Supporting Information:

Ni-Catalyzed Dehydrogenative Coupling of Primary and Secondary Alcohols with Methyl-N-Heteroaromatics

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1. General Information

All catalytic experiments were carried out using standard Schlenk techniques. Unless otherwise stated reaction were conducted in flame-dried glassware under an atmosphere of nitrogen and commercially obtained reagent were used as received. All solvents were reagent grade or better. Toluene was refluxed over sodium/benzophenone, followed by distilled under argon atmosphere and stored over sodium. Chemicals used in catalysis reactions were used without additional purification. Thin layer chromatography (TLC) was performed using silica gel precoated aluminium foil which was visualized with UV light at 254 nm or under iodine. Column chromatography was performed with SiO$_2$ (Silicycle Siliaflash F60 (230-400 mesh). $^1$H NMR (500, 200 MHz), $^{13}$C NMR (126, 50 MHz) spectra were recorded on the NMR spectrometer. Deuterated chloroform (CDCl$_3$) was used as the solvent, and chemical shift values ($\delta$) are reported in parts per million relative to the residual signals of this solvent [$\delta$ 7.27 for $^1$H (chloroform-d), $\delta$ 77.0 for $^{13}$C{$^1$H} (chloroform-d). Abbreviations used in the NMR follow-up experiments: s, singlet; d, doublet; dd, doublet of doublet; t, triplet; tt, triplet of triplet; td, triplet of doublet; q, quartet; br, broad; m, multiplet. GC analysis was carried out using a HP-5 column (30 m, 0.25 mm, 0.25$\mu$). Mass spectra were obtained on a GCMS-QP 5000 instruments with ionization voltages of 70 eV. High resolution mass spectra (HRMS) were obtained on a High-resolution mass spectra (HRMS) were obtained by fast atom bombardment (FAB) using a double focusing magnetic sector mass spectrometer and electron impact (EI) ionization technique (magnetic sector-electric sector double focusing mass analyzer).
2. Optimization of the reaction condition

Table S1: Screening of catalyst

<table>
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<tr>
<th>Entry</th>
<th>Ni-Catalyst</th>
<th>Product</th>
<th>Product</th>
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<tbody>
<tr>
<td>1</td>
<td>NiBr₂+TMEDA(L₁)</td>
<td>88</td>
<td>6</td>
</tr>
<tr>
<td>2</td>
<td>NiCl₂(DME)</td>
<td>72</td>
<td>25</td>
</tr>
<tr>
<td>3</td>
<td>NiBr₂</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>4</td>
<td>Nickel(II) bromide 2-methoxyethyl ether complex</td>
<td>65</td>
<td>25</td>
</tr>
<tr>
<td>5</td>
<td>Bis(cyclopentadienyl)nickel(II)</td>
<td>37</td>
<td>63</td>
</tr>
</tbody>
</table>

*aReaction conditions: 1a (0.5 mmol), benzyl alcohol 2a (1.5 mmol), Ni-catalyst (10 mol%), TMEDA (0.25 mmol), KO'Bu (1.0 mmol) using 2 ml of toluene as solvent at 130 °C. bConversion based on GC analysis using m-xylene as an internal standard.

Table S2: Screening of Ni-catalyst and ligand ratio

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<tr>
<th>Entry</th>
<th>NiBr₂:L₁</th>
<th>Product</th>
<th>Product</th>
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<tbody>
<tr>
<td>1</td>
<td>1:5</td>
<td>88</td>
<td>6</td>
</tr>
<tr>
<td>2</td>
<td>1:3</td>
<td>69</td>
<td>25</td>
</tr>
<tr>
<td>3</td>
<td>1:2</td>
<td>55</td>
<td>45</td>
</tr>
<tr>
<td>4</td>
<td>1:1</td>
<td>51</td>
<td>49</td>
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**Table S3**: Screening of base$^{a,b}$

<table>
<thead>
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<th>Base</th>
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<td></td>
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<td>3a</td>
<td>3a'</td>
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<td>1</td>
<td>KOtBu</td>
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<td>6</td>
</tr>
<tr>
<td>2</td>
<td>LiOtBu</td>
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<td>25</td>
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<td></td>
<td>NaOtBu</td>
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<tr>
<td>3</td>
<td>KOH</td>
<td>NR</td>
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<tr>
<td>5</td>
<td>KH</td>
<td>NR</td>
<td>NR</td>
</tr>
<tr>
<td>6</td>
<td>K$_2$CO$_3$</td>
<td>NR</td>
<td>NR</td>
</tr>
</tbody>
</table>

$^a$Reaction conditions: 1a (0.5 mmol), benzyl alcohol 2a (1.5 mmol), Ni-catalyst (10 mol%), KOtBu (1.0 mmol) using 2 ml of toluene as solvent at 130 °C. $^b$Conversion based on GC analysis using m-xylene as an internal standard.
**Table S4**: Screening of amount of base amount\textsuperscript{a,b}

\[
\begin{align*}
\text{1a} + \text{PhOH} & \xrightarrow{\text{Ni-cat (10 mol\%)} \quad \text{L1 (0.25 mmol)}} \text{3a} + \text{Ph} \\
\text{Base (X.0 mmol)} & \quad \text{Toluene, 130 °C}
\end{align*}
\]

<table>
<thead>
<tr>
<th>Entry</th>
<th>Base</th>
<th>GC-Conversion</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>3a</td>
<td>3a'</td>
</tr>
<tr>
<td>1</td>
<td>KO'Bu (2.0 equiv)</td>
<td>88</td>
</tr>
<tr>
<td>2</td>
<td>KO'Bu (1.0 equiv)</td>
<td>56</td>
</tr>
<tr>
<td>3</td>
<td>KO'Bu (0.5 equiv)</td>
<td>25</td>
</tr>
<tr>
<td>4</td>
<td>KO'Bu (0.2 equiv)</td>
<td>NR</td>
</tr>
</tbody>
</table>

\textsuperscript{a}Reaction conditions: 1a (0.5 mmol), benzyl alcohol 2a (1.5 mmol), Ni-catalyst (10 mol\%), TMEDA (0.25 mmol), using 2 ml of toluene as solvent at 130 °C. \textsuperscript{b}Conversion based on GC analysis using m-xylene as an internal standard. NR = No reaction.

**Table S5**: Screening of alcohol amount\textsuperscript{a,b}

\[
\begin{align*}
\text{1a} + \text{PhOH} & \xrightarrow{\text{Ni-cat (10 mol\%)} \quad \text{L1 (0.25 mmol)}} \text{3a} + \text{Ph} \\
\text{Base (1.0 mmol)} & \quad \text{Toluene, 130 °C}
\end{align*}
\]

<table>
<thead>
<tr>
<th>Entry</th>
<th>Benzyl alcohol (2a, equiv)</th>
<th>GC-Conversion</th>
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</thead>
<tbody>
<tr>
<td></td>
<td>3a</td>
<td>3a'</td>
</tr>
<tr>
<td>1</td>
<td>3</td>
<td>88</td>
</tr>
<tr>
<td>2</td>
<td>2</td>
<td>75</td>
</tr>
<tr>
<td>3</td>
<td>1</td>
<td>60</td>
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</table>

\textsuperscript{a}Reaction conditions: 1a (0.5 mmol), benzyl alcohol 2a, Ni-catalyst (10 mol\%), TMEDA (0.25 mmol), KO'Bu (1.0 mmol) using 2 mL of toluene as solvent at 130 °C. \textsuperscript{b}Conversion based on GC analysis using m-xylene as an internal standard.
3. General experimental procedure

In a 10 mL oven dried sealed tube, alcohol 2 (1.5 mmol), and methyl N-Heteroaromatics 1 (0.5 mmol), NiBr₂ (10 mol%), TMEDA (0.25 mmol) KO'Bu (1.0 mmol) were added under an argon atmosphere in toluene (2.0 mL). The flask was sealed tightly with a teflon plug under an argon atmosphere, and the solution was stirred at 130°C (oil bath temperature) for 24 h. Then the reaction mixture was cooled to room temperature, and the reaction mixture was quenched with water (20 mL) and extracted with dichloromethane (2 x 20 mL). The organic layer was combined, washed with brine (20 mL) and then dried over Na₂SO₄. After concentration under reduced pressure, the residue was purified by 230-400 mesh silica-gel column chromatography using petroleum ether/ethyl acetate (50/1) to afford the pure product 3.

4. Mechanistic Studies

3a. Detection of H₂ gas liberation

In a 10 ml head space vial, 1a (0.5 mmol), 2a (1.5 mmol), NiBr₂ (10 mol%), TMEDA (0.25 mmol), KO'Bu (1.0 mmol) were added under an argon atmosphere in toluene (2.0 mL). After 4 h of reaction, the gaseous phase of the crude reaction mixture was analyzed through gas phase GC analysis. The evolution of H₂ gas during the alkylation process was qualitatively observed using GC analysis which reveals the reaction takes place via Ni-catalyzed hydrogen auto-transfer pathway.

![Figure S1. Gas phase GC for the identification of molecular hydrogen](image-url)
3b. Intermediate Determination

(E)-2-(4-methylstyryl)quinoline (6)

To a reaction mixture of 2-methyl quinoline 1a and KO\textsubscript{t}Bu in THF, \(p\)-tolualdehyde was added slowly under argon atmosphere at room temperature. The reaction mixture was stirred for 12 h. The reaction mixture was quenched with water (20 mL) and extracted with dichloromethane (2 x 20 mL). The organic layer was combined, washed with brine (20 mL) and then dried over Na\textsubscript{2}SO\textsubscript{4}. After concentration under reduced pressure, residue was purified by 230-400 mesh silica-gel column chromatography using petroleum ether/ethyl acetate (50/1) to afford the pure product 6 as colourless solid. Isolated yield: 65%. Next, \(\alpha,\beta\)-unsaturated quinoline derivative 6 was applied under standard catalytic conditions in the presence of 4-methyl benzyl alcohol 2b as hydrogen donor. The GC analysis of crude mixture showed the formation of alkylated quinoline derivative 3b confirmed by GC-MS, which confirmed the formation of 6 as a key intermediate in the catalytic process.
Figure S2. GC of the crude reaction mixture.

Figure S3. GC-MS data of the crude reaction mixture.
3c. Deuterium experiment

a) To a 15 mL clean and oven-dried screw cap reaction tube, 1a (0.3 mmol) and 2a-[d] (90%) (0.3 mmol) were added under standard reaction conditions. Then the reaction was performed under standard condition for 24 h. The percentage of deuterium incorporation in the product was calculated based on NMR analysis.

5. Characterization data

2-phenethylquinoline (3a)

The general procedure was followed to afford the title compound as pale yellow liquid, isolated yield: 82%, 95 mg.

\[ ^1\text{H NMR} \ (500 \text{ MHz, CDCl}_3) \delta 8.12 \ (d, J = 8.7 \text{ Hz, 1H}), 8.06 \ (d, J = 8.3 \text{ Hz, 1H}), 7.81 \ (d, J = 7.7 \text{ Hz, 1H}), 7.76-7.68 \ (m, 2H), 7.53 \ (t, J = 7.7 \text{ Hz, 1H}), 7.34-7.28 \ (m, 4H), 7.26-7.22 \ (m, 1H), 3.36-3.31 \ (m, 2H), 3.23-3.18 \ (m, 2H). \]

\[ ^{13}\text{C NMR} \ (126 \text{ MHz, CDCl}_3) \delta 161.8, 147.9, 141.5, 136.2, 129.4, 128.8, 128.5, 128.4, 127.5, 126.7, 125.9, 125.7, 121.5, 40.9, 35.9. \]

HRMS(EI) m/z Calcd for C\textsubscript{17}H\textsubscript{16}N [M+H]\textsuperscript{+}: 234.1277; Found: 234.1279.
2-(2-methylphenethyl)quinoline (3b)

The general procedure was followed to afford the title compound as pale yellow liquid, isolated yield: 69%, 85 mg.

$^1$H NMR (500 MHz, CDCl$_3$) $\delta$ 8.12 (d, $J = 8.7$ Hz, 1H), 8.06 (d, $J = 8.3$ Hz, 1H), 7.80 (d, $J = 8.3$ Hz, 1H), 7.73 (t, $J = 6.7$ Hz, 1H), 7.52 (t, $J = 6.7$ Hz, 1H), 7.25-7.21 (m, 2H), 7.20-7.14 (m, 3H), 3.30-3.26 (m, 2H), 3.19-3.15 (m, 2H), 2.38 (s, 3H).

$^{13}$C NMR (126 MHz, CDCl$_3$) $\delta$ 161.9, 147.9, 139.6, 136.1, 135.9, 130.1, 129.3, 128.9, 128.8, 127.5, 126.7, 126.1, 125.9, 125.7, 121.4, 39.6, 33.2, 19.3.

HRMS (EI) m/z Calcd for C$_{18}$H$_{18}$N [M+H]$^+$: 248.1434; Found: 248.1436.

2-(3-methylphenethyl)quinoline (3c)

The general procedure was followed to afford the title compound as pale yellow liquid, isolated yield: 71%, 87 mg.

$^1$H NMR (500 MHz, CDCl$_3$) $\delta$ 8.16-8.05 (m, 2H), 7.82 (d, $J = 7.8$ Hz, 1H), 7.73 (t, $J = 7.8$ Hz, 1H), 7.53 (t, $J = 6.7$ Hz, 1H), 7.30-7.26 (m, 1H), 7.20 (t, $J = 6.7$ Hz, 1H), 7.15-7.03 (m, 3H), 3.37-3.28 (m, 2H), 3.20-3.11 (m, 2H), 2.36 (s, 3H).

$^{13}$C NMR (126 MHz, CDCl$_3$) $\delta$ 161.9, 147.9, 141.4, 137.9, 136.2, 129.4, 129.3, 128.3, 127.5, 126.8, 126.7, 125.5, 121.5, 41.1, 35.9, 21.4.

HRMS (EI) m/z Calcd for C$_{18}$H$_{18}$N [M+H]$^+$: 248.1434; Found: 248.1436.
2-(4-methylphenethyl)quinoline (3d)

The general procedure was followed to afford the title compound as pale yellow liquid, isolated yield: 73%, 90 mg.

$^1$H NMR (200 MHz, CDCl$_3$) δ 8.20-8.09 (m, 2H), 7.90-7.74 (m, 2H), 7.62-7.54 (m, 1H), 7.36-7.20 (m, 1H), 7.26-7.05 (m, 4H), 3.42-3.31 (m, 2H), 3.27-3.12 (m, 2H), 2.41 (s, 3H).

$^{13}$C NMR (50 MHz, CDCl$_3$) δ 161.8, 147.9, 138.3, 136.1, 135.3, 129.3, 128.9, 128.8, 128.3, 127.4, 126.7, 125.6, 121.5, 41.1, 35.4, 20.9.

HRMS (EI) m/z Calcd for C$_{18}$H$_{18}$N [M+H]$^+$: 248.1434; Found: 248.1436.

2-(4-methoxyphenethyl)quinoline (3e)

The general procedure was followed to afford the title compound as pale yellow liquid, isolated yield: 70%, 92 mg.

$^1$H NMR (200 MHz, CDCl$_3$) δ 8.13-8.05 (m, 2H), 7.81 (d, $J = 8.4$ Hz, 1H), 7.73 (t, $J = 7.6$ Hz, 1H), 7.52 (t, $J = 7.6$ Hz, 1H), 7.26 (d, $J = 7.6$ Hz, 1H), 7.18 (d, $J = 8.4$ Hz, 2H), 6.84 (d, $J = 8.4$ Hz, 2H), 3.81 (s, 3H), 3.31-3.26 (m, 2H), 3.15-3.10 (m, 2H).

$^{13}$C NMR (50 MHz, CDCl$_3$) δ 161.9, 157.9, 147.9, 136.1, 133.6, 129.4, 129.3, 128.9, 128.8, 127.5, 126.8, 125.7, 121.6, 113.8, 55.2, 41.3, 35.1.

HRMS (EI) m/z Calcd for C$_{18}$H$_{18}$NO [M+H]$^+$: 264.1383; Found: 264.1379.
2-(2-(Naphthalen-2-yl)ethyl)quinoline (3g)
The general procedure was followed to afford the title compound as pale yellow solid, isolated yield: 91%, 128 mg.

$^1$H NMR (500 MHz, CDCl$_3$) $\delta$ 8.16 (d, $J = 8.8$ Hz, 1H), 8.05 (d, $J = 8.3$ Hz, 1H), 7.93-7.68 (m, 6H), 7.60-7.37 (m, 4H), 7.26 (d, $J = 8.3$ Hz, 1H), 3.40 (m, 4H).

$^{13}$C NMR (126 MHz, CDCl$_3$) $\delta$ 161.7, 147.9, 138.9, 136.2, 133.6, 132.0, 129.4, 128.8, 127.9, 127.6, 127.5, 127.4, 127.3, 126.8, 126.5, 125.8, 125.7, 125.2, 121.5, 40.8, 36.0.

HRMS (EI) m/z Calcd for C$_{21}$H$_{18}$N [M+H]$^+$: 284.1434; Found: 284.1433.

2-(2-(Naphthalen-1-yl)ethyl)quinoline (3h)
The general procedure was followed to afford the title compound as pale yellow solid, isolated yield: 83%, 117 mg.

$^1$H NMR (500 MHz, CDCl$_3$) $\delta$ 8.26-8.11 (m, 2H), 8.03(d, $J = 8.3$ Hz, 1H), 7.95-7.85 (m, 1H), 7.84-7.69 (m, 3H), 7.62-7.47 (m, 3H), 7.43-7.35 (m, 2H), 7.22 (d, $J = 6.8$ Hz, 1H), 3.70-3.63 (m, 2H), 3.51-3.39 (m, 2H).

$^{13}$C NMR (126 MHz, CDCl$_3$) $\delta$ 161.9, 148.0, 137.5, 136.1, 133.8, 131.8, 129.4, 128.9, 128.8, 127.5, 126.8, 126.1, 125.9, 125.7, 125.5, 125.4, 123.7, 121.5, 40.0, 32.9.

HRMS (EI) m/z Calcd for C$_{21}$H$_{18}$N [M+H]$^+$: 284.1434; Found: 284.1433.
2-(2-(furan-2-yl)ethyl)quinoline (3i)
The general procedure was followed to afford the title compound as pale yellow liquid, isolated yield: 72%, 80 mg.

$^1$H NMR (500 MHz, CDCl$_3$) $\delta$ 8.10 (d, $J = 8.8$ Hz, 2H), 7.83 (d, $J = 8.8$ Hz, 1H), 7.70 (t, $J = 7.2$ Hz, 1H), 7.53 (t, $J = 7.2$ Hz, 1H), 7.39-7.29 (m, 2H), 6.30 (br, 1H), 6.04 (br, 1H), 3.37 (t, $J = 7.2$ Hz, 2H), 3.23 (t, $J = 8.0$ Hz, 2H).

$^{13}$C NMR (126 MHz, CDCl$_3$) $\delta$ 161.2, 140.9, 136.3, 129.4, 128.8, 127.5, 126.8, 125.9, 121.3, 110.1, 105.4, 37.4, 27.9.

HRMS (EI) m/z Calcd for C$_{15}$H$_{14}$ON [M+H]$^+$: 224.1070; Found: 224.1069.

2-(2-cyclohexylethyl)naphthalene (3j)
The general procedure was followed to afford the title compound as colorless liquid, isolated yield: 71%, 85 mg.

$^1$H NMR (500 MHz, CDCl$_3$) $\delta$ 8.13-7.97 (dd, $J = 7.3$, 2.3 Hz, 2H), 7.85-7.61 (m, 2H), 7.54-7.41 (m, 1H), 7.33-7.25 (m, 1H), 3.07-2.87 (m, 2H), 1.88-1.64 (m, 7H), 1.46-1.10 (m, 4H), 1.07-0.85 (m, 2H).

$^{13}$C NMR (126 MHz, CDCl$_3$) $\delta$ 163.5, 147.9, 136.2, 129.3, 128.8, 127.5, 126.7, 125.6, 121.4, 37.8, 37.7, 36.9, 33.3, 26.7, 26.4.

HRMS (EI) m/z Calcd for C$_{17}$H$_{22}$N [M+H]$^+$: 240.1747; Found: 240.1746.
2-(2-cyclopropylethyl)quinoline (3k)

The general procedure was followed to afford the title compound as colorless liquid, isolated yield: 70%, 69 mg.

$^1$H NMR (500 MHz, CDCl$_3$) δ 8.05 (d, $J = 8.3$ Hz, 2H), 7.80-7.62 (m, 2H), 7.47 (t, $J = 7.8$ Hz, 1H), 7.30 (d, $J = 8.7$ Hz, 1H), 3.08 (t, $J = 7.8$ Hz, 2H), 1.72 (q, $J = 7.4$ Hz, 2H), 0.85-0.67 (m, 1H), 0.51-0.35 (m, 2H), 0.12-0.03 (m, 2H).

$^{13}$C NMR (126 MHz, CDCl$_3$) δ 162.8, 147.9, 136.0, 129.3, 128.8, 127.4, 126.7, 125.6, 121.5, 39.3, 35.0, 10.9, 4.6.

HRMS (EI) m/z Calcd for C$_{14}$H$_{16}$N [M+H]$^+$: 198.1277; Found: 198.1179.

2-(4-phenylbutyl)quinoline (3m)

The general procedure was followed to afford the title compound as colourless liquid, isolated yield: 68%, 89 mg.

$^1$H NMR (500 MHz, CDCl$_3$) δ 8.02 (d, $J = 8.5$ Hz, 2H), 7.76 (d, $J = 7.6$ Hz, 2H), 7.67 (t, $J = 8.5$ Hz, 1H), 7.47 (t, $J = 7.6$ Hz, 1H), 7.34-7.13 (m, 6H), 3.00 (t, $J = 8.5$ Hz, 2H), 2.67 (t, $J = 7.6$ Hz, 2H), 1.87 (pent, $J = 8.5$ Hz, 2H), 1.75 (pent, $J = 7.6$ Hz, 2H)

$^{13}$C NMR (126 MHz, CDCl$_3$) δ 162.7, 147.9, 142.4, 136.2, 129.3, 128.8, 128.4, 128.2, 127.4, 126.7, 125.6, 121.3, 39.1, 35.8, 31.3, 29.6.

HRMS (EI) m/z Calcd for C$_{19}$H$_{20}$N [M+H]$^+$: 262.1590; Found: 262.1589.
2-(2,2-diphenylethyl)quinoline (3n)

The general procedure was followed to afford the title compound as colourless liquid, isolated yield: 45%, 69 mg.

$^1$H NMR (200 MHz, CDCl$_3$) $\delta$ 8.06 (d, $J = 7.8$ Hz, 1H), 7.90 (d, $J = 8.4$ Hz, 1H), 7.76-7.63 (m, 2H), 7.48-7.32 (m, 6H), 7.24-7.12 (m, 5H), 7.00 (d, $J = 8.4$ Hz, 1H), 4.73 (t, $J = 7.8$ Hz, 1H), 3.74 (d, $J = 8.1$ Hz, 2H).

$^{13}$C NMR (126 MHz, CDCl$_3$) $\delta$ 160.6, 147.9, 144.3, 135.8, 129.3, 128.8, 128.5, 128.4, 128.1, 127.6, 127.5, 126.6, 126.2, 125.8, 122.1, 51.1, 44.9.

HRMS (EI) m/z Calcd for C$_{23}$H$_{20}$N [M+H]$^+$: 310.1590; Found: 310.1591.

2-(2-phenyl-2-0-tolylethyl)quinoline (3o)

The general procedure was followed to afford the title compound as colourless liquid, isolated yield: 42%, 68 mg.

$^1$H NMR (500 MHz, CDCl$_3$) $\delta$ 8.06 (d, $J = 8.8$ Hz, 1H), 7.89 (d, $J = 8.3$ Hz, 1H), 7.73 (d, $J = 7.3$ Hz, 1H), 7.69 (dt, $J = 6.9$, 1.2 Hz, 1H), 7.53-7.46 (m, 2H), 7.24-7.18 (m, 5H), 7.16-7.05 (m, 3H), 6.95 (d, $J = 8.3$ Hz, 1H), 4.96 (t, $J = 7.8$ Hz, 1H), 3.72 (d, $J = 7.8$ Hz, 2H), 2.21 (s, 3H).

$^{13}$C NMR (126 MHz, CDCl$_3$) $\delta$ 160.7, 147.9, 143.9, 142.1, 136.4, 135.6, 130.4, 129.2, 128.9, 128.2, 128.1, 127.4, 126.9, 126.7, 126.1, 126.0, 125.9, 125.7, 122.0, 46.8, 45.4, 19.8.
HRMS(EI) m/z Calcd for C_{24}H_{22}N [M+H]^+: 324.1747; Found: 324.1749.

2-(4-methylphenethyl)quinoxaline (4a)
The general procedure was followed to afford the title compound as pale yellow liquid, isolated yield: 78%, 97 mg.

^1^H NMR (200 MHz, CDCl_3) δ 8.63 (s, 1H), 8.13-8.03 (m, 2H), 7.82-7.68 (m, 2H), 7.20-7.01 (m, 4H), 3.39-3.27 (m, 2H), 3.21-3.09 (m, 2H), 2.33 (s, 3H).

^1^3^C NMR (50 MHz, CDCl_3) δ 156.6, 145.9, 142.3, 141.3, 137.6, 135.8, 129.9, 129.2, 129.0, 128.9, 128.4, 38.3, 34.9, 21.0.

HRMS(EI) m/z Calcd for C_{17}H_{17}N_2 [M+H]^+: 249.1386; Found: 249.1385.

2-(4-chlorophenethyl)quinoxaline (4b)
The general procedure was followed to afford the title compound as pale yellow liquid, isolated yield: 71%, 95 mg.

^1^H NMR (200 MHz, CDCl_3) δ 8.63 (s, 1H), 8.15-8.02 (m, 2H), 7.81-7.65 (m, 2H), 7.31-7.15 (m, 4H), 3.40-3.27 (m, 2H), 3.16-3.11 (m, 2H).

^1^3^C NMR (50 MHz, CDCl_3) δ 156.4, 145.8, 142.2, 141.3, 140.7, 129.9, 129.2, 129.0, 128.9, 128.5, 128.4, 126.2, 38.1, 35.2.
**2-heptylquinoxaline (4c)**

The general procedure was followed to afford the title compound as colourless liquid, isolated yield: 70%, 80 mg.

**$^1$H NMR** (200 MHz, CDCl$_3$) δ 8.74 (s, 1H), 8.12-8.01 (m, 2H), 7.79-7.62 (m, 2H), 3.01 (t, $J = 8.1$ Hz, 2H), 1.94-1.77 (m, 2H), 1.48-1.17 (m, 8H), 0.93-0.77 (m, 3H).

**$^{13}$C NMR** (50 MHz, CDCl$_3$) δ 157.7, 145.8, 142.2, 141.2, 129.9, 129.2, 128.9, 36.5, 31.7, 29.5, 29.4, 29.1, 22.6, 14.0.

**HRMS (EI) m/z Calcd for C$_{15}$H$_{21}$N$_2$ [M+H]$^+$: 229.1699; Found: 229.1698.**

**2-(2-(thiophen-2-yl)ethyl)quinoxaline (4d)**

The general procedure was followed to afford the title compound as pale yellow liquid, isolated yield: 62%, 74 mg.

**$^1$H NMR** (500 MHz, CDCl$_3$) δ 8.6 (s, 1H), 8.07- 8.05 (m, 2H), 7.77-7.68 (m, 2H), 7.11 (dd, $J = 5.1$, 1.1 Hz, 1H), 6.89 (dd, $J = 5.1$, 3.3 Hz, 1H), 6.80 (dd, $J = 3.3$, 1.0 Hz, 1H), 3.45-3.41 (m, 2H), 3.36-3.34 (m, 2H).
$^{13}$C NMR (126 MHz, CDCl$_3$) $\delta$ 155.6, 145.6, 143.2, 142.1, 141.2, 129.9, 129.1, 129.0, 128.8, 126.7, 124.7, 123.4, 38.0, 28.9.

HRMS(EL) m/z Calcd for C$_{14}$H$_{13}$N$_2$S [M+H]$^+$: 241.0794; Found: 241.0793.

6-methoxy-2-(4-methylphenethyl)quinoline (5a)
The general procedure was followed to afford the title compound as pale yellow liquid, isolated yield: 81%, 112 mg.

$^1$H NMR (500 MHz, CDCl$_3$) $\delta$ 7.99-7.93 (m, 2H), 7.37 (dd, $J = 6.0$, 3.1 Hz, 1H), 7.20 (d, $J = 8.3$ Hz, 1H), 7.15 (d, $J = 8.1$ Hz, 2H), 7.10 (d, $J = 7.6$ Hz, 2H), 7.06 (d, $J = 2.8$ Hz, 1H), 3.93 (s, 3H), 3.27-3.22 (m, 2H), 3.14-3.09 (m, 2H), 2.33 (s, 3H).

$^{13}$C NMR (126 MHz, CDCl$_3$) $\delta$ 159.4, 157.2, 144.0, 138.5, 135.4, 134.9, 130.3, 129.0, 128.4, 127.6, 121.8, 121.7, 105.2, 55.5, 40.8, 35.6, 20.9.

HRMS(EL) m/z Calcd for C$_{19}$H$_{20}$ON [M+H]$^+$: 278.1539; Found: 278.1542.

2-phenethylquinoxaline (5b)
The general procedure was followed to afford the title compound as pale yellow liquid, isolated yield: 86%, 100 mg.

$^1$H NMR (500 MHz, CDCl$_3$) $\delta$ 8.63 (s, 1H), 8.14-8.01 (m, 2H), 7.81-7.65 (m, 2H), 7.31-7.15 (m, 5H), 3.40-3.27 (m, 2H), 3.24-3.11 (m, 2H).
$^{13}$C NMR (126 MHz, CDCl$_3$) $\delta$ 156.4, 145.8, 142.2, 141.2, 140.7, 129.9, 129.2, 129.0, 128.9, 128.5, 128.4, 126.2, 38.1, 35.2.

HRMS (EI) m/z Calcd for C$_{16}$H$_{15}$N$_2$ [M+H]$^+$/ Found: 235.1229.

(E)-2-(4-methylstyryl)quinoline

$^1$H NMR (500 MHz, CDCl$_3$) $\delta$ 8.14 (d, $J$ = 8.5 Hz, 1H), 8.08 (d, $J$ = 8.5 Hz, 1H), 7.79 (d, $J$ = 8.0 Hz, 1H), 7.71-7.65 (m, 3H), 7.56 (d, $J$ = 8.0 Hz, 2H), 7.50 (t, $J$ = 7.6 Hz, 1H), 7.38 (d, $J$ = 16.3 Hz, 1H), 7.22 (d, $J$ = 7.5 Hz, 2H), 2.40 (s, 3H).

$^{13}$C NMR (126 MHz, CDCl$_3$) $\delta$ 156.2, 148.2, 138.7, 136.3, 134.4, 133.7, 129.7, 129.5, 129.1, 127.9, 127.5, 127.2, 126.0, 119.2, 21.4.

HRMS (EI) m/z Calcd for C$_{18}$H$_{16}$N [M+H]$^+$/ Found: 246.1275.

$^1$H NMR (500 MHz, CDCl$_3$) $\delta$ 8.12 (t, $J$ = 8.7 Hz, 2H), 7.83-7.71 (m, 2H), 7.56 (dt, $J$ = 8.5, 1.3 Hz, 1H), 7.37-7.28 (m, 5H), 3.42-3.29 (m, 1.92H), 3.28-3.14 (m, 1.70H).
6. Copies of NMR Spectra

\[ \text{Chemical Shift (ppm)} \]

\[ \text{1H & 13C NMR of 3a} \]

S20
$^1$H & $^{13}$C NMR of 3b
$^1$H & $^{13}$C NMR of 3c

S22
$^{1}H$ & $^{13}C$ NMR of 3d
$^{1}H$ & $^{13}C$ NMR of 3e

S24
$^{1}H$ & $^{13}C$ NMR of 3g
$^1$H & $^{13}$C NMR of 3h
$\text{H} \& \text{C NMR of 3i}$

S27
$^1$H & $^{13}$C NMR of 3j
H & $^{13}$C NMR of 3k
$^{1}$H & $^{13}$C NMR of 3m
$^1$H & $^{13}$C NMR of 3n
$^{1}$H & $^{13}$C NMR of 3n
$^1$H & $^{13}$C NMR of 4a
$^{1}$H & $^{13}$C NMR of 4b
$^1$H & $^{13}$C NMR of 4c
\[ \text{\(^1H\) NMR of 4d} \]

\[ \text{\(^{13}C\) NMR of 4d} \]
$^{1}H$ & $^{13}C$ NMR of 5a
$^1$H & $^{13}$C NMR of 5b

![NMR spectra of 5b](image)

$^1$H NMR spectrum showing chemical shifts at 1.00, 2.07, 3.00 ppm, and $^{13}$C NMR spectrum showing chemical shifts at 156.16, 133.68, 127.96 ppm.

Chemical structure of 5b with highlighted peaks on the NMR spectra.
$^{1}H$ & $^{13}C$ NMR of $3d'$

$^{1}H$ NMR of [D]-3a