# ESI <br> Manganese catalyzed C-alkylation of methyl $N$-heteroarenes with primary alcohols 

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## 1. General information.

All the catalytic and stoichiometric reactions have been carried out under argon or nitrogen atmosphere using a standard Schlenk line and glove box technique in oven dried glassware. Reaction temperatures are disclosed as the temperature of the bath surrounding the vessel unless otherwise mentioned.

Chemicals. Commercially available chemicals were purchased from Avra Synthesis, TCI, Sigma Aldrich, and Alfa Aesar chemicals without further purifications. Dry and deoxygenated solvents were prepared according to standard procedures.

Analytical: ${ }^{1} \mathrm{H},{ }^{13} \mathrm{C}\{1 \mathrm{H}\},{ }^{19} \mathrm{~F}$ NMR spectra were collected using Bruker $\left({ }^{1} \mathrm{H}: 500 \mathrm{MHz},{ }^{13} \mathrm{C}\{1 \mathrm{H}\}: 126 \mathrm{MHz}\right)$ and JEOL ( ${ }^{1} \mathrm{H}: 400 \mathrm{MHz},{ }^{13} \mathrm{C}\{1 \mathrm{H}\}: 100 \mathrm{MHz}$ ) and were referenced to the resonances of the solvent used. Coupling constants (J) are reported in Hertz (Hz). Coupling patterns are indicated as: br (broad), s (singlet), d (doublet), t (triplet), dd (doublet of doublet), or m (multiplet). FT-IR spectra were recorded by PerkinElmer FT-IR Spectrometer. The elemental analyses were carried out with a Perkin-Elmer 240C elemental analyzer. Mass spectral analyses were done in Bruker micrOTOF-Q II Spectrometer.

Chromatography. Gas chromatography were recorded in the Thermofisher GC-MS spectrometer with an appropriate internal standard. For thin layer chromatography (TLC) analysis Merck pre-coated TLC plates (silica gel 60 F254 0.25 mm ) were used. Visualization was accomplished by UV light ( 254 nm ), $\mathrm{KMnO}_{4}$, and ceric ammonium molybdate strain.

## 2. Synthesis of manganese complexes.

### 2.1 Synthesis of manganese complex $\left.\left[\mathrm{Mn}(\mathrm{CO})_{2}(\mathrm{Br}) \mathrm{C}_{12} \mathrm{H}_{12} \mathrm{~N}_{4}\right](\mathrm{Mn}-1)\right]$.

To a solution of (E)-2-(2-(1-(pyridin-2-yl)ethylidene)hydrazineyl)pyridine ( $21 \mathrm{mg}, 0.1 \mathrm{mmol}, 1.0$ equiv.) in Toluene ( 2 mL ) was added $\mathrm{Mn}(\mathrm{CO})_{s} \mathrm{Br}\left(27.4 \mathrm{mg}, 1.0\right.$ equiv.) and the mixture was heated at $80^{\circ} \mathrm{C}$ for 2 h . Orange color precipitate formed. Solvent was removed from the reaction mixture and solid compound was washed with hexane ( $3 \times 2 \mathrm{~mL}$ ). Orange color solid compound was found as a mixture of cationic and neutral complex. The analytical data are consistent with those previously reported literature. ${ }^{1}$ Selected IR ( $\mathrm{KBr}, \mathrm{cm}^{-1}$ ): 2022 (C=O), 1913 (C=O), 1857 (C=O), 1611, 1463, 1278, 1246, 1109, 775.

### 2.2 Synthesis of manganese complex [(4-Ph)Triaz $\left.\left(\mathbf{N H P}^{i} \mathbf{P r}_{2}\right)_{2} \mathbf{M n}(\mathbf{C O})_{2} \mathbf{B r}\right](\mathbf{M n}-2)$.


$\mathbf{M n - 2}$ haxene and dried in vacuo to afford [(4-Ph)Triaz $\left.\left(\mathrm{NHP}^{i} \mathrm{Pr}_{2}\right)_{2} \mathrm{Mn}(\mathrm{CO})_{2} \mathrm{Br}\right](\mathbf{M n - 2})$ as a bright yellow powder $(91 \%)$. The analytical data are consistent with those previously reported literature. ${ }^{2}$ Selected IR (KBr, cm ${ }^{-1}$ ): 1937 (C=O), 1867 (C=O).

### 2.3 Synthesis of manganese complex $\left[\mathrm{Mn}(\mathrm{CO})_{2}(\mathrm{Br}) \mathrm{NH}\left(\mathrm{C}_{2} \mathbf{H}_{4} \mathbf{P}^{i} \mathrm{Pr}_{2}\right)_{2}\right](\mathrm{Mn}-3)$.



Mn-3

In a 15 mL schlenk tube under an urgon atmosphere, $\mathrm{Mn}(\mathrm{CO})_{5} \operatorname{Br}(85.3 \mathrm{mg}, 0.31 \mathrm{mmol})$ was suspended in toluene $(4 \mathrm{~mL})$.Then $\left[\mathrm{NH}\left(\mathrm{C}_{2} \mathrm{H}_{4} \mathrm{P}^{i} \mathrm{Pr}_{2}\right)_{2}\right](100 \mathrm{mg}, 0.33 \mathrm{mmol})$ was added dropwise via syringe at room temperature. After 10 min of stirring the mixture was heated at $100^{\circ} \mathrm{C}$ for 24 h . After removing solvent under reduced pressure yellow solid compound was observed. Washing this solid with hexane $(3 \times 2 \mathrm{~mL})$ and drying under high vacuum provided $\left[\mathrm{Mn}(\mathrm{CO})_{2}(\mathrm{Br}) \mathrm{NH}\left(\mathrm{C}_{2} \mathrm{H}_{4} \mathrm{P}^{i} \mathrm{Pr}_{2}\right)_{2}\right](\mathbf{M n}-3)$ as a yellow solid $(98 \%, 0.30 \mathrm{mmol}, 150 \mathrm{mg})$ as complex. The analytical data are consistent with those previously reported literature. ${ }^{3}$ Selected IR (ATR, $\mathrm{cm}^{-1}$ ): 1903 (C=O), 1815(C=O), 1464.8, 1406.8, 1384.5, 1366.2, 1248.4, 1091.6, 828.5.

## $2.4 \quad$ Synthesis of manganese complex $\left[\mathrm{Mn}(\mathrm{CO})_{2}(\mathrm{Br}) \mathrm{NH}\left(\mathrm{C}_{2} \mathbf{H}_{4} \mathrm{PPh}_{2}\right)_{2}\right](\mathrm{Mn}-4)$.


$\mathrm{Mn}-4 \quad$ toluene $(1.2 \mathrm{~mL})$ and $\operatorname{MnBr}(\mathrm{CO})_{5}(0.1 \mathrm{mmol}, 27.4 \mathrm{mg}, 1$ equiv.) were added to the schlenk tube. The reaction mixture was stirred for 20 h at reflux temperature. After removing solvent under reduced pressure yellow solid compound was observed. Washing this solid with hexane ( $3 * 2 \mathrm{~mL}$ ) and drying under high vacuum provided $\left[\mathrm{Mn}(\mathrm{CO})_{2}(\mathrm{Br}) \mathrm{NH}\left(\mathrm{C}_{2} \mathrm{H}_{4} \mathrm{PPh}_{2}\right)_{2}\right](\mathbf{M n}-4)$ as a yellow solid $(91 \%, 58 \mathrm{mg}$,
$0.091 \mathrm{mmol})$ as a complex. The analytical data are matched with the previously reported literature. ${ }^{4}$ Selected IR (ATR, $\mathrm{cm}^{-1}$ ): 1910 (C=O), 1826 (C=O).

### 2.5 Synthesis of manganese complex $\left[\mathrm{Mn}(\mathrm{CO})_{3}(\mathrm{Br}) \mathrm{C}_{11} \mathrm{H}_{11} \mathrm{~N}_{3} \mathrm{~S}\right](\mathrm{Mn}-5)$.



Mn-5

In a schlenk tube, the hydrazone ligand ( $21.7 \mathrm{mg}, 0.1 \mathrm{mmol}$ ) prepared from corresponding ketone and hydrazine and $\mathrm{Mn}(\mathrm{CO})_{5} \mathrm{Br}$ were taken. After adding THF $(2 \mathrm{~mL})$ to the reaction mixture, schlenk tube was sealed and heated at $90^{\circ} \mathrm{C}$ for 4 h . Yellow color crystals started to coming out upon cooling. Hexane was added and the yellow crystals are collected upon decanting the solvent from the Schlenk tube, washed with hexane and dried. $40.1 \mathrm{mg}, 92 \%$ yield of $\left[\mathrm{Mn}(\mathrm{CO})_{3}(\mathrm{Br}) \mathrm{C}_{11} \mathrm{H}_{11} \mathrm{~N}_{3} \mathrm{~S}\right](\mathbf{M n}-\mathbf{5})$ was obtained. The analytical data are matches with our previously reported literature. ${ }^{5}$ Selected IR ( $\mathrm{KBr}, \mathrm{cm}^{-1}$ ): $2026(\mathrm{C}=\mathrm{O})$, 1934.8 (C=O), 1908.7 (C=O), 1617.4, 1574, 1487, 1104.3.
$\begin{array}{lllllll}2.6 & \text { Synthesis of } \quad \text { manganese complex } \quad\left[\mathrm{Mn}(\mathrm{CO})_{3}(\mathrm{Br}) \mathrm{C}_{11} \mathrm{H}_{12} \mathrm{~N}_{2} \mathrm{~S}\right] & (\mathrm{Mn}-6) & \text { and } \\ & {\left[\mathrm{Mn}(\mathrm{CO})_{3}(\mathrm{Br}) \mathrm{C}_{14} \mathrm{H}_{16} \mathrm{~N}_{2} \mathrm{~S}\right](\mathrm{Mn}-7) .}\end{array}$


Mn-6


Mn-7

Manganese complexes Mn-6 and Mn-7 were prepared according to our previously published literature. ${ }^{6}$ In a schlenk tube, amine ligand ( 0.1 mmol ) prepared from the corresponding aldehyde and 2 aminomethyl pyridine, $\mathrm{Mn}(\mathrm{CO})_{5} \mathrm{Br}(28 \mathrm{mg}, 1.02$ equiv.) and THF ( 2 mL ) were taken and the schlenk tube was sealed and heated at $90^{\circ} \mathrm{C}$ for 4 h . The color of the solution turns into red during that time. After evaporation of solvent under Ar atmosphere it turns amorphous yellow color solids which were washed with hexane ( $3 \times$ 2 mL ) and dried. Brown color solid compounds were obtained in $70 \%$ and $96 \%$ yields, respectively. For Mn-6, Selected IR (ATR, $\mathrm{cm}^{-1}$ ): 3182.3 ( $\mathrm{N}-\mathrm{H}$ ), 2019.7 (C=O), 1938.1 (C=O), 1865.3 (C=O), 1619.9, 1462.9, 1271.1, 1120.2, 1026.4, 965.2, 791.8, 706.1 and for Mn-7, Selected IR (ATR, $\mathrm{cm}^{-1}$ ): 3045, 2928, 2860, 2025 (C=O), 1962 (C=O), 1913(C=O), 1605, 1478, 1429, 1088, 751, 697.

## 3. Detailed optimization of the reaction conditions.

General procedure: In a 15 mL reaction tube $[\mathbf{M n}](2 \mathrm{~mol} \%)$ and base $(0.2 \mathrm{mmol})$ were taken. After that ${ }^{t} \mathrm{AmOH}(0.1 \mathrm{~mL}), \mathbf{1 a}(0.2 \mathrm{mmol})$ and $\mathbf{2 a}(0.3 \mathrm{mmol})$ were added and the tube was closed before the mixture was placed in a preheated oil bath at $140^{\circ} \mathrm{C}$ for 24 h . Upon completion the reaction mixture was quenched with water ( 2 mL ) and extracted with ethyl acetate $(3 \times 5 \mathrm{~mL}$ ). The combined organic layers were dried over $\mathrm{Na}_{2} \mathrm{SO}_{4}$, filtered, and concentrated. The residue was purified by column chromatography over silica gel (100-200 mesh) with hexane/ethyl acetate mixture as eluent.

Table S1. Catalyst optimization. ${ }^{a}$

|  |  |  |  <br> 4aa |
| :---: | :---: | :---: | :---: |
| Entry | [Mn] (2 mol\%) | Yield\%(3aa) | Yield\% (4aa) |
| $1 .{ }^{\text {b }}$ | $\mathbf{M n - 1}$ (2.5 mol\%) in ${ }^{\text {t }} \mathrm{BuOH}$ ) | - | 89 |
| $2 .{ }^{\text {c }}$ | Mn-2 (0.5 mol\%), KOH in ${ }^{\text {t }} \mathrm{BuOH} / \mathrm{PhMe}$ ) | ) | 94 |
| 3. | Mn-3 | 98 (95) | trace |
| 4. | Mn-4 | 96 (92) | trace |
| 5. | Mn-5 | trace | trace |
| 6. | Mn-6 | trace | trace |
| 7. | Mn-7 | 55 | 19 |

${ }^{a} 2$-methylquinoline 1a ( 0.2 mmol ), benzyl alcohol 2a ( 0.3 mmol ), [ $\left.\mathbf{M n}\right]$ ( $2 \mathrm{~mol} \%$ ), ${ }^{\dagger} \mathrm{BuOK}(0.2 \mathrm{mmol}$ ), ${ }^{t} \mathrm{AmOH}(0.1 \mathrm{~mL})$ at $140^{\circ} \mathrm{C}, 24 \mathrm{~h}$. Yields were measured by gas chromatography using mesitylene as an internal standard. ${ }^{b}$ ref -1 . ${ }^{c}$ ref $-2 b$

Table S2. Solvent optimization. ${ }^{a}$

${ }^{a} 2$-methylquinoline 1a ( 0.2 mmol ), benzylalcohol 2a ( 0.3 mmol ), Mn-3 (2 mol\%), ${ }^{t} \mathrm{BuOK}(0.2 \mathrm{mmol})$, Solvent ( 0.1 mL ) at $140{ }^{\circ} \mathrm{C}, 24 \mathrm{~h}$. Yields were measured by GC-MS taking mesitylene as an internal standard.

## Table S3. Base optimization ${ }^{a}$


${ }^{a} 2$-methylquinoline 1a $(0.2 \mathrm{mmol})$, benzylalcohol 2a ( 0.3 mmol ), Mn-3 ( $2 \mathrm{~mol} \%$ ), Base $(0.2 \mathrm{mmol})$, ${ }^{t} \mathrm{AmOH}(0.1 \mathrm{~mL})$ at $140{ }^{\circ} \mathrm{C}, 24 \mathrm{~h}$. Yields were measured by GC-MS taking mesitylene as an internal standard.

Table S4. Alcohol optimization. ${ }^{a}$

${ }^{a} 2$-methylquinoline 1a ( 0.2 mmol ), benzylalcohol 2a ( $1-2$ equiv.), Mn-3 (2 mol\%), ${ }^{t} \mathrm{BuOK}(0.2 \mathrm{mmol}$ ), ${ }^{t} \mathrm{AmOH}(0.1 \mathrm{~mL})$ at $140^{\circ} \mathrm{C}, 24 \mathrm{~h}$. Yields were measured by GC-MS taking mesitylene as an internal standard.

Table S5. Optimization of base equivalency. ${ }^{a}$

${ }^{a} 2$-methylquinoline 1a ( 0.2 mmol ), benzylalcohol 2a ( 0.3 mmol ), Mn-3 ( $2 \mathrm{~mol} \%$ ), ${ }^{t} \mathrm{BuOK}$ ( $0.1-1$ equiv.), ${ }^{t} \mathrm{AmOH}(0.1 \mathrm{~mL})$ at $140{ }^{\circ} \mathrm{C}, 24 \mathrm{~h}$. Yields were measured by GC-MS taking mesitylene as an internal standard.

## 4. Manganese catalysed C-alkylations of methyl N-heteroarenes with primary alcohols.

## General procedure:

In a 15 mL reaction tube $\mathbf{M n - 3}(0.004 \mathrm{mmol})$ and ${ }^{t} \mathrm{BuOK}(0.2 \mathrm{mmol})$ were taken. After that ${ }^{t} \mathrm{AmOH}(0.1$ $\mathrm{mL}), \mathbf{1 a}(0.2 \mathrm{mmol})$ and $\mathbf{2 a}(0.3 \mathrm{mmol})$ were added and the tube was closed before the mixture was placed in a preheated oil bath at $140^{\circ} \mathrm{C}$ for 24 h . Upon completion the reaction mixture was quenched with water $(2 \mathrm{~mL})$ and extracted with ethyl acetate $(3 \times 5 \mathrm{~mL})$. The combined organic layers were dried over $\mathrm{Na}_{2} \mathrm{SO}_{4}$, filtered, and concentrated. The residue was purified by column chromatography over silica gel (100-200 mesh) with hexane/ethyl acetate mixture as eluent.

2-phenethylquinoline (3aa): ${ }^{7}$ Yield: $95 \% ~(44 \mathrm{mg}, 0.190 \mathrm{mmol})$. The title compound was isolated as a light
 brown oil eluting with $2 \%$ ethyl acetate in hexane. ${ }^{1} \mathbf{H}$ NMR $(400 \mathrm{MHz}$, $\left.\mathrm{CDCl}_{3}\right) \delta 8.10(\mathrm{~d}, J=8.5 \mathrm{~Hz}, 1 \mathrm{H}), 8.05(\mathrm{~d}, J=8.4 \mathrm{~Hz}, 1 \mathrm{H}), 7.78(\mathrm{~d}, J=8.1$ $\mathrm{Hz}, 1 \mathrm{H}), 7.71$ (ddd, $J=8.3,6.9,1.3 \mathrm{~Hz}, 1 \mathrm{H}), 7.50(\mathrm{dd}, J=11.3,4.2 \mathrm{~Hz}, 1 \mathrm{H})$, $7.34-7.17(\mathrm{~m}, 6 \mathrm{H}), 3.35-3.28(\mathrm{~m}, 2 \mathrm{H}), 3.18(\mathrm{dd}, J=9.8,6.2 \mathrm{~Hz}, 2 \mathrm{H}) .{ }^{\mathbf{1 3}} \mathbf{C} \mathbf{N M R}\left(126 \mathrm{MHz}, \mathrm{CDCl}_{3}\right) \delta$ $161.9,148.1,141.7,136.3,129.5,129.0,128.6,128.5,127.6,126.9,126.1,125.9,121.7,41.1,36.0$.

2-(4-methylphenethyl)quinolone (3ab): ${ }^{\mathbf{8}}$ Yield: $91 \% ~(45 \mathrm{mg}, 0.186 \mathrm{mmol})$. The title compound was
 isolated as a light brown oil with $2 \%$ ethyl acetate in hexane. ${ }^{1} \mathbf{H}$ NMR $\left(400 \mathrm{MHz}, \mathrm{CDCl}_{3}\right) \delta 8.07(\mathrm{dd}, J=19.8,8.2 \mathrm{~Hz}, 2 \mathrm{H}), 7.78(\mathrm{dd}, J=8.0$, $0.9 \mathrm{~Hz}, 1 \mathrm{H}), 7.70(\mathrm{ddd}, J=8.2,6.8,1.3 \mathrm{~Hz}, 1 \mathrm{H}), 7.55-7.45(\mathrm{~m}, 1 \mathrm{H})$, $7.24(\mathrm{~d}, J=8.5 \mathrm{~Hz}, 1 \mathrm{H}), 7.16(\mathrm{~d}, J=8.0 \mathrm{~Hz}, 2 \mathrm{H}), 7.10(\mathrm{~d}, J=7.9 \mathrm{~Hz}$, $2 \mathrm{H}), 3.33-3.25(\mathrm{~m}, 2 \mathrm{H}), 3.13(\mathrm{dd}, J=9.8,6.4 \mathrm{~Hz}, 2 \mathrm{H}), 2.33(\mathrm{~s}, 3 \mathrm{H}) .{ }^{\mathbf{1 3}} \mathbf{C} \mathbf{N M R}\left(101 \mathrm{MHz}, \mathrm{CDCl}_{3}\right) \delta 162.1$, $148.1,138.5,136.4,135.6,129.5,129.2,129,128.5,127.6,126.9,126,121.7,41.2,35.7,21.1$.
2-(4-methoxyphenethyl)quinoline (3ac): ${ }^{7}$ Yield: $91 \% ~(48 \mathrm{mg}, 0.182 \mathrm{mmol})$. The title compound was
 isolated as a light brown oil with $2 \%$ ethyl acetate in hexane. ${ }^{\mathbf{1}} \mathbf{H}$ NMR $\left(400 \mathrm{MHz}, \mathrm{CDCl}_{3}\right) \delta 8.09(\mathrm{~d}, J=8.5 \mathrm{~Hz}, 1 \mathrm{H}), 8.03(\mathrm{~d}, J=8.4 \mathrm{~Hz}, 1 \mathrm{H})$, $7.77(\mathrm{~d}, J=8.0 \mathrm{~Hz}, 1 \mathrm{H}), 7.70(\mathrm{ddd}, J=8.3,6.9,1.3 \mathrm{~Hz}, 1 \mathrm{H}), 7.50(\mathrm{dd}$, $J=11.1,4.1 \mathrm{~Hz}, 1 \mathrm{H}), 7.22(\mathrm{~d}, J=8.5 \mathrm{~Hz}, 1 \mathrm{H}), 7.16(\mathrm{~d}, J=8.6 \mathrm{~Hz}, 2 \mathrm{H})$, $6.83(\mathrm{~d}, J=8.6 \mathrm{~Hz}, 2 \mathrm{H}), 3.78(\mathrm{~s}, 3 \mathrm{H}), 3.27(\mathrm{dd}, J=9.7,6.4 \mathrm{~Hz}, 2 \mathrm{H}), 3.11(\mathrm{dd}, J=9.6,6.5 \mathrm{~Hz}, 2 \mathrm{H}) .{ }^{13} \mathrm{C}$ NMR (101 MHz, $\mathrm{CDCl}_{3}$ ) $\delta 162.0,158,148.1,136.3,133.7,129.5,129,127.6,126.9,125.9,121.7,113.9$, 55.3, 41.4, 35.2.

2-(2-([1,1'-biphenyl]-4-yl)ethyl)quinoline (3ad): Yield: $74 \%$ ( $46 \mathrm{mg}, 0.148 \mathrm{mmol}$ ). The title compound
 was isolated as a white solid with $2 \%$ ethyl acetate in hexane. Selected IR (DCM, $\mathrm{cm}^{-1}$ ): 2950.6, 2926.8, 2852.0, 1603.2, 1561.1, 1501.0, 1487.3, 1451.2, 1425.5, 1405.7, 1116.4, 977.3, 762.1, 689.4, 489.0. ¹H NMR $\left(500 \mathrm{MHz}, \mathrm{CDCl}_{3}\right) \delta 8.11(\mathrm{~d}, J=8.4 \mathrm{~Hz}, 1 \mathrm{H}), 8.06(\mathrm{~d}, J=8.4 \mathrm{~Hz}, 1 \mathrm{H}), 7.79(\mathrm{~d}, J=8.1 \mathrm{~Hz}, 1 \mathrm{H}), 7.72(\mathrm{t}, J$
$=7.6 \mathrm{~Hz}, 1 \mathrm{H}), 7.60(\mathrm{~d}, J=7.8 \mathrm{~Hz}, 2 \mathrm{H}), 7.52(\mathrm{dd}, J=16.8,7.8 \mathrm{~Hz}, 3 \mathrm{H}), 7.44(\mathrm{t}, J=7.6 \mathrm{~Hz}, 2 \mathrm{H}), 7.34(\mathrm{~d}, J$ $=7.9 \mathrm{~Hz}, 3 \mathrm{H}), 7.27(\mathrm{~d}, J=8.3 \mathrm{~Hz}, 1 \mathrm{H}), 3.35(\mathrm{dd}, J=9.6,6.5 \mathrm{~Hz}, 2 \mathrm{H}), 3.26-3.19(\mathrm{~m}, 2 \mathrm{H})$, 13C NMR ( $126 \mathrm{MHz}, \mathrm{CDCl}_{3}$ ) $\delta 161.9,148.2,141.2,140.8,139.1,136.4,129.5,129.1,129.0,128.8,127.7,127.3$, 127.2, 127.1, 127.0, 125.9, 121.7, 41.0, 35.6; HRMS (ESI) m/z: $[\mathrm{M}+\mathrm{H}]^{+}$Calcd for $\mathrm{C}_{23} \mathrm{H}_{19} \mathrm{~N}: 310.1590$; Found 310.1580.

2-(4-chlorophenethyl)quinoline (3ae): ${ }^{9}$ Yield: $72 \% ~(38 \mathrm{mg}, 0.144 \mathrm{mmol})$. The title compound was
 isolated as a light brown oil with $2 \%$ ethyl acetate in hexane. ${ }^{1} \mathbf{H}$ NMR ( $400 \mathrm{MHz}, \mathrm{CDCl}_{3}$ ) $\delta 8.06(\mathrm{t}, J=8.7 \mathrm{~Hz}, 2 \mathrm{H}), 7.81-7.75(\mathrm{~m}, 1 \mathrm{H}), 7.70$ (ddd, $J=8.4,7.0,1.4 \mathrm{~Hz}, 1 \mathrm{H}), 7.53-7.47$ (m, 1H), 7.26 ( $\mathrm{s}, 1 \mathrm{H}$ ), $7.24-$ 7.15 (m, 3H), $7.13-7.08(\mathrm{~m}, 1 \mathrm{H}), 3.30-3.24(\mathrm{~m}, 2 \mathrm{H}), 3.14$ (dd, $J=9.6$, $6.2 \mathrm{~Hz}, 2 \mathrm{H}) ;{ }^{13} \mathbf{C}$ NMR (101 MHz, $\mathrm{CDCl}_{3}$ ) $\delta 161.3,148.1,143.7,136.5,134.2,129.8,129.6,129,128.8$, 127.7, 127, 126.9, 126.3, 126.0, 121.6, 40.7, 35.5.

2-(3-methoxyphenethyl)quinolone (3af): ${ }^{8}$ Yield: $95 \%$ ( $50 \mathrm{mg}, 0.190 \mathrm{mmol}$ ). The title compound was
 isolated as a light brown oil with $2 \%$ ethyl acetate in hexane. ${ }^{1} \mathbf{H}$ NMR $\left(400 \mathrm{MHz}, \mathrm{CDCl}_{3}\right) \delta 8.06(\mathrm{dd}, J=19.3,8.5 \mathrm{~Hz}, 2 \mathrm{H}), 7.77(\mathrm{~d}, J=8.0$
$\mathrm{Hz}, 1 \mathrm{H}), 7.70$ (ddd, $J=8.5,7.0,1.4 \mathrm{~Hz}, 1 \mathrm{H}), 7.49$ (ddd, $J=7.9,6.8,0.9$ $\mathrm{Hz}, 1 \mathrm{H}), 7.22(\mathrm{dd}, J=16.6,8.2 \mathrm{~Hz}, 2 \mathrm{H}), 6.89-6.80(\mathrm{~m}, 2 \mathrm{H}), 6.76(\mathrm{dd}, J=8.2,2.7 \mathrm{~Hz}, 1 \mathrm{H}), 3.76(\mathrm{~s}, 3 \mathrm{H})$, $3.33-3.25(\mathrm{~m}, 2 \mathrm{H}), 3.15(\mathrm{dd}, J=9.8,6.3 \mathrm{~Hz}, 2 \mathrm{H}) ;{ }^{13} \mathbf{C}$ NMR ( $101 \mathrm{MHz}, \mathrm{CDCl}_{3}$ ) $\delta 161.9,159.7,148.1$, 143.2, 136.3, 129.5, 129.4, 128.9, 127.6, 126.9, 125.9, 121.7, 121, 114.2, 111.6, 55.2, 41, 36.1.

2-(2-methylphenethyl)quinoline (3ag): ${ }^{8}$ Yield: $92 \%$ ( $45 \mathrm{mg}, 0.184 \mathrm{mmol}$ ). The title compound was
 isolated as a light brown oil with $2 \%$ ethyl acetate in hexane. ${ }^{1} \mathbf{H}$ NMR (400 $\left.\mathrm{MHz}, \mathrm{CDCl}_{3}\right) \delta 8.11(\mathrm{~d}, J=8.5 \mathrm{~Hz}, 1 \mathrm{H}), 8.04(\mathrm{~d}, J=8.4 \mathrm{~Hz}, 1 \mathrm{H}), 7.78(\mathrm{~d}, J=$ $8.0 \mathrm{~Hz}, 1 \mathrm{H}), 7.71(\mathrm{ddd}, J=8.4,7.1,1.5 \mathrm{~Hz}, 1 \mathrm{H}), 7.54-7.46(\mathrm{~m}, 1 \mathrm{H}), 7.21(\mathrm{dd}$, $J=8.3,4.6 \mathrm{~Hz}, 2 \mathrm{H}), 7.15(\mathrm{dt}, J=8.9,4.6 \mathrm{~Hz}, 3 \mathrm{H}), 3.32-3.23(\mathrm{~m}, 2 \mathrm{H}), 3.21$ - 3.12 (m, 2H), $2.36(\mathrm{~s}, 3 \mathrm{H}) ;{ }^{13} \mathbf{C}$ NMR ( $101 \mathrm{MHz}, \mathrm{CDCl}_{3}$ ) $\delta 162.1,148.1,139.8,136.3,136.1,130.3$, $129.5,129.0,128.9,127.6,126.9,126.3,126.2,125.9,121.6,39.8,33.4,19.5$.
2-(3,5-dimethoxyphenethyl)quinoline (3ah): ${ }^{\mathbf{1 0}}$ Yield: $82 \%$ ( $48 \mathrm{mg}, 0.164 \mathrm{mmol}$ ). The title compound was
 isolated as a light brown oil with $2 \%$ ethyl acetate in hexane. ${ }^{1} \mathbf{H}$ NMR $\left(500 \mathrm{MHz}, \mathrm{CDCl}_{3}\right) \delta 8.07(\mathrm{dd}, J=19.4,8.4 \mathrm{~Hz}, 2 \mathrm{H}), 7.78(\mathrm{~d}, \mathrm{~J}=8.1$ $\mathrm{Hz}, 1 \mathrm{H}$ ), 7.71 (ddd, $J=8.3,6.9,1.3 \mathrm{~Hz}, 1 \mathrm{H}), 7.54-7.46(\mathrm{~m}, 1 \mathrm{H}), 7.26$ $(\mathrm{t}, J=5.7 \mathrm{~Hz}, 1 \mathrm{H}), 6.44(\mathrm{~d}, \mathrm{~J}=2.1 \mathrm{~Hz}, 2 \mathrm{H}), 6.34(\mathrm{t}, J=2.2 \mathrm{~Hz}, 1 \mathrm{H})$, 3.76 (s, 6H), 3.30 (dd, $J=9.5,6.7 \mathrm{~Hz}, 2 \mathrm{H}$ ), 3.12 (dd, $J=9.6,6.7 \mathrm{~Hz}$, $2 \mathrm{H}) .{ }^{13} \mathbf{C}$ NMR ( $126 \mathrm{MHz}, \mathrm{CDCl}_{3}$ ) $\delta 161.7,160.8,148.0,143.9,136.2,129.4,128.8,127.5,126.8,125.8$, 121.5, 106.5, 98.2, 55.2, 55.1, 40.7, 36.2.

2-(3,4-dimethoxyphenethyl)quinoline (3ai): ${ }^{11}$ Yield: $92 \%$ ( $54 \mathrm{mg}, 0.184 \mathrm{mmol}$ ). The title compound was
 isolated as a light brown oil with $10 \%$ ethyl acetate in hexane. ${ }^{1} \mathbf{H}$ NMR $\left(500 \mathrm{MHz}, \mathrm{CDCl}_{3}\right) \delta 8.09(\mathrm{dd}, J=18.5,8.4 \mathrm{~Hz}, 2 \mathrm{H}), 7.80(\mathrm{~d}, J=8.1$ $\mathrm{Hz}, 1 \mathrm{H}), 7.72(\mathrm{t}, J=7.7 \mathrm{~Hz}, 1 \mathrm{H}), 7.52(\mathrm{t}, J=7.5 \mathrm{~Hz}, 1 \mathrm{H}), 7.25(\mathrm{~d}, J=$ $8.4 \mathrm{~Hz}, 1 \mathrm{H}), 6.79(\mathrm{~d}, J=15.5 \mathrm{~Hz}, 3 \mathrm{H}), 3.87(\mathrm{~s}, 3 \mathrm{H}), 3.82(\mathrm{~s}, 3 \mathrm{H}), 3.30(\mathrm{dd}, J=9.3,6.8 \mathrm{~Hz}, 2 \mathrm{H}), 3.13$ (dd, $J=9.4,6.7 \mathrm{~Hz}, 2 \mathrm{H}$ ); ${ }^{13} \mathbf{C}$ NMR ( $126 \mathrm{MHz}, \mathrm{CDCl}_{3}$ ) $\delta 161.8,148.8,147.9,147.3,136.3,134.1,129.5,128.8$, $127.5,126.8,125.8,121.6,120.3,112,111.3,55.9,55.7,41.2,35.6$.

2-(2-(naphthalen-2-yl)ethyl)quinoline (3aj): ${ }^{\mathbf{8}}$ Yield: $62 \%$ ( $35 \mathrm{mg}, 0.124 \mathrm{mmol}$ ). The title compound was isolated as a white solid with $2 \%$ ethyl acetate in hexane. ${ }^{\mathbf{1}} \mathbf{H} \mathbf{N M R}\left(400 \mathrm{MHz}, \mathrm{CDCl}_{3}\right) \delta 8.10(\mathrm{~d}, J=8.2$
 $\mathrm{Hz}, 1 \mathrm{H}), 8.04(\mathrm{~d}, J=8.4 \mathrm{~Hz}, 1 \mathrm{H}), 7.83-7.75(\mathrm{~m}, 4 \mathrm{H}), 7.74-7.68(\mathrm{~m}$, $2 \mathrm{H}), 7.51$ (ddd, $J=7.8,6.8,1.0 \mathrm{~Hz}, 1 \mathrm{H}), 7.46-7.39$ (m, 3H), $7.28-7.22$ (m, 1H), 3.40 (ddd, $J=9.1,5.9,2.0 \mathrm{~Hz}, 2 \mathrm{H}), 3.37-3.30(\mathrm{~m}, 2 \mathrm{H}) ;{ }^{13} \mathbf{C}$ NMR (126 MHz, $\mathrm{CDCl}_{3}$ ) $\delta 161.9,148.2,139.2,136.4,133.8,132.2,129.6,129.0,128.1,127.8,127.7$, $127.6,127.5,127.0,126.7,126.1,126.0,125.4,121.7,41.0,36.2$.

2-(2-(furan-2-yl)ethyl)quinoline (3ak): ${ }^{12}$ Yield: $77 \%$ ( $34 \mathrm{mg}, 0.154 \mathrm{mmol}$ ). The title compound was isolated as a light brown oil with $2 \%$ ethyl acetate in hexane. ${ }^{1} \mathbf{H} \mathbf{~ N M R ~}\left(400 \mathrm{MHz}, \mathrm{CDCl}_{3}\right) \delta 8.05(\mathrm{dd}, J=$
 $8.4,4.3 \mathrm{~Hz}, 2 \mathrm{H}), 7.79-7.75(\mathrm{~m}, 1 \mathrm{H}), 7.69$ (ddd, $J=8.3,6.8,1.3 \mathrm{~Hz}, 1 \mathrm{H}), 7.50$ (dd, $J=11.1,4.2 \mathrm{~Hz}, 1 \mathrm{H}), 7.32(\mathrm{~d}, J=1.6 \mathrm{~Hz}, 1 \mathrm{H}), 7.23(\mathrm{~d}, J=8.4 \mathrm{~Hz}, 1 \mathrm{H})$, 6.26 (dd, $J=3.0,2.0 \mathrm{~Hz}, 1 \mathrm{H}), 6.00(\mathrm{~d}, J=2.9 \mathrm{~Hz}, 1 \mathrm{H}), 3.36-3.30(\mathrm{~m}, 2 \mathrm{H})$, 3.22 - 3.16 (m, 2H), ${ }^{13} \mathbf{C}$ NMR ( $126 \mathrm{MHz}, \mathrm{CDCl}_{3}$ ) $\delta 161.4,155.2,148.1,141.1,136.4,129.5,129,127.6$, 127, 126, 121.5, 110.3, 105.5, 37.5, 28.0.

2-(2-(pyridin-3-yl)ethyl)quinolone (3al): ${ }^{8}$ Yield: $98 \% ~(46 \mathrm{mg}, 0.196 \mathrm{mmol})$. The title compound was
 isolated as a light brown oil with $30 \%$ ethyl acetate in hexane. ${ }^{1} \mathbf{H}$ NMR (500 $\left.\mathrm{MHz}, \mathrm{CDCl}_{3}\right) \delta 8.49(\mathrm{~s}, 2 \mathrm{H}), 8.05(\mathrm{dd}, J=8.1,4.9 \mathrm{~Hz}, 2 \mathrm{H}), 7.83-7.63(\mathrm{~m}$, $2 \mathrm{H}), 7.59-7.41$ (m, 2H), 7.20 (d, $J=8.3 \mathrm{~Hz}, 2 \mathrm{H}$ ), $3.34-3.25(\mathrm{~m}, 2 \mathrm{H}), 3.22$ $-3.13(\mathrm{~m}, 2 \mathrm{H}) ;{ }^{13} \mathbf{C}$ NMR ( $126 \mathrm{MHz}, \mathrm{CDCl}_{3}$ ) $\delta 160.9,148.1,136.5,129.7$, 129, 127.7, 126.9, 126.1, 121.6, 40.3, 33.

2-pentylquinoline (3am): ${ }^{\mathbf{1 2}}$ Yield: $73 \%$ ( $29 \mathrm{mg}, 0.146 \mathrm{mmol}$ ). The title compound was isolated as a light brown oil with $2 \%$ ethyl acetate in hexane. ${ }^{1} \mathbf{H}$ NMR $\left(400 \mathrm{MHz}, \mathrm{CDCl}_{3}\right) \delta 8.05(\mathrm{dd}, J=8.4,2.5 \mathrm{~Hz}, 2 \mathrm{H})$,
 $7.76(\mathrm{~d}, J=8.0 \mathrm{~Hz}, 1 \mathrm{H}), 7.67$ (ddd, $J=8.3,6.9,1.4 \mathrm{~Hz}, 1 \mathrm{H}), 7.50-7.43(\mathrm{~m}$, $1 \mathrm{H}), 7.29(\mathrm{~d}, J=8.4 \mathrm{~Hz}, 1 \mathrm{H}), 2.96(\mathrm{dd}, J=8.6,7.2 \mathrm{~Hz}, 2 \mathrm{H}), 1.87-1.73(\mathrm{~m}$, $2 \mathrm{H}), 1.38(\mathrm{pd}, J=9.4,3.0 \mathrm{~Hz}, 4 \mathrm{H}), 0.90(\mathrm{t}, J=7.0 \mathrm{~Hz}, 3 \mathrm{H}) ;{ }^{13} \mathbf{C}$ NMR ( $126 \mathrm{MHz}, \mathrm{CDCl}_{3}$ ) $\delta 163.3,148.1$, $136.3,129.4,129,127.6,126.8,125.7,121.5,39.5,31.9,29.9,22.7,14.1$.

2-octylquinoline (3an): ${ }^{8}$ Yield: $75 \% ~(36 \mathrm{mg}, 0.15 \mathrm{mmol})$. The title compound was isolated as a light brown oil with $2 \%$ ethyl acetate in hexane. ${ }^{1} \mathbf{H}$ NMR ( $\left.500 \mathrm{MHz}, \mathrm{CDCl}_{3}\right) \delta 8.05(\mathrm{dd}, J=8.4,2.7 \mathrm{~Hz}, 2 \mathrm{H}), 7.76(\mathrm{~d}$,
 $J=8.1 \mathrm{~Hz}, 1 \mathrm{H}), 7.70-7.64(\mathrm{~m}, 1 \mathrm{H}), 7.47(\mathrm{dd}, J=7.9,7.0 \mathrm{~Hz}, 1 \mathrm{H})$, $7.29(\mathrm{~d}, J=8.4 \mathrm{~Hz}, 1 \mathrm{H}), 3.02-2.92(\mathrm{~m}, 2 \mathrm{H}), 1.87-1.75(\mathrm{~m}, 2 \mathrm{H})$, $1.48-1.24(\mathrm{~m}, 12 \mathrm{H}), 0.87(\mathrm{t}, J=6.8 \mathrm{~Hz}, 3 \mathrm{H}) .{ }^{13} \mathbf{C}$ NMR $\left(126 \mathrm{MHz}, \mathrm{CDCl}_{3}\right) \delta 163.27,148.06,136.2,129.4$, $129,127.6,126.8,125.7,121.5,39.6,32.0,30.2,29.8,29.7,29.6,29.4,22.8,14.2$.

2-undecylquinoline (3ao): ${ }^{12}$ Yield: $70 \% ~(40 \mathrm{mg}, 0.140 \mathrm{mmol})$. The title compound was isolated as a light brown oil with $1 \%$ ethyl acetate in hexane. ${ }^{1} \mathbf{H} \mathbf{N M R}\left(400 \mathrm{MHz}, \mathrm{CDCl}_{3}\right) \delta 8.05(\mathrm{dd}, J=8.4,5.8 \mathrm{~Hz}, 2 \mathrm{H})$,
 $7.80-7.75(\mathrm{~m}, 1 \mathrm{H}), 7.68$ (ddd, $J=8.3,6.8,1.3 \mathrm{~Hz}, 1 \mathrm{H}), 7.51-7.45(\mathrm{~m}, 1 \mathrm{H})$, $7.30(\mathrm{~d}, J=8.5 \mathrm{~Hz}, 1 \mathrm{H}), 3.01-2.92(\mathrm{~m}, 2 \mathrm{H}), 1.86-1.78(\mathrm{~m}, 2 \mathrm{H}), 1.45-1.25$ $(\mathrm{m}, 16 \mathrm{H}), 0.88(\mathrm{t}, \mathrm{J}=6.9 \mathrm{~Hz}, 3 \mathrm{H}) ;{ }^{13} \mathbf{C}$ NMR ( $126 \mathrm{MHz}, \mathrm{CDCl}_{3}$ ) $\delta 163.3$, 148.1, $136.3,129.4,129.0,127.6,126.9,125.8,121.5,39.6,32.1,31.0,30.2,29.8,29.75,29.72,29.70,29.67$, 29.5, 22.8, 14.3 .

2-heptadecylquinoline (3ap): Yield: $68 \%$ ( $50 \mathrm{mg}, 0.136 \mathrm{mmol}$ ). The title compound was isolated as a amorphous brown solid with $1 \%$ ethyl acetate in hexane. Selected IR (DCM, $\mathrm{cm}^{-1}$ ): 2920.1, 2850.7, 1738.5,
 1601.2, 1563.2, 1504.8, 1471.5, 1426.7, 1374.4, 1264.3, 740.3; ${ }^{\mathbf{1}} \mathbf{H}$ NMR (500 $\left.\mathrm{MHz}, \mathrm{CDCl}_{3}\right) \delta 7.95(\mathrm{t}, J=8.1 \mathrm{~Hz}, 2 \mathrm{H}), 7.67(\mathrm{~d}, J=8.0 \mathrm{~Hz}, 1 \mathrm{H}), 7.62-7.52(\mathrm{~m}$, $1 \mathrm{H}), 7.38(\mathrm{t}, J=7.4 \mathrm{~Hz}, 1 \mathrm{H}), 7.20(\mathrm{~d}, J=8.4 \mathrm{~Hz}, 1 \mathrm{H}), 2.91-2.80(\mathrm{~m}, 2 \mathrm{H}), 1.71$ $(\mathrm{dt}, J=15.6,7.7 \mathrm{~Hz}, 2 \mathrm{H}), 1.35-1.14(\mathrm{~m}, 28 \mathrm{H}), 0.78(\mathrm{t}, J=6.9 \mathrm{~Hz}, 3 \mathrm{H}) ;{ }^{13} \mathbf{C} \mathbf{N M R}\left(126 \mathrm{MHz}, \mathrm{CDCl}_{3}\right) \delta$ 163.1, 147.9, 136.1, 129.2, 128.8, 127.4, 126.7, 125.6, 121.3, 39.4, 31.9, 30.0, 29.56 (overlapped), 29.3, 22.6, 14.1; HRMS (ESI) m/z: [M+H] ${ }^{+}$Calcd for $\mathrm{C}_{26} \mathrm{H}_{41} \mathrm{~N}: 368.3312$; Found 368.3306 .

2-nonadecylquinoline (3aq): Yield: $53 \%$ ( $42 \mathrm{mg}, 0.106 \mathrm{mmol}$ ). The title compound was isolated as a amorphous white solid with $1 \%$ ethyl acetate in hexane. Selected IR (DCM, $\mathrm{cm}^{-1}$ ): 2019.0, 2849.5, 1618.7,
 1601.0, 1562.8, 1504.1, 1472.0, 1427.1, 826.6, 717.4, 619.3; ${ }^{1} \mathbf{H}$ NMR (500
$\left.\mathrm{MHz}, \mathrm{CDCl}_{3}\right) \delta 8.05(\mathrm{t}, J=8.0 \mathrm{~Hz}, 2 \mathrm{H}), 7.77(\mathrm{~d}, J=7.9 \mathrm{~Hz}, 1 \mathrm{H}), 7.71-7.64$ (m, 1H), 7.48 (t, $J=7.4 \mathrm{~Hz}, 1 \mathrm{H}$ ), $7.30(\mathrm{~d}, J=8.4 \mathrm{~Hz}, 1 \mathrm{H}), 2.99-2.95(\mathrm{~m}, 2 \mathrm{H}), 1.86-1.75(\mathrm{~m}, 2 \mathrm{H}), 1.47$ $-1.13(\mathrm{~m}, 32 \mathrm{H}), 0.88(\mathrm{t}, J=6.9 \mathrm{~Hz}, 3 \mathrm{H}),{ }^{13} \mathbf{C}$ NMR ( $126 \mathrm{MHz}, \mathrm{CDCl}_{3}$ ) $\delta 163.3,148.1,136.3,129.4,129.0$, 127.6, 126.9, 125.8, 121.5, 39.6, 32.1, 30.2, 30.08 - 29.68 (overlapped), 22.8, 14.3. HRMS (ESI) m/z: $[\mathrm{M}+\mathrm{H}]^{+}$Calcd for $\mathrm{C}_{28} \mathrm{H}_{45} \mathrm{~N}$ : 396.3625; Found 396.3624.

2-(2-cyclohexylethyl)quinoline (3ar): ${ }^{12}$ Yield: $79 \%$ ( $38 \mathrm{mg}, 0.158 \mathrm{mmol}$ ). The title compound was isolated as a light brown oil with $2 \%$ ethyl acetate in hexane. ${ }^{1} \mathbf{H}$ NMR $\left(400 \mathrm{MHz}, \mathrm{CDCl}_{3}\right) \delta 8.04(\mathrm{~d}, J=$
 $8.3 \mathrm{~Hz}, 2 \mathrm{H}), 7.76(\mathrm{dd}, J=8.1,1.2 \mathrm{~Hz}, 1 \mathrm{H}), 7.70-7.63(\mathrm{~m}, 1 \mathrm{H}), 7.47(\mathrm{dd}, J=$ $11.1,4.1 \mathrm{~Hz}, 1 \mathrm{H}), 7.28(\mathrm{~d}, J=8.4 \mathrm{~Hz}, 1 \mathrm{H}), 3.03-2.92(\mathrm{~m}, 2 \mathrm{H}), 1.88-1.76$ $(\mathrm{m}, 2 \mathrm{H}), 1.76-1.64(\mathrm{~m}, 5 \mathrm{H}), 1.39-1.15(\mathrm{~m}, 4 \mathrm{H}), 0.97(\mathrm{qd}, J=12.2,3.0 \mathrm{~Hz}$,
$2 \mathrm{H}) ;{ }^{13} \mathbf{C}$ NMR ( $126 \mathrm{MHz}, \mathrm{CDCl}_{3}$ ) $\delta 163.6,148.1,136.3,129.4,128.9,127.6,126.8,125.7,121.5,37.9$, 37.8, 37.0, 33.4, 26.8, 26.5.

2-(2-cyclopropylethyl)quinoline (3as): ${ }^{\mathbf{1 2}}$ Yield: $82 \%$ ( $32 \mathrm{mg}, 0.164 \mathrm{mmol}$ ). The title compound was isolated as a light brown oil with $2 \%$ ethyl acetate in hexane. ${ }^{1} \mathbf{H} \mathbf{~ N M R ~}\left(400 \mathrm{MHz}, \mathrm{CDCl}_{3}\right) \delta 8.04(\mathrm{~d}, J=$
 $8.4 \mathrm{~Hz}, 2 \mathrm{H}), 7.78-7.73(\mathrm{~m}, 1 \mathrm{H}), 7.70-7.64(\mathrm{~m}, 1 \mathrm{H}), 7.47(\mathrm{t}, J=7.5 \mathrm{~Hz}, 1 \mathrm{H})$, $7.30(\mathrm{~d}, J=8.4 \mathrm{~Hz}, 1 \mathrm{H}), 3.07(\mathrm{dd}, J=8.7,7.0 \mathrm{~Hz}, 2 \mathrm{H}), 1.77-1.68(\mathrm{~m}, 2 \mathrm{H}), 0.84$ - $0.72(\mathrm{~m}, 1 \mathrm{H}), 0.47-0.39(\mathrm{~m}, 2 \mathrm{H}), 0.07(\mathrm{q}, J=5.0 \mathrm{~Hz}, 2 \mathrm{H}) ;{ }^{13} \mathbf{C}$ NMR (126 $\left.\mathrm{MHz}, \mathrm{CDCl}_{3}\right) \delta 163,148.1,136.2,129.4,129,127.6,126.8,125.7,121.7,39.5,35.2,11.0,4.7$.
(R)-2-(4,8-dimethylnon-7-en-1-yl)quinoline (3at): ${ }^{12}$ Yield: $93 \% ~(52 \mathrm{mg}, 0.186 \mathrm{mmol}$ ). The title compound was isolated as a colorless oil with $2 \%$ ethyl acetate in hexane. ${ }^{1} \mathbf{H} \mathbf{N M R}\left(500 \mathrm{MHz}, \mathrm{CDCl}_{3}\right) \delta$
 $8.05(\mathrm{dd}, J=8.4,4.3 \mathrm{~Hz}, 2 \mathrm{H}), 7.77(\mathrm{~d}, J=8.1 \mathrm{~Hz}, 1 \mathrm{H}), 7.67(\mathrm{t}, J=7.7 \mathrm{~Hz}$, $1 \mathrm{H}), 7.47(\mathrm{t}, J=7.5 \mathrm{~Hz}, 1 \mathrm{H}), 7.29(\mathrm{~d}, J=8.4 \mathrm{~Hz}, 1 \mathrm{H}), 5.09(\mathrm{t}, J=6.7 \mathrm{~Hz}, 1 \mathrm{H})$, $3.01-2.89(\mathrm{~m}, 2 \mathrm{H}), 1.96(\mathrm{qd}, J=14.5,7.3 \mathrm{~Hz}, 2 \mathrm{H}), 1.89-1.78(\mathrm{~m}, 2 \mathrm{H}), 1.67$ $(\mathrm{s}, 3 \mathrm{H}), 1.58(\mathrm{~s}, 3 \mathrm{H}), 1.51-1.40(\mathrm{~m}, 2 \mathrm{H}), 1.34(\mathrm{dt}, J=15.1,5.8 \mathrm{~Hz}, 1 \mathrm{H}), 1.25$ $(\mathrm{dt}, J=10.9,5.5 \mathrm{~Hz}, 1 \mathrm{H}), 1.15(\mathrm{dt}, J=22.3,7.0 \mathrm{~Hz}, 1 \mathrm{H}), 0.89(\mathrm{~d}, J=6.3 \mathrm{~Hz}, 3 \mathrm{H}) ;{ }^{13} \mathbf{C}$ NMR $(126 \mathrm{MHz}$, $\left.\mathrm{CDCl}_{3}\right) \delta 163.2,148.1,136.3,131.2,129.4,129.0,127.6,126.9,125.8,125.1,121.5,39.8,37.2,37,32.5$, 27.7, 25.8, 25.7, 19.7, 17.8 .

6-methyl-2-phenethylquinoline (3ba): ${ }^{7}$ Yield: $82 \% ~(41 \mathrm{mg}, 0.164 \mathrm{mmol})$. The title compound was isolated as a light brown oil with $2 \%$ ethyl acetate in hexane. ${ }^{1} \mathbf{H} \mathbf{N M R}\left(400 \mathrm{MHz}, \mathrm{CDCl}_{3}\right) \delta 8.00-7.93$
 (m, 2H), $7.57-7.51(\mathrm{~m}, 2 \mathrm{H}), 7.27(\mathrm{dt}, J=11.0,7.0 \mathrm{~Hz}, 4 \mathrm{H}), 7.23-7.16$ (m, 2H), $3.31-3.24(\mathrm{~m}, 2 \mathrm{H}), 3.15(\mathrm{dd}, J=9.8,5.9 \mathrm{~Hz}, 2 \mathrm{H}), 2.53(\mathrm{~s}, 3 \mathrm{H})$; ${ }^{13} \mathbf{C}$ NMR ( $101 \mathrm{MHz}, \mathrm{CDCl}_{3}$ ) $\delta 161,146.7,141.7,135.7,131.8,128.7$, 128.5, 126.9, 126.6, 126.1, 121.7, 41.1, 36.2, 21.6.

6-methoxy-2-phenethylquinoline (3ca): ${ }^{8}$ Yield: $75 \% ~(40 \mathrm{mg}, 0.150 \mathrm{mmol}$ ). The title compound was isolated as a light brown oil with $2 \%$ ethyl acetate in hexane.

${ }^{1} \mathbf{H}$ NMR ( $400 \mathrm{MHz}, \mathrm{CDCl}_{3}$ ) $\delta 7.94(\mathrm{dd}, J=14.5,8.8 \mathrm{~Hz}, 2 \mathrm{H}), 7.35(\mathrm{dd}$, $J=9.2,2.8 \mathrm{~Hz}, 1 \mathrm{H}), 7.25(\mathrm{dd}, J=12.0,6.8 \mathrm{~Hz}, 4 \mathrm{H}), 7.18(\mathrm{t}, J=8.4 \mathrm{~Hz}$, $2 \mathrm{H}), 7.04(\mathrm{~d}, J=2.8 \mathrm{~Hz}, 1 \mathrm{H}), 3.91(\mathrm{~s}, 3 \mathrm{H}), 3.24(\mathrm{dd}, J=9.7,6.0 \mathrm{~Hz}$, 2 H ), 3.13 (dd, $J=9.8,6.1 \mathrm{~Hz}, 2 \mathrm{H}$ ). ${ }^{13} \mathbf{C}$ NMR ( $126 \mathrm{MHz}, \mathrm{CDCl}_{3}$ ) $\delta$ 159.3, 157.4, 141.7, 135.2, 130.4, 128.6, 128.5, 127.8, 126.1, 122.0, 121.9, 105.3, 55.6, 40.8, 36.2.

7-chloro-2-phenethylquinoline (3da): ${ }^{13}$ Yield: $71 \%$ ( $38 \mathrm{mg}, 0.142 \mathrm{mmol}$ ). The title compound was
 isolated as a light brown oil with $2 \%$ ethyl acetate in hexane. ${ }^{1} \mathbf{H}$ NMR $\left(500 \mathrm{MHz}, \mathrm{CDCl}_{3}\right) \delta 8.09(\mathrm{~d}, J=1.7 \mathrm{~Hz}, 1 \mathrm{H}), 8.00(\mathrm{~d}, J=8.4 \mathrm{~Hz}, 1 \mathrm{H})$, 7.69 (d, $J=8.7 \mathrm{~Hz}, 1 \mathrm{H}), 7.44(\mathrm{dd}, J=8.6,2.0 \mathrm{~Hz}, 1 \mathrm{H}), 7.32-7.27(\mathrm{~m}$,
$2 \mathrm{H}), 7.25(\mathrm{t}, J=5.7 \mathrm{~Hz}, 2 \mathrm{H}), 7.23-7.18(\mathrm{~m}, 2 \mathrm{H}), 3.29(\mathrm{dd}, J=9.6,6.4 \mathrm{~Hz}, 2 \mathrm{H}), 3.16(\mathrm{dd}, J=9.5,6.5 \mathrm{~Hz}$, $2 \mathrm{H}) ;{ }^{13} \mathbf{C}$ NMR (126 MHz, $\mathrm{CDCl}_{3}$ ) $\delta 163.1,148.5,141.6,136.0,135.3,128.8,128.6,128.5,128.1,126.9$, 126.2, 125.2, 121.9, 41, 35.8.

5,7-dichloro-2-phenethylquinoline (3ea): Yield: $60 \%$ ( $36 \mathrm{mg}, 0.119 \mathrm{mmol}$ ). The title compound was isolated as a light brown solid with $2 \%$ ethyl acetate in hexane. Selected IR (DCM, $\mathrm{cm}^{-1}$ ): 3062.8, 3027.3,
 $2925.2,2854.6,1605.8,1553.2,1453.6,1391.0,1331.9,1136.8,1061.0$, 967.0, 859.6, 747.3; ${ }^{1} \mathbf{H}$ NMR ( $400 \mathrm{MHz}, \mathrm{CDCl}_{3}$ ) $\delta 8.38(\mathrm{~d}, J=8.6 \mathrm{~Hz}$, $1 \mathrm{H}), 8.00(\mathrm{~d}, J=1.6 \mathrm{~Hz}, 1 \mathrm{H}), 7.56(\mathrm{~d}, J=1.9 \mathrm{~Hz}, 1 \mathrm{H}), 7.32-7.25(\mathrm{~m}$, $3 \mathrm{H}), 7.22(\mathrm{dd}, J=8.8,4.3 \mathrm{~Hz}, 3 \mathrm{H}), 3.34-3.26(\mathrm{~m}, 2 \mathrm{H}), 3.16(\mathrm{dd}, J=9.4$, 6.4 Hz, 2H); ${ }^{13} \mathbf{C}$ NMR (101 MHz, $\mathrm{CDCl}_{3}$ ) $\delta 164.0,148.8,141.3,134.7$, 133.0, 132.2, 128.6, 127.5, 126.8, 126.3, 123.6, 122.7, 40.8, 35.6. HRMS (ESI) m/z: $[\mathrm{M}+\mathrm{H}]^{+}$Calcd for $\mathrm{C}_{17} \mathrm{H}_{13} \mathrm{Cl}_{2} \mathrm{~N}: 302.0498$, Found 302.0510.

4-phenethylquinoline (3fa): ${ }^{\mathbf{1 2}}$ Yield: $92 \%$ ( $43 \mathrm{mg}, 0.184 \mathrm{mmol}$ ). The title compound was isolated as a light brown oil with $2 \%$ ethyl acetate in hexane. ${ }^{1} \mathbf{H} \mathbf{N M R}\left(400 \mathrm{MHz}, \mathrm{CDCl}_{3}\right) \delta 8.79(\mathrm{~d}, J=4.4 \mathrm{~Hz}, 1 \mathrm{H}), 8.14(\mathrm{~d}$,
 $J=8.4 \mathrm{~Hz}, 1 \mathrm{H}), 8.08(\mathrm{~d}, J=8.3 \mathrm{~Hz}, 1 \mathrm{H}), 7.72(\mathrm{ddd}, J=8.3,6.9,1.1 \mathrm{~Hz}, 1 \mathrm{H}), 7.58(\mathrm{t}, J=$ $7.6 \mathrm{~Hz}, 1 \mathrm{H}), 7.31(\mathrm{t}, J=7.3 \mathrm{~Hz}, 2 \mathrm{H}), 7.22(\mathrm{ddd}, J=17.4,10.3,3.6 \mathrm{~Hz}, 4 \mathrm{H}), 3.39(\mathrm{dd}, J=$ $9.3,6.9 \mathrm{~Hz}, 2 \mathrm{H}), 3.08(\mathrm{dd}, J=9.4,6.7 \mathrm{~Hz}, 2 \mathrm{H}) ;{ }^{13} \mathbf{C} \mathbf{N M R}\left(101 \mathrm{MHz}, \mathrm{CDCl}_{3}\right) \delta 150.3$, $148.5,147.5,141.1,130.4,129.2,128.7,128.5,127.6,126.6,126.5,123.5,121.0,36.28$, 34.2 .

2-phenethylquinoxaline (3ga): ${ }^{8}$ Yield: $69 \% ~(32 \mathrm{mg}, 0.138 \mathrm{mmol}$ ). The title compound was isolated as a pale yellow oil with $2 \%$ ethyl acetate in hexane.

${ }^{\mathbf{1}} \mathbf{H}$ NMR $\left(400 \mathrm{MHz}, \mathrm{CDCl}_{3}\right) \delta 8.61(\mathrm{~s}, 1 \mathrm{H}), 8.06(\mathrm{dd}, J=7.9,1.7 \mathrm{~Hz}, 2 \mathrm{H})$, $7.78-7.67(\mathrm{~m}, 2 \mathrm{H}), 7.30-7.16(\mathrm{~m}, 5 \mathrm{H}), 3.32(\mathrm{dd}, J=9.3,6.4 \mathrm{~Hz}, 2 \mathrm{H}), 3.18$ $(\mathrm{dd}, J=9.4,6.4 \mathrm{~Hz}, 2 \mathrm{H}) ;{ }^{\mathbf{1 3}} \mathbf{C} \mathbf{N M R}\left(126 \mathrm{MHz}, \mathrm{CDCl}_{3}\right) \delta 156.6,145.9,142.4$, $141.4,140.9,130.1,129.3,129.2,129.0,128.7,128.6,126.4,38.2,35.4$.

1-benzyl-2-phenethyl-1H-benzo[d]imidazole (3ha): ${ }^{7}$ Yield: $97 \%$ ( $61 \mathrm{mg}, 0.194 \mathrm{mmol}$ ). The title compound was isolated as a light brown solid with $15 \%$ ethyl acetate in hexane. ${ }^{1} \mathbf{H} \mathbf{N M R}(400 \mathrm{MHz}$,
 $\left.\mathrm{CDCl}_{3}\right) \delta 7.84(\mathrm{~d}, J=7.6 \mathrm{~Hz}, 1 \mathrm{H}), 7.27(\mathrm{~d}, J=5.8 \mathrm{~Hz}, 6 \mathrm{H}), 7.22(\mathrm{~d}, J=4.3$ $\mathrm{Hz}, 3 \mathrm{H}), 7.17(\mathrm{~d}, J=7.2 \mathrm{~Hz}, 2 \mathrm{H}), 7.02-6.95(\mathrm{~m}, 2 \mathrm{H}), 5.18(\mathrm{~s}, 2 \mathrm{H}), 3.16(\mathrm{~d}, J$ $=10.0 \mathrm{~Hz}, 4 \mathrm{H}) ;{ }^{13} \mathbf{C} \mathbf{N M R}\left(101 \mathrm{MHz}, \mathrm{CDCl}_{3}\right) \delta 154.6,142.6,140.9,136$, $135.4,129.1,128.6,128.5,128,126.4,126.2,122.5,122.2,119.4,109.6,46.7$, 34.1, 29.7.

1-benzyl-5,6-dichloro-2-phenethyl-1H-benzo[d]imidazole (3ia): Yield: $87 \%$ ( $66 \mathrm{mg}, 0.174 \mathrm{mmol}$ ). The
 title compound was isolated as a light brown solid with $10 \%$ ethyl acetate in hexane. Selected IR (DCM, $\mathrm{cm}^{-1}$ ): 3027.2, 2855.0, 1605.2, 1511.2, 1496.6, 1453.6, 1403.0, 1308.5, 1095.8, 1076.9, 947.2, 841.0, 697.64. ¹H NMR (400 $\left.\mathrm{MHz}, \mathrm{CDCl}_{3}\right) \delta 7.84(\mathrm{~s}, 1 \mathrm{H}), 7.32-7.17(\mathrm{~m}, 7 \mathrm{H}), 7.12(\mathrm{dd}, J=5.0,3.2 \mathrm{~Hz}$, $2 \mathrm{H}), 6.92(\mathrm{dd}, J=6.5,2.9 \mathrm{~Hz}, 2 \mathrm{H}), 5.08(\mathrm{~s}, 2 \mathrm{H}), 3.19-3.04(\mathrm{~m}, 4 \mathrm{H}) ;{ }^{13} \mathbf{C}$ NMR ( $\left.126 \mathrm{MHz}, \mathrm{CDCl}_{3}\right) \delta 156.9$, $142.2,140.6,135.2,134.8,129.3,128.8,128.5,128.4,126.7,126.6,126.4,126.1,120.7,111.1,47.1,34.0$, 29.8; HRMS (ESI) m/z: $[\mathrm{M}+\mathrm{H}]^{+}$Calcd for $\mathrm{C}_{22} \mathrm{H}_{28} \mathrm{Cl}_{2} \mathrm{~N}_{2}$ : 381.0920; Found 381.0930 .

2-phenethylbenzo[d]oxazole (3ja): ${ }^{\mathbf{8}}$ Yield: $78 \%$ ( $35 \mathrm{mg}, 0.157 \mathrm{mmol}$ ). The title compound was isolated as a light brown oil with $2 \%$ ethyl acetate in hexane. ${ }^{1} \mathbf{H} \mathbf{N M R}\left(400 \mathrm{MHz}, \mathrm{CDCl}_{3}\right) \delta 7.70-7.65(\mathrm{~m}, 1 \mathrm{H})$,
 $7.50-7.45(\mathrm{~m}, 1 \mathrm{H}), 7.33-7.17(\mathrm{~m}, 7 \mathrm{H}), 3.23(\mathrm{~d}, J=3.1 \mathrm{~Hz}, 4 \mathrm{H}) ;{ }^{13} \mathbf{C}$ NMR $\left(101 \mathrm{MHz}, \mathrm{CDCl}_{3}\right) \delta 156.8,144.8,144.2,142.4,140.9,128.6,128.5,126.3$, 37.3, 35.5.

4-phenethylpyrimidine (3ka): ${ }^{\mathbf{1 4}}$ Yield: $77 \%$ ( $28 \mathrm{mg}, 0.154 \mathrm{mmol}$ ). The title compound was isolated as a
 light brown oil with $5 \%$ ethyl acetate in hexane. ${ }^{\mathbf{1}} \mathbf{H} \mathbf{N M R}\left(500 \mathrm{MHz}, \mathrm{CDCl}_{3}\right) \delta$ $9.18(\mathrm{~s}, 1 \mathrm{H}), 8.59(\mathrm{~d}, J=3.0 \mathrm{~Hz}, 1 \mathrm{H}), 7.30(\mathrm{t}, J=7.4 \mathrm{~Hz}, 2 \mathrm{H}), 7.21(\mathrm{dd}, J=15.8$, $7.5 \mathrm{~Hz}, 3 \mathrm{H}), 7.10(\mathrm{~d}, J=4.2 \mathrm{~Hz}, 1 \mathrm{H}), 3.10(\mathrm{~s}, 4 \mathrm{H}) ;{ }^{13} \mathbf{C} \mathbf{N M R}\left(126 \mathrm{MHz}, \mathrm{CDCl}_{3}\right)$ $\delta 169.7,158.9,156.8,140.7,128.6,128.5,126.4,120.8,39.6,34.8$

N,N-dibenzyl-4-phenethylpyrimidin-2-amine (3la): Yield: $82 \%$ ( $62 \mathrm{mg}, 0.164 \mathrm{mmol}$ ). The title
 compound was isolated as a light brown oil with $2 \%$ ethyl acetate in hexane. Selected IR (DCM, $\mathrm{cm}^{-1}$ ): 3085.4, 3061.4, 3028.2, 1575.4, 1556.9, 1503.6, $1452.6,1421.8,1348.9,696.6 ;{ }^{1} \mathbf{H} \mathbf{N M R}\left(500 \mathrm{MHz}, \mathrm{CDCl}_{3}\right) \delta 8.23(\mathrm{~d}, J=$ $4.9 \mathrm{~Hz}, 1 \mathrm{H}), 7.37-7.31(\mathrm{~m}, 4 \mathrm{H}), 7.31-7.24(\mathrm{~m}, 8 \mathrm{H}), 7.19(\mathrm{dd}, J=12.6,7.1 \mathrm{~Hz}, 3 \mathrm{H}), 6.39(\mathrm{~d}, J=4.9 \mathrm{~Hz}$, $1 \mathrm{H}), 4.92(\mathrm{~s}, 4 \mathrm{H}), 3.04(\mathrm{t}, J=7.7 \mathrm{~Hz}, 2 \mathrm{H}), 2.93(\mathrm{t}, J=7.8 \mathrm{~Hz}, 2 \mathrm{H}),{ }^{13} \mathbf{C} \mathbf{N M R}\left(126 \mathrm{MHz}, \mathrm{CDCl}_{3}\right) \delta 170.3$, $162.3,157.8,141.7,138.9,128.6,126.5,128.4,127.9,127.1,126.0,109.3,49.14,39.50,34.29$. HRMS (ESI) m/z: $[\mathrm{M}+\mathrm{H}]^{+}$Calcd for $\mathrm{C}_{26} \mathrm{H}_{24} \mathrm{~N}_{3}: 380.2121$; Found 380.2133.

2-phenethylpyrazine (3ma): ${ }^{\mathbf{1 4}}$ Yield: $99 \% ~(36 \mathrm{mg}, 0.198 \mathrm{mmol}$ ). The title compound was isolated as a light brown oil with $5 \%$ ethyl acetate in hexane. ${ }^{1} \mathbf{H} \mathbf{N M R}\left(400 \mathrm{MHz}, \mathrm{CDCl}_{3}\right) \delta 8.52-8.48(\mathrm{~m}, 1 \mathrm{H}), 8.41$
 $-8.32(\mathrm{~m}, 2 \mathrm{H}), 7.26(\mathrm{t}, J=7.3 \mathrm{~Hz}, 2 \mathrm{H}), 7.21-7.12(\mathrm{~m}, 3 \mathrm{H}), 3.14-3.08(\mathrm{~m}, 2 \mathrm{H})$, $3.08-3.02(\mathrm{~m}, 2 \mathrm{H}) ;{ }^{13} \mathbf{C}$ NMR ( $126 \mathrm{MHz}, \mathrm{CDCl}_{3}$ ) $\delta 156.9,144.8,144.2,142.5$, $140.9,128.6,128.5,126.3,37.3,35.5$.

3-phenethylpyridazine: ${ }^{15}$ (3na) Yield: $60 \% ~(22 \mathrm{mg}, 0.120 \mathrm{mmol})$. The title compound was isolated as a light brown oil with $40 \%$ ethyl acetate in hexane. ${ }^{1} \mathbf{H}$ NMR $\left(500 \mathrm{MHz}, \mathrm{CDCl}_{3}\right) \delta 9.08(\mathrm{~d}, J=3.9 \mathrm{~Hz}, 1 \mathrm{H})$,
 7.35 (dd, $J=8.1,4.6 \mathrm{~Hz}, 1 \mathrm{H}), 7.32-7.27(\mathrm{~m}, 2 \mathrm{H}), 7.21(\mathrm{q}, J=7.5 \mathrm{~Hz}, 4 \mathrm{H}), 3.35$ $-3.29(\mathrm{~m}, 2 \mathrm{H}), 3.19-3.13(\mathrm{~m}, 2 \mathrm{H}) ;{ }^{13} \mathbf{C}$ NMR ( $126 \mathrm{MHz}, \mathrm{CDCl}_{3}$ ) $\delta 170.2,163$, 149.7, 140.7, 128.5, 126.5, 126.3, 126.2, 38.2, 35.6.
 was isolated as a white solid with $10 \%$ ethyl acetate in hexane. ${ }^{1} \mathbf{H} \mathbf{N M R}\left(400 \mathrm{MHz}, \mathrm{CDCl}_{3}\right) \delta 8.58(\mathrm{~d}, J=$
 $4.7 \mathrm{~Hz}, 1 \mathrm{H}), 7.62-7.55(\mathrm{~m}, 3 \mathrm{H}), 7.52(\mathrm{~d}, J=8.2 \mathrm{~Hz}, 2 \mathrm{H}), 7.43(\mathrm{t}, J=7.6 \mathrm{~Hz}$, 2H), $7.36-7.25(\mathrm{~m}, 3 \mathrm{H}), 7.16-7.09(\mathrm{~m}, 2 \mathrm{H}), 3.18-3.07(\mathrm{~m}, 4 \mathrm{H})$; 13C NMR $\left(126 \mathrm{MHz}, \mathrm{CDCl}_{3}\right) \delta 161.3,149.5,141.2,140.9,139.0,136.5,129.0,128.9$, 127.3, 127.2, 127.1, 123.2, 121.3, 40.3, 35.8.

2-(2-(naphthalen-2-yl)ethyl)pyridine (30j): ${ }^{17}$ Yield: $54 \%$ ( $25 \mathrm{mg}, 0.108 \mathrm{mmol}$ ). The title compound was isolated as a white solid with $10 \%$ ethyl acetate in hexane. ${ }^{1} \mathbf{H} \mathbf{N M R}\left(400 \mathrm{MHz}, \mathrm{CDCl}_{3}\right) \delta 8.58(\mathrm{dd}, J=4.8$,

$1.3 \mathrm{~Hz}, 1 \mathrm{H}), 7.77(\mathrm{ddd}, J=9.1,8.1,5.2 \mathrm{~Hz}, 3 \mathrm{H}), 7.63(\mathrm{~s}, 1 \mathrm{H}), 7.55(\mathrm{td}, J=7.7$,
$1.9 \mathrm{~Hz}, 1 \mathrm{H}), 7.47-7.39$ (m, 2H), 7.36 (dd, $J=8.4,1.7 \mathrm{~Hz}, 1 \mathrm{H}$ ), 7.11 (ddd, $J$
$=15.4,7.6,4.3 \mathrm{~Hz}, 2 \mathrm{H}), 3.26-3.16(\mathrm{~m}, 4 \mathrm{H}) ;{ }^{13} \mathbf{C} \mathbf{N M R}\left(126 \mathrm{MHz}, \mathrm{CDCl}_{3}\right) \delta$ $161.3,149.5,139.2,136.5,133.8,132.2,128.0,127.7,127.6,127.5,126.7,126.0,125.3,123.2,121.3,40.2$, 36.3.

4-(2-([1,1'-biphenyl]-4-yl)ethyl)pyridine (3pd): ${ }^{\mathbf{1 4}}$ Yield: $77 \%$ ( $40 \mathrm{mg}, 0.154 \mathrm{mmol}$ ). The title compound was isolated as a white solid with $10 \%$ ethyl acetate in hexane. ${ }^{1} \mathbf{H} \mathbf{~ N M R ~}\left(500 \mathrm{MHz}, \mathrm{CDCl}_{3}\right) \delta 8.52(\mathrm{~d}, J=$
 $5.2 \mathrm{~Hz}, 2 \mathrm{H}), 7.60(\mathrm{~d}, J=7.6 \mathrm{~Hz}, 2 \mathrm{H}), 7.54(\mathrm{~d}, J=8.0 \mathrm{~Hz}, 2 \mathrm{H}), 7.45(\mathrm{t}, J=$ $7.6 \mathrm{~Hz}, 2 \mathrm{H}), 7.35(\mathrm{t}, J=7.3 \mathrm{~Hz}, 1 \mathrm{H}), 7.24(\mathrm{~d}, J=8.0 \mathrm{~Hz}, 2 \mathrm{H}), 7.13(\mathrm{~d}, J=$ $5.4 \mathrm{~Hz}, 2 \mathrm{H}), 2.99(\mathrm{~s}, 4 \mathrm{H}) ;{ }^{13} \mathbf{C}$ NMR ( $126 \mathrm{MHz}, \mathrm{CDCl}_{3}$ ) $\delta 150.4,149.7,140.8,139.7,139.2,128.8,128.7$, 127.2, 127.1, 126.9, 123.9, 37.0, 36.1.

4-(2-(naphthalen-2-yl)ethyl)pyridine (3pj): ${ }^{\mathbf{1 4}}$ Yield: $81 \%$ ( $38 \mathrm{mg}, 0.162 \mathrm{mmol}$ ). The title compound was isolated as a white solid with $10 \%$ ethyl acetate in hexane. ${ }^{1} \mathbf{H}$ NMR ( $500 \mathrm{MHz}, \mathrm{CDCl}_{3}$ ) $\delta 8.49(\mathrm{~d}, J=4.7$
 $\mathrm{Hz}, 2 \mathrm{H}), 7.85-7.71(\mathrm{~m}, 3 \mathrm{H}), 7.58(\mathrm{~s}, 1 \mathrm{H}), 7.50-7.39(\mathrm{~m}, 2 \mathrm{H}), 7.30(\mathrm{~d}, J=$ $8.3 \mathrm{~Hz}, 1 \mathrm{H}), 7.10(\mathrm{~d}, J=5.0 \mathrm{~Hz}, 2 \mathrm{H}), 3.14-3.06$ (m, 2H), $3.05-2.98$ (m, $2 \mathrm{H}),{ }^{13} \mathbf{C}$ NMR ( $126 \mathrm{MHz}, \mathrm{CDCl}_{3}$ ) $\delta$ 150.6, 149.9, 138.3, 133.7, 132.3, 128.2, 127.8, 127.6, 127.2, 126.7, 126.2, 125.5, 124.1, 37.1, 36.9.

4-(2-cyclopropylethyl)pyridine (3ps): Yield: $65 \%$ ( $19 \mathrm{mg}, 0.130 \mathrm{mmol}$ ). The title compound was isolated as a light brown oil with 5\% ethyl acetate in hexane. Selected IR (DCM, $\mathrm{cm}^{-1}$ ): 3076.2, 2998.1, 2923.4,
 2855.5, 1557.8, 1602.7, 1415.7, 1016.0, 799.8, 521.9; ${ }^{1} \mathbf{H}$ NMR ( $500 \mathrm{MHz}, \mathrm{CDCl}_{3}$ ) $\delta$ 8.47 (s, 2H), 7.11 (d, $J=3.2 \mathrm{~Hz}, 2 \mathrm{H}), 2.70(\mathrm{t}, J=7.6 \mathrm{~Hz}, 2 \mathrm{H}), 1.52(\mathrm{dd}, J=15.0,7.2$ $\mathrm{Hz}, 2 \mathrm{H}), 0.68(\mathrm{dd}, J=9.7,4.7 \mathrm{~Hz}, 1 \mathrm{H}), 0.43(\mathrm{q}, J=5.0 \mathrm{~Hz}, 2 \mathrm{H}), 0.08-0.02(\mathrm{~m}, 2 \mathrm{H})$; ${ }^{13}$ C NMR ( $126 \mathrm{MHz}, \mathrm{CDCl}_{3}$ ) $\delta 151.7,149.7,124.2,35.6,35.5,10.7,4.7$; HRMS (ESI) m/z: $[\mathrm{M}+\mathrm{H}]^{+}$Calcd for $\mathrm{C}_{10} \mathrm{H}_{13} \mathrm{~N}: 148.1121$; Found 148.1118.
(R)-4-(4,8-dimethylnon-7-en-1-yl)pyridine (3pt): Yield: $63 \%$ ( $29 \mathrm{mg}, 0.126 \mathrm{mmol}$ ). The title compound
 was isolated as a light brown oil with 5\% ethyl acetate in hexane Selected IR (DCM, $\mathrm{cm}^{-1}$ ): 2926.1, 2856.1, 1603.4, 1558.7, 1456.0, 1415.5, 1376.9, 1219.4, 1069.1, 993.0, 797.4, ${ }^{1} \mathbf{H}$ NMR ( $500 \mathrm{MHz}, \mathrm{CDCl}_{3}$ ) $\delta 8.47(\mathrm{~d}, J=4.9 \mathrm{~Hz}, 2 \mathrm{H}), 7.09(\mathrm{~d}, J=$ $5.0 \mathrm{~Hz}, 2 \mathrm{H}), 5.08(\mathrm{t}, J=6.9 \mathrm{~Hz}, 1 \mathrm{H}), 2.57(\mathrm{td}, J=8.1,3.3 \mathrm{~Hz}, 2 \mathrm{H}), 2.02-1.87(\mathrm{~m}$, $2 \mathrm{H}), 1.67(\mathrm{~s}, 3 \mathrm{H}), 1.66-1.59(\mathrm{~m}, 2 \mathrm{H}), 1.58(\mathrm{~s}, 3 \mathrm{H}), 1.42(\mathrm{dt}, J=13.0,6.6 \mathrm{~Hz}, 1 \mathrm{H}), 1.37-1.27(\mathrm{~m}, 2 \mathrm{H})$, 1.15 (tdd, $J=12.9,8.2,4.5 \mathrm{~Hz}, 2 \mathrm{H}), 0.86(\mathrm{~d}, J=6.6 \mathrm{~Hz}, 3 \mathrm{H}) ;{ }^{13} \mathbf{C}$ NMR ( $126 \mathrm{MHz}, \mathrm{CDCl}_{3}$ ) $\delta 151.9,149.7$, 131.3, 125, 124.0, 37.1, 36.6, 35.7, 32.4, 27.9, 25.8, 25.6, 19.6, 17.8; HRMS (ESI) m/z: [M+H] Calcd for $\mathrm{C}_{16} \mathrm{H}_{25} \mathrm{~N}: ~ 232.2060$; Found 232.2072 .

2,5-diphenethylpyrazine (3qaa): ${ }^{14}$ Yield: $52 \%$ ( $30 \mathrm{mg}, 0.104 \mathrm{mmol}$ ). The title compound was isolated as
 a light yellow solid with $2 \%$ ethyl acetate in hexane. ${ }^{1} \mathbf{H}$ NMR $(500 \mathrm{MHz}$, $\left.\mathrm{CDCl}_{3}\right) \delta 8.25(\mathrm{~s}, 2 \mathrm{H}), 7.28-7.22(\mathrm{~m}, 4 \mathrm{H}), 7.16(\mathrm{dd}, J=16.9,7.7 \mathrm{~Hz}, 6 \mathrm{H})$, $3.09-2.99(\mathrm{~m}, 8 \mathrm{H}) ;{ }^{13} \mathbf{C} \mathbf{~ N M R}\left(126 \mathrm{MHz}, \mathrm{CDCl}_{3}\right) \delta 154,143.8,141.1,128.6$,
128.5, 126.3, 37, 35.7.

2,4,6-triphenethyl-1,3,5-triazine (3raaa): Yield: $50 \%$ ( $39 \mathrm{mg}, 0.099 \mathrm{mmol}$ ). The title compound was isolated as a light brown solid with 5\% ethyl acetate in hexane. Selected IR $\left(\mathrm{CDCl}_{3}, \mathrm{~cm}^{-1}\right): 3085.8,3063.0$,
 3027.0, 2929.5, 2860.9, 1541.5, 1496.2, 1453.5, 1383.4, 1076.5, 1029.0, 909.8, 696.8, $747.7,544.8,488.6$; ${ }^{1} \mathbf{H}$ NMR ( $500 \mathrm{MHz}, \mathrm{CDCl}_{3}$ ) $\delta 7.27$ (dq, $J$ $=16.7,7.4 \mathrm{~Hz}, 15 \mathrm{H}), 3.23-3.11(\mathrm{~m}, 12 \mathrm{H}) ;{ }^{13} \mathbf{C}$ NMR $\left(126 \mathrm{MHz}, \mathrm{CDCl}_{3}\right) \delta$ 178.2, 141, 128.5, 128.4, 126.1, 40.4, 33.6; HRMS (ESI) m/z: [M+H] ${ }^{+}$Calcd for $\mathrm{C}_{27} \mathrm{H}_{27} \mathrm{~N}_{3}: 394.2278$; Found 394.2285.

## 5. Synthesis of drug molecules ( $\pm$ )-cuspareine (5ai) ${ }^{18}$ and ( $\pm$ )-angustureine (5am) ${ }^{19}$. 5.1 ( $\pm$ )-Cuspareine (5ai):



2-(3,4-dimethoxyphenethyl)quinoline 3ai ( $77 \mathrm{mg}, 0.26 \mathrm{mmol}$ ) and $\mathrm{NiCl}_{2} .6 \mathrm{H}_{2} \mathrm{O}(0.052 \mathrm{mmol})$ were taken in a 50 mL round bottom flask and dissolved in 3 mL of methanol. After that, $\mathrm{NaBH}_{4}$ ( 1.105 mmol ) was added in portion at $0^{\circ} \mathrm{C}$ and stirred for 30 min at RT. After completion of reaction, methanol was evaporated and dissolve in $10 \% \mathrm{HCl}$, the acidic solution was then basified by adding concentrated ammonium hydroxide solution and extracted with ether. The extract was dried over $\mathrm{Na}_{2} \mathrm{SO}_{4}$, evaporated and purified by column chromatography. The desired product, 2-(3,4-dimethoxyphenethyl)-1,2,3,4-tetrahydroquinoline was obtained in $93 \%$ ( $72 \mathrm{mg}, 0.24 \mathrm{mmol}$ ) isolated yield. 2-(3,4-dimethoxyphenethyl)-1,2,3,4tetrahydroquinoline was obtained in $93 \%(72 \mathrm{mg}, 0.24 \mathrm{mmol}) \mathrm{K}_{2} \mathrm{CO}_{3}(33 \mathrm{mg}, 0.24 \mathrm{mmol})$ and MeI ( 1.44 mmol ) in THF ( 3 mL ) were charged in a 15 mL sealed tube and reflux for 20 h . After completion of reaction, the reaction mixture was cooled to room temperature and quenched by adding $\mathrm{H}_{2} \mathrm{O}$. The reaction mixture was extracted with EtOAC, dried over $\mathrm{Na}_{2} \mathrm{SO}_{4}$ then concentrated in vacuo. Purification was done by column chromatography to yield of the desired product 5ai in $80 \%$ ( $60 \mathrm{mg}, 0.192 \mathrm{mmol}$ ).

2-(3,4-dimethoxyphenethyl)-1-methyl-1,2,3,4-tetrahydroquinoline (5ai): ${ }^{\mathbf{1 8}}{ }^{\mathbf{1}} \mathbf{H} \mathbf{N M R}$ (500 MHz, $\left.\mathrm{CDCl}_{3}\right) \delta 7.12(\mathrm{t}, J=7.7 \mathrm{~Hz}, 1 \mathrm{H}), 7.02(\mathrm{~d}, J=7.3 \mathrm{~Hz}, 1 \mathrm{H}), 6.82(\mathrm{~d}, J=8.0 \mathrm{~Hz}, 1 \mathrm{H}), 6.78-6.73(\mathrm{~m}, 2 \mathrm{H})$, 6.63 (t, $J=7.3 \mathrm{~Hz}, 1 \mathrm{H}$ ), 6.57 (d, $J=8.2 \mathrm{~Hz}, 1 \mathrm{H}$ ), $3.90(\mathrm{~s}, 3 \mathrm{H}), 3.88(\mathrm{~s}, 3 \mathrm{H}), 3.32(\mathrm{td}, J=8.4,4.2 \mathrm{~Hz}, 1 \mathrm{H})$, $2.95(\mathrm{~s}, 3 \mathrm{H}), 2.93-2.84(\mathrm{~m}, 1 \mathrm{H}), 2.76-2.67(\mathrm{~m}, 2 \mathrm{H}), 2.57(\mathrm{ddd}, J=14.0,10.1,6.5 \mathrm{~Hz}, 1 \mathrm{H}), 2.03-1.90$ $(\mathrm{m}, 3 \mathrm{H}), 1.82-1.72(\mathrm{~m}, 1 \mathrm{H}) ;{ }^{13} \mathbf{C}$ NMR ( $126 \mathrm{MHz}, \mathrm{CDCl}_{3}$ ) $\delta 149.0,147.3,145.4,134.8,128.8,127.2$, $121.8,120.2,115.5,111.8,111.5,110.7,58.5,56.00,55.9,38.2,33.2,32.0,24.5,23.7$.

## 5.2 ( $\pm$ )-Angustureine (5am) ${ }^{19}$.



2-pentylquinoline (3am) ( 0.16 mmol ) and $\mathrm{NiCl}_{2} \cdot 6 \mathrm{H}_{2} \mathrm{O}(0.028 \mathrm{mmol})$ were taken in a 50 mL RB and dissolve in 2 mL of methanol. After that, $\mathrm{NaBH}_{4}(0.64 \mathrm{mmol})$ was added in portion at $0^{\circ} \mathrm{C}$ and stirred for 30 min at RT. After completion of reaction, methanol was evaporated and dissolve in $10 \% \mathrm{HCl}$, the acidic solution was then basified by adding concentrated ammonium hydroxide solution and extracted with ether. The extract was dried over $\mathrm{Na}_{2} \mathrm{SO}_{4}$, evaporated and purified by column chromatography. The desired product 2-pentyl-1,2,3,4-tetrahydroquinoline was obtained in $89 \%$ ( $29 \mathrm{mg}, 0.142 \mathrm{mmol}$ ) isolated yield. 2-pentyl-1,2,3,4-tetrahydroquinoline ( $29 \mathrm{mg}, 0.142 \mathrm{mmol}$ ), $\mathrm{K}_{2} \mathrm{CO}_{3}(20 \mathrm{mg}, 0.142 \mathrm{mmol})$ and MeI $(0.62$ mmol ) in THF ( 2 mL ) were charged in a 15 mL sealed tube and reflux for 20 h . After completion of reaction, the reaction mixture was cooled to room temperature and quenched by adding $\mathrm{H}_{2} \mathrm{O}$. The reaction mixture was extracted with EtOAC, dried over $\mathrm{Na}_{2} \mathrm{SO}_{4}$ then concentrated in vacuo. Purification was done by column chromatography to yield of the desired product 5am in $82 \%$ ( $25 \mathrm{mg}, 0.115 \mathrm{mmol}$ ).

1-methyl-2-pentyl-1,2,3,4-tetrahydroquinoline (5am): ${ }^{\mathbf{1 2}}{ }^{\mathbf{1}} \mathbf{H} \mathbf{N M R}\left(400 \mathrm{MHz}, \mathrm{CDCl}_{3}\right) \delta 7.09(\mathrm{t}, \mathrm{J}=7.7$ $\mathrm{Hz}, 1 \mathrm{H}), 6.98(\mathrm{~d}, J=7.2 \mathrm{~Hz}, 1 \mathrm{H}), 6.59(\mathrm{t}, J=7.3 \mathrm{~Hz}, 1 \mathrm{H}), 6.53(\mathrm{~d}, J=8.2 \mathrm{~Hz}, 1 \mathrm{H}), 3.24(\mathrm{td}, J=8.5,4.1$ $\mathrm{Hz}, 1 \mathrm{H}), 2.94(\mathrm{~s}, 3 \mathrm{H}), 2.87-2.76(\mathrm{~m}, 1 \mathrm{H}), 2.66(\mathrm{dt}, J=16.2,4.2 \mathrm{~Hz}, 1 \mathrm{H}), 1.90(\mathrm{dt}, J=12.3,4.5 \mathrm{~Hz}, 2 \mathrm{H})$, $1.66-1.57(\mathrm{~m}, 1 \mathrm{H}), 1.45-1.26(\mathrm{~m}, 7 \mathrm{H}), 0.91(\mathrm{t}, J=6.8 \mathrm{~Hz}, 3 \mathrm{H}) ;{ }^{13} \mathbf{C}$ NMR ( $126 \mathrm{MHz}, \mathrm{CDCl}_{3}$ ) $\delta 145.6$, $128.8,127.2,122.0,115.3,110.6,59.1,38.1,32.2,31.4,25.9,24.6,23.7,22.8,14.2$.

## 6. Mechanistic studies.

### 6.1. Reaction with isotope labeled alcohol in ${ }^{t} \mathrm{AmOH}$ solvent.



In a 15 mL reaction tube, $\mathbf{1 a}(0.1 \mathrm{mmol}), \alpha, \alpha-\mathrm{D}_{2}-\mathbf{2 d}(0.15 \mathrm{mmol}), \mathbf{M n}-3(2 \mathrm{~mol} \%)$ and ${ }^{\dagger} \mathrm{BuOK}$ ( 1 equiv.) were taken. Then ${ }^{t} \mathrm{AmOH}(0.05 \mathrm{~mL})$ was added and the tube was closed before the reaction mixture was placed in a preheated oil bath at $140^{\circ} \mathrm{C}$ for 24 h . After completion, reaction mixture was quenched with water $(0.05 \mathrm{~mL})$ and extracted with ethylacetate $(3 \times 2)$. The combined organic layers were dried over $\mathrm{Na}_{2} \mathrm{SO}_{4}$, filtered, and concentrated. The residue was purified by column chromatography over silica gel (100-200 mesh) with hexane/ethyl acetate mixture as eluent. $28 \mathrm{mg}, 0.091 \mathrm{mmol}(91 \%)$ yield of the desired product (3ad-D) was obtained.


${ }^{1} \mathrm{H}$ NMR in $\mathrm{CDCl}_{3}(500 \mathrm{MHz})$



Figure S1. ${ }^{1} \mathrm{H}$ NMR of 3ad-D for the estimation of deuterium incorporation.

### 6.2.1 Reaction with isotope labeled alcohol in dioxane solvent.



In a 15 mL reaction tube, $\mathbf{1 a}(0.1 \mathrm{mmol}), \alpha, \alpha-\mathrm{D}_{2}-\mathbf{2 d}(0.15 \mathrm{mmol}), \mathbf{M n}-3(2 \mathrm{~mol} \%)$ and ${ }^{t} \mathrm{BuOK}$ ( 1 equiv.) were taken. Then dioxane $(0.05 \mathrm{~mL})$ was added and the tube was closed before the reaction mixture was placed in a preheated oil bath at $140^{\circ} \mathrm{C}$ for 24 h . After completion, reaction mixture was quenched with water $(0.05 \mathrm{~mL})$ and extracted with ethylacetate $(3 \times 2)$. The combined organic layers were dried over $\mathrm{Na}_{2} \mathrm{SO}_{4}$, filtered, and concentrated. The residue was purified by column chromatography over silica gel (100-200 mesh) with hexane/ethyl acetate mixture as eluent. $29 \mathrm{mg}, 0.093 \mathrm{mmol}(93 \%)$ yield of the desired product (3ad-D) was obtained.


Figure S2. ${ }^{1} \mathrm{H}$ NMR of 3ad-D for the estimation of deuterium incorporation.

### 6.2.2 Determination of kinetic isotope effect.



Two parallel reactions were carried out by $\mathbf{1 a}(0.1 \mathrm{mmol})$ with $\mathbf{2 d}(0.15 \mathrm{mmol})$ and $\alpha, \alpha-D_{2}-2 d(0.15 \mathrm{mmol})$ under the standard reaction condition in dioxane solvent for 1 h . GC analysis revealed $39 \%$ and $21 \%$ yields of the desired product respectively. This corresponds to $k_{\mathrm{H}} / k_{\mathrm{D}}=1.85$.

### 6.3. Olefination of 2 -methyl quinoline (1a) with benzaldehyde without catalyst.



2-methyl quinoline 1a ( 0.1 mmol ), benzaldehyde 2'a ( 0.1 mmol ) and ${ }^{t} \mathrm{BuOK}$ ( 1 equiv.) in ${ }^{t} \mathrm{AmOH}$ were taken in a 15 mL sealed tube under argon atmosphere. After that, the reaction mixture was placed in a preheated oil bath at $140^{\circ} \mathrm{C}$. After 2 h , the crude reaction mixture was analyzed by GC and $20 \%$ yield of 4aa was obtained using mesitylene as an internal standard.

### 6.4. Olefination of 2-methyl quinoline (1a) with benzaldehyde with catalyst.



2-methyl quinoline 1a ( 0.1 mmol ), benzaldehyde 2'a ( 0.1 mmol ), $\mathbf{M n - 3}$ ( $2 \mathrm{~mol} \%$ ) and ${ }^{t} \mathrm{BuOK}$ ( 1 equiv.) in ${ }^{t} \mathrm{AmOH}$ were taken in a 15 mL sealed tube under argon atmosphere. After that, the reaction mixture was placed in a preheated oil bath at $140^{\circ} \mathrm{C}$. After 2 h , the crude reaction mixture was analyzed by GC and $25 \%$ yield of 4aa was obtained using mesitylene as an internal standard.
6.5. Manganese catalyzed hydrogenation of $(E)-2-(2-([1,1$ '-biphenyl]-4-yl)vinyl)quinoline (4ad) with 2d.


In a 15 mL sealed tube, $\mathbf{M n}-\mathbf{3}$ ( $2 \mathrm{~mol} \%$ ), 4ad ( 0.1 mmol ), biphenyl methanol $\mathbf{2 d}(0.1 \mathrm{mmol})$, ${ }^{\mathrm{t}} \mathrm{BuOK}(1$ equiv.) and dioxane ( 0.05 mL ) were taken and tube was sealed. After that, the reaction mixture was placed in a preheated oil bath at $140^{\circ} \mathrm{C}$ for 12 h under argon atmosphere. Upon completion of reaction, the reaction mixture was quenched with water and extracted with ethyl acetate. $83 \%$ of the isolated yield of the hydrogenation product $\mathbf{3 a d}$ was obtained. The formation of corresponding ester $\mathbf{5 d}$ in $\mathbf{6 2 \%}$ yield was observed. We could also notice the aldehyde $\mathbf{2}$ 'd in trace amount, which were confirmed by ${ }^{1} \mathrm{H}$ NMR spectroscopy.


Figure S3. ${ }^{1} \mathrm{H}$ NMR of a mixture of ester ( $\mathbf{5 d}$ ) and aldehyde ( $\mathbf{2}^{\prime} \mathbf{d}$ ).

### 6.6. Manganese catalyzed hydrogenation of (E)-2-(2-([1,1'-biphenyl]-4-yl)vinyl)quinoline (4ad) with

 $\alpha, \alpha-D_{2}-2 d$.

In a 15 mL sealed tube, $\mathbf{M n}-\mathbf{3}(2 \mathrm{~mol} \%), \mathbf{4 a d}(0.1 \mathrm{mmol}), \alpha, \alpha-\mathrm{D}_{2}-\mathbf{2 d}(0.1 \mathrm{mmol}),{ }^{\text {t }} \mathrm{BuOK}(1$ equiv.) in dioxane $(0.05 \mathrm{~mL})$ were taken and tube was sealed. After that, the reaction mixture was placed in a preheated oil bath at $140^{\circ} \mathrm{C}$ for 12 h under argon atmosphere. Upon completion of reaction, the reaction mixture was quenched with water and extracted with ethyl acetate. $97 \%$ of the isolated yield of the desired product was obtained (3ad-D) with $35 \%$ deuterium incorporation at the $\beta$ position and $22 \%$ deuterium incorporation at $\alpha$-position of the desired saturated product.


Figure S4. ${ }^{1} \mathrm{H}$ NMR of 3ad-D for the estimation of deuterium incorporation.

### 6.7 Kinetic monitoring of the reaction.

In a 15 mL sealed tube, 2-methylquinoline $\mathbf{1 a}(0.1 \mathrm{mmol})$, benzyl alcohol $\mathbf{2 a}(0.15 \mathrm{mmol}), \mathbf{M n} \mathbf{- 3}(2 \mathrm{~mol} \%)$ and ${ }^{\text {' }} \mathrm{BuOK}(0.1 \mathrm{mmol})$ were taken under argon atmosphere. After that the tube was closed before the reaction mixture was placed in preheated oil bath at $140{ }^{\circ} \mathrm{C}$. The reaction mixture was analyzed by GC using mesitylene as an internal standard at specified time interval.
Table S5. Kinetic monitoring of the reaction of 1a with 2a.

| Time $(\mathrm{h})$ | $[\mathbf{1 a}] \mathrm{mmol}$ | $[\mathbf{2 a}] \mathrm{mmol}$ | $[\mathbf{3 a}] \mathrm{mmol}$ | $[\mathbf{4 a a}] \mathrm{mmol}$ | $[\mathbf{2} \mathbf{a}] \mathrm{mmol}$ |
| :---: | :---: | :---: | :---: | :---: | :---: |
| 0 | 0.1 | 0.15 | 0 | 0 | 0 |
| 0.5 | 0.07 | 0.107 | 0.01 | 0.019 | 0.001 |
| 1 | 0.051 | 0.073 | 0.032 | 0.014 | 0.003 |
| 2 | 0.025 | 0.028 | 0.06 | 0.013 | 0.002 |
| 4 | 0.02 | 0.012 | 0.077 | 0.004 | 0.0015 |
| 6 | 0.015 | 0.011 | 0.081 | 0.003 | 0.0015 |
| 8 | 0.011 | 0.001 | 0.085 | 0.002 | 0.001 |
| 12 | 0.001 | 0 | 0.095 | 0 | 0 |



Figure S5: Graphical representation for the kinetic profile.

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## 8. Copies of ${ }^{1} \mathrm{H}$ and ${ }^{13} \mathrm{C}$ NMR spectra.




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${ }^{13} \mathrm{C}$ NMR in $\mathrm{CDCl}_{3}(101 \mathrm{MHz})$










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${ }^{13} \mathrm{C}$ NMR in $\mathrm{CDCl}_{3}(101 \mathrm{MHz})$







${ }^{13} \mathrm{C}$ NMR in $\mathrm{CDCl}_{3}(126 \mathrm{MHz})$





${ }^{1} \mathrm{H}$ NMR in $\mathrm{CDCl}_{3}(400 \mathrm{MHz})$


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${ }^{13} \mathrm{C}$ NMR in $\mathrm{CDCl}_{3}(126 \mathrm{MHz})$



${ }^{13} \mathrm{C}$ NMR in $\mathrm{CDCl}_{3}(126 \mathrm{MHz})$


${ }^{1} \mathrm{H}$ NMR in $\mathrm{CDCl}_{3}(500 \mathrm{MHz})$



${ }^{13} \mathrm{C} \mathrm{NMR} \mathrm{in}^{\mathrm{CDCl}} 3$ ( 126 MHz )




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${ }^{1} \mathrm{H}$ NMR in $\mathrm{CDCl}_{3}(400 \mathrm{MHz})$


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${ }^{1} \mathrm{H}$ NMR in $\mathrm{CDCl}_{3}(400 \mathrm{MHz})$

${ }^{13} \mathrm{C}$ NMR in $\mathrm{CDCl}_{3}(126 \mathrm{MHz})$



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${ }^{13} \mathrm{C}$ NMR in $\mathrm{CDCl}_{3}(101 \mathrm{MHz})$





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${ }^{13} \mathrm{C}$ NMR in $\mathrm{CDCl}_{3}(101 \mathrm{MHz})$



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${ }^{13} \mathrm{C}$ NMR in $\mathrm{CDCl}_{3}(126 \mathrm{MHz})$



${ }^{1} \mathrm{H}$ NMR in $\mathrm{CDCl}_{3}(500 \mathrm{MHz})$



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${ }^{13} \mathrm{C}$ NMR in $\mathrm{CDCl}_{3}(126 \mathrm{MHz})$


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