Tin-Free Radical Alkoxyamine Addition and Isomerization Reactions by Using the Persistent Radical Effect: Variation of the Alkoxyamine Structure

Kian Molawi, Tobias Schulte, Kai Oliver Siegenthaler, Christian Wetter, and Armido Studer*[a]

Abstract: Various C-centered radicals can efficiently be generated through thermal C–O-bond homolysis of alkoxyamines. This method is used to perform environmentally benign radical cyclization and intermolecular addition reactions. These alkoxyamine isomerizations and intermolecular carboaminoxylations are mediated by the persistent radical effect (PRE). In the paper, the effect of the variation of the alkoxyamine structure—in particular steric effects in the nitroxide moiety—on the outcome of the PRE mediated radical reactions will be discussed. Fourteen different nitroxides were used in the studies. It will be shown that reaction times can be shortened about 100 times upon careful tuning of the alkoxyamine structure. Activation energies for the C–O-bond homolysis of the various alkoxyamines are provided. The kinetic data are used to explain the reaction outcome of the PRE-mediated processes.

Keywords: C–C coupling · kinetics · persistent radical effect · radical reactions · synthetic methods

Introduction

Organotin compounds have found widespread application for conducting various types of radical reactions.[1] However, there are drawbacks associated with tin-based radical chemistry, namely toxicity, hazardous handling, and problems with product purification. Therefore, many research groups have initiated programs towards tin-free radical chemistry.[2] Herein we report on environmentally benign radical cyclization and addition reactions using the so-called persistent radical effect (PRE).

The PRE is a general principle that explains the highly specific formation of the cross-coupling product R^1–R^2 between two radicals R^1 and R^2 when one species is persistent (R^1) and the other transient (R^2) and the two radicals are formed at equal rates.[3] Nonselective statistical reaction between the two different radical intermediates is suppressed. The reason behind this reactivity lies in the reluctance of the persistent radicals to undergo homo-coupling. Therefore, the persistent radicals can only be consumed through cross-reaction with a transient radical. The transient species, however, can also react in a homo-coupling process to form R^2–R^2 and the corresponding disproportionation products. This leads to a build up of the persistent radical and eventually to the highly selective cross-coupling reaction.

Recently, we communicated first results on environmentally benign radical alkoxyamine isomerization reactions using the PRE.[4] For example, alkoxyamine **1** was isomerized to the corresponding cyclized alkoxyamines **2** (70%) and **3** (13%, Scheme 1). Heating of alkoxyamine **1** reversibly generates a transient C-radical **4** and the persistent TEMPO radical. 5-*exo* or 6-*endo* cyclization leads to the transients **5** and **6** which upon trapping with TEMPO finally provide the alkoxyamine isomerization products **2** and **3**. The coupling of the transient species **4**, **5** and **6** with the persistent TEMPO is a highly selective process steered by the PRE.[5]

We have also shown that these reactions can be conducted under microwave conditions.[6] Herein we report in full details on alkoxyamine isomerization and addition reactions. Structure/reactivity profiles of various new alkoxyamines will be discussed. In addition, C–O-bond dissociation energies of the new alkoxyamines are provided.

[a] Dipl.-Chem. K. Molawi, Dipl.-Chem. T. Schulte, Dipl.-Chem. K. O. Siegenthaler, Dr. C. Wetter, Prof. Dr. A. Studer
Organisch Chemisches-Institut
Westfälische Wilhelms-Universität, Corrensstrasse 40
48149 Münster (Germany)
Fax: (+49) 251-833-6523
E-mail: studer@uni-muenster.de

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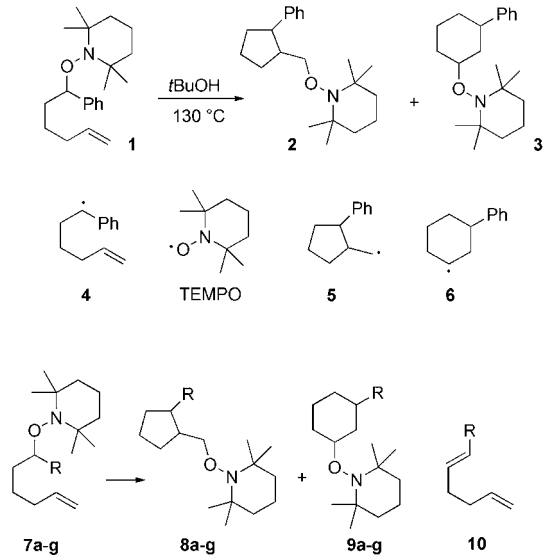


Scheme 1. Alkoxyamine isomerization using the PRE.

Results and Discussion

Intramolecular processes—Radical alkoxyamine isomerizations: The synthesis of the alkoxyamines **1** and **7a–h** has previously been described.[7] All the radical isomerizations were conducted in sealed tubes at 130–132 °C under an argon atmosphere. Optimizations were performed by using alkoxyamine **1**. Various solvents were tested. Best results were obtained in *t*BuOH (0.02 M) in the presence of 10% camphor sulfonic acid (CSA) for 24 h (**2**: 70%, *trans*:*cis* 2.5:1; **3**: 13%, *trans*/*cis* 1:1). CSA is used to decrease the concentration of TEMPO. If the TEMPO concentration is too high, the desired cyclization reaction of radical **4** cannot efficiently compete with TEMPO trapping.[8] In fact, isomerization without CSA was not completed after 36 h. The relative configuration of the major isomer was assigned after N–O cleavage in **2** by using standard conditions (Zn, AcOH, H_2O, THF) to form the corresponding known alcohol.[9]

In DMF isomerization occurred faster (16 h), however, slightly lower yields were obtained (**2**: 56%; **3**: 10%). Reactions in *tert*-butylbenzene, *N*,*N*′-dimethyl-*N*,*N*′-propylene urea (DMPU) and water did not work.

Under the optimized conditions alkoxyamines **7a–f** were successfully isomerized. The results are summarized in Table 1. Isomerization of bromide **7a** afforded **8a** (71%, *trans*:*cis* 2.7:1) and **9a** in 8% yield (run 1). Reaction of **7b** led to 10% of the side product **10** (R = Ph-4-OMe). The side product either derives from a disproportionation reaction of TEMPO with the corresponding transient C-radical or from a direct ionic elimination of TEMPOH.[10] The products **8b** and **9b** were isolated in 54% combined yield (**8b**:**9b** 2.8:1, run 2). Clean reactions were observed for heteroarenes **7c** and **7d** (runs 3 and 4). The reaction with nitrile **7e** afforded 61% of the 5-*exo* product **8e** and 7% of **9e** (run 5). With **7f**, no 6-*endo* product was formed and **8f** was isolated in 67% (*dr* 1:1, run 6) along with 10% of **10** (R = CO_2*t*Bu). No isomerization occurred with **7g**, **h**, and **i** (runs 7–9).

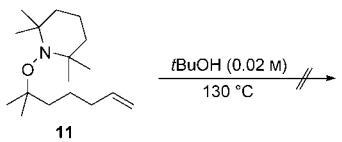
In Table 1 the activation energies (E_a) of the C–O-bond homolysis of the alkoxyamines **7a–i** are listed. One can readily see that the success of the reaction depends on the activation energy of the C–O-bond homolysis. For alkoxyamines with $E_a < 140$ kJ mol^{-1} isomerization readily occurred (runs 1–6, E_a(**1**) = 131.9 kJ mol^{-1}) whereas for alkoxyamines **7g–i** the C–O bonds are too strong and homolysis cannot be accomplished under the applied conditions (E_a values are above 160 kJ mol^{-1}, runs 7–9).

It would be important to know the upper limit for alkoxyamine E_a for which isomerization is still feasible. The 140–160 kJ mol^{-1} range extracted from Table 1 is certainly too large for synthetic planning. Therefore, we looked for other substrates for which the E_a lies in between this range. We found that isomerization of alkoxyamine **11**, for which an E_a of 144.0 kJ mol^{-1} was measured,[7] did not work under the standard conditions (Scheme 2). Even at 150 °C reaction could not be performed. Since the statistical error in the kinetic experiments lies between 2 and 3 kJ mol^{-1}, we assume that isomerizations should work for alkoxyamines with E_a values below 142 kJ mol^{-1}.

Table 1. Isomerization of **7a–i** (*t*BuOH (0.02 M), 10% CSA, 130–132 °C, 24 h, sealed tube) and activation energies for the C–O-bond homolysis of alkoxyamines **7a–i**.

Run	Compd	R	**8** [%]	*dr* (**8**) (*trans*/*cis*)	**9** [%][a]	**10** [%]	E_a[b] [kJ mol^{-1}]
1	**7a**	4-BrC_6H_4	71	2.7:1	8	<2	127.2
2	**7b**	4-$CH_3OC_6H_4$	46	2.8:1	8	10	132.8
3	**7c**	2-thienyl	67	2.1:1	11	5	112.4
4	**7d**	2-pyridyl	57	1.6:1	12	5	129.7
5	**7e**	NC	61	1.1:1[c]	7	<2	137.9
6	**7f**	*t*BuO_2C	67	1:1	<2	10	139.0[d]
7	**7g**	H	<2	–	<2	<2	>165.3
8	**7h**	CH_3	<2	–	<2	<2	>165.3[d]
9	**7i**	PhS	<2	–	<2	<2	162.7[b,e]

[a] The 6-*endo* product was formed as a 1:1 mixture of the diastereoisomers. [b] Ref. [7]. [c] The relative configuration of the two isomers was not assigned. [d] Estimated from data on similar compounds published in ref. [11]. [e] 4-Hydroxy-TEMPO was used instead of TEMPO for the preparation of the alkoxyamine.



Scheme 2. Attempted isomerization of **11**.

The activation energy for the C–O-bond homolysis of an alkoxyamine depends on the stability of the released radical and on the structure of the corresponding nitroxide.[7,11,12] Steric and polar effects in the nitroxide moiety play an important role.[12] In order to improve the efficiency of the PRE-mediated isomerizations, we decided to test other nitroxides. As a model reaction the cyclization of the 1-phenyl-5-hexenyl radical **4** was investigated. The nitroxide moiety was systematically varied. The synthesis of the alkoxyamines **13a**, **15a** and **16a** has previously been described.[7] The alkoxyamines **12a**, **14a** and **17–24a** were prepared from the corresponding nitroxides[12–16] and 1-bromo-1-phenyl-5-hexene as described in the Experimental Section.

In sealed tubes the alkoxyamines **12–24a** were heated under standard conditions (*t*BuOH, 0.02 M, with or without CSA, 130 °C) and the time necessary to get complete conversion was determined. Samples were taken after appropriate time intervals and were analyzed by ^{1}H NMR spectroscopy. The 5-*exo* (**12–24b**, *trans*:*cis* mixture of isomers) and 6-*endo* products (**12–24c**) were obtained in moderate to good yields. The *endo*/*exo* isomers were not separated. The isomer ratio for the compounds **12** and **13** was determined by using ^{1}H NMR spectroscopy. The relative configuration of the major isomer of the *exo*-cyclization products **12b** and **13b** was assigned in analogy to alkoxyamine **2**. Due to the complexity of the ^{1}H NMR spectra of the isomerization products **14–24** their isomer ratio was not determined. The results are summarized in Table 2. In addition, we also included the activation energies for the alkoxyamine C–O-bond homolysis into Table 2. Most of the kinetic data have previously been published. The E_a for C–O-bond homolysis for alkoxyamine **19a** and for the other new alkoxyamines described herein (see below) was determined by kinetic EPR experiments (see Experimental Section).[7]

Isomerization of the hydroxy-TEMPO-derivative **12** was completed in 14 h in the presence of CSA. The *exo*/*endo*-isomers **12b**,**c** were isolated in 73 % combined yield (run 1). A faster cyclization was obtained for the di-*tert*-butyl nitroxide derived alkoxyamine **13a**. Isomerization for 3 h afforded the alkoxyamines **13b**,**c** in 87 % yield (run 2). Since the addition of CSA led to decomposition of the starting alkoxyamine **13a**, the reaction had to be conducted without CSA. A short reaction time was also observed for the phosphonate **14a** (4.5 h, run 3).[17,18] Hydrogen bonding in nitroxides has been shown to lead to a stabilization of the nitroxides and hence to decreased reactivity towards C-centered radicals.[19] Moreover, we have shown that intramolecular H-bonding in alkoxyamines influences the C–O-bond homolysis. Faster homolysis was obtained for alkoxyamines capable of forming intramolecular hydrogen bonds.[7] Thus, H-bonding in alkoxyamines and nitroxides should lead to a shift of the equilibrium of the reversible alkoxyamine C–O-bond homolysis towards the radical pair. This eventually should lead to faster isomerization reactions. In fact, upon going from the parent Hawker–Braslau-type[20] alkoxyamine **15a** to the H-bonding system **16a** a small decrease of the reaction time was noticed (runs 4,5). With alkoxyamine **17a**, bearing three OH groups appropriately positioned for intramolecular H-bonding, a further decrease of the isomerization time was obtained (4 h, run 6). However, at the same time the yield is steadily decreasing from 97 to 73 to 69 %. This is due to the instability of the nitroxides capable of forming intramolecular H-bonds.[14]

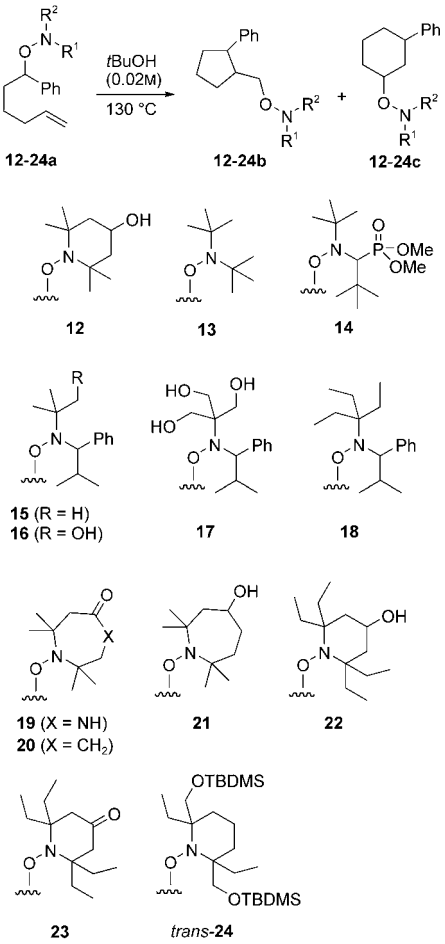
We have recently shown that substitution of the *tert*-butyl group in Hawker–Braslau-type alkoxyamines of type **15a** by the larger triethylmethyl group provides effective shielding of the nitroxide moiety and this in turn leads to reactive alkoxyamines.[16] To our delight, a highly efficient isomerization was observed for alkoxyamine **18a**: Reaction was completed in less than 15 minutes and CSA addition did not show any effect (Table 2, run 7).

Encouraged by these results we decided to prepare other sterically highly hindered alkoxyamines (see Scheme 3, Table 2). On the basis of experimental results and on calculations, it has been predicted that in cyclic nitroxides the ring size influences the C–O-bond dissociation energy (BDE) of the corresponding alkoxyamines.[13,21] The BDE increases from seven- to six- to five-membered cyclic nitroxides. Therefore, alkoxyamines prepared from seven-membered cyclic nitroxides were tested in the model isomerization reaction. Disappointingly, alkoxyamine **19a** isomerized sluggishly (entry 8). A slightly better result was obtained for the seven-membered ketone **20a** (entry 9). A further improvement was observed upon reduction of the keto functionality. Isomerization of alcohol **21a** was completed in 3 h (entry 9). The switching of the hybridization from sp^2 to sp^3 in the nitroxide ring at position 4 probably leads to a conformational change which eventually provides better shielding and hence faster homolysis.

Finally, we tested TEMPO analogues in which the four methyl substituents are replaced by larger ethyl and silyloxymethyl groups, respectively. A highly efficient isomerization was observed for alkoxyamine **22a** (<0.25 h, entry 11). As with the seven-membered ring systems, the corresponding ketone **23a** isomerized far less efficiently (entry 12). We believe that the decreased stability of the ketoalkoxyamine due to a possible β-elimination may be the reason for the different reactivity. In fact, decomposition products were identified in the crude ^{1}H NMR spectrum. A very good result was also obtained for the bissilyl ether **24a** for which reaction was completed in 20 minutes (entry 13).

From these structure–activity studies we can state that 6-membered cyclic nitroxides with bulky α-substituents perform very well in the PRE-mediated test reaction. Steric effects seem to play a major role for increasing the reactivity of a given alkoxyamine. For efficient alkoxyamines CSA addition is not necessary.

The isomerization results correlate fairly well with the activation energies for the C–O-bond homolysis of the corresponding alkoxyamines. Slow isomerizations were observed for alkoxyamines with E_a values above 133 kJ mol^{-1} (**12a**, **19a** and **20a**). For alkoxyamines with E_a values between 124–127 kJ mol^{-1} reaction took 3–8 h for completion. For systems with E_a values below 123 kJ mol^{-1} efficient isomeri-



Scheme 3. Various alkoxyamines tested in the alkoxyamine isomerization.

Table 2. Effect of the nitroxide structure on the isomerization; activation energies for the alkoxyamine C–O-bond homolysis.

Run	Cpd	Yield [%] (*exo* + *endo*)	*t* [h]	E_a [kJ mol^{-1}]	Ref.
1	**12**	73[a]	14[b]	133.6	[13]
2	**13**	87[c]	3	119.1	[7]
3	**14**	80	4.5[b]	124.5	[11]
4	**15**	97	8[b]	127.1	[7]
5	**16**	73	7.5[b]	126.5	[7]
6	**17**	69	4[b]	124.1	[7]
7	**18**	90	< 0.25	121.7	[16]
8	**19**	61	> 36[b,d,e]	133.0	this work
9	**20**	74	20[b]	133.1	[13]
10	**21**	75	3[b]	124.4	[13]
11	**22**	95	< 0.25	122.8	[15]
12	**23**	38	> 24[d]	123.7	[15]
13	**24**	84	0.33	122.2	[14]

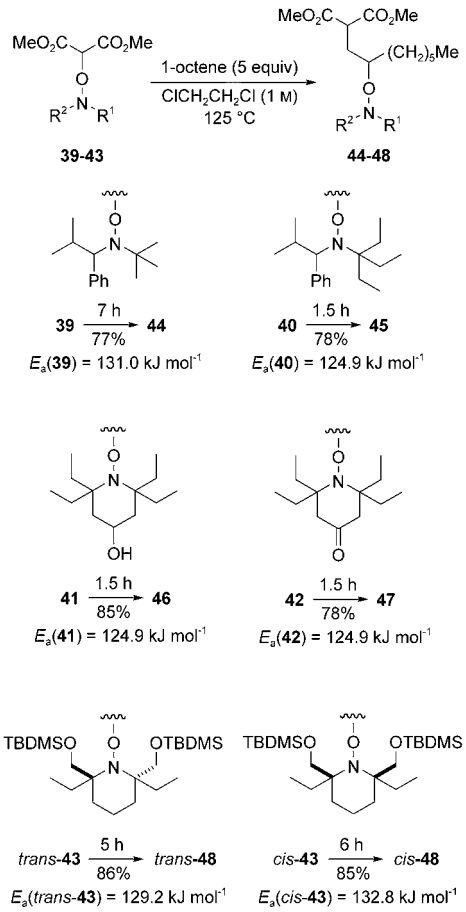
[a] *exo*/*endo* 2.2:1; *trans*/*cis* (**12b**) 2.2:1. [b] 10% CSA was added. [c] *exo*/*endo* 13.5:1; *trans*/*cis* (**13b**) 2.2:1. [d] Reaction was not completed. [e] Yield determined by ^{1}H NMR spectroscopy. Remaining material is unreacted **19a** (39%).

zations were obtained. However, the correlation is not perfect. The di-*tert*-butyl-nitroxide derived alkoxyamine **13a**, for which the lowest activation energy was determined, isomerized in 3 h, whereas for the slower homolysing alkoxyamines **22a** and **24a** less than 20 minutes is necessary to get complete conversion. It is important to note that the trapping of the nitroxide with the C-centered radical is as important as the C–O-bond homolysis. It is the equilibrium constant which is important and which should provide a better correlation. Unfortunately, the equilibrium constants for our alkoxyamines are not known. We assume that the trapping reaction of radical **4** with the nitroxides derived from **22a** and **24a** is slower than the analogous reaction with the di-*tert*-butyl-nitroxide. This leads to a higher life time of the intermediate radicals in systems **22** and **24** and eventually to faster isomerizations.

Intermolecular processes—Radical alkoxyamine additions: We next decided to study nitroxide-mediated intermolecular alkoxyamine additions, so-called carboaminoxylations.[22] Along with the strength of the C–O bond, the reactivity of the C-centered radical in the intermolecular addition has to be considered. As a model reaction the addition onto 1-octene was investigated. It is obvious that the attempted intermolecular carboaminoxylation will only work for stabilized radicals which at the same time are reactive in intermolecular additions. Malonyl radicals, which have successfully been used in atom transfer reactions,[23] fulfill these criteria. Indeed, we have already shown that intermolecular carboaminoxylation of TEMPO-malonate **25**[24] in $ClCH_2CH_2Cl$ onto 1-octene provided carboaminoxylation product **26** in 66% yield (Table 3, run 1).[22] To study the scope and the limitations we decided to look at other TEMPO-alkoxyamines derived from stabilized radicals which are reactive in intermolecular additions. The alkoxyamines **27**–**32** were prepared via deprotonation of the corresponding C–H acidic compounds with subsequent oxidation ($CuCl_2$) in the presence of TEMPO. The compounds were obtained as racemates. Alkoxyamine additions were studied by using 1-octene as acceptor under the optimized conditions ($ClCH_2CH_2Cl$, 1 M, 135 °C, 3 d, Table 3). Products derived from **27**, **30** and **31** were obtained as 1:1 mixture of diastereoisomers. Reaction of Weinreb amide **27** with 1-octene afforded addition product **33** in 33% yield (run 2). Alkoxyamine addition by using **28**, derived from methyl acetylacetate, failed (run 3). The starting alkoxyamine was not stable under the applied conditions. The same behavior was observed for alkoxyamine **29** (run 4). Probably, the α-H-atoms at C(4) of the β-ketoester are the reason for the failure. Intramolecular 1,5-proton transfer to the alkoxyamine N atom may initiate the decomposition, as suggested by a referee.[25] Indeed, the pivaloylated alkoxyamine **30** lacking α-H-atoms at C(4) delivered the desired carboaminoxylation product **36** in 51% yield. The Horner-type alkoxyamine **31** was successfully added onto 1-octene (**37**, 56%, run 6).[26] Moreover, we showed that functionalized geminal bisphosphonates can be prepared using our methodology (**38**, 57%, run 7).[27] Thus, various functional groups, which are highly useful for further synthetic manipulations, can be introduced using our method.

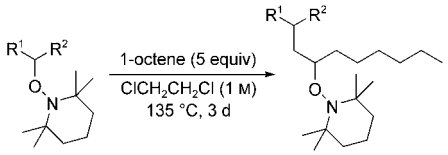
We also measured the E_a values for alkoxyamines **25**, **27**, **30–32** (see Table 3). As expected for successful PRE-mediated processes, all values lie below 142 kJ mol^{-1}. The change of the ester functionality by an amide, such as the Weinreb amide, does not alter the E_a to a large extent (compare runs 1 and 2, 140.0 vs 137.7 kJ mol^{-1}). The introduction of a dialkylphosphonyl group leads to a lowering of E_a (135.3 kJ mol^{-1}, run 6). This is probably due to steric factors. For the bisphosphonate **32** the lowest activation energy was measured (123.8 kJ mol^{-1}, run 7). The replacement of the methoxycarbonyl group by a pivaloyl group also leads to a decrease of the E_a (compare run 1 and 5, 140.0 versus 132.1 kJ mol^{-1}). Electronic as well as steric factors are contributing in this case.

We have to admit that a disadvantage of our method is the long reaction times necessary to get high conversions (three days!). We thought that the change of the TEMPO moiety by sterically more hindered nitroxides should lead to decreased reaction times, as already observed for the alkoxyamine isomerizations described above. To this end, alkoxyamines **39–43** were prepared and tested in the 1-octene carboaminoxylation reaction (**44–48**, Scheme 4). The experiments were conducted in sealed tubes at 125 °C in $ClCH_2CH_2Cl$ (1 M) by using 5 equiv of 1-octene. The time necessary to get complete conversion was determined. The results are summarized in Scheme 4. With malonate **39** reaction was completed after 7 h and alkoxyamine **44** was isolated in 77 % yield. With the more bulky triethylmethyl congener **40** an even faster addition was obtained. Reaction was finished in just 1.5 h and **45** was isolated in 78 % yield. Similar results were obtained for the alkoxyamines **41** and **42**. Interestingly, although the ketonitroxide derived from **42** did not perform well in the cyclization reaction described above, highly efficient intermolecular addition was obtained by using **42**. The alkoxyamines **43** (*cis* and *trans*-isomer) underwent intermolecular addition onto 1-octene in 5 and 6 h, respectively, providing the corresponding carboaminoxylation products *trans* and *cis*-**48** in high yields.



Scheme 4. Carboaminoxylation of 1-octene by using alkoxyamines **39–43**.

Table 3. Intermolecular carboaminoxylations of various TEMPO-derived alkoxyamines onto 1-octene. E_a for the starting alkoxyamines.



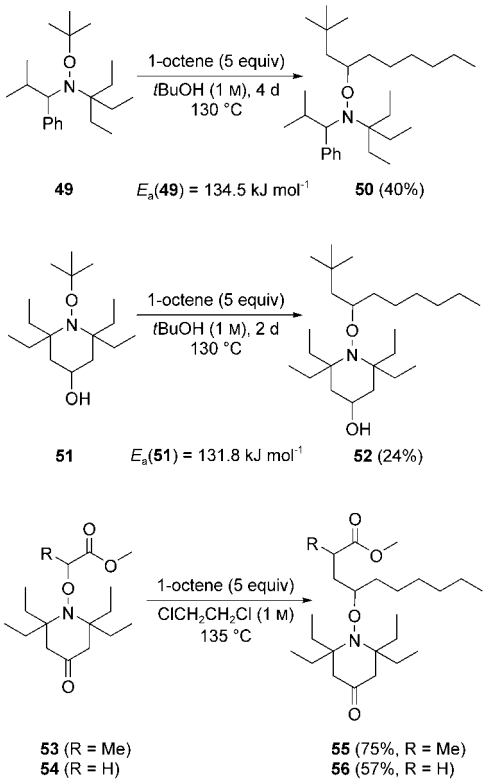
25,27–32 **26,33–38**

Run	Compd	R^1	R^2	Product	Yield [%]	E_a [kJ mol^{-1}]
1	**25**	CO_2Me	CO_2Me	**26**	66	140.0
2	**27**	CO_2Me	CON(Me)OMe	**33**	33	137.7
3	**28**	CO_2Me	COMe	**34**	–	n.d.
4	**29**	CO_2Me	COEt	**35**	–	n.d.
5	**30**	CO_2Et	CO*t*Bu	**36**	51	132.1
6	**31**	CO_2Et	$PO(OEt)_2$	**37**	56	135.3
7	**32**	$PO(OMe)_2$	$PO(OMe)_2$	**38**	57	123.8

We also measured the activation energies for the C–O-bond homolysis of malonates **39–43**. The kinetic data correlate well with the reaction times. For TEMPO-malonate **25** with an E_a of 140.0 kJ mol^{-1} three days were necessary for the carboaminoxylation at 135 °C. The alkoxyamines **39**, *cis*-**43** and *trans*-**43** with E_a values in the range of 131 kJ mol^{-1} reacted in 5–7 h at 125 °C. For malonates **40–42** (E_a = 124.9 kJ mol^{-1} for each) addition was completed in just 1.5 h. Hence, the reaction time could be shortened from 3 d to 1.5 h upon simply switching the nitroxide moiety, clearly showing the benefits of our nitroxide design.

With highly efficient nitroxides in hand we also attempted intermolecular addition of tertiary alkyl radicals. The *tert*-butyl alkoxyamines **49** and **51** were readily prepared from *t*BuLi oxidation in the presence of the corresponding nitroxide. The intermolecular carboaminoxylations were per-

formed in *t*BuOH at 130 °C by using 1-octene as radical acceptor (Scheme 5). A 40 % yield was obtained using alkoxyamine **49** (*dr* 1:1). The reaction with **51** provided adduct **52** in a moderate yield (24 %). Increasing the reaction time did not improve the result. Surprisingly, the E_a for C–O-bond homolysis of alkoxyamine **51** is smaller than the E_a for **49**, although with the latter a better result was obtained in the 1-octene addition. Alkoxyamine stability may be the reason for the improved yield using **49**.



Scheme 5. Intermolecular carboaminoxylation by using the PRE.

We could also show that with efficient nitroxides, additions of α-methoxycarbonyl alkyl radicals are feasible. Addition of **53** onto 1-octene provided ester **55** as a 1:1 mixture of diastereoisomers in 75 % yield (24 h). A slower reaction was observed using alkoxyamine **54**. The carboaminoxylation was stopped after four days. Product **56** was isolated in 57 % yield along with 14 % of unreacted starting alkoxyamine.

Conclusion

We reported radical alkoxyamine isomerization and intermolecular addition reaction using the PRE. We showed that the nitroxide structure effects the reaction outcome to a large extent. In particular steric effects play a major role. For the alkoxyamine isomerization investigated comprising the ubiquitous 5-hexenyl radical cyclization, reaction time could be shortened from 24 h to 15 minutes upon simply switching the nitroxide moiety. For the intermolecular addition of TEMPO-malonate **25** to 1-octene three days were necessary for high conversions, whereas for alkoxyamines **40** and **41**, deriving from sterically highly hindered nitroxides, only 1.5 h were necessary for the same reaction. Importantly, reactions which cannot be conducted by using TEMPO-derived alkoxyamines can be performed in moderate to good yields using alkoxyamines derived from sterically highly hindered alkoxyamines. Various functional groups, such as the Weinreb amide, Horner-phosphonates or geminal bisphosphonates can be introduced using our methodology. The environmentally benign reactions are easy to perform. No special equipment is necessary.

We could also show that the reaction times correlate fairly well with the activation energies for the C–O-bond homolysis of the starting alkoxyamines. Hence, upon simply looking at the kinetics of the homolysis process, the success of the reaction can be predicted. Of course this is important for careful reaction planning.

Finally, it is worth mentioning that alkoxyamines are also used as regulators for the nitroxide mediated stable free radical polymerization.[28] The results presented herein will lead to new ideas for the design of alkoxyamine polymerization regulators.

Experimental Section

General: All reactions involving air- or moisture-sensitive reagents or intermediates were carried out in dried glassware under an argon atmosphere. THF was freshly distilled from potassium under argon. Et_2O was freshly distilled from K/Na under argon. CH_2Cl_2 was freshly distilled from P_2O_5. All other solvents and reagents were purified according to standard procedures or were used as received from Aldrich or Fluka. ^1H and ^{13}C NMR spectra were recorded on a Bruker AMX 500, AMX 400, AC 300, ARX 300, ARX 200, a Varian-Gemini 300 or a Varian-Gemini 200. Chemical shifts δ in ppm relative to $CHCl_3$ at 7.26 ppm as external standard. TLC was performed by using Merck silica gel coated 60 F_{254} glass plates; detection with UV or dipping into a solution of $KMnO_4$ (1.5 g in 400 mL H_2O, 5 g $NaHCO_3$) or a solution of $Ce(SO_4)_2 \cdot H_2O$ (10 g), phosphormolybdic acid hydrate (25 g), concentrated H_2SO_4 (60 mL), and H_2O (940 mL), followed by heating. Flash column chromatography (FC) was performed using Merck or Fluka silica gel 60 (40–63 μm) applying a pressure of about 0.4 bar. Melting points were determined with a Büchi 510 or a Büchi SMP-20 apparatus and are uncorrected. IR spectra were recorded on a Perkin Elmer 1600, a Perkin Elmer 782, a Bruker IFS-200 or a Nicolet Magna-IR 750 spectrophotometer. Mass spectra were recorded on a VG Tribid, a CG Tribid, Varian CH7 (EI); IonSpec Ultima, QStarPulsar i, Finnigan MAT TSQ 700 or a Finnigan MAT *95S* (ESI) and peaks are given in *m/z* (% of basis peak). Kinetic EPR experiments were performed on a Bruker ESP 300 E at 130 °C. The temperature of the probe was regulated in a gas flow (92 % N_2, 8 % H_2) by a Bruker Variable Temperature Unit BVT 2000. The nitroxide concentrations were determined by double integration of the EPR spectra and calibration with a TEMPO solution in *tert*-butylbenzene (0.1 mM).

General procedure 1 (GP 1)—Isomerization of alkoxyamines: The alkoxyamine and in some cases CSA (10 %) were dissolved in degassed *t*BuOH (0.02 M solution) under argon. The mixture was heated to 130–132 °C in a sealed tube for 0.25–40 h. After removal of the solvent in vacuo the residue was purified by FC.

General procedure 2 (GP 2)—Synthesis of alkoxyamines according to the method of Matyjaszewski:[29] The bromide, nitroxide, copper powder, $Cu(OTf)_2$ and 4,4′-di-*tert*-butyl-[2,2′]bipyridine were dissolved in benzene under argon. The reaction mixture was heated to 65–75 °C in a sealed tube for 6–20 h. Afterwards the mixture was filtered through silica gel and the solvents were removed in vacuo. FC finally yielded the desired alkoxyamine. For highly efficient nitroxides the alkoxyamine synthesis should be performed at lower temperatures (< 40 °C).

General procedure 3 (GP 3)—Oxidative coupling of 1,3-dicarbonyl-compounds and phosphonates with nitroxides: LDA was prepared from diisopropylamine (DIPA) and *n*-butyl lithium (*n*BuLi) in dimethoxyethane (DME) at −60 °C. The 1,3-dicarbonyl-compound or the phosphonate, respectively, was added and the mixture was stirred for 30 min at −60 °C. Then the nitroxide and anhydrous $CuCl_2$ were added followed by stirring for 90 min at 0 °C and 2–20 h at room temperature. The reaction was stopped upon addition of NH_4Cl (aq. sat.) and the aqueous layer was extracted (3×) with Et_2O. The combined organic layers were dried over $MgSO_4$ and the solvents were removed in vacuo. FC finally yielded the desired alkoxyamine.

General procedure 4 (GP 4)—Intermolecular additions of alkoxyamines to alkenes: The alkoxyamine was dissolved under argon in degassed 1,2-dichloroethane (DCE, 1 M solution) and the alkene was added (5 equiv). The mixture was heated in a sealed tube to 125–135 °C for 1.5–72 h. After evaporation of the solvent in vacuo the residue was purified by FC to yield the desired products.

2,2,6,6-Tetramethyl-1-(2-phenyl-cyclopentylmethoxy)-piperidine (2), 2,2,6,6-tetramethyl-1-(2-phenyl-cyclohexyloxy)-piperidine (3): The isomerization was performed according to GP 1 by using alkoxyamine **1** (210 mg, 0.67 mmol), CSA (15.6 mg, 0.067 mmol) and *t*BuOH (33.5 mL) at 130–132 °C for 24 h. FC (Et_2O/pentane 1:100) yielded a mixture (174 mg, 83 %) of **2** and **3** (**2**/**3** 5.4:1, *cis*/*trans* (**2**) 1:2.5, *cis*/*trans* (**3**) 1:1; all ratios determined by analysis of ^{1}H NMR spectra).

Compound **2**: ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.31–7.11 (m, 5H, Ph-H), 3.72–3.63 (m, 2H, CH_2O, *trans*), 3.38–3.29 (m, 2H, CH_2O, *cis*), 3.27–3.21 (m, 1H, CHPh, *cis*), 2.78–2.72 (m, 1H, CHPh, *trans*), 2.55–0.99 (m, 25H, both isomers); ^{13}C NMR (100 MHz, $CDCl_3$): *cis*-**2**: δ = 143.2 (C), 128.4 (CH), 128.0 (CH), 125.7 (CH), 77.5 (CH_2), 59.6 (C), 47.3 (CH), 43.6 (CH), 39.6 (CH_2), 32.8 (CH_3), 32.7 (CH_3), 30.8 (CH_2), 29.1 (CH_2), 23.7 (CH_2), 20.1 (CH_3); *trans*-**2**: δ = 145.9 (C), 128.2 (CH), 127.5 (CH), 125.7 (CH), 79.3 (CH_2), 59.7 (C), 49.2 (CH), 47.2 (CH), 39.6 (CH_2), 35.9 (CH_2), 33.2 (CH_3), 32.9 (CH_3), 24.8 (CH_2), 20.1 (CH_3), 17.1 (CH_3).

Compound **3**: ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.31–7.15 (m, 5H, Ph-H, both isomers), 4.07–4.04 (m, 1H, HCO, single isomer), 3.79–3.70 (m, 1H, HCO, single isomer), 3.00–2.92 (m, 1H, CHPh, single isomer), 2.60–2.40 (m, 1H, CHPh, single isomer), 2.40–1.00 (m, 26H, both isomers); ^{13}C NMR (100 MHz, $CDCl_3$): both isomers: δ = 147.7 (C), 146.9 (C), 128.3 (2×CH), 126.9 (2×CH), 125.9 (CH), 125.8 (CH), 82.2 (CH), 78.5 (CH), 59.8 (C), 59.7 (C), 43.5 (CH), 40.4 (CH_2), 40.3 (2×CH_2), 38.7 (CH), 38.5 (CH_2), 34.6 (CH_3), 34.0 (CH_2), 33.9 (CH_2), 32.7 (CH_2), 30.4 (CH_2), 25.0 (CH_2), 21.6 (CH_2), 20.3 (CH_3), 17.3 (CH_2), 17.2 (CH_2); IR($CHCl_3$): $\tilde{\nu}$ = 2933s, 2871s, 1601w, 1492m, 1470m, 1452m, 1374m, 1360m, 1260w, 1132m, 1046m, 994w, 957w cm^{-1}; MS (EI): *m*/*z*: 315 (5) $[M]^+$, 300 (35), 159 (13), 157 (18), 142 (100), 91 (35); elemental analysis calcd (%) for $C_{21}H_{33}NO$ (315.50): C 79.95 H 10.54, N 4.44; found: C 80.05, H 10.78, N 4.67.

The syntheses of the alkoxyamines **7a–e** have previously been published.[7]

2-(2,2,6,6-Tetramethyl-piperidin-1-yloxy)-hept-6-enoic acid *tert*-butylester (7f): A solution of hept-6-enoic acid *tert*-butyl ester (200 mg, 1.09 mmol) in THF (1.8 mL) was added to a solution of LDA (1.20 mmol) in THF (5 mL) at −78 °C. After stirring for 30 min at −78 °C a suspension of TEMPO (157 mg, 1.00 mmol) and $CuCl_2$ (161 mg, 1.20 mmol) in THF (4 mL) was added. The mixture was allowed to warm to room temperature (over 5 h) and was stirred over night. The reaction was stopped by addition of NH_4Cl (aq. sat.) followed by extraction (3×) of the aqueous layer with Et_2O. The combined organic layers were washed with brine, dried over $MgSO_4$ and the solvents were removed in vacuo. FC (Et_2O/pentane 1:45) yielded **7f** (200 mg, 59 %). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 5.83–5.73 (m, 1H, H_2C=C*H*), 5.03–4.93 (m, 2H, H_2C=CH), 4.14–4.10 (m, 1H, HCO), 2.17–2.00 (m, 2H), 1.87–1.79 (m, 2H), 1.60–1.20 (m, 8H), 1.46 (s, 9H, $C(CH_3)_3$), 1.16 (s, 3H, CH_3), 1.12 (s, 3H, CH_3), 1.11 (s, 6H, CH_3); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 172.9 (C), 138.4 (CH), 114.7 (CH_2), 85.8 (CH), 80.8 (C), 59.9 (C), 59.5 (C), 40.3 (CH_2), 33.7 (CH_3), 33.5 (CH_2, CH_3), 31.9 (CH_2), 28.1 (CH_3), 23.7 (CH_2), 20.2 (CH_3), 17.1 (CH_2); IR ($CHCl_3$): $\tilde{\nu}$ = 2979s, 2935s, 2871s, 1732s, 1640w, 1457m, 1368s, 1153s, 915s, 843s cm^{-1}; MS (EI): *m*/*z*: 339 (2) $[M]^+$, 156 (100); elemental analysis calcd (%) for $C_{20}H_{37}NO_3$ (339.52): C 70.75, H 10.98, N 4.13; found: C 70.84, H 10.75, N 4.28.

2,2,6,6-Tetramethyl-1-(1-methyl-hex-5-enoyloxy)-piperidine (7h): A solution of 6-iodo-hept-1-ene (224 mg, 1.0 mmol) and TEMPO (941 mg, 6.0 mmol) in benzene (10 mL) was heated under reflux under argon. Tris(trimethylsilyl)silane (TTMSH) (1.23 mL, 4.0 mmol) was added in three portions every 60 min. After the last addition of TTMSH the mixture was heated under reflux for another 30 min. The solvent was removed in vacuo and the residue was purified by FC (Et_2O/pentane 1:100) to yield **7h** (246 mg, 97 %). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 5.88–5.78 (m, 1H, H_2C=C*H*), 5.04–4.93 (m, 2H, H_2C=CH), 3.91–3.83 (m, 1H, HCO), 2.09–2.03 (m, 2H), 1.69–1.27 (m, 10H), 1.16–1.07 (m, 15H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 139.1 (CH), 114.3 (CH_2), 78.2 (CH), 60.1 (C), 59.1 (C), 40.3 (CH_2), 35.9 (CH_2), 34.4 (2×CH_3), 34.1 (CH_2), 25.3 (CH_2), 20.4 (2 CH_3), 19.9 (CH_3), 17.4 (CH_2); IR ($CHCl_3$): $\tilde{\nu}$ = 2973s, 2933s, 2871w, 1639w, 1457m, 1376s, 1361s, 1132s, 915m cm^{-1}; MS (EI): *m*/*z*: 253 (< 1) $[M]^+$, 157 (11), 142 (100); elemental analysis calcd (%) for $C_{16}H_{31}NO$ (253.43): C 75.83, H 12.33, N 5.53; found: C 75.97, H 12.44, N 5.27.

2,2,6,6-Tetramethyl-1-(1-phenylsulfanyl-hex-5-enoyloxy)-piperidine (7i): Calcium ascorbate dihydrate (1.50 g, 3.80 mmol) was added to a suspension of TEMPO (468 mg, 3.00 mmol) in H_2O (26 mL) and the mixture was stirred at room temperature for 15 min. H_2O was added and the reaction mixture was extracted with Et_2O (3×). The combined organic layers were dried over $MgSO_4$ and the solvent was removed in vacuo. The resulting hydroxylamine was dissolved in THF (2 mL) under argon and then added dropwise to a suspension of NaH (148 mg, 60 %, 3.70 mmol) in THF (5 mL). The mixture was stirred for 30 min at room temperature. Afterwards a solution of 1-Chlor-1-phenylsulfanyl-5-hexene (566 mg, 2.50 mmol)[30] in THF (2 mL) was added and the reaction mixture was heated under reflux for 20 h. The reaction was stopped upon the addition of H_2O followed by extraction of the aqueous layer with Et_2O (2×). The combined organic layers were dried over $MgSO_4$ and the solvents were removed in vacuo. FC (pentane/$CHCl_3$ 20:1→2:1) yielded **7i** (174 mg, 20 %). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.62–7.52 (m, 2H, Ph-H), 7.39–7.17 (m, 3H, Ph-H), 5.80–5.70 (m, 1H, H_2C=C*H*), 5.19 (dd, J_1 = 9.0, J_2 = 3.9 Hz, 1H, HCO), 4.99–4.90 (m, 2H, H_2C=CH), 2.10–1.95 (m, 3H), 1.82–1.72 (m, 1H), 1.70–1.13 (m, 20H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 138.6 (CH), 135.8 (C), 132.1 (CH), 128.5 (CH), 126.5 (CH_2), 114.6 (CH_2), 93.9 (CH), 60.7 (C), 59.8 (C), 40.4 (CH_2), 34.7 (CH_3), 34.0 (CH_2), 33.5 (CH_3), 33.4 (CH_2), 25.5 (CH_2), 20.6 (2×CH_3), 17.2 (CH_2); IR ($CHCl_3$): $\tilde{\nu}$ = 2933s, 1639w, 1583w, 1377m, 1362m, 1132m, 973m, 914s cm^{-1}; MS (EI): *m*/*z*: 347 (< 1) $[M+H]^+$, 234 (10), 218 (25), 191 (33), 157 (22), 142 (24), 140 (48), 126 (85), 110 (100); elemental analysis calcd (%) for $C_{21}H_{33}NOS$ (347.56): C 72.57, H 9.57, N 4.03; found: C 72.51, H 9.53, N 3.93.

Isomerization of 7a: Applying GP 1 **7a**[7] (250 mg, 0.63 mmol), CSA (14.6 mg, 0.063 mmol) and *t*BuOH (31.5 mL) were heated for 24 h. FC (Et_2O/pentane 1:100) yielded a mixture (201 mg, 80 %) of **8a** (71 %) and **9a** (8 %). The *trans*/*cis* ratios (2.8:1 for **8a**, 1:1 for **9a**) were determined by ^{1}H NMR spectroscopy.

1-[2-(4-Bromophenyl)-cyclopentylmethoxy]-2,2,6,6-tetramethyl-piperidine (8a): ^{1}H NMR (400 MHz, $CDCl_3$): *trans*-**8a**: δ = 7.38 (d, *J* = 8.4 Hz, 2H, Ph-H), 7.10 (d, *J* = 8.3 Hz, 2H, Ph-H), 3.70–3.62 (m, 2H, H_2CO), 2.75–2.69 (m, 1H, HCPh), 2.40–0.90 (m, 25H); *cis*-**8a**: δ = 7.36 (d, *J* = 8.3 Hz, 2H, Ph-H), 7.06 (d, *J* = 8.1 Hz, 2H, Ph-H), 3.37–3.28 (m, 2H, H_2CO), 3.22–3.16 (m, 1H, HCPh), 2.47–2.42 (m, 1H), 2.20–1.00 (m, 21H), 0.86 (s, 3H, CH_3); ^{13}C NMR (100 MHz, $CDCl_3$): *trans*-**8a**: δ = 145.0 (C), 131.2 (CH), 129.2 (CH), 119.3 (C), 79.2 (CH_2), 59.7 (C), 48.8 (CH), 47.2 (CH), 39.6 (CH_2), 39.6 (CH_2), 36.0 (CH_2), 33.1 (CH_3), 33.0

(CH_3), 30.1 (CH_2), 24.7 (CH_3), 20.1 (CH_3), 17.1 (CH_2); *cis*-**8a**: $\delta = 142.3$ (C), 131.0 (CH), 130.1 (CH), 119.4 (C), 77.4 (CH_2), 59.6 (C), 59.5 (C), 46.7 (CH), 43.5 (CH), 32.8 (CH_3), 32.8 (CH_3), 30.9 (CH_2), 29.1 (CH_2), 23.7 (CH_2), 20.1 (CH_2); IR ($CHCl_3$): $\tilde{\nu} = 2933$s, 2872s, 1488s, 1374s, 1360s, 1260w, 1131s, 1074s, 1046s, 1010s cm^{-1}; MS (EI): *m*/*z*: 395 (4) $[M]^+$, 380 (38) $[M-CH_3]^+$, 171 (25), 156 (24), 142 (100); elemental analysis calcd (%) for $C_{21}H_{32}NOBr$ (394.39): C 63.95, H 8.18, N 3.55; found: C 64.07, H 8.04, N 3.23.

Isomerization of 7b: Applying GP 1 **7b**[7] (37 mg, 0.11 mmol), CSA (2.5 mg, 0.011 mmol) and *t*BuOH (5.5 mL) were heated for 24 h. FC (Et_2O/pentane 1:60) yielded a mixture (21 mg, 54%) of **8b** (46%) and **9b** (8%). The *trans*/*cis* ratios (2.8:1 for **8b**, 1:1 for **9b**) were determined by ^1H NMR spectroscopy. **10c** (10%) was isolated as a by-product.

1-[2-(4-Methoxyphenyl)-cyclopentylmethoxy]-2,2,6,6-tetramethyl-piperidine (8b): ^1H NMR (400 MHz, $CDCl_3$): *trans*-**8b**: $\delta = 7.14$ (d, $J = 8.5$ Hz, 2H, Ph-H), 6.82 (d, $J = 8.8$ Hz, 2H, Ph-H), 3.78 (s, 3H, OCH_3), 3.69 (dd, $J_1 = 8.5$, $J_2 = 5.0$ Hz, 1H, H_2CO), 3.63 (dd, $J_1 = 8.4$, $J_2 = 7.0$ Hz, 1H, H_2CO), 2.73–2.67 (m, 1H, HCPh), 2.20–1.00 (m, 25H). *cis*-**8b**: $\delta = 7.09$ (d, $J = 8.3$ Hz, 2H, Ph-H), 6.79 (d, $J = 8.8$ Hz, 2H, Ph-H), 3.78 (s, 3H, OCH_3), 3.37 (dd, $J_1 = 8.8$, $J_2 = 5.7$ Hz, 1H, H_2CO), 3.30 (dd, $J_1 = 8.6$, $J_2 = 8.6$ Hz, 1H, H_2CO), 3.22–3.16 (m, 1H, HCPh), 2.20–1.00 (m, 22H), 0.88 (s, 3H, CH_3); ^{13}C NMR (100 MHz, $CDCl_3$): *trans*-**8b**: $\delta = 157.7$ (C), 137.9 (C), 128.3 (CH), 113.6 (CH), 79.3 (CH_2), 59.7 (C), 55.3 (CH_3), 48.3 (CH), 47.3 (CH), 39.6 (CH_2), 35.9 (CH_2), 33.2 (CH_3), 33.0 (CH_3), 30.2 (CH_2), 24.6 (CH_2), 20.1 (CH_3), 17.1 (CH_2); *cis*-**8b**: $\delta = 157.6$ (C), 135.3 (C), 129.2 (CH), 113.4 (CH), 77.6 (CH_2), 59.8 (C), 55.3 (CH_3), 46.4 (CH), 43.6 (CH), 40.2 (CH_2), 32.8 (CH_3), 32.6 (CH_3), 31.0 (CH_2), 29.1 (CH_2), 23.7 (CH_2), 20.1 (CH_3); IR ($CHCl_3$): $\tilde{\nu} = 2938$s, 2871s, 1611m, 1512s, 1467s, 1374m, 1359m, 1132s, 1037s, 828s cm^{-1}; MS (EI): *m*/*z*: 345 (5) $[M]^+$, 330 (22) $[M-CH_3]^+$, 189 (76), 142 (46), 121 (100); elemental analysis calcd (%) for $C_{22}H_{35}NO_2$ (345.52): C 76.48, H 10.21, N 4.05; found: C 76.64, H 10.35, N 4.23.

Isomerization of 7c: Applying GP 1 **7c**[7] (200 mg, 0.62 mmol), CSA (14.4 mg, 0.062 mmol) and *t*BuOH (31 mL) were heated for 24 h. FC (Et_2O/pentane 1:100) yielded a mixture (156 mg, 78%) of **8c** (67%) and **9c** (11%). The *trans*/*cis* ratios (2.1:1 for **8c**, 1:1 for **9c**) were determined by ^1H NMR spectroscopy. **10c** (5%) was isolated as a by-product.

2,2,6,6-Tetramethyl-1-(2-thiophene-2-yl-cyclopentyl-methoxy)-piperidine (8c): ^1H NMR (400 MHz, $CDCl_3$): *trans*-**8c**: $\delta = 7.10$–7.08 (m, 1H, arom. H), 6.90–6.88 (m, 1H, arom. H), 6.83–6.80 (m, 1H, arom. H), 3.79 (dd, $J_1 = 8.5$, $J_2 = 5.2$ Hz, 1H, H_2CO), 3.72 (dd, $J_1 = 8.5$, $J_2 = 6.7$ Hz, 1H, H_2CO), 3.15–3.09 (m, 1H, HC_{Aryl}), 2.30–1.20 (m, 13H), 1.20–1.00 (m, 12H, CH_3); *cis*-**8c**: $\delta = 7.12$–7.08 (m, 1H, arom. H), 6.94–6.88 (m, 1H, arom. H), 6.78–6.76 (m, 1H, arom. H), 3.53–3.47 (m, 2H, H_2CO), 3.42–3.38 (m, 1H, HC_{Aryl}), 2.43–2.34 (m, 1H), 2.30–1.20 (m, 12H), 1.20–1.00 (m, 9H, CH_3), 0.93 (s, 3H, CH_3); ^{13}C NMR (100 MHz, $CDCl_3$): *trans*-**8c**: $\delta = 150.2$ (C), 126.4 (CH), 123.0 (CH), 122.4 (CH), 79.0 (CH_2), 59.8 (C), 48.1 (CH), 43.8 (CH), 40.0 (CH_2), 36.6 (CH_2), 33.2 (CH_3), 33.1 (CH_3), 29.9 (CH_2), 24.6 (CH_2), 20.2 (CH_3), 17.1 (CH_2); *cis*-**8c**: $\delta = 146.6$ (C), 126.3 (CH), 124.2 (CH), 122.9 (CH), 77.3 (CH_2), 59.6 (C), 44.1 (CH), 42.9 (CH), 39.6 (CH_2), 32.9 (CH_3), 32.7 (CH_2), 32.4 (CH_3), 28.5 (CH_2), 23.0 (CH_2), 20.2 (CH_3), 17.1 (CH_2); IR ($CHCl_3$): $\tilde{\nu} = 2934$s, 2871s, 1468s, 1375m, 1360m, 1132m, 1045m cm^{-1}; MS (EI): *m*/*z*: 321 (4) $[M]^+$, 306 (42) $[M-CH_3]^+$, 165 (70), 156 (22), 142 (100); elemental analysis calcd (%) for $C_{19}H_{31}NOS$ (321.53): C 70.98, H 9.72, N 4.36; found: C 71.21, H 9.58, N 4.34.

Isomerization of 7d: Applying GP 1 **7d**[7] (76 mg, 0.24 mmol), CSA (5.6 mg, 0.024 mmol) and *t*BuOH (12 mL) were heated for 24 h. FC (Et_2O/pentane 1:6→1:4) yielded a mixture (55 mg, 72%) of **8d** (57%) and **9d** (15%). The *trans*/*cis* ratios (1.6:1 for **8d**, 1:1 for **9d**) were determined by ^1H NMR spectroscopy. **10d** (5%) was isolated as a by-product.

2-[2-(2,2,6,6-Tetramethyl-piperidin-1-yloxymethyl)-cyclopentyl]-pyridine (8d): ^1H NMR (400 MHz, $CDCl_3$): *trans*-**8d**: $\delta = 8.55$–8.53 (m, 1H, arom. H), 7.57–7.53 (m, 1H, arom. H), 7.18–7.16 (m, 1H, arom. H), 7.08–7.04 (m, 1H, arom. H), 3.74–3.68 (m, 2H, H_2CO), 2.97–2.91 (m, 1H, HC_{Aryl}), 2.54–2.45 (m, 1H), 2.13–1.97 (m, 2H), 1.96–1.68 (m, 4H), 1.61–1.14 (m, 6H), 1.08 (s, 3H, CH_3), 1.04 (s, 3H, CH_3), 0.95 (s, 3H, CH_3), 0.93 (s, 3H, CH_3); ^{13}C NMR (100 MHz, $CDCl_3$): *trans*-**8d**: $\delta = 165.0$ (C), 149.2 (CH), 136.0 (CH), 122.6 (CH), 120.9 (CH), 79.7 (CH_2), 59.7 (C), 51.6 (CH), 46.1 (CH), 39.6 (CH_2), 34.7 (CH_2), 33.0 (CH_3), 33.0 (CH_3), 30.1 (CH_2), 25.0 (CH_2), 20.0 (CH_3), 20.0 (CH_3), 17.1 (CH_2); IR ($CHCl_3$): $\tilde{\nu} = 2935$s, 2870s, 1592s, 1474s, 1435s, 1374m, 1360m, 1132m, 1047m cm^{-1}; MS (EI): *m*/*z*: 317 (< 1) $[M+H]^+$, 301 (< 1) $[M-CH_3]^+$, 160 (100); elemental analysis calcd (%) for $C_{20}H_{32}N_2O$ (316.49): C 75.90, H 10.19, N 8.85; found: C 75.85, H 9.98, N 8.84.

Isomerization of 7e: Applying GP 1 **7e**[7] (200 mg, 0.76 mmol), CSA (17.6 mg, 0.076 mmol) and *t*BuOH (38 mL) were heated for 24 h. FC (Et_2O/pentane 1:40→1:20) yielded a mixture (135 mg, 68%) of **8e** (61%) and **9e** (7%). The *trans*/*cis* ratios (1.1:1 for **8e**, 1:1 for **9e**) were determined by ^1H NMR spectroscopy.

2-(2,2,6,6-Tetramethyl-piperidin-1-yloxymethyl)-cyclopentane-1-nitrile (8e): ^1H NMR (400 MHz, $CDCl_3$): isomer A: $\delta = 3.87$–3.83 (m, 1H, H_2CO), 3.72 (dd, $J_1 = 9.0$, $J_2 = 6.6$ Hz, 1H, H_2CO), 2.70–2.64 (m, 1H, HCCN), 2.35–2.25 (m, 1H), 2.15–1.40 (m, 12H), 1.40–1.00 (m, 12H, CH_3); isomer B: $\delta = 3.96$ (dd, $J_1 = 9.2$, $J_2 = 8.5$ Hz, 1H, H_2CO), 3.87–3.83 (m, 1H, H_2CO), 3.05–3.01 (m, 1H, HCCN), 2.47–2.38 (m, 1H), 2.15–1.40 (m, 12H), 1.40–1.00 (m, 12H, CH_3); ^{13}C NMR (100 MHz, $CDCl_3$): isomer A: $\delta = 123.0$ (C), 77.1 (CH_2), 60.0 (C), 44.8 (CH), 39.6 (CH_2), 33.3 (CH_3), 32.3 (CH), 31.2 (CH_2), 27.4 (CH_2), 22.8 (CH_2), 20.2 (2×CH_3), 20.2 (CH_3), 17.0 (CH_2); isomer B: $\delta = 121.3$ (C), 77.1 (CH_2), 59.9 (C), 42.4 (CH), 39.6 (CH_2), 33.1 (CH_3), 31.2 (CH_2), 30.8 (CH), 28.5 (CH_2), 24.6 (CH_2), 20.1 (CH_3), 20.0 (CH_3), 17.1 (CH_2); IR ($CHCl_3$): $\tilde{\nu} = 2974$s, 2935s, 2875s, 2238m, 1470m, 1453m, 1375m, 1360m, 1132s, 1049s cm^{-1}; MS (EI): *m*/*z*: 264 (6) $[M]^+$, 249 (100) $[M-CH_3]^+$, 156 (25), 142 (14); elemental analysis calcd (%) for $C_{16}H_{28}N_2O$ (264.41): C 72.68, H 10.67, N 10.59; found: C 72.51, H 10.89, N 10.59.

Isomerization of 7f: Applying GP 1 **7f** (200 mg, 0.59 mmol), CSA (13.7 mg, 0.059 mmol) and *t*BuOH (29.5 mL) were heated for 24 h. FC (Et_2O/pentane 1:60) yielded **8f** (134 mg, 67%). The *trans*/*cis* ratio (1:1) was determined by ^1H NMR spectroscopy. **10f** (10%) was isolated as a by-product.

2-(2,2,6,6-Tetramethyl-piperidin-1-yloxymethyl)-cyclopentanoic acid *tert*-butylester (8f): ^1H NMR (400 MHz, $CDCl_3$): Isomer A: $\delta = 3.81$ (dd, $J_1 = 8.6$, $J_2 = 5.3$ Hz, 1H, H_2CO), 3.61 (dd, $J_1 = 9.6$, $J_2 = 8.6$ Hz, 1H, H_2CO), 2.87–2.71 or 2.52–2.46 (m, 1H, $HCCO_2R$), 2.38–2.28 (m, 1H, $HCCH_2ON$), 2.00–1.30 (m, 12H), 1.44 (s, 9H, $C(CH_3)_3$), 1.16–1.09 (m, 12H, CH_3); isomer B: $\delta = 3.77$ (dd, $J_1 = 8.4$, $J_2 = 5.8$ Hz, 1H, H_2CO), 3.73 (dd, $J_1 = 8.4$, $J_2 = 6.4$ Hz, 1H, H_2CO), 2.87–2.71 or 2.52–2.46 (m, 1H, $HCCO_2R$), 2.38–2.28 (m, 1H, $HCCH_2ON$), 2.00–1.30 (m, 12H), 1.44 (s, 9H, $C(CH_3)_3$), 1.16–1.09 (m, 12H, CH_3); ^{13}C NMR (100 MHz, $CDCl_3$): isomer A: $\delta = 175.9$ (C), 79.7 (C), 79.0 (CH_2), 59.9 (C), 47.8 (CH), 43.4 (CH), 39.6 (CH_2), 33.1 (CH_3), 30.0 (CH_2), 28.2 (CH_2), 28.1 (CH_3), 25.4 (CH_2), 20.1 (CH_3), 17.1 (CH_2); isomer B: $\delta = 174.2$ (C), 79.9 (C), 76.9 (CH_2), 59.9 (C), 47.3 (CH), 42.4 (CH), 39.6 (CH_2), 33.1 (CH_3), 30.5 (CH_2), 29.1 (CH_2), 28.2 (CH_3), 23.3 (CH_2), 20.2 (CH_3), 17.2 (CH_2); IR ($CHCl_3$): $\tilde{\nu} = 2975$s, 2934s, 2872s, 1715s, 1471s, 1454s, 1368s, 1151s, 1047m cm^{-1}; MS (EI): *m*/*z*: 339 (1) $[M]^+$, 324 (9) $[M-CH_3]^+$, 157 (20), 142 (100), 127 (33); elemental analysis calcd (%) for $C_{20}H_{37}NO_3$ (339.52): C 70.75, H 10.98, N 4.13; found: C 70.67, H 10.79, N 4.16.

2,2,6,6-Tetramethyl-1-(1-phenyl-hex-5-enyloxy)-piperidin-4-ol (12a): Calcium ascorbate dihydrate (2.77 g, 6.50 mmol) was added to a suspension of 4-*tert*-butyldimethylsilyloxy-TEMPO (1.72 mg, 6.0 mmol) in H_2O (25 mL) and the mixture was stirred at room temperature for 15 min. H_2O was added and the reaction mixture was extracted with Et_2O (3×). The combined organic layers were dried over $MgSO_4$ and the solvent was removed in vacuo. The resulting hydroxylamine was dissolved in THF under argon and then added dropwise to a suspension of NaH (240 mg, 60%, 6.00 mmol) in THF (10 mL). The mixture was stirred for 30 min at room temperature. Afterwards a solution of 1-bromo-1-phenyl-5-hexene (703 mg, 3.00 mmol) in THF (2 mL) was added and the reaction mixture was heated under reflux for 14 h. The reaction was stopped by the addition of H_2O followed by extraction of the aqueous layer with Et_2O (2×). The combined organic layers were dried over $MgSO_4$ and the solvents were removed in vacuo. FC (Et_2O/pentane 1:130) yielded silylated-**12a** (493 mg, 37%). Desilylation was achieved by dissolving silylated-**12a** (490 mg, 1.10 mmol) in THF (13 mL) and adding TBAF·3H_2O (868 mg,

2.75 mmol) at room temperature. The mixture was stirred for 6 h. The reaction was stopped upon the addition of NH_4Cl (aq. sat.) followed by extraction (3×) of the aqueous layer with Et_2O. The combined organic layers were washed with brine, dried over $MgSO_4$ and the solvents were removed in vacuo. FC (Et_2O/pentane 2:3) yielded **12a** (336 mg, 92%). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.32–7.21 (m, 5H, Ph-H), 5.76–5.66 (m, 1H, H_2C=C*H*), 4.96–4.87 (m, 2H, H_2C=C*H*), 4.57 (dd, J_1 = 9.9, J_2 = 4.1 Hz, 1H, HCO), 3.96–3.88 (m, 1H, HCOH), 2.13–1.91 (m, 3H), 1.84–1.74 (m, 2H), 1.70–1.51 (m, 1H), 1.51–1.46 (m, 1H), 1.33 (s, 3H, CH_3), 1.22 (s, 3H, CH_3), 1.33–1.00 (m, 3H), 1.04 (s, 3H, CH_3), 0.53 (s, 3H, CH_3); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 143.4 (C), 138.7 (CH), 127.9 (CH), 127.9 (CH), 127.1 (CH), 114.5 (CH_2), 87.5 (CH), 63.3 (CH), 60.5 (C), 59.8 (C), 48.9 (CH_2), 48.9 (CH_2), 35.3 (CH_2), 34.3 (CH_3), 34.1 (CH_3), 33.7 (CH_2), 24.7 (CH_2), 21.3 (2CH_3); IR ($CHCl_3$): $\tilde{\nu}$ = 3604m, 3440br, 2975s, 2940s, 1639m, 1456s, 1363s, 1046s, 1027m, 996m, 913m cm^{-1}; MS (EI): *m*/*z*: 316 (< 1) $[M-CH_3]^+$, 173 (29), 158 (100), 117 (35); elemental analysis calcd (%) for $C_{21}H_{33}NO_2$ (331.50): C 76.09, H 10.03, N 4.23; found: C 76.17, H 9.89, N 4.26.

2,2,6,6-Tetramethyl-1-(2-phenyl-cyclopentylmethyl)-piperidin-4-ol (12b): GP 1 was applied by using alkoxyamine **12a** (200 mg, 0.60 mmol) and CSA (13.0 mg, 0.06 mmol) in *t*BuOH (30 mL) at 130°C for 14 h. The desired isomerization product could be isolated after FC (Et_2O/pentane 1:2) in an overall yield of 73% (*exo*/*endo* 12.2:1, *trans*/*cis* (**12b**) 2.2:1). M.p. 94–95°C. ^{1}H NMR (400 MHz, $CDCl_3$): *trans*-**12b**: δ = 7.31–7.12 (m, 5H, Ph-H), 3.92–3.87 (m, 1H, *H*COH), 3.70 (dd, J_1 = 8.6, J_2 = 5.4 Hz, 1H, HCON), 3.65 (dd, J_1 = 8.5, J_2 = 6.8 Hz, 1H, HCON), 2.77–2.70 (m, 1H, HC-Ph), 2.50–1.00 (m, 23H, CH, CH_2, CH_3); *cis*-**12b**: δ = 7.31–7.12 (m, 5H, Ph-H), 3.92–3.87 (m, 1H, *H*COH), 3.37 (dd, J_1 = 8.8, J_2 = 5.9 Hz, 1H, HCON), 3.65 (dd, J_1 = 8.7, J_2 = 8.7 Hz, 1H, HCON), 3.27–3.21 (m, 1H, HC-Ph), 2.50–1.00 (m, 22H, CH, CH_2, CH_3), 0.87 (s, 1H, CH_3); ^{13}C NMR (100 MHz, $CDCl_3$): *trans*-**12b**: δ = 145.7 (C), 128.2 (CH), 127.4 (CH), 125.8 (CH), 79.5 (CH_2), 63.3 (CH), 60.1 (C), 60.0 (C), 49.3 (CH), 48.3 (CH_2), 47.1 (CH), 35.9 (CH_2), 33.2 (CH_3), 33.0 (CH_3), 30.2 (CH_2), 24.7 (CH_2), 21.0 (CH_3); *cis*-**12b**: δ = 143.1 (C), 128.4 (CH), 127.4 (CH), 125.7 (CH), 77.6 (CH_2), 63.3 (CH), 59.9 (C), 59.8 (C), 48.3 (CH_2), 47.2 (CH), 35.9 (CH_2), 32.8 (CH_3), 32.6 (CH_3), 30.9 (CH_2), 29.2 (CH_2), 23.7 (CH_2), 21.0 (CH_3); IR ($CHCl_3$): $\tilde{\nu}$ = 3606m, 3428br, 2941s, 2872m, 1601w, 1492w, 1453m, 1375s, 1364s, 1044s, 1027s, 952m, 897w cm^{-1}; MS (EI): *m*/*z*: 331 (8) $[M]^+$, 316 (42) $[M-CH_3]^+$, 173 (41) $[M-C_{12}H_{14}]^+$, 158 (100) $[M-ONC_9H_{18}OH]^+$, 91 (68); elemental analysis calcd (%) for $C_{21}H_{33}NO_2$ (331.50): C 76.09, H 10.03, N 4.32; found: C 76.02, H 10.24, N 4.27.

***N*,*N*-Di-*tert*-butyl-*O*-(1-phenyl-hex-5-enyl)-hydroxylamine (13a)**: Calcium ascorbate dihydrate (1.194 g, 2.80 mmol) was added to a suspension of *N*,*N*-di-*tert*-butylnitroxide (403 mg, 2.80 mmol) in water (10 mL). The mixture was stirred at room temperature for 15 min. After the addition of water and extraction with Et_2O (2×) evaporation of the solvent led to the corresponding hydroxylamine which was then dissolved in THF under argon. The solution was added slowly to a suspension of NaH (112 mg, 60%, 2.80 mmol) in THF (5 mL) prior to the addition of a solution of 1-bromo-1-phenyl-5-hexene (300 mg, 1.28 mmol) in THF (1 mL). The reaction mixture was heated to reflux for 44 h. After the addition of water the mixture was extracted with Et_2O twice and the combined organic layers was dried over $MgSO_4$. Evaporation of the solvent in vacuo and purification with FC (Et_2O/pentane 1:120) yielded alkoxyamine **13a** (185 mg, 24%). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.35–7.20 (m, 5H, Ph-H), 5.76–5.66 (m, 1H, C*H*=CH_2), 4.96–4.87 (m, 2H, CH=CH_2), 4.60 (dd, J_1 = 3.9, J_2 = 10.3 Hz, 1H, HCO), 2.21–2.12 (m, 1H), 2.07–1.91 (m, 2H), 1.83–1.73 (m, 1H), 1.31 (s, 9H, $C(CH_3)_3$), 1.20–1.00 (m, 2H), 0.97 (s, 9H, $C(CH_3)_3$); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 143.10 (C), 138.79 (CH), 128.29 (CH), 127.82 (CH), 127.13 (CH), 114.39 (CH_2), 87.44 (CH), 62.07 (C), 61.68 (C), 34.47 (CH_2), 33.79 (CH_2), 30.70 (CH_3), 30.62 (CH_3), 25.13 (CH_2); IR ($CHCl_3$): $\tilde{\nu}$ = 2971s, 2931s, 2861w, 1639w, 1494m, 1453m, 1386m, 1362s, 976m, 912s cm^{-1}; MS (FAB): *m*/*z*: 304.3 (25) $[M+H]^+$, 248.3 (26), 159.2 (83), 145.2 (100), 128.1 (40), 117.0 (28); elemental analysis calcd (%) for $C_{20}H_{33}NO$ (303.49): C 79.15, H 10.96, N 4.62; found: C 79.24, H 11.02, N 4.51.

***N*,*N*-Di-*tert*-butyl-*O*-(2-phenyl-cyclopentylmethyl)-hydroxylamine (13b)**: According to GP 1 alkoxyamine **13a** (60 mg, 0.198 mmol) was isomerized in *t*BuOH (10 mL) at 130–132°C in 3 h. The crude product was purified by FC (Et_2O/pentane 1:120) and the isomerization product was isolated in an overall yield of 87% (*exo*/*endo* 13.5:1, *trans*/*cis* (**13b**) 2.2:1). ^{1}H NMR (400 MHz, $CDCl_3$): *trans*-**13b**: δ = 7.30–7.10 (m, 5H, Ph-H), 3.69–3.62 (m, 2H, OCH_2), 2.70–2.64 (m, 1H, HC-Ph), 2.25–2.15 (m, 1H, OCH_2CH), 2.12–1.50 (m, 6H, CH_2), 1.16 (s, 9H, $C(CH_3)_3$), 1.10 (s, 9H, $C(CH_3)_3$); *cis*-**13b**: δ = 7.30–7.10 (m, 5H, Ph-H), 3.36–3.19 (m, 3H, OCH_2, HCPh), 2.12–1.50 (m, 7H, OCH_2CH,CH_2), 1.15 (s, 9H, $C(CH_3)_3$), 1.05 (s, 9H, $C(CH_3)_3$); ^{13}C NMR (100 MHz, $CDCl_3$): *trans*-**13b**: δ = 145.8 (C), 128.2 (CH), 127.4 (CH), 125.7 (CH), 79.7 (CH_2), 62.4 (C), 62.2 (C), 49.5 (CH), 47.0 (CH), 35.7 (CH_2), 30.7 (CH_2), 29.9 (CH_3), 29.8 (CH_3), 24.7 (CH_2); *cis*-**13b**: δ = 128.3 (CH), 128.0 (CH), 126.9 (CH), 77.2 (CH_2), 62.3 (C), 62.2 (C), 47.3 (CH), 43.3 (CH), 30.7 (CH_2), 29.9 (CH_3), 29.7 (CH_3), 29.3 (CH_2), 23.6 (CH_2); IR ($CHCl_3$): $\tilde{\nu}$ = 3008m, 2940s, 2868m, 1703s, 1450m, 1361m, 1312m, 1120m, 1053w, 1018m, 913m cm^{-1}; MS (FAB): *m*/*z*: 303 (100) $[M]^+$, 248 (91) $[M-C_4H_7]^+$, 232 (94), 159 (93) $[M-ONC_8H_{18}]^+$, 145 (87) $[M-C_{12}H_{14}]^+$, 90 (98), 71 (96); elemental analysis calcd (%) for $C_{20}H_{33}NO$ (303.49): C 79.15, H 10.96, N 4.62; found: C 79.11, H 10.97, N 4.41.

{1-[*tert*-Butyl-(1-phenyl-hex-5-enyloxy)-amino]-2,2-dimethyl-propyl}-phosphonic acid dimethylester (14a): GP 2 was applied by using (1-bromo-hex-5-enyl)-benzene (235 mg, 1.00 mmol), corresponding nitroxide[17] (303 mg, 1.20 mmol), Cu (67 mg, 1.05 mmol), $Cu(OTf)_2$ (3.5 mg, 10 μmol) and 4,4′-di-*tert*-butyl-[2,2′]bispyridine (1 mg, 40 μmol) in benzene (1.5 mL) for 22 h at 70°C. FC (Et_2O/pentane 1:2) yielded **14a** (77 mg, 19%) as a mixture of diastereoisomers. ^{1}H NMR (400 MHz, $CDCl_3$): isomer A: δ = 7.45–7.43 (m, 2H, Ph-H), 7.33–7.20 (m, 3H, Ph-H), 5.76–5.64 (m, 1H, H_2C=C*H*), 5.00–4.82 (m, 3H, H_2C=CH, HCO), 3.51 (d, J_{HP} = 11.1 Hz, 3H, OCH_3), 3.41 (d, J_{HP} = 26.1 Hz, 1H, HCP), 2.97 (d, J_{HP} = 11.4 Hz, 3H, OCH_3), 2.65–2.57 (m, 1H), 2.10–1.95 (m, 2H), 1.75–1.50 (m, 2H), 1.10–0.90 (m, 1H), 1.20 (s, 9H, $C(CH_3)_3$), 1.18 (s, 9H, $C(CH_3)_3$); isomer B: δ = 7.33–7.20 (m, 5H, Ph-H), 5.76–5.64 (m, 1H, H_2C=C*H*), 5.00–4.82 (m, 2H, H_2C=CH), 4.74 (dd, J_1 = 11.9, J_2 = 3.3 Hz, 1H, HCO), 3.86 (d, J_{HP} = 11.2 Hz, 3H, OCH_3), 3.64 (d, J_{HP} = 11.0 Hz, 3H, OCH_3), 3.35 (d, J_{HP} = 26.0 Hz, 1H, HCP), 2.76–2.67 (m, 1H), 2.00–1.80 (m, 2H), 1.75–1.50 (m, 2H), 1.10–0.90 (m, 1H), 1.22 (s, 9H, $C(CH_3)_3$), 0.82 (s, 9H, $C(CH_3)_3$); ^{13}C NMR (100 MHz, $CDCl_3$): isomer A: δ = 141.7 (C), 138.8 (CH), 128.8 (CH), 127.9 (CH), 114.4 (CH_2), 83.5 (CH), 70.2 (d, J = 139.2 Hz, CH), 61.4 (C), 52.9 (d, J = 6.2 Hz, CH_3), 49.1 (d, J = 7.5 Hz, CH_3), 35.2 (d, J = 5.1 Hz, C), 34.0 (CH_2), 33.0 (CH_2), 28.5 (CH_3), 28.1 (CH_3), 24.7 (CH_2); isomer B: δ = 143.5 (C), 138.9 (CH), 128.0 (CH), 127.7 (CH), 127.2 (CH), 114.2 (CH_2), 90.5 (CH), 70.0 (d, J = 138.1 Hz, CH), 61.2 (C), 53.0 (d, J = 7.4 Hz, CH_3), 36.1 (CH_2), 35.7 (d, J = 6.1 Hz, C), 33.6 (CH_2), 30.6 (CH_2), 30.5 (CH_3), 29.9 (CH_3), 25.4 (CH_2); IR ($CHCl_3$): $\tilde{\nu}$ = 2979s, 1639w, 1454m, 1394m, 1365s, 1070s, 1035s, 914m cm^{-1}; MS (FAB): *m*/*z*: 426 (89) $[M+H]^+$, 316 (36), 267 (56), 210 (44), 158 (100), 154 (30); elemental analysis calcd (%) for $C_{23}H_{40}NO_4P$ (425.55): C 64.92, H 9.47, N 3.29; found: C 65.08, H 9.61, N 3.26.

{1-[*tert*-Butyl-(2-phenyl-cyclopentylmethoxy)-amino]-2,2-dimethyl-propyl}-phosphonic acid dimethyl ester (14b): Applying a variation of GP 2 a solution of alkoxyamine **14a** in *t*BuOH (6.3 mL, 0.05 M) was heated to 130°C for 4.5 h. FC (Et_2O/pentane 1:2) yielded the desired cyclization product as a mixture of **14b** and **14c** (102 mg, 80%). ^{1}H NMR (400 MHz, $CDCl_3$) (4 isomers): δ = 7.27–7.22 (m, 5H, Ph-H), 4.23–4.04 (m, 1H, OCH_2), 3.81–3.35 (m, 7H, OCH_2, OCH_3), 3.21–3.10 (m, 1H, PCH), 2.64–1.35 (m, 8H, CH, CH_2), 1.19–0.94 (m, 18H, CH_3); due to its complexity (4 isomers) the ^{13}C NMR spectrum was not interpreted; IR ($CHCl_3$): $\tilde{\nu}$ = 3400br, 2956s, 2873w, 1601w, 1468s, 1392m, 1365s, 1070s, 1032s cm^{-1}; MS (FAB): *m*/*z*: 426 (11) $[M+H]^+$, 368 (18) $[M-C_4H_9]^+$, 316 (100) $[M-C_2H_6O_3P]^+$, 260 (81), 210 (20); elemental analysis calcd (%) for $C_{23}H_{40}NO_4P$ (425.55): C 64.92, H 9.47, N 3.29; found: C 64.86, H 9.50, N 3.22.

The syntheses of alkoxyamines **15a**, **16a** and **17a** have previously been published.[7]

***N*-*tert*-Butyl-*N*-(2-methyl-1-phenyl-propyl)-*O*-(2-phenyl-cyclopentyl-methyl)-hydroxylamine (15b)**: Applying a variation of GP 1 a solution of alkoxyamine **15a** (350 mg, 0.92 mmol) and CSA (20.1 mg, 0.092 mmol) in *t*BuOH (1.75 mL, 0.05 M) was heated in a sealed tube to 130°C for 8 h.

FC (pentane/MTBE 20:1) yielded **15b** as a colourless oil (338 mg, 97%). **15b** was isolated as an unseparable mixture of diastereoisomers. Due to the complexity of the ^{1}H NMR spectrum the diastereomeric ratio could not be determined. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.20–7.10 (m, 10H, Ph-H), 3.89–3.12 (m, 4H, CH_2ON, PhCH), 2.74–0.28 (m, 23H); ^{13}C NMR (75 MHz, $CDCl_3$): δ = 145.6, 142.8, 131.1, 130.9, 129.4, 128.3, 127.4, 126.9, 126.2, 125.8, 79.5, 72.3, 72.1, 60.0, 49.2, 47.1, 35.9, 31.4, 30.9, 28.4, 27.6, 24.7, 21.9, 21.1; IR (neat): $\tilde{\nu}$ = 3061w, 2954s, 2869m, 1491w, 1452m, 1384m, 1359m, 1213w, 1040w, 756m, 701s cm^{-1}; MS (ESI): *m*/*z*: 411 (100), 380 (47) $[M+H]^+$, 325 (54), 222(82); HRMS (ESI): *m*/*z*: calcd for $C_{26}H_{38}NO$: 380.2953; found: 380.2953 $[M+H]^+$.

2-Methyl-2-[(1-methyl-1-phenyl-ethyl)-(2-phenyl-cyclopentylmethoxy)-amino]-propane-1-ol (16b): A solution of alkoxyamine **16a** (102 mg, 0.258 mmol) and CSA (6 mg, 0.026 mmol) in *t*BuOH (13 mL) was heated under argon in a sealed tube to 130°C for 7.5 h. Evaporation of the solvent and purification by FC (Et_2O/pentane 1:20→1:10) yielded the isomerization product (74 mg, 73%). Due to their complexity (4 isomers) the ^{1}H NMR spectrum and the ^{13}C NMR spectrum were not interpreted. IR ($CHCl_3$): $\tilde{\nu}$ = 3482br, 3007w, 2957s, 2871m, 1601w, 1492m, 1452s, 1409m, 1383s, 1365m, 1322w, 1162m, 1042s cm^{-1}; MS (MALDI): *m*/*z*: 418 (23) $[M+Na]^+$, 264 (42), 200 (100); HRMS (MALDI): *m*/*z*: calcd for $C_{26}H_{37}NO_2Na$: 418.2716; found: 418.2712 $[M+Na]^+$; elemental analysis calcd (%) for $C_{26}H_{37}NO_2$ (395.58): C 78.94, H 9.43, N 3.54; found: C 78.78, H 9.49, N 3.55.

2-Hydroxymethyl-2-[(1-methyl-1-phenyl-ethyl)-(2-phenyl-cyclopentylmethoxy)-amino]-propane-1,3-diol (17b): The isomerization was performed according to GP 1 by using alkoxyamine **17a**, CSA and *t*BuOH. FC (Et_2O/pentane 1:2) yielded the cyclization product **17b**. Due to their complexity (4 isomers) the ^{1}H NMR spectrum and the ^{13}C NMR spectrum were not interpreted. IR ($CHCl_3$): $\tilde{\nu}$ = 3503br, 2960s, 2872m, 1601m, 1496w, 1452m, 1385m, 1111m, 1045s, 881w cm^{-1}; MS (FAB): *m*/*z*: 450 (8) $[M+Na]^+$, 428 (88) $[M+H]^+$, 396 (31) $[M-CH_2OH]^+$, 384 (63) $[M-C_3H_7]^+$, 296 (32) $[M-C_{10}H_{11}]^+$, 264 (35), 133 (100) $[M-C_{12}H_{15}ONC_4H_9O_3]^+$, 90 (75).

***N*-(1,1-Diethylpropyl)-*N*-(2-methyl-1-phenylpropyl)-*O*-(1-phenylhex-5-enyl)hydroxylamine (18a)**: GP 2 was applied by using (1-bromo-hex-5-enyl)-benzene (137 mg, 0.57 mmol), the corresponding nitroxide[16] (150 mg, 0.57 mmol), Cu (36 mg, 0.57 mmol), $Cu(OTf)_2$ (10.0 mg, 29 μmol) and 4,4′-di-*tert*-butyl-[2,2′]bipyridine (15.0 mg, 0.114 mmol) in benzene (2.0 mL) for 14 h at 75°C. FC (Et_2O/pentane 1:250) yielded **18a** (162 mg, 67%) as a mixture of diastereoisomers (*dr* 1:1, determined by ^{1}H NMR analysis). ^{1}H NMR (400 MHz, $CDCl_3$): isomer A: δ = 7.41–7.14 (m, 10H, CH), 5.79–5.68 (m, 1H, CH), 5.01–4.90 (m, 2H, CH_2), 4.68 (dd, J_1 = 10.8, J_2 = 3.7 Hz, 1H, CH), 3.88 (d, J = 7.0 Hz, 1H, CH), 2.42–1.04 (m, 13H), 0.94–0.17 (m, 15H); isomer B: δ = 7.41–7.14 (m, 10H, CH), 5.79–5.68 (m, 1H, CH), 5.01–4.90 (m, 2H, CH_2), 4.63 (dd, J_1 = 10.8, J_2 = 3.7 Hz, 1H, CH), 3.42 (d, J = 7.0 Hz, 1H, CH), 2.42–1.04 (m, 13H), 0.94–0.17 (m, 15H); ^{13}C NMR (100 MHz, $CDCl_3$): both isomers: δ = 145.4 (C), 143.7 (C), 143.2 (C), 138.6 (C), 128.7 (CH), 128.5 (CH), 128.1 (CH), 127.9 (CH), 127.2 (CH), 126.9 (CH), 126.0 (CH), 125.8 (CH), 114.5 (CH_2), 114.4 (CH_2), 87.8 (CH), 87.3 (CH), 71.2 (CH), 70.8 (CH), 67.2 (C), 67.0 (C), 36.4 (CH_2), 36.3 (CH_2), 35.4 (CH), 35.3 (CH), 27.2 (CH_2), 27.1 (CH_2), 25.2 (CH_2), 25.0 (CH_2), 24.6 (CH_3), 24.5 (CH_3), 22.2 (CH_3), 22.1 (CH_3), 9.0 (CH_3), 8.9 (CH_3); IR (neat): $\tilde{\nu}$ = 3442br, 3061w, 3026w, 2956s, 2873m, 1601w, 1492w, 1453m, 1382w, 1029m cm^{-1}; MS (ESI): *m*/*z*: 422 (27) $[M+H]^+$, 409 (100); HRMS (ESI): *m*/*z*: calcd for $C_{29}H_{44}NO$: 422.3423; found: 422.3414 $[M+H]^+$.

***N*-(1,1-Diethylpropyl)-*N*-(2-methyl-1-phenylpropyl)-*O*-(2-phenylcyclopentylmethyl)hydroxylamin (18b)**: Applying GP 1 a solution of alkoxyamine **18a** (71.5 mg, 0.170 mol) in *t*BuOH (8.5 mL) was heated for 20 min. FC (Et_2O/pentane 1:200) yielded the cyclization product (64.1 mg, 90%). ^{1}H NMR (200 MHz, $CDCl_3$): *trans*-**18b**: δ = 7.39–7.17 (m, 10H, Ph-H), 3.90–3.87 (m, 1H, CH), 3.78–3.67 (m, 2H, CH_2), 3.51–3.40 (m, 1H, CH), 2.35–1.12 (m, 14H), 0.93–0.35 (m, 15H, CH_3); *cis*-**18b**: δ = 7.39–7.17 (m, 10H, Ph-H), 3.90–3.87 (m, 1H, CH), 3.51–3.40 (m, 2H, CH_2), 3.34–3.11 (m, 1H, CH), 2.35–1.12 (m, 14H), 0.93–0.35 (m, 15H, CH_3); ^{13}C NMR (50 MHz, $CDCl_3$): mixture of isomers: δ = 145.4 (C), 143.8 (C), 130.4 (CH), 128.3 (CH), 128.2 (CH), 127.4 (CH), 127.3 (CH), 127.2 (CH), 126.2 (CH), 125.9 (CH), 79.2 (CH_2), 78.9 (CH_2), 71.1 (CH), 71.0 (CH), 67.1 (C), 66.9 (C), 49.1 (CH), 47.5 (CH), 47.1 (CH), 35.7 (CH), 35.6 (CH), 32.2 (CH_2), 32.0 (CH_2), 31.1 (CH_2), 30.8 (CH_2), 27.3 (CH_2), 27.1 (CH_2), 24.6 (CH_3), 24.5 (CH_3), 22.2 (CH_3), 22.1 (CH_3), 21.4 (CH_2), 8.7 (CH_3); IR (neat): $\tilde{\nu}$ = 3026w, 2955s, 2872s, 1644s, 1492m, 1452s, 1382m, 1029m cm^{-1}; MS (ESI): *m*/*z*: 481 (100), 444 (14) $[M+Na]^+$, 437 (78); HRMS (ESI): *m*/*z*: calcd for $C_{29}H_{43}NNaO$: 444.3242; found: 444.3249 $[M+Na]^+$.

2,2,7,7-Tetramethyl-1-(1-phenylhex-5-enyloxyl)[1,4]diazepane-5-one (19a): GP 2 was applied by using (1-bromo-hex-5-enyl)-benzene (253 mg, 1.06 mmol), the corresponding nitroxide (150 mg, 0.57 mmol), Cu (72 mg, 1.12 mmol), $Cu(OTf)_2$ (4.0 mg, 10.6 μmol) and 4,4′-di-*tert*-butyl-[2,2′]bipyridine (7.0 mg, 42.4 μmol) in benzene (4.0 mL) for 14 h at 75°C. FC (ethyl acetate/MeOH 30:1) yielded **19a** (169 mg, 39%). ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.33–7.23 (m, 5H, Ph-H), 6.94 (1H, NH), 5.75–5.63 (m, 1H, H_2C=C*H*), 4.96–4.88 (m, 2H, *H*$_2$C=CH), 4.60 (dd, J_1 = 10.6, J_2 = 3.9 Hz, 1H, OCH), 3.40–3.18 (m, 1H, NCH_2), 2.96–2.67 (m, 2H, NCH_2, $OCCH_2$), 2.44–2.05 (m, 1H, OCH_2), 2.31–1.80 (m, 4H, CH_2), 1.44–1.03 (m, 12H, CH_2, CH_3), 0.70 (brs, 1H, CH_3), 0.60 (brs, 1H, CH_3); ^{13}C NMR (75 MHz, $CDCl_3$): δ = 175.7 (C), 143.8 (C), 138.5 (CH), 128.0 (CH), 127.4 (CH), 114.6 (CH_2), 87.9 (CH), 63.5 (C), 61.8 (C), 51.0 (CH_2), 47.2 (CH_2), 34.8 (CH_2), 34.2 (CH_3), 33.6 (CH_2), 30.1 (CH_3), 24.7 (CH_2), 22.8 (CH_3), 20.4 (CH_3); IR (neat): $\tilde{\nu}$ = 3426br, 3214m, 3081w, 2078w, 2949m, 1676s, 1493w, 1434w, 1381m, 1247m cm^{-1}; MS (ESI): *m*/*z*: 367 (33) $[M+Na]^+$, 345 (100) $[M+H]^+$, 255 (17), 227 (21), 195 (28); HRMS (ESI): *m*/*z*: calcd for $C_{21}H_{33}N_2O_2$: 345.2542; found: 345.2540 $[M+H]^+$.

2,2,7,7-Tetramethyl-1-(-2-phenyl-cyclopentylmethyloxy)-[1,4]diazepan-5-one (19b), 2,2,7,7-tetramethyl-1-(-2-phenyl-cyclohexyloxy)-[1,4]diazepan-5-one (19c): According to GP 1 a solution of alkoxyamine **19a** (25 mg, 0.073 mmol) and CSA (1.8 mg, 0.0073 mmol) in *t*BuOH (3.65 mL, 0.02 M) was heated to 130°C for 36 h. The reaction was not yet completed and the products could not be separated from the starting material. Due to the complexity of the NMR spectra (starting material **19a**, 2 isomers of **19b**, 2 isomers of **19c**) the reaction product was not analyzed.

2,2,7,7-Tetramethyl-1-(1-phenyl-hex-5-enyloxy)-azepane-4-one (20a): GP 2 was applied by using the corresponding nitroxide[13] (527 mg, 2.86 mmol), (1-bromo-hex-5-enyl)-benzene (570 mg, 2.38 mmol), $Cu(OTf)_2$ (8.6 mg, 0.024 mmol), Cu (159 mg, 2.50 mmol) and 4,4′-di-*tert*-butyl-[2,2′]bipyridine (12.8 mg, 0.095 mmol). FC (pentane/MTBE 4:1) yielded alkoxyamine **20a** as a yellowish oil (204 mg, 25%). ^{1}H NMR (300 MHz, $CDCl_3$): both isomers: δ = 7.23–7.19 (m, 5H, Ph-H), 5.70–5.57 (m, 1H, CH_2=C*H*), 4.90–4.82 (m, 2H, C*H*$_2$=CH), 4.51 (dd, J_1 = 3.6, J_2 = 9.9, 1H, CHON), 2.86 (d, J = 11.6 Hz, 1H, CHC=O, single isomer), 2.72 (d, J = 11.6 Hz, 1H, CHC=O, single isomer), 2.39 (d, J = 11.6 Hz, 1H, CHC=O, single isomer), 2.24 (d, J = 11.6 Hz, 1H, CHC=O, single isomer), 2.13–1.60 (m, 8H, CH_2), 1.42–1.06 (m, 11H, CH_2, CH_3), 0.69, 0.55 (2s, 3H, CH_3, both isomers); ^{13}C NMR (75 MHz, $CDCl_3$): both isomers: δ = 211.4, 211.2, 142.1, 138.3, 128.2, 127.7, 127.2, 125.7, 114.4, 87.1, 63.4, 62.2, 37.7, 36.3, 36.0, 33.9, 33.4, 32.5, 32.3, 25.1, 24.7, 24.3; IR (film): $\tilde{\nu}$ = 2974s, 2937s, 1714s, 1454m, 1363m, 911m, 700s cm^{-1}; MS (ESI): *m*/*z*: 366 (33) $[M+Na]^+$, 207 (100); HRMS (ESI): *m*/*z*: calcd for $C_{22}H_{33}NNaO_2$: 366.2409; found: 366.2396 $[M+Na]^+$.

2,2,7,7-Tetramethyl-1-(2-phenyl-cyclopentylmethoxy)-azepan-4-one (20b), 2,2,7,7-tetramethyl-1-(3-phenyl-cyclohexyloxy)-azepan-4-one (20c): According to GP 1 a solution of alkoxyamine **20b** (90.0 mg, 0.26 mmol) and CSA (5.70 mg, 0.026 mmol) in *t*BuOH (0.02 M) was heated in a sealed tube to 130°C for 20 h. FC (pentane/MTBE 4:1) yielded the desired product as a yellow oil (66.0 mg, 0.19 mmol, 74%). The isomerization product was isolated as an unseparable mixture of **20b** (two diastereoisomers) and **20c** (due to the complexity of the NMR spectra the product ratios could not be determined). ^{1}H NMR (200 MHz, $CDCl_3$): δ = 7.22–7.07 (m, 5H, Ph-H), 3.68–3.46 (m, 2H, CH_2ON), 3.25–3.07 (m, 1H, CHPh), 2.79–0.82 (m, 25H, CH_2, CH, CH_3); IR (neat): $\tilde{\nu}$ = 2946s, 2873s, 1710s, 1493m, 1451m, 1363m, 1222m, 1031s, 759m, 703s cm^{-1}; MS (ESI): *m*/*z*: 366 (100) $[M+Na]^+$, 344 (21) $[M+H]^+$, 288 (10), 242 (31), 232 (11); HRMS (ESI): *m*/*z*: calcd for $C_{22}H_{34}NO_2$: 344.2590; found: 344.2588 $[M+H]^+$.

2,2,7,7-Tetramethyl-1-(1-phenyl-5-hexenyloxy)-azepan-4-ol (21a): A solution of alkoxyamine **20a** (500 mg, 1.46 mmol) in MeOH (50 mL) with molecular sieves (3) Å) was cooled to 0 °C and $NaBH_4$ (275 mg, 7.28 mmol) was added portionwise. After gas development ceased MeOH (70 mL) was added to dissolve the solid formed. The solution was stirred at room temperature for 24 h prior to the addition of NH_4Cl (aq. sat., 30 mL). The resulting suspension was filtered, washed with Et_2O (3×30 mL) and the combined organic layers were dried over $MgSO_4$. Evaporation of the solvent and purification by FC (pentane/MTBE 4:1) yielded **21a** as a yellow oil (450 mg, 89 %). Alkoxyamine **21a** was isolated as an unseparable mixture of diastereoisomers. Due to the complexity of the NMR spectra the diastereomeric ratios could not be determined. ^{1}H NMR (300 MHz, $CDCl_3$): $\delta=7.33$–7.19 (m, 5H, Ph-H), 5.77–5.62 (m, 1H, CH_2=C*H*), 5.47–5.26 (m, 1H, OH, both isomers), 4.96–4.88 (m, 2H, CH_2=CH), 4.62–4.53 (m, 1H, CHON), 4.08–3.93 (m, 1H, C*H*OH), 2.36–1.01 (m, 21H, CH_2, CH_3), 0.72, 0.64, 0.53 (3s, 3H, CH, both isomers); IR (neat): $\tilde{\nu}$ = 3352m, 2936s, 1478m, 1454m, 1361s, 1160m, 911m, 700m cm^{-1}; MS (ESI): *m*/*z*: 346 (100) $[M+H]^+$, 188 (34), 171 (30).

2,2,7,7-Tetramethyl-1-(2-phenyl-cyclopentylmethoxy)-azepan-4-ol (21b), 2,2,7,7-tetramethyl-1-(2-phenyl-cyclohexyloxy)-azepan-4-ol (21c): According to GP 1 a solution of alkoxyamine **21a** (79.0 mg, 0.23 mmol) and CSA (5.00 mg, 0.023 mmol) in *t*BuOH (0.02 M) was heated to 130 °C for 3 h. FC (pentane/MTBE 4:1) yielded the isomerization product as a yellow oil (60.0 mg, 75 %). Both **21b** (*cis* and *trans* isomers) and **21c** were observed. Due to the complexity of the NMR spectra the product ratios could not be determined. ^{1}H NMR (200 MHz, $CDCl_3$): $\delta=7.24$–7.09 (m, 5H, Ph-H), 4.92 (brs, 1H, OH), 3.99–3.60 (brm, 3H, C*H*OH, CH_2ON), 3.42–3.17 (m, 1H, PhCH), 2.76–0.93 (m, 25H); IR (neat): $\tilde{\nu}$ = 3359brm, 2936s, 2871s, 1474m, 1451m, 1359m, 1238w, 1161m, 1036s, 755m, 699s cm^{-1}; MS (ESI): *m*/*z*: 368 (18) $[M+Na]^+$, 346 (100) $[M+H]^+$, 328 (13), 290 (7), 242 (25), 192 (10), 171 (8).

2,2,6,6-Tetraethyl-1-(1-phenylhex-5-enyloxy)-piperidin-4-ol (22a): GP 2 was applied by using (1-bromo-hex-5-enyl)-benzene (281 mg, 1.17 mmol), corresponding nitroxide[15] (295 mg, 1.29 mmol), Cu (78 mg, 1.23 mmol), $Cu(OTf)_2$ (9.4 mg, 0.026 mmol) and 4,4′-di-*tert*-butyl-[2,2′]bipyridine (13.8 mg, 0.103 mmol) in benzene (4.0 mL) for 14 h at 75 °C. FC (Et_2O/pentane 1:3) yielded **22a** (146 mg, 32 %). ^{1}H NMR (200 MHz, $CDCl_3$): $\delta=7.30$–7.11 (m, 5H, Ph-H), 5.76–5.62 (m, 1H, H_2C=C*H*), 4.97–4.87 (m, 2H, H_2C=CH), 4.73 (s, 1H, OH), 4.49 (dd, $J_1=10.1$, $J_2=3.4$ Hz, 1H, NOCH), 4.01–3.79 (m, 1H, HOC*H*), 2.14–0.58 (m, 30H, CH_2, CH_3); ^{13}C NMR (50 MHz, $CDCl_3$): $\delta=138.6$ (C), 128.2 (CH), 127.3 (CH), 127.0 (CH), 125.7 (CH), 114.4 (CH_2), 86.0 (CH), 65.4 (C), 65.0 (C), 62.5 (CH), 39.9 (CH_2), 39.6 (CH_2), 35.7 (CH_2), 33.6 (CH_2), 30.3 (CH_2), 30.1 (CH_2), 29.5 (CH_2), 29.1 (CH_2), 24.6 (CH_2), 10.2 (CH_3), 10.0 (CH_3), 8.2 (CH_3), 8.0 (CH_3); IR (neat): $\tilde{\nu}$ = 3325br, 3027w, 2959s, 2877s, 1942w, 1803w, 1640w, 1603w, 1493m, 1464s, 1377m cm^{-1}; MS (ESI): *m*/*z*: 410 (27) $[M+Na]^+$, 388 (82) $[M+H]^+$, 372 (77), 260 (41), 242 (72), 184 (100); HRMS (ESI): *m*/*z*: calcd for $C_{25}H_{42}NO_2$: 388.3216; found: 388.3209 $[M+H]^+$.

2,2,6,6-Tetraethyl-1-(2-phenylcyclopentylmethoxy)-piperidin-4-ol (22b), 2,2,6,6-tetraethyl-1-(3-phenylcyclohexyloxy)-piperidin-4-ol (22c): GP 1 was applied by using alkoxyamine **22a** (49.0 mg, 0.133 mmol) in *t*BuOH (6.6 mL) for 15 min. FC (Et_2O/pentane 1:3) yielded the products **22b** and **22c** (48.1 mg, 95 %) as mixture of isomers (**22b**/**22c** 12.5:1; **22b**: *trans*/*cis* 2.7:1). ^{1}H NMR (500 MHz, $CDCl_3$): *trans*-**22b**: $\delta=7.37$–7.17 (m, 5H, Ph-H), 4.02–3.84 (m, 1H, CH), 3.64–3.59 (m, 2H, CH_2), 2.69 (dt, $J_1=8.3$, $J_2=8.3$ Hz, 1H, CH), 2.18–1.07 (m, 20H, CH_2, CH, OH), 1.10–0.81 (m, 12H, CH_3); *cis*-**22b**: $\delta=7.37$–7.17 (m, 5H, Ph-H), 4.02–3.84 (m, 1H, CH), 3.27–3.22 (m, 2H, CH_2), 2.43–2.35 (m, 1H), 2.18–1.07 (m, 20H, CH_2, OH), 1.06–0.68 (m, 12H, CH_3); ^{13}C NMR (125 MHz, $CDCl_3$): mixture of isomers: $\delta=145.5$ (C), 138.4 (C), 128.4 (CH), 128.3 (CH), 128.2 (CH), 128.1 (CH), 127.9 (CH), 127.3 (CH), 126.8 (CH), 125.8 (CH), 127.7 (CH), 76.5 (CH), 75.4 (CH), 65.4 (C), 65.3 (C), 65.0 (C), 64.8 (C), 64.7 (C), 62.9 (C H), 49.1 (CH), 47.5 (CH), 47.3 (CH), 43.6 (CH), 40.1 (CH_2), 40.0 (CH_2), 39.9 (CH_2), 39.6 (CH_2), 35.7 (CH_2), 30.9 (CH_2), 30.3 (CH_2), 29.5 (CH_2), 29.3 (CH_2), 29.2 (CH_2), 29.1 (CH_2), 28.9 (CH_2), 27.4 (CH_2), 27.1 (CH_2), 24.6 (CH_2), 23.8 (CH_2), 10.2 (CH_3), 10.1 (CH_3), 8.3 (CH_3), 8.2 (CH_3), 8.1 (CH_3), 8.0 (CH_3), 7.9 (CH_3); IR (neat): $\tilde{\nu}$ = 3338br, 3062w, 3027w, 2959s, 2877m, 1603w, 1493w, 1466m, 1378m, 1038s cm^{-1}; MS (ESI): *m*/*z*: 389 (27), 388 (100) $[M+H]^+$, 320 (10), 260 (11), 192 (11), 184 (13); HRMS (ESI): *m*/*z*: calcd for $C_{25}H_{42}NO_2$: 388.3216; found: 388.3216 $[M+H]^+$.

2,2,6,6-Tetraethyl-1-(1-phenylhex-5-enyloxy)-piperidin-4-one (23a): GP 2 was applied by using (1-bromo-hex-5-enyl)benzene (191 mg, 0.80 mmol), corresponding nitroxide[15] (200 mg, 0.88 mmol), Cu (53 mg, 0.84 mmol), $Cu(OTf)_2$ (3.0 mg, 8.4 μmol) and 4,4′-di-*tert*-butyl-[2,2′]bipyridine (4.5 mg, 0.034 mmol) in benzene (2.6 mL) for 14 h at 75 °C. FC (Et_2O/pentane 1:20) yielded alkoxyamine **23a** (86 mg, 28 %). ^{1}H NMR (300 MHz, $CDCl_3$): $\delta=7.23$–7.19 (m, 5H, Ph-H), 5.68–5.59 (m, 1H, CH), 4.90–4.82 (m, 2H, CH_2), 4.44 (dd, $J_1=10.0$, $J_2=3.9$ Hz, 1H, CH), 2.24 (brs, 4H, CH_2), 1.98–1.89 (m, 4H, CH_2), 1.69–1.62 (m, 6H, CH_2), 1.10–0.49 (m, 4H, CH_2), 0.99 (brs, 3H, CH_3), 0.86 (brs, 3H, CH_3), 0.65 (brs, 3H, CH_3), 0.52 (brs, 3H, CH_3); ^{13}C NMR (75 MHz, $CDCl_3$): $\delta=211.0$ (C), 142.8 (C), 138.4 (CH), 127.8 (CH), 127.6 (2 CH), 127.4 (CH), 114.5 (CH_2), 87.0 (CH), 66.2 (C), 66.1 (C), 46.5 (CH_2), 35.3 (CH_2), 33.5 (CH_2), 30.9 (CH_2), 30.0 (CH_2), 29.5 (CH_2), 28.6 ($2\times CH_2$), 24.7 (CH_2), 9.7 (CH_3), 9.5 (CH_3), 8.6 (CH_3), 8.3 (CH_3); IR (CCl_4): $\tilde{\nu}$ = 3444w, 3065w, 2971s, 2940s, 2881m, 1718s, 1463m, 1329m cm^{-1}; MS (ESI): *m*/*z*: 408 (83) $[M+Na]^+$, 386 (4) $[M+H]^+$, 281 (65), 249 (100); HRMS (ESI): *m*/*z*: calcd for $C_{25}H_{39}NNaO_2$: 408.2879; found: 408.2879 $[M+Na]^+$.

2,2,6,6-Tetraethyl-1-(2-cyclopentylmethyloxy)-piperidin-4-one (23b), 2,2,6,6-tetraethyl-1-(2-cyclohexyloxy)-piperidin-4-one (23c): According to GP 1 a solution of alkoxyamine **23a** (10 mg, 26.0 μmol) and CSA (0.6 mg, 2.6 μmol) in *t*BuOH (1.3 mL) was heated to 130 °C for 24 h. The reaction was not yet completed and the products could not be separated from the starting material. Due to the complexity of the NMR spectra (starting material **23a**, 2 isomers of **23b**, 2 isomers of **23c**) the reaction product was not analyzed.

***trans*-2,6-Bis(*tert*-butyldimethylsilyloxymethyl)-2,6-diethyl-1-(1-phenylhex-5-enyloxy)-piperidin (24a)**: GP 2 was applied by using (1-bromohex-5-enyl)benzene (76 mg, 0.319 mmol), the corresponding nitroxide[14] (142 mg, 0.319 mmol), Cu (20 mg, 0.319 mmol), $Cu(OTf)_2$ (5.8 mg, 0.016 mmol), 4,4′-di-*tert*-butyl-[2,2′]bipyridine (8.6 mg, 0.064 mmol) in benzene (2.0 mL) for 16 h at 75 °C. FC (pentane) yielded alkoxyamine **24a** (183 mg, 93 %) as a mixture of diastereoisomers (*dr* 1:1). Isomer A: ^{1}H NMR (400 MHz, $CDCl_3$): $\delta=7.34$–7.13 (m, 5H, Ph-H), 5.74–5.64 (m, 1H, CH), 4.95–4.87 (m, 2H, CH_2), 4.77–4.73 (m, 1H, CH), 4.00–3.92 (m, 4H, CH_2), 2.14–0.50 (m, 40H), 0.10–(−0.07) (m, 12H, CH_3); ^{13}C NMR (100 MHz, $CDCl_3$): $\delta=144.2$ (C), 138.7 (CH), 128.2 (CH), 127.6 ($2\times$CH), 127.1 ($2\times$CH), 114.4 (CH_2), 86.8 (CH), 78.0 (CH_2), 76.3 (CH_2), 65.7 (C), 65.0 (C), 36.7 (CH_2), 33.9 (CH_2), 31.0 (CH_2), 30.4 (CH_2), 28.9 (CH_2), 28.7 (CH_2), 25.9 ($6\times CH_3$), 24.8 (CH_2), 18.2 ($2\times$C), 15.8 (CH_2), 10.1 (CH_3), 7.9 (CH_3), −5.5 (CH_3); isomer B: ^{1}H NMR (400 MHz, $CDCl_3$): $\delta=7.34$–7.13 (m, 5H, CH), 5.74–5.64 (m, 1H, CH), 4.95–4.87 (m, 2H, CH_2), 4.57 (dd, $J_1=10.2$, $J_2=3.3$ Hz, 1H, CH), 4.00–3.92 (m, 4H, CH_2), 2.14–0.50 (m, 40H), 0.10–(−0.01) (m, 12H, CH_3); ^{13}C NMR (100 MHz, $CDCl_3$): $\delta=144.2$ (C), 138.7 (CH), 128.3 (CH), 127.3 ($2\times$CH), 126.8 ($2\times$CH), 114.4 (CH_2), 86.8 (CH), 78.0 (CH_2), 76.3 (CH_2), 68.7 (C), 68.0 (C), 36.7 (CH_2), 33.9 (CH_2), 31.7 (CH_2), 31.2 (CH_2), 30.4 (CH_2), 28.9 (CH_2), 25.9 ($6\times CH_3$), 24.8 (CH_2), 18.2 ($2\times$C), 15.8 (CH_2), 10.3 (CH_3), 8.0 (CH_3), −5.5 (CH_3); IR (neat): $\tilde{\nu}$ = 2954s, 2930s, 2881m, 2857m, 1641br, 1471m, 1254m, 1089s cm^{-1}; MS (ESI): *m*/*z*: 604 (100) $[M+H]^+$, 569 (79); HRMS (ESI): *m*/*z*: calcd for $C_{35}H_{66}NO_3Si_2$: 604.4581; found: 604.4583 $[M+H]^+$.

***trans*-2,6-Bis(*tert*-butyldimethylsilyloxymethyl)-2,6-diethyl-1-(2-phenylcyclopentylmethoxy)-piperidine (24b), *trans*-2,6-bis(*tert*-butyldimethylsilyloxymethyl)-2,6-diethyl-1-(3-phenylcyclohexyloxy)-piperidine (24c)**: GP 1 was applied by using alkoxyamine **24a** (46.0 mg, 76.2 μmol) in *t*BuOH (3.8 mL, 0.02 M) for 20 min. FC (Et_2O/pentane 1:250) yielded the products **24b** and **24c** (39.2 mg, 84 %) as a mixture of isomers (**24b**/**24c** 10.6:1; **24b**: *trans*/*cis* 2.9:1; **24c**: *dr* 1.1:1; the diastereoisomers due to the stereogenic centre of the nitroxide moiety are formed in a 1:1 ratio). ^{1}H NMR (500 MHz, $CDCl_3$): *trans*-**24b**: $\delta=7.33$–7.13 (m, 5H, CH), 4.00–3.24 (m, 6H, CH_2), 2.70–2.59 (m, 1H, CH), 2.15–1.15 (m, 23H), 0.90–0.77 (m, 18H, CH_3), 0.07–(−0.13) (m, 12H, CH_3); *cis*-**24b**: $\delta=7.33$–7.13 (m, 5H, CH), 4.00–3.24 (m, 4H, CH_2), 3.23–3.17 (m, 3H), 2.15–1.15 (m, 23H), 0.90–0.77 (m, 18H, CH_3), 0.07–(−0.13) (m, 12H, CH_3); **24c** (isomer A): $\delta=7.33$–7.13 (m, 5H, CH), 4.00–3.24 (m, 5H), 2.90–2.84 (m,

1H, CH), 2.15–1.15 (m, 24H), 0.90–0.77 (m, 18H, CH_3), 0.07–(−0.13) (m, 12H, CH_3); **24c** (isomer B): δ = 7.33–7.13 (m, 5H, CH), 4.00–3.24 (m, 5H), 2.49–2.46 (m, 1H, CH), 2.15–1.15 (m, 24H), 0.90–0.77 (m, 18H, CH_3), 0.07–(−0.13) (m, 12H, CH_3); ^{13}C NMR (125 MHz, $CDCl_3$): mixture of isomers: δ = 145.8 (C), 145.6 (C), 128.3 (CH), 128.2 (CH), 127.4 (CH), 127.3 (CH), 125.8 (CH), 125.7 (CH), 78.0 (CH_2), 77.9 (CH_2), 68.1 (CH_2), 65.8 (C), 65.6 (C), 65.5 (C), 65.0 (C), 63.6 (CH_2), 49.5 (CH), 49.1 (CH), 47.3 (CH), 35.9 (CH_2), 35.8 (CH_2), 31.7 (CH_2), 31.5 (CH_2), 30.4 (CH_2), 30.2 (CH_2), 28.7 (CH_2), 28.1 (CH_2), 26.0 (CH_3), 24.9 (CH_2), 24.8 (CH_2), 24.6 (CH_2), 18.2 (C), 15.8 (CH_2), 10.3 (CH_3), 10.2 (CH_3), 7.9 (CH_3), 7.7 (CH_3), −5.5 (CH_3); IR (neat): $\tilde{\nu}$ = 3063w, 3027w, 2955s, 2880s, 2857s, 1939w, 1603w, 1471m, 1462m, 1254s, 1089s cm^{-1}; MS (ESI): *m/z*: 605 (43), 604 (100) $[M+H]^+$, 569 (78); HRMS (ESI): *m/z*: calcd for $C_{35}H_{66}NO_3Si_2$: 406.4582; found: 406.4559 $[M+H]^+$.

***N*-Methoxy-*N*-methyl-2-(2,2,6,6-tetramethyl-piperidin-1-yloxy)-malonamic acid methylester (27)**: GP 3 was applied by using *N*-methoxy-*N*-methyl malonamic acid methylester (483 mg, 3.00 mmol), DIPA (0.47 mL, 3.30 mmol), *n*BuLi (2.35 M in hexane, 1.40 mL, 3.30 mmol), TEMPO (516 mg, 3.30 mmol) and $CuCl_2$ (1.210 g, 9.00 mmol) in DME (18 mL) and stirring for 5 h at room temperature. FC (Et_2O/pentane 1:5) yielded alkoxyamine **27** (746 mg, 2.36 mmol, 79%) as a colourless oil. ^{1}H NMR (500 MHz, $CDCl_3$): δ = 5.27 (s, 1H, CCH_3), 3.74 (s, 3H, $NOCH_3$), 3.73 (s, 3H, $COCH_3$), 3.16 (s, 3H, NCH_3), 1.57–1.25 (m, 6H, CH_2), 1.22 (s, 3H, CCH_3), 1.16 (s, 3H, CCH_3), 1.11 (s, 3H, CCH_3), 1.05 (s, 3H, CCH_3); ^{13}C NMR (125 MHz, $CDCl_3$): δ = 168.8 ((CO)O), 167.8 ((CO)N), 84.3 (CH), 61.5 ($NOCH_3$), 60.5 ($NC(CH_3)_2$), 59.9 ($NC(CH_3)_2$), 52.1 (OCH_3), 40.1 (CH_2), 32.6 (NCH_3), 32.4 (CH_3), 20.3 (CH_3), 20.0 (CH_3), 16.9 (CH_2); IR (neat): $\tilde{\nu}$ = 3501m, 2958s, 2922w, 1761s, 1670s, 1473m, 1428m, 1384m, 1361w, 1307w, 1264s, 1199s, 1176w, 1136w, 1080s, 1018w, 999w, 944w, 931w, 652m, 588m cm^{-1}; MS (ESI): *m/z*: 317 (100) $[M+H]^+$, 183 (6), 156 (33), 140 (8), 126 (7); HRMS (ESI): *m/z*: calcd for $C_{15}H_{29}N_2O_5$: 317.2076; found: 317.2074 $[M+H]^+$.

3-Oxo-2-(2,2,6,6-tetramethyl-piperidin-1-yloxy)-methylbutanoate (28): GP 3 was applied by using 3-oxo butyric acid methylester (1.858 g, 16.00 mmol), DIPA (2.49 mL, 17.60 mmol), *n*BuLi (2.19 M in hexane, 8.05 mL, 17.60 mmol), TEMPO (2.750 g, 17.60 mmol) and $CuCl_2$ (2.366 g, 17.60 mmol) in DME (64 mL) and stirring at room temperature for 2 h. FC (Et_2O/pentane 1:20) yielded alkoxyamine **28** (2.065 g, 7.61 mmol, 48%). ^{1}H NMR (300 MHz, $CDCl_3$): δ = 4.83 (s, 1H, CH), 3.76 (s, 3H, OCH_3), 2.32 (s, 3H, $OCCH_3$), 1.60–1.26 (m, 6H, CH_2), 1.20 (s, 6H, CH_3), 1.04 (s, 3H, CH_3), 1.00 (s, 3H, CH_3); ^{13}C NMR (75 MHz, $CDCl_3$): δ = 202.3 (H_3CCO), 167.8 (OCO), 92.9 (CH), 59.8 (NC), 59.5 (NC), 51.9 (OCH_3), 39.6 (CH_2), 32.5 (CH_3), 32.0 (CH_3), 26.0 (CH_3), 19.7 (CH_3), 16.4 (CH_2); IR (KBr): $\tilde{\nu}$ = 3004m, 2986m, 2931s, 1749s, 1717s, 1455m, 1435m, 1376w, 1362m, 1315m, 1236m, 1198s, 1172s, 1133w, 1085s, 993w, 975w, 958w, 925m, 523m cm^{-1}; MS (ESI): *m/z*: 272 (55) $[M+H]^+$, 156 (77), 142 (25), 126 (100); HRMS (ESI): *m/z*: calcd for $C_{14}H_{26}NO_4$: 272.1862; found: 272.1858 $[M+H]^+$.

3-Oxo-2-(2,2,6,6-tetramethyl-piperidin-1-yloxy)-pentanoic acid methyl ester (29): Applying GP 3 by using LDA (5.50 mmol), 3-oxo-pentanoic acid methyl ester (651 mg, 5.00 mmol), TEMPO (859 mg, 5.50 mmol) and $CuCl_2$ (1.345 g, 10.00 mmol) in DME (23 mL). Stirring at 0 °C for 6 h. FC (Et_2O/pentane 1:15→1:9) yielded **29** (841 mg, 59%). M.p. 53 °C; ^{1}H NMR (300 MHz, $CDCl_3$): δ = 4.85 (s, 1H, OCH), 3.73 (d, J = 0.6 Hz, 3H, OCH_3), 2.80 (dq, J_1 = 18.6, J_2 = 7.2 Hz, 1H, $OCCH_2$), 2.57 (dq, J_1 = 18.6, J_2 = 7.2 Hz, 1H, $OCCH_2$), 1.44–0.96 (m, 18H, CH_2, CH_3), 1.06 (t, J = 7.2 Hz, 3H, CH_2CH_3); ^{13}C NMR (75 MHz, $CDCl_3$): δ = 205.3 (C), 168.5 (C), 93.1 (CH), 60.3 (C), 60.0 (C), 52.3 (CH_3), 40.1 (CH_2), 33.0 (CH_3), 32.5 (CH_3), 32.3 (CH_2), 24.2 (CH_2), 20.1 (CH_3), 16.9 (CH_2), 7.0 (CH_3); IR (neat): $\tilde{\nu}$ = 2980m, 2938s, 2875w, 1740s, 1708s, 1651w, 1452m, 1436w, 1377w, 1360m, 1313m, 1237m, 1169m, 1137s, 1085s, 1051m, 992w, 973w, 957w, 925m, 875w, 839w, 794s, 740m, 689w, 632w, 581w, 516w cm^{-1}; MS (ESI): *m/z*: 308 (31) $[M+Na]^+$, 286 (22) $[M+H]^+$, 118 (36), 104 (75), 90 (100), 76 (64), 72 (49), 58 (38); HRMS (ESI): *m/z*: calcd for $C_{15}H_{27}NO_4Na$: 308.1832; found: 308.1820 $[M+Na]^+$.

4,4-Dimethyl-3-oxo-2-(2,2,6,6-tetramethyl-piperidin-1-yloxy)- pentanoic acid ethylester (30): GP 3 was applied by using 4,4-dimethyl-3-oxo-pentanoic acid methylester (334 mg, 1.94 mmol), DIPA (0.30 mL, 2.13 mmol), *n*BuLi (2.35 M in hexane, 0.91 mL, 2.13 mmol), TEMPO (333 mg, 2.13 mmol) and $CuCl_2$ (782 g, 5.82 mmol) in DME (12 mL) and stirring at room temperature for 17 h. FC (Et_2O/pentane 1:10) yielded alkoxyamine **30** (447 mg, 1.37 mmol, 48%). ^{1}H NMR (300 MHz, $CDCl_3$): δ = 5.30 (s, 1H, CH), 4.20 (q, J = 7.1 Hz, 2H, OCH_2), 1.69–1.39 (m, 6H, 3× CH_2), 1.28 (t, J = 7.1 Hz, 3H, CH_2CH_3), 1.23–1.11 (m, 15H, $C(CH_3)_3$, CH_3), 0.97 (s, 3H, CH_3), 0.93 (s, 3H, CH_3); ^{13}C NMR (75 MHz, $CDCl_3$): δ = 208.1 ($(H_3C)_3CCO$), 167.7 (COOEt), 89.5 (CH), 61.4 (OCH_2), 60.5 (NC), 59.8 (NC), 44.2 ($(CH_3)_3C$), 40.1 (CH_2), 33.0 (CH_3), 27.1 ($(CH_3)_3C$), 20.3 (CH_3), 20.1 (CH_3), 17.0 (CH_2), 14.0 (CH_3); IR (neat): $\tilde{\nu}$ = 2987s, 2936s, 2872w, 1750s, 1716s, 1472m, 1362m, 1325m, 1271w, 1242m, 1174m, 1093s, 1048w, 1016m, 986m cm^{-1}; MS (ESI): *m/z*: 328 (100) $[M+H]^+$, 158 (53), 156 (16), 142 (15), 126 (35); HRMS (ESI): *m/z*: calcd for $C_{18}H_{34}NO_4$: 328.2488; found: 328.2461 $[M+H]^+$.

Diethoxyphosphoryl-(2,2,6,6-tetramethyl-piperidin-1-yloxy)-acetic acid ethyl ester (31): GP 3 was applied by using diethoxyphosphoryl-acetic acid ethyl ester (0.68 mL, 3.46 mmol), DIPA (0.54 mL, 3.84 mmol), *n*BuLi (1.6 M in hexane, 2.4 mL, 3.84 mmol), TEMPO (600 mg, 3.84 mmol) and $CuCl_2$ (4.66 g, 34.6 mmol) in DME (60 mL). FC (acetone/pentane 1:4) yielded **31** (1.1 g, 83%). ^{1}H NMR (200 MHz, $CDCl_3$): δ = 4.81 (d, J = 18.0 Hz, 1H, CH), 4.32–4.10 (m, 6H, OCH_2), 1.43–1.05 (m, 27H, 3×CH_3CH_2, TEMPO); ^{13}C NMR (75 MHz, $CDCl_3$): δ = 168.6 (C), 83.6 (d, J = 147.6 Hz, CHP), 63.4–62.9 (m, CH_2-O-P), 61.2 (CH_2), 60.0 (C), 40.7 (CH_2), 16.9 (CH_2), 16.4 (CH_2), 16.3 (CH_3), 16.3 (CH_3), 13.9 (CH_3); IR (neat): $\tilde{\nu}$ = 2978s, 2934s, 1788s, 1468m, 1379m, 1366m, 1263s, 1213m, 1150m, 1097m, 1024s, 975m, 902w, 875s, 789m, 599m, 540m cm^{-1}; MS (EI): *m/z*: 379 (75) $[M]^+$, 364 (100), 296 (66), 156 (71) $[TEMPO]^+$; HRMS (EI): *m/z*: calcd for $C_{17}H_{34}NO_6P$: 379.2124; found: 379.2124 $[M]^+$.

[(Dimethoxyphosphoryl)-(2,2,6,6-tetramethylpiperidin-1-yloxy)-methyl]-phosphonic acid dimethylester (32): GP 3 was applied by using DIPA (0.72 mL, 5.19 mmol), *n*BuLi (1.62 M in hexane, 3.2 mL, 5.19 mmol), (dimethoxyphosphorylmethyl)-phosphonic acid dimethylester (803 mg, 3.46 mmol), TEMPO (600 mg, 3.81 mmol) and $CuCl_2$ (4.66 g, 34.60 mmol) in DME (40 mL) and stirring at −60 °C for 90 min before allowing to warm up and stirring at room temperature for another 3 h. FC (acetone) yielded alkoxyamine **32** (526 mg, 39%). ^{1}H NMR (300 MHz, $CDCl_3$): δ = 4.85 (t, J = 26.3 Hz, 1H, CH), 3.87–3.81 (m, 12H, OCH_3), 1.61–1.22 (m, 18H, TEMPO); ^{13}C NMR (75 MHz, $CDCl_3$): δ = 76.3 (t, J_{CP} = 148.9 Hz, CH), 61.7 (CH_2), 53.3 (CH_3), 40.9 (CH_2), 33.5 (CH_3), 20.5 (CH_3), 16.9 (CH_2); IR (neat): $\tilde{\nu}$ = 2955s, 2853s, 1467s, 1369m, 1365m, 1260s, 1183m, 1132m, 1039s, 862m, 832m, 784m, 603m, 529m cm^{-1}; MS (EI): *m/z*: 387 (61) $[M]^+$, 304 (80), 323 (91), 157 (74) $[TEMPO-H]^+$, 156 (100) [TEMPO], 124 (77); HRMS (EI): *m/z*: calcd for $C_{14}H_{31}NO_7P_2$: 387.1576; found: 387.1576 $[M]^+$.

2-(Methoxy-methyl-carbamoyl)-4-(2,2,6,6-tetramethyl-piperidin-1-yloxy)-decanoic acid methylester (33): GP 4 was applied by using alkoxyamine **29** (160 mg, 0.51 mmol) and 1-octene (284 mg, 2.53 mmol) in DCE (0.5 mL) at 135 °C for 3 d. FC (Et_2O/pentane 1:5) yielded **33** (71 mg, 0.17 mmol, 33%). Alkoxyamine **33** was isolated as an unseparable mixture of diastereoisomers (*dr* 1:1). ^{1}H NMR (400 MHz, $CDCl_3$): both isomers: δ = 4.06 (t, J = 7.1 Hz, 1H, OCCHCO), 3.84–3.75 (m, 1H, OCH), 3.71 (s, 3H, $NOCH_3$), 3.70 (s, 3H, $COCH_3$), 3.20 (s, 3H, NCH_3), 2.19–2.06 (m, 2H, CH_2), 1.66–1.37 (m, 6H, CH_2), 1.35–1.16 (m, 10H, CH_2), 1.07 (s, 12H, CH_3), 0.87 (t, J = 6.3 Hz, 3H, CH_3); ^{13}C NMR (100 MHz, $CDCl_3$): both isomers: δ = 170.9 (OCO), 170.5 (CON), 79.2 (OCH), 61.2 ($NOCH_3$), 60.0 ($NC(CH_3)_2$), 59.3 ($NC(CH_3)_2$), 52.2 (OCH_3), 45.5 (OCCHCO), 40.4 (CH_2), 40.2 (CH_2), 34.2 (NCH_3), 33.2 (CH_2), 32.9 (CH_2), 32.7 (CH_3), 31.9 (CH_2), 29.6 (CH_2), 25.8 (CH_2), 22.6 (CH_2), 20.5 (CH_3), 17.4 (CH_2), 14.1 (CH_3); IR (neat): $\tilde{\nu}$ = 3470w, 2930s, 2871m, 1745s, 1675s, 1465s, 1377s, 1361m, 1259m, 1181m, 1133m, 992m, 958w, 721w, 593w cm^{-1}; MS (ESI): *m/z*: 429 (100) $[M+H]^+$; HRMS (ESI): *m/z*: calcd for $C_{23}H_{45}N_2O_5$: 429.3328; found: 429.3338 $[M+H]^+$.

2-(2,2-Dimethylpropionyl)-4-(2,2,6,6-tetramethyl-piperidin-1-yloxy)-decanoic acid ethylester (36): GP 4 was applied by using alkoxyamine **30** (100 mg, 0.31 mmol) and 1-octene (171 mg, 1.53 mmol) in DCE (0.31 mL) at 135 °C for 3 d. FC (Et_2O/pentane 1:10) yielded **36** (68 mg, 0.15 mmol, 51%). Alkoxyamine **36** was isolated as an unseparable mixture of diastereoisomers (*dr* 1:1). ^{1}H NMR (200 MHz, $CDCl_3$): both iso-

mers: $\delta = 4.46$ (dd, $J = 8.8$, $J = 2.8$ Hz, 2H, OCCHCO), 4.16 (q, $J = 7.0$ Hz, 2H, OCH_2), 4.13 (q, $J = 7.3$ Hz, 2H, OCH_2), 3.81–3.65 (m, 2H, NOCH), 2.34–1.98 (m, 4H, CH_2), 1.68–1.41 (m, 12H, CH_2), 1.27–1.15 (m, 25H, $C(CH_3)_3$, CH_3, CH_2), 1.06 (s, 9H, CH_3), 1.05 (s, 9H, CH_3), 0.87 (t, $J = 6.3$ Hz, 6H, CH_3); ^{13}C NMR (75 MHz, $CDCl_3$): both isomers: $\delta = 210.8$ ($(H_3C)_3CCO$), 169.9 (OCO), 169.8 (OCO), 79.8 (OCH), 79.4 (OCH), 61.1 (NC), 61.0 (OCH_2), 60.3 (NC), 50.0 (OC*C*HCO), 48.9 (OC*C*HCO), 45.5 ($(H_3C)_3C$), 45.4 ($(H_3C)_3C$), 40.5 (CH_2), 40.2 (CH_2), 40.1 (CH_2), 34.5 (CH_2), 34.4 (CH_3), 34.1 (CH_3), 33.6 (CH_2), 33.2 (CH_2), 32.7 (CH_3), 31.9 (CH_2), 29.6 (CH_2), 29.6 (CH_2), 26.5 (CH_3), 26.2 (CH_3), 26.0 (CH_2), 25.8 (CH_2), 22.6 (CH_2), 22.6 (CH_2), 20.7 (CH_3), 20.6 (CH_3), 17.4 (CH_2), 17.3 (CH_2), 14.7 (CH_3), 14.6 (CH_3), 14.3 (CH_3); IR (neat): $\tilde{\nu} = 3441$w, 2930s, 2872m, 1748s, 1709s, 1466m, 1366m, 1226w, 1182m, 1132w, 1043w, 989w, 957w, 942w, 716w cm^{-1}; MS (ESI): *m*/*Z*: 440 (100) $[M+H]^+$, 321 (73), 158 (26), 126 (39); HRMS (ESI): *m*/*z*: calcd for $C_{26}H_{50}NO_4$: 440.3740; found: 440.3741 $[M+H]^+$.

2-(Diethoxyphosphoryl)-4-(2,2,6,6-tetramethylpiperidin-1-yloxy)-decanoic acid ethylester (37): GP 4 was applied by using alkoxyamine **31** (100 mg, 0.26 mmol) and 1-octene (0.21 mL, 1.32 mmol) in DCE (0.26 mL) at 135 °C for 3 d. FC (pentane/acetone 10:1) yielded the desired product **37** (72 mg, 56 %). ^{1}H NMR (300 MHz, $CDCl_3$): both isomers: $\delta = 4.35$–3.98 (m, 7H, OCH_2CH_3, CHO), 3.78–3.57 (m, 2H, CH_2CHP), 3.56–3.29 (m, 1H, EtO_2CCHP, single isomer), 3.16–2.87 (m, 1H, EtO_2CCHP, single isomer), 2.44–0.83 (m, 37H), 0.85 (t, $J = 6.6$ Hz, 3H, $CH_3CH_2CH_2$); ^{13}C NMR (75 MHz, $CDCl_3$): both isomers: $\delta = 169.1$ (3 signals), 80.3, 80.1, 79.0, 78.8, 65.8, 65.7, 65.6, 65.5, 65.4, 62.9, 62.8, 62.7 (2 signals), 62.5 (2 signals), 62.4, 62.3, 62.2, 61.4, 61.1, 61.0, 60.1, 59.6, 59.2, 58.8, 43.7, 42.7, 42.0, 40.9, 40.2, 40.1, 39.9, 34.0, 33.9, 32.6, 32.1, 31.6, 31.2, 31.1, 30.3, 30.2, 29.3 (2 signals), 25.8, 25.4, 22.4, 20.3, 17.1, 16.1, 13.8; IR (neat): $\tilde{\nu} =$ 2930s, 2871s, 1736s, 1466m, 1369m, 1258s, 1157m, 1133m, 1027s, 966s, 867w, 786w, 733w cm^{-1}; MS (ESI): *m*/*z*: 1005 (11) $[2M+Na]^+$, 492 (100) $[M+H]^+$; HRMS (ESI): *m*/*z*: calcd for $C_{25}H_{51}NO_6P$: 492.3455; found: 492.3454 $[M+H]^+$.

[1-(Dimethoxyphosphoryl)-3-(2,2,6,6-tetramethylpiperidin-1-yloxy)-nonyl]-phosphonic acid dimethylester (38): GP 4 was applied by using alkoxyamine **32** (100 mg, 0.258 mmol) and 1-octene (0.20 mL, 1.29 mmol) in DCE (0.258 mL) at 135 °C for 3 d. FC (pentane/acetone 4:1→acetone) yielded the desired product **38** (73 mg, 57 %). ^{1}H NMR (300 MHz, $CDCl_3$): $\delta = 3.98$–3.77 (m, 1H, CHON), 3.76–3.71 (m, 13H, OCH_3, CHP), 2.87–2.67 (m, 1H, CH_2CHP), 2.05–1.92 (m, 3H, CH_2-CHP, CH_2CHO), 1.92–0.78 (m, 17H), 1.03 (s, 6H, CH_3 (TEMPO)), 0.98 (s, 6H, CH_3 (TEMPO)); ^{13}C NMR (50 MHz, $CDCl_3$): $\delta = 79.2$–79.0 (m, CH-ON), 59.9 (C), 59.1 (C), 53.3–52.8 (m, OCH_3), 40.2 (m, CH_2), 32.4 (CH_2), 32.1 (t, $J = 89.1$ Hz, CH-P), 31.8 (CH_2), 29.8–29.7 (m, CH_2), 29.4 (CH_2), 25.7 (CH_2), 22.5 (CH_2), 20.5 (CH_3), 20.3 (CH_3), 17.2 (CH_2), 14.0 (CH_3); IR (neat): $\tilde{\nu} =$ 2955s, 2929s, 2855s, 1464s, 1376m, 1360m, 1257s, 1183m, 1132m, 1034s, 958w, 828m, 733m, 530m cm^{-1}; MS (ESI): *m*/*z*: 1021 (51) $[2M+Na]^+$, 500 (100) $[M+H]^+$; HRMS (ESI): *m*/*z*: calcd for $C_{22}H_{48}NO_7P_2$: 500.2907; found: 500.2906 $[M+H]^+$.

2-[*N*-*tert*-Butyl-*N*-(2-methyl-1-phenyl-propyl)-aminooxy]-malonic acid dimethylester (39): GP 3 was applied by using DIPA (1.87 mL, 13.20 mmol), *n*BuLi (2.35 M in hexane, 5.61 mL, 13.20 mmol), dimethylmalonate (1.585 g, 12.00 mmol), corresponding nitroxide[20] (2.908 g, 13.20 mmol) and $CuCl_2$ (4.840 g, 36.00 mmol) in DME (72 mL) and stirring at room temperature for 5 h. FC (Et_2O/pentane 1:10) yielded alkoxyamine **39** (2.724 g, 7.75 mmol, 65 %). M.p. 88–91 °C; ^{1}H NMR (300 MHz, $CDCl_3$): $\delta = 7.64$ (brs, 2H, Ph-H), 7.45–7.30 (m, 3H, Ph-H), 5.26 (s, 1H, NOCH), 3.97 (s, 3H, OCH_3), 3.90 (s, 3H, OCH_3), 3.49 (d, $J = 10.5$ Hz, 1H, NCH), 2.12–2.00 (m, 1H, $(H_3C)_2CH$), 1.23 (d, $J = 6.3$ Hz, 3H, $CHCH_3$), 1.06 (s, 9H, $C(CH_3)_3$), 0.59 (d, $J = 6.6$ Hz, 3H, $CHCH_3$); ^{13}C NMR (75 MHz, $CDCl_3$): $\delta = 168.1$ (OCO), 167.3 (OCO), 141.5 (C), 130.5 (CH), 127.7 (CH), 126.6 (CH), 86.0 (NOCH), 72.9 (NCH), 61.2 ($C(CH_3)_3$), 52.6 (OCH_3), 52.6 (OCH_3), 31.3 (CH), 27.6 ($C(CH_3)_3$), 21.7 (CH_3), 21.2 (CH_3); IR (KBr): $\tilde{\nu} =$ 3068w, 2971m, 2867w, 1766s, 1734s, 1736w, 1436m, 1362m, 1350m, 1283m, 1236s, 1197m, 1166m, 1105s, 917m, 703s cm^{-1}; MS (ESI): *m*/*z*: 374 (100) $[M+Na]^+$, 220 (20), 154 (6), 133 (9); HRMS (ESI): *m*/*z*: calcd for $C_{19}H_{29}NO_5Na$: 374.1938; found: 374.1943 $[M+Na]^+$.

2-[*N*-(1,1-Diethyl-propyl)-*N*-(2-methyl-1-phenyl-propyl)-aminooxy]-malonic acid dimethyl ester (40): GP 3 was applied by using LDA (2.20 mmol), malonic acid dimethyl ester (229 μL, 2.00 mmol), corresponding nitroxide[16] (525 mg, 2.00 mmol) and $CuCl_2$ (296 mg, 2.20 mmol) in DME (9.0 mL). Stirring at 0 °C for 6 h. FC (Et_2O/pentane 1:30) yielded alkoxyamine **40** (438 mg, 56 %). ^{1}H NMR (300 MHz, $CDCl_3$): $\delta = 7.62$–7.18 (m, 5H, Ph-H), 5.13 (s, 1H, OCH), 3.84 (s, 3H, OCH_3), 3.79 (s, 3H, OCH_3), 3.41 (d, $J = 10.5$ Hz, 1H, NCH), 1.97 (dhept, $J_1 = 10.5$, $J_2 = 6.6$ Hz, 1H, $HC(CH_3)_2$), 1.43–1.25 (m, 6H, CH_2), 1.14 (d, $J = 6.6$ Hz, 3H, $HCCH_3$), 0.71 (t, $J = 7.5$ Hz, 9H, CH_2CH_3), 0.47 (d, $J = 6.6$ Hz, 3H, $HCCH_3$); ^{13}C NMR (75 MHz, $CDCl_3$): $\delta = 168.1$ (COO), 167.2 (C), 142.5 (C), 130.6 (CH), 127.6 (CH), 126.6 (CH), 86.2 (CH), 71.7 (CH), 68.6 (C), 52.6 (CH_3), 52.5 (CH_3), 32.0 (CH), 27.4 (CH_2), 22.0 (CH_3), 21.6 (CH_3), 8.6 (CH_3); IR (neat): $\tilde{\nu} =$ 3481w, 3061w, 2958s, 2881s, 1771w, 1749s, 1600w, 1492w, 1455s, 1435m, 1383m, 1326m, 1274m, 1219s, 1154m, 1095s, 1075w, 1019s, 914s, 853m, 808m, 759m, 735m, 707s, 614w, 571w, 540w cm^{-1}; MS (ESI): *m*/*z*: 432 (47) $[M+K]^+$, 416 (47) $[M+Na]^+$, 262 (100) $[M-C_5H_7O_4]^+$, 170 (38), 164 (26), 133 (69), 91 (14); HRMS (ESI): *m*/*z*: calcd for $C_{22}H_{35}NO_5K$: 432.2152; found: 432.2161 $[M+K]^+$.

2-(2,2,6,6-Tetraethyl-4-hydroxy-piperidin-1-yloxy)-malonic acid dimethyl ester (41): Alkoxyamine **42** (100 mg, 0.28 mmol) was dissolved in isopropanol (0.4 mL) and $NaBH_4$ (5.3 mg, 0.14 mmol) was added. After stirring for 18 h at room temperature the reaction was stopped by the addition of HCl (1 M). The aqueous layer was extracted (2×) with Et_2O and the combined organic layers were dried over $MgSO_4$. After removal of the solvents FC (Et_2O/pentane 1:10→1:2) yielded **41** (65 mg, 65 %). M.p. 114–116 °C; ^{1}H NMR (300 MHz, $CDCl_3$): $\delta = 4.93$ (s, 1H, OCH), 3.90 (tt, $J_1 = 11.4$, $J_2 = 3.9$ Hz, 1H, CHOH), 3.77 (s, 6H, OCH_3), 2.23–2.11 (m, 2H, CH_2), 1.81–1.69 (m, 4H, $OCCH_2$), 1.52 (brs, 1H, OH), 1.45–1.22 (m, 6H, CH_2), 0.88 (t, $J = 7.5$ Hz, 6H, CH_3), 0.85 (t, $J = 7.5$ Hz, 6H, CH_3); ^{13}C NMR (75 MHz, $CDCl_3$): $\delta = 167.5$ (C), 84.4 (CH), 66.3 (C), 62.1 (CH), 52.7 (CH_3), 39.3 (CH_2), 29.3 (CH_2), 27.0 (CH_2), 9.9 (CH_3), 7.9 (CH_3); IR (KBr): $\tilde{\nu} =$ 3527s, 3350s, 2968s, 2880w, 1760s, 1738w, 1454m, 1436w, 1413w, 1382w, 1331m, 1275m, 1222s, 1153m, 1101m, 1060s, 1038w, 1013m, 984w, 956w, 904m, 839w, 791m, 732m, 627w, 494m cm^{-1}; MS (ESI): *m*/*z*: 382 (47) $[M+Na]^+$, 250 (33), 232 (22), 228 (100) $[M-C_5H_7O_4]^+$, 200 (23), 170 (52), 154 (13); HRMS (ESI): *m*/*z*: calcd for $C_{18}H_{33}NO_6Na$: 382.2206; found: 382.2215 $[M+Na]^+$.

2-(2,2,6,6-Tetraethyl-4-oxo-piperidin-1-yloxy)-malonic acid dimethyl ester (42): Applying GP 3 by using LDA (1.70 mmol), malonic acid dimethyl ester (177 μL, 1.55 mmol), the corresponding nitroxide[15] (350 mg, 1.55 mmol) and $CuCl_2$ (416 mg, 3.09 mmol) in DME (6.2 mL). The mixture was stirred at 0 °C for 4.5 h. FC (Et_2O/pentane 1:20→1:10) yielded **42** (403 mg, 73 %). M.p. 53–55 °C; ^{1}H NMR (300 MHz, $CDCl_3$): $\delta = 4.95$ (s, 1H, OCH), 3.77 (s, 6H, OCH_3), 2.42–2.27 (m, 4H, $OCCH_2$), 2.18–2.11 (m, 2H, CH_2), 1.70–1.63 (m, 2H, CH_2), 1.52–1.39 (m, 4H, CH_2), 0.87 (t, $J = 6.9$ Hz, 12H, CH_3); ^{13}C NMR (75 MHz, $CDCl_3$): $\delta = 209.1$ (C), 170.0 (C), 85.0 (CH), 67.6 (C), 52.7 (CH_3), 46.3 (CH_2), 30.0 (CH_2), 28.3 (CH_2), 9.5 (CH_3), 8.1 (CH_3); IR (KBr): $\tilde{\nu} =$ 2971s, 2881w, 1764s, 1728m, 1453s, 1426m, 1379m, 1326m, 1278m, 1215s, 1149s, 1098s, 986m, 961w, 917m, 840w, 823w, 799s, 742m, 646m, 625w, 579w, 518m, 451w, 435w, 405w cm^{-1}; MS (ESI): *m*/*z*: 396 (10) $[M+K]^+$, 380 (30) $[M+Na]^+$, 226 (100) $[M-C_5H_7O_4]^+$, 170 (34), 154 (62), 86 (34); HRMS (ESI): *m*/*z*: calcd for $C_{18}H_{31}NO_6Na$: 380.2049; found: 380.2057 $[M+Na]^+$.

2-(*cis*-2,6-Bis-(*tert*-butyl-dimethylsilanoxymethyl)-2,6-diethylpiperidin-1-yloxy)-malonic acid dimethylester (*cis*-43): GP 3 was applied by using DIPA (0.11 mL, 787 μmol), *n*BuLi (1.64 M in hexane; 0.48 mL, 787 μmol), dimethyl malonate (86 μL, 749 μmol), corresponding nitroxide[14] (350 mg, 787 μmol) and $CuCl_2$ (252 mg, 1.87 mmol) in DME (10 mL). The mixture was stirred at 0 °C for 2 h and at room temperature for 18 h. FC (MTBE/pentane 1:19) yielded alkoxyamine *cis*-**43** (337 mg, 585 μmol, 78 %). M.p. 51–57 °C; ^{1}H NMR (300 MHz, $CDCl_3$): $\delta = 4.93$ (s, 1H, CH), 3.94–3.80 (m, 3H, $OCHH$), 3.78 (s, 6H, OCH_3), 3.40 (s, 1H, $OCHH$), 2.19–1.15 (m, 10H, 5×CH_2), 0.82–0.93 (m, 24H, 2×$C(CH_3)_3$, 2×CH_2CH_3), 0.04 (s, 12H, $Si(CH_3)_2$); ^{13}C NMR (75 MHz, $CDCl_3$): $\delta = 167.4$, 85.2, 68.2, 66.8, 65.9, 63.9, 52.7, 31.6, 28.6, 28.4, 25.9, 24.3, 22.3, 18.2, 15.5, 9.9, 7.8, −5.4, −5.5; IR (KBr): $\tilde{\nu} =$ 2955s, 2884m, 2857m, 1771s, 1752s, 1471m, 1435w, 1255s, 1218m, 1089s, 837s, 776s, 669w cm^{-1}; MS (ESI):

m/z: 614 (7) $[M+K]^+$, 598 (47) $[M+Na]^+$, 576 (6) $[M+H]^+$, 483 (43), 467 (100), 444 (35) $[M-$malonyl$]^+$, 337 (35), 284 (23); HRMS (ESI): *m/z*: calcd for $C_{28}H_{57}NO_7Si_2Na$: 598.3571; found: 598.3581 $[M+Na]^+$.

2-[*trans*-2,6-Bis-(*tert*-butyl-dimethylsilanoxymethyl)-2,6-diethylpiperidin-1-yloxy]-malonic acid dimethylester (*trans*-43): GP 3 was applied by using DIPA (0.16 mL, 1.12 mmol), *n*BuLi (1.64 M in hexane, 0.68 mL, 1.12 mmol), malonic acid dimethylester (122 μL, 1.07 mmol), corresponding nitroxide[14] (500 mg, 1.12 mmol) and $CuCl_2$ (376 mg, 2.80 mmol, 2.60 equiv) in dimethoxyethane (19 mL). The reaction mixture was stirred at room temperature for 18 h. FC (MTBE/pentane 1:9) yielded alkoxyamine *trans*-**43** (580 mg, 1.01 mmol, 94%). M.p. 67–69 °C; ^{1}H NMR (300 MHz, $CDCl_3$): $\delta = 5.30$ (s, 1H, CH), 3.96 (d, $J = 9.8$ Hz, 1H, OC*H*H), 3.76 (s, 3H, OCH_3), 3.76 (s, 3H, OCH_3), 3.75 (d, $J = 8.5$ Hz, 1H, OCH*H*), 3.47 (d, $J = 10.5$ Hz, 1H, OC*H*H), 3.25 (d, $J = 10.5$ Hz, 1H, OCH*H*), 2.18–1.20 (m, 10H, $5\times CH_2$), 0.92–0.79 (m, 24H, $2\times C(CH_3)_3$, $2\times CH_2CH_3$), 0.11–(−0.07) (m, 12H, $Si(CH_3)_2$); ^{13}C NMR (50 MHz, $CDCl_3$): $\delta = 167.9$, 167.7, 84.7, 66.6, 66.4, 65.9, 63.5, 52.5, 52.4, 30.2, 28.6, 28.3, 25.9, 25.8, 23.7, 18.1 (2 signals), 15.7, 9.4, 7.6, −5.5 (2 signals), −5.6, −5.7; IR (neat): $\tilde{\nu}$ = 2954s, 2885m, 2857m, 1770s, 1752s, 1471m, 1435w, 1255s, 1220m, 1089s, 837s, 776s cm^{-1}; MS (ESI): *m/z*: 598 (7) $[M+Na]^+$, 467 (18), 444 (100) $[M-$malonyl$]^+$; HRMS (ESI): *m/z*: calcd for $C_{28}H_{57}NO_7Si_2Na$: 598.3571; found: 598.3572 $[M+Na]^+$.

2-{2-[*N*-*tert*-Butyl-*N*-(2-methyl-1-phenyl-propyl)-aminooxy]-octyl}-malonic acid dimethylester (44): GP 4 was applied using alkoxyamine **39** (100 mg, 0.29 mmol) and 1-octene (160 mg, 1.42 mmol) in DCE (0.29 mL) at 125 °C for 7 h. FC (pentane/diethylamine 30:1) yielded the desired product **44** (103 mg, 0.22 mmol, 77%). Alkoxyamine **44** was isolated as an unseparable mixture of diastereoisomers (*dr* 1:1). ^{1}H NMR (200 MHz, $CDCl_3$): both isomers: $\delta = 7.31$–7.16 (m, 5H, Ph-H), 3.92–3.59 (m, 8H, OCCHCO, NOCH, OCH_3), 3.45 (d, $J = 10.2$ Hz, 1H, NCH, single isomer), 3.40 (d, $J = 10.3$ Hz, 1H, NCH, single isomer), 2.41–2.19 (m, 2H, CH_2), 2.16–1.97 (m, 1H, $(H_3C)_2CH$), 1.50–1.23 (m, 10H, CH_2), 1.17 (d, $J = 6.5$ Hz, 3H, $CHCH_3$, single isomer), 1.16 (d, $J = 6.3$ Hz, 3H, $CHCH_3$, single isomer), 0.99–0.85 (m, 12H, $C(CH_3)_3$, $CHCH_3$), 0.43 (t, $J = 6.5$ Hz, 3H, CH_2CH_3); ^{13}C NMR (75 MHz, $CDCl_3$): both isomers: $\delta = 170.1$ (OCO), 170.0 (OCO), 141.5 (C), 131.4 (CH), 131.0 (CH), 127.2 (CH), 127.0 (CH), 126.3 (CH), 126.2 (CH), 79.3 (NOCH), 79.1 (NOCH), 72.4 (NCH), 71.9 (NCH), 61.2 ($C(CH_3)_3$), 60.2 ($C(CH_3)_3$), 52.4 (OCH_3), 52.3 (OCH_3), 48.4 (OC*C*HCO), 48.1 (OC*C*HCO), 32.9 (CH_2), 32.6 (CH_2), 32.4 (CH_2), 32.4 (CH_2), 32.3 (CH), 31.8 (CH_2), 31.7 (CH_2), 31.6 (CH_2), 29.6 (CH_2), 29.5 (CH_2), 28.4 ($C(CH_3)_3$), 28.4 ($C(CH_3)_3$), 27.2 (CH_3), 25.8 (CH_2), 25.2 (CH_2), 22.6 (CH_2), 22.1 (CH_3), 21.7 (CH_3), 21.5 (CH_3), 21.0 (CH_3), 14.0 (CH_3); IR (neat): $\tilde{\nu}$ = 3474w, 2955s, 2870s, 1739s, 1454m, 1436s, 1385m, 1362m, 1254s, 1203s, 1155s, 1046m, 957w, 864w, 835w, 773w, 744w, 703s, 599w cm^{-1}; MS (ESI): *m/z*: 486 (100) $[M+Na]^+$, 464 (43) $[M+H]^+$, 332 (58), 265 (22), 150 (12), 94 (9); HRMS (ESI): *m/z*: calcd for $C_{27}H_{46}NO_5$: 464.3376; found: 464.3367 $[M+H]^+$.

2-{2-[*N*-(1,1-Diethyl-propyl)-*N*-(2-methyl-1-phenyl-propyl)-aminooxy]-octyl}-malonic acid dimethyl ester (45): Applying GP 4 alkoxyamine **40** (50 mg, 0.13 mmol), 1-octene (100 μL, 0.64 mmol) and DCE (127 μL) were heated to 125 °C for 1.5 h. FC (Et_2O/pentane 1:10) yielded **45** (50 mg, 78%) as a mixture of diastereoisomers (*dr* (*syn*/*anti*) 1:1, determined by ^{1}H NMR analysis). ^{1}H NMR (300 MHz, $CDCl_3$): both isomers: $\delta = 7.36$–7.12 (m, 5H, Ph-H), 3.85–3.61 (m, 2H, OCH, OCCHCO), 3.76 (s, 3H, OCH_3, single isomer), 3.73 (s, 3H, OCH_3, single isomer), 3.72 (s, 3H, OCH_3, single isomer), 3.70 (s, 3H, OCH_3, single isomer), 3.49–3.42 (m, 1H, NCH), 2.37–2.01 (m, 3H, $OCHCH_2$, $HC(CH_3)_2$), 1.52–1.15 (m, 19H, CH_2, CH_3), 0.92–0.87 (m, 3H, $HCCH_3$), 0.68, 0.65 (2 *t*, $J = 7.8$ Hz, 9H, CH_2CH_3), 0.44, 0.41 (2d, $J = 6.6$ Hz, 3H, $HCCH_3$); ^{13}C NMR (75 MHz, $CDCl_3$): both isomers: $\delta = 170.2$ (C), 170.1 (C), 170.2 (C), 167.2 (C), 142.8 (C), 142.1 (C), 131.5 (CH), 131.0 (CH), 127.0 (CH), 126.8 (CH), 126.2 (CH), 126.1 (CH), 79.2 (CH), 78.8 (CH), 71.4 (CH), 70.8 (CH), 68.4 (C), 67.6 (C), 52.5 (CH_3), 52.5 (CH_3), 52.5 (CH_3), 52.3 (CH_3), 48.3 (CH), 48.2 (CH), 33.0 (CH_2), 32.9 (CH), 32.7 (CH_2), 32.6 (CH_2), 32.6 (CH_2), 32.1 (CH), 31.8 (CH_2), 31.7 (CH_2), 29.7 (CH_2), 29.6 (CH_2), 27.6 (CH_2), 27.4 (CH_2), 25.6 (CH_2), 25.3 (CH_2), 22.6 (CH_2), 22.4 (CH_3), 21.9 (CH_3), 21.5 (CH_3), 14.1 (CH_3), 14.1 (CH_3), 8.8 (CH_3), 8.7 (CH_3); IR (neat): $\tilde{\nu}$ = 3472w, 2956s, 2872w, 1740s, 1600w, 1457m, 1436s, 1380m, 1341m, 1253s, 1196w, 1155s, 1011s, 911s, 863m, 754s, 734w, 704s, 593m, 526m cm^{-1}; MS (ESI): *m/z*: 544 (22) $[M+K]^+$, 528 (100) $[M+Na]^+$, 428 (6), 408 (7); HRMS (ESI): *m/z*: calcd for $C_{30}H_{51}NO_5Na$: 528.3665; found: 528.3660 $[M+Na]^+$.

2-[2-(2,2,6,6-Tetraethyl-4-hydroxy-piperidin-1-yloxy)-octyl]-malonic acid dimethyl ester (46): Applying GP 4 alkoxyamine **41** (47 mg, 0.13 mmol), 1-octene (103 μL, 0.65 mmol) and DCE (131 μL) were heated to 125 °C for 1.5 h. FC (Et_2O/pentane 2:3) yielded **46** (52 mg, 85%). ^{1}H NMR (400 MHz, $CDCl_3$): $\delta = 3.97$–3.78 (m, 1H, OCH), 3.73 (s, 3H, OCH_3), 3.72 (s, 3H, OCH_3), 3.68–3.53 (m, 2H, HOC*H*, OCCHCO), 2.21–1.10 (m, 25H, CH_2, CH_3, OH), 0.89–0.86 (m, 15H, CH_3); ^{13}C NMR (100 MHz, $CDCl_3$): $\delta = 170.0$ (C), 169.9 (C), 78.6 (CH), 66.1 (C), 62.7 (CH), 52.5 (CH_3), 52.4 (CH_3), 48.4 (CH), 40.4 (CH_2), 32.8 (CH_2), 32.7 (CH_2), 31.7 (CH_2), 30.5 (CH_2), 30.3 (CH_2), 29.5 (CH_2), 27.3 (CH_2), 27.1 (CH_2), 25.3 (CH_2), 22.5 (CH_2), 14.0 (CH_3), 10.3 (CH_3), 10.0 (CH_3), 8.7 (CH_3), 7.8 (CH_3); IR (neat): $\tilde{\nu}$ = 3371s, 2956s, 2879m, 1739s, 1464s, 1436s, 1378m, 1337m, 1256s, 1197w, 1155s, 1107w, 1060m, 1040m, 1012m, 913m, 789w, 734s, 648w cm^{-1}; MS (ESI): *m/z*: 510 (29) $[M+K]^+$, 494 (100) $[M+Na]^+$, 472 (36) $[M+H]^+$, 344 (28), 276 (16), 228 (14), 170 (10); HRMS (ESI): *m/z*: calcd for $C_{26}H_{49}NO_6Na$: 494.3458; found: 494.3463 $[M+Na]^+$.

2-[2-(2,2,6,6-Tetraethyl-4-oxo-piperidin-1-yloxy)-octyl]-malonic acid dimethyl ester (47): Applying GP 4 alkoxyamine **42** (70 mg, 0.20 mmol), 1-octene (154 μL, 0.98 mmol) and DCE (196 μL) were heated to 125 °C for 1.5 h. FC (Et_2O/pentane 1:20→1:4) yielded **47** (72 mg, 78%). ^{1}H NMR (300 MHz, $CDCl_3$): $\delta = 3.73$ (s, 3H, OCH_3), 3.73 (s, 3H, OCH_3), 3.64–3.59 (m, 2H, OCH, OCCHCO), 2.46–2.27 (m, 4H, CH_2), 2.23–2.00 (m, 2H, CH_2), 1.77–1.49 (m, 8H, CH_2), 1.32–1.17 (m, 10H, CH_2), 0.89–0.83 (m, 15H, CH_3); ^{13}C NMR (75 MHz, $CDCl_3$): $\delta = 210.8$ (C), 169.9 (C), 169.8 (C), 79.2 (CH), 66.1 (C), 65.4 (C), 52.6 (CH_3), 52.5 (CH_3), 48.4 (CH), 47.0 (CH_2), 32.6 (CH_2), 32.5 (CH_2), 31.9 (CH_2), 31.7 (CH_2), 29.5 (CH_2), 29.3 (CH_2), 29.1 (CH_2), 25.4 (CH_2), 22.5 (CH_2), 14.0 (CH_3), 9.8 (CH_3), 9.4 (CH_3), 8.7 (CH_3), 8.3 (CH_3); IR (neat): $\tilde{\nu}$ = 3469w, 2959s, 2882w, 1755w, 1738s, 1464w, 1436s, 1378w, 1331m, 1253s, 1197w, 1155m, 1045m, 970w, 920w, 806w, 733m cm^{-1}; MS (ESI): *m/z*: 492 (100) $[M+Na]^+$, 470 (12) $[M+H]^+$, 287 (42), 144 (66), 60 (30); HRMS (ESI): *m/z*: calcd for $C_{26}H_{47}NO_6Na$: 492.3301; found: 492.3300 $[M+Na]^+$.

2-[2-(*cis*-2,6-Bis-(*tert*-butyl-dimethylsilanoxymethyl)-2,6-diethylpiperidin-1-yloxy)octyl]-malonic acid dimethylester (*cis*-48): Applying GP 4 alkoxyamine *cis*-**43** (52 mg, 90 μmol) and 1-octene (71 μL, 452 μmol, 5.00 equiv) were heated in DCE (0.11 mL) to 125 °C for 6 h. FC (MTBE/pentane 1:19) yielded the addition product *cis*-**48** (53 mg, 77 μmol, 85%). ^{1}H NMR (300 MHz, $CDCl_3$): $\delta = 3.94$–3.22 (m, 6H, C*H*(CO), OCH, $2\times OCH_2$), 3.73 (s, 6H, OCH_3), 2.23–1.01 (m, 22H, CH_2, CH_3), 1.00–0.76 (m, 27H, $2\times C(CH_3)_3$, CH_2, CH_3), 0.09–(−0.08) (m, 12H, $2\times Si(CH_3)_2$); ^{13}C NMR (75 MHz, $CDCl_3$): $\delta = 169.9$, 79.2, 66.1, 64.5, 52.5, 52.4, 48.5, 32.4, 31.8, 29.6, 29.3, 27.0, 25.9, 22.6, 18.3, 18.2, 15.9, 14.1, 8.8, 7.9, −5.5; IR (neat): $\tilde{\nu}$ = 2955s, 2930s, 2883m, 2857s, 1758s, 1742s, 1463m, 1436m, 1254s, 1196w, 1153m, 1089s, 1007w, 862s, 837s, 776s cm^{-1}; MS (ESI): *m/z*: 726 (18) $[M+K]^+$, 710 (71) $[M+Na]^+$, 688 (30) $[M+H]^+$, 284 (100), 195 (73), 163(70); HRMS (ESI): *m/z*: calcd for $C_{36}H_{73}NO_7Si_2Na$: 710.4823; found: 710.4833 $[M+Na]^+$.

2-[2-(*trans*-2,6-Bis-(*tert*-butyl-dimethylsilanoxymethyl)-2,6-diethylpiperidin-1-yloxy)octyl]-malonic acid dimethylester (*trans*-48): Applying GP 4 alkoxyamine *trans*-**43** (65 mg, 113 μmol) and 1-octene (89 μL, 568 μmol) were heated in DCE (0.11 mL) to 125 °C for 5 h. FC (MTBE/pentane 1:19) yielded the addition product *trans*-**48** (67 mg, 97 μmol, 86%). Separation of the formed diastereoisomers (*dr* 1:1, determined by ^{13}C NMR analysis) was not possible. ^{1}H NMR (300 MHz, $CDCl_3$): both isomers: $\delta = 4.11$–3.31 (m, 6H, C*H*(CO), OCH, OCH_2), 3.73 (s, 6H, OCH_3), 2.34–1.05 (m, 25H, $11\times CH_2$, $CH_2CH_2CH_3$), 1.00–0.77 (m, 24H, $2\times C(CH_3)_3$, $2\times CCH_2CH_3$), 0.06–0.00 (m, 12H, $2\times Si(CH_3)_2$); ^{13}C NMR (50 MHz, $CDCl_3$): both isomers: $\delta = 170.3$, 170.0, 169.9 (2 signals), 79.0, 78.9, 52.5, 52.4 (2 signals), 48.6, 48.2, 33.2, 32.7, 32.5, 32.4, 31.9, 31.8, 29.7, 25.9, 25.6, 22.6, 18.2, 16.0, 14.1 (2 signals), −5.5 (2 signals); IR (neat): $\tilde{\nu}$ = 2955s, 2883s, 2857s, 1758s, 1742s, 1463m, 1435m, 1254s, 1089s, 866s, 837s, 775s cm^{-1}; MS (ESI): *m/z*: 727 (3) $[M+K]^+$, 711 (60), 688 (24) $[M+H]^+$, 284 (78), 222 (49), 195 (97), 163 (100), 130 (100); HRMS (ESI): *m/z*: calcd for $C_{36}H_{73}NO_7Si_2Na$: 710.4823; found: 710.4829 $[M+Na]^+$.

***O*-*tert*-Butyl-*N*-(1,1-diethyl-propyl)-*N*-(2-methyl-1-phenyl-propyl)-hydroxylamine (49)**: Corresponding nitroxide[16] (380 mg, 1.49 mmol) was dissolved in THF (6 mL) under argon. The mixture was cooled to −78 °C followed by the addition of *t*BuLi (2.90 mmol) and $CuCl_2$ (214 mg, 1.59 mmol). After stirring for 23 h at room temperature the reaction was stopped upon the addition of NH_4Cl (aq. sat.). The aqueous layer was extracted with Et_2O (3×) and the combined organic layers were dried over $MgSO_4$. Evaporation of the solvents in vacuo followed by FC (pentane) yielded **49** (207 mg, 45 %). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.51–7.46 (m, 2H, Ph-H), 7.26–7.15 (m, 3H, Ph-H), 3.45 (d, J = 10.4 Hz, 1H, NCH), 2.16 (dhept, J_1 = 10.4, J_2 = 6.4 Hz, 1H, $HC(CH_3)_2$), 1.48–1.38 (m, 6H, CH_2), 1.41 (s, 9H, $C(CH_3)_3$), 1.20 (d, J = 6.0 Hz, 3H, $HCCH_3$), 0.66 (t, J = 7.2 Hz, 9H, CH_2CH_3), 0.43 (d, J = 6.4 Hz, 3H, $HCCH_3$); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 143.7 (C), 131.5 (CH), 126.8 (CH), 125.9 (CH), 78.9 (C), 71.4 (CH), 67.7 (C), 32.5 (CH), 29.9 (CH_3), 28.0 (CH_2), 23.0 (CH_3), 21.6 (CH_3), 8.8 (CH_3); IR (neat): $\tilde{\nu}$ = 3059w, 2970s, 2876w, 1601w, 1456s, 1385m, 1362s, 1252w, 1222w, 1173s, 1072w, 1006m, 910m, 867s, 780w, 754s, 737w, 700s, 665m, 593m, 522w, 454w cm^{-1}; MS (ESI): *m*/*z*: 320 (12) $[M+H]^+$, 222 (100) $[M-C_7H_{13}]^+$, 166 (33) $[M-C_{11}H_{21}]^+$, 148 (16) $[M-C_{11}H_{20}O]^+$, 133 (16) $[M-ONC_{11}H_{24}]^+$; HRMS (ESI): *m*/*z*: calcd for $C_{21}H_{38}NO$: 320.2948; found: 320.2963 $[M+H]^+$.

***N*-(1,1-Diethyl-propyl)-*O*-[1-(2,2-dimethylpropyl)-heptyl]-*N*-(2-methyl-1-phenyl-propyl)-hydroxylamine (50)**: Alkoxyamine **49** (55 mg, 0.17 mmol) was dissolved in degassed *t*BuOH (172 μL) under an argon atmosphere and 1-octene (136 μL, 0.86 mmol) was added. The mixture was heated to 130 °C in a sealed tube for 4 d. After removal of the solvent in vacuo the residue was purified by FC (pentane) to yield **50** (30 mg, 40 %) as a mixture of diastereoisomers (*dr* (*syn*/*anti*) 1:1, determined by ^{1}H NMR analysis). ^{1}H NMR (300 MHz, $CDCl_3$): both isomers: δ = 7.51–7.31 (m, 2H, Ph-H), 7.26–7.12 (m, 3H, Ph-H), 3.92–3.79 (m, 1H, OCH), 3.47–3.34 (m, 1H, NCH), 2.24–2.00 (m, 2H, CH_2), 1.85, 1.80 (2 d, J = 5.4 Hz, 1H, CH), 1.54–1.17 (m, 22H, CH_2, CH_3), 1.00–0.98 (m, 3H, CH_3), 0.93–0.86 (m, 6H, CH_3), 0.75–0.63 (m, 9H, CH_3), 0.50–0.39 (m, 3H, CH_3); ^{13}C NMR (75 MHz, $CDCl_3$): both isomers: δ = 142.9 (C), 142.6 (C), 131.7 (CH), 131.5 (CH), 126.7 (CH), 126.7 (CH), 125.9 (CH), 79.7 (CH), 79.7 (CH), 71.2 (CH), 70.8 (CH), 68.2 (C), 68.2 (C), 46.9 (CH_2), 46.4 (CH_2), 35.1 (C), 34.2 (C), 32.5 (CH), 32.4 (CH), 31.9 (CH_2), 31.9 (CH_2), 30.8 ($C(CH_3)_3$), 30.7 (CH_3), 30.0 (CH_2), 30.0 (CH_2), 29.9 (CH_2), 29.9 (CH_2), 28.0 (CH_2), 27.9 (CH_2), 27.5 (CH_2), 25.5 (CH_2), 25.5 (CH_2), 23.0 (CH_3), 23.0 (CH_3), 22.7 (CH_2), 22.6 (CH_2), 21.8 (CH_3), 21.6 (CH_3), 14.1 (CH_3), 14.1 (CH_3), 9.0 (CH_3), 8.9 (CH_3); IR (neat): $\tilde{\nu}$ = 3060w, 2956s, 2871w, 1600w, 1467s, 1381s, 1363m, 1248w, 1158m, 1072w, 1033w, 1009m, 910m, 863m, 753m, 702s, 676w, 595w, 525w cm^{-1}; MS (ESI): *m*/*z*: 432 (22) $[M+H]^+$, 331 (100) $[M-C_7H_{16}]^+$, 202 (3), 165 (3), 147 (59), 132 (29) $[M-C_{19}H_{41}NO]^+$; HRMS (ESI): *m*/*z*: calcd for $C_{29}H_{54}NO$: 432.4200; found: 432.4219 $[M+H]^+$.

1-*tert*-Butoxy-2,2,6,6-tetraethylpiperidin-4-ol (51): *t*BuLi (5.94 mmol) was added dropwise at −78 °C to a solution of the corresponding nitroxide[15] (616 mg, 2.70 mmol) in THF (10 mL). After 5 min anhydrous $CuCl_2$ (399 mg, 2.97 mmol) was added and the reaction mixture was allowed to warm to room temperature and was stirred overnight. The reaction was quenched with NH_4Cl (aq. sat.) and extracted with MTBE. Drying over $MgSO_4$ and evaporation of the solvent in vacuo yielded alkoxyamine **51** (312 mg, 41 %). ^{1}H NMR (300 MHz, $CDCl_3$): δ = 3.91–3.83 (m, 1H, CH), 2.05–1.93 (m, 2H, CH_2), 1.81–1.66 (m, 4H, CH_2), 1.55–1.47 (m, 3H, CH_2), 1.34–1.19 (m, 1H, CH_2), 1.55 (s, 9H, CH_3), 1.05–0.96 (m, 2H, CH_2), 0.93–0.85 (m, 12H, CH_3); ^{13}C NMR (75 MHz, $CDCl_3$): δ = 77.9 (C), 65.2 (2×C), 61.9 (CH), 40.2 (2×CH_2), 29.8 (2×CH_2), 29.0 (3×CH_3), 26.6 (2×CH_2), 10.0 (2×CH_3), 8.3 (2×CH_3); IR (neat): $\tilde{\nu}$ = 3333br, 2966s, 2879m, 1463m, 1383m, 1279w, 1257w, 1223w, 1175m cm^{-1}; MS (ESI): *m*/*z*: 286 (56) $[M+H]^+$, 230 (100), 184 (34); HRMS (ESI): *m*/*z*: calcd for $C_{17}H_{36}NO_2$: 286.2741; found: 286.2741 $[M+H]^+$.

1-[1-(2,2-Dimethyl-propyl)-heptyloxy]-2,2,6,6-tetraethylpiperidin-4-ol (52): Alkoxyamine **51** (50 mg, 0.175 mmol) and 1-octene (98 mg, 0.875 mmol) were dissolved in *t*BuOH (0.18 mL) and heated to 130 °C in a sealed tube for 2 d (5 mL) under an argon atmosphere. The solvent was removed in vacuo and the residue was purified by FC (Et_2O/pentane 1:2) yielding the addition product **52** (17 mg, 24 %). ^{1}H NMR (200 MHz, $CDCl_3$): δ = 3.97–3.86 (m, 1H, CH), 3.73–3.59 (m, 1H, CH), 2.17–1.91 (m, 4H, CH_2), 1.81–1.43 (m, 12H, CH_2), 1.39–1.14 (m, 12H), 1.04–0.83 (m, 20H); ^{13}C NMR (50 MHz, $CDCl_3$): δ = 69.8 (C), 64.8 (C), 62.8 (C), 61.9 (CH), 48.2 (CH_2), 40.6 (CH_2), 40.2 (CH_2), 32.6 (CH_2), 31.7 (CH_2), 29.9 (CH_2), 29.8 (CH_2), 29.4 (3×CH_3), 29.2 (CH_2), 27.4 (CH_2), 27.1 (CH_2), 25.7 (CH_2), 22.8 (C), 22.4 (CH_2), 13.9 (CH_2), 10.6 (CH_3), 10.1 (CH_3), 8.8 (CH_3), 8.0 (CH_3); IR (neat): $\tilde{\nu}$ = 3353br, 2961s, 2878m, 1464m, 1379m, 1148w, 1039m cm^{-1}; MS (ESI): *m*/*z*: 447 (100), 398 (12) $[M+H]^+$, 235 (67); HRMS (ESI): *m*/*z*: calcd for $C_{25}H_{52}NO_2$: 398.3998; found: 398.4011 $[M+H]^+$.

2-(2,2,6,6-Tetraethyl-4-oxo-piperidin-1-yloxy)-propionic acid methyl ester (53): GP 2 was applied by using 3-bromo-propionic acid methyl ester (181 μL, 1.58 mmol), the corresponding nitroxide[15] (340 mg, 1.50 mmol), Cu (100 mg, 1.58 mmol), $Cu(OTf)_2$ (5.4 mg, 15 μmol) and 4,4′-di-*tert*-butyl-[2,2′]bipyridine (16.0 mg, 60 μmol) in benzene (3.0 mL) for 18 h at 75 °C. FC (Et_2O/pentane 1:6) yielded **53** (436 mg, 93 %). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 4.37 (q, J = 6.8 Hz, 1H, OCH), 3.72 (s, 3H, OCH_3), 2.36 (d, J = 6.8 Hz, 4H, $OCCH_2$), 2.24–1.97 (m, 2H, CH_2), 1.64–1.60 (m, 4H, CH_2), 1.49–1.35 (m, 2H, CH_2), 1.39 (d, J = 6.8 Hz, 3H, $OCCH_3$), 0.97–0.81 (m, 12H, CH_3); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 210.0 (C), 174.1 (C), 80.6 (CH), 66.6 (C), 51.6 (CH_3), 46.6 (CH_2), 31.0 (CH_2), 28.8 (CH_2), 18.4 (CH_3), 9.4 (CH_3), 8.2 (CH_3); IR (neat): $\tilde{\nu}$ = 3423w, 2969s, 2882m, 1751m, 1717s, 1614w, 1460s, 1377m, 1333m, 1272m, 1198s, 1129s, 1078s, 1036m, 976m, 761w, 582w, 521w cm^{-1}; MS (ESI): *m*/*z*: 336 (100) $[M+Na]^+$, 267 (41), 249 (33), 212 (42), 109 (32), 85 (64); HRMS (ESI): *m*/*z*: calcd for $C_{17}H_{31}NO_4Na$: 336.2145; found: 336.2153 $[M+Na]^+$.

(2,2,6,6-Tetraethyl-4-oxo-piperidin-1-yloxy)-acetic acid methyl ester (54): GP 2 was applied by using bromo-acetic acid methyl ester (102 μL, 1.05 mmol), corresponding nitroxide[15] (226 mg, 1.00 mmol), Cu (67 mg, 1.05 mmol), $Cu(OTf)_2$ (3.6 mg, 10 μmol) and 4,4′-Di-*tert*-butyl-[2,2′]bipyridine (11.0 mg, 40 μmol) in benzene (2.0 mL) for 16 h at 75 °C. FC (Et_2O/pentane 1:10) yielded **54** (145 mg, 48 %). ^{1}H NMR (300 MHz, $CDCl_3$): δ = 4.41 (s, 2H, OCH_2), 3.71 (s, 3H, OCH_3), 2.35, 2.30 (2 brs, 4H, $OCCH_2$), 2.03 (brs, 2H, CH_2), 1.59 (brs, 6H, CH_2), 0.91 (brs, 12H, CH_3); ^{13}C NMR (75 MHz, $CDCl_3$): δ = 209.3 (C), 169.3 (C), 73.6 (CH_2), 67.6 (C), 51.4 (CH_3), 46.4 (CH_2), 29.8 (CH_2), 28.2 (CH_2), 9.4 (CH_3), 8.0 (CH_3); IR (neat): $\tilde{\nu}$ = 2968s, 2882m, 1759m, 1716s, 1522w, 1462m, 1436m, 1377m, 1333m, 1280m, 1201s, 1087s, 1016m, 922w, 898w, 802m, 733m, 650w, 580m, 524m cm^{-1}; MS (ESI): *m*/*z*: 300 (22) $[M+H]^+$, 215 (13), 194 (4), 173 (100), 110 (9), 83 (13), 56 (8); HRMS (ESI): *m*/*z*: calcd for $C_{16}H_{29}NO_4Na$: 322.1989; found: 322.1953 $[M+Na]^+$.

2-Methyl-4-(2,2,6,6-tetraethyl-4-oxo-piperidin-1-yloxy)-decanoic acid methyl ester (55): Applying GP 4 alkoxyamine **53** (52 mg, 0.17 mmol), 1-octene (130 μL, 0.83 mmol) and DCE (165 μL) were heated to 135 °C for 24 h. FC (Et_2O/pentane 1:10) yielded **55** (53 mg, 75 %) as a mixture of diastereoisomers (*dr* (*syn*/*anti*) 1:1, determined by ^{1}H NMR analysis). ^{1}H NMR (400 MHz, $CDCl_3$): both isomers: δ = 3.66 (s, 3H, OCH_3, single isomer), 3.65 (s, 3H, OCH_3, single isomer), 3.66–3.58 (m, 1H, OCH), 2.72–1.28 (m, 25H, CH, CH_2), 1.17 (t, J = 8.8 Hz, 3H, CH_3), 0.90–0.81 (m, 15H, CH_3); ^{13}C NMR (100 MHz, $CDCl_3$): both isomers: δ = 210.8 (C), 177.1 (C), 177.0 (C), 79.9 (CH), 79.6 (CH), 65.7 (C), 51.4 (CH_3), 51.4 (CH_3), 47.1 (CH_2), 37.5 (CH_2), 37.2 (CH_2), 36.3 (CH), 36.2(CH), 33.0 (CH_2), 32.9 (CH_2), 32.5 (CH_2), 31.7 (CH_2), 29.6 (CH_2), 25.5 (CH_2), 25.3 (CH_2), 22.5 (CH_2), 18.3 (CH_3), 18.1 (CH_3), 14.0 (CH_3), 9.5 (CH_3), 8.8 (CH_3); IR (neat): $\tilde{\nu}$ = 3433w, 2964s, 2932s, 2881m, 1736s, 1718s, 1597w, 1461s, 1377w, 1331w, 1253m, 1196s, 1169s, 1145w, 1093m, 979m, 922w, 806w, 763w, 537w cm^{-1}; MS (ESI): *m*/*z*: 448 (79) $[M+Na]^+$, 212 (100) $[M-C_{12}H_{21}O_3]^+$, 152 (100), 85 (45); HRMS (ESI): *m*/*z*: calcd for $C_{25}H_{47}NO_4Na$: 448.3397; found: 448.3421 $[M+Na]^+$.

4-(2,2,6,6-Tetraethyl-4-oxo-piperidin-1-yloxy)-decanoic acid methyl ester (56): Applying GP 4 alkoxyamine **54** (42 mg, 0.14 mmol), 1-octene (110 μL, 0.70 mmol) and DCE (140 μL) were heated to 135 °C for 4 d. FC (Et_2O/pentane 1:20) yielded **56** (33 mg, 57 %). Some of the starting material **54** could be reisolated (6 mg, 14 %). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 3.68–3.60 (m, 1H, OCH), 3.67 (s, 3H, OCH_3), 2.41–2.32 (m, 6H, $OCCH_2$), 2.08–1.58 (m, 12H, CH_2), 1.34–1.17 (m, 8H, CH_2), 0.95–0.77 (m, 15H, CH_3); ^{13}C NMR (75 MHz, $CDCl_3$): δ = 210.8 (C), 174.0 (C),

80.8 (CH), 67.8 (C), 51.5 (CH_3), 47.1 (CH_2), 32.3 (CH_2), 31.8 (CH_2), 30.2 (CH_2), 29.9 (CH_2), 29.6 (CH_2), 28.4 (CH_2), 27.9 (CH_2), 25.6 (CH_2), 22.6 (CH_2), 14.0 (CH_3), 9.6 (CH_3), 8.7 (CH_3); IR (neat): $\tilde{\nu}$ = 3427w, 2960s, 2930s, 2882m, 1739m, 1718s, 1462m, 1438m, 1376w, 1331w, 1253m, 1197s, 1169s, 1091m, 1013m, 966m, 804m, 726w, 700w, 578w, 529w cm^{-1}; MS (ESI): *m*/*z*: 434 (100) $[M+Na]^+$, 412 (6) $[M+H]^+$, 322 (33); HRMS (ESI): *m*/*z*: calcd for $C_{24}H_{45}NO_4Na$: 434.3241; found: 434.3193 $[M+Na]^+$.

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