Supporting Information

Ag(I)-Catalyzed Cyclization of \( o \)-Alkynylacetophenones Facilitated Through Acetal Formation: Synthesis of C3-Naphthyl Indole Derivatives

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1. General information

Unless otherwise mentioned, chemicals obtained from commercial suppliers were used without further purification. AgOTf and TMOF were purchased from Sigma-Aldrich, and Avra synthesis respectively, and were used without further purification. All the reactions were performed in oven-dried glassware with magnetic stirring. Dichloromethane (DCM) was dried in the presence of calcium hydride and distilled before use. Reactions were monitored using silica gel plates 60 F254 and were visualized with UV light (254 nm), with Seebach stain followed by heating. Column chromatography was carried out using silica gel (100-200 mesh) packed in glass columns. NMR spectra were recorded at 400, 500 MHz (1H) and at 100, 125 MHz (13C), respectively. Chemical shifts (δ) are reported in ppm, using the residual solvent peak in CDCl3 (H: δ = 7.26 and C: δ = 77.0 ppm) as internal standard, and coupling constants (J) are indicated in Hz. HRMS were recorded using ESI-TOF techniques.

2. Synthesis of N-protected indoles

*N*-protected indoles 2a-2e, 2g, 2h, and 2o-2q were synthesized according to the previous reports.1 The other indole derivative 2f was synthesized by the following procedure.

**Procedure for the synthesis of 1-benzyl-6-bromo-7-methyl-1H-indole 2f**

To a stirred solution of 6-bromo-7-methyl-1H-indole 8 (120 mg, 0.4 mmol) in DMF (3 mL) was added NaH (22 mg, 0.48 mmol) at 0 °C under nitrogen atmosphere. The reaction mixture was brought to room temperature and stirred for 30 minutes before adding benzyl bromide 9 (53 µL, 0.44 mmol) at 0 °C. Then, the reaction mixture was allowed to stir overnight at room temperature. After completion of the reaction, the reaction mixture was quenched with saturated aqueous NH4Cl
solution and extracted with ethyl acetate (3 x 10 mL). The combined organic layers were washed with saturated brine solution, dried over anhydrous Na$_2$SO$_4$, and concentrated under reduced pressure. The residue was purified by column chromatography (silica gel, hexane/EtOAc mixture as eluent) to afford the pure product 2f as a white solid (137 mg, 91%). mp 98-100 °C. $R_f = 0.51$ (in 5% EtOAc/Hex). IR (neat, cm$^{-1}$): 1514, 1492, 1447, 1371, 1384, 1353, 1315, 1177, 1101, 1027, 972, 798, 721, 693. $^1$H NMR (400 MHz, CDCl$_3$): $\delta$ 7.35-7.33 (m, 1H), 7.31-7.26 (m, 4H), 7.06 (d, $J = 3.2$ Hz, 1H), 6.91-6.89 (m, 2H), 6.53 (d, $J = 3.2$ Hz, 1H), 5.57 (s, 2H), 2.60 (s, 3H). $^{13}$C NMR (100 MHz, CDCl$_3$): $\delta$ 139.1, 135.5, 131.3, 129.1, 128.9, 127.4, 125.3, 124.7, 120.7, 119.9, 119.8, 102.1, 52.8, 18.4. HRMS (ESI): calcd. for [C$_{16}$H$_{15}$BrN] [M+H]$^+$: 300.0382; found: 300.0381.

3. Synthesis of o-alkynylacetophenones 1

o-Alkynylacetophenones 1a-1e, 1g, 1h-1j, 1l-1m were synthesized according to the previous reports. Other o-alkynylacetophenone derivatives 1f and 1k were synthesized by the following procedures.

Procedure for the synthesis of N-(3-(2-Acetylphenyl)prop-2-yn-1-yl)-4-methylbenzenesulfonamide 1f

2-Iodoacetophenone 10 (400 mg, 1.62 mmol), and 4-methyl-N-(prop-2-yn-1-yl)benzenesulfonamide 11 (405 mg, 1.94 mmol), were dissolved in dry THF (17 mL). Then diisopropylamine (DIPA) (1.2 mL, 8.1 mmol) was added to the above solution under stirring before cooling down to the 0 °C. Later, Pd(PPh)$_3$Cl$_2$ (12 mg, 0.064 mmol), and CuI (22 mg, 0.03 mmol) were added and the reaction mixture was allowed to warm to room temperature and stirred for overnight. After completion of the reaction, the reaction mixture was quenched with saturated aqueous NH$_4$Cl solution and
extracted with ethyl acetate (3 x 20 mL). The combined organic layers were washed with saturated brine solution, dried over Na₂SO₄, and concentrated under reduced pressure. The residue was purified by flash column chromatography (silica gel, hexane/EtOAc mixture as eluent) to afford the pure product 1f as a yellow solid (461 mg, 86%). mp 103-105 °C. Rᵣ = 0.33 (in 40% EtOAc/Hex). IR (neat, cm⁻¹): 3282, 1682, 1594, 1478, 1426, 1322, 1246, 1157, 1067, 964, 812, 767, 662, 608. ¹H NMR (500 MHz, CDCl₃): δ 7.79 (dt, J = 8.5, 2.0 Hz, 2H), 7.67-7.65 (m, 1H), 7.40-7.34 (m, 2H), 7.24 (d, J = 8.0 Hz, 2H), 7.22-7.20 (m, 1H), 4.90 (t, J = 5.5 Hz, 1H), 4.10 (d, J = 6.0 Hz, 2H), 2.55 (s, 3H), 2.33 (s, 3H). ¹³C {¹H} NMR (100 MHz, CDCl₃): δ 199.7, 143.6, 140.3, 136.7, 134.1, 131.1, 129.6, 128.5, 128.4, 127.3, 126.3, 120.5, 88.8, 83.6, 33.8, 29.4, 21.3. HRMS (ESI): calcd. for [C₁₈H₁₇NNaO₃S] [M+Na]⁺: 350.0821; found: 350.0827.

Procedure for the synthesis of 1-(5-nitro-2-(phenylethynyl)phenyl)ethan-1-one 1k

To a stirred solution of 1-(2-bromo-5-nitrophenyl)ethan-1-one 12 (500 mg, 2.05 mmol) in triethylamine (10 mL), Pd(PPh₃)₄ (47 mg, 0.041 mmol) was added under nitrogen atmosphere. The resulting solution was stirred for 5 min before adding CuI (4 mg, 0.021 mmol). Then, phenylacetylene 13 (0.27 mL, 2.46 mmol) was added, and the reaction mixture was stirred at 60 °C for 12 h. It was then diluted with EtOAc, filtered through a celite pad, and evaporated under reduced pressure. The crude reaction mixture was purified by column chromatography to obtain pure 1-(5-nitro-2-(phenylethynyl)phenyl)ethan-1-one 1k as a yellow solid (461 mg, 84%). mp = 111-113 °C, Rᵣ = 0.46 (in 10% EtOAc/Hex). IR (neat, cm⁻¹): 3103, 2214, 1686, 1599, 1574, 1509, 1490, 1340, 1294, 1259, 1109, 1061, 910, 890, 845, 743, 685. ¹H NMR (500 MHz, CDCl₃): δ 8.61 (d, J = 2.0 Hz, 1H), 8.31 (dd, J = 8.5, 2.5 Hz, 1H), 7.79 (d, J = 8.5 Hz, 1H), 7.59-7.57 (m, 2H), 7.45-7.39 (m, 3H), 2.83
(s, 3H). $^{13}$C NMR (100 MHz, CDCl$_3$): $\delta$ 197.6, 146.7, 141.3, 134.9, 131.8, 129.8, 128.6, 128.0, 125.5, 123.9, 121.8, 100.5, 87.1, 29.7. HRMS (ESI): calcd. for [C$_{16}$H$_{12}$NO$_3$] [M+H]$^+$: 266.0812; found: 266.0813.

4. General procedure for the synthesis of C3-naphthyl indole derivatives 3

![Chemical Structure](image)

To a stirred solution of $o$-alkynylacetophenone 1 (1.2 equiv), $N$-protected indole 2 (0.4 mmol, 1.0 equiv) and TMOF (2.0 equiv) in DCM (4 mL) was added AgOTf (10 mol %) at room temperature. The reaction mixture was stirred at the same temperature. After completion of the reaction, the reaction mixture was concentrated under reduced pressure. The residue was purified by column chromatography (silica gel, hexane/EtOAc mixture as eluent) to afford the pure product 3.

5. Characterization data of compounds 3, 4aa, 5aa, 5ak, 6k, and 7

1-Benzyl-3-(3-phenylnaphthalene-1-yl)-1H-indole 3aa

White solid (140 mg, 85%). mp 88-90 °C. $R_f$ = 0.5 (in 5% EtOAc/Hex). IR (neat, cm$^{-1}$): 1549, 1493, 1451, 1383, 1337, 1257, 1167, 1074, 1014, 883, 763, 736, 693. $^1$H NMR (500 MHz, CDCl$_3$): $\delta$ 8.15 (d, $J$ = 8.5 Hz, 1H), 8.08 (s, 1H), 8.49 (d, $J$ = 8.0 Hz, 1H), 7.94-7.93 (m, 1H), 7.81-7.79 (m, 2H), 7.61 (dd, $J$ = 8.0, 0.5 Hz, 1H), 7.55 (d, $J$ = 7.5 Hz, 1H), 7.52-7.49 (m, 2H), 7.45-7.40 (m, 3H), 7.38-7.35 (m, 3H), 7.33-7.28 (m, 2H), 7.26 (d, $J$ = 7.0 Hz, 2H), 7.18-7.15 (m, 1H), 5.46 (s, 2H). $^{13}$C $\{^1$H$\}$ NMR (125 MHz, CDCl$_3$): $\delta$ 141.1, 138.2, 137.3, 136.6, 134.4, 133.5, 131.7, 128.9, 128.8, 128.6, 128.4, 127.7, 127.5, 127.4, 127.0, 126.4, 126.1, 125.8, 124.9, 122.2, 120.6, 119.9, 115.6, 110.0, 50.3. HRMS (ESI): calcd. for [C$_{31}$H$_{24}$N] [M+H]$^+$: 410.1903; found: 410.1905.
1-Benzyl-5-fluoro-3-(3-phenylnaphthalene-1-yl)-1H-indole 3ab

White solid (121 mg, 71%). mp 140-142 °C. $R_f = 0.38$ (in 5% EtOAc/Hex). IR (neat, cm$^{-1}$): 1542, 1480, 1447, 1246, 1181, 955, 895, 853, 790, 761, 693, 651. $^1$H NMR (500 MHz, CDCl$_3$): $\delta$ 8.08 (d, $J = 8.5$ Hz, 2H), 7.98 (d, $J = 8.5$ Hz, 1H), 7.87 (d, $J = 2.0$ Hz, 1H), 7.78 (dd, $J = 8.5$, 1.0 Hz, 2H), 7.55-7.52 (m, 1H), 7.51-7.48 (m, 2H), 7.45-7.42 (m, 1H), 7.42 (s, 1H), 7.39-7.38 (m, 1H), 7.37-7.35 (m, 2H), 7.33-7.28 (m, 2H), 7.26-7.20 (m, 3H), 7.00 (td, $J = 9.5$, 2.5 Hz, 1H), 5.43 (s, 2H). $^{13}$C {$^1$H} NMR (125 MHz, CDCl$_3$): $\delta$ 159.1, 157.2, 141.0, 138.2, 136.9, 134.3, 133.1, 132.9, 131.5, 129.2, 128.9, 128.8, 128.6, 127.8, 127.4, 127.3, 127.2, 126.8, 126.1 (d, $J_{CF} = 30$ Hz), 125.9, 125.0, 115.5 (d, $J_{CF} = 20$ Hz), 110.7 (d, $J_{CF} = 15$ Hz), 110.6, 110.5, 105.4, 105.2, 50.5. $^{19}$F NMR (470 MHz, CDCl$_3$), -124.0. HRMS (ESI): calcd. for [C$_{31}$H$_{23}$FN] [M+H]$^+$: 428.1809; found: 428.1809.

1-Benzyl-5-chloro-3-(3-phenylnaphthalene-1-yl)-1H-indole 3ac

White solid (130 mg, 73%). mp 158-160 °C. $R_f = 0.41$ (in 5% EtOAc/Hex). IR (neat, cm$^{-1}$): 1595, 1494, 1467, 1349, 1267, 1169, 1065, 1028, 884, 851, 747, 693, 642. $^1$H NMR (500 MHz, CDCl$_3$): $\delta$ 8.07 (s, 1H), 8.03 (d, $J = 8.5$ Hz, 1H), 7.98 (d, $J = 8.0$ Hz, 1H), 7.85 (d, $J = 1.5$ Hz, 1H), 7.77 (d, $J = 7.5$ Hz, 2H), 7.54 (d, $J = 7.0$ Hz, 1H), 7.51-7.48 (m, 3H), 7.45-7.42 (m, 1H), 7.41-7.39 (m, 1H), 7.37 (s, 1H), 7.35 (d, $J = 7.5$ Hz, 2H), 7.30-7.29 (m, 2H), 7.23-7.19 (m, 3H), 5.42 (s, 2H). $^{13}$C {$^1$H} NMR (125 MHz, CDCl$_3$): $\delta$ 140.9, 138.2, 136.8, 134.9, 134.3, 132.7, 131.6, 129.3, 128.9, 128.8, 128.6, 127.9, 127.4(4), 127.4(0), 127.3, 126.8, 126.2, 126.0, 125.9, 125.8, 125.2, 122.5, 119.8, 115.2, 111.0, 50.4. HRMS (ESI): calcd. for [C$_{31}$H$_{23}$ClN] [M+H]$^+$: 444.1514; found: 444.1514.

1-Benzyl-5-bromo-3-(3-phenylnaphthalene-1-yl)-1H-indole 3ad

1-Benzyl-5-fluoro-3-(3-phenylnaphthalene-1-yl)-1H-indole 3ab

White solid (121 mg, 71%). mp 140-142 °C. $R_f = 0.38$ (in 5% EtOAc/Hex). IR (neat, cm$^{-1}$): 1542, 1480, 1447, 1246, 1181, 955, 895, 853, 790, 761, 693, 651. $^1$H NMR (500 MHz, CDCl$_3$): $\delta$ 8.08 (d, $J = 8.5$ Hz, 2H), 7.98 (d, $J = 8.5$ Hz, 1H), 7.87 (d, $J = 2.0$ Hz, 1H), 7.78 (dd, $J = 8.5$, 1.0 Hz, 2H), 7.55-7.52 (m, 1H), 7.51-7.48 (m, 2H), 7.45-7.42 (m, 1H), 7.42 (s, 1H), 7.39-7.38 (m, 1H), 7.37-7.35 (m, 2H), 7.33-7.28 (m, 2H), 7.26-7.20 (m, 3H), 7.00 (td, $J = 9.5$, 2.5 Hz, 1H), 5.43 (s, 2H). $^{13}$C {$^1$H} NMR (125 MHz, CDCl$_3$): $\delta$ 159.1, 157.2, 141.0, 138.2, 136.9, 134.3, 133.1, 132.9, 131.5, 129.2, 128.9, 128.8, 128.6, 127.8, 127.4, 127.3, 127.2, 126.8, 126.1 (d, $J_{CF} = 30$ Hz), 125.9, 125.0, 115.5 (d, $J_{CF} = 20$ Hz), 110.7 (d, $J_{CF} = 15$ Hz), 110.6, 110.5, 105.4, 105.2, 50.5. $^{19}$F NMR (470 MHz, CDCl$_3$), -124.0. HRMS (ESI): calcd. for [C$_{31}$H$_{23}$FN] [M+H]$^+$: 428.1809; found: 428.1809.
White solid (156 mg, 80%). mp 64-66 °C. $R_f$ = 0.48 (in 5% EtOAc/Hex). IR (neat, cm$^{-1}$): 1595, 1493, 1466, 1349, 1266, 1168, 1027, 884, 789, 749, 693. $^1$H NMR (400 MHz, CDCl$_3$): $\delta$ 8.07 (d, $J = 1.6$ Hz, 1H), 7.99 (dd, $J = 13.6$, 8.4 Hz, 2H), 7.83 (d, $J = 2.0$ Hz, 1H), 7.78-7.75 (m, 2H), 7.65 (d, $J = 2.0$ Hz, 1H), 7.55-7.47 (m, 3H), 7.45-7.40 (m, 1H), 7.39-7.35 (m, 3H), 7.34-7.30 (m, 3H), 7.25 (d, $J = 8.4$ Hz, 1H), 7.21 (d, $J = 6.8$ Hz, 2H), 5.42 (s, 2H). $^{13}$C NMR (100 MHz, CDCl$_3$): $\delta$ 140.9, 138.2, 136.8, 135.1, 134.3, 132.6, 131.6, 130.0, 128.9, 128.8, 128.7, 128.6, 127.9, 127.4, 127.3, 126.8, 126.2, 126.0(9), 126.0(0), 125.2, 125.1, 122.9, 115.1, 113.4, 111.4, 50.4. HRMS (ESI): calcd. for [C$_{31}$H$_{23}$BrN] [M+H]$^+$: 488.1008; found: 488.1008.

1-Benzyl-5-methoxy-3-(3-phenylnaphthalene-1-yl)-1$H$-indole 3ae

White solid (159 mg, 90%). mp 62-64 °C. $R_f$ = 0.4 (in 5% EtOAc/Hex). IR (neat, cm$^{-1}$): 1482, 1448, 1338, 1282, 1213, 1175, 1040, 886, 790, 748, 694. $^1$H NMR (500 MHz, CDCl$_3$): $\delta$ 8.11 (d, $J = 8.5$ Hz, 1H), 8.06 (d, $J = 1.5$ Hz, 1H), 7.98 (d, $J = 8.0$ Hz, 1H), 7.89 (d, $J = 2.0$ Hz, 1H), 7.79-7.77 (m, 2H), 7.54-7.51 (m, 1H), 7.50-7.47 (m, 2H), 7.44-7.40 (m, 1H), 7.39 (dt, $J = 7.5$, 1.0 Hz, 1H), 7.36 (dt, $J = 3.5$, 1.0 Hz, 1H), 7.35-7.33 (m, 2H), 7.30-7.27 (m, 2H), 7.24-7.22 (m, 2H), 6.98 (d, $J = 2.0$ Hz, 1H), 6.91 (dd, $J = 9.0$, 2.5 Hz, 1H), 5.41 (s, 2H), 3.71 (s, 3H). $^{13}$C {${^1}$H} NMR (100 MHz, CDCl$_3$): $\delta$ 154.4, 141.0, 138.2, 137.3, 134.3, 133.6, 131.7, 131.6, 128.8, 128.6, 128.5, 128.3, 127.7, 127.4, 127.3, 127.2, 126.8, 126.5, 126.1, 125.7, 124.8, 115.1, 112.6, 110.8, 101.9, 55.8, 50.4. HRMS (ESI): calcd. for [C$_{32}$H$_{26}$NO] [M+H]$^+$: 440.2009; found: 440.2009.

1-Benzyl-6-bromo-7-methyl-3-(3-phenylnaphthalen-1-yl)-1$H$-indole 3af
White solid (156 mg, 77%). mp 164-166 ºC. $R_f = 0.58$ (in 10% EtOAc/Hex). IR (neat, cm$^{-1}$): 1599, 1493, 1448, 1410, 1351, 1171, 1014, 963, 877, 820, 790, 757, 689. $^1$H NMR (500 MHz, CDCl$_3$): $\delta$ 8.06 (d, $J = 1.5$ Hz, 1H), 8.01 (d, $J = 8.5$ Hz, 1H), 7.97 (d, $J = 8.5$ Hz, 1H), 7.85 (d, $J = 2.0$ Hz, 1H), 7.76 (dt, $J = 8.0$, 1.5 Hz, 2H), 7.53-7.47 (m, 3H), 7.42-7.41 (m, 1H), 7.39 (dt, $J = 7.5$, 1.0 Hz, 1H), 7.36-7.33 (m, 2H), 7.31-7.28 (m, 3H), 7.21 (dd, $J = 8.5$, 0.5 Hz, 1H), 7.05 (d, $J = 7.0$ Hz, 2H), 5.70 (s, 2H), 2.69 (s, 3H).

$^{13}$C {H} NMR (125 MHz, CDCl$_3$): $\delta$ 140.9, 138.9, 138.1, 135.7, 134.3, 132.7, 131.6, 130.6, 129.0, 128.8, 128.7, 128.6, 127.5, 127.49, 127.43, 127.3, 126.2, 126.1, 125.8, 125.4, 125.1, 124.9, 121.0, 120.3, 119.3, 115.6, 52.9, 18.4. HRMS (ESI): calcd. for [C$_{32}$H$_{25}$BrN] [M+H]$^+$: 502.1165; found: 502.1164.

1-Benzyl-7-methyl-3-(3-phenylnaphthalen-1-yl)-1H-indole 3ag

White solid (136 mg, 80%). mp 102-104 ºC. $R_f = 0.57$ (in 10% EtOAc/Hex). IR (neat, cm$^{-1}$): 1597, 1493, 1448, 1414, 1375, 1169, 1074, 1028, 883, 812, 745, 693. $^1$H NMR (MHz, CDCl$_3$): $\delta$ 8.12 (d, $J = 8.5$ Hz, 1H), 8.08 (s, 1H), 7.99 (d, $J = 8.0$ Hz, 1H), 7.92 (d, $J = 2.0$ Hz, 1H), 7.79 (dt, $J = 8.0$, 1.0 Hz, 2H), 7.55-7.49 (m, 3H), 7.45-7.43 (m, 1H), 7.42 (dt, $J = 7.0$, 1.5 Hz, 1H), 7.39 (dt, $J = 7.5$, 1.5 Hz, 1H), 7.35 (tt, $J = 7.0$, 1.0 Hz, 2H), 7.31 (s, 1H), 7.30-7.27 (s, 1H), 7.08 (d, $J = 7.5$ Hz, 2H), 7.04 (t, $J = 7.0$ Hz, 1H), 6.99 (d, $J = 7.0$ Hz, 1H), 5.71 (s, 2H), 2.64 (s, 3H).

$^{13}$C {H} NMR (100 MHz, CDCl$_3$): $\delta$ 141.0, 139.4, 138.1, 135.2, 134.3, 133.4, 131.7, 129.6, 129.3, 128.9, 128.8, 128.5, 127.4, 127.3, 126.4, 126.1, 125.7, 125.5, 125.0, 124.8, 121.3, 120.1, 118.6, 115.5, 52.3, 19.6. HRMS (ESI): calcd. for [C$_{32}$H$_{26}$N] [M+H]$^+$: 424.2060; found: 424.2060.

1-Methyl-3-(3-phenylnaphthalen-1-yl)-1H-indole 3ah

White solid (100 mg, 75%). mp 92-94 ºC. $R_f = 0.58$ (in 5% EtOAc/Hex). IR (neat, cm$^{-1}$): 1594, 1472, 1355, 1227, 1154, 1114, 1064, 1012, 883, 735, 694. $^1$H NMR (400 MHz, CDCl$_3$): $\delta$ 8.14 (d, $J = 8.4$ Hz, 1H), 8.06 (s, 1H), 7.98
(d, J = 8.0 Hz, 1H), 7.90 (d, J = 1.6 Hz, 1H), 7.80-7.78 (m, 2H), 7.58 (d, J = 8.0 Hz, 1H), 7.55-7.49 (m, 3H), 7.48-7.43 (m, 2H), 7.42-7.39 (m, 1H), 7.37-7.33 (m, 1H), 7.31 (s, 1H), 7.17-7.13 (m, 1H), 3.93 (s, 3H).

$^{13}$C {$^1$H} NMR (100 MHz, CDCl$_3$): $\delta$ 141.1, 138.1, 136.9, 134.3, 133.6, 131.7, 128.8, 128.5, 128.3, 128.0, 127.4, 127.2(8), 127.2(4), 126.4, 126.1, 125.6, 124.7, 121.9, 120.4, 119.6, 114.9, 109.4, 32.8. HRMS (ESI): calcd. for [C$_{25}$H$_{20}$N] $[M+H]^+$: 334.1590; found: 334.1593.

3-(3-Phenylnaphthalen-1-yl)-1H-indole 3ai

White solid (80 mg, 60%). mp 95-97 °C. $R_f$ = 0.30 (in 10% EtOAc/Hex). IR (neat, cm$^{-1}$): 3412, 1594, 1492, 1452, 1418, 1243, 1092, 884, 739, 694. $^1$H NMR (400 MHz, CDCl$_3$): $\delta$ 8.36 (bs, 1H), 8.11-8.08 (m, 2H), 7.99 (d, J = 8.4 Hz, 1H), 7.91 (d, J = 2.0 Hz, 1H), 7.80-7.78 (m, 2H), 7.57 (d, J = 8.0 Hz, 1H), 7.56-7.53 (m, 1H), 7.52-7.48 (m, 3H), 7.44-7.41 (m, 2H), 7.38 (dt, J = 7.2, 2.0 Hz, 1H), 7.32-7.28 (m, 1H), 7.18-7.14 (m, 1H). $^{13}$C {$^1$H} NMR (100 MHz, CDCl$_3$): $\delta$ 141.0, 138.1, 136.0, 134.3, 133.5, 131.7, 128.8, 128.5, 127.6, 127.4, 127.3(4), 127.3(3), 126.3, 126.1, 125.7, 124.9, 123.6, 122.4, 120.3, 120.1, 116.4, 111.2. HRMS (ESI): calcd. for [C$_{24}$H$_{18}$N] $[M+H]^+$: 320.1434; found: 320.1436.

2-Methyl-3-(3-phenylnaphthalen-1-yl)-1H-indole 3aj

Yellow liquid (87 mg, 65%). $R_f$ = 0.33 (in 20% EtOAc/Hex). IR (neat, cm$^{-1}$): 3399, 1595, 1494, 1457, 1324, 1303, 1244, 1212, 1011, 883, 741, 694. $^1$H NMR (500 MHz, CDCl$_3$): $\delta$ 8.11 (bs, 1H), 8.09 (s, 1H), 7.99 (d, J = 8.0 Hz, 1H), 7.81-7.77 (m, 4H), 7.53-7.46 (m, 3H), 7.42-7.36 (m, 3H), 7.30 (d, J = 8.0 Hz, 1H), 7.20 (dt, J = 7.5, 1.5 Hz, 1H), 7.08-7.04 (m, 1H), 2.37 (s, 3H). $^{13}$C {$^1$H} NMR (100 MHz, CDCl$_3$): $\delta$ 141.1, 138.1, 135.2, 134.2, 133.5, 132.7, 132.1, 129.3, 128.8, 128.5, 128.1, 127.4, 127.3, 126.6, 126.0, 125.6, 124.9, 121.4, 119.8, 119.3, 112.8, 110.2, 12.5. HRMS (ESI): calcd. for [C$_{25}$H$_{20}$N] $[M+H]^+$: 334.1590; found: 334.1603.

1-Benzyl-3-(3-(p-tolyl)naphthalen-1-yl)-1H-indole 3ba
White solid (140 mg, 82%). mp 66–68 °C. $R_f = 0.59$ (in 10% EtOAc/Hex). IR (neat, cm$^{-1}$): 1597, 1495, 1464, 1336, 1255, 1168, 1016, 887, 813, 731, 698. $^1$H NMR (400 MHz, CDCl$_3$): $\delta$ 8.12 (d, $J = 8.4$ Hz, 1H), 8.04 (d, $J = 1.6$ Hz, 1H), 7.96 (d, $J = 8.0$ Hz, 1H), 7.89 (d, $J = 2.0$ Hz, 1H), 7.68 (dt, $J = 8.0$, 2.4 Hz, 2H), 7.59 (dt, $J = 8.0$, 1.2 Hz, 1H), 7.53–7.49 (m, 1H), 7.42–7.40 (m, 2H), 7.38–7.33 (m, 3H), 7.31–7.28 (m, 3H), 7.26–7.24 (m, 3H), 7.16–7.12 (m, 1H), 5.45 (s, 2H), 2.42 (s, 3H). $^{13}$C $^1$H NMR (100 MHz, CDCl$_3$): $\delta$ 138.1, 138.0, 137.2, 137.0, 136.5, 134.3, 133.3, 131.5, 129.5, 128.8, 128.5, 128.3, 127.7, 127.6, 127.2, 126.8, 126.3, 126.0, 125.5, 124.4, 122.1, 120.5, 119.8, 115.5, 109.9, 50.1, 21.1. HRMS (ESI): calcd. for [C$_{32}$H$_{26}$N][M+H]$^+$: 424.2060; found: 424.2061.

**1-benzyl-3-(3-(o-tolyl)naphthalen-1-yl)-1H-indole 3bb**

Yellow liquid (136 mg, 80%). $R_f = 0.41$ (in 5% EtOAc/Hex). IR (neat, cm$^{-1}$): 1595, 1492, 1463, 1336, 1168, 1015, 905, 889, 725, 647. $^1$H NMR (500 MHz, CDCl$_3$): $\delta$ 8.16 (d, $J = 8.5$ Hz, 1H), 7.93 (d, $J = 8.0$ Hz, 1H), 7.62 (d, $J = 1.5$ Hz, 1H), 7.58 (d, $J = 8.0$ Hz, 1H), 7.54–7.51 (m, 1H), 7.45–7.41 (m, 1H), 7.40–7.39 (m, 2H), 7.36–7.30 (m, 6H), 7.29–7.27 (m, 2H), 7.24–7.23 (m, 2H), 7.15–7.12 (m, 1H), 5.44 (s, 2H), 2.39 (s, 3H). $^{13}$C $^1$H NMR (100 MHz, CDCl$_3$): $\delta$ 141.8, 139.2, 137.2, 136.6, 135.5, 133.9, 132.6, 131.3, 130.3, 129.4, 128.8, 128.3(7), 128.3(3), 127.7(S), 127.7(2), 127.3, 126.9, 126.8, 126.4, 125.9, 125.7, 125.6, 122.1, 120.5, 119.8, 115.5, 109.9, 50.2, 20.6. HRMS (ESI): calcd. for [C$_{32}$H$_{26}$N][M+H]$^+$: 424.2060; found: 424.2060.

**1-benzyl-3-(3-(3-methoxyphenyl)naphthalen-1-yl)-1H-indole 3bc**

Yellow liquid (136 mg, 77%). $R_f = 0.39$ (in 5% EtOAc/Hex). IR (neat, cm$^{-1}$): 1595, 1490, 1383, 1247, 1169, 1041, 780, 730, 693, 618. $^1$H NMR (500 MHz, CDCl$_3$): $\delta$ 8.11 (d, $J = 8.0$ Hz, 1H), 8.04 (s, 1H), 7.96 (d, $J =
8.5 Hz, 1H), 7.87 (d, J = 2.0 Hz, 1H), 7.56 (d, J = 8.0 Hz, 1H), 7.52-7.49 (m, 1H), 7.41-7.38 (m, 3H), 7.37-7.36 (m, 2H), 7.34-7.32 (m, 2H), 7.29-7.28 (m, 2H), 7.25-7.23 (m, 3H), 7.12 (t, J = 7.0 Hz, 1H), 6.93-6.91 (m, 1H), 5.44 (s, 2H), 3.88 (s, 3H).

13C {1H} NMR (100 MHz, CDCl₃): δ 159.9, 142.6, 138.0, 137.2, 136.5, 134.3, 134.3, 131.7, 129.7, 128.8, 128.5, 128.3, 127.7, 127.3, 126.9, 126.4, 126.1, 125.7, 124.9, 122.1, 120.5, 119.9(8), 119.9(2), 115.5, 113.1, 112.8, 109.9, 55.3, 50.2. HRMS (ESI): calcd. for [C₃₂H₂₆NO] [M+H]+: 440.2009; found: 440.2010.

1-Benzyl-3-(3-(4-methoxyphenyl)naphthalen-1-yl)-1H-indole 3bd

Yellow liquid (152 mg, 86%). Rₕ = 0.31 (in 5% EtOAc/Hex). IR (neat, cm⁻¹): 1606, 1512, 1462, 1244, 1029, 827, 730, 698. ¹H NMR (500 MHz, CDCl₃): δ 8.10 (d, J = 8.0 Hz, 1H), 8.00 (s, 1H), 7.95 (d, J = 8.0 Hz, 1H), 7.86 (s, 1H), 7.71 (d, J = 8.5 Hz, 2H), 7.58 (d, J = 7.5 Hz, 1H), 7.50 (t, J = 7.0 Hz, 1H), 7.40 (t, J = 8.0 Hz, 1H), 7.36 (s, 1H), 7.34 (d, J = 7.0 Hz, 1H), 7.29 (t, J = 7.0 Hz, 1H), 7.26-7.24 (m, 3H), 7.13 (t, J = 7.5 Hz, 1H), 7.02 (d, J = 8.5 Hz, 2H), 5.45 (s, 2H), 3.87 (s, 3H). ¹³C {¹H} NMR (100 MHz, CDCl₃): δ 159.1, 137.7, 137.2, 136.5, 134.4, 133.5, 133.3, 131.3, 128.7, 128.4, 128.3, 127.7, 127.1, 126.8, 126.3, 126.0, 125.4, 124.0, 122.1, 120.5, 119.8, 115.5, 114.2, 109.9, 55.2, 50.1. HRMS (ESI): calcd. for [C₃₂H₂₆NO] [M+H]+: 440.2009; found: 440.2009.

1-Benzyl-3-(3-hexynaphthalen-1-yl)-1H-indole 3be

Yellow liquid (122 mg, 73%). Rₕ = 0.7 (in 10% EtOAc/Hex). IR (neat, cm⁻¹): 1599, 1543, 1495, 1463, 1386, 1352, 1252, 1168, 1075, 1014, 955, 877, 783, 737, 694, 616. ¹H NMR (500 MHz, CDCl₃): δ 8.06 (d, J = 8.5 Hz, 1H), 7.85 (d, J = 8.0 Hz, 1H), 7.63 (s, 1H), 7.54 (d, J = 8.0 Hz, 1H), 7.48 (d, J = 1.5 Hz, 1H), 7.47-7.44 (m, 1H), 7.39 (d, J = 8.0 Hz, 1H), 7.35 (tt, J = 7.0, 1.5 Hz, 3H), 7.33-7.26 (m, 3H), 7.25-7.23 (m, 3H), 7.14-7.11 (m, 1H), 5.44 (s, 2H), 2.81 (t, J = 7.5 Hz, 2H), 1.78-1.72 (m, 2H), 1.45-1.39 (m, 2H), 1.37-1.31 (m, 4H), 0.90 (t, J = 7.0 Hz, 3H). ¹³C {¹H} NMR (125 MHz, CDCl₃): δ 140.1, 137.4, 136.5, 134.3, 132.6, 130.9, 129.3, 128.8, 127.7, 127.6(9), 127.6(0), 126.9, 126.3, 125.6, 125.4, 124.0, 122.1, 120.5, 119.8, 115.5, 114.2, 109.9, 55.2, 50.1. HRMS (ESI): calcd. for [C₃₂H₂₆NO] [M+H]+: 440.2009; found: 440.2009.

N-((4-(1-benzyl-1H-indol-3-yl)naphthalen-2-yl)methyl)-4-methylbenzenesulfonamide 3bf

Yellow liquid (143 mg, 69%). \( R_f = 0.28 \) (in 20% EtOAc/Hex). IR (neat, cm\(^{-1}\)): 3276, 3029, 2923, 1598, 1494, 1464, 1452, 1323, 1153, 1091, 880, 812, 739, 663, 547. \(^1\)H NMR (500 MHz, CDCl\(_3\)): \( \delta \) 8.03 (d, \( J = 8.5 \) Hz, 1H), 7.79 (d, \( J = 8.0 \) Hz, 1H), 7.76 (d, \( J = 8.0 \) Hz, 2H), 7.61 (s, 1H), 7.47 (t, \( J = 7.0 \) Hz, 1H), 7.41-7.36 (m, 5H), 7.34 (d, \( J = 7.5 \) Hz, 2H), 7.31-7.28 (m, 2H), 7.22 (t, \( J = 7.5 \) Hz, 5H), 7.10 (t, \( J = 7.5 \) Hz, 1H), 5.42 (s, 2H), 4.73 (t, \( J = 6.0 \) Hz, 1H), 4.33 (d, \( J = 6.5 \) Hz, 2H), 2.32 (s, 3H). \(^{13}\)C \(^{1}\)H NMR (125 MHz, CDCl\(_3\)): \( \delta \) 143.4, 137.2, 136.9, 136.5, 133.8, 133.7, 133.2, 131.9, 129.6, 128.8, 128.1, 127.7, 127.6, 127.2, 127.1, 126.9, 126.5, 126.1, 125.9, 125.7, 122.2, 120.4, 119.9, 115.1, 109.9, 50.2, 47.4, 21.3. HRMS (ESI): calcd. for [C_{33}H_{29}N_{2}O_{2}S] [M+H]^+: 517.1944; found: 517.1945.

1-Benzyl-3-(3-(thiophen-2-yl)naphthalen-1-yl)-1H-indole 3bg

Yellow liquid (130 mg, 78%). \( R_f = 0.4 \) (in 5% EtOAc/Hex). IR (neat, cm\(^{-1}\)): 1596, 1542, 1494, 1463, 1385, 1352, 1234, 1167, 1028, 1012, 880, 853, 821, 729, 693. \(^1\)H NMR (500 MHz, CDCl\(_3\)): \( \delta \) 8.07-8.06 (m, 2H), 7.92 (d, \( J = 8.0 \) Hz, 1H), 7.90 (d, \( J = 1.5 \) Hz, 1H), 7.56 (d, \( J = 8.0 \) Hz, 1H), 7.52-7.48 (m, 1H), 7.46 (dd, \( J = 3.5 \) 1.0 Hz, 1H), 7.42-7.38 (m, 2H), 7.37 (s, 1H), 7.35-7.36 (m, 2H), 7.33-7.32 (m, 1H), 7.30-7.28 (m, 1H), 7.26-7.25 (m, 3H), 7.16-7.12 (m, 2H), 5.45 (s, 2H). \(^{13}\)C \(^{1}\)H NMR (125 MHz, CDCl\(_3\)): \( \delta \) 144.5, 137.2, 136.5, 134.3, 133.6, 131.8, 131.4, 128.8, 128.3, 128.2, 128.0, 127.7, 126.9, 126.4, 126.3, 126.0, 125.7, 124.9, 123.4, 123.3, 122.2, 120.4, 119.9, 115.2, 109.9, 50.2. HRMS (ESI): calcd. for [C_{29}H_{22}NS] [M+H]^+: 416.1467; found: 416.1472.

1-Benzyl-3-(7-fluoro-3-phenylnaphthalen-1-yl)-1H-indole 3bh
White solid (130 mg, 76%). mp 60–62 °C. $R_f = 0.5$ (in 10% EtOAc/Hex). IR (neat, cm$^{-1}$): 1598, 1543, 1497, 1451, 1386, 1328, 1241, 1173, 1075, 958, 915, 881, 805, 760, 725, 693. $^1$H NMR (400 MHz, CDCl$_3$): $\delta$: 8.04 (s, 1H), 7.98–7.93 (m, 2H), 7.77–7.74 (m, 3H), 7.58 (dt, $J = 7.6$, 1.2 Hz, 1H), 7.51–7.47 (m, 2H), 7.43–7.38 (m, 2H), 7.37–7.34 (m, 3H), 7.33–7.25 (m, 6H), 7.18–7.14 (m, 1H), 5.46 (s, 2H). $^{13}$C {$^1$H} NMR (125 MHz, CDCl$_3$): $\delta$ 160.8 (d, $J = 244.0$ Hz), 140.8, 137.5 (d, $J = 2.5$ Hz), 137.1, 136.6, 132.8 (dd, $J = 50$, 5 Hz), 131.3, 130.9, 130.8, 128.8(7), 128.8(5), 128.1(9), 128.1(0), 127.7, 127.6, 127.3, 126.9, 124.6, 122.3, 120.2 (d, $J = 21.2$ Hz), 116.4 (d, $J = 26.2$ Hz), 115.0, 110.0, 109.8 (d, $J = 21.2$ Hz), 50.2. $^{19}$F NMR (470 MHz, CDCl$_3$): $\delta$ -114.0. HRMS (ESI): calcd. for [C$_{31}$H$_{23}$FN] [M+H]$^+$: 428.1809; found: 428.1809.

1-Benzyl-3-(7-phenynaphtho[2,3-d][1,3]dioxol-5-yl)-1H-indole 3bi

Yellow liquid (146 mg, 80%). $R_f = 0.27$ (in 5% EtOAc/Hex). IR (neat, cm$^{-1}$): 2922, 1603, 1494, 1455, 1278, 1231, 1173, 1035, 951, 882, 737, 693. $^1$H NMR (400 MHz, CDCl$_3$): $\delta$ 7.88 (d, $J = 2.0$ Hz, 1H), 7.74–7.72 (m, 3H), 7.56 (dt, $J = 8.0$, 1.0 Hz, 1H), 7.48–7.44 (m, 2H), 7.40 (d, $J = 9.0$ Hz, 2H), 7.37–7.33(7) (m, 3H), 7.33 (s, 1H), 7.31–7.27 (m, 1H), 7.25–7.23 (m, 3H), 7.15–7.12 (m, 1H), 6.02 (s, 2H), 5.44 (s, 2H). $^{13}$C {$^1$H} NMR (125 MHz, CDCl$_3$): $\delta$ 147.7, 147.6, 141.1, 137.3, 136.8, 136.5, 132.6, 131.5, 128.9, 128.8, 128.7, 128.2, 127.7, 127.4, 127.2, 127.0, 126.9, 126.0, 124.1, 122.1, 120.5, 119.9, 115.9, 109.9, 104.3, 102.9, 101.0, 50.2. HRMS (ESI): calcd. for [C$_{32}$H$_{24}$NO$_2$] [M+H]$^+$: 454.1802; found: 458.1802.

1-Benzyl-3-(2-methyl-3-phenylnaphthalen-1-yl)-1H-indole 3bj
White solid (105 mg, 62%). mp 62−64 °C. R<sub>f</sub> = 0.35 (in 5% EtOAc/Hex). IR (neat, cm<sup>-1</sup>): 1595, 1493, 1464, 1451, 1422, 1385, 1349, 1259, 1212, 1171, 1149, 908, 886, 734, 693. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>): δ 7.85 (d, J = 8.0 Hz, 1H), 7.78 (s, 1H), 7.65 (d, J = 8.4 Hz, 1H), 7.49-7.46 (m, 4H), 7.44-7.36 (m, 4H), 7.35-7.30 (m, 3H), 7.29-7.26 (m, 1H), 7.25-7.22 (m, 3H), 7.18 (s, 1H), 7.10-7.06 (m, 1H), 5.47 (s, 2H), 2.18 (s, 3H).

<sup>13</sup>C {<sup>1</sup>H} NMR (100 MHz, CDCl<sub>3</sub>): δ 142.7, 141.2, 137.6, 136.5, 133.9, 133.5, 131.8, 131.4, 129.4, 128.9, 128.8, 128.0(9), 128.0(4), 127.9, 127.7, 127.6, 126.8, 126.7, 126.6, 125.6, 125.1, 121.9, 120.5, 119.6, 114.2, 109.8, 50.1, 19.4. HRMS (ESI): calcd. for [C<sub>32</sub>H<sub>26</sub>N] [M+H]<sup>+</sup>: 424.2060; found: 424.2061.

**1-Benzyl-3-(7-nitro-3-phenylnaphthalen-1-yl)-1H-indole derivative 3bk**

Yellow solid (132 mg, 73%). mp 160-162 °C. R<sub>f</sub> = 0.40 (in 10% EtOAc/Hex). IR (neat, cm<sup>-1</sup>): 2919, 2850, 1615, 1520, 1487, 1461, 1334, 1157, 1078, 886, 828, 735, 628. <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>): δ 9.15 (d, J = 2.5 Hz, 1H), 8.26 (dd, J = 9.0, 2.5 Hz, 1H), 8.09-8.08 (m, 2H), 8.05 (d, J = 9.0 Hz, 1H), 7.94-7.77 (m, 2H), 7.62 (dt, J = 5.0, 1.0 Hz, 1H), 7.53-7.50 (m, 2H), 7.47-7.45 (m, 1H), 7.44 (tt, J = 7.5, 1.0 Hz, 1H), 7.40 (s, 1H), 7.39-7.37 (m, 1H), 7.33-7.29 (m, 4H), 7.20-7.16 (m, 1H), 5.49 (s, 2H). <sup>13</sup>C {<sup>1</sup>H} NMR (100 MHz, CDCl<sub>3</sub>): δ 145.4, 142.1, 140.0, 137.1, 136.8, 123.2, 130.3, 129.0(6), 129.0(0), 128.8, 128.2, 128.1, 127.9, 127.5, 127.1, 124.2, 123.5, 122.7, 120.6, 119.6, 113.8, 110.2, 50.3. HRMS (ESI): calcd. for [C<sub>31</sub>H<sub>23</sub>N<sub>2</sub>O<sub>2</sub>] [M+H]<sup>+</sup>: 455.1754; found: 455.1754.

**1-Methyl-3-(3-propylnaphthalen-1-yl)-1H-indole 3hl**

Yellow liquid (70 mg, 59%). R<sub>f</sub> = 0.4 (in 10% EtOAc/Hex). IR (neat, cm<sup>-1</sup>): 1613, 1597, 1574, 1540, 1498, 1476, 1372, 1333, 1244, 1225, 1149, 1130, 1113, 1056, 1011, 920, 850, 823, 807, 734, 647. <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>): δ 8.12 (d, J = 8.0 Hz, 1H), 7.89 (d, J = 8.0 Hz, 1H), 7.67 (s, 1H), 7.58-7.57 (m, 1H), 7.51-7.48 (m, 2H), 7.46 (d, J = 8.5 Hz, 1H), 7.40-7.33 (m, 2H), 7.28 (s, 1H), 7.19-7.16 (m, 1H), 3.92 (s, 3H), 2.84 (t, J = 7.0 Hz, 2H), 1.83 (sext, J = 7.5 Hz, 2H), 1.06 (t, J = 7.0 Hz, 3H). <sup>13</sup>C {<sup>1</sup>H} NMR (125 MHz, CDCl<sub>3</sub>): δ 139.8, 136.9, 134.2, 132.7, 130.9, 129.2,
128.1, 128.0, 127.7, 126.3, 125.6, 125.4, 124.7, 121.8, 120.4, 119.5, 115.0, 109.3, 38.1, 32.8, 24.4, 13.9. HRMS (ESI): calcd. for [C_{22}H_{22}N][M+H]^+: 300.1747; found: 300.1747.

3-(3-Butynaphthalen-1-yl)-1-methyl-1H-indole 3hm

Yellow liquid (78 mg, 62%). $R_f = 0.5$ (in 5% EtOAc/Hex). IR (neat, cm$^{-1}$): 1598, 1542, 1463, 1422, 1358, 1332, 1245, 1227, 1152, 1130, 1115, 1059, 1011, 875, 810, 735, 646. $^1$H NMR (500 MHz, CDCl$_3$): $\delta$ 8.06 (d, $J = 8.5$ Hz, 1H), 7.84 (d, $J = 8.5$ Hz, 1H), 7.62 (s, 1H), 7.52 (d, $J = 8.0$ Hz, 1H), 7.47-7.45 (m, 2H), 7.43 (d, $J = 8.5$ Hz, 1H), 7.35-7.29 (m, 2H), 7.25(5)-7.25(2) (m, 1H), 7.14-7.11 (m, 1H), 3.92 (s, 3H), 2.81 (t, $J = 8.0$ Hz, 2H), 1.77-1.70 (m, 2H), 1.47-1.39 (m, 2H), 0.96 (t, $J = 7.5$ Hz, 3H). $^{13}$C $\{^1$H$\}$ NMR (125 MHz, CDCl$_3$): $\delta$ 140.0, 136.9, 134.2, 132.7, 130.9, 129.2, 128.1, 128.0, 127.7, 126.3, 125.6, 125.3, 124.7, 121.8, 120.4, 119.5, 115.0, 109.3, 35.8, 33.5, 32.8, 22.4, 14.0. HRMS (ESI): calcd. for [C$_{23}$H$_{24}$N][M+H]^+: 314.1903; found: 314.1904.

1-Benzyl-3-(3-butynaphthalen-1-yl)-5-chloro-1H-indole 3cm

Yellow liquid (110 mg, 65%). $R_f = 0.6$ (in 10% EtOAc/Hex). IR (neat, cm$^{-1}$): 1600, 1495, 1468, 1386, 1352, 1261, 1169, 1065, 1025, 956, 872, 849, 789, 747, 729, 696. $^1$H NMR (500 MHz, CDCl$_3$): $\delta$ 7.98 (d, $J = 8.5$ Hz, 1H), 7.85 (d, $J = 8.5$ Hz, 1H), 7.64 (s, 1H), 7.48-7.43 (3H), 7.38-7.36 (m, 2H), 7.34-7.33 (m, 2H), 7.32 (d, $J = 7.0$ Hz, 1H), 7.28 (d, $J = 9.0$ Hz, 1H), 7.21 (d, $J = 7.5$ Hz, 2H), 7.19-7.17 (m, 1H), 5.41 (s, 2H), 2.82 (t, $J = 8.0$ Hz, 2H), 1.74 (quint, $J = 7.5$ Hz, 2H), 1.44 (sext, $J = 7.5$ Hz, 2H), 0.98 (t, $J = 7.5$ Hz, 3H). $^{13}$C $\{^1$H$\}$ NMR (125 MHz, CDCl$_3$): $\delta$ 140.0, 136.9, 134.2, 134.8, 134.2, 131.8, 130.8, 129.4, 129.3, 128.9, 128.8, 128.7(5), 127.8(3), 126.7, 125.9, 125.8, 125.7(7), 125.7(1), 125.0, 122.4, 119.9, 115.3, 110.9, 50.3, 35.7, 33.5, 22.4, 14.0. HRMS (ESI): calcd. for [C$_{29}$H$_{27}$ClN][M+H]^+: 424.1827; found: 424.1827.

1-Benzyl-5-fluoro-3-(3-propynaphthalen-1-yl)-1H-indole 3bl
Yellow liquid (108 mg, 68%). $R_f = 0.51$ (in 5% EtOAc/Hex). IR (neat, cm$^{-1}$): 1599, 1576, 1481, 1451, 1353, 1245, 1181, 1092, 1024, 988, 889, 850, 789, 748, 702, 651. $^1$H NMR (400 MHz, CDCl$_3$): $\delta$ 8.03 (d, $J = 8.4$ Hz, 1H), 7.86 (d, $J = 8.0$ Hz, 1H), 7.65 (s, 1H), 7.50-7.45 (m, 2H), 7.39-7.36 (m, 3H), 7.35-7.30 (m, 2H), 7.29-7.26 (m, 1H), 7.24-7.22 (m, 2H), 7.18 (dd, $J = 9.6$, 2.4 Hz, 1H), 6.99 (td, $J = 8.8$, 2.4 Hz, 1H), 5.41 (s, 2H), 2.80 (t, $J = 7.6$ Hz, 2H), 1.8 (sext, $J = 7.6$ Hz, 2H), 1.03 (t, $J = 7.2$ Hz, 3H).

$^{13}$C {$^1$H} NMR (100 MHz, CDCl$_3$): $\delta$ 158.1 (d, $J = 233$ Hz), 139.8, 137.0, 134.2, 133.1, 132.0, 130.8, 129.2 (d, $J = 4.0$ Hz), 128.9, 128.7 (d, $J = 10$ Hz), 127.8 (d, $J = 2.0$ Hz), 126.8, 126.0, 125.7 (d, $J = 7.0$ Hz), 125.0, 115.6 (d, $J = 5.0$ Hz), 110.6 (d, $J = 3.0$ Hz), 110.5, 110.4, 105.3 (d, $J = 24$ Hz), 50.5, 38.1, 24.4, 13.9. $^{19}$F NMR (470 MHz, CDCl$_3$): $\delta$ -124.3. HRMS (ESI): calcd. for [C$_{28}$H$_{25}$FN] $[M+H]^+$: 394.1966; found: 394.1966.

### 1-Benzyl-6-fluoro-3-(3-(4-methoxyphenyl)naphthalen-1-yl)-1H-indole 3oe

White solid (143 mg, 78%). mp 78-80 °C. $R_f = 0.48$ (in 5% EtOAc/Hex). IR (neat, cm$^{-1}$): 1606, 1579, 1545, 1512, 1466, 1452, 1332, 1281, 1244, 1170, 1112, 1089, 1029, 951, 907, 859, 826, 749, 701, 615. $^1$H NMR (500 MHz, CDCl$_3$): $\delta$ 8.05 (d, $J = 8.5$ Hz, 1H), 8.00 (s, 1H), 7.95 (d, $J = 8.5$ Hz, 1H), 7.83 (d, $J = 1.5$ Hz, 1H), 7.70 (dt, $J = 9.0$, 3.0 Hz, 2H), 7.52-7.49 (m, 1H), 7.45 (dd, $J = 8.5$, 5.5 Hz, 1H), 7.41-7.39 (m, 1H), 7.38-7.35 (m, 2H), 7.34 (s, 1H), 7.32 (m, 1H), 7.24-7.23 (m, 2H), 7.05 (dd, $J = 10.0$, 5.0 Hz, 1H), 7.02 (dt, $J = 9.0$, 3.0 Hz, 2H), 6.88 (td, $J = 9.0$, 2.0 Hz, 1H), 5.38 (s, 2H), 3.87 (s, 3H). $^{13}$C {$^1$H} NMR (125 MHz, CDCl$_3$): $\delta$ 160.0 (d, $J = 236$ Hz), 159.2, 137.7, 136.8, 136.5 (d, $J = 11.2$ Hz), 134.4, 133.4, 132.9, 131.2, 128.9, 128.4(8), 128.4(2), 127.9(3), 127.9(1), 127.8, 127.1, 126.9, 126.1 (d, $J = 20$ Hz), 125.5, 124.9, 124.3, 121.4 (d, $J = 40$ Hz), 115.8, 114.2, 108.6 (d, $J = 25$ Hz), 96.3 (d, $J = 25$ Hz), 55.3, 50.4. $^{19}$F NMR (470 MHz, CDCl$_3$): $\delta$ -120.1. HRMS (ESI): calcd. for [C$_{32}$H$_{25}$FNO] $[M+H]^+$: 458.1915; found: 458.1922.

### 1-Benzyl-6-methoxy-3-(3-(3-methoxyphenyl)naphthalen-1-yl)-1H-indole 3pd
White solid (141 mg, 75%). mp 143–145 °C. \( R_f = 0.48 \) (in 5% EtOAc/Hex). IR (neat, cm\(^{-1}\)): 1595, 1571, 1488, 1453, 1331, 1257, 1212, 1168, 1094, 1040, 955, 879, 780, 748, 694. \(^1\)H NMR (500 MHz, CDCl\(_3\)): \( \delta \) 8.13 (d, \( J = 8.5 \) Hz, 1H), 8.03 (s, 1H), 7.96 (d, \( J = 8.0 \) Hz, 1H), 7.86 (d, \( J = 2.0 \) Hz, 1H), 7.53-7.49 (m, 1H), 7.44-7.38 (m, 3H), 7.37-7.34 (m, 3H), 7.31-7.28 (m, 2H), 7.26-7.24 (m, 4H), 6.93 (ddd, \( J = 8.0, 2.5, 1.0 \) Hz, 1H), 6.84 (d, \( J = 2.0 \) Hz, 1H), 6.80 (dd, \( J = 9.0, 2.5 \) Hz, 1H), 5.39 (s, 2H), 3.89 (s, 3H), 3.84 (s, 3H). \(^{13}\)C \(^1\)H NMR (125 MHz, CDCl\(_3\)): \( \delta \) 159.9, 156.6, 142.6, 138.0, 137.3, 137.2, 134.2, 133.5, 131.7, 129.7, 128.8, 128.5, 127.7, 127.1, 126.9, 126.6, 126.4, 126.1, 125.7, 124.8, 122.7, 121.2, 119.9, 115.5, 113.0, 112.7, 93.5, 55.7, 55.3, 50.1. HRMS (ESI): calcd. for [C\(_{33}\)H\(_{27}\)NNaO\(_2\)] [M+Na]+: 492.1934; found: 492.1932.

N-((4-(1-Benzyl-7-methoxy-1H-indol-3-yl)naphthalen-2-yl)methyl)-4-methylbenzenesulfonamide 3qg

White solid (156 mg, 71%). mp 90–92 °C. \( R_f = 0.41 \) (in 20% EtOAc/Hex). IR (neat, cm\(^{-1}\)): 1573, 1494, 1452, 1426, 1324, 1257, 1213, 1155, 1089, 1060, 811, 748, 695, 660. \(^1\)H NMR (500 MHz, CDCl\(_3\)): \( \delta \) 7.98 (d, \( J = 8.5 \) Hz, 1H), 7.76 (d, \( J = 8.5 \) Hz, 1H), 7.74 (dt, \( J = 8.0, 2.0 \) Hz, 2H), 7.58 (s, 1H), 7.47-7.44 (m, 1H), 7.37-7.34 (m, 1H), 7.33-7.29 (m, 3H), 7.26-7.23 (m, 1H), 7.21-7.19 (dd, \( J = 7.5, 1.5 \) Hz, 4H), 7.13 (s, 1H), 7.00-6.97 (m, 1H), 6.96-6.94 (m, 1H), 6.68 (dd, \( J = 7.0, 1.0 \) Hz, 1H), 5.72 (s, 2H), 4.75 (t, \( J = 6.0 \) Hz, 1H), 4.31 (d, \( J = 6.0 \) Hz, 2H), 3.88 (s, 3H), 2.31 (s, 3H). \(^{13}\)C \(^1\)H NMR (125 MHz, CDCl\(_3\)): \( \delta \) 147.6, 143.4, 139.3, 136.7, 133.8, 133.7, 133.1, 131.8, 130.1, 129.6, 128.5, 128.0, 127.2, 127.1, 126.8, 126.5, 126.1, 125.8, 125.7, 120.2, 115.3, 113.0, 103.0, 55.4, 52.5, 47.4, 21.3. HRMS (ESI): calcd. for [C\(_{34}\)H\(_{31}\)N\(_2\)O\(_3\)S] [M+H]+: 547.2050; found: 547.2049.

1-Benzyl-3-(1-methyl-3-phenyl-1H-isochromen-1-yl)-1H-indole 5aa
Yellow solid. mp 150-152 °C. $R_f = 0.46$ (in 10% EtOAc/Hex). IR (neat, cm$^{-1}$): 1594, 1494, 1450, 1384, 1167, 1027, 905, 733. $^1$H NMR (500 MHz, CDCl$_3$): $\delta$ 7.74-7.72 (m, 2H), 7.67 (dt, $J = 8.0$, 1.0 Hz, 1H), 7.33-7.29 (m, 4H), 7.28-7.27 (m, 2H), 7.23 (dd, $J = 7.5$, 1.5 Hz, 1H), 7.21 (dt, $J = 8.0$, 1.0 Hz, 1H), 7.14 (dd, $J = 7.5$, 1.0 Hz, 1H), 7.12-7.07 (m, 4H), 7.02-6.98 (m, 1H), 6.97 (dt, $J = 7.5$, 1.0 Hz, 1H), 6.89 (s, 1H), 6.44 (s, 1H), 5.26 (s, 2H), 2.17 (s, 3H).

$^{13}$C NMR (100 MHz, CDCl$_3$): $\delta$ 151.4, 137.5, 137.4, 135.2, 135.0, 131.2, 128.8, 128.5, 128.2, 127.8, 127.6, 126.6, 126.5, 125.3, 124.5, 123.9, 122.0, 121.8, 119.6, 119.4, 109.9, 100.2, 79.6, 50.1, 26.0. HRMS (ESI): calcd. for [C$_{31}$H$_{26}$NO] [M+H]$^+$: 428.2009; found: 428.2009.

(5-Benzyl-11-methyl-5H-benzo[b]carbazol-6-yl)(phenyl)methanone 4aa

Yellow solid. mp 185-187 °C. $R_f = 0.36$ (in 5% EtOAc/Hex). IR (neat, cm$^{-1}$): 1663, 1594, 1470, 1398, 1316, 1228, 1157, 1026, 929, 731. $^1$H NMR (500 MHz, CDCl$_3$): $\delta$ 8.49 (d, $J = 7.5$ Hz, 1H), 8.38 (dq, $J = 1.0$, 0.5 Hz, 1H), 7.57 (dq, $J = 1.5$, 1.0 Hz, 3H), 7.49-7.42 (m, 2H), 7.37 (dt, 7.0, 1.5 Hz, 1H), 7.35-7.31 (m, 2H), 7.24 (d, $J = 8.5$ Hz, 1H), 7.15 (t, $J = 8.0$ Hz, 2H), 6.98-6.92 (m, 3H), 6.73-6.71 (m, 2H), 5.39 (s, 2H), 3.36 (s, 3H). $^{13}$C NMR (100 MHz, CDCl$_3$): $\delta$ 199.3, 138.3, 136.6, 133.3, 131.1, 130.2, 129.9, 128.4, 128.2, 127.1, 126.8, 126.7, 125.8, 125.5, 124.9, 124.2, 124.0, 123.8, 123.4, 122.8, 119.8, 114.3, 108.9, 48.1, 15.9. HRMS (ESI): calcd. for [C$_{31}$H$_{24}$NO] [M+H]$^+$: 426.1852; found: 426.1857.

6. Procedure for the synthesis of 1-Benzyl-3-(1-methyl-7-nitro-3-phenyl-1H-isochromen-1-yl)-1H-indole 5ak and 1-Methoxy-1-methyl-7-nitro-3-phenyl-1H-isochromene 6k:
To a stirred solution of 1-(5-nitro-2-(phenylethynyl)phenyl)ethan-1-one 1k (127 mg, 0.48 mmol), 1-benzyl-1H-indole 2a (83 mg, 0.48 mmol) and TMOF (88 µL, 0.8 mmol) in DCM (4 mL) was added AgOTf (10 mg, 0.04 mmol) at room temperature under nitrogen atmosphere. The reaction mixture was stirred at the same temperature. After completion of the reaction, reaction mixture was concentrated under reduced pressure. The residue was purified by column chromatography (silica gel, hexane/EtOAc mixture as eluent) to afford the pure products 1-benzyl-3-(1-methyl-7-nitro-3-phenyl-1H-isochromen-1-yl)-1H-indole 5ak and 1-methoxy-1-methyl-7-nitro-3-phenyl-1H-isochromene 6k in 41% and 22% respectively.

**1-Benzyl-3-(1-methyl-7-nitro-3-phenyl-1H-isochromen-1-yl)-1H-indole 5ak**

Yellow solid (78 mg, 41%). mp 142-144 °C. R_f = 0.15 (in 10% EtOAc/Hex). IR (neat, cm⁻¹): 1568, 1493, 1450, 1325, 1246, 1102, 1056, 899, 763, 718, 690. ¹H NMR (500 MHz, CDCl₃): δ 8.11 (dd, J = 8.0, 2.0 Hz, 1H), 7.79-7.77 (m, 3H), 7.59 (d, J = 8.0 Hz, 1H), 7.37-7.36 (m, 3H), 7.34 (d, J = 7.5 Hz, 2H), 7.30-7.27 (m, 2H), 7.23 (d, J = 8.5 Hz, 1H), 7.15 (d, J = 7.5 Hz, 1H), 7.12 (d, J = 8.5 Hz, 2H), 7.01 (t, J = 7.0 Hz, 2H), 6.53 (s, 1H), 5.33 (s, 2H), 2.19 (s, 3H). ¹³C NMR (100 MHz, CDCl₃): δ 155.5, 145.9, 137.9, 137.6, 137.1, 135.3, 134.0, 129.8, 128.9, 128.4, 127.7, 127.4, 126.7, 126.2, 125.8, 124.0, 123.7, 122.3, 121.5, 120.4, 119.8, 118.3, 110.1, 98.6, 80.3, 50.1, 26.0. HRMS (ESI): calcd. for [C₃₁H₂₅N₂O₃] [M+H]^+: 473.1860; found: 473.1864.

**1-Methoxy-1-methyl-7-nitro-3-phenyl-1H-isochromene 6k**

Yellow solid (30 mg, 22%). mp 86-88 °C. R_f = 0.35 (in 10% EtOAc/Hex). IR (neat, cm⁻¹): 1670, 1579, 1526, 1349, 1196, 911, 836, 735, 666. ¹H NMR (400 MHz, CDCl₃): δ 8.23 (d, J = 2.4 Hz, 1H), 8.18 (dd, J = 8.4, 2.4 Hz, 1H), 7.85-7.81 (m, 2H), 7.47-7.42 (m, 3H), 7.25 (d, J = 8.4 Hz, 1H), 6.51 (s, 1H), 3.32 (s, 3H), 1.97 (s, 3H). ¹³C {¹H} NMR (100 MHz, CDCl₃): δ 154.4, 146.1, 137.8, 133.1, 130.5, 130.0, 128.6, 125.3, 124.6, 124.4, 120.6, 102.8, 97.9, 50.6, 25.7. HRMS (ESI): calcd. for [C₁₄H₁₂NO₃] [M-Ome]^+: 266.0812; found: 266.0817.

**7. Synthesis of 1-benzyl-3-(7-nitro-3-phenynaphthalen-1-yl)-1H-indole 3bk from 5ak**
To a stirred solution of 1-benzyl-3-(1-methyl-3-phenyl-1H-isochromen-1-yl)-1H-indole 5ak (12 mg, 0.028 mmol) in DCM (1 mL) was added AgOTf (0.7 mg, 0.0028 mmol) at room temperature under nitrogen atmosphere. The reaction mixture was stirred at the same temperature. After completion of the reaction, reaction mixture was concentrated under reduced pressure. The residue was purified by column chromatography (silica gel, hexane/EtOAc mixture as eluent) to afford the pure 1-benzyl-3-(7-nitro-3-phenylnaphthalen-1-yl)-1H-indole derivative 3bk (10 mg, 78%).

8. Synthesis of 5ak from 1-methoxy-1-methyl-7-nitro-3-phenyl-1H-isochromene 6k and 1-benzyl-1H-indole 2a

To a stirred solution of 1-methoxy-1-methyl-7-nitro-3-phenyl-1H-isochromene 6k (15 mg, 0.06 mmol) and 1-benzyl-1H-indole 2a (10 mg, 0.05 mmol) in DCM (1 mL) was added AgOTf (1.2 mg, 0.005 mmol) at room temperature under nitrogen atmosphere. The reaction mixture was stirred at the same temperature. After completion of the reaction, reaction mixture was concentrated under reduced pressure. The residue was purified by column chromatography (silica gel, hexane/EtOAc mixture as eluent) to afford the pure 1-benzyl-3-(1-methyl-7-nitro-3-phenyl-1H-isochromen-1-yl)-1H-indole 5ak as a yellow solid (10 mg, 84%).

9. Synthesis of 1-benzyl-3-(3-phenylnaphthalen-1-yl)-1H-indole 3aa from 1-benzyl-3-(1-methyl-3-phenyl-1H-isochromen-1-yl)-1H-indole 5aa
To a stirred solution of 1-benzyl-3-(1-methyl-3-phenyl-1H-isochromen-1-yl)-1H-indole 5aa (23 mg, 0.05 mmol) in DCM (1 mL) was added AgOTf (1.4 mg, 0.005 mmol) at room temperature under nitrogen atmosphere. The reaction mixture was stirred at the same temperature. After completion of the reaction, the reaction mixture was concentrated under reduced pressure. The residue was purified by column chromatography (silica gel, hexane/EtOAc mixture as eluent) to afford the pure 1-benzyl-3-(3-phenylnaphthalen-1-yl)-1H-indole 3aa in 83% (17 mg) yield along with trace amount of (5-benzyl-11-methyl-5H-benzo[b]carbazol-6-yl)(phenyl)methanone 4aa.

10. Procedure for the synthesis of 1-(1,1-dimethoxyethyl)-2-(phenylethynyl)benzene 7

A solution of 1-(2-(phenylethynyl)phenyl)ethan-1-one 1a (250 mg, 1.1 mmol), MeOH (712 µL, 17.6 mmol), TMOF (182 µL, 1.65 mmol), tetrabutylammonium tribromide (TBATB) (16 mg, 0.03 mmol) and THF (2 mL) were stirred for 4 h at room temperature. Then, the reaction mixture was diluted with EtOAc (15 mL), and washed with saturated aqueous solution of NaHCO₃. The resulting organic layer was concentrated under reduced pressure and purified by column chromatography (silica gel, hexane/EtOAc mixture as
eluent) to afford the pure product 1-(1,1-dimethoxyethyl)-2-(phenylethynyl)benzene 7 as a yellow liquid (170 mg, 58%). $R_f = 0.43$ (in 5% EtOAc/Hex). IR (neat, cm$^{-1}$): 1678, 1592, 1491, 1440, 1355, 1275, 1244, 1068, 956, 753, 688, 595. $^1$H NMR (500 MHz, CDCl$_3$): $\delta$ 7.72 (dd, $J = 8.0, 1.5$ Hz, 1H), 7.57 (dd, $J = 7.5, 1.5$ Hz, 1H), 7.55-7.53 (m, 2H), 7.36-7.32 (m, 3H), 7.32-7.30 (m, 1H), 7.28 (dd, $J = 7.5, 1.5$ Hz, 1H), 3.25 (s, 6H), 1.75 (s, 3H). $^{13}$C $^1$H NMR (125 MHz, CDCl$_3$): $\delta$ 144.0, 134.0, 131.4, 128.2, 128.04, 128.02, 127.5, 127.4, 123.9, 120.8, 101.5, 93.1, 89.1, 48.8, 23.7. HRMS (ESI): calcd. for [C$_{18}$H$_{18}$NO$_2$][M+Na]$^+$: 289.1199; found: 289.1194.

11. Synthesis of 3aa from 1-(1,1-dimethoxyethyl)-2-(phenylethynyl)benzene 7 and 1-benzyl-1$H$-indole 2a

To a stirred solution of 1-(1,1-dimethoxyethyl)-2-(phenylethynyl)benzene 7 (64 mg, 0.24 mmol) and 1-benzyl-1$H$-indole 2a (41 mg, 0.2 mmol) in DCM (2 mL) was added AgOTf (5 mg, 0.02 mmol) at room temperature under nitrogen atmosphere. The reaction mixture was stirred at the same temperature. After completion of the reaction, the reaction mixture was concentrated under reduced pressure. The residue was purified by column chromatography (silica gel, hexane/EtOAc mixture as eluent) to afford the pure 1-benzyl-3-(3-phenylnaphthalen-1-yl)-1$H$-indole 3aa in 80% (66 mg) yield.

12. Procedure for scale-up reaction for the synthesis of 3aa

To a stirred solution of 1-(2-(phenylethynyl)phenyl)ethan-1-one 1a (1.32 g, 6 mmol), 1-benzyl-1$H$-indole 2a (1.03 g, 5 mmol) and TMOF (1.09 mL, 10 mmol) in DCM (40 mL) was added AgOTf (128 mg, 0.5 mmol) at room temperature under nitrogen atmosphere. The reaction mixture was stirred at the same temperature. After completion of the reaction, the reaction mixture was
concentrated under reduced pressure. The residue was purified by column chromatography (silica gel, hexane/EtOAc mixture as eluent) to afford the pure product 3aa in 80% (1.65 g) yield along with 10% (212 mg) of the product 4aa.
13. Copies of NMR Spectra

1H NMR (400 MHz, CDCl₃)

[Chemical structure and NMR spectrum diagram]
$^{13}$C \((^{1}H)\) NMR (100 MHz, CDCl$_3$)
$^1$H NMR (500 MHz, CDCl$_3$)
$^{13}$C ($^1$H) NMR (100 MHz, CDCl$_3$)
$\text{O}_2\text{N}$

$\text{H NMR (500 MHz, CDCl}_3\text{)}$

$^1\text{H NMR (500 MHz, CDCl}_3\text{)}$
$^1H$ NMR (100 MHz, CDCl$_3$)
$^{1}$H NMR (500 MHz, CDCl$_3$)
$\text{C}^1\text{H}$ NMR (125 MHz, CDCl$_3$)
$^{1}H$ NMR (500 MHz, CDCl$_3$)
$^{13}$C ($^1$H) NMR (125 MHz, CDCl$_3$)
$^{19}$F NMR (470 MHz, CDCl$_3$)
$^{13}$C ($^1$H) NMR (125 MHz, CDCl$_3$)
$^1$H NMR (400 MHz, CDCl$_3$)
$^{13}$C ($^1$H) NMR (100 MHz, CDCl$_3$)
$^1$H NMR (500 MHz, CDCl$_3$)
$^{13}$C ($^1$H) NMR (100 MHz, CDCl$_3$)
$^{1}H$ NMR (500 MHz, CDCl$_3$)
$^{1}$H NMR (500 MHz, CDCl$_3$)
$\text{Me}^3\text{ag}^1\text{C} \{^1\text{H}\}$ NMR (100 MHz, CDCl$_3$)
$^1$H NMR (400 MHz, CDCl$_3$)
$^{13}$C ($^1$H) NMR (125 MHz, CDCl$_3$)
$^{1}$H NMR (400 MHz, CDCl$_3$)
$^{13}$C ($^1$H) NMR (125 MHz, CDCl$_3$)
$\text{NH}$

$\text{Me}$

$3\text{aj}$

$\text{H NMR (500 MHz, CDCl}_3\text{)}$
$^{13}$C ($^1$H) NMR (100 MHz, CDCl$_3$)
$^1$H NMR (400 MHz, CDCl$_3$)
$\text{H}$}{NMR (100 MHz, CDCl$_3$)
$^1$H NMR (500 MHz, CDCl$_3$)
$^{13}$C ($^1$H) NMR (100 MHz, CDCl$_3$)
$^{1}H$ NMR (500 MHz, CDCl$_3$)
$^{13}$C NMR (500 MHz, CDCl$_3$)
$\text{S-58}$

$\text{N}$

$\text{Bn}$

$\text{3bd}$

$\text{H}$

$\text{NMR (500 MHz, CDCl}_3$)

$\text{OMe}$

$\text{1H NMR (500 MHz, CDCl}_3$)

\begin{align*}
\text{ppm} & \quad \text{ppm} \\
11 & \quad 10 \\
9 & \quad 8 \\
8 & \quad 7 \\
7 & \quad 6 \\
6 & \quad 5 \\
5 & \quad 4 \\
4 & \quad 3 \\
3 & \quad 2 \\
2 & \quad 1 \\
1 & \quad 0 \\
0 & \quad \text{ppm}
\end{align*}
$\text{NMR (100 MHz, CDCl}_3$)

$^{13}\text{C H NMR}$
$^1$H NMR (500 MHz, CDCl$_3$)
$^{13}$C ($^1$H) NMR (125 MHz, CDCl$_3$)
$^{13}$C ($^1$H) NMR (125 MHz, CDCl$_3$)
$^1$H NMR (125 MHz, CDCl$_3$)
$^1$H NMR (500 MHz, CDCl$_3$)
$^{1}$H NMR (400 MHz, CDCl$_3$)
$^{13}$C ($^1$H) NMR (125 MHz, CDCl$_3$)
$\text{\textsuperscript{19}F NMR, (470 MHz, CDCl$_3$)}$
$\text{H NMR (500 MHz, CDCl}_3\text{)}$
$^{13}$C ($^1$H) NMR (125 MHz, CDCl$_3$)
$^{1}$H NMR (400 MHz, CDCl$_3$)

3bj

$\text{Me}$

$\text{Bn}$
$\{^{1}H\}$ NMR (100 MHz, CDCl$_3$)

$\text{Me}$

$\text{Bn}$

$\text{3bj}$

$^{13}$C ($^{1}H$) NMR (100 MHz, CDCl$_3$)

ppm

200 180 160 140 120 100 80 60 40 20 0
$^1$H NMR (500 MHz, CDCl$_3$)
$^{13}$C ($^1$H) NMR (100 MHz, CDCl$_3$)
$^{1}H$ NMR (500 MHz, CDCl$_3$)
$^{13}\text{C} (\text{H}) \text{ NMR (125 MHz, CDCl}_3)$
$\text{Me}$

$\text{H}$

$\text{NMR}$ (500 MHz, CDCl$_3$)

$3\text{hm}$

$^1\text{H NMR}$ (500 MHz, CDCl$_3$)
$\text{Me}$

$\text{3hm}$

$^{13}\text{C}\left({}^1\text{H}\right)\text{NMR (MHz, CDCl}_3\right)$
$^1$H NMR (500 MHz, CDCl$_3$)
$\text{Cl}$

$\text{NMR (125 MHz, CDCl$_3$)}$

$^{13}\text{C}\{^1\text{H}\}$ NMR (125 MHz, CDCl$_3$)
$^{1}$H NMR (400 MHz, CDCl$_3$)
$^{13}$C ($^1$H) NMR (100 MHz, CDCl$_3$)
$^{19}$F NMR, (470 MHz, CDCl$_3$)
$^{1}$H NMR (500 MHz, CDCl$_3$)
$^{13}$C ($^1$H) NMR (125 MHz, CDCl$_3$)
$^{19}$F NMR (470 MHz, CDCl$_3$)
$^1$H NMR (500 MHz, CDCl$_3$)
$^13$C ($^1$H) NMR (125 MHz, CDCl$_3$)
$^1$H NMR (500 MHz, CDCl$_3$)
$^1$H NMR (100 MHz, CDCl$_3$)
$\text{H NMR (500 MHz, CDCl}_3\text{)}$
$^{13}$C ($^1$H) NMR (100 MHz, CDCl$_3$)
$^1$H NMR (500 MHz, CDCl$_3$)
\textbf{13C ($^1$H) NMR (100 MHz, CDCl$_3$)}

\begin{itemize}
  \item 151.39
  \item 137.42
  \item 137.37
  \item 134.92
  \item 131.11
  \item 128.73
  \item 128.13
  \item 128.72
  \item 127.72
  \item 126.62
  \item 126.25
  \item 125.43
  \item 124.89
  \item 123.48
  \item 121.76
  \item 119.52
  \item 119.38
  \item 118.09
  \item 109.39
  \item 79.59
  \item 77.32
  \item 77.70
  \item 76.87
  \item 76.68
  \item 50.03
  \item 25.93
\end{itemize}
$^1$H NMR (400 MHz, CDCl$_3$)
$^{13}\text{C} \quad {^1\text{H}} \text{NMR (100 MHz, CDCl}_3\text{)}$
$\text{O}_2\text{N}$

$\text{Ph}$

$\text{Me}$

$\text{O}$

$\text{N}$

$\text{Bn}$

5ak

$^1\text{H NMR (500 MHz, CDCl}_3)$
$^{13}$C ($^1$H) NMR (100 MHz, CDCl$_3$)
$^1$H NMR (125 MHz, CDCl$_3$)

$^{13}$C NMR (125 MHz, CDCl$_3$)
14. $^1$H NMR monitoring of the reaction of 1a with 2a in the presence of TMOF

**Figure S1**: $^1$H NMR monitoring of the reaction of 1a with 2a in the presence of TMOF (Spectrum 1: Reaction mixture before adding AgOTf, Spectrum 2: Reaction mixture after 1h of adding AgOTf).
15. X-ray data of 3af and 5ak

X-ray data of 3af

![ORTEP representation of 3af](image)

**Figure 2**: ORTEP representation of 3af. Thermal ellipsoids are drawn with 50% probability.

**Table S2. Crystallographic data of compound 3af**

<table>
<thead>
<tr>
<th>Compound</th>
<th>3af</th>
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<tbody>
<tr>
<td>Identification code</td>
<td>RB61</td>
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<tr>
<td>CCDC</td>
<td><strong>2209520</strong></td>
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<tr>
<td>Empirical formula</td>
<td>C\textsubscript{32}H\textsubscript{24}BrN</td>
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<tr>
<td>Formula weight</td>
<td>502.46</td>
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<tr>
<td>Temperature/K</td>
<td>300</td>
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<tr>
<td>Crystal system</td>
<td>Triclinic</td>
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<tr>
<td>Property</td>
<td>Value</td>
</tr>
<tr>
<td>--------------------------------</td>
<td>------------------------------</td>
</tr>
<tr>
<td>Space group</td>
<td>P -1</td>
</tr>
<tr>
<td>a/Å</td>
<td>9.1848 (2)</td>
</tr>
<tr>
<td>b/Å</td>
<td>9.7094 (2)</td>
</tr>
<tr>
<td>c/Å</td>
<td>14.2815 (2)</td>
</tr>
<tr>
<td>α/°</td>
<td>95.361 (2)</td>
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<tr>
<td>β/°</td>
<td>92.618 (1)</td>
</tr>
<tr>
<td>γ/°</td>
<td>109.065 (2)</td>
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<tr>
<td>Volume/Å³</td>
<td>1194.55 (4)</td>
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<tr>
<td>Z</td>
<td>2</td>
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<td>Density(ρ)calc g/cm³</td>
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<td>F(000)</td>
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<td>Reflections collected</td>
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<tr>
<td>Independent reflections</td>
<td>3396</td>
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<tr>
<td>Completeness to theta = 24.995</td>
<td>99.9%</td>
</tr>
<tr>
<td>R (reflections)</td>
<td>0.0385 (3396)</td>
</tr>
</tbody>
</table>
X-ray data of 5ak

**Figure 1:** ORTEP representation of 5ak. Thermal ellipsoids are drawn with 50% probability.

**Table S1. Crystallographic data of compound 5ak**

<table>
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<tr>
<th>Compound</th>
<th>5ak</th>
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<tr>
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<td>CCDC</td>
<td><strong>2204406</strong></td>
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<tr>
<td>Empirical formula</td>
<td>C\textsubscript{31}H\textsubscript{24}N\textsubscript{2}O\textsubscript{3}</td>
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<tr>
<td>Formula weight</td>
<td>472.52</td>
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<tr>
<td>Temperature/K</td>
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<td>Crystal system</td>
<td>Monoclinic</td>
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<tr>
<td>Property</td>
<td>Value</td>
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<tr>
<td>----------------------------------</td>
<td>----------------------------</td>
</tr>
<tr>
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<td>b/Å</td>
<td>9.6103(12)</td>
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<tr>
<td>c/Å</td>
<td>22.543(3)</td>
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<tr>
<td>α/°</td>
<td>90</td>
</tr>
<tr>
<td>β/°</td>
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<tr>
<td>γ/°</td>
<td>90</td>
</tr>
<tr>
<td>Volume/Å³</td>
<td>4986.5(11)</td>
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<tr>
<td>Z</td>
<td>8</td>
</tr>
<tr>
<td>Density(ρ)calc g/cm³</td>
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<tr>
<td>Absorption Coefficient(μ) (mm⁻¹)</td>
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<td>F(000)</td>
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<tr>
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<tr>
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<tr>
<td>R (reflections)</td>
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</table>
16. References


