Catalytic oxidative dehydrogenation of N-heterocycles with nitrogen/phosphorus co-doped porous carbon materials

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Abstract: A metal-free oxidative dehydrogenation of N-heterocycles utilizing a nitrogen/phosphorus co-doped porous carbon (NPCH) catalyst is reported. The optimal material is robust against traditional poisoning agents and shows high antioxidant resistance. It exhibits good catalytic performance for the synthesis of various quinoline, indole, isoquinoline, and quinoxaline ‘on-water’ under air atmosphere. The active sites in the NPCH catalyst are proposed to be phosphorus and nitrogen centers within the porous carbon network.
1. General experimental details

All chemicals such as 2-methylimidazole (2-Melm), Zn(NO$_3$)$_2$.6H$_2$O, benzylamine, triphenylphosphine and 1,2,3,4-tetrahydroquinoline were purchased from commercial suppliers and used directly without further purification.

$^1$H NMR and $^{13}$C NMR spectra were recorded on Bruker 300/400 and Bruker AV500M spectrometer. GC-MS was performed on an ISQ Trace 1300 in the electron ionization (EI) mode. GC analyses are performed on an Agilent 7890A instrument (Column: Agilent 19091J-413: 30 m × 320 μm × 0.25 μm, carrier gas: H$_2$, FID detection. XRD analysis was performed on Shimadzu X-ray diffractometer (XRD-6000) with Cu Ka irradiation. Transmission electron microscopy (TEM) images were taken using a PHILIPS Tecnai 12 microscope operating at 120 kv. Scanning electron microscopy (SEM) images were performed using a Hitachi S-4800 apparatus on a sample powder previously dried and sputter-coated with a thin layer of gold. X-ray photoelectron spectroscopy (XPS) was performed on an ESCALAB 250Xi spectrometer, using an Al Ka X-ray source (1350 eV of photons) and calibrated by setting the C 1s peak to 284.80 eV. Inductively coupled plasma mass spectrometry (ICP-OES) was analyzed on Varian (Agilent) 715-ES ICP-Emission-Spectrometer. BET surface area and pore size measurements were performed with N$_2$ adsorption/desorption isotherms at 77 K on a Micromeritics ASAP 2020 instrument. Before measurements, the samples were degassed at 150°C for 12 h.

2. Procedure for the preparation of catalysts

Synthesis of ZIF-8-Bn, ZIF-8-BnP and ZIF-8

ZIF-8-Bn was synthesized with the following steps. Typically, 8 mmol Zn(NO$_3$)$_2$.6H$_2$O was added to 80 mL H$_2$O under ultrasonic. Meanwhile, 32 mmol 2-Melm and 32 mmol benzylamine were added to 80 mL H$_2$O by sonication for 10 min. The obtained salt solution was added to the above 2-Melm solution under vigorous stirring at room temperature for 4 h. The obtained sample was centrifuged and washed with methanol. The final product was dried under vacuum at 80°C for 12 h. The same procedure was used for the synthesis of ZIF-8 except that no benzylamine was used. Mix ZIF-8-Bn (1 g) and PPh$_3$ uniformly through grinding to synthesize ZIF-8-BnP. Accordingly, the catalysts with different P loadings were prepared in same procedure with only changing of the added amount of PPh$_3$ (e.g. ZIF-8-BnP150, ZIF-8-BnP300, ZIF-8-BnP450).

Synthesis of lignin

First place 10 g of wood chips in the pressure tube. Then, 100 mL of 1, 4-dioxane and 8 mL of 2M HCl aqueous solution were added and stirred at 120°C for 12 h to obtain a brown solid-liquid mixture. The mixture was filtered to remove solid, and the obtained filtrate was concentrated by decompresion distillation to afford a viscous liquid. A large amount of brown solids were precipitated out when deionized water was poured into the viscous liquid. The brown solid was collected and dried overnight at 80°C to produce the final organosolv lignin.

Synthesis of NC, NC-Bn, NPC-X, C-L(lignin), and NPCH

The pyrolysis of ZIF-8-BnP (ZIF-8-BnP150, ZIF-8-BnP300, ZIF-8-BnP450) was carried out in a tubular furnace under a nitrogen atmosphere. The sample was heated from room temperature to 900°C at a heating rate of 5 °C/min and kept at this temperature for 2 h. The resulting catalyst was denoted as NPC-150, NPC-300, and NPC-450. The NC, NC-Bn, and C-L(lignin) were prepared by a similar method using, ZIF-8, ZIF-8-Bn and lignin instead of ZIF-8-BnP, respectively. The obtained sample (NPC-300) was then treated with 2M of HCl to remove the zinc species. The residual was completely washed with distilled water and ethanol before drying in an oven at 80°C overnight, obtaining the final N,P co-doped carbon, which was designated as NPCH.
3. Catalytic tests

Catalytic reactions

Typically, NPCH (5 mg) was placed in a 25 mL sealed tube, and 1.2.3.4-tetrahydroquinoline (0.2 mmol) and H₂O (1.5 mL) were added to the mixture under atmospheric air with a magnetic to initiate the reaction at 120°C for 12 h. After reaction, the mixture was extracted with ethyl acetate and the product were analyzed by GC/MS (ISQ Trace 1300). The conversion and yield were determined by GC (Agilent 7890A) with hexadecane as an internal standard. The corresponding product was purified by column chromatography.

Gram scale reactions and catalyst recycling

To a Teflon or glass fitted 300 mL autoclave, the magnetic stirring bar, and corresponding substrates (20 mmol) were transferred and then 100 mL of H₂O was added. Then after, the required amount of catalyst (NPCH; 200 mg) was added. The autoclave was pressurized with 20 bar air. The autoclave was placed into an aluminum block preheated at 100°C and the reaction was stirred for 12 h. After completion of the reaction, the autoclave was cooled to room temperature. The remaining air was discharged, and the products were removed from the autoclave. The mixture was extracted with ethyl acetate and the catalyst was isolated from the solution by centrifugation. The yield of the product was determined by GC (Agilent 7890A) with hexadecane as an internal standard. After each cycle, the catalyst was isolated from the solution by centrifugation, washed three times with methanol, and dried under vacuum to remove the residual solvent and then reused for another reaction cycle.

4. Supplementary figures and tables

Fig. S1 XRD patterns (A) Simulated ZIF-8, as-synthesized ZIF-8 and ZIF-8-Bn; (B) NPC-300 and NPCH; * NPCH is the catalyst after six cycles.

Fig. S2 Raman spectra of NC, NC-Bn, NPC-300, and NPCH.
Fig. S3 Nitrogen adsorption–desorption isotherms and the pore size distributions of NC, NC-Bn, NPC-300, and NPCH.

Fig. S4 XPS survey spectrum of NPC-300 and NPCH.

Fig. S5 Digital photos of catalyst dispersed in water.

Fig. S6 The characterization of the NPCH catalyst after six runs. (A) $N_2$ adsorption-desorption isotherms; (B) The pore size distributions; (C) Raman spectra; (D) TEM image.
Fig. S7 The particle size distribution of NPC-300 and NPCH.

Scheme S1. Mechanistic investigations.

Scheme S2. The proposed reaction mechanism.

Table S1. ICP-OES analysis of NPC-300 and NPCH.

| Catalysts | P mg/kg | Zn mg/kg |
|-----------|---------|----------|
|           |         |          |
| Catalysts | BET Surface area (m²/g) | Pore volume (cm³/g) | Mean pore size (nm) |
|-----------|----------------------|-------------------|-------------------|
| NC        | 572                  | 0.26              | 3.52              |
| NC-Bn     | 1046                 | 0.72              | 3.39              |
| NPC-300   | 1017                 | 0.72              | 3.25              |
| NPCH      | 829                  | 0.68              | 3.16              |
| NPCH⁶      | 662                  | 0.50              | 2.95              |

⁶ NPCH is the catalyst after six cycles.

| Catalysts | C [at%] | N [at%] | O [at%] | P [at%] | Zn [at%] |
|-----------|---------|---------|---------|---------|----------|
| NPC-300   | 90.88   | 3.43    | 4.68    | 0.65    | 0.36     |
| NPCH      | 91.52   | 2.88    | 5.13    | 0.35    | 0.12     |

5. NMR data

**Quinoline (2a)**

\[^1\text{H} \text{NMR}\] (300 MHz, Chloroform-d) δ 8.90 (dd, J = 4.2, 1.7 Hz, 1H), 8.18 – 8.08 (m, 2H), 7.79 (dd, J = 8.3, 1.5 Hz, 1H), 7.70 (ddd, J = 8.5, 6.9, 1.5 Hz, 1H), 7.52 (ddd, J = 8.1, 6.9, 1.2 Hz, 1H), 7.37 (dd, J = 8.3, 4.2 Hz, 1H). \[^{13}\text{C} \text{NMR}\] (75 MHz, Chloroform-d) δ 150.37, 148.22, 136.13, 129.50, 129.41, 128.29, 127.80, 126.57, 121.08.

**Quinaldine (2b)**

\[^1\text{H} \text{NMR}\] (300 MHz, Chloroform-d) δ 8.07 – 7.99 (m, 2H), 7.80 – 7.73 (m, 1H), 7.68 (ddd, J = 8.4, 6.9, 1.5 Hz, 1H), 7.47 (ddd, J = 8.1, 6.9, 1.2 Hz, 1H), 7.27 (d, J = 8.4 Hz, 1H), 2.75 (s, 3H). \[^{13}\text{C} \text{NMR}\] (75 MHz, Chloroform-d) δ 158.97, 147.82, 136.20, 129.44, 128.59, 127.49, 126.48, 125.68, 122.00, 25.36.

**3-Methylquinoline (2c)**

\[^1\text{H} \text{NMR}\] (300 MHz, DMSO-d6) δ 8.77 (d, J = 2.2 Hz, 1H), 8.10 (d, J = 1.1 Hz, 1H), 7.99 (d, J = 8.4 Hz, 1H), 7.88 (d, J = 6.8 Hz, 1H), 7.68 (ddd, J = 8.4, 6.9, 1.6 Hz, 1H), 7.56 (ddd, J = 8.1, 6.9, 1.3 Hz, 1H), 2.47 (s, 3H). \[^{13}\text{C} \text{NMR}\] (75 MHz, DMSO-d6) δ 152.80, 146.49, 134.78, 131.02, 129.13, 128.91, 128.19, 127.84, 127.01, 18.66.

**4-Methylquinoline (2d)**

\[^1\text{H} \text{NMR}\] (500 MHz, DMSO-d6) δ 8.71 (d, J = 4.4 Hz, 1H), 7.99 (d, J = 9.7 Hz 2H), 7.69 (t, J = 7.6 Hz, 1H), 7.55 (t, J = 8.3 Hz, 1H), 7.27 (d, J = 4.4 Hz, 1H), 2.58 (s, 3H). \[^{13}\text{C} \text{NMR}\] (126 MHz, DMSO-d6) δ 150.60, 148.01, 144.42, 129.96, 129.57, 128.22, 126.75, 124.64, 122.37, 18.50.

**6-Methoxyquinoline (2e)**

\[^{13}\text{C} \text{NMR}\] (DMSO-d6) δ 150.60, 148.01, 144.42, 129.96, 129.57, 128.22, 126.75, 124.64, 122.37, 18.50.
1H NMR (300 MHz, Chloroform-d) δ 8.75 (dd, J = 4.3, 1.7 Hz, 1H), 8.08 – 7.97 (m, 2H), 7.40 – 7.32 (m, 2H), 7.06 (d, J = 2.8 Hz, 1H), 3.92 (s, 3H). 13C NMR (75 MHz, Chloroform-d) δ 157.81, 147.71, 144.15, 135.04, 130.63, 129.35, 122.45, 121.37, 105.13, 55.55.

8-Methylquinoline (2f)

1H NMR (500 MHz, DMSO-d6) δ 8.88 (dd, J = 4.2, 1.9 Hz, 1H), 8.25 (dd, J = 8.3, 1.8 Hz, 1H), 7.73 (d, J = 8.2 Hz, 1H), 7.54 (d, J = 7.0 Hz, 1H), 7.48 – 7.39 (m, 2H), 2.68 (s, 3H). 13C NMR (126 MHz, DMSO-d6) δ 149.91, 147.17, 136.85, 136.66, 129.85, 128.31, 126.57, 126.46, 121.65, 18.14.

7-Methylquinoline (2g)

1H NMR (300 MHz, DMSO-d6) δ 8.85 (d, J = 2.5 Hz, 1H), 8.30 (d, J = 8.8 Hz, 1H), 7.89 – 7.81 (m, 2H), 7.45 (dd, J = 8.2, 4.1 Hz, 2H), 2.52 (s, 3H). 13C NMR (75 MHz, DMSO-d6) δ 150.91, 148.44, 139.79, 136.11, 129.14, 128.27, 128.20, 126.43, 121.11, 21.84.

6-Fluoroquinoline (2i)

1H NMR (300 MHz, DMSO-d6) δ 8.90 (dd, J = 4.2, 1.7 Hz, 1H), 8.36 (ddd, J = 8.4, 1.8, 0.8 Hz, 1H), 8.09 (dd, J = 9.2, 5.5 Hz, 1H), 7.79 (dd, J = 8.5, 2.9 Hz, 1H), 7.74 – 7.52 (m, 2H). 13C NMR (75 MHz, DMSO-d6) δ 161.69, 150.52, 150.48, 145.39, 136.09, 136.02, 132.31, 132.18, 129.13, 128.99, 122.65, 120.21, 119.87, 111.64, 111.35.

6-Chloroquinoline (2j)

1H NMR (500 MHz, DMSO-d6) δ 8.92 (dd, J = 4.2, 1.8 Hz, 1H), 8.34 (d, J = 7.6 Hz, 1H), 8.10 (d, J = 2.4 Hz, 1H), 8.03 (d, J = 8.9 Hz, 1H), 7.75 (dd, J = 9.0, 2.4 Hz, 1H), 7.58 (dd, J = 8.4, 4.2 Hz, 1H). 13C NMR (126 MHz, DMSO-d6) δ 151.51, 146.56, 135.85, 131.50, 131.36, 130.49, 129.12, 127.20, 122.86.

5-Bromoquinoline (2k)

1H NMR (300 MHz, DMSO-d6) δ 8.98 (dd, J = 4.2, 1.6 Hz, 1H), 8.48 (dd, J = 8.5, 1.7, 0.9 Hz, 1H), 8.07 (dt, J = 8.5, 1.0 Hz, 1H), 7.96 (dd, J = 7.5, 1.1 Hz, 1H), 7.73 – 7.66 (m, 2H). 13C NMR (75 MHz, DMSO-d6) δ 151.95, 148.91, 135.15, 130.92, 130.66, 129.77, 127.32, 123.50, 121.58.

7-Nitroquinoline (2l)

1H NMR (300 MHz, DMSO-d6) δ 9.11 (dd, J = 4.2, 1.7 Hz, 1H), 8.78 (d, J = 2.3 Hz, 1H), 8.57 (dd, J = 8.4, 1.8, 0.9 Hz, 1H), 8.32 (dd, J = 9.0, 2.3 Hz, 1H), 8.25 (d, J = 8.6 Hz, 1H), 7.76 (dd, J = 8.4, 4.2 Hz, 1H). 13C NMR (75 MHz, DMSO-d6) δ 153.61, 148.09, 146.72, 136.75, 131.72, 130.83, 125.10, 124.94, 120.25.

2-Phenylquinoline (2m)

1H NMR 1H NMR (300 MHz, DMSO-d6) δ 8.47 (d, J = 8.7 Hz, 1H), 8.32 – 8.25 (m, 2H), 8.16 (d, J = 8.7 Hz, 1H), 8.09 (d, J = 8.5 Hz, 1H), 8.01 (d, J = 6.7 Hz, 1H), 7.79 (ddd, J = 8.4, 6.9, 1.5 Hz, 1H), 7.64 – 7.47 (m, 4H). 13C NMR (75 MHz, DMSO-d6) δ 156.55, 148.01, 139.12, 137.68, 130.41, 130.08, 129.57, 129.33, 128.28, 127.69, 127.46, 126.93, 119.22.

8-Hydroxyquinoline (2n)

1H NMR (300 MHz, DMSO-d6) δ 9.81 (s, 1H), 8.85 (dd, J = 4.1, 1.7 Hz, 1H), 8.32 (dd, J = 8.3, 1.7 Hz, 1H), 7.60 – 7.35 (m, 3H), 7.09 (dd, J = 7.2, 1.7 Hz, 1H). 13C NMR (75 MHz, DMSO-d6) δ 153.79, 148.61, 138.95, 136.53, 129.27, 127.98, 122.31, 118.19, 111.76.

6-(Methoxycarbonyl)quinoline (2o)
H NMR (300 MHz, DMSO-d6) δ 9.00 (dd, J = 4.2, 1.8 Hz, 1H), 8.62 (d, J = 2.0 Hz, 1H), 8.56 – 8.50 (m, 1H), 8.16 (dd, J = 8.8, 2.0 Hz, 1H), 8.06 (dt, J = 8.8, 0.8 Hz, 1H), 7.59 (dd, J = 8.3, 4.2 Hz, 1H), 3.90 (s, 3H).

13C NMR (75 MHz, DMSO-d6) δ 166.28, 153.31, 149.82, 137.94, 131.41, 129.92, 128.76, 127.75, 127.58, 122.75, 52.81.

4-Methyl-6-bromoquinoline (2q)

H NMR (300 MHz, Chloroform-d) δ 8.77 (d, J = 4.5 Hz, 1H), 8.14 (dd, J = 2.2, 0.4 Hz, 1H), 7.97 (dd, J = 8.9, 0.5 Hz, 1H), 7.76 (dd, J = 8.9, 2.2 Hz, 1H), 7.25 (dd, J = 4.4, 1.0 Hz, 1H), 2.67 (d, J = 0.9 Hz, 3H).

13C NMR (75 MHz, DMSO-d6) δ 150.37, 148.50, 144.08, 138.20, 136.99, 132.27, 129.72, 128.45, 127.92, 123.56, 119.88, 118.00, 112.56, 111.59, 110.81, 102.15, 25.41.

6-Fluoro-2-methylquinoline (2r)

H NMR (300 MHz, DMSO-d6) δ 8.23 (d, J = 8.9 Hz, 1H), 7.39 (dd, J = 2.6, 0.7 Hz, 1H), 7.02 (dt, J = 2.6, 0.7 Hz, 1H), 6.69 (dd, J = 2.0, 0.7 Hz, 1H), 2.35 (s, 3H).

13C NMR (101 MHz, DMSO-d6) δ 136.56, 135.92, 129.12, 120.33, 119.34, 119.01, 110.92, 99.49, 13.86.

5-Methylindole (4b)

H NMR (500 MHz, DMSO-d6) δ 10.89 (s, 1H), 7.42 – 7.12 (m, 3H), 6.87 (d, J = 8.1 Hz, 1H), 6.44 – 6.11 (m, 1H), 2.34 (s, 3H).

13C NMR (126 MHz, DMSO-d6) δ 134.71, 128.38, 127.57, 125.62, 122.96, 120.07, 111.52, 100.93, 21.67.

2-Methylindole (4c)

H NMR (500 MHz, Chloroform-d) δ 10.82 (s, 1H), 7.36 (d, J = 7.8 Hz, 1H), 7.24 (d, J = 8.0 Hz, 1H), 6.92 (dt, J = 31.1, 7.3 Hz, 2H), 6.08 (s, 1H), 2.35 (s, 3H).

13C NMR (126 MHz, Chloroform-d) δ 136.56, 135.92, 129.12, 120.33, 119.34, 119.01, 110.92, 99.49, 13.86.

5-Methoxyindole (4d)

H NMR (400 MHz, DMSO-d6) δ 10.91 (s, 1H), 7.32 – 7.25 (m, 2H), 7.04 (dt, J = 2.6, 0.7 Hz, 1H), 6.73 (ddt, J = 8.8, 2.1, 0.9 Hz, 1H), 6.34 (ddt, J = 3.0, 2.0, 1.0 Hz, 1H), 3.75 (s, 3H).

13C NMR (101 MHz, DMSO-d6) δ 153.70, 131.47, 128.45, 126.18, 112.42, 111.58, 102.10, 101.27, 55.71.

5-Chloroindole (4e)

H NMR (300 MHz, Chloroform-d) δ 8.15 (s, 1H), 7.63 (dt, J = 2.0, 0.7 Hz, 1H), 7.31 (dt, J = 8.6, 0.7 Hz, 1H), 7.23 (ddt, J = 3.0, 2.5, 0.4 Hz, 1H), 7.16 (ddt, J = 8.6, 2.0, 0.4 Hz, 1H), 6.51 (ddt, J = 3.1, 2.0, 0.9 Hz, 1H).

13C NMR (75 MHz, Chloroform-d) δ 134.15, 128.97, 125.55, 125.49, 122.34, 120.14, 112.01, 102.43.

5-Bromoindole (4f)

H NMR (500 MHz, DMSO-d6) δ 11.27 (s, 1H), 7.71 (d, J = 2.0 Hz, 1H), 7.40 – 7.34 (m, 2H), 7.17 (dd, J = 8.6, 2.0 Hz, 1H), 6.41 (d, J = 2.8 Hz, 1H).

13C NMR (126 MHz, DMSO-d6) δ 135.03, 130.02, 127.37, 123.82, 122.66, 113.82, 111.83, 101.24.

6-Fluoroindole (4g)
$^1$H NMR (500 MHz, DMSO-d$_6$) δ 11.13 (s, 1H), 7.50 (dd, $J = 8.7, 5.5$ Hz, 1H), 7.31 (t, $J = 2.8$ Hz, 1H), 7.17 (dd, $J = 10.3, 2.4$ Hz, 1H), 6.87 – 6.79 (m, 1H), 6.46 – 6.38 (m, 1H).

$^13$C NMR (126 MHz, DMSO-d$_6$) δ 160.13, 158.28, 136.25, 136.15, 126.38, 126.35, 124.90, 121.41, 121.33, 107.84, 107.65, 101.66, 97.89, 97.68.

6-Nitroindole (4h)

$^1$H NMR (500 MHz, DMSO-d$_6$) δ 11.83 (s, 1H), 8.35 (d, $J = 2.2$ Hz, 1H), 7.87 (dd, $J = 8.8, 2.2$ Hz, 1H), 7.77 (t, $J = 2.8$ Hz, 1H), 7.71 (d, $J = 8.7$ Hz, 1H), 6.63 (d, $J = 2.7$ Hz, 1H).

$^13$C NMR (126 MHz, DMSO-d$_6$) δ 142.30, 134.75, 133.14, 132.79, 120.68, 114.50, 108.71, 102.79.

4-Cyanoindole (4i)

$^1$H NMR (500 MHz, DMSO-d$_6$) δ 11.73 (s, 1H), 7.76 (d, $J = 8.2$ Hz, 1H), 7.64 (t, $J = 2.9$ Hz, 1H), 7.51 (d, $J = 7.4$ Hz, 1H), 7.22 (t, $J = 7.8$ Hz, 1H), 6.63 – 6.52 (m, 1H).

$^13$C NMR (126 MHz, DMSO-d$_6$) δ 136.11, 136.83, 132.90, 126.11, 122.83, 121.72, 120.88, 118.81, 106.78, 51.09.

3-Methoxycarbonylindole (4j)

$^1$H NMR (400 MHz, DMSO-d$_6$) δ 11.97 (s, 1H), 8.14 – 8.11 (m, 1H), 8.08 – 8.02 (m, 1H), 7.56 – 7.50 (m, 1H), 7.29 – 7.18 (m, 2H), 3.85 (s, 3H).

$^13$C NMR (101 MHz, DMSO-d$_6$) δ 165.25, 136.83, 132.90, 126.11, 122.83, 121.72, 120.88, 118.81, 106.78, 51.09.

7-Bromo-5-nitro-1H-indole (4k)

$^1$H NMR (300 MHz, DMSO-d$_6$) δ 12.08 (s, 1H), 8.54 (dd, $J = 2.1$, 0.6 Hz, 1H), 8.10 (dd, $J = 2.0$, 0.4 Hz, 1H), 7.66 – 7.57 (m, 1H), 6.84 (dd, $J = 3.2$, 1.8 Hz, 1H).

$^13$C NMR (75 MHz, DMSO-d$_6$) δ 141.42, 137.77, 130.61, 128.22, 118.88, 117.22, 106.01, 104.38.

5-Bromo-2-methyl-1H-indole (4l)

$^1$H NMR (300 MHz, DMSO-d$_6$) δ 11.12 (s, 1H), 7.56 (dd, $J = 2.0$, 0.6 Hz, 1H), 7.23 (dt, $J = 8.5$, 0.7 Hz, 1H), 7.09 (dd, $J = 8.5$, 2.0 Hz, 1H), 6.11 (dp, $J = 1.9$, 0.9 Hz, 1H), 2.38 (d, $J = 0.9$ Hz, 3H).

$^13$C NMR (75 MHz, DMSO-d$_6$) δ 137.88, 135.21, 131.03, 122.71, 121.51, 112.81, 111.60, 99.32, 13.81.

7-Azaindole (4n)

$^1$H NMR (300 MHz, DMSO-d$_6$) δ 11.62 (s, 1H), 8.21 (ddd, $J = 4.7$, 1.6, 0.4 Hz, 1H), 7.95 (dd, $J = 7.8$, 1.6 Hz, 1H), 7.46 (d, $J = 3.4$ Hz, 1H), 7.05 (dd, $J = 7.8$, 4.7 Hz, 1H), 6.44 (d, $J = 3.5$ Hz, 1H).

$^13$C NMR (75 MHz, DMSO-d$_6$) δ 148.89, 142.88, 128.49, 126.45, 120.07, 115.86, 100.23.

Quinoxaline (6a)

$^1$H NMR (300 MHz, Chloroform-d) δ 8.84 (s, 2H), 8.14 – 8.07 (m, 2H), 7.81 – 7.72 (m, 2H).

$^13$C NMR (75 MHz, Chloroform-d) δ 144.93, 143.00, 130.11, 129.49.

6-Nitroquinoxaline (6c)

$^1$H NMR (400 MHz, DMSO-d$_6$) δ 9.16 (s, 2H), 8.90 (dd, $J = 2.6$, 0.5 Hz, 1H), 8.56 (dd, $J = 9.2$, 2.6 Hz, 1H), 8.34 (dd, $J = 9.2$, 0.5 Hz, 1H).

$^13$C NMR (101 MHz, DMSO-d$_6$) δ 149.32, 149.59, 148.05, 145.11, 141.45, 131.72, 125.70, 123.99.
2-Phenylquinoxaline (6d)

![2-Phenylquinoxaline](image)

$^1$H NMR 1H NMR (300 MHz, Chloroform-d) $\delta$ 9.32 (s, 1H), 8.21 – 8.09 (m, 4H), 7.84 – 7.64 (m, 2H), 7.59 – 7.48 (m, 3H). $^{13}$C NMR (75 MHz, Chloroform-d) $\delta$ 151.85, 143.37, 142.32, 141.59, 136.79, 130.30, 130.21, 129.65, 129.55, 129.17, 129.14, 127.57.

1-Phenyl-3,4-dihydroisoquinoline (6g)

![1-Phenyl-3,4-dihydroisoquinoline](image)

$^1$H NMR 1H NMR (300 MHz, Chloroform-d) $\delta$ 9.32 (s, 1H), 8.21 – 8.09 (m, 4H), 7.84 – 7.64 (m, 2H), 7.59 – 7.48 (m, 3H). $^{13}$C NMR (75 MHz, Chloroform-d) $\delta$ 151.85, 143.37, 142.32, 141.59, 136.79, 130.30, 130.21, 129.65, 129.55, 129.17, 129.14, 127.57.

Acridine (6h)

![Acridine](image)

$^1$H NMR 1H NMR (300 MHz, Chloroform-d) $\delta$ 9.32 (s, 1H), 8.21 – 8.09 (m, 4H), 7.84 – 7.64 (m, 2H), 7.59 – 7.48 (m, 3H). $^{13}$C NMR (75 MHz, Chloroform-d) $\delta$ 151.85, 143.37, 142.32, 141.59, 136.79, 130.30, 130.21, 129.65, 129.55, 129.17, 129.14, 127.57.

7,8-Benzquinoline (6i)

![7,8-Benzquinoline](image)

$^1$H NMR 1H NMR (300 MHz, Chloroform-d) $\delta$ 9.32 (s, 1H), 8.21 – 8.09 (m, 4H), 7.84 – 7.64 (m, 2H), 7.59 – 7.48 (m, 3H). $^{13}$C NMR (75 MHz, Chloroform-d) $\delta$ 151.85, 143.37, 142.32, 141.59, 136.79, 130.30, 130.21, 129.65, 129.55, 129.17, 129.14, 127.57.

1,10-Phenanthroline (6k)

![1,10-Phenanthroline](image)

$^1$H NMR 1H NMR (300 MHz, Chloroform-d) $\delta$ 9.32 (s, 1H), 8.21 – 8.09 (m, 4H), 7.84 – 7.64 (m, 2H), 7.59 – 7.48 (m, 3H). $^{13}$C NMR (75 MHz, Chloroform-d) $\delta$ 151.85, 143.37, 142.32, 141.59, 136.79, 130.30, 130.21, 129.65, 129.55, 129.17, 129.14, 127.57.

9-Fluorenone (6l)

![9-Fluorenone](image)

$^1$H NMR 1H NMR (300 MHz, Chloroform-d) $\delta$ 9.32 (s, 1H), 8.21 – 8.09 (m, 4H), 7.84 – 7.64 (m, 2H), 7.59 – 7.48 (m, 3H). $^{13}$C NMR (75 MHz, Chloroform-d) $\delta$ 151.85, 143.37, 142.32, 141.59, 136.79, 130.30, 130.21, 129.65, 129.55, 129.17, 129.14, 127.57.

Xanth-9-one (6m)

![Xanth-9-one](image)

$^1$H NMR 1H NMR (300 MHz, Chloroform-d) $\delta$ 9.32 (s, 1H), 8.21 – 8.09 (m, 4H), 7.84 – 7.64 (m, 2H), 7.59 – 7.48 (m, 3H). $^{13}$C NMR (75 MHz, Chloroform-d) $\delta$ 151.85, 143.37, 142.32, 141.59, 136.79, 130.30, 130.21, 129.65, 129.55, 129.17, 129.14, 127.57.

7H-indeno[2,1-c]quinolin-7-one (6n)

![7H-indeno[2,1-c]quinolin-7-one](image)

$^1$H NMR 1H NMR (300 MHz, Chloroform-d) $\delta$ 9.32 (s, 1H), 8.21 – 8.09 (m, 4H), 7.84 – 7.64 (m, 2H), 7.59 – 7.48 (m, 3H). $^{13}$C NMR (75 MHz, Chloroform-d) $\delta$ 151.85, 143.37, 142.32, 141.59, 136.79, 130.30, 130.21, 129.65, 129.55, 129.17, 129.14, 127.57.

$^{13}$C NMR (75 MHz, Chloroform-d) $\delta$ 151.85, 143.37, 142.32, 141.59, 136.79, 130.30, 130.21, 129.65, 129.55, 129.17, 129.14, 127.57.
4-(4-Fluorophenyl)quinoline (6o)

$^1$H NMR: $^1$H NMR (500 MHz, DMSO-$d_6$) $\delta$ 8.90 (d, $J$ = 4.4 Hz, 1H), 8.08 (d, $J$ = 8.4 Hz, 1H), 7.83 – 7.72 (m, 2H), 7.59 – 7.51 (m, 3H), 7.42 – 7.34 (m, 3H).$^{13}$C NMR: $^{13}$C NMR (126 MHz, DMSO-$d_6$) $\delta$ 163.76, 161.80, 150.59, 148.62, 146.80, 134.10, 134.08, 132.07, 132.00, 130.04, 129.95, 127.51, 126.37, 125.71, 122.06, 116.25, 116.08.

6. NMR spectra
7. GC-MS spectra
