Copper-Catalyzed Oxidative Cross-coupling of α-Aminocarbonyl Compounds with Aliphatic Primary Amines and Other Amines toward 2-Oxoacetamidines

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Table of Contents

1. General Information…………………………………………………………………………………………. S2

2. Preparation of α-Amino Carbonyl Compounds ........................................................................ S2

3. General Procedure for the Synthesis of Product 3aa ............................................................ S2

4. All Products .......................................................................................................................... S3-S11

5. Reference ............................................................................................................................ S11

6. 1H and 13C NMR Spectra ..................................................................................................... S12-S37

7. Crystal Structure Data ........................................................................................................ S38
1. **General Information.**

Chemicals were either purchased or purified by standard techniques. All reactions were carried out under a nitrogen atmosphere unless otherwise noted. Column chromatography separations were performed on silica gel (200–300 mesh). $^1$H and $^{13}$C NMR spectra were recorded on a Varian Inova-400 spectrometer (400MHz for $^1$H, 100 MHz for $^{13}$C). NMR chemical shifts were measured relative to the signals of residual CHCl$_3$ ($\delta$H 7.26 ppm and $\delta$C 77.16 ppm) or DMSO-$d_6$ ($\delta$H 2.50 ppm) and DMSO-$d_6$ ($\delta$C 39.520 ppm). LRMS was performed on a GC-MS instrument and HRMS was measured on an electrospray ionization (EI) apparatus using time-of-flight (TOF) mass spectrometry. Melting points are uncorrected.

2. **Preparation of α-Amino Carbonyl Compounds$^{[1-2]}$**

The synthesis of α-amino carbonyl compounds is carried out in two steps. The first step, synthesis of α-bromoacetophenone: to a solution of the acetophenone (15.0 mmol, 1 equiv) in 8 mL of acetonitrile were added NBS (2.72 g, 15.3 mmol, 1.02 equiv) and p-toluenesulfonic acid (2.85 g, 15.0 mmol, 1 equiv). The reaction mixture was stirred for 24 h at 50 °C. After that time, the solvent was evaporated under reduced pressure. A water solution of saturated NaHCO$_3$ (30 mL) was then added, and the solution was extracted with dichloromethane (3 × 30 mL). The organic layers were combined and dried over Na$_2$SO$_4$. The solvent was evaporated, and the residue was purified by silica gel column chromatography (petroleum ether/ethyl acetate = 25:1, V/V) to afford the desired product in 82% yield as a white solid. After that, the next step is that a solution of α-bromoacetophenone (5 mmol) with aniline (5 mmol) and NaHCO$_3$ (5 mmol) in EtOH (20mL) was stirred at room temperature for 12 h and the crude products could be obtained as yellow precipitates, which was recrystallized by EtOH and the yellow solid 1a was isolated in 81% yield.

3. **General Procedure for the Synthesis of Product 3aa**

To a flame-dried Round-bottomed flask with a magnetic stirring bar were charged 1a (63.3 mg, 0.3 mmol), aniline 2a (55.8 mg, 0.6 mmol), Cu(OAc)$_2$·H$_2$O (6 mg, 0.03 mmol), TBHP (38.5 mg, 0.3 mmol) in DCE (2 mL) under nitrogen atmosphere. The reaction mixture was stirred at 60 °C until complete consumption of the starting material as detected by TLC or GC-MS analysis. After the reaction was finished, the reaction mixture was washed with brine. The aqueous phase was re-extracted with ethyl acetate. The combined organic extracts were dried over Na$_2$SO$_4$ and concentrated in vacuum, and the resulting residue was purified by silica gel column chromatography (petroleum ether/ethyl acetate = 8:1, V/V) to afford the desired product 3aa in 91% yield (82 mg) as a yellow solid.
4. All Products

2-oxo-N,N',2-triphenylacetimidamide (3aa). Yellow solid, mp 111-112 °C. Yield 82 mg (91%) at 0.3 mmol scale. $^1$H NMR (400 MHz, DMSO-$d_6$) $\delta$ 9.79 (s, 1H), 7.82 (dd, $J = 14.8, 7.8$ Hz, 4H), 7.62 (t, $J = 7.2$ Hz, 1H), 7.48 (t, $J = 7.6$ Hz, 2H), 7.34 (t, $J = 7.6$ Hz, 2H), 7.04 (t, $J = 7.2$ Hz, 3H), 6.78 (t, $J = 7.2$ Hz, 1H), 6.70 (d, $J = 7.6$ Hz, 2H). $^{13}$C NMR (100 MHz, DMSO-$d_6$) $\delta$ 192.1, 152.1, 148.4, 140.1, 134.7, 129.3, 129.1, 128.7, 128.5, 122.7, 122.4, 121.8, 119.5. HRMS (EI) m/z: [M]$^+$ calcld for C$_{20}$H$_{16}$N$_2$O 300.1246; found 300.1257.

2-oxo-N,N'-diphenyl-2-(p-tolyl)acetimidamide (3ba). Yellow solid, mp 107-108 °C. Yield 88 mg (93%) at 0.3 mmol scale. $^1$H NMR (400 MHz, DMSO-$d_6$) $\delta$ 9.76 (s, 1H), 7.84 (d, $J = 7.6$ Hz, 2H), 7.71 (d, $J = 7.8$ Hz, 2H), 7.31 (dd, $J = 19.4, 7.6$ Hz, 4H), 7.04 (s, 3H), 6.79 (t, $J = 7.0$ Hz, 1H), 6.71 (d, $J = 7.2$ Hz, 2H), 2.32 (s, 3H). $^{13}$C NMR (100 MHz, DMSO-$d_6$) $\delta$ 191.5, 152.2, 148.5, 145.5, 140.2, 131.3, 129.7, 129.5, 128.7, 128.5, 122.7, 122.4, 121.8, 119.5, 21.4. HRMS (EI) m/z: [M]$^+$ calcld for C$_{21}$H$_{18}$N$_2$O 314.1411; found 314.1422.

2-oxo-N,N'-diphenyl-2-(m-tolyl)acetimidamide (3ca). Yellow oil. Yield 69 mg (73%) at 0.3 mmol scale. $^1$H NMR (400 MHz, DMSO-$d_6$) $\delta$ 9.77 (s, 1H), 7.84 (d, $J = 7.0$ Hz, 2H), 7.61 (d, $J = 10.4$ Hz, 2H), 7.44 (d, $J = 7.2$ Hz, 1H), 7.36 (dd, $J = 15.0, 7.3$ Hz, 3H), 7.05 (s, 3H), 6.79 (s, 1H), 6.71 (d, $J = 6.8$ Hz, 2H), 2.31 (s, 3H). $^{13}$C NMR (100 MHz, DMSO-$d_6$) $\delta$ 192.1, 152.1, 148.5, 140.2, 138.6, 135.4, 133.7, 129.4, 129.1, 128.8, 128.6, 126.9, 122.6 (d, $J = 25.5$ Hz), 122.5 – 122.1 (m), 121.9, 119.5, 20.8. HRMS (EI) m/z: [M]$^+$ calcld for C$_{21}$H$_{18}$N$_2$O 314.1411; found 314.1421.
2-oxo-N,N'-diphenyl-2-(o-tolyl)acetimidamide (3da). Yellow oil. Yield 58 mg (62%) at 0.3 mmol scale. $^1$H NMR (400 MHz, DMSO-$_d$6) $\delta$ 9.80 (s, 1H), 7.85 (d, J = 7.8 Hz, 2H), 7.68 (d, J = 7.6 Hz, 1H), 7.40 (t, J = 7.4 Hz, 1H), 7.37 – 7.26 (m, 3H), 7.16 (d, J = 7.4 Hz, 1H), 7.03 (dd, J = 16.8, 7.8 Hz, 3H), 6.77 (t, J = 7.0 Hz, 1H), 6.62 (d, J = 7.4 Hz, 2H), 2.33 (s, 3H). $^{13}$C NMR (100 MHz, DMSO-$_d$6) $\delta$ 194.3, 153.1, 148.4, 140.3, 139.5, 133.3 (d, J = 8.8 Hz), 131.9, 128.8, 128.4, 126.2, 122.7, 122.4, 121.7, 119.5, 20.7. HRMS (EI) m/z: [M]$^+$ calcd for C$_{21}$H$_{18}$N$_2$O 314.1411; found 314.1421.

2-(4-methoxyphenyl)-2-oxo-N,N'-diphenylacetimidamide (3ea). Yellow oil. Yield 84 mg (85%) at 0.3 mmol scale. $^1$H NMR (400 MHz, DMSO-$_d$6) $\delta$ 9.73 (s, 1H), 7.84 (d, J = 7.4 Hz, 2H), 7.78 (d, J = 8.2 Hz, 2H), 7.33 (t, J = 7.0 Hz, 2H), 7.03 (dd, J = 15.6, 8.0 Hz, 5H), 6.80 (t, J = 6.8 Hz, 1H), 6.72 (d, J = 7.2 Hz, 2H), 3.80 (s, 3H). $^{13}$C NMR (100 MHz, DMSO-$_d$6) $\delta$ 190.2, 164.2, 152.4, 148.6, 140.3, 131.9, 128.7, 128.5, 126.7, 122.4, 121.8, 119.5, 114.5, 55.8. HRMS (EI) m/z: [M]$^+$ calcd for C$_{21}$H$_{18}$N$_2$O$_2$ 330.1356; found 330.1364.

2-(4-fluorophenyl)-2-oxo-N,N'-diphenylacetimidamide (3fa). Yellow solid, mp 145-146 °C. Yield 72 mg (75%) at 0.3 mmol scale. $^1$H NMR (400 MHz, DMSO-$_d$6) $\delta$ 9.81 (s, 1H), 7.86 (dd, J = 17.6, 7.2 Hz, 4H), 7.32 (dd, J = 19.8, 8.4 Hz, 4H), 7.05 (t, J = 7.0 Hz, 3H), 6.80 (t, J = 7.0 Hz, 1H), 6.70 (d, J = 7.4 Hz, 2H). $^{13}$C NMR (100 MHz, DMSO-$_d$6) $\delta$ 190.6, 151.9, 148.4, 140.1, 132.5 (d, J = 9.7 Hz), 130.7, 128.8, 128.6, 122.9, 122.6, 121.9, 119.6, 116.6, 116.4. HRMS (EI) m/z: [M]$^+$ calcd for C$_{20}$H$_{15}$FN$_2$O 318.1176; found 318.1163.

2-(4-chlorophenyl)-2-oxo-N,N'-diphenylacetimidamide (3ga). Yellow oil. Yield 58 mg (62%) at 0.3 mmol scale. $^1$H NMR (400 MHz, DMSO-$_d$6) $\delta$ 9.80 (s, 1H), 7.85 (d, J = 7.8 Hz, 2H), 7.68 (d, J = 7.6 Hz, 1H), 7.40 (t, J = 7.4 Hz, 1H), 7.37 – 7.26 (m, 3H), 7.16 (d, J = 7.4 Hz, 1H), 7.03 (dd, J = 16.8, 7.8 Hz, 3H), 6.77 (t, J = 7.0 Hz, 1H), 6.62 (d, J = 7.4 Hz, 2H), 2.33 (s, 3H). $^{13}$C NMR (100 MHz, DMSO-$_d$6) $\delta$ 194.3, 153.1, 148.4, 140.3, 139.5, 133.3 (d, J = 8.8 Hz), 131.9, 128.8, 128.4, 126.2, 122.7, 122.4, 121.7, 119.5, 20.7. HRMS (EI) m/z: [M]$^+$ calcd for C$_{21}$H$_{18}$N$_2$O 314.1411; found 314.1421.
Yellow solid, 139-140 °C. Yield 79 mg (79%) at 0.3 mmol scale. $^1$H NMR (400 MHz, DMSO-$d_6$) δ 9.81 (s, 1H), 7.86 (dd, $J = 18.2$, 7.2 Hz, 4H), 7.32 (dd, $J = 19.6$, 8.4 Hz, 4H), 7.05 (t, $J = 7.2$ Hz, 3H), 6.80 (t, $J = 7.2$ Hz, 1H), 6.70 (d, $J = 7.4$ Hz, 2H). $^{13}$C NMR (100 MHz, DMSO-$d_6$) δ 152.3, 148.8, 140.5, 132.9 (d, $J = 10.2$ Hz), 131.0, 129.2, 128.9, 123.2, 122.9, 122.2, 119.9, 116.9, 116.7. HRMS (EI) m/z: [M]$^+$ calcld for C$_{20}$H$_{15}$ClN$_2$O 334.0864; found 334.0875.

2-(3-chlorophenyl)-2-oxo-N,N'-diphenylacetimidamide (3ha). Yellow solid, mp 101-102 °C. Yield 84 mg (84%) at 0.3 mmol scale. $^1$H NMR (400 MHz, DMSO-$d_6$) δ 9.86 (s, 1H), 7.83 (d, $J = 7.6$ Hz, 2H), 7.76 (d, $J = 7.6$ Hz, 1H), 7.69 (d, $J = 8.0$ Hz, 2H), 7.52 (t, $J = 7.8$ Hz, 1H), 7.35 (t, $J = 7.2$ Hz, 2H), 7.06 (t, $J = 6.8$ Hz, 3H), 6.81 (t, $J = 6.8$ Hz, 1H), 6.69 (d, $J = 7.2$ Hz, 2H). $^{13}$C NMR (100 MHz, DMSO-$d_6$) δ 191.1, 151.4, 148.2, 135.5, 134.4, 133.9, 131.4, 128.9, 128.7, 128.3, 128.1, 123.0, 122.7, 121.9, 119.6. HRMS (EI) m/z: [M]$^+$ calcld for C$_{20}$H$_{15}$ClN$_2$O 334.0864; found 334.0876.

2-(3-bromophenyl)-2-oxo-N,N'-diphenylacetimidamide (3ia). Yellow solid, mp 118-119 °C. Yield 87 mg (77%) at 0.3 mmol scale. $^1$H NMR (400 MHz, DMSO-$d_6$) δ 9.85 (s, 1H), 7.80 (d, $J = 9.0$ Hz, 5H), 7.46 (t, $J = 7.6$ Hz, 1H), 7.35 (t, $J = 7.2$ Hz, 2H), 7.06 (s, 3H), 6.81 (t, $J = 7.0$ Hz, 1H), 6.70 (d, $J = 7.4$ Hz, 2H). $^{13}$C NMR (100 MHz, DMSO-$d_6$) δ 191.0, 151.4, 148.2, 137.3, 135.6, 131.6, 131.1, 128.8, 128.7, 122.9, 122.7, 122.3, 121.8, 119.6. HRMS (EI) m/z: [M]$^+$ calcld for C$_{20}$H$_{15}$BrN$_2$O 378.0359; found 378.0366.

2-(4-cyanophenyl)-2-oxo-N,N'-diphenylacetimidamide (3ja). Yellow oil. Yield 61 mg (63%) at 0.3 mmol scale. $^1$H NMR (400 MHz,
DMSO-$d_6$ δ 9.89 (s, 1H), 7.93 (q, J = 7.8 Hz, 4H), 7.82 (d, J = 7.4 Hz, 2H), 7.35 (t, J = 6.8 Hz, 2H), 7.12 – 6.99 (m, 3H), 6.81 (d, J = 7.0 Hz, 1H), 6.68 (d, J = 7.2 Hz, 2H). $^{13}$C NMR (100 MHz, DMSO-$d_6$) δ 191.6, 151.3, 148.0, 139.9, 136.8, 133.2, 129.7, 128.8, 128.7, 123.0, 122.8, 121.9, 119.6, 117.9, 116.2. HRMS (EI) m/z: [M]$^+$ calcd for C$_{21}$H$_{15}$N$_3$O 325.1221; found 325.1212.

2-oxo-N,N'$'$-diphenyl-2-(4-(trifluoromethyl)phenyl)acetimidamide (3ka). Yellow oil. Yield 79 mg (72%) at 0.3 mmol scale. $^1$H NMR (400 MHz, DMSO-$d_6$) δ 9.88 (s, 1H), 7.98 (d, J = 7.8 Hz, 2H), 7.91 – 7.77 (m, 4H), 7.35 (t, J = 7.2 Hz, 2H), 7.12 – 6.99 (m, 3H), 6.79 (t, J = 6.8 Hz, 1H), 6.70 (d, J = 7.2 Hz, 2H). $^{13}$C NMR (100 MHz, DMSO-$d_6$) δ 191.6, 151.5, 148.1, 134.0, 136.8, 133.4, 130.1, 128.75 (d, J = 19.2 Hz), 126.2, 122.88 (d, J = 25.5 Hz), 122.2, 121.9, 119.6. HRMS (EI) m/z: [M]$^+$ calcd for C$_{21}$H$_{15}$F$_3$N$_2$O 368.1129; found 368.1141.

2-oxo-2-phenyl-N,N'$'$-di-p-tolylacetimidamide (3ab). Yellow solid, mp 140-141 °C. Yield 81 mg (82%) at 0.3 mmol scale. $^1$H NMR (400 MHz, DMSO-$d_6$) δ 9.62 (s, 1H), 7.79 (d, J = 7.6 Hz, 2H), 7.71 (d, J = 7.6 Hz, 2H), 7.62 (t, J = 7.2 Hz, 1H), 7.48 (t, J = 7.4 Hz, 2H), 7.13 (d, J = 7.6 Hz, 2H), 6.84 (d, J = 7.4 Hz, 2H), 6.59 (d, J = 7.4 Hz, 2H), 2.27 (s, 3H), 2.08 (s, 3H). $^{13}$C NMR (100 MHz, DMSO-$d_6$) δ 192.4, 152.0, 145.9, 137.7, 134.7, 133.7, 131.5, 131.0, 129.3, 129.21 – 128.91 (m), 121.7, 119.5, 20.5, 20.3. HRMS (EI) m/z: [M]$^+$ calcd for C$_{22}$H$_{20}$N$_2$O 328.1563; found 328.1579.

2-oxo-2-phenyl-N,N'$'$-di-m-tolylacetimidamide (3ac). Yellow oil. Yield 79 mg (80%) at 0.3 mmol scale. $^1$H NMR (400 MHz, DMSO-$d_6$) δ 9.68 (s, 1H), 7.79 (d, J = 7.2 Hz, 2H), 7.67 (s, 1H), 7.61 (d, J = 7.0 Hz, 2H), 7.49 (t, J = 7.0 Hz, 2H), 7.21 (s, 1H), 6.97 – 6.79 (m, 2H), 6.66 – 6.41 (m, 3H), 2.29 (s, 3H), 2.08 (s, 3H), 2.06 (s, 3H). $^{13}$C NMR (100 MHz, DMSO-$d_6$) δ 192.4, 152.0, 145.9, 137.7, 134.7, 133.7, 131.5, 131.0, 129.3, 129.21 – 128.91 (m), 121.7, 119.5, 20.5, 20.3. HRMS (EI) m/z: [M]$^+$ calcd for C$_{22}$H$_{20}$N$_2$O 328.1563; found 328.1579.
N,N'-bis(3-methoxyphenyl)-2-oxo-2-phenylacetimidamide (3ad). Yellow oil. Yield 81 mg (75%) at 0.3 mmol scale. $^\text{1}^\text{H}$ NMR (400 MHz, DMSO-$d_6$) $\delta$ 9.78 (s, 1H), 7.81 (d, $J = 7.4$ Hz, 2H), 7.63 (t, $J = 7.2$ Hz, 1H), 7.58 (s, 1H), 7.50 (t, $J = 7.4$ Hz, 2H), 7.33 (d, $J = 7.6$ Hz, 1H), 7.23 (t, $J = 7.8$ Hz, 1H), 6.94 (t, $J = 7.6$ Hz, 1H), 6.64 (d, $J = 7.8$ Hz, 1H), 6.36 (d, $J = 7.8$ Hz, 1H), 6.29 (d, $J = 6.8$ Hz, 2H), 3.73 (s, 3H), 3.55 (s, 3H). $^{13}$C NMR (100 MHz, DMSO-$d_6$) $\delta$ 192.0, 159.6, 159.4, 152.1, 149.7, 141.2, 134.7, 133.8, 129.6, 129.4, 129.3, 129.2, 114.4, 112.0, 108.5, 107.9, 107.5, 105.7, 55.1, 54.9. HRMS (EI) m/z: [M]$^+$ calcd for C$_{22}$H$_{20}$N$_2$O$_3$ 360.1466; found 360.1479.

N,N'-bis(2-methoxyphenyl)-2-oxo-2-phenylacetimidamide (3ae). Yellow oil. Yield 72 mg (67%) at 0.3 mmol scale. $^\text{1}^\text{H}$ NMR (400 MHz, DMSO-$d_6$) $\delta$ 8.92 (s, 1H), 7.78 (d, $J = 7.2$ Hz, 2H), 7.56 (d, $J = 6.4$ Hz, 1H), 7.43 (t, $J = 6.8$ Hz, 2H), 7.11 – 6.85 (m, 4H), 6.79 – 6.49 (m, 4H), 3.81 (s, 3H), 3.55 (s, 3H). $^{13}$C NMR (100 MHz, DMSO-$d_6$) $\delta$ 191.4, 152.6, 134.4 (d, $J = 8.0$ Hz), 129.5, 128.9, 124.3 – 123.7 (m), 122.7 (d, $J = 14.7$ Hz), 122.4 (d, $J = 5.8$ Hz), 120.6, 111.5, 55.4. HRMS (EI) m/z: [M]$^+$ calcd for C$_{22}$H$_{20}$N$_2$O$_3$ 360.1467; found 360.1478.

N,N'-bis(4-(tert-butyl)phenyl)-2-oxo-2-phenylacetimidamide (3af). Yellow solid, mp 118-119 °C. Yield 105 mg (85%) at 0.3 mmol scale. $^\text{1}^\text{H}$ NMR (400 MHz, DMSO-$d_6$) $\delta$ 9.65 (s, 1H), 7.80 (d, $J = 7.4$ Hz, 2H), 7.74 (d, $J = 7.8$ Hz, 2H), 7.62 (t, $J = 7.2$ Hz, 1H), 7.48 (t, $J = 7.2$ Hz, 2H), 7.34 (d, $J =
7.8 Hz, 2H), 7.05 (d, J = 7.6 Hz, 2H), 6.63 (d, J = 7.6 Hz, 2H), 1.27 (s, 9H), 1.13 (s, 9H). $^{13}$C NMR (100 MHz, DMSO- $d_6$) $\delta$ 192.4, 151.8, 145.8, 144.9, 144.4, 137.6, 134.5, 134.0, 129.3, 129.1, 125.3, 125.1, 34.0, 33.8, 31.3, 31.2. HRMS (EI) m/z: [M]$^+$ calec for C$_{28}$H$_{32}$N$_2$O 412.2502; found 412.2519.

N,N'-bis(4-fluorophenyl)-2-oxo-2-phenylacetimidamide (3ag). Yellow solid, mp 115-116 °C.

Yield 71 mg (70%) at 0.3 mmol scale. $^1$H NMR (400 MHz, DMSO- $d_6$) $\delta$ 9.89 (s, 1H), 7.86 (s, 2H), 7.80 (d, J = 7.6 Hz, 2H), 7.64 (t, J = 7.2 Hz, 1H), 7.50 (t, J = 7.2 Hz, 2H), 7.19 (t, J = 8.2 Hz, 2H), 6.87 (t, J = 8.2 Hz, 2H), 6.71 (d, J = 4.8 Hz, 2H).$^{13}$C NMR (100 MHz, DMSO- $d_6$) $\delta$ 192.1, 159.2, 152.5, 144.8, 136.4, 134.9, 133.6, 129.3, 129.2, 123.24 (d, J = 7.7 Hz, 121.24 (d, J = 7.5 Hz), 115.4, 115.2, 115.0. HRMS (EI) m/z: [M]$^+$ calec for C$_{20}$H$_{14}$F$_2$N$_2$O 336.1082; found 336.1069.

N,N'-bis(4-chlorophenyl)-2-oxo-2-phenylacetimidamide (3ah). Yellow solid, mp 129-130 °C. Yield 102 mg(92%) at 0.3 mmol scale. $^1$H NMR (400 MHz, DMSO- $d_6$) $\delta$ 10.06 (s, 1H), 7.86 (d, J = 8.2 Hz, 2H), 7.81 (d, J = 7.6 Hz, 2H), 7.65 (t, J = 7.2 Hz, 1H), 7.50 (t, J = 7.4 Hz, 2H), 7.40 (d, J = 8.2 Hz, 2H), 7.09 (d, J = 7.8 Hz, 2H), 6.72 (d, J = 7.8 Hz, 2H).$^{13}$C NMR (100 MHz, DMSO- $d_6$) $\delta$ 191.5, 152.4, 147.2, 138.8, 135.0, 133.4, 129.4, 129.3, 128.7, 128.5, 126.7, 126.5, 123.5, 121.2. HRMS (EI) m/z: [M]$^+$ calec for C$_{20}$H$_{14}$Cl$_2$N$_2$O 368.0495; found 368.0486.

N,N'-bis(4-bromophenyl)-2-oxo-2-phenylacetimidamide (3ai). Yellow solid, mp 126-127 °C.

Yield 100 mg (73%) at 0.3 mmol scale. $^1$H NMR (400 MHz, DMSO- $d_6$) $\delta$ 10.06 (s, 1H), 7.80 (d, J = 6.8 Hz, 4H), 7.66 (t, J = 7.2 Hz, 1H), 7.51 (t, J = 8.4 Hz, 4H), 7.22 (d, J = 7.8 Hz, 2H), 6.66 (d, J = 7.8 Hz, 2H).$^{13}$C NMR (100 MHz, DMSO- $d_6$) $\delta$ 191.5, 152.3, 147.6, 139.2, 135.1, 133.4,
N-isopropyl-2-oxo-N',2-diphenylacetimidamide (3ak). Yellow solid, mp 144-145 °C. Yield 49 mg (62%) at 0.3 mmol scale. $^1$H NMR (400 MHz, DMSO-$d_6$) $\delta$ 7.73 (d, $J = 7.4$ Hz, 2H), 7.58 (t, $J = 7.2$ Hz, 1H), 7.52 – 7.36 (m, 3H), 6.97 (t, $J = 7.2$ Hz, 2H), 6.70 (t, $J = 7.0$ Hz, 1H), 6.60 (d, $J = 7.4$ Hz, 2H), 4.16 (s, 1H), 1.22 (d, $J = 6.2$ Hz, 6H). $^{13}$C NMR (100 MHz, DMSO-$d_6$) $\delta$ 193.6, 154.2, 149.6, 134.4, 134.0, 129.2, 129.0, 128.4, 122.3, 121.7, 42.0, 22.1. HRMS (EI) m/z: [M$^+$]$^+$ calcd for C$_{20}$H$_{14}$Br$_2$N$_2$O 455.9462; found 455.9475.

N-(tert-butyl)-2-oxo-N',2-diphenylacetimidamide (3al). Yellow solid, mp 131-132 °C. Yield 47 mg (56%) at 0.3 mmol scale. $^1$H NMR (400 MHz, DMSO-$d_6$) $\delta$ 7.72 (d, $J = 7.8$ Hz, 2H), 7.57 (t, $J = 7.4$ Hz, 1H), 7.45 (t, $J = 7.6$ Hz, 2H), 7.10 (s, 1H), 6.96 (t, $J = 7.6$ Hz, 2H), 6.68 (t, $J = 7.4$ Hz, 1H), 6.57 (d, $J = 7.8$ Hz, 2H), 1.48 (s, 9H). $^{13}$C NMR (100 MHz, DMSO-$d_6$) $\delta$ 193.6, 154.2, 149.6, 134.4, 134.0, 129.2, 129.0, 128.4, 122.1, 121.4, 51.8, 28.3. HRMS (EI) m/z: [M$^+$]$^+$ calcd for C$_{18}$H$_{20}$N$_2$O 280.1563; found 280.1581.

N-cyclopentyl-2-oxo-N',2-diphenylacetimidamide (3am). Yellow solid, mp 115-116 °C. Yield 42 mg (48%) at 0.3 mmol scale. $^1$H NMR (400 MHz, DMSO-$d_6$) $\delta$ 7.72 (d, $J = 7.4$ Hz, 2H), 7.58 (t, $J = 7.4$ Hz, 1H), 7.46 (t, $J = 7.4$ Hz, 2H), 6.97 (t, $J = 7.4$ Hz, 2H), 6.69 (t, $J = 7.2$ Hz, 1H), 6.60 (d, $J = 7.6$ Hz, 2H), 4.29 (s, 1H), 1.97 (s, 2H), 1.62 (d, $J = 44.2$ Hz, 7H). $^{13}$C NMR (100 MHz, DMSO-
$d_0 \delta 193.6, 154.5, 149.6, 134.3, 134.0, 129.1, 129.0, 128.3, 122.2, 121.6, 51.9, 32.1, 23.6$. HRMS (EI) m/z: [M]$^+$ calcd for C$_{19}$H$_{20}$N$_2$O 292.1589; found 292.1573.

N-cyclohexyl-2-oxo-N',2-diphenylacetimidamide (3an). Yellow solid, mp 104-105 °C. Yield 36 mg (39%) at 0.3 mmol scale. $^1$H NMR (400 MHz, DMSO-$d_6$) $\delta$ 7.73 (d, $J = 7.4$ Hz, 2H), 7.58 (t, $J = 7.2$ Hz, 1H), 7.46 (t, $J = 7.2$ Hz, 2H), 6.96 (t, $J = 7.2$ Hz, 2H), 6.69 (t, $J = 7.0$ Hz, 1H), 6.58 (d, $J = 7.6$ Hz, 2H), 3.87 (s, 1H), 2.04 (d, $J = 9.8$ Hz, 2H), 1.73 (d, $J = 10.8$ Hz, 2H), 1.59 (d, $J = 11.8$ Hz, 1H), 1.24 (tt, $J = 23.2$, 12.2 Hz, 6H). $^{13}$C NMR (100 MHz, DMSO-$d_6$) $\delta$ 193.5, 154.0, 149.5, 134.3, 134.0, 129.2, 129.0, 128.3, 122.2, 121.5, 49.0, 32.0, 25.5, 24.7. HRMS (EI) m/z: [M]$^+$ calcd for C$_{20}$H$_{22}$N$_2$O 306.1719; found 306.1728.

N-benzyl-2-oxo-N',2-diphenylacetimidamide (3ao). Yellow solid, mp 111-112 °C. Yield 34 mg (36%) at 0.3 mmol scale. $^1$H NMR (400 MHz, DMSO-$d_6$) $\delta$ 8.08 (s, 1H), 7.73 (d, $J = 7.3$ Hz, 2H), 7.59 (t, $J = 7.1$ Hz, 1H), 7.52 – 7.41 (m, 3H), 7.38 (t, $J = 7.2$ Hz, 2H), 7.33 – 7.22 (m, 1H), 6.98 (t, $J = 7.2$ Hz, 2H), 6.71 (t, $J = 7.0$ Hz, 1H), 6.61 (d, $J = 7.4$ Hz, 2H), 4.59 (d, $J = 4.3$ Hz, 2H). $^{13}$C NMR (100 MHz, DMSO-$d_6$) $\delta$ 194.0, 155.3, 149.6, 139.7, 134.9, 134.2, 129.6, 129.4, 128.8 (d, $J = 4.5$ Hz), 128.1 (s), 127.3, 122.6, 122.4 (d, $J = 29.4$ Hz), 44.1. HRMS (EI) m/z: [M]$^+$ calcd for C$_{21}$H$_{18}$N$_2$O 314.1415; found 314.1421.

2-morpholino-1-phenyl-2-(phenylimino)ethanone (3aq). Yellow oil. Yield 52 mg (57%) at 0.3 mmol scale. $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 7.80 (d, $J = 7.8$ Hz, 2H), 7.52 (t, $J = 7.4$ Hz, 1H), 7.39 (t, $J = 7.6$ Hz, 2H), 7.00 (t, $J = 7.6$ Hz, 2H), 6.77 (t, $J = 7.4$ Hz, 1H), 6.70 (d, $J = 7.8$ Hz, 2H), 3.75 (s, 4H), 3.52 (s, 4H). $^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ 194.1, 156.1, 148.1, 134.6,
134.5, 129.2, 128.9, 128.4, 122.6, 122.2, 66.6, 45.3. HRMS (EI) m/z: [M]+ calcd for C_{18}H_{18}N_{2}O_{2} 294.1381; found 294.1364.

5. Reference

6. $^1$H and $^{13}$C NMR Spectra
6. crystal structure data

A single crystal for X-ray analysis of 3aa was obtained by recrystallation from EtOAc/petroleumether.

CCDC-1555783 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

Compound 3aa: Displacement ellipsoids are drawn at the 30% probability level.