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Homogeneous Catalysis

A Bifunctional Tungstate Catalyst for Chemical Fixation of CO_2 at Atmospheric Pressure**

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Chemical fixation of carbon dioxide (CO_2) into useful and valuable chemicals is a key technology for sustainable low-carbon society because CO_2 is a renewable and environmentally friendly C_1 source, which is in contrast to toxic CO and phosgene.[1] However, CO_2 is much less reactive than CO and phosgene, and a large energy input (e.g., highly reactive reagents, high pressures of CO_2, and stoichiometric amounts of strong acids or bases) is usually required to transform CO_2 into various chemicals. Therefore, the low-energy catalytic fixation of CO_2 is highly desirable. Catalytic CO_2 fixation at atmospheric pressure has been limited to reactive substrates (strained cyclic molecules, unsaturated compounds, etc.),[1] and bifunctional catalysts, which allow a concerted action on both CO_2 and substrates, are promising candidates for highly efficient CO_2 fixation at atmospheric pressure.[1d]

Catalytic C−N and C−O bond-formation processes with CO_2 are important in both industry and academia because they offer economical and environmental advantages such as high atom efficiency and water is the only by-product.[1a,d–f] Urea derivatives, made from CO_2, are important end products or intermediates for pharmaceuticals, agricultural pesticides, antioxidants in gasoline, dyes, and resin precursors.[2] Although various base catalysts such as CsOH, Cs_2CO_3, and ionic liquids have been used for the synthesis of urea derivatives with CO_2, these systems have disadvantages: 1) high CO_2 pressures (2.5–8.0 MPa) and reaction temperatures (423–453 K), 2) narrow applicability to substrates, and 3) need of dehydrating agents or additives (see Table S1 in the Supporting Information).[3]

Recently, we have developed a series of polyoxometalates (POMs) as catalysts for various functional-group transformations.[4] While acid and oxidation catalysis by POMs have extensively been investigated, there are no successful examples of base catalysis including chemical fixation of CO_2.[4,5] The charges and sizes of POMs strongly affect the basicities of the oxygen atoms, and increase with an increase in the charge densities (i.e., the negative charge per size). On the basis of this concept, we focus on the basic property of a monomeric tungstate, $[WO_4]^{2-}$, having a high charge density. First, the structures of various tungstates were optimized by the density functional theory (DFT) calculations, and the basicities of oxygen atoms in various POMs were compared with the natural bond orbital (NBO) charges (Figure 1a). The NBO charge of an oxygen atom in $[WO_4]^{2-}$ was −0.934, which is much lower than those (−0.569–−0.753) in the other POMs such as $[W_6O_{19}]^{2-}$, $[W_{10}O_{32}]^{4-}$, and $[\alpha\text{-SiW}_{12}O_{40}]^{4-}$, thus suggesting that $[WO_4]^{2-}$ is the most basic among these tungstates. Herein, we report the first example of tungstate-based catalytic chemical fixation of CO_2. A simple monomeric tungstate, $TBA_2[WO_4]$ (**A**, TBA = $[(n\text{-}C_4H_9)_4N]^+$), can act as a highly efficient homogeneous catalyst for chemical fixation of CO_2 with amines, 2-aminobenzonitriles, and propargylic alcohols to give urea derivatives, quinazoline-2,4(1*H*,3*H*)-diones, and cyclic carbonates, respectively. The ^1H and ^{13}C NMR spectra show the specific interaction of the tungsten-oxo moiety in **A** with both CO_2 and the substrate. Such simultaneous activation by **A** results in the following advantages: 1) accomplishment of CO_2 transformations at

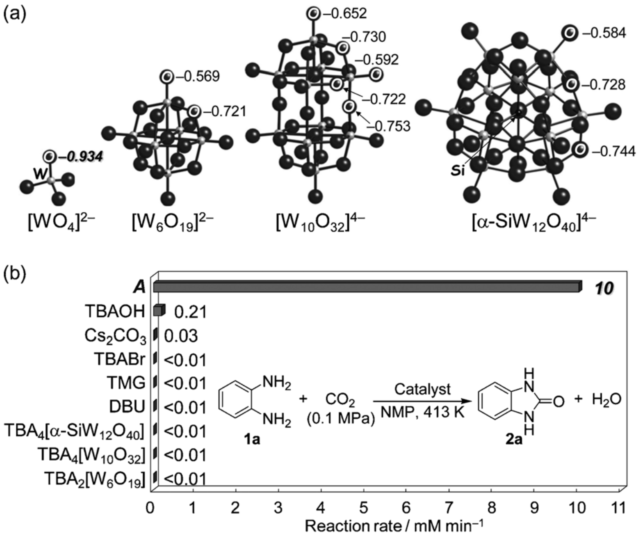

Figure 1. a) Calculated molecular structures of various tungstates and NBO charges of oxygen atoms. b) Reaction of **1a** with CO_2 at atmospheric pressure using various catalysts. Reaction conditions: Catalyst (150 μmol), **1a** (1 mmol), CO_2 (0.1 MPa), NMP (1 mL), 413 K. Reaction rates were determined from the reaction profiles at low conversions (< 10%) of **1a**.

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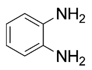
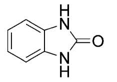
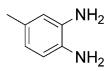
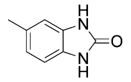
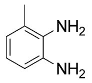
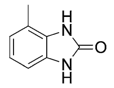
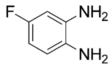
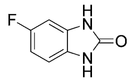
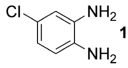
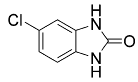
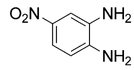
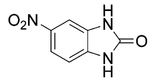
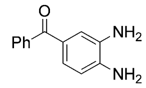
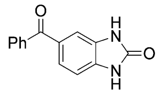
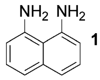
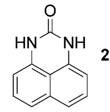
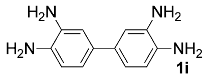
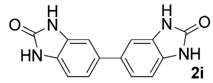
atmospheric pressure, 2) high yields and turnover numbers (TONs), and 3) applicability to a wide range of substrates.

A benchmark reaction of 1,2-phenylenediamine (**1a**) with CO_2 to give 2-benzimidazolone (**2a**) in *N*-methylpyrrolidone (NMP) was carried out (Figure 1b and see Table S2 in the Supporting Information). Since reactivities of less nucleophilic arylamines with CO_2 are very low, which is in sharp contrast with those of alkylamines,[6] **2a** has not yet been obtained in the absence of catalysts even under harsh reaction conditions (6 MPa of CO_2 pressure at 423 K).[7] Notably, the **A**-catalyzed reaction proceeded efficiently with CO_2 at atmospheric pressure (0.1 MPa) to give **2a** in 91% yield. Reactions hardly proceeded in the absence of **A** or in the presence of the other POMs such as $TBA_2[W_6O_{19}]$, $TBA_4[W_{10}O_{32}]$, and $TBA_4[\alpha\text{-}SiW_{12}O_{40}]$, and is in accord with the computational results. The reaction rate (10 mM min^{-1}) of **A** was 48-fold faster compared with those (< 0.01–0.21 mM min^{-1}) of typical inorganic and organic strong bases such as Cs_2CO_3, TBAOH, 1,8-diazabicyclo[5.4.0]undec-7-ene (DBU), and 1,1,3,3-tetramethylguanidine (TMG). To the best of our knowledge, no successful example of either stoichiometric or catalytic synthesis from aromatic diamines and CO_2 has been reported.

The **A**-catalyzed system could be applied to various kinds of structurally diverse aromatic diamines (Table 1). Various kinds of 1,2-phenylenediamines (**1a**–**1g**) having electron-donating as well as electron-withdrawing substituents were converted into the corresponding 2-benzimidazolones **2a**–**2g** in moderate to high yields using CO_2 at atmospheric pressure (Table 1, entries 3, 5, 7, 9, 11, and 13). 1,8-Diaminonaphthalene (**1h**) and 3,3′-diaminobenzidine (**1i**) were also effectively converted into the corresponding cyclic urea derivatives (**2h** and **2i**) in 87 and 85% yields, respectively (Table 1, entries 15 and 17). For the reactions of various aromatic diamines at 2 MPa of CO_2, high to excellent yields of the corresponding urea derivatives could be obtained even with low catalyst loadings (2–10 mol%; Table 1, entries 2, 4, 6, 8, 10, 12, 14, 16, and 18). The 4 mmol scale reaction of **1b** with CO_2 (2 MPa), catalyzed by **A** (0.5 mol% with respect to **1b**) at 413 K for 96 h, gave **2b** in 93% yield. The TON got up to 186, and the value was much higher than those (0–52) reported for the base-catalyzed reactions of amines to urea derivatives (see Table S1 in the Supporting Information).[3]

Despite the weaker basicity of $[WO_4]^{2-}$ (pK_a of conjugate acid in water: 3.5) compared with those of the inorganic and organic strong bases such as $[CO_3]^{2-}$ (10.3), DBU (12.0), and TMG (13.6),[8] **A** showed much higher catalytic activity. To elucidate the role of **A**, the reactivity of **A** with **1a** and CO_2 were investigated by using ^1H, ^{13}C, and ^{183}W NMR spectroscopy. The ^1H NMR spectrum of **1a** showed the downfield shift of the signal of the NH_2 protons from $\delta = 4.22$ to 4.76 ppm by addition of one equivalent of **A** (relative to **1a**; Figures 2a,b, and Figure S1 in the Supporting Information), thus indicating the hydrogen-bonding interaction between **A** and **1a** described in reference [9] (Figure S2). The downfield shift of the signal for the NH_2 protons ($\Delta\delta = +0.54$ ppm) with **A** was much larger than that ($\Delta\delta = +<0.01$ ppm) with DBU, thus suggesting the stronger interaction of **1a** with **A**. The signal at $\delta = 16.4$ ppm in the ^{183}W NMR spectrum of **A** also shifted (to $\delta = 1.7$ ppm) upon addition of **1a** (Figures 2d,e). The hydrogen bond could weaken the N−H bond and facilitate the nucleophilic attack of the NH_2 group in **1a** on the carbon atom of CO_2.

Table 1: Reactions of aromatic diamines with CO_2 catalyzed by **A**.[a]

Entry	Substrate	CO_2 [MPa]	Product	Yield [%]
1	 **1a**	0.1	 **2a**	91
2		2		90
3	 **1b**	0.1	 **2b**	85
4		2		99
5	 **1c**	0.1	 **2c**	78
6		2		98
7	 **1d**	0.1	 **2d**	87
8		2		94
9	 **1e**	0.1	 **2e**	50
10		2		76
11	 **1f**	0.1	 **2f**	45
12		2		70
13	 **1g**	0.1	 **2g**	56
14		2		83
15	 **1h**	0.1	 **2h**	87
16		2		97
17[b]	 **1i**	0.1	 **2i**	85
18[b]		2		94

[a] Reaction conditions: Substrate (1 mmol), **A** (20 μmol for entries 2, 4, 6, 16, and 18), (50 μmol for entries 8 and 10, 100 μmol for entries 3, 5, 12, 14, and 15, and 150 μmol for entries 1, 7, 9, 11, 13, and 17), NMP (1 mL), 413 K, 24 h. Yields were determined by GC (entries 1–10, 15, and 16) or LC (entries 11–14) analysis. [b] Substrate (0.5 mmol). Yields are those of the isolated products.

When the DMF solution of **A** was exposed to CO_2 (0.1 MPa), a new ^{13}C signal appeared at $\delta = 163.6$ ppm (Figure 2c and see Figure S1 in the Supporting Information) with satellites [coupling constants ($^2J_{\text{W-C}}$, 14% satellite intensities) of 6.7 Hz], thus suggesting the presence of a W-O-C bond. The α-carbon atoms of the terminal O-*i*Pr ligands in $W_2R_2(R'C{\equiv}CR'')_2(O\text{-}i\text{Pr})_4$ (R = CH_2Ph, CH_2SiMe_3, *n*Pr, and C_6H_4-*p*-Me; R′CCR″ = MeC≡CMe, MeC≡CEt, and EtC≡CEt) show similar coupling constants $^2J_{\text{W-C}}$ (4–12 Hz).[10] The chemical shift was different from those of free CO_2 ($\delta = 125.3$ ppm) and $TBAHCO_3$ ($\delta = 160.7$ ppm). Therefore, the new ^{13}C signal at $\delta = 163.6$ ppm could arise from the **A**/CO_2 adduct, which is similar to Lewis base/CO_2 adducts such as amidines, guanidines, and N-heterocyclic carbenes (Figure S2).[11] These base/CO_2 adducts are key carrier intermediates for accomplishing the fixation through nucleophilic incorporation of the O=C=O unit.[1,12] Upon introduction of CO_2 (0.1 MPa), a new ^{183}W signal appeared at $\delta = 57.8$ ppm

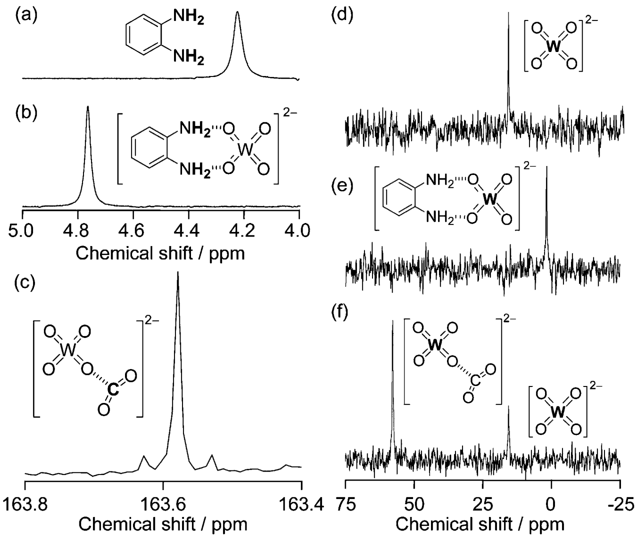
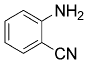
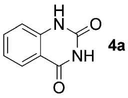
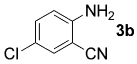
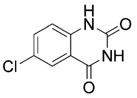
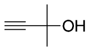
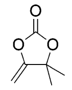
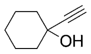
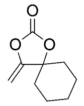
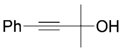
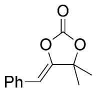
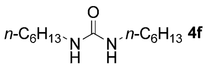
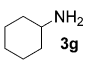
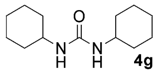


Figure 2. ^{1}H NMR spectra of a) **1a** (0.05 M) and b) **1a** (0.05 M) in the presence of **A** (0.05 M). c) ^{13}C NMR spectrum of **A** (0.5 M) with CO_2 at atmospheric pressure (0.1 MPa). ^{183}W NMR spectra of d) **A** (0.5 M), e) **A** (0.5 M) in the presence of **1a** (0.5 M), and f) **A** (0.5 M) with CO_2 at atmospheric pressure (0.1 MPa). Conditions: DMF/[D$_7$]DMF (2:1, v/v), 298 K for (a) and (b), and 233 K for (c), (d), (e), and (f).

Table 2: Reactions of various substrates with CO_2 catalyzed by **A**.[a]

Entry	Substrate	CO_2 [MPa]	Product	*t* [h]	Yield [%]
1	 **3a**	0.1	 **4a**	120	90
2		2		24	90
3	 **3b**	0.1	 **4b**	120	93
4		2		24	96, TON 480
5	 **3c**	0.1	 **4c**	15	76, TON 228
6		2		24	95, TON 473
7	 **3d**	0.1	 **4d**	15	84, TON 252
8		2		24	95, TON 475
9	 **3e**	0.1	 **4e**	24	31
10		2		12	82
11	$n\text{-}C_6H_{13}\text{–}NH_2$ **3f**	0.1	 **4f**	30	62
12		2		24	76
13	 **3g**	0.1	 **4g**	30	56
14		2		24	70

[a] Reaction conditions: Substrate (1 mmol for entries 1–3 and 9–14), (3 mmol for entries 5 and 7), and (5 mmol for entries 4, 6, and 8), **A** (10 μmol for entries 4–6 and 10), 20 μmol for entries 1–3, 12, and 14), 100 μmol for entries 11 and 13), and (150 μmol for entry 9); solvent: DMSO (2 mL; entries 1–4), CH_3CN (0.1 mL, entries 5–10), and NMP (1 mL, entries 11–14); reaction temperature: 333 K (entries 5 and 7), 353 K (entries 6 and 8–10), 373 K (entries 1–3), 393 K (entry 4), and 413 K (entries 11–14). Yields were determined by GC analysis.

with a decrease in the intensity of the signal at $\delta = 16.4$ ppm (Figures 2d,f). In contrast, no interaction of the other POMs such as TBA$_4$[α-SiW$_{12}$O$_{40}$] and TBA$_2$[W$_6$O$_{19}$] with both **1a** and CO_2 was observed, thus showing the specific bifunctional interaction of **A** with both **1a** and CO_2. The ^{183}W NMR spectrum of **A** in the presence of both **1a** and CO_2 also showed the signals at $\delta = 55.9$ and -0.2 ppm, which are assignable to **A**/**1a** and **A**/CO_2 adducts, respectively, thus supporting the bifunctionality of **A**.

The reaction of *N,N'*-dimethyl-1,2-phenylenediamine with CO_2 catalyzed by **A** did not proceed, thus suggesting that the reaction proceeds via the isocyanate intermediate, which cannot be formed from a secondary aromatic amine.[13] On the basis of these results, the present reaction of **1a** with CO_2 possibly proceeds as follows (see Figure S3 in the Supporting Information): First, the activation of both **1a** and CO_2 by **A** facilitates the nucleophilic attack of the NH_2 group on the carbon atom of CO_2 to give the corresponding carbamic acid.[14] Then, the carbamic acid is converted into the isocyanate intermediate. Finally, the nucleophilic attack of NH group on carbon atom of isocyanate takes place to give the corresponding urea derivative.

To investigate the effectiveness of the present simultaneous activation of CO_2 and a nucleophile, we explored **A**-catalyzed CO_2 transformations of various nucleophiles such as amines and alcohols (Table 2). The **A**-catalyzed reactions of 2-aminobenzonitiriles (**3a** and **3b**), terminal propargylic alcohols (**3c** and **3d**), and primary alkylamines (**3f** and **3g**) using an atmospheric pressure of CO_2 efficiently proceeded to give the corresponding quinazoline-2,4(1*H*,3*H*)-diones (**4a** and **4b**), cyclic carbonates (**4c** and **4d**), and 1,3-disubstituted urea derivatives (**4f** and **4g**; Table 2, entries 1, 3, 5, 9, 11, and 13), whereas higher CO_2 pressures (0.5–14 MPa) are generally required to attain high yields with other catalysts (Tables S1 and S3–S5 in the Supporting Information).[3,12a,15] Catalytic synthesis of 1,3-disubstituted urea derivatives using CO_2 at atmospheric pressure is unprecedented. In addition, the reactions of various kinds of substrates including an inactive internal propargylic alcohol (**3d**) at 2 MPa of CO_2 efficiently proceeded even with low catalyst loading (0.2–2 mol%; Table 2, entries 2, 4, 6, 8, 10, 12, and 14).[16,17] Notably, the reactions of **3b**–**3d** with CO_2 using 0.2 mol% of **A** efficiently proceeded to give **4b**–**4d** in 96, 95, and 95% yields, respectively. In these cases, the TONs were 480, 473, and 475, respectively, and the values were much larger than those (3–22, < 1–12, and < 1–96 for **3b**, **c**, and **d**, respectively) of the reported systems (Tables S3–S5).[12a,15]

Our study shows the importance of developing bifunctional catalysts which can activate both CO_2 and a nucleophile (amines, alcohols, etc.). This approach is a promising strategy for the development of highly efficient chemical fixation of CO_2 to generate various useful chemicals under the very mild reaction conditions.

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[1] a) T. Sakakura, J.-C. Choi, H. Yasuda, *Chem. Rev.* **2007**, *107*, 2365–2387; b) P. G. Jessop, T. Ikariya, R. Noyori, *Science* **1995**, *269*, 1065–1069; c) G. A. Olah, B. Török, J. P. Joschek, I. Bucsi, P. M. Esteves, G. Rasul, G. K. S. Prakash, *J. Am. Chem. Soc.* **2002**, *124*, 11379–11391; d) M. Peters, B. Köhler, W. Kuckshinrichs, W. Leitner, P. Markewitz, T. E. Müller, *ChemSusChem* **2011**, *4*, 1216–1240; e) M. Cokoja, C. Bruckmeier, B. Rieger, W. A. Herrmann, F. E. Kühn, *Angew. Chem.* **2011**, *123*, 8662–8690; *Angew. Chem. Int. Ed.* **2011**, *50*, 8510–8537; f) M. Aresta, *Carbon Dioxide as Chemical Feedstock*, Wiley-VCH, Weinheim, **2010**; g) D. Yu, Y. Zhang, *Proc. Natl. Acad. Sci. USA* **2010**, *107*, 20184–20189.

[2] N. Volz, J. Clayden, *Angew. Chem.* **2011**, *123*, 12354–12361; *Angew. Chem. Int. Ed.* **2011**, *50*, 12148–12155.

[3] a) F. Shi, Y. Deng, T. SiMa, J. Peng, Y. Gu, B. Qiao, *Angew. Chem.* **2003**, *115*, 3379–3382; *Angew. Chem. Int. Ed.* **2003**, *42*, 3257–3260; b) A. Ion, V. Parvulescu, P. Jacobs, D. De Vos, *Green Chem.* **2007**, *9*, 158–161; c) T. Jiang, X. Ma, Y. Zhou, S. Liang, J. Zhang, B. Han, *Green Chem.* **2008**, *10*, 465–469.

[4] N. Mizuno, K. Yamaguchi, K. Kamata in *Topics in Organometallics Chemistry—Chemistry of Bifunctional Molecular Catalysis* (Eds.: T. Ikariya, M. Shibasaki), Springer, Berlin, **2011**, pp. 127–160.

[5] a) T. Okuhara, N. Mizuno, M. Misono, *Adv. Catal.* **1996**, *41*, 113–252; b) I. V. Kozhevnikov, *Catalysts for Fine Chemical Synthesis, Vol. 2*, Wiley, Chichester, **2002**; c) C. L. Hill in *Comprehensive Coordination Chemistry II, Vol. 4* (Eds.: J. A. McCleverty, T. J. Meyer), Elsevier Pergamon, Amsterdam, **2004**, pp. 679–759; d) R. Neumann, A. M. Khenkin, *Chem. Commun.* **2006**, 2529–2538.

[6] K. Masuda, Y. Ito, M. Horiguchi, H. Fujita, *Tetrahedron* **2005**, *61*, 213–229.

[7] B. M. Bhanage, S. Fujita, Y. Ikushima, M. Arai, *Green Chem.* **2003**, *5*, 340–342.

[8] a) M. T. Pope, *Heteropoly and Isopoly Oxometalates*, Springer, Berlin, **1983**; b) *CRC Handbook of Chemistry and Physics, 82nd ed.* (Ed.: D. R. Lide), CRC, Boca Ratton, **2001–2002**; c) D. Granitza, M. Beyermann, H. Wenschuh, H. Haber, L. A. Carpino, G. A. Truran, M. Bienert, *J. Chem. Soc. Chem. Commun.* **1995**, 2223–2224; d) I. M. Kolthoff, M. K. Chantooni, Jr., S. Bhowmik, *J. Am. Chem. Soc.* **1968**, *90*, 23–28.

[9] a) D.-W. Yoon, H. Hwang, C.-H. Lee, *Angew. Chem.* **2002**, *114*, 1835–1837; *Angew. Chem. Int. Ed.* **2002**, *41*, 1757–1759; b) I. M. Jones, A. D. Hamilton, *Angew. Chem.* **2011**, *123*, 4693–4696; *Angew. Chem. Int. Ed.* **2011**, *50*, 4597–4600.

[10] M. H. Chisholm, B. W. Eichhorn, K. Folting, J. C. Huffman, *Organometallics* **1989**, *8*, 49–66.

[11] a) C. Villiers, J.-P. Dognon, R. Pollet, P. Thuéry, M. Ephritikhine, *Angew. Chem.* **2010**, *122*, 3543–3546; *Angew. Chem. Int. Ed.* **2010**, *49*, 3465–3468; b) F. S. Pereira, E. R. deAzevedo, E. F. da Silva, T. J. Bonagamba, D. L. da S. Agostíni, A. Magalhães, A. E. Job, E. R. P. González, *Tetrahedron* **2008**, *64*, 10097–10106; c) H. A. Duong, T. N. Tekavec, A. M. Arif, J. Louie, *Chem. Commun.* **2004**, 112–113.

[12] a) Y. Kayaki, M. Yamamoto, T. Ikariya, *Angew. Chem.* **2009**, *121*, 4258–4261; *Angew. Chem. Int. Ed.* **2009**, *48*, 4194–4197; b) L. Gu, Y. Zhang, *J. Am. Chem. Soc.* **2010**, *132*, 914–915.

[13] C. Wu, *Green Chem.* **2010**, *12*, 1811–1816.

[14] Upon introduction of CO_2 (0.4 MPa) into the DMF solution containing **1a** (0.9 M) and **A** (0.2 M), seven new ^{13}C signals appeared at $\delta = 159.6$, 139.7, 132.0, 120.9, 120.5, 117.1, and 116.2 ppm (see Figure S4 in the Supporting Information). It has been reported that the ^{13}C signal of the carboxy carbon atom in carbamic acid appears in the range of $\delta = 157$–160 ppm.[6] Therefore, these seven ^{13}C signals are likely to correspond to the carbamic acid. New ^{1}H signals also appeared at $\delta = 7.19$ and 6.78 ppm and are assigned as the aromatic and NH protons of the carbamic acid, respectively, while other signals overlapped with those of **1a**. In contrast, these ^{13}C and ^{1}H signals were not observed in the absence of **A**.

[15] a) J. Gao, L.-N. He, C.-X. Miao, S. Chanfreau, *Tetrahedron* **2010**, *66*, 4063–4067; b) H.-F. Jiang, A.-Z. Wang, H.-L. Liu, C.-R. Qi, *Eur. J. Org. Chem.* **2008**, 2309–2312; c) N. D. Ca', B. Gabriele, G. Ruffolo, L. Veltri, T. Zanetta, M. Costa, *Adv. Synth. Catal.* **2011**, *353*, 133–146; d) T. Mizuno, Y. Ishino, *Tetrahedron* **2002**, *58*, 3155–3158; e) Y. P. Patil, P. J. Tambade, K. M. Deshmukh, B. M. Bhanagae, *Catal. Today* **2009**, *148*, 355–360; f) Y. Kayaki, M. Yamamoto, T. Ikariya, *J. Org. Chem.* **2007**, *72*, 647–649; g) Y. Gu, F. Shi, Y. Deng, *J. Org. Chem.* **2004**, *69*, 391–394; h) I. Tommasi, F. Sorrentino, *Tetrahedron Lett.* **2009**, *50*, 104–107; i) M. Costa, G. P. Chiusoli, M. Rizzardi, *Chem. Commun.* **1996**, 1699–1700; j) G.-Q. Yuan, G.-J. Zhu, X.-Y. Chang, C.-R. Qi, H.-F. Jiang, *Tetrahedron* **2010**, *66*, 9981–9985.

[16] The reaction of aniline with CO_2 did not proceed under the same reaction conditions as those used for **3f** and **3g** (Table 2, entries 12 and 14).

[17] The reactions of 2-aminobenzonitriles and propargylic alcohols possibly proceed via the corresponding carbamic and carbonic acids and subsequent transformations to the corresponding quinazoline-2,4(1*H*,3*H*)-diones and cyclic carbonates, respectively, in a similar way to those of the reported systems.[15]