Supplementary information for

Quinonediimines as a redox-active organocatalyst for oxidative coupling of aryland alkenylmagnesium compounds under molecular oxygen

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Fig.S1 Enlarged figure of Fig. 2 (¹H NMR experiment to follow the redox cycle of **1a** in the oxidative coupling of **2a** and reoxidation under molecular oxygen.).

General

¹H NMR (400 MHz) spectra were measured on a JEOL JNM-ECS400 spectrometer. Chemical shifts in CDCl₃ were reported in ppm on the δ scale relative to a residual solvent (δ 7.26 for ¹H NMR) as an internal standard. Anhydrous THF was prepared using a Glass Contour Solvent Dispensing System. Grignard reagents **2b-h** were purchased from commercial sources. Grignard reagents **2a** and **2i-j** were prepared from the corresponding bromides according to a classical procedure using Mg turning in THF, where the reaction mixture was warmed to 60 °C. Titration of Grignard reagents was carried out using iodine. All of coupling products **3a-j** were known compounds. The CAS number is shown below: **3a** (2548-47-2), **3b** (92-52-4), **3c** (2132-80-1), **3d** (398-23-2), **3e** (613-33-2), **3f** (605-39-0), **3g** (4482-03-5), **3h** (612-78-2), **3i** (75416–81–8) and **3j** (75416-80-7). Confirmation of products **3i-j** was carried out by comparison with the reported ¹H NMR data.^{S1} Products **3a-h** were isolated by silica-gel column chromatography, and the ¹H NMR chemical shifts and charts were described below. A representative procedure for the coupling reaction is described in the main text.

Preparation of N,N'-diphenyl-p-benzoquinonediimine (1a)



To a mixture of *N*,*N*-diphenyl-*p*-phenylenediamine (1.0 g, 3.9 mmol) and iodosylbenzene (880 mg, 4.0 mmol) was added CH₂Cl₂ (200 mL) at room temperature under molecular nitrogen. The reaction mixture was stirred at room temperature overnight. The solvent was evaporated *in vacuo*. The residue was purified by silica-gel chromatography (from CH₂Cl₂ to hexane/ethyl acetate = 4/1). The obtained **1a** was further purified by recrystalization with toluene to give **1a** as a red solid (769 mg, 2.95 mmol, 76%). Chemical shifts of the ¹H NMR spectrum were identical with the reported one.^{S2}

References

S1 (a) For **3i**: M. Shimizu, T. Kurahashi, K. Shimono, K. Tanaka, I. Nagao, S. Kiyomoto and T. Hiyama, *Chem. Asian J.*, 2007, **2**, 1400; (b) for **3j**: T. Yamamoto, T. Yasuda, K. Kobayashi, I. Yamaguchi, T. Koizumi, D. Ishii, M. Nakagawa, Y. Mashiko and N. Shimizu, *Bull. Chem. Soc. Jpn.*, 2006, **79**, 498.

S2 (a) M. Sandberg and T. Hjertberg, *Stnth. Met.*, 1989, **29**, E257; (b) C.-C. Han, R. Balakumar, D. Thirumalai and M.-T. Chung, *Org. Biomol. Chem.*, 2006, **4**, 3511.

¹H NMR chemical shifts and the charts for the coupling products

Buta-1,3-diene-2,3-diyldibenzene (**3a**): ¹H NMR (400 MHz, CDCl₃) δ = 7.37-7.41 (m, 4H), 7.19-7.30 (m, 6H), 5.54 (d, *J* = 1.8 Hz, 2H) and 5.31 (d, *J* = 1.8 Hz, 2H) ppm.



1,1'-Biphenyl (**3b**): ¹H NMR (400 MHz, CDCl₃) *δ* = 7.57-7.64 (m, 4H), 7.40-7.50 (m, 4H) and 7.32-7.39 (m, 2H) ppm.



4,4'-Dimethoxy-1,1'-biphenyl (**3c**): ¹H NMR (400 MHz, CDCl₃) δ = 7.48 (d, *J* = 8.7 Hz, 4H), 6.96 (d, *J* = 8.7 Hz, 4H) and 3.85 (s, 6H) ppm.



4,4'-Difluoro-1,1'-biphenyl (**3d**): ¹H NMR (400 MHz, CDCl₃) δ = 7.49 (dd, *J* = 5.5, 8.7 Hz, 4H) and 7.12 (dd, *J* = 8.7, 8.7 Hz, 4H) ppm.



4,4'-Dimethyl-1,1'-biphenyl (**3e**): ¹H NMR (400 MHz, CDCl₃) δ = 7.49 (d, *J* = 8.2 Hz, 4H), 7.24 (d, *J* = 8.2 Hz, 4H) and 2.40 (s, 6H) ppm.





2,2'-Dimethyl-1,1'-biphenyl (**3f**): ¹H NMR (400 MHz, CDCl₃) δ = 7.19-7.29 (m, 6H), 7.11 (d, *J* = 6.9 Hz, 2H) and 2.06 (s, 6H) ppm.



2,2',4,4',6,6'-hexamethyl-1,1'-biphenyl (**3g**): ¹H NMR (400 MHz, CDCl₃) δ = 6.98 (s, 4H), 2.37 (s, 6H) and 1.91 (s, 12H) ppm.



2,2'-binaphthalene (**3h**): ¹H NMR (400 MHz, CDCl₃) δ = 8.18 (s, 2H), 7.87-7.99 (m, 4H) and 7.48-7.57 (m, 2H) ppm.

