

Supporting Information

Synthesis of Pyrrolo[1,2-*a*]quinolines and Ullazines by Visible Light mediated one- and twofold Annulation of *N*-Arylpyrroles with Arylalkynes

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1) General Information

Solvents and reagents were obtained from commercial sources and used without further purification. Spectroscopic grade DMF and DMSO were dried with 3 Å molecular sieves according to a reported procedure¹. Rhodamine 6G (**Rh-6G**) (dye content ~ 95%) was purchased from Sigma Aldrich. Proton NMR spectra were recorded on a Bruker Avance 300 MHz spectrometer and 600 MHz spectrometer in CDCl₃ solution with internal solvent signal peak at 7.26 ppm. Carbon NMR were recorded at 75 MHz spectrometer and 151 MHz spectrometer in CDCl₃ solution and referenced to the internal solvent signal at 77.26 ppm. Proton NMR data are reported as follows: chemical shift (ppm), multiplicity (s = singlet, d = doublet, t = triplet, q = quartet, quint = quintet, dd = doublet of doublets, ddd = doublet of doublet of doublets, td = triplet of doublets, qd = quartet of doublets, m = multiplet, br. s. = broad singlet), and coupling constants (Hz). High resolution mass spectra (HRMS) were obtained from the central analytic mass spectrometry facilities of the Faculty of Chemistry and Pharmacy, Regensburg University and are reported according to the IUPAC recommendations 2013. All reactions were monitored by thin-layer chromatography using Merck silica gel plates 60 F254; visualization was accomplished with short wave length UV light (254 nm). UV-Vis and fluorescence measurements were performed with Varian Cary 50 UV/Vis spectrophotometer and FluoroMax-4 spectrofluorometer, respectively. Electrochemical studies were carried out under argon atmosphere. The measurements were performed in dimethylformamide (DMF) containing 0.1 M tetra-n-butylammonium tetrafluoroborate using ferrocene/ferrocenium (Fc/Fc⁺) as an internal reference. A glassy carbon electrode (working electrode), platinum wire counter electrode, and Ag quasi-reference electrode were employed. Spectroelectrochemical studies were carried out in an optically transparent thin layer electrochemical cell (OTTLE). Standard flash chromatography was performed using silica gel of particle size 40–63 µm. Photoreduction and annulation reactions were performed with 455 nm LEDs (OSRAM Oslon SSL 80 royal-blue LEDs (λ = 455 nm ($\pm$ 15 nm), 3.5 V, 700 mA).

2) General Procedures

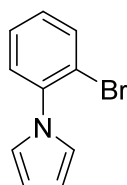
Synthesis of Starting materials:

Procedure for the synthesis of *N*-Aryl Pyrroles:

N-Aryl Pyrroles 1(a-c, e and f) were prepared by Paal-Knorr synthesis from the respective aniline, according to the procedure reported by Lee *et al.*²

General Method: A solution of aniline (1 equiv.) and acetic acid (0.07 mL/mmol aniline) in DCE (1.86 mL/mmol aniline) and water (1.12 mL/mmol aniline) were heated to 80° C. 2,5- Dimethoxytetrahydrofuran (1.05 equiv.) was then added in one portion and the heating was continued at 80° C overnight. Once cooled, the layers were separated and the aqueous layer was extracted with DCM. The combined organic layers were then dried with MgSO₄, filtered, and the solvent was removed in vacuo to yield the crude pyrrole.

Synthesis of 1-(2-Bromo-phenyl)-1*H*-pyrrole (**1a**):



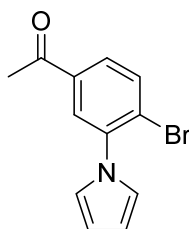
Synthesized according to the general procedure using 2-bromo-aniline (1.0 g, 4.5 mmol). Purified by flash column chromatography (hexane : ethyl acetate, 99:1) to yield the title compound as a colourless oil (0.64 g, 75%).

¹H NMR (CDCl₃, 300 MHz, ppm): δ 7.70 (dd, J = 8.1 Hz, J = 1.2 Hz, 1H), 7.4-7.31 (m, 2H), 7.25-7.20 (m, 1H), 6.88 (t, J = 2.1 Hz, 2H), 6.34 (t, J = 2.1 Hz, 2H).

¹³C NMR (CDCl₃, 75 MHz, ppm): δ 140.4, 133.8, 128.8, 128.3, 128.1, 122.2, 119.9, 109.2

HRMS: C₁₀H₉BrN [M+H]⁺ calculated 221.9913 was found 221.9919, spectral data are consistent with those reported in the literature.³

Synthesis of 1-(4-bromo-3-(1H-pyrrol-1-yl)phenyl)ethan-1-one (1b):



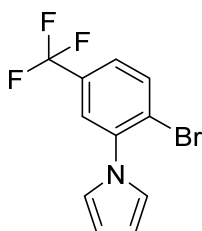
Synthesized according to the general procedure using 2-bromo-aniline (1.0 g, 4.6 mmol). Purified by flash column chromatography (hexane : ethyl acetate, 96:4) to yield the compound as a white solid (1.04 g, 85%).

¹H NMR (CDCl₃, 300 MHz, ppm): δ 7.89 (t, *J* = 1.2 Hz, 1H), 7.80 (m, 2H), 6.90 (t, *J* = 2.2 Hz, 2H), 6.37 (t, *J* = 2.1 Hz, 2H), 2.61 (s, 3H).

¹³C NMR (CDCl₃, 75 MHz, ppm): δ 196.4, 140.9, 137.2, 134.4, 128.2, 128.0, 125.6, 122.3, 109.9, 26.8.

HRMS: [M⁺] C₁₂H₁₀BrNO calculated 262.9940 found 262.9937

Synthesis of 1-(2-bromo-5-(trifluoromethyl)phenyl)-1H-pyrrole (1c):



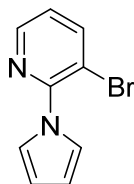
Synthesized according to the general procedure using 2-bromo-aniline (1.0 g, 4.1 mmol). Purified by flash column chromatography (hexane : ethyl acetate, 99:1) to yield the desired compound as a colourless oil (0.96 g, 80%).

¹H NMR (CDCl₃, 300 MHz, ppm): δ 7.84 (d, *J* = 8.3 Hz, 1H), 7.6 (s, 1H), 7.49 (s, 1H), 6.94 (t, *J* = 1.8 Hz, 2H), 6.41 (t, *J* = 1.8 Hz, 2H).

¹³C NMR (CDCl₃, 75 MHz, ppm): δ 141.1, 134.8, 131.7, 131.3, 130.8, 130.4, 125.5, 125.4, 125.4, 125.3, 125.2, 123.9, 122.3, 110.2

HRMS: [M⁺] C₁₁H₇NF₃Br calculated 288.9704 found 288.9703.

Synthesis of 3-bromo-2-(1H-pyrrol-1-yl)pyridine (1e):



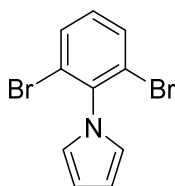
Synthesized according to the general procedure using 2-bromo-aminopyridine (1.0 g, 5.7 mmol). Purified by flash column chromatography (hexane : ethyl acetate, 99:1) to yield the desired compound as a colorless solid (0.65 g, 51%).

¹H NMR (CDCl₃, 300 MHz, ppm): δ 8.44 (dd, *J* = 4.6, 1.6 Hz, 1H), 8.0 (dd, *J* = 7.9, 1.6 Hz, 1H), 7.29 (t, *J* = 2.2 Hz, 2H), 7.1 (dd, *J* = 7.9, 4.6 Hz, 1H), 6.36 (t, *J* = 2.2 Hz, 2H).

¹³C NMR (CDCl₃, 75 MHz, ppm): δ 150.1, 147.6, 143.7, 122.7, 121.5, 112.5, 110.2

HRMS: [M⁺] C₉H₇N₂Br calculated 221.97871 found 221.97878

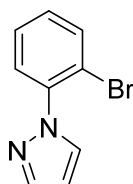
Synthesis of 1-(2,6-dibromophenyl)-1*H*-pyrrole (1f):



Synthesized according to the general procedure using 2,6-dibromo-aniline (1.0 g, 3.3 mmol). Purified by flash column chromatography (hexane:ethyl acetate, 98:2) to yield the desired compound as white solid (1.01 g, 84%). ¹H NMR (CDCl₃, 300 MHz, ppm): δ 7.67 (s, 1H), 7.64 (s, 1H), 7.20 – 7.11 (m, 1H), 7.84 – 6.25 (m, 8H), 6.69 (t, *J* = 2.1 Hz, 2H), 6.40 (t, *J* = 2.1 Hz, 2H).

¹³C NMR (CDCl₃, 75 MHz, ppm): δ 139.8, 132.4, 130.6, 124.31, 121.5, 109.3. data identical to those reported.⁴

Synthesis of 1-(2-bromophenyl)-1*H*-pyrazole (1d):



A round bottomed flask was charged with pyrazole (14.6 mmol), 2-bromo-fluorobenzene (5.1 g, 29.3 mmol, 2.0 equiv.) and K₃PO₄ (15.5 g, 73.4 mmol, 5.0 equiv.) in DMF (140 mL) and refluxed under nitrogen for 24 hrs. After the reaction, the mixture was cooled to room temperature. It was mixed with H₂O and the organic layer was extracted with ethyl acetate. The solvent was removed and the crude product was purified by flash column chromatography on silica gel using (hexane : ethyl acetate, 91:9) to yield the desired compound as colorless liquid in 83% yield.

¹H NMR (CDCl₃, 300 MHz, ppm): δ 7.81 (d, *J* = 2.3 Hz, 1H), 7.75 (d, *J* = 1.6 Hz, 1H), 7.70 (dd, *J* = 7.9, 1.4 Hz, 1H), 7.52 (dd, *J* = 7.9, 1.7 Hz, 1H), 7.42 (ddd, *J* = 7.9, 7.4, 1.4 Hz, 1H), 7.28 (ddd, *J* = 8.0, 7.4, 1.7 Hz, 1H), 6.47 (t, *J* = 2.1 Hz, 1H).

¹³C NMR (CDCl₃, 75 MHz, ppm): δ 140.8, 139.9, 133.8, 131.3, 129.6, 128.3, 128.2, 118.6, 106.5 data identical to those reported.⁵

3) General procedure for C–H arylation followed by intramolecular cyclization reactions:

In a 5 mL snap vial with magnetic stirring bar the aryl halide (0.1 mmol, 1.0 equiv.), the corresponding alkyne (20.0 equiv.) and **Rh-6G** (0.01 mmol, 0.2 equiv.) were added and the mixture was degassed by “pump-freeze-thaw” cycles (×3) via a syringe needle. DIPEA (2.2 equiv.) and dry DMSO (total volume of the solution 1.5 mL), were added under N₂ and the resulting mixture was again degassed twice by syringe needle. This reaction mixture was transferred into a microreactor (capacity 1.7mL) and irradiated with blue light (455nm) under nitrogen at 25° C. The reaction progress was monitored by GC analysis. After 2.5 h to 24 h of irradiation, the reaction mixture was transferred to separating funnel, diluted with ethyl acetate and washed with 15 mL of water. The aqueous layer was washed three times (3 × 15 mL) with ethyl acetate. The combined organic phases were dried over MgSO₄, filtered and concentrated in vacuum. Purification of the crude product was achieved by flash column chromatography using petrol ether/ethyl acetate as eluent.

Glass microreactors and irradiation setup used for photocatalysis:

The reaction mixture (1.5mL) was injected by syringe into the glass microreactor (LTF, 11×5.7cm×1.7mL internal volume, 0.3 mL volume of the reactor tubing) previously flushed with nitrogen. The flow reactor was cooled down to 25°C with a custom-made aluminum cooling block placed opposite to LEDs with a mirror to minimize loss of the light.

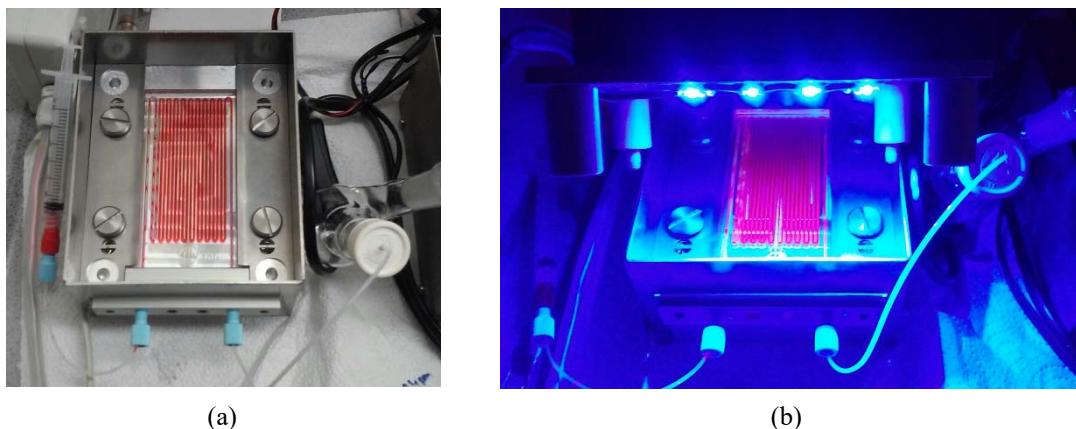


Fig 1. a) Glass microreactor with suspension of reaction mixture (no flow method). b) irradiation setup for the reaction in microreactor with 455nm blue LED.

Absorption spectra of Rh-6G and Rh-6G^{•-}:

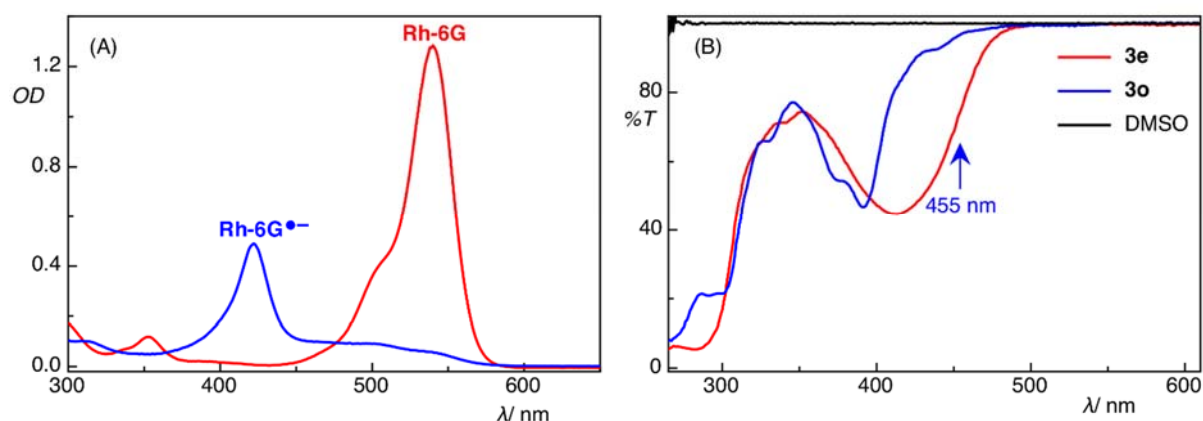
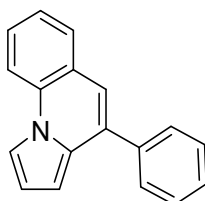


Fig 2: (A) Absorption spectra of Rh-6G and Rh-6G^{•-}, (generated electrochemically). (B) Transmittance spectra of compound **3e** and **3o** in DMSO.

4-Phenylpyrrolo[1,2-*a*]quinoline (**3a**):⁶

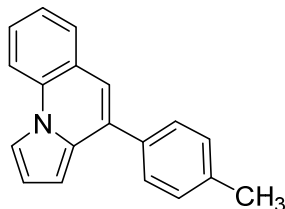


The compound was prepared according to the general procedure using 22.2 mg of 1-(2-bromophenyl)-1*H*-pyrrole, 9.5 mg of **Rh-6G**, 219.6μL of phenylacetylene, 38.3μL of DIPEA and 1.5mL dry DMSO. The reaction mixture was irradiated for 24h under N₂. Purification of the crude product was achieved by flash column chromatography using petrol ether as eluent to yield the desired compound as greenish solid (13.8 mg, 60%).

¹H NMR (CDCl₃, 300 MHz, ppm): δ 7.92 (m, 1H), 7.89 (d, *J* = 8.4 Hz, 1H), 7.71 (d, *J* = 8.4 Hz, 2H), 7.67 (d, *J* = 8.0 Hz, 1H), 7.51–7.4 (m, 4H), 7.32 (t, *J* = 7.6 Hz, 1H), 6.99 (s, 1H), 6.80 (t, *J* = 3.2 Hz, 1H), 6.61 (d, *J* = 4 Hz, 1H).

¹³C NMR (CDCl₃, 75 MHz, ppm): δ 139.3, 133.0, 132.9, 131.1, 129.0, 128.7, 128.6, 128.3, 127.8, 124.5, 123.9, 118.3, 114.3, 113.0, 112.8, 103.6

4-(*p*-Tolyl)pyrrolo[1,2-*a*]quinoline (3b):⁷

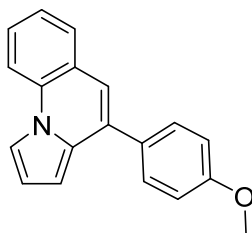


The compound was prepared according to the general procedure using 22.2 mg of 1-(2-bromophenyl)-1*H*-pyrrole, 9.5 mg of **Rh-6G**, 253.6 μL of 1-ethynyl-4-methylbenzene, 38.3 μL of DIPEA and 1.5 mL dry DMSO. The reaction mixture was irradiated for 3 h under N₂. Purification of the crude product was achieved by flash column chromatography using petrol ether as eluent to yield the desired compound as greenish solid (12.4 mg, 51%).

¹H NMR (CDCl₃, 300 MHz, ppm): δ 7.91–7.87 (m, 2H), 7.66–7.64 (m, 1H), 7.60 (d, *J* = 8.1 Hz, 2H), 7.50–7.45 (m, 1H), 7.32–7.30 (m, 1H), 7.29–7.27 (m, 2H), 6.96 (s, 1H), 6.79–6.78 (m, 1H), 6.61–6.60 (m, 1H), 2.43 (s, 3H).

¹³C NMR (CDCl₃, 75 MHz, ppm): δ 137.8, 136.1, 132.64, 132.59, 130.9, 129.2, 128.6, 128.2, 127.4, 124.3, 123.6, 117.7, 114.0, 112.7, 112.5, 103.3, 21.3

4-(4-Methoxyphenyl)pyrrolo[1,2-*a*]quinoline (3c):⁸

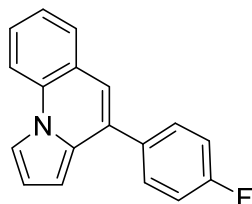


The compound was prepared according to the general procedure using 22.2 mg of 1-(2-bromophenyl)-1*H*-pyrrole, 9.5 mg of **Rh-6G**, 259.3 μL of 1-ethynyl-4-methoxybenzene, 38.3 μL of DIPEA and 1.5 mL dry DMSO. The reaction mixture was irradiated for 2.5 h under N₂. Purification of the crude product was achieved by flash column chromatography using petrol ether as eluent to yield the desired compound as greenish solid (13 mg, 50%).

¹H NMR (CDCl₃, 300 MHz, ppm): δ 7.85–7.80 (m, 2H), 7.59–7.57 (m, 3H), 7.42–7.38 (m, 1H), 7.26–7.22 (m, 1H), 6.94 (dd, *J* = 2.2, 6.6 Hz, 2H), 6.87 (s, 1H), 6.72 (t, *J* = 3.3 Hz, 1H), 6.54 (dd, *J* = 1.5, 3.7 Hz, 1H), 3.80 (s, 3H).

¹³C NMR (CDCl₃, 75 MHz, ppm): δ 159.5, 132.5, 132.3, 131.4, 131.0, 129.4, 128.5, 127.3, 124.3, 123.6, 117.5, 114.0, 113.9, 112.7, 112.5, 103.2, 55.3

4-(4-Fluorophenyl)pyrrolo[1,2-*a*]quinoline (3d):⁶



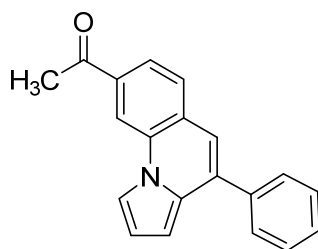
The compound was prepared according to the general procedure using 22.2 mg of 1-(2-bromophenyl)-1*H*-pyrrole, 9.5 mg of **Rh-6G**, 229.2 μL of 1-ethynyl-4-fluorobenzene, 38.3 μL of DIPEA and 1.5 mL dry DMSO. The reaction

mixture was irradiated for 2.5 h under N₂. Purification of the crude product was achieved by flash column chromatography using petrol ether as eluent to yield the desired compound as light green solid (11.9 mg, 48%).

¹H NMR (CDCl₃, 300 MHz, ppm): δ 7.93 (dd, *J* = 3.2, 1.6 Hz, 1H), 7.89 (d, *J* = 8.4 Hz, 1H), 7.68 (m, 3H), 7.51 (t, *J* = 7.2 Hz, 1H), 7.35 (t, *J* = 6.8 Hz, 1H), 7.17 (t, *J* = 8.8 Hz, 2H), 6.95 (s, 1H), 6.80 (dd, *J* = 3.6, 2.8 Hz, 1H), 6.56 (dd, *J* = 4.0, 1.6 Hz, 1H).

¹³C NMR (CDCl₃, 75 MHz, ppm): δ 164.0, 161.6, 135.2, 135.1, 132.8, 131.8, 131.0, 130.3, 130.2, 130.1, 128.9, 127.9, 124.3, 124.0, 118.3, 115.8, 115.6, 114.3, 113.0, 112.9, 104.9, 103.4

1-(4-Phenylpyrrolo[1,2-*a*]quinolin-8-yl)ethan-1-one (3e):



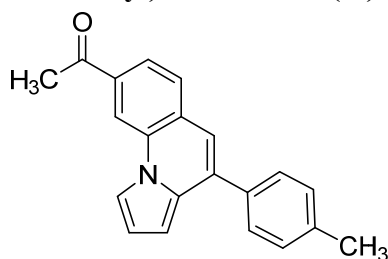
The compound was prepared according to the general procedure using 26.4 mg of 1-(4-bromo-3-(1*H*-pyrrol-1-yl)phenyl)ethan-1-one, 9.5 mg of **Rh-6G**, 219.6 μL of phenylacetylene, 38.3 μL of DIPEA and 1.5 mL dry DMSO. The reaction mixture was irradiated for 3 h under N₂. Purification of the crude product was achieved by flash column chromatography using petrol ether/ethyl acetate (95:5) as eluent to yield the desired compound as yellow solid (16.5 mg, 58%).

¹H NMR (CDCl₃, 300 MHz, ppm): δ 8.52 (s, 1H), 8.08 (dd, *J* = 3, 1.4 Hz, 1H), 7.88 (dd, *J* = 8.1, 1.4 Hz, 1H), 7.72 (d, *J* = 8.1 Hz, 3H), 7.60 – 7.46 (m, 3H), 6.99 (s, 1H), 6.84 (dd, *J* = 3.6, 3.3 Hz, 1H), 6.68 (dd, *J* = 4.7, 0.9 Hz, 1H), 2.73 (s, 3H).

¹³C NMR (CDCl₃, 75 MHz, ppm): δ 197.4, 138.6, 135.5, 128.8, 128.7, 128.5, 128.4, 123.8, 117.3, 114.2, 114.0, 113.5, 105.0, 27.0.

HRMS [M+H]⁺ C₂₀H₁₅NO calculated 286.1226 found 286.1229.

1-(4-(*p*-Tolyl)pyrrolo[1,2-*a*]quinolin-8-yl)ethan-1-one (3f):



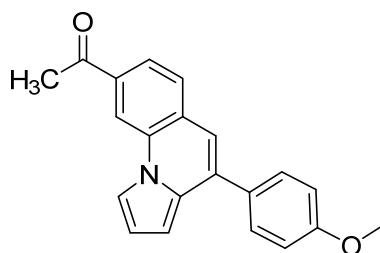
The compound was prepared according to the general procedure using 26.4 mg of 1-(4-bromo-3-(1*H*-pyrrol-1-yl)phenyl)ethan-1-one, 9.5 mg of **Rh-6G**, 253.6 μL of 1-ethynyl-4-methylbenzene, 38.3 μL of DIPEA and 1.5 mL dry DMSO. The reaction mixture was irradiated for 3 h under N₂. Purification of the crude product was achieved by flash column chromatography using petrol ether/ethyl acetate (95:5) as eluent to yield the desired compound as yellow solid (16.2 mg, 54%).

¹H NMR (CDCl₃, 300 MHz, ppm): δ 8.52 (s, 1H), 8.07 (dd, *J* = 3.0, 1.4 Hz, 1H), 7.87 (dd, *J* = 8.2, 1.6 Hz, 1H), 7.71 (d, *J* = 8.2 Hz, 1H), 7.67 – 7.57 (m, 2H), 7.42 – 7.28 (m, 2H), 6.97 (s, 1H), 6.84 (dd, *J* = 3.9, 2.9 Hz, 1H), 6.68 (dd, *J* = 3.9, 1.2 Hz, 1H), 2.73 (s, 3H), 2.45 (s, 3H).

¹³C NMR (CDCl₃, 75 MHz, ppm): δ 197.4, 138.6, 135.7, 135.6, 135.4, 132.5, 129.5, 128.7, 128.5, 128.4, 123.7, 117.0, 114.2, 113.9, 113.5, 105.0, 27.0, 21.5.

HRMS [M⁺] C₂₁H₁₇NO calculated 299.1304 found 299.1305

1-(4-(4-Methoxyphenyl)pyrrolo[1,2-*a*]quinolin-8-yl)ethan-1-one (3g):



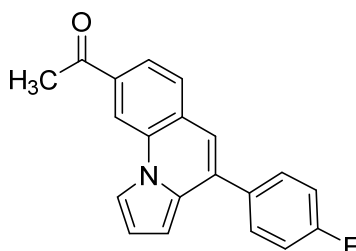
The compound was prepared according to the general procedure using 26.4 mg of 1-(4-bromo-3-(1*H*-pyrrol-1-yl)phenyl)ethan-1-one, 9.5 mg of **Rh-6G**, 259.3 μ L of 1-ethynyl-4-methoxybenzene, 38.3 μ L of DIPEA and 1.5 mL dry DMSO. The reaction mixture was irradiated for 2.5 h under N_2 . Purification of the crude product was achieved by flash column chromatography using petrol ether/ethyl acetate (95:5) as eluent to yield the desired compound as yellow solid (23.6 mg, 75%).

¹H NMR ($CDCl_3$, 300 MHz, ppm): δ 8.52 (s, 1H), 8.07 (dd, J = 2.9, 1.4 Hz, 1H), 7.88 (dd, J = 8.1, 1.6 Hz, 1H), 7.72 (d, J = 8.1 Hz, 1H), 7.69 – 7.65 (m, 2H), 7.06 – 7.01 (m, 2H), 6.96 (s, 1H), 6.84 (dd, J = 3.8, 2.9 Hz, 1H), 6.68 (dd, J = 3.9, 1.3 Hz, 1H), 3.90 (s, 3H), 2.73 (s, 3H).

¹³C NMR ($CDCl_3$, 151 MHz, ppm): δ 197.4, 160.1, 135.4, 135.3, 132.5, 131.2, 131.1, 129.7, 128.7, 128.6, 123.8, 116.8, 114.3, 114.2, 113.9, 113.5, 105.0, 55.6, 27.0

HRMS [M^+] $C_{21}H_{17}NO_2$ calculated 315.1253 found 315.1255

1-(4-(4-Fluorophenyl)pyrrolo[1,2-*a*]quinolin-8-yl)ethan-1-one (3h):



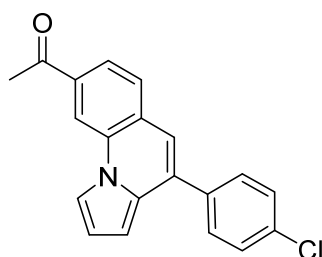
The compound was prepared according to the general procedure using 26.4 mg of 1-(4-bromo-3-(1*H*-pyrrol-1-yl)phenyl)ethan-1-one, 9.5 mg of **Rh-6G**, 229.2 μ L of 1-ethynyl-4-fluorobenzene, 38.3 μ L of DIPEA and 1.5 mL dry DMSO. The reaction mixture was irradiated for 2.5 h under N_2 . Purification of the crude product was achieved by flash column chromatography using petrol ether/ethyl acetate (95:5) as eluent to yield the desired compound as yellow solid (15.1 mg, 50%).

¹H NMR ($CDCl_3$, 300 MHz, ppm): δ 8.52 (s, 1H), 8.08 (dd, J = 3.0, 1.4 Hz, 1H), 7.88 (dd, J = 8.2, 1.6 Hz, 1H), 7.79 – 7.60 (m, 3H), 7.19 (t, J = 8.7 Hz, 2H), 6.96 (s, 1H), 6.84 (dd, J = 3.9, 2.9 Hz, 1H), 6.62 (dd, J = 3.9, 1.4 Hz, 1H), 2.73 (s, 3H).

¹³C NMR ($CDCl_3$, 75 MHz, ppm): δ 197.4, 164.7, 161.4, 135.7, 134.68, 134.63, 132.6, 130.9, 130.2, 130.1, 128.8, 128.3, 123.8, 117.3, 116.0, 115.7, 114.2, 114.1, 113.6, 104.9, 27.0.

HRMS [M^+] $C_{20}H_{14}FNO$ calculated 303.1053 found 303.1051

1-(4-(4-Chlorophenyl)pyrrolo[1,2-*a*]quinolin-8-yl)ethan-1-one (3i):



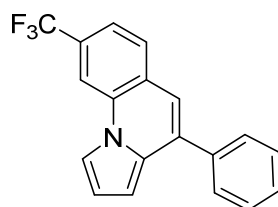
The compound was prepared according to the general procedure using 26.4 mg of 1-(4-bromo-3-(1*H*-pyrrol-1-yl)phenyl)ethan-1-one, 9.5 mg of **Rh-6G**, 273 mg of 1-chloro-4-ethynylbenzene, 38.3 μ L of DIPEA and 1.5 mL dry DMSO. The reaction mixture was irradiated for 2.5 h under N₂. Purification of the crude product was achieved by flash column chromatography using petrol ether/ethyl acetate (95:5) as eluent to yield the desired compound as yellow solid (15.9 mg, 50%).

¹H NMR (CDCl₃, 600 MHz, ppm): δ 8.53 (s, 1H), 8.08 (dd, *J* = 2.9, 1.4 Hz, 1H), 7.89 (dd, *J* = 8.1, 1.6 Hz, 1H), 7.73 (d, *J* = 8.1 Hz, 1H), 7.70 – 7.56 (m, 2H), 7.55 – 7.40 (m, 2H), 6.97 (s, 1H), 6.85 (dd, *J* = 3.9, 2.9 Hz, 1H), 6.62 (dd, *J* = 3.9, 1.4 Hz, 1H), 2.73 (s, 3H).

¹³C NMR (CDCl₃, 151 MHz, ppm): δ 197.4, 137.1, 135.8, 134.6, 134.5, 132.7, 130.7, 129.8, 129.8, 129.1, 128.9, 128.2, 123.9, 117.4, 114.3, 114.2, 113.6, 104.9, 27.0.

HRMS [*M*⁺] C₂₀H₁₄ClNO calculated 319.0758 found 319.0759

4-Phenyl-8-(trifluoromethyl)pyrrolo[1,2-*a*]quinoline (3j):



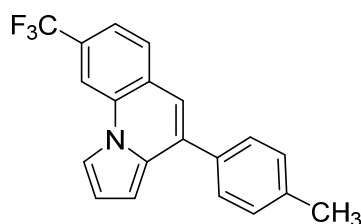
The compound was prepared according to the general procedure using 29 mg of 1-(2-bromo-5-(trifluoromethyl)phenyl)-1*H*-pyrrole, 9.5 mg of **Rh-6G**, 219.6 μ L of phenylacetylene, 38.3 μ L of DIPEA and 1.5 mL dry DMSO. The reaction mixture was irradiated for 4 h under N₂. Purification of the crude product was achieved by flash column chromatography using petrol ether as eluent to yield the desired compound as light green solid (15 mg, 52%).

¹H NMR (CDCl₃, 600 MHz, ppm): δ 8.14 (s, 1H), 7.99 (dd, *J* = 2.8, 1.2 Hz, 1H), 7.78 (d, *J* = 8.2 Hz, 1H), 7.75 – 7.62 (m, 2H), 7.59 – 7.48 (m, 4H), 7.00 (s, 1H), 6.86 (dd, *J* = 3.9, 2.9 Hz, 1H), 6.67 (dd, *J* = 3.9, 1.3 Hz, 1H).

¹³C NMR (CDCl₃, 151 MHz, ppm): δ 138.6, 135.3, 132.4, 131.1, 129.4, 129.3, 128.8, 128.7, 127.1, 125.2, 123.4, 121.6, 120.26, 120.24, 117.1, 113.8, 113.5, 111.7, 111.67, 111.64, 111.62, 104.8

HRMS [*M*⁺] C₁₉H₁₂F₃N calculated 311.0916 found 311.0907

4-(*p*-Tolyl)-8-(trifluoromethyl)pyrrolo[1,2-*a*]quinoline (3k):



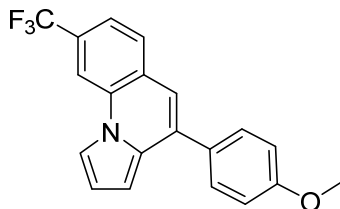
The compound was prepared according to the general procedure using 29 mg of 1-(2-bromo-5-(trifluoromethyl)phenyl)-1*H*-pyrrole, 9.5 mg of **Rh-6G**, 253.6 μ L of 1-ethynyl-4-methylbenzene, 38.3 μ L of DIPEA and 1.5 mL dry DMSO. The reaction mixture was irradiated for 4 h under N₂. Purification of the crude product was achieved by flash column chromatography using petrol ether as eluent to yield the desired compound as light green solid (18.2 mg, 56%).

¹H NMR (CDCl₃, 300 MHz, ppm): δ 8.13 (s, 1H), 7.97 (dd, *J* = 2.9, 1.4 Hz, 1H), 7.76 (d, *J* = 8.1 Hz, 1H), 7.70 – 7.59 (m, 2H), 7.59 – 7.49 (m, 1H), 7.40 – 7.27 (m, 2H), 6.98 (s, 1H), 6.85 (dd, *J* = 3.9, 2.9 Hz, 1H), 6.68 (dd, *J* = 3.9, 1.3 Hz, 1H), 2.46 (s, 3H).

¹³C NMR (CDCl₃, 75 MHz, ppm): δ 138.6, 135.7, 135.2, 132.3, 131.1, 129.5, 129.3, 128.4, 127.1, 120.24, 116.8, 113.7, 113.5, 111.6, 104.8, 21.5.

HRMS [M^+] C₂₀H₁₄F₃N calculated 325.1072 found 325.1064

4-(4-Methoxyphenyl)-8-(trifluoromethyl)pyrrolo[1,2-*a*]quinoline (3l):



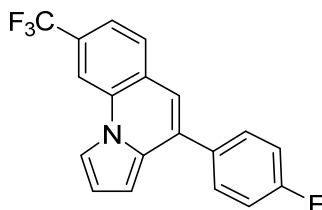
The compound was prepared according to the general procedure using 29 mg of 1-(2-bromo-5-(trifluoromethyl)phenyl)-1*H*-pyrrole, 9.5 mg of **Rh-6G**, 259.3 μL of 1-ethynyl-4-methoxybenzene, 38.3 μL of DIPEA and 1.5 mL dry DMSO. The reaction mixture was irradiated for 4 h under N₂. Purification of the crude product was achieved by flash column chromatography using petrol ether as eluent to yield the desired compound as green solid (14 mg, 41%).

¹H NMR (CDCl₃, 300 MHz, ppm): δ 8.14 (s, 1H), 7.97 (dd, *J* = 3.0, 1.3 Hz, 1H), 7.76 (d, *J* = 8.1 Hz, 1H), 7.72 – 7.62 (m, 2H), 7.54 (dd, *J* = 8.1, 1.0 Hz, 1H), 7.12 – 7.00 (m, 2H), 6.96 (s, 1H), 6.85 (dd, *J* = 3.7, 2.9 Hz, 1H), 6.68 (dd, *J* = 3.8, 1.3 Hz, 1H), 3.90 (s, 3H).

¹³C NMR (CDCl₃, 151 MHz, ppm): δ 160.1, 134.9, 132.3, 131.2, 131.0, 129.7, 129.2, 129.1, 128.8, 127.2, 127.0, 125.2, 123.4, 121.6, 120.25, 120.23, 120.21, 120.18, 116.6, 114.3, 113.5, 111.66, 111.63, 111.60, 111.57, 104.8, 55.6.

HRMS [M^+] C₂₀H₁₄F₃NO calculated 341.1020 found 341.1019

4-(4-Fluorophenyl)-8-(trifluoromethyl)pyrrolo[1,2-*a*]quinoline (3m):



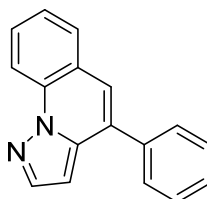
The compound was prepared according to the general procedure using 29 mg of 1-(2-bromo-5-(trifluoromethyl)phenyl)-1*H*-pyrrole, 9.5 mg of **Rh-6G**, 229.2 μL of 1-ethynyl-4-fluorobenzene, 38.3 μL of DIPEA and 1.5 mL dry DMSO. The reaction mixture was irradiated for 4 h under N₂. Purification of the crude product was achieved by flash column chromatography using petrol ether as eluent to yield the desired compound as green solid (13.5 mg, 41%).

¹H NMR (600 MHz, CDCl₃, ppm): δ 8.1 (s, 1H), 7.98 (dd, *J* = 2.8, 1.3 Hz, 1H), 7.77 (d, *J* = 8.1 Hz, 1H), 7.72 – 7.65 (m, 2H), 7.55 (dd, *J* = 8 Hz, 1H), 7.23 – 7.16 (m, 2H), 6.96 (s, 1H), 6.86 (dd, *J* = 3.7, 2.9 Hz, 1H), 6.62 (dd, *J* = 3.8, 1.2 Hz, 1H).

¹³C NMR (151 MHz, CDCl₃, ppm): δ 163.9, 162.2, 134.6, 134.5, 134.2, 132.4, 131.0, 130.2, 129.5, 129.2, 126.9, 123.3, 120.34, 120.32, 117.1, 115.9, 115.8, 113.8, 113.7, 111.7, 111.6, 104.7

HRMS [$M+H$]⁺ C₁₉H₁₁F₄N calculated 330.09 found 330.09

4-Phenylpyrazolo[1,5-*a*]quinoline (3n):



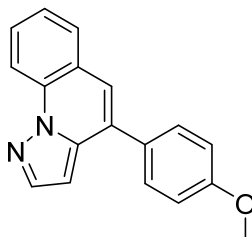
The compound was prepared according to the general procedure using 22.3 mg of 1-(2-bromophenyl)-1*H*-pyrazole, 9.5 mg of **Rh-6G**, 219.6 μ L of phenylacetylene, 38.3 μ L of DIPEA and 1.5 mL dry DMSO. The reaction mixture was irradiated for 24 h under N₂. Purification of the crude product was achieved by flash column chromatography using petrol ether : ethyl acetate (96:4) as eluent to yield the desired compound as light green solid (9.5 mg, 39%).

¹H NMR (300 MHz, CDCl₃, ppm): δ 8.60 (d, *J* = 8.4 Hz, 1H), 8.06 (d, *J* = 2.1 Hz, 1H), 7.82-7.65 (m, 4H), 7.55-7.46 (m, 4H), 7.43 (s, 1H), 6.75 (d, *J* = 2.1 Hz, 1H).

¹³C NMR (75 MHz, CDCl₃, ppm): δ 141.4, 138.4, 138.3, 134.3, 131.1, 129.4, 129.0, 128.7, 128.6, 128.3, 125.1, 123.8, 123.3, 115.7, 100.4

HRMS [*M*⁺] C₁₇H₁₂N₂ calculated 244.0995 found 244.0991

4-(4-Methoxyphenyl)pyrazolo[1,5-*a*]quinoline (3o):



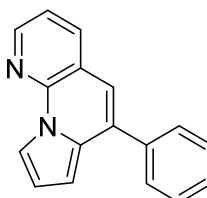
The compound was prepared according to the general procedure using 22.3 mg of 1-(2-bromophenyl)-1*H*-pyrazole, 9.5 mg of **Rh-6G**, 259.3 μ L of 1-ethynyl-4-methoxybenzene, 38.3 μ L of DIPEA and 1.5 mL dry DMSO. The reaction mixture was irradiated for 24 h under N₂. Purification of the crude product was achieved by flash column chromatography using petrol ether : ethyl acetate (96:4) as eluent to yield the desired compound as light green solid (10 mg, 35%).

¹H NMR (300 MHz, CDCl₃, ppm): δ 8.59 (d, *J* = 8.4 Hz, 1H), 8.05 (d, *J* = 2.1 Hz, 1H), 7.79 (dd, *J* = 7.9, 1.1 Hz, 1H), 7.68-7.63 (m, 3H), 7.48-7.42 (m, 1H), 7.38 (s, 1H), 7.07-7.02 (m, 2H), 6.73 (d, *J* = 2.1 Hz, 1H), 3.89 (s, 3H).

¹³C NMR (75 MHz, CDCl₃, ppm): δ 160.0, 141.4, 138.6, 134.1, 130.7, 130.7, 129.5, 129.1, 128.5, 125.1, 122.7, 115.7, 114.4, 100.3, 55.6

HRMS [*M*⁺] C₁₈H₁₄N₂O calculated 274.1100 found 274.1103

6-Phenylpyrrolo[1,2-*a*][1,8]naphthyridine (3p):



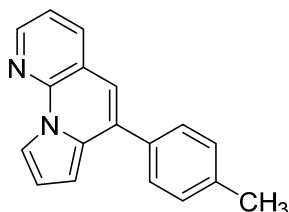
The compound was prepared according to the general procedure using 22.3 mg of 3-bromo-2-(1*H*-pyrrol-1-yl)pyridine, 9.5 mg of **Rh-6G**, 219.6 μ L of phenylacetylene, 38.3 μ L of DIPEA and 1.5 mL dry DMSO. The reaction mixture was irradiated for 16 h under N₂. Purification of the crude product was achieved by flash column chromatography using petrol ether : ethyl acetate (96:4) as eluent to yield the desired compound as yellow solid (12 mg, 49%).

¹H NMR (300 MHz, CDCl₃, ppm): δ 8.55 (dd, *J* = 4.8, 1.8 Hz, 1H), 8.44 (dd, *J* = 2.9, 1.4 Hz, 1H), 7.98 (dd, *J* = 7.7, 1.7 Hz, 1H), 7.73-7.69 (m, 2H), 7.53-7.74 (m, 3H), 7.31 (dd, *J* = 7.7, 4.7 Hz, 1H), 6.91 (s, 1H), 6.83 (dd, *J* = 3.7, 3 Hz, 1H), 6.67 (dd, *J* = 3.8, 1.5 Hz, 1H).

¹³C NMR (75 MHz, CDCl₃, ppm): δ 146.8, 144.1, 138.6, 136.3, 134.3, 128.8, 128.6, 128.5, 120.2, 119.3, 116.3, 114.5, 113.4, 105.3

HRMS [*M*⁺] C₁₇H₁₂N₂ calculated 244.0995 found 244.0999

6-(*p*-Tolyl)pyrrolo[1,2-*a*][1,8]naphthyridine (3q):



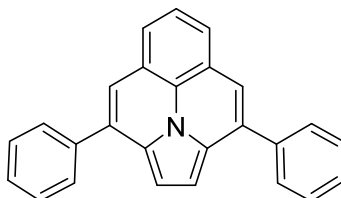
The compound was prepared according to the general procedure using 22.3 mg of 3-bromo-2-(1*H*-pyrrol-1-yl)pyridine, 9.5 mg of **Rh-6G**, 253.6 μL of 1-ethynyl-4-methylbenzene, 38.3 μL of DIPEA and 1.5 mL dry DMSO. The reaction mixture was irradiated for 16 h under N₂. Purification of the crude product was achieved by flash column chromatography using petrol ether : ethyl acetate (96:4) as eluent to yield the desired compound as yellow solid (13 mg, 50%).

¹H NMR (300 MHz, CDCl₃, ppm): δ 8.53 (dd, *J* = 4.7, 1.7 Hz, 1H), 8.43 (dd, *J* = 2.8, 1.4 Hz, 1H), 7.96 (dd, *J* = 7.8, 1.7 Hz, 1H), 7.63-7.59 (m, 2H), 7.32-7.26 (m, 3H), 6.89 (s, 1H), 6.83 (dd, *J* = 3.7, 3.0 Hz, 1H), 6.68 (dd, *J* = 3.7, 1.5 Hz, 1H), 2.45 (s, 3H).

¹³C NMR (75 MHz, CDCl₃, ppm): δ 146.7, 144.0, 138.5, 136.2, 135.7, 134.2, 131.7, 129.5, 128.4, 120.1, 119.3, 116.0, 114.4, 113.3, 105.2, 21.5

HRMS [*M*⁺] C₁₈H₁₄N₂ calculated 258.11515 found 258.11516

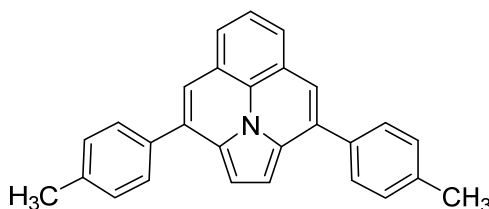
3,9-Diphenylindolizino[6,5,4,3-*ija*]quinoline (3r):⁹



¹H NMR (600 MHz, CDCl₃, ppm): δ 7.83 – 7.78 (m, 4H), 7.53 (s, 7H), 7.24 (s, 2H), 7.07 (s, 2H).

¹³C NMR (CDCl₃, 151 MHz, ppm): δ 138.9, 133.7, 132.8, 128.9, 128.5, 128.4, 127.0, 126.0, 124.0, 119.7, 119.5, 106.2.

3,9-di-*p*-Tolylindolizino[6,5,4,3-*ija*]quinoline (3s):



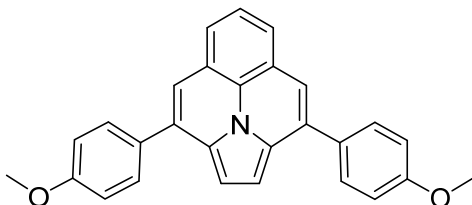
The compound was prepared according to the general procedure using 30 mg of 1-(2,6-dibromophenyl)-1*H*-pyrrole, 9.5 mg of **Rh-6G**, 253.6 μL of 1-ethynyl-4-methylbenzene, and 38.3 μL of DIPEA. The reaction mixture was irradiated for 24 h under N₂. Purification of the crude product was achieved by flash column chromatography using petrol ether as eluent to yield the desired compound as yellow solid (11.1 mg, 30%).

¹H NMR (600 MHz, CDCl₃): δ 7.72 – 7.69 (m, 4H), 7.49 – 7.45 (m, 2H), 7.42 (m, 1H), 7.35 – 7.32 (m, 4H), 7.21 (s, 2H), 7.06 (s, 2H), 2.46 (s, 6H).

¹³C NMR (CDCl₃, 151 MHz, ppm): δ 138.3, 136.0, 133.6, 132.7, 129.65, 129.6, 128.2, 127.0, 126.1, 124.0, 119.4, 119.2, 106.1, 21.5.

EI-MS [M⁺] C₂₈H₂₁N calculated 371.16685 found 371.16695.

3,9-Bis(4-methoxyphenyl)indolizino[6,5,4,3-*ija*]quinoline (3t):



The compound was prepared according to the general procedure using 30 mg of 1-(2,6-dibromophenyl)-1*H*-pyrrole, 9.5 mg of **Rh-6G**, 259.3 μL of 1-ethynyl-4-methoxybenzene, and 38.3 μL of DIPEA. The reaction mixture was irradiated for 24 h under N₂. Purification of the crude product was achieved by flash column chromatography using petrol ether as eluent to yield the desired compound as yellow solid (12.1 mg, 30%).

¹H NMR (600 MHz, CDCl₃): δ 7.75 – 7.72 (m, 4H), 7.46 – 7.70 (m, 3H), 7.39 (s, 2H), 7.07 – 7.04 (m, 6H), 3.90 (s, 6H).

¹³C NMR (CDCl₃, 151 MHz, ppm): δ 159.9, 134.2, 133.2, 132.5, 131.4, 129.5, 127.1, 126.1, 124.0, 119.3, 118.9, 114.3, 106.1, 55.6.

EI-MS [M⁺] C₂₈H₂₁NO₂ calculated 403.15668 found 403.15664.

References:

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¹H- and ¹³C NMR spectra of synthesized compounds.

