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Supporting Information

DDQ/FeCl₃-mediated tandem oxidative carbon-carbon bond formation to the Synthesis of indole-fluorene hybrid

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General: All ¹H NMR spectral data were recorded by Bruker 300, 400, 500 (300, 400, 500 MHz) spectrometer in CDCl₃ solutions expressing chemical shifts in parts per million (ppm, δ) and are referenced to CHCl₃ (δ = 7.26 ppm) as an internal standard. All coupling constants are absolute values and are expressed in Hz. The description of the signals include: s = singlet, d = doublet, t = triplet, m = multiplet, dd = doublet of doublets and brs = broad singlet.td = triplet of doublet. ¹³C NMR spectra were recorded with a Bruker 300, 400, 500 (75, 100, 125 respectively MHz) spectrometer as solutions in CDCl₃ with complete proton decoupling. Chemical shifts are expressed in parts per million (ppm, δ) and are referenced to CDCl₃ (δ = 77.0 ppm) as an internal standard. High-Resolution Mass Spectra (HRMS) were performed with a Qtof Micro YA263 spectrometer in trichloromethane solvent. The molecular fragments are quoted as the relation between mass and charge (*m*/*z*). The routine monitoring of reactions was performed with silica gel coated glass slides (Merck, silica gel G for TLC), and pre-coated Al plate, which were analyzed with iodine and uv light respectively. Solvents, reagents and chemicals were purchased from Aldrich, Fluka, Merck, SRL, Spectrochem and Process Chemicals. All reactions involving moisture sensitive reactants were executed with oven-dried glassware.

Empirical formula	$C_{28}H_{21}NO_2S$
Formula weight	435.52
Temperature/K	293
Crystal system	monoclinic
Space group	'P 21/n'
a/Å	9.730(2)
b/Å	20.980(4)
c/Å	11.450(2)
α/°	90
β/°	104.39(3)
γ/°	90
Volume/ų	2264.0(8)
Z	4
$\rho_{calc}g/cm^3$	1.278
µ/mm ⁻¹	0.168
F(000)	912
Crystal size/mm ³	.4 × .25 × .1
Radiation	Μο Κα (λ = 0.71073)
θ range/°	1.94 to 27.46
Index ranges	-12 ≤ h ≤ 12, -27 ≤ k ≤ 27, -13 ≤ l ≤ 14
Data/restraints/parameters	5164/0/289
Goodness-of-fit on F ²	0.861
Largest diff. peak/hole/e	0.18/-0.38

Representative experimental procedure for the synthesis of *N*-(3-(2-phenylphenyl)prop-2-yn-1-yl)-*N*-(2-bromophenyl)-4-methylbenzenesulfonamide (1a):



To a solution of *N*-(2-bromophenyl)-4-methyl-*N*-(prop-2-yn-1-yl)benzenesulfonamide (363 mg, 1mmol) in dimethyl sulfoxide (2 mL) and 2-phenyliodobenzene (308 mg, 1.1 mmol), triethylamine (202 mg, 2 mmol), Cul (4 mg, 0.02 mmol) and Pd(PPh₃)₄ (12 mg, 0.02 mmol) were added successively. The resulting solution was stirred at room temperature under argon atmosphere for overnight. After the completion of the reaction (monitored by TLC), the crude reaction mixture was extracted with ethyl acetate. The organic extract was washed with brine solution, dried over anhydrous Na₂SO₄ and concentrated. The product was subjected to column chromatography (silica gel, 60-120 mesh), eluting with pet ether/EtOAc 90:10 (v/v) to afford the product **1a** as a yellow semisolid (463 mg, 0.90mmol, 90%).¹H NMR (CDCl₃, 300 MHz) δ 2.42 (s, 3H), 4.28 (d, *J* = 18.0 Hz, 1H), 4.93 (d, *J* = 18.0 Hz, 1H), 6.99 (d, *J* = 6.3Hz, 1H), 7.13 (d, *J* = 6.6 Hz, 1H), 7.18–7.26 (m, 4H), 7.29–7.36 (m, 6H), 7.42 (t, *J* = 4.2 Hz, 2H), 7.64 (d, *J* = 8.7 Hz, 1H), 7.70 (d, *J* = 8.1 Hz, 2H) ppm. ¹³C NMR (CDCl₃, 75 MHz) δ 21.7, 41.4, 85.3, 85.9, 120.7, 125.8, 127.0, 127.5, 127.9, 128.1, 128.8, 129.1, 129.5, 129.6, 130.2, 132.3, 133.6, 133.8, 137.2, 137.6, 140.3, 143.7, 143.8 ppm.

Compounds **1b-1o** were synthesised by the above similar procedure.

Representative experimental procedure for the synthesis of (z)-2-((1-tosylindolin-3ylidene)methyl)bipheny/(2a):



То а solution of N-(3-([1,1'-biphenyl]-2-yl)prop-2-yn-1-yl)-N-(2-bromophenyl)-4methylbenzenesulfonamide 1a (155 mg, 0.3 mmol) in 2.5 M K₂CO₃(2 mL) and 2 mL ethanol-toluene (1:1), PCy₃ (8 mg, 0.03 mmol) and Pd(OAc)₂ (4 mg, 0.015 mmol) were added successively. The resulting solution was stirred at 75 °C under argon atmosphere for 3 h. After the completion of the reaction (monitored by TLC), the crude reaction mixture was extracted with ethyl acetate. The organic extract was washed with brine solution, dried over anhydrous Na₂SO₄ and concentrated. The product was subjected to column chromatography (silica gel, 60-120 mesh), eluting with pet ether/EtOAc 95:5 (v/v) to afford the product 2a as a greenish white solid (109 mg, 0.25 mmol, 82%); m. p. 116-118 °C. ¹H NMR (CDCl₃, 400 MHz) δ 2.37 (s, 3H), 4.80 (d, J= 2.8 Hz, 2H) , 6.70 (d, J = 2.8 Hz, 1H), 6.96 (t, J= 7.6 Hz,1H), 7.16 (d, J= 7.6 Hz, 1H), 7.20–7.27 (m, 5H), 7.29–7.44 (m, 7H), 7.72 (t, J= 8.0 Hz,3H) ppm. 13 C NMR (CDCl₃, 100MHz) δ 21.7, 54.5, 115.0, 118.2, 120.6, 123.9, 127.3, 127.4, 127.5, 127.6, 127.7, 128.2, 129.8, 129.9, 130.6, 131.4, 132.8, 134.0, 134.2, 140.9, 141.9, 143.4, 144.4, ppm.

(z)-2-(1-(1-tosylindolin-3-ylidene)methyl)-4'-methoxybiphenyl (2b):



То N-(2-bromophenyl)-N-(3-(4'-methoxy-[1,1'-biphenyl]-2-yl)prop-2-yn-1-yl)-4а solution of methylbenzenesulfonamide 1b (164 mg, 0.3 mmol) in 2.5 M K₂CO₃(2 mL) and 2 mL ethanol-toluene (1:1), PCy₃(8 mg, 0.03 mmol) and Pd(OAc)₂ (4 mg, 0.015 mmol) were added successively. The resulting solution was stirred at 75 °C under argon atmosphere for 4 h. After the completion of the reaction (monitored by TLC), the crude reaction mixture was extracted with ethyl acetate. The organic extract was washed with brine solution, dried over anhydrous Na₂SO₄and concentrated. The product was subjected to column chromatography (silica gel, 60-120 mesh), eluting with pet ether/EtOAc 95:5 (v/v) to afford the product 2b as a greenish white solid (117 mg, 0.25 mmol, 83%); m. p. 130-132°C. ¹H NMR (CDCl₃, 500 MHz) δ 2.39 (s, 3H), 3.84 (s, 3H) 4.78 (d, J= 3.0 Hz, 2H) , 6.72 (t, J = 3.0Hz, 1H), 6.90 (d, J= 8.5 Hz, 2H), 6.97 (t, J= 7.5 Hz, 1H), 7.16–7.25 (m, 4H), 7.31–7.41 (m, 6H), 7.72 (dd, J= 8.5, 12.0, Hz,3H) ppm. 13 C NMR (CDC_{I3}, 100 MHz) δ 21.6, 54.5, 55.4 113.7, 115.0, 118.4, 120.5, 123.9, 127.2, 127.3, 127.5, 127.6, 129.7, 129.9, 130.6, 130.9, 131.4, 132.6, 133.2, 134.1, 134.2, 141.5, 143.4, 144.3, 159.0 ppm.

(z)-2-((1-tosylindolin-3-ylidene)methyl)-4'-methylbiphenyl (2c):



То N-(2-bromophenyl)-4-methyl-N-(3-(4'-methyl-[1,1'-biphenyl]-2-yl)prop-2-yn-1а solution of yl)benzenesulfonamide 1c (159 mg, 0.3 mmol) in 2.5 M $K_2CO_3(2 mL)$ and 2 mL ethanol-toluene (1:1), PCy_3 (8 mg, 0.03 mmol) and Pd(OAc)₂ (4 mg, 0.015 mmol) were added successively. The resulting solution was stirred at 70-75 °C under argon atmosphere for 4 h. After the completion of the reaction (monitored by TLC), the crude reaction mixture was extracted with ethyl acetate. The organic extract was washed with brine solution, dried over anhydrous Na₂SO₄ and concentrated. The product was subjected to column chromatography (silica gel, 60-120 mesh), eluting with pet ether/EtOAc 95:5 (v/v) to afford the product 2cas a greenish white solid (106 mg, 0.24mmol, 81%); m. p. 138-140 °C.¹H NMR (CDCl₃, 400 MHz) δ 2.28 (s, 3H), 2.30 (s, 3H), 4.72 (d, J= 3.2 Hz, 2H), 6.63 (t, J = 3.2Hz, 1H), 6.88 (t, J= 7.6 Hz, 1H), 7.07-7.11 (m, 5H), $^{7.14-7.17}$ (m, 3H), 7.22-7.31 (m, 4H), 7.63 (t, J= 8.4 Hz,3H). ppm. 13 C NMR (CDCl₃, 100 MHz) δ 21.3, 21.6, Me $^{-1.2}$ (m, 3H), 7.22-7.31 (m, 4H), 7.63 (t, J= 8.4 Hz,3H). 54.5, 114.9, 118.4, 120.6, 123.9, 127.3, 127.4, 127.6, 128.9, 129.7, 129.9, 130.6, 131.4, 132.5, 134.0, 134.1, 137.0, 137.8, 141.8, 143.3, 144.4 ppm.

(z)-2-((1-tosylindolin-3-ylidene)methyl)-4'-chlorobiphenyl (2d):



То а solution of N-(2-bromophenyl)-N-(3-(4'-chloro-[1,1'-biphenyl]-2-yl)prop-2-yn-1-yl)-4methylbenzenesulfonamide 1d (165 mg, 0.3 mmol) in 2.5 M $K_2CO_3(2 mL)$ and 2 mL ethanol-toluene (1:1), PCy₃ (8 mg, 0.03 mmol) and Pd(OAc)₂ (4 mg, 0.015 mmol) were added successively. The resulting solution was stirred at 70-75 °C under argon atmosphere for 4 h. After the completion of the reaction (monitored by TLC), the crude reaction mixture was extracted with ethyl acetate. The organic extract was washed with brine solution, dried over anhydrous Na₂SO₄ and concentrated. The product was subjected to column chromatography (silica gel, 60-120 mesh), eluting with pet ether/EtOAc 95:5 (v/v) to afford the product 2d as a greenish white solid (118 mg, 0.25mmol, 85%); m. p. 142-144 °C. ¹H NMR (CDCl₃, 400 MHz) δ 2.26 (s, 3H), 4.66 (d, J= 2.8 Hz, 2H), 6.55 (t, J = 2.8Hz, 1H), 6.88 (t, J = 7.6 Hz, 1H), 7.09 (d, J= 8.8 Hz, 3H), 7.15 (t, J = 8.0 Hz, 3H), 7.21–7.27 (m, 5H), 7.32 (dd, J= 7.6, 2.4 Hz, 1H), 7.62 (dd, J= 11.2, 8.4 Hz, 3H). ppm. ¹³C NMR $(CDCI_3, 100 \text{ MHz}) \delta 21.6, 54.3, 114.9, 117.6, 120.5, 123.9, 127.2, 127.5, 127.7, 127.9, 128.4, 129.9, 130.4,$ 131.0, 133.2, 133.4, 134.0, 139.2, 140.3, 143.3, 144.4. ppm.

(z)-2-((1-tosylindolin-3-ylidene)methyl)-5-methylbiphenyl (2e):



N-(2-bromophenyl)-4-methyl-N-(3-(5-methyl-[1,1'-biphenyl]-2-yl)prop-2-yn-1-То а solution of yl)benzenesulfonamide 1e (159 mg, 0.3 mmol) in 2.5 M K₂CO₃(2 mL) and 2 mL ethanol-toluene (1:1), PCy₃ (8 mg, 0.03 mmol) and Pd(OAc)₂ (4 mg, 0.015 mmol) were added successively. The resulting solution was stirred at 70-75 °C under argon atmosphere for 4 h. After the completion of the reaction (monitored by TLC), the crude reaction mixture was extracted with ethyl acetate. The organic extract was washed with brine solution, dried over anhydrous Na₂SO₄ and concentrated. The product was subjected to column chromatography (silica gel, 60-120 mesh), eluting with pet ether/EtOAc 95:5 (v/v) to afford the product 2e as a yellowish white solid (108 mg, 0.24mmol, 81%); m. p. 126-128 °C.¹H NMR (CDCl₃, 300 MHz) δ 2.37 (s, 3H), 2.42 (s, 3H), 4.80 (d, J= 3.0 Hz, 2H), 6.68 (bs, 1H), 6.95 (t, J = 7.5 Hz, 1H), 7.14 (d, J= 7.5 Hz, 1H), 7.19– 7.26 (m, 8H), 7.32-7.36 (m, 3H), 7.70 (dd, J= 7.8, 4.5 Hz, 3H). ppm. ¹³C NMR (CDCl₃, 75 MHz) δ 21.4, 21.7, 54.6, 114.9, 118.1, 120.5, 123.9, 127.4, 128.2, 128.4, 129.6, 129.8, 129.9, 131.2, 131.4, 131.6, 131.9, 134.2, 137.5, 141.0, 141.9, 143.3, 144.4. ppm.

(z)-2-((5-methyl-1-tosylindolin-3-ylidene)methyl)biphenyl (2f):



То N-(3-([1,1'-biphenyl]-2-yl)prop-2-yn-1-yl)-N-(2-bromo-4-methylphenyl)-4а solution of methylbenzenesulfonamide 1f (159 mg, 0.3 mmol) in 2.5 M K₂CO₃(2 mL) and 2 mL ethanol-toluene (1:1), PCy₃ (8 mg, 0.03 mmol) and Pd(OAc)₂ (4 mg, 0.015 mmol) were added successively. The resulting solution was stirred at 75 °C under argon atmosphere for 4 h. After the completion of the reaction (monitored by TLC), the crude reaction mixture was extracted with ethyl acetate. The organic extract was washed with brine solution, dried over anhydrous Na2SO4 and concentrated. The product was subjected to column chromatography (silica gel, 60-120 mesh), eluting with pet ether/EtOAc 95:5 (v/v) to afford the product 2f as a yellowish white solid (108 mg, 0.24 mmol, 80%); m. p. 136-138 °C. 1 H NMR (CDCl₃, 400 MHz) δ 2.24 (s, 3H), 2.37 (s, 3H), 4.76 (d, J= 2.8 Hz, 2H) , 6.65 (t, J = 2.8 Hz, 1H), 6.96 (s,1H), 7.05 (d, J= 8.4 Hz, 1H), 7.22– 7.29 (m, 4H), 7.30–7.44 (m, 7H), 7.62 (d, J= 8.0 Hz,1H), 7.68 (d, J= 8.4 Hz,2H). ppm. ¹³C NMR (CDCl₃, 100 MHz) δ 21.1, 21.7, 54.7, 114.98, 117.94, 120.9, 127.3, 127.4, 127.5, 127.5, 127.6, 128.2, 129.8, 129.9, 130.7, 131.5, 133.1, 133.7, 134.1, 134.2, 140.9, 141.3, 141.7, 144.3 ppm.

(z)-2-((5,7-dimethyl-1-tosylindolin-3-ylidene)methyl)biphenyl (2g):



N-(3-([1,1'-biphenyl]-2-yl)prop-2-yn-1-yl)-N-(2-bromo-4,6-dimethylphenyl)-4-То а solution of methylbenzenesulfonamide 1g (163 mg, 0.3 mmol) in 2.5 M $K_2CO_3(2 mL)$ and 2 mL ethanol-toluene (1:1), PCy₃ (8 mg, 0.03 mmol) and Pd(OAc)₂ (4 mg, 0.015 mmol) were added successively. The resulting solution was stirred at 75 °C under argon atmosphere for 5 h. After the completion of the reaction (monitored by TLC), the crude reaction mixture was extracted with ethyl acetate. The organic extract was washed with brine solution, dried over anhydrous Na₂SO₄ and concentrated. The product was subjected to column chromatography (silica gel, 60-120 mesh), eluting with pet ether/EtOAc 95:5 (v/v) to afford the product 2g as a greenish white solid (116 mg, 0.25 mmol, 84%); m. p. 138-140 °C. ¹H NMR (CDCl₃, 400 MHz) δ 2.25 (s, 3H), 2.34 (s, 3H), 2.58 (s, 3H), 4.70 (d, J= 2.4 Hz, 2H) , 6.32 (d, J = 2.4Hz, 1H), 6.71 (s,1H),6.96 (s, 1H),7.00-7.05 (m, 4H), 7.15 (d, J= 6.8 Hz,1H), 7.20–7.29 (m, 2H), 7.31 (dd, J= 2.0, 4.8 Hz,3H), 7.35-7.38 (m, 3H). ppm. ^{13}C NMR (CDCl₃, 100 MHz) δ 19.8, 21.2, 21.8, 56.8, 118.3, 118.6, 125.0, 127.2, 127.5, 127.6, 127.7, 128.1, 128.2, 129.2, 129.8, 130.4, 132.3, 133.0, 133.2, 134.1, 135.1, 136.4, 137.7, 140.8, 141.1, 141.4, 143.8 ppm.



То solution ofN-(3-([1,1'-biphenyl]-2-yl)prop-2-yn-1-yl)-N-(2-bromo-4-fluorophenyl)-4а methylbenzenesulfonamide **1h** (160 mg, 0.3 mmol) in 2.5 M K₂CO₃(2 mL) and 2 mL ethanol-toluene (1:1), PCy₃ (8 mg, 0.03 mmol) and Pd(OAc)₂ (4 mg, 0.015 mmol) were added successively. The resulting solution was stirred at 70-75 °C under argon atmosphere for 4 h. After the completion of the reaction (monitored by TLC), the crude reaction mixture was extracted with ethyl acetate. The organic extract was washed with brine solution, dried over anhydrous Na2SO4 and concentrated. The product was subjected to column chromatography (silica gel, 60-120 mesh), eluting with pet ether/EtOAc 95:5 (v/v) to afford the product 2has a greenish white solid (114 mg, 0.25mmol, 83%); m. p. 152-154 °C. ¹H NMR (CDCl₃, 400 MHz) δ 2.29 (s, 3H), 4.72 (d, J= 2.8 Hz, 2H), 6.54 (t, J = 2.8 Hz, 1H), 6.71 (dd, J = 8.0, 2.4Hz, 1H), 6.84 (td, J= 9.2, 2.8 Hz, 1H), 7.14 (dd, J = 7.6, 2.0Hz, 3H), 7.16 (s, 1H), 7.21 (d, J= 7.2 Hz, 1H) 7.25-7.30 (m, 5H), 7.32-7.34 (m, 1H), 7.56–7.61 (m, 3H). ppm. ¹³C NMR (CDCl₃, 100 MHz) δ 21.7, 54.9, 107.2 (d, , J_{C-F} = 24.0 Hz), 116.4 (d, , J_{C-F} = 9.0 Hz), 116.5, 119.5, 127.3, 127.4, 127.4, 127.6, 127.9, 128.2, 129.7, 129.9, 130.6, 132.0 (d, , J_{C-F} = 3.0 Hz), 133.3, 133.4, 133.5, 133.7, 139.4, 140.6, 142.0, 144.5, 160.0 (d, , J_{CF} = 241.0 Hz). ppm.

(z)-2-((5-trifluoromethyl-1-tosylindolin-3-ylidene)methyl)biphenyl (2i)



To a solution of *N*-(3-([1,1'-biphenyl]-2-yl)prop-2-yn-1-yl)-*N*-(2-bromo-4-(trifluoromethyl)phenyl)-4methylbenzenesulfonamide **1i** (175 mg, 0.3 mmol) in 2.5 M K₂CO₃(2 mL) and 2 mL ethanol-toluene (1:1), PCy₃ (8 mg, 0.03 mmol) and Pd(OAc)₂ (4 mg, 0.015 mmol) were added successively. The resulting solution was stirred at 70-75 °C under argon atmosphere for 5 h. After the completion of the reaction (monitored by TLC), the crude reaction mixture was extracted with ethyl acetate. The organic extract was washed with brine solution, dried over anhydrous Na₂SO₄ and concentrated. The product was subjected to column chromatography (silica gel, 60-120 mesh), eluting with pet ether/EtOAc 95:5 (v/v) to afford the product **2i** as a pale greenish solid (116 mg, 0.23mmol, 78%); m. p. 124-126 °C. ¹H NMR (CDCl₃, 400 MHz) δ 2.40 (s, 3H), 4.80 (d, *J* = 3.2 Hz, 2H), 6.80 (t, *J* = 3.2Hz, 1H), 7.25–7.29 (m, 4H), 7.32 (d, *J* = 7.2 Hz, 1H), 7.35–7.43 (m, 7H), 7.47 (d, *J* = 8.8 Hz, 1H), 7.72 (d, *J* = 8.0 Hz, 2H), 7.77 (d, *J* = 8.4 Hz, 1H). ppm. ¹³C NMR (CDCl₃, 100 MHz) δ 21.7, 54.8, 114.4, 117.7, 120.1, 126.8, 127.2, 127.6, 127.6, 128.1, 128.3, 129.7, 130.1, 130.8, 131.2, 133.5, 134.0, 140.5, 142.0, 144.9, 145.8. ppm. (z)-2-((5-chloro-1-tosylindolin-3-ylidene)methyl)-4'-methoxybiphenyl (2j):



To a solution of *N*-(2-bromo-4-chlorophenyl)-*N*-(3-(4'-methoxy-[1,1'-biphenyl]-2-yl)prop-2-yn-1-yl)-4methylbenzenesulfonamide **1j** (175 mg, 0.3 mmol) in 2.5 M K₂CO₃(2 mL) and 2 mL ethanol-toluene (1:1), PCy₃ (8 mg, 0.03 mmol) and Pd(OAc)₂ (4 mg, 0.015 mmol) were added successively. The resulting solution was stirred at 70-75 °C under argon atmosphere for 4 h. After the completion of the reaction (monitored by TLC), the crude reaction mixture was extracted with ethyl acetate. The organic extract was washed with brine solution, dried over anhydrous Na₂SO₄ and concentrated. The product was subjected to column chromatography (silica gel, 60-120 mesh), eluting with pet ether/EtOAc 95:5 (v/v) to afford the product **2j** as a white solid (116 mg, 0.23mmol, 75%)as a mixture of non-separable isomers (E:Z=1:1.2); m. p. 144-146 °C. ¹H NMR (CDCl₃, 400 MHz) δ 2.28 (s, 3.6H), 2.30 (s, 3H), 3.75 (s, 3.6H), 3.76 (s, 3H), 4.67 (d, *J*= 2.8 Hz, 2H), 4.70 (d, *J*= 3.2 Hz, 2.4H), 6.62 (dt, *J* = 12.0, 3.2 Hz, 2H), 6.80–6.83 (m, 4H), 6.88 (td, *J*= 8.0, 1.0Hz, 1H), 7.05–7.16 (m, 14H), 7.18–7.23 (m, 2H), 7.26–7.30 (m, 6H),7.60 (dt, *J*= 21.6, 9.6Hz, 6H). ppm. ¹³C NMR (CDCl₃, 100 MHz) δ 21.6, 54.4. 54.8, 55.3, 113.6, 113.8, 114.9, 116.0, 118.4, 119.9, 120.5, 120.5, 123.9, 127.2, 127.3, 127.4, 127.5, 127.6, 128.0, 129.4, 129.5, 129.7, 129.9, 130.0, 130.6, 130.7, 130.8, 130.9, 131.4, 132.5, 133.2, 133.6, 133.7, 134.0, 134.1, 141.4, 141.6, 141.9, 144.3, 144.3, 144.6, 158.9, 159.0. ppm.

(z)-2-((5-fluoro-1-tosylindolin-3-ylidene)methyl)-4'-methoxybiphenyl (2k):



ofN-(2-bromo-4-fluorophenyl)-N-(3-(4'-methoxy-[1,1'-biphenyl]-2-yl)prop-2-yn-1-yl)-4-То solution а methylbenzenesulfonamide 1k (169 mg, 0.3 mmol) in 2.5 M K₂CO₃(2 mL) and 2 mL ethanol-toluene (1:1), PCy₃ (8 mg, 0.03 mmol) and Pd(OAc)₂ (4 mg, 0.015 mmol) were added successively. The resulting solution was stirred at 70-75 °C under argon atmosphere for 4 h. After the completion of the reaction (monitored by TLC), the crude reaction mixture was extracted with ethyl acetate. The organic extract was washed with brine solution, dried over anhydrous Na₂SO₄ and concentrated. The product was subjected to column chromatography (silica gel, 60-120 mesh), eluting with pet ether/EtOAc 95:5 (v/v) to afford the product 2k as a greenish white solid (112 mg, 0.23mmol, 78%); m. p. 158-160 °C. 1 H NMR (CDCl₃, 400 MHz) δ 2.28 (s, 3H), 3.75 (s, 3H), 4.69 (d, J= 3.2 Hz, 2H), 6.56 (t, J = 3.2 Hz, 1H), 6.75 (dd, J= 8.0, 2.4Hz, 1H), 6.78–6.86 (m, 3H), 7.06 (dt, J= 6.8, 2.0 Hz, 2H) 7.14–7.18 (m, 3H), 7.20–7.30 (m, 3H), 7.55–7.60 (m, 3H). ppm. ¹³C NMR $(CDCI_3, 100 \text{ MHz}) \delta 21.6, 54.3, 54.9, 107.2 \text{ (d, } J_{C-F} = 24.0 \text{ Hz}), 113.7, 116.3 \text{ (d, } J_{C-F} = 7.0 \text{ Hz}), 116.4 \text{ (d, } J_{C-F} = 7.0 \text{ Hz})$ 9.0 Hz), 119.8, 127.2, 127.3, 127.4, 127.9, 129.9, 130.6, 130.8, 131.8 (d, , J_{C-F} = 2.0 Hz), 132.9, 133.3, 133.4, 133.5, 133.6, 139.4, 141.6, 144.5, 159.0, 160.0 (d, , J_{C-F} = 241.0 Hz), ppm.

(z)-2-((5-methyl-1-tosylindolin-3-ylidene)methyl)-5-methylbiphenyl (2l):



To a solution of *N*-(2-bromo-4-methylphenyl)-4-methyl-*N*-(3-(5-methyl-[1,1'-biphenyl]-2-yl)prop-2-yn-1yl)benzenesulfonamide **1I** (164 mg, 0.3 mmol) in 2.5 M K₂CO₃(2 mL) and 2 mL ethanol-toluene (1:1), PCy₃ (8 mg, 0.03 mmol) and Pd(OAc)₂ (4 mg, 0.015 mmol) were added successively. The resulting solution was stirred at 70-75 °C under argon atmosphere for 5 h. After the completion of the reaction (monitored by TLC), the crude reaction mixture was extracted with ethyl acetate. The organic extract was washed with brine solution, dried over anhydrous Na₂SO₄ and concentrated. The product was subjected to column chromatography (silica gel, 60-120 mesh), eluting with pet ether/EtOAc 95:5 (v/v) to afford the product **2I** as a greenish solid (112 mg, 0.24mmol, 80%); m. p. 162-164 °C. ¹H NMR (CDCl₃, 400 MHz) δ 2.23 (s, 3H), 2.36 (s, 3H),2.41 (s, 3H), 4.76 (d, *J*= 2.8 Hz, 2H), 6.62 (t, *J* = 3.2Hz, 1H), 6.94 (s, 1H), 7.03 (d, *J*= 8.0 Hz, 1H), 7.18–7.26 (m, 7H), 7.32-7.38 (m, 3H), 7.61 (d, *J*= 8.0 Hz, 1H), 7.67 (d, *J*= 8.0 Hz, 2H). ppm. ¹³C NMR (CDCl₃, 100 MHz) δ 21.0, 21.3, 21.6, 54.7, 114.9, 117.8, 120.8, 127.2, 127.3, 127.4, 128.2, 128.3, 129.8, 129.8, 130.4, 131.3, 131.4, 131.6, 132.2, 133.6, 134.1, 137.4, 141.0, 141.2, 141.7, 144.2. ppm.

(z)-2-((1-mesylindolin-3-ylidene)methyl)-4'-methoxybiphenyl (2m):



То solution ofN-(2-bromophenyl)-N-(3-(4'-methoxy-[1,1'-biphenyl]-2-yl)prop-2-yn-1а yl)methanesulfonamide 1m (141 mg, 0.3 mmol) in 2.5 M K₂CO₃(2 mL) and 2 mL ethanol-toluene (1:1), PCy₃(8 mg, 0.03 mmol) and Pd(OAc)₂ (4 mg, 0.015 mmol) were added successively. The resulting solution was stirred at 75 °C under argon atmosphere for 3 h. After the completion of the reaction (monitored by TLC), the crude reaction mixture was extracted with ethyl acetate. The organic extract was washed with brine solution, dried over anhydrous Na₂SO₄and concentrated. The product was subjected to column chromatography (silica gel, 60-120 mesh), eluting with pet ether/EtOAc 95:5 (v/v) to afford the product 2mas a white solid (102 mg, 0.26 mmol, 85%); m. p. 146-148 °C. ¹H NMR (CDCl₃, 500 MHz) δ 2.88 (s, 3H), 3.85 (s, 3H) 4.83 (d, J= 3.0 Hz, 2H) , 6.88 (t, J = 3.5 Hz, 1H), 6.95 (dd, J= 7.0, 2.0 Hz,2H), 7.04 (td, J= 7.5, 0.5 Hz, 1H), 7.24 (d, J= 7.5 Hz, 1H), 7.27 (dd, J= 5.0, 4.5 Hz, 2H), 7.29 (dd, J= 6.5, 2.0 Hz, 1H), 7.33 (d, J= 7.5 Hz, 1H) 7.34–7.39 (m, 3H), 7.51 (d, J= 8.5 Hz,1H) ppm. ¹³C NMR (CDC₁₃, 125 MHz) δ 35.3, 54.8, 55.4, 113.7, 113.8, 114.2, 118.8, 120.8, 124.1, 127.3, 127.5, 127.8, 129.9, 130.5, 130.6, 131.0, 131.2, 132.3, 133.3, 134.0, 141.6, 143.2, 159.0 ppm.



То solution of N-(3-([1,1'-biphenyl]-2-yl)prop-2-yn-1-yl)-N-(3-bromopyridin-2-yl)-4а methylbenzenesulfonamide **1n** (155 mg, 0.3 mmol) in 2.5 M K₂CO₃(2 mL) and 2 mL ethanol-toluene (1:1), PCy₃ (8 mg, 0.03 mmol) and Pd(OAc)₂ (4 mg, 0.015 mmol) were added successively. The resulting solution was stirred at 75 °C under argon atmosphere for 5 h. After the completion of the reaction (monitored by TLC), the crude reaction mixture was extracted with ethyl acetate. The organic extract was washed with brine solution, dried over anhydrous Na2SO4 and concentrated. The product was subjected to column chromatography (silica gel, 60-120 mesh), eluting with pet ether/EtOAc 90:10 (v/v) to afford the product **2n** as a yellow solid (100 mg, 0.23 mmol, 75%); m. p. 148-150 °C. ¹H NMR (CDCl₃, 500 MHz) δ 2.39 (s, 3H), 4.95 (d, J= 3.0 Hz, 2H), 6.78 (t, J = 3.0Hz, 1H), 6.81 (dd, J= 7.5, 5.5 Hz,1H), 7.28 (dd, J= 14.5, 7.0 Hz, 2H), 7.31 (dd, J= 4.5, 2.0 Hz, 2H), 7.32-7.41 (m, 7H), 7.44 (dd, J= 6.0, 3.0 Hz, 1H), 8.01 (dd, J= 8.5, 2.0 Hz, 2H), 8.18 (dd, J= 5.0, 1.5 Hz, 1H). ppm. 13 C NMR (CDCl $_3$, 125 MHz) δ 21.7, 53.3, 118.4, 120.7, 124.4, 127.4, 127.5, 127.7, 128.0, 128.1, 128.2, 128.3, 129.5, 129.6, 129.8, 130.7, 133.4, 135.6, 140.7, 142.0, 144.4, 148.6, 156.5 ppm.

(z)-2-((5-methyl-1-tosyl-7-azaindolin-3-ylidene)methyl)biphenyl (2o):



N-(3-([1,1'-biphenyl]-2-yl)prop-2-yn-1-yl)-N-(3-bromo-5-methylpyridin-2-yl)-4-То а solution of methylbenzenesulfonamide 1o (159 mg, 0.3 mmol) in 2.5 M K₂CO₃(2 mL) and 2 mL ethanol-toluene (1:1), PCy₃ (8 mg, 0.03 mmol) and Pd(OAc)₂ (4 mg, 0.015 mmol) were added successively. The resulting solution was stirred at 75 °C under argon atmosphere for 5 h. After the completion of the reaction (monitored by TLC), the crude reaction mixture was extracted with ethyl acetate. The organic extract was washed with brine solution, dried over anhydrous Na₂SO₄ and concentrated. The product was subjected to column chromatography (silica gel, 60-120 mesh), eluting with pet ether/EtOAc 90:10 (v/v) to afford the product **20** as a yellow solid (95 mg, 0.21 mmol, 70%); m. p. 156-158 °C. ¹H NMR (CDCl₃, 400 MHz) δ 2.21 (s, 3H), 2.40 (s, 3H), 4.94 (d, J= 3.2 Hz, 2H), 6.77 (t, J = 3.2Hz, 1H), 7.22 (d, J= 1.6 Hz,1H), 7.29 (d, J= 8.0 Hz, 2H),7.32–7.35 (m, 2H), 7.38–7.40 (m, 6H),7.42 (dd, J= 5.6, 1.6 Hz, 1H), 8.00 (d, J= 8.0 Hz, 2H), 8.03 (d, J= 1.0 Hz, 1H). ppm. ¹³C NMR (CDCl₃, 100 MHz) δ 18.0, 21.7, 53.5, 120.4, 127.4, 127.6, 127.7, 127.9, 128.0, 128.3, 128.9, 129.6, 129.8, 129.8, 130.7, 133.5, 140.8, 141.9, 144.3, 148.8, 154.8 ppm.



To a solution of **2a** (66 mg, 0.15 mmol) in dry nitromethane (1.5 mL) was added DDQ (0.15 mmol) in presence of anhydrous FeCl₃ (5 mg, 0.03 mmol) and 4Å molecular sieves as additive. The reaction mixture was stirred at 60 °C temperature under an argon atmosphere for 3 h. After the completion of the reaction (monitored by TLC), the crude reaction mixture was extracted with DCM. The organic extract was dried over anhydrous Na₂SO₄ and product was purified by column chromatography (silica gel, 60-120 mesh), eluting with pet ether/EtOAc 97:3 (v/v) to afford the product **3a** as a white solid (56 mg, 0.13 mmol, 85%), m. p. 166-168 °C. . ¹H NMR (CDCl₃, 300 MHz) δ 2.37 (s, 3H), 5.24 (s, 1H), 6.70 (d, *J*= 7.8 Hz, 1H), 6.95 (t, *J*= 8.1 Hz, 1H), 7.17–7.23 (m, 5H), 7.24–7.29 (m, 2H), 7.40 (t, *J*= 7.2 Hz, 2H), 7.57 (s, 1H), 7.76 (d, *J*= 8.1 Hz, 2H), 7.84 (d, *J*= 6.9 Hz, 2H), 7.93 (d, *J*= 8.1 Hz, 1H).ppm. ¹³C NMR (CDCl₃, 75MHz) δ 21.7, 45.8, 113.9, 120.2, 120.3, 122.3, 123.2, 124.5, 124.8, 125.1, 126.9, 127.5, 127.7, 129.8, 130.0, 135.3, 135.9, 141.0, 145.0, 146.0 ppm. HRMS: cacld for C₂₈H₂₁NO₂S [M]⁺ 435.1293; found 435.1292.

3-(2-methoxy-9H-fluoren-9-yl)-1-tosyl-1H-indole (3b):



Compound **2b** (70 mg, 0.15 mmol) was treated with DDQ(0.15 mmol) in combination with anhydrous FeCl₃ (5 mg, 0.03 mmol) and 4Å molecular sieves under argon atmosphere at 60°C temperature as described for the synthesis of **3b** for 2 h to afford **3b** as a off white solid (60 mg, 0.13 mmol, 84%), m. p. 147-149 °C.¹H NMR (CDCl₃, 300 MHz) δ 2.39 (s, 3H), 3.77 (s, 3H), 5.20 (s, 1H), 6.71 (d, *J*= 7.2 Hz,1H), 6.82 (s, 1H), 6.95 (d, *J*= 7.2Hz,2H), 7.15–7.19 (m, 2H),7.22–7.28 (m, 3H), 7.38 (t, *J*= 7.2 Hz, 1H), 7.60 (s, 1H), 7.77 (t, *J*= 8.7 Hz, 4H), 7.95 (d, *J*= 8.4 Hz, 1H).ppm. ¹³C NMR (CDCl₃, 75MHz) δ 21.7, 45.8, 55.5, 110.6, 113.8, 119.3, 120.3, 122.4, 123.2, 124.5, 124.8, 124.9, 126.3, 126.9, 127.7, 129.7, 129.9, 133.9, 135.3, 135.9, 141.0, 145.0, 145.5, 147.8, 159.7 ppm. HRMS: cacld for C₂₉H₂₃NO₃S [M+H]⁺ 466.1432; found 466.1478.

3-(2-methyl-9H-fluoren-9-yl)-1-tosyl-1H-indole (3c):



Compound **2c** (68 mg, 0.15 mmol) was treated with DDQ(0.15 mmol) in combination with anhydrous FeCl₃ (5 mg, 0.03 mmol)and 4Å molecular sieves under argon atmosphere at 60 °C temperature as described for the synthesis of **3c** for 2.5 h to afford **3c** as a white solid (58 mg, 0.13 mmol, 90%), m. p. 168-170 °C.¹H NMR (CDCl₃, 400 MHz) δ 2.32 (s, 3H), 2.37 (s, 3H), 5.20 (s, 1H), 6.70 (d, *J*= 6.0 Hz,1H), 6.95 (t, *J*= 7.2 Hz,1H), 7.08 (s, 1H), 7.17–7.26 (m, 6H), 7.39 (t, *J*= 7.2 Hz, 1H), 7.59 (s, 1H), 7.72–7.81 (m, 4H), 7.96 (d, *J*= 8.4 Hz, 1H). ppm. ¹³C NMR (CDCl₃, 100 MHz) δ 21.4, 21.6, 21.7, 45.6, 113.9, 119.8, 120.3, 122.6, 123.2, 124.5, 124.7, 125.0, 125.7, 126.8, 126.9, 127.7, 128.6, 129.0, 129.8, 129.9, 135.3, 135.9, 137.3, 138.3, 141.1, 144.9, 145.8, 146.2 ppm. HRMS: cacld for C₂₉H₂₃NO₂SNa [M+Na]⁺ 472.1347; found 472.1350.

N Ts



Compound **2d** (71 mg, 0.15 mmol) was treated with DDQ (0.15 mmol) in combination with anhydrous FeCl₃ (5 mg, 0.03 mmol) and 4Å molecular sieves under argon atmosphere at 60 °C temperature as described for the synthesis of **3d** for 2 h to afford **3d** as a off white solid (52 mg, 0.11 mmol, 74%), m. p. 158-160 °C.¹H NMR (CDCl₃, 400 MHz) δ 2.37 (s, 3H), 5.22 (s, 1H), 6.66 (d, *J*= 5.6 Hz,1H), 6.96 (t, *J*= 7.6 Hz,1H),7.21–7.30 (m, 6H), 7.36–7.42 (m, 2H),7.59 (s, 1H), 7.78 (td, *J*= 8.4, 13.2 Hz, 4H), 7.98 (d, *J*= 8.4 Hz,1H). ppm. ¹³C NMR (CDCl₃, 100 MHz) δ 21.6, 45.7, 114.0, 120.0, 120.2, 121.0, 121.6, 123.3, 124.7, 124.9, 125.1, 125.3, 126.9, 127.8, 128.1, 129.5, 130.0, 133.1, 135.1, 135.9, 139.5, 139.9, 145.1, 145.8, 147.8ppm. HRMS: cacld for C₂₈H₂₀ClNO₂SNa [M+Na]⁺ 492.0801; found 492.0800.

3-(3-methyl-9H-fluoren-9-yl)-1-tosyl-1H-indole (3e):



Compound **2e** (68 mg, 0.15 mmol) was treated with DDQ (0.15 mmol) in combination with anhydrous FeCl₃ (5 mg, 0.03 mmol) and 4Å molecular sieves under argon atmosphere at 60 °C temperature as described for the synthesis of **3e** for 2 h to afford **3e** as a off white solid (54 mg, 0.12 mmol, 83%), m. p. 156-158 °C.¹H NMR (CDCl₃, 300 MHz) δ 2.37 (s, 3H), 2.46 (s, 3H), 5.20 (s, 1H), 6.71 (d, *J*= 7.8 Hz,1H), 6.95 (t, *J*= 7.8 Hz,1H), 7.04 (d, *J*= 7.8 Hz,1H), 7.19 (dd, *J*= 7.8, 15.6 Hz,2H), 7.25–7.41 (m, 4H), 7.38 (t, *J*= 7.5 Hz, 1H), 7.55 (s, 1H), 7.65 (s, 1H), 7.79 (dd, *J*= 8.4, 15.6 Hz, 3H), 7.93 (d, *J*= 8.4 Hz,1H). ppm. ¹³C NMR (CDCl₃, 125MHz) δ 21.6, 45.4, 113.9, 120.0, 120.3, 120.7, 122.7, 123.2, 124.8, 125.1, 126.9, 127.3, 127.7, 128.4, 129.9, 135.6, 136.0, 137.5, 141.1, 141.2, 143.2, 144.9, 146.5ppm. HRMS: cacld for C₂₉H₂₃NO₂SNa [M+Na]⁺ 472.1347; found 472.1385.

3-(9H-fluoren-9-yl)-5-methyl-1-tosyl-1H-indole (3f):



Compound **2f** (68 mg, 0.15 mmol) was treated with DDQ(0.15 mmol) in combination with anhydrous FeCl₃ (5 mg, 0.03 mmol) and 4Å molecular sieves under argon atmosphere at 60 °C temperature as described for the synthesis of **3f** for 2 h to afford **3f** as a off white solid (59 mg, 0.13 mmol, 88%), m. p. 183-185 °C.¹H NMR (CDCl₃, 400 MHz) δ 2.20 (s, 3H), 2.36 (s, 3H), 5.23 (s, 1H), 6.60 (bs, 1H), 7.05 (d, *J*= 8.4 Hz,1H), 7.21–7.26 (m, 4H), 7.29 (d, *J*= 7.2 Hz, 2H), 7.41 (t, *J*= 7.6 Hz, 2H),7.46 (s, 1H), 7.74 (d, *J*= 8.4 Hz, 2H), 7.84 (t, *J*= 8.4 Hz, 3H). ppm. ¹³C NMR (CDCl₃, 100 MHz) δ 21.4, 21.6, 45.6, 113.6, 120.0, 120.2, 122.3, 124.5, 125.0, 126.3, 126.9, 127.4, 127.7, 128.3, 129.9, 130.2, 132.9, 134.1, 135.3, 141.0, 144.9, 146.0 ppm. HRMS: cacld for C₂₉H₂₃NO₂SNa [M+Na]⁺472.1347; found 472.1385.



Compound **2g** (70 mg, 0.15 mmol) was treated with DDQ(0.15 mmol) in combination with anhydrous FeCl₃ (5 mg, 0.03 mmol)and 4Å molecular sieves under argon atmosphere at 60 °C temperature as described for the synthesis of **3g** for 3.5 h to afford **3g** as a off white solid (57 mg, 0.12 mmol, 82%), m. p. 152-154 °C.¹H NMR (CDCl₃, 300 MHz) δ 2.16 (s, 3H), 2.37 (s, 3H), 2.54 (s, 3H), 5.21 (s, 1H), 6.51 (bs, 1H), 6.80 (s, 1H), 7.16–7.25 (m, 4H), 7.26–7.28 (m, 2H), 7.38–7.53 (m, 5H), 7.84 (d, *J*= 7.5 Hz, 2H). ppm. ¹³C NMR (CDCl₃, 75MHz) δ 21.1, 21.7, 21.7, 45.4, 117.7, 120.1, 122.6, 124.9, 125.6, 126.6, 127.4, 127.6, 128.2, 129.7, 130.0, 132.7, 133.5, 134.5, 136.3, 141.0, 144.4, 146.1 ppm. HRMS: cacld for C₃₀H₂₅NO₂SNa [M+Na]⁺ 486.1504; found 486.1502.

3-(9H-fluoren-9-yl)-5-fluoro-1-tosyl-1H-indole (3h):



Compound **2h** (68 mg, 0.15 mmol) was treated with DDQ (0.15 mmol) in combination with anhydrous FeCl₃ (5 mg, 0.03 mmol) and 4Å molecular sieves under argon atmosphere at 60°C temperature as described for the synthesis of **3h** for 3 h to afford **3h** as a white solid (54 mg, 0.12 mmol, 80%), m. p. 208-210 °C.¹H NMR (CDCl₃, 400 MHz) δ 2.38 (s, 3H), 5.20 (s, 1H), 6.25 (d, *J*= 8.0 Hz,1H), 6.93 (t, *J*= 8.0 Hz,1H), 7.24–7.28 (m, 6H),7.43 (t, *J*= 8.0 Hz, 2H), 7.66 (s, 1H), 7.76 (d, *J*= 8.8 Hz,2H), 7.88 (dd, *J*= 8.0, 8.0 Hz, 3H). ppm. ¹³C NMR (CDCl₃, 100 MHz) δ 21.7, 45.7,106.0 (d, , *J*_{C-F} = 24.0 Hz), 112.9 (d, , *J*_{C-F} = 26.0 Hz),114.9 (d, , *J*_{C-F} = 9.0 Hz), 122.2 (d, , *J*_{C-F} = 4.0 Hz), 125.0, 126.8, 126.9, 127.5, 127.9, 128.3, 129.1, 129.9, 130.0, 130.6, 130.7, 132.3, 135.1, 141.0, 145.2, 145.5, 159.3 (d, , *J*_{C-F} = 239.0 Hz),ppm. HRMS: cacld for C₂₈H₂₀FNO₂SNa [M+Na]⁺ 476.1096; found 476.1091.

3-(9H-fluoren-9-yl)-5-(trifluoromethyl)-1-tosyl-1H-indole (3i):



Compound **2i** (76 mg, 0.15 mmol) was treated with DDQ (0.15 mmol) in combination with anhydrous FeCl₃ (5 mg, 0.03 mmol) and 4Å molecular sieves under argon atmosphere at 60 °C temperature as described for the synthesis of **3i** for 3.5 h to afford **3i** as a off white solid (55 mg, 0.11 mmol, 75%), m. p. 170-172 °C.¹H NMR (CDCl₃, 400 MHz) δ 2.38 (s, 3H), 5.27 (s, 1H), 7.06 (s, 1H), 7.22–7.28 (m, 6H), 7.41–7.47 (m, 3H), 7.62 (s, 1H), 7.77 (d, *J*= 8.4 Hz, 2H), 7.86 (d, *J*= 7.6 Hz, 2H), 8.04 (d, *J*= 8.8 Hz, 1H). ppm. ¹³C NMR (CDCl₃, 100 MHz) δ 21.7, 45.3, 114.2, 117.7 (q, *J*_{C-F} = 4.0 Hz), 120.3, 121.6 (q, *J*_{C-F} = 4.0 Hz), 122.6, 123.0, 124.9, 125.1, 125.4, 125.7 (d, *J*_{C-F} = 5.0 Hz), 126.9, 127.6, 128.0, 128.4, 129.6, 130.2, 135.0, 137.2, 141.0, 145.5 (d, *J*_{C-F} = 8.0 Hz).ppm. HRMS: cacld for C₂₉H₂₀F₃NO₂SNa [M+Na]⁺ 526.1065; found 526.1068.



Compound **2j** (75 mg, 0.15 mmol) was treated with DDQ (0.15 mmol) in combination with anhydrous FeCl₃ (5 mg, 0.03 mmol) and 4Å molecular sieves under argon atmosphere at 60 °C temperature as described for the synthesis of **3j** for 3 h to afford **3j** as a pale yellow solid (57 mg, 0.11 mmol, 76%, 1:1.7 dr), m. p. 120-122 °C.¹H NMR (CDCl₃, 300 MHz) δ 2.36 (s, 3H), 2.37 (s, 5H), 3.74 (s, 3H) 3.75 (s, 5H), 5.13 (s, 1.7H), 5.18 (s, 1H)6.63 (s, 1H), 6.70 (d, *J*= 7.8 Hz,1H), 6.79 (dd, *J*= 1.8, 10.8 Hz,3H), 6.95 (dt, *J*= 2.1, 8.4 Hz,3H), 7.11–7.26 (m, 14H),7.33–7.40 (m, 3H), 7.58 (s, 3H), 7.60–7.61 (m, 10H), 7.72 (d, *J*= 3.3 Hz, 2H), 7.75 (d, *J*= 3.3 Hz, 1H). ppm. ¹³C NMR (CDCl₃, 100 MHz) δ 21.6, 21.7, 45.5, 45.8, 55.5, 55.5, 110.6, 110.7, 113.8, 114.9, 119.3, 119.5, 119.9, 120.3, 120.8, 121.0, 122.0, 123.2, 124.5, 124.7, 124.8, 124.9, 125.2, 125.8, 126.3, 126.4, 126.9, 127.7, 127.9, 129.1, 129.8, 130.0, 130.9, 133.9, 134.0, 134.3, 135.0, 140.9, 145.0, 145.0, 145.3, 145.5, 147.4, 147.9, 159.8, 159.8 ppm. HRMS: cacld for C₂₉H₂₂ClNO₃SNa [M+Na]⁺ 522.0907; found 522.0908.

5-fluoro-3-(2-methoxy-9H-fluoren-9-yl)-1-tosyl-1H-indole (3k):



Compound **2k** (73 mg, 0.15 mmol) was treated with DDQ (0.15 mmol) in combination with anhydrous FeCl₃ (5 mg, 0.03 mmol) and 4Å molecular sieves under argon atmosphere at 60°C temperature as described for the synthesis of **3k** for 3 h to afford **3k** as a white solid (58 mg, 0.12 mmol, 78%), m. p. 138-140°C.¹H NMR (CDCl₃, 400 MHz) δ 2.37 (s, 3H), 3.74 (s, 3H), 5.11 (s, 1H), 6.21 (d, *J* = 8.0 Hz,1H), 6.22 (s, 1H), 6.89–6.95 (m, 2H), 7.16 (dd, *J* = 7.6, 13.2 Hz,2H), 7.23–7.25 (m, 2H) 7.36 (t, *J* = 7.2 Hz, 1H), 7.64 (s, 1H), 7.71–7.75 (m, 4H) 7.86 (dd, *J* = 4.4, 8.8 Hz,1H). ppm. ¹³C NMR (CDCl₃, 125MHz) δ 21.7, 45.7, 55.5, 106.0 (d, *J* _{C-F} = 23.7 Hz), 110.7, 112.9 (d, *J* _{C-F} = 25.0 Hz), 113.8, 114.9 (d, *J* _{C-F} = 8.7 Hz), 119.5, 121.0, 122.4 (d, *J* _{C-F} = 3.7 Hz), 126.3 (d, *J* _{C-F} = 8.7 Hz), 126.9, 127.4, 127.9, 129.9 (d, *J* _{C-F} = 26.2 Hz), 130.6 (d, *J* _{C-F} = 8.7 Hz), 135.0, 141.0, 145.1 (d, *J* _{C-F} = 26.2 Hz), 147.4, 159.8 159.4 (d, *J* _{C-F} = 238.7 Hz) ppm. HRMS: cacld for C₂₉H₂₂FNO₃S [M+H]⁺ 484.1383; found 484.1374.

5-methyl-3-(3-methyl-9H-fluoren-9-yl)-1-tosyl-1H-indole (3I):



Compound **2I** (70 mg, 0.15 mmol) was treated with DDQ(0.15 mmol) in combination with anhydrous FeCl₃ (5 mg, 0.03 mmol) and 4Å molecular sieves under argon atmosphere at 60 °C temperature as described for the synthesis of **3I** for 3 h to afford **3I** as a off white solid (56 mg, 0.12 mmol, 80%), m. p. 168-170 °C.¹H NMR (CDCl₃, 400 MHz) δ 2.20 (s, 3H), 2.35 (s, 3H), 2.46 (s, 3H), 5.17 (s, 1H), 6.61 (bs, 1H), 7.03–7.05 (m, 2H), 7.15–7.26 (m, 5H), 7.39 (dd, *J*= 8.8, 15.6 Hz, 2H), 7.65 (s, 1H), 7.72 (d, *J*= 8.0 Hz, 2H), 7.81 (d, *J*= 8.4 Hz, 2H). ppm. ¹³C NMR (CDCl₃, 100MHz) δ 21.4, 21.7, 5.2, 113.6, 120.0, 120.0, 120.7, 122.6, 124.4, 124.7, 125.0, 126.2, 126.9, 127.3, 127.6, 128.4, 129.9, 132.8, 134.1, 135.3, 137.4, 141.1, 143.2, 144.8, 146.4ppm. HRMS: cacld for C₃₀H₂₅NO₂SNa [M+Na]⁺ 486.1504; found 486.1506.



Compound **2m** (59 mg, 0.15 mmol) was treated with DDQ (0.15 mmol) in combination with anhydrous FeCl₃ (5 mg, 0.03 mmol) and 4Å molecular sieves under argon atmosphere at 60 °C temperature as described for the synthesis of **3m** for 2 h to afford **3m** as a white solid (47 mg, 0.12 mmol, 81%), m. p. 160-162 °C.¹H NMR (CDCl₃, 400 MHz) δ 3.13 (s, 3H), 3.80 (s, 3H), 5.26 (s, 1H), 6.91 (d, *J*= 7.6 Hz,1H), 6.95 (s, 1H), 6.99 (d, *J*= 8.4 Hz, 1H), 7.08 (t, *J*= 7.6 Hz, 1H), 7.20 (t, *J*= 7.2 Hz, 1H), 7.28–7.42 (m, 3H), 7.46 (s, 1H), 7.78 (d, *J*= 8.0 Hz, 2H), 7.89 (d, *J*= 8.4 Hz, 1H) .ppm. ¹³C NMR (CDCl₃, 75MHz) δ 40.7, 45.7, 55.6, 110.9, 113.2, 113.7, 119.4, 120.6, 120.9, 122.2, 123.4, 123.9, 125.0, 125.1, 126.4, 127.8, 129.7, 134.0, 135.8, 141.0, 145.5, 147.8, 159.8 ppm. HRMS: cacld for C₂₃H₁₉NO₃SNa [M+Na]⁺ 412.0983; found 412.0985.

3-(9H-fluoren-9-yl)-1-tosyl-1H-pyrrolo[2,3-b]pyridine (3n):



Compound **2n** (66 mg, 0.15 mmol) was treated with DDQ (0.19 mmol) in combination with anhydrous FeCl₃ (5 mg, 0.03 mmol) and 4Å molecular sieves under argon atmosphere at 60 °C temperature as described for the synthesis of **3n** for 5 h to afford **3n** as a off white solid (44 mg, 0.10 mmol, 66%),The organic extract was dried over anhydrous Na₂SO₄ and product was purified by column chromatography (silica gel, 60-120 mesh), eluting with pet ether/EtOAc 97:5 (v/v),m. p. 176-178 °C.¹H NMR (CDCl₃, 300 MHz) δ 2.38 (s, 3H), 5.21 (s, 1H), 6.75–6.84 (m, 2H), 7.20–7.31 (m, 6H), 7.38–7.43 (m, 2H), 7.84 (t, *J*= 4.2 Hz, 3H), 8.08–8.12 (m, 2H), 8.27 (dd, *J*= 1.8, 4.5 Hz, 1H). ppm. ¹³C NMR (CDCl₃, 100 MHz) δ 21.7, 46.0, 118.5, 118.6, 120.2, 121.7, 124.2, 125.2, 127.5, 127.9, 128.2, 128.7, 129.7, 135.6, 140.9, 145.0, 145.2, 145.6, 147.9 ppm. HRMS: cacld for C₂₇H₂₀N₂O₂S [M+H]⁺ 437.1324; found 437.1322.

3-(9H-fluoren-9-yl)-5-methyl-1-tosyl-1H-pyrrolo[2,3-b]pyridine (3o):



Compound **2o** (68 mg, 0.15 mmol) was treated with DDQ (0.19 mmol) in combination with anhydrous FeCl₃ (5 mg, 0.03 mmol) and 4Å molecular sieves under argon atmosphere at 60 °C temperature as described for the synthesis of **3o** for 5 h to afford **3o** as a white solid (45 mg, 0.10 mmol, 68%),The organic extract was dried over anhydrous Na₂SO₄ and product was purified by column chromatography (silica gel, 60-120 mesh), eluting with pet ether/EtOAc 97:5 (v/v),m. p. 194-196 °C.¹H NMR (CDCl₃, 400 MHz) δ 2.03 (s, 3H), 2.31 (s, 3H), 5.11 (s, 1H), 6.52 (s, 1H), 7.15–7.24 (m, 6H), 7.34 (t, *J*= 7.6 Hz, 2H), 7.68 (s, 1H), 7.77 (d, *J*= 7.6 Hz, 2H), 7.98–8.05 (m, 3H). ppm. ¹³C NMR (CDCl₃, 100 MHz) δ 18.4, 21.7, 46.0, 118.3, 120.2, 121.7, 124.4, 125.1, 127.5, 127.9, 128.0, 128.1, 128.6, 129.7, 135.7, 141.0, 145.0, 145.7, 145.9, 146.5 ppm. HRMS: cacld for C₂₈H₂₃N₂O₂SNa [M+Na]⁺ 473.1300; found 473.1303.

NMR data of compound 3-indolyl biphenyl ketone:



¹H NMR (CDCl₃, 400 MHz) δ 2.38 (s, 3H), 7.14 (d, *J*= 7.2 Hz, 1H), 7.18–7.26 (m, 4H),7.30 (dd, *J*= 3.2, 3.2 Hz, 2H), 7.37 (d, *J*= 7.2 Hz, 2H), 7.48–7.55 (m, 3H), 7.59 (d, *J*= 8.4 Hz, 3H), 7.62 (s, 1H), 7.75 (dd, *J*= 3.2, 2.4 Hz, 1H), 8.25 (dd, *J*= 2.8, 2.8 Hz, 1H) ppm. ¹³C NMR (CDCl₃, 100 MHz) δ 21.8, 112.9, 121.4, 123.0, 124.8, 125.7, 127.2, 127.3, 127.6, 127.8, 128.6, 128.9 130.2, 130.3, 130.5, 130.6, 134.5, 134.7, 135.0, 139.9,140.2, 140.5 145.8, 193.5 ppm. HRMS: cacld for C₂₈H₂₁NO₃SNa [M+Na]⁺ 474.1140; found 474.1143.

Two view of ortep diagram for the crystal structure of the compound 3a (Thermal ellipsoid contour at 50% probability level)



CCDC no.1964540























¹³C NMR of 2g, CDCl₃, 100 MHz



¹³C NMR expansion of 2g, CDCl₃, 100 MHz











¹³C NMR expansion of 2k, CDCl₃, 100 MHz



¹³C NMR of 2I, CDCl₃, 100 MHz



¹H NMR of 2m, CDCl₃, 500 MHz





¹³C NMR of 2n, CDCl₃, 125 MHz



¹H NMR of 2o, CDCl₃, 400 MHz

















¹³C NMR expansion of 3d, CDCl₃, 100 MHz









MHz







$^{\rm 13}{\rm C}$ NMR of 3i, CDCl₃, 100 MHz



¹³C NMR expansion of 3i, CDCl₃, 100 MHz



¹H NMR of 3j, CDCl₃, 300 MHz









¹H NMR of 3m, CDCl₃, 400 MHz





200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 ppm





