Supporting information

Highly Efficient Fixation of Carbon Dioxide into 2-Oxazolidinones under Mild Medium by Using Reusable Ionic Liquid/CuI Catalyst System

Mayumi Egashira, Hsiu-Hui Chen*

Department of Molecular Science and Engineering, National Taipei University of Technology, Taipei 106, Taiwan.

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1. Experimental Section

**Materials and Characterization Techniques.** All chemicals and solvents (AR quality) were used as received without further purification. The chemicals and their purities (as received) are listed as follows: ethynylbenzene (Alfa Aesar, >98%), 1-butyl-4-ethynylbenzene (TCI, >97%), hept-1-yne (TCI, >97%), 2-Methyl-3-butyn-2-ol (Alfa Aesar, >98%), benzaldehyde (Alfa Aesar, >99%), 4-bromobenzaldehyde (Alfa Aesar, >98%), 4-methoxybenzaldehyde (Alfa Aesar, >98%), 4-formylbenzonitrile (Matrix Scientific, 97%), 2-chlorobenzaldehyde (Acros, 99%), 3-chlorobenzaldehyde (TCI, >98%), 4-chlorobenzaldehyde (Acros, >98.5%), benzylamine (Alfa Aesar, >98%), 4-methylbenzylamine (Acros, 98%), butan-1-amine (Alfa Aesar, 99%), 4-(trifluoromethyl)benzylamine (Combi-Blocks, 98%), 1-butyl-2,3-dimethylimidazolium hexafluorophosphate (TCI, >97.0%), 1-butyl-3-methylimidazolium tetrafluoroborate (Acros, 98%), 1-butyl-3-methylimidazolium hexafluorophosphate (TCI, >98%), 1-ethyl-3-methylimidazolium hexafluorophosphate (TCI, >98%), 1-butyl-2,3-dimethylimidazolium tetrafluoroborate (TCI, >98%), 1-butyl-2,3-dimethylimidazolium bis(trifluoromethanesulfonyl)imide (TCI, >98%), 1-butyl-2,3-dimethylimidazolium trifluoromethanesulfonate (TCI, >98%), 1,8-diazabicyclo(5.4.0)undec-7-ene (TCI, 99%), acetic acid (Scharlau, >99%), copper(I) iodide (AK Scientific, >99%). Column chromatography was performed on silica gel (230–400 mesh). Thin-layer chromatography (TLC) was performed on glass sheets precoated with silica gel (Merck, Kieselgel 60, F254). $^1$H NMR and $^{13}$C NMR spectra were recorded in CDCl$_3$ on Agilent Technologies 300 and 400 MHz NMR spectrometers with the residue solvent proton or carbon signal as the internal standard ($^1$H NMR: 7.26 ppm; $^{13}$C NMR: 77.0 ppm). Multiplicities are given as s (singlet), d (doublet), t (triplet), q (quartet), and m (multiplet). Mass spectra were obtained by fast atom bombardment (FAB), electron ionization (EI), both equipped with a magnetic sector analyzer, and electrospray ionization (ESI), equipped with a TOF analyzer. IR spectra were measured on a Nicolet 6700 FT-IR spectrometer from Thermo Scientific. X-ray diffraction data were obtained by an Xcalibur, an Atlas, and a Gemini diffractometer.

**General Procedure for the Synthesis of Compound 5.** 50 mL Schlenk tube equipped with a stir bar was filled with CuI (57 mg, 30 mol %), ionic liquid (180μL, 5.7 M), alkyn (1.0 mmol), and amine (1.3 mmol) under N$_2$. After the neck was capped with a rubber septum, the tube was purged with CO$_2$ by freeze-pump-thaw three times. The mixture was stirred with a magnetic stirrer for 5 min, and then aldehyde (1.3 mmol) was added. The rubber septum was replaced with a glass stopper, and the tube was attached to a balloon of CO$_2$. The tube was placed in the chemical reactor set stirring speed at 350 rpm. The reaction was continued at different temperatures for 48-56 h. After the reaction was completed, ionic liquid and CuI were removed by silica gel column chromatography (EtOAc/hexane = 1:5) from the obtained mixture. Finally, the yield was determined by the $^1$H NMR internal standard method.
General Procedure for the recyclability investigation of ionic liquid/ CuI system. After the reaction was completed, 10 mL diethyl ether was directly added to the tube. The mixture solution was stirred with a magnetic stirrer for 2 min, and agitated by an ultrasonic cleaner for 2 min. Then, the upper layer was collected. Repeat the above steps ten times. After these steps, the upper layer was further purified by column chromatography (EtOAc/hexane = 1:5), and the solvent was removed by a rotary evaporator. Finally, the yield was determined by the $^1$H NMR internal standard method. The lower layer was reused for the next round after drying under 70 °C for 4 h.

(Z)-3-benzyl-5-benzylidene-4-phenyloxazolidin-2-one (5a). White solid; yield: 99%; $^1$H NMR (CDCl$_3$, 300 MHz): δ = 7.50 (d, J = 6.0 Hz, 2H), 7.43 (m, 3H), 7.33 (m, 3H), 7.27 (m, 4H), 7.19 (m, 3H), 5.19 (s, 1H), 5.15 (s, 1H), 4.96 (d, J = 15.0 Hz, 1H), 3.68 (d, J = 15.0 Hz, 1H); $^{13}$C NMR (CDCl$_3$, 75 MHz): δ = 155.08, 147.47, 136.76, 134.72, 133.30, 129.37, 129.30, 128.88, 128.56, 128.40, 128.30, 128.21, 128.01, 126.95, 104.81, 62.78, 45.53; HRMS (FAB-Magnetic Sector): m/z [M+H]$^{+}$ calcd for C$_{23}$H$_{20}$NO$_2$: 342.1494, found 342.1487; IR (KBr): 2924.6, 1783.9 ($\nu$ C=O), 1688.4, 1408.8, 1037.5 cm$^{-1}$.

(Z)-3-benzyl-5-(4-butylbenzylidene)-4-(4-methoxyphenyl)oxazolidin-2-one (5b). White solid; yield: 89%; $^1$H NMR (CDCl$_3$, 300 MHz): δ = 7.42 (d, J = 9.0 Hz, 2H), 7.34 (m, 3H), 7.17 (m, 4H), 7.11 (d, J = 9.0 Hz, 2H), 6.93 (d, J = 6.0 Hz, 2H), 5.17 (s, 1H), 5.11 (s, 1H), 4.93 (d, J = 15.0 Hz, 1H), 3.85 (d, J = 3.0 Hz, 3H), 3.66 (d, J = 15.0 Hz, 1H), 2.57 (t, J = 7.5 Hz, 2H), 1.57 (t, J = 7.5 Hz, 2H), 1.34 (m, 2H), 0.91 (t, J = 7.5 Hz, 3H); $^{13}$C NMR (CDCl$_3$, 75 MHz): 160.28, 155.13, 147.16, 141.83, 134.86, 130.74, 129.47, 128.85, 128.71, 128.55, 128.48, 128.21, 128.14, 114.56, 104.62, 62.25, 55.36, 45.34, 35.35, 33.53, 22.30, 13.93; HRMS (ESI-QTOF): m/z [M+H]$^{+}$ calcd for C$_{28}$H$_{30}$NO$_3$: 428.2226, found 428.2230; IR (KBr): 2931, 1784 ($\nu$ C=O), 1690, 1513, 1053 cm$^{-1}$.

(Z)-3-benzyl-4-(4-bromophenyl)-5-(4-butylbenzylidene)oxazolidin-2-one (5c). White solid; yield: 51%; $^1$H NMR (CDCl$_3$, 300 MHz): δ = 7.56 (d, J = 9.0 Hz, 2H), 7.41 (d, J = 9.0 Hz, 2H), 7.34 (m, 3H), 7.13 (m, 6H), 5.15 (s, 1H), 5.10 (s, 1H), 4.95 (d, J = 15.0 Hz, 1H), 3.67 (d, J = 15.0 Hz, 1H), 2.57 (t, J = 7.5 Hz, 2H), 1.54 (m, 2H), 1.32 (m, 2H), 0.90 (t, J = 7.5 Hz, 3H); $^{13}$C NMR (CDCl$_3$, 75 MHz): 155.07, 146.09, 142.10, 135.91, 134.46, 132.47, 130.38, 129.69, 128.93, 128.64, 128.51, 128.30, 128.23, 123.47, 105.14, 62.00, 45.58, 35.33, 34.48, 22.27, 13.91; HRMS (ESI-QTOF): m/z [M+Na]$^{+}$ calcd for C$_{27}$H$_{26}$NO$_2$BrNa: 498.1045, found 498.1042; IR (KBr): 2929, 1780 ($\nu$C=O), 1687, 1400, 1070 cm$^{-1}$.

(Z)-4-(3-benzyl-5-(4-butylbenzylidene)-2-oxooxazolidin-4-yl)benzonitrile (5d). White solid; yield: 61%; $^1$H NMR (CDCl$_3$, 300 MHz): δ = 7.72 (d, J = 9.0 Hz, 2H), 7.40 (d, J = 9.0 Hz, 3H), 7.35 (m, 4H), 7.11 (m, 4H), 5.18 (s, 1H), 5.13 (s, 1H), 4.96 (d, J = 15.0 Hz, 1H), 3.72 (d, J = 15.0 Hz, 1H), 2.57 (t, J = 7.5 Hz, 2H), 1.56 (m, 2H), 1.33 (m, 2H), 0.90 (t, J = 7.5 Hz, 3H); $^{13}$C NMR (CDCl$_3$, 75 MHz): 154.98, 145.20,
142.38, 142.16, 134.07, 130.05, 129.00, 128.65, 128.56, 128.47, 128.26, 118.02, 113.32, 105.67, 62.19, 45.96, 35.32, 33.45, 22.25, 13.89; HRMS (ESI-QTOF): m/z [M+H]^+ calecd for C_{28}H_{27}N_{2}O_{4} 423.2073, found 423.2048; IR (KBr): 2928.4, 1783.8 (νC=O), 1689.3, 1405.9 cm\(^{-1}\).

(Z)-5-benzylidene-3-butyl-4-(4-methoxyphenyl)oxazolidin-2-one (5e).\(^5\) White solid; yield: 77%; \(^1\)H NMR (CDCl\(_3\), 300 MHz): δ = 7.54 (d, J = 9.0 Hz, 2H), 7.25 (m, 5H), 6.96 (d, J = 9.0 Hz, 2H), 5.37 (d, J = 3.0 Hz, 1H), 5.26 (d, J = 3.0 Hz, 1H), 3.85 (s, 3H), 3.50 (m, 1H), 2.85 (m, 1H), 1.47 (m, 2H), 1.30 (m, 2H), 0.90 (t, J = 7.5 Hz, 3H); \(^1\)C NMR (CDCl\(_3\), 75 MHz): 160.27, 154.91, 148.07, 133.48, 129.16, 129.09, 128.39, 128.25, 126.81, 114.56, 104.28, 63.32, 55.32, 41.41, 28.89, 19.79, 13.60; HRMS (ESI-QTOF): m/z [M+H]^+ calecd for C\(_{21}\)H\(_{24}\)NO\(_{3}\) 338.1756, found 338.1737; IR (KBr): 2931.3, 1782.9 (νC=O), 1690.3, 1512.9, 1034.6 cm\(^{-1}\).

(Z)-5-benzylidene-4-(4-bromophenyl)-3-butyloxazolidin-2-one (5f).\(^6\) White solid; yield: 82%; \(^1\)H NMR (CDCl\(_3\), 300 MHz): δ = 7.59 (d, J = 9.0 Hz, 2H), 7.53 (d, J = 9.0 Hz, 2H), 7.31 (m, 2H), 7.22 (m, 3H), 5.37 (s, 1H), 5.24 (s, 1H), 3.53 (m, 1H), 2.83 (m, 1H), 1.47 (m, 2H), 1.31 (m, 2H), 0.91 (t, J = 7.5 Hz, 3H); \(^1\)C NMR (CDCl\(_3\), 75 MHz): 154.85, 147.02, 136.32, 133.13, 132.52, 129.40, 128.44, 128.30, 127.06, 123.48, 104.83, 63.16, 41.61, 28.87, 19.74, 13.58; HRMS (ESI-QTOF): m/z [M+H]^+ calecd for C\(_{20}\)H\(_{21}\)NO\(_{2}\)Br 386.0756, found 386.0709; IR (KBr): 2959.2, 1784.8 (νC=O), 1691.3, 1404.9, 1070.3 cm\(^{-1}\).

(Z)-5-(4-butylbenzylidene)-3-(4-methylbenzyl)-4-phenyloxazolidin-2-one (5h). White solid; yield: 87%; \(^1\)H NMR (CDCl\(_3\), 400 MHz): δ = 7.42 (m, 5H), 7.26 (m, 2H), 7.14 (d, J = 8.0 Hz, 2H), 7.10 (d, J = 8.0 Hz, 2H), 7.06 (d, J = 8.0 Hz, 2H), 5.16 (s, 1H), 5.13 (s, 1H), 4.92 (d, J = 16.0 Hz, 1H), 3.62 (d, J = 16.0 Hz, 1H), 2.56 (t, J = 8.0 Hz, 2H), 2.35 (s, 3H), 1.56 (m, 2H), 1.32 (m, 2H), 0.91 (t, J = 6.0 Hz, 3H); \(^1\)C NMR (CDCl\(_3\), 100 MHz): 155.19, 146.84, 141.86, 137.99, 137.00, 131.72, 130.72, 129.52, 129.24, 128.56, 128.48, 128.22, 128.04, 104.73, 62.64, 45.22, 35.35, 33.51, 22.29, 21.14, 13.90; HRMS (ESI-QTOF): m/z [M+H]^+ calecd for C\(_{28}\)H\(_{30}\)NO\(_{2}\) 412.2277, found 412.2248. IR (KBr): 2928.4, 1788.6 (νC=O), 1690.3, 1512.9, 1054.9 cm\(^{-1}\).

(Z)-5-benzylidene-4-(4-methoxyphenyl)-3-(4-methylbenzyl)oxazolidin-2-one (5i). White solid; yield: 76%; \(^1\)H NMR (CDCl\(_3\), 400 MHz): δ = 7.48 (d, J = 8.0 Hz, 2H), 7.27 (m, 2H), 7.15 (m, 5H), 7.02 (d, J = 8.0 Hz, 2H), 6.93 (d, J = 12.0 Hz, 2H), 5.16 (s, 1H), 5.09 (s, 1H), 4.88 (d, J = 16.0 Hz, 1H), 3.83 (s, 3H), 3.60 (d, J = 16.0 Hz, 1H), 2.33 (s, 3H); \(^1\)C NMR (CDCl\(_3\), 100 MHz): 160.34, 154.99, 148.00, 137.96, 133.45, 131.77, 129.52, 129.45, 128.70, 128.56, 128.40, 128.30, 126.87, 114.62, 104.54, 62.22, 55.37, 45.11, 21.14; HRMS (ESI-QTOF): m/z [M+H]^+ calecd for C\(_{25}\)H\(_{30}\)NO\(_{3}\) 386.1756, found 386.1732; IR (KBr): 2923.2, 1784.8 (νC=O), 1690.3, 1512.9, 1247.7, 1053.9 cm\(^{-1}\).
(Z)-5-benzylidene-4-(4-bromophenyl)-3-(4-methylbenzyl)oxazolidin-2-one (5j). White solid; yield: 30%; 1H NMR (CDCl$_3$, 400 MHz): $\delta = 7.56$ (d, $J = 8.0$ Hz, 2H), 7.49 (d, $J = 8.0$ Hz, 2H), 7.29 (t, $J = 8.0$ Hz, 2H), 7.20 (d, $J = 8.0$ Hz, 1H), 7.14 (m, 4H), 7.04 (d, $J = 8.0$ Hz, 2H), 5.16 (s, 1H), 5.10 (s, 1H), 4.92 (d, $J = 16.0$ Hz, 1H), 3.63 (d, $J = 16.0$ Hz, 1H), 2.35 (s, 3H); 13C NMR (CDCl$_3$, 100 MHz): 154.93, 146.96, 138.19, 135.93, 133.11, 132.53, 131.37, 129.70, 129.62, 128.55, 128.45, 128.33, 127.12, 123.52, 105.06, 62.09, 45.39, 21.14; HRMS (ESI-QTOF): m/z [M+H]$^+$ calcd for C$_{24}$H$_{21}$NO$_2$Br 434.0756, found 434.0690; IR (KBr): 2921.6, 1782.9 (νC=O), 1690.3, 1401.0, 1052.9 cm$^{-1}$.

(2)-5-benzylidene-4-(4-methoxyphenyl)-3-(4-(trifluoromethyl)benzyl)oxazolidin-2-one (5k). White solid; yield: 83%; 1H NMR (CDCl$_3$, 300 MHz): $\delta = 7.59$ (d, $J = 6.0$ Hz, 2H), 7.51 (d, $J = 9.0$ Hz, 2H), 7.30 (m, 4H), 7.18 (m, 3H), 6.93 (d, $J = 9.0$ Hz, 2H), 5.22 (s, 1H), 5.13 (s, 1H), 4.89 (d, $J = 15.0$ Hz, 1H), 3.82 (m, 4H); 13C NMR (CDCl$_3$, 75 MHz): 160.46, 154.99, 147.49, 139.01, 133.18, 131.04, 130.61, 130.18, 129.75, 129.44, 129.29, 128.76, 128.44, 128.33, 128.15, 127.04, 125.86, 125.81, 125.76, 125.71, 122.08, 118.48, 114.88, 105.02, 62.65, 55.35, 45.01; HRMS (ESI-QTOF): m/z [M+H]$^+$ calcd for C$_{25}$H$_{21}$NO$_3$F$_3$ 440.1474, found 440.1476; IR (KBr): 1783 (νC=O), 1689, 1416, 1063 cm$^{-1}$.

(Z)-3-benzyl-5-(2-hydroxy-2-methylpropylidene)-4-phenyloxazolidin-2-one (5m). White solid; yield: 71%; 1H NMR (CDCl$_3$, 400 MHz): $\delta = 7.41$ (m, 3H), 7.33 (m, 3H), 7.17 (m, 4H), 4.96 (s, 1H), 4.88 (d, $J = 16.0$ Hz, 1H), 4.52 (s, 1H), 3.61 (d, $J = 16.0$ Hz, 1H), 2.31 (s, 1H), 1.36 (d, $J = 8.0$ Hz, 6H); 13C NMR (CDCl$_3$, 100 MHz): 154.64, 146.32, 136.75, 134.64, 129.32, 129.28, 128.87, 128.62, 128.23, 127.91, 112.77, 70.00, 62.03, 45.49, 30.14; HRMS (ESI-QTOF): m/z [M+H]$^+$ calcd for C$_{20}$H$_{22}$NO$_3$ 324.1600, found 324.1579; IR (KBr): 3444.2, 2972.7, 1783.8 (νC=O), 1702.8, 1410.7, 1060.7 cm$^{-1}$.

(Z)-3-benzyl-5-benzylidene-4-(2-chlorophenyl)oxazolidin-2-one (5n). White solid; yield: 39 %; 1H NMR (CDCl$_3$, 400 MHz): $\delta = 7.44$ (m, 3H), 7.28 (m, 8H), 7.15 (m, 3H), 5.81 (s, 1H), 5.27 (s, 1H), 4.90 (d, $J = 12.0$ Hz, 1H), 3.73 (d, $J = 12.0$ Hz, 1H), 2.31 (s, 1H), 1.36 (d, $J = 8.0$ Hz, 6H); 13C NMR (CDCl$_3$, 100 MHz): 155.22, 146.01, 134.51, 133.25, 130.37, 129.30, 128.85, 128.63, 128.56, 128.39, 128.36, 128.25, 128.01, 127.85, 127.26, 126.99, 104.31, 58.41, 45.93, 58.41, 45.93; HRMS (ESI-QTOF): m/z [M+H]$^+$ calcd for C$_{23}$H$_{19}$NO$_2$Cl 376.1104, found 376.1086; IR (KBr): 3028.6, 1784.8 (νC=O), 1701.7, 1060.7 cm$^{-1}$.

(Z)-3-benzyl-5-benzylidene-4-(3-chlorophenyl)oxazolidin-2-one (5o). White solid; yield: 95%; 1H NMR (CDCl$_3$, 300 MHz): $\delta = 7.52$ (d, $J = 6.0$ Hz, 2H), 7.41 (s, 1H), 7.37 (m, 4H), 7.28 (m, 3H), 7.18 (m, 4H), 5.22 (d, $J = 3.0$ Hz, 1H), 5.13 (d, $J = 3.0$ Hz, 1H), 4.98 (d, $J = 15.0$ Hz, 1H), 3.74 (d, $J = 15.0$ Hz, 1H); 13C NMR (CDCl$_3$, 75 MHz): 154.91, 146.59, 138.80, 135.23, 134.37, 132.99, 130.82, 129.62, 128.94, 128.50, 128.44, 128.35, 127.97, 127.14, 126.07, 105.19, 62.15, 45.68; HRMS (ESI-QTOF): m/z [M+H]$^+$ calcd for C$_{22}$H$_{19}$NO$_2$Cl 376.1104, found 376.1085; IR (KBr): 1781 (νC=O), 1691, 1405, 1047 cm$^{-1}$.
(Z)-3-benzyl-5-benzylidene-4-(4-chlorophenyl)oxazolidin-2-one (5p). White solid; yield: 73%; 1H NMR (CDCl₃, 300 MHz): δ = 7.52 (d, J = 9.0 Hz, 2H), 7.43 (d, J = 9.0 Hz, 2H), 7.36 (m, 3H), 7.30 (m, 2H), 7.22 (m, 5H), 5.19 (s, 1H), 5.14 (s, 1H), 4.97 (d, J = 15.0 Hz, 1H), 3.70 (d, J = 15.0 Hz, 1H); 13C NMR (CDCl₃, 75 MHz): 154.91, 146.93, 135.34, 135.23, 134.41, 133.02, 129.55, 129.38, 128.93, 128.50, 128.44, 128.32, 128.30, 127.11, 105.08, 62.04, 45.57; HRMS (ESI-QTOF): m/z [M+H]+ calcd for C₂₃H₁₉NO₂Cl 376.1104, found 376.1052; IR (KBr): 3029.6, 1782.9 (νC=O), 1690.3, 1493.6, 1090.5 cm⁻¹.

(Z)-3-benzyl-5-hexylidene-4-phenyloxazolidin-2-one (5q). White solid; yield: 55%; 1H NMR (CDCl₃, 300 MHz): δ = 7.40 (m, 3H), 7.33 (m, 3H), 7.21 (m, 2H), 7.16 (m, 2H), 4.98 (s, 1H), 4.90 (d, J = 15.0 Hz, 1H), 4.30 (t, J = 6.0 Hz, 1H), 3.62 (d, J = 15.0 Hz, 1H), 2.10 (m, 2H), 1.24 (m, 6H), 0.85 (t, J = 6.0 Hz, 3H); 13C NMR (CDCl₃, 75 MHz): 155.61, 147.00, 137.43, 135.02, 129.15, 129.10, 128.82, 128.62, 128.10, 127.93, 105.30, 61.65, 45.39, 31.31, 28.89, 24.78, 22.40, 14.06; HRMS (ESI-QTOF): m/z [M+H]+ calcd for C₂₂H₂₅NO₂ 336.1964, found 336.1966; IR (KBr): 2930, 1777 (νC=O), 1654, 1457, 1079 cm⁻¹.

General procedure for the preparation of [DBUH][OAc]. 10 mmol of DBU and acetic acid were mixed in 100 ml round bottom flask. The mixture was stirred for 24 h at room temperature. Then, the obtained mixture was dried in vacuo at 60 °C for 24 h. 1H NMR (D₂O, 400 MHz): δ = 3.48-3.46 (m, 2H), 3.45-3.41 (m, 2H), 3.24-3.21 (m, 2H), 2.54-2.51 (m, 2H), 1.93–1.90 (m, 2H), 1.81 (s, 3H), 1.65–1.59 (m, 6H); 13C NMR (D₂O, 100 MHz): δ = 181.42, 165.95, 54.13, 48.20, 37.94, 32.79, 28.45, 25.85, 23.29, 18.90.

Procedure for the Reaction on a 10 mmol Scale. A two-necked round-bottom flask was charged with CuI (0.57 g, 30 mol %), 1-butyl-2,3-dimethylimidazolium hexafluorophosphate (2.42 g, 5.7 M) phenylacetylene (1.02 g, 9.99 mmol), benzylamine (1.42 g, 13.25 mmol), and a magnetic stir bar under N₂. Then, the reaction vessel was sealed and flushed with CO₂ by the freeze–pump–thaw method. The mixture was stirred with a magnetic stirrer for 5 min, and then benzaldehyde (1.41 g, 13.29 mmol) was added. The flask was attached with a balloon of CO₂, heated up to 75 °C with an oil bath, and stirred for 48 h. After the reaction was completed, the reaction mixture was allowed to cool to room temperature and was passed through a plug of silica gel. The crude reaction mixtures were further purified by silica gel column chromatography (EtOAc/hexanes = 1/18) to provide the desired oxazolidinone 5 (2.39 g, 70%) as a colorless solid.
2. Optimal reaction conditions

\[
\begin{align*}
1a & \quad \text{Ph} \quad \text{NH}_2 + \quad \text{Ph} \quad \text{O} \quad \text{H} + \quad \text{Ph} \quad \equiv \\
& \quad \text{Cul (30 mol\%), CO}_2 \quad \text{(balloon)} \\
& \quad \text{[BMMIM][PF}_6\text{]}, \text{75 °C, 48 h} \\
& \quad \text{Ph} \quad \text{NH} \\
& \quad \text{Ph} \\
& \quad \text{4a} \\
& \quad \text{+} \\
& \quad \text{Ph} \quad \text{N} \quad \text{O} \\
& \quad \text{Ph} \\
& \quad \text{5a}
\end{align*}
\]

Figure S1. Optimal reaction conditions with 1 eq. phenylacetylene (1.0 mmol), benzaldehyde (1.0 mmol), and benzyamine (1.0 mmol) in the [BMMIM][PF₆] under CO₂ pressure (with a balloon) at a temperature of 75 °C for 48 h.
Table S1. Optimization of reaction conditions for different reaction times

All reactions were conducted using phenylacetylene (0.3 mmol), benzaldehyde (0.39 mmol), and benzylamine (0.39 mmol) in [BMMIM][PF₆] (c. 5.7 M) under CO₂ pressure (with a balloon) at a temperature of 75 °C. "Reported yields were determined using the ¹H-NMR internal standard method.

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<tr>
<td>11</td>
<td>44</td>
<td>4</td>
<td>93</td>
</tr>
<tr>
<td>12</td>
<td>48</td>
<td>trace</td>
<td>99</td>
</tr>
</tbody>
</table>
Table S2. Optimization of reaction conditions different temperatures and reaction times

\[
\text{Ph}_2\text{NH}_2 + \text{Ph}-\text{CH} + \text{Ph}_2\text{C} \xrightarrow{\text{Cul (30 mol\%), CO}_2 \text{ (balloon)}} \text{[BMMIM][PF}_6\text{], T °C, x h}} \rightarrow \text{Ph}_2\text{C} = \text{NH} + \text{Ph}_2\text{N} - \text{OC} \text{Ph}
\]

<table>
<thead>
<tr>
<th>T (°C)(^a)</th>
<th>x (h)</th>
<th>yield of 4a (%)(^b)</th>
<th>yield of 5a (%)(^b)</th>
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</thead>
<tbody>
<tr>
<td>55</td>
<td>48</td>
<td>7</td>
<td>78</td>
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<tr>
<td>56</td>
<td>&lt;5</td>
<td></td>
<td>87</td>
</tr>
<tr>
<td>60</td>
<td>&lt;5</td>
<td></td>
<td>90</td>
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<tr>
<td>65</td>
<td>48</td>
<td>&lt;5</td>
<td>83</td>
</tr>
<tr>
<td>56</td>
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<td>&lt;5</td>
<td></td>
<td>93</td>
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<tr>
<td>75</td>
<td>48</td>
<td>trace</td>
<td>99</td>
</tr>
</tbody>
</table>

\(^a\)All reactions were conducted using phenylacetylene (1.0 mmol), benzaldehyde (1.3 mmol), and benzylamine (1.3 mmol) in [BMMIM][PF\(_6\)] (c. 5.7 M) under CO\(_2\) pressure (with a balloon). \(^b\)Reported yields were determined using the \(^1\)H-NMR internal standard method.
3. Single-crystal X-ray diffraction data of 5k

Figure S2. Crystal structure of 5k with Thermal Ellipsoids at 50% Probability.

Table S3. Crystal data and structure refinement for 5k.

<table>
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<tr>
<th>Property</th>
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<tr>
<td>Empirical formula</td>
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<tr>
<td>Formula weight</td>
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<tr>
<td>Crystal system</td>
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<tr>
<td>T(K)</td>
<td>200(2)</td>
</tr>
<tr>
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<td>P2_1/c</td>
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<tr>
<td>a/Å</td>
<td>20.0518(4)</td>
</tr>
<tr>
<td>b/Å</td>
<td>10.0983(2)</td>
</tr>
<tr>
<td>c/Å</td>
<td>10.6704(3)</td>
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<tr>
<td>α(°)</td>
<td>90</td>
</tr>
<tr>
<td>β(°)</td>
<td>104.6280(10)</td>
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<tr>
<td>γ(°)</td>
<td>90</td>
</tr>
<tr>
<td>V/ Å³</td>
<td>2090.60(8)</td>
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<tr>
<td>Z</td>
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</tr>
<tr>
<td>D_0/Mg m³</td>
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<tr>
<td>μ/mm⁻¹</td>
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<td>θ/deg</td>
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</tr>
<tr>
<td>Range h</td>
<td>-28 to 23</td>
</tr>
<tr>
<td>Range k</td>
<td>-14 to 14</td>
</tr>
</tbody>
</table>
4. \(^1\)H NMR, \(^{13}\)C NMR, MS, and IR spectra

4.1 \(^1\)H and \(^{13}\)C NMR spectra for compound 5.

![Figure S3. \(^1\)H NMR (300 MHz, CDCl\(_3\)) of Compound 5a.](image-url)
Figure S4. $^{13}$C NMR (75 MHz, CDCl$_3$) of Compound 5a.

Figure S5. $^{1}$H NMR (300 MHz, CDCl$_3$) of Compound 5b.
Figure S6. $^{13}$C NMR (75 MHz, CDCl$_3$) of Compound 5b.

Figure S7. $^1$H NMR (300 MHz, CDCl$_3$) of Compound 5c.
Figure S8. $^{13}$C NMR (75 MHz, CDCl$_3$) of Compound 5c.

Figure S9. $^1$H NMR (300 MHz, CDCl$_3$) of Compound 5d.
Figure S10. $^{13}$C NMR (75 MHz, CDCl$_3$) of Compound 5d.

Figure S11. $^1$H NMR (300 MHz, CDCl$_3$) of Compound 5e.
Figure S12. $^{13}$C NMR (75 MHz, CDCl$_3$) of Compound 5e.

Figure S13. $^1$H NMR (300 MHz, CDCl$_3$) of Compound 5f.
Figure S14. $^{13}$C NMR (75 MHz, CDCl$_3$) of Compound 5f.

Figure S15. $^1$H NMR (400 MHz, CDCl$_3$) of Compound 5h.
Figure S16. $^{13}$C NMR (100 MHz, CDCl$_3$) of Compound 5h.

Figure S17. $^1$H NMR (400 MHz, CDCl$_3$) of Compound 5i.
Figure S18. $^{13}$C NMR (100 MHz, CDCl$_3$) of Compound 5i.

Figure S19. $^1$H NMR (400 MHz, CDCl$_3$) of Compound 5j.
Figure S20. $^{13}$C NMR (100 MHz, CDCl$_3$) of Compound 5j.

Figure S21. $^1$H NMR (300 MHz, CDCl$_3$) of compound 5k.
Figure S22. $^1$C NMR (75MHz, CDCl$_3$) of compound 5k.

Figure S23. $^1$H NMR (400 MHz, CDCl$_3$) of Compound 5m.
Figure S24. $^{13}$C NMR (100 MHz, CDCl$_3$) of Compound 5m.

Figure S25. $^1$H NMR (400 MHz, CDCl$_3$) of Compound 5n.
Figure S26. $^{13}$C NMR (100 MHz, CDCl$_3$) of Compound 5n.

Figure S27. $^1$H NMR (300 MHz, CDCl$_3$) of Compound 5o.
Figure S28. $^{13}$C NMR (75 MHz, CDCl$_3$) of Compound 5o.

Figure S29. $^1$H NMR (300 MHz, CDCl$_3$) of Compound 5p.
**Figure S30.** $^{13}$C NMR (75 MHz, CDCl$_3$) of Compound 5p.

**Figure S31.** $^1$H NMR (300 MHz, CDCl$_3$) of Compound 5q.
Figure S32. $^{13}$C NMR (75 MHz, CDCl$_3$) of Compound 5q.

4.2 Mass spectra for compound 5.

Figure S33. The mass spectrum of Compound 5a.
Figure S34. The mass spectrum of Compound 5b.

Figure S35. The Mass Spectrum of Compound 5c.
Figure S36. The Mass Spectrum of Compound 5d.

Figure S37. The Mass Spectrum of Compound 5e.
Figure S38. The Mass Spectrum of Compound 5f.

Figure S39. The Mass Spectrum of Compound 5h.
Figure S40. The Mass Spectrum of Compound 5i.

Figure S41. The Mass Spectrum of Compound 5j.
Figure S42. The Mass Spectrum of Compound 5k.

Figure S43. The Mass Spectrum of Compound 5m.
Figure S44. The Mass Spectrum of Compound 5n.

Figure S45. The Mass Spectrum of Compound 5o.
Figure S46. The Mass Spectrum of Compound 5p.
Figure S47. The Mass Spectrum of Compound 5q.
4.3 IR spectra for compound 5.

Figure S48. The IR Spectrum of Compound 5a.

Figure S49. The IR Spectrum of Compound 5b.
Figure S50. The IR Spectrum of Compound 5c.

Figure S51. The IR Spectrum of Compound 5d.
Figure S52. The IR Spectrum of Compound 5e.

Figure S53. The IR Spectrum of Compound 5f.
Figure S54. The IR Spectrum of Compound 5h.

Figure S55. The IR Spectrum of Compound 5i.
Figure S56. The IR Spectrum of Compound 5j.

Figure S57. The IR Spectrum of Compound 5k.
Figure S58. The IR Spectrum of Compound 5m.

Figure S59. The IR Spectrum of Compound 5n.
Figure S60. The IR Spectrum of Compound $5_0$.

Figure S61. The IR Spectrum of Compound $5_p$. 

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Figure S62. The IR Spectrum of Compound 5q.

Figure S63. The $^{31}$P NMR Spectra of [BMMIM][PF$_6$] and [BMMIM][PF$_6$] + CO$_2$. 
Figure S64. The $^{19}$F NMR Spectra of [BMMIM][PF$_6$] and [BMMIM][PF$_6$] + CO$_2$. 
References