

Supporting Information for:

Cooperation between Cu⁺ and Cu²⁺ species in CuCoAl layered double hydroxide and substrate promoting effect afford a really simple protocol for the efficient synthesis of quinazolines

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Experimental

Chemicals and reagents

All the reagents and solvents in the study were analytically pure and were all purchased from Energy or Aladdin and used as received. 2-phenyl-1,2,3,4-tetrahydroquinazoline (**5**) were prepared from 2-aminobenzylamine and benzaldehyde according to the reported method.¹

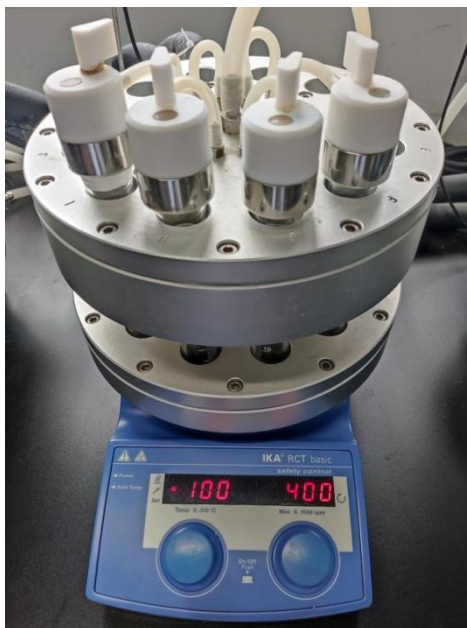
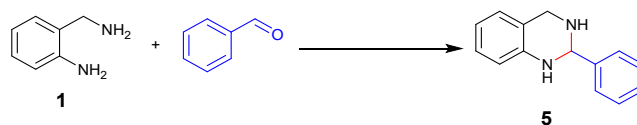


Fig. S1 The photographs of the reactor and the reaction.

Preparation and characterization of catalysts

CuCoAl-LDH sample was synthesized by a coprecipitation method. Specific preparation steps were as follows: a mixed solution of Cu(NO₃)₂·6H₂O (0.05 mol, 12.1 g), Co(NO₃)₂·6H₂O (0.05 mol, 14.6 g) and Al(NO₃)₃·9H₂O (0.05 mol, 18.8 g) in 150 mL of deionized water, and a solution of NaOH (0.33 mol, 13.2 g) in 150 mL deionized water were added dropwise into a solution of Na₂CO₃ (0.1 mol, 10.6 g) in 100 mL water with stirring (350 r/min) under 60 °C. The pH of the mixture was maintained at 10±0.2. After the complete of the adding, the suspension was stirred for another 5 h under the same temperature and then digested overnight. The resulting precipitate was filtrated and washed to neutrality with deionized water. The residue was then dried at 80 °C for 12 h to give the powdery CuCoAl-LDH sample. The contents of Cu, Co, and Al obtained from inductively coupled plasma (ICP) analysis in a Varian Vista-AX device were 21.60%, 19.38% and 8.95%, respectively. Similar procedures were employed to obtain the other LDHs samples.

X-ray diffraction (XRD) was conducted on a Rigaku powered diffraction unit with Cu K α radiation ($\lambda=1.5402$ Å, 40 kV, 300 mA). Scanning electron micrograph (SEM) was performed on a ZEISS/SUPRA55 instrument. X-ray photoelectron spectroscopy (XPS) was performed using a Thermo Scientific K-Alpha with a monochromatic Al X-ray source (excitation energy 1486.6 eV). The C 1s peak at 284.80 eV was used as calibration. X-band continuous-wave EPR spectra were obtained using a Bruker spectrometer equipped (EPR A300-10/12). The solution of 2-aminobenzylamine (1.0 mmol), benzyl alcohol

(1.0 mmol), CuCoAl-LDH (100 mg) in toluene (2 mL) was stirred for 1 h at 100 °C and 100 μ L of the solution was sampled in EPR tube, which were cooled 5 K prior to measurements. EPR analysis was carried out at low temperature on EPR spectrometer operated at 9.802 GHz.

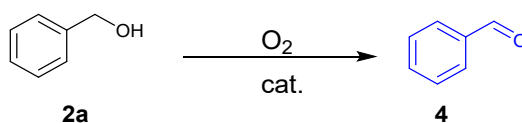
Catalytic cascade coupling/cyclization reaction between 2-aminobenzylamine and alcohols

Typically, a mixture of 2-aminobenzylamine (1.0 mmol), benzyl alcohol (1.0 mmol), CuCoAl-LDH (100 mg) and toluene (2 mL) was magnetically stirred in a carousel reaction tube (Fig. S1) at 100 °C under pure oxygen atmosphere (1 atm). TLC (thin-layer chromatography, petroleum ether/ethyl acetate (10:1, v/v)) was employed to monitor the reaction, and the conversion of the substrate and the selectivity of quinoline were obtained on the basis of the GC-MS analysis (SHIMADZU, GCMS-QP2010 SE). After the reaction, the catalyst was retrieved from the reaction mixture by simple filtration, and tested by recycling of the catalyst under the selected conditions.

The catalytic cascade coupling/cyclization between 2-aminobenzylamine and other alcohols were performed with similar procedure. After completion of the reaction, the reaction mixture was concentrated on a rotary evaporator under vacuum, then the residue was purified by flash column chromatography on silica gel (petroleum ether/ethyl acetate (10:1, v/v)) to yield corresponding quinolines. NMR spectra were recorded on a Bruker ADVANCE NMR spectrometer (500 MHz). The melting point was analyzed on a OptiMelt Automated Melting Point System.

Catalytic oxidation of benzyl alcohol

A mixture of benzyl alcohol (1.0 mmol), catalyst (100 mg) and toluene (2 mL) was magnetically stirred in a carousel reaction tube at 100 °C under pure oxygen atmosphere (1 atm). GC-MS (SHIMADZU, GCMS-QP2010 SE) was employed to monitor the reaction and analyze the conversion of benzyl alcohol.

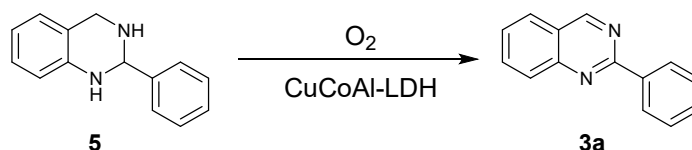


Catalytic cyclization reaction between 2-aminobenzylamine and benzaldehyde

A mixture of 2-aminobenzylamine (1.0 mmol), benzaldehyde (1.0 mmol), CuCoAl-LDH (100 mg) and toluene (2 mL) was magnetically stirred in a carousel reaction tube at 100 °C under nitrogen atmosphere (1 atm). GC-MS (SHIMADZU, GCMS-QP2010 SE) was employed to monitor the reaction and analyze the conversion of 2-aminobenzylamine.

Catalytic dehydrogenation of 2-phenyl-1,2,3,4-tetrahydroquinazoline (5)

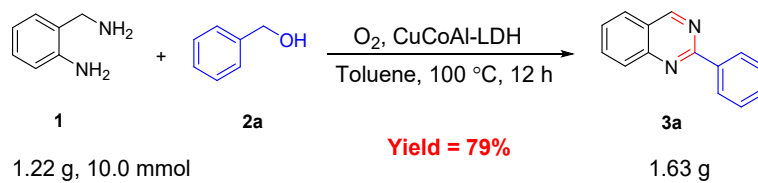
A mixture of 2-phenyl-1,2,3,4-tetrahydroquinazoline (5) (1.0 mmol), CuCoAl-LDH (100 mg) and toluene (2 mL) was magnetically stirred in a carousel reaction tube at 100 °C under pure oxygen atmosphere (1 atm). GC-MS (SHIMADZU, GCMS-QP2010 SE) was employed to monitor the reaction and analyze the conversion and yield of quinoline.



Large scale reaction between 2-aminobenzylamine and benzyl alcohol

A mixture of a mixture of 2-aminobenzylamine (1.22 g, 10.0 mmol), benzyl alcohol (1.08 g, 10.0 mmol), CuCoAl-LDH (1.0

g) and toluene (20 mL) in a 50 mL round-bottom flask was magnetically stirred at 100 °C under a 1 atm of pure oxygen atmosphere. The reaction was monitored by TLC (petroleum ether/ethyl acetate (10:1, v/v)). After completion of the reaction (12 h), the reaction mixture was cooled and separated by filtration to remove the catalyst. The filtrate was purified using flash chromatography to give 1.63 g of **3a** in a 79% yield (Scheme S1).



Scheme S1 Larger scale reaction.

Catalysts characterization

The hydrotalcite crystalline phase for the CuCoAl-LDH sample was confirmed by XRD pattern (Fig. S2A). The characteristic diffraction peaks of hydrotalcite around at $2\theta = 11.8^\circ, 23.7^\circ, 34.6^\circ, 39.4^\circ, 47.1^\circ, 60.4^\circ,$ and 61.7° , are assigned to planes (003), (006), (009), (015), (018), (110) and (113), respectively.²⁻⁵ The value of cell parameter $c = 3d(003)$ was calculated to be 2.25 nm, suggesting that the interlayers of the sample are mainly intercalated with CO_3^{2-} besides H_2O and OH^- .⁶ No obvious impurity peak was detected, suggestive of the high purity of the synthesized CuCoAl-LDH sample. These observations indicate that Cu, Co and Al species were doped into the lattices of hydrotalcite structure. To determine the microstructural property of CuCoAl-LDH, SEM characterization was employed. The SEM image depicted in Fig. S2B indicates that the morphology of CuCoAl-LDH shows the characteristic layered structure, which agreed with the anticipated layered LDH structure recognized by the XRD result. As shown in Fig. 1B, a lateral diameter distribution of about 50–150 nm is observed for the sample. ICP analysis showed that the ratio of the Cu/Co/Al was 1.03: 0.99:1, consistent with the theoretical value, suggesting that all the metallic ions have been precipitated during the preparation.

The FT-IR spectrum of CuCoAl-LDH depicted in Fig. S2C shows a broad and intense band around 3445 cm^{-1} , which can be assigned to the stretching vibration of the layer hydroxyl groups ($\nu_{\text{O-H}}$) and interlayer water molecules, and the broadening arises from extended hydrogen bonding.^{4, 7} A rather weak band at 1637 cm^{-1} is related to the bending mode of interlayer water molecules, and the band observed at about 1359 cm^{-1} is due to the asymmetric ν_3 mode of the interlayers carbonate anion.⁴ The absence of any band close to 1080 cm^{-1} suggests that the D_{3h} symmetry of the carbonate anion is retained in the interlayer region of the CuCoAl-LDH samples.⁷ In addition, Me–OH stretching and Me–O(H)–Me' bending vibrations could be found in the range of $400 - 1000\text{ cm}^{-1}$.^{4, 8}

The thermal behavior of the prepared CuCoAl-LDH was tracked by TG and the results are displayed in Fig. S2D. It is clear that TG curve, together with the corresponding differential (DTG) curve involve three stages for the weight loss. The first stage happened in the region from $120\text{ }^\circ\text{C}$ to about $180\text{ }^\circ\text{C}$, identified by a rather sharp peak of DTG curve, should correspond the loss of interlayer water without collapse of structure. This weight loss is immediately followed by a second weight loss arranged ca. $200 - 270\text{ }^\circ\text{C}$, generally ascribed to dehydroxylation of the brucite-like layers, and the loss of CO_2 from the interlayer,⁹ further demonstrating the interlayer anions of CO_3^{2-} . The corresponding DTG curve in this temperature range is rather broad, consistent with the reported results.⁷ The third small weight loss recorded between ca. $500 - 530\text{ }^\circ\text{C}$ with a relative weaker minimum is observed in the DTG curve, unlike the LDHs built up by Mg and Al, for which generally no further weight loss is recorded above $500\text{ }^\circ\text{C}$. The characteristic behavior for CuCoAl-LDH sample should probably result from the presence of some carbonate ions strongly held to the brucite-like sheets in Cu containing hydrotalcite like compounds.¹⁰

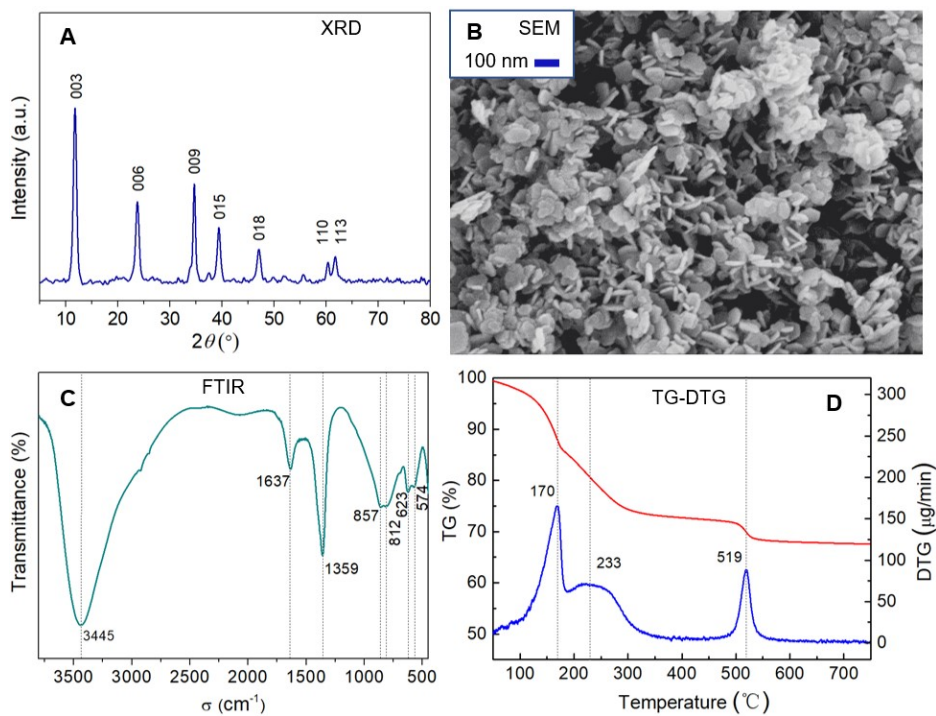


Fig. S2 XRD pattern (A), SEM image (B), FTIR spectrum (C) and TG-DTG curve (D) of the prepared CuCoAl-LDH.

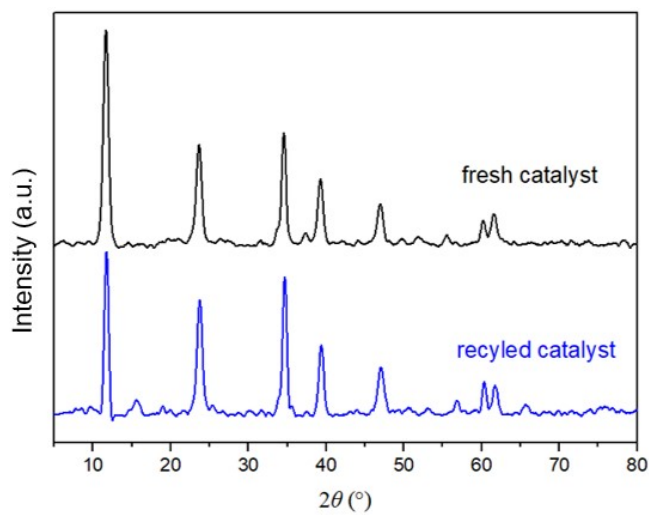


Fig. S3 XRD for fresh and recycled CuCoAl-LDH catalyst.

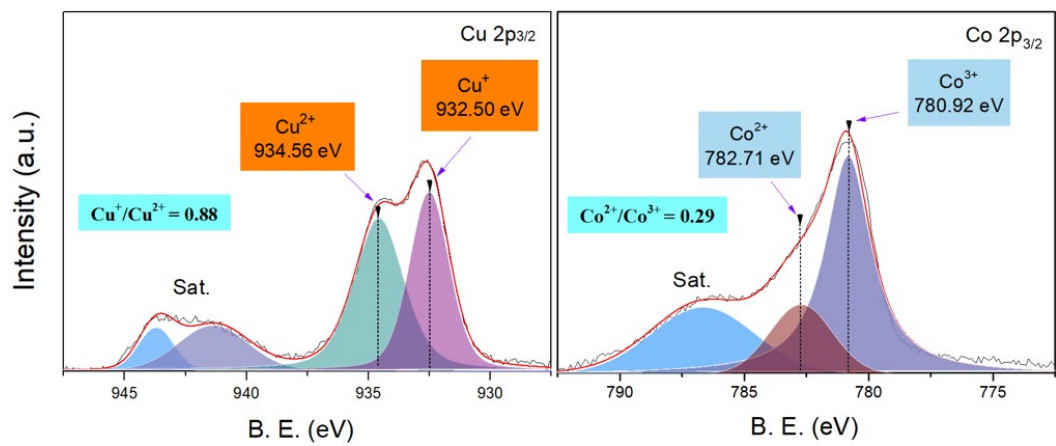
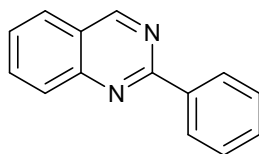
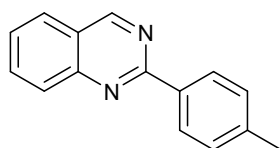


Fig. S4 XPS spectra for recycled CuCoAl-LDH catalyst.

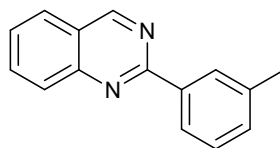
Spectrometric data for the products:



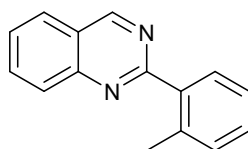
2-phenylquinazoline (**3a**)^{11, 12}: Yellow solid, mp. 104.0 – 104.6 °C. **¹H NMR** (500 MHz, CDCl₃) δ 9.47 (s, 1H), 8.66 (dd, *J* = 8.0, 1.3 Hz, 2H), 8.10 (d, *J* = 8.8 Hz, 1H), 7.90 (t, *J* = 7.3 Hz, 2H), 7.63-7.52 (m, 4H). **¹³C NMR** (126 MHz, CDCl₃) δ 161.05, 160.51, 150.77, 138.07, 134.12, 130.65, 128.67 (2C), 128.65 (2C), 128.62, 127.27, 127.14, 123.60. **HRMS** (ESI⁺) Calcd for C₁₄H₁₀N₂ [M+H]⁺ 206.0844, found 206.0843.



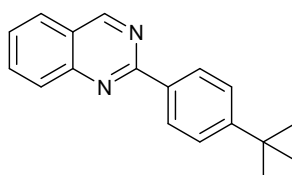
2-(*p*-tolyl)quinazoline (**3b**)¹¹: Yellow solid, mp. 111.5 – 112.2 °C. **¹H NMR** (500 MHz, CDCl₃) δ 9.44 (s, 1H), 8.55 (d, *J* = 8.2 Hz, 2H), 8.08 (d, *J* = 8.9 Hz, 1H), 7.93-7.85 (m, 2H), 7.58 (t, *J* = 7.4 Hz, 1H), 7.37 (d, *J* = 8.1 Hz, 2H), 2.47 (s, 3H). **¹³C NMR** (126 MHz, CDCl₃) δ 161.14, 160.44, 150.80, 140.88, 135.36, 134.04 (2C), 129.44 (2C), 128.57 (2C), 127.13, 127.03, 123.52, 21.56. **HRMS** (ESI⁺) Calcd for C₁₅H₁₂N₂ [M+H]⁺ 220.1000, found 220.1002.



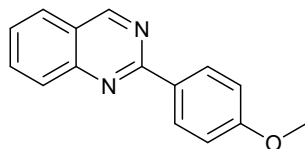
2-(*m*-tolyl)quinazoline (**3c**)¹¹: Yellow solid, mp. 101.1 – 102.2 °C. **¹H NMR** (500 MHz, CDCl₃) δ 9.49 (s, 1H), 8.50-8.39 (m, 2H), 8.12 (d, *J* = 8.4 Hz, 1H), 7.98-7.90 (m, 2H), 7.64 (t, *J* = 7.5 Hz, 1H), 7.46 (t, *J* = 7.6 Hz, 1H), 7.36 (d, *J* = 7.5 Hz, 1H), 2.52 (s, 3H). **¹³C NMR** (126 MHz, CDCl₃) δ 161.24, 160.47, 150.79, 138.30, 137.97, 134.11, 131.45, 129.11, 128.63, 128.60, 127.23, 127.14, 125.79, 123.59, 21.57. **HRMS** (ESI⁺) Calcd for C₁₅H₁₂N₂ [M+H]⁺ 220.1000, found 220.1001.



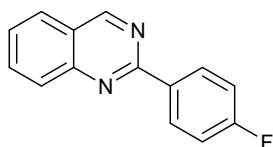
2-(*o*-tolyl)quinazoline (**3d**)¹¹: Yellow solid, mp. 100.5 – 102.5 °C. **¹H NMR** (500 MHz, CDCl₃) δ 9.53 (d, *J* = 0.5 Hz, 1H), 8.12 (dd, *J* = 8.4, 0.7 Hz, 1H), 8.02-7.90 (m, 3H), 7.71-7.66 (m, 1H), 7.39 (dd, *J* = 8.9, 6.7 Hz, 3H), 2.63 (s, 3H). **¹³C NMR** (126 MHz, CDCl₃) δ 164.07, 160.12, 150.41, 138.61, 137.38, 134.16, 131.31, 130.65, 129.33, 128.60, 127.57, 127.10, 126.01, 122.93, 21.04. **HRMS** (ESI⁺) Calcd for C₁₅H₁₂N₂ [M+H]⁺ 220.1000, found 220.1003.



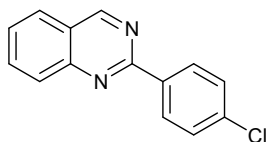
2-(4-(*tert*-butyl)phenyl)quinazoline (**3e**)¹¹: Yellow solid, mp. 81.1 – 83.2 °C. ¹H NMR (500 MHz, CDCl₃) δ 9.48-9.42 (m, 1H), 8.62-8.57 (m, 2H), 8.10 (d, *J* = 8.9 Hz, 1H), 7.91-7.85 (m, 2H), 7.62-7.54 (m, 3H), 1.43 (s, 9H). ¹³C NMR (126 MHz, CDCl₃) δ 161.13, 160.44, 153.95, 150.82, 135.37, 134.00, 128.61, 128.43, 127.12, 127.02, 125.66 (2C), 123.52 (2C), 34.91, 31.33 (3C). HRMS (ESI⁺) Calcd for C₁₈H₁₈N₂ [M+H]⁺ 262.1470, found 262.1475.



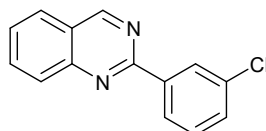
2-(4-methoxyphenyl)quinazoline (**3f**)^{11, 12}: Yellow solid, mp. 86.0 – 87.5 °C. ¹H NMR (500 MHz, CDCl₃) δ 9.53 (s, 1H), 8.12 (d, *J* = 8.5 Hz, 1H), 7.99 (d, *J* = 8.1 Hz, 1H), 7.97-7.92 (m, 2H), 7.68 (t, *J* = 7.5 Hz, 1H), 7.41-7.35 (m, 3H), 2.64 (s, 3H). ¹³C NMR (126 MHz, CDCl₃) δ 161.8, 160.8, 160.4, 150.8, 134.1, 130.7, 130.2 (2C), 128.4, 127.2, 126.8, 123.3, 114.0 (2C), 55.4. HRMS (ESI⁺) Calcd for C₁₅H₁₂N₂O [M+H]⁺ 232.0950, found 232.0953. This compound was known: X.F. Cheng, H.M. Wang, F.H. Xiao, G.J. Deng, Green Chem., 2016, 18, 5773-5776.



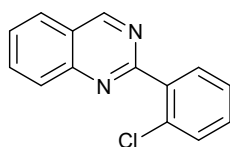
2-(4-fluorophenyl)quinazoline (**3g**)¹: Yellow solid, mp. 139.6 – 140.2 °C. ¹H NMR (500 MHz, CDCl₃) δ 9.43 (s, 1H), 8.64 (dd, *J* = 8.6, 5.7 Hz, 2H), 8.06 (d, *J* = 8.8 Hz, 1H), 7.90 (dd, *J* = 7.7, 5.6 Hz, 2H), 7.60 (t, *J* = 7.4 Hz, 1H), 7.22 (t, *J* = 8.6 Hz, 2H). ¹³C NMR (126 MHz, CDCl₃) δ 160.50, 160.08, 150.70, 134.20 (2C), 130.72, 130.65, 128.54 (2C), 127.28, 127.14, 123.48, 115.65, 115.47. HRMS (ESI⁺) Calcd for C₁₄H₉FN₂ [M+H]⁺ 224.0750, found 224.0754.



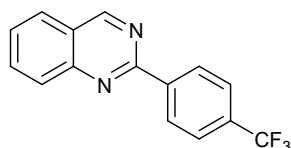
2-(4-chlorophenyl)quinazoline (**3h**)¹: Yellow solid, mp. 135.5 – 136.4 °C. ¹H NMR (500 MHz, CDCl₃) δ 9.47 (s, 1H), 8.63-8.55 (m, 2H), 8.09 (d, *J* = 8.5 Hz, 1H), 7.98-7.90 (m, 2H), 7.65 (dd, *J* = 11.0, 4.0 Hz, 1H), 7.55-7.49 (m, 2H). ¹³C NMR (126 MHz, CDCl₃) δ 160.56, 160.06, 150.70, 136.85, 136.53, 134.29, 129.92 (2C), 128.85 (2C), 128.61, 127.49, 127.18, 123.63. HRMS (ESI⁺) Calcd for C₁₄H₉ClN₂ [M+H]⁺ 240.0454, found 240.0450.



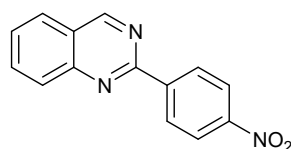
2-(3-chlorophenyl)quinazoline (**3i**)^{1, 12}: Yellow solid, mp. 150.4 – 152.0 °C. ¹H NMR (500 MHz, CDCl₃) δ 9.49-9.43 (m, 1H), 8.64 (t, *J* = 1.8 Hz, 1H), 8.58-8.47 (m, 1H), 8.13-8.05 (m, 1H), 7.97-7.89 (m, 2H), 7.64 (td, *J* = 7.3, 1.0 Hz, 1H), 7.48 (dd, *J* = 5.1, 2.8 Hz, 2H). ¹³C NMR (126 MHz, CDCl₃) δ 160.56, 159.68, 150.65, 139.87, 134.78, 134.32, 130.55, 129.86, 128.68, 128.66, 127.65, 127.16, 126.65, 123.75. HRMS (ESI⁺) Calcd for C₁₄H₉ClN₂ [M+H]⁺ 240.0454, found 240.0453.



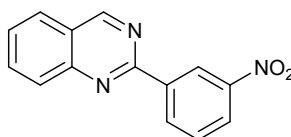
2-(2-chlorophenyl)quinazoline (**3j**)^{12, 13}: Yellow solid, mp. 66.5 – 67.8 °C. **¹H NMR** (500 MHz, CDCl₃) δ 9.56 (d, *J* = 0.5 Hz, 1H), 8.16 (dd, *J* = 8.5, 0.6 Hz, 1H), 8.06-7.96 (m, 2H), 7.88-7.82 (m, 1H), 7.73 (ddd, *J* = 8.0, 7.0, 1.0 Hz, 1H), 7.60-7.54 (m, 1H), 7.46-7.41 (m, 2H). **¹³C NMR** (126 MHz, CDCl₃) δ 161.99, 160.29, 150.37, 138.27, 134.45, 132.91, 131.80, 130.57, 130.37, 128.65, 128.11, 127.19, 126.93, 123.30. **HRMS** (ESI⁺) Calcd for C₁₄H₉ClN₂ [M+H]⁺ 240.0454, found 240.0453.



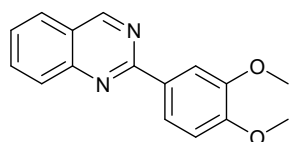
2-(4-(trifluoromethyl)phenyl)quinazoline (**3k**)^{11, 12}: Yellow solid, mp. 146.6 – 148.5 °C. **¹H NMR** (500 MHz, CDCl₃) δ 9.50 (d, *J* = 0.4 Hz, 1H), 8.76 (d, *J* = 8.1 Hz, 2H), 8.15-8.10 (m, 1H), 8.00-7.93 (m, 2H), 7.80 (d, *J* = 8.2 Hz, 2H), 7.72-7.64 (m, 1H). **¹³C NMR** (126 MHz, CDCl₃) δ 160.63, 159.61, 150.66, 141.31, 134.39, 132.25, 131.99, 128.83, 128.77, 127.88, 127.18, 125.53, 125.50, 125.47, 125.31, 123.84. **HRMS** (ESI⁺) Calcd for C₁₅H₉F₃N₂ [M+H]⁺ 274.0718, found 274.0714.



2-(4-nitrophenyl)quinazoline (**3l**)¹⁴: Yellow solid, mp. 163.4 – 165.0 °C. **¹H NMR** (500 MHz, CDCl₃) δ 9.52 (s, 1H), 8.81 (d, *J* = 8.9 Hz, 2H), 8.14 (d, *J* = 8.4 Hz, 1H), 8.09 (d, *J* = 8.6 Hz, 2H), 8.00 (dd, *J* = 12.2, 5.5 Hz, 2H), 7.72 (t, *J* = 7.5 Hz, 1H). **¹³C NMR** (126 MHz, CDCl₃) δ 160.73, 158.77, 150.59, 149.17, 143.84, 140.05, 134.63, 129.39 (2C), 128.85, 128.36, 127.25, 123.76 (2C). **HRMS** (ESI⁺) Calcd for C₁₄H₉N₃O₂ [M+H]⁺ 251.0695, found 251.0693.

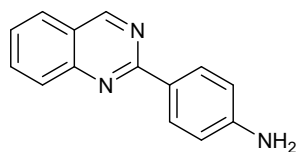


2-(3-nitrophenyl)quinazoline (**3m**)¹³: Pale yellow solid, mp. 100.7 – 102.3 °C. **¹H NMR** (500 MHz, CDCl₃) δ 9.53 (s, 2H), 9.00 (d, *J* = 7.8 Hz, 1H), 8.36 (d, *J* = 1.3 Hz, 1H), 8.15 (d, *J* = 8.4 Hz, 1H), 8.12-7.83 (m, 2H), 7.72 (q, *J* = 8.1 Hz, 2H). **¹³C NMR** (126 MHz, CDCl₃) δ 160.80, 158.70, 150.62, 139.91, 134.63, 134.61, 134.24, 129.56, 128.78, 128.12, 127.25, 125.04, 123.97, 123.62. **HRMS** (ESI⁺) Calcd for C₁₄H₉N₃O₂ [M+H]⁺ 251.0695, found 251.0695. This compound was known: (a) A.R. Tiwari, B.M. Bhanage, *Org. Biomol. Chem.*, 2016, 14, 10567-10571.

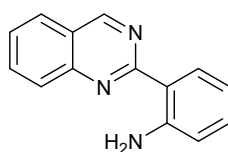


2-(3,4-dimethoxyphenyl)quinazoline (**3n**)¹⁵: Yellow solid, mp. 112.2 – 113.8 °C. **¹H NMR** (500 MHz, CDCl₃) δ 9.42 (d, *J* = 0.4 Hz, 1H), 8.27 (dd, *J* = 8.4, 2.0 Hz, 1H), 8.21 (d, *J* = 2.0 Hz, 1H), 8.06 (dd, *J* = 8.3, 0.8 Hz, 1H), 7.93-7.85 (m, 2H), 7.61-7.55 (m, 1H), 7.03 (d, *J* = 8.5 Hz, 1H), 4.08 (s, 3H), 3.99 (s, 3H). **¹³C NMR** (126 MHz, CDCl₃) δ 160.72, 160.36, 151.37,

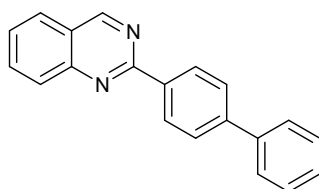
150.80, 149.05, 134.07, 130.91, 128.41, 127.16, 126.87, 123.35, 122.00, 111.07, 110.85, 56.03, 55.99. **HRMS** (ESI⁺) Calcd for C₁₆H₁₄N₂O₂ [M+H]⁺ 266.1055, found 266.1056.



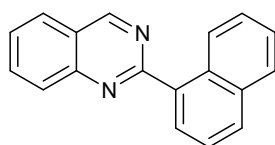
4-(quinazolin-2-yl)aniline (**3o**)¹⁶: Pale yellow solid, mp. 171.4 – 172.2 °C. **¹H NMR** (500 MHz, CDCl₃) δ 9.51-9.42 (m, 1H), 8.66 (d, *J* = 8.1 Hz, 2H), 8.05-7.98 (m, 1H), 7.92 (dt, *J* = 8.4, 7.2 Hz, 2H), 7.64-7.59 (m, 1H), 6.88-6.80 (m, 2H), 6.59 (s, 2H). **¹³C NMR** (126 MHz, CDCl₃) δ 160.73, 158.77, 150.59, 149.17, 143.84, 140.05, 134.63 (2C), 129.39, 128.85, 128.36, 127.25, 123.76 (2C). **HRMS** (ESI⁺) Calcd for C₁₄H₁₁N₃ [M+H]⁺ 221.0953, found 221.0954. This compound was known: M. Saha, P. Mukherjee, A.R. Das, Tetrahedron lett., 2017, 58, 2044-2049.



2-(quinazolin-2-yl)aniline (**3p**)¹⁷: Pale yellow solid, mp. 86.4 – 88.2 °C. **¹H NMR** (500 MHz, CDCl₃) δ 9.54-9.34 (m, 1H), 8.66 (dd, *J* = 8.1, 1.6 Hz, 1H), 8.09-7.97 (m, 1H), 7.91 (ddd, *J* = 8.4, 7.8, 4.4 Hz, 2H), 7.68-7.58 (m, 1H), 7.29 (s, 1H), 6.91-6.78 (m, 2H), 6.59 (s, 2H). **¹³C NMR** (126 MHz, CDCl₃) δ 162.49, 159.80, 149.65, 148.93, 134.09, 131.78, 131.39, 127.91, 127.18, 126.90, 122.52, 119.06, 117.14, 116.97. **HRMS** (ESI⁺) Calcd for C₁₄H₁₁N₃ [M+H]⁺ 221.0953, found 221.0953. This compound was known: T.T. Duan, T.R. Zhai, H.H. Liu, Z.L. Yan, Y. Zhao, L. Feng, C. Ma, Org. Biomol. Chem., 2016, 14, 6561-6567.

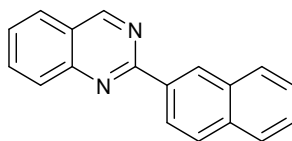


2-([1,1'-biphenyl]-4-yl)quinazoline (**3q**)¹⁸: White solid, mp. 137.4 – 141.8 °C. **¹H NMR** (500 MHz, CDCl₃) δ 9.42 (s, 1H), 8.68 (d, *J* = 8.1 Hz, 2H), 8.07 (d, *J* = 8.8 Hz, 1H), 7.86 (dd, *J* = 7.6, 6.1 Hz, 2H), 7.76 (d, *J* = 8.0 Hz, 2H), 7.68 (d, *J* = 7.9 Hz, 2H), 7.55 (t, *J* = 7.5 Hz, 1H), 7.46 (t, *J* = 7.5 Hz, 2H), 7.36 (t, *J* = 7.2 Hz, 1H). **¹³C NMR** (126 MHz, CDCl₃) δ 160.83, 160.53, 150.83, 143.27 (2C), 140.63, 137.03, 134.17 (2C), 129.11, 128.90 (2C), 128.65, 127.73, 127.38, 127.28, 127.24, 127.19 (2C), 123.63. **HRMS** (ESI⁺) Calcd for C₂₀H₁₄N₂ [M+H]⁺ 282.1157, found 282.1155. This compound was known: J.N. Yang, Z.B. Xie, L. Jin, X.H. Chen, Z.G. Le, Org. Biomol. Chem., 2022, 20, 3558-3563.

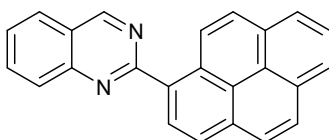


2-(naphthalen-1-yl)quinazoline (**3r**)¹²: Yellow solid, mp. 126.3 – 128.5 °C. **¹H NMR** (500 MHz, CDCl₃) δ 9.60 (s, 1H), 8.76 (d, *J* = 8.4 Hz, 1H), 8.26-8.17 (m, 2H), 8.03 (d, *J* = 8.2 Hz, 1H), 8.00-7.94 (m, 3H), 7.67 (td, *J* = 7.6, 2.9 Hz, 2H), 7.58 (ddd, *J* = 15.3, 8.1, 3.9 Hz, 2H). **¹³C NMR** (126 MHz, CDCl₃) δ 163.48, 160.46, 150.58, 136.35, 134.37, 134.23, 131.27, 130.45, 129.71, 128.66, 128.55, 127.77, 127.18, 126.93, 125.97 (2C), 125.37, 123.14. **HRMS** (ESI⁺) Calcd for C₁₈H₁₂N₂ [M+H]⁺

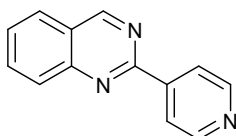
256.1000, found 256.1000. This compound was known: R. Gujjarappa, S.K. Maity, C.K. Hazra, N. Vodnala, S. Dhiman, A. Kumar, U. Beifuss, C.C. Malakar, Eur. J. Org. Chem., 2018, 33, 4628-4638.



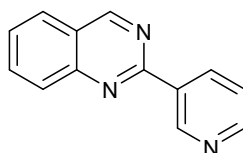
2-(naphthalen-2-yl)quinazoline (**3s**)^{12, 19}: Yellow solid, mp. 131.5 – 133.0 °C. **¹H NMR** (500 MHz, CDCl₃) δ 9.50 (s, 1H), 9.19 (s, 1H), 8.77 (dd, *J* = 8.6, 1.6 Hz, 1H), 8.15 (d, *J* = 8.8 Hz, 1H), 8.10-8.06 (m, 1H), 8.02 (d, *J* = 8.6 Hz, 1H), 7.94-7.90 (m, 3H), 7.58 (ddd, *J* = 10.2, 9.3, 4.8 Hz, 3H); **¹³C NMR** (126 MHz, CDCl₃) δ 161.00, 160.53, 150.83, 135.40, 134.71, 134.20, 133.45, 129.32, 129.00, 128.64, 128.32, 127.76, 127.32, 127.19, 127.14, 126.27, 125.46, 123.63. **HRMS** (ESI⁺) Calcd for C₁₈H₁₂N₂ [M+H]⁺ 256.1000, found 256.1000. This compound was known: S. Yao, K.J. Zhou, J.B. Wang, H.G. Cao, L. Yu, J.Z. Wu, P.H. Qiu, Q. Xu, Green Chem., 2017, 19, 2945-2951.



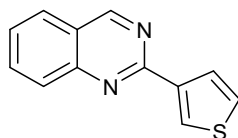
2-(4,6-dihydropyren-1-yl)quinazoline (**3t**)^{13, 18}: Yellow solid, mp. 157.4 – 163.3 °C. **¹H NMR** (500 MHz, CDCl₃) δ 9.64 (d, *J* = 0.6 Hz, 1H), 9.07 (d, *J* = 9.3 Hz, 1H), 8.71 (d, *J* = 8.0 Hz, 1H), 8.32 (d, *J* = 8.0 Hz, 1H), 8.25 – 8.19 (m, 3H), 8.19 – 8.10 (m, 3H), 8.05 – 7.93 (m, 3H), 7.68 (ddd, *J* = 8.1, 7.0, 1.0 Hz, 1H). **¹³C NMR** (126 MHz, CDCl₃) δ 163.83, 160.54, 150.73, 134.46, 133.38, 132.45, 131.34, 130.88, 129.52, 129.08, 128.70, 128.48, 127.84 (2C), 127.50, 127.24, 126.07, 125.63, 125.38, 125.29, 125.27, 124.96, 124.77, 122.99. **HRMS** (ESI⁺) Calcd for C₂₄H₁₆N₂ [M+H]⁺ 332.1313, found 332.1317. This compound was known: R. Gujjarappa, S.K. Maity, C.K. Hazra, N. Vodnala, S. Dhiman, A. Kumar, U. Beifuss, C.C. Malakar, Eur. J. Org. Chem., 2018, 33, 4628-4638.



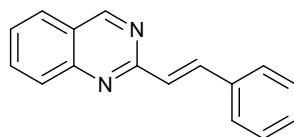
2-(pyridin-4-yl)quinazoline (**3u**)^{12, 13}: Yellow solid, mp. 125.3 – 126.3 °C. **¹H NMR** (500 MHz, CDCl₃) δ 9.41 (s, 1H), 8.76 (d, *J* = 4.2 Hz, 2H), 8.39 (d, *J* = 4.6 Hz, 2H), 8.05 (d, *J* = 8.7 Hz, 1H), 7.89 (dd, *J* = 9.8, 4.1 Hz, 2H), 7.61 (t, *J* = 7.5 Hz, 1H). **¹³C NMR** (126 MHz, CDCl₃) δ 160.65, 158.78, 150.43 (3C), 145.20, 134.45, 128.80, 128.25, 127.13, 124.07, 122.28 (2C). **HRMS** (ESI⁺) Calcd for C₁₃H₉N₃ [M+H]⁺ 207.0796, found 207.0796. This compound was known: X.F. Cheng, H.M. Wang, F.H. Xiao, G.J. Deng, Green Chem., 2016, 18, 5773-5776.



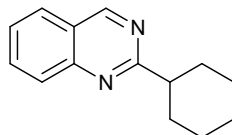
2-(pyridin-3-yl)quinazoline (**3v**)^{11, 20}: Yellow oil. **¹H NMR** (500 MHz, CDCl₃) δ 9.77 (d, *J* = 1.2 Hz, 1H), 9.41 (s, 1H), 8.82 (dt, *J* = 8.0, 1.8 Hz, 1H), 8.70 (dd, *J* = 4.6, 1.1 Hz, 1H), 8.04 (d, *J* = 8.8 Hz, 1H), 7.95-7.84 (m, 2H), 7.60 (t, *J* = 7.5 Hz, 1H), 7.42 (dd, *J* = 7.9, 4.8 Hz, 1H). **¹³C NMR** (126 MHz, CDCl₃) δ 160.62, 159.03, 151.10, 150.52, 150.15, 135.80, 134.40, 133.52, 128.58, 127.79, 127.18, 123.75, 123.43. **HRMS** (ESI⁺) Calcd for C₁₃H₉N₃ [M+H]⁺ 207.0796, found 207.0794.



2-(thiophen-3-yl)quinazoline (**3w**)¹¹: Yellow solid, mp. 100.1 – 101.2 °C. **¹H NMR** (500 MHz, CDCl₃) δ 9.40 (d, *J* = 0.6 Hz, 1H), 8.45 (dd, *J* = 3.1, 1.2 Hz, 1H), 8.08 (dd, *J* = 5.0, 1.2 Hz, 1H), 8.04 (d, *J* = 8.9 Hz, 1H), 7.92-7.85 (m, 2H), 7.59 (ddd, *J* = 7.9, 7.0, 1.0 Hz, 1H), 7.44 (dd, *J* = 5.1, 3.1 Hz, 1H). **¹³C NMR** (126 MHz, CDCl₃) δ 160.56, 158.25, 150.72, 142.06, 134.16, 128.39, 128.33, 127.72, 127.19, 127.05, 126.13, 123.39. **HRMS** (ESI⁺) Calcd for C₁₂H₈N₂S [M+H]⁺ 212.0408, found 212.0407.



(*E*)-2-styrylquinazoline (**3x**)²⁰: White solid, mp. 122 – 123 °C. **¹H NMR** (500 MHz, CDCl₃) δ 9.33 (s, 1H), 8.15 (d, *J* = 16.0 Hz, 1H), 7.97 (d, *J* = 8.8 Hz, 1H), 7.85 (t, *J* = 6.9 Hz, 2H), 7.67 (d, *J* = 7.8 Hz, 2H), 7.54 (t, *J* = 7.4 Hz, 1H), 7.44 – 7.36 (m, 3H), 7.36 – 7.30 (m, 1H). **¹³C NMR** (126 MHz, CDCl₃) δ 161.27, 160.24, 150.56, 138.57, 136.20, 134.24 (2C), 129.09 (2C), 128.84 (2C), 128.12, 127.91, 127.71, 127.20, 123.35. **HRMS** (ESI⁺) Calcd for C₁₆H₁₂N₂ [M+H]⁺ 232.1000, found 232.1005. This compound was known: (a) B. Han, X.L. Yang, C. Wang, Y.W. Bai, T.C. Pan, X. Chen, W. Yu, J. Org. Chem., 2012, 77, 1136-1142. (b) R. Gujjarappa, S.K. Maity, C.K. Hazra, N. Vodnala, S. Dhiman, A. Kumar, U. Beifuss, C.C. Malakar, Eur. J. Org. Chem., 2018, 33, 4628-4638.



2-cyclohexylquinazoline (**3y**)¹²: Yellow oil. **¹H NMR** (500 MHz, CDCl₃) δ 9.38 (s, 1H), 8.02 (s, 1H), 7.91 (s, 2H), 7.60 (s, 1H), 3.12-3.04 (m, 1H), 2.11 (dd, *J* = 13.6, 1.8 Hz, 2H), 1.96-1.90 (m, 2H), 1.82-1.74 (m, 4H), 1.50 (dt, *J* = 12.8, 3.3 Hz, 2H). **¹³C NMR** (126 MHz, CDCl₃) δ 170.94, 159.79, 149.64, 133.89, 127.90, 126.88, 126.86, 123.29, 47.97, 31.98 (2C), 26.35, 26.06 (2C). **HRMS** (ESI⁺) Calcd for C₁₄H₁₆N₂ [M+H]⁺ 212.1313, found 212.1312.

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NMR spectra

