Acceptorless Ruthenium Catalyzed Dehydrogenation of Alcohols to Ketones and Esters

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Electronic Supplementary Informations

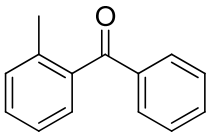
General Considerations

All reactions were carried out with flame-dried glassware using standard Schlenk techniques under an inert atmosphere of dry argon. Toluene was dried over Braun MB-SPS-800 solvent purification system while reagent grade diethyl ether and pentane for chromatography were procured from Aldrich and used as obtained. Catalyst **A** [$RuCl_2$(*p*-cymene)IMes] was synthesized using literature procedures.[i] Analytical TLC was performed on Merck 60F254 silica gel plates (0.25 mm thickness). Column chromatography was performed on Acros Organics Ultrapure silica gel (mesh size 40-60μm, 60A). NMR spectra were recorded on Bruker spectrometers (^{1}H NMR at 300 MHz or 400 MHz and ^{13}C NMR at 125 MHz). Deuterated $CDCl_3$ was stored over 4 Å molecular sieves. GC analyses were carried out using dodecane as an internal standard on Shimadzu GC-2014 instrument.

Sample experimental procedure

In a typical experiment, *DL*-sec-phenylethyl alcohol (Acros Organics, 100μL, 0.8284 mmol), Ru catalyst (12.6 mg, 0.02071 mmol), dodecane (10μL, 0.04403 mmol) and K_3PO_4 (87.9 mg, 0.4142 mmol) were added in a Schlenk tube under argon. Dry, purged toluene (1 mL) was then added to the mixture and a reflux condenser with a bubbler was fitted to the Schlenk tube. Under an atmosphere of argon, the Schlenk tube was then placed in an oil bath pre-heated to 125°C. The mixture was refluxed for 48 h under a flow of argon to ensure removal of liberated hydrogen all the while maintaining a constant substrate concentration. The reaction mixture was cooled to room temperature and loaded on a silica gel column pre-soaked with pure pentane. The column was then eluted with pentane to completely remove toluene. Then, the column was eluted with a mixture of pentane/diethyl ether (9.8/0.2) to afford acetophenone.

Phenyl (2-tolyl)methanone

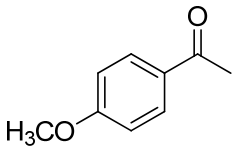


Light yellow solid. Yield 84%.

NMR data were consistent with reported data.[ii]

^{1}H NMR (500 MHz, $CDCl_3$): δ 7.84 (dd, *J* = 7.8, *J* =1.4 Hz, 2H), 7.58 (tt, *J* = 7.4Hz, *J* = 1.2Hz, 1H), 7.48 (m, 2H), 7.41 (td, *J* = 7.4 Hz, *J* = 1.2, 1H), 7.35-7.27 (m, 3H), 2.37 (s, 3H). **^{13}C NMR** (125 MHz, $CDCl_3$): δ 198.6, 138.6, 137.7, 136.7, 133.1, 131.0, 130.2, 130.1, 128.5, 128.4, 125.2, 20.

1-(4-methoxyphenyl)ethanone

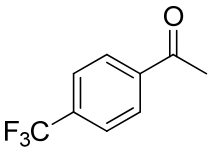


Colourless oil. Yield 96%.

NMR data were consistent with reported data.[iii]

^{1}H NMR (300 MHz, $CDCl_3$): δ 7.96 (d, *J* = 9 Hz, 2H), 6.95 (d, *J* = 6 Hz, 2H), 3.88 (s, 3H), δ 2.56 (s, 3H). **^{13}C NMR** (125 MHz, $CDCl_3$): δ 196.7, 163.4, 130.5, 130.3, 113.6, 55.4, 26.3.

1-(4-trifluoromethyl)ethanone

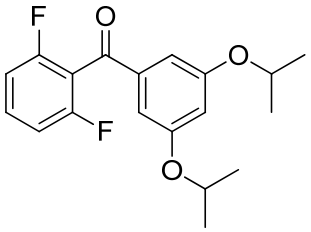


Colorless oil. Yield 50%.

NMR data were consistent with reported data.[iv]

^{1}H NMR (300 MHz, $CDCl_3$): δ 8.07 (d, *J* = 9.2 Hz, 2H), 7.74 (d, *J* = 9.2 Hz, 2H), 2.64 (s, 3H). **^{13}C NMR** (125 MHz, $CDCl_3$): δ 196.8, 139.6 (q, *J* = 1.5 Hz), 134.5 (q, *J* = 32.0 Hz), 128.5, 125.6 (q, *J* = 3.6 Hz), 124.6 (q, J = 271.9 Hz), 26.6.

(2, 6-difluorophenyl)(3, 5-diisopropoxyphenyl) methanone

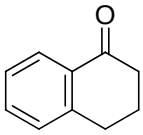


Colourless oil. Yield 45%.

NMR data were consistent with reported data.[v]

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.47-7.41 (m, 1H), 7.03-6.96 (m, 4H), 6.68 (bs, 1H), 4.57 (hept, *J* = 6.0 Hz, 2H), 1.35 (m, 12H, CH_3) **^{13}C NMR** (100 MHz, $CDCl_3$): δ 188.8, 159.7 (dd, *J* = 251.5, J = 7.6 Hz), 159.3, 138.7 , 131.7 (t, *J* = 9.8 Hz), 117.2 (t, *J* = 22.0 Hz), 111.8 (dd, *J* = 19.5 Hz, *J* = 5.6 Hz), 109.7, 70.3, 21.9

3, 4-dihydronaphthalen-1(2H)-one

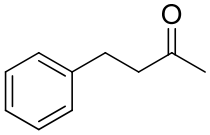


Colorless oil. Yield 73%.

NMR data were consistent with reported data.[vi]

^{1}H NMR (300 MHz, $CDCl_3$): δ 8.04 (d, *J* = 7.5 Hz, 1H), 7.45 (m, 1H) 7.31-7.23 (m, 2H), 2.95 (m, 2H), 2.64 (m 2H), 2.12 (m, 2H). **^{13}C NMR** (125 MHz, $CDCl_3$): δ 198.2, 144.4, 133.3, 132.6, 128.7, 127.1, 126.6, 39.1, 29.6, 23.2.

4-Phenyl-butan-2-one

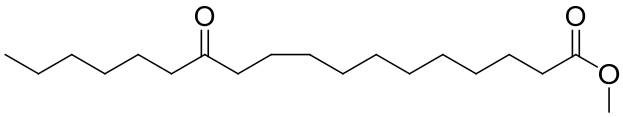


Clear colorless oil. Yield 56%.

NMR data were consistent with reported data.[vii]

^{1}H NMR (300 MHz, $CDCl_3$): δ 7.33 (m, 2H), 7.22 (m, 3H), 2.93 (t, *J* =7.5 Hz, 2H), 2.78 (t, *J* =7.5 Hz, 2H), 2.16 (s, 3H). **^{13}C NMR** (125 MHz, $CDCl_3$): 207.8, 141.0, 128.4, 128.3, 126.1, 45.1, 30.0, 29.7.

Methyl 12-oxooctadecanoate

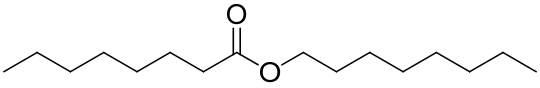


White flakes. Yield 90%.

NMR data were consistent with reported data.[viii]

^{1}H NMR (300 MHz, $CDCl_3$): δ 3.64 (s, 3H), 2.36 (t, *J* = 7.5 Hz, 4H), 2.28 (t, *J* =7.5 Hz, 2H), 1.55 (br, 6H), 1.25 (bs, 18H), 0.85 (t, *J* = 6.0 Hz, 3H). **^{13}C NMR** (100 MHz, $CDCl_3$): 211.6, 174.2, 51.4, 42.8, 42.7, 34.0, 31.6, 39.3, 29.2, 29.1, 28.9, 24.9, 23.8, 22.5, 14.0. HRMS (ESI) : calcd for $C_{19}H_{36}O_3Na$ 335.2562, measured 335.2563.

Octyl octanoate

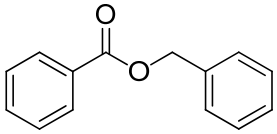


Colorless oil.

NMR data were consistent with reported data.[ix]

^{1}H NMR (500 MHz, $CDCl_3$): δ 4.08 (t, *J* = 6.75 Hz, 2H), 2.31 (t, *J* =7.5 Hz, 2H), 1.64 (t, *J* =7.5 Hz, 4H), 1.37-1.26 (m, 18H), 0.88 (t, *J* =7.0 Hz, 3H). **^{13}C NMR** (125 MHz, $CDCl_3$): δ 174.0, 64.3, 34.43, 31.7, 31.6, 29.2, 29.18, 29.12, 28.9, 28.6, 25.9, 25.0, 22.6, 22.5, 14.07, 14.05. **LRMS** (EI) calcd. for $C_{16}H_{32}O_2$ 256, found 256. **$C_{16}H_{32}O_2$** (256.42) calcd. C 74.94, H 12.58, found C 74.17, H 12.46.

Benzyl benzoate

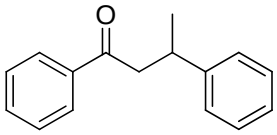


Colorless oil. Yield 30%.

NMR data were consistent with reported data.[x]

^{1}H NMR (300 MHz, $CDCl_3$): δ 8.12 (d, *J* = 6.0 Hz, 2H), 7.61-7.31 (m, 8H), 5.4 (s, 2H). **^{13}C NMR** (100 MHz, $CDCl_3$): δ 166.4, 136.1, 133.0, 130.1, 129.7, 129.6, 128.4, 128.3, 128.2, 128.1, 127.2, 66.7; **LRMS** (EI) calcd. for $C_{14}H_{12}O_2$ 212, found 212.

1.3-diphenylbutan-1-one (Partially reduced aldol product)



White powder.

NMR data were consistent with reported data.[xi]

^{1}H NMR (300 MHz, $CDCl_3$): δ 7.97 (d, *J* =7.5 Hz, 2H), 7.57 (t, *J* =6 Hz, 1H), 7.47 (t, *J* = 7.5 Hz, 2H), 7.35-7.22 (m, 5H), 3.57-3.37 (m, 2H), 3.37-3.17 (m, 1H), 1.36 (d, *J* =6 Hz, 3H). **^{13}C NMR** (125 MHz, $CDCl_3$): δ 199.1, 146.6, 137.2, 132.9, 128.6, 128.5, 128.09, 126.8, 126.3, 47.0, 35.6, 21.9; **HRMS** (ESI) calcd. for $C_{16}H_{16}ONa$ 247.10988, measured 247.1098.

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[i] Lo C., Cariou R., Fischmeister C., Dixneuf P. H., *Adv. Synth. Catal.*, **2007**, 349, 546-550.
[ii] Miao,T., Wang, G-W. *Chem.Comm*. **2011**, 97, 9501-9503.
[iii] Yuan, Y., Shi, X., Liu, W. *Synlett.* **2011**, 4, 559-564.
[iv] Coleman, M.G., Brown, A.N., Bolton, B.A., Hairong, G. *Adv.Synth.Catal.* **2010**, 352, 967-970.
[v] Kabro A., Ghattas G., Fischmeister C., Bruneau C., *Dalton Trans*., DOI:10.1039/C2DT12271E
[vi] Beldar, A.G., Sharma,M. *E-J.Chem*. **2011**, 8, 288-292.
[vii] Fox, D.J., Pedersen, D.D., Warren, S. *Org.Biomol.Chem.* **2011**, 16, 3102-3107.
[viii] Aldrich data base. http://www.sigmaaldrich.com/spectra/fnmr/FNMR006240.PDF
[ix] Masuyama, Y., Takahashi, M., Kurushi, Y. *Tetrahedron. Lett.* **1984**, 8, 4417-4420.
[x] Li,L., Sheng, H., Xu, F., Shen,Q. *Chin. J. Chem.* **2009**, 27, 1127-1131.
[xi] Jana, U., Biswas, S., Maiti, S. *Eur. J. Org.Chem.* **2008**, 5798-5804.