Support Information

Radical-mediated multicomponent cascade reaction for the synthesis of azide-biindole derivatives

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1. General information

All chemicals and reagents were used of commercial grade and were used without no further purification. The reactions were monitored by thin-layer chromatography (TLC) using silica gel GF254. Column chromatography was performed with 200–300 mesh silica gel. All yields refer to isolated products after purification. The intermediates and the products synthesized were fully characterized by spectroscopic data. The NMR spectra were recorded on Bruker DRX-600 ($^1$H: 600 MHz, $^{13}$C: 151 MHz) using DMSO-$d_6$ as solvents. The following abbreviation were used to explain the multiplicities: (s) = singlet, (d) = doublet, (t) = triplet, (q) = quartet, (sept) = septuplet, (dd) = double doublet, (dt) = double triplet, (dq) = double quartet, (ddd) = double-double doublet, (m) = multiplet; Chemical shifts ($\delta$) are expressed in parts per million (ppm) and $J$ values are given in hertz (Hz). IR spectra were recorded on an FT-IR Thermo Nicolet Avatar 360 using a KBr pellet. HRMS was performed on an Agilent LC/MSD TOF instrument. The melting points were measured by the XT-4A melting point apparatus without correction.

2. General Procedure for preparing 3-azido-biindoles 3-4 and triazol product 8

Under air atmosphere, benzimidazole 1 (1 mmol), indole 2 (2.2 mmol), PIFA (1.1 mmol, 473 mg), Cu(OAc)$_2$ (20 mol%, 36.2 mg), NaN$_3$ (1.5 mmol, 97.5 mg) and EA (30 mL) were added to 100 mL reaction tube. The mixture was stirred at reflux temperature in oil bath for 5 h. After cooling to room temperature, the reaction was quenched with saturated NaCl solution and extracted with 60 mL EtOAc for three times. The organic layers were combined, dried over Na$_2$SO$_4$, filtered and evaporated under reduced pressure. The residues were purified by flash column chromatography.
on silica gel to provide the products 3a-3s. The products were further identified by FTIR spectroscopy, NMR spectroscopy, and HRMS.

Under air atmosphere, imidazole 1 (1 mmol), indole 2 (2.2 mmol), PIFA (1.1 mmol, 473 mg), Cu(OAc)$_2$ (20 mol%, 36.2 mg), NaN$_3$ (1.5 mmol, 97.5 mg) and EA (30 mL) were added to 100 mL reaction tube. The mixture was stirred at reflux temperature in oil bath for 5 h. After cooling to room temperature, the reaction was quenched with saturated NaCl solution and extracted with 60 mL EtOAc for three times. The organic layers were combined, dried over Na$_2$SO$_4$, filtered and evaporated under reduced pressure. The residues were purified by flash column chromatography on silica gel to provide the products 4a-4q. The products were further identified by FTIR spectroscopy, NMR spectroscopy, and HRMS.

The reaction of 3-azido-biindole product 3a (7.1 mmol, 2.76 g), methyl but-3-ynoate (8 mmol, 784 mg), CuSO$_4$·5H$_2$O (10 mol%, 177.5 mg), and Cu powder (28.4 mmol, 1.8 g) were placed in a flame-dried Schlenk tube under air, followed by the addition of DMSO (80 mL). The reaction was conducted at room temperature for 3 h in dark place. After that, 120 mL water was added and the reaction was extracted by ethyl acetate. The crude product was purified by flash column chromatography on silica gel to afford the product 8 as reddish brown solid (3.17 g, 92%). The product 8 was
further identified by FTIR spectroscopy, NMR spectroscopy, and HRMS.

3. Spectroscopic Data of 3-8

3'-Azido-2'-(1H-benzo[d]imidazol-1-yl)-1H,3'H-3,3'-biindole (3a)

Reddish brown solid; Mp: 213.4 - 214.1 °C; 295 mg, yield: 76%; IR (KBr): 3440, 2254, 2128, 1662, 826, 763, 633, 603, 550, 503, 454 cm⁻¹; ¹H NMR (600 MHz, DMSO-d₆) δ 11.56 (d, J = 2.9 Hz, 1H, NH), 8.65 (d, J = 8.2 Hz, 1H, ArH), 8.60 (d, J = 2.8 Hz, 1H, ArH), 8.01 (d, J = 7.7 Hz, 1H, ArH), 7.72 (d, J = 8.2 Hz, 1H, ArH), 7.28 (m, 1H, ArH), 7.23 – 7.19 (m, 1H, ArH), 6.73 (t, J = 7.6 Hz, 1H, ArH), 6.64 (d, J = 8.2 Hz, 1H, ArH); ¹³C NMR (151 MHz, DMSO-d₆) δ 165.26, 151.96, 143.31, 141.51, 137.47, 136.03, 131.79, 131.71, 127.29, 126.03, 125.45, 125.19, 123.68, 123.35, 122.46, 121.39, 120.57, 120.24, 117.30, 116.38, 112.78, 109.16, 74.40. HRMS (ESI-TOF) m/z: [M + H]⁺ calcd for C₂₃H₁₆N₇ 390.1462; Found 390.1459.

3'-Azido-2'-(1H-benzo[d]imidazol-1-yl)-5,5'-dichloro-1H,3'H-3,3'-biindole (3b)

Reddish brown solid; Mp: 221.7 - 222.9 °C; 310 mg, yield: 68%; IR (KBr): 3436, 2255, 2124, 1660, 1652, 824, 762, 649, 626, 618, 521, 508, 494 cm⁻¹; ¹H NMR (600 MHz, DMSO-d₆) δ 11.83 (d, J = 2.3 Hz, 1H, NH), 8.64 (d, J = 8.2 Hz, 1H, ArH), 8.56 (s, 1H, ArH), 8.07 (d, J = 2.8 Hz, 1H, ArH), 7.89 (d, J = 8.3 Hz, 1H, ArH), 7.76 (d, J = 8.2 Hz, 1H, ArH), 7.67 (dd, J = 8.3, 2.2 Hz, 1H, ArH), 7.56 (d, J = 7.2 Hz, 1H, ArH), 7.54 (d, J = 2.2 Hz, 1H, ArH), 7.45 (d, J = 7.7 Hz, 1H, ArH), 7.42 (d, J = 8.7 Hz, 1H, ArH), 7.05 (dd, J = 8.7, 2.1 Hz, 1H, ArH), 6.66 (s, 1H, ArH); ¹³C NMR (151 MHz, DMSO-d₆) δ 165.47, 151.96, 143.35, 141.51, 137.47, 136.03, 131.79, 131.71, 127.29, 126.03, 125.45, 125.19, 123.68, 123.35, 122.46, 121.39, 120.57, 120.24, 117.30, 116.38, 112.78, 109.16, 74.40. HRMS (ESI-TOF) m/z: [M + H]⁺ calcd for C₂₃H₁₄Cl₂N₇ 458.0682; Found 458.0680.

3'-Azido-2'-(1H-benzo[d]imidazol-1-yl)-6,6'-dichloro-1H,3'H-3,3'-biindole (3c)
Reddish brown solid; Mp: 226.1 -226.6 °C; 320 mg, yield: 70%; **IR** (KBr): 3437, 2253, 2126, 1659, 823, 763, 625 cm⁻¹; **¹H NMR** (600 MHz, DMSO-d₆) δ 11.75 (s, 1H, NH), 8.65 (d, J = 8.2 Hz, 1H, ArH), 8.60 (s, 1H, ArH), 8.07 (d, J = 2.8 Hz, 1H, ArH), 7.97 (d, J = 1.9 Hz, 1H, ArH), 7.78 (d, J = 7.9 Hz, 1H, ArH), 7.57 (t, J = 7.2 Hz, 1H, ArH), 7.48 – 7.44 (m, 3H, ArH), 7.41 (dd, J = 8.0, 1.9 Hz, 1H, ArH), 6.87 (dd, J = 8.6, 2.0 Hz, 1H, ArH), 6.70 (d, J = 8.7 Hz, 1H, ArH); **¹³C NMR** (151 MHz, DMSO-d₆) δ 166.44, 153.38, 143.37, 141.51, 137.90, 136.12, 134.58, 127.45, 127.12, 126.61, 126.19, 125.72, 125.01, 122.95, 122.03, 121.71, 120.87, 120.69, 118.57, 116.42, 112.50, 109.01, 73.88. **HRMS** (ESI-TOF) m/z: [M + H]⁺ calcd for C₂₅H₁₄Cl₂N₇ 458.0682; Found 458.0677.

3'-Azido-2'-{(1H-benzo[d]imidazol-1-yl)-7,7'-dichloro-1H,3'H-3,3'-biindole (3d)}

Reddish brown solid; Mp: 244.5 -245.3 °C; 233 mg, yield: 51%; **IR** (KBr): 3445, 2252, 2126, 1661, 824, 762, 624, 551, 500, 453 cm⁻¹; **¹H NMR** (600 MHz, DMSO-d₆) δ 12.05 (s, 1H, NH), 8.66 (d, J = 8.1 Hz, 1H, ArH), 8.61 (s, 1H, ArH), 8.12 (d, J = 2.9 Hz, 1H, ArH), 7.76 (d, J = 7.9 Hz, 1H, ArH), 7.68 (d, J = 7.0 Hz, 1H, ArH), 7.62 – 7.54 (m, 1H, ArH), 7.45 (t, J = 7.0 Hz, 1H, ArH), 7.40 (d, J = 6.3 Hz, 1H, ArH), 7.34 (t, J = 7.7 Hz, 1H, ArH), 7.13 (d, J = 7.6 Hz, 1H, ArH), 6.83 (t, J = 7.9 Hz, 1H, ArH), 6.63 (d, J = 8.1 Hz, 1H, ArH); **¹³C NMR** (151 MHz, DMSO-d₆) δ 165.74, 148.64, 143.37, 141.52, 137.63, 134.32, 132.03, 131.71, 128.88, 126.87, 126.31, 125.79, 125.43, 125.10, 122.56, 122.22, 121.66, 120.72, 117.27, 116.39, 116.18, 109.99, 74.94. **HRMS** (ESI-TOF) m/z: [M + H]⁺ calcd for C₂₅H₁₄Cl₂N₇ 458.0682; Found 458.0677.

3'-Azido-2'-{(1H-benzo[d]imidazol-1-yl)-5,5'-dibromo-1H,3'H-3,3'-biindole (3e)}
Reddish brown solid; Mp: 236.8 -237.4 °C; 344 mg, yield: 63%; IR (KBr): 3444, 2250, 2128, 1660, 829, 757, 621, 544, 486, 456, 414 cm\(^{-1}\); \(^1\)H NMR (600 MHz, DMSO-\(d_6\)) \(\delta\) 11.84 (d, \(J = 2.9\) Hz, 1H, NH), 8.64 (d, \(J = 8.2\) Hz, 1H, ArH), 8.54 (s, 1H, ArH), 8.05 (d, \(J = 2.8\) Hz, 1H, ArH), 7.86 – 7.77 (m, 2H, ArH), 7.75 (d, \(J = 7.9\) Hz, 1H, ArH), 7.64 (d, \(J = 1.9\) Hz, 1H, ArH), 7.55 (t, \(J = 7.7\) Hz, 1H, ArH), 7.44 (t, \(J = 7.0\) Hz, 1H, ArH), 7.37 (d, \(J = 8.7\) Hz, 1H, ArH), 7.15 (dd, \(J = 8.6, 1.9\) Hz, 1H, ArH), 6.82 (s, 1H, ArH); \(^{13}\)C NMR (151 MHz, DMSO-\(d_6\)) \(\delta\) 165.35, 151.03, 143.34, 141.45, 137.95, 136.18, 134.83, 131.69, 127.22, 126.67, 126.24, 125.70, 125.21, 124.90, 123.27, 120.69, 119.74, 119.35, 116.34, 115.02, 112.89, 108.11, 74.16. HRMS (ESI-TOF) m/z: [M + H]\(^+\) calcd for C\(_{23}\)H\(_{14}\)Br\(_2\)N\(_7\) 547.9651; Found 547.9654.

3’-Azido-2’-(1H-benzo[d]imidazol-1-yl)-6,6’-dibromo-1H,3’H-3,3’-biindole (3f)

Reddish brown solid; Mp: 201.1 -201.8 °C; 338 mg, yield: 62%; IR (KBr): 3444, 2255, 2125, 1657, 823, 762, 701, 654, 630, 609, 592, 534, 510, 492 cm\(^{-1}\); \(^1\)H NMR (600 MHz, DMSO-\(d_6\)) \(\delta\) 11.73 (d, \(J = 2.5\) Hz, 1H, NH), 8.62 (d, \(J = 8.3\) Hz, 1H, ArH), 8.56 (s, 1H, ArH), 8.07 (d, \(J = 1.8\) Hz, 1H, ArH), 8.03 (d, \(J = 2.8\) Hz, 1H, ArH), 7.76 (d, \(J = 7.8\) Hz, 1H, ArH), 7.61 – 7.50 (m, 3H, ArH), 7.44 (t, \(J = 7.0\) Hz, 1H, ArH), 7.37 (d, \(J = 7.9\) Hz, 1H, ArH), 6.96 (dd, \(J = 8.6, 1.8\) Hz, 1H, ArH), 6.64 (d, \(J = 8.7\) Hz, 1H, ArH); \(^{13}\)C NMR (151 MHz, DMSO-\(d_6\)) \(\delta\) 166.27, 153.46, 143.34, 141.46, 138.33, 134.98, 131.68, 130.03, 126.49, 126.19, 125.77, 125.72, 125.34, 124.50, 123.42, 122.26, 120.68, 118.92, 116.42, 115.46, 115.41, 108.97, 73.93. HRMS (ESI-TOF) m/z: [M + H]\(^+\) calcd for C\(_{23}\)H\(_{14}\)Br\(_2\)N\(_7\) 547.9651; Found 547.9650.

3’-Azido-2’-(1H-benzo[d]imidazol-1-yl)-5,5’-difluoro-1H,3’H-3,3’-biindole (3g)
Reddish brown solid; Mp: 214.2 -214.7 °C; 272 mg, yield: 64%; **IR** (KBr): 3435, 2255, 2129, 1664, 825, 762, 700, 668, 623, 547, 541, 511, 451 cm⁻¹; **¹H NMR** (600 MHz, DMSO-\(d_6\)) \(\delta\) 11.73 (s, 1H, NH), 8.63 (d, \(J = 8.3\) Hz, 1H, ArH), 8.59 (s, 1H, ArH), 8.07 (d, \(J = 2.9\) Hz, 1H, ArH), 7.89 (dd, \(J = 8.5, 4.4\) Hz, 1H, ArH), 7.75 (d, \(J = 7.9\) Hz, 1H, ArH), 7.60 - 7.50 (m, 1H, ArH), 7.47 - 7.37 (m, 4H, ArH), 6.92 (td, \(J = 28.1, 9.2, 2.5\) Hz, 1H, ArH), 6.35 (d, \(J = 7.6\) Hz, 1H, ArH); **¹³C NMR** (151 MHz, DMSO-\(d_6\)) \(\delta\) 165.50, 161.82 (d, \(J = 243\) Hz), 157.81 (d, \(J = 232.5\) Hz), 148.40, 143.71, 141.87, 138.21, 134.53, 132.11, 127.91, 126.53, 125.95, 123.77 (d, \(J = 10.5\) Hz), 123.17 (d, \(J = 9\) Hz), 121.04, 118.75, (d, \(J = 24\) Hz), 116.70, 114.61 (d, \(J = 10.5\) Hz), 112.26 (d, \(J = 25.5\) Hz), 111.33 (d, \(J = 25.5\) Hz), 109.07 (d, \(J = 4.5\) Hz), 102.38 (d, \(J = 25.5\) Hz), 74.77; **¹⁹F NMR** (565 MHz, DMSO-\(d_6\)) \(\delta\) -124.27, -125.17. **HRMS** (ESI-TOF) m/z: [M + H]+ calcd for \(C_{23}H_{14}F_2N_7\) 426.1273; Found 426.1265.

3'-Azido-2'-(1H-benzo[\(d\)]imidazol-1-yl)-6,6'-difluoro-1H,3'H-3,3'-biindole (3h)

Reddish brown solid; Mp: 250.8 -252.1 °C; 255 mg, yield: 60%; **IR** (KBr): 3437, 2257, 2128, 1663, 824, 762, 665, 618, 535, 512, 463, 426 cm⁻¹; **¹H NMR** (600 MHz, DMSO-\(d_6\)) \(\delta\) 11.65 (s, 1H, NH), 8.62 (d, \(J = 8.2\) Hz, 1H, ArH), 8.60 (s, 1H, ArH), 8.02 (d, \(J = 2.7\) Hz, 1H, ArH), 7.80 – 7.70 (m, 2H, ArH), 7.59 – 7.52 (m, 1H, ArH), 7.48 – 7.40 (m, 2H, ArH), 7.16 (td, \(J = 9.2, 8.5, 4.3\) Hz, 2H, ArH), 6.69 (td, \(J = 9.3, 2.4\) Hz, 1H, ArH), 6.63 (dd, \(J = 8.9, 5.2\) Hz, 1H, ArH); **¹³C NMR** (151 MHz, DMSO-\(d_6\)) \(\delta\) 166.80, 164.45 (d, \(J = 244.5\) Hz), 159.46 (d, \(J = 235.5\) Hz), 153.82 (d, \(J = 12\) Hz), 143.34, 141.46, 137.53 (d, \(J = 13.5\) Hz), 131.78 (d, \(J = 24\) Hz), 126.17, 126.12, 125.68, 125.14 (d, \(J = 10.5\) Hz), 120.67, 120.11, 118.32 (d, \(J = 10.5\) Hz), 116.41, 113.72 (d, \(J = 22.5\) Hz), 109.54 (d, \(J = 24\) Hz), 109.21, 109.18, 109.01, 98.87 (d, \(J = 22.5\) Hz), 73.83; **¹⁹F NMR** (565 MHz, DMSO-\(d_6\)) \(\delta\) -109.13, -120.30. **HRMS** (ESI-TOF) m/z: [M + H]+ calcd for \(C_{23}H_{14}F_2N_7\) 426.1273; Found 426.1268.

3'-Azido-2'-(1H-benzo[\(d\)]imidazol-1-yl)-7,7'-dimethyl-1H,3'H-3,3'-biindole (3i)
Reddish brown solid; Mp: 204.7 -205.3 °C; 200 mg, yield: 48%; IR (KBr): 3444, 2252, 2125, 1666, 822, 625, 583 cm⁻¹; ¹H NMR (600 MHz, DMSO-d₆) δ 11.53 (s, 1H, NH), 8.69 (d, J = 8.2 Hz, 1H, ArH), 8.59 (s, 1H, ArH), 7.99 (d, J = 2.9 Hz, 1H, ArH), 7.73 (d, J = 7.9 Hz, 1H, ArH), 7.54 (t, J = 7.8 Hz, 1H, ArH), 7.44 – 7.41 (m, 1H, ArH), 7.40 (d, J = 3.3 Hz, 1H, ArH), 7.20 (t, J = 7.4 Hz, 1H, ArH), 7.16 (d, J = 7.3 Hz, 1H, ArH), 6.79 (d, J = 7.1 Hz, 1H, ArH), 6.64 (t, J = 7.6 Hz, 1H, ArH), 6.46 (d, J = 8.1 Hz, 1H, ArH), 2.71 (s, 3H, CH₃), 2.40 (s, 3H, CH₃); ¹³C NMR (151 MHz, DMSO-d₆) δ 164.24, 150.26, 143.31, 141.47, 136.96, 135.86, 132.81, 131.85, 130.79, 127.10, 126.01, 125.38, 124.76, 123.13, 122.91, 122.07, 121.00, 120.52, 120.45, 116.39, 114.94, 109.76, 74.70, 17.09, 16.76. HRMS (ESI-TOF) m/z: [M + H]⁺ calcd for C₂₅H₂₀N₇ 418.1775; Found 418.1770.

3’-Azido-2’-(1H-benzo[d]imidazol-1-yl)-5,5’-dimethoxy-1H,3’H,3’,3’-biindole (3j)

Reddish brown solid; Mp: 248.9 -250.2 °C; 296 mg, yield: 66%; IR (KBr): 3655, 3442, 2258, 2122, 2001, 1660, 1220, 824, 768, 626, 566, 554, 499, 420 cm⁻¹; ¹H NMR (600 MHz, DMSO-d₆) δ 11.45 (s, 1H, NH), 8.67 (d, J = 8.2 Hz, 1H, ArH), 8.62 (s, 1H, ArH), 7.99 (s, 1H, ArH), 7.82 (d, J = 8.5 Hz, 1H, ArH), 7.78 (d, J = 8.0 Hz, 1H, ArH), 7.57 (t, J = 7.8 Hz, 1H, ArH), 7.46 (t, J = 7.7 Hz, 1H, ArH), 7.30 (d, J = 8.6 Hz, 1H, ArH), 7.17 (d, J = 7.3 Hz, 1H, ArH), 7.01 (s, 1H, ArH), 6.71 (d, J = 8.9 Hz, 1H, ArH), 6.13 (s, 1H, ArH), 3.81 (s, 3H, CH₃), 3.44 (s, 3H, CH₃); ¹³C NMR (151 MHz, DMSO-d₆) δ 163.56, 159.04, 153.91, 145.03, 143.27, 141.39, 137.58, 132.50, 131.78, 125.87, 125.71, 125.26, 123.76, 121.95, 120.53, 116.13, 115.82, 113.45, 111.93, 110.46, 108.67, 99.61, 74.50, 56.26, 55.40. HRMS (ESI-TOF) m/z: [M + H]⁺ calcd for C₂₅H₂₄N₇O₂ 450.1673; Found 450.1665.

3’-Azido-2’-(5-fluoro-1H-benzo[d]imidazol-1-yl)-1H,3’H-3,3’-biindole (3k)
Reddish brown solid; Mp: 265.3 -266.6 °C; 260 mg, yield: 64%; **IR** (KBr): 3447, 2255, 2129, 1659, 517, 451 cm⁻¹; **¹H NMR** (600 MHz, DMSO-<sub>d₆</sub>) δ 11.58 (s, 1H, NH), 8.60 (s, 1H, ArH), 8.41 (dd, <i>J</i> = 9.1, 2.6 Hz, 1H, ArH), 8.02 (d, <i>J</i> = 2.8 Hz, 1H, ArH), 7.87 (d, <i>J</i> = 7.8 Hz, 1H, ArH), 7.76 (dd, <i>J</i> = 8.7, 4.9 Hz, 1H, ArH), 7.59 (t, <i>J</i> = 7.7 Hz, 1H, ArH), 7.38 (t, <i>J</i> = 8.5 Hz, 2H, ArH), 7.35 – 7.27 (m, 2H, ArH), 7.01 (t, <i>J</i> = 7.6 Hz, 1H, ArH), 6.75 (t, <i>J</i> = 7.6 Hz, 1H, ArH), 6.64 (d, <i>J</i> = 8.2 Hz, 1H, ArH); **¹³C NMR** (151 MHz, DMSO-<sub>d₆</sub>) δ 165.16, 160.62 (d, <i>J</i> = 238.5 Hz), 151.71, 142.12, 139.84, 138.86, 137.46, 135.96, 131.74, 127.46, 125.28, 123.68, 123.30 (d, <i>J</i> = 10.5 Hz), 122.49, 121.74 (d, <i>J</i> = 10.5 Hz), 121.56, 120.29, 117.31, 113.37 (d, <i>J</i> = 24 Hz), 112.80, 108.89, 103.31 (d, <i>J</i> = 28.5 Hz), 74.32; **¹⁹F NMR** (565 MHz, DMSO-d₆) δ -115.38. **HRMS** (ESI-TOF) m/z: [M + H]+ calcd for C₂₃H₁₅F₇N₇ 408.1367; Found 408.1361.

3'-Azido-5,5'-dichloro-2'-(5-fluoro-1H-benzo[d]imidazol-1-yl)-1H,3'H-3,3'-biindole (3l)

Reddish brown solid; Mp: 244.4 -245.3 °C; 280 mg, yield: 59%; **IR** (KBr): 3442, 2259, 2127, 1660, 1478, 824, 763, 622, 553, 516, 453 cm⁻¹; **¹H NMR** (600 MHz, DMSO-<sub>d₆</sub>) δ 11.86 (s, 1H, NH), 8.62 (s, 1H, ArH), 8.63 – 8.61 (m, 1H, ArH), 8.08 (d, <i>J</i> = 2.8 Hz, 1H, ArH), 7.87 (d, <i>J</i> = 8.3 Hz, 1H, ArH), 7.65 (dd, <i>J</i> = 8.3, 2.1 Hz, 1H, ArH), 7.59 (t, <i>J</i> = 9.0, 2.6 Hz, 1H, ArH), 7.54 (d, <i>J</i> = 2.1 Hz, 1H, ArH), 7.44 – 7.37 (m, 2H, ArH), 7.04 (dd, <i>J</i> = 8.7, 2.1 Hz, 1H, ArH), 6.65 (s, 1H, ArH); **¹³C NMR** (151 MHz, DMSO-<sub>d₆</sub>) δ 165.23, 159.55, 150.44, 143.18, 137.70, 135.94, 131.93, 131.80, 128.34, 127.48, 124.92, 124.18, 124.00, 122.91, 122.67, 117.29 (d, <i>J</i> = 10.5 Hz), 116.27, 114.61, 114.05, 113.88, 108.09, 106.96 (d, <i>J</i> = 24 Hz), 74.04; **¹⁹F NMR** (565 MHz, DMSO-d₆) δ -115.96. **HRMS** (ESI-TOF) m/z: [M + H]+ calcd for C₂₅H₁₅Cl₂F₇N₇ 476.0588; Found 476.0583.

3'-Azido-6,6'-dichloro-2'-(5-fluoro-1H-benzo[d]imidazol-1-yl)-1H,3'H-3,3'-biindole (3m)

S10
Reddish brown solid; Mp: 249.1 -249.5 °C; 285 mg, yield: 60%; IR (KBr): 3442, 2255, 2126, 1651, 823, 763, 624, 585, 533, 486, 434 cm⁻¹; ¹H NMR (600 MHz, DMSO-d₆) δ 11.74 (s, 1H, NH), 8.56 (s, 1H, ArH), 8.38 (dd, J = 9.1, 2.6 Hz, 1H, ArH), 8.04 (d, J = 2.8 Hz, 1H, ArH), 7.97 (d, J = 1.9 Hz, 1H, ArH), 7.78 (dd, J = 8.7, 4.8 Hz, 1H, ArH), 7.47 – 7.40 (m, 2H, ArH), 7.39 (dd, J = 7.9, 1.9 Hz, 1H, ArH), 7.31 (td, J = 9.1, 2.6 Hz, 1H, ArH), 6.85 (dd, J = 8.7, 1.9 Hz, 1H, ArH), 6.69 (d, J = 8.7 Hz, 1H, ArH); ¹³C NMR (151 MHz, DMSO-d₆) δ 166.33, 159.89, 153.12, 142.07, 139.89, 137.90, 136.15, 134.51, 132.00, 127.48, 127.27, 126.68, 125.00, 122.01, 121.91, 120.90, 118.60, 113.67, 113.51, 112.50, 108.76, 103.47 (d, J = 30 Hz), 73.81; ¹⁹F NMR (565 MHz, DMSO-d₆) δ -115.19. HRMS (ESI-TOF) m/z: [M + H]⁺ calcd for C₂₃H₁₃Cl₂FN₇ 476.0588; Found 476.0586.

3’-Azido-7,7’-dichloro-2’-(5-fluoro-1H-benzo[d]imidazol-1-yl)-1H,3’H-3,3’-biindole (3n)

Reddish brown solid; Mp: 277.3 -278.5 °C; 247 mg, yield: 52%; IR (KBr): 3447, 2252, 2126, 1666, 826, 766, 624, 590, 529, 501, 479 cm⁻¹; ¹H NMR (600 MHz, DMSO-d₆) δ 12.06 (d, J = 2.9 Hz, 1H, NH), 8.62 (s, 1H, ArH), 8.39 (dd, J = 9.0, 2.7 Hz, 1H, ArH), 8.12 (d, J = 2.9 Hz, 1H, ArH), 7.80 (dd, J = 8.8, 4.8 Hz, 1H, ArH), 7.69 (dd, J = 8.1, 1.1 Hz, 1H, ArH), 7.41 (dd, J = 7.4, 1.1 Hz, 1H, ArH), 7.39 – 7.31 (m, 2H, ArH), 7.14 (d, J = 6.9 Hz, 1H, ArH), 6.85 (t, J = 7.9 Hz, 1H, ArH), 6.64 (d. J = 8.2 Hz, 1H, ArH); ¹³C NMR (151 MHz, DMSO-d₆) δ 165.67, 160.67 (d, J = 238.5 Hz), 148.36, 142.16, 139.90, 137.56, 134.31, 132.05, 131.95 (d, J = 30 Hz), 129.08, 126.96, 125.55, 125.08, 122.58, 122.24, 121.94 (d, J = 9 Hz), 121.72, 117.27, 116.23, 113.68 (d, J = 25.5 Hz), 109.71, 103.37 (d, J = 30 Hz), 74.88; ¹⁹F NMR (565 MHz, DMSO-d₆) δ -114.95. HRMS (ESI-TOF) m/z: [M + H]⁺ calcd for C₂₃H₁₃Cl₂FN₇ 476.0588; Found 476.0582.

3’-Azido-5,5’-dibromo-2’-(5-fluoro-1H-benzo[d]imidazol-1-yl)-1H,3’H-3,3’-biindole (3o)
Reddish brown solid; Mp: 269.8 - 270.6 °C; 315 mg, yield: 56%; **IR** (KBr): 3442, 2253, 1717, 1660, 1478, 826, 763, 622, 516, 455 cm⁻¹; **¹H NMR** (600 MHz, DMSO-d₆) δ 11.83 (s, 1H, NH), 8.63 (dd, J = 9.0, 4.9 Hz, 1H, ArH), 8.59 (s, 1H, ArH), 8.04 (d, J = 2.8 Hz, 1H, ArH), 7.85 - 7.76 (m, 2H, ArH), 7.67 - 7.59 (m, 2H, ArH), 7.42 (tt, J = 9.1, 2.6 Hz, 1H, ArH), 7.37 (d, J = 8.6 Hz, 1H, ArH), 7.16 (dd, J = 8.4, 2.0 Hz, 1H, ArH), 6.81 (s, 1H, ArH); **¹³C NMR** (151 MHz, DMSO-d₆) δ 165.14, 160.39 (d, J = 238.5 Hz), 150.85, 144.19 (d, J = 13.5 Hz), 143.16, 137.98, 136.17, 134.87, 128.37, 127.31, 126.71, 125.21, 124.89, 123.34, 119.88, 119.35, 117.30 (d, J = 9 Hz), 115.03, 114.00 (d, J = 24 Hz), 112.89, 107.99, 106.99 (d, J = 25.5 Hz), 74.06; **¹⁹F NMR** (565 MHz, DMSO-d₆) δ -116.74. **HRMS** (ESI-TOF) m/z: [M + H]⁺ calcd for C₂₃H₁₃Br₂F₅N₇ 565.9557; Found 565.9553.

3'-Azido-5,5'-dichloro-2'-(5-chloro-1H-benzo[d]imidazol-1-yl)-1H,3'H-3,3'-biindole (3p)

Reddish brown solid; Mp: 255.2 - 256.5 °C; 324 mg, yield: 66%; **IR** (KBr): 3439, 2243, 2124, 1656. 829, 759, 617, 571, 527 cm⁻¹; **¹H NMR** (600 MHz, DMSO-d₆) δ 11.83 (d, J = 2.9 Hz, 1H, NH), 8.61 (t, J = 4.4 Hz, 2H, ArH), 8.06 (d, J = 2.8 Hz, 1H, ArH), 7.88 (d, J = 8.3 Hz, 1H, ArH), 7.85 (d, J = 2.1 Hz, 1H, ArH), 7.67 (dd, J = 8.3, 2.2 Hz, 1H, ArH), 7.59 (dd, J = 8.7, 2.2 Hz, 1H, ArH), 7.55 (d, J = 2.1 Hz, 1H, ArH), 7.41 (d, J = 8.7 Hz, 1H, ArH), 7.05 (dd, J = 8.7, 2.1 Hz, 1H, ArH), 6.66 (d, J = 2.0 Hz, 1H, ArH); **¹³C NMR** (151 MHz, DMSO-d₆) δ 165.28, 150.39, 144.36, 142.94, 137.72, 135.96, 131.94, 131.90, 130.58, 129.98, 127.49, 126.29, 124.96, 124.21, 124.00, 122.97, 122.68, 120.38, 117.53, 116.31, 114.61, 107.99, 74.13. **HRMS** (ESI-TOF) m/z: [M + H]⁺ calcd for C₂₃H₁₃Cl₃N₇ 492.0293; Found 492.0284.

3'-Azido-6,6'-dichloro-2'-(5-chloro-1H-benzo[d]imidazol-1-yl)-1H,3'H-3,3'-biindole (3q)
Reddish brown solid; Mp: 272.3 -273.7 °C; 299 mg, yield: 61%; IR (KBr): 3441, 2269, 1656, 1497, 1455, 821, 764, 578, 529, 495, 484, 447 cm⁻¹; ¹H NMR (600 MHz, DMSO-d₆) δ 11.73 (d, J = 2.8 Hz, 1H, NH), 8.65 (d, J = 2.1 Hz, 1H, ArH), 8.59 (s, 1H, ArH), 8.04 (d, J = 2.8 Hz, 1H, ArH), 8.02 (d, J = 1.9 Hz, 1H, ArH), 7.77 (d, J = 8.5 Hz, 1H, ArH), 7.48 (dd, J = 8.5, 2.1 Hz, 1H, ArH), 7.43 (d, J = 8.1 Hz, 2H, ArH), 7.39 (dd, J = 7.9, 1.9 Hz, 1H, ArH), 6.85 (dd, J = 8.7, 1.9 Hz, 1H, ArH), 6.70 (d, J = 8.7 Hz, 1H, ArH); ¹³C NMR (151 MHz, DMSO-d₆) δ 166.28, 153.06, 142.33, 142.19, 137.90, 136.18, 134.52, 132.38, 130.55, 127.47, 127.32, 126.70, 125.97, 124.98, 122.06, 122.02, 121.99, 120.92, 118.64, 116.20, 112.49, 108.75, 73.81. HRMS (ESI-TOF) m/z: [M + H]⁺ calcd for C₂₃H₁₃Cl₃N₇ 492.0293; Found 492.0287.

3'-Azido-5,5'-dibromo-2'-(5-chloro-1H-benzo[d]imidazol-1-yl)-1H,3'H-3,3'-biindole (3r)

Reddish brown solid; Mp: 240.6 -241.4 °C; 346 mg, yield: 60%; IR (KBr): 3443, 2364, 2254, 2127, 1659, 1461, 821, 769, 625, 546, 455, 430 cm⁻¹; ¹H NMR (600 MHz, DMSO-d₆) δ 11.84 (d, J = 2.9 Hz, 1H, NH), 8.61 (s, 1H, ArH), 8.60 (s, 1H, ArH), 8.04 (d, J = 2.8 Hz, 1H, ArH), 7.85 - 7.81 (m, 1H, ArH), 7.79 (dd, J = 10.0, 8.1 Hz, 1H, ArH), 7.64 (dd, J = 8.7, 2.0 Hz, 1H, ArH), 7.57 (dd, J = 8.8, 2.1 Hz, 1H, ArH), 7.36 (d, J = 8.7 Hz, 1H, ArH), 7.14 (dd, J = 8.6, 1.9 Hz, 1H, ArH), 6.87 (d, J = 8.3 Hz, 1H, ArH), 6.81 (s, 1H, ArH); ¹³C NMR (151 MHz, DMSO-d₆) δ 165.15, 159.42, 150.79, 144.38, 142.94, 140.53, 137.97, 136.19, 134.86, 130.00, 127.35, 126.71, 126.28, 125.22, 123.37, 120.38, 119.96, 119.39, 117.52, 115.01, 112.92, 107.89, 74.10. HRMS (ESI-TOF) m/z: [M + H]⁺ calcd for C₂₃H₁₃Br₂ClN₇ 579.9282; Found 579.9284.

3'-Azido-6,6'-dichloro-2'-(5,6-dimethyl-1H-benzo[d]imidazol-1-yl)-1H,3'H-3,3'-biindole (3s)
Reddish brown solid; Mp: 229.6 - 231.2 °C; 227 mg, yield: 47%; IR (KBr): 3448, 2269, 2129, 1662, 829, 768, 626, 550, 511, 422 cm⁻¹; \(^1\)H NMR (600 MHz, DMSO-\(d_6\)) \(\delta\) 11.73 (s, 1H, NH), 8.42 (s, 1H, ArH), 8.39 (s, 1H, ArH), 8.03 (d, \(J = 2.7\) Hz, 1H, ArH), 7.94 (d, \(J = 1.7\) Hz, 1H, ArH), 7.51 (s, 1H, ArH), 7.45 - 7.39 (m, 2H, ArH), 7.38 - 7.34 (m, 1H, ArH), 6.84 (dd, \(J = 8.6, 1.8\) Hz, 1H, ArH), 6.66 (d, \(J = 8.7\) Hz, 1H, ArH), 2.41 (s, 3H, \(CH_3\)), 2.33 (s, 3H, \(CH_3\)) \(^{13}\)C NMR (151 MHz, DMSO-\(d_6\)) \(\delta\) 166.33, 153.51, 141.84, 140.62, 137.88, 136.09, 134.98, 134.37, 130.02, 127.44, 126.91, 126.45, 124.95, 122.02, 121.60, 120.85, 120.70, 118.54, 116.47, 112.48, 109.19, 73.81, 20.65, 20.22. HRMS (ESI-TOF) m/z: [M - H]⁻ calcd for C\(_{25}\)H\(_{18}\)Cl\(_2\)N\(_7\) 484.0850; Found 484.0847.

3'-Azido-2'-(1H-imidazol-1-yl)-1H,3'H-3,3'-biindole (4a)

Reddish brown solid; Mp: 142.9 - 144.2 °C; 247 mg, yield: 73%; IR (KBr): 3448, 2256, 2121, 1655, 1452, 1307, 829, 767, 667, 626, 575, 511, 453, 424 cm⁻¹; \(^1\)H NMR (600 MHz, Acetone-\(d_6\)) \(\delta\) 10.67 (s, 1H, NH), 8.11 (s, 1H, ArH), 7.76 (d, \(J = 2.7\) Hz, 1H, ArH), 7.64 (t, \(J = 1.5\) Hz, 1H, ArH), 7.58 (d, \(J = 7.7\) Hz, 1H, ArH), 7.41 (td, \(J = 7.6, 1.3\) Hz, 1H, ArH), 7.28 (d, \(J = 8.2\) Hz, 1H, ArH), 7.23 (d, \(J = 6.2\) Hz, 1H, ArH), 7.17 (td, \(J = 7.5, 1.0\) Hz, 1H, ArH), 6.94 – 6.89 (m, 1H, ArH), 6.87 (d, \(J = 1.6\) Hz, 1H, ArH), 6.72 – 6.62 (m, 2H, ArH); \(^{13}\)C NMR (151 MHz, Acetone-\(d_6\)) \(\delta\) 164.53, 151.60, 137.50, 136.81, 136.21, 131.09, 130.23, 126.90, 124.20, 123.43, 123.37, 122.35, 120.95, 119.92, 117.50, 116.72, 112.14, 109.23, 73.91. HRMS (ESI-TOF) m/z: [M + H]⁺ calcd for C\(_{19}\)H\(_{14}\)N\(_7\) 340.1305; Found 340.1302.

3'-Azido-6,6'-dichloro-2'-(1H-imidazol-1-yl)-1H,3'H-3,3'-biindole (4b)
Reddish brown solid; Mp: 202.7 -203.4 °C; 260 mg, yield: 64%; **IR** (KBr): 3448, 2248, 2117, 1648, 826, 769, 630, 568, 534, 480, 435, 412 cm⁻¹; **¹H NMR** (600 MHz, DMSO-d₆) δ 11.72 (d, J = 2.8 Hz, 1H, NH), 8.30 (s, 1H, ArH), 7.98 (d, J = 2.7 Hz, 1H, ArH), 7.86 (d, J = 1.6 Hz, 1H, ArH), 7.76 (s, 1H, ArH), 7.44 (d, J = 1.9 Hz, 1H, ArH), 7.41 - 7.36 (m, 2H, ArH), 7.15 - 7.06 (m, 1H, ArH), 6.89 (dd, J = 8.6, 1.9 Hz, 1H, ArH), 6.62 (d, J = 8.6 Hz, 1H, ArH); **¹³C NMR** (151 MHz, DMSO-d₆) δ 165.70, 152.70, 137.84, 136.75, 136.11, 135.38, 131.09, 127.41, 126.71, 125.12, 122.05, 121.75, 120.83, 118.67, 117.43, 116.59, 112.48, 108.31, 73.23. **HRMS** (ESI-TOF) m/z: [M + H]⁺ calcld for C₁₉H₁₁Cl₂N₄ 408.0526; Found 408.0520.

3'-Azido-6,6'-dibromo-2'-(1H-imidazol-1-yl)-1H,3'H-3,3'-biindole (4c)

![Structure of 3'-Azido-6,6'-dibromo-2'-(1H-imidazol-1-yl)-1H,3'H-3,3'-biindole (4c)](image)

Reddish brown solid; Mp: 191.3 -192.5 °C; 292 mg, yield: 59%; **IR** (KBr): 3448, 2259, 2124, 1658, 1306, 828, 769, 630, 544, 513, 455, 422 cm⁻¹; **¹H NMR** (600 MHz, DMSO-d₆) δ 11.76 (d, J = 2.8 Hz, 1H, NH), 8.33 (d, J = 1.1 Hz, 1H, ArH), 8.03 (d, J = 1.8 Hz, 1H, ArH), 8.00 (d, J = 2.7 Hz, 1H, ArH), 7.80 (t, J = 1.5 Hz, 1H, ArH), 7.63 (d, J = 1.8 Hz, 1H, ArH), 7.57 (dd, J = 7.9, 1.8 Hz, 1H, ArH), 7.37 (d, J = 7.9 Hz, 1H, ArH), 7.13 (d, J = 1.6 Hz, 1H, ArH), 7.05 (dd, J = 8.6, 1.8 Hz, 1H, ArH), 6.62 (d, J = 8.6 Hz, 1H, ArH); **¹³C NMR** (151 MHz, DMSO-d₆) δ 165.54, 152.78, 138.28, 136.73, 135.78, 131.08, 130.33, 126.58, 125.45, 124.53, 124.47, 123.39, 122.27, 119.02, 117.42, 115.44, 115.38, 108.28, 73.28. **HRMS** (ESI-TOF) m/z: [M + H]⁺ calcld for C₁₉H₁₂Br₂N₇ 497.9495; Found 497.9488.

3'-Azido-6,6'-difluoro-2'-(1H-imidazol-1-yl)-1H,3'H-3,3'-biindole (4d)

![Structure of 3'-Azido-6,6'-difluoro-2'-(1H-imidazol-1-yl)-1H,3'H-3,3'-biindole (4d)](image)
Reddish brown solid; Mp: 130.7 -131.4 °C; 228 mg, yield: 61%; **IR** (KBr): 3442, 2258, 2128, 1998, 1654, 1213, 1150, 821, 768, 632, 573, 456, 424 cm⁻¹; **¹H NMR** (600 MHz, DMSO-\(d_6\)) \(\delta\) 11.64 (s, 1H, NH), 8.31 (s, 1H, ArH), 7.77 (t, \(J = 1.5\) Hz, 1H, ArH), 7.67 (dd, \(J = 8.9, 2.4\) Hz, 1H, ArH), 7.41 (dd, \(J = 8.2, 5.2\) Hz, 1H, ArH), 7.17 (dd, \(J = 9.9, 2.4\) Hz, 1H, ArH), 7.15 - 7.12 (m, 1H, ArH), 7.09 (s, 1H, C= ArH), 6.73 (td, \(J = 9.3, 2.4\) Hz, 1H, ArH), 6.55 (dd, \(J = 8.9, 5.2\) Hz, 1H, ArH); **¹³C NMR** (151 MHz, DMSO-\(d_6\)) \(\delta\) 166.05, 164.37 (d, \(J = 244.5\) Hz), 159.46 (d, \(J = 235.5\) Hz), 153.14 (d, \(J = 12\) Hz), 137.46 (d, \(J = 12\) Hz), 136.73, 132.69, 131.04, 126.25, 125.26 (d, \(J = 9\) Hz), 120.14, 118.44 (d, \(J = 10.5\) Hz), 117.40, 113.98 (d, \(J = 24\) Hz), 109.64 (d, \(J = 24\) Hz), 109.04 (d, \(J = 25.5\) Hz), 108.49, 98.84 (d, \(J = 25.5\) Hz), 73.17; **¹⁹F NMR** (565 MHz, DMSO-\(d_6\)) \(\delta\) -109.13, -120.42. **HRMS** (ESI-TOF) m/z: [M + H]⁺ calcd for C₁₉H₁₂F₂N₇ 376.1117; Found 376.1112.

3'-Azido-2'-(1H-imidazol-1-yl)-5,5'-dimethyl-1H,3'H-3,3'-biindole (4e)

Reddish brown solid; Mp: 205.1 -205.8 °C; 231 mg, yield: 63%; **IR** (KBr): 3448, 2255, 2129, 1665, 1475, 1328, 835, 769, 694, 596, 573, 453 cm⁻¹; **¹H NMR** (600 MHz, DMSO-\(d_6\)) \(\delta\) 11.40 (s, 1H, NH), 8.25 (s, 1H, ArH), 7.83 (t, \(J = 1.5\) Hz, 1H, ArH), 7.76 (s, 1H, ArH), 7.64 (d, \(J = 7.9\) Hz, 1H, ArH), 7.35 (d, \(J = 7.9\) Hz, 1H, ArH), 7.27 (d, \(J = 8.3\) Hz, 1H, ArH), 7.15 (s, 1H, ArH), 7.05 (s, 1H, ArH), 6.87 (d, \(J = 8.3\) Hz, 1H, ArH), 6.40 (s, 1H, ArH), 2.29 (s, 3H, CH₃), 2.12 (s, 3H, CH₃); **¹³C NMR** (151 MHz, DMSO-\(d_6\)) \(\delta\) 163.75, 148.95, 137.26, 137.04, 136.48, 135.80, 131.95, 130.66, 128.71, 125.02, 124.19, 124.11, 123.66, 120.98, 117.32, 116.97, 112.46, 108.04, 73.80, 21.70, 21.35. **HRMS** (ESI-TOF) m/z: [M + H]⁺ calcd for C₂₁H₁₈N₇ 368.1618; Found 368.1615.

3'-Azido-2'-(1H-imidazol-1-yl)-6,6'-dimethyl-1H,3'H-3,3'-biindole (4f)
Reddish brown solid; Mp: 171.2 -172.5 °C; 220 mg, yield: 60%; IR (KBr): 3441, 2258, 2128, 1997, 1655, 1306, 834, 753, 621, 579, 524, 481, 414 cm⁻¹; ¹H NMR (600 MHz, DMSO-\textit{d}_6) δ 11.34 (s, 1H, NH), 8.25 (t, \(J = 1.0\) Hz, 1H, ArH), 7.79 (d, \(J = 2.7\) Hz, 1H, ArH), 7.75 (t, \(J = 1.5\) Hz, 1H, ArH), 7.59 – 7.52 (m, 1H, ArH), 7.20 (d, \(J = 7.5\) Hz, 1H, ArH), 7.15 (s, 1H, ArH), 7.11 (dt, \(J = 7.3\), 1.2 Hz, 1H, ArH), 7.05 (dd, \(J = 1.6\), 0.8 Hz, 1H, ArH), 6.62 (dd, \(J = 8.3\), 1.5 Hz, 1H, ArH), 6.46 (d, \(J = 8.3\) Hz, 1H, ArH), 2.42 (s, 3H, CH₃), 2.27 (s, 3H, CH₃); ¹³C NMR (151 MHz, DMSO-\textit{d}_6) δ 164.66, 151.51, 141.60, 137.85, 136.53, 133.96, 131.74, 130.69, 127.87, 124.36, 123.40, 122.04, 121.93, 121.35, 117.33, 117.17, 112.39, 108.60, 73.64, 21.70, 21.57. HRMS (ESI-TOF) m/z: [M + H]^+ calcd for C₂₁H₁₈N₇ 368.1618; Found 368.1622.

3'-Azido-2'-(1H-imidazol-1-yl)-7,7'-dimethyl-1H,3'H-3,3'-biindole (4g)

Reddish brown solid; Mp: 180.8 - 181.8 °C; 158 mg, yield: 43%; IR (KBr): 3439, 2258, 2126, 1659, 1388, 828, 769, 625, 563, 536, 454 cm⁻¹; ¹H NMR (600 MHz, DMSO-\textit{d}_6) δ 11.55 (s, 1H, NH), 8.33 (s, 1H, ArH), 7.95 (d, \(J = 2.8\) Hz, 1H, ArH), 7.82 (t, \(J = 1.4\) Hz, 1H, ArH), 7.44 (d, \(J = 7.6\) Hz, 1H, ArH), 7.25 (t, \(J = 7.5\) Hz, 1H, ArH), 7.18 (d, \(J = 7.3\) Hz, 1H, ArH), 7.13 – 7.05 (m, 1H, ArH), 6.88 (d, \(J = 7.2\) Hz, 1H, ArH), 6.74 (t, \(J = 7.6\) Hz, 1H, ArH), 6.45 (d, \(J = 8.1\) Hz, 1H, ArH), 2.66 (s, 3H, CH₃), 2.47 (s, 3H, CH₃); ¹³C NMR (151 MHz, DMSO-\textit{d}_6) δ 163.47, 149.60, 136.93, 136.76, 136.53, 132.85, 130.93, 130.63, 127.32, 124.83, 123.19, 122.90, 122.04, 121.09, 120.40, 117.34, 115.12, 109.14, 74.07, 71.10, 16.69. HRMS (ESI-TOF) m/z: [M + H]^+ calcd for C₂₁H₁₈N₇ 368.1618; Found 368.1613.

3'-Azido-2'-(1H-imidazol-1-yl)-5,5'-dimethoxy-1H,3'H-3,3'-biindole (4h)
Reddish brown solid; Mp: 121.9 -122.6 °C; 263 mg, yield: 66%; IR (KBr): 3491, 2976, 2258, 2129, 1665, 1222, 762, 691, 643, 590, 550, 493, 452 cm⁻¹; ¹H NMR (600 MHz, DMSO-d₆) δ 11.38 (d, J = 2.8 Hz, 1H, NH), 8.28 (s, 1H, ArH), 7.76 (t, J = 1.4 Hz, 1H, ArH), 7.69 (d, J = 8.5 Hz, 1H, ArH), 7.28 (d, J = 8.8 Hz, 1H, ArH), 7.10 (dd, J = 8.5, 2.6 Hz, 1H, ArH), 7.05 (s, 1H, ArH), 6.92 (d, J = 2.6 Hz, 1H, ArH), 6.71 (dd, J = 8.8, 2.5 Hz, 1H, ArH), 6.00 (d, J = 2.4 Hz, 1H, ArH), 3.74 (s, 3H, CH₃), 3.48 (s, 3H, CH₃); ¹³C NMR (151 MHz, DMSO-d₆) δ 162.63, 159.16, 153.93, 144.36, 138.49, 136.37, 132.48, 130.57, 125.83, 123.83, 121.97, 117.25, 115.73, 113.44, 111.89, 110.61, 107.95, 99.80, 73.85, 56.24, 55.49. HRMS (ESI-TOF) m/z: [M + H]+ calcd for C₂₁H₁₈N₇O₂ 400.1516; Found 400.1512.

3'-Azido-2'-(2-methyl-1H-imidazol-1-yl)-1H,3'H-3,3'-biindole (4i)

Reddish brown solid; Mp: 121.3 -122.2 °C; 144 mg, yield: 41%; IR (KBr): 3444, 2972, 2263, 2129, 1657, 1306, 824, 763, 626, 551, 518, 480, 454, 423 cm⁻¹; ¹H NMR (600 MHz, DMSO-d₆) δ 11.47 (d, J = 2.7 Hz, 1H, NH), 7.81 (d, J = 2.7 Hz, 1H, ArH), 7.54 (td, J = 7.4, 1.8 Hz, 1H, ArH), 7.47 (d, J = 1.7 Hz, 1H, ArH), 7.37 (d, J = 8.2 Hz, 1H, ArH), 7.34 – 7.28 (m, 2H, ArH), 7.03 (ddd, J = 8.2, 6.9, 1.2 Hz, 1H, ArH), 6.81 (td, J = 7.5, 7.0, 1.1 Hz, 1H, ArH), 6.78 (d, J = 1.7 Hz, 1H, ArH), 6.64 (d, J = 8.1 Hz, 1H, ArH), 2.71 (s, 3H, CH₃); ¹³C NMR (151 MHz, DMSO-d₆) δ 165.51, 151.43, 146.88, 137.35, 136.47, 131.57, 128.34, 127.55, 125.12, 123.67, 123.35, 122.40, 121.50, 120.17, 118.09, 117.38, 112.74, 108.39, 74.96, 17.74. HRMS (ESI-TOF) m/z: [M + H]+ calcd for C₂₀H₁₆N₇ 354.1462; Found 354.1459.

3'-Azido-2'-(4-methyl-1H-imidazol-1-yl)-1H,3'H-3,3'-biindole (4j)

Reddish brown solid; Mp: 115.8 -117.3 °C; 208 mg, yield: 59%; IR (KBr): 3449, 2262, 2139, 1658, 1451, 821, 759, 629, 572, 455, 429 cm⁻¹; ¹H NMR (600 MHz, DMSO-d₆) δ 11.56 (d, J = 2.8 Hz, 1H, NH), 8.20 (d, J = 1.3 Hz, 1H, ArH), 7.94 (d, J = 2.7 Hz, 1H, ArH), 7.75 (d, J = 7.7 Hz, 1H, ArH), 7.57 (td, J = 7.7, 1.4 Hz, 1H, ArH), 7.55 – 7.52 (m, 1H, ArH), 7.42 (d, J = 7.9 Hz, 1H, ArH), 7.36 (dd, J = 7.5, 1.4 Hz, 1H, ArH), 7.32 (td, J = 7.5, 1.1 Hz, 1H, ArH), 7.07 (ddd, J = 8.2, 7.1, 1.1 Hz, 1H, ArH), 6.82 (ddd, J = 8.2, 7.0, 1.1 Hz, 1H, ArH), 6.63 (d, J = 8.1 Hz, 1H, ArH), 2.10 (s, 3H, CH₃); ¹³C NMR (151 MHz, DMSO-d₆) δ 164.23, 151.47, 139.64, 137.42, 136.81,
136.12, 131.63, 127.29, 125.12, 123.72, 122.43, 121.20, 120.17, 117.46, 113.23, 108.70, 73.68, 13.70. **HRMS** (ESI-TOF) m/z: [M + H]^+ calcld for C_{20}H_{16}N_{7} 354.1462; Found 354.1464.

3’-Azido-6,6’-dichloro-2’-(4-methyl-1H-imidazol-1-yl)-1H,3'H-3,3’-biindole (4k)

![Chemical structure of 3’-Azido-6,6’-dichloro-2’-(4-methyl-1H-imidazol-1-yl)-1H,3'H-3,3’-biindole (4k)](attachment)

Reddish brown solid; Mp: 123.6 -124.8 °C; 240 mg, yield: 57%; **IR** (KBr): 3448, 2259, 2121, 1655, 834, 773, 631, 572, 517, 483, 452, 424 cm⁻¹; **¹H NMR** (600 MHz, DMSO-d_6) δ 11.70 (d, J = 2.8 Hz, 1H, NH), 8.16 (s, 1H, ArH), 7.95 (d, J = 2.7 Hz, 1H, ArH), 7.82 (d, J = 1.7 Hz, 1H, ArH), 7.51 – 7.42 (m, 2H, ArH), 6.89 (dd, J = 8.6, 1.9 Hz, 1H, ArH), 6.64 (d, J = 8.6 Hz, 1H, ArH), 2.08 (s, 3H, CH₃); **¹³C NMR** (151 MHz, DMSO-d_6) δ 165.46, 152.90, 140.01, 137.85, 136.26, 136.04, 135.33, 127.41, 127.13, 126.54, 125.04, 122.08, 121.53, 120.80, 118.70, 113.22, 112.47, 108.55, 73.16, 13.70. **HRMS** (ESI-TOF) m/z: [M + H]^+ calcld for C_{20}H_{14}Cl_{2}N_{7} 422.0682; Found 422.0680.

3’-Azido-6,6’-dibromo-2’-(4-methyl-1H-imidazol-1-yl)-1H,3'H-3,3’-biindole (4l)

![Chemical structure of 3’-Azido-6,6’-dibromo-2’-(4-methyl-1H-imidazol-1-yl)-1H,3'H-3,3’-biindole (4l)](attachment)

Reddish brown solid; Mp: 154.1 -154.7 °C; 275 mg, yield: 54%; **IR** (KBr): 3447, 2256, 2137, 1996, 1653, 1306, 821, 773, 674, 624, 542, 514, 456, 413 cm⁻¹; **¹H NMR** (600 MHz, DMSO-d_6) δ 11.70 (d, J = 2.7 Hz, 1H, NH), 8.15 (d, J = 1.3 Hz, 1H, ArH), 7.95 (d, J = 1.8 Hz, 1H, ArH), 7.93 (d, J = 2.7 Hz, 1H, ArH), 7.59 (d, J = 1.8 Hz, 1H, ArH), 7.49 (dd, J = 7.9, 1.8 Hz, 1H, ArH), 7.48 – 7.45 (m, 1H, ArH), 7.30 (d, J = 7.9 Hz, 1H, ArH), 7.00 (dd, J = 8.6, 1.8 Hz, 1H, ArH), 6.58 (d, J = 8.6 Hz, 1H, ArH), 2.07 (s, 3H, CH₃); **¹³C NMR** (151 MHz, DMSO-d_6) δ 165.29, 152.97, 140.02, 138.28, 136.25, 135.73, 130.07, 126.42, 125.38, 124.42, 124.31, 123.36, 122.30, 119.05, 115.43, 115.36, 113.22, 108.51, 73.20, 13.69. **HRMS** (ESI-TOF) m/z: [M + H]^+ calcld for C_{20}H_{14}Br_{2}N_{7} 511.9651; Found 511.9652.

3’-Azido-6,6’-difluoro-2’-(4-methyl-1H-imidazol-1-yl)-1H,3'H-3,3’-biindole (4m)
3'-Azido-5,5'-dimethyl-2'-(4-methyl-1H-imidazol-1-yl)-1H,3'H-3,3'-biindole (4n)

Reddish brown solid; Mp: 162.2 -163.3 °C; 210 mg, yield: 54%; **IR (KBr)**: 3462, 3078, 2342, 2256, 2124, 1665, 825, 761, 694, 622, 595, 532, 498, 441 cm⁻¹; **1H NMR** (600 MHz, DMSO-d₆) δ 11.61 (d, J = 2.7 Hz, 1H, NH), 8.17 (d, J = 1.4 Hz, 1H, ArH), 7.92 (d, J = 2.7 Hz, 1H, ArH), 7.63 (dd, J = 8.9, 2.4 Hz, 1H, ArH), 7.52 – 7.44 (m, 1H, ArH), 7.38 (dd, J = 8.2, 5.2 Hz, 1H, ArH), 7.17 (dd, J = 9.8, 2.4 Hz, 1H, ArH), 7.12 (ddd, J = 9.4, 8.2, 2.4 Hz, 1H, ArH), 6.73 (td, J = 9.3, 2.4 Hz, 1H, ArH), 6.57 (dd, J = 8.9, 5.2 Hz, 1H, ArH), 2.08 (s, 3H, CH₃); **13C NMR** (151 MHz, DMSO-d₆) δ 165.80, 164.36 (d, J = 244.5 Hz), 159.45 (d, J = 235.5 Hz), 153.32 (d, J = 12 Hz), 139.95, 137.44 (d, J = 12 Hz), 136.26, 132.61, 126.10, 125.19 (d, J = 10.5 Hz), 120.15, 118.45 (d, J = 9 Hz), 113.72 (d, J = 24 Hz), 113.21, 109.42 (d, J = 24 Hz), 109.01 (d, J = 24 Hz), 108.72, 98.83 (d, J = 27 Hz), 73.06, 13.72; **19F NMR** (565 MHz, DMSO-d₆) δ -109.23, -120.44. **HRMS** (ESI-TOF) m/z: [M + H]+ calecd for C₂₀H₁₄F₂N₇ 390.1273; Found 390.1267.

3'-Azido-6,6'-dimethyl-2'-(4-methyl-1H-imidazol-1-yl)-1H,3'H-3,3'-biindole (4o)

Reddish brown solid; Mp: 107.3 -108.4 °C; 221 mg, yield: 58%; **IR (KBr)**: 3444, 2258, 2126, 1655, 814, 762, 621, 574, 530, 454, 418 cm⁻¹; **1H NMR** (600 MHz, DMSO-d₆) δ 11.39 (s, 1H, NH), 8.12 (t, J = 1.3 Hz, 1H, ArH), 7.81 (d, J = 2.5 Hz, 1H, ArH), 7.60 (d, J = 7.9 Hz, 1H, ArH), 7.48 (q, J = 1.3 Hz, 1H, ArH), 7.38 – 7.29 (m, 1H, ArH), 7.27 (d, J = 8.3 Hz, 1H, ArH), 7.12 (s, 1H, ArH), 6.87 (d, J = 8.3 Hz, 1H, ArH), 6.42 (s, 1H, ArH), 2.28 (s, 3H, CH₃), 2.12 (s, 3H, CH₃), 2.07 (s, 3H, CH₃); **13C NMR** (151 MHz, DMSO-d₆) δ 163.54, 149.13, 139.50, 139.50, 136.99, 135.98, 135.80, 131.88, 128.65, 124.86, 124.12, 124.07, 123.69, 120.78, 117.03, 113.18, 112.44, 108.27, 73.74, 21.72, 21.33, 13.72. **HRMS** (ESI-TOF) m/z: [M + H]+ calecd for C₂₂H₂₀N₇ 382.1775; Found 382.1772.
Reddish brown solid; Mp: 128.8 -129.7 °C; 213 mg, yield: 56%; IR (KBr): 3445, 2242, 2129, 1660, 1457, 819, 758, 621, 526, 455, 422 cm\(^{-1}\); \(^1\)H NMR (600 MHz, DMSO-\(d_6\)) δ 11.32 (d, \(J = 2.7\) Hz, 1H, NH), 8.11 (s, 1H, ArH), 7.77 (d, \(J = 2.7\) Hz, 1H, ArH), 7.53 (s, 1H, ArH), 7.47 (s, 1H, ArH), 7.17 (d, \(J = 7.5\) Hz, 1H, ArH), 7.15 (s, 1H, ArH), 7.08 (d, \(J = 7.6\) Hz, 1H, ArH), 6.62 (d, \(J = 8.3\) Hz, 1H, ArH), 6.47 (d, \(J = 8.2\) Hz, 1H, ArH), 2.40 (s, 3H, CH\(_3\)), 2.27 (s, 3H, CH\(_3\)), 2.06 (s, 3H, CH\(_3\)); \(^{13}\)C NMR (151 MHz, DMSO-\(d_6\)) δ 164.44, 151.65, 141.53, 139.54, 137.84, 136.04, 133.88, 131.74, 127.64, 124.17, 123.33, 121.90, 121.84, 121.35, 117.19, 113.18, 112.37, 108.85, 73.56, 21.69, 21.57, 13.68. HRMS (ESI-TOF) m/z: [M + H]\(^+\) calcd for C\(_{22}\)H\(_{20}\)N\(_3\) 382.1775; Found 382.1771.

3'-Azido-7,7'-dimethyl-2'-(4-methyl-1H-imidazol-1-yl)-1H,3'H-3,3'-biindole (4p)

Reddish brown solid; Mp: 144.1 -144.9 °C; 160 mg, yield: 42%; IR (KBr): 3444, 2243, 2119, 2009, 1667, 821, 758, 625, 572, 495, 450, 418 cm\(^{-1}\); \(^1\)H NMR (600 MHz, DMSO-\(d_6\)) δ 11.49 (d, \(J = 2.8\) Hz, 1H, NH), 8.14 (s, 1H, ArH), 7.88 (d, \(J = 2.8\) Hz, 1H, ArH), 7.51 (t, \(J = 1.4\) Hz, 1H, ArH), 7.36 (d, \(J = 7.7\) Hz, 1H, ArH), 7.17 (t, \(J = 7.5\) Hz, 1H, ArH), 7.11 (d, \(J = 7.3\) Hz, 1H, ArH), 6.83 (d, \(J = 7.1\) Hz, 1H, ArH), 6.70 (t, \(J = 7.6\) Hz, 1H, ArH), 6.43 (d, \(J = 8.1\) Hz, 1H, ArH), 2.60 (s, 3H, CH\(_3\)), 2.42 (s, 3H, CH\(_3\)), 2.08 (s, 3H, CH\(_3\)); \(^{13}\)C NMR (151 MHz, DMSO-\(d_6\)) δ 163.26, 149.76, 139.49, 136.91, 136.69, 136.03, 132.78, 130.67, 127.07, 124.69, 123.20, 122.86, 122.01, 121.03, 120.36, 115.15, 113.23, 109.35, 73.96, 17.11, 16.69, 13.70. HRMS (ESI-TOF) m/z: [M + H]\(^+\) calcd for C\(_{22}\)H\(_{20}\)N\(_3\) 382.1775; Found 382.1776.

3'-Azido-5,5'-dimethoxy-2'-(4-methyl-1H-imidazol-1-yl)-1H,3'H-3,3'-biindole (4q)
Reddish brown solid; Mp: 123.6 -124.5 °C; 231 mg, yield: 56%; **IR** (KBr): 3446, 2252, 2129, 2001, 1656, 1489, 821, 620, 559, 537, 482, 456, 425 cm⁻¹; **¹H NMR** (600 MHz, DMSO-⁵⁶) δ 11.36 (d, J = 2.8 Hz, 1H, NH), 8.14 (s, 1H, ArH), 7.84 (d, J = 2.8 Hz, 1H, ArH), 7.65 (d, J = 8.5 Hz, 1H, ArH), 7.52 – 7.43 (m, 1H, ArH), 7.28 (d, J = 8.8 Hz, 1H, ArH), 7.08 (d, J = 2.6 Hz, 1H, ArH), 6.90 (d, J = 2.6 Hz, 1H, ArH), 6.72 (dd, J = 8.8, 2.5 Hz, 1H, ArH), 6.03 (d, J = 2.5 Hz, 1H, ArH), 3.73 (s, 3H, CH₃), 3.48 (s, 3H, CH₃), 2.07 (s, 3H, CH₃); **¹³C NMR** (151 MHz, DMSO-⁵⁶) δ 162.46, 158.99, 153.92, 144.55, 139.39, 138.42, 135.86, 132.49, 125.68, 123.86, 121.74, 115.68, 113.41, 113.12, 111.86, 110.54, 108.20, 99.89, 73.81, 56.21, 55.51, 13.73. **HRMS** (ESI-TOF) m/z: [M + H]⁺ calcd for C₂₂H₂₀N₇O₂ 414.1673; Found 414.1667.

4-((1H-benzo[d]imidazol-1-yl)methyl)-2,6-di-tert-butylphenol (5)

![Structure of 4-((1H-benzo[d]imidazol-1-yl)methyl)-2,6-di-tert-butylphenol](image)

White solid; Mp: 151.4 -152.6 °C; 141 mg, yield: 42%; **IR** (KBr): 3624, 2910, 2746, 2577, 1703, 1628, 1481, 1365, 1197, 964, 847, 732 cm⁻¹; **¹H NMR** (600 MHz, DMSO-⁶) δ 8.40 (s, 1H, ArH), 7.67 (d, J = 8.1 Hz, 1H, ArH), 7.63 (d, J = 8.0 Hz, 1H, ArH), 7.24 (t, J = 7.6 Hz, 1H, ArH), 7.19 (t, J = 7.5 Hz, 1H, ArH), 7.15 (s, 2H, ArH), 7.06 (s, 1H, OH), 5.38 (s, 2H, CH₂), 1.35 (s, 18H, CH₃); **¹³C NMR** (151 MHz, DMSO-⁶) δ 153.92, 144.46, 143.95, 139.95, 134.25, 128.32, 124.53, 122.76, 121.96, 119.90, 111.20, 48.47, 34.94, 30.75. **HRMS** (ESI-TOF) m/z: [M + H]⁺ calcd for C₂₂H₂₉N₂O 337.2274; Found 337.2269.

2-(1H-benzo[d]imidazol-1-yl)-1H,1'H-3,3'-biindole (6)

![Structure of 2-(1H-benzo[d]imidazol-1-yl)-1H,1'H-3,3'-biindole](image)

Reddish brown solid; Mp: 282.4 -283.8 °C; 309 mg, yield: 89%; **IR** (KBr): 3767, 3426, 3060, 2355, 1655, 824, 766, 611, 503, 450 cm⁻¹; **¹H NMR** (600 MHz, DMSO-⁶) δ 12.08 (s, 1H, NH), 11.20 (d, J = 2.6 Hz, 1H, NH), 8.45 (s, 1H, ArH), 7.71 (d, J = 7.9 Hz, 1H, ArH), 7.60 (d, J = 8.0 Hz, 1H, ArH), 7.51 (d, J = 8.1 Hz, 1H, ArH), 7.38 – 7.33 (m, 2H, ArH), 7.29 (td, J = 8.0, 2.9 Hz, 2H, ArH), 7.26 – 7.19 (m, 2H, ArH), 7.16 (t, J = 7.5 Hz, 1H, ArH), 7.05 – 7.00 (m, 2H, ArH), 6.77 (t, J = 7.5 Hz, 1H, ArH); **¹³C NMR** (151 MHz, DMSO-⁶) δ 144.90, 143.14, 136.57, 134.94, 134.49, 127.43, 126.92, 126.38, 124.46, 123.97, 123.12, 122.97, 121.64, 120.45, 120.29, 120.12, 119.29, 119.15, 112.19, 112.12, 111.36, 106.50, 104.74. **HRMS** (ESI-TOF) m/z: [M + H]⁺ calcd for C₂₃H₁₉N₄ 349.1448; Found 349.1440.
4-((2-(1H-benzo[d]imidazol-1-yl)-1H-indol-3-yl)methyl)-2,6-di-tert-butylphenol (7)

HRMS (ESI-TOF) m/z: [M + H]$^+$ calcd for C$_{30}$H$_{34}$N$_3$O 452.2696; Found 452.2690.

methyl 2-(1-(2'-((1H-benzo[d]imidazol-1-yl)-1H,3'H-[3,3'-biindol]-3'-yl)-1H-1,2,3-triazol-4-yl)acetate (8)

Reddish brown solid; Mp: 267.2 - 268.5 °C; 3.17 g, yield: 92%; IR (KBr): 3760, 3414, 3018, 2127, 1788, 1651, 826, 760, 613, 504, 453 cm$^{-1}$; $^1$H NMR (600 MHz, DMSO-$_d_6$) $\delta$ 9.11 (s, 1H, NH), 8.19 (s, 1H, ArH), 7.94 (dd, $J =$ 7.9, 1.5 Hz, 1H, ArH), 7.85 (t, $J =$ 1.2 Hz, 1H, ArH), 7.76 (s, 1H, ArH), 7.69 – 7.61 (m, 2H, ArH), 7.54 – 7.47 (m, 3H, ArH), 7.40 (td, $J =$ 7.5, 1.3 Hz, 1H, ArH), 7.32 (ddd, $J =$ 8.3, 7.1, 1.4 Hz, 1H, ArH), 7.22 (td, $J =$ 7.6, 4.8, 1.4 Hz, 2H, ArH), 7.11 (dt, $J =$ 11.5, 7.6, 1.5 Hz, 2H, ArH), 3.85 (d, $J =$ 1.2 Hz, 2H, CH$_2$), 3.75 (s, 3H, CH$_3$); $^{13}$C NMR (151 MHz, DMSO-$_d_6$) $\delta$ 169.72, 155.73, 145.68, 142.87, 140.48, 140.02, 138.47, 138.19, 132.53, 130.56, 130.26, 128.72, 127.26, 124.93, 124.65, 122.19, 122.04, 121.58, 120.88, 120.49, 120.35, 118.68, 116.90, 111.44, 108.98, 61.08, 52.08, 33.28. HRMS (ESI-TOF) m/z: [M + H]$^+$ calcd for C$_{29}$H$_{22}$N$_7$O$_2$ 488.1829; Found 488.1826.
4. Reaction Condition Optimizations

![Reaction diagram]

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<sup>a</sup> Reagents and conditions: In a 25 mL reaction tube, benzimidazole 1a (0.5 mmol), indole 2a (1.1 mmol), oxidant (0.55 mmol), catalyst (20 mol%), azide source (0.75 mmol), solvent 10 mL, under aerobic atmosphere (1 atm), stirred for 5 h. <sup>b</sup> rt = room temperature. <sup>c</sup> Isolated yield based on 1a. <sup>d</sup>acac = acetylacetone. <sup>e</sup>Catalyst (10 mol%). <sup>f</sup>Catalyst (5 mol%). <sup>g</sup> under argon (1 atm) atmosphere.

Table S1. Reaction Condition Optimizations<sup>a,c</sup>

Our initial attempt involved the cascade reaction of benzimidazole (1a) and indole (2a) was studied in the presence of a series of catalysts by using PIFA as an oxidant in
dichloromethane. Different catalysts were screened for their ability to catalyze the cascade reaction at room temperature (Table S1, entries 1–8). The results indicated that the use of Cu(OAc)$_2$ led to the highest yield (32%) of the model azide-biindole product 3a (Table S1, entry 6). Encouraged by this result, we sought to enhance the yield of this cascade reaction by screening a variety of different solvents (Table S1, entries 9–13). Using Cu(OAc)$_2$ as the catalyst in the presence of PIFA and sodium azide, the highest yield of 3a was obtained when using ethyl acetate as the solvent (56% yield, Table S1, entry 13). Subsequent screening of other oxidants indicated that PIFA remained the best oxidant for furnishing 3a in the highest yield (Table S1, entries 14–17). In addition to NaN$_3$, azidotrimethylsilane (TMSN$_3$) and diphenyl phosphoryl azide (DPPA) were screened as the azide source (Table S1, entries 18–19). The results showed that NaN$_3$ was more reactive than the other organic azides (Table S1, entry 13). Then, increasing the reaction temperature from 40°C to reflux afforded increasingly higher yields compared to at r.t., with the highest yield being obtained under refluxing conditions (76% yield, Table S1, entry 22). In addition, the amount of the catalyst was screened, showing that a decrease in the amount of the catalyst decreased the yield of the reaction; approximately 20 mol% was identified as the optimal amount (Table S1, entry 23, 24 vs entry 22). Finally, the reaction proceeded under argon atmosphere to test whether the inert gas (argon) environment affected the yield of this cascade reaction, we found that under inert atmosphere, the reaction yield did not change significantly (Table S1, entry 25). Therefore, the results of the reaction optimization indicated that ethyl acetate as the solvent, 1.1 equiv. of PIFA as the oxidant, 20 mol% Cu(OAc)$_2$ as the catalyst, 1.5 equiv. of NaN$_3$ as the azide source, a temperature of reflux temperature was best-suited for the synthesis of compound 3a (Table S1, entry 22).
5. X-ray Structure and Data of 3a

Figure S1. X-Ray crystal structure of 3a
Compound 3a (50 mg) was added to a 10 mL sample bottle, following to add DCM (2 mL), n-hexane (2.5 mL) and toluene (0.1 mL), then seal the bottle with parafilm, and poke 15 small holes on the parafilm, place the sample bottle in a safe place to allow it to volatilize and separate out the single crystal. Take out the single crystal and send it for single crystal diffraction test to obtain relevant data. Instrument model: Intensity data for single crystals of each complex were collected on a BRUKER SMART APEX II CCD detector with graphite-monochromatized Mo Kα radiation (k = 0.071073 nm). The structures were solved by direct method using the program SHELXS-97 and subsequent Fourier difference techniques, and refined anisotropically by full matrix least-squares on F2 using SHELXL-97.
6. X-ray Structure and Data of 4p

Figure S2. X-Ray crystal structure of 4p
Compound 4p (50 mg) was added to a 10 mL sample bottle, following to add DCM (2 mL), n-hexane (2.5 mL) and toluene (0.1 mL), then seal the bottle with a parafilm, and poke 15 small holes on the parafilm, place the sample bottle in a safe place to allow it to volatilize and separate out the single crystal. Take out the single crystal and send it for single crystal diffraction test to obtain relevant data. Instrument model: Intensity data for single crystals of each complex were collected on a BRUKER SMART APEX II CCD detector with graphite-monochromatized Mo Kα radiation (k = 0.071073 nm). The structures were solved by direct method using the program SHELXS-97 and subsequent Fourier difference techniques, and refined anisotropically by full matrix least-squares on F2 using SHELXL-97.
7. X-ray Structure and Data of 6

Figure S3. X-Ray crystal structure of 6
Table S4. Crystal data and structure refinement for 6

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<td><strong>Hall group</strong></td>
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**Correction method= Not given**

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Compound 6 (50 mg) was added to a 10 mL sample bottle, following to add DCM (2 mL), n-hexane (2.5 mL) and toluene (0.1 mL), then seal the bottle with a parafilm, and poke 15 small holes on the parafilm, place the sample bottle in a safe place to allow it to volatilize and separate out the single crystal. Take out the single crystal and send it for single crystal diffraction test to obtain relevant data. Instrument model: Intensity data for single crystals of each complex were collected on a BRUKER SMART APEX II CCD detector with graphite-monochromatized Mo Kα radiation (k = 0.071073 nm). The structures were solved by direct method using the program SHELXS-97 and subsequent Fourier difference techniques, and refined anisotropically by full matrix least-squares on F2 using SHELXL-97.
8. $^1$H NMR and $^{13}$C NMR Spectra of These Compounds

$^1$H-NMR (600 MHz, DMSO) Spectra of compound 3a

$^{13}$C-NMR (151 MHz, DMSO) Spectra of compound 3a
$^1$H-NMR (600 MHz, DMSO) Spectra of compound 3b

$^{13}$C-NMR (151 MHz, DMSO) Spectra of compound 3b
$^1$H-NMR (600 MHz, DMSO) Spectra of compound 3c

$^{13}$C-NMR (151 MHz, DMSO) Spectra of compound 3c
$^1$H-NMR (600 MHz, DMSO) Spectra of compound 3d

$^{13}$C-NMR (151 MHz, DMSO) Spectra of compound 3d
$^{1}$H-NMR (600 MHz, DMSO) Spectra of compound 3e

$^{13}$C-NMR (151 MHz, DMSO) Spectra of compound 3e
$^1$H-NMR (600 MHz, DMSO) Spectra of compound 3f

$^{13}$C-NMR (151 MHz, DMSO) Spectra of compound 3f
$^1$H-NMR (600 MHz, DMSO) Spectra of compound 3g

$^{13}$C-NMR (151 MHz, DMSO) Spectra of compound 3g
$^{19}$F-NMR (565MHz, DMSO) spectrum of compound 3g
$^1$H-NMR (600 MHz, DMSO) Spectra of compound 3h

$^{13}$C-NMR (151 MHz, DMSO) Spectra of compound 3h
$^1$H-NMR (565MHz, DMSO) spectrum of compound 3h
$^1$H-NMR (600 MHz, DMSO) Spectra of compound 3i

$^{13}$C-NMR (151 MHz, DMSO) Spectra of compound 3i
$^1$H-NMR (600 MHz, DMSO) Spectra of compound 3j

$^{13}$C-NMR (151 MHz, DMSO) Spectra of compound 3j
$^1$H-NMR (600 MHz, DMSO) Spectra of compound 3k

$^{13}$C-NMR (151 MHz, DMSO) Spectra of compound 3k
$^{19}$F-NMR (565MHz, DMSO) spectrum of compound 3k
$^1$H-NMR (600 MHz, DMSO) Spectra of compound 3l

$^{13}$C-NMR (151 MHz, DMSO) Spectra of compound 3l
$^{19}$F-NMR (565MHz, DMSO) spectrum of compound 3I
$^1$H-NMR (600 MHz, DMSO) Spectra of compound 3m

$^{13}$C-NMR (151 MHz, DMSO) Spectra of compound 3m
$^{19}$F-NMR (565MHz, DMSO) spectrum of compound 3m
$^1$H-NMR (600 MHz, DMSO) Spectra of compound 3n

$^{13}$C-NMR (151 MHz, DMSO) Spectra of compound 3n
$^{19}$F-NMR (565MHz, DMSO) spectrum of compound 3n
$^1$H-NMR (600 MHz, DMSO) Spectra of compound 3o

$^{13}$C-NMR (151 MHz, DMSO) Spectra of compound 3o

SS2
$^{19}\text{F-NMR (565MHz, DMSO) spectrum of compound 3o}$
$^{1}H$-NMR (600 MHz, DMSO) Spectra of compound 3p

$^{13}C$-NMR (151 MHz, DMSO) Spectra of compound 3p
$^1$H-NMR (600 MHz, DMSO) Spectra of compound 3q

$^{13}$C-NMR (151 MHz, DMSO) Spectra of compound 3q
$^1$H-NMR (600 MHz, DMSO) Spectra of compound 3r

$^{13}$C-NMR (151 MHz, DMSO) Spectra of compound 3r
$^1$H-NMR (600 MHz, DMSO) Spectra of compound 3s

$^{13}$C-NMR (151 MHz, DMSO) Spectra of compound 3s
**$^{1}$H-NMR (600 MHz, DMSO) Spectra of compound 4a**

![H-NMR Spectrum](image)

**$^{13}$C-NMR (151 MHz, DMSO) Spectra of compound 4a**

![C-NMR Spectrum](image)
$^1$H-NMR (600 MHz, DMSO) Spectra of compound 4b

$^{13}$C-NMR (151 MHz, DMSO) Spectra of compound 4b
\(^1\text{H-NMR (600 MHz, DMSO) Spectra of compound 4c}\)

\(^{13}\text{C-NMR (151 MHz, DMSO) Spectra of compound 4c}\)
$^1$H-NMR (600 MHz, DMSO) Spectra of compound 4d

$^{13}$C-NMR (151 MHz, DMSO) Spectra of compound 4d
$^{19}$F-NMR (565MHz, DMSO) spectrum of compound 4d
$^1$H-NMR (600 MHz, DMSO) Spectra of compound 4e

$^{13}$C-NMR (151 MHz, DMSO) Spectra of compound 4e
$^{1}H$-NMR (600 MHz, DMSO) Spectra of compound 4f

$^{13}C$-NMR (151 MHz, DMSO) Spectra of compound 4f
$^1$H-NMR (600 MHz, DMSO) Spectra of compound 4g

$^{13}$C-NMR (151 MHz, DMSO) Spectra of compound 4g
$^1$H-NMR (600 MHz, DMSO) Spectra of compound 4h

$^{13}$C-NMR (151 MHz, DMSO) Spectra of compound 4h
\(^1\)H-NMR (600 MHz, DMSO) Spectra of compound \(4i\)

\(^{13}\)C-NMR (151 MHz, DMSO) Spectra of compound \(4i\)
$^1$H-NMR (600 MHz, DMSO) Spectra of compound 4j

$^{13}$C-NMR (151 MHz, DMSO) Spectra of compound 4j
$^1$H-NMR (600 MHz, DMSO) Spectra of compound 4k

$^{13}$C-NMR (151 MHz, DMSO) Spectra of compound 4k
$^1$H-NMR (600 MHz, DMSO) Spectra of compound 4l

$^{13}$C-NMR (151 MHz, DMSO) Spectra of compound 4l
$^1$H-NMR (600 MHz, DMSO) Spectra of compound $4m$

$^{13}$C-NMR (151 MHz, DMSO) Spectra of compound $4m$
$^{19}$F-NMR (565MHz, DMSO) spectrum of compound 4m
$^{1}$H-NMR (600 MHz, DMSO) Spectra of compound 4n

$^{13}$C-NMR (151 MHz, DMSO) Spectra of compound 4n
$^1$H-NMR (600 MHz, DMSO) Spectra of compound 4o

$^{13}$C-NMR (151 MHz, DMSO) Spectra of compound 4o
$^{1}$H-NMR (600 MHz, DMSO) Spectra of compound 4p

$^{13}$C-NMR (151 MHz, DMSO) Spectra of compound 4p
$^1$H-NMR (600 MHz, DMSO) Spectra of compound 4q

$^{13}$C-NMR (151 MHz, DMSO) Spectra of compound 4q
$^{1}$H-NMR (600 MHz, DMSO) Spectra of compound 5

$^{13}$C-NMR (151 MHz, DMSO) Spectra of compound 5
$^1$H-NMR (600 MHz, DMSO) Spectra of compound 6

$^{13}$C-NMR (151 MHz, DMSO) Spectra of compound 6
HRMS spectrum of compound 7
$^{1}$H-NMR (600 MHz, DMSO) Spectra of compound 8

$^{13}$C-NMR (151 MHz, DMSO) Spectra of compound 8