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Naturally occurring α-amino acid: a simple and inexpensive catalyst for the selective synthesis of 5-aryl-2-oxazolidinones from CO_2 and aziridines under solvent-free conditions

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ABSTRACT

Naturally occurring α-amino acid successfully catalyzed cycloaddition of aziridine with carbon dioxide to afford 5-aryl-2-oxazolisinones under mild conditions without the need of any additives. The scope of this reaction is very general, providing the corresponding products in good yields and excellent regioselectivity (87:13–100:0) regardless of the α-amino acid examined and a wide variety of N-substituted aziridines employed. Two possible reaction pathways for the reaction were also discussed.

Within the space of a few years, development of highly efficient methods for chemical fixation of carbon dioxide has been drawing intensive interest in organic synthesis and chemical industry. This is due to the fact that carbon dioxide, main greenhouse gas, can be used as a safe and cheap C1 building block to produce useful organic compounds.[1] One of the attractive methods to fix CO_2 is the coupling of CO_2 with aziridines to form oxazolidinones, which are widely available in organic synthesis as chiral auxiliaries or as biologically active pharmaceutical agents.[2] In this respect, numerous catalysts have been reported for this reaction, such as nickel complexes,[3] iodine,[4] alkali metal halide,[5–7] salen Cr(III)/DMAP,[8] phenol/DMAP,[9] and $PEG_{6000}(NBu_3Br)_2$.[10] However, most catalysts cannot meet the current industrial demands because of some drawbacks, such as the need for a cosolvent or cocatalyst, and their high cost. Therefore, development of efficient catalysts for this transformation using cheap and non-toxic reagents and conducting the reactions under solvent-free conditions is still desirable.

As our ongoing interest in CO_2 incorporation into fine organic chemicals,[11] we recently reported the use of naturally occurring α-amino acid in the cycloaddition of CO_2 with epoxides to form carbonates.[11b] Herein, we have successfully extended the scope of this catalytic system to aziridines without the need of any toxic organic solvents or cocatalysts. To the best of our knowledge, this is the first work to use this natural catalyst system to chemical fixation of CO_2 with aziridines. Furthermore, α-amino acids are very active for both epoxides and aziridines. Comparing to the majority of reported catalysts for the carboxylation of CO_2 with aziridines, α-amino acids have many advantages, such as natural, simple, accessible, inexpensive, and non-toxic. We believe that this simple, cheaper, and ecological catalyst system would have great potential in industrial application for chemical fixation of carbon dioxide.

At first, L-histidine, which is one of the most effective catalysts for the cycloaddition of CO_2 with epoxides, was employed as the catalyst for the reaction of 1-propyl-2-phenylazirdine (**1a**)[12] with CO_2.[13] Results in Table 1 showed that L-histidine was very active for this transformation. Hence, experiments with L-histidine as a catalyst were examined carefully to study the carboxylation of **1a** under a variety of reaction conditions, which included changes in catalyst loading (0.2–0.8 mol %), temperature (70–130 °C), CO_2 pressure (3–11 MPa), reaction time (12–48 h).

As is easily seen from Table 1, the activity of our catalytic system is strongly dependent on reaction temperature. In the lower temperature region (70–110 °C), the total yields of oxazolidinone **2a** and **3a** increased rapidly with increasing temperature, while no significant change observed from 110 to 130 °C (Table 1, entries 1–5). In an attempt to determine the suitable dosage of L-histidine used, we found that even when the catalyst loading was as low as 0.2 mol %, the coupling reaction still proceeded smoothly to give oxazolidinones in 70% yield (Table 1, entries 6, 9, and 10). At 8 MPa of CO_2 pressure and 110 °C, **1a** could be completely converted into oxazolidines after 36 h (Table 1, entries 2, 6–8). When the reaction time was shortened to 12 h, the total yield of oxazolidinones was decreased from 99% to 32%. It is worth mentioning that 5-phenyl-3-propyloxazolidin-2-one (**2a**) was predominately formed in all cases which resulted from the opening of the aziridine ring at the most substituted carbon.

Figure 1 illustrates CO_2 pressure dependence on the yield and regioselectivity of oxazolidinones. The yield of oxazolidinones also strongly depended on CO_2 pressure, while variation of pressure had no influence on the regioselectivity of **2a**. The maximum yield reached 99% at about 8 MPa near the critical pressure of CO_2 and a further increase in pressure to 12 MPa led to a depression in yield.

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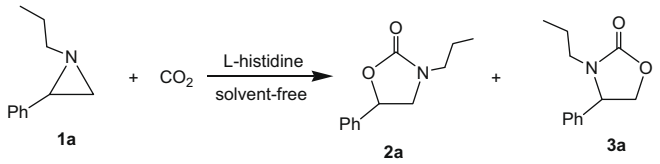
Table 1
Carboxylation of aziridine into oxazolidinone



Entry	Catalyst (mol %)	Temperature (°C)	Time (h)	Yield (%)	**2a**:**3a** (%)
1	0.6	130	48	99	95:5
2	0.6	110	48	99	94:6
3	0.6	100	48	88	94:6
4	0.6	90	48	65	92:8
5	0.6	70	48	8	93:7
6	0.6	110	36	99	93:7
7	0.6	110	24	83	93:7
8	0.6	110	12	32	92:8
9	0.4	110	36	84	92:8
10	0.2	110	36	70	93:7

Yield: the total yield of **2a** and **3a**; regioselectivity: molar ratio of **2a:3a**; reaction conditions: **1a** (322 mg, 2 mmol), L-histidine (1.9 mg, 0.012 mmol), 36 h, 110 °C.

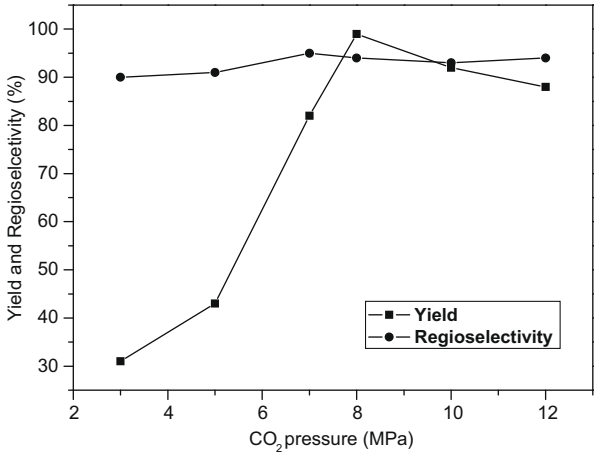


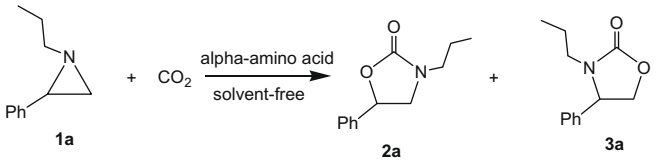
Figure 1. CO_2 pressure-yield and regioselectivity plots in the reaction of **1a** with CO_2.

This interesting phenomenon is almost certainly due to the phase behavior in this set of experiments and is in general agreement with previous report.[14]

Encouraged by the successful results of CO_2-fixation using L-histidine as the catalyst, we next examined the cycloaddition reactions of 1-propyl-2-phenylazirdine (**1a**) with CO_2 using various common α-amino acids as catalysts under the given conditions. The results were summarized in Table 2. Almost all of the amino acids examined could catalyze the reaction to give oxazolidinones in good to excellent yields with a large excess of the 5-substituted isomer over the 4-substituted one (from 87:13 to 96:4).

The reaction was then extended to the carboxylation of several monosubstituted aziridines **1b**–**1l** which were primarily varied as to their N-substitution in the catalysis of L-histidine.[15] The results were listed in Table 3. L-Histidine was a highly effective catalyst for the conversion of various monosubstituted aziridines into oxazolidinones under the optimal conditions. Substrate **1b** and **1c** afforded a relatively low yield of the desired product because self-oligomers were formed during the reaction (Table 3, entries 1 and 2). The substrates **1d–1h** bearing alkyl groups or cyclohexyl at the nitrogen atom afforded corresponding oxazolidinones in good to excellent yields, and 5-substituted oxazolidinones were the major isomer (Table 3, entries 3–7). However, substrate **1i** with a *tert*-butyl substitution at nitrogen atom afforded lower yield (42%) after 72 h, although it gave 3-*tert*-butyl-5-phenyloxazolidin-2-one (**2i**) as the sole product (Table 3, entry 8). Table 3 also showed that aziridines with either electron-donating group or electron-withdrawing group on the C1-aryl group could smoothly react with CO_2 and give oxazolidinones in high yield and regioselectivity (Table 3, entries 9–11). It can be suggested from the above-mentioned results in Tables 2 and 3 that the product yields and regioselectivity depends on the catalyst structure, the electron nature of the sub-

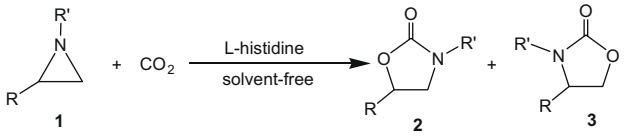
Table 2
Coupling of CO_2 with 1-*n*-propyl-2-phenylaziridine (**1a**) catalyzed by various α-amino acid[a]

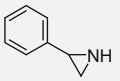
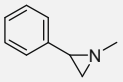
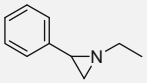
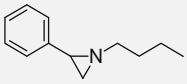
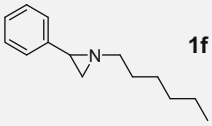
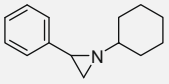
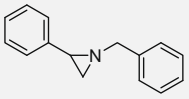
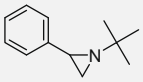
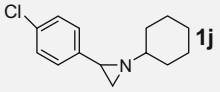
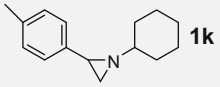
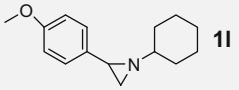


Entry	α-Amino acid	Yield[b] (%)	**2a**:**3a**[c] (%)
1	L-Glycine	96	92:8
2	L-Alanine	48	89:11
3	L-Leucine	99	91:9
4	L-Isoleucine	94	87:13
5	L-Valine	99	91:9
6	L-Serine	84	94:6
7	L-Threonine	99	93:7
8	L-Cysteine	99	92:8
9	L-Methionine	99	90:10
10	L-Tyrosine	83	92:8
11	L-Phenylalanine	82	91:9
12	L-Tryptophan	86	89:11
13	L-Arginine	88	96:4
14	L-Histidine	99	93:7
15	L-Lysine	96	95:5
16	L-Aspartic acid	74	96:4
17	L-Glutamic acid	62	95:5
18	L-Asparagine	99	92:8
19	L-Glutamine	87	91:9
20	L-Proline	99	92:8

[a] Reaction conditions: **1a** (322 mg, 2 mmol); 36 h, CO_2 8 MPa, 110 °C.
[b] The total yield of **2a** and **3a**, determined by GC with biphenyl as an internal standard.
[c] Molar ratio of **2a** to **3a**.

Table 3
Substrate scope of L-histidine in the reaction of CO_2 and N-substituted aziridines[a]

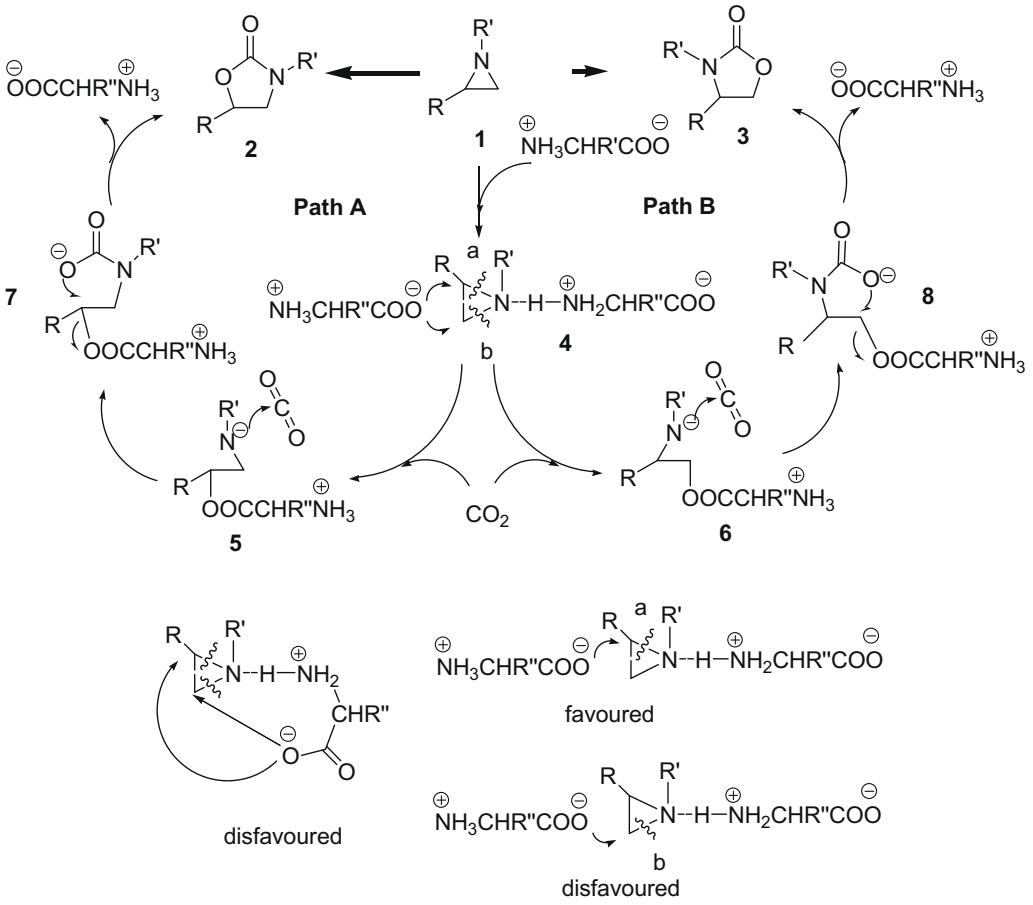


Entry	Substrate	Conversion[b] (%)	Isolated yield[c] (%)	**2**:**3**[d] (%)
1	 **1b**	>99	54	87:13
2	 **1c**	>99	79	94:6
3	 **1d**	>99	97	98:2
4	 **1e**	>99	97	95:5
5	 **1f**	>99	97	99.5:0.5
6	 **1g**	>99	95	98:2
7	 **1h**	>99	96	100:0
8[e]	 **1i**	45	42	100:0
9	 **1j**	>99	94	99:1
10	 **1k**	>99	96	99:1
11	 **1l**	>99	92	100:0

[a] Reaction conditions: substrates (2 mmol) L-histidine (1.9 mg, 0.012 mmol), 36 h, CO_2 8 MPa, 110 °C.
[b] Determined by GC with biphenyl as an internal standard.
[c] The total yield of **2** and **3**.
[d] Molar ratio of **2** to **3**, determined by ^1H NMR.
[e] The reaction time is 72 h.

strates, and the steric hindrance of the substituent group at the nitrogen atom. These regiospecific results are similar to those of the reaction of aziridines in the presence of salen Cr(III)/DMAP[8] or $PEG_{6000}(NBu_3Br)_2$.[10]

It has been suggested that hydrogen binding can activate the ring-opening reaction of epoxides.[16] In our catalytic system, there was a hydrogen bond donor from amino acids. On the basis of the special structure of amino acid[17] and our experimental results, we proposed a plausible reaction mechanism for the formation of oxazolidinones involving Lewis acid activation and Lewis base nucleophilic attack of the aziridines by different amino acids, which was shown in Scheme 1. Firstly, the aziridine ring was activated by an amino acid through hydrogen bond to form the intermediate **4**. Next, it has been reported that the nucleophilic attack would not occur by the carboxylate ion of the same amino acid which activated the aizridine ring through hydrogen bonding according to the Baldwin's rule.[18] Thus, the activated ring was nucleophilic attacked by the carboxylate ion of another amino acid. Since the bond dissocaiation energy of ArCH–NR is lower than that of $ArCHCH_2$–NHR in aziridine ring,[19] the intermediate **5** was favorably formed via Path A although ring-opening reaction occurred at the more sterically hindered side of the aziridine ring. Regioselectivity in this ring-opening reaction results in the regioselective formation of oxazolidinones. Then, the interaction was occurred between the zwitterion **5** and CO_2 to form intermediate **7**. Finally the intramolecular cyclization via nucleophilic attack led to the final product and regenerated the catalyst. Path B is a difavorable route on energy, however if intermediate **6** was formed, regioisomer **3** could be obtained through a similar way.



Scheme 1. A proposed mechanism for the coupling of CO_2 and aziridines by the α-amino acids catalyst system.

In conclusion, a novel catalytic system for incorporation of CO_2 into aziridines for the synthesis of oxazolidinones was developed. Almost all the naturally occurring α-amino acids were efficient catalysts for the reaction of CO_2 with aziridines to obtain the corresponding oxazolidinones in excellent yield and high regioselectivity. This CO_2-fixation method can be operated under supercritical conditions without any additives. The hopeful method for chemical fixation of CO_2 will be further improved in order to develop more environmentally benign progress.

Acknowledgments

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12. All of the aziridines were synthesized according to the following literatures (a) Capriati, V.; Florio, S.; Luisi, R.; Musio, B. *Org. Lett.* **2005**, *7*, 3749; (b) Ref. 10.
13. *General procedure for carboxylation of aziridine with CO_2*: Aziridine (2 mmol), L-histidine (1.9 mg, 0.012 mmol) was added to a 15 mL stainless autoclave reactor with a magnetic stirrer. CO_2 was introduced into the autoclave and then the pressure was generally adjusted to 8 MPa at 110 °C. The mixture was stirred continuously at 110 °C for 36 h, and the pressure was kept constant during the reaction. After the reaction, the reactor was cooled in ice-water and extra CO_2 was vented slowly. An aliquot of sample was taken from the resultant mixture and dissolved in CH_2Cl_2 for GC analysis. The residue was purified by flash silica gel chromatography using petroleum ether/ethyl acetate = 10:1 to 1:1 as eluant to afford the product. The products were further identified by NMR and MS.
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15. *Spectroscopic data of the 5-aryl-2-oxazolidinones*: *5-Phenyl-3-propyloxazolidin-2-one* (**2a**): ^{1}H NMR (400 MHz, $CDCl_3$) δ 0.91 (t, ^3J = 7.2 Hz, 3H), 1.52–1.61 (m, 2H), 3.18–3.31 (m, 2H), 3.40 (t, ^3J = 8.0 Hz, 1H), 3.90 (t, ^3J = 8.8 Hz, 1H), 5.46 (t, ^3J = 8.0 Hz, 1H), 7.32–7.39 (m, 5H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 11.0, 20.5, 45.7, 52.0, 74.2, 125.4, 128.6, 128.7, 138.8, 157.9; MS (EI) *m*/*z* (%): 205, 144, 132, 105, 91, 70, 43.
5-Phenyloxazolidin-2-one (**2b**): ^{1}H NMR (400 MHz, $CDCl_3$) δ 3.53 (t, ^3J = 8.4 Hz, 1H), 3.97 (t, ^3J = 8.4 Hz, 1H), 5.60 (t, ^3J = 8.2 Hz, 1H), 6.68 (s, 1H), 7.36–7.41 (m, 5H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 48.2, 77.7, 125.5, 128.7, 138.3, 160.1; MS (EI) *m*/*z* (%): 163, 107, 91, 79, 77, 32.
3-Methyl-5-phenyloxazolidin-2-one(**2c**): ^{1}H NMR (400 MHz, $CDCl_3$) δ 2.91 (s, 3H), 3.43 (t, ^3J = 8.4 Hz, 1H), 3.91 (t, ^3J = 8.8 Hz, 1H), 5.46 (t, ^3J = 8.0 Hz, 1H),

7.35–7.41 (m, 5H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 30.9, 54.2, 74.0, 125.4, 128.6, 128.7, 138.5, 158.0. MS (EI) *m*/*z* (%): 177, 132, 91, 77, 43.

3-Ethyl-5-phenyloxazolidin-2-one (**2d**): ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.05 (t, ^3J = 7.2 Hz, 3H), 1.29–1.38 (m, 2H), 1.48–1.56 (m, 2H), 3.21–3.35 (m, 2H), 3.40 (t, ^3J = 8.0 Hz, 1H), 3.89 (t, ^3J = 8.8 Hz, 1H), 5.45 (t, ^3J = 8.0 Hz, 1H), 7.32–7.39 (m, 5H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 13.6, 19.7, 29.2, 43.7, 52.0, 74.2, 125.4, 128.6, 128.7, 138.8, 157.8; MS (EI) *m*/*z* (%): 191, 146, 130, 91, 57.

3-Butyl-5-phenyloxazolidin-2-one (**2e**): ^{1}H NMR (400 MHz, $CDCl_3$) δ 0.92 (t, ^3J = 7.2 Hz, 3H), 1.29–1.38 (m, 2H), 1.48–1.56 (m, 2H), 3.21–3.35 (m, 2H), 3.40 (t, ^3J = 8.0 Hz, 1H), 3.89 (t, ^3J = 8.8 Hz, 1H), 5.45 (t, ^3J = 8.0 Hz, 1H), 7.32–7.39 (m, 5H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 13.6, 19.7, 29.2, 43.7, 52.0, 74.2, 125.4, 128.6, 128.7, 138.8, 157.8; MS (EI) *m*/*z* (%): 219, 176, 132, 105, 91, 84.

3-tert-Butyl-5-phenyloxazolidin-2-one (**2f**): ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.41 (s, 9H), 3.45 (t, ^3J = 8.4 Hz, 1H), 3.95 (t, ^3J = 8.6 Hz, 1H), 5.36 (t, ^3J = 8.2 Hz, 1H), 7.32–7.41 (m, 5H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 27.3, 50.9, 53.4, 73.3, 125.4, 128.5, 128.7, 138.9, 156.6; MS (EI) *m*/*z* (%): 219, 204, 160, 91, 57.

3-Hexyl-5-phenyloxazolidin-2-one (**2g**): ^{1}H NMR (400 MHz, $CDCl_3$) δ 0.79 (t, ^3J = 6.6 Hz, 3H), 1.20–1.24 (m, 6H), 1.43–1.47 (m, 2H), 3.13–3.23 (m, 2H), 3.31 (t, ^3J = 8.0 Hz, 1H), 3.82 (t, ^3J = 8.8 Hz, 1H), 5.37 (t, ^3J = 8.0 Hz, 3H), 7.25–7.31 (m, 5H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 13.6, 22.1, 25.9, 26.9, 31.0, 43.7, 51.7, 73.9, 125.1, 128.3, 128.5, 138.7, 157.5; MS (EI) *m*/*z* (%): 247, 176, 156, 132, 104, 91, 77.

3-Cyclohexyl-5-phenyloxazolidin-2-one (**2h**): ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.0–1.9 (m, 10H), 3.39 (t, ^3J = 8.0 Hz, 1H), 3.71–3.78 (m, 1H), 3.88 (t, ^3J = 8.6 Hz, 1H), 5.46 (t, ^3J = 8.0 Hz, 1H), 7.33–7.41 (m, 5H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 25.1, 29.9, 30.4, 48.2, 52.4, 74.4, 125.3, 128.6, 128.7, 138.9, 157.1; MS (EI) *m*/*z* (%): 245, 200, 164, 110, 104, 91, 55.

3-Benzyl-5-phenyloxazolidin-2-one (**2i**): ^{1}H NMR (400 MHz, $CDCl_3$) δ 3.29 (t, ^3J = 8.2 Hz, 1H), 3.75 (t, ^3J = 8.8 Hz, 1H), 4.46 (ABq, *JAB* = 15.0 Hz, $\Delta\nu$AB = 36.0 Hz, 2H), 5.45 (t, ^3J = 8.0 Hz, 1H), 7.26–7.36 (m, 10H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 48.3, 51.5, 74.5, 125.5, 128.0, 128.1, 128.7, 128.8, 135.6, 138.5, 157.9; MS (EI) *m*/*z* (%): 253, 165, 118, 104, 91, 65.

5-(4-Chlorophenyl)-3-cyclohexyloxazolidin-2-one (**2j**): ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.05–1.83 (m, 10H), 3.34 (t, ^3J = 8.0 Hz, 1H), 3.69–3.76 (m, 1H), 3.89 (t, ^3J = 8.7 Hz, 1H), 5.44 (t, ^3J = 8.0 Hz, 1H), 7.27–7.38 (m, 4H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 25.2, 25.3, 30.0, 30.4, 48.2, 52.6, 73.8, 126.8, 129.0, 134.5, 137.6, 156.8; MS (EI) *m*/*z* (%): 279, 267, 236, 198, 192, 180, 154, 138, 110, 103, 55.

3-Cyclohexyl-5-p-tolyloxazolidin-2-one (**2k**): ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.02–1.82 (m, 10H), 2.36 (s, 3H), 3.38 (t, ^3J = 8.0 Hz, 1H), 3.71–3.75 (m, 1H), 3.85 (t, ^3J = 8.7 Hz, 1H), 5.43 (t, ^3J = 8.0 Hz, 1H), 7.17–7.26 (m, 4H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 21.1, 25.2, 25.3, 25.4, 30.1, 30.5, 48.3, 52.5, 74.5, 125.5, 129.5, 136.0, 138.6, 157.3; MS (EI) *m*/*z* (%): 259, 220, 214, 172, 158, 134, 118, 105, 91, 55.

3-Cyclohexyl-5-(4-methoxyphenyl)oxazolidin-2-one (**2l**): ^{1}H NMR (400 MHz, $CDCl_3$) δ 0.86–1.86 (m, 10H), 3.39 (t, ^3J = 8.0 Hz, 1H), 3.72–3.87 (m, 5H), 5.41 (t, ^3J = 8.0 Hz, 1H), 6.91 (d, *J* = 8.8 Hz, 2H), 7.27 (d, *J* = 8.8 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 25.2, 25.3, 30.0, 30.5, 48.2, 52.4, 55.3, 74.5, 114.1, 127.1, 130.8, 157.2, 159.8; MS (EI) *m*/*z* (%): 275, 230, 188, 148, 134, 121, 110, 83.

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