Article

Cobalt(II)[salen] Catalyzed Selective Aerobic Oxidative Cross-Coupling between Electron-Rich Phenols and 2-Naphthols

Hagai Reiss, Hadas Shalit, Vlada Vershinin, Nagnath Yadav More, Hagit Forckosh, and Doron Pappo

J. Org. Chem., **Just Accepted Manuscript** • DOI: 10.1021/acs.joc.9b00822 • Publication Date (Web): 08 May 2019

Cobalt(II)[salen] Catalyzed Selective Aerobic Oxidative Cross-Coupling between Electron-Rich Phenols and 2-Naphthols

Hagai Reiss,[a] Hadas Shalit,[a] Vlada Vershinin,[a] Nagnath Yadav More,[a] Hagit Forckosh[a], and Doron Pappo[a,*]

Department of Chemistry, Ben-Gurion University of the Negev, Beer-Sheva 84105, Israel

E-mail: Pappod@bgu.ac.il

A selectivity-driven catalyst design approach was adopted to address chemoselectivity issues in the oxidative coupling of phenols. This approach was utilized for developing a Co(II)[salen] catalyzed aerobic oxidative cross-coupling of phenols in a recyclable 1,1,1,3,3,3-hexafluoropropan-2-ol solvent. The waste-free conditions offer a sustainable entry to non-symmetric biphenols via a mechanistic scheme that involves coupling of a liberated phenoxyl radical with a ligated 2-naphthoxyl radical.

INTRODUCTION

Metal-catalyzed oxidative phenol coupling reactions offer a sustainable method to prepare biaryl compounds directly from unfunctionalized arenes.[1-3] This process requires a redox catalyst that can transfer two electrons and two protons from the coupling partners to an oxidant, such as a dioxygen molecule or peroxide, while forging a new biaryl bond.[4] Previous studies have shown that first-row vanadium(V)[5-13] chromium(III),[14] manganese(III),[14] iron(III),[15-25] cobalt(II)[26, 27], and copper(II)[28-31] complexes are effective catalysts for oxidative homo- and cross-coupling of phenols.[32, 33] Consequently, biaryl compounds that are important for natural products synthesis and that play a valuable role as catalysts and ligands in asymmetric transformations are easily prepared in a single step from simple phenols. Recent mechanistic studies revealed that the selectivity in these reactions is catalyst dependent.[34] Therefore, in order to take this chemistry one step further and establish it as a benign method to complement traditional cross-coupling reactions, new catalytic conditions should be developed.

One possible approach to identify efficient catalytic systems is to map the reactivity of complexes as catalysts in the oxidative coupling of two phenols (**A** and **B**). This reaction can afford either biphenol **A**–**A**, biphenol **B**–**B,** or the cross-coupling product, biphenol **A**–**B**, depending on the identity of the catalyst and the reaction mechanism (Scheme 1A). In 2015, our group introduced a model for predicting the chemoselectivity outcome of oxidative coupling reactions between two different phenols.[4, 21] According to the suggested model, the formation of biphenol **A**–**B** via a radical-anion/nucleophile coupling mechanism is favorable when ligated phenolate **A** is selectively oxidized to phenoxyl radical **A•** in the presence of a stronger nucleophilic phenol(ate) **B** (E_{ox}**A** < E_{ox}**B** and $\Delta N > 0$, $\Delta N = N_{\mathbf{B}} - N_{\mathbf{A}}$, N = theoretical global nucleophilicity, Scheme 1A).[21] However, when phenolate **A** is the superior nucleophile ($\Delta N < 0$), biphenol **A**–**A** formation predominates. The multi-coordinated $FeCl_3$,[21] Fe[phosphate]$_3$,[17, 19] and Katsuki's Fe[salen] complexes[23-25] were found to mediate the oxidative cross-coupling of phenols in accordance with this predictive model. To overcome the mechanistic restriction that limits the cross-coupling between phenols with a high negative nucleophilicity difference ($\Delta N << 0$), our group turned to the Fe[TPP]Cl (TPP = tetraphenylporphyrin) complex, which has a single available site for phenol ligation. The Fe[TPP]Cl catalyst proved to be efficient for coupling phenols of type **A** with weak nucleophilic phenols of type **B**, through postulated outer-sphere coupling between ligated phenoxyl radical **B•** and liberated phenoxyl radical **A•** (Scheme 1A).[16] The chemoselectivity in these reactions is obtained by the selective binding of phenol **B** to the metal in 1,1,1,3,3,3-hexafluoropropan-2-ol (HFIP).[16] In both mechanisms, the first requirement for achieving high cross-coupling selectivity is that the oxidation of phenol **A** in the presence of phenol **B** (E_{ox}**A** < E_{ox}**B**) will be selective. Indeed, achieving chemoselectivity when both phenolic reactants have relatively low oxidation potentials (E_{ox}**A** ≈ E_{ox}**B**) is a challenge. For example, the oxidative coupling between readily oxidized 2-methoxy-4-methylphenol (**2a,** E_{ox} = 0.46V [HFIP, Ag *vs* $AgNO_3$) and 3-carbomethoxy-2-naphthol (**3a**, E_{ox} = 0.80V) by $FeCl_3$ [10 mol %, *t*-BuOO*t*-Bu, HFIP, rt] exhibited high cross-coupling selectivity, affording the desired cross-coupling product **6a** in 82% yield (Scheme 1B).[21] However, under the same conditions, the coupling of phenol **2a** and 3-methoxy-2-naphthol (**3b**), which has a relatively low oxidation potential (E_{ox}(**3b**) = 0.56V), was not selective, affording a complex mixture of homo-, cross-coupling, and dehydrogenation products (*vide infra*). To overcome the mechanistic constraints that limit the selectivity in coupling two readily oxidized phenols, a selectivity-driven catalyst design approach was adopted.

The Kozlowski group reported the aerobic oxidative homo- and cross-coupling of phenols by different M[salen] and M[salan] complexes (M = Cr, Cu, Fe, Mn, Ru or V), which is an important attempt to deal with the selectivity issues of the reaction.[14] In contrast to the attention devoted to the latter metals, previous studies have only rarely focused on the ability of cobalt(II) complexes to mediate oxidative phenolic coupling.[26, 27] The few available examples include the Co[salen] catalyzed aerobic oxidative polymerization of 2,3-dihydroxynaphthalene[35, 36]

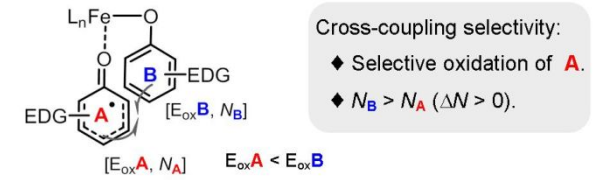
and Guo's aerobic Co[TPP] **1a**, catalyzed oxidative dimerization of readily oxidized phenols.[37] Other related studies focused on the activity of Co[salen] complexes as atmospheric dioxygen carriers[38] and as aerobic catalysts in the dehydrogenation of phenols to quinones.[39-47] To the best of our knowledge, suitable conditions for the aerobic oxidative cross-coupling of phenols by Co(II) complexes have never been reported.

Here we describe a selectivity-driven catalyst design study that resulted in the development of highly selective and sustainable cobalt[salen]-catalyzed aerobic oxidative cross-coupling between readily oxidized phenols and 2-naphthols (E_{ox}**A** ≈ E_{ox}**B**). This sustainable reaction can be performed on a multi-gram scale in HFIP as a recyclable solvent under air atmosphere (open flask); H_2O is produced as the only waste product. On the basis of our mechanistic investigation a catalytic cycle that involves coupling between ligated naphthoxyl radical with a liberated phenoxyl radical is postulated.

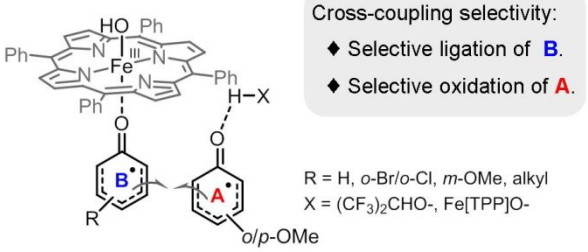
Scheme 1. Selective oxidative cross-coupling of phenols by iron catalysis.

[A] Postulated oxidative coupling modes

Inner-sphere radical-anion coupling

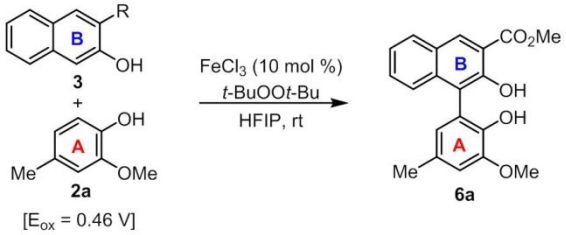


Outer-sphere ligated radical-radical coupling



[B] The chemoselectivity challenge:

Selective Cross-coupling when E_{ox}A ≈ E_{ox}B

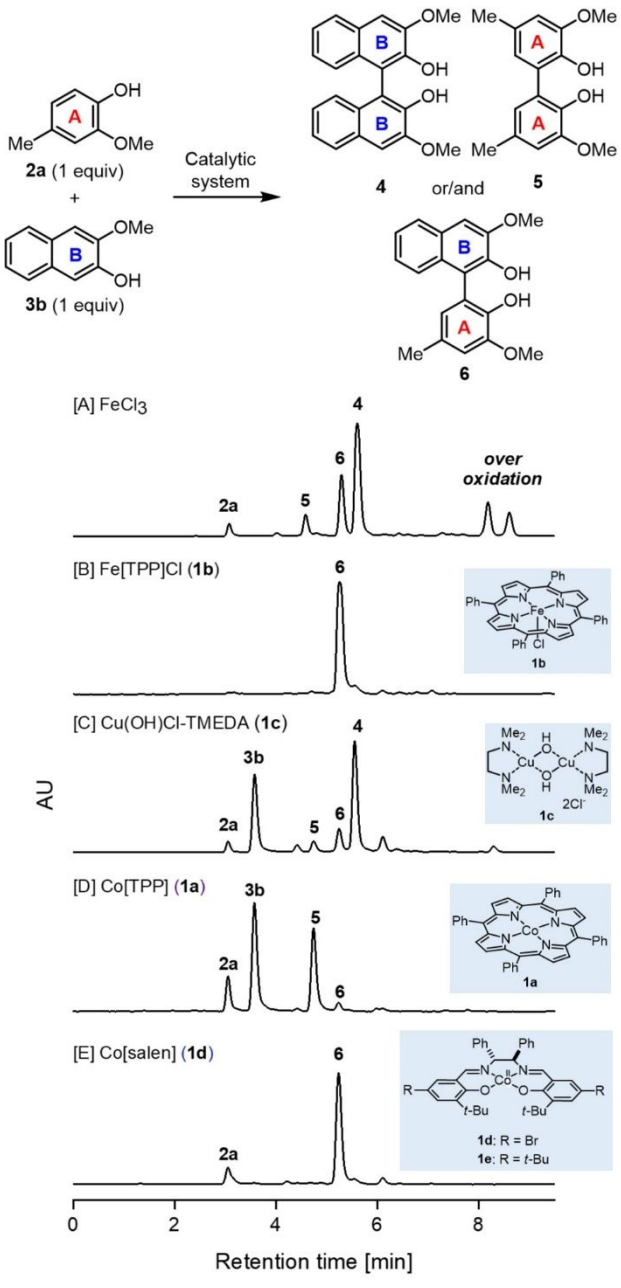


	R	E_{ox} [V]	yield [%]
3a	CO_2Me	0.80	**6a**, 82%
3b	OMe	0.56	complex mixture

RESULTS AND DICUSSION

Catalyst-controlled chemoselectivity in oxidative phenol coupling. We initiated this study by screening different redox catalytic systems that will enable the oxidative coupling between phenols with relatively close oxidation potentials. For that purpose, 2-methoxy-4-methylphenol (**2a**, 1 equiv) and 3-methoxy-2-naphthol (**3b**, 1 equiv) were chosen (Scheme 2).

Scheme 2. Catalyst-controlled chemoselectivity in the oxidative coupling of phenols. [a,b,c]



[a]*Conditions*: [A] $FeCl_3$ (10 mol %), *t*-BuOO-*t*Bu (1.5 equiv), HFIP, rt, 16 h; [B] Fe[TPP]Cl (**1b**, 1 mol %), *t*-BuOOH (1.1 equiv), HFIP, rt, 16 h; [C] Cu(OH)Cl-TMEDA (**1c**, 1 mol %), O_2, CH_2Cl_2, rt, 19 h; [D] Co[TPP] (**1a**, 0.2 mol %), O_2, Na_2CO_3, MeOH-H_2O, 60 °C, 16 h; [E] Co[salen] (**1d**, 1 mol

%), air, HFIP, rt, 16 h; [b]λ=230 nm; [c]See Scheme S2 in the SI for the exact conditions.

$FeCl_3$/t-BuOOt-Bu/HFIP catalytic system. The oxidative coupling reaction between phenol **2a** and 2-naphthol **3b** was first carried out using the multi-coordinated $FeCl_3$ catalyst under previously developed conditions by our group [$FeCl_3$ (10 mol %), *t*-BuO*t*-Bu, and HFIP at room temperature].[15, 18, 20, 21, 48] HPLC analysis of the reaction crude revealed the formation of all three possible coupling products **4**, **5,** and **6,** together with other undefined over-oxidation compounds (Scheme 2A). As mentioned above, under these conditions, $FeCl_3$ mediates the coupling of two phenols via an inner-sphere oxidative radical-anion coupling mechanism.[21] The poor chemoselectivity here is attributed to the inability of the catalyst to distinguish between the two ligated phenolic partners.

Fe[TPP]Cl/t-BuOOH/HFIP catalytic system. The oxidative cross-coupling between phenol **2a** and 2-naphthol **3b** by Fe[TPP]Cl catalyst **1b** [(1 mol %), *t*-BuOOH, and HFIP, rt] exhibited excellent cross-coupling selectivity, affording unsymmetrical biphenol **6** as a single product (Scheme 2B). On the basis of previously reported competitive NMR studies,[16] phenol **2a** was found to be a weak ligand for iron in HFIP, whereas 2-naphthol **3b** binds strongly to complex **1b** in the presence of HFIP (see the supporting information, Figure S1-S4). As a result, selective binding of 2-naphthol **3b** to the iron porphyrin complex is assumed to be the origin of the chemoselectivity.[16] The postulated mechanism proceeds with the formation of a high valence [**3b**][TPP]Fe^{IV}=O porphyryl radical intermediate that selectively oxidizes phenol **2a** to a phenoxyl radical **2a•** [E_{ox}**2a** < E_{ox}**3b**]. This transient radical species reacts with a persistent ligated naphthoxyl radical [**3b•**][TPP]Fe^{III}-OH intermediate (see Scheme 1A) via an intermolecular radical−radical coupling mechanism.[16] The fact that two structurally distinctive iron complexes ($FeCl_3$ and Fe[TPP]Cl) mediate the same reaction with different selectivities emphasizes the tight relation between the catalysts' structural properties and the mechanism.

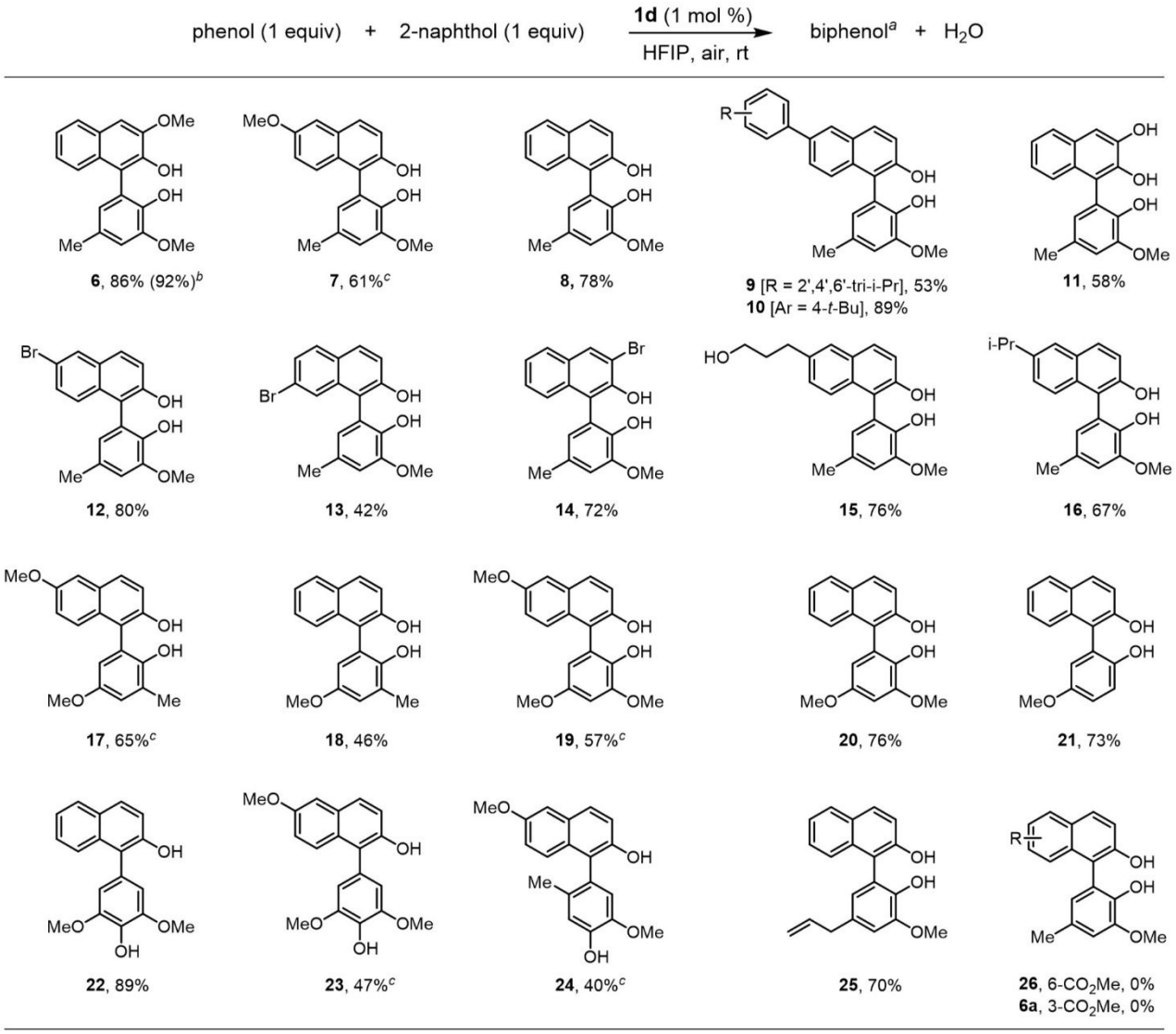
Cu(OH)Cl-TMEDA/air/CH_2Cl_2 catalytic system. The aerobic oxidative coupling of phenol **2a** and 2-naphthol **3b** using Nakajima and Koga's Cu(OH)Cl-TMEDA (**1c**) catalytic system[49, 50] was not selective (Scheme 2C). Roithová has shown – with the aid of infrared multiphoton dissociation (IRMPD) spectroscopy and DFT calculations – that the mechanism underlying this reaction involves the coupling of 2-naphthoxyl radicals bound in a binuclear copper cluster.[51, 52] Whereas 2-naphthol **3b** underwent oxidative dimerization to afford BINOL **4**, phenol **2a** was too reactive under the reaction conditions, affording a mixture of dehydrogenation products. Interestingly, the cross-coupling product **6** was almost not formed under these conditions.

Co[TPP]/O_2/Na_2CO_3/MeOH-H_2O catalytic system. The conditions developed by Guo for aerobic oxidative homocoupling of phenols using Co[TPP] **1a** [(0.2 mol %), O_2 (1 atm), and Na_2CO_3, MeOH-H_2O, 60 °C] exhibited unique selectivity. Under his reported conditions, the phenol **2a** underwent oxidative dimerization while naphthol **3b** was left almost unreacted (Scheme 2D). Guo postulated an oxidative radical-radical coupling mechanism between two phenoxyl radicals. However, the factors that lead to the selective formation of biphenol **5** remain in the dark.[37] Nevertheless, it is reasonable to assume that Co[TPP] mediates the reaction by a mechanism that differs from that of the above copper and iron catalysts.

Co[salen] catalytic system. Encouraged by the finding that Co[TPP] can selectively oxidize phenol **2a** in the presence of naphthol **3b**, we examined the reactivity of cobalt(II) salen complexes, which are known as superior oxygen carriers.[44, 45, 53-55] Therefore, they offer excellent opportunities for developing sustainable catalytic systems based on free air as the terminal oxidant. First, phenol **2a** (1 equiv) and naphthol **3b** (1 equiv) were mixed with Co[salen] **1d** (1 mol %) in MeOH under air atmosphere at room temperature. Yet, under these conditions no reaction took place. However, when the reaction performed in HFIP (Scheme 2E) a high degree of cross-coupling selectivity was observed affording unsymmetrical biphenol **6** in an excellent 86% isolated yield (see Figure 1). The fact that atmospheric air serves as the terminal oxidant in this reaction, makes this method to be highly attractive for large-scale production of biaryl products.

Scope and limitation. The scope of the newly established catalytic system was examined. The general conditions include mixing the phenol (1 equiv) and the 2-naphthol (1 equiv) reactants with Co[salen] (1 mol %) in HFIP at room temperature in an open flask. Under these conditions, different unsymmetrical biphenols **6**-**25** were isolated in moderate to high yields (Figure 1). In general, readily oxidized phenols with either *ortho*- or *para*-methoxy groups and 2-naphthols substituted with electron-donating groups (such as alkyl, aryl, hydroxy, or methoxy) or weak electron-withdrawing groups (*e.g.* Br) are suitable coupling partners. In addition, oxidizable functional groups, such as primary alcohol (see **15**) and allyl (see **25**) groups were stable under the mild reaction conditions. 6-methoxy-2-naphthol has oxidation potential comparable to its phenolic partners, and as a result, only moderate selectivity was observed under the general conditions. To improve the yield of the cross-coupling products, 1.5 equiv of the phenolic reactant was used and the reactions were performed at 4 °C (see **7**, **17**, **19**, **23** and **24**). The reaction between phenol **2a** and 3-(CO_2Me)-2-naphthol (**3a**) or 6-(CO_2Me)-2-naphthol, which are the preferred coupling partners in the $FeCl_3$/*t*-BuOO*t*-Bu/HFIP catalytic system (*vide-supra*),[21] failed to afford the corresponding biaryl coupling products **6a** and **26**.

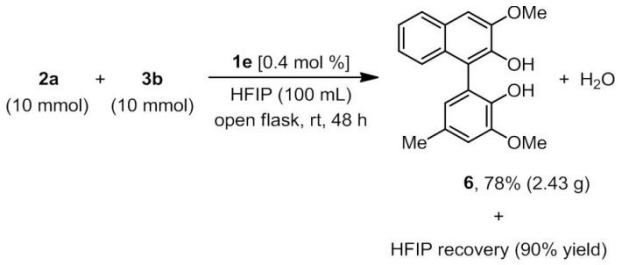
Figure 1. The reaction scope.



Conditions: A solution of phenol (1 equiv), 2-naphthol (1 equiv) and Co[salen] **1d** (1 mol %) was stirred at room temperature up to 24 hours in HFIP (0.1 M). [a]Isolated yields of pure products; [b]Co[salen] **1e** was used instead of **1d**; [c]The Reaction was performed with 1.5 equiv of the phenol at 4 °C.

Several other Co[salen] complexes that differ in their electronic properties were also tested. These readily available complexes mediate the reaction with similar catalytic activity, implying that in this reaction electronic and steric changes have only minor influence over the catalytic activity. For example, under similar conditions cobalt salen **1e** (Scheme 2, R = *t*-Bu), which differs from complex **1d** (R = Br) in its electronic nature, successfully mediated the oxidative coupling of phenol **2a** and **3b** affording biphenol **6** in an improved 92% yield.

The scalability of the process was illustrated by performing the coupling of phenol **2a** with 2-naphthol **3b** (1:1 ratio, 10 mmol) on a multi-gram scale [Scheme 3, Co[salen] **1e** (0.4 mol %), HFIP, air, rt, 48 h]. This simple-setting reaction afforded the desired coupling product **6** in 78% yield (2.43 g). Since H_2O is the only side product formed in this process, the expensive fluorinated alcohol solvent was successfully recovered by simple distillation (90% yield).[56] This experiment demonstrates that this technology is suitable for benign preparative applications.



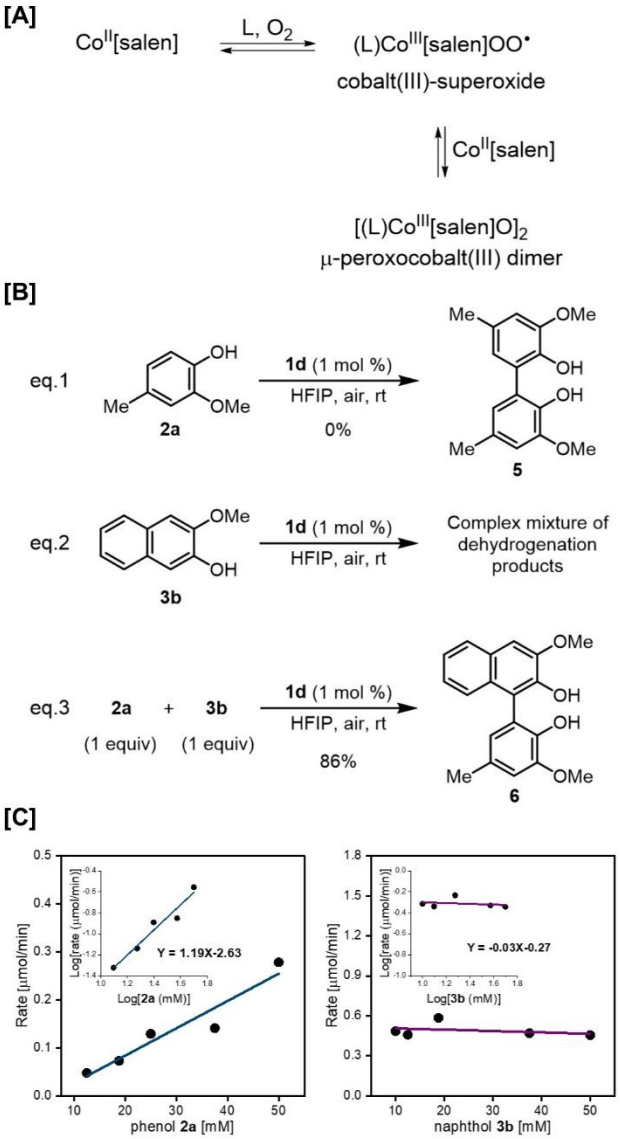
Scheme 3. Large-scale aerobic oxidative coupling of phenols **2a** and **3b** by Co[salen] catalyst.

To clarify the observed selectivity and reactivity of the reaction, we performed a mechanistic investigation. In recent years, HFIP has become the solvent of choice in oxidation processes[57-64] as it stabilizes cationic radical species.[61, 65] In oxidative phenol coupling reactions, HFIP forms strong hydrogen-bonds with the oxidant,[64, 66, 67] the phenoxyl radicals,[16, 21] and the redox catalysts.[16, 68] As a result it significantly enhances the reaction rate and the selectivity.[4, 20] Cobalt(II) salen complexes reversibly uptake dioxygen molecules in strong coordination solvents, such as pyridine, DMSO, and DMF,[69-71] forming monomeric cobalt(III)-superoxide complexes that exist in equilibrium with μ-peroxocobalt(III) dimer complexes (Scheme 4A). [39, 42, 43, 45, 53, 72] A similar trend was observed when complexes **1d** or **1e** dissolved in HFIP under air atmosphere. The UV spectra of these complexes revealed a rapid change in the oxidation state of complex **1e** in HFIP and the formation of cobalt(III) species (see Supporting Information, Figure S5), whereas the absorbance change for complex **1d** took a longer time (several hours). Furthermore, the initial red-orange color of the complexes in HFIP turned black for complex **1e** (R = *t*-Bu) and upon solvent removal, a black solid[69] with a molecular weight compatible with a μ-peroxocobalt(III) dimer was detected by mass-spectroscopy. The elemental analysis of this solid afforded mass fractions of carbon, nitrogen, oxygen, fluorine, and hydrogen, which support a molecular formula of a μ-peroxocobalt(III) dimer bound to HFIP and H_2O molecules ($[(HFIP)_2(H_2O)_6(\mathbf{1e})O]_2$) (**1f**, eq. 3, see the Supporting Information, Table S1).[62, 64] This dimeric complex disassembled to complex **1e** when dissolved in $CDCl_3$ or methanol.

A series of control experiments and kinetic studies were carried out to uncover the coupling mechanism. When phenol **2a** alone, which is a weak ligand in HFIP,[16] was mixed with the cobalt catalyst **1d** in HFIP no oxidation processes took place (Scheme 4B, eq.1). On the other hand, under similar conditions, 2-naphthol **3b** was not stable affording a mixture of dehydrogenation products (Scheme 4B, eq.2). However, a highly chemoselective cross-coupling reaction occurred when phenol **2a** and 2-napthol **3b** were mixed together with the catalyst, affording unsymmetrical biphenol **6** in 86% isolated yield (eq.3 indicating that 2-naphthol **3b** probably act as a fifth ligand and activates the Co[salen] catalyst. This assumption was confirmed by initial-rate kinetic studies. A first-order behavior for phenol **2a** and a zero-order behavior for 2-naphthol **3b** were revealed (Scheme 4C).[73, 74] This supports the premise that coordination of the 2-naphthol to the metal occurs prior to the oxidation of the phenol, which is probably the rate determining step.

The Co[salen] and the Fe[TPP]Cl catalytic systems exhibited similar cross-coupling selectivity for the oxidative coupling of phenol **2a** and naphthol **3b** (Scheme 2). Since selectivity is closely related to the coupling mechanism, it is reasonable to assume that the two catalytic systems would mediate the reaction by closely related outer-sphere radical-radical coupling mechanisms.[16]

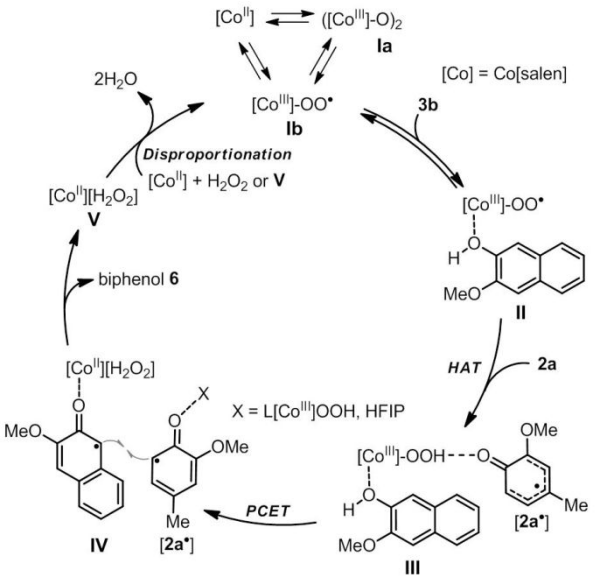
Scheme 4. Mechanistic studies



A] Dimerization of cobalt(II) salen complexes in the presence of O_2. B] Control experiments for studying the role of the fifth ligand of the Co[salen] **1d** catalyst. C] Dependence of the initial rate on 2-methoxy-4-methylphenol (**2a**) and 3-methoxy-2-naphthol (**3b**) concentrations.

Based on these findings, a mechanism for the oxidative coupling of electron-rich phenols with 2-naphthol derivatives is postulated (Scheme 5). The catalytic cycle

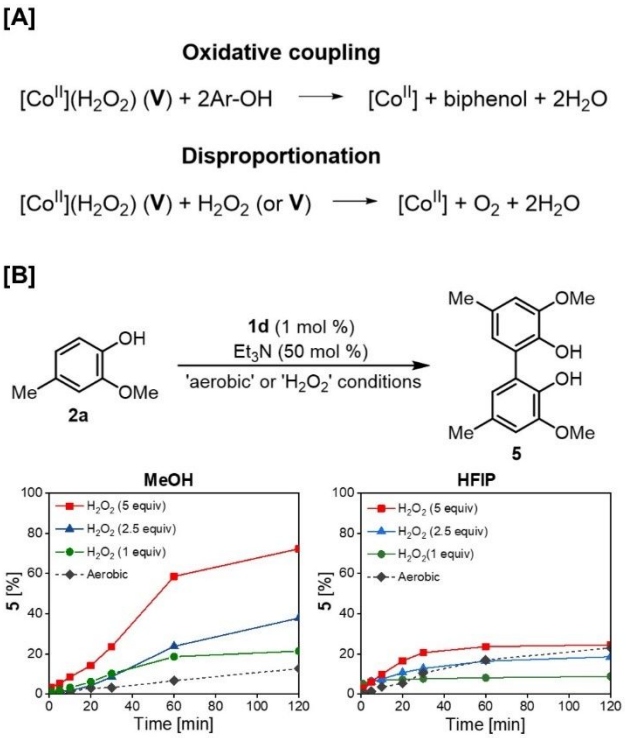
begins with the formation of μ-peroxocobalt(III) dimer complex **Ia**, which is found in equilibrium with cobalt(III)-superoxide complex **Ib**. Conversion of these complexes to intermediate **II** takes place upon 2-naphthol **3b** ligation. The abstraction of a hydrogen atom from phenol **2a,** by the cobalt-superoxide complex **II**, generates complex **III** and a liberated phenoxyl radical **2a•** with a relatively long lifetime in HFIP. Although the subsequent steps in the catalytic cycle are kinetically invisible, it is suggested, based on the independent EPR studies of Bolzacchini et al.[54] and Tkáč,[75] that complex **III** undergoes a rapid consecutive proton-coupled-electron transfer (PCET) process to form a cobalt-ligated naphthoxyl radical species (complex **IV**).[54] The ligated naphthoxyl radical in **IV** and the liberated phenoxyl radical [**2a•**] can then couple, undergo coupling to afford biphenol **6** and complex **V**. Thus, the observed chemoselectivity can be explained in terms of the different roles played by the two coupling partners during the catalytic cycle.



Scheme 5. Postulated mechanism for the Co[salen]-catalyzed aerobic oxidative cross-coupling of phenols in HFIP.

Complex **V** (Scheme 5) can mediate either: 1) the formation of a second biaryl bond, while utilizing hydrogen peroxide as the oxidant,[76, 77] and/or 2) the co-catalyzed disproportionation of two molecules of H_2O_2 into two molecules of H_2O and a single O_2 molecule, which in turn, enters the aerobic catalytic cycle (Figure 2A). To distinguish between the two possible routes, we studied the oxidative homocoupling reactions of phenol **2a** (1 equiv) by catalyst **1d** (1 mol %) in the presence of triethylamine (TEA, 0.5 equiv). As mentioned above, phenol **2a** is stable under our reaction conditions in the absence of a fifth ligand (Scheme 4B, eq. 1), therefore, TEA was needed to promote the homocoupling. The dimerization of **2a** was succesfully carried out in methanol or in HFIP (Figure 2B) either under air (open flask, gray diamonds, dashed line) or in the presence of different amounts of hydrogen peroxide urea complex (UHP; 1, 2.5, and 5 equiv, green circles, blue triangles and red squares, solid lines, respectively) under Ar atmosphere. This part of the study revealed that in methanol the oxidative dimerization of phenol **2a** is H_2O_2 dependent (solid lines) and that the reaction proceeds significantly faster with UHP rather than under aerobic conditions (compare the red squares with the gray diamonds). This suggests that in methanol, hydrogen peroxide serves as a terminal oxidant in the oxidative coupling reaction. These results are in agreement with the findings of the Stahl group,[77, 78] who reported that in methanol the aerobic oxidation of hydroquinone (HQ) to benzoquinone (BQ) by Co[salophen] catalyst involves a slow HQ to BQ oxidation step ($O_2 \rightarrow H_2O_2$), followed by an extremely rapid second oxidation step (HQ to BQ and $H_2O_2 \rightarrow 2H_2O$). In contrast, the oxidative coupling of phenol **2a** in HFIP under aerobic conditions (dashed gray line, Figure 2B) exhibited reactivity similar to that in the presence of UHP (solid lines, Figure 2B), indicating that the oxidative coupling using hydrogen peroxide as the terminal oxidant is a slow process in HFIP and that H_2O_2 disproportionation is a competitive process that terminates the catalytic cycle, while regenerating complex **Ib**. The latter complex could re-enter the aerobic catalytic cycle; hence, O_2 alone serves as the terminal oxidant in this oxidative coupling reaction.

Figure 2. Comparison between terminal oxidants (O_2 and H_2O_2) in the Co[salen]-catalyzed oxidative coupling of **2a** in methanol or in HFIP.



Conditions: 'H_2O_2' conditions = phenol **2a** (0.05 mmol), **1d** (1 mol %), Et_3N (0.025 mmol), hydrogen peroxide urea complex [1 equiv (green circles), 2.5 equiv (blue triangles) and 5 equiv (red squares)] in MeOH or HFIP (1 mL), Ar

atm, rt; 'aerobic' conditions = phenol **2a** (0.05 mmol), **1d** (1 mol %), Et_3N (0.025 mmol) in MeOH or HFIP (1 mL), under air (open flask), rt.

Conclusions

In summary, a selectivity-driven catalyst design approach was successfully applied to develop an efficient, highly selective aerobic oxidative cross-coupling of phenols. The catalytic reaction, which relies on the readily available Co[salen] catalysts **1d** and **1e**, is both scalable and sustainable. The latter advantage was conferred by the recyclability of the HFIP solvent and the mild waste-free conditions (an open flask at room temperature). The postulated mechanism involves coupling between a liberated phenoxyl radical and a ligated naphthoxyl radical, whereas the selectivity is attributed to the difference in the binding ability of the two phenols to the catalyst in HFIP.

Experimental Section

General Methods. All reagents were of reagent grade quality, purchased commercially from Sigma-Aldrich, Alfa-Aesar, or Fluka, and used without further purification. Purification by column chromatography was performed on Sigma-Aldrich chromatographic silica gel (40-60 μm). TLC analyses were performed using Merck silica gel glass plates 60 F254. NMR spectra were recorded on Bruker DPX400 or DMX500 instruments; chemical shifts, given in ppm, are relative to Me_4Si as an internal standard or to the residual solvent peak. HR-MS data were obtained using a LTQ Orbitrap XL ETD (Thermo Fisher Scientific, Germany & USA) high resolution mass spectrometer. HPLC analysis was carried out on Agilent 1260 instrument equipped with a G4212-60008 photodiode array detector. Gas chromatography measurements were carried out in an Agilent 7820A GC equipped with a FID detector working under standard conditions and an Agilent HP-5 column. Spectrophotometer measurements were carried out in Thermo Scientific UV-vis Helios Omega.

General procedure for aerobic oxidative coupling of phenols by Co[salen] 1d catalyst. A solution of phenol (0.25 mmol), 2-naphthol (0.25 mmol) and Co[salen] **1d** (1.8 mg, 1 mol %) in HFIP (0.1 M, 2.5 mL) was stirred at room temperature[a]. After complete consumption of the starting materials (indicated by TLC or HPLC within 24 h) the reaction was quenched by addition of CH_2Cl_2 and HCl 1 M. The organic phase was separated and dried over $MgSO_4$. The volatiles were removed under reduced pressure and the crude residue was purified by column chromatography (silica gel 40-60 μm), affording the biphenol cross-coupling product.

[a]Except for reactions with 6-methoxy-2-naphthol that were performed at 4 °C with 1.5 equiv of the phenol.

*1-(2-hydroxy-3-methoxy-5-methylphenyl)-3-methoxynaphthalen-2-ol (**6**).*[79] 2-methoxy-4-methylphenol (32 μL, 0.25 mmol) and 3-methoxy-2-naphthol (44 mg, 0.25 mmol) were reacted according to the general method. The crude residue was purified by column chromatography (ethyl acetate/hexane 20:80) to afford compound **6** (67 mg, 86% yield) as an amorphous light pink solid. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.74 (d, J = 8.0 Hz, 1H), 7.43 (d, J = 8.2 Hz, 1H), 7.34 (t, J = 7.2 Hz, 1H), 7.27 (t, J = 7.3 Hz, 1H), 7.20 (s, 1H), 6.82 (s, 1H), 6.72 (s, 1H), 5.99 (s, 1H, OH), 5.49 (s, 1H, OH), 4.05 (s, 3H), 3.95 (s, 3H), 2.37 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 147.2, 146.9, 142.9, 141.5, 129.4, 129.0, 128.8, 126.8, 124.9, 124.3, 124.2, 124.0, 120.8, 117.4, 111.6, 105.9, 56.0 (2XC), 21.3.

*1-(2-hydroxy-3-methoxy-5-methylphenyl)-6-methoxynaphthalen-2-ol (**7**).* 2-methoxy-4-methylphenol (47 μL, 0.375 mmol) and 6-methoxy-2-naphthol (44 mg, 0.25 mmol) were reacted according to the general method at 4 °C. The crude residue was purified by column chromatography (ethyl acetate/hexane 20:80) to afford compound **7** (47.4 mg, 61% yield) as an amorphous light yellow solid. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.71 (d, J = 8.8 Hz, 1H), 7.37 (d, J = 9.2 Hz, 1H), 7.25 (d, J = 8.8 Hz, 1H), 7.14 (d, J = 2.6 Hz, 1H), 7.04 (dd, J = 9.2, 2.6 Hz, 1H), 6.82 (d, J = 1.8 Hz, 1H), 6.70 (broad multiplet, J = 1.8, 0.9 Hz, 1H), 5.59 (s, 1H, OH), 5.26 (s, 1H, OH), 3.97 (s, 3H), 3.90 (s, 3H), 2.35 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 155.9, 149.3, 147.2, 141.6, 130.3, 130.1, 128.5, 126.4, 124.4, 119.8, 119.5, 118.9, 118.2, 116.9, 112.0, 106.5, 56.1, 55.4, 21.2. HRMS (ESI): m/z $[M+H]^+$ calcd for $C_{19}H_{19}O_4$ 311.1278, found 311.1278.

*1-(2-hydroxy-3-methoxy-5-methylphenyl)naphthalen-2-ol (**8**).*[20] 2-methoxy-4-methylphenol (32 μL, 0.25 mmol) and 2-naphthol (36 mg, 0.25 mmol) were reacted according to the general method. The crude residue was purified by column chromatography (ethyl acetate/hexane 20:80) to afford compound **8** (54.8 mg, 78% yield) as an amorphous a light brown solid. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.77 (d, J = 8.9 Hz, 2H), 7.42 (dd, J = 8.0, 1.1 Hz, 1H), 7.35 – 7.26 (m, 2H), 7.26 – 7.19 (m, 1H), 6.79 (d, J = 1.4 Hz, 1H), 6.67 (d, J = 0.9 Hz, 1H), 5.56 (s, 1H, OH), 5.37 (s, 1H, OH), 3.92 (s, 3H), 2.32 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 150.8, 147.2, 141.7, 133.1, 130.4, 129.8, 129.2, 128.1, 126.5, 124.8, 124.4, 123.3, 119.3, 117.8, 116.6, 112.1, 56.1, 21.2.

*1-(2-hydroxy-3-methoxy-5-methylphenyl)-6-(2,4,6-triisopropylphenyl)naphthalen-2-ol (**9**).* 2-methoxy-4-methylphenol (41 μL, 0.325 mmol due to low solubility of the naphthol) and 6-(1,3,5-tri-*i*-propyl-phenyl)-2-naphthol (87 mg, 0.25 mmol) were reacted according to the general method. The crude residue was purified by column chromatography (ethyl acetate/hexane 25:75) to afford compound **9** (64.4 mg, 53% yield) as an amorphous yellow solid. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.81 (d, J = 8.8 Hz, 1H), 7.63 (d, J = 1.6 Hz, 1H), 7.50 (d, J = 8.6 Hz, 1H), 7.33 (d, J = 8.9 Hz, 1H), 7.23 (dd, J = 8.6, 1.7 Hz, 1H), 7.10 (s, 2H), 6.87 (d, J = 1.8 Hz, 1H), 6.82 (d, J = 1.6 Hz, 1H), 5.68 (s, 1H, OH), 5.44 (s, 1H, OH), 3.99 (s, 3H), 2.98 (hept, J = 6.9 Hz, 1H), 2.68 (m, 2H), 2.41 (s, 3H), 1.34 (d, J = 6.9 Hz, 6H), 1.17 – 0.99 (m, 12H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 150.8, 147.9, 147.3, 147.0, 146.9, 141.7, 137.0, 135.8, 131.8, 130.5, 129.9, 129.2, 128.9, 128.4, 124.5, 124.4, 120.6, 120.5, 119.3, 117.9, 116.4, 112.1, 56.1, 34.3, 30.3 (2XC), 24.4, 24.2 (2XC),

24.1, 21.3. HRMS (ESI): m/z $[M+H]^+$ calcd for $C_{33}H_{39}O_3$ 483.2894, found 483.2892.

*6-(4-(tert-butyl)phenyl)-1-(2-hydroxy-3-methoxy-5-ethylphenyl)naphthalen-2-ol (**10**).* 2-methoxy-4-methylphenol (32 µL, 0.25 mmol) and 6-*t*-butyl-phenyl-2-naphthol (69 mg, 0.25 mmol) were reacted according to the general method. The crude residue was purified by column chromatography (ethyl acetate/hexane 20:80) to afford compound **10** (92 mg, 89% yield) as a yellow solid. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.06 (d, J = 1.9 Hz, 1H), 7.90 (d, J = 8.8 Hz, 1H), 7.70 – 7.67 (m, 3H), 7.59 (d, J = 8.8 Hz, 1H), 7.56 – 7.52 (m, 2H), 7.35 (d, J = 8.9 Hz, 1H), 6.88 (d, J = 1.8 Hz, 1H), 6.79 (dd, J = 1.9 Hz, 0.8 Hz, 1H), 5.73 (s, 1H, OH), 5.56 (s, 1H, OH), 3.98 (s, 3H), 2.41 (s, 3H), 1.43 (s, 9H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 150.9, 150.1, 147.3, 141.8, 138.3, 136.0, 132.3, 130.4, 130.1, 129.5, 126.9, 126.2, 125.9, 125.8, 125.4, 124.5, 119.4, 118.3, 116.7, 112.1, 56.1, 34.6, 31.5, 21.3. HRMS (ESI): m/z $[M+H]^+$ calcd for $C_{28}H_{29}O_3$ 413.2111, found 413.2104.

*1-(2-hydroxy-3-methoxy-5-methylphenyl)naphthalene-2,3-diol (**11**).* 2-methoxy-4-methylphenol (32 µL, 0.25 mmol) and 2,3 dihydroxynaphthalene (40 mg, 0.25 mmol) were reacted according to the general method. The crude residue was purified by column chromatography (ethyl acetate/hexane 30:70) to afford compound **11** (43 mg, 58% yield) as a white solid. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.69 (d, J = 7.6 Hz, 1H), 7.50 (d, J = 8.3 Hz, 1H), 7.37 – 7.28 (m, 2H), 7.24 (ddd, J = 8.2, 6.8, 1.4 Hz, 1H), 6.83 (d, J = 1.7 Hz, 1H), 6.76 (d, J = 1.0 Hz, 1H), 5.95 (s, 3H, OH), 3.97 (s, 3H), 2.36 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 147.0, 145.1, 141.0, 140.9, 130.3 (2XC), 127.9, 126.8, 125.0, 124.6, 124.2, 123.9, 119.6, 118.2, 111.8, 109.9, 56.1, 21.2. HRMS (ESI): m/z $[M+H]^+$ calcd for $C_{18}H_{17}O_4$ 297.1121, found 297.1119.

*6-bromo-1-(2-hydroxy-3-methoxy-5-methylphenyl)naphthalen-2-ol (**12**).*[20] 2-methoxy-4-methylphenol (32 µL, 0.25 mmol) and 6-bromo-2-naphthol (55.8 mg, 0.25 mmol) were reacted according to the general method. The crude residue was purified by column chromatography (ethyl acetate/hexane 20:80) to afford compound **12** (72 mg, 80% yield) as an amorphous yellow solid. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.95 (d, J = 2.0 Hz, 1H), 7.71 (d, J = 8.9 Hz, 1H), 7.40 (dd, J = 9.0, 2.0 Hz, 1H), 7.33 (d, J = 9.0 Hz, 1H), 7.29 (d, J = 8.9 Hz, 1H), 6.84 (d, J = 1.7 Hz, 1H), 6.68 (d, J = 1.8 Hz, J = 0.8 Hz, 1H), 5.64 (s, 1H, OH), 5.43 (s, 1H, OH), 3.97 (s, 3H), 2.36 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 151.1, 147.2, 141.7, 131.7, 130.5, 130.3, 130.0, 129.6, 128.8, 126.8, 124.2, 118.9, 118.7, 117.1, 117.0, 112.2, 56.1, 21.2.

*7-bromo-1-(2-hydroxy-3-methoxy-5-methylphenyl)naphthalen-2-ol (**13**).* 2-methoxy-4-methylphenol (32 µL, 0.25 mmol) and 7-bromo-2-naphthol (55.8 mg, 0.25 mmol) were reacted according to the general method. The crude residue was purified by column chromatography (ethyl acetate/hexane 20:80) to afford compound **13** (38 mg, 42% yield) as a yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.76 (d, J = 9.0 Hz, 1H), 7.66 (d, J = 8.7 Hz, 1H), 7.59 (d, J = 1.8 Hz, 1H), 7.39 (dd, J = 8.7, 1.8 Hz, 1H), 7.28 (d, J = 9.0 Hz, 1H), 6.85 (s, 1H), 6.67 (s, 1H), 5.67 (s, 1H, OH), 5.46 (s, 1H, OH), 3.97 (s, 3H), 2.37 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 151.6, 147.2, 141.7, 134.5, 130.6, 129.8, 129.7, 127.5, 127.0, 126.7, 124.2, 121.0, 118.4, 118.2, 116.2, 112.3, 56.1, 21.2. HRMS (ESI): m/z $[M+Na]^+$ calcd for $C_{18}H_{15}BrO_3Na$ 381.0097, 383.0076 found 381.0092, 383.0070.

*3-bromo-1-(2-hydroxy-3-methoxy-5-methylphenyl)naphthalen-2-ol (**14**).*[20] 2-methoxy-4-methylphenol (32 µL, 0.25 mmol) and 3-bromo-2-naphthol (55.8 mg, 0.25 mmol) were reacted according to the general method. The crude residue was purified by column chromatography (ethyl acetate/hexane 20:80) to afford compound **14** (65 mg, 72% yield) as a yellow liquid. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.11 (s, 1H), 7.73 (d, J = 7.4 Hz, 1H), 7.44 (d, J = 7.7 Hz, 1H), 7.43 – 7.28 (m, 2H), 6.85 (s, 1H), 6.70 (s, 1H), 5.77 (s, 1H, OH), 5.62 (s, 1H, OH), 3.96 (s, 3H), 2.37 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 147.1 (2XC), 141.6, 132.6, 131.8, 130.2, 129.6, 127.2, 126.7, 125.2, 124.3, 124.1, 119.6, 118.6, 112.2, 112.1, 56.1, 21.2.

*1-(2-hydroxy-3-methoxy-5-methylphenyl)-6-(3-hydroxypropyl)-naphthalen-2-ol (**15**).* 2-methoxy-4-methylphenol (32 µL, 0.25 mmol) and 6-(3-hydroxypropyl)-2-naphthol (50.5 mg, 0.25 mmol) were reacted according to the general method. The crude residue was purified by column chromatography (ethyl acetate/hexane 20:80) to afford compound **15** (64 mg, 76% yield) as an amorphous yellow solid. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.76 (d, J = 8.8 Hz, 1H), 7.62 (d, J = 1.4 Hz, 1H), 7.42 (d, J = 8.6 Hz, 1H), 7.27 (d, J = 8.8 Hz, 1H), 7.22 (dd, J = 8.7, 1.8 Hz, 1H), 6.84 (d, J = 1.7 Hz, 1H), 6.72 (dd, J = 1.9, 0.8 Hz, 1H), 5.61 (s, 1H, OH), 5.38 (s, 1H, OH), 3.97 (s, 3H), 3.42 (t, J = 6.6 Hz, 2H), 2.90 (t, J = 7.3 Hz, 2H), 2.37 (s, 3H), 2.23 (quin., J = 6.7 Hz, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 150.6, 147.3, 141.8, 135.4, 131.8, 130.5, 129.4 (2XC), 127.9, 127.2, 125.2, 124.5, 119.4, 118.1, 116.6, 112.1, 56.2, 34.2, 33.9, 33.3, 21.3. HRMS (ESI): m/z $[M+H]^+$ calcd for $C_{21}H_{23}O_4$ 339.1591, found 339.1589.

*1-(2-hydroxy-3-methoxy-5-methylphenyl)-6-isopropylnaphthalen-2-ol (**16**).* 2-methoxy-4-methylphenol (32 µL, 0.25 mmol) and 6-i-propyl-2-naphthol (47 mg, 0.25 mmol) were reacted according to the general method. The crude residue was purified by column chromatography (ethyl acetate/hexane 20:80) to afford compound **16** (54 mg, 67% yield) as a yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.78 (d, J = 8.8 Hz, 1H), 7.63 (d, J = 1.6 Hz, 1H), 7.42 (d, J = 8.8 Hz, 1H), 7.29 (dd, J = 8.7 Hz, J = 1.9 Hz, 1H), 7.27 (d, J = 8.7 Hz, 1H), 6.84 (d, J = 1.8 Hz, 1H), 6.73 (d, J = 1.8 Hz, 1H), 5.63 (s, 1H, OH), 5.41 (s, 1H, OH), 3.96 (s, 3H), 3.04 (hept, J = 6.9 Hz, 1H), 2.37 (s, 3H), 1.33 (d, J = 6.9 Hz, 6H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 150.3, 147.2, 143.7, 141.7, 131.6, 130.3, 129.5, 129.3, 126.4, 124.8, 124.5, 124.4, 119.6, 117.7, 116.4, 112.0, 56.1, 33.9, 24.0, 24.0 (2XC), 21.2. HRMS (ESI): m/z $[M+H]^+$ calcd for $C_{21}H_{23}O_3$ 323.1642, found 323.1637.

*1-(2-hydroxy-5-methoxy-3-methylphenyl)-6-methoxynaphthalen-2-ol (**17**).* 2-methyl-4-methoxy phenol (51.8 mg, 0.375 mmol) and 6-methoxy-2-naphthol (44 mg, 0.25 mmol) were reacted according to the general method at 4 °C. The crude residue was purified by column chromatography (ethyl acetate/hexane 20:80) to afford compound **17** (50.5 mg, 65% yield) an

amorphous pale brown solid. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.75 (d, J = 8.9 Hz, 1H), 7.31 (d, J = 9.1 Hz, 1H), 7.26 (d, J = 8.9 Hz, 1H), 7.16 (d, J = 2.4 Hz, 1H), 7.08 (dd, J = 9.1, 2.4 Hz, 1H), 6.87 (d, J = 2.8 Hz, 1H), 6.61 (d, J = 2.8 Hz, 1H), 3.90 (s, 3H), 3.76 (s, 3H), 2.33 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 156.3, 153.5, 150.0, 146.5, 130.1, 129.4, 128.1, 127.0, 125.8, 119.7, 118.8, 118.3, 118.1, 114.6, 112.9, 106.7, 55.7, 55.4, 16.6. HRMS (ESI): m/z $[M+H]^+$ calcd for $C_{19}H_{19}O_4$ 310.1278, found 310.1273.

*1-(2-hydroxy-5-methoxy-3-methylphenyl)naphthalen-2-ol (**18**).*[79] 2-methyl-4-methoxyphenol (34.5 mg, 0.25 mmol) and 2-naphthol (36 mg, 0.25 mmol) were reacted according to the general method. The crude residue was purified by column chromatography (ethyl acetate/hexane 20:80) to afford compound **18** (32 mg, 46% yield) as an amorphous yellow solid. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.85 (t, J = 8.9 Hz, 2H), 7.39 (m, Hz, 3H), 7.29 (d, J = 8.9 Hz, 1H), 6.89 (s, 1H), 6.63 (s, 1H), 5.38 (s, 1H, OH), 4.57 (s, 1H, OH), 3.76 (s, 3H), 2.35 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 153.6, 151.7, 146.6, 133.0, 130.8, 129.2, 128.3, 127.3, 127.1, 124.3, 123.9, 118.7, 118.4, 117.7, 114.4, 113.0, 55.7, 16.6.

*1-(2-hydroxy-3,5-dimethoxyphenyl)-6-methoxynaphthalen-2-ol (**19**).* 2,4-dimethoxyphenol (58 mg, 0.375 mmol) and 6-methoxy-2-naphthol (44 mg, 0.25 mmol) were reacted according to the general method at 4 °C. The crude residue was purified by column chromatography (ethyl acetate/hexane 10:90) to afford compound **19** (46.7 mg, 57% yield) as a pale brown solid. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.72 (d, J = 8.8 Hz, 1H), 7.41 (d, J = 9.2 Hz, 1H), 7.26 (d, J = 8.8 Hz, 1H), 7.15 (d, J = 2.6 Hz, 1H), 7.05 (dd, J = 9.2, 2.6 Hz, 1H), 6.63 (d, J = 2.8 Hz, 1H), 6.40 (d, J = 2.8 Hz, 1H), 5.41 (s, 1H, OH), 5.36 (s, 1H, OH), 3.95 (s, 3H), 3.90 (s, 3H), 3.76 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 156.0, 153.7, 149.3, 148.1, 138.0, 130.1, 128.6, 128.2, 126.4, 119.5, 119.0, 118.3, 116.9, 106.5 (2XC), 100.1, 56.1, 55.8, 55.4. HRMS (ESI): m/z $[M+H]^+$ calcd for $C_{19}H_{19}O_5$ 327.1227, found 327.1234.

*1-(2-hydroxy-3,5-dimethoxyphenyl)naphthalen-2-ol (**20**).*[21] 2,4-dimethoxyphenol (38.6 mg, 0.25 mmol) and 2-naphthol (36 mg, 0.25 mmol) were reacted according to the general method. The crude residue was purified by column chromatography (ethyl acetate/hexane 15:85) to afford compound **20** (56.4 mg, 76% yield) as a yellow-orange liquid. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.85 – 7.81 (m, 2H), 7.52 – 7.50 (m, 1H), 7.40 – 7.31 (m, 2H), 7.30 (d, J = 8.9 Hz, 1H), 6.65 (d, J = 2.8 Hz, 1H), 6.42 (d, J = 2.8 Hz, 1H), 5.49 (s, 1H, OH), 5.42 (s, 1H, OH), 3.95 (s, 3H), 3.76 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 153.8, 150.9, 148.3, 138.2, 133.1, 130.1, 129.3, 128.3, 126.7, 124.9, 123.5, 119.4, 118.0, 116.6, 106.6, 100.3, 56.2, 55.9.

*1-(2-hydroxy-5-methoxyphenyl)naphthalen-2-ol (**21**).*[16] 4-metho-xyphenol (31.1 mg, 0.25 mmol) and 2-naphthol (36 mg, 0.25 mmol) were reacted according to the general method. The crude residue was purified by column chromatography (ethyl acetate/hexane 10:90) to afford compound **21** (48.4 mg, 73% yield) as a yellow liquid. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.86 – 7.82 (m, 2H), 7.41 – 7.35 (m, 3H), 7.28 (d, J = 8.9 Hz, 1H), 7.06 (d, J = 8.9 Hz, 1H), 6.97 (dd, J = 8.9, 3.1 Hz, 1H), 6.79 (d, J = 3.0 Hz, 1H), 5.41 (s, 1H, OH), 4.62 (s, 1H, OH), 3.76 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 154.2, 151.8, 148.3, 133.0, 131.0, 129.3, 128.4, 127.5, 124.3, 124.0, 119.7, 117.9, 117.6, 116.9, 116.2, 114.3, 55.9.

*1-(4-hydroxy-3,5-dimethoxyphenyl)naphthalen-2-ol (**22**).*[80] 2,6-dimethoxyphenol (38.5 mg, 0.25 mmol) and 2-naphthol (36 mg, 0.25 mmol) were reacted according to the general method. The crude residue was purified by column chromatography (ethyl acetate/hexane 25:75) to afford compound **22** (66.3 mg, 89% yield) as an amorphous brown solid. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.84 – 7.78 (m, 2H), 7.51 – 7.46 (m, 1H), 7.41 – 7.32 (m, 3H), 7.28 (d, J = 8.9 Hz, 1H), 6.65 (s, 2H), 5.78 (s, 1H, OH), 5.43 (s, 1H, OH), 3.89 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 150.4, 148.0, 134.8, 133.6, 129.5, 128.9, 128.1, 126.6, 124.7 (2XC), 123.4, 121.1, 117.3, 107.5, 56.5.

*1-(4-hydroxy-3,5-dimethoxyphenyl)-6-methoxynaphthalen-2-ol (**23**).* 2,6-dimethoxyphenol (58 mg, 0.375 mmol) and 6-methoxy-2-naphthol (44 mg, 0.25 mmol) were reacted according to the general method at 4 °C. The crude residue was purified by column chromatography (ethyl acetate/hexane 25:75) to afford compound **23** (38.6 mg, 47% yield) as a brown liquid. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.69 (d, J = 8.9 Hz, 1H), 7.39 (d, J = 9.2 Hz, 1H), 7.24 (d, J = 8.9 Hz, 1H), 7.14 (d, J = 2.6 Hz, 1H), 7.05 (dd, J = 9.2, 2.6 Hz, 1H), 6.62 (s, 2H), 5.73 (s, 1H, OH), 5.21 (s, 1H, OH), 3.91 (s, 3H), 3.88 (s, 6H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 155.9, 148.8, 148.0, 134.8, 129.8, 128.8, 128.2, 126.3, 124.9, 121.4, 119.1, 117.7, 107.4, 106.4, 56.5, 55.5. HRMS (ESI): m/z $[M+H]^+$ calcd for $C_{19}H_{19}O_5$ 327.1227, found 327.1221.

*1-(4-hydroxy-5-methoxy-2-methylphenyl)-6-methoxynaphthalen-2-ol (**24**).* 2-methoxy-5-methylphenol (52 mg, 0.375 mmol) and 6-methoxy-2-naphthol (44 mg, 0.25 mmol) were reacted according to the general method at 4 °C. The crude residue was purified by column chromatography (ethyl acetate/hexane 25:75) to afford compound **24** (30.8 mg, 40% yield) as a white solid. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.71 (d, J = 8.9 Hz, 1H), 7.25 (d, J = 8.9 Hz, 1H), 7.17 (dd, J = 6.8, 6.1 Hz, 2H), 7.04 (dd, J = 9.1, 2.7 Hz, 1H), 6.99 (s, 1H), 6.74 (s, 1H), 5.75 (s, 1H, OH), 4.95 (s, 1H, OH), 3.91 (s, 3H), 3.83 (s, 3H), 1.93 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 156.0, 149.0, 146.0, 145.5, 132.0, 129.9, 128.8, 128.1, 126.2, 124.0, 120.6, 119.1, 117.7, 117.0, 113.6, 106.6, 56.2, 55.5, 18.9. HRMS (ESI): m/z $[M+H]^+$ calcd for $C_{19}H_{19}O_4$ 311.1278, found 311.1276.

*1-(5-allyl-2-hydroxy-3-methoxyphenyl)naphthalen-2-ol (**25**).* Eugenol (38.5 µL, 0.25 mmol) and 2-naphthol (36 mg, 0.25 mmol) were reacted according to the general method. The crude residue was purified by column chromatography (ethyl acetate/hexane 10:90) to afford compound **25** (54 mg, 70% yield) as an amorphous brown solid. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.83 (d, J = 8.7 Hz, 2H), 7.47 (d, J = 8.1 Hz, 1H), 7.40 – 7.31 (m, 2H), 7.30 (d, J = 8.7 Hz, 1H), 6.86 (s, 1H), 6.76 (s, 1H), 6.00 (m, 1H), 5.67 (s, 1H, OH), 5.41 (s, 1H, OH), 5.12 (m, 2H), 3.98 (s, 3H), 3.40 (d, J = 6.6 Hz, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 150.9, 147.4, 142.3, 137.4, 133.1, 132.7, 129.9, 129.2, 128.2,

126.5, 124.8, 124.1, 123.4, 119.5, 117.8, 116.5, 116.1, 111.4, 56.1, 39.9. HRMS (ESI): m/z $[M+H]^+$ calcd for $C_{20}H_{19}O_3$ 307.1334, found 307.1324.

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the

ACS Publications website at DOI:

Kinetic data and mechanistic studies as well as full spectroscopic data for all compounds,

Conflicts of interest

There are no conflicts to declare.

Acknowledgments

This work was supported by the Israel Science Foundation (grant number 164/16). The authors would like to thank the *COST-CHAOS* organization for funding the participation in the conference.

Notes and references

1. Yi, H.; Zhang, G.; Wang, H.; Huang, Z.; Wang, J.; Singh, A. K.; Lei, A., Recent Advances in Radical C–H Activation/Radical Cross-Coupling. *Chem. Rev.* **2017,** *117* (13), 9016-9085.
2. Liu, C.; Zhang, H.; Shi, W.; Lei, A., Bond formations between two nucleophiles: transition metal catalyzed oxidative cross-coupling reactions. *Chem. Rev.* **2011,** *111* (3), 1780-824.
3. Liu, C.; Liu, D.; Lei, A., Recent Advances of Transition-Metal Catalyzed Radical Oxidative Cross-Couplings. *Acc. Chem. Res.* **2014,** *47* (12), 3459-3470.
4. Shalit, H.; Dyadyuk, A.; Pappo, D., Selective Oxidative Phenol Coupling by Iron Catalysis. *J. Org. Chem.* **2019,** *84* (4), 1677-1686.
5. Kang, H.; Lee, Y. E.; Reddy, P. V. G.; Dey, S.; Allen, S. E.; Niederer, K. A.; Sung, P.; Hewitt, K.; Torruellas, C.; Herling, M. R.; Kozlowski, M. C., Asymmetric Oxidative Coupling of Phenols and Hydroxycarbazoles. *Org. Lett.* **2017,** *19* (20), 5505-5508.
6. Liu, L.; Carroll, P. J.; Kozlowski, M. C., Vanadium-Catalyzed Regioselective Oxidative Coupling of 2-Hydroxycarbazoles. *Org. Lett.* **2015,** *17* (3), 508-511.
7. Guo, Q.-X.; Wu, Z.-J.; Luo, Z.-B.; Liu, Q.-Z.; Ye, J.-L.; Luo, S.-W.; Cun, L.-F.; Gong, L.-Z., Highly Enantioselective Oxidative Couplings of 2-Naphthols Catalyzed by Chiral Bimetallic Oxovanadium Complexes with Either Oxygen or Air as Oxidant. *J. Am. Chem. Soc.* **2007,** *129* (45), 13927-13938.
8. Luo, Z.; Liu, Q.; Gong, L.; Cui, X.; Mi, A.; Jiang, Y., Novel achiral biphenol-derived diastereomeric oxovanadium(IV) complexes for highly enantioselective oxidative coupling of 2-naphthols. *Angew. Chem. Int. Ed.* **2002,** *41* (23), 4532-4535.
9. Sako, M.; Takizawa, S.; Yoshida, Y.; Sasai, H., Enantioselective and aerobic oxidative coupling of 2-naphthol derivatives using chiral dinuclear vanadium(V) complex in water. *Tetrahedron: Asymmetry* **2015,** *26* (12–13), 613-616.
10. Takizawa, S.; Kodera, J.; Yoshida, Y.; Sako, M.; Breukers, S.; Enders, D.; Sasai, H., Enantioselective oxidative-coupling of polycyclic phenols. *Tetrahedron* **2014,** *70* (9), 1786-1793.
11. Takizawa, S.; Katayama, T.; Sasai, H., Dinuclear chiral vanadium catalysts for oxidative coupling of 2-naphtholsvia a dual activation mechanism. *Chem. Commun.* **2008,** (35), 4113-4122.
12. Takizawa, S.; Katayama, T.; Somei, H.; Asano, Y.; Yoshida, T.; Kameyama, C.; Rajesh, D.; Onitsuka, K.; Suzuki, T.; Mikami, M.; Yamataka, H.; Jayaprakash, D.; Sasai, H., Dual activation in oxidative coupling of 2-naphthols catalyzed by chiral dinuclear vanadium complexes. *Tetrahedron* **2008,** *64* (15), 3361-3371.
13. Somei, H.; Asano, Y.; Yoshida, T.; Takizawa, S.; Yamataka, H.; Sasai, H., Dual activation in a homolytic coupling reaction promoted by an enantioselective dinuclear vanadium(IV) catalyst. *Tetrahedron Lett.* **2004,** *45* (9), 1841-1844.
14. Lee, Y. E.; Cao, T.; Torruellas, C.; Kozlowski, M. C., Selective Oxidative Homo- and Cross-Coupling of Phenols with Aerobic Catalysts. *J. Am. Chem. Soc.* **2014,** *136* (19), 6782-6785.
15. Vershinin, V.; Dyadyuk, A.; Pappo, D., Iron-catalyzed selective oxidative arylation of phenols and biphenols. *Tetrahedron* **2017,** *73* (26), 3660-3668.
16. Shalit, H.; Libman, A.; Pappo, D., meso-Tetraphenylporphyrin Iron Chloride Catalyzed Selective Oxidative Cross-Coupling of Phenols. *J. Am. Chem. Soc.* **2017,** *139* (38), 13404-13413.
17. Narute, S.; Pappo, D., Iron Phosphate Catalyzed Asymmetric Cross-Dehydrogenative Coupling of 2-Naphthols with β-Ketoesters. *Org. Lett.* **2017,** *19* (11), 2917-2920.
18. Dyadyuk, A.; Sudheendran, K.; Vainer, Y.; Vershinin, V.; Shames, A. I.; Pappo, D., Direct Synthesis of Polyaryls by Consecutive Oxidative Cross-Coupling of Phenols with Arenes. *Org. Lett.* **2016,** *18* (17), 4324-7.
19. Narute, S.; Parnes, R.; Toste, F. D.; Pappo, D., Enantioselective Oxidative Homocoupling and Cross-Coupling of 2-Naphthols Catalyzed by Chiral Iron Phosphate Complexes. *J. Am. Chem. Soc.* **2016,** *138* (50), 16553-16560.
20. Gaster, E.; Vainer, Y.; Regev, A.; Narute, S.; Sudheendran, K.; Werbeloff, A.; Shalit, H.; Pappo, D., Significant Enhancement in the Efficiency and Selectivity of Iron-Catalyzed Oxidative Cross-Coupling of Phenols by Fluoroalcohols. *Angew. Chem. Int. Ed.* **2015,** *54* (14), 4198-4202.
21. Libman, A.; Shalit, H.; Vainer, Y.; Narute, S.; Kozuch, S.; Pappo, D., Synthetic and Predictive Approach to Unsymmetrical Biphenols by Iron-Catalyzed Chelated Radical-Anion Oxidative Coupling. *J. Am. Chem. Soc.* **2015,** *137* (35), 11453-11460.
22. Oguma, T.; Katsuki, T., Asymmetric oxidation of alcohols and phenol derivatives with air as oxidant. *RSC Green Chem. Ser.* **2015,** *28* (Transition Metal Catalysis in Aerobic Alcohol Oxidation), 231-255.
23. Matsumoto, K.; Egami, H.; Oguma, T.; Katsuki, T., What factors influence the catalytic activity of iron-salan complexes for aerobic oxidative coupling of 2-naphthols? *Chem. Commun.* **2012,** *48* (47), 5823-5825.
24. Egami, H.; Matsumoto, K.; Oguma, T.; Kunisu, T.; Katsuki, T., Enantioenriched Synthesis of C1-Symmetric BINOLs: Iron-Catalyzed Cross-Coupling of 2-Naphthols and Some Mechanistic Insight. *J. Am. Chem. Soc.* **2010,** *132* (39), 13633-13635.
25. Egami, H.; Katsuki, T., Iron-Catalyzed Asymmetric Aerobic Oxidation: Oxidative Coupling of 2-Naphthols. *J. Am. Chem. Soc.* **2009,** *131*, 6082-6083.

26. Baleizão, C.; Garcia, H., Chiral Salen Complexes: An Overview to Recoverable and Reusable Homogeneous and Heterogeneous Catalysts. *Chem. Rev.* **2006,** *106* (9), 3987-4043.
27. Pellissier, H.; Clavier, H., Enantioselective Cobalt-Catalyzed Transformations. *Chem. Rev.* **2014,** *114* (5), 2775-2823.
28. Kozlowski, M. C.; Morgan, B. J.; Linton, E. C., Total synthesis of chiral biaryl natural products by asymmetric biaryl coupling. *Chem. Soc. Rev.* **2009,** *38* (11), 3193-207.
29. Hewgley, J. B.; Stahl, S. S.; Kozlowski, M. C., Mechanistic Study of Asymmetric Oxidative Biaryl Coupling: Evidence for Self-Processing of the Copper Catalyst to Achieve Control of Oxidase vs Oxygenase Activity. *J. Am. Chem. Soc.* **2008,** *130* (37), 12232-12233.
30. Li, X.; Hewgley, J. B.; Mulrooney, C. A.; Yang, J.; Kozlowski, M. C., Enantioselective Oxidative Biaryl Coupling Reactions Catalyzed by 1,5-Diazadecalin Metal Complexes: Efficient Formation of Chiral Functionalized BINOL Derivatives. *J. Org. Chem.* **2003,** *68* (14), 5500-5511.
31. Li, X.; Yang, J.; Kozlowski, M. C., Enantioselective oxidative biaryl coupling reactions catalyzed by 1,5-diazadecalin metal complexes. *Org. Lett.* **2001,** *3* (8), 1137-1140.
32. Elsler, B.; Schollmeyer, D.; Dyballa, K. M.; Franke, R.; Waldvogel, S. R., Metal- and Reagent-Free Highly Selective Anodic Cross-Coupling Reaction of Phenols. *Angew. Chem. Int. Ed.* **2014,** *53* (20), 5210-5213.
33. Morimoto, K.; Sakamoto, K.; Ohnishi, Y.; Miyamoto, T.; Ito, M.; Dohi, T.; Kita, Y., Metal-Free Oxidative para Cross-Coupling of Phenols. *Chem. -Eur. J.* **2013,** *19* (27), 8726-8731.
34. Kozlowski, M. C., Oxidative Coupling in Complexity Building Transforms. *Acc. Chem. Res.* **2017,** *50* (3), 638-643.
35. Habaue, S.; Aoyagi, H.; Murakami, S.; Higashimura, H., Asymmetric oxidative coupling polymerization of dihydroxynaphthalene derivatives with cobalt-salen complexes. *Polymer Bull.* **2007,** *59* (3), 303-310.
36. Haikarainen, A.; Sipilä, J.; Pietikäinen, P.; Pajunen, A.; Mutikainen, I., Salen complexes with bulky substituents as useful tools for biomimetic phenol oxidation research. *Bioorg. Med. Chem.* **2001,** *9* (6), 1633-1638.
37. Jiang, Q.; Sheng, W.; Tian, M.; Tang, J.; Guo, C., Cobalt(II)-Porphyrin-Catalyzed Aerobic Oxidation: Oxidative Coupling of Phenols. *Eur. J. Org. Chem.* **2013,** *2013* (10), 1861-1866.
38. Cozzi, P. G., Metal–Salen Schiff base complexes in catalysis: practical aspects. *Chem. Soc. Rev.* **2004,** *33* (7), 410-421.
39. Zombeck, A.; Drago, R. S.; Corden, B. B.; Gaul, J. H., Activation of molecular oxygen. Kinetic studies of the oxidation of hindered phenols with cobalt-dioxygen complexes. *J. Am. Chem. Soc.* **1981,** *103* (25), 7580-7585.
40. Bozell, J. J.; Hames, B. R.; Dimmel, D. R., Cobalt-Schiff base complex catalyzed oxidation of para-substituted phenolics. Preparation of benzoquinones. *J. Org. Chem.* **1995,** *60* (8), 2398-2404.
41. Maruyama, K.; Kusukawa, T.; Mashino, T.; Nishinaga, A., Co(salen)-Catalyzed tert-Butyl Hydroperoxide Oxidation of tert-Butylphenols Bearing an Unsaturated Side Chain. *J. Org. Chem.* **1996,** *61* (10), 3342-3349.
42. Cedeno, D.; Bozell, J. J., Catalytic oxidation of para-substituted phenols with cobalt–Schiff base complexes/O2—selective conversion of syringyl and guaiacyl lignin models to benzoquinones. *Tetrahedron Lett.* **2012,** *53* (19), 2380-2383.
43. Carter, M. J.; Rillema, D. P.; Basolo, F., Oxygen carrier and redox properties of some neutral cobalt chelates. Axial and in-plane ligand effects. *J. Am. Chem. Soc.* **1974,** *96* (2), 392-400.
44. Corden, B. B.; Drago, R. S.; Perito, R. P., Steric and electronic effects of ligand variation on cobalt dioxygen catalysts. *J. Am. Chem. Soc.* **1985,** *107* (10), 2903-2907.
45. Bailey, C. L.; Drago, R. S., Utilization of O2 for the specific oxidation of organic substrates with cobalt (II) catalysts. *Coord. Chem. Rev.* **1987,** *79* (3), 321-332.
46. Ortiz, B.; Park, S.-M., Electrochemical and spectroelectrochemical studies of cobalt salen and salophen as oxygen reduction catalysts. *B. Kor. Chem. Soc.* **2000,** *21* (4), 405-411.
47. Larionov, V. A.; Peregudova, S. M.; Maleev, V. I.; Belokon, Y. N., A novel type of catalysts for asymmetric oxidative coupling of 2-naphthol. *Russ. Chem. Bull.* **2016,** *65* (3), 685-688.
48. Regev, A.; Shalit, H.; Pappo, D., Iron-Catalyzed Oxidative C–C and C–O Coupling of Halophenols to α-Substituted β-Keto Esters. *Synthesis* **2015,** *47* (12), 1716-1725.
49. Noji, M.; Nakajima, M.; Koga, K., A new catalytic system for aerobic oxidative coupling of 2-naphthol derivatives by the use of CuCl-amine complex: A practical synthesis of binaphthol derivatives. *Tetrahedron Lett.* **1994,** *35* (43), 7983-7984.
50. Wendlandt, A. E.; Suess, A. M.; Stahl, S. S., Copper-Catalyzed Aerobic Oxidative C–H Functionalizations: Trends and Mechanistic Insights. *Angew. Chem. Int. Ed.* **2011,** *50* (47), 11062-11087.
51. Roithova, J., Characterization of reaction intermediates by ion spectroscopy. *Chemical Society reviews* **2012,** *41* (2), 547-559.
52. Roithová, J.; Milko, P., Naphthol Coupling Monitored by Infrared Spectroscopy in the Gas Phase. *J. Am. Chem. Soc.* **2010,** *132* (1), 281-288.
53. Drago, R. S., Homogeneous metal-catalyzed oxidations by O2. *Coord. Chem. Rev.* **1992,** *117*, 185-213.
54. Bolzacchini, E.; Canevali, C.; Morazzoni, F.; Orlandi, M.; Rindone, B.; Scotti, R., Spectromagnetic investigation of the active species in the oxidation of propenoidic phenols catalysed by [N,N[prime or minute]-bis(salicylidene)ethane-1,2-diaminato]cobalt(II) *. *J. Chem. Soc., Dalton Trans.* **1997,** (24), 4695-4700.
55. Drago, R. S.; Cannady, J. P.; Leslie, K. A., Hydrogen-bonding interactions involving metal-bound dioxygen. *J. Am. Chem. Soc.* **1980,** *102* (19), 6014-6019.
56. Brenek, S. J.; Caron, S.; Chisowa, E.; Delude, M. P.; Drexler, M. T.; Ewing, M. D.; Handfield, R. E.; Ide, N. D.; Nadkarni, D. V.; Nelson, J. D.; Olivier, M.; Perfect, H. H.; Phillips, J. E.; Teixeira, J. J.; Weekly, R. M.; Zelina, J. P., Development of a Practical and Convergent Process for the Preparation of Sulopenem. *Org. Proc. Res. Dev.* **2012,** *16* (8), 1348-1359.
57. Chen, X.-L.; Ai, B.-R.; Dong, Y.; Zhang, X.-M.; Wang, J.-Y., Hexafluoro-2-propanol-assisted quick and chemoselective nitro reduction using iron powder as catalyst under mild conditions. *Tetrahedron Lett.* **2017,** *58*, 3646-3649.
58. Colomer, I.; Chamberlain, A. E. R.; Haughey, M. B.; Donohoe, T. J., Hexafluoroisopropanol as a highly versatile solvent. *Nature Rev. Chem.* **2017,** *1*, 88.
59. Ilardi, E. A.; Stivala, C. E.; Zakarian, A., Hexafluoroisopropanol as a Unique Solvent for Stereoselective Iododesilylation of Vinylsilanes. *Org. Lett.* **2008,** *10* (9), 1727-1730.
60. Ravikumar, K. S.; Zhang, Y. M.; Bégué, J.-P.; Bonnet-Delpon, D., Role of Hexafluoro-2-propanol in Selective Oxidation of Sulfide to Sulfoxide: Efficient Preparation of Glycosyl Sulfoxides. *Eur. J. Org. Chem.* **1998,** *1998* (12), 2937-2940.
61. Eberson, L.; Hartshorn, M. P.; Persson, O.; Radner, F., Making radical cations live longer. *Chem. Commun.* **1996,** (18), 2105-2112.
62. Gaster, E.; Kozuch, S.; Pappo, D., Selective Aerobic Oxidation of Methylarenes to Benzaldehydes Catalyzed by N-Hydroxyphthalimide and Cobalt(II) Acetate in Hexafluoropropan-2-ol. *Angew. Chem. Int. Ed.* **2017,** *56* (21), 5912-5915.
63. Elsler, B.; Wiebe, A.; Schollmeyer, D.; Dyballa, K. M.; Franke, R.; Waldvogel, S. R., Source of Selectivity in Oxidative Cross-Coupling of

Aryls by Solvent Effect of 1,1,1,3,3,3-Hexafluoropropan-2-ol. *Chem. Eur. J.* **2015,** *21* (35), 12321-5.

64. Berkessel, A.; Adrio, J. A.; Hüttenhain, D.; Neudörfl, J. M., Unveiling the "Booster Effect" of Fluorinated Alcohol Solvents: Aggregation-Induced Conformational Changes and Cooperatively Enhanced H-Bonding. *J. Am. Chem. Soc.* **2006,** *128* (26), 8421-8426.

65. Eberson, L.; Hartshorn, M. P.; Persson, O., 1,1,1,3,3,3-Hexafluoropropan-2-ol as a solvent for the generation of highly persistent radical cations. *J. Chem. Soc., Perkin Trans. 2* **1995,** (9), 1735-1744.

66. Shuklov, I. A.; Dubrovina, N. V.; Börner, A., Fluorinated Alcohols as Solvents, Cosolvents and Additives in Homogeneous Catalysis. *Synthesis* **2007,** *2007*, 2925-2943.

67. Bégué, J.-P.; Bonnet-Delpon, D.; Crousse, B., Fluorinated Alcohols: A New Medium for Selective and Clean Reaction. *Synlett* **2004,** *2004*, 18-29.

68. Schubert, M.; Leppin, J.; Wehming, K.; Schollmeyer, D.; Heinze, K.; Waldvogel, S. R., Powerful fluoroalkoxy molybdenum(V) reagent for selective oxidative arene coupling reaction. *Angew. Chem. Int. Ed.* **2014,** *53* (9), 2494-7.

69. Floriani, C.; Calderazzo, F., Oxygen adducts of Schiff's base complexes of cobalt prepared in solution. *J. Chem. Soc. A* **1969,** (0), 946-953.

70. Hester, R.; Nour, E., Resonance Raman studies of transition metal peroxo complexes: 5—The oxygen carrier cobalt (II)-salen and its μ-peroxo complexes,[(L)(salen) Co] 2O2; L= DMSO, py, DMF, pyO and no L. *J. Raman Spec.* **1981,** *11* (2), 49-58.

71. Stynes, D. V.; Stynes, H. C.; Ibers, J. A.; James, B. R., Kinetics of the reaction of amine complexes of cobalt (II) protoporphyrin IX dimethyl ester with oxygen. Evidence for hydrogen bonding with coordinated oxygen. *J. Am. Chem. Soc.* **1973,** *95* (4), 1142-1149.

72. Tovrog, B. S.; Kitko, D. J.; Drago, R. S., Nature of the bound oxygen in a series of cobalt dioxygen adducts. *J. Am. Chem. Soc.* **1976,** *98* (17), 5144-5153.

73. Cook, A. K.; Sanford, M. S., Mechanism of the Palladium-Catalyzed Arene C–H Acetoxylation: A Comparison of Catalysts and Ligand Effects. *J. Am. Chem. Soc.* **2015,** *137* (8), 3109-3118.

74. King, A. E.; Ryland, B. L.; Brunold, T. C.; Stahl, S. S., Kinetic and Spectroscopic Studies of Aerobic Copper(II)-Catalyzed Methoxylation of Arylboronic Esters and Insights into Aryl Transmetalation to Copper(II). *Organometallics* **2012,** *31* (22), 7948-7957.

75. A., T.; L., O., Radical reactions in the co-ordination field of transition metals. VIII—σ-phenoxy and σ-cyclohexadienoneoxy radicals co-ordinated to cobalt (III) and their generation by tert-butylperoxy radicals or by molecular oxygen complexed to cobalt. *Org. Magn. Reson.* **1980,** *14* (2), 109-119.

76. Wang, Y.-H.; Pegis, M. L.; Mayer, J. M.; Stahl, S. S., Molecular Cobalt Catalysts for O2 Reduction: Low-Overpotential Production of H2O2 and Comparison with Iron-Based Catalysts. *J. Am. Chem. Soc.* **2017**.

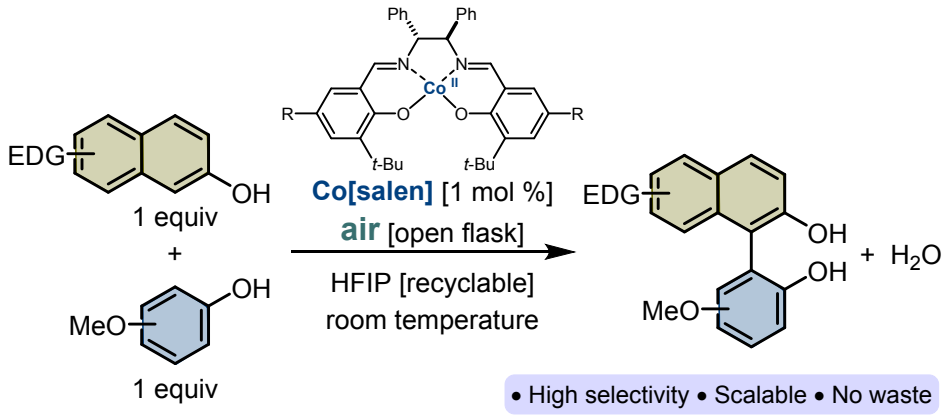
77. Anson, C. W.; Ghosh, S.; Hammes-Schiffer, S.; Stahl, S. S., Co(salophen)-Catalyzed Aerobic Oxidation of p-Hydroquinone: Mechanism and Implications for Aerobic Oxidation Catalysis. *J. Am. Chem. Soc.* **2016,** *138* (12), 4186-4193.

78. Wang, Y.-H.; Goldsmith, Z. K.; Schneider, P. E.; Anson, C. W.; Gerken, J. B.; Ghosh, S.; Hammes-Schiffer, S.; Stahl, S. S., Kinetic and Mechanistic Characterization of Low-Overpotential, H2O2-Selective Reduction of O2 Catalyzed by N2O2-Ligated Cobalt Complexes. *J. Am. Chem. Soc.* **2018,** *140* (34), 10890-10899.

79. Sharma, S.; Parumala, S. K. R.; Peddinti, R. K., Lewis Acid-Mediated Site-Selective Synthesis of Oxygenated Biaryls from Methoxyphenols and Electron-Rich Arenes. *J. Org. Chem.* **2017,** *82* (18), 9367-9383.

80. More, N. Y.; Jeganmohan, M., Oxidative Cross-Coupling of Two Different Phenols: An Efficient Route to Unsymmetrical Biphenols. *Org. Lett.* **2015,** *17* (12), 3042-5.

TOC:


Ph
Ph
N
N
Co II
R
O
O
R
t-Bu
t-Bu
EDG
OH
1 equiv
+
MeO
OH
1 equiv
Co[salen] [1 mol %]
air [open flask]
HFIP [recyclable]
room temperature
EDG
OH
OH
MeO
+ H2O
• High selectivity • Scalable • No waste