Electronic Supplementary Information

Catalytic chemoselective addition of acetonitrile to enolizable aldehydes with cationic Ru complex/DBU combination

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1. General

Infrared (IR) spectra were recorded on a JASCO FT/IR 410 Fourier transform infrared spectrophotometer. NMR spectra were recorded on a JEOL JNM-LA500 spectrometer, operating at 500 MHz for $^1$H NMR, 125.65 MHz for $^{13}$C NMR, and 202.35 MHz for $^{31}$P NMR. Chemical shifts in CDCl$_3$ were reported downfield from TMS (= 0) or in the scale relative to CHCl$_3$ (7.24 ppm) for $^1$H NMR. For $^{13}$C NMR, chemical shifts were reported in the scale relative to CHCl$_3$ (77.0 ppm for $^{13}$C NMR) as an internal reference. Chemical shifts in C$_6$D$_6$ were reported in the scale relative to C$_6$D$_6$ (7.15 ppm) for $^1$H NMR. For $^{13}$C NMR, chemical shifts were reported in the scale relative to C$_6$D$_6$ (128.0 ppm for $^{13}$C NMR) as an internal reference. Chemical shifts for $^{31}$P NMR were reported in the scale relative to 85% phosphoric acid as an external standard. FAB mass spectra were measured on JEOL JMS-MS700V. ESI mass spectra were measured on Waters-ZQ4000. Column chromatography was performed with silica gel Merck 60 (230–400 mesh ASTM). Acetonitrile was distilled from CaH$_2$. Monophosphine and diphosphine CpRu complex were prepared from CpRu(CH$_3$CN)$_3$PF$_6$ (section 2). CpRu(CH$_3$CN)$_3$PF$_6$ was prepared as reported in the literature (Gill, P. T.; Mann, K. R. Organometallics 1982, 1, 485. (b) Trost, B. M.; Older, C. M. Organometallics 2002, 21, 2544.).

2. Preparation of Acetonitrile Solution of Ru-phosphine Complex

$CpRu(PPh$_3$)(CH$_3$CN)$_2$PF$_6$ (1a)$

A flame-dried flask was charged with CpRu(CH$_3$CN)$_3$PF$_6$ (21.7 mg, 0.05 mmol) and triphenylphosphine (13.1 mg, 0.05 mmol) under Ar. To the flask was added dry acetonitrile (833 μL) and stirred for 1 h at room temperature. The resulting 0.06 M CH$_3$CN solution of CpRu(PPh$_3$)(CH$_3$CN)$_2$PF$_6$ (1a) was used as catalyst.

$CpRu(PPh$_3$)$_2$(CH$_3$CN)PF$_6$ (1b)$

A flame-dried flask was charged with CpRu(CH$_3$CN)$_3$PF$_6$ (50 mg, 0.115 mmol) and PPh$_3$ (60.4 mg, 0.23 mmol) under Ar. To the mixture was added CDCl$_3$ (2.0 mL) and the resulting yellow solution was stirred at 50 °C for 2 h. The formation of diphosphine complex 1b was confirmed by $^1$H NMR and $^{31}$P NMR (δ 42.5 ppm) analysis of small aliquot of the reaction mixture. The solvent was removed under reduced pressure and
CH$_3$CN (1.92 mL) was refilled to the resulting residue to give 0.06 M CH$_3$CN solution of 1b.

3. ESI-MS Analysis of Ru Complex.

Although the reactions in Table 1 and 2 were performed in CH$_3$CN/HMPA solvent, ESI-MS analysis of Ru complexes was performed in THF solvent. In the absence of external CH$_3$CN, it was much easier to compare the stability of Ru monophosphine complex 1a and diphosphine complex 1b toward ligand exchange of CH$_3$CN with DBU.

Preparation of ESI-MS sample

A dried test tube was charged with acetonitrile solution of CpRu(PPh$_3$)$_2$(CH$_3$CN)PF$_6$ (1b) (166 µL, 0.01 mmol) under Ar. The solvent was removed under reduced pressure and dried THF (0.5 mL) was refilled. To the THF solution of 1b was added 0.5 M THF solution of DBU (20 µL, 0.01 mmol) and the resulting mixture was stirred at 50 °C.

Acetonitrile ligands in Ru complex CpRu(PPh$_3$)$_2$(CH$_3$CN)PF$_6$ (1a) were readily exchangeable with DBU in THF at 50 °C to give CpRu(PPh$_3$)(DBU)(CH$_3$CN)PF$_6$ (6a) as shown in Chart S1. Upon addition of DBU (1 equiv to 1a) to the THF solution of 1a, the color of the mixture turned to dark brown from yellow and the peak derived from Ru-DBU complex (6a) was observed predominantly in ESI-MS spectrum (Chart S1). Although a full characterization of complex 6a was not accomplished due to its low stability, the formation of 6a was supported by the intense peak (m/z = 581 for [6a-CH$_3$CN]$^+$, m/z = 622 for [6a]$^+$) derived from 6a in ESI-MS spectra (Chart S1). Although the peak of [6a-CH$_3$CN]$^+$ is much more prominent than the peak of [6a]$^+$ under ESI-MS conditions, [6a]$^+$ would probably exist in the solution as a dominant species over a coordinatively-unsaturated 16e complex [6a-CH$_3$CN]$^+$.

In contrast, when diphosphine complex CpRu(PPh$_3$)$_2$(CH$_3$CN)PF$_6$ (1b) was treated with 1 equiv of DBU in THF at 50 °C, Ru-DBU complex CpRu(PPh$_3$)$_2$(DBU)PF$_6$ was not
observed in ESI-MS analysis even after 12 h (Chart S2). This observation indicated that coordination of DBU to the Ru center of the diphosphine complex 1b was disfavored even in the absence of acetonitrile solvent (competitive ligand to the Ru center). Therefore, unstable Ru-DBU complex 6b generated in catalytic cycle would be readily transformed into acetonitrile complex 1b, avoiding the accumulation of the unstable Ru-DBU complex 6b.

*Chart S2.* ESI-MS spectrum of 1b in THF in the presence of DBU (1 equiv to 1b).

4. **Spectral Data**

3a, 3b, 3d, are known compound. Registry number: 3a: 155486-16-1, 3b: 70102-88-4, 3d: 113576-56-0
3-Hydroxy-6-phenylhexanitrile (3c)
Colorless oil; IR (neat) ν 3452, 2251 cm\(^{-1}\); \(^1\)H NMR (CDCl\(_3\)) δ 1.55-1.70 (m, 3H), 1.72-1.83 (m, 1H), 2.43 (dd, \(J = 6.8, 16.6\) Hz, 1H), 2.47 (brs, 1H), 2.50 (dd, \(J = 5.0, 16.6\) Hz, 1H), 2.64 (t, \(J = 7.5\) Hz 2H), 3.88-3.95 (m, 1H), 7.15-7.20 (m, 3H), 7.26-7.29 (m, 2H); \(^13\)C NMR (CDCl\(_3\)) δ 26.1, 27.1, 35.3, 35.9, 67.5, 117.7, 125.9, 128.3, 128.4, 141.6; ESI-MS \(m/z\) 212 [M+Na]; HRMS (FAB\(^+\)) calcd. for C\(_{12}\)H\(_{14}\)N [M–H\(_2\)O+H\(^+\)] 172.1121 found 172.1127.

12-Cyano-11-hydroxydodec-1-ene (3e)
Colorless oil; IR (neat) ν 3435, 2252, 1640 cm\(^{-1}\); \(^1\)H NMR (CDCl\(_3\)) δ 1.19-1.32 (m, 12H), 1.53-1.55 (m, 2H), 1.92 (brs, 1H), 1.94-1.99 (m, 2H), 2.41 (dd, \(J = 6.4, 16.5\) Hz, 1H), 2.45 (dd, \(J = 5.0, 16.5\) Hz, 1H), 3.85-3.96 (m, 1H), 4.86 (brd, \(J = 10.4\) Hz, 1H), 4.92 (brd, \(J = 17.1\) Hz, 1H), 5.73 (dddd, \(J = 6.7, 6.7, 10.4, 17.1\) Hz, 1H); \(^13\)C NMR (CDCl\(_3\)) δ 25.3, 26.1, 28.8, 29.0, 29.2, 29.3, 29.4, 33.7, 36.5, 67.8, 114.1, 117.7, 139.1; ESI-MS \(m/z\) 232 [M+Na]\(^+\); HRMS (FAB\(^+\)) calcd. for C\(_{13}\)H\(_{24}\)NO [M+H\(^+\)] 210.1852, found 210.1856.

4-Cyclohexyl-3-hydroxybutanitrile (3f)
Colorless solid; IR (KBr) ν 3436, 2251 cm\(^{-1}\); \(^1\)H NMR (CDCl\(_3\)) δ 0.84-0.99 (m, 2H), 1.10-1.23 (m, 3H), 1.33-1.45 (m, 2H), 1.48-1.52 (m, 1H), 1.61-1.73 (m, 5H), 2.28 (brd, \(J = 3.7\) Hz, 1H), 2.44 (dd, \(J = 6.4, 16.7\) Hz, 1H), 2.53 (dd, \(J = 4.6, 16.7\) Hz, 1H), 4.03 (m, 1H); \(^13\)C NMR (CDCl\(_3\)) δ 25.3, 36.8, 37.1, 64.6, 67.1, 117.6, 128.4, 128.5, 128.7, 137.0, 157.6; ESI-MS \(m/z\) 190 [M+Na]\(^+\); HRMS (FAB\(^+\)) calcd. for C\(_{10}\)H\(_{18}\)NO [M+H\(^+\)] 168.1382, found 168.1383.

5-Benzoxycarbamoyl-3-hydroxypentanitrile (3g)
Colorless solid; IR (KBr) ν 3352, 2251, 1698, 1533 cm\(^{-1}\); \(^1\)H NMR (C\(_6\)D\(_6\)) δ 0.98-1.07 (m, 2H), 1.66 (dd, \(J = 5.8, 16.8\) Hz, 1H), 1.72 (dd, \(J = 6.1, 16.8\) Hz, 1H), 2.46-2.52 (m, 1H), 3.07-3.12 (m, 1H), 3.28-3.35 (m, 1H), 3.60 (brd, \(J = 4.5\) Hz, 1H), 4.19 (brs, 1H), 4.98 (s, 2H), 7.04-7.28 (m, 5H); \(^13\)C NMR (C\(_6\)D\(_6\)) δ 25.3, 36.8, 37.1, 64.6, 67.1, 117.6, 128.4, 128.5, 128.7, 137.0, 157.6; ESI-MS \(m/z\) 271 [M+Na]\(^+\); HRMS (FAB\(^+\)) calcd. for C\(_{13}\)H\(_{17}\)N\(_2\)O\(_3\) [M+H\(^+\)] 249.1239, found 249.1238.
10-Benzoyloxy-3-hydroxydecanitrile (3h)
Colorless oil; IR (neat) ν 3479, 2251, 1698, 1716 cm⁻¹; ¹H NMR (CDCl₃) δ 1.33-1.44 (m, 8H), 1.54-1.59 (m, 2H), 1.70-1.77 (m, 2H), 2.46 (dd, J = 6.4, 16.5 Hz, 1H), 2.52 (dd, J = 4.5, 16.5 Hz, 1H), 2.53 (brs, 1H), 3.85-3.95 (m, 1H), 4.28 (t, J = 6.7 Hz, 2H), 7.41 (dd, J = 7.6, 7.9 Hz, 2H), 7.53 (t, J = 7.6 Hz, 1H), 8.01 (d, J = 7.9 Hz, 2H); ¹³C NMR (CDCl₃) δ 25.2, 25.8, 26.0, 28.5, 29.0, 29.1, 36.4, 65.0, 67.6, 117.7, 128.3, 129.4, 130.3, 132.8, 166.7; ESI-MS m/z 312 [M+Na]+; HRMS (FAB+) calcd. for C₁₇H₂₄NO₃ [M+H]+ 290.1751, found 290.1750.

3,10-Dihydroxydecanitrile (3i)
Colorless oil; IR (neat) ν 3391, 2252 cm⁻¹; ¹H NMR (CDCl₃) δ 1.32-1.45 (m, 9H), 1.51-1.60 (m, 4H), 2.08 (d, J = 5.2 Hz, 1H), 2.46 (dd, J = 6.5, 16.5 Hz, 1H), 2.54 (dd, J = 4.8, 16.5 Hz, 1H), 3.62 (t, J = 6.8 Hz, 2H), 3.89-3.94 (m, 1H); ¹³C NMR (CDCl₃) δ 25.1, 25.4, 26.0, 29.1, 29.1, 32.4, 36.3, 62.6, 67.4, 117.9; ESI-MS m/z 208 [M+Na]+; HRMS (FAB+) calcd. for C₁₀H₂₀NO₂ [M+H]+ 186.1489, found 186.1494.

3-Hydroxy-6-(4-acetyl)phenylhexanitrile (3j)
Colorless oil; IR (neat) ν 3455, 2250, 1678 cm⁻¹; ¹H NMR (CDCl₃) δ 1.56-1.70 (m, 3H), 1.77-1.86 (m, 1H), 2.46 (dd, J = 6.3, 16.6 Hz, 1H), 2.52 (dd, J = 5.1, 16.6 Hz, 1H), 2.55 (s, 3H), 2.66-2.70 (m, 2H), 2.78 (brd, J = 5.1Hz, 1H), 3.85-3.92 (m, 1H), 7.23 (d, J = 8.0 Hz, 2H), 7.84 (d, J = 8.0 Hz, 2H); ¹³C NMR (CDCl₃) δ 26.2, 26.5, 26.8, 35.4, 35.8, 67.4, 117.6, 128.5, 128.6, 135.0, 147.6, 198.1; ESI-MS m/z 254 [M+Na]+; HRMS (FAB+) calcd. for C₁₄H₁₈NO₂ [M+H]+ 232.1332, found 232.1340.