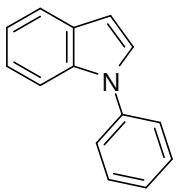
Supporting Information

General Methods

All reactions were performed under an atmosphere of dry nitrogen gas in oven-dried glassware unless otherwise specified. Distilled water was used as solvent in the reaction and degassed with nitrogen gas immediately before use. Hexanes, chloroform and ethyl acetate used for extraction and chromatography were used as purchased. ^{1}H and ^{13}C NMR spectra were recorded on a Bruker 500 MHz NMR spectrometer at room temperature in $CDCl_3$ with the solvent residual peak as internal reference ($CDCl_3$: 1H = 7.26 ppm) unless otherwise stated. Data are reported in the following order: chemical shifts (δ); multiplicities (s (singlet), d (doublet), t (triplet), q (quartet), m (multiplet)); coupling constants, J (Hz); integration. All the reagents were purchased from Aladdin-Reagent Inc. and used as obtained.

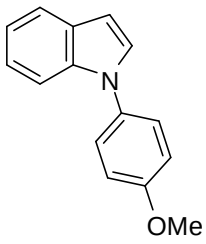
General procedure for the copper-catalyzed coupling N-arylation of indoles in water

To a mixture of CuI (0.04 mmol), 2,2'-bipyridine (0.08 mmol), betaine (0.8 mmol), K_3PO_4 (0.8 mmol), indole (0.4 mmol) and iodobenzene (0.8 mmol) was added nitrogen degassed water (2 mL). The reaction mixture was stirred for 10 h at 90 ^{o}C. Then the reaction mixture was extracted with EtOAc, dried over $MgSO_4$. The solvent was evaporated under reduced pressure. The resultant material was purified by preparatory TLC with silica gel to afford the desired product.

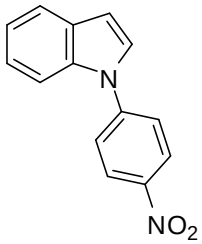


Yield: 96%. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.70 (d, J = 8.0 Hz, 1 H), 7.58 (d, J = 8.0 Hz, 1 H), 7.55-7.50 (m, 4 H) 7.40-7.33 (m, 2 H), 7.23 (t, J = 8.0, 1 H), 7.18 (t, J = 8.0, 1 H), 6.70 (d, J = 3.0,

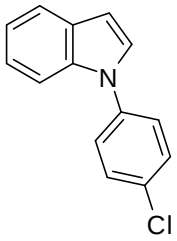
1 H).[1]



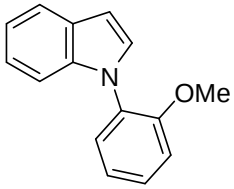
Yield: 81%. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.69 (d, J = 8.0 Hz, 1 H), 7.47 (d, J = 8.0 Hz, 1 H), 7.42 (d, J = 9.0 Hz, 2 H), 7.29 (d, J = 3.5, 1 H), 7.22 (t, J = 8.0, 1 H), 7.16 (t, J = 8.0, 1 H), 7.04 (d, J = 9.0, 2 H), 6.66 (d, J = 3.5, 1 H), 3.89 (s, 3 H).[2]



Yield: 95%. ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.44-8.39 (m, 2 H), 7.74-7.66 (m, 4 H), 7.39 (d, J = 3.5 Hz, 1 H), 7.34-7.23 (m, 2 H), 6.78 (d, J = 3.5 Hz, 1 H).[3]

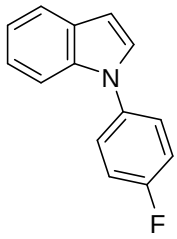


Yield: 82%. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.70 (d, J = 8.0 Hz, 1 H), 7.54-7.43 (m, 5H), 7.30 (d, J = 3.0 Hz, 1 H), 7.27-7.17 (m, 2 H), 6.70 (d, J =3.0 Hz, 1 H).[4]

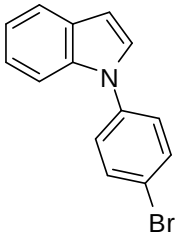


[1] R. K. Rao, A. B. Naidu, E.A. Jaseer and G. Sekar, *Tetrahedron*, 2009, **65**, 4619.
[2] G. Yan, C. Kuang, Y. Zhang and J. Wang, *Org. Lett.*, 2010, **12**, 1052.
[3] H.-G. Lee, J.-E. Won, M.-J. Kim, S,-E, Park, K,-J, Jung, B, R, Kim, S,-G, Lee and Y.-J. Yoon, *J. Org. Chem.*, 2009, **74**, 5675.
[4] H.-C. Ma and X.-Z. Jiang, *J. Org. Chem.*, 2007, **72**, 8943.

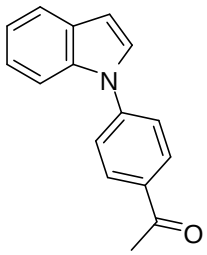
Yield: 62%. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.68 (d, J = 8.0 Hz, 1 H), 7.43-7.37 (m, 2 H), 7.29 (d, J = 3.5 Hz, 1 H), 7.25-7.06 (m, 5 H) 6.67 (d, J = 3.5 Hz, 1 H), 3.78 (s, 3 H).[5]



Yield: 76%. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.70 (d, J = 8.0 Hz, 1 H), 7.50-7.44 (m, 3 H), 7.29 (d, J = 3.5 Hz, 1 H), 7.26-7.16 (m, 4 H) 6.69 (d, J = 3.5 Hz, 1 H).[6]



Yield: 57%. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.69 (d, J = 8.0 Hz, 1 H), 7.64 (d, J = 8.5 Hz, 2 H), 7.52 (d, J = 8.0 Hz, 1 H), 7.40 (d, J = 8.5 Hz, 2 H), 7.30 (d, J = 3.5 Hz, 1 H), 7.24 (t, J = 8.0 Hz, 1 H), 7.18 (t, J = 8.0 Hz, 1 H), 6.70 (d, J =3.5 Hz, 1 H).[7]



Yield: 63%. ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.13 (d, J = 8.0 Hz, 2 H), 7.70 (d, J = 8.0 Hz, 1 H), 7.65 (d, J =8.0 Hz, 1 H), 7.63 (d, J = 8.0 Hz, 2 H), 7.39 (d, J = 3.5 Hz, 1 H), 7.27 (t, J = 8.0 Hz, 1 H), 7.21(t, J = 8.0 Hz, 1 H), 6.74 (d, J = 3.5 Hz, 1 H), 2.66 (s, 3 H).[8]

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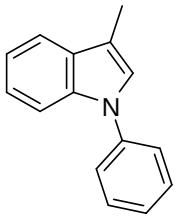
[5] F.-F. Yong, Y.-C. Teo, S.-H. Tay, B. Y.-H. Tan and K.-H. Lim, *Tetrahedron Lett.*, 2011, **52**, 1161.

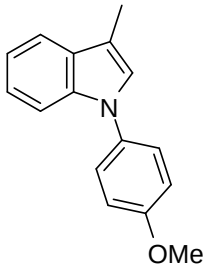
[6] E.-C. Elliott, E. R. Bowkett, J. L. Maggs, J. Bacsa, B. K. Park, S. L. Regan, P. M. O'Neill and A. V. Stachulski, *Org. Lett.*, 2011, **13**, 5592.

[7] C. Cheng, G. Sun, J. Wan and C. Sun, *Synlett*, 2009, 2663.

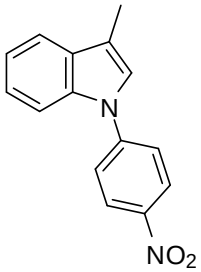
[8] Q. Cai, W. Zhu, H. Zhang, Y. Zhang and D. Ma, *Synthesis*, 2005, 496.



Yield: 78%. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.64 (d, J = Hz, 1 H), 7.57 (d, J = Hz, 1 H), 7.53-7.48 (m, 3 H), 7.36-7.30 (m, 2 H), 7.27-7.14 (m, 3 H), 2.41 (s, 3 H).[9]



Yield: 78%. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.63 (d, J = 8.0 Hz, 1 H), 7.44 (d, J = 8.0 Hz, 1 H), 7.39 (d, J = 8.0 Hz, 2 H), 7.21 (t, J = 8.0 Hz, 1 H), 7.16 (t, J = 8.0 Hz, 1 H), 7.08 (s, 1 H), 7.02 (d, J = 8.0 Hz, 2 H), 3.88 (s, 3 H), 2.40 (s, 3 H).



Yield: 69%. ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.38 (d, J = 8.5 Hz, 2 H), 7.67-7.63 (m, 4 H), 7.31 (t, J = 8.0 Hz, 1 H), 7.25 (t, J = 8.0 Hz, 1 H), 7.18 (s, 1 H), 2.40 (s, 3 H).[10]

[9] A. K. Verma, J. Singh. and R. C. Larock, *Tetrahedron*, 2009, **65**, 8434.
[10] H. Xu, W.-Q. Liu, L.-L. Fan, Y. Chen, L.-M. Yang, L. Lv and Y.-T. Zheng, *Chem. Pharm. Bull.*, 2008, **56**, 720.