Electronic Supplementary Information

Iridium-catalyzed decarbonylation of aldehydes under mild conditions

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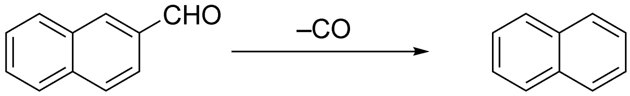
General procedures and materials

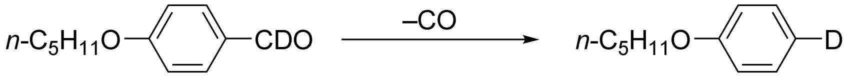
The reactions in Table 1 were performed under an argon atmosphere using standard Schlenk-type glasswares on a dual-manifold Schlenk line. Reagents and solvents were dried and purified by usual procedures.[1] $[\mathrm{IrCl(cod)}]_2$,[2] $[\mathrm{Ir(cod)_2}]\mathrm{BF_4}$,[3] $[\mathrm{IrCl_2Cp^*}]_2$[4] and 2-methyl-2-(4-methylphenyl)propanal[5] were prepared as described in their literatures. *p*-Amyloxybenzaldehyde-d_1 was purchased from CDN isotopes Inc. and distilled under Ar. Other chemicals were purchased from commercial sources. ^{1}H and ^{13}C NMR spectra were measured with a JEOL ECX-400P spectrometer. The ^{1}H NMR chemical shifts are reported relative to tetramethylsilane (TMS, 0.00 ppm) or residual protiated solvent (7.26 ppm) in $\mathrm{CDCl_3}$. The ^{13}C NMR chemical shifts are reported relative to $\mathrm{CDCl_3}$ (77.0 ppm). EI-MS were recorded on a Shimadzu GCMS-QP5050A with a direct inlet. Column chromatography was carried out on silica gel (Kanto N60, spherical, neutral, 63-210 μm). GC analysis was carried out using Shimadzu GC-17A equipped with an integrator (C-R8A) with a capillary column (CBP-5, 0.25 mm i.d. × 25 m).

Decarbonylation of 2-naphthaldehyde (Table 1, entry 5)



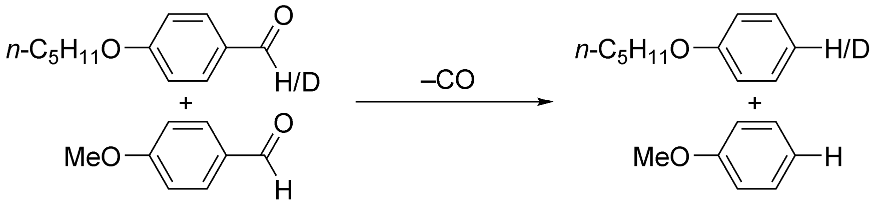
To a 10 cm^3 Schlenk flask with a reflux condenser were added [IrCl(cod)]$_2$ (8.4 mg, 0.0125 mmol) and PPh$_3$ (6.6 mg, 0.025 mmol). The flask was evacuated and backfilled with argon three times. Then a degassed dioxane (1.0 cm^3) was added to the flask and the resultant solution was stirred at room temperature for 10 min. 2-Naphthaldehyde (78.1 mg, 0.50 mmol) was added to the flask and the mixture was heated under reflux (bath temp. 110 °C) for 48 h under an argon atmosphere (balloon). After cooling to room temperature, the reaction mixture was diluted with diethyl ether (5.0 cm^3) and added tridecane (0.205 mmol) as an internal standard. The yield of the product, naphthalene, was determined by GC analysis (95%).

Decarbonylation of *p*-amyloxybenzaldehyde-d_1 (Table 2, entry 10)



To a 10 cm^3 Schlenk flask with a reflux condenser were added [IrCl(cod)]$_2$ (16.8 mg, 0.025 mmol) and PPh$_3$ (13.1 mg, 0.050 mmol). Then dioxane (unpurified, 1.0 cm^3) was added to the flask and the resultant solution was stirred at room temperature for 10 min under an air. *p*-Amyloxybenzaldehyde-d_1 (193 mg, 1.0 mmol, 99.7%-*d*) was added to the flask and the mixture was heated under reflux (bath temp. 110 °C) for 72 h. After cooling to room temperature, the mixture was diluted with pentane and washed with water and brine. The organic layer was dried over Na$_2$SO$_4$, filtered and evaporated carefully. The crude product was purified by silica gel column chromatography using pentane as an eluent to give *p*-amyloxybenzene-d_1 (134 mg, 81%, deuterium incorporation >99% determined by ^{1}H NMR) as a colorless oil: ^{1}H NMR (400 MHz, CDCl$_3$): δ 7.25 (d, J = 8.2 Hz, 2H), 6.88 (d, J = 8.7 Hz, 2H), 3.92 (t, J = 6.6 Hz, 2H), 1.73-1.80 (quintet, 2H, J = 7.2 Hz), 1.32-1.47 (m, 4H), 0.92 (t, J = 7.0 Hz, 3H). ^{13}C NMR (100 MHz, CDCl$_3$) 159.1, 129.2, 120.1($^1J_{\mathrm{C\text{-}D}}$ = 24 Hz), 114.4, 67.8, 29.0, 28.2, 22.5, 14.0. EI-MS: *m/z* 166 ([M+H]$^+$, 1%), 165 ([M]$^+$, 8), 95 (100).

General procedure for kinetic study



To a 10 cm^3 Schlenk flask with a reflux condenser were added $[IrCl(cod)]_2$ (16.8 mg, 0.025 mmol) and PPh_3 (13.1 mg, 0.050 mmol). The flask was evacuated and backfilled with argon three times. Then a degassed dioxane (1.0 cm^3) was added to the flask and the resultant solution was stirred at room temperature for 10 min. *p*-Amyloxybenzaldehyde-d_0 or *p*-amyloxybenzaldehyde-d_1 (1.0 mmol), *p*-methoxybenzaldehyde (1.0 mmol) and bibenzyl (0.50 mmol) as an internal standard were added to the flask and the mixture was heated under reflux (bath temp. 110 °C) under an argon atmosphere (balloon). A small aliquot (0.01 cm^3) was taken out from the reaction mixture at suitable interval. The samples were diluted with diethyl ether (0.05 cm^3) and analyzed by GC (Figure 1). The data during 4-20 h (the conversions after 20 h were 72% for *p*-amyloxybenzaldehyde-d_0 and 52% for *p*-amyloxybenzaldehyde-d_1) were used for the kinetic measurement because these reactions had the induction periods.

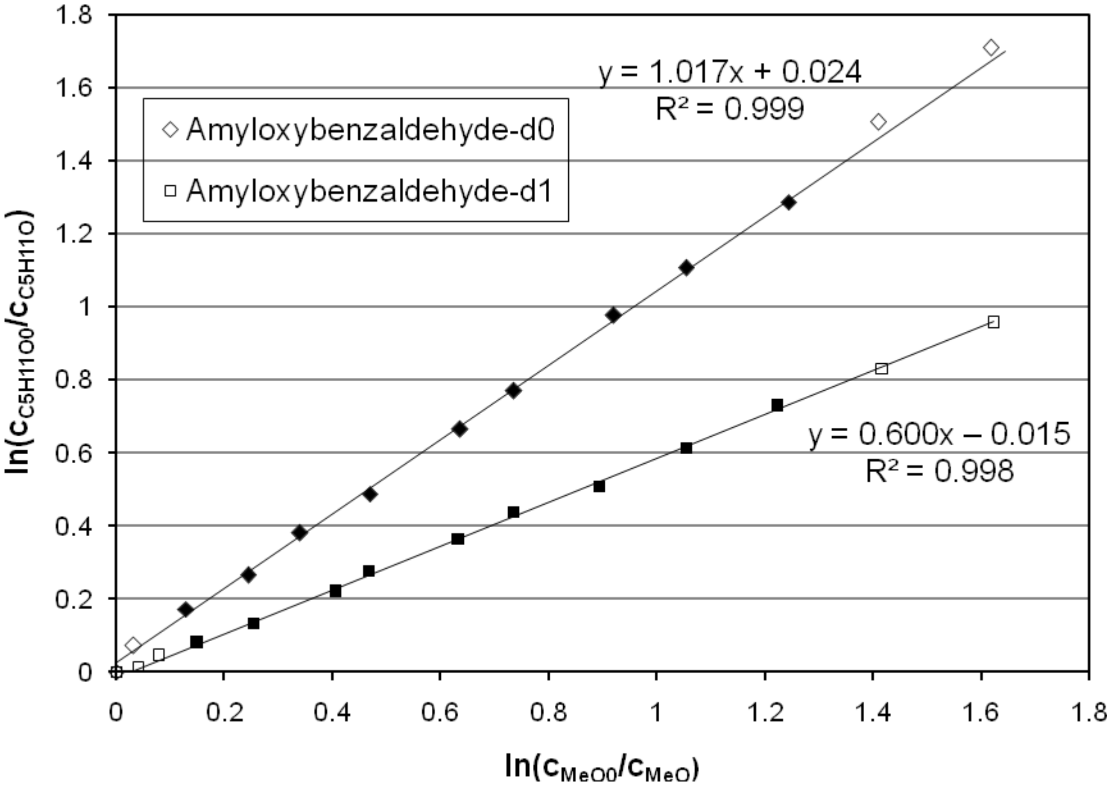


Figure 1 The kinetic isotope effect (k_H/k_D) measurement for the *p*-amyloxybenzaldehydes.

References

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