Transition-metal-free, Visible-light Induced Cyclization of Arylsulfonyl Chlorides with *o*-Azidoarylalkynes: A Regiospecific Route to Unsymmetrical 2,3-Disubstituted Indoles

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Supporting Information

List of Contents

- (A) Materials and equipment
- (B) Typical experimental procedure
- (C) Analytical data
- (D) References
- (E) Spectra

(A) Materials and equipment

Reagents were obtained commercially and used as received. Solvents were purified and dried by standard methods. *o*-Azidoarylalkynes **2** were prepared according the literature methods.¹ All title products were characterized by ¹H NMR, ¹³C NMR, MS and High Resolution mass spectrometer (HRMS). ¹H NMR spectra were recorded on 400 MHz in CDCl₃, and ¹³C NMR spectra were recorded on 100 MHz in CDCl₃ using tetramethylsilane (TMS) as an internal standard. Chemical shift values (δ) are given in ppm. Coupling constants (*J*) were measured in Hz. Mass spectra were obtained with ionization voltages of 70 eV. HRMS spectra were obtained by ESI on a TOF mass. 200-300 mesh silica gel was used for column chromatography.

(B) Typical experimental procedure

Typical Experimental Procedure for the Synthesis of compounds 3:

To a Schlenk tube were added arylsulfonyl chlorides **1** (0.35 mmol), *o*-azidoarylalkynes **2** (0.3 mmol), Eosin Y (3 mol%), MeCN (2.0 mL), 1,4-CHD (0.45 mmol), Na₂HPO₄ (0.3 mmol). Then the tube was charged with argon, and was stirred at room temperature with the irradiation of a 5 W blue LED (λ max = 455 nm) for about 12 h. After the reaction was finished, the reaction mixture was diluted in 35 mL ethyl acetate, washed with a saturated solution of brine (8 mL), saturated NaHCO₃ (10 mL), a saturated solution of brine (8 mL), dried (Na₂SO₄) and concentrated in vacuum, and the resulting residue was purified by silica gel column chromatography (hexane/ethyl acetate) to afford the desired products **3**.

(C) Analytical data



2,3-Diphenyl-1H-indole (3aa):

¹H NMR (400 MHz, CDCl₃) δ : 8.23 (brs, 1H), 7.71 (d, J = 8.0 Hz, 1H), 7.54-7.27 (m, 12H), 7.16 (d, J = 8.4 Hz, 1H); ¹³C NMR (100 MHz, CDCl₃) δ : 136.0 135.1, 134.2, 132.8, 132.6, 130.2, 128.8, 128.7, 128.5, 128.2, 127.7, 126.4, 122.8, 120.5, 119.7, 110.6; LRMS (EI 70 ev) m/z (%): 269 (M⁺, 100); HRMS m/z (ESI) calcd for C₂₀H₁₆N (M+H)⁺ 270.1283, found 270.1279.



2-Phenyl-3-p-tolyl-1H-indole (3ab):

¹H NMR (400 MHz, CDCl₃) δ : 8.20 (brs, 1H), 7.74 (d, J = 80 Hz, 1H), 7.50-7.20 (m, 12H), 2.44 (s, 3H); ¹³C NMR (100 MHz, CDCl₃) δ : 136.0, 135.9, 134.1, 132.8, 132.1, 130.0, 129.3, 129.0, 128.7, 128.2, 127.7, 122.7, 120.5, 119.8, 115.1, 111.1, 21.5; LRMS (EI 70 ev) m/z (%): 283 (M⁺, 100); HRMS m/z (ESI) calcd for C₂₁H₁₈N (M+H)⁺ 284.1435, found 284.1441.



3ac

3-(4-Methoxyphenyl)-2-phenyl-1H-indole (3ac):

¹H NMR (400 MHz, CDCl₃) δ : 8.20 (brs, 1H), 7.55-7.51 (m, 3H), 7.48-7.46 (m, 1H), 7.35-7.30 (m, 4H), 7.27-7.25 (m, 1H), 7.16 (t, *J* = 6.8 Hz, 1H), 7.06 (t, *J* = 6.8 Hz, 1H), 6.98 (t, *J* = 7.6 Hz, 2H), 3.84 (s, 3H); ¹³C NMR (100 MHz, CDCl₃) δ : 158.2, 136.4, 133.8, 133.2, 130.9, 128.8, 128.4, 128.3, 128.1, 127.6, 127.1, 122.1, 119.6, 118.7, 114.1, 111.3, 54.5; LRMS (EI 70 ev) *m/z* (%): 299 (M⁺, 100); HRMS m/z (ESI) calcd for C₂₁H₁₈NO (M+H)⁺ 300.1383, found 300.1390.



3-(4-Fluorophenyl)-2-phenyl-1H-indole (3ad):

¹H NMR (400 MHz, CDCl₃) δ : 8.18 (s, 1H), 7.63 (d, J = 8.0 Hz, 1H), 7.40-7.34 (m, 5H), 7.31-7.28 (m, 3H), 7.23-7.20 (m, 1H), 7.16-7.13 (m, 1H), 7.09-7.04 (m, 2H); ¹³C NMR (100 MHz, CDCl₃) δ : 162.7 (d, J = 241.3 Hz), 136.0, 134.3, 132.7, 131.88 (d, J = 6.0 Hz), 131.1, 131.0, 129.05 (d, J = 34.5 Hz), 128.4, 128.0, 122.9, 120.7, 119.5, 115.4 (d, J = 26.5 Hz), 114.2, 111.1; LRMS (EI 70 ev) *m/z* (%): 287 (M⁺, 100); HRMS m/z (ESI) calcd for C₂₀H₁₅FN (M+H)⁺ 288.1189, found 288.1193.



3-(4-Chlorophenyl)-2-phenyl-1H-indole (3ae):

¹H NMR (400 MHz, CDCl₃) δ : 8.19 (brs, 1H), 7.65 (d, J = 8.0 Hz, 1H), 7.46-7.30 (m, 10H), 7.25 (t, J = 6.2 Hz, 1H), 7.18 (t, J = 8.0 Hz, 1H); ¹³C NMR (100 MHz, CDCl₃) δ : 136.1, 134.5, 133.7, 132.4, 132.0, 131.4, 129.1, 128.8, 128.5, 128.3, 128.1, 123.0, 120.8, 119.5, 113.9, 111.0; LRMS (EI 70 ev) m/z (%): 303 (M⁺, 72); HRMS m/z (ESI) calcd for C₂₀H₁₅ClN (M+H)⁺ 304.0894, found 304.0898.



2-Phenyl-3-o-tolyl-1H-indole (3af):

¹H NMR (400 MHz, CDCl₃) δ : 8.25 (brs, 1H), 7.47 (d, J = 8.0 Hz, 1H), 7.37-7.29 (m, 7H), 7.25-7.19 (m, 4H), 7.12 (dd, J = 10.8 Hz, J = 1.6 Hz,1H), 2.08 (s, 3H); ¹³C NMR (100 MHz, CDCl₃) δ : 137.8, 136.1, 134.6, 133.8, 133.1, 131.7, 130.3, 129.8, 128.8, 127.7, 127.2, 126.8, 125.9, 122.8, 120.3, 120.2, 114.9, 110.8, 20.4; LRMS (EI 70 ev) m/z (%): 283 (M⁺, 100); HRMS m/z (ESI) calcd for $C_{21}H_{18}N$ (M+H)⁺ 284.1435, found 284.1444.



2-Phenyl-3-m-tolyl-1H-indole (3ag):

¹H NMR (400 MHz, CDCl₃) δ : 8.24 (brs, 1H), 7.78 (d, J = 8.0 Hz, 1H), 7.50-7.46 (m, 3H), 7.41-7.35 (m, 4H), 7.34-7.19 (m, 5H), 2.43 (s, 3H); ¹³C NMR (100 MHz, CDCl3) δ : 138.8, 136.4, 136.1, 135..5, 134.1, 133.0, 129.3, 129.0, 128.8, 128.3, 127.4, 126.0, 125.3, 124.3, 122.1, 120.1, 118.7, 111.4, 25.1; LRMS (EI 70 ev) *m/z* (%): 283 (M⁺, 100); HRMS m/z (ESI) calcd for C₂₁H₁₈NO (M+H)⁺ 284.1435, found 284.1439.



3-(Naphthalen-1-yl)-2-phenyl-1H-indole (3ah):

¹H NMR (400 MHz, CDCl₃) δ : 8.21 (brs, 1H), 7.99 (d, J = 7.2 Hz, 1H), 7.84 (d, J = 8.0 Hz, 1H), 7.58-7.45 (m, 5H), 7.40-7.36 (m, 2H), 7.33-7.24 (m, 3H), 7.18 (t, J = 7.4 Hz, 3H), 7.09-7.05 (m, 1H); ¹³C NMR (100 MHz, CDCl₃) δ : 137.5, 136.4, 134.6, 134.2, 133.4, 132.2, 130.2, 129.9, 129.5, 129.1, 129.0, 128.3, 127.1, 126.9, 126.7, 126.4, 126.0, 123.1, 120.8, 116.7, 112.3, 111.9; LRMS (EI 70 ev) m/z (%): 319 (M⁺, 100); HRMS m/z (ESI) calcd for C₂₄H₁₈N (M+Na)⁺ 320.1434, found 320.1429.



2-Phenyl-3-(thiophen-2-yl)-1H-indole (3ai):

¹H NMR (400 MHz, CDCl₃) δ : 8.23 (brs, 1H), 7.80 (d, J = 5.6 Hz, 1H), 7.54-7.49 (m, 2H), 7.41 (d, J = 7.2 Hz, 1H), 7.38-7.31 (m, 3H), 7.30 (dd, J = 0.8 Hz, J = 4.8 Hz, 1H), 7.27-7.23 (m, 1H), 7.20-7.17 (m, 1H), 7.08 (dd, J = 2.8 Hz, J = 3.6 Hz, 1H), 7.05 (dd, J = 1.2 Hz, J = 0.8, 1H); ¹³C NMR (100 MHz, CDCl₃) δ : 136.3, 135.6, 135.2, 132.3, 128.8, 128.6, 128.3, 128.0, 127.3, 126.3, 124.6, 122.9, 120.7, 119.8, 110.8, 108.1; LRMS (EI 70 ev) m/z (%): 275 (M⁺, 100); HRMS m/z (ESI) calcd for C₁₈H₁₄NS (M+H)⁺ 276.0841, found 276.0837.



3-(Trifluoromethyl)-2-phenyl-1H-indole (3aj):

¹H NMR (400 MHz, CDCl₃) δ : 8.30 (brs, 1H), 7.84 (d, J = 8.0 Hz, 1H), 7.60-7.57 (m, 2H), 7.51-7.47 (m, 3H), 7.41-7.39 (m, 1H), 7.30-7.23 (m, 2H); ¹³C NMR (100 MHz, CDCl₃) δ : 138.7 (q, J = 4.7 Hz), 135.0, 131.1, 129.9, 129.5, 129.2, 129.1, 128.8, 127.8, 127.3, 125.8 (d, J = 1.7 Hz), 123.6, 121.9, 120.2 (d, J = 2.2 Hz), 111.1, 104.1 (q, J = 35.8 Hz); LRMS (EI 70 ev) m/z (%): 261 (M⁺, 100); HRMS m/z (ESI) calcd for C₁₅H₁₁F₃N (M+H)⁺ 262.0839, found 262.0845.



2-(4-Methoxyphenyl)-3-phenyl-1H-indole (3ba):

¹H NMR (400 MHz, CDCl₃) δ : 8.20 (brs, 1H), 7.75 (d, J = 7.2 Hz, 1H), 7.58 (d, J = 8.0 Hz, 1H), 7.54-7.36 (m, 7H), 7.29 (t, J = 7.2 Hz, 1H), 7.18 (d, J = 5.4 Hz, 1H), 6.85 (d, J = 8.0 Hz, 2H), 3.82 (s, 3H); ¹³C NMR (100 MHz, CDCl₃) δ : 160.3, 137.2, 136.7, 135.1, 130.8, 130.2, 129.5, 129.2, 126.7, 126.0, 122.7, 120.6, 119.5, 114.7, 112.0, 111.8, 55.4; LRMS (EI 70 ev) m/z (%): 299 (M⁺, 100); HRMS m/z (ESI) calcd for C₂₁H₁₈NO (M+H)⁺ 300.1383, found 300.1389.



2-(4-Fluorophenyl)-3-phenyl-1H-indole (3ca):

¹H NMR (400 MHz, CDCl₃) δ : 8.17 (brs, 1H), 7.67 (d, J = 7.6 Hz, 1H), 7.47-7.37 (m, 5H), 7.32-7.29 (m, 1H), 7.27-7.21 (m, 2H), 7.16 (dd, J = 10.4 Hz, J = 2.0 Hz, 2H), 7.10-7.06 (m, 1H), 6.99-6.93 (m, 1H); ¹³C NMR (100 MHz, CDCl₃) δ : 164.1 (d, J = 244.4 Hz), 136.0, 134.8 (d, J = 13.6 Hz), 134.6, 132.7, 130.4, 130.3, 128.9, 128.8, 126.7, 123.9 (d, J = 3.4 Hz), 123.2, 120.7, 120.0, 116.0, 115.1 (d, J = 24.6 Hz), 114.7, 114.5, 111.0; LRMS (EI 70 ev) m/z (%): 287 (M⁺, 100); HRMS m/z (ESI) calcd for C₂₀H₁₅FN (M+H)⁺ 288.1189, found 288.1197.



3-Phenyl-2-(thiophen-2-yl)-1H-indole (3da):

¹H NMR (400 MHz, CDCl₃) δ : 8.26 (brs, 1H), 7.56-7.52 (m, 3H), 7.49 (dd, J = 10.0 Hz, J = 2.4

Hz, 2H), 7.42-7.37 (m, 3H), 7.23 (dd, J = 1.2 Hz, J = 8.4 Hz, 1H), 7.14-7.10 (m, 1H), 6.38 (dd, J = 3.2 Hz, J = 2.8 Hz, 1H), 6.35 (d, J = 3.6 Hz, 2H); ¹³C NMR (100 MHz, CDCl₃) δ : 147.2, 141.5, 135.4, 134.7, 130.3, 128.9, 128.5, 127.1, 125.4, 123.0, 120.4, 119.5, 114.7, 112.0, 1108, 106.9; HRMS m/z (ESI) calcd for C₁₈H₁₄NS (M+H)⁺ 276.0841, found 276.0844.



2-(Naphthalen-1-yl)-3-phenyl-1H-indole (3ea):

¹H NMR (400 MHz, CDCl₃) δ : 8.15 (brs, 1H), 7.91-7.82 (m, 4H), 7.46-7.37 (m, 4H), 7.34-7.31 (m, 3H), 7.28 (t, *J* = 6.8 Hz, 1H), 7.22-7.14 (m, 3H), 7.11 (t, *J* = 7.4 Hz, 1H); ¹³C NMR (100 MHz, CDCl₃) δ : 136.0, 135.0, 133.7, 133.2, 132.3, 130.7, 129.3, 128.8, 128.5, 128.2, 127.7, 126.7, 126.2, 126.1, 125.8, 125.4, 122.7, 120.5, 119.8, 116.8, 111.1; LRMS (EI 70 ev) *m/z* (%): 319 (M⁺, 100); HRMS m/z (ESI) calcd for C₂₄H₁₈N (M+H)⁺ 320.1434, found 320.1439.



5-Fluoro-2,3-diphenyl-1H-indole (3ga):

¹H NMR (400 MHz, CDCl₃) δ : 8.21 (brs, 1H), 7.54-7.41 (m, 6H), 7.40-7.28 (m, 6H), 7.03-6.99 (m, 1H); ¹³C NMR (100 MHz, CDCl₃) δ : 159.4 (d, J = 234.1 Hz), 135.7, 134.4, 132.4, 130.0, 129.2 (d, J = 8.4 Hz), 128.8 (d, J = 9.8 Hz), 128.0, 127.8, 126.5, 115.2, 111.6 (d, J = 10.7 Hz), 111.2, 110.9, 104.7 (d, J = 23.8 Hz); LRMS (EI 70 ev) m/z (%): 287 (M⁺, 100); HRMS m/z (ESI) calcd for C₂₀H₁₅FN (M+H)⁺ 288.1189, found 288.1196.



5-Chloro-2,3-diphenyl-1H-indole (3ha):

¹H NMR (400 MHz, CDCl₃) δ : 8.24 (brs, 1H), 7.67 (d, J = 2.8 Hz, 1H), 7.51-7.43 (m, 5H), 7.41-7.29 (m, 6H), 7.22 (dd, J = 6.8 Hz, J = 2.4 Hz, 1H); ¹³C NMR (100 MHz, CDCl₃) δ : 135.3, 134.2, 134.1, 132.0, 130.1, 129.8, 128.7, 128.6, 128.1, 128.0, 126.6, 126.2, 122.9, 119.1, 114.8, 111.7; LRMS (EI 70 ev) m/z (%): 303 (M⁺, 66); HRMS m/z (ESI) calcd for C₂₀H₁₅ClN (M+H)⁺ 304.0894, found 304.0890.



7-Fluoro-2,3-diphenyl-1H-indole (3ia):

¹H NMR (400 MHz, CDCl₃) δ : 8.39 (brs, 1H), 7.55-7.29 (m, 11H), 7.10-7.04 (m, 1H), 7.03 (ddd, J = 6.0 Hz, J = 2.4 Hz, J = 4.4 Hz, 1H); ¹³C NMR (100 MHz, CDCl₃) δ : 151.1 (d, J = 353.8 Hz), 135.1, 134.7, 132.5 (d, J = 2.5 Hz), 132.3, 130.1, 128.9, 128.3 (d, J = 28.9 Hz), 126.5, 124.4, 124.1, 120.7, 115.7 (d, J = 10.8 Hz), 115.3, 107.5 (d, J = 14.3 Hz); LRMS (EI 70 ev) m/z (%): 287 (M⁺, 100); HRMS m/z (ESI) calcd for C₂₀H₁₅FN (M+H)⁺ 288.1189, found 288.1191.



5,6-Dichloro-2,3-diphenyl-1H-indole (3ja):

¹H NMR (400 MHz, CDCl₃) δ : 8.22 (brs, 1H), 7.69 (s, 1H), 7.53 (s, 1H), 7.45-7.29 (m, 10H); ¹³C NMR (100 MHz, CDCl₃) δ : 135.8, 134.5, 133.7, 131.6, 129.8, 128.8, 128.7, 128.5, 128.1, 128.0, 126.6, 126.1, 124.5, 120.5, 114.6, 112.2; LRMS (EI 70 ev) *m/z* (%): 337 (M⁺, 67); HRMS m/z (ESI) calcd for C₂₀H₁₄Cl₂N (M+H)⁺ 338.0504 found 338.0510



5-Methoxy-2,3-diphenyl-1H-indole (3ka):

¹H NMR (400 MHz, CDCl₃) δ : 8.14 (brs, 1H), 7.47-7.34 (m, 6H), 7.32-7.28 (m, 5H), 7.15 (d, J

= 2.4 Hz, 1H), 6.94 (dd, J = 10.0 Hz, J = 2.4 Hz, 1H), 3.83 (s, 3H); ¹³C NMR (100 MHz, CDCl₃) δ : 154.7, 135.3, 134.8, 132.6, 131.1, 130.0, 129.2, 128.6, 128.5, 128.1, 127.6, 126.2, 114.8, 112.9, 111.7, 101.2, 55.8; LRMS (EI 70 ev) m/z (%): 299 (M⁺, 100); HRMS m/z (ESI) calcd for C₂₁H₁₈NO (M+H)⁺ 300.1383, found 300.1380.



6-Methyl-2,3-diphenyl-1H-indole (3la):

¹H NMR (400 MHz, CDCl₃) δ : 8.09 (brs, 1H), 7.61 (d, J = 8.0 Hz, 1H), 7.51-7.29 (m, 10H), 7.23 (s, 1H), 7.05 (dd, J = 8.4 Hz, J = 0.8 Hz, 1H), 2.51 (s, 3H); ¹³C NMR (100 MHz, CDCl₃) δ : 136.3, 135.2, 133.4, 132.7, 132.5, 130.0, 128.7, 128.3, 127.9, 127.4, 126.5, 126.0, 122.1, 119.5, 114.9, 110.6, 21.4; LRMS (EI 70 ev) m/z (%): 283 (M⁺, 100); HRMS m/z (ESI) calcd for C₂₁H₁₈N (M+H)⁺ 284.1435, found 284.1437.

References

1. Lu, B.; Luo, Y.; Liu, L.; Ye, L.; Wang, Y.; Zhang, L. Angew. Chem. Int. Ed. 2011, 50, 8358.



¹H NMR of Compound 3aa



¹³C NMR of Compound 3aa



¹H NMR of Compound 3ab



¹³C NMR of Compound 3ab



¹H NMR of Compound 3ac



¹³C NMR of Compound 3ac



¹H NMR of Compound 3ad



¹³C NMR of Compound 3ad



¹H NMR of Compound 3ae



¹³C NMR of Compound 3ae



¹H NMR of Compound 3af



¹³C NMR of Compound 3af



¹H NMR of Compound 3ag



¹³C NMR of Compound 3ag



¹H NMR of Compound 3ah



¹³C NMR of Compound 3ah



¹H NMR of Compound 3ai



¹³C NMR of Compound 3ai



¹H NMR of Compound 3aj



¹³C NMR of Compound 3aj



¹H NMR of Compound 3ba



¹³C NMR of Compound 3ba



¹H NMR of Compound 3ca



¹³C NMR of Compound 3ca



¹H NMR of Compound 3da



¹³C NMR of Compound 3da



¹H NMR of Compound 3ea



¹³C NMR of Compound 3ea



¹H NMR of Compound 3ga



¹³C NMR of Compound 3ga



¹H NMR of Compound 3ha



¹³C NMR of Compound 3ha



¹H NMR of Compound 3ia



¹³C NMR of Compound 3ia



¹H NMR of Compound 3ja



¹³C NMR of Compound 3ja



¹H NMR of Compound 3ka



¹³C NMR of Compound 3ka



¹H NMR of Compound 3la



¹³C NMR of Compound 3la