EurJOC
European Journal of Organic Chemistry

Chemistry Europe
European Chemical Societies Publishing

Accepted Article

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To be cited as: *Eur. J. Org. Chem.* 10.1002/ejoc.202000771

Link to VoR: https://doi.org/10.1002/ejoc.202000771

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10.1002/ejoc.202000771

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FULL PAPER

Triethylamine Hydroiodide as a Bifunctional Catalyst for the Solvent-Free Synthesis of 2-Oxazolidinones

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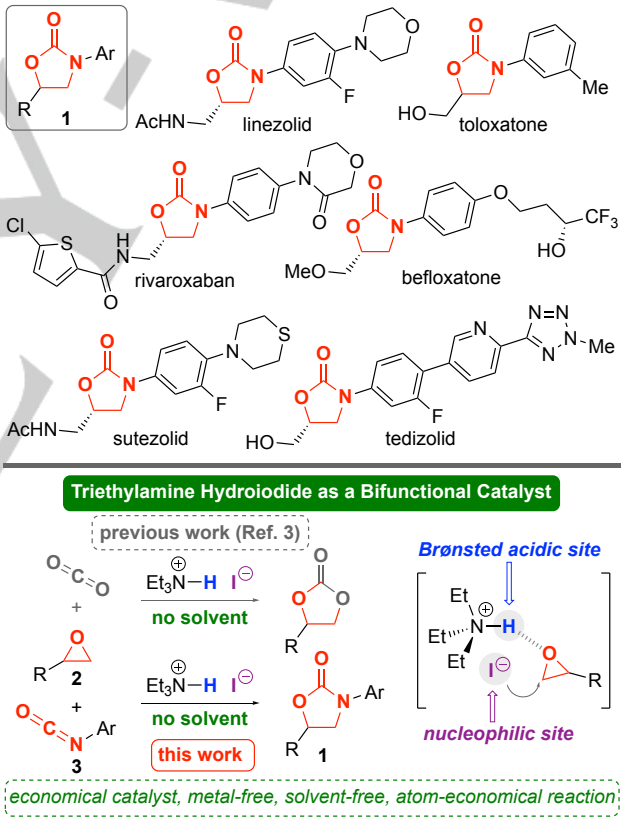
Abstract: Among the wide variety of heterocycles, 2-oxazolidinones are recognized as some of the most important heterocyclic compounds in medicinal chemistry. Therefore, the development of a practical methods for their synthesis would be an important development. Herein, we report a practical method for the synthesis of 2-oxazolidinones under solvent-free conditions using triethylamine hydroiodide as a simple and effective bifunctional organocatalyst.

Introduction

Five-membered heterocycles are very important structural units for drug design.[1] Among the wide variety of five-membered heterocycles, 2-oxazolidinones **1** are recognized as some of the most important heterocyclic compounds in medicinal chemistry. Many important pharmaceuticals have been designed and prepared based on a 2-oxazolidinone core (Scheme 1).[2] For example, anticoagulant agent, rivaroxaban ranked as one of the top-selling drugs. Thus, the development of an efficient and practical method for the synthesis of 2-oxazolidinones **1** would be important in the field of synthetic organic chemistry. In the course of our recent study on the development of practical methods for the synthesis of five-membered cyclic carbonates from epoxides and carbon dioxide using triethylamine hydroiodide as a simple and effective bifunctional catalyst,[3–5] we became interested in the synthesis of 2-oxazolidinones **1** under a similar catalytic system. The coupling reactions of epoxides **2** and aryl isocyanates **3** under the influence of a triethylamine hydroiodide provides 2-oxazolidinones **1** without the formation of by-products.[6] Herein, we report a practical and efficient method for the synthesis of 2-oxazolidinones under solvent and metal-free environmentally benign conditions with an economical and readily available triethylamine hydroiodide catalyst.

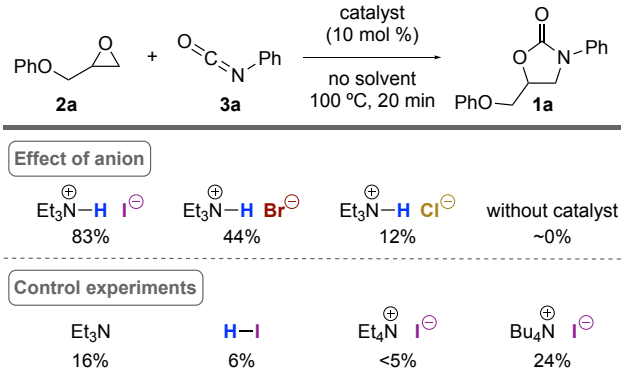


Scheme 1. Important 2-oxazolidinones and our synthetic approach.

Results and Discussion

Our initial aim was to clarify the catalytic activity of triethylamine hydroiodide as a bifunctional organocatalyst in the synthesis of 2-oxazolidinone **1a** (Scheme 2). The reaction proceeds under very simple conditions. A mixture of glycidyl phenyl ether **2a**, phenyl isocyanate **3a** (1.1 equiv), and triethylamine hydroiodide (10 mol %) was heated at 100 °C. After stirring the mixture for 20 min

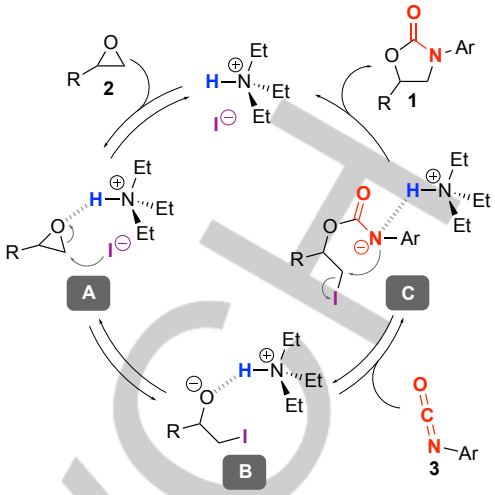
at 100 °C, we obtained the target product **1a** in an 83% yield.[7] We next investigated the effects of anions in the bifunctional catalyst. The catalytic activity of ammonium salts largely depends on the halide anion, and bromide and chloride anions showed a lower level of catalytic activity compared with that of the iodide anion. The reaction using triethylamine hydrobromide provided product **1a** in a moderate yield (44%), but triethylamine hydrochloride could only produce **1a** in a low yield (12%). The use of halide anions resulted in a similar trend during our previous study of the cyclic carbonate synthesis.[3] It should be noted that no target product was obtained when the reaction was performed without a catalyst.



Scheme 2. Effect of ammonium salt catalysts.

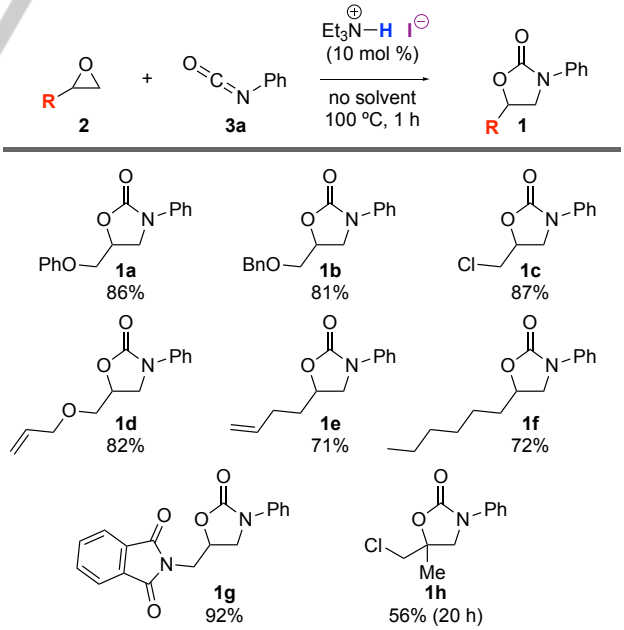
To clarify the importance of the bifunctional properties of triethylamine hydroiodide, several control experiments were examined (Scheme 2). When the reactions were performed with either triethylamine or hydroiodic acid catalysts, target 2-oxazolidinone **1a** was obtained in low yields (16 and 6%, respectively). In addition, the catalytic activities of tetraalkylammonium iodides were compared with that of triethylamine hydroiodide.[6a,k] The reactions using tetraethylammonium and tetrabutylammonium iodide catalysts proceeded slowly under the reaction conditions to provide **1a** in low yields (<5 and 24%, respectively). These results clearly suggested that both an iodide counter anion and an acidic hydrogen on the nitrogen of the triethylamine hydroiodide catalyst were essential to achieve good catalytic performance.

Based on the results listed in Scheme 2, the assumed catalytic cycle for the present reaction using the triethylamine hydroiodide catalyst was proposed, and it appears in Scheme 3. In this cycle, epoxide **2** is activated *via* a hydrogen-bonding interaction with an acidic hydrogen on the catalyst, as proven in our previous study (intermediate **A**).[3] The activated epoxide then undergoes nucleophilic attack from an iodide anion to form intermediate **B**. The nucleophilic alkoxide anion in intermediate **B** attacks isocyanate **3** to yield intermediate **C**. The intramolecular ring-closing of intermediate **C** affords the target 2-oxazolidinone **1** with a regeneration of the triethylamine hydroiodide catalyst. The positive effect of the iodide anion in comparison with other halide anions in Scheme 2 can be explained by a lower ability to coordinate with an acidic hydrogen (intermediate **A**) and by the ability of the higher leaving groups (intermediate **C**).



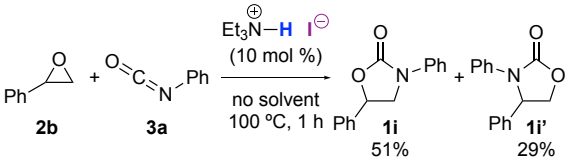
Scheme 3. Assumed catalytic cycle.

With the assumed catalytic cycle in hand, the substrate generality of epoxides **2** was examined with phenyl isocyanate **3a** under the influence of the triethylamine hydroiodide catalyst (Scheme 4). Epoxides containing various functional groups could be applied to this reaction. The target 2-oxazolidinones **1a**–**1g** were obtained in good to high yields as a result of the reaction at 100 °C for 1 h under solvent-free conditions.[8] The present catalytic system could be applied to the reaction with 2,2-disubstituted epoxide. We could obtain a disubstituted 2-oxazolidinone **1h** in a moderate yield as a result of the reaction for 20 h. It should be mentioned that several 2-oxazolidinone products in Scheme 4 have been reported as biologically active compounds.[9]



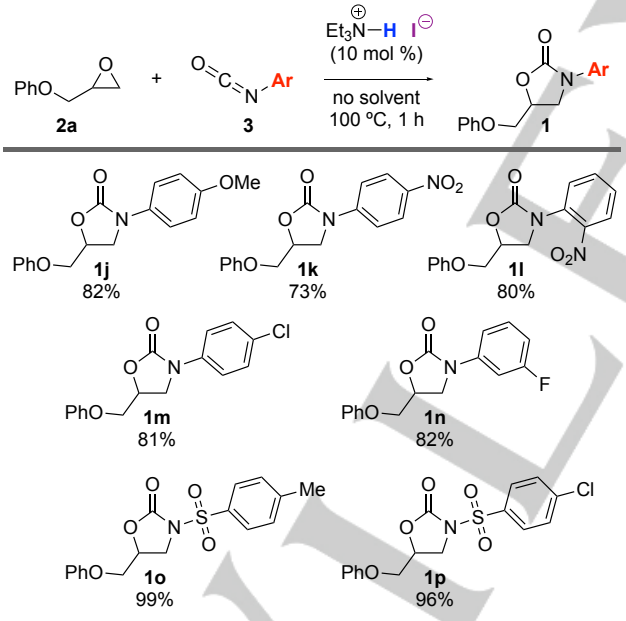
Scheme 4. Scope of epoxides **2**.

The reaction was also performed with styrene oxide **2b** under standard reaction conditions (Scheme 5). Although the reaction of styrene oxide **2b** and phenyl isocyanate **3a** was efficiently promoted using a triethylamine hydroiodide catalyst, we obtained not only the target 2-oxazolidinone **1i** (51% yield) but also regioisomer **1i'** (29% yield). Regioisomeric products such as a **1i'** are generally observed in reactions with styrene oxide derivatives.[6]



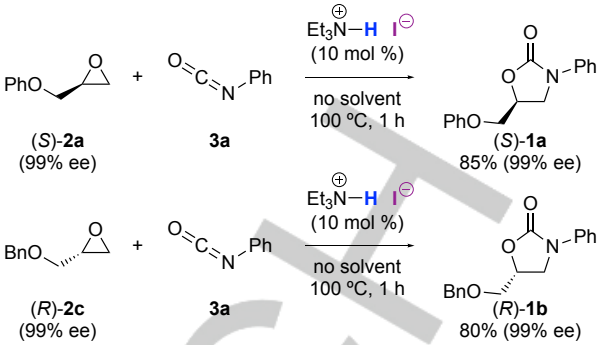
Scheme 5. Reaction with styrene oxide **2b**.

The scope of aryl isocyanates **3** was also investigated (Scheme 6).[10] A series of aryl isocyanates **3** possessing electron-donating and -withdrawing functionalities at the para, meta, and ortho positions could be applied to the reaction with glycidyl phenyl ether **2a** under the influence of triethylamine hydroiodide catalyst to provide 2-oxazolidinones **1j**–**1n** in good yields. Arylsulfonyl isocyanates could also be applied to this reaction system to provide products **1o** and **1p** in excellent yields.



Scheme 6. Scope of isocyanates **3**.

To expand the utility of the present reaction system using triethylamine hydroiodide as a bifunctional catalyst, enantiopure epoxides (*S*)-**2a** and (*R*)-**2c** were submitted to produce optically active 2-oxazolidinones (Scheme 7). To our delight, optically pure 2-oxazolidinones (*S*)-**1a** and (*R*)-**1b** were obtained in good yields with retention of the chirality.



Scheme 7. Synthesis of optically active 2-oxazolidinones.

Conclusion

In summary, we successfully developed a practical method for the synthesis of medicinally important 2-oxazolidinones by using triethylamine hydroiodide as a simple, yet effective, bifunctional organocatalyst. The atom-economical coupling reactions of epoxides and isocyanates with triethylamine hydroiodide proceeded under solvent-free conditions. The importance of the bifunctional feature of the catalyst was clarified in the control experiments. Additionally, the present catalytic system could be applied to the asymmetric synthesis of chiral 2-oxazolidinones. The reported reaction system is one of the most economical processes yet documented for the efficient synthesis of 2-oxazolidinones.

Experimental Section

General Procedure for the Reaction of Epoxides 2 and Isocyanates 3 Catalyzed by Triethylamine Hydroiodide. A mixture of epoxide **2** (2.0 mmol), isocyanate **3** (2.2 mmol), and triethylamine hydroiodide (0.20 mmol, 10 mol %) was heated to 100 °C and stirred for 1 h. After cooling to room temperature, the reaction mixture was purified by flash column chromatography on silica gel (hexane/EtOAc or hexane/CH_2Cl_2 as eluent) to afford the corresponding 2-oxazolidinone **1**.

5-(Phenoxymethyl)-3-phenyl-oxazolidin-2-one (1a):[6] ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.58 (dd, *J* = 0.8, 8.8 Hz, 2H), 7.40 (t, *J* = 8.0 Hz, 2H), 7.30 (dt, *J* = 1.2, 8.2 Hz, 2H), 7.16 (t, *J* = 7.2 Hz, 1H), 7.00 (t, *J* = 7.2 Hz, 1H), 6.92 (dd, *J* = 0.8, 8.4 Hz, 2H), 4.96–5.01 (m, 1H), 4.18–4.27 (m, 3H), 4.08 (dd, *J* = 6.0, 8.8 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 158.0, 154.4, 138.1, 129.6, 129.1, 124.2, 121.7, 118.3, 114.6, 70.3, 67.8, 47.4; IR (neat): 1738, 1506, 1499, 1414, 1254, 1225, 752, 744 cm^{-1}. (*S*)-**1a:**[6] $[\alpha]^{21}_D$ +59.7 (*c* = 0.90, $CHCl_3$, 99% ee); HPLC analysis: Daicel Chiralpak IC-3, hexane/2-propanol = 3:1, flow rate = 0.5 mL/min, 254 nm; retention time: 57.0 min (minor) and 73.1 min (major).

5-(Benzyloxymethyl)-3-phenyl-oxazolidin-2-one (1b):[6] ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.54 (dd, *J* = 1.2, 8.4 Hz, 2H), 7.28–7.40 (m, 7H), 7.14 (t, *J* = 7.2 Hz, 1H), 4.75–4.81 (m, 1H), 4.64 (d, *J* = 12.0 Hz, 1H), 4.60 (d, *J* = 11.6 Hz, 1H), 4.07 (dd, *J* = 8.8, 8.8 Hz, 1H), 3.93 (dd, *J* = 6.4, 8.8 Hz, 1H), 3.73 (d, *J* = 4.4 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 154.5, 138.2, 137.3, 129.0, 128.5, 127.9, 127.7, 123.9, 118.1, 73.7, 71.2, 70.0, 47.2; IR (neat): 1743, 1504, 1408, 1223, 1129, 1104, 753 cm^{-1}. (*R*)-**1b:**[6] $[\alpha]^{19}_D$ –32.3 (*c* = 0.80, $CHCl_3$, 99% ee); HPLC analysis: Daicel Chiralpak IC-3, hexane/2-propanol = 3:1, flow rate = 0.5 mL/min, 214 nm; retention time: 73.0 min (minor) and 78.1 min (major).

5-(Chloromethyl)-3-phenyl-oxazolidin-2-one (1c):[6] ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.55 (d, *J* = 8.8 Hz, 2H), 7.40 (t, *J* = 8.8 Hz, 2H), 7.17 (t, *J* = 8.0 Hz, 1H), 4.84–4.91 (m, 1H), 4.18 (dd, *J* = 8.8, 9.6 Hz, 1H), 3.97 (dd, *J* = 6.0, 9.6 Hz, 1H), 3.80 (dd, *J* = 4.4, 11.6 Hz, 1H), 3.75 (dd, *J* = 6.8, 11.6 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 153.9, 137.7, 129.1, 124.3, 118.3, 70.8, 48.0, 44.6; IR (neat): 1742, 1502, 1408, 1307, 1225, 1128, 748 cm^{-1}.

5-(Allyloxymethyl)-3-phenyl-oxazolidin-2-one (1d):[6] ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.56 (dd, *J* = 0.8, 8.8 Hz, 2H), 7.38 (t, *J* = 8.0 Hz, 2H), 7.14 (t, *J* = 7.6 Hz, 1H), 5.84–5.94 (m, 1H), 5.20–5.32 (m, 2H), 4.75–4.81 (m, 1H), 4.06–4.10 (m, 3H), 3.95 (dd, *J* = 6.4, 8.8 Hz, 1H), 3.67–3.74 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 154.5, 138.2, 133.9, 129.0, 123.9, 118.1, 117.7, 72.6, 71.2, 70.0, 47.2; IR (neat): 1744, 1503, 1409, 1223, 1131, 1107, 754 cm^{-1}.

5-(3-Buten-1-yl)-3-phenyl-oxazolidin-2-one (1e):[11] ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.54 (d, *J* = 8.0 Hz, 2H), 7.38 (t, *J* = 8.0 Hz, 2H), 7.14 (t, *J* = 7.6 Hz, 1H), 5.78–5.89 (m, 1H), 5.04–5.14 (m, 2H), 4.63–4.70 (m, 1H), 4.09 (dd, *J* = 8.4, 8.8 Hz, 1H), 3.67 (dd, *J* = 6.8, 8.8 Hz, 1H), 2.20–2.36 (m, 2H), 1.94–2.03 (m, 1H), 1.78–1.87 (m, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 154.7, 138.2, 136.5, 128.9, 123.8, 118.0, 115.9, 72.2, 50.3, 34.1, 28.7; IR (neat): 1741, 1503, 1407, 1218, 1130, 912, 754, 729 cm^{-1}.

5-Hexyl-3-phenyl-oxazolidin-2-one (1f):[11] ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.54 (dd, *J* = 0.8, 8.8 Hz, 2H), 7.38 (t, *J* = 8.0 Hz, 2H), 7.13 (t, *J* = 7.2 Hz, 1H), 4.60–4.67 (m, 1H), 4.08 (dd, *J* = 8.4, 8.8 Hz, 1H), 3.66 (dd, *J* = 6.8, 8.4 Hz, 1H), 1.68–1.91 (m, 2H), 1.25–1.55 (m, 8H), 0.90 (t, *J* = 6.8 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 154.9, 138.3, 128.9, 123.8, 118.1, 73.0, 50.4, 35.0, 31.5, 28.8, 24.4, 22.4, 14.0; IR (neat): 2953, 2917, 2855, 1738, 1721, 1505, 1416, 1233, 1147, 756, 747 cm^{-1}.

3-Phenyl-5-(phthalimidomethyl)-oxazolidin-2-one (1g):[6] ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.86–7.90 (m, 2H), 7.73–7.78 (m, 2H), 7.52 (d, *J* = 7.6 Hz, 2H), 7.37 (t, *J* = 8.0 Hz, 2H), 7.14 (t, *J* = 7.6 Hz, 1H), 4.95–5.02 (m, 1H), 4.12–4.18 (m, 2H), 3.98 (dd, *J* = 5.6, 14.4 Hz, 1H), 3.92 (dd, *J* = 5.6, 9.2 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 167.9, 153.9, 137.8, 134.3, 131.6, 128.9, 124.1, 123.5, 118.2, 69.5, 48.2, 40.7; IR (neat): 1750, 1742, 1709, 1414, 1398, 1389, 1225, 1138, 1040, 754, 725, 713 cm^{-1}.

5-(Chloromethyl)-5-methyl-3-phenyl-oxazolidin-2-one (1h): ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.55 (d, *J* = 8.0 Hz, 2H), 7.39 (t, *J* = 8.0 Hz, 2H), 7.16 (t, *J* = 7.2 Hz, 1H), 4.11 (d, *J* = 9.2 Hz, 1H), 3.77 (d, *J* = 9.2 Hz, 1H), 3.74 (d, *J* = 11.2 Hz, 1H), 3.63 (d, *J* = 11.2 Hz, 1H), 1.67 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 153.5, 137.9, 129.0, 124.2, 118.2, 77.3, 53.4, 49.2, 24.1; IR (neat): 1739, 1503, 1405, 1319, 1216, 1146, 1094, 751 cm^{-1}; HRMS (FAB) calcd for $C_{11}H_{12}ClNO_2$: 225.0557 ([M]$^+$), found 225.0557.

3,5-Diphenyl-oxazolidin-2-one (1i):[6] ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.56 (d, *J* = 8.4 Hz, 2H), 7.36–7.45 (m, 7H), 7.15 (t, *J* = 7.6 Hz, 1H), 5.64 (dd, *J* = 7.6, 8.4 Hz, 1H), 4.38 (dd, *J* = 8.8, 8.8 Hz, 1H), 3.97 (dd, *J* = 7.6, 9.2 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 154.6, 138.03, 138.00, 128.98. 128. 91, 125.6, 124.0, 118.2, 73.9, 52.5; IR (neat): 1744, 1502, 1400, 1369, 1222, 1210, 1136, 984, 751 cm^{-1}.

3,4-Diphenyl-oxazolidin-2-one (1i'):[6] ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.23–7.40 (m, 9H), 7.06 (t, *J* = 7.6 Hz, 1H), 5.39 (dd, *J* = 5.6, 8.8 Hz, 1H), 4.77 (dd, *J* = 8.8, 8.8 Hz, 1H), 4.19 (dd, *J* = 5.6, 8.8 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 155.9, 138.2, 137.0, 129.3. 128.85, 128.77, 126.2, 124.6, 120.8, 69.8, 60.6; IR (neat): 1744, 1500, 1394, 1354, 1209, 1125, 1046, 756 cm^{-1}.

3-(4-Methoxyphenyl)-5-(phenoxymethyl)-oxazolidin-2-one (1j):[6] ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.47 (d, *J* = 9.2 Hz, 2H), 7.31 (t, *J* = 8.4 Hz, 2H), 7.00 (t, *J* = 7.6 Hz, 1H), 6.90–6.95 (m, 4H), 4.94–4.99 (m, 1H), 4.15–4.25 (m, 3H), 4.03 (dd, *J* = 5.6, 8.8 Hz, 1H), 3.81 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 158.0, 156.4, 154.7, 131.2, 129.6, 121.7, 120.3, 114.6, 114.3, 70.3, 67.9, 55.5, 47.9; IR (neat): 1732, 1519, 1253, 1244, 1226, 1147, 1095, 1085, 1042, 988, 819, 755 cm^{-1}.

3-(4-Nitrophenyl)-5-(phenoxymethyl)-oxazolidin-2-one (1k):[11] ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.28 (d, *J* = 9.6 Hz, 2H), 7.77 (d, *J* = 9.6 Hz, 2H), 7.31 (t, *J* = 8.0 Hz, 2H), 7.02 (t, *J* = 7.2 Hz, 1H), 6.90 (d, *J* = 8.0 Hz, 2H), 5.03–5.09 (m, 1H), 4.23–4.30 (m, 3H), 4.17 (dd, *J* = 5.6, 8.8 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 157.8, 153.8, 143.6, 143.4, 129.7, 125.0, 122.0, 117.4, 114.6, 70.6, 67.6, 47.0; IR (neat): 1741, 1597, 1515, 1505, 1491, 1403, 1329, 1304, 1214, 1146, 753 cm^{-1}.

3-(2-Nitrophenyl)-5-(phenoxymethyl)-oxazolidin-2-one (1l): ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.04 (d, *J* = 8.8 Hz, 1H), 7.68 (t, *J* = 8.0 Hz, 1H), 7.46–7.50 (m, 2H), 7.32 (t, *J* = 8.4 Hz, 2H), 7.02 (t, *J* = 7.2 Hz, 1H), 6.96 (d, *J* = 8.0 Hz, 2H), 5.06–5.12 (m, 1H), 4.24–4.30 (m, 3H), 4.09 (dd, *J* = 5.6, 8.8 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 157.9, 155.3, 145.3, 133.9, 131.1, 129.6, 128.0, 127.6, 125.8, 121.6, 114.5, 71.9, 67.6, 49.1; IR (neat): 1752, 1529, 1490, 1413, 1354, 1225, 1153, 747, 733 cm^{-1}; HRMS (FAB) calcd for $C_{16}H_{14}N_2O_5$: 314.0903 ([M]$^+$), found 314.0903.

3-(4-Chlorophenyl)-5-(phenoxymethyl)-oxazolidin-2-one (1m):[6] ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.53 (d, *J* = 9.6 Hz, 2H), 7.35 (d, *J* = 8.8 Hz, 2H), 7.30 (t, *J* = 8.0 Hz, 2H), 7.01 (t, *J* = 7.6 Hz, 1H), 6.91 (d, *J* = 7.6 Hz, 2H), 4.96–5.03 (m, 1H), 4.23 (d, *J* = 4.4 Hz, 2H), 4.18 (dd, *J* = 8.8, 8.8 Hz, 1H), 4.06 (dd, *J* = 6.0, 8.8 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 157.9, 154.2, 136.7, 129.6, 129.4, 129.1, 121.8, 119.4, 114.5, 70.4, 67.7, 47.2; IR (neat): 1737, 1498, 1251, 1224, 1146, 1096, 754 cm^{-1}.

3-(3-Fluorophenyl)-5-(phenoxymethyl)-oxazolidin-2-one (1n): ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.48 (td, *J* = 2.4, 11.2 Hz, 1H), 7.28–7.37 (m, 4H), 7.01 (t, *J* = 7.6 Hz, 1H), 6.91 (dd, *J* = 0.8, 8.8 Hz, 2H), 6.86 (ddt, *J* = 0.8, 2.4, 8.0 Hz, 1H), 4.97–5.03 (m, 1H), 4.23 (d, *J* = 4.4 Hz, 2H), 4.19 (dd, *J* = 8.8, 8.8 Hz, 1H), 4.06 (dd, *J* = 6.0, 8.8 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 163.0 (d, *J* = 244 Hz), 157.9, 154.1, 139.6 (d, *J* = 10.7 Hz), 130.2 (d, *J* = 9.1 Hz), 129.6, 121.8, 114.6, 113.2 (d, *J* = 3.3 Hz), 110.8 (d, *J* = 21.4 Hz), 105.8 (d, *J* = 27.2 Hz), 70.4, 67.7, 47.2; IR (neat): 1735, 1590, 1496, 1405, 1252, 1227, 1093, 756 cm^{-1}; HRMS (FAB) calcd for $C_{16}H_{14}FNO_3$: 287.0958 ([M]$^+$), found 287.0958.

5-(Phenoxymethyl)-3-tosyl-oxazolidin-2-one (1o):[6] ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.97 (d, *J* = 8.0 Hz, 2H), 7.37 (d, *J* = 8.4 Hz, 2H), 7.26 (t, *J* = 8.4 Hz, 2H), 6.99 (t, *J* = 7.6 Hz, 1H), 6.71 (d, *J* = 8.0 Hz, 2H), 4.83–4.87 (m, 1H), 4.21 (dd, *J* = 8.8, 9.2 Hz, 1H), 4.06–4.14 (m, 3H), 2.47 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 157.6, 151.3, 145.8, 134.1, 129.9, 129.5, 128.2, 121.9, 114.5, 71.5, 67.3, 46.2, 21.7; IR (neat): 1773, 1372, 1245, 1173, 1145, 1095, 1044, 814, 747 cm^{-1}.

3-(4-Chlorobenzenesulfonyl)-5-(phenoxymethyl)-oxazolidin-2-one (1p): ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.03 (d, *J* = 8.0 Hz, 2H), 7.55 (d, *J* = 8.8 Hz, 2H), 7.27 (t, *J* = 8.0 Hz, 2H), 7.00 (t, *J* = 7.2 Hz, 1H), 6.69 (d, *J* = 8.0 Hz, 2H), 4.85–4.91 (m, 1H), 4.22 (dd, *J* = 8.8, 9.2 Hz, 1H), 4.06–4.16 (m, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 157.5, 151.2, 141.3, 135.5, 129.62, 129.57, 121.9, 114.4, 71.8, 67.3, 46.1; IR (neat): 1779, 1371, 1172, 1145, 1084, 751, 730 cm^{-1}; HRMS (FAB) calcd for $C_{16}H_{15}ClNO_5S$: 368.0359 ([M+H]$^+$), found 368.0359.

Acknowledgements

We thank Professor Satoshi Minakata (Osaka University) for valuable comments regarding the present work. This work was supported by JSPS KAKENHI Grant Number JP19K05480, by the Cooperative Research Program of "Network Joint Research Center for Materials and Devices" (20201298), and by Takahashi Industrial and Economic Research Foundation. This work was the result of using research equipment shared in MEXT Project for

promoting public utilization of advanced research infrastructure (Program for supporting introduction of the new sharing system) Grant Numbers JPMXS0422500320 and JPMXS0422300120.

Keywords: Bifunctional catalysts • Green chemistry • Heterocycles • Organocatalysis • Sustainable chemistry

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[7] Reduction of the catalyst loading caused a decrease in the yield.

[8] The reaction with 3,3-dimethyl-1,2-epoxybutane proceeded sluggishly.

[9] Products **1a** and **1f** were tested as positive allosteric modulators of mGluR2: E. J. Brnardic, M. E. Fraley, R. M. Garbaccio, M. E. Layton, J. M. Sanders, C. Culberson, M. A. Jacobson, B. C. Magliaro, P. H. Hutson, J. A. O'Brien, S. L. Huszar, J. M. Uslaner, K. L. Fillgrove, C. Tang, Y. Kuo, S. M. Sur, G. D. Hartman, *Bioorg. Med. Chem. Lett.* **2010**, *20*, 3129–3133.

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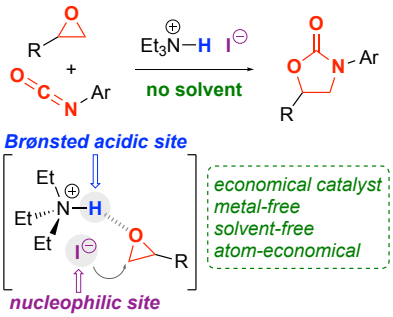

This efficient synthesis of 2-oxazolidinones from epoxides and isocyanates features the use of triethylamine hydroiodide as a simple and effective bifunctional organocatalyst.

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