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FULL PAPER

Iron-Catalyzed Oxidative C–C Cross-Coupling Reaction of Tertiary Anilines with Hydroxyarenes Using Air as Sole Oxidant**

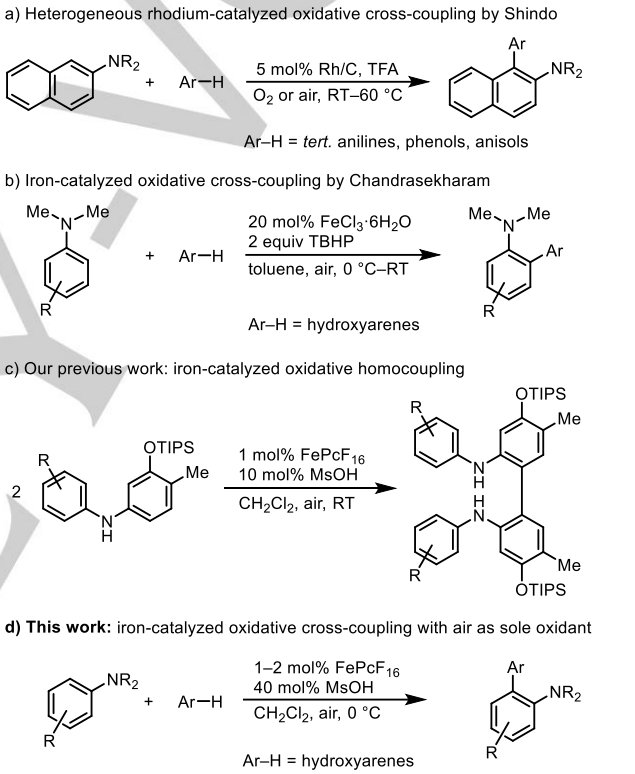
Alexander Purtsas,[a] Olga Kataeva,[b] and Hans-Joachim Knölker*[a]

Abstract: We describe a mild procedure for the oxidative C–C cross-coupling of tertiary anilines with phenols which provides the products generally in high yields and with excellent selectivity. The reaction is catalyzed by the hexadecafluorinated iron–phthalocyanine complex $FePcF_{16}$ in the presence of substoichiometric amounts of methanesulfonic acid and ambient air as sole oxidant.

Introduction

The development of transition metal-catalyzed cross-coupling reactions represents a useful and powerful tool for C–C bond formation. While noble metals have been used as catalysts for classical cross-coupling reactions (e.g., Heck, Negishi, Suzuki–Miyaura),[1] first-row transitions metals have been extensively studied over the past two decades due to their low cost, large abundance in the earth's crust and lower toxicity.[2] Thus for economic and ecological reasons, iron-catalyzed organic transformations have received most attention in recent years.[3] Moreover, the pre-functionalized substrates required for classical cross-coupling reactions lead to a low atom economy and the formation of by-products as unavoidable drawbacks. Oxidative (or dehydrogenative) cross-coupling reactions for C–C bond formation by activation of two C–H bonds are a highly useful synthetic alternative and represent a perfect example of a green and economical chemical process.[4,5] However, most of the iron-catalyzed oxidative coupling reactions require peroxides,[6–8] peracids,[9] or quinones[10] as stoichiometric oxidants to re-oxidize iron(II) to iron(III). Reactions using molecular oxygen or air as sole oxidant have rarely been explored.[11,12] Recently, Shindo and co-workers described a heterogeneous Rh-catalyzed aerobic oxidative cross-coupling for the synthesis of unsymmetrical biaryl compounds (Scheme 1).[13]

Iron as first-row transition metal is environmentally safe and thus has become a highly promising catalyst.[3] The groups of Li,[6] Chandrasekharam,[7] and Pappo[8] reported iron-catalyzed oxidative cross-coupling reactions which were achieved by re-oxidation of iron with different peroxides. Despite the recent advances, this process still remains a challenge because of the formation of homocoupling products and oxidized by-products resulting from stoichiometric amounts of a strong oxidant (e.g., peroxide).[6–8] Recently, we have developed an iron-catalyzed oxidative homocoupling by using the hexadecafluorinated iron–phthalocyanine complex $FePcF_{16}$ as catalyst (Figure 1) and air as re-oxidant.[14] This reaction has been applied to the homocoupling of diarylamines and 1- and 2-hydroxycarbazoles.[14,15] In contrast to most of the alternative iron-catalyzed oxidative cross-coupling reactions,[6–10] our procedure is using ambient air as sole oxidant.



Scheme 1. Biaryl bond formation by transition metal-catalyzed oxidative cross-coupling reactions. TFA = trifluoroacetic acid, TBHP = *tert*-butyl hydroperoxide, TIPS = Triisopropylsilyl.

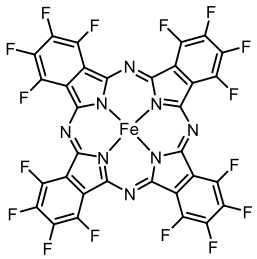


Figure 1. Structure of iron(II)–hexadecafluorophthalocyanine ($FePcF_{16}$).

Biaryl compounds represent key structural motifs in many biologically active natural products and pharmaceutical

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[**] Transition Metals in Organic Synthesis, Part 143. For Part 142, see: J. R. Suresh, G. Whitener, D. J. Bröcher, G. Theumer, I. Bauer, W. Massa, H.-J. Knölker, *Chem. Eur. J.* **2019**, *25*, 13759–13765.

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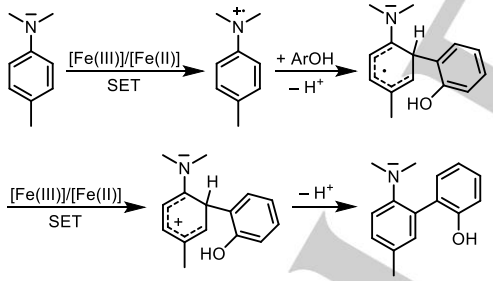
compounds and therefore, diverse methods for their synthesis have been established.[16] Herein, we report a mild and efficient synthesis of unsymmetrical biaryl compounds by an iron-catalyzed oxidative cross-coupling of tertiary anilines and hydroxyarenes in the presence of air.

Results and Discussion

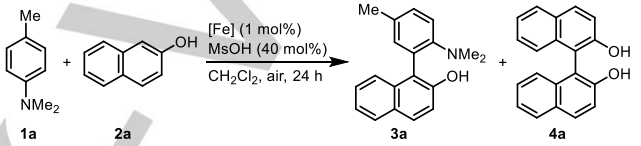
The oxidative homocoupling of diarylamines and hydroxycarbazoles has been achieved under mild reaction conditions and in high yields with catalytic amounts of iron(II)–hexadecafluorophthalocyanine ($FePcF_{16}$)[14,17] in the presence of methanesulfonic acid or acetic acid and ambient air as final oxidant.[14,15] Oxidative cross-coupling reactions with iron–phthalocyanine (FePc) or iron–porphyrin complexes as catalysts have been reported previously.[18,19] However in order to regenerate the catalytically active iron(III) complex, an oxidant (e.g. peroxide) had to be added in stoichiometric amounts.[8c,8d] Based on our previous studies,[14,15,20] we envisaged to develop an iron-catalyzed cross-coupling of anilines with phenols by using air as sole oxidant. Moreover, we wanted to avoid the need for a transient connection between the two reactants for cross coupling.[21] According to previous reports,[7,13,14,22] we hypothesized that the homocoupling of anilines could be suppressed by substituents causing a steric hindrance at the amino group. Reaction of a radical cation generated by SET oxidation of a tertiary aniline with a sterically less hindered phenol should preferentially form a C–C bond either via radical or electrophilic aromatic substitution (Scheme 2). A second SET and final proton loss with concomitant re-aromatization would lead to the cross-coupling product.



Scheme 2. Proposed mechanism for the iron-catalyzed oxidative cross-coupling of tertiary anilines and phenols.

Thus, we selected *N*,*N*-dimethyl-*p*-toluidine (**1a**) and 2-naphthol (**2a**) as model system for optimizing the reaction conditions of the iron-catalyzed oxidative cross-coupling. Various temperatures and iron catalysts have been tested for the reaction of **1a** with two equivalents of **2a** in dichloromethane under air (Table 1). Using catalytic amounts (1 mol%) of $FePcF_{16}$ and substoichiometric amounts (40 mol%) of methanesulfonic acid as additive at room temperature afforded the cross-coupling product **3a** in 64% yield along with the homocoupling product 1,1'-binaphthyl-2,2'-diol (BINOL) (**4a**)[23] in 9% yield (entry 1). The structure of **3a** was confirmed by an X-ray analysis (Figure 2). Variation of the reaction temperature (entries 2 and 3) showed that the cross-coupling reaction proceeds even better at 0 °C and provides the biaryl compound **3a** in 84% yield.[7a] In the following, we have performed several blank experiments in order to support our hypothesis of an iron(III)-catalyzed oxidative coupling which is promoted by the Brønsted acid additive. Reaction in the absence of iron catalyst gave no product at all (entry 4). The same result was obtained when the reaction was performed in the presence of 1 mol% of $FePcF_{16}$ but under argon instead of air (entry 5). These experiments confirm that $FePcF_{16}$ as well as its oxidation by air to the μ-oxo-diiron(III) complex are essential for the catalytic [Fe(III)]/[Fe(II)] cycle leading to the oxidative biaryl coupling.[14,18–20] The iron-catalyzed oxidative cross-coupling in the absence of methanesulfonic acid resulted in a significantly lower yield (17%) of the biaryl compound **3a** (entry 6) and an excess of a weaker acid (acetic acid) as additive led to **3a** in only 37% yield (entry 7).

Table 1. Optimization of the iron-catalyzed oxidative cross-coupling reaction.[a]



Entry	T (°C)	[Fe]	Yield **3a** (%)	Yield **4a** (%)
1	20	$FePcF_{16}$	64	9
2[b]	70	$FePcF_{16}$	trace	–
3	0	$FePcF_{16}$	84	18
4	0	–	–	–
5[c]	0	$FePcF_{16}$	–	–
6[d]	0	$FePcF_{16}$	17	27
7[e]	0	$FePcF_{16}$	37	26
8	0	FePc	66	20
9	0	$FePc(SO_3)_4H_3Na$	14	trace
10[f]	0	$FePc(SO_3)_4H_3Na$	20	–
11	0	$FePc(CO_2C_5H_{11})_8$	33	trace
12	0	$FePcCl_{16}$	–	–
13	0	FePpz	–	–
14	0	$FePpzCl_8$	–	–
15	0	$FePpz(Ph)_8$	–	–
16	0	$ClFeTPPF_{20}$	–	–
17	0	$FeCl_2$ (99.99%)	–	–

[a] **1a** (1.0 equiv), **2a** (2.0 equiv). [b] Solvent: $(CH_2Cl)_2$, 4 h. [c] Reaction under argon. [d] Reaction without MsOH. [e] Reaction with AcOH (3.0 equiv) instead of MsOH. [f] Solvent: H_2O. $FePcF_{16}$ = iron(II)–hexadecafluorophthalocyanine, FePc = iron(II)–phthalocyanine, $FePc(SO_3)_4H_3Na$ = iron(II)–phthalocyaninetetrasulfonic acid monosodium salt · x H_2O, FePpz = iron(II)–pyrazinoporphyrazine, ClFeTPP = tetraphenylporphyrin–iron(III) chloride (structures shown in the Supporting Information).

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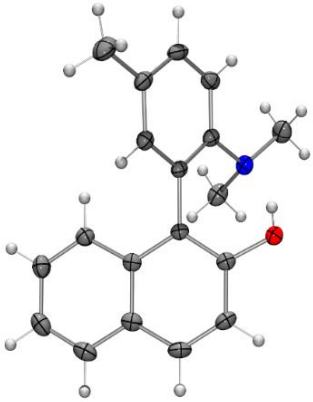
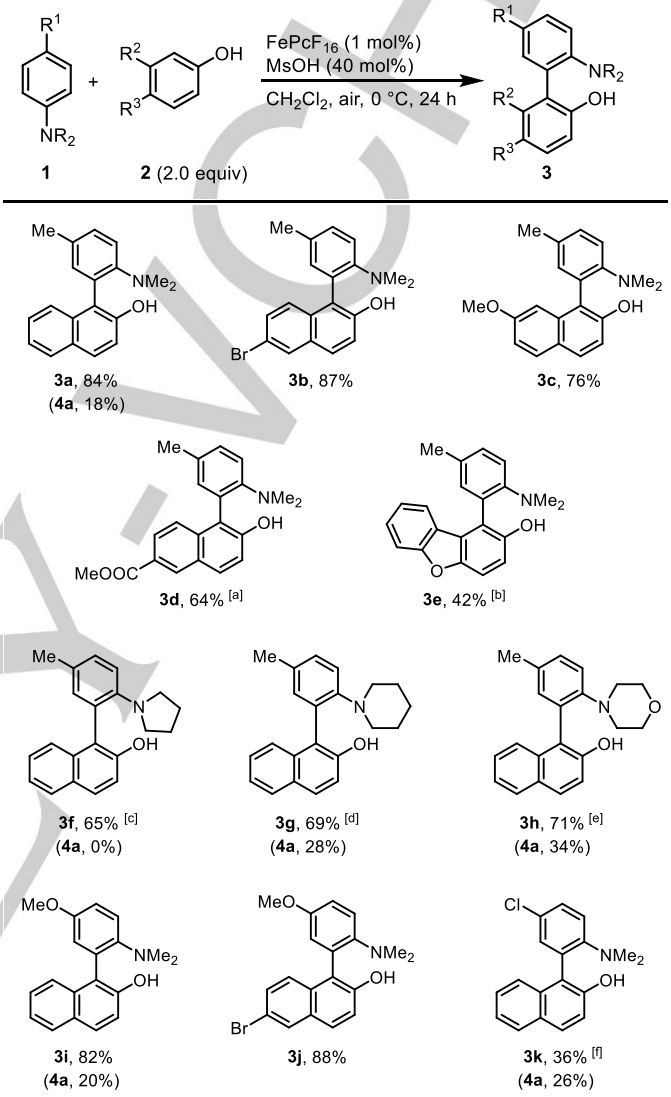


Figure 2. Molecular structure of the biaryl compound **3a** in the crystal (thermal ellipsoids are shown at the 50% probability level).

The unsubstituted iron(II)–phthalocyanine complex (FePc) afforded the cross-coupling product **3a** in 66% yield (entry 8), whereas other iron complexes led to either low yields of **3a** (entries 9–11) or no product formation at all (entries 12–17). The present results confirm previous findings that $FePcF_{16}$ has a higher activity compared to the parent complex FePc which is ascribed to the electronic effect of the fluorine atoms.[14,20,24] It is noteworthy that using the tetrasulfonato-substituted iron–phthalocyanine complex as catalyst, the oxidative cross coupling to **3a** could successfully be achieved in water as solvent (entry 10), albeit yet in low yield (20%).

Using the optimized reaction conditions, we have studied the synthetic scope of this cross-coupling reaction between various tertiary arylamines **1** and hydroxyarenes **2** (Table 2). As the simple monocyclic phenols we have tested gave no cross-coupling products, we focused on polycyclic hydroxyarenes as substrates. The iron-catalyzed oxidative coupling of *N*,*N*-dimethyl-*p*-toluidine (**1a**) with the substituted 2-naphthols **2a–d** provided selectively the corresponding cross-coupling products **3a–d** in 64–87% yield. Interestingly, a homocoupling of the 2-naphthol was observed only for the parent compound **2a**. The results emphasize the functional group tolerance of this reaction. The cross coupling of 2-hydroxydibenzofuran **2e** with **1a** appeared to be more difficult and afforded compound **3e** only in 42% yield. The structure of the 1-aryl-coupled dibenzofuran-2-ol **3e**, which was reported to show anti-TB activity and previously obtained as a red liquid,[7b] was confirmed by an X-ray analysis (Figure 3). The iron-catalyzed cross coupling of a range of tertiary anilines **1** with 2-naphthols **2** proceeded well and led to the corresponding products **3f–j** in high yields (65–88%). Whereas the reaction between *p*-chloro-*N*,*N*-dimethylaniline and 2-naphthol (**2a**) afforded the coupling product **3k** only in moderate yield.

Table 2. Synthesis of unsymmetrical biaryls **3** by iron-catalyzed oxidative cross-coupling of *N*,*N*-dialkylanilines **1** with various hydroxyarenes **2**.



[a] 0 °C to RT. [b] 2 mol% of $FePcF_{16}$. [c] Reaction time: 4 h. [d] 6.0 equiv of **2a**, 48 h. [e] 6.0 equiv of **2a**. [f] 4.0 equiv of **2a**.

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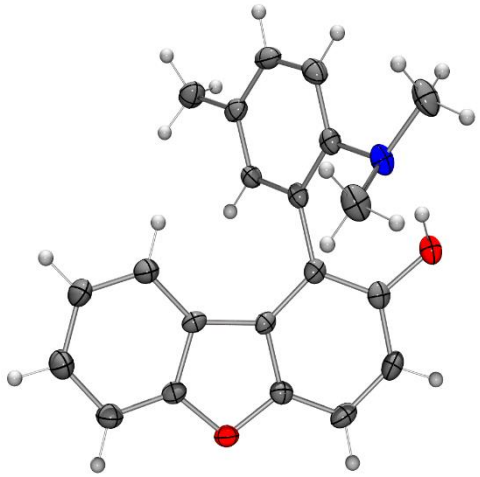
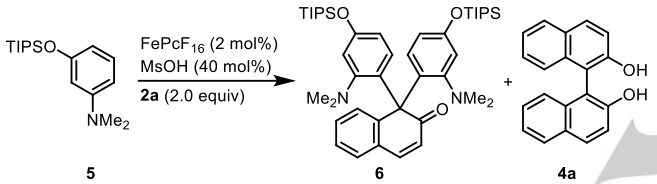
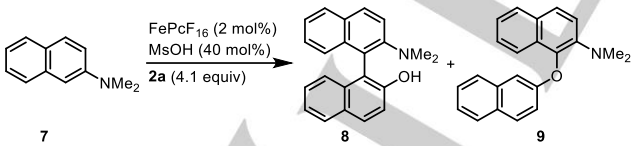


Figure 3. Molecular structure of the biaryl compound **3e** in the crystal (thermal ellipsoids are shown at the 50% probability level).



Scheme 3. Iron-catalyzed oxidative cross coupling of 2-naphthol (**2a**) with *N*,*N*-dimethyl-3-(triisopropylsilyloxy)aniline (**5**). Reaction conditions: CH_2Cl_2, air, 0 °C, 24 h; **6**: 37%, **4a**: 19% yield.

The *meta*-silyloxy-substituted *N*,*N*-dimethylaniline **5** is very electron-rich and highly reactive at the positions *ortho*/*para* to the dimethylamino group (Scheme 3). Thus, the iron-catalyzed reaction led to an oxidative coupling of two molecules of **5** at their sterically least hindered reactive position (C-6) with C-1 of 2-naphthol (**2a**) and provided compound **6** by dearomatization of one benzo ring.



Scheme 4. Iron-catalyzed oxidative cross-coupling of 2-naphthol (**2a**) with 2-*N*,*N*-dimethylaminonaphthalene (**7**). Reaction conditions: CH_2Cl_2, air, 0 °C, 24 h; **8**: 62%, **9**: 11%, **4a**: 20% yield.

The application of our iron-catalyzed C–C cross coupling to the reaction of 2-*N*,*N*-dimethylaminonaphthalene (**7**) with **2a** provided *N*,*N*-dimethyl-NOBIN (2-dimethylamino-2'-hydroxy-1,1'-binaphthyl) (**8**) (Scheme 4).[25] Compound **8** was obtained in 62% yield and confirmed by an X-ray crystal structure determination (Figure 4). NOBIN derivatives were shown to be highly useful as axially chiral biaryl ligands in asymmetric catalysis and efficient routes for their synthesis are still being searched.[25,26] Remarkably, this reaction afforded the C–O cross-coupled compound **9** as a by-product, thus indicating that ethers may be accessible by iron-catalyzed C–O cross-coupling reactions using air as oxidant.

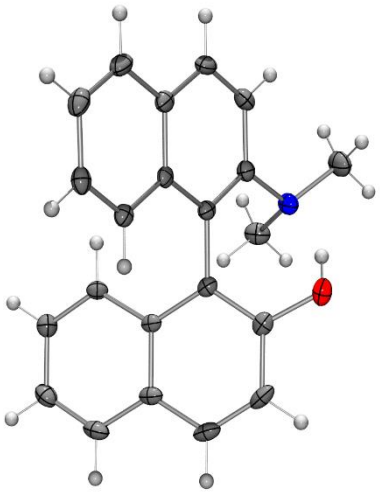


Figure 4. Molecular structure of *N*,*N*-dimethyl-NOBIN (**8**) in the crystal (thermal ellipsoids are shown at the 50% probability level).

Conclusions

We have developed an efficient and environmentally friendly method for the synthesis of unsymmetrical biaryl compounds by iron-catalyzed oxidative cross-coupling of tertiary anilines and hydroxyarenes. Our procedure requires 1–2 mol% of the hexadecafluorinated iron–phthalocyanine complex $FePcF_{16}$ as catalyst, substoichiometric amounts of methanesulfonic acid as additive, and air as the sole oxidant. The unsymmetrical biaryls are obtained with excellent selectivity. Further studies of this process and applications are in progress.

Experimental Section

All iron-catalyzed reactions were performed with non-dried solvents in an atmosphere of air unless stated otherwise. All other reactions were performed in oven-dried glassware with dry solvents. Dichloromethane and THF were dried by using a solvent-purification system (MBraun-SPS). Chemicals were used as received from commercial sources. Reaction mixtures were cooled by using a Lauda Compact Pl 1 cryostat. Automated flash column chromatography was performed with silica gel (Acros Organics; 0.035–0.070 mm) on a Büchi Sepacore system equipped with an UV monitor. TLC analysis was performed on TLC plates from Merck (60 F254) with UV light for visualization. Melting points were measured on a Gallenkamp MPD 350 melting-point apparatus. UV spectra were recorded on a PerkinElmer 25 UV/Vis spectrometer. Fluorescence spectra were measured on a Varian Cary Eclipse spectrophotometer. Wavelengths are reported in nm. IR spectra were recorded on a Thermo Nicolet Avatar 360 FTIR spectrometer using the attenuated total reflectance (ATR) method. Wavenumbers are reported in cm^{-1}. NMR spectra were recorded on Bruker DRX 500 and Avance III 600 spectrometers. Chemical shifts δ are reported in ppm with the solvent signal as an internal standard. The following abbreviations have been

used: s = singlet, d = doublet, t = triplet, q = quartet, quin = quintet, spt = septet, m = multiplet, and br = broad. EI mass spectra were recorded by GC-MS coupling on an Agilent Technologies 6890 N GC system equipped with a 5973 mass-selective detector (70 eV). ESI mass spectra were recorded on a Bruker Esquire LC mass spectrometer with an ion-trap detector. Positive and negative ions were detected. ESI-HRMS were recorded on a Waters Xevo G2-XS QTOF. Elemental analyses were measured on a EuroVector EuroEA3000 elemental analyser. Weight portions are given in percent. X-ray crystal structure analyses were performed with a Bruker Kappa Apex II CCD that was equipped with a 700 series Cryostream low temperature device from Oxford Cryosystems. SHELXS-97,[27] SADABS version 2.10,[28] SHELXL-97,[29] POV-Ray for Windows version 3.7.0.msvc10.win64, and ORTEP-3 for Windows[30] were used as software.

2-Acetyldibenzofuran: [7b] A solution of dibenzofuran (3.11 g, 18.5 mmol) in chloroform (30 mL) was added over a period of 10 min via syringe pump to a mixture of aluminum trichloride (2.99 g, 22.4 mmol), freshly distilled acetyl chloride (1.6 mL, 1.8 g, 22 mmol) and chloroform (30 mL) at room temperature under argon. After stirring over 45 min, the reaction mixture was poured into a mixture of ice water (100 mL) and 1 N HCl (50 mL). The aqueous layer was extracted three times with dichloromethane. The combined organic layers were dried over $MgSO_4$ and the solvent was removed in vacuo. Purification of the crude product by column chromatography on silica gel with isohexane/ethyl acetate (10:1) afforded 2-acetyldibenzofuran (3.47 g, 16.5 mmol, 89%) as a colorless solid. M.p. 66.5 °C; UV (MeOH): λ = 216, 238, 253, 287 nm; fluorescence (MeOH): λ_{ex} = 253 nm, λ_{em} = 415 nm; IR (ATR): $\tilde{\nu}$ = 3319, 3061, 3041, 2991, 2962, 2912, 2056, 2030, 2009, 1907, 1844, 1794, 1772, 1735, 1717, 1699, 1667, 1633, 1583, 1553, 1488, 1476, 1453, 1421, 1364, 1345, 1327, 1304, 1278, 1215, 1199, 1185, 1119, 1103, 1064, 1022, 955, 907, 893, 871, 841, 820, 769, 748, 729, 711, 652, 632 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$): δ = 2.72 (s, 3 H), 7.40 (td, J = 7.5, 0.9 Hz, 1 H), 7.51 (m, 1 H), 7.60 (m, 2 H), 8.01 (m, 1 H), 8.11 (dd, J = 8.5, 1.9 Hz, 1 H), 8.59 (dd, J = 1.8, 0.5 Hz, 1 H) ppm; ^{13}C NMR and DEPT (125 MHz, $CDCl_3$): δ = 26.94 (CH_3), 111.72 (CH), 112.09 (CH), 121.09 (CH), 121.75 (CH), 123.53 (CH), 123.87 (C), 124.71 (C), 128.11 (CH), 128.13 (CH), 132.65 (C), 157.00 (C), 159.06 (C), 197.46 (C=O) ppm; MS (EI): *m/z* (%) = 210 (42, $[M]^+$), 195 (100), 167 (35), 139 (68), 113 (10); elemental analysis (%) calcd for $C_{14}H_{10}O_2$: C 79.98, H 4.79; found: C 79.62, H 4.80.

2-Hydroxydibenzofuran (***2e***): [7b] Trifluoroacetic acid (1.8 mL, 2.7 g, 23 mmol) and then *m*-chloroperoxybenzoic acid (2.49 g, 14.4 mmol) were slowly added to a solution of 2-acetyldibenzofuran (1.16 g, 5.52 mmol) in dry dichloromethane (20 mL) at 0 °C. The reaction mixture was stirred at room temperature for 3 days and quenched with sat. aqueous iron(II) sulfate. The aqueous layer was extracted three times with dichloromethane. The combined organic layers were washed with a sat. aqueous solution of Na_2CO_3, then with water and dried over $MgSO_4$. After evaporation of the solvent, the crude product was suspended in MeOH (25 mL), sodium methoxide (1.26 g, 23.2 mmol) was added, the mixture was stirred at room temperature for 1 h, and quenched with 2 N HCl (15 mL). The aqueous layer was extracted three times with dichloromethane, the combined organic layers were dried over $MgSO_4$, and the solvent was removed in vacuo. Purification of the crude product by column chromatography on silica gel with isohexane/ethyl acetate (10:1) provided 2-hydroxydibenzofuran (**2e**) (779 mg, 4.23 mmol, 76% over two steps) as a colorless solid. M.p. 129 °C; UV (MeOH): λ = 236, 242, 252, 290, 308 nm; fluorescence (MeOH): λ_{ex} = 252 nm, λ_{em} = 354 nm; IR (ATR): $\tilde{\nu}$ = 3193 (br), 3061, 3035, 2011, 1974, 1934, 1894, 1845, 1740, 1635, 1598, 1574, 1475, 1440, 1420, 1397, 1361, 1332, 1306, 1279, 1210, 1188, 1165, 1148, 1117, 1100, 1015, 933, 898, 867, 840, 798, 740, 717, 621 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$): δ = 4.80 (br s, 1 H), 6.96 (dd, J = 8.8, 2.5 Hz, 1 H), 7.33 (td, J = 7.5, 1.1 Hz, 1 H), 7.38 (d, J = 2.5 Hz, 1 H), 7.43 (d, J = 8.8 Hz, 1 H), 7.45 (td, J = 7.8, 1.4 Hz, 1 H), 7.54 (d, J = 8.2 Hz, 1 H), 7.89 (d, J = 7.9 Hz, 1 H) ppm; ^{13}C NMR and DEPT (125 MHz, $CDCl_3$): δ = 106.40 (CH), 111.89 (CH), 112.25 (CH), 115.39 (CH), 120.84 (CH), 122.59 (CH), 124.35 (C), 125.19 (C), 127.44 (CH), 151.13 (C), 151.55 (C), 157.14 (C) ppm; MS (EI): *m/z* (%) = 184 (100, $[M]^+$), 155 (10), 128 (16), 102 (8), 92 (8); elemental analysis (%) calcd for $C_{12}H_8O_2$: C 78.25, H 4.38; found: C 78.59, H 4.21.

1-(4-Tolyl)pyrrolidine: 1,4-Dibromobutane (475 mg, 2.20 mmol) was added to a mixture of K_2CO_3 (692 mg, 5.01 mmol) and *para*-toluidine (214 mg, 2.00 mmol) in anhydrous DMF (10 mL) and the reaction mixture was heated to 80 °C for 24 h under inert atmosphere. Subsequently, the reaction mixture was cooled to room temperature and diluted with ethyl acetate and water. The layers were separated and the organic layer was extracted three times with 1 N HCl. The aqueous layers were combined, adjusted to pH 8 with 1 N NaOH, and then extracted three times with ethyl acetate. The combined organic layers were washed with brine and dried over $MgSO_4$. Evaporation of the solvent in vacuo and purification of the crude product by column chromatography on silica gel with isohexane/ethyl acetate (20:1) afforded 1-(4-tolyl)pyrrolidine (251 mg, 1.56 mmol, 78%) as a pale yellow solid. ^1H NMR (500 MHz, $CDCl_3$): δ = 2.00 (m, 4 H), 2.27 (s, 3 H), 3.27 (m, 4 H), 6.53 (d, J = 7.2 Hz, 2 H), 7.06 (d, J = 8.3 Hz, 2 H) ppm; ^{13}C NMR and DEPT (125 MHz, $CDCl_3$): δ = 20.41 (CH_3), 25.53 (2 CH_2), 47.98 (2 CH_2), 111.92 (2 CH), 124.52 (C), 129.76 (2 CH), 146.23 (C) ppm; MS (EI): *m/z* (%) = 161 (72, $[M]^+$), 160 (100), 118 (20), 105 (40); elemental analysis (%) calcd for $C_{11}H_{15}N$: C 81.94, H 9.38, N 8.69; found: C 82.24, H 9.39, N 8.66. For further analytical data, see ref. [31].

1-(4-Tolyl)piperidine and *4-(4-tolyl)morpholine* (by adaptation of a literature procedure[32]): A mixture of 4-bromotoluene (180 mg, 1.05 mmol), piperidine (86.1 mg, 1.01 mmol) or morpholine (87.2 mg, 1.00 mmol), $Pd(OAc)_2$ (2.7 mg, 12 µmol), RuPhos (9.5 mg, 20 µmol), and powdered NaO*t*Bu (124 mg, 1.29 mmol) was stirred at 110 °C overnight. After cooling to room temperature, the mixture was dissolved in CH_2Cl_2/H_2O (1:1), and the aqueous layer was extracted twice with CH_2Cl_2 (5 mL). The combined organic layers were dried over $MgSO_4$, the solvent was evaporated in vacuo, and the crude product was purified by column chromatography on silica gel with isohexane/ethyl acetate (20:1).

1-(4-Tolyl)piperidine (118 mg, 0.672 mmol, 67%) was obtained as a colorless oil. ^1H NMR (500 MHz, $CDCl_3$): δ = 1.56 (m, 2 H), 1.73 (m, 4 H), 2.27 (s, 3 H), 3.10 (t, J = 5.4 Hz, 4 H), 6.88 (d, J = 8.2 Hz, 2 H), 7.07 (d, J = 8.2 Hz, 2 H) ppm; ^{13}C NMR and DEPT (125 MHz, $CDCl_3$): δ = 20.58 (CH_3), 24.39 (CH_2), 26.04 (2 CH_2), 51.55 (2 CH_2), 117.17 (2 CH), 129.05 (C), 129.69 (2 CH), 150.36 (C) ppm; MS (EI): *m/z* (%): 175 (66, $[M]^+$), 174 (100), 146 (10), 119 (43), 91 (48), 65 (14); elemental analysis (%) calcd for $C_{12}H_{17}N$: C 82.23, H 9.78, N 7.99; found: C 82.22, H 9.50, N 8.14. For further analytical data, see ref. [31].

4-(4-Tolyl)morpholine (163 mg, 0.921 mmol, 92%) was obtained as a colorless solid. ^1H NMR (500 MHz, $CDCl_3$): δ = 2.29 (s, 3 H), 3.11 (m, 4 H), 3.87 (m, 4 H), 6.85 (d, J = 8.5 Hz, 2 H), 7.10 (d, J = 8.2 Hz, 2 H) ppm; ^{13}C NMR and DEPT (125 MHz, $CDCl_3$): δ = 20.55 (CH_3), 50.10 (2 CH_2), 67.08 (2 CH_2), 116.21 (2 CH), 129.72 (C), 129.84 (2 CH), 149.24 (C) ppm; MS (EI): *m/z* (%) = 177 (45, $[M]^+$), 119 (100), 91 (40), 65 (13); HRMS (ESI) calcd for $C_{11}H_{16}NO^+$ ($[M+H]^+$): 178.1232; found: 178.1230. For further analytical data, see ref. [31].

4-Methoxy-N,N-*dimethylaniline*, *4-chloro*-N,N-*dimethylaniline*, and *2*-N,N-*dimethylaminonaphthalene* (***7***): Aqueous formaldehyde (37%, 12.2 mL, 164 mmol) was slowly added to a solution of *p*-anisidine (1.28 g, 10.4 mmol) or *p*-chloroaniline (1.32 g, 10.4 mmol) or naphthalen-2-amine (1.49 g, 10.4 mmol) in dry THF (110 mL) and the solution was stirred at room temperature. After 15 min, sodium cyanoborohydride (4.63 g, 73.7 mmol) was added and the mixture was stirred at room temperature

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for 15 min. Subsequently, acetic acid (1.7 mL) was added dropwise while keeping the reaction at room temperature. The reaction mixture was stirred at room temperature for 2–4 h until all starting material was consumed as indicated by TLC and quenched with 2 N NaOH (pH >7). The mixture was extracted three times with ethyl acetate and the combined organic layers were dried over $MgSO_4$. After evaporation of the solvent in vacuo, the crude product was purified by column chromatography on silica gel with isohexane/ethyl acetate (gradient elution from 15:1 to 10:1).

4-Methoxy-*N*,*N*-dimethylaniline (1.21 g, 8.01 mmol, 77%) was obtained as a grey solid. M.p. 35 °C; UV (MeOH): λ = 246, 306 nm; fluorescence (MeOH): λ_{ex} = 246 nm, λ_{em} = 373 nm; IR (ATR): $\tilde{\nu}$ = 3071, 3038, 2993, 2949, 2884, 2831, 2798, 1851, 1613, 1574, 1558, 1539, 1513, 1441, 1341, 1300, 1244, 1225, 1180, 1129, 1064, 1034, 945, 816, 801, 681 cm^{-1}; ^1H NMR (600 MHz, $CDCl_3$): δ = 2.88 (s, 6 H), 3.77 (s, 3 H), 6.78 (d, *J* = 8.7 Hz, 2 H), 6.86 (d, *J* = 8.7 Hz, 2 H) ppm; ^{13}C NMR and DEPT (151 MHz, $CDCl_3$): δ = 42.03 (2 CH_3), 55.90 (CH_3), 114.80 (2 CH), 115.15 (2 CH), 145.81 (C), 152.26 (C) ppm; MS (EI): *m/z* (%) = 151 (58, $[M]^+$), 136 (100), 120 (11), 108 (22), 92 (10), 65 (12); elemental analysis (%) calcd for $C_9H_{13}NO$: C 71.49, H 8.67, N 9.26; found: C 71.45, H 8.64, N 9.34.

4-Chloro-*N*,*N*-dimethylaniline (1.47 g, 9.45 mmol, 91%) was obtained as a colorless solid. M.p. 43.5 °C; UV (MeOH): λ = 259, 313 nm; fluorescence (MeOH): λ_{ex} = 259 nm, λ_{em} = 364 nm; IR (ATR): $\tilde{\nu}$ = 3091, 2989, 2886, 2853, 2803, 2109, 1956, 1865, 1755, 1613, 1590, 1559, 1490, 1442, 1340, 1222, 1188, 1164, 1124, 1093, 1060, 994, 941, 806, 758, 697 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$): δ = 2.93 (s, 6 H), 6.65 (d, *J* = 8.5 Hz, 2 H), 7.18 (d, *J* = 8.8 Hz, 2 H) ppm; ^{13}C NMR and DEPT (125 MHz, $CDCl_3$): δ = 40.86 (2 CH_3), 113.83 (2 CH), 121.60 (C), 128.95 (2 CH), 149.26 (C) ppm; MS (EI): *m/z* (%) = 155 (78, $[M]^+$),154 (100), 139 (23), 118 (12), 111 (17), 77 (14), 75 (19), 50 (11), 42 (13); elemental analysis (%) calcd for $C_8H_{10}ClN$: C 61.74, H 6.48, N 9.00; found: C 61.82, H 6.47, N 9.06.

2-*N*,*N*-Dimethylaminonaphthalene (**7**) (1.65 g, 9.62 mmol, 93%) was obtained as a pale yellow solid. M.p. 43.5 °C; UV (MeOH): λ = 214, 247, 287, 297, 352 nm; fluorescence (MeOH): λ_{ex} = 247 nm, λ_{em} = 409 nm; IR (ATR): $\tilde{\nu}$ = 3048, 3021, 2975, 2889, 2869, 2801, 1736, 1699, 1624, 1595, 1559, 1540, 1507, 1484, 1440, 1365, 1328, 1277, 1241, 1198, 1145, 1062, 1014, 956, 865, 824, 803, 740, 614 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$): δ = 3.06 (s, 6 H), 6.97 (br s, 1 H), 7.19 (dd, *J* = 8.8, 2.5 Hz, 1 H), 7.23 (m, 1 H), 7.38 (td, *J* = 7.6, 1 Hz, 1 H), 7.67 (d, *J* = 8.2 Hz, 1 H), 7.70 (d, *J* = 8.4 Hz, 1 H), 7.72 (d, *J* = 8.5 Hz, 1 H) ppm; ^{13}C NMR and DEPT (125 MHz, $CDCl_3$): δ = 41.21 (2 CH_3), 107.02 (CH), 116.63 (CH), 122.36 (CH), 126.38 (2 CH), 127.17 (C), 127.58 (CH), 128.87 (CH), 135.03 (C) 148.58 (C) ppm; MS (EI): *m/z* (%) = 171 (100, $[M]^+$), 170 (97), 155 (22), 154 (11), 129 (12), 128 (36), 127 (30), 126 (11), 115 (12), 77 (11); elemental analysis (%) calcd for $C_{12}H_{13}N$: C 84.17, H 7.65, N 8.18; found: C 84.46, H 7.73, N 8.24.

N,N-*Dimethyl-3-(triisopropylsilyloxy)aniline* (***5***): Triisopropylsilyl triflate (2.70 mL, 3.08 g, 10.1 mmol) was added dropwise to a solution of *N*,*N*-dimethyl-3-aminophenol (1.00 g, 7.29 mmol) and triethylamine (2.70 mL, 1.97 g, 19.5 mmol) in dichloromethane (62 mL) at 0 °C under an argon atmosphere. After stirring of the solution for 22 h at room temperature, water (20 mL) was added and the aqueous layer was extracted three times with dichloromethane. The combined organic layers were dried over $MgSO_4$ and the solvent was removed. Purification of the crude product by column chromatography on silica gel with isohexane/ethyl acetate (15:1) provided compound **5** (2.08 g, 7.09 mmol, 97%) as a reddish oil. UV (MeOH): λ = 212, 253, 296 nm; fluorescence (MeOH): λ_{ex} = 212 nm, λ_{em} = 348 nm; IR (ATR): $\tilde{\nu}$ = 2943, 2889, 2865, 2800, 1604, 1573, 1499, 1452, 1396, 1353, 1248, 1168, 1151, 1062, 1002, 925, 881, 827, 783, 756, 681 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$): δ = 1.11 (d, *J* = 7.6 Hz, 18 H), 1.26 (m, 3 H), 2.91 (s, 6 H), 6.29 (m, 2 H), 6.35 (d, *J* = 7.9 Hz, 1 H), 7.06 (t, *J* = 8.0 Hz, 1 H) ppm; ^{13}C NMR and DEPT (125 MHz, $CDCl_3$): δ = 12.88 (6 CH_3), 18.13 (3 CH), 40.91 (2 CH_3), 104.95 (CH), 106.08 (CH), 108.64 (C), 129.64 (2 CH), 157.11 (C) ppm; ESI-MS (+25 V): *m/z* = 294.3 $[M+H]^+$; elemental analysis (%) calcd for $C_{17}H_{31}NOSi$: C 69.56, H 10.65, N 4.77; found: C 69.40, H 10.87, N 5.00.

1,2,3,4,8,9,10,11,15,16,17,18,22,23,24,25-Hexadecafluorophthalocyaninato–iron(II): (for experimental details, see refs. [14,17,20]); $FePcF_{16}$ (70% yield) was obtained as a dark blue to violet powder. IR (ATR): $\tilde{\nu}$ = 3636, 3180, 2645, 2436, 2043, 1772, 1733, 1682, 1618, 1559, 1520, 1484, 1459, 1399, 1318, 1266, 1147, 958, 944, 837, 751, 655 cm^{-1}; ESI-MS (+100 V): *m/z* = 857.1 $[M+H]^+$; ESI-MS (–50 V): *m/z* = 914.7 $[M+OAc]^-$, 886.7 $[M+OMe]^-$; elemental analysis (%) calcd for $C_{32}F_{16}FeN_8$: C 44.89, N 13.09; found: C 44.33, N 13.18.

General procedure for the iron-catalyzed oxidative cross-coupling: A 0.1 M solution of the tertiary aniline **1** (1.0 equiv) in dichloromethane (2–6 mL) was added to a mixture of the hydroxyarene **2** (2.0 equiv), methanesulfonic acid (40 mol%), and $FePcF_{16}$ (1.0 mol%). The reaction mixture was vigorously stirred at 0 °C for 4–48 h under air and then quenched with a sat. aqueous solution of Na_2CO_3 (5 mL). The aqueous layer was extracted three times with dichloromethane and the combined organic layers were evaporated in vacuo. Purification of the crude product by automated column chromatography on silica gel provided the biaryl compound **3**.

1-(2-(Dimethylamino)-5-methylphenyl)naphthalen-2-ol (***3a***): *N*,*N*-Dimethyl-*p*-toluidine (**1a**) (83.1 mg, 615 µmol), dichloromethane (6 mL), 2-naphthol (**2a**) (173 mg, 1.20 mmol), methanesulfonic acid (23.2 mg, 241 µmol), $FePcF_{16}$ (5.1 mg, 6.0 µmol). Reaction time: 24 h, column chromatography (isohexane/ethyl acetate, 1–3%, 1 h, 3–15%, 0.5 h, 15%, 20 min). **3a** (144 mg, 519 µmol, 84%) was obtained as a pale yellow solid. M.p. 166.5 °C; UV (MeOH): λ = 231, 286, 333 nm; fluorescence (MeOH): λ_{ex} = 231 nm, λ_{em} = 422 nm; IR (ATR): $\tilde{\nu}$ = 3028, 2995, 2955, 2916, 2873, 2842, 2795, 1892, 1619, 1590, 1558, 1497, 1458, 1397, 1358, 1334, 1296, 1231, 1177, 1156, 1130, 1093, 1037, 1015, 955, 925, 891, 868, 816, 751, 720, 688, 662, 634 cm^{-1}; ^1H NMR (600 MHz, $CDCl_3$): δ = 2.33 (s, 3 H), 2.68 (s, 6 H), 7.19 (m, 1 H), 7.22 (m, 2 H), 7.28 (d, *J* = 8.7 Hz, 1 H), 7.34 (m, 1 H), 7.38 (m, 1 H), 7.78 (d, *J* = 8.8 Hz, 1 H), 7.80 (d, *J* = 8.5 Hz, 1 H), 7.82 (dd, *J* = 8.4, 1.1 Hz, 1 H), 10.15 (br s, 1 H) ppm; ^{13}C NMR and DEPT (151 MHz, $CDCl_3$): δ = 20.80 (CH_3), 43.95 (2 CH_3), 118.23 (CH), 120.82 (CH), 121.07 (C), 123.20 (CH), 125.48 (CH), 126.20 (CH), 128.28 (CH), 129.19 (CH), 129.45 (CH), 130.05 (C), 130.66 (C), 132.82 (C), 133.51 (C), 135.87 (CH), 147.50 (C), 152.27 (C) ppm; ESI-MS (+10 V): *m/z* = 278.1 $[M+H]^+$; elemental analysis (%) calcd for $C_{19}H_{19}NO$: C 82.28, H 6.90, N 5.05; found: C 81.90, H 7.00, N 4.89.

1,1'-Binaphthyl-2,2'-diol (BINOL) (**4a**): (30.5 mg, 107 µmol, 18%) was obtained as a brown solid. ^1H NMR (600 MHz, $CDCl_3$): δ = 5.06 (br s, 2 H), 7.16 (d, *J* = 8.3 Hz, 2 H), 7.31 (td, *J* = 7.7, 1.1 Hz, 2 H), 7.38 (m, 4 H), 7.90 (d, *J* = 8.3 Hz, 2 H), 7.98 (d, *J* = 9.0 Hz, 2 H) ppm; ^{13}C NMR and DEPT (151 MHz, $CDCl_3$): δ = 110.94 (2 C), 117.90 (2 CH), 124.19 (2 CH), 124.35 (2 CH), 127.64 (2 CH), 128.57 (2 CH), 129.61 (2 C), 131.60 (2 CH), 133.54 (2 C), 152.89 (2 C) ppm; ESI-MS (+25 V): *m/z* = 287.2 $[M+H]^+$. For further analytical data, see ref. [23].

Crystallographic data for compound ***3a***: $C_{19}H_{19}NO$, *M* = 277.35 g mol^{-1}, crystal size 0.250 × 0.300 × 0.330 mm^3, monoclinic, space group $P2_1/c$, *a* = 9.2180(17), *b* = 8.8167(17), *c* = 18.835(4) Å, *V* = 1491.1(5) $Å^3$, Z = 4, ρ_{calcd} = 1.235 g cm^{-3}, μ = 0.076 mm^{-1}, λ = 0.71073 Å, *T* = 120(2) K, θ range = 2.22–28.49°, reflections collected 17145, independent reflections 3766 (R_{int} = 0.0477), 197 parameters. The structure was solved by direct methods and refined by full-matrix least-squares on F^2; final *R* indices [$I>2\sigma(I)$] R_1 = 0.0462 and wR_2 = 0.1105 maximal residual electron density 0.282 e $Å^{-3}$. CCDC 1963408 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre.

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6-Bromo-1-(2-(dimethylamino)-5-methyl-phenyl)naphthalen-2-ol ***(3b)***: *N*,*N*-Dimethyl-*p*-toluidine (**1a**) (81.0 mg, 599 µmol), dichloromethane (6 mL), 6-bromo-2-naphthol (268 mg, 1.20 mmol), methanesulfonic acid (23.1 mg, 240 µmol), $FePcF_{16}$ (5.1 mg, 6.0 µmol). Reaction time: 24 h, column chromatography (isohexane/ethyl acetate, 2–6%, 1 h, 6–15%, 0.5 h, 15–20%, 20 min). Biaryl **3b** (186 mg, 522 µmol, 87%) was obtained as a brownish yellow solid. M.p. 189.5 °C; UV (MeOH): λ = 236, 291, 343 nm; fluorescence (MeOH): λ_{ex} = 343 nm, λ_{em} = 423 nm; IR (ATR): $\tilde{\nu}$ = 3064, 3041, 3025, 2988, 2949, 2912, 2876, 2840, 2797, 1908, 1585, 1490, 1449, 1417, 1358, 1334, 1295, 1278, 1233, 1175, 1134, 1098, 1074, 1036, 952, 923, 897, 816, 755, 694, 670 cm^{-1}; ^1H NMR (600 MHz, $CDCl_3$): δ = 2.32 (s, 3 H), 2.66 (s, 6 H), 7.17 (s, 1 H), 7.18 (d, *J* = 5.6 Hz, 1 H), 7.23 (dd, *J* = 8.3, 1.9 Hz, 1 H), 7.28 (d, *J* = 8.7 Hz, 1 H), 7.43 (dd, *J* = 9.0, 2.3 Hz, 1 H), 7.68 (d, *J* = 3.8 Hz, 1 H), 7.69 (d, *J* = 4.1 Hz, 1 H), 7.96 (d, *J* = 2.3 Hz, 1 H), 10.27 (br s, 1 H) ppm; ^{13}C NMR and DEPT (151 MHz, $CDCl_3$): δ = 20.78 (CH_3), 43.87 (2 CH_3), 116.88 (C), 118.32 (CH), 121.44 (C), 121.96 (CH), 127.44 (CH), 128.42 (CH), 129.35 (CH), 129.44 (CH), 130.12 (CH), 130.22 (C), 131.23 (C), 132.11 (C), 132.82 (C), 135.72 (CH), 147.73 (C), 152.66 (C) ppm; ESI-MS (+10 V): *m/z* = 356.1 $[M+H]^+$; ESI-MS (–10 V): *m/z* = 354.2 $[M–H]^–$; elemental analysis (%) calcd for $C_{19}H_{18}BrNO$: C 64.06, H 5.09, N 3.93; found: C 63.75, H 5.08, N 3.91.

1-(2-(Dimethylamino)-5-methylphenyl)-7-methoxynaphthalen-2-ol ***(3c)***: *N*,*N*-Dimethyl-*p*-toluidine (**1a**) (81.1 mg, 599 µmol), dichloromethane (6 mL), 7-methoxy-2-naphthol (209 mg, 1.20 mmol), methanesulfonic acid (23.1 mg, 240 µmol), $FePcF_{16}$ (5.1 mg, 6.0 µmol). Reaction time: 24 h, column chromatography (isohexane/ethyl acetate, 2–8%, 1 h, 8–15%, 0.5 h, 15–20%, 20 min). Biaryl **3c** (141 mg, 459 µmol, 76%) was obtained as a beige solid. M.p. 116 °C; UV (MeOH): λ = 238, 301 nm; fluorescence (MeOH): λ_{ex} = 301 nm, λ_{em} = 412 nm; IR (ATR): $\tilde{\nu}$ = 2995, 2958, 2932, 2916, 2873, 2840, 2797, 1988, 1904, 1733, 1697, 1619, 1559, 1493, 1454, 1397, 1373, 1358, 1327, 1297, 1263, 1230, 1214, 1175, 1160, 1136, 1092, 1038, 1018, 980, 933, 877, 863, 841, 817, 751, 679, 662, 640, 615 cm^{-1}; ^1H NMR (600 MHz, $CDCl_3$): δ = 2.33 (s, 3 H), 2.70 (s, 6 H), 3.76 (s, 3 H), 7.01 (dd, *J* = 2.6, 1.0 Hz, 1 H), 7.10 (m, 1 H), 7.14 (d, *J* = 8.7 Hz, 1 H), 7.22 (m, 2 H), 7.30 (s, 1 H), 7.70 (d, *J* = 9.0 Hz, 1 H), 7.72 (d, *J* = 8.7 Hz, 1 H), 10.09 (br s, 1 H) ppm; ^{13}C NMR and DEPT (151 MHz, $CDCl_3$): δ = 20.75 (CH_3), 44.08 (2 CH_3), 55.38 (CH_3), 104.91 (CH), 115.00 (CH), 118.29 (CH), 118.54 (CH), 119.94 (C), 125.39 (C), 129.24 (CH), 129.37 (CH), 129.88 (CH), 130.72 (C), 133.34 (C, HMBC), 134.76 (C), 135.44 (CH), 146.93 (C), 152.86 (C), 158.16 (C) ppm; ESI-MS (+10 V): *m/z* = 308.1 $[M+H]^+$; ESI-MS (–10 V): *m/z* = 305.8 $[M–H]^–$; elemental analysis (%) calcd for $C_{20}H_{21}NO_2$: C 78.15, H 6.89, N 4.56; found: C 77.89, H 6.92, N 4.53.

Methyl 5-(2-(dimethylamino)-5-methylphenyl)-6-hydroxy-2-naphthoate ***(3d)***: *N*,*N*-Dimethyl-*p*-toluidine (**1a**) (81.0 mg, 600 µmol), dichloromethane (6 mL), methyl 6-hydroxy-2-naphthoate (245 mg, 1.21 mmol), methanesulfonic acid (23.1 mg, 240 µmol), $FePcF_{16}$ (5.1 mg, 6.0 µmol). The reaction mixture was warmed up slowly from 0 °C to room temperature. Reaction time: 24 h, column chromatography (isohexane/ethyl acetate, 3–7%, 1.5 h, 7–15%, 0.5 h). Biaryl **3d** (128 mg, 382 µmol, 64%) was obtained as a reddish solid. M.p. 112 °C; UV (MeOH): λ = 246, 303 nm; fluorescence (MeOH): λ_{ex} = 246 nm, λ_{em} = 441 nm; IR (ATR): $\tilde{\nu}$ = 3025, 2953, 2909, 2876, 2839, 2794, 1917, 1844, 1792, 1771, 1733, 1709, 1653, 1635, 1618, 1593, 1495, 1472, 1436, 1366, 1341, 1291, 1230, 1196, 1176, 1154, 1135, 1106, 1092, 1038, 975, 957, 929, 909, 819, 790, 753, 694, 674 cm^{-1}; ^1H NMR (600 MHz, $CDCl_3$): δ = 2.33 (s, 3 H), 2.67 (s, 6 H), 3.97 (s, 3 H), 7.18 (m, 2 H), 7.24 (dd, *J* = 8.3, 1.3 Hz, 1 H), 7.32 (d, *J* = 8.7 Hz, 1 H), 7.84 (m, 1 H), 7.88 (d, *J* = 8.7 Hz, 1 H), 7.94 (dd, *J* = 9.0, 1.5 Hz, 1 H), 8.57 (d, *J* = 1.5 Hz, 1 H) ppm; ^{13}C NMR and DEPT (151 MHz, $CDCl_3$): δ = 20.78 (CH_3), 43.89 (2 CH_3), 52.23 (CH_3), 118.34 (CH), 121.30 (C), 121.67 (CH), 124.72 (C), 125.62 (CH), 125.68 (CH), 128.99 (C), 129.47 (CH), 130.23 (C), 130.86 (CH), 131.43 (CH), 132.94 (C), 135.81 (CH), 136.06 (C), 147.59 (C), 154.58 (C), 167.57 (C=O) ppm; ESI-MS (+10 V): *m/z* = 336.2 $[M+H]^+$; ESI-MS (–10 V): *m/z* = 333.9 $[M–H]^–$; elemental analysis (%) calcd for $C_{21}H_{21}NO_3$: C 75.20, H 6.31, N 4.18; found: C 74.92, H 6.51, N 4.09.

1-*(2-(Dimethylamino)-5-methylphenyl)dibenzo[*b,d*]furan-2-ol* ***(3e)****:* *N*,*N*-Dimethyl-*p*-toluidine (**1a**) (81.3 mg, 601 µmol), dichloromethane (6 mL), 2-hydroxydibenzofuran (**2e**) (223 mg, 1.21 mmol), methanesulfonic acid (23.2 mg, 241 µmol), $FePcF_{16}$ (10.3 mg, 12.0 µmol, 2 mol%). Reaction time: 24 h, column chromatography (isohexane/ethyl acetate, 1–5%,1 h, 5–10%, 45 min, 10–15%, 15 min). Biaryl **3e** (80.8 mg, 255 µmol, 42%) was obtained as a light pink solid. M.p. 115.5 °C; UV (MeOH): λ = 218, 292 nm; fluorescence (MeOH): λ_{ex} = 292 nm, λ_{em} = 400 nm; IR (ATR): $\tilde{\nu}$ = 3002, 2959, 2919, 2873, 2839, 2793, 1907, 1845, 1727, 1613, 1559, 1542, 1499, 1469, 1440, 1423, 1367, 1339, 1299, 1259, 1213, 1185, 1156, 1130, 1112, 1083, 1064, 1041, 1017, 963, 932, 903, 887, 860, 840, 826, 805, 783, 751, 694, 644, 629 cm^{-1}; ^1H NMR (600 MHz, $CDCl_3$): δ = 2.33 (s, 3 H), 2.71 (s, 6 H), 7.09 (m, 1 H), 7.17 (d, *J* = 8.7 Hz, 1 H), 7.21 (d, *J* = 8.3 Hz, 1 H), 7.28 (dd, *J* = 8.3, 1.5 Hz, 1 H), 7.39 (m, 2 H), 7.48 (m, 2 H), 7.55 (d, *J* = 8.3 Hz, 1 H), 9.89 (br s, 1 H) ppm; ^{13}C NMR and DEPT (151 MHz, $CDCl_3$): δ = 20.68 (CH_3), 44.14 (2 CH_3), 111.68 (CH), 111.80 (CH), 118.19 (CH), 118.75 (CH), 121.94 (CH), 122.25 (CH), 122.35 (C), 122.42 (C), 124.76 (C), 126.72 (CH), 129.85 (CH), 130.14 (C), 133.22 (C), 134.72 (CH), 147.09 (C), 150.73 (C), 151.54 (C), 157.13 (C) ppm; ESI-MS (+10 V): *m/z* = 318.1 $[M+H]^+$; elemental analysis (%) calcd for $C_{21}H_{19}NO_2$: C 79.47, H 6.03, N 4.41; found: C 79.18, H 6.31, N 4.35.

Crystallographic data for compound ***3e***: $C_{21}H_{19}NO_2$, *M* = 317.37 g mol^{-1}, crystal size 0.486 × 0.628 × 0.673 mm^3, orthorhombic, space group $P2_12_12_1$, *a* = 7.9372(6), *b* = 12.2884(9), *c* = 17.0584(13) Å, *V* = 1663.8(2) $Å^3$, Z = 4, ρ_{calcd} = 1.267 g cm^{-3}, μ = 0.081 mm^{-1}, λ = 0.71073 Å, *T* = 150(2) K, θ range = 2.91–28.00°, reflections collected 12725, independent reflections 4017 (R_{int} = 0.0879), 224 parameters. The structure was solved by direct methods and refined by full-matrix least-squares on F^2; final *R* indices [$I>2\sigma(I)$] R_1 = 0.0472 and wR_2 = 0.0876 maximal residual electron density 0.199 e $Å^{-3}$. CCDC 1963409 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre.

1-(5-Methyl-2-(pyrrolidin-1-yl)phenyl)naphthalen-2-ol ***(3f)****:* 1-(4-Tolyl)pyrrolidine (64.0 mg, 397 µmol), dichloromethane (4 mL), 2-naphthol (**2a**) (116 mg, 805 µmol), methanesulfonic acid (15.5 mg, 161 µmol), $FePcF_{16}$ (3.4 mg, 4.0 µmol). Reaction time: 4 h, column chromatography (isohexane/ethyl acetate, 1–5%, 1 h, 5–15%, 20 min). Biaryl **3f** (79.0 mg, 260 µmol, 65%) was obtained as a pale reddish solid. M.p. 145 °C; UV (MeOH): λ = 231, 323 nm; fluorescence (MeOH): λ_{ex} = 323 nm, λ_{em} = 480 nm; IR (ATR): $\tilde{\nu}$ = 3051, 3032, 2970, 2922, 2876, 2853, 1740, 1621, 1591, 1499, 1466, 1396, 1335, 1297, 1276, 1221, 1186, 1154, 1110, 1091, 1041, 1015, 956, 933, 890, 815, 787, 753, 674, 633 cm^{-1}; ^1H NMR (600 MHz, $CDCl_3$): δ = 1.79 (m, 4 H), 2.32 (s, 3 H), 2.83 (m, 2 H), 3.08 (m, 2 H), 7.08 (d, *J* = 8.3 Hz, 1 H), 7.18 (m, 2 H), 7.25 (d, *J* = 8.7 Hz, 1 H), 7.35 (m, 1 H), 7.40 (m, 1 H), 7.78 (d, *J* = 9.0 Hz, 1 H), 7.82 (d, *J* = 7.5 Hz, 1 H), 7.85 (d, *J* = 8.7 Hz, 1 H), 8.73 (br s, 1 H) ppm; ^{13}C NMR and DEPT (151 MHz, $CDCl_3$): δ = 20.64 (CH_3), 24.64 (2 CH_2), 51.07 (2 CH_2), 116.59 (CH), 119.68 (CH), 122.13 (C), 123.19 (CH), 125.83 (CH), 126.17 (CH), 127.22 (C), 128.16 (CH), 129.15 (CH), 129.20 (CH), 129.75 (C), 130.57 (C), 133.45 (C), 135.44 (CH), 145.75 (C), 151.96 (C) ppm; ESI-MS (+10 V): *m/z* = 304.1 $[M+H]^+$; ESI-MS (–10 V): *m/z* = 301.8 $[M–H]^–$; elemental analysis (%) calcd for $C_{21}H_{21}NO$: C 83.13, H 6.98, N 4.62; found: C 83.05, H 7.20, N 4.57.

1-(5-Methyl-2-(piperidin-1-yl)phenyl)naphthalen-2-ol ***(3g)****:* 1-(4-Tolyl)piperidine (35.5 mg, 203 µmol), dichloromethane (2 mL), 2-naphthol (**2a**) (116 mg, 806 µmol), methanesulfonic acid (7.8 mg, 81 µmol), $FePcF_{16}$ (1.8 mg, 2.1 µmol), after 24 h, addition of further **2a** (57.9 mg, 402 µmol).

Reaction time: 48 h, column chromatography (isohexane/ethyl acetate, 1–3%, 1 h, 3–8%, 0.5 h, 8–15%, 20 min). Biaryl **3g** (44.2 mg, 139 µmol, 69%) was obtained as a colorless solid. M.p. 126.5 °C; UV (MeOH): λ = 231, 286, 335 nm; fluorescence (MeOH): λ_{ex} = 231 nm, λ_{em} = 411 nm; IR (ATR): $\tilde{\nu}$ = 3058, 3028, 2936, 2920, 2844, 1590, 1495, 1465, 1438, 1378, 1332, 1276, 1227, 1147, 1099, 1063, 1030, 953, 918, 903, 867, 817, 751, 726, 676, 635 cm^{-1}; ^{1}H NMR (600 MHz, $CDCl_3$): δ = 1.55 (m, 6 H), 2.32 (s, 3 H), 2.89 (m, 4 H), 7.13 (d, *J* = 8.3 Hz, 1 H), 7.21 (m, 2 H), 7.30 (d, *J* = 8.7 Hz, 1 H), 7.34 (m, 1 H), 7.38 (m, 1 H), 7.77 (d, *J* = 9.0 Hz, 1 H), 7.82 (m, 2 H) ppm; ^{13}C NMR and DEPT (151 MHz, $CDCl_3$): δ = 20.81 (CH_3), 23.93 (CH_2), 26.22 (2 CH_2), 53.72 (2 CH_2), 118.69 (CH), 121.02 (CH), 121.31 (C), 123.14 (CH), 125.60 (CH), 126.06 (CH), 128.26 (CH), 129.15 (CH), 129.34 (CH), 130.16 (C), 131.19 (C), 132.63 (C), 133.63 (C), 135.87 (CH), 148.09 (C), 151.83 (C) ppm; ESI-MS (+10 V): *m/z* = 318.2 [M+H]$^+$; elemental analysis (%) calcd for $C_{22}H_{23}NO$: C 83.24, H 7.30, N 4.41; found: C 83.44, H 7.42, N 4.35.
4a (49.0 mg, 171 µmol, 28%).

1-(5-Methyl-2-morpholinophenyl)naphthalen-2-ol ***(3h)****:* 4-(4-Tolyl)morpholine (70.9 mg, 400 µmol), dichloromethane (4 mL), 2-naphthol (**2a**) (346 mg, 2.40 mmol), methanesulfonic acid (15.5 mg, 161 µmol), $FePcF_{16}$ (3.4 mg, 4.0 µmol). Reaction time: 24 h, column chromatography (isohexane/ethyl acetate, 2–5%, 1 h, 5–8%, 45 min, 8–15%, 0.5 h). Biaryl **3h** (90.3 mg, 283 µmol, 71%) was obtained as a brown solid. M.p. 94 °C; UV (MeOH): λ = 230, 288, 334 nm; fluorescence (MeOH): λ_{ex} = 334 nm, λ_{em} = 412 nm; IR (ATR): $\tilde{\nu}$ = 3055, 2960, 2912, 2851, 1726, 1618, 1593, 1497, 1450, 1362, 1334, 1298, 1275, 1227, 1154, 1113, 1068, 1045, 954, 916, 877, 815, 749, 730, 676, 662, 635, 613 cm^{-1}; ^{1}H NMR (600 MHz, $CDCl_3$): δ = 2.34 (s, 3 H), 2.99 (m, 4 H), 3.68 (m, 4 H), 7.18 (d, *J* = 8.3 Hz, 1 H), 7.23 (dd, *J* = 17.4, 1.5 Hz, 2 H), 7.32 (d, *J* = 8.7 Hz, 1 H), 7.36 (m, 1 H), 7.38 (m, 1 H), 7.73 (d, *J* = 8.3 Hz, 1 H), 7.79 (d, *J* = 8.7 Hz, 1 H), 7.83 (dd, *J* = 7.9, 1.5 Hz, 1 H), 9.69 (br s, 1 H) ppm; ^{13}C NMR and DEPT (151 MHz, $CDCl_3$): δ = 20.84 (CH_3), 52.49 (2 CH_2), 66.84 (2 CH_2), 118.52 (CH), 120.60 (CH), 120.64 (C), 123.45 (CH), 125.35 (CH), 126.40 (CH), 128.34 (CH), 129.58 (CH), 129.77 (CH), 130.12 (C), 130.44 (C), 133.40 (C), 133.73 (C), 135.97 (CH), 146.26 (C), 151.42 (C) ppm; ESI-MS (+10 V): *m/z* = 320.2 [M+H]$^+$; ESI-MS (–10 V): *m/z* = 318.1 [M–H]$^-$, HRMS (ESI) calcd for $C_{21}H_{22}NO_2^+$ ([M+H]$^+$): 320.1651; found: 320.1654.
4a (116 mg, 405 µmol, 34%).

1-(2-(Dimethylamino)-5-methoxyphenyl)naphthalen-2-ol ***(3i)****:* 4-Methoxy-*N*,*N*-dimethylaniline (90.7 mg, 600 µmol), dichloromethane (6 mL), 2-naphthol (**2a**) (177 mg, 1.23 mmol), methanesulfonic acid (23.3 mg, 241 µmol), $FePcF_{16}$ (5.1 mg, 6.0 µmol). Reaction time: 24 h, column chromatography (isohexane/ethyl acetate, 2–8%, 1.5 h, 8–15%, 20 min). Biaryl **3i** (144 mg, 491 µmol, 82%) was obtained as a colorless solid. M.p. 141.5 °C; UV (MeOH): λ = 233, 287, 336 nm; fluorescence (MeOH): λ_{ex} = 233 nm, λ_{em} = 412 nm; IR (ATR): $\tilde{\nu}$ = 3045, 3004, 2972, 2954, 2919, 2873, 2829, 2790, 1619, 1594, 1558, 1542, 1500, 1460, 1408, 1361, 1337, 1308, 1292, 1238, 1192, 1168, 1037, 1005, 954, 922, 879, 861, 816, 754, 724, 698, 675, 636, 605 cm^{-1}; ^{1}H NMR (600 MHz, $CDCl_3$): δ = 2.67 (s, 6 H), 3.75 (s, 3 H), 6.98 (m, 2 H), 7.24 (d, *J* = 8.3 Hz, 1 H), 7.29 (d, *J* = 8.7 Hz, 1 H), 7.34 (m, 1 H), 7.38 (m, 1 H), 7.80 (d, *J* = 8.7 Hz, 1 H), 7.83 (m, 2 H), 10.49 (br s, 1 H) ppm; ^{13}C NMR and DEPT (151 MHz, $CDCl_3$): δ = 44.26 (2 CH_3), 55.78 (CH_3), 114.33 (CH), 119.40 (CH), 120.11 (CH), 120.65 (C), 120.94 (CH), 123.25 (CH), 125.30 (CH), 126.31 (CH), 128.33 (CH), 129.70 (CH), 129.99 (C), 132.30 (C), 133.49 (C), 143.20 (C), 152.39 (C), 155.44 (C) ppm; ESI-MS (+10 V): *m/z* = 294.1 [M+H]$^+$; elemental analysis (%) calcd for $C_{19}H_{19}NO_2$: C 77.79, H 6.53, N 4.77; found: C 77.76, H 6.81, N 4.77.
4a (34.2 mg, 120 µmol, 20%).

6-Bromo-1-(2-(dimethylamino)-5-methoxyphenyl)naphthalen-2-ol ***(3j)****:* 4-Methoxy-*N*,*N*-dimethylaniline (90.7 mg, 600 µmol), dichloromethane (6 mL), 6-bromo-2-naphthol (268 mg, 1.20 mmol), methanesulfonic acid (23.2 mg, 241 µmol), $FePcF_{16}$ (5.1 mg, 6.0 µmol). Reaction time: 24 h, column chromatography (isohexane/ethyl acetate, 2–8%, 1.5 h, 8–15%, 20 min). Biaryl **3j** (196 mg, 526 µmol, 88%) was obtained as a dark yellow solid. M.p. 169 °C; UV (MeOH): λ = 235, 282, 348 nm; fluorescence (MeOH): λ_{ex} = 235 nm, λ_{em} = 422 nm; IR (ATR): $\tilde{\nu}$ = 3058, 3021, 2985, 2949, 2924, 2850, 2830, 2790, 1736, 1679, 1630, 1574, 1490, 1451, 1415, 1360, 1331, 1290, 1233, 1203, 1163, 1068, 1038, 1003, 953, 925, 877, 813, 769, 672, 615 cm^{-1}; ^{1}H NMR (600 MHz, $CDCl_3$): δ = 2.67 (s, 6 H), 3.75 (s, 3 H), 6.91 (d, *J* = 3.0 Hz, 1 H), 6.98 (dd, *J* = 8.7, 3.0 Hz, 1 H), 7.23 (d, *J* = 8.7 Hz, 1 H), 7.30 (d, *J* = 9.0 Hz, 1 H), 7.42 (dd, *J* = 9.0, 2.3 Hz, 1 H), 7.69 (d, *J* = 6.0 Hz, 1 H), 7.70 (d, *J* = 6.4 Hz, 1 H), 7.96 (d, *J* = 2.3 Hz, 1 H), 10.51 (br s, 1 H) ppm; ^{13}C NMR and DEPT (151 MHz, $CDCl_3$): δ = 44.30 (2 CH_3), 55.78 (CH_3), 114.54 (CH), 116.91 (C), 119.56 (CH), 119.98 (CH), 120.83 (C), 122.09 (CH), 127.18 (CH), 128.74 (CH), 129.45 (CH), 130.20 (CH), 131.16 (C), 131.83 (C), 132.07 (C), 143.11 (C), 152.79 (C), 155.56 (C) ppm; ESI-MS (+10 V): *m/z* = 372.1 [M+H]$^+$; ESI-MS (–10 V): *m/z* = 369.9 [M–H]$^-$, elemental analysis (%) calcd for $C_{19}H_{18}BrNO_2$: C 61.30, H 4.87, N 3.76; found: C 60.97, H 4.83, N 3.52.

1-(5-Chloro-2-(dimethylamino)phenyl)naphthalen-2-ol ***(3k)***: 4-Chloro-*N*,*N*-dimethylaniline (93.4 mg, 600 µmol), dichloromethane (6 mL), 2-naphthol (**2a**) (347 mg, 2.41 mmol), methanesulfonic acid (23.1 mg, 240 µmol), $FePcF_{16}$ (5.1 mg, 6.0 µmol). Reaction time: 24 h, column chromatography (isohexane/ethyl acetate, 1–3%, 0.5 h, 3–7%, 1.5 h, 7–15%, 20 min). Biaryl **3k** (63.8 mg, 214 µmol, 36%) was obtained as a brownish yellow solid. M.p. 128 °C; UV (MeOH): λ = 230, 282, 333 nm; fluorescence (MeOH): λ_{ex} = 230 nm, λ_{em} = 364, 422 nm; IR (ATR): $\tilde{\nu}$ = 3051, 2959, 2916, 2876, 2845, 2797, 2056, 1701, 1632, 1592, 1510, 1474, 1455, 1391, 1358, 1336, 1299, 1272, 1234, 1176, 1150, 1127, 1112, 1038, 997, 952, 924, 890, 849, 815, 787, 746, 721, 686, 640, 624 cm^{-1}; ^{1}H NMR (600 MHz, $CDCl_3$): δ = 2.67 (s, 6 H), 7.20 (d, *J* = 8.7 Hz, 1 H), 7.27 (d, *J* = 8.8 Hz, 1 H), 7.37 (m, 2 H), 7.40 (d, *J* = 2.4 Hz, 1 H), 7.42 (m, 1 H), 7.76 (d, *J* = 8.5 Hz, 1 H), 7.81 (d, *J* = 8.8 Hz, 1 H), 7.83 (m, 1 H), 9.66 (br s, 1 H) ppm; ^{13}C NMR and DEPT (151 MHz, $CDCl_3$): δ = 43.72 (2 CH_3), 119.62 (CH), 119.85 (C), 120.70 (CH), 123.51 (CH), 124.97 (CH), 126.72 (CH), 128.33 (C), 128.39 (CH), 128.40 (CH), 130.04 (C), 130.09 (CH), 132.50 (C), 133.13 (C), 134.81 (CH), 148.72 (C), 152.26 (C) ppm; ESI-MS (+10 V): *m/z* = 298.1 [M+H]$^+$; elemental analysis (%) calcd for $C_{18}H_{16}ClNO$: C 72.60, H 5.42, N 4.70; found: C 72.63, H 5.50, N 4.39.
4a (90.5 mg, 316 µmol, 26%).

1,1-Bis(2-(dimethylamino)-4-(triisopropylsilyloxy)phenyl)naphthalen-2(1H)-one ***(6)***: *N*,*N*-Dimethyl-3-(triisopropylsilyloxy)aniline (**5**) (173 mg, 589 µmol), dichloromethane (6 mL), 2-naphthol (**2a**) (173 mg, 1.20 mmol), methanesulfonic acid (23.1 mg, 240 µmol), $FePcF_{16}$ (10.5 mg, 12.3 µmol). Reaction time: 24 h, column chromatography (isohexane/ethyl acetate, 1–3%,1 h, 3–15%, 0.5 h, 15%, 20 min). Compound **6** was obtained as a pale yellow solid (78.2 mg, 108 µmol, 37%). M.p. 261 °C; UV (MeOH): λ = 219, 259, 293 nm; fluorescence (MeOH): λ_{ex} = 259 nm, λ_{em} = 443 nm; IR (ATR): $\tilde{\nu}$ = 2942, 2886, 2864, 2790, 1738, 1690, 1651, 1606, 1557, 1542, 1508, 1453, 1423, 1356, 1255, 1185, 1122, 1091, 998, 922, 882, 798, 752, 680, 641 cm^{-1}; ^{1}H NMR (500 MHz, $CDCl_3$): δ = 0.83 (d, *J* = 7.6 Hz, 9 H), 0.88 (d, *J* = 7.6 Hz, 9 H), 0.94 (d, *J* = 7.6 Hz, 9 H), 1.01 (d, *J* = 7.6 Hz, 9 H), 1.06 (m, 3 H), 1.33 (m, 3 H), 2.86 (s, 6 H), 2.87 (s, 6 H), 5.94 (d, *J* = 10.1 Hz, 1 H), 6.04 (m, 2 H), 6.13 (d, *J* = 2.2 Hz, 1 H), 6.21 (br d, *J* = 9.1 Hz, 2 H), 6.75 (m, 2 H), 6.97 (d, *J* = 10.1 Hz, 1 H), 7.09 (m, 1 H), 7.19 (m, 2 H) ppm; ^{13}C NMR and DEPT (125 MHz, $CDCl_3$): δ = 13.23 (3 CH), 13.61 (3 CH), 18.09 (3 CH_3), 18.19 (3 CH_3), 18.29 (3 CH_3), 18.42 (3 CH_3), 40.49 (2 CH_3), 41.50 (2 CH_3), 63.91 (C), 103.24 (CH), 104.23 (CH), 104.86 (CH), 105.03 (CH), 116.07 (C), 119.06 (C), 126.57 (CH), 127.37 (CH), 128.28 (CH), 128.76 (CH), 129.52 (CH), 130.43 (CH), 132.33 (C), 133.29 (CH), 139.09

(CH), 146.27 (C), 151.21 (C), 154.33 (C), 157.57 (C), 194.74 (C=O) ppm (the signal for one C is missing due to overlapping); ESI-MS (+25 V): *m/z* = 727.8 $[M+H]^+$; elemental analysis (%) calcd for $C_{44}H_{66}N_2O_3Si_2$: C 72.67, H 9.15, N 3.85; found: C 72.97, H 9.19, N 4.10.
4a (33.4 mg, 117 µmol, 19%).

*2'-Dimethylamino-2-hydroxy-1,1'-binaphthyl (*N,N*-dimethyl-NOBIN) (**8**) and* N,N*-dimethyl-1-(naphthalen-2-yloxy)naphthalen-2-amine (**9**)*: A solution of 2-*N*,*N*-dimethylaminonaphthalene (**7**) (413 mg, 2.41 mmol) in dichloromethane (26 mL) was added to a mixture of 2-naphthol (**2a**) (1.41 g, 9.80 mmol), methanesulfonic acid (93.2 mg, 967 µmol), and $FePcF_{16}$ (41.1 mg, 48.0 µmol). The reaction mixture was vigorously stirred at 0 °C for 24 h under air and then quenched with a saturated solution of Na_2CO_3 (25 mL). The aqueous layer was extracted three times with dichloromethane (25 mL) and the combined organic layers were dried over $MgSO_4$. Evaporation of the solvent in vacuo and purification of the crude product by automated column chromatography on silica gel (isohexane/ethyl acetate, 0–2%, 0.5 h, 2–6%, 2 h, 6–18%, 0.5 h) afforded the coupling products **8**, **9**, and **4a**. *N*,*N*-Dimethyl-NOBIN (**8**) (470 mg, 1.50 mmol, 62%) was obtained as a yellow solid. M.p. 151.5 °C; UV (MeOH): λ = 219, 254, 290, 335 nm; fluorescence (MeOH): λ_{ex} = 254 nm, λ_{em} = 423 nm; IR (ATR): $\tilde{\nu}$ = 3061, 2975, 2953, 2866, 2835, 2789, 1737, 1618, 1590, 1542, 1507, 1458, 1440, 1397, 1353, 1325, 1293, 1271, 1223, 1195, 1142, 1092, 1068, 1039, 988, 952, 935, 857, 816, 748, 697, 655, 631 cm^{-1}; ^1H NMR (600 MHz, $CDCl_3$): δ = 2.66 (s, 6 H), 7.04 (d, *J* = 8.7 Hz, 1 H), 7.09 (d, *J* = 8.5 Hz, 1 H), 7.16 (ddd, *J* = 8.5, 7.0, 1.1 Hz, 1 H), 7.21 (ddd, *J* = 8.5, 7.0, 1.1 Hz, 1 H), 7.32 (m, 2 H), 7.38 (d, *J* = 8.8 Hz, 1 H), 7.52 (d, *J* = 9.0 Hz, 1 H), 7.84 (d, *J* = 8.3 Hz, 1 H), 7.87 (d, *J* = 8.1 Hz, 1 H), 7.90 (d, *J* = 8.8 Hz, 1 H), 7.96 (d, *J* = 9.0 Hz, 1 H) ppm; ^{13}C NMR and DEPT (151 MHz, $CDCl_3$): δ = 43.85 (2 CH_3), 118.41 (C), 118.45 (CH), 119.60 (CH), 122.48 (C), 123.38 (CH), 124.46 (CH), 125.84 (CH), 126.10 (CH), 126.48 (CH), 126.71 (CH), 128.07 (CH), 128.31 (CH), 129.42 (C), 129.90 (CH), 130.12 (CH), 130.34 (C), 134.07 (C), 134.27 (C), 149.24 (C), 151.79 (C) ppm; ESI-MS (+25 V): *m/z* = 314.1 $[M+H]^+$; ESI-MS (–25 V): *m/z* = 311.8 $[M-H]^-$; elemental analysis (%) calcd for $C_{22}H_{19}NO$: C 84.31, H 6.11, N 4.47; found: C 84.44, H 6.12, N 4.43.

*Crystallographic data for compound **8***: $C_{22}H_{19}NO$, *M* = 313.38 g mol^{-1}, crystal size 0.210 × 0.320 × 0.670 mm^3, orthorhombic, space group $P2_12_12_1$, *a* = 8.3318(7), *b* = 10.8815(9), *c* = 18.0791(15) Å, *V* = 1639.1(2) $Å^3$, Z = 4, ρ_{calcd} = 1.270 g cm^{-3}, μ = 0.077 mm^{-1}, λ = 0.71073 Å, *T* = 100(2) K, θ range = 2.25–28.98°, reflections collected 30910, independent reflections 4356 (R_{int} = 0.0578), 223 parameters. The structure was solved by direct methods and refined by full-matrix least-squares on F^2; final *R* indices [$I>2\sigma(I)$] R_1 = 0.0450 and wR_2 = 0.1027; maximal residual electron density 0.290 e $Å^{-3}$. CCDC 1963410 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre.

N,*N*-Dimethyl-1-(naphthalen-2-yloxy)naphthalen-2-amine (**9**) (81.1 mg, 25.9 µmol, 11%) was obtained as a beige solid. M.p. 102 °C; UV (MeOH): λ = 215, 226, 254, 303, 328 nm; fluorescence (MeOH): λ_{ex} = 226 nm, λ_{em} = 416 nm; IR (ATR): $\tilde{\nu}$ = 3058, 2948, 2843, 2800, 1734, 1697, 1653, 1624, 1596, 1559, 1540, 1504, 1457, 1428, 1375, 1320, 1249, 1231, 1212, 1158, 1115, 1070, 991, 957, 910, 844, 801, 747, 713, 685, 634 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$): δ = 2.91 (s, 6 H), 6.91 (d, *J* = 2.5 Hz, 1 H), 7.28 (dd, *J* = 8.8, 2.5 Hz, 1 H), 7.34 (m, 5 H), 7.54 (d, *J* = 8.2 Hz, 1 H), 7.74 (d, *J* = 8.83 Hz, 1 H), 7.78 (m, 2 H), 7.82 (m, 1 H), 7.86 (m, 1 H) ppm; ^{13}C NMR and DEPT (125 MHz, $CDCl_3$): δ = 42.89 (2 CH_3), 109.58 (CH), 117.80 (CH), 119.46 (CH), 121.31 (CH), 123.84 (CH), 123.87 (CH), 125.78 (CH), 126.35 (CH), 126.58 (CH), 127.04 (C), 127.74 (CH), 127.76 (CH), 129.38 (CH), 129.60 (CH), 129.88 (C), 134.59 (C), 138.41 (C), 142.12 (C), 156.35 (C) ppm (the signal for one C is missing due to overlapping); MS (EI): *m/z* (%) = 313 (70, $[M]^+$), 186 (26), 184 (10), 173 (13), 172 (100), 170 (12), 142 (15), 141 (23), 128 (14), 127 (49), 126 (12), 102 (10), 77 (11), 42 (42); elemental analysis (%) calcd for $C_{22}H_{19}NO$: C 84.31, H 6.11, N 4.47; found: C 84.67, H 6.38, N 4.54. **4a** (281 mg, 981 µmol, 20%).

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Keywords: C–H bond activation • homogeneous catalysis • iron • oxidative cross-coupling • phthalocyanines

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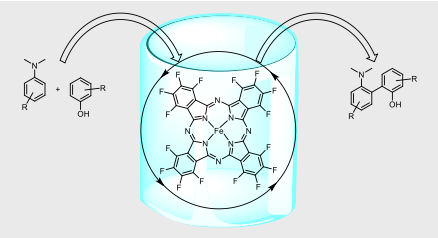
FULL PAPER

In contrast to most of the iron-catalyzed oxidative cross-coupling reactions, we used ambient air as sole oxidant for the C–C bond formation between tertiary anilines and hydroxyarenes. Using iron(II)–hexadecafluorophthalocyanine as catalyst, the reaction proceeds under mild conditions and affords the coupling products with excellent selectivity.



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Iron-Catalyzed Oxidative C–C Cross-Coupling Reaction of Tertiary Anilines with Hydroxyarenes Using Air as Sole Oxidant