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Supporting Information

Cucurbit[6]uril supported β -Ni(OH)₂ nanoparticles as heterogeneous catalyst for the synthesis of quinazolines *via* acceptorless dehydrogenative coupling of alcohols with nitriles

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Materials and Instrumentations

All chemicals and reagents were purchased from Alfa Aeser, TCI chemicals, Sigma Aldrich and Loba. FTIR spectroscopic analysis was recorded on a Perkin Elmer spectrometer between 400 and 4000 cm⁻¹ using KBr pellets. The surface morphology was observed by Field Emission Microscope (FESEM) of model FESEM Supra 55 (Carl Zeiss, Germany). The energy-dispersive X-ray spectroscopy (EDX) analysis was carried out on an electron probe microscope Supra 55 (Carl Zeiss, Germany). Powdered X-ray diffraction (PXRD) of the catalyst was done by Rigaku Smartlab with CuK α radiation ($\lambda = 0.15418$ nm). X-ray photoelectron (XPS) analysis was performed on a 5000 Versa probe III. High Resolution Transmission Electron Microscope (HRTEM-200 kV) image was observed using model Talos F200X G2. The thermogravimetric analysis (TGA) was done using EXSTAR, SI 6300 EXSTAR. Inductively Coupled Plasma – Atomic Emission Spectroscopy (ICP-OES) was carried out using Thermo Fisher Scientific, USA, Icap 7400Duo.



Figure S1. EDX of β -Ni(OH)₂-CB[6] nanocomposite



Figure S2: TGA thermograph of β -Ni(OH)₂-CB[6] nanocomposite



Figure S3. FTIR of β -Ni(OH)₂-CB[6] nanocomposite after 4th cycle

Synthesis of Cucurbit[6]uril, CB[6]

CB[6] was synthesised by the reported method.¹ To a mixture of glycouril (40 mmol) and formaldehyde (37% in water, 91 mmol), 9M sulphuric acid (20 ml) was added. The mixture was heated for 24 h at 75 °C to give a clear solution. The temperature was further raised to 100 °C for 12 h. The clear reaction solution so obtained was then allowed to cool and poured into water (200 ml) followed by acetone (~950 ml) to produce a white precipitate. The precipitate was separated by decantation, washed with the acetone/water (1:4) and then filtered. By the fractional dissolution of other CB counterparts with acetone/water (1:2) the primary product CB[6] was isolated.

Spectral data (¹H and ¹³C NMR) of quinazolines.



2-phenylquinazoline (Table 2, 3a): White solid (90% yield), ¹H NMR (400 MHz, CDCl₃): δ = 9.46 (s, 1H), 8.64-8.61 (m, 2H), 8.08 (d, *J* = 12 Hz, 1H), 7.91-7.87 (m, 2H), 7.61-7.51 (m, 4H), ¹³C NMR (CDCl₃, 100 MHz): 161.0, 160.5, 150.7, 138.0, 134.1, 130.6, 128.6, 128.6, 127.2, 127.1, 123.6.



2-(4-fluorophenyl)quinazoline (Table 2, 3b): White solid (91% yield), ¹H NMR (400 MHz, CDCl₃): δ = 9.42 (s, 1H), 8.64-8.59 (m, 2H), 8.04 (d, *J* = 12 Hz, 1H), 7.90-7.86 (m, 2H), 7.61-7.51 (t, 1H), 7.22-7.17 (m, 2H), ¹³C NMR (CDCl₃, 100 MHz): 160.5, 160.1, 150.8, 134.2, 130.7, 130.6, 128.5, 127.2, 127.1, 123.4, 115.6, 115.4.



2-(4-chlorophenyl)quinazoline (Table 2, 3c): White solid (94% yield), ¹H NMR (400 MHz, CDCl₃): δ = 9.44 (s, 1H), 8.58-8.55 (m, 2H), 8.06 (d, *J* = 12 Hz, 1H), 7.93-7.89 (m, 2H), 7.64-7.60 (m, 1H), 7.50-7.48 (m, 2H), ¹³C NMR (CDCl₃, 100 MHz): 160.5, 160.0, 150.7, 136.8, 136.5, 134.2, 129.9, 128.8, 128.6, 127.5, 127.1, 123.5.



2-(4-bromophenyl)quinazoline (Table 2, 3d): White solid (92% yield), ¹H NMR (400 MHz, CDCl₃): $\delta = 9.43$ (s, 1H), 8.50-8.47 (m, 2H), 8.06 (d, J = 8 Hz, 1H), 7.92-7.88 (m, 2H), 7.66-7.60

(m, 3H), ¹³C NMR (CDCl₃, 100 MHz): 160.5, 160.1, 150.6, 136.9, 134.3, 131.8, 130.2, 128.5, 127.5, 127.1, 125.4, 123.6.



2-(3-bromophenyl)quinazoline (Table 2, 3e): White solid (82% yield), ¹H NMR (400 MHz, CDCl₃): δ = 9.47 (s, 1H), 8.80 (s, 1H), 8.56 (d, *J* = 8 Hz, 1H), 8.09 (d, *J* = 12 Hz, 1H), 7.96-7.91 (m, 2H), 7.67-7.62 (m, 2H), 7.43-7.39 (m, 1H), ¹³C NMR (CDCl₃, 100 MHz): 160.6, 159.7, 150.7, 140.1, 134.4, 133.4, 131.6, 130.1, 128.6, 127.8, 127.1, 127.1, 123.7, 122.9.



2-(4-(trifluoromethyl)phenyl)quinazoline (Table 2, 3f): White solid (96% yield), ¹H NMR (400 MHz, CDCl₃): δ = 9.48 (s, 1H), 8.73 (d, *J* = 8 Hz, 1H), 8.10 (d, *J* = 8 Hz, 1H), 7.96-7.92 (m, 2H), 7.78 (d, *J* = 8 Hz, 2H), 7.67-7.63 (m, 1H), ¹³C NMR (CDCl₃, 100 MHz): 160.6, 159.6, 150.6, 141.3, 134.4, 132.2, 131.9, 128.8, 128.7, 127.8, 127.1, 125.58, 125.51, 125.47, 123.8.



2-p-tolylquinazoline (Table 2, 3g): White solid (92% yield), ¹H NMR (400 MHz, CDCl₃): δ = 9.44 (s, 1H), 8.51 (d, *J* = 8 Hz, 2H), 8.07 (d, *J* = 8 Hz, 1H), 7.92-7.87 (m, 2H), 7.61-7.57 (m, 2H), 7.34 (d, *J* = 8 Hz, 2H), 2.44 (s, 3H), ¹³C NMR (CDCl₃, 100 MHz): 161.2, 160.4, 150.8, 140.8, 135.3, 134.0, 129.4, 128.5, 127.1, 127.5, 123.5, 21.3.



2-(4-methoxyphenyl)quinazoline (Table 2, 3h): White solid (93% yield), ¹H NMR (400 MHz, CDCl₃): δ = 9.41 (s, 1H), 8.59-8.55 (m, 2H), 8.03 (d, *J* = 8 Hz, 1H), 7.89-7.85 (m, 2H), 7.57-7.54 (m, 1H), 7.06-7.02 (m, 2H), 3.91 (s, 3H), ¹³C NMR (CDCl₃, 100 MHz): 161.8, 160.8, 160.4, 150.9, 134.0, 130.6, 130.1, 128.4, 127.1, 126.8, 123.3, 114.0, 55.42.



2-(3-methoxyphenyl)quinazoline (Table 2, 3i): White solid (79% yield), ¹H NMR (400 MHz, CDCl₃): δ = 9.43 (s, 1H), 8.24-8.18 (m, 2H), 8.08 (d, *J* = 8 Hz, 1H), 7.90-786 (m, 2H), 7.60-7.56 (m, 1H), 7.46-7.42 (t, 1H), 7.08-7.05 (m, 1H), ¹³C NMR (CDCl₃, 100 MHz): 160.8, 160.4, 150.7, 139.4, 134.1, 129.5, 128.6, 127.3, 127.1, 123.6, 121.1, 117.2, 113.0, 55.2.



2-(pyridin-3-yl)quinazoline (Table 2, 3j): Yellow solid (83% yield), ¹H NMR (400 MHz, CDCl₃): δ = 9.49 (s, 1H), 8.80-8.79 (m, 2H), 8.45-8.44 (m, 2H), 8.13-8.10 (m, 1H), 8.97-8.93 (m, 2H), 7.70-7.66 (m, 1H), ¹³C NMR (CDCl₃, 100 MHz): 160.7, 158.9, 150.5, 150.4, 145.3, 134.5, 128.8, 128.3, 127.2, 124.1, 122.4.



2-(thiophen-2-yl)quinazoline (Table 2, 3k): White solid (81% yield), ¹H NMR (400 MHz, CDCl₃): δ = 9.26 (s, 1H), 8.06 (d, *J* = 4 Hz, 1H), 7.92 (d, *J* = 8 Hz, 1H), 7.80-7.77 (m, 2H), 7.49-7.43 (m, 2H), 7.12-7.10 (m, 1H), ¹³C NMR (CDCl₃, 100 MHz): 160.5, 157.7, 150.5, 143.8, 134.4, 129.9, 129.1, 128.4, 128.1, 127.3, 127.0, 123.4.



6-chloro-2-phenylquinazoline (Table 2, 3l): White solid (76% yield), ¹H NMR (400 MHz, CDCl₃): δ = 9.38 (s, 1H), 8.60-8.57 (m, 2H), 8.02 (d, *J* = 8 Hz, 1H), 7.88 (d, *J* = 4 Hz, 1H), 7.83-7.80 (m, 1H), 7.55-7.51 (m, 3H), ¹³C NMR (CDCl₃, 100 MHz): 161.3, 159.5, 149.2, 137.5, 135.1, 132.8, 130.9, 130.3, 128.7, 125.8, 123.9.



6-chloro-2-(4-fluorophenyl)quinazoline (Table 2, 3m): White solid (80% yield), ¹H NMR (400 MHz, CDCl₃): δ = 9.29 (s, 1H), 8.55-8.51 (m, 2H), 7.93 (d, *J* = 8 Hz, 1H), 7.82 (d, *J* = 4 Hz, 1H), 7.76-7.74 (m, 1H), 7.15-7.10 (m, 2H), ¹³C NMR (CDCl₃, 100 MHz): 160.3, 159.4, 149.2, 135.3, 133.7, 132.7, 130.7, 130.6, 130.2, 125.8, 123.8, 115.7, 115.5.



6-chloro-2-(4-chlorophenyl)quinazoline (Table 2, 3n): White solid (82% yield), ¹H NMR (400 MHz, CDCl₃): δ = 9.29 (s, 1H), 8.46 (d, *J* = 8 Hz, 2H), 8.93 (d, *J* = 8 Hz, 1H), 7.83 (s, 1H), 7.77-7.74 (m, 1H), 7.41 (d, *J* = 12 Hz, 2H), ¹³C NMR (CDCl₃, 100 MHz): 160.2, 159.4, 149.1, 135.1, 136.0, 135.2, 133.0, 130.3, 129.8, 128.9, 125.8, 124.0



2-(4-bromophenyl)-6-chloroquinazoline (Table 2, 30): White solid (78% yield), ¹H NMR (400 MHz, CDCl₃): δ = 9.29 (s, 1H), 8.39 (d, *J* = 8 Hz, 2H), 7.93 (d, *J* = 8 Hz, 1H), 7.83 (s, 1H), 7.77-7.74 (m, 1H), 7.59-7.57 (m, 2H), ¹³C NMR (CDCl₃, 100 MHz): 160.3, 159.5, 149.1, 136.5, 135.2, 133.0, 131.8, 130.3, 130.1, 128.7, 128.5, 125.8, 124.0.



6-chloro-2-(4-(trifluoromethyl)phenyl)quinazoline (Table 2, 3p): White solid (85% yield), ¹H NMR (400 MHz, CDCl₃): δ = 9.26 (s, 1H), 8.58 (d, *J* = 8 Hz, 2H), 7.90 (d, *J* = 8 Hz, 1H), 7.78 (s, 1H), 7.74-7.71 (m, 1H), 7.66 (d, *J* = 8 Hz, 2H), ¹³C NMR (CDCl₃, 100 MHz): 159.7, 159.5, 149.0, 140.7, 135.3, 133.4, 132.5, 132.1, 130.3, 130.4, 128.8, 125.8, 125.3, 124.2, 122.8.



6-chloro-2-p-tolylquinazoline (Table 2, 3q): White solid (77% yield), ¹H NMR (400 MHz, CDCl₃): δ = 9.29 (s, 1H), 8.41-8.39 (m, 2H), 7.93 (d, *J* = 8 Hz, 1H), 7.80 (d, *J* = 4 Hz, 1H), 7.75-7.72 (m, 1H), 7.26 (d, *J* = 8 Hz, 2H), 2.37 (s, 3H), ¹³C NMR (CDCl₃, 100 MHz): 161.3, 159.4, 149.2, 141.2, 135.0, 134.8, 132.4, 130.3, 129.4, 128.6, 125.8, 123.9, 21.6.



6-chloro-2-(4-methoxyphenyl)quinazoline (Table 2, 3r): White solid (79% yield), ¹H NMR (400 MHz, CDCl₃): δ = 9.29 (s, 1H), 8.51-8.48 (m, 2H), 7.92 (d, *J* = 12 Hz, 1H), 7.82 (s, 1H), 7.76-7.73 (m, 1H), 7.00-6.97 (m, 2H), 3.85 (s, 3H), ¹³C NMR (CDCl₃, 100 MHz): 162.5, 161.1, 159.4, 141.4, 135.0, 132.2, 130.2, 130.1, 125.8, 123.7, 114.0, 55.7.



6-chloro-2-(3-methoxyphenyl)quinazoline (Table 2, 3s): White solid (67% yield), ¹H NMR (400 MHz, CDCl₃): $\delta = 9.32$ (s, 1H), 8.41-8.11 (m, 2H), 7.96 (d, J = 8 Hz, 1H), 7.83 (d, J = 4 Hz, 1H), 7.75-7.74 (m, 1H), 7.37 (t, J = 8 Hz, 1H), 7.01-6.98 (m, 1H), 3.87 (s, 3H), ¹³C NMR (CDCl₃, 100 MHz): 160.0, 159.4, 149.2, 139.0, 135.1, 132.8, 130.4, 129.7, 125.8, 124.0, 121.1, 117.5, 113.0, 55.4. HRMS (M+H) 271.0638 calculated for C₁₅H₁₂N₂OCl : 271.056; found 271.0632



6-chloro-2-(pyridin-3-yl)quinazoline (Table 2, 3t): Yellow solid (73% yield), ¹H NMR (400 MHz, CDCl₃): δ = 9.37 (s, 1H), 8.73 (d, *J* = 4 Hz, 2H), 8.36 (d, *J* = 8 Hz, 2H), 8.00 (d, *J* = 12 Hz, 1H), 7.89 (s, 1H), 7.83-7.80 (m, 1H), ¹³C NMR (CDCl₃, 100 MHz): 159.8, 159.2, 150.5, 149.1, 144.9, 135.6, 134.0, 130.6, 125.8, 124.6, 122.3.



6-chloro-2-(thiophen-2-yl)quinazoline (Table 2, 3u): White solid (71% yield), ¹H NMR (400 MHz, CDCl₃): δ = 9.21 (s, 1H), 8.07-8.05 (m, 1H), 7.87 (d, *J* = 12 Hz, 1H), 7.78 (d, *J* = 4 Hz, 1H), 7.74-7.71 (m, 1H), 7.46-7.45 (m, 1H), 7.13-7.10 (m, 1H), ¹³C NMR (CDCl₃, 100 MHz): 159.5, 158.1, 149.1, 143.4, 135.4, 132.6, 130.3, 129.9, 129.6, 128.5, 126.0, 123.7.

¹H and ¹³C spectra of quinazoline



Figure S4: ¹H NMR spectrum of 2-phenylquinazoline



Figure S5: ¹³C NMR spectrum of 2-phenylquinazoline



Figure S6: ¹H NMR spectrum of 2-(4-fluorophenyl)quinazoline



Figure S7: ¹³C NMR spectrum of 2-(4-fluorophenyl)quinazoline



Figure S8: ¹H NMR spectrum of 2-(4-chlorophenyl)quinazoline



Figure S9: ¹³C NMR spectrum of 2-(4-chlorophenyl)quinazoline



Figure S10: ¹H NMR spectrum of 2-(4-bromophenyl)quinazoline



Figure S11: ¹³C NMR spectrum of 2-(4-bromophenyl)quinazoline



Figure S12: ¹H NMR spectrum of 2-(3-bromophenyl)quinazoline



Figure S13: ¹³C NMR spectrum of 2-(3-bromophenyl)quinazoline



Figure S14: ¹H NMR spectrum of 2-(4-(trifluoromethyl)phenyl)quinazoline



Figure S15: ¹³C NMR spectrum of 2-(4-(trifluoromethyl)phenyl)quinazoline



Figure S16: ¹H NMR spectrum of 2-p-tolylquinazoline



Figure S17: ¹³C NMR spectrum of 2-p-tolylquinazoline



Figure S18: ¹H NMR spectrum of 2-(4-methoxyphenyl)quinazoline



Figure S19: ¹³C NMR spectrum of 2-(4-methoxyphenyl)quinazoline



Figure S20: ¹H NMR spectrum of 2-(3-methoxyphenyl)quinazoline



Figure S21: ¹³C NMR spectrum of 2-(3-methoxyphenyl)quinazoline



Figure S22: ¹H NMR spectrum of 2-(pyridin-3-yl)quinazoline



Figure S23: ¹³C NMR spectrum of 2-(pyridin-3-yl)quinazoline



Figure S24: ¹H NMR spectrum of 2-(thiophen-2-yl)quinazoline



Figure S25: ¹³C NMR spectrum of 2-(thiophen-2-yl)quinazoline



Figure S26: ¹H NMR spectrum of 6-chloro-2-phenylquinazoline



Figure S27: ¹³C NMR spectrum of 6-chloro-2-phenylquinazoline



Figure S28: ¹H NMR spectrum of 6-chloro-2-(4-fluorophenyl)quinazoline



Figure S29: ¹³C NMR spectrum of 6-chloro-2-(4-fluorophenyl)quinazoline



Figure S30: ¹H NMR spectrum of 6-chloro-2-(4-chlorophenyl)quinazoline



Figure S31: ¹³C NMR spectrum of 6-chloro-2-(4-chlorophenyl)quinazoline



Figure S32: ¹H NMR spectrum of 2-(4-bromophenyl)-6-chloroquinazoline



Figure S33: ¹³C NMR spectrum of 2-(4-bromophenyl)-6-chloroquinazoline



Figure S34: ¹H NMR spectrum of 6-chloro-2-(4-(trifluoromethyl)phenyl)quinazoline



Figure S35: ¹³C NMR spectrum of 6-chloro-2-(4-(trifluoromethyl)phenyl)quinazoline



Figure S36: ¹H NMR spectrum of 6-chloro-2-p-tolylquinazoline



Figure S37: ¹³C NMR spectrum of 6-chloro-2-p-tolylquinazoline



Figure S38: ¹H NMR spectrum of 6-chloro-2-(4-methoxyphenyl)quinazoline



Figure S39: ¹³C NMR spectrum of 6-chloro-2-(4-methoxyphenyl)quinazoline



Figure S40: ¹H NMR spectrum of 6-chloro-2-(3-methoxyphenyl)quinazoline



Figure S41: ¹³C NMR spectrum of 6-chloro-2-(3-methoxyphenyl)quinazoline



Figure S42: ¹H NMR spectrum of 6-chloro-2-(pyridin-3-yl)quinazoline



Figure S43: ¹³C NMR spectrum of 6-chloro-2-(pyridin-3-yl)quinazoline



Figure S44: ¹H NMR spectrum of 6-chloro-2-(thiophen-2-yl)quinazoline



Figure S45: ¹³C NMR spectrum of 6-chloro-2-(thiophen-2-yl)quinazoline





Turnover number (TON) calculations:¹²

 $\frac{Moles \ of \ reagent \ \times \ yield}{TON = }$ $\frac{Moles \ of \ Nickel \ hydroxide \ NPs}{Moles \ of \ Nickel \ hydroxide \ NPs}$

Calculation of green chemistry matrices:



a) (total mass of stiochiomtric reactant) – (total mass of product formed) Mass of product

 $=\frac{(0.123+0.103)-0.185}{0.185}$

= 0.221

(*M.Wt of product*) **b)** Atom economy: $\overline{\sum(M.Wt \ of \ stiochiometric \ reactants)} \times 100$

$$\frac{206.08}{123.15 + 103.04} \times 100$$

= 91 %

c) Carbon efficiency: $\frac{[(No. of moles of product)(No. of carbons in product)]}{\sum[(No. of moles of reactant)(No. of carbon in reactant)]} \times 100$

$$= \frac{0.89 \times 14}{(1 \times 7)(1 \times 7)} \times 100$$

$$= 89\%$$
d) Process mass intensity :
$$\frac{\sum (mass \ of \ stiochiometric \ reactants)}{mass \ of \ products}$$

$$= \frac{0.123 + 0.103}{0.185}$$

= 1.221

Alternatively Process mass intensity = E-factor+1

$$= 0.221 + 1$$

=1.221

e) Reaction mass efficiency:
$$\frac{mass \ of \ product}{\sum(mass \ of \ stiochiometric \ reactants)} \times 100$$

 $=\frac{0.185}{0.123+0.103}\times100$

= 82 %

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