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Coupling of CO_2 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,[4] PCP,[5] POP,[6] OCO,[7] SCS,[8] CNC,[9] or CCC[10] 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-workers[12] has shown that carbazole derived CNC coordinating ligands are valuable precursors for the design of effective catalysts[13] 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 CO_2 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

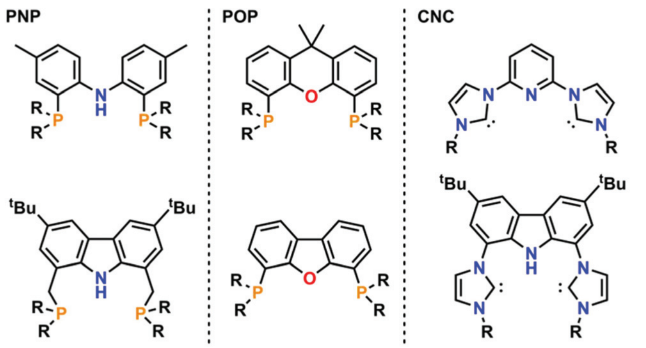

Fig. 1 Selected examples of the most commonly used pincer-type ligands scaffolds with PNP (left), POP (middle) and CNC (right) coordination modes.

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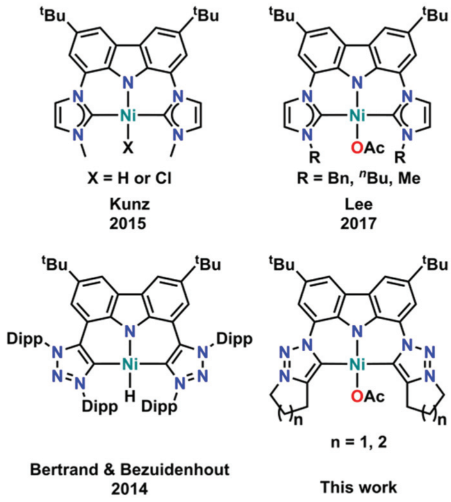


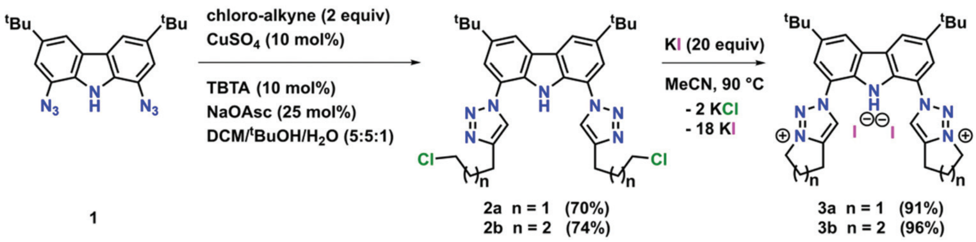
Fig. 2 Overview of all literature known carbene decorated nickel(II) carbazolide complexes, including the two new examples reported in this work.

NHC donors for mesoionic carbene (MIC) donors.[17j,18] Pioneering work by Sarkar and co-workers has shown that MIC-derived catalysts often exceed the catalytic potential of their NHC congeners.[18,19,20–26] Transferring this concept to carbazolide-derived mesoionic carbenes, Bertrand and Bezuidenhout reported the first CNC pincer-type MIC ligands in 2014 (Fig. 2, bottom left).[27] While this ligand was capable of stabilising a rare rhodium(I)–dioxygen adduct[28] as well as a rare T-shaped gold(I) complex,[29] its synthesis is tedious and requires the use of harmful and explosive reagents such as *tert*-butylhypochlorite and *in situ* generated 3-chlorotriazenes. Additionally, this synthetic route is limited by the availability of stable triazene derivatives, which means that it only serves to synthesise sterically demanding systems.

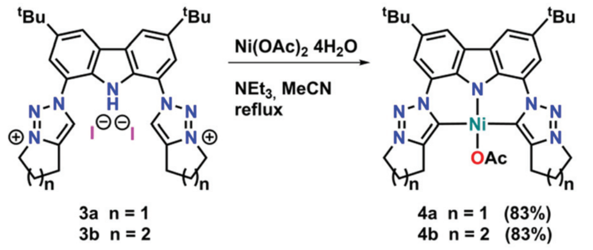
Aiming for a less hazardous synthetic protocol and reducing the steric bulk of carbazole-derived triazolium salts, we recently reported a tandem Finkelstein–cyclisation strategy which gave access to highly luminescent bis-*N*-fused triazolylidene carbazolide complexes of lithium and magnesium.[30] In this contribution we investigate the coordination behaviour of these novel carbazole functionalized triazolylidene ligands towards nickel(II) and their application in the copolymerisation of CO_2 with epoxides.

Results and discussion

To expand the versatility of our recently reported synthetic strategy to prepare bis(triazolylidene)-carbazolide ligands,[30] 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-pentyne and 1,8-diazido-3,6-di-*tert*-butyl-carbazole,[31] 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-5*H* 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-5*H* 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) $-CH_2Cl$ protons from δ = 3.69 ppm for **2a** to δ = 4.90 ppm for **3a**, and (iii) the coupling of this methylene group to the triazole nitrogen atoms ($\delta(^{15}N)$ = 266.6 ppm) as seen in the ^1H–^{15}N HMBC NMR spectrum (compare Fig. S10†). Finally, X-ray quality crystals[32] 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 $P\bar{1}$ 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-N*H* proton H10 to one of the iodide counterions (Fig. 3, left), in **3b** such an interaction is absent.[30] Apart from the hydrogen bonding, the structural parameters in **3a** reflect the ones in **3b**[30] and previously reported 1,2,3-triazolium salts.[20,22] A detailed discussion of



Scheme 1 Synthesis of *N*-fused triazolium salts **3a** and **3b** from the corresponding chloroalkyl-triazoles **2a** and **2b**, which can be obtained following standard CuAAC reaction conditions between 1,8-diazido-3,6-di-*tert*-butylcarbazole **1** and the corresponding chloro-alkynes 5-chloro-1-pentyne or 6-chloro-1-hexyne.



Scheme 2 Synthesis of the nickel(II) triazolylidene complexes **4a** and **4b**.

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(II) 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 $Ni(OAc)_2 \cdot 4H_2O$ in the presence of excess triethylamine at 80 °C (see Scheme 2). Despite the fact that **4a** and **4b** differ only by one methylene group, their solubility differs drastically. While complex **4b** is soluble in a range of coordinating, aromatic and halogenated solvents, **4a** does only dissolve to a minimal extent in halogenated or coordinating solvents, but is insoluble in aromatic solvents. Successful formation of the new triazolylidene nickel(II) complexes was supported by several features in the ^1H and $^{13}C\{^1H\}$ NMR spectra of the complexes: (i) the disappearance of the carbazole-N*H* and triazolium-5*H* resonances in the ^1H NMR spectra of the complexes (Fig. S11 and S16†) as well as the N*H* absorption band in the IR spectrum (Fig. S56 and S57†), (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 $^{13}C\{^1H\}$ NMR spectra of **4a** and **4b** (compare Fig. S12 and S17†), which are in a comparable range of previously reported nickel(II) triazolylidene complexes.[33,34] Additionally, a signal at δ = 177.7 ppm and δ = 177.1 ppm in the $^{13}C\{^1H\}$ 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 $P\bar{1}$ as either a water solvate (**4a**) or a dichloromethane solvate (**4b**). In both complexes the nickel(II) ion is in a slightly distorted square planar coordination environment, with N10–Ni1–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 τ'_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(II) ions.[14,27] The nickel–carbene carbon 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(II) triazolylidene complexes.[33,34] The intra ligand distances within the triazolylidene ring are in the expected region and comparable to previously reported triazolylidene complexes.[21–26,33,34] 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 (CO_2) are shown in Table 1. It is noteworthy that compared to the report by Lee and co-workers,

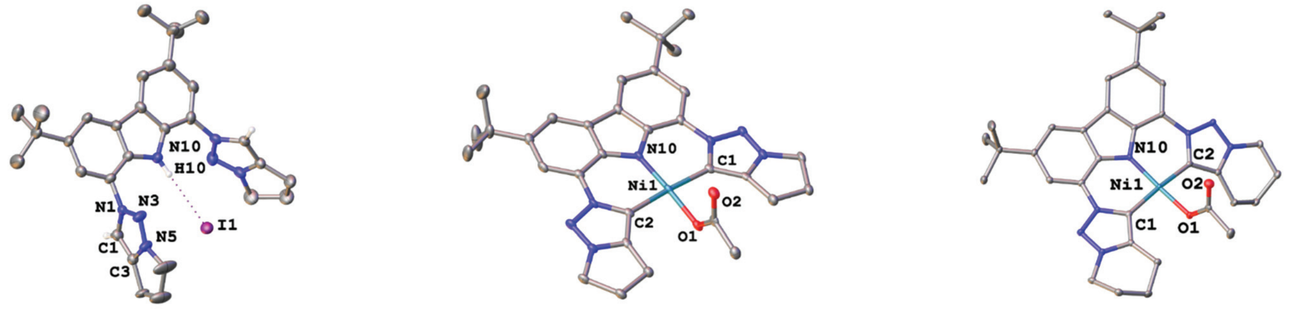


Fig. 3 Thermal ellipsoid plots of **3a**, **4a** and **4b** (left to right). Second iodide counteranion (**3a**), solvent atoms and hydrogen atoms have been omitted for clarity. Thermal ellipsoids are shown at a probability level of 50%.

Table 1 Overview of the performed catalytic reactions using pro-catalysts **4a** and **4b** as well as various epoxide monomers. All reactions were performed neat in a 2.77 mmol scale with 0.1 mol% catalyst and co-catalyst

Entry	Epoxide	Cat. (mol%)	Co-catalyst	Time [h]	*T* [°C]	$p\mathrm{CO_2}$ [bar]	Epoxide conv.[a] [%]	Ratio CC : PE[a]	TON[b,d]	TOF[c,d]
1	CHO	**4a** (0.5)	—	18	130	20	53	64 : 36	67	4
2	CHO	**4b** (0.5)	—	18	130	20	19	63 : 37	24	1
3	CHO	**4a** (0.25)	—	18	130	20	50	33 : 67	67	4
4	CHO	**4b** (0.25)	—	18	130	20	55	24 : 76	53	3
5[e]	CHO	**4a** (0.1)	—	18	130	20	38	15 : 85	58	3
6[e]	CHO	**4a** (0.1)	[PPN]Cl	18	130	20	46	43 : 57	195	11
7	CHO	**4b** (0.1)	—	18	130	20	69	8 : 92	55	3
8	CHO	**4b** (0.1)	[PPN]Cl	18	130	20	70	32 : 68	220	12
9	CHO	**4a** (0.1)	—	120	130	20	73	53 : 47	392	3
10	CHO	**4a** (0.1)	[PPN]Cl	120	130	20	>99	100 : 0	>999	8
11	CHO	**4b** (0.1)	—	120	130	20	95	78 : 22	739	6
12	CHO	**4b** (0.1)	[PPN]Cl	120	130	20	>99	93 : 7	930	8
13	CHO	**4a** (0.1)	[PPN]Cl	18	130	2	4	37 : 63	16	1
14	CHO	**4b** (0.1)	[PPN]Cl	18	130	2	7	27 : 73	19	1
15	CHO	—	—	18	130	20	85	0 : 100	0	0
16	CHO	—	[PPN]Cl	18	130	20	56	53 : 47	301	17
17	CHO	—	—	18	130	—	99	0 : 100	0	0
18[f]	GMPE	**4a** (0.1)	—	18	RT	20	0	—	0	0
19[f]	GMPE	**4a** (0.1)	[PPN]Cl	18	RT	20	0	—	0	0
20[f]	GMPE	**4a** (0.1)	—	18	80	20	0	—	0	0
21[f]	GMPE	**4a** (0.1)	[PPN]Cl	18	80	20	15	100 : 0	153	8
22	GMPE	**4a** (0.1)	—	18	130	20	41	100 : 0	411	23
23	GMPE	**4a** (0.1)	[PPN]Cl	18	130	20	>99	100 : 0	>999	55
24	GMPE	**4b** (0.1)	—	18	130	20	>99	100 : 0	>999	55
25	GMPE	**4b** (0.1)	[PPN]Cl	18	130	20	>99	100 : 0	>999	55
26	GMPE	—	—	18	130	20	0	—	0	0
27	GMPE	—	[PPN]Cl	18	130	20	11	100 : 0	110	6
28	AGE	**4a** (0.1)	—	18	130	20	73	100 : 0	733	41
29	AGE	**4a** (0.1)	[PPN]Cl	18	130	20	98	100 : 0	981	54
30	AGE	**4b** (0.1)	—	18	130	20	96	100 : 0	962	53
31	AGE	**4b** (0.1)	[PPN]Cl	18	130	20	98	100 : 0	975	54
32	E5H	**4a** (0.1)	—	18	130	20	52	100 : 0	519	29
33	E5H	**4a** (0.1)	[PPN]Cl	18	130	20	77	100 : 0	770	43
34	E5H	**4b** (0.1)	—	18	130	20	33	100 : 0	331	18
35	E5H	**4b** (0.1)	[PPN]Cl	18	130	20	84	100 : 0	839	47
36	*t*BOMC	**4a** (0.1)	—	18	130	20	>99	48 : 52	482	27
37	*t*BOMC	**4a** (0.1)	[PPN]Cl	18	130	20	>99	82 : 18	820	46
38	*t*BOMC	**4b** (0.1)	—	18	130	20	>99	64 : 36	638	35
39	*t*BOMC	**4b** (0.1)	[PPN]Cl	18	130	20	>99	81 : 19	808	45

[a] Determined by ^{1}H NMR. [b] TON = moles of CC formed by mole of catalyst. [c] TOF = TON per hour. [d] Both, TON and TOF were calculated on the basis of the epoxide conversion determined by ^{1}H NMR. [e] Reaction performed in a 3.06 mmol scale. [f] Performed in DCM.

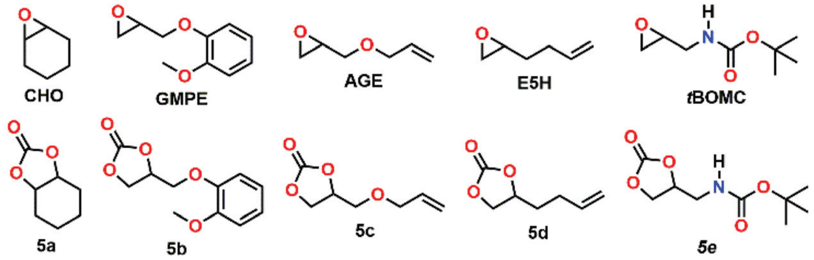


Fig. 4 Epoxides used for the coupling reaction with $\mathrm{CO_2}$. The corresponding cyclic carbonates **5a–5e** are listed underneath.

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,[35,36] recent literature reports show that nickel (II)-based catalysts can efficiently couple carbon dioxide and epoxides to the desired polycarbonates even at 20 bar.[37] In an initial check, wether **4a** and **4b** could be active (pro)-catalysts in the copolymerisation of CHO and CO_2, 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.[15] 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(II) complex, which is capable of performing efficient CC coupling at 1 bar and 100 °C.[38] 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),[39] in order to probe if the trends for cyclohexene oxide can be reproduced for other epoxides. Treating 3-(*o*-methoxyphenoxy)-1,2-epoxypropane (GMPE) (entries 18–27) under the same conditions as applied for our initial cyclohexene oxide studies (130 °C, 20 bar of CO_2 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*-butyl(oxiran-2-ylmethyl)carbamate (*t*BOMC). Similar to the glycidyl ethers, full conversion of the starting material was achieved for both catalysts **4a** and **4b**. However, for *t*BOMC 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)-carbazolide ligands by applying a straight-forward intramolecular cyclisation reaction, avoiding hazardous and explosive *tert*-butylhypochlorite. Furthermore, following a simple deprotonation protocol using only triethylamine as a base, we have been able to synthesise new nickel(II) complexes **4a,b**.

In contrast to their imidazolylidene Ni(II) congeners, which previously have been found to be good polymerisation catalysts,[15] 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 CO_2, and even subtle changes in catalyst design can have a large impact.[36] 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 $CDCl_3$ and CD_2Cl_2 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.

NMR spectra were collected at 298 K on a Bruker AV-500 or an Ascent 700 spectrometer using regular NMR tubes. All chemical shifts (δ) are reported in ppm. ^1H and ^{13}C chemical shifts were calibrated to residual solvent peaks. ^{15}N chemical shifts were calibrated to liquid ammonia (NH_3). Elemental analyses were performed using an Elementar vario microcube instrument at the University of Paderborn. 1,8-Diazido-3,6-di-*tert*-butylcarbazole **1**[31] and triazolium salt **3b**[30] were prepared following literature known procedures. All reagents were used as received without further purification.

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-pentyne (564 mg, 0.58 mL, 5.5 mmol, 2.3 equiv.), sodium ascorbate (125 mg, 0.6 mmol, 0.25 equiv.) and tris[(1-benzyl-1*H*-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 ($CDCl_3$, 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, $-CH_2Cl$), 3.06 (t, *J* = 7.3 Hz, 4H, CH_2), 2.32 (pent, *J* = 6.3 Hz, 4H, CH_2), 1.52 (s, 18H, $C(CH_3)_3$); $^{13}C\{^1H\}$ NMR ($CDCl_3$, 298 K, 125 MHz, in ppm): 146.6 (Aryl-C), 143.5 (Aryl-C), 130.3 (Aryl-C), 125.9 (Aryl-C), 121.5 (Aryl-C), 119.3 (Triazolyl-5C), 116.7 (Aryl-CH), 114.6 116.7 (Aryl-CH), 44.4 ($-CH_2Cl$), 35.1 ($C(CH_3)_3$), 32.1 ($C(CH_3)_3$), 31.9 (CH_2), 22.9 (CH_2); Hi-Res mass (ESI+) calcd. for $[C_{30}H_{37}N_7Cl_2 + H^+]$ 566.2566 found: 566.2567; Elemental analysis calcd. for $C_{30}H_{37}N_7Cl_2 \cdot 0.25\ CH_2Cl_2$ C 61.81 H 6.46 N 16.68 found C 62.01 H 6.62 N 16.53.

3,6-Di-*tert*-butyl-1,8-bis-(4,5,6-trihydropyrrolo-1,2,3-triazoliumyl)-carbazole-diiodide (3a). A mixture of 3,6-Di-*tert*-butyl-1,8-bis-(4-(3-chloropropyl)-1,2,3-triazolyl)-carbazole (932 mg, 1.64 mmol, 1 equiv.) and potassium iodide (5.46 g, 32.9 mmol, 20 equiv.) was heated in acetonitrile (50 mL) at 90 °C for 44 h. All volatiles of the reaction mixture were removed under reduced pressure. The remaining solid was extracted with dichloromethane (3 × 50 mL) and filtered. The filtrate was concentrated to 20 mL and added dropwise to a stirred solution of diethylether (300 mL). The precipitate was filtered off and washed with diethylether (100 mL) and *n*-pentane (30 mL). The beige-colored solid was dried *in vacuo* to yield the desired product in 91% yield (1.11 g, 1.49 mmol). ^1H NMR (CD_2Cl_2, 298 K, 500 MHz, in ppm): 10.97 (s, 1H, Carbazole-NH), 8.67 (s, 2 h, triazole-5H), 8.43 (d, *J* = 1.7 Hz, 2H, Aryl-H), 7.81 (d, *J* = 1.7 Hz, 2H, Aryl-H), 4.90 (t, *J* = 6.3 Hz, 4H, N-CH_2), 3.40 (t, *J* = 7.5 Hz, 4H, CH_2), 2.96 (m, 8H, CH_2), 1.50 (s, 18H, $C(CH_3)_3$; $^{13}C\{^1H\}$ NMR (CD_2Cl_2, 298 K, 125 MHz, in ppm): 149.2 (Aryl-C), 144.9 (Aryl-C), 133.2 (Aryl-C), 127.3 (triazolium-5C), 126.1 (Aryl-C), 121.4 (Aryl-CH), 121.2 (Aryl-CH), 119.9(Aryl-C), 52.5 (N-CH_2), 35.4 ($C(CH_3)_3$), 31.9 ($C(CH_3)_3$), 26.7 (CH_2), 23.9 (CH_2); Hi-Res mass (ESI+) calcd. for $[C_{30}H_{37}N_7]^{2+}$ 247.6555; found: 247.6566 Elemental analysis calcd. for $C30H_{37}N_7I_2 \cdot CH_2Cl_2$ C 44.62 H 4.71 N 11.75; found: C 44.46 H 4.88 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 $Ni(OAc)_2 \cdot 4H_2O$ (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 (CD_2Cl_2, 298 K, 700 MHz, in ppm): 8.24 (s, 2H, Aryl-H), 8.14 (s, 2H, Aryl-H), 4.48 (s, 4H, N-CH_2), 3.15 (s, 4H, CH_2), 2.74 (s, 4H, CH_2), 2.18 (s, 3H, acetate-CH_3), 1.50 (s, 18H, $C(CH_3)_3$); $^{13}C\{^1H\}$ NMR (CD_2Cl_2, 298 K, 125 MHz, in ppm): 177.7 (acetate-CO_2) 152.0 (triazolylidene-5C), 145.9 (Aryl-C), 140.8 (Aryl-C), 137.4 (Aryl-C), 127.9 (Aryl-C), 124.0 (Aryl-C), 116.9 (Aryl-CH), 111.2 (Aryl-CH), 48.8 (N-CH_2), 35.3 ($C(CH_3)_3$), 32.4 ($C(CH_3)_3$), 26.9 (CH_2), 25.8 (acetate-CH_3), 25.6 (CH_2); Hi-Res mass (ESI+) calcd. for $[C_{30}H_{34}N_7Ni]^+$ 550.2229; found: 550.2228. Elemental analysis calcd. for $C_{32}H_{37}N_7O_2Ni \cdot 0.9\ CH_2Cl_2$ C 57.53, H 5.69, N 14.28; found C 57.42, H 5.81, N 14.39.

(3,6-Di-*tert*-butyl-1,8-bis-(2,4,5,6-tetrahydropyridin-1,2,3-triazolylidene)-carbazolid) nickel(II) (4b). Triazolium salt **3a** (233 mg, 0.3 mmol, 1 equiv.) and $Ni(OAc)_2 \cdot 4H_2O$ (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 an orange solution with a fine white precipitate. 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 **4b**, which was isolated by filtration and dried in air to give **4b** as a free-flowing powder in a yield of 83%. (159 mg, 0.249 mmol) ^1H NMR (CD_2Cl_2, 298 K, 700 MHz, in ppm): 8.23 (s, 2H, Aryl-H), 8.15 (s, 2H, Aryl-H), 4.49 (s, 4H, N-CH_2), 3.26 (s, 4H, CH_2), 2.15 (s, 4H, CH_2), 2.08 (s, 3H, acetate-CH_3), 1.96 (s, 4H, CH_2), 1.51 (s, 18H, $C(CH_3)_3$); $^{13}C\{^1H\}$ NMR (CD_2Cl_2, 298 K, 125 MHz, in ppm): 177.1 (acetate-CO_2), 146.9 (triazolyldiene-5C), 145.0 (Aryl-C), 140.7

(Aryl-C), 137.5 (Aryl-C), 127.9 (Aryl-C), 123.5 (Aryl-C), 116.9 (Aryl-CH), 111.5 (Aryl-CH), 48.8 (N-CH_2), 35.3 ($C(CH_3)_3$), 32.5 ($C(CH_3)_3$), 25.3 (acetate-CH_3), 24.4 (CH_2), 22.5 (CH_2), 20.8 (CH_2); Hi-Res mass (ESI+) calcd. for $[C_{32}H_{38}N_7Ni]^+$ 578.2542; found: 578.2578. Elemental analysis calcd. for $C_{34}H_{41}N_7O_2Ni\cdot0.5\ CH_2Cl_2$ C 60.86, H 6.22, N 14.40; found C 60.79, H 6.48, N 14.18.

General procedure for the cyclisation to products 5a–e. In a GC-vial with a magnetic stir bar a mixture of the epoxide (2.77 mmol, 1000 eq.), the catalyst (2.77 μmol; 1 eq.) and the cocatalyst (2.77 μmol; 1 eq.) was given in an autoclave. After a pressure of 20 bar of CO_2 was applied, the reaction was stirred at 130 °C for 18 h. The reaction was quenched by cooling with an ice bath and carefully releasing the excess of CO_2. Immediately an NMR sample was taken from the mixture, measured and the remaining mixture diluted with $CHCl_3$ and precipitated from MeOH to isolate eventually formed polycarbonate. Please note that in none of our experiments PC could be precipitated. Epoxide conversion was determined from the integrals in the proton NMR spectra of the reaction mixture. Using the Integrals of the formed cyclic carbonate I_{CC}, polyether I_{PE} and the residual monomer $I_{Monomer}$ and the following formula:

$$\text{Conv.} = \frac{I_{CC} + I_{PE}}{I_{CC} + I_{PE} + I_{Monomer}}$$

CHO. The crude product was analyzed by ^1H NMR spectroscopy in deuterated chloroform. Therefore, the determination of the conversions where done by the methanetriyl resonances from cyclohexene oxide (dd, δ = 3.12 ppm), polyether linkages (br., δ = 3.70–3.20 ppm), and cyclic carbonate (multiplet, δ = 4.67 ppm, *cis* cyclic carbonate).

GMPE. The crude product was analyzed by ^1H NMR spectroscopy in deuterated chloroform. Therefore, the determination of the conversions where done by the methanetriyl resonances from glycidyl methoxyphenyl ether (dd, δ = 3.36 ppm), and cyclic carbonate (multiplet, δ = 5.24 ppm, *cis* cyclic carbonate).

AGE. The crude product was analyzed by ^1H NMR spectroscopy in deuterated chloroform. Therefore, the determination of the conversions where done by the methanetriyl resonances from allyl glycidyl ether (dd, δ = 3.15 ppm), and cyclic carbonate (multiplets, δ = 4.81 ppm, *cis* cyclic carbonate).

E5H. The crude product was analyzed by ^1H NMR spectroscopy in deuterated chloroform. Therefore, the determination of the conversions where done by the methanetriyl resonances from 1,2-epoxyhex-5-ene (dd, δ = 2.93 ppm), and cyclic carbonate (multiplet, δ = 4.72 ppm, *cis* cyclic carbonate).

***t*BOMC.** The crude product was analyzed by ^1H NMR spectroscopy in deuterated chloroform. Therefore, the determination of the conversions where done by the epoxide methylene resonances from *tert*-butyl(oxiran-2-ylmethyl)carbamate (dd, δ = 2.54 ppm, and dd, δ = 2.72 ppm), and cyclic carbonate (dd, δ = 4.28 ppm, and dd, δ = 4.51 ppm). Several additional resonances could be observed but the substance/substances causing these could not be isolated.

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] ^1H NMR ($CDCl_3$, 303 K, 500 MHz, in ppm): 4.67 (m, 2H, CH), 1.89 (dd;$^3J_{HH}$ = 5.4 Hz, $^3J_{HH}$ = 10.8 Hz, 4H, CH_2), 1.61 (m, 2H, CH_2), 1.43 (m, 2H, CH_2); $^{13}C\{^1H\}$ NMR ($CDCl_3$, 303 K, 175 MHz, in ppm): 155.4 (C_q), 75.8 (CH), 26.9 (CH_2), 19.3 (CH_2); Hi-Res mass (ESI+) calcd. for $[C_8H_{15}O_2N + H^+]$ 143.0703 found: 143.0716.

4-((2-methoxyphenoxy)methyl)-1,3-dioxolan-2-one (5b). The NMR data obtained agrees with the literature.[41] ^1H 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 (d, $^3J_{HH}$ = 4.3 Hz, 2H, OCH_2), 3.84 (s, 3H, OCH_3); $^{13}C\{^1H\}$ NMR ($CDCl_3$, 303 K, 175 MHz, in ppm): 155.8 (Dioxolane-C_q), 150.6 (Aryl-C_q), 147.6 (Aryl-C_q), 123.6 (Aryl-CH), 121.2 (Aryl-CH), 117.0 (Aryl-CH), 112.0 (Aryl-CH), 74.6 (Dioxolane-CH), 69.5 (OCH_2), 66.5 (Allyl-CH_2),56.0 (OCH_3); Hi-Res mass (ESI+) calcd. for $[C_8H_{15}O_2N + H^+]$ 224.0685 found: 224.0688.

4-((Allyloxy)methyl)-1,3-dioxolan-2-one (5c). The NMR data obtained agrees with the literature.[42] ^1H NMR ($CDCl_3$, 303 K, 500 MHz, in ppm): 5.86 (m, 1H, Allyl-CH), 5.28 (m, 1H, Allyl-CH_2), 5.22 (m, Allyl-CH_2), 4.81 (m, 1H, Dioxolane-CH), 4.49 (dd, $^2J_{HH,trans}$ = 8.4 Hz, $^3J_{HH}$ = 8.4 Hz, 1H, Dioxolane-CH_2), 4.39 (dd, $^2J_{HH,cis}$ = 6.1 Hz, $^3J_{HH}$ = 8.4 Hz, 1H, Dioxolane-CH_2), 4.05 (m, 2H, Allyl-OCH_2), 3.68 (m, 2H, Dioxolane-CH_2); $^{13}C\{^1H\}$ NMR ($CDCl_3$, 303 K, 175 MHz, in ppm): 155.0 (C_q), 133.8 (Allyl-CH), 118.0 (Allyl-CH_2), 75.1 (Dioxolane-CH), 72.7 (Allyl-OCH_2), 69.0 (Dioxolane-CH_2), 66.4 (Dioxolane-OCH_2).

4-(But-3-en-1-yl)-1,3-dioxolan-2-one (5d). The NMR data obtained agrees with the literature.[43] ^1H NMR ($CDCl_3$, 303 K, 500 MHz, in ppm): 5.78 (m, 1H, Allyl-CH), 5.07 (m, 2H, Allyl-CH_2), 4.72 (m, 1H, Dioxolane-CH), 4.52 (dd, $^2J_{HH,trans}$ = 7.9 Hz, $^3J_{HH}$ = 8.4 Hz, 1H, Dioxolane-CH_2), 4.07 (dd, $^2J_{HH,cis}$ = 7.2 Hz, $^3J_{HH}$ = 8.5 Hz, 1H, Dioxolane-CH_2), 1.61 (m, 2H, CH_2), 2.22 (m, 2H, CH_2); 2.00–1.70 (m, 2H, CH_2); $^{13}C\{^1H\}$ NMR ($CDCl_3$, 303 K, 175 MHz, in ppm): 155.0 (C_q), 136.2 (Allyl-CH), 116.6 (Allyl-CH_2), 75.1 (Dioxolane-CH), 72.7 (Allyl-OCH_2), 69.0 (Dioxolane-CH_2), 66.4 (Dioxolane-OCH_2).

***tert*-Butyl ((2-oxo-1,3-dioxolan-4-yl)methyl)carbamate (5e).** The NMR data obtained agrees with the literature.[44] ^1H NMR ($CDCl_3$, 303 K, 500 MHz, in ppm): 5.03 (br., 1H, NH), 4.80 (m, 1H, CH), 4.49 (dd, $^2J_{HH,trans}$ = 8.8 Hz, $^3J_{HH}$ = 8.8 Hz, 1H, Dioxolane-CH_2), 4.26 (dd, $^2J_{HH,cis}$ = 6.8 Hz, $^3J_{HH}$ = 8.8 Hz, 1H, Dioxolane-CH_2), 3.47 (dd, $^3J_{HH}$ = 6.2 Hz, $^4J_{HH}$ = 4.4 Hz, 2H, NCH_2), 1.43 (s, 9H, $C(CH_3)_3$); $^{13}C\{^1H\}$ 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+) calcd. for $[C_8H_{15}O_2N + Na^+]$ 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 decarbonate

(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 Na_2SO_4, the solvent was removed and the crude product purified by column chromatography (silica, *n*-hexane/ethyl acetate 9 : 1, R_f = 0.58) to obtain a colorless solid with 85% yield. (44.7 mmol, 7.03 g) ^{1}H NMR ($CDCl_3$, 303 K, 500 MHz, in ppm): 5.84 (m, 1H, Allyl-CH), 5.18 (m, 1H, Allyl-CH_2), 5.11 (m, 1H, Allyl-CH_2), 4.75 (br., 1H, NH), 3.74 (s, 2H, NCH_2), 1.45 (s, 9H, $C(CH_3)_3$); $^{13}C\{^1H\}$ NMR ($CDCl_3$, 303 K, 175 MHz, in ppm): 155.9 (C_q), 135.1 (Allyl-CH), 115.8 (Allyl-CH_2), 79.5 ($C(CH_3)_3$), 43.2 (NCH_2), 28.5 ($C(CH_3)_3$); Hi-Res mass (ESI+) calcd. for $[C_8H_{15}O_2N + Na^+]$ 180.1000 found: 180.1000.

***O-tert*-Butyl-*N*-(oxiran-2-ylmethyl) carbamate (*t*BOMC).** The synthesis was performed after a procedure of Teerawutgulrag and co-workers.[45] To a cooled solution of *O-tert*-butyl-*N*-allyl-carbamate (10.00 g, 63.6 mmol, 1 equiv.) in dichloro-methane (500 mL) at 0 °C was *meta*-chlorperbenzoic acid (44.15 g, 50–55%, 127.2 mmol, 2.0 equiv.) in portions. The mixture was stirred at RT for 18 h before washed with saturated sodium sulfite solution (2 × 130 mL) and saturated sodium bicarbonate solution (2 × 150 mL). The water layers were extracted with ethyl acetate (3 × 125 mL), the combined organic layers dried over Na_2SO_4 and the solvent removed under reduced pressure. The crude product was purified by column chromatography (silica, *n*-hexane/ethyl acetate 4 : 1, R_f = 0.33) to yield in 81% of a slightly yellow oil. (51.5 mmol, 8.92 g) ^{1}H NMR ($CDCl_3$, 303 K, 500 MHz, in ppm): 4.81 (br., 1H, NH), 3.47 (br, 1H, N-CH_2), 3.18 (m, 1H, Epoxide-CH), 3.05 (br., 1H, NCH_2), 2.75 (dd, $^2J_{HH}$ = 4.7 Hz, $^3J_{HH,trans}$ = 4.2 Hz, 1H, Epoxide-CH_2), 2.57 (dd, $^2J_{HH}$ = 4.8 Hz, $^3J_{HH,cis}$ = 2.7 Hz, 1H, Allyl-CH_2), 1.42 (s, 9H, $C(CH_3)_3$). $^{13}C\{^1H\}$ NMR ($CDCl_3$, 303 K, 175 MHz, in ppm): 155.9 (C_q), 79.6 ($C(CH_3)_3$), 50.9 (Epoxide-CH), 45.1 (NCH_2), 41.8 (Epoxide-CH_2), 28.5 ($C(CH_3)_3$); Hi-Res mass (ESI+) calcd. for $[C_8H_{15}O_2N + Na^+]$ 196.0944 found: 196.0950.

Conflicts of interest

There are no conflicts to declare.

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