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Amine-Responsive Disassembly of Au(I)-Cu(I) Double Salts for the Oxidative Carbonylation

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Abstract: Herein, a sensitive amine-responsive disassembly of self-assembled Au(I)-Cu(I) double salts was observed and its utilization for the synergistic catalysis was further enlightened. Investigation of the disassembly of $[\text{Au}(\text{NHC})_2][\text{Cu}_2]$ revealed the contribution of Cu-assisted ligand exchange of N-heterocyclic carbene (NHC) by amine in $[\text{Au}(\text{NHC})_2]^+$ and the capacity of $[\text{Cu}_2]^-$ on the oxidative step. By integrating the implicative information coded in the responsive behaviour and inherent catalytic functions of d^{10} metal complexes, we have developed a novel catalyst for the oxidative carbonylation of amines. The advantages of this protocol were clearly reflected on mild reaction conditions and the significantly expanded scope (51 examples); both primary and steric secondary amines can be employed as substrates. The cooperative reactivity from Au and Cu centers, as an indispensable prerequisite for the excellent catalytic performance, was validated in the synthesis of (un)symmetric ureas and carbamates.

Expanding applications of supramolecular organometallic complexes that bear diverse coordination chemistry is a fanatical pursuit.^[1] As an attractive family of functional materials, d^8/d^{10} double salts with infinite metallic chains have engendered extensive attention, especially for potential use in emission-relevant fields, such as detection, sensing and optical devices.^[2] Compared to the considerable progress on the fabrication of self-assembled double salts, researches on disassembly processes are relatively sparse.^[3] This situation is somewhat surprising since the metallophilic interactions that involved in the double salts formation are weak and susceptible to the influence of external stimuli,^[4] resulting in frequently encountered disassembly behaviours. Considering the disassembly of supramolecular

metal complexes is often associated with subtle changes in the metal-metal/ligand bonds,^[5] we envisage that this dynamic nature could be harnessed for catalysis, in which the coordination state of metal centers play a vital role for the reactivity.^[6] Despite numerous reports have highlighted the intrinsic catalytic functions of d^8/d^{10} metal complexes,^[7] there no precedent for the fabrication of sophisticated catalytic systems based on the understanding of disassembly of metallophilic double salt.

Herein, on the basis of d^{10} double salts constructed by our former developed facile modular protocol,^[3a-c] we report our finding and understanding on the amine-responsive disassembly of self-assembled Au(I)-Cu(I) double salts and their applications in catalysis. The investigation of disassembly phenomenon inferred the contribution of Cu-assisted ligand exchange of N-heterocyclic carbene (NHC) by amine in $[\text{Au}(\text{NHC})_2]^+$ and the capacity of $[\text{Cu}_2]^-$ on the oxidative step. By integratedly using the implicative information and inherent catalytic functions of d^{10} metal complexes, we apply these heterobimetallic complexes for the oxidative carbonylation of amines to (un)symmetric ureas and carbamates (51 examples). The remarkable cooperative reactivity between Au and Cu rendered the transformation of primary and steric secondary amines proceed smoothly under mild conditions. Regarding the monomer of these two coinage metals complexes are practically unreactive under the same conditions, the present system represents an illustration for synergistic catalysis.^[8]

The synthesis started from an anion metathesis reaction between $[\text{Au}(\text{NHC})_2]\text{Cl}$ (cation, $[\text{Au}(\text{NHC})_2]\text{BF}_6$ could also be used as cation precursors, **C1**) and $\text{Bu}_4\text{N}[\text{Cu}_2]$ (anion, **A1**), by mixing the methanol solution of the cation and the acetonitrile solution of the anion (Figure 1, the self-assembled materials named as **C1-A1**). In contrast to the colourlessness of both cation **C1** and anion **A1** precursors under UV irradiation, the emission from **C1-A1** was brightly yellow, confirming the existence of $d^{10} \cdots d^{10}$ interactions.

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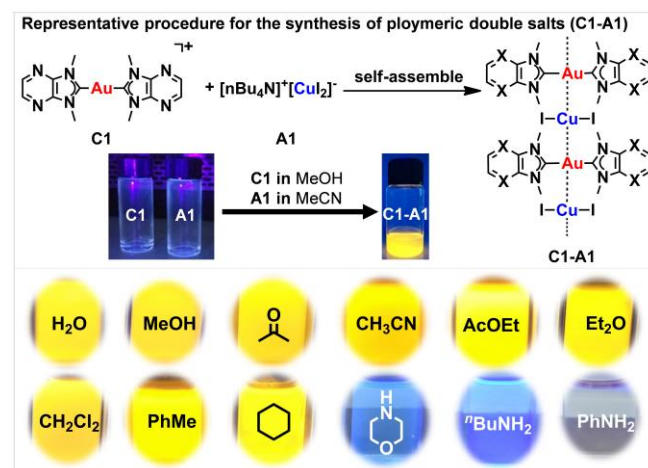


Figure 1. The synthesis of polymeric Au(I)-Cu(I) double salts and the colour of **C1-A1** in various suspension under UV irradiation ($\lambda = 365 \text{ nm}$).

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The colour remained intact upon the exposure to polar and non-polar solvents such as water, methanol, acetone, acetonitrile, ethyl acetate, ethyl ether, methylene chloride, toluene, and cyclohexane. Interestingly, in morpholine and butylamine solutions the colour of the suspension changed to light blue, whereas in aniline a transparent solution was formed (Figure 1; Figure S1-S2 for luminescence spectra).

The salient amine-responsive behaviour of Au(I)-Cu(I) double salts drew our attention and was investigated by spectroscopic techniques. The solid sample exhibited intense phosphorescence at 590 nm, while a characteristic peak at 390 nm attributed to free or azolium-form NHC ligand (see reference peak in Figure S3) emerged in morpholine (Figure 2a) and butylamine (Figure S4) solutions. The formation of $[\text{Au}(\text{NHC})(\text{morpholine})]^+$ was verified by observing the molecular ion peak of $m/z = 432$ on the mass spectrum (Figure S5). In aniline solution, the peak at 590 nm faded out without the peak arising at 390 nm (Figure S6), hinting that the dissociation occurred without ligand exchange. Intriguingly, without the moiety of **A1**, no measurable emission signal of NHC ligand of **C1** was observed. But once ${}^t\text{Bu}_4\text{N}[\text{CuI}_2]$ was introduced, the signal ($\lambda_{\text{max}} = 390 \text{ nm}$) rose up within minutes (Figure 2b), indicating that the presence of $[\text{CuI}_2]^-$ was critical in mediating the ligand exchange on the fragment of $[\text{Au}(\text{NHC})_2]^+$. Analysis of single-crystal structure (Figure 2c) showed that Au-C (carbene C) bond distances in $[\text{Au}(\text{NHC})_2]\text{Cl}$ (2.006 and 2.017 Å) and $[\text{Au}(\text{NHC})_2]\text{BF}_6$ (2.005 Å) are relatively shorter than that in $[\text{Au}(\text{NHC})_2][\text{CuI}_2]$ (2.014, 2.017, and 2.027 Å). These X-ray crystallographic data illustrate that intermolecular Au-Cu interactions weaken the interaction between Au-C (carbene), which would contribute to the essential ligand exchange step.

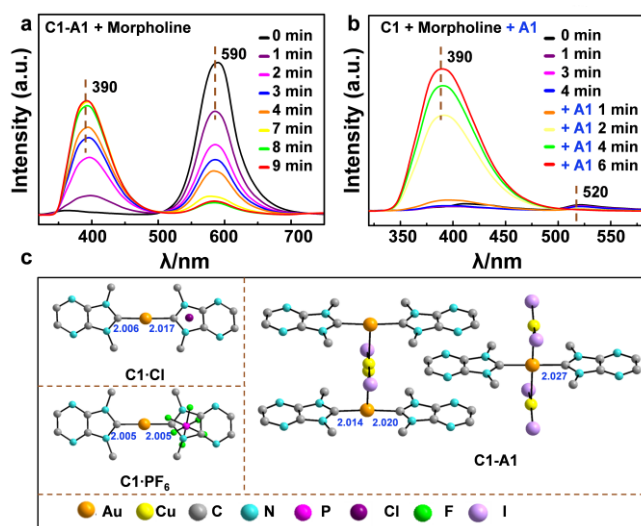


Figure 2. The time-resolved photoluminescent behaviors of **C1-A1** in amines and crystal structure of **C1** ($[\text{Au}(\text{NHC})_2]\text{Cl}$ and $[\text{Au}(\text{NHC})_2]\text{BF}_6$); both of them can be used as cation precursors for the preparation of double salts and **C1-A1**.

By X-ray absorption spectroscopy (XAS),^[9] the absorption edge position of fresh **C1-A1** solid and **C1-A1** in morpholine under either nitrogen or aerobic atmospheres indicated the unchanged oxidation state of Au (Figure 3a). Oppositely, the absorption edge on Cu K-edge XANES was shifted to higher energy when the solution was exposed to air, suggesting Cu(I) species were oxidized to Cu(II), then the absorption edge was shifted back to lower energy. Further heating this solution sample to 60 °C, the

absorption edge curve was shifted back to its original position, hinting the recovery of Cu(I) species (Figure 3b). Then, the electron paramagnetic resonance (EPR) was employed to track the transformation of morpholine during copper redox process.^[10] Two kinds of signals were observed in the toluene solution dissolving **C1-A1** and morpholine in the open air (Figure 3c,d). The Cu(II) signal ($g_z = 2.14$, $g_y = 2.11$, $g_x = 2.08$) and the sign of N-centred radical cation ($g = 2.006$, $A_N = 14\text{G}$, $A_H = 24\text{G}$, linewidth = 4G) was observed simultaneously (Figure 3c). When 5,5-dimethyl-1-pyrroline N-oxide (DMPO) was added, a N-centred radical trapped by DMPO ($g = 2.007$, $A_{N1} = 13.7\text{G}$, $A_H = 15.92\text{G}$, $A_{N2} = 2.0\text{G}$) was observed (see details in SI Figure S7).^[11] The swing of absorption edge on Cu K-edge XANES and observation of oxidized morpholine N-centred radical cation on X-band EPR spectra signified the occurrence of oxidation-reduction cycle on Cu complex in the presence of morpholine.

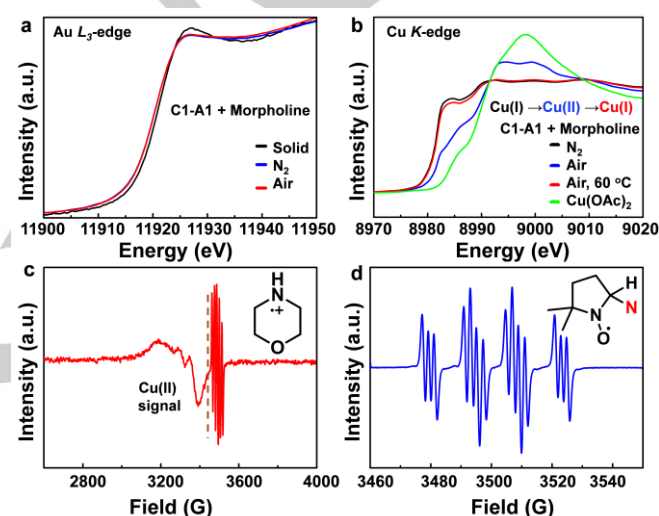


Figure 3. XANES spectra of Au and Cu under different atmospheres conditions (a, b); EPR spectra of **C1-A1** (X band, 9.8 GHz, 293 K); **C1-A1** (1 mg) and morpholine (0.5 mmol) dissolved in toluene.

Afore mentioned indications transpired from spectroscopic characterization, concerning the distinct capacity of cation $[\text{Au}(\text{NHC})_2]^+$ on interacting with amine and speciality of anion $[\text{CuY}_2]^-$ on aerobic oxidation, encouraged us to scrutinize the potential synergism of these Au(I)-Cu(I) double salts in metal catalysis. Given the well-established CO coordination ability of coinage metal complexes,^[12] the catalytic oxidative carbonylation of amines,^[13] a promising alternative to implementing the phosgene-free synthesis of urea,^[14] was targeted as an ideal benchmark reaction. In a preliminary verification, we found that aliphatic amines (morpholine and butylamine) gave an exceptional outcome to afford the desired ureas with **C1-A1** as the catalyst, whereas no reaction proceeded with aniline (Figure S8). These results implied the essentiality of Cu-assisted ligand exchange of N-heterocyclic carbene (NHC) by amine in $[\text{Au}(\text{NHC})_2]^+$ for the substrate activation.

When different d^{10} double salts with various cations and anions were employed, the significant synergistic effect of **C1-A1**^[15] from the delicate cooperation between Au and Cu as well as the indispensable contributions of NHC and iodide ligands on the activity was highlighted.^[16] Under the same conditions, **C1-A2** and **C2-A1** resulted in low yields, whereas **C1-A3**, **C2-A2**, **C2-A3** did not promote the reaction at all. No or very poor conversion were

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identified for using $[\text{Au}_2]^+$ (**C1-A4** and **C2-A4**), $[\text{Ag}_2]^+$ (**C1-A5**), $[\text{Ag}(\text{NHC})_2]$ (**C3-A1** and **C4-A1**), monomeric complexes **C1**, **A1**, and **CuI**. For **C1-A1**, notably, the catalyst can be reassembled into supramolecular complexes after the reaction and reused for at least four runs without appreciable loss of the original activity (Figure S9-S10).

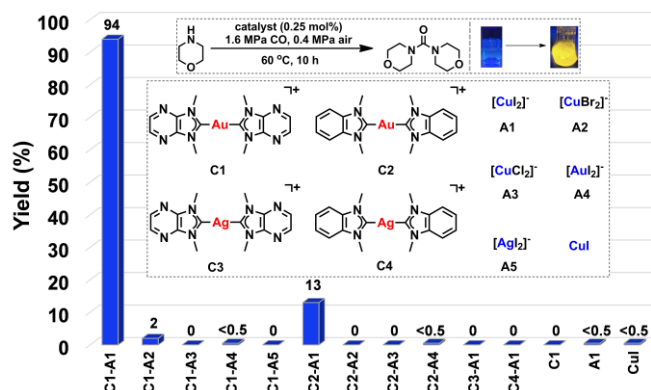
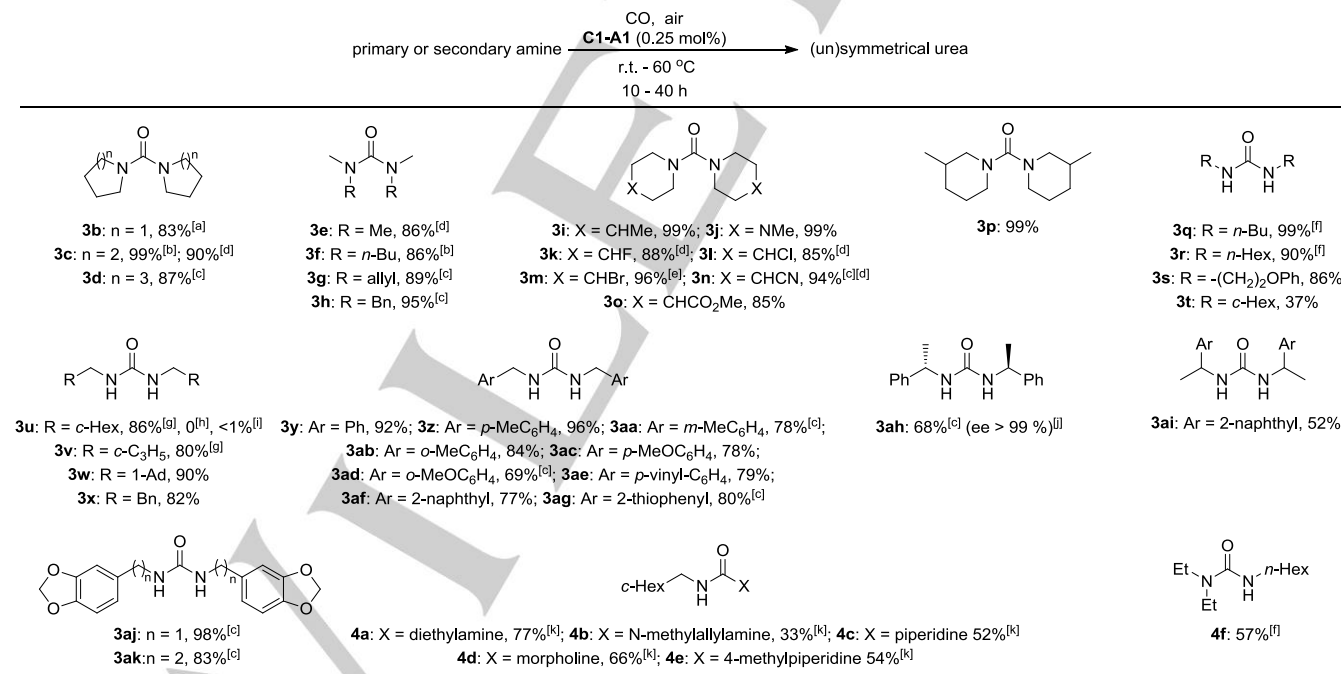


Figure 4. Oxidative carbonylation of morpholine. Reaction conditions: catalyst (0.25 mol% **Cn-Am**: Au-Cu, Au-Ag, Ag-Cu, Au-Au), **1a** (0.5 mmol, 1.0 equiv.), toluene (2 mL), 60 °C, CO (1.6 MPa), air (0.4 MPa), 10 h, Yield determined by GC with biphenyl as the calibrated internal standard.

The cooperative reactivity of Au and Cu facilitated the catalytic

Table 1. The synthesis of (un)symmetrical ureas



Reaction conditions: For symmetrical ureas: **C1-A1** (0.25 mol%), toluene (2 mL), amine (0.5 mmol), 60 °C, CO (1.6 MPa), air (0.4 MPa). Unless other stated, 24 h for secondary amines and 40 h for primary amines, isolate yield. [a] 30 h. [b] 12 h. [c] **C1-A1** (0.5 mol%). [d] Corresponding secondary ammonium chloride with 2 equiv. Na₂CO₃. [e] 4-Bromopiperidinium bromide with 2 equiv. Na₂CO₃. [f] Room temperature. [g] 24 h. [h] **C1** instead of **C1-A1**. [i] **A1** instead of **C1-A1**. [j] ee value of product was determined by HPLC with a chiral column. [k] for unsymmetrical ureas: **C1-A1** (0.25 mol%), toluene (5 mL), 0.6 mmol secondary amine, 0.5 mmol primary amine (1.0 equiv.), 50 °C, CO (3.6 MPa), air (0.4 MPa), 40 h, yields were determined by GC, biphenyl as calibrated internal standard. Ad = adamantyl.

Also, the present oxidative carbonylation system of amine shows promise for the synthesis of carbamates with alcohol as

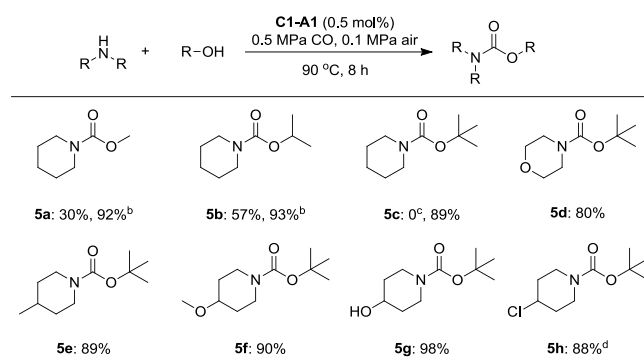
efficiency on the oxidative carbonylation of an assortment of amines. Structurally diverse secondary amines reacted with CO/air to afford tetrasubstituted ureas in excellent yields (**3b-p**). This performance is remarkable, as commonly, transition metal-catalyzed carbonylation of secondary amines selectively produces formamides or gives no conversion at all.^[17] Such mild oxidative conditions allowed the easily-oxidized olefin group (**3g**) and secondary benzylamine^[18] (**3h**) as well as those reactive functional groups including aliphatic tertiary amine, halogen, cyano groups and carboxylic ester (**3j-o**) to stay intact. The conversion of primary amines to disubstituted ureas also proceeded well with this protocol (**3q-ak**). The synergism between Au and Cu was still manifested on primary amine (**3u**). The reactions of aliphatic amines went smoothly (**3q-x**); *n*-butylamine (**3q**) and *n*-hexylamine (**3r**) were even able to be transformed at room temperature. Various substituted benzylamines (**3y-3ai**) could be converted to the corresponding ureas in high yields. Mild conditions tolerated the highly strained cyclopropyl group (**3v**), vinyl (**3ae**) and thiophene ring (**3ag**) well. Chiral center in the vicinity of the amino group was retained (**3ah**). Since both primary and secondary amines were reactive, the notoriously difficult carbonylative cross-coupling between two different amines represents a challenging task. Gratifyingly, the preparation of unsymmetrical ureas in moderate to good selectivity was possible if the primary amine was carbonylated in the presence of slightly excess secondary amine (**4a-4f**).

nucleophiles (Table 2). Strikingly, the notoriously difficult reaction with tert-butanol as starting materials perform smoothly under the

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optimized condition, affording N-Boc protection amines.^[19] As the direct conversion of amines, CO/O₂ with steric tertiary alcohols has proven to be difficult and no effective catalyst systems reported, till recently, the synthesis of N-Boc-protected amines is via the reaction of secondary amines with (Boc)₂O,^[20] which is commonly prepared by the reaction of toxic phosgene or its derivatives with tert-butanol.^[21] Thus in consideration of the whole process, the preparation of N-Boc protected amines by (Boc)₂O belongs to a phosgene-mediated route; beyond that more than a half of atoms in (Boc)₂O were wasted as by-products (tert-butanol and carbon dioxide). Alternatively, the ready availability of the substrates (amines, tert-butanol, CO and air) makes this [Au(NHC)₂][CuI₂]-catalyzed carbonylative protocol attractive for generating a series of N-Boc protected amines derivatives.

Table 2. The synthesis of carbamates



Reaction conditions: **C1-A1** (0.5 mol%), alcohol (5 mL), amine (0.5 mmol), 90 °C, CO (0.5 MPa), air (0.1 MPa), 8 h; [b] 24 h; [c] **C1** or **A1** instead of **C1-A1**; [d] Corresponding secondary ammonium chloride with 2 equiv. Na₂CO₃.

In summary, a sensitive amine-responsive disassembly of self-assembled Au(I)-Cu(I) double salts was unearthed. Inspired by this discovery and relevant spectroscopic hints, the oxidative carbonylation of amine catalyzed by these metal complexes was explored. Though the precise interactions of Au(I)-Cu(I) complexes during the reaction remain to be clarified at this stage, it is rationally considered that the cooperation of Au and Cu centers in the activation of amine and oxidative carbonylation step play an integrated role for the excellent catalytic performance in the synthesis of various ureas and carbamates. Currently, the elaborated investigation of the nature of this catalytic system is in progress.

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Conflict of interest

The authors declare no conflict of interest.

Keywords: amine-responsive, synergistic catalysis, supramolecular chemistry, oxidative carbonylation, urea and carbamates

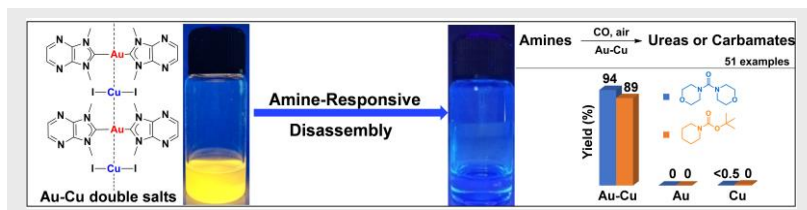
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COMMUNICATION



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**Amine-Responsive Disassembly
of Au(I)-Cu(I) Double Salts for the
Oxidative Carbonylation**

Disassembly for catalysis: A sensitive amine-induced disassembly of self-assembled Au(I)-Cu(I) double salts was observed. Stimulated by the finding and understanding on this dynamic feature, a synergistic catalytic system for the oxidative carbonylation of primary and secondary amines (51 examples) to ureas and carbamates, has been developed.