Electronic Supplementary Material (ESI) for Organic and Biomolecular Chemistry

Supporting Information for:

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

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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_2O solutions using the solvent peak as an internal standard (4.76 ppm) 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 *t*1, 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.

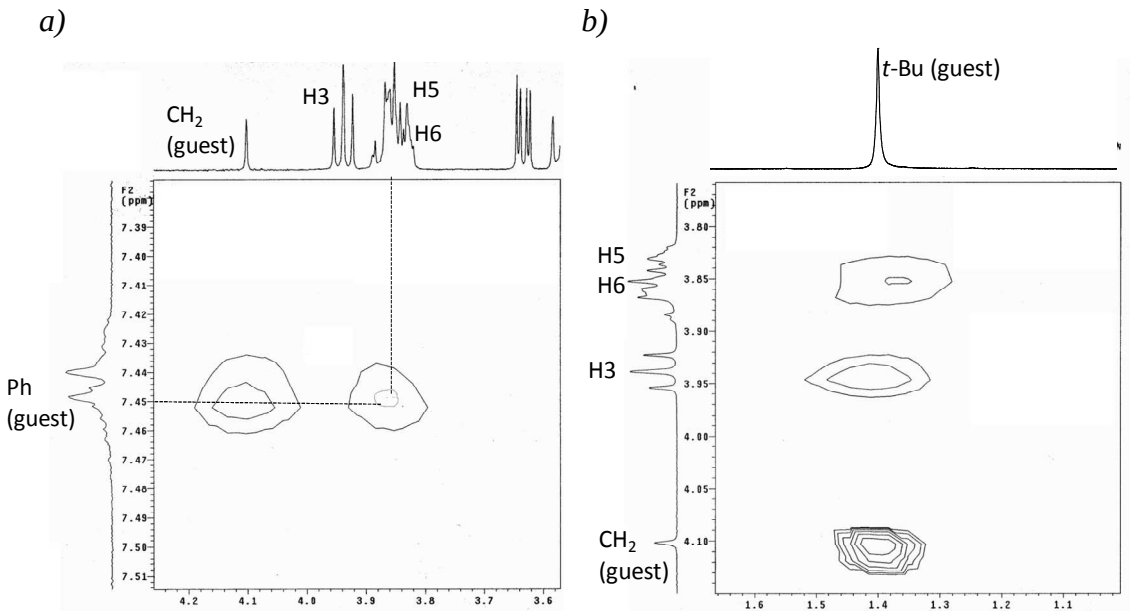

FIGURE S1. Portions of the ROESY (600 MHz, D_2O, 298 K) spectra of a 0.5 mM solution of **1a** (right, X range from 1.00 to 1.66 ppm, Y range from 3.76 to 4.15 ppm; left, X range from 3.56 to 4.25 ppm, Y range from 7.38 to 7.51 ppm) containing an equimolar amount of β-CD. The dotted lines in the spectrum *a* evidence the cross peak connecting phenyl ring protons of **1a** with H5/H6 CD protons only, not observed with H3.

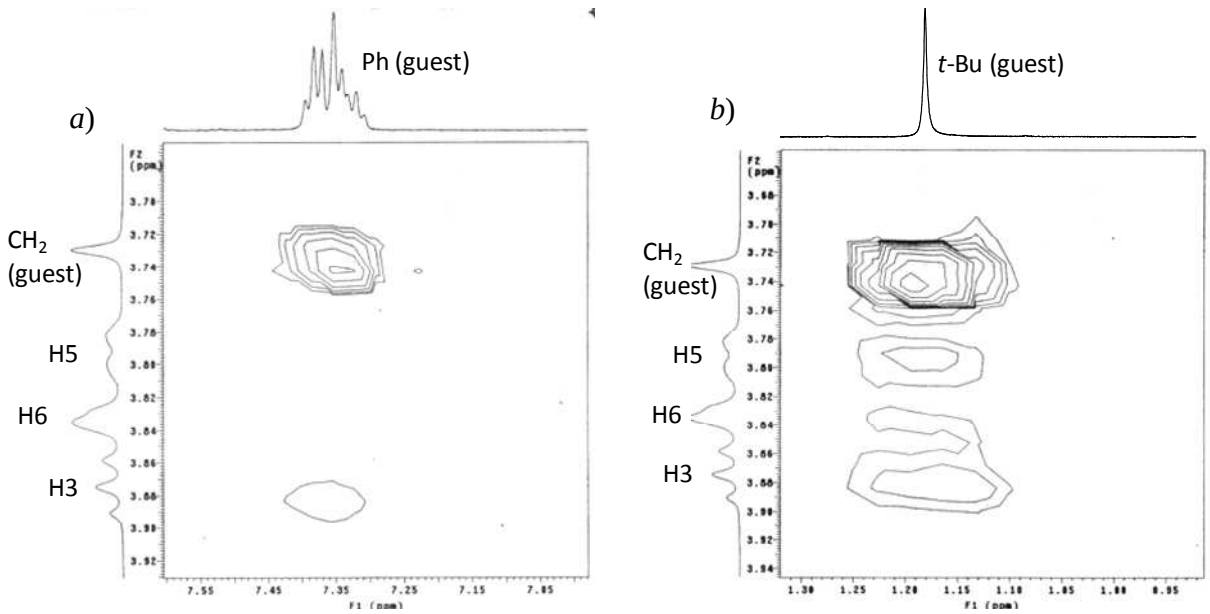

FIGURE S2. Portions of the ROESY (600 MHz, D_2O, 298 K) spectra of a 0.5 mM solution of **1a** (right, X range from 0.90 to 1.32 ppm, Y range from 3.50 to 3.94 ppm; left, X range from 7.00 to 7.60 ppm, Y range from 3.66 to 3.93 ppm) containing 0.13 mM γ-CD. The *a* spectrum evidences the cross peak connecting phenyl ring protons of **1a** with H3 CD protons only, not observed with H5 or H6.

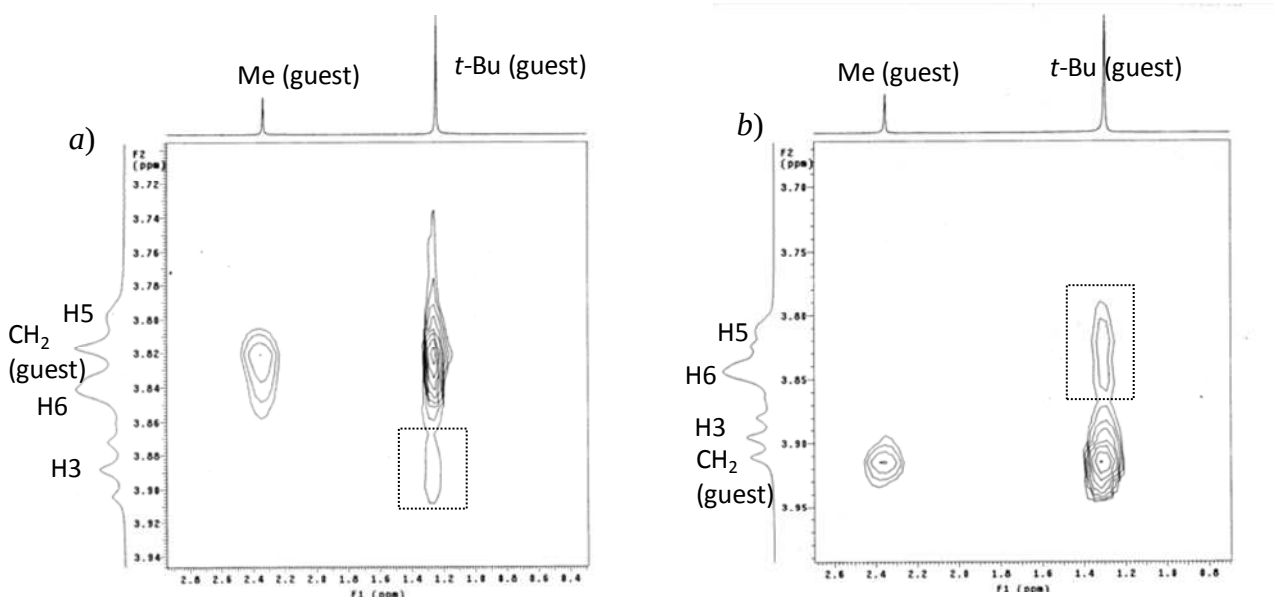

FIGURE S3. Portions of the ROESY (600 MHz, D_2O, 298 K) spectra of a 0.5 mM solution of **2a** (right, X range from 0.0 to 2.7 ppm, Y range from 3.60 to 4.00 ppm; left, X range from 0.2 to 2.9 ppm, Y range from 3.70 to 3.95 ppm) containing *a*) 0.22 mM γ-CD; *b*) 0.64 mM γ-CD. The square in plot *a* 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.

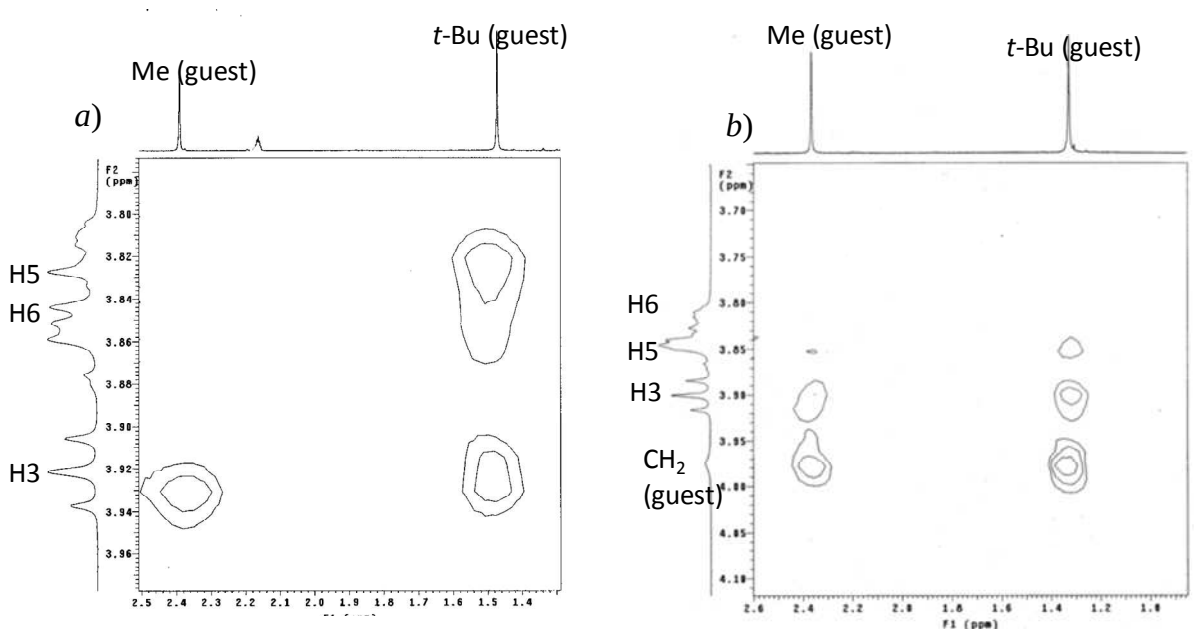

FIGURE S4. Portions of the ROESY (600 MHz, D_2O, 298 K) spectra of a 0.5 mM solution of **3a** (right, X range from 0.9 to 2.0 ppm, Y range from 3.65 to 4.12 ppm; left, X range from 1.3 to 2.5 ppm, Y range from 3.78 to 3.98 ppm) containing *a*) 0.5 mM β-CD; *b*) 0.4 mM γ-CD. The presence of cross peaks 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.

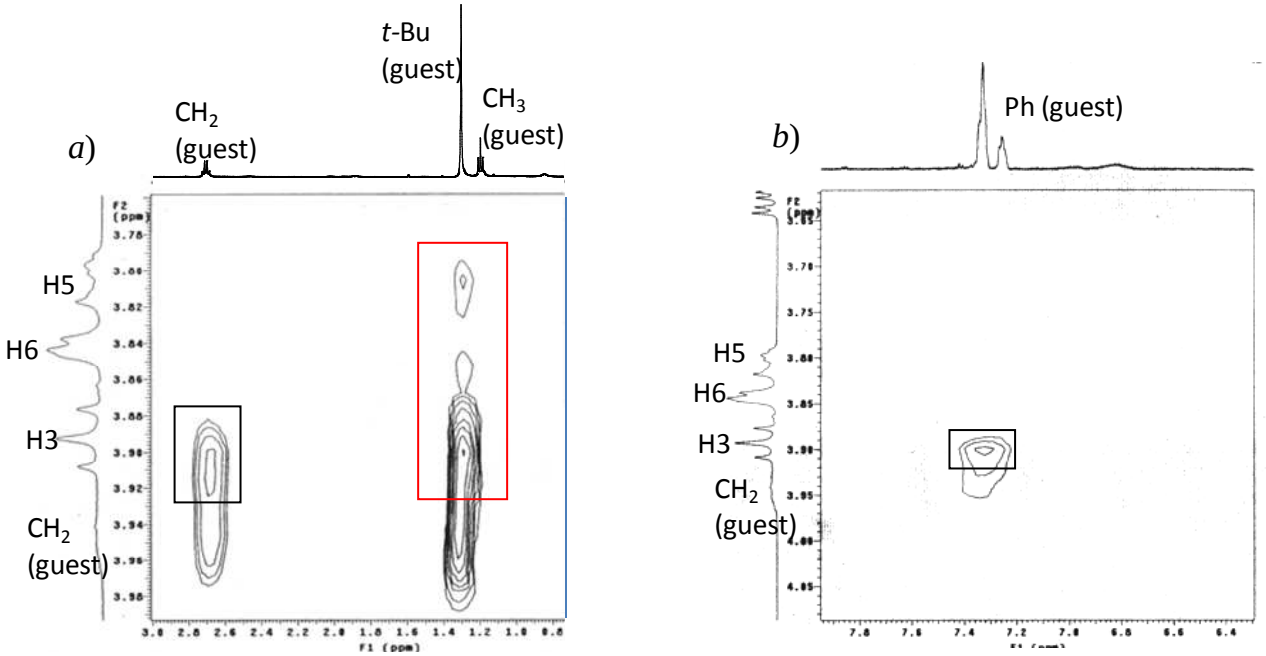

FIGURE S5. Portions of the ROESY (600 MHz, D_2O, 298 K) spectra of a 0.5 mM solution of **6a** (right, X range from 6.5 to 7.9 ppm, Y range from 3.62 to 4.08 ppm; left, X range from 0.0 to 3.0 ppm, Y range from 3.76 to 3.99 ppm) containing *a*) 0.1 mM β-CD; *b*) 0.4 mM β-CD. The presence of cross peaks 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.