A Robust Iron Catalyst for the Selective Hydrogenation of Substituted (Iso)Quinolines

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1. General Information

The metal precursor Iron(II) acetate (>99.99 trace analysis) was obtained from Sigma-Aldrich. All reagents were used directly without further purification. Solvents were used directly without purification. Unless otherwise mentioned, all the reactions were performed in autoclaves.

NMR-spectra were recorded on Bruker AV 300 and 400 spectrometers. Chemical shifts (δ) are reported in ppm downfield of tetramethylsilane. The residual solvent signals were used as references for 1H and 13C NMR spectra (CDCl₃: δH = 7.26 ppm, δC = 77.12 ppm; DMSO-d₆: δH = 2.50 ppm, δC = 39.52 ppm). 19F NMR spectra are not calibrated by an internal reference. Coupling constants (J) are quoted in Hz. Mass spectra were recorded on an AMD 402/3 or a HP 5973 mass selective detector.

XRD powder patterns were recorded either on a Panalytical X'Pert diffractometer equipped with a Xcelerator detector, automatic divergence slits and Cu Kα radiation (40 kV, 40 mA). Cu β-radiation was excluded by using nickel filter foil. The samples were mounted on silicon zero background holders. Peak positions and profile were fitted with Pseudo-Voigt function using the the Panalytical HighScore Plus software package. Phase identification was done by using the PDF-2 database of the International Center of Diffraction Data (ICDD).

X-ray photoelectron spectra (XPS) were collected using an ESCALAB220xi spectrometer equipped with a monochromatized Al Kα X-ray radiation source (hv = 1486.6 eV). Electron binding energies were calibrated on C1s contribution at 284.8 eV in C1s region. The XPS peaks were analyzed using a Shirley-type background and a nonlinear least square fitting of the experimental data based on a mixed Gaussian/Lorentzian peak shape. Peak areas were divided by a sensitivity factor obtained from the element specific Scofield factor and the transmission function of the spectrometer.

The TEM measurements were performed at 200kV with an 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 977 ER (Gatan) electron energy loss spectrometer (EELS) with an annular dark field (ADF) detector placed at the spectrometer entrance for chemical analysis and spectrum imaging.

The aberration corrected STEM imaging (High-Angle Annular Dark Field (HAADF) and Annular Bright Field (ABF)) were performed under the following conditions. HAADF and ABF both were done with a spot size of approximately 0.13nm. Preparation of the TEM sample: The sample was deposed without any pretreatment on a holey carbon supported Cu-grid (mesh 300) and transferred to the microscope.

The Raman spectra were collected on a Renishaw inVia Raman microscope using a 633 nm laser with a laser power between 0.081 and 0.161 mW. The samples were mounted onto object slides and an objective with a magnification of 50x was applied. The band intensities were evaluated manually by adjusting the baseline carefully to the region between 2200 and 600 cm⁻¹.

No attempts were made for the optimization of substrate synthesis.
2. Synthesis of Catalysts:

2.1 Procedure for Catalyst Preparation

\[ \text{Schiff Base Ligand} \]

\[ \begin{align*}
\text{L1: } R &= \text{H} \quad (24 \text{ h}) \\
\text{L2: } R &= \text{CN} \quad (48 \text{ h}) \\
\text{L3: } R &= \text{OMe} \quad (12 \text{ h}) \\
\text{L4: } (6 \text{ h})
\end{align*} \]

Scheme S1: General procedure for the synthesis of Fe-based heterogeneous catalysts.

In a 100 mL round bottomed flask equipped with magnetic stir bar, 2-pyridinecarboxaldehyde (643 mg, 6.00 mmol, 2.00 equiv.) was added to the suspension of 1,4-phenylenediamine (324 mg, 3.00 mmol, 1.00 equiv.) in toluene (15 mL). The resulting suspension was stirred for 6 h at rt. The solvent was removed under reduced pressure to obtain yellow ligand L4. The obtained ligand L4 was directly used for next step. 1H NMR (300 MHz, CDCl3): δ (ppm): 8.72 (ddd, J = 4.9, 1.7, 0.9 Hz, 2H), 8.66 (s, 2H), 8.21 (dt, J = 8.0, 1.1 Hz, 2H), 7.79 – 7.85 (m, 2H), 7.35 – 7.39 (m, 2H), 7.37 (s, 4H); 13C NMR (75 MHz, CDCl3): δ (ppm): 160.3, 154.7, 149.9, 149.7, 136.8, 125.3, 122.3, 122.1; HR-MS (ESI): m/z calculated for [C18H15N4]+ ([M+H]+): 287.1291, found: 287.1296. The obtained spectroscopic data were in agreement with the reported data for this compound [ref.1].

Next, the obtained ligand L4 (ca. 3.00 mmol) was dissolved in abs. ethanol (25 mL) in a 100 mL round bottomed flask equipped with a reflux condenser and magnetic stir bar. The resulting suspension was stirred at 70 °C for 5 min for complete dissolution of the ligand and then Fe(OAc)2 (117 mg, 0.670 mmol) was added to the solution. After 1 h stirring at 70 °C, carbon powder: VULCAN® XC72R (925 mg) was added to the reaction mixture and continued stirring for another 4 h at same temperature. After cooling the reaction mixture to rt, ethanol was removed slowly under reduced pressure. The obtained black solids was dried for 3 h at 60 °C under vacuum. The dried sample was transferred into a ceramic crucible and then placed in an oven. The oven was evacuated to ca. 5 mbar and then flushed with argon. Then the oven was heated to temperature 800 °C with a temperature gradient 25 °C/min and the final temperature was held for 2 h under argon atmosphere. After that the oven was cooled down to rt. During the whole process, argon was purged through the oven constantly. The as-prepared catalyst (designated as Fe(1)/L4(4.5)@C-800) was stored in a screw capped vial without any special protection from air at room temperature.

Additionally, several Fe-based materials with different ligands (L1, L2 and L3) using carbon powder: VULCAN® XC72R as support and ligand L4 using various supports (Al2O3(α), SiO2, TiO2 and CeO2) were prepared under the similar conditions. Furthermore, a series of Fe-based materials using ligand L4 and carbon powder: VULCAN® XC72R as support was prepared at various temperature (500-900 °C). Moreover, a series of Fe-based materials with different metal-to-ligand ratio with ligand L4 using carbon powder: VULCAN® XC72R as support were prepared.
2.2 Thermogravimetry (TG) and Differential Scanning Calorimetry (DSC) Measurement:

Thermogravimetry (TG) and Differential Scanning Calorimetry (DSC) curves obtained during the heat treatment of dried Fe(OAc)$_2$-L4 complex impregnated on VULCAN® XC72R under nitrogen atmosphere are illustrated in Figure S1. As noticed in Figure S1, rapid mass loss was noticed after 260 °C (rest mass: 92%) till 500 °C (rest mass: 64 wt%). However, the mass loss was continued at very slow rate increasing the temperature upto 1000 °C. At 800 °C, the rest mass of the material was 61 wt%.

![Figure S1: Thermogravimetry (TG) and Differential Scanning Calorimetry (DSC) analysis of Fe(1)/L4(4.5)/C composite.](image)

3. Optimisation and Control Experiments for the Hydrogenation of Quinoline:

3.1 Optimisation Studies

\[
\text{catalyst} \quad \text{solvent, T (°C), t (h), H$_2$ (bar)} \quad \text{product}
\]

\[
\text{L1, R = H; L2, R = CN; L3, R = OMe; L4}
\]
<table>
<thead>
<tr>
<th>Entry</th>
<th>Catalyst (mol%)</th>
<th>Solvent</th>
<th>H₂ (MPa)</th>
<th>T (°C)</th>
<th>t (h)</th>
<th>Conv.(Yield) (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Fe(1)/L₁(3.0)@C-800 (12% Fe)</td>
<td>iPrOH</td>
<td>5</td>
<td>140</td>
<td>28</td>
<td>16 (16)</td>
</tr>
<tr>
<td>2</td>
<td>Fe(1)/L₂(3.0)@C-800 (12% Fe)</td>
<td>iPrOH</td>
<td>5</td>
<td>140</td>
<td>28</td>
<td>12 (12)</td>
</tr>
<tr>
<td>3</td>
<td>Fe(1)/L₃(3.0)@C-800 (12% Fe)</td>
<td>iPrOH</td>
<td>5</td>
<td>140</td>
<td>28</td>
<td>15 (15)</td>
</tr>
<tr>
<td>4</td>
<td>Fe(1)/L₄(1.5)@C-800 (12% Fe)</td>
<td>iPrOH</td>
<td>5</td>
<td>140</td>
<td>28</td>
<td>55 (50)</td>
</tr>
<tr>
<td>5</td>
<td>Fe(1)/L₄(1.5)@Al₂O₃-800 (12% Fe)</td>
<td>iPrOH</td>
<td>5</td>
<td>140</td>
<td>28</td>
<td>47 (46)</td>
</tr>
<tr>
<td>6</td>
<td>Fe(1)/L₄(1.5)@SiO₂-800 (12% Fe)</td>
<td>iPrOH</td>
<td>5</td>
<td>140</td>
<td>28</td>
<td>32 (32)</td>
</tr>
<tr>
<td>7</td>
<td>Fe(1)/L₄(1.5)@TiO₂-800 (12% Fe)</td>
<td>iPrOH</td>
<td>5</td>
<td>140</td>
<td>28</td>
<td>24 (24)</td>
</tr>
<tr>
<td>8</td>
<td>Fe(1)/L₄(1.5)@C-500 (12% Fe)</td>
<td>iPrOH</td>
<td>5</td>
<td>140</td>
<td>28</td>
<td>&lt;5 (4)</td>
</tr>
<tr>
<td>9</td>
<td>Fe(1)/L₄(1.5)@C-600 (12% Fe)</td>
<td>iPrOH</td>
<td>5</td>
<td>140</td>
<td>28</td>
<td>7 (7)</td>
</tr>
<tr>
<td>10</td>
<td>Fe(1)/L₄(1.5)@C-700 (12% Fe)</td>
<td>iPrOH</td>
<td>5</td>
<td>140</td>
<td>28</td>
<td>35 (31)</td>
</tr>
<tr>
<td>11</td>
<td>Fe(1)/L₄(1.5)@C-900 (12% Fe)</td>
<td>iPrOH</td>
<td>5</td>
<td>140</td>
<td>28</td>
<td>48 (47)</td>
</tr>
<tr>
<td>12</td>
<td>Fe(1)/L₄(1.5)@C-800 (12% Fe)</td>
<td>Toluene</td>
<td>5</td>
<td>140</td>
<td>24</td>
<td>34 (34)</td>
</tr>
<tr>
<td>13</td>
<td>Fe(1)/L₄(1.5)@C-800 (12% Fe)</td>
<td>1,4-Dioxane</td>
<td>5</td>
<td>140</td>
<td>24</td>
<td>41 (41)</td>
</tr>
<tr>
<td>14</td>
<td>Fe(1)/L₄(1.5)@C-800 (12% Fe)</td>
<td>AmylOH</td>
<td>5</td>
<td>140</td>
<td>24</td>
<td>42 (42)</td>
</tr>
<tr>
<td>15</td>
<td>Fe(1)/L₄(1.5)@C-800 (12% Fe)</td>
<td>iPrOH</td>
<td>5</td>
<td>140</td>
<td>24</td>
<td>45 (45)</td>
</tr>
<tr>
<td>16</td>
<td>Fe(1)/L₄(1.5)@C-800 (12% Fe)</td>
<td>iPrOH/H₂O (3/1)</td>
<td>5</td>
<td>140</td>
<td>24</td>
<td>52 (52)</td>
</tr>
<tr>
<td>17</td>
<td>Fe(1)/L₄(3.0)@C-800 (12% Fe)</td>
<td>iPrOH/H₂O (3/1)</td>
<td>5</td>
<td>140</td>
<td>24</td>
<td>77 (70)</td>
</tr>
<tr>
<td>18</td>
<td>Fe(1)/L₄(4.5)@C-800 (12% Fe)</td>
<td>iPrOH/H₂O (3/1)</td>
<td>5</td>
<td>140</td>
<td>24</td>
<td>96 (84)</td>
</tr>
<tr>
<td>19</td>
<td>Fe(1)/L₄(6.0)@C-800 (12% Fe)</td>
<td>iPrOH/H₂O (3/1)</td>
<td>5</td>
<td>140</td>
<td>24</td>
<td>91 (82)</td>
</tr>
<tr>
<td>20</td>
<td>Fe(1)/L₄(4.5)@C-800 (12% Fe)</td>
<td>iPrOH/H₂O (3/1)</td>
<td>5</td>
<td>140</td>
<td>30</td>
<td>&gt;99 (85)</td>
</tr>
</tbody>
</table>
21 Fe(1)/L4(4.5)@C-800 (12% Fe) \text{ iPrOH/H}_2\text{O (3/1)} 5 130 30 80 (73)

22 Fe(1)/L4(4.5)@C-800 (12% Fe) \text{ iPrOH/H}_2\text{O (3/1)} 5 120 30 47 (45)

23 Fe(1)/L4(4.5)@C-800 (12% Fe, 64 mg) \text{ iPrOH/H}_2\text{O (3/1)} 4 130 56 >99(87)

24 Fe(1)/L4(4.5)@C-800 (10% Fe) \text{ iPrOH/H}_2\text{O (3/1)} 4 130 56 87(79)

25 Fe(1)/L4(4.5)@C-800 (after leaching) (10% Fe, 64 mg) \text{ iPrOH/H}_2\text{O (3/1)} 4 130 56 >99(91)

26 Fe(OAc)$_2$-L4-C (~12% Fe) \text{ iPrOH/H}_2\text{O (3/1)} 4 130 56 --

27 Fe@C-800 (12% Fe) \text{ iPrOH/H}_2\text{O (3/1)} 4 130 56 --

28 L4@C-800 \text{ iPrOH/H}_2\text{O (3/1)} 4 130 56 --

29 Fe$_3$O$_3$ (12% Fe) \text{ iPrOH/H}_2\text{O (3/1)} 4 130 56 --

30$^b$ Fe(1)/L4(4.5)@C-800 (12% Fe) \text{ iPrOH} -- 130 56 --

$^a$Conversion of the reaction and yield were determined by GC analysis using hexadecane as internal standard. $^b$The reaction was performed under N$_2$(4 MPa) atmosphere.

### 3.2 Comparison between the Catalyst before and after Leaching:

#### Table S1’

<table>
<thead>
<tr>
<th>Entry</th>
<th>Catalyst (mol%)</th>
<th>Solvent</th>
<th>H$_2$ (bar)</th>
<th>T (°C)</th>
<th>t (h)</th>
<th>Conversion (%)$^a$</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Fe(1)/L4(4.5)@C-800 (64 mg)</td>
<td>\text{ iPrOH/H}_2\text{O (3/1)}</td>
<td>40</td>
<td>130</td>
<td>56</td>
<td>&gt;99(93)</td>
</tr>
<tr>
<td>2</td>
<td>Fe(1)/L4(4.5)@C-800 (after leaching) (64 mg)</td>
<td>\text{ iPrOH/H}_2\text{O (3/1)}</td>
<td>40</td>
<td>130</td>
<td>56</td>
<td>&gt;99(95)</td>
</tr>
</tbody>
</table>

$^a$Conversion of the reaction and yield were determined by GC analysis using hexadecane as internal standard.
4. Catalyst Characterisation

4.1 Elemental Analysis:

Table S2

<table>
<thead>
<tr>
<th>Entry</th>
<th>Catalyst (mol%)</th>
<th>C (wt%)</th>
<th>H (wt%)</th>
<th>N (wt%)</th>
<th>Fe (wt%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Fe(1)/L4(1.5)@C-500</td>
<td>91.70</td>
<td>0.209</td>
<td>2.499</td>
<td>2.519</td>
</tr>
<tr>
<td>2</td>
<td>Fe(1)/L4(1.5)@C-800</td>
<td>90.10</td>
<td>0.336</td>
<td>1.435</td>
<td>2.511</td>
</tr>
<tr>
<td>3</td>
<td>Fe(1)/L4(3.0)@C-800</td>
<td>88.91</td>
<td>0.165</td>
<td>2.154</td>
<td>2.456</td>
</tr>
<tr>
<td>4</td>
<td>Fe(1)/L4(4.5)@C-800</td>
<td>89.09</td>
<td>0.165</td>
<td>3.222</td>
<td>2.138</td>
</tr>
<tr>
<td>5</td>
<td>Fe(1)/L4(6.0)@C-800</td>
<td>89.17</td>
<td>0.115</td>
<td>4.118</td>
<td>2.058</td>
</tr>
<tr>
<td>6</td>
<td>Fe(1)/L4(4.5)@C-800 (after 7th Run)</td>
<td>85.19</td>
<td>0.520</td>
<td>3.155</td>
<td>1.911</td>
</tr>
<tr>
<td>6</td>
<td>Fe(1)/L4(4.5)@C-800 (leaching with HCl)</td>
<td>85.22</td>
<td>0.341</td>
<td>3.154</td>
<td>1.726</td>
</tr>
</tbody>
</table>

4.2 X-Ray Diffraction (XRD) Measurement:

Figure S2: X-Ray Diffraction (XRD) pattern of Fe(1)/L1(1.5)@C-800 (black) and Fe(1)/L4(x)@C-800 (x = 1.5 equiv. (red), x = 3.0 equiv. (blue), x = 4.5 equiv. (purple) and x = 6.0 equiv. (green)). Phases are shown as triangle (Fe₃C, ICDD 00-034-0001), empty circle (Fe, 00-006-0696), empty square (FeNx, ICDD 01-075-2127).
**Figure S3:** Powder X-ray diffraction pattern of Fe(1)/L4(4.5)@C-800 (fresh catalyst (black) and used catalyst after 7th Run (red)). Phases are shown as filled circles (Fe$_3$O$_4$, ICDD 01-084-2782), triangle (Fe$_3$C, ICDD 00-034-0001), empty circle (Fe, ICDD 00-006-0696), empty square (FeN$_x$, ICDD 01-075-2127).

### 3.3 X-Ray Photoelectron Spectroscopic (XPS) Measurement:

**Table S3**

<table>
<thead>
<tr>
<th>Entry</th>
<th>Catalyst</th>
<th>C (At%)</th>
<th>O (At%)</th>
<th>N (At%)</th>
<th>Fe (At%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>2</td>
<td>Fe(1)/L4(4.5)@C-800</td>
<td>91.26</td>
<td>4.48</td>
<td>3.74</td>
<td>0.51</td>
</tr>
<tr>
<td>3</td>
<td>Fe(1)/L4(1.5)@C-800</td>
<td>93.64</td>
<td>3.35</td>
<td>2.59</td>
<td>0.40</td>
</tr>
<tr>
<td>4</td>
<td>Fe(1)/L4(1.5)@C-500</td>
<td>70.50</td>
<td>15.18</td>
<td>11.18</td>
<td>3.14</td>
</tr>
<tr>
<td>5</td>
<td>Fe(1)/L4(4.5)@C-800 (used)</td>
<td>89.02</td>
<td>6.03</td>
<td>4.15</td>
<td>0.80</td>
</tr>
</tbody>
</table>
Figure S4: XPS measurements for Fe(1)/L4(4.5)@C-800.
Figure S5: XPS measurements for Fe(1)/L4(1.5)@C-800.
**Figure S6:** XPS measurements for Fe(1)/L4(1.5)@C-500.
Figure S7: XPS spectra for Fe(1)/L4(4.5)@C-800, Fe(1)/L4(1.5)@C-800 and Fe(1)/L4(1.5)@C-500: 
a) N1s XPS spectra; b) C1s XPS spectra.
Figure S8: XPS measurements for Fe(1)/L4(4.5)@C-800 after 7th Run.
Figure S9: XPS spectra of the Fe(1)/L4(4.5)@C-800 after 7th Run: a) Fe2p XPS spectra; b) N1s XPS spectra; c) C1s spectra.
4.4 Scanning Transmission Electron Microscopy (STEM) Measurement:

4.4.1 Analytical STEM Data of Catalyst Fe(1)/L4(4.5)@C-800:

Figure S10. STEM-ADF (annular dark field) image (a) from the sample area used for elemental mapping of catalyst Fe(1)/L4(4.5)@C-800 in the main text marked with areas from which the electron energy loss spectra (EELS) (b,c) are extracted. The EELS data has been background subtracted, deconvolved and scaled to matching maximum intensities of the carbon edge. Area 1 and 3 differ slightly in carbon edge structure and nitrogen content with area 1 probably stemming from the ligand and area 3 from the vulcan support. Area 2 shows a Fe particle (probably carbide). The STEM-HAADF and -ABF pairs (d,e,f) of the general area used for spectrum imaging show the typical morphology of the catalyst (d), while the higher magnification shows the structural differences between the carbon phase probably stemming from the ligand and the Vulcan support, with the high resolution pair (f) showing the presence of a heavier type of element in the extra carbon phase which is not visible in the ABF image due to contrast mechanisms.
STEM-ADF (annular dark field) image (a) from another sample area of catalyst Fe(1)/L4(4.5)@C-800 marked with areas from which EELS (b,c) and EDXS (d) are extracted. The EELS data is background subtracted, deconvolved and scaled to matching intensities in front of the Fe-L edge. Area 1 contains small amounts of nitrogen, whereas Area 2 contains no nitrogen, no oxygen and no Fe. Area 3 shows an iron containing particle, iron carbide is probable considering the form of the carbon fine structure. However no firm statement can be made due to coverage with graphitic carbon. The STEM-ADF image (e) overlaid with the elemental map data generated from the EELS data show the distribution of nitrogen compared to the different carbon structure in the catalyst. Additionally the carbon nanotube structure is visible in in the STEM-HAADF (annular dark field) and STEM-ABF (annular bright field) images (f), with (g) showing a higher magnified image pair of the carbon covered Fe containing particle attached to the carbon tube.
4.4.2 Analytical STEM Data of Catalyst Fe(1)/L4(1.5)@C-800:

Figure S12. STEM-ADF image (a) of the sample (Fe(1)/L4(1.5)@C-800) marked with the areas used for EELS (b, c) and EDXS (d). Area 1 shows a faint amount of nitrogen and iron in the EELS data within a carbon matrix, whereas area 2 includes a small Fe containing particle. The EELS data has been subtracted with a background fit in front of the C-K edge, deconvolved and scaled to matching integrated C-K edge intensities. The elemental maps calculated from the EELS data and the false colour image overlaid on the STEM-ADF image (e) show the distribution of the nitrogen containing carbon phase while the Fe containing particle is represented by a bright blue pixel. The STEM-HAADF and corresponding STEM-ABF images (f) show the general area used for the spectrum imaging with only one Fe containing particles present in the imaged area. The higher magnified detail (g) is of the region containing the nitrogen containing carbon phase where small agglomerations of an element heavier than C are present. Another pair of STEM-HAADF and -ABF images (h) shows a different region of the specimen containing lots of iron carbide particles of different sizes and (i) showing high resolution images of a iron carbide particle surrounded by few layers of graphene.
4.4.3 Analytical STEM Data of Catalyst Fe(1)/L4(1.5)@C-500:

Figure S13. STEM-ADF image (a) of the sample (Fe(1)/L4(1.5)@C-500) marked with the areas used for EELS (b, c) and EDXS (d). Area 1 shows a certain content of nitrogen and iron in the EELS data lacking in area 2, leading to the assumption, that area 1 represents a ligand based carbon structure. Also, this carbon structure shows no oxygen signal distinguishable from the background. The EELS data has been subtracted with a background fit in front of the C-K edge, deconvolved and scaled to matching integrated C-K edge intensities. The elemental maps calculated from the EELS data and the false colour image overlaid on the STEM-ADF image (e) shows the distribution of the ligand based carbon phase. The STEM-HAADF and corresponding STEM-ABF images (f) show the general area used for the spectrum imaging with only one Fe containing particles present in the imaged area. The higher magnified detail (g) is of the region containing the ligand based carbon phase. Another pair of STEM-HAADF and -ABF images (h) shows a region of the specimen containing lots of Fe based particles of different sizes and morphology.
4.4.4 HR-STEM Images of Catalyst Fe(1)/L4(4.5)@C-800 after 7th Run:

Figure S14. STEM-ADF (annular dark field) image (a) from the sample (Fe(1)/L4(4.5)@C-800) after 7th run marked with the areas from where the EELS data (b,c) has been extracted. Area 1 and 3 show a small amount of nitrogen, whereas area 2 the nitrogen is not discernible from the background. In general, the distribution is comparable to the fresh sample albeit some minor modifications in the morphology of the nitrogen containing carbon phase. EELS data has been background subtracted, deconvolved and scaled to matching integrated intensities of the C-K edge. STEM-ADF image (d) overlaid with EELS elemental maps of (Fe(1)/L4(4.5)@C-800) after 7th run showing the distribution of N, O and Fe on the carbon support. STEM-HAADF and -ABF pair (e) showing the surrounding area of the sample position used for spectrum imaging. Seldom Si and Fe containing structures similar to phyllosilicates could be found as shown in STEM-HAADF and -ABF image pairs (f,g) and STEM-ADF image (h) with corresponding EDXS data. These structure are not present in fresh samples. The source of the Si is unknown, the general Si content of the sample is very low (Si = 0.07% by elemental analysis).
4.5 Raman Spectroscopic Measurement:

**Figure S15:** Raman Spectra of L4(4.5)@C-800 (red), Fe(1)/L4(1.5)@C-800 (green), Fe(1)/L4(3.0)@C-800 (blue), Fe(1)/L4(4.5)@C-800 (purple) and Fe(1)/L4(6.0)@C-800 (black) materials. Two distinct peaks: G-band ($I_G$) and D-band ($I_D$) were appeared at ~1590 cm$^{-1}$ and ~1590 cm$^{-1}$ respectively.

**Table S4:** Determination of $I_G/I_D$ ratio

<table>
<thead>
<tr>
<th>Entry</th>
<th>Catalyst</th>
<th>$I_G/I_D$</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>L4(4.5)@C-800</td>
<td>0.83</td>
</tr>
<tr>
<td>2</td>
<td>Fe(1)/L4(1.5)@C-800</td>
<td>0.89</td>
</tr>
<tr>
<td>3</td>
<td>Fe(1)/L4(3.0)@C-800</td>
<td>0.86</td>
</tr>
<tr>
<td>4</td>
<td>Fe(1)/L4(4.5)@C-800</td>
<td>0.86</td>
</tr>
<tr>
<td>5</td>
<td>Fe(1)/L4(6.0)@C-800</td>
<td>0.86</td>
</tr>
</tbody>
</table>
5 Scope and Limitations Studies

5.1 Synthesis of Substrates

Substrate $5'$, $19'$, and $30'$ were synthesized according to the cited literature reports. Substrate $5'$, $9'$, $10'$, $20'$, $24'$, $28'$, $29'$, $38'$ and $39'$ were synthesized according to the methods described below. Rest of the substrates was commercially available.

Synthesis of (Hetero)Aryl-substituted (Iso)Quinolines:

In an oven dried Schlenck flask equipped with a magnetic stir bar, 3-, 6- or 8-bromoquinoline or 4-bromoisoquinoline (1.0 equiv.) and Arylboronic acid or ester (1.1 equiv.) were dissolved in 1,4-dioxane (0.1M, Condition A) or isopropanol (0.1M, Condition B) under argon atmosphere. Then aq. 2M $K_2CO_3$ solution (10.0 equiv. for arylboronic acids or 1.1 equiv. for arylboronic esters, Condition A) or 4M $K_3PO_4$ solution (10.0 equiv., Condition B) was added to the reaction mixture and the resulting solution was degassed for 20 min purging argon through it. Afterwards, $[Pd(PPh_3)_4]$ (5 mol%, Condition A) or $[Pd(PPh_3)_2Cl_2]$ (5 mol%, Condition B) was added to the solution and the resulting reaction mixture was heated at 100 °C (Condition A) and 60 °C (Condition B) for 12-15 h. After cooling to rt, the reaction mixture was diluted with water and extracted with ethyl acetate. The organic layers were washed with brine solution and dried with sodium sulphate. The organic phase was concentrated under reduced pressure and the crude reaction mixture was purified by flash column chromatography through silica gel (eluent: heptane/ethyl acetate or dichloromethane/ethyl acetate or dichloromethane/methanol) to afford pure product.

3-(4-Methoxyphenyl)quinoline ($5'$)

Isolated Yield: 99% (936 mg, 3.98 mmol, white solid) with 3-bromoquinoline (832 mg, 4.00 mmol) and (4-methoxyphenyl)boronic acid (669 mg, 4.40 mmol) following Condition A; $^1$H NMR (300 MHz, CDCl$_3$): $\delta$ (ppm): 9.19 (d, $J = 2.3$ Hz, 1H), 8.24 (d, $J = 2.3$ Hz, 1H), 8.17 (d, $J = 8.4$ Hz, 1H), 7.86 (d, $J = 8.1$ Hz, 1H), 7.64 – 7.75 (m, 3H), 7.57 (ddd, $J = 8.0$, 6.9, 1.2 Hz, 1H), 7.05 – 7.10 (m, 2H), 3.89 (s, 3H); $^{13}$C NMR (75 MHz, CDCl$_3$): $\delta$ (ppm): 159.9, 149.8, 147.0, 133.5, 132.4, 130.3, 129.2, 129.1, 128.5, 128.2, 127.9, 127.0, 114.7, 55.4; HR-MS (EI): $m/z$ calculated for [C$_{16}$H$_{13}$N$_2$O] ([M]): 235.0992, found: 235.0994.
6-(4-Fluorophenyl)quinoline (9')

**Isolated Yield:** 94% (630 mg, 2.82 mmol, pale yellow solid) with 6-bromoquinoline (624 mg, 3.00 mmol) and (4-fluorophenyl)boronic acid (462 mg, 3.30 mmol) following Condition A; $^1$H NMR (300 MHz, CDCl$_3$): $\delta$ (ppm): 8.91 (dd, $J = 4.2, 1.7$ Hz, 1H), 8.18 – 8.20 (m, 2H), 7.89 – 7.93 (m, 2H), 7.62 – 7.69 (m, 2H), 7.41 (dd, $J = 8.3, 4.2$ Hz, 1H), 7.13 – 7.21 (m, 2H); $^{13}$C NMR (75 MHz, CDCl$_3$): $\delta$ (ppm): 162.9 (d, $J = 247.4$ Hz), 150.6, 147.7, 138.4, 136.6 (d, $J = 3.3$ Hz), 136.3, 130.1, 129.2, 129.12 (d, $J = 3.1$ Hz), 128.6, 125.4, 121.7, 116.0 (d, $J = 21.5$ Hz); $^{19}$F NMR (282 MHz, CDCl$_3$): $\delta$ (ppm): –114.85; HR-MS (EI): $m/z$ calculated for [C$_{15}$H$_{10}$N$_{1}$F$_{1}$] ([M]): 223.0792, found: 223.0786.

6-(4-(Trifluoromethoxy)phenyl)quinoline (10')

**Isolated Yield:** 90% (920 mg, 3.18 mmol, brown solid) with 6-bromoquinoline (624 mg, 3.00 mmol) and (4-(trifluoromethoxy)phenyl)boronic acid (680 mg, 3.3 mmol) following Condition A; $^1$H NMR (300 MHz, CDCl$_3$): $\delta$ (ppm): 8.93 (dd, $J = 4.2, 1.7$ Hz, 1H), 8.17 – 8.22 (m, 2H), 7.92 – 7.96 (m, 2H), 7.69 – 7.74 (m, 2H), 7.43 (dd, $J = 8.3, 4.2$ Hz, 1H), 7.32 – 7.36 (m, 2H), 7.32 – 7.36 (m, 2H); $^{13}$C NMR (75 MHz, CDCl$_3$): $\delta$ (ppm): 150.8, 149.13 (q, $J = 1.8$ Hz), 147.9, 139.2, 138.1, 136.4, 130.3, 129.0, 128.9, 128.5, 125.8, 121.8, 121.5 (q, $J = 1.0$ Hz), 120.7 (q, $J = 257.3$ Hz); $^{19}$F NMR (282 MHz, CDCl$_3$): $\delta$ (ppm): –57.78; HR-MS (EI): $m/z$ calculated for [C$_{13}$H$_{10}$N$_{1}$O$_{1}$F$_{3}$] ([M]): 289.0709, found: 289.0714.

6-(1-Methyl-1H-pyrazol-5-yl)quinoline (11')

**Isolated Yield:** 96% (605 mg, 2.89 mmol, brown solid) with 6-bromoquinoline (624 mg, 3.00 mmol) and 1-methyl-5-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-1H-pyrazole (687 mg, 3.30 mmol) following Condition A; $^1$H NMR (300 MHz, CDCl$_3$): $\delta$ (ppm): 8.96 (dd, $J = 4.3, 1.7$ Hz, 1H), 8.18 – 8.21 (m, 1H), 8.19 (d, $J = 8.7$ Hz, 1H), 8.16 (d, $J = 2.0$ Hz, 1H), 7.76 (dd, $J = 8.7, 2.0$ Hz, 1H), 7.56 (d, $J = 1.9$ Hz, 1H), 7.46 (dd, $J = 8.3, 4.2$ Hz, 1H), 6.62 (d, $J = 1.9$ Hz, 1H), 3.96 (s, 3H); $^{13}$C NMR (75 MHz, CDCl$_3$): $\delta$ (ppm): 151.3, 147.9, 142.9, 138.8, 136.3, 130.1, 129.1, 128.2, 127.8, 122.0, 106.8, 37.8; HR-MS (EI): $m/z$ calculated for [C$_{13}$H$_{11}$N$_{3}$] ([M]): 209.0948, found: 209.0944.

3-(Quinolin-6-yl)benzonitrile (24')

- 522 -
**Isolated Yield**: 94% (433 mg, 1.88 mmol, white solid) with 6-bromoquinoline (416 mg, 2.00 mmol) and (3-cyanophenyl)boronic acid (323 mg, 2.20 mmol) following Condition B; 

\[ ^1H \text{NMR (300 MHz, CDCl}_3) \]: \( \delta \text{ (ppm): 8.92 (dd, } J = 4.2, 1.7 \text{ Hz, 1H), 8.19 (dd, } J = 8.1, 1.3 \text{ Hz, 1H), 8.18 (d, } J = 8.6, 1\text{H), 7.93 – 7.95 (m, 2H), 7.85 – 7.66 (m, 2H), 7.43 (dd, } J = 8.3, 4.2 \text{ Hz, 1H); } ^{13}C \text{ NMR (75 MHz, CDCl}_3) \]: \( \delta \text{ (ppm): 151.1, 148.0, 141.6, 136.9, 136.4, 131.8, 131.1, 131.0, 130.5, 129.9, 128.5, 128.4, 126.0, 121.9, 118.7, 113.2; HR-MS (EI): } m/z \text{ calculated for [C}_{16}H_{10}N_2} ([M]): 230.0839, found: 230.0835.

8-(Thiophen-3-yl)quinoline (28’)

![8-(Thiophen-3-yl)quinoline](image)

**Isolated Yield**: 81% (342 mg, 1.62 mmol, pale yellow oil) with 8-bromoquinoline (416 mg, 2.00 mmol) and thiophen-3-ylboronic acid (282 mg, 2.20 mmol) following Condition A; 

\[ ^1H \text{NMR (300 MHz, CDCl}_3) \]: \( \delta \text{ (ppm): 9.00 (dd, } J = 4.2, 1.8 \text{ Hz, 1H), 8.20 (dd, } J = 8.3, 1.9 \text{ Hz, 1H), 7.91 (dd, } J = 3.0, 1.3 \text{ Hz, 1H), 7.88 (dd, } J = 7.2, 1.5 \text{ Hz, 1H), 7.79 (dd, } J = 8.2, 1.5 \text{ Hz, 1H), 7.58 (dd, } J = 8.2, 7.2 \text{ Hz, 1H), 7.45 (dd, } J = 5.0, 3.0 \text{ Hz, 1H), 7.43 (dd, } J = 8.2, 4.2 \text{ Hz, 1H); } ^{13}C \text{ NMR (75 MHz, CDCl}_3) \]: \( \delta \text{ (ppm): 150.2, 146.0, 139.7, 136.5, 135.3, 129.9, 129.6, 127.5, 126.5, 124.9, 124.7, 121.2; HR-MS (EI): } m/z \text{ calculated for [C}_{13}H_8N_1S_1} ([M]): 210.0372, found: 210.0370. The obtained spectroscopic data were in agreement with the reported data for this compound [ref.5].

(4-(Isoquinolin-4-yl)phenyl)(morpholino)methanone (29’)

![4-(Isoquinolin-4-yl)phenyl)(morpholino)methanone](image)

**Isolated Yield**: 69% (440 mg, 1.38 mmol, light yellow solid after further recrystallization) with 4-bromoisoquinoline (416 mg, 2.0 mmol) and morpholino(4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)phenyl)methanone (698 mg, 2.20 mmol) following Condition A; 

\[ ^1H \text{NMR (300 MHz, CDCl}_3) \]: \( \delta \text{ (ppm): 9.27 (d, } J = 0.9 \text{ Hz, 1H), 8.47 (s, 1H), 8.04 – 8.07 (m, 1H), 7.85 – 7.89 (m, 1H), 7.62 – 7.72 (m, 2H), 7.57 (s, 4H), 3.61 – 3.76 (m, 8H); } ^{13}C \text{ NMR (101 MHz, CDCl}_3) \]: \( \delta \text{ (ppm): 170.1, 152.5, 142.8, 138.8, 135.0, 134.0, 132.4, 130.9, 130.3, 128.4, 128.0, 127.5, 127.4, 124.5, 67.0, 48.4, 42.7; HR-MS (EI): } m/z \text{ calculated for [C}_{20}H_{18}N_1O_1} ([M]): 318.1363, found: 318.1363.

6-(Pyren-1-yl)quinoline (38’)

![6-(Pyren-1-yl)quinoline](image)
**Isolated Yield:** 98% (650 mg, 1.97 mmol, pale yellow solid) with 6-bromoquinoline (416 mg, 2.00 mmol) and pyren-1-ylboronic acid (541 mg, 2.20 mmol) following Condition A; $^1$H NMR (400 MHz, CDCl$_3$): $\delta$ (ppm): 9.02 (dd, $J = 4.3$, 1.7 Hz, 1H), 8.16 – 8.32 (m, 6H), 8.13 (s, 2H), 8.01 – 8.07 (m, 5H), 7.49 (dd, $J = 8.2$, 4.3 Hz, 1H); $^{13}$C NMR (101 MHz, CDCl$_3$): $\delta$ (ppm): 150.7, 147.6, 139.8, 136.8, 136.4, 132.7, 131.6, 131.1, 131.0, 129.4, 129.2, 128.8, 128.4, 128.0, 127.9, 127.8, 127.5, 126.3, 125.5, 125.2, 125.1, 125.0, 124.8, 121.7; HR-MS (EI): m/z calculated for [C$_{25}$H$_{15}$N] ([M]): 329.1199, found: 329.1194.

**2-Methyl-6-(pyren-1-yl)quinoline (39’)**

![2-Methyl-6-(pyren-1-yl)quinoline](image)

**Isolated Yield:** 99% (680 mg, 1.98 mmol, pale yellow solid) with 6-bromo-2-methylquinoline (444 mg, 2.00 mmol) and pyren-1-ylboronic acid (541 mg, 2.20 mmol) following Condition A; $^1$H NMR (300 MHz, CDCl$_3$): $\delta$ (ppm): 8.12 – 8.27 (m, 8H), 7.96 – 8.07 (m, 5H), 7.37 (d, $J = 8.4$ Hz, 1H), 2.83 (s, 3H); $^{13}$C NMR (75 MHz, CDCl$_3$): $\delta$ (ppm): 159.4, 147.2, 138.8, 137.0, 136.5, 132.6, 131.6, 131.1, 130.9, 129.0, 128.6, 127.9, 127.9, 127.7, 127.5, 126.6, 126.2, 125.4, 125.2, 125.1, 125.1, 125.0, 124.8, 122.6, 25.6; HR-MS (EI): m/z calculated for [C$_{26}$H$_{17}$N] ([M]): 343.1356, found: 343.1348.

**Synthesis of (+)-α-Tocopherol-modified quinoline substrate (20’):**

![Synthesis of (+)-α-Tocopherol-modified quinoline substrate (20')](image)

In an oven dried Schlenk tube, substrate 35 (794 mg, 3.58 mmol, 1.00 equiv.), (+)-α-Tocopherol (3.10 g, 7.20 mmol, 2.00 equiv.) and K$_2$CO$_3$ (990 mg, 7.16 mmol, 2.00 equiv.) were dissolved in DMF (11 mL). Then, sodium iodide (108 mg, 0.72 mmol, 0.20 equiv.) was added to the resulting solution and allowed to stir at 120 °C for 15 h. After cooling down to rt, the reaction mixture was diluted with water (7 mL) and the organic phase was extracted with ethyl acetate (3×15 mL). The combined

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1 The synthesis of substrate 35 has been described in section 5.5.3
organic layers were washed with water followed by brine solution and finally solvents were removed
under reduced pressure. The crude reaction mixture was purified by flash column chromatography
through silica (eluent: heptane/ethylacetate = 90/10) to afford pure product 20' (1.25 g, 2.03 mmol,
57%) as brown viscous liquid.

\[ \text{H NMR (400 MHz, CDCl}_3\text{): } \delta (ppm): 8.78 (dd, } J = 4.3, 1.7 \text{ Hz, 1H}), 8.05 (ddd, } J = 8.3, 4.2 \text{ Hz, 1H}), 7.35 (dd, } J = 8.3, 4.2 \text{ Hz, 1H}), 7.14 (d, } J = 2.7 \text{ Hz, 1H}), 4.39 (t, } J = 6.1 \text{ Hz, 2H}), 2.56 (t, } J = 6.8 \text{ Hz, 2H}), 2.30 – 2.36 \text{ (m, 2H}), 2.11 (s, 3H), 2.08 (s, 3H), 1.71 – 1.85 \text{ (m, 2H), 1.02 – 1.59 \text{ (m, 2H), 0.84 – 0.88 (m, 12H); C NMR (101 MHz, CDCl}_3\text{): } \delta (ppm): 157.2, 148.1, 148.0, 147.9, 144.6, 134.9, 131.0, 129.5, 127.9, 125.9, 123.0, 122.6, 121.4, 117.7, 106.0, 74.9, 68.9, 64.9, 40.2, 39.5, 37.6, 37.5, 37.4, 32.9, 32.8, 31.4, 30.1, 28.1, 26.7, 24.0, 23.9, 23.8, 21.2, 20.8, 19.9, 19.8, 12.8, 11.9, 11.9; HR-MS (EI): } m/z \text{ calculated for [C}_{41}\text{H}_{61}\text{N}_{1}\text{O}_{3}\text{] ([M]): 615.4646, found: 615.4634.}

5.2 General Procedure for the Hydrogenation of N-Heteroarenes (GP)

\[ \text{Fe(1)/L4(4.5)@C-800 (10-15 mol% Fe)} \]
\[ \text{iPrOH/H}_2\text{O or MeOH/H}_2\text{O (3/1)} \]
\[ 120-150^\circ \text{C, 56-72 h} \]
\[ \text{H}_2 (3-5 \text{ MPa)} \]

In a 4 or 8 mL glass vial fitted with a septum cap containing a magnetic stirring bar, Fe(1)/L4(4.5)@C-800 and substrate (N-Heteroarene) were added to a solvent mixture of iPrOH/H\text{O or MeOH/H}_2\text{O (3/1). The reaction vial was then placed into a 300 mL autoclave, flashed with hydrogen five times and finally pressurized to 3-5 MPa. The reaction mixture was stirred at 120-150°C for 56-72 h. After cooling the reaction mixture to room temperature, the autoclave was slowly depressurized. Solvents were removed and the crude reaction mixture was purified by flash column chromatography through silica (eluent: heptane/ethyl acetate or dichloromethane/methanol) to afford pure product. [N.B. The mentioned reaction temperature is the temperature at inner wall of glass vials inside the autoclave]

The yields of product 1 and 23 were calculated based on GC analysis using hexadane as internal standard.

5.3 Characterization Data of Isolated Products

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

Prepared from 2-Methylquinoline (2', 57 mg, 0.4 mmol, 1.00 equiv.), Fe(1)/L4(4.5)@C-800 (106 mg, 10 mol% Fe) and H\text{2 (4 MPa) in iPrOH/H}_2\text{O (3/1, 2 mL) at 130 \text{ °C for 60 h following GP. Isolated Yield: 98% (58 mg, 0.39 mmol, colourless liquid); H NMR (300 MHz, CDCl}_3\text{): } \delta (ppm): 6.99 – 7.05 (m, 2H), 6.66 (td, } J = 7.4, 1.2 \text{ Hz, 1H}), 6.52 (dd, } J = 8.3, 1.3 \text{ Hz, 1H}), 3.66 (bs, 1H), 3.39 – 3.50 \text{ (m, 1H)}, 2.73 – 2.96 (m, 2H), 1.94 – 2.02 \text{ (m, 1H), 1.58 – 1.71 (m, 1H), 1.26 (d, } J = 6.3 \text{ Hz, 3H); C NMR (75 MHz, CDCl}_3\text{): } \delta (ppm): 144.9, 129.3, 126.8, 121.2, 117.0, 114.1, 47.2, 30.2, 26.7, 22.7;
HR-MS (EI): \( m/z \) calculated for \([\text{C}_{10}\text{H}_{13}\text{N}]^+\) ([M]): 147.1043, found: 147.1043. The obtained spectroscopic data were in agreement with the reported data for this compound [ref.6,7].

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

![2-Phenyl-1,2,3,4-tetrahydroquinoline](image)

Prepared from 2-Phenylquinoline (3', 83 mg, 0.40 mmol, 1.00 equiv.), Fe(1)/L4(4.5)@C-800 (106 mg, 10 mol% Fe) and \( \text{H}_2 \) (4 MPa) in \( \text{PrOH/H}_2\text{O} \) (3/1, 2 mL) at 140 °C for 72 h following GP. **Isolated Yield:** 98% (82 mg, 0.40 mmol, colourless oil); **\(^1\)H NMR (300 MHz, CDCl\(_3\))**: \( \delta \) (ppm): 7.35 – 7.50 (m, 5H), 7.08 – 7.13 (m, 2H), 6.75 (td, \( J = 7.4, 1.2 \) Hz, 1H), 6.63 – 6.69 (m, 1H), 4.51 (dd, \( J = 9.2, 3.4 \) Hz, 1H), 4.09 (bs, 1H), 2.95 – 3.07 (m, 1H), 2.82 (dt, \( J = 16.3, 4.8 \) Hz, 1H), 2.02 – 2.25 (m, 2H); **\(^13\)C NMR (75 MHz, CDCl\(_3\))**: \( \delta \) (ppm): 144.9, 144.8, 129.4, 128.6, 127.5, 127.0, 126.6, 120.9, 117.2, 114.1, 56.3, 31.1, 26.5; **HR-MS (EI):** \( m/z \) calculated for \([\text{C}_{15}\text{H}_{15}\text{N}]^+\) ([M]): 209.1199, found: 209.1199. The obtained spectroscopic data were in agreement with the reported data for this compound [ref.6].

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

![3-Methyl-1,2,3,4-tetrahydroquinoline](image)

Prepared from 3-Methylquinoline (4', 57 mg, 0.4 mmol, 1.00 equiv.), Fe(1)/L4(4.5)@C-800 (106 mg, 10 mol% Fe) and \( \text{H}_2 \) (4 MPa) in \( \text{PrOH/H}_2\text{O} \) (3/1, 2 mL) at 140 °C for 72 h following GP. **Isolated Yield:** 90% (53 mg, 0.36 mmol, pale yellow liquid); **\(^1\)H NMR (300 MHz, CDCl\(_3\))**: \( \delta \) (ppm): 6.99 – 7.05 (m, 2H), 6.66 (td, \( J = 7.4, 1.2 \) Hz, 1H), 6.53 (dd, \( J = 7.6, 0.8 \) Hz, 1H), 3.80 (bs, 1H), 3.31 (ddd, \( J = 11.0, 3.7, 2.0 \) Hz, 1H), 2.94 (dd, \( J = 11.0, 9.6 \) Hz, 1H), 2.83 (ddd, \( J = 16.0, 4.9, 1.9 \) Hz, 1H), 2.49 (dd, \( J = 16.0, 10.2 \) Hz, 1H), 2.03 – 2.19 (m, 1H), 1.31 (d, \( J = 6.6 \) Hz, 3H); **\(^13\)C NMR (75 MHz, CDCl\(_3\))**: \( \delta \) (ppm): 144.9, 144.8, 129.4, 128.6, 127.5, 127.0, 126.6, 120.9, 117.2, 114.1, 56.3, 31.1, 26.5; **HR-MS (EI):** \( m/z \) calculated for \([\text{C}_{10}\text{H}_{13}\text{N}]^+\) ([M]): 147.1043, found: 147.1039. The obtained spectroscopic data were in agreement with the reported data for this compound [ref.7].

3-(4-Methoxyphenyl)-1,2,3,4-tetrahydroquinoline (5)

![3-(4-Methoxyphenyl)-1,2,3,4-tetrahydroquinoline](image)

Prepared from 3-(4-Methoxyphenyl)quinoline (5', 94 mg, 0.4 mmol, 1.00 equiv.), Fe(1)/L4(4.5)@C-800 (127 mg, 12 mol% Fe) and \( \text{H}_2 \) (5 MPa) in \( \text{PrOH/H}_2\text{O} \) (3/1, 2 mL) at 150 °C for 70 h following GP. **Isolated Yield:** 91% (87 mg, 0.36 mmol, white solid); **\(^1\)H NMR (300 MHz, CDCl\(_3\))**: \( \delta \) (ppm): 7.17 – 7.22 (m, 2H), 7.01 – 7.04 (m, 2H), 6.89 – 6.94 (m, 2H), 6.46 – 6.70 (m, 1H), 6.55 – 6.58 (m, 1H), 3.99 (bs, 1H), 3.83 (s, 3H), 3.42 – 3.48 (m, 1H), 3.31 (t, \( J = 10.5 \) Hz, 1H), 3.06 – 3.18 (m, 1H), 1.92 – 2.04 (m, 2H); **\(^13\)C NMR (75 MHz, CDCl\(_3\))**: \( \delta \) (ppm): 158.4, 144.1, 136.1, 129.6, 128.2, 127.1,
121.5, 117.2, 114.1, 114.1, 55.4, 48.7, 37.9, 34.9; **HR-MS (ESI):** m/z calculated for \([\text{C}_{16}\text{H}_{18}\text{NO}]^+\) ([M+H]+): 240.1383, found: 240.1380.

3-(Benzo[d][1,3]dioxol-5-ylmethyl)-2-methyl-1,2,3,4-tetrahydroquinoline (6)

![Chemical Structure of 3-(Benzo[d][1,3]dioxol-5-ylmethyl)-2-methyl-1,2,3,4-tetrahydroquinoline (6)](image)

Prepared from 3-(Benzo[d][1,3]dioxol-5-ylmethyl)-2-methylquinoline (6′, 111 mg, 0.4 mmol, 1.00 equiv.), Fe(1)/L4(4.5)@C-800 (127 mg, 12 mol% Fe) and \(\text{H}_2\) (5 MPa) in \(\text{iPrOH/H}_2\text{O}\) (3/1, 2 mL) at 150 °C for 72 h following GP. **Isolated Yield:** 77% as inseparable mixture of daistereomers (87 mg, 0.31 mmol, pale yellow liquid, d.r. = 1.3:1, determined by GC analysis); **\(^1\text{H NMR (400 MHz, CDCl}_3\):** \(\delta\) (ppm): 6.98 – 7.04 (m, 2H), 6.94 (t, \(J = 8.3\) Hz, 2H), 6.76 – 6.79 (m, 2H), 6.60 – 6.72 (m, 6H), 6.50 – 6.52 (m, 2H), 6.40 – 6.46 (m, 2H), 5.95 – 5.96 (m, 4H), 3.76 (bs, 2H), 3.51 – 3.56 (m, 1H), 3.22 (quin, \(J = 6.3\) Hz, 1H), 2.86 (dd, \(J = 13.6, 5.7\) Hz, 1H), 2.66 – 2.76 (m, 3H), 2.52 – 2.58 (m, 1H), 2.40 – 2.48 (m, 2H), 2.31 (dd, \(J = 13.5, 9.4\) Hz, 1H), 2.15 – 2.23 (m, 1H), 1.83 – 1.91 (m, 1H), 1.27 (d, \(J = 6.3\) Hz, 3H), 1.22 (d, \(J = 6.5\) Hz, 3H); **13C NMR (101 MHz, CDCl\(_3\):** \(\delta\) (ppm): 147.6, 147.6, 145.8, 145.8, 144.0, 143.8, 143.6, 134.9, 129.9, 129.6, 126.9, 122.1, 122.0, 120.0, 119.8, 117.2, 116.9, 114.1, 113.6, 109.6, 109.5, 108.2, 108.2, 106.9, 106.9, 50.6, 49.3, 39.6, 38.3, 38.3, 35.5, 30.5, 30.0, 21.8, 17.7; **HR-MS (EI):** m/z calculated for \([\text{C}_{18}\text{H}_{19}\text{N}_1\text{O}_2]\) ([M]): 281.1410, found: 281.1409.

2,4-Dimethyl-1,2,3,4-tetrahydroquinoline (7)

![Chemical Structure of 2,4-Dimethyl-1,2,3,4-tetrahydroquinoline (7)](image)

Prepared from 2,4-Dimethylquinoline (7′, 63 mg, 0.4 mmol, 1.00 equiv.), Fe(1)/L4(4.5)@C-800 (106 mg, 10 mol% Fe) and \(\text{H}_2\) (5 MPa) in \(\text{iPrOH/H}_2\text{O}\) (3/1, 2 mL) at 150 °C for 72 h following GP. **Isolated Yield:** 71% as inseparable mixture of daistereomers (46 mg, 0.29 mmol, colourless liquid, d.r.: cis:trans = 4.5:1, determined by GC analysis); **\(^1\text{H NMR (300 MHz, CDCl}_3\):** **cis isomer:** \(\delta\) (ppm): 7.18 (dt, \(J = 7.7, 1.2\) Hz, 1H), 7.01 (dddd, \(J = 8.0, 7.3, 1.5, 0.9\) Hz, 1H), 6.70 (td, \(J = 7.4, 1.3\) Hz, 1H), 6.50 (dd, \(J = 8.0, 1.2\) Hz, 1H), 3.67 (bs, 1H), 3.45 – 3.55 (m, 1H), 2.91 – 3.07 (m, 1H); 1.97 (ddd, \(J = 12.8, 5.4, 2.6\) Hz, 1H), 1.31 – 1.44 (m, 1H), 1.36 (d, \(J = 6.8\) Hz, 3H), 1.23 (d, \(J = 6.2\) Hz, 3H); **13C NMR (75 MHz, CDCl\(_3\):** **cis isomer:** \(\delta\) (ppm): 144.9, 126.9, 126.8, 126.3, 117.3, 114.0, 47.5, 40.7, 31.0, 22.9, 20.4; **HR-MS (EI):** m/z calculated for \([\text{C}_{11}\text{H}_{15}\text{N}_1]\) ([M]): 161.1199, found: 161.1203. The obtained spectroscopic data were in agreement with the reported data for this compound [ref.8].

6-Isopropyl-1,2,3,4-tetrahydroquinoline (8)
Prepared from 6-Isopropylquinoline (8', 69 mg, 0.4 mmol, 1.00 equiv.), Fe(1)/L4(4.5)@C-800 (106 mg, 10 mol% Fe) and H₂ (4 MPa) in PrOH/H₂O (3/1, 2 mL) at 140 °C for 60 h following GP. 
**Isolated Yield:** 67% (47 mg, 0.27 mmol, colourless liquid); ¹H NMR (300 MHz, CDCl₃): δ (ppm): 6.82 – 6.88 (m, 2H), 6.45 (d, J = 7.9 Hz, 1H), 3.57 (bs, 1H), 3.26 – 3.30 (m, 2H), 2.78 (sept, J = 6.9 Hz, 1H), 2.77 (t, J = 6.4 Hz, 2H), 1.91 – 1.99 (m, 2H), 1.22 (d, J = 6.9 Hz, 6H); ¹³C NMR (75 MHz, CDCl₃): δ (ppm): 142.8, 137.8, 127.5, 124.7, 121.5, 114.5, 42.3, 33.3, 27.2, 24.4, 22.5; HR-MS (EI): m/z calculated for [C₁₂H₁₇N₁] ([M]): 175.1356, found: 175.1355. The obtained spectroscopic data were in agreement with the reported data for this compound [ref.9].

**6-(4-Fluorophenyl)-1,2,3,4-tetrahydroquinoline (9)**

Prepared from 6-(4-Fluorophenyl)quinoline (9', 90 mg, 0.4 mmol, 1.00 equiv.), Fe(1)/L4(4.5)@C-800 (106 mg, 10 mol% Fe) and H₂ (4 MPa) in PrOH/H₂O (3/1, 2 mL) at 140 °C for 60 h following GP. 
**Isolated Yield:** 94% (84 mg, 0.37 mmol, white solid); ¹H NMR (300 MHz, CDCl₃): δ (ppm): 7.45 – 7.52 (m, 2H), 7.18 – 7.21 (m, 2H), 7.05 – 7.13 (m, 2H), 6.53 – 6.57 (m, 1H), 3.76 (bs, 1H), 3.33 – 3.37 (m, 2H), 2.84 (t, J = 6.4 Hz, 2H), 1.96 – 2.04 (m, 2H); ¹³C NMR (75 MHz, CDCl₃): δ (ppm): 161.8 (d, J = 244.3 Hz), 144.3, 137.8 (d, J = 3.1 Hz), 129.1, 128.1, 127.7 (d, J = 7.8 Hz), 125.5, 121.7, 115.4 (d, J = 21.2 Hz), 114.6, 42.1, 27.2, 22.2; ¹⁹F NMR (282 MHz, CDCl₃): δ (ppm): -117.84; HR-MS (EI): m/z calculated for [C₁₅H₁₄N₁F₁] ([M]): 227.1102, found: 227.1105.

**6-(4-(Trifluoromethoxy)phenyl)-1,2,3,4-tetrahydroquinoline (10)**

Prepared from 6-(4-(Trifluoromethoxy)phenyl)quinoline (10', 116 mg, 0.4 mmol, 1.00 equiv.), Fe(1)/L4(4.5)@C-800 (106 mg, 10 mol% Fe) and H₂ (5 MPa) in PrOH/H₂O (3/1, 2 mL) at 150 °C for 72 h following GP. 
**Isolated Yield:** 87% (104 mg, 0.35 mmol, white solid); ¹H NMR (300 MHz, CDCl₃): δ (ppm): 7.51 – 7.56 (m, 2H), 7.19 – 7.25 (m, 4H), 6.53 – 6.56 (m, 1H), 3.88 (bs, 1H), 3.34 – 3.37 (m, 2H), 2.84 (t, J = 6.4 Hz, 2H), 1.95 – 2.03 (m, 2H); ¹³C NMR (75 MHz, CDCl₃): δ (ppm): 147.7 (q, J = 2.0 Hz), 144.7, 140.6, 128.5, 128.3, 127.5, 125.6, 121.7, 121.3 (q, J = 0.9 Hz), 120.7 (q, J = 257 Hz), 114.5, 42.1, 27.3, 22.2; ¹⁹F NMR (282 MHz, CDCl₃): δ (ppm): -57.82; HR-MS (EI): m/z calculated for [C₁₃H₁₂N₁O₁F₃] ([M]): 293.1022, found: 293.1022.

**6-(1-Methyl-1H-pyrazol-5-yl)-1,2,3,4-tetrahydroquinoline (11)**

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Prepared from 6-(1-Methyl-1H-pyrazol-5-yl)quinoline (11’, 84 mg, 0.4 mmol, 1.00 equiv.), Fe(1)/L4(4.5)@C-800 (106 mg, 10 mol% Fe) and H2 (4 MPa) in PrOH/H2O (3/1, 2 mL) at 140 °C for 60 h following GP. **Isolated Yield:** 97% (83 mg, 0.39 mmol, white solid); 1H NMR (300 MHz, CDCl3): δ (ppm): 7.46 (d, J = 1.9 Hz, 1H), 6.97 – 7.01 (m, 2H), 6.48 – 6.51 (m, 1H), 6.19 (d, J = 1.9 Hz, 1H), 4.11 (bs, 1H), 3.86 (s, 3H), 3.31 – 3.35 (m, 2H), 2.79 (t, J = 6.4 Hz, 2H), 1.92 – 2.00 (m, 2H); 13C NMR (75 MHz, CDCl3): δ (ppm): 145.0, 144.3, 138.3, 129.9, 127.3, 121.2, 118.8, 113.8, 105.1, 41.9, 37.4, 27.1, 21.9; HR-MS (ESI): m/z calculated for [C13H16N3]+ ([M+H]+): 214.1339, found: 214.1339.

6-Methoxy-2-methyl-1,2,3,4-tetrahydroquinoline (12)

Prepared from 6-Methoxy-2-methylquinoline (12’, 70 mg, 0.4 mmol, 1.00 equiv.), Fe(1)/L4(4.5)@C-800 (106 mg, 10 mol% Fe) and H2 (4 MPa) in PrOH/H2O (3/1, 2 mL) at 130 °C for 72 h following GP. **Isolated Yield:** 93% (66 mg, 0.37 mmol, pale yellow liquid); 1H NMR (300 MHz, CDCl3): δ (ppm): 6.60 – 6.65 (m, 2H), 6.44 – 6.49 (m, 1H), 3.75 (s, 3H), 3.44 (bs, 1H), 3.29 – 3.40 (m, 1H), 2.81 – 2.93 (m, 1H), 2.69 – 2.77 (m, 1H), 1.90 – 1.98 (m, 1H), 1.53 – 1.66 (m, 1H), 1.22 (d, J = 6.2 Hz, 3H); 13C NMR (75 MHz, CDCl3): δ (ppm): 151.9, 139.0, 122.5, 115.4, 114.7, 112.9, 55.8, 47.5, 30.4, 27.0, 22.6; HR-MS (EI): m/z calculated for [C11H15NO]+ ([M]+): 177.1148, found: 177.1148. The obtained spectroscopic data were in agreement with the reported data for this compound [ref.10].

6-Fluoro-2-methyl-1,2,3,4-tetrahydroquinoline (13)

Prepared from 6-Fluoro-2-methylquinoline (13’, 65 mg, 0.4 mmol, 1.00 equiv.), Fe(1)/L4(4.5)@C-800 (106 mg, 10 mol% Fe) and H2 (4 MPa) in PrOH/H2O (3/1, 2 mL) at 130 °C for 60 h following GP. **Isolated Yield:** 94% (62 mg, 0.38 mmol, colourless liquid); 1H NMR (282 MHz, CDCl3): δ (ppm): 6.65 – 6.72 (m, 2H), 6.38 – 6.43 (m, 1H), 3.46 (bs, 1H), 3.30 – 3.41 (m, 1H), 2.66 – 2.90 (m, 2H), 1.88 – 1.97 (m, 1H), 1.50 – 1.64 (m, 1H), 1.21 (d, J = 6.3 Hz, 3H); 13C NMR (75 MHz, CDCl3): δ (ppm): 155.6 (d, J = 234.5 Hz), 141.1 (d, J = 1.7 Hz), 122.6 (d, J = 6.6 Hz), 115.5 (d, J = 21.6 Hz), 114.8 (d, J = 7.1 Hz), 113.2 (d, J = 22.4 Hz), 47.4, 30.0, 26.8, 22.6; 19F NMR (300 MHz, CDCl3): δ (ppm): −128.33; HR-MS (EI): m/z calculated for [C10H12N1F1] ([M]): 165.0948, found: 165.0946. The obtained spectroscopic data were in agreement with the reported data for this compound [ref.6].

7-Fluoro-2-methyl-1,2,3,4-tetrahydroquinoline (14)
Prepared from 7-Fluoro-2-methylquinoline (14', 65 mg, 0.4 mmol, 1.00 equiv.), Fe(1)/L4(4.5)@C-800 (106 mg, 10 mol% Fe) and H₂ (4 MPa) in 1PrOH/H₂O (3/1, 2 mL) at 140 °C for 60 h following GP. **Isolated Yield:** 88% (58 mg, 0.35 mmol, white solid); ¹H NMR (300 MHz, CDCl₃): δ (ppm): 6.86 (ddt, J = 8.4, 6.5, 1.0 Hz, 1H), 6.28 (td, J = 8.5, 2.6 Hz, 1H), 6.16 (dd, J = 10.8, 2.5 Hz, 1H), 6.65 – 6.72 (m, 2H), 6.38 – 6.43 (m, 1H), 3.85 (bs, 1H), 3.34 – 3.45 (m, 1H), 2.63 – 2.83 (m, 2H), 1.88 – 1.97 (m, 1H), 1.49 – 1.62 (m, 1H), 1.21 (d, J = 6.3 Hz, 3H); ¹³C NMR (75 MHz, CDCl₃): δ (ppm): 162.3 (d, J = 240.4 Hz), 145.9 (d, J = 10.5 Hz), 130.2 (d, J = 9.8 Hz), 116.6 (d, J = 2.5 Hz), 103.5 (d, J = 21.5 Hz), 100.3 (d, J = 24.5 Hz), 47.2, 30.1, 26.1, 22.6; ¹⁹F NMR (282 MHz, CDCl₃): δ (ppm): −117.15; HR-MS (EI): m/z calculated for [C₁₀H₁₂N₁F₁] ([M]): 165.0948, found: 165.0951. The obtained spectroscopic data were in agreement with the reported data for this compound [ref.6].

2,8-Dimethyl-1,2,3,4-tetrahydroquinoline (15)

Prepared from 2,8-Dimethylquinoline (15', 63 mg, 0.4 mmol, 1.00 equiv.), Fe(1)/L4(4.5)@C-800 (106 mg, 10 mol% Fe) and H₂ (4 MPa) in 1PrOH/H₂O (3/1, 2 mL) at 140 °C for 72 h following GP. **Isolated Yield:** 82% (53 mg, 0.33 mmol, colourless liquid); ¹H NMR (300 MHz, CDCl₃): δ (ppm): 6.82 – 6.84 (m, 2H), 6.43 – 6.46 (m, 1H), 3.53 (bs, 1H), 3.35 – 3.45 (m, 1H), 2.25 (s, 3H), 1.92 – 2.00 (m, 1H), 1.55 – 1.69 (m, 1H), 1.24 (d, J = 6.3 Hz, 3H); ¹³C NMR (75 MHz, CDCl₃): δ (ppm): 142.5, 129.9, 127.3, 126.3, 121.3, 114.3, 47.4, 30.5, 26.7, 22.7, 20.5; HR-MS (EI): m/z calculated for [C₁₁H₁₄N₁] ([M]): 161.1199, found: 161.1202.

8-Ethoxy-1,2,3,4-tetrahydroquinoline (16)

Prepared from 8-Ethoxyquinoline (16', 69 mg, 0.4 mmol, 1.00 equiv.), Fe(1)/L4(4.5)@C-800 (106 mg, 10 mol% Fe) and H₂ (4 MPa) in 1PrOH/H₂O (3/1, 2 mL) at 140 °C for 72 h following GP. **Isolated Yield:** 92% (65 mg, 0.37 mmol, pale yellow liquid); ¹H NMR (300 MHz, CDCl₃): δ (ppm): 6.56 – 6.68 (m, 3H), 4.25 (bs, 1H), 4.07 (q, J = 7.0 Hz, 2H), 3.36 – 3.40 (m, 2H), 2.82 (t, J = 6.4 Hz, 2H), 2.90 – 2.92 (m, 2H), 2.25 (s, 3H), 1.96 – 2.04 (m, 2H), 1.46 (t, J = 7.0 Hz, 3H); ¹³C NMR (75 MHz, CDCl₃): δ (ppm): 145.6, 134.6, 121.6, 121.4, 115.8, 108.3, 63.6, 41.6, 26.8, 22.2, 15.1; HR-MS (EI): m/z calculated for [C₁₁H₁₅O₁N₁] ([M]): 177.1148, found: 177.1145. The obtained spectroscopic data were in agreement with the reported data for this compound [ref.6].

1,2,3,4-Tetrahydroquinolin-8-ol (17)

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Prepared from Quinolin-8-ol (17', 58 mg, 0.4 mmol, 1.00 equiv.), Fe(1)/L4(4.5)@C-800 (127 mg, 12 mol% Fe) and H₂ (5 MPa) in iPrOH/H₂O (3/1, 2 mL) at 150 °C for 72 h following GP. **Isolated Yield:** 64% (38 mg, 0.26 mmol, white solid); **¹H NMR (300 MHz, CDCl₃):** δ (ppm): 6.61 (m, 1H), 6.53 (m, 2H), 4.48 (s, 2H), 3.31 (t, J = 4.8 Hz, 2H), 2.78 (t, J = 6.0 Hz, 2H), 1.95 (dt, J = 10.8, 6.2 Hz, 2H); **¹³C NMR (75 MHz, CDCl₃):** δ (ppm): 143.2, 133.5, 123.7, 122.0, 117.2, 112.5, 41.9, 26.7, 22.4; **HR-MS (EI):** m/z calculated for [C₉H₁₁O₁N₁] ([M]): 149.0835, found: 149.0835.

4-Methyl-1,2,3,4-tetrahydroquinoline (18)

Prepared from 4-Methylquinoline (18', 57 mg, 0.4 mmol, 1.00 equiv.), Fe(1)/L4(4.5)@C-800 (106 mg, 10 mol% Fe) and H₂ (4 MPa) in iPrOH/H₂O (3/1, 2 mL) at 140 °C for 72 h following GP. **Isolated Yield:** 65% (38 mg, 0.26 mmol, pale yellow liquid); **¹H NMR (300 MHz, CDCl₃):** δ (ppm): 7.08 – 7.12 (m, 1H), 6.98 – 7.03 (m, 1H), 6.68 (td, J = 7.4, 1.3 Hz, 1H), 6.49 – 6.52 (m, 1H), 3.76 (bs, 1H), 3.26 – 3.41 (m, 2H), 2.95 (sept, J = 6.6 Hz, 1H), 1.97 – 2.07 (m, 1H); 1.67 – 1.77 (m, 1H), 1.33 (d, J = 7.0 Hz, 3H); **¹³C NMR (75 MHz, CDCl₃):** δ (ppm): 144.3, 128.5, 126.8, 126.7, 117.0, 114.3, 39.1, 30.3, 30.0, 22.7; **HR-MS (EI):** m/z calculated for [C₁₀H₁₃N₁] ([M]): 147.1043, found: 147.1045.

The obtained spectroscopic data were in agreement with the reported data for this compound [ref.6].

2-(4-(tert-Butyl)phenyl)-6-isopropyl-1,2,3,4-tetrahydroquinoline (19)

Prepared from 2-(4-(tert-Butyl)phenyl)-6-isopropylquinoline (19', 152 mg, 0.5 mmol, 1.00 equiv.), Fe(1)/L4(4.5)@C-800 (160 mg, 12 mol% Fe) and H₂ (5 MPa) in iPrOH/H₂O (3/1, 2 mL) at 150 °C for 72 h following GP. **Isolated Yield:** 93% (143 mg, 0.47 mmol, white solid); **¹H NMR (300 MHz, CDCl₃):** δ (ppm): 7.40 – 7.48 (m, 4H), 6.95 – 6.99 (m, 2H), 6.54 – 6.57 (m, 1H), 4.46 (dd, J = 9.6, 3.2 Hz, 1H), 3.98 (bs, 1H), 2.95 – 3.09 (m, 1H), 2.78 – 2.93 (m, 2H), 2.01 – 2.23 (m, 2H), 1.42 (s, 9H), 1.31 (d, J = 6.9 Hz, 6H); **¹³C NMR (75 MHz, CDCl₃):** δ (ppm): 150.4, 143.0, 142.0, 137.8, 127.3, 126.4, 125.5, 124.9, 118.2, 114.2, 56.3, 34.6, 33.4, 31.5, 31.4, 27.0, 24.5; **HR-MS (EI):** m/z calculated for [C₂₂H₂₉N₁] ([M]): 307.2295, found: 307.2290.

6-(3-(((R)-2,5,7,8-tetramethyl-2-((4R,8R)-4,8,12-trimethyltridecyl)chroman-6-yl)oxy)propoxy)-1,2,3,4-tetrahydroquinoline (20)
Prepared from 6-(3-(((R)-2,5,7,8-tetramethyl-2-((4R,8R)-4,8,12-trimethyltridecyl)chroman-6-yl)oxy)propoxy)quinoline (20', 200 mg, 0.32 mmol, 1.00 equiv.), Fe(1)/L4(4.5)@C-800 (129 mg, 15 mol% Fe) and H₂ (5 MPa) in rPrOH/H₂O (3/1, 2 mL) at 150 °C for 72 h following GP. **Isolated Yield:** 76% (151 mg, 0.24 mmol, pale yellow viscous liquid; ¹H NMR (300 MHz, CDCl₃): δ (ppm): 6.64 – 6.69 (m, 2H), 6.47 (dd, J = 8.2, 0.7 Hz, 1H), 4.19 (t, J = 6.1 Hz, 2H), 3.87 (t, J = 6.1 Hz, 2H), 3.50 (bs, 1H), 3.27 – 3.31 (m, 2H), 2.79 (t, J = 6.5 Hz, 2H), 2.62 (t, J = 6.8 Hz, 2H), 2.21 – 2.29 (m, 2H), 2.21 (s, 3H), 2.14 (s, 3H), 1.92 – 2.01 (m, 2H), 1.74 – 1.89 (m, 2H), 1.08 – 1.63 (m, 24H), 0.89 – 0.94 (m, 12H); ¹³C NMR (75 MHz, CDCl₃): δ (ppm): 151.2, 148.3, 147.8, 139.0, 127.9, 125.9, 122.9, 122.9, 117.6, 116.1, 115.6, 113.9, 74.8, 69.4, 65.5, 42.4, 40.2, 39.5, 37.6, 37.6, 37.5, 37.4, 32.9, 32.8, 31.4, 30.5, 28.1, 27.3, 24.9, 24.6, 24.0, 22.9, 22.8, 22.6, 21.1, 20.8, 19.9, 19.8, 12.8, 12.0, 11.9; HR-MS (EI): m/z calculated for [C₄₁H₆₅N₁O₃] ([M]): 619.4959, found: 619.4958.

3-Methyl-1,2,3,4-tetrahydrobenzo[f]quinoline (21)

Prepared from 3-Methylbenzo[f]quinoline (21', 77 mg, 0.4 mmol, 1.00 equiv.), Fe(1)/L4(4.5)@C-800 (160 mg, 15 mol% Fe) and H₂ (5 MPa) in rPrOH/H₂O (3/1, 2 mL) at 150 °C for 72 h following GP. **Isolated Yield:** 91% (72 mg, 0.36 mmol, pale yellow liquid; ¹H NMR (400 MHz, CDCl₃): δ (ppm): 7.59 (dq, J = 8.5, 0.9 Hz, 1H), 7.54 (ddd, J = 8.6, 1.3, 0.6 Hz, 1H), 7.36 (d, J = 8.7 Hz, 1H), 7.28 (ddd, J = 8.4, 6.8, 1.4 Hz, 1H), 7.08 (ddd, J = 8.0, 6.8, 1.1 Hz, 1H), 6.61 (d, J = 8.7 Hz, 1H), 3.69 (bs, 1H), 3.23 – 3.30 (m, 1H), 2.93 – 3.00 (m, 1H), 2.78 – 2.87 (m, 1H), 1.93 – 1.99 (m, 1H), 1.52 – 1.62 (m, 1H), 1.11 (d, J = 6.3 Hz, 3H); ¹³C NMR (101 MHz, CDCl₃): δ (ppm): 142.0, 133.5, 128.5, 127.9, 127.2, 126.3, 121.7, 121.4, 118.3, 111.6, 47.0, 30.2, 22.7, 22.2; HR-MS (EI): m/z calculated for [C₁₄H₁₅N₁] ([M]): 197.1199, found: 197.1200. The obtained spectroscopic data were in agreement with the reported data for this compound [ref.6,7].

9,10-Dihydroacridine (22)

Prepared from Acridine (22', 72 mg, 0.4 mmol, 1.00 equiv.), Fe(1)/L4(4.5)@C-800 (106 mg, 10 mol% Fe) and H₂ (4 MPa) in rPrOH/H₂O (3/1, 2 mL) at 140 °C for 60 h following GP. **Isolated Yield:** 91% (66 mg, 0.36 mmol, white solid; ¹H NMR (300 MHz, CDCl₃): δ (ppm): 7.07 – 7.15 (m, 4H), 6.88 (td, J = 7.4, 1.2 Hz, 2H), 6.66 – 6.69 (m, 2H), 5.95 (bs, 1H), 4.08 (s, 2H); ¹³C NMR (75 MHz, CDCl₃): δ (ppm): 140.2, 128.7, 127.1, 120.8, 120.2, 113.6, 31.5; HR-MS (EI): m/z calculated for [C₁₃H₁₀N₁] ([M-H]): 180.0808, found: 180.0810. The obtained spectroscopic data were in agreement with the reported data for this compound [ref.6].
3-(1,2,3,4-Tetrahydroquinolin-6-yl)benzonitrile (24)

Prepared from 3-(Quinolin-6-yl)benzonitrile (24', 92 mg, 0.4 mmol, 1.00 equiv.), Fe(1)/L4(4.5)@C-800 (106 mg, 10 mol% Fe) and H₂ (5 MPa) in iPrOH/H₂O (4/1, 2.5 mL) at 150 °C for 72 h following GP. Isolated Yield: 78% (73 mg, 0.31 mmol, colourless liquid); ¹H NMR (300 MHz, CDCl₃): δ (ppm): 7.78 – 7.79 (m, 1H), 7.73 (dt, J = 7.4, 1.8 Hz, 1H), 7.42 – 7.51 (m, 2H), 7.17 – 7.21 (m, 2H), 6.53 – 6.56 (m, 1H), 3.94 (bs, 1H), 3.33 – 3.37 (m, 2H), 2.83 (t, J = 6.4 Hz, 2H), 1.96 – 2.02 (m, 2H); ¹³C NMR (75 MHz, CDCl₃): δ (ppm): 145.2, 142.7, 130.4, 129.6, 129.4, 129.2, 128.1, 127.0, 125.5, 121.7, 119.3, 114.5, 112.7, 42.0, 27.2, 22.0; HR-MS (EI): m/z calculated for [C₁₆H₁₄N₂] ([M]): 234.1152, found: 234.1149.

Methyl 1,2,3,4-tetrahydroquinoline-6-carboxylate (25)

Prepared from Methyl quinoline-6-carboxylate (25', 75 mg, 0.4 mmol, 1.00 equiv.), Fe(1)/L4(4.5)@C-800 (106 mg, 10 mol% Fe) and H₂ (5 MPa) in iPrOH/H₂O (3/1, 2 mL) at 150 °C for 72 h following GP. Isolated Yield: 52% (40 mg, 0.21 mmol, pale yellow solid); ¹H NMR (300 MHz, CDCl₃): δ (ppm): 7.62 – 7.66 (m, 2H), 6.38 (d, J = 8.9 Hz, 1H), 4.36 (bs, 1H), 3.83 (s, 3H), 3.32 – 3.36 (m, 2H), 2.76 (t, J = 6.3 Hz, 2H), 1.88 – 1.96 (m, 2H); ¹³C NMR (75 MHz, CDCl₃): δ (ppm): 167.6, 148.9, 131.4, 129.2, 120.0, 117.5, 112.7, 51.6, 41.8, 27.0, 21.5; HR-MS (EI): m/z calculated for [C₁₁H₁₃N₂O₂] ([M]): 191.0941, found: 191.0939. The obtained spectroscopic data were in agreement with the reported data for this compound [ref.7].

7-Chloro-2-methyl-1,2,3,4-tetrahydroquinoline (26)

Prepared from 7-Chloro-2-methylquinoline (26', 71 mg, 0.4 mmol, 1.00 equiv.), Fe(1)/L4(4.5)@C-800 (106 mg, 10 mol% Fe) and H₂ (3 MPa) in iPrOH/H₂O (3/1, 2 mL) at 120 °C for 72 h following GP. Isolated Yield: 7-Chloro-2-methyl-1,2,3,4-tetrahydroquinoline (26, 70%) and 2-Methyl-1,2,3,4-tetrahydro-quinoline (2, 7%), due to hydrodechlorination, were obtained as inseparable mixture (55 mg); ¹H NMR (300 MHz, CDCl₃) for 26: δ (ppm): 6.86 (dt, J = 8.0, 1.0 Hz, 1H), 6.56 (dd, J = 8.0, 2.1 Hz, 1H), 6.44 (d, J = 2.1 Hz, 1H), 3.72 (bs, 1H), 3.34 – 3.45 (m, 1H), 2.70 – 2.78 (m, 2H), 1.89 – 1.96 (m, 1H), 1.45 – 1.62 (m, 1H), 1.21 (d, J = 6.3 Hz, 3H); ¹³C NMR (75 MHz, CDCl₃) for 26: δ (ppm): 145.8, 132.0, 130.3, 119.4, 116.3, 113.4, 47.1, 30.0, 26.2, 22.6; HR-MS (EI) for 26: m/z calculated for [C₁₆H₁₄N₂Cl₂] ([M]): 181.0653, found: 181.0658.

8-Chloro-2-methyl-1,2,3,4-tetrahydroquinoline (27)
Prepared from 8-Chloro-2-methylquinoline (27', 71 mg, 0.4 mmol, 1.00 equiv.), Fe(1)/L4(4.5)@C-800 (106 mg, 10 mol% Fe) and H₂ (4 MPa) in PrOH/H₂O (3/1, 2 mL) at 130 °C for 70 h following GP. **Isolated Yield:** 77% (56 mg, 0.31 mmol, colourless liquid); ¹H NMR (300 MHz, CDCl₃): δ (ppm): 7.07 – 7.11 (m, 1H), 6.87 – 6.91 (m, 1H), 6.53 (t, J = 7.7 Hz, 1H), 4.29 (bs, 1H), 3.43 – 3.54 (m, 1H), 2.78 – 2.87 (m, 2H), 1.93 – 1.99 (m, 1H), 1.54 – 1.67 (m, 1H), 1.30 (d, J = 6.3 Hz, 3H); ¹³C NMR (75 MHz, CDCl₃): δ (ppm): 140.8, 127.5, 126.8, 122.4, 117.8, 116.4, 47.2, 29.7, 26.8, 22.6; HR-MS (EI): m/z calculated for [C₁₀H₁₂NCl₁] ([M]): 181.0653, found: 181.0651. The obtained spectroscopic data were in agreement with the reported data for this compound [ref.6].

**8-(Thiophen-3-yl)-1,2,3,4-tetrahydroquinoline (28)**

Prepared from 8-(Thiophen-3-yl)quinoline (28', 53 mg, 0.25 mmol, 1.00 equiv.), Fe(1)/L4(4.5)@C-800 (100 mg, 15 mol% Fe) and H₂ (5 MPa) in PrOH/H₂O (3/1, 1.2 mL) at 150 °C for 72 h following GP. **Isolated Yield:** 89% (48 mg, 0.22 mmol, colourless liquid); ¹H NMR (300 MHz, CDCl₃): δ (ppm): 7.42 (dd, J = 4.9, 3.0 Hz, 1H), 7.34 (dd, J = 3.0, 1.3 Hz, 1H), 7.24 (ddd, J = 4.9, 1.3, 0.2 Hz, 1H), 7.00 (dddt, J = 13.9, 7.5, 1.7, 0.8 Hz, 2H), 6.66 (t, J = 7.5 Hz, 1H), 4.23 (bs, 1H), 3.27 – 3.31 (m, 2H), 2.85 (t, J = 6.4 Hz, 2H), 1.93 – 2.01 (m, 2H); ¹³C NMR (75 MHz, CDCl₃): δ (ppm): 142.3, 140.0, 129.0, 128.8, 128.0, 126.0, 122.7, 121.5, 116.3, 42.1, 27.6, 22.1; HR-MS (EI): m/z calculated for [C₁₃H₁₃N₁S₁] ([M]): 215.0763, found: 215.0758.

**Morpholino(4-(1,2,3,4-tetrahydroisoquinolin-4-yl)phenyl)methanone (29)**

Prepared from (4-(isoquinolin-4-yl)phenyl)(morpholino)methanone (29', 127 mg, 0.4 mmol, 1.00 equiv.), Fe(1)/L4(4.5)@C-800 (106 mg, 10 mol% Fe) and H₂ (5 MPa) in PrOH/H₂O (3/1, 2.0 mL) at 150 °C for 72 h following GP. **Isolated Yield:** 71% (91 mg, 0.28 mmol, colourless liquid); ¹H NMR (400 MHz, CDCl₃): δ (ppm): 7.30 – 7.33 (m, 2H), 7.11 – 7.18 (m, 3H), 7.05 – 7.09 (m, 2H), 6.84 – 6.86 (m, 1H), 4.04 – 4.16 (m, 3H), 3.49 – 3.67 (m, 8H), 3.39 (dd, J = 12.9, 5.1 Hz, 1H), 3.06 (dd, J = 12.9, 6.4 Hz, 1H), 2.43 (bs, 1H); ¹³C NMR (101 MHz, CDCl₃): δ (ppm): 170.3, 146.9, 136.6, 136.0, 133.4, 130.2, 129.1, 127.3, 126.6, 126.5, 126.0, 66.9, 52.0, 48.3, 48.2, 44.7, 42.6; HR-MS (EI): m/z calculated for [C₂₀H₂₂O₂N₂] ([M]): 322.1676, found: 322.1679.
5.4 Large Scale Reaction

The reaction with 6-Fluoro-2-methylquinoline (13') was performed in large scale (1.0 g, 6.2 mmol) with Fe(1)/L4(4.5)@C-800 (1.43 g, 8 mol% Fe) and H₂ (4 MPa) in PrOH/H₂O (3/1, 20 mL) at 130 °C for 66 h delivering desired product, 6-Fluoro-2-methyl-1,2,3,4-tetrahydroquinoline (13, 968 mg, 5.86 mmol) in 95% yield.

5.5 Applications

5.5.1 Synthesis of (±)-Angustureine (31):

In a 4 mL glass vial fitted with a septum containing a magnetic stirring bar, Fe(1)/L4(4.5)@C-800 (133 mg, 10 mol% Fe) and 2-Pentylquinoline (30', 100 mg, 0.50 mmol, 1.0 equiv.) were added to a solvent mixture of PrOH/H₂O (3/1, 2.5 mL). The reaction vial was then placed into a 300 mL autoclave, flashed with hydrogen five times and finally pressurized to 40 bar. The reaction mixture was stirred at 140°C for 72 h. After cooling the reaction mixture to room temperature, the autoclave was slowly depressurized. Solvents were removed and the crude reaction mixture was purified by flash column chromatography through silica (eluent: heptane/ethyl acetate = 90/10) to afford pure product 2-Pentyl-1,2,3,4-tetrahydroquinoline (30, 99 mg, 0.48 mmol, 97%) as pale yellow liquid.

\[^{1}H\text{NMR (400 MHz, CDCl}_3\text{)}:\delta\text{ (ppm): 7.02 – 7.06 (m, 2H), 6.68 (td, J = 7.3, 1.2 Hz, 1H), 6.54 (d, J = 8.2 Hz, 1H), 3.80 (bs, 1H), 3.27 – 3.33 (m, 1H), 2.77 – 2.93 (m, 2H), 2.00 – 2.07 (m, 1H), 1.63 – 1.72 (m, 1H), 1.36 – 1.59 (m, 8H), 1.00 (t, J = 6.8 Hz, 3H);}^{13}C\text{NMR (101 MHz, CDCl}_3\text{)}:\delta\text{ (ppm): 144.8, 129.3, 126.7, 121.4, 116.9, 114.1, 51.7, 51.6, 32.1, 28.2, 26.5, 25.5, 22.8, 14.2; GC-MS: EI-MS [m/z (%)]: (M⁺ = 203) major peaks found: 203 (11), 132 (100), 130 (11). The obtained spectroscopic data were in agreement with the reported data for this compound [ref.10].}

In a 8 mL glass vial fitted with a septum containing a magnetic stirring bar, 2-Pentyl-1,2,3,4-tetrahydroquinoline (30, 94 mg, 0.46 mmol, 1.00 equiv.), formic acid (43 mg, 0.92 mmol, 2.00 equiv.), Co(BF₄)₂·6H₂O (4.70 mg, 0.014 mmol, 0.03 equiv.) and Triphos(p-anisole) (23 mg, 0.028 mmol, 0.06 equiv.) were dissolved in 1,4-dioxane (2.0 mL). The reaction vial was then placed into a 300 mL autoclave, flashed with hydrogen five times and finally pressurized to 40 bar. The reaction mixture was stirred at 100°C for 24 h. After cooling the reaction mixture to room temperature, the autoclave
was slowly depressurized. Solvents were removed and the crude reaction mixture was purified by flash column chromatography through silica (eluent: heptane/ethyl acetate = 96/4) to afford pure product 31 (92 mg, 0.42 mmol, 91%) as pale yellow liquid.

\[\text{\(1^H\) NMR (300 MHz, CDCl}_3\): } \delta (ppm): 7.14 (t, \(J = 7.6\) Hz, 1H), 7.03 (d, \(J = 7.2\) Hz, 1H), 6.64 (tt, \(J = 7.3, 1.0\) Hz, 1H), 6.58 (d, \(J = 8.2\) Hz, 1H), 3.25 – 3.32 (m, 1H), 2.98 (s, 3H), 2.81 – 2.92 (m, 1H), 2.67 – 2.75 (m, 1H), 1.91 – 1.98 (m, 2H), 1.60 – 1.71 (m, 1H), 1.29 – 1.52 (m, 7H), 0.96 (t, \(J = 6.4\) Hz, 3H); \[\text{\(13C\) NMR (75 MHz, CDCl}_3\): } \delta (ppm): 145.5, 128.7, 127.2, 121.9, 115.3, 110.5, 59.1, 38.1, 32.2, 31.3, 25.9, 24.5, 23.7, 22.8, 14.2; HR-MS (EI): \(m/z\) calculated for [C\(_{15}\)H\(_{23}\)N\(_1\)] ([M]): 271.1825, found: 271.1826. The obtained spectroscopic data were in agreement with the reported data for this compound [ref.10].

5.5.2 Synthesis of Tubulin Polymerization Inhibitor (33):

In a 4 mL glass vial fitted with a septum cap containing a magnetic stirring bar, Fe(1)/L4(4.5)@C-800 (106 mg, 10 mol% Fe) and 6-Methoxyquinoline (32', 64 mg, 0.40 mmol, 1.0 equiv.) were added to a solvent mixture of \(i\)-PrOH/H\(_2\)O (3/1, 2.0 mL). The reaction vial was then placed into a 300 mL autoclave, flushed with hydrogen five times and finally pressurized to 40 bar. The reaction mixture was stirred at 130°C for 70 h. After cooling the reaction mixture to room temperature, the autoclave was slowly depressurized. Solvents were removed and the crude reaction mixture was purified by filtering through a silica pad to afford pure product 6-Methoxy-1,2,3,4-tetrahydroquinoline (32, 62 mg, 0.38 mmol, 95%) as pale yellow liquid. 

\[\text{\(1^H\) NMR (300 MHz, CDCl}_3\): } \delta (ppm): 6.57 – 6.63 (m, 2H), 6.45 – 6.48 (m, 1H), 7.05 – 7.13 (m, 2H), 6.53 – 6.57 (m, 1H), 3.74 (s, 3H), 3.47 (bs, 1H), 3.24 – 3.28 (m, 2H), 2.77 (t, \(J = 6.5\) Hz, 2H), 1.90 – 1.98 (m, 2H); \[\text{\(13C\) NMR (75 MHz, CDCl}_3\): } \delta (ppm): 151.9, 138.9, 123.0, 115.7, 115.0, 113.0, 55.9, 42.4, 27.3, 21.5; HR-MS (EI): \(m/z\) calculated for [C\(_{10}\)H\(_{13}\)N\(_1\)O\(_1\)] ([M]): 163.0992, found: 163.0994. The obtained spectroscopic data were in agreement with the reported data for this compound [ref.6].

In an oven dried Schlenk flask, 6-Methoxy-1,2,3,4-tetrahydroquinoline (32, 65.3 mg, 0.40 mmol, 1.00 equiv.) was dissolved in dry dichloromethane (1.5 mL). Triethylamine (84 µL, 0.60 mmol, 1.50 equiv.) followed by 3,4,5-trimethoxybenzoyl chloride (120 mg, 0.52 mmol, 1.30 equiv.) was added to the resulting solution and allowed to stir at rt for 20 h. The crude reaction mixture was directly purified by flash column chromatography through silica (eluent: heptane/ethyl acetate = 80/20) to afford pure product 6-Methoxy-1,2,3,4-tetrahydroquinoline (32, 62 mg, 0.38 mmol, 95%) as pale yellow liquid.

\[\text{\(1^H\) NMR (300 MHz, CDCl}_3\): } \delta (ppm): 6.66 – 6.73 (m, 2H), 6.56 (s, 2H), 6.46 (dd, \(J = 8.9, 2.9\) Hz, 1H), 3.85 (t, \(J = 6.6\) Hz, 2H), 3.80 (s, 3H), 3.71 (s, 3H), 3.67 (s, 6H), 2.78 (t, \(J = 6.6\) Hz, 2H), 1.96 – 2.04 (m, 2H); \[\text{\(13C\) NMR (75 MHz, CDCl}_3\): } \delta (ppm): 169.4, 156.6, 152.7, 139.6, 133.0, 132.6, 131.3, 126.3, 113.2, 111.5, 106.3, 60.9, 56.1, 55.5, 44.6, 27.2, 24.2; HR-MS (EI): \(m/z\) calculated for
[C₂₀H₂₃NO₅] ([M]): 357.1571, found: 357.1571. The obtained spectroscopic data were in agreement with the reported data for this compound [ref.6].

5.5.3 Synthesis of Histamine H₃-Receptor antagonist (37):

In a heat gun dried Schlenk tube, sodium methoxide (568 mg, 10.50 mmol, 1.05 equiv.) was dissolved in MeOH (40 mL). The substrate, 6-quinolinol (34, 1.45 g, 10.00 mmol, 1.00 equiv.) was added to the solution at rt and stirred for 20 min. Then, 3-bromo-1-chloropropane (1.78 mL, 18.20 mmol, 1.80 equiv.) was added to the resulting solution and finally refluxed at 80 °C for 36 h. After cooling down to rt, the solvent was removed under reduced pressure and the crude reaction mixture was purified by flash column chromatography through silica (eluent: heptane/ethyl acetate = 4/1) to afford pure product 35 (1.41 g, 6.36 mmol, 64%) as pale yellow solid upon cooling.

1H NMR (300 MHz, CDCl₃): δ (ppm): 8.76 (dd, J = 4.3, 1.6 Hz, 1H), 8.01 – 8.04 (m, 1H), 8.00 (d, J = 9.6 Hz, 1H), 7.32 – 7.38 (m, 2H), 7.08 (d, J = 2.8 Hz, 1H), 4.23 (t, J = 5.9 Hz, 2H), 3.78 (t, J = 6.3 Hz, 2H), 2.26 – 2.34 (m, 2H); 13C NMR (75 MHz, CDCl₃): δ (ppm): 156.9, 148.2, 144.6, 134.9, 131.0, 129.4, 122.5, 121.5, 106.1, 64.7, 41.6, 32.3; HR-MS (ESI): m/z calculated for [C₁₂H₁₃ClNO]⁺ ([M+H]⁺): 222.0680, found: 222.0680.

In an oven dried Schlenk tube, substrate 35 (510 mg, 2.30 mmol, 1.00 equiv.), piperidine (455 µL, 4.60 mmol, 2.00 equiv.) and K₂CO₃ (636 mg, 4.60 mmol, 2.00 equiv.) were dissolved in DMF (7 mL). Then, sodium iodide (69 mg, 0.46 mmol, 0.20 equiv.) was added to the resulting solution and allowed to stir at 120 °C for 15 h. After cooling down to rt, the reaction mixture was diluted with water (7 mL) and the organic phase was extracted with ethyl acetate (3×10 mL). The combined organic layers were washed with water followed by brine solution and finally solvents were removed under reduced pressure. The crude reaction mixture was purified by flash column chromatography through silica (eluent: dichloromethane/methanol = 99/1 to 90/10) to afford pure product 36' (560 mg, 2.07 mmol, 90%) as pale yellow solid.

1H NMR (300 MHz, CDCl₃): δ (ppm): 8.75 (dd, J = 4.3, 1.7 Hz, 1H), 8.00 – 8.03 (m, 1H), 7.98 (d, J = 9.6 Hz, 1H), 7.31 – 7.37 (m, 2H), 7.03 (d, J = 2.8 Hz, 1H), 1.59 – 1.66 (m, 4H), 1.41 – 1.49 (m, 2H); 13C NMR (75 MHz, CDCl₃): δ (ppm): 157.2, 148.0, 144.5, 134.9, 130.9, 129.4, 122.6, 121.4, 106.0, 66.9, 56.1, 54.8, 26.7, 25.9, 24.4; HR-MS (ESI): m/z calculated for [C₁₇H₂₃N₂O⁺ ([M+H]⁺): 271.1805, found: 271.1804.
In a 4 mL glass vial fitted with a septum cap containing a magnetic stirring bar, Fe(1)/L4(4.5)@C-800 (159 mg, 15 mol% Fe) and the compound 36’ (108 mg, 0.40 mmol, 1.0 equiv.) were added to a solvent mixture of PrOH/H$_2$O (3/1, 2.0 mL). The reaction vial was then placed into a 300 mL autoclave, flashed with hydrogen five times and finally pressurized to 50 bar. The reaction mixture was stirred at 150°C for 72 h. After cooling the reaction mixture to room temperature, the autoclave was slowly depressurized. Solvents were removed and the crude reaction mixture was purified by flash column chromatography through silica (eluent: heptane/ethyl acetate/triethylamine = 80/20/2 to 70/30/2) to afford pure product 36 (88 mg, 0.32 mmol, 80%) as colourless liquid.

1H NMR (300 MHz, CDCl$_3$): δ (ppm): 6.54 – 6.60 (m, 2H), 6.38 – 6.43 (m, 1H), 3.90 (t, J = 6.4 Hz, 2H), 3.54 (bs, 1H), 3.21 – 3.24 (m, 2H), 2.73 (t, J = 6.5 Hz, 2H), 2.42 – 2.47 (m, 2H), 2.38 (t, J = 4.9 Hz, 4H), 1.86 – 1.96 (m, 4H), 1.54 – 1.62 (m, 4H), 1.38 – 1.46 (m, 4H), 1.86 – 1.96 (m, 4H), 1.54 – 1.62 (m, 4H), 1.38 – 1.46 (m, 4H); 13C NMR (75 MHz, CDCl$_3$): δ (ppm): 151.2, 138.9, 122.8, 115.8, 115.5, 113.7, 67.3, 56.2, 54.7, 42.4, 27.2, 27.1, 26.1, 24.5, 22.5; HR-MS (EI): m/z calculated for [C$_{17}$H$_{26}$N$_2$O$_1$] ([M]): 274.2040, found: 274.2043.

In an oven dried Schlenk flask, compound 36 (83 mg, 0.30 mmol, 1.00 equiv.) was dissolved in dry dichloromethane (3 mL). Triethylamine (84 µL, 0.60 mmol, 2.00 equiv.) followed by benzenesulfonyl chloride (58 µL, 0.45 mmol, 1.50 equiv.) was added to the resulting solution and allowed to stir at rt for 20 h. The crude reaction mixture was directly purified by flash column chromatography through silica (eluent: heptane/ethyl acetate/triethylamine = 80/20/2 to 70/30/2) to afford pure product 37 (122 mg, 0.29 mmol, 98%) as colourless liquid.

1H NMR (300 MHz, CDCl$_3$): δ (ppm): 7.65 (d, J = 9.0 Hz, 1H), 7.45 – 7.53 (m, 3H), 7.32 – 7.38 (m, 2H), 6.73 (dd, J = 9.0, 3.0 Hz, 1H), 6.49 (d, J = 2.8 Hz, 1H), 3.93 (t, J = 6.4 Hz, 2H), 3.70 – 3.74 (m, 2H), 2.20 – 2.45 (m, 2H), 2.36 (t, J = 5.8 Hz, 4H), 2.26 (t, J = 6.8 Hz, 2H), 1.88 – 1.97 (m, 2H), 1.36 – 1.69 (m, 8H); 13C NMR (75 MHz, CDCl$_3$): δ (ppm): 156.6, 139.5, 132.7, 132.6, 129.6, 128.9, 127.1, 126.9, 114.2, 112.8, 66.6, 56.0, 54.7, 46.4, 26.9, 26.5, 26.0, 24.5, 21.3; HR-MS (EI): m/z calculated for [C$_{23}$H$_{30}$N$_2$O$_3$S] [(M+H)$^+$]: 414.1972, found: 414.1970.

5.5.4 Conversion of Photoluminescent Materials (38’ and 39’)

6-(Pyren-1-yl)-1,2,3,4-tetrahydroquinoline (38)

Prepared from 6-(Pyren-1-yl)quinoline (38’, 99 mg, 0.3 mmol, 1.00 equiv.), Fe(1)/L4(4.5)@C-800 (80 mg, 10 mol% Fe) and H$_2$ (5 MPa) in PrOH/H$_2$O (3/1, 1.6 mL) at 150 °C for 72 h following GP. Isolated Yield: 90% (90 mg, 0.27 mmol, yellow solid); 1H NMR (400 MHz, CDCl$_3$): δ (ppm): 8.34 (d, J = 9.2 Hz, 1H), 8.14 – 8.21 (m, 3H), 7.98 – 8.10 (m, 5H), 7.27 – 7.29 (m, 2H), 6.66 – 6.69 (m, 1H), 3.98 (bs, 1H), 3.40 – 3.43 (m, 2H), 2.91 (t, J = 6.4 Hz, 2H), 2.03 – 2.09 (m, 2H); 13C NMR (101 MHz, CDCl$_3$): δ (ppm): 144.1, 138.5, 131.8, 131.7, 131.2, 130.1, 129.8, 129.3, 128.6, 127.8, 127.6, 127.1, 127.0, 126.0, 125.2, 125.2, 124.9, 124.8, 124.6, 121.5, 114.2, 42.2, 27.2, 22.3 (note: two peaks at δ (ppm) = 126.0 are merged together); HR-MS (ESI): m/z calculated for [C$_{25}$H$_{20}$N]$^+$ ([M+H]$^+$): 334.1590, found: 334.1590.
2-Methyl-6-(pyren-1-yl)-1,2,3,4-tetrahydroquinoline (39)

Prepared from 2-Methyl-6-(pyren-1-yl)quinoline (39', 138 mg, 0.4 mmol, 1.00 equiv.), Fe(1)/L4(4.5)@C-800 (106 mg, 10 mol% Fe) and H₂ (5 MPa) in iPrOH/H₂O (3/1, 2 mL) at 150 °C for 72 h following GP. Isolated Yield: 92% (128 mg, 0.37 mmol, yellow solid); ¹H NMR (300 MHz, CDCl₃): δ (ppm): 8.33 (d, J = 9.3 Hz, 1H), 8.13 – 8.21 (m, 3H), 7.97– 8.11 (m, 5H), 7.27 – 7.30 (m, 2H), 6.67 – 6.70 (m, 1H), 3.91 (bs, 1H), 3.48 – 3.59 (m, 1H), 2.81 – 3.05 (m, 2H), 1.99 – 2.07 (m, 1H), 1.66 – 1.79 (m, 1H), 1.30 (d, J = 6.2 Hz, 3H); ¹³C NMR (75 MHz, CDCl₃): δ (ppm): 144.1, 138.6, 131.7, 131.6, 131.3, 130.1, 129.9, 129.3, 128.6, 127.8, 127.6, 127.1, 127.0, 126.0, 126.0, 125.2, 125.2, 124.9, 124.8, 124.6, 121.2, 114.0, 47.5, 30.3, 26.9, 22.8 (note: two peaks at δ (ppm) = 126.0 are merged together); HR-MS (EI): m/z calculated for [C₂₆H₂₁N₁] ([M]): 347.1669, found: 347.1660.

5.5.5 Photophysical Studies of Photoluminescent Materials (38’, 39’, 38 and 39)

The UV-Visible absorption of 20 µM solutions of compound 38’, 39’, 38 and 39 in dichloromethane was recorded by SPECORD® S600 of Analytik Jena, whereas the emission of same solutions was measured by Cary Eclipse Fluorescence Spectrophotometer (from Varian) equipped with a sample holder respectively. The recorded absorption spectra and normalized emission spectra are depicted in Figure 5.

6 Catalyst Recycling Experiments

The recycling experiments were carried out in 4.0 mmol scale: Quinaldine (2’, 4.0 mmol, 1.00 equiv.), Fe(1)/L4(4.5)@C-800 (1.06 g, 10 mol% Fe) and H₂ (4 MPa) in iPrOH/H₂O (3/1, 20 mL) at 130 °C for 60 h following general procedure. After cooling the reaction mixture to room temperature, the hydrogen gas was released. The reaction mixture was diluted with ethyl acetate and then hexadecane (internal standard) was added to the reaction mixture for the GC yield analysis. The catalyst was separated via centrifugation and washed with fresh ethanol and ethyl acetate. The separated catalyst was dried for 6 h under vacuum and reused for next run. The results of seven runs of this catalyst have been summarized in Table S7. The supernatant liquids obtained after each run of the catalyst in this reaction were tested for leaching by atomic absorption spectroscopy (AAS) analysis (see Table S8). No significant amount of leaching of iron (Fe) was noticed. However, the recycling experiments upto 5 runs were also performed for shorter reaction time (10 h) and the results are summarized in Table S9, which showed a slight reactivity drop at 3rd run.

Table S5: Recycling experiments of Fe(1)/L4(4.5)@C-800 catalyst for the hydrogenation of quinaldine (2’) after 60 h

<table>
<thead>
<tr>
<th>Number of Run</th>
<th>Yield (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>98</td>
</tr>
<tr>
<td>2</td>
<td>98</td>
</tr>
<tr>
<td>3</td>
<td>96</td>
</tr>
</tbody>
</table>
Table S6: Leaching Tests

<table>
<thead>
<tr>
<th>Number of Run</th>
<th>Iron Content (ppm)\textsuperscript{a}</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>0.06</td>
</tr>
<tr>
<td>2</td>
<td>0.10</td>
</tr>
<tr>
<td>3</td>
<td>0.11</td>
</tr>
<tr>
<td>4</td>
<td>0.10</td>
</tr>
<tr>
<td>5</td>
<td>0.33</td>
</tr>
<tr>
<td>6</td>
<td>0.07</td>
</tr>
<tr>
<td>7</td>
<td>0.08</td>
</tr>
</tbody>
</table>

\textsuperscript{a}GC Yield determined using hexadecane as internal reference.

**Table S7:** Recycling experiments of Fe(1)/L4(4.5)@C-800 catalyst for the hydrogenation of quinaldine (2') after 10 h

<table>
<thead>
<tr>
<th>Number of Run</th>
<th>Yield (%)\textsuperscript{a}</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>39</td>
</tr>
<tr>
<td>2</td>
<td>40</td>
</tr>
<tr>
<td>3</td>
<td>34</td>
</tr>
<tr>
<td>4</td>
<td>33</td>
</tr>
<tr>
<td>5</td>
<td>33</td>
</tr>
</tbody>
</table>

\textsuperscript{a}GC Yield determined using hexadecane as internal reference.

### 7 Comparison Study with State-of-the-Art Catalyst

In a 4 mL glass vial fitted with a septum cap containing a magnetic stirring bar, 5% Ru/C (50 mg, 12 mol%) and quinoline were added to a solvent mixture of iPrOH/H\textsubscript{2}O (1 mL, 3/1). The reaction vial was then placed into a 300 mL autoclave, flashed with hydrogen five times and finally pressurized to 4 MPa. The reaction mixture was stirred at 130°C for 56 h. After cooling the reaction mixture to room temperature, the autoclave was slowly depressurized. The reaction mixture was analyzed by GC-MS. In figure S16, the GC-MS spectra showed that decahydroquinoline (1a) and N-isopropyl decahydroquinoline (1b) were obtained as major and minor product respectively, due to over reduction of in situ-formed tetrahydroquinoline.
Figure S16: Comparison study with state-of-the-art catalyst (Ru/C): decahydroquinoline (1a) at t = 9.3 min. and N-isopropyl decahydroquinoline (1b) at t = 12.6 min.
8 References:


5. R. Tan, D. Song Organometallics 2011, 30, 1637-1645.


9 NMR Spectra of Isolated Compounds

Ligand 4:

\[ \text{Sahoo BS-475-L PROTON CDCl}_3 \{\text{C:Bruker TopSpin3.5pl6}\} 1706 3 \]
29'

PROTON CDCl3

Au13C CDCl3

Sahoo, BS-734-R

- S51 -
38°
Au13C CDCl3 (C:\Bruker\TopSpin3.5pl6) 1711 27

121.71 124.84 124.97 125.06 125.11 125.17 125.47 126.27 127.52 127.83 127.89 128.00 128.44 128.75 129.19 129.41 131.03 131.05 131.60 132.71 136.43 136.77 139.75 147.62 150.69

PROTON CDCl3 (C:\Bruker\TopSpin3.5pl6) 1712 44

3.03 0.98 5.00 8.00 2.83 7.35 7.38 7.97 8.00 8.00 8.02 8.03 8.04 8.04 8.05 8.05 8.07 8.12 8.14 8.16 8.19 8.20 8.20 8.21 8.23 8.23 8.24 8.27

39'

PROTON CDCl3 (C:\Bruker\TopSpin3.5pl6) 1712 44

10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
Sahoo, BS-737

Au13C CDCl3 {C:\Bruker\TopSpin3.5pl6} 1802.43

- S85 -