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Isolation and Characterization of a Trinuclear Cobalt Complex Containing Trigonal-Prismatic Cobalt in Secondary Alcohol Aerobic Oxidation

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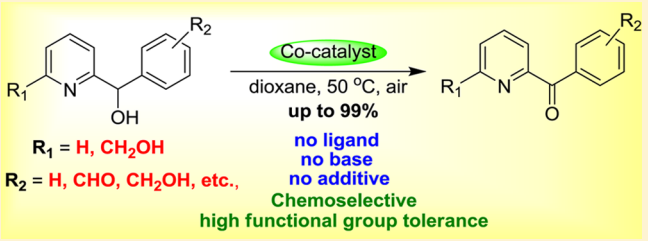
Supporting Information

ABSTRACT: An unusual trinuclear cobalt complex was successfully isolated and characterized in the $Co(OAc)_2 \cdot 4H_2O$-catalyzed aerobic oxidation of pyridine-based secondary alcohols. In this complex, a cobalt ion (the one in the middle, labeled Co2) has a novel trigonal-prismatic structure coordinated with six oxygen atoms from the substrate. The molecular oxygen present in air plays a major role in enabling this transformation to be catalytic. This aerobic catalytic reaction is very selective to pyridine-based secondary alcohols over primary alcohols.

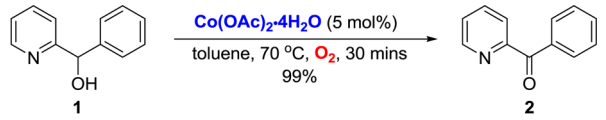


Aryl(di)azinyl ketone derivatives have shown a wide range of biological activities such as being antihistamines, antimalarial and antiarrhythmic agents, β_2-adrenergic agonists, and anticancer therapeutics.[1] Owing to their biological importance and usefulness, various synthetic approaches have been developed to prepare these ketone derivatives. In particular, the oxidation of secondary alcohols[2] and benzylic oxidation of the methylene group of aryl(di)azinylmethanes have proven to be versatile synthetic strategies.[3] Despite their merits, the aforementioned methods suffer from harsh reaction conditions, less functional group tolerance, multistep preparation of starting materials, the need for ligands to the metal catalysts, and moderately sustainable oxidizing agents. Also, it is difficult to address the exact reaction pathway with appropriate evidence. Hence, it is important to develop a new catalytic method which will be more economical, environmentally benign, and easily available and have high functional group tolerance and high selectivity with proper understanding of the reaction pathway.

Recently, we had used chiral cobalt catalysts for the synthesis of enantiomerically enriched benzoins and α-hydroxy esters through oxidative kinetic resolution.[4] Further extending the scope of cobalt catalysts, in this paper we report for the first time a $Co(OAc)_2$-catalyzed selective secondary pyridine based alcohol oxidation reaction and the isolation and characterization of an unusual trinuclear cobalt complex, which is formed in the course of this oxidation reaction.

To begin with, we carried out the aerobic oxidation of (2-pyridyl)phenylmethanol (**1**) as a model substrate using a catalytic amount of cobalt acetate (5 mol %) in the presence of oxygen in toluene at 70 °C. This aerobic oxidation reaction yielded 99% of the corresponding ketone, phenyl(pyridin-2-yl)methanone (**2**), in 30 min (Scheme 1). It is interesting to note that this aerobic oxidation reaction took place without any external ligand, base, or additive. To increase the efficiency of the reaction, the oxidation reaction was further screened with different types of cobalt salts, solvents, ratios of catalyst, and temperatures to optimize the reaction conditions for this aerobic oxidation reaction. The results are summarized in Table 1.

Scheme 1. Cobalt-Catalyzed Aerobic Oxidation of Alcohol 1



Initially, various cobalt salts were screened. Cobalt acetate turned out to be the best reagent, and it resulted in 99% isolated yield of the product in 30 min (Table 1, entry 1).

These results indicate that the counteranion acetate plays a prominent role in this oxidation. Next, various solvents were tested for this oxidation reaction, and among them dioxane proved to be the most efficient solvent for this oxidation reaction (99% isolated yield in 3.5 h; Table 1, entry 9). Ketone **2** was obtained with other solvents also, but the reaction time was longer. It is possible that the coordinating nature of the substrate with cobalt acetate could be more favorable in dioxane than that in the other solvents.

Then the reaction was carried out in an open air atmosphere; it took 4 h to provide 98% isolated yield (Table 1, entry 14) which clearly shows that molecular oxygen present in the air is sufficient. Therefore, we decided to carry out the reaction further in an open air atmosphere. Finally, upon cobalt catalyst screening, it was found that 10 mol % of catalyst gave 99%

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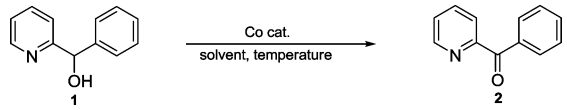
Table 1. Optimization of Cobalt-Catalyzed Aerobic Oxidation of Secondary Alcohol



entry	cobalt source	loading (mol %)	solvent	T (°C)	atmosphere	time (h)	yield (%)[a]
1	$Co(OAc)_2{\cdot}4H_2O$	5	toluene	70	O_2	0.5	99
2	$Co(NO)_3{\cdot}7H_2O$	5	toluene	70	O_2	48	84
3	$CoSO_4{\cdot}7H_2O$	5	toluene	70	O_2	48	
4	CoO	5	toluene	70	O_2	48	14
5	$CoCl_2{\cdot}6H_2O$	5	toluene	70	O_2	48	
6	$Co(OAc)_2{\cdot}4H_2O$	5	toluene	50	O_2	4	98
7	$Co(OAc)_2{\cdot}4H_2O$	5	benzene	50	O_2	21	94
8	$Co(OAc)_2{\cdot}4H_2O$	5	THF	50	O_2	9	98
9	$Co(OAc)_2{\cdot}4H_2O$	5	dioxane	50	O_2	3.5	99
10	$Co(OAc)_2{\cdot}4H_2O$	5	$CHCl_3$	50	O_2	48	37
11	$Co(OAc)_2{\cdot}4H_2O$	5	DMF	50	O_2	23	98
12	$Co(OAc)_2{\cdot}4H_2O$	5	CH_3CN	50	O_2	8	98
13	$Co(OAc)_2{\cdot}4H_2O$	5	MeOH	50	O_2	48	34
14	$Co(OAc)_2{\cdot}4H_2O$	5	dioxane	50	air	4	98[b]
15	$Co(OAc)_2{\cdot}4H_2O$	1	dioxane	50	air	18	96
16	$Co(OAc)_2{\cdot}4H_2O$	2.5	dioxane	50	air	6.5	98
17	$Co(OAc)_2{\cdot}4H_2O$	5	dioxane	50	air	3.5	96
18	$Co(OAc)_2{\cdot}4H_2O$	10	dioxane	50	air	2.5	99
19	$Co(OAc)_2{\cdot}4H_2O$	20	dioxane	50	air	1	97

[a]Isolated yield. [b]Reaction carried out in an open air atmosphere.

isolated yield in just 2.5 h (entry 18). After having optimized the reaction conditions, we tested the substrate scope for this oxidation reaction. Several pyridine-based secondary alcohols containing both electron-withdrawing and electron-donating groups were successfully oxidized to the corresponding ketones in quantitative yield, as summarized in Figure 1.

Interestingly, even groups typically sensitive toward oxidation such as aldehydic (**1n**) and benzylic alcoholic groups (**1m**) were well tolerated under the optimized reaction conditions and yielded selectively the corresponding oxidized products 95% (**2n**) and 97% (**2m**), respectively (Scheme 2).

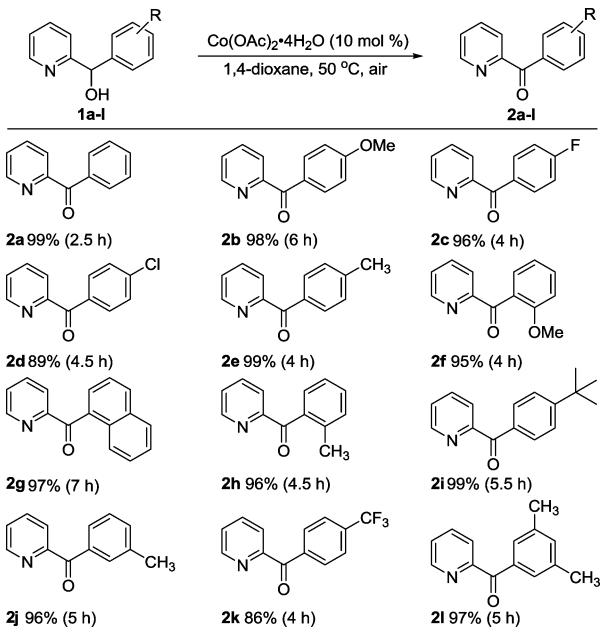
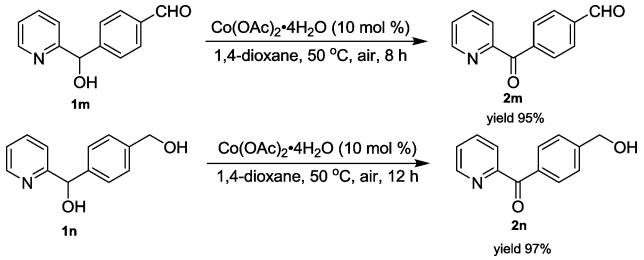


Figure 1. Substrate scope of the aerobic oxidation reaction.

Scheme 2. High Functional Group Tolerance of Cobalt-Catalyzed Aerobic Oxidation Reaction



Our cobalt acetate catalyzed aerobic oxidation reaction is very selective to 2-pyridinyl-based secondary alcohols over primary alcohols. When pyridine-based alcohols containing both primary and secondary alcohol groups such as substrates **3** were made to react under the optimized reaction conditions, in all of the reactions only the secondary alcohol groups were selectively oxidized over the primary alcoholic group (Table 2). In particular, when the diol **3b** was oxidized with the $Co(OAc)_2$ catalyst, it only yielded the selective secondary alcohol oxidized product **4b** with 88% isolated yield (entry 2). However, the same diol **3b** when treated with other typical oxidizing agents such as PDC, PCC, and DMP and under Swern oxidation conditions gave almost a 1:1 mixture of products without any selectivity, and the results are summarized in Table 3. These results clearly show that the cobalt acetate catalyzed aerobic oxidation is very selective for secondary alcohols due to the increased acidity of doubly activated benzylic protons.

Motivated by the excellent selectivity afforded in the Co-catalyzed oxidation protocol, we then strived to find out how

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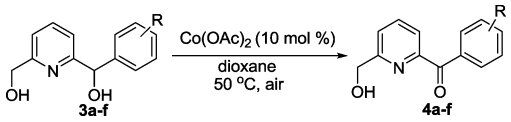
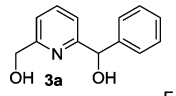
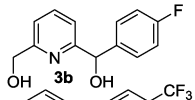
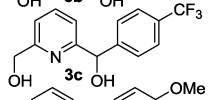
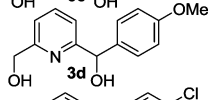
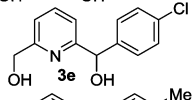
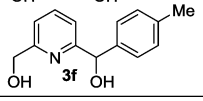
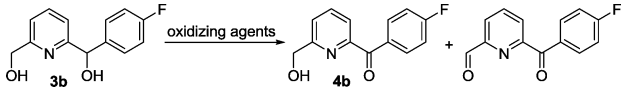
Table 2. Selective Aerobic Oxidation of Secondary Alcohols over Primary Alcohols by Cobalt Acetate



entry	substrate	time(d)	yield (%)[a]
1		4.0	60[b]
2		4.0	88[b]
3		4.5	73[b]
4		5.0	48[b]
5		5.0	79[b]
6		8.0	60[b]

[a]Isolated yield. [b]The appropriate quantity of starting material was recovered.

Table 3. Various Typical Oxidizing Agent Mediated Selective Oxidations of Diol[a]



entry	reagent	time	yield (%)	yield (%)
1	**$Co(OAc)_2{\cdot}4H_2O$**	**4 days**	**88**	**0**
2	PCC	4 h	24	18
3	PDC	4 h	29	34
4	DMP	2 days	21	30
5	Swern oxidation	9 h	23	31

[a]All the oxidizing reagents were used in a 2 equiv amount in dichloromethane solvent (5 mL). Swern oxidation was carried out in DMSO as solvent.

the cobalt acetate alone is responsible for the catalytic oxidation without any ligand, additives, or base. We started with the diphenylmethanol substrate **5** and noticed that it failed to undergo any oxidation reaction, even when an external ligand such as 1,10-phenanthroline or tetramethylethylenediamine (TMEDA) was used along with cobalt acetate.

Surprisingly, other pyridine-based secondary alcohols such as (3-pyridyl)phenylmethanol (**6**) and 4-pyridylphenylmethanol (**7**) also failed to provide any oxidized product. In order to further understand the selectivity of this oxidation reaction, we performed the reaction with a mixture of the substrates (2-pyridyl)phenylmethanol (**1**) and 2-pyridinemethanol. As we expected, only substrate **1** was oxidized to provide the corresponding ketone **2** in 96% isolated yield in 4 h, whereas 2-pyridinemethanol was recovered in a quantitative amount. These results clearly indicate that there can be a complex formation between cobalt acetate and the 2-pyridinyl-based secondary alcohol **1**, which can act as a bidentate ligand (β-imino alcohol) to putatively give a five-membered cyclic complex with cobalt acetate whose formation is not possible in the case of other secondary alcohols **5**–**7** (Figure 2).

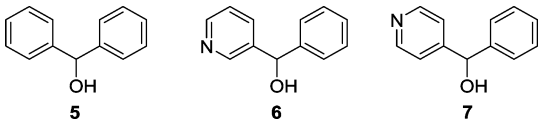


Figure 2. Substrates which failed to undergo oxidation.

Thus, the pyridine nitrogen atom of alcohol **1** may coordinate with cobalt acetate and this coordination may increase the acidity of the benzylic methine proton, whereas this is not possible in the case of diphenylmethanol, (3-pyridyl)phenylmethanol, and (4-pyridyl)phenylmethanol. In addition, the nitrogen atom of **1** can act as a base as well. To investigate the exact mechanistic pathway of this aerobic oxidation reaction, particularly the complexation nature of the substrate **1** with $Co(OAc)_2$, we attempted to isolate the reaction complex from cobalt acetate and pyridinyl alcohol **1**. When a 1:1 ratio of cobalt acetate and pyridinyl alcohol **1** was stirred in dioxane at room temperature for 30 min followed by the slow evaporation of the solvent, pink crystals (crystal **A**) were obtained and a notable quantity of the oxidized product ketone **2** was found in the mother liquor. The XRD analysis of this crystal **A** revealed that the very unusual trinuclear cobalt species **8a** was complexed with six molecules of (2-pyridyl)-phenylmethanol along with a cocrystal of cobalt acetate trimer **8b** (Figure 3).

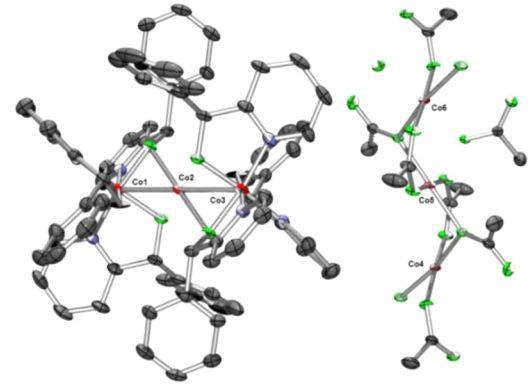


Figure 3. ORTEP diagram of the cobalt trinuclear complex in crystal **A**. H atoms have been omitted for clarity. Relevant bond lengths (Å) and angles (deg): Co1–Co2 2.6351(8), Co1–N1 1.921(7), Co1–N2 1.927(6), Co1–N3 1.930(4), Co1–O1 1.881(3), Co1–O2 1.883(3), Co1–O3 1.871(3), Co3–O4 2.102(2), Co3–O5 2.167(3); N1–Co1–N2 99.0(2), N1–Co1–N3 98.4(2), N1–Co1–O1 86.0(2), N1–Co1–O2 171.2(2), N1–Co1–O3 87.4(2). CCDC No.: 781092.

In order to accurately study the properties of complex **8a**, it is necessary to avoid the formation of cocrystal **8b**. We found that the cobalt acetate trimer cocrystal formation could be avoided if the required or an excess quantity of alcohol is present in the medium, as in the case of aerobic oxidation reaction. Thus, when 1:10 ratios of cobalt acetate and pyridinyl alcohol **1** were used for complex formation under the same conditions, black crystals (crystal **B**) were isolated and a reasonable quantity of the oxidation product **2** was seen in the

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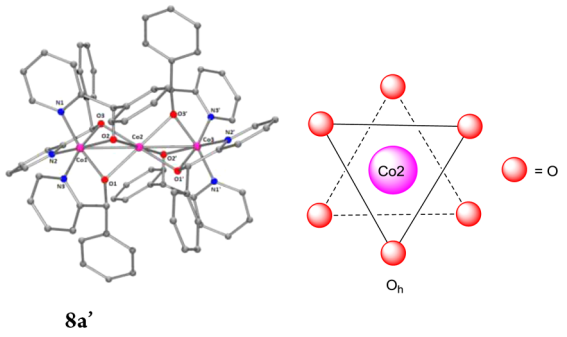
mother liquor. The solid-state X-ray structure of the Co complex **8a′** is shown in Figure 4. As expected, the cobalt



8a′

Figure 4. ORTEP diagram of cobalt trinuclear complex **8a′** (crystal **B**). H atoms and acetic acid molecule have been omitted for clarity. Relevant bond lengths (Å) and angles (deg): Co1−Co2 2.6351(8), Co1−N1 1.929(7), Co1−N2 1.920(6), Co1−N3 1.920(4), Co1−O1 1.885(3), Co1−O2 1.882(5), Co1−O3 1.879(4); N1−Co1−N2 98.9(2), N1−Co1−N3 97.8(2), N1−Co1−O1 85.2(2), N1−Co1−O2 170.3(2), N1−Co1−O3 90.4(2). CCDC No.: 789671.

triacetate cocrystal **8b** is absent in this case and only the trinuclear cobalt complex, bereft of any contaminations (**8a′**), is present: the space group of crystal **8a′** is *C*2/*c* with unit dimensions a = 29.163(2) Å, b = 17.1312(12) Å, and c = 18.0064(13) Å and cell angles α = 90.00°, β = 122.096(2)°, and γ = 90.00°.

In complex **8a′**, all three cobalt atoms are present in a linear arrangement and both of the terminal cobalt atoms (Co1 and Co3) have a distorted-octahedral geometry with a coordination number of 6 with 3 oxygen and 3 nitrogen atoms from 3 molecules of alcohol **1**. The geometry of the cobalt (Co2) atom present in the middle corresponds to a trigonal-prismatic structure with 6 oxygen bridgehead coordination from all 6 alcohols. Thus, the middle cobalt (Co2) represents an unusual trigonal-prismatic coordination geometry with a coordination sphere of 6 oxygen atoms.[5] In general, these types of complexes have been reported only with a dithiolate ligand.[6] The trigonal-prismatic structure belongs to the O_h point group, as shown in Figure 4. It can also be seen that the oxygen atoms attached to the middle Co are arranged at the corners of the trigonal prism with Co−O distances of Co2−O1 2.901(4) Å, Co2−O2 2.082(3) Å, and Co2−O3 2.078(5) Å. The triangular faces are almost perfect triangles with O−O distances of O1−O2 2.568 Å, O2−O3 2.541 Å, and O3−O1 2.568 Å and angles of 60.33, 60.37, and 59.29°. These values are also consistent with previous report.[5] Finally, the utilization of complex **8a′** as a catalyst for the aerobic oxidation reaction of **1** gave ketone **2** in 93% yield in 4.5 h.

When the isolated complex **8a′** was subjected to the optimal reaction conditions without alcohol **1**, it produced ketone **2** as the product in 43% isolated yield in 6 h and cobalt remains were recovered from the reaction mixture. Powder XRD data of the recovered cobalt remains were found to be is very close to the powder XRD data of cobalt(II) acetate tetrahydrate (Figure 5). The recovered cobalt remains from the decomposition of complex **8a′** were then used as a catalyst for the oxidation of alcohol **1**, and as expected, oxidation took place to yield ketone **2**. However, the reaction was slightly slow (4.5 h) and the isolated yield of ketone **2** was 87%. Finally, when instead of cobalt acetate other acetates of metals such as Pd, Mn, Cd, Rh,

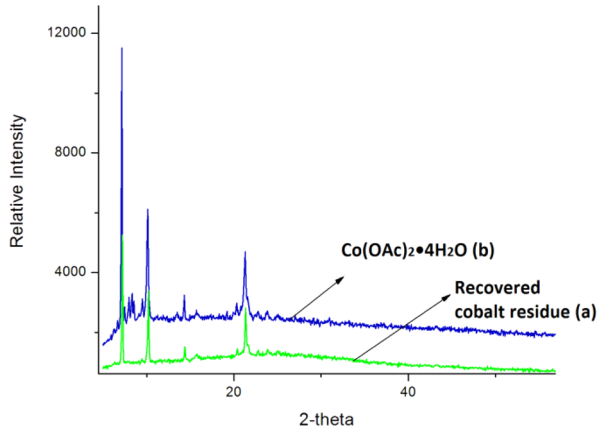
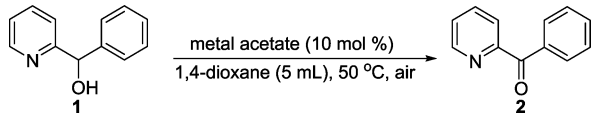


Figure 5. Powder XRD spectrum of recovered residue and cobalt acetate tetrahydrate.

Fe, and Zn were used as catalysts for the oxidation reaction of **1**, all of them led to either very poor conversion or no reaction at all. The results are summarized in Table 4. Then, when the

Table 4. Various Metal Acetate Catalyzed Oxidations of Secondary Alcohols



entry	metal salt	time (h)	yield (%)[a]
1	$Fe(OAc)_2$	48	35
2	$[Rh(OAc)_2]_2$	48	
3	$Pd(OAc)_2$	48	34
4	$Cd(OAc)_2$	48	
5	$Zn(OAc)_2$	48	
6	$Mn(OAc)_2$	48	23

[a]Isolated yield.

oxidation reaction of **1** was carried out under a nitrogen atmosphere, the reaction faced a serious setback and the yield was drastically reduced to 10%. However, the same reaction under a nitrogen atmosphere with 1 equiv of cobalt acetate gave a 93% yield of ketone.[7]

This result clearly indicates that molecular oxygen[8] present in air is helping the cobalt catalyst to regenerate for the next catalytic cycle to provide a quantitative yield of the product. Other cobalt salts such as $CoCl_2$ did not provide any oxidation product even after 2 days at 70 °C, which clearly shows that in cobalt acetate the acetate counteranion plays a prominent role in the oxidation reaction. To investigate this scenario, 10 mol % (1 equiv with respect to cobalt chloride) of sodium acetate was used along with $CoCl_2$ under the optimized conditions.[9] As we expected, the aerobic oxidation reaction went smoothly and provided 88% isolated yield in 3 h, which indicates the importance of acetate ion in the oxidation reaction.

In summary, we have developed an efficient and selective method to oxidize pyridine-based secondary alcohols using $Co(OAc)_2$ as a catalyst. An interesting trinuclear cobalt complex was isolated and characterized. In this structure, the cobalt ion (Co2) located in the middle has an unusual trigonal-prismatic structure and is surrounded by the six oxygen atoms. The molecular oxygen present in air plays a major role in ensuring that the oxidation reaction is a catalytic process.

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Finally, our $Co(OAc)_2$-catalyzed aerobic oxidation of pyridine-based alcohols is very selective to secondary alcohols over primary alcohols, thus providing a useful synthetic platform in complicated organic syntheses.

EXPERIMENTAL SECTION

General Considerations. Reactions were performed in an oven-dried reaction tube in an open air atmosphere. Extra pure analytical grade 1,4-dioxane and cobalt acetate tetrahydrate were purchased from Sisco Research Laboratories (India) PVT. Ltd. Solvents used for extraction and purification were technical grade and were distilled before use. Reactions were monitored by thin-layer chromatography on precoated aluminum-packed plates (0.25 mm, Merck Kieselgel 60 with fluorescent indicator UV254) and visualized by fluorescence quenching. Column chromatography was performed with silica gel (particle size 100−120 mesh, RANKEM). The wavenumbers of recorded IR signals are quoted in cm^{-1}. ^1H and ^{13}C NMR spectra were recorded in $CDCl_3$ solvent on a 400 MHz spectrometer. Data are expressed as chemical shifts in parts per million (ppm) relative to residual chloroform and $CDCl_3$ (^1H δ 7.26 and ^{13}C δ 77.16, respectively; likewise for other solvents where applicable) and TMS as internal standard on the δ scale. ^1H coupling constants J are given in Hz and are rounded to the nearest 0.1 Hz.

Experimental Procedure for Cobalt Complex 8a′ (Crystals A and B) Preparation. *Crystal B.* In a clean 50 mL round-bottom flask, $Co(OAc)_2{\cdot}4H_2O$ (24.9 mg, 0.1 mmol) and (2-pyridyl)-phenylmethanol (**1**; 185 mg, 1 mmol) were added to 30 mL of 1,4-dioxane, and the mixture was stirred at room temperature for 30 min. The resulting mixture was filtered through Whatman filter paper, and the resulting homogeneous solution was allowed to slowly evaporate at room temperature. After 4 days, black crystals of **B** (**8a′**) started to form; these were suitable for single-crystal X-ray analysis. Yield: 86 mg (twice recovered from mother liquor), 67%. Mp: 138 °C. IR (KBr): 3049, 3069, 3027, 1568, 1022, 768 cm^{-1}. Anal. Calcd for $C_{76}H_{72}Co_3N_6O_{15}$: C, 61.29; H, 5.28; N, 5.79. Found: C, 62.03; H, 5.21; N, 5.63.

Crystal A. Pink crystals of **A** (**8a,b**) were prepared by the same procedure as for crystal **B**; $Co(OAc)_2{\cdot}4H_2O$ (249 mg, 1 mmol) and (2-pyridyl)phenylmethanol (**1**; 185 mg, 1 mmol) were added in a 1:1 ratio. Yield: 173 mg, 81%. Mp: 129 °C. IR (KBr): 3419, 3064, 2851, 1570, 1482, 1444, 1396, 1033, 767 cm^{-1}. Anal. Calcd for $C_{88}H_{110}Co_6N_6O_{34}$: C, 49.17; H, 5.16; N, 3.91. Found: C, 48.69; H, 4.52; N, 3.87.

Experimental Procedure for Oxidation of Alcohol 1 using Complex 8a′ and Recovery, Reusing the Complex 8a′ Residue. In a reaction tube, complex **8a′** (128.2 mg, 0.1 mmol) in 5 mL of 1,4-dioxane was stirred at 50 °C for 4.5 h. The reaction progress was monitored by TLC. The reaction mixture was concentrated, the resulting residue was washed with diethyl ether until product **2** disappeared from the reaction mixture, and the combined organic layers were concentrated and filtered through a silica pad to provide phenyl(2-pyridyl)methanone (**2**; yield 46.9 mg, 43%). Solvent was removed from the recovered cobalt remains, and the leftover cobalt compound was considered as cobalt(II) acetate (on the basis of a powder XRD study) and further used as a catalyst (24.9 mg, 0.1 mmol) to oxidize the alcohol **1** (185 mg, 1 mmol) to yield phenyl(2-pyridyl)methanone (**2**; 159 mg, yield 87%) in 4.5 h.

Typical Experimental Procedure for Aerobic Oxidation. In a reaction tube, a mixture of cobalt(II) acetate tetrahydrate (24.9 mg, 0.1 mmol) and phenyl(2-pyridyl)methanol (**1**; 185 mg, 1 mmol) in 5 mL of 1,4-dioxane was stirred at 50 °C in an open air atmosphere for 3.5 h. The progress of the reaction was monitored by TLC. The reaction mixture was concentrated, and the resulting residue was directly purified by silica gel column chromatography (eluents: hexanes and ethyl acetate) to give phenyl(2-pyridyl)methanone (**2**; 181 mg, 99% yield).

*Phenyl(pyridin-2-yl)methanone (**2a**):* white solid; mp 42−43 °C (lit.[10] mp 42 °C); R_f = 0.48 (hexanes/ethyl acetate, 80/20 v/v); ^1H NMR (400 MHz, $CDCl_3$) δ 8.61 (d, J = 4.4 Hz, 1H), 7.89−8.01 (m, 3H), 7.78 (td, J = 1.6 Hz, J = 7.6 Hz, 1H), 7.48 (t, J = 7.6 Hz, 1H), 7.32−7.42 (m, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 193.9, 155.1, 148.5, 137.1, 136.3, 132.9, 131.0, 128.2, 126.2, 124.6; IR (neat) 3057, 2926, 1661, 1576, 1308, 932, 742, 693 cm^{-1}; HRMS (m/z) $[M + H]^+$ calcd for $C_{12}H_{10}NO$ 184.0762, found 184.0768.

*(4-Methoxyphenyl)(pyridin-2-yl)methanone (**2b**):* white solid; mp 92−94 °C (lit.[11] mp 95−97 °C); R_f = 0.42 (hexanes/ethyl acetate, 70/30 v/v); ^1H NMR (400 MHz, $CDCl_3$) δ 8.71 (d, J = 4.4 Hz, 1H), 8.12 (d, J = 8.8 Hz, 2H), 7.99 (d, J = 7.6 Hz, 1H), 7.88 (td, J = 1.6 Hz, J = 7.6 Hz, 1H), 7.43−7.50 (m, 1H), 6.97 (d, J = 8.8 Hz, 2H), 3.88 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 192.4, 163.7, 155.9, 148.5, 137.1, 133.6, 129.2, 125.9, 124.6, 113.7, 55.6; IR (neat) 3053, 3001, 2348, 2251, 1648, 1598, 1258, 912, 741 cm^{-1}; HRMS (m/z) $[M + Na]^+$ calcd for $C_{13}H_{11}NO_2Na$ 236.0687, found 236.0692.

*(4-Fluorophenyl)(pyridin-2-yl)methanone (**2c**):* white solid; mp 68−70 °C (lit.[12] mp 68−69 °C); R_f = 0.71 (hexanes/ethyl acetate, 80/20 v/v); ^1H NMR (400 MHz, $CDCl_3$) δ 8.70−8.74 (m, 1H), 8.13−8.20 (m, 2H), 8.06(d, J = 8 Hz, 1H), 7.91 (td, J = 1.6 Hz J = 7.6 Hz, 1H), 7.47−7.53 (m, 1H), 7.12−7.20 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 192.1, 165.7 (d, J = 253.1 Hz), 154.9, 148.5, 137.3, 133.9 (d, J = 9.3 Hz), 132.5, 126.4, 124.7, 115.4 (d, J = 21.6 Hz); IR (neat) 2362, 1655, 1590, 1306, 909, 736 cm^{-1}; HRMS (m/z) $[M + H]^+$ calcd for $C_{12}H_9NOF$ 202.0668, found 202.0663.

*(4-Chlorophenyl)(pyridin-2-yl)methanone (**2d**):* white solid; mp 58−60 °C (lit.[11] mp 60−61 °C); R_f = 0.75 (hexanes/ethyl acetate, 80/20 v/v); ^1H NMR (400 MHz, $CDCl_3$) δ 8.72 (d, J = 3.6 Hz, 1H), 8.02−8.12 (m, 3H), 7.93 (d, J = 7.6 Hz, 1H), 7.49−7.55 (m, 1H), 7.46 (d, J = 8.4 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 192.5, 154.7, 148.6, 139.5, 137.4, 134.6, 132.6, 128.6, 126.6, 124.8; IR (neat) 3058, 2927, 2855, 1665, 1581, 1308, 922, 740 cm^{-1}; HRMS (m/z) $[M + H]^+$ calcd for $C_{12}H_9NOCl$ 218.0373, found 218.0370.

*(Pyridin-2-yl)(p-tolyl)methanone (**2e**):* white solid; mp 43−45 °C (lit.[13] mp 43−44 °C); R_f = 0.71 (hexanes/ethyl acetate, 80/20 v/v); ^1H NMR (400 MHz, $CDCl_3$) δ 8.63 (d, J = 4.4 Hz, 1H), 7.85−7.99 (m, 3H), 7.75−7.84 (m, 1H), 7.34−7.44 (m, 1H), 7.20 (d, J = 8 Hz, 2H), 2.34 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 193.6, 155.5, 148.5, 143.9, 137.1, 133.7, 131.2, 129.0, 126.1, 124.1, 21.8; IR (neat) 3055, 2925, 2856, 2361, 2105, 1659, 1606, 1309, 929, 740 cm^{-1}; HRMS (m/z) $[M + H]^+$ calcd for $C_{13}H_{12}NO$ 198.0919, found 198.0924.

*(2-Methoxyphenyl)(pyridin-2-yl)methanone (**2f**):* white solid; mp 78−80 °C (lit.[14] mp 77−79 °C); R_f = 0.50 (hexanes/ethyl acetate, 70/30 v/v); ^1H NMR (400 MHz, $CDCl_3$) δ 8.52−8.57 (m, 1H), 7.88 (dd, J = 0.8 Hz, J = 6.8 Hz, 1H), 7.75 (td, J = 1.6 Hz, J = 7.6 Hz, 1H), 7.44 (dd, J = 1.6 Hz, J = 7.6 Hz, 1H), 7.36 (m, 1H), 7.29−7.35 (m, 1H), 6.93−6.99 (m, 1H), 6.88 (d, J = 8.4 Hz, 1H), 3.55 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 196.2, 158.3, 155.5, 148.9, 136.8, 132.9, 130.4, 128.2, 126.2, 123.2, 120.6, 111.7, 55.7; IR (neat) 3060, 2928, 2845, 2360, 1669, 1590, 1242, 923, 745 cm^{-1}; HRMS (m/z) $[M + H]^+$ calcd for $C_{13}H_{12}NO_2$ 214.0868, found 214.0867.

*(Naphthalen-1-yl)(pyridin-2-yl)methanone (**2g**):* yellow solid; mp 43−45 °C (lit.[13] mp 43−45 °C); R_f = 0.48 (hexanes/ethyl acetate, 70/30 v/v); ^1H NMR (400 MHz, $CDCl_3$) δ 8.69 (d, J = 4.4 Hz, 1H), 8.22−8.29 (m, 1H), 8.16 (d, J = 7.6 Hz, 1H), 8.03 (d, J = 8.4 Hz, 1H),7.87−7.96 (m, 2H), 7.72(dd, J = 0.8 Hz, J = 7.2 Hz, 1H), 7.44−7.58 (m, 4H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 196.7, 156.6, 149.3, 137.1, 134.8, 134.0, 132.3, 131.4, 130.0, 128.6, 127.6, 126.6, 126.4, 125.8, 124.7, 124.3; IR (neat) 3055, 2928, 2250, 1665, 1577, 1298, 914, 738 cm^{-1}; HRMS (m/z) $[M + H]^+$ calcd for $C_{16}H_{12}NO$ 234.0919, found 234.0923.

*(Pyridin-2-yl)(o-tolyl)methanone (**2h**):*[13] colorless oil; R_f = 0.41 (hexanes/ethyl acetate, 70/30 v/v); ^1H NMR (400 MHz, $CDCl_3$) δ 8.72 (d, J = 2.8 Hz, 1H), 8.11 (d, J = 7.6 Hz, 1H), 7.92 (t, J = 7.6 Hz, 1H), 7.39−7.54 (m, 3H), 7.24−7.36(m, 2H), 2.40 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 197.5, 155.1, 149.3, 138.0, 137.5, 137.2, 131.3, 131.1, 130.2, 126.6, 125.2, 124.3, 20.6; IR (neat) 3056, 2978, 2928, 2860, 1672, 1578, 1314, 1273, 927, 743 cm^{-1}; HRMS (m/z) $[M + H]^+$ calcd for $C_{13}H_{12}NO$ 198.0919, found 198.0917.

*(4-tert-Butylphenyl)(pyridin-2-yl)methanone (**2i**):* colorless oil; R_f = 0.60 (hexanes/ethyl acetate, 70/30 v/v); ^1H NMR (400 MHz,

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$CDCl_3$) δ 8.72 (d, J = 4.8 Hz, 1H), 7.98−8.04 (m, 3H), 7.88 (td, J = 1.6 Hz, J = 7.6 Hz, 1H), 7.44−7.53(m, 3H), 1.34 (s, 9H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 193.7, 156.7, 155.5, 148.6, 137.1, 133.6, 131.1, 126.1, 125.3, 124.7, 35.2, 31.2; IR (neat) 3056, 2963, 2867, 1661, 1604, 1309, 1271, 758 cm^{-1}; HRMS (m/z) [M + H]$^+$ calcd for $C_{16}H_{18}NO$ 240.1388, found 240.1382.

(Pyridin-2-yl)(m-tolyl)methanone ***(2j)****:* yellow oil; R_f = 0.54 (hexanes/ethyl acetate, 70/30 v/v); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.69 (d, J = 4.0 Hz, 1H), 7.98 (d, J = 7.6 Hz, 1H), 7.76−7.90 (m, 2H), 7.29−7.50 (m, 3H), 2.39 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 194.3, 155.2, 148.6, 137.9, 137.0, 136.3, 133.8, 131.3, 128.3, 128.1, 126.1, 124.6, 21.4; IR (neat) 3055, 2921, 2859, 1662, 1577, 1309, 747, 711 cm^{-1}; HRMS (m/z) [M + H]$^+$ calcd for $C_{13}H_{12}NO$ 198.0919, found 198.0920.

(Pyridin-2-yl)(4-(trifluoromethyl)phenyl)methanone ***(2k)****:* yellow oil; R_f = 0.73 (hexanes/ethyl acetate, 70/30 v/v); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.70 (d, J = 4.4 Hz, 1H), 8.17 (d, J = 8.0 Hz, 2H), 8.10 (d, J = 8.0 Hz, 1H), 7.91 (td, J = 1.6 Hz, J = 7.8 Hz, 1H), 7.72 (d, J = 8.0 Hz, 2H), 7.47−7.53 (m, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 192.9, 154.2, 148.8, 139.4, 137.4, 134.0 (q, J = 32.4 Hz), 131.3, 126.9, 125.2 (q, J = 3.6 Hz), 124.9, 122.5; IR (neat) 3062, 2926, 2853, 1671, 1581, 1316, 1121, 743 cm^{-1}; HRMS (m/z) [M + H]$^+$ calcd for $C_{13}H_9NOF_3$ 252.0636, found 252.0641.

(3,5-Dimethylphenyl)(pyridin-2-yl)methanone ***(2l)****:* pale yellow oil; R_f = 0.42 (hexanes/ethyl acetate, 80/20 v/v); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.71 (dt, J = 4.8 Hz, J = 0.8 Hz, 1H), 7.98 (dd, J = 8.0 Hz, J = 0.8 Hz, 1H), 7.84−7.91 (m, 1H), 7.61 (s, 2H), 7.43−7.49 (m, 1H), 7.21 (d, J = 0.4 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 194.6, 155.5, 148.7, 137.8, 137.0, 136.5, 134.8, 128.7, 126.1, 124.6, 21.3; IR (neat) 3055, 2921, 2859, 1662, 1577, 1309, 747 cm^{-1}; HRMS (m/z) [M + Na]$^+$ calcd for $C_{14}H_{13}NONa$ 234.0895, found 234.0905.

4-(Hydroxy(pyridin-2-yl)methyl)benzaldehyde ***(1m)****:* colorless oil; R_f = 0.20 (hexanes/ethyl acetate, 70/30 v/v); ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.86 (s, 1H), 8.43 (s, 1H), 7.73 (d, J = 8 Hz, 2H), 7.55 (t, J = 7.6 Hz, 1H), 7.48 (d, J = 8 Hz, 2H), 7.07−7.17 (m, 2H), 5.75 (s, 1H), 4.99 (bs, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 192.0, 160.1, 149.9, 148.1, 137.3, 135.8, 130.0, 127.5, 122.9, 121.3, 74.7; IR (neat) 3435, 2834, 2738, 2252, 1698, 1601, 1431, 1207, 1054, 910, 734 cm^{-1}; HRMS (m/z) [M + H]$^+$ calcd for $C_{13}H_{12}NO_2$ 214.0868, found 214.0874.

4-Picolinoylbenzaldehyde ***(2m)****:* white solid; mp 52−53 °C; R_f = 0.50 (hexanes/ethyl acetate, 70/30 v/v); ^{1}H NMR (400 MHz, $CDCl_3$) δ 10.12 (s, 1H), 8.73 (d, J = 3.2 Hz, 1H), 8.21 (d, J = 8 Hz, 2H), 8.13 (d, J = 7.6 Hz, 1H), 7.89−8.06 (m, 3H), 7.49−7.60 (m, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 193.1, 191.1, 154.2, 148.8, 141.3, 138.7, 137.4, 131.5, 129.3, 126.9, 124.8; IR (neat) 2927, 2849, 2749, 1704, 1657, 1574, 1305 cm^{-1}; HRMS (m/z) [M + H]$^+$ calcd for $C_{13}H_{10}NO_2$ 212.0712, found 212.0716.

(4-(Hydroxymethyl)phenyl)(pyridin-2-yl)methanol ***(1n)****:* yellow solid; mp 62−63 °C; R_f = 0.20 (hexanes/ethyl acetate, 50/50 v/v); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.53 (d, J = 4.8 Hz, 1H), 7.61 (td, J = 1.2 Hz, J = 7.8 Hz, 1H), 7.27−7.37 (m, 4H), 7.12−7.21 (m, 2H), 5.72 (s, 1H), 4.63 (s, 2H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 161.0, 147.9, 142.7, 140.7, 137.1, 127.3, 122.6, 121.5, 74.9, 65.1; IR (neat) 3301, 3135, 2917, 2887, 2841, 2734, 1062, 1001, 761 cm^{-1}; HRMS (m/z) [M + H]$^+$ calcd for $C_{13}H_{14}NO_2$ 216.1025, found 216.1026.

(4-(Hydroxymethyl)phenyl)(pyridin-2-yl)methanone ***(2n)****:* colorless oil; R_f = 0.20 (hexanes/ethyl acetate, 70/30 v/v); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.71 (d, J = 3.6 Hz, 1H), 8.02 (d, J = 8 Hz, 3H), 7.90 (t, J = 7.6 Hz, 1H), 7.49 (d, J = 6.8 Hz, 1H), 7.45 (d, J = 8 Hz, 2H), 4.74 (s, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 193.7, 155.1, 148.6, 146.6, 137.3, 135.3, 131.3, 126.3, 126.2, 124.7, 64.5; IR (neat) 3375, 2925, 2861, 1662, 1606, 1577, 1414, 1311, 745 cm^{-1}; HRMS (m/z) [M + H]$^+$ calcd for $C_{13}H_{12}NO_2$ 214.0868, found 214.0870.

(6-(Hydroxymethyl)pyridin-2-yl)phenylmethanol ***(3a)****:* yellow oil; R_f = 0.28 (hexanes/ethyl acetate, 50/50 v/v); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.49−7.57 (m, 1H), 7.16−7.31 (m, 5H), 7.11 (d, J = 7.6 Hz, 1H), 7.01 (d, J = 8.0 Hz, 1H), 5.70 (s, 1H), 4.68 (s, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 160.4, 158.2, 142.8, 137.9, 128.7, 128.5, 128.0, 127.1, 120.1, 119.5, 75.2, 64.5; IR (neat) 3376, 2923, 2859, 1712, 1588, 1452, 1053, 913, 739 cm^{-1}; HRMS (m/z) [M + H]$^+$ calcd for $C_{13}H_{14}NO_2$ 216.1025, found 216.1028.

(6-(Hydroxymethyl)pyridin-2-yl)phenylmethanone ***(4a)****:* yellow oil; R_f = 0.53 (hexanes/ethyl acetate, 50/50 v/v); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.02 (d, J = 7.6 Hz, 2H), 7.92 (q, J = 7.6 Hz, 2H), 7.60 (t, J = 7.6 Hz, 1H), 7.44−7.53 (m, 3H), 4.84 (s, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 193.6, 158.4, 153.7, 138.0, 136.2, 133.2, 131.0, 128.3, 123.5, 123.2, 64.0; IR (neat) 3438, 3069, 2929, 2845, 1715, 1664, 913, 740 cm^{-1}; HRMS (m/z) [M + H]$^+$ calcd for $C_{13}H_{12}NO_2$ 214.0868, found 214.0872.

(4-Fluorophenyl)(6-(hydroxymethyl)pyridin-2-yl)methanol ***(3b)****:* yellow oil; R_f = 0.28 (hexanes/ethyl acetate, 50/50 v/v); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.49 (t, J = 7.6 Hz, 1H), 7.17−7.24 (m, 2H), 7.08 (d, J = 7.6 Hz, 1H), 6.95 (d, J = 7.6 Hz, 1H), 6.87 (t, J = 8.4 Hz, 2H), 5.63 (s, 1H), 4.60 (s, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 162.4 (d, J = 244.6), 160.4, 158.5, 138.7, 137.8, 128.7 (d, J = 8.1 Hz), 119.8, 119.5, 115.4 (d, J = 21.4 Hz), 74.6, 64.5; IR (neat) 3355, 2869, 2828, 1599, 1508, 1223, 1057, 913, 742 cm^{-1}; HRMS (m/z) [M + H]$^+$ calcd for $C_{13}H_{13}NO_2F$ 234.0930, found 234.0936.

(4-Fluorophenyl)(6-(hydroxymethyl)pyridin-2-yl)methanone ***(4b)****:* yellow oil; R_f = 0.43 (hexanes/ethyl acetate, 50/50 v/v); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.07−8.15 (m, 2H), 7.88−7.98 (m, 2H), 7.47 (d, J = 7.6 Hz, 1H), 7.16 (t, J = 8.4 Hz, 2H), 4.84 (s, 2H), 3.52 (bs, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 192.0, 165.9 (d, J = 253.9 Hz), 158.2, 153.8, 138.0, 133.8 (d, J = 9.3 Hz), 132.6, 123.5, 123.2, 115.5 (d, J = 21.7 Hz), 64.1; IR (neat) 3429, 2923, 1662, 1591, 1230, 908, 727 cm^{-1}; HRMS (m/z) [M + H]$^+$ calcd for $C_{13}H_{11}NO_2F$ 232.0774, found 232.0770.

(6-(Hydroxymethyl)pyridin-2-yl)(4-(trifluoromethyl)phenyl)-methanol ***(3c)****:* yellow oil; R_f = 0.26 (hexanes/ethyl acetate, 50/50 v/v); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.59 (t, J = 7.6 Hz, 1H), 7.52 (d, J = 8 Hz, 2H), 7.46 (d, J = 8 Hz, 2H), 7.17 (d, J = 7.6 Hz, 1H), 7.06 (d, J = 7.6 Hz, 1H), 5.78 (s, 1H), 5.50 (bs, 1H), 4.70 (s, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 159.8, 158.6, 146.7, 138.0, 129.9 (q, J = 32.1 Hz), 127.2, 126.1, 125.5 (d, J = 3.7 Hz), 122.8, 119.9 (d, J = 8.7 Hz), 74.8, 64.5; IR (neat) 3361, 2935, 2866, 1587, 1325, 1122, 1065, 913, 740 cm^{-1}; HRMS (m/z) [M + H]$^+$ calcd for $C_{14}H_{13}NO_2F_3$ 284.0898, found 284.0900.

(6-(Hydroxymethyl)pyridin-2-yl)(4-(trifluoromethyl)phenyl)-methanone ***(4c)****:* yellow oil; R_f = 0.66 (hexanes/ethyl acetate, 50/50 v/v); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.13 (d, J = 8 Hz, 2H), 8.02 (d, J = 7.6 Hz, 1H), 7.94 (t, J = 7.6 Hz, 1H), 7.75 (d, J = 8 Hz, 2H), 7.51 (d, J = 7.6 Hz, 1H), 4.83 (s, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 192.6, 158.7, 152.9, 139.3, 138.2, 134.0, 131.2, 125.3, 125.2, 123.8, 123.6, 64.1; IR (neat) 3451, 2922, 1672, 1589, 1322, 760 cm^{-1}; HRMS (m/z) [M + H]$^+$ calcd for $C_{14}H_{11}NO_2F_3$ 282.0742, found 282.0748.

(6-(Hydroxymethyl)pyridin-2-yl)(4-methoxyphenyl)methanol ***(3d)****:* white solid; mp 116 °C; R_f = 0.18 (hexanes/ethyl acetate, 50/50 v/v); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.55 (t, J = 7.6 Hz, 1H), 7.17−7.23 (m, 2H), 7.12 (d, J = 7.6 Hz, 1H), 6.99 (d, J = 7.6 Hz, 1H), 6.75−6.81 (m, 2H), 5.66 (s, 1H), 4.70 (s, 2H), 3.70 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 160.8, 159.4, 158.1, 137.9, 135.1, 128.4, 120.1, 119.4, 114.1, 74.8, 64.6, 55.4; IR (neat) 3355, 2923, 2361, 1604, 1510, 1244, 1032, 740 cm^{-1}; HRMS (m/z) [M + H]$^+$ calcd for $C_{14}H_{16}NO_3$ 246.1130, found 246.1135.

(6-(Hydroxymethyl)pyridin-2-yl)(4-methoxyphenyl)methanone ***(4d)****:* colorless oil; R_f = 0.48 (hexanes/ethyl acetate, 50/50 v/v); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.00−8.07 (m, 2H), 7.80−7.90 (m, 2H), 7.44 (d, J = 6.8 Hz, 1H), 6.89−6.97 (m, 2H), 4.81 (s, 2H), 3.85 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 192.1, 163.7, 158.3, 154.4, 137.9, 133.5, 128.8, 123.2, 122.8, 113.6, 64.1, 55.6; IR (neat) 3394, 2248, 1656, 1594, 1319, 1259, 913, 739 cm^{-1}; HRMS (m/z) [M + H]$^+$ calcd for $C_{14}H_{14}NO_3$ 244.0974, found 244.0973.

(4-Chlorophenyl)(6-(hydroxymethyl)pyridin-2-yl)methanol ***(3e)****:* white solid; mp 121 °C; R_f = 0.30 (hexanes/ethyl acetate, 50/50 v/v); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.64 (t, J = 8.0 Hz, 1H), 7.25−7.33 (m, 4H), 7.21 (d, J = 7.6 Hz, 1H), 7.06 (d, J = 8.0 Hz, 1H), 5.75 (s, 1H), 4.77 (s, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 160.0, 158.4, 141.4, 138.1, 133.8, 128.8, 128.5, 120.0, 119.7, 74.6, 64.5; IR (neat)

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3359, 1588, 1326, 1268, 756 cm^{-1}; HRMS (m/z) $[M + H]^+$ calcd for $C_{13}H_{13}NO_2Cl$ 250.0635, found 250.0635.

*(4-Chlorophenyl)(6-(hydroxymethyl)pyridin-2-yl)methanone (**4e**):* white solid; mp 116 °C; R_f = 0.66 (hexanes/ethyl acetate, 50/50 v/v); ^1H NMR (400 MHz, $CDCl_3$) δ 7.89−8.03 (m, 4H), 7.44−7.51 (m, 3H), 4.84 (s, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 192.2, 158.5, 153.4, 139.7, 138.2, 134.6, 132.5, 128.7, 123.6, 123.5, 64.1; IR (neat) 3412, 2923, 2854, 1663, 1583, 849, 756 cm^{-1}; HRMS (m/z) $[M + H]^+$ calcd for $C_{13}H_{11}NO_2Cl$ 248.0478, found 248.0478.

*(6-(Hydroxymethyl)pyridin-2-yl)(p-tolyl)methanol (**3f**):* yellow oil; R_f = 0.28 (hexanes/ethyl acetate, 50/50 v/v); ^1H NMR (400 MHz, $CDCl_3$) δ 7.62 (t, J = 7.6 Hz, 1H), 7.25 (d, J = 8.0 Hz, 2H), 7.18 (d, J = 7.6 Hz, 1H), 7.13 (d, J = 7.6 Hz, 2H), 7.08 (d, J = 8.0 Hz, 1H), 5.74 (s, 1H), 4.77 (s, 2H) 2.32 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 160.7, 158.1, 140.0, 137.7, 129.4, 127.1, 120.0, 119.3, 75.2, 64.6, 21.3; IR (neat) 3355, 2923, 2361, 1604, 1510, 1244, 1032, 740 cm^{-1}; HRMS (m/z) $[M + H]^+$ calcd for $C_{14}H_{16}NO_2$ 230.1181, found 230.1184.

*(6-(Hydroxymethyl)pyridin-2-yl)(p-tolyl)methanone (**4f**):* colorless oil; R_f = 0.48 (hexanes/ethyl acetate, 50/50 v/v); ^1H NMR (400 MHz, $CDCl_3$) δ 7.84 (d, J = 8.0 Hz, 2H), 7.77 (d, J = 4.4 Hz, 2H), 7.36 (t, J = 4.4 Hz, 1H), 7.18 (d, J = 8.0 Hz, 2H), 4.72 (s, 2H), 2.33 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 193.4, 158.5, 154.1, 144.0, 137.7, 133.5, 131.1, 129.0, 123.2, 122.9, 64.1, 21.8; IR (neat) 3394, 2248, 1656, 1594, 1319, 1259, 913, 739 cm^{-1}; HRMS (m/z) $[M + H]^+$ calcd for $C_{14}H_{14}NO_2$ 228.1025, found 228.1028.

■ ASSOCIATED CONTENT

Supporting Information

Figures, tables, and CIF files giving NMR spectra of ketones and secondary alcohols, powder XRD data for the recovered cobalt product, and crystallographic data for **8a,b** and **8a′**. This material is available free of charge via the Internet at http://pubs.acs.org. CCDC 781092 (crystal **A**) and 789671 (crystal **B**) also contain supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

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Notes

The authors declare no competing financial interest.

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