Iridium-Catalyzed Oppenauer Oxidations of Primary Alcohols Using Acetone or 2-Butanone as the Oxidants

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Supporting Information

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Instruments and Materials. Melting points were obtained with a Yanagimoto Micro Melting Point Apparatus and are uncorrected. Infrared (IR) spectra were recorded on a JASCO FT/IR 5300 spectrometer. ^1H NMR spectra were recorded on a JEOL EX-270 NMR spectrometer at 270 MHz with tetramethylsilane used as an internal standard. The chemical shifts are reported in ppm on the δ scale downfield from tetramethylsilane, and signal patterns are indicated as follows: s, singlet; d, doublet; t, triplet; m, multiplet; br, broad peak. ^{13}C NMR spectra were measured on a JEOL EX-270 NMR spectrometer at 67.8 MHz. The chemical shifts are reported in ppm with chloroform-*d* (77.0 ppm) as an internal standard. Gas chromatographic analyses were performed on a Shimadzu GC-14B gas chromatograph. The preparation method for Ir catalyst **4** is given in Ref. 5.

3,4-Dimethoxybenzaldehyde (2a). IR (neat) 1682, 1269, 1242 cm^{-1} . ^1H NMR (CDCl_3) δ 3.95 (s, 3H), 3.98 (s, 3H), 6.99 (d, $J = 8.3$ Hz), 7.41-7.48 (m, 2H), 9.86 (s, 1H). ^{13}C NMR (CDCl_3) δ 190.4, 154.0, 149.2, 129.7, 126.4, 110.1, 108.6, 55.9, 55.7. Pouchert, C.J.; Behnke, J. In *The Aldrich Library of ^{13}C and ^1H FT NMR Spectra*, 1st Ed.; Aldrich Chemical: Milwaukee, 1993; Vol. 2, p 955–B

***p*-Anisaldehyde (2b).** IR (neat) 1684, 1260 cm^{-1} . ^1H NMR (CDCl_3) δ 3.90 (s, 3H), 7.01(d, $J = 8.8$ Hz, 2H), 7.85 (d, $J = 8.8$ Hz, 2H), 9.89 (s, 1H). ^{13}C NMR (CDCl_3) δ 190.3, 164.2, 131.6, 129.6, 114.0, 55.3. Pouchert, C.J.; Behnke, J. In *The Aldrich Library of ^{13}C and ^1H FT NMR Spectra*, 1st Ed.; Aldrich Chemical: Milwaukee, 1993; Vol. 2, p 941–A

***p*-Methylbenzaldehyde (2c).** GC (column, TC-WAX, 0.25 mm x 30 m, GL Sciences Inc.); carrier gas, helium (40 kPa); initial column temp, 130 $^{\circ}\text{C}$; final column temp, 250 $^{\circ}\text{C}$; progress rate, 10 $^{\circ}\text{C}/\text{min}$; injection temp, 250 $^{\circ}\text{C}$; retention time (*tR*) of *p*-methylbenzylalcohol, 14.9 min; *tR* of *p*-methylbenzaldehyde, 11.3 min.; anisole as an internal standard. Physical properties: consistent with the commercially available authentic sample.

4-(Methylthio)benzaldehyde (2d). IR (neat) 1694 cm^{-1} . ^1H NMR (CDCl_3) δ 2.54 (s, 3H), 7.33(d, $J = 8.5$ Hz, 2H), 7.78 (d, $J = 8.5$ Hz, 2H), 9.93 (s, 1H). ^{13}C NMR (CDCl_3) δ 190.8, 147.6, 132.6, 129.6, 124.8, 14.5. Pouchert, C.J.; Behnke, J. In *The Aldrich*

Library of ^{13}C and ^1H FT NMR Spectra, 1st Ed.; Aldrich Chemical: Milwaukee, 1993; Vol. 2, p 943–B

Benzaldehyde (2e). GC (column, TC-WAX, 0.25 mm x 30 m, GL Sciences Inc.); carrier gas, helium (40 kPa); initial column temp, 130 °C; final column temp, 250 °C; progress rate, 10 °C/min; injection temp, 250 °C; retention time (*t_R*) of benzylalcohol, 12.7 min; *t_R* of benzaldehyde, 8.9 min.; anisole as an internal standard. Physical properties: consistent with the commercially available authentic sample.

***p*-Bromobenzaldehyde (2f).** mp. 57 °C. IR (KBr) 1689 cm^{-1} . ^1H NMR (CDCl_3) δ 7.69 (d, J = 8.7 Hz, 2H), 7.76 (d, J = 8.7 Hz, 2H), 9.98 (s, 1H). ^{13}C NMR (CDCl_3) δ 190.8, 134.9, 132.3, 130.8, 129.6. Pouchert, C.J.; Behnke, J. In *The Aldrich Library of ^{13}C and ^1H FT NMR Spectra*, 1st Ed.; Aldrich Chemical: Milwaukee, 1993; Vol. 2, p 940–C

***trans*-Cinnamaldehyde (2g).** IR (neat) 1678, 1626 cm^{-1} . ^1H NMR (CDCl_3) δ 6.73 (dd, J = 15.9, 7.7 Hz, 1H), 7.42–7.60(m, 6H), 9.72 (d, J = 7.7 Hz, 1H). ^{13}C NMR (CDCl_3) δ 193.3, 152.4, 133.7, 130.9, 128.8, 128.2. Pouchert, C.J.; Behnke, J. In *The Aldrich Library of ^{13}C and ^1H FT NMR Spectra*, 1st Ed.; Aldrich Chemical: Milwaukee, 1993; Vol. 2, p 926–C

Octanal (2h) GC (column, TC-WAX, 0.25 mm x 30 m, GL Sciences Inc.); carrier gas, helium (40 kPa); initial column temp, 130 °C; final column temp, 250 °C; progress rate, 10 °C/min; injection temp, 250 C; retention time (*t_R*) of 1-octanol, 8.7 min; *t_R* of octanal, 6.7 min.; anisole as an internal standard. Physical properties: consistent with the commercially available authentic sample.