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Copper(I)-2-(2′-pyridyl)benzimidazole catalyzed N-arylation of indoles

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ABSTRACT

CuI-2-(2′-pyridyl)benzimidazole catalyst system can serve efficiently to promote N-arylation of various indoles to afford the N-arylated indoles. The bidentate ligand, 2-(2′-pyridyl)benzimidazole was proved superior to monodentate nitrogen-based ligands and well-known bidentate ligands such as 2,2′-bipyridyl and 1,10-phenanthroline.

1. Introduction

In 1983, Kosugi and Migita first reported the coupling reaction of aryl bromides with tin amide in the presence of $PdCl_2$-(P(*o*-tol)$_3$)$_2$.[1] The disadvantage of this reaction is to use stoichiometric amounts of tributyltin amides. After their pioneering works, Buchwald[2] and Hartwig[3] reported the amination of aryl halides using free amine by the use of palladium and phosphine ligands such as P(*o*-tol)$_3$ and BINAP in 1995. After that, Yamamoto and Koike in Tosoh group introduced *t*-Bu$_3$P as a phosphine ligand in 1998. [4] In this system, that is, Pd(OAc)$_2$, *t*-Bu$_3$P and NaO*t*-Bu, aryl chloride can be used as a substrate. The characteristic features of *t*-Bu$_3$P, that have, steric hindrance and electron rich substituent gave the guidelines for development of the design of phosphine ligands. In most cases of these reactions, strong bases such as NaO*t*-Bu or LiHMDS are often used.[5] On the other hand, we have interested in coupling reaction using metal–nitrogen ligand system. For example, we reported monodentate imidazole or imidazoline derivatives as ligands for the palladium-catalyzed Mizoroki–Heck reaction and Suzuki–Miyaura coupling reaction.[6,7] We also reported bidentate 2-(2′-pyridyl)benzimidazole–$PdCl_2$ complex efficiently catalyzed Mizoroki–Heck reaction.[8,9,10] On the other hand, copper-catalyzed coupling reactions have much attention these days. There are some advantages in the use of copper as coupling catalyst; abundant reserve, low toxicity and low cost. As the ligands, diamines,[11] diols,[12] amino acids and amino alcohols,[13] oxime phosphines,[14] salicylaldoximes,[15] β-diketones and β-keto esters,[16] and so on have been used in copper-catalyzed coupling reactions.[17,18] We have interest in the ability of ligand acceleration of 2-(2′-pyridyl)benzimidazole in copper-catalyzed coupling reaction. Herein, we report copper(I)-2-(2′-pyridyl)benzimidazole catalyzed N-arylation of indoles.[19]

2. Results and discussion

2.1. Screening of ligands

We first examined the effect of the nitrogen-based ligands in the reaction of N-arylation of indoles with 4-iodotoluene using CuI–nitrogen-based ligand system. 4-Bromotoluene and 4-chlorotoluene were inert for N-arylation of indoles in our system. We examined the effect of solvents such as toluene, dioxane, CH_3CN, DMF, DMSO and NMP (*N*-methylpyrrolidone) and bases such as *t*-BuOK, $CsCO_3$, K_2CO_3, CsF and K_3PO_4. Among those, the combination of DMF and K_3PO_4 gave the best results. As for the reaction temperature, 110 °C wad proved to be necessary for this reaction. As shown entries 2 and 3 in Table 1, imidazoline and imidazole derived monodentate ligands **1** and **2** did not accelerate the reaction (44% and 15% yield, respectively) compared with none catalyst system (37%). Therefore, we turned our attention to bidentate ligands such as 2-(2′-pyridyl)imidazoline **3** and 2-(2′-pyridyl)benzimidazole 4. It should be mentioned that well-known bidentate nitrogen ligands, such as 2,2′-bipyridyl **5** and 1,10-phenanthroline **6** did not give the product in high yield (47% and 40%, respectively). 2-(2′-Pyridyl)benzimidazole **4** was easily prepared by the reaction of 2-pyridyncarbaldehyde with 1,2-phenylenediamine in the presence of activated carbon under oxygen atmosphere (Scheme 1).[20]

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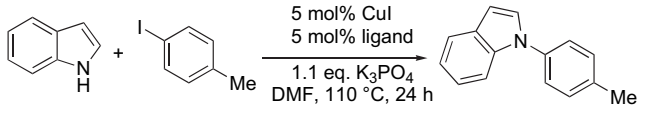
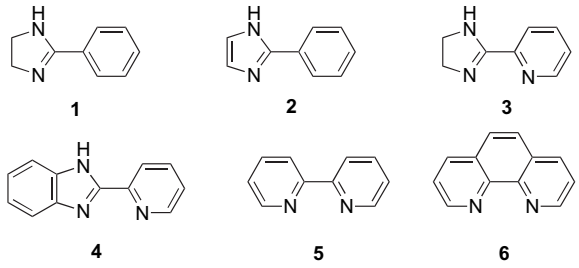
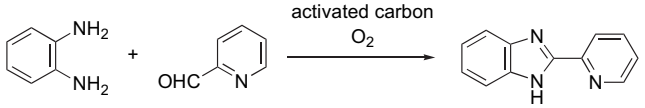
Table 1
Ligand effect in the Cu-catalyzed N-arylation of indole with 4-iodotoluene[a]



Entry	Ligand	Yield[b]/%
1	None	37
2[c]	**1**	44
3[c]	**2**	15
4	**3**	81
5	**4**	83
6	**5**	47
7	**6**	40



[a] All reactions were carried out using 4-iodotoluene (2 mmol) and indole (3 mmol) in DMF (4 mL) at 110 °C.
[b] Isolated yields after silica-gel column chromatography.
[c] 10 mol % of ligand was used.

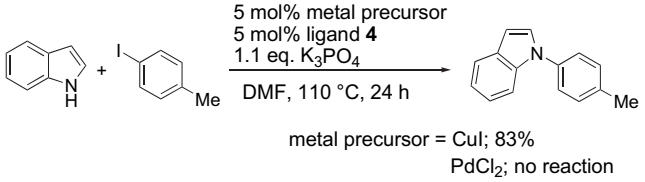


Scheme 1.

2.2. CuI-2-(2′-pyridyl)benzimidazole catalyzed N-arylation of indoles

Then, we examined the reaction of substituted indoles with 4-iodotoluene. The reactions were carried out using 5 mol % of CuI, 5 mol % of ligand **4** in the presence of 1.1 equiv of K_3PO_4 in DMF at 110 °C for 24 h. The obtained results are summarized in Table 2. All substituted indoles except for having substituents at R^1 gave the products in high yield. Low yield in the case of entries 9 and 10 (R^1=Me and Ph) may be due to the steric hindrance.

Next, we examined the reaction of indole with substituted aryl iodides (Table 3). All the substituted aryl iodides reacted with indole to afford the coupling products in good to high yield. We did not observe any limitation as for aryl iodide derivative.

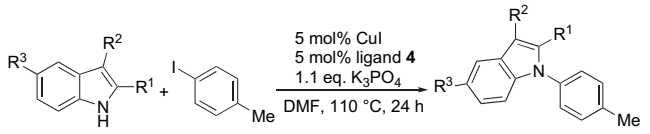


It should be mentioned that the combination of $PdCl_2$ and ligand **4** did not give the product.

2.3. C–N vs C–O

The present CuI-2-(2′-pyridyl)benzimidazole also catalyzes C–O bond formation.[21–24] Actually, when 4-iodotoluene was treated with 5-hydroxyindole, the mixture of *N*-(4-methylphenoxy)-1*H*-indole (**8**) and *N*-(4-methylphenyl)-5-(4-methylphenoxy)indole (**9**) was obtained (Table 4). *N*-(4′-Methylphenyl)-5-hydroxyindole (**7**) was not obtained. These results indicate the formation of C–O bond takes place faster than C–N bond formation.

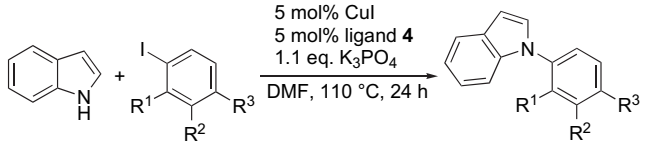
Table 2
Reaction of substituted indoles with 4-iodotoluene[a]



Entry	R^1	R^2	R^3	Yield[b]/%
1	H	H	H	83
2	H	H	Me	92
3	H	H	OMe	83
4	H	H	Cl	82
5	H	H	CN	88
6	H	H	NH_2	76
7	H	Me	H	83
8	H	CO_2Me	H	97
9	Me	H	H	23
10	Ph	H	H	38

[a] All reactions were carried out using 4-iodotoluene (2 mmol) and indole (3 mmol) in DMF (4 mL) at 110 °C.
[b] Isolated yields after silica-gel column chromatography.

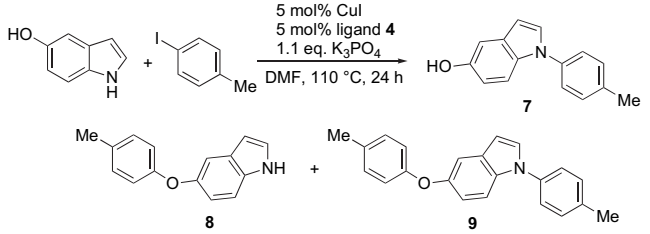
Table 3
Reaction of indole with substituted aryl iodides[a]



Entry	R^1	R^2	R^3	Yield[b]/%
1	H	H	Me	83
2	H	H	OMe	78
3	H	H	Cl	86
4	H	Cl	H	89
5	Me	H	H	73

[a] All reactions were carried out using 4-iodotoluene (2 mmol) and indole (3 mmol) in DMF (4 mL) at 110 °C.
[b] Isolated yields after silica-gel column chromatography.

Table 4
Reaction of 5-hydroxyindole with 4-iodotoluene[a]



Entry	Ratio		Yield[b]/%		
	5-Hydroxyindole	4-Iodotoluene	**7**	**8**	**9**
1	1	2	0	82	16
2	1	1	0	55	19
3	2	1	0	69	10

[a] All reactions were carried out in DMF (4 mL) at 110 °C.
[b] Isolated yields after silica-gel column chromatography.

3. Conclusions

We found the CuI-2-(2′-pyridyl)benzimidazole catalyst system works efficiently to promote N-arylation of various indoles to afford the *N*-arylated indoles. The bidentated ligand, 2-(2′-pyridyl)benzimidazole was proved superior to monodentate nitrogen-based ligands and well-known bidentate ligands such as 2,2′-bipyridyl and 1,10-phenanthroline.

4. Experimental section

4.1. General procedure for N-arylation of indole

K_3PO_4 (467.0 mg, 2.2 mmol) was added to a Schlenk tube equipped with a stirring bar and the tube was dried under vacuum and then filled with an argon. CuI (19.0 mg, 0.1 mmol) and ligand (0.1 mmol) and DMF (4.0 mL) were added and the mixture was stirred at 50 °C for 1 h, aryl iodide (2.0 mmol) and indole (3.0 mmol) were added, and then the mixture was stirred at 110 °C for 24 h. After the completion of the reaction, the mixture was cooled, then the precipitate was removed by filtration and the product was extracted with diethyl ether. The combined organic layer was dried over anhydrous Na_2SO_4 and filtered. After evaporation, the obtained residue was purified by silica-gel column chromatography to give the *N*-arylated product.

4.1.1. N-(4-Methylphenyl)indole[25]. Yield: 83%; R_f=0.78 (hexane:ethyl acetate=5:1); IR (KBr): ν_{max} (cm^{-1}) 3042, 1529, 1526, 1495, 1480, 1330, 1221, 1153, 822, 694; ^1H NMR (400 MHz, $CDCl_3$): δ 7.67 (d, J=7.7 Hz, 1H), 7.57 (d, J=8.4 Hz, 1H), 7.37 (d, J=7.7 Hz, 2H), 7.30–7.2 (m, 3H); 7.2–7.1 (m, 2H), 6.65 (d, J=2.8 Hz, 1H), 2.42 (s, 3H); ^{13}C NMR (100.6 MHz, $CDCl_3$): δ 137.3, 136.3, 136.0, 130.1, 129.1, 128.0, 124.3, 122.1, 121.1, 120.1, 110.4, 103.2, 21.0.

4.1.2. N-(4-Methylphenyl)-5-methylindole[26]. Yield: 92%; R_f=0.24 (hexane); IR (KBr): ν_{max} (cm^{-1}) 3033, 2918, 1529, 1526, 1480, 1333, 1221, 1158, 822, 793; ^1H NMR (400 MHz, $CDCl_3$): δ 7.5–7.4 (m, 4H), 7.3–7.2 (m, 3H), 7.02 (d, J=10.0 Hz, 1H), 6.57 (d, J=2.8 Hz, 1H); 2.46 (s, 3H), 2.42 (s, 3H); ^{13}C NMR (100.6 MHz, $CDCl_3$): δ 137.4, 135.9, 134.3, 130.0, 129.5, 129.4, 127.9, 124.0, 123.8, 120.7, 110.2, 102.7, 21.3, 21.0.

4.1.3. N-(4-Methylphenyl)-5-methoxyindole[27]. Yield: 83%; R_f=0.63 (hexane:ethyl acetate=5:1); mp 59–60 °C (lit.[27] 57–58 °C); IR (KBr): ν_{max} (cm^{-1}) 3106, 2954, 1480, 1447, 1262, 1221, 1160, 1028, 799, 765; ^1H NMR (400 MHz, $CDCl_3$): δ 7.61 (d, J=8.0 Hz, 1H), 7.4–7.3 (m, 2H), 7.3–7.2 (m, 2H), 7.25 (s, 1H), 7.13 (d, J=2.0 Hz, 1H), 6.86 (dd, J=7.1, 4.8 Hz, 1H), 6.58 (d, J=2.0 Hz, 1H), 3.87 (s, 3H), 2.43 (s, 3H); ^{13}C NMR (100.6 MHz, $CDCl_3$): δ 154.4, 137.4, 136.1, 131.2, 130.1, 129.7, 128.4, 123.9, 112.4, 111.3, 102.8, 102.6, 55.8, 21.0.

4.1.4. N-(4-Methylphenyl)-5-chloroindole. Yield: 82%; R_f=0.26 (hexane); mp 42–43 °C; IR (KBr): ν_{max} (cm^{-1}) 3107, 1519, 1457, 1329, 1224, 1204, 1063, 799.5, 712.2; ^1H NMR (400 MHz, $CDCl_3$): δ 7.63 (s, 1H), 7.41 (d, J=8.8 Hz, 2H), 7.4–7.3 (m, 4H), 7.14 (d, J=8.8 Hz, 1H), 6.60 (d, J=0.8 Hz, 1H), 2.43 (s, 3H); ^{13}C NMR (100.6 MHz, $CDCl_3$): δ 136.8, 136.7, 134.4, 130.2, 130.1, 129.3, 125.8, 124.9, 124.2, 122.4, 120.3, 111.9, 111.5, 102.7, 21.0. Anal. Calcd for $C_{15}H_{12}ClN$: C, 74.53; H, 5.00. Found: C, 74.87; H, 5.01.

4.1.5. N-(4-Methylphenyl)-5-cyanoindole. Yield: 88%; R_f=0.50 (hexane:ethyl acetate=5:1); mp 88–89 °C; IR (KBr): ν_{max} (cm^{-1}) 2955, 2255, 1519, 1480, 1447, 1262, 1160, 1028, 799, 765; ^1H NMR (400 MHz, $CDCl_3$): δ 8.02 (s, 1H), 7.51 (d, J=8.4 Hz, 1H), 7.4–7.3 (m, 5H), 6.73 (d, J=3.6 Hz, 1H), 2.45 (s, 3H), 2.43 (s, 3H); ^{13}C NMR (100.6 MHz, $CDCl_3$): δ 137.4, 137.3, 135.9, 130.4, 130.2, 128.6, 126.4, 124.8, 124.4, 111.2, 124.1, 103.7, 103.1, 20.9. Anal. Calcd for $C_{16}H_{12}N_2$: C, 82.73; H, 5.21. Found: C, 82.91; H, 5.26.

4.1.6. N-(4-Methylphenyl)-5-aminoindole. Yield: 67%; R_f=0.58 (hexane:ethyl acetate=1:1); mp 92–93 °C; IR (KBr): ν_{max} (cm^{-1}); 3752, 3744, 3741, 2336, 1734, 1653, 1218, 1162, 823, 795; ^1H NMR (400 MHz, $CDCl_3$): δ 7.4–7.3 (m, 3H), 7.3–7.2 (m, 3H), 6.96 (s, 1H), 6.67 (d, J=12.0 Hz, 1H), 6.50 (d, J=3.2 Hz, 1H), 3.50 (br, 2H), 2.41 (s, 3H), ^{13}C NMR (100.6 MHz, $CDCl_3$): δ 139.9, 137.5, 135.8, 130.8, 130.2, 130.0, 128.3, 123.8, 115.8, 112.9, 111.1, 105.7, 102.1, 20.9. Anal. Calcd for $C_{15}H_{14}N_2$: C, 81.05; H, 6.33. Found: C, 80.96; H, 6.44.

4.1.7. N-(4-Methylphenyl)-3-methylindole[26]. Yield: 83%; R_f=0.70 (hexane:ethyl acetate=10:1); mp 43–44 °C (lit.[25] 43–44 °C); IR (KBr): ν_{max} (cm^{-1}) 3042, 2943, 1653, 1608, 1507, 1457, 1517, 1221, 786, 731; ^1H NMR (400 MHz, $CDCl_3$): δ 7.62 (d, J=7.2 Hz, 1H), 7.51 (d, J=7.0 Hz, 1H), 7.36 (d, J=7.2 Hz, 2H), 7.21 (t, J=7.2 Hz, 1H), 7.16 (t, J=7.1 Hz, 1H), 7.11 (s, 1H), 2.42 (s, 3H), 2.38 (s, 3H); ^{13}C NMR (100.6 MHz, $CDCl_3$): δ 137.4, 136.0, 135.7, 130.0, 129.6, 125.5, 123.9, 122.2, 119.5, 119.1, 112.4, 110.3, 21.0, 9.5.

4.1.8. N-(4-Methylphenyl)methyl indole-3-carboxylate[26]. Yield: 97%; R_f=0.30 (hexane); IR (KBr): ν_{max} (cm^{-1}) 3037, 2947, 1694, 1538, 1455, 1211, 1108, 1050, 823, 776; ^1H NMR (400 MHz, $CDCl_3$): δ 8.24 (d, J=8.4 Hz, 1H), 7.99 (s, 1H), 7.48 (d, J=8.4 Hz, 1H), 7.5–7.3 (m, 6H), 3.98 (s, 3H), 2.45(s, 3H); ^{13}C NMR (100.6 MHz, $CDCl_3$): δ 165.4, 137.7, 136.7, 135.9, 134.2, 130.3, 126.8, 124.6, 123.2, 122.3, 121.7, 110.9, 108.7, 60.3, 51.0, 21.0, 14.1.

4.1.9. N-(4-Methylphenyl)-2-methylindole[28]. Yield: 23%; R_f=0.70 (hexane:ethyl acetate=10:1); IR (KBr): ν_{max} (cm^{-1}) 3042, 2943, 1653, 1608, 1507, 1457, 1517, 1221, 786, 731; ^1H NMR (400 MHz, $CDCl_3$): δ 7.56 (d, J=8.0 Hz, 1H), 7.32 (d, J=7.9 Hz, 2H), 7.22 (d, J=8.0 Hz, 2H), 7.1–7.0 (m, 3H), 6.38 (s, 1H), 2.46 (s, 3H), 2.29 (s, 3H); ^{13}C NMR (100.6 MHz, $CDCl_3$): δ 138.2, 137.5, 137.0, 135.2, 130.1, 129.9, 128.1, 127.7, 126.3, 120.9, 119.8, 119.4, 109.9, 100.9, 21.1, 13.3.

4.1.10. N-(4-Methoxyphenyl)indole[27,29]. Yield: 78%; R_f=0.63 (hexane:ethyl acetate=5:1); mp 57–58 °C (lit.[26,28] 57–58 °C); IR (KBr): ν_{max} (cm^{-1}) 3048, 1517, 1457, 1247, 1229, 1214, 1027, 762, 746; ^1H NMR (400 MHz, $CDCl_3$): δ 7.45 (d, J=7.6 Hz, 1H), 7.40 (d, J=7.6 Hz, 2H), 7.28 (d, J=7.0 Hz, 2H), 7.20 (t, J=7.6 Hz, 1H), 7.17 (t, J=1.6 Hz, 1H), 7.03 (d, J=7.6 Hz, 2H), 6.65 (d, J=0.8 Hz, 1H), 3.88 (s, 3H); ^{13}C NMR (100.6 MHz, $CDCl_3$) δ 158.2, 136.3, 132.8, 128.9, 128.2, 126.9, 122.1, 120.9, 120.0, 114.7, 110.3, 102.8, 55.5.

4.1.11. N-(4-Chlorophenyl)indole[30]. Yield: 86%; R_f=0.26 (hexane); IR (KBr): ν_{max} (cm^{-1}) 1595, 1497, 1495, 1456, 1332, 1234, 1211, 1089, 831, 761, 742; ^1H NMR (400 MHz, $CDCl_3$): δ 7.67 (d, J=8.4 Hz, 1H), 7.5–7.4 (m, 5H), 7.28 (d, J=8.4 Hz, 1H), 7.2–7.1 (m, 2H), 6.68 (d, J=0.8 Hz, 1H); ^{13}C NMR (100.6 MHz, $CDCl_3$) δ 138.3, 135.7, 131.9, 129.7, 129.3, 127.6, 125.4, 122.6, 121.2, 120.6, 110.2, 104.0.

4.1.12. N-(3-Chlorophenyl)indole[31]. Yield: 89%; R_f=0.26 (hexane); IR (KBr): ν_{max} (cm^{-1}) 1594, 1517, 1487, 1455, 1333, 1234, 1135, 760, 740, 688; ^1H NMR (400 MHz, $CDCl_3$): δ 7.68 (d, J=7.6 Hz, 1H), 7.55 (d, J=7.6 Hz, 1H), 7.51 (d, J=7.6 Hz, 1H), 7.42–7.40 (m, 2H), 7.3–7.2 (m, 2H), 7.24 (t, J=6.8 Hz, 1H), 6.69 (d, J=0.8 Hz, 1H); ^{13}C NMR (100.6 MHz, $CDCl_3$): δ 140.9, 135.6, 135.1, 130.6, 129.4, 127.5, 126.4, 124.3, 122.7, 122.2, 121.3, 120.7, 110.3, 104.3.

4.1.13. N-(2-Methylphenyl)indole[25]. Yield: 73%; R_f=0.24 (hexane); IR (KBr): ν_{max} (cm^{-1}) 3053, 1603, 1581, 1512, 1510, 1496, 1457, 1306, 764, 740; ^1H NMR (400 MHz, $CDCl_3$): δ 7.70 (d, J=6.4 Hz, 1H), 7.4–7.3 (m, 4H), 7.2–7.1 (m, 4H), 6.67 (d, J=2.8 Hz, 1H), 2.06 (s, 3H); ^{13}C NMR

(100.6 MHz, $CDCl_3$): δ 138.3, 136.9, 135.8, 131.2, 128.6, 128.3, 128.2, 128.1, 126.7, 122.0, 120.8, 119.8, 110.5, 102.5, 17.6.

4.1.14. N-(4-Methylphenyl)-2-phenylindole[32]. Yield: 38%; R_f=0.30 (hexane); IR (KBr): ν_{max} (cm^{-1}) 3029, 1500, 1459, 1449, 1324, 1257, 1212, 1134, 793, 742, 710, 692; ^1H NMR (400 MHz, $CDCl_3$): δ 7.67 (d, J=6.0 Hz, 1H), 7.3–7.1 (m, 12H), 6.78 (s, 1H), 2.38 (s, 3H); ^{13}C NMR (100.6 MHz, $CDCl_3$): δ 140.7, 139.1, 137.0, 135.8, 132.6, 129.8, 128.8, 128.2, 128.1, 127.7, 127.2, 122.2, 120.5, 120.4, 110.6, 103.4, 21.1.

4.1.15. 5-(4-Methylphenoxy)-1H-indole (entry 1 in Table 4). Yield: 82%; R_f=0.68 (hexane:ethyl acetate=1:1); IR (KBr): ν_{max} (cm^{-1}) 3019, 1516, 1474, 1454, 1324, 1217, 1212, 1153, 1115, 1070, 788, 753; ^1H NMR (400 MHz, $CDCl_3$): δ 7.6–7.4 (m, 3H), 7.3–7.2 (m, 3H), 7.07 (s, 1H), 6.77 (d, J=8.0 Hz, 1H), 6.63 (s, 1H), 4.54 (s, 1H), 2.42 (s, 3H); ^{13}C NMR (100.6 MHz, $CDCl_3$): δ 149.8, 137.3, 136.2, 131.4, 130.1, 130.0, 128.8, 124.0, 111.8, 111.3, 105.3, 102.4, 21.0. Anal. Calcd for $C_{15}H_{13}NO$: C, 80.69; H, 5.87. Found: C, 80.30; H, 5.92.

4.1.16. N-(4-Methylphenyl)-5-(4-methylphenoxy)indole[27] *(entry 2 in Table 4).* Yield: 19%; R_f=0.85 (hexane:ethyl acetate=1:1); IR (KBr): ν_{max} (cm^{-1}) 3058, 3032, 1609, 1518, 1470, 1250, 1219, 1167, 756, 736; ^1H NMR (400 MHz, $CDCl_3$): δ 7.46 (d, J=9.2 Hz, 2H), 7.36 (d, J=6.0 Hz, 3H), 7.3–7.2 (m, 4H), 7.08 (d, J=8.8 Hz, 2H), 6.9–6.8 (m, 3H), 7.08 (d, J=8.8 Hz, 2H), 6.57 (s, 1H), 2.41 (s, 3H), 2.30 (s, 3H); ^{13}C NMR (100.6 MHz, $CDCl_3$): δ 156.7, 150.1, 137.2, 136.4, 132.7, 131.5, 130.1, 130.0, 129.7, 129.0, 124.1, 117.7, 115.5, 1113.3, 110.7, 103.0, 21.0, 20.6.

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Supplementary data

Supplementary data associated with this article can be found in the online version, at doi:10.1016/j.tet.2009.10.014.

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