Supporting Information

Manganese Catalyzed $\alpha$-Alkylation of Ketones, Esters and Amides Using Alcohols

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1. General Procedure

All experiments with metal complexes and phosphine ligands were carried out under an atmosphere of purified nitrogen in a Vacuum Atmospheres glovebox equipped with a MO 40-2 inert gas purifier or using standard Schlenk techniques under argon atmosphere. All solvents were reagent grade or better. Non-deuterated solvents were dried over sodium/benzophenoneketyl (tetrahydrofuran, n-pentane, 1,4-dioxane, and toluene), and distilled under argon atmosphere. All solvents were degassed with argon and kept in the glove box over activated 4Å molecular sieves. Deuterated solvents were purchased from Aldrich, purged with argon and stored over activated 4Å molecular sieves in the glove box. $^1$H, and $^{13}$C NMR spectra were recorded using Bruker AMX-300 and 500 NMR spectrometer. All spectra were recorded at 295 K, unless otherwise noted. $^1$H NMR and $^{13}$C{H} NMR chemical shifts are reported in ppm downfield from tetramethylsilane and referenced to the residual signals of an appropriate deuterated solvent. NMR spectroscopy abbreviations: br, broad; s, singlet; d, doublet; m, multiplet. GCMS was carried out on HP 6890 (flame ionization detector and thermal conductivity detector) and HP 5973 (MS detector) instruments equipped with a 30 m column (Restek 5MS, 0.32 mm internal diameter) with a 5% phenylmethylsilicone coating (0.25 mm) and helium as carrier gas. Most of the commercially available reagents were used as received. Catalyst 1, 2, 3 were prepared according to the literature procedure.1-3

2. Experimental

General procedure for the catalytic reactions

For Table 1: 1 mmol of benzyl alcohol and 1 mmol of acetophenone were added to 0.01 mmol of catalyst 1 (catalyst 2 and 3 for entry 9 and 10) and 3 mol% of $^t$BuOK (or other base, as mentioned in Table 1) and the mixture was dissolved in 2 mL of toluene (or 1,4-dioxane or THF; Table 1, entries 1, 2, 3, respectively) and placed in a 25 mL Teflon Schlenk tube under N2. The tube was heated at 125 ºC (or 110 ºC, Table 1, entry 7) with stirring for the mentioned time. The reaction mixture was then cooled down in an ice bath and the products were analyzed by GC-MS using m-xylene as internal standard.
For Table 2: 1 mmol of primary alcohol and 1 mmol of ketone substrate were added to 0.01 mmol of catalyst 1 with 3 mol% of tBuOK and the mixture was dissolved in 2 mL of toluene and placed in a 25 mL Teflon Schlenk tube under N₂. The tube was heated at 125 ºC with stirring for 18h (for entries J-N: 0.5 mmol alcohol, 0.5 mmol ketone, 0.01 mmol cat, 6 mol% tBuOK were used). The reaction mixture was then cooled down in an ice bath and the products were analyzed by GC-MS and NMR. Most of the products were isolated after column chromatography passing through silica with 10% ethylacetate and hexane solvent mixture.

For Scheme 3: 1 mmol of benzyl alcohol derivatives and 1 mmol of 1-phenylethanol were added to 0.01 mmol of catalyst 1 with 3 mol% of tBuOK and the mixture was dissolved in 2 mL of toluene, placed in a 25 mL Teflon Schlenk tube under N₂. The tube was heated at 125 ºC with stirring for 18h. The reaction mixture was then cooled down in an ice bath and H₂ was vented off. The reaction products were analyzed by GC-MS and NMR.

For Table 3, esters alkylation: 1 mmol of primary alcohol, and 4 mmol of t-butyl acetate were added to 0.05 mmol of catalyst 1 with 1.5 equivalent (with respect to alcohol) of tBuOK and the mixture was dissolved in 2 mL of t-butanol, placed in a 25 mL Teflon Schlenk tube under N₂. The tube was heated at 125 ºC with stirring for 18h. The reaction mixture was then cooled down and products were analysed by GC-MS. Most of the products were isolated after column chromatography passing through silica with 1% diethylether and hexane solvent mixture.

For Table 3, amide alkylation: 1 mmol of primary alcohol, and 2 mmol of N,N-dimethylacetamide were added to 0.05 mmol of catalyst 1 with 1.5 equivalent (with respect to alcohol) of tBuOK and the mixture was dissolved in 2 mL of toluene, placed in a 25 mL Teflon Schlenk tube under N₂. The tube was heated at 125 ºC with stirring for 18h. The reaction mixture was then cooled down and products were analysed by GC-MS. Most of the products were isolated after column chromatography passing through silica with 30% ethylacetate and hexane solvent mixture.
Reaction of methanol or ethanol with acetophenone catalyzed by 1:

1 mmol of acetophenone and 4 mmol of methanol or ethanol were added to 0.01 mmol of catalyst 1 with 3 mol% of tBuOK and the mixture was dissolved in 2 mL of toluene and placed in a 25 mL Teflon Schlenk tube under N\textsubscript{2}. The tube was heated at 125 °C with stirring for 18h. The reaction mixture was then cooled down in an ice bath and the products were analyzed by GC-MS.

For methanol: overall 40% conversion was observed. 20% of the 1-phenylpropanone was formed along with other high molecular weight condensed product.

For ethanol: overall 80% of the conversion was observed, with formation of 1-phenyl ethanol and 35% of the 1-phenylbutanone was formed as the targeted product.

Gas phase analysis of the reaction and hydrogen gas detection:

1 mmol of benzyl alcohol and 1 mmol of 1-phenylethanol were added to 0.01 mmol of catalyst 1 with 3 mol% of tBuOK and the mixture was dissolved in 2 mL of toluene, placed in a 25 mL Teflon Schlenk tube under N\textsubscript{2}. The tube was heated at 125 °C with stirring for 18h. The reaction mixture was then cooled down in an ice bath. The gas mixture was injected into a GC instrument equipped with a thermal conductivity detector, showing formation of H\textsubscript{2}.
Figure S1. GC chromatogram of the gas phase using a thermal conductivity detector for H$_2$ analysis. Top: blank run; bottom: reaction gas phase (arrow marks the H$_2$ peak)
3. GC-MS data of the products

**Table S1:** GC-MS data of the products was obtained using an HP 6890 GC chromatograph equipped with flame ionization and thermal conductivity detectors, and a HP 5973 (MS detector) instruments, equipped with a 30 m column (Restek 5MS, 0.32 mm internal diameter) with a 5% phenylmethylsilicone coating (0.25 mm) and helium as carrier gas with a flow rate of 1 ml/min:

| Compound  | Retention Time (min) | Mass/Charge Ratio (m/z) |
|-----------|----------------------|-------------------------|
| 1. Ph-O   | 17.61               | 210                     |
| 2. Me₂N-Ph-O | 18.26             | 253                     |
| 3. F₃C-Ph-O | 15.58             | 278                     |
| 4. Br-Ph-O | 17.74               | 288                     |
| 5. Me-Ph-O | 16.35               | 224                     |
| 6. MeO-Ph-O | 18.42              | 270                     |
| 7. F-Ph-O | 15.61               | 228                     |
| 8. MeO-Ph-O | 17.38              | 240                     |
| 9. MeO-Ph-O | 19.23              | 260                     |
| 10. OMe-Ph | 18.96               | 240                     |
| 11. Ph-CO | 13.07               | 190                     |
| 12. Ph-CO | 14.186              | 204                     |
| 13. Ph-CO | 15.451              | 211                     |
| 14. Ph-CO | 15.778              | 216                     |

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|        |        |        |
|--------|--------|--------|
| ![Structure 1](image1.png) | ![Structure 2](image2.png) | ![Structure 3](image3.png) |
| tr = 12.04 m/z = 206 | tr = 14.91 m/z = 220 | tr = 15.68 m/z = 240 |
| ![Structure 4](image4.png) | ![Structure 5](image5.png) | ![Structure 6](image6.png) |
| tr = 14.11 m/z = 274 | tr = 13.66 m/z = 177 | tr = 14.45 m/z = 191 |
| ![Structure 7](image7.png) | ![Structure 8](image8.png) | ![Structure 9](image9.png) |
| MeO | F₃C | NC |
| tr = 15.07 m/z = 207 | tr = 16.78 m/z = 245 | tr = 16.78 m/z = 235 |
| ![Structure 10](image10.png) | ![Structure 11](image11.png) | ![Structure 12](image12.png) |
| tr = 12.18 m/z = 134 | tr = 12.69 m/z = 148 | tr = 18.19 m/z = 219 |
| ![Structure 13](image13.png) | ![Structure 14](image14.png) |
| tr = 16.13 m/z = 202 |
4. $^1$H and $^{13}$C{$^1$H} NMR data of isolated product

![Chemical structure](image)

$^1$H NMR (500 MHz, CDCl$_3$) $\delta$: 3.11 (t, J= 7.6Hz, 2H), 3.34 (d, J= 7.6Hz, 2H), 7.24 (t, J= 7.8Hz, 1H), 7.28-7.35 (m, 4H), 7.48 (t, J= 7.6Hz, 2H), 7.58 (t, J= 7.3Hz, 1H), 7.99 (d, J=7.3Hz, 2H); $^{13}$C NMR (125 MHz, CDCl$_3$): 31.1, 40.4, 126.1, 128.0 (2C), 128.4, 128.5 (2C), 128.6 (2C), 133.0, 136.8, 141.3, 144.9, 199.2.

The $^1$H and $^{13}$C NMR spectra showed good agreement with the literature data.$^{4a}$

![Chemical structure](image)

$^1$H NMR (500 MHz, CDCl$_3$) $\delta$: 3.04 (t, J= 7.7Hz, 2H), 3.29 (t, J= 7.7Hz, 2H), 3.81 (s, 3H), 6.87 (d, J= 8.5Hz, 2H), 7.20 (d, J= 8.5Hz, 2H), 7.47 (t, J=7.6Hz, 2H), 7.57 (t, J=7.7Hz, 2H), 7.98 (d, J= 7.7Hz, 2H); $^{13}$C NMR (125 MHz, CDCl$_3$): 29.3, 40.7, 55.2, 113.9 (2C), 128.1 (2C), 128.6 (2C), 129.3 (2C), 133.0, 133.3, 136.9, 158.0, 199.4.

The $^1$H and $^{13}$C NMR spectra showed good agreement with the literature data.$^{4a}$

![Chemical structure](image)

$^1$H NMR (500 MHz, CDCl$_3$) $\delta$: 2.35 (s, 3H), 3.06 (t, J= 7.6Hz, 2H), 3.31 (t, J= 7.6Hz, 2H), 7.15 (dd, J=7.2Hz, J=20.0Hz, 4H), 7.48 (t, J=7.7Hz, 2H), 7.58 (t, J=7.7Hz, 1H), 7.98 (d, J= 7.7Hz, 2H); $^{13}$C NMR (125 MHz, CDCl$_3$): 21.0, 29.7, 40.6, 128.0 (2C), 128.3 (2C), 128.6 (2C), 129.2 (2C), 133.0, 135.6, 138.2, 144.9, 199.3.

The $^1$H and $^{13}$C NMR spectra showed good agreement with the literature data.$^{4a}$

![Chemical structure](image)

$^1$H NMR (500 MHz, CDCl$_3$) $\delta$: 2.98 (s, 6H), 3.05 (t, J= 7.5Hz, 2H), 3.36 (t, J= 7.5Hz, 2H) 6.70 (b, 3H), 7.24 (t, J=7.6Hz, 1H), 7.49 (t, J=7.6Hz, 2H), 760 (t, J=7.2Hz, 1H), 8.00 (d, J=7.6Hz, 2H); $^{13}$C NMR (125 MHz, CDCl$_3$): 30.7, 40.7, 40.8, 110.9, 113.1, 117.1, 128.1 (2C), 128.6 (2C), 129.2, 132.9, 136.9, 142.3, 150.6, 199.5.

The $^1$H and $^{13}$C NMR spectra showed good agreement with the literature data.$^{4a}$
$^1$H NMR (500 MHz, CDCl$_3$) $\delta$: 3.10 (t, $J= 7.6$Hz, 2H), 3.31 (d, $J= 7.6$Hz, 2H), 3.86 (s, 3H), 6.89-6.895 (m, 2H), 7.24-7.25 (m, 2H), 7.48 (t, $J=7.4$Hz, 2H), 7.58 (t, $J=7.4$Hz, 2H), 8.02(d, $J= 7.6$Hz, 2H); $^{13}$C NMR (125 MHz, CDCl$_3$): 25.7, 38.9, 55.2, 110.2, 120.5, 127.5, 128.1 (2C), 128.5 (2C), 129.5, 130.2, 132.9, 137.0, 157.5, 200.0.

The $^1$H and $^{13}$C NMR spectra showed good agreement with the literature data.\textsuperscript{4a}

![Chemical Structure](image)

$^1$H NMR (500 MHz, CDCl$_3$) $\delta$: 3.04 (t, $J= 7.9$Hz, 2H), 3.30 (t, $J= 7.9$Hz, 2H), 3.87 (s, 3H), 3.88 (s, 3H), 6.79-6.82 (m, 3H), 7.47 (t, $J=7.3$Hz, 2H), 7.57 (t, $J=7.3$Hz, 1H), 7.98 (d, $J= 7.4$Hz, 2H); $^{13}$C NMR (125 MHz, CDCl$_3$): 29.8, 40.7, 55.8, 55.9, 111.3, 111.8, 120.1, 128.0 (2C), 128.6 (2C), 133.0, 133.9, 136.9, 147.4, 148.9, 199.4.

The $^1$H and $^{13}$C NMR spectra showed good agreement with the literature data.\textsuperscript{4a}

![Chemical Structure](image)

$^1$H NMR (500 MHz, CDCl$_3$) $\delta$: 3.16 (t, $J=7.3$Hz, 2H), 3.35 (t, $J=7.3$Hz, 2H), 7.39 (d, $J=7.9$Hz, 2H), 7.48 (t, $J=7.6$Hz, 2H), 7.57 (d, $J=7.9$Hz, 2H), 7.59 (t, $J=7.6$Hz, 2H), 7.98 (d, $J= 7.5$Hz, 2H); $^{13}$C NMR (125 MHz, CDCl$_3$): 29.7, 39.8, 125.39-125.48 (q, $^3$J$_{CF} = 3.8$Hz, 2C, q, $^1$J$_{C-F} = 271.8$Hz, CF$_3$), 128.0 (2C), 128.6 (2C), 128.8 (2C), 133.2 (2C), 136.6, 145.4, 198.5.

The $^1$H and $^{13}$C NMR spectra showed good agreement with the literature data.\textsuperscript{4a}

![Chemical Structure](image)

$^1$H NMR (500 MHz, CDCl$_3$) $\delta$: 3.05 (t, $J= 7.5$Hz, 2H), 3.30 (t, $J= 7.5$Hz, 2H), 7.15 (d, $J= 7.6$Hz, 2H), 7.43 (d, $J= 7.6$Hz, 2H), 7.48 (t, $J=7.0$Hz, 2H), 7.58 (t, $J=7.0$Hz, 1H), 7.97 (d, $J= 7.6$Hz, 2H); $^{13}$C NMR (125 MHz, CDCl$_3$): 29.4, 40.0, 119.9, 128.0 (2C), 128.6 (2C), 130.2 (2C), 131.5 (2C), 133.2, 136.7, 140.2, 198.8.

The $^1$H and $^{13}$C NMR spectra showed good agreement with the literature data.\textsuperscript{4a}
$^1$H NMR (500 MHz, CDCl$_3$) $\delta$: 3.46 (t, J=7.2Hz, 2H), 3.58 (t, J=7.2Hz, 2H), 7.44-7.49 (m, 4H), 7.51-7.59 (m, 3H), 7.77-7.79 (m, 1H), 7.91 (d, J=7.7Hz, 1H), 7.99 (d, J=7.7Hz, 2H), 8.10 (d, J=7.7Hz, 1H); $^{13}$C NMR (125 MHz, CDCl$_3$): 27.2, 39.7, 123.5, 125.6, 125.7, 126.1, 126.2, 127.0, 128.0 (2C), 128.6 (2C), 128.9, 131.7, 133.1, 133.9, 136.8, 137.4, 199.3.

The $^1$H and $^{13}$C NMR spectra showed good agreement with the literature data.$^{4a}$

$^1$H NMR (500 MHz, CDCl$_3$) $\delta$: 3.09 (t, J=7.6Hz, 2H), 3.60 (t, J=7.6Hz, 2H), 7.20-7.22 (m, 1H), 7.30 (m, 4H), 7.47-7.50 (m, 1H), 7.85 (t, J=7.4Hz, 1H), 8.07 (d, J=7.9Hz, 1H), 8.69 (d, J=5.1Hz, 1H); $^{13}$C NMR (125 MHz, CDCl$_3$): 29.8, 39.4, 121.8, 125.9, 127.1, 128.4 (2C), 128.5 (2C), 136.9, 141.4, 148.9, 153.2, 201.2.

The $^1$H and $^{13}$C NMR spectra showed good agreement with the literature data.$^{4a}$

$^1$H NMR (500 MHz, CDCl$_3$) $\delta$: 3.10 (t, J=7.2Hz, 2H), 3.26 (t, J=7.2Hz, 2H), 3.60H (J=4.1Hz, 1H), 7.24 (t, J=7.1Hz, 1H), 7.27-7.29 (m, 2H), 7.33 (t, J=7.3Hz, 2H), 7.65 (d, J=5.1Hz, 1H), 7.71 (d, J=4.1Hz, 1H); $^{13}$C NMR (125 MHz, CDCl$_3$): 30.3, 41.4, 126.2, 128.1, 128.4 (2C), 128.6 (2C), 131.8, 133.6, 141.0, 144.1, 192.2.

The $^1$H and $^{13}$C NMR spectra showed good agreement with the literature data.$^{4a}$

$^1$H NMR (500 MHz, CDCl$_3$) $\delta$: 3.010 (t, J=7.4Hz, 2H), 3.33 (t, J=7.4Hz, 2H), 7.22-7.26 (m, 3H), 7.32-7.33 (m, 2H), 7.77 (d, J=8.4Hz, 2H), 8.04 (d, J=8.4Hz, 2H); $^{13}$C NMR (125 MHz, CDCl$_3$): 29.8, 40.7, 116.3, 117.9, 126.3, 128.4 (2C), 128.5, 128.6 (2C), 128.7, 132.5 (2C), 139.7, 140.6, 197.8.

The $^1$H and $^{13}$C NMR spectra showed good agreement with the literature data.$^{4b}$
The $^1$H and $^{13}$C NMR spectra showed good agreement with the literature data.\textsuperscript{4a}

The $^1$H and $^{13}$C NMR spectra showed good agreement with the literature data.\textsuperscript{4c}

The $^1$H and $^{13}$C NMR spectra showed good agreement with the literature data.\textsuperscript{4d}
The $^1$H and $^{13}$C NMR spectra showed good agreement with the literature data.\(^{4d}\)

\begin{center}
\includegraphics[width=0.2\textwidth]{structure1}
\end{center}

$^1$H NMR (500 MHz, CDCl\(_3\)) $\delta$: 2.59 (t, $J=8.1$ Hz, 2H), 2.92 (t, $J=8.1$ Hz, 2H), 2.94-2.96 (b, 6H), 3.80 (s, 3H), 6.84 (d, $J=8.3$ Hz, 2H), 7.16 (d, $J=8.3$ Hz, 2H); $^{13}$C NMR (125 MHz, CDCl\(_3\)): 30.5, 35.4, 35.5, 37.1, 55.2, 113.8, 129.3, 133.5, 157.9, 172.3.

The $^1$H and $^{13}$C NMR spectra showed good agreement with the literature data.\(^{4d}\)

\begin{center}
\includegraphics[width=0.2\textwidth]{structure2}
\end{center}

$^1$H NMR (500 MHz, CDCl\(_3\)) $\delta$: 2.63 (t, $J=8.1$ Hz, 2H), 3.00 (t, $J=8.1$ Hz, 2H), 3.37 (t, $J=4.7$ Hz, 2H), 3.53 (t, $J=4.7$ Hz, 2H), 3.64 (bs, 4H), 7.21-7.24 (m, 3H), 7.29-7.32 (m, 2H); $^{13}$C NMR (125 MHz, CDCl\(_3\)): 31.4, 34.8, 41.9, 45.9, 66.4, 66.8, 126.2, 128.4 (2C), 128.5 (2C), 141.0, 170.9.

The $^1$H and $^{13}$C NMR spectra showed good agreement with the literature data.\(^{4d}\)

\begin{center}
\includegraphics[width=0.2\textwidth]{structure3}
\end{center}

$^1$H NMR (500 MHz, CDCl\(_3\)) $\delta$: 1.43 (s, 9H), 2.56 (t, $J=7.9$ Hz, 2H), 2.93 (t, $J=7.9$ Hz, 2H), 7.16-7.22 (m, 3H), 7.29-7.32 (m, 2H); $^{13}$C NMR (125 MHz, CDCl\(_3\)): 28.2, 31.1, 37.1, 80.4, 126.1, 128.3, 128.4, 140.7, 172.4.

The $^1$H and $^{13}$C NMR spectra showed good agreement with the literature data.\(^{4d}\)

\begin{center}
\includegraphics[width=0.2\textwidth]{structure4}
\end{center}

$^1$H NMR (500 MHz, CDCl\(_3\)) $\delta$: 1.55 (s, 9H), 6.39 (d, $J=16.1$ Hz, 1H), 7.38-7.39 (m, 3H), 7.52-7.54 (m, 2H), 7.61 (d, $J=16.1$ Hz, 1H); $^{13}$C NMR (125 MHz, CDCl\(_3\)): 28.0, 80.5, 120.1, 127.9, 129.0, 134.6, 143.5, 166.3.
$^1$H NMR (500 MHz, CDCl$_3$) $\delta$: 1.44 (s, 9H), 2.33 (s, 3H), 2.53 (t, J= 7.9Hz, 2H), 2.89 (t, J= 7.9Hz, 2H), 7.11 (s, 4H); $^{13}$C NMR (125 MHz, CDCl$_3$): 21.0, 28.2, 30.7, 37.2, 80.4, 128.2, 129.0, 135.5, 137.7, 172.4.

The $^1$H and $^{13}$C NMR spectra showed good agreement with the literature data.$^{4d}$

$^1$H NMR (500 MHz, CDCl$_3$) $\delta$: 1.55 (s, 9H), 2.39 (s, 3H), 6.35 (d, J= 15.7Hz, 1H), 7.20 (d, J= 7.8Hz, 2H), 7.43 (d, J= 7.8Hz, 1H), 7.58 (d, J= 15.7Hz, 1H); $^{13}$C NMR (125 MHz, CDCl$_3$): 21.4, 28.0, 84.3, 119.0, 127.7, 129.5, 131.9, 140.3, 143.5, 166.5.

The $^1$H and $^{13}$C NMR spectra showed good agreement with the literature data.$^{4d}$
5. Selected $^1$H and $^{13}$C NMR spectra of isolated products

Figure S2. $^1$H NMR of 1,3-diphenylpropan-1-one

Figure S3. $^{13}$C NMR of 1,3-diphenylpropan-1-one
Figure S4. $^1$H NMR of A

Figure S5. $^1$H NMR of A
Figure S6. $^1$H NMR of B

Figure S7. $^{13}$C NMR of B
Figure S8. $^1$H NMR of C

Figure S9. $^{13}$C\{${^1}$H\} NMR of C
Figure S10. $^1$H NMR of D

Figure S11. $^{13}$C($^1$H) NMR of D
Figure S12. $^1$H NMR of E

Figure S13. $^{13}$C($^1$H) NMR of E
Figure S14. $^1$H NMR of F

Figure S15. $^{13}$C{$^1$H} NMR of F
Figure S16. $^1$H NMR of H

Figure S17. $^{13}$C{$^1$H} NMR of H
Figure S18. $^1$H NMR of K

Figure S19. $^{13}$C{$^1$H} NMR of K
Figure S20. $^1$H NMR of L

Figure S21. $^{13}$C($^1$H) NMR of L
Figure S22. $^1$H NMR of M

Figure S23. $^{13}$C{ $^1$H} NMR of M
Figure S24. $^{13}\text{C}^\{1\text{H}\}$ NMR of I

Figure S25. $^{13}\text{C}^\{1\text{H}\}$ NMR of I
Figure S26. $^1$H NMR of J

Figure S27. $^{13}$C$^1$H NMR of J
Figure S28. $^{13}$C{$^{1}$H} NMR of Q

Figure S29. $^{13}$C{$^{1}$H} NMR of Q
**Figure S30.** $^1$H NMR of 3-(phenyl)-N,N-dimethylpropanamide

**Figure S31.** $^{13}$C{$^1$H} NMR of 3-(phenyl)-N,N-dimethylpropanamide
Figure S32. $^1$H NMR of 3-(4-methylphenyl)-N,N-dimethylpropanamide

Figure S33. $^{13}$C($^1$H) NMR of 3-(4-methylphenyl)-N,N-dimethylpropanamide
Figure S34. $^1$H NMR of 3-(4-methoxyphenyl)-N,N-dimethylpropanamide

Figure S35. $^{13}$C{$^1$H} NMR of 3-(4-methoxyphenyl)-N,N-dimethylpropanamide
Figure S36. $^1$H NMR of 1-morpholino-3-phenylpropan-1-one

Figure S37. $^{13}$C{$^1$H} NMR of 1-morpholino-3-phenylpropan-1-one
Figure S38. $^1$H NMR of tert-butyl 3-(phenyl)propanoate

Figure S39. $^{13}$C{$^1$H} NMR of tert-butyl 3-(phenyl)propanoate
**Figure S40.** $^1$H NMR of tert-butyl 3-(4-methylphenyl)propanoate

**Figure S41.** $^{13}$C{$^1$H} NMR of tert-butyl 3-(4-methylphenyl)propanoate
Figure S42. $^1$H NMR of tert-butyl 3-(4-chlorophenyl)propanoate

Figure S43. $^{13}$C($^1$H) NMR of tert-butyl 3-(4-chlorophenyl)propanoate
6. REFERENCES

(1) Chakraborty, S.; Gellrich, U.; Diskin-Posner, Y.; Leitus, G.; Avram, L.; Milstein, D. Manganese-Catalyzed N-Formylation of Amines by Methanol Liberating H₂: A Catalytic and Mechanistic Study. Angew. Chem. Int. Ed. 2017, 56, 4229-4233.

(2) Mukherjee, A.; Nerush, A.; Leitus, G.; Shimon, L. J. W.; Ben-David, Y.; Espinosa Jalapa, N. A.; Milstein, D. Manganese-Catalyzed Environmentally Benign Dehydrogenative Coupling of Alcohols and Amines to Form Aldimines and H₂: A Catalytic and Mechanistic Study. J. Am. Chem. Soc. 2016, 138, 4298-4301.

(3) Espinosa-Jalapa, N. A.; Kumar, A.; Milstein. D. Synthesis of Cyclic Imides by Acceptorless Dehydrogenative Coupling of Diols and Amines Catalyzed by a Manganese Pincer Complex. J. Am. Chem. Soc. 2017, 139, 11722-11725.

(4) (a) Tan, D. –W.; Li, H.-X.; Zhu, D.-L; Li, H.-Y.; Young, D. J.; Yao, J.-L.; Lang, J.-P. Ligand-Controlled Copper(I)-Catalyzed Cross-Coupling of Secondary and Primary Alcohols to α-Alkylated Ketones, Pyridines and Quinolines. Org. Lett., 2018, 20, 608–611. (b) Yang, J.; Seto, Y. W.; Yoshikai, N. Cobalt-Catalyzed Intermolecular Hydroacylation of Olefins through Chelation-Assisted Imidoyl C-H Activation. ACS Catal., 2015, 5, 3054–3057. (c) Jensen, T.; Madsen, R. Ruthenium-Catalyzed Alkylation of Oxindole with Alcohols. J. Org. Chem., 2009, 74, 3990–3992. (d) Deibl, N.; Kempe, R. General and Mild Cobalt-Catalyzed C-Alkylation of Unactivated Amides and Esters with Alcohols. J. Am. Chem. Soc., 2016, 138, 10786–10789.