Supporting Information
for DOI: 10.1055/s-0036-1588101
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One-pot synthesis of imidazolyl isoquinolines under a Pd-catalysed C–H activation/annulation (CHAA) reaction

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1. General Information

Flash chromatography was performed on silica gel 100-200 µm. The solvent system used was a gradient of petroleum ether/ethyl acetate, increasing in polarity to ethyl acetate. Thin layer chromatography (TLC) was performed on glass backed plates pre-coated with silica (GF254), which were developed using standard visualizing agents. $^1$H and $^{13}$C NMR spectra were recorded on a 600 MHz or 400 MHz BRUKER AVANCE spectrometer at 25 °C. $^1$H: Chemical shifts are reported in ppm with the solvent resonance as the internal standard (CHCl$_3$: δ 7.26 ppm; DMSO: δ 2.50 ppm). Data are reported as follows: chemical shift, multiplicity (s = singlet, d = doublet, t = triplet, q = quartet, br = broad, m = multiplet, sept = septet), integration, coupling constants ($J$) in Hz. $^{13}$C NMR spectra were recorded with complete proton decoupling. Chemical shifts are reported in ppm with the solvent resonance as the internal standard. Low resolution mass spectra were recorded on Micromass Autospec, operating in Agilent GC-MS operating in either E.I. or C.I mode. High-resolution mass spectra (HRMS) recorded for accurate mass analysis, were performed on either a Q-TOF micro (Bruker Compass Data Analysis 4.0) spectrometer. The UV-vis and fluorescence spectra were performed on HITACHI (U-3900) and EDINBURGH (FLS 980). All the IR date were recorded by FTIR Spectrometer (Bruker Optics Tensor 27).

2. Experimental Section

2.1 Preparation of substrates

Reagents and solvents were commercially available and were used without further purification. Penylacetylene and imidazole were purchased from Heowns. Diphenylethyn were prepared via Sonogashira coupling reactions of the corresponding phenylacetylene and iodobenzene using the literature procedures. The analytical data of products are agreed with those data which have been reported
previously in the literature.

2.2 Synthesis of imidazo[2,1-a]isoquinoline and analogues

To a 10 mL microwave vial was weighed phenylacetylene (0.3 mmol), imidazol (2.0 equiv.), and K$_2$PO$_4$ (2.0 equiv.). The vial was charged with a magnetic stir bar and subsequently added NMP (1.0 mL) as the solvent. The microwave vial cap was affixed onto the vial and the reaction mixture was heated at 120 °C (300 W) for 10-120 minutes. After the first step was completed, the mixture was added with Pd(OAc)$_2$ (10% mmol), Cu(OAc)$_2$ (2 equiv.), HOAc (200 ul), dioxane (1.0 mL) and without be purified. Then the reaction mixture was heated at 120 °C (300 W) use the microwave for 5-9 hours. The reaction course was monitored by GC-MS or TLC. After the vessel was cooled down to room temperature the mixture was diluted with EtOAc (20 mL), transferred to a separatory funnel and washed with water (30 mL × 3) and Brine (45 mL × 1). The organic phase was dried over Na$_2$SO$_4$, filtered and the solvent was removed under reduced pressure to provide the crude product. The purification was performed by flash column chromatography on silica gel. The analytical data of products are agreed with those data which have been reported previously in the literature.$^{1,2}$

imidazo[2,1-a]isoquinoline (4a)

Following the general procedure, imidazo[2,1-a]isoquinoline 4a (36 mg, 72%) was isolated as a yellow solid. Mp: 69-70 °C; $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 8.63 (d, $J = 8.0$ Hz, 1H), 7.91 (d, $J = 7.0$ Hz, 1H), 7.69 (d, $J = 8.0$ Hz, 1H), 7.67-7.53 (m, 4H), 7.03 (d, $J = 7.0$ Hz, 1H); $^{13}$C NMR (101 MHz, CDCl$_3$) $\delta$ 143.2, 131.4, 129.4, 128.2, 128.2, 126.9, 124.0, 123.2, 123.1, 114.2, 113.2.; HRMS (ESI) m/z calcd for C$_{11}$H$_8$N$_2$
Following the general procedure, 9-chloroimidazo[2,1-a]isoquinoline 4b (27 mg, 45%) was isolated as a yellow solid; Mp: 70-72 °C; $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 8.60 (d, $J$ = 2.0 Hz, 1H), 7.89 (d, $J$ = 7.0 Hz, 1H), 7.60 (m, 3H), 7.49 (dd, $J$ = 9.0, 2.0 Hz, 1H), 7.00 (d, $J$ = 7.5 Hz, 1H); $^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ 142.0, 134.1, 131.8, 128.6, 128.4, 127.6, 125.0, 123.3, 122.8, 114.6, 112.5.; HRMS (ESI) m/z calcd for C$_{11}$H$_7$ClN$_2$ 202.0298; found 202.0299.

Following the general procedure, 9-fluoroimidazo[2,1-a]isoquinoline 4c (22 mg, 40%) was isolated as a yellow solid; Mp: 65-66 °C; $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 8.27 (dd, $J$ = 9.5, 2.5 Hz, 1H), 7.90 (d, $J$ = 7.5 Hz, 1H), 7.70 (dd, $J$ = 9.0, 5.5 Hz, 1H), 7.62 (s, 1H), 7.59 (s, 1H), 7.30 (td, $J$ = 9.0, 2.5 Hz, 1H), 7.04 (d, $J$ = 7.5 Hz, 1H); $^{13}$C NMR (101 MHz, CDCl$_3$) $\delta$ 162.3 (d, $J$ = 248.5 Hz), 131.7, 129.3 (d, $J$ = 8.8 Hz), 125.9 (d, $J$ = 2.1 Hz), 125.5, 122.4 (d, $J$ = 2.1 Hz), 116.9 (d, $J$ = 24.0 Hz), 114.6, 112.6, 110.8, 108.6 (d, $J$ = 23.8 Hz); HRMS (ESI) m/z calcd for C$_{11}$H$_7$FN$_2$ 186.0593; found 186.0597.
9-methylimidazo[2,1-a]isoquinoline (4d)

Following the general procedure, 9-methylimidazo[2,1-a]isoquinoline 4d (35 mg, 64%) was isolated as a yellow solid; Mp: 78-79 °C; $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 8.45 (s, 1H), 7.86 (d, $J = 7.5$ Hz, 1H), 7.55-7.61 (m, 3H), 7.39 (d, $J = 8.0$ Hz, 1H), 7.02 (d, $J = 7.5$ Hz, 1H), 2.56 (s, 3H); $^{13}$C NMR (101 MHz, CDCl$_3$) $\delta$ 138.4, 131.3, 129.7, 129.4, 127.2, 126.8, 124.0, 123.0, 122.3, 114.2, 113.0, 21.8; HRMS (ESI) m/z calcd for C$_{12}$H$_{10}$N$_2$ 182.0844; found 182.0846.

5-phenylimidazo[2,1-a]isoquinoline (4e)

Following the general procedure, 5-phenylimidazo[2,1-a]isoquinoline 4e (36 mg, 50%) was isolated as a yellow solid; Mp: 120-122 °C; $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 8.67 (d, $J = 5.5$ Hz, 1H), 7.72 (d, $J = 5.5$ Hz, 1H), 7.67-7.63 (m, 3H), 7.61-7.50 (m, 6H), 7.02 (s, 1H); $^{13}$C NMR (151 MHz, CDCl$_3$) $\delta$ 143.7, 135.9, 134.4, 131.0, 129.9, 129.7, 129.1, 128.6, 128.4, 128.0, 126.9, 123.3, 123.1, 113.1, 99.9; HRMS (ESI) m/z calcd for C$_{17}$H$_{12}$N$_2$ 244.1000; found 244.1000. IR (KBr): 3552, 2989, 2413, 1720, 1617, 1449, 1324, 766 cm$^{-1}$.

Following the general procedure, benzo[4,5]imidazo[2,1-a]isoquinoline 4f (34 mg, 52%) was isolated as a yellow solid; Mp: 111-112 °C; $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 8.83 (m, 1H), 8.16 (d, $J = 8.0$ Hz, 1H), 8.02 (d, $J = 8.5$ Hz, 1H), 7.83 (d, $J = 8.0$ Hz, 1H), 7.74 (m, 1H), 7.68 (m, 2H), 7.52 (td, $J = 7.5$, 1.0 Hz, 1H), 7.42 (td, $J = 8.0$, 1.0 Hz, 1H), 7.07 (d, $J = 7.0$ Hz, 1H); $^{13}$C NMR (101 MHz, CDCl$_3$) $\delta$ 146.3, 142.8, 130.6, 129.1, 129.0, 127.2, 126.0, 124.0, 123.7, 122.6, 120.8, 120.4, 118.9, 110.3, 108.8; HRMS (ESI) m/z calcd for C$_{15}$H$_{10}$N$_2$ 218.0844; found 218.0842.

![4g](image)

2-chlorobenzo[4,5]imidazo[2,1-a]isoquinoline (4g)

Following the general procedure, 2-chlorobenzo[4,5]imidazo[2,1-a]isoquinoline 4g (33 mg, 44%) was isolated as a yellow solid; Mp: 152-155 °C; $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 8.74 (d, $J = 2.0$ Hz, 1H), 8.05 (d, $J = 7.0$ Hz, 1H), 7.99 (d, $J = 8.0$ Hz, 1H), 7.76 (d, $J = 8.5$ Hz, 1H), 7.59 (d, $J = 8.5$ Hz, 1H), 7.51 (m, 2H), 7.39 (t, $J = 8.0$ Hz, 1H), 6.95 (d, $J = 7.0$ Hz, 1H); $^{13}$C NMR (101 MHz, CDCl$_3$) $\delta$ 145.9, 143.6, 134.1, 130.3, 129.9, 129.7, 128.4, 125.0, 124.5, 124.4 122.3, 121.5, 120.0, 110.5, 109.9; HRMS (ESI) m/z calcd for C$_{15}$H$_9^{35}$ClN$_2$ 252.0454; found 252.0455.

![4h](image)

2-fluorobenzo[4,5]imidazo[2,1-a]isoquinoline (4h)
Following the general procedure, 2-fluorobenzo[4,5]imidazo[2,1-a]isoquinoline 4h (24 mg, 35%) was isolated as a brown solid; Mp: 172-174 °C; $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 8.47 (dd, $J$ = 9.5, 2.5 Hz, 1H), 8.15 (d, $J$ = 7.5 Hz, 1H), 8.02 (d, $J$ = 8.5 Hz, 1H), 7.85 (d, $J$ = 8.0 Hz, 1H), 7.75 (dd, $J$ = 8.5, 5.5 Hz, 1H), 7.53 (t, $J$ = 8.0 Hz, 1H), 7.47–7.37 (m, 2H), 7.07 (d, $J$ = 7.5 Hz, 1H); $^{13}$C NMR (101 MHz, CDCl$_3$) $\delta$ 162.2 (d, $J$ = 249.0 Hz), 143.6 (s), 129.4 (d, $J$ = 8.5 Hz), 128.1, 128.1, 125.1 (d, $J$ = 9.5 Hz), 125.0, 122.3, 120.7 (d, $J$ = 2.5 Hz), 120.0, 118.7 (d, $J$ = 24.0 Hz), 110.8, 110.8, 110.5 (d, $J$ = 24.0 Hz), 110.0; HRMS (ESI) m/z calcd for C$_{15}$H$_9$FN$_2$ 236.0750; found 236.0751.

2,9,10-trimethylbenzo[4,5]imidazo[2,1-a]isoquinoline (4i)

Following the general procedure, 2,9,10-trimethylbenzo[4,5]imidazo[2,1-a]isoquinoline 4i (30.5 mg, 39%) was isolated as a yellow solid; Mp: 197-199 °C; $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 8.59 (s, 1H), 8.00 (d, $J$ = 7.0 Hz, 1H), 7.74 (s, 1H), 7.60 (d, $J$ = 8.0 Hz, 1H), 7.53 (s, 1H), 7.45 (d, $J$ = 8.0 Hz, 1H), 6.96 (d, $J$ = 7.5 Hz, 1H), 2.57 (s, 3H), 2.45 (s, 6H); $^{13}$C NMR (101 MHz, CDCl$_3$) $\delta$ 146.7, 142.4, 138.3, 133.7, 131.1, 129.1, 128.6, 126.9, 124.5, 123.7, 120.6, 119.7, 110.8, 109.9, 21.6, 20.70, 20.68; HRMS (ESI) m/z calcd for C$_{18}$H$_{16}$N$_2$ 260.1313; found 260.1314. IR (KBr): 3020, 2920, 2853, 1732, 1518, 1458, 1363, 1003, 824 cm$^{-1}$.

Following the general procedure, 2-methoxybenzo[4,5]imidazo[2,1-a]isoquinoline 4j (33 mg, 45%) was isolated as a white solid; Mp: 124-125 °C; $^1$H NMR (400 MHz, CDCl$_3$) δ 8.19 (d, $J = 2.5$ Hz, 1H), 8.09 (d, $J = 7.5$ Hz, 1H), 8.03 (d, $J = 8.0$ Hz, 1H), 7.84 (d, $J = 8.0$ Hz, 1H), 7.67 (d, $J = 8.5$ Hz, 1H), 7.52 (td, $J = 8.0$, 1.5 Hz, 1H), 7.41 (td, $J = 8.0$, 1.5 Hz, 1H), 7.28 (dd, $J = 9.0$, 3.0 Hz, 1H), 7.04 (d, $J = 7.5$ Hz, 1H), 4.04 (s, 3H); $^{13}$C NMR (101 MHz, CDCl$_3$) δ 159.7, 147.2, 143.8, 130.2, 128.7, 125.7, 124.9, 124.7, 121.8, 120.8, 119.8, 119.2, 111.2, 110.0, 105.1, 55.9; HRMS (ESI) m/z calcd for C$_{16}$H$_{12}$N$_2$O 248.0950; found 248.0953.

![Diagram of 4j](image)

6-phenylbenzo[4,5]imidazo[2,1-a]isoquinoline (4k)

Following the general procedure, 6-phenylbenzo[4,5]imidazo[2,1-a]isoquinoline 4k (35 mg, 40%) was isolated as a yellow solid; Mp: 171-173 °C; $^1$H NMR (400 MHz, CDCl$_3$) δ 8.89 (m, 1H), 7.99 (d, $J = 8.0$ Hz, 1H), 7.77-7.54 (m, 8H), 7.40 (td, $J = 8.0$, 1.0 Hz, 1H), 7.00 (td, $J = 8.0$, 1.0 Hz, 1H), 6.91 (s, 1H), 6.49 (d, $J = 9.0$ Hz, 1H); $^{13}$C NMR (101 MHz, CDCl$_3$) δ 148.3, 144.3, 137.5, 134.7, 131.6, 130.7, 130.1, 129.7, 129.4, 129.0, 127.9, 126.7, 125.1, 124.2, 122.9, 121.3, 119.7, 114.1, 112.6; HRMS (ESI) m/z calcd for C$_{21}$H$_{14}$N$_2$ 294.1157; found 294.1158. IR (KBr): 3552, 3235, 2027, 1617, 1527, 1394, 1311, 1274, 878 cm$^{-1}$.

2.3 General procedure for the synthesis of imidazoyl isoquinolium salts 5 (a-j)$^3$
Freshly made imidazo[2,1-a]isoquinoline and analogues 4 (0.2 mmol) was dissolved in toluene (1 ml) and the electrophilic agent R-X (10-20 equiv.)\textsuperscript{*1} was added. The reaction was stirred 24 hours under reflux. The final product precipitates from the solution and is recovered by filtration. The residue was washed extensively with diethyl ether and dried to yield the corresponding imidazolyl isoquinolium salts framework 5 (a-j).

\textsuperscript{*1} The quantity of electrophilic reactive added in excess depends on the its physical properties: 20 equivalents were used with inexpensive liquid with low boiling point.

\begin{center}
\includegraphics[width=0.2\textwidth]{5a.png}
\end{center}

1-methyl-1H-imidazo[2,1-a]isoquinolin-4-ium iodide (5a)

Following the general procedure, 1-methyl-1H-imidazo[2,1-a]isoquinolin-4-ium iodide 5a (44 mg, 71%) as a white solid; Mp: 251-254 °C; \textsuperscript{1}H NMR (400 MHz, DMSO) δ 8.79 (d, \( J = 8.0 \) Hz, 1H), 8.67 (d, \( J = 7.5 \) Hz, 1H), 8.45 (d, \( J = 2.0 \) Hz, 1H), 8.26 (d, \( J = 2.0 \) Hz, 1H), 8.24 (d, \( J = 8.0 \) Hz, 1H), 8.00 (m, 2H), 7.90 (d, \( J = 7.2 \) Hz, 1H), 4.48 (s, 3H); \textsuperscript{13}C NMR (101 MHz, DMSO) δ 136.9, 132.4, 132.2, 130.2, 129.0, 127.5, 125.1, 124.8, 118.4, 117.9, 116.5, 39.1; HRMS (ESI) m/z caled for C_{12}H_{11}N_{2} (M-I) 183.0922; found 183.0924. IR (KBr): 3549, 3236, 2024, 1618, 1548, 1483, 1455, 803, 746 cm\textsuperscript{-1}. 

\textsuperscript{1}
1-butyl-1H-imidazo[2,1-a]isoquinolin-4-ium iodide (5b)

Following the general procedure, 1-butyl-1H-imidazo[2,1-a]isoquinolin-4-ium iodide 5b (46 mg, 65%) was isolated as a yellow solid; Mp: 138-141 °C; $^1$H NMR (400 MHz, DMSO) $\delta$ 8.67 (d, $J = 7.0$ Hz, 1H), 8.64 (dd, $J = 7.5$, 2.0 Hz, 1H), 8.49 (d, $J = 2.0$ Hz, 1H), 8.31 (d, $J = 2.0$ Hz, 1H), 8.27-8.22 (m, 1H), 8.06-7.96 (m, 2H), 7.91 (d, $J = 7.5$ Hz, 1H), 4.87 (t, $J = 7.5$ Hz, 2H), 2.04-1.85 (m, 2H), 1.46 (m, 2H), 0.95 (t, $J = 7.5$ Hz, 3H); $^{13}$C NMR (101 MHz, DMSO) $\delta$ 136.2, 132.7, 132.2, 130.5, 129.3, 126.8, 125.3, 124.4, 118.1, 117.9, 116.93, 50.60, 31.11, 19.47, 14.01; HRMS (ESI) $m/z$ calcd for C$_{15}$H$_{17}$IN$_2$ (M-I) 225.1392; found 225.1392. IR (KBr): 3550, 3065, 2953, 1726, 1545, 1521, 1214, 1070, 815 cm$^{-1}$.

1-benzyl-1H-imidazo[2,1-a]isoquinolin-4-ium bromide (5c)

Following the general procedure, 1-benzyl-1H-imidazo[2,1-a]isoquinolin-4-ium bromide 5c (68 mg, 88%) was isolated as a white solid; Mp: 245-247 °C; $^1$H NMR (600 MHz, DMSO) $\delta$ 8.78 (d, $J = 7.5$ Hz, 1H), 8.63 (s, 1H), 8.43 (d, $J = 8.5$ Hz, 1H), 8.38 (s, 1H), 8.22 (d, $J = 8.0$ Hz, 1H), 7.95 (m, 2H), 7.81 (t, $J = 8.0$ Hz, 1H), 7.40 (t, $J = 7.5$ Hz, 2H), 7.34 (t, $J = 7.5$ Hz, 1H), 7.29 (d, $J = 7.5$ Hz, 2H), 6.22 (s, 2H); $^{13}$C NMR (151 MHz, DMSO) $\delta$ 136.3, 134.2, 132.3, 131.9, 129.7, 129.1, 128.6, 128.2, 126.8, 126.4, 125.0, 124.0, 117.9, 117.1, 117.0, 53.1; HRMS (ESI) $m/z$ calcd for
C_{16}H_{15}BrN_{2} (M-Br) 259.1235; found 259.1236. IR (KBr): 3551, 3148, 3065, 1617, 1546, 1463, 1359, 1181, 806 cm\(^{-1}\).

![Diagram 5d]


Following the general procedure, 12-methyl-12H-benzo[4,5]imidazo[2,1-a]isoquinolin-7-ium iodide 5d (60 mg, 83%) was isolated as a white solid; Mp: 280-283 °C; \(^1\)H NMR (400 MHz, DMSO) \(\delta\) 9.34 (d, \(J = 7.5\) Hz, 1H), 9.10 (d, \(J = 8.5\) Hz, 1H), 8.69 (d, \(J = 8.5\) Hz, 1H), 8.35 (m, 2H), 8.16 (t, \(J = 8.0\) Hz, 1H), 8.11-8.02 (m, 2H), 7.93 (t, \(J = 8.5\) Hz, 1H), 7.84 (t, \(J = 8.5\) Hz, 1H), 4.65 (s, 3H); \(^{13}\)C NMR (101 MHz, DMSO) \(\delta\) 141.5, 134.9, 133.9, 133.6, 130.3, 129.2, 129.0, 127.1, 126.7, 126.2, 123.3, 118.12, 117.2, 113.9, 113.4, 35.4; HRMS (ESI) \(m/z\) calcd for C_{16}H_{13}IN_{2}(M-I) 233.1079; found 233.1078. IR (KBr): 3549, 3018, 1617, 1528, 1478, 1419, 1252, 1001, 755 cm\(^{-1}\).

![Diagram 5e]


Following the general procedure, 12-butyl-12H-benzo[4,5]imidazo[2,1-a]isoquinolin-7-ium iodide 5e (50 mg, 62%) was isolated as a white solid; Mp: 252-254°C; \(^1\)H NMR (400 MHz, DMSO) \(\delta\) 9.35 (d, \(J = 7.5\) Hz, 1H), 8.87 (d, \(J = 8.5\) Hz, 1H), 8.70 (d, \(J = 8.5\) Hz, 1H), 8.35 (m, 2H), 8.20-8.04 (m, 3H), 7.92 (t, \(J = 7.5\) Hz, 1H), 7.84 (t, \(J = 8.0\) Hz, 1H), 5.16 (t, \(J = 7.5\) Hz, 2H), 2.01 (dt, \(J = 15.0, 7.5\) Hz, 2H), 1.55 (dq, \(J = 15.0, 7.5\) Hz, 2H), 0.95 (t, \(J = 7.3\) Hz,
$^{13}$C NMR (101 MHz, DMSO) δ 140.6, 135.1, 133.8, 133.4, 130.8, 129.5, 129.1, 127.3, 126.3, 126.0, 123.6, 117.7, 117.3, 114.0, 113.5, 46.9, 31.1, 19.8, 14.2; HRMS (ESI) m/z calcd for C$_{21}$H$_{19}$IN$_2$ (M−I) 275.1548; found 275.1550.

IR (KBr): 3550, 3037, 1920, 1617, 1526, 1472, 1455, 1367, 750 cm$^{-1}$.

12-benzyl-12H-benzo[4,5]imidazo[2,1-a]isoquinolin-7-ium iodide (5f)

Following the general procedure, 12-benzyl-12H-benzo[4,5]imidazo[2,1-a]isoquinolin-7-ium iodide 5f, (75 mg, 87%) was isolated as a white solid; Mp: 253-255 °C; $^1$H NMR (400 MHz, DMSO) δ 9.44 (d, $J = 7.5$ Hz, 1H), 8.77 (dd, $J = 7.5$ Hz, 1H), 8.61 (d, $J = 8.5$ Hz, 1H), 8.33 (d, $J = 8.0$ Hz, 1H), 8.27 (dd, $J = 8.0$ Hz, $J = 2.0$ Hz, 1H), 8.16 (d, $J = 7.5$ Hz, 1H), 8.08 (t, $J = 8.0$ Hz, 1H), 7.93-7.83 (m, 3H), 7.44-7.30 (m, 5H), 6.48 (s, 2H); $^{13}$C NMR (101 MHz, DMSO) δ 141.4, 135.3, 134.6, 134.0, 133.8, 130.4, 129.6, 129.4, 129.3, 128.6, 127.6, 126.6, 126.5, 125.9, 123.8, 117.6, 117.3, 114.2, 113.3, 50.

HRMS (ESI) m/z calcd for C$_{22}$H$_{17}$IN$_2$Br (M−Br) 309.1386; found 309.1387.

IR (KBr): 3550, 3413, 2995, 1617, 1525, 1472, 1327, 803, 752 cm$^{-1}$.

2,12-dimethyl-12H-benzo[4,5]imidazo[2,1-a]isoquinolin-7-ium iodide (5g)

Following the general procedure, 2,12-dimethyl-12H-benzo[4,5]imidazo
[2,1-a]isoquinolin-7-ium iodide 5g, (59 mg, 80%) was isolated as a white solid; Mp: 287-290 °C; $^1$H NMR (400 MHz, DMSO) δ 9.27 (d, $J = 7.5$ Hz, 1H), 8.84 (s, 1H), 8.67 (d, $J = 8.5$ Hz, 1H), 8.35 (d, $J = 8.5$ Hz, 1H), 8.22 (d, $J = 8.5$ Hz, 1H), 8.03 (d, $J = 7.0$ Hz, 1H), 7.98 (d, $J = 8.0$ Hz, 1H), 7.91 (t, $J = 7.5$ Hz, 1H), 7.82 (t, $J = 7.5$ Hz, 1H), 4.66 (s, 3H), 2.71 (s, 3H); $^{13}$C NMR (101 MHz, DMSO) δ 141.2, 140.7, 135.4, 133.6, 132.8, 129.0, 128.9, 127.1, 126.1, 125.6, 122.5, 118.2, 117.1, 113.9, 113.4, 35.5, 22.0; HRMS (ESI) $m/z$ calcld for C$_{17}$H$_{15}$IN$_2$ (M-I) 247.1235; found 247.1235. IR (KBr): 3550, 3413, 3019, 1619, 1532, 1500, 1448, 1035, 770 cm$^{-1}$.

![5h](image)

**2-chloro-12-methyl-12H-benzo[4,5]imidazo[2,1-a]isoquinolin-7-ium iodide (5h)**

Following the general procedure, 2-chloro-12-methyl-12H-benzo[4,5]imidazo[2,1-a]isoquinolin-7-ium iodide 5h, (55 mg, 70%) was isolated as a white solid; Mp: 238-241 °C; $^1$H NMR (400 MHz, DMSO) δ 9.38 (d, $J = 6.5$ Hz, 1H), 9.00 (s, 1H), 8.70 (d, $J = 8.0$ Hz, 1H), 8.38 (t, $J = 8.0$ Hz, 2H), 8.22 (d, $J = 8.0$ Hz, 1H), 8.12 (d, $J = 6.0$ Hz, 1H), 7.94 (t, $J = 7.0$ Hz, 1H), 7.87 (t, $J = 7.0$ Hz, 1H), 4.68 (s, 3H); $^{13}$C NMR (101 MHz, DMSO) δ 140.5, 134.9, 134.1,133.6, 133.5, 131.2, 129.3, 127.0, 126.5, 125.5, 123.9, 119.3, 116.7, 114.0, 113.6, 35.2; HRMS (ESI) $m/z$ calcld for C$_{16}$H$_{12}$ClIN$_2$ (M-I) 267.0689; found 267.0688. IR (KBr): 3529, 3030, 1950, 1534, 1446, 1413, 1318, 879, 764 cm$^{-1}$.

![5i](image)
2-fluoro-12-methyl-12H-benzo[4,5]imidazo[2,1-a]isoquinolin-7-ium iodide (5i)

Following the general procedure, 2-fluoro-12-methyl-12H-benzo[4,5]imidazo[2,1-a]isoquinolin-7-ium iodide 5i, (56 mg, 75%) was isolated as a yellow solid; Mp: 255-259 °C; \(^{1}H\) NMR (400 MHz, DMSO) \(\delta\) 9.35 (d, \(J = 7.5 \text{ Hz, 1H}\)), 8.84 (dd, \(J = 10.5, 2.5 \text{ Hz, 1H}\)), 8.70 (d, \(J = 8.0 \text{ Hz, 1H}\)), 8.44 (dd, \(J = 9.0, 6.0 \text{ Hz, 1H}\)), 8.38 (d, \(J = 8.5 \text{ Hz, 1H}\)), 8.16-8.06 (m, 2H), 7.94 (t, \(J = 8.0 \text{ Hz, 1H}\)), 7.85 (t, \(J = 7.5 \text{ Hz, 1H}\)), 4.66 (s, 3H); \(^{13}C\) NMR (101 MHz, DMSO) \(\delta\) 162.1 (d, \(J = 248.5 \text{ Hz}\)), 140.8 (d, \(J = 4.5 \text{ Hz}\)), 133.6, 132.2 (d, \(J = 9.5 \text{ Hz}\)), 131.8, 129.2, 127.0, 126.4, 122.96 (d, \(J = 23.7 \text{ Hz}\)), 122.92 (d, \(J = 2.5 \text{ Hz}\)), 119.3 (d, \(J = 10.5 \text{ Hz}\)), 116.7, 114.0, 113.5, 112.1 (d, \(J = 26.0 \text{ Hz}\)), 35.1; HRMS (ESI) \(m/z\) calcd for C\(_{16}\)H\(_{12}\)FIN\(_{2}\) (M-I) 251.0985; found 251.0986.

IR (KBr): 3013, 1648, 1620, 1503, 1412, 1287, 1036, 714 cm\(^{-1}\).

References:


UV-vis and Fluorescence spectra

The UV-vis spectra were performed on a spectrofluorimeter, and the fluorescent measurement was carried out on a fluorescent spectrofluorimeter. All the compounds were with a concentration of 10 \(\mu\) M in methanol. The liquid samples are measured in standard (10mm x 10mm) quartz cuvettes. Need 2 identical cuvettes, one containing the sample, the other containing the solvent only. Before measured the quantum yields, make sure that all the compounds were with an optical density of 0.1 at the excitation wavelength.
UV spectra of imidazolyl isoquinolines

Fluorescence spectra of imidazolyl isoquinolines
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<th>Compound</th>
<th>$\lambda_{\text{abs}}$ (nm)</th>
<th>$\lambda_{\text{em}}$ (nm)</th>
<th>Stokes shift (nm)</th>
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$^1\text{H}$ and $^{13}\text{C}$ NMR Spectra