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 [IrCl(cod)]2, 2 [Ir(cod)2]BF4, 3 [IrCl2Cp*]2 and 2-methyl-2-(4-methylphenyl)propanal5 were prepared as described in their literatures. p-Amyloxybenzaldehyde-d1 was purchased from CDN isotopes Inc. and distilled under Ar. Other chemicals were purchased from commercial sources. 1H and 13C NMR spectra were measured with a JEOL ECX-400P spectrometer. The 1H NMR chemical shifts are reported relative to tetramethylsilane (TMS, 0.00 ppm) or residual protiated solvent (7.26 ppm) in CDCl3. The 13C NMR chemical shifts are reported relative to CDCl3 (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 $p$-amylxybenzaldehyde-$d_1$ (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$_3$): $\delta$ 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 ($^{1}J_{C,D} = 24$ 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 ($k_{\text{H}}/k_{\text{D}}$) measurement for the $p$-amyloxybenzaldehydes.

References