Supporting Information

A General Catalyst Based on Cobalt Core–Shell Nanoparticles for the Hydrogenation of N-Heteroarenes Including Pyridines

Kathiravan Murugesan, Vishwas G. Chandrashekhar, Carsten Kreyenschulte, Matthias Beller,* and Rajenahally V. Jagadeesh*

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Supplementary Information

Table of contents
S1. Materials and methods
S2. Procedure for catalyst preparation
S3. Catalysts characterization
S4. General procedure for the hydrogenation of N-heteroarenes
S5. Gram scale reactions
S6. General procedure for dehydrogenation reaction
S7. Catalyst recycling
S8. Reaction optimization
S9. NMR data
S10. NMR spectra

S1. Materials and methods
All substrates were obtained commercially from various chemical companies. Purity of all the substrates has been checked before they used for the reaction. Cobalt(II) nitrate hexahydrate (cat no. 139267-100G) and terephthalic acid (cat no.185361; 98%) were obtained from Sigma Aldrich. Pyromellitic acid (cat no. B23099; 96%) and trimesic acid (1,3,5-benzenetricarboxylic acid; cat no. A15947; 98%) was obtained from Alfa Aesar. Silica (Aerosil OX-50) was obtained from Evonik. tert-Butanol, 2-propanol (i-PrOH) and benzene were obtained from Across chemicals. Pyrolysis
experiments were carried out in Nytech-Qex oven. Before using, purity of all the substrates has been checked by GC-MS.

XRD powder pattern were recorded either on a Panalytical X'Pert diffractometer equipped with a Xcelerator detector or on a Panalytical Empyrean diffractometer equipped with a PIXcel 3D detector system. Both were used with automatic divergence slits and Cu ka1/ka2 radiation (40 kV, 40 mA; \(\lambda = 0.015406 \text{ nm}, 0.0154443 \text{ nm}\)). Cu beta-radiation was excluded by using nickel filter foil. Peak positions and profile were fitted with Pseudo-Voigt function using the High Score Plus software package (Panalytical). Phase identification was done by using the PDF-2 database of the International Center of Diffraction Data (ICDD).

STEM measurements were performed at 200kV with a probe aberration-corrected JEM-ARM200F (JEOL, Corrector: CEOS). The microscope is equipped with a JED-2300 (JEOL) energy-dispersive x-ray-spectrometer (EDXS) and an Enfinium ER (Gatan) electron energy loss spectrometer (EELS). STEM imaging was performed using High-Angle Annular Dark Field (HAADF) and Annular Bright Field (ABF) detectors, while the annular dark field (ADF) detector was used during EELS acquisition. The solid samples were deposed without any pretreatment on a holey carbon supported Cu-grid (mesh 300) and transferred to the microscope. EELS elemental maps were calculated using the internal standards method in Digital Micrograph 3.4 (Gatan).

XPS data was obtained with a VG ESCALAB220iXL (ThermoScientific) with monochromatic Al K\(\alpha\) (1486.6 eV) radiation. The electron binding energies EB were obtained without charge compensation. For quantitative analysis the peaks were deconvoluted with Gaussian-Lorentzian curves, the peak area was divided by a sensitivity factor obtained from the element specific Scofield factor and the transmission function of the spectrometer. CasaXPS was used for XPS peak deconvolution.

BET surface areas (BET-SA) of the catalysts were determined on NOVA 4200e instrument by N\(_2\)-physisorption at -196 °C. Prior to the measurements, the known amount of catalyst was evacuated for 2 h at 220 °C to remove physically adsorbed water.

All catalytic experiments were carried out in 300 mL and 100 mL autoclaves (PARR Instrument Company). In order to avoid unspecific reactions, all catalytic reactions were carried out either in glass vials, which were placed inside the autoclave, or glass/Teflon vessel fitted autoclaves.

GC and GC-MS were recorded on Agilent 6890N instrument. GC conversion and yields were determined by GC-FID, HP6890 with FID detector, column HP530 m x 250 mm x 0.25 μm.

\(^1\)H and \(^{13}\)C NMR data were recorded on a Bruker ARX 300 and Bruker ARX 400 spectrometers using DMSO-d6, CD\(_3\)OD and CDCl\(_3\) solvents.
S2. Procedure for the catalyst preparation

S2.1. Preparation of Co-pyromellitic acid @SiO₂-800 catalyst (Co/Co₃O₄@SiO₂)

In a 50 mL round bottomed flask, 444.5 mg of cobalt(II) nitrate hexahydrate and 1.16 g of pyromellitic acid in 20 mL N,N-dimethylformamide (DMF) were stirred at 150 °C for 30-45 min by placing round bottom flask containing reaction mixture into an aluminum block preheated at 150 °C. Then, 1.2 g of silica (Aerosil-OX-50) was added followed by the addition of 15 mL of DMF and the reaction mixture again was stirred at 150 °C for 4-5 h by fixing reflux condenser to the round bottomed flask. Then, the reflux condenser was removed and the round bottomed flask containing reaction product was allowed to stand without stirring and closing for 20 h at 150 °C in order to slow evaporation of DMF. After the evaporation of the solvent and ensuring the complete drying, the material was cooled to room temperature and grinded into fine powder. The powdered material was pyrolyzed at 800 °C for 2 hours under an argon atmosphere and then cooled to room temperature after pyrolysis.

Elemental analysis (Wt%): Co-pyromellitic acid@SiO₂-800 (Co/Co₃O₄@SiO₂): Co=5.4%, C=8.35%, H=0.29%, Si=43.05% N=0.33%.

Same procedure was applied to prepare other materials such as Co-benzoic acid@SiO₂-800 Co-terephthalic acid@SiO₂-800, Co-trimesic acid @SiO₂-800 and cobalt nitrate@SiO₂-800

S3. Catalysts characterization

XRD spectra and data
**Fig. S1.** XRD spectrum of Co/Co$_3$O$_4$@SiO$_2$ catalyst.
Fig. S2. XRD spectrum of cobalt nitrate@SiO2-800 catalyst.
Fig. S3. STEM-HAADF (A) and ABF-STEM (B) images of an overview of the Co containing particles on the support. STEM-HAADF (C) image (left) and corresponding EDX spectra of the marked areas of Co/Co₃O₄@SiO₂ catalyst. Constant Si to O signal ratios in the spectrum from the support (013) and from the particle (012) implies that this particle is of metal character.
**Fig. S4.** STEM-ADF image (A) overlaid with false color elemental map showing the distribution of C, O and maps of the different oxidation states of Co, with the single-color elemental maps in (B). Especially in the Co overlay plot the metal core and oxide shell nature of the Co particles is clearly shown. To distinguish between Co metal and Co oxide internal reference spectra from clearly distinguishable sample regions were fitted pixel-wise to the spectrum imaging dataset. STEM-ADF image (C) is marked with the areas used for the EEL spectra in (D) from the same spectrum imaging dataset used in (A) & (B). The differences in fine structure of O relate to the local elemental composition in area 1, where the O edge signal is dominated by the SiO$_2$ support, whereas areas 2 and 3 show less silica-based oxygen but more Co oxide.
Fig. S5. STEM-HAADF (A) and STEM-ABF (B) image showing an overview of the one time used catalyst with details of the starting redeposition of the Co phase towards a thin structure in the higher resolution STEM-HAADF (C) and STEM-ABF (D) images.
Fig. S6. STEM-ADF image (A) of the once used catalyst overlaid with false color elemental map showing the distribution of C, O and maps of the different oxidation states of Co, with the single-color elemental maps in (B). The Co maps indicate the remaining presence of the core metal oxide shell structure, but also an additional structure containing Co and O appears to have formed (arrow, cf. S10 C, D). The intensity in the left half of the C map is due to the carbon foil of the specimen grid. The data was treated as before in the fresh specimen.
Fig. S7. STEM-HAADF (A) and STEM-ABF (B) image showing an overview of the seven-times used catalyst with details of the remaining particles in STEM-HAADF (C) and STEM-ABF (D) images and further details of the continuing redeposition of the Co phase towards a thin structure in the STEM-HAADF (E) and STEM-ABF (F) images.
Fig. S8. STEM-ADF image (A) of the 7-times used catalyst overlaid with a false color elemental map showing the distribution of C, O and maps of the different oxidation states of Co, with the single-color elemental maps in (B). Especially in the Co oxide treatment the continued growth of the new Co oxide phase is recognizable, while the original core shell structure still remains although electron microscopy data cannot answer if there is a shift in balance between the amount of core shell particles versus the amount of the new phase. The data was treated as before in the fresh specimen.
**XPS Analysis**

**Fig. S9.** XP spectra of the Co2p for Co/Co3O4@SiO2 catalyst.
Fig. S10. BET of Co-Co₃O₄@SiO₂ catalyst.
S4. General procedure for the N-heteroarenes hydrogenation

A magnetic stirring bar and 0.5 mmol of the corresponding substrate were transferred to 8 mL glass vial and then 3 mL solvent (2:1 i-PrOH-H₂O) was added. Then, 40-60 mg of catalyst was added depending on the substrate and the vial was fitted with septum, cap and needle. The reaction vials (8 vials with different substrates at a time) were placed into a 300 mL autoclave. The autoclave was flushed with 30 bar hydrogen twice and then it was pressurized with 10-50 bar of hydrogen. The autoclave was placed into an aluminum block preheated at 80-145 °C (placed 30 minutes before counting the reaction time in order to attain reaction temperature) and the reactions were stirred for required time. During the reaction the inside temperature of the autoclave was measured to be 70-135 °C and this temperature was used as the reaction temperature. After the completion of the reactions, the autoclave was cooled to room temperature. The remaining hydrogen was discharged and the vials containing reaction products were removed from the autoclave. The solid catalyst was filtered off and washed thoroughly with ethyl acetate. The reaction products were analyzed by GC-MS. The corresponding products were purified by column chromatography (silica; n-hexane-ethyl acetate mixture). The resulting products were characterized by NMR and GC-MS spectral analysis.

Procedure for the yields determined by GC for selected compounds: After completion of the reactions, n-hexadecane (100µL) as standard was added to the reaction vials and the reaction products were diluted with THF followed by filtration using plug of silica and then analyzed by GC.

S5. General procedure for gram scale reactions

To a Teflon or glass fitted 100 mL, a magnetic stirring bar and the corresponding heteroarene were transferred and 10-20 mL of i-PrOH: H₂O (2:1) was added. After adding the 40-60 mg Co-pyromellitic acid@SiO₂-800 catalyst (7.5 to 11 mol %) the autoclave was flushed with 30 bar hydrogen twice, and then it was pressurized with 10 -50 bar hydrogen depending on the substrate. The autoclave was placed into a heating set-up and the inside temperature of the autoclave was set to 70 - 135 °C (based on reaction conditions mentioned in Fig. S8) and this temperature was used as the reaction temperature. After completion of the reaction, the autoclave was cooled to room temperature. The remaining hydrogen was discharged, and the reaction products were removed from the autoclave. The solid catalyst was filtered off and washed thoroughly with methanol and ethyl acetate. The reaction products were analyzed by GC-MS and the corresponding products were purified by column chromatography (silica; n-hexane-ethyl acetate mixture) and characterized by NMR and GC-MS spectral analysis.
Fig. S11. Practical applicability of cobalt-catalyzed N-heteroarenes hydrogenation protocol for gram scale reactions. Reaction conditions: [a] For 0.5 mmol substrate, 40 mg Co-pyromellitic acid@SiO$_2$-800, 50 bar H$_2$, 3 mL solvent (i-PrOH:H$_2$O; 2:1), 120 °C, 24h, isolated yields. [b] Same as [a] at 135 °C with 60 mg Co-pyromellitic acid@SiO$_2$-800 for 48h. [c] 0.5 mmol substrate, 50 Co-pyromellitic acid@SiO$_2$-800, 10 bar H$_2$, 3 mL solvent (i-PrOH: H$_2$O; 2:1), 70 °C, 24h, yields were determined by GC using n-hexadecane standard. [d] Same as [c] at 120°C with 30 bar H$_2$.

S6. General procedure for dehydrogenation reaction

To a 100 mL autoclave, a magnetic stirring bar and the corresponding 2-methyl-1,2,3,4-tetrahydroquinoline (2 mmol, 290 mg) were transferred and 10 mL of t-BuOH was added. After adding 240 mg of Co-pyromellitic acid@SiO$_2$-800 (11 mol % of Co) the autoclave was flushed with 10 bar nitrogen twice. The autoclave was placed into a heating set-up, and the temperature inside the autoclave set to 200 °C and this temperature was used as the reaction temperature. After completion of the reaction, the autoclave was cooled to room temperature and the generated H$_2$ was analyzed by GC. The remaining gas was discharged, and the reaction products were removed from the autoclave. The solid catalyst was filtered off and washed thoroughly with ethyl acetate. The reaction products were analyzed by GC-MS and yields were determined by GC using n-hexadecane standard.

S7. Catalyst recycling

A magnetic stirring bar and 10 mmol of 2-methyl quinoline were transferred to a 100 mL autoclave and then 15 mL t-BuOH was added. Then, 1 g of catalyst Co-pyromellitic acid@SiO$_2$-800 (9 mol% Co) was added. The autoclave was flushed with 20 bar hydrogen and then it was pressurized with 10 bar hydrogen. The autoclave was placed into heating system and reactions were allowed to progress at 120 °C (temperature inside the autoclave) by stirring for the required time. After the completion of the reaction, the autoclave was cooled, and the remaining hydrogen was discharged. To the reaction products, 250 µL n-hexadecane as standard was added. The catalyst was separated by centrifugation and the centrifugate containing reaction products was subjected to GC analysis for determining the yield of 2-methyl-1,2,3,4-tetrahydroquinoline. The separated catalyst was washed with ethyl acetate, dried under vacuum and used without further purification or reactivation for the next run.
**Fig. S12.** Catalyst recycling for the hydrogenation of 2-methyl quinoline to 2-methyl-1,2,3,4 tetrahydroquinoline. Reaction conditions: 1.4 gram 2-methyl quinoline (10 mmol), 1 g of Co-pyromellitic acid@SiO$_2$-800 (9 mol % Co), 10 bar H$_2$, 15 mL t-BuOH, 120 °C, 24 h.
S8. Reaction optimization

Table S1: Screening of different solvents for the hydrogenation of nicotinamide using Co-pyromellitic acid@SiO₂-800 catalyst.

| Entry | Solvent | Conversion (%) | Yield (%) |
|-------|---------|----------------|-----------|
| 1ᵃ    | i-PrOH  | 60             | 58        |
| 2ᵃ    | t-BuOH  | 10             | 8         |
| 3ᵃ    | MeOH    | 55             | 52        |
| 4ᵃ    | EtOH    | 54             | 51        |
| 5ᵃ    | TFE     | 50             | 48        |
| 6ᵃ    | Toluene | 40             | 38        |
| 7ᵃ    | THF     | 10             | 8         |
| 8ᵃ    | i-PrOH:H₂O (3 mL: 100 µL) | 85 | 83 |
| 9ᵃ    | i-PrOH:H₂O (2 mL: 1 mL) | >99 | 97 |
| 10ᵇ   | i-PrOH:H₂O (2 mL: 1 mL) | 2 | 1 |
| 11ᶜ   | i-PrOH:H₂O (2 mL: 1 mL) | 4 | 2 |
| 12ᵈ   | i-PrOH:H₂O (2 mL: 1 mL) | 10 | 8 |

Reaction conditions: 0.5 mmol substrate, 40 mg Co-pyromellitic acid@SiO₂-800 (7.5 mol% Co), 50 bar H₂, 3 mL solvent, 120 °C, 24h, yields were determined by GC using n-hexadecane standard. [b] same as [a] at 100 °C [c] same as [a] using 6 mol% of catalyst [d] Same as [a] with 30 bar H₂.
S9. NMR Data

Piperidin-3-carboxamide

\[ \text{O} \]
\[ \text{NH}_2 \]

$^{1}$H NMR (300 MHz, Chloroform-$d$) $\delta$ 7.22 (br s, 1H), 5.88 (br s, 1H), 3.01 – 2.84 (m, 2H), 2.85 – 2.62 (m, 2H), 2.40 – 2.20 (m, 1H), 2.00 – 1.89 (m, 1H), 1.85 – 1.58 (m, 3H), 1.52 – 1.34 (m, 1H). $^{13}$C NMR (75 MHz, Chloroform-$d$) $\delta$ 177.93, 48.57, 46.57, 42.19, 27.66, 23.83. White solid.

N-Methyl-1-(piperidin-3-yl)methanamine

\[ \text{O} \]
\[ \text{NH} \]

$^{1}$H NMR (400 MHz, DMSO-$d_6$) $\delta$ 3.19 – 3.02 (m, 1H), 2.91 – 2.53 (m, 3H), 2.47 (s, 3H), 2.30 – 2.10 (m, 2H), 1.93 – 1.58 (m, 4H), 1.31 – 1.16 (m, 1H). $^{13}$C NMR (75 MHz, Chloroform-$d$) $\delta$ 51.42, 46.08, 43.50, 33.60, 31.16, 26.56, 21.60. Brown gum.

2-Pentylpiperidine

\[ \text{O} \]
\[ \text{NH} \]

$^{1}$H NMR (300 MHz, Chloroform-$d$) $\delta$ 3.43 – 3.13 (m, 1H), 2.92 – 2.56 (m, 2H), 1.97 – 1.50 (m, 6H), 1.42 – 1.16 (m, 8H), 0.81 (t, $J$ = 6.8 Hz, 3H). $^{13}$C NMR (75 MHz, Chloroform-$d$) $\delta$ 57.31, 45.17, 34.03, 31.57, 28.91, 26.23, 25.20, 23.02, 22.51, 13.96. Colorless gum.
2-(p-Tolyl)piperidine

\[
\begin{align*}
\text{H NMR (300 MHz, Chloroform-}d\text{) } & \delta 7.16 (d, J = 8.1 \text{ Hz}, 2\text{H}), 7.03 (d, J = 8.2 \text{ Hz}, 2\text{H}), 3.56 – 3.36 \\
& \text{(m, 1\text{H}), 3.21 – 2.98 (m, 1\text{H}), 2.80 – 2.58 (m, 1\text{H}), 2.23 (s, 3\text{H}), 1.92 – 1.23 (m, 7\text{H}).} \\
\text{C NMR (75 MHz, Chloroform-}d\text{) } & \delta 142.62, 136.54, 129.04, 126.55, 62.11, 47.87, 35.04, 25.94, 25.50, 21.09 \\
& \text{White solid.}
\end{align*}
\]

2-(4-(Trifluoromethyl)phenyl)piperidine

\[
\begin{align*}
\text{H NMR (300 MHz, Chloroform-}d\text{) } & \delta 7.50 (d, J = 8.6 \text{ Hz}, 2\text{H}), 7.42 (d, J = 8.7 \text{ Hz}, 2\text{H}), 3.72 – 3.40 \\
& \text{(m, 1\text{H}), 3.22 – 2.92 (m, 1\text{H}), 2.88 – 2.59 (m, 1\text{H}), 2.21 (br s, 1\text{H}), 2.00 – 1.07 (m, 6\text{H}).} \\
\text{C NMR (75 MHz, Chloroform-}d\text{) } & \delta 149.23, 129.33 (q, J = 32.2 \text{ Hz}), 127.01, 125.33 (q, J = 3.8 \text{ Hz}), 124.24 (q, J = 271.9 \text{ Hz}), 61.88, 47.57, 34.95, 25.61, 25.23 \\
& \text{Colorless gum.}
\end{align*}
\]

2-(4-Methoxyphenyl)piperidine

\[
\begin{align*}
\text{H NMR (300 MHz, Chloroform-}d\text{) } & \delta 7.20 (d, J = 8.3 \text{ Hz}, 2\text{H}), 6.76 (d, J = 8.7 \text{ Hz}, 2\text{H}), 3.70 (s, 3\text{H}), \\
& 3.56 – 3.33 (m, 1\text{H}), 3.18 – 2.92 (m, 1\text{H}), 2.82 – 2.55 (m, 1\text{H}), 2.12 – 1.17 (m, 7\text{H}). \\
\text{C NMR (75 MHz, Chloroform-}d\text{) } & \delta 158.64, 137.79, 127.72, 113.72, 61.75, 55.27, 47.90, 35.00, 25.91, 25.50 \\
& \text{Colorless gum.}
\end{align*}
\]
8-Chloro-1,2,3,4-tetrahydroquinoline

\[ \text{H NMR} (300 \text{ MHz, Chloroform-}d) \delta 7.02 - 6.92 \text{ (m, 1H)}, 6.81 - 6.71 \text{ (m, 1H)}, 6.47 - 6.35 \text{ (m, 1H)}, 4.29 \text{ (br s, 1H)}, 3.42 - 3.13 \text{ (m, 2H)}, 2.68 \text{ (t, } J = 6.4 \text{ Hz, 2H)}, 2.07 - 1.58 \text{ (m, 2H).} \]

\[ \text{C NMR} (75 \text{ MHz, Chloroform-}d) \delta 140.75, 127.69, 126.80, 122.66, 118.07, 116.31, 41.85, 27.27, 21.70. \]

6-Methoxy-1,2,3,4-tetrahydroquinoline

\[ \text{H NMR} (300 \text{ MHz, Chloroform-}d) \delta 6.53 - 6.44 \text{ (m, 2H)}, 6.34 \text{ (dd, } J = 8.4, 0.6 \text{ Hz, 1H)}, 3.62 \text{ (s, 3H)}, 3.52 \text{ (br s, 1H)}, 3.26 - 3.01 \text{ (m, 2H)}, 2.74 - 2.42 \text{ (m, 2H)}, 2.00 - 1.60 \text{ (m, 2H).} \]

\[ \text{C NMR} (75 \text{ MHz, Chloroform-}d) \delta 151.84, 138.92, 122.89, 115.62, 114.90, 112.93, 55.82, 42.37, 27.22, 22.48. \]

2-Methyl-1,2,3,4-tetrahydroquinoline

\[ \text{H NMR} (300 \text{ MHz, Chloroform-}d) \delta 6.96 - 6.85 \text{ (m, 2H)}, 6.57 \text{ (td, } J = 7.4, 1.2 \text{ Hz, 1H)}, 6.47 \text{ (dd, } J = 8.3, 1.2 \text{ Hz, 1H)}, 3.42 - 3.24 \text{ (m, 1H)}, 2.88 - 2.57 \text{ (m, 2H)}, 2.02 - 1.76 \text{ (m, 1H)}, 1.67 - 1.41 \text{ (m, 1H)}, 1.17 \text{ (d, } J = 6.3 \text{ Hz, 3H).} \]

\[ \text{C NMR} (75 \text{ MHz, Chloroform-}d) \delta 143.97, 129.32, 126.74, 121.63, 117.65, 114.56, 47.39, 29.97, 26.49, 22.36. \]
6-Chloro-1,2,3,4-tetrahydroquinoline

\[
\begin{array}{c}
\text{Cl} \\
\text{N} \\
\text{H}
\end{array}
\]

\(^1\text{H} \text{ NMR (300 MHz, Chloroform-}d) \ \delta 6.94 – 6.66 (m, 2H), 6.45 – 6.09 (m, 1H), 3.70 (br s, 1H), 3.31 – 3.02 (m, 2H), 2.79 – 2.43 (m, 2H), 2.07 – 1.61 (m, 2H). \ ^{13}\text{C NMR (75 MHz, Chloroform-}d) \ \delta 143.20, 129.03, 126.51, 122.96, 121.24, 115.19, 41.87, 26.88, 21.75.

6-Fluoro-2-methyl-1,2,3,4-tetrahydroquinoline

\[
\begin{array}{c}
\text{F} \\
\text{N} \\
\text{H}
\end{array}
\]

\(^1\text{H} \text{ NMR (300 MHz, Chloroform-}d) \ \delta 6.74 – 6.46 (m, 2H), 6.43 – 6.17 (m, 1H), 3.52 (br s, 1H), 3.41 – 3.08 (m, 1H), 2.91 – 2.44 (m, 2H), 2.02 – 1.69 (m, 1H), 1.61 – 1.28 (m, 1H), 1.12 (d, J = 6.3 Hz, 3H). \ ^{13}\text{C NMR (75 MHz, Chloroform-}d) \ \delta 155.58 (d, J = 234.7 Hz), 140.82 (d, J = 1.9 Hz), 122.61 (d, J = 6.7 Hz), 115.40 (d, J = 21.6 Hz), 114.85 (d, J = 7.6 Hz), 113.17 (d, J = 22.4 Hz), 47.37, 29.86, 26.70, 22.44.

Methyl 1,2,3,4-tetrahydroquinoline-6-carboxylate

\[
\begin{array}{c}
\text{O} \\
\text{N} \\
\text{H}
\end{array}
\]

\(^1\text{H} \text{ NMR (300 MHz, Chloroform-}d) \ \delta 7.70 – 7.39 (m, 2H), 6.29 (d, J = 8.9 Hz, 1H), 4.27 (br s, 1H), 3.74 (s, 3H), 3.35 – 3.09 (m, 2H), 2.78 – 2.50 (m, 2H), 1.96 – 1.69 (m, 2H). \ ^{13}\text{C NMR (75 MHz, Chloroform-}d) \ \delta 167.59, 148.84, 131.27, 129.11, 119.89, 117.27, 112.67, 51.44, 41.69, 26.93, 21.39.
2-Methyl-1,2,3,4-tetrahydroquinolin-8-ol

\[
\begin{align*}
\text{H NMR (300 MHz, Chloroform-} & \text{d) } \delta 6.71 - 6.24 (m, 3H), 4.70 (br s, 2H), 3.44 - 3.07 (m, 1H), 2.92 - 2.44 (m, 2H), 2.11 - 1.71 (m, 1H), 1.71 - 1.39 (m, 1H), 1.18 (d, J = 6.3 Hz, 3H). \\
\text{C NMR (75 MHz, Chloroform-} & \text{d) } \delta 143.11, 132.74, 123.65, 121.68, 117.71, 112.58, 47.46, 30.03, 26.41, 22.27.
\end{align*}
\]

6-Bromo-1,2,3,4-tetrahydroquinoline

\[
\begin{align*}
\text{H NMR (400 MHz, Chloroform-} & \text{d) } \delta 7.09 - 6.89 (m, 2H), 6.36 (d, J = 8.3 Hz, 1H), 3.33 - 3.01 (m, 2H), 2.67 (t, J = 6.4 Hz, 2H), 2.01 - 1.56 (m, 2H). \\
\text{C NMR (101 MHz, Chloroform-} & \text{d) } \delta 142.51, 131.98, 129.47, 124.18, 116.32, 109.41, 41.82, 26.67, 21.48.
\end{align*}
\]

2-Phenyl-1,2,3,4-tetrahydroquinoline

\[
\begin{align*}
\text{H NMR (400 MHz, Chloroform-} & \text{d) } \delta 7.34 - 7.15 (m, 5H), 6.96 - 6.87 (m, 2H), 6.57 (td, J = 7.4, 1.2 Hz, 1H), 6.49 - 6.40 (m, 1H), 4.34 (dd, J = 9.3, 3.3 Hz, 1H), 4.10 (br s, 1H), 2.90 - 2.77 (m, 1H), 2.70 - 2.58 (m, 1H), 2.12 - 1.73 (m, 2H). \\
\text{C NMR (101 MHz, Chloroform-} & \text{d) } \delta 144.76, 144.63, 129.35, 128.62, 127.50, 126.96, 126.62, 121.01, 117.32, 114.13, 56.32, 31.00, 26.43.
\end{align*}
\]
6-Methyl-1,2,3,4-tetrahydroquinoline

\[
\begin{align*}
\text{H NMR (400 MHz, Chloroform-}^d\text{) } & \delta 6.79 - 6.59 (m, 2\text{H}), 6.34 (d, J = 8.6 \text{ Hz, 1H}), 3.68 (\text{br s, 1H}), 3.29 - 3.00 (m, 2\text{H}), 2.65 (t, J = 6.4 \text{ Hz, 2H}), 2.12 (s, 3\text{H}), 1.96 - 1.70 (m, 2\text{H}). \\
\text{C NMR (101 MHz, Chloroform-}^d\text{) } & \delta 142.16, 130.11, 127.28, 126.49, 121.77, 114.65, 42.22, 26.92, 22.42, 20.46.
\end{align*}
\]

2,6-Dimethyl-1,2,3,4-tetrahydroquinoline

\[
\begin{align*}
\text{H NMR (300 MHz, Chloroform-}^d\text{) } & \delta 6.78 - 6.57 (m, 2\text{H}), 6.33 (d, J = 8.7 \text{ Hz, 1H}), 3.56 (\text{br s, 1H}), 3.37 - 3.09 (m, 1\text{H}), 2.95 - 2.47 (m, 2\text{H}), 2.12 (s, 3\text{H}), 1.94 - 1.71 (m, 1\text{H}), 1.64 - 1.33 (m, 1\text{H}), 1.11 (d, J = 6.3 \text{ Hz, 3H}). \\
\text{C NMR (75 MHz, Chloroform-}^d\text{) } & \delta 142.36, 129.91, 127.31, 126.45, 121.40, 114.45, 47.45, 30.42, 26.66, 22.63, 20.52.
\end{align*}
\]

6-((3-(2,5,7,8-Tetramethyl-2-(4,8,12-trimethyltridecyl)chroman-6-yl)oxy)propoxy)-1,2,3,4-tetrahydroquinoline

\[
\begin{align*}
\text{H NMR (300 MHz, Chloroform-}^d\text{) } & \delta 6.65 - 6.49 (m, 2\text{H}), 6.42 (d, J = 8.4 \text{ Hz, 1H}), 4.06 (t, J = 6.2 \text{ Hz, 2H}), 3.93 (\text{br s, 1H}), 3.74 (t, J = 6.1 \text{ Hz, 2H}), 3.29 - 3.08 (m, 2\text{H}), 2.68 (t, J = 6.5 \text{ Hz, 2H}), 2.48 (t, J = 6.8 \text{ Hz, 2H}), 2.12 (t, J = 6.2 \text{ Hz, 2H}), 2.08 (s, 3\text{H}), 2.03 (s, 3\text{H}), 2.00 (s, 3\text{H}), 1.91 - 1.82 (m, 2\text{H}), 1.77 - 1.62 (m, 2\text{H}), 1.53 - 0.93 (m, 24\text{H}), 0.84 - 0.68 (m, 12\text{H}). \\
\text{C NMR (75 MHz, Chloroform-}^d\text{) } & \delta 151.64, 148.23, 147.79, 138.09, 127.91, 125.90, 123.40, 122.85, 117.54, 116.07, 116.03, 113.93, 74.81, 69.33, 65.49, 42.42, 40.16, 39.45, 37.53, 37.48, 37.46, 37.36, 32.85, 32.75,
\end{align*}
\]
31.38 , 30.39 , 28.06 , 27.12 , 24.88 , 24.52 , 23.95 , 22.81 , 22.37 , 21.11 , 20.73 , 19.83 , 19.77 , 12.78 , 11.92 , 11.86.

**5,6,7,8-Tetrahydroimidazo[1,2-a]pyridine**

![Structure](image)

$^1$H NMR (300 MHz, Chloroform-$d$) $\delta$ 7.05 – 6.63 (m, 2H), 3.90 (t, $J =$ 5.6 Hz, 2H), 2.79 (t, $J =$ 6.1 Hz, 2H), 2.05 – 1.60 (m, 4H). $^{13}$C NMR (75 MHz, Chloroform-$d$) $\delta$ 144.69 , 127.34 , 117.82 , 44.83 , 24.54 , 23.11 , 21.16 . Brown gum.

**1,2,3,4-Tetrahydroquinoxaline**

![Structure](image)

$^1$H NMR (300 MHz, Chloroform-$d$) $\delta$ 6.55 – 6.47 (m, 2H), 6.45 – 6.38 (m, 2H), 3.62 (br s, 2H), 3.33 (s, 4H). $^{13}$C NMR (75 MHz, Chloroform-$d$) $\delta$ 133.60 , 118.89 , 114.85 , 41.40 .

**1,2,3,4-Tetrahydro-1,5-naphthyridine**

![Structure](image)

$^1$H NMR (300 MHz, Chloroform-$d$) $\delta$ 7.76 (dd, $J =$ 4.7, 1.5 Hz, 1H), 6.87 – 6.70 (m, 1H), 6.63 (dd, $J =$ 8.1, 1.5 Hz, 1H), 3.87 (br s, 1H), 3.37 – 3.05 (m, 2H), 2.84 (t, $J =$ 6.5 Hz, 2H), 2.09 – 1.65 (m, 2H). $^{13}$C NMR (75 MHz, Chloroform-$d$) $\delta$ 142.60 , 141.01 , 137.66 , 121.87 , 120.15 , 41.42 , 30.25 , 21.70 . Brown gum.
3-Methyl-1,2,3,4-tetrahydrobenzo[f]quinoline

![Chemical structure of 3-Methyl-1,2,3,4-tetrahydrobenzo[f]quinoline](image)

**$^1$H NMR (300 MHz, Chloroform-$d$)** δ 7.67 – 7.56 (m, 1H), 7.59 – 7.53 (m, 1H), 7.43 – 7.33 (m, 1H), 7.37 – 7.25 (m, 1H), 7.16 – 7.04 (m, 1H), 6.63 (d, $J = 8.7$ Hz, 1H), 3.79 (br s, 1H), 3.36 – 3.23 (m, 1H), 3.08 – 2.75 (m, 2H), 2.07 – 1.89 (m, 1H), 1.70 – 1.49 (m, 1H), 1.14 (d, $J = 6.3$ Hz, 3H). **$^{13}$C NMR (75 MHz, Chloroform-$d$)** δ 141.98, 133.46, 128.47, 127.90, 127.23, 126.32, 121.69, 121.41, 118.32, 111.55, 46.95, 30.19, 22.69, 22.24.

1,2,3,4-Tetrahydrobenzo[h]quinolone

![Chemical structure of 1,2,3,4-Tetrahydrobenzo[h]quinolone](image)

**$^1$H NMR (300 MHz, Chloroform-$d$)** δ 7.99 – 7.77 (m, 2H), 7.63 – 7.52 (m, 2H), 7.42 – 7.27 (m, 2H), 4.46 (s, 1H), 3.74 – 3.42 (m, 2H), 3.08 (t, $J = 6.4$ Hz, 2H), 2.31 – 1.84 (m, 2H). **$^{13}$C NMR (75 MHz, Chloroform-$d$)** δ 139.12, 133.23, 128.77, 128.68, 125.09, 124.87, 123.45, 119.68, 117.12, 116.00, 42.56, 27.64, 22.27.

1,2,3,4-Tetrahydro-1,10-phenanthroline

![Chemical structure of 1,2,3,4-Tetrahydro-1,10-phenanthroline](image)

**$^1$H NMR (400 MHz, Chloroform-$d$)** δ 8.61 (dd, $J = 4.3, 1.7$ Hz, 1H), 7.99 (dd, $J = 8.3, 1.7$ Hz, 1H), 7.25 (dd, $J = 8.2, 4.3$ Hz, 1H), 7.11 (d, $J = 8.2$ Hz, 1H), 6.91 (d, $J = 8.2$ Hz, 1H), 3.62 – 3.30 (m, 2H), 2.85 (t, $J = 6.3$ Hz, 2H), 2.16 – 1.78 (m, 2H). **$^{13}$C NMR (101 MHz, Chloroform-$d$)** δ 146.12, 140.27, 137.02, 132.49, 129.47, 127.58, 120.37, 117.35, 113.05, 41.27, 27.17, 21.62.

S25
S10. NMR spectra
