Synthesis of Heterofunctionalised Diamines and Triamines by Hydroaminomethylation of Diallyl Ethers, -silanes, or -amines

Peter Eilbracht,*[a] Christian Ludger Kranemann,[a] and Lars Bärfacker[a]

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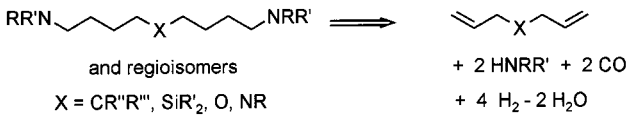
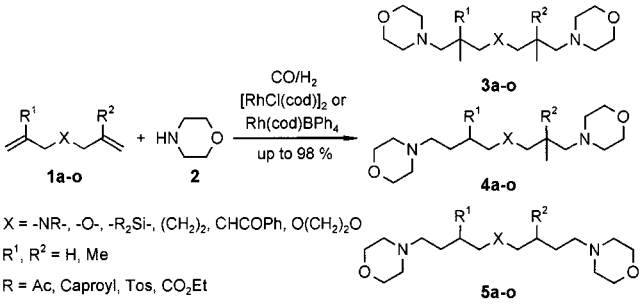
Starting from diallyl ethers, -silanes, or -amines various di- or triamines with potential biological activity are obtainable in one step by Rh^I-catalysed hydroaminomethylation of the alkene moieties in the presence of synthesis gas.

Introduction

Various α,ω-di- and triamines[1−6] are known to have biological activity. In all cases the amine moieties are connected by methylene chains. The synthesis of these amines is usually achieved by classical nucleophilic substitution pathways starting from halides and secondary or primary amines. Alternatively, a retrosynthetic analysis of the amine structure also leads back to olefinic functionalities by application of the hydroaminomethylation methodology.[7]



This method involves selective alkylation of primary or secondary amines by hydroformylation of alkenes and subsequent reductive amination of the oxo aldehydes in a one-pot procedure. We here report the hydroaminomethylation of α,ω-diolefins **1a−b** and diallyl systems **1c−o** as a model study. Hydroaminomethylation of diallylamines **1j−o** conveniently leads to triamines.[8] According to the same procedure the carba, oxa and sila analogues **1a−i** give the corresponding diamines. α,ω-Diamines connected by nine carbon atoms possess antimalarial activities,[9] whereas sila compounds of this type thus obtained are known to exhibit antifungal[10] and antiviral[11] activities.



Scheme 1. Bis(hydroaminomethylation) of diallylamines, diallyl ethers, and diallylsilanes **1a−o**

[a] Fachbereich Chemie, Universität Dortmund,
Otto-Hahn-Str. 6, D-44221 Dortmund, Germany
Fax: (internat.) + 49(0)231/755-5363
E-mail: eilbrach@citrin.chemie.uni-dortmund.de

Results and Discussion

Hydroaminomethylation of α,ω-diolefins **1a−e** is performed in almost quantitative yields (see Table 1). While the methallyl compound **1e** only gives the *n*/*n* product **5e**, the non-substituted allyl systems lead to mixtures of *n*/*n*, *n*/*iso*, and *iso*/*iso* products. The observed *n*/*iso* ratio is 2.1. This ratio drops to 1.1 if moieties with potential precoordinating ability are introduced (entry 2).

Hitherto only few examples of hydroformylation or hydroaminomethylation of allylsilanes are reported[7e,12] and to our knowledge no conversions of diallylsilanes under hydroformylation conditions have been investigated. Hydroaminomethylation of diallylsilanes **1c−e** with morpholine (entry 3 and 5) proceeds with slightly lower yields compared to the dienes **1a**,**b**. The regioselectivity is in line with the hydroaminomethylation of monoallylsilanes[7e] and comparable to the carbon analogue **1a** (entry 1).

Under similar conditions the diallylsilane **1e** is converted with benzylamine **6** as a primary amine into the corresponding diamine **7** in 88% yield. In line with earlier results[7d] no tertiary amines are formed under these conditions.

In analogy to the results above diallyl ethers undergo bis-(hydroaminomethylation) with good yields. The *n*/*iso* ratio decreases to 0.9. This may be caused by a coordinating or chelating effect of the oxygen atom to the rhodium centre during the catalytic cycle. A conversion of bis(methallyl) ethers **1g**,**i** results in a mixture of the *N*,*N*-bis(hydroaminomethylation) products **5g**,**i** and products **8g**,**i**, **9g**,**i** arising from a double-bond migration. This type of isomerisation is known to be catalysed by transition-metal complexes.[9] The enol ethers **8g**,**i** thus generated contain a triply substituted double bond which usually is hydroformylated or hydroaminomethylated only under harsh conditions. Generally, less substituted enol ethers are carbonylated in α position to the oxygen atom.[12] In addition the vinyl ethers **8** are disubstituted in β position. Therefore exclusive α carbonylation is observed (**9**).

In order to test the methodology for the preparation of triamines the hydroaminomethylation of diallylamines **1j−o** was investigated. The conversion of monoallylamines under hydroformylation conditions usually leads to γ-lactams as demonstrated by other research groups.[14] Diallylamines

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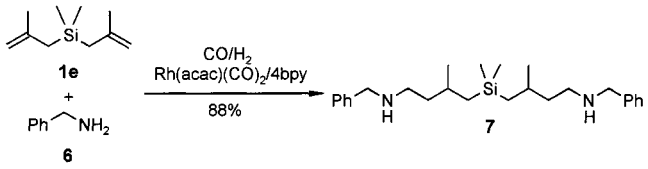
Table 1. Bis(hydroaminomethylation) of α,ω-diolefins **1a**,**b** and their sila analogues **1c−e** with **2**

Entry	**1**	X	R^1	R^2	p_{total}[a]		Total yield[b] (%)	Yield[b] **3** (%)	Yield[b] **4** (%)	Yield[b] **5** (%)	*n*/*iso* ratio
1[7c]	**a**	$[CH_2]_2$	H	H	80	**a**	96	10	42	44	2.1
2	**b**	CHCOPh	H	H	80	**b**	92	21	47	24	1.1
3	**c**	$SiMe_2$	H	H	80	**c**	51	ca. 5	23	23	2.1
5	**d**	$SiPh_2$	H	H	80	**d**	78	14	35	29	1.5
4	**e**	$SiMe_2$	Me	Me	100	**e**	93	–	–	93	–

[a] $p(CO) = p(H_2)$. – [b] Isolated yields.



Scheme 2. Hydroaminomethylation of bis(methallyl)dimethylsilane (**1e**) with benzylamine (**6**)

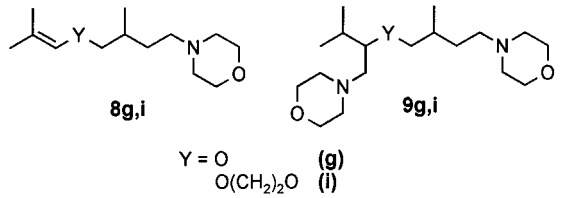
in order to achieve hydroaminomethylation of both double bonds protecting groups have to be employed in order to suppress the lactam formation.

As presented in Table 3 protecting groups with different electron-withdrawing properties are tolerated in the hydroaminomethylation procedure. In all cases a lower *n*/*iso* ratio is observed if compared with nonsubstituted diolefins, diallylsilanes, or diallyl ethers. This effect is interpreted as a result of chelating effects involved in the catalytic cycle. The

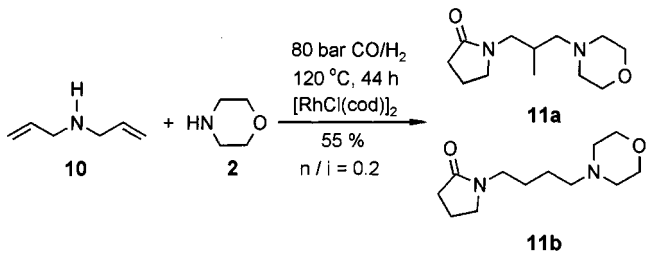
Table 2. Results of the bis(hydroaminomethylation) of diallyl ethers **1f−i** with **2**

Entry	**1**	X	R^1	R^2	p_{total}[a]		Total yield[b] (%)	Yield[b] **3** (%)	Yield[b] **4** (%)	Yield[b] **5** (%)	*n*/*iso* ratio
6	**f**	O	H	H	80	**f**	83	25	38	20	0.9
7	**g**	O	Me	Me	80	**g**	99	–	–	59[c]	–
8	**h**	$O[CH_2]_2O$	H	H	80	**h**	78	25	38	15	0.8
9	**i**	$O[CH_2]_2O$	Me	Me	80	**i**	87	–	–	55[d]	–

[a] $p(CO) = p(H_2)$. – [b] Isolated yields. – [c] And 28% yield of **8g** and 12% yield of **9g**. – [d] And 24% yield of **8i** and 8% yield of **9i**.



react in a tandem hydrocarboxylation/hydroaminomethylation sequence in which the diamines **11** are generated. The reaction sequence may start with pyrrolidinone formation, while the remaining allylic function is hydroaminomethylated leading to the bicyclic products **11** with high *iso* selectivity. The chronological order of these steps, however, is unclear yet and it may as well proceed vice versa. Thus, olefin insertion predominantly proceeds to generate the branched isomers since in this case a six-membered ring system[15] with an exocyclic methyl group is the intermediate. For the *n* product a less favoured seven-membered ring has to be formed. Therefore it can be assumed that the regioselectivity of the reaction is strongly influenced by the donor ability of the hetero function used. This is in line with the observation that the amides (entries 10, 11, and 14) are more directing towards the *iso* products than the weaker donating tosylates and carbamates (entries 12, 13). The replacement of the allylic moieties by methallylic ones after a similar reaction time leads to incomplete conversion into the expected *n*-carbonylation products involving monohydroaminomethylation leading to side product **12**.



Scheme 3. Carbonylative cyclohydroamination/hydroaminomethylation of diallylamine (**10**) with morpholine (**2**)

Conclusion

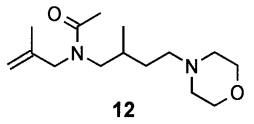
In conclusion we have shown that hydroaminomethylation of hetero-functionalised diolefins offers an effective novel access to a large number of highly functionalised diamine and triamine compounds. Precoordinating effects significantly influence the regioselectivity of the hydroaminomethylation procedure.

Various di- and triamines with different biological function are described.[1−6] In most cases these systems are characterised by linear carbon spacers between the nitrogen

Table 3. Results of the bis(hydroaminomethylation) of diallylamines **1j−o** with **2**

Entry	**1**	X	R^1	R^2	p_{total}[a]		Total yield[b] (%)	Yield[b] **3** (%)	Yield[b] **4** (%)	Yield[b] **5** (%)	*n*/*iso* ratio
10	**j**	NAc	H	H	80	**j**	89	38	46	< 5	0.4
11	**k**	NCap	H	H	80	**k**	93	35	53	< 5	0.4
12	**l**	NTos	H	H	80	**l**	98	35	46	17	0.7
13	**m**	NCO_2Et	H	H	80	**m**	93	32	45	16	0.7
14	**n**	NAc	Me	H	80	**n**	91	−	67	24	0.4
15	**o**	NAc	Me	Me	80	**o**	89	−	−	66[c]	−

[a] $p(CO) = p(H_2)$. − [b] Isolated yields. − [c] And 23% yield of **12**.



12

atoms. This may be due to the ubiquity of unbranched di- and polyamines. The method described here leads to either linear or branched products. To our knowledge it is yet unknown whether the branched derivatives provide similar or different activities. In addition the regioselectivity can be controlled by phosphanes or phosphites. According to preliminary results use of $Rh(acac)(CO)_2$ and BIPHEPHOS[16] exclusively leads to the *n*,*n* products.

Experimental Section

General Remarks: The diolefinic silanes were obtained by common Grignard cross coupling routes. Diolefinic ethers are accessible by Williamson ether synthesis, diolefinic amine derivatives are available by a classical nucleophilic substitution reactions. The catalyst precursors $[RhCl(cod)]_2$[17] and $Rh(cod)(\eta^6\text{-}BPh_4)$[18] were prepared as described. − NMR: Bruker DRX 400, $CDCl_3$ as solvent and TMS ($\delta_H = 0$) or CH_2Cl_2 ($\delta_H = 5.30$) as internal standard. − IR: Nicolet Impact 400 D. − MS/HRMS: Finnigan CA 5. − Elemental analysis: Leco, CHNS-932. − Analytical gas chromatography: Fisons 8130 gas chromatograph with 30-m CP sil-5 capillaries. − GC MS: Spectra were obtained by using a comparable capillary and a Finnigan MAT 8320 instrument. Pressure reactions were carried out in autoclaves (type A, 250 mL, PTFE insert) from Berghof, Eningen.

General Procedure. − Hydroaminomethylation of 1a,b and 1f−o with Morpholine (2): The diolefin **1** (7.0 mmol), amine **2** (14.2 mmol), $[Rh(cod)Cl]_2$ (0.5 mol-% based on the amount of the diolefin) and dry acetonitrile (10 mL) were placed in an autoclave. After flushing with argon, the reactor was pressurised with 50 bar of hydrogen and 50 bar of carbon monoxide and heated to 120°C for 20 h. The autoclave was allowed to cool to room temp. and after removal of the solvent by rotary evaporation the catalyst was removed by filtration through a small pad of neutral alumina (activity III) with MTBE.

Column Chromatography: The column chromatography was carried out on alumina N (activity III) from ICN Biomedicals, Eschwege, or with silica gel 60 from Merck, Darmstadt. For 1 g of product mixture 120 g of stationary phase was employed using columns with 2.5 cm inner diameter. In all cases the *iso*/*iso* product was eluted first, followed by the *n*/*iso* and the *n*/*n* isomer. MTBE = *tert*-butyl methyl ether, PE = petroleum ether (boiling range: 30−60°C). For further details see below.

Hydroaminomethylation of 1b with 2: According to the general procedure **1b** and **2** were converted into 2.80 g of a mixture of **3b**, **4b**, **5b**. Purification by column chromatography (MTBE/PE, 3:1 as eluent) led to 0.60 g (21%) of **3b** as a 1:1:1:1 mixture of diastereoisomers (determined by ^1H and ^{13}C NMR), 1.33 g (47%) of **4b** as a 1:1 mixture of diastereoisomers (determined by ^1H and ^{13}C NMR) and 0.68 g (24%) of **5b**.

4-Methyl-2-[2-methyl-3-(morpholin-4-yl)propyl]-5-(morpholin-4-yl)-1-phenylpentan-1-one (3b): ^1H NMR (400 MHz, $CDCl_3$, 20 °C): δ = 0.87 (d, ^3J = 6.5 Hz, 3 H), 0.96 (2 × d, ^3J = 6.5 Hz, 3 H), 1.22 (m, 1 H), 1.55 (m, 3 H), 1.75 (m, 1 H), 2.05 (m, 3 H), 2.14 (m, 2 H), 2.30 (2 × s, 8 H), 3.60 (m, 8 H), 3.78 (m) and 3.89 (m) [1H], 7.51 (m, 2 H), 7.60 (m, 1 H), 8.01 (m, 2 H). − ^{13}C NMR (100 MHz, $CDCl_3$, 20°C): δ = 18.5, 18.8, 19.2, 19.2 (2 × CH_3), 27.7, 27.9, 27.9, 27.9 (CH), 37.0, 38.0, 38.8, 39.0 (CH_2), 41.2, 41.6, 41.7 (CH), 51.9, 54.0, 54.0 (CH_2), 66.2, 66.3, 66.5, 66.6 (CH_2), 66.8, 66.9 (CH_2), 128.2, 128.2 (CH), 128.6, 128.6 (CH), 132.8 (CH), 136.8, 137.2, 137.4 (C_q), 203.9, 203.9, 204.3 (C_q). − IR (neat): ṽ [cm^{-1}] = 2956 vs, 1682 vs, 1596 m, 1459 s, 1447 s, 1119 vs, 865 vs, 704 vs. − MS (EI, 70 eV); *m*/*z* (%): 402 (1) [M^+], 115 (10), 105 (13), 100 (100), 73 (63), 57 (37), 43 (39). − $C_{24}H_{38}N_2O_3$ (402.6): calcd. C 71.6, H 9.5, N 7.0; found C 71.5, H 9.4, N 7.2.

2-[2-Methyl-3-(morpholin-4-yl)propyl]-6-(morpholin-4-yl)-1-phenylhexan-1-one (4b): ^1H NMR (400 MHz, $CDCl_3$, 20 °C): δ = 0.87 (2 × d, ^3J = 6.5 Hz, 3 H), 1.20 (m) and 1.58 (m) [2 H], 1.28 (m, 2 H), 1.45 (m, 3 H), 1.73 (m) and 2.03 (m) [3H], 2.13 (m, 1 H), 2.31 (10 H), 3.55 (m, 1 H), 3.68 (t*, ^3J = 4.8 Hz, 8 H), 7.48 (t, ^3J = 7.5 Hz, 2 H), 7.57 (td*, ^3J = 7.5 Hz, ^4J = 1.1 Hz, 1 H), 7.98 (td*, ^3J = 7.5 Hz, ^4J = 1.5 Hz, 2 H). − ^{13}C NMR (100 MHz, $CDCl_3$, 20°C): δ = 18.8, 19.0 (CH_3), 25.3, 25.3 (CH_2), 26.6, 26.6 (CH_2), 27.8, 27.9 (CH), 32.2, 33.4 (CH_2), 37.5, 38.0 (CH_2), 43.6, 43.6 (CH), 53.8, 53.9 (CH_2), 58.7, 58.7 (CH_2), 66.2, 66.3 (CH_2), 66.8, 66.8 (CH_2), 128.1, 128.1 (CH), 128.6, 128.6 (CH), 132.8 (CH), 137.2, 137.4 (C_q), 204.0 (C_q). − IR (neat): ṽ [cm^{-1}] = 2953 vs, 2853 vs, 1681 vs, 1456 s, 1447 s, 1118 vs, 864 s, 706 s. − MS (EI, 70 eV); *m*/*z* (%): 402 (9) [M^+], 372 (3), 105 (5), 100 (100), 77 (4), 56 (6). − $C_{24}H_{38}N_2O_3$ (403.6): calcd. C 71.6, H 9.4, N 7.0; found C 71.5, H 9.4, N 7.1.

6-(Morpholin-4-yl)-2-[4-(morpholin-4-yl)butyl]-1-phenylhexan-1-one (5b): ^1H NMR (400 MHz, $CDCl_3$, 20 °C): δ = 1.28 (quint*, ^3J = 7.5 Hz, 4 H), 1.48 (m, 6 H), 1.80 (m, 2 H), 2.26 (dd, ^3J = 6.5 Hz, ^2J = 12.8 Hz, 4 H), 2.37 (br. s, 8 H), 3.48 (quint*, ^3J = 6.5 Hz, 1 H), 3.68 (t*, ^3J = 4.5 Hz, 8 H), 7.48 (t, ^3J = 7.3 Hz, 2 H), 7.58 (tt, ^3J = 7.3 Hz, ^4J = 1.4 Hz, 1 H), 7.95 (d, ^3J = 7.3 Hz, 2 H). − ^{13}C NMR (100 MHz, $CDCl_3$, 20°C): δ = 25.3 (CH_2), 26.6 (CH_2), 32.2 (CH_2), 45.9 (CH), 53.6 (CH_2), 58.7 (CH_2), 66.8 (CH_2), 128.0 (CH), 128.6 (CH), 132.8 (CH), 137.4 (C_q), 204.2 (C_q). − IR (neat): ṽ [cm^{-1}] = 2939 vs, 1680 vs, 1596 w, 1447 m, 1118 vs, 865 s, 706 s. − MS (EI, 70 eV); *m*/*z* (%): 402 (20) [M^+], 372 (10), 105 (12), 100

(100), 56 (9). − $C_{24}H_{38}N_2O_3$ (403.6): calcd. C 71.6, H 9.4, N 7.0; found C 71.5, H 9.6, N 7.1.

Hydroaminomethylation of 1c with 2: A mixture of diallyldimethylsilane (**1c**) (0.67 g, 4.8 mmol), amine **2** (0.92 g, 10.5 mmol), Rh(cod)BPh_4 (1 mol-%), and dry toluene (10 mL) was placed in an autoclave. After flushing with argon, the reactor was pressurised with 40 bar of hydrogen and 40 bar of carbon monoxide and heated to 120°C for 20 h. 1.74 g of a crude mixture of **4c** and **5c** is obtained. The isolation of the products was carried out by column chromatography (PE/MTBE = 1:1) leading to 0.38 g (23%) of **4c** and 0.38 g (23%) of **5c**.

Dimethyl[2-methyl-3-(morpholin-4-yl)propyl][4-(morpholin-4-yl)-butyl]silane (4c): ^{1}H NMR (400 MHz, $CDCl_3$, 20 °C): δ = 0.04 (s, 3 H), 0.04 (s, 3 H), 0.24 (dd, ^2J = 14.6 Hz, ^3J = 9.3 Hz, 1 H), 0.47 (m, 2 H), 0.69 (dd, ^2J = 14.6 Hz, ^3J = 4.0 Hz, 1 H), 0.85 (d, ^3J = 6.5 Hz, 3 H), 1.25 (m, 2 H), 1.48 (m, 2 H), 1.73 (m, 1 H), 2.01−2.04 (2 H), 2.29−2.40 (10 H), 3.65−3.70 (8 H). − ^{13}C NMR (100 MHz, $CDCl_3$, 20°C): δ = −2.4 (CH_3), −2.3 (CH_3), 16.1 (CH_2), 21.3 (CH_2), 21.3 (CH_3), 21.8 (CH_2), 26.4 (CH), 30.5 (CH_2), 53.8 (CH_2), 54.0 (CH_2), 58.9 (CH_2), 66.9 (CH_2), 67.0 (CH_2), 68.9 (CH_2). − IR (neat): ṽ [cm^{-1}] = 2955 vs 1456 m, 1371 m, 1119 vs, 864 s. − GC MS (EI, 70 eV); *m/z* (%): 342 (10) [M^+ − 1], 100 (100), 70 (13).

Dimethylbis[4′-(morpholin-4-yl)butyl]silane (5c): ^{1}H NMR (400 MHz, $CDCl_3$, 20 °C): δ = 0.11 (s, 6 H), 0.44 (m, 4 H), 1.24 (m, 4 H), 1.45 (m, 4 H), 2.26 (t, ^3J = 7.3 Hz, 4 H), 2.38 (br. s, 8 H), 3.66 (t*, ^3J = 4.5 Hz, 8 H). − ^{13}C NMR (100 MHz, $CDCl_3$, 20°C): δ = −3.5 (CH_3), 15.1 (CH_2), 21.8 (CH_2), 30.4 (CH_2), 53.8 (CH_2), 66.9 (CH_2). − IR (neat): ṽ [cm^{-1}] = 2953 vs, 1456 m, 1445 m, 1119 vs, 862 s. − GC MS (EI, 70 eV); *m/z* (%): 343 (22) [M^+], 172 (8), 100 (100). − $C_{18}H_{38}N_2O_2Si$ (342.6): calcd. C 63.1, H 11.2, N 8.2; found C 63.1, H 10.9, N 8.2.

Hydroaminomethylation of 1d with 2: A mixture of diallyldiphenylsilane (**1d**) (1.26 g, 4.8 mmol), amine **2** (0.92 g, 10.5 mmol), Rh(cod)BPh_4 (1 mol-%), and dry toluene (15 mL) was placed in an autoclave. After flushing with argon, the reactor was pressurised with 40 bar of hydrogen and 40 bar of carbon monoxide and heated to 120°C for 20 h. 2.30 g of crude product was obtained. The isolation of the products was carried out by column chromatography (2-propanol/$CHCl_3$ = 1:15) leading to 0.31 g (14%) of **3d** as a 1:1 mixture of diastereoisomers (determined by ^{1}H and ^{13}C NMR), 0.78 g (35%) of **4d** and 0.65 g (29%) of **5d**. Data obtained from mixture of **3d**, **4d**, **5d**. − IR (neat): ṽ [cm^{-1}] = 3068 m, 2954 s, 1427 m, 1118 vs, 701 vs. − MS (EI, 70 eV); *m/z* (%): 466 (16) [M^+ − 1], 183 (11), 149 (59), 100 (100), 57 (11). − $C_{28}H_{42}N_2O_2Si$ (466.7): calcd. C 72.1, H 9.1, N 6.0; found C 72.1, H 9.2, N 6.0.

Bis[(2-methyl-3-(morpholin-4-yl)propyl]diphenylsilane (3d): ^{1}H NMR (400 MHz, $CDCl_3$, 20 °C): δ = 0.80 (d, ^3J = 6.0 Hz, 3 H), 0.80 (d, ^3J = 6.0 Hz, 3 H), 0.90 (dd, ^3J = 8.8 Hz, ^3J = 14.8 Hz, 1 H), 0.92 (dd, ^3J = 8.8 Hz, ^3J = 14.8 Hz, 1 H), 1.46 (dd, ^3J = 5.0 Hz, ^3J = 14.8 Hz, 1 H), 1.47 (dd, ^3J = 5.0 Hz, ^3J = 14.8 Hz, 1 H), 1.74 (m, 2 H), 2.03 (m, 4 H), 2.23 (m, 8 H), 3.64 (t*, ^3J = 4.8 Hz, 8 H), 7.32−7.60 (10 H). − ^{13}C NMR (100 MHz, $CDCl_3$, 20°C): δ = 19.1 (CH_2), 19.3 (CH_2), 21.4, 21.4 (CH_3), 26.1, 26.1 (CH), 53.8 (CH_2), 53.9 (CH_2), 66.9, 66.9 (CH_2), 68.6, 68.6 (CH_2), 68.7 (CH_2), 127.6, 127.6 (CH), 128.9 (CH), 135.0, 135.0 (CH), 136.9, 136.9 (C_q).

[2-Methyl-3-(morpholin-4-yl)propyl][4-(morpholin-4-yl)butyl]-diphenylsilane (4d): ^{1}H NMR (400 MHz, $CDCl_3$, 20 °C): δ = 0.84 (d, ^3J = 6.5 Hz, 3 H), 0.87 (dd, ^3J = 9.1 Hz, ^3J = 15.0 Hz, 1 H), 1.16 (m, 2 H), 1.39 (m, 2 H), 1.47 (dd, ^3J = 9.8 Hz, ^3J = 15.1 Hz, 1 H), 1.55 (m, 2 H), 1.77 (m, 1 H), 2.04 (dd, ^3J = 6.8 Hz, ^3J = 12.0 Hz, 1 H), 2.07 (dd, ^3J = 7.8 Hz, ^3J = 12.0 Hz, 1 H), 2.24 (br. s, 4 H), 2.31 (m, 2 H), 2.41 (br. s, 4 H), 3.63 (t*, ^3J = 4.5 Hz, 4 H), 3.71 (t*, ^3J = 4.5 Hz, 4 H), 7.32−7.60 (10 H). − ^{13}C NMR (100 MHz, $CDCl_3$, 20°C): δ = 13.2 (CH_2), 18.1 (CH_2), 21.3 (CH_3), 21.5 (CH_2), 26.0 (CH), 30.2 (CH_2), 53.6 (CH_2), 53.9 (CH_2), 58.4 (CH_2), 66.8 (CH_2), 68.7 (CH_2), 127.6 (CH), 127.7 (CH), 129.0, 129.0 (CH), 134.8, 134.8 (CH), 136.4, 136.6 (C_q).

Bis[4′-(morpholin-4-yl)butyl]diphenylsilane (5d): ^{1}H NMR (400 Hz, $CDCl_3$, 20 °C): δ = 1.10 (m, 4 H), 1.38 (m, 4 H), 1.53 (m, 4 H), 2.30 (mc, 4 H), 2.39 (br. s, 8 H), 3.70 (t*, ^3J = 4.5 Hz, 8 H), 7.32−7.53 (10 H). − ^{13}C NMR (100 MHz, $CDCl_3$, 20°C): δ = 12.4 (CH_2), 21.6 (CH_2), 30.3 (CH_2), 53.7 (CH_2), 58.5 (CH_2), 66.9 (CH_2), 127.7 (CH), 129.1 (CH), 134.8, 136.1 (C_q).

Hydroaminomethylation of 1e and 2: A mixture of bis(methallyl)dimethylsilane (**1e**) (0.50 g, 3.0 mmol), amine **2** (0.52 g, 5.9 mmol), Rh(cod)BPh_4 (1 mol-%), and dry toluene (10 mL) was placed in an autoclave. After flushing with argon, the reactor was pressurised with 50 bar of hydrogen and 50 bar of carbon monoxide and heated to 120°C for 48 h. 1.14 g of crude product was obtained. Further purification was carried out by kugelrohr distillation leading to 1.03 g (93%) of **5e**.

Dimethylbis[2-methyl-4-(morpholin-4-yl)butyl]silane (5e): ^{1}H NMR (400 MHz, $CDCl_3$, 20 °C): δ = −0.54 (s, 6 H), 0.35 (dd, ^2J = 14.8 Hz, ^3J = 8.8 Hz, 2 H), 0.56 (dd, ^2J = 14.8 Hz, ^3J = 3.8 Hz, 2 H), 0.84 (d, ^2J = 7.5 Hz, 6 H), 1.27 (m, 2 H), 1.39 (m, 2 H), 1.54 (m, 2 H), 2.24 (m, 4 H), 2.35 (br. s, 8 H), 3.64 (t*, ^3J = 3.8 Hz, 8 H). − ^{13}C NMR (100 MHz, $CDCl_3$, 20°C): δ = −1.4 (CH_3), −1.3 (2 × CH_3), 23.0 (2 × CH_3), 24.6 (2 × CH_2), 28.0 (CH), 37.2 (2 × CH_2), 53.8 (CH_2), 57.2 (CH_2), 66.9 (CH_2). − IR (neat): ṽ [cm^{-1}] = 2955 vs, 1457 m, 1373 m, 1119 vs, 869 s. − GC MS (EI, 70 eV); *m/z* (%): 370 (15) [M^+ − 1], 214 (9), 100 (100), 72 (42), 56 (18). − $C_{20}H_{42}N_2O_2Si$ (370.7): calcd. C 64.8, H 11.4, N 7.6; found C 64.8, H 10.9, N 7.6.

Hydroaminomethylation of 1d and 6: A mixture of bis(methallyl)dimethylsilane (**1d**) (0.833 g, 4.8 mmol), amine **6** (1.13 g, 10.5 mmol), Rh(cod)BPh_4 (1 mol-%), 2,2′-bipyridyl (4 mol-%), and dry toluene (50 mL) was placed in an autoclave. After flushing with argon, the reactor was pressurised with 40 bar of hydrogen and 40 bar of carbon monoxide and heated to 100°C for 48 h. 1.92 g of crude product was obtained. The isolation of the products was carried out by column chromatography (*n*-pentane/*i*PrOH = 10:1) on silica gel leading to 1.73 g (88%) of **7**.

Bis[4-(benzylamino)-2-methylbutyl]dimethylsilane (7): ^{1}H NMR (400 MHz, $CDCl_3$, 20 °C): δ = 0.07 (s, 6 H), 0.45 (dd, ^3J = 8.5 Hz, ^3J = 14.6 Hz, 1 H), 0.46 (dd, ^3J = 8.8 Hz, ^3J = 14.8 Hz, 1 H), 0.67 (dd, ^3J = 4.6 Hz, ^3J = 14.6 Hz, 2 H), 0.96 (d, ^3J = 6.5 Hz, 3 H), 0.96 (d, ^3J = 6.8 Hz, 3 H), 1.39−1.60 (4 H), 1.70 (m, 2 H), 2.67 (m, 4 H), 3.82 (s, 4 H), 7.24−7.40 (10 H). − ^{13}C NMR (100 MHz, $CDCl_3$, 20°C): δ = −1.3 (CH_3), 22.9 (CH_3), 23.0 (CH_3), 24.6, 24.6 (CH_2), 27.6 (CH), 40.9, 40.9 (CH_2), 47.4 (CH_2), 54.1 (CH_2), 126.7 (CH), 127.9 (CH), 128.3 (CH), 140.4 (C_q). − IR (neat): ṽ [cm^{-1}] = 3302 w, 2952 s, 1453 s, 1248 s, 836 s, 697 s. − MS (EI, 70 eV); *m/z* (%): 411 (17) [M^+], 410 (47), 319 (72), 234 (32), 120 (52), 91 (100), 59 (10).

Hydroaminomethylation of 1f with 2: According to thegeneral procedure **1f** and **2** were converted into 2.00 g of a mixture of **3f**, **4f**, **5f**. Purification by column chromatography (MTBE/PE = 1:1 as eluent) led to 0.53 g (25%) of **3f** as a 1:1 mixture of diastereoisomers (determined by ^{1}H and ^{13}C NMR), 0.80 g (38%) of **4f** and 0.42 g (20%) of **5f**.

Bis[2-methyl-3-(morpholin-4-yl)propyl] Ether (3f): ^{1}H NMR (400 MHz, $CDCl_3$, 20 °C): δ = 0.94 (d, ^3J = 6.8 Hz, 6 H), 1.94

(oct*, ^3J = 6.8 Hz, 2 H), 2.10 (m, 2 H), 2.28 (m, 2 H), 2.39 (br. s, 8 H), 3.18 (dd, ^3J = 6.5 Hz, ^2J = 9.0 Hz, 1 H), 3.20 (dd, ^3J = 6.5 Hz, ^2J = 9.0 Hz, 1 H), 3.34 (dd, ^3J = 5.3 Hz, ^2J = 9.0 Hz, 1 H), 3.39 (dd, ^3J = 5.3 Hz, ^2J = 9.0 Hz, 1 H), 3.69 (t*, ^3J = 4.5 Hz, 8 H). − ^{13}C NMR (100 MHz, $CDCl_3$, 20°C): δ = 15.9, 16.0 (CH_3), 30.8, 30.8 (CH), 54.0 (CH_2), 62.5 (CH_2), 66.9 (CH_2), 74.8 (CH_2). − IR (neat): $\tilde{\nu}$ [cm^{-1}] = 2957 vs, 1685 m, 1456 s, 1446 m, 1119 vs, 865 s. − GC MS (EI, 70 eV); *m/z* (%): 301 (19) [M^+ + 1], 142 (12), 100 (100), 70 (15), 57 (11). − $C_{16}H_{32}N_2O_3$ (300.4): calcd. C 64.0, H 10.7, N 9.3; found C 63.7, H 11.1, N 9.3.

2-Methyl-3-(morpholin-4-yl)propyl 4-(Morpholin-4-yl)butyl Ether (4f): ^{1}H NMR (400 MHz, $CDCl_3$, 20 °C): δ = 0.98 (d*, ^3J = 6.5 Hz, 3 H), 1.58 (m, 4 H), 1.91 (m, 1 H), 2.11 (m, 1 H), 2.28 (m, 1 H), 2.41 (m, 10 H), 3.19 (m, 1 H), 3.41 (m, 3 H), 3.71 (s, 8 H). − ^{13}C NMR (100 MHz, $CDCl_3$, 20°C): δ = 16.0 (CH_3), 23.1 (CH_2), 27.5 (CH_2), 30.8 (CH), 53.6 (CH_2), 54.0 (CH_2), 58.8 (CH_2), 62.5 (CH_2), 66.8 (CH_2), 66.9 (CH_2), 70.8 (CH_2), 74.7 (CH_2). − IR (neat): $\tilde{\nu}$ [cm^{-1}] = 2955 vs, 1456 m, 1447 m, 1119 vs, 866 s. − GC MS (EI, 70 eV); *m/z* (%): 301 (21) [M^+ + 1], 142 (21), 112 (10), 100 (100), 70 (15), 56 (15). − $C_{16}H_{32}N_2O_3$ (300.4): calcd. C 64.0, H 10.7, N 9.3; found C 63.8, H 11.0, N 9.7.

Bis[4-(morpholin-4-yl)butyl] Ether (5f):[19] ^{1}H NMR (400 MHz, $CDCl_3$, 20 °C): δ = 1.57 (m, 8 H), 2.35 (m, 4 H), 2.43 (s, 8 H), 3.41 (m, 4 H), 3.71 (t*, ^3J = 4.5 Hz, 8 H). − ^{13}C NMR (100 MHz, $CDCl_3$, 20°C): δ = 23.1 (CH_2), 27.5 (CH_2), 53.6 (CH_2), 58.7 (CH_2), 66.8 (CH_2), 70.5 (CH_2). − IR (neat): $\tilde{\nu}$ [cm^{-1}] = 2951 vs, 1456 s, 1447 s, 1119 vs. − GC MS (EI, 70 eV); *m/z* (%): 301 (48) [M^+ + 1], 270 (10), 142 (45), 112 (18), 100 (100), 70 (21), 56 (20). − $C_{16}H_{32}N_2O_3$ (300.4): calcd. C 64.0, H 10.7, N 9.3; found C 63.6, H 10.8, N 9.3.

Hydroaminomethylation of 1g with 2: According to thegeneral procedure **1g** and **2** were converted into 2.13 g of a mixture of **5g**, **8g**, and **9g**. Purification by column chromatography (MTBE/PE = 5:1 as eluent) led to 1.36 g (59%) of **5g** as a 1:1 mixture of diastereoisomers (determined by ^{1}H and ^{13}C NMR), 0.45 g (28%) of **8g** and 0.28 g (12%) of **9g** as a 1:1 mixture of diastereoisomers (determined by ^{1}H and ^{13}C NMR).

4-{3-Methyl-4-[2-methyl-4-(morpholin-4-yl)butoxy]butyl}-morpholine (5g): ^{1}H NMR (400 MHz, $CDCl_3$, 20 °C): δ = 0.92 (d, ^3J = 6.7 Hz, 6 H), 1.28 (m, 2 H), 1.64 (m, 2 H), 1.76 (oct*, ^3J = 6.7 Hz, 2 H), 2.38 (dt*, ^2J = 10.0 Hz, ^3J = 6.0 Hz, 4 H), 2.44 (br. s, 8 H), 3.21 (m, 4 H), 3.70 (t*, ^3J = 4.5 Hz, 8 H). − ^{13}C NMR (100 MHz, $CDCl_3$, 20°C): δ = 17.1 (CH_3), 30.3 (CH_2), 31.7 (CH), 53.6 (CH_2), 56.8 (CH_2), 66.8 (CH_2), 76.3 (CH_2). − IR (neat): $\tilde{\nu}$ [cm^{-1}] = 2955 vs, 1457 m, 1374 m, 1358 m, 1119 vs. − GC MS (EI, 70 eV); *m/z* (%): 329 (65) [M^+ + 1], 156 (51), 126 (14), 112 (18), 100 (100), 70 (22), 56 (19). − $C_{18}H_{36}N_2O_3$ (328.5): calcd. C 65.8, H 11.0, N 8.5; found C 65.9, H 11.2, N 8.7.

4-[3-Methyl-4-(2-methyl-1-propenyloxy)butyl]morpholine (8g): ^{1}H NMR (400 MHz, $CDCl_3$, 20 °C): δ = 0.92 (d, ^3J = 6.7 Hz, 3 H), 1.30 (m, 1 H), 1.52 (s, 3 H), 1.58 (s, 3 H), 1.65 (m, 1 H), 1.81 (oct*, ^3J = 6.7 Hz, 1 H), 2.37 (m, 2 H), 2.42 (br. s, 4 H), 3.48 (m, 2 H), 3.70 (t*, ^3J = 4.5 Hz, 4 H), 5.77 (s, 1 H). − ^{13}C NMR (100 MHz, $CDCl_3$, 20°C): δ = 14.8 (CH_3), 16.7 (CH_3), 19.3 (CH_3), 30.0 (CH_2), 31.8 (CH), 53.6 (CH_2), 56.6 (CH_2), 66.8 (CH_2), 76.7 (CH_2), 109.7 (C_q), 140.1 (CH). − IR (neat): $\tilde{\nu}$ [cm^{-1}] = 2957 vs, 1691 s, 1457 s, 1170 vs, 1144 vs, 1120 vs. − GC MS (EI, 70 eV); *m/z* (%): 228 (34) [M^+ + 1], 156 (69), 140 (11), 100 (100), 70 (13), 56 (17). − $C_{13}H_{25}NO_2$ (227.3): calcd. C 68.7, H 11.1, N 6.2; found C 68.5, H 11.2, N 6.7.

4-{3-Methyl-4-[2-methyl-1-(morpholin-4-ylmethyl)propoxy]-butyl}morpholine (9g): ^{1}H NMR (400 MHz, $CDCl_3$, 20 °C): δ = 0.84 (m, 9 H), 1.20 (m, 1 H), 1.60 (m, 2 H), 1.81 (m, 1 H), 2.31 (m, 12 H), 3.03 (q*, ^3J = 4.9 Hz, 1 H), 3.12 (dd, ^3J = 6.4 Hz, ^2J = 8.8 Hz) and 3.28 (dd, ^3J = 5.8 Hz, ^2J = 8.8 Hz) [1H], 3.19 (dd, ^3J = 5.9 Hz, ^2J = 8.8 Hz) and 3.35 (dd, ^3J = 5.8 Hz, ^2J = 8.8 Hz) [1H], 3.61 (2 × t, ^3J = 4.7 Hz, 8 H). − ^{13}C NMR (100 MHz, $CDCl_3$, 20°C): δ = 17.2, 17.3 (CH_3), 17.7, 17.7 (CH_3), 18.4, 18.4 (CH_3), 30.1, 30.2 (CH), 30.3 (CH_2), 32.3 (CH), 53.7 (CH_2), 54.3 (CH_2), 56.9 (CH_2), 59.8, 59.8 (CH_2), 66.9 (CH_2), 67.0 (CH_2), 75.4 (CH_2), 81.7, 81.8 (CH). − IR (neat): $\tilde{\nu}$ [cm^{-1}] = 2957 vs, 1457 s, 1373 s, 1360 s, 1120 vs, 1088 vs, 868 s. − GC MS (EI, 70 eV); *m/z* (%): 329 (25) [M^+ + 1], 156 (52), 126 (19), 112 (21), 100 (100), 70 (22), 56 (18). − $C_{18}H_{36}N_2O_3$ (328.5): calcd. C 65.8, H 11.0, N 8.5; found C 65.5, H 10.6, N 8.6.

Hydroaminomethylation of 1h with 2: According to thegeneral procedure **1h** and **2** were converted into 2.37 g of a mixture of **3h**, **4h**, **5h**. Purification by column chromatography (MTBE/*n*-hexane = 1:1 as eluent) led to 0.59 g (25%) of **3h** as a 1:1 mixture of diastereoisomers (determined by ^{1}H and ^{13}C NMR), 0.93 g (38%) of **4h**, and 0.36 g (15%) of **5h**.

Ethylene Glycol Bis[2-methyl-3-(morpholin-4-yl)propyl] Ether (3h): ^{1}H NMR (400 MHz, $CDCl_3$, 20 °C): δ = 0.95 (2 × d, ^3J = 6.5 Hz, 6 H), 1.78 (oct*, ^3J = 6.8 Hz, 2 H), 2.12 (dd, ^2J = 12.0 Hz, ^3J = 6.4 Hz, 2 H), 2.28 (dd, ^2J = 12.0 Hz, ^3J = 7.1 Hz, 2 H), 2.39 (s, 8 H), 3.32 (m, 2 H), 3.48 (dd, ^2J = 9.2 Hz, ^3J = 5.1 Hz, 2 H), 3.58 (s, 4 H), 3.69 (t*, ^3J = 3.7 Hz, 8 H). − ^{13}C NMR (100 MHz, $CDCl_3$, 20°C): δ = 16.0 (CH_3), 30.8 (CH), 54.1 (CH_2), 62.6 (CH_2), 67.0 (CH_2), 70.4 (CH_2), 75.3 (CH_2). − IR (neat): $\tilde{\nu}$ [cm^{-1}] = 2955 s, 1456 m, 1372 m, 1119 vs, 865 s. − GC MS (EI, 70 eV); *m/z* (%): 345 (21) [M^+ + 1], 142 (8), 100 (100), 70 (12). − $C_{18}H_{36}N_2O_4$ (344.5): calcd. C 62.8, H 10.5, N 8.1; found C 62.6, H 10.4, N 8.3.

Ethylene Glycol 2-Methyl-3-(morpholin-4-yl)propyl 4-(Morpholin-4-yl)butyl Ether (4h): ^{1}H NMR (400 MHz, $CDCl_3$, 20 °C): δ = 0.97 (d, ^3J = 6.8 Hz, 3 H), 1.59 (m, 4 H), 1.98 (m, 1 H), 2.10 (dd, ^2J = 12.3 Hz, ^3J = 7.4 Hz, 1 H), 2.28 (dd, ^2J = 12.3 Hz, ^3J = 7.0 Hz, 1 H), 2.32 (t*, ^3J = 7.3 Hz, 2 H), 2.38 (s, 4 H), 2.42 (s, 4 H), 3.26 (dd, ^2J = 9.1 Hz, ^3J = 6.8 Hz, 1 H), 3.48 (m, 3 H), 3.58 (br. s, 4 H), 3.68 (t*, ^3J = 4.8 Hz, 4 H), 3.72 (t*, ^3J = 4.5 Hz, 4 H). − ^{13}C NMR (100 MHz, $CDCl_3$, 20°C): δ = 16.0 (CH_3), 23.1 (CH_2), 27.5 (CH_2), 30.7 (CH), 53.6 (CH_2), 54.0 (CH_2), 58.7 (CH_2), 62.5 (CH_2), 66.9 (CH_2), 66.9 (CH_2), 69.9 (CH_2), 70.4 (CH_2), 71.1 (CH_2), 75.2 (CH_2). − IR (neat): $\tilde{\nu}$ [cm^{-1}] = 2955 vs, 1456 s, 1446 s, 1119 vs, 865 s. − GC MS (EI, 70 eV); *m/z* (%): 345 (15) [M^+ + 1], 142 (8), 100 (100), 70 (16). − $C_{18}H_{36}N_2O_4$ (344.5): calcd. C 62.8, H 10.5, N 8.1; found C 62.6, H 10.4, N 8.3.

Ethylene Glycol Bis[4-(morpholin-4-yl)butyl] Ether (5h): ^{1}H NMR (400 MHz, $CDCl_3$, 20 °C): δ = 1.59 (m, 8 H), 2.34 (t*, ^3J = 7.4 Hz, 4 H), 2.42 (s, 8 H), 3.55 (s, 4 H), 3.70 (t*, ^3J = 4.5 Hz, 8 H). − ^{13}C NMR (100 MHz, $CDCl_3$, 20°C): δ = 23.5 (CH_2), 27.9 (CH_2), 54.1 (CH_2), 59.2 (CH_2), 67.4 (CH_2), 70.5 (CH_2), 71.6 (CH_2). − IR (neat): $\tilde{\nu}$ [cm^{-1}] = 2952 vs, 1456 vs, 1398 m, 1372 s, 1357 s, 1263 s, 1118 vs, 866 vs. − GC MS (EI, 70 eV); *m/z* (%): 345 (38) [M^+ + 1], 314 (6), 142 (28), 112 (13), 100 (100), 84 (11), 70 (25). − $C_{18}H_{36}N_2O_4$ (344.5): calcd. C 62.8, H 10.5, N 8.1; found C 62.6, H 10.4, N 8.3.

Hydroaminomethylation of 1i with 2: According to the general procedure **1i** and **2** were converted into 2.42 g of a mixture of **5i**, **8i** and **9i**. Purification by column chromatography (MTBE/PE = 2:1 as eluent) led to 1.44 g (55%) of **5i** as a 1:1 mixture of diastereoisomers (determined by ^{1}H and ^{13}C NMR), 0.47 g (24%) of **8i** and 0.21 g (8%) of **9i** as a 1:1 mixture of diastereoisomers (determined by ^{1}H and ^{13}C NMR).

4-(3-Methyl-4-{2-[2-methyl-4-(morpholin-4-yl)butoxy]-ethoxy}butyl)morpholine (5i): ^{1}H NMR (400 MHz, $CDCl_3$, 20 °C): δ = 0.92 (d, ^3J = 6.7 Hz, 6 H), 1.26 (m, 2 H), 1.65 (m, 2 H), 1.78 (oct, ^3J = 6.7 Hz, 2 H), 2.35 (m, 4 H), 2.42 (br. s, 8 H), 3.28 (m, 4 H), 3.54 (s, 4 H), 3.69 (t*, ^3J = 4.3 Hz, 8 H). − ^{13}C-NMR (100 MHz, $CDCl_3$, 20°C): δ = 17.0 (CH_3), 30.3 (CH_2), 31.7 (CH), 53.7 (CH_2), 56.8 (CH_2), 66.9 (CH_2), 70.2 (CH_2), 76.7 (CH_2). − IR (neat): ṽ [cm^{-1}] = 2955 vs, 1457 s, 1398 m, 1373 m, 1119 vs, 868 s. − GC MS (EI, 70 eV); *m/z* (%): 373 (98) [M^+ + 1], 156 (15), 126 (10), 112 (12), 100 (100). − $C_{20}H_{40}N_2O_4$ (372.5): calcd. C 64.5, H 10.8, N 7.5; found C 64.7, H 10.8, N 7.4.

4-{3-Methyl-4-[2-(2-methylpropenyloxy)ethoxy]butyl}morpholine (8i): ^{1}H NMR (400 MHz, $CDCl_3$, 20 °C): δ = 0.92 (d, ^3J = 6.8 Hz, 3 H), 1.28 (m, 1 H), 1.53 (d, ^4J = 1.0 Hz, 3 H), 1.59 (d, ^4J = 1.0 Hz, 3 H), 1.65 (m, 1 H), 1.78 (m, 1 H), 2.35 (m, 2 H), 2.43 (br. s, 4 H), 3.29 (dd, ^2J = 9.3 Hz, ^3J = 6.4 Hz, 1 H), 3.31 (dd, ^2J = 9.3 Hz, ^3J = 6.4 Hz, 1 H), 3.57 (m, 2 H), 3.70 (t*, ^3J = 4.8 Hz, 4 H), 3.79 (m, 2 H), 5.83 (sept, ^4J = 1.0 Hz, 1 H). − ^{13}C NMR (100 MHz, $CDCl_3$, 20°C): δ = 14.9 (CH_3), 17.0 (CH_3), 19.4 (CH_3), 30.2 (CH_2), 31.7 (CH), 53.7 (CH_2), 56.8 (CH_2), 66.9 (CH_2), 70.0 (CH_2), 70.8 (CH_2), 76.7 (CH_2), 110.5 (C_q), 140.1 (CH). − IR (neat): ṽ [cm^{-1}] = 2957 vs, 1691 s, 1456 s, 1376 m, 1172 vs, 1120 vs. − GC MS (EI, 70 eV); *m/z* (%): 272 (42) [M^+ + 1], 172 (11), 156 (23), 100 (100), 59 (10). − $C_{15}H_{29}NO_3$ (271.4): calcd. C 66.4, H 10.8, N 5.2; found C 66.4, H 10.8, N 5.1.

4-(3-Methyl-4-{2-[2-methyl-1-(morpholin-4-yl)methyl-propoxy]ethoxy}butyl)morpholine (9i): ^{1}H NMR (400 MHz, $CDCl_3$, 20 °C): δ = 0.90 (m, 9 H), 1.28 (m, 1 H), 1.62 (m, 1 H), 1.78 (m, 1 H), 1.89 (m, 1 H), 2.42 (m, 12 H), 3.27 (m, 2 H), 3.54 (m, 3 H), 3.61 (m, 1 H), 3.70 (m, 9 H). − ^{13}C NMR (100 MHz, $CDCl_3$, 20°C): δ = 17.0, 17.1 (CH_3), 17.9, 18.0 (CH_3), 30.2 (CH), 30.3, 30.3 (CH_2), 31.7, 31.8 (CH), 53.7 (CH_2), 54.4, 60.0 (CH_2), 56.8, 56.8 (CH_2), 66.9 (CH_2), 67.0, 69.4 (CH_2), 70.2, 70.6 (CH_2), 76.7, 76.7 (CH_2), 82.2 (CH). − IR (neat): ṽ [cm^{-1}] = 2956 vs, 1455 m, 1119 vs. − GC MS (EI, 70 eV); *m/z* (%): 373 (25) [M^+ + 1], 156 (11), 100 (100), 70 (11). − $C_{20}H_{40}N_2O_4$ (372.5): calcd. C 64.5, H 10.8, N 7.5; found C 64.3, H 10.8, N 7.4.

Hydroaminomethylation of 10 with 2: According to the general procedure **10** and **2** were converted during 44 h into 1.19 g of a mixture of **11a** and **11b**. Purification by column chromatography (PE/MTBE = 5:1) led to 0.71 g (45%) of pure **11a** and 0.21 g of a mixture of **11a** and **11b** containig 75 % of **11b** (not isolated, detected by GC and GC-MS analysis).

1-[2-Methyl-3-(morpholin-4-yl)propyl]pyrrolidin-2-one (11a): ^{1}H NMR (400 MHz, $CDCl_3$, 20 °C): δ = 0.89 (d, ^3J = 6.6 Hz, 3 H), 1.52 (m, 1 H), 2.02 (m, 2 H), 2.20 (m, 2 H), 2.39 (m, 6 H), 3.11 (dd, ^2J = 13.7 Hz, ^3J = 8.1 Hz, 1 H), 3.28 (m, 1 H), 3.39 (m, 2 H), 3.69 (t*, ^3J = 4.5 Hz, 4 H). − ^{13}C NMR (100 MHz, $CDCl_3$, 20°C): δ = 16.5 (CH_3), 18.0 (CH_2), 28.6 (CH), 31.0 (CH_2), 47.4 (CH_2), 47.9 (CH_2), 54.0 (CH_2), 63.6 (CH_2), 66.9 (CH_2), 174.2 (C_q). − IR (neat): ṽ [cm^{-1}] = 2958 s, 1686 vs, 1461 s, 1442 s, 1426 s, 1399 s, 1118 vs, 864 s, 799 s. − GC MS (EI, 70 eV); *m/z* (%): 227 (36) [M^+ + 1], 141 (31), 110 (11), 100 (100), 70 (38), 56 (27).

Hydroaminomethylation of 1j with 2: According to the general procedure **1j** and **2** were converted into 2.20 g of a mixture of **3j**, **4j**. Purification by column chromatography (ethyl acetate as eluent) led to 0.91 g (38%) **3j** as a 1:1 mixture of diastereoisomers (determined by ^{1}H and ^{13}C NMR) and 1.10 g (46 %) of **4j**.

***N*,*N*-Bis[2-methyl-3-(morpholin-4-yl)propyl]-acetamide (3j):** ^{1}H NMR (400 MHz, $CDCl_3$, 20 °C): δ = 0.88 (d*, ^3J = 5.6 Hz, 3 H), 0.94 (d*, ^3J = 6.3 Hz, 3 H), 2.11 (2 × s, 3 H), 2.16 (m, 6 H), 2.37 (s, 4 H), 2.44 (s, 4 H), 3.04 (m, 2 H), 3.50 (m, 2 H), 3.69 (s, 8 H). − ^{13}C NMR (100 MHz, $CDCl_3$, 20°C): δ = 16.7, 16.8 (CH_3), 21.8, 21.9 (CH_3), 28.4 (CH), 30.0, 30.2 (CH), 50.5, 50.8 (CH_2), 53.9 (CH_2), 54.1, 54.1 (CH_2), 63.5, 63.7 (CH_2), 63.8, 63.9 (CH_2), 66.9, 67.0 (CH_2), 170.7 (C_q). − IR (neat): ṽ [cm^{-1}] = 2957 s, 1645 vs, 1456 s, 1445 m, 1118 vs, 863 s. − MS (EI, 70 eV); *m/z* (%): 341 (63) [M^+], 311 (56), 255 (43), 241 (62), 214 (46), 214 (46), 211 (20), 183 (25), 171 (25), 154 (28), 141 (70), 128 (64), 112 (42), 100 (100), 86 (45), 70 (70), 56 (75), 43 (95).

***N*-[2-Methyl-3-(morpholin-4-yl)propyl]-*N*-[4-(morpholin-4-yl-butyl])acetamide (4j):** ^{1}H NMR (400 MHz, $CDCl_3$, 20 °C): δ = 0.88 (d, ^3J = 5.8 Hz) and 0.94 (d, ^3J = 6.5 Hz) [3H], 1.55 (m, 4 H), 2.09 (2 × s, 3 H), 2.16 (m, 3 H), 2.35 (m, 6 H), 2.42 (s, 4 H), 3.01 (m, 1 H), 3.29 (m, 2 H), 3.47 (m, 1 H), 3.69 (m, 8 H). − ^{13}C NMR (100 MHz, $CDCl_3$, 20°C): δ = 16.5, 16.6 (CH_3), 21.4, 21.7 (CH_3), 23.6, 23.8 (CH_2), 25.0, 26.3 (CH_2), 28.7, 30.0 (CH), 45.7, 49.2 (CH_2), 50.0, 52.9 (CH_2), 53.5 (CH_2), 53.8, 54.0 (CH_2), 58.1, 58.5 (CH_2), 63.6, 63.4 (CH_2), 66.7, 66.8 (CH_2), 66.8 (CH_2), 170.3 (C_q). − IR (neat): ṽ [cm^{-1}] = 2955 s, 1646 vs, 1456 m, 1446 m, 1422 m, 1118 vs. − MS (EI, 70 eV); *m/z* (%): 341 (24) [M^+], 311 (16), 141 (17), 100 (100). Data obtained from mixture of **3j** and **4j**. − $C_{18}H_{35}N_3O_3$ (341.5): calcd. C 63.3, H 10.3, N 12.3; found C 63.0, H 10.1, N 12.1.

Hydroaminomethylation of 1k with 2: According to the general procedure **1k** and **2** were converted into 2.54 g of a mixture of **3k**, **4k**. Purification by column chromatography (PE/MTBE = 1:10 as eluent) led to 0.97 g (35%) of **3k** as a 1:1 mixture of diastereoisomers (determined by ^{1}H and ^{13}C NMR) and 1.47 g (53%) of **4k**.

***N*,*N*-Bis[2-methyl-3-(morpholin-4-yl)-propyl]capramide (3k):** ^{1}H NMR (400 MHz, $CDCl_3$, 20 °C): δ = 0.89 (m, 9 H), 1.31 (m, 4 H), 1.64 (quint, ^3J = 7.3 Hz, 2 H), 2.00 (m, 1 H), 2.18 (m, 5 H), 2.40 (m, 10 H), 2.99 (m, 2 H), 3.51 (m, 2 H), 3.69 (s, 8 H). − ^{13}C NMR (100 MHz, $CDCl_3$, 20°C): δ = 13.9 (CH_3), 16.8, 16.8 (CH_3), 22.4 (CH_2), 25.3 (CH_2), 28.5, 30.4, 30.7 (CH), 31.7 (CH_2), 33.3 (CH_2), 50.9, 51.4 (CH_2), 53.3, 53.5 (CH_2), 53.9, 54.0, 54.1, 54.1 (CH_2), 63.6, 63.7, 63.9 (CH_2), 66.9, 67.0 (CH_2), 173.5 (C_q). − IR (neat): ṽ [cm^{-1}] = 2956 vs, 1643 vs, 1457 s, 1422 m, 1119 vs, 863 s. − MS (EI, 70 eV); *m/z* (%): 397 (3) [M^+], 141 (7), 100 (100), 70 (10), 56 (15), 42 (27). − Data obtained from mixture of **3k** and **4k**. − $C_{22}H_{43}N_3O_3$ (397.6): calcd. C 66.5, H 10.9, N 10.6; found C 66.3, H 10.8, N 10.4.

***N*-[2-Methyl-3-(morpholin-4-yl)propyl]-*N*-[4-(morpholin-4-yl)-butyl]capramide (4k):** ^{1}H NMR (400 MHz, $CDCl_3$, 20 °C): δ = 0.90 (m, 6 H), 1.30 (m, 4 H), 1.57 (m, 6 H), 1.98 (m) and 2.15 (m) [3H], 2.38 (m, 12 H), 2.97 (m, 1 H), 3.27 (m, 2 H), 3.48 (m, 1 H), 3.70 (m, 8 H). − ^{13}C NMR (100 MHz, $CDCl_3$, 20°C): δ = 13.9 (CH_3), 16.6, 16.7 (CH_3), 22.4 (CH_2), 23.7, 23.9 (CH_2), 25.1, 25.2 (CH_2), 26.7 (CH_2), 28.8, 30.4 (CH), 31.1, 33.1 (CH_2), 31.6 (CH_2), 46.1, 48.7 (CH_2), 50.4, 52.2 (CH_2), 53.6, 53.9, 54.1 (CH_2), 58.2, 58.6 (CH_2), 63.5, 63.8 (CH_2), 66.8, 66.9 (CH_2), 173.0 (C_q). − IR (neat): ṽ [cm^{-1}] = 2956 vs, 1645 vs, 1456 s, 1423 m, 1119 vs, 865 s. − MS (EI, 70 eV); *m/z* (%): 397 (65) [M^+], 367 (56), 297 (43), 141 (74), 125 (41), 111 (52), 100 (100), 84 (35), 70 (47), 56 (56), 43 (76). − $C_{22}H_{43}N_3O_3$ (397.6): calcd. C 66.5, H 10.9, N 10.6; found C 66.6, H 10.9, N 10.8.

Hydroaminomethylation of 1l with 2: According to the general procedure **1l** and **2** were converted into 3.26 g of a mixture of **3l**, **4l**, **5l**. Purification by column chromatography (PE/MTBE = 1:5 as eluent) led to 0.97 g (35%) of **3l** as a 1:1 mixture of diastereoisomers (determined by ^{1}H and ^{13}C NMR), 1.28 g (46%) of **4l** and 0.47 g (17%) of **5l**.

4-Methyl-*N*,*N*-bis[2-methyl-3-(morpholin-4-yl)propyl]-benzenesulfonamide (3l): ^{1}H NMR (400 MHz, $CDCl_3$, 20 °C): δ = 0.92 (d, ^3J = 6.3 Hz, 3 H), 0.94 (d, ^3J = 6.3 Hz, 3 H), 2.10 (m, 6 H), 2.37 (m, 8 H), 2.43 (s, 3 H), 2.78 (m, 2 H), 3.18 (m, 2 H), 3.68 (m, 8 H), 7.53 (dd, ^3J = 8.1 Hz, ^4J = 1.8 Hz, 2 H), 7.68 (d, ^3J = 8.1 Hz, 2 H). − ^{13}C NMR (100 MHz, $CDCl_3$, 20°C): δ = 16.9, 16.9 (CH_3), 21.5 (CH_3), 29.5, 29.6 (CH), 54.0, 54.1 (CH_2), 54.9, 55.3 (CH_2), 63.6, 63.6 (CH_2), 67.0 (CH_2), 127.4, 127.5 (CH), 129.5 (CH), 135.8, 136.2 (C_q), 143.1, 143.1 (C_q). − IR (neat): ṽ [cm^{-1}] = 2958 vs, 1599 m, 1494 m, 1456 vs, 1338 vs, 1118 vs, 1014 vs, 864 s. − MS (EI, 70 eV); *m*/*z* (%): 453 (66) [M^+], 423 (40), 298 (53), 211 (56), 197 (64), 171 (44), 155 (39), 141 (65), 128 (61), 126 (71), 112 (87), 100 (100), 96 (25), 91 (59), 86 (36), 73 (77), 56 (78), 43 (82). − HRMS; $C_{23}H_{39}N_3SO_4$: calcd. 453.2661; found 453.2631.

4-Methyl-*N*-[2-methyl-3-(morpholin-4-yl)propyl]-*N*-[4-(morpholin-4-yl)-butyl]benzenesulfonamide (4l): ^{1}H NMR (400 MHz, $CDCl_3$, 20 °C): δ = 0.94 (d, ^3J = 6.5 Hz, 3 H), 1.43 (quint*, ^3J = 7.3 Hz, 2 H), 1.52 (m, 2 H), 2.04 (m, 1 H), 2.11 (m, 2 H), 2.29 (t*, ^3J = 7.3 Hz, 2 H), 2.39 (br. s, 8 H), 2.42 (s, 3 H), 2.79 (dd, ^3J = 8.6 Hz, ^2J = 13.9 Hz, 1 H), 3.09 (m, 2 H), 3.19 (dd, ^3J = 5.4 Hz, ^2J = 13.9 Hz, 1 H), 3.68 (m, 8 H), 7.30 (d, ^3J = 8.1 Hz, 2 H), 7.68 (d, ^3J = 8.1 Hz, 2 H). − ^{13}C NMR (100 MHz, $CDCl_3$, 20°C): δ = 16.8 (CH_3), 21.4 (CH_3), 23.8 (CH_2), 26.4 (CH_2), 29.7 (CH), 49.3 (CH_2), 53.4 (CH_2), 53.6 (CH_2), 54.0 (CH_2), 58.3 (CH_2), 63.5 (CH_2), 66.9 (CH_2), 67.0 (CH_2), 127.2 (CH), 129.5 (CH), 136.5 (C_q), 143.0 (C_q). − IR (neat): ṽ [cm^{-1}] = 2956 vs, 1599 m, 1498 m, 1456 m, 1339 vs, 1159 vs, 1119 vs, 864 s, 655 vs. − MS (EI, 70 eV); *m*/*z* (%): 453 (62) [M^+], 423 (48), 298 (62), 268 (19), 211 (25), 171 (42), 157 (44), 142 (58), 139 (59), 128 (54), 126 (57), 112 (37), 110 (53), 100 (100), 98 (59), 91 (67), 86 (51), 73 (61), 56 (78), 42 (77).

4-Methyl-*N*,*N*-bis[4-(morpholin-4-yl)butyl]benzenesulfonamide (5l): ^{1}H NMR (400 MHz, $CDCl_3$, 20 °C): δ = 1.52 (m, 8 H), 2.32 (t*, ^3J = 7.3 Hz, 4 H), 2.42 (s, 11 H), 3.11 (t*, ^3J = 7.3 Hz, 4 H), 3.71 (s, 8 H), 7.29 (d, ^3J = 8.3 Hz, 2 H), 7.67 (d, ^3J = 8.3 Hz, 2 H). − ^{13}C NMR (100 MHz, $CDCl_3$, 20°C): δ = 21.4 (CH_3), 23.5 (CH_2), 26.5 (CH_2), 48.0 (CH_2), 53.6 (CH_2), 58.3 (CH_2), 66.8 (CH_2), 127.0 (CH), 129.5 (CH), 136.8 (C_q), 143.0 (C_q). − IR (neat): ṽ [cm^{-1}] = 2951 vs, 1598 m, 1494 w, 1456 vs, 1399 s, 1373 s, 1357 s, 1335 vs, 1305 vs, 1118 vs, 1091 vs, 865 vs. − MS (EI, 70 eV); *m*/*z* (%): 453 (45) [M^+], 298 (22), 142 (54), 126 (23), 100 (100), 84 (18), 56 (16). − Data obtained from mixture of **3l**, **4l** and **5l**. − $C_{23}H_{39}N_3SO_4$ (453.6): calcd. C 60.9, H 8.7, N 9.3; found C 61.0, H 8.6, N 8.9.

Hydroaminomethylation of 1m with 2: According to the general procedure **1m** and **2** were converted into 2.66 g of a mixture of **3m**, **4m**, **5m**. Purification by column chromatography (MTBE as eluent) led to 0.82 g (32%) of **3m** as a 1:1 mixture of diastereoisomers (determined by ^{1}H and ^{13}C NMR), 1.18 g (45%) of **4m** and 0.42 g (16%) of **5m**.

Ethyl *N*,*N*-Bis[2-methyl-3-(morpholin-4-yl)propyl]carbamate (3m): ^{1}H NMR (400 MHz, $CDCl_3$, 20 °C): δ = 0.89 (d, ^3J = 5.6 Hz, 6 H), 1.24 (2 × t, ^3J = 7.0 Hz, 3 H), 2.13 (m, 6 H), 2.36 (m, 8 H), 2.87 (m, 1 H), 3.02 (m, 1 H), 3.34 (m, 1 H), 3.50 (m, 1 H), 3.69 (t*, ^3J = 4.6 Hz, 8 H), 4.10 (q, ^3J = 7.0 Hz, 2 H). − ^{13}C NMR (100 MHz, $CDCl_3$, 20°C): δ = 14.5 (CH_3), 16.6 (CH_3), 29.6, 29.8 (CH), 52.1, 52.4, 52.6, 52.9 (CH_2), 53.8, 53.9 (CH_2), 60.7 (CH_2), 63.6 (CH_2), 66.8 (CH_2), 156.5, 156.6 (C_q). − IR (neat): ṽ [cm^{-1}] = 2957 vs, 1698 vs, 1472 s, 1458 s, 1444 m, 1422 s, 1259 vs, 1118 vs, 864 s. − MS (EI, 70 eV); *m*/*z* (%): 371 (16) [M^+], 100 (100). − $C_{19}H_{37}N_3O_4$ (371.5): calcd. C 61.4, H 10.0, N 11.3; found C 61.5, H 9.9, N 11.5.

Ethyl *N*-[2-Methyl-3-(morpholin-4-yl)propyl]-*N*-[4-(morpholin-4-yl)-butyl]carbamate (4m): ^{1}H NMR (400 MHz, $CDCl_3$, 20 °C): δ = 0.89 (d, ^3J = 6.3 Hz, 3 H), 1.24 (br. s, 3 H), 1.50 (m, 4 H), 2.11 (m, 3 H), 2.34 (t*, ^3J = 7.5 Hz, 2 H), 2.43 (s, 8 H), 2.92 (m, 1 H), 3.25 (m, 3 H), 3.70 (m, 8 H), 4.12 (q, ^3J = 6.8 Hz, 2 H). − ^{13}C NMR (100 MHz, $CDCl_3$, 20°C): δ = 14.6 (CH_3), 16.5 (CH_3), 23.7 (CH_2), 25.6, 26.2 (CH_2), 29.2, 29.7 (CH), 47.5, 47.8 (CH_2), 51.2, 51.9 (CH_2), 53.6, 53.9 (CH_2), 58.6, 58.6 (CH_2), 60.8 (CH_2), 63.6 (CH_2), 66.9, 66.9 (CH_2), 156.5, 156.5 (C_q). − IR (neat): ṽ [cm^{-1}] = 2955 s, 1698 vs, 1473 s, 1458 s, 1445 s, 1422 s, 1119 vs, 865 s. − MS (EI, 70 eV); *m*/*z* (%): 371 (10) [M^+], 100 (100), 58 (8). − $C_{19}H_{37}N_3O_4$ (371.5): calcd. C 61.4, H 10.0, N 11.3; found C 61.3, H 9.9, N 11.5.

Ethyl *N*,*N*-Bis[4-(morpholin-4-yl)butyl]carbamate (5m): ^{1}H NMR (400 MHz, $CDCl_3$, 20 °C): δ = 1.24 (t, ^3J = 7.1 Hz, 3 H), 1.51 (m, 8 H), 2.34 (t*, ^3J = 7.6 Hz, 4 H), 2.42 (s, 8 H), 3.22 (br. s, 4 H), 3.71 (t*, ^3J = 4.6 Hz, 8 H), 4.11 (q, ^3J = 7.1 Hz, 2 H). − ^{13}C NMR (100 MHz, $CDCl_3$, 20°C): δ = 14.7 (CH_3), 23.7 (CH_2), 26.0, 26.4 (CH_2), 46.5, 47.0 (CH_2), 53.6 (CH_2), 58.6 (CH_2), 60.9 (CH_2), 66.9, (CH_2), 156.3 (C_q). − IR (neat): ṽ [cm^{-1}] = 2940 s, 1698 vs, 1471 m, 1457 m, 1118 vs. − MS (EI, 70 eV); *m*/*z* (%): 371 (55) [M^+], 341 (31), 142 (17), 111 (15), 100 (100). − $C_{19}H_{37}N_3O_4$ (371.5): calcd. C 61.4, H 10.0, N 11.3; found C 61.4, H 10.3, N 11.5.

Hydroaminomethylation of 1n with 2: According to the general procedure **1n** and **2** were converted into 2.34 g of a mixture of **4n**, **5n**. Purification by column chromatography (toluene/ethanol = 50:1 as eluent) led to 1.67 g (67%) of **4n** as a 1:1 mixture of diastereoisomers (determined by ^{1}H and ^{13}C NMR) and 0.58 g (24%) of **5n**.

***N*-[2-Methyl-4-(morpholin-4-yl)butyl]-*N*-[2-methyl-3-(morpholin-4-yl)propyl]acetamide (4n):** ^{1}H NMR (400 MHz, $CDCl_3$, 20 °C): δ = 0.83 (2 × d, ^3J = 6.5 Hz, 3 H), 0.90 (d, ^3J = 6.6 Hz, 3 H), 1.29 (m, 1 H), 1.53 (m, 1 H), 1.71 (m, 1 H), 2.11 (2 × s, 3 H), 2.17 (m, 1 H), 2.35 (m, 4 H), 2.40 (br. s, 8 H), 3.03 (m, 1 H), 3.18 (m, 1 H), 3.29 (m, 1 H), 3.51 (m, 1 H), 3.69 (t*, ^3J = 5.3 Hz, 8 H). − ^{13}C NMR (100 MHz, $CDCl_3$, 20°C): δ = 16.5, 16.6, 16.6, 16.7 (CH_3), 17.4, 17.4, 17.5 (CH_3), 21.7, 21.8 (CH_3), 28.2, 28.2, 29.6, 29.7 (CH), 29.9, 29.9, 30.6, 30.8 (CH), 30.8, 30.9, 31.0 (CH_2), 50.2, 50.4, 51.3, 51.4 (CH_2), 53.6, 53.6, 53.8, 54.0 (CH_2), 53.2, 53.3, 55.3, 55.4 (CH_2), 56.3, 56.4, 56.7, 56.8 (CH_2), 63.4, 63.5, 63.7 (CH_2), 66.7, 66.8 (CH_2), 170.6 (C_q). − IR (neat): ṽ [cm^{-1}] = 2957 s, 1651 vs, 1645 vs, 1456 s, 1446 s, 1423 s, 1119 vs. − MS (EI, 70 eV); *m*/*z* (%): 355 (4) [M^+], 141 (6), 100 (100), 43 (7).

***N*-[2-Methyl-4-(morpholin-4-yl)butyl]-*N*-[4-(morpholin-4-yl)-butyl]acetamide (5n):** ^{1}H NMR (400 MHz, $CDCl_3$, 20 °C): δ = 0.88 (d, ^3J = 6.5 Hz) and 0.92 (d, ^3J = 6.8 Hz) [3H], 1.28 (m, 1 H), 1.52 (m, 5 H), 1.87 (m, 1 H), 2.08 (2 × s, 3 H), 2.34 (m, 4 H), 2.41 (br. s, 8 H), 3.05 (dd, ^3J = 8.3 Hz, ^2J = 14.6 Hz, 1 H), 3.18 (m, 1 H), 3.25 (m, 1 H), 3.32 (dd, ^3J = 6.9 Hz, ^2J = 14.7 Hz, 1 H), 3.69 (t*, ^3J = 4.5 Hz, 8 H). − ^{13}C NMR (100 MHz, $CDCl_3$, 20°C): δ = 17.4, 17.5 (CH_3), 21.5, 21.8 (CH_3), 23.6, 23.9 (CH_2), 25.1, 26.3 (CH_2), 30.1, 30.7 (CH), 30.8, 31.0 (CH_2), 45.5, 48.7 (CH_2), 53.5, 53.6 (CH_2), 51.0, 54.5 (CH_2), 56.5, 56.8 (CH_2), 58.1, 58.5 (CH_2), 66.8, 66.8 (CH_2), 170.3, 170.3 (C_q). − IR (neat): ṽ [cm^{-1}] = 2954 s, 1647 vs, 1456 s, 1447 s, 1423 s, 1118 vs, 876 s. − MS (EI, 70 eV); *m*/*z* (%): 355 (14) [M^+], 325 (11), 100 (100), 70 (12), 57 (18), 43 (18).

Hydroaminomethylation of 1o with 2: According to the general procedure **1o** and **2** were converted into 2.30 g of a mixture of **5o** and **12**. Purification by column chromatography (MTBE/PE = 10:1 as eluent) led to 1.72 g (66%) of **5o** as a 1:1 mixture of diastereoisomers (determined by ^{1}H and ^{13}C NMR) and 0.44 g (23%) of **12**.

***N*,*N*-Bis[2-methyl-4-(morpholin-4-yl)butyl]acetamide (5o):** ^{1}H NMR (400 MHz, $CDCl_3$, 20 °C): 0.88 (2 × d, ^3J = 6.8 Hz, 6 H), 1.29 (m,

2 H), 1.52 (m, 2 H), 1.91 (m, 2 H), 2.10 (s, 3 H), 2.32 (m, 4 H), 2.40 (br. s, 8 H), 3.07 (m, 1 H), 3.21 (m, 3 H), 3.70 (t*, ^3J = 4.5 Hz, 4 H). − ^{13}C NMR (100 MHz, $CDCl_3$, 20°C): δ = 17.3, 17.3, 17.4, 17.4 (CH_3), 21.7 (CH_3), 29.4, 29.5, 30.3, 30.4 (CH), 30.7, 30.7, 30.8, 30.9 (CH_2), 53.5, 53.5 (CH_2), 50.9, 51.0, 54.5, 54.6 (CH_2), 56.2, 56.2, 56.6, 56.6 (CH_2), 66.6 (CH_2), 170.5 (C_q). − IR (neat): $\tilde{\nu}$ [cm^{-1}] = 2956 vs, 1647 vs, 1456 s, 1447 s, 1424 s, 1119 vs. − MS (EI, 70 eV); *m/z* (%): 369 (22) [M^+], 339 (17), 269 (12), 156 (17), 140 (12), 100 (100). − $C_{20}H_{39}N_3O_3$ (369.5): calcd. C 65.0, H 10.6, N 11.4; found C 64.9, H 10.4, N 11.4.

***N*-(2-Methylallyl)-*N*-[2-methyl-4-(morpholin-4-yl)butyl]acetamide (12):** ^{1}H NMR (400 MHz, $CDCl_3$, 20 °C): δ = 0.90 (2 × d, ^3J = 6.8 Hz, 3 H), 1.30 (m, 1 H), 1.54 (m, 1 H), 1.68 (2 × s, 3 H), 1.88 (m, 1 H), 2.10 (2 × s, 3 H), 2.38 (m, 6 H), 3.05 (m) and 3.28 (m) [1H], 3.18 (m, 1 H), 3.69 (t*, ^3J = 4.5 Hz, 4 H), 3.87 (m, 2 H), 4.74 (2 × s, 1 H), 4.90 (2 × s, 1 H). − ^{13}C NMR (100 MHz, $CDCl_3$, 20°C): δ = 17.4, 17.5 (CH_3), 19.8, 19.9 (CH_3), 21.4, 21.5 (CH_3), 30.2 (CH), 30.9, 31.0 (CH_2), 50.0, 51.5 (CH_2), 53.6, 53.6 (CH_2), 53.1, 55.4 (CH_2), 56.4, 56.7 (CH_2), 66.8, 66.8 (CH_2), 110.9, 111.8 (CH_2), 139.7, 140.4 (C_q), 171.2 170.4 (C_q). − IR (neat): $\tilde{\nu}$ [cm^{-1}] = 3080 w, 2957 s, 1651 vs, 1446 s, 1422 s, 1119 vs. − GC−MS (EI, 70 eV); *m/z* (%): 269 (55) [M^+ + 1], 155 (11), 100 (100), 84 (15), 70 (13), 56 (21). − $C_{15}H_{28}N_2O_2$ (268.4): calcd. C 67.1, H 10.5, N 10.4; found C 66.9, H 10.3, N 10.7.

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