

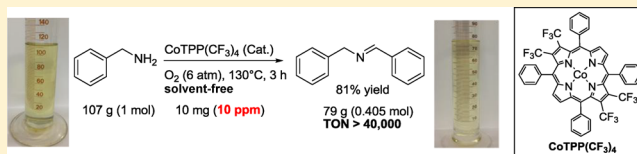
# Oxidative Coupling of Benzylamines to Imines by Molecular Oxygen Catalyzed by Cobalt(II) $\beta$ -Tetrakis(trifluoromethyl)-*meso*-tetraphenylporphyrin

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## S Supporting Information

**ABSTRACT:** Oxidative coupling of benzylamines to imines by molecular oxygen is efficiently realized in the presence of very low catalyst loadings of Co(II)  $\beta$ -tetrakis(trifluoromethyl)-*meso*-tetraphenylporphyrin. Due to the effect of four  $\beta$ -CF<sub>3</sub> groups, the catalyst shows good selectivity and very high turnover number. The reaction is easily scaled up and may provide a convenient way to prepare many imines in large scale.



Porphyrins, due to the unique  $18\pi$ -electron macrocycle, have emerged as useful ligands for transition metal catalysts in organic synthesis in a variety of atom/group transfer reactions, including oxygen, carbene, and nitrene transfer reactions.<sup>1</sup> As model catalysts of cytochrome P450,<sup>2</sup> metalloporphyrins were extensively studied and used as efficient catalysts in practical aerobic oxidation reactions of various organic compounds,<sup>1e–8</sup> such as oxidation of olefins to epoxides, cycloalkanes to alcohols or ketones, alcohols to aldehydes, etc. Though great progress has been achieved, the desire to further improve the catalytic efficiency remains. Low catalytic efficiency is mainly due to the rapid destruction by self-oxidation or formation of inactive  $\mu$ -oxo dimers. Introduction of electron-withdrawing groups into the periphery of the porphyrin macrocycle has been proven to be a good solution because it is possible to avoid catalyst self-degradation or the formation of inactive  $\mu$ -oxo dimers by creating a cage around the metal-oxo intermediate.<sup>1f</sup> Moreover, the electron-withdrawing groups may enhance the electrophilicity of an active metal-oxo intermediate and subsequently improve the catalytic efficiency.<sup>1f,3</sup>

A number of porphyrins with steric and electron-withdrawing groups including halogens, CN, NO<sub>2</sub>, CF<sub>3</sub> groups, etc. have been reported, and some of them have been used as good catalysts for various oxidation reactions.<sup>1f</sup> Among them, the CF<sub>3</sub> group shows unique influence on the porphyrin macrocycle due to its steric and electronic effects.<sup>4</sup> We found that  $\beta$ -tetrakis(trifluoromethyl)-*meso*-tetraphenylporphyrin (H<sub>2</sub>TPP(CF<sub>3</sub>)<sub>4</sub>) with a severely distorted macrocycle induced by the bulky CF<sub>3</sub> groups is easily reduced to  $20\pi$ -electron  $\beta$ -tetrakis(trifluoromethyl)-*meso*-tetraphenylporphyrins but is relatively hard to be oxidized due to the four strong electron-withdrawing CF<sub>3</sub> groups.<sup>4e</sup> In view of these great effects, we supposed that H<sub>2</sub>TPP(CF<sub>3</sub>)<sub>4</sub> may have potential applications in catalytic oxidation reactions.

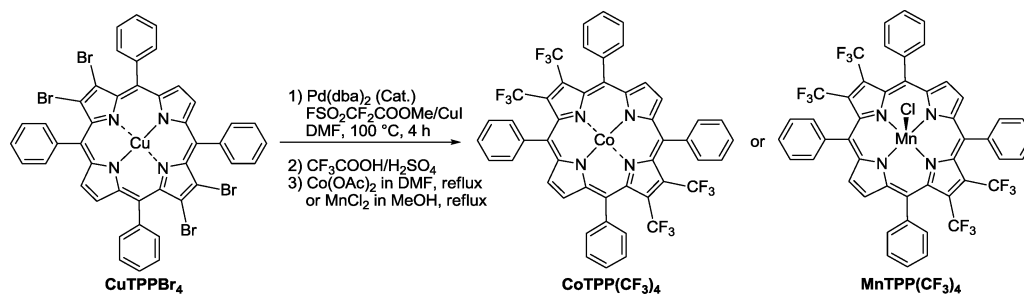
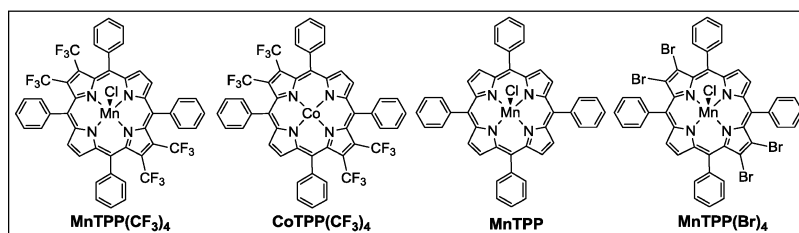
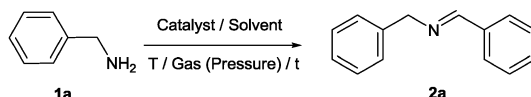
On the other hand, imines are very useful and important intermediates in pharmaceutical, biological, and chemical syntheses.<sup>5</sup> Many synthetic methods were developed for efficient synthesis of various imines.<sup>6</sup> Among them, oxidation of primary amines to imines is a fundamental and practical approach. However, comparatively little attention has been devoted to it probably due to the product selectivity issue. Although much progress has been made in this area in recent years by using green oxidants with different catalysts, such as Au,<sup>7</sup> Ru,<sup>8</sup> Cu,<sup>9</sup> Fe,<sup>10</sup> Co,<sup>11</sup> AIBN,<sup>12</sup> photocatalyst,<sup>13</sup> manganese metalloporphyrins,<sup>14</sup> etc., it is always desired to further improve the catalytic efficiency and easily scale up the reaction in order to obtain the product in large quantity. During our ongoing efforts in the synthesis (Scheme 1) and application of fluoroporphyrins, it was found that cobalt(II)  $\beta$ -tetrakis(trifluoromethyl)-*meso*-tetraphenylporphyrin (CoTPP(CF<sub>3</sub>)<sub>4</sub>) showed very good catalytic selectivity and activity on the oxidative coupling of benzylamines to imines with environmentally friendly oxidant molecular oxygen, and the reaction could be easily scaled up. Herein we present the results.

Free-base porphyrin H<sub>2</sub>TPP(CF<sub>3</sub>)<sub>4</sub> was conveniently prepared by palladium-catalyzed trifluoromethylation of CuTPPBr<sub>4</sub> and subsequent demetalation according to our previous report.<sup>4d</sup> Insertion of Co(II) and Mn(III) into H<sub>2</sub>TPP(CF<sub>3</sub>)<sub>4</sub> afforded the catalysts used in our following study, CoTPP(CF<sub>3</sub>)<sub>4</sub> and manganese(III)  $\beta$ -tetrakis(trifluoromethyl)-*meso*-tetraphenylporphyrin chloride (MnTPP(CF<sub>3</sub>)<sub>4</sub>), respectively. Benzylamine **1a** was chosen as the model substrate. Our study was conducted with the oxidative coupling of **1a** with catalytic amounts of MnTPP(CF<sub>3</sub>)<sub>4</sub> or CoTPP(CF<sub>3</sub>)<sub>4</sub> (0.01 mol %) under oxygen atmosphere. The results are summarized in Table 1.

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Scheme 1. Synthesis of the Catalysts

Table 1. Oxidative Coupling of Benzylamines to Imines Catalyzed by Metalloporphyrin under Various Conditions<sup>a</sup>

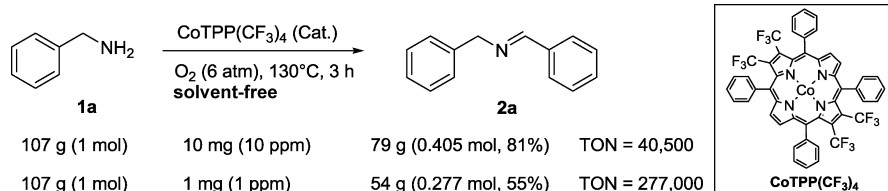
entry	catalyst	solvent	t (h)	T (°C)	conversion (%)	yield <sup>b</sup> (%)
1	MnTPP(CF <sub>3</sub> ) <sub>4</sub>	dioxane	3	130	67	66
2	CoTPP(CF <sub>3</sub> ) <sub>4</sub>	dioxane	3	130	65	65
3	MnTPP	dioxane	3	130	100	0
4	none	dioxane	3	130	100	0
5	MnTPP(Br) <sub>4</sub>	dioxane	3	130	35	29
6 <sup>c</sup>	MnTPP(CF <sub>3</sub> ) <sub>4</sub>	dioxane	6	reflux	9	9
7	MnTPP(CF <sub>3</sub> ) <sub>4</sub>	dioxane	66	80	55	55
8	MnTPP(CF <sub>3</sub> ) <sub>4</sub>	dioxane	7	130	100	0
9	MnTPP(CF <sub>3</sub> ) <sub>4</sub>	hexane	3	130	49	47
10	MnTPP(CF <sub>3</sub> ) <sub>4</sub>	MeCN	3	130	36	36
11	MnTPP(CF <sub>3</sub> ) <sub>4</sub>	toluene	3	130	60	55
12	MnTPP(CF <sub>3</sub> ) <sub>4</sub>	DMF	3	130	100	0
13	MnTPP(CF <sub>3</sub> ) <sub>4</sub>	DCE	4	130	100	0
14	MnTPP(CF <sub>3</sub> ) <sub>4</sub>	DME	4	130	83	47
15	MnTPP(CF <sub>3</sub> ) <sub>4</sub>	DG	4	130	100	0
16	MnTPP(CF <sub>3</sub> ) <sub>4</sub>	EtOH	3	130	18	18
17	MnTPP(CF <sub>3</sub> ) <sub>4</sub>	dioxane/H <sub>2</sub> O <sup>d</sup>	3	130	83	83
18	CoTPP(CF <sub>3</sub> ) <sub>4</sub>	dioxane/H <sub>2</sub> O <sup>d</sup>	3	130	94	92

<sup>a</sup>The reactions were carried out with benzylamine **1a** (535 mg, 5 mmol) and catalyst ( $5 \times 10^{-4}$  mmol) in solvent (5 mL) under O<sub>2</sub> atmosphere of 6 atm. <sup>b</sup>Conversion of benzylamine and yield of product were determined by GC-MS. <sup>c</sup>O<sub>2</sub> (1 atm). <sup>d</sup>Dioxane/H<sub>2</sub>O = 5:1 v/v.

Among several  $\beta$ -sterically hindered metalloporphyrin catalysts screened, both CoTPP(CF<sub>3</sub>)<sub>4</sub> and MnTPP(CF<sub>3</sub>)<sub>4</sub> were highly selective catalysts for the oxidative coupling reaction, affording the desired imine with >98% selectivity and moderate conversion (Table 1, entries 1 and 2). As a comparison, without a catalyst or with Mn(III) *meso*-tetraphenylporphyrin chloride (MnTPP) as catalyst under the similar conditions, no desired product was observed despite complete conversion of the starting benzylamine **1a** (Table 1, entries 3 and 4). Also, Mn(III)  $\beta$ -tetrakisbromo-*meso*-tetraphenylporphyrin chloride (MnTPPBr<sub>4</sub>) afforded lower conversion and selectivity, indicating the important role of CF<sub>3</sub> groups (Table 1, entry 5). According to GC-MS analysis, the possible byproducts were PhCOOH, PhCN, and PhCONH<sub>2</sub>. These byproducts may induce and accelerate the degradation of

desired imine formed in the reaction. As a result, without a catalyst or with a poor catalyst, the byproducts were formed at the beginning of the reaction and destroyed the desired imine immediately (Table 1, entries 3 and 4). However, with a good catalyst, only the desired imine was produced and its decomposition was avoided (Table 1, entries 1, 2, and 5). The oxygen pressure of 6 atm seems necessary to the reaction because reduced pressure resulted in lower conversion and yield (Table 1, entry 6). Elevated reaction temperatures were beneficial to the formation of the oxidative coupling product because lower reaction temperatures significantly slowed the reaction rate. Both the conversion and yield were reduced to 55% with a reaction temperature of 80 °C and even prolonged reaction time of 66 h (Table 1, entry 7). Reaction time was another crucial factor. Prolonged reaction time did not further

Scheme 2. Scale-up Experiments of the Oxidative Coupling Reactions of Benzylamine

Table 2. Oxidative Coupling of Various Benzylamines to Imines Catalyzed by  $\text{CoTPP(CF}_3)_4$ <sup>a</sup>

entry	Substrate	product	yield <sup>b</sup>
1	<b>1a</b>	<b>2a</b>	87% (94%)
2	<b>1b</b>	<b>2b</b>	84%
3	<b>1c</b>	<b>2c</b>	84%
4	<b>1d</b>	<b>2d</b>	89%
5	<b>1e</b>	<b>2e</b>	85%
6	<b>1f</b>	<b>2f</b>	85%
7	<b>1g</b>	<b>2g</b>	71%
8	<b>1h</b>	<b>2h</b>	(91%)
9	<b>1i</b>	<b>2i</b>	74%
10	<b>1j</b>	<b>2j</b>	81%
11	<b>1k</b>	<b>2k</b>	52%

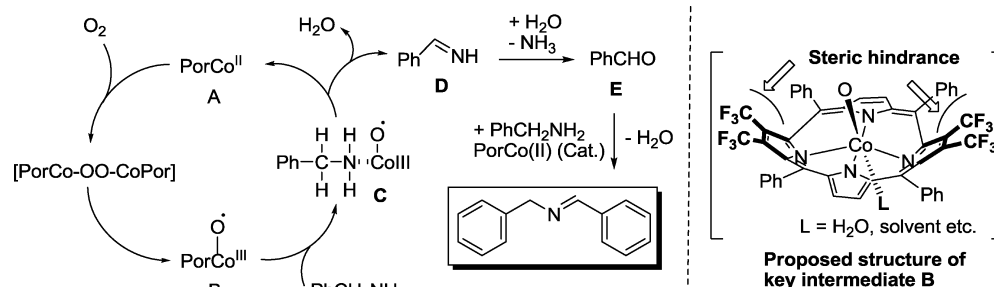
<sup>a</sup> Amine (5 mmol), catalyst ( $5 \times 10^{-4}$  mmol),  $\text{O}_2$  (6 atm), dioxane/ $\text{H}_2\text{O}$  (10 mL/2 mL),  $130^\circ\text{C}$ , 3 h. <sup>b</sup> Isolated yields based on the starting primary amines used; GC yields in parentheses.

improve yield of the desired imine but may lead to decomposition of the desired product (Table 1, entry 8). During the first 3 h, only the conversion of amine to imine was observed; no decomposition of the desired imine occurred. However, after about 3 h, decomposition of the desired imine started. It seems that this result is not related to the concentration of the desired imine because the reaction shows similar results on a large scale (1 mol) under solventless conditions (Scheme 2). Reduced reaction time led to decreased conversion of the starting benzylamine and yield of the desired imine. Among various solvents screened, such as hexane, acetonitrile, toluene, DMF, dichloromethane, DME, DG, and ethanol, dioxane stood out to be the best one (Table 1, entries 9–16). To our delight, when a small amount of water was used as cosolvent (dioxane/ $\text{H}_2\text{O}$  = 5:1 v/v), the yield of desired

imine increased up to 83% for  $\text{MnTPP(CF}_3)_4$  catalyst and 92% for  $\text{CoTPP(CF}_3)_4$  catalyst (Table 1, entries 17 and 18). All of these systematic studies indicated that a combination of 6 atm oxygen in dioxane/ $\text{H}_2\text{O}$  (5:1 v/v) at  $130^\circ\text{C}$  for 3 h with a catalytic amount of  $\text{CoTPP(CF}_3)_4$  was the most effective system for the oxidative coupling of benzylamines to imines.

With the optimized reaction conditions in hand (Table 1, entry 18), we examined the  $\text{CoTPP(CF}_3)_4$ -catalyzed oxidative coupling of various benzylamines. The results are summarized in Table 2. In general, a variety of substituted benzylamines with either electron-withdrawing or -donating groups were suitable substrates in the reaction, affording the desired imines in good yields. The electronic properties of the substituents on the aryl ring have little influence on the efficiency of the oxidation reactions (Table 2, entries 2–6 and 8). It was found

Scheme 3. Proposed Mechanism of the Oxidative Coupling of Benzylamines to Imines



that the reaction is sensitive to the steric hindrance of the substituents on the aryl ring. Lower yield of the desired imine was obtained for *ortho*-methyl benzylamine (Table 2, entry 7). It should be mentioned that heteroaromatic amine **1k**, which might deactivate the catalyst due to the coordination with metal ion of the catalyst, can also be applied to the reaction, providing a moderate yield of the desired imine (Table 2, entry 11). However, aliphatic amines are not suitable substrates for the reaction, resulting in complex reaction mixtures.

To demonstrate the applicability of this method, the oxidative coupling of benzylamine **1a** was conducted on a 1 mol (107 g) scale (Scheme 2). The reaction proceeded smoothly and provided the desired imine in good isolated yield of 81%. It should be noted that a quite low catalyst loading of 10 ppm was used in this case, and the mole turnover number (TON) and mole turnover frequency (TOF) are as high as 40 500 and 13 500 h<sup>-1</sup>, respectively, indicating the high efficiency and stability of the catalyst. When the catalyst loading was further reduced to 1 ppm, the oxidative coupling reaction afforded a lower yield of the desired imine with a very high TON and TOF of 277 000 and 92 300 h<sup>-1</sup>, respectively. It is worth mentioning that the reaction showed a high selectivity and resulted in only the desired imine besides a bit of unconsumed starting benzylamine. Moreover, for large-scale preparation, no solvent is needed for the reaction if a liquid amine is used.

On the basis of above experiments and previous reports,<sup>6,15</sup> a plausible reaction mechanism for the oxidative coupling of benzylamine with CoTPP(CF<sub>3</sub>)<sub>4</sub> as catalyst has been proposed as shown in Scheme 3. CoTPP(CF<sub>3</sub>)<sub>4</sub> reacts with oxygen under reaction conditions to generate the active intermediate **B**, which coordinates with benzylamine to form intermediate **C**. It is subsequently converted to a Schiff base intermediate **D**. Hydrolysis of this imine intermediate **D** induced by H<sub>2</sub>O with the elimination of a molecule of NH<sub>3</sub> results in the formation of benzaldehyde **E**, which reacted with another benzylamine molecule to generate the desired imine product with the release of a molecule of H<sub>2</sub>O.

The key step might be the activation of molecule oxygen with CoTPP(CF<sub>3</sub>)<sub>4</sub>. It is easier for Co(II) than Mn(III) in the catalyst to react with molecular oxygen to form active intermediate **B**.<sup>15</sup> As a result, CoTPP(CF<sub>3</sub>)<sub>4</sub> shows higher catalytic activation. The high efficiency and selectivity of CoTPP(CF<sub>3</sub>)<sub>4</sub> catalyst might arise from the effect of the four bulky and electron-withdrawing β-CF<sub>3</sub> groups. As shown in Scheme 3, based on the previous reports,<sup>4</sup> a proposed structure of key intermediate **B** demonstrates a saddle conformation due to the steric hindrance of four CF<sub>3</sub> groups, which creates a cage around the active metal-oxo intermediate **B** and prevents

catalyst self-degradation and the formation of an inactive μ-oxo dimer. At the same time, this structure might be beneficial for the high selectivity of the reaction. In addition, the strong electron-withdrawing abilities of four CF<sub>3</sub> groups might increase the reactivity of the key active metal-oxo intermediate **B**, resulting in rapid formation of the desired product.

In conclusion, an efficient and practical method for oxidative coupling of benzylamines to imines by molecular oxygen catalyzed by Co(II) β-tetrakis(trifluoromethyl)-*meso*-tetraphenylporphyrin has been developed. The reaction shows good selectivity and high turnover number, which might be due to the effect of the four bulky electron-withdrawing β-CF<sub>3</sub> groups on the catalyst. In addition, the reaction is easily scaled up and leads to a high yield of the desired imine, which makes it applicable for large-scale preparation.

## EXPERIMENTAL SECTION

**General Remarks.** NMR spectra were recorded on a NMR spectrometer at 400 MHz for <sup>1</sup>H and 376 MHz for <sup>19</sup>F NMR spectra. All spectra were obtained at room temperature in CDCl<sub>3</sub>. Chemical shifts are reported in parts per million (ppm) relative to tetramethylsilane (TMS) as an internal standard (δ<sub>TMS</sub> = 0 ppm) for <sup>1</sup>H NMR spectra and CFCl<sub>3</sub> as an external standard (negative for upfield) for <sup>19</sup>F NMR spectra. Thin-layer chromatography (TLC) analysis was performed on a silica gel plate and flash column chromatography over silica gel (mesh 300–400). All solvents and chemicals were reagent grade, purchased commercially, and used without further purification if not noted. The catalyst CoTPP(CF<sub>3</sub>)<sub>4</sub> was readily prepared according to reported procedures with slight modifications.<sup>4</sup>

**Procedures for the Synthesis of CoTPP(CF<sub>3</sub>)<sub>4</sub>.** *Synthesis of CuTPP(CF<sub>3</sub>)<sub>4</sub>.*<sup>4d</sup> FSO<sub>2</sub>CF<sub>2</sub>COOMe (1.94 g, 10.1 mmol, 20 equiv) was added at room temperature to a mixture of CuTPPBr<sub>4</sub> (500 mg, 0.5 mmol, 1 equiv), Pd(dba)<sub>2</sub> (14 mg, 5 mol %), and CuI (1.92 g, 10.1 mmol, 20 equiv) in dry DMF (100 mL). The reaction mixture was stirred at 100 °C under nitrogen for 4 h. After being cooled to room temperature, the reaction mixture was diluted with CH<sub>2</sub>Cl<sub>2</sub> and filtered through a pad of Celite. The filtrate was washed three times with water, dried over anhydrous Na<sub>2</sub>SO<sub>4</sub>, and evaporated to dryness. The resulting solid was purified by flash chromatography using petroleum ether/dichloromethane (10:1) as the eluent to give the target product CuTPP(CF<sub>3</sub>)<sub>4</sub> (408 mg, 86%) as a dark green solid.

**Demetalation of CuTPP(CF<sub>3</sub>)<sub>4</sub>.**<sup>4a,d</sup> CuTPP(CF<sub>3</sub>)<sub>4</sub> (400 mg, 0.43 mmol) was dissolved in CH<sub>2</sub>Cl<sub>2</sub> (40 mL). H<sub>2</sub>SO<sub>4</sub>/CF<sub>3</sub>COOH (1:10, 4 mL) was added dropwise, the resulting dark brown mixture stirred at room temperature for about 4 h, until TLC indicated that the substrate disappeared completely. Then the mixture was poured into brine (80 mL) and neutralized with NaHCO<sub>3</sub>. The organic layer was washed with water and brine, passed through dry silica gel, and evaporated to dryness. The resulting residue was purified by flash chromatography using petroleum ether/dichloromethane (1:2) as the eluent to give the desired product H<sub>2</sub>TPP(CF<sub>3</sub>)<sub>4</sub> (275 mg, 70%) as a brown solid.



**Insertion of Cobalt(II) into  $H_2TPP(CF_3)_4$ .**  $H_2TPP(CF_3)_4$  (500 mg, 0.564 mmol, 1 equiv) was dissolved in DMF (100 mL) and heated to reflux, then  $Co(OAc)_2 \cdot 4H_2O$  (0.7 g, 2.82 mmol, 5 equiv) was added. The reaction mixture was stirred at reflux for 30 min. After being cooled to room temperature, the reaction mixture was diluted with  $CH_2Cl_2$  (200 mL) and washed three times with water. The organic layer was separated, dried with anhydrous  $Na_2SO_4$ , and evaporated to dryness. The resulting residue was purified by flash chromatography using petroleum ether/dichloromethane (5:1) as the eluent to give the desired product  $CoTPP(CF_3)_4$  (483 mg, 91%) as a dark green solid.

$H_2TPP(CF_3)_4$ :  $^1H$  NMR (400 MHz,  $C_6D_6$ )  $\delta$  8.12–8.14 (m, 8H, Ph-ortho), 8.01 (s, 4H,  $\beta$ -H), 8.42–8.51 (m, 12H, Ph-meta, para), –1.41 (s, 2H, N–H);  $^{19}F$  NMR (376 MHz,  $C_6D_6$ )  $\delta$  –49.27 (s, 12F,  $\beta$ - $CF_3$ ); MS (MALDI)  $m/z$  = 887.6 ( $M + H$ )<sup>+</sup>.<sup>4a,d</sup>

$CoTPP(CF_3)_4$ :  $^1H$  NMR (400 MHz,  $CDCl_3$ )  $\delta$  15.44 (br s, 4H,  $\beta$ -H), 13.56 (br s, 8H, Ph-ortho), 9.51–9.57 (m, 12H, Ph-meta, para);  $^{19}F$  NMR (376 MHz,  $CDCl_3$ )  $\delta$  –53.41 (br s, 12F,  $\beta$ - $CF_3$ ); HRMS (MALDI) calcd for  $C_{48}H_{24}CoF_{12}N_4$  ( $M^+$ ) 943.1136, found 943.1145.<sup>4c</sup>

**General Procedure for the Synthesis of 2a–2m.** A solution of benzylamine **1a** (535 mg, 5 mmol, 1 equiv) and  $CoTPP(CF_3)_4$  (0.5 mg,  $10^{-4}$  equiv) in dioxane/ $H_2O$  (12 mL, 5:1 v/v) was stirred in a 100 mL autoclave under oxygen (6 atm) at 130 °C for 3 h. After being cooled to room temperature, the reaction mixture was evaporated to dryness directly and the resulting residue was purified by flash column chromatography (eluent, PE/EA/ $NEt_3$  = 100:10:1) to give the desired target product **2a**.

**Imine 2a:** yellow oil (423 mg, 87% yield);  $^1H$  NMR (400 MHz,  $CDCl_3$ )  $\delta$  8.41 (s, 1H), 7.79–7.81 (m, 2H), 7.44–7.25 (m, 8H), 4.81 (s, 2H); MS (EI)  $m/z$  = 195.1 ( $M^+$ ).<sup>9f</sup>

**Imine 2b:** yellow oil (485 mg, 84% yield);  $^1H$  NMR (400 MHz,  $CDCl_3$ )  $\delta$  8.35 (s, 1H), 7.78 (dd,  $J$  = 5.6, 8.4 Hz, 2H), 7.30 (dd,  $J$  = 5.6, 8.4 Hz, 2H), 7.11 (t,  $J$  = 8.8 Hz, 2H), 7.03 (t,  $J$  = 8.8 Hz, 2H), 4.74 (s, 2H);  $^{19}F$  NMR (376 MHz,  $CDCl_3$ )  $\delta$  –109.22 (s, 1F), –115.99 (s, 1F); MS (EI)  $m/z$  = 231.1 ( $M^+$ ).<sup>9f</sup>

**Imine 2c:** yellow oil (552 mg, 84% yield);  $^1H$  NMR (400 MHz,  $CDCl_3$ )  $\delta$  8.33 (s, 1H), 7.71 (d,  $J$  = 8.4 Hz, 2H), 7.39 (d,  $J$  = 8.4 Hz, 2H), 7.32 (d,  $J$  = 8.4 Hz, 2H), 7.27 (d,  $J$  = 8.4 Hz, 2H), 4.76 (s, 2H); MS (EI)  $m/z$  = 263.0 ( $M^+$ ).<sup>9f</sup>

**Imine 2d:** yellow oil (585 mg, 89% yield);  $^1H$  NMR (400 MHz,  $CDCl_3$ )  $\delta$  8.34 (s, 1H), 7.82 (m, 1H), 7.62–7.64 (m, 1H), 7.40–7.43 (m, 1H), 7.33–7.38 (m, 2H), 7.21–7.31 (m, 3H), 4.78 (s, 2H); MS (EI)  $m/z$  = 263.0 ( $M^+$ ).<sup>9f</sup>

**Imine 2e:** yellow oil (750 mg, 85% yield);  $^1H$  NMR (400 MHz,  $CDCl_3$ )  $\delta$  8.33 (s, 1H), 7.64 (d,  $J$  = 8.4 Hz, 2H), 7.56 (d,  $J$  = 8.4 Hz, 2H), 7.47 (d,  $J$  = 8.4 Hz, 2H), 7.21 (d,  $J$  = 8.4 Hz, 2H), 4.75 (s, 2H); MS (EI)  $m/z$  = 352.9 ( $M^+$ ).<sup>16</sup>

**Imine 2f:** yellow oil (473 mg, 85% yield);  $^1H$  NMR (400 MHz,  $CDCl_3$ )  $\delta$  8.36 (s, 1H), 7.69 (d,  $J$  = 8.4 Hz, 2H), 7.24 (d,  $J$  = 4.4 Hz, 2H), 7.22 (d,  $J$  = 4.4 Hz, 2H), 7.17 (d,  $J$  = 8.4 Hz, 2H), 4.79 (s, 2H), 2.40 (s, 3H), 2.36 (s, 3H); MS (EI)  $m/z$  = 223.1 ( $M^+$ ).<sup>9f</sup>

**Imine 2g:** yellow oil (396 mg, 71% yield);  $^1H$  NMR (400 MHz,  $CDCl_3$ )  $\delta$  8.68 (s, 1H), 7.94 (d,  $J$  = 7.5 Hz, 1H), 7.31–7.18 (m, 7H), 4.84 (s, 2H), 2.52 (s, 3H), 2.40 (s, 3H); MS (EI)  $m/z$  = 223.1 ( $M^+$ ).<sup>9f</sup>

**Imine 2h:** yellow oil (580 mg, 91% yield);  $^1H$  NMR (400 MHz,  $CDCl_3$ )  $\delta$  8.28 (s, 1H), 7.70 (d,  $J$  = 8.8 Hz, 2H), 7.24 (d,  $J$  = 8.8 Hz, 2H), 6.86–6.92 (m, 4H), 4.71 (s, 2H), 3.81 (s, 3H), 3.77 (s, 3H); MS (EI)  $m/z$  = 255.1 ( $M^+$ ).<sup>9f</sup>

**Imine 2i:** yellow oil (472 mg, 74% yield);  $^1H$  NMR (400 MHz,  $CDCl_3$ )  $\delta$  8.36 (s, 1H), 7.41 (s, 1H), 7.34–7.26 (m, 3H), 7.00 (dq,  $J$  = 1.6, 7.6 Hz, 1H), 6.95–6.92 (m, 2H), 6.83 (dd,  $J$  = 2.4, 8.0 Hz, 1H), 4.81 (s, 2H), 3.85 (s, 3H), 3.82 (s, 3H); MS (EI)  $m/z$  = 255.1 ( $M^+$ ).<sup>9f</sup>

**Imine 2j:** white solid (946 mg, 81% yield);  $^1H$  NMR (400 MHz,  $CDCl_3$ )  $\delta$  8.56 (s, 1H), 8.27 (s, 2H), 7.97 (s, 1H), 7.85 (s, 2H), 7.82 (s, 1H), 4.98 (s, 2H);  $^{19}F$  NMR (376 MHz,  $CDCl_3$ )  $\delta$  –62.99 (s, 6F), –63.15 (s, 6F); MS (EI)  $m/z$  = 467.1 ( $M^+$ ).<sup>17</sup>

**Imine 2k:** yellow oil (269 mg, 52% yield);  $^1H$  NMR (400 MHz,  $CDCl_3$ )  $\delta$  8.42 (s, 1H), 7.42 (d,  $J$  = 5.2, 1H), 7.33 (dd,  $J$  = 0.8, 3.6, 1H), 7.24 (dd,  $J$  = 1.2, 5.2, 1H), 7.07 (dd,  $J$  = 3.6, 4.8, 1H), 7.34–7.26 (m, 3H), 7.00 (dq,  $J$  = 1.6, 7.6 Hz, 1H), 6.98–7.01 (m, 2H), 4.95 (s, 2H); MS (EI)  $m/z$  = 207.0 ( $M^+$ ).<sup>12</sup>

## ■ ASSOCIATED CONTENT

### § Supporting Information

Copies of  $^1H$  and  $^{19}F$  NMR spectra. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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### Notes

The authors declare no competing financial interest.

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