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Fast equilibrium of zwitterionic adduct formation in reversible fixation—release system of CO₂ by amidines under dry conditions

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ABSTRACT

We investigated the fixation of CO₂ by several amidines in solution and found that simple monocyclic amidines fixed CO₂ under dry conditions to quantitatively afford the corresponding bicarbonates through hydrolysis of the zwitterionic adducts by adventitious water. In contrast, linear amidines did not form the bicarbonates under the same conditions, while 1,8-diazabicyclo[5.4.0]undec-7-ene (DBU) could not effectively trap CO₂. The CO₂ fixed by the monocyclic amidines was quantitatively released by argon bubbling at a temperature as low as 60 °C. The CO₂ fixation—release process could be repeated several times without loss of the high efficiency.

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1. Introduction

The increasing concentration of carbon dioxide (CO_2) in the atmosphere has resulted in the rising global temperature and serious environmental problems, while CO_2 is also regarded as a cheap, green C1 resource.¹ Development of efficient methods for CO_2 adsorption has thus become an important research area in recent years. One of the most well-researched processes for CO_2 capture is based on chemically reversible CO_2 fixation by primary or secondary amines at ambient temperature to give ammonium carbamates, and CO_2 release from the ammonium carbamates upon heating.² Styrene- or siloxane-based polymers bearing amino groups have been also studied for application to CO_2 fixation.³ However, these processes require 2 equiv of amines for CO_2 fixation and high temperature for CO_2 release.^{2,3}

The use of amidines and guanidines, such as 1,8-diazabicyclo [5.4.0]undec-7-ene (DBU) for reversible CO₂ fixation—release processes is considered more attractive than the use of primary or secondary amines, since the CO₂ fixation requires 1 equiv of the amidines and the CO₂ release proceeds readily at low temperature.^{4,5} We have also reported reversible CO₂ fixation by polymers bearing cyclic amidines under wet conditions.⁶ In addition,

amidines and guanidines have been utilized as efficient catalysts for CO₂-insertion reactions.⁷ The CO₂-binding reactions seem to occur simultaneously with the capture of water molecules to yield bicarbonates and have been recently applied to switchable ionic liquids and surfactant.^{4b-e} On the other hands, the amidines are unable to efficiently trap CO₂ even at high pressure of CO₂ under dry conditions and their CO₂-binding process requires a certain amount of water (e.g., 700 ppm for DBU) for the formation of the bicarbonate salts.^{5b} The CO₂-binding reactions have been suggested to involve a zwitterionic adduct between the amidine and CO₂, the existence of which was also reported to occur between CO₂ and the free amino groups of proteins.⁸ Recently, Villiers et al. reported the isolation and full characterization including single crystal X-ray analysis of the zwitterionic adduct between 1,5,7-triazabicyclo [4.4.0]dec-5-ene (TBD) and CO₂.^{5d} However, all attempts to isolate and characterize the zwitterionic adducts between amidines, such as DBU and CO₂ especially in solution have not yet been successful, although several solid-state ¹³C NMR studies revealed that zwitterionic carbamate species are contained in the solid mixtures obtained by evaporation of reaction mixture of amidines and CO₂ in dry organic solvents, such as CH₃CN.^{5a,e} The development of CO₂ recycling and catalytic reactions with amidines requires comprehensive information of the mechanism for CO₂ capture and release in various reaction media. Moreover, the effect of the chemical structures of amidines on their binding and release of CO₂ would be quite useful knowledge for further design and





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synthesis of amidine-based CO_2 -binding materials as well as catalysts. Accordingly, we have investigated the reversible fixation-release behavior of CO_2 by several amidines including DBU under dry conditions, highlighting the mechanism of their CO_2 binding in solution (Scheme 1).



Scheme 1. CO₂ fixation by amidines.

2. Results and discussion

First, we examined the CO₂ fixation by four linear amidines, N,N-1a,⁹ dimethyl-N'-octylacetamidine N,N-dimethyl-N'-cyclohexylacetamidine **1b**,¹⁰ *N*,*N*-dimethyl-*N'*-octylformamidine **1c**,¹¹ and *N*,*N*-dimethyl-*N'*-cyclohexylformamidine **1d**,¹² with dry bubbling CO₂ (200 mL/min, H₂O content <5 ppm) for 1 h in anhydrous acetonitrile (CH₃CN) under the dry conditions (Table 1, entries 1-4). In all cases, the reaction mixtures remained homogeneous and colorless with no indication of precipitate formation under the dry conditions. Although trace amounts (<1%) of the bicarbonates were obtained from the acetamidines, 1a and 1b, under the wet conditions, the formamidines, 1c and 1d, did not form the bicarbonates at all in the presence of equimolar amount of water. In most cases, the amidines were completely recovered as colorless liquids by evaporation at 25 °C, whereas the linear amidines were reported to react smoothly and quantitatively with CO₂ to give the bicarbonate salts as white precipitates in wet CH₃CN containing

Table 1

CO₂ fixation by the amidines under dry and wet conditions^a

| X 1 | $\begin{array}{c} CO_2 \\ \hline \\ Ar \end{array} \begin{bmatrix} +X-C \\ 1 \\ C \\ \hline \end{array}$ | $\left[\begin{array}{c} CO_2^{-} \end{array}\right] \xrightarrow{+ H_2O^{c,d}}$ | XH⁺•HCO₃ [−] ↓ 2 |
|--------|---|---|-------------------------------------|
| Entry | Amidine | Yield/% ^b | |
| | | Dry condition ^c | Wet condition ^d |
| 1 | 1a | 0 | <1 |
| 2 | 1b | 0 | <1 |
| 3 | 1c | 0 | 0 |
| 4 | 1d | 0 | 0 |
| 5 | 1e | 27 | 92 |
| 6 | 1f | 39 | 91 |
| 7 | 1g | 95 | 94 |
| 8 | 1h | >99 | >99 |

^a Reaction conditions: 5 mmol of 1a-h, 10 mL of anhydrous CH₃CN, CO₂ bubbling (200 mL/min, H₂O content <5 ppm) at 25 °C for 1 h.

^b Isolated.

 $^{\rm c}$ Water only came from the $\rm CO_2$ gas and/or adventitiously.

 $^{\rm d}$ After completion of $\rm CO_2$ bubbling, water (5 mmol, 1 equiv) was added via a syringe.

a sufficient amount of water.⁴ These results clearly showed that the reactions of linear amidines with CO_2 were greatly influenced by the amounts of water in the reaction mixtures.

In contrast with these linear amidines, the bicyclic amidines, 1e (DBN) and 1f (DBU), reacted with the dry CO₂ at ambient temperature under the dry conditions, and small amounts of white precipitates started to form in anhydrous CH₃CN within 1 h. After addition of anhydrous ether, the bicarbonate salts, **2e** and **2f**, were precipitated as white solids in low yields (Table 1, entries 5 and 6). The bicarbonates 2 may form through hydrolysis of the zwitterionic intermediates between the amidines **1** and CO₂ by adventitious water during the reaction and/or the isolation procedure owing to their hygroscopic nature.⁵ The compositional formula of the salt **2f** was confirmed by elemental analysis, showing that the salt consists of the amidinium and bicarbonate ions (Found: C, 55.99; H, 8.44; N, 13.07. Calc. for C₁₀H₁₈N₂O₃: C, 56.06; H, 8.47; N, 13.07%). The higher reactivities of **1e** and **1f** toward CO₂ than those of **1a–d** can be attributed to its higher nucleophilicity, owing to their cyclic structures. However, the fixation efficiencies using 1e and 1f (yields of 2e and 2f) were 27% and 39% under the above conditions, which was less satisfactory in economical and practical usages. In contrast, the use of an equimolar amount of water as hydrolytic agent resulted in remarkably increased yields of 92% and 91%, respectively (entries 5 and 6). On the other hand, no precipitation was observed when much drier CO₂ (H₂O content<0.5 ppm) was employed in dry CH₃CN.^{5b} This result suggested that the amount of water contained in the reaction system is an important factor for the CO₂ fixation by the cyclic amidine.

Next, we investigated the CO₂ fixation behavior of two monocyclic amidines, 1-methyl-1,4,5,6-tetrahydropyrimidine $1g^{13}$ and 1,4,5,6-tetrahydropyrimidine 1h.¹⁴ Upon bubbling the dry CO₂ into an anhydrous CH₃CN solution of 1g (0.5 M), white solids started to exothermically precipitate in anhydrous CH₃CN within 10 min. After 1 h, the bicarbonate salt 2g was isolated in an almost quantitative yield,⁵ which indicates that the adsorbability of 1g under the dry CO₂ atmosphere was comparable to that in sufficiently wet CO₂ atmosphere (Table 1, entry 7).⁶ The compositional formula of 2g was also confirmed by elemental analysis and it was further characterized by ¹H and ¹³C NMR. Furthermore, the structure of 2g was unambiguously confirmed by X-ray crystallographic analysis (Fig. 1).¹⁵ However, the highly deliquescent character of the bicarbonate salt



Fig. 1. Single crystal X-ray structure of 2g with thermal ellipsoids of 50% probability.

2g hampered gaining its precise thermogravimetric analysis (TGA) data and melting point. The monocyclic amidine **1h** was also shown to react exothermically with the dry CO₂ in anhydrous CH₃CN and the bicarbonate salt **2h** was isolated quantitatively in 1 h (Table 1, entry 8). The **2h** thus obtained did not deliquesce in the air for, at least, a couple of days. The compositional formula of **2h** was also confirmed by elemental analysis and it was further characterized by ¹H and ¹³C NMR. The higher ability of **1g** and **1h** to trap CO₂ could be attributed to the less steric hindrance around the nucleophilic nitrogen atoms when compared to those in **1e** and **1f**.

The thermal stability of **2h** was studied by TGA. The analytical value of the first weight loss at 106 °C corresponded to that of CO_2 and H_2O (anal. 40.1%, calcd 41.8%), and the second weight loss at 159 °C corresponded to that of the amidine (anal. 56.2%, calcd. 58.2%). **2h** also released CO_2 within 1 h at 60 °C under nitrogen bubbling (200 mL/min) in anhydrous dimethyl sulfoxide (DMSO).

The high efficiency of the CO₂ fixation–release cycle using **1h** was demonstrated in anhydrous DMSO by bubbling the dry CO₂ at 25 °C and bubbling Ar at 60 °C in an alternate manner. The mixture was preheated at 60 °C under bubbling Ar for 30 min before the initial CO₂ fixation step. The CO₂ fixation efficiency of 1h was estimated from the weight change of the reaction mixture by using a blank DMSO solution. As shown in Fig. 2, both the fixation and release proceeded quantitatively within 1 h by bubbling CO₂ and Ar, respectively. Furthermore, the CO₂ fixing efficiency did not change between the first and third fixation steps. The bicarbonate salt 2h was isolated in an almost quantitative yield (98%) from the reaction mixture after the third fixation step and it was also subjected to elemental analysis, which showed that the salt was highly pure as the salt obtained after the first CO₂ fixation step (Found: C, 41.30; H, 7.13; N, 19.21. Calc. for C₅H₁₀N₂O₃: C, 41.09; H, 6.90; N, 19.17%). These results proved that **1h** was a highly efficient recyclable CO₂ adsorbent in the presence of an extremely low amount of water.



Fig. 2. Reversible CO_2 fixation and release by **1h**. (a) Flow rate of CO_2 and Ar: 200 mL/ min; (b) the CO_2 fixation efficiency was calculated based on the formation of the bicarbonate **2h**.

We further investigated the CO₂-binding reaction of **1g** in dry CD₃CN by ¹³C and ¹H NMR spectroscopy, focusing on the initial stage of the reaction (Figs. 3 and S4). Upon bubbling the dry CO₂ into a solution of **1g** in CD₃CN at ambient temperature for 1 min, the signal of the methine carbon (N–C=N) shifted to a lower magnetic field of 153.1 ppm and a new signal assignable to the CO₂⁻ moiety of



Fig. 3. Partial 13 C NMR spectra (100 MHz, 25 °C) of a solution of 1g in CD₃CN (0.1 M) with bubbling CO₂ gas followed by addition of an excess water.

the zwitterionic carbamate **1g**-CO₂ appeared at 131.3 ppm, which was different from that of dissolved CO_2 in CD_3CN (125.6 ppm).¹⁶ The CO_2^- signal shifted to a high magnetic field with increasing bubbling time, while the methine signal did not change very much. This chemical shift change indicates that **1g**-CO₂ exchanged its CO₂⁻ moiety with the dissolved CO₂ faster than the NMR time scale. Accordingly, the CO_2^- moiety of **1g**-CO₂ and the dissolved CO_2 gave the one signal with the averaged chemical shift, which shifted to a higher magnetic field with bubbling time, as the amount of the dissolved CO₂ increased. After 2 min of CO₂ bubbling, an excess water was added to the CD₃CN solution, a new signal attributable to HCO_3^- appeared at 160.6 ppm¹⁷ along with that of the dissolved CO₂ at 125.6 ppm, showing the formation of the bicarbonate **2g** by hydrolysis of 1g-CO₂. The ¹H NMR spectral change of the reaction mixture was consistent with the ¹³C NMR result. We have similarly confirmed the zwitterionic adduct formation between **1f** and CO₂ in anhydrous CD₃CN at the initial stage of the CO₂-binding reaction as the intermediate for the bicarbonate 2f (Fig. S3).

Contrary to our expectation, we found by ¹³C NMR that the linear acetamidine **1a** also formed the zwitterionic adduct **1a**-CO₂ with CO₂ in anhydrous CD₃CN (Fig. S1). Upon bubbling the dry CO₂ into an anhydrous CD₃CN solution of **1a**, the amidine signal (N-C= N) shifted to a low magnetic field by *ca*. 2 ppm and a new signal derived from the carbamic CO_2^- group at 125.8 ppm, which was shown to exist in a fast equilibrium with the dissolved CO₂ molecules. Upon addition of an excess of water, a new signal assignable to HCO_3^- ion appeared at 160.5 ppm, accompanied by a low magnetic field shift of the amidine carbon by ca. 2 ppm. The fact that the reaction of **1a** with CO₂ in CH₃CN resulted in the complete recovery of **1a** (Table 1, entry 1) indicated that the zwitterionic adduct **1a**-CO₂ (or the bicarbonate **2a** formed by hydrolysis of **1a**-CO₂) was highly soluble in CH₃CN owing to the octyl substituent and the captured CO₂ was released during evaporation of the CH₃CN. In contrast, the ¹³C NMR spectrum of **1c** in CD₃CN did not show any significant change after bubbling CO₂ gas, indicating that the carbamic zwitterion 1c-CO₂ was not present in a detectable amount, or the equilibrium state exists very close to the side of the free 1c and CO₂ (Fig. S2). The difference in the CO₂-binding behavior could be attributed to the methyl group on the amidine methine moiety of 1a, which enhances the nucleophilicity of the amidine

nitrogen atom by its electron-donating nature. However, ¹³C NMR study revealed that upon addition of an excess water, **1c** was completely converted to the bicarbonate **2c**, probably because the excess water shifted the equilibrium of **1c** with CO_2 to the side of **2c**. Thus, the ¹³C NMR results revealed that the carbamic zwitterion formation was highly affected by the chemical structures of amidines under anhydrous conditions, whereas the amidines gave the bicarbonates in the presence of a sufficient amount of water irrespective of the structures.

3. Conclusion

In conclusion, we found that the simple monocyclic amidines fixed CO₂ quantitatively under dry conditions to afford the corresponding bicarbonates through hydrolysis of the zwitterionic adducts by adventitious water. In contrast, use of the linear amidines did not form the bicarbonates under the same dry conditions, while DBU and DBN cannot effectively trap CO₂. The CO₂ fixed by the monocyclic amidines was quantitatively released after heating at 60 °C with Ar bubbling. The CO₂ fixation–release efficiency remained unchanged after the second cycles under the dry conditions. We also disclosed by the ¹³C and ¹H NMR studies that the zwitterionic adduct formation between the amidines and CO₂ in solution is reversible and in equilibrium faster than the NMR time scale. This can account for why characterization of zwitterionic carbamates in solution was not successful despite tremendous efforts. In addition, the effect of the chemical structures of amidines on the CO_2 capture is remarkable: the acetamidine can bind CO_2 to form a zwitterionic adduct in solution as effectively as the cyclic amidines, while the formamidine formed the zwitterionic adduct with CO₂ in a detectable amount under the same conditions. This can be explained in terms of the nucleophilicity of the amidine nitrogen atoms as well as the steric hindrance, and could be quite important information for further design and synthesis of amidineand guanidine-based materials for CO₂ fixation and catalysts for CO₂ insertion. Although the zwitterionic adducts between amidines and CO₂ are less stable than their guanidine counterparts, we believe that incorporation of bulky substituents would kinetically increase their stability, and such attempts to isolate and characterize zwitterionic amidines-CO₂ adducts are ongoing in our laboratory.

4. Experimental section

4.1. General

4.1.1. Materials and instruments. All starting materials and dehydrated solvents were purchased from Aldrich, Wako Pure Chemical Industries (Osaka, Japan), and Tokyo Kasei Kogyo (Tokyo, Japan), and were distilled prior to use. The melting points were measured using a Yanaco MP-S3 melting point apparatus (Kyoto, Japan) and were uncorrected. The NMR spectra were obtained using a JEOL ECS-400 spectrometer operating at 400 MHz for ¹H and 100 MHz for ¹³C. The IR spectra were recorded as KBr discs or pellets on a JASCO FT/IR-460 Plus spectrometer. The elemental analyses were performed by the Perkin Elmer 2400II CHNS/O Analyzer. Thermogravimetric analysis (TGA) was performed at heating and cooling ratio of 5 °C/min over the temperature range of 25–200 °C on a Seiko EXSTER6000 system with TGA-6200 instruments under nitrogen atmosphere (flow rate: 200 mL/min). The single crystal Xray data were collected on a Bruker Smart Apex CCD-based X-ray diffractometer with Mo-K α radiation (λ =0.71073 Å).

4.2. Preparation of the cyclic amidines

4.2.1. 1-Methyl-1,4,5,6-tetrahydropyrimidine (**1g**).¹³ N,N-Dimethylformamide dimethyl acetal (6.26 g, 52.5 mmol) was added to the mixture of *N*-methyl-1,3-diaminopropane (4.41 g, 50 mmol) in anhydrous toluene (50 mL) at room temperature, and the mixture was stirred at 80 °C for 24 h. The mixture was evaporated in vacuo, and the residue was distilled under reduced pressure to give **1g** (4.63 g, 94%) as a colorless liquid; Bp 57–59 °C/1.0 kPa. ¹H NMR (400 MHz, CDCl₃, 25 °C) δ (ppm): 1.84 (quin, *J*=6.0 Hz, 2H, NCH₂CH₂CH₂NCH₃), 3.27 (t, *J*=6.0 Hz, 2H, NCH₂CH₂CH₂NCH₃), 6.92 (s, 1H, NCHN). ¹³C NMR (100 MHz, CDCl₃, 25 °C) δ (ppm): 20.6 (NCH₂CH₂CH₂NCH₃), 149.8 (NCHN). IR (neat, cm⁻¹): 2928, 2848 (CH), 1634 (C=N), 1313 (CH₂NCH₃).

4.2.2. 1,4,5,6-*Tetrahydropyrimidine* (**1h**).¹⁴ N,N-Dimethylformamide dimethyl acetal (6.26 g, 52.5 mmol) was added to the mixture of 1,3-diaminopropane (3.71 g, 50 mmol) in anhydrous toluene (50 mL) at room temperature, and the mixture was stirred at 80 °C for 24 h. The mixture was evaporated in vacuo, and the residue was distilled under reduced pressure to give **1h** (3.71 g, 88%) as a colorless liquid; Bp 80–82 °C/0.1 kPa. ¹H NMR (400 MHz, CDCl₃, 25 °C) δ (ppm): 1.83 (quin, *J*=6.0 Hz, 2H, NCH₂CH₂CH₂N), 3.30 (t, *J*=6.0 Hz, 4H, NCH₂CH₂CH₂NH), 4.28 (br s, 1H, NH), 7.11 (s, 1H, NCHN). ¹³C NMR (100 MHz, CDCl₃, 25 °C) δ (ppm): 21.2 (NCH₂CH₂CH₂NH), 41.2 (NCH₂CH₂CH₂NH), 147.3 (NCHN). IR (neat, cm⁻¹): 3309 (NH), 2932, 2851 (CH), 1635 (C=N).

4.3. Typical procedure for CO₂ fixation

Dry CO₂ gas (>99.999%, H₂O <5 ppm) was bubbled into a solution (0.2 L/min) of the amidine (5 mmol) in anhydrous CH₃CN (10 mL) at 25 °C. After 1 h under bubbling CO₂, anhydrous Et₂O (20 mL) was added to a suspension of the salt in CH₃CN. The resulting white precipitate was filtered off, washed with anhydrous Et₂O (10 mL×2) and dried in a stream of CO₂ to give amidinium bicarbonate as a white powder.

4.3.1. 1-Methyl-1,4,5,6-tetrahydropyrimidinium bicarbonate (**2g**). Yield 763 mg, 95%. ¹H NMR (400 MHz, D₂O, 25 °C) δ (ppm): 2.03 (quin, *J*=6.0 Hz, 2H, NCH₂CH₂CH₂N), 3.16 (s, 3H, NCH₃), 3.32 (t, *J*=6.0 Hz, 2H, NCH₂CH₂CH₂NCH₃), 3.40 (t, *J*=6.0 Hz, 2H, NCH₂CH₂CH₂NCH₃), 3.40 (t, *J*=6.0 Hz, 2H, NCH₂CH₂CH₂NCH₃), 7.82 (s, 1H, NCHN). ¹³C NMR (100 MHz, D₂O, 0.4% dioxane (67.4 ppm), 25 °C) δ (ppm): 18.8 (NCH₂CH₂CH₂NCH₃), 37.3 (NCH₃), 42.1 (NCH₂CH₂CH₂NCH₃), 46.1 (NCH₂CH₂CH₂NCH₃), 152.7 (NCHN), 161.2 (HCO₃⁻). IR (KBr, cm⁻¹): 3412 (OH), 2950 (CH), 1696 (C=N), 1407 (OCO₂⁻). Anal. Calcd for C₆H₁₂N₂O₃: C, 44.99; H, 7.55; N, 17.49. Found: C, 45.14; H, 7.81; N, 17.47.

4.3.2. 1,4,5,6-*Tetrahydropyrimidinium bicarbonate* (**2h**). Yield 728 mg, >99%. Mp 90–92 °C. ¹H NMR (400 MHz, D₂O, 25 °C) δ (ppm): 2.00 (quin, *J*=6.0 Hz, 2H, NCH₂CH₂CH₂N), 3.40 (t, *J*=6.0 Hz, 4H, NCH₂CH₂CH₂N), 7.87 (s, 1H, NCHN). ¹³C NMR (100 MHz, D₂O, 0.4% dioxane (67.4 ppm), 25 °C) δ (ppm): 18.5 (NCH₂CH₂CH₂N), 38.6 (NCH₂CH₂CH₂N), 152.1 (NCHN), 161.2 (HCO₃⁻). IR (KBr, cm⁻¹): 3433 (OH, NH), 2980 (CH), 1685 (C=N), 1402 (OCO₂⁻). Anal. Calcd for C₅H₁₀N₂O₃: C, 41.09; H, 6.90; N, 19.17. Found: C, 41.13; H, 7.13; N, 19.25.

4.4. X-ray crystallographic data of 2g

X-ray diffraction data for **2g** were collected on a Bruker Smart APEX-II CCD-based X-ray diffractometer with Mo-K α radiation (λ =0.71073 Å) at 90 K.

Single crystals of **2g** [C₆H₁₂N₂O₃, MW=160.18] suitable for X-ray analysis were grown from a solution in anhydrous acetone, and a single colorless crystal with dimensions $0.20 \times 0.20 \times 0.15$ mm³ was selected for intensity measurements. The unit cell was monoclinic with the space group *P*2₁/n. Lattice constants with *Z*=4,

 $ρ_{calcd}=1.436$ g cm⁻³, μ(MoKα)=0.115 mm⁻¹, F(000)=340, $2θ_{max}=57.30^{\circ}$ were a=6.7400(7) Å, b=10.7652(11), c=10.4216(11) Å, β=103.1400(10)°, and V=736.37(13) Å³. A total of 3396 reflections were collected, of, which 1295 reflections were independent (R_{int} =0.0097). The structure was refined to final R_1 =0.0268 for 1293 data [I>2σ(I)] with 144 parameters and wR_2 =0.0737 for all data, GOF=1.044, and residual electron density max/min=0.164/ -0.217 e Å⁻³.

Supplementary data

¹H and ¹³C spectra of isolated compounds and experimental data of linear amidines (1a-d) and amidinium bicarbonates (2e and 2f) are available. Supplementary data related to this article can be found at http://dx.doi.org/10.1016/j.tet.2013.04.110.

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