Tetrahedron Letters 53 (2012) 6999–7002

Contents lists available at SciVerse ScienceDirect

Tetrahedron Letters

journal homepage: www.elsevier.com/locate/tetlet

Copper (I) catalyzed synthesis of 1,3-oxazolidin-2-ones from alkynes, amines, and carbon dioxide under solvent-free conditions

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ARTICLE INFO

Article history:
Received 19 May 2012
Revised 12 October 2012
Accepted 18 October 2012
Available online 24 October 2012

Keywords:
Carbon dioxide
Oxazolidinone
Solvent-free
Copper-catalyzed

ABSTRACT

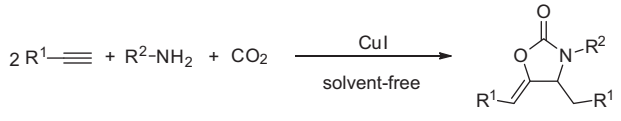
It was described that 1,3-oxazolidin-2-ones could be produced from alkynes, amines, and CO_2 catalyzed by copper (I) iodide under the solvent-free conditions. Terminal aryl alkynes and aliphatic primary amine are good substances for the transformation of CO_2 into the target oxazolidinones in good yields.

The 1,3-oxazolidin-2-ones constitute a very important class of heterocyclic compounds which could be used not only as multipurpose chiral synthons in asymmetric syntheses of biologically active compounds or their synthetic intermediates,[1] but also as chiral auxiliaries in many asymmetric transformations such as alkylation, acylation, and Diels–Alder reactions, and aldolic condensations.[2] Moreover, some oxazolidinones such as DUP-105, DUP-721, and linezolid (Zyvox) have drawn interest as monodrug- or multidrug-resistant antibacterial agents.[3] The importance of these heterocyclic derivatives justifies the continuous endeavors to develop novel routes to their synthesis and a number of procedures to synthesize 1,3-oxazolidin-2-ones have been developed.[4]

The use of industrially produced CO_2 as a chemical feedstock is attracting growing attention. CO_2 is a major contributor to the greenhouse effect, and a number of strategies have been developed to reduce its concentration in the atmosphere. Although the employment of CO_2 in chemical synthesis contributes relatively little to mitigation of the CO_2 concentration in the atmosphere, several other factors render CO_2 an interesting chemical feedstock, such as low cost, relative nontoxicity, nonflammability, and renewal.[5]

In our continuing efforts to chemical fixation of CO_2, we have developed a number of protocols to transform CO_2 into value-added products, such as 1,3-oxazolidin-2-ones from propargylic alcohols, and primary amines or aziridines,[6,7] cyclic carbonates from epoxides or propargylic alcohols,[8,9] β-oxopropylcarbamates from propargylic alcohols, and secondary amines.[10] As a part of our works in this field, we recently developed an efficient approach to synthesize oxazolin-2-ones via the cycloaddition of terminal alkynes, primary amines, and CO_2 under the catalysis of copper (I) iodide (Scheme 1). Compared to the reported starting materials for chemical fixation of CO_2 to 1,3-oxazolidin-2-ones, alkynes is much cheaper than aziridines,[11] propargylic amines,[12] or propargylic alcohols.[13]

In order to explore the optimum reaction conditions, the interaction of CO_2, phenylacetylene, and *n*-butylamine was selected as the model reaction. The experimental data are collected in Table 1. On the basis of our experience on using supercritical carbon dioxide as the reaction medium,[14] we initially carried out the reaction in supercritical carbon dioxide catalyzed by CuBr under CO_2 pressure of 7.5 MPa at 110 °C for 24 h. It was found that the desired (*Z*)-4-benzyl-5-benzylidene-3-butyloxazolidin-2-one was obtained in 71% yield (Table 1, entry 1). The target compound was formed in 86% in the above reaction system catalyzed by CuI instead (Table 1, entry 2). Other cuprous salts, for instance, CuCl and CuOTf, gave inferior results (Table 1, entries 3 and 4). Although monovalent silver and gold reagents are usually employed to activate alkynes,



Scheme 1. Synthesis of 1,3-oxazolidin-2-ones from alkynes, amines, and CO_2 catalyzed by copper (I) iodide.

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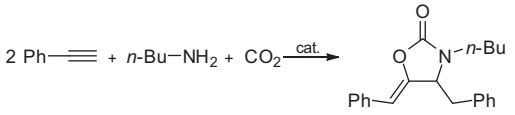
http://dx.doi.org/10.1016/j.tetlet.2012.10.073

Table 1
Optimizing the reaction conditions for the synthesis of 1,3-oxazolidin-2-one from alkynes, amines, and CO_2[a]



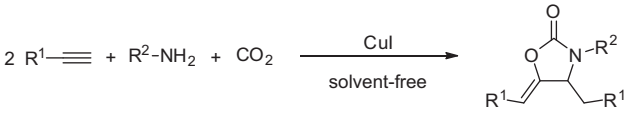
Entry	Cat.	P (MPa)	*T*. (°C)	Yield[b] (%)
1	CuBr	7.5	110	71
2	CuI	7.5	110	86
3	CuCl	7.5	110	35
4	CuOTf	7.5	110	27
5	AgBr	7.5	110	0
6	AgOTf	7.5	110	0
7	AuCl	7.5	110	Trace
8	Ph_3PAuCl	7.5	110	9
9	CuI	5	110	86
10	CuI	2	110	86
11	CuI	1	110	77
12	CuI	0.5	110	29
13	CuI	2	90	86
14	CuI	2	70	72
15	CuI	2	130	85

[a] Reagents and conditions: phenyl acetylene (2 mmol), butylamine (2 mmol), catalyst (0.1 mmol).
[b] Determined by ^1H NMR.

AgBr and AgOTf had no ability to drive the transformation (Table 1, entries 5 and 6). Aurous chloride and Chloro(triphenylphosphine)gold (I) exhibited extremely weak activity (Table 1, entries 7 and 8). The effect of CO_2 pressure was then investigated. As the experimental results had shown, when CO_2 pressure was gradually tuned from 7.5 MPa to 2 MPa, the yield of target oxazolidinone had no significant change (Table 1, entries 9 and 10). This result was beyond our expectation because our original destination was to develop a transformation in supercritical carbon dioxide. The following study suggested that further reduction of the pressure resulted in a decline of the yield (Table 1, entry 11). When CO_2 pressure was set at 0.5 MPa, the yield of the desired product plunged to 29% (Table 1, entry 12) The influence of the reaction temperature was finally examined and it was found that the yield had not been impacted when the temperature was regulated from 110 °C to 90 °C (Table 1, entry 13). The reaction temperature decreased to 70 °C or increased to 130 °C led to a lower yield (Table 1, entries 14 and 15).

With the optimized reaction conditions in hand, we next evaluated the generality and scope of the methodology for the synthesis of 1,3-oxazolidin-2-ones via the cycloaddition of alkynes, primary amines, and CO_2. And the results are summarized in Table 2. A variety of amines were firstly subjected to the cycloaddition reaction with phenyl acetylene and CO_2. As the results showed, *sec*-butyl amine gave a lower yield compared with *n*-butylamine(Table 2, entries 1 and 2),[15] The reaction of phenyl acetylene with ethyl

Table 2
Synthesis of 1,3-oxazolidin-2-ones from alkynes, amines, and CO_2 catalyzed by CuI under solvent-free conditions[a]



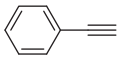
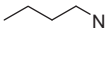
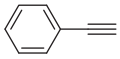
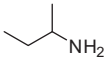
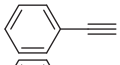
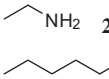
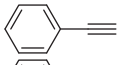
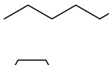
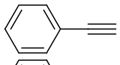
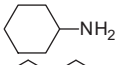
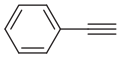
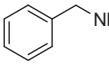
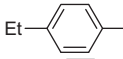
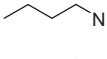
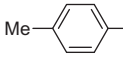
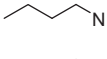
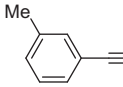
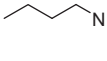
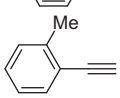
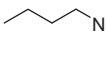
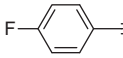
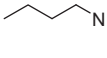
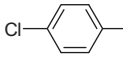
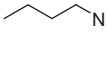
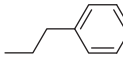
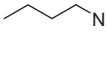
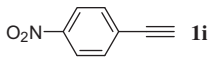
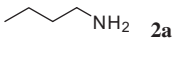
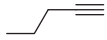
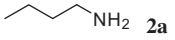
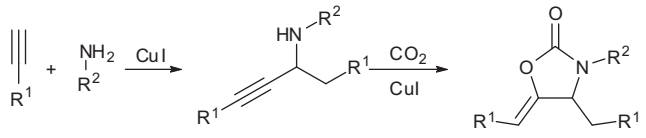
Entry	Alkyne	Amine	Product no.	Yield[b] (%)
1	 **1a**	 **2a**	**3aa**	84
2	 **1a**	 **2b**	**3ab**	80
3	 **1a**	 **2c**	**3ac**	86
4	 **1a**	 **2d**	**3ad**	73
5	 **1a**	 **2e**	**3ae**	87
6	 **1a**	 **2f**	**3af**	69
7	 **1b**	 **2a**	**3ba**	86
8	 **1c**	 **2a**	**3ca**	89
9	 **1d**	 **2a**	**3da**	79
10	 **1e**	 **2a**	**3ea**	58
11	 **1f**	 **2a**	**3fa**	83
12	 **1g**	 **2a**	**3ga**	81
13	 **1h**	 **2a**	**3ha**	52

Table 2 (*continued*)

Entry	Alkyne	Amine	Product no.	Yield[b] (%)
14	 **1i**	 **2a**	**3ia**	0
15	 **1j**	 **2a**	**3ja**	0

[a] Reagents and conditions: alkyne (2 mmol), amine (2 mmol), CuI (0.1 mmol), P = 2 MPa, 90 °C.
[b] Isolated yields.



Scheme 2. The probable pathway of the formation of 1,3-oxazolidin-2-ones from alkynes, amines, and CO_2 catalyzed by copper (I) iodide.

amine and *n*-hexyl amine proceeded smoothly with 3ac and 3ad obtained in yields of 86% and 73%, respectively (Table 2, entries 3 and 4). Cyclohexylamine and benzylamine gave the corresponding products 3ae and 3af in yields of 87% and 69%, respectively (Table 2, entries 5 and 6). Various terminal alkynes were treated with *n*-butyl amine and our studying results indicated that alkyl substituted aryl terminal alkynes could all go across the reaction despite the alkyl groups in *para*-, *meta*-, or *ortho*-position of aryl rings (Table 2, entries 7–10), the transformation could also tolerate halogen groups (Table 2, entries 11 and 12). Substrate 1 h, bearing a bulky substituent, could also undergo the cycloaddition (Table 2, entry 13). Our experimental results indicated that substrate 1i, bearing a strongly electron-withdrawing nitro group failed to furnish the desired 1,3-oxazolidin-2-one and aliphatic alkyne that appeared less reactive (Table 2, entries 14 and 15).

The probable pathway of the cycloaddition of terminal alkynes, primary amines, and CO_2 is described in Scheme 2. Alkyne interacted with amine via a copper-catalyzed tandem anti-markovnikov hydroamination and alkyne addition to furnish propargylamine which then went across the cycloadditon with CO_2 to afford 5-arylidene-1,3-oxazolidin-2-one.[16,12]

In conclusion, we have disclosed that copper (I) iodide could catalyze the chemical fixation of CO_2 into 1,3-oxazolidin-2-ones with alkynes and amines under solvent-free conditions. This procedure supplies an alternative route to 1,3-oxazolidin-2-ones from relatively low-cost alkynes and amines.

Acknowledgments

We thank the National Natural Science Foundation of China (20932002 and 21172076), the National Basic Research Program of China (973 Program) (2010CB-732206), the Doctoral Fund of the Ministry of Education of China (20090172110014), the Guangdong Natural Science Foundation (10351064101000000), and the Fundamental Research Funds for the Central Universities (2011ZZ007) for financial support.

Supplementary data

Supplementary data associated with this article can be found, in the online version, at http://dx.doi.org/10.1016/j.tetlet.2012.10.073.

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15. *Typical experimental procedure for the copper (I) catalyzed synthesis of 1, 3-oxazolidin-2-ones from alkynes, amines, and carbon dioxide under solvent-free conditions*. A 15 mL polytetrafluoroethylene (PTFE) reaction vessel was charged with CuI (0.1 mmol), alkyne (2 mmol), and amine (2 mmol). The vessel was fixed into a stainless steel autoclave with a pressure-regulating system. The autoclave was sealed and CO_2 was introduced from a cylinder. The autoclave was heated by an oil bath. The reaction continued under magnetic stirring for 24 h. When the reaction was complete, the vessel was cooled with an ice bath and the pressure was released slowly to atmospheric pressure. The residue was extracted with ethyl acetate (10 mL). The collected filtrate was concentrated under reduced pressure. The product was purified by chromatography on a silica gel column using light petroleum ether/ethyl acetate as eluent. (*Z*)-4-Benzyl-5-benzylidene-3-butyloxazolidin-2-one (**3aa**) ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.46 (d, J = 7.4 Hz, 2H), 7.44–7.13 (m, 8H), 5.19 (d, J = 1.5 Hz, 1H), 4.71–4.62 (m, 1H), 3.68–3.55 (m, 1H), 3.19–2.92 (m, 3H), 1.62–1.46 (m, 2H), 1.31 (m, 2H), 0.92 (t, J = 7.3 Hz, 1H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 155, 146, 135, 133, 130, 129, 128, 128, 127, 127, 104, 59, 42, 40, 29, 20, 14. IR (KBr): 2959, 1775, 1410. MS (EI, 70 eV): m/z (%) = 230 (100), 174 (35), 103 (10). HRMS Calcd for $C_{21}H_{23}NO_2$: 321.1729, Found: 321.1721. (*Z*)-4-Benzyl-5-benzylidene-3-sec-butyloxazolidin-2-one (**3ab**) ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.46–7.16 (m, 10H), 4.83 (d, J = 3.8 Hz, 1H), 4.62 (td, J = 8.7, 4.0 Hz, 1H), 3.67–3.48 (m, 1H), 3.33 (m, 1H), 2.90 (m, 1H), 2.00–1.77 (m, 2H), 1.42 (dd, J = 16.8, 6.9 Hz, 3H), 0.98 (dd, J = 17.1, 7.5 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 155, 146, 135, 133, 130, 129, 128, 127, 104, 62, 53, 42, 28, 19, 11. MS (EI, 70 eV): m/z (%) = 230(72), 175(10), 174(100), 103(20). IR (KBr): 2978, 1780, 1420, 698. HRMS Calcd for $C_{21}H_{23}NO_2$: 321.1729, Found: 321. 1725. (*Z*)-4-Benzyl-5-benzylidene-3-ethyloxazolidin-2-one (**3ac**) ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.50 (d, J = 7.6 Hz, 2H), 7.33 (t, J = 7.2 Hz, 5H), 7.26–7.20 (m, 3H), 5.22 (s, 1H), 4.72 (t, J = 5.5 Hz, 1H), 3.71 (m, 1H), 3.22–3.13 (m, 2H), 3.00 (dd, J = 14.0, 6.6 Hz, 1H), 1.22 (t, J = 7.2 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 155, 146, 135, 133, 130, 129, 128, 127. 104, 59, 40, 37, 13. MS (EI, 70 eV): m/z (%) = 202(100), 174(9), 103(9), 91(11), 56(22). IR (KBr): 2970, 1775, 1376, 699. HRMS Calcd for $C_{19}H_{19}NO_2$: 293.1416, Found: 293. 1427. (*Z*)-4-Benzyl-5-benzylidene-3-hexyloxazolidin-2-one (**3ad**) ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.46 (d, J = 7.5 Hz, 2H), 7.32–7.25 (m, 5H), 7.22–7.14 (m, 3H), 5.19 (d, J = 1.1 Hz, 1H), 4.66 (t, J = 5.0 Hz, 1H), 3.64–3.55 (m, 1H), 3.17–2.94

(m, 3H), 1.27 (s, 6H), 0.88 (t, J = 6.6 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 155, 146, 135, 133, 130, 129, 128, 127, 104, 59, 42, 40, 31, 27, 26, 23, 14. MS (EI, 70 eV): m/z (%) = 258(100), 174(44), 103(12), 43(11) IR (KBr): 2924, 1771, 1410, 695. HRMS Calcd for $C_{23}H_{27}NO_2$: 349.2042, Found: 349.2037. (*Z*)-4-Benzyl-5-benzylidene-3-cyclohexyloxazolidin-2-one (**3ae**) ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.39 (d, J = 7.5 Hz, 2H), 7.33–7.23 (m, 5H), 7.22–7.13 (m, 3H), 4.85 (s, 1H), 4.64–4.57 (m, 1H), 3.41–3.31 (m, 1H), 3.27 (m, 1H), 2.87 (m, 1H), 2.01–1.62 (m, 6H), 1.35–1.12 (m, 4H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 154, 146, 135, 134, 130, 129, 128, 127, 104, 60, 55, 42, 31, 30, 26. MS (EI, 70 eV): m/z (%) = 256(63), 174(100), 103(19), 55(17) IR (KBr): 2931, 1775, 1376, 696. HRMS Calcd for $C_{23}H_{25}NO_2$: 347.1885, Found: 347. 1879. (*Z*)-3,4-Dibenzyl-5-benzylideneoxazolidin-2-one (**3af**) ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.45 (d, J = 7.4 Hz, 2H), 7.35–7.24 (m, 8H), 7.17 (dd, J = 10.3, 4.3 Hz, 3H), 7.13–7.08 (m, 2H), 5.13 (d, J = 1.5 Hz, 1H), 4.96 (d, J = 15.2 Hz, 1H), 4.10 (m, 1H), 4.05 (s, 1H), 4.02 (s, 1H), 3.15–2.91 (m, 1H) ^{13}C NMR (101 MHz, $CDCl_3$) δ 155, 146, 135, 135, 133, 130, 129, 128, 127, 104, 59, 46, 40. MS (EI, 70 eV): m/z (%) = 264(53), 91(100). IR (KBr): 3029, 1783, 1416, 1054, 670. HRMS Calcd for $C_{24}H_{21}NO_2$: 355.1572, Found: 355.1572. (*Z*)-3-Butyl-4-(4-ethylbenzyl)-5-(4-ethylbenzylidene)oxazolidin-2-one (**3ba**) ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.39 (d, J = 8.2 Hz, 2H), 7.17–7.08 (m, 6H), 5.20 (d, J = 1.3 Hz, 1H), 4.64 (dd, J = 5.5, 4.0 Hz, 1H), 3.66–3.54 (m, 2H), 3.13–2.90 (m, 2H), 2.67–2.55 (m, 4H), 1.23 (m, 10H), 0.90 (dd, J = 12.8, 5.5 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 155, 145, 143, 132, 131, 130, 129, 128, 104, 59, 42, 39, 29, 28, 20, 16, 14. MS (EI, 70 eV): m/z (%) = 258(100), 202(21), 131(13). IR (KBr): 2963, 1773, 1411, 1957. HRMS Calcd for $C_{25}H_{31}NO_2$: 377.2355, Found: 377, 2357. (*Z*)-3-Butyl-4-(4-methylbenzyl)-5-(4-methylbenzylidene)oxazolidin-2-one (**3ca**) ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.37 (d, J = 8.0 Hz, 2H), 7.14–7.04 (m, 6H), 5.21 (s, 1H), 4.63 (t, J = 5.0 Hz, 1H), 3.67–3.57 (m, 1H), 3.12–3.00 (m, 2H), 2.94 (m, 1H), 2.33 (s, 6H), 1.62–1.49 (m, 2H), 1.37–1.24 (m, 2H), 0.92 (t, J = 7.4 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 155, 145, 137, 132, 131, 129, 128, 104, 59, 42, 39, 29, 21, 20, 14. MS (EI, 70 eV): m/z (%) = 244(100), 207(17), 188(28), 117(11), 105(12), 32(12). IR (KBr): 2929, 1738, 1407, 757. HRMS Calcd for $C_{23}H_{27}NO_2$: 349.2042, Found: 349, 2041. (*Z*)-3-Butyl-4-(3-methylbenzyl)-5-(3-methylbenzylidene)oxazolidin-2-one (**3da**) ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.34–7.00 (m, 8H), 5.19 (d, J = 1.2 Hz, 1H), 4.68 (t, J = 5.0 Hz, 1H), 3.68–3.58 (m, 1H), 3.18–3.03 (m, 2H), 2.95 (m, 1H), 2.42–2.30 (d, J = 3.8 Hz, 6H), 1.62–1.53 (m, 2H), 1.39–1.27 (m, 2H), 0.95 (t, J = 7.4 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 155, 146, 138, 135, 133, 130, 129, 128, 127, 126, 104, 60, 43, 40, 29, 21, 20, 14. MS (EI, 70 eV): m/z (%) = 244(100), 188(31), 117(11), 105(8). IR (KBr): 2924, 1779, 1417, 1045. HRMS Calcd for $C_{23}H_{27}NO_2$: 349.2042, Found: 349. 2045. (*Z*)-3-Butyl-4-(2-methylbenzyl)-5-(2-methylbenzylidene)oxazolidin-2-one (**3ea**) ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.37 (d, J = 8.1 Hz, 2H), 7.14–7.04 (m, 6H), 5.21 (d, J = 1.4 Hz, 1H), 4.64 (t, J = 4.7 Hz, 1H), 3.61 (m, 1H), 3.11–3.01 (m, 2H), 2.95 (m, 1H), 2.32 (s, 6H), 1.59–1.51 (m, 2H), 1.36–1.24 (m, 2H), 0.92 (t, J = 7.4 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 155, 145, 1376, 132, 131, 129, 128, 104, 59, 42, 39, 29, 21, 20, 14. MS (EI, 70 eV): m/z (%) = 244(100), 188(25), 117(11), 105(11). IR (KBr): 2926, 1780, 1417, 1049. HRMS Calcd for $C_{23}H_{27}NO_2$: 349.2042, Found: 349.2041. (*Z*)-3-Butyl-4-(4-fluorobenzyl)-5-(4-fluorobenzylidene)oxazolidin-2-one (**3fa**) ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.43 (dd, J = 8.6, 5.5 Hz, 2H), 7.14 (dd, J = 8.3, 5.5 Hz, 2H), 6.99 (td, J = 8.6, 6.4 Hz, 4H), 5.18 (s, 1H), 4.64 (t, J = 5.0 Hz, 1H), 3.69–3.59 (m, 1H), 3.13–3.02 (m, 2H), 2.97 (m, 1H), 1.57 (m, 2H), 1.34 (m, 2H), 0.94 (t, J = 7.3 Hz, 3H) ^{13}C NMR (101 MHz, $CDCl_3$) δ 163, 161, 155, 145, 131, 130, 129, 116, 115, 103, 59, 42, 39, 29, 20, 14. MS (EI, 70 eV): m/z (%) = 248(100), 192(51), 121(17), 109(16). IR (KBr): 2928, 1778, 1508, 1227, 830. HRMS Calcd for $C_{21}H_{21}F_2NO_2$: 357.1540, Found: 357.1550. (*Z*)-3-Butyl-4-(4-chlorobenzyl)-5-(4-chlorobenzylidene)oxazolidin-2-one (**3ga**) ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.39 (d, J = 8.5 Hz, 2H), 7.27 (dd, J = 10.3, 5.1 Hz, 4H), 7.10 (d, J = 8.2 Hz, 2H), 5.19 (s, 1H), 4.65 (t, J = 4.9 Hz, 1H), 3.69–3.59 (m, 1H), 3.13–3.02 (m, 2H), 2.98 (m, 1H), 1.57 (m, 2H), 1.34 (m, 2H), 0.94 (t, J = 7.4 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 155, 146, 131, 130, 129, 103, 59, 42, 39, 29, 20, 14. MS (EI, 70 eV): m/z (%) = 266(32), 264(100), 210(12), 208(40) IR (KBr): 2930, 1684, 1406, 1091, 761. HRMS Calcd for $C_{21}H_{21}Cl_2NO_2$: 389.0949, Found: 389. 0948. (*Z*)-3-Butyl-4-((4′-propylbiphenyl-4-yl)methyl)-5-((4′-propylbiphenyl-4-yl)methylene)oxazolidin-2-one (**3ha**) ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.59–7.46 (m, 10H), 7.25 (m, 6H), 5.27 (s, 1H), 4.72 (s, 1H), 3.71–3.61 (m, 1H), 3.23–2.99 (m, 3H), 2.64 (m, 4H), 1.68 (m, 4H), 1.58 (m, 2H), 1.33 (m, 2H), 1.02–0.89 (m, 9H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 155, 146, 142, 140, 139, 138, 134, 132, 130, 129, 127, 103, 60, 42, 40, 38, 29, 25, 20, 14. IR (KBr): 2957, 1914, 1395, 808. HRMS Calcd for $C_{39}H_{43}NO_2$: 557.3294, Found: 557.3289.

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