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Bifunctional silanol-based HBD catalysts for CO_2 fixation into cyclic carbonates†

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First examples of unprecedented silanol-based bifunctional HBD catalysts $[({}^tBuO)_2\{(N(CH_2CH_2)_3N)\text{-}CH_2CH_2O\}Si(OH)]^+I^-$ and (*Rac*)- and (*R*)-$[({}^tBuO)_2\{(N(CH_2CH_2)_3N)CH_2(Et)CHO)\}Si(OH)]^+I^-$ with tetraalkylammonium units directly incorporated into their structures were prepared from tailor-made silanols. These bifunctional silanols were used together with other mixed alkoxysilanols of general formula $({}^tBuO)_2(RO)SiOH$ (R = Me, Et, ^{i}Pr, $-CH_2CH_2I$ and $-CH(Et)CH_2I$) in a systematic study of their catalytic properties for the preparation of cyclic carbonates using a library of epoxides and industrial-grade carbon dioxide. With 4 mol% catalyst loading in the absence of a solvent and an external nucleophile source, the bifunctional catalysts showed good to very good conversion of epoxides to the corresponding cyclic carbonates within 10 h at 70 °C and 75 psi of CO_2. Furthermore, the developed synthetic approach used in the preparation of these mixed alkyl silanols *via* the hydrolysis of the corresponding acetoxysilyl alkoxides $({}^tBuO)_2(RO)Si(OAc)$ (R = organic moiety) allowed a straightforward route to the modification of the steric bulk around the silicon atom and the introduction of functional groups for further derivatization.

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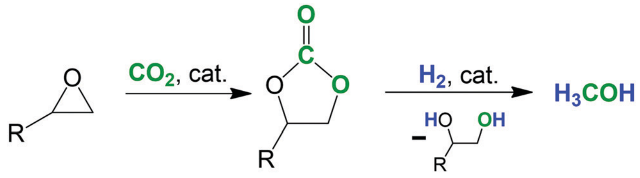
Introduction

Carbon dioxide is an ideal C1 building block in organic synthesis because it is abundant, inexpensive and nontoxic. In this sense, the development of chemical transformations involving CO_2 as a starting material has attracted attention in green and sustainable chemistry.[1–5] Particularly, the synthesis of cyclic carbonates through cycloaddition of CO_2 with epoxides is considered as one of the most promising processes due to its 100% atom utilization ratio.[6,7] Furthermore, cyclic carbonates find high utility as polar aprotic solvents, electrolytes in lithium batteries, starting materials for different polymeric materials, and as chemical precursors.[8–12] Moreover, the presence of five-membered cyclic carbonate fragments in the structure of some natural products has been described.[13] Additionally, cyclic carbonates can be catalytically reduced, producing methanol and 1,2-diols,[14,15] where the latter can be converted back to the epoxide (Scheme 1).[16]

Therefore, the development of new and inexpensive catalytic systems capable of selectively producing these cyclic carbonates under mild reaction conditions without the formation of polymers attracts wide attention both in academia and industry.[7,17,18] A dynamic field in this area is the use of metal-free catalysts since they are usually cheaper, readily available, less toxic than metal-containing species and do not tend to initiate the polymerization of the cyclic carbonates.[17] A variety of hydrogen bond donors (HBD) have been identified as metal-free catalysts to facilitate the synthesis of cyclic carbonates, as they are capable of activating the epoxide moiety *via* the formation of a hydrogen bond with the oxygen atom as an acceptor.[19–22] However, these HBDs need to be accompanied by suitable nucleophiles such as quaternary ammonium salts acting as cocatalysts, resulting in two-component catalytic systems. These systems allow the synthesis of cyclic carbonates at low temperature and low pressure due to the synergistic effect of hydrogen bonding and nucleophilic anions, making the ring-opening of the epoxide more efficient.[6,23] In this regard, HBDs such as phenols,[24] alcohols,[25–27] carboxylic[28] or boronic acids[29] and ionic liquids[30] have been used to facilitate the synthesis of cyclic carbonates usually in combination with



Scheme 1 Synthesis of cyclic carbonates from epoxides and the catalytic reduction of the carbonate to methanol.

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tetraalkylammonium salts. Therefore, one way to improve the HBD catalytic systems for the synthesis of carbonates is the specific design of new bifunctional catalysts that would contain in their molecule the required nucleophile and a few of such systems have been reported recently, but they usually need high pressures and/or temperatures.[28,31–35]

Silanols are compounds with at least one Si–OH group and are an emerging class of HBD catalysts. In this regard, a bis(1-naphthyl)silanediol/TBAI system was used for the cycloaddition of CO_2 with different epoxides under mild reaction conditions,[36] and our research group evaluated the catalytic activity of the more acidic but less stable alkoxysilanetriols and alkoxybis(silanetriols) in the synthesis of styrene carbonate.[37] A quantitative conversion was achieved after 15 h at 60 °C and 1 atm of CO_2, using tetrabutylammonium iodide (TBAI) as the nucleophile source. In both cases, the use of a cocatalyst was necessary to facilitate the opening of the epoxide. Despite their good catalytic activity, more extensive use of silanols is hampered by difficulties during their synthesis and purification and especially the propensity of the silanols to self-condense, which increases with the number of OH groups attached to the same silicon atom.[36,37]

We envisioned the use of trialkoxysilanols with a general formula $(^t\mathrm{BuO})_2(\mathrm{RO})\mathrm{SiOH}$, where the SiO_4 unit increases the acidity of the Si–OH group when compared to the analogue with Si–C bonds, while the two bulky ^{t}Bu groups help to increase the stability of the silanols against hydrolysis and condensation. The variation of the third alkoxy group allows fine-tuning of the steric properties and incorporation of further functional groups into the molecule. However, the synthesis of such mixed-alkyl trialkoxysilanols is a synthetic challenge due to poor control over the degree of substitutions with two different alkoxy groups. Herein we report a straightforward synthesis of such mixed-alkyl $(^t\mathrm{BuO})_2(\mathrm{RO})\mathrm{Si(OH)}$ silanols from silicon tetraacetate and simple alcohols. Furthermore, silanols with $-\mathrm{O}-\mathrm{CH_2CH_2I}$ and $-\mathrm{O}-\mathrm{CH(Et)CH_2I}$ groups were used in the synthesis of the first examples of ionic silanol-based HBD catalysts $[(^t\mathrm{BuO})_2\{(\mathrm{N(CH_2CH_2)_3N)CH_2CH_2O}\}\mathrm{Si(OH)}]^+\mathrm{I}^-$ and (*Rac*)- and (*R*)-$[(^t\mathrm{BuO})_2\{(\mathrm{N(CH_2CH_2)_3N)CH_2(Et)CHO}\}\mathrm{Si(OH)}]^+\mathrm{I}^-$ (Fig. 1) that contain in the same molecule the acidic Si–OH HBD group and a quaternary ammonium ion with an I^- anion. Finally, the tailor-made silanols were evaluated as HBD catalysts in the synthesis of cyclic carbonates using a library of epoxides and industrial-grade carbon dioxide.

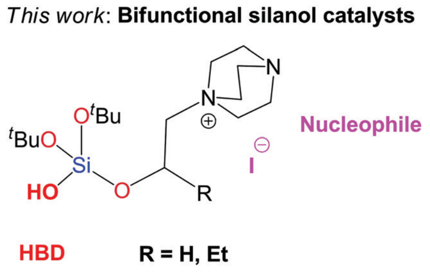
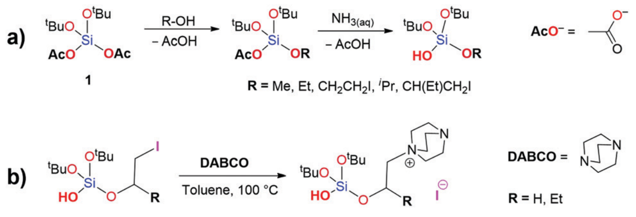


Fig. 1 Bifunctional silanol-based HBD catalysts proposed in this work.

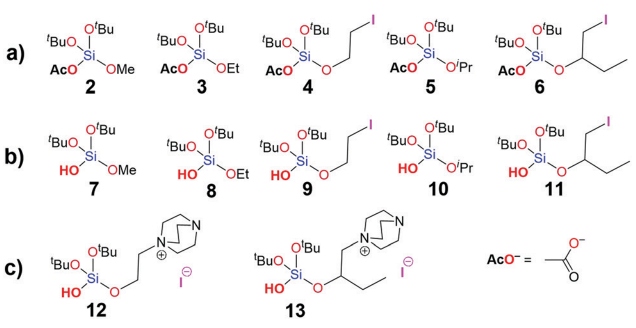
Results and discussion

Synthesis and characterization

The traditional synthetic methods for silanols starting from $SiCl_4$[38–42] or alkoxysilanes[43,44] present significant disadvantages as especially the use of chlorosilanes requires the use of large quantities of dry solvents and bases such as aliphatic amines,[45] anilines,[46] or pyridine[38] to capture the HCl produced during the reaction and the subsequent hydrolysis of the trialkoxychlorosilane to the final silanol. Furthermore, any trace of acid or base in the final product catalyzes the condensation of the Si–OH groups and this tendency increases with the number of Si–OH groups attached to the same silicon atom due to their higher acidity.[47] In addition, silanols with at least one alkoxy group with a lower steric bulk are oils further hampering their purification.[42] In this regard, we have recently reported a green method for the synthesis of alkoxysilanetriols from triacetoxysilylalkoxides[37] where the only byproduct is acetic acid or acetamide that helps stabilize the target silanols. Therefore, to obtain the silanols $(^t\mathrm{BuO})_2(\mathrm{RO})\mathrm{Si(OH)}$ we have designed a two-step synthesis from $(^t\mathrm{BuO})_2\mathrm{Si(OAc)}_2$ (**1**) (obtained from $\mathrm{Si(OAc)}_4$ and 2 equivalents of ^{t}BuOH)[48] and the corresponding alcohol (methanol, ethanol, iodoethanol, isopropanol or 1-iodo-2-butanol) yielded the monoacetoxysilylalkoxides $(^t\mathrm{BuO})_2(\mathrm{RO})\mathrm{Si(OAc)}$ (**2**, R = Me; **3**, R = Et; **4**, R = CH_2CH_2I; **5**, R = ^{i}Pr; **6**, R = $CH(Et)CH_2I$) with increasing steric bulk around the silicon atom (Schemes 2 and 3). As anticipated, the higher volume of the alcohol increases the difficulty in substituting one of the acetate groups. However, it is possible to obtain compounds **2–6** in a pure form in nearly quantitative yields varying the concentration of the alcohol and reaction times without any purification. Stirring of



Scheme 2 General method for the preparation of (a) monoacetoxysilylalkoxides and silanols, (b) silanol-based bifunctional HBD catalysts.



Scheme 3 Prepared (a) monoacetoxysilylalkoxides **2–6**; (b) the corresponding silanols **7–11** and (c) silanol-based bifunctional HBD catalysts **12** and **13**.

compounds **2–6** for 1 to 6 hours in an aqueous ammonia solution at ambient temperature (see the Experimental section) yielded the corresponding monosilanols **7–11**.

The hydrolysis proceeds *via* a nucleophilic attack of ammonia on the C═O group of the acetate substituent as evidenced by the formation of acetamide. Again, higher steric bulk of the R group requires longer reaction times and a higher concentration of the ammonia solution to achieve complete conversion. Under these conditions, no evidence of condensation of the silanols or hydrolysis of the alkoxide groups was observed. It is noteworthy that both the acetoxysilanes and the silanols, even those with small R substituents, are air- and moisture-stable facilitating their handling and storage. Furthermore, the exceptional stability of these silanols was demonstrated by using compounds **9** and **11** in reactions with 1,4-diazabicyclo[2.2.2]octane (DABCO) in boiling toluene to synthesize the first examples of unprecedented silanol-based bifunctional HBD catalysts $[({}^t\mathrm{BuO})_2\{(\mathrm{N}(\mathrm{CH_2CH_2})_3\mathrm{N})\text{-}\mathrm{CH_2CH_2O}\}\mathrm{Si(OH)}]^+\mathrm{I}^-$ (**12**) and $[({}^t\mathrm{BuO})_2\{(\mathrm{N}(\mathrm{CH_2CH_2})_3\mathrm{N})\mathrm{CH_2(Et)}\text{-}\mathrm{CHO}\}\mathrm{Si(OH)}]^+\mathrm{I}^-$ (**13**), respectively (Schemes 2 and 3). Compounds **11** and **13** were prepared both as racemic mixtures and as pure *R* enantiomers that are labeled here as (*Rac*)- and (*R*)-, respectively.

All compounds were characterized by ^{29}Si, ^{13}C, and ^{1}H NMR and IR spectroscopy, elemental analysis, and mass spectrometry. Additionally, the molecular structures of the ionic silanols **12** and **13** were determined by single crystal X-ray diffraction studies. The bands associated with the C═O stretching vibration of the acetate group in the $({}^t\mathrm{BuO})_2(\mathrm{RO})\mathrm{Si(OAc)}$ compounds are shifted to lower wavenumbers ($\tilde{\nu}$ 1736–1742 cm^{-1}) when compared with those for $\mathrm{Si(OAc)_4}$ ($\tilde{\nu}$ 1760 cm^{-1}) or $({}^t\mathrm{BuO})_2\mathrm{Si(OAc)_2}$ ($\tilde{\nu}$ 1744 cm^{-1}). These bands are absent in silanols **7–11** that contain broad bands at $\tilde{\nu}$ 3384–3403 cm^{-1} corresponding to the OH groups. The complete conversion of the acetates into the silanols has also been corroborated by ^{1}H NMR spectra of silanols **7–11** that are devoid of the signals for the acetate group but contain a broad signal for the hydrogen of the OH moiety. Furthermore, ^{1}H NMR spectra of **12** and **13** contain also the signals corresponding to the monoalkylated DABCO fragment. The IR spectra of **12**, (*Rac*)-**13** and (*R*)-**13** contain the broad bands ($\tilde{\nu}$ 3275–3300 cm^{-1}) of the OH group, that are shifted to lower wavenumbers compared to those of precursors **9** ($\tilde{\nu}$ 3396 cm^{-1}), (*Rac*)-**11** ($\tilde{\nu}$ 3398 cm^{-1}) or (*R*)-**11** ($\tilde{\nu}$ 3403 cm^{-1}).

Description of crystal structures

The molecular structures of the ionic silanols **12**, (*Rac*)-**13** and (*R*)-**13** were determined by single crystal X-ray diffraction studies. Single crystals were obtained from a saturated THF/acetonitrile solution (**12**, (*Rac*)-**13**) and a THF/toluene ((*R*)-**13**) solution at −30 °C. Compound **12** crystallizes in the monoclinic space group $P2_1/c$, while compound **13** ((*Rac*)- and (*R*)-) was solved in the monoclinic $P2_1$ space group (Fig. 2 and Table S2 in the ESI†). The molecular structures confirm the incorporation of the DABCO moiety into the molecule and the formation of the ionic species. The main feature of these compounds is the presence of an O–H···I hydrogen bond with distances of 2.62(4) Å (**12**), 2.74(2) ((*Rac*)-**13**) and 2.58(2) ((*R*)-**13**) Å, respectively, that are shorter than the sum of the van der Waals radii of *H* and *I* ($\sum r_{\mathrm{vdw}}$ (*I*,*H*) 3.16 Å) and explain the rather large shift in the frequency of the stretching vibration for the OH group in the IR spectra (*vide supra*).[49] In all structures, the SiO$_4$ unit has a distorted tetrahedral geometry with angles ranging from 101.6(8) to 114.0(4)°. The $\mathrm{Si{-}O^tBu}$ (1.598(5)–1.618(6) Å), Si–OR (1.625(5)–1.647(6) Å) and Si–O(H) (1.614(6)–1.628(7) Å) bond lengths are only slightly influenced by the different alkyl substituents. Selected bond lengths and angles for compounds **12**, (*Rac*)-**13** and (*R*)-**13** are listed in Table 1.

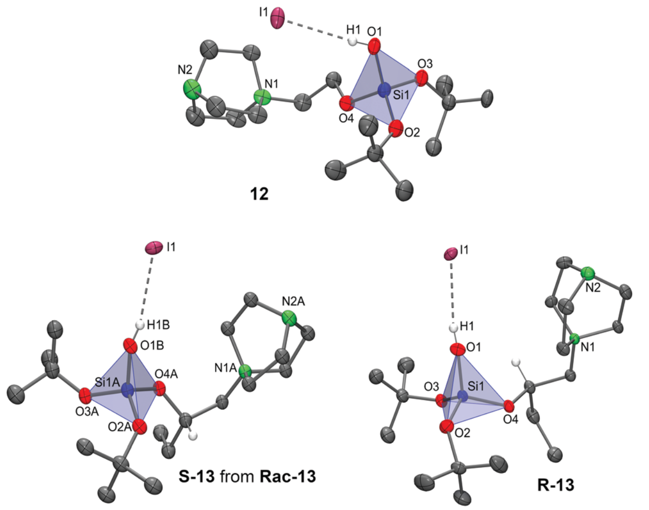


Fig. 2 Molecular structures of compounds **12**, (*Rac*)-**13** and (*R*)-**13**, with thermal ellipsoids set at the 50% probability level. Carbon-bound hydrogen atoms (except in the chiral carbon of **13**) were eliminated for the sake of clarity.

Table 1 Selected bond distances (Å) and angles (°) for compounds **12**, (*Rac*)-**13** and (*R*)-**13**

	12	(*Rac*)-13	(*R*)-13
Si–OH	1.628(7)	1.615(4)	1.620(3)
$\mathrm{Si{-}O^tBu}$	1.598(5)–1.618(6)	1.593(5)–1.611(4)	1.609(3)–1.611(3)
Si–OR	1.625(5)	1.645(4)	1.637(3)
O···I	3.404(8)	3.392(4)	3.403(3)
OH···I	2.62(4)	2.67(3)	2.584(19)
O–C (range)	1.419(8)–1.464(9)	1.424(6)–1.440(7)	1.432(4)–1.443(3)
$\mathrm{N{-}C_{exo}}$	1.518(8)	1.507(6)	1.513(4)
O–Si–O (range)	103.9(4)–109.3(4)	103.5(2)–116.1(3)	103.4(1)–115.6(2)
Si–O–H	125(6)	119(3)	125(3)
O–H···I	0.841(11)	0.828(14)	0.840(14)
C–O–Si (range)	123.4(6)–134.9(5)	122.8(3)– 136.6(4)	122.7(2)–134.4(2)
$\mathrm{C{-}N{-}C_{exo}}$	108.8(6)–111.1(5)	106.8(4)–113.1(4)	106.5(3)–112.7(3)

Catalytic studies

Initial screening. The bifunctional HBD catalysts **12** and **13**, together with silanols **7–11** and $({}^t\mathrm{BuO})_3\mathrm{SiOH}$, were evaluated as catalysts in the cycloaddition of CO$_2$ with styrene oxide (SO) to produce styrene carbonate (SC) (Fig. 3). Tetrabutylammonium iodide (TBAI) was used as a cocatalyst in the case of silanols **7–11**, while ionic silanols **12** and **13** were used without any additional iodide source. The single crystal analysis of **12** and **13** revealed a strong interaction between the silanol group and the iodide anion, suggesting that higher temperature will be necessary to increase the competitivity of the epoxides with the

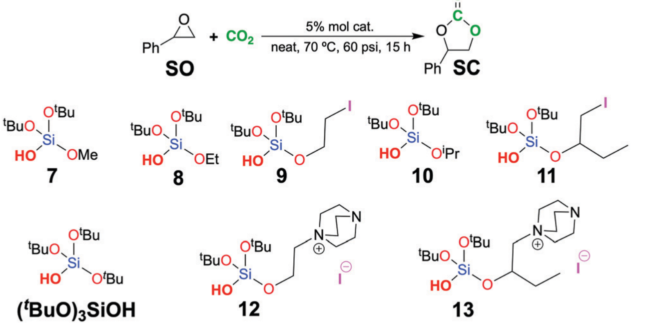


Fig. 3 Silanols, including the bifunctional HBD catalysts **12** and **13**, used in the cycloaddition of CO_2 with styrene oxide.

Table 2 Hydrogen-bond donor catalyst screening

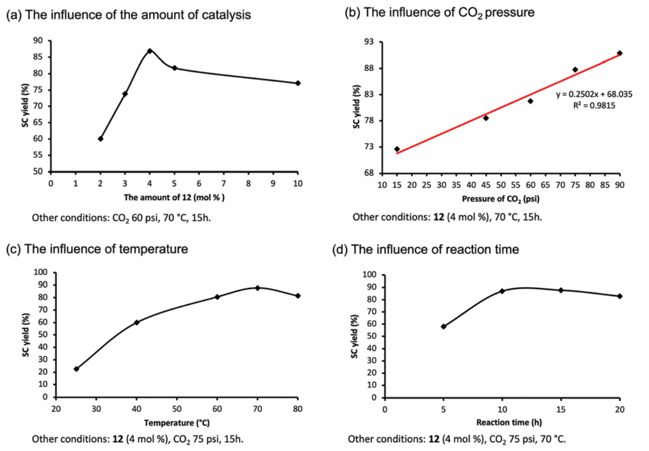
Entry	Catalyst	Catalyst (mol%)	TBAI (mol%)	Yield
1	**7**	5	5	77
2	**8**	5	5	60
3	**9**	5	5	81
4	**10**	5	5	63
5	(*Rac*)-**11**	5	5	86
6	(*R*)-**11**	5	5	85
7	(^{t}BuO)$_3$SiOH	5	5	70
8	**12**	5	—	82
9	(*Rac*)-**13**	5	—	75
10	(*R*)-**13**	5	—	72
11		—	5	38

iodide anions for the coordination to the Si–OH group. Therefore, the reaction conditions for the initial screening were set to 70 °C, 60 psi CO_2, 5 mol% catalyst loading, and 15 hour reaction time.

Under these conditions, a synergistic effect between the ammonium salt and the silanol is observed, as the reaction does not proceed in the absence of TBAI, while the absence of silanol leads to only 38% conversion (Table 2). On the other hand, monosilanols **7**, **8** and **10** (**7**, R = Me; **8**, R = Et; **10**, R = ^{i}Pr) present moderate catalytic activity (60–77%) similar to the bulkier monosilanol (^{t}BuO)$_3$SiOH (70%), while compounds **9**, (*Rac*)-**11** and (*R*)-**11** that contain a covalently bound iodine atom show conversions of 81–86%. Finally, the use of the functionalized silanols **12**, (*Rac*)-**13** and (*R*)-**13** (based on **9** and **11**) led under the same conditions to conversions of 72–82% even in the absence of TBAI (Table 2).

Optimization of the reaction parameters

Based on the initial screening, optimization of the reaction conditions for the preparation of styrene carbonate was undertaken. The bifunctional HBD catalyst **12** was used to evaluate its potential because it showed one of the highest conversions under the screening conditions. Fig. 4 shows the effect of the amount of catalyst, CO_2 pressure, reaction temperature, and reaction time on the SC yield, while the different reaction conditions for this optimization, including the final optimized reaction parameters are tabulated in Table 3. Increasing the amount of **12** from 2 to 4 mol% led to a significant increase of the SC formed (60 to 87%). However, a further increase of the catalyst loading to 5 and 10 mol% led to lower SC conversions (82 and 77%, respectively; Fig. 4a). A nearly linear dependence (R^2 = 0.9815) was observed between the CO_2 pressure and the yield of SC due to the increased interaction of CO_2 with the epoxide and the catalyst (Fig. 4b). Increasing temperature led to a higher yield, reaching a maximum at 70 °C (Fig. 4c). However, a further increase in temperature caused a decrease in the yield, possibly due to side reactions.[50] The influence of reaction time on the yield was also evaluated (Fig. 4d), indicating that a reaction time of 10 h was necessary for the maximum conversion of styrene oxide under the selected conditions. Longer reaction time resulted in a decrease in the yield. Therefore, the optimized reaction conditions for the reaction are 70 °C, 75 psi, 4 mol% of **12**, and 10 h.


(a) The influence of the amount of catalysis

(b) The influence of CO_2 pressure

(c) The influence of temperature

(d) The influence of reaction time

Other conditions: CO_2 60 psi, 70 °C, 15h.

Other conditions: **12** (4 mol %), 70 °C, 15h.

Other conditions: **12** (4 mol %), CO_2 75 psi, 15h.

Other conditions: **12** (4 mol %), CO_2 75 psi, 70 °C.

Fig. 4 The effects of different parameters on the yield of SC catalyzed by **12**.

Cycloaddition of CO_2 with various epoxides

To study the general applicability of the neutral and ionic bifunctional silanol catalysts, the cycloaddition reactions of CO_2 with a broad range of different epoxides were investigated, using silanols **9**, **11–13** as catalysts (Fig. 5 and Table 4). Epoxides with electron-withdrawing and electron-donating substituents can be converted to the respective carbonates in good to very good yields at 70 °C, 75 psi within 10 h, using neutral silanols **9** and **11** (with TBAI as cocatalyst) or in the case of the bifunctional catalysts **12** and **13**, even in the absence of an external nucleophile source. The very good conversions of 1,2-epoxy-3-phenoxypropane can be explained by the electron-withdrawing substituent, which facilitates the nucleophilic attack of the iodine during the ring opening of the epoxide. Cyclohexene oxide shows none to a very low conversion to the corresponding cyclic carbonate, due to its high steric hindrance.[30,31]

Furthermore, to confirm that the activity is related to the combination of silanol and the iodide nucleophile, a control experiment using only 1,4-diazabicyclo[2.2.2]octane was carried out using the optimized conditions (4% DABCO loading, 70 °C, 75 psi, 10 h). However, DABCO was found to be inactive in the synthesis of styrene carbonate (<1% conversion) and even epichlorohydrin (highly reactive epoxide with an electron-withdrawing substituent) was converted to the corresponding carbonate only from 8%. Therefore, both the acidic Si–OH HBD and the quaternary ammonium ion with I^- anions are necessary for the catalytic activity.

Table 3 All conditions used in the optimization of the reaction conditions for the preparation of styrene carbonate. Numbers in bold gave the best results

Optimized condition	Catalyst loading (mol%)	Temperature (°C)	Pressure of CO_2 (psi)	Time (h)
Initial screening	5	70	60	15
Catalyst loading	2, 3, **4**, 5, 10	70	60	15
CO_2 pressure	4	70	15, 45, 60, **75**, 90	15
Temperature	4	25, 40, 60, **70**, 80	75	15
Time	4	70	75	5, **10**, 15, 20
Best conditions	**4**	**70**	**75**	**10**

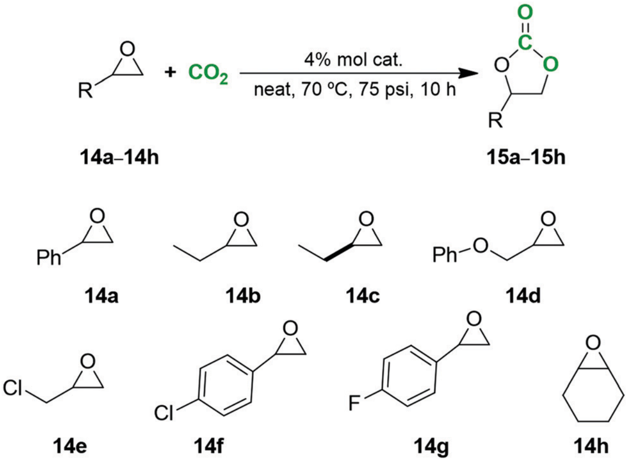


Fig. 5 Library of epoxides used in the study.

The enantiopure (*R*)-1,2-butylene oxide was used as a substrate with the (*R*)-**13** catalyst under the optimized conditions to determine the degree of retention of the chirality of the epoxide. (*R*)-1,2-Butylene carbonate was isolated with 99% enantiomeric excess (ee) confirming nucleophilic attack of the iodide ion at the less hindered C1-carbon of the epoxide. The reaction of (*Rac*)-1,2-butylene with CO_2 using the chiral catalyst (*R*)-**13** produced a racemic mixture of the corresponding carbonate probably due to the use of elevated temperature (70 °C) and longer distance of the chiral center from the Si–OH group that hamper the control of enantioselectivity.[51–53]

Furthermore, the recyclability of catalyst **12** was examined using SO as the substrate under the optimized reaction conditions. After the reaction, catalyst **12** was precipitated from the reaction mixture using diethyl ether. A gradual loss of the catalytic activity after the first run was observed (Fig. 6) probably due to catalyst inactivation.

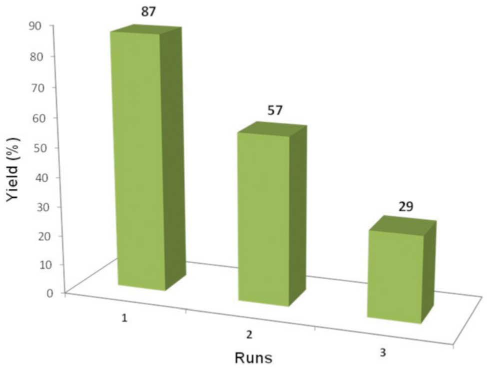


Fig. 6 Comparative yields of SC obtained after three consecutive runs using recycled catalyst **12**.

Conclusions

We described the first bifunctional silanol-based HBD catalysts **12** and **13** that can be synthesized using an easy methodology *via* the (^{t}BuO)$_2$(RO)Si(OAc) and (^{t}BuO)$_2$(RO)Si(OH) intermediates. Furthermore, this synthetic method opens the possibility for the introduction of a wide range of functional groups (even chiral ones) and therefore easy access to tailor-made silanol-based HBD catalysts. Compounds **12** and **13** proved to be efficient catalysts for the cycloaddition of various epoxides and CO_2 under mild reaction conditions (70 °C, 75 psi bar CO_2, 10 h) without a solvent and in the absence of any metal or external nucleophile source. Good to very good conversion was observed, even if the epoxide needs to compete for the Si–OH···O(epoxide) interaction with the iodide anion. Therefore, these systems represent an exciting starting point for a new class of bifunctional HBD catalysts based on silanols. This work is currently underway in our laboratory.

Table 4 Cycloaddition of CO_2 with various epoxides catalyzed by silanols **9**, **11–13**

			Cyclic carbonate (conversion)							
Catalyst	Cat. (mol%)	TBAI (mol%)	**15a** (%)	**15b** (%)	**15c** (%)	**15d** (%)	**15e** (%)	**15f** (%)	**15g** (%)	**15h** (%)
9	4	4	74	83	—	97	96	91	92	12
11-(*Rac*)	4	4	87	92	92	>99	89	85	93	12
11-(*R*)	4	4	81	95	91	>99	84	84	95	10
12	4	—	87	72	—	98	98	82	76	4
13-(*Rac*)	4	—	76	73	75	98	95	87	75	0
13-(*R*)	4	—	79	72	85	98	92	85	72	0

Experimental section

General information

Extra dry industrial grade carbon dioxide with 99.8% purity was purchased from INFRA, S.A. de C.V. and used without further purification. The synthesis of compounds **1–6** was performed under a dried dinitrogen atmosphere using Schlenk and glovebox techniques. On the other hand, the synthesis of silanols **7–13** did not require the use of an inert atmosphere. Solvents were purchased from Sigma-Aldrich and where necessary dried before use with an MBraun SPS solvent purification system using Grubs' columns. ^{t}BuOH was dried with metallic sodium and distilled before use; tetrabutylammonium iodide (TBAI) was purchased from Sigma-Aldrich and recrystallized from a $\mathrm{CH_2Cl_2}$/diethyl ether mixture. 1,4-Diazabicyclo[2.2.2]octane (DABCO), 2-iodoethanol, (*Rac*)- and (*R*)-1,2-epoxybutane, epichlorohydrin, styrene oxide, cyclohexene oxide, 2-(4-fluorophenyl)-oxirane, 2-(4-chlorophenyl)oxirane and 1,2-epoxy-3-phenoxypropane were purchased from Sigma-Aldrich and used without further purification, whereas $(^t\mathrm{BuO})_2\mathrm{Si(OAc)_2}$ **1** was prepared according to the literature procedure from $\mathrm{Si(OAc)_4}$ and ^{t}BuOH.[48] 1-iodobutan-2-ol was prepared using a modified methodology for 1-iodopropan-2-ol.[54] $\mathrm{CDCl_3}$ was used without further purification. NMR spectroscopic data were recorded on a Bruker Avance III 300 MHz or a Varian Inova 500 MHz spectrometer. FT-IR spectra were measured on a Bruker Tensor 27 using the ATR technique with a diamond window in the range of $\tilde{\nu}$ 500–4000 cm^{-1}. Electron impact mass spectrometry (EI-MS) measurements were carried on a Shimadzu GCMS-QP2010 Plus using direct insertion in the detection range of *m*/*z* 20–1090. Elemental analyses (C, H, N) were performed on an Elemental vario MICRO Cube analyzer. It is noteworthy that the carbon content in most of the compounds is low, probably due to the formation of silicon carbide, which is difficult to pyrolyze. Melting points were measured on a Büchi B-540 apparatus.

Cycloaddition reactions were conducted in Q-tube systems using the neat epoxide and the catalyst. Before the reaction, the reactor was purged with $\mathrm{CO_2}$ and subsequently pressurized with $\mathrm{CO_2}$ to the selected pressure. The reactor was heated to the desired temperature for a preset time, whereupon it was cooled to room temperature. THF (10 mL) was added, and the reaction mixture was filtered. The obtained solution was analyzed using gas chromatography on an Agilent 7890B instrument with an FID using an HP-5 capillary column (30 m, 0.320 mm, 0.25 μm) with nitrogen as the carrier gas. The analysis conditions for most of the carbonates were as follows: initial temperature 50 °C, kept for 5 minutes, then increased at a ramp rate of 10 °C min^{-1} to 250 °C, and held at the final temperature for 5 minutes. Cyclic carbonates were purified by distillation or crystallization and the isolated carbonate products were characterized by ^{1}H NMR and matched with previously reported data[34,36] (see the ESI†).

General synthetic route for monoacetoxysilylalkoxides 2–6

Monoacetoxysilylalkoxides $(^t\mathrm{BuO})_2\mathrm{(RO)Si(OAc)}$ (R = Me, Et, $\mathrm{ICH_2CH_2}$, ^{i}Pr, $\mathrm{ICH_2(Et)CH}$, ^{t}Bu) were prepared as follows: a solution of the corresponding alcohol in THF was added to $(^t\mathrm{BuO})_2\mathrm{Si(OAc)_2}$ **1**. The reaction mixture was stirred at ambient temperature (20 °C) for 16 to 72 h. Afterward, all volatiles were removed under reduced pressure, and the product was isolated as a colorless oil.

$(^t\mathrm{BuO})_2\mathrm{(MeO)Si(OAc)}$ (**2**): methanol (1.5 M in THF, 4.6 mL, 6.84 mmol); **1** (2.00 g, 6.84 mmol); stirring for 16 h. Yield: 1.65 g, 91%. Elemental analysis (%) calcd for $\mathrm{C_{11}H_{24}O_5Si}$ (264.39 g mol^{-1}): C 49.97, H 9.15; found: C 49.38, H 8.72. FT-IR (ATR) (cm^{-1}) 2977, 2935 (w, C–H, $\mathrm{CH_3}$), 1739 (m, C=O), 1067 (s, Si–O–C). ^{1}H NMR (300.53 MHz, $\mathrm{CDCl_3}$): δ (ppm) 3.60 (s, 3H, $\mathrm{C}\mathit{H}_3$), 2.10 (s, 3H, $\mathrm{OCC}\mathit{H}_3$), 1.33 (s, 18H, $\mathrm{C(C}\mathit{H}_3)_3$). $^{13}\mathrm{C}\{^1\mathrm{H}\}$ NMR (75.57 MHz, $\mathrm{CDCl_3}$): δ (ppm) 168.9 ($\mathrm{O}\mathit{C}\mathrm{CH_3}$), 74.2 $\mathit{C}\mathrm{(CH_3)_3}$, 51.3 ($\mathit{C}\mathrm{H_3}$), 31.2 ($\mathrm{C(}\mathit{C}\mathrm{H_3)_3}$), 23.0 ($\mathrm{OC}\mathit{C}\mathrm{H_3}$). ^{29}Si NMR (59.63 MHz, $\mathrm{CDCl_3}$): δ (ppm) −95.2. EI-MS: *m*/*z* (%) 249 (13) $[\mathrm{M-Me}]^+$, 191 (21) $[\mathrm{M-O^tBu}]^+$, 135 (100) $[\mathrm{M-2\ ^tBu-Me}]^+$.

$(^t\mathrm{BuO})_2\mathrm{(EtO)Si(OAc)}$ (**3**): ethanol (1.5 M in THF, 4.6 mL, 6.84 mmol); **1** (2.00 g, 6.84 mmol); stirring for 48 h. Yield: 1.75 g, 95%. Elemental analysis (%) calcd for $\mathrm{C_{12}H_{26}O_5Si}$ (278.42 g mol^{-1}): C 51.77, H 9.41; found: C 50.42, H 9.00. FT-IR (ATR) (cm^{-1}) 2976, 2932 (w, C–H, $\mathrm{CH_3}$, $\mathrm{CH_2}$), 1742 (w, C=O), 1060 (s, Si–O–C). ^{1}H NMR (300.53 MHz, $\mathrm{CDCl_3}$): δ (ppm) 3.90 (q, 2H, $^3J_{\mathrm{H-H}}$ = 7.0 Hz, $\mathrm{C}\mathit{H}_2\mathrm{CH_3}$, 2.10 (s, 3H, $\mathrm{OCC}\mathit{H}_3$), 1.33 (s, 18H, $\mathrm{C(C}\mathit{H}_3)_3$), 1.23 (t, 3H, $^3J_{\mathrm{H-H}}$ = 7.0 Hz, $\mathrm{CH_2C}\mathit{H}_3$). $^{13}\mathrm{C}\{^1\mathrm{H}\}$ NMR (75.57 MHz, $\mathrm{CDCl_3}$): δ (ppm) 168.6 ($\mathrm{O}\mathit{C}\mathrm{CH_3}$), 74.0 $\mathit{C}\mathrm{(CH_3)_3}$, 59.4 ($\mathit{C}\mathrm{H_2CH_3}$), 31.0 ($\mathrm{C(}\mathit{C}\mathrm{H_3)_3}$), 22.8 ($\mathrm{OC}\mathit{C}\mathrm{H_3}$), 17.7 ($\mathrm{CH_2}\mathit{C}\mathrm{H_3}$). ^{29}Si NMR (59.63 MHz, $\mathrm{CDCl_3}$): δ (ppm) −96.6. EI-MS: *m*/*z* (%) 263 (21) $[\mathrm{M-Me}]^+$, 219 (2) $[\mathrm{M-OAc}]^+$, 205 (36) $[\mathrm{M-O^tBu}]^+$, 149 (100) $[\mathrm{M-2\ ^tBu-Me}]^+$.

$(^t\mathrm{BuO})_2\mathrm{(ICH_2CH_2O)Si(OAc)}$ (**4**): 2-iodoethanol (1.3 M in THF, 5.3 mL, 6.84 mmol); **1** (2.00 g, 6.84 mmol); stirring for 72 h. Yield: 2.57 g, 93%. Elemental analysis (%) calcd for $\mathrm{C_{12}H_{25}O_5SiI}$ (404.31 g mol^{-1}): C 35.65, H 6.23; found: C 34.73, H 6.13. FT-IR (ATR) (cm^{-1}) 2976, 2934 (w, C–H, $\mathrm{CH_3}$, $\mathrm{CH_2}$), 1736 (m, C=O), 1065 (s, Si–O–C). ^{1}H NMR (300.53 MHz, $\mathrm{CDCl_3}$): δ (ppm) 4.06 (t, 2H, $^3J_{\mathrm{H-H}}$ = 7.0 Hz, $\mathrm{C}\mathit{H}_2\mathrm{CH_2I}$), 3.26 (t, 2H, $^3J_{\mathrm{H-H}}$ = 7.0 Hz, $\mathrm{CH_2C}\mathit{H}_2\mathrm{I}$), 2.09 (s, 3H, $\mathrm{OCC}\mathit{H}_3$), 1.34 (s, 18H, $\mathrm{C(C}\mathit{H}_3)_3$). $^{13}\mathrm{C}\{^1\mathrm{H}\}$ NMR (75.57 MHz, $\mathrm{CDCl_3}$): δ (ppm) 169.1 ($\mathrm{O}\mathit{C}\mathrm{CH_3}$), 74.6 $\mathit{C}\mathrm{(CH_3)_3}$, 64.8 ($\mathit{C}\mathrm{H_2CH_2I}$), 31.3 ($\mathrm{C(}\mathit{C}\mathrm{H_3)_3}$), 23.1 ($\mathrm{OC}\mathit{C}\mathrm{H_3}$), 5.8 ($\mathrm{CH_2}\mathit{C}\mathrm{H_3I}$). ^{29}Si NMR (59.63 MHz, $\mathrm{CDCl_3}$): δ (ppm) −97.0. EI-MS: *m*/*z* (%) 389 (16) $[\mathrm{M-Me}]^+$, 331 (36) $[\mathrm{M-O^tBu}]^+$, 345 (3) $[\mathrm{M-OAc}]^+$, 275 (100) $[\mathrm{M-2\ ^tBu-Me}]^+$.

$(^t\mathrm{BuO})_2(^i\mathrm{PrO})\mathrm{Si(OAc)}$ (**5**): isopropanol (2.6 M in THF, 2.7 mL, 6.84 mmol); **1** (2.0 g, 6.84 mmol); stirring for 48 h. Yield: 1.85 g, 92%. Elemental analysis (%) calcd for $\mathrm{C_{13}H_{28}O_5Si}$ (292.44 g mol^{-1}): C 53.39, H 9.65; found: C 52.03, H 9.21. FT-IR (ATR) (cm^{-1}) 2976, 2935 (w, C–H, $\mathrm{CH_3}$), 1739 (m, C=O), 1068 (s, Si–O–C).^{1}H NMR (300.53 MHz, $\mathrm{CDCl_3}$): δ (ppm) 4.34 (sept, 1H, $^3J_{\mathrm{H-H}}$ = 6.1 Hz, $\mathrm{C}\mathit{H}\mathrm{(CH_3)_2}$, 2.09 (s, 3H, $\mathrm{OCC}\mathit{H}_3$, 1.33 (s, 18H, $\mathrm{C(C}\mathit{H}_3)_3$), 1.21 (d, 6H, $^3J_{\mathrm{H-H}}$ = 6.1 Hz, $\mathrm{CH(C}\mathit{H}_3)_2$), $^{13}\mathrm{C}\{^1\mathrm{H}\}$ NMR (75.57 MHz, $\mathrm{CDCl_3}$): δ (ppm) 169.0 ($\mathrm{O}\mathit{C}\mathrm{CH_3}$), 74.2 $\mathit{C}\mathrm{(CH_3)_3}$ 66.7 ($\mathit{C}\mathrm{H(CH_3)_2}$), 31.3 ($\mathrm{C(}\mathit{C}\mathrm{H_3)_3}$), 25.2 ($\mathrm{CH(}\mathit{C}\mathrm{H_3)_2}$), 23.3 ($\mathrm{OC}\mathit{C}\mathrm{H_3}$). ^{29}Si NMR (59.63 MHz, $\mathrm{CDCl_3}$): δ (ppm) −97.9. EI-MS: *m*/*z* (%) 277 (18) $[\mathrm{M-Me}]^+$, 233 (20) $[\mathrm{M-OAc}]^+$, 219 (47) $[\mathrm{M-O^tBu}]^+$, 163 (100) $[\mathrm{M-2\ ^tBu-Me}]^+$.

$(^t\mathrm{BuO})_2\{\mathrm{(ICH_2(Et)CHO)}\}\mathrm{Si(OAc)}$ (*Rac*)-**6**: (*Rac*)-1-iodobutan-2-ol (1.37 g, 6.84 mmol); **1** (2.00 g, 6.84 mmol); no solvent; stirring for 72 h. Yield: 2.65 g, 90%. Elemental analysis (%) calcd for $C_{14}H_{29}O_5SiI$ (432.37 g mol^{-1}): C 38.89, H 6.76; found: C 37.15, H 6.50. FT-IR (ATR) (cm^{-1}) 2975, 2935 (w, C–H, CH_3, CH_2), 1736 (m, C═O), 1068 (s, Si–O–C). ^{1}H NMR (300.53 MHz, $CDCl_3$): δ (ppm) 3.83 (pent, 1H, $^3J_{H-H}$ = 7.0 Hz, C*H*O), 3.34 (m, 2H, $CHC\mathit{H}_2I$), 2.09 (s, 3H, $OCC\mathit{H}_3$), 1.67 (pent, 2H, $^3J_{H-H}$ = 7.3 Hz, $C\mathit{H}_2CH_3$), 1.34 (s, 18H, $C(C\mathit{H}_3)_3$), 0.90 (t, 3H, $^3J_{H-H}$ = 7.3 Hz, $CH_2C\mathit{H}_3$). $^{13}C\{^1H\}$ NMR (75.57 MHz, $CDCl_3$): δ (ppm) 168.9 ($O\mathit{C}CH_3$), 74.6 $\mathit{C}(CH_3)_3$, 73.4 *C*HO, 31.3 ($C(\mathit{C}H_3)_3$), 29.3 ($CH\mathit{C}H_2I$), 23.2 ($OC\mathit{C}H_3$), 13.0 ($\mathit{C}H_2CH_3$), 9.2 ($CH_2\mathit{C}H_3$). ^{29}Si NMR (59.63 MHz, $CDCl_3$): δ (ppm) −98.2. EI-MS: *m*/*z* (%) 417 (10) $[M - Me]^+$, 359 (40) $[M - O^tBu]^+$, 303 (58) $[M - 2\ ^tBu - Me]^+$.

$(^tBuO)_2\{(ICH_2(Et)CHO)\}Si(OAc)$ (*R*)-**6**: (*R*)-1-iodobutan-2-ol (1.37 g, 6.84 mmol); **1** (2.00 g, 6.84 mmol); no solvent; stirring for 72 h. Yield: 2.70 g, 91%. Elemental analysis (%) calcd for $C_{14}H_{29}O_5SiI$ (432.37 g mol^{-1}): C 38.89, H 6.76; found: C 37.15, H 6.50. FT-IR (ATR) (cm^{-1}) 2974, 2935 (w, C–H, CH_3, CH_2), 1736 (m, C═O), 1068 (s, Si–O–C). ^{1}H NMR (300.53 MHz, $CDCl_3$): δ (ppm) 3.83 (pent, 1H, $^3J_{H-H}$ = 7.3 Hz, C*H*O, 3.34 (m, 2H, $CHC\mathit{H}_2I$), 2.10 (s, 3H, $OCC\mathit{H}_3$), 1.66 (pent, 2H, $^3J_{H-H}$ = 7.3 Hz, $C\mathit{H}_2CH_3$), 1.34 (s, 18H, $C(C\mathit{H}_3)_3$), 0.90 (t, 3H, $^3J_{H-H}$ = 7.3 Hz, $CH_2C\mathit{H}_3$). $^{13}C\{^1H\}$ NMR (75.57 MHz, $CDCl_3$): δ (ppm) 169.2 ($O\mathit{C}CH_3$), 74.6 ($\mathit{C}(CH_3)_3$), 73.4 *C*HO, 31.3 ($C(\mathit{C}H_3)_3$), 29.4 ($CH\mathit{C}H_2I$), 23.2 ($OC\mathit{C}H_3$), 13.2 ($\mathit{C}H_2CH_3$), 9.2 ($CH_2\mathit{C}H_3$). ^{29}Si NMR (59.63 MHz, $CDCl_3$): δ (ppm) −98.0. EI-MS: *m*/*z* (%) 417 (8) $[M - Me]^+$, 359 (37) $[M - O^tBu]^+$, 303 (48) $[M - 2\ ^tBu - Me]^+$.

General synthetic route for monosilanols 7–11

The corresponding monoacetoxysilylalkoxide was suspended in a solution of aqueous ammonia. The reaction mixture was vigorously stirred at room temperature for 1 to 6 h. Subsequently, the silanol was extracted with ethyl acetate and dried with Na_2SO_4. Finally, all volatiles were removed under reduced pressure, and the product was isolated as a colorless oil.

$(^tBuO)_2(MeO)Si(OH)$ (**7**): **2** (1.65 g, 6.22 mmol); aqueous ammonia (3.8 M, 10 mL); stirring for **1** h. Yield: 1.24 g, 90%. Elemental analysis (%) calcd for $C_9H_{22}O_4Si$ (222.35 g mol^{-1}): C 48.61, H 9.97; found: C 47.24, H 9.26. FT-IR (ATR) (cm^{-1}) 3392 (w, br, O–H), 2975, 2932 (w, C–H, CH_3), 1056 (s, Si–O–C). ^{1}H NMR (300.53 MHz, $CDCl_3$): δ (ppm) 4.32 (s, br, 1H, OH), 3.53 (s, 3H, $C\mathit{H}_3$), 1.33 (s, 18H, $C(C\mathit{H}_3)_3$). $^{13}C\{^1H\}$ NMR (75.57 MHz, $CDCl_3$): δ (ppm) 73.2 $\mathit{C}(CH_3)_3$, 50.7 ($\mathit{C}H_3$), 31.3 ($C(\mathit{C}H_3)_3$). ^{29}Si NMR (59.63 MHz, $CDCl_3$): δ (ppm) −85.9. EI-MS: *m*/*z* (%) 207 (94) $[M - Me]^+$, 151 (100) $[M - C_4H_8 - Me]^+$.

$(^tBuO)_2(EtO)Si(OH)$ (**8**): **3** (1.75 g, 6.30 mmol); aqueous ammonia (3.8 M, 10 mL); stirring for 2 h. Yield: 1.37 g, 92%. Elemental analysis (%) calcd for $C_{10}H_{24}O_4Si$ (236.38 g mol^{-1}): C 50.81, H 10.23; found: C 48.80, H 9.99. FT-IR (ATR) (cm^{-1}) 3384 (w, br, O–H), 2975, 2931 (w, C–H, CH_3, CH_2), 1056 (s, Si–O–C). ^{1}H NMR (300.53 MHz, $CDCl_3$): δ (ppm) 4.22 (s, br, 1H, OH), 3.82 (q, 2H, $^3J_{H-H}$ = 7.0 Hz, $C\mathit{H}_2CH_3$), 1.33 (s, 18H, $C(C\mathit{H}_3)_3$), 1.22 (t, 3H, $^3J_{H-H}$ = 7.0 Hz, $CH_2C\mathit{H}_3$).$^{13}C\{^1H\}$ NMR (75.57 MHz, $CDCl_3$): δ (ppm) 73.2 $\mathit{C}(CH_3)_3$, 59.0 ($\mathit{C}H_2CH_3$), 31.3 ($C(\mathit{C}H_3)_3$), 17.9 ($CH_2\mathit{C}H_3$). ^{29}Si NMR (59.63 MHz, $CDCl_3$): δ (ppm) −86.7. EI-MS: *m*/*z* (%) 221 (94) $[M - Me]^+$, 165 (100) $[M - C_4H_8 - Me]^+$.

$(^tBuO)_2(ICH_2CH_2O)Si(OH)$ (**9**): **4** (2.57 g, 6.34 mol); aqueous ammonia (7.5 M, 10 mL); stirring for 4 h. Yield: 2.21 g, 96%. Elemental analysis (%) calcd for $C_{10}H_{23}O_4SiI$ (362.28 g mol^{-1}): C 33.15, H 6.40; found: C 33.17, H 6.58. FT-IR (ATR) (cm^{-1}) 3396 (w, br, O–H), 2974, 2933 (w, C–H, CH_3, CH_2), 1056 (s, Si–O–C). ^{1}H NMR (300.53 MHz, $CDCl_3$): δ (ppm) 3.99 (t, 2H, $^3J_{H-H}$ = 7.0 Hz, $C\mathit{H}_2CH_2I$, 3.28 (t, 2H, $^3J_{H-H}$ = 7.0 Hz, $CH_2C\mathit{H}_2I$), 2.51 (s, br, 1H, O*H*), 1.34 (s, 18H, $C(C\mathit{H}_3)_3$). $^{13}C\{^1H\}$ NMR (75.57 MHz, $CDCl_3$): δ (ppm) 73.7 $\mathit{C}(CH_3)_3$, 64.3 ($\mathit{C}H_2CH_2I$), 31.4 ($C(\mathit{C}H_3)_3$), 6.1 ($\mathit{C}H_2CH_2I$). ^{29}Si NMR (59.63 MHz, $CDCl_3$): δ (ppm) −87.4. EI-MS: *m*/*z* (%) 437 (100) $[M - Me]^+$, 289 (38) $[M - O^tBu]^+$, 233 (62) $[M - C_4H_8 - Me]^+$.

$(^tBuO)_2(^iPrO)Si(OH)$ (**10**): **5** (1.85 g, 6.31 mmol); aqueous ammonia (7.5 M, 10 mL); stirring for 6 h. Yield: 1.45 g, 92%. Elemental analysis (%) calcd for $C_{11}H_{26}O_4Si$ (250.16 g mol^{-1}): C 52.76, H 10.47; found: C 51.38, H 10.33. FT-IR (ATR) (cm^{-1}) 3393 (w, br, O–H), 2974, 2933 (m, C–H, CH_3), 1057 (s, Si–O–C). ^{1}H NMR (300.53 MHz, $CDCl_3$): δ (ppm) 4.24 (sept, 1H, $^3J_{H-H}$ = 6.1 Hz, $C\mathit{H}(CH_3)_2$, 2.62 (s, br, 1H, O*H*), 1.33 (s, 18H, $C(C\mathit{H}_3)_3$), 1.21 (d, 6H, $^3J_{H-H}$ = 6.1 Hz, $CH(C\mathit{H}_3)_2$), $^{13}C\{^1H\}$ NMR (75.57 MHz, $CDCl_3$): δ (ppm) 73.1 ($\mathit{C}(CH_3)_3$), 65.9 ($\mathit{C}H(CH_3)_2$, 31.3 ($C(\mathit{C}H_3)_3$), 25.2 ($CH(\mathit{C}H_3)_2$) ^{29}Si NMR (59.63 MHz, $CDCl_3$): δ (ppm) −87.6. EI-MS: *m*/*z* (%) 235 (100) $[M - Me]^+$, 179 (100) $[M - C_4H_8 - Me]^+$.

$(^tBuO)_2\{(ICH_2(Et)CHO)\}Si(OH)$ (*Rac*)-**11**: **6** (2.65 g, 6.13 mmol) was suspended in a solution of aqueous ammonia (7.5 M, 10 mL) for 4 hours. Yield: 2.22 g, 93%. Elemental analysis (%) calcd for $C_{12}H_{27}O_4SiI$ (390.33 g mol^{-1}): C 36.92, H 6.97; found: C 36.16, H 6.73. FT-IR (ATR) (cm^{-1}) 3398 (w, br, O–H), 2974, 2934 (w, C–H, CH_3, CH_2), 1057 (s, Si–O–C). ^{1}H NMR (300.53 MHz, $CDCl_3$): δ (ppm) 3.74 (m, C*H*O), 3.33 (m, 2H, $CHC\mathit{H}_2I$), 2.44 (s, br, 1H, O*H*), 1.66 (m, 2H, $C\mathit{H}_2CH_3$), 1.34 (s, 18H, $C(C\mathit{H}_3)_3$), 0.92 (t, 3H, $^3J_{H-H}$ = 7.3 Hz, $CH_2C\mathit{H}_3$). $^{13}C\{^1H\}$ NMR (75.57 MHz, $CDCl_3$): δ (ppm) 73.5 $\mathit{C}(CH_3)_3$, 73.2 (*C*HO), 31.5 ($C(\mathit{C}H_3)_3$), 29.5 $I\mathit{C}H_2(CH_2CH_3)$, 13.4 ($\mathit{C}H_2CH_3$), 9.4 ($CH_2\mathit{C}H_3$). ^{29}Si NMR (59.63 MHz, $CDCl_3$): δ (ppm) −88.2 EI-MS: *m*/*z* (%) 375 (62) $[M - Me]^+$, 317 (45) $[M - O^tBu]^+$, 261 (70) $[M - C_4H_8 - Me]^+$.

$(^tBuO)_2\{(ICH_2(Et)CHO)\}Si(OH)$ (*R*)-**11**: (*R*)-**6** (2.70 g, 6.24 mol) was suspended in a solution of aqueous ammonia (7.5 M, 10 mL) for 4 hours. Yield: 2.33 g, 96%. Elemental analysis (%) calcd. for $C_{12}H_{27}O_4SiI$ (390.33 g mol^{-1}): C 36.92, H 6.97; found: C 36.43, H 6.97. FT-IR (ATR) (cm^{-1}) 3403 (w, br, O–H), 2973, 2934 (w, C–H, CH_3, CH_2), 1058 (s, Si–O–C). ^{1}H NMR (300.53 MHz, $CDCl_3$): δ (ppm) 3.74 (m, C*H*O), 3.34 (m, 2H, $CHC\mathit{H}_2I$), 2.44 (s, br, 1H, O*H*), 1.67 (m, 2H, $C\mathit{H}_2CH_3$), 1.34 (s, 18H, $C(C\mathit{H}_3)_3$), 0.92 (t, 3H, $^3J_{H-H}$ = 7.3 Hz, $CH_2C\mathit{H}_3$). $^{13}C\{^1H\}$ NMR (75.57 MHz, $CDCl_3$): δ (ppm) 73.5 $\mathit{C}(CH_3)_3$, 73.2 (*C*HO), 31.5 ($C(\mathit{C}H_3)_3$), 29.5 $I\mathit{C}H_2(CH_2CH_3)$, 13.4 ($\mathit{C}H_2CH_3$), 9.4 ($CH_2\mathit{C}H_3$). ^{29}Si NMR (59.63 MHz, $CDCl_3$): δ (ppm) −88.2 EI-MS: *m*/*z* (%) 375 (98) $[M - Me]^+$, 317 (58) $[M - O^tBu]^+$, 261 (100) $[M - C_4H_8 - Me]^+$.

Preparation of bifunctional catalysts 12, (*Rac*)-13 and (*R*)-13

$[(^tBuO)_2\{(N(CH_2CH_2)_3N)CH_2CH_2O\}Si(OH)]^+I^-$ **12**: to a mixture of monosilanol **9** (1.00 g, 2.76 mmol) and DABCO (0.31 g, 2.76 mmol) was added toluene (3 mL). The reaction mixture was heated to 100 °C over a period of 3 h. Afterward, the solvent was removed under reduced pressure and **12** was washed with diethyl ether (2 × 3 mL) and hexane (2 × 3 mL). Yield: 1.09 g, 83%. M.p. 190–191 °C. Elemental analysis (%) calcd for $\text{C}_{16}\text{H}_{35}\text{O}_4\text{N}_2\text{SiI}$ (474.45 g mol^{-1}): C 40.50, H 7.44, N 5.90; found: C 40.07, H 7.51, N 6.11. FT-IR (ATR) (cm^{-1}) 3275 (w, br, O–H), 2970, 2934 (w, C–H, CH_3, CH_2), 1055 (s, Si–O–C). ^{1}H NMR (300.53 MHz, CDCl_3): δ (ppm) 5.25 (s, br, 1H, OH), 4.22 (m, 2H, $\text{OC}H_2\text{CH}_2$), 3.77 (m, 8H, $\text{OCH}_2\text{C}H_2$, $\text{C}H_2\text{N}^+$), 3.22 (t, 6H, $^3J_{\text{H–H}}$ = 7.1 Hz, $\text{C}H_2\text{N}_{\text{terciary}}$), 1.28 (s, 18H, $\text{C}(\text{C}H_3)_3$). ^{13}C{^{1}H} NMR (75.57 MHz, CDCl_3): δ (ppm) 73.5 ($C(\text{CH}_3)_3$), 66.0 ($\text{O}C\text{H}_2\text{CH}_2$), 56.6 ($\text{OCH}_2C\text{H}_2$), 53.4 ($C\text{H}_2\text{N}^+$), 45.3 $C\text{H}_2\text{N}_{\text{terciary}}$, 31.6 $\text{C}(C\text{H}_3)$. ^{29}Si NMR (59.63 MHz, CDCl_3): δ (ppm) −87.7. EI-MS: m/z (%) 347 (30) $[\text{M} - \text{I}]^+$, 112 (15) $[\text{C}_6\text{H}_{12}\text{N}_2]^+$, 56 (100) $[\text{C}_4\text{H}_8]^+$.

(Rac)-$[(^t\text{BuO})_2\{(\text{N}(\text{CH}_2\text{CH}_2)_3\text{N})\text{CH}_2(\text{Et})\text{CHO})\}\text{Si}(\text{OH})]^+\text{I}^-$ *(Rac)*-**13**. To a mixture of monosilanol *(Rac)*-**11** (0.80 g, 2.05 mmol) and DABCO (0.23 g, 2.05 mmol) was added toluene (3 mL). The reaction mixture was heated to 100 °C over 24 hours. Afterward, the solvent was removed under reduced pressure and the resulting white powder was washed with diethyl ether (2 × 3 mL) and hexane (2 × 3 mL). Yield: 0.81 g, 79%. M.p. 209–210 °C. Elemental analysis (%) calcd for $\text{C}_{18}\text{H}_{39}\text{O}_4\text{NSiI}$ (502.50 g mol^{-1}): C 43.02, H 7.82, N 5.57; found: C 42.29, H 7.80, N 5.22. FT-IR (ATR) (cm^{-1}) 3300 (w, br, O–H), 2971, 2934 (w, C–H, CH_3, CH_2), 1056 (s, Si–O–C). ^{1}H NMR (300.53 MHz, CDCl_3): δ (ppm) 5.05 (s, br, 1H, OH), 4.66 (m, 1H, OCH), 3.82 (m, 6H, $\text{CHC}H_2\text{N}^+$), 3.65 (m, 1H, $\text{C}H_2\text{N}^+$), 3.38 (m, 1H, $\text{C}H_2\text{N}^+$), 3.26 (m, 6H, $\text{C}H_2\text{N}_{\text{terciary}}$), 1.75 (m, 2H, $\text{C}H_2\text{CH}_3$), 1.34 (s, 18H, $\text{C}(\text{C}H_3)_3$), 1.00 (t, 3H, $^3J_{\text{H–H}}$ = 7.3 Hz, $\text{CH}_2\text{C}H_3$). ^{13}C{^{1}H} NMR (75.57 MHz, CDCl_3): δ (ppm) 73.8 $C(\text{CH}_3)_3$, 69.4 (OCH), 67.8 ($\text{CH}C\text{H}_2\text{N}^+$), 53.6 ($C\text{H}_2\text{N}^+$), 45.5 ($C\text{H}_2\text{N}_{\text{terciary}}$), 31.7 ($\text{C}(C\text{H}_3)_3$), 28.7 ($C\text{H}_2\text{CH}_3$), 9.1 ($\text{CH}_2C\text{H}_3$). ^{29}Si NMR (59.63 MHz, CDCl_3): δ (ppm) −88.9. EI-MS: m/z (%) 375 (5) $[\text{M} - \text{I}]^+$, 112 (12) $[\text{C}_6\text{H}_{12}\text{N}_2]^+$, 56 (80) $[\text{C}_4\text{H}_8]^+$.

(R)-$[(^t\text{BuO})_2\{(\text{N}(\text{CH}_2\text{CH}_2)_3\text{N})\text{CH}_2(\text{Et})\text{CHO})\}\text{Si}(\text{OH})]^+\text{I}^-$ *(R)*-**13**. To a mixture of monosilanol *(R)*-**11** (0.80 g, 2.05 mmol) and DABCO (0.23 g, 2.05 mmol) was added toluene (3 mL). The reaction mixture was heated to 100 °C over 24 hours. Afterward, the solvent was removed under reduced pressure and the resulting white powder was washed with diethyl ether (2 × 3 mL) and hexane (2 × 3 mL). Yield: 0.83 g, 81%. M.p. 209–210 °C. Elemental analysis (%) calcd. for $\text{C}_{18}\text{H}_{39}\text{O}_4\text{NSiI}$ (502.50 g mol^{-1}): C 43.02, H 7.82, N 5.57; found: C 42.20, H 7.77, N 5.52. FT-IR (ATR) (cm^{-1}) 3296 (w, br, O–H), 2971, 2934 (w, C–H, CH_3, CH_2), 1058 (s, Si–O–C). ^{1}H NMR (300.53 MHz, CDCl_3): 5.04 (s, br, 1H, OH), 4.66 (m, 1H, OCH), 3.80 (m, 6H, $\text{CHC}H_2\text{N}^+$), 3.65 (m, 1H, $\text{C}H_2\text{N}^+$), 3.38 (m, 1H, $\text{C}H_2\text{N}^+$), 3.26 (m, 6H, $\text{C}H_2\text{N}_{\text{terciary}}$), 1.75 (m, 2H, $\text{C}H_2\text{CH}_3$), 1.34 (s, 18H, $\text{C}(\text{C}H_3)_3$), 1.00 (t, 3H, $^3J_{\text{H–H}}$ = 7.3 Hz, $\text{CH}_2\text{C}H_3$). ^{13}C{^{1}H} NMR (75.57 MHz, CDCl_3): δ (ppm) 73.7 ($C(\text{CH}_3)_3$), 69.3 (OCH), 67.7 ($\text{CH}C\text{H}_2\text{N}^+$), 53.5 ($C\text{H}_2\text{N}^+$), 45.5 ($C\text{H}_2\text{N}_{\text{terciary}}$), 31.7 ($\text{C}(C\text{H}_3)_3$), 28.7 ($C\text{H}_2\text{CH}_3$), 9.0 ($\text{CH}_2C\text{H}_3$). ^{29}Si NMR (59.63 MHz, CDCl_3): δ (ppm) −88.8. EI-MS: m/z (%) 375 (5) $[\text{M} - \text{I}]^+$, 112 (12) $[\text{C}_6\text{H}_{12}\text{N}_2]^+$, 56 (80) $[\text{C}_4\text{H}_8]^+$.

Conflicts of interest

There are no conflicts to declare.

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