Electronic Supplementary Information

Pt, Pd and Au Nanoparticles Supported on DNA-MMT Hybrid: Efficient Catalysts for Highly Selective Oxidation of Primary Alcohols to Aldehydes, Acids and Esters

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General Remarks

All substrates were purchased commercially without further purification. Fish sperm DNA (CAS: 100403-24-5). The morphology and size of the Pd NPs were characterized on transmission electron microscopy (TEM) (JEOL–2010 and Hitachi H7650). The diluted solutions of the as-synthesized metal/DNA-MMT nanohybrid were used as samples directly and dried on the carbon-coated Cu grids. X-ray powder diffraction (XRD) experiments were carried out with a Philips X’Pert Pro Super diffractometer with Cu KR radiation ($\lambda = 1.54178 \text{ Å}$). The accurate concentrations of metal/DNA-MMT nanohybrid and other supported metal catalysts were directly determined by ICP-OES (Inductively Coupled Plasma Optical Emission Spectrometer) using Perkin Elmer Optima 7300 DV. $^1$H NMR, $^{13}$C NMR and $^{31}$P NMR were recorded on a Bruker AC-300 FT ($^1$H NMR 300 MHz, $^{13}$C NMR 75 MHz) or Bruker AC-400 FT ($^1$H NMR 400 MHz, $^{13}$C NMR 100 MHz) using TMS as internal reference. HRMS were recorded on a MicroMass GCT TOF-MS. GC-MS samples were recorded on a Shimadzu QP-5050 GC-MS system. And the yields were determined using 1,3,5-trimethylbenzene as an internal standard. X-ray photoelectron spectroscopy (XPS) measurements were performed on an ESCALAB 250 electron spectrometer using monochromatized Al K$\alpha$ excitation source ($h \nu = 1486.6$ eV).

General procedures for the synthesis of heterogeneous catalysts

Synthesis of metal/DNA

0.2 mmol of the corresponding metal salt (PdCl$_2$, KAuCl$_4$, K$_2$PtCl$_6$) and 20 mg of fish sperm DNA were dissolved in 24 ml Tris buffer (10 mM, pH = 7.4). The combined solution was stirred for 24 h to ensure the corresponding metal ion (Pd$^{2+}$, Au$^{3+}$, Pt$^{4+}$) thoroughly bind to DNA. After this aging process, 1.0 mmol of freshly dissolved NaBH$_4$ in 16 ml Tris buffer was added dropwise under N$_2$ atmosphere at 0 °C. After reduction, the solution was stirred for another 24 h in N$_2$ from 0 °C to room temperature to obtain the resulting M/DNA nanohybrids (c.a. 5 mM in Tris). This synthesis method can be scaled up to hundreds of millilitres easily at a time.

Synthesis of metal/MMT

0.2 mmol of the corresponding metal salt (PdCl$_2$, KAuCl$_4$, K$_2$PtCl$_6$) and 40 mg of Na-MMT were dissolved in 24 ml Tris buffer (10 mM, pH = 7.4). The combined solution was stirred for 24 h to ensure the corresponding metal ion (Pd$^{2+}$, Au$^{3+}$, Pt$^{4+}$)
thoroughly bind to Na-MMT. After this aging process, 1.0 mmol of freshly dissolved NaBH₄ in 16 ml Tris buffer was added dropwise under N₂ atmosphere at 0 °C. After reduction, the solution was stirred for another 24 h in N₂ from 0 °C to room temperature to obtain the resulting M/Na-MMT nanohybrids (c.a. 5 mM in Tris).

**Synthesis of metal/DNA-MMT**

To synthesize the hybrid of DNA-MMT, Na-MMT and fish sperm DNA were dispersed in deionized water with the desired concentration (MMT/DNA (w/w) = 2.0). After adjusting the pH value to 8 with 0.1 M Na₂CO₃, the above system was left under vigorous stirring for 12 h at 50 °C. Then the hybrid was centrifuged, washed with deionized water and dried under vacuum.

0.2 mmol of the corresponding metal salt (PdCl₂, KAuCl₄, K₂PtCl₆) and 60 mg of the as-synthesized DNA-MMT hybrid were dissolved in 36 ml Tris buffer (10 mM, pH = 7.4). The combined solution was stirred for 24 h to ensure the corresponding metal ion (Pd²⁺, Au³⁺, Pt⁴⁺) thoroughly bind to DNA. After this aging process, 1.0 mmol of freshly dissolved NaBH₄ in 14 ml Tris buffer was added dropwise under N₂ atmosphere at 0 °C. After reduction, the solution was stirred for another 24 h in N₂ from 0 °C to room temperature to obtain the resulting M/DNA-MMT catalysts (c.a. 4 mM in Tris).

**Detailed characterization of heterogeneous catalysts**

**XRD patterns for Na-MMT and DNA-MMT**

![Figure S1 XRD patterns of Na-MMT and DNA-MMT hybrid](image_url)
the XRD analyses for MMT and DNA-MMT show that 001 crystal face of origin Na-MMT'20 is 6.39°, while DNA-MMT'20 is 4.20°. The layer spacing of MMT increases from 1.38 nm to 2.09 nm through the Bragg law. The hybrid of DNA-MMT has been obtained.

XRD patterns for metal/DNA-MMT heterogeneous catalysts

Figure S2 XRD patterns of Pt/DNA-MMT, Pd/DNA-MMT and Au/DNA-MMT heterogeneous catalysts

XPS experiments for metal/DNA-MMT heterogeneous catalysts
TEM analyses for metal/DNA-MMT heterogeneous catalysts

Pt/DNA-MMT  Pd/DNA-MMT

Au/DNA-MMT

Figure S3 TEM analyses for Pt/DNA-MMT, Pd/DNA-MMT and Au/DNA-MMT heterogeneous catalysts
General procedure for selective oxidation of alcohols

selective oxidation of primary alcohols to aldehydes: For Pt/DNA-MMT catalyst: To 3 ml of as-synthesized Pt/DNA-MMT catalyst was precipitated by adding excess EtOH (3 times of the volume). After sitting for 1 h and then centrifuged at 6000 \text{ r min}^{-1} for 4 min, the decantate was poured off. The obtained solid residue was dried by N\textsubscript{2} flow and redispersed in a water solution (1 mL) containing K\textsubscript{3}PO\textsubscript{4}•3H\textsubscript{2}O (6.7 mg, 0.025 mmol). Benzyl alcohol (54.1 mg, 0.50 mmol) was then added to the solution. The air in the reaction mixture was removed under vacuum and the reaction vessel refilled with O\textsubscript{2}. This procedure was repeated for three times. The reaction mixture was then stirred under an O\textsubscript{2} balloon at 60 °C for 12 h. After the reaction was finished, 3 times the volume of EtOH and 5 times the volume of EtOAc was added to the reaction mixture. This mixture was left undisturbed for 2 h to allow precipitation and then centrifuged at 6000 \text{ r min}^{-1} for 4 min. The decantate was poured off. The solid residue was dried and used as the catalyst for the next round. The organic phase and the aqueous phase in the decantate were separated. The obtained aqueous phase was treated with hydrochloric acid and then extracted by EtOAc. The combined organic phase was evaporated with a rotary evaporator. The obtained residue was analyzed by GC-MS.

selective oxidation of primary alcohols to acids: For Pd/DNA-MMT catalyst: To 3 ml of as-synthesized Pd/DNA-MMT catalyst was precipitated by adding excess EtOH (3 times of the volume). After sitting for 1 h and then centrifuged at 6000 \text{ r min}^{-1} for 4 min, the decantate was poured off. The obtained solid residue was dried by N\textsubscript{2} flow and redispersed in a water solution (1 mL) containing LiOH•H\textsubscript{2}O (31.4 mg, 0.750 mmol). Benzyl alcohol (54.1 mg, 0.50 mmol) was then added to the solution. The air in the reaction mixture was removed under vacuum and the reaction vessel refilled with O\textsubscript{2}. This procedure was repeated for three times. The reaction mixture was then stirred under an O\textsubscript{2} balloon at 25 °C for 12 h. After the reaction was finished, 3 times the volume of EtOH and 5 times the volume of EtOAc was added to the reaction mixture. This mixture was left undisturbed for 2 h to allow precipitation and then centrifuged at 6000 \text{ r min}^{-1} for 4 min. The decantate was poured off. The solid residue was dried and used as the catalyst for the next round. The organic phase and the aqueous phase in the decantate were separated. The obtained aqueous phase was treated with hydrochloric acid and then extracted by EtOAc. The combined organic phase was evaporated with a rotary evaporator. The obtained residue was analyzed by GC-MS and then purified with column chromatography over silica gel. The resulting products were characterized by \textsuperscript{1}H NMR, \textsuperscript{13}C NMR and HRMS.

selective oxidation of primary alcohols to esters: For Au/DNA-MMT catalyst: To 2 ml of as-synthesized Au/DNA-MMT catalyst was precipitated by adding excess EtOH (3 times of the volume). After sitting for 1 h and then centrifuged at 6000 \text{ r min}^{-1} for 4 min, the decantate was poured off. The obtained solid residue was dried by N\textsubscript{2} flow
and redispersed in a water solution (1 mL) containing Cs$_2$CO$_3$ (61.1 mg, 0.1875 mmol). Benzyl alcohol (54.1 mg, 0.50 mmol) was then added to the solution. The air in the reaction mixture was removed under vacuum and the reaction vessel refilled with O$_2$. This procedure was repeated for three times. The reaction mixture was then stirred under an O$_2$ balloon at 50 °C for 12 h. After the reaction was finished, 3 times the volume of EtOH and 5 times the volume of EtOAc was added to the reaction mixture. This mixture was left undisturbed for 2 h to allow precipitation and then centrifuged at 6000 r min$^{-1}$ for 4 min. The decantate was poured off. The solid residue was dried and used as the catalyst for the next round. The organic phase and the aqueous phase in the decantate were separated. The obtained aqueous phase was treated with hydrochloric acid and then extracted by EtOAc. The combined organic phase was evaporated with a rotary evaporator. The obtained residue was analyzed by GC-MS and then purified with column chromatography over silica gel. The resulting products were characterized by $^1$H NMR, $^{13}$C NMR and HRMS.

**Comparsion of different heterogenous catalysts in selective oxidation of benzyl alcohol$^{[a]}$**

**Table S1**

<table>
<thead>
<tr>
<th>Entry</th>
<th>Catalyst</th>
<th>Base (equiv)</th>
<th>T (°C)</th>
<th>2a Yield (%)</th>
<th>3a Yield (%)</th>
<th>4a Yield (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Pd/DNA-MMT</td>
<td>LiOH·H$_2$O (1.5)</td>
<td>25</td>
<td>&lt; 1</td>
<td>99</td>
<td>n.d.</td>
</tr>
<tr>
<td>2</td>
<td>Pd/DNA</td>
<td>LiOH·H$_2$O (1.5)</td>
<td>25</td>
<td>3</td>
<td>95</td>
<td>n.d.</td>
</tr>
<tr>
<td>3</td>
<td>Pd/MMT</td>
<td>LiOH·H$_2$O (1.5)</td>
<td>25</td>
<td>3</td>
<td>96</td>
<td>n.d.</td>
</tr>
<tr>
<td>4</td>
<td>Pt/DNA-MMT</td>
<td>K$_3$PO$_4$·H$_2$O (0.05)</td>
<td>60</td>
<td>86</td>
<td>7</td>
<td>n.d.</td>
</tr>
<tr>
<td>5</td>
<td>Pt/DNA</td>
<td>K$_3$PO$_4$·H$_2$O (0.05)</td>
<td>60</td>
<td>75</td>
<td>20</td>
<td>n.d.</td>
</tr>
<tr>
<td>6</td>
<td>Pt/MMT</td>
<td>K$_3$PO$_4$·H$_2$O (0.05)</td>
<td>60</td>
<td>50</td>
<td>35</td>
<td>n.d.</td>
</tr>
<tr>
<td>7</td>
<td>Au/DNA-MMT</td>
<td>Cs$_2$CO$_3$ (0.75)</td>
<td>50</td>
<td>3</td>
<td>&lt; 1</td>
<td>95</td>
</tr>
<tr>
<td>8</td>
<td>Au/DNA</td>
<td>Cs$_2$CO$_3$ (0.75)</td>
<td>50</td>
<td>6</td>
<td>9</td>
<td>81</td>
</tr>
<tr>
<td>9</td>
<td>Au/MMT</td>
<td>Cs$_2$CO$_3$ (0.75)</td>
<td>50</td>
<td>10</td>
<td>21</td>
<td>68</td>
</tr>
</tbody>
</table>

$^{[a]}$ Reaction conditions: 1a (0.50 mmol), Cat. (Pt: 1.5 mol%, Pd: 1.7 mol%, Au: 2.9 mol%). $^{[b]}$ Determined by GC-MS with an internal standard, n.d. = not detected.
Selective oxidation of alcohol catalyzed by different metal salt\[a\]

Table S2

![Chemical structure diagram]

<table>
<thead>
<tr>
<th>Entry</th>
<th>Catalyst</th>
<th>Base (equiv)</th>
<th>T (°C)</th>
<th>2a (%)</th>
<th>3a (%)</th>
<th>4a (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>PdCl₂</td>
<td>LiOH·H₂O (1.5)</td>
<td>25</td>
<td>5</td>
<td>70</td>
<td>n.d.</td>
</tr>
<tr>
<td>4</td>
<td>K₂PtCl₆</td>
<td>K₃PO₄·H₂O (0.05)</td>
<td>60</td>
<td>4</td>
<td>trace</td>
<td>n.d.</td>
</tr>
<tr>
<td>7</td>
<td>KAuCl₄</td>
<td>Cs₂CO₃ (0.75)</td>
<td>50</td>
<td>11</td>
<td>7</td>
<td>trace</td>
</tr>
</tbody>
</table>

[a] Reaction conditions: 1a (0.50 mmol), Cat. (K₂PtCl₆: 1.5 mol%, PdCl₂: 1.7 mol%, KAuCl₄: 2.9 mol%). [b] Determined by GC-MS with an internal standard, n.d. = not detected.

The recycling of heterogeneous catalysts in selective oxidation of alcohol

The recycling of Pt/DNA-MMT\[a\]

Table S3

![Chemical structure diagram]

<table>
<thead>
<tr>
<th>Run</th>
<th>Yield (%)[b]</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>86</td>
</tr>
<tr>
<td>2</td>
<td>83</td>
</tr>
<tr>
<td>3</td>
<td>80</td>
</tr>
</tbody>
</table>

[a] Reaction conditions: 1a (0.50 mmol), Cat. (Pt: 1.5 mol%). [b] GC yield.
The recycling of Pt/DNA \[^a\]

Table S4

![Chemical reaction diagram](image)

<table>
<thead>
<tr>
<th>Run</th>
<th>Yield (%)[^b]</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>75</td>
</tr>
<tr>
<td>2</td>
<td>70</td>
</tr>
<tr>
<td>3</td>
<td>67</td>
</tr>
</tbody>
</table>

\[^a\] Reaction conditions: \(1\text{a} \) (0.50 mmol), Cat. (Pt: 1.5 mol\%). \[^b\] GC yield.

The recycling of Pd/DNA-MMT\[^a\]

Table S5

![Chemical reaction diagram](image)

<table>
<thead>
<tr>
<th>Run</th>
<th>Yield (%)[^b]</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>98</td>
</tr>
<tr>
<td>2</td>
<td>95</td>
</tr>
<tr>
<td>3</td>
<td>93</td>
</tr>
<tr>
<td>4</td>
<td>91</td>
</tr>
<tr>
<td>5</td>
<td>89</td>
</tr>
</tbody>
</table>

\[^a\] Reaction conditions: \(1\text{a} \) (0.50 mmol), Cat. (Pd: 1.7 mol\%). \[^b\] Isolated yield.

The recycling of Au/DNA-MMT\[^a\]

Table S6

![Chemical reaction diagram](image)

<table>
<thead>
<tr>
<th>Run</th>
<th>Yield (%)[^b]</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>94</td>
</tr>
<tr>
<td>2</td>
<td>90</td>
</tr>
<tr>
<td>3</td>
<td>87</td>
</tr>
<tr>
<td>4</td>
<td>84</td>
</tr>
<tr>
<td>5</td>
<td>81</td>
</tr>
</tbody>
</table>

\[^a\] Reaction conditions: \(1\text{a} \) (0.50 mmol), Cat. (Au: 1.7 mol\%). \[^b\] Isolated yield.
[a] Reaction conditions: 1a (0.50 mmol), Cat. (Au: 2.9 mol%). [b] Isolated yield.

ICP-OES measurement of heterogenous catalysts

For the as-synthesized metal/DNA-MMT nanohybrids (2 mL), with the aid of centrifugation at 5000 r/min for 5 minutes, then the decantate were poured out. The residues were dried by N₂ flow and dissolved in aqua regia. Then the mixture was filtered and washed. Subsequently, the filtrate was transferred to a 50 ml volumetric flask. The accurate Pt, Pd and Au content in the corresponding metal/DNA-MMT was 1.463 mg, 0.905 mg and 1.428 mg respectively with ICP-OES measurement. After three cycles the Pt content was decreased to 1.287 mg, the Pd content was decreased to 0.830 mg and the Au content was decreased to 1.251 mg after five cycles, respectively. In contrast, the Pt content was decreased to 1.194 mg from 1.463 mg in the Pt/DNA after three cycles

Characterization data of products

Benzoic acid (3a)

\[
\begin{align*}
\text{C} & \quad \text{O} \\
\text{H} & \quad \text{OH}
\end{align*}
\]

\[^1\text{H NMR (300 MHz, d}^6\text{-DMSO)}: \delta \text{ [ppm]} = 12.919 \text{ (s, 1H), 7.948 \text{ (d, 7.2 Hz, 2H), 7.620 \text{ (t, 7.5 Hz, 1H), 7.497 \text{ (t, 7.5 Hz, 2H);}^{13}\text{C NMR (75 MHz, CDCl}_3\text{)}: \delta \text{ [ppm]} = 172.6, 134.0, 130.4, 129.5, 128.6; HRMS (M\text{+}) \text{calcd for C}_7\text{H}_6\text{O}_2: 122.0368 found 122.0367.}\]

4-Fluorobenzoic acid (3b)

\[
\begin{align*}
\text{F} & \quad \text{C} & \quad \text{O} \\
\text{H} & \quad \text{OH}
\end{align*}
\]

\[^1\text{H NMR (300 MHz, d}^6\text{-DMSO)}: \delta \text{ [ppm]} = 13.021 \text{ (s, 1H), 8.002 \text{ (m, 2H), 7.316 \text{ (t, 9.0 Hz, 2H);}^{13}\text{C NMR (100 MHz, CDCl}_3\text{)}: \delta \text{ [ppm]} = 171.2, 166.5 \text{ (d, J}_{\text{CF} = 253.7 \text{ Hz), 133.1 \text{ (d, J}_{\text{CF} = 9.5 \text{ Hz), 125.7 \text{ (d, J}_{\text{CF} = 2.9 \text{ Hz), 115.9 \text{ (d, J}_{\text{CF} = 22.0 \text{ Hz);} HRMS (M\text{+}) \text{calcd for C}_7\text{H}_5\text{FO}_2: 140.0274 found 140.0278.}\]

3-Fluorobenzoic acid (3c)

\[
\begin{align*}
\text{F} & \quad \text{C} & \quad \text{O} \\
\text{H} & \quad \text{OH}
\end{align*}
\]
1H NMR (400 MHz, d$_6$-DMSO): $\delta$ [ppm] = 13.240 (s, 1H), 7.785 (d, 7.6 Hz, 1H), 7.664-7.631 (m, 1H), 7.577-7.523 (m, 1H), 7.492-7.444 (m, 1H); $^{13}$C NMR (100 MHz, d$_6$-DMSO): $\delta$ [ppm] = 166.2 (d, $J_{CF} = 2.8$ Hz), 162.0 (d, $J_{CF} = 243.2$ Hz), 133.3 (d, $J_{CF} = 7.2$ Hz), 130.8 (d, $J_{CF} = 7.9$ Hz), 125.4 (d, $J_{CF} = 2.8$ Hz), 119.8 (d, $J_{CF} = 21.0$ Hz), 115.7 (d, $J_{CF} = 22.5$ Hz); HRMS (M+) calcd for C$_7$H$_5$FO$_2$: 140.0274 found 140.0275.

4-Chlorobenzoic acid (3d)

4-Methylbenzoic acid (3f)

3-Methylbenzoic acid (3g)

4-Methoxybenzoic acid (3h)
4-Nitrobenzoic acid (3i)

\[
\begin{align*}
\text{1H NMR (400 MHz, d6-DMSO): } & \delta [\text{ppm}] = 13.644 (s, 1H), 8.316 (d, 8.6 Hz, 2H), 8.179-8.146 (m, 2H); \ \\
\text{13C NMR (100 MHz, d6-DMSO): } & \delta [\text{ppm}] = 165.8, 150.0, 136.4, 130.7, 123.7; \ \\
\text{HRMS (M+) calcd for C7H5NO4: } & 167.0219 \text{ found } 167.0222.
\end{align*}
\]

4-(Trifluoromethyl)benzoic acid (3j)

\[
\begin{align*}
\text{1H NMR (400 MHz, d6-DMSO): } & \delta [\text{ppm}] = 13.444 (s, 1H), 8.130 (d, 8.3 Hz, 2H), 7.860 (d, 8.3 Hz, 2H); \ \\
\text{13C NMR (100 MHz, d6-DMSO): } & \delta [\text{ppm}] = 166.2, 134.6, 132.5 (q, J_{CF} = 31.7), 130.1, 125.6 (q, J_{CF} = 37 Hz), 123.8 (q, J_{CF} = 270.7 Hz); \ \\
\text{HRMS (M+) calcd for C8H5F3O2: } & 190.0242 \text{ found } 190.0240.
\end{align*}
\]

Thiophene-2-carboxylic acid (3k)

\[
\begin{align*}
\text{1H NMR (300 MHz, d6-DMSO): } & \delta [\text{ppm}] = 13.006 (s, 1H), 7.878-7.857 (m, 1H), 7.734-7.718 (m, 1H), 7.190-7.161 (m, 1H); \ \\
\text{13C NMR (75 MHz, d6-DMSO): } & \delta [\text{ppm}] = 162.9, 134.7, 133.22, 133.19, 128.2; \ \\
\text{HRMS (M+) calcd for C5H4O2S: } & 127.9932 \text{ found } 127.9936.
\end{align*}
\]

Furan-2-carboxylic acid (3l)

\[
\begin{align*}
\text{1H NMR (400 MHz, d6-DMSO): } & \delta [\text{ppm}] = 12.972 (s, 1H), 7.907-7.901 (m, 1H), 7.211-7.200 (m, 1H), 6.652-6.638 (m, 1H); \ \\
\text{13C NMR (100 MHz, d6-DMSO): } & \delta [\text{ppm}] = 159.3, 147.0, 144.9, 117.7, 112.1; \ \\
\text{HRMS (M+) calcd for C5H4O3: } & 112.0160 \text{ found } 112.0161.
\end{align*}
\]
$^{1}$H NMR (400 MHz, CDCl$_3$): $\delta$ [ppm] = 8.110-8.082 (m, 2H), 7.588-7.544 (m, 1H), 7.476-7.444 (m, 3H), 7.430-7.332 (m, 4H), 5.382 (s, 2H); $^{13}$C NMR (100 MHz, CDCl$_3$): $\delta$ [ppm] = 166.6, 136.2, 133.2, 130.3, 129.9, 128.7, 128.5, 128.4, 128.3, 66.8; HRMS (M$^+$) calcd for C$_{14}$H$_{12}$O$_2$: 212.0837 found 212.0841.

4-Fluorobenzyl 4-fluorobenzoate (4b)

$^{1}$H NMR (400 MHz, CDCl$_3$): $\delta$ [ppm] = 8.093-8.050 (m, 2H), 7.441-7.406 (m, 2H), 7.135-7.045 (m, 4H), 5.316 (s, 2H); $^{13}$C NMR (100 MHz, CDCl$_3$): $\delta$ [ppm] = 166.0 (d, $J_{CF} = 252.7$ Hz), 165.6, 162.9 (d, $J_{CF} = 245.5$ Hz), 132.4 (d, $J_{CF} = 9.1$ Hz), 131.9 (d, $J_{CF} = 3.0$ Hz), 130.4 (d, $J_{CF} = 8.4$ Hz), 126.4 (d, 2.9 Hz), 115.7 (d, $J_{CF} = 21.8$ Hz), 66.3; HRMS (M$^+$) calcd for C$_{14}$H$_{10}$F$_2$O$_2$: 248.0649 found 248.0647.

4-Chlorobenzyl 4-chlorobenzoate (4c)

$^{1}$H NMR (400 MHz, CDCl$_3$): $\delta$ [ppm] = 8.008-7.974 (m, 2H), 7.428-7.391 (m, 2H), 7.382-7.343 (m, 4H), 5.316 (s, 2H); $^{13}$C NMR (100 MHz, CDCl$_3$): $\delta$ [ppm] = 165.6, 139.8, 134.5, 134.4, 131.2, 129.8, 129.0, 128.9, 128.5, 66.3; HRMS (M$^+$) calcd for C$_{14}$H$_{10}$Cl$_2$O$_2$: 280.0058 found 280.0063.

4-Bromobenzyl 4-bromobenzoate (4d)

$^{1}$H NMR (400 MHz, CDCl$_3$): $\delta$ [ppm] = 7.930-7.896 (m, 2H), 7.598-7.565 (m, 2H), 7.534-7.501 (m, 2H), 7.326-7.293 (m, 2H), 5.297 (s, 2H); $^{13}$C NMR (100 MHz, CDCl$_3$): $\delta$ [ppm] = 165.7, 134.9, 131.97, 131.95, 131.4, 130.1, 129.0, 128.5, 122.6, 66.3; HRMS (M$^+$) calcd for C$_{14}$H$_{10}$Br$_2$O$_2$: 367.9048 found 367.9042.

2-Bromobenzyl 2-bromobenzoate (4e)

O

Br

Br
$^1$H NMR (400 MHz, CDCl$_3$): $\delta$ [ppm] = 7.884-7.860 (m, 1H), 7.688-7.665 (m, 1H), 7.624-7.587 (m, 1H), 7.553-7.530 (m, 1H), 7.394-7.316 (m, 3H), 7.241-7.198 (m, 1H), 5.465 (s, 2H); $^{13}$C NMR (100 MHz, CDCl$_3$): $\delta$ [ppm] = 165.8, 135.1, 134.6, 134.5, 133.1, 132.9, 131.7, 130.5, 130.1, 127.7, 127.4, 123.8, 122.1, 67.1; HRMS (M+) calcd for C$_{14}$H$_{10}$Br$_2$O$_2$: 367.9048 found 367.9044.

4-Methylbenzyl 4-methylbenzoate (4f)

![4-Methylbenzyl 4-methylbenzoate](image)

$^1$H NMR (400 MHz, CDCl$_3$): $\delta$ [ppm] = 7.967 (d, 7.6 Hz, 2H), 7.348 (d, 8.0 Hz, 2H), 7.240-7.190 (m, 4H), 5.318 (s, 2H), 2.407 (s, 3H), 2.371 (s, 3H); $^{13}$C NMR (100 MHz, CDCl$_3$): $\delta$ [ppm] = 166.7, 143.8, 138.1, 133.4, 129.9, 129.4, 129.2, 128.5, 127.7, 66.6, 21.8, 21.3; HRMS (M+) calcd for C$_{16}$H$_{16}$O$_2$: 240.1150 found 240.1155.

3-Methylbenzyl 3-methylbenzoate (4g)

![3-Methylbenzyl 3-methylbenzoate](image)

$^1$H NMR (400 MHz, CDCl$_3$): $\delta$ [ppm] = 7.886 (t, 8.6 Hz, 2H), 7.381-7.243 (m, 5H), 7.161 (d, 6.8 Hz, 1H), 5.329 (s, 2H), 2.400 (s, 3H), 2.381 (s, 3H); $^{13}$C NMR (100 MHz, CDCl$_3$): $\delta$ [ppm] = 166.8, 138.4, 138.3, 136.2, 133.9, 130.4, 130.3, 129.13, 129.10, 128.7, 128.4, 127.0, 125.4, 66.9, 21.5, 21.4; HRMS (M+) calcd for C$_{16}$H$_{16}$O$_2$: 240.1150 found 240.1153.

4-Methoxybenzyl 4-methoxybenzoate (4h)

![4-Methoxybenzyl 4-methoxybenzoate](image)

$^1$H NMR (400 MHz, CDCl$_3$): $\delta$ [ppm] = 8.023-8.000 (m, 2H), 7.381 (d, 8.8 Hz, 2H), 6.922-6.890 (m, 4H), 5.271 (s, 2H), 3.848 (s, 3H), 3.815 (s, 3H); $^{13}$C NMR (100 MHz, CDCl$_3$): $\delta$ [ppm] = 166.4, 163.6, 159.8, 131.9, 130.1, 128.6, 122.9, 114.1, 113.7, 66.4, 55.6, 55.4; HRMS (M+) calcd for C$_{16}$H$_{16}$O$_4$: 272.1049 found 272.1043.

4-Nitrobenzyl 4-nitrobenzoate (4i)

![4-Nitrobenzyl 4-nitrobenzoate](image)

$^1$H NMR (400 MHz, CDCl$_3$): $\delta$ [ppm] = 8.318-8.292 (m, 2H), 8.273-8.232 (m, 4H), 7.622 (d, 8.8 Hz, 2H), 5.503 (s, 2H); $^{13}$C NMR (100 MHz, CDCl$_3$): $\delta$ [ppm] = 164.4, 151.0, 148.2, 142.5, 135.0, 131.0, 128.8, 124.1, 123.8, 66.2; HRMS (M+) calcd for C$_{14}$H$_{10}$N$_2$O$_6$: 302.0539 found 302.0544.
naphthalen-1-ylmethyl 1-naphthoate (4k)

\[ \text{1H NMR (400 MHz, CDCl}_3\text{): } \delta [ppm] = 8.881 (d, 8.7 Hz, 1H), 8.108-8.072 (m, 2H), 7.902 (d, 8.2 Hz, 1H), 7.835-7.762 (m, 3H), 7.603 (d, 6.8 Hz, 1H), 7.523-7.466 (m, 2H), 7.449-7.386 (m, 3H), 7.358-7.320 (m, 1H), 5.823 (s, 2H); \text{13C NMR (100 MHz, CDCl}_3\text{): } \delta [ppm] = 167.5, 134.5, 134.0, 133.7, 132.0, 131.7, 131.6, 130.6, 129.5, 128.9, 128.7, 128.0, 127.8, 127.0, 126.8, 126.4, 126.1, 125.6, 125.5, 124.6, 123.8, 65.3; \text{HRMS (M+) calcd for C}_{22}H_{16}O_2: 312.1150 found 312.1161. \]

2-Nitrobenzyl benzoate (4l)

\[ \text{1H NMR (400 MHz, CDCl}_3\text{): } \delta [ppm] = 8.148-8.087 (m, 3H), 7.700-7.637 (m, 2H), 7.623-7.580 (m, 1H), 7.528-7.457 (m, 3H), 5.787 (s, 2H); \text{13C NMR (100 MHz, CDCl}_3\text{): } \delta [ppm] = 166.1, 147.8, 133.9, 133.5, 132.5, 129.9, 129.7, 129.1, 128.9, 128.7, 125.3, 63.5; \text{HRMS (M+) calcd for C}_{14}H_{11}NO_4: 257.0688 found 257.0694. \]

2-Nitrobenzyl 4-methylbenzoate (4m)

\[ \text{1H NMR (400 MHz, CDCl}_3\text{): } \delta [ppm] = 8.108 (t, 8.6 Hz, 1H), 7.977-7.957 (m, 2H), 7.665-7.607 (m, 2H), 7.496-7.454 (m, 1H), 7.241 (s, 2H), 5.745 (s, 2H), 2.406 (s, 3H); \text{13C NMR (100 MHz, CDCl}_3\text{): } \delta [ppm] = 166.1, 147.8, 144.3, 133.9, 132.7, 129.9, 129.4, 129.0, 128.8, 127.0, 125.2, 63.3, 21.8; \text{HRMS (M+) calcd for C}_{15}H_{13}NO_4: 271.0845 found 271.0844. \]

2-Nitrobenzyl 3-methylbenzoate (4n)

\[ \text{1H NMR (400 MHz, CDCl}_3\text{): } \delta [ppm] = 8.149-8.127 (m, 1H), 7.909-7.889 (m, 2H), 7.687-7.634 (m, 2H), 7.524-7.482 (m, 1H), 7.421-7.358 (m, 2H), 5.778 (s, 2H), 2.421 (s, 3H); \text{13C NMR (100 MHz, CDCl}_3\text{): } \delta [ppm] = 166.3, 147.8, 138.6, 134.3, 133.9, 132.6, 130.5, 129.7, 129.1, 128.9, 128.6, 127.1, 125.3, 63.4, 21.4; \text{HRMS (M+) calcd for C}_{15}H_{13}NO_4: 271.0845 found 271.0841. \]
2-Nitrobenzyl 4-methoxybenzoate (4o)

\[
\text{H} \quad \text{O} \quad \text{O} \quad \text{NO}_2
\]

\[ ^1H \text{ NMR (400 MHz, CDCl}_3): \delta [ppm] = 8.119 (t, 8.4 \text{ Hz}, 1\text{H}), 8.065-8.029 (m, 2\text{H}), 7.682-7.622 (m, 2\text{H}), 7.511-7.469 (m, 1\text{H}), 6.964-6.928 (m, 2\text{H}), 5.748 (s, 2\text{H}), 3.870 (s, 3\text{H}); \]
\[ ^{13}C \text{ NMR (100 MHz, CDCl}_3): \delta [ppm] = 165.8, 163.9, 147.8, 133.9, 132.8, 132.0, 129.0, 128.8, 125.2, 122.1, 114.0, 63.2, 55.6; \]
\[ \text{HRMS (M+)} \text{ calcd for C}_{15}\text{H}_{13}\text{NO}_5: 287.0794 \text{ found 287.0799.} \]

2-Nitrobenzyl 4-fluorobenzoate (4p)

\[
\text{F} \quad \text{O} \quad \text{O} \quad \text{NO}_2
\]

\[ ^1H \text{ NMR (400 MHz, CDCl}_3): \delta [ppm] = 8.143-8.089 (m, 3\text{H}), 7.669-7.642 (m, 2\text{H}), 7.538-7.495 (m, 1\text{H}), 7.164-7.121 (m, 2\text{H}), 5.468 (s, 2\text{H}); \]
\[ ^{13}C \text{ NMR (100 MHz, CDCl}_3): \delta [ppm] = 166.2 (d, J_{\text{CF}} = 253 \text{ Hz}), 165.1, 147.9, 133.9, 132.5 (d, J_{\text{CF}} = 9.0 \text{ Hz}), 132.2, 129.2, 129.1, 126.0 (d, J_{\text{CF}} = 3.0 \text{ Hz}), 125.3, 115.9 (d, J_{\text{CF}} = 22.0 \text{ Hz}), 63.6; \]
\[ \text{HRMS (M+)} \text{ calcd for C}_{14}\text{H}_{10}\text{FNO}_4: 275.0594 \text{ found 275.0591.} \]
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