Supplementary Information

Electrochemical [3+2] Cycloaddition of Anilines and Enamine ketone: Construction of 3-benzoylindole

derivatives

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1. General Information

Compounds and solvents were purchased from commercial sources and were used as received without further purification unless stated otherwise. All products were purified by flashchromatography on silica gel (200-300 mesh). The chemical yields referred are isolated products. ¹H NMR spectra were recorded at 600 MHz, ¹³C NMR spectra were recorded at 150 MHz, ¹⁹F NMR spectra were recorded at 470 MHz (Bruker Avance). Chemical shifts are reported in part per million (ppm) relative to residual solvent of CDCl₃ (7.26 ppm for ¹H NMR, 77.16 ppm for ¹³C NMR). The used abbreviations are as follows: s (singlet), d (doublet), t (triplet), dd (double of doublet), dt (doublet of triplet), m (multiplet). Multiplets which arise from accidental equality of coupling constants of magnetically non-equivalent protons are marked as virtual (virt.). High resolution mass spectra (HRMS) data were measured on a FT-ICR-MS SolariX 7T. Reactions were monitored by TLC analysis using silica gel 60 Å F-254 thin layer plates and compounds were visualized with a UV light at 254 nm or 365 nm. Flash column chromatography was performed on silica gel 60 Å, 10-40 µm. CV curves were recorded using a three-electrode scheme. The working electrode was a glassy carbon electrode, A platinum electrode served as counter electrode. Ag/AgCl (KCl sat'd) was used as the reference electrode. The working electrode was polished before recording each CV curve.

2. General procedure of the synthesis of the products



In an undivided cell constructed from non-borosilicate glass and equipped with a magnetic stirrer, a nickel plate $(1.5 \times 1.0 \text{ cm}^2)$ served as the cathode, while a graphite felt $(1.5 \times 1.0 \text{ cm}^2)$ acted as the anode. Substrate aniline **1a** (0.3 mmol, 1.0 equiv.), enamine **2a** (0.6 mmol, 2.0 equiv.), and the electrolyte LiBF₄ (0.3 mmol, 1.0 equiv.) were introduced into the solvent DCE (6 mL). The reaction proceeded under a constant current of 3 mA, with the internal temperature maintained at approximately 80 °C. Upon completion, the solvent was removed using a rotary evaporator. The remaining crude product was then purified by silica gel column chromatography

with a petroleum ether/ethyl acetate solvent system ((PE/EA = 10:1) to yield the corresponding product.

3. Further functionalization of product

(a) The synthesis of 3c



3aa (0.1 mmol, 1.0 equiv.) and sodium hydroxide (NaOH, 0.2 mmol, 2.0 equiv.) were sequentially added to a 25 mL round-bottom flask charged with 10 mL of anhydrous ethanol, and the mixture was stirred thoroughly to ensure complete dissolution. The reaction flask was then placed in a thermostatically controlled oil bath, gradually heated to 80 °C, and maintained at this temperature under vigorous stirring for 10 hours. The reaction progress was monitored by thin-layer chromatography every 2 hours using a petroleum ether/ethyl acetate mixture (v/v = 5:1) as the eluent until the starting material spot disappeared, indicating reaction completion. After cooling to room temperature, the ethanol solvent was removed under reduced pressure via rotary evaporation to yield the crude product. Purification was carried out by silica gel column chromatography with a gradient elution system of petroleum ether/ethyl acetate (v/v from 10:1 to 7:1), and the target fractions were collected and concentrated under reduced pressure to afford the final pure product.

(b)The synthesis of 4a



(5-Methoxy-*1H*-indol-3-yl)(phenyl)methanone (**3c**, 0.1 mmol, 1.0 equiv.) was added to a dry 50 mL round-bottom flask charged with 10 mL of anhydrous N,N-dimethylformamide (DMF), followed by the slow addition of sodium hydride (NaH, 0.15 mmol, 1.5 equiv.). The mixture was

stirred at room temperature for 30 minutes. Allyl bromide (0.2 mmol, 2.0 equiv.) was then slowly added dropwise to the reaction mixture, and stirring was continued at room temperature. The reaction progress was monitored every hour by thin-layer chromatography using a petroleum ether/ethyl acetate mixture (v/v = 5:1) as the eluent until the starting material spot disappeared, indicating completion. After quenching the reaction with 10 mL of water, the mixture was extracted three times with ethyl acetate (20 mL each). The combined organic layers were washed with 20 mL of saturated brine, dried over anhydrous sodium sulfate, and filtered. The solvent was removed under reduced pressure via rotary evaporation to yield the crude product. Purification was performed by silica gel column chromatography using a gradient elution system of petroleum ether/ethyl acetate (v/v from 10:1 to 7:1). The target fractions were collected and concentrated under reduced pressure to afford the final pure product.

(c)The synthesis of 4b



Intermediate (5-methoxy-*1H*-indol-3-yl)(phenyl)methanone (**3c**, 0.2 mmol, 1.0 equiv.), naproxen (0.4 mmol, 2.0 equiv.), di-tert-butyl dicarbonate (Boc₂O, 0.2 mmol, 1.0 equiv.), 4-dimethylaminopyridine (DMAP, 5 mol%), and 2,6-lutidine (10 mol%) were sequentially added to a dry 50 mL round-bottom flask charged with 10 mL of acetonitrile. The reaction mixture was stirred at 28 °C for 24 hours, with aliquots withdrawn every 4 hours to monitor progress by thin-layer chromatography using a petroleum ether/ethyl acetate mixture (v/v = 3:1) as the eluent until the starting material spot disappeared, confirming completion. The acetonitrile was subsequently removed under reduced pressure to afford the crude product, which was purified via silica gel column chromatography using a gradient elution system of ethyl acetate/petroleum ether (v/v = 6:1). The target compound 4b was collected and concentrated under reduced pressure to yield the final product.

(d)The synthesis of 4c



Intermediate (5-methoxy-*1H*-indol-3-yl)(phenyl)methanone (**3c**, 0.2 mmol, 1.0 equiv.), aspirin (0.4 mmol, 2.0 equiv.), di-tert-butyl dicarbonate (Boc₂O, 0.2 mmol, 1.0 equiv.), 4dimethylaminopyridine (DMAP, 5 mol%), and 2,6-lutidine (10 mol%) were sequentially added to a dry 50 mL round-bottom flask charged with 10 mL of acetonitrile. The reaction mixture was stirred at 28 °C for 24 hours, with aliquots withdrawn every 4 hours to monitor progress by thinlayer chromatography using a petroleum ether/ethyl acetate mixture (v/v = 4:1) as the eluent until the starting material spot disappeared, confirming completion. The acetonitrile was subsequently removed under reduced pressure to afford the crude product, which was purified via silica gel column chromatography using a gradient elution system of ethyl acetate/petroleum ether (v/v =6:1). The target compound 4c was collected and concentrated under reduced pressure to yield the final product.

4. Cyclic voltammetry studies.

The cyclic voltammograms were recorded in an electrolyte of $LiBF_4$ (0.1 M) in DCE (10.0 mL) using a glassy carbon disk working electrode (diameter, 3 mm), a Ni wire auxiliary electrode and an Ag/AgCl reference electrode. The scan rate is 100 mV/s.



Figure S1. Cyclic voltammograms.

5. Spectra data of products



(5-methoxy-1-tosyl-1H-indol-3-yl)(phenyl)methanone(3aa)

Yellow solid, 80% yield. 97 mg ¹H NMR (600 MHz, Chloroform-*d*) δ 7.98 (s, 1H), 7.92 – 7.86 (m, 3H), 7.80 (s, 1H), 7.74 (d, *J* = 8.1 Hz, 2H), 7.62 (m, 1H), 7.56 (t, *J* = 7.5 Hz, 2H), 7.26 (d, *J* = 8.1 Hz, 2H), 7.02 (m, 1H), 3.84 (s, 3H), 2.34 (s, 3H). ¹³C NMR (150 MHz, Chloroform-*d*) δ 191.2, 157.8, 146.0, 139.3, 134.6, 134.2, 132.5, 130.3, 129.7, 129.6, 129.1, 128.8, 127.2, 120.3, 115.9, 114.2, 104.5, 55.8, 21.8. HRMS (ESI) calculated for C₂₃H₂₀NO₄S⁺ [M+H]⁺: 406.1113; found: 406.1112.



(4-fluorophenyl)(5-methoxy-1-tosyl-1H-indol-3-yl)methanone(3ab)

Yellow solid, 76 % yield. 96 mg ¹**H NMR** (600 MHz, Chloroform-*d*) δ 7.95 (s, 1H), 7.92 – 7.87 (m, 3H), 7.79 – 7.75 (m, 3H), 7.26 (d, *J* = 7.5 Hz, 2H), 7.22 (t, *J* = 8.7 Hz, 2H), 7.02 (dd, *J* = 9.0, 2.7 Hz, 1H), 3.85 (s, 3H), 2.36 (s, 3H). ¹³C NMR (150 MHz, Chloroform-*d*) δ 189.5, 166.2, 164.5(s, J = 252.5 Hz), 157.7, 145.9, 134.4, 133.7, 131.5 (d, J = 8.9 Hz), 130.2, 129.6 (d, J = 17.6 Hz), 129.5, 127.1, 120.0, 115.9 (d, J = 5.3 Hz), 115.8, 114.1, 104.3, 55.7, 21.6. ¹⁹F NMR (470 MHz, CDCl₃) δ - 106.14. HRMS (ESI) calculated for C₂₃H₁₉FNO₄S⁺ [M+H]⁺: 424.1019; found: 424.1021.



(3-chlorophenyl)(5-methoxy-1-tosyl-1H-indol-3-yl)methanone(3ac)

Yellow solid, 70 % yield. 92 mg ¹H NMR (600 MHz, Chloroform-*d*) δ 7.88 (s, 1H), 7.80 (d, J = 9.3 Hz, 1H), 7.72 – 7.69 (m, 4H), 7.64 (dt, J = 7.5, 1.3 Hz, 1H), 7.54 – 7.51 (m, 1H), 7.41 (t, J = 7.5 Hz, 1H), 7.19 (s, 2H), 6.95 (dd, J = 9.0, 2.7 Hz, 1H), 3.79 (s, 3H), 2.29 (s, 3H).¹³C NMR (150 MHz, Chloroform-*d*) δ 189.5, 157.8, 146.0, 140.8, 134.9, 134.4, 134.2, 132.3, 130.3, 130.0, 129.6, 129.4, 128.9, 127.8, 127.1, 119.9, 116.0, 114.1, 104.3, 55.8, 21.7. HRMS (ESI) calculated for C₂₃H₁₉ClNO₄S⁺ [M+H]⁺: 440.0123; found: 440.0120.



(4-bromophenyl)(5-methoxy-1-tosyl-1H-indol-3-yl)methanone(3ad)

Yellow solid, 74 % yield. 107 mg ¹**H NMR** (600 MHz, Chloroform-*d*) δ 7.93 (s, 1H), 7.86 (d, J = 9.3 Hz, 1H), 7.77 (dd, J = 5.4, 3.0 Hz, 3H), 7.72 (d, J = 8.1 Hz, 2H), 7.68 (d, J = 8.1 Hz, 2H), 7.25 (d, J = 7.8 Hz, 2H), 7.02 (d, J = 8.7 Hz, 1H), 3.85 (s, 3H), 2.36 (s, 3H).¹³**C NMR** (150 MHz, Chloroform-*d*) δ 189.8, 157.7, 146.0, 137.9, 134.40, 133.9, 132.0, 130.5, 130.3, 129.6, 129.5, 129.4, 127.1, 119.9, 116.0, 114.1, 104.3, 55.8, 21.7. **HRMS (ESI)** calculated for C₂₃H₁₉BrNO₄S⁺ [M+H]⁺: 484.0281; found: 484.0282.



(5-methoxy-1-tosyl-1H-indol-3-yl)(p-tolyl)methanone(3ae)

Yellow solid, 65 % yield. 82 mg ¹H NMR (600 MHz, Chloroform-*d*) δ 7.97 (s, 1H), 7.86 (d, J = 9.3 Hz, 1H), 7.77 (dd, J = 15.0, 6.6 Hz, 5H), 7.34 (d, J = 7.8 Hz, 2H), 7.28 – 7.22 (m, 2H), 7.01 (dd, J = 9.0, 2.4 Hz, 1H), 3.85 (s, 3H), 2.47 (s, 3H), 2.35 (s, 3H).¹³C NMR (150 MHz, Chloroform-*d*) δ 190.8, 157.6, 145.9, 143.2, 136.5, 134.5, 133.8, 130.2, 129.8, 129.5, 129.4, 129.2, 127.1, 120.3, 115.8, 114.1, 104.3, 55.7, 21.7, 21.6. HRMS (ESI) calculated for C₂₄H₂₂NO₄S⁺ [M+H]⁺: 420.1269; found: 420.1266.



(5-methoxy-1-tosyl-1H-indol-3-yl)(m-tolyl)methanone(3af)

Yellow solid, 60 % yield. 75 mg ¹H NMR (600 MHz, Chloroform-*d*) δ 7.97 (d, J = 0.9 Hz, 1H), 7.87 (d, J = 9.3 Hz, 1H), 7.80 (d, J = 2.7 Hz, 1H), 7.77 (d, J = 8.1 Hz, 2H), 7.64 (d, J = 13.2 Hz, 3H), 7.42 (d, J = 7.5 Hz, 2H), 7.24 (s, 1H), 7.01 (dd, J = 9.0, 2.4 Hz, 1H), 3.85 (s, 3H), 2.46 (s, 3H), 2.35 (s, 3H).¹³C NMR (150 MHz, Chloroform-*d*) δ 191.3, 157.6, 145.9, 139.3, 138.6, 134.5, 134.1, 133.2, 130.2, 129.7, 129.5, 129.5, 128.5, 127.1, 126.3, 120.4, 115.8, 114.1, 104.4, 55.7, 21.6, 21.5. HRMS (ESI) calculated for C₂₄H₂₂NO₄S⁺ [M+H]⁺: 420.1269; found: 420.1272.



(5-methoxy-1-tosyl-1H-indol-3-yl)(o-tolyl)methanone(3ag)

Yellow solid, 55 % yield. 69 mg ¹H NMR (600 MHz, Chloroform-*d*) δ 7.84 (d, J = 9.3 Hz, 2H), 7.77 – 7.75 (m, 3H), 7.42 (d, J = 7.5 Hz, 2H), 7.35 – 7.27 (m, 3H), 7.25 (s, 1H), 7.01 (dd, J = 9.0, 2.7 Hz, 1H), 3.86 (s, 3H), 2.39 (s, 3H), 2.36 (s, 3H).¹³C NMR (150 MHz, Chloroform-*d*) δ 193.5,157.8,146,139.5,136.6,135.2,134.6,131.4,130.5,130.3,129.7,129.2,128.2,127.2,125.6,121.7, 116,114.2,104.5,55.9,21.8,19.9. HRMS (ESI) calculated for C₂₄H₂₂NO₄S⁺ [M+H]⁺: 420.1269; found: 420.1266.



(2,5-dimethylphenyl)(5-methoxy-1-tosyl-1H-indol-3-yl) methanone(3ah)

Yellow solid, 62 % yield. 80 mg ¹H NMR (600 MHz, Chloroform-*d*) δ 7.86 – 7.82 (m, 2H), 7.77 – 7.75 (m, 3H), 7.26 (d, *J* = 7.8 Hz, 2H), 7.23 (d, *J* = 7.8 Hz, 1H), 7.20 (d, *J* = 8.1 Hz, 2H), 7.01 (dd, *J* = 9.0, 2.7 Hz, 1H), 3.86 (s, 3H), 2.38 (s, 3H), 2.36 (s, 3H), 2.33 (s, 3H).¹³C NMR (150 MHz, Chloroform-*d*) δ 193.7, 157.7, 145.9, 139.4, 135.1, 134.9, 134.5, 133.2, 131.1, 131.1, 130.2, 129.7, 129.1, 128.7, 127.1, 121.7, 115.8, 114.1, 104.4, 55.8, 21.7, 21.0, 19.3. HRMS (ESI) calculated for C₂₅H₂₄NO₄S⁺ [M+H]⁺: 434.1426; found: 434.1423.



(4-ethylphenyl)(5-methoxy-1-tosyl-1H-indol-3-yl)methanone(3ai)

Yellow solid, 64 % yield. 83 mg ¹H NMR (600 MHz, Chloroform-*d*) δ 7.98 (s, 1H), 7.87 (d, J = 9.3 Hz, 1H), 7.80 (d, J = 8.1 Hz, 3H), 7.77 (d, J = 8.7 Hz, 2H), 7.37 (d, J = 7.8 Hz, 2H), 7.24 (d, J = 8.1 Hz, 2H), 7.01 (dd, J = 9.0, 2.7 Hz, 1H), 3.86 (s, 3H), 2.78 (t, J = 7.8 Hz, 2H), 2.35 (s, 3H), 1.32 (s, 3H).¹³C NMR (150 MHz, Chloroform-*d*) δ 190.8, 157.6, 149.4, 145.8, 136.7, 134.5, 133.8, 130.2, 129.8, 129.5, 129.3, 128.2, 127.1, 120.3, 115.8, 114.1, 104.3, 55.7, 28.9, 21.6, 15.4. HRMS (ESI) calculated for C₂₅H₂₄NO₄S⁺ [M+H]⁺: 434.1426; found: 434.1428.



(4-isopropylphenyl)(5-methoxy-1-tosyl-1H-indol-3-yl)methanone(3aj)

Yellow solid, 60 % yield. 80 mg ¹H NMR (600 MHz, Chloroform-*d*) δ 8.00 (d, J = 6.0 Hz, 1H), 7.86 (d, J = 9.3 Hz, 1H), 7.81 (dt, J = 7.8, 3.9 Hz, 3H), 7.77 (d, J = 8.7 Hz, 2H), 7.56 (d, J = 8.4Hz, 1H), 7.40 (d, J = 8.1 Hz, 1H), 7.25 (d, J = 8.1 Hz, 2H), 7.01 (dd, J = 9.0, 2.7 Hz, 1H), 3.86 (s, 3H), 3.03 (p, J = 6.9 Hz, 1H), 2.35 (s, 3H), 1.40 (s, 3H), 1.33 (d, J = 6.9 Hz, 3H).¹³C NMR (150 MHz, Chloroform-d) δ 190.7, 157.6, 156.1, 153.9, 145.8, 136.9, 134.5, 133.8, 130.2, 129.3, 127.1, 126.8, 125.7, 120.3, 115.8, 114.1, 104.3, 104.3, 55.7, 31.2, 23.8, 21.6. HRMS (ESI) calculated for C₂₆H₂₆NO₄S⁺ [M+H]⁺: 448.1582; found: 448.1585.



(4-(tert-butyl)phenyl)(5-methoxy-1-tosyl-1H-indol-3-yl)methanone (3ak)

Yellow solid, 61 % yield. 84 mg¹H NMR (600 MHz, Chloroform-*d*) δ 7.93 (s, 1H), 7.79 (d, J = 9.3 Hz, 1H), 7.74 (d, J = 8.1 Hz, 3H), 7.69 (d, J = 8.1 Hz, 2H), 7.48 (d, J = 8.1 Hz, 2H), 7.17 (d, J = 8.1 Hz, 2H), 6.93 (dd, J = 9.0, 2.7 Hz, 1H), 3.78 (s, 3H), 2.27 (s, 3H), 1.32 (s, 9H).¹³C NMR (150 MHz, Chloroform-*d*) δ 189.7, 156.6, 155.1, 144.8, 135.4, 133.5, 132.8, 129.2, 128.7, 128.6, 128.5, 127.9, 126.8, 126.0, 124.6, 119.3, 114.8, 113.0, 103.3, 54.7, 34.1, 30.2, 20.6. HRMS (ESI) calculated for C₂₇H₂₈NO₄S⁺ [M+H]⁺: 462.1739; found: 462.1742.



(5-methoxy-1-tosyl-1H-indol-3-yl)(4-methoxyphenyl)methanone (3al)

Yellow solid, 72 % yield. 94 mg ¹H NMR (600 MHz, Chloroform-*d*) δ 7.96 (s, 1H), 7.89 (d, J = 1.8 Hz, 1H), 7.88 – 7.86 (m, 2H), 7.77 – 7.73 (m, 3H), 7.24 (d, J = 8.1 Hz, 2H), 7.04 – 6.99 (m, 3H), 3.92 (s, 3H), 3.85 (s, 3H), 2.35 (s, 3H).¹³C NMR (150 MHz, Chloroform-*d*) δ 189.6, 163.2, 157.5, 145.8, 134.53, 133.1, 131.7, 131.4, 130.2, 129.9, 129.5, 127.0, 120.4, 115.8, 114.1, 113.9, 104.2, 55.7, 55.6, 21.6. HRMS (ESI) calculated for C₂₄H₂₂NO₄S⁺ [M+H]⁺: 436.1218; found: 436.1217.



(5-methoxy-1-tosyl-1*H*-indol-3-yl)(4-(trifluoromethyl)phenyl) methanone (3am) Yellow solid, 69 % yield. 98 mg ¹H NMR (600 MHz, Chloroform-*d*) δ 7.92 (d, *J* = 6.3 Hz, 3H), 7.86 (d, *J* = 9.3 Hz, 1H), 7.80 (dd, *J* = 5.4, 2.7 Hz, 3H), 7.80 – 7.74 (m, 2H), 7.26 (d, *J* = 8.1 Hz, 2H), 7.02 (dd, *J* = 9.0, 2.7 Hz, 1H), 3.84 (s, 3H), 2.34 (s, 3H).¹³C NMR (150 MHz, Chloroform-*d*) δ 189.9, 157.8, 146.1, 142.3, 134.4, 134.3 (d, *J* = 4.5 Hz), 130.3, 129.5, 129.3, 129.1, 127.1, 125.8 (q, *J* = 3.6 Hz), 124.6, 122.8, 119.8, 116.1, 114.1, 104.4, 55.8, 21.7.¹⁹F NMR (470 MHz, Chloroform-*d*) δ -62.94. HRMS (ESI) calculated for C24H19F3NO4S+ [M+H]+: 474.0987; found: 474.0985.



methyl 4-(5-methoxy-1-tosyl-1H-indole-3-carbonyl)benzoate(3an)

Yellow solid, 78 % yield. 108 mg ¹H NMR (600 MHz, Chloroform-*d*) δ 8.21 (d, *J* = 8.4 Hz, 2H), 7.94 (s, 1H), 7.88 (t, *J* = 8.7 Hz, 3H), 7.81 (d, *J* = 2.7 Hz, 1H), 7.78 (d, *J* = 8.1 Hz, 2H), 7.27 (d, *J* = 6.9 Hz, 2H), 7.03 (dd, *J* = 9.0, 2.7 Hz, 1H), 3.99 (s, 3H), 3.87 (s, 3H), 2.37 (s, 3H).¹³C NMR (150 MHz, Chloroform-*d*) δ 190.4, 166.3, 157.8, 146.1, 142.8, 134.4, 134.4, 133.2, 130.3, 129.9, 129.5, 129.3, 128.8, 127.1, 119.9, 116.1, 114.1, 104.4, 55.8, 52.5, 21.7. HRMS (ESI) calculated for C₂₅H₂₂NO₆S⁺ [M+H]⁺: 464.1168; found: 464.1164.



4-(5-methoxy-1-tosyl-1H-indole-3-carbonyl)benzonitrile (3ao)

Yellow solid, 74 % yield. 95 mg ¹H NMR (600 MHz, Chloroform-*d*) δ 7.94 – 7.92 (m, 2H), 7.91 (s, 1H), 7.87 – 7.83 (m, 3H), 7.80 – 7.77 (m, 3H), 7.27 (d, J = 8.4 Hz, 2H), 7.04 (dd, J = 9.0, 2.7 Hz, 1H), 3.86 (s, 3H), 2.37 (s, 3H).¹³C NMR (150 MHz, Chloroform-*d*) δ 189.3, 157.9, 146.2, 142.8, 134.3, 134.2, 132.6, 130.3, 129.5, 129.3, 129.2, 127.2, 119.5, 118.0, 116.2, 115.6, 114.1, 104.4, 55.8, 21.7. HRMS (ESI) calculated for C₂₄H₁₉N₂O₄S⁺ [M+H]⁺: 431.1065; found: 431.1069.



benzo[d][1,3]dioxol-5-yl(5-methoxy-1-tosyl-1H-indol-3-yl)methanone (3ap)

Yellow solid, 60 % yield. 81 mg ¹H NMR (600 MHz, Chloroform-*d*) δ 7.89 (s, 1H), 7.79 (d, J = 9.3 Hz, 1H), 7.70 (d, J = 8.4 Hz, 2H), 7.65 (d, J = 2.7 Hz, 1H), 7.40 (d, J = 9.6 Hz, 1H), 7.18 (d, J = 10.2 Hz, 3H), 6.93 (dd, J = 9.0, 2.7 Hz, 1H), 6.86 (d, J = 8.1 Hz, 1H), 6.03 (s, 2H), 3.78 (s, 3H), 2.29 (s, 3H).¹³C NMR (150 MHz, Chloroform-*d*) δ 188.1, 156.5, 150.5, 147.2, 144.8, 133.5, 132.5, 132.1, 129.2, 128.7, 128.5, 126.0, 124.2, 119.2, 114.8, 113.1, 108.0, 107.0, 103.1, 100.9, 54.7, 20.6. HRMS (ESI) calculated for C₂₄H₂₀NO₆S⁺ [M+H]⁺: 450.1011; found: 450.1009.



phenyl(5-tosyl-5*H*-[1,3]dioxolo[4,5-f]indol-7-yl)methanone (3ba)

Yellow solid, 50 % yield. 63 mg ¹H NMR (600 MHz, Chloroform-*d*) δ 7.80 (s, 1H), 7.76 (d, J = 6.9 Hz, 2H), 7.68 (d, J = 8.4 Hz, 2H), 7.64 (s, 1H), 7.57 – 7.51 (m, 2H), 7.45 (t, J = 7.5 Hz, 2H), 7.19 (d, J = 2.4 Hz, 1H), 7.15 – 7.12 (m, 1H), 5.94 (s, 2H), 2.30 (s, 3H).¹³C NMR (150 MHz, Chloroform-d) δ 189.9, 146.3, 144.9, 138.1, 133.4, 131.3, 129.2, 128.6, 127.9, 127.6, 126.3, 126.1, 121.9, 119.5, 107.8, 104.4, 100.6, 93.5, 20.6. HRMS (ESI) calculated for C₂₃H₁₈NO₅S⁺ [M+H]⁺: 420.0905; found: 420.0909.



(5-ethoxy-1-tosyl-1H-indol-3-yl)(phenyl)methanone (3ca)

Yellow solid, 77 % yield. 97 mg ¹H NMR (600 MHz, Chloroform-*d*) δ 7.97 (s, 1H), 7.86 (dd, J = 8.7, 4.5 Hz, 3H), 7.81 – 7.74 (m, 3H), 7.62 (t, J = 7.5 Hz, 1H), 7.54 (t, J = 7.8 Hz, 2H), 7.24 (d, J = 8.1 Hz, 2H), 7.01 (dd, J = 9.0, 2.7 Hz, 1H), 4.09 (q, J = 6.9 Hz, 2H), 2.35 (s, 3H), 1.42 (t, J = 6.9 Hz, 3H).¹³C NMR (150 MHz, Chloroform-*d*) δ 191.0, 157.0, 145.9, 139.3, 134.5, 134.1, 132.3, 130.2, 129.6, 129.5, 129.0, 128.7, 127.1, 120.2, 116.3, 114.1, 105.1, 63.9, 21.7, 14.8. HRMS (ESI) calculated for C₂₄H₂₂NO₄S⁺ [M+H]⁺: 420.1269; found: 420.1272.



(5-methoxy-6-methyl-1-tosyl-1H-indol-3-yl)(phenyl)methanone (3ea)

Yellow solid, 70 % yield. 88 mg ¹H NMR (600 MHz, Chloroform-*d*) δ 7.83 (s, 1H), 7.77 (dt, J = 6.9, 1.4 Hz, 2H), 7.70 – 7.66 (m, 3H), 7.65 (s, 1H), 7.53 (d, J = 7.5 Hz, 1H), 7.45 (t, J = 7.5 Hz, 2H), 7.17 (d, J = 8.1 Hz, 2H), 3.80 (s, 3H), 2.27 (s, 6H).¹³C NMR (150 MHz, Chloroform-*d*) δ 191.2, 156.2, 145.8, 139.3, 134.7, 133.1, 132.3, 130.2, 129.2, 129.0, 128.7, 127.4, 127.0, 126.7, 120.3, 114.5, 102.4, 55.7, 21.7, 17.5. HRMS (ESI) calculated for C₂₄H₂₂NO₄S⁺ [M+H]⁺: 420.1269; found: 420.1265.



(5-methoxy-1-((4-methoxyphenyl)sulfonyl)-*1H*-indol-3-yl)(phenyl) methanone (3ia) Yellow solid, 62 % yield. 78 mg ¹H NMR (600 MHz, Chloroform-*d*) δ 7.89 (s, 1H), 7.77 – 7.74 (m, 3H), 7.73 – 7.70 (m, 3H), 7.51 – 7.49 (m, 1H), 7.42 (t, *J* = 7.5 Hz, 2H), 6.91 (dd, *J* = 9.0, 2.7 Hz, 1H), 6.78 (d, *J* = 9.0 Hz, 2H), 3.75 (s, 3H), 3.66 (s, 3H).¹³C NMR (150 MHz, Chloroform-*d*) δ 191.1, 164.4, 157.6, 139.3, 134.2, 132.3, 129.7, 129.5, 129.4, 128.9, 128.7, 120.0, 115.8, 114.8, 114.1, 114.1, 104.4, 55.8, 55.7. HRMS (ESI) calculated for C₂₃H₂₀NO₅S⁺ [M+H]⁺: 422.1062; found: 422.1065.



(6-methoxy-1-(phenylsulfonyl)-1H-indol-3-yl)(phenyl)methanone (3ja)

Yellow solid, 57 % yield. 67 mg ¹H NMR (600 MHz, Chloroform-*d*) δ 7.79 (s, 1H), 7.70 – 7.65 (m, 5H), 7.61 (d, J = 2.7 Hz, 1H), 7.44 – 7.42 (m, 1H), 7.40 – 7.32 (m, 4H), 7.27 (s, 1H), 6.83 (dd, J = 9.0, 2.7 Hz, 1H), 3.66 (s, 3H).¹³C NMR (150 MHz, Chloroform-*d*) δ 189.9, 156.7, 138.1, 136.4, 133.5, 132.9, 131.4, 128.6, 128.6, 128.5, 127.9, 127.7, 125.9, 119.3, 114.9, 113.0, 103.3, 54.7. HRMS (ESI) calculated for C₂₂H₁₈NO₄S⁺ [M+H]⁺: 392.0956; found: 392.0958.



(5-methoxy-1-((4-(trifluoromethyl)phenyl)sulfonyl)-1H-indol-3-yl) (phenyl)

methanone (3ka)

Yellow solid, 40 % yield. 55 mg ¹H NMR (600 MHz, Chloroform-*d*) δ 8.04 (d, J = 8.4 Hz, 2H), 7.98 (s, 1H), 7.92 – 7.86 (m, 3H), 7.80 (d, J = 2.7 Hz, 1H), 7.74 (d, J = 8.4 Hz, 2H), 7.68 – 7.62 (m, 1H), 7.56 (d, J = 7.8 Hz, 2H), 7.08 (dd, J = 9.0, 2.7 Hz, 1H), 3.90 (s, 3H).¹³C NMR (150 MHz, Chloroform-*d*) δ 190.8, 157.9, 140.8, 138.9, 133.5, 132.6, 129.8, 129.5, 129.0, 128.8, 127.6, 126.8 (q, J = 3.6 Hz), 121.1, 116.3, 113.9, 104.7, 77.3, 77.1, 76.8, 55.8.¹⁹F NMR (470 MHz, CDCl₃) δ -63.44. HRMS (ESI) calculated for C₂₃H₁₇F₃NO₄S⁺ [M+H]⁺: 460.0830; found: 460.0828.



(1-((4-bromophenyl)sulfonyl)-5-methoxy-1H-indol-3-yl)(phenyl) methanone(3la)

Yellow solid, 50 % yield. 70 mg ¹H NMR (600 MHz, Chloroform-*d*) δ 7.94 (s, 1H), 7.87 – 7.83 (m, 3H), 7.80 (d, J = 2.7 Hz, 1H), 7.74 (d, J = 8.7 Hz, 2H), 7.60 (d, J = 8.7 Hz, 3H), 7.55 (t, J = 7.8 Hz, 2H), 7.03 (dd, J = 9.0, 2.7 Hz, 1H), 3.87 (s, 3H).¹³C NMR (150 MHz, Chloroform-*d*) δ 190.9, 157.9, 139.1, 136.4, 133.7, 132.9, 132.5, 130.1, 129.8, 129.4, 129.0, 128.7, 128.4, 120.8, 116.1, 113.9, 104.6, 55.8. HRMS (ESI) calculated for C₂₂H₁₇BrNO₄S⁺ [M+H]⁺: 470.0061; found: 470.0065.



(1-((4-chlorophenyl)sulfonyl)-5-methoxy-1H-indol-3-yl)(phenyl) methanone(3ma)

Yellow solid, 54 % yield. 69 mg ¹H NMR (600 MHz, Chloroform-*d*) δ 7.86 (s, 1H), 7.78 – 7.75 (m, 3H), 7.73 (d, J = 9.0 Hz, 3H), 7.54 (t, J = 7.5 Hz, 1H), 7.45 (t, J = 7.5 Hz, 2H), 7.33 (d, J = 8.7 Hz, 2H), 6.94 (dd, J = 9.0, 2.7 Hz, 1H), 3.77 (s, 3H).¹³C NMR (150 MHz, Chloroform-*d*) δ 189.8, 156.8, 140.4, 138.0, 134.7, 132.6, 131.4, 128.9, 128.7, 128.3, 127.9, 127.7, 127.3, 119.6, 115.0, 112.9, 103.5, 54.7. HRMS (ESI) calculated for C₂₂H₁₇ClNO₄S⁺ [M+H]⁺: 426.0567; found: 426.0565.



(1-((4-iodophenyl)sulfonyl)-5-methoxy-1H-indol-3-yl)(phenyl) methanone(3na)

Yellow solid, 58 % yield. 90 mg ¹H NMR (600 MHz, Chloroform-*d*) δ 7.85 (s, 1H), 7.75 (t, J = 8.4 Hz, 3H), 7.71 (d, J = 8.7 Hz, 3H), 7.54 (t, J = 7.5 Hz, 1H), 7.49 – 7.44 (m, 4H), 6.93 (dd, J = 9.0, 2.7 Hz, 1H), 3.77 (s, 3H).¹³C NMR (150 MHz, Chloroform-*d*) δ 190.9, 157.839, 139.1, 138.9, 136.9, 133.7, 132.5, 129.8, 129.4, 129.0, 128.8, 128.1, 120.7, 116.1, 113.9, 104.6, 102.8, 55.8. HRMS (ESI) calculated for C₂₂H₁₇INO₄S⁺ [M+H]⁺: 517.9923; found: 517.9925.



(5-methoxy-1-(o-tolylsulfonyl)-1H-indol-3-yl)(phenyl) methanone(3oa)

Yellow solid, 66 % yield. 80 mg ¹H NMR (600 MHz, Chloroform-*d*) δ 8.00 (s, 1H), 7.88 – 7.84 (m, 4H), 7.81 (d, J = 2.7 Hz, 1H), 7.69 (d, J = 1.5 Hz, 2H), 7.61 (d, J = 5.4 Hz, 1H), 7.53 (s, 1H), 7.51 (d, J = 3.9 Hz, 1H), 7.35 (s, 1H), 7.02 (dd, J = 9.0, 2.7 Hz, 1H), 3.84 (s, 3H), 2.34 (s, 3H).¹³C NMR (150 MHz, Chloroform-*d*) δ 191.0, 157.7, 140.1, 139.2, 137.3, 136.5, 135.5, 134.1, 133.3, 132.4, 130.1, 129.0, 128.7, 127.2, 124.3, 120.2, 115.9, 114.1, 104.4, 55.7, 21.4. HRMS (ESI) calculated for C₂₃H₁₉NO₄S⁺ [M+H]⁺: 406.1113; found: 406.1115.



(6-methoxy-1-(m-tolylsulfonyl)-1H-indol-3-yl)(phenyl)methanone (3pa)

Yellow solid, 68 % yield. 83 mg ¹H NMR (600 MHz, Chloroform-*d*) δ 7.98 (s, 1H), 7.89 – 7.87 (m, 1H), 7.76 (d, J = 2.4 Hz, 3H), 7.50 (t, J = 7.2 Hz, 2H), 7.43 (s, 1H), 7.42 (s, 1H), 7.41 (s, 1H), 7.39 (s, 1H), 7.13 (d, J = 3.6 Hz, 1H), 6.83 (dd, J = 9.0, 2.7 Hz, 1H), 3.74 (s, 3H), 2.37 (s, 3H).¹³C NMR (150 MHz, Chloroform-*d*) δ 189.9, 156.5, 138.2, 137.0, 135.1, 133.6, 133.1, 132.2, 131.3, 129.0, 128.4, 127.8, 127.6, 125.9, 125.8, 118.0, 114.7, 112.6, 103.4, 54.6, 19.1. HRMS (ESI) calculated for C₁₆H₁₃NO₂⁺ [M+H]⁺: 406.1113; found: 406.1110.



(5-Methoxy-1H-indol-3-yl)(phenyl)methanone(3c)

Yellow solid, 23 mg,yield: 90 % ¹H NMR (600 MHz, DMSO-d6) δ 11.99 (s, 1H), 7.88 (m, 1H), 7.82 – 7.77 (m, 3H), 7.60 (t, J = 7.2 Hz, 1H), 7.54 (t, J = 7.5 Hz, 2H), 7.43 (m, 1H), 6.91 (m, 1H), 3.82 (s, 3H).¹³C NMR (150 MHz, DMSO-d6) δ 190.3, 155.9, 141.0, 136.3, 131.9, 131.3, 128.7, 128.6, 127.4, 115.2, 113.4, 113.4, 103.5, 55.6. HRMS (ESI) calculated for C₁₆H₁₃NO₂⁺ [M+H]⁺: 252.1025; found: 252.1022.



(1-Allyl-5-methoxy-1H-indol-3-yl)(phenyl)methanone(4a)

Yellow solid, 25 mg,yield: 86 % ¹H NMR (600 MHz, Chloroform-*d*) δ 7.90 (m, 1H), 7.73 (d, J = 7.2 Hz, 2H), 7.45 (d, J = 12.9 Hz, 2H), 7.42 – 7.38 (m, 2H), 7.17 (m, 1H), 6.88 (m, 1H), 5.94 – 5.86 (m, 1H), 5.19 (m, 1H), 5.07 (m, 1H), 4.64 (d, J = 5.1 Hz, 2H), 3.83 (s, 3H).¹³C NMR (150 MHz, Chloroform-*d*) δ 189.9, 155.6, 139.9, 135.9, 131.0, 130.8, 130.0, 127.6, 127.3, 127.2, 117.5, 114.5, 113.23, 109.9, 102.8, 54.8, 48.6. HRMS (ESI) calculated for C₁₉H₁₇NO₂S⁺ [M+H]⁺: 292.1338; found: 292.1340.



1-(3-Benzoyl-5-methoxy-1H-indol-1-yl)-2-(6-methoxynaphthalen-2-yl)propan-1-one(4b)

Yellow solid, 68 mg,yield: 74 % ¹**H NMR** (600 MHz, Chloroform-*d*) δ 8.48 (m, 1H), 7.86 (s, 1H), 7.78 (m, 1H), 7.75 (m, 1H), 7.67 (m, 1H), 7.61 (s, 1H), 7.49 (t, *J* = 7.5 Hz, 1H), 7.35 (d, *J* = 6.9 Hz, 2H), 7.29 (m, 1H), 7.26 – 7.12 (m, 5H), 7.06 (m, 1H), 4.46 (q, *J* = 6.9 Hz, 1H), 3.92 (s, 3H), 3.87 (s, 3H), 1.68 (d, *J* = 6.6 Hz, 2H).¹³**C NMR** (150 MHz, Chloroform-*d*) δ 191.1, 172.3, 158.1, 157.8, 139.1, 135.9, 133.9, 133.8, 132.0, 130.9, 129.3, 129.2, 128.8, 128.4, 128.4, 125.8, 125.2, 119.7, 117.4, 115.7, 105.7, 104.1, 55.7, 55.4, 46.6, 20.2. **HRMS (ESI)** calculated for C₃₀H₂₅NO₄⁺ [M+H]⁺: 464.1862; found: 464.1865.



2-(3-Benzoyl-5-methoxy-1H-indole-1-carbonyl)phenyl acetate(4c)

Yellow solid, 57 mg,yield: 69 % ¹H NMR (600 MHz, Chloroform-*d*) δ 8.30 (m, 1H), 7.88 – 7.78 (m, 6H), 7.57 (dt, J = 52.8, 7.7 Hz, 5H), 7.05 – 7.02 (m, 1H), 3.89 (s, 3H), 2.64 (s, 3H).¹³C NMR (150 MHz, Chloroform-*d*) δ 191.4, 168.5, 157.6, 139.5, 133.08, 132.3, 130.7, 129.23, 128.9, 128.7, 128.5, 120.5, 117.1, 115.7, 104.2, 55.7, 23.8. HRMS (ESI) calculated for C₂₅H₂₀NO₅⁺ [M+H]⁺: 414.1341; found: 414.1339.

6. NMR Spectra

3aa





3ab

S16



90 70 50 30 10 -10 -30 -50 -70 -90 -110 -130 -150 -170 -190 -210 -230 -250 -270 -290 f1 (ppa)





190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 f1 (ppa)

S19





Ts ¹H CDCl₃ 600 MHz

3ae







¹H CDCl₃ 600 MHz











¹H CDCl₃ 600 MHz



-2.351 -2.356 -2.356 -2.356 -2.356 -2.356 -2.351 -2.351 -2.351 -2.351 -2.351 -2.351





3ai





190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 f1 (ppm)

S26





¹H CDCl₃ 600 MHz





3am



90 70 50 30 10 -10 -30 -50 -70 -90 -110 -130 -150 -170 -190 -210 -230 -250 -270 -290 f1 (ppa)



3an





¹H CDCl₃ 600 MHz



190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 f1 (ppa)

3ao





3ba



¹H CDCl₃ 600 MHz









S35



3ia



~3.746 ~3.662



¹H CDCl₃ 600 MHz





3ja





-290 50 30 10 -10 -30 -50 -70 -90 -110 f1 (ppm) -250 -270 -130 -170 -190 -210 -230 -150



3la

7.033 7.1859 7.1807 7.1807 7.1803 7.7.793 7.7.793 7.7.595 7.7.595 7.7.595 7.7.535 7.7.535 7.7.535 7.7.038 7.7.038



¹H CDCl₃ 600 MHz



-3.772

-3.768



¹H CDCl₃ 600 MHz









3pa



¹H CDCl₃ 600 MHz





4a



190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 f1 (ppm)



¹H CDCl₃ 600 MHz

4b



190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 f1 (ppm)



¹H CDCl₃ 600 MHz



--3.890