

## SUPPORTING INFORMATION

### Reaction of 2,5-dihydroxy-[1,4]-benzoquinone with nucleophiles – *ipso*-substitution vs. addition/elimination

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## Experimental Methods

### General information on methods

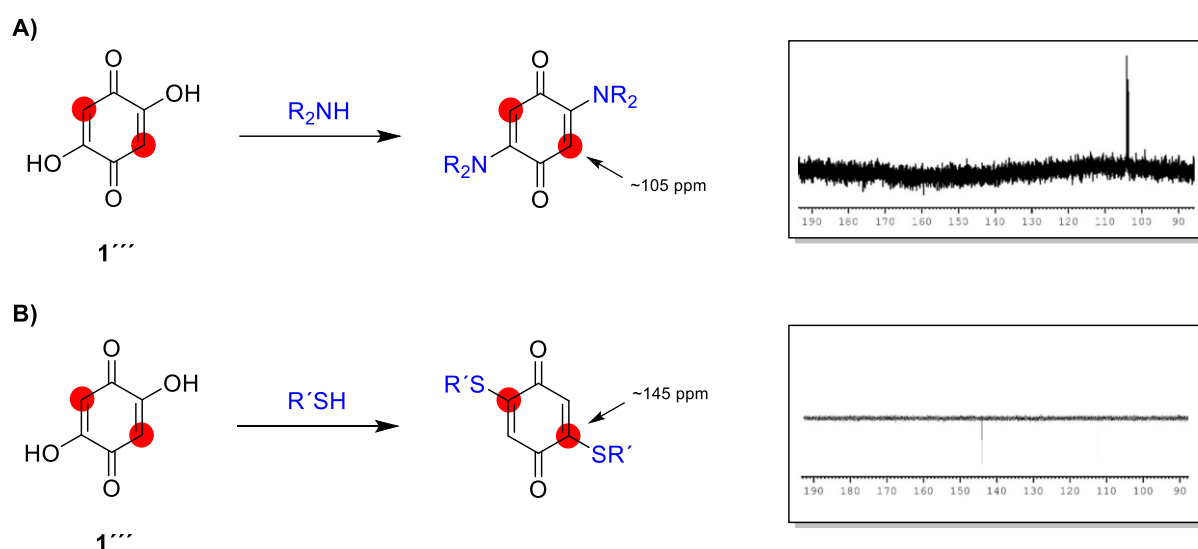
Chemicals and reagents (DHBQ, amines, thiols) as well as solvents were purchased from Sigma-Aldrich (Schnelldorf, Germany) or ABCR (Karlsruhe, Germany). Chemicals were of the highest grade available and used without further purification, unless otherwise stated. DHBQ was recrystallized from glacial acetic acid. NMR solvents were purchased from Eurisotop (Saint-Aubin, France) and Sigma-Aldrich.

The NMR spectroscopic experiments were performed on a Bruker Avance II 400 instrument (<sup>1</sup>H resonance at 400.13 MHz, <sup>13</sup>C resonance at 100.61 MHz) with a 5 mm broadband probe head (BBFO) equipped with a z-gradient using standard Bruker pulse programs. Data were collected with 32k data points and apodized with a Gaussian window function (GB = 0.3) prior to Fourier transformation. Enhancement of the S/N ratio was achieved by multiplication of the FID with an exponential window function (lb = 1Hz). Bruker TopSpin software was used for data processing. All chemical shifts are given in ppm, referenced to the residual solvent signals.

### General procedure for the reaction of DHBQ with nucleophiles:

The reactions with isotopically labelled DHBQ were performed in the NMR tube in either deuterated or non-deuterated solvents (in case only  $^{13}\text{C}$  spectra were recorded). In a typical procedure, the DHBQ isotopomer (1.5 mg) was dissolved in 1 mL of solvent (acetonitrile, water, amines) in a glass vial and vortexed for 10 s. The nucleophile (2.0 eq.) was added (with the exception of amines that were solvent and co-reactant at the same time) and the mixture vortexed again. The vial was closed, heated to  $40^\circ\text{C}$  for 15 min, cooled to r.t. and a drop of  $\text{CD}_3\text{CN}$  (NMR lock) was added. The solution was transferred to the NMR tube and the  $^{13}\text{C}$  NMR spectra (4 scans) were recorded. In some cases, the reaction was directly performed in the standard NMR tube with only 0.6 mL of solvent.

### Structural Characterization



**Scheme S1.** A) *Ipso*-substitution in case of the reaction of the  $^{13}\text{C}$ -3/ $^{13}\text{C}$ -6 DHBQ isotopomer with morpholine to 2,5-dimorpholino-[1,4]-benzoquinone (inset:  $^{13}\text{C}$  NMR, 4 scans); B) Addition/elimination sequence in case of the reaction of the  $^{13}\text{C}$ -3/ $^{13}\text{C}$ -6 DHBQ isotopomer reacting with thiophenol to 2,5-bis(thiophenyl)-[1,4]-benzoquinone (inset:  $^{13}\text{C}$  NMR, 4 scans).