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Cobalt(II)-Catalyzed Oxidative Esterification of Aldehydes: A

Cooperative Effect between Cobalt and Iodide Ion

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Supporting Information

General Procedures. All reactions were carried out under argon using Schlenk-type glassware or in a glovebox. Solvents were dried and distilled under argon prior to use. NMR spectra were recorded on a bruker ASCEND spectrometer (¹H, 600 MHz; ¹³C{¹H}, 151 MHz) or a JEOL JNM-ECA600 spectrometer (¹H, 600 MHz; ¹³C{¹H}, 151 MHz). ¹H NMR and ¹³C NMR, chemical shift δ is given relative to TMS and referenced to the solvent signal. Column chromatography was performed using silica gel. Analytical TLC was done using pre-coated silica gel 60 F₂₅₄ plates. GC analysis was performed using Aglient GC-7890B equipped with a capillary column (DB-FFAP, 30m×0.32mm) using a flame ionization detector. GC-MS was performed using Aglient 6890N-5975B with HP-5MS (30m×0.32mm) column.

1. Comparison of n-Bu₄NI and KI with CoI₂ Catalyst Systems.

Table S1. Comparison of CoI₂ with n-Bu₄NI and KI catalyst systems for the oxidative esterification of aldehydes bearing

$R \stackrel{\text{II}}{\underset{l}{\text{II}}} + MeOH \\ 1 (8 \text{ equiv.}) \\ 1 (8 \text{ equiv.}) \\ R \stackrel{\text{Catalyst}}{\underset{TBHP}{\text{AlCl}_3 (5 \text{ mol}\%)}} R \stackrel{\text{O}}{\underset{l}{\text{II}}} + R \stackrel{\text{O}}{\underset{l}{\text{II}}} \\ R \stackrel{\text{O}}{\underset{l}{\text{II}}} \\ 3 \\ 4 \\ R \stackrel{\text{O}}{\underset{l}{\text{II}}} \\ R \stackrel{\text{O}}{\underset{I}} \\ R \stackrel{\text{O}{\underset{I}}{\underset{I}} \\$					
Entry	Cata. (mol%)	R-	Conv. (%)	Select. (%)	
				3	4
1	Col ₂ (5)		98	94	3
2	KI (10)	H (1a)	71	68	6
3	<i>n</i> -Bu ₄ NI (10)		95	88	6
4	Col ₂ (5)		100	94	6
5	KI (10)	<i>p</i> -OMe (1c)	54	51	2
6	<i>n</i> -Bu ₄ NI (10)		98	92	5
7	CoI ₂ (5)		81	80	0
8	KI (10)	<i>p</i> -NO ₂ (1b)	81	80	0
9	<i>n</i> -Bu ₄ NI (10)		88	87	0

functional groups with MeOH.^a

^a reaction conditions: Aldehyde (1 mmol, 1.0 equiv.), MeOH (8.0 equiv.), AlCl₃ (5 mol%), TBHP (2.0 equiv), 100 °C, 24 h, yields were determined by GC with biphenyl as internal standard.

2. Results for equation 6.

Procedure. To a solution of aldehyde (1 mmol, 1 equiv) in MeOH (8 mmol, 8 equiv.) and methyl acrylate (8 mmol, 8 equiv.) in a glass tube with a stirbar was added CoI_2 (15.7 mg, 0.05 mmol, 5 mol%), AlCl₃ (6.7 mg, 0.05 mmol, 5 mol%), and 5.5M TBHP in decane (91µL, 0.5 mmol, 0.5 equiv.) under argon. The mixture was heated to 100°C for 24h during which three another equal amount of TBHP were added. The mixture was then diluted with CH₃CN (15 mL), and analysised by GC, the unkown trace peaks were also analysed by GC-MS and no peaks of acyl radical and methyl acrylate adduct were found .

GC methods: Aglient GC-7890B equipped with a capillary column (DB-FFAP, 30m×0.32mm) was used. The oven temperature was held at 60 °C for 2 min, increased to 180 °C at a rate of 10 °C/min, and then to 240 °C at a rate of 30 °C/min and held at this temperature for 5 min. The injector temperature was set at 250 °C. The detector (FID) temperature was held at 300 °C.



Fig. S1 GC analysis of the mixture and raw materials.

3. Electrochemical Methods and Cyclic Voltammograms.

Instrumentation. Cyclic voltammetry (CV) measurements were performed on a CH Instruments electrochemical analyzer with CHI 660D software. A three-electrode system was used, consisting of a platinum disk (2 mm diameter) working electrode, platinum wire (0.5 mm diameter and 6 cm length) counter electrode, and Ag/Ag^+ (containing 10 mM AgNO₃ with 0.1 M lithium perchlorate solution in CH₃CN) reference electrode.

General Procedure. The cyclic voltammetry was performed in a glovebox and CH_3CN solvent was dried and degased before use. Lithium perchlorate (0.1 M in CH_3CN) was used as supporting electrolyte. Each date was collected using 5 mL supporting electrolyte solution containing the sample in a electrochemical cell at a scan rate of 50 mV/s.



Fig. S2 Comparison of cyclic voltammograms of NaI, *n*-Bu₄NI and CoI₂ (each case: 1 mM).

4. UV-Visible Spectroscopic Measurements.

Instrumentation. UV-Visible spectra were acquired with an Shimadzu UV-2550 UV–Visible spectrophotometer equiped with a S-1700 thermoelectric cell holder.

Methods for Fig. 4. The CoI₂, KI or n-Bu₄IN solution in CH₃CN was prepared seperately in glovebox, and 2 mL of the solution was celled in a 10mm quartz cell with a rubber cap and a stirrer. The mixture was fixed in the cell holder, stirred and heated to required temperature. The photometric measurement was monitored at 362 nm. For Fig. 4A, a certain amount of TBHP (5.5M in decane) was injected to the solution by syringe and data were recorded at fixed intervals. Amount: 0.05 mM CoI₂, 1.38 mM TBHP; 2.5 mM KI, 6.88 mM TBHP; 5 mM n-Bu₄NI, 100 mM TBHP. For Fig. 4B, TBHP (5.5M in decane) was added successively at 60°C and data were recorded each time at 20 min late after adding TBHP. Amount: 0.2 mM CoI₂; 0.4 mM KI; 0.4 mM Bu₄NI.

Generel Procedure for Fig. 2, Fig. S3 and Fig. S5. The CoI_2 or n-Bu₄IN solution in CH₃CN was prepared seperately in glovebox, and 2 mL of the solution was celled in a 10mm quartz cell with a rubber cap and a stirrer. Afterwards a certain amount of TBHP (5.5M in decane) or different amount of I₂ solution in CH₃CN was injected to the solution by syringe. The mixture was fixed in the cell holder, stirred at room tempetrature or heated to 60°C and spectrum were recorded at fixed intervals.

Procedure for Fig. S4. Bu_4IN (36.9 mg, 0.1 mmol) was dissolved in 1 mL CH₃CN in a little vial with a stirrer in glovebox. Afterwards 364 μ L TBHP (5.5M in decane) was added to the solution by syringe and the mixture was heated to 60°C. For each spectrum, 1 μ L liquid was taken by microsyringe and diluted with CH₃CN to 2 mL.

The UV-Visible Spectroscopic Time Course Measurements of n-Bu₄NI with TBHP.

At first, analogous amount of TBHP to low concentration of CoI_2 case (Fig. 2, B) was used. But there were hardly any changes of spectra even at 60°C for 30 min (Fig. S2). Then the concentration of n-Bu₄NI and TBHP was increased greatly for reaction and some changes of spectra were observed (Fig. S3).



Fig. S3 UV-visible spectra acquired from monitoring the reaction time course of the oxidation of 0.05 mM Bu_4NI in CH₃CN by TBHP. (Bu_4NI : TBHP = 1: 26).



Fig. S4 UV–visible spectra acquired from monitoring the reaction time course of the oxidation of n-Bu₄NI by TBHP. (reaction condition: **0.1 M** n-Bu₄NI, n-Bu₄NI: TBHP = 20)

The UV-Visible Spectroscopic of Different Ratio of I₂ and CoI₂.



Fig. S5 UV-visible spectra of Different Ratio of I₂ and CoI₂ in CH₃CN. (left: 0.05 mM CoI₂, 10 mM I₂; right: CoI₂: 1.3 mM CoI₂, 67 mM I₂.)

The absorptions of the characteristic peaks of CoI_2 (Fig. S3, blank line, peak at 247 nm and peaks around 700 nm) decrease slightly with the increase of I_2 :CoI₂ ratio. That's caused by the increase of solution volume by adding I_2 solution to CoI_2 solution.

5. X-ray photoelectron spectroscopy (XPS) measurements.

XPS measurements were carried out with a Thermo Fisher Scientific ESCALAB 250Xi spectrometer with a hemispherical analyzer. The monochromatized Al K α X-ray source (E = 1486.6 eV) was operated at 15 kV and 10 mA. The standard mode was used as lens mode. The base pressure during the experiment in the analysis chamber was 4 × 10⁻⁷ mbar. To account for charging effects of carbonized samples, the binding energy values were referred to C 1s at 284.8 eV. Spectral analysis consisted in a shirley + linear background subtraction and deconvolution using a mixed Gaussian and Lorentzian lineshapes for each spectral component.



Fig. S6 I3d XPS sepctra of the standard sample of CoI₂, n-Bu₄NI and the n-Bu₄NI+TBHP residue under the same condition

with Fig. 3C.

6. Preparation of Esters

General procedure for Table 2. To a solution of aldehyde (1 mmol, 1 equiv) in MeOH (8 mmol, 8 equiv.) in a glass tube with a stirbar was added CoI₂ (15.7 mg, 0.05 mmol, 5 mol%), AlCl₃ (6.7 mg, 0.05 mmol, 5 mol%), and 5.5M TBHP in decane (91 μ L, 0.5 mmol, 0.5 equiv.) under argon. The mixture was heated to 100°C for 24h during which three another equal amount of TBHP were added. At the end of the reaction, saturated ammonium chloride solution (10 mL) was added to the mixture. The products were extracted by ethyl acetate (3 × 10mL). The combined organic extract was dried by Na₂SO₄ overnight and concentrated, then purified by column chromatography.

Preparation of 3aa. To a solution of benzaldehyde (0.11g, 1 mmol, 1 equiv) in MeOH (0.32mL, 8 mmol, 8 equiv.) in a glass tube with a stirbar was added CoI₂ (15.7 mg, 0.05 mmol, 5 mol%), AlCl₃ (6.7 mg, 0.05 mmol, 5 mol%), and 5.5M TBHP in decane (91µL, 0.5 mmol, 0.5 equiv.) under argon. The mixture was heated to 100°C for 24h during which three another equal amount of TBHP were added. At the end of the reaction, saturated ammonium chloride solution (10 mL) was added to the mixture. The products were extracted by ethyl acetate (3 × 10mL). The combined organic extract was dried by Na₂SO₄ overnight and concentrated, then purified by column chromatography (petroleum ether/ethyl acetate 20:1) provided **3aa** in a yield of 94%. ¹H NMR (600 MHz, CDCl₃, 298 K): $\delta = 8.04$ (dd, ³*J*_{HH} = 8.3 Hz, ³*J*_{HH} = 1.3 Hz, 2H, *o*-Ph), 7.54 (tt, ³*J*_{HH} = 7.6 Hz, ³*J*_{HH} = 1.3 Hz, 1H, *p*-Ph), 7.43 (ddm, ³*J*_{HH} = 8.3 Hz, ³*J*_{HH} = 7.6 Hz, 2H, *m*-Ph), 3.91 (s, 3H, OCH₃). ¹³C {¹H} NMR (151 MHz, CDCl₃, 298 K): $\delta = 167.2$ (C=O), 133.0, 130.3, 129.7, 128.4 (Ph), 52.2 (OCH₃).

Preparation of 3ba. To a solution of 4-nitrobenzaldehyde (1 mmol, 1 equiv) in MeOH (0.32mL, 8 mmol, 8 equiv.) in a glass tube with a stirbar was added CoI₂ (15.7 mg, 0.05 mmol, 5 mol%), AlCl₃ (6.7 mg, 0.05 mmol, 5 mol%), and 5.5M TBHP in decane (91µL, 0.5 mmol, 0.5 equiv.) under argon. The mixture was heated to 100°C for 24h during which three another equal amount of TBHP were added. At the end of the reaction, saturated ammonium chloride solution (10 mL) was added to the mixture. The products were extracted by ethyl acetate (3 × 10mL). The combined organic extract was dried by Na₂SO₄ overnight and concentrated, then purified by column chromatography (petroleum ether/ethyl acetate 20:1) provided **3ba** in a yield of 80%. ¹H NMR (600 MHz, CDCl₃, 298 K): $\delta = 8.27$ (d, ³*J*_{HH} = 8.3 Hz, 2H, Ph), 8.19 (d, ³*J*_{HH} = 8.3 Hz, 2H, Ph), 3.97 (s, 3H, OCH₃). ¹³C{¹H} NMR (151 MHz, CDCl₃, 298 K): $\delta = 165.3$ (C=O), 150.6 (*i*-Ph^{NO2}), 135.60 (*i*-Ph^{C=O}), 130.8, 123.7 (Ph), 52.9 (OCH₃).

Preparation of 3ca. To a solution of 4-methoxybenzaldehyde (1 mmol, 1 equiv) in MeOH (0.32mL, 8 mmol, 8 equiv.) in a glass tube with a stirbar was added CoI₂ (15.7 mg, 0.05 mmol, 5 mol%), AlCl₃ (6.7 mg, 0.05 mmol, 5 mol%), and 5.5M TBHP in decane (91µL, 0.5 mmol, 0.5 equiv.) under argon. The mixture was heated to 100°C for 24h during which three another equal amount of TBHP were added. At the end of the reaction, saturated ammonium chloride solution (10 mL) was added to the mixture. The products were extracted by ethyl acetate (3 × 10mL). The combined organic extract was dried by Na₂SO₄ overnight and concentrated, then purified by column chromatography (petroleum ether/ethyl acetate 10:1) provided **3ca** in a yield of 94%. ¹H NMR (600 MHz, CDCl₃, 298 K): $\delta = 7.97$ (dt, ³*J*_{HH} = 8.9, ³*J*_{HH} = 2.3 Hz, 2H, Ph), 6.89 (dt, ³*J*_{HH} = 8.9, ³*J*_{HH} = 2.3 Hz, 2H, Ph), 3.86, 3.83 (each s, each 3H, OCH₃). ¹³C {¹H} NMR (151 MHz, CDCl₃) $\delta = 166.9$ (C=O), 163.4, 131.6 (each *i*-Ph), 122.6, 113.6 (each Ph), 55.4, 51.9 (each OCH₃).

Preparation of 3da. To a solution of 4-methylbenzaldehyde (1 mmol, 1 equiv) in MeOH (0.32mL, 8 mmol, 8 equiv.) in a glass tube with a stirbar was added CoI₂ (15.7 mg, 0.05 mmol, 5 mol%), AlCl₃ (6.7 mg, 0.05 mmol, 5 mol%), and 5.5M TBHP in decane (91µL, 0.5 mmol, 0.5 equiv.) under argon. The mixture was heated to 100°C for 24h during which three another equal amount of TBHP were added. At the end of the reaction, saturated ammonium chloride solution (10 mL) was added to the mixture. The products were extracted by ethyl acetate (3 × 10mL). The combined organic extract was dried by Na₂SO₄ overnight and concentrated, then purified by column chromatography (petroleum ether/ethyl acetate 20:1) provided **3da** in a yield of 89%. ¹H NMR (600 MHz, CDCl₃, 298 K): δ = 7.93 (dm, ³*J*_{HH} = 8.2 Hz, 2H, Ph), 7.22 (dm, ³*J*_{HH} = 8.2 Hz, 2H, Ph), 3.89 (s, 3H, OCH₃), 2.39 (s, 3H, CH₃). ¹³C{¹H} NMR (151 MHz, CDCl₃, 298 K): δ = 167.2 (C=O), 143.6 (*i*-Ph), 129.7, 129.1 (Ph), 127.51 (*i*-Ph), 52.0 (OCH₃), 21.7 (CH₃).

Preparation of 3ea. To a solution of 4-chlorobenzaldehyde (1 mmol, 1 equiv) in MeOH (0.32mL, 8 mmol, 8 equiv.) in a glass tube with a stirbar was added CoI₂ (15.7 mg, 0.05 mmol, 5 mol%), AlCl₃ (6.7 mg, 0.05 mmol, 5 mol%), and 5.5M TBHP in decane (91µL, 0.5 mmol, 0.5 equiv.) under argon. The mixture was heated to 100°C for 24h during which three another equal amount of TBHP were added. At the end of the reaction, saturated ammonium chloride solution (10 mL) was added to the mixture. The products were extracted by ethyl acetate (3 × 10mL). The combined organic extract was dried by Na₂SO₄ overnight and concentrated, then purified by column chromatography (petroleum ether/ethyl acetate 20:1) provided **3ea** in a yield of 88%. ¹H NMR (600 MHz, CDCl₃, 298 K): δ = 7.95 (dm, ³*J*_{HH} = 8.5 Hz, 2H, Ph), 7.39 (dm, ³*J*_{HH} = 8.5 Hz, 2H, Ph), 3.89 (s, 3H, OCH₃). ¹³C{¹H} NMR (151 MHz, CDCl₃, 298 K): δ = 166.3 (C=O), 139.4 (*i*-Ph), 131.1, 128.8 (Ph), 128.7 (*i*-Ph), 52.3 (OCH₃).

Preparation of 3fa. To a solution of 3-nitrobenzaldehyde (1 mmol, 1 equiv) in MeOH (0.32 mL, 8 mmol, 8 equiv.) in a glass tube with a stirbar was added CoI₂ (15.7 mg, 0.05 mmol, 5 mol%), AlCl₃ (6.7 mg, 0.05 mmol, 5 mol%), and 5.5M TBHP in decane (91µL, 0.5 mmol, 0.5 equiv.) under argon. The mixture was heated to 100°C for 24h during which three another equal amount of TBHP were added. At the end of the reaction, saturated ammonium chloride solution (10 mL) was added to the mixture. The products were extracted by ethyl acetate (3 × 10mL). The combined organic extract was dried by Na₂SO₄ overnight and concentrated, then purified by column chromatography (petroleum ether/ethyl acetate 10:1) provided **3fa** in a yield of 92%. ¹H NMR (600 MHz, CDCl₃, 298 K): $\delta = 8.86$ (t, ³*J*_{HH} = 1.9 Hz, 1H, Ph), 8.41 (dm, ³*J*_{HH} = 8.1 Hz, 1H, Ph), 8.36 (dm, ³*J*_{HH} = 7.8 Hz, 1H, Ph), 7.65 (dd, ³*J*_{HH} = 8.1 Hz, ³*J*_{HH} = 7.8 Hz, 1H, Ph), 7.65 (dd, ³*J*_{HH} = 8.1 Hz, ³*J*_{HH} = 7.8 Hz, 1H, Ph), 52.9 (OCH₃).

Preparation of 3ga. To a solution of 3-methoxybenzaldehyde (1 mmol, 1 equiv) in MeOH (0.32 mL, 8 mmol, 8 equiv.) in a glass tube with a stirbar was added CoI₂ (15.7 mg, 0.05 mmol, 5 mol%), AlCl₃ (6.7 mg, 0.05 mmol, 5 mol%), and 5.5M TBHP in decane (91µL, 0.5 mmol, 0.5 equiv.) under argon. The mixture was heated to 100°C for 24h during which three another equal amount of TBHP were added. At the end of the reaction, saturated ammonium chloride solution (10 mL) was added to the mixture. The products were extracted by ethyl acetate (3 × 10mL). The combined organic extract was dried by Na₂SO₄ overnight and concentrated, then purified by column chromatography (petroleum ether/ethyl acetate 20:1) provided **3ga** in a yield of 92%. ¹H NMR (600 MHz, CDCl₃, 298 K): δ = 7.62 (dm, ³*J*_{HH} = 7.7 Hz, 1H, Ph), 7.55 (m, 1H, Ph), 7.33 (t, ³*J*_{HH} = 8.0 Hz, 1H, Ph), 7.09 (dm, ³*J*_{HH} = 8.0 Hz, 1H, Ph), 3.90 (s, 3H, OCH₃), 3.83 (s, 3H, OCH₃). ¹³C {¹H} NMR (151 MHz, CDCl₃, 298 K): δ = 167.1 (C=O), 159.7, 131.5 (*i*-Ph), 129.5, 122.1, 119.6, 114.1 (Ph), 55.5 (OCH₃), 52.2 (OCH₃).

Preparation of 3ha. To a solution of 3-methylbenzaldehyde (1 mmol, 1 equiv) in MeOH (0.32 mL, 8 mmol, 8 equiv.) in a glass tube with a stirbar was added CoI₂ (15.7 mg, 0.05 mmol, 5 mol%), AlCl₃ (6.7 mg, 0.05 mmol, 5 mol%), and 5.5M TBHP in decane (91µL, 0.5 mmol, 0.5 equiv.) under argon. The mixture was heated to 100°C for 24h during which three another equal amount of TBHP were added. At the end of the reaction, saturated ammonium chloride solution (10 mL) was added to the mixture. The products were extracted by ethyl acetate (3 × 10mL). The combined organic extract was dried by Na₂SO₄ overnight and concentrated, then purified by column chromatography (petroleum ether/ethyl acetate 20:1) provided **3ha** in a yield of 93%. ¹H NMR (600 MHz, CDCl₃, 298 K) δ = 7.85 (br s, 1H, *o*-Ph), 7.83 (dm, ³*J*_{HH} = 7.5 Hz, 1H, *o*'-Ph), 7.33 (dm, ³*J*_{HH} = 7.8 Hz, 1H, *p*-Ph), 7.30 (tm, ³*J*_{HH} = 7.5 Hz, 1H, *m*'-Ph), 3.89 (s, 3H, OCH₃), 2.37 (s, 3H, CH₃). ¹³C{¹H} NMR (151 MHz, CDCl₃, 298 K): δ = 167.1 (C=O), 138.0 (*m*-Ph), 133.6 (*p*-Ph), 130.1 (*i*-Ph and *o*-Ph), 128.2 (*m*'-Ph), 126.7 (*o*'-Ph), 51.9 (OCH₃), 21.1 (CH₃).

Preparation of 3ia. To a solution of 3-chlorobenzaldehyde (1 mmol, 1 equiv) in MeOH (0.32 mL, 8 mmol, 8 equiv.) in a glass tube with a stirbar was added CoI₂ (15.7 mg, 0.05 mmol, 5 mol%), AlCl₃ (6.7 mg, 0.05 mmol, 5 mol%), and 5.5M TBHP in decane (91µL, 0.5 mmol, 0.5 equiv.) under argon. The mixture was heated to 100°C for 24h during which three another equal amount of TBHP were added. At the end of the reaction, saturated ammonium chloride solution (10 mL) was added to the mixture. The products were extracted by ethyl acetate (3 × 10mL). The combined organic extract was dried by Na₂SO₄ overnight and concentrated, then purified by column chromatography (petroleum ether/ethyl acetate 10:1) provided **3ia** in a yield of 94%. ¹H NMR (600 MHz, CDCl₃, 298 K): $\delta = 8.00$ (t, ³*J*_{HH} = 1.7 Hz, 1H, Ph), $\delta = 7.91$ (d, ³*J*_{HH} = 7.8Hz, 1H,

Ph), $\delta = 7.51$ (dm, ${}^{3}J_{HH} = 8.0$ Hz, 1H, Ph), $\delta = 7.36$ (t, ${}^{3}J_{HH} = 7.9$ Hz, 1H, Ph), 3.91 (s, 3H, OCH₃). ${}^{13}C{}^{1}H$ NMR (151 MHz, CDCl₃, 298 K): $\delta = 165.9$ (C=O), 134.6, 132.0 (*i*-Ph), 133.0, 129.7(7), 129.7(6), 127.8 (Ph), 52.5 (OCH₃).

Preparation of 3ja. To a solution of 2-methoxybenzaldehyde (1 mmol, 1 equiv) in MeOH (0.32 mL, 8 mmol, 8 equiv.) in a glass tube with a stirbar was added CoI₂ (15.7 mg, 0.05 mmol, 5 mol%), AlCl₃ (6.7 mg, 0.05 mmol, 5 mol%), and 5.5M TBHP in decane (91µL, 0.5 mmol, 0.5 equiv.) under argon. The mixture was heated to 100°C for 24h during which three another equal amount of TBHP were added. At the end of the reaction, saturated ammonium chloride solution (10 mL) was added to the mixture. The products were extracted by ethyl acetate (3 × 10mL). The combined organic extract was dried by Na₂SO₄ overnight and concentrated, then purified by column chromatography (petroleum ether/ethyl acetate 10:1) provided **3ja** in a yield of 85%. ¹H NMR (600 MHz, CDCl₃, 298 K): $\delta = 7.76$ (dd, ³*J*_{HH} = 7.9, ³*J*_{HH} = 1.8 Hz, 1H, Ph), 7.42 (m, 1H, Ph), 6.94 (m, 1H, Ph), 6.92 (m, 1H, Ph), 3.86 (s, 3H, OCH₃), 3.84 (s, 3H, OCH₃). ¹³C {¹H} NMR (151 MHz, CDCl₃, 298 K): $\delta = 166.7$ (C=O), 159.1, 112.0 (*i*-Ph), 133.5, 131.6, 120.1, 120.0 (Ph), 55.9, 52.0 (OCH₃).

Preparation of 3ka. To a solution of 2-chlorobenzaldehyde (1 mmol, 1 equiv) in MeOH (0.32 mL, 8 mmol, 8 equiv.) in a glass tube with a stirbar was added CoI₂ (15.7 mg, 0.05 mmol, 5 mol%), AlCl₃ (6.7 mg, 0.05 mmol, 5 mol%), and 5.5M TBHP in decane (91µL, 0.5 mmol, 0.5 equiv.) under argon. The mixture was heated to 100°C for 24h during which three another equal amount of TBHP were added. At the end of the reaction, saturated ammonium chloride solution (10 mL) was added to the mixture. The products were extracted by ethyl acetate (3 × 10mL). The combined organic extract was dried by Na₂SO₄ overnight and concentrated, then purified by column chromatography (petroleum ether/ethyl acetate 20:1) provided **3ka** in a yield of 49%. ¹H NMR (600 MHz, CDCl₃, 298 K): $\delta = 7.79$ (dd, ³*J*_{HH} = 7.8, ³*J*_{HH} = 1.6 Hz, 1H, Ph), 7.42 (dd, ³*J*_{HH} = 8.0, ³*J*_{HH} = 0.9 Hz, 1H, Ph), 7.38 (dt, ³*J*_{HH} = 8.0, ³*J*_{HH} = 1.6 Hz, 1H, Ph), 7.28 (dt, ³*J*_{HH} = 7.8, ³*J*_{HH} = 0.9 Hz, 2H, Ph), 3.90 (s, 3H, OCH₃). ¹³C{¹H} NMR (151 MHz, CDCl₃, 298 K): $\delta = 165.2$ (C=O), 132.7, 129.1 (*i*-Ph), 131.6, 130.4, 130.1, 125.6 (Ph), 51.4 (OCH₃).

Preparation of 3la. To a solution of n-hexanal (1 mmol, 1 equiv) in MeOH (0.32mL, 8 mmol, 8 equiv.) in a glass tube with a stirbar was added CoI₂ (15.7 mg, 0.05 mmol, 5 mol%), AlCl₃ (6.7 mg, 0.05 mmol, 5 mol%), and 5.5M TBHP in decane (91 μ L, 0.5 mmol, 0.5 equiv.) under argon. The mixture was heated to 100°C for 24h during which three another equal amount of TBHP were added. At the end of the reaction, saturated ammonium chloride solution (10 mL) was added to the mixture. The products were analysised by GC-MS and provided a yield of 65%.

Preparation of 3ma. To a solution of 3-phenylpropion aldehyde (1 mmol, 1 equiv) in MeOH (0.32 mL, 8 mmol, 8 equiv.) in a glass tube with a stirbar was added CoI₂ (15.7 mg, 0.05 mmol, 5 mol%), AlCl₃ (6.7 mg, 0.05 mmol, 5 mol%), and 5.5M TBHP in decane (91µL, 0.5 mmol, 0.5 equiv.) under argon. The mixture was heated to 100°C for 24h during which three another equal amount of TBHP were added. At the end of the reaction, saturated ammonium chloride solution (10 mL) was added to the mixture. The products were extracted by ethyl acetate (3 × 10mL). The combined organic extract was dried by Na₂SO₄ overnight and concentrated, then purified by column chromatography (petroleum ether/ethyl acetate 10:1) provided **3ma** in a yield of 72%. ¹H NMR (600 MHz, CDCl₃, 298 K): $\delta = 7.31$ (m, 2H, *m*-Ph), 7.22 (m, 1H, *p*-Ph), 7.22 (m, 1H, *o*-Ph), 3.68 (s, 3H, OCH₃), 2.97 (t, ³J_{HH} = 8.1 Hz, 2H), 2.65 (t, ³J_{HH} = 8.1 Hz, 2H). ¹³C {¹H} NMR (151 MHz, CDCl₃, 298 K): $\delta = 173.4$ (C=O), 140.6 (*i*-Ph), 128.6, 128.35 (*m*-Ph, *o*-Ph), 126.35 (*p*-Ph), 51.7 (OCH₃), 35.77 (CH₂), 31.02 (CH₂).

Preparation of 3na. To a solution of 4-pyridylaldehyde (1 mmol, 1 equiv) in MeOH (0.32 mL, 8 mmol, 8 equiv.) in a glass tube with a stirbar was added CoI₂ (15.7 mg, 0.05 mmol, 5 mol%), AlCl₃ (6.7 mg, 0.05 mmol, 5 mol%), and 5.5M TBHP in decane (91µL, 0.5 mmol, 0.5 equiv.) under argon. The mixture was heated to 100°C for 24h during which three another equal amount of TBHP were added. At the end of the reaction, saturated ammonium chloride solution (10 mL) was added to the mixture. The products were extracted by ethyl acetate (3 × 10mL). The combined organic extract was dried by Na₂SO₄ overnight and concentrated, then purified by column chromatography (petroleum ether/ethyl acetate 5:1) provided **3na** in a yield of 75%. ¹H NMR (600 MHz, CDCl₃, 298 K): δ = 8.76 (m, 2H, Py), 7.82 (m, 2H, Py), 3.94 (s, 3H, OCH₃). ¹³C {¹H} NMR (151 MHz, CDCl₃, 298 K): δ = 164.7 (C=O), 149.7 (Py), 136.4 (*i*-Py), 121.9 (Py), 51.8 (OCH₃).

Preparation of 30a. To a solution of 2-furanaldehyde (1 mmol, 1 equiv) in MeOH (0.32 mL, 8 mmol, 8 equiv.) in a glass tube with a stirbar was added CoI₂ (15.7 mg, 0.05 mmol, 5 mol%), AlCl₃ (6.7 mg, 0.05 mmol, 5 mol%), and 5.5M TBHP in decane (91µL, 0.5 mmol, 0.5 equiv.) under argon. The mixture was heated to 100°C for 24h during which three another equal amount of TBHP were added. At the end of the reaction, saturated ammonium chloride solution (10 mL) was added to the mixture. The products were extracted by ethyl acetate (3 × 10mL). The combined organic extract was dried by Na₂SO₄ overnight and concentrated, then purified by column chromatography (petroleum ether/ethyl acetate 40:1) provided **30a** in a yield of 66%. ¹H NMR (600 MHz, CDCl₃, 298 K): δ = 7.58 (m, 1H, furyl), 7.18 (d, ³*J*_{HH} = 3.4 Hz, 1H, furyl), 6.51 (dd, ³*J*_{HH} = 3.4, ³*J*_{HH} = 1.7 Hz, 1H, furyl), 3.90 (s, 3H, OCH₃). ¹³C{¹H}</sup> NMR (151 MHz, CDCl₃, 298 K): δ = 159.3 (C=O), 146.4 (furyl), 144.8 (*i*-furyl), 118.1 (furyl), 112.0 (furyl), 52.1 (OCH₃).

Preparation of 3pa. To a solution of 2-thiophenaldehyde (1 mmol, 1 equiv) in MeOH (0.32 mL, 8 mmol, 8 equiv.) in a glass tube with a stirbar was added CoI₂ (15.7 mg, 0.05 mmol, 5 mol%), AlCl₃ (6.7 mg, 0.05 mmol, 5 mol%), and 5.5M TBHP in decane (91µL, 0.5 mmol, 0.5 equiv.) under argon. The mixture was heated to 100°C for 24h during which three another equal amount of TBHP were added. At the end of the reaction, saturated ammonium chloride solution (10 mL) was added to the mixture. The products were extracted by ethyl acetate (3 × 10mL). The combined organic extract was dried by Na₂SO₄ overnight and concentrated, then purified by column chromatography (petroleum ether/ethyl acetate 10:1) provided **3pa** in a yield of 69%. ¹H NMR (600 MHz, CDCl₃, 298 K): $\delta = 7.81$ (dd, ³*J*_{HH} = 3.7, ³*J*_{HH} = 0.9 Hz, 1H, thiophen), 7.55 (dd, ³*J*_{HH} = 4.9, ³*J*_{HH} = 0.9 Hz, 1H, thiophen), 7.10 (dd, ³*J*_{HH} = 4.9, ³*J*_{HH} = 3.7 Hz, 1H, thiophen), 3.89 (s, 3H, OCH₃). ¹³C {¹H} NMR (151 MHz, CDCl₃, 298 K): $\delta = 162.9$ (C=O), 133.6 (thiophen), 132.5 (thiophen), 130.1 (*i*-thiophen), 127.9 (thiophen), 52.3 (OCH₃).

Preparation of 3ab. To a solution of benzaldehyde (1 mmol, 1 equiv) in ethonal (8 mmol, 8 equiv.) in a glass tube with a stirbar was added CoI₂ (15.7 mg, 0.05 mmol, 5 mol%), AlCl₃ (6.7 mg, 0.05 mmol, 5 mol%), and 5.5M TBHP in decane (91µL, 0.5 mmol, 0.5 equiv.) under argon. The mixture was heated to 100°C for 24h during which three another equal amount of TBHP were added. At the end of the reaction, saturated ammonium chloride solution (10 mL) was added to the mixture. The products were extracted by ethyl acetate (3 × 10mL). The combined organic extract was dried by Na₂SO₄ overnight and concentrated, then purified by column chromatography (petroleum ether/ethyl acetate 20:1) provided **3ab** in a yield of 96%. ¹H NMR (600 MHz, CDCl₃, 298 K): $\delta = 8.05$ (dm, ³*J*_{HH} = 8.4 Hz, 2H, *o*-Ph), 7.53 (tm, ³*J*_{HH} = 7.5 Hz, 1H, *p*-Ph), 7.42 (ddm, ³*J*_{HH} = 8.4 Hz, ³*J*_{HH} = 7.5 Hz, 2H, *m*-Ph), 4.37 (q, ³*J*_{HH} = 7.1 Hz, 2H, CH₂^{Et}), 1.39 (t, ³*J*_{HH} = 7.1 Hz, 3H, CH₃^{Et}). ¹³C{¹H} NMR (151 MHz, CDCl₃, 298 K): $\delta = 166.7$ (C=O), 132.9 (*p*-Ph), 130.6 (*i*-Ph), 129.6, 128.4 (Ph), 61.0 (OCH₂), 14.4 (CH₃^{Et}).

Preparation of 3ac. To a solution of benzaldehyde (1 mmol, 1 equiv) in n-butanol (8 mmol, 8 equiv.) in a glass tube with a stirbar was added CoI₂ (15.7 mg, 0.05 mmol, 5 mol%), AlCl₃ (6.7 mg, 0.05 mmol, 5 mol%), and 5.5M TBHP in decane (91µL, 0.5 mmol, 0.5 equiv.) under argon. The mixture was heated to 100°C for 24h during which three another equal amount of TBHP were added. At the end of the reaction, saturated ammonium chloride solution (10 mL) was added to the mixture. The products were extracted by ethyl acetate (3 × 10mL). The combined organic extract was dried by Na₂SO₄ overnight and concentrated, then purified by column chromatography (petroleum ether/ethyl acetate 20:1) provided **3ac** in a yield of 94%. ¹H NMR (600 MHz, CDCl₃, 298 K): $\delta = 8.05$ (dm, ³*J*_{HH} = 7.5 Hz, 2H, *o*-Ph), 7.54 (tm, ³*J*_{HH} = 7.4 Hz, 1H, *p*-Ph), 7.43 (ddm, ³*J*_{HH} = 7.5 Hz, 3*H*_L, 2H, *m*-Ph), 4.33 (t, ³*J*_{HH} = 6.6 Hz, 2H, OCH₂^{Bu}), 1.75 (m, 2H, CH₂^{Bu}), 1.48 (m, 2H, CH₂^{Bu}), 0.98 (³*J*_{HH} = 7.3 Hz, 3H, CH₃^{Bu}). ¹³C{¹H} NMR (151 MHz, CDCl₃, 298 K): $\delta = 166.7$ (C=O), 132.8 (*p*-Ph), 130.6 (*i*-Ph), 129.6, 128.4 (Ph), 64.9 (OCH₂), 30.9, 19.4 (CH₂^{Bu}), 13.8 (CH₃^{Bu}).

Preparation of 3ad. To a solution of benzaldehyde (1 mmol, 1 equiv) in isopropanol (8 mmol, 8 equiv.) in a glass tube with a stirbar was added CoI₂ (15.7 mg, 0.05 mmol, 5 mol%), AlCl₃ (6.7 mg, 0.05 mmol, 5 mol%), and 5.5M TBHP in decane (91 μ L, 0.5 mmol, 0.5 equiv.) under argon. The mixture was heated to 100°C for 24h during which three another equal amount of TBHP were added. At the end of the reaction, saturated ammonium chloride solution (10 mL) was added to the mixture. The products were extracted by ethyl acetate (3 × 10mL). The combined organic extract was dried by Na₂SO₄ overnight and concentrated, then purified by column chromatography (petroleum ether/ethyl acetate 20:1) provided **3ad** in a

yield of 73%. ¹H NMR (600 MHz, CDCl₃, 298 K): $\delta = 8.05$ (dm, ³*J*_{HH} = 7.6 Hz, 2H, *o*-Ph), 7.53 (tm, ³*J*_{HH} = 7.4 Hz, 2H, *p*-Ph), 7.42 (ddm, ³*J*_{HH} = 7.6 Hz, ³*J*_{HH} = 7.4 Hz, 2H, *m*-Ph), 5.26 (hept, ³*J*_{HH} = 6.3 Hz, 1H, CH^{i-Pr}), 1.37 (d, ³*J*_{HH} = 6.3 Hz, 6H, CH₃^{i-Pr}). ¹³C{¹H} NMR (151 MHz, CDCl₃, 298 K): $\delta = 166.2$ (C=O), 132.7 (*p*-Ph), 131.0 (*i*-Ph), 129.6, 128.3 (Ph), 68.4 (CH^{i-Pr}), 22.0 (CH₃^{i-Pr}).

Preparation of 3ae. To a solution of benzaldehyde (1 mmol, 1 equiv) in tert-butanol (8 mmol, 8 equiv.) in a glass tube with a stirbar was added CoI₂ (15.7 mg, 0.05 mmol, 5 mol%), AlCl₃ (6.7 mg, 0.05 mmol, 5 mol%), and 5.5M TBHP in decane (91µL, 0.5 mmol, 0.5 equiv.) under argon. The mixture was heated to 100°C for 24h during which three another equal amount of TBHP were added. At the end of the reaction, saturated ammonium chloride solution (10 mL) was added to the mixture. The products were extracted by ethyl acetate (3 × 10mL). The combined organic extract was dried by Na₂SO₄ overnight and concentrated, then purified by column chromatography (petroleum ether/ethyl acetate 20:1) provided **3ae** in a yield of 58%. ¹H NMR (600 MHz, CDCl₃, 298 K): δ = 7.99 (dm, ³*J*_{HH} = 7.2 Hz, 2H, *o*-Ph), 7.52 (tm, ³*J*_{HH} = 7.4 Hz, 1H, *p*-Ph), 7.41 (ddm, ³*J*_{HH} = 7.6 Hz, ³*J*_{HH} = 7.4 Hz, 2H, *m*-Ph), 1.60 (s, 9H, 3×CH₃^{t-Bu}). ¹³C{¹H} NMR (151 MHz, CDCl₃, 298 K): δ = 165.9 (C=O), 132.5 (*p*-Ph), 132.2 (*i*-Ph), 129.5, 128.3 (*o*,*m*-Ph), 81.1 (Cq^{t-Bu}), 28.3 (CH₃^{t-Bu}).