Supporting Information

Ruthenium complexes bearing α-diimine ligands and their catalytic applications in $N$-alkylation of amines, $\alpha$-alkylation of ketones and $\beta$-alkylation of secondary alcohols

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![FT-IR spectrum of ligand 1](image)

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**Table S1**: Crystal data and structure refinement parameters for complexes L₁, 1, 3 & 4.

|                  | L₁         | 1          | 3          | 4          |
|------------------|------------|------------|------------|------------|
| **CCDC Number**  | 2086813    | 2103005    | 2086814    | 2086865    |
| **Chem. formula**| C₂₆H₁₈N₄O₂ | C₆₃H₄₈N₄O₃P₂Ru | C₅₉H₴₄N₄O₃P₂RuS₂ | C₅₉H₴₂As₂N₄O₃RuS₂ |
| **Formula weight**| 418.44     | 1072.06    | 1084.11    | 1170.00    |
| **Temperature (K)** | 273(2) K   | 296(2) K   | 293(2) K   | 296(2) K   |
| **Wavelength (Å)** | 0.71073 Å  | 0.71073 Å  | 0.71073 Å  | 0.71073 Å  |
| **Crystal system** | Monoclinic | Monoclinic | Monoclinic | Triclinic   |
| **Space group**   | Cc         | P2₁/c      | P2₁/c      | P-1        |
| **Unit cell dimensions** |            |            |            |            |
| a (Å)             | 26.13 (3) Å| 17.0764(12) Å| 16.9512(8) Å| 11.7291(9) Å|
| b (Å)             | 4.761 (7) Å| 16.0690(11) Å| 19.1318(10) Å| 22.1650(18) Å|
| c (Å)             | 19.97 (3) Å| 19.1558(10) Å| 9.0961(2)° | 88.653(3)° |
| α (°)             | 90°        | 90°        | 90°        | 79.879(3)° |
| β (°)             | 128.26 (3)°| 90.961(2)° | 92.053 (2)°| 88.653(3)° |
| γ (°)             | 90°        | 90°        | 90°        | 83.134(3)° |
| **Volume (Å³)**   | 1951(5) Å³ | 5255.6(6) Å³| 5085.3(4) Å³| 5513.4 (8) Å³|
| **Z**             | 4          | 4          | 4          | 4          |
| **Density (Calcd)** | 1.425 Mg/m³ | 1.355 Mg/m³ | 1.416 Mg/m³ | 1.410 Mg/m³ |
| **Absorption coefficient** | 0.093 mm⁻¹ | 0.410 mm⁻¹ | 0.504 mm⁻¹ | 1.598 mm⁻¹ |
| **F(000)**        | 872        | 2208       | 2224       | 2360       |
| **Crystal Size (mm³)** | 0.20 x 0.10 x 0.10 | 0.19 x 0.13 x 0.08 | 0.53 x 0.37 x 0.36 | 0.22 x 0.19 x 0.11 |
| **Theta range for data collection** | 2.074 to 27.372° | 2.386 to 30.958° | 2.596 to 28.304° | 0.933 to 27.268° |
| **Index ranges**  | -33<=h<=33, -19<=h<=24, -19<=k<=23, -25<=l<=25 | -20<=h<=22, -20<=k<=20, -27<=k<=27, -25 <=l<=25 | -15<=h<=15, -20<=k<=20, -27<=k<=27, -28<=l<=28 |
| **Reflections collected** | 26748 | 80189 | 69970 | 133072 |
| **Independent reflections** | 4427 [R(int) = 0.0836] | 16366 [R(int) = 0.0683] | 12579 [R(int) = 0.0424] | 24755 [R(int) = 0.0415] |
| **Data/restraints/parameters** | 4427 / 2 / 289 | 16366 / 107/ 636 | 12579 / 402 / 621 | 24593 / 0 / 1295 |
| **Goodness-of-fit on F²** | 1.041 | 1.017 | 1.079 | 0.899 |
| **Final R indices** | | | | |
| [I>2sigma(I)]    | R1 = 0.0570, R1 = 0.0554, R1 = 0.0801, R1 = 0.0354, | wR² = 0.1076 wR² = 0.1187 wR² = 0.2022 wR² = 0.0916 | |
| **R indices (all data)** | R1 = 0.1150, R1 = 0.1153, R1 = 0.1056, R1 = 0.0568, | wR² = 0.1237 wR² = 0.1433 wR² = 0.2200 wR² = 0.1075 | |
Table S2: Selected geometrical parameters for complexes $L_1, 1, 3 \& 4$

| Bond lengths (Å) | $L_1$ | 1 | 3 |
|------------------|-------|---|---|
| O(1)-C(13)       | 1.194 (5) | Ru(1)-C(63) | 1.840 (4) | Ru(1)-C(1) | 1.873(6) |
| O(2)-C(13)       | 1.215 (5) | Ru(1)-O(2)  | 2.1312 (18) | Ru(1)-O(2) | 2.134(3) |
| N(1)-C(12)       | 1.272 (5) | Ru(1)-H     | 1.781 (19) | Ru(1)-H    | 1.76(3)  |
| N(3)-C(11)       | 1.282 (5) | Ru(1)-N(3)  | 2.183 (2)  | Ru(1)-N(1) | 2.186(4) |
| N(3)-N(4)        | 1.369 (5) | Ru(1)-P(1)  | 2.3652 (8) | Ru(1)-P(1) | 2.3634(12) |
| N(1)-N(2)        | 1.349 (5) | Ru(1)-P(2)  | 2.3770(8)  | Ru(1)-P(2) | 2.3658(12) |
| N(2)-H2A         | 0.860    |             |             |            |            |
| N(4)-H4A         | 0.860    |             |             |            |            |

| Bond angles(°)   | $L_1$ | 1 | 3 |
|------------------|-------|---|---|
| N(1)-N(2)-C(13)  | 119.1 (3) | C(63)-Ru(1)-O(2) | 99.48 (11) | C(1)-Ru(1)-O(2) | 99.49 (19) |
| N(1)-N(2)-C(12)  | 116.7 (4) | C(63)-Ru(1)-N(3) | 174.31(11) | C(1)-Ru(1)-N(1) | 174.41 (19) |
| C(20)-N(4)-N(3)  | 117.7 (4) | C(63)-Ru(1)-P(1) | 89.28 (11) | C(1)-Ru(1)-P(1) | 92.67 (17) |
| O(2)-C(20)-N(4)  | 121.9 (4) | C(63)-Ru(1)-H    | 82.6 (7)   | C(1)-Ru(1)-H    | 84.9 (11) |
| O(2)-C(20)-C(21) | 123.2 (4) | O(2)-Ru(1)-H     | 175.9(7)   | O(2)-Ru(1)-H    | 170.3 (10) |
| N(4)-C(20)-C(21) | 114.9 (4) | O(2)-Ru(1)-P(1)  | 91.71 (6)  | O(2)-Ru(1)-P(2) | 92.37 (9) |
| O(1)-C(13)-C(21) | 121.9 (4) | O(2)-Ru(1)-P(2)  | 91.86 (6)  | O(2)-Ru(1)-P(1) | 91.41 (9) |
| O(1)-C(13)-C(14) | 117.5 (4) | O(2)-Ru(1)-N(3)  | 74.84 (7)  | O(2)-Ru(1)-N(1) | 74.99 (12) |
| N(2)-C(13)-C(14) | 115.6 (4) | N(3)-Ru(1)-P(1)  | 91.30 (6)  | N(1)-Ru(1)-P(1) | 88.42 (10) |
| H2A-N(2)-N(1)    | 120.5   | N(3)-Ru(1)-P(2)  | 87.71 (6)  | N(1)-Ru(1)-P(2) | 91.26 (10) |
| H2A-N(2)-C(13)   | 120.4   | N(3)-Ru(1)-H     | 103.1(6)   | N(1)-Ru(1)-H    | 100.7 (10) |
| N(3)-N(4)-H4A    | 121.2   | P(1)-Ru(1)-H     | 91.8 (7)   | P(1)-Ru(1)-H    | 78.8 (10) |
| H4A-N(4)-C(20)   | 121.1   | P(2)-Ru(1)-H     | 84.5(7)    | P(2)-Ru(1)-H    | 97.3 (10) |
|                  |        | P(2)-Ru(1)-P(1)  | 175.91 (2) | P(2)-Ru(1)-P(1) | 175.98 (4) |
### Bond lengths (Å)

| Bond                  | Length (Å) |
|-----------------------|------------|
| Ru(1)-C (59)          | 1.869 (3)  |
| Ru(1)-O (2)           | 2.082 (19) |
| Ru(1)-N (2)           | 2.080 (2)  |
| Ru(1)-N (3)           | 2.056 (2)  |
| Ru(1)-As (1)          | 2.4730 (4) |
| Ru(1)-As (2)          | 2.4778 (4) |

### Bond angles (°)

| Bond                  | Angle (°) |
|-----------------------|-----------|
| C(59)-Ru(1)-O(2)      | 95.69 (11) |
| C(59)-Ru(1)-N(2)      | 96.62 (12) |
| C(59)-Ru(1)-N(3)      | 172.09 (12) |
| C(59)-Ru(1)-As(1)     | 90.24 (9)  |
| C(59)-Ru(1)-As(2)     | 91.41 (9)  |
| O(2)-Ru(1)-As(1)      | 86.19 (6)  |
| O(2)-Ru(1)-As(2)      | 88.84 (6)  |
| N(3)-Ru(1)-N(2)       | 91.27 (10) |
| N(3)-Ru(1)-O(2)       | 76.44 (8)  |
| N(3)-Ru(1)-As(1)      | 90.05 (7)  |
| N(3)-Ru(1)-As(2)      | 87.65 (7)  |
| N(2)-Ru(1)-O(2)       | 167.56 (9) |
| N(2)-Ru(1)-As(1)      | 91.71 (7)  |
| N(2)-Ru(1)-As(2)      | 92.89 (7)  |
| As(2)-Ru(1)-As(1)     | 174.904 (14) |
2. Catalysis

2.1 General methods

Thin-layer chromatography (TLC) was carried out on Merck 1.05554 aluminum sheets precoated with silica gel 60 F254, and the spots were monitored by UV light at 254 nm. Column chromatography purifications were executed using Merck silica mesh (100-200). Infrared spectra of the ligands and the metal complexes were recorded in the range of 4000-400 cm\(^{-1}\) using a Bruker model FT-IR spectrophotometer. The \(^1\)H & \(^13\)C NMR spectra were measured on a Bruker AV400 instrument by using CDCl\(_3\) as a solvent. Tetramethylsilane was used as an internal standard for the measuring of chemical shifts (ppm).

2.2 General experimental procedure for \(N\)-alkylation of aromatic amines with alcohols

To a mixture of ruthenium(II) catalyst (0.5 mmol), 5 mmol of benzyl alcohol, 5 mmol of substituted amine, 5 mol% of KOH and 5 mL of toluene were taken in 25mL of RB flask and the reaction was carried out by 12 hrs at 110\(^\circ\)C. Upon completion (as monitored by TLC), the reaction mixture was cooled at ambient temperature, H\(_2\)O (3 ml) was added and the organic layer was extracted with ethyl acetate (3-10 mL). The combined organic layers were dried with sodium sulphate anhydrous and concentrated. The crude sample was purified by column chromatography (ethyl acetate/n-hexane). Conversions were monitored by NMR spectroscopy.

2.3 General experimental procedure for \(\alpha\)-alkylation of aromatic ketones with alcohols

To a solution of Ru(II) catalyst (0.5 mmol) and KOH (5 mol%) in toluene (3ml) was added the corresponding ketone (5mmol) followed by the corresponding alcohol (5mmol). The mixture was stirred and heated at 110\(^\circ\)C for a period of 12 hrs. After completion of the reaction, the reaction mixture was cooled and as tested by TLC. Then the mixture was diluted with 3 ml of H\(_2\)O and extracted with DCM (5 ml). The combined organic layers were dried over anhydrous Na\(_2\)SO\(_4\), filtered. The resulting residue was purified by column chromatography on silica gel using suitable mixtures of Pet ether/Ethyl acetate to get a pure product and analysed by NMR spectroscopy.
2.4 General experimental procedure for β-alkylation of secondary alcohols with primary alcohols

In a 25 mL RB flask were placed with secondary alcohol (2.5 mmol), primary alcohol (2.5 mmol), 5 mol% of ruthenium(II) catalyst, and base KOH (5 mol%) in Toluene (3 mL). The reaction mixture was heated at 110 °C for 12h. After completion of the reaction, the mixture was cooled to room temperature, diluted with dichloromethane and hexane mixture and filtered. The filtrate was concentrated and the crude sample was purified by column chromatography (hexane/ethyl acetate) to provide the desired product. The products were characterized by NMR spectroscopy.

2.5 Characterization data of compounds. (6a-6k), (7a-7i), (8a-8f).

N-Benzylaniline (6a):

\[
\text{The title compound (1a) was synthesized according to the general procedure, using aniline (5.0 mmol) and benzyl alcohol (5.0 mmol). 1a was isolated by column chromatography (hexane/EtOAc, 8:2) as a colorless liquid (93 %).} \]

\[ \text{\textsuperscript{1}H NMR (400MHz, CDCl}_3\text{):} \delta = 7.36 (t, J = 4 \text{ Hz}, 2\text{H}), 7.34 (d, J = 4 \text{ Hz}, 2\text{H}), 7.31 (t, J = 4 \text{ Hz}, 1\text{H}), 7.29 (d, J = 8 \text{ Hz}, 1\text{H}), 7.27 (t, J = 4 \text{ Hz}, 1\text{H}), 7.29 (d, J = 8 \text{ Hz}, 3\text{H}), 4.62 (s, NH, 1\text{H}), 2.59 (s, -\text{CH}_2, 2\text{H}). \text{ Data agrees with literature values.}^{1,2,3,4} \]

Dibenzylamine (6b):
The title compound (6b) was synthesized according to the general procedure, using benzylamine (5.0 mmol) and benzyl alcohol (5.0 mmol). 1a was isolated by column chromatography (hexane/EtOAc, 8:2) as a yellow liquid (95 %). $^1$H NMR (400MHz, CDCl$_3$): δ = 7.51 (t, J = 4 Hz, 4H), 7.16 (d, J = 8 Hz, 4H), 6.99 (t, J = 4 Hz, 2H), 5.12 (s, NH, 1H), 4.17 (s, -CH$_2$, 4H). Data agrees with literature values.$^{5,6}$

$N$-benzyl-2,4,6-trimethylaniline (6c):

The title compound (6c) was synthesized according to the general procedure, using 2,4,6-trimethylamine (5.0 mmol) and benzyl alcohol (5.0 mmol). 6c was isolated by column chromatography (hexane/EtOAc, 8:2) as a colourless liquid (90 %). $^1$H NMR (400MHz, CDCl$_3$): δ = 7.51 (t, J = 4 Hz, 4H), 7.16 (d, J = 8 Hz, 4H), 6.99 (t, J = 4 Hz, 2H), 4.17 (s, -CH$_2$, 4H), 5.12 (s, NH, 1H). $^{13}$C NMR (100 MHz, CDCl3): δ = 141.85, 140.41, 131.92, 129.34, 128.72, 127.58, 127.30, 64.76, 20.85, 17.80. Data agrees with literature values.$^7$

$N$-benzyl-2,6-diethylaniline (6e):

The title compound (6e) was synthesized according to the general procedure, using 2,6-dimethylamine (5.0 mmol) and benzyl alcohol (5.0 mmol). 6e was isolated by column chromatography (hexane/EtOAc, 8:2) as a colourless liquid (81 %). $^1$H NMR (400MHz, CDCl$_3$): δ = 7.55 (t, J = 4 Hz, 4H), 7.50 (d, J = 8 Hz, 2H), 7.41 (d, J = 4 Hz, 2H), 7.05 (t, J= 4 Hz, 1H), 6.75 (t, J = 4 Hz), 7.29 (t, J = 4 Hz, 2H), 5.35 (s, NH, 1H), 4.65 (s, -CH$_2$, 2H), 2.53 (q, -CH$_3$, 6H). $^{13}$C NMR (100 MHz, CDCl3): δ = 135.54, 127.73, 124.04, 122.39, 119.93, 118.06, 113.81, 55.01, 23.22, 17.74. Data agrees with literature values.$^8$
$N$-benzyl-2,6-diisopropylaniline (6f):

![Chemical structure of 6f]

The title compound (6f) was synthesized according to the general procedure, using 2,6-diisopropylamine (5.0 mmol) and benzyl alcohol (5.0 mmol). 6f was isolated by column chromatography (hexane/EtOAc, 8:2) as a brownish liquid (79%). $^1$H NMR (400MHz, CDCl$_3$): $\delta$ = 7.66 (t, J = 4 Hz, 1H), 7.49 (d, J = 4 Hz, 2H), 7.39 (d, J = 8 Hz, 2H), 6.83 (t, J = 4 Hz, 3H), 5.35 (s, 1H, NH), 3.72 (s, -CH$_2$, 2H), 2.89 – 3.01 (m, -CH$_3$, 2H), 1.28 (d, J = 8 Hz, 6H), 1.18 (d, J = 8 Hz, 6H). $^{13}$C NMR (100 MHz, CDCl$_3$): $\delta$ = 140.53, 137.83, 130.25, 128.45, 127.65, 124.52, 123.04, 56.45, 28.21, 23.80. Data agrees with literature values.$^9$

$N$-benzyl cyclohexanamine (6g):

![Chemical structure of 6g]

The title compound (6g) was synthesized according to the general procedure, using cyclohexylamine (5.0 mmol) and benzyl alcohol (5.0 mmol). 6g was isolated by column chromatography (hexane/EtOAc, 8:2) as a colourless liquid (75%). $^1$H NMR (400MHz, CDCl$_3$): $\delta$ = 8.08 (d, J = 8 Hz, 2H), 7.40 (t, J = 4 Hz, 2H), 7.29 (t, J = 4 Hz, 1H), 4.63 (s, 1H, NH), 4.63 (s, NH, 1H), 3.81 (s, -CH$_2$, 2H), 3.21 – 3.16 (q, 4H), 1.64 – 1.54 (m, cyclohexane, 4H), 1.36 – 1.27 (m, cyclohexane, 4H). $^{13}$C NMR (100 MHz, CDCl$_3$): $\delta$ = 140.53, 137.83, 130.25, 128.45, 127.65, 124.52, 123.04, 56.45, 28.21, 23.80. Data agrees with literature values.$^{10}$

$N$-benzyl-1-(pyridine-3-yl)methanamine (6h):

![Chemical structure of 6h]
The title compound (6h) was synthesized according to the general procedure, using picolylamine (5.0 mmol) and benzyl alcohol (5.0 mmol). 6h was isolated by column chromatography (hexane/EtOAc, 8:2) as a colourless liquid (87 %). $^1$H NMR (400MHz, CDCl$_3$): $\delta = 8.10$ (d, J = 8 Hz, 2H), 7.92 (d, J = 8 Hz, 1H), 7.89 (t, J = 4 Hz, 1H), 7.86 (t, J = 4 Hz, 1H), 7.86 (t, J = 4 Hz, 1H), 7.58 (t, J = 4 Hz), 7.29 (d, J = 8 Hz, 1H), 7.06 (t, J = 4 Hz, 2H), 4.68 (s, NH, 1H), 3.23 (s, -CH$_2$, 4H). $^{13}$C NMR (100 MHz, CDCl$_3$): $\delta = 150.91, 165.62, 141.50, 136.82, 130.47, 128.34, 127.19, 126.87, 118.26, 64.65$. Data agrees with literature values.$^{11}$

$N$-butyl-$N$-butan-1-amine (6i)

The title compound (6i) was synthesized according to the general procedure, using dibutyl amine (5.0 mmol) and benzyl alcohol (5.0 mmol). 6i was isolated by column chromatography (hexane/EtOAc, 8:2) as a colourless liquid (82 %). $^1$H NMR (400MHz, CDCl$_3$): $\delta = 7.41 - 7.32$ (t, J = 4 Hz, 1H), 7.31 (d, J = 4 Hz, 2H), 7.29 (t, J = 4 Hz, 2H), 4.54 (s, -CH$_2$, 2H), 2.48 - 2.44 (t, J = 4 Hz, 2H), 1.43 – 1.35 (q, -CH$_2$, 4H), 1.26 – 1.21 (m, -CH$_2$, 4H), 0.88 – 0.84 (t, -CH$_3$, J = 4 Hz, 6H). $^{13}$C NMR (100 MHz, CDCl$_3$): $\delta = 128.87, 124.52, 123.33, 77.50, 66.95, 28.27, 23.8, 22.7$. Data agrees with literature values.$^{12}$

$N$-benzyl-2-methylpropan-2-amine (6j):

The title compound (6j) was synthesized according to the general procedure, using tert-butyl amine (5.0 mmol) and benzyl alcohol (5.0 mmol). 6j was isolated by column chromatography (hexane/EtOAc, 8:2) as a colourless liquid (78 %). $^1$H NMR (400MHz, CDCl$_3$): $\delta = 7.59$ (t, J = 4 Hz, 2H), 7.55 (d, J = 8 Hz, 2H), 7.35 (t, J = 4 Hz, 1H), 5.37 (s, NH, 1H), 3.70 (s, -CH$_2$, 2H), 1.13 (s, -CH$_3$, 9H). Data agrees with literature values.$^{13}$
**N- benzyl-ethane-1,2-diamine (6k):**

The title compound (6k) was synthesized according to the general procedure, using Ethylene diamine (5.0 mmol) and benzyl alcohol (5.0 mmol). 6k was isolated by column chromatography (hexane/EtOAc, 8:2) as a colourless liquid (81 %). $^1$H NMR (400MHz, CDCl$_3$): $\delta$ = 7.72 (d, J = 8 Hz, 2H), 7.13 (t, J = 4 Hz, 1H), 6.75 (t, J = 4 Hz, 2H), 5.27 (s, NH, 1H), 3.66 (s, -CH$_2$, 2H), 2.40 (t, J = 4 Hz, 2H), 2.04 (t, J = 4 Hz, 2H), 1.26 (s, -NH$_2$, 2H). Data agrees with literature values.$^{14,15}$

**1,3 – diphenylpropan -1-one (7a):**

Acetophenone (1 mmol), benzyl alcohol (1 mmol): yield of (7a): 97%. $^1$H NMR (400MHz, CDCl$_3$): $\delta$ = 7.62 (d, J = 5.44 Hz, 2H), 7.53 (d, J = 5.88 Hz, 2H), 7.30 – 7.27 (m, 6H), 3.09 (t, J = 6.36 Hz, -CH$_2$, 2H), 2.72 (t, J = 6.04 Hz, -CH$_2$, 2H). $^{13}$C NMR (100 MHz, CDCl$_3$): $\delta$ = 203.11, 136.92, 134.27, 130.89, 128.55, 123.89, 120.69, 118.73, 47.32, 29.95. Data agrees with literature values.$^{16,17,18}$

**3-(4- methoxyphenyl)-1-phenylpropan-1-one (7b):**

Acetophenone (1 mmol), 4-methoxy benzyl alcohol (1 mmol): yield of (7b): 94%. $^1$H NMR (400MHz, CDCl$_3$): $\delta$ = 7.62 (d, J = 5.44 Hz, 2H), 7.53 (d, J = 5.88 Hz, 2H), 7.30 – 7.27 (m, 6H), 3.81 (s, -CH$_3$, 3H), 3.09 (t, J = 6.36 Hz, -CH$_2$, 2H), 2.72 (t, J = 6.04 Hz, -CH$_2$, 2H). $^{13}$C NMR
(100 MHz, CDCl3): δ = 202.78, 156.63, 144.60, 140.60, 138.57, 135.55, 133.40, 129.34, 128.34, 114.87, 54.32, 43.55, 31.30. Data agrees with literature values.\textsuperscript{19,20}

1-Phenyl-3-(o-tolyl) propan-1-one (7c):

Acetophenone (1 mmol), 4-methyl benzyl alcohol (1 mmol): yield of (7c): 90%.

\textsuperscript{1}H NMR (400MHz, CDCl\textsubscript{3}): δ = 7.84 (d, J = 4.50 Hz, 2H), 7.44 – 7.41 (t, J = 4 Hz, 1H), 7.36 - 7.33 (t, J = 4.01 Hz, 6H), 3.06 (t, J = 5.06 Hz, -CH\textsubscript{2}, 2H), 2.84 (t, J = 5.61 Hz, -CH\textsubscript{2}, 2H), 2.33 (s, -CH\textsubscript{3}, 3H).

\textsuperscript{13}C NMR (100 MHz, CDCl3): δ = 199.77, 137.87, 137.05, 133.13, 129.22, 128.63, 127.79, 124.06, 122.65, 120.84, 43.38, 31.64, 19.87. Data agrees with literature values.\textsuperscript{21,22}

1-(2- hydroxy phenyl) -3 - phenyl propan-1-one (7e):

o-hydroxy acetophenone (1 mmol), benzyl alcohol (1 mmol): yield of (7e): 91%.

\textsuperscript{1}H NMR (400MHz, CDCl\textsubscript{3}): δ = 12.16 (s, OH, 1H), 7.81 (d, J = 6.52 Hz, 2H), 6.90 – 6.81 (m, 7H), 3.48 (t, J = 6.76 Hz, -CH\textsubscript{2}, 2H), 3.35 (t, J = 6.52 Hz, -CH\textsubscript{2}, 2H). Data agrees with literature values.\textsuperscript{23}

1-(2- hydroxyl phenyl)-3- (4- methoxyphenyl) propan-1-one (7f):
o-hydroxy acetophenone (1 mmol), 4- methoxy benzyl alcohol (1 mmol): yield of (7f): 95%. \( ^1H \) NMR (400MHz, CDCl\(_3\)): \( \delta = 10.74 \) (s, OH, 1H), 8.07 (d, J = 4 Hz, 2H), 7.96 (d, J = 4 Hz, 1H), 7.93 (d, J = 4 Hz, 1H), 7.89 (d, J = 8 Hz, 1H), 7.48 – 7.44 (t, J = 4 Hz, 6H), 2.92 - 2.89 (t, J = Hz, -CH\(_2\), 2H), 2.88 - 2.84 (t, J = Hz, -CH\(_2\), 2H), 3.06 (s, -CH\(_3\), 3H). Data agrees with literature values.\(^{24,25}\)

1-(2- hydroxyphenyl)-3-phenylpropan-1-one (7i):

4-methoxy 2- hydroxy acetophenone (1 mmol), benzyl alcohol (1 mmol): yield of (7i): 89%. \( ^1H \) NMR (400MHz, CDCl\(_3\)): \( \delta = 7.83 \) (d, J = 5.6 Hz, 2H), 7.48 – 7.44 (m, 7H), 5.29 (s, OH, 1H), 3.78 (s, -CH\(_3\), 3H), 3.55 (t, J = 4.01 Hz, -CH\(_2\), 2H), 3.39 (t, J = 3.09 Hz, -CH\(_2\), 2H). Data agrees with literature values.\(^{28}\)
(1,3-Diphenylpropan-1-ol (8a):

![Structural formula](image)

1-Phenyl ethanol (2.5 mmol), benzyl alcohol (2.5 mmol): Yield: 98%; $^1$H NMR (400 MHz; CDCl$_3$; ppm): 7.94 (d, J = 7.6 Hz, 4H), 7.56 (t, J = 4.12 Hz, 4H), 7.45 (t, J = 3.46 Hz, 2H), 4.88 – 4.83 (q, -CH$_2$, 2H), 3.30 (t, J = 3.56 Hz, 1H), 3.08 (t, J = 4.36 Hz, 2H). $^{13}$C NMR (100 MHz; CDCl$_3$, ppm): 142.88, 139.52, 129.15, 128.63, 128.22, 127.18, 126.32, 125.49, 125.48, 74.20, 30.33, 25.31. Data agrees with literature values.$^{29}$

3- (4-methoxyphenyl)-1-phenylpropan-1-ol (8b):

![Structural formula](image)

1-Phenyl ethanol (2.5 mmol), 4-Methoxy benzyl alcohol (2.5 mmol): Yield: 96%; $^1$H NMR (400 MHz; CDCl$_3$; ppm): 7.95 (d, J = 8.4 Hz, 4H), 7.57 (t, J = 7.88 Hz, 4H), 7.45 (t, J = 8.04 Hz, 1H), 4.93 – 4.80 (q, -CH$_2$, 2H), 4.13 (s, -CH$_3$, 3H), 3.32 (t, J = 7.08 Hz, 1H), 3.07 (t, J = 6.91 Hz, 2H), 1.46 (s,OH, 3H). 4.88 – 4.83 (q, -CH$_2$, 2H), 3.30 (t, J = 3.56 Hz, 1H), 3.08 (t, J = 4.36 Hz, 2H). Data agrees with literature values.$^{30}$

1-Phenylpentan-3-ol (8e):

![Structural formula](image)
Butanol (2.5 mmol), benzyl alcohol (2.5 mmol): Yield: 89%; $^1$H NMR (400 MHz; CDCl$_3$; ppm): 7.19 – 7.12 (m, 4H), 4.73 – 4.68 (m, 4H), 1.90 (s, OH, 1H), 3.50 (m, 8H). Data agrees with literature values.$^{31}$

1-(4-methoxyphenyl) pentan-3-ol (8f):

Butanol (2.5 mmol), 4-methoxy benzyl alcohol (2.5 mmol): Yield: 85%; $^1$H NMR (400 MHz; CDCl$_3$; ppm): 7.62 – 7.43 (m, 7 H), 4.91 (m, 1H), 4.39 – 4.34 (m, 6H), 1.49 (s, OH, 1H), 2.00 (s, -CH$_3$, 3H). Data agrees with literature values.$^{32}$
2.6 NMR spectra of catalytic products (6a-6k), (7a-7m), (8a-8f).

**Figure S44:** $^1$H NMR (400 MHz, CDCl$_3$) spectrum of 6a
Figure S45: $^1$H NMR (400 MHz, CDCl$_3$) spectrum of 6b
Figure S46: $^1$H NMR (400 MHz, CDCl$_3$) spectrum of 6c
Figure S47: $^1$H NMR (400 MHz, CDCl$_3$) spectrum of 6e
Figure S48: $^1$H NMR (400 MHz, CDCl$_3$) spectrum of 6f
Figure S49: $^1$H NMR (400 MHz, CDCl$_3$) spectrum of 6g
Figure S50: $^1$H NMR (400 MHz, CDCl$_3$) spectrum of 6h
Figure S51: $^1$H NMR (400 MHz, CDCl$_3$) spectrum of 6i
Figure S52: $^1$H NMR (400 MHz, CDCl$_3$) spectrum of 6j
Figure S53: $^1$H NMR (400 MHz, CDCl$_3$) spectrum of 6k
Figure S54: $^1$H NMR (400 MHz, CDCl$_3$) spectrum of 7a
Figure S55: $^1$H NMR (400 MHz, CDCl$_3$) spectrum of 7b
Figure S56: $^1$H NMR (400 MHz, CDCl$_3$) spectrum of 7c
Figure S57: $^1$H NMR (400 MHz, CDCl$_3$) spectrum of 7e
Figure S58: $^1$H NMR (400 MHz, CDCl$_3$) spectrum of 7f
Figure S59: $^1$H NMR (400 MHz, CDCl$_3$) spectrum of 7h
Figure S60: $^1$H NMR (400 MHz, CDCl$_3$) spectrum of 7i
Figure S61: $^1$H NMR (400 MHz, CDCl$_3$) spectrum of 8a
Figure S62: $^1$H NMR (400 MHz, CDCl$_3$) spectrum of 8b
Figure S63: $^1$H NMR (400 MHz, CDCl$_3$) spectrum of 8e
Figure S64: $^1$H NMR (400 MHz, CDCl$_3$) spectrum of 8f
Figure S65: $^{13}$C NMR (100 MHz, CDCl$_3$) spectrum of 6c
Figure S66: $^{13}$C NMR (100 MHz, CDCl$_3$) spectrum of 6e
Figure S67: $^{13}$C NMR (100 MHz, CDCl$_3$) spectrum of 6f
Figure S68: $^{13}$C NMR (100 MHz, CDCl$_3$) spectrum of 6i
Figure S69: $^{13}$C NMR (100 MHz, CDCl$_3$) spectrum of 6h
Figure S70: $^{13}$C NMR (100 MHz, CDCl$_3$) spectrum of 7a
Figure S71: $^{13}$C NMR (100 MHz, CDCl$_3$) spectrum of 7b
Figure S72: $^{13}$C NMR (100 MHz, CDCl$_3$) spectrum of 7c
Figure S73: $^{13}$C NMR (100 MHz, CDCl$_3$) spectrum of 8a
2.7 Control experiments

\textit{α-alkylation of acetophenone with benzyl alcohol in absence of catalyst}

Acetophenone (1 mmol), benzylalcohol (1 mmol), KOH (0.5 mmol) and toluene (2 mL) were charged into a round neck flask and heated at 110 °C. After 12 h, the crude reaction mixture was analysed by $^{13}$C-NMR (See Figure S37; 7a), there was no intermediate was observed.

\textit{α-alkylation of acetophenone with benzyl alcohol in presence of catalyst}

Acetophenone (1 mmol), benzylalcohol (1 mmol), catalyst 3 (0.5 mol%), KOH (0.5 mmol) and toluene (2 mL) were charged into a round neck flask and heated at 110 °C. After 12 h, the crude reaction mixture was analysed by $^{13}$C-NMR (See Figure S57) and the conversion of desired chalcone intermediate was found to be 71%.

\[
\begin{align*}
\text{Acetophenone} & \quad + \quad \text{Benzyl alcohol} \\
& \quad \xrightarrow{3 \text{ (0.5 mol %)}} \quad \text{Chalcone} \\
& \quad \text{KOH, toluene} \\
& \quad 110^\circ C, 12 \text{ hrs} \\
& \quad \text{Observed 71%}
\end{align*}
\]
Figure S74: $^{13}$C NMR (100 MHz, CDCl$_3$) spectrum of scheme 6.
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