



Supporting Information

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**Transition Metal Free Homocoupling of Organomagnesium
compounds**

Supporting Information

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General All reactions were carried out under a nitrogen atmosphere in dried glassware. All starting materials were purchased from commercial sources and used without further purification. THF was continuously refluxed and freshly distilled from sodium benzophenone ketyl under nitrogen. Yields refer to isolated yields of compounds estimated to be > 95 % pure as determined by ¹H-NMR, ¹³C-NMR and capillary GC. The analytical data for the known compounds was found to match the literature data.

Preparation of the reagent 3,3',5,5'-tetra-tert-butyl-4,4'-diphenoquinone (1): although phenoquinone (1) can be easily prepared according *Kharasch* procedure¹ using oxygen we report herein a practical procedure using air as oxidant. Thus, the bubbling of air through solution of 2,6-di-tert-butylphenol (20.6 g, 0.1 mol) and potassium hydroxide (20 g in 30 mL of water) in tert-butyl alcohol (250 mL) within 48 h at room temperature leads to the formation of a brown precipitate. The reaction mixture was diluted with water (250 ml) and the precipitate was collected on filter. Upon recrystallization from iso-propanol brown needles were obtained (17 g, 86 %, mp = 246 °C).

Typical procedure. **Preparation of diethyl biphenyl-4,4'-dicarboxylate (4e):** A dry and argon flushed 10 mL flask, equipped with a magnetic stirrer and a septum, was charged

with ethyl 4-iodobenzoate (552 mg, 2.0 mmol) in THF (2 mL). The reaction mixture was cooled to -20°C and *i*-PrMgCl·LiCl² (2 mL, 1.05 M in THF, 2.1 mmol) was added dropwise. After 20 min at -20°C the I/Mg-exchange was complete (checked by GC analysis of reaction aliquots, the conversion was more than 98%) and solution of phenoquinone (**1**, 449 mg, 1.1 mmol) in THF (5 mL) was added dropwise. The reaction mixture was stirred for 2 h at 0°C and was then quenched with sat. aqueous NH₄Cl solution (2 mL). The aqueous phase was extracted with ether (3 x 4 mL), dried with Na₂SO₄ and concentrated *in vacuo*. The crude residue was purified by flash chromatography (pentane:CH₂Cl₂) yielding the diethyl biphenyl-4,4'-dicarboxylate (**4e**, 184 mg, 93%) as a white crystals.

2,2'-bis(allyloxy)-5,5'-dibromobiphenyl (6c):

¹H-NMR (CDCl₃, 200 MHz): δ = 7.38 (dd, *J* = 2.6 Hz, *J* = 8.7 Hz, 2 H); 7.37 (d, *J* = 2.6 Hz, 2 H); 6.79 (brd, *J* = 8.7 Hz, 2 H); 6.00 - 5.78 (m, 2 H); 5.27-5.12 (m, 4 H); 4.47 (dt, *J* = 1.7 Hz, *J* = 4.8 Hz, 4 H).

¹³C-NMR (CDCl₃, 75 MHz): δ = 150.3; 134.7; 130.8; 127.2; 117.6; 117.5; 116.9; 110.8, 69.0.

HR-MS: (C₈H₈BrN) calculated 421.9517
 found 421.9493

tetraethyl 5,5'-dibromobiphenyl-2,2',4,4'-tetracarboxylate (97b):

¹H-NMR (CDCl₃, 200 MHz): δ = 8.40 (s, 2 H); 7.44 (s, 2 H); 4.38 (q, *J* = 7.2 Hz, 4 H); 4.04 (q, *J* = 7.2 Hz, 4 H); 1.36 (t, *J* = 7.2 Hz, 6 H); 1.01 (t, *J* = 7.2 Hz, 6 H).

¹³C-NMR (CDCl₃, 75 MHz): δ = 165.4; 165.3; 145.2; 135.9; 133.3; 132.2; 129.0; 125.9; 62.4; 61.8; 14.6; 14.2.

MS (EI, 70 eV): *m/z* (%) = 602 (M⁺, ⁸¹Br₂, 0.54); 600 (M⁺, ⁷⁹Br⁸¹Br 0.95); 598 (M⁺, ⁷⁹Br₂, 0.39); 577 (11); 555 (20); 553 (10); 529 (50); 528 (24); 527 (100); 526 (12); 525 (49); 501 (34); 500 (14); 499 (63); 497 (33); 419 (18).

HR-MS: (C₈H₈BrN) calculated 597,9838 found 597,9809

(6E,8E)-2,2,3,3,12,12,13,13-octamethyl-4,11-dioxa-3,12-disilatetradeca-6,8-diene (12d):

¹H-NMR (CDCl₃, 200 MHz): d = 6.15 (brd, *J* = 14.5 Hz, 2 H); 5.66 (m, 2 H); 4.14 (brd, *J* = 4.5 Hz, 4 H); 0.84 (s, 9 H); 0.00 (s, 6 H).

¹³C-NMR (CDCl₃, 75 MHz): d = 132.6; 129.7; 63.9; 26.3; 18.8; -4.8.

MS (EI, 70 eV): m/z (%) = 327 (M⁺ - CH₃, 0.4); 189 (10); 148 (14); 147 (100); 79 (14); 75 (36); 73 (44).

HR-MS: (C₁₈H₃₈O₂Si₂ - CH₃) calculated 327,2176 found 327,2156

(6Z,8Z)-2,2,3,3,12,12,13,13-octamethyl-4,11-dioxa-3,12-disilatetradeca-6,8-diene (12e):

¹H-NMR (CDCl₃, 200 MHz): d = 6.14 (m, *J* = 8.5 Hz, 2 H); 5.55 (m, 2 H); 4.27 (brd, *J* = 5.9 Hz, 4 H); 0.82 (s, 9 H); 0.00 (s, 6 H).

¹³C-NMR (CDCl₃, 75 MHz): d = 132.6; 123.7; 59.8; 26.3; 18.7; -4.8.

MS (EI, 70 eV): m/z (%) = 342 (M⁺, 1.5); 285 (24); 197 (33); 148 (14); 147 (100); 79 (14); 75 (35); 73 (92).

HR-MS: (C₁₈H₃₈O₂Si₂) calculated 342,2410 found 342,2383

UV/Vis monitoring of the interaction of Grignard reagents with phenoquinone 6 using a stopped-flow technique. All operations were performed under atmosphere of dry Ar. Samples were prepared in well-dried and Ar-flushed vessels sealed with rubber septa. THF solutions of phenoquinone 1 and Grignard reagents (titrated with I₂) were mixed in a volume ratio 1 : 10 using syringes with pneumatically driven pistons on a Hi-Tech SF-61DX2 stopped flow diode array spectrophotometer system. Multiwavelength absorption spectra were taken in constant time intervals.

Reduction of phenoquinone 1 with sodium. Pieces of sodium (1.5 g) were put in a brown THF solution of diphenoquinone 1 (25

ml, 5.63×10^{-5} M) and a reaction mixture was kept overnight at room temperature. The UV/Vis spectrum indicated a complete conversion of phenoquinone **1** ($\lambda_{\max} = 423$ nm) to phenoxide radical ($\lambda_{\max} = 459$ nm). This radical anion decomposes immediately if it is diluted with THF, which was freshly distilled over Na/benzophenone and kept under rubber septum for one hour. Therefore for dilution and further stopped-flow measurements of the reaction of phenoxide radical with 2-naphtelenylmagnesium bromide **7j** we used THF containing trace amounts of LiAlH_4 , which does not react with phenoxide radical.

References and Notes:

- 1 M. S. Kharasch, B. S. Joshi, *J. Org. Chem.* **1957**, *22*, 1439.
- 2 *i*-PrMgCl·LiCl is commercially available from Chemetall GmbH (Frankfurt am Main)