Coupling of CO₂ and epoxides catalysed by novel N-fused mesoionic carbene complexes of nickel (II)†

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We report the syntheses of two rigid mesoionic carbene (MIC) ligands with a carbazole backbone via an intramolecular Finkelstein–cyclisation cascade and investigate their coordination behavior towards nickel(II) acetate. Despite the nickel(II) carbene complexes 4a,b showing only minor differences in their chemical composition, they display curious differences in their chemical properties, e.g. solubility. Furthermore, the potential of these novel MIC complexes in the coupling of carbon dioxide and epoxides as well as the differences in reactivity compared to classical NHC-derived complexes are evaluated.

Introduction

Pincer-type ligands have opened many new avenues in modern-day chemistry, giving rise to stable and robust catalysts as well as allowing for the isolation of highly reactive metal complexes.1,2 Therefore, a large variety of neutral and monoanionic pincer ligands have been synthesised in the past decades (Fig. 1).2,3 Due to their unique profiles and modular chemical designs, especially regarding the nature of the coordinating donor atoms (ranging from PNP,5 PCP,5 POP,6 OCO,7 SCS,8 CNC,9 or CCC10 just to mention a few), numerous breakthroughs have been achieved. One moiety of ever-increasing focus in this context is the monoanionic carbazole fragment. Its planar and rigid geometry in combination with its persistent fluorescence and its unique ability to partake in redox-reactions led to a plethora of applications in catalysis and small molecule activation.11 However, until now most of the carbazole systems have been derived from the classical PNP substitution pattern, while CNC coordination motifs, e.g. by using N-heterocyclic carbenes (NHCs), have found less attention. Nevertheless, seminal work by Kunz and co-workers12 has shown that carbazole derived CNC coordinating ligands are valuable precursors for the design of effective catalysts13 and can stabilize highly reactive group 10 metal complexes (Fig. 2, top left).14 This is supported by a recent report of Lee and co-workers who showed that nickel(II) complexes (Fig. 2, top right) are potent catalysts in the copolymerisation of CO₂ and cyclohexene oxide.15 However, given the relatively high temperatures required for catalysis, especially in comparison to systems with early transition metals,16 we felt that the improvement of these catalysts should be a valuable goal.

One strategy for the improvement of the catalytic potential of NHC-derived catalysts in recent years was the exchange of the

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Fig. 1 Selected examples of the most commonly used pincer-type ligands scaffolds with PNP (left), POP (middle) and CNC (right) coordination modes.
Results and discussion

To expand the versatility of our recently reported synthetic strategy to prepare bis(triazolylidene)-carbazolide ligands, in addition to the known compound 3b with a six-membered piperidine-based ring, we also synthesised ligand precursor 3a with a five-membered pyrrolidine-based annulated ring, which has a slightly lower steric bulk (Scheme 1). Compound 3a was synthesised using standard CuAAC (copper catalysed alkyne azide cycloaddition) conditions with 5-chloro-1-pentylene and 1,8-diazido-3,6-di-tert-butyl-carbazole, resulting in the clean formation of the desired chloro-propyl 1,2,3-triazole 2a in 70% yield (Scheme 1, middle). Indicative for the successful formation of the desired triazole is the disappearance of the characteristic azide stretching band in the IR spectrum at 2099 cm⁻¹ (compare Fig. S53 and S54†). Additionally, successful formation of 2a was evidenced by ¹H NMR spectroscopy, showing a characteristic triazole-5H low-field resonance at δ = 8.02 ppm. Addition of an excess of potassium iodide (20 equiv.) and heating the mixture to 90 °C for 48 h led to the formation of the desired N-fused triazolium salt 3a in quantitative yields (Scheme 1, right). Successful cyclisation was evident by various features in the NMR spectra: (i) the typical low-field shift of the triazolium-5H resonance in the ¹H NMR spectrum from δ = 8.02 ppm for 2a to δ = 8.67 ppm for 3a, (ii) the low-field shift of the resonance of the (former) –CH₂Cl protons from δ = 4.90 ppm for 2a to δ = 4.69 ppm for 3a, and (iii) the coupling of this methylene group to the triazole nitrogen atoms (δ¹⁵N) = 266.6 ppm) as seen in the ¹H–¹⁵N HMBC NMR spectrum (compare Fig. S10†). Finally, X-ray quality crystals of 3a were obtained by layering a concentrated dichloromethane solution with n-hexane in a NMR tube and storage at room temperature for several days. Compound 3a crystallises in the triclinic space group P1 with five dichloromethane solvent molecules in the crystal lattice and two independent molecules in the asymmetric unit. Despite the relatively small change from an N-fused piperidine to a pyrrolidine ring, the structures of 3a,b reveal notable differences. While 3a shows hydrogen bonding of the carbazole-NH proton H10 to one of the iodide counterions (Fig. 3, left), in 3b such an interaction is absent. Apart from the hydrogen bonding, the structural parameters in 3a reflect the ones in 3b and previously reported 1,2,3-triazolium salts. A detailed discussion of
the structural parameters is therefore omitted. For more details on the structural metrics please see Tables S1 and S2 in the ESI† (Fig. 3).

Although mesoionic carbene complexes of nickel(i) are still scarce and often rely on the use of precursors which are unstable under ambient (air and moisture) conditions, such as nickelocene,33,34 we found that complexation could be achieved using Ni(OAc)₂·4H₂O in the presence of excess triazole and carbon dioxide (CO₂) are shown in Table 1. It is noteworthy that compared to the report by Lee and co-workers, noteworthy that compared to the report by Lee and co-workers,14,27 the triazole nitrogen atoms from complexes: (i) the disappearance of the carbazole-N and carbazole-CH resonances in the 1H NMR spectra of the complexes (Fig. S11 and S16†), as well as (ii) a high-field shift of the resonance of the methylene protons adjacent to the triazole nitrogen atoms from δ = 4.90 ppm and δ = 4.79 ppm for 3a and 3b to δ = 4.48 ppm and δ = 4.49 ppm for 4a and 4b (compare Fig. S11 and S16†), and (iii) the presence of the characteristic triazolylidene-5C resonance at δ = 152.0 ppm and δ = 146.9 ppm in the 13C{1H} NMR spectra of 4a and 4b (compare Fig. S12 and S17†), which are in a comparable range of previously reported nickel(i) triazolylidene complexes.33,34 Additionally, a signal at δ = 177.7 ppm and δ = 177.1 ppm in the 13C{1H} NMR spectra of 4a and 4b was detected, corresponding to the carbonyl carbon atom of the acetate anion. Ultimate prove for the successful formation of the desired triazolylidene complexes 4a and 4b was given by X-ray diffraction analysis. Single crystals suitable for structure analysis were obtained by layering a concentrated dichloromethane solution of the respective complexes with n-hexane in an NMR tube at room temperature (Fig. 3, middle and right). Both compounds crystallise in the triclinic space group P1 as either a water solvate (4a) or a dichloromethane solvate (4b). In both complexes the nickel(i) ion is in a slightly distorted square planar coordination environment, with Ni1–N1–O1 and C1–Ni1–C2 angles of 175.44(7)°/176.30(9)° (4a) and 176.11(7)°/173.39(7)° (4b), as well as r′₄ values of 0.06 and 0.07 in 4a and 4b, respectively. The Ni1–N10 distances are 1.854(2) Å (4a) and 1.861(2) Å (4b) and lie in the range of previously reported carbazolide and pyrrolide coordinated nickel(i) ions.34 The nickel-carbene atom distances were found to be 1.945(2) Å and 1.947(2) Å in 4a and 1.943(2) Å and 1.931(2) Å in 4b for Ni1–C1 and Ni1–C2, respectively. These distances also compare well to those of previously reported nickel(i) triazolylidene complexes.33,34 The intra ligand distances within the triazolylidene ring are in the expected region and comparable to previously reported triazolylidene complexes.33,34 Further information regarding the crystal structures and selected bond lengths and angles can be found in the ESI, Tables S1 and S2.†

Having the new complexes in hand, and given the fact, that MIC-derived complexes are known to often surpass their NHC congeners' activities in catalytic reactions,18 we next turned our focus towards their catalytic potential in the copolymerisation of carbon dioxide and cyclohexene oxide. Lee et al.15 have previously shown that corresponding NHC-derived catalysts (Fig. 1, top right) are moderately active catalysts for the polymerisations of carbon dioxide and cyclohexene oxide to give copolymers. Thus, we applied similar conditions to our catalysts and used cyclohexene oxide (CHO, Fig. 4) as monomer as well. The results for the catalysed coupling reactions of epoxide and carbon dioxide (CO₂) are shown in Table 1. It is noteworthy that compared to the report by Lee and co-workers,
who were able to apply a carbon dioxide pressure of 500 psi (34.5 bar), our synthetic setup was limited to a pressure of 290 psi (20 bar). Although it has been accepted as a common rule, that higher pressures favour the formation of polycarbonates, recent literature reports show that nickel (n)-based catalysts can efficiently couple carbon dioxide and

![Diagram]

**Fig. 4** Epoxides used for the coupling reaction with CO$_2$. The corresponding cyclic carbonates 5a–5e are listed underneath.
epoxides to the desired polycarbonates even at 20 bar. In an initial check, wether 4a and 4b could be active (pro)-catalysts in the copolymerisation of CHO and CO₂, we applied different catalyst loadings 0.5, 0.25 and 0.1 mol% of 4a or 4b (entries 1–5 and 7), similar to the experiments performed by Lee and co-workers. Crude ¹H NMR spectra of the reaction mixtures indicated the possible formation of polymers showing broad peaks (Fig. S21†). However, after work-up cyclic carbonate (CC) 5a was isolated as the sole product from these reactions. Notably, when the reaction was performed either without catalysts or without carbon dioxide, small amounts of polyether (PE) could be isolated (vide infra, entries 15–17).

While the TONS to CC seem to be barely affected by the catalyst loading for 4a (entries 1, 3 and 5), the formation of PE by-products increased with lower catalyst loadings. Contrary, for catalyst 4b (entries 2, 4 and 7), TONS as well as the formation of PE by-product increased concurrently with lower catalyst loadings. Applying the established cocatalyst bis(triphenyl-phosphine) iminium chloride ([PPN]Cl) (entries 6 and 8) resulted in higher conversion of the monomer and TONS/TOFs up to 220/12 h⁻¹. Since no significant polycarbonate formation could be detected for all of these conditions, we proceeded with the lowest catalyst loading (0.1 mol%) to improve the conditions leading to cyclic carbonates. Increasing the reaction time from 18 h to 120 h (entries 9–12) led to increasing amounts of cyclic carbonate 5a, while polyether formation was suppressed. Similarly, the addition of [PPN]Cl shifted the selectivity of the reaction towards the formation of cyclic carbonates. Furthermore, complex 4a seems to have a lower activity at this catalyst loading compared to 4b, which is most likely related to the lower solubility of 4a. Reducing the carbon dioxide pressure to 2 bars (entries 13 and 14) resulted in a drastic drop of the conversions and a preferred formation of polyether. Notably, Mayilmurugan et al. have recently reported a nickel(u) complex, which is capable of performing efficient CC coupling at 1 bar and 100 °C. No catalyst (entry 15) for CHO gave solely PE, only co-catalyst resulted in lower TOFs and PE by-product of 47% (entry 16). Heating of the monomer led to pure PE (entry 17).

Next we turned our interest towards the reactivity of other, functionalised epoxides, especially glycidyl ethers (see Fig. 4), in order to prove if the trends for cyclohexene oxide can be reproduced for other epoxies. Treating 3-(o-methoxy-phenoxo)-1,2-epoxypropane (GMPE) (entries 18–27) under the same conditions as applied for our initial cyclohexene oxide studies (130 °C, 20 bar of CO₂ and 18 h), the overall conversions for GMPE were found to be higher (entries 22–25). The TOF for complex 4b without co-catalyst was >55 h⁻¹ and the TOF for 4a only 23 h⁻¹. Therefore, a higher reactivity of 4b for the reaction of GMPE to 5b can be assumed, which might as well be related to the higher solubility of 4b. With increasing temperature, the formation of CC is entropically favoured over PC formation. Therefore, experiments with GMPE at RT (entries 18 and 19) and at 80 °C (entries 20 and 21) were performed. While at RT no reaction was observed, at 80 °C the use of complex 4b gave CC with a moderate TOF of 8 h⁻¹. In all cases, the addition of [PPN]Cl resulted in a drastic enhancement of the catalytic activity of the systems. Using no catalyst and only co-catalyst for GMPE resulted in no conversion. Using no catalyst and only [PPN]Cl gave low TOFs of 6 h⁻¹ (entries 26 and 27). The same trends were also observed for other glycidyl ethers such as allyl glycidyl ether (AGE, entries 28–31), and 1,2-epoxyhex-5-ene (E5H, entries 32–35).

Finally, we examined the influence of a protic substrate, for which purpose we synthesized tert-butylic(oxygen-2-ylmethyl)carbamate (tBOMC). Similar to the glycidyl ethers, full conversion of the starting material was achieved for both catalysts 4a and 4b. However, for tBOMC the carbonate selectivity of the complexes dropped and the PE by-product was formed in significant amounts. Nevertheless, PE formation can be decreased by addition of [PPN]Cl as co-catalyst (entries 36–39).

Conclusion

We extended the route to 1,8-bis(1,2,3-triazolylidene)-carbazole ligands by applying a straight-forward intramolecular cyclisation reaction, avoiding hazardous and explosive tert-butylic(hydropochlorite. Furthermore, following a simple deprotonation protocol using only triethyamine as a base, we have been able to synthesise new nickel(u) complexes 4a,b.

In contrast to their imidazoylidene Ni(u) congeners, which previously have been found to be good polymerisation catalysts, the 1,2,3-triazolylidene complexes 4a,b presented in this work turned out to be moderate catalysts for the cyclisation of carbon dioxide and epoxides to cyclic carbonates. However, it should be pointed out again, that the selectivity of cyclisation vs. polymerisation is strongly balanced by electronic and steric effects of the catalysts, as well as the applied pressure of CO₂, and even subtle changes in catalyst design can have a large impact. Nevertheless, these results represent a rare case, in which the replacement of normal by mesoionic carbenes in a catalyst has not led to an increase of its catalytic potential, but to an inversion of selectivity. We are currently investigating the cause of this selectivity switch and further applications of the new carbazole-derived MIC ligands in early transition metal coordination chemistry and photochemistry.

Experimental section

General remarks

If not otherwise mentioned, all transformations involving nickel precursors were carried out under inert conditions using the Schlenk technique or an argon-filled glovebox. Organic syntheses were carried out under ambient conditions without taking precautions to exclude moisture or air. Solvents were dried by a MBraun SPS system and stored over activated molecular sieves (3 Å) for at least 24 h. The deuterated solvents CDCl₃ and CD₂Cl₂ were used as received without any prior drying. IR spectra were recorded at room temperature under inert conditions using a Bruker Vertex 70 with ATR equipment.
The beige-colored solid was dried washed with diethylether (100 mL) and concentrated to 20 mL and added dropwise to a stirred solution of reduced pressure. The remaining solid was extracted with dichloromethane (2 × 25 mL) and filtered. All volatiles of the filtrate were removed under reduced pressure. The slightly pink-coloured solid was further dried in vacuo to yield the desired product in 70% yield (953 mg, 1.68 mmol).

Synthetic procedures

3,6-Di-tert-butyl-1,8-bis-(4-(3-chloropropyl)-1,2,3-triazolyl)-carbazole (2a). To a mixture of 3,6-di-tert-butyl-carbazole-1,8-diazide (867 mg, 2.4 mmol, 1 equiv.), 5-chloro-1-pentyn-1-ol (564 mg, 5.58 mmol, 2.3 equiv.), sodium ascorbate (125 mg, 0.66 mmol, 0.25 equiv.) and tris[(1-benzyl-1H-1,2,3-triazol-4-yl)methyl]amine (TBTA, 133 mg, 0.25 mmol, 0.1 equiv.) in dichloromethane (10 mL), tert-butanol (10 mL) and water (2 mL) a solution of copper sulfate (40 mg, 0.25 mmol, 0.1 equiv.) in water (2 mL) was added. The resulting reaction mixture was stirred at room temperature under an atmosphere of argon for 16 h. The beige-coloured suspension was filtered, and the precipitate washed with n-pentane (2 × 10 mL). The solid was extracted with dichloromethane (2 × 25 mL) and filtered. All volatiles of the filtrate were removed under reduced pressure. The slightly pink-coloured solid was further dried in vacuo to yield the desired product in 70% yield (953 mg, 1.68 mmol).

1H NMR (CDCl3, 298 K, 500 MHz, in ppm): 10.82 (s, 1H, Carbazole-NH), 8.16 (d, J = 1.3 Hz, 2H, Aryl-H), 8.02 (s, 2H, triazole-5H), 7.60 (d, J = 1.3 Hz, 2H, Aryl-H), 3.69 (t, J = 6.3 Hz, 4H, -CH2Cl), 3.06 (t, J = 7.3 Hz, 4H, CH2), 2.32 (pent, J = 6.3 Hz, 4H, CH2), 1.52 (s, 18H, C(CH3)3); 13C{1H} NMR (CDCl3, 298 K, 125 MHz, in ppm): 177.7 (acetate-CO2), 154.9 (Aryl-C), 149.8 (Aryl-C), 143.5 (Aryl-C), 130.3 (Aryl-C), 125.9 (Aryl-C), 121.5 (Aryl-C), 119.3 (Triazolyl-C), 116.7 (Aryl-CH), 114.6 116.7 (Aryl-CH), 44.4 (−CH2Cl), 35.1 (C(CH3)3), 32.1 (C(CH3)3), 31.9 (CH2), 22.9 (CH2); Hi-Res mass (ESI+) calcd. for [C30H34N7Ni]+ 550.2229; found: 550.2266. Elemental analysis calcd. for C30H34N7Ni·0.9CH2Cl2 C 44.83 H 4.71 N 11.75; found: C 44.46 H 4.87 N 12.15.

3,6-Di-tert-butyl-1,8-bis-(4,5,6-trihydropyrrolo-1,2,3-triazolylidene)carbazolid) nickel(II) (4a). Triazolium salt 3a (225 mg, 0.3 mmol, 1 equiv.) and Ni(OAc)2·4H2O (74.6 mg, 0.3 mmol, 1 equiv.) was dissolved in dry acetonitrile and excess triethylamine (304 mg, 3 mmol, 0.42 mL, 10 equiv.) was added. The mixture was sealed and stirred at 82 °C overnight resulting in the formation of a thick yellow suspension. The solvent was reduced under reduced pressure, and the residue was dissolved in dichloromethane (20 mL) and filtered through a pad of Celite. The clear orange-red solution was extracted with water and brine, dried over magnesium sulphate and concentrated under reduced pressure to 3 mL. Addition of hexane (50 mL) cause the precipitation of the desired complex 4a, which was isolated by filtration and dried in air to give 4a as a free-flowing powder in a yield of 83%. (152 mg, 0.249 mmol)

1H NMR (CD2Cl2, 298 K, 700 MHz, in ppm): 8.24 (s, 2H, Aryl-H), 8.14 (s, 2H, Aryl-H), 4.48 (s, 4H, N-CH2), 3.15 (s, 4H, CH2), 2.74 (s, 4H, CH2), 2.18 (s, 3H, acetate-CH3), 1.50 (s, 18H, C(CH3)3); 13C{1H} NMR (CD2Cl2, 298 K, 125 MHz, in ppm): 177.7 (acetate-CO2), 154.9 (Aryl-C), 149.8 (Aryl-C), 143.5 (Aryl-C), 130.3 (Aryl-C), 125.9 (Aryl-C), 121.5 (Aryl-C), 119.3 (Triazolyl-C), 116.7 (Aryl-CH), 114.6 116.7 (Aryl-CH), 44.4 (−CH2Cl), 35.1 (C(CH3)3), 32.1 (C(CH3)3), 31.9 (CH2), 22.9 (CH2); Hi-Res mass (ESI+) calcd. for [C30H34N7Ni]+ 550.2229; found: 550.2266. Elemental analysis calcd. for C30H34N7Ni·0.9CH2Cl2 C 57.53, H 5.69, N 14.28; found C 57.42, H 5.81, N 14.39.
In order to isolate the cyclic carbonate, the solvent was removed under reduced pressure and purified by column chromatography (silica, CH/EE).

**Hexahydro-1,3-benzodioxol-2-one (5a).** The NMR data obtained agrees with the literature.\(^{15,40}\) \(^1\)H NMR (CDCl\(_3\), 303 K, 500 MHz, in ppm): 4.67 (m, 2H, CH), 1.89 (dd, \(^{1}J_{HH} = 5.4\) Hz, \(^{3}J_{HH} = 10.8\) Hz, 4H, CH\(_2\)), 1.61 (m, 2H, CH\(_2\)), 1.43 (m, 2H, CH\(_2\)); \(^{13}\)C\(^{(1)}\)H) NMR (CDCl\(_3\), 303 K, 175 MHz, in ppm): 155.4 (C\(_6\)), 75.8 (CH), 26.9 (CH\(_2\)), 19.3 (CH\(_2\)); Hi-Res mass (ESI+) calc. for \([\text{C}_8\text{H}_15\text{O}_2\text{N}^+\text{H}^+]\) 240.0846 found: 240.0846.

**4-(2-methoxyphenoxymethyl)-1,3-dioxolan-2-one (5b).** The NMR data obtained agrees with the literature.\(^{41}\) \(^1\)H NMR (CDCl\(_3\), 303 K, 500 MHz, in ppm): 7.06-6.95 (m, 4H, Aryl-H), 5.00 (m, 1H, CH), 4.61 (m, 2H, Dioxolane-CH\(_2\)), 4.22 (dd, \(^{3}J_{HH} = 4.3\) Hz, 2H, OCH\(_2\)), 3.84 (s, 3H, OCH\(_3\)); \(^{13}\)C\(^{(1)}\)H) NMR (CDCl\(_3\), 303 K, 175 MHz, in ppm): 155.8 (Dioxolane-C\(_q\)), 150.6 (Aryl-C\(_q\)), 147.6 (Aryl-C\(_q\)), 133.8 (Aryl-C\(_q\)), 121.2 (Aryl-CH), 117.0 (Aryl-CH), 112.0 (Aryl-CH), 74.6 (Dioxolane-CH), 69.5 (OCH\(_3\)), 66.5 (Allyl-CH), 56.0 (OCH\(_3\)); Hi-Res mass (ESI+) calc. for \([\text{C}_8\text{H}_15\text{O}_2\text{N}^+\text{H}^+]\) 240.0846 found: 240.0846.

**4-((Allylxy)methoxymethyl)-1,3-dioxolan-2-one (5c).** The NMR data obtained agrees with the literature.\(^{42}\) \(^1\)H NMR (CDCl\(_3\), 303 K, 500 MHz, in ppm): 5.86 (m, 1H, Allyl-CH), 5.28 (m, 1H, Allyl-CH), 5.22 (m, Allyl-CH), 4.81 (m, 1H, Dioxolane-CH), 4.49 (dd, \(^{3}J_{HH,\text{trans}} = 8.4\) Hz, \(^{3}J_{HH} = 8.4\) Hz, 1H, Dioxolane-CH), 4.39 (dd, \(^{2}J_{HH,\text{cis}} = 6.1\) Hz, \(^{3}J_{HH} = 8.4\) Hz, 1H, Dioxolane-CH), 4.05 (m, 2H, Allyl-OCH\(_2\)), 3.68 (m, 2H, Dioxolane-CH); \(^{13}\)C\(^{(1)}\)H) NMR (CDCl\(_3\), 303 K, 175 MHz, in ppm): 155.0 (C\(_q\)), 133.8 (Allyl-CH), 118.0 (Allyl-CH), 75.1 (Dioxolane-CH), 72.7 (Allyl-OCH\(_2\)), 69.0 (Dioxolane-CH), 66.4 (Dioxolane-OCH\(_3\)).

**4-(But-3-en-1-yl)-1,3-dioxolan-2-one (5d).** The NMR data obtained agrees with the literature.\(^{43}\) \(^1\)H NMR (CDCl\(_3\), 303 K, 500 MHz, in ppm): 5.78 (m, 1H, Allyl-CH), 5.07 (m, 2H, Allyl-CH), 4.72 (m, 1H, Dioxolane-CH), 4.52 (dd, \(^{3}J_{HH,\text{trans}} = 7.9\) Hz, \(^{3}J_{HH} = 8.4\) Hz, 1H, Dioxolane-CH), 4.07 (dd, \(^{2}J_{HH,\text{cis}} = 7.2\) Hz, \(^{3}J_{HH} = 8.5\) Hz, 1H, Dioxolane-CH), 1.61 (m, 2H, CH\(_2\)), 2.22 (m, 2H, CH\(_2\)), 2.00-1.70 (m, 2H, CH\(_2\)); \(^{13}\)C\(^{(1)}\)H) NMR (CDCl\(_3\), 303 K, 175 MHz, in ppm): 155.0 (C\(_q\)), 136.2 (Allyl-CH), 116.6 (Allyl-CH), 75.1 (Dioxolane-CH), 72.7 (Allyl-OCH\(_2\)), 69.0 (Dioxolane-CH), 66.4 (Dioxolane-OCH\(_3\)).

**tert-Butyl (2-oxo-1,3-dioxolan-4-yl)methyl)carbamate (5e).** The NMR data obtained agrees with the literature.\(^{44}\) \(^1\)H NMR (CDCl\(_3\), 303 K, 500 MHz, in ppm): 5.03 (br, 1H, NH), 4.80 (m, 1H, CH), 4.49 (dd, \(^{3}J_{HH,\text{trans}} = 8.8\) Hz, \(^{3}J_{HH} = 8.8\) Hz, 1H, Dioxolane-CH), 4.26 (dd, \(^{2}J_{HH,\text{cis}} = 6.8\) Hz, \(^{3}J_{HH} = 8.8\) Hz, 1H, Dioxolane-CH), 3.47 (dd, \(^{2}J_{HH} = 6.2\) Hz, \(^{3}J_{HH} = 4.4\) Hz, 2H, NCH\(_2\)), 1.43 (s, 9H, C(CH\(_3\))\(_3\)); \(^{13}\)C\(^{(1)}\)H) NMR (CDCl\(_3\), 303 K, 175 MHz, in ppm): 156.4 (Dioxolane-C\(_q\)), 154.8 (Carbamate-C\(_q\)), 80.6 (C(CH\(_3\))\(_3\)); 75.9 (CH), 66.8 (Dioxolane-CH\(_2\)), 42.3 (NCH\(_2\)), 28.3 (C(CH\(_3\))\(_3\)); Hi-Res mass (ESI+) calc. for \([\text{C}_8\text{H}_13\text{O}_3\text{N}^+\text{H}^+]\) 240.0842 found: 240.0846.

**O-tert-Butyl-N-allylcarbamate.** The synthesis was performed after a procedure of Teerawutgulrag and co-workers.\(^{45}\) A solution of allyl amine (3.00 g, 52.6 mmol, 1 equiv.) and triethyl amine (9.5 mL, 68.0 mmol, 1.3 equiv.) in dry DCM (10 mL) was cooled to 0 °C. After addition of di-tert-butyl decarboxate
(14.6 mL, 68.0 mmol, 1.3 equiv.) in portions, the mixture was stirred at RT over 18 h. The mixture was washed with NaOH (10 weight%, 20 mL) and the water layer extracted with ethyl acetate (3 × 50 mL). After the combined organic layers were dried over Na2SO4, the solvent was removed and the crude product purified by column chromatography (silica, n-hexane/ethyl acetate 9:1, Rf = 0.58) to obtain a colorless solid with 85% yield. (44.7 mmol, 7.03 g) 1H NMR (CDCl3, 303 K, 500 MHz, in ppm): 4.81 (br., 1H, Epoxide-CH2), 5.11 (m, 1H, Allyl-CH2), 4.75 (br., 1H, NH), 3.74 (s, 3H, NCH2), 3.05 (br., 1H, NCH2), 2.75 (dd, JHH = 4.2 Hz, JHN = 4.8 Hz, CH2-nitrogen), 2.57 (dd, JHH = 4.2 Hz, JHN = 4.8 Hz, CH2-nitrogen), 2.41 (s, 9H, C(CH3)3); 13C{1H} NMR (CDCl3, 303 K, 125 MHz, in ppm): 155.9 (Cq), 135.1 (Allyl-CH), 115.8 (Allyl-CH2), 79.5 (C(CH3)3); Hi-Res mass (ESI+) calcd. for [C8H15O2N+Na+] 180.1000 found: 180.1000.

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