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Tosylated glycerol carbonate, a versatile bis-electrophile to access new functionalized glycidol derivatives

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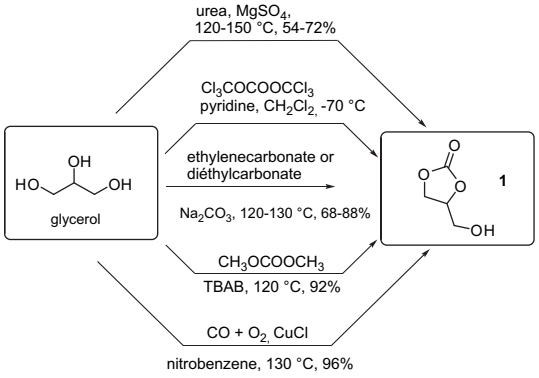
ABSTRACT

The reactivity of tosylated glycerol carbonate **2** toward nucleophiles has been exploited to generate glycidol analogues protected with carbonate or carbamate groups. The activated glycerol **2** is a reasonable linking agent with thiol and alcohol nucleophiles and an excellent and selective one with primary amines, allowing efficient bis-functionalizations of glycerol.

1. Introduction

Valorization of glycerol as renewable resource is becoming a crucial challenge for industrial companies: this small molecule appears as a major by-product in manufacturing biodiesels, fatty acids, and surfactants.[1] Glycerol 1,2-carbonate ((4-hydroxymethyl)-1,3-dioxolan-2-one; GC) **1**, which bears a primary hydroxymethyl group, can be prepared directly and in high yield from glycerol by different methods (Scheme 1). The cheapest method to obtain GC is to react urea with glycerol in the presence of catalysts like zinc oxide and magnesium or sodium sulfate.[2] GC can also be prepared by reacting glycerol with phosgene[3] but to avoid the use of that highly toxic reagent, production of GC can be effected by transesterification of dialkyl carbonates under alkaline conditions.[4] Reacting dimethyl carbonate with glycerol in the presence of tetra-*n*-butylammonium bromide furnishes GC in very good yield.[5] A direct process to achieve GC formation involves Cu(I)-catalyzed reaction of glycerol with carbon monoxide and oxygen.[6] Recently the reaction of transcarbonation of ethylene carbonate with carbon dioxide under super critical conditions was also reported.[7]



Scheme 1. Main routes to obtain glycerol 1,2-carbonate (GC) **1**.

As a plurifunctional inexpensive compound, GC has a considerable potential for different transformations in fine chemistry. The resolution of racemic GC has already been investigated using lipase-catalyzed acetylation and/or alcoholysis.[8] More recently, self-condensation of GC to oligomers was explored[9] to show that like glycidol, the cyclic carbonate could serve as a source of new polymeric materials, high-valued constituents in the production of a number of polymers.[10a,b] Conversion of GC into glycidol can be performed by two processes: (a) in the presence of ethylene carbonate at high temperature and reduced pressure;[10c] (b) in the presence of Na_3PO_4.[10d] The primary hydroxyl group of GC may be reacted with aldehydes,[11] anhydrides[12] or isocyanates[13] to form enol ethers, esters or urethanes.

GC was employed as a source to mixed carbonate, which reacted with diamines to obtain polyurethanes without the use of hazardous isocyanates.[14] Eventually this stable and low-toxic molecule, like other cyclic carbonates, has found use as a solvent in cosmetic, personal care, medicine, and chemical industry, as a biolubricant owing to its adhesion to metallic surfaces and resistance to oxidation, hydrolysis, and pressure or a component of gas-separation membranes.[15–18] Cyclic carbonates may undergo a number of reactions with various nucleophiles—aromatic and aliphatic amines,

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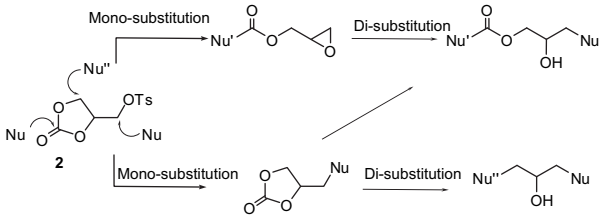
thiols, alcohols, and carboxylic acids.[19] Despite its unsophisticated preparation, glycerol 1,2-carbonate has been scarcely studied as a precursor for the development of new synthons in organic chemistry. Recently, we reported our preliminary results on the reactivity of nucleophiles toward *O*-sulfonylated GCs.[20] In the present work, we have investigated the behavior of the activated GC **2** when opposed to miscellaneous oxygen-, nitrogen-, and sulfur-nucleophiles, with a view to enlarging the scope of modular transformations of this multi-electrophilic synthon, which could be seen as a possible alternative reagent to glycidol or epichlorhydrin[21] (Scheme 2).

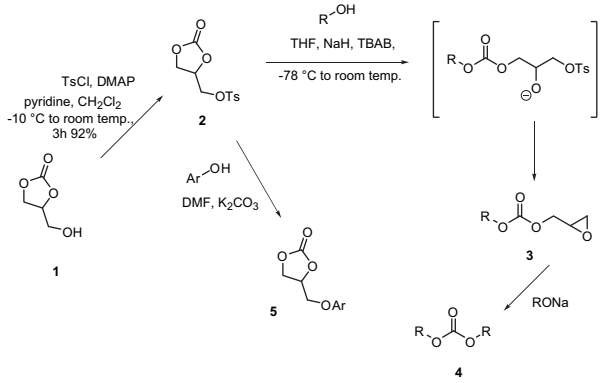


Scheme 2. Modular reactivity of tosylated GC **2**.

2. Results and discussion

2.1. Formation of alkyl glycidyl carbonates

Following our previous approach, the primary hydroxyl of GC **1** was activated by tosylation (Scheme 3), the choice of a tosyl group being based not only on the high conversion yield but also on the stability and crystallinity of tosylated GC **2**.[20]



Scheme 3. Formation of alkyl glycidyl carbonates via transcarbonatation.

Tosylated GC **2** was first exposed to *m*-methoxyphenol in order to compare with results previously obtained with *m*-methoxythiophenol.[20] The reaction with *m*-methoxyphenol and potassium carbonate in DMF proved to be far less efficient than with the thioanalogue: only 41% of the aryloxy derivative **5** was obtained, while 55% of the arylsulfanyl analogue could be obtained under the same conditions from *m*-methoxythiophenol. Therefore, in connection with a procedure described by Clements et al. for the preparation of glycidyl carbonates,[22] aliphatic alkoxides were reacted with **2** leading to selective formation of alkyl glycidyl carbonates (Table 1).

Reaction of solketal with **2** was examined first, with a view to synthesizing a non-symmetrically protected diglycerol;[23] benzyl alcohol (entries 2 and 3) was also studied as a more standard example. Variations of the base (K_2CO_3, *t*-BuOK, NaH, BuLi) and solvent (DMF, THF) were thus evaluated, showing optimal yields by using NaH and a catalytic amount of tetra-*n*-butylammonium bromide (TBAB) in THF.

Table 1
Formation of alkyl glycidyl carbonates

Entry	Alcohol	Solvent	Product (yield)	Side-product (yield)
1	Solketal[a]	DMF	**3a** (35)	—
2	Benzyl alcohol[a]	DMF	**3b** (46)	**4b** (21)
3		THF	**3b** (49)	**4b** (33)
4	Pentan-1-ol[a]	THF	**3c** (83)	—
5	Heptan-1-ol[a]	THF	**3d** (72)	—
6	Decan-1-ol[a]	THF	**3e** (67)	**4e** (12)
7	Dodecan-1-ol[a]	THF	**3f** (56)	**4f** (13)
8	Allyl alcohol[a]	THF	**3g** (47)	**4g** (12)
9	Cyclohexanol[a]	THF	**3h** (20)	—
10	Pentan-3-ol[a]	THF	**3i** (6)	—
11	*tert*-Butanol[a]	THF	**3j** (—)	—
12	*t*-BuOK[b]	THF	**3j** (87)	—
13	*m*-Methoxyphenol	THF	**3k** (—)	**5** (41)
14	*m*-Methoxyphenol [c]	DMF	**3k** (—)	**5** (65)

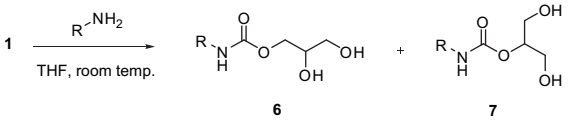
[a] Complete disappearance of the starting material was observed.
[b] *t*-BuOK, THF, TBAB, from −70 °C to rt, 24 h.
[c] $NaHCO_3$ was used as the base.

Alkyl glycidyl carbonates **3b–j** were obtained in variable yields as major compounds of the nucleophilic displacement. In the case of benzyl alcohol, the double nucleophilic attack at the carbonyl was largely observed leading to the formation of dibenzyl carbonate **4f** in 21–33% yield. Such transcarbonatation was not detected when the reaction was efficient enough as with *n*-pentanol or *n*-heptanol (entries 4 and 5) whereas symmetrical carbonates were isolated in low yields with other primary alkoxides (entries 6–8). Both secondary alcohols tested—pentan-3-ol and cyclohexanol (entries 9 and 10)—showed dramatically lowered reactivity mainly due to flexibility and increased steric hindrance. In the fixed conditions, *tert*-butanol proved totally inefficient but in contrast, using *t*-BuOK led to an impressive 87% yield of the *tert*-butyl glycidyl carbonate **3j** (entry12). From the above results, it appears that under the conditions applied, primary alcohols generally react fairly with tosylated GC **2** to yield the corresponding glycidyl carbonates **3** together with a transcarbonated side-product **4**. Secondary or tertiary alcohols proved much less efficient—in part because of steric hindrance, but most likely owing to defective formation of the sodium alkoxide under the conditions applied. This was reinforced by the efficient conversion into the expected **3j** when using pure *t*-BuOK in THF. Taking this into consideration, a modified procedure involving reaction of *t*-BuOH with sodium hydride for 2 h finally gave a 66% yield of carbonate **3j**. A reactivity test involving *m*-methoxyphenol was effected under the same conditions: the expected substitution at the tosylated center afforded the aryl ether **5** in 41% yield; however this could be augmented to 65% yield by changing both the solvent to DMF and the base to $NaHCO_3$. In summary, the reactivity of tosylated GC **2** with *O*-nucleophiles is clearly governed by HSAB criteria: hard alkoxide reagents regioselectively attack the carbonyl center, whereas a softer phenolic ion preferentially interacts with the *O*-sulfonylated appendage.

2.2. Formation of alkyl glycidyl carbamates

The most widely explored reaction of cyclic carbonates in functional polymers has been amine condensations. Cyclic carbonates react with primary and some secondary amines at rt in the absence of catalyst: similarly to aliphatic alcohols, aliphatic amines attack the carbonyl center, to effect ring-opening of the carbonate.[19,24] Previous studies on non-symmetrical cyclic carbonates have shown that both regioisomeric carbamates can be formed, the primary prevailing over the secondary.[25,26] *O*-Benzoylated GC reacted smoothly with benzylamine to produce a mixture of glycerol-derived carbamates without benzoate aminolysis.[25] The isomeric ratio of those carbamates was mostly dependent on the amine and solvent used.[26]

In a first set of trials, we have explored the reactivity of GC **1** (Scheme 4) with some simple amines.



Scheme 4. Reaction of primary amines with GC **1**.

Similarly to the results obtained by Keul et al.[17]—standard aminolysis (rt, 21 h) of **1** in DMSO yielding a 53:47 mixture of two carbamates—the condensation proceeded smoothly in good to excellent yields, giving in a similar 60–40 ratio the expected mixtures of carbamate regioisomers **6** and **7**, which could not be separated (Table 2).[25]

Table 2
Production from GC **1** of glycerol-derived carbamates **6** and **7**

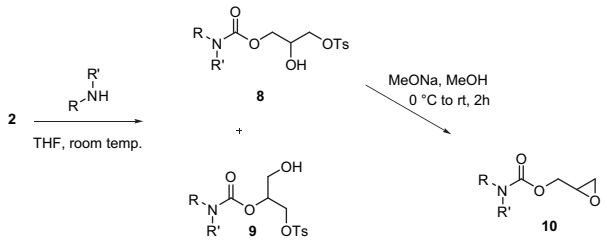
Entry	Amine	Product mixture	Yield (%)	Ratio (prim/sec)[a]
1	1-Decylamine	**6a**/**7a**	71	62:38
2	1-Dodecylamine	**6b**/**7b**	87	59:41
3	Allylamine	**6c**/**7c**	88	69:31
4	Benzylamine	**6d**/**7d**	99	63:37

[a] Based on ^{1}H NMR spectra.

It is known that the isomeric ratio in the ring cleavage of a cyclic carbonate can be influenced by the character of the side chain, in which an electron-withdrawing effect would favor the primary carbamate.[24,25] Urethane formation was investigated from a glycerol carbonate activated as a primary phenoxycarbonyl derivative: chemoselective substitution was observed at low temperature (0–25 °C) whereas ring-opening occurred at higher temperature (25–60 °C), but only after total consumption of the phenyl carbonate.[17] Thus temperature should be a critical factor to control the reaction selectivity.

In other respects, the effect of a sulfonate moiety might be crucial in bringing chemoselectivity improvement: this would be an opportunity to explore the direct reactivity of aliphatic amines with tosylated GC **2**.

Aminolysis of tosylated GC **2** (Scheme 5) was performed at rt by adding an aliphatic amine (1.2 equiv) in aprotic solvent until total consumption of the starting carbonate. The first experiments were efficiently conducted in DMF, however, particularly because of troublesome carbamate recovery, THF was preferred in the procedure, in which no double nucleophilic attack was observed, even with an amine excess of up to 6 equiv. The reaction was chemoselective in all of our cases on the contrary to previous publications.[25,26] No tosyl substitution occurred and only carbamates of type **8** were detected and isolated (Table 3). This confirmed the influence of an electron-withdrawing group on the regioselectivity of the ring-opening of GC, isomeric secondary carbamates **9** remaining undetected. In the narrow panel of amines tested, better reactivities were expectedly observed for primary amines (entries 1–4, 71–97%) than for heterocyclic secondary amines (53–68%),



Scheme 5. Two-step sequence of carbamate then oxirane formation.

Table 3
Production from **2** of carbamates **8** and oxiranes **10**

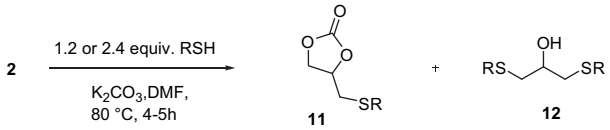
Entry	Amine	Carbamate (yield)	Oxirane (yield)
1	1-Decylamine	**8a** (97)	**10a** (97)
2	1-Dodecylamine	**8b** (97)	**10b** (83)
3	Allylamine	**8c** (96)	**10c** (75)
4	Benzylamine	**8d** (71)	**10d** (80)
5	Morpholine	**8e** (68)	**10e** (58)
6	Piperidine	**8f** (58)	**10f** (61)
7	*N*-Benzylpiperazine	**8g** (53)	**10g** (69)
8	*N*,*N*-Diisopropylamine	—	—

while bulky *N*,*N*-diisopropylamine proved unreactive. Aromatic amines such as aniline or indoline have shown no reactivity when the same conditions were used.

The oxiranyl moiety is a key structural segment in organic synthesis, especially when inserted into C-3 synthons of the glycidol and epichlorhydrin family. In that way, conversion of compounds **8** into oxirane–urethanes would be of high value. The glycidyl alkylcarbamates **10a–g** were readily obtained from precursors **8a–g** (Table 3) using standard treatment by stoichiometric sodium methoxide in methanol, with yields ranging from reasonable to excellent (58–97%).

2.3. Reaction with *S*-centered and other soft nucleophiles

The next family of aliphatic nucleophiles to be explored was thiol compounds. According to our previous results, the SH group of aliphatic thiols should be prone to attack onto the *O*-sulfonylated appendage of **2** (Scheme 6).[20] Applying with aliphatic thiols the reaction conditions (Et_3N or $NaHCO_3$) used in our precedent work proved unsuccessful, while a stronger base like K_2CO_3 effected smooth conversion (Table 4) into thio-derivatives. All the thiols tested gave the expected reaction at the tosylated center of the glycerol backbone, thus following the Pearson orientation of the reaction to the softer electrophilic site of GC **2**.



Scheme 6. Reaction of thiols with tosylated GC **2**.

Table 4
Nucleophilic displacement by aliphatic thiols

Entry	Thiols	Product	Product
	Hexanethiol **a**	**11a**	**12a**
1	1.2 equiv	84%	—
2	2.4 equiv	23%	26%
	Benzylmercaptan **b**	**11b**	**12b**
3	1.2 equiv	38%	9%
4	2.4 equiv	34%	39%
	Cyclopentanethiol **c**	**11c**	**12c**
5	1.2 equiv	68%	3%
6	2.4 equiv	33%	50%
	6-Mercaptohexanol **d**	**11d**	**12d**
7	1.2 equiv	39%	—
8	2.4 equiv	39%	—

Using a slight excess of thiol, the monosubstituted derivatives **11a–d** (Table 4) were obtained in reasonable to good yields. On the contrary, a larger excess of thiol (2.4 equiv) allowed 1,3-disubstitution to afford bis-sulfides **12**, albeit in rather moderate yields. Typically, hexanethiol reacted efficiently to give the monosulfide **11a** in 84% yield (entry 1), whereas the bis-sulfide **12a** was

obtained in only 26% yield together with 23% **11a** (the silica gel chromatography separation of **12a** and **11a** proved troublesome, entry 2). Initially involved with a view to testing the chemoselectivity of the reaction, 6-mercaptohexanol gave disappointing results: in both cases, only the monosulfide **11d** could be isolated in moderate yields, mainly because of tedious separation of the starting thiol from the resulting monosulfide.

Moving from simple aliphatic thiols to a more complex example led to unexpectedly good results: the regioselective reaction under identical conditions of 2,3,4,6-tetra-*O*-acetyl-β-D-glucopyranosylthiol **13** (a standard nucleophilic partner in our laboratory) with tosylated GC **2** (Scheme 7) afforded an 83% yield of the thioglucoside **14** as a diastereoisomeric mixture.

Scheme 7. Reaction of a glyco-mercaptan with tosylated GC **2**.

Some other standard 'soft' nucleophiles were also tested (Table 5). Iodide ion nucleophilic displacement converted **2** into the iodomethylcarbonate **15**[11b] in 89% yield, whereas the analogous azido derivative **16**[20] was obtained in 84% yield.

Table 5
Reactivity of soft nucleophiles

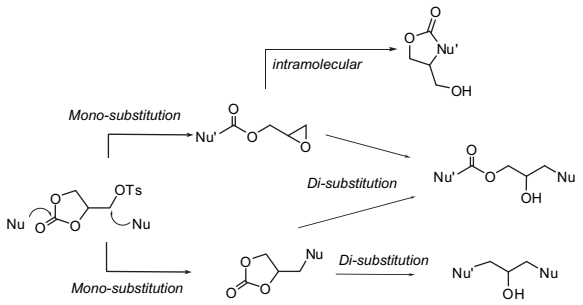
Entry	Nu (2 equiv)	Solvent	Product	Yield (%)
1	NaI	Acetone	**15**	89
2	NaN_3	DMF	**16**	84
3	KSCN	DMSO	**17**	47
4	AcSK	DMF	**18**	62
5	Thiourea	DMF	**19a** Thiol	71
			19b Disulfide	56

Under the same conditions, KSCN afforded the expected thiocyanate **17** in 25% yield only; changing the solvent to DMSO improved the reactivity and a reasonable 47% yield of **17** was reached. Similarly, the thioester **18** was produced from **2** in 62% yield. In contrast, thiourea failed to react and therefore the analogous iodide **15** was engaged instead of tosylated GC **2**: the expected isothiouronium salt was formed but it could not be separated from the remaining thiourea. Hydrolysis under reductive conditions was performed on the crude salt and afforded the previously unknown 1-thioglycerol-2,3-carbonate **19a** was obtained in 71% yield over three steps from **2**. However **19a** spontaneously and rapidly underwent oxidation into the dimeric disulfide **19b**, which could be isolated in 56% yield.

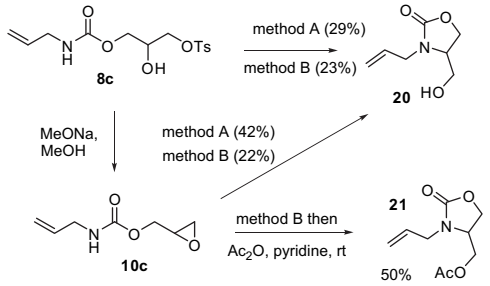
2.4. Tandem functionalization

With a view to further exemplifying the functional diversity prospect opened above, we were interested in exploring the potential of versatile reagent **2** in nucleophile-induced combined modifications of glycerol (Scheme 8).

A first tandem functionalization of glycerol was performed with intramolecular formation of *N*-substituted 1,3-oxazolidin-2-ones, a well-known class of heterocyclic compounds.[27] The test-substrate initially selected was *N*-allylcarbamate **8c**, which reacted with NaH or *t*-BuOK to undergo intramolecular cyclization (Scheme 9); however the reaction revealed less efficient than expected, the expected oxazolidinone **20** being obtained in poor yields (23–29%) whatever the base used. By replacing **8c** by the epoxide **10c** in the reaction with *t*-BuOK, the oxazolidinone **20** was obtained with a poor yield of 22% while using NaH increased the yield to 42%. The



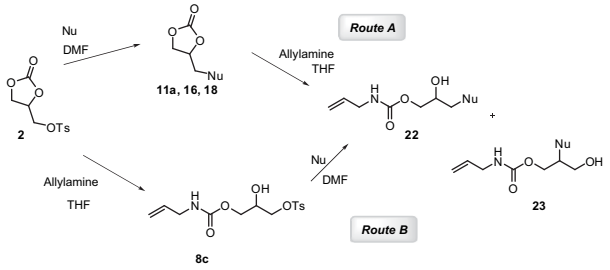
Scheme 8. Tosylated GC **2** in combined modifications of glycerol.



Scheme 9. Conversion of linear carbamates into oxazolidones—method A: NaH, THF, −70 °C to rt, method B: *t*-BuOK, THF, −70 °C to rt, 2 h.

process was slightly improved by in situ acetylation of the hydroxyl group, to afford the *O*-acetylated oxazolidinone **21** in 50% yield.

Tandem functionalization to afford non-symmetric disubstituted glycerols was performed through combining some of the most efficient nucleophiles tested above—allylamine, hexanethiol, NaN_3, and AcSK (Scheme 10).



Scheme 10. Tandem functionalization of tosylated GC **2**.

For the preparation of **22a** (Nu=SAc, 44% overall yield), route B was compulsory: indeed in route A, allylamine attack did not occur on the cyclic carbonate but most likely on the thioacetate. Azide **22b** was obtained in excellent overall yields either via **8c** while via **16** (route A) the yields drop to a moderate 32%. The reaction with hexanethiol was more complex: aminolysis of the cyclic carbonate never exceeded 21%, which resulted in a 16% overall yield for route A. Using route B furnished with 70% yield two regioisomeric thioethers **22c** and **23** in ca. 4:1 ratio.

We have also compared the efficiency of reactivity to obtain **22c** and **23** from two analogues of **8c**. We have tested the iodo derivative **24** (obtained by nucleophilic substitution of tosylated **8c** in 51% yield) and the epoxide **10c**. The reactivity with hexanethiol of the epoxide **10c** (**22c**: 31%, **23**: 7%) and the iodohydrin **24** (**22c**: 31%, **23**:7%) clearly showed that the tosyl intermediate **8c** leads to far better results in terms of efficiency and yield.

The compared results according to different routes, reported in Table 6, showed that route B appears more efficient even though the yields of this two-step sequence are in some cases moderate.

Table 6
Routes A and B comparison for bis-functionalization of tosylated GC

Product: Nu	**22a**: SAc	**22b**: N_3	**22c**: SHexyl	**23**: SHexyl
Route A (two steps)	*	48% (32%)	21% (16%)	
Route B	45% (44%)[a]	98% (97%)	55% (53%)	15%

* means not tested.
[a] Overall yields (%) of the two-step sequence.

3. Conclusion

Exploration of the reactivity of tosylated glycerol carbonate **2** toward nucleophiles has shown this reagent to be a good selective linker for primary and secondary amines and a productive precursor to various glycidol analogues either bearing a carbonate or a carbamate moiety. As expected the reaction with thiols was much less efficient but, depending on the thio-compound involved, formation in good conditions of glycerol-based thioethers was observed. Taking advantage of marked chemo- and regioselective behavior of **2**, efficient bis-functionalizations of glycerol could also be performed. The above results should help promoting tosylated glycerol carbonate as a good surrogate of glycidol and epichlorohydrin in some chemical synthetic applications.[21] Further work will focus on enantioselective approaches for exploration of new linking strategies with adapted nucleophiles.

4. Experimental

4.1. General

Solvents were dried and distilled by standard methods before use. Reactions were monitored by TLC analysis on precoated silica gel plates (Kieselgel 60F_{254}, E. Merck); spots were visualized with UV light and charring after a 1% $KMnO_4$ solution spray. Column chromatography was performed on silica gel SI 60 (43–60 μm; E. Merck) using mixtures of hexane (Hex) or petroleum ether (PE) and ethyl acetate (EA) or dichloromethane (CH_2Cl_2) and methanol (MeOH). Melting points (mp) were determined on a Büchi Melting Point B-540 apparatus and are uncorrected. IR spectra were measured either on a Perkin–Elmer Paragon 1000 PC or FT-IR Thermo Scientific Nicolet iS10 spectrophotometers; IR absorption frequencies are given in cm^{-1}. ^1H and ^{13}C NMR spectra were recorded on a Bruker Avance DPX-250 instrument (250 MHz, respectively), a Varian Unity Inova instrument (300 MHz, respectively), or on a Bruker Avance DPX-400 instrument (400 MHz). Chemical shifts (δ) are reported in parts per million downfield from internal TMS standard; coupling constants (J) are reported in hertz and refer to apparent peak multiplicity. Mass spectra (MS) were recorded on Perkin–Elmer SCIEX API 300 (ion spray) and Agilent 110 (serie MS with VL) apparatuses. Elemental analysis was performed with an Exeter Analytical CE-440 Elemental Analyzer. High resolution mass spectra (HRMS) were recorded with a TOF spectrometer in ESI or CI mode.

Glycerol 1,2-carbonate (4-hydroxymethyl-1,3-dioxolan-2-one) **1** [931-40-8] was prepared according to Ref. 11a; NMR spectra are in agreement with literature data. 3-*O*-Tosyl glycerol 1,2-carbonate **2** [949895-84-5] was prepared according to Ref. 11b; NMR spectra are in agreement with literature data.

4.2. Standard procedure for the synthesis of 3a–k[22]

To a solution of alkoxide (1.2 equiv; pre-formed by reacting the alcohol with sodium hydride) in THF or DMF (4 mL) maintained at −70 °C was slowly added a solution of compound **2** (0.5 g, 1.836 mmol) and *n*-Bu_4NBr (59 mg, 0.183 mmol, 0.1 equiv) in THF or DMF (5 mL). After 2 h stirring at −70 °C, the mixture was allowed to slowly warm up to rt and was then diluted with ethyl acetate and water. The organic layer was washed with water and brine, then dried over $MgSO_4$. After filtration and concentration of the solution in vacuo, the residue was purified by flash column chromatography (eluent: Hex/EA 9/1, then 4/1).

*4.2.1. (2,2-Dimethyl-1,3-dioxolan)-4-ylmethyl glycidyl carbonate **3a**.* Compound **3a** was isolated in 35% yield as a colorless oil. ^1H NMR (250 MHz, $CDCl_3$) δ 4.38 (dd, 1H, J_{gem}=12.1, J_{vic}=3.3, H-1a-glycidyl), 4.30 (dd, 1H, J=5.8, 5.9, H-4-dioxolanyl), 4.20–4.11 (m, 2H, OCH_2-dioxolanyl), 4.08–3.95 (m, 2H, H-5b, H-1b-glycidyl), 3.75 (dd, 1H, J_{gem}=8.5 Hz, H-5a), 3.20 (m, 1H, H-2-glycidyl), 2.82 (t, 1H, J_{gem}=J_{vic}=4.5, H-3a-glycidyl), 2.64 (dd, 1H, J_{vic}=2.5, H-3b-glycidyl), 1.40, 1.33 (2s, 6H, CH_3). ^{13}C NMR (62.5 MHz) δ 154.8 (CO), 110.0 (Me_2C), 73.3 (C-4), 68.5, 68.2, 66.3 (OCH_2-dioxolanyl, C-1-glycidyl, C-5), 49.0 (C-2-glycidyl), 44.6 (C-3-glycidyl), 26.7, 25.4 (Me_2C). MS (IS) m/z 233.5 $[M+H]^+$, 250.5 $[M+NH_4]^+$, 255.5 $[M+Na]^+$. IR (NaCl) 1761 (CO).

*4.2.2. Benzyl glycidyl carbonate **3b** [131118-94-0][22b].* Compound **3b** was isolated in 49% yield as a colorless oil. ^1H NMR (250 MHz, $CDCl_3$) δ 7.29–7.54 (m, 5H, Ph), 5.18 (s, 2H, CH_2Ph), 4.41 (dd, 1H, J_{gem}=12.1, J_{vic}=3.3, H-1a), 4.06 (dd, 1H, J_{vic}=6.1, H-1b), 3.24 (m, 1H, H-2), 2.84 (t, 1H, J_{gem}=J_{vic}=4.8, H-3a), 2.66 (dd, 1H, J_{vic}=2.3, H-3b). ^{13}C NMR (62.5 MHz) δ 154.9 (CO), 135.1 (C_{IV}–Ar), 128.4, 128.6 (CH–Ar), 69.9, 68.4 (C-1, PhCH_2), 49.1 (C-2), 44.6 (C-3). MS (IS) m/z 226.5 $[M+NH_4]^+$, 231.0 $[M+Na]^+$. IR (NaCl) 3065, 3035, 3005, 2955 (CH–Ar), 1760 (CO), 1250 (C–O–C). Anal. Calcd for $C_{11}H_{12}O_4$ (208.21): C, 63.45; H, 5.81. Found: C, 63.50; H, 5.96.

*4.2.3. n-Pentyl glycidyl carbonate **3c**.* Compound **3c** was isolated in 83% yield as a colorless oil. ^1H NMR (300 MHz, $CDCl_3$) δ 4.38 (dd, 1H, J_{gem}=12.0, J_{vic}=3.3, H-1a), 4.14 (t, 2H, J_{vic}=6.7, OCH_2-pentyl), 4.02 (dd, 1H, J_{vic}=6.1, H-1b), 3.23 (m, 1H, H-2), 2.84 (t, 1H, J_{gem}=J_{vic}=4.8, H-3a), 2.66 (dd, 1H, J_{vic}=2.7, H-3b), 1.66 (m, 2H, CH_2-pentyl), 1.33 (m, 4H, CH_2-pentyl), 0.89 (br t, 3H, CH_3). ^{13}C NMR (75 MHz, $CDCl_3$) δ 155.0 (CO), 68.5 (C-1), 68.1 (OCH_2-pentyl), 49.1 (C-2), 44.6 (C-3), 28.4, 27.7, 22.2 (CH_2-pentyl), 13.9 (CH_3). MS (IS): m/z 189.4 $[M+H]^+$, 211.4 $[M+Na]^+$. IR (NaCl): 2959, 2934, 2873 (CH), 1747 (CO), 1262 (C–O–C). Anal. Calcd for $C_9H_{16}O_4$ (188.22): C, 57.41; H, 8.57. Found: C, 57.16; H, 8.72.

*4.2.4. n-Heptyl glycidyl carbonate **3d**.* Compound **3c** was isolated in 72% yield as a colorless oil. ^1H NMR (300 MHz, $CDCl_3$) δ 4.37 (dd, 1H, J_{gem}=12.1, J_{vic}=3.3, H-1a), 4.13 (t, 2H, J_{vic}=6.7, OCH_2-heptyl), 4.02 (dd, 1H, J_{vic}=6.1, H-1b), 3.22 (m, 1H, H-2), 2.83 (t, 1H, J_{gem}=J_{vic}=4.8, H-3a), 2.65 (dd, 1H, J_{vic}=2.6, H-3b), 1.65 (m, 2H, CH_2-heptyl), 1.32 (m, 8H, CH_2-heptyl), 0.86 (br t, 3H, CH_3). ^{13}C NMR (62.5 MHz, $CDCl_3$) δ 155.2 (CO), 68.7 (C-1), 68.2 (OCH_2-heptyl), 49.2 (C-2), 44.7 (C-3), 31.8, 29.0, 28.7, 25.7, 22.7 (CH_2-heptyl), 14.1 (CH_3). MS (IS): m/z 234.5 $[M+NH_4]^+$, 239.0 $[M+Na]^+$. IR (NaCl) 2957, 2930, 2873, 2860 (CH), 1765 (CO), 1263 (C–O–C). Anal. Calcd for $C_{11}H_{20}O_4$ (216.28): C, 61.09; H, 9.32. Found: C, 61.31; H, 9.41.

*4.2.5. n-Decyl glycidyl carbonate **3e**.* Compound **3e** was isolated in 67% yield as a white solid, mp 36–37 °C (CH_2Cl_2). ^1H NMR (300 MHz, $CDCl_3$) δ 4.39 (dd, 1H, J_{gem}=12.0, J_{vic}=3.3, H-1a), 4.14 (t, 2H, J_{vic}=6.6, OCH_2-decyl), 4.01 (dd, 1H, J_{vic}=6.0, H-1b), 3.24 (m, 1H, H-2), 2.85 (t, 1H, J_{gem}=J_{vic}=4.8, H-3a), 2.67 (dd, 1H, J_{vic}=2.6, H-3b), 1.66 (m, 2H, CH_2-decyl), 1.38–1.19 (m, 14H, CH_2-decyl), 0.87 (br t, 3H, CH_3). ^{13}C NMR (75 MHz, $CDCl_3$) δ 155.2 (CO), 68.5 (C-1), 68.0 (OCH_2-decyl), 49.1 (C-2), 44.5 (C-3), 31.9, 29.5, 29.3, 29.2, 28.6, 25.7, 22.7 (CH_2-decyl), 14.1 (CH_3). MS (APCI$^+$): m/z 259.5 $[M+H]^+$, 281.5 $[M+Na]^+$. IR (KBr) 2958, 2924, 2854 (CH), 1742 (CO), 1265 (C–O–C). Anal. Calcd for $C_{14}H_{26}O_4$ (258.36): C, 65.07; H, 10.15. Found: C, 65.25; H, 10.19.

*4.2.6. n-Dodecyl glycidyl carbonate **3f**.* Compound **3f** was isolated in 56% yield as a white solid, mp 41–42 °C (CH_2Cl_2). ^1H NMR (300 MHz, $CDCl_3$) δ 4.39 (dd, 1H, J_{gem}=12.0, J_{vic}=3.3, H-1a), 4.14 (t, 2H, J_{vic}=6.6, OCH_2-dodecyl), 4.01 (dd, 1H, J_{vic}=6.0, H-1b), 3.23 (m,

1H, H-2), 2.85 (t, 1H, J_{gem}=J_{vic}=4.8, H-3a), 2.67 (dd, 1H, J_{vic}=2.7, H-3b), 1.66 (m, 2H, CH_2-dodecyl), 1.38–1.19 (m, 18H, CH_2-dodecyl), 0.87 (m, 3H, CH_3). ^{13}C NMR (75 MHz, $CDCl_3$) δ 155.0 (CO), 68.6 (C-1), 68.1 (OCH_2-dodecyl), 49.1 (C-2), 44.6 (C-3), 31.9, 29.7, 29.6, 29.5, 29.3, 29.2, 28.6, 25.6, 22.7 (CH_2-dodecyl), 14.1 (CH_3). MS (APCI$^+$): m/z 287.5 [M+H]$^+$, 309.5 [M+Na]$^+$. IR (KBr) 2957, 2923, 2853 (CH), 1743 (CO), 1267 (C–O–C). Anal. Calcd for $C_{16}H_{30}O_4$ (286.41): C, 67.10; H, 10.56. Found: C, 67.39; H, 10.68.

4.2.7. Allyl glycidyl carbonate ***3g*** *[68404-09-1]*[22b]. Compound **3g** was isolated in 47% yield as a colorless oil. ^{1}H NMR (300 MHz, $CDCl_3$) δ 5.97–5.84 (m, 1H, =CH), 5.37–5.23 (m, 2H, =CH_2), 4.63–4.59 (m, 2H, OCH_2-allyl), 4.38 (dd, 1H, J_{gem}=12.3, J_{vic}=3.3, H-1a), 4.01 (dd, 1H, J_{vic}=6.3, H-1b), 3.21 (m, 1H, H-2), 2.82 (t, 1H, J_{gem}=J_{vic}=4.8, H-3a), 2.64 (dd, 1H, J_{vic}=2.4, H-3b). ^{13}C NMR (75 MHz, $CDCl_3$) δ 154.8 (CO), 131.4 (=*CH*), 119.1 (=CH_2), 68.8 (C-1), 68.3 (OCH_2-allyl), 49.1 (C-2), 44.6 (C-3). MS (APCI$^+$): m/z 159.3 [M+H]$^+$. IR (NaCl) 2986, 2955, 2873 (CH), 1751 (CO), 1263 (C–O–C).

4.2.8. Cyclohexyl glycidyl carbonate ***3h***. Compound **3h** was isolated (after 48 h stirring) in 20% yield as a colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 4.62–4.55 (m, 1H, *CH*-cyclohexyl), 4.32 (dd, 1H, J_{gem}=12.2, J_{vic}=3.2, H-1a), 3.98 (ddd, 1H, J_{vic}=6.4, J=1.2, H-1b), 3.20 (m, 1H, H-2), 2.81 (dt, 1H, J=5.2, 6.7, H-3a), 2.62 (m, 1H, H-3b), 1.89–1.86 (m, 2H), 1.76–1.70 (m, 2H), 1.52–1.16 (m, 6H, CH_2-cyclohexyl). ^{13}C NMR (100 MHz, $CDCl_3$) δ 154.2 (CO), 77.0 (*CH*-cyclohexyl), 67.8 (C-1), 48.9 (C-2), 44.5 (C-3), 31.3, 25.0, 23.5 (CH_2-cyclohexyl). MS (IS): m/z 223.0 [M+Na]$^+$. IR (neat) 2937, 2860 (CH), 1738 (CO). ESI-HRMS calcd for $C_{10}H_{16}O_4Na$: 223.0946. Found: 223.0944 [M+Na]$^+$.

4.2.9. Pent-3-yl glycidyl carbonate ***3i***. Compound **3i** was isolated (after 48 h stirring) in 6% yield as a colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 4.62–4.56 (m, 1H, *CH*-pentyl), 4.37 (dd, 1H, J_{gem}=12.0, J_{vic}=3.6, H-1a), 4.04 (dd, 1H, J_{vic}=6.0, H-1b), 3.24 (m, 1H, H-2), 2.85 (t, 1H, J_{gem}=J_{vic}=4.6, H-3a), 2.66 (dd, 1H, J=4.6 Hz, J_{vic}=2.8, H-3b), 1.66–1.59 (m, 4H, CH_2-pentyl), 0.89 (m, 6H, CH_3). ^{13}C NMR (100 MHz, $CDCl_3$) δ 155.0 (CO), 81.8 (*CH*-pentyl), 69.7 (C-1), 49.1 (C-2), 44.6 (C-3), 26.3 (CH_2-pentyl), 9.4 (CH_3). MS (IS): m/z 211.4 [M+Na]$^+$. IR (neat) 2970 (CH), 1740 (CO). ESI-HRMS calcd for $C_9H_{16}O_4Na$: 211.0946. Found: 211.0952 [M+Na]$^+$.

4.2.10. tert-Butyl glycidyl carbonate ***3j*** *[379220-30-1]*[22a]. By using *t*-BuOK as reagent, compound **3j** was obtained (after 48 h stirring) in 87% yield as a colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 4.29 (dd, 1H, J_{gem}=12.0, J_{vic}=3.6, H-1a), 3.98 (dd, 1H, J_{vic}=6.0, H-1b), 3.22 (m, 1H, H-2), 2.84 (t, 1H, J_{gem}=J_{vic}=4.8, H-3a), 2.64 (dd, 1H, J_{vic}=2.6, H-3b), 1.49 (d, 9H, J=0.8, *t-Bu*). ^{13}C NMR (100 MHz, $CDCl_3$) δ 153.2 (CO), 82.6 (C_{IV}–*t*-Bu), 67.4 (C-1), 49.1 (C-2), 44.7 (C-3), 27.7 (3$^*CH_3$). MS (IS): m/z 175.3 [M+H]$^+$, 197.3 [M+Na]$^+$. IR (neat) 2981 (CH), 1739 (CO).

4.2.11. Dibenzyl carbonate ***4b*** *[3459-92-5].* Carbonate **4b** (co-product of **3b**) was isolated in 33% yield as a colorless oil.

4.2.12. Di-n-decyl carbonate ***4e*** *[6290-55-7].* Carbonate **4e** (co-product of **3e**) was isolated in 12% yield as a colorless oil.

4.2.13. Di-n-dodecyl carbonate ***4f*** *[6627-45-8].* Carbonate **4f** (co-product of **3f**) was isolated in 13% yield as a colorless oil.

4.2.14. Diallyl carbonate ***4g*** *[15022-08-9].* Carbonate **4g** (co-product of **3f**) was isolated in 12% yield as a colorless oil.

4.2.15. 4-(3-Methoxyphenoxy)methyl-1,3-dioxolan-2-one ***5***. 3-Methoxyphenol (0.137 g, 1.1 mmol) and $NaHCO_3$ (0.062 g, 0.74 mmol) were added to a solution of **2** (0.1 g, 0.37 mmol) in DMF (2.5 ml), which was then heated at 80 °C for 23 h. After cooling to rt, the mixture was hydrolyzed and extracted (3×) with ethyl acetate; the organic phase was washed (3×) with water and brine, then dried over $MgSO_4$. After filtration and concentration of the solution in vacuo, the residue was purified by flash column chromatography (eluent: PE/EA 1/1). Compound **5** (54 mg, 65% yield) was isolated as an oil. ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.19 (t, 1H, J_{vic}=8.1, *CH*–Ar), 6.65–6.42 (m, 3H, *CH*–Ar), 5.02 (m, 1H, H-4), 4.60 (t, 1H, J_{gem}=J_{vic}=8.4, H-5a), 4.52 (dd, 1H, J_{vic}=6.0, H-5b), 4.22 (dd, 1H, J_{gem}=10.6, J_{vic}=4.0, CH_2OAr), 4.11 (dd, 1H, J_{vic}=3.6, CH_2OAr), 3.79 (s, 3H, OCH_3). ^{13}C NMR (75 MHz, $CDCl_3$) δ 161.0, 159.0 (2$^*C_{IV}$–Ar), 154.9 (CO), 130.2, 107.7, 106.5, 101.3 (*CH*–Ar), 74.2 (C-4), 67.0, 66.3 (C-5, CH_2OAr), 55.5 (OCH_3). MS (APCI$^+$): m/z 242.0 [M+NH_4]$^+$. IR (NaCl) 1787 (CO).

4.3. Standard procedure for the synthesis of isomeric carbamates 6a–d and 7a–d[28]

The appropriate amine (1.2 equiv) was added to a THF (3 ml) solution of glycerol carbonate **1** (0.118 g, 1 mmol) maintained at 0 °C. The reaction mixture was stirred at rt until total consumption of **1**. After concentration of the solution in vacuo, the residue was purified by flash column chromatography (eluent: PE/EA or pure EA).

4.3.1. 1-(2,3-Dihydroxypropyl)-N-decylcarbamate ***6a*** *and 2-(1,3-dihydroxypropyl)-N-decylcarbamate* ***7a***. A mixture of regioisomers **6a** and **7a** was isolated (after 72 h stirring; eluent: Hex/EA 3/2) in an 87% yield as an amorphous solid. ^{1}H NMR (300 MHz, DMSO-d_6) δ 7.11–7.01 (m, NH), 4.78–4.50 (m, H-2_{7a}, OH), 3.96–3.78 (m, H-1_{6a}), 3.62–3.30 (m, H-2_{6a}, CH_2OH), 2.93 (dd, 2H, J_{gem}=12.6, J_{vic}=6.3, CH_2NH), 1.38–1.34 (m, 2H, CH_2-decyl), 1.32–1.23 (m, 14H, CH_2-decyl), 0.85 (m, 3H, CH_3). ^{13}C NMR (75 MHz, DMSO-d_6) δ 156.3, 156.1 (CO), 75.2 (C-2_{7a}), 69.8 (C-1_{6a}), 65.4 (C-2_{6a}), 62.8 (C-3_{6a}), 60.0 (C-1_{7a}, C-3_{7a}), 40.2 (CH_2NH), 31.4, 29.4, 29.0, 28.7, 26.2, 22.1 (CH_2-decyl), 13.9 (CH_3). MS (APCI$^+$) m/z 276.6 [M+H]$^+$. IR (KBr) 3349 (OH), 2851, 2922, 2958 (N–H, CH), 1684 (CO), 1535 (NHCO), 1257 (C–O–C). Anal. Calcd for $C_{14}H_{29}NO_4$ (275.39): C, 61.06; H, 10.61; N, 5.09. Found: C, 61.81; H, 10.61; N, 5.25.

4.3.2. 1-(2,3-Dihydroxypropyl)-N-dodecylcarbamate ***6b*** *[133685-16-2] and 2-(1,3-dihydroxypropyl)-N-dodecylcarbamate* ***7b***. A mixture of regioisomers **6b** and **7b** was isolated (after 72 h stirring; eluent: Hex/EA 3/2) in 71% yield as an amorphous solid. ^{1}H NMR (300 MHz, DMSO-d_6) δ 7.10–7.01 (m, NH), 4.78–4.51 (m, H-2_{7b}, OH), 3.96–3.78 (m, H-1_{6a}), 3.63–3.30 (m, H-2_{6b}, CH_2OH), 2.93 (dd, 2H, J_{gem}=12.9, J_{vic}=6.6, CH_2NH), 1.38–1.31 (m, 2H, CH_2-dodecyl), 1.29–1.15 (m, 18H, CH_2-dodecyl), 0.85 (m, 3H, CH_3). ^{13}C NMR (75 MHz, DMSO-d_6) δ 156.3, 156.1 (CO), 75.2 (C-2_{7b}), 69.8 (C-1_{6b}), 65.4 (C-2_{6b}), 62.8 (C-3_{6b}), 60.0 (C-1_{7b}, C-3_{7b}), 40.2 (CH_2NH), 31.3, 29.4, 29.1, 29.0, 28.8, 28.7, 26.3, 22.1 (CH_2-dodecyl), 13.9 (CH_3). MS (APCI$^+$) m/z 304.5 [M+H]$^+$. IR (KBr) 3351 (OH), 2850, 2921, 2958 (N–H, CH), 1684 (CO), 1535 (NHCO). Anal. Calcd for $C_{16}H_{33}NO_4$ (303.44): C, 63.33; H, 10.96; N, 4.62. Found: C, 63.66; H, 11.29; N, 4.56.

4.3.3. 1-(2,3-Dihydroxypropyl)-N-allylcarbamate ***6c*** *[82771-98-0] and 2-(1,3-dihydroxypropyl)-N-allylcarbamate* ***7c***. A mixture of regioisomers **6c** and **7c** was isolated (after 5 days stirring; eluent: pure EA) in 88% yield as a colorless oil. ^{1}H NMR (300 MHz, DMSO-d_6) δ 7.29–7.23 (m, NH), 5.90–5.77 (m, 1H, =CH), 5.59–5.55 (m, 1H, NH′), 5.42–5.38 (m, 1H, H-1′), 5.23–5.12 (m, 4H, 2×CH_{2allyl}), 4.82–4.75 (m, 1H, H-1′), 4.20–4.10 (m, 2H, H-1), 3.92–3.55 (m, CH_2NH, H-2_{6c}, CH_2OH). ^{13}C NMR (75 MHz, DMSO-d_6) δ 156.4, 156.1 (CO), 135.7 (=*CH*), 114.9 (=CH_2), 75.5 (C-2_{7c}), 69.8 (C-1_{6c}), 65.8 (C-2_{6c}), 62.8 (C-3_{6c}), 60.1 (C-1_{7c}, C-3_{7c}), 43.4 (CH_2NH). MS (APCI$^+$) m/z 176.4

$[M+H]^+$. IR (NaCl) 3332 (OH), 2933 (N–H), 1700 (CO), 1539 (NHCO), 1255 (C–O–C).

4.3.4. 1-(2,3-Dihydroxypropyl)-N-benzylcarbamate ***6d*** *and 2-(1,3-dihydroxypropyl)-N-benzylcarbamate* ***7d***. A mixture of regioisomers **6d** and **7d** was isolated (after 5 days stirring; eluent: pure EA) in 99% yield as an amorphous solid. ^{1}H NMR (300 MHz, DMSO-d_6) δ 7.72–7.61 (m, NH), 7.34–7.22 (m, 5H, Ph), 4.84–4.61 (m, H-2_{7d}, OH), 4.18 (d, 2H, J_{vic}=6.3, PhCH_2NH), 4.02–3.83 (m, H-1_{6d}), 3.65–3.32 (m, H-2_{6d}, CH_2OH). ^{13}C NMR (75 MHz, DMSO-d_6) δ 156.7 (2^*CO), 139.9 (C_{IV}-Ar), 128.2, 127.0, 126.7 (*CH*–Ar), 75.6 (2_{7d}), 69.8 (C-1_{6d}), 65.8 (C-2_{6d}), 62.8 (C-3_{6d}), 60.1 (C-1_{7d}, C-3_{7d}), 43.7 (PhCH_2NH). MS (APCI$^+$) *m*/*z* 226.4 $[M+H]^+$. IR (KBr) 3310 (OH), 3086, 3065, 3032, 2939 (N–H, CH_{Ar}), 1685 (CO), 1556 (NHCO). Anal. Calcd for $C_{11}H_{15}NO_4$ (225.24): C, 58.66; H, 6.71; N, 6.22. Found: C, 59.05; H, 6.78; N, 6.34.

4.4. Standard procedure for the synthesis of carbamates 8a–g

The appropriate amine (1.2 equiv) was added to a THF (5 mL) solution of tosylate **2** (0.5 g, 1.836 mmol) maintained at 0 °C. The reaction mixture was stirred at rt until total consumption of **2**. After dilution with EA and water, the organic layer was washed with water and brine, then dried over $MgSO_4$. After filtration and concentration of the solution in vacuo, the residue was purified by flash column chromatography (eluents: Hex/EA, PE/EA or DCM/MeOH).

4.4.1. (2-Hydroxy-3-tosyloxypropyl)-N-decylcarbamate ***8a***. Compound **8a** was isolated (after 48 h stirring; eluent: Hex/EA 7/3) in 62% yield as a colorless oil. ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.79 (d, 2H, J_{vic}=8.1, H–Ar), 7.35 (d, 2H, J_{vic}=7.8, H–Ar), 4.83 (br s, 1H, NH), 4.20–4.00 (m, 5H, H-1, H-2, H-3), 3.13 (m, 2H, CH_2NH), 2.68 (br s, 1H, OH), 2.45 (s, 3H, ArCH_3), 1.49–1.44 (m, 2H, CH_2-decyl), 1.33–1.21 (m, 14H, CH_2-decyl), 0.87 (m, 3H, CH_3). ^{13}C NMR (75 MHz, $CDCl_3$) δ 145.1 (CO), 137.7, 132.4 (2^*C_{IV}–Ar), 129.9, 128.0 (CH–Ar), 69.9 (C-1), 68.7 (C-3), 65.4 (C-2), 41.2 (CH_2NH), 31.9, 29.8, 29.5, 29.3, 29.2, 26.7, 22.7 (CH_2-decyl), 21.7 (ArCH_3), 14.1 (CH_3). MS (APCI$^+$): *m*/*z* 430.4 $[M+H]^+$. IR (NaCl) 3383 (OH), 2925, 2855 (N–H, CH_{al}), 1705 (CO), 1177 (C–O). Anal. Calcd for $C_{21}H_{35}NO_6S$ (429.57): C, 58.72; H, 8.21; N, 3.26. Found: C, 58.50; H, 8.30; N, 3.61.

4.4.2. 1-(2-Hydroxy-3-tosyloxypropyl)-N-dodecylcarbamate ***8b***. Compound **8b** was isolated (after 24 h stirring; eluent: Hex/EA 7/3) in 54% yield as a colorless oil. ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.79 (d, 2H, J_{vic}=8.4, H–Ar), 7.35 (d, 2H, J_{vic}=8.1, H–Ar), 4.85 (br s, 1H, NH), 4.19–3.99 (m, 5H, H-1, H-2, H-3), 3.12 (m, 2H, CH_2NH), 2.81 (br s, 1H, OH), 2.45 (s, 3H, ArCH_3), 1.48–1.44 (m, 2H, CH_2-dodecyl), 1.32–1.24 (m, 18H, CH_2-dodecyl), 0.86 (m, 3H, CH_3). ^{13}C NMR (75 MHz, $CDCl_3$) δ 145.1 (CO), 138.4, 132.4 (2^*C_{IV}–Ar), 129.9, 128.0 (CH–Ar), 69.9 (C-1), 68.3 (C-3), 65.3 (C-2), 41.2 (CH_2NH), 31.9, 29.6, 29.5, 29.3, 29.2, 26.7, 22.7 (CH_2-decyl), 21.7 (ArCH_3), 14.1 (CH_3). MS (APCI$^+$): *m*/*z* 458.5 $[M+H]^+$. IR (NaCl) 3340 (OH), 2924, 2854, 1704 (CO), 1177 (C–O). Anal. Calcd for $C_{23}H_{39}NO_6S$ (457.63): C, 60.37; H, 8.59; N, 3.06. Found: C, 60.44; H, 8.74; N, 3.49.

4.4.3. 1-(2-Hydroxy-3-tosyloxypropyl)-N-allylcarbamate ***8c***. Compound **8c** was isolated (after 48 h stirring; eluent: Hex/EA 7/3) in 86% yield as a colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.79 (d, 2H, J_{vic}=6.3, H–Ar), 7.34 (d, 2H, J_{vic}=6.0, H–Ar), 5.85–5.75 (m, 1H, =CH), 5.19–5.11 (m, 2H, $=CH_2$), 5.04 (s, 1H, NH), 4.23–4.00 (m, 5H, H-1, H-2, H-3), 3.78–3.74 (m, 2H, CH_2NH), 3.41 (s, 1H, OH), 2.44 (s, 3H, ArCH_3). ^{13}C NMR (100 MHz, $CDCl_3$) δ 156.5 (CO), 145.1, 132.4 (2^*C_{IV}–Ar), 134.0 (=*CH*), 129.9, 128.0 (CH–Ar), 116.3 ($=CH_2$), 70.0 (C-1), 68.1 (C-3), 65.4 (C-2), 43.5 (CH_2NH), 21.6 (ArCH_3). MS (APCI$^+$): *m*/*z* 330.3 $[M+H]^+$. IR (NaCl) 3383 (OH), 3068, 2956, 2925, 1705 (C=O), 1175 (C–O). ESI-HRMS calcd for $C_{14}H_{19}NO_6SNa$: 352.0831. Found: 352.0827 $[M+Na]^+$.

4.4.4. 1-(2-Hydroxy-3-tosyloxypropyl)-N-benzylcarbamate ***8d***. Compound **8d** was isolated (after 5 days stirring; eluent: DCM/MeOH 98/2) in 71% yield as a colorless oil. ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.78 (d, 2H, J_{vic}=8.1, H–Ar), 7.35–7.24 (m, 7H, H–Ar), 5.25 (s, 1H, NH), 4.32 (d, 2H, J_{vic}=6.0, CH_2NH), 4.21–4.00 (m, 5H, H-1, H-2, H-3), 3.33 (s, 1H, OH), 2.43 (s, 3H, ArCH_3). ^{13}C NMR (75 MHz, $CDCl_3$) δ 156.7 (CO), 145.1, 137.9, 132.3 (3^*C_{IV}–Ar), 129.9, 128.7, 128.0, 127.6, 127.5 (*CH*–Ar), 70.0 (C-1), 68.2 (C-3), 65.5 (C-2), 45.1 (CH_2NH), 21.6 (ArCH_3). MS (APCI$^+$): *m*/*z* 380.4 $[M+H]^+$. IR (NaCl) 3407 (OH), 1709 (CO), 1175 (C–O). ESI-HRMS calcd for $C_{18}H_{21}NO_6S$: 379.1090. Found: 379.1087.

4.4.5. 1-(2-Hydroxy-3-tosyloxypropyl)-N-morpholinylcarbamate ***8e***. Compound **8e** was isolated (after 4 days stirring; eluent: Hex/EA 7/3) in 68% yield as a colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.80 (d, 2H, J_{vic}=8.2, H–Ar), 7.36 (d, 2H, J_{vic}=8.2, H–Ar), 4.27–4.17 (m, 2H, H-1), 4.06–4.01 (m, 3H, H-2, H-3), 3.64 (br s, 4H, CH_2O-morph), 3.44 (br s, 4H, CH_2N-morph), 2.53 (br s, 1H, OH), 2.45 (s, 3H, ArCH_3). ^{13}C NMR (100 MHz, $CDCl_3$) δ 155.7 (CO), 145.2, 132.4 (2^*C_{IV}–Ar), 130.0, 128.0 (CH–Ar), 69.8 (C-1), 68.4 (C-3), 66.5, 66.4 (CH_2O), 66.2 (C-2), 44.3, 44.1 (CH_2N), 21.7 (ArCH_3). MS (IS): *m*/*z* 360.5 $[M+H]^+$, 382.0 $[M+Na]^+$. IR (neat) 3411 (OH), 2966, 1684 (CO), 1431 (CH). ESI-HRMS calcd for $C_{15}H_{22}NO_7S$: 360.1117. Found: 360.1113 $[M+H]^+$.

4.4.6. 1-(2-Hydroxy-3-tosyloxypropyl)-N-piperidinylcarbamate ***8f***. Compound **8f** was isolated (after 4 days stirring; eluent: Hex/EA 6/4) in 58% yield as a colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.80 (d, 2H, J_{vic}=8.4, H–Ar), 7.36 (d, 2H, J_{vic}=8.4, H–Ar), 4.25–4.13 (m, 2H, H-1), 4.05–4.00 (m, 3H, H-2, H-3), 3.37 (br s, 4H, CH_2N), 2.45 (s, 3H, ArCH_3), 1.67 (br s, 1H, OH), 1.58 (m, 2H, CH_2), 1.51 (br s, 4H, CH_2). ^{13}C NMR (100 MHz, $CDCl_3$) δ 156.0 (CO), 145.0, 132.5 (2^*C_{IV}–Ar), 129.9, 128.0 (CH–Ar), 69.7 (C-1), 68.6 (C-3), 66.0 (C-2), 45.0 (CH_2N), 25.7, 25.4, 24.2 (CH_2-pip), 21.6 (ArCH_3). MS (IS): *m*/*z* 358.5 $[M+H]^+$, 380.0 $[M+Na]^+$. IR (neat) 3398 (OH), 2938, 1674 (CO), 1435 (CH_{al}). ESI-HRMS calcd for $C_{16}H_{24}NO_6S$: 358.1324. Found: 358.1321 $[M+H]^+$.

4.4.7. 1-(2-Hydroxy-3-tosyloxypropyl)-N-(4-benzyl)piperazinylcarbamate ***8g***. Compound **8g** was isolated (after 48 h stirring; eluent: Hex/EA 4/6) in 53% yield as a colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.78 (d, 2H, J_{vic}=8.4, H–Ar), 7.34–7.26 (m, 7H, H–Ar), 4.20–4.12 (m, 2H, H-1), 4.05–4.00 (m, 3H, H-2, H-3), 3.78 (br s, 1H, OH), 3.54 (s, 2H, CH_2Ph), 3.44 (br s, 4H, CH_2N), 2.45–2.40 (s, 7H, CH_2N, ArCH_3). ^{13}C NMR (100 MHz, $CDCl_3$) δ 155.5 (CO), 145.0, 132.4 (2^*C_{IV}–Ar), 129.9, 129.1, 128.9, 128.3, 127.9, 127.3, 125.8 (CH–Ar), 69.9 (C-1), 68.0 (C-3), 65.9 (C-2), 62.7 (CH_2Ph), 52.4, 43.7, 43.6 (CH_2N), 21.6 (ArCH_3). MS (IS): *m*/*z* 449.0 $[M+H]^+$. IR (neat) 3399 (OH), 2920 (=N–), 1682 (CO). ESI-HRMS calcd for $C_{22}H_{29}N_2O_6S$: 449.1746. Found: 449.1754 $[M+H]^+$.

4.5. Standard procedure for the synthesis of 10a–g[29]

To a solution of tosylate **8** (1 mmol) in methanol (2 mL) cooled at 0 °C was added a freshly prepared 0.5 M solution of sodium methoxide in methanol (2 mL, 1 equiv). The mixture was stirred for 2 h while warming up to rt. After dilution with ethyl acetate and water, the organic layer was washed with water and brine, then dried over $MgSO_4$. After filtration and concentration of the solution in vacuo the residue was purified by flash column chromatography (eluent: Hex/EA or PE/EA).

4.5.1. Glycidyl N-decylcarbamate ***10a***. Compound **10a** was isolated (eluent: Hex/EA 4/1) in 97% yield as a white solid, mp 45–46 °C (CH_2Cl_2). ^{1}H NMR (300 MHz, $CDCl_3$) δ 4.79 (br s, 1H, NH), 4.42 (dd, 1H, J_{gem}=12.3, J_{vic}=3.0, H-1a), 3.86 (dd, 1H, J_{vic}=6.3, H-1b), 3.22–

3.12 (m, 3H, H-2, CH_2NH), 2.83 (t, 1H, J_{gem}=J_{vic}=4.8, H-3a), 2.64 (dd, 1H, J_{vic}=2.4, H-3b), 1.50–1.46 (m, 2H, CH_2-decyl), 1.25–1.20 (m, 14H, CH_2-decyl), 0.87 (m, 3H, CH_3). ^{13}C NMR (75 MHz, $CDCl_3$) δ 156.0 (CO), 65.4 (C-1), 49.8 (C-2), 44.6 (C-3), 41.1 (CH_2NH), 35.4 (CH_2), 31.8, 29.9, 29.5, 29.2, 26.7, 22.6 (CH_2-decyl), 14.1 (CH_3). MS (APCI$^+$): m/z 258.6 [M+H]$^+$. IR (KBr) 2955, 2917, 2848 (CH), 1686 (CO), 1565 (NHCO). Anal. Calcd for $C_{14}H_{27}NO_3$ (257.37): C, 65.33; H, 10.57; N, 5.44. Found: C, 65.05; H, 10.58; N, 5.42.

4.5.2. Glycidyl N-dodecylcarbamate ***10b****.* Compound **10b** was isolated (eluent: Hex/EA 4/1) in 83% yield as a white solid, mp 50–52 °C (CH_2Cl_2). ^{1}H NMR (300 MHz, $CDCl_3$) δ 4.79 (br s, 1H, NH), 4.42 (dd, 1H, J_{gem}=12.3, J_{vic}=3.0, H-1a), 3.86 (dd, 1H, J_{vic}=6.6, H-1b), 3.22–3.12 (m, 3H, H-2, CH_2NH), 2.83 (t, 1H, J_{gem}=J_{vic}=4.8, H-3a), 2.63 (dd, 1H, J_{vic}=2.7, H-3b), 1.50–1.45 (m, 2H, CH_2-dodecyl), 1.32–1.20 (m, 18H, CH_2-dodecyl), 0.87 (m, 3H, CH_3). ^{13}C NMR (75 MHz, $CDCl_3$) δ 156.0 (CO), 65.2 (C-1), 49.8 (C-2), 44.6 (C-3), 41.1 (CH_2NH), 31.9, 29.9, 29.6, 29.5, 29.3, 26.7, 22.7 (CH_2-dodecyl), 14.1 (CH_3). MS (APCI$^+$): m/z 286.6 [M+H]$^+$. IR (KBr) 2955, 2917, 2848 (CH_{al}), 1686 (CO), 1565 (NHCO). Anal. Calcd for $C_{16}H_{31}NO_3$ (285.43): C, 67.33; H, 10.95; N, 4.91. Found: C, 67.75; H, 11.16; N, 5.21.

4.5.3. Glycidyl N-allylcarbamate ***10c****.* Compound **10c** was isolated (eluent: Hex/EA 3/2) in 64% yield as a colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 5.89–5.80 (m, 1H, =CH), 5.23–5.11 (m, 2H, =CH_2), 5.03 (br s, 1H, NH), 4.45 (dd, 1H, J_{gem}=12.4, J_{vic}=2.8, H-1a), 3.86 (dd, 1H, J_{vic}=6.4, H-1b), 3.81 (t, 2H, J_{vic}=5.6, CH_2NH), 3.21 (m, 1H, H-2), 2.84 (t, 1H, J_{gem}=J_{vic}=4.8, H-3a), 2.64 (dd, 1H, J_{vic}=2.4, H-3b). ^{13}C NMR (100 MHz, $CDCl_3$) δ 155.9 (CO), 134.2 (=*CH*), 116.0 (=CH_2), 65.4 (C-1), 49.7 (C-2), 44.5 (C-3), 43.4 (CH_2NH). MS (APCI$^+$): m/z 158.3 [M+H]$^+$. IR (NaCl) 3068, 3006, 2929 (C), 1711 (CO), 1531 (NHCO), 1245 (C–O–C). Anal. Calcd for $C_7H_{11}NO_3$ (157.17): C, 53.49; H, 7.05; N, 8.91. Found: C, 52.89; H, 7.15; N, 8.90.

4.5.4. Glycidyl N-benzylcarbamate ***10d*** *[170956-42-0]*[22b]*.* Compound **10d** was isolated (eluent: Hex/EA 7/3) in 80% yield as a colorless oil. ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.38–7.26 (m, 5H, H–Ar), 5.13 (br s, 1H, NH), 4.48 (dd, 1H, J_{gem}=12.3, J_{vic}=3.0, H-1a), 4.39 (d, 2H, J_{vic}=6.0, CH_2NH), 3.92 (dd, 1H, J_{vic}=6.3, H-1b), 3.22 (m, 1H, H-2), 2.85 (t, 1H, J_{gem}=J_{vic}=4.8, H-3a), 2.65 (dd, 1H, J_{vic}=2.4, H-3b). ^{13}C NMR (75 MHz, $CDCl_3$) δ 156.0 (CO), 138.2 (C_{IV}–Ar), 128.6, 127.5 (*CH*–Ar), 65.5 (C-1), 49.7 (C-2), 45.1 (CH_2NH), 44.6 (C-3). MS (APCI$^+$): m/z 208.4 [M+H]$^+$. IR (NaCl) 3063, 3031, 2943 (CH_{Ar}), 1706 (CO), 1534 (NHCO), 1256 (C–O–C). Anal. Calcd for $C_{11}H_{13}NO_3$ (207.23): C, 63.76; H, 6.32; N, 6.76. Found: C, 63.62; H, 6.44; N, 6.57.

4.5.5. Glycidyl N-morpholinylcarbamate ***10e*** *[117382-54-4].* Compound **10e** was isolated (eluent: Hex/EA 2/3) in 53% yield as a colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 4.47 (dd, 1H, J_{gem}=12.0, J_{vic}=2.8,, H-1a), 3.91 (dd, 1H, J_{vic}=6.4, H-1b), 3.65 (m, 4H, CH_2O-morph), 3.49 (m, 4H, CH_2N-morph), 3.23 (m, 1H, H-2), 2.85 (t, 1H, J_{gem}=J_{vic}=5.0, H-3a), 2.63 (dd, 1H, J_{vic}=2.8, H-3b). ^{13}C NMR (100 MHz, $CDCl_3$) δ 154.9 (CO), 66.5 (CH_2O), 66.2 (C-1), 49.7 (C-2), 44.5 (C-3), 44.1, 44.0 (CH_2N). MS (IS): m/z 188.0 [M+H]$^+$, 210.0 [M+Na]$^+$. IR (neat) 2972, 2923, 2867 (CH), 1694 (CO), 1534 (NHCO), 1256 (C–O–C). ESI-HRMS calcd for $C_8H_{13}NO_4Na$: 210.0742. Found: 210.0748 [M+Na]$^+$.

4.5.6. Glycidyl N-piperidinylcarbamate ***10f*** *[96426-72-1].* Compound **10f** was isolated (eluent: Hex/EA 2/3) in 61% yield as a colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 4.43 (dd, 1H, J_{gem}=12.4, J_{vic}=3.2, H-1a), 3.91 (dd, 1H, J_{vic}=6.4, H-1b), 3.43 (m, 4H, CH_2N), 3.23 (m, 1H, H-2), 2.84 (t, 1H, J_{gem}=J_{vic}=4.8, H-3a), 2.63 (dd, 1H, J_{vic}=2.8, H-3b), 1.62–1.54 (m, 6H, CH_2-pip). ^{13}C NMR (100 MHz, $CDCl_3$) δ 155.0 (CO), 65.7 (C-1), 49.9 (C-2), 44.9 (CH_2N), 44.6 (C-3), 25.6, 25.5, 24.3 (CH_2-pip). MS (IS) m/z 186.0 [M+H]$^+$, 208.0 [M+Na]$^+$. IR (neat) 2935, 2856 (CH_{al}), 1693 (CO). ESI-HRMS calcd for $C_9H_{15}NO_3Na$: 208.0950. Found: 208.0949 [M+Na]$^+$.

4.5.7. Glycidyl N-(4-benzyl)piperazinyl carbamate ***10g****.* Compound **10g** was isolated (eluent: Hex/EA 2/3) in 69% yield as a colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.31–7.20 (m, 5H, H–Ar), 4.40 (dd, 1H, J_{gem}=12.0, J_{vic}=2.8, H-1a), 3.86 (dd, 1H, J_{vic}=6.4, H-1b), 3.46 (m, 6H, CH_2N, CH_2Ph), 3.18 (m, 1H, H-2), 2.79 (t, 1H, J_{gem}=J_{vic}=4.8, H-3a), 2.59 (dd, 1H, J_{vic}=2.8, H-3b), 2.38 (br s, 4H, CH_2N). ^{13}C NMR (100 MHz, $CDCl_3$) δ 154.7 (CO), 137.6 (C_{IV}–Ar), 129.0, 128.2, 127.1 (*CH*–Ar), 65.8 (C-1), 62.9 (CH_2Ph), 52.5, 43.7 (CH_2N), 49.7 (C-2), 44.4 (C-3). MS (IS): m/z 277.0 [M+H]$^+$, 299.0 [M+Na]$^+$. IR (neat) 2942, 2809 (CH), 1697 (CO). ESI-HRMS calcd for $C_{15}H_{21}N_2O_3$: 277.1552. Found: 277.1539 [M+H]$^+$.

4.6. Standard procedure for the synthesis of 11a–d

To a solution of tosylated GC **2** (0.272 g, 1 mmol) in DMF (2 mL) cooled at 0 °C, were added potassium carbonate (0.166 g, 1.2 equiv) and the appropriate thiol (1.2 equiv). The reaction mixture was heated at 80 °C for 4 h. After dilution with ethyl acetate and water, the organic layer was washed with water, brine, then dried over $MgSO_4$. After filtration and concentration of the solution in vacuo, the residue was purified by flash column chromatography (eluent: PE/EA).

4.6.1. 4-(n-Hexylsulfanyl)methyl-1,3-dioxolan-2-one ***11a****.* Compound **11a** was isolated (eluent: Hex/EA 9/1) in 84% yield as a colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 4.83 (m, 1H, H-4), 4.57 (t, 1H, J_{gem}=J_{vic}=8.4, H-5a), 4.29 (dd, 1H, J_{vic}=6.4, H-5b), 2.92 (dd, 1H, J_{gem}=14.0, J_{vic}=4.8, S*CH*a), 2.79 (dd, 1H, J_{vic}=8.0, S*CH*b), 2.62–2.58 (m, 2H, SCH_2-hexyl), 1.62–1.55 (m, 2H), 1.42–1.23 (m, 6H, CH_2-hexyl), 0.89 (t, 3H, J_{vic}=8.6, CH_3). ^{13}C NMR (100 MHz, $CDCl_3$) δ 154.5 (CO), 75.5 (C-4), 68.6 (C-5), 34.6 (SCH_2), 33.0 (SCH_2-hexyl), 31.3, 29.5, 28.3, 22.4 (CH_2-hexyl), 13.9 (CH_3). MS (IS): m/z 219.0 [M+H]$^+$, 241.0 [M+Na]$^+$. IR (NaCl) 3019 (CH), 1806 (CO). ESI-HRMS calcd for $C_{10}H_{18}O_3SNa$: 241.0874. Found: 241.0883 [M+Na]$^+$.

4.6.2. 4-(Benzylsulfanyl)methyl-1,3-dioxolan-2-one ***11b****.* Compound **11b** was isolated (eluent: Hex/EA 9/1) in 38% yield as a colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.37–7.27 (m, 5H, H–Ar), 4.67 (m, 1H, H-4), 4.44 (t, 1H, J_{gem}=J_{vic}=8.4, H-5a), 4.16 (dd, 1H, J_{vic}=6.6, H-1b), 3.81 and 3.77 (2d, AB system, 2H, J_{gem}=13.7, PhCH_2), 2.79 (dd, 1H, J_{gem}=14.3, J_{vic}=4.7, S*CH*a), 2.68 (dd, 1H, J_{vic}=7.3, S*CH*b). ^{13}C NMR (100 MHz, $CDCl_3$) δ 154.5 (CO), 137.3 (C_{IV}–Ar), 128.9, 128.8, 127.6 (*CH*–Ar), 75.4 (C-4), 68.5 (C-5), 36.8 (PhCH_2), 33.4 (SCH_2). MS (IS): m/z 247.4 [M+Na]$^+$. IR (NaCl) 1793 (CO), 1167, 1064 (CH). ESI-HRMS calcd for $C_{11}H_{12}O_3SNa$: 247.0405. Found: 247.0395 [M+Na]$^+$.

4.6.3. 4-(Cyclopentylsulfanyl)methyl-1,3-dioxolan-2-one ***11c****.* Compound **11c** was isolated (eluent: Hex/EA 9/1) in 68% yield as a colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 4.84 (m, 1H, H-4), 4.56 (t, 1H, J_{gem}=J_{vic}=8.8, H-5a), 4.28 (dd, 1H, J_{vic}=6.8, H-5b), 3.20–3.13 (m, 1H, *CHS*), 2.96 (dd, 1H, J_{gem}=14.0, J_{vic}=4.8, S*CH*a), 2.79 (dd, 1H, J_{vic}=8.0, S*CH*b), 2.04–1.97 (m, 2H), 1.80–1.68 (m, 2H), 1.64–1.43 (m, 4H, CH_2-cyclopentyl), 1.64–1.43 (m, 4H, CH_2). ^{13}C NMR (100 MHz, $CDCl_3$) δ 154.6 (CO), 75.4 (C-4), 68.7 (C-5), 44.5 (*CHS*), 34.4 (SCH_2), 33.99 (CH_2), 33.80 (CH_2), 24.7, 24.6 (CH_2-cyclopentyl). MS (IS): m/z 203.0 [M+H]$^+$, 225.0 [M+Na]$^+$. IR (neat) 2954 (CH_{al}), 1790 (CO).

4.6.4. 4-(6-Hydroxyhexylsulfanyl)methyl-1,3-dioxolan-2-one ***11d****.* Compound **11d** was isolated (eluent: PE/EA 3/2) in 39% yield as a colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 4.84 (m, 1H, H-4), 4.54 (t, 1H, J_{gem}=J_{vic}=8.4, H-5a), 4.25 (dd, 1H, J_{vic}=6.4, H-5b), 3.58 (t, 2H,

J_{vic}=6.8, CH_2OH), 2.87 (dd, 1H, J_{gem}=14.0, J_{vic}=4.8, SC*H*a), 2.76 (dd, 1H, J_{vic}=7.2, SC*H*b), 2.57 (dt, 2H, J=7.2, 1.6, SCH_2-hexyl), 1.96 (br s, 1H, OH), 1.60–1.48 (m, 4H), 1.42–1.29 (m, 4H, CH_2-hexyl). ^{13}C NMR (100 MHz, $CDCl_3$) δ 154.6 (CO), 75.5 (C-4), 68.5 (C-5), 62.5 (CH_2O), 34.5 (SCH_2), 32.8 (SCH_2-hexyl), 32.3, 29.3, 28.2, 25.2 (CH_2-hexyl). MS (IS): m/z 235.5 $[M+H]^+$, 257.0 $[M+Na]^+$. IR (NaCl) 3684 (OH), 1805 (CO). ESI-HRMS calcd for $C_{10}H_{18}O_4SNa$: 257.0824. Found: 257.0828 $[M+Na]^+$.

4.7. Standard procedure for the synthesis of 12a–c

To a solution of tosylated GC **2** (0.272 g, 1 mmol) in DMF (2 mL) cooled at 0 °C were added potassium carbonate (0.304 g, 2.2 equiv) and the appropriate thiol (2.2 equiv). The reaction mixture was heated at 80 °C for 5 h. After dilution with ethyl acetate and water, the organic layer was washed with water, brine, then dried over $MgSO_4$. After filtration and concentration of the solution in vacuo, the residue was purified by flash column chromatography (eluent: PE/EA).

4.7.1. 1,3-Bis(hexylsulfanyl)propan-2-ol ***12a*** *[32338-87-7]*[29]. Compound **12a** was isolated (eluent: PE/EA 19/1→4/1) in 26% yield as a colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 3.82–3.72 (m, 1H, H-2), 2.93 (br s, 1H, OH), 2.76 (dd, 2H, J_{gem}=13.5, J_{vic}=4. 8, H-1a, H-3a), 2.63 (dd, 2H, J_{vic}=7.5, H-1b, H-3b), 2.55 (t, 4H, J_{vic}=8.8, SCH_2), 1.62–1.50 (m, 4H), 1.41–1.20 (m, 12H, CH_2-hexyl), 0.86 (t, 6H, J_{vic}=6.8, CH_3). ^{13}C NMR (100 MHz, $CDCl_3$) δ 68.8 (C-2), 38.3 (C-1, C-3), 32.6 (SCH_2-hexyl), 31.3, 29.6, 28.4, 22.5 (CH_2-hexyl), 14.0 (CH_3). MS (IS): m/z 315 $[M+Na]^+$. IR (NaCl) 3229 (OH), 2954, 2925, 2856 (C_{al}).

4.7.2. 1,3-Bis(benzylsulfanyl)propan-2-ol ***12b*** *[1631-59-0]*[30]. Compound **12b** was isolated (eluent: PE/EA 9/1) in 39% yield as a colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.33–7.25 (m, 10H, H–Ar), 3.70–3.65 (m, 5H, H-2, CH_2Ph), 2.72 (d, 1H, OH), 2.59 (dd, 2H, J_{gem}=13.8, J_{vic}=4.7, H-1a, H-3a), 2.48 (dd, 2H, J_{vic}=7.5, H-1b, H-3b). ^{13}C NMR (100 MHz, $CDCl_3$) δ 138.0 (C_{IV}–Ar), 128.9 (*CH*–Ar_{ortho}), 128.5 (*CH*–Ar_{meta}), 127.1 (*CH*–Ar_{para}), 68.6 (C-2), 37.3 (C-1), 36.5 (C-3). MS ($APCI^+$): m/z 327.3 $[M+Na]^+$. IR (NaCl) 3440 (OH).

4.7.3. 1,3-Bis(cyclopentylsulfanyl)propan-2-ol ***12c***. After 5 h stirring at 70 °C, compound **12c** was isolated (eluent: PE/EA 9/1) in 50% yield as a colorless oil (33% **11c** was also produced). ^{1}H NMR (400 MHz, $CDCl_3$) δ 3.80–3.87 (m, 1H, H-2), 3.10–3.17 (m, 2H, *CHS*), 2.93 (d, 1H, J_{vic}=3.2, OH), 2.80 (dd, 2H, J_{gem}=13.2, J_{vic}=4.8, H-1a, H-3a), 2.66 (dd, 2H, J_{vic}=7.5, H-1b, H-3b), 2.05–1.97 (m, 4H), 1.80–1.69 (m, 4H), 1.63–1.48 (m, 8H, CH_2-cyclopentyl). ^{13}C NMR (100 MHz, $CDCl_3$) δ 68.9 (C-2), 44.3 (*CHS*), 38.2 (C-1, C-3), 33.9 (4×CH_2), 24.7 (CH_2-cyclopentyl). MS (IS): m/z 277.0 $[M+NH_3]$, 299.0 $[M+K]^+$. IR (neat) 3432 (OH), 2952 (CH, CH_2), 1206 (C–O).

4.7.4. 4-(2,3,4,6-Tetra-O-acetyl-β-D-glucopyranosylthiomethyl)-1,3-dioxolan-2-one ***14***. To a solution of **2** (0.250 g, 0.92 mmol) in DMF (2 mL) cooled at 0 °C were added potassium carbonate (0.152 g, 1.1 mmol) and 1-thio-β-D-glucose tetraacetate (0.4 g, 1.1 mmol). After stirring 4 h at rt, the reaction mixture was diluted with ethyl acetate and water. The organic layer was washed with water, brine, then dried over $MgSO_4$. After filtration and concentration of the solution in vacuo, the residue was purified by flash chromatography (eluent: PE/EA 3/2) to afford 0.354 g (83% yield) of the diastereoisomeric mixture **14**. An analytical sample of the faster moving diastereoisomer was obtained $[\alpha]_D$ −21 (c 1, $CHCl_3$). ^{1}H NMR (400 MHz, $CDCl_3$) δ 5.24 (t, 1H, J_{vic}=9.7, H-3′), 5.08 (t, 1H, J_{vic}=10.0, H-4′), 5.03 (t, 1H, J_{vic}=10.0, H-2′), 4.95–4.86 (m, 1H, H-4), 4.55 (t, 1H, J_{gem}=J_{vic}=8.4, H-5a), 4.54 (d, 1H, J_{vic}=10.0, H-1′), 4.38 (dd, 1H, J_{vic}=6.4, H-5b), 4.25 (dd, 1H, $J_{6'a,6'b}$=12.5, $J_{6'a,5'}$=4.8, H-6′a), 4.18 (dd, 1H, $J_{6'b,5'}$=2.3 Hz, H-6′b), 3.76 (ddd, 1H, H-5′), 3.25 (dd, 1H, J_{gem}=14.4, J_{vic}=5.0, SC*H*a), 2.79 (dd, 1H, J_{vic}=7.8, SC*H*b), 2.10, 2.07, 2.04, 2.02 (4s, 12H, CH_3). ^{13}C NMR (100 MHz, $CDCl_3$) δ 170.7, 170.3, 169.6, 169.4 (CH_3CO), 152.8 (OCOO), 82.4 (C-1′), 76.5 (C-5′), 75.6 (C-4), 73.5 (C-3′), 69.4 (C-2′), 68.5 (C-5), 68.1 (C-4′), 61.8 (C-6′), 31.6 (CH_2S), 20.8, 20.7, 20.6 (CH_3). ESI-HRMS calcd for $C_{18}H_{24}O_{12}NaS$: 487.0886. Found: 487.0886.

4.8. Standard procedure for the synthesis of 15–18

To a solution of tosylated GC **2** (0.5 g, 1.836 mmol) in the appropriate solvent (4 mL), 2 equiv MX salt (M=Na, K; X=I, N_3, SCN, SAc) was added and the reaction mixture was heated. After dilution with ethyl acetate and water, the organic layer was washed with water, brine, then dried over $MgSO_4$. After filtration and concentration of the solution in vacuo, the residue was purified by flash column chromatography (eluent: PE/EA).

4.8.1. 4-(Iodomethyl)-1,3-dioxolan-2-one ***15*** *[78947-99-6]*[11b,31]. NaI was reacted 3 h with **2** in refluxing acetone. Compound **15** was isolated (eluent: PE/EA 1/1) in 89% yield as a white solid, mp 67–69 °C (CH_2Cl_2). ^{1}H NMR (250 MHz, $CDCl_3$) δ 4.80–4.50 (m, 1H, H-4), 4.58 (t, 1H, J_{gem}=J_{vic}=8.8, H-5a), 4.19 (dd, 1H, J_{vic}=6.2, H-5b), 3.40 (dd, 1H, J_{gem}=10.7, J_{vic}=4.5, IC*H*a), 3.34 (dd, 1H, J_{vic}=7.2, H-IC*H*b). ^{13}C NMR (62.5 MHz, $CDCl_3$) δ 154.3 (CO), 74.7 (C-4), 69.8 (C-5), 4.4 (CH_2I). MS (IS): m/z 246.0 $[M+NH_4]^+$, 251.0 $[M+Na]^+$. IR (KBr) 1775 (CO).

4.8.2. 4-(Azidomethyl)-1,3-dioxolan-2-one ***16*** *[949896-03-1]*[21]. NaN_3 was reacted 18 h with **2** in DMF at 70 °C. Compound **16** was isolated (without chromatography) in 84% yield as a colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 4.88–4.82 (m, 1H, H-2), 4.53 (t, 1H, J_{gem}=J_{vic}=8.6, H-5a), 4.31 (dd, 1H, J_{vic}=6.0, H-5b), 3.72 (dd, 1H, J_{gem}=13.6, J_{vic}=4.0, NC*H*a), 3.55 (dd, 1H, J_{vic}=4.4, NC*H*b). ^{13}C NMR (100 MHz, $CDCl_3$) δ 154.2 (CO), 74.2 (C-4), 66.3 (C-5), 52.0 (CH_2N). MS (IS): m/z 161.0 $[M+NH_4]^+$. IR (NaCl) 2927 (CH), 2103 (N_3), 1782 (CO).

4.8.3. 4-(Thiocyanatomethyl)-1,3-dioxolan-2-one ***17***. KSCN was reacted 24 h with **2** in DMSO at 70 °C. Compound **17** was isolated (eluent: PE/EA 7/3) in 47% yield as a white solid, mp 58–60 °C (CH_2Cl_2). ^{1}H NMR (400 MHz, $CDCl_3$) δ 5.09–5.03 (m, 1H, H-2), 4.70 (dd, 1H, J_{gem}=9.2, J_{vic}=8.4 Hz, H-5a), 4.36 (dd, 1H, J_{vic}=6.0, H-5b), 3.33 (dd, 1H, J_{gem}=14.0, J_{vic}=6.0, SC*H*a), 3.29 (dd, 1H, J_{vic}=6.0, SC*H*b). ^{13}C NMR (100 MHz, $CDCl_3$) δ 153.5 (CO), 110.4 (CN), 74.2 (C-4), 67.7 (C-5), 35.7 (CH_2S). MS (IS): m/z 192.0 $[M+Na]^+$. IR (NaCl) 2994, 2940 (CH), 2159 (CN), 1773 (CO). ESI-HRMS calcd for $C_5H_5NO_3NaS$: 181.9888. Found: 181.9882.

4.8.4. 4-(Acetylsulfanylmethyl)-1,3-dioxolan-2-one ***18*** *[97900-31-7]*[32]. CH_3COSK was reacted 6 h with **2** in DMF at 70 °C. Compound **18** was isolated (eluent: PE/EA 7/3) in 62% yield as a colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 4.86 (m, 1H, H-4), 4.52 (dd, 1H, J_{gem}=8.8, J_{vic}=8.0, H-5a), 4.12 (dd, 1H, J_{vic}=6.4, H-5b), 3.29 (dd, 1H, J_{gem}=14.4, J_{vic}=5.2, SC*H*a), 3.23 (dd, 1H, J_{vic}=6.0, SC*H*b), 2.40 (s, 3H, CH_3). ^{13}C NMR (100 MHz, $CDCl_3$) δ 194.3 (*SCO*), 154.2 (OCOO), 74.6 (C-4), 68.1 (C-5), 31.4 (CH_2S), 30.5 (CH_3). MS (IS): m/z 199.0 $[M+Na]^+$. IR (neat) 2926 (CH), 1791 (CO), 1691 (CO). ESI-HRMS calcd for $C_6H_8O_4NaS$: 199.0041. Found: 199.0050.

4.8.5. 4-(Mercaptomethyl)-1,3-dioxolan-2-one ***19a*** *and related disulfide* ***19b***. A solution of iodide **15** (0.564 g, 2.47 mmol) and thiourea (0.414 g, 5.44 mmol) in acetone (15 mL) was refluxed for 2 h. The residue left after evaporation was taken in water (20 mL) containing $Na_2S_2O_5$ (4.70 g, 24.7 mmol) and the resulting suspension was refluxed for 10 min. After cooling and extraction with

ethyl acetate (3×50 mL), the organic phase was washed with brine (2×30 mL), dried over $MgSO_4$, and evaporated to give thiol **19a** in 71% yield. ^{1}H NMR (250 MHz, $CDCl_3$) δ 4.88–4.77 (m, 1H, H-4), 4.60 (ft, 1H, J_{gem}=J_{vic}=8.5, H-5a), 4.23 (dd, 1H, J_{vic}=6.3, H-5b), 3.43 (dd, 1H, J_{gem}=10.5, J_{vic}=4.1, SC*H*a), 3.32 (ft, 1H, J_{vic}=8.5, SC*H*b), 1.26 (t, 1H, SH).

Upon standing at rt, **19a** quantitatively oxidized into its disulfide **19b**. ^{1}H NMR (400 MHz, $CDCl_3$) δ 4.87–4.56 (dddd, 1H, $J_{4,5a}$=8.0 Hz, $J_{4,5b}$=6.3 Hz, $J_{4,6a}$=4.1 Hz, $J_{4,6b}$=8.3 Hz, H-4), 4.60 (ft, 1H, J_{gem}=J_{vic}=8.8, H-5a), 4.22 (dd, 1H, J_{vic}=6.3,H-5b), 3.43 (dd, 1H, J_{gem}=10.5, J_{vic}=4.1, SC*H*a), 3.30 (dd, 1H, J_{vic}=8.4, SC*H*b). ^{13}C NMR (100 MHz, $CDCl_3$) δ 154.2 (C-2), 73.4 (C-4), 69.9 (C-5), 3.7 (*C*H_2S). MS (IS): *m*/*z* 289 $[M+Na]^+$. ESI-HRMS calcd for $C_8H_{10}O_6S_2$: 265.9919. Found: 265.9917.

4.8.6. 3-Allyl-4-hydroxymethyl-2-oxazolidinone ***20*** *[205680-42-8]*[27c]. To a suspension of sodium hydride (60% dispersion in mineral oil) (0.111 g, 2.77 mmol) in anhydrous THF (5 mL) cooled at −70 °C was added a solution of carbamate **10c** (0.397 g, 2.526 mmol) in anhydrous THF (5 mL). The mixture was stirred for 2 h while warming up to rt. After dilution with dichloromethane and water, the organic layer was washed with water, brine, then dried over $MgSO_4$. After filtration and concentration of the solution in vacuo, the residue was purified by flash column chromatography (eluent: PE/EA 3/2 → 2/3) to give compound **20** in 42% yield as a colorless oil.

4.8.7. 4-Acetoxymethyl-3-allyl-2-oxazolidinone ***21***. To a suspension of *t*-BuOK (0.260 g, 2.317 mmol) in anhydrous THF (4 mL) cooled at −70 °C was added a solution of carbamate **10c** (0.331 g, 2.106 mmol) in anhydrous THF (3 mL). The mixture was stirred for 4 h while warming up to rt, then acetic anhydride (0.398 ml, 4.212 mmol) was added and the mixture stirred at rt for an additional 18 h. After dilution with ethyl acetate and water, the organic layer was washed with water, brine, then dried over $MgSO_4$. After filtration and concentration of the solution in vacuo, the residue was purified by flash column chromatography (eluent: PE/EA 7/3) to give compound **21** in 50% yield as a colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 5.82–5.71 (m, 1H, =CH), 5.29–5.23 (m, 2H, =CH_2), 4.38 (dt, 1H, J_{gem}=J_{vic}=8.6, J=0.4, H-5a), 4.24 (dd, 1H, J_{gem}=12.0, J_{vic}=4.4, *CHa*OAc), 4.19–4.08 (m, 3H, H-5b, *CHb*OAc, *CHa*N), 3.99 (m, 1H, H-4), 3.70–3.64 (m, 1H, *CHb*N), 2.10 (s, 3H, CH_3). ^{13}C NMR (100 MHz, $CDCl_3$) δ 170.5 (CH_3CO), 157.8 (N*CO*), 131.9 (=*CH*), 119.0 (=CH_2), 64.5 (C-5), 62.2 (*C*H_2OAc), 53.4 (C-4), 45.2 (*C*H_2N), 20.6 (CH_3). MS (IS): *m*/*z* 200.0 $[M+H]^+$, 222.0 $[M+Na]^+$. IR (neat) 2921 (CH), 1733 (CO). ESI-HRMS calcd for $C_9H_{14}NO_4$: 200.0923. Found: 200.0919 $[M+H]^+$.

4.8.8. 1-(3-Acetylsulfanyl-2-hydroxypropyl)-N-allylcarbamate ***22a***. AcSK (0.151 g, 1.319 mmol) was dissolved in anhydrous DMF (2 ml) and cooled to −70 °C. Then, compound **8c** (0.184 g, 0.55 mmol) in anhydrous DMF (2 ml) was added. The reaction mixture was allowed to warm to rt and stirred for 6 h. The reaction mixture was diluted with ethyl acetate and water. After extraction (two times), the organic layers were collected, washed thoroughly with water, brine and then dried over $MgSO_4$. After filtration the solvent was removed by evaporation in vacuo. The resulting residue was purified by flash chromatography (eluent: PE/EA 7/3) to give (0.062 g, 0.27 mmol) compound **22a** (47%) as a colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 5.85–5.77 (m, 1H, =CH), 5.20–5.10 (m, 3H, NH, =CH_2), 4.15 (dd, 1H, J_{gem}=11.4, J_{vic}=3.6, H-1a), 4.08 (dd, 1H, J_{vic}=6.0, H-1b), 4.00–3.85 (m, 1H, H-2), 3.79 (m, 2H, *CH*$_2$NH), 3.23 (br s, 1H, OH), 3.09 (dd, 1H, J_{gem}=14.0, J_{vic}=5.2, H-3a), 2.99 (dd, 1H, J_{vic}=6.8, H-3b), 2.34 (s, 3H, CH_3). ^{13}C NMR (100 MHz, $CDCl_3$) δ 196.0 (S*CO*), 156.5 (N*CO*), 134.1 (=*CH*), 116.2 (=CH_2), 69.4 (C-2), 67.5 (C-1), 43.5 (*C*H_2N), 32.4 (*C*H_2S), 30.5 (CH_3). MS (IS) *m*/*z* 256.0 $[M+Na]^+$. IR (neat) 3338 (OH, NH), 2926 (C_{Al}), 1689 (CO). ESI-HRMS calcd for $C_9H_{15}NO_4NaS$: 256.0619. Found: 256.0623.

4.8.9. 1-(3-Azido-2-hydroxypropyl)-N-allylcarbamate ***22b***. A solution of compound **8c** (0.4 g, 1.214 mmol) and sodium azide (0.158 g, 2.43 mmol) in anhydrous DMF (3 mL) was heated at 70 °C for 24 h. After cooling, the mixture was diluted with ethyl acetate and water and the aqueous phase was extracted three times with ethyl acetate. The organic phase was washed with water, brine, then dried over $MgSO_4$. After filtration and concentration of the solution in vacuo, the residue was purified by flash column chromatography (eluent: PE/EA 7/3) to give compound **22b** in 56% yield as a colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 5.82–5.71 (m, 1H, =CH), 5.29–5.23 (m, 2H, =CH_2), 5.07 (br s, 1H, NH), 4.21 (dd, 1H, J_{gem}=12.0, J_{vic}=3.6, H-1a), 4.15 (dd, 1H, J_{vic}=6.0, H-1b), 3.99 (m, 1H, H-2), 3.82 (m, 2H, *CH*$_2$NH), 3.40 (dd, 1H, J_{gem}=12.4, J_{vic}=4.8, H-3a), 3.37 (dd, 1H, J_{vic}=6.0, H-3b), 3.10 (br s, 1H, OH). ^{13}C NMR (100 MHz, $CDCl_3$) δ 156.6 (N*CO*), 134.0 (=*CH*), 116.4 (=CH_2), 69.6 (C-2), 66.6 (C-1), 53.3 (C-3), 43.6 (*C*H_2N). MS (IS): *m*/*z* 201.0 $[M+H]^+$, 223.0 $[M+Na]^+$. IR (neat) 3334 (OH, NH), 2925 (CH), 2099 (N_3), 1695 (C=O). ESI-HRMS calcd for $C_7H_{12}N_4O_3Na$: 223.0807. Found: 223.0809.

4.8.10. 1-(3-Hexylsulfanyl-2-hydroxypropyl)-N-allylcarbamate ***22c*** *and 1-(2-hexylsulfanyl-3-hydroxypropyl)-allylcarbamate* ***23***. To a suspension of sodium hydride (60% dispersion in mineral oil) (0.018 g, 0.459 mmol) and TBAB (0.012 g, 0.038 mmol) in anhydrous THF (2 mL) cooled at −70 °C hexanethiol (0.065 ml, 0.459 mmol) was added and stirring was continued for 15 min. Compound **8c** (0.126 g, 0.383 mmol) dissolved in anhydrous THF (2 mL) was added and the reaction mixture was stirred for 3 h more while warming up to rt. After dilution with ethyl acetate and water, the organic layer was washed with water, brine, then dried over $MgSO_4$. After filtration and concentration of the solution in vacuo, the residue was purified by flash column chromatography (eluent: PE/EA 4/1) to give compound **22c** in 55% yield as a colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 5.89–5.79 (m, 1H, =CH), 5.22–5.12 (m, 2H, =CH_2), 4.88 (br s, 1H, NH), 4.25 (dd, 1H, J_{gem}=11.2, J_{vic}=3.6, H-1a), 4.11 (dd, 1H, J_{vic}=6.0, H-1b), 3.95–3.87 (m, 1H, H-2), 3.80 (m, 2H, *CH*$_2$NH), 3.02 (m, 1H, OH), 2.71 (m, 1H, H-3a), 2.59–2.52 (m, 3H, H-3b, SCH_2), 1.62–1.54 (m, 2H), 1.41–1.24 (m, 6H, *CH*$_2$-hexyl), 0.88 (t, 3H, J_{vic}=6.8, CH_3). ^{13}C NMR (100 MHz, $CDCl_3$) δ 156.5 (N*CO*), 134.2 (=*CH*), 116.3 (=CH_2), 68.6 (C-2), 67.7 (C-1), 43.5 (*C*H_2N), 35.8 (C-3), 32.5 (SCH_2-hexyl), 31.4, 29.6, 28.5, 22.5 (*CH*$_2$-hexyl), 14.0 (CH_3). MS (IS): *m*/*z* 276.0 $[M+H]^+$, 298.0 $[M+Na]^+$. IR (neat) 3327 (OH, NH), 2925, 2856 (C_{Al}), 1697 (CO). ESI-HRMS calcd for $C_{13}H_{25}NO_3NaS$: 298.1453. Found: 298.1466.

Compound **23** was isolated in 15% yield as a colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 5.86–5.78 (m, 1H, =CH), 5.21–5.10 (m, 2H, =CH_2), 5.05 (br s, 1H, NH), 4.87–4.82 (m, 1H, H-2), 3.84–3.74 (m, 4H, H-1a, H-1b, *CH*$_2$NH), 2.72 (d, 2H, J=6.8 Hz, H-3a, H-3b), 2.67 (m, 1H, OH), 2.55 (t, 2H, J_{vic}=7.2, SCH_2), 1.56 (m, 2H), 1.40–1.22 (m, 6H, *CH*$_2$-hexyl), 0.86 (t, 3H, J_{vic}=6.8, CH_3). ^{13}C NMR (100 MHz, $CDCl_3$) δ 156.1 (N*CO*), 134.2 (=*CH*), 116.2 (=CH_2), 74.8 (C-2), 63.5 (C-1), 43.4 (*C*H_2N), 32.7 (SCH_2-hexyl), 32.3 (C-3), 31.3, 29.5, 28.4, 22.5 (*CH*$_2$-hexyl), 14.0 (CH_3). MS (IS): *m*/*z* 276.0 $[M+H]^+$, 298.0 $[M+Na]^+$. IR (neat) 3325 (OH, NH), 2925, 2856 (CH), 1696 (CO). ESI-HRMS calcd for $C_{13}H_{25}NO_3NaS$: 298.1453. Found: 298.1458.

4.8.11. 1-(2-Hydroxy-3-iodopropyl)-N-allylcarbamate ***24***. A solution of compound **8c** (0.669 g, 2.031 mmol) and sodium iodide (0.609 g, 4.062 mmol) in anhydrous acetone (5 mL) was heated under reflux for 18 h. After cooling, the mixture was diluted with ethyl acetate and water and the aqueous phase was extracted three times with ethyl acetate. The organic phase was washed with water, brine, then dried over $MgSO_4$. After filtration and concentration of the solution in vacuo, the residue was purified by flash column

chromatography (eluent: PE/EA 3/2) to give compound **24** in 51% yield as a colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 5.87–5.77 (m, 1H, =CH), 5.21–5.12 (m, 3H, $=CH_2$, NH), 4.22 (m, 2H, H-1a, H-1b), 3.84–3.78 (m, 3H, H-2, CH_2NH), 3.37 (br s, 1H, OH), 3.30–3.20 (m, 2H, H-3a, H-3b). ^{13}C NMR (100 MHz, $CDCl_3$) δ 156.5 (*NCO*), 134.0 (=*CH*), 116.5 ($=CH_2$), 69.8 (C-2), 67.6 (C-1), 43.5 (CH_2N), 8.3 (C-3). MS (IS): *m*/*z* 286.0 $[M+H]^+$, 308.0 $[M+Na]^+$. IR (neat) 3327 (OH, NH), 2953 (C_{Al}), 2099 (N_3), 1693 (CO). ESI-HRMS calcd for $C_7H_{12}NO_3INa$: 307.9760. Found: 307.9751.

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