

Supplementary Information for:

Tetraarylethylene having two nitroxide groups: redox-switching of through-bond magnetic interaction by conformation change

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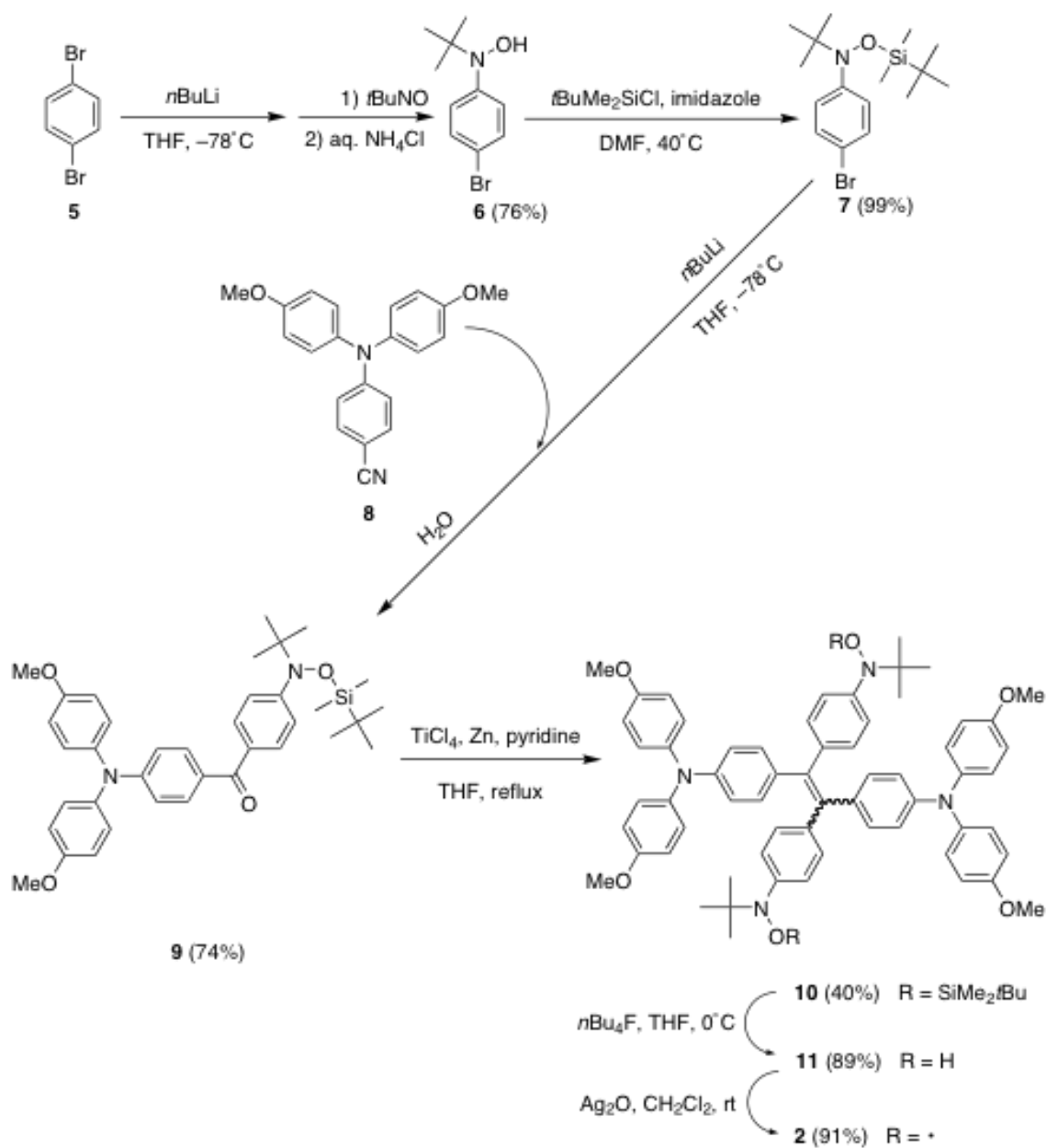
Synthesis of **2**

The synthesis of bisnitroxide **2** is outlined in Scheme S1. Monolithiated 1,4-dibromobenzene (**5**) was coupled with 2-methyl-2-nitrosopropane to give hydroxylamine (**6**). The hydroxylamine **6** was protected with *tert*-butyldimethylsilyl group. Asymmetrically substituted diarylketone (**9**) was prepared by addition of the nitrile (**8**) to the lithiated **7** and subsequent hydrolysis. The reductive coupling of the ketone **9** with a low-valent titanium reagent¹ gave a mixture of *cis*- and *trans*-isomers of **10**. After desilylation of **10** with tetrabutylammonium fluoride, the desired bisnitroxide **2** was obtained by oxidation of the bishydroxylamine **11** with Ag₂O. The ratio of the two isomers for the precursor **11** was estimated to be 41:59 from the ¹H- and ¹³C-NMR spectra. This ratio is in fairly good accordance with that estimated from the temperature dependence of the magnetic susceptibility of **2** (see text).

Experimental data for **11**: ^1H NMR (CDCl_3 , 400 MHz): δ 6.53–7.01 (m, 32H for *cis-trans* mixture), 3.74 and 3.72 (s, 12H for *cis-trans* mixture), 1.09 and 1.04 (s, 18H for *cis-trans* mixture) ppm; ^{13}C NMR (CDCl_3 , 100 Mhz): δ 155.4, 146.5, 146.4, 140.8, 140.6, 139.3, 136.6, 135.8, 132.1, 132.0, 130.7, 130.5, 126.4, 126.2, 123.3, 119.5, 118.8, 114.4, 60.6, 60.3, 55.4, 26.0, 25.9 ppm (23 peaks for *cis-trans* mixture). For **2**: HR-MS (FAB+, NBA): m/z calc. for $\text{C}_{62}\text{H}_{63}\text{N}_4\text{O}_6$ [MH^+] 959.4748, found 959.4763; calc. for $\text{C}_{62}\text{H}_{64}\text{N}_4\text{O}_6$ [MH_2^+] 960.4826, found 960.4818; Anal. calc. for $\text{C}_{62}\text{H}_{62}\text{N}_4\text{O}_6$: C, 77.64; H, 6.52; N, 5.84; O, 10.01. Found: C, 77.46; H, 6.68; N, 5.57; O, 10.00. For **3**: ^1H NMR (CDCl_3 , 400 MHz): δ 6.61–7.16 (m, 34H for *cis-trans* mixture), 3.77 (s, 12H for *cis-trans* mixture) ppm; ^{13}C NMR (CDCl_3 , 100 MHz): δ 155.5, 155.4, 146.6, 146.5, 144.2, 143.9, 140.9, 140.8, 139.8, 139.7, 136.4, 136.1, 131.9, 131.4, 127.4, 126.3, 126.2, 126.0, 119.6, 114.5, 114.4, 55.5 ppm (22 peaks for *cis-trans* mixture); HR-MS (FAB+, NBA): m/z calcd for $\text{C}_{54}\text{H}_{46}\text{N}_2\text{O}_4$ [M^+] 786.3458, found 786.3484; Anal. calcd for $\text{C}_{54}\text{H}_{46}\text{N}_2\text{O}_4$: C, 82.42; H, 5.89; N, 3.56; O, 8.13. Found: C, 82.14; H, 6.14; N, 3.37; O, 8.04.

Reference

- 1 I. Agranat, S. Cohen, R. Isaksson, J. Sandström and M. R. Suissa, *J. Org. Chem.*, 1990, **55**, 4943.



Scheme S1 Synthetic route for **2**.