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Polystyrene-bound diethanolamine based ionic liquids for chemical fixation of CO_2

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ABSTRACT

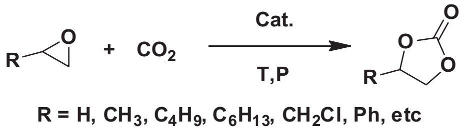
Polystyrene-bound diethanolamine based ionic liquids (PS-DHEEAB and PS-THEAB) were synthesized and applied for the chemical fixation of CO_2 into cyclic carbonates without any additional co-catalyst and solvent. The effect of the catalysts with different number of hydroxyl group in the cation of the IL on the reaction was systematically investigated. Highest activity and selectivity were achieved in the presence of polystyrene supported diethanolamine ethyl bromide (PS-DHEEAB) in comparison with other catalysts employed. The catalyst was tough in stability and also found to be extended to a variety of terminal epoxides and aziridines. The relationship between high catalytic reactivity and the –OH functional groups was proposed.

Cyclic carbonates, which can serve as excellent aprotic polar solvents and extensively as intermediates in the production of pharmaceuticals and fine chemicals, have drawn much more attention recently.[1] Their current synthesis routes by cycloaddition of CO_2 to epoxides are regarded as an effective way of utilizing CO_2 as a Cl resource (Scheme 1).[1]

Various catalysts have been employed for this transformation.[2–8] Among which, ionic liquids (ILs) and their immobilization catalysts are especially highlighted.[3–6] This is because that as a novel substitute, ILs can be tailored by designing functional groups in their cations or anions to adapt different applications.[9] Besides, ILs can also be chemically immobilized onto solid supports such as silica, molecular sieves, chitosan, and polystyrene (PS) resin with the advantages of high activity and separability. Among the above functionalized groups, –OH group is widely investigated for enhancing the activity of catalysts for the synthesis of cyclic carbonates.[3–6] Our recent works proposed that –OH group in the ILs could exhibit a positive behavior on the ring opening of epoxides.[5] This effect combined with the nucleophilic synergetic effect of halide anion could make the cycloaddition reaction proceed smoothly.[5] Since most natural building blocks, such as carbohydrates, amino acids, and nucleic acids, offer a rich source of H-bond donors, hydrogen bonding resulted in many diverse and flexible 'platform' to establish a highly effective catalytic system.

Diethanolamine and its N-substituted derivatives, which are currently used for CO_2 industrial absorption,[10] could also serve as valuable intermediates,[11] group protective agent,[12] and excellent ligand for organometallic catalysts.[13] However, studies on the utilization of diethanolamine based ILs for chemical fixations of CO_2 to produce cyclic carbonates are scarce. The synthesized ILs contains a large amount of –OH groups that may show excellent activity with respect. Herein, we report the first examples of supported diethanolamine based ILs for the synthesis of cyclic carbonates. Polystyrene resin was chosen as a support due to its high mechanical and chemical stability as well as good anti-swelling properties in various solvents.[14] Based on the comparison in activity and stability of Cl^-, Br^-, and I^- in our previous work,[5] Br^- was chosen as the best anion of the IL catalysts. The corresponding catalyst structures (PS-DHEEAB and PS-THEAB) were described in Scheme 2. The synthesis procedures of the catalysts were illustrated in Scheme 3[15–17].

Using propylene oxide (PO) as a model substrate, the activities of the synthesized catalysts on the synthesis of propylene carbonate (PC) were investigated without any additional Lewis acid reagent and solvent[18]. For comparison, we also investigated the



Scheme 1. Synthesis of cyclic carbonates from CO_2 and epoxides.

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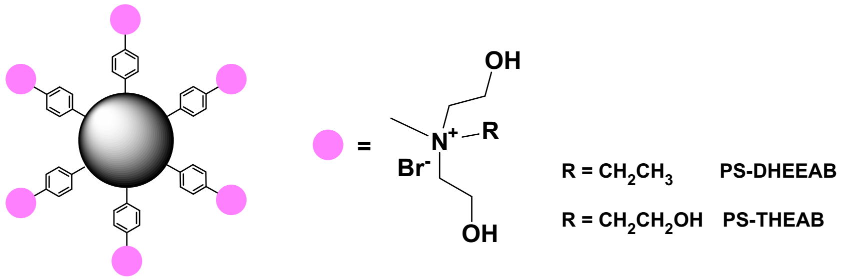
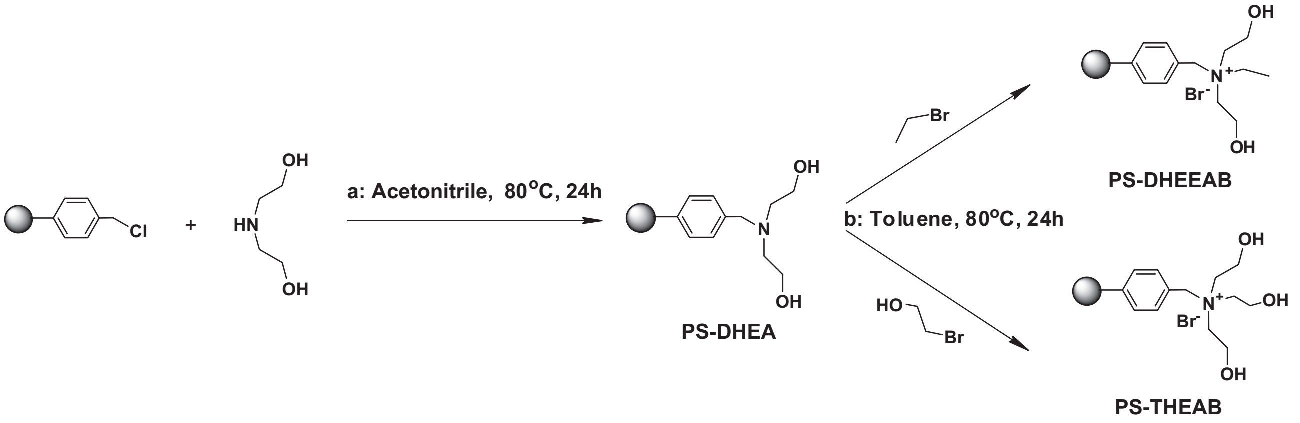
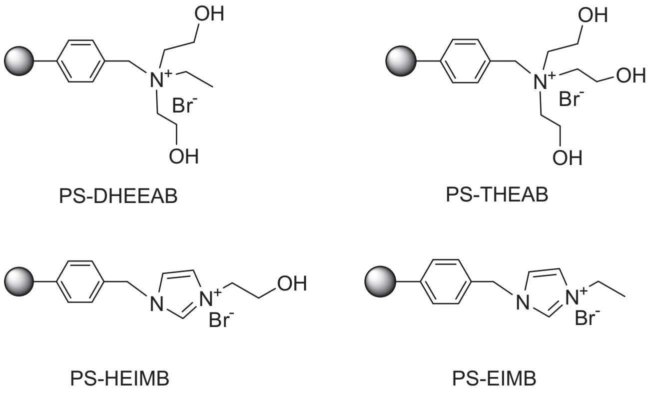


Scheme 2. Structures of PS-DHEEAB and PS-THEAB.



Scheme 3. Synthesis procedure of PS-DHEEAB and PS-THEAB.



Scheme 4. Structures of the PS supported IL catalysts.

Table 1
Synthesis of PC catalyzed by different catalysts[a]

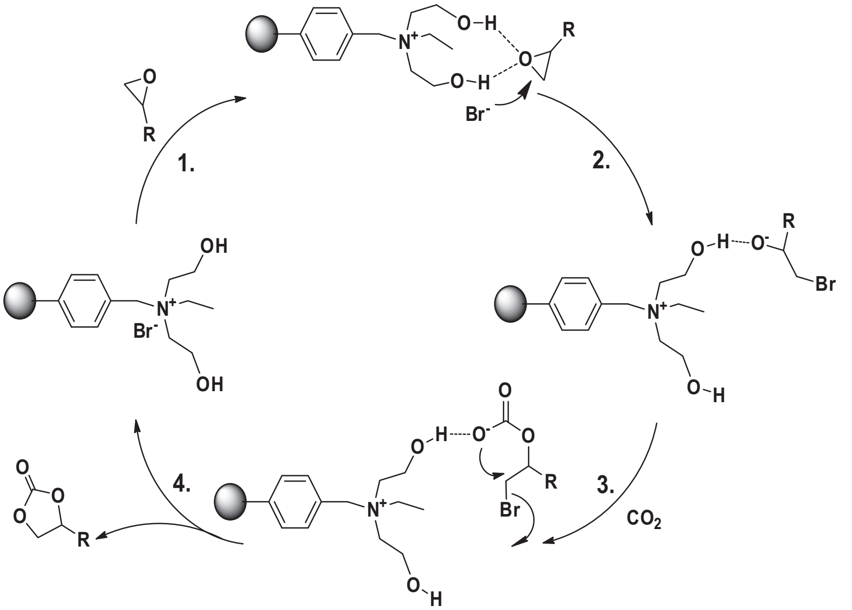
Entry	Catalyst	Conversion[b] (%)	Selectivity[b] (%)
1	PS	–	–
2	Diethanolamine	4	99
3	DHEDEAB	86	99
4	PS-DHEEAB	69	99
5	PS-DHEEAB[c]	92	99
6	PS-DHEEAB[d]	99	99
7	PS-THEAB	65	99
8	PS-HEIMB	52	99
9	PS-EIMB	35	99

[a] Reaction conditions: PO (0.1 mol), catalyst (2.0 mmol), temperature: 110 °C, CO_2 pressure: 2.0 MPa, reaction time: 2 h.
[b] Determined by GC.
[c] Reaction time: 3 h.
[d] Reaction time: 4 h.

activities of the corresponding homogeneous IL (DHEDEAB) and the catalysts we synthesized in our previous work (PS-HEIMB and PS-EIMB).[5] All of the PS supported IL catalysts were used without grinding (particle size: 1 mm, 18 mesh). The structures of the PS supported IL catalysts are shown in Scheme 4, and the corresponding results are listed in Table 1.

PS and diethanolamine (Table 1, entries 1 and 2) are ineffective catalysts as respected. DHEDEAB (entry 3), which was the homogeneous state of PS-DHEEAB, showed excellent activity. The main reason for this was that the homogenous IL had a better miscibility in the substrate. The catalytic activities of PS-DHEEAB (entry 4), PS-THEAB (entry 7) and PS-HEIMB (entry 8), which have different number of –OH groups, were also investigated in our experiment. PS-DHEEAB and PS-THEAB showed higher activities than PS-HEIMB, which may be due to the role of more –OH groups in the ring opening of epoxides. PS-THEAB showed a little lower activity than PS-DHEEAB, which possibly because that the two –OH groups in the cation of PS-DHEEAB could form two hydrogen bonding effect with the O atom of the epoxide, which was calculated by molecular simulation in our previous work,[5] by which the ring opening of epoxide could be promoted. This similar effect could also be found in the other work.[8a] However, the excess –OH group in the cation of PS-THEAB might prefer to form intramolecular hydrogen bond with halide anion, by which the nucleophilic behavior of the anion was weakened.[19] The catalytic activity of PS-EIMB (entry 9) was significantly lower than that of the –OH containing catalysts, and it further proved the synergistic catalysis role of –OH groups.

According to the above results, a proposed mechanism was exhibited in Scheme 5. As proposed in Scheme 5, the coordination of H atoms in the –OH groups with the O atom of the epoxide through a hydrogen bond resulted in the polarization of C–O bonds, and the Br anion made a nucleophilic attack on the less sterically hindered carbon atom of the epoxide at the same time. As a



Scheme 5. Proposed mechanism.

result, the ring of the epoxide was opened easily. Then, the interaction occurred between the oxygen anion and CO_2, forming an alkylcarbonate anion which would be transformed into a cyclic carbonate by the intramolecular substitution of the halide in the next step. From the viewpoint of exhibiting improved yield of PC, increased number of –OH groups might reinforce the ring opening effect.

Due to the high activity and selectivity for the coupling reaction of PO and CO_2, PS-DHEEAB was used for further investigation. In the recycling experiment, we used PS-DHEEAB for six times. As shown in Figure 1, no significant decrease in PO conversions and selectivity for six repeated runs indicates the high stability of the catalyst.

The highly efficient PS-DHEEAB catalyst was also found to be extended to a variety of terminal substrates under the optimal reaction conditions, including epoxides and aziridines[20]. The results are summarized in Table 2. Aromatic **1a**, **1b**, **1c**, **1d,** and **1e**

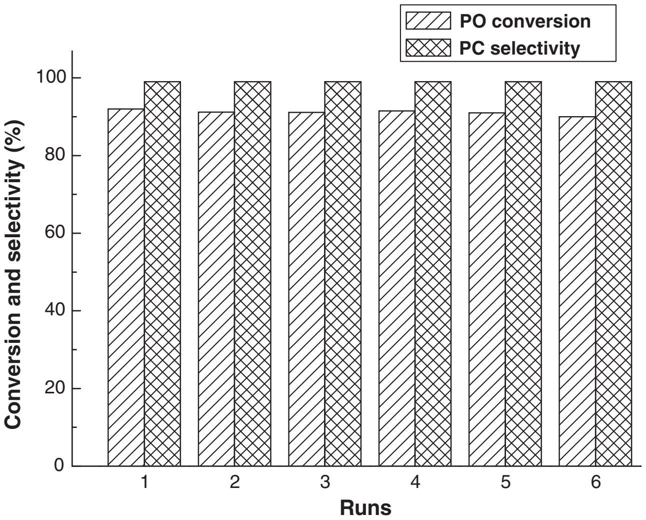


Figure 1. Recycling experiments for PS-DHEEAB. Reaction conditions: PO (0.1 mol), catalyst (2.0 mmol), temperature: 110 °C, CO_2 pressure: 2.0 MPa, reaction time: 3 h.

Table 2
Synthesis of other products catalyzed by PS-DHEEAB[a]

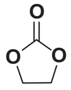
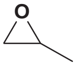
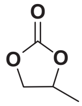
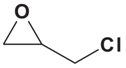
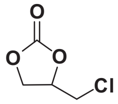
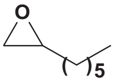
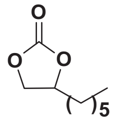
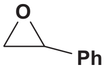
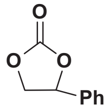
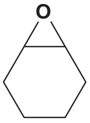
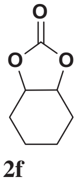
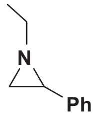
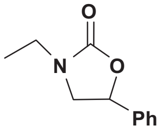
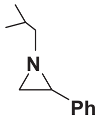
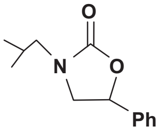
Entry	Substrate	Product	Time (h)	Conversion[b] (%)	Selectivity[b] (%)
1	 **1a**	 **2a**	2	99	99
2	 **1b**	 **2b**	4	99	99
3	 **1c**	 **2c**	3	99	99
4[c]	 **1d**	 **2d**	6	99	99
5	 **1e**	 **2e**	6	96	99
6[c]	 **1f**	 **2f**	24	87	99

Table 2 (*continued*)

Entry	Substrate	Product	Time (h)	Conversion[b] (%)	Selectivity[b] (%)
7[d]	 **1g**	 **2g**	0.5	99	97[e]
8[d]	 **1h**	 **2h**	2	99	98[f]

[a] Reaction conditions: epoxides (0.1 mol), catalyst (2.0 mmol), 110 °C, CO$_2$ 2.0 MPa.

[b] Determined by GC.

[c] Reaction temperature: 120 °C.

[d] Reaction temperature: 50 °C.

[e] The byproduct was 3-ethyl-4-phenyloxazolidin-2-one, determined by GC–MS.

[f] The byproduct was 3-isopropyl-4-phenyloxazolidin-2-one, determined by GC–MS.

epoxides were the preferred substrates for the reaction and these reactions could be completed in less than 6 h. While **1f**, which needs 24 h to reach 87% yield due to the higher hindrance originated from the two rings. The selectivity of all the reactions to the cyclic carbonates was more than 99%. The catalyst also showed excellent activity to the reactions of **1g**, **1h** aziridines and CO$_2$ to produce 5-aryl-2-oxazolidinones. The reactions could be processed at mild conditions to achieve high conversion and regioselectivity.

In conclusion, a series of PS-bound diethanolamine based ionic liquids were developed and used for the synthesis of cyclic carbonates under mild conditions without any co-catalyst and any co-solvents. Catalysts with different number of hydroxyl groups in the cation of the IL had a remarkable influence on the reaction. Among all the supported IL catalysts investigated, PS-DHEEAB was the most effective. The catalyst could be applicable to a series of terminal epoxides and aziridines with good activities. Moreover, the catalyst could be recycled for six times without significant loss in activity and selectivity. The result of this work is an example of the application of diethanolamine based ILs as environmentally benign alternatives in organic synthesis and catalysis.

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15. *Typical synthesis procedure of hydroxyl-functionalized ionic liquids*: (a) For the synthesis of PS-DHEEAB, a mixture of PS (10.0 g, 53.4 mmol, 18.05% Cl content), diethanolamine (5.6 g, 53.5 mmol) and acetonitrile (50 mL) was heated at 80 °C for 24 h in a 125 mL three-necked flask with vigorous stirring. After cooled down to room temperature, the solid residue was collected by filtration and washed separately with water and acetone. Then, the solid was dried under vacuum at 60 °C for 12 h and PS-DHEA was obtained. The loading of diethanolamine attached on the PS was 3.7 mmol/g determined by nitrogen content from elementary analysis (Vario EL, Elementar Analysensysteme GmbH), 98% of the –Cl was reacted through the calculation. (b) Bromoethane (5.9 g, 54.1 mmol), PS-DHEA (10.0 g) and acetonitrile (70 mL) were added into a 125 mL three-necked flask equipped with a magnetic stirrer, the mixture was heated at 80 °C for another 24 h. After reaction, the reaction mixture was cooled down to room temperature. The liquid phase was poured off, and the solid residue was washed with ethyl acetate three times. Then, the solid was dried under vacuum at 60 °C for 12 h and PS-DHEEAB was obtained. Based on the similar procedure, PS-THEAB was synthesized respectively, using 2-bromoethanol instead of bromoethane.
16. *The amount of ionic liquid attached on the PS was determined from elemental analysis*: PS-DHEEAB (loading, 2.6 mmol/g), PS-THEAB (loading, 2.6 mmol/g), PS-HEIMB (loading, 3.2 mmol/g), and PS-EIMB (loading, 3.2 mmol/g).
17. FT-IR spectroscopic studies were firstly carried out with PS-DHEEAB, support PS and the active specie DHEDEAB. The results were compared with those of the corresponding monomeric analogues. The samples were dried over phosphorus pentoxide under vacuum at 70 °C for 48 h before detecting. Both DHEDEAB and PS-DHEEAB display a typical strong peak corresponding to –OH stretching frequency centered at about 3420 cm^{-1}, and a typical peak centered at 1265 cm^{-1} in PS corresponding to the stretching frequency of the functional group –CH$_2$Cl disappears in the spectra of PS-DHEEAB, suggesting the complete modification of PS.
18. *Cycloaddition procedure for the reaction of propylene oxide (PO) with CO$_2$*: All the coupling reactions were conducted in a 100 mL stainless-steel reactor equipped with a magnetic stirrer and automatic temperature control system. A typical reaction was carried out as follows: In the reactor, an appropriate CO$_2$ (≈1.0 MPa) was added to a mixture of PO (7.0 mL, 0.1 mol), and catalyst (2.0 mmol) at room temperature. Then, the temperature was raised to 110 °C with the addition of CO$_2$ from a reservoir tank to maintain a constant pressure (2.0 MPa). After the reaction had proceeded for 2.0 h, the reactor was cooled to ambient temperature, and the remaining CO$_2$ and PO were removed and absorbed in the saturation solution of Na$_2$CO$_3$. The catalyst was separated by filtration, and the products were isolated and analyzed by Agilent 6890/5973 GC–MS equipped with a FID detector and a DB-wax. The catalyst was washed

with acetone for three times and dried under vacuum for the recycling experiment.

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20. Spectral characteristics of the products (**2a**–**h**) in Table 2 were provided as follows: *1,3-Dioxolan-2-one* (**2a**): ^{1}H NMR ($CDCl_3$, TMS, 400 MHz): 4.2 (t, *J* = 10 Hz, 4H); ^{13}C NMR ($CDCl_3$, TMS, 100 MHz): 63.3, 155 (C=O); Anal. Calcd for **2a**: C, 40.92; H, 4.58; O, 54.50. Found: C, 40.82; H, 4.56; O, 54.62. *4-methyl-1,3-dioxolan-2-one* (**2b**): ^{1}H NMR ($CDCl_3$, TMS, 400 MHz):1.49 (d, *J* = 6.0 Hz, 3H); 4.05 (t, *J* = 8.8 Hz, 1H); 4.60 (t, *J* = 8.0 Hz, 1H); 4.86–4.94 (m, 1H); ^{13}C NMR ($CDCl_3$, TMS, 100 MHz): 18.95, 70.46, 73.51, 154.95 (C=O); Anal. Calcd for **2b**: C, 47.06; H, 5.92; O, 47.02. Found: C, 46.93; H, 5.94; O, 47.13. *4-chloromethyl-1,3-dioxolan-2-one* (**2c**): ^{1}H NMR ($CDCl_3$, TMS, 400 MHz): 1.490 (d, *J* = 6.0 Hz, 3H); 4.05 (t, *J* = 8.4 Hz, 1H); 4.60 (t, *J* = 8.0 Hz, 1H); 4.86–4.94 (m, 1H); ^{13}C NMR ($CDCl_3$, TMS, 100 MHz): 18.95, 70.46, 73.51, 154.95 (C=O); Anal. Calcd for **2c**: C, 35.19; H, 3.69; Cl, 25.97; O, 35.15. Found: C, 35.11; H, 3.72; Cl, 25.88; O, 35.29. *4-hexyl-1,3-dioxolan-2-one* (**2d**): ^{1}H NMR ($CDCl_3$, TMS, 400 MHz): 0.84 (t, *J* = 13.1 Hz, 3H); 1.24–1.28 (m, 7H); 1.34 (t, *J* = 9.6 Hz, 1H); 1.65 (t, *J* = 11.7 Hz, 2H); 4.08 (t, *J* = 15.8 Hz, 1H); 4.53 (t, *J* = 15.8 Hz, 1H); 4.74 (t, *J* = 6.9 Hz, 1H); ^{13}C NMR ($CDCl_3$, TMS, 100 MHz): 14.29, 22.52, 24.45, 28.87, 31.63, 33.44, 69.69, 77.49, 155.35 (C=O); Anal. Calcd for **2d**: C, 62.77; H, 9.36; O, 27.87. Found: C, 62.70; H, 9.38; O, 27.92. *4-phenyl-1,3-dioxolan-2-one* (**2e**): ^{1}H NMR ($CDCl_3$, TMS, 400 MHz): 4.34 (t, *J* = 8.4 Hz, 1H); 4.80 (t, *J* = 8.4 Hz, 1H); 5.68 (t, *J* = 8.0 Hz, 1H); 7.35–7.44 (m, 5H); ^{13}C NMR ($CDCl_3$, TMS, 100 MHz): 71.10, 77.92, 125.81, 129.12, 129.63, 135.70, 154.81 (C=O); Anal. Calcd for **2e**: C, 65.85; H, 4.91; O, 29.24. Found: C, 65.72; H, 4.92; O, 29.36. *4,5-tetramethylene-1,3-dioxolan-2-one* (**2f**): ^{1}H NMR ($CDCl_3$, TMS, 400 MHz): 1.80–1.86 (m, 2H); 1.97–2.05 (m, 2H); 2.28 (d, *J* = 4.8 Hz, 4H); 5.06–5.11 (m, 2H); ^{13}C NMR ($CDCl_3$, TMS, 100 MHz): 19.00, 26.61, 75.65, 155.27 (C=O); Anal. Calcd for **2f**: C, 59.14; H, 7.09; O, 33.77. Found: C, 59.06; H, 7.14; O, 33.80. *3-Ethyl-5-phenyloxazolidin-2-one* (**2g**): ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.19 (t, *J* = 9.2 Hz, 3H), 3.30–3.51 (m, 3H), 3.89 (t, *J* = 11.5 Hz, 1H), 5.47 (t, *J* = 6.9 Hz, 1H), 7.33–7.40 (m, 5H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 12.7, 39.0, 51.7, 74.4, 125.6, 129.0, 129.2, 138.7, 157.8; Anal. Calcd for **2g**: C, 69.09; H, 6.85; N, 7.32; O, 16.73. Found: C, 68.92; H, 6.95; N, 7.28; O, 16.85. *3-Isopropyl-5-phenyloxazolidin-2-one* (**2h**): ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.16 (d, *J* = 9.2 Hz, 3H), 1.21 (d, *J* = 9.0 Hz, 3H), 3.40 (t, *J* = 6.0 Hz, 1H), 3.89 (t, *J* = 11.4 Hz, 1H), 4.11–4.22 (m, 1H), 5.48 (t, *J* = 10.5 Hz, 1H), 7.34–7.40 (m, 5H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 20.0, 21.0, 41.6, 48.5, 74.4, 125.5, 128.3, 128.8, 138.7, 158.3; Anal. Calcd for **2h**: C, 71.21; H, 7.81; N, 6.39; O, 14.59. Found: C, 71.12; H, 7.85; N, 7.23; O, 14.69.