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## Supporting Information

for

## Acceptorless Dehydrogenation and Dehydrogenative Coupling of Alcohols

# by Protic NHC Ruthenium Complexes

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#### **1. General Information**

All reactions dealing with air- or moisture-sensitive compounds were performed by standard Schlenk techniques or in the nitrogen-filled Vigor glove box. Analytical thin-layer chromatography (TLC) was performed on HSGF254 silica gel plates. THF, xylene, toluene, diethyl ether and hexane were distilled from sodium and stored over fresh Na chips in a glovebox. <sup>1</sup>H and <sup>13</sup>C nuclear magnetic resonance (NMR) spectra of organic products were recorded on a Bruker AVIII 400 MHz spectrometer instrument. Data are reported as follows: chemical shift in ppm ( $\delta$ ), multiplicity (s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet, br = broad signal), coupling constant (Hz), and integration.

#### 2. Catalytic reactions

General procedure for acceptorless dehydrogenation of alcohols: In a nitrogen-filled glovebox, 1phenylethanol (120 mg, 0.98 mmol), complex 2 (5.5 mg, 1% mol),  $Cs_2CO_3$  (3.2 mg, 1% mol) and xylene (1 mL) were charged in a seal bottle, which was heated at 140 °C. The reaction was monitored by GC-MS. After reaction, the solution was allowed to cool to room temperature, filtered through a silica gel column, and eluted with petroleum ether. The resulted solution was evaporated carefully under vacuum to afford acetophenone (100 mg, 85% yield). The <sup>1</sup>H NMR and MS spectra of acetophenone were matched with the previous reports.

General procedure for dehydrogenative coupling of secondary alcohols with primary alcohols: In a nitrogen-filled glovebox, 1-phenylethanol (60 mg, 0.49 mmol), benzyl alcohol (55 mg, 0.51 mmol), complex 2 (5.5 mg, 2% mol),  $Cs_2CO_3$  (3.2 mg, 2% mol) and xylene (1 mL) were charged in a seal bottle, which was heated at 150 °C for 48 h. After reaction, the solution was allowed to cool to room temperature. The pure product **8a** was obtained as a white solid (87 mg, 85% yield) by column chromatography with petroleum ether/ethyl acetate (100:1) as eluent.

Entry	Cat. (2 mol%)	Solution	Temp (°C)	Base	GC Yield (%)
1	4	toluene	120	Cs <sub>2</sub> CO <sub>3</sub>	43
2	4	xylene	150	Cs <sub>2</sub> CO <sub>3</sub>	90
3	4	xylene	120	Cs <sub>2</sub> CO <sub>3</sub>	38
4	4	xylene	150	none	0
5	2	xylene	150	none	0
6	2	xylene	150	Cs <sub>2</sub> CO <sub>3</sub>	89
7	2	xylene	150	KO'Bu	3
8	2	xylene	150	NaO'Bu	24
9	2	xylene	150	NaOAc	0

Table S1 Optimization of dehydrogenative coupling of 1-phenylethanol and benzyl alcohol

 1, 3-diphenylpropan-1-one (8a), White solid (85%). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>):

 δ

 7.97 (d, J = 7.2 Hz, 2H), 7.56 (t, J = 7.4 Hz, 1H), 7.46 (t, J = 7.6 Hz, 2H), 7.25 –

 7.34 (m, 4H), 7.22 (t, J = 7 Hz, 1H), 3.32 (t, J = 7.6 Hz, 2H), 3.09 (t, J = 7.8 Hz, 2H);

<sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>): δ 199.2, 141.3, 136.9, 133.1, 128.6, 128.6, 128.5, 128.1, 126.2, 40.5, 30.2.
Data are consistent with previously reported data. [D. W. Wang, K. Y. Zhao, C. Y. Xu, H. Y. Miao, Y. Q. Ding, *ACS Catal.* **2014**, *4*, 3910-3918]



**3-(4-chlorophenyl)-1-phenylpropan-1-one (8b)**, pale yellow solid (71%). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>): δ 7.96 – 7.94 (m, 2H), 7.56 (t, *J* = 7.4 Hz, 1H), 7.46 (t, *J* = 7.6 Hz, 2H), 7.27 (s, 1H), 7.25 (s, 1H), 7.20 – 7.17 (m, 2H), 3.28 (t, *J* = 7.6

Hz, 2H), 3.05 (t, *J* = 7.6 Hz, 2H); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>): δ 198.9, 139.7, 136.8, 133.2, 131.9, 129.8, 128.6 (2C), 128.0, 40.1, 29.4. Data are consistent with previously reported data. [D. W. Wang, K. Y. Zhao, C. Y. Xu, H. Y. Miao, Y. Q. Ding, *ACS Catal.* **2014**, *4*, 3910-3918]



**3-(4-methoxyphenyl)-1-phenylpropan-1-one (8c),** colorless oil (95%). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>): δ 7.96 (d, *J* = 7.2, 2H), 7.56 (t, *J* = 7.2 Hz, 1H), 7.45 (t, *J* = 7.4 Hz, 2H), 7.17 (d, *J* = 8.4 Hz, 2H), 6.84 (d, *J* = 8.8 Hz, 2H), 3.79 (s,

3H), 3.27 (t, J = 7.6 Hz, 2H), 3.02 (t, J = 7.8 Hz, 2H); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>): δ 199.4, 158.0, 136.9, 133.3, 133.1, 129.4, 128.6, 128.1, 114.0, 55.3, 40.7, 29.3. Data are consistent with previously reported data.
[D. W. Wang, K. Y. Zhao, C. Y. Xu, H. Y. Miao, Y. Q. Ding, ACS Catal. 2014, 4, 3910-3918]

**1-phenyl-3-(***p***-tolyl)propan-1-one (8d)**, yellow oil (75%). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>): δ 7.97 (d, *J* = 7.2 Hz, 2H), 7.56 (t, *J* = 7.4 Hz, 1H), 7.46 (t, *J* = 7.6 Hz, 2H), 7.16 (d, *J* = 8.4, 2H), 7.12 (d, *J* = 8.2, 2H), 3.29 (t, *J* = 7.8 Hz, 2H), 3.04 (t, *J* 

= 7.6 Hz, 2H), 2.33 (s, 3H); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>): δ 199.4, 138.2, 136.9, 135.6, 133.1, 129.2, 128.6, 128.3, 128.1, 40.6, 29.7, 21.0. Data are consistent with previously reported data. [S. Musa, L. Ackermann, D. Gelman, *Adv. Synth. Catal.* 2013, *355*, 3077-3080]

**1-phenyl-3-(***o***-tolyl)propan-1-one (8e)**, white solid (74%). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>): δ 7.98 (d, *J* = 7.2 Hz, 2H), 7.57 (t, *J* = 7.4 Hz, 1H), 7.47 (t, *J* = 7.6 Hz, 2H), 7.12 - 7.22 (m, 4H), 3.26 (t, *J* = 8 Hz, 2H), 3.06 (t, *J* = 7.8 Hz, 2H), 2.36 (s, 3H); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>): δ 199.4, 139.4, 136.9, 136.0, 133.1, 130.4, 128.7, 128.6, 128.1, 126.3, 126.2, 39.1, 27.5, 19.4. Data are consistent with previously reported data. [X. Liu, R. S. Ding, L. He, Y. M. Liu, Y. Cao, H. Y. He, K. N. Fan, *ChemSusChem*, **2013**, *6*, 604-608]

 $\begin{array}{l} \textbf{3-([1,1'-biphenyl]-4-yl)-1-phenylpropan-1-one} \quad \textbf{(8f)}, \quad \text{yellow solid} \quad (58\%); \quad ^{1}\text{H} \\ \textbf{NMR} \quad \textbf{(400 MHz, CDCl_3): } \delta \quad \textbf{8.00} \quad \textbf{(d, } J = 7.2 \text{ Hz}, \text{ 2H}), \quad \textbf{7.52} - 7.61 \quad \textbf{(m, 5H)}, \quad \textbf{7.40} - \\ 7.50 \quad \textbf{(m, 4H)}, \quad \textbf{7.32} - 7.36 \quad \textbf{(m, 3H)}, \quad \textbf{3.36} \quad \textbf{(t, } J = 7.2 \text{ Hz}, \text{ 2H}), \quad \textbf{3.13} \quad \textbf{(t, } J = 7.6 \text{ Hz}, \text{ 2H}); \\ \end{array}$ 

<sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>): δ 199.2, 141.0, 140.4, 139.2, 136.9, 133.1, 128.9, 128.8, 128.6, 128.1, 127.3, 127.1, 127.0, 40.4, 29.8. Data are consistent with previously reported data. [T. Kuwahara, T. Fukuyama, I.



3-(benzo[d][1,3]dioxol-5-yl)-1-phenylpropan-1-one (8g), colorless oil (58%). <sup>1</sup>**H** NMR (400 MHz, CDCl<sub>3</sub>):  $\delta$  7.95 (d, J = 8.4 Hz, 2H), 7.56 (t, J = 6.8, 1H), 7.46 (t, J = 6.8 Hz, 2H), 6.67 – 6.75 (m, 3H), 5.92 (d, J = 1.2 Hz, 2H), 3.26 (t, J =8.4 Hz, 2H), 3.00 (t, *J* = 7.6 Hz, 2H); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>): δ 199.2, 147.7, 145.9, 136.9, 135.1, 133.1, 128.6, 128.0, 121.2, 108.9, 108.3, 100.8, 40.7, 29.9. Data are consistent with previously reported data. [X. J. Cui, Y. Zhang, F. Shi, Y. Q. Deng, Chem. Eur. J. 2011, 17, 1021-1028]

3-(furan-2-yl)-1-phenylpropan-1-one (8h), yellow oil (94%). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>): δ 7.98 (d, *J* = 7.2 Hz, 2H), 7.57 (t, *J* = 7.4 Hz, 1H), 7.47 (t, *J* = 7.6 Hz, 2H), 7.32 (d, J = 0.8 Hz, 1H), 6.29 (dd, J = 2.9, 2.0 Hz, 1H), 6.06 (d, J = 2.4 Hz, 1H), 3.34 (t, J = 7.6 Hz, 2H), 3.10 (t, J = 7.4 Hz, 2H); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>): δ 198.7, 154.8, 141.1, 136.8, 133.1, 128.6, 128.0, 110.3, 105.3, 36.9, 22.5. Data are consistent with previously reported data. [D. W. Wang, K. Y. Zhao, C. Y. Xu, H. Y. Miao, Y. Q. Ding, ACS Catal. 2014, 4, 3910-3918]

1-phenyl-3-(thiophen-2-yl)propan-1-one (8i), yellow oil (75%). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>): δ 7.97 (d, *J* = 7.6 Hz, 2H), 7.57 (t, *J* = 7.2 Hz, 1H), 7.47 (t, *J* = 7.6 Hz, 2H), 7.13 (dd, J = 1.2, 2.6, 1H), 6.90 – 6.94 (m, 1H), 6.87 (d, J = 2.8 Hz, 1H), 3.35 – 3.40 (m,

2H), 3.20 – 3.33 (m, 2H); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>): δ 198.6, 143.9, 136.8, 133.2, 128.7, 128.1, 126.9, 124.7, 123.4, 40.6, 24.2. Data are consistent with previously reported data. [T. Kuwahara, T. Fukuyama, I. Ryu, Org. Lett. 2012, 14, 4703-4705]



3-(naphthalen-2-yl)-1-phenylpropan-1-one (8j), white solid (86%); <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>): δ 7.99 (d, *J* = 7.2 Hz, 2H), 7.79 – 7.82 (m, 3H), 7.70 (s, 1H), 7.56 (t, J = 7.2 Hz, 1H), 7.38 – 7.50 (m, 5H), 3.40 (t, J = 7.6 Hz, 2H), 3.25 (t, J = 7.6 Hz, 2H); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>): δ 199.2, 138.8, 136.9, 133.7, 133.1, 132.1, 128.6, 128.14, 128.07, 127.6, 127.5, 127.2, 126.5, 126.0, 125.3, 40.4, 30.3. Data are consistent with previously reported data. [B. Q. Ding, Z. F. Zhang, Y. G. Liu, M. Sugiya, T. Imamoto, W. Zhang, *Org. Lett.* **2013**, *14*, 3690-3693]

1-p CD

**1-phenyl-1-**(*p*-tolyl)propan-1-one (8k), white solid (76%); <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>): δ 7.87 (d, *J* = 8.4 Hz, 2H), 7.19 – 7.34 (m, 7H), 3.29 (t, *J* = 7.6 Hz, 2H), 3.07 (t, *J* = 7.8 Hz, 2H), 2.42 (s, 3H); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>): δ 199.0, 144.0,

141.5, 134.5, 129.4, 128.6, 128.5, 128.3, 126.2, 40.5, 30.4, 21.8. Data are consistent with previously reported data. [X. Liu, R. S. Ding, L. He, Y. M. Liu, Y. Cao, H. Y. He, K. N. Fan, *ChemSusChem*, **2013**, *6*, 604-608]

1-(4-chlorophenyl)-3-phenylpropan-1-one (8l), yellow solid (68%). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>):  $\delta$  7.89 (d, J = 8.4 Hz, 2H), 7.43 (d, J = 8.4 Hz, 2H), 7.20 – 7.31(m, 5H), 3.27 (t, J = 7.8 Hz, 2H), 3.07 (t, J = 7.8 Hz, 2H); <sup>13</sup>C NMR (100

MHz, CDCl<sub>3</sub>): δ 198.0, 141.1, 139.2, 135.2, 129.5, 128.9, 128.6, 128.4, 128.2, 40.4, 30.1. Data are consistent with previously reported data. [D. W. Wang, K. Y. Zhao, C. Y. Xu, H. Y. Miao, Y. Q. Ding, *ACS Catal.* **2014**, *4*, 3910-3918]



**1-(4-methoxyphenyl)-3-phenylpropan-1-one (8m)**, white solid (90%). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>): δ7.95 (d, *J* = 8 Hz, 2H), 7.19-7.33 (m, 5H), 6.93 (d, *J* = 8.4 Hz, 2H), 3.87 (s, 3H), 3.26 (t, *J* = 7.8 Hz, 2H), 3.06 (t, *J* = 7.6 Hz, 2H); <sup>13</sup>C NMR (100

MHz, CDCl<sub>3</sub>): δ 197.8, 163.5, 141.5, 130.3, 130.0, 128.5, 128.4, 126.1, 113.7, 55.5, 40.1, 30.4. Data are consistent with previously reported data. [X. Liu, R. S. Ding, L. He, Y. M. Liu, Y. Cao, H. Y. He, K. N. Fan, *ChemSusChem*, **2013**, *6*, 604-608]



CDCl<sub>3</sub>): δ 198.2, 145.8, 141.3, 133.2, 128.54, 128.47(2C), 126.2, 125.0, 40.3, 30.2, 14.8. Data are consistent with previously reported data. [F. Caturla, J.-M. Jiménez, N. Godessart, M. Amat, A. Cárdenas, L. Soca, J. Beleta, H. Ryder, M. Crespo, J. Med. Chem. 2004, 47, 3874-3886]

1-(2,4-dimethylphenyl)-3-phenylpropan-1-one (80), colorless oil (58%). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>): δ 7.56 (s, 1H), 7.16 – 7.32 (m, 5H), 7.03 – 7.06 (m, 2H), 3.22 (t, J = 7.8 Hz, 2H), 3.04 (t, J = 7.6 Hz, 2H), 2.48 (s, 3H), 2.35 (s, 3H);  ${}^{13}$ C NMR (100 MHz, CDCl<sub>3</sub>): 8 202.6, 141.9, 141.4, 138.7, 134.9, 132.9, 129.0, 128.5, 128.4, 126.3, 126.1, 42.9, 30.5, 21.5, 21.3. Data are consistent with previously reported data. [Q. B. Jiang, T. L. Guo, Q. F. Wang, P. Wu, Z. K. Yu, Adv. Synth. Catal. 2013, 355, 1874-1880]



1-(benzo[d][1,3]dioxol-5-yl)-3-phenylpropan-1-one (8p), white solid (87%). <sup>1</sup>H **NMR** (400 MHz, CDCl<sub>3</sub>):  $\delta$  7.56 (dd, J = 8.2, 1.5 Hz, 1H), 7.45 (d, J = 1.6 Hz, 1H), 7.19 – 7.33 (m, 5H), 6.83 (d, J = 8 Hz, 1H), 6.03 (s, 2H), 3.22 (t, J = 7.6 Hz, 2H), 3.05 (t, J = 7.6 Hz, 2H); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>): δ 197.3, 151.7, 148.2, 141.4, 131.8, 128.8, 128.5, 128.4, 126.1, 124.2, 107.9, 101.8, 40.2, 30.4. Data are consistent with previously reported data. [P. Colbon, J. Ruan, M. Purdie, J. L. Xiao, Org. Lett. 2010, 12, 3670-3673]



1-(naphthalen-2-yl)-3-phenylpropan-1-one (8q), White solid (93%). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>): δ 8.47 (s, 1H), 8.05 (d, *J* = 8.4 Hz, 1H), 7.80 – 7.96 (m, 3H), 7.50 - 7.63 (m, 2H), 7.20 - 7.35 (m, 4H), 3.45 (t, J = 7.8 Hz, 2H), 3.14 (t, J = 7.8

Hz, 2H); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>): δ 199.2, 141.4, 135.6, 134.2, 132.6, 129.7, 129.6, 128.6, 128.5 (3C), 127.8, 126.8, 126.2, 123.9, 40.6, 30.3. Data are consistent with previously reported data. [K. Chakrabarti, B. Paul, M. Maji, B. C. Roy, S. Shee, S. Kundu, Org. Biomol. Chem, 2016, 14, 10988-10997]



**1-([1,1'-biphenyl]-4-yl)-3-phenylpropan-1-one (8r)**, white solid (66%); <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>): δ 8.05 (d, *J* = 8.4 Hz, 2H), 7.69 (d, *J* = 8.4 Hz, 2H), 7.64 (d, *J* = 7.6 Hz, 2H), 7.48 (t, *J* = 7.6 Hz, 2H), 7.42 (d, *J* = 7.2 Hz, 1H), 7.20 - 7.36 (m, 5H), 3.35 (t, *J* = 7.6 Hz, 2H), 3.12 (t, *J* = 7.8 Hz, 2H); <sup>13</sup>C

NMR (100 MHz, CDCl<sub>3</sub>): δ 198.8, 145.8, 141.4, 139.9, 135.6, 129.0, 128.7, 128.6, 128.5, 128.3, 127.3 (2C signals), 126.2, 40.5, 30.2. Data are consistent with previously reported data. [A. Zanardi, J A. Mata, E. Peris, *J. Am. Chem. Soc.* **2009**, *131*, 14531-14537.]

## 3. X-ray structures and data of 2 and 4



ORTEP of **2** with thermal ellipsoids at the 30% probability level. Hydrogen atoms have been omitted for clarity (CCDC No: 1529097).

# Table S2: Crystal data and structure refinement for 2

Complex 2
C <sub>27</sub> H <sub>42</sub> ClN <sub>2</sub> PRu
562.12
104.4
Monoclinic
$P2_1/c$
12.74606(16),10.64439(15),19.7255(3)
90.00,98.7804(13),90.00
2644.88(6)
4
1.412
0.772
1176
$0.25{\times}\;0.24{\times}\;0.09$
6.2 to 52°
$-15 \le h \le 12, -12 \le k \le 13, -24 \le l \le 22$
11464
5191[R(int) = 0.0265 (inf-0.9Å)]
5191/0/300
1.051
$R_1 = 0.0285, wR_2 = 0.0598$
$R_1 = 0.0340, wR_2 = 0.0626$
0.418/-0.488
Ν
0.998



ORTEP of **3** with thermal ellipsoids at the 30% probability level. Hydrogen atoms and  $C_6H_6$  have been omitted for clarity (CCDC No: 1529098).

### Table S3: Crystal data and structure refinement for 3

Identification code	Complex 3·C <sub>6</sub> H <sub>6</sub>
Empirical formula	$C_{27}H_{42}N_2NaPRu\cdot C_6H_6$
Formula weight	627.76
Temperature / K	163(2)K
Wavelength	0.71073 A
Crystal system	Triclinic
Space group	P-1
a / Å, b / Å, c / Å	10.123(3),12.566(3),13.275(4)
$\alpha/\text{deg}, \beta/\text{deg}, \gamma/\text{deg}$	83.199(5),84.143(5),68.651(4)
Volume / Å <sup>3</sup>	1559.3(7)
Z	2
$\rho_{calc} / \text{ mg m}^{-3}$	1.337
μ / mm <sup>-1</sup>	0.59
F (000)	660
Crystal size / mm <sup>3</sup>	$0.23{\times}\ 0.16{\times}\ 0.14$
20 range for data collection	1.6 to 28.31 deg
Index ranges	$\text{-13} \le h \le 11,  \text{-16} \le k \le 16,  \text{-17} \le l \le 11$
Reflections collected	10055
Independent reflections	6939[R(int) = 0.0404]
Absorption correction	None
Max. and min. transmission	0.920 and 0.893
Refinement method	Full-matrix least-squares on F <sup>2</sup>
Data/restraints/parameters	6939/0/349
Goodness-of-fit on F <sup>2</sup>	0.95
Final R indexes [I>2sigma(I)]	$R_1 = 0.0538, wR_2 = 0.1268$
Final R indexes [all data]	$R_1 = 0.0747, wR_2 = 0.1377$
Largest diff.peak/hole/ e Å <sup>-3</sup>	0.615/-0.65
Completeness	0.922













140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -110 -130 -150 -170 -190 -210 -230 f1 (ppm)









140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -110 -130 -150 -170 -190 -210 -230 f1 (ppm)





















210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10 fl (ppm)















































9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5 -1.C fl (ppm)

9.5



210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10 f1 (ppm)







60 150 140 130 120 110 100 90 80 70 60 50 40 f1 (ppm)





























