Supporting Information

*Ortho*-amino group functionalized 2,2’-bipyridine based Ru(II) complex catalysed alkylation of secondary alcohols, nitriles and amines using alcohols

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**Text S1: X-ray crystallographic studies:** Single-crystal X-ray data of all the complexes were collected at 100 K by using a Bruker SMART APEX II CCD diffractometer and Bruker D8 Quest single crystal diffractometer with graphite monochromated MoKα radiation ($\lambda = 0.71073$ Å). The frames were indexed, integrated and scaled using SMART and SAINT software package\(^1\) and the data were corrected for absorption using the SADABS program.\(^2\) The structures were solved and refined using WINGX and SHELX programs.\(^3\) The crystallographic figures have been generated using Diamond 3 software 10 (30% probability thermal ellipsoids).\(^4\) The CCDC number of complex 1a, 1b and 1c are CCDC 1568230, CCDC 1568231 and CCDC 1568232 respectively.

![Crystallographic structure](image)

**Figure S1:** Solid state structure of complex 1a (30% thermal ellipsoids; counter chloride anion and solvent molecules are omitted for clarity).

**Table S1.** Crystallographic data and refinement parameters for complex 1a.

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Identification code</td>
<td>Complex1a</td>
</tr>
<tr>
<td>Empirical formula</td>
<td>C$<em>{51}$H$</em>{51}$N$_4$O$_2$Cl$_5$P$_2$Ru</td>
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<tr>
<td>Formula weight</td>
<td>1092.21</td>
</tr>
<tr>
<td>Temperature/K</td>
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</tr>
<tr>
<td>Crystal system</td>
<td>monoclinic</td>
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<tr>
<td>Space group</td>
<td>P2$_1$/c</td>
</tr>
<tr>
<td>a/Å</td>
<td>12.074(3)</td>
</tr>
<tr>
<td>b/Å</td>
<td>22.964(6)</td>
</tr>
<tr>
<td>c/Å</td>
<td>17.711(5)</td>
</tr>
<tr>
<td>α/°</td>
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<tr>
<td>β/°</td>
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<td>γ/°</td>
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<td>Volume/Å$^3$</td>
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Table S2. Crystallographic data and refinement parameters for complex 1b.

<table>
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<th>Parameter</th>
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<tbody>
<tr>
<td>Identification code</td>
<td>Complex1b</td>
</tr>
<tr>
<td>Empirical formula</td>
<td>C₄₈H₄₄N₄RuCl₂P₂</td>
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<tr>
<td>Formula weight</td>
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</table>
Figure S3: Solid state structure of complex 1c (30% thermal ellipsoids; counter PF$_{6}$ anion is omitted for clarity).
**Table S3**: Crystallographic data and refinement parameters for complex 1c.

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</tr>
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<td>Empirical formula</td>
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<td>Temperature/K</td>
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<td>Crystal system</td>
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<td>a/Å</td>
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<tr>
<td>b/Å</td>
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<tr>
<td>β/°</td>
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<tr>
<td>γ/°</td>
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<td>Volume/Å^3</td>
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<td>Z</td>
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<td>ρ_{calc}/g/cm^3</td>
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<tr>
<td>μ/mm^3</td>
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<td>F(000)</td>
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<td>Crystal size/mm^3</td>
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<td>Radiation</td>
<td>MoKα (λ = 0.71073)</td>
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<tr>
<td>2Θ range for data collection/°</td>
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<td>Index ranges</td>
<td>-28 ≤ h ≤ 29, -15 ≤ k ≤ 10, -9 ≤ l ≤ 9</td>
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<tr>
<td>Independent reflections</td>
<td>4256 [R_{int} = 0.0446, R_{sigma} = 0.0481]</td>
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<tr>
<td>Data/restraints/parameters</td>
<td>4256/1/321</td>
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<tr>
<td>Goodness-of-fit on F^2</td>
<td>1.041</td>
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<tr>
<td>Final R indexes [I&gt;=2σ (I)]</td>
<td>R_1 = 0.0357, wR_2 = 0.0819</td>
</tr>
<tr>
<td>Final R indexes [all data]</td>
<td>R_1 = 0.0411, wR_2 = 0.0865</td>
</tr>
<tr>
<td>Largest diff. peak/hole / e Å^-3</td>
<td>0.88/-0.35</td>
</tr>
<tr>
<td>Flack parameter</td>
<td>-0.01(3)</td>
</tr>
</tbody>
</table>

**Table S4**: β-Alkylation of different secondary alcohols with benzyl alcohol.\(^a\)

\[
\begin{align*}
\text{R-CHOH} + \text{Ph-OH} & \xrightarrow{\text{Cat. 1a (0.1 mol %)}} \text{R-CHOH} \xrightarrow{\text{KO' Bu (0.5 equiv.)}} \text{R-OH} + \text{Ph-C=O} \\
\text{Toluene, 130 °C, 1.5-5 h} & \text{A} + \text{B}
\end{align*}
\]
<table>
<thead>
<tr>
<th>Entry</th>
<th>Secondary alcohol</th>
<th>Product</th>
<th>Conv. (%)&lt;sup&gt;b&lt;/sup&gt;</th>
<th>A/B ratio&lt;sup&gt;b&lt;/sup&gt;</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td><img src="image1" alt="Secondary alcohol 1" /></td>
<td><img src="image2" alt="Product 1" /></td>
<td>100</td>
<td>92:8</td>
</tr>
<tr>
<td>2</td>
<td><img src="image3" alt="Secondary alcohol 2" /></td>
<td><img src="image4" alt="Product 2" /></td>
<td>100</td>
<td>88:12</td>
</tr>
<tr>
<td>3</td>
<td><img src="image5" alt="Secondary alcohol 3" /></td>
<td><img src="image6" alt="Product 3" /></td>
<td>99</td>
<td>91:9</td>
</tr>
<tr>
<td>4</td>
<td><img src="image7" alt="Secondary alcohol 4" /></td>
<td><img src="image8" alt="Product 4" /></td>
<td>93</td>
<td>93:7</td>
</tr>
<tr>
<td>5</td>
<td><img src="image9" alt="Secondary alcohol 5" /></td>
<td><img src="image10" alt="Product 5" /></td>
<td>100</td>
<td>87:13</td>
</tr>
<tr>
<td>6</td>
<td><img src="image11" alt="Secondary alcohol 6" /></td>
<td><img src="image12" alt="Product 6" /></td>
<td>100</td>
<td>81:19</td>
</tr>
<tr>
<td>7</td>
<td><img src="image13" alt="Secondary alcohol 7" /></td>
<td><img src="image14" alt="Product 7" /></td>
<td>80</td>
<td>85:15</td>
</tr>
<tr>
<td>8&lt;sup&gt;c&lt;/sup&gt;</td>
<td><img src="image15" alt="Secondary alcohol 8" /></td>
<td><img src="image16" alt="Product 8" /></td>
<td>95</td>
<td>93:7</td>
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<tr>
<td>9</td>
<td><img src="image17" alt="Secondary alcohol 9" /></td>
<td><img src="image18" alt="Product 9" /></td>
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<td>99:1</td>
</tr>
<tr>
<td>10&lt;sup&gt;d,e&lt;/sup&gt;</td>
<td><img src="image19" alt="Secondary alcohol 10" /></td>
<td><img src="image20" alt="Product 10" /></td>
<td>100</td>
<td>99:1</td>
</tr>
<tr>
<td>11&lt;sup&gt;d,e&lt;/sup&gt;</td>
<td><img src="image21" alt="Secondary alcohol 11" /></td>
<td><img src="image22" alt="Product 11" /></td>
<td>97</td>
<td>93:7</td>
</tr>
</tbody>
</table>

<sup>a</sup>Reaction condition: Cat. 1a (0.1 mol %), secondary alcohol (1.1 mmol), benzyl alcohol (1.1 mmol) and KOtBu (0.55 mmol) in 2 mL toluene at 130 °C for 1.5 h; closed argon condition in Schlenk tube. <sup>b</sup>Determined by 1H NMR using 1,3,5-trimethoxybenzene as internal standard. <sup>c</sup>2 h heating. <sup>d</sup>5 h heating. <sup>e</sup>2.2 mmol secondary alcohol and 1.1 mmol benzyl alcohol were used.
Table S5: β-Alkylation of 1-phenylethanol with different primary alcohols.\textsuperscript{a}

\[
\begin{array}{cccc}
\text{Entry} & \text{Primary alcohol} & \text{Product} & \text{Conv. (\%)}^b & \text{A/B ratio}^b \\
1 & \begin{array}{c}
\text{Cl} \\
\text{OH}
\end{array} & \begin{array}{c}
\text{OH} \\
\text{Cl}
\end{array} & 97 & 91:9 \\
2 & \begin{array}{c}
\text{Br} \\
\text{OH}
\end{array} & \begin{array}{c}
\text{OH} \\
\text{Br}
\end{array} & 98 & 90:10 \\
3 & \begin{array}{c}
\text{F} \\
\text{OH}
\end{array} & \begin{array}{c}
\text{OH} \\
\text{F}
\end{array} & 100 & 89:11 \\
4 & \begin{array}{c}
\text{Me} \\
\text{OH}
\end{array} & \begin{array}{c}
\text{OH} \\
\text{Me}
\end{array} & 100 & 90:10 \\
5 & \begin{array}{c}
\text{MeO} \\
\text{OH}
\end{array} & \begin{array}{c}
\text{OH} \\
\text{MeO}
\end{array} & 100 & 88:12 \\
6 & \begin{array}{c}
\text{Cl} \\
\text{OH}
\end{array} & \begin{array}{c}
\text{OH} \\
\text{Cl}
\end{array} & 99 & 84:16 \\
7 & \begin{array}{c}
\text{OMe} \\
\text{OH}
\end{array} & \begin{array}{c}
\text{OH} \\
\text{OMe}
\end{array} & 96 & 90:10 \\
8 & \begin{array}{c}
\text{Cl} \\
\text{OH}
\end{array} & \begin{array}{c}
\text{OH} \\
\text{Cl}
\end{array} & 97 & 92:8 \\
9 & \begin{array}{c}
\text{OMe} \\
\text{OH}
\end{array} & \begin{array}{c}
\text{OH} \\
\text{OMe}
\end{array} & 100 & 79:21
\end{array}
\]

\textsuperscript{a} Conditions: Cat. 1a (0.1 mol %) with KO\textsubscript{Bu} (0.5 equiv.) in toluene at 130 °C for 1.5-7 h.

\textsuperscript{b} Determined by GC analysis.

\textsuperscript{c} Naphthalene derivative.
**Text S2: Procedure for the control experiments of β-alkylation secondary alcohol:** Under argon condition, a mixture of cat. 1a (0.1 mol %), KO'Bu (0.55 mmol), 1-phenylethanol (1.1 mmol) and benzaldehyde (1.1 mmol) was added with 2 mL toluene and refluxed at 130 °C (oil bath temperature) for 30 min (reaction a). After it was cooled to room temperature, the crude reaction mixture was analysed by GC check the conversion of 1-phenylethanol and further evaporating the solvent, the resulting mixture was submitted for $^1$H NMR to calculate the product selectivity.

In the similar way, reaction b also was performed with cat. 1a (0.1 mol %), KO'Bu (0.55 mmol), acetophenone (1.1 mmol), and benzyl alcohol (1.1 mmol) in 2 mL toluene at 130 °C (oil bath temperature) for 30 min under closed argon condition.

**Text S3: Procedure for time dependence product distribution of β-alkylation of secondary alcohol:** To check the conversion and product selectivity of β-alkylation of secondary alcohol at different time interval, six identical reactions were performed following standard reaction condition in six Schlenk tubes using 1-phenylethanol and benzyl alcohol as model substrates only varying the reaction time (15 min, 30 min, 45 min, 60 min, 75 min and 90 min). After the reaction,
the conversion and product selectivity were determined by $^1$H NMR and the data was plotted in % Mol vs. time (min) (figure S4).

Figure S4. Time dependence product distribution of β-alkylation of 1-phenylethanol with benzyl alcohol using cat. 1a.

Text S4: TON Calculation in β-alkylation of secondary alcohols: 32 µL solution of cat. 1a (4.4 x 10$^{-4}$ mol % cat. 1a) was taken from stock solution (1.5 mg cat. 1a in 1.5 mL acetonitrile) and added in a Schlenk flask. After evaporating acetonitrile under reduced pressure, 1-phenylethanol (8.05 mmol), benzyl alcohol (8.05 mmol), KO$^t$Bu (4.025 mmol) and 15 mL toluene were taken into the flask, equipped with a magnetic stir bar. Then the flask was heated at 130 °C (oil bath temperature) for 30 hour. Based on the GC analysis conversion of 1-phenylethanol was 43.5%.

Text S5: Hg$^0$ poisoning experiment: To investigate the homogeneous nature of the catalyst in reaction condition, Hg$^0$ poisoning test was performed. Following the general procedure for β-alkylation of secondary alcohols, two identical reactions were performed in parallel using 1-phenylethanol and benzyl alcohol as substrates where one acted as the control reaction. Under argon condition, a mixture of cat. 1a (0.1 mol %), KO$^t$Bu (0.55 mmol), 1-phenylethanol (1.1 mmol) and benzyl alcohol (1.1 mmol) was added in two different Schlenk tube with 2 mL toluene and refluxed at 130 °C (oil bath temperature) for 10 min. After 10 min, the two reaction mixtures were cooled down to room temperature under argon flow and a drop of Hg$^0$ was added in one tube, re-sealed and refluxed again at 130 °C (oil bath temperature) for another 80 min (the control Schlenk tube was also treated identically, without adding of Hg$^0$). After the reaction, the conversion of 1-phenylethanol was monitored by GC. The conversion of 1-phenylethanol without and with Hg$^0$ were 100% and 96% respectively.

Table S6: Substrate scope of α-alkylation of arylacetonitriles with primary alcohols.$^a$
<table>
<thead>
<tr>
<th>Entry</th>
<th>Nitrile</th>
<th>Alcohol</th>
<th>Product</th>
<th>Time (h)</th>
<th>Yield (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>( \text{Ph-CH}_2\text{CN} )</td>
<td>( \text{Ph-OH} )</td>
<td>( \text{Ph-CH}_2\text{CN} )</td>
<td>2</td>
<td>99</td>
</tr>
<tr>
<td>2</td>
<td>( \text{Me-Ph-CH}_2\text{CN} )</td>
<td>( \text{Ph-OH} )</td>
<td>( \text{Me-Ph-CH}_2\text{CN} )</td>
<td>1.5</td>
<td>&gt;99</td>
</tr>
<tr>
<td>3</td>
<td>( \text{MeO-Ph-CH}_2\text{CN} )</td>
<td>( \text{Ph-OH} )</td>
<td>( \text{MeO-Ph-CH}_2\text{CN} )</td>
<td>2</td>
<td>&gt;99</td>
</tr>
<tr>
<td>4</td>
<td>( \text{Br-Ph-CH}_2\text{CN} )</td>
<td>( \text{Ph-OH} )</td>
<td>( \text{Br-Ph-CH}_2\text{CN} )</td>
<td>1.5</td>
<td>98</td>
</tr>
<tr>
<td>5</td>
<td>( \text{N-pyridyl-CH}_2\text{CN} )</td>
<td>( \text{Ph-OH} )</td>
<td>( \text{N-pyridyl-Ph-CH}_2\text{CN} )</td>
<td>3</td>
<td>98</td>
</tr>
<tr>
<td>6</td>
<td>( \text{Ph-CH}_2\text{CN} )</td>
<td>( \text{Me-Ph-OH} )</td>
<td>( \text{Ph-CH}_2\text{CN} )</td>
<td>3</td>
<td>99</td>
</tr>
<tr>
<td>7</td>
<td>( \text{Ph-CH}_2\text{CN} )</td>
<td>( \text{Ph-OH} )</td>
<td>( \text{Ph-CH}_2\text{CN} )</td>
<td>3</td>
<td>99</td>
</tr>
<tr>
<td>8</td>
<td>( \text{Ph-CH}_2\text{CN} )</td>
<td>( \text{O-Ph-OH} )</td>
<td>( \text{Ph-CH}_2\text{CN} )</td>
<td>2</td>
<td>98</td>
</tr>
</tbody>
</table>
Reaction conditions: Cat. 1a (0.5 mol %), arylacetonitrile (0.5 mmol), alcohol (2.5 mmol) and KOH (0.25 mmol) refluxed in 2 mL dioxane at 115 °C in necessary time; closed argon condition in Schlenk tube. Determined by GC using mesitylene as an internal standard. 1 mol % cat. 1a. Heated at 130 °C. 1 equiv. KOH.

Table S7: Substrate scope for the α-methylation of arylacetonitriles using methanol.

<table>
<thead>
<tr>
<th>Entry</th>
<th>Nitrile</th>
<th>Product</th>
<th>Yield (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td><img src="image1.png" alt="Nitrile" /></td>
<td><img src="image2.png" alt="Product" /></td>
<td>92</td>
</tr>
<tr>
<td>2</td>
<td><img src="image3.png" alt="Nitrile" /></td>
<td><img src="image4.png" alt="Product" /></td>
<td>88</td>
</tr>
<tr>
<td>3</td>
<td><img src="image5.png" alt="Nitrile" /></td>
<td><img src="image6.png" alt="Product" /></td>
<td>76</td>
</tr>
<tr>
<td>4</td>
<td><img src="image7.png" alt="Nitrile" /></td>
<td><img src="image8.png" alt="Product" /></td>
<td>68</td>
</tr>
<tr>
<td>5</td>
<td><img src="image9.png" alt="Nitrile" /></td>
<td><img src="image10.png" alt="Product" /></td>
<td>81</td>
</tr>
</tbody>
</table>
Reaction conditions: Cat. 1a (1 mol %), arylacetonitrile (0.6 mmol) and NaOMe (0.6 mmol) in MeOH (1.0 mL) at 135 °C for 16 h; closed argon condition in pressure tube. Determined by GC using mesitylene as an internal standard.

**Table S8:** Monoalkylation of acetonitrile using different alcohols.°

\[ R-OH + CH_3CN \xrightarrow{\text{Cat. 1a (5 mol %), NaOH (2 equiv.)}} R-CN \]

<table>
<thead>
<tr>
<th>Entry</th>
<th>Substrate</th>
<th>Product</th>
<th>Yield (%)^b</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Phenol</td>
<td>Phenyl-C orphenyl</td>
<td>94</td>
</tr>
<tr>
<td>2</td>
<td>(Me)</td>
<td>Phenyl-C orphenyl</td>
<td>81</td>
</tr>
<tr>
<td>3</td>
<td>(MeO)</td>
<td>Phenyl-C orphenyl</td>
<td>85</td>
</tr>
<tr>
<td>4</td>
<td>(F)</td>
<td>Phenyl-C orphenyl</td>
<td>77</td>
</tr>
<tr>
<td>5</td>
<td>OMe</td>
<td>Phenyl-C orphenyl</td>
<td>69</td>
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<tr>
<td>6</td>
<td>OMe</td>
<td>Phenyl-C orphenyl</td>
<td>87</td>
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<tr>
<td>7</td>
<td>OMe</td>
<td>Phenyl-C orphenyl</td>
<td>83</td>
</tr>
<tr>
<td>8</td>
<td>Phenol</td>
<td>Phenyl-C orphenyl</td>
<td>72</td>
</tr>
<tr>
<td>9</td>
<td>Phenol</td>
<td>Phenyl-C orphenyl</td>
<td>64</td>
</tr>
</tbody>
</table>

° Reaction conditions: Cat. 1a (5 mol %), alcohol (0.5 mmol), NaOH (1.0 mmol) and CH3CN (62.5 mmol) heated in 1 mL toluene at 120 °C for 24 h; closed argon condition in Schlenk tube. Determined by GC using mesitylene as an internal standard.

**Table S9:** N-methylation of amines using methanol.°

\[ R-NH_2 + MeOH \xrightarrow{\text{Cat. 1a (1 mol %), NaOMe (1 equiv.)}} R-NH-Me \]

° Reaction conditions: Cat. 1a (1 mol %), alcohol (0.5 mmol), NaOH (1.0 mmol) and CH3CN (62.5 mmol) heated in 1 mL toluene at 120 °C for 24 h; closed argon condition in Schlenk tube. Determined by GC using mesitylene as an internal standard.
<table>
<thead>
<tr>
<th>Entry</th>
<th>Substrate</th>
<th>Product</th>
<th>Yield (%)&lt;sup&gt;b&lt;/sup&gt;</th>
</tr>
</thead>
<tbody>
<tr>
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<sup>a</sup>Reaction conditions: Cat. 1a (1 mol %), amine (0.8 mmol), NaOMe (0.8 mmol) in methanol (1.0 mL) refluxed at 110 °C for 15 h; closed argon condition in pressure tube. <sup>b</sup>Determined by GC using mesitylene as an internal standard. <sup>c</sup>12 h. <sup>d</sup>24 h.

Text S6: NMR Characterization Data of Isolated Products:

β-Alkylated alcohols

Secondary alcohol variation products: 1,3-diphenylpropan-1-ol (2a)<sup>5</sup>: Colourless oil (203 mg, 87% isolated yield);<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>): \(\delta = 7.36-7.34 (m, 4H), 7.31-7.25 (m, 3H), 7.21-7.17 (m, 3H), 4.68 (dd, \(J_{HH} = 8.0, 5.6 \text{ Hz, 1H}), 2.79-2.63 (m, 2H), 2.15-2.04 (m, 2H), 1.91 (bs, 1H); \)<sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>): \(\delta = 144.66, 141.88, 128.63, 128.55, 128.50, 127.75, 126.04, 125.98, 73.98, 40.56, 32.16.\)
1-(4-Chlorophenyl)-3-phenylpropan-1-ol (2b): Colourless oil (228 mg, 84% isolated yield); $^1$H NMR (400 MHz, CDCl$_3$): $\delta =$ 7.33-7.25 (m, 6H), 7.21-7.17 (m, 3H), 4.65 (dd, $J_{H,H} =$ 7.6, 5.2 Hz, 1H), 2.77-2.62 (m, 2H), 2.14-1.94 (m, 2H), 1.85 (bs, 1H); $^{13}$C NMR (100 MHz, CDCl$_3$): $\delta =$ 143.13, 141.60, 133.35, 128.75, 128.57, 128.53, 127.42, 126.09, 73.26, 40.60, 32.03.

1-(4-Bromophenyl)-3-phenylpropan-1-ol (2c): Colourless oil (272 mg, 85% isolated yield); $^1$H NMR (400 MHz, CDCl$_3$): $\delta =$ 7.48-7.46 (m, 2H), 7.31-7.28 (m, 2H), 7.22-7.17 (m, 5H), 4.62 (dd, $J_{H,H} =$ 8.0, 5.6 Hz, 1H), 2.76-2.61 (m, 2H), 2.20 (bs, 1H), 2.13-1.93 (m, 2H); $^{13}$C NMR (100 MHz, CDCl$_3$): 143.58, 141.53, 131.63, 128.53, 128.49, 127.75, 126.05, 121.39, 73.19, 40.49, 31.95.

1-(4-Fluorophenyl)-3-phenylpropan-1-ol (2d): Light yellow oil (203 mg, 80% isolated yield); $^1$H NMR (500 MHz, CDCl$_3$): $\delta =$ 7.32-7.25 (m, 4H), 7.20-7.17 (m, 3H), 7.05-7.01 (m, 2H), 4.66 (t, $J_{H,H} =$ 6.5 Hz, 1H), 2.75-2.62 (m, 2H), 2.14-1.96 (m, 3H); $^{13}$C NMR (125 MHz, CDCl$_3$): $\delta =$ 163.29, 161.34, 141.68, 140.41, 140.39, 128.54, 128.52, 127.70, 127.64, 126.04, 115.49, 115.32, 73.30, 40.65, 32.10.

1-(4-Methylphenyl)-3-phenylpropan-1-ol (2e): Colourless oil (204 mg, 82% isolated yield); $^1$H NMR (400 MHz, CDCl$_3$): $\delta =$ 7.30-7.16 (m, 9H), 4.65 (dd, $J_{H,H} =$ 7.6, 5.6 Hz, 1H), 2.78-2.62 (m, 2H), 2.35 (s, 3H), 2.18-1.97 (m, 2H), 1.82 (bs, 1H); $^{13}$C NMR (100 MHz, CDCl$_3$): $\delta =$ 141.97, 141.69, 137.45, 128.31, 128.56, 128.49, 126.02, 125.94, 73.85, 40.47, 32.21, 21.24.

1-(4-Methoxyphenyl)-3-phenylpropan-1-ol (2f): Pale yellow oil (203 mg, 76% isolated yield); $^1$H NMR (400 MHz, CDCl$_3$): $\delta =$ 7.29-7.16 (m, 7H), 6.90-6.87 (m, 2H), 4.63 (dd, $J_{H,H} =$ 7.6, 6.0 Hz, 1H), 3.81 (s, 3H), 2.76-2.60 (m, 2H), 2.18-1.97 (m, 2H), 1.79 (bs, 1H); $^{13}$C NMR (100 MHz, CDCl$_3$): $\delta =$ 159.24, 141.95, 136.81, 128.57, 128.50, 127.34, 125.96, 114.01, 73.63, 55.43, 40.47, 32.26.

2-Benzyl-1,2,3,4-tetrahydronaphalen-1-ol (2g): White solid (157 mg, 60% isolated yield); $^1$H NMR (400 MHz, CDCl$_3$): $\delta =$ 7.52-7.49 (m, 1H), 7.32-7.29 (m, 2H), 7.24-7.19 (m, 5H), 7.10-7.08 (m, 1H), 4.50 (d, $J_{H,H} =$ 8.0 Hz, 1H), 3.07 (dd, $J_{H,H} =$ 12, 4 Hz, 1H), 2.77-2.74 (m, 2H), 2.51 (dd, $J_{H,H} =$ 12, 4 Hz, 1H), 2.10-1.94 (m, 2H), 1.70 (bs, 1H), 1.55-1.45 (m, 1H); $^{13}$C NMR (100 MHz, CDCl$_3$): $\delta =$ 140.48, 138.69, 136.93, 130.50, 129.41, 128.86, 128.49, 127.57, 126.42, 126.15, 73.14, 44.13, 38.49, 27.75, 24.66.

1-(Naphthalen-2-yl)-3-phenylpropan-1-ol (2h): White solid (237 mg, 82% isolated yield); $^1$H NMR (400 MHz, CDCl$_3$): $\delta =$ 7.85-7.82 (m, 3H), 7.79 (s, 1H), 7.50-7.46 (m, 3H), 7.30-7.27 (m, 2H), 7.21-7.17 (m, 3H), 4.86 (dd, $J_{H,H} =$ 7.6, 5.6 Hz, 1H), 2.82-2.66 (m, 2H), 2.27-2.12 (m, 2H), 1.89 (bs, 1H); $^{13}$C NMR (100 MHz, CDCl$_3$): $\delta =$ 142.00, 141.86, 133.40, 133.14, 128.59, 128.54, 128.52, 128.05, 127.82, 126.31, 126.01, 124.81, 124.17, 74.11, 40.45, 32.18.

1,5-Diphenylpentan-3-ol (2i): White solid (132 mg, 50% isolated yield); $^1$H NMR (500 MHz, CDCl$_3$): $\delta =$ 7.30-7.19 (m, 10H), 3.67 (m, 1H), 2.80-2.65 (m, 4H), 1.87-1.75 (m, 4H), 1.54 (s, 1H); $^{13}$C NMR (125 MHz, CDCl$_3$): $\delta =$ 142.17, 128.58, 128.54, 126.00, 71.00, 39.37, 32.20.

1-cyclopropyl-3-phenylpropan-1-ol (2j): Colourless oil (178 mg, 92% isolated yield); $^1$H NMR (400 MHz, CDCl$_3$): $\delta =$ 7.32-7.18 (m, 5H), 2.94-2.71 (m, 3H), 2.14 (bs, 1H), 1.98-1.92 (m, 2H).
$^{13}$C NMR (100 MHz, CDCl$_3$): $\delta = 142.28, 128.43, 128.38, 125.70, 75.96, 38.75, 32.03, 17.93, 2.70, 2.60.$

4-Methyl-1-phenylpentan-3-ol (2k)$^9$: Colourless oil (168 mg, 86% isolated yield); $^1$H NMR (400 MHz, CDCl$_3$): $\delta = 7.30-7.27$ (m, 2H), 7.22-7.16 (m, 3H), 3.40 (sept, $J_{H,H} = 3.6$ Hz, 1H), 2.88-2.81 (m, 1H), 2.69-2.61 (m, 1H), 1.84-1.64 (m, 3H), 0.92 (dd, $J_{H,H} = 6.8$, 1.2 Hz, 6H); $^{13}$C NMR (100 MHz, CDCl$_3$): $\delta = 142.47, 128.56, 128.51, 125.91, 76.26, 36.08, 33.80, 32.60, 18.90, 17.29.$

**Primary alcohol variation products: 3-(4-Chlorophenyl)-1-phenylpropan-1-ol (3a)$^{10}$:** White solid (222 mg, 82% isolated yield); $^1$H NMR (400 MHz, CDCl$_3$): $\delta = 7.38-7.22$ (m, 7H), 7.13-7.09 (m, 2H) 4.66 (t, $J_{H,H} = 5.9$ Hz, 1H), 2.75-2.60 (m, 2H), 2.14-1.94 (m, 2H), 1.83 (d, $J_{H,H} = 2.4$ Hz, 1H); $^{13}$C NMR (100 MHz, CDCl$_3$): $\delta = 144.51, 140.33, 131.66, 129.92, 128.70, 128.58, 127.88, 126.00, 73.83, 40.43, 31.50.$

3-(4-Bromophenyl)-1-phenylpropan-1-ol (3b)$^{11}$: Colourless oil (266 mg, 83% isolated yield); $^1$H NMR (400 MHz, CDCl$_3$): $\delta = 7.40-7.25$ (m, 7H), 7.05 (d, $J_{H,H} = 8.0$ Hz, 2H), 4.65 (dd, $J_{H,H} = 8.0$, 5.5 Hz, 1H), 2.72-2.59 (m, 2H), 2.13-1.96 (m, 3H); $^{13}$C NMR (100 MHz, CDCl$_3$): $\delta = 144.49, 140.85, 131.52, 130.32, 128.67, 127.85, 125.99, 119.67, 73.78, 40.32, 31.53.$

3-(4-Fluorophenyl)-1-phenylpropan-1-ol (3c)$^{12}$: Colourless oil (208 mg, 82% isolated yield); $^1$H NMR (400 MHz, CDCl$_3$): $\delta = 7.37-7.26$ (m, 5H), 7.15-7.11 (m, 2H), 6.97-6.93 (m, 2H) 4.66 (t, $J_{H,H} = 6.4$ Hz, 1H), 2.75-2.60 (m, 2H), 2.14-1.94 (m, 2H), 1.87 (bs, 1H); $^{13}$C NMR (100 MHz, CDCl$_3$): $\delta = 162.58, 160.16, 144.58, 137.48, 129.89, 129.82, 128.67, 127.83, 126.01, 115.31, 115.10, 73.86, 40.68, 31.33.$

3-(4-Methylphenyl)-1-phenylpropan-1-ol (3d)$^{13}$: White solid (214 mg, 86% isolated yield); $^1$H NMR (400 MHz, CDCl$_3$): $\delta = 7.35-7.33$ (m, 4H), 7.31-7.26 (m, 1H), 7.08 (s, 4H), 4.68 (dd, $J_{H,H} = 7.6$, 5.2 Hz, 1H), 2.74-2.59 (m, 2H), 2.31 (s, 3H), 2.16-1.96 (m, 2H), 1.75 (bs, 1H); $^{13}$C NMR (100 MHz, CDCl$_3$): $\delta = 144.70, 138.75, 135.39, 129.18, 128.60, 128.42, 127.71, 126.04, 73.98, 40.65, 31.69, 21.11.$

3-(4-Methoxyphenyl)-1-phenylpropan-1-ol (3e)$^{13}$: White solid (218 mg, 82% isolated yield); $^1$H NMR (400 MHz, CDCl$_3$): $\delta = 7.34-7.25$ (m, 5H), 7.10 (d, $J_{H,H} = 8.4$ Hz, 2H), 6.82 (d, $J_{H,H} = 8.4$ Hz, 2H), 4.66 (dd, $J_{H,H} = 7.6$, 5.2 Hz, 1H), 3.77 (s, 3H), 2.71-2.57 (m, 2H), 1.24-1.94 (m, 2H), 1.76 (bs, 1H); $^{13}$C NMR (100 MHz, CDCl$_3$): $\delta = 157.83, 144.72, 133.95, 129.40, 128.57, 127.66, 126.02, 113.89, 73.88, 55.32, 40.77, 31.20.$

3-(2-Chlorophenyl)-1-phenylpropan-1-ol (3f)$^{14}$: Colourless dense oil (211 mg, 78% isolated yield); $^1$H NMR (400 MHz, CDCl$_3$): $\delta = 7.37-7.11$ (m, 9H), 4.72 (dd, $J_{H,H} = 7.8$, 5.3 Hz, 1H), 2.93-2.87 (m, 1H), 2.80-2.74 (m, 1H), 2.13-2.02 (m, 2H), 1.94 (bs, 1H); $^{13}$C NMR (100 MHz, CDCl$_3$): $\delta = 144.50, 139.53, 134.06, 130.55, 129.63, 128.66, 127.82, 127.52, 126.92, 126.03, 74.12, 38.84, 30.19.$

3-(2-Methoxyphenyl)-1-phenylpropan-1-ol (3g)$^{15}$: Pale yellow oil (213 mg, 80% isolated yield); $^1$H NMR (400 MHz, CDCl$_3$): $\delta = 7.37-7.32$ (m, 4H), 7.28-7.25 (m, 1H), 7.22-7.14 (m, 2H), 6.92-6.85 (m, 2H), 4.63 (dd, $J_{H,H} = 8.4$, 4.8 Hz, 1H), 3.83 (s, 3H), 2.78-2.74 (m, 2H), 2.29 (bs, 1H),
2.12-1.95 (m, 2H); $^{13}$C NMR (100 MHz, CDCl$_3$): $\delta = 157.45, 144.73, 130.17, 130.08, 128.45, 127.45, 127.31, 126.00, 120.78, 73.63, 55.42, 39.47, 26.53.

3-(3-Chlorophenyl)-1-phenylpropan-1-ol (3h)$_{16}$: Colourless dense liquid (222 mg, 82% isolated yield); $^1$H NMR (400 MHz, CDCl$_3$): $\delta = 7.37-7.27$ (m, 5H), 7.22-7.14 (m, 3H), 7.07-7.05 (m, 1H). $\delta$ = 6.87 (dd, $J_{H,H} = 8, 5.6$ Hz, 1H), 2.77-2.61 (m, 2H), 2.16-1.95 (m, 2H), 1.83 (bs, 1H); $^{13}$C NMR (100 MHz, CDCl$_3$): $\delta = 144.49, 143.99, 134.25, 129.74, 128.71, 127.90, 126.77, 126.18, 126.00, 73.84, 40.30, 31.85.

3-(Naphthalen-1-yl)-1-phenylpropan-1-ol (3i)$_{17}$: Pale yellow oil (216 mg, 75% isolated yield); $^1$H NMR (500 MHz, CDCl$_3$): $\delta = 8.00-7.98$ (m, 1H), 7.86-7.85 (m, 1H), 7.72 (d, $J_{H,H} = 8.0$ Hz, 1H), 7.51-7.46 (m, 2H), 7.42-7.34 (m, 6H), 7.32-7.28 (m, 1H), 4.81-4.78 (m, 1H), 3.28-3.22 (m, 1H), 3.14-3.08 (m, 1H), 2.30-2.13 (m, 2H), 2.04 (d, $J_{H,H} = 3.5$ Hz, 1H); $^{13}$C NMR (125 MHz, CDCl$_3$): $\delta = 144.65, 138.13, 134.04, 131.97, 128.88, 128.65, 127.80, 126.80, 126.07, 125.91, 125.66, 125.57, 123.90, 74.30, 39.95, 29.23.

3-Cyclohexyl-1-phenylpropan-1-ol (3j)$_{15}$: Colourless dense liquid (211 mg, 88% isolated yield); $^1$H NMR (400 MHz, CDCl$_3$): $\delta = 7.36-7.29$ (m, 4H), 7.28-7.26 (m, 1H), 1.82-1.74 (m, 2H), 1.55 (bs, 1H), 1.36-1.09 (m, 10H), 0.89-0.81 (m, 2H); $^{13}$C NMR (100 MHz, CDCl$_3$): $\delta = 145.09, 128.57, 126.05, 75.21, 37.79, 36.61, 33.62, 33.50, 33.42, 26.79, 26.50.

1-Phenylhex-1-ol (3k)$_{5}$: Colourless oil (160 mg, 82% isolated yield); $^1$H NMR (500 MHz, CDCl$_3$): $\delta = 7.37-7.33$ (m, 4H), 7.30-7.27 (m, 1H), 1.80-1.68 (m, 2H), 1.46-1.30 (m, 6H), 0.90 (t, $J_{H,H} = 7.0$ Hz, 3H); $^{13}$C NMR (125 MHz, CDCl$_3$): $\delta = 145.08, 128.46, 127.49, 126.00, 74.72, 39.15, 31.82, 25.59, 22.66, 14.11

1-Phenyloctan-1-ol (3l)$_{16}$: Colourless oil (163 mg, 72% isolated yield); $^1$H NMR (400 MHz, CDCl$_3$): $\delta = 7.36-7.31$ (m, 4H), 7.30-7.26 (m, 1H), 1.78-1.66 (m, 2H), 1.32-1.22 (m, 10H), 0.88 (t, $J_{H,H} = 7.2$ Hz, 3H); $^{13}$C NMR (100 MHz, CDCl$_3$): $\delta = 145.10, 128.49, 127.52, 126.01, 74.76, 39.22, 31.92, 29.61, 29.48, 29.32, 25.92, 22.74, 14.17

$\alpha$-Alkylation of arylacetanilides: 2,3-Diphenylpropanenitrile (4a)$_{17}$: Colourless solid (98 mg, 94% isolated yield); $^1$H NMR (400 MHz, CDCl$_3$): $\delta = 7.38-7.35$ (m, 8H), 7.15-7.13 (m, 2H), 4.0 (dd, $J_{H,H} = 8.3, 6.5$ Hz, 1H), 3.22-3.10 (m, 2H); $^{13}$C NMR (100 MHz, CDCl$_3$): $\delta = 136.36, 135.29, 129.32, 129.12, 128.31, 127.59, 127.49, 120.49, 42.30, 39.91; GC-MS: [M$^+$] = 207.1

3-Phenyl-2-p-tolylpropanenitrile (4b)$_{18}$: Colourless solid (105 mg, 95% isolated yield); $^1$H NMR (400 MHz, CDCl$_3$): $\delta = 7.31-7.11$ (m, 10H), 3.95 (dd, $J_{H,H} = 8.4, 6.6$ Hz, 1H), 3.19-3.07 (m, 2H), 2.34 (s, 3H); $^{13}$C NMR (100 MHz, CDCl$_3$): $\delta = 138.10, 136.50, 132.30, 129.75, 129.29, 128.69, 127.41, 120.63, 42.33, 39.55, 29.79, 21.18; GC-MS: [M$^+$] = 221.1

2-(4-Methoxyphenyl)-3-phenylpropanenitrile (4c)$_{18}$: Colourless solid (111 mg, 94% isolated yield); $^1$H NMR (400 MHz, CDCl$_3$): $\delta = 7.29-7.25$ (m, 3H), 7.17-7.11(m, 4H), 6.86 (d, $J_{H,H} = 8.8$ Hz, 2H), 3.94 (dd, $J_{H,H} = 8.2, 6.6$ Hz, 1H), 3.80 (s, 3H), 3.19-3.06 (m, 2H); $^{13}$C NMR (100 MHz, CDCl$_3$): $\delta = 159.48, 136.47, 129.34, 128.72, 128.69, 127.41, 127.28, 120.74, 114.43, 55.42, 42.36, 39.06; GC-MS: [M$^+$] = 237.1

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2-(4-Bromophenyl)-3-phenylpropanenitrile (4d): Pale Yellow Solid (130 mg, 91% isolated yield); $^1$H NMR (400 MHz, CDCl$_3$): $\delta$ = 7.48-7.45 (m, 2H), 7.31-7.25 (m, 3H), 7.11-7.08 (m, 4H), 3.96 (dd, $J_{H,H} = 7.7, 6.9$ Hz, 1H), 3.20-3.07 (m, 2H). $^{13}$C NMR (100 MHz, CDCl$_3$): $\delta$ = 135.82, 134.19, 132.23, 129.23, 128.79, 127.63, 122.40, 119.95, 42.04, 39.31, 29.79; GC-MS: [M$^+$] = 285.0.

3-Phenyl-2-(pyridin-3-yl)propanenitrile (4e): Colourless solid (94 mg, 90% isolated yield); $^1$H NMR (400 MHz, CDCl$_3$): $\delta$ = 8.58 (d, $J_{H,H} = 2.7$ Hz, 1H), 8.46 (s, 1H), 7.58 (d, $J_{H,H} = 6.4$ Hz, 1H), 7.31-7.25 (m, 2H), 7.10 (m, 2H), 4.05 (t, $J_{H,H} = 5.8$ Hz, 1H), 3.25-3.12 (m, 2H). $^{13}$C NMR (125 MHz, CDCl$_3$): $\delta$ = 149.65, 148.83, 135.37, 131.17, 129.33, 128.90, 127.82, 123.84, 119.46, 41.89, 37.35, 29.78; GC-MS: [M$^+$] = 208.1.

2-Phenyl-3-p-tolylpropanenitrile (4f): Colourless liquid (104 mg, 94% isolated yield); $^1$H NMR (400 MHz, CDCl$_3$): $\delta$ = 7.38-7.32 (m, 3H), 7.28-7.25 (m, 2H), 7.10 (d, $J_{H,H} = 7.9$ Hz, 2H), 7.03 (d, $J_{H,H} = 8.0$ Hz, 2H), 3.97 (dd, $J_{H,H} = 8.3, 7.7$ Hz, 1H), 3.17-3.06 (m, 2H), 2.32 (s, 3H). $^{13}$C NMR (100 MHz, CDCl$_3$): $\delta$ = 137.10, 135.42, 133.32, 129.40, 129.17, 129.09, 128.25, 127.58, 120.56, 41.93, 40.06, 21.20; GC-MS: [M$^+$] = 221.1.

3-(2-Methoxypyphenyl)-2-phenylpropanenitrile (4g): Colourless liquid (107 mg, 90% isolated yield); $^1$H NMR (400 MHz, CDCl$_3$): $\delta$ = 7.37-7.23 (m, 6H), 7.07 (dd, $J_{H,H} = 7.7, 1.7$ Hz, 1H), 6.89-6.85 (m, 2H), 4.16 (dd, $J_{H,H} = 9.0, 6.4$ Hz, 1H), 3.84 (s, 3H), 3.21-3.09 (m, 2H). $^{13}$C NMR (100 MHz, CDCl$_3$): $\delta$ = 157.49, 136.12, 131.26, 128.97, 128.93, 128.04, 127.45, 124.99, 120.92, 120.69, 110.37, 55.37, 37.86, 37.73; GC-MS: [M$^+$] = 237.1.

3-(Benzod[d][1,3]dioxol-5-yl)-2-phenylpropanenitrile (4h): Colourless liquid (114 mg, 91% isolated yield); $^1$H NMR (400 MHz, CDCl$_3$): $\delta$ = 7.38-7.24 (m, 5H), 6.71 (d, $J_{H,H} = 7.9$ Hz, 1H), 6.58 (m, 2H), 5.93 (s, 2H), 3.94 (dd, $J_{H,H} = 8.2, 6.6$ Hz, 1H), 3.12-3.01 (m, 2H). $^{13}$C NMR (100 MHz, CDCl$_3$): $\delta$ = 147.82, 146.96, 135.19, 130.01, 129.13, 128.32, 127.55, 122.58, 120.42, 109.56, 108.45, 101.15, 42.06, 40.15; GC-MS: [M$^+$] = 250.8.

3-(Naphthalen-1-yl)-2-phenylpropanenitrile (4i): White solid (118 mg, 92% isolated yield); $^1$H NMR (400 MHz, CDCl$_3$): $\delta$ = 7.94-7.88 (m, 2H), 7.79 (d, $J_{H,H} = 8.2$ Hz, 1H), 7.57-7.49 (m, 2H), 7.41-7.29 (m, 7H), 4.16 (dd, $J_{H,H} = 8.6, 6.7$ Hz, 1H), 3.67-3.57 (m, 2H). $^{13}$C NMR (100 MHz, CDCl$_3$): 135.69, 134.04, 134.28, 131.36, 129.35, 129.22, 128.42, 128.39, 128.22, 127.44, 126.64, 125.88, 125.57, 122.67, 120.56, 39.70, 38.91, 29.79; GC-MS: [M$^+$] = 257.1.

2-Phenyhexanenitrile (4j): Colourless liquid (78 mg, 90% isolated yield); $^1$H NMR (400 MHz, CDCl$_3$): $\delta$ = 7.39-7.28 (m, 5H), 3.76 (dd, $J_{H,H} = 8.5, 6.4$ Hz, 1H), 1.97-1.87 (m, 2H), 1.54-1.31 (m, 4H), 0.91 (t, $J_{H,H} = 7.3$ Hz, 3H). $^{13}$C NMR (100 MHz, CDCl$_3$): 136.10, 129.03, 129.97, 127.23, 120.93, 37.38, 35.62, 29.12, 22.08, 13.75; GC-MS: [M$^+$] = 173.1.

3-Phenylquinolin-2-amine (4k): Off-white solid (90 mg, 82% isolated yield); $^1$H NMR (500 MHz, CDCl$_3$): $\delta$ = 7.78 (s, 1H), 7.69 (d, $J_{H,H} = 8.4$ Hz, 1H), 7.64 (dd, $J_{H,H} = 8.0, 1.2$ Hz, 1H), 7.58-7.54 (m, 1H), 7.53-7.48 (m, 4H), 7.43 (tt, $J_{H,H} = 7.0, 1.7$ Hz, 1H), 7.28-7.25 (m, 1H), 5.01 (bs, 2H). $^{13}$C NMR (100 MHz, CDCl$_3$): 155.26, 147.21, 137.66, 137.35, 129.76, 125.25, 129.00, 128.33, 127.60, 125.67, 125.12, 124.30, 122.89; ESI-MS: m/z 221.1077 [(M+H)$^+$, predicted: 221.1079].
\textbf{\(\alpha\)-Methylation of aryl acetonitrile: 2-Phenylpropanenitrile (5a)\textsuperscript{22}:\) Colourless liquid (69 mg, 88\% isolated yield); \(^1\)H NMR (400 MHz, CDCl\(_3\)): \(\delta = 7.40-7.30\) (m, 5H), 3.89 (q, \(J_{\text{H,H}} = 7.2\) Hz, 1H), 1.64 (d, \(J_{\text{H,H}} = 7.2\) Hz, 3H); \(^{13}\)C NMR (100 MHz, CDCl\(_3\)): \(\delta = 137.20, 129.28, 128.18, 126.83, 121.71, 31.39, 21.61\); GC-MS: [M\(^+\)] = 131.1

\textbf{2-\(P\)-tolylpropanenitrile (5b)\textsuperscript{22}:\) Colourless liquid (72 mg, 83\% isolated yield); \(^1\)H NMR (500 MHz, CDCl\(_3\)): \(\delta = 7.26-7.18\) (m, 4H), 3.86 (q, \(J_{\text{H,H}} = 7.0\) Hz, 1H), 2.35 (s, 3H), 1.62 (d, \(J_{\text{H,H}} = 7.2\) Hz, 3H); \(^{13}\)C NMR (125 MHz, CDCl\(_3\)): \(\delta = 137.96, 134.19, 129.89, 126.69, 121.90, 30.98, 21.62, 21.16\); GC-MS: [M\(^+\)] = 145.1

\textbf{2-(4-Methoxyphenyl)propanenitrile (5c)\textsuperscript{22}:\) Colourless liquid (70 mg, 72\% isolated yield); \(^1\)H NMR (500 MHz, CDCl\(_3\)): \(\delta = 7.26\) (d, \(J_{\text{H,H}} = 9.0\) Hz, 2H), 6.90 (d, \(J_{\text{H,H}} = 9.0\) Hz, 2H), 3.85 (q, \(J_{\text{H,H}} = 7.5\) Hz, 1H), 3.80 (s, 3H), 1.60 (d, \(J_{\text{H,H}} = 7.5\) Hz, 3H); \(^{13}\)C NMR (125 MHz, CDCl\(_3\)): \(\delta = 159.37, 129.17, 127.94, 121.99, 114.56, 55.45, 30.55, 21.63\); GC-MS: [M\(^+\)] = 161.1

\textbf{2-(4-Bromophenyl)propanenitrile (5d)\textsuperscript{22}:\) Colourless liquid (81 mg, 64\% isolated yield); \(^1\)H NMR (500 MHz, CDCl\(_3\)): \(\delta = 7.51\) (d, \(J_{\text{H,H}} = 8.5\) Hz, 2H), 7.26-7.22 (m, 2H), 3.86 (q, \(J_{\text{H,H}} = 7.5\) Hz, 1H), 1.62 (d, \(J_{\text{H,H}} = 7.5\) Hz, 3H); \(^{13}\)C NMR (125 MHz, CDCl\(_3\)): \(\delta = 136.17, 132.43, 128.55, 122.23, 121.15, 30.93, 21.45\); GC-MS: [M\(^+\)] = 209.0

\textbf{2-(Pyridin-3-yl)propanenitrile (5e)\textsuperscript{25}:\) Colourless liquid (60 mg, 76\% isolated yield); \(^1\)H NMR (500 MHz, CDCl\(_3\)): \(\delta = 8.60-8.59\) (m, 1H), 7.74 (dt, \(J_{\text{H,H}} = 8.0, 1.5\) Hz, 1H), 7.35 (q, \(J_{\text{H,H}} = 8.0\) Hz, 1H), 3.95 (q, \(J_{\text{H,H}} = 7.0\) Hz, 1H), 1.67 (d, \(J_{\text{H,H}} = 7.5\) Hz, 3H); \(^{13}\)C NMR (125 MHz, CDCl\(_3\)): \(\delta = 149.69, 148.34, 134.43, 133.00, 124.06, 120.65, 29.15, 21.37\); GC-MS: [M\(^+\)] = 132.0

\textbf{Monoalkylation of acetonitrile: 3-Phenylpropanenitrile (6a)\textsuperscript{26}:\) Yellow oil (59 mg, 90\% isolated yield); \(^1\)H NMR (400 MHz, CDCl\(_3\)): \(\delta = 7.36-7.22\) (m, 5H), 2.95 (t, \(J_{\text{H,H}} = 7.44\) Hz, 2H), 2.60 (t, \(J_{\text{H,H}} = 7.44\) Hz, 2H), 2.32 (s, 3H); \(^{13}\)C NMR (100 MHz, CDCl\(_3\)): \(\delta = 138.18, 128.97, 128.39, 127.33, 119.30, 31.64, 19.45\). GC-MS: [M\(^+\)] = 131.1

\textbf{3-P-tolylpropanenitrile (6b)\textsuperscript{26}:\) Colourless oil (55 mg, 76\% isolated yield); \(^1\)H NMR (400 MHz, CDCl\(_3\)): \(\delta = 7.15-7.09\) (m, 4H), 2.91 (t, \(J_{\text{H,H}} = 7.44\) Hz, 2H), 2.58 (t, \(J_{\text{H,H}} = 7.44\) Hz, 2H), 2.32 (s, 3H); \(^{13}\)C NMR (100 MHz, CDCl\(_3\)): \(\delta = 141.44, 136.96, 135.08, 129.61, 128.21, 119.32, 31.26, 21.14, 19.60\). GC-MS: [M\(^+\)] = 145.0

\textbf{3-(4-Methoxyphenyl)propanenitrile (6c)\textsuperscript{26}:\) Yellow oil (64 mg, 80\% isolated yield); \(^1\)H NMR (400 MHz, CDCl\(_3\)): \(\delta = 7.14\) (d, \(J_{\text{H,H}} = 8.60\) Hz, 2H), 6.86 (d, \(J_{\text{H,H}} = 8.64\) Hz, 2H), 3.78 (s, 3H), 2.89 (t, \(J_{\text{H,H}} = 7.40\) Hz, 2H), 2.57 (t, \(J_{\text{H,H}} = 7.44\) Hz, 2H); \(^{13}\)C NMR (100 MHz, CDCl\(_3\)): \(\delta = 158.82, 130.20, 129.41, 119.34, 114.32, 55.37, 30.85, 19.80\). GC-MS: [M\(^+\)] = 161.1

\textbf{3-(4-Fluorophenyl)propanenitrile (6d)\textsuperscript{26}:\) Colourless oil (52 mg, 70\% isolated yield); \(^1\)H NMR (400 MHz, CDCl\(_3\)): \(\delta = 7.21-7.17\) (m, 2H), 7.04-7.00 (m, 2H), 2.92 (t, \(J_{\text{H,H}} = 7.36\) Hz, 2H), 2.59 (t, \(J_{\text{H,H}} = 7.48\) Hz, 2H); \(^{13}\)C NMR (100 MHz, CDCl\(_3\)): \(\delta = 163.33, 160.88, 133.78, 129.99, 129.91, 119.00, 115.96, 115.75, 30.87, 19.68\). GC-MS: [M\(^+\)] = 149.0

\textbf{3-(2-Methoxyphenyl)propanenitrile (6e)\textsuperscript{26}:\) Yellow oil (51 mg, 64\% isolated yield); \(^1\)H NMR (400 MHz, CDCl\(_3\)): \(\delta = 7.27-7.22\) (m, 1H), 7.16 (dd, \(J_{\text{H,H}} = 7.34, 1.36\) Hz 1H), 6.93-6.85 (m, 2H),
3.83 (s, 3H), 2.95 (t, J\textsubscript{H,H} = 7.44 Hz, 2H), 2.61 (t, J\textsubscript{H,H} = 7.44 Hz, 2H), $^1$H NMR (100 MHz, CDCl\textsubscript{3}): δ = 157.35, 130.29, 128.72, 126.38, 120.74, 119.77, 110.41, 56.26, 27.14, 17.54. GC-MS: [M+] =161.0

3-(Benzod[d][1,3]dioxol-5-yl)propanonitrile (6f)$^{27}$: Colourless oil (72 mg, 82% isolated yield); $^1$H NMR (400 MHz, CDCl\textsubscript{3}): δ = 6.77-6.66 (m, 3H), 5.94 (s, 2H), 2.86 (t, J\textsubscript{H,H} = 7.32 Hz, 2H), 2.56 (t, J\textsubscript{H,H} = 7.40 Hz, 2H). $^{13}$C NMR (100 MHz, CDCl\textsubscript{3}): δ = 148.01, 146.81, 131.80, 121.46, 119.16, 108.71, 108.63, 101.16, 31.41, 19.81. GC-MS: [M+] =175.2

3-(Naphthalen-1-yl)propanonitrile (6g)$^{28}$: Yellow oil (71 mg, 78% isolated yield); $^1$H NMR (400 MHz, CDCl\textsubscript{3}): δ = 7.93-7.87 (m, 2H), 7.79 (d, J\textsubscript{H,H} = 7.96 Hz, 1H), 7.58-7.49 (m, 2H), 7.45-7.38 (m, 2H), 3.44 (t, J\textsubscript{H,H} = 7.64 Hz, 2H), 2.76 (t, J\textsubscript{H,H} = 7.68 Hz, 2H). $^{13}$C NMR (100 MHz, CDCl\textsubscript{3}): δ = 134.03, 133.93, 129.28, 128.24, 126.66, 125.99, 125.70, 122.68, 119.97, 28.93, 18.60. GC-MS: [M+] =136.1

3-Cyclohexylpropanonitrile (6h)$^{29}$: Yellow oil (45 mg, 66% isolated yield); $^1$H NMR (500 MHz, CDCl\textsubscript{3}): δ = 2.33 (t, J\textsubscript{H,H} = 7.40 Hz, 2H), 1.72-1.64 (m, 5H), 1.56-1.52 (m, 2H), 1.39-1.34 (m, 1H), 1.28-1.13 (m, 3H), 0.93-0.87 (m, 2H). $^{13}$C NMR (125 MHz, CDCl\textsubscript{3}): δ = 120.14, 36.69, 32.66, 32.61, 26.40, 26.04, 14.74. GC-MS: [M+] =136.1

Octanenitrile (6i)$^{30}$: Yellow oil (37 mg, 60% isolated yield); $^1$H NMR (500 MHz, CDCl\textsubscript{3}): δ = 2.32 (t, J\textsubscript{H,H} = 7.20 Hz, 2H), 1.64 (q, J\textsubscript{H,H} = 7.44 Hz, 1H), 1.46-1.39 (m, 2H), 1.34-1.24 (m, 8H), 0.87 (t, J\textsubscript{H,H} = 7.0 Hz, 3H). $^{13}$C NMR (100 MHz, CDCl\textsubscript{3}): δ = 119.97, 31.56, 29.73, 28.70, 28.51, 25.44, 22.60, 17.21, 14.11. GC-MS: [M+] =124.1

N-methylation of amines: N-methylaniline (7a): Yellow oil (81 mg, 95% isolated yield); $^1$H NMR (400 MHz, CDCl\textsubscript{3}): δ = 7.20 (d, J\textsubscript{H,H} = 7.4 Hz, 2H), 6.72 (t, J\textsubscript{H,H} = 7.3 Hz, 1H), 6.62 (t, J\textsubscript{H,H} = 7.6 Hz, 2H), 3.46 (bs, 1H), 2.84 (s, 3H). $^{13}$C NMR (100 MHz, CDCl\textsubscript{3}): δ = 149.37, 129.32, 117.40, 112.56, 30.87. GC-MS: [M+] =107.0

N,4-dimethylaniline (7b)$^{31}$: Yellow oil (91 mg, 94% isolated yield); $^1$H NMR (500 MHz, CDCl\textsubscript{3}): δ = 6.96 (d, J\textsubscript{H,H} = 8.25 Hz, 2H), 6.52 (d, J\textsubscript{H,H} = 8.4 Hz, 2H), 2.92 (bs, 1H), 2.76 (s, 3H), 2.20 (s, 3H). $^{13}$C NMR (125 MHz, CDCl\textsubscript{3}): δ = 147.16, 129.68, 126.73, 112.88, 31.14, 20.30. GC-MS: [M+] =121.0

4-Methoxy-N-methylaniline (7c)$^{31}$: Yellow oil (103 mg, 94% isolated yield); $^1$H NMR (500 MHz, CDCl\textsubscript{3}): δ = 6.79 (d, J\textsubscript{H,H} = 8.9 Hz, 2H), 6.59 (d, J\textsubscript{H,H} = 8.9 Hz, 2H), 3.75 (s, 3H), 2.81 (s, 3H). $^{13}$C NMR (125 MHz, CDCl\textsubscript{3}): δ = 152.36, 143.70, 115.09, 113.91, 56.02, 31.85. GC-MS: [M+] =137.0

4-Bromo-N-methylaniline (7d)$^{32}$: Yellow oil (137 mg, 92% isolated yield); $^1$H NMR (500 MHz, CDCl\textsubscript{3}): δ = 7.26-7.24 (m, 2H), 6.48-6.46 (m, 2H), 3.72 (bs, 1H), 2.80 (s, 3H). $^{13}$C NMR (125 MHz, CDCl\textsubscript{3}): δ = 148.41, 131.99, 114.06, 108.92, 30.83. GC-MS: [M+] =184.9

3-Chloro-N-methylaniline (7e)$^{33}$: Yellow oil (105 mg, 93% isolated yield); $^1$H NMR (500 MHz, CDCl\textsubscript{3}): δ = 7.01 (t, J\textsubscript{H,H} = 7.9 Hz, 1H), 6.59 (d, J\textsubscript{H,H} = 8.0 Hz, 1H), 6.51 (t, J\textsubscript{H,H} = 1.9 Hz, 1H),
6.42 (dd, J_{H,H} = 8.0, 1.8 Hz, 1H), 2.73 (s, 3H). $^{13}$C NMR (125 MHz, CDCl$_3$): $\delta$ = 150.55, 134.94, 130.08, 116.92, 111.94, 110.87, 30.34. GC-MS: [M$^+$] = 141.0

**N-methylnaphthalen-1-amine (7f)**$^{34}$: Colourless oil (91 mg, 72% isolated yield); $^1$H NMR (500 MHz, CDCl$_3$): $\delta$ = 7.83 (d, J_{H,H} = 8.1 Hz, 1H), 7.79 (d, J_{H,H} = 8.2 Hz, 1H), 7.50-7.40 (m, 3H), 7.29 (d, J_{H,H} = 8.0 Hz, 1H), 6.63 (d, J_{H,H} = 7.5 Hz, 1H), 4.38 (bs, 1H), 3.03 (s, 3H). $^{13}$C NMR (125 MHz, CDCl$_3$): $\delta$ = 144.61, 134.34, 128.75, 126.78, 125.81, 124.78, 123.57, 119.91, 117.43, 103.92, 31.12. GC-MS: [M$^+$] = 157.0

**N-methylpyridin-3-amine (7g)**$^{35}$: Pale yellow oil (78 mg, 90% isolated yield); $^1$H NMR (500 MHz, CDCl$_3$): $\delta$ = 7.96 (d, J_{H,H} = 2.8 Hz, 1H), 7.89 (dd, J_{H,H} = 4.6, 1.0 Hz, 1H), 7.07 (q, J_{H,H} = 4.5 Hz, 1H), 6.85 (dq, J_{H,H} = 8.0, 1.0 Hz, 1H), 2.81 (s, 3H). $^{13}$C NMR (125 MHz, CDCl$_3$): $\delta$ = 145.35, 138.33, 135.49, 123.90, 118.35, 30.30. GC-MS: [M$^+$] = 108.0

**N,N-dimethylhexan-1-amine (7h)**$^{36}$: Pale yellow oil (57 mg, 55% isolated yield); $^1$H NMR (400 MHz, CDCl$_3$): $\delta$ = 2.21-2.17 (m, 8H), 1.44-1.40 (m, 2H), 1.27-1.23 (m, 6H), 0.85 (t, J_{H,H} = 6.7 Hz, 3H). $^{13}$C NMR (100 MHz, CDCl$_3$): $\delta$ = 60.10, 45.62, 31.97, 27.87, 27.32, 22.74, 14.17. GC-MS: [M$^+$] = 129.1
$^1$H and $^{13}$C NMR Spectra of isolated products: $^1$H and $^{13}$C NMR of all the isolated compounds are given below.
2d

$\begin{align*}
\text{H} & \quad 7.32 \\
\text{H} & \quad 7.31 \\
\text{H} & \quad 7.28 \\
\text{H} & \quad 7.27 \\
\text{H} & \quad 7.20 \\
\text{H} & \quad 7.19 \\
\text{H} & \quad 7.17 \\
\text{H} & \quad 7.03 \\
\text{F} & \quad 4.07 \\
\text{F} & \quad 4.04 \\
\end{align*}$
2g

OH

\[
\begin{align*}
    &7.52 \quad 7.49 \quad 7.42 \quad 7.39 \quad 7.25 \quad 7.24 \quad 7.23 \quad 7.21 \quad 7.20 \quad 7.19 \quad 7.17 \quad 7.08 \\
    &3.10 \quad 3.05 \quad 2.77 \quad 2.74 \quad 2.74 \quad 2.74 \quad 2.74 \quad 2.74 \quad 2.74 \quad 2.74 \quad 2.74 \quad 2.74 \\
    &1.06 \quad 1.06 \quad 1.06 \quad 1.06 \quad 1.06 \quad 1.06 \quad 1.06 \quad 1.06 \quad 1.06 \quad 1.06 \quad 1.06 \quad 1.06 \\
    &1.23 \quad 1.23 \quad 1.23 \quad 1.23 \quad 1.23 \quad 1.23 \quad 1.23 \quad 1.23 \quad 1.23 \quad 1.23 \quad 1.23 \quad 1.23 \\
\end{align*}
\]

\[140.48 \quad 138.69 \quad 129.41 \quad 128.62 \quad 77.43 \quad 76.63 \quad 73.14 \quad -41.13 \quad -30.48 \quad -27.68 \quad -27.68 \quad -27.68 \]

f1 (ppm) 190 170 150 130 110 90 70 50 30 10 0
$\text{6h}$

$\text{CN}$

$\text{6h}$

$\text{CN}$

$\text{6h}$
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