3-Acetylcoumarin as a Practical Ligand for Copper-Catalyzed C–N Coupling Reactions at Room Temperature

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Abstract: The use of coumarin-based ligands was examined in copper-catalyzed C–N cross-coupling reactions. It was found that 3-acetylcoumarin constituted a new, practical ligand for the copper-catalyzed N-arylation of aliphatic amines and imidazole with aryl iodides at room temperature. Aryl bromides could also be aminated efficiently at 80 °C. This readily available catalyst system, namely copper(I) iodide and 3-acetylcoumarin, provides a mild and practical method for the synthesis of aromatic amines.

Key words: copper, catalysis, cross-coupling, 3-acetylcoumarin, room temperature

Transition-metal-catalyzed formation of carbon–nitrogen bonds via cross-coupling reactions represents a powerful means for the preparation of numerous important products in pharmaceutical and material sciences.[1] Although palladium-catalyzed C–N coupling reactions have been extensively studied,[2] copper-based catalyst systems have also attracted much attention[3] because of the low price of copper. Several reviews have detailed the recent progress of copper-catalyzed C–N coupling reactions.[3,4]

To date a number of efficient ligands have been developed for the copper-catalyzed coupling of aliphatic amines with aryl halides, including *N*,*N*-diethylsalicylamide,[5] amino acids,[6] amino alcohols,[7] oxime-phosphine oxide,[8] and phosphoramidite.[9] However, copper-catalyzed N-arylation of aliphatic amines at room temperature remained limited. Recently, Buchwald et al. (diketone ligand),[10] Zhao et al. (BINOL ligand)[11] and Ding et al (2-pyridyl β-ketone ligand)[12] have successfully performed the copper-catalyzed arylation of alkylamines at room temperature; it remains important to find new and more efficient ligands for room temperature catalysis. In this paper, we report a new and readily available catalyst system using 3-acetylcoumarin (3-acetyl-2*H*-1-benzopyran-2-one, **L5**) as the ligand to construct C(aryl)–N bonds at room temperature. While the coumarin scaffold has been successful in fluorescence probe chemistry,[13] its utility in the copper-catalyzed Ullmann reaction has not yet been demonstrated.

Iodobenzene (**1a**) and hexylamine (**2a**) were selected as the model system to optimize the catalytic conditions using different copper catalysts, ligands, bases, and solvents in the N-arylation reaction at room temperature (Table 1). Several coumarin-based ligands (Figure 1) including coumarin-3-carboxylic acid (**L1**), ethyl coumarin-3-carboxylate (**L2**), coumarin-3-carboxamides **L3** and **L4**, 3-acetylcoumarin (**L5**), and 3-(1-hydroxyethyl)coumarin (**L6**) were examined (Table 1, entries 1–6). It was found that moderate yields can be obtained in the presence of coumarin-3-carboxylate **L2** and coumarin-3-carboxamides **L3** and **L4** (entries 2–4). However, the yield was zero when coumarin-3-carboxylic acid (**L1**) and 3-(1-hydroxyethyl)coumarin (**L6**) were used (entries 1, 6). We were pleased to find that 3-acetylcoumarin (**L5**) dramatically increase the coupling yield to 90% (entry 5). It is noteworthy that crystalline 3-acetylcoumarin is readily available from commercial sources or can be simply synthesized from salicylal.

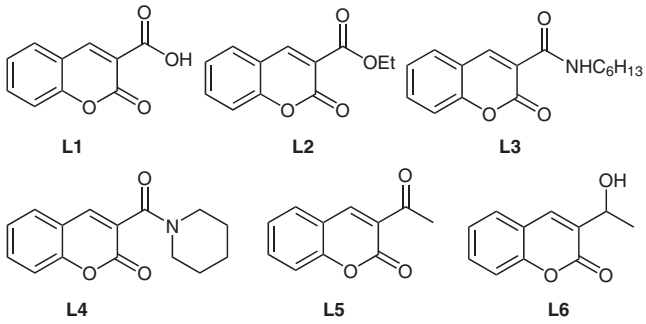

Figure 1 Coumarin-based ligands

Subsequently, using 3-acetylcoumarin (**L5**) as the ligand, a range of combinations of copper sources, bases, and solvents were examined (entries 7–14) and the following standard coupling reaction conditions were identified: 10 mol% copper(I) iodide as the catalyst and 20 mol% 3-acetylcoumarin as the ligand, relative to the aryl iodide, *N*,*N*-dimethylformamide as the solvent, and cesium carbonate as the base at room temperature.

The substrate scope of this reaction was then examined using a variety of aryl iodides and amines under the optimized condition (Table 2). We were delighted to find that the N-arylation of hexylamine with a variety of aryl iodides proceeded smoothly to give the corresponding products **3a–f** in good to excellent yields (68–92%) (entries 1–6). However, aryl iodides with an *ortho*-substituent do not readily participate in the reaction. For instance, 2-iodoaniline gave **3g** in 13% isolated yield (entry 7). Other

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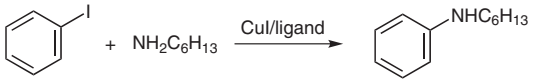
alkylamines, such as butylamine, phenethylamine, and benzylamine, were examined and good yields of product **3h–k** were obtained (entries 8–11). Sterically more hindered amines, such as cyclohexylamine and piperidine, however, resulted in significant reduction in the yield (entries 12 and 13).

Table 1 Copper-Catalyzed Cross-Coupling of Iodobenzene (**1a**) with Hexylamine (**2a**)[a]



1a **2a** **3a**

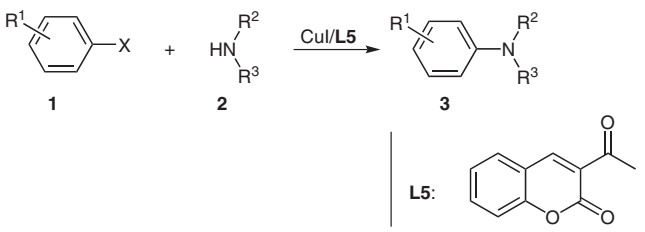
Entry	Catalyst	Ligand	Base	Solvent	Yield[b] (%)
1	CuI	**L1**	Cs_2CO_3	DMF	0
2	CuI	**L2**	Cs_2CO_3	DMF	55
3	CuI	**L3**	Cs_2CO_3	DMF	40
4	CuI	**L4**	Cs_2CO_3	DMF	37
5	CuI	**L5**	Cs_2CO_3	DMF	90
6	CuI	**L6**	Cs_2CO_3	DMF	0
7	CuBr	**L5**	Cs_2CO_3	DMF	55
8	CuCl	**L5**	Cs_2CO_3	DMF	74
9	Cu_2O	**L5**	Cs_2CO_3	DMF	12
10	$CuSO_4$	**L5**	Cs_2CO_3	DMF	10
11	CuI	**L5**	Cs_2CO_3	dioxane	16
12	CuI	**L5**	Cs_2CO_3	toluene	17
13	CuI	**L5**	K_2CO_3	DMF	42
14	CuI	**L5**	K_3PO_4	DMF	50

[a] Reaction conditions: PhI (**1a**, 1.0 mmol), hexylamine (**2a**, 1.5 mmol), CuI (10 mol%), ligand (20 mol%), base (2.0 mmol), solvent (0.5mL), r.t., 24 h.
[b] Isolated yields.

In addition to aryl iodides, aryl bromides could also undergo amination mediated by the same ligand when the temperature was raised to 80 °C (entries 14–17). It was found that both electron-rich and electron-deficient aryl bromides can be smoothly converted into the desired products with moderate isolated yields (55–70%). Furthermore, we found that this catalyst system could be applied to C–N cross-coupling reactions of imidazole (entries 18–21). Electron-rich and electron-deficient aryl iodides were reacted with imidazole at room temperature and products **3o–r** were obtained in excellent isolated yields (81–95%).

To conclude, in the present study we have developed a new and practical catalyst system, i.e. copper(I) iodide/3-acetylcoumarin. This system could catalyze N-arylation

Table 2 Copper(I) Iodide/3-Acetylcoumarin (**L5**) Catalyzed N-Arylation of Alkylamines and Imidazole **2** with Aryl Iodides and Bromides **1**[a]



Entry	Aryl halide		R^2R^3NH	Product	Yield[b] (%)
	R^1	X			
1	H	I	$Me(CH_2)_5NH_2$	**3a**	90
2	4-Me	I	$Me(CH_2)_5NH_2$	**3b**	85
3	4-OMe	I	$Me(CH_2)_5NH_2$	**3c**	68
4	4-Br	I	$Me(CH_2)_5NH_2$	**3d**	92
5	4-Cl	I	$Me(CH_2)_5NH_2$	**3e**	91
6	3-CO_2Me	I	$Me(CH_2)_5NH_2$	**3f**	80
7	2-NH_2	I	$Me(CH_2)_5NH_2$	**3g**	13
8	H	I	$BuNH_2$	**3h**	88
9	H	I	$Ph(CH_2)_2NH_2$	**3i**	85
10	4-Cl	I	$Ph(CH_2)_2NH_2$	**3j**	89
11	H	I	$BnNH_2$	**3k**	81
12	H	I	$CyNH_2$	**3l**	39 (64[c])
13	H	I	piperidine	**3m**	15
14	H	Br	$Me(CH_2)_5NH_2$	**3a**	65[d]
15	4-Cl	Br	$Me(CH_2)_5NH_2$	**3e**	70[d]
16	4-Ac	Br	$Me(CH_2)_5NH_2$	**3n**	68[d]
17	4-OMe	Br	$Me(CH_2)_5NH_2$	**3c**	55[d]
18	H	I	imidazole	**3o**	93
19	4-Me	I	imidazole	**3p**	90
20	4-OMe	I	imidazole	**3q**	81
21	4-Ac	I	imidazole	**3r**	95

[a] Reaction conditions: aryl halide (1.0 mmol), amine (1.5 mmol), CuI (10 mol%), 3-acetylcoumarin (**L5**, 20 mol%), Cs_2CO_3 (2.0 mmol), DMF (0.5mL), r.t. (~25 °C), 24 h.
[b] Isolated yields.
[c] At 50 °C.
[d] At 80 °C

of aliphatic amines and imidazole at room temperature. 3-Acetylcoumarin is commercially available or can be easily synthesized from salicylal, hence, we believe that the new ligand system may find useful applications in the synthesis of aromatic amines. Further study on the mechanism of the reactions and the applications of this catalytic

system to other cross-coupling reactions are ongoing in our laboratory.

All reactions were carried out in an oven-dried Schlenk tube under N_2 atmosphere. DMF, dioxane, and toluene were distilled from CaH_2, respectively. 3-Acetylcoumarin (L5) was purchased from Acros, and L1–L4, L6 were prepared following known procedures. All aryl halides and amines were purchased from Alfa Aesar or Acros and used directly. Flash column chromatography was performed on silica 230–400 mesh. IR spectra were recorded on a Nicolet FT IR-500 spectrophotometer. ^1H and ^{13}C NMR spectra were recorded on a Bruker Advance 400 spectrometer at r.t. in $CDCl_3$; chemical shifts are relative to TMS. GC-MS analysis was performed on Thermo Scientific AS 3000 Series GC-MS System. HRMS analysis was performed on Finnigan LCQ Advantage Max Series MS System.

Coupling of Aryl Iodides with Amines at Room Temperature; General Procedure

An oven-dried Schlenk tube was charged with CuI (20 mg, 10 mol%), Cs_2CO_3 (652 mg, 2 mmol), and 3-acetylcoumarin (**L5**, 38 mg, 20 mol%). The tube was evacuated and backfilled with N_2 (this procedure was repeated 3 ×). Then aryl halide (1.0 mmol), amine (1.5 mmol), and DMF (0.5 mL) were added under N_2. The tube was sealed and the mixture was stirred at r.t. for 24 h. The resulting suspension was filtered through a pad of silica gel with the help of CH_2Cl_2 (50 mL). The filtrate was concentrated and the residue was purified by column chromatography (silica gel, EtOAc–PE) to afford the product.

***N*-Hexylaniline (3a)**

IR (KBr): 3422, 3062, 2936, 2864, 1606, 1510, 1461, 1320, 1259, 1131, 1069, 744, 688 cm^{-1}.

^1H NMR (400 MHz, $CDCl_3$): δ = 7.16 (t, *J* = 7.8 Hz, 2 H), 6.67 (t, *J* = 7.3 Hz, 1 H), 6.59 (d, *J* = 8.0 Hz, 2 H), 3.50 (br s, 1 H), 3.09 (t, *J* = 7.1 Hz, 2 H), 1.66–1.52 (m, 2 H), 1.44–1.24 (m, 6 H), 0.90 (t, *J* = 6.8 Hz, 3 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 148.7, 129.3, 117.2, 112.8, 44.1, 31.8, 29.7, 27.0, 22.8, 14.2.

GC-MS (EI): *m*/*z* = 177.13 $[M]^+$.

HRMS (EI): *m*/*z* $[M]^+$ calcd for $C_{12}H_{19}N$: 177.1517; found: 177.1510.

***N*-Hexyl-4-methylaniline (3b)[14]**

IR (KBr): 3418, 2936, 2864, 1620, 1524, 1477, 1319, 1253, 1134, 1069, 803 cm^{-1}.

^1H NMR (400 MHz, $CDCl_3$): δ = 6.98 (d, *J* = 8.1 Hz, 2 H), 6.53 (d, *J* = 8.3 Hz, 2 H), 3.34 (br s, 1 H), 3.07 (t, *J* = 7.1 Hz, 2 H), 2.23 (s, 3 H), 1.77–1.48 (m, 2 H), 1.48–1.13 (m, 6 H), 0.89 (t, *J* = 6.8 Hz, 3 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 146.5, 129.8, 126.4, 113.1, 44.6, 31.8, 29.7, 27.0, 22.8, 20.5, 14.2.

GC-MS (EI): *m*/*z* = 191.07 $[M]^+$.

***N*-Hexyl-4-methoxyaniline (3c)**

IR (KBr): 3402, 2936, 2864, 1621, 1461, 1235, 1135, 1068, 815 cm^{-1}.

^1H NMR (400 MHz, $CDCl_3$): δ = 6.78 (d, *J* = 8.7 Hz, 2 H), 6.56 (d, *J* = 8.1 Hz, 2 H), 3.74 (s, 3 H), 3.08 (br s, 3 H), 1.73–1.47 (m, 2 H), 1.46–1.17 (m, 6 H), 0.90 (t, *J* = 6.8 Hz, 3 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 152.2, 142.8, 115.0, 114.3, 56.0, 45.1, 31.8, 29.9, 27.0, 22.8, 14.2.

GC-MS (EI): *m*/*z* = 207.15 $[M]^+$.

HRMS (EI): *m*/*z* $[M]^+$ calcd for $C_{13}H_{21}NO$: 207.1623; found: 177.1614.

4-Bromo-*N*-hexylaniline (3d)[14]

IR (KBr): 3426, 2936, 2864, 1599, 1501, 1321, 1259, 1130, 808 cm^{-1}.

^1H NMR (400 MHz, $CDCl_3$): δ = 7.26–7.18 (m, 2 H), 6.51–6.39 (m, 2 H), 3.60 (br s, 1 H), 3.05 (t, *J* = 7.1 Hz, 2 H), 1.64–1.51 (m, 2 H), 1.43–1.23 (m, 6 H), 0.90 (t, *J* = 6.8 Hz, 3 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 147.6, 132.0, 114.3, 108.6, 44.1, 31.7, 29.5, 26.9, 22.7, 14.1.

GC-MS (EI): *m*/*z* = 255.00, 257.00 $[M]^+$.

4-Chloro-*N*-hexylaniline (3e)

IR (KBr): 3436, 2936, 2864, 1604, 1502, 1322, 1135, 1071, 811 cm^{-1}.

^1H NMR (400 MHz, $CDCl_3$): δ = 7.10 (d, *J* = 8.8 Hz, 2 H), 6.50 (d, *J* = 8.8 Hz, 2 H), 3.59 (br s, 1 H), 3.05 (t, *J* = 7.1 Hz, 2 H), 1.65–1.50 (m, 2 H), 1.44–1.20 (m, 6 H), 0.90 (t, *J* = 6.8 Hz, 3 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 147.2, 129.1, 121.6, 113.8, 44.2, 31.7, 29.5, 26.9, 22.7, 14.1.

GC-MS (EI): *m*/*z* = 211.11 $[M]^+$.

HRMS (EI): *m*/*z* $[M]^+$ calcd for $C_{12}H_{18}NCl$: 211.1128; found: 211.1135.

Methyl 3-(Hexylamino)benzoate (3f)

IR (KBr): 3416, 2936, 2864, 1712, 1611, 1585, 1525, 1492, 1476, 1441, 1342, 1274, 1244, 1224, 1136, 1107, 744 cm^{-1}.

^1H NMR (400 MHz, $CDCl_3$): δ = 7.38 (d, *J* = 7.7 Hz, 1 H), 7.30 (s, 1 H), 7.23 (t, *J* = 7.9 Hz, 1 H), 6.82 (dd, *J* = 8.0, 1.8 Hz, 1 H), 3.89 (s, 3 H), 3.14 (t, *J* = 7.2 Hz, 2 H), 1.69–1.58 (m, 2 H), 1.45–1.22 (m, 6 H), 0.90 (t, *J* = 6.8 Hz, 3 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 167.6, 148.0, 131.2, 129.3, 118.9, 117.8, 113.9, 52.1, 44.5, 31.7, 29.4, 26.9, 22.7, 14.1.

GC-MS (EI): *m*/*z* = 235.10 $[M]^+$.

HRMS (EI): *m*/*z* $[M]^+$ calcd for $C_{14}H_{21}NO_2$: 235.1572; found: 235.1567.

***N*-Butylaniline (3h)[15]**

IR (KBr): 3406, 2928, 2867, 1602, 1505, 1476, 1429, 1374, 1319, 1262, 1177, 1149, 747, 691 cm^{-1}.

^1H NMR (400 MHz, $CDCl_3$): δ = 7.19–7.15 (m, 2 H), 6.68 (t, *J* = 7.3 Hz, 1 H), 6.62–6.60 (m, 2 H), 3.75 (br s, 1 H), 3.11 (t, *J* = 7.1 Hz, 2 H), 1.64–1.57 (m, 2 H), 1.47–1.40 (m, 2 H), 0.95 (t, *J* = 7.3 Hz, 3 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 148.5, 129.2, 117.0, 112.7, 43.6, 31.7, 20.3, 13.9.

GC-MS (EI): *m*/*z* = 149.12 $[M]^+$.

***N*-Phenethylaniline (3i)**

IR (KBr): 3422, 3032, 2936, 1604, 1509, 1321, 1261, 1122, 1069, 745, 689 cm^{-1}.

^1H NMR (400 MHz, $CDCl_3$): δ = 7.31 (t, *J* = 7.3 Hz, 2 H), 7.20 (m, 5 H), 6.70 (t, *J* = 7.3 Hz, 1 H), 6.61 (d, *J* = 7.7 Hz, 2 H), 3.65 (br s, 1 H), 3.40 (t, *J* = 7.0 Hz, 2 H), 2.91 (t, *J* = 7.0 Hz, 2 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 148.1, 139.4, 129.4, 128.9, 128.7, 126.5, 117.6, 113.1, 45.1, 35.6.

GC-MS (EI): *m*/*z* = 197.03 $[M]^+$.

HRMS (EI): *m*/*z* $[M]^+$ calcd for $C_{14}H_{15}N$: 197.1204; found: 197.1197.

4-Chloro-*N*-phenethylaniline (3j)[16]
IR (KBr): 3436, 2936, 2864, 1604, 1502, 1322, 1135, 1071, 811 cm^{-1}.

^1H NMR (400 MHz, $CDCl_3$): δ = 7.31 (t, *J* = 7.3 Hz, 2 H), 7.24 (d, *J* = 7.3 Hz, 1 H), 7.20 (d, *J* = 7.1 Hz, 2 H), 7.14–7.06 (m, 2 H), 6.51 (d, *J* = 8.8 Hz, 2 H), 3.66 (br s, 1 H), 3.36 (t, *J* = 6.9 Hz, 2 H), 2.89 (t, *J* = 7.0 Hz, 2 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 146.7, 139.1, 129.2, 128.9, 128.8, 126.6, 122.1, 114.1, 45.2, 35.5.

GC-MS (EI): *m*/*z* = 231.04 $[M]^+$.

***N*-Benzylaniline (3k)**
IR (KBr): 3430, 3032, 1605, 1510, 1493, 1450, 1329, 1276, 734, 685 cm^{-1}.

^1H NMR (400 MHz, $CDCl_3$): δ = 7.40–7.30 (m, 4 H), 7.27 (dd, *J* = 8.1, 5.6 Hz, 1 H), 7.21–7.12 (m, 2 H), 6.71 (t, *J* = 7.3 Hz, 1 H), 6.63 (d, *J* = 7.7 Hz, 2 H), 4.32 (s, 2 H), 4.02 (br s, 1 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 148.3, 139.6, 129.4, 128.8, 127.6, 127.4, 117.7, 113.0, 48.5.

GC-MS (EI): *m*/*z* = 183.08 $[M]^+$.

HRMS (EI): *m*/*z* $[M]^+$ calcd for $C_{13}H_{13}N$: 183.1048; found: 183.1041.

1-[4-(Hexylamino)phenyl]ethanone (3n)[17]
IR (KBr): 3436, 2936, 2851, 1665, 1594, 1510, 1391, 1358, 1262, 810 cm^{-1}.

^1H NMR (400 MHz, $CDCl_3$): δ = 7.82 (d, *J* = 8.8 Hz, 2 H), 6.54 (d, *J* = 8.6 Hz, 2 H), 4.16 (br s, 1 H), 3.18 (br s, 2 H), 2.49 (s, 3 H), 1.70–1.53 (m, 2 H), 1.45–1.23 (m, 6 H), 0.90 (t, *J* = 6.8 Hz, 3 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 196.4, 152.4, 130.9, 126.7, 111.4, 43.5, 31.7, 29.4, 26.9, 26.1, 22.7, 14.1.

GC-MS (EI): *m*/*z* = 219.06 $[M]^+$.

1-Phenyl-1*H*-imidazole (3o)[18]
IR (KBr): 3112, 1602, 1510, 1305, 1260, 1057, 960, 903, 814, 757, 688, 655, 515 cm^{-1}.

^1H NMR (400 MHz, $CDCl_3$): δ = 7.86 (s, 1 H), 7.52–7.44 (m, 2 H), 7.42–7.33 (m, 3 H), 7.28 (s, 1 H), 7.21 (s, 1 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 137.4, 135.6, 130.4, 129.9, 127.6, 121.6, 118.3.

GC-MS (EI): *m*/*z* = 144.04 $[M]^+$.

1-(4-Tolyl)-1*H*-imidazole (3p)[18]
IR (KBr): 3126, 1523, 1460, 1301, 1243, 1110, 1053, 959, 899, 814, 731, 656, 525 cm^{-1}.

^1H NMR (400 MHz, $CDCl_3$): δ = 7.82 (s, 1 H), 7.31–7.22 (m, 5 H), 7.19 (s, 1 H), 2.39 (s, 3 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 137.5, 135.7, 135.0, 130.4, 130.1, 121.5, 118.4, 20.9.

GC-MS (EI): *m*/*z* = 158.05 $[M]^+$.

1-(4-Methoxyphenyl)-1*H*-imidazole (3q)
IR (KBr): 3118, 1613, 1520, 1461, 1303, 1269, 1243, 1061, 1029, 824 cm^{-1}.

^1H NMR (400 MHz, $CDCl_3$): δ = 7.77 (s, 1 H), 7.30 (d, *J* = 8.9 Hz, 2 H), 7.19 (d, *J* = 9.5 Hz, 2 H), 7.03–6.92 (m, 2 H), 3.85 (s, 3 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 159.0, 135.9, 130.7, 130.0, 123.3, 118.9, 114.9, 55.6.

GC-MS (EI): *m*/*z* = 174.04 $[M]^+$.

HRMS (EI): *m*/*z* $[M]^+$ calcd for $C_{10}H_{10}N_2O$: 174.0793; found: 174.0784.

1-[4-(1*H*-Imidazol-1-yl)phenyl]ethanone (3r)
IR (KBr): 3116, 1679, 1608, 1520, 1492, 1426, 1363, 1307, 1252, 1189, 1111, 1060, 956, 820 cm^{-1}.

^1H NMR (400 MHz, $CDCl_3$): δ = 8.09 (d, *J* = 8.7 Hz, 2 H), 7.96 (s, 1 H), 7.50 (d, *J* = 8.7 Hz, 2 H), 7.36 (s, 1 H), 7.25 (s, 1 H), 2.64 (s, 3 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 196.6, 140.9, 136.0, 135.5, 131.3, 130.5, 120.9, 117.9, 26.7.

GC-MS (EI): *m*/*z* = 186.04 $[M]^+$.

HRMS (EI): *m*/*z* $[M]^+$ calcd for $C_{11}H_{10}N_2O$: 186.0793; found: 186.0788.

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