

Oxidative coupling revisited: solvent-free, heterogeneous and in water†

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Fe(III) treated K-10 montmorillonite and FeCl₃ (both hydrated and anhydrous) are compared as catalysts for oxidative coupling of phenol substrates under a range of conditions. While the commonly reported coupling of 2-naphthol proceeds under a range of conditions, other substrates are far less readily coupled. Counterintuitively, biphasic reactions of poorly water soluble substrates in contact with aqueous solutions of FeCl₃ are the most universally applicable conditions while many homogeneous reaction mixtures yield little or no coupling product. Fe(III) treated K-10 proved to be a poor catalyst for oxidative coupling of most substrates. Comparison of coupling conditions provides a framework for optimisation of green methodologies using oxidative coupling catalysts.

Introduction

The formation of C–C linked biaryl dimers is an important synthetic tool, and is involved in the biosynthesis of natural products containing biaryl linkages.¹ Additionally, oxidative coupling is believed to be an important process in the formation of humic materials in soils *via* enzymatic and abiotic routes.² Understanding such synthetic processes on a molecular scale is the basis of ongoing study within our group. The knowledge obtained from soil chemistry studies and from the wider soil literature, aids understanding of the inorganic/abiotic processes which promote C–C bond formation, from a synthetic point of view.³

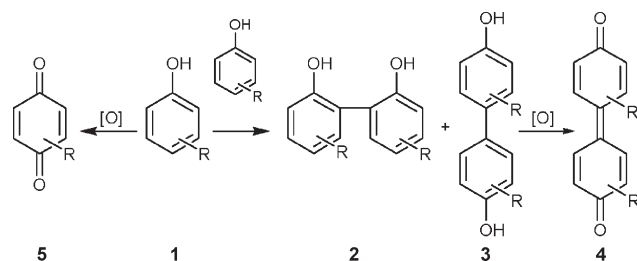
The oxidative dimerisation of phenols is a long-established reaction, which can be promoted stoichiometrically by FeCl₃·6H₂O,^{4,5} and catalytically by Cu(II)-amine complexes⁶ as well as supported transition metals.⁷ The coupling mechanism is believed to involve either one two-electron or two one-electron oxidations to form an aryl-aryl coupled dimer through the *ortho* **2** and/or *para* positions **3** (Scheme 1).^{5,8} Protonation

of the phenol, as determined by pH, can also influence the coupling mechanism, and overall two protons and two electrons are lost during coupling.⁹ In some cases, competing and/or subsequent oxidation to form quinones occurs, either from the coupled product **4** or the original substrate **5**.

Modified clay minerals are commonly used as heterogeneous catalysts in organic synthesis¹⁰ and oxidative coupling of phenols has been effected using clay-supported transition metals,^{7,11,12} as naturally derived, environmentally benign and re-useable heterogeneous catalysts. Treating clays with transition metal ions, such as Cu(II) or Fe(III) salts, causes ion-exchange and surface adsorption of these hydrated cations, increasing the Lewis acidity and redox activity of the clay. K-10 montmorillonite is a commercially available clay that is acid-treated to increase surface area, and to effect protonation of the remaining negatively charged exchange sites. While K-10 is not a particularly pure or structurally intact clay, it is easily obtained and modified for use in organic synthesis, hence its ongoing popularity.

Remarkably, when we sought to compare the activity of the potentially green catalysts, Fe(III) treated clays, with various other methods described in the literature, it appeared that many of the greener methods described were so highly substrate specific, that procedures to effect oxidative coupling were not universally applicable and also exhibited some surprising phase dependence.

In this paper a range of coupling conditions, utilising either FeCl₃ (both in the hexahydrate and anhydrous forms), or Fe(III) treated clays as oxidants/catalysts in solvents (toluene, acetonitrile, water) or solvent-free, were compared in the oxidative coupling of a varied group of substrates.



Scheme 1 Coupling of substituted phenols to form *o*-*o'* **2** or *p*-*p'* **3** dimers.

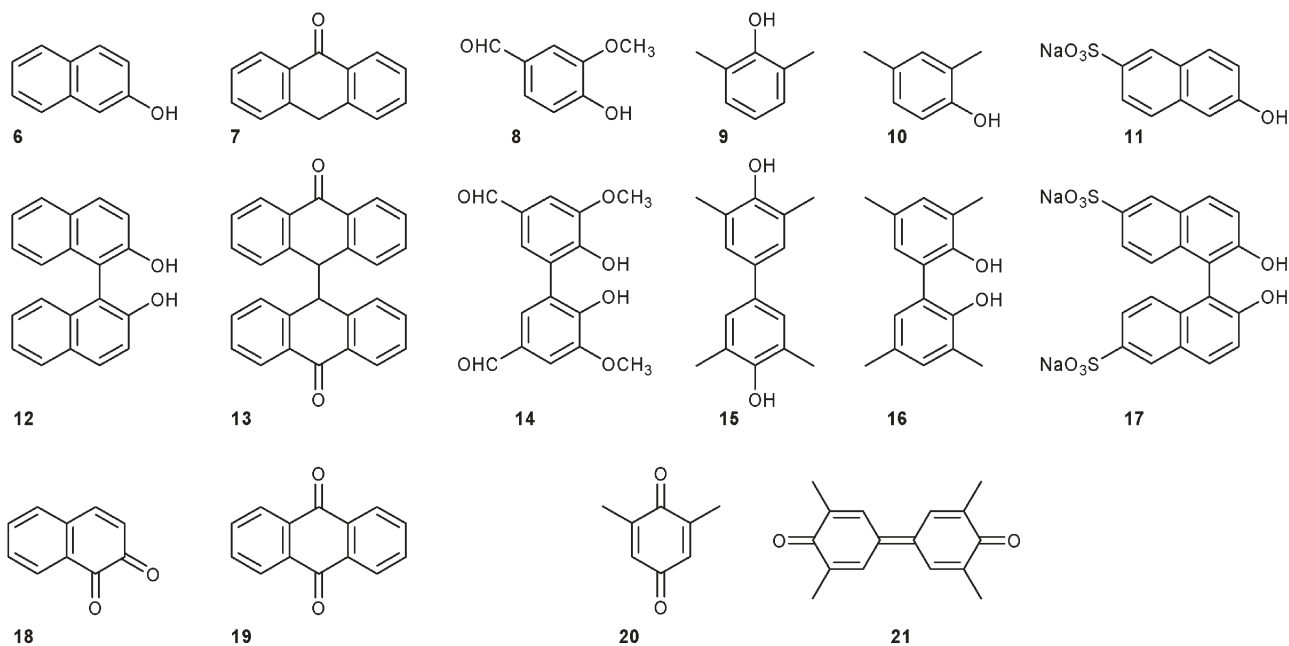
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Results and discussion

Substrates for oxidative coupling are depicted in Scheme 2. 2-Naphthol **6**, as the most often referred to substrate in reports of new or more effective oxidative coupling reactions, was tested alongside anthrone **7**, vanillin **8**, 2,6-dimethylphenol **9**, 2,4-dimethylphenol **10** and sodium 6-hydroxynaphthalene-2-sulfonate **11** to yield variously, C–C biaryl coupled products



Scheme 2 Substrates and products. Substrates **6**, **7**, **8**, **10** and **11** yield coupled products **12**, **13**, **14**, **16** and **17** while **9** provides the further oxidised diphenoquinone **21** along with **15**. Oxidation of substrates **6**, **7** and **9** to yield **18**, **19** and **20** competes with biaryl coupling.

12–17 or diphenoquinone **21**. Anthrone is reported to undergo keto-enol tautomerism to 9-anthrol in the presence of transition metals, including FeCl_3 .¹³ Some competitive substrate oxidation without coupling to yield naphthoquinone **18**, anthraquinone **19** or benzoquinone **20** occurred under some conditions tested.

Catalysts Fe(III) treated K-10 montmorillonite and $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$ (or dehydrated) were employed under a range of conditions similar to those previously described: Fe(III) treated clays,⁷ in biphasic systems with aqueous FeCl_3 ,^{4,14} so-called ‘solid-state’,⁵ and using acetonitrile as solvent, as well as a two-phase toluene/molten $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$ system.

Results are summarised in Table 1 and additionally depicted as maximum recoverable yields of coupled product in Fig. 1. This graphically illustrates the huge differences in efficacy of the various conditions. Many reports of greener conditions

describe only the coupling of 2-naphthol or substituted 2-naphthol, yet, coupling of 2-naphthol **6** to yield BINOL **12** is readily achieved under a range of conditions including: with $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$ in toluene, neat, or in water and, to a reasonable extent, by reaction in toluene (replacing the chlorobenzene reported by Kantam *et al.*⁷) with the catalyst Fe(III) treated K-10. Thus, this reaction is readily achieved under conditions that may prove useless for other substrates and is not a good probe for comparison of green oxidative coupling protocols.

Remarkably, in spite of the poor aqueous solubility exhibited by most of these substrates, reaction at 50 °C in aqueous FeCl_3 solution provided significant conversion to coupled products for most substrates, except anthrone. These reactions were biphasic (except for **11**) and Ding *et al.* suggest that reaction occurs at the crystalline substrate surface, *via* an interaction between solid and liquid phases.^{4,15} This does not

Table 1 Mass recovery and product distribution in oxidative coupling reactions, compound number in parentheses

Catalyst: Fe^{3+} -K10																
(A) Toluene, 111 °C, 6 h				(B) Water, 100 °C, 6 h				(C) Neat, 50 °C, 24 h				(D) Neat, 160 °C, 24 h				
Rec ^a	Sm ^b	Cp ^c	Ox ^d	Rec	Sm	Cp	Ox	Rec	Sm	Cp	Ox	Rec	Sm	Cp	Ox	
6	79	33	67(12)		88	96	4(12)		96	93	7(12)		100	82	18(12)	
7	94	21	78(13)	1(19)	91	65	32(13)	3(19)	90	82	4(13)	14(19)	82	58	2(13)	40(19)
8	96	100	0(14)		90	100	0(14)		100	100	0(14)		70	72	28(20)	
9	86	100	0(15,21)	0(20)	24	0	29(15,21)	71(20)	99	100	0(15,21)	0(20)	13	10	90(15,21)	0(20)
10	81	85	15(16)		17	36	64(16)		100	100	0(16)		10	98	2(16)	
11	100	100	0(17)		97	100	0(17)		97	100	0(17)		100	100	0(17)	
Catalyst: $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$																
(E) Water, 50 °C, 4 h				(F) Acetonitrile, 82 °C, 4 h				(G) Neat, 50 °C, 4 h				(H) Toluene, 50 °C, 4 h				
Rec ^a	Sm ^b	Cp ^c	Ox ^d	Rec	Sm	Cp	Ox	Rec	Sm	Cp	Ox	Rec	Sm	Cp	Ox	
6	99	0	100(12)		99	80	18(12)	2(18)	99	0	100(12)		86	0	100(12)	
7	87	88	3(13)	9(19)	78	27	64(13)	9(19)	80	7	30(13)	63(19)	82	0	89(13)	11(19)
8	68	43	57(14)		65	97	3(14)		99	100	0(14)		95	100	0(14)	
9	89	12	87(15,21)	1(20)	85	57	16(15,21)	27(20)	88	100	0(15,21)	0(20)	25	55	15(15,21)	30(20)
10	75	25	75(16)		100	100	0(16)		92	31	69(16)		63	92	8(16)	
11	97	0	100(17)		58	100	0(17)		99	100	0(17)		99	100	0(17)	

^a Mass recovery (%) ^b Starting material (%) ^c Coupled products (%) ^d Oxidised products (%)

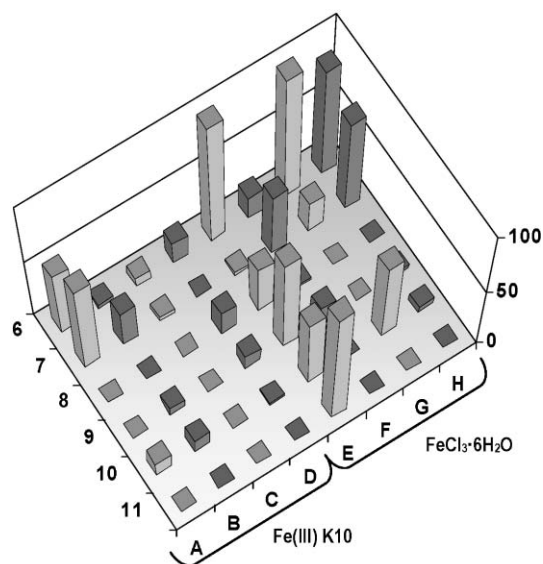


Fig. 1 Quantities of coupled products, represented as (mass recovery/100 × % Cp), recovered under various reaction conditions. **Fe³⁺-K10**: A = toluene reflux, 6 h; B = water reflux, 6 h; C = solvent-free 50 °C, 24 h; D = solvent-free 160 °C, 24 h. **FeCl₃·6H₂O**: E = water, 50 °C, 4h; F = CH₃CN reflux, 4 h; G = solvent-free, 50 °C, 4 h; H = toluene 50 °C, 4 h.

appear to be supported by the lack of reactivity of anthrone, the least water soluble material, and instead it is postulated that it is indeed dissolved substrate which reacts (as previously suggested¹⁶) possibly *via* a phenoxide radical mechanism due to the low pH of FeCl₃ solutions (measured to be 2.5). Coupled products, which (bar 17) exhibited poor aqueous solubility, largely separated from the aqueous solution, facilitating easy recovery, along with other benefits associated with reactions 'on water'.¹⁷

It was expected that reaction in acetonitrile (F), which yielded a homogeneous solution, would proceed rapidly, however, reasonable conversion was only obtained with anthrone 7. Attempts to effect coupling in other solvents including diethyl ether and ethyl acetate (both yielding homogeneous reaction mixtures) were also unsuccessful. When dissolved in toluene (H), anthrone readily reacted, yielding coupled product 13 almost as efficiently as 2-naphthol. FeCl₃·6H₂O is insoluble in toluene and forms a separate molten lower phase at 50 °C. Nonetheless, some reactions proceeded rapidly and such conditions provided for easy product recovery by simple filtration of the Fe salt residue and evaporation of the toluene solution post reaction. Given that, above 37 °C, FeCl₃·6H₂O is a liquid comprised of Fe(H₂O)₄Cl₂⁺ and FeCl₄⁻, with excess water molecules,¹⁸ this might be described as a biphasic reaction with an ionic liquid catalyst.

Previous reports of direct solvent-free reaction of 2-naphthol 6 with FeCl₃·6H₂O,⁵ coupled with the observation that this hydrated salt may form low melting mixtures with certain substrates,¹⁹ led to the examination of solvent-free reaction mixtures (G). Grinding of solid FeCl₃·6H₂O with substrates 6–11 and gentle heating (50 °C) resulted in reaction mixtures that differed significantly in physical appearance (Fig. 2): 6 yields the yellow reaction mixture noted previously¹⁹ as does 7;

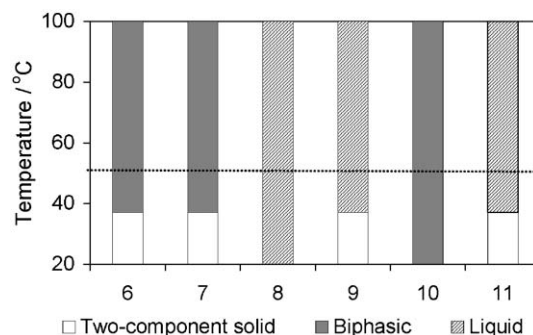


Fig. 2 Observed phase-changes with changes in *T* for solvent-free reaction mixtures (G) for substrates 6–11.

vanillin 8, forms a black liquid upon contact with the Fe salt; the mixture with 9 liquefies completely above the melting point of FeCl₃·6H₂O; 10, a liquid at room temperature (at 37 °C the entire mixture melts and immediately solid Fe residues begin to separate), yields a mixture of solid and liquid across the entire temperature range and 11 remains a mixture of two solids up to 37 °C.

Only the reaction mixtures that were designated as biphasic at the chosen reaction temperature in Fig. 2 yielded significant quantities of coupled products. A powder-XRD trace obtained immediately for the reaction mixture of 6 and FeCl₃·6H₂O on heating to 50 °C, indicated a dramatic loss of overall crystallinity. (A similar order of reactivity was demonstrated using anhydrous FeCl₃ (m.p. 304 °C) at 21 °C in a glove box challenging the suggestion that this was due to separation of products from the hydrated ionic liquid or concentrated aqueous solution of Fe(H₂O)₄Cl₂⁺ and FeCl₄⁻.)

A final observation: in the presence of FeCl₃, substrates 9 and 10 were usually recovered as dark red oils, indicating the possible formation of charge-transfer complexes. However, these are unlikely to play a mechanistic role due to their appearance in both reactive and unreactive systems.

Conclusion

Biphasic oxidative coupling of poorly water soluble substrates in contact with aqueous solutions of FeCl₃ were the most universally applicable conditions, while many homogeneous reaction mixtures yielded little or no coupling product. Fe(III) treated K-10 proved to be a poor catalyst for oxidative coupling of most substrates. The more successful conditions for Fe(III)-promoted coupling were observed when reactions were biphasic, indicating that homogeneous conditions may not always be the best choice for similar synthetic processes.

Experimental

2-Naphthol, anthrone, 2,6-dimethylphenol, 2,4-dimethylphenol, sodium 6-hydroxynaphthalene-2-sulfonate, K-10 montmorillonite clay, and anhydrous FeCl₃, were purchased from Sigma–Aldrich chemical company, vanillin from Ajax Chemicals Ltd and FeCl₃·6H₂O from BDH. All reagents and organic solvents were used as purchased from the supplier without any further purification.

^1H nuclear magnetic resonance (NMR) and ^{13}C NMR spectra were recorded on 200 MHz, 300 MHz or 400 MHz Bruker spectrometers in CDCl_3 , $\text{DMSO}-d_6$ or D_2O with tetramethylsilane (TMS) as an internal standard ($\delta = 0$ ppm), except in the case of D_2O (H_2O $\delta = 4.79$ ppm). Gas chromatography (GC) was performed on an Agilent 6850 Series II Network GC System, equipped with an FID detector and an HP-1 column (30 m \times 0.32 mm ID). Helium was used as a carrier gas at a flow-rate of 2.0 ml min^{-1} , and a temperature program of 100–300 $^\circ\text{C}$ at 10 $^\circ\text{C}$ min^{-1} was employed. Conversions were deduced from comparison of integrated areas of well-resolved signals in ^1H NMR spectra ($\pm 1\%$ error was determined for this method), or from resolved signals in GC analysis (compared to mixtures of standards made up to known concentrations). In addition, GC-MS analysis was used to confirm identity of the components of product mixtures. GC-MS was performed on a ThermoQuest TRACE DSQ GC-MS using an SGE BP5 column (30 m \times 0.22 mm ID) and an Electron Impact (EI) detector with an ionisation energy of 70 eV. Helium was used as a carrier gas at a flow-rate of 0.8 ml min^{-1} , and a temperature program of 50 $^\circ\text{C}$ for 2 min, 20 $^\circ\text{C}$ min^{-1} to 250 $^\circ\text{C}$ held for 16 min was employed. Atomic absorption spectroscopy (AAS) was carried out using a Perkin Elmer atomic absorption spectrometer Model 3110. Inductively coupled plasma optical emission spectroscopy (ICP-OES) was carried out using a Varian VistaPro ICP-OES with simultaneous CCD and axial view torch detectors. Melting points were recorded on a Gallenkamp variable heat melting point apparatus at a heating rate of 1 $^\circ\text{C}$ min^{-1} .

Preparation of Fe(III)-treated K-10 montmorillonite

Commercially available acid treated K-10 montmorillonite was washed with cold, dilute hydrochloric acid to remove exchangeable cations. The clay was then stirred in an aqueous FeCl_3 solution containing five times the metal ion concentration, compared with the approximated cation exchange capacity of the clay (~ 100 mequiv per 100 g). The clay was washed thoroughly with deionised water until chloride ions could no longer be detected in the washings. After drying (105 $^\circ\text{C}$) and milling, the clay thus obtained was independently analysed by AAS and ICP-OES to determine the Fe content of the clay. Fe content determination by AAS involved acid-washing of a small amount of Fe(III)-treated K-10 and its precursor (~ 300 mg) in 0.1 M HCl twice, and analysing the combined washings bracketed by Fe standards. Fe content determination by ICP-OES involved digestion of Fe(III)-treated K-10 and its precursor (~ 1 g) in *aqua regia* followed by multi-elemental analysis bracketed by mixed-standards. The exchangeable Fe content of the clay was determined to be 0.0098 g Fe per 1.000 g of clay by AAS and 0.0083 g Fe per 1.000 g of clay by ICP-OES (average 0.0090 g Fe per 1.000 g of clay). Assuming saturation with Fe(III), the CEC of the clay was calculated to be ~ 50 mequiv per 100 g.

Example procedure for clay-catalysed reactions in toluene (A)

Fe(III)-treated K10 montmorillonite (0.2368 g, 0.0380 mmol Fe) was added to a solution of anthrone **7** (0.2002 g,

1.0310 mmol) in toluene (30 ml) at reflux (111 $^\circ\text{C}$) for 6 h. After cooling, solids were removed by filtration, the organic solution was dried (MgSO_4), filtered and the solvent removed *in vacuo* to give a yellow solid (0.1883 g, 94% mass recovery). ^1H NMR (CDCl_3 , TMS, 300 MHz) revealed 21% anthrone **7**, 78% bianthranyl **13** and 1% anthraquinone **19**.

Example procedure for clay-catalysed reactions in water (B)

Anthrone **7** (0.1980 g, 1.0190 mmol) was added to a suspension of Fe(III)-treated K-10 montmorillonite (0.2345 g, 0.0380 mmol Fe) in water (30 ml) and stirred at reflux (100 $^\circ\text{C}$) for 6 h. The mixture was filtered, extracted with dichloromethane, dried (MgSO_4), filtered and the solvent removed *in vacuo* to give a yellow solid (0.1807 g, 91% mass recovery). ^1H NMR (CDCl_3 , TMS, 300 MHz) revealed 65% anthrone **7**, 32% bianthranyl **13**, and 3% anthraquinone **19**.

Example procedure for solvent-free reactions with clays (C,D)

2-Naphthol **6** (0.2008 g, 1.3930 mmol) and Fe(III)-treated K-10 montmorillonite (0.3231 g, 0.0520 mmol Fe) were ground together, placed in a sealed Pyrex test-tube in an aluminium dry block heater and kept at 50 $^\circ\text{C}$ (160 $^\circ\text{C}$ for high-temp experiments (D)) for 24 hours. The organic component was extracted with dichloromethane, filtered to remove clay, dried (MgSO_4), filtered and the solvent removed *in vacuo* to give a white solid (0.1931 g, 96% mass recovery). ^1H NMR (CDCl_3 , TMS, 300 MHz) revealed 93% 2-naphthol **6** and 7% 1,1'-binaphthalene-2,2'-diol **12**.

Example procedure for reactions with Fe salt in water (E)

2,6-Dimethylphenol **9** (0.2024 g, 1.6570 mmol) was added to a solution of $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$ (1.7695 g, 6.5470 mmol) in distilled water (30 ml) and slurried at 50 $^\circ\text{C}$ for 4 h. The solid organic phase was filtered off after cooling, and the remaining mixture was extracted with dichloromethane, dried (MgSO_4), filtered, combined and the solvent removed *in vacuo* to give a red solid (0.1801 g, 89% mass recovery). ^1H NMR (CDCl_3 , TMS, 300 MHz) revealed 12% 2,6-dimethylphenol **9**, 68% 3,3',5,5'-tetramethyldiphenylquinone **21**, 19% 3,3',5,5'-tetramethyl-1,1'-biphenyl-4,4'-diol **15**, and 1% 2,6-dimethylbenzoquinone **20**.

Example procedure for reactions with Fe salt in acetonitrile (F)

2-Naphthol **6** (0.2010 g, 1.3940 mmol) was added to a solution of $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$ (0.7531 g, 2.7860 mmol) in acetonitrile (30 ml) and stirred at reflux (82 $^\circ\text{C}$) for 4 h. The reaction was quenched with 1 M HCl (10 ml), partitioned with an aliquot of dichloromethane, dried (MgSO_4), filtered and the solvent removed *in vacuo* to give a white solid (0.1995 g, 99% mass recovery). ^1H NMR (CDCl_3 , TMS, 400 MHz) revealed 80% 2-naphthol **6**, 18% 1,1'-binaphthalene-2,2'-diol **12**, and 2% 1,4-naphthoquinone **18**.

Example procedure for neat reactions with Fe salts (G)

2,4-Dimethylphenol **10** (0.2000 g, 1.6370 mmol) and $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$ (0.8825 g, 3.2650 mmol) were placed in a sealed

test-tube, mixed together and kept at 50 °C for 4 h. The reaction was quenched with 1 M HCl (10 ml), washed with an aliquot of distilled water and the organic component extracted with dichloromethane. The solution was dried (MgSO₄), filtered and the solvent removed *in vacuo* to give a red solid (0.1835 g, 92% mass recovery). ¹H NMR (CDCl₃, TMS, 200 MHz) revealed 31% 2,4-dimethylphenol **10** and 69% 3,3',5,5'-tetramethyl-1,1'-biphenyl-2,2'-diol **16**.

Example procedure for reactions with Fe salt in toluene (H)

FeCl₃·6H₂O (0.7484 g, 2.7690 mmol) was added to a solution of 2-naphthol **6** (0.1999 g, 1.3870 mmol) in toluene (30 ml) and slurried at 50 °C for 4 h. The mixture was filtered and the solvent removed *in vacuo* to give a white solid (0.1770 g, 86% mass recovery). ¹H NMR (CDCl₃, TMS, 200 MHz) revealed 0% 2-naphthol **6** and 100% 1,1'-binaphthalene-2,2'-diol **12**.

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References

- 1 P. P. Reddy, C. Y. Chu, D. R. Hwang, S. K. Wang and B. J. Uang, *Coord. Chem. Rev.*, 2003, **237**, 257.
- 2 S. Pal, J. M. Bollag and P. M. Huang, *Soil Biol. Biochem.*, 1994, **26**, 813.
- 3 J. M. Bollag, J. Dec and P. M. Huang, *Adv. Agron.*, 1998, **63**, 237.
- 4 K. Ding, Y. Wang, L. Zhang and Y. Wu, *Tetrahedron*, 1996, **52**, 1005.
- 5 F. Toda, K. Tanaka and S. Iwata, *J. Org. Chem.*, 1989, **54**, 3007.
- 6 J. Brussee, J. L. G. Groenendijk, J. M. te Koppele and A. C. A. Jansen, *Tetrahedron*, 1985, **41**, 3313.
- 7 M. L. Kantam, B. Kavita and F. Figueras, *Catal. Lett.*, 1998, **51**, 113.
- 8 S. Kobayashi and H. Higashimura, *Prog. Polym. Sci.*, 2003, **28**, 1015.
- 9 G. Lessene and K. S. Feldman, in *Modern Arene Chemistry*, Wiley-VCH, 2002.
- 10 M. Balogh and P. Laszlo, in *Organic Chemistry Using Clays*, Springer-Verlag, 1993.
- 11 M. L. Kantam and P. L. Santhi, *Synth. Commun.*, 1996, **26**, 3075.
- 12 T. S. Li, H. Y. Duan, B. Z. Li, B. B. Tewari and S. H. Li, *J. Chem. Soc., Perkin Trans. 1*, 1999, 291.
- 13 T. Fujii, N. Tanaka, K. Kodaira, Y. Kawai, H. Yamashita and M. Anpo, *J. Photochem. Photobiol., A*, 1999, **125**, 85.
- 14 R. G. R. Bacon and A. R. Izzat, *J. Chem. Soc. C*, 1966, 791.
- 15 H. Dianin, *Ber. Dtsch. Chem. Ges.*, 1873, **6**, 1252.
- 16 Š. Vyskočil, M. Smrčina, M. Lorenc, V. Hanuš, M. Polášek and P. Kočovský, *Chem. Commun.*, 1998, 585.
- 17 S. Narayan, J. Muldoon, M. G. Finn, V. V. Fokin, H. C. Kolb and K. B. Sharpless, *Angew. Chem.*, 2005, **117**, 3339.
- 18 K. Murata and D. E. Irish, *Spectrochim. Acta, Part A*, 1988, **44**, 739.
- 19 G. Rothenberg, A. P. Downie, C. L. Raston and J. L. Scott, *J. Am. Chem. Soc.*, 2001, **123**, 8701.