Supporting information

Guerbet-Type β-alkylation of Secondary Alcohols Catalyzed by Chromium Chloride and its Corresponding NNN Pincer Complex

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1. Optimization:

Table S1. Optimization of the chromium catalyzed solvent-free β-alkylation of 1-phenylethanol with benzyl alcohol under conventional heating

![Reaction Diagram]

<table>
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<tr>
<th>Entry</th>
<th>Base (X mol%)</th>
<th>Catalyst (Y mol%)</th>
<th>Yield (%) and [TON]</th>
<th>Selectivity of 4=((Yield of 4/Total yield 4+3)*100)</th>
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<tbody>
<tr>
<td>1</td>
<td>Na₂CO₃ (5)</td>
<td>CrCl₃.6H₂O(0.005)</td>
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<tr>
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<td>4±0[800]</td>
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<td>11±2[2200]</td>
<td>5±1[1000]</td>
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<td>12±1[2400]</td>
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<td>20</td>
<td>5(0.005)</td>
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<td>21</td>
<td>5(0.005)</td>
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[^a]: Conditions: Benzyl alcohol (4 mmol), 1-phenylethanol (4 mmol), base (X mol%), and Cr catalyst (Y mol%) were heated together at 140 °C for 3 hours. [^b]: Mol% of base is with respect to total alcohol content (1+2). [^c]: Yield determined from ¹H NMR analysis using toluene as an internal standard. Yields reported are the average of two runs. [^d]: Reaction performed at 120 °C. [^e]: Reaction performed at 100 °C. [^f]: TON are written in the parenthesis.
Table S2. Chromium catalyzed solvent-free β-alkylation of 1-phenyl ethanol with benzyl alcohol under microwave conditions$^a$

![Diagram of the reaction]

<table>
<thead>
<tr>
<th>Entry</th>
<th>Temperature (°C)</th>
<th>Catalyst</th>
<th>Yield (%)$^b$ and [TON]$^c$</th>
<th>Selectivity of 4 = ((Yield of 4/Total yield 3+4)*100)</th>
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<td>5</td>
<td>90[18000]</td>
<td>7[1400]</td>
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<tr>
<td>2</td>
<td>120</td>
<td>5</td>
<td>26[5200]</td>
<td>2[400]</td>
</tr>
<tr>
<td>3</td>
<td>100</td>
<td>5</td>
<td>8[1600]</td>
<td>2[400]</td>
</tr>
<tr>
<td>4</td>
<td>140</td>
<td>CrCl$_3$-6H$_2$O</td>
<td>76[15200]</td>
<td>3[600]</td>
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<td>5</td>
<td>120</td>
<td>CrCl$_3$-6H$_2$O</td>
<td>31[6200]</td>
<td>3[600]</td>
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$^a$Conditions: Benzyl alcohol (2 mmol), 1-phenyl ethanol (2 mmol), NaO$_2$Bu (5 mol%), and Cr catalyst (0.005 mol%) were heated together in air at 140 °C for 1.5 hours under 75 W microwave irradiation. $^b$Mol% of base and catalyst is with respect to total alcohol content (1+2). $^c$Yield determined from $^1$H NMR analysis using toluene as an internal standard. Yields reported are the average of two runs. $^d$TON are written in the parenthesis.
Table S3. Effect of hot filtration and mercury drop test in the chromium catalyzed solvent-free β-alkylation of 1-phenyl ethanol with benzyl alcohol under conventional heating

<table>
<thead>
<tr>
<th>Entry</th>
<th>Base (5 mol%)a</th>
<th>Catalyst (Y mol %)b</th>
<th>Yield (%)c and [TON]d</th>
<th>Selectivity of 4 = ( \frac{\text{Yield of 4}}{\text{Total yield 4+3}} \times 100 )</th>
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<tbody>
<tr>
<td>1</td>
<td>NaO\text{Bu}</td>
<td>5</td>
<td>84±0.3[16800]</td>
<td>8±1[1600]</td>
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<tr>
<td>2d</td>
<td>NaO\text{Bu}</td>
<td>5</td>
<td>82[16400]</td>
<td>11[2200]</td>
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<tr>
<td>3e</td>
<td>NaO\text{Bu}</td>
<td>5</td>
<td>81[16200]</td>
<td>6[1200]</td>
</tr>
<tr>
<td>4</td>
<td>NaO\text{Bu}</td>
<td>CrCl\text{3.6H}_2\text{O}</td>
<td>79±2[15800]</td>
<td>12±1[2400]</td>
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<tr>
<td>5d</td>
<td>NaO\text{Bu}</td>
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<td>NaO\text{Bu}</td>
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<td>6[1200]</td>
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\( ^a \)Conditions: Benzyl alcohol (2 mmol), 1-phenyl ethanol (2 mmol), base (5 mol%), and Cr catalyst (Y mol%) were heated together in air at 140 °C for 3 hours. \( ^b \)Mol% of base and catalyst is with respect to total alcohol content (1+2). \( ^c \)Yield determined from \(^1\)H NMR analysis using toluene as an internal standard. Yields reported are the average of two runs. \( ^d \)Result obtained from heating the filtrate for 2.5 h post hot-filtration after 30 minutes of reaction. \( ^e \)Reaction performed in the presence of excess mercury. \( ^f \)TON are written in the parenthesis.
2. HRMS analysis:

![HRMS analysis image](image)

**Figure S1.** HRMS (ESI) plot of complex 5.

![HRMS expanded spectra image](image)

**Figure S2.** HRMS (ESI) expanded spectra of m/z 406.9962 (a) Observed (b) Simulated.
Figure S3. HRMS (ESI) expanded spectra of m/z 429.1622 (a) Observed (b) Simulated.

Figure S4. HRMS (ESI) expanded spectra of m/z 461.1829 (a) Observed (b) Simulated.
**Figure S5.** HRMS (ESI) expanded spectra of m/z 506.2228 (a) Observed (b) Simulated.

**Figure S6.** HRMS (ESI) plot of the reaction mixture containing 1(4 mmol) and 2(4 mmol) in the presence of 5 mol% CrCl₃·6H₂O and 5 mol% NaOᵀBu at t = 0 h at 140 °C.
Figure S7. HRMS (ESI) expanded spectra of m/z 243.073 (a) Observed (b) Simulated.

Figure S8. HRMS (ESI) expanded spectra of m/z 431.5330 (a) Observed (b) Simulated.
**Figure S9.** HRMS(ESI) expanded spectra of m/z 687.3843 (a) Observed (b) Simulated.

**Figure S10.** HRMS (ESI) plot of the reaction mixture containing 1(4 mmol) and 2(4 mmol) in the presence of 5 mol% CrCl₃·6H₂O and 5 mol% NaO'Bu at t = 0 h at 140 °C.
**Figure S11.** HRMS (ESI) expanded spectra of m/z 352.2153 (a) Observed (b) Simulated.

**Figure S12.** HRMS (ESI) expanded spectra of m/z 766.2749 (a) Observed (b) Simulated.
Figure S13. HRMS (ESI) plot of the reaction mixture containing 1 (4 mmol) and 2 (4 mmol) in the presence of 5 mol% 5 and 5 mol% NaO\textsubscript{t}Bu at t = 0 h at 140 °C.

Figure S14. HRMS (ESI) expanded spectra of m/z 443.1747 (a) Observed (b) Simulated.
Figure S15. HRMS (ESI) plot of the reaction mixture containing 1 (4 mmol) and 2 (4 mmol) in the presence of 5 mol% 5 and 5 mol% NaO\textsubscript{Bu} at t = 1 h at 140 °C.

Figure S16. HRMS (ESI) expanded spectra of m/z 457.1656 (a) Observed (b) Simulated.
**Figure S17.** HRMS (ESI) expanded spectra of m/z 679.2920 (a) Observed (b) Simulated.

**Figure S18.** HRMS (ESI) expanded spectra of m/z 859.3874 (a) Observed (b) Simulated.
3. Gas Chromatography Analysis:

GC analysis (TCD detection) was performed on an Agilent 7820-GC instrument fitted with Agilent Front SSZ Inlet N2 HP-PLOT Q column (30 m length x 530 μm x 40 μm) using the following method:

Agilent 7820-GC back detector TCD
Oven temperature: 50 °C
Time at starting temp: 0 min
Hold time = 10 min
Inlet temperature: 100 °C
Detector temperature (TCD): 250 °C
Detector temperature (FID): 300 °C
Flow rate (carrier): 5 mL/min (N2)
Split ratio: 10

Figure S19: Evidence for H₂ evolution in the dehydrogenation of benzyl alcohol (1) catalyzed by 5 (0.01 mol %) and NaO'Bu (10 mol%) at 140 °C via GC analysis.
Figure S20: Evidence for H₂ evolution in the dehydrogenation of benzyl alcohol (1) catalyzed by CrCl₃.6H₂O (0.01 mol %) and NaO'Bu (10 mol%) at 140 °C via GC analysis.

Figure S21: Evidence for H₂ evolution in the dehydrogenation of 1-Phenyl ethanol (2) catalyzed by 5 (0.01 mol %) and NaO'Bu (10 mol%) at 140 °C via GC analysis.
Figure S22: Evidence for H₂ evolution in the dehydrogenation of 1-Phenyl ethanol (2) catalyzed by CrCl₃·6H₂O (0.01 mol %) and NaO'Bu (10 mol%) at 140 °C via GC analysis.

4. EPR analysis:

Figure S23. The X-band EPR spectra of the complex 5 recorded on a JES-FA200 ESR spectrometer at room temperature with microwave power of 0.998 mW and microwave frequency of 9.14 GHz.
5. NMR Data and Spectra:

1,3-diphenylpropan-1-ol (4a):

$^1$H NMR (500 MHz, CDCl$_3$): $\delta$ 7.26 (d, $J = 4.3$ Hz, 4H), 7.18 (q, $J = 6.0$ Hz, 3H), 7.10 (d, $J = 7.5$ Hz, 3H), 4.60 (t, $J = 6.4$ Hz, 1H), 2.62-2.55 (m, 2H), 2.10 – 1.89 (m, 2H), 1.80 (s, 1H). $^{13}$C($^1$H) NMR (126 MHz, CDCl$_3$): $\delta$ 144.70, 141.92, 128.66, 127.79, 126.00, 74.04, 40.60, 32.20.

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

$^1$H NMR (500 MHz, CDCl$_3$): $\delta$ 7.33 – 7.18 (m, 6H), 6.94 (d, $J = 6.5$ Hz, 2H), 6.84 (d, $J = 8.0$ Hz, 1H), 4.69 (s, 1H), 3.83 (s, 3H), 2.80-2.66 (m, 2H), 2.19 – 2.00 (m, 2H), 1.92 (s, 1H). $^{13}$C($^1$H) NMR (151 MHz, CDCl$_3$): $\delta$ 146.43, 141.89, 129.68, 128.52, 125.99, 118.36, 113.22, 111.52, 73.95, 55.37, 40.53, 32.17.

1-(4-(tert-butyl)phenyl)-3-phenylpropan-1-ol (4d):

$^1$H NMR (500 MHz, CDCl$_3$): $\delta$ 7.37 (d, $J = 8.2$ Hz, 2H), 7.26 (dd, $J = 15.2, 7.2$ Hz, 4H), 7.18 (dd, $J = 13.2, 7.2$ Hz, 3H), 4.66 (t, $J = 7.8$ Hz, 1H), 2.80 – 2.63 (m, 2H), 2.18 – 1.99 (m, 2H), 1.85 (d, $J = 2.9$ Hz, 1H), 1.32 (s, 9H). $^{13}$C($^1$H) NMR (126 MHz, CDCl$_3$): $\delta$ 150.76, 142.01, 141.68, 128.49, 125.94, 125.81, 73.82, 40.39, 34.66, 32.27, 31.49.

3-phenyl-1-(thiophen-2-yl)propan-1-ol (4f):

$^1$H NMR (600 MHz, CDCl$_3$): $\delta$ 7.34 – 7.30 (m, 2H), 7.30 – 7.28 (m, 1H), 7.24 (d, $J = 7.9$ Hz, 3H), 7.02 – 6.99 (m, 2H), 4.99 – 4.93 (m, 1H), 2.84 – 2.71 (m, 2H), 2.30 – 2.15 (m, 2H), 2.05 (d, $J = 4.2$ Hz, 1H). $^{13}$C($^1$H) NMR (151 MHz, CDCl$_3$): $\delta$ 150.62, 141.57, 128.57, 126.09, 124.83, 124.07, 69.65, 40.82, 32.14.

1-(4-chlorophenyl)-3-phenylpropan-1-ol (4g):

$^1$H NMR (500 MHz, CDCl$_3$): $\delta$ 7.32 (d, $J = 8.6$ Hz, 2H), 7.30 – 7.25 (m, 4H), 7.21 – 7.17 (m, 3H), 4.67 (ddd, $J = 8.3, 5.1, 3.3$ Hz, 1H), 2.76-2.63 (m, 2H), 2.14 – 1.95 (m, 2H), 1.88 (d, $J = 3.5$ Hz, 1H). $^{13}$C($^1$H) NMR (126 MHz, CDCl$_3$): $\delta$ 143.16, 141.62, 133.40, 128.78, 128.59, 128.55, 127.44, 126.10, 73.30, 40.64, 32.06.

1-(3-chlorophenyl)-3-phenylpropan-1-ol (4i):

$^1$H NMR (600 MHz, CDCl$_3$): $\delta$ 7.38 (s, 1H), 7.34 – 7.26 (m, 4H), 7.23 (dd, $J = 13.4, 8.0$ Hz, 4H), 4.69 (dt, $J = 8.0, 4.1$ Hz, 1H), 2.80-2.68 (m, 2H), 2.16 – 2.00 (m, 2H), 1.98 (d, $J = 3.3$ Hz, 1H).
1-(3-bromophenyl)-3-phenylpropan-1-ol(4j):

$^1$H NMR (600 MHz, CDCl$_3$): $\delta$ 7.54 (s, 1H), 7.43 (d, $J = 7.8$ Hz, 1H), 7.34 – 7.27 (m, 3H), 7.26 – 7.20 (m, 4H), 4.68 (dt, $J = 8.2$, 4.4 Hz, 1H), 2.81 – 2.67 (m, 2H), 2.16 – 1.97 (m, 3H). $^{13}$C($^1$H) NMR (151 MHz, CDCl$_3$): $\delta$ 147.07, 141.55, 130.77, 130.22, 129.15, 128.59, 128.55, 126.11, 124.63, 122.77, 73.26, 40.61, 32.03.

3-phenyl-1-(p-tolyl)propan-1-ol(4l):

$^1$H NMR (600 MHz, CDCl$_3$): $\delta$ 7.31 (t, $J = 7.6$ Hz, 2H), 7.28 (d, $J = 8.0$ Hz, 2H), 7.21 (dd, $J = 16.2$, 7.7 Hz, 5H), 4.68 (t, $J = 8.1$, 4.3 Hz, 1H), 2.79 – 2.67 (m, 2H), 2.39 (s, 3H), 2.20 – 2.02 (m, 2H), 1.91 (t, 1H). $^{13}$C($^1$H) NMR (151 MHz, CDCl$_3$): $\delta$ 141.97, 141.69, 137.45, 129.31, 128.56, 128.49, 126.02, 125.94, 73.85, 40.47, 32.21, 21.24.

3-phenyl-1-(4-(trifluoromethyl)phenyl)propan-1-ol(4m):

$^1$H NMR (600 MHz, CDCl$_3$): $\delta$ 7.61 (d, $J = 8.1$ Hz, 2H), 7.46 (d, $J = 8.2$ Hz, 2H), 7.30 (t, $J = 7.6$ Hz, 2H), 7.20 (t, $J = 8.1$, 4.3 Hz, 1H), 4.76 (dt, $J = 8.1$, 4.3 Hz, 1H), 2.79 – 2.67 (m, 2H), 2.15 – 2.00 (m, 3H). $^{13}$C($^1$H) NMR (151 MHz, CDCl$_3$): $\delta$ 148.65, 141.44, 128.63, 128.54, 126.29, 126.17, 125.61, 125.58, 125.56, 125.53, 73.29, 40.69, 31.97.

1-(naphthalen-2-yl)-3-phenylpropan-1-ol(4p):

$^1$H NMR (600 MHz, CDCl$_3$): $\delta$ 7.88 – 7.77 (m, 4H), 7.59 – 7.48 (m, 3H), 7.39 – 7.21 (m, 5H), 4.89 (pt, $J = 7.9$, 3.1 Hz, 1H), 2.82 – 2.70 (m, 2H), 2.30 – 2.15 (m, 2H), 2.03 (s, 1H). $^{13}$C($^1$H) NMR (151 MHz, CDCl$_3$): $\delta$ 142.01, 141.86, 133.41, 133.15, 128.59, 128.54, 128.52, 128.06, 127.83, 126.32, 126.01, 124.82, 124.17, 74.12, 40.46, 32.18.

1-(4-methoxyphenyl)-3-phenylpropan-1-ol(4q):

$^1$H NMR (600 MHz, CDCl$_3$): $\delta$ 7.32 – 7.28 (m, 4H), 7.21 (d, $J = 7.1$ Hz, 3H), 6.92 (d, $J = 8.7$ Hz, 2H), 4.66 (t, $J = 6.6$, 1H), 3.83 (s, 3H), 2.76 – 2.64 (m, 2H), 2.20 – 2.00 (m, 2H), 1.86 (s, 1H). $^{13}$C($^1$H) NMR (151 MHz, CDCl$_3$): $\delta$ 159.24, 141.95, 136.80, 128.56, 127.34, 125.96, 114.02, 73.63, 55.42, 40.46, 32.25.

3-(3-methoxyphenyl)-1-phenylpropan-1-ol (4r):

$^1$H NMR (500 MHz, CDCl$_3$): $\delta$ 7.25 – 7.06 (m, 6H), 6.70 – 6.61 (m, 3H), 4.57 – 4.51 (m, 1H), 3.66 (s, 3H), 2.65 – 2.48 (m, 2H), 2.14 (s, 1H), 1.95 (ddt, $J = 49.6$, 14.1, 7.3 Hz, 2H). $^{13}$C($^1$H) NMR (126 MHz, CDCl$_3$): $\delta$ 159.68, 143.52, 129.38, 128.52, 127.63, 125.97, 120.93, 114.26, 111.24, 77.09, 76.90, 73.82, 55.16, 40.37, 32.14.
1-phenyl-3-(m-tolyl)propan-1-ol (4s):

\(^1\)H NMR (600 MHz, CDCl\(_3\)): \(\delta\) 7.36 (d, \(J = 4.3\) Hz, 4H), 7.32 – 7.27 (m, 1H), 7.17 (t, \(J = 7.4\) Hz, 1H), 7.03 – 6.98 (m, 3H), 4.72 – 4.68 (m, 1H), 2.75-2.61 (m, 2H), 2.32 (s, 3H), 2.16 – 2.00 (m, 3H), 1.85 (s, 1H). \(^{13}\)C\({^1}\)H NMR (151 MHz, CDCl\(_3\)): \(\delta\) 144.71, 141.83, 138.08, 129.39, 128.65, 128.42, 127.77, 126.73, 126.06, 125.56, 74.10, 40.63, 32.12, 21.53.

1-phenyl-3-(pyridin-3-yl)propan-1-ol (4t):

\(^1\)H NMR (600 MHz, CDCl\(_3\)): \(\delta\) 8.43 – 8.38 (m, 2H), 7.52 (dt, \(J = 7.9, 2.0\) Hz, 1H), 7.37 (d, \(J = 4.5\) Hz, 4H), 7.32 – 7.28 (m, 1H), 7.21 (dd, \(J = 7.8, 4.8\) Hz, 1H), 4.70 (dd, \(J = 8.0, 5.2\) Hz, 1H), 2.80-2.68 (m, 3H), 2.17-1.99 (m, 3H). \(^{13}\)C\({^1}\)H NMR (151 MHz, CDCl\(_3\)): \(\delta\) 147.44, 144.72, 137.43, 136.21, 128.79, 127.94, 126.10, 73.59, 40.33, 29.39.

3-(naphthalen-1-yl)-1-phenylpropan-1-ol (4u):

\(^1\)H NMR (600 MHz, CDCl\(_3\)): \(\delta\) 8.02 – 7.99 (m, 1H), 7.89 – 7.85 (m, 1H), 7.74 (d, \(J = 8.1\) Hz, 1H), 7.53 – 7.47 (m, 3H), 7.43 – 7.35 (m, 6H), 7.34 – 7.30 (m, 1H), 4.83 (dt, \(J = 8.0, 4.2\) Hz, 1H), 3.31 – 3.10 (m, 2H), 2.32 – 2.15 (m, 2H), 1.96 (d, \(J = 3.3\) Hz, 1H). \(^{13}\)C\({^1}\)H NMR (151 MHz, CDCl\(_3\)): \(\delta\) 144.65, 138.12, 134.04, 131.96, 128.89, 128.69, 127.85, 126.82, 126.09, 125.93, 125.68, 125.59, 123.91, 74.35, 39.98, 29.26.

3-(3-chlorophenyl)-1-phenylpropan-1-ol (4z):

\(^1\)H NMR (600 MHz, CDCl\(_3\)): \(\delta\) 7.36 (d, \(J = 6.5\) Hz, 4H), 7.29 (ddd, \(J = 8.5, 5.8, 2.1\) Hz, 1H), 7.22 – 7.15 (m, 3H), 7.07 (dt, \(J = 7.4, 1.5\) Hz, 1H), 4.68 (t, \(J = 6.4\) Hz, 1H), 2.77 – 2.62 (m, 2H), 2.15 – 1.97 (m, 2H), 1.89 (s, 1H). \(^{13}\)C\({^1}\)H NMR (151 MHz, CDCl\(_3\)): \(\delta\) 144.49, 143.99, 134.25, 129.75, 128.72, 127.91, 126.19, 126.00, 73.84, 40.30, 31.85.

3-(4-chlorophenyl)-1-phenylpropan-1-ol (4zb):

\(^1\)H NMR (600 MHz, CDCl\(_3\)): \(\delta\) 7.41 – 7.35 (m, 4H), 7.32 (t, \(J = 7.6\) Hz, 1H), 7.29 – 7.25 (m, 2H), 7.14 (d, \(J = 8.3\) Hz, 2H), 4.70 (ddd, \(J = 8.2, 3.4\) Hz, 1H), 2.78 – 2.63 (m, 2H), 2.17 – 1.98 (m, 2H), 1.90 (d, \(J = 3.3\) Hz, 1H). \(^{13}\)C\({^1}\)H NMR (151 MHz, CDCl\(_3\)): \(\delta\) 144.53, 140.34, 131.69, 129.92, 128.71, 128.60, 127.89, 126.01, 73.85, 40.44, 31.51.
1-phenyl-3-(p-tolyl)propan-1-ol(4ze):

$^1$H NMR (600 MHz, CDCl$_3$): $\delta$ 7.40 – 7.35 (m, 4H), 7.30 (tt, $J = 6.5$, 3.0 Hz, 1H), 7.12 (s, 4H), 4.71 – 4.67 (m, 1H), 2.76 – 2.62 (m, 2H), 2.35 (s, 3H), 2.17 – 2.00 (m, 3H).$^{13}$C($^1$H) NMR (151 MHz, CDCl$_3$): $\delta$ 144.71, 135.38, 129.18, 128.60, 128.42, 127.70, 126.05, 73.98, 40.65, 21.10.

Figure S24. $^1$H NMR spectra of 1,3-diphenylpropan-1-ol (4a) recorded in CDCl$_3$.
Figure S25. $^{13}$C($^1$H) NMR spectra of 1,3-diphenylpropan-1-ol(4a) recorded in CDCl$_3$.

Figure S26: $^1$H NMR spectra of 1-(3-methoxyphenyl)-3-phenylpropan-1-ol(4b) recorded in CDCl$_3$. 
Figure S27: $^{13}$C($^1$H) NMR spectra of 1-(3-methoxyphenyl)-3-phenylpropan-1-ol(4b) recorded in CDCl$_3$.

Figure S28: $^1$H NMR spectra of 1-(4-(tert-butyl)phenyl)-3-phenylpropan-1-ol(4d) recorded in CDCl$_3$. 
Figure S29: $^{13}$C($^1$H) NMR spectra of 1-(4-(tert-butyl)phenyl)-3-phenylpropan-1-ol(4d) recorded in CDCl$_3$.

Figure S30: $^1$H NMR spectra of 3-phenyl-1-(thiophen-2-yl)propan-1-ol(4f) recorded in CDCl$_3$. 
Figure S31: $^{13}$C($^1$H) NMR spectra of 3-phenyl-1-(thiophen-2-yl)propan-1-ol(4f) recorded in CDCl$_3$.

Figure S32: $^1$H NMR spectra of 1-(4-chlorophenyl)-3-phenylpropan-1-ol(4g) recorded in CDCl$_3$. 
Figure S33: $^{13}$C ($^1$H) NMR spectra of 1-(4-chlorophenyl)-3-phenylpropan-1-ol (4g) recorded in CDCl$_3$.

Figure S34: $^1$H NMR spectra of 1-(3-chlorophenyl)-3-phenylpropan-1-ol(4i) recorded in CDCl$_3$. 
Figure S35: $^1$H NMR spectra of 1-(3-bromophenyl)-3-phenylpropan-1-ol(4j) recorded in CDCl$_3$.

Figure S36: $^{13}$C($^1$H) NMR spectra of 1-(3-bromophenyl)-3-phenylpropan-1-ol(4j) recorded in CDCl$_3$. 
Figure S37: $^1$H NMR spectra of 3-phenyl-1-(p-tolyl)propan-1-ol (4l) recorded in CDCl$_3$.

Figure S38: $^{13}$C($^1$H) NMR spectra of 3-phenyl-1-(p-tolyl)propan-1-ol (4l) recorded in CDCl$_3$. 
Figure S39: $^1$H NMR spectra of 3-phenyl-1-(4-(trifluoromethyl)phenyl)propan-1-ol (4m) recorded in CDCl$_3$.

Figure S40: $^{13}$C($^1$H) NMR spectra of 3-phenyl-1-(4-(trifluoromethyl)phenyl)propan-1-ol (4m) recorded in CDCl$_3$. 
Figure S41: $^1$H NMR spectra of 1-(naphthalen-2-yl)-3-phenylpropan-1-ol(4p) recorded in CDCl$_3$.

Figure S42: $^{13}$C($^1$H) NMR spectra of 1-(naphthalen-2-yl)-3-phenylpropan-1-ol(4p) recorded in CDCl$_3$. 
**Figure S43:** $^1$H NMR spectra of 1-(4-methoxyphenyl)-3-phenylpropan-1-ol(4q) recorded in CDCl$_3$.

**Figure S44:** $^{13}$C($^1$H) NMR spectra of 1-(4-methoxyphenyl)-3-phenylpropan-1-ol(4q) recorded in CDCl$_3$. 
Figure S45: $^1$H NMR spectra of 3-(3-methoxyphenyl)-1-phenylpropan-1-ol(4r) recorded in CDCl$_3$.

Figure S46: $^{13}$C($^1$H) NMR spectra of 3-(3-methoxyphenyl)-1-phenylpropan-1-ol(4r) recorded in CDCl$_3$. 
**Figure S47:** $^1$H NMR spectra of 1-phenyl-3-(m-tolyl) propan-1-ol (4s) recorded in CDCl$_3$.

**Figure S48:** $^{13}$C($^1$H) NMR spectra of 1-phenyl-3-(m-tolyl)propan-1-ol (4s) recorded in CDCl$_3$. 
Figure S49: $^1$H NMR spectra of 1-phenyl-3-(pyridin-3-yl)propan-1-ol(4t) recorded in CDCl$_3$.

Figure S50: $^{13}$C($^1$H) NMR of 1-phenyl-3-(pyridin-3-yl)propan-1-ol(4t) recorded in CDCl$_3$. 
**Figure S51:** $^1$H NMR spectra of 3-(naphthalen-1-yl)-1-phenylpropan-1-ol(4u) recorded in CDCl$_3$.

**Figure S52:** $^{13}$C($^1$H) NMR spectra of 3-(naphthalen-1-yl)-1-phenylpropan-1-ol(4u) recorded in CDCl$_3$. 
**Figure S53:** $^1$H NMR spectra of 3-(3-chlorophenyl)-1-phenylpropan-1-ol(4z) recorded in CDCl$_3$.

**Figure S54:** $^{13}$C($^1$H) NMR spectra of 3-(3-chlorophenyl)-1-phenylpropan-1-ol(4z) recorded in CDCl$_3$. 
**Figure S55:** $^1$H NMR spectra of 3-(4-chlorophenyl)-1-phenylpropan-1-ol (4zb) recorded in CDCl$_3$.

**Figure S56:** $^{13}$C($^1$H) NMR spectra of 3-(4-chlorophenyl)-1-phenylpropan-1-ol (4zb) recorded in CDCl$_3$. 

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Figure S57: $^1$H NMR spectra of 1-phenyl-3-(p-tolyl)propan-1-ol(4ze) recorded in CDCl$_3$.

Figure S58: $^{13}$C($^1$H) NMR spectra of 1-phenyl-3-(p-tolyl)propan-1-ol(4ze) recorded in CDCl$_3$. 

S37
6. Calculation of Kinetic Isotopic Effect (KIE):

\[
\frac{k_{\text{Ha}}}{k_{\text{D}}} = \text{KIE}
\]

Where, \( k_{\text{Ha}} \) and \( k_{\text{D}} \) are the proton content and deuterium content at C<sub>a</sub> of the product 4a as determined by \(^1\text{H}-\text{NMR}\)

\[
k_{\text{Ha}} = \frac{\text{Integral value}}{\text{Number of protons}} \times 100 = A \times 100
\]

\[
k_{\text{D}} = (1-A)\times100
\]

7. Magnetic moment of 5 in solution (Evan’s method):

Magnetic moment in solution was measured by following the Evan’s NMR method.\(^{1-3}\) A solution of \((^\text{Ph}_2\text{NNN})\text{CrCl}_3\) (0.00055 g, 0.00125 mmol) in a 0.5 mL mixture of MeOH-d<sub>4</sub>/t-BuOH (98:2) was prepared. To the same NMR tube a capillary containing the 2% t-BuOH in MeOH-d<sub>4</sub> solution was inserted. NMR spectrum was recorded on a Bruker ASCEND 600 operating at 600 MHz. A chemical shift difference of 30 Hz was observed for the t-BuOH peak for the samples in the inner and outer tubes. Based on the equation\(^2\)

\[
\mu_0=798(\chi_M T)^{0.5} \text{[T= temperature of measurement and } \chi_M = 3\Delta f/1000fc, \text{where } \Delta f \text{ is the paramagnetic shift of the solvent in Hz, } f \text{ is the frequency of the NMR instrument in Hz, and } c \text{ is the molar concentration of the metal complex]}, \text{ we have observed the magnetic moment } \mu_{\text{eff}} = 3.4 \mu_0 \text{ which is in agreement with a octahedral Cr(III) species.}\(^4\)

Subsequently, NaOH (0.044g, 1.1 mmol) was added to a stock solution of \((^\text{Ph}_2\text{NNN})\text{CrCl}_3\) (0.0006 g, 0.00145 mmol) in a 0.5 mL mixture of MeOH-d<sub>4</sub>/t-BuOH (98:2). To the same NMR tube a capillary containing the 2% t-BuOH in MeOH-d<sub>4</sub> solution was inserted. NMR spectrum was recorded on a Bruker ASCEND 600 operating at 600 MHz. A chemical shift difference of 72 Hz was observed for the t-BuOH peak for the samples in the inner and outer tubes which gave a magnetic moment of 4.8 \(\mu_0\) which is in agreement with a octahedral Cr(II) species.\(^4\)

8. References: