Synthesis of Dibenzo-Fused Seven-Membered Heterocycles via Copper-Catalyzed Cyclization of 2-Haloaniline Compounds

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Abstract: A one-step synthesis of dibenzo-fused seven-membered nitrogen heterocycles from acetophenones/benzophenones and 2-haloanilines, via a copper-catalyzed amination, was developed. The reaction involves amination followed by intramolecular cyclization.

Key words: heterocycles, copper catalyst, arylation–cyclization, 2-haloaniline

Heterocycles are one of the most studied subjects as their structural units are widely found in numerous natural products.[1] In particular, seven- and eight-membered ring heterocycles constitute a number of biologically interesting molecules.[2] The abundance of these medium-sized rings in pharmaceuticals and agrochemicals continues to ensure that they are important synthetic targets for organic chemists.

In recent years, transition-metal-catalyzed arylation of amines has been shown to be extremely effective for application in the field of organic synthesis.[3–5] The formation of carbon–heteroatom bond via a copper-catalyzed amination reaction has been also successfully developed during the past few years.[6] However, the use of ligands (amino acids,[7] diamines,[8] and diols[9]), poor substrate scope, or the need to use stoichiometric amounts of copper reagents have limited the utility of these reactions in some cases.[10] A significant challenge in this case is combination of amination and construction of medium-sized heterocycles using copper salts in the absence of ligands. Hence, we want to report an arylation–cyclization reaction for the synthesis of seven-membered nitrogen heterocycles in the presence of a ligand-free catalyst (Scheme 1).

Our initial study began with the reaction of **1a** (1.5 equiv), **2a** (1.0 equiv, 0.30 mmol), Cu_2O (10 mol%) as the catalyst, and K_2CO_3 (1.5 equiv) in toluene at 110 °C under argon for 12 hours. The desired product **3a** was isolated in a 45% yield (Table 1, entry 1). The effect of the base on the coupling–cyclization reaction was examined. In general, the use of K_2CO_3 gave yields superior to those achieved with Cs_2CO_3, K_3PO_4 or Et_3N (entries 2–4). Further optimization of the reaction conditions revealed that the use of xylene was more effective than toluene, dimethyl sulfoxide (DMSO), *N*,*N*-dimethylformamide (DMF), benzene or *N*-methyl-2-pyrrolidinone (NMP) (entries 5–9). The use of PPh_3 as a ligand did not improve the product yield (entry 10). Other catalyst systems were also tested, such as CuO, $Cu(PPh_3)_2NO_3$, CuI, CuI–PPh_3, Cu, and were found to be less effective (entries 11–15).

Under the optimized reaction conditions, the breadth and the scope of the reaction were next investigated. The reactions of 1-(2-aminophenyl)ethanone (**1a**) with 2-iodoanilines having various substituents produced high yields of the dibenzo-fused seven-membered nitrogen derivatives and only a very small amount of the cross-coupling products was isolated (Table 2, entries 1–4). However, 2-iodoaniline **2e** bearing an electron-withdrawing group was unable to afford the desired product. Instead, only the cross-coupling product was obtained (entry 5). Similarly, the reactions of 2-aminobenzophenones were also studied. Moderate to good yields of the expected products were obtained and the cross-coupling products were not observed (entries 6–10, 12 and 13). However, when the 2-iodoaniline **2f** was used we could not get the target product (entry 11). Presumably, the difficulty for cyclization was due to the presence of electron-withdrawing groups.

We also attempted to extend the method to the less reactive 2-bromoaniline (**2g**). However, a lower yield was obtained and longer reaction time was required (entry 14). The use of 2-aminobenzaldehyde (**1f**) gave the corresponding product in 60% yield (entry 15). When methyl 2-aminobenzoate (**1g**) was subjected to the copper-catalyzed reaction, only the amination product was isolated (entry 16).

To clarify the effect of catalyst, we examined the reaction of **1a** and **2a** in the absence of the copper catalyst. Neither dehydration (products **A**, **B**) nor amination (product **C**) was observed (Scheme 2).

In summary, we have developed a novel methodology for the synthesis of dibenzo-fused seven-membered nitrogen heterocycles, based on the N-arylation of 2-haloaniline, followed by intramolecular cyclization in the presence of a common and cheap catalyst. This is an efficient strategy for the synthesis of a variety of dibenzo-fused seven-membered heterocycles.

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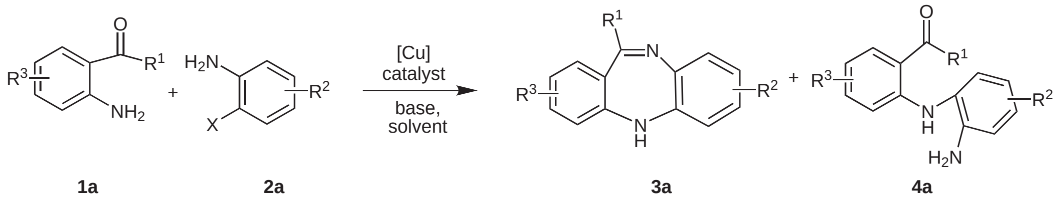
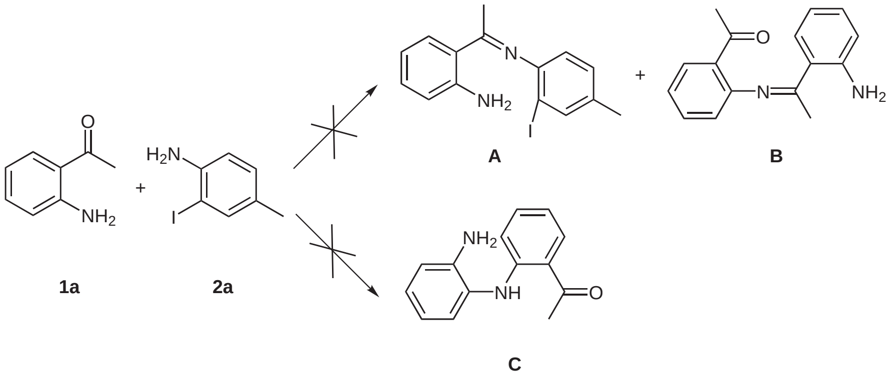


Scheme 1



Scheme 2

Table 1 Optimization of the Copper-Catalyzed Cyclization of **1a** with 2-Iodoaniline **2a**[a]

Entry	Catalyst	Base	Solvent	Temp (°C)	Time (h)	Yield[b] (%) of **3a**	Yield[b] (%) of **4a**
1	Cu_2O	K_2CO_3	toluene	110	12	45	–
2	Cu_2O	Cs_2CO	toluene	110	12	38	–
3	Cu_2O	K_3PO_4	xylene	145	8	48	15
4	Cu_2O	Et_3N	toluene	110	12	31	–
5	Cu_2O	K_2CO_3	DMSO	110	12	trace	–
6	Cu_2O	K_2CO_3	DMF	110	12	10	–
7	Cu_2O	K_2CO_3	benzene	145	8	–[c]	–
8	Cu_2O	K_2CO_3	NMP	110	12	trace	–
9	Cu_2O	K_2CO_3	xylene	145	8	88	6
10	$Cu_2O–PPh_3$	K_2CO_3	xylene	145	8	84	6
11	CuO	K_2CO_3	xylene	145	8	75	7
12	[Cu][d]	K_2CO_3	xylene	145	8	76	6
13	CuI	K_2CO_3	xylene	145	8	–[c]	–
14	$CuI–PPh_3$	K_2CO_3	xylene	145	8	–[c]	–
15	Cu	K_2CO_3	xylene	145	8	83	9

[a] Reactions were carried out on a 0.3-mmol scale in solvent (1.0 mL) under argon for the specified period of time with **1a** (1.5 equiv), **2a** (1.0 equiv), base (1.5 equiv), and catalyst (0.10 equiv).

[b] Isolated yields.

[c] No reaction.

[d] [Cu] = $Cu(PPh_3)_2NO_3$.

Table 2 Synthesis of Dibenzo-Fused Seven-Membered Nitrogen Heterocycles[a,11]

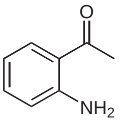
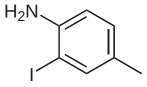
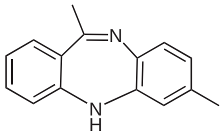
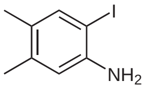
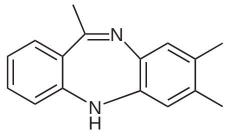
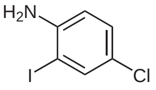
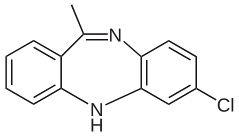
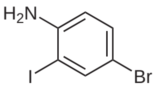
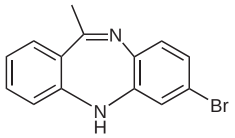
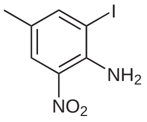
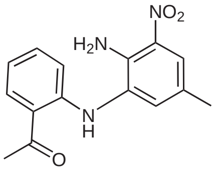
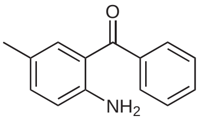
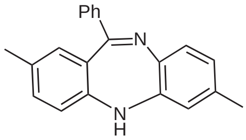
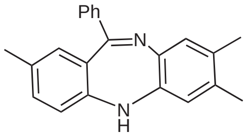
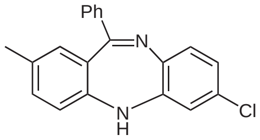
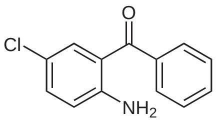
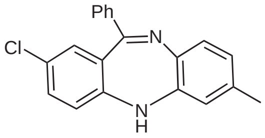
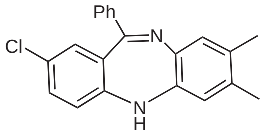
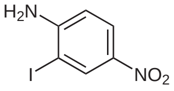
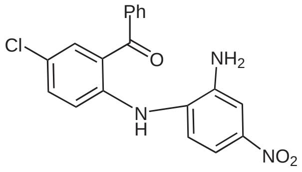
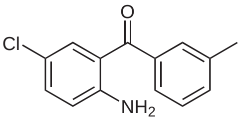
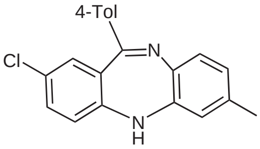
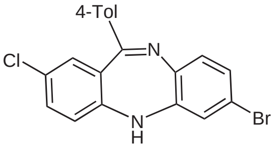
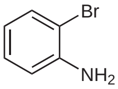
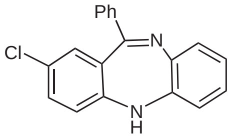
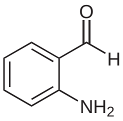
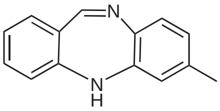
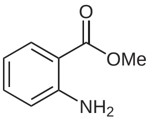
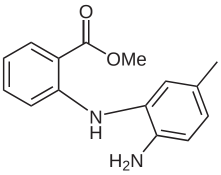
Entry	Ketone	Aniline	Product	Time (h)	Yield[b] (%) of **3**	Yield[b] (%) of **4**
1	**1a** 	**2a** 	**3a** 	8	88	5
2	**1a**	**2b** 	**3b** 	8	90	5
3	**1a**	**2c** 	**3c** 	4.5	85	6
4	**1a**	**2d** 	**3d** 	6	75	7
5	**1a**	**2e** 	**4e** 	12	–	85
6	**1b** 	**2a**	**3f** 	5	80	–
7	**1b**	**2b**	**3g** 	5	76	–
8	**1b**	**2c**	**3h** 	7	80	–
9	**1c** 	**2a**	**3i** 	8	80	–
10	**1c**	**2b**	**3j** 	2.5	78	–
11	**1c**	**2f** 	**4k** 	20	–	75

Table 2 Synthesis of Dibenzo-Fused Seven-Membered Nitrogen Heterocycles[a,11] (continued)

Entry	Ketone	Aniline	Product	Time (h)	Yield[b] (%) of **3**	Yield[b] (%) of **4**
12	**1d** 	**2a**	**3l** 	6	82	–
13	**1d**	**2d**	**3m** 	13	68	–
14	**1d**	**2g** 	**3n** 	20	40	–
15	**1f** 	**2a**	**3o** 	7	60	9
16	**1g** 	**2a**	**4p** 	8	–	70

[a] All reactions were carried out under the optimal conditions reported in the text.
[b] Isolated yields.

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(11) **Typical Procedure for the Preparation of Dibenzo-Fused Seven-Membered Nitrogen Heterocycles Compounds**: A mixture of **1a** (60.8 mg, 0.45 mmol), **2b** (69.9 mg, 0.3 mmol), Cu_2O (4.3 mg, 0.03 mmol) and K_2CO_3 (62.1 mg, 0.45mmol) was placed in xylene (1.0 mL) under Ar at 145 °C in a round-bottomed flask. When the reaction was considered complete as determined by TLC analysis, the reaction mixture was allowed to cool to r.t., and the mixture was extracted with EtOAc. The combined organic extracts were washed with H_2O and sat. brine. The organic layers were dried over $MgSO_4$, and filtered. Solvents were evaporated under reduced pressure. The residue was purified by chromatography on silica gel (hexanes–EtOAc, 10:1) to afford 7,11-dimethyl-5*H*-dibenzo[*b*,*e*][1,4]diazepine (**3a**; 53.9 mg, 88%) as a yellow solid; mp 133–135 °C. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 2.23 (s, 3 H), 2.54 (s, 3 H), 4.86 (s, 1 H), 6.48 (s, 1 H), 6.65–6.68 (d, *J* = 8.4 Hz, 1 H), 6.80–6.83 (d, *J* = 7.5 Hz, 1 H), 6.94–6.99 (m, 1 H), 7.03–7.05 (d, *J* = 6.0 Hz, 1 H), 7.19–7.31 (m, 2 H). ^{13}C NMR (75 MHz, $CDCl_3$): δ = 20.6, 28.4, 119.2, 120.2, 122.8, 124.8, 127.9, 129.0, 129.3, 131.6, 136.6, 138.1, 142.2, 153.0, 168.9. IR (KBr): 761, 1281, 1459, 1630, 3278, 3348 cm^{-1}. EI–MS: *m*/*z* = 222 [M^{+}], 207, 192, 111 cm^{-1}. Anal. Calcd for $C_{15}H_{14}N_2$: C, 81.05; H, 6.35; N, 12.60. Found: C, 80.87; H, 6.09; N, 12.71.

7-Chloro-11-methyl-5*H*-dibenzo[*b*,*e*][1,4]diazepine (3c): The reaction mixture was chromatographed using hexanes–EtOAc (10:1) to afford **3c** (58.2 mg, 85%) as a brown solid. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 2.52–2.53 (m, 3 H), 4.89 (s, 1 H), 6.65–6.68 (d, *J* = 7.5 Hz, 2 H), 6.95–7.06 (m, 3 H), 7.22–7.32 (m, 2 H). ^{13}C NMR (75 MHz, $CDCl_3$): δ = 28.5, 119.5, 119.6, 123.3, 124.1, 129.0, 129.4, 131.8, 131.9, 134.8, 139.2, 143.4, 152.3, 170.1. IR (KBr): 758, 1456, 1631, 3272, 3356 cm^{-1}. EI–MS: *m*/*z* = 242 [M^{+}], 207. Anal. Calcd for $C_{14}H_{11}ClN_2$: C, 69.28; H, 4.57; N, 11.54. Found: C, 69.37; H, 4.38; N, 11.45.

1-[2-(2-Amino-5-methyl-3-nitrophenylamino)phenyl]ethanone (4e): The reaction mixture was chromatographed using hexanes–EtOAc (30:1) to afford **4e** (68.4 mg, 85%) as an orange solid. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 2.26 (s, 3 H), 2.67 (s, 3 H), 6.26 (s, 2 H), 6.55–6.58 (d, *J* = 8.7 Hz, 1 H), 6.76–6.82 (t, *J* = 7.2 Hz, 1 H), 7.23–7.34 (m, 2 H), 7.84–7.90 (t, *J* = 7.5 Hz, 2 H), 10.03 (s, 1 H). ^{13}C NMR (75 MHz, $CDCl_3$): δ = 20.1, 28.0, 114.2, 117.2, 119.0, 123.7, 125.2, 128.4, 132.4, 132.6, 135.1, 135.5, 140.6, 148.8, 201.8. IR (KBr): 750, 1225, 1450, 1576, 1638, 3373, 3472 cm^{-1}. EI–MS: *m*/*z* = 285 [M^{+}], 195, 120. Anal. Calcd for $C_{15}H_{15}N_3O_3$: C, 63.15; H, 5.30; N, 14.73. Found: C, 63.31; H, 5.10; N, 14.87.

2,7,8-Trimethyl-11-phenyl-5*H*-dibenzo[*b*,*e*][1,4]diazepine (3g): The reaction mixture was chromatographed using hexanes–EtOAc (50:1) to afford **3g** (66.5 mg, 76%) as a yellow solid. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 2.13 (s, 6 H), 2.17 (s, 3 H), 4.81 (s, 1 H), 6.45 (s, 1 H), 6.61–6.64 (d, *J* = 7.5 Hz, 1 H), 6.78 (s, 1 H), 7.02–7.09 (m, 1 H), 7.22 (s, 1 H), 7.36–7.41 (m, 3 H), 7.70–7.74 (m, 2 H). ^{13}C NMR (75 MHz, $CDCl_3$): δ = 18.8, 19.0, 20.4, 119.4, 120.8, 127.2, 127.9, 129.5, 129.6, 131.6, 131.9, 132.1, 132.4, 135.2, 138.4, 140.2, 141.5, 152.0, 168.7. IR (KBr): 695, 731, 1464, 1613, 2920, 3329 cm^{-1}. EI–MS: *m*/*z* = 312 [M^{+}], 297. Anal. Calcd for $C_{22}H_{20}N_2$: C, 84.58; H, 6.45; N, 8.97. Found: C, 84.59; H, 6.53; N, 8.89.

2-Chloro-7-methyl-11-phenyl-5*H*-dibenzo[*b*,*e*][1,4]diazepine (3i): The reaction mixture was chromatographed using hexanes–EtOAc (50:1) to afford **3i** (71.7 mg, 80%) as an orange solid. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 2.25 (s, 3 H), 4.90 (s, 1 H), 6.49 (s, 1 H), 6.67–6.70 (d, *J* = 8.1 Hz, 1 H), 6.86–6.89 (d, *J* = 8.1 Hz, 1 H), 6.96–6.97 (m, 1 H), 7.18–7.25 (m, 2 H), 7.38–7.45 (m, 3 H), 7.68–7.71 (m, 2 H). ^{13}C NMR (75 MHz, $CDCl_3$): δ = 20.7, 120.4, 121.0, 125.2, 127.7, 128.1, 128.7, 128.9, 129.4, 130.1, 131.4, 131.6, 137.3, 138.1, 140.8, 141.7, 152.8, 167.1. IR (KBr): 1450, 1615, 3269, 3348 cm^{-1}. EI–MS: *m*/*z* = 318 [M^{+}], 283, 268, 214. Anal. Calcd for $C_{20}H_{15}ClN_2$: C, 75.35; H, 4.74; N, 8.79. Found: C, 75.43; H, 4.87; N, 8.98.

2-Chloro-7,8-dimethyl-11-phenyl-5*H*-dibenzo[*b*,*e*][1,4]diazepine (3j): The reaction mixture was chromatographed using hexanes–EtOAc (50:1) to afford **3j** (72.8 mg, 78%) as a yellow solid. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 2.11–2.24 (m, 6 H), 4.87 (s, 1 H), 6.43 (s, 1 H), 6.64–6.66 (m, 1 H), 6.95–6.96 (m, 1 H), 7.09 (s, 1 H), 7.15–7.23 (m, 1 H), 7.37–7.46 (m, 3 H), 7.68–7.71 (m, 2 H). ^{13}C NMR (75 MHz, $CDCl_3$): δ = 18.8, 19.1, 120.9, 120.9, 127.6, 128.1, 128.8, 129.3, 129.6, 130.0, 131.4, 131.5, 132.5, 135.7, 138.2, 139.4, 140.8, 153.1, 167.1. IR (KBr): 696, 731, 1462, 1617, 2920, 3341 cm^{-1}. EI–MS: *m*/*z* = 332 [M^{+}], 297, 214, 111. Anal. Calcd for $C_{21}H_{17}ClN_2$: C, 75.78; H, 5.15; N, 8.42. Found: C, 75.67; H, 5.05; N, 8.48.

7-Bromo-2-chloro-11-*m*-tolyl-5*H*-dibenzo[*b*,*e*][1,4]diazepine (3m): The reaction mixture was chromatographed using hexanes–EtOAc (50:1) to afford **3m** (75.1 mg, 68%) as a yellow solid. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 3.26 (s, 3 H), 4.94 (s, 1 H), 6.71–6.73 (d, *J* = 8.1 Hz, 1 H), 6.87 (s, 1 H), 6.99–7.00 (m, 1 H), 7.14–7.18 (m, 2 H), 7.24–7.30 (m, 3 H), 7.38 (s, 1 H), 7.56 (s, 1 H). ^{13}C NMR (75 MHz, DMSO-d_6): δ = 21.7, 120.1, 122.7, 123.3, 126.8, 127.0, 127.1, 128.8, 129.2, 130.1, 130.5, 131.3, 131.9, 132.8, 138.2, 140.3, 140.7, 145.7, 154.8, 168.7. IR (KBr): 628, 764, 825, 1026, 1652, 2253, 3414 cm^{-1}. EI–MS: *m*/*z* = 396 [M^{+}], 361. Anal. Calcd for $C_{20}H_{14}BrClN_2$: C, 60.40; H, 3.55; N, 7.04. Found: C, 60.55; H, 3.36; N, 7.18.

7-Methyl-5*H*-dibenzo[*b*,*e*][1,4]diazepine (3o): The reaction mixture was chromatographed using hexanes–EtOAc (10:1) to afford **3o** (34.3 mg, 60%) as a dark red solid. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 2.20 (s, 3 H), 4.84 (s, 1 H), 6.30 (s, 1 H), 6.44–6.47 (d, *J* = 7.5 Hz, 1 H), 6.72–6.74 (d, *J* = 7.5 Hz, 2 H), 6.83–6.88 (t, *J* = 7.5 Hz, 1 H), 6.99–7.04 (t, *J* = 7.5 Hz, 2 H), 7.11–7.16 (t, *J* = 14.7 Hz, 1 H), 8.04 (s, 1 H). ^{13}C NMR (75 MHz, $CDCl_3$): δ = 20.6, 118.3, 120.5, 122.4, 124.6, 126.3, 130.5, 131.9, 132.6, 137.6, 138.7, 142.3, 151.8, 162.1. IR (KBr): 746, 1456, 1588, 2920, 3355 cm^{-1}. EI–MS: *m*/*z* = 208 [M^{+}]. Anal. Calcd for $C_{14}H_{12}N_2$: C, 80.74; H, 5.81; N, 13.45. Found: C, 80.64; H, 5.67; N, 13.53.