Supporting Information for:

**Kinetic Control of the Direction of Inclusion of Nitroxide Radicals into Cyclodextrins**

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**General notes**

- 2D-ROESY spectrum of 1a@β-CD
- 2D-ROESY spectrum of 1a@γ-CD
- 2D-ROESY spectra of 2a@γ-CD
- 2D-ROESY spectrum of 3a@β-CD
- 2D-ROESY spectrum of 3a@γ-CD
- 2D-ROESY spectra of 6a@β-CD
General.

EPR spectra were recorded by using a Bruker ELEXYS E500 spectrometer equipped with an NMR gaussmeter for field calibration and a microwave frequency counter for g factor determination. Digitised EPR spectra were transferred to a PC and analysed by comparison with simulated spectra. ESR spectra has been recorded by using the following instrument settings: microwave power 0.79 mW, modulation amplitude 0.04 mT, modulation frequency 100 kHz, scan time 180 s, 2K data points.

1D and 2D NMR spectra were recorded at 298 K on a Varian Inova spectrometer operating at 600 MHz in D$_2$O solutions using the solvent peak as an internal standard (δ scale). Chemical shifts are reported in parts per million (δ scale). ROESY data were collected using a 90° pulse width of 7.2 µs and a spectral width of 6000 Hz in each dimension, respectively. The data were recorded in the phase sensitive mode using a CW spin-lock field of 2 KHz, without spinning the sample. Acquisitions were recorded at mixing times 300 ms. Other instrumental settings were: 64 increments of 2K data points, 8 scans per t1, 1.5 s delay time for each scan.

ESI-MS spectra were recorded with Micromass ZMD spectrometer by using the following instrumental settings: positive ions; desolvation gas (N$_2$) 230 L/h; cone gas (skimmer): 50 L/h; desolvation temp. 120° C; capillary voltage: 3.2 kV; cone voltage: 40 and 100 V; hexapole extractor: 3 V.
**FIGURE S1.** Portions of the ROESY (600 MHz, D$_2$O, 298 K) spectra of a 0.5 mM solution of 1a (right, X range from 1.00 to 1.66 ppm, Y range from 3.76 to 4.15 ppm; left, X range from 3.56 to 4.25 ppm, Y range from 7.38 to 7.51 ppm) containing an equimolar amount of β-CD. The dotted lines in the spectrum a evidence the cross peak connecting phenyl ring protons of 1a with H5/H6 CD protons only, not observed with H3.

**FIGURE S2.** Portions of the ROESY (600 MHz, D$_2$O, 298 K) spectra of a 0.5 mM solution of 1a (right, X range from 0.90 to 1.32 ppm, Y range from 3.50 to 3.94 ppm; left, X range from 7.00 to 7.60 ppm, Y range from 3.66 to 3.93 ppm) containing 0.13 mM γ-CD. The a spectrum evidences the cross peak connecting phenyl ring protons of 1a with H3 CD protons only, not observed with H5 or H6.
**FIGURE S3.** Portions of the ROESY (600 MHz, D$_2$O, 298 K) spectra of a 0.5 mM solution of 2a (right, X range from 0.0 to 2.7 ppm, Y range from 3.60 to 4.00 ppm; left, X range from 0.2 to 2.9 ppm, Y range from 3.70 to 3.95 ppm) containing a) 0.22 mM γ-CD; b) 0.64 mM γ-CD. The square in plot a evidences the cross peak connecting tert-butyl protons of 2a with CD H3 signal, and the square in plot b shows the intermolecular interaction of the tert-butyl of 2a with CD H5 or H6 protons. The largest cross peaks in both plots represent intramolecular interactions between tert-butyl and ortho-methyl with benzyl signals of 2a. No intermolecular correlations were detected for phenyl ring and the inner protons of the host.

**FIGURE S4.** Portions of the ROESY (600 MHz, D$_2$O, 298 K) spectra of a 0.5 mM solution of 3a (right, X range from 0.9 to 2.0 ppm, Y range from 3.65 to 4.12 ppm; left, X range from 1.3 to 2.5 ppm, Y range from 3.78 to 3.98 ppm) containing a) 0.5 mM β-CD; b) 0.4 mM γ-CD. The presence of cross peaks in plot a connecting methyl ring-substituents of 3a with H3 β-CD protons only, not observed with H5 and H6 and the pattern of interactions for the tert-butyl portion indicate the inclusion of the amine into the CD from the tert-butyl side. Same considerations are valid also for the complex with γ-CD. In both complexes no intermolecular correlations were detected for phenyl ring and the inner protons of the hosts.
**FIGURE S5.** Portions of the ROESY (600 MHz, D$_2$O, 298 K) spectra of a 0.5 mM solution of 6a (right, X range from 6.5 to 7.9 ppm, Y range from 3.62 to 4.08 ppm; left, X range from 0.0 to 3.0 ppm, Y range from 3.76 to 3.99 ppm) containing a) 0.1 mM β-CD; b) 0.4 mM β-CD. The presence of cross peaks in plot a connecting methylene ring-substituent (of ethyl group) of 6a with H3 β-CD protons only (black square), not observed with H5 and H6, together with interactions of the tert-butyl portion with H3 (strong) and H5 (medium) and H6 (weak) (red square), and connection of phenyl ring protons with H3 (black square) in plot b, indicate that the inclusion of the amine into the CD occurs from the tert-butyl side. The out-of-square cross-peaks present in both plots are relative to intramolecular interactions of the amine.