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N-Heterocyclic Carbene Catalyzed Domino Cyclization of Propargylic Alcohols and Benzoyl Isocyanates

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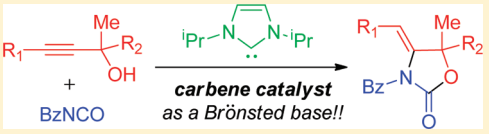
Supporting Information

ABSTRACT: *N*-Hetereocyclic carbenes (NHCs) were found to be efficient catalysts for the cyclization of propargylic alcohols and isocyanates. Domino cyclization reactions were carried out using isopropyl-substituted imidazolium salt as a precatalyst, and a wide range of substituted oxazolidinones were obtained in high yields.



N-Heterocyclic carbenes (NHCs) have come to be heavily researched for the role of nucleophilic organocatalysts and ligands, and the remarkable success of NHCs is innately caused by their powerful capacity as two-electron donors.[1] The most attractive catalytic role of NHCs is to convert aldehydes into acyl anion equivalents during transformations such as benzoin and Stetter reactions. Although the development of these reactions to trigger umpolungs has received significant attention, different modes of reactivity for NHCs has received considerably less attention. In this study, we have discovered another Brönsted basic property[2] of various NHCs in the benzylidene oxazolidinone synthesis.

Oxazolidinones and their derivatives are a very important class of heterocyclic compounds in terms of bioactive and chiral molecules. They exhibit a wide range of biological properties including monoamine oxidase inhibitors, renin inhibitors, sigma receptors, cytokine modulators and antibiotics,[3] and also been used as chiral synthons or auxiliaries, allowing high levels of diastereoselectivity in the chirality transfer reactions and asymmetric reactions.[4] Due to the importance of their structures, several methods for the synthesis of 1,3-oxazolidin-2-ones have been developed. Classical methods for the oxazolidinone formations involve condensation reactions with amino alcohols and carbonyl precursors such as phosgene, chloroformate, and dialkyl carbonates. An alternative approach is the cyclization reaction of vinyl or propargyl carbamate catalyzed by base[5] or transition metal[6] catalysts under mild conditions. Although another method using CO_2 as a carbonyl source has been developed recently,[7] these procedures were mostly applied to the construction of 4-*methylene*-1,3-oxazolidin-2-one, and only a few 4-*arylidene* compounds have been reported. In this context, concise catalytic methods for the direct synthesis of 4-arylideneoxazolidinones are presented as an atom-economical and environmentally benign process using propargylic alcohols and isocyanates.

To examine the possibility of using internal propargyl alcohols as potential substrates, phenyl-substituted propargyl alcohol (**1a**) and benzoyl isocyanate were used to create oxazolidinone heterocycles, having pre-existing issues of lower reactivities of internal propargylic alcohols compared to terminal ones[7e] and benzoyl isocyanates compared to phenyl isocyanates (Table 1).[6a] *N*-Heterocyclic carbene catalysts have previously been shown to activate CO_2 in 1,3-dioxolan-2-ones synthesis with internal propargylic alcohols,[8] which led us to investigate their use as potential catalysts. The use of 1,3-diisopropylimidazolium chloride and DBU resulted in the synthesis of benzylideneoxazolidinone with a 62% yield, which was accompanied by an unreacted propargyl alcohol. An increase in reaction temperature resulted in little improvement; however, when KO^{t}Bu was used as a base, a remarkable increase in reactivity and isolated yield was achieved even with a reduced reaction time. Screening tests with other imidazolium, triazolium, and thiazolium catalysts demonstrated that precatalyst **I** was the most effective, and we hypothesized that this higher reactivity was due to the lower steric hindrance in isopropyl substituents. During solvent optimization studies, other polar solvents, such as CH_3CN and CH_3NO_2, were shown to provide little benefit relative to DCE. On the basis of these results, we performed a control experiment with only the DBU base catalyst, which resulted in a 50% yield even with a prolonged reaction time (12 h). Remarkably, this reaction resulted in the exclusive formation of the (*E*)-configured isomer, and ^{1}H NMR experiments did not show any trace of the (*Z*)-isomer. The structure of the product was determined by 1D NOE and subsequently confirmed by X-ray crystallography.[9] The (*E*)-conformer, which is accessed by the *anti*-addition of amine nucleophile and proton, could provide a mechanistic insight into this reaction, which will be discussed later. For the reactivities of other isocyanates bearing various *N*-substituents, no reaction occurred with *n*-butyl or benzyl isocyanates, and phenyl isocyanate induced cyclization even in the presence of the DBU catalyst.[10] In addition, tosyl or trichloromethyl isocyanate having an electron withdrawing

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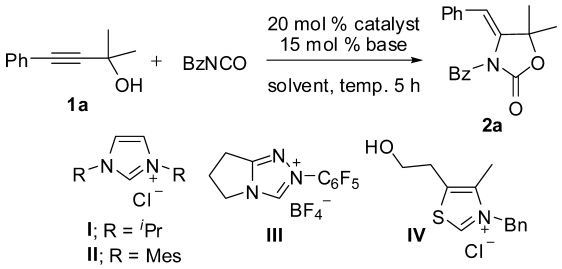
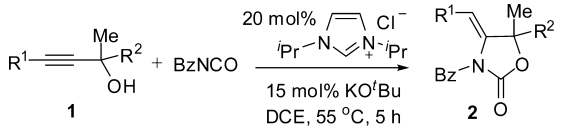
Table 1. Optimization of Conditions for Benzylidene Oxazolidinone Synthesis[a]



entry	catalyst	base	solvent	temp (°C)	yield[b] (%)
1[c]	**I**	DBU	DCE	rt	62
2[c]	**I**	DBU	DCE	55	68
3	**I**	TEA	DCE	55	0
4	**I**	KO^{t}Bu	DCE	55	92
5	**I**	Cs_2CO_3	DCE	55	54
6	**I**	KHMDS	DCE	55	90
7	**II**	KO^{t}Bu	DCE	55	50
8	**III**	KO^{t}Bu	DCE	55	35
9	**IV**	KO^{t}Bu	DCE	55	0
10	**I**	KO^{t}Bu	CH_3CN	55	28
11	**I**	KO^{t}Bu	CH_3NO_2	55	51
12[d]	**I**	KO^{t}Bu	DCE	55	55

[a]Reactions and conditions: propargylic alcohol (**1a**: 0.25 mmol), BzNCO (0.375 mmol), NHC catalyst (20 mol %), base (15 mol %), solvent (0.2 M) under N_2, unless otherwise specified. [b]Isolated yield after chromatographic purification. [c]Reaction for 12 h. [d]Reaction with 15 mol % of catalyst and 12 mol % of base.

Table 2. Synthesis of Arylidene Oxazolidinones: Substrate Scope[a]



entry	R^1	R^2	product	yield[b] (%)
1	Ph	Me	**2a**	92
2	4-MeC_6H_4	Me	**2b**	71
3	4-MeOC_6H_4	Me	**2c**	51
4	4-FC_6H_4	Me	**2d**	99
5	4-ClC_6H_4	Me	**2e**	99
6	4-BrC_6H_4	Me	**2f**	76
7	2-ClC_6H_4	Me	**2g**	84
8	3-ClC_6H_4	Me	**2h**	49
9	4-Cl-2-F- C_6H_4	Me	**2i**	77
10	4-CN-C_6H_4	Me	**2j**	10
11	4-CH_3CO-C_6H_4	Me	**2k**	0
12	4-NO_2−C_6H_4	Me	**2l**	0
13	1-naphthyl	Me	**2m**	56
14	2-thienyl	Me	**2n**	78
15	2-pyridyl	Me	**2o**	65
16	4-ClC_6H_4	Et	**2p**	99
17	Ph	^{i}Pr	**2q**	77
18	H	Et	**2r**	56
19	^{n}Bu	Me	**2s**	0

[a]Reactions and conditions: propargylic alcohol (**1**: 0.25 mmol), BzNCO (0.375 mmol), NHC catalyst (20 mol %), base (15 mol %), solvent (0.2 M) under N_2, unless otherwise specified. [b]Isolated yield after chromatographic purification.

group could not produce the corresponding oxazolidinone, whereas the tosyl-substituted carbamate was formed in good yield within 1 h.

Encouraged by this initial result, we explored the generality of this process (Table 2). Preparation of the required propargylic alcohols was straightforward and was performed either by Sonogasira coupling with aryl iodide and 2-methyl-3-butyn-2-ol or alternatively via alkynylation with lithiated phenyl acetylene to various ketones. The presence of the electron-donating groups on the phenyl group led to slightly lower

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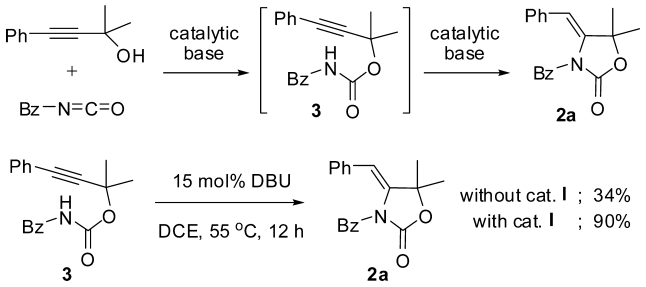
yields of the oxazolidinone products (entries 2, 3). Propargylic alcohols containing halogen groups on an aryl ring were converted into the corresponding oxazolidinones **2d-i** with good to excellent yield, and the reaction of substrates **1d** and **1e**, which have *p*-fluorophenyl and *p*-chlorophenyl groups resulted in the exclusive formation of oxazolidinones with 99% yields. Substrates bearing electron-withdrawing substitutents on an aryl group did not participate in the cyclization reactions, even under harsh conditions (CH_3NO_2, 100 °C, 48 h). Heterocycles such as thiophene and pyridine were able to tolerate these reaction conditions (entries 14 and 15) and substrates **1p** and **1q**, which have different dialkyl substituents also afforded the expected product with excellent yield. On the basis of the cyclization results for substrates **1r** and **1s**, it was inferred that the substituents on the alkynyl group delicately affected reactivity (entries 18 and 19). The reaction with terminal propargylic alcohol **1r** afforded 4-methylene-1,3-oxazolidin-2-one; however, the reaction with *n*-butyl substituted alkyne **1s** did not produce any product.

On the basis of the results shown in Tables 1 and 2, it is very clear that *N*-heterocyclic carbene plays a vital role in reducing the reaction time and improving the yield of oxazolidinone formation, rendering a plausible pathway proposed in Scheme 1. Base promoted reaction, with the *N*-heterocyclic carbene

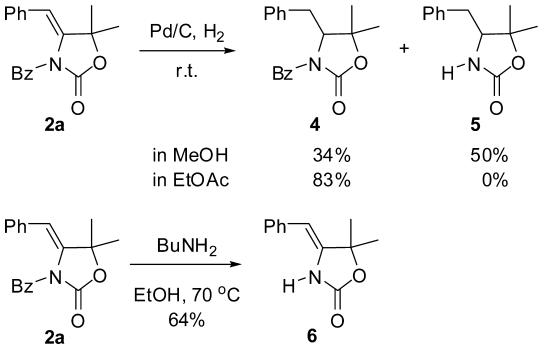
Scheme 1. Mechanistic Investigation of 4-Benzylideneoxazolidinone Formation



serving as an active Brönsted base,[2] starts by an initial nucleophilic addition of the anionic oxygen of propargylic alcohol to the electrophilic carbon of isocyanate. The consecutive intramolecular cyclization of carbamate intermediate affords the arylidene oxazolidinone synthesis. Although the alternative route of zwitterionic NHC-NCO adduct generation could not be exclusively ruled out,[11] formation of carbamate **3** as an intermediate confirmed by isolating in the middle of the reaction, also the verification test of base-catalyzed cyclization of carbamate **3** was conducted. Comparison between two reactions, *N*-heterocyclic carbene or DBU catalyzed cyclization,[12] led us to theorize that NHC as a more active Brönsted base is indispensable for cyclization of the benzoyl substituted carbamate **3**, whereas the phenyl substituted carbamates provided satisfactory results in the DBU-catalyzed reaction between propargylic alcohols and PhNCO.[10]

The synthesized 4-benzylidene oxazolidinones would act as synthetic precursors in the further transformation reactions (Scheme 2). Hydrogenation of **2a** in MeOH provided the reduced product **4**,[13] which was accompanied by the unexpected debenzoylated one **5**,[14] while the change of solvent to EtOAc afforded the formation of only **4** with a yield of 83%. We also examined the alkylamine mediated hydrolysis to form debenzoylated oxazolidinone, which could be applied in the synthesis of the chiral auxiliary. Benzylidene oxazolidinone **2a**

Scheme 2. Further Synthetic Transformations of 4-Benzylideneoxazolidinones



underwent the debenzoylation reactions with $BuNH_2$ under heating in EtOH, resulting in amine **6** with a yield of 64%.

In summary, we have developed an NHC-catalyzed intermolecular domino cyclization of propargylic alcohol and BzNCO to afford a range of arylidene oxazolidinones in a mild one-step synthesis. In particular, the first use of the NHC catalyst to activate isonitriles has a significant advantage in regard to oxazolidinone formation relative to previously reported conditions. Enantioselective hydrogenation of oxazolidinone products could be used to build a wide range of chiral synthons in asymmetric organic transformations.[15] The NHC catalyzed cyclization reactions using various accumulated double bond systems are currently being investigated.

■ EXPERIMENTAL SECTION

General Procedure for Preparation of 4-Benzylideneoxazolidinones. Propargylic alcohol (0.25 mmol) in DCE (0.2 M) was treated with benzoyl isocyanate (55.2 mg, 0.375 mmol), 1,3-diisopropylimidazolium chloride (9.4 mg, 0.05 mmol), and KO^{t}Bu (4.2 mg, 0.0375 mmol) at 55 °C under N_2 atmosphere. After stirring for 5 h, the reaction mixture was concentrated and purified by silica column chromatography.

(*Z*)-3-Benzoyl-4-benzylidene-5,5-dimethyloxazolidin-2-one (2a): ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.74 (d, 2H, J = 8.4 Hz), 7.57 (t, 1H, J = 7.5 Hz), 7.41 (t, 2H, J = 7.7 Hz), 7.11−7.08 (m, 3H), 7.03−7.00 (m, 2H), 5.92 (s, 1H), 1.74 (s, 6H) ppm; ^{13}C NMR (75 MHz, $CDCl_3$) δ 166.8, 152.8, 139.0, 134.6, 133.7, 132.5, 130.2, 130.1, 128.2, 128.2, 127.6, 127.2, 107.2, 84.1, 27.8 ppm; MS m/z (EI, relative intensity) 307 (M^+, 12), 248 (2), 122 (6), 105 (100), 77 (28); HRMS (EI) calcd for $C_{19}H_{17}NO_3$ (M^+) 307.1208, found 307.1206.

(*Z*)-3-Benzoyl-5,5-dimethyl-4-(4-methylbenzylidene)-oxazolidin-2-one (2b): ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.74 (d, 2H, J = 8.6 Hz), 7.56 (t, 1H, J = 7.5 Hz), 7.41 (t, 2H, J = 7.6 Hz), 6.89 (s, 4H), 5.88 (s, 1H), 2.19 (s, 3H) 1.71 (s, 6H) ppm; ^{13}C NMR (75 MHz, $CDCl_3$): δ 166.9, 152.9, 138.1, 136.9, 133.6, 132.6, 131.6, 130.2, 128.9, 128.2, 127.4, 107.4, 84.1, 27.7, 21.1 ppm; MS m/z (EI, relative intensity) 321 (M^+, 48), 159 (44), 143 (42), 119 (49), 105 (100), 77 (61); HRMS (EI) calcd for $C_{20}H_{19}NO_3$ (M^+) 321.1365, found 321.1363.

(*Z*)-3-Benzoyl-4-(4-methoxybenzylidene)-5,5-dimethyloxazolidin-2-one (2c): ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.76 (d, 2H, J = 7.3 Hz), 7.58 (t, 1H, J = 7.4 Hz), 7.43 (t, 2H, J = 7.6 Hz), 6.95 (d, 2H, J = 8.6 Hz), 6.63 (d, 2H, J = 8.6 Hz), 5.87 (s, 1H), 3.70 (s, 3H) 1.72 (s, 6H) ppm; ^{13}C NMR (75 MHz, $CDCl_3$): δ 166.8, 158.4, 137.4, 133.6, 130.2, 128.9, 128.2, 127.0, 113.6, 107.2, 84.1, 55.1, 27.7 ppm; MS m/z (EI, relative intensity) 337 (M^+, 21), 105 (100), 77 (57); HRMS (EI) calcd for $C_{20}H_{19}NO_4$ (M^+) 337.1314, found 337.1316.

(*Z*)-3-Benzoyl-4-(4-fluorobenzylidene)-5,5-dimethyloxazolidin-2-one (2d): ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.68 (d, 2H, J = 8.4 Hz), 7.53 (t, 1H, J = 7.3 Hz), 7.37 (t, 2H, J = 7.6 Hz), 6.91 (dd, 2H, J = 8.2, 5.3 Hz), 6.73 (t, 1H, J = 8.6 Hz), 5.81 (s, 1H), 1.67 (s, 6H)

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ppm; ^{13}C NMR (75 MHz, $CDCl_3$) δ 166.8, 161.4 (d, J = 245.4 Hz), 152.7, 139.1, 133.9, 132.3, 130.7, 130.6, 130.1, 129.2, 129.1, 128.3, 115.3 (d, J = 21.6 Hz), 106.1, 84.1, 27.8 ppm; MS m/z (EI, relative intensity) 325 (M^+, 8), 105 (100), 77 (24); HRMS (EI) calcd for $C_{19}H_{16}FNO_3$ (M^+) 325.1114, found 325.1118.

(*Z*)-3-Benzoyl-4-(4-chlorobenzylidene)-5,5-dimethyloxazolidin-2-one (2e): ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.68 (d, 2H, J = 7.5 Hz), 7.53 (t, 1H, J = 7.3 Hz), 7.38 (t, 2H, J = 7.6 Hz), 7.00 (d, 2H, J = 8.5 Hz), 6.87 (d, 2H, J = 8.2 Hz), 5.79 (s, 1H), 1.66 (s, 6H) ppm; ^{13}C NMR (75 MHz, $CDCl_3$) δ 166.8, 152.6, 139.5, 134.0, 133.1, 132.8, 132.3, 130.2, 128.8, 128.4, 128.4, 106.0, 84.1, 27.8 ppm; MS m/z (EI, relative intensity) 341 (M^+, 8), 297 (6), 282 (5), 105 (100), 77 (27); HRMS (EI) calcd for $C_{19}H_{16}ClNO_3$ (M^+) 341.0819, found 341.0821.

(*Z*)-3-Benzoyl-4-(4-bromobenzylidene)-5,5-dimethyloxazolidin-2-one (2f): ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.78 (d, 2H, J = 8.4 Hz), 7.64 (t, 1H, J = 7.3 Hz), 7.48 (t, 2H, J = 7.6 Hz), 7.28 (d, 2H, J = 7.5 Hz), 6.91 (d, 2H, J = 8.4 Hz), 5.87 (s, 1H), 1.76 (s, 6H) ppm; ^{13}C NMR (75 MHz, $CDCl_3$) δ 166.8, 152.6, 139.5, 134.0, 133.5, 132.2, 131.3, 130.2, 129.1, 128.3, 121.0, 106.0, 84.1, 27.7 ppm; MS m/z (EI, relative intensity) 387 (M^++2, 6), 385 (M^+, 6), 105 (100), 77 (24); HRMS (EI) calcd for $C_{19}H_{16}BrNO_3$ (M^+) 385.0313, found 385.0314.

(*Z*)-3-Benzoyl-4-(2-chlorobenzylidene)-5,5-dimethyloxazolidin-2-one (2g): ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.59 (d, 2H, J = 8.4 Hz), 7.50 (t, 2H, J = 7.5 Hz), 7.34 (t, 2H, J = 7.7 Hz), 7.14 (d, 2H, J = 7.5 Hz), 7.05–6.95 (m, 3H), 5.86 (s, 1H), 1.76 (s, 6H) ppm; ^{13}C NMR (75 MHz, $CDCl_3$) δ 166.5, 152.5, 141.2, 133.6, 133.3, 133.0, 132.2, 129.7, 129.7, 129.3, 129.2, 128.6, 128.2, 128.2, 126.3, 103.4, 83.8, 28.0 ppm; MS m/z (EI, relative intensity) 341 (M^+, 13), 105 (100), 77 (40); HRMS (EI) calcd for $C_{19}H_{16}ClNO_3$ (M^+) 341.0819, found 341.0816.

(*Z*)-3-Benzoyl-4-(3-chlorobenzylidene)-5,5-dimethyloxazolidin-2-one (2h): ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.73 (d, 2H, J = 8.2 Hz), 7.58 (t, 1H, J = 7.5 Hz), 7.42 (t, 2H, J = 7.6 Hz), 7.01–6.89 (m, 4H), 5.82 (s, 1H), 1.72 (s, 6H) ppm; ^{13}C NMR (75 MHz, $CDCl_3$): δ 166.9, 152.6, 140.4, 136.4, 134.2, 134.0, 132.1, 130.2, 129.5, 128.4, 127.5, 127.2, 125.6, 105.5, 84.0, 27.7 ppm; MS m/z (EI, relative intensity) 341 (M^+, 24), 105 (100), 77 (64); HRMS (EI) calcd for $C_{19}H_{16}ClNO_3$ (M^+) 341.0819, found 341.0821.

(*Z*)-3-Benzoyl-4-(4-chloro-2-fluorobenzylidene)-5,5-dimethyloxazolidin-2-one (2i): ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.73 (d, 2H, J = 7.5 Hz), 7.57 (t, 1H, J = 7.5 Hz), 7.42 (t, 2H, J = 7.2 Hz), 7.03–6.98 (m, 2H), 6.83 (d, 2H, J = 10.1 Hz), 5.74 (s, 1H), 1.73 (s, 6H) ppm; ^{13}C NMR (75 MHz, $CDCl_3$) δ 166.4, 158.8 (d, J = 249.1 Hz), 152.3, 141.1, 133.8, 133.7, 133.6, 132.4, 130.1, 129.9, 129.9, 128.1, 125.0, 124.2, 121.5 (d, J = 15.5 Hz), 116.0 (d, J = 25.3 Hz), 99.2, 83.9, 28.1 ppm; MS m/z (EI, relative intensity) 359 (M^+, 10), 105 (100), 77 (24); HRMS (EI) calcd for $C_{19}H_{15}FClNO_3$ (M^+) 359.0724, found 359.0722.

(*Z*)-4-((3-Benzoyl-5,5-dimethyl-2-oxooxazolidin-4-ylidene)methyl)benzonitrile (2j): ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.74 (d, 2H, J = 7.3 Hz), 7.61 (t, 1H, J = 7.5 Hz), 7.44 (t, 1H, J = 7.6 Hz), 7.36 (d, 2H, J = 8.2 Hz), 7.08 (d, 2H, J = 8.0 Hz), 5.88 (s, 1H), 1.73 (s, 6H) ppm; ^{13}C NMR (75 MHz, $CDCl_3$) δ 166.8, 152.4, 141.6, 139.6, 134.3, 132.0, 131.9, 130.3, 128.5, 128.1, 118.6, 110.4, 105.0, 84.1, 27.8 ppm; MS m/z (EI, relative intensity) 332 (M^+, 10), 288 (2), 228 (4), 105 (100), 77 (61); HRMS (EI) calcd for $C_{20}H_{16}N_2O_3$ (M^+) 332.1161, found 332.1164.

(*Z*)-3-Benzoyl-5,5-dimethyl-4-(naphthalen-1-ylmethylene)-oxazolidin-2-one (2m): ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.66–7.63 (m, 2H), 7.57 (d, 1H, J = 7.0 Hz), 7.36–7.32 (m, 4H), 7.20–7.12 (m, 3H), 7.03 (t, 2H, J = 7.4 Hz), 6.17 (s, 1H), 1.85 (s, 6H) ppm; ^{13}C NMR (75 MHz, $CDCl_3$) δ 166.6, 152.5, 142.1, 133.3, 132.9, 131.9, 131.6, 130.5, 129.0, 128.3, 128.1, 127.8, 125.95, 125.86, 125.79, 124.9, 124.2, 103.5, 83.6, 28.1 ppm; MS m/z (EI, relative intensity) 357 (M^+, 28), 105 (100), 77 (22); HRMS (EI) calcd for $C_{23}H_{19}NO_3$ (M^+) 357.1365, found 357.1360.

(*Z*)-3-Benzoyl-5,5-dimethyl-4-(thiophene-2-ylmethylene)-oxazolidin-2-one (2n): ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.84 (d, 1H, J = 8.4 Hz), 7.60 (t, 1H, J = 7.4 Hz), 7.45 (t, 2H, J = 7.6 Hz), 7.10 (d, 1H, J = 5.1 Hz), 6.82 (dd, 1H, J = 5.0, 3.7 Hz), 6.74 (d, 1H, J = 3.5 Hz), 6.07 (s, 1H), 1.70 (s, 6H) ppm; ^{13}C NMR (75 MHz, $CDCl_3$) δ 167.0, 152.6, 138.0, 136.4, 133.8, 132.7, 130.6, 128.2, 127.2, 126.9, 125.9, 101.7, 84.3, 27.5 ppm; MS m/z (EI, relative intensity) 313 (M^+, 23), 105 (100), 77 (39); HRMS (EI) calcd for $C_{17}H_{15}NO_3S$ (M^+) 313.0772, found 313.0770.

(*Z*)-3-Benzoyl-5,5-dimethyl-4-(pyridin-2-ylmethylene)-oxazolidin-2-one (2o): ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.96 (d, 1H, J = 7.5 Hz), 7.63 (d, 1H, J = 4.2 Hz), 7.55 (t, 1H, J = 7.2 Hz), 7.47–7.41 (m, 2H), 7.01 (d, 1H, J = 7.9 Hz), 6.79 (t, 1H, J = 6.0 Hz), 5.77 (s, 1H), 1.68 (s, 6H) ppm; ^{13}C NMR (75 MHz, $CDCl_3$) δ 167.8, 152.0, 146.9, 142.9, 136.3, 133.6, 133.3, 130.7, 128.9, 128.2, 127.9, 123.1, 121.1, 102.9, 84.4, 27.7 ppm; MS m/z (EI, relative intensity) 308 (M^+, 31), 204(47), 105 (100), 77 (68); HRMS (EI) calcd for $C_{18}H_{16}N_2O_3$ (M^+) 308.1161, found 308.1162.

(*Z*)-3-Benzoyl-4-(4-chlorobenzylidene)-5-ethyl-5-methyloxazolidin-2-one (2p): ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.74 (d, 2H, J = 7.3 Hz), 7.59 (t, 1H, J = 7.4 Hz), 7.43 (t, 2H, J = 7.7 Hz), 7.05 (d, 2H, J = 8.2 Hz), 6.92 (d, 2H, J = 8.3 Hz), 5.78 (s, 1H), 2.05–1.86 (m, 2H), 1.69 (s, 3H), 1.06 (t, 3H, J = 7.3 Hz) ppm; ^{13}C NMR (75 MHz, $CDCl_3$) δ 166.8, 153.1, 138.2, 134.0, 133.2, 132.7, 132.4, 130.2, 128.8, 128.4, 105.9, 86.7, 34.0, 26.3, 7.6 ppm; MS m/z (EI, relative intensity) 355 (M^+, 11), 139(66), 105 (100), 77 (60); HRMS (EI) calcd for $C_{20}H_{18}ClNO_3$ (M^+) 355.0975, found 355.0980.

(*Z*)-3-Benzoyl-4-benzylidene-5-isopropyl-5-methyloxazolidin-2-one (2q): ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.70 (d, 2H, J = 8.2 Hz), 7.52 (t, 1H, J = 7.3 Hz), 7.37 (t, 2H, J = 7.6 Hz), 7.03–6.95 (m, 5H), 5.81 (s, 1H), 2.02 (m, 1H), 1.64 (s, 3H), 1.06 (t, 6H, J = 6.6 Hz) ppm; ^{13}C NMR (75 MHz, $CDCl_3$) δ 166.8, 153.5, 138.0, 134.9, 133.7, 132.7, 130.3, 128.3, 128.2, 127.5, 127.1, 107.5, 88.6, 38.0, 24.4, 16.5, 16.5 ppm; MS m/z (EI, relative intensity) 335 (M^+, 14), 105 (100), 77 (22); HRMS (EI) calcd for $C_{21}H_{21}NO_3$ (M^+) 335.1521, found 335.1519.

3-Benzoyl-5-ethyl-5-methyl-4-methyleneoxazolidin-2-one (2r): ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.60 (d, 2H, J = 7.1 Hz), 7.52 (t, 1H, J = 7.4 Hz), 7.39 (t, 2H, J = 7.5 Hz), 5.53 (d, 1H, J = 2.5 Hz), 4.49 (d, 1H, J = 2.4 Hz), 1.93–1.84 (m, 1H), 1.79–1.71 (m, 1H), 1.55 (s, 3H), 0.97 (t, 3H, J = 7.3 Hz) ppm; ^{13}C NMR (75 MHz, $CDCl_3$) δ 169.1, 152.5, 144.6, 133.5, 133.0, 129.03, 129.00, 128.21, 128.17, 91.2, 85.6, 33.9, 26.7, 7.5 ppm; MS m/z (EI, relative intensity) 245 (M^+, 10), 201(7), 105 (100), 77 (49); HRMS (EI) calcd for $C_{14}H_{15}NO_3$ (M^+) 245.1052, found 245.1056.

2-Methyl-4-phenylbut-3-yn-2-yl benzoylcarbamate (3): ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.92 (s, 1H), 7.75 (d, 2H, J = 8.4 Hz), 7.51 (t, 1H, J = 7.3 Hz), 7.43–7.37 (m, 4H), 7.24–7.20 (m, 3H), 1.79 (s, 6H) ppm; ^{13}C NMR (75 MHz, $CDCl_3$) δ 164.9, 148.6, 133.1, 132.9, 131.9, 128.8, 128.5, 128.2, 127.5, 122.2, 89.1, 84.8, 75.1, 29.0 ppm; MS m/z (EI, relative intensity) 307 (M^+, 11), 160 (28), 143 (40), 105 (100), 77 (55); HRMS (EI) calcd for $C_{19}H_{17}NO_3$ (M^+) 307.1208, found 307.1207.

General Procedure for Hydrogenation Reactions of 2a. A solution of **2a** (1 mmol) in anhydrous methanol or ethyl acetate (3 mL) was treated with palladium (10 wt % on charcoal) under a hydrogen atmosphere (H_2 balloon). The reaction mixture was stirred for 2 h at room temperature. The progress of the reaction was followed by TLC. After completion, the reaction was filtered through Celite and the residue washed with solvent used. The filtrate was concentrated under reduced pressure and purified by column chromatography (EtOAc/hexane).

3-Benzoyl-4-benzyl-5,5-dimethyloxazolidin-2-one (4): ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.60 (d, 2H, J = 7.1 Hz), 7.47 (t, 1H, J = 7.3 Hz), 7.36 (t, 2H, J = 7.5 Hz), 7.25–7.21 (m, 3H), 7.18–7.12 (m, 2H), 4.59 (dd, 1H, J = 9.7, 4.2 Hz), 3.41 (dd, 1H, J = 14.1, 4.2 Hz), 2.82 (dd, 1H, J = 14.0, 9.8 Hz) 1.43 (s, 3H), 1.21 (s, 3H) ppm; ^{13}C NMR (75 MHz, $CDCl_3$): δ 170.4, 152.6, 136.4, 133.4, 132.6, 129.2, 129.2, 129.1, 128.7, 128.4, 127.9, 127.0, 82.3, 64.5, 34.4, 28.1, 22.6 ppm; MS m/z (EI, relative intensity) 309 (M^+, 15), 176 (34), 149, (9), 105, (100), 77 (25); HRMS (EI) calcd for $C_{19}H_{19}NO_3$ (M^+) 309.1365, found 309.1364.

4-Benzyl-5,5-dimethyloxazolidin-2-one (5): ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.36–7.23 (m, 3H), 7.16–7.15 (m, 2H), 4.81 (s, 1H), 3.66 (dd, 1H, J = 10.8, 3.7 Hz), 2.82 (dd, 1H, J = 13.3, 3.6 Hz), 2.64

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(dd, 1H, J = 13.2, 11.0 Hz), 1.47 (s, 3H), 1.44 (s, 3H) ppm; ^{13}C NMR (75 MHz, $CDCl_3$) δ 157.8, 136.8, 129.1, 128.8, 127.2, 83.2, 63.0, 37.0, 27.5, 21.9 ppm; MS m/z (EI, relative intensity) 205 (M^+, 5), 114 (100), 91 (46), 71 (91); HRMS (EI) calcd for $C_{12}H_{15}NO_2$ (M^+) 205.1103, found 205.1105.

General Procedure for Debenzoylation Reactions of 2a. A stirred solution of **2a** (1 mmol) in ethanol (3 mL) was treated with butylamine (1.5 mmol) at room temperature. The resulting mixture was heated to 70 °C for 12 h. The progress of the reaction was monitored by TLC. After completion, the reaction mixture was cooled to room temperature and extracted with EtOAc (2 × 5 mL). The combined organic portions were washed with water and brine, dried over anhydrous $MgSO_4$, and concentrated under reduced pressure. The residue was purified by column chromatography over silica gel (EtOAc/hexane) to give the desired product **6**.

(*Z*)-4-Benzylidene-5,5-dimethyloxazolidin-2-one (6): ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.81 (s, 1H), 7.40 (t, 2H, J = 7.6 Hz), 7.29−7.22 (m, 3H), 5.39 (s, 1H), 1.66 (s, 6H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ 155.8, 141.7, 135.2, 129.4, 129.0, 129.0, 128.6, 126.99, 126.97, 126.6, 97.4, 85.2, 27.9 ppm; MS m/z (EI, relative intensity) 203 (M^+, 100), 188 (8), 158 (23), 144 (59), 132 (84), 117 (60), 105 (48), 77 (21); HRMS (EI) calcd for $C_{12}H_{13}NO_2$ (M^+) 203.0946, found 203.0947.

■ ASSOCIATED CONTENT

Supporting Information

Copies of ^{1}H NMR and ^{13}C NMR spectra for all products and X-ray crystallographic information for **2a** including an ORTEP diagram and CIF. This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes

The authors declare no competing financial interest.

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