Supplementary information for

Synthesis of an oligomer ruthenium complex and its catalysis in the oxidation of alcohols

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Supporting Information

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I. Characterization of the ligand precursor(3) and the ligand

Dimethyl 4-(4-(2,2′:6′,2″-terpyridin-4′-yl)benzyloxy)pyridine-2,6-dicarboxylate (3):
white solid; $^1$H NMR (DMSO-d$_6$, 400 MHz): $\delta$ 3.92 (s, 6H), 5.51 (s, 2H), 7.53~7.56 (m, 2H), 7.72 (d, $J$ = 8.1 Hz, 2H), 7.89 (s, 2H), 8.00~8.07 (m, 4H), 8.69 (d, $J$ = 8.0 Hz, 2H), 8.75 (s, 2H), 8.78 (d, $J$ = 4.0 Hz, 2H). $^{13}$C NMR (CDCl$_3$, 101 MHz) $\delta$ 53.3, 70.4, 114.9, 118.9, 121.4, 123.9, 127.9, 128.2, 135.5, 136.9, 139.0, 149.2, 149.5, 149.9, 156.0, 156.1, 165.1, 166.7.

Figure S1. $^1$H NMR of dimethyl 4-(4-(2,2′:6′,2″-terpyridin-4′-yl)benzyloxy)pyridine-2,6-dicarboxylate (3) (DMSO-d$_6$)

Figure S2. $^{13}$C NMR of dimethyl 4-(4-(2,2′:6′,2″-terpyridin-4′-yl)benzyloxy)pyridine-2,6-dicarboxylate (3) (CDCl$_3$)

Potassium 4-(4-(2,2′:6′,2″-terpyridin-4′-yl)benzyloxy)pyridine-2,6-dicarboxylate (4)
$^1$H NMR (400 MHz, D$_2$O): δ 4.87 (s, 2H), 7.11～7.16 (m, 4H), 7.30 (d, $J = 8.2$ Hz, 2H), 7.40 (s, 2H), 7.62～7.67 (m, 4H), 7.89 (d, $J = 7.9$ Hz, 2H), 8.19 (d, $J = 4.4$ Hz, 2H). $^{13}$C NMR (101 MHz, DMSO-d$_6$:H$_2$O=1:3) δ 69.4, 111.8, 118.1, 122.2, 124.7, 126.8, 128.2, 135.9, 137.0, 138.2, 148.7, 148.8, 154.2, 155.2, 166.3, 172.2. HRMS (ESI): m/z calcd for C$_{29}$H$_{19}$K$_2$N$_4$O$_5$: 581.0630 [M+H]$^+ $; found: 581.0625.

Figure S3. $^1$H NMR of potassium 4-(4-(2,2':6',2''-terpyridin-4'-yl)benzyloxy)pyridine-2,6-dicarboxylate (4) (D$_2$O)

Figure S4. $^{13}$C NMR of potassium 4-(4-(2,2':6',2''-terpyridin-4'-yl)benzyloxy)pyridine-2,6-dicarboxylate (4) (DMSO-d$_6$:H$_2$O=1:3)
II. Optimization of oxidation of 1-phenylethanol

To explore the catalytic activity of oligomer-Ru(terpy)(pydic), oxidation of 1-phenylethanol was chosen as a model reaction. Initially, molecular oxygen was used as oxidant to conduct the conversion, but almost no oxidation reaction took place (Table S1, entry 1). Then hydrogen peroxide was tried because of its good performance in the Ru(terpy)(pydic) catalyzed oxidation of various alcohols. However, very low conversion was obtained (Table S1, entry 2). No big improvement was received by extending reaction time (Table S1, entry 3). Gratifyingly, TBHP showed good performance in the reaction and the conversion of 1-phenylethanol reached up to 96.3% with a selectivity of 99% in 16.0 h at 60°C (Table S1, entry 4).

The effect of several solvents was also screened. Results showed that n-hexane gave the best results among the tested solvents, the other solvents afforded low conversion compared to n-hexane in the same reaction time (Table S1, entries 4-8). Furthermore, the catalyst has best recyclability in n-hexane among all the tested solvents.

**Table S1** The oxidation of 1-phenylethanol catalyzed by oligomer-Ru(terpy)(pydic) with different oxidants and solvents
Entry  | Oxidant | Solvent   | Time (h) | Conv. (%) | Select. (%) |
---|---------|----------|----------|-----------|-------------|
1    | O$_2$   | Cyclohexane | 16.0     | N. R      | —           |
2    | 30% H$_2$O$_2$ | Cyclohexane | 16.0     | 32        | >99         |
3    | 30% H$_2$O$_2$ | Cyclohexane | 24.0     | 44        | >99         |
4    | 70% TBHP | Cyclohexane | 16.0     | 96        | >99         |
5    | 70% TBHP | Toluene    | 16.0     | 85        | >99         |
6    | 70% TBHP | DCE       | 16.0     | 95        | >99         |
7    | 70% TBHP | MTBE      | 16.0     | 78        | >99         |
8    | 70% TBHP | n-Hexane  | 16.0     | >99       | >99         |

Reaction condition: 1-phenylethanol (2 mmol), catalyst (0.2 mol%), oxidant (4 mmol), solvent (2 mL), reaction temperature 60°C.

The effect of the amount of TBHP on the oxidation of 1-phenylethanol was investigated at 60°C and the results are shown in Table S2. It is obvious that increasing TBHP loading can accelerate the reaction. When the molar ratio of TBHP to 1-phenylethanol was 3:1, the reaction could quantitatively complete in 6.0 h (Table S2, entry 3). With further increase of TBHP loading the accelerate rate decreased. Therefore, the molar ratio of TBHP to substrate was chosen as 3:1 in the later experiments.

Table S2 Effect of the amount of TBHP on the oxidation of 1-phenylethanol

<table>
<thead>
<tr>
<th>Entry</th>
<th>Substrate:TBHP</th>
<th>Time (h)</th>
<th>Conv. (%)</th>
<th>Select. (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>1:1</td>
<td>16.0</td>
<td>80</td>
<td>&gt;99</td>
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<td>4</td>
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<td>&gt;99</td>
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<tr>
<td>5</td>
<td>1:5</td>
<td>4.5</td>
<td>&gt;99</td>
<td>&gt;99</td>
</tr>
</tbody>
</table>

Reaction condition: 1-phenylethanol (2 mmol), catalyst (0.2 mol%), n-hexane (2 mL), reaction temperature 60°C.

* Determined by GC.
The amount of catalyst was optimized under the same TBHP loading and the results are listed in Table S3. The reaction conversion was only 31.1% in the absence of the catalyst in 10.5 h (Table S3, entry 1). The time to complete the reaction was shortened with increasing the catalyst loading from 0.05 to 0.20 mol % (Table S3, entries 2-5). When the catalyst loading was 0.10 mol%, almost a quantitative yield of acetophenone was obtained in 8.0 h (Table S3, entry 3). Though further increasing the catalyst loading can still accelerate the reaction, it is not necessary in view of the high cost of the catalyst. Thus, the catalyst loading was determined as 0.10 mol% of the substrate.

<table>
<thead>
<tr>
<th>Entry</th>
<th>Catalyst (mol%)</th>
<th>Time (h)</th>
<th>Conv. (%) a</th>
<th>Select. (%) a</th>
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<td>0.05</td>
<td>10.5</td>
<td>&gt;99</td>
<td>&gt;99</td>
</tr>
<tr>
<td>3</td>
<td>0.10</td>
<td>8.0</td>
<td>&gt;99</td>
<td>&gt;99</td>
</tr>
<tr>
<td>4</td>
<td>0.15</td>
<td>6.5</td>
<td>&gt;99</td>
<td>&gt;99</td>
</tr>
<tr>
<td>5</td>
<td>0.20</td>
<td>6.0</td>
<td>&gt;99</td>
<td>&gt;99</td>
</tr>
</tbody>
</table>

Table S3 Effect of the amount of catalyst on the oxidation of 1-phenylethanol

Reaction condition: 1-phenylethanol (2 mmol), oxidant (6 mmol), n-hexane (2 mL), reaction temperature 60°C.

a Determined by GC.

Finally, the effect of temperature on the reaction was evaluated and the results are listed in Table S4. The reaction rate increased with the increase of temperature from 40°C to 70°C. When the temperature was 50°C, the conversion of 1-phenylethanol reached 100% with a selectivity of acetophenone higher than 99% in 9.5 h (Table S4, entry 2). Further increasing reaction temperature can still shorten reaction time, but high temperature will lead safety problem due to thermal decomposition of TBHP. Therefore, the optimal temperature was 50°C in the oxidation of alcohols with TBHP as oxidant catalyzed by the oligomer ruthenium complex.
Table S4 Effect of reaction temperature on the oxidation of 1-phenylethanol

<table>
<thead>
<tr>
<th>Entry</th>
<th>Temperature (°C)</th>
<th>Time (h)</th>
<th>Conv. (%)</th>
<th>Select. (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>40</td>
<td>13.5</td>
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<td>&gt;99</td>
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<td>50</td>
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<td>4</td>
<td>70</td>
<td>7.0</td>
<td>&gt;99</td>
<td>&gt;99</td>
</tr>
</tbody>
</table>

Reaction condition: 1-phenylethanol (2 mmol), catalyst (0.1 mol%), n-hexane (2 mL), oxidant (6 mmol).

III. Characterization of the Products

Acetophenone: colourless oil; $^1$H NMR (CDCl$_3$, 400 MHz) $\delta$ ppm = 2.61 (s, -CH$_3$, 3H), 7.45~7.49 (m, Ar-H, 2H), 7.55~7.59 (m, Ar-H, 1H), 7.95~7.98 (m, Ar-H, 2H).

Figure S6. $^1$H NMR of acetophenone (CDCl$_3$) (Table 1, entry 1)

4-Fluoroacetophenone: yellow oil; $^1$H NMR (CDCl$_3$, 400 MHz) $\delta$ ppm = 2.60 (s, -CH$_3$, 3H), 7.12~7.16 (m, Ar-H, 2H), 7.97~8.01 (m, Ar-H, 2H).
4-Chloroacetophenone: yellow oil; $^1$H NMR (DMSO, 400 MHz) $\delta$ ppm = 2.59 (s, -CH$_3$, 3H), 7.60 (d, $J$ = 8.8 Hz, Ar-H, 2H), 7.98 (d, $J$ = 8.8 Hz, Ar-H, 2H).

3-Chloroacetophenone: yellow oil; $^1$H NMR (CDCl$_3$, 400 MHz) $\delta$ ppm = 2.60 (s, -CH$_3$, 3H), 7.41 (t, $J$ = 7.8 Hz, Ar-H, 1H), 7.53 (d, $J$ = 8.0 Hz, Ar-H, 1H), 7.83(d, $J$ = 7.8 Hz, Ar-H, 1H), 7.92 (s, Ar-H, 1H).
2-Chloroacetophenone: yellow oil; $^1$H NMR (CDCl$_3$, 400 MHz) $\delta$ ppm = 2.66 (s, -CH$_3$, 3H), 7.31~7.33 (m, Ar-H, 1H), 7.34~7.44 (m, Ar-H, 2H), 7.54~7.57 (m, Ar-H, 1H).

4-Bromoacetophenone: white crystal; $^1$H NMR (CDCl$_3$, 400 MHz) $\delta$ ppm = 2.60 (s, -CH$_3$, 3H), 7.61 (d, $J$ = 8.8 Hz, Ar-H, 2H), 7.83 (d, $J$ = 8.8 Hz, Ar-H, 2H).
Figure S11. $^1$H NMR of 4-bromoacetophenone (CDCl$_3$) (Table 1, entry 6)

4-Methylacetophenone: faint yellow oil; $^1$H NMR (CDCl$_3$, 400 MHz) $\delta$ ppm = 2.41 (s, -CH$_3$, 3H), 2.58 (s, -CH$_3$, 3H), 7.26 (d, $J = 8.2$ Hz, Ar-H, 2H), 7.86 (d, $J = 8.0$ Hz, Ar-H, 2H).

Figure S12. $^1$H NMR of 4-methoxyacetophenone (CDCl$_3$) (Table 1, entry 7)

4-Methoxyacetophenone: white crystal; $^1$H NMR (CDCl$_3$, 400 MHz) $\delta$ ppm = 2.56 (s, -CH$_3$, 3H), 3.87 (s, -CH$_3$, 3H), 6.93 (d, $J = 8.8$ Hz, Ar-H, 2H), 7.94 (d, $J = 8.8$ Hz, Ar-H, 2H).
2-Methoxyacetophenone: yellow oil; $^1$H NMR (CDCl$_3$, 400 MHz) $\delta$ ppm = 2.62 (s, -CH$_3$, 3H), 3.91 (s, -CH$_3$, 3H), 6.96~7.02 (m, Ar-H, 2H), 7.44~7.49 (m, Ar-H, 1H), 7.72~7.75 (m, Ar-H, 1H).

2-Acetonaphthone: white crystal; $^1$H NMR (CDCl$_3$, 400 MHz) $\delta$ ppm = 2.74 (s, -CH$_3$, 3H), 6.96~7.02 (m, Ar-H, 2H), 7.44~7.49 (m, Ar-H, 1H), 7.72~7.75 (m, Ar-H, 1H).
Figure S15. $^1$H NMR of 2-acetonaphthone (CDCl$_3$) (Table 1, entry 10)

Benzophenone: white crystal; $^1$H NMR (CDCl$_3$, 400 MHz) $\delta$ ppm = 7.46~7.58 (m, Ar-H, 4H), 7.59~7.61 (m, Ar-H, 2H), 7.79~7.82 (m, Ar-H, 4H).

Figure S16. $^1$H NMR of benzophenone (CDCl$_3$) (Table 1, entry 11)

1-Phenyl-1-propanone: colourless oil; $^1$H NMR (CDCl$_3$, 400 MHz) $\delta$ ppm = 1.23 (t, $J$...
= 7.2 Hz, -CH$_3$, 3H), 3.01 (q, $J = 7.2$ Hz, -CH$_2$, 2H), 7.46 (t, $J = 7.2$ Hz, Ar-H, 2H), 7.55 (t, $J = 7.2$ Hz, Ar-H, 1H), 7.97 (d, $J = 7.2$ Hz, Ar-H, 2H).

**Figure S17.** $^1$H NMR of 1-phenyl-1-propanone (CDCl$_3$) (Table 1, entry 12)

1-Indanone: yellow oil; $^1$H NMR (CDCl$_3$, 400 MHz) δ ppm = 2.68~2.71 (m, -CH$_2$, 2H), 3.14~3.17 (m, -CH$_2$, 2H), 7.37 (t, $J = 7.2$ Hz, Ar-H, 1H), 7.49 (d, $J = 8.4$ Hz, Ar-H, 1H), 7.59 (t, $J = 7.2$ Hz, Ar-H, 1H), 7.77 (d, $J = 7.6$ Hz, Ar-H, 1H).

**Figure S18.** $^1$H NMR of 1-indanone (CDCl$_3$) (Table 1, entry 13)

$\alpha$-Tetralone: faint yellow oil; $^1$H NMR (CDCl$_3$, 400 MHz) δ ppm = 2.01~2.07 (m, -
CH₂, 2H), 2.60 (t, $J = 6.5$ Hz, -CH₂, 2H), 2.94 (t, $J = 6.0$ Hz, -CH₂, 2H), 7.33 ~ 7.37 (m, Ar-H, 2H), 7.55 (t, $J = 7.4$ Hz, Ar-H, 1H), 7.86 (d, $J = 7.8$ Hz, Ar-H, 1H).

Figure S19. $^1$H NMR of α-tetralone (CDCl₃) (Table 1, entry 14)

Cyclohexanone: colourless oil, $^1$H NMR (CDCl₃, 400 MHz) $\delta$ ppm = 1.70 ~ 1.76 (m, -CH₂, 2H), 1.84 ~ 1.90 (4H), 2.33 ~ 2.36 (4H).

Figure S20. $^1$H NMR of cyclohexanone (CDCl₃) (Table 1, entry 15)

Menthone: colourless oil, $^1$H NMR (CDCl₃, 400 MHz) 0.85 (d, $J = 6.8$ Hz, -CH₃, 3H), 0.91 (d, $J = 6.8$ Hz, -CH₃, 3H), 1.01 (d, $J = 6.3$ Hz, -CH₃, 3H), 1.29 ~ 1.44 (m,
2H), 1.80~1.92 (m, 2H), 1.96~1.99 (m, 1H), 2.02~2.10 (m, 2H), 2.12~2.18 (m, 1H), 2.33~2.38 (m, 1H).

Figure S21. $^1$H NMR of menthone (CDCl$_3$) (Table 1, entries 16, 17)

2-Pentanone: colourless oil, $^1$H NMR (CDCl$_3$, 400 MHz) $\delta$ ppm = 0.92 (t, $J = 7.4$ Hz, -CH$_3$, 3H), 1.56~1.66 (m, -CH$_2$, 2H), 2.14 (s, -CH$_3$, 3H), 2.42 (t, $J = 7.3$ Hz, -CH$_2$, 2H).

Figure S22. $^1$H NMR of 2-pentanone (CDCl$_3$) (Table 1, entries 18, 19)

Benzoic acid: white crystal; $^1$H NMR (CDCl$_3$, 400 MHz) $\delta$ ppm = 7.47~7.51 (m, Ar-H, 2H), 7.60~7.65 (m, Ar-H, 1H), 8.12~8.15 (m, Ar-H, 2H), 12.61 (s, -COOH, 1H).

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Benzaldehyde: colourless oil; $^1$H NMR (CDCl$_3$, 400 MHz) $\delta$: 7.53 (2H, t, $J_1 = 7.6$ Hz, $J_2 = 7.2$ Hz, Ar-H), 7.61$\sim$7.65 (1H, m, Ar-H), 7.88 (2H, dd, $J_1 = 8.4$ Hz, $J_2 = 1.2$ Hz, ArH), 10.02 (1H, s, -CHO).

4-Fluorobenzoic acid: white crystal; $^1$H NMR (DMSO-d$_6$, 400 MHz) $\delta$ ppm $= 7.30 \sim 7.35$ (m, Ar-H, 2H), 8.00$\sim$8.02 (m, Ar-H, 2H), 13.06 (s, -COOH, 1H).

Figure S23. $^1$H NMR of benzoic acid (CDCl$_3$) (Table 1, entry 20)

Figure S24. $^1$H NMR of benzaldehyde (CDCl$_3$) (Table 1, entry 20)
4-Fluorobenzoic acid: white crystal; $^1$H NMR (DMSO-d$_6$, 400 MHz) $\delta$: 7.47~7.52 (m, Ar-H, 1H), 7.54~7.60 (m, Ar-H, 1H), 7.66 (d, $J = 9.2$ Hz, Ar-H, 1H), 7.66 (d, $J = 7.6$ Hz, Ar-H, 1H).
Hz, Ar-H, 1H), 13.31 (s, COOH, 1H).

Figure S27. $^1$H NMR of 2-fluorobenzoic acid (DMSO-d$_6$) (Table 1, entry 22)

2-Fluorobenzaldehyde: colourless oil; $^1$H NMR (CDCl$_3$, 400 MHz) $\delta$: 7.32~7.37 (1H, m, Ar-H), 7.51~7.59 (2H, m, Ar-H), 7.69 (1H, dt, $J_1 = 4.0$ Hz, $J_2 = 8.0$ Hz, Ar-H), 10.00 (1H, d, $J = 4$ Hz, -CHO).

$p$-Toluic acid: white crystal; $^1$H NMR (DMSO-d$_6$, 400 MHz) $\delta$: 2.37 (s, -CH$_3$, 3H), 7.30 (d, $J = 7.6$ Hz, Ar-H, 2H), 7.83 (d, $J = 7.1$ Hz, Ar-H, 2H), 12.80 (s, -COOH, 1H).

Figure S28. $^1$H NMR of 2-fluorobenzaldehyde (CDCl$_3$) (Table 1, entry 22)
p-Tolualdehyde: colourless oil; $^1$H NMR (CDCl$_3$, 400 MHz) $\delta$: 2.43 (3H, s, -CH$_3$), 7.33 (2H, d, $J = 7.6$ Hz, Ar-H), 7.77 (2H, d, $J = 7.6$ Hz, Ar-H), 9.96 (1H, s, -CHO).

4-tert-Butoxybenzoic acid: white crystal; $^1$H NMR (CDCl$_3$, 400 MHz) $\delta$ 1.43 (9H, s, -C(CH$_3$)$_3$), 7.04 (2H, d, $J = 8.7$ Hz, Ar-H), 8.03 (2H, d, $J = 8.7$ Hz, Ar-H).
3-Hydroxy-1-phenylpropan-1-one: colourless oil; $^1$H NMR (CDCl$_3$, 400 MHz) $\delta$: 2.76 (1H, s, -OH), 3.24 (2H, t, $J$=5.3 Hz, -CH$_2$), 4.04 (2H, d, $J$=5.3 Hz, -CH$_2$), 7.46~7.50 (2H, m, Ar-H), 7.57~7.61 (1H, m, Ar-H), 7.97 (2H, d, $J$=8.0 Hz, Ar-H).

Figure S31. $^1$H NMR of 4-tert-butoxybenzoic acid (CDCl$_3$) (Table 1, entry 24)

Figure S32. $^1$H NMR of 3-hydroxy-1-phenylpropan-1-one (CDCl$_3$) (Table 1, entry 25)

IV. References