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Aerobic Oxidative Coupling of 2-Aminonaphthalenes by Homogenous Nonheme Iron Catalysts

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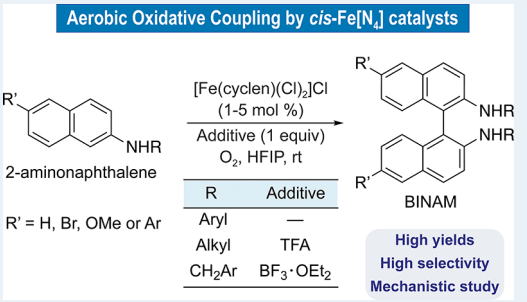
ABSTRACT: An efficient and general aerobic oxidative coupling method to prepare 1,1′-binaphthyl-2,2′-diamines (BINAMs) from *N*-substituted-2-aminonaphthalene (**1**) based on [Fe^{III}(cyclen)$(Cl)_2$]Cl catalyst in 1,1,1,3,3,3-hexafluoropropan-2-ol (HFIP) at room temperature is reported. The highly selective conditions were applied to prepare a list of *N*,*N*′-dialkyl-, *N*,*N*′-dibenzyl-, and *N*,*N*′-diaryl-BINAMs with moderate to high yields. Based on mechanistic studies, which include control experiments and variable time normalization analysis, it is suggested that the coupling between [Fe^{III}(cyclen)-(**1**)(OOH)]$^{+2}$ and 2-aminonaphthalene **1** is the key irreversible step in the catalytic cycle.



KEYWORDS: *nonheme iron catalysis, aerobic oxidative coupling, 2-aminonaphthalene, 1,1′-binaphthyl-2,2′-diamine (BINAM), variable time normalization analysis*

INTRODUCTION

1,1′-Binaphthyl-2,2′-diamines (BINAMs, Scheme 1a)[1] alongside 1,1′-bi-2-naphthols (BINOLs)[2] and 2-amino-2′-hydroxy-1,1′-binaphthyls (NOBINs) are members of the axially chiral binaphthyl family.[3] These privileged C1- and C2-symmetric molecules have made significant contributions to the advancement of asymmetric catalysis and related fields.[2−4] As a result, there is an ongoing effort to develop efficient methods for their synthesis, starting from simple and readily available naphthalene units.

Over the years, various strategies have been developed for synthesizing optically enriched binaphthalene compounds, including multistep synthesis,[5] resolution,[6] catalytic atroposelective arylation of quinone acetals,[7] and asymmetric oxidative coupling reactions.[8] Among these, the latter method is particularly attractive due to its simplicity and sustainability. A range of catalytic systems based on redox-active chiral V,[9] Cu,[10] and Fe[11] have been applied for the oxidative coupling of two 2-naphthol units, as well as oxidative cross-coupling between 2-naphthol and 2-aminonaphthalene (**1**). These methods provide a direct pathway to enantioenriched BINOLs and NOBINs, typically involving the coupling step of a chiral metal-ligated naphthoxyl radical intermediate (Figure 1a).[9l,10i,11c,e,g,12] However, chiral metal complexes capable of promoting the atroposelective synthesis of BINAMs via a mechanism involving M−[**1**·] intermediate (Figure 1a) remain relatively underdeveloped.[10g]

To develop methods for the asymmetric synthesis of BINAMs, it is essential to identify chiral redox-active metal complexes capable of catalyzing an inner-sphere oxidative coupling of 2-aminonaphthalenes. Currently, reported conditions for BINAM preparation via oxidative coupling rely on electrochemistry,[13] stoichiometric amounts of Cu(II) amine complexes,[6f] heterogeneous catalysts (such as Rh/C and Pd/Al_2O_3, Scheme 1b),[14] or processes involving free naphthylamino radical (**1**·) intermediates.[15] Consequently, these methods are less suitable for asymmetric transformations. In a recent study, the Knölker group utilized chiral phosphoric acids (CPA) to induce atroposelectivity in a Fenton-type $FePcF_{16}$-catalyzed oxidative coupling reaction of *N*-aryl-2-aminonaphthalenes. This approach demonstrated partial success, affording *N*,*N*′-diaryl-BINAMs with low to moderate enantioselectivity ratios (Scheme 1c).[16] While this study represents a significant milestone, it underscores the need to identify a class of chiral iron catalysts capable of facilitating this reaction through alternative mechanisms that involve chiral Fe−[**1**·] intermediates.

Iron(III) complexes with *N*- and O-based ligands easily change between oxidation states promoting oxidative coupling reactions through different mechanisms.[8b,17] Fe[N_4] complexes (N_4 = tetradentate nitrogen (*N*)-based ligands) are a promising class of nonheme oxidants that form oxygenated

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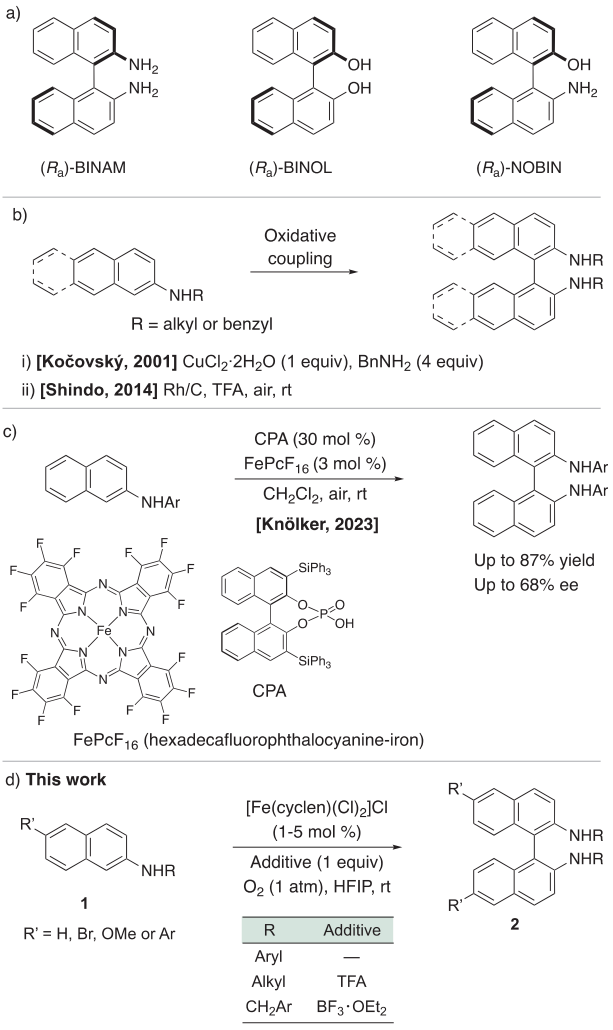
Scheme 1. Oxidative Coupling of 2-Aminonaphthalenes



iron intermediates ($[N_4]Fe^{IV/V}{=}O$, $[N_4]Fe^{III}{-}OOH$, or $[N_4]Fe^{III}{-}OO^{\bullet}$)[18] while transferring oxygen atoms to substrates.[19] The *cis*-Fe[N_4] complexes have two available coordination sites for the substrates to interact with the oxidant (Figure 1b).[20] These important complexes promote oxidation reactions, such as water oxidation,[21] hydrocarbon hydroxylation,[18c,22] *cis*-dihydroxylation,[23] and epoxidation,[24] by pathways that are not involved in the release of highly reactive hydroxyl radicals (Fenton-like processes).[25] Indeed, chiral *cis*-Fe[N_4] complexes are highly efficient catalysts for asymmetric transformations.[18a,26] Nevertheless, their application as aerobic catalysts in biaryl bond-forming reactions remains underdeveloped.

To establish the scientific foundation for advancing the asymmetric iron-catalyzed oxidative coupling of 2-aminonaphthalenes, we investigated the potential of *cis*-$Fe^{III}[N_4]$ complexes to act as catalysts in this process. Here, we present highly effective conditions for the aerobic oxidative coupling of 2-aminonaphthalenes utilizing the readily accessible $[Fe^{III}(cyclen)(Cl)_2]Cl$ catalyst in 1,1,1,3,3,3-hexafluoropropan-2-ol (HFIP, Scheme 1d). This methodology provides a straightforward route to various racemic *N*,*N*′-disubstituted-BINAMs with outstanding efficiency. Through a series of control experiments and variable time normalization analyses, we propose a mechanism involving a key coupling step

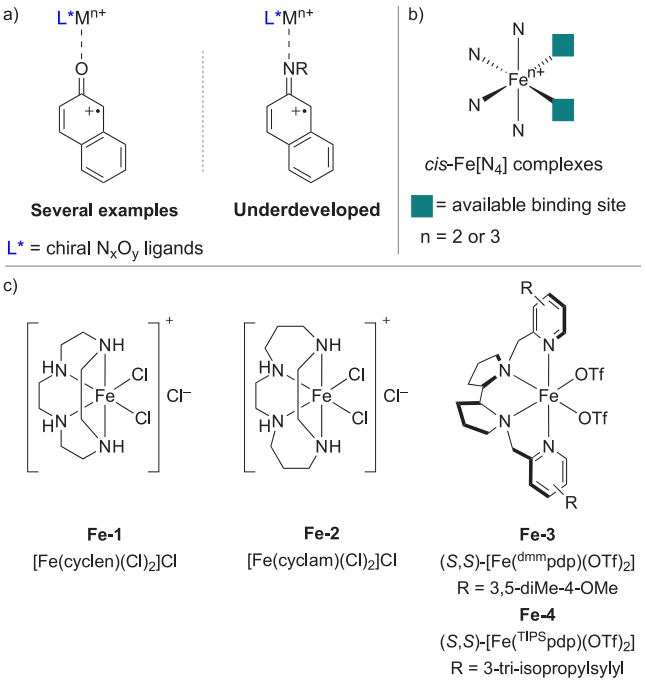


Figure 1. (a) Key intermediates in the oxidative coupling of 2-naphthols and 2-aminonaphthalenes; (b) the general structure of *cis*-Fe[N_4] complexes; (c) the specific *cis*-Fe[N_4] complexes that were used in this study.

between $[Fe^{III}(cyclen)(\mathbf{1})(OOH)]^{2+}$ and a second 2-aminonaphthalene partner.

RESULTS AND DISCUSSION

Method Development and Reaction Generality. The investigation commenced with the assessment of $FeCl_3$ to facilitate the oxidative homocoupling of *N*-(4-chlorophenyl)-2-aminonaphthalene (**1a**). We utilized conditions developed in our group for the oxidative coupling of phenols with 2-aminonaphthalenes, comprising $FeCl_3$ (10 mol %), *t*-BuOO*t*-Bu (1.5 equiv) as the terminal oxidant, and TFA additive (1 equiv) in 1,1,1,3,3,3-hexafluoroisopropanol (HFIP).[11g,17c] Under these conditions, BINAM **2a** was obtained in 69% yield (Table 1, entry 1), albeit with a notable amount of benz[*a*]acridin **2aa** (26% yield, Scheme 2). Control experiments confirmed that compound **2aa** resulted from the oxidative dearomatization of BINAM **2a** through a metal-free aerobic oxidative annulation process that occurs upon exposing compound **2a** to *t*-BuOO*t*-Bu and TFA in HFIP (Scheme 2). To prevent the formation of benz[*a*]acridin **2aa**, we omitted the peroxide and conducted the reaction under O_2 atmosphere [(1 atm), $FeCl_3$ (5 mol %), HFIP, rt, entry 2]. Although the reaction exhibited high chemoselectivity, yielding BINAM **2a** in 93% isolated yield, prolonged time (approximately 48 h) was necessary to achieve complete conversion. Moreover, the method demonstrated limited generality, failing to facilitate the coupling of less reactive *N*-alkyl-2-aminonaphthalenes.

We then investigated the potential of Fe[N_4] ligands in mediating the aerobic oxidative coupling of compound **1a**. Commercially available aza-crown compounds, 1,4,7,10-tetraazacyclododecane (cyclen) and 1,4,8,11-tetraazacyclotetradecane (cyclam), are known to form structurally defined *cis*-Fe[N_4] complexes, namely $[Fe^{III}(cyclen)Cl_2]Cl$ (**Fe-1**) and $[Fe^{III}(cyclam)Cl_2]Cl$ (**Fe-2**) complexes.[27] Fortunately, both

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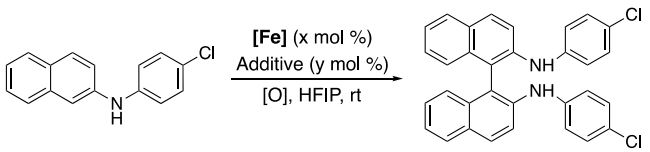
Table 1. Optimization of the Reaction Conditions[a]

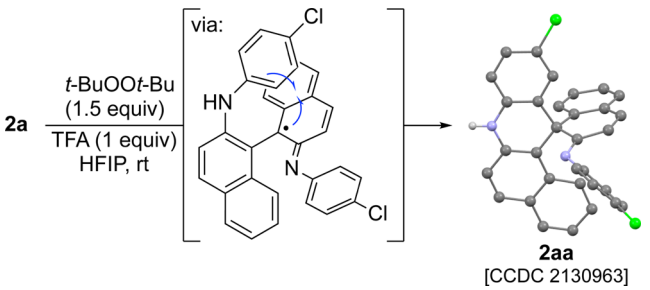


1a 2a

entry	[Fe] (*x* mol %), additive (*y* mol %)	oxidant	time [h]	2a (%)[b]
1	$FeCl_3$ (10), TFA (100)	*t*-BuOO*t*-Bu	24	69 (**2aa**, 26%)
2	$FeCl_3$ (5)	O_2 (1 atm)	48	93
3	**Fe-1** (2)	O_2 (1 atm)	4	99, [97][c]
4	**Fe-2** (2)	O_2 (1 atm)	4	97
5	**Fe-3** (1)	O_2 (1 atm)	24	93[d]
6	**Fe-4** (1)	O_2 (1 atm)	24	99[d]
7	--	O_2 (1 atm)	4	*NR*

[a]Reaction conditions: **1a** (0.1 mmol), *t*-BuOO*t*-Bu (0.15 mmol, 1.5 equiv), HFIP (700 μL, 0.14M), at room temperature. [b]Isolated yield. [c]In brackets is the isolated yield of **2a** from a large-scale experiment (**1a**, 5 mmol). [d]Racemate (0% ee), based on chiral HPLC.; NR = no reaction.

Scheme 2. Formation of Benz[*a*]acridin 2aa via Oxidative Annulation of 2a



Fe-1 and **Fe-2** complexes (2 mol %) exhibited high catalytic activity in HFIP [O_2 (1 atm), rt], affording BINAM **2a** in 99 and 97% yields, respectively, within only 4 h (entries 3 and 4). Other *cis*-Fe[N_4] complexes, such as (*S*,*S*′)-[Fe^{II}(^{dmm}pdp)-($OTf)_2$] (**Fe-3**) and (*S*,*S*′)-[Fe^{II}(^{TIPS}pdp)($OTf)_2$] (**Fe-4**), which have been utilized in asymmetric epoxidation reactions by Costas,[28] also showed promising results, affording racemic BINAM **2a** in excellent yields of 93% and 99%, respectively (entries 5 and 6). The control experiment without the iron (entry 7) confirmed the necessity of the catalyst in this process. Finally, we demonstrated the scalability of the method for producing large quantities of BINAM **2a** by conducting the oxidative coupling of **1a** on a 5 mmol scale using **Fe-1** as the catalyst (97% yield, entry 3, square brackets). Notably, since H_2O is the sole byproduct, we successfully recovered most of the HFIP solvent (83% yield) through simple distillation.

We then examined the generality of the method for the oxidative coupling of different 2-(*N*-substituted-2-aminonaphthalenes. The general conditions [**Fe-1** (2 mol %), O_2 (1 atm), HFIP, rt] were successfully applied for preparing (*N*,*N*′-diaryl)-BINAMs **2b-j** in good to excellent isolated yields (66–99%, Figure 2). However, our initial attempts to couple less oxidizable *N*-alkyl-2-aminonaphthaleness **1k–p** resulted in poor conversions. This reactivity problem was addressed by increasing the loading of **Fe-1** to 3 mol %, and by the addition of TFA (1 equiv) to the reaction mixture. Under these

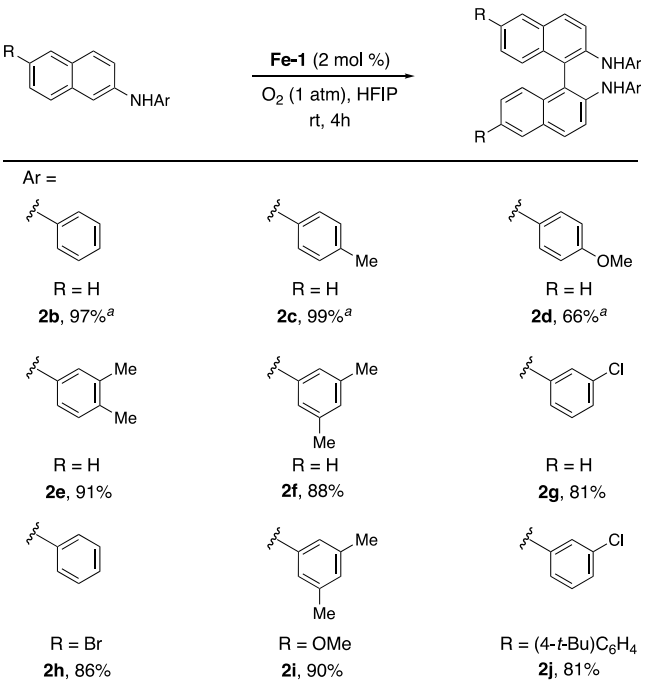


Figure 2. Aerobic oxidative coupling of *N*-aryl-2-aminonaphthalenes. [a]The reaction was performed on a 0.25 mmol scale.

modified conditions, full conversions were obtained within 24 h, affording (*N*,*N*′-dialkyl)-BINAMs **2k–p** in good to excellent yields (68–96%, Figure 3).

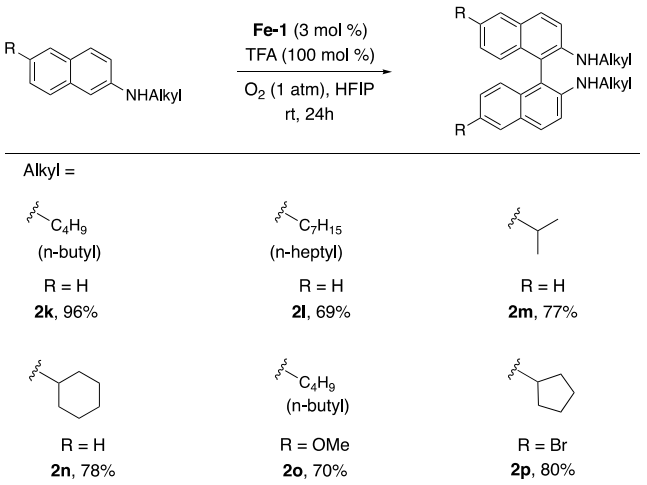


Figure 3. Aerobic oxidative coupling of *N*-alkyl-2-aminonaphthalenes.

Next, a regioselectivity issue arose when *N*-benzyl-2-aminonaphthalene **1q** was subjected to the above conditions with a slightly higher catalyst loading [**Fe-1** (5 mol %), TFA (100 mol %), O_2 (1 atm), HFIP, rt]. Under these conditions, we isolated both the C–C coupling product, BINAM **2q** (52% yield), and the C–N coupling product **3q** in 30% yield (Figure 4). The formation of compound **3q** as a side product implies that the spin density in the **1q**• intermediate is mainly distributed between the nitrogen and the C-1 atom. Interestingly, replacing the TFA with $BF_3{\cdot}(OEt)_2$ (100 mol %) completely suppressed the C–N pathway, affording BINAM **2q** in 70% yield.[11g] A similar reactivity trend was observed for other *N*-benzyl-2-aminonaphthalenes, such as 2-

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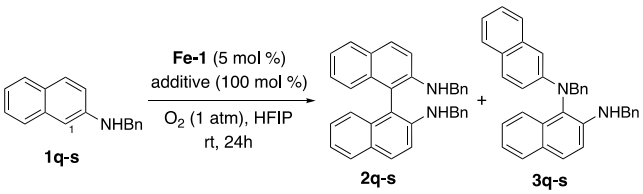


Bn =			Cl		OMe	
additive	2q	3q	2r	3r	2s	3s
TFA	52%	30%	50%	36%	50%	18%
$BF_3{\cdot}OEt_2$	70%	—	75%	—	76%	—

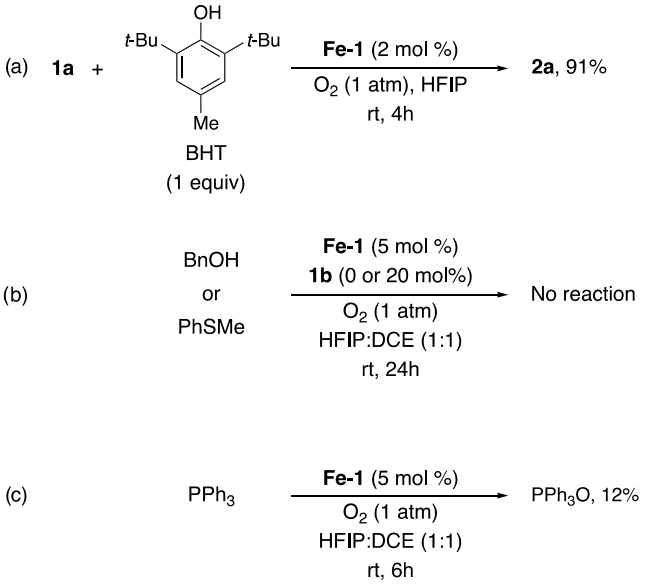
Figure 4. Aerobic oxidative coupling of *N*-($ArCH_2$)-2-aminonaphthalenes.

[*N*-((4-Cl)C_6H_4)CH_2]-aminonaphthalene **1r** and 2-[*N*-((4-Me)C_6H_4)CH_2]-aminonaphthalene **1s**. Their oxidative coupling in the presence of $BF_3{\cdot}(OEt)_2$ additive afforded the desired BINAM products **2r** and **2s** in 75% and 76% yields, respectively.

Mechanistic Investigation. To gain a deeper insight into the coupling mechanism and the mode of action of the **Fe-1** catalyst, we conducted control experiments and kinetic studies.

Initially, we ruled out the involvement of a Fenton-type mechanism by demonstrating that the oxidative coupling of compound **1a** proceeds with comparable efficiency in the presence of butylated hydroxytoluene (BHT, 1 equiv, Scheme 3a), a free-radical scavenger.

Scheme 3. Control Experiments (a–c)



Oxygen transfer experiments provide valuable insights into the type of oxygenated Fe[N_4] intermediates formed under oxidation conditions. Previous studies by Nam demonstrated that nonheme iron(IV) oxo species could oxygenate benzyl alcohols, sulfides, and triphenylphosphine.[18h,24] In contrast, nonheme iron(III) hydroperoxo complexes are weak oxidants, primarily limited to the oxidation of PPh_3 to PPh_3O. Our control experiments revealed that benzyl alcohol and thioanisole substrates remained unaffected under the coupling conditions [**Fe-1** (5 mol %), **1b** (0 or 20 mol %), HFIP/DCE (1:1), O_2 (1 atm), rt, Scheme 3b]. Conversely, slow oxidation of PPh_3 occurred under similar conditions (without **1b**, 12% yield, Scheme 3c and Figure 5a, asterisk marks). These findings

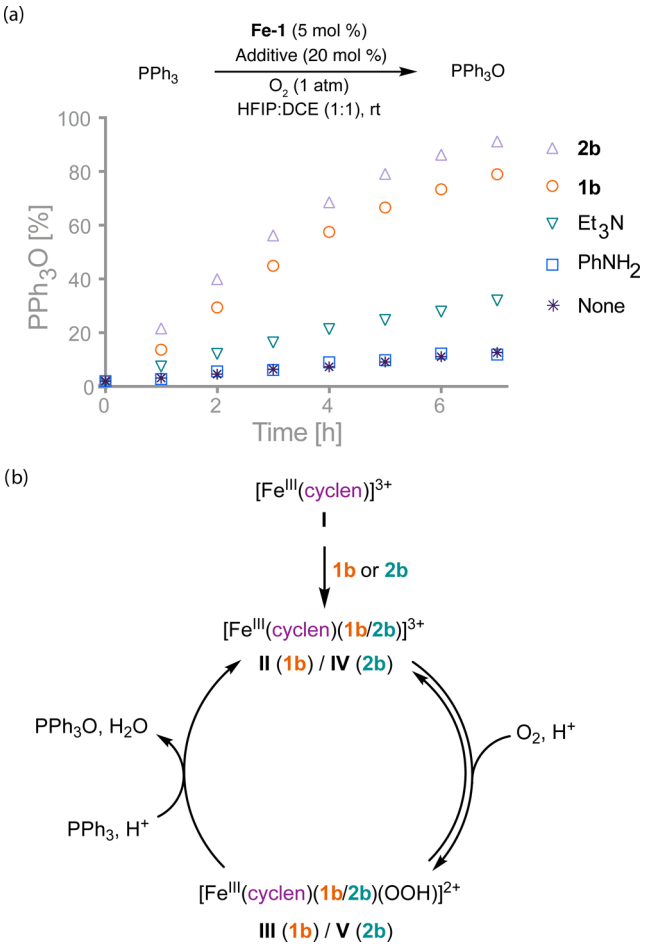


Figure 5. $[Fe^{III}(cyclen)]^{3+}$-catalyzed aerobic PPh_3 oxidation. (a) The influence of additives on the rate of PPh_3O formation; (b) a postulated mechanism for the oxidation of PPh_3.

suggest that iron(III) hydroperoxo complexes, rather than iron(IV) oxo intermediates, serve as the active oxidants formed during the reaction conditions.

Next, to evaluate the influence of substrates on the oxygenation of **Fe-1**, we monitored the rate of PPh_3O formation under the reaction conditions [**Fe-1** (5 mol %), O_2 (1 atm), HFIP/DCE (1:1), rt] with or without additives (20 mol %, Figure 5a). The data revealed a notable acceleration in the production of PPh_3O in the presence of the *N*-phenyl-2-aminonaphthalene substrate **1b** (circle marks) or the BINAM product **2b** (triangle marks). As control experiments, other bases, such as triethylamine (triangle-down marks) and aniline (squares marks), were tested, displaying a no effect to mild effect on the oxidation rate. These results suggest that the strong *N*-ligands **1b** and **2b** bind to the **Fe-1** catalyst, forming the $[Fe^{III}(cyclen)(\mathbf{1b})]^{3+}$ (**II**) and $[Fe^{III}(cyclen)(\mathbf{2b})]^{3+}$ (**IV**) intermediates (Figure 5b). These Fe[N_5] complexes act as effective reductants of O_2, generating iron hydroperoxo complexes, such as $[Fe^{III}(cyclen)(\mathbf{1b})(OOH)]^{2+}$ (**III**) and $[Fe^{III}(cyclen)(\mathbf{2b})(OOH)]^{2+}$ (**V**), which subsequently transfer oxygen to PPh_3 while releasing

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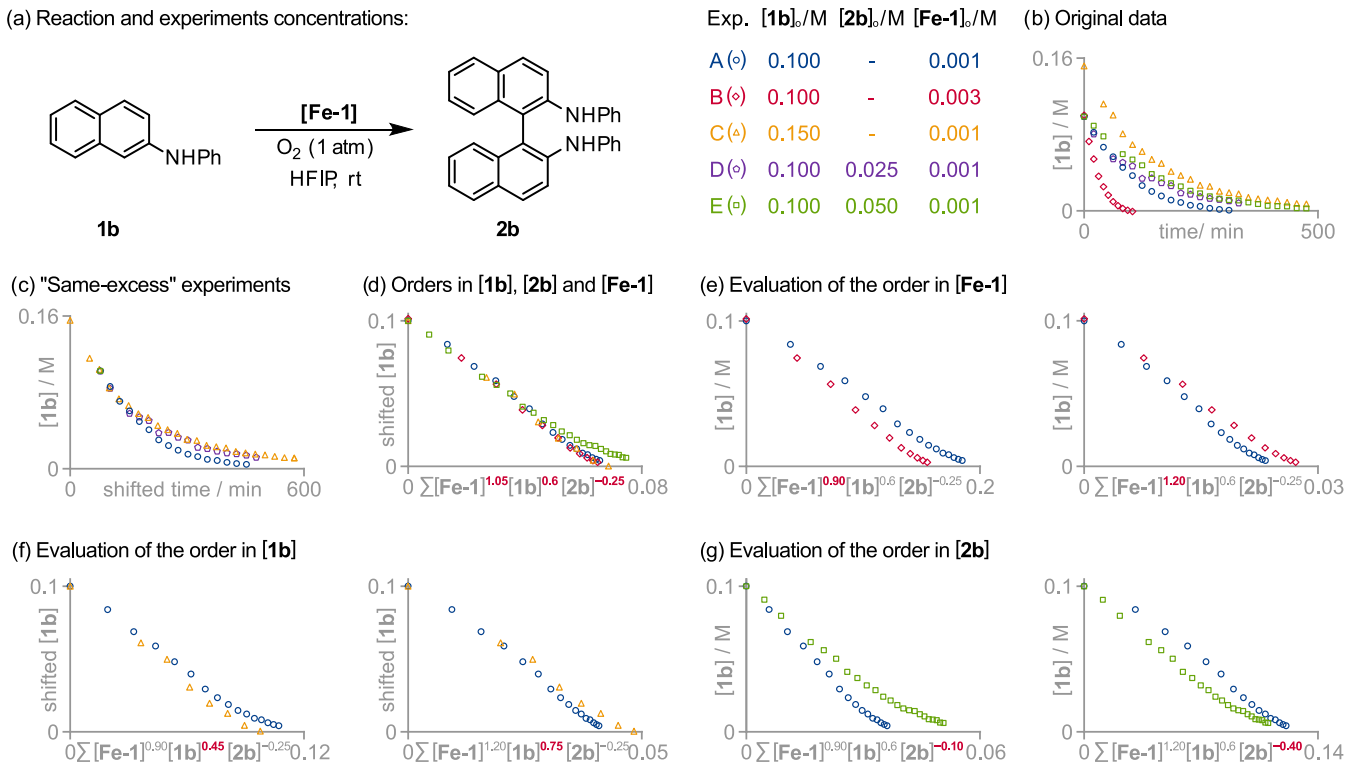

Figure 6. Kinetic studies using the variable time normalization analysis method.

H_2O. Notably, we observed that the oxidative coupling of **1b** commences only after the concentration of PPh_3 decreases, indicating that the two processes compete and likely involve a similar iron oxidant species, likely complex **III**.

Kinetic studies were performed to propose a catalytic cycle for the aerobic oxidative coupling of **1b** by the **Fe-1** catalyst. Five reactions with different initial concentrations of the reaction components **1b**, **2b**, and **Fe-1** (Figure 6a) were sampled and analyzed in HPLC at different reaction times (Figure 6b). The kinetic study of reactions involving reactants in different phases might be complicated due to mass transfer phenomena, which become kinetically relevant during the reaction. Based on initial experiments, involving reactions under air atmosphere and different stirring rates, we inferred that the overall process is not limited by the oxygen transfer into the solution.

The stability of the catalyst during the reaction was evaluated with a "same-excess" experiment (Figure 6c).[29] The reaction profile of the standard reaction (reaction A) was time-shifted[30] to compare it with the reaction profile with a different initial concentration of **1b** (reaction C). When reaction C reached 0.10 M of **1b**, it was slower than the standard reaction that started at 0.10 M (Figure 6c). This result indicates the presence of significant catalyst deactivation or product inhibition. A reaction with 0.10 M of **1b** and 0.025 M of BINAM **2b** (reaction D) was monitored to discern between these possibilities. The time-shifted reaction profile of reaction D overlays with the profile of reaction C (Figure 6c), indicating that the BINAM product inhibits the reaction, whereas the catalyst deactivation is insignificant.

The partial orders of the reaction, the degree of product inhibition, and the effect of **1b** on the reaction rate were determined using the time normalization[31] and the variable time normalization analyses.[32] The best overlay between the profiles of reactions with a different catalyst loading (reactions A and B) was obtained when using an order of 1.05 in the catalyst (Figure 6d,e). Given the noise in the experimental data, due to the intrinsic challenges associated with the sampling and the analysis of this reaction, the order in the catalyst was not considered to be sufficiently greater than 1, which could imply a step involving more than one catalytic species or a significant catalyst inhibition with an impurity in the solvent.[33] The order in the substrate was found to be 0.6 (Figure 6d,f) by normalizing the reaction profiles of experiments with different initial concentrations of **1b** (reactions A and C). The variable normalization analysis of reactions started with different amounts of the product (reactions A and E) clearly shows that the order in the BINAM product is negative. However, it does not provide a good overlay of the entire reaction profiles when a constant order is used (Figure 6d,g). This slight discrepancy between the normalized reaction profiles may be due to factors other than the concentration of the product, which can affect the kinetics of the reactions. For example, the addition of product **2b** also affects the acidity of the reaction media, which may have a different effect on the reaction rate at different stages of the reaction.

Based on all of the evidence provided, we propose the mechanism shown in Figure 7. The order 1 in the catalyst, the partial positive order in **1b**, and the partial negative order in **2b** could be explained by the partial saturation of the catalyst with **1b** (complex **II**) and the competition for the catalyst with **2b** (complex **IV**). The high reactivity toward PPh_3 oxidation complexes **II** and **IV** supports the premise that these Fe[**N5**]-type complexes are stronger O_2-reducing agents than complex **I** (Figure 5b). Thus, we propose that the reaction of complex **II** with the dioxygen molecule will afford the key **1b**-ligated iron hydroperoxo complex **III** that promotes oxidative coupling with a second molecule of 2-aminonaphthalene **1b**.

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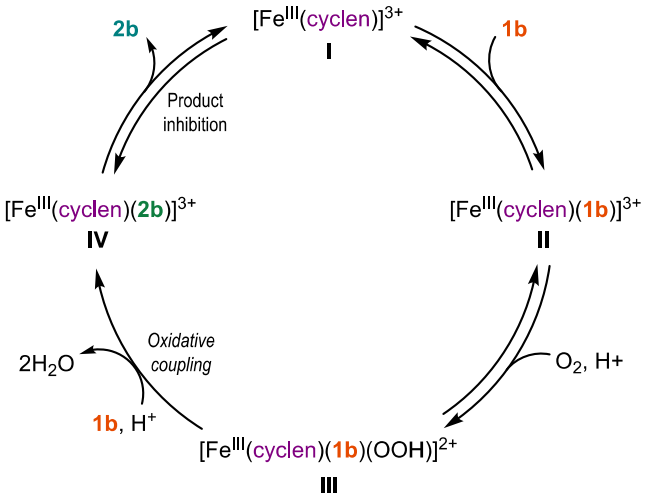

Figure 7. A postulated mechanism for the Fe-1-catalyzed aerobic oxidative coupling of 2-aminonaphthalene **1b**.

This irreversible step will afford complex **IV** that reversibly releases the BINAM product in the terminate step.

CONCLUSIONS

In conclusion, a general and simple method for preparing BINAMs by the Fe[N_4]-catalyzed aerobic oxidative coupling of *N*-substituted-2-aminonaphthalenes is reported. The highly effective conditions involve mixing compound **1** with [Fe^{III}(cyclen)Cl_2]Cl (2−5 mol %) and with or without an acid additive (0−1 equiv) under O_2 atmosphere (1 atm) in HFIP at room temperature. Under these set of conditions, a long list of *N*,*N*′-dialkyl, *N*,*N*′-dibenzyl, and *N*,*N*′-diaryl-BINAMs **2** were prepared in high yields. Our mechanistic studies support the binding of the substrate to the catalyst, forming the [Fe^{III}(cyclen)(**1**)(OOH)]$^{+2}$ intermediate that reacts with a second molecule of **1**. This study described the suitability of the homogeneous *cis*-Fe[N_4] complexes to facilitate the oxidative coupling of 2-aminonaphthalenes through a non-Fenton-type mechanism, laying the groundwork for the future development of an asymmetric version of this transformation.

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acscatal.4c01839.

Experimental procedures, spectral characterization, and additional data (PDF)

Compound 2aa (CIF)

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Author Contributions

The manuscript was written through the contributions of all authors.

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Notes

The authors declare no competing financial interest.

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