Supporting Information
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Supporting Information

for

Novel Oxidation of Tertiary Amines with Osmium Tetroxide

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Amide 2b

1H NMR (CDCl₃, 300 MHz): δ = 1.05–1.25 (m, 1H), 1.41–2.09 (m, 6H), 2.54–2.75 (m, 1.4H), 2.86–2.16 (m, 1.6H), 3.35 (dd, J = 4.8, 13.5 Hz, 0.6H), 3.73–3.91 (m, 2H), 3.86 (s, 3H), 3.93–4.06 (m, 1.4H), 4.12–4.29 (m, 1.4H), 4.47 (s, 1H), 4.86–4.94 (m, 0.6H), 6.62 (d, J = 8.1 Hz, 0.4H), 6.63 (d, J = 8.1 Hz, 0.6H), 6.76 (d, J = 8.1 Hz, 1H), 7.97 (s, 0.6H), 8.14 (s, 0.4H). IR (film): 1646 cm⁻¹. HRMS (FAB): m/z calcd for C₂₀H₂₄NO₅ [M+H]+: 358.1654; Found: 358.1647.

Ketolactam 4b

1H NMR (CDCl₃, 300 MHz): δ = 1.34–1.58 (m, 2H), 1.66–1.81 (m, 2H), 2.65–2.74 (m, 1H), 2.77 (dd, J = 3.9, 18.0 Hz, 1H), 3.04 (dd, J = 1.7, 18.0 Hz, 1H), 3.15 (s, 3H), 3.74–4.02 (m, 4H), 3.85 (s, 3H), 4.19–4.28 (m, 1H), 5.39 (s, 1H), 6.66 (d, J = 8.4 Hz, 1H), 6.84 (d, J = 8.1 Hz, 1H). IR (film): 3417, 1730, 1659 cm⁻¹. HRMS (FAB): m/z calcd for C₂₀H₂₂NO₆ [M+H]+: 372.1447; Found: 372.1445.

Hydroxylactam 5b

1H NMR (CDCl₃, 300 MHz): δ = 1.18–1.33 (m, 1H), 1.53–1.73 (m, 3H), 2.61–2.71 (m, 2H), 2.90 (dd, J = 1.5, 17.7 Hz, 1H), 3.02 (s, 3H), 3.41 (br s, 1H), 3.64–3.69 (m, 1H), 3.70–3.79 (m, 1H), 3.82–3.99 (m, 3H), 3.87 (s, 3H), 4.17–4.25 (m, 1H), 5.14 (s, 1H), 6.61 (d, J = 8.1 Hz, 1H), 6.80 (d, J = 8.1 Hz, 1H). IR (film): 1623 cm⁻¹. HRMS (FAB): m/z calcd for C₂₀H₂₄NO₆ [M+H]+: 374.1604; Found: 374.1588.
Amide 2c

[Chemical structure image]

$^1$H NMR (CDCl$_3$, 300 MHz): $\delta = 1.07$ (d, $J = 6.9$ Hz, 2H), 1.10–1.20 (m, 1H), 1.13 (d, $J = 6.9$ Hz, 2H), 1.15 (d, $J = 6.6$ Hz, 0.9H), 1.17 (d, $J = 6.6$ Hz, 0.9H), 1.42–1.83 (m, 5H), 1.90–1.98 (m, 0.7H), 1.99–2.08 (m, 0.3H), 2.50–2.66 (m, 1.3 H), 2.69–3.10 (m, 2.7H), 3.64 (m, 0.7H), 3.75–3.92 (m, 2H), 3.86 (s, 3H), 3.97–4.08 (m, 1H), 4.12–4.22 (m, 1H), 4.28–4.33 (m, 0.3H), 4.41–4.54 (m, 0.3H), 4.47 (s, 1H), 5.13–5.21 (m, 0.7H), 6.62 (d, $J = 8.4$ Hz, 0.3H), 6.63 (d, $J = 8.1$ Hz, 0.7H), 6.77 (d, $J = 8.1$ Hz, 1H). IR (film): 3303, 1636 cm$^{-1}$. HRMS (FAB): m/z calcd for C$_{23}$H$_{30}$NO$_5$ [M+H]$^+$: 400.2124; Found: 400.2055.

Ketolactam 4c

[Chemical structure image]

$^1$H NMR (CDCl$_3$, 300 MHz): $\delta = 0.93$ (d, $J = 6.6$ Hz, 3H), 0.98 (d, $J = 6.6$ Hz, 3H), 1.35–1.60 (m, 2H), 1.68–1.81 (m, 2H), 2.07–2.23 (m, 1H), 2.60–2.75 (m, 1H), 2.67 (dd, $J = 7.5$, 13.5 Hz, 1H), 2.77 (dd, $J = 4.5$, 18.0 Hz, 1H), 3.01 (br d, $J = 18.0$ Hz, 1H), 3.74–4.03 (m, 5H), 3.86 (s, 3H), 4.21–4.29 (m, 1H), 5.40 (s, 1H), 6.65 (d, $J = 8.4$ Hz, 1H), 6.84 (d, $J = 8.1$ Hz, 1H). IR (film): 1734, 1670 cm$^{-1}$. HRMS (FAB): m/z calcd for C$_{23}$H$_{28}$NO$_6$ [M+H]$^+$: 414.1917; Found: 414.1869.

Hydroxylactam 5c

[Chemical structure image]

$^1$H NMR (CDCl$_3$, 300 MHz): $\delta = 0.91$ (d, $J = 6.3$ Hz, 3H), 0.96 (d, $J = 6.3$ Hz, 3H), 1.17–1.31 (m, 1H), 1.54–1.74 (m, 3H), 2.03–2.18 (m, 1H), 2.54 (dd, $J = 7.1$, 13.4 Hz, 1H), 2.59–2.74 (m, 2H), 2.86 (br d, $J = 17.7$ Hz, 1H), 3.67–4.00 (m, 6H), 3.87 (s, 3H), 4.15–4.25 (m, 1H), 5.14 (s, 1H), 6.59 (d, $J = 8.1$ Hz, 1H), 6.79 (d, $J = 8.4$ Hz, 1H). IR (film): 3303, 2957, 1623, 1127, 753 cm$^{-1}$. HRMS (FAB): m/z calcd for C$_{23}$H$_{30}$NO$_6$ [M+H]$^+$: 416.2073; Found:
Lactam 13a

\begin{align*}
\begin{array}{c}
\text{H NMR (CDCl}_3\text{, 300 MHz): } \delta = 0.20–0.38 (m, 2H), 0.46–0.61 (m, 2H), 0.96–1.11 (m, 1H), 2.00–2.16 (m, 1H), \\
2.18–2.30 (m, 1H), 2.65 (dd, \ J = 10.5, 17.4 Hz, 1H), 2.82 (ddd, \ J = 1.8, 5.4, 17.4 Hz, 1H), 3.22–3.59 (m, 5H), 7.36 \\
(dd, \ J = 1.8, 8.7 Hz, 1H), 7.42–7.52 (m, 2H), 7.64 (br s, 1H), 7.77–7.88 (m, 3H). \text{ IR (film): 1637 cm}^{-1}. \text{ HRMS}
\end{array}
\end{align*}

Hydroxylactam 14a

\begin{align*}
\begin{array}{c}
\text{H NMR (CDCl}_3\text{, 300 MHz): } \delta = 0.25–0.35 (m, 2H), 0.49–0.64 (m, 2H), 0.98–1.13 (m, 1H), 2.11–2.36 (m, 2H), \\
3.19 (dt, \ J = 4.1, 11.4 Hz, 1H), 3.29 (dd, \ J = 7.2, 13.8 Hz, 1H), 3.42 (dd, \ J = 6.9, 14.1 Hz, 1H), 3.53 (ddd, \ J = 2.7, \\
6.0, 12.3 Hz, 1H), 3.64 (dt, \ J = 5.2, 11.7 Hz, 1H), 3.83 (br s, 1H), 7.40–7.51 (m, 3H), 7.75 (br s, 1H), 7.77–7.89 (m, \\
3H). \text{ IR (film): 3430, 1631 cm}^{-1}. \text{ HRMS (FAB): m/z calcd for C}_{19}\text{H}_{22}\text{NOM}[M+H]^+: 296.1651; \text{ Found: 296.1657.}
\end{array}
\end{align*}

Lactam 13b

\begin{align*}
\begin{array}{c}
\text{H NMR (CDCl}_3\text{, 300 MHz): } \delta = 2.01–2.26 (m, 2H), 2.61 (dd, \ J = 10.8, 17.4 Hz, 1H), 2.81 (ddd, \ J = 2.0, 5.3, 17.3
\end{array}
\end{align*}
Hz, 1H), 3.01 (s, 3H), 3.20–3.32 (m, 1H), 3.35 (ddd, \( J = 3.6, 5.7, 12.3 \) Hz, 1H), 3.44 (ddd, \( J = 4.9, 10.5, 12.2 \) Hz, 1H), 7.32 (dd, \( J = 1.8, 8.7 \) Hz, 1H), 7.42–7.52 (m, 2H), 7.62 (br d, \( J = 1.2 \) Hz, 1H), 7.78–7.86 (m, 3H). IR (film): 1639 cm\(^{-1}\). HRMS (FAB): m/z calcd for C\(_{16}\)H\(_{18}\)NO [M+H]\(^{+}\): 240.1388; Found: 240.1377.

**Hydorxylactam 14b**

![Hydorxylactam 14b](image)

\(^1\)H NMR (CDCl\(_3\), 300 MHz): \( \delta = 2.08–2.36 \) (m, 2H), 3.04 (s, 3H), 3.09–3.24 (m, 1H), 3.41 (ddd, \( J = 2.0, 6.0, 12.2 \) Hz, 1H), 3.52 (dt, \( J = 5.1, 11.9 \) Hz, 1H), 3.80 (s, 1H), 4.26 (d, \( J = 10.8 \) Hz, 1H), 7.39–7.50 (m, 3H), 7.74 (br s, 1H), 7.78–7.88 (m, 3H). IR (film): 1697, 1637, 1611 cm\(^{-1}\). HRMS (FAB): m/z calcd for C\(_{16}\)H\(_{18}\)NO [M+H]\(^{+}\): 256.1388; Found: 256.1313.

**Lactam 13c**

![Lactam 13c](image)

\(^1\)H NMR (CDCl\(_3\), 300 MHz): \( \delta = 0.92–0.95 \) (m, 6H), 1.97–2.26 (m, 3H), 2.66 (dd, \( J = 10.5, 17.4 \) Hz, 1H), 2.70–2.88 (m, 1H), 3.08–3.49 (m, 5H), 7.36 (dd, \( J = 1.8, 10.2 \) Hz, 1H), 7.37–7.51 (m, 2H), 7.63 (br s, 1H), 7.75–7.87 (m, 3H). IR (film): 2957, 1643 cm\(^{-1}\). HRMS (FAB): m/z calcd for C\(_{16}\)H\(_{24}\)NO [M+H]\(^{+}\): 282.1858; Found: 282.1718.
**Hydroxylactam 14c**

![Image of Hydroxylactam 14c](image)

$^1$H NMR (CDCl$_3$, 300 MHz): $\delta$ = 0.90–0.99 (m, 6H), 2.06–2.29 (m, 3H), 3.05–3.56 (m, 5H), 3.84 (s, 1H), 4.28 (d, $J$ = 10.8 Hz, 1H), 7.39–7.51 (m, 3H), 7.74 (br s, 1H), 7.76–7.87 (m, 3H). IR (film): 3429, 3057, 1624, 745 cm$^{-1}$. HRMS (FAB): m/z calcd for C$_{19}$H$_{24}$NO$_2$ [M+H]$^+$: 298.1807; Found: 298.1808.

**Ketolactam 15c**

![Image of Ketolactam 15c](image)

$^1$H NMR (CDCl$_3$, 300 MHz): $\delta$ = 0.74 (d, $J$ = 6.9 Hz, 3H), 0.80 (d, $J$ = 6.9 Hz, 3H), 1.84–1.98 (m, 1H), 2.56 (ddd, $J$ = 5.3, 12.0, 14.1 Hz, 1H), 2.84 (dt, $J$ = 14.1, 3.2 Hz, 1H), 3.08–3.24 (m, 2H), 3.27–3.41 (m, 2H), 3.82 (br s, 1H), 7.47–7.57 (m, 4H), 7.74–7.89 (m, 2H), 7.93 (d, $J$ = 9.3 Hz, 1H). IR (film): 1735, 1632 cm$^{-1}$. HRMS (FAB): m/z calcd for C$_{19}$H$_{22}$NO$_2$ [M+H]$^+$: 296.1651; Found: 296.1642.

**Lactam 13d**

![Image of Lactam 13d](image)

$^1$H NMR (CDCl$_3$, 300 MHz): $\delta$ = 1.91–2.05 (m, 1H), 2.07–2.17 (m, 1H), 2.49 (dd, $J$ = 11.1, 17.3 Hz, 1H), 2.72 (ddd, $J$ = 2.1, 5.2, 17.3 Hz, 1H), 2.99 (s, 3H), 3.09 (ddt, $J$ = 3.2, 5.1, 11.2 Hz, 1H), 3.32 (ddd, $J$ = 3.3, 5.7, 12.2 Hz, 1H), 3.40 (ddd, $J$ = 4.8, 10.7, 12.2 Hz, 1H), 7.16–7.27 (m, 3H), 7.30–7.37 (m, 2H). IR (film): 3456, 2927, 1630, 1498, 1452, 1340 cm$^{-1}$. HRMS (EI): m/z calcd for C$_{12}$H$_{15}$NO [M]$^+$: 189.1154; Found: 189.1158.
Hydroxylactam 14d

\[
\text{Me} \quad \text{OH} \\
\text{14d}
\]

$^1$H NMR (CDCl$_3$, 300 MHz): $\delta = 1.98–2.17$ (m, 2H), 2.92–3.02 (m, 1H), 2.98 (s, 3H), 3.34 (ddd, $J = 2.2, 6.0, 12.2$ Hz, 1H), 3.49 (dt, $J = 5.3, 11.9$ Hz, 1H), 3.73 (br s, 1H), 4.11 (d, $J = 10.8$ Hz, 1H), 7.18–7.27 (m, 3H), 7.29–7.36 (m, 2H). IR (film): 3420, 2649, 1322, 1240, 1105 cm$^{-1}$. HRMS (FAB): m/z calcd for C$_{12}$H$_{18}$NO$_2$[M+H]$^+$: 206.1181; Found: 206.1177.

**Discussion about the deprotonation of the osmate ester**

Treatment of cis- or trans-stilbene S1 with OsO$_4$ in the presence of K$_2$CO$_3$ (catalytic reaction conditions (condition II): OsO$_4$ (0.1 equiv), K$_3$Fe(CN)$_6$ (9 equiv), K$_2$CO$_3$ (9 equiv), r-BuOH/H$_2$O = 1/1, r.t.) gave $\alpha$-diketone (benzil) S2 as a main product along with hydroxyketone (benzoin) S3 and 1,2-diol (hydrobenzoin) S4. Oxidation of meso- or rac-diol S4, which is the product of the syn-dihydroxylation reaction of either cis- or trans-stilbene S1, respectively, under the same reaction conditions also provided the $\alpha$-diketone S2. Both protons located on the oxygens of the intermediate osmate ester S5 would be deprotonated to afford $\alpha$-diketone S2. The oxidation rate of either cis-stilbene S1 or meso-diol S4 was faster than that of either the trans-stilbene S1 or rac-diol S4, respectively. This result may be explained by a steric acceleration effect on the deprotonation of the osmate ester S5. Although dihydroxylation of the olefin with OsO$_4$ is a reliable method, the $\alpha$-diketone was reported as a byproduct in some cases.$^1$ Under those conditions, deprotonation of the osmate ester may proceed before the osmate is hydrolyzed. These observations strongly support our plausible reaction mechanism of oxidation reaction of tertiary amines with OsO$_4$. 
References