

SUPPORTING INFORMATION

**Expanding applications of zeolite imidazolate frameworks in catalysis: Synthesis of
quinazolines using ZIF-67 as an efficient heterogeneous catalyst**

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1 Materials and instrumentation

All reagents and starting materials were obtained commercially from Sigma-Aldrich and Acros, and were used as received without any further purification unless otherwise noted. Nitrogen physisorption measurements were conducted using a Micromeritics 2020 volumetric adsorption analyzer system. Samples were pretreated by heating under vacuum at 200 °C for 6 h. A Netzsch Thermoanalyzer STA 409 was used for thermogravimetric analysis (TGA) with a heating rate of 5 °C/min under a nitrogen atmosphere. X-ray powder diffraction (XRD) patterns were recorded using a Cu K α radiation source on a D8 Advance Bruker powder diffractometer. Scanning electron microscopy studies were conducted on a S4800 Scanning Electron Microscope (SEM). Transmission electron microscopy studies were performed using a JEOL JEM 1400 Transmission Electron Microscope (TEM) at 80 kV. The ZIF-67 sample was dispersed on holey carbon grids for TEM observation. Elemental analysis with Inductively Coupled Plasma Atomic Emission Spectroscopy (ICP-MS) was performed on a Shimadzu ICPE-9000. Fourier transform infrared (FT-IR) spectra were obtained on a Nicolet 6700 instrument, with samples being dispersed on potassium bromide pellets.

Gas chromatographic (GC) analyses were performed using a Shimadzu GC 2010-Plus equipped with a flame ionization detector (FID) and an SPD-5 column (length = 30 m, inner diameter = 0.25 mm, and film thickness = 0.25 μ m). The temperature program for GC analysis heated samples from 100 to 130 °C at 40 °C/min; heated from 130 to 180 °C at 50 °C/min; heated them from 180 to 280 °C at 50 °C/min and held them at 280 °C for 3.5 min. Inlet and detector temperature were set constant at 280 °C. Diphenyl ether was used as

internal standard to calculate the conversion of reaction. The ^1H and ^{13}C NMR were recorded on a Bruker AV 500 MHz with tetramethylsilane as standard.

2 Synthesis of Co-MOFs and Co-ZIFs

ZIF-67

The ZIF-67 was prepared according to literature procedure [1]. In a typical preparation, a mixture of 2-methylimidazole (3.284 g, 40 mmol) and triethylamine (5.6 ml, 40 mmol) was dissolved in water (10 mL). A solution of $\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ (0.73 g, 2.5 mmol) in water (10 mL) was then added, and the resulting solution was stirred for 10 min at room temperature. The purple precipitates were separated by centrifugation, washed with water (3 x 10 mL) and methanol (3 x 10 mL) at room temperature. The material was evacuated under vacuum at 150 °C for 6 h, yielding 0.314 g of ZIF-67 in the form of purple crystals (56% yield).

Elemental analysis of ZIF-67 with ICP-MS indicated a cobalt loading of 4.32 mmol/g, is close to theoretical value of 4.48 mmol/g.

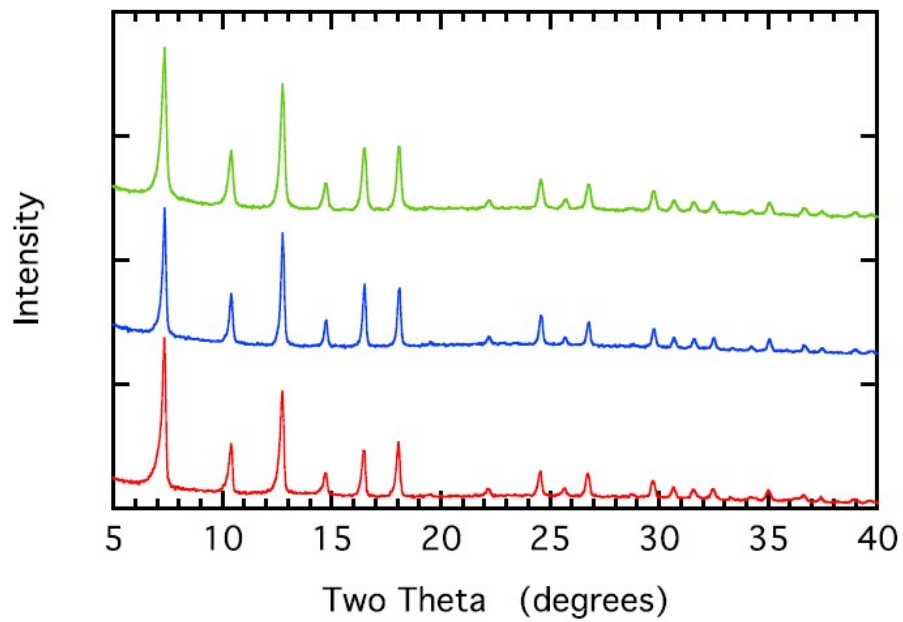


Fig. S1. X-ray powder diffractograms of ZIF-67 in the previous study [1].

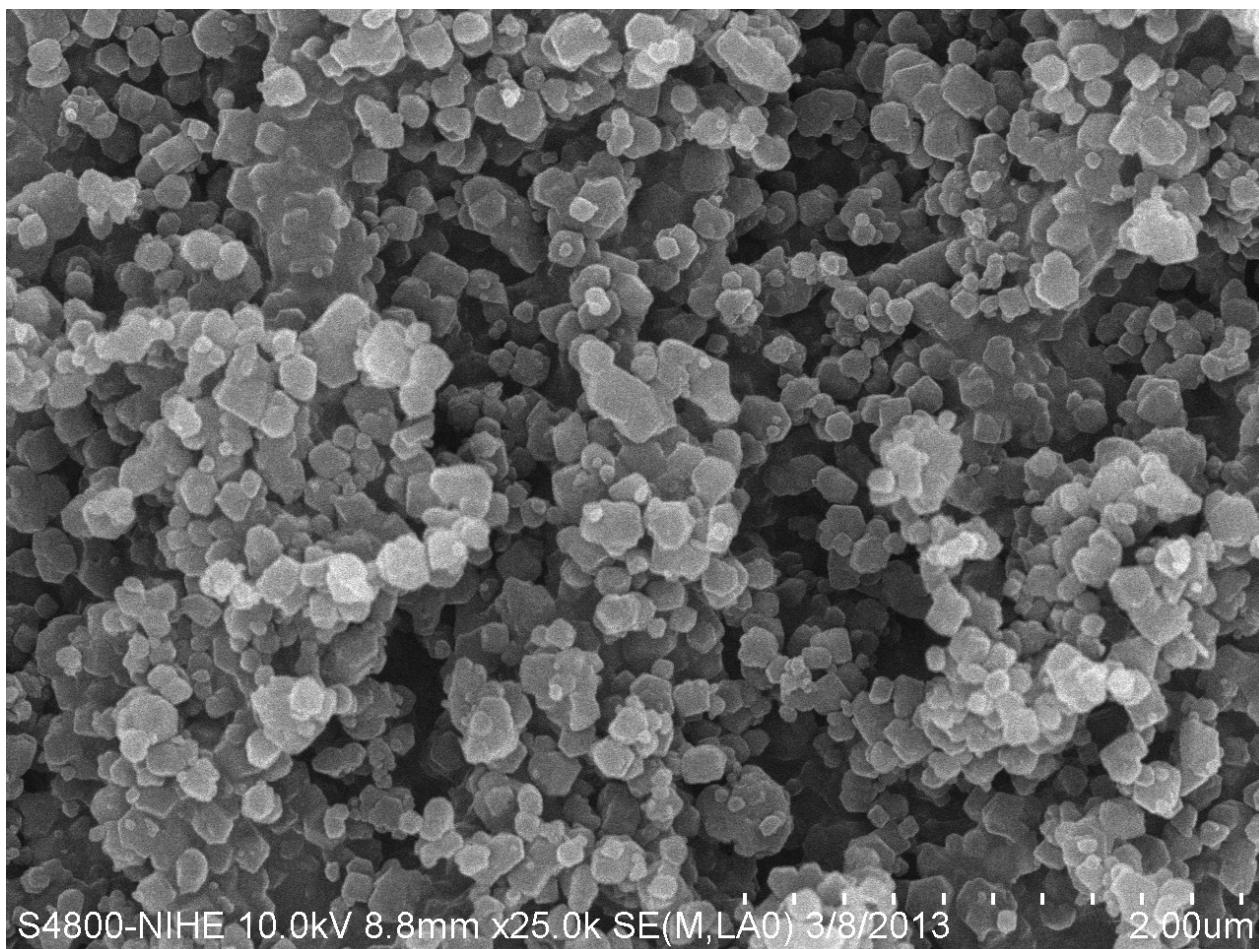
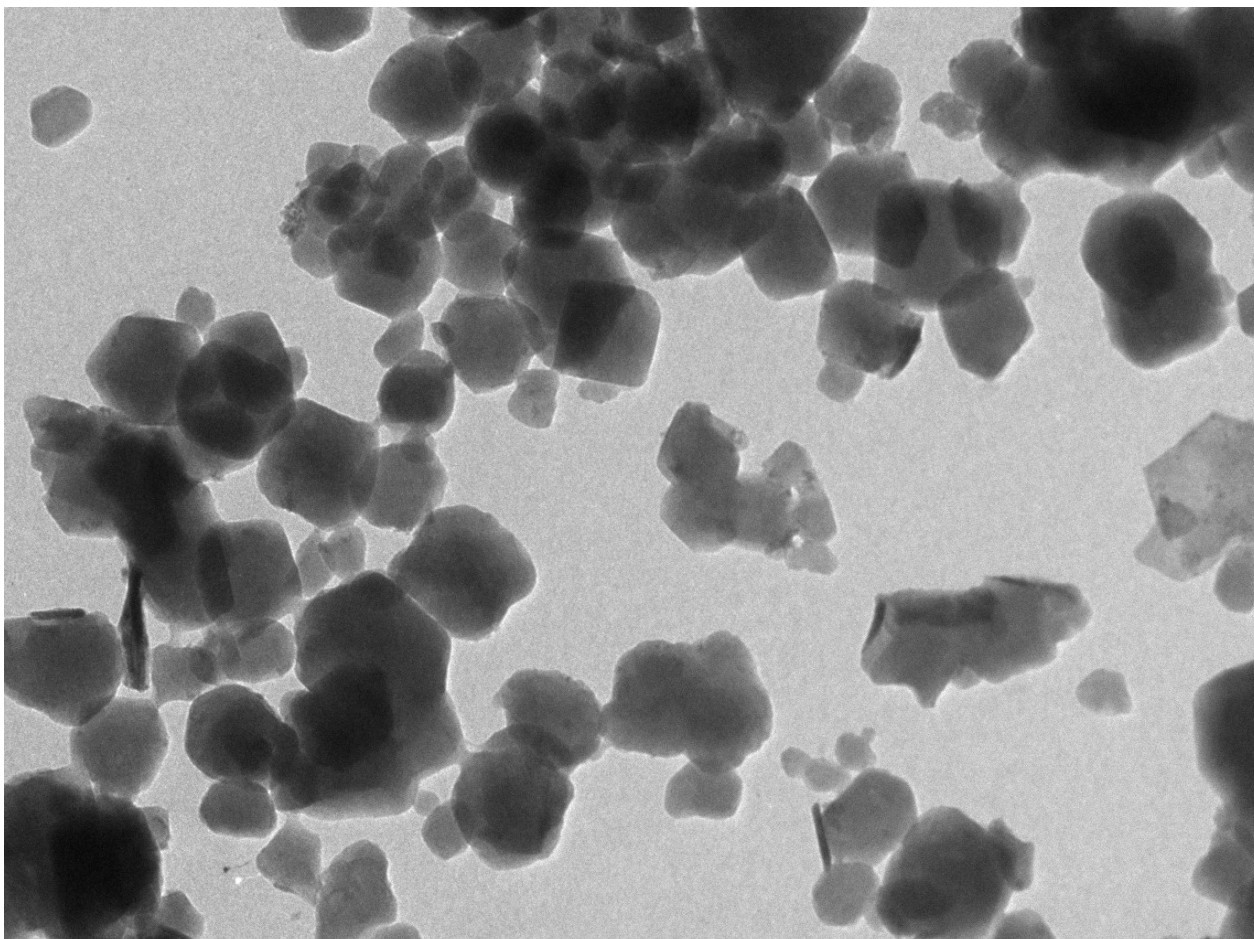


Fig. S2. SEM micrograph of the ZIF-67.



ZIF - 67.008

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Fig. S3. TEM micrograph of the ZIF-67.

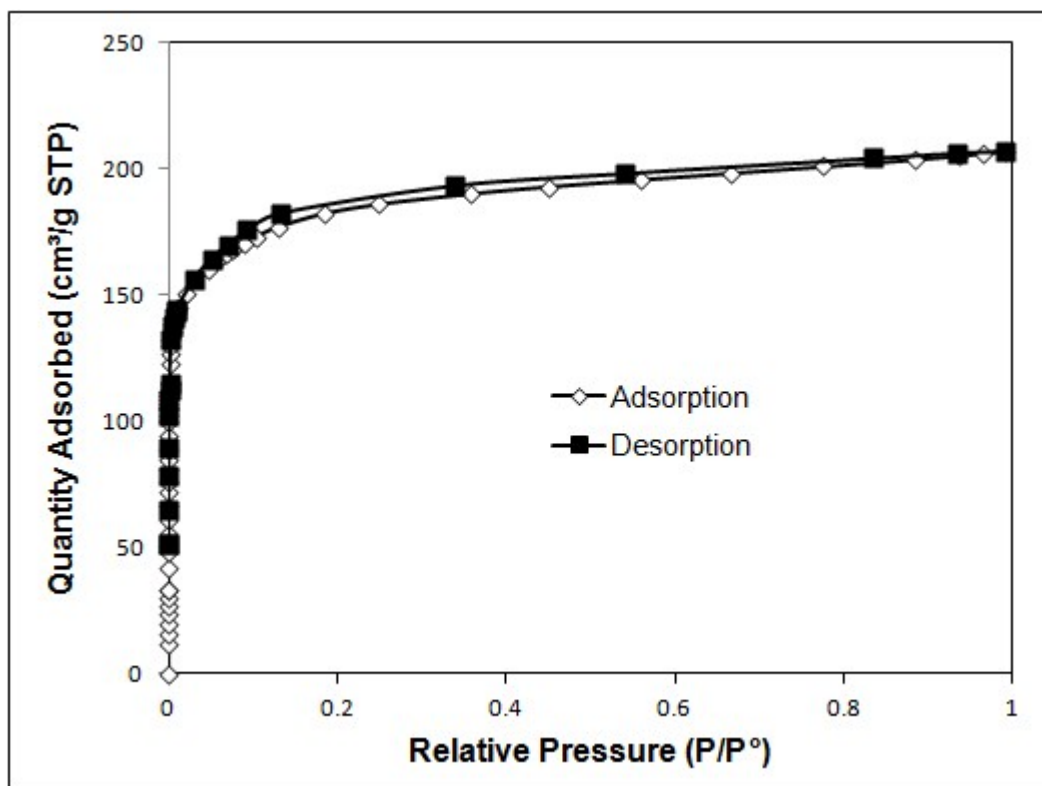


Fig. S4. Nitrogen adsorption/desorption isotherm of the ZIF-67.

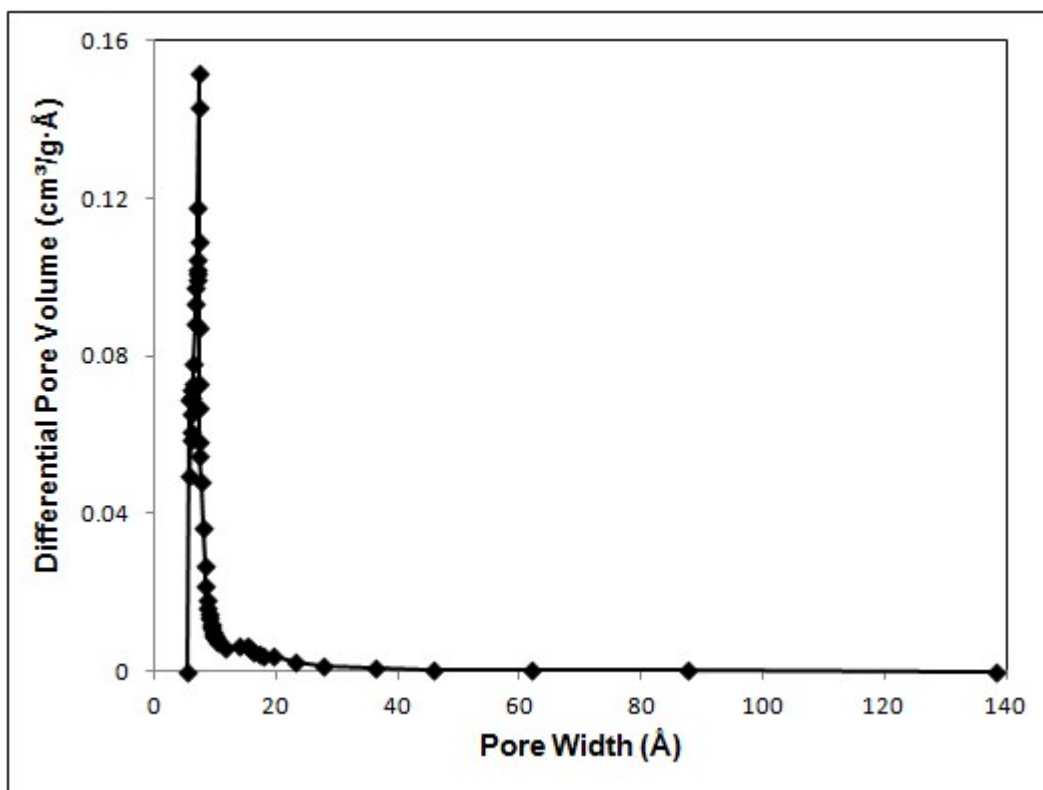


Fig. S5. Pore size distribution of the ZIF-67.

Pore size distribution measurement parameters:

Sample Mass: 0.2843 g

Thermal Correction: No

Cold Free Space: 47.9826 cm³

Warm Free Space: 16.2399 cm³

Ambient temperature: 22.00 °C

Measured

Automatic Degas: Yes

Equilibration Interval: 5 s

Analysis Adsorptive: N₂

Low Pressure Dose: None

Analysis Bath Temp.: 77.300 K

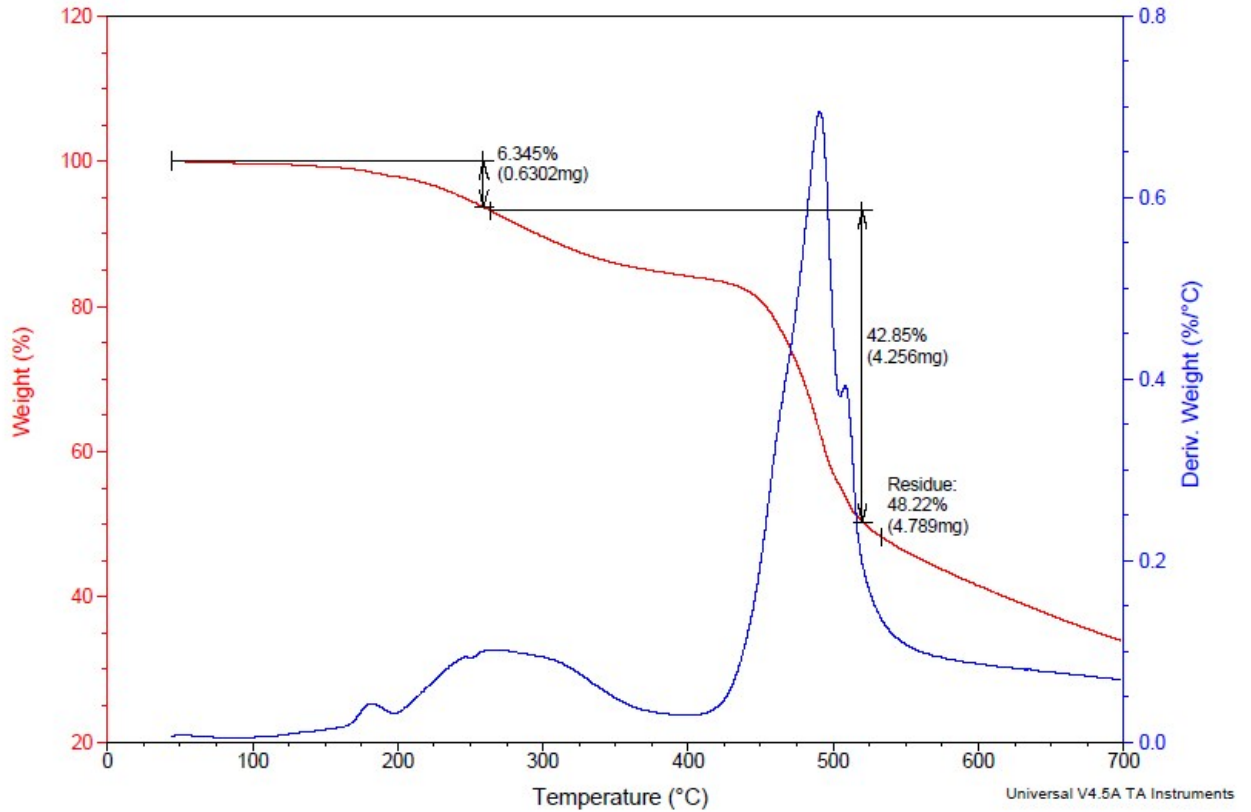


Fig. S6. TGA analysis of the ZIF-67.

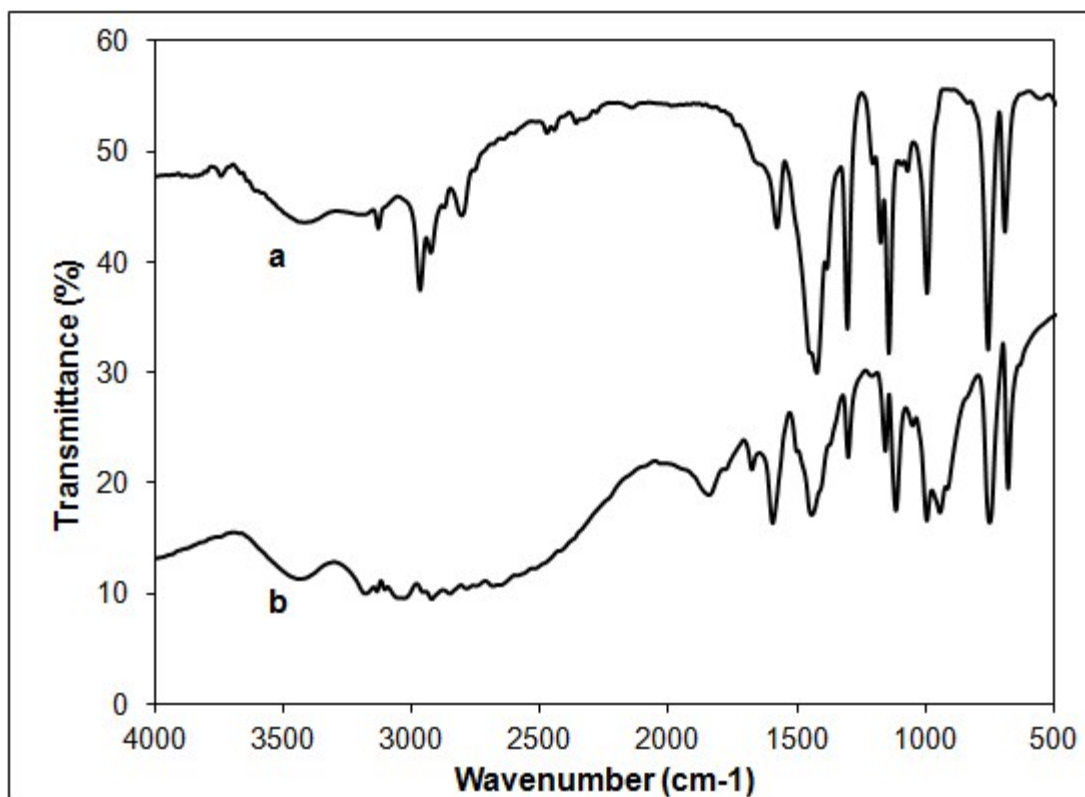


Fig. S7. FT-IR spectrum of the ZIF-67 (a) and 2-methylimidazole (b).

ZIF-9:

The ZIF-9 was prepared according to literature procedure [2]. In a typical preparation, a solid mixture of cobalt nitrate hexahydrate (2.10 g, 7.21 mmol) and benzimidazole (0.60 g, 5.08 mmol) was dissolved in 180 mL of *N,N'*-dimethylformamide (DMF), and then distributed in 20 mL vials. The vials were tightly capped and heated at a rate of 5 °C min⁻¹ to 140 °C in a programmable oven and held at this temperature for 48 h, then cooled at a rate of 0.4 °C min⁻¹ to room temperature. The purple crystals were collected from the mother liquor, washed with DMF (3 x 15 mL) for 3 days. After that, the DMF was exchanged by

dichloromethane (3 x 15 mL) for 3 days. The residual solvents were removed under vacuum at 200 °C for 6 h, yielding 0.25 g of purple crystals (25% based on benzimidazole).

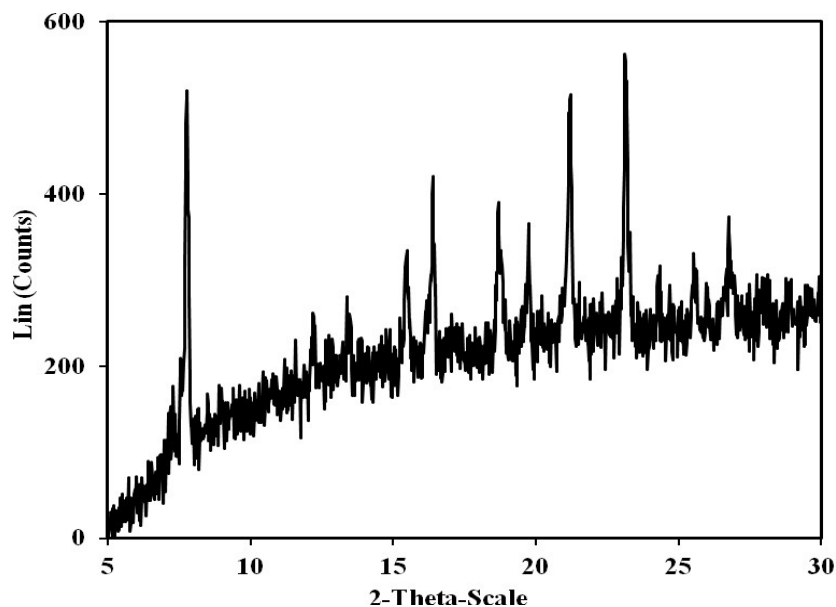


Fig. S8. X-ray powder diffractogram of the ZIF-9.

Co₂(BDC)₂(DABCO):

The Co₂(BDC)₂(DABCO) was prepared according to the modified literature procedure [3]. H₂BDC (H₂BDC = 1,4-benzenedicarboxylic acid; 0.332 g, 2 mmol), DABCO (DABCO = 1,4-diazabicyclo[2.2.2]octane; 0.112 g, 1 mmol), and Co(NO₃)₂·6H₂O (0.58 g, 2 mmol) was dissolved in DMF (DMF = *N,N*'-dimethylformamide; 15 ml). The resulting solution was distributed to two 20 ml vials. The vials were then heated at 100 °C in an isothermal oven for 48 h. After cooling the vials to room temperature, the solid product was removed by decanting with mother liquor and washed in DMF (3 x 10 mL) for 3 days. Solvent exchange was carried out with methanol (3 x 10 mL) at room temperature for 3 days. The material was

then evacuated under vacuum at 140 °C for 6 h, yielding 0.407 g of $\text{Co}_2(\text{BDC})_2(\text{DABCO})$ in the form of purple crystals (73% yield based on cobalt salt).

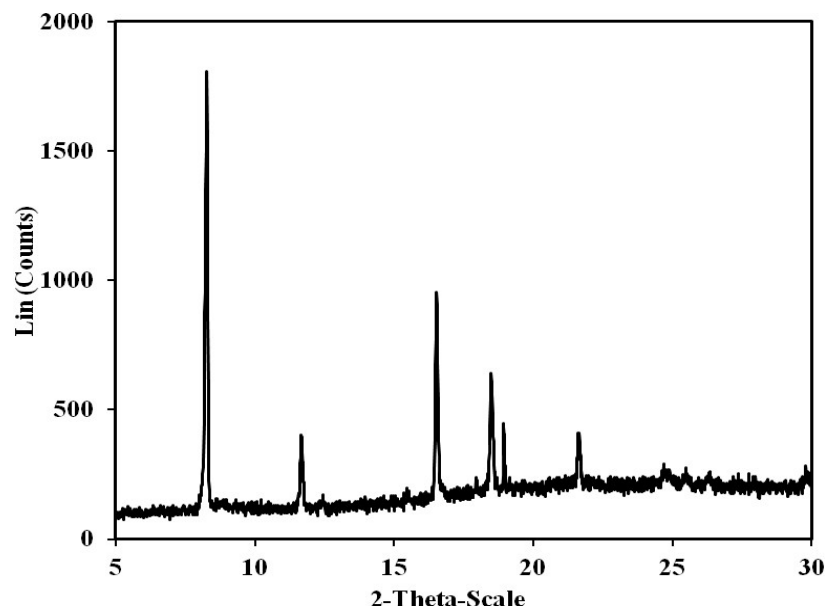


Fig. S9. X-ray powder diffractogram of the $\text{Co}_2(\text{BDC})_2(\text{DABCO})$.

Co-MOF-74:

The Co-MOF-74 was prepared according to literature procedure [4]. In a typical preparation, a mixture of 2,5- dihydroxyterephthalic acid (DHTA) (0.05 g, 0.25 mmol), and $\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ (0.150 g, 0.52 mmol) was dissolved in a mixture of DMF (10 mL), ethanol (10 mL) and water (10 mL) and the resulting solution was distributed to two 20 mL vials. The vial was then heated at 100 °C in an isothermal oven for 48 h. After cooling the vial to room temperature, the solid product was removed by decanting with mother liquor and washed in DMF (3 x 10 mL) for 3 days. Solvent exchange was then carried out with methanol (3 x 10 mL) at room temperature for 3 day. The material was then evacuated under vacuum at 200 °C

for 6 h, yielding 0.051g of Co-MOF-74 in the form of deep purple crystals (80% based on 2,5- dihydroxyterephthalic acid).

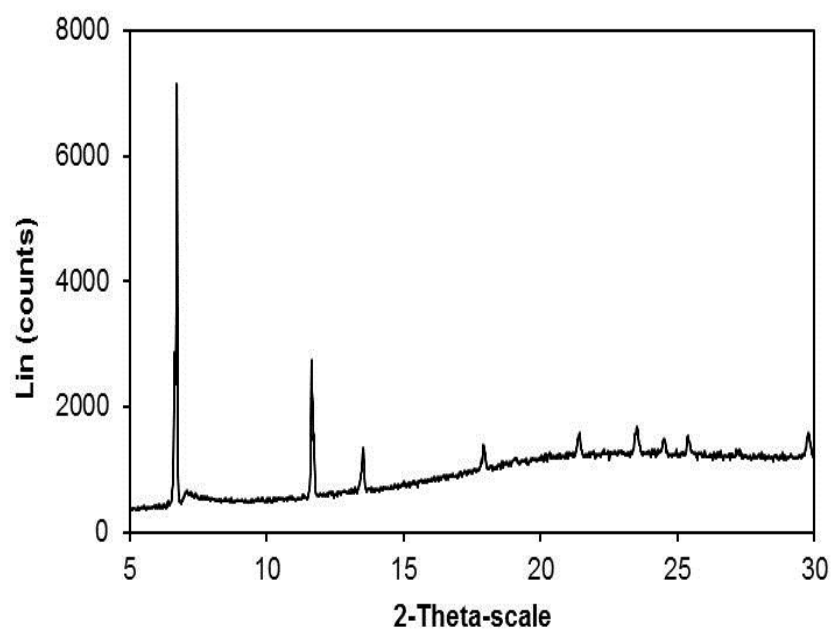


Fig. S10. X-ray powder diffractogram of the Co-MOF-74.

3 Product isolation and characterization

Conversion was calculated as equation:

$$Y(t) = \frac{\frac{S_{(SM)}}{S_{(diphenyl\ ether)}}(t_0) - \frac{S_{(SM)}}{S_{(diphenyl\ ether)}}(t)}{\frac{S_{(SM)}}{S_{(diphenyl\ ether)}}(t_0)} \times 100\%$$

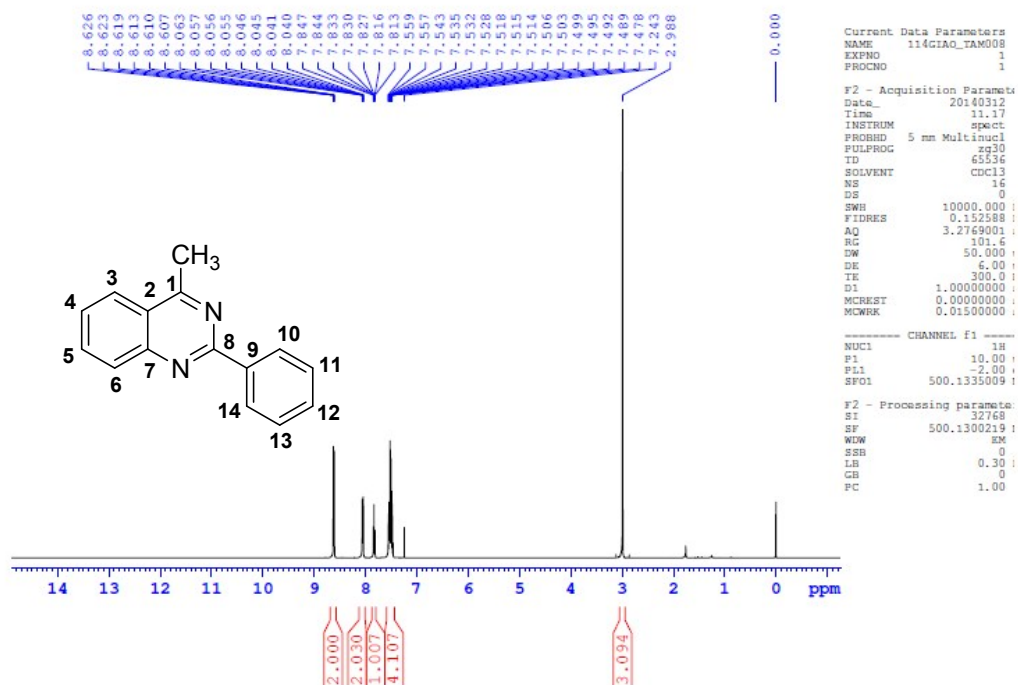
In which:

S_{SM} : peak area of starting material.

$S_{diphenyl\ ether}$: peak area of standard diphenyl ether.

Isolation of products: In a typical experiment, a mixture of 2-aminobenzoketone (1 mmol), benzylamines (1.5 mmol), *tert*-butyl hydroperoxide 70% in water (685 μ l, 5 mmol), and toluene (5 ml) was added into a 25 mL flask containing ZIF-67 catalyst (0.0066g, 0.03 mmol). The reaction mixture was stirred at 80 °C for 180 min. After the completion of reaction, catalyst was filtered off. The solution was washed with NaCl (saturated aqueous solution, 3 x 15 mL) and extracted with ethyl acetate (3 x 20 mL). The combined organic phase was then dried over Na_2SO_4 and concentrated under vacuum. After chromatography (ethylacetate/hexane = 1:15), pure products were obtained.

TAM008-CDC13-1H



TAM008-CDC13-C13CPD

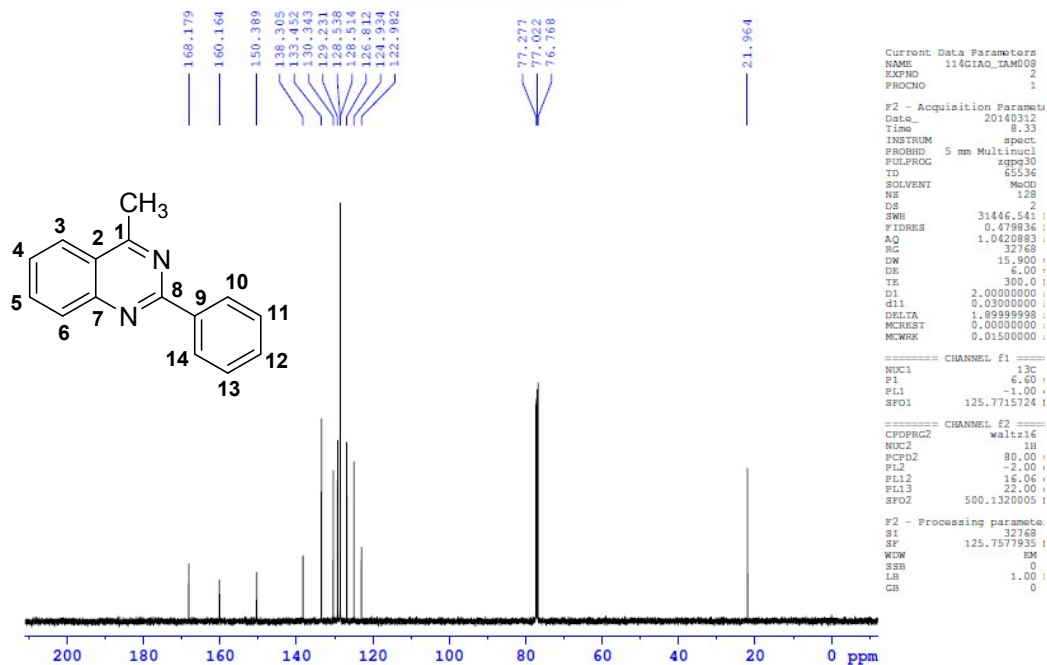
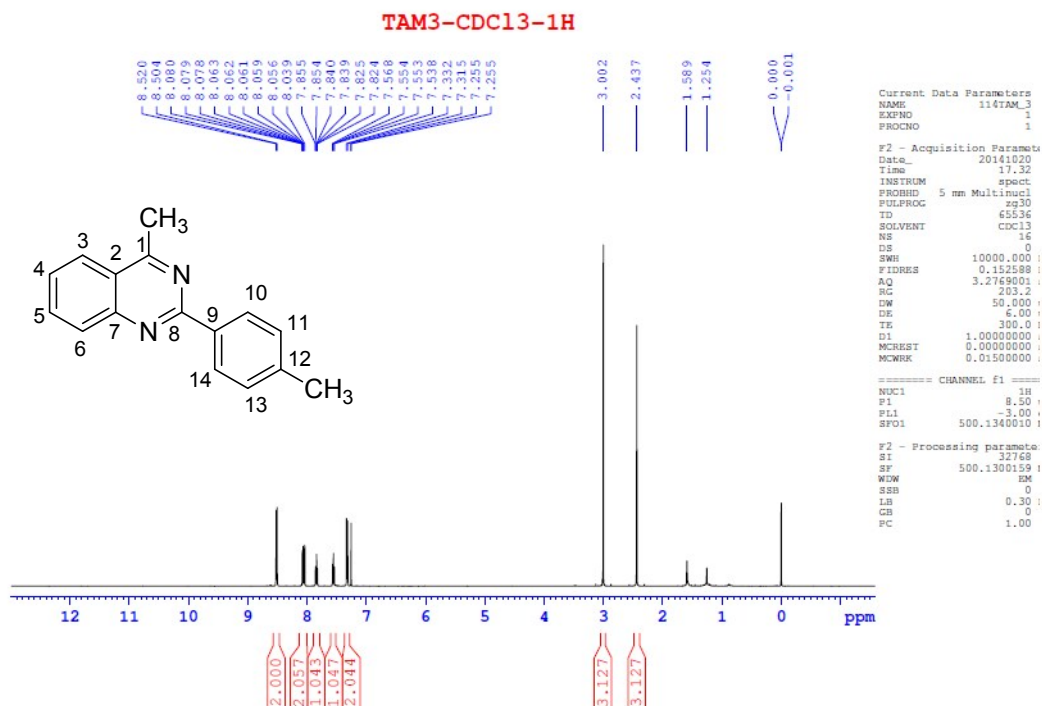


Fig. S11. ¹H NMR spectra and ¹³C NMR of 4-methyl-2-phenylquinazoline in CDCl₃.

4-methyl-2-phenylquinazoline: a white solid (191 mg, yield: 87%). This compound is known [5]. ^1H NMR (500 MHz, CDCl_3 , TMS): δ (ppm) = 2.99 (s, 3H, CH_3), 7.48-7.56 (m, 4H, $H_{\text{C}_4, \text{C}_{11}, \text{C}_{12}, \text{C}_{13}}$), 7.81-7.85 (m, 1H, H_{C_6}), 8.04-8.06 (m, 2H, $H_{\text{C}_3, \text{C}_5}$), 8.61-8.63 (m, 2H, $H_{\text{C}_{10}, \text{C}_{14}}$). ^{13}C NMR (125MHz, CDCl_3 , TMS): δ (ppm) = 22.0, 123.0, 124.9, 126.8, 128.5, 128.5, 129.2, 130.3, 133.4, 138.3, 150.4, 160.2, 168.2.



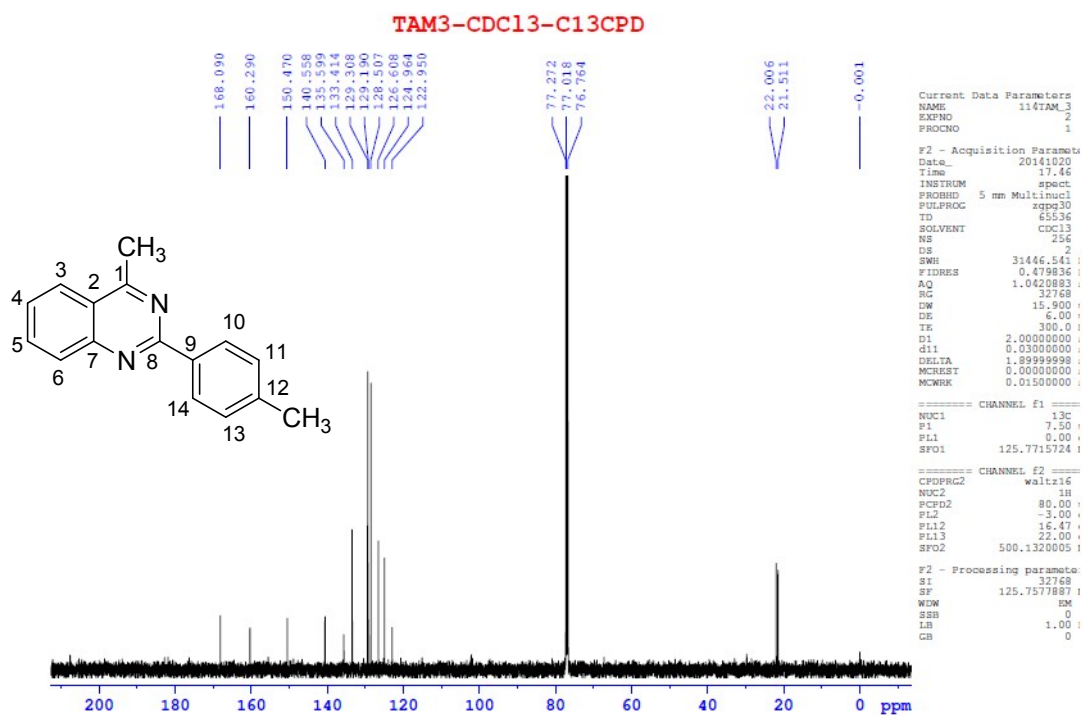


Fig. S12. ^1H NMR spectra and ^{13}C NMR of 4-methyl-2-(p-tolyl)quinazoline in CDCl_3 .

4-methyl-2-(p-tolyl)quinazoline: a pale yellow solid (176 mg, yield: 75%). This compound is known [6]. ^1H NMR (500 MHz, CDCl_3 , TMS): δ (ppm) = 2.44 (s, 3H, C_{12}CH_3), 3.00 (s, 3H, C_1CH_3), 7.32 (d, $J = 8.3$ Hz, 2H, $H_{\text{C}_{11},\text{C}_{13}}$), 7.55 (t, $J = 7.3$ Hz, 1H, H_{C_4}), 7.84 (dt, $J = 0.5$ Hz, $J = 7.5$ Hz, 1H, H_{C_6}), 8.04-8.08 (m, 2H, $H_{\text{C}_3,\text{C}_5}$), 8.51 (d, $J = 8.3$ Hz, 2H, $H_{\text{C}_{10},\text{C}_{14}}$). ^{13}C NMR (125MHz, CDCl_3 , TMS): δ (ppm) = 21.5, 22.0, 123.0, 125.0, 126.6, 128.5, 129.2, 129.3, 133.4, 135.6, 140.6, 150.5, 160.3, 168.1.

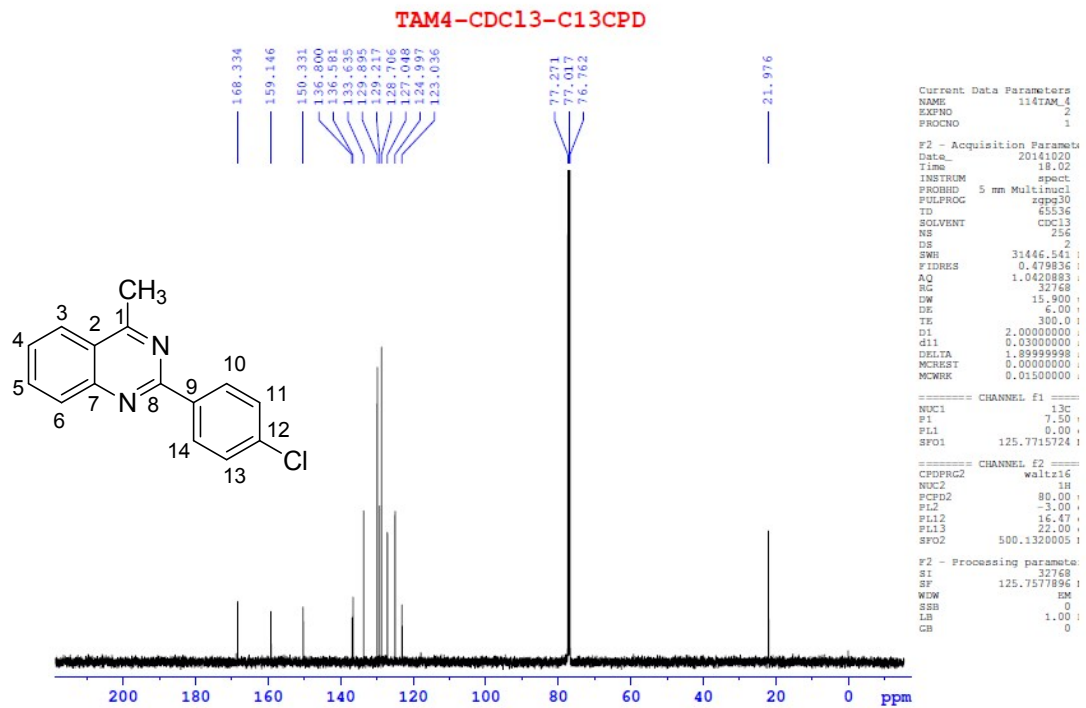
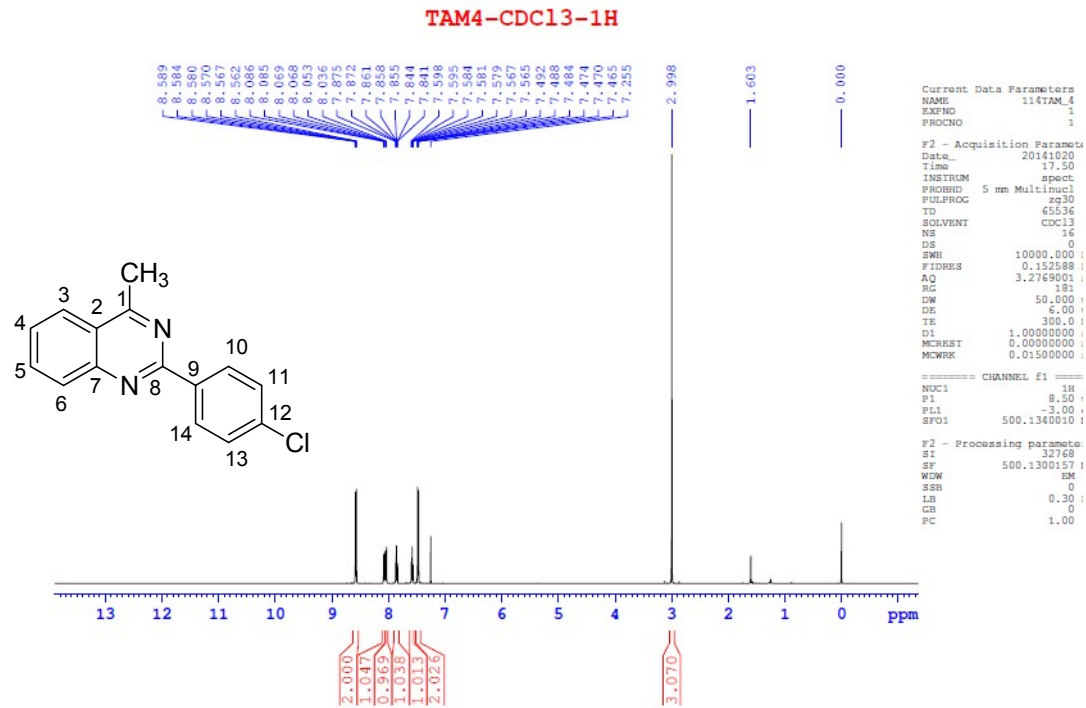
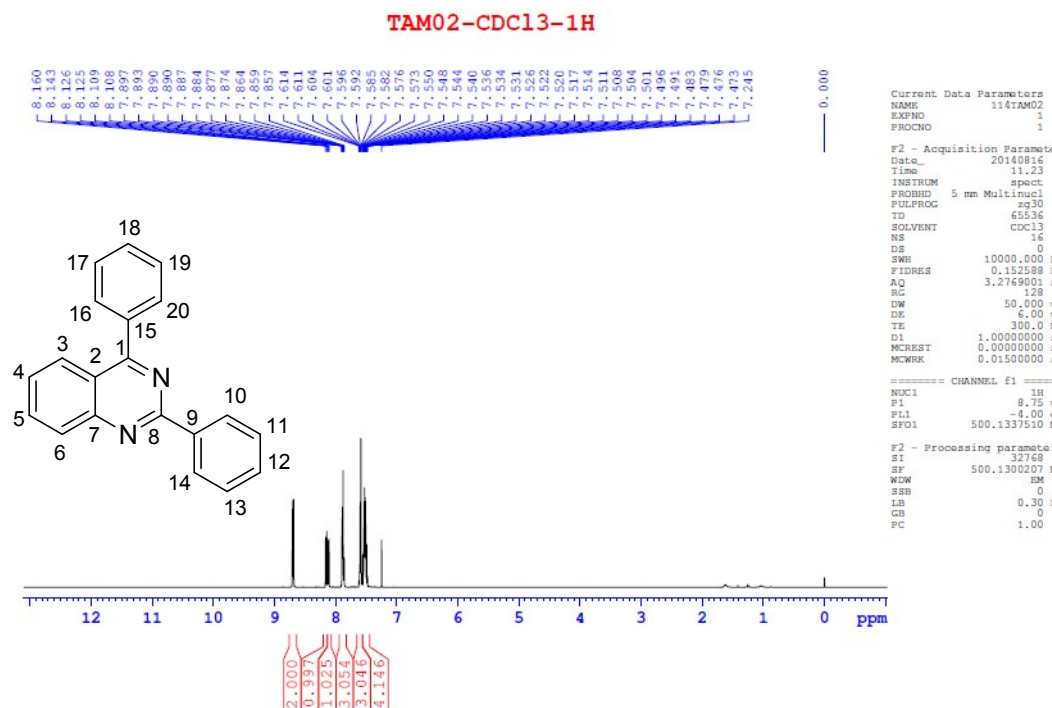


Fig. S13. ¹H NMR spectra and ¹³C NMR of 2-(4-chlorophenyl)-4-methylquinazoline in CDCl₃.

2-(4-chlorophenyl)-4-methylquinazoline: a pale yellow solid (210 mg, yield: 83%). This compound is known [6]. ^1H NMR (500 MHz, CDCl_3 , TMS): δ (ppm) = 3.00 (s, 3H, CH_3), 7.47-7.49 (m, 2H, $H_{\text{C11,C13}}$), 7.57-7.60 (m, 1H, H_{C4}), 7.84-7.88 (m, 1H, H_{C6}), 8.05 (d, $J = 8.5$ Hz, 1H, H_{C3}), 8.08 (dd, $J = 0.5$ Hz, $J = 8.5$ Hz, H_{C5}), 8.56-8.59 (m, 2H, $H_{\text{C10,C14}}$). ^{13}C NMR (125MHz, CDCl_3 , TMS): δ (ppm) = 22.0, 123.0, 125.0, 127.0, 128.7, 129.2, 129.9, 133.6, 139.6, 136.8, 150.3, 159.1, 168.3.



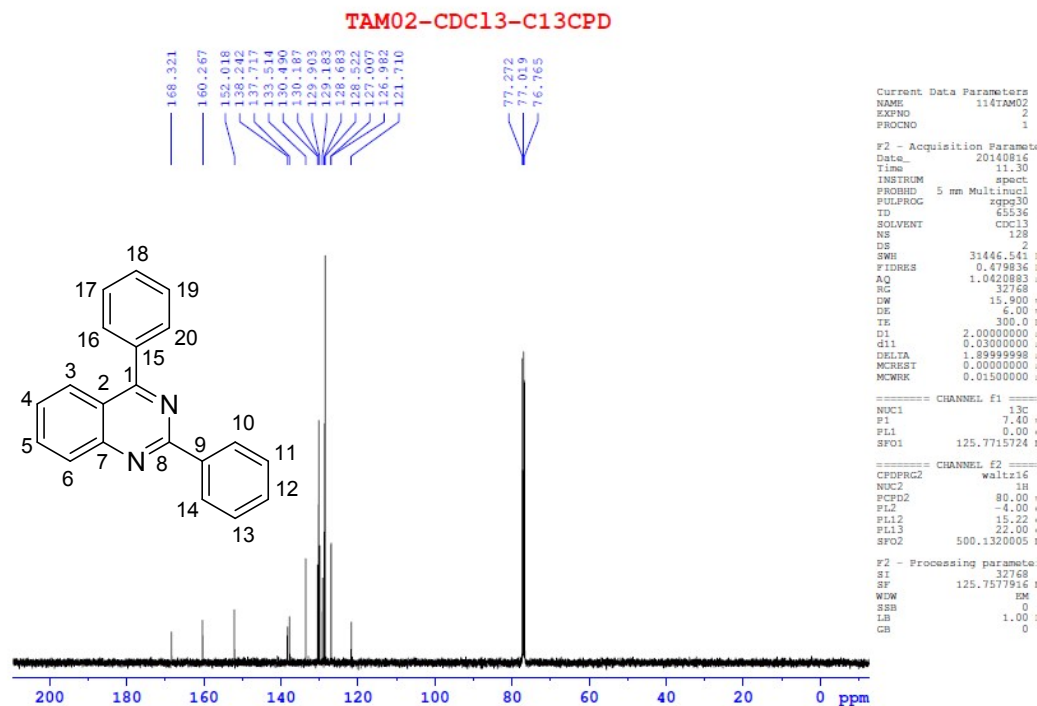


Fig. S14. ^1H NMR spectra and ^{13}C NMR of 2,4-diphenylquinazoline in CDCl_3 .

2,4-diphenylquinazoline: a white solid (250 mg, yield: 89%). This compound is known [5]. ^1H NMR (500 MHz, CDCl_3 , TMS): δ (ppm) = 7.47-7.55 (m, 4H, $H_{\text{C11,C13,C17,C19}}$), 7.57-7.61 (m, 3H, $H_{\text{C4,C12,C18}}$), 7.86-7.90 (m, 3H, $H_{\text{C6,C16,C20}}$), 8.11 (dd, $J = 0.5$ Hz, $J = 8.5$ Hz, 2H, H_{C3}), 8.15 (d, $J = 8.5$ Hz, H_{C5}), 8.68-8.71 (m, 2H, $H_{\text{C10,C14}}$). ^{13}C NMR (125MHz, CDCl_3 , TMS): δ (ppm) = 121.7, 127.0, 127.0, 128.5, 128.7, 129.2, 129.9, 130.2, 130.5, 133.5, 137.7, 138.2, 152.0, 160.3, 168.3.

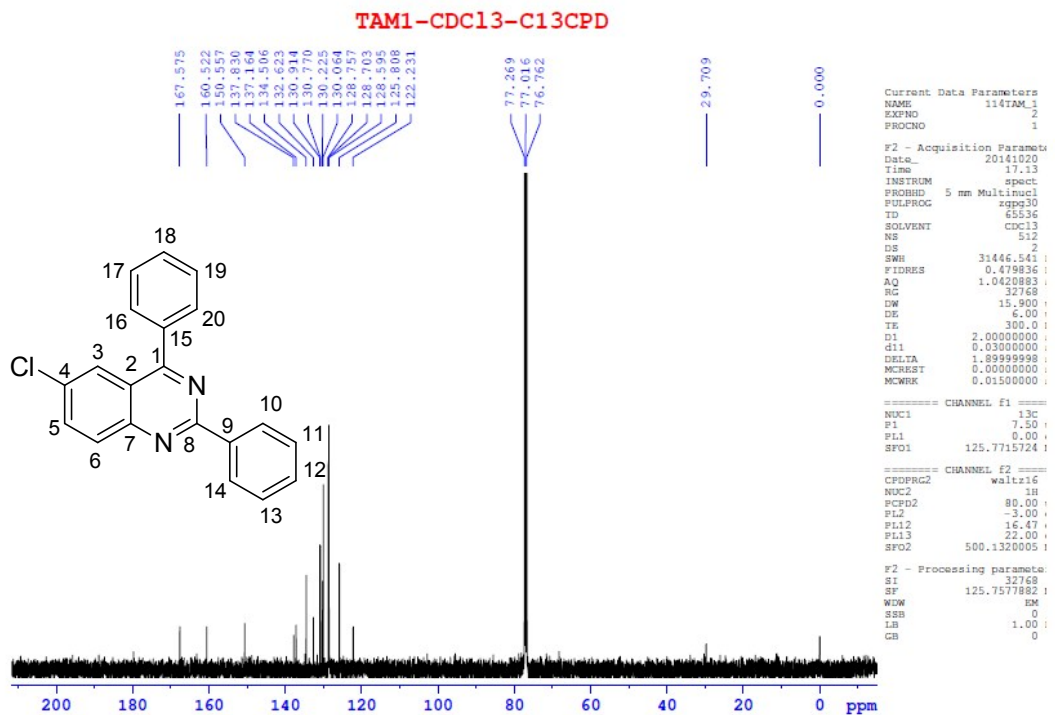
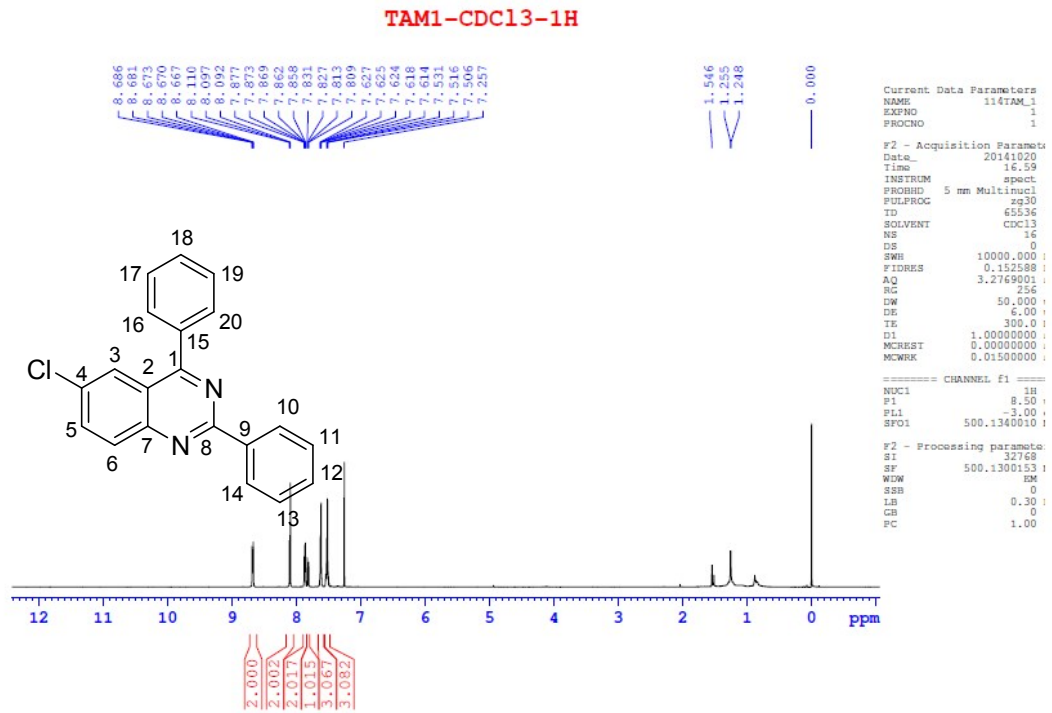


Fig. S15. ^1H NMR spectra and ^{13}C NMR of 6-chloro-2,4-diphenylquinazoline in CDCl_3 .

6-chloro-2,4-diphenylquinazoline: a pale yellow solid (246 mg, yield: 78%). This compound is known [5]. ¹H NMR (500 MHz, CDCl₃, TMS): δ (ppm) = 7.51-7.53 (m, 3H, *H*_{C17,C18,C19}), 7.61-7.63 (m, 3H, *H*_{C11,C12,C13}), 7.81-7.88 (dd, *J* = 2.0 Hz, *J* = 9.0 Hz, 1H, *H*_{C5}), 7.86-7.88 (m, 2H, *H*_{C16,C20}), 8.09-8.11 (m, 2H, *H*_{C3,C6}), 8.67-8.69 (m, 2H, *H*_{C10,C14}). ¹³C NMR (125 MHz, CDCl₃, TMS): δ (ppm) = 122.2, 125.8, 128.6, 128.7, 128.8, 130.1, 130.2, 130.8, 130.9, 132.6, 134.5, 137.2, 137.8, 150.6, 160.5, 167.6.

References

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