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"Catalysis in a Tea Bag": Synthesis, Catalytic Performance and Recycling of Dendrimer-Immobilised Bis- and Trisoxazoline Copper Catalysts

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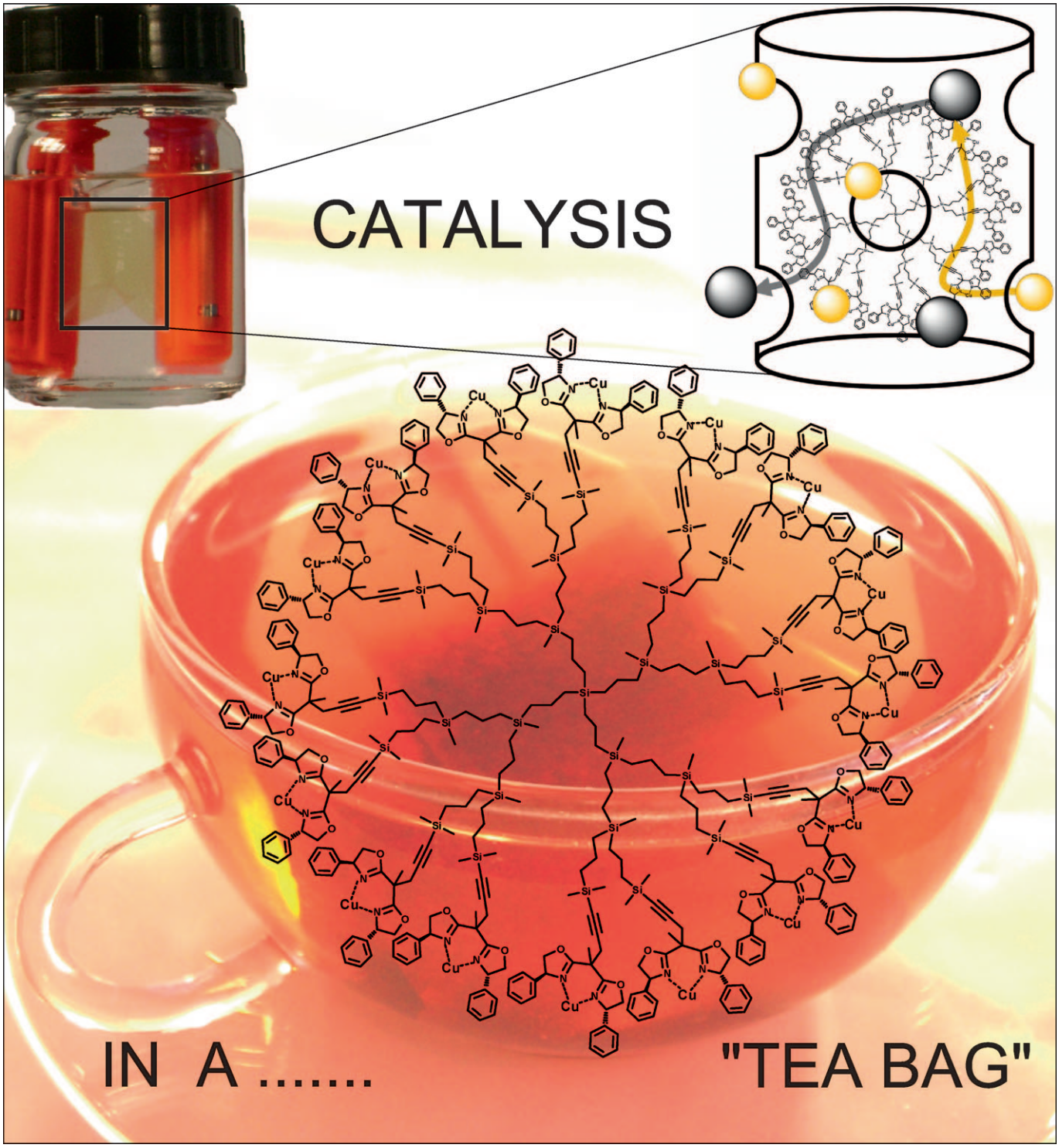

Abstract: Bis- and trisoxazolines (BOX and trisox), containing a linker unit in the ligand backbone that allows their covalent attachment to carbosilane dendrimers, have been employed as polyfunctional ligands for recyclable Cu^{II} Lewis acid catalysts that were immobilised in a membrane bag. The oxazolines contained an alkynyl unit attached to their backbone that was deprotonated with LDA or BuLi and then reacted with the chlorosilyl termini of zeroth-, first- and second-generation carbosilane dendrimers in the presence of $TlPF_6$. The functionalised dendritic systems were subsequently separated from excess ligand by way of dialysis. The general catalytic potential of these systems was assessed by studying two benchmark reactions, the α-hydrazination of a β-keto ester as well as the Henry reaction of 2-nitrobenzaldehyde with nitromethane. For both reactions the bisoxazoline-based catalysts displayed superior selectivity and, in particular, catalyst activity. The latter was interpreted as being due to the hindered decoordination of the third oxazoline unit, the key step in the generation of the active catalyst, in the immobilised trisox–copper complexes. Solutions of the second-generation dendrimer catalysts were placed in membrane bags, fabricated from commercially available dialysis membranes, with the purpose of catalyst recycling based on dialysis. Overall, the supported BOX catalyst gave good and highly reproducible results throughout the study, whereas the performance of the trisox dendrimer system decreased monotonically. The reason for the different behaviour is the markedly lower activity of trisox-based catalysts relative to those based on the BOX ligand. This necessitated an increased reaction time for each cycle of the trisox derivatives, resulting in higher levels of catalyst leaching, which was attributed to a modification of the structure of the membrane by its exposure to the solvent trifluoroethanol at 40 °C.

Keywords: bisoxazolines · dendrimers · homogeneous catalysis · membranes · trisoxazolines

Introduction

The exploitation of ultra- and nanofiltration techniques based on dialysis in the reaction engineering of catalytic processes was originally developed for biotechnological applications.[1] Kula, Wandrey and others used continuous-flow membrane reactors for enzymatic transformations since the early 1980s,[2] and a simple, practical variation of this approach for batch reactions was put forward by Whitesides and co-workers in 1987 who employed membrane bags to recycle the enzymatic catalyst.[3] The application of this technique to organometallic homogeneous catalysis has been a more recent development. Kragl and others made key contributions to the development of continuously operating membrane reactors for this type of catalytic systems,[4] using, amongst others, a polymer-supported proline-derivative as a chiral catalyst.[5] Finally, van Koten and van Leeuwen and their co-workers first reported the application of this technique to dendrimer catalysis and led to its establishment in dendrimer chemistry.[6,7]

These techniques require membranes that are adapted to the reaction conditions to achieve good catalytic performance.[8] The pore size of the membrane should guarantee retention of the catalyst and smooth transport of the reactants and products. Possible interactions of the various compounds/intermediates with the membrane surface have to be considered. Finally, a membrane that is mechanically, thermally and chemically stable in the required solvent and at the required temperature should be chosen. This is a major issue with polymeric membranes that may swell, change their structure and, therefore, their pore size, leading to increased catalyst leaching.[9]

Driven by a gradient, the substrates/reactants are transported through the membrane, whereas the catalyst is retained due to its size. The driving force may be a pressure, concentration or temperature gradient or a difference in electrical potential. Several types of membrane-based reactors have been reported, some of which require sophisticated engineering.[6e–h] The simplest approach is based on catalyst trapping within a membrane "bag". It provides adequate dispersion of the catalyst and guarantees minimal interaction between the catalyst and the polymer, thus allowing the use of relatively labile catalyst systems. This is certainly the case for the copper(II)-based Lewis acid catalysts employed in this work that are attached to dendrimer supports and are held within a dialysis membrane "tea bag",[10] which may be "dipped" into a reactant solution and recycled several times.

Whereas many examples of immobilised bisoxazolines have been reported, relatively few contributions to the field report the use of dendrimers as soluble supports,[11,12] and in most of these studies the immobilised catalysts only displayed moderate activity and selectivity. A notable exception has been Majoral's and Reiser's series of dendritic azabis(oxazolines), which gave good yields, and good to excellent enantioselectivities at 5 mol% catalyst loading and were recycled up to three times.[13] In this work, well-estab-

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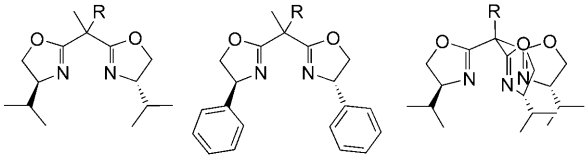
lished carbosilane dendrimers[14] are employed that guarantee a minimum interaction of the catalytic centres with the dendritic core structure.

Results and Discussion

In this section we first describe the synthesis of bis- and trisoxazolines[15] containing a linker unit in the ligand backbone that allows their covalent attachment to carbosilane dendrimers. Our systems of reference are the bisoxazolines (BOX) **A** and **B** as well as the trisoxazoline (trisox) **C** (Scheme 1).



A: R=Me
2a: R=propargyl
4a: R=propargyl-TBDMS
G0-**2a** R=G0-(**2a**)$_3$
G1-**2a** R=G1-(**2a**)$_7$
G2-**2a** R=G2-(**2a**)$_{15}$

B: R=Me
2b: R=propargyl
4b: R=propargyl-TBDMS
G0-**2b** R=G0-(**2b**)$_3$
G1-**2b** R=G1-(**2b**)$_7$
G2-**2b** R=G2-(**2b**)$_{15}$

C: R=Me
3a: R=propargyl
5: R=propargyl-TBDMS
G0-**3a** R=G0-(**3a**)$_3$
G1-**3a** R=G1-(**3a**)$_7$
G2-**3a** R=G2-(**3a**)$_{15}$

Scheme 1. Structures of the BOX- and trisox-functionalised ligands used in this study. **A**, **B** and **C** are reference ligands; G0, G1 and G2 = zeroth-, first-, second-generation dendrimers, respectively; TBDMS = *tert*-butyldimethylsilyl.

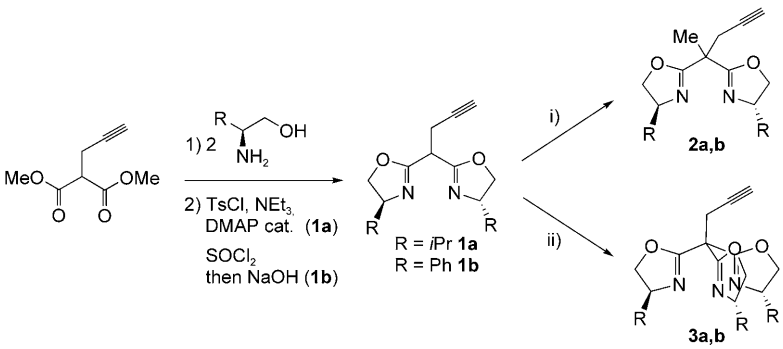
The choice of the appropriate linker is based on two principal requirements: a relatively inert binding to the supporting macromolecule and minimised interference with the catalytic sites.[16] A propargyl function at the bridging position of the BOX ligand or the apical position of the trisox ligand appeared to meet these requirements. Moreover, the terminal alkyne subsequently allowed facile linkage to the dendrimers through deprotonation and reaction with chlorosilane termini.[17]

Synthesis of propargyl-functionalised BOX and trisox derivatives: The synthesis of the new propargyl-functionalised BOX derivatives and trisox ligands is based on a modular strategy and derives from an intermediate bisoxazoline **1a**,**b** (Scheme 2). (*S*)-Valinol and (*S*)-α-phenylglycinol were used to introduce groups with different steric bulk, and the tethered ligands **2a**,**b** (BOX derivatives) and **3a**,**b** (trisox ligands) were synthesised from commercially available dimethyl propargylmalonate.

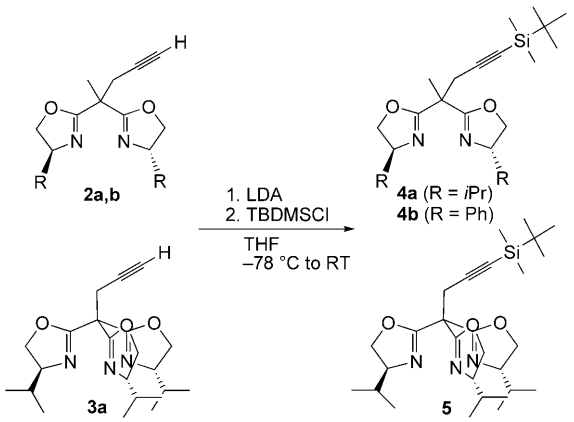
Based on established procedures, the formation of both diamide intermediates in the synthesis of the bisoxazolines proceeded cleanly and almost quantitatively. For (*S*)-valinol, this was directly followed by cyclisation using tosyl chloride to give **1a** in 68% yield.[18] The reaction of dimethyl propargylmalonate with (*S*)-α-phenylglycinol proceeded less cleanly; however, treatment with $SOCl_2$ and subsequent cyclisation with NaOH generated BOX **1b** in a reasonable yield (41%).[19] After lithiation of **1a,b**, they were reacted with MeI to give propargyl-BOX(*i*Pr) (**2a**) and propargyl-BOX(Ph) (**2b**) in excellent yields over 90%. The replacement of the acidic atom at the bridgehead in **1a,b** was required to avoid competitive reactions in the following immobilisation reaction.

The synthesis of C_3 symmetric propargyl-trisox(*i*Pr) (**3a**) and propargyl-trisox(Ph) (**3b**) was achieved by the established coupling[20] of a lithiated bisoxazoline with a 2-bromooxazoline.[21] The presence of the propargyl moiety necessitated more vigorous conditions as well as longer reaction times and a higher stoichiometric excess of the bromooxazolines than previously reported for the parent trisox derivatives. Under these conditions **3a** was obtained in 69% yield. In the case of **3b**, high temperatures had to be avoided because 2-bromophenyloxazoline is far less stable than 2-bromoisopropyloxazoline. It is especially prone to rearrange and form a 2-bromoisocyanate.[22] Accordingly, compound **3b** could only be isolated in 35% yield.

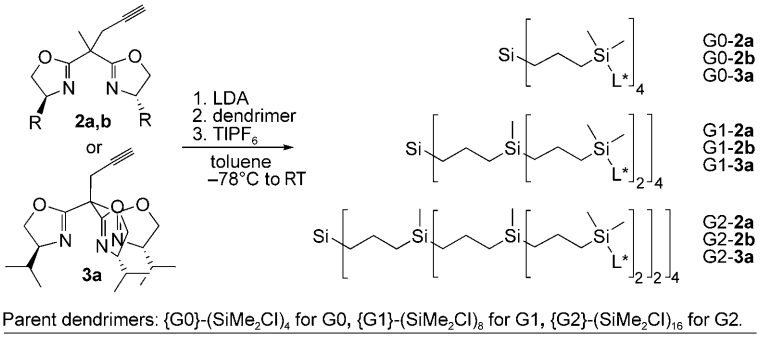
Preparation of the oxazoline-functionalised dendrimers: The parent carbosilane dendrimers {G0}-($SiMe_2Cl$)$_4$, {G1}-($SiMe_2Cl$)$_8$ and {G2}-($SiMe_2Cl$)$_{16}$ were synthesised according to literature procedures,[14e–j] with the aim of a subsequent nucleophilic substitution at the terminal chlorosilane groups. To test the potential of ligands **2a,b** and **3a,b** for this kind of reaction *t*BuMe_2SiCl was chosen as a model system. After deprotonation of **2a,b** and **3a** by LDA or BuLi and reaction with the chlorosilane, clean and complete product formation (**4a,b** and **5**) was observed (Scheme 3). However, employing the same reaction conditions with {G0}-($SiMe_2Cl$)$_4$, {G1}-($SiMe_2Cl$)$_8$ and {G2}-($SiMe_2Cl$)$_{16}$ only led to low or moderate conversion and inseparable product mixtures of in part defective dendritic systems.



Scheme 2. Synthesis of the propargyl-functionalised BOX **2a,b** and trisox **3a,b** ligands. Reaction conditions: i) *n*BuLi, then MeI; ii) *t*BuLi, then 2-bromooxazoline.



Scheme 3. Synthesis of TBDMS-functionalised model systems **4a,b** (77% and 62% yield) and **5** (95% yield) for the dendritic BOX and trisox ligands.



Scheme 4. Synthesis of the BOX- and trisox-functionalised carbosilane dendrimers G0-L*, G1-L*, G2-L* (L* = **2a**,**b** and **3a**).

The sluggish and incomplete conversion could be overcome by addition of one equivalent of $TlPF_6$ per acetylide unit and the use of an excess of the linker-ligand reagent (Scheme 4). Applying of this strategy, conversions of around 70% for all dendrimer and ligand combinations were achieved.

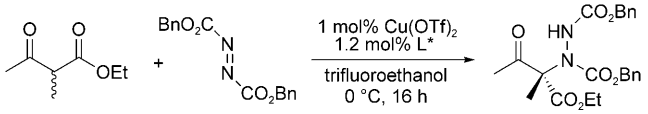
The purification of the new dendritic compounds was carried out by applying van Koten's strategy of dendrimer isolation by dialysis.[23] The zeroth-generation trisox derivative G0-**3a** as well as all first- and second-generation dendrimers G1-L* and G2-L* (L* = **2a**,**b** and **3a**) could be purified efficiently and were obtained in pure form in moderate to good yields (49–77%). However, the zeroth-generation G0-L* derivatives (L* = **2a**,**b**) were too small to be efficiently retained by the membrane pores and therefore had to be purified by flash column chromatography. As they tend to decompose slowly on silica, this explains their low yields (28 and 22%). Characterisation (and assessment of purity) of the oxazoline-functionalised dendrimers was provided by ^{13}C and ^{29}Si NMR spectroscopy, elemental analysis as well as by mass spectrometry for the lower generations.

Comparative studies of copper(II) Lewis acid catalysts. The general catalytic potential of compounds G0-L*, G1-L*, G2-L* (L* = **2a**,**b** and **3a**) as polyfunctional chiral ligand systems for asymmetric copper(II) Lewis acid catalysis was assessed by studying two benchmark reactions, the α-hydrazination of a β-keto ester as well as the Henry reaction of 2-nitrobenzaldehyde with nitromethane. Both reactions had previously been studied using various BOX derivatives as stereodirecting ligands.[24,25] Ligands **A**, **B** and **C** (shown above), bearing only a methyl group at the bridgehead or the apical position, were employed as reference systems for both of these reactions.

α-Hydrazination of ethyl 2-methylacetoacetate: This reaction has been studied extensively[24] and therefore lent itself to assess the influence of the dendritic support (and subsequently the recycling in a membrane bag, vide infra) on the catalytic system. The results obtained for the catalytic α-hydrazination of ethyl 2-methylacetoacetate are displayed in Table 1. A remarkably low catalyst loading of 1 mol% was found to be sufficient and generally high yields and selectivities were obtained.

The highest enantioselectivities were observed for the BOX(Ph) derivatives—a trend which had already been noted earlier.[24] Enantiomeric excesses of between 97 and 99% were obtained with these catalysts, whereas BOX(*i*Pr) and trisox(*i*Pr) ranged between 90 and 97% *ee*. There are some notable aspects concerning the results obtained with BOX(*i*Pr) and trisox(*i*Pr) derivatives, namely an increase of *ee* values from 94% *ee* for the catalysts with the parent ligand systems **A** and **C** to 97 and 96% with propargyl-substituted ligands **3a** and **2a**, respectively. Similar observations were made for the smaller dendritic species G0-**3a**/G0-**2a** as well as G1-**3a**/G1-**2a**. In general,

Table 1. Catalytic asymmetric α-hydrazination of ethyl 2-methylacetoacetate with the polyfunctional dendritic ligands and monofunctional reference systems.



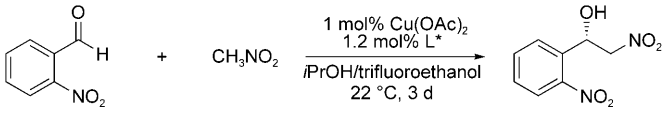
Ligand	*ee* [%]	Ligand	*ee* [%]	Ligand	*ee* [%]
C	94	**A**	94	**B**	98
3a	96	**2a**	97	**2b**	99
5	93	**4a**	96	**4b**	99
G0-**3a**	92	G0-**2a**	93	G0-**2b**	97
G1-**3a**	95	G1-**2a**	95	G1-**2b**	97
G2-**3a**	90	G2-**2a**	94	G2-**2b**	98

[a] Structures of the ligands are shown in Scheme 1. Quantitative yields were obtained for all catalysts.

enantioselectivities were slightly higher (3–4%) for the bisoxazoline with respect to the trisox systems.

Henry reaction of nitromethane and 2-nitrobenzaldehyde: The Henry reaction was chosen as a complementary test system to assess the trend observed in the α-hydrazination. BOX ligands had already been applied successfully in the reaction of various benzaldehyde derivatives with nitromethane at 5 mol% catalyst loading, yielding products with good enantioselectivities of around 90%.[25] To prove the effect of the varying catalyst environments in this study, a reference reaction was chosen that only gave moderate enantiomeric excesses, this allowing both increase and decrease in enantioselectivities. Table 2 summarises the reaction conditions as well as the catalytic results for the different copper(II) catalysts.

Table 2. Catalytic asymmetric Henry reaction of 2-nitrobenzaldehyde and nitromethane with the polyfunctional dendritic ligands and monofunctional reference systems.



Ligand	*ee* [%]	Yield [%]	Ligand	*ee* [%]	Yield [%]	Ligand	*ee* [%]	Yield [%]
C	75	93	**A**	74	95	**B**	71	89
3a	67	32	**2a**	77	45	**2b**	74	74
5	50	24	**4a**	77	36	**4b**	74	65
G0-**3a**	52	42	G0-**2a**	84	86	G0-**2b**	84	83
G1-**3a**	53	58	G1-**2a**	87	87	G1-**2b**	83	85
G2-**3a**	53	54	G2-**2a**	83	87	G2-**2b**	81	82

[a] Structures of the ligands are shown in Scheme 1.

First of all, we note a significant difference between the BOX- and trisox-based catalysts. BOX(Ph) and BOX(*i*Pr) gave similar *ee* values (71–77% *ee*) and yields for all mononuclear catalysts. On the other hand, the dendritic BOX derivatives all gave reaction products with significantly higher enantiomeric excesses (81–87% *ee*). In contrast, the performance of all the trisox-based catalysts proved to be inferior, both in terms of the activities and enantioselectivities. The negative trend with respect to the trisox-based catalysts observed for the α-hydrazination discussed above is thus enhanced for the Henry reaction.

Comparison of the BOX– and trisox–copper catalysts: To gain some insight into the different behaviour of the immobilised BOX and trisox ligands for both types of reactions, the rates of conversion were monitored. For this purpose the α-hydrazination of ethyl 2-methylacetoacetate was chosen because it had already been the object of a detailed kinetic study and proceeded very cleanly.[24c] The corresponding conversion curves are shown in Figure 1. To allow for a better comparison Figure 2 depicts the time each catalyst required to achieve 90% conversion.

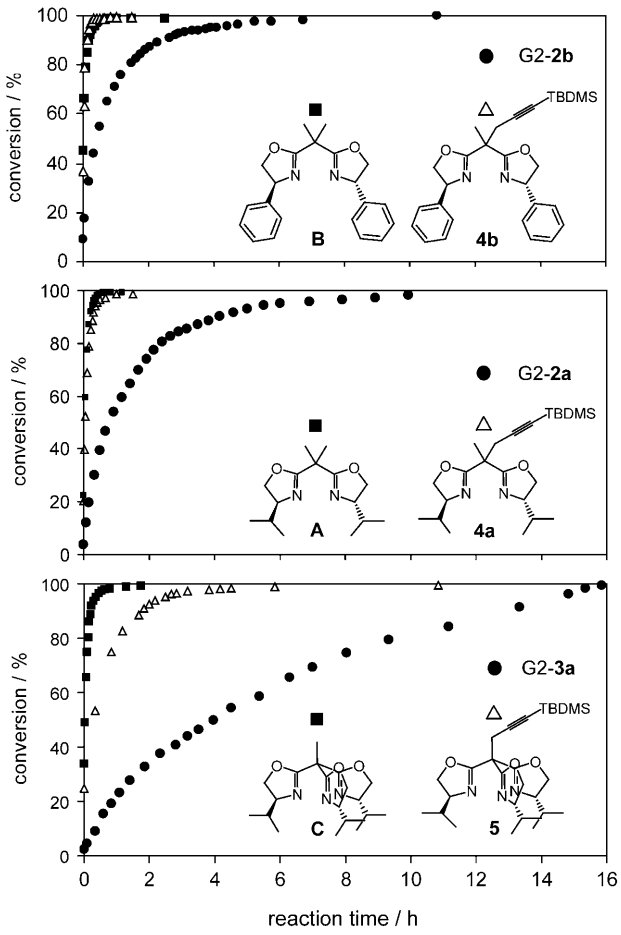


Figure 1. Conversion curves for the α-hydrazination of ethyl 2-methylacetoacetate using catalysts with different steric bulk.

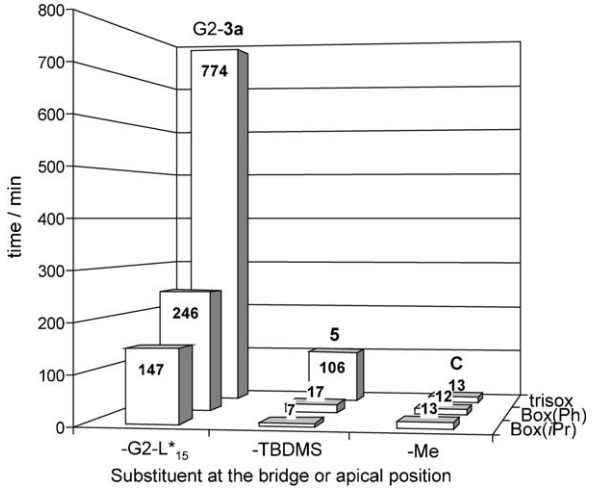


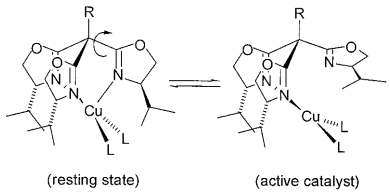
Figure 2. Comparison of the time needed to achieve 90% conversion with the different catalysts.

Both the BOX-based catalysts and the TBDMS-functionalised derivatives (TBDMS = *tert*-butyldimethylsilyl) display similar rates of conversion, whereas the G2-supported catalysts are markedly less active (Figure 1, top and middle). In

contrast, the conversion curves recorded for the three trisox species reveal different behaviour. Whereas the parent catalyst containing ligand **C** displays an activity similar to the BOX-based catalysts, the TBDMS-substituted trisox catalyst **5** is significantly less active, and the conversion is even slower for the dendritic catalyst G2-**3a** (Figure 1, bottom and Figure 2). In summary, whilst the attachment of a linker at the ligand backbone and the immobilisation only moderately affect the BOX-based catalysts for the two reactions studied in this work, the effect on the trisox-based catalysts is dramatic. Attachment of trisox to a second generation carbosilane dendrimer increases the reaction times by an order of magnitude!

This observation may be understood on the basis of the previously proposed role of the third ligand arm in trisox–copper(II) Lewis acid catalysts.[24b,c] In solution, an equilibrium between κ^3- and κ^2-trisox coordinated complexes is thought to exist, for which the coordination of the third ligand arm stabilises the resting state but leads to a deactivation of the copper complexes by reduction of the Lewis acidity as was shown in a theoretical study on BOX–Cu catalysts.[26] We note though that Reiser et al. have found that in some cases pentacoordinate Cu^{II} species may be effective as catalysts,[27] but apparently not with strong donors such as the third oxazoline moiety present in the trisox ligands employed in this study.

The transformation of the stabilised but inactive resting state into the active (17 electron Cu^{II}) species therefore requires the decoordination of an oxazoline unit, which then adopts a remote position from the centre, as depicted in Scheme 5.[24b,c] The resulting vacant coordination site can



Scheme 5. Equilibrium between κ^3- and κ^2-trisox-coordinated complexes. In the κ^2-coordinated species the third oxazoline adopts a remote position from the metal centre.

only then be occupied by the enolate form of ethyl 2-methylacetoacetate. Enantiodescrimination is thus effected by similar Cu species in the BOX and trisox systems.

However, decoordination of the third arm and a fast equilibration of the κ^3- and κ^2-trisox-coordinated complexes require sufficient space for the intramolecular movement of one of the oxazoline rings. Introduction of a bulky substituent (in the form of the linker or even more so of the dendrimer) to the apical position hinders this process sterically and therefore only a fraction of the actually employed trisox–Cu catalyst will be catalytically active. For immobilised trisox, the catalyst loading is thus effectively reduced and the background reaction leading to a racemic product gains in importance. In summary, increasing steric bulk in the periphery of the immobilised trisox ligands is thought to result in the negative observed effect on both the catalyst activity and selectivity. On the other hand, increasing steric bulk may be beneficial for the enantiodiscrimination in the case of the more "open" BOX as manifested in an increase of the *ee* values by about 10%!

Recycling through dialysis: As indicated above, the dendrimer catalysts were developed with the purpose of catalyst recycling based on dialysis, using membrane bags fabricated from a commercially available dialysis membrane (Sigma-Aldrich: benzoylated dialysis tubing, MWCO 2000). As reactors we chose simple screw cap vials as depicted in Figure 3.

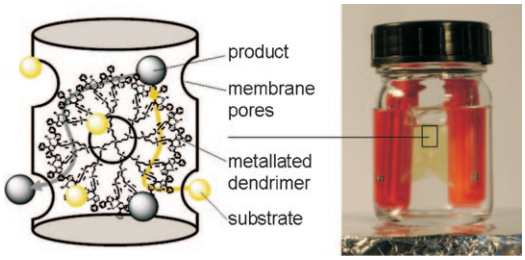


Figure 3. General setup for the recycling using the "catalyst in a tea bag" principle. An enlarged schematic view clarifies the operational principle.

Two of the highest generation dendrimers (G2-**2b** and G2-**3a**) were applied to compare the behaviour of BOX and trisox in the recycling study of the α-hydrazination. The metalated analogues G2-**2b**–Cu and G2-**3a**–Cu of these dendritic ligands possess molecular weights of around 14500 g mol^{-1}, whereas the membrane allows only the migration of molecules up to 2000 g mol^{-1}. On the other hand, the transport of the substrates and the product in and out of the membrane bag occurs by diffusion, which was accelerated by operating at an elevated temperature of 40 °C, consequently resulting in somewhat lower enantioselectivity. The substrates migrate into the membrane bag, in which they interact with the catalytically active terminal groups of the dendrimer and are converted to the product. Consequently, the latter is enriched in the interior and then passes through the membrane to the exterior part of the reactor following the concentration gradient. The practical handling of such a catalyst "tea bag" is illustrated in Figure 4.

Initially the dendrimer-filled membrane bag was placed into the vial containing the yellow solution of the substrates, the colour being due to the diazodicarboxylate (Figure 4a). After their complete conversion to the product, which is accompanied by a decolouration of the solution (Figure 4b), the bag was transferred into another vial containing fresh substrates (Figure 4c). For monitoring the rate of decolouration, reactions times of 10 and 24 h were chosen per cycle with G2-**2b**–Cu and G2-**3a**–Cu, respectively, in order to ach-

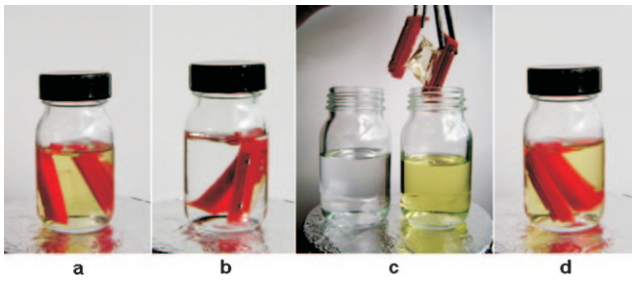


Figure 4. Series showing the course of one recycling: a) dendrimer-filled membrane bag in the yellow solution of the substrates; b) colourless solution after complete conversion; c) transfer of the bag into another vial; d) subsequent reaction cycle.

ieve reasonable conversions. The results obtained for seven successive runs are summarised in Figure 5.

It is notable that the enantioselectivities obtained with G2-**2b**–Cu vary only slightly from 82% in the first to 77% *ee* in the last run. A maximum *ee* of 88% was reached during the third and fourth cycle. The corresponding yields reflect the classical behaviour of membrane systems showing increase between the first (67%) and the second run (86%), reflecting the establishment of a stationary state and then drop gradually to 69% again in the seventh cycle. Overall, the supported BOX catalyst G2-**2b**–Cu gave good and highly reproducible results throughout the study. The trisox dendrimer system G2-**3a**–Cu, on the other hand, started out with a moderate performance (69% *ee*, 55% yield) which decreased monotonically to 14% *ee* and 38% yield for the final run. The reason for the different behaviour of the two dendrimer catalysts is to a large extent the markedly lower activity of G2-**3a** compared to G2-**2b**. This necessitated increased reaction times for each cycle, leading to higher levels of metal-ion leaching, which were investigated by atomic absorption spectrometry. This established a loss in Cu of 2% per cycle of 10 h with G2-**2b**, whereas 4% of the initially applied amount of Cu was leached after cycles of 24 h in the catalyses with G2-**3a**. The level of leaching is proportional to the reaction time and may result in part from the substitutional lability of the copper(II)-oxazoline complexes as well as the modification of the membrane structure due to its exposure to trifluoroethanol at 40°C.

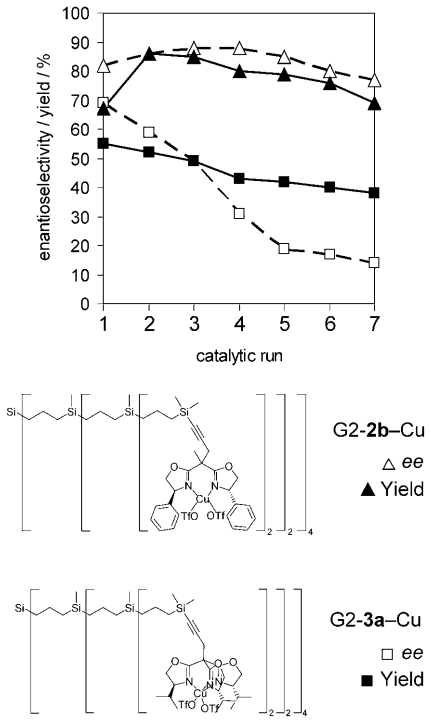


Figure 5. Results of the catalytic performance obtained in the recycling study. Seven successive runs with G2-**2b**–Cu and G2-**3a**–Cu are presented.

Conclusion

In this study bis- and trisoxazolines bearing an alkynyl linker unit have been attached to second-generation carbosilane dendrimers and their copper(II) complexes have been immobilised in dialysis membrane bags. Only the bisoxazoline-based catalysts displayed sufficient activity to allow recycling without significant decrease in activity and selectivity. This has allowed to effect catalytic conversions by dipping the catalyst-filled dialysis bags into reaction vessels containing the substrate. Similar to previously reported enzymatic systems, the dendrimers provided the basis of a catalytic "tea bag", which may be conveniently recycled several times. Ongoing research addresses the problems associated with the transport phenomena which govern the properties of this type of system.

Experimental Section

All manipulations were carried out by using standard Schlenk line or drybox techniques under an atmosphere of argon, unless stated otherwise. Solvents were pre-dried over activated 4 Å molecular sieves and heated to reflux over potassium (THF), sodium (toluene) or calcium hydride (CH_2Cl_2, NEt_3) under an argon atmosphere and collected by distillation. ^1H, $^{13}C\{^1H\}$, $^{29}Si\{^1H\}$ NMR spectra were recorded on a Bruker Avance II 400 or a Bruker Avance III 600 spectrometer. ^1H and ^{13}C assignments were confirmed when necessary by DEPT-135 and two-dimensional ^1H-^1H as well as ^{13}C-^1H NMR experiments. ^1H and ^{13}C NMR spectra were referenced internally to residual protio-solvent (^1H) or solvent (^{13}C) resonances and are reported relative to tetramethylsilane. ^{29}Si NMR spectra were referenced externally to tetramethylsilane. Infrared spectra were prepared as KBr pellets and were recorded on a Varian Excalibur 3100 series FTIR spectrometer. Mass spectra were recorded by the mass spectrometry service and elemental analyses by the analytical service of the Chemical Institutes of the University of Heidelberg. Analytical separation of enantiomers was provided by high pressure liquid chromatography on a Finnigan Surveyor machine. Daicel Chiralcel columns AD-H and OD-H (250×4.6 mm, 5 μm) and the corresponding guard cartridge (10×4 mm, 5 μm) were used. For gas chromatography a Finnigan Focus GC apparatus equipped with a capillary column (BPX5, 5% phenyl, polysilphenylenesiloxane, nonpolar, 30 m×0.25 mm×0.5 μm) was applied. Membranes for dialysis were purchased from Sigma-Aldrich (dialysis tubing, benzoylated, av. flat width 32 mm). (*S*)-Valinol,[28] (*S*)-α-phenylglycinol,[28] (*S*)-4-isopropyloxazoline,[29] (*S*)-4-phenyloxazoline,[29] (*S*)-2-

bromo-4-isopropyloxazoline,[21] (*S*)-2-bromo-phenyloxazoline,[21] 1,1,1-tris[(*S*)-4-isopropyloxazolin-2-yl]ethane (**C**)[20] and the chlorosilyl-functionalised carbosilane dendrimers[14e–j] were prepared according to published procedures. 2,2-Bis[(*S*)-4-isopropyloxazolin-2-yl]propane (**A**) and 2,2-bis[(*S*)-4-phenyloxazolin-2-yl]propane (**B**) were obtained by methylation of the corresponding 2,2-bis(oxazolin-2-yl)ethanes.[18,30] All other compounds and reagents were purchased from commercial chemical suppliers and used without further purification. The absolute configuration for the product ee's was determined by HPLC and comparison with the literature data.[24]

Preparation of the ligands

***N,N′*-Bis[(*S*)-1-(hydroxymethyl)-2-methylpropyl]-2-prop-2-yn-1-ylmalonamide (1a′)**: In a sealed Schlenk tube, L-valinol (7.57 g, 73.4 mmol) and dimethyl propargylmalonate (5.58 mL, 36.7 mmol) were heated at 120 °C until a solid formed (about 1.5 h). Dry toluene was added to the warm mixture to generate a suspension that was heated at 120 °C for another 2 h. The product was precipitated by addition of hexane at room temperature. Subsequent filtration, another washing with hexane, and removal of the residual solvent in vacuo yielded the diamide as an off-white powder (10.62 g, 93 %). ^{1}H NMR (600.13 MHz, [D$_6$]DMSO, 293 K): δ = 7.59 (d, ^3J = 9.26 Hz, 1H; NH), 7.52 (d, ^3J = 9.19 Hz, 1H; NH), 4.64 (br dd, ^3J = 9.03 Hz, ^3J = 5.30 Hz, 2H; OH), 3.61 (m, 1H; NCH), 3.54 (m, 1H; NCH), 3.44–3.26 (m, 5H; CH$_2$OH, CHCH$_2$C≡CH), 2.73 (t, ^4J = 2.59 Hz, 1H; CH$_2$C≡CH), 2.56 (ddd, ^2J = 16.66 Hz, ^3J = 8.62 Hz, ^4J = 2.62 Hz, 1H; CH$_2$C≡CH), 2.46 (ddd, ^2J = 16.67 Hz, ^3J = 6.21 Hz, ^4J = 2.63 Hz, 1H; CH$_2$C≡CH), 1.86 (m, 1H; CH(CH$_3$)$_2$), 1.80 (m, 1H; CH(CH$_3$)$_2$), 0.86 (d, ^3J = 6.83 Hz, 3H; CH(CH$_3$)$_2$), 0.82 (d, ^3J = 6.66 Hz, 3H; CH(CH$_3$)$_2$), 0.81 (d, ^3J = 6.59 Hz, 3H; CH(CH$_3$)$_2$), 0.78 ppm (d, ^3J = 6.83 Hz, 3H; CH(CH$_3$)$_2$); ^{13}C{^{1}H} NMR (150.90 MHz, [D$_6$]DMSO, 293 K): δ = 167.65/167.30 (NCO), 82.22 (C≡CH), 71.79 (C≡CH), 61.16/61.07 (CH$_2$OH), 55.53/55.24 (NCH), 51.70 (CHCH$_2$C≡CH), 28.22/27.57 (CH(CH$_3$)$_2$), 19.65/19.55 (CH(CH$_3$)$_2$), 18.28 (CH$_2$C≡CH), 17.92/17.38 ppm (CH(CH$_3$)$_2$); IR (KBr): $\tilde{\nu}$ = 3520–3320 (s, br; OH), 3320–3200 (m; NH), 2980–2870 (m; CH$_2$), 2121 (w; C≡C), 1634, 1559 cm^{-1} (s, CO); MS (FAB): *m*/*z* (%): 625.5 (3) [2*M*+H]$^+$, 313.3 (100) [*M*+H]$^+$, 295.3 (95) [*M*−OH]$^+$; elemental analysis calcd (%) for C$_{16}$H$_{28}$N$_2$O$_4$ (312.41): C 61.51, H 9.03, N 8.97; found C 61.25, H 8.92, N 8.95.

***N,N′*-Bis[(*S*)-2-hydroxy-1-phenylethyl]-2-prop-2-yn-1-ylmalonamide (1b′)**: In a sealed Schlenk tube, L-α-phenylglycinol (13.77 g, 100.4 mmol) and dimethyl propargylmalonate (7.63 mL, 50.2 mmol) were heated at 110 °C until a solid formed (about 3 h). Then, dry toluene was added to the warm mixture to generate a suspension that was heated at 100 °C for another 2 h. The product was precipitated by addition of pentane at room temperature. Subsequent filtration, another washing with pentane, and removal of the residual solvent in vacuo yielded the diamide as a white powder (18.20 g, 95 %). ^{1}H NMR (600.13 MHz, [D$_6$]DMSO, 293 K): δ = 8.51 (d, ^3J = 7.93 Hz, 1H; NH), 8.45 (d, ^3J = 7.87 Hz, 1H; NH), 7.36–7.21 (m, 10H; CH$_{aryl}$), 5.04 (s, 2H; OH), 4.84 (m, 2H; NCH), 3.64–3.59 (m, 4H; CH$_2$OH), 3.57 (t, ^3J = 7.38 Hz, 1H; CHCH$_2$C≡CH), 2.76 (t, ^4J = 2.35 Hz, 1H; CH$_2$C≡CH), 2.53 ppm (d, ^3J = 5.76 Hz, 2H; CH$_2$C≡CH); ^{13}C{^{1}H} NMR (150.90 MHz, [D$_6$]DMSO, 293 K): δ = 166.99/166.88 (NCO), 140.90/140.68 (C$_{q,\ aryl}$), 127.98/126.69/126.66/126.62 (C$_{aryl}$), 82.18 (C≡H), 71.95 (C≡CH), 64.73/64.42 (CH$_2$OH), 54.94/54.89 (NCH), 51.48 (CHCH$_2$C≡CH), 17.91 (CH$_2$C≡CH); IR (KBr): $\tilde{\nu}$ = 3520–3340 (m, br; OH), 3340–3240 (m; NH), 3100–3040 (w; CH$_{aryl}$), 2990–2860 (w; CH$_2$), 1665, 1541 cm^{-1} (s; CO); MS (FAB): *m*/*z* (%): 381.2 (100) [*M*+H]$^+$; HRMS (FAB): *m*/*z* calcd for C$_{22}$H$_{25}$N$_2$O$_4$ [*M*+H]$^+$: 381.1814; found: 381.1808; elemental analysis calcd (%) for C$_{22}$H$_{24}$N$_2$O$_4$ (380.44): C 69.46, H 6.36, N 7.36; found C 69.03, H 6.43, N 7.28.

***N,N′*-Bis[(*S*)-2-chloro-1-phenylethyl]-2-prop-2-yn-1-ylmalonamide (1b″)**: A suspension of dihydroxy diamide **1b′** (6.75 g, 17.7 mmol) in dry toluene (140 mL) was cooled to 0 °C and SOCl$_2$ (7.77 mL, 107.1 mmol) was added slowly. The reaction proceeded at room temperature over night, yielding a greyish green solution. Removal of the solvent in vacuo gave a yellow glass, which was redissolved in dichloromethane, washed with KHCO$_3$ (10 % w/w in H$_2$O) and dried over Na$_2$SO$_4$. Subsequent filtration and removal of the residual solvent in vacuo yielded the product as a reddish orange powder of sufficient purity for direct use in the next step (7.39 g, 99 %). ^{1}H NMR (600.13 MHz, [D$_4$]MeOH, 293 K): δ = 7.34–7.25 (m, 10H; CH$_{aryl}$), 5.18 (m, 2H; NCH), 3.86–3.71 (m, 4H; CH$_2$Cl), 3.49 (t, ^3J = 7.59 Hz, 1H; CHCH$_2$C≡CH), 2.76–2.68 (m, 2H; CH$_2$C≡CH), 2.31 ppm (t, ^4J = 2.63 Hz, 1H; CH$_2$C≡CH); ^{13}C{^{1}H} NMR (150.90 MHz, [D$_4$]MeOH, 293 K): δ = 170.20/170.19 (NCO), 140.03/139.93 (C$_{q,aryl}$), 129.80/129.72/129.12/129.04/128.00/127.92 (C$_{aryl}$), 82.29 (C≡CH), 72.14 (C≡CH), 56.39/56.25 (NCH), 54.11 (CHCH$_2$C≡CH), 47.84/47.65 (CH$_2$Cl), 20.78 ppm (CH$_2$C≡CH); IR (KBr): $\tilde{\nu}$ = 3295 (m; NH), 3120–3000 (w; CH$_{aryl}$), 3000–2850 (w; CH$_2$), 2121 (w; C≡C), 1670, 1558 cm^{-1} (s; CO); MS (FAB): *m*/*z* (%): 417.2 (50) [*M*+H]$^+$, 367.2 (6) [*M*−CH$_2$Cl]$^+$; HRMS (FAB): *m*/*z* calcd for C$_{22}$H$_{23}$N$_2$O$_2$^{35}Cl$_2$ [*M*+H]$^+$: 417.1163; found: 417.1136; *m*/*z* calcd for C$_{22}$H$_{23}$N$_2$O$_2$^{35}Cl^{37}Cl [*M*+H]$^+$: 419.1108; found: 419.1143; *m*/*z* calcd for C$_{22}$H$_{23}$N$_2$O$_2$^{37}Cl$_2$ [*M*+H]$^+$: 421.1078; found: 421.1134.

4,4-Bis[(*S*)-4-isopropyloxazolin-2-yl]but-1-yne (1a): Dry NEt$_3$ (12.17 mL, 87.6 mmol) and DMAP (241 mg, 2.0 mmol) were added to a suspension of dihydroxy diamide **1a′** (6.15 g, 19.7 mmol) in dry dichloromethane (250 mL). The mixture was cooled to 0 °C and solid TsCl (7.50 g, 39.3 mmol) was added over a period of 3 h. After warming the resulting off-white suspension to room temperature, a yellow solution formed that was stirred for another 4 d. Completion of conversion was achieved by subsequent heating at 40 °C for 8 h. The resulting mixture was diluted by addition of dichloromethane, washed with NH$_4$Cl$_{aq}$ as well as brine, and dried over Na$_2$SO$_4$. Filtration and removal of the solvent in vacuo afforded an oily crude product that was purified by column chromatography (pentane/EtOAc 60:40) yielding the product as a pale yellow oil (3.97 g, 73 %). ^{1}H NMR (600.13 MHz, CDCl$_3$, 293 K): δ = 4.27–4.22 (m, 2H; CH$_2$O), 4.03–3.94 (m, 4H; CH$_2$O, NCH), 3.65 (t, ^3J = 7.74 Hz, 1H; CHCH$_2$C≡CH), 2.86 (ddd, ^2J = 16.89 Hz, ^3J = 7.71 Hz, ^4J = 2.65 Hz, 1H; CH$_2$C≡CH), 2.81 (ddd, ^2J = 16.88 Hz, ^3J = 7.80 Hz, ^4J = 2.66 Hz, 1H; CH$_2$C≡CH), 1.98 (t, ^4J = 2.65 Hz, 1H; CH$_2$C≡CH), 1.78 (m, 2H; CH(CH$_3$)$_2$), 0.92 (d, ^3J = 6.80 Hz, 6H; CH(CH$_3$)$_2$), 0.86 ppm (d, ^3J = 6.78 Hz, 6H; CH(CH$_3$)$_2$); ^{13}C{^{1}H} NMR (150.90 MHz, CDCl$_3$, 293 K): δ = 163.14/163.08 (NCO), 80.69 (C≡CH), 71.88/71.82 (NCH), 70.30 (CH$_2$O), 70.05 (C≡CH), 39.08 (CHCH$_2$C≡CH), 32.28/32.21 (CH(CH$_3$)$_2$), 19.78 (CH$_2$C≡CH), 18.56/18.51 (CH(CH$_3$)$_2$), 17.72 ppm (CH(CH$_3$)$_2$); IR (KBr): $\tilde{\nu}$ = 2960–2874 (m; CH$_2$), 2108 (w; C≡C), 1665 cm^{-1} (s; C=N); MS (FAB): *m*/*z* (%): 277.2 (100) [*M*+H]$^+$, 191.1 (4) [*M*+H−C$_5$H$_{10}$O]$^+$; HRMS (FAB): *m*/*z* calcd for C$_{16}$H$_{25}$N$_2$O$_2$ [*M*+H]$^+$: 277.1916; found: 277.1944; elemental analysis calcd (%) for C$_{16}$H$_{24}$N$_2$O$_2$ (276.37): C 69.53, H 8.75, N 10.14; found C 69.57, H 8.75, N 9.96.

4,4-Bis[(*S*)-4-phenyloxazolin-2-yl]but-1-yne (1b): In air, dichloride **1b″** (7.39 g, 17.7 mmol) was dissolved in methanolic NaOH (2.13 g, 53.3 mmol in 260 mL) and heated to reflux for 14 h, during which NaCl precipitated. The solvent was removed in vacuo, and the residue was redissolved in dichloromethane, washed with NH$_4$Cl$_{aq}$ and dried over Na$_2$SO$_4$. Filtration and removal of the solvent in vacuo afforded an orange foam that was purified by column chromatography (pentane/EtOAc 70:30) yielding the bisoxazoline as an orange, viscous oil (2.61 g, 43 %). ^{1}H NMR (600.13 MHz, CDCl$_3$, 293 K): δ = 7.35–7.26 (m, 10H; CH$_{aryl}$), 5.28 (m, 2H; NCH), 4.71 (m, 2H; CH$_2$O), 4.19 (m, 2H; CH$_2$O), 3.90 (t, ^3J = 7.71 Hz, 1H; CHCH$_2$C≡CH), 3.02 (m, 2H; CH$_2$C≡CH), 2.10 ppm (dt, ^4J = 2.50 Hz, ^5J = 1.18 Hz, 1H; CH$_2$C≡CH); ^{13}C{^{1}H} NMR (150.90 MHz, CDCl$_3$, 293 K): δ = 164.75/164.67 (NCO), 141.94/141.87 (C$_{q,\ aryl}$), 128.69/128.68/127.65/126.75/126.65 (C$_{aryl}$), 80.58 (C≡CH), 75.55/75.47 (CH$_2$O), 70.49 (C≡CH), 69.69/69.60 (NCH), 39.14 (CHCH$_2$C≡CH), 19.97 ppm (CH$_2$C≡CH); IR (KBr): $\tilde{\nu}$ = 3295 (m; C≡CH), 3070–3005 (w; CH$_{aryl}$), 2980–2860 (m; CH$_2$), 2121 (w; C≡C), 1664 (s; C=N); MS (FAB): *m*/*z* (%): 345.1 (100) [*M*+H]$^+$, 225.1 (2) [*M*+H−C$_8$H$_8$O]$^+$; HRMS (FAB): *m*/*z* calcd for C$_{22}$H$_{21}$N$_2$O$_2$ [*M*+H]$^+$: 345.1603; found: 345.1600; elemental analysis calcd (%) for C$_{22}$H$_{20}$N$_2$O$_2$ (344.41): C 76.72, H 5.85, N 8.13; found C 76.55, H 5.90, N 7.99.

4,4-Bis[(*S*)-4-isopropyloxazolin-2-yl]pent-1-yne (propargyl-BOX(*i*Pr); 2a): A solution of bisoxazoline **1a** (2.40 g, 8.7 mmol) in THF (50 mL) was cooled to −78 °C and *n*BuLi (5.97 mL, 1.6 M in hexane) was added. The resulting bright yellow mixture was stirred at −40 °C for 30 min prior to the addition of MeI (1.62 mL, 26.0 mmol). The mixture was slowly warmed to room temperature over night. After removal of the solvent in vacuo, the residue was redissolved in dichloromethane, washed with

NH_4Cl_{aq} and dried over Na_2SO_4. Filtration and removal of the solvent gave the crude product that was purified by column chromatography (pentane/EtOAc 60:40) yielding **2a** as a pale yellow oil (2.30 g, 91%). ^{1}H NMR (600.13 MHz, $CDCl_3$, 293 K): δ = 4.23–4.19 (m, 2H; CH_2O), 4.03–3.95 (m, 4H; CH_2O, NCH), 2.90 (dd, ^2J = 16.80 Hz, ^4J = 2.64 Hz, 1H; CH_2C≡CH), 2.85 (dd, ^2J = 16.79 Hz, ^4J = 2.63 Hz, 1H; CH_2C≡CH), 1.98 (t, ^4J = 2.60 Hz, 1H; CH_2C≡CH), 1.80 (m, 2H; CH(CH_3)$_2$), 1.63 (s, 3H; CCH_3), 0.91 (m, 6H; CH(CH_3)$_2$), 0.86 ppm (m, 6H; CH(CH_3)$_2$); ^{13}C{^{1}H} NMR (150.90 MHz, $CDCl_3$, 293 K): δ = 166.67/166.54 (NCO), 80.02 (C≡CH), 71.79/71.54 (NCH), 70.79 (C≡CH), 70.12/70.09 (CH_2O), 41.72 (CCH$_2$C≡CH), 32.18/32.13 (CH(CH_3)$_2$), 26.95 (CH_2C≡CH), 21.25 (CCH_3), 18.64/18.47 (CH(CH_3)$_2$), 17.55/17.39 ppm (CH(CH_3)$_2$); IR (KBr): $\tilde{\nu}$ = 2960–2874 (m; CH_2), 2121 (w; C≡C), 1661 cm^{-1} (s; C=N); MS (FAB): m/z (%): 291.2 (100) [M+H]$^+$, 289.1 (4) [M−H]$^+$, 247.1 (2) [M−C_3H_7]$^+$, 205.1 (4) [M+H−C_5H_{10}O]$^+$; HRMS (FAB): m/z calcd for $C_{17}H_{27}N_2O_2$ [M+H]$^+$: 291.2072; found: 291.2066; elemental analysis calcd (%) for $C_{17}H_{26}N_2O_2$ (290.40): C 70.31, H 9.02, N 9.65; found C 70.13, H 8.95, N 9.08.

4,4-Bis[(*S*)-4-phenyloxazolin-2-yl]pent-1-yne (propargyl-BOX(Ph); 2b): A solution of bisoxazoline **1b** (858 mg, 2.5 mmol) in THF (10 mL) was cooled to −78°C and *n*BuLi (1.70 mL, 1.6 M in hexane) was added. The resulting bright yellow mixture was stirred at −40°C for 30 min prior to adding MeI (0.47 mL, 7.5 mmol). The solution was warmed to room temperature over night. After removal of the solvent in vacuo, the residue was redissolved in dichloromethane, washed with NH_4Cl_{aq} and dried over Na_2SO_4. Filtration and removal of the solvent yielded the crude product which was purified by column chromatography (pentane/EtOAc 60:40) yielding **2b** as a colourless, extremely viscous oil (847 mg, 95%). ^{1}H NMR (600.13 MHz, $CDCl_3$, 293 K): δ = 7.35–7.26 (m, 10H; CH_{aryl}), 5.26 (m, 2H; NCH), 4.70 (m, 2H; CH_2O), 4.18 (m, 2H; CH_2O), 3.05 (d, ^4J = 2.48 Hz, 2H; CH_2C≡CH), 2.10 (t, ^4J = 2.39 Hz, 1H; CH_2C≡CH), 1.81 ppm (s, 3H; CCH_3); ^{13}C{^{1}H} NMR (150.90 MHz, $CDCl_3$, 293 K): δ = 168.29/168.20 (NCO), 142.13/142.05 ($C_{q,\ aryl}$), 128.69/128.62/127.61/126.84/126.63 (C_{aryl}), 79.85 (C≡CH), 75.71/75.63 (CH_2O), 71.28 (C≡CH), 69.74/69.52 (NCH), 42.08 (CCH$_3$), 27.12 (CH$_2$C≡CH), 21.41 ppm (CCH_3); IR (KBr): $\tilde{\nu}$ = 3291 (m; C≡CH), 3070–3000 (w; CH_{aryl}), 3000–2840 (m; CH_2), 2121 (w; C≡C), 1654 cm^{-1} (s; C=N); MS (FAB): m/z (%): 359.1 (100) [M+H]$^+$, 357.1 (6) [M−H]$^+$, 239.0 (5) [M+H−C_8H_8O]$^+$; HRMS (FAB): m/z calcd for $C_{23}H_{23}N_2O_2$ [M+H]$^+$: 359.1760; found: 359.1771; elemental analysis calcd (%) for $C_{23}H_{22}N_2O_2$ (358.43): C 77.07, H 6.19, N 7.82; found C 76.85, H 6.25, N 7.48.

4,4,4-Tris[(*S*)-4-isopropyloxazolin-2-yl]but-1-yne (propargyl-trisox(*i*Pr); 3a): A solution of bisoxazoline **1a** (970 mg, 3.5 mmol) in dry toluene (100 mL) was cooled to −78°C and *t*BuLi (2.27 mL, 1.7 M in hexane) was added; 15 min later (*S*)-2-bromo-4-isopropyloxazoline (943 mg, 4.9 mmol, 62% w/w in THF) was transferred to the yellow solution, giving rise to an orange-brown colour. The mixture was warmed to room temperature, concentrated to eliminate the hexane originating from *t*BuLi, and heated at 100°C for 10 d. The resulting deep brown solution was evaporated to dryness and the residue was redissolved in dichloromethane (100 mL), washed with H_2O (20 mL) and dried over Na_2SO_4. Filtration and removal of the solvent in vacuo yielded a brown oil which was purified by column chromatography (EtOAc/MeOH 97.5/2.5) yielding **3b** as a yellow, viscous oil (934 mg, 69%). ^{1}H NMR (399.89 MHz, $CDCl_3$, 293 K): δ = 4.27 (dd, ^2J = 9.48 Hz, ^3J = 8.07 Hz, 3H; CH_2O), 4.07 (m, 3H; CH_2O), 4.03–3.98 (m, 3H; NCH), 3.24 (dd, ^2J = 16.69 Hz, ^4J = 2.64 Hz, 1H; CH_2C≡CH), 3.14 (dd, ^2J = 16.70 Hz, ^4J = 2.66 Hz, 1H; CH_2C≡CH), 1.99 (t, ^4J = 2.64 Hz, 1H; CH_2C≡CH), 1.80 (m, 3H; CH(CH$_3$)$_2$), 0.92 (d, ^3J = 6.80 Hz, 9H; CH(CH_3)$_2$), 0.87 ppm (d, ^3J = 6.77 Hz, 9H; CH(CH_3)$_2$); ^{13}C{^{1}H} NMR (100.56 MHz, $CDCl_3$, 293 K): δ = 162.44 (NCO), 80.00 (C≡CH), 71.66 (NCH), 70.28 (CH_2O), 70.22 (C≡CH), 47.92 (CCH$_2$C≡CH), 32.21 (CH(CH$_3$)$_2$), 25.44 (CH$_2$C≡CH), 18.64/18.46 (CH(CH_3)$_2$), 17.87/17.71 ppm (CH(CH_3)$_2$); IR (KBr): $\tilde{\nu}$ = 2960–2874 (m; CH_2), 2108 (w; C≡C), 1665 cm^{-1} (s; C=N); MS (EI): m/z (%): 387.2 (4) [M]$^+$, 344.1 (100) [M−C_3H_7]$^+$, 275.1 (30) [M−C_6H_{10}NO]$^+$; HRMS (FAB): m/z calcd for $C_{22}H_{34}N_3O_3$ [M+H]$^+$: 388.2600; found: 388.2597; elemental analysis calcd (%) for $C_{22}H_{33}N_3O_3$ (387.52): C 68.19, H 8.58, N 10.84; found C 68.39, H 8.56, N 10.29.

4,4,4-Tris[(*S*)-4-phenyloxazolin-2-yl]but-1-yne (propargyl-trisox(Ph); 3b): A solution of bisoxazoline **1b** (442 mg, 1.3 mmol) in dry toluene (70 mL) was cooled to −78°C and *t*BuLi (0.94 mL, 1.7 M in hexane) was added; 15 min later (*S*)-2-bromo-4-phenyloxazoline (406 mg, 1.8 mmol, 54% w/w in THF) was transferred to the yellow solution, giving rise to an orange-brown colour. The mixture was warmed to room temperature, concentrated to eliminate the hexane originating from *t*BuLi, and heated at 70°C for 10 d. The resulting pale brown solution was evaporated to dryness and the residue was redissolved in dichloromethane (50 mL), washed with H_2O (10 mL) and dried over Na_2SO_4. Filtration and removal of the solvent in vacuo yielded a brown oil which was purified by column chromatography (pentane/EtOAc 40:60, then EtOAc and EtOAc/MeOH 99:1) yielding **3b** as an extremely viscous oil, which turned into a glass upon standing (220 mg, 35%). ^{1}H NMR (600.13 MHz, $CDCl_3$, 293 K): δ = 7.36–7.26 (m, 15H; CH_{aryl}), 5.35 (dd, ^3J = 10.09 Hz, ^3J = 7.88 Hz, 3H; NCH), 4.78 (dd, ^2J = 10.13 Hz, ^3J = 8.35 Hz, 3H; CH_2O), 4.26 (m, 3H; CH_2O), 3.45 (dd, ^2J = 16.81 Hz, ^4J = 2.62 Hz, 1H; CH_2C≡CH), 3.39 (dd, ^2J = 16.80 Hz, ^4J = 2.65 Hz, 1H; CH_2C≡CH), 2.11 ppm (t, ^4J = 2.62 Hz, 1H; CH_2C≡CH); ^{13}C{^{1}H} NMR (150.90 MHz, $CDCl_3$, 293 K): δ = 164.25 (NCO), 141.90 ($C_{q,\ aryl}$), 128.58/127.57/126.93 (C_{aryl}), 79.77 (C≡CH), 76.04 (CH_2O), 71.03 (C≡CH), 69.64 (NCH), 48.47 (CCH$_2$C≡CH), 25.68 ppm (CH$_2$C≡CH); IR (KBr): $\tilde{\nu}$ = 3291 (m; C≡CH), 3070–3005 (w; CH_{aryl}), 2980–2850 (m; CH_2), 2108 (w; C≡C), 1663 cm^{-1} (s; C=N); MS (FAB): m/z (%): 490.1 (100) [M+H]$^+$, 464.1 (5) [M−C_2H]$^+$, 345.0 (10) [M−C_2H−C_8H_8O]$^+$; HRMS (FAB): m/z calcd for $C_{31}H_{28}N_3O_3$ [M+H]$^+$: 490.2130; found: 490.2145; elemental analysis calcd (%) for $C_{31}H_{27}N_3O_3$ (489.56)·0.9 MeOH: C 73.91, H 5.95, N 8.11; found C 73.96, H 6.00, N 7.85.

General procedure for the preparation of TBDMS-functionalised ligands: A solution of the corresponding ligand (0.3–1.3 mmol) in THF (10–20 mL) was cooled to −78°C and LDA, *n*BuLi or *t*BuLi (1.1–1.2 equiv) were added. The resulting mixture was stirred for 30 min and a solution of TBDMSCl (1.2–1.3 equiv) in THF was added. After warming to room temperature, it was additionally stirred for 3–4 d. The solvent was removed in vacuo and the residue redissolved in dichloromethane, washed with NH_4Cl_{aq} and dried over Na_2SO_4. Filtration and removal of the solvent gave an oily crude product which was purified by column chromatography.

1-[*tert*-Butyl(dimethyl)silyl]-4,4-bis[(*S*)-4-isopropyloxazolin-2-yl]pent-1-yne (TBDMS-propargyl-BOX(*i*Pr); 4a): Yield: 77%; ^{1}H NMR (600.13 MHz, $CDCl_3$, 293 K): δ = 4.21 (m, 2H; CH_2O), 4.02–3.91 (m, 4H; CH_2O, NCH), 3.00 (d, ^2J = 16.93 Hz, 1H; CH_2C≡C), 2.84 (d, ^2J = 16.93 Hz, 1H; CH_2C≡C), 1.83–1.73 (m, 2H; CH(CH$_3$)$_2$), 1.63 (s, 3H; CCH_3), 0.93 (d, ^3J = 6.82 Hz, 3H; CH(CH_3)$_2$), 0.91–0.89 (m, 12H; C(CH_3)$_3$, CH(CH_3)$_2$), 0.85 (m, 6H; CH(CH_3)$_2$), 0.05 ppm (s, 6H; Si(CH_3)$_2$); ^{13}C{^{1}H} NMR (150.90 MHz, $CDCl_3$, 293 K): δ = 166.73 (NCO), 102.99 (C≡C-TBDMS), 85.27 (C≡C-TBDMS), 71.88/71.55 (NCH), 70.23/69.99 (CH_2O), 41.88 (CCH$_2$C≡C), 32.37/32.13 (CH(CH$_3$)$_2$), 28.32 (CH$_2$C≡C), 26.05 (C(CH_3)$_3$), 21.29 (CCH$_3$), 18.74/18.54 (CH(CH_3)$_2$), 17.71/17.33 (CH(CH_3)$_2$), 16.49 (C(CH$_3$)$_3$), −4.57 ppm (Si(CH_3)$_2$); ^{29}Si{^{1}H} NMR (79.44 MHz, $CDCl_3$, 293 K): δ = −8.86; IR (KBr): $\tilde{\nu}$ = 2958–2858 (m; CH_2), 2177 (m; C≡C), 1662 cm^{-1} (s; C=N); MS (FAB): m/z (%): 405.2 (100) [M+H]$^+$, 361.2 (2) [M−C_3H_7]$^+$; HRMS (FAB): m/z calcd for $C_{23}H_{41}N_2O_2Si$ [M+H]$^+$: 405.2937; found: 405.2925; elemental analysis calcd (%) for $C_{23}H_{40}N_2O_2Si$ (404.66): C 68.27, H 9.96, N 6.92; found C 68.10, H 9.86, N 6.84.

1-[*tert*-Butyl(dimethyl)silyl]-4,4-bis[(*S*)-4-phenyloxazolin-2-yl]pent-1-yne (TBDMS-propargyl-BOX(Ph); 4b): Yield: 62%; ^{1}H NMR (600.13 MHz, $CDCl_3$, 293 K): δ = 7.34–7.26 (m, 10H; CH_{aryl}), 5.24 (m, 2H; NCH), 4.68 (m, 2H; CH_2O), 4.19–4.11 (m, 2H; CH_2O), 3.17 (d, ^2J = 16.91 Hz, 1H; CH_2C≡C), 3.01 (d, ^2J = 16.90 Hz, 1H; CH_2C≡C), 1.80 (s, 3H; CCH_3), 0.94 (s, 9H; C(CH_3)$_3$), 0.10 ppm (s, 6H; Si(CH_3)$_2$); ^{13}C{^{1}H} NMR (150.90 MHz, $CDCl_3$, 293 K): δ = 168.56/168.33 (NCO), 142.26/142.07 ($C_{q,\ aryl}$), 128.66/127.55/126.72/126.67 (C_{aryl}), 102.64 (C≡C-TBDMS), 85.81 (C≡C-TBDMS), 75.63/75.58 (CH_2O), 69.71/69.57 (NCH), 42.32 (CCH$_3$), 28.53 (CH$_2$C≡C), 26.04 (C(CH_3)$_3$), 21.42 (CCH$_3$), 16.51 (C(CH$_3$)$_3$), −4.52 ppm (Si(CH_3)$_2$); ^{29}Si{^{1}H} NMR (79.44 MHz, $CDCl_3$, 293 K): δ = −8.61 ppm; IR (KBr): $\tilde{\nu}$ = 3090–3004 (w; CH_{aryl}), 3000–2854 (m; CH_2),

2175 (m; C≡C), 1668, 1664 cm^{-1} (s; C=N); MS (FAB): *m/z* (%): 473.2 (100) $[M+H]^+$, 471.2 (3) $[M-H]^+$, 353.1 (1) $[M+H-C_8H_8O]^+$, 319.1 (4) $[M-C_9H_{17}Si]^+$; HRMS (FAB): *m/z* calcd for $C_{29}H_{37}N_2O_2Si$ $[M+H]^+$: 473.2624; found: 473.2693; elemental analysis calcd (%) for $C_{29}H_{36}N_2O_2Si$ (472.69): C 73.69, H 7.68, N 5.93; found C 73.28, H 7.61, N 5.92.

1-[*tert*-Butyl(dimethyl)silyl]-4,4,4-tris[(*S*)-4-isopropyloxazolin-2-yl]but-1-yne (TBDMS-propargyl-trisox(*i*Pr); 5): Yield: 96%; ^1H NMR (399.89 MHz, $CDCl_3$, 293 K): $\delta=4.25$ (dd, $^2J=9.37$, $^3J=8.39$ Hz, 3H; CH_2O), 4.05 (m, 3H; CH_2O), 3.97 (ddd, $^3J=9.60$ Hz, $^3J=7.34$ Hz, $^3J=6.10$ Hz, 3H; NC*H*), 3.31 (d, $^2J=16.88$ Hz, 1H; CH_2C≡C), 3.15 (d, $^2J=16.81$ Hz, 1H; CH_2C≡C), 1.78 (m, 3H; C*H*(CH_3)$_2$), 0.92 (d, $^3J=6.87$ Hz, 9H; CH(CH_3)$_2$), 0.90 (s, 9H; C(CH_3)$_3$), 0.87 (d, $^3J=6.77$ Hz, 9H; CH-(CH_3)$_2$), 0.04 (s, 3H; Si(CH_3)$_2$), 0.03 ppm (s, 3H; Si(CH_3)$_2$); $^{13}C\{^1H\}$ NMR (100.56 MHz, $CDCl_3$, 293 K): $\delta=162.56$ (N*C*O), 102.84 (*C*≡C-TBDMS), 84.29 (C≡*C*-TBDMS), 71.88 (N*C*H), 70.60 (*C*H_2O), 48.05 (*C*CH$_2$C≡C), 32.43 (*C*H(CH$_3$)$_2$), 26.88 (*C*H$_2$C≡C), 26.07 C(*C*H$_3$)$_3$), 18.69 (CH(*C*H$_3$)$_2$), 17.91 (CH(*C*H$_3$)$_2$), 16.57 (*C*(CH$_3$)$_3$), −4.55 ppm (Si(*C*H$_3$)$_2$); $^{29}Si\{^1H\}$ NMR (79.44 MHz, $CDCl_3$, 293 K): $\delta=-9.09$; IR (KBr): $\tilde{\nu}=$ 2961–2858 (m; CH_2), 2180 (w; C≡C), 1677 cm^{-1} (s; C=N); MS (FAB): *m/z* (%): 502.3 (100) $[M+H]^+$, 348.3 (4) $[M-C_9H_{17}Si]^+$; HRMS (FAB): *m/z* calcd for $C_{28}H_{48}N_3O_3Si$ $[M+H]^+$: 502.3465; found: 502.3445; elemental analysis calcd (%) for $C_{28}H_{47}N_3O_3Si$ (501.78): C 67.02, H 9.44, N 8.37; found C 67.01, H 9.26, N 8.19.

General procedure for the preparation of the functionalised dendrimers: The appropriate amount of ligand (1.1–1.8 equiv with respect to each chlorosilyl function of the carbosilane dendrimer) was dissolved in dry toluene (3 mL), cooled to −78 °C and LDA (1.0 equiv with respect to the amount of ligand, 1.8 M in THF/heptane/ethylbenzene) was added slowly. The resulting solution was stirred at −40 °C for 30 min. A solution of the corresponding chlorosilyl-functionalised dendrimer (10–70 μmol) in dry toluene (2 mL) and solid $TlPF_6$ (1.1–1.6 equiv per chlorosilyl function) were added. The mixture was warmed to room temperature over night and stirred for several days. After removal of the solvent in vacuo, the residue was redissolved in dichloromethane, washed with H_2O (1–2 mL), and dried over Na_2SO_4. The solvent was again removed, the residue redissolved in MeOH, and filtered through a biochemical filter (0.45 μm pore size). This step was repeated once or twice. {G0}-[propargyl-BOX-(*i*Pr)]$_4$ and {G0}-[propargyl-BOX(Ph)]$_4$ were then purified by flash filtration through silica gel (pentane/EtOAc 60:40, later EtOAc/MeOH 97.5:2.5 to 95:5). All other derivatives were purified by dialysis: the membrane was washed with dichloromethane (3×) and filled with a concentrated solution of the crude product in dichloromethane. The resulting bag was placed into pure dichloromethane (200 mL) and gently stirred for 8–16 h. Then the exterior solvent was replaced. This was repeated up to four times, depending on the amount of residual free ligand and other impurities in the sample.

{G0}-[propargyl-BOX(*i*Pr)]$_4$ (G0-2a): Yield: 28%; ^1H NMR (600.13 MHz, $CDCl_3$, 293 K): $\delta=4.20$ (dd, $^2J=9.47$ Hz, $^3J=8.12$ Hz, 4H; CH_2O), 4.18 (dd, $^2J=9.47$ Hz, $^3J=8.17$ Hz, 4H; CH_2O), 4.02–3.98 (m, 8H; CH_2O), 3.98–3.93 (m, 8H; NC*H*), 2.96 (d, $^2J=16.92$ Hz, 4H; CH_2C≡C), 2.84 (d, $^2J=16.92$ Hz, 4H; CH_2C≡C), 1.79 (m, 8H; C*H*(CH$_3$)$_2$), 1.61 (s, 12H; CCH_3), 1.34 (m, 8H; H_c), 0.93 (d, $^3J=6.81$ Hz, 12H; CH(CH_3)$_2$), 0.90 (d, $^3J=6.82$ Hz, 12H; CH(CH_3)$_2$), 0.87 (d, $^3J=6.78$ Hz, 12H; CH-(CH_3)$_2$), 0.85 (d, $^3J=6.79$ Hz, 12H; CH(CH_3)$_2$), 0.64 (m, 8H; H_b), 0.56 (m, 8H; H_d), 0.081 (s, 12H; H_a), 0.080 ppm (s, 12H; H_a); $^{13}C\{^1H\}$ NMR (150.90 MHz, $CDCl_3$, 293 K): $\delta=166.75/166.60$ (N*C*O), 102.67 (*C*≡C-Si), 86.56 (C≡*C*-Si), 71.75/71.44 (N*C*H), 70.11/69.96 (*C*H_2O), 41.79 (*C*CH$_3$), 32.27/32.10 (*C*H(CH$_3$)$_2$), 28.23 (*C*H$_2$C≡C), 21.25 (C*C*H$_3$), 21.06 (C_b), 18.70/18.43 (CH(*C*H$_3$)$_2$), 18.31 (C_c), 17.69/17.36 (CH(*C*H$_3$)$_2$), 17.02 (C_d), −1.63/-1.65 ppm (C_a); $^{29}Si\{^1H\}$ NMR (79.44 MHz, $CDCl_3$, 293 K): $\delta=0.73$ (*Si*(CH$_2$)$_4$), −17.93 ppm (*Si*(CH$_3$)$_2$); IR (KBr): $\tilde{\nu}=2960$, 2915, 2875 (s; CH_2), 2177 (w; C≡C), 1662 cm^{-1} (s; C=N); MS (FAB): *m/z* (%): 1856 (17) $[M+H]^+$, 1196 (5) $[M-C_{22}H_{37}N_2O_2Si]^+$, 807 (2) $[M-C_{44}H_{74}N_4O_4Si_2]^+$, 389 (24) $[C_{22}H_{37}N_2O_2Si]^+$; HRMS (MALDI): *m/z* calcd for $C_{88}H_{149}N_8O_8Si_5$ $[M+H]^+$: 1586.0339; found: 1586.0330,.

{G1}-[propargyl-BOX(*i*Pr)]$_8$ (G1-2a): Yield: 77%; ^1H NMR (600.13 MHz, $CDCl_3$, 293 K): $\delta=4.19$ (dd, $^2J=18.97$ Hz, $^3J=9.27$ Hz, 16H; CH_2O), 4.04–3.92 (m, 32H; CH_2O, NC*H*), 2.95 (d, $^2J=17.06$ Hz, 8H; CH_2C≡C), 2.84 (d, $^2J=17.00$ Hz, 8H; CH_2C≡C), 1.83–1.75 (m, 16H; C*H*(CH$_3$)$_2$), 1.61 (s, 24H; CCH_3), 1.39–1.31 (m, 24H; H_c, H_g), 0.93 (d, $^3J=6.68$ Hz, 24H; CH(CH_3)$_2$), 0.90 (d, $^3J=6.74$ Hz, 24H; CH(CH_3)$_2$), 0.86 (d, $^3J=6.79$ Hz, 24H; CH(CH_3)$_2$), 0.85 (d, $^3J=7.71$ Hz, 24H; CH-(CH_3)$_2$), 0.66–0.60 (m, 16H; H_b), 0.58–0.51 (m, 32H; H_d, H_f, H_h), 0.08 (s, 48H; H_a), −0.08 ppm (s, 12H; H_e); $^{13}C\{^1H\}$ NMR (150.90 MHz, $CDCl_3$, 293 K): $\delta=166.69/166.64$ (N*C*O), 102.73 (*C*≡C-Si), 86.59 (C≡*C*-Si), 71.77/71.48 (N*C*H), 70.16/70.01 (*C*H_2O), 41.83 (*C*CH$_3$), 32.15/32.12 (*C*H-(CH$_3$)$_2$), 28.29 (*C*H$_2$C≡C), 21.30 (C*C*H$_3$), 20.98 (C_b), 18.75/18.48 (CH-(*C*H$_3$)$_2$), 18.44 (C_d, C_f, C_h), 18.31 (C_c, C_g), 17.74/17.38 (CH(*C*H$_3$)$_2$), −1.53 (C_a), −5.07 ppm (C_e); $^{29}Si\{^1H\}$ NMR (79.44 MHz, $CDCl_3$, 293 K): $\delta=1.04$ (*Si*(CH$_2$)$_3$CH$_3$), 0.42 (*Si*(CH$_2$)$_4$), −17.85 ppm (*Si*(CH$_3$)$_2$); IR (KBr): $\tilde{\nu}=$ 2960, 2915, 2875 (s; CH_2), 2177 (w; C≡C), 1655 cm^{-1} (s; C=N); MS (MALDI): *m/z* (%): 3485 (76) $[M+H]^+$, 3231 (24) $[M+H-C_{14}H_{24}N_2O_2]^+$, 3136 (31) $[M+H-C_{19}H_{31}N_2O_2Si]^+$; HRMS (MALDI): *m/z* calcd for $C_{192}H_{333}N_{16}O_{16}Si_{13}$ $[M+H]^+$: 3483.2731; found: 3483.2798.

{G2}-[propargyl-BOX(*i*Pr)]$_{16}$ (G2-2a): Yield: 66%; ^1H NMR (600.13 MHz, $CDCl_3$, 293 K): $\delta=4.19$ (m, 32H; CH_2O), 4.03–3.92 (m, 64H; CH_2O, NC*H*), 2.96 (d, $^2J=16.92$ Hz, 16H; CH_2C≡C), 2.84 (d, $^2J=16.87$ Hz, 16H; CH_2C≡C), 1.84–1.74 (m, 32H; C*H*(CH$_3$)$_2$), 1.61 (s, 48H; CCH_3), 1.40–1.31 (m, 56H; H_c, H_g, H_k), 0.93 (d, $^3J=6.79$ Hz, 48H; CH-(CH_3)$_2$), 0.90 (d, $^3J=6.79$ Hz, 48H; CH(CH_3)$_2$), 0.87 (d, $^3J=6.83$ Hz, 48H; CH(CH_3)$_2$), 0.85 (d, $^3J=6.85$ Hz, 48H; CH(CH_3)$_2$), 0.67–0.60 (m, 32H; H_b), 0.59–0.49 (m, 80H; H_d, H_f, H_h, H_j, H_l), 0.08 (s, 96H; H_a), −0.08 (s, 24H; H_e), −0.09 ppm (s, 12H; H_l); $^{13}C\{^1H\}$ NMR (150.90 MHz, $CDCl_3$, 293 K): $\delta=166.78/166.63$ (N*C*O), 102.70 (*C*≡C-Si), 86.57 (C≡*C*-Si), 71.77/71.46 (N*C*H), 70.14/69.98 (*C*H_2O), 41.81 (*C*CH$_3$), 32.25/32.13 (*C*H(CH$_3$)$_2$), 28.27 (*C*H$_2$C≡C), 21.28 (C*C*H$_3$), 20.96 (C_b), 18.74/18.47 (CH(*C*H$_3$)$_2$), 18.41 (C_d, C_f, C_h, C_j, C_l), 18.31 (C_c, C_g, C_k), 17.73/17.39 (CH-(*C*H$_3$)$_2$), −1.55 (C_a), −5.05 ppm (C_e, *Ci*); $^{29}Si\{^1H\}$ NMR (79.44 MHz, $CDCl_3$, 293 K): $\delta=1.09/0.85$ (*Si*(CH$_2$)$_3$CH$_3$), 0.46 (*Si*(CH$_2$)$_4$), −17.88 ppm (*Si*(CH$_3$)$_2$); IR (KBr): 2959, 2913, 2874 (s; CH_2), 2177 (w; C≡C), 1662 cm^{-1} (s; C=N); elemental analysis calcd (%) for $C_{400}H_{700}N_{32}O_{32}Si_{29}$ (7284.51): C 65.95, H 9.69, N 6.15; found C 65.26, H 9.25, N 5.85.

{G0}-[propargyl-BOX(Ph)]$_4$ (G0-2b): Yield: 22%; ^1H NMR (600.13 MHz, $CDCl_3$, 293 K): $\delta=7.36–7.26$ (m, 40H; CH_{aryl}), 5.25 (m, 8H; NC*H*), 4.68 (m, 8H; CH_2O), 4.14 (m, 8H; CH_2O), 3.13 (d, $^2J=16.90$ Hz, 4H; CH_2C≡C), 3.03 (d, $^2J=16.90$ Hz, 4H; CH_2≡C), 1.80 (s, 12H; CCH_3), 1.38 (m, 8H; H_c), 0.69 (m, 8H; H_b), 0.59 (m, 8H; H_d), 0.14 ppm (s, 24H; H_a); $^{13}C\{^1H\}$ NMR (150.90 MHz, $CDCl_3$, 293 K): $\delta=$ 168.44/168.38 (N*C*O), 142.23/142.07 ($C_{q,\ aryl}$), 128.65/127.54/126.75/126.62 (C_{aryl}), 102.44 (*C*≡C-Si), 87.15 (C≡*C*-Si), 75.63/75.58 (*C*H_2O), 69.72/69.50 (N*C*H), 42.26 (*C*CH$_3$), 28.50 (*C*H$_2$C≡C), 21.43 (C*C*H$_3$), 21.09 (C_b), 18.38 (C_c), 17.06 (C_d), −1.52 ppm (C_a); $^{29}Si\{^1H\}$ NMR (79.44 MHz, $CDCl_3$, 293 K): $\delta=0.89$ (*Si*(CH$_2$)$_4$), −17.68 ppm (*Si*(CH$_3$)$_2$); IR (KBr): $\tilde{\nu}=3086$, 3063, 3030 (w; CH_{aryl}), 2960, 2915, 2875 (s; CH_2), 2177 (m; C≡C), 1662 cm^{-1} (s; C=N); MS (MALDI): *m/z* (%): 1858 (73) $[M+H]^+$, 1618 (5) $[M+H-C_{16}H_{16}O_2]^+$; HRMS (MALDI): *m/z* calcd for $C_{112}H_{133}N_8O_8Si_5$ $[M+H]^+$: 1857.9087; found: 1857.9106.

{G1}-[propargyl-BOX(Ph)]$_8$ (G1-2b): Yield: 52%; ^1H NMR (600.13 MHz, $CDCl_3$, 293 K): $\delta=7.35–7.25$ (m, 80H; CH_{aryl}), 5.23 (m, 16H; NC*H*), 4.67 (m, 16H; CH_2O), 4.13 (m, 16H; CH_2O), 3.12 (d, $^2J=16.88$ Hz, 8H; CH_2C≡C), 3.02 (d, $^2J=16.85$ Hz, 8H; CH_2C≡C), 1.79 (s, 24H; CCH_3), 1.38 (m, 24H; H_c, H_g), 0.68 (m, 16H; H_b), 0.63–0.49 (m, 32H; H_d, H_f, H_h), 0.13 (s, 48H; H_a), −0.07 ppm (s, 12H; H_e); $^{13}C\{^1H\}$ NMR (150.90 MHz, $CDCl_3$, 293 K): $\delta=168.33$ (N*C*O), 142.33/142.11 ($C_{q,aryl}$), 128.66/127.55/126.76/126.63 (C_{aryl}), 102.36 (*C*≡C-Si), 87.12 (C≡*C*-Si), 75.63 (*C*H_2O), 70.41 (N*C*H), 42.41 (*C*CH$_3$), 28.47 (*C*H$_2$C≡C), 21.44 (C*C*H$_3$), 21.09 (C_b), 18.63 (C_d, C_f, C_h), 18.28 (C_c, C_g), −1.46 (C_a), −4.93 ppm (C_e); $^{29}Si\{^1H\}$ NMR (79.44 MHz, $CDCl_3$, 293 K): $\delta=1.05$ (*Si*-(CH$_2$)$_3$CH$_3$), 0.44 (*Si*(CH$_2$)$_4$), −17.64 ppm (*Si*(CH$_3$)$_2$); IR (KBr): $\tilde{\nu}=3086$, 3063, 3030 (w; CH_{aryl}), 2956, 2913, 2874 (s; CH_2), 2177 (m; C≡C), 1655 cm^{-1} (s; C=N); MS (MALDI-TOF): *m/z* (%): 4051 (100) $[M+Na]^+$, 4029 (71) $[M+H]^+$, 3707 (37) $[M-C_{20}H_{19}N_2O_2]^+$, 3028 (28) $[M+H-C_{60}H_{75}N_4O_4Si_3]^+$; MS (MALDI-TOF): *m/z* (%): 2038 (98) $[M+2Na]^{2+}$.

{G2}-[propargyl-BOX(Ph)]$_{16}$ (G2-2b): Yield: 49%; ^{1}H NMR (600.13 MHz, $CDCl_3$, 293 K): δ = 7.36–7.18 (m, 160H; CH_{aryl}), 5.22 (m, 32H; NCH), 4.65 (m, 32H; CH_2O), 4.11 (m, 32H; CH_2O), 3.11 (d, ^2J = 16.73 Hz, 16H; CH_2C≡C), 3.00 (d, ^2J = 16.69 Hz, 16H; CH_2C≡C), 1.77 (s, 48H; CCH_3), 1.44–1.31 (m, 56H; H_c, H_g, H_k), 0.71–0.63 (m, 32H; H_b), 0.63–0.44 (m, 80H; H_d, H_f, H_h, H_j, H_l), 0.12 (s, 96H; H_a), −0.09 ppm (s, 36H; H_e, H_i); ^{13}C{^{1}H} NMR (150.90 MHz, $CDCl_3$, 293 K): δ = 168.40 (NCO), 142.22/142.06 ($C_{q,aryl}$), 128.65/127.55/126.75/126.62 (C_{aryl}), 102.45 (C≡C-Si), 87.13 (C≡C-Si), 75.64/75.59 (CH_2O), 69.71/69.50 (NCH), 42.26 (CCH_3), 28.50 (CH_2C≡C), 21.45 (CCH_3), 20.96 (C_b), 19.03 (C_d, C_f, C_h, C_j, C_l), 18.35 (C_c, C_g, C_k), −1.46 (C_a), −5.03 ppm (C_e, Ci); ^{29}Si{^{1}H} NMR (79.44 MHz, $CDCl_3$, 293 K): δ = 1.03/0.82 (Si(CH$_2$)$_3$CH$_3$), 0.40 (Si(CH$_2$)$_4$), −17.65 ppm (Si(CH$_3$)$_2$); IR (KBr): $\tilde{\nu}$ = 3086, 3062, 3031 (w; CH_{aryl}), 2956, 2913, 2876 (s; CH_2), 2177 (m; C≡C), 1655 cm^{-1} (s; C=N); elemental analysis calcd (%) for $C_{496}H_{636}N_{32}O_{32}Si_{29}$ (8373.03): C 71.15, H 7.66, N 5.35; found C 70.06, H 7.21, N 5.19.

{G0}-[propargyl-trisox(*i*Pr)]$_4$ (G0-3a): Yield: 33%; ^{1}H NMR (600.13 MHz, $CDCl_3$, 293 K): δ = 4.23 (m, 12H; CH_2O), 4.05 (m, 12H; CH_2O), 3.99 (td, ^3J = 9.10 Hz, ^3J = 6.95 Hz, 12H; NCH), 3.30 (d, ^2J = 16.72 Hz, 4H; CH_2C≡C), 3.07 (d, ^2J = 16.77 Hz, 4H; CH_2C≡C), 1.79 (m, 12H; CH(CH$_3$)$_2$), 1.30 (m, 8H; H_c), 0.91 (d, ^3J = 6.62 Hz, 36H; CH-(CH_3)$_2$), 0.86 (d, ^3J = 6.61 Hz, 36H; CH(CH_3)$_2$), 0.62 (m, 8H; H_b), 0.52 (m, 8H; H_d), 0.05 (s, 12H; H_a), 0.04 ppm (s, 12H; H_a); ^{13}C{^{1}H} NMR (150.90 MHz, $CDCl_3$, 293 K): δ = 162.44 (NCO), 102.50 (C≡C-Si), 85.57 (C≡C-Si), 71.80 (NCH), 70.55 (CH_2O), 47.98 (CCH_2C≡C), 32.40 (CH-(CH$_3$)$_2$), 26.73 (CH_2C≡C), 21.14 (C_b), 18.58 (CH(CH_3)$_2$), 18.24 (C_c), 17.93 (CH(CH_3)$_2$), 17.17 (C_d), −1.70 ppm (C_a); ^{29}Si{^{1}H} NMR (79.44 MHz, $CDCl_3$, 293 K): δ = 0.73 (Si(CH$_2$)$_4$), −18.29 ppm (Si(CH$_3$)$_2$); IR (KBr): $\tilde{\nu}$ = 2961, 2919, 2877 (s; CH_2), 2181 (m; C≡C), 1669, 1666 cm^{-1} (s; C=N); MS (MALDI): m/z (%): 1974 (39) $[M+H]^+$, 1863 (75) $[M+H-C_6H_{10}NO]^+$; HRMS (MALDI): m/z calcd for $C_{108}H_{177}N_{12}O_{12}Si_5$ $[M+H]^+$: 1974.2450; found: 1974.2461.

{G1}-[propargyl-trisox(*i*Pr)]$_8$ (G1-3a): Yield: 54%; ^{1}H NMR (600.13 MHz, $CDCl_3$, 293 K): δ = 4.21 (m, 24H; CH_2O), 4.02 (m, 24H; CH_2O), 3.95 (td, ^3J = 9.37 Hz, ^3J = 6.85 Hz, 24H; NCH), 3.28 (d, ^2J = 16.73 Hz, 8H; CH_2C≡C), 3.05 (d, ^2J = 16.72 Hz, 8H; CH_2C≡C), 1.74 (m, 24H; CH(CH$_3$)$_2$), 1.29 (m, 24H; H_c, H_g), 0.88 (d, ^3J = 6.73 Hz, 72H; CH-(CH_3)$_2$), 0.83 (d, ^3J = 6.72 Hz, 72H; CH(CH_3)$_2$), 0.59 (m, 16H; H_b), 0.49 (m, 32H; H_d, H_f, H_h), 0.03 (s, 48H; H_a), 0.01 ppm (s, 12H; H_e); ^{13}C{^{1}H} NMR (150.90 MHz, $CDCl_3$, 293 K): δ = 162.48 (NCO), 102.54 (C≡C-Si), 85.58 (C≡C-Si), 71.82 (NCH), 70.58 (CH_2O), 48.01 (CCH_2C≡C), 32.43 (CH(CH$_3$)$_2$), 26.78 (CH_2C≡C), 21.03 (C_b), 18.61 (CH(CH_3)$_2$), 18.54 (C_d, C_f, C_h), 18.24 (C_c, C_g), 17.96 (CH(CH_3)$_2$), −1.60 (C_a), −5.00 ppm (C_e); ^{29}Si{^{1}H} NMR (79.44 MHz, $CDCl_3$, 293 K): δ = 1.05 (Si(CH$_2$)$_3$CH$_3$), 0.53 (Si(CH$_2$)$_4$), −18.22 ppm (Si(CH$_3$)$_2$); IR (KBr): $\tilde{\nu}$ = 2961, 2915, 2876 (s; CH_2), 2182 (m; C≡C), 1665, 1660 cm^{-1} (s; C=N); MS (MALDI-TOF): m/z (%): 4327 (<1) $[M+C_2H_8O_2]^+$, 3201 (<1) $[M-C_{58}H_{97}N_6O_6Si_3]^+$; elemental analysis calcd (%) for $C_{232}H_{388}N_{24}O_{24}Si_{13}$ (4262.82): C 65.37, H 9.17, N 7.89; found C 65.04, H 9.02, N 7.34.

{G2}-[propargyl-Trisox(*i*Pr)]$_{16}$ (G2-3a): Yield: 50%; ^{1}H NMR (600.13 MHz, $CDCl_3$, 293 K): δ = 4.25 (m, 48H; CH_2O), 4.06 (m, 48H; CH_2O), 3.98 (td, ^3J = 9.09 Hz, ^3J = 6.86 Hz, 48H; NCH), 3.31 (d, ^2J = 16.76 Hz, 16H; CH_2C≡C), 3.09 (d, ^2J = 16.83 Hz, 16H; CH_2C≡C), 1.82–1.74 (m, 48H; CH(CH$_3$)$_2$), 1.38–1.28 (m, 56H; H_c, H_g, H_k), 0.92 (d, ^3J = 6.74 Hz, 144H; CH(CH_3)$_2$), 0.87 (d, ^3J = 6.71 Hz, 144H; CH(CH_3)$_2$), 0.65–0.59 (m, 32H; H_b), 0.57–0.46 (m, 80H; H_d, H_f, H_h, H_j, H_l), 0.06 (s, 96H; H_a), −0.09 (s, 24H; H_e), −0.10 ppm (s, 12H; H_i); ^{13}C{^{1}H} NMR (150.90 MHz, $CDCl_3$, 293 K): δ = 162.45 (NCO), 102.51 (C≡C-Si), 85.54 (C≡C-Si), 71.81 (NCH), 70.56 (CH_2O), 47.97 (CCH_2C≡C), 32.43 (CH-(CH$_3$)$_2$), 26.74 (CH_2C≡C), 21.02 (C_b), 18.62 (CH(CH_3)$_2$), 18.51 (C_d, C_f, C_h, C_j, C_l), 18.24 (C_c, C_g, C_k), 17.98 (CH(CH_3)$_2$), −1.59 (C_a), −5.03 (C_e), −5.04 ppm (Ci); ^{29}Si{^{1}H} NMR (79.44 MHz, $CDCl_3$, 293 K): δ = 1.03/0.82 (Si(CH$_2$)$_3$CH$_3$), 0.40 (Si(CH$_2$)$_4$), −17.65 ppm (Si(CH$_3$)$_2$); IR (KBr): $\tilde{\nu}$ = 2961, 2916, 2877 (s; CH_2), 2182 (m; C≡C), 1669, 1665 cm^{-1} (s; C=N); elemental analysis calcd (%) for $C_{480}H_{812}N_{48}O_{48}Si_{29}$ (8838.36): C 65.23, H 9.26, N 7.61; found C 64.26, H 9.02, N 7.65.

General procedure for the catalytic α-hydrazination of ethyl 2-methylacetoacetate: Stock solutions of [Cu(OTf)$_2$] (10.9 mg) and of the corresponding ligand or functionalised dendrimer (respective amount) in MeOH (1.00 mL) were prepared under air. Successive aliquots of both homogeneous solutions (containing 1.5 μmol of [Cu(OTf)$_2$] and 1.8 μmol of the corresponding ligand species) were taken and reacted for 1 h to obtain the catalyst for each run. The resulting turquoise/light-green solution was evaporated to dryness (30 min) and the complex redissolved in trifluoroethanol (1.00 mL). Ethyl 2-methylacetoacetate (21.5 μL, 0.15 mmol) was added to the solution prior to cooling to 0 °C and addition of a precooled solution of dibenzylazodicarboxylate (54.7 mg, 0.18 mmol) in trifluoroethanol (0.50 mL). After 16 h at 0 °C, the products were isolated by flash column chromatography (pentane/EtOAc 80:20). The enantioselectivity of the product was determined by HPLC, using a Daicel Chiralpak AD-H column (hexane/*i*PrOH 90:10, 82 bar, 10 μL, 0.95 mL min^{-1}, detection 213 nm, 225 nm, 254 nm, t_R(maj) = 33.0 min, t_R(min) = 36.3 min). All given values were determined as average of three corroborating runs.

Monitoring of conversion curves: Catalyses were conducted as described above. The progress of the reaction was monitored by measuring the disappearance of ethyl 2-methylacetoacetate by GC, using methyl hexanoate as internal standard. The following GC method was applied: T_{inj} = 200 °C, T_{det} = 250 °C, 20 mL min^{-1} He flow, splitless, temperature program: 40 °C, 1 min, 25 °C min^{-1} up to 270 °C, 270 °C, 2 min; t_R (methyl hexanoate) = 4.3 min, t_R (substrate) = 4.9 min.

General procedure for the catalytic Henry reaction of nitromethane and 2-nitrobenzaldehyde: Stock solutions of [Cu(OAc)$_2$] hydrate (9 mg) in MeOH (1.50 mL) and of the corresponding ligand or functionalised dendrimer (respective amount) in MeOH (1.00 mL) were prepared under air. Successive aliquots of both homogeneous solutions (containing 1.5 μmol of [Cu(OAc)$_2$] hydrate and 1.8 μmol of the corresponding ligand species) were taken and reacted for 1 h to obtain the catalyst for each run. The resulting green solution was evaporated to dryness (30 min) and the complex redissolved in trifluoroethanol/*i*PrOH 2:1 (1.00 mL) prior to the addition of nitromethane (410 μL) and a solution of 2-nitrobenzaldehyde (22.7 mg, 0.15 mmol) in trifluoroethanol/*i*PrOH 2:1 (0.50 mL). The resulting brownish solution was stirred at 23 °C for 3 d. Then, the mixture was filtered through a small pad of silica gel to remove the catalyst. The solvent was removed in vacuo and the product was isolated by flash column chromatography (pentane/EtOAc 80:20). The enantioselectivity of the product was determined by HPLC, using a Daicel Chiralpak OD-H column (hexane/*i*PrOH 90:10, 64 bar, 10 μL, 0.8 mL min^{-1}, detection 225 nm, 254 nm, t_R(min) = 17.8 min, t_R(maj) = 19.6 min). All given values were determined as average of at least two corroborating runs.

General procedure for the catalytic recycling using a dialysis membrane: Membrane pieces (Sigma-Aldrich: benzoylated dialysis tubing, avg. flat width 32 mm) of identical length (6.5 cm) were washed with trifluoroethanol (4×). Stock solutions of [Cu(OTf)$_2$] (10.9 mg) and G2-**2b** or G2-**3a** (respective amount) in MeOH (1.00 mL) were prepared. Successive aliquots of both homogeneous solutions (containing 1.5 μmol of [Cu(OTf)$_2$] and 0.11 μmol of the corresponding dendrimer) were taken and reacted for 1 h to obtain the catalyst for each run. The solvent was removed in vacuo (30 min). Then, the residue was redissolved in trifluoroethanol (5 mL) and transferred into the membrane. The resulting bag was placed into a screw cap vial and gently stirred in pure trifluoroethanol (10 mL) at 40 °C for 10 h and subsequently transferred into a screw cap vial containing a solution of ethyl 2-methylacetoacetate (21.5 μL, 0.15 mmol) and dibenzylazodicarboxylate (54.7 mg, 0.18 mmol) in trifluoroethanol (10 mL). The reaction was allowed to proceed for the appropriate time (10 h with G2-**2b**, 24 h with G2-**3a**) at 40 °C and then, the catalyst bag was directly transferred into another vial containing a fresh solution of substrates for the next run whereas the solution from the preceding run was concentrated in vacuo. Isolation of the product was provided by flash column chromatography (pentane/EtOAc 80:20). The enantioselectivity of the product was determined by HPLC, using a Daicel Chiralpak AD-H column (hexane/*i*PrOH 90:10, 82 bar, 10 μL, 0.95 mL min^{-1}, detection 213 nm, 225 nm, 254 nm, t_R(maj) = 33.0 min, t_R(min) = 36.3 min). Values given for each run were determined as average of at least five corroborating experiments.

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