Supporting Information

High binding yet accelerated guest rotation within a cucurbit[7]uril complex. Toward paramagnetic gyroscopes and rolling nanomachines.

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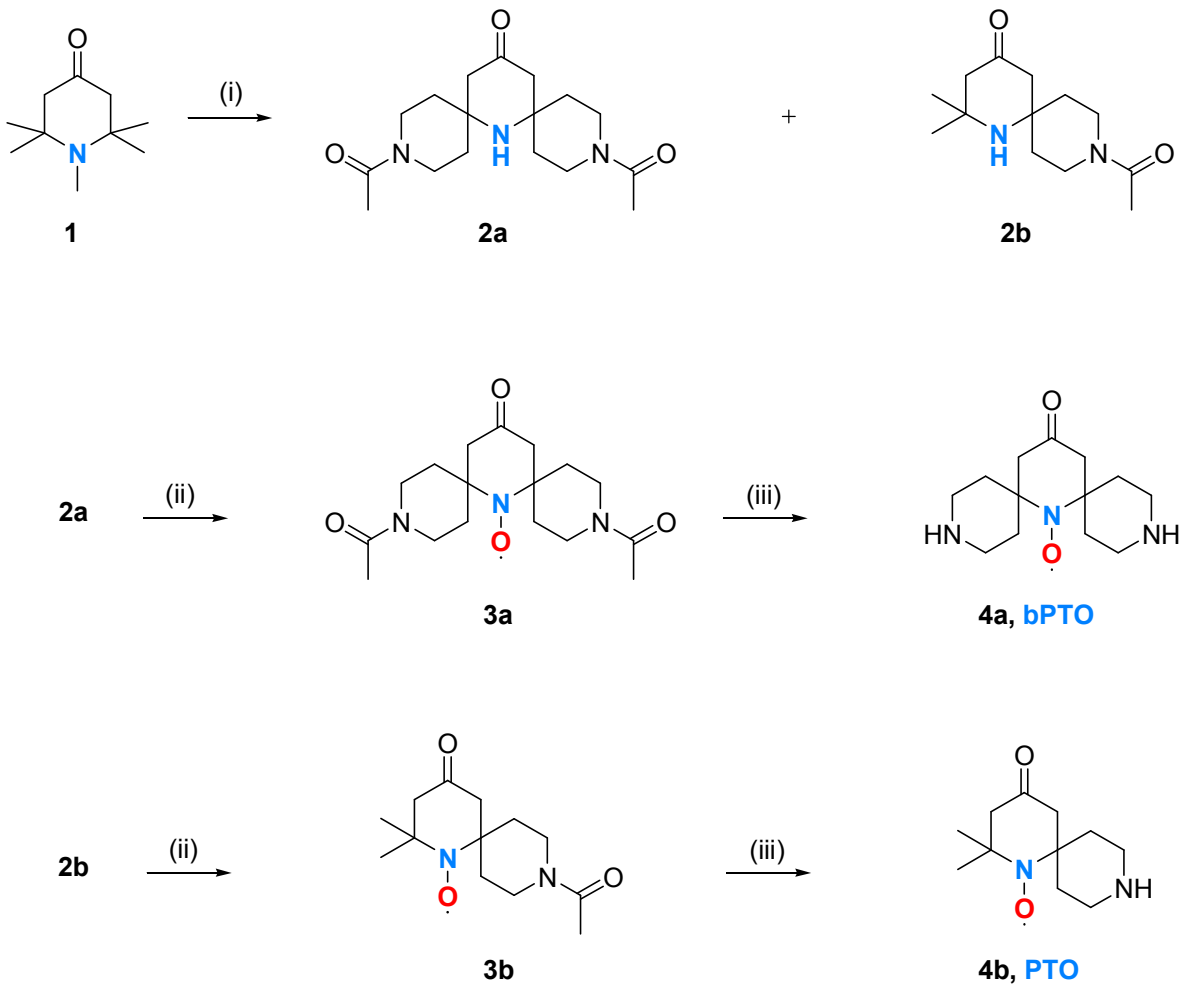


Figure S1. Reagents and conditions : (i) 1-acetylpiperidin-4-one, NH_4Cl, DMSO, 60°C, 16h. (ii) H_2O_2(30%), $Na_2WO_4.2H_2O$, EtOH, 25°C, 24h. (iii) KOH (6M), EtOH, 50°C, 12h.

General procedure: **bPTO** (**4**) and **PTO** (**6**) were synthesized in a three-steps sequence starting from 1,2,2,6,6-pentamethylpiperidin-4-one (**1**). First, the spiro(hetero)cyclohexyl moieties were introduced by Utsumi's method, using 1-acetylpiperidin-4-one as reactant, a mixture of 2,6-spirosubstituted piperidin-4-one (**2a**) and the corresponding mono spirosubstituted piperidin-4-one (**2b**) was obtained.[1] Then, compounds **2a** and **2b** were oxidized by hydrogen peroxide in the presence of sodium tungstate to yield nitroxide radicals **3a** and **3b** respectively. Finally, acetamido groups were removed in aqueous basic conditions to give **bPTO** (**4a**) and **PTO** (**4b**). CB[7] and CB[8] were obtained from a previously reported procedure.[2]

Experimental section. 1,2,2,6,6-Pentamethylpiperidin-4-one **1**, 1-acetylpiperidin-4-one and **bPyTO** were synthesized according to the literature procedures.[1,3,4] All chemicals used in syntheses were purchased from Aldrich Chemical Co. Purification of products was accomplished by flash column chromatography on silica gel (Merck silica gel 60, 230-400 mesh). NMR measurements were recorded on a Bruker AVL 300 spectrometer (^{1}H-NMR 300.1 MHz and ^{13}C-NMR 75.5 MHz) using $CDCl_3$ as the solvent (internal reference). Splitting patterns are indicated as follows: br, broad; s, singlet; m, multiplet. Mass spectral analyses were carried out using a Q-STAR Elite at the Aix-Marseille Université Mass

Spectrum Facility, Spectropole Saint Jérôme Marseille. Melting points were determined using a Bibby SMP3 apparatus and are uncorrected. The final product was purified to ≥ 95% and was confirmed by HPLC and LC-MS analysis. HPLC experiments were performed using Agilent 1200 system equipped with UV-Vis absorption and fluorescence detectors. A fused core C18 column (Phenomenex, Kinetex C18, 100 mm x 4.6 mm, 2.6 µm) was used. Typically, a gradient elution using aqueous mobile phase with increasing fractions of acetonitrile (from 10% to 40% over 5 min and from 40 to 100% over 5 min) in the presence of 0.1% TFA was used. The compounds were eluted using a flow rate of 1.5 ml/min. LC-MS analysis were performed using Agilent 1260 equipped with UV-Vis absorption and mass spectrum detector. Typically, an isocratic elution using 40% H_2O and 60% MeOH over 5 min was used. The compounds were eluted using a flow rate of 0.1 ml/min. **bPTO** (1.2 mg) and ascorbic acid (5.2 mg) were dissolved in doubly distilled deionized water (0.5 mL). After few minutes, ^{1}H NMR of this sample was achieved using a small capillary containing $CDCl_3$. α-CD was from ACROS. β-CD, DM-β-CD, TEMPO (sublimed, 99%), ascorbic acid and sodium ascorbate were from Aldrich and used as received. ESR measurements were performed on a Bruker Elexsys spectrometer operating at 9.4 GHz (X-band) in 50 µL capillaries using the following parameters: microwave power 5 mW and modulation amplitude 0.1 G. DFT calculations were performed with the Gaussian09 Rev.D01 package. All the structures were fully optimized at the B3LYP/6-31G(d) level of theory taking into account solvation effects (water) with CPCM model.[5]

Synthesis of 3,11-Diacetyl-7-azadispiro[5.1.5.3]hexadecan-15-one (2a) and 9-acetyl-2,2-dimethyl-1,9-diazaspiro[5.5]undecan-4-one (2b).

To a stirred mixture of 1,2,2,6,6-pentamethylpiperidin-4-one **1** (3.74 g, 22.13 mmol) and 1-acetyl-piperidin-4-one (9.37 g, 66.45 mmol) in dimethylsulfoxide (50 mL), NH_4Cl (7.10 g, 132.78 mmol) was added at room temperature. The mixture was heated at 60°C during 16 h before being diluted with water (100 mL). Afterwise pH was adjusted at 2 with 1N HCl aqueous solution (50 mL) and the mixture was extracted with diethylether (3 x 100 mL). The aqueous layer was adjusted to pH 11 by adding 100 mL of a 30% K_2CO_3 aqueous solution and then extracted with chloroform (4 x 350 mL). The organic phase was concentrated under reduced pressure, washed with brine (100 mL), dried over Na_2SO_4, and the solvent was distilled under reduced pressure. The crude product was purified by SiO_2 column chromatography with chloroform/methanol (95/5) to afford **2a** (1.25 g, 18 %) as a pale yellow solid. mp: 165°C (lit[1]. mp: 164.2°C). $C_{17}H_{27}N_3O_3$. ^{1}H NMR (300 MHz, $CDCl_3$) δ 1.45-1.60 (m, 8H), 1.96 (s, 6H), 2.28 (s, 4H), 3.30-3.60 (m, 8H). ^{13}C NMR (300 MHz, $CDCl_3$) δ 21.12, 37.24, 38.94, 39.58, 42.21, 52.06, 55.57, 168.53, 208.33. ESI-MS *m/z* = 322 $[M+H]^+$; 344 $[M+Na]^+$ and **2b** (1.05 g, 20%) as a pale yellow solid. NMR and characterized details are the same as described in the following reference.[6]

***Synthesis of 3,11-Diacetyl-15-oxo-3,7,11-triazadispiro[5.1.5.3]hexadec-7-yl-7-oxyl* (3a)**.

Compound **2a** (0.39 g, 1.21 mmol) and $Na_2WO_4.2H_2O$ (48 mg, 0.14 mmol) were stirred in ethanol (25 mL) and H_2O_2 (30%, 5.08 mmol, 580 µL) was slowly added at 0°C. The mixture was stirred for 24 h at room temperature, then K_2CO_3 (0.50 g) was added and the solution was extracted twice with chloroform (50 mL). The organic layer was dried over Na_2SO_4 and distilled under reduced pressure. The crude product was purified by SiO_2 column chromatography using CH_2Cl_2 / EtOH (99/1) as eluent to provide **3a** (0.22 g, 54%) as a pale red solid. X-band EPR spectrum (293 K, in CH_2Cl_2): triplet, A_N = 1.43 mT. ESI-MS *m/z* = 337 $[M+H]^+$; 359 $[M+Na^+]$.

***Synthesis of* (3b)**.

Compound **2b** (0.15g, 0.63 mmol) was oxidized according to the method described for compound **3a**. The product was purified by SiO_2 column chromatography using CH_2Cl_2 / EtOH (99/1) as eluent to provide **3b** (85 mg, 53%) as a pale yellow solid. X-band EPR spectrum (293 K, in CH_2Cl_2): triplet, A_N = 1.45 mT. ESI-MS *m/z* = 254 $[M+H]^+$; 276 $[M+Na^+]$. 292 $[M+K^+]$.

***Synthesis of bPTO* (4a)**.

Compound **3a** (0.17 g, 0.51 mmol) was dissolved in ethanol (4.3 mL), before a 6M KOH aqueous solution (1 mL) was added at room temperature. The solution was then stirred at 50°C overnight. After cooling, the mixture was concentrated under reduced pressure, diluted in dichloromethane (20 mL), washed with water (5 mL), dried over Na_2SO_4 and the solvent was distilled under reduced pressure. The residue was precipitated into AcOEt to give **bPTO (4a)** as a red solid (25 mg, 20%). X-band EPR spectrum (293 K, in H_2O): triplet, A_N = 1.53 mT. ESI-MS *m/z* = 253 $[M+H]^+$; 275 $[M+Na^+]$. HRMS-ESI calcd for $C_{13}H_{22}N_3O_2^{\cdot}$ 253.1785, ($[M+H]^+$) found: 253.1784. ^1H NMR of reduced **bPTO** (400 MHz) δ 1.80-1.86 (m, 4H), 2.35-2.45 (m, 4H), 2.79 (s, 4H), 3.10-3.17 (m, 4H), 3.39-3.44 (m, 4H).

Synthesis of PTO (4b).

Compound **3b** (50 mg, 0.197 mmol) was dissolved in ethanol (1.75 mL), before a 6M KOH aqueous solution (460 µl) was added at room temperature. The solution was then stirred at 50°C overnight. After cooling, the mixture was concentrated under reduced pressure, diluted in dichloromethane (10 mL), washed with water (3 mL), dried over Na_2SO_4 and the solvent was distilled under reduced pressure to give **PTO (4b)** as a red solid (30 mg, 72%). X-band EPR spectrum (293 K, in H_2O): triplet, A_N = 1.57 mT. ESI-MS *m/z* = 212 $[M+H]^+$. HRMS-ESI calcd for $C_{11}H_{19}N_2O_2^{\cdot}$ 212.1519, ($[M+H]^+$) found: 212.1519. ^1H NMR of reduced **PTO** (400 MHz) δ 1.25 (s, 6H), 1.80-1.85 (m, 2H), 2.36-2.45 (m, 2H), 2.62 (brs, 2H), 2.75 (brs, 2H), 3.08-3.14 (m, 2H), 3.40-3.45 (m, 2H). Elemental analysis: calculated for $C_{11}H_{19}N_2O_2^{\cdot}$ • 0.5 AcOH: C 59.73 H 8.77 N 11.61; found C 59.82 H 8.73 N 11.65.

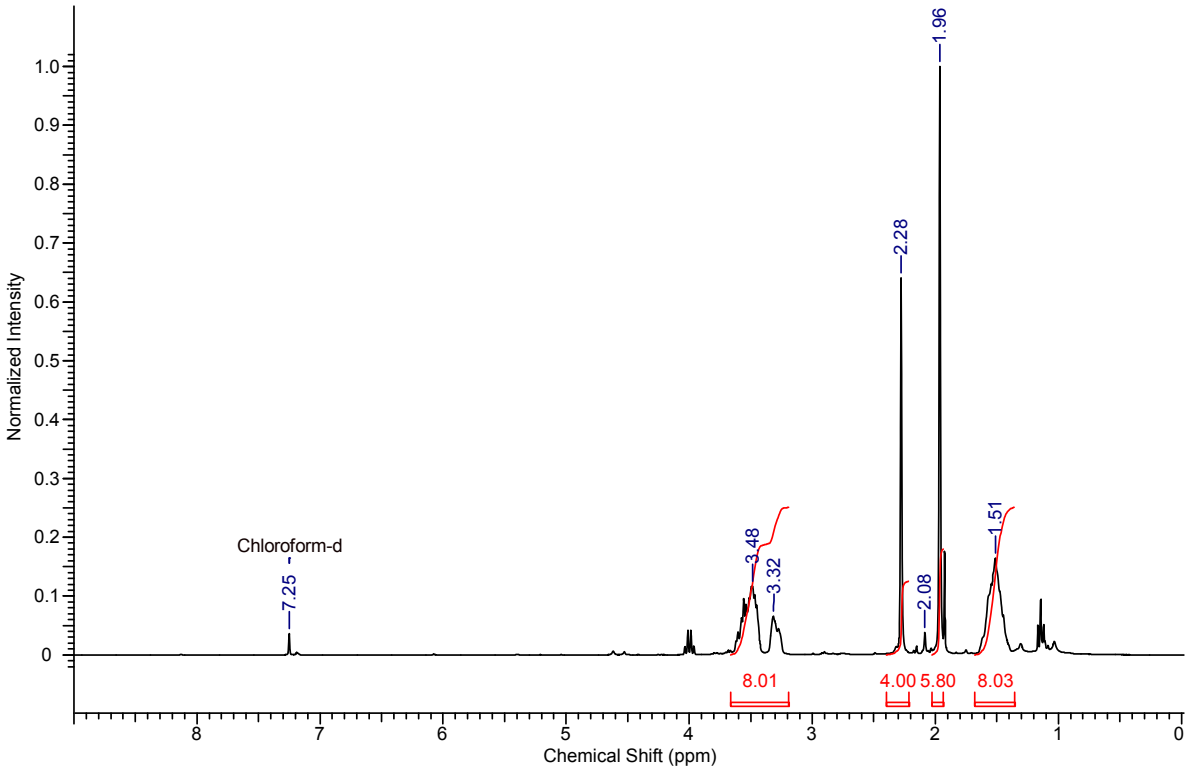


Figure S2. ^{1}H NMR spectrum of *3,11-Diacetyl-7-azadispiro[5.1.5.3]hexadecan-15-one* (**2a**).

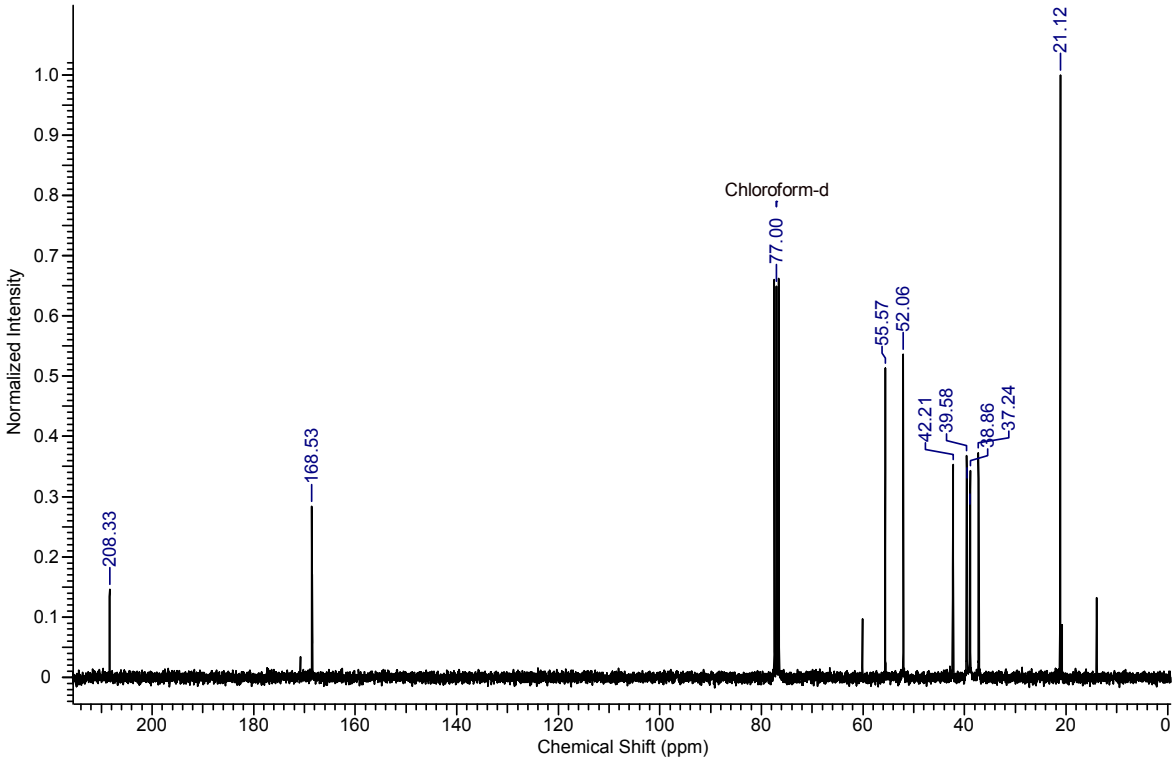


Figure S3. ^{13}C NMR spectrum of *3,11-Diacetyl-7-azadispiro[5.1.5.3]hexadecan-15-one* (**2a**).

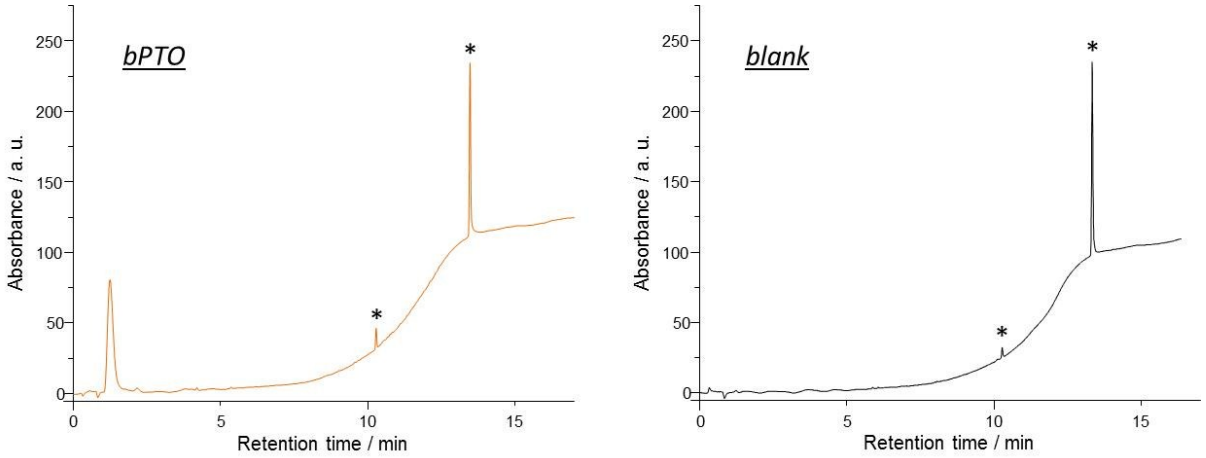


Figure S4. HPLC chromatogram of **bPTO** (**4a**) (*: internal standards)**.** (water/acetonitrile/0.1% TFA gradient, RPC18, UV detection).

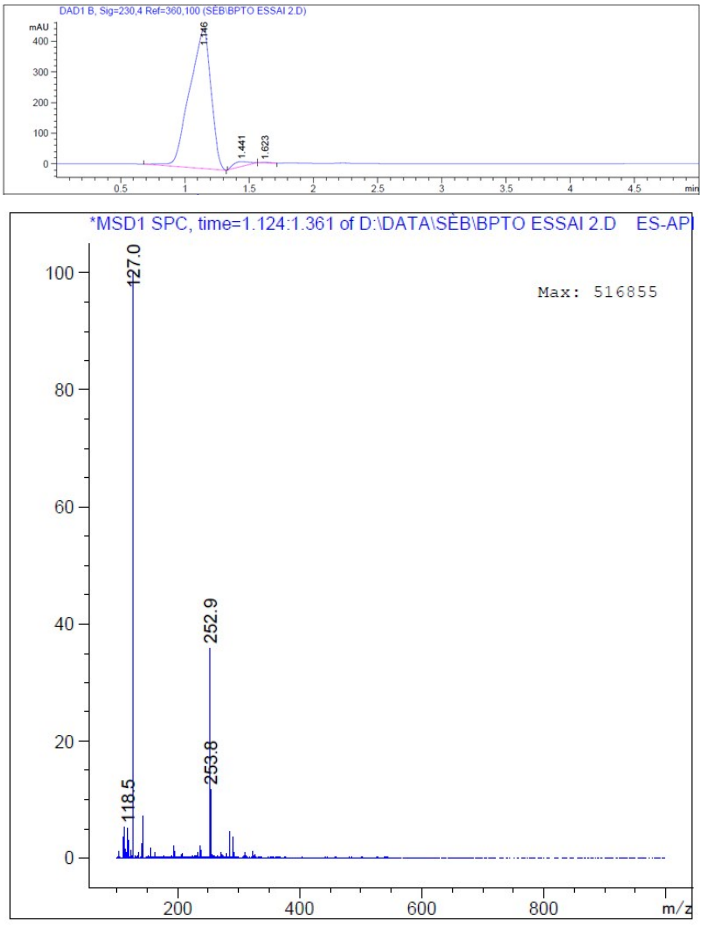


Figure S5. LC-MS analysis of **bPTO** (**4a**). (H_2O/MeOH, isocratic elution, C18, UV detection and mass detector).

As nitroxides are paramagnetic, conventional ^{1}H NMR cannot be performed. In order to get a ^{1}H NMR of the most closely related molecule, bPTO was reduced with ascorbic acid, in pure water to avoid deuterium exchange with the 4 acidic protons next to the carbonyl function that would have occurred in D_2O. $CDCl_3$, with trace amounts of $CHCl_3$ and water, was used as an external standard in a capillary tube placed inside the NMR tube for the lock.

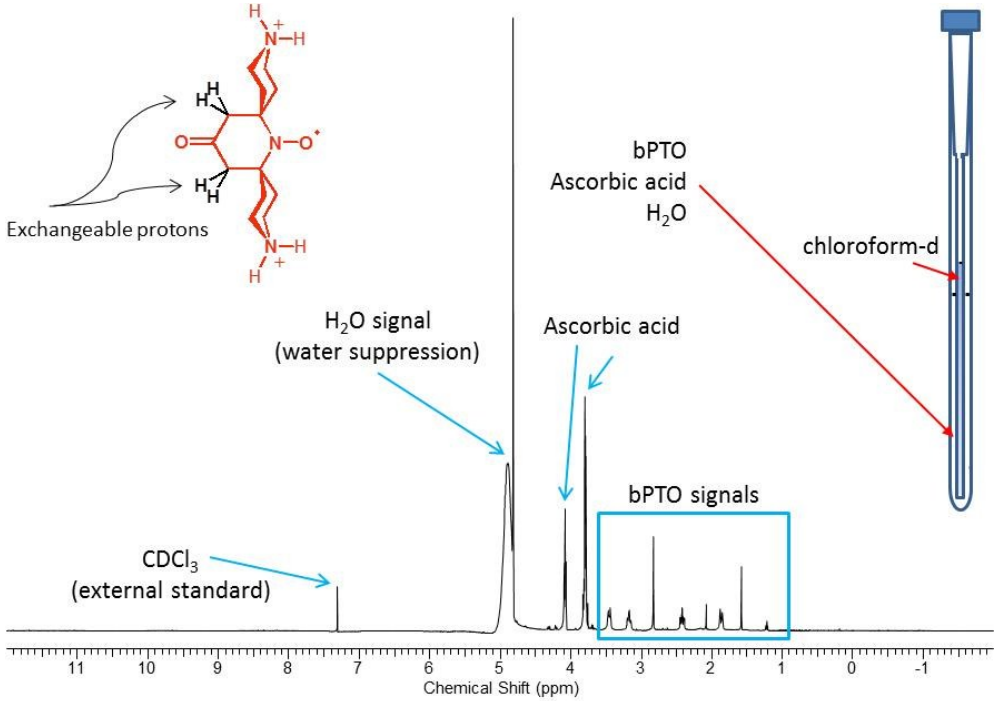


Figure S6. ^{1}H NMR spectrum of reduced **bPTO** (**4a**) in pure water with ascorbic acid.

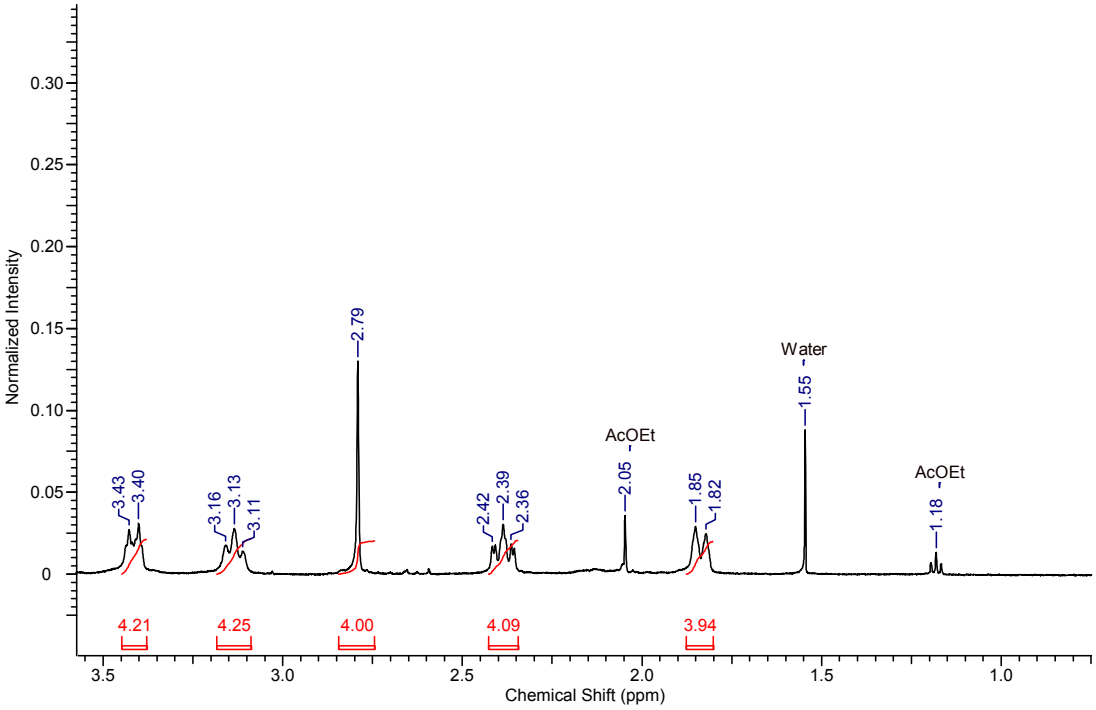


Figure S7. Excerpt of the ^{1}H NMR spectrum of Figure S6.

The same procedure as for bPTO was used to record the ^{1}H NMR spectrum of reduced PTO.

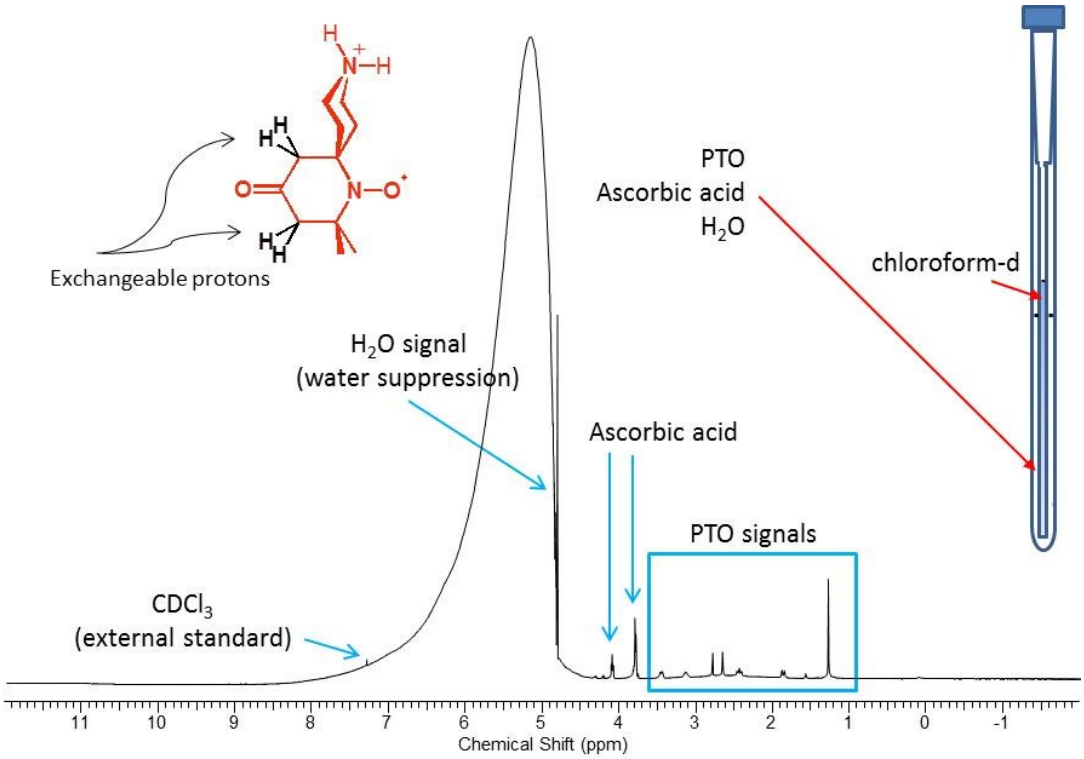


Figure S8. ^{1}H NMR spectrum of reduced **PTO** (**4b**) in pure water with ascorbic acid.

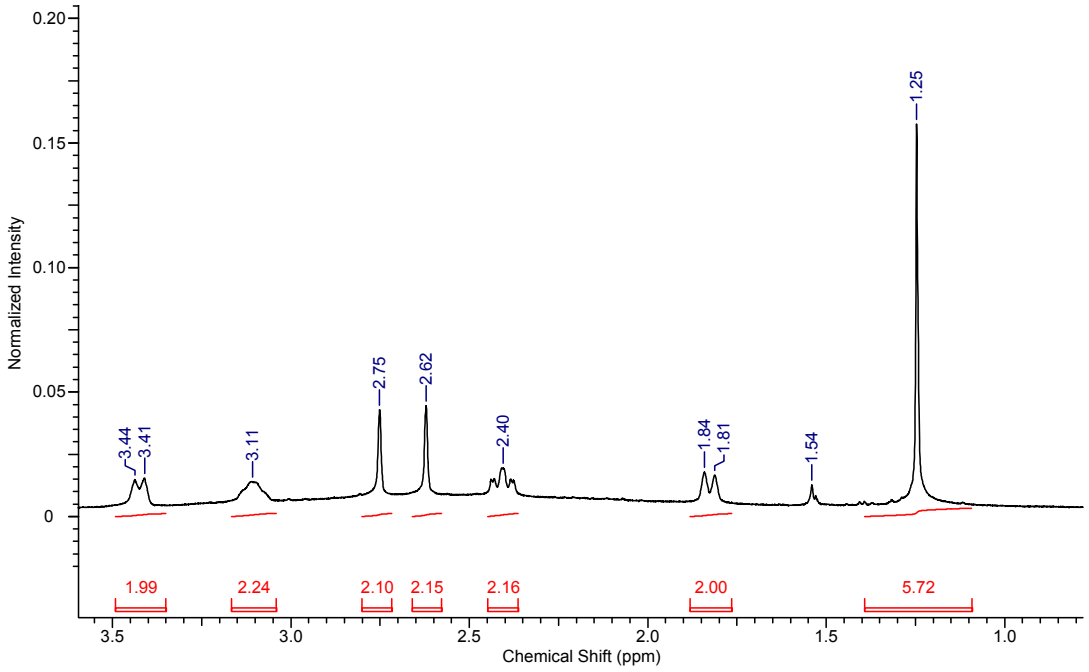


Figure S9. Excerpt of the ^{1}H NMR spectrum of Figure S8.

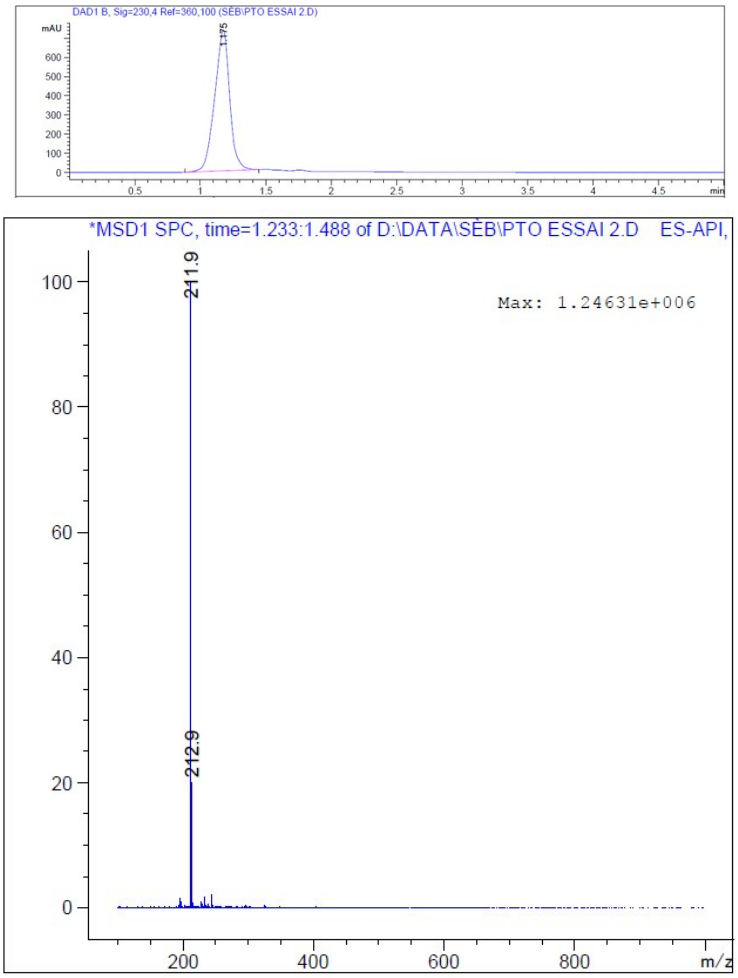
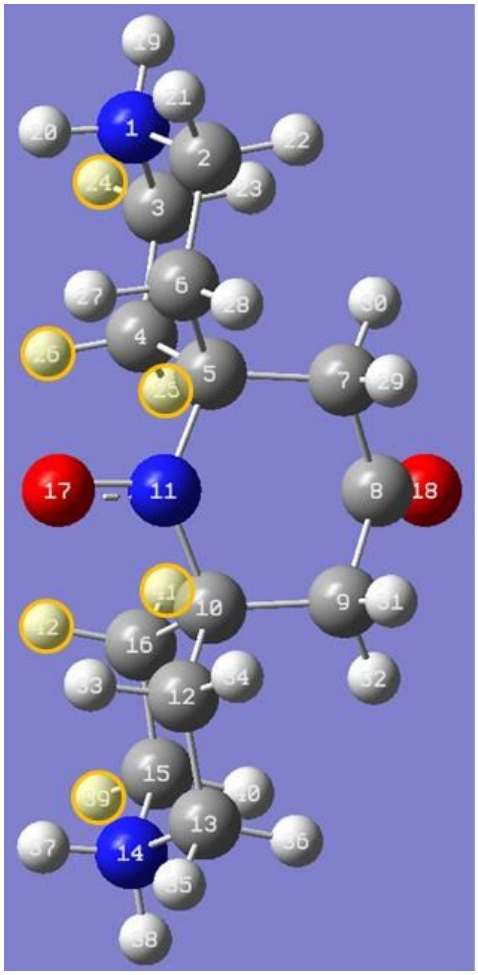


Figure S10. LC-MS analysis of **PTO** (**4b**). (H_2O/MeOH, isocratic elution, C18, UV detection and mass detector).

The calculations for the coupling constants were done at the PBE0/6-31G(d) level of theory taking into account solvation effects (water) with CPCM model.[5] This method is known to provide more reliable coupling constants.[7]



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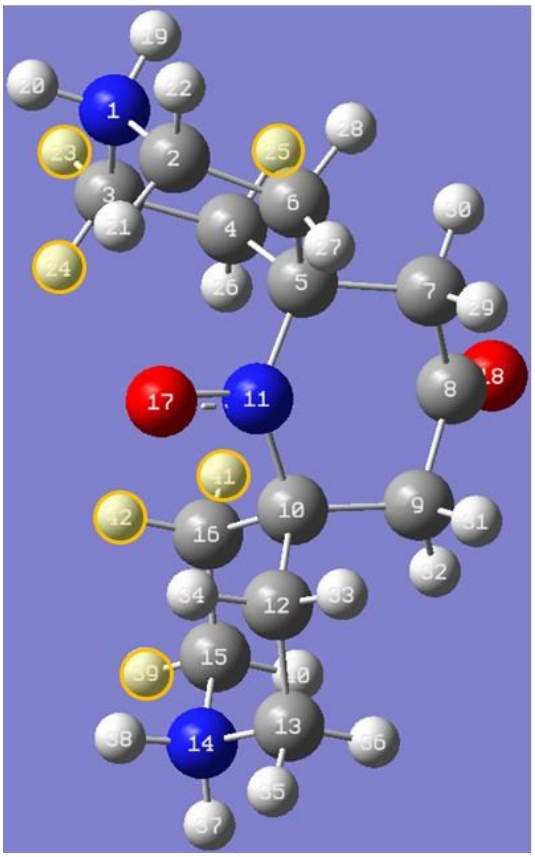
Isotropic Fermi Contact Couplings

	Atom	a.u.	MegaHertz	Gauss
1	N(14)	-0.00003	-0.01080	-0.00385
2	C(13)	-0.00072	-0.80472	-0.28715
3	C(13)	0.00187	2.09669	0.74815
4	C(13)	0.01419	15.95147	5.69188
5	C(13)	-0.00833	-9.36530	-3.34177
6	C(13)	0.00667	7.49955	2.67603
7	C(13)	0.00070	0.79182	0.28254
8	C(13)	-0.00065	-0.73154	-0.26103
9	C(13)	0.00066	0.74006	0.26407
10	C(13)	-0.00835	-9.38999	-3.35058
11	N(14)	0.12750	41.19613	14.69980
12	C(13)	0.00676	7.59859	2.71137
13	C(13)	-0.00071	-0.79928	-0.28520
14	N(14)	-0.00003	-0.00934	-0.00333
15	C(13)	0.00183	2.06121	0.73549
16	C(13)	0.01410	15.85491	5.65743
17	O(17)	0.07828	-47.45398	-16.93276
18	O(17)	0.00017	-0.10035	-0.03581
19	H(1)	-0.00003	-0.12540	-0.04475
20	H(1)	-0.00001	-0.03807	-0.01359
21	H(1)	0.00023	1.04809	0.37398
22	H(1)	0.00011	0.47289	0.16874
23	H(1)	0.00012	0.55040	0.19640
24	H(1)	0.00099	4.44309	1.58541
25	H(1)	-0.00048	-2.14833	-0.76658
26	H(1)	-0.00072	-3.21430	-1.14694
27	H(1)	-0.00028	-1.23748	-0.44156
28	H(1)	-0.00020	-0.90251	-0.32204
29	H(1)	-0.00020	-0.88434	-0.31556
30	H(1)	-0.00042	-1.87808	-0.67015
31	H(1)	-0.00020	-0.88774	-0.31677
32	H(1)	-0.00042	-1.88237	-0.67168
33	H(1)	-0.00028	-1.24395	-0.44387
34	H(1)	-0.00020	-0.91015	-0.32476
35	H(1)	0.00023	1.04258	0.37202
36	H(1)	0.00011	0.48108	0.17166
37	H(1)	-0.00001	-0.03886	-0.01386
38	H(1)	-0.00003	-0.12693	-0.04529
39	H(1)	0.00100	4.44800	1.58716
40	H(1)	0.00013	0.57877	0.20652
41	H(1)	-0.00048	-2.14416	-0.76509
42	H(1)	-0.00072	-3.22736	-1.15160

Figure S11. Protons showing long range coupling for the **bPTO** trans-trans conformer.

All protons giving coupling constants > 0.7 Gauss have been highlighted.



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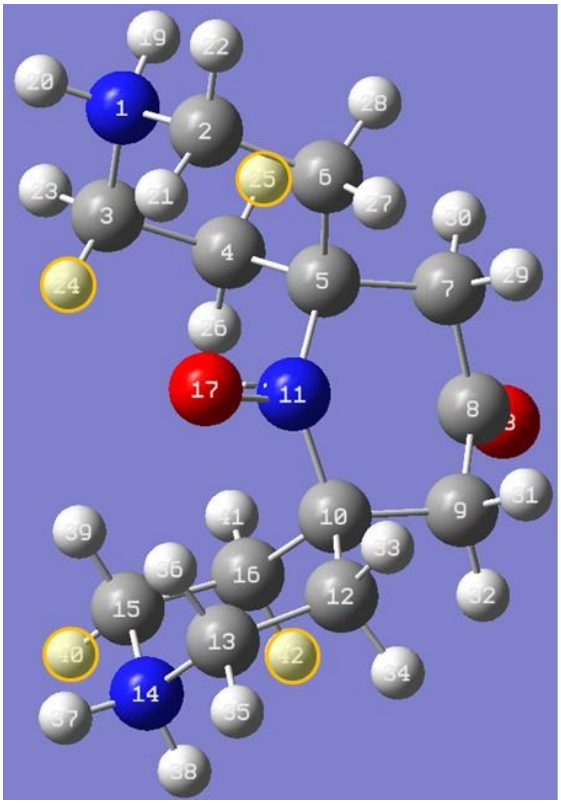
Isotropic Fermi Contact Couplings

	Atom	a.u.	MegaHertz	Gauss
1	N(14)	-0.00011	-0.03526	-0.01258
2	C(13)	-0.00039	-0.43967	-0.15688
3	C(13)	0.00088	0.98960	0.35311
4	C(13)	0.02134	23.98796	8.55950
5	C(13)	-0.01066	-11.98433	-4.27631
6	C(13)	0.00749	8.42116	3.00488
7	C(13)	0.00130	1.45588	0.51949
8	C(13)	-0.00065	-0.73299	-0.26155
9	C(13)	0.00066	0.74342	0.26527
10	C(13)	-0.01048	-11.77787	-4.20264
11	N(14)	0.12327	39.82845	14.21178
12	C(13)	0.00713	8.01287	2.85919
13	C(13)	-0.00069	-0.77990	-0.27829
14	N(14)	0.00000	-0.00065	-0.00023
15	C(13)	0.00167	1.87890	0.67044
16	C(13)	0.01516	17.04561	6.08230
17	O(17)	0.07934	-48.09338	-17.16091
18	O(17)	0.00022	-0.13633	-0.04865
19	H(1)	0.00000	-0.01391	-0.00496
20	H(1)	-0.00002	-0.09780	-0.03490
21	H(1)	0.00010	0.44457	0.15863
22	H(1)	0.00020	0.90011	0.32118
23	H(1)	0.00118	5.29148	1.88813
24	H(1)	0.00045	2.02216	0.72156
25	H(1)	0.00225	10.07906	3.59646
26	H(1)	-0.00031	-1.40204	-0.50028
27	H(1)	-0.00025	-1.13947	-0.40659
28	H(1)	-0.00035	-1.55743	-0.55573
29	H(1)	-0.00015	-0.68923	-0.24593
30	H(1)	-0.00023	-1.03739	-0.37017
31	H(1)	-0.00022	-0.98615	-0.35188
32	H(1)	-0.00041	-1.85155	-0.66068
33	H(1)	-0.00023	-1.03265	-0.36847
34	H(1)	-0.00031	-1.38157	-0.49298
35	H(1)	0.00029	1.30059	0.46408
36	H(1)	0.00013	0.56723	0.20240
37	H(1)	-0.00003	-0.13883	-0.04954
38	H(1)	-0.00001	-0.04008	-0.01430
39	H(1)	0.00095	4.25907	1.51974
40	H(1)	0.00010	0.45881	0.16371
41	H(1)	-0.00051	-2.29109	-0.81752
42	H(1)	-0.00071	-3.17518	-1.13298

Figure S12. Protons showing long range coupling for the **bPTO** cis-trans conformer.



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Isotropic Fermi Contact Couplings

	Atom	a.u.	MegaHertz	Gauss
1	N(14)	-0.00006	-0.02005	-0.00715
2	C(13)	-0.00032	-0.35689	-0.12735
3	C(13)	0.00056	0.62950	0.22462
4	C(13)	0.02138	24.03949	8.57789
5	C(13)	-0.01247	-14.01475	-5.00081
6	C(13)	0.00834	9.38087	3.34733
7	C(13)	0.00101	1.13433	0.40476
8	C(13)	-0.00063	-0.70323	-0.25093
9	C(13)	0.00162	1.82515	0.65126
10	C(13)	-0.01240	-13.94545	-4.97608
11	N(14)	0.12010	38.80387	13.84619
12	C(13)	0.00732	8.22482	2.93482
13	C(13)	-0.00052	-0.58750	-0.20963
14	N(14)	-0.00002	-0.00668	-0.00238
15	C(13)	0.00021	0.23677	0.08449
16	C(13)	0.02175	24.44592	8.72291
17	O(17)	0.08034	-48.70228	-17.37818
18	O(17)	0.00031	-0.18639	-0.06651
19	H(1)	-0.00001	-0.04471	-0.01595
20	H(1)	-0.00002	-0.10144	-0.03620
21	H(1)	0.00013	0.59101	0.21089
22	H(1)	0.00027	1.19246	0.42550
23	H(1)	0.00113	5.06708	1.80806
24	H(1)	0.00042	1.88179	0.67147
25	H(1)	0.00196	8.77474	3.13104
26	H(1)	-0.00039	-1.72282	-0.61475
27	H(1)	-0.00031	-1.36431	-0.48682
28	H(1)	-0.00030	-1.33018	-0.47464
29	H(1)	-0.00020	-0.87265	-0.31138
30	H(1)	-0.00026	-1.14434	-0.40833
31	H(1)	-0.00018	-0.82564	-0.29461
32	H(1)	-0.00019	-0.86169	-0.30747
33	H(1)	-0.00027	-1.19314	-0.42574
34	H(1)	-0.00035	-1.56225	-0.55745
35	H(1)	0.00020	0.90240	0.32200
36	H(1)	0.00011	0.49290	0.17588
37	H(1)	-0.00002	-0.10274	-0.03666
38	H(1)	-0.00001	-0.04998	-0.01783
39	H(1)	0.00042	1.88247	0.67171
40	H(1)	0.00110	4.89635	1.74714
41	H(1)	-0.00037	-1.63787	-0.58443
42	H(1)	0.00203	9.07448	3.23800

Figure S13. Protons showing long range coupling for the **bPTO** cis-cis conformer.

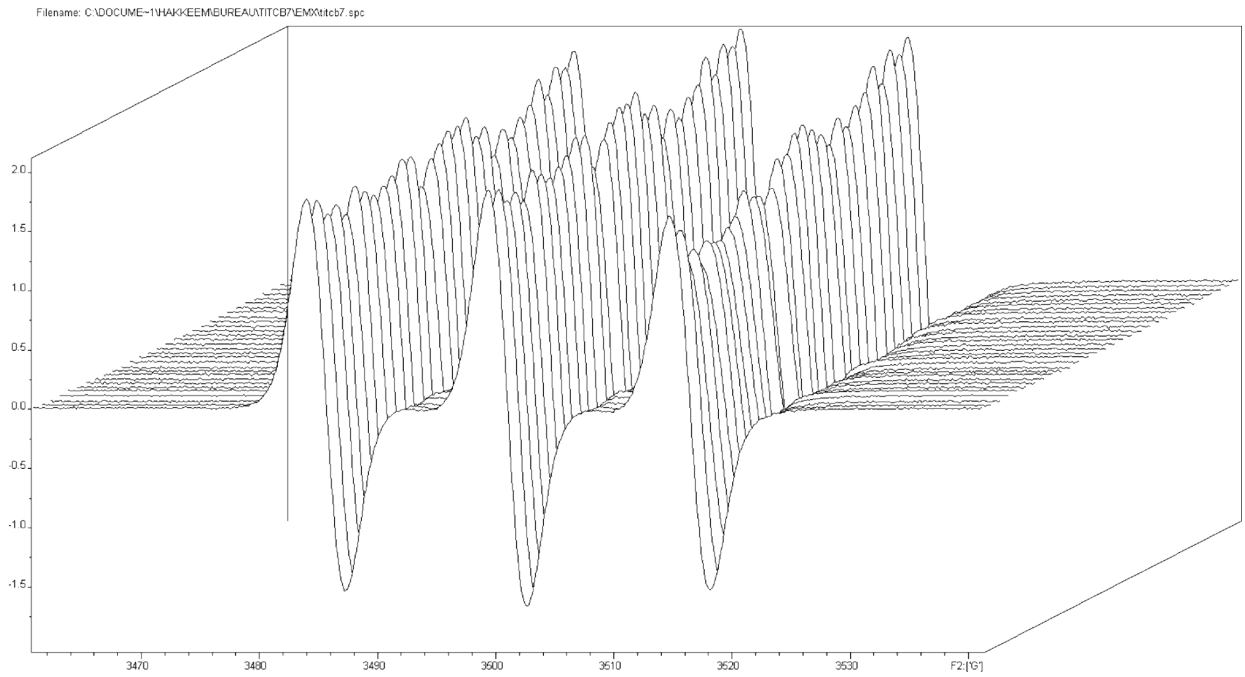

Figure S14. ESR titration of **bPTO** with CB[7].

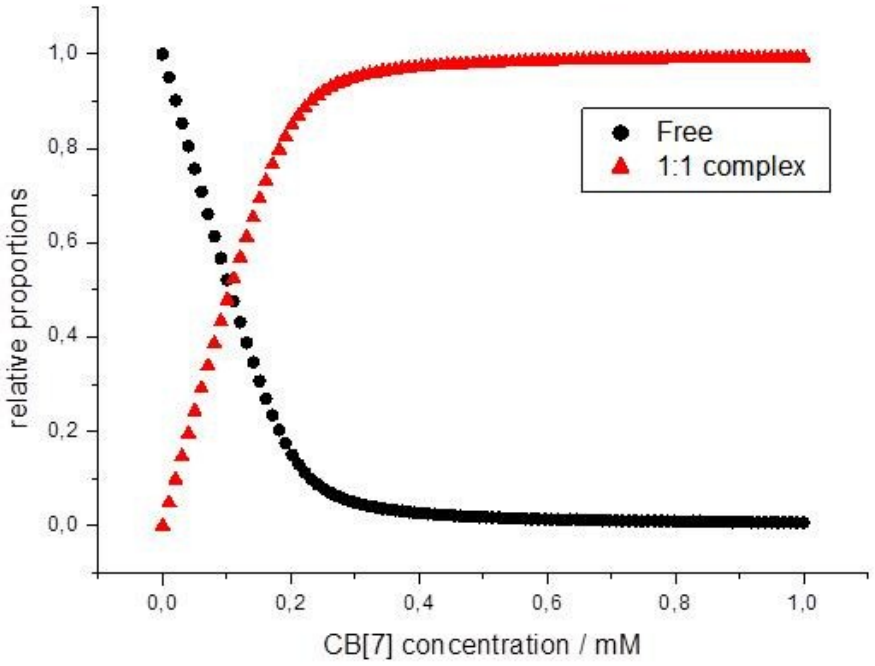

Figure S15. Distribution of free and included **bPTO** over a [0, 1] mM window with CB[7].

The binding constants were determined using the specially developed program for multiple equilibria paramagnetic species.[8]

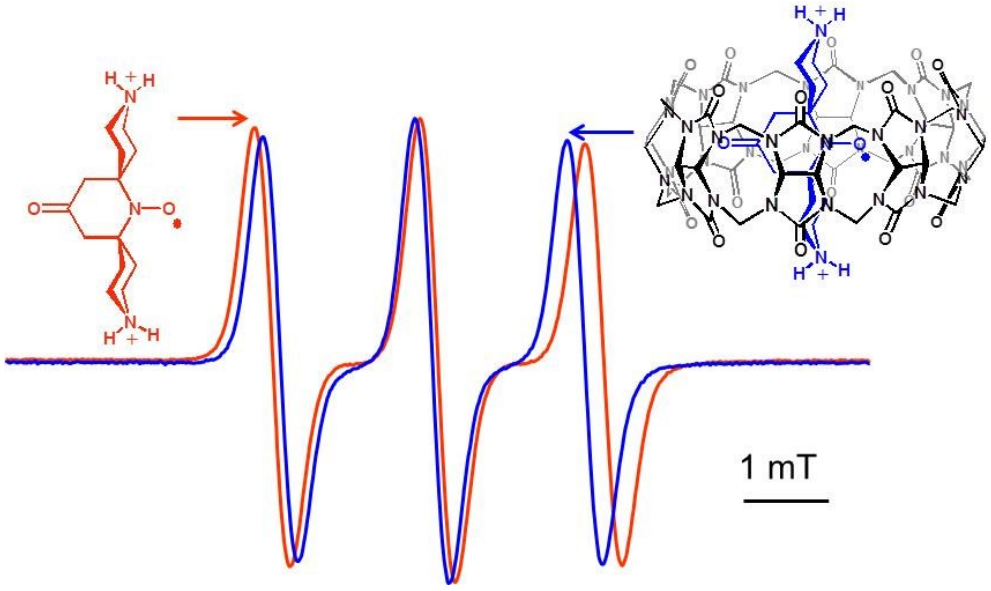

Figure S16. ESR spectra of **bPTO** without (0.2 mM) and with CB[8] (0.2 mM).

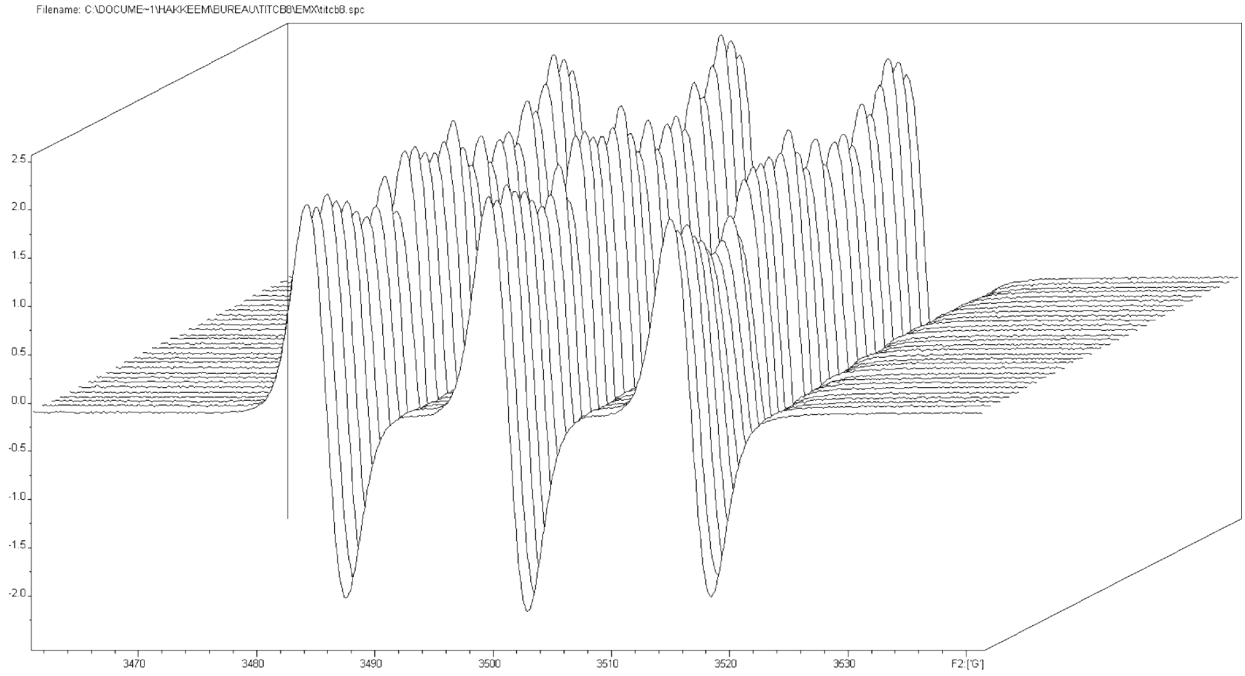

Figure S17. ESR titration of **bPTO** with CB[8].

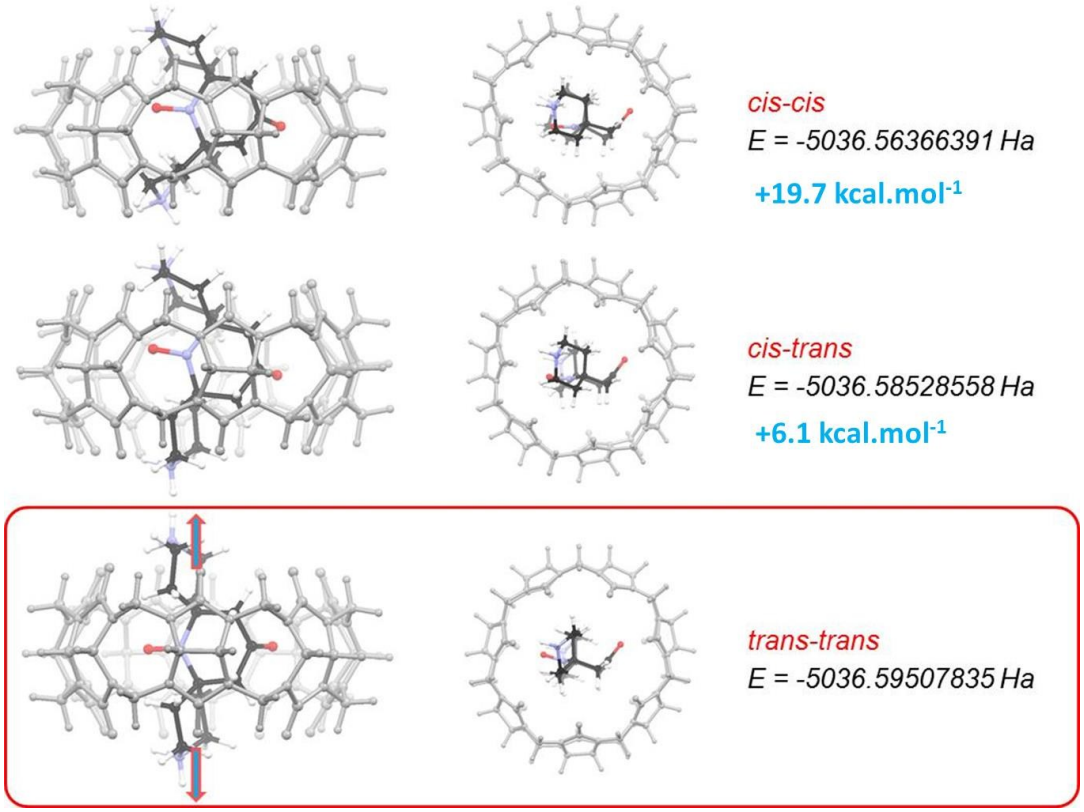

Figure S18. DFT minimized structures of inclusion complexes of **bPTO** with CB[7].

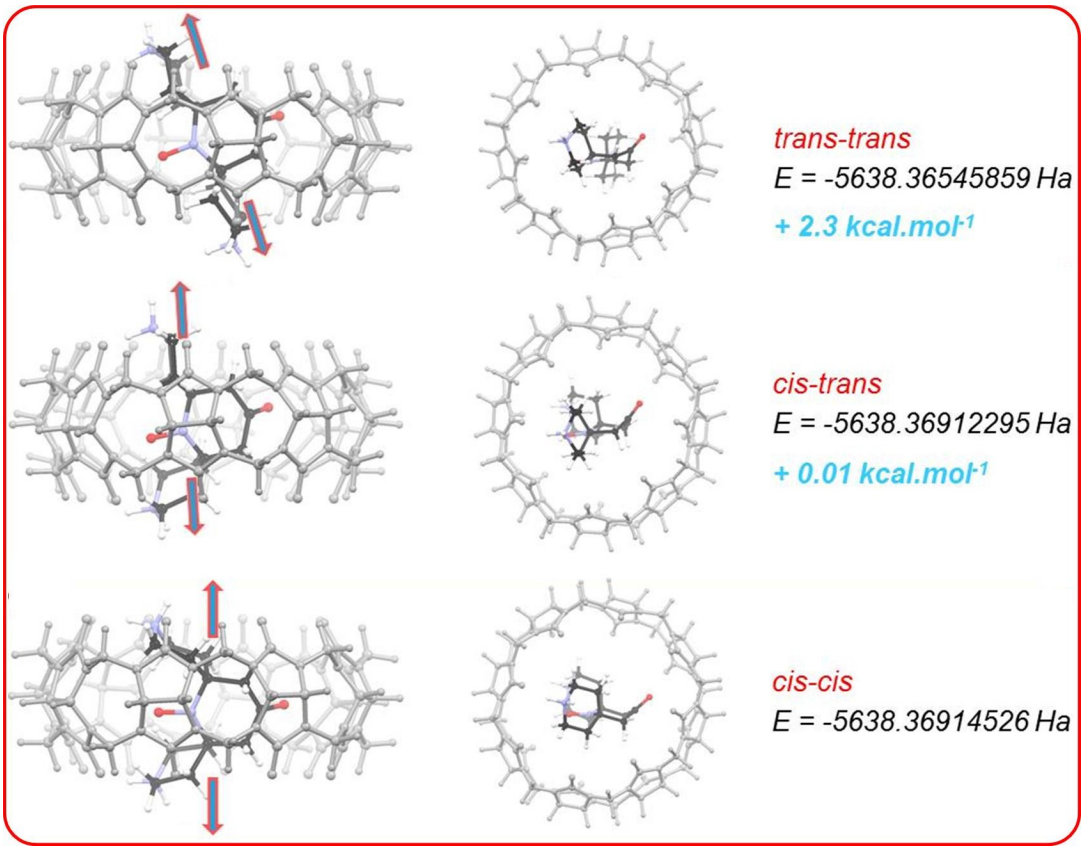

Figure S19. DFT minimized structures of inclusion complexes of **bPTO** with CB[8].

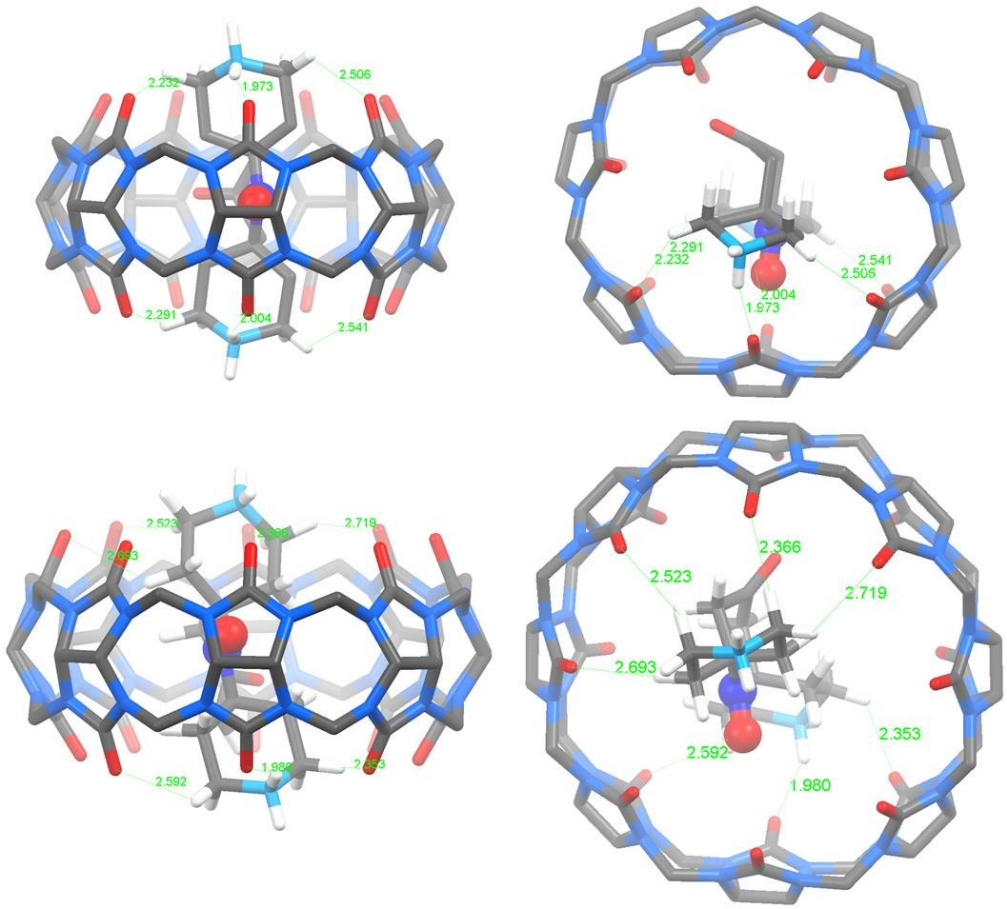

Figure S20. Stabilizing interactions in the inclusion complex of **bPTO** with CB[7] and CB[8] (*trans-trans* conformers).

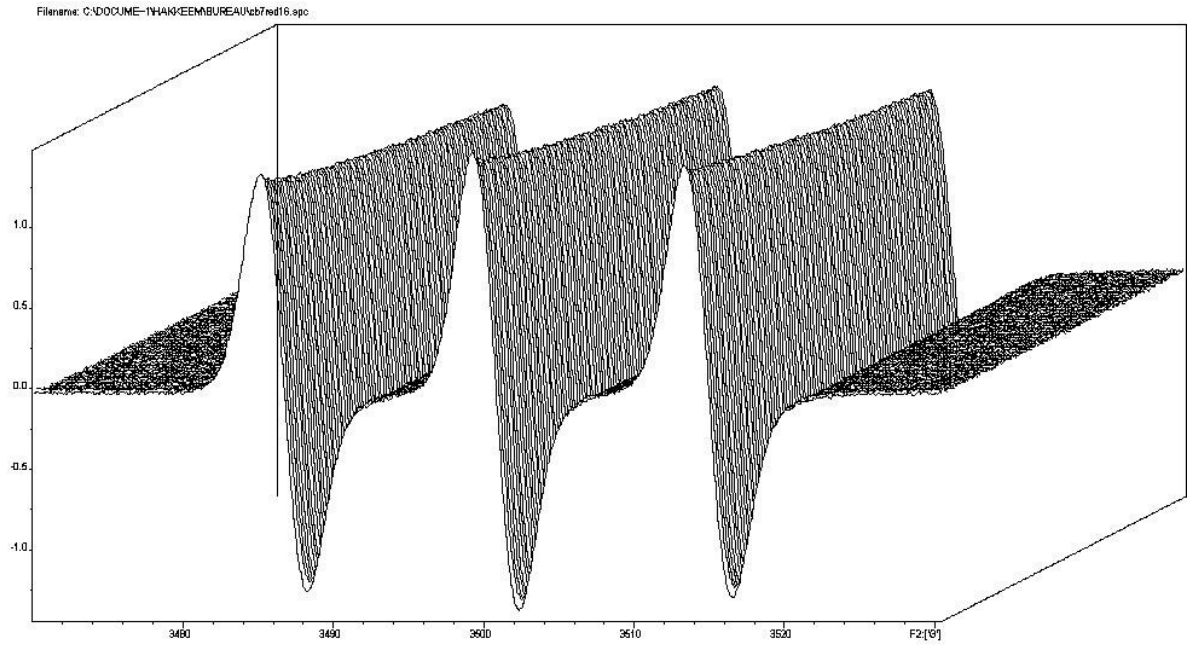

Figure S21. Decay of the three-line ESR spectrum of the **bPTO**@CB[7] complex in the presence of ascorbic acid (2 mM) in water over 16 hours (**bPTO** 0.2 mM and CB[7] 0.35 mM).

Simulations of ESR spectra with decreasing intensity over time with CB[7].

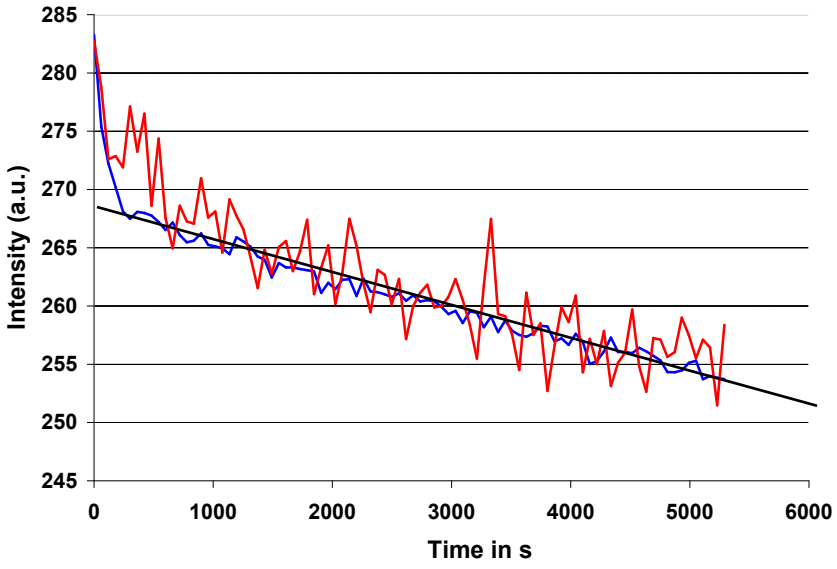

Figure S22. Variation of ESR intensity for **bPTO**-CB[7] in a.u (**bPTO** 0.2 mM, CB[7] 0.35 mM and ascorbic acid 2 mM). Red line: second integral, blue line: computer simulation, black line: linear trend line for points measured after 5 minutes.

The concentration decreased quickly during the starting four minutes, afterwhile the decrease is rather slow. The scatter of data is much larger for the second integral indicating the advantage of computer simulation. For this reason the decay analysis is carried out for the concentration data obtained by computer simulation. In order to analyze the fast initial decay, we subtracted the concentration measured after five minutes from the data obtained in the first few minutes. The corrected data points for **bPTO**-CB[7] together with an exponential trend line are shown in Figure S20.

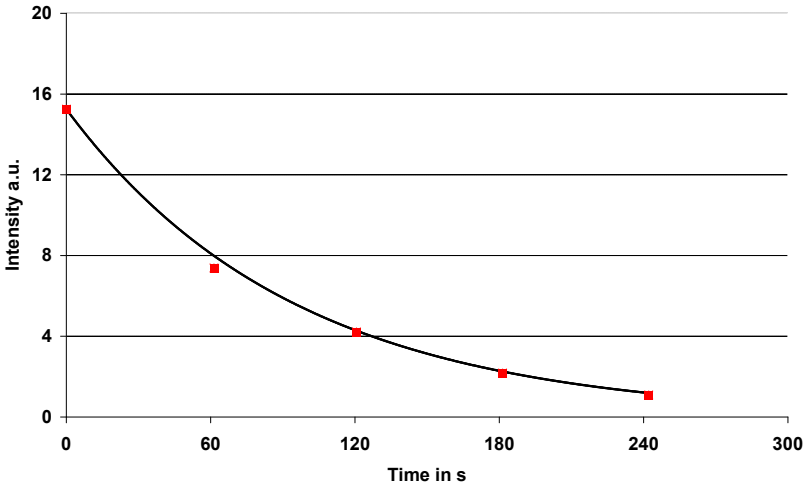

Figure S23. The initial decay of radical concentration when the concentration data were reduced by the value measured before five minutes. Exponential fit of decay : black line.

The initial decay shows a first order kinetics with a half life time standing around 1 min (66 s). The short lifetime is typical for nitroxide radicals in the presence of ascorbic acid. The results can be interpreted by the presence of ~5% non-associated radicals. The 2D ESR analysis for **bPTO**-CB[7] gave log*K*=5.2577, which corresponds to ~3.5% of non-associated radical. The decay kinetics for data measured after five minutes is also analyzed, see Figure S21.

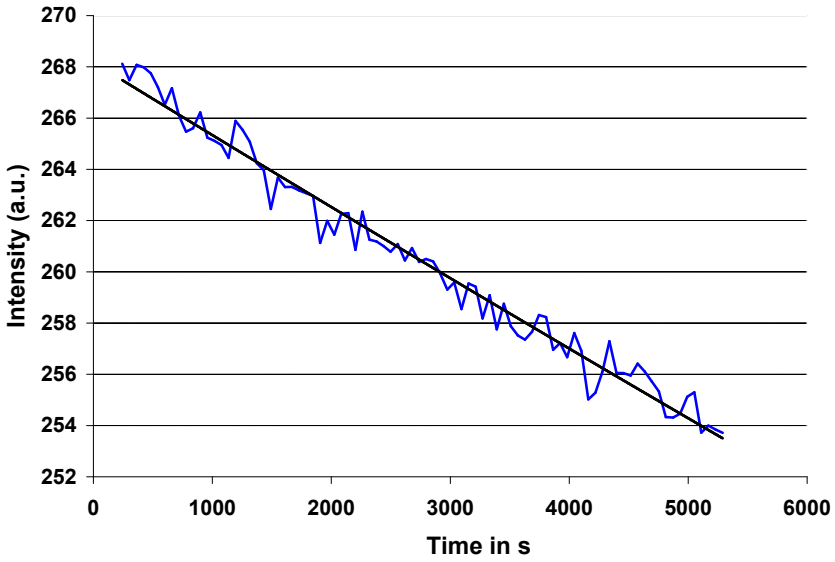

Figure S24. The decay of **bPTO** radical concentration measured between 5 and 90 minutes. The fit gives a half life time of 17 h when first order kinetics is applied.

Simulations of ESR spectra with decreasing intensity over time with CB[8].

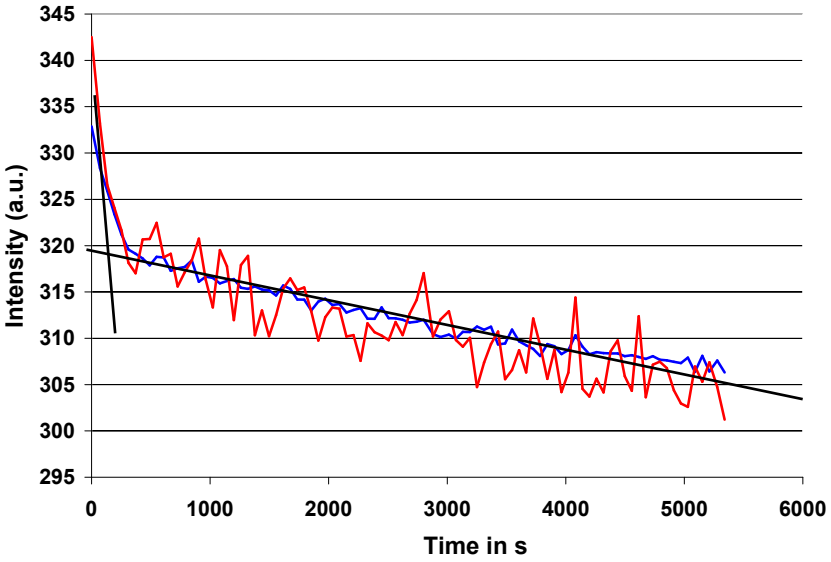

Figure S25. Variation of ESR intensity for **bPTO**-CB[8] in a.u (**bPTO** 0.2 mM, CB[8] 0.35 mM and ascorbic acid 2 mM). Red line: second integral, blue line: computer simulation, black lines: linear trend lines for points before and after 5 minutes.

As for CB[7], the decay curves have been fitted affording half-life times of ~1 min (first trend within the first 5 minutes) and 21 H for the second trend (included radical in CB[8]).

Table S1. Rotational dynamic parameters for the two nitroxides **bPTO** and **bPyTO** with CB[7], CB[8] or DM-β-CD.

compound	**Model 1**[1] **IBRD**[2] τ_c (ps) *(r.m.s.d.)*[4]	**Model 1 ABRD**[3] τ_{II} (ps) $\tau_{\perp}$ *(r.m.s.d.)*	**Model 2**[1] τ_{II} (ps) $\tau_{\perp}$ *(r.m.s.d.)*
bPTO	102 *(0.0878)*	51 550 *(0.0846)*	40 600 (*0*)
CB[7]@**bPTO**	27 *(0.0766)*	13 537 *(0.0726)*	0.4 740 (*0.029735*)
CB[8]@**bPTO**	58 *(0.0668)*	20 776 *(0.0586)*	2 1140 (*0.001102*)
DM-β-CD@**bPTO**	257 *(0.0631)*	151 1189 *(0.0591)*	140 1015 (*0*)
bPyTO	41 *(0.0526)*	7.6 348 *(0.0505)*	18.8 183 (*0*)
CB[7]@**bPyTO**	361 *(0.1140)*	260 776 *(0.1140)*	230 1178 (*0*)
PTO	13 (*0.0597*)	4.6 351 (*0.0555*)	26 162 (*0*)
CB[7]@**PTO**	24 (*0.0949*)	0.4 705 (*0.0828*)	0.3 535 (*0.0339*)
CB[8]@**PTO**	14 (*0.0908*)	0.3 373 (*0.0861*)	0.8 348 (*0.0294*)

[1]See part "rotational dynamics" in the manuscript.[2] Isotropic Brownian Rotational Diffusion. [3]Anisotropic Brownian Rotational Diffusion. [4] Root mean square deviation.

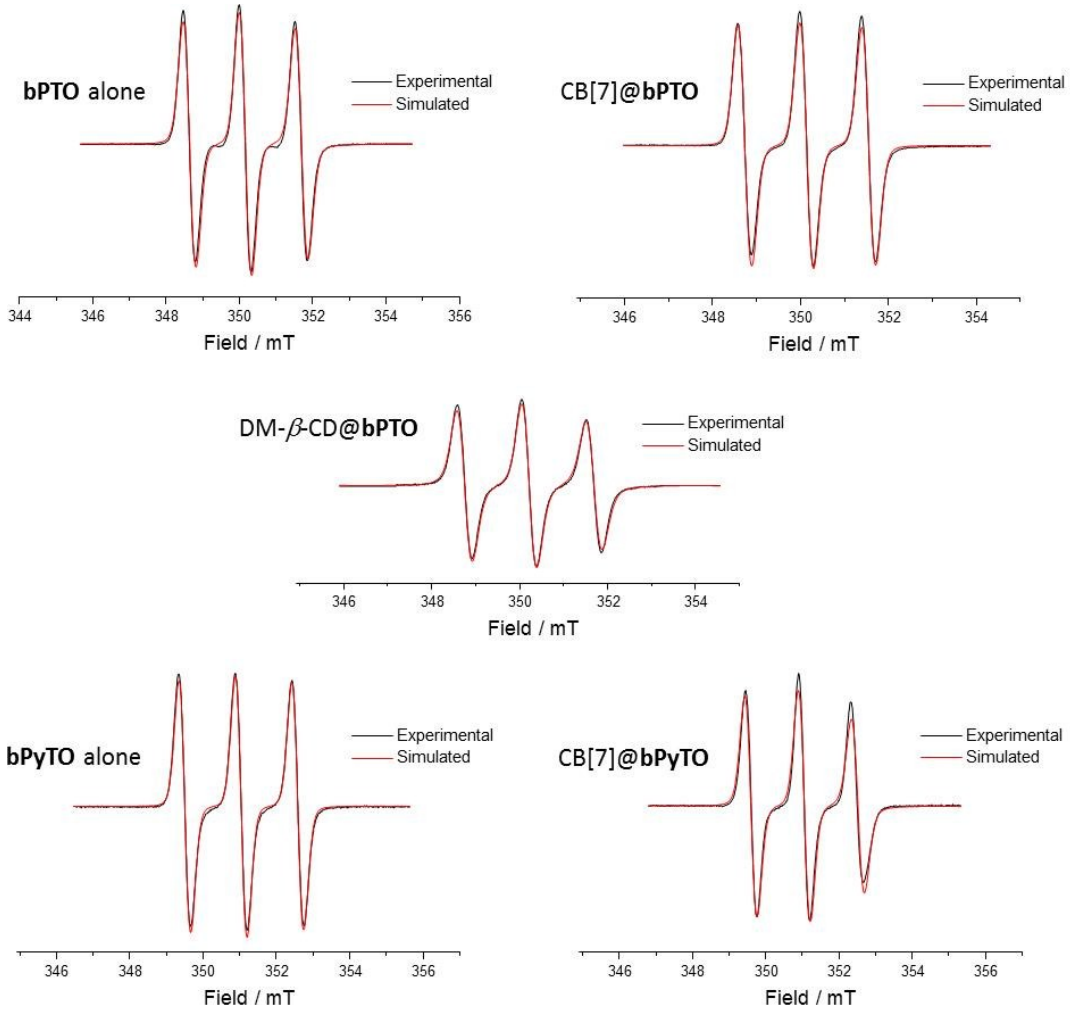

Figure S26. Simulations of EPR spectra of nitroxides **bPTO** and **bPyTO** in the presence of CB[7], CB[8] or DM-β-CD.

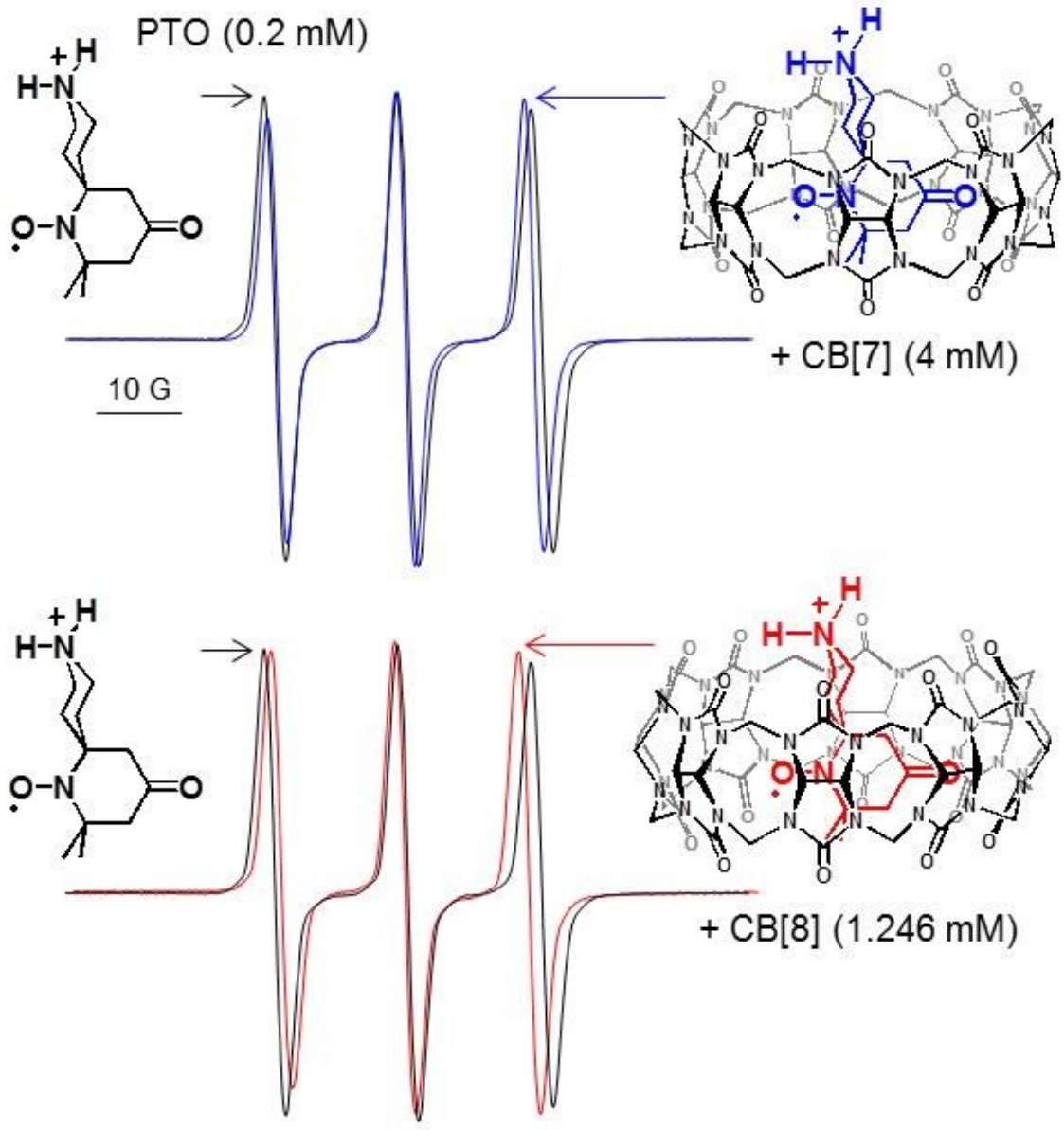

Figure S27. EPR spectra of nitroxide **PTO** alone, and with CB[7] and CB[8].

Absolute energies (in Hartrees) and coordinates of the atoms of bPTO@CB[*n*] complexes.

bPTO@CB[7] (cis-cis conformer).

```
  168
scf done: -5036.563664
 N     0.220507    -0.200633     0.065576
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 C     2.305200     1.165832    -0.142593
 C     2.593752     1.082938     1.369823
 C     1.234735     0.912632     2.089021
 C     3.196265     2.420163     1.870119
 C     4.689677     2.400302     1.719657
 C     5.353829     1.320932     2.516798
 C     5.031505     0.029738     1.743557
 N     3.528675    -0.072683     1.655054
 C     5.591233    -1.155864     2.548926
 C     5.733019    -2.466012     1.793139
 N     6.478473    -2.269483     0.507503
 C     5.815072    -1.243511    -0.363102
 C     5.729196     0.087560     0.355905
 O     3.033128    -1.258503     1.567428
 O     5.300049     3.043285     0.884104
 H    -0.433281     0.521310    -0.252041
 H    -0.168493    -1.111069    -0.215990
 H     0.679147    -1.167749     1.854753
 H    -0.694779    -0.063349     1.952759
 H     1.288063     0.089182    -1.706325
 H     2.078585    -0.960207    -0.503812
 H     1.742447     2.085713    -0.333741
 H     3.225873     1.254197    -0.723286
 H     1.381570     0.743480     3.156612
 H     0.732703     1.883138     1.990398
 H     2.935671     2.545679     2.923633
 H     2.768478     3.246574     1.303267
 H     4.946393     1.250605     3.525510
 H     6.433982     1.459248     2.559175
 H     4.946120    -1.326352     3.411349
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 H     6.281926    -3.198761     2.378211
 H     4.756525    -2.855154     1.520722
 H     6.534556    -3.153910    -0.027454
 H     7.446654    -1.987553     0.696841
 H     4.830475    -1.641301    -0.612809
 H     6.420219    -1.159841    -1.261795
 H     5.248594     0.803548    -0.311519
 H     6.743816     0.474595     0.512199
 O     0.502198    -1.920426    -2.584260
 O     1.772691     1.721956    -3.192162
 O     2.883263     4.762142    -0.601552
 O     2.920624     5.311869     2.956416
 O     1.921925     2.277275     5.143104
 O     0.645096    -1.282505     4.323225
 O     0.137590    -3.074995     0.857188
 O     6.440021    -3.698251    -1.929723
 O     7.733194    -0.142577    -2.827421
 O     8.681807     2.833692    -0.710408
 O     8.644361     2.881836     2.716615
 O     7.699376     0.061074     5.075489
 O     6.487023    -3.630045     4.605726
 O     5.909106    -5.358505     1.174165
 N     2.573674    -2.027622    -3.649297
 N     3.339340     0.266189    -4.106433
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 N     4.643030     4.244036    -2.031125
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N	1.945725	-3.210423	4.287659
N	1.589355	-4.361025	2.149512
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N	4.265892	-4.483796	-2.135334
N	4.917361	-2.766152	-3.420814
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N	7.383520	4.709807	-0.252021
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C	3.014074	1.972066	5.607238
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C	1.055234	-4.000532	3.454250
C	1.027038	-3.914716	0.966267
C	1.094818	-4.505486	-1.441608
C	3.118386	-4.249910	-2.997435
C	3.574843	-3.055213	-3.901547
C	4.706939	0.343618	-4.575138
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C	6.335500	5.481660	-0.904039
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C	6.194811	4.932642	4.215952
C	5.214251	2.186366	6.421675
C	4.672397	0.756787	6.760485
C	3.429821	-2.594356	6.031609
C	2.996867	-3.784093	5.109591
C	2.458606	-5.508748	1.939250
C	2.478639	-5.669029	0.381840
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C	5.320248	-3.652649	-2.443286
C	5.848761	-1.894527	-4.119429
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C	7.323171	2.700651	-3.243225
C	7.771004	3.605175	-0.983333
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C	7.787359	3.714965	2.981014
C	7.387617	2.939241	5.299709
C	6.698256	0.559381	5.573133
C	5.737983	-1.554804	6.472262
C	5.313121	-3.427729	4.890482
C	4.371558	-5.372706	3.646919
C	4.682679	-5.393963	1.172472
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H	1.416360	-0.455677	-4.318045
H	4.071453	4.305423	-4.035356

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 H     2.882698    -5.158859    -3.561477
 H     3.601776    -3.305271    -4.967893
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 H     5.287613     2.438561    -5.098915
 H     6.164967     5.207144    -3.122383
 H     6.699772     6.492997    -1.118009
 H     6.823735     6.661808     2.934464
 H     6.482131     5.548641     5.076095
 H     5.440070     2.788043     7.309497
 H     4.607354     0.560273     7.836754
 H     3.290016    -2.802637     7.098928
 H     2.612928    -4.645905     5.668090
 H     2.060366    -6.385552     2.462201
 H     2.107003    -6.640743     0.038085
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```

bPTO@CB[7] (cis-trans conformer).

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  168
scf done: -5036.585286
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 C     2.862347     1.151158     1.371507
 C     1.471822     1.041563     2.036384
 C     3.488635     2.504315     1.777164
 C     4.935493     2.469855     1.369993
 C     5.746115     1.508209     2.190918
 C     5.287447     0.086449     1.795273
 N     3.772511     0.029353     1.809282
 C     5.793202    -0.943255     2.821603
 C     7.301707    -1.162199     2.771757
 N     7.707044    -1.577430     1.382471
 C     7.320022    -0.550576     0.354190
 C     5.811569    -0.310917     0.389447
 O     3.268140    -1.153988     1.803625
 O     5.368017     3.006614     0.365014
 H    -0.086640     0.486405    -0.357572
 H     0.165191    -1.139166    -0.186812
 H     0.911047    -1.052212     1.917167
 H    -0.456588     0.065814     1.870363
 H     1.696835    -0.048160    -1.690029
 H     2.423902    -1.020305    -0.385570
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H	2.108909	2.032547	-0.441474
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H	0.980321	2.004429	1.852050
H	3.399591	2.630559	2.859217
H	2.955242	3.308799	1.271397
H	5.553895	1.667579	3.254108
H	6.810177	1.649292	2.001307
H	5.529745	-0.614451	3.827878
H	5.280767	-1.889149	2.644530
H	7.581251	-1.962300	3.454659
H	7.869881	-0.264798	3.023187
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O	1.072127	-2.059158	-2.631533
O	1.961436	1.655584	-3.264264
O	2.511617	4.662446	-0.807800
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O	0.664725	-1.181399	4.294774
O	0.590648	-3.098699	0.916850
O	7.187028	-2.911269	-1.539732
O	8.028354	0.634916	-2.567894
O	8.534288	3.737467	-0.608681
O	8.196125	3.702728	2.915037
O	7.338995	0.799924	5.473687
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N	-2.292095	-4.172510	-1.085275

N	-1.294112	-6.508674	1.034475
N	-0.986315	-6.242558	-1.164719
C	4.741191	0.957958	5.817992
C	6.761634	-0.056103	6.475503
C	5.583192	-0.699020	7.273789
C	6.719878	-2.384107	6.085771
C	3.100647	-0.126827	7.308963
C	5.061178	-3.160367	7.756694
C	1.107395	-1.314989	6.481546
C	2.573165	-2.563839	7.844448
C	1.315011	-3.422364	7.505583
C	3.253838	-4.534438	6.751364
C	-0.938352	-2.723017	6.523728
C	1.115778	-5.715853	6.397872
C	-1.946903	-3.128234	4.300597
C	-1.143403	-5.030218	5.438730
C	-1.866224	-5.479820	4.128877
C	0.339353	-6.312633	4.127545
C	-3.175488	-4.121343	2.403757
C	-1.148639	-7.138625	2.329369
C	-2.475844	-3.509309	0.105385
C	-2.489292	-5.807210	0.610824
C	-2.271407	-5.616637	-0.925108
C	-0.436012	-6.786744	-0.016536
C	-2.422395	-3.511380	-2.367854
C	-0.461680	-6.534063	-2.482675
H	-1.343533	-4.893869	-4.538328
H	0.354319	-3.661801	-5.793316
H	3.579257	-5.114918	-4.875309
H	2.762582	-4.188813	-6.167772
H	0.933648	-1.263494	-5.929552
H	0.552287	-0.266446	-4.496706
H	3.320990	-1.777242	-6.315553
H	5.333430	-0.523122	-5.725801
H	7.477083	-2.788186	-3.813633
H	7.525665	-1.345728	-4.867362
H	5.631976	1.612511	-4.564502
H	4.422334	2.041031	-3.319833
H	7.839269	0.846382	-3.748902
H	9.157697	1.290463	-1.736234
H	10.216247	-0.128484	0.003337
H	9.485273	-1.739178	0.264992
H	8.734254	3.014143	-0.009246
H	7.025457	3.433093	0.301515
H	9.836646	1.548260	1.752580
H	9.391586	1.366224	4.150443
H	8.847575	-2.158742	4.812699
H	9.296840	-0.618908	5.601304
H	6.112743	2.864056	4.871160
H	7.634798	2.387540	5.677414
H	7.540953	0.380458	7.110643
H	5.627946	-0.513133	8.352914
H	2.511742	0.692666	6.896546
H	3.207430	0.006835	8.394179
H	5.603184	-4.086219	7.564380
H	5.123112	-2.911498	8.822371
H	2.665241	-2.318201	8.908333
H	0.787916	-3.802868	8.387738
H	-1.389783	-1.753267	6.314082
H	-1.381967	-3.147176	7.432410
H	1.838650	-6.484622	6.124347
H	0.549983	-6.040122	7.281382
H	-1.607313	-5.419974	6.352304
H	-2.749424	-6.104268	4.306843
H	-3.520275	-3.088045	2.367429
H	-4.029810	-4.786539	2.580372
H	-2.071670	-7.682436	2.567337
H	-0.318640	-7.841218	2.252543

H	-3.387790	-6.381539	0.862107
H	-3.048452	-6.078058	-1.544177
H	-3.137069	-4.076164	-2.977885
H	-2.811287	-2.510475	-2.182400
H	0.304718	-7.300005	-2.361523
H	-1.274155	-6.922384	-3.109297

Molecular Dynamics of the bPTO@CB[7] complex.

Molecular Dynamics (MD) calculations were performed with the Gromacs 5.0.4[9] package. The complex was solvated in a quasi-cubic box which contained 1157 water molecules. Two chloride counterions were added to obtain a neutral system. Concerning the force fields used in the MD simulations, we used the TIP3P[10] force field to describe the water molecules, the AMBER force field (ff99SB)[11] including additional parameters for nitroxide moieties developed by Barone et al.[12] and the atomic charges were computed at the HF/6-31G(d) level of theory with the RESP scheme.[13]
In order to optimize the simulation box size, we performed a NPT calculation at 300K and 1 bar during 300 ps with a time step of 2.5 fs. After this first stage, we performed two NVT trajectories at 300K during 100 ns with a time step of 2.5 fs. We kept the last 99.5 ns of the two trajectories for the data analysis calculations.

References

[1] Sakai, K.; Yamada, K-I.; Yamasaki, T.; Kinoshita, Y.; Mito, F.; Utsumi, H. *Tetrahedron* **2010**, *66*, 2311-2315.

[2] Bardelang, D.; Udachin, K. A.; Leek, D. M.; Margeson, J.; Chan, G.; Ratcliffe, C. I.; Ripmeester, J. A. *Cryst. Growth Des.* **2011**, *11*, 5598-5614.

[3] Carrozza, P.; Ferri, G. *Eur. Pat. Appl.* **1996**, EP 729947 A1 19960904.

[4] Gless, Richard D., Jr.; Anandan, Sampath Kumar; Aavula, Bhaskar R. PCT, **2008**, WO2008112022.

[5] Cossi, M.; Rega, N.; Scalmani, G.; Barone, V. *J. Comp. Chem.* **2003**, *24*, 669-681.

[6] Zagdoun, A., Casano, G., Ouari, O., Schwarzwälder, M., Rossini, A.J., Aussenac, F., Yulikov, M., Jeschke, G., Coperet, C., Lesage, A., Tordo, P. and Emsley, L. *J. Am. Chem. Soc.* **2013**, *135*, 12790-12797.

[7] Adamo, C. and Barone, V. *J. Chem. Phys.* **1999**, *110*, 6158-6159.

[8] Rockenbauer, A.; Szabó-Plánka, T.; Árkosi, Zs.; Korecz, L. *J. Am. Chem. Soc.* **2001**, *123*, 7646-7654.

[9] Hess, B.; Kutzner, C.; van der Spoel, D. and Lindahl, E. *J. Chem. Theory Comput.* **2008**, *4*, 435-447.

[10] Jorgensen, W. L. and Madura, J. D. *J. Am. Chem. Soc.* **1983**, *105*, 1407-1473.

[11] Hornak, V.; Abel, R.; Okur, A.; Strockbine, B.; Roitberg, A. and Simmerling, C. *Proteins: Struct., Funct., Bioinf.* **2006**, *65*, 712-725.

[12] Stendardo, E.; Pedone, A.; Cimino, P.; Menziani, M. C.; Crescenzi, O. and Barone, V. *Phys. Chem. Chem. Phys.* **2010**, *12*, 11697-11709.

[13] Wang, J.; Cieplak, P. and Kollman, P. A. *J. Comput. Chem.* **2000**, *21*, 1049-1074.