SUPPORTING INFORMATION

Multi-State Regulation of the Dihydrogen Phosphate Binding Affinity to a Light- and Heat-Responsive Bis-Urea Receptor

Sander J. Wezenberg,* Matea Vlatković, Jos C. M. Kistemaker and Ben L. Feringa*

Centre for Systems Chemistry, Stratingh Institute for Chemistry, University of Groningen, Nijenborgh 4, 9747 AG, Groningen, The Netherlands

Email: s.j.wezenberg@rug.nl; b.l.feringa@rug.nl

Table of Contents

Experimental section S2

^{1}H and ^{13}C NMR spectra of new compounds S6

^{1}H NMR dilution studies S10

^{1}H NMR isomerization studies S12

UV-Vis spectra and Eyring plot analysis S14

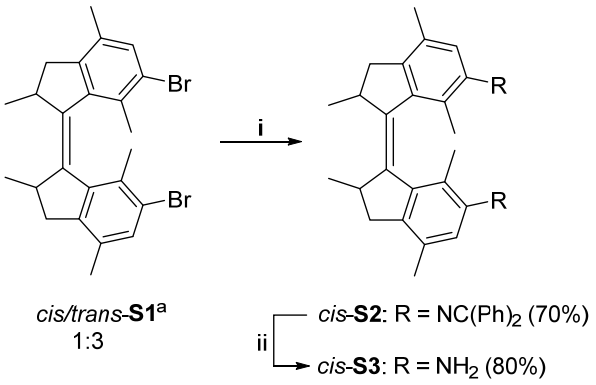
^{1}H NMR titrations and data analysis S15

^{31}P NMR reversible switching studies S28

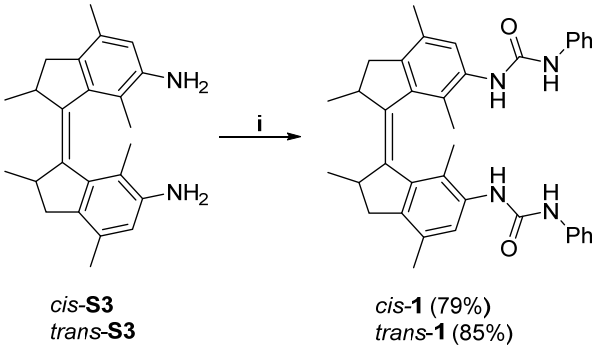
DFT Calculations S29

References and notes S37

Experimental section



Scheme S1. Synthesis of diamine *cis*-**S3** identical to the procedure previously reported for *trans*-**S3**[1]: (i) benzophenone imine, [Pd(OAc)$_2$] (5 mol%), DPPF (7.5 mol%), NaOtBu, toluene, 90 °C; (ii) 2M aqueous HCl, THF. [a)] Only the *cis*-isomer is drawn.



Scheme S2. Synthesis of bis-urea receptors *cis*-**1** and *trans*-**1** (only the *cis*-isomers are drawn): (i) phenyl isocyanate, CH_2Cl_2.

General methods and materials:

Toluene and CH_2Cl_2 were dried by using an MBraun solvent purification system and THF was distilled from benzophenone/sodium. DMSO-d_6 was stored under N_2 over molecular sieves (4Å) and purified by standing overnight with freshly heated/cooled alumina followed by reflux over CaO and distillation from CaH_2 under reduced pressure. Solvents were degassed by purging with N_2 for 30 min. Bis-bromide **S1**[2] (*cis/trans* mixture) and bis-amine *trans*-**S3**[1] were prepared according to procedures described in the literature. All other chemicals were commercial products and were used as received. Flash chromatography (FC) was performed using silica gel (SiO_2) purchased from Merck (type 9385, 230-400 mesh) and thin-layer chromatography (TLC) was carried out on aluminum sheets coated with silica 60

F254 obtained from Merck; compounds were visualized with a UV lamp (254 nm) or by staining with phosphomolybdic acid (PMA). Melting points (m.p.) were determined using a Büchi-B545 capillary melting point apparatus. ^{1}H, ^{13}C and ^{31}P NMR spectra were recorded on Varian VXR-300S, Varian Mercury Plus-400 and Varian Inova-500 spectrometers at 298 K. Chemical shifts (δ) are denoted in parts per million (ppm) relative to $CDCl_3$ (for ^{1}H detection, δ = 7.26 ppm; for ^{13}C detection, δ = 77.16 ppm), CD_2Cl_2 (for ^{1}H detection, δ = 5.32 ppm; for ^{13}C detection, δ = 53.50 ppm), DMSO-d_6 (for ^{1}H detection, δ = 2.50 ppm; for ^{13}C detection, δ = 39.52 ppm) or aqueous 85% H_3PO_4 (for ^{31}P detection, δ = 0.00). For ^{1}H NMR spectroscopy, the splitting pattern of peaks is designated as follows: s (singlet), d (doublet), t (triplet), (multiplet), br (broad), or dd (doublet of doublets). High-resolution mass spectrometry (ESI-MS) was performed on a LTQ Orbitrap XL spectrometer with ESI or APCI ionization. UV-vis spectra were recorded on a Hewlet-Packard HP 8543 diode array in a 1 cm quartz cuvette. Irradiation experiments were carried out using a Spectroline model ENB-280C/FE lamp positioned at a distance of 3 cm from the sample, of which the temperature was maintained in a water bath at 20 °C.

***cis*-(±)-*N*,*N'*-(2,2',4,4',7,7'-hexamethyl-2,2',3,3'-tetrahydro-[1,1'-biindenylidene]-6,6'-diyl)bis(1,1-diphenylmethanimine) (*cis*-(±)-S2):**

Compound *cis*-(±)-**S2** was prepared following a previously reported protocol.[1] Palladium(II) acetate (35 mg, 0.16 mmol), DPPF (131 mg, 0.24 mmol) and sodium *tert*-butoxide (607 mg, 6.32 mmol) were brought under a nitrogen atmosphere in a Schlenk tube via three vacuum/nitrogen cycles. Degassed toluene (17 mL) was added, and the resulting suspension was stirred and treated with benzophenone (1.7 mL, 9.5 mmol) and a solution of bis-bromide (±)-**S1** (1:3 cis/trans mixture, 1.50 g, 3.16 mmol). The mixture was heated to 90 °C for 16 h, cooled to rt and diluted with water (20 mL). The aqueous layer was extracted with EtOAc (3× 25 mL) and the combined organic phases were dried over Na_2SO_4. FC (SiO_2, pentane/Et_2O 19:1) afforded *cis*-(±)-**S2** (373 mg, 17%; ~70% of theoretical maximum) and *trans*-(±)-**S2** (1.24 mg, 58%; ~78% of theoretical maximum) as yellow solids. An analytically pure sample of *cis*-(±)-**S2** was obtained by recrystallization from pentane/Et_2O: ^{1}H NMR (400 MHz, CD_2Cl_2): δ 7.72 (m, 4H; ArH), 7.47-7.33 (m, 6H; ArH), 7.09 (m, 10H; ArH), 6.08 (s, 2H; ArH), 3.29 (m, 2H; CH), 2.97 (dd, J = 14.7, 6.3 Hz, 2H; CH), 2.32 (d, J = 14.7 Hz, 2H; CH), 2.03 (s, 6H; $ArCH_3$), 1.26 (s, 6H; $ArCH_3$), 1.01 (d, J = 6.7 Hz, 6H; CH_3); 13C NMR (100 MHz, CD_2Cl_2): δ 166.4, 148.6, 142.1, 141.3, 140.4, 139.8, 137.0, 130.7 (2×), 129.4, 129.3,

128.7, 128.4, 128.2, 124.7, 119.6, 42.55, 38.7, 20.6, 18.5, 16.3; HRMS (APCI) *m/z*: 675.3472 ([M + H]$^+$, calcd for $C_{50}H_{47}N_2^+$: 675.3738).

cis-(±)-2,2',4,4',7,7'-hexamethyl-2,2',3,3'-tetrahydro-[1,1'-biindenylidene]-6,6'-diamine (_cis_-(±)-S3):

Compound *cis*-(±)-**S2** was prepared via an identical procedure as *trans*-(±)-**S2**.[1] A 2M aqueous HCl solution (0.6 mL) was added to *cis*-(±)-**S2** (370 mg, 0.55 mmol) in THF (1 mL). The solution was stirred for 20 min, diluted with 0.5M aqueous HCl (10 mL) and washed with Et_2O (3× 5 mL). The water layer was then made basic by addition of Na_2CO_3 (pH ~ 10) and extracted with EtOAc (3× 15 mL). The combined extracts were dried over Na_2SO_4 and concentrated to afford *cis*-(±)-**S3** (152 mg, 80%) as a white solid. ^{1}H NMR (300 MHz, $CDCl_3$): δ 6.43 (s, 2H; ArH), 3.42-3.26 (br. m, 6H; NH_2, CH), 3.04 (dd, J = 14.4, 6.1 Hz, 2H; CH), 2.37 (d, J = 14.5 Hz, 2H; CH), 2.20 (s, 6H; $ArCH_3$), 1.36 (s, 6H; $ArCH_3$) 1.09 (d, J = 6.6 Hz, 6H; CH_3); ^{13}C NMR (75 MHz, $CDCl_3$): δ 142.8, 142.0, 140.9, 134.9, 131.2, 118.2, 115.3, 41.7, 38.3, 20.7, 18.6, 15.3; HRMS (APCI) *m/z*: 347.2482 ([M + H]$^+$, calcd for $C_{24}H_{31}N_2^+$: 347.2482)

cis-(±)-1,1'-(2,2',4,4',7,7'-hexamethyl-2,2',3,3'-tetrahydro-[1,1'-biindenylidene]-6,6'-diyl)bis(3-phenylurea) (_cis_-(±)-1):

Under a N_2 atmosphere, *cis*-(±)-**S3** (103 mg, 0.30 mmol) was dissolved in CH_2Cl_2 (5 mL) and treated with phenyl isocyanate (65 µL, 0.59 mmol). The solution was stirred for 16 h and the precipitate was filtered off and washed with CH_2Cl_2 to yield *cis*-(±)-**1** (138 mg, 79%) as a white solid. M.p. 295 °C (dec); ^{1}H NMR (400 MHz, DMSO-d_6, assignments based on COSY and NOESY): δ 8.97 (s, 2H; NH), 7.71 (s, 2H; NH), 7.59 (s, 2H; ArH), 7.44 (d, J = 7.9 Hz, 4H; ArH), 7.22 (t, J = 7.6 Hz, 4H; ArH), 6.92 (t, J = 7.2 Hz, 2H; ArH), 3.05 (dd, J = 14.8, 5.9 Hz, 2H; CH), 2.42 (d, J = 14.9 Hz, 2H; CH), 2.23 (s, 6H; $ArCH_3$), 1.38 (s, 6H; $ArCH_3$), 1.06 (d, J = 6.5 Hz, 6H; CH_3), one CH signal hidden under the H_2O residual peak ; ^{13}C NMR (100 MHz, DMSO-d_6): δ 152.7, 140.7, 140.5, 140.0, 138.1, 135.5, 130.1, 128.8, 122.6, 121.5, 121.1, 117.8, 41.0, 37.9, 20.4, 18.5, 15.9; HRMS (ESI) *m/z*: 607.3011 ([M + Na]$^+$, calcd for $C_{38}H_{40}N_4O_2Na^+$: 607.3044), 585.3192 ([M + H]$^+$, calcd for $C_{38}H_{41}N_4O_2^+$: 585.3224).

***trans*-(±)-1,1'-(2,2',4,4',7,7'-hexamethyl-2,2',3,3'-tetrahydro-[1,1'-biindenylidene]-6,6'-diyl)bis(3-phenylurea) (*trans*-(±)-1):**

Under a N_2 atmosphere, *trans*-(±)-**S3** (84 mg, 0.24 mmol) was dissolved in CH_2Cl_2 (4 mL) and treated with phenyl isocyanate (53 µL, 0.48 mmol). The solution was stirred for 16 h and the precipitate was filtered off and washed with CH_2Cl_2 to yield *trans*-(±)-**1** (121 mg, 85%) as a white solid. M.p. 204 – 207 °C; ^{1}H NMR (400 MHz, DMSO-d_6, assignments based on COSY and NOESY): δ 8.92 (s, 2H; NH), 7.95 (s, 2H; NH), 7.48 (d, J = 7.9 Hz, 4H; ArH), 7.41 (s, 2H; ArH), 7.28 (t, J = 7.7 Hz, 4H; ArH), 6.96 (t, J = 7.3 Hz, 2H; ArH), 2.81 (m, 2H; CH), 2.57 (overlapped with the DMSO residual peak, 2H; CH), 2.30 (s, 6H; $ArCH_3$), 2.23 (d, J = 14.3 Hz, 2H; CH), 2.15 (s, 6H; $ArCH_3$), 1.08 (d, J = 6.2 Hz, 6H; CH_3); ^{13}C NMR (125 MHz, DMSO-d_6): δ 152.9, 141.3, 141.0, 140.1, 136.6, 135.9, 130.9, 128.8, 122.8, 122.3, 121.6, 118.0, 41.5, 38.2, 19.1, 18.2, 18.1; HRMS (ESI) *m/z*: 607.3009 ($[M + Na]^+$, calcd for $C_{38}H_{40}N_4O_2Na^+$: 607.3044), 585.3191 ($[M + H]^+$, calcd for $C_{38}H_{41}N_4O_2^+$: 585.3224).

^{1}H NMR titrations:

A 5 mM solution of either stable *cis*-**1** or *trans*-**1** (receptor solution) was prepared in DMSO-d_6/0.5%H_2O (v/v). This solution was then used to dissolve the selected tetrabutyl ammonium anion (50 mM). The solution containing the anion was added stepwise to the receptor solution (0.5 mL) in and NMR tube and after each addition a ^{1}H NMR spectrum was recorded. For the competitive titration to the stable *trans*-**1**/unstable *cis*-**1** mixture, a 5 mM solution of the *trans*-isomer was irradiated with 312 nm light for 2 h in an NMR tube,[3] which was maintained at 20 °C in a water bath. The resulting solution containing an equimolar *cis*/*trans* mixture of **1** was used to prepare the 50 mM anion solution.

In situ switching of phosphate levels:

All glassware was dried by heating with a heat gun under vacuum. In a glove box, tetrabutyl ammonium dihydrogen phosphate (0.7 mg, 2.0 µmol) and stable *trans*-**1** (1.2 mg, 2.0 µmol) were dissolved in 2 mL dried DMSO-d_6 (1 mM). The solution was transferred to a J. Young NMR tube and sealed airtight. The tube contained a closed capillary with a 0.1 M solution of triphenylphosphine oxide in DMSO-d_6 used for referencing (δ = 25.95 ppm). The sample was sequentially irradiated with 312 or 365 nm light at 20 °C in a water bath or heated at 60 °C in an oil bath. After each step ^{1}H and ^{31}P NMR spectra were recorded.

^{1}H and ^{13}C NMR spectra of new compounds

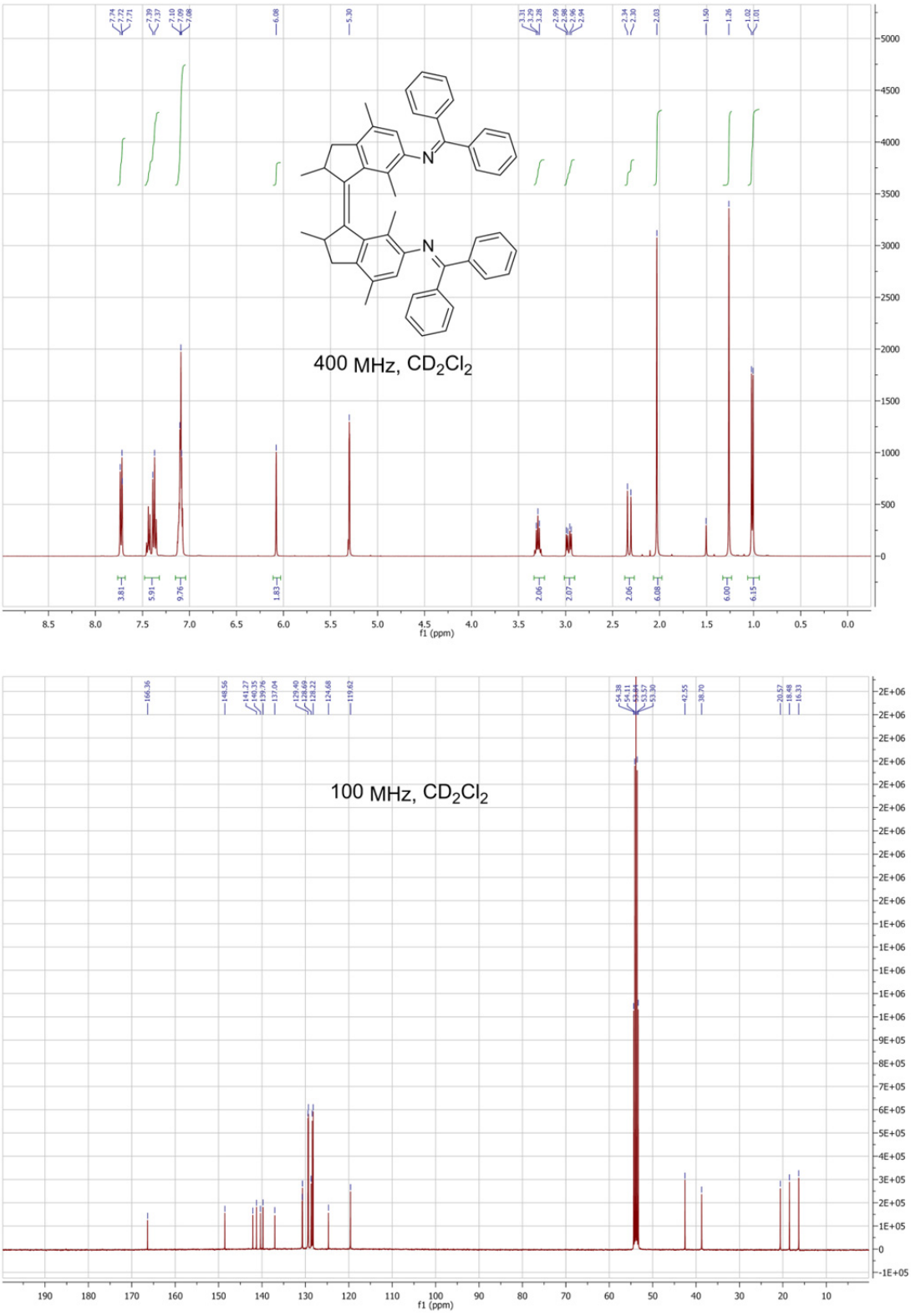


Figure S1. ^{1}H NMR (top) and ^{13}C NMR (bottom) spectra of *cis*-(±)-**S2**.

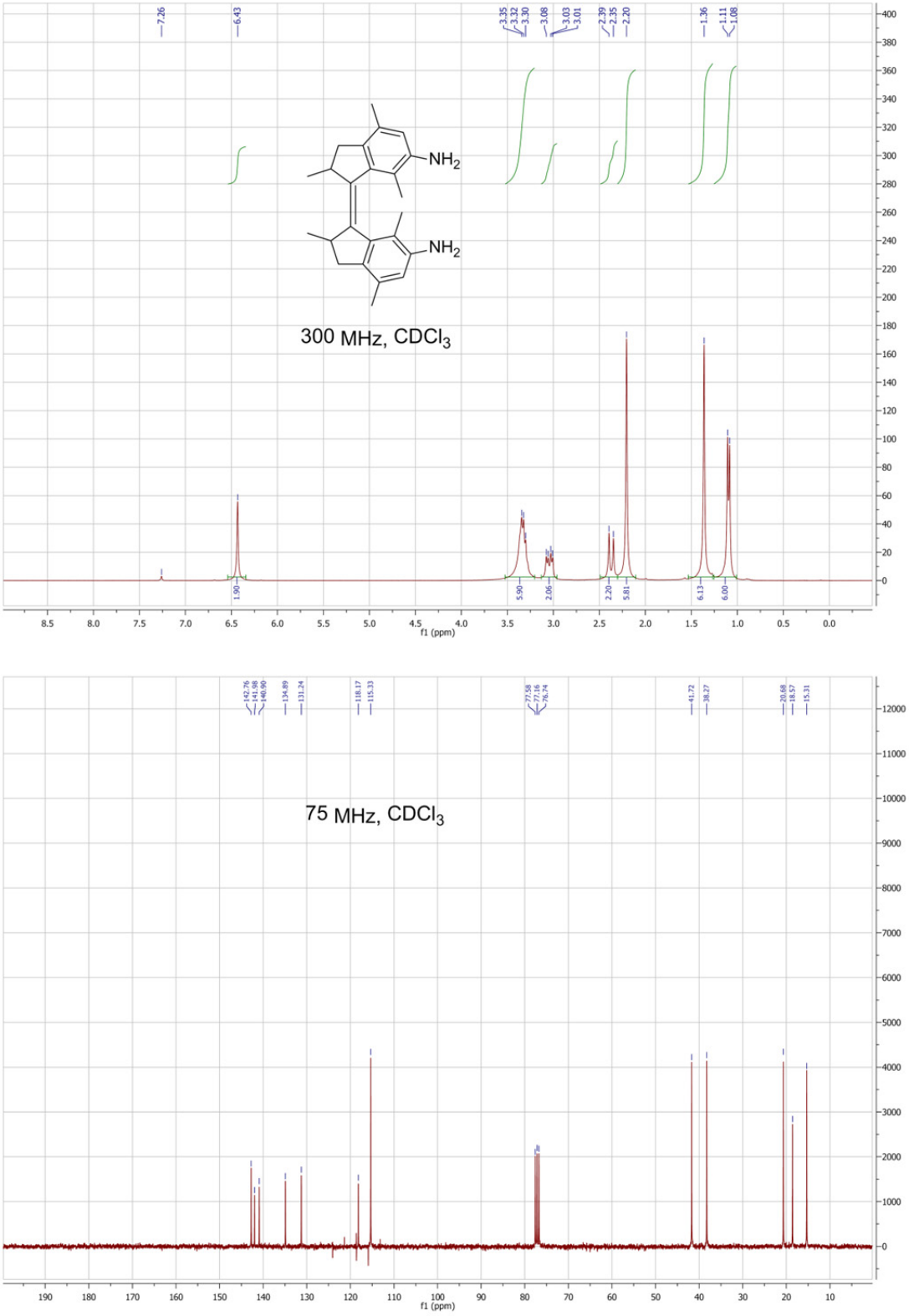


Figure S2. ^{1}H NMR (top) and ^{13}C NMR (bottom) spectra of *cis*-(±)-**S3**.

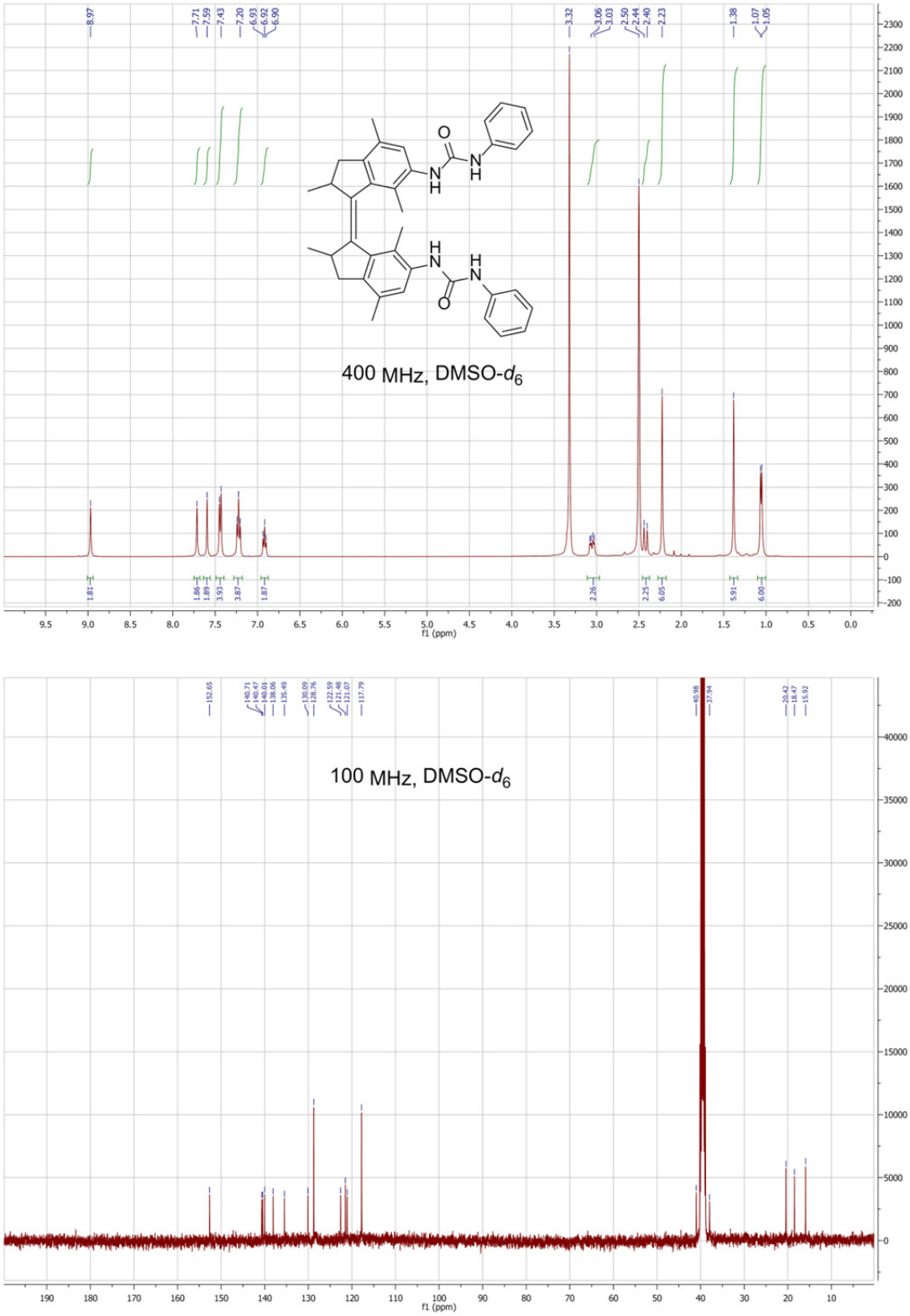


Figure S3. ^{1}H NMR (top) and ^{13}C NMR (bottom) spectra of *cis*-(±)-**1**.

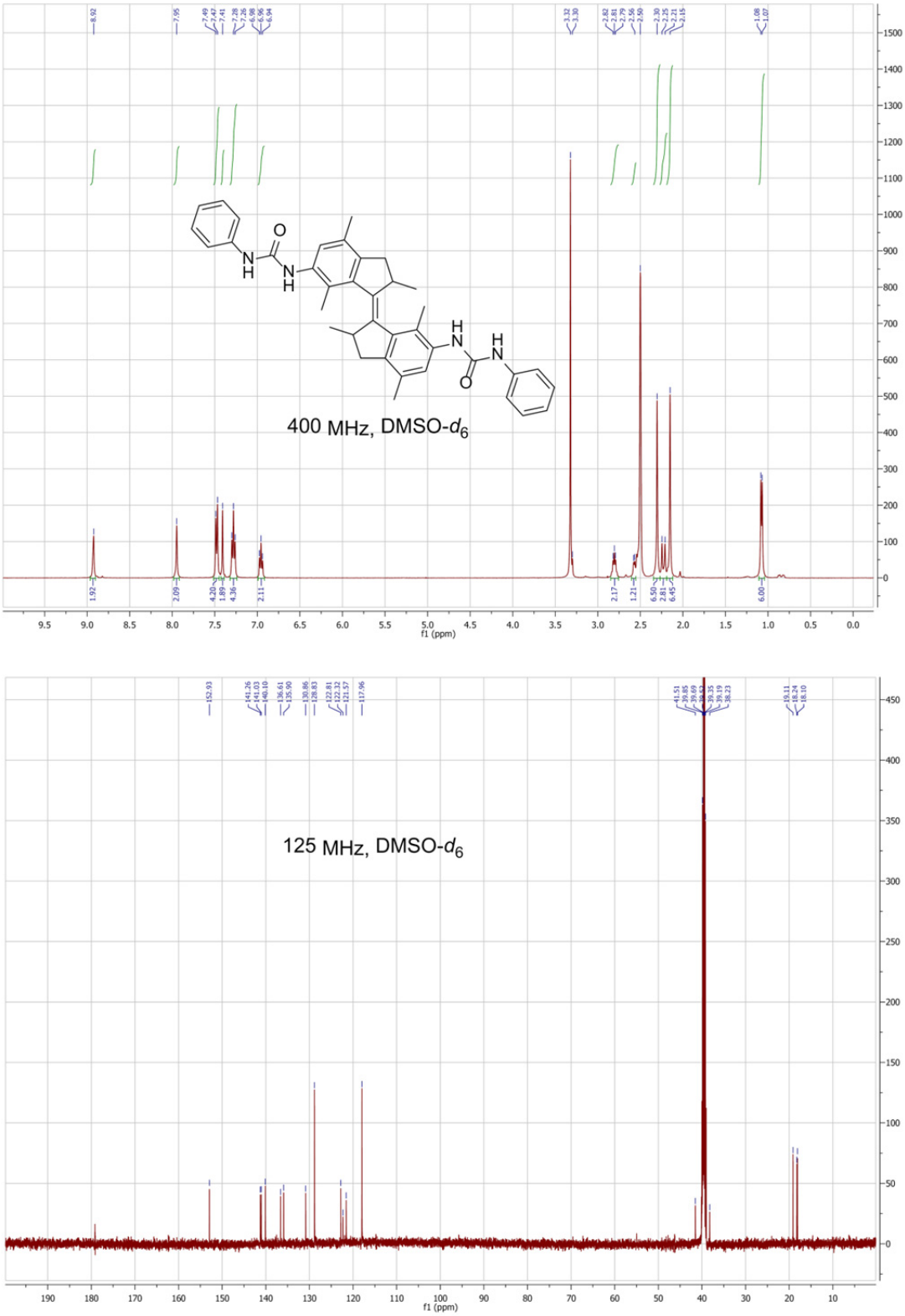


Figure S4. ^{1}H NMR (top) and ^{13}C NMR (bottom) spectra of *trans*-(±)-**1**.

^{1}H NMR dilution studies

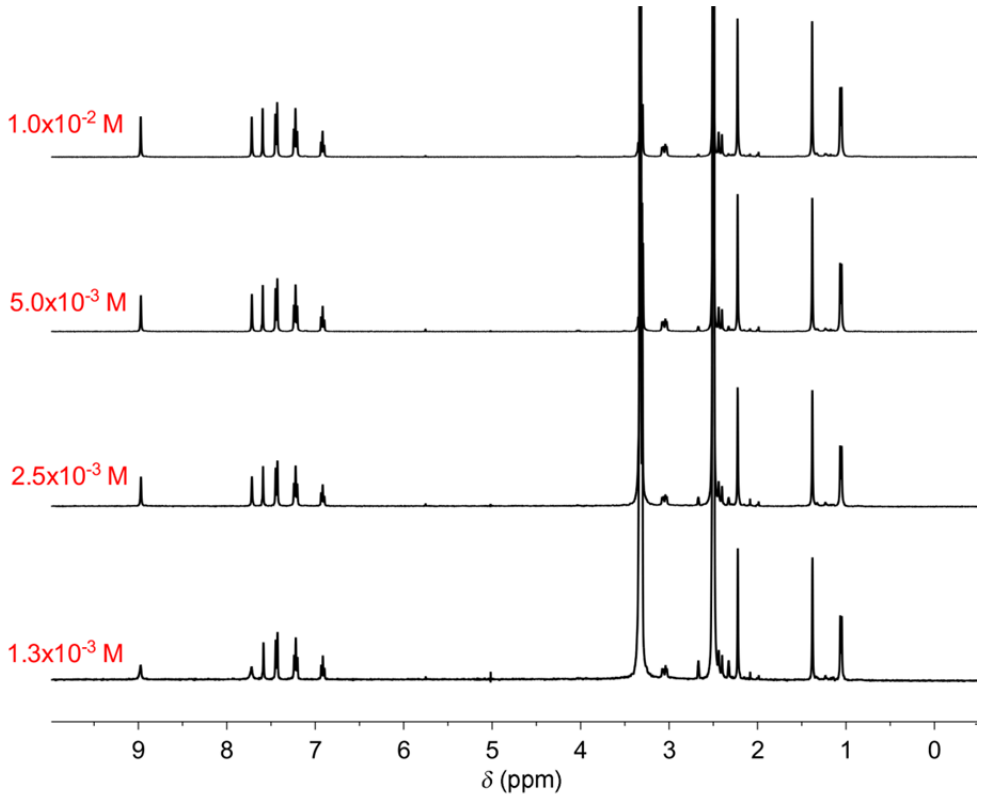


Figure S5. ^{1}H NMR spectra (400 MHz) of stable *cis*-**1** in DMSO-d_6 at four different concentrations (1×10^{-2} M – 1.3×10^{-3} M). The absence of changes in chemical shifts upon dilution indicates that no self-association occurs in this concentration regime.

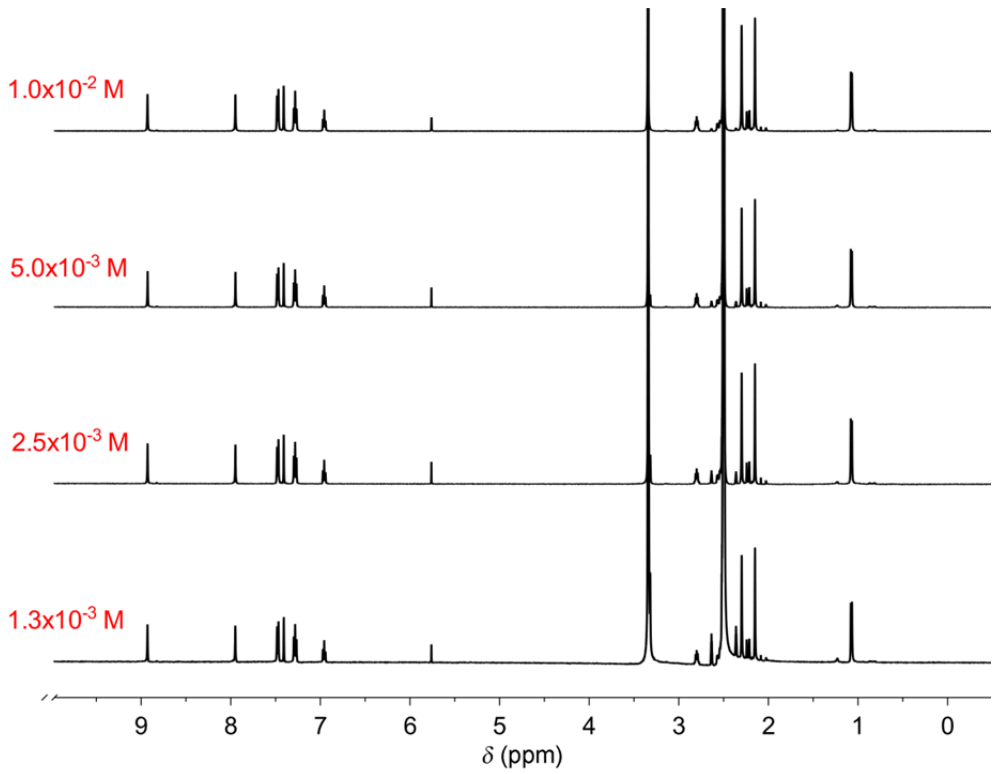


Figure S6. ^{1}H NMR spectra (500 MHz) of stable *trans*-**1** in DMSO-d_6 at four different concentrations (1×10^{-2} M – 1.3×10^{-3} M). The absence of changes in chemical shifts upon dilution indicates that no self-association occurs in this concentration regime.

^{1}H NMR isomerization studies

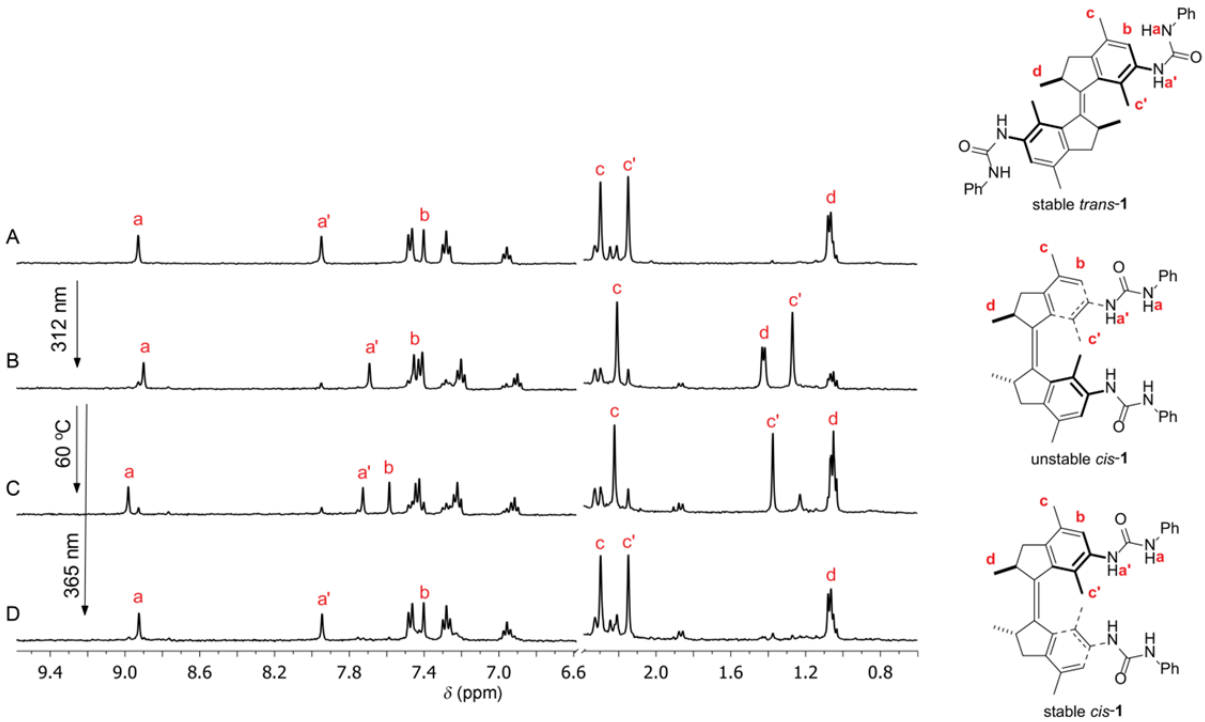


Figure S7. Aromatic and aliphatic region in the ^{1}H NMR spectrum (400 MHz) of stable *trans*-**1** (A) in DMSO-d_6/0.5%H_2O (1×10^{-3} M) and spectral changes after irradiation with 312 nm light at 20 °C for 2 h giving predominantly unstable *cis*-**1** (B). Subsequent heating at 60°C for 24 h induces the thermal isomerization to stable *cis*-**1** (C), whereas the stable *trans*-isomer is regenerated upon irradiation of the same sample with 365 nm light at 20 °C for 1.5 h (D).

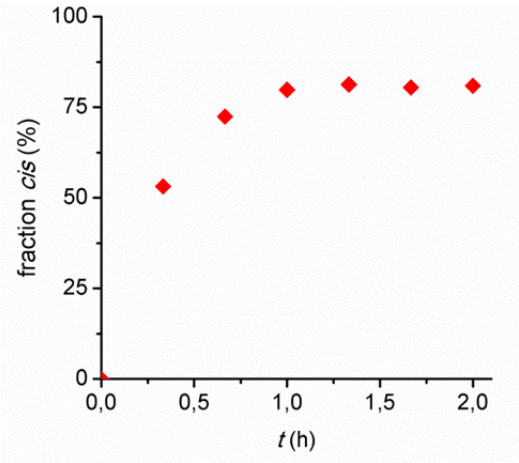


Figure S8. PSS determination for the irradiation of stable *trans*-**1** to give unstable *cis*-**1** (1×10^{-3} M in DMSO-d_6/0.5%H_2O). The *cis*/*trans* ratio was determined in time by averaging the integrals of $H_{a'}$ and $H_{c'}$ signals in the ^{1}H NMR spectrum.

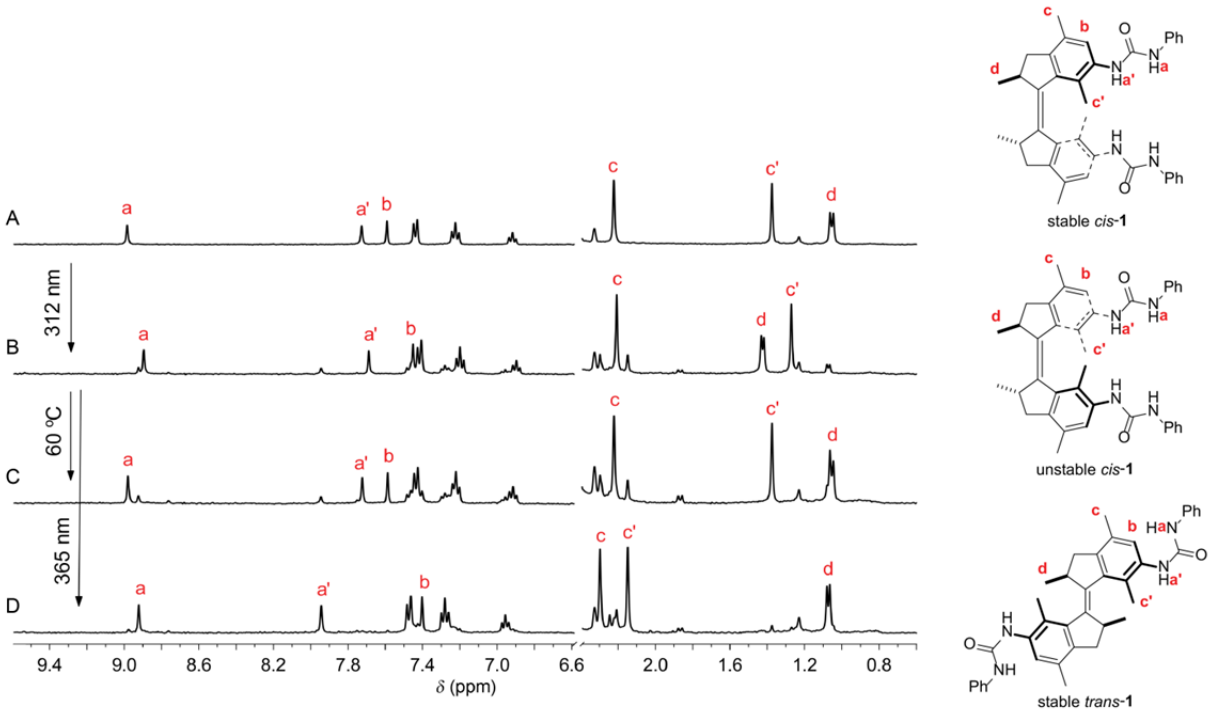


Figure S9. Aromatic and aliphatic region in the ^{1}H NMR spectrum (400 MHz) of stable *cis*-**1** (A) in DMSO-d_6/0.5%H_2O (1×10^{-3} M) and spectral changes after irradiation with 312 nm light at 20 °C for 2 h giving the PSS stable *trans*-**1**/unstable *cis*-**1** mixture (B). Subsequent heating at 60°C for 24 h induces thermal isomerization to stable *cis*-**1** (C), whereas the stable *trans*-isomer is formed upon irradiation with 365 nm light at 20 °C for 1.5 h (D).

UV-Vis spectra and Eyring plot analysis

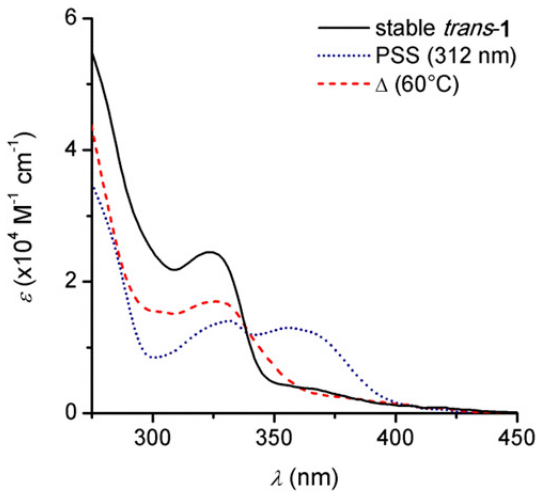


Figure S10. UV-vis absorption spectrum (1×10^{-5} M in DMSO/0.5%H_2O) of stable *trans*-**1**, before (black, solid) and after irradiation with 312 nm light at 20 °C for 1 h (blue, dotted) and subsequent heating at 60 °C for 24 h (red, dashed).

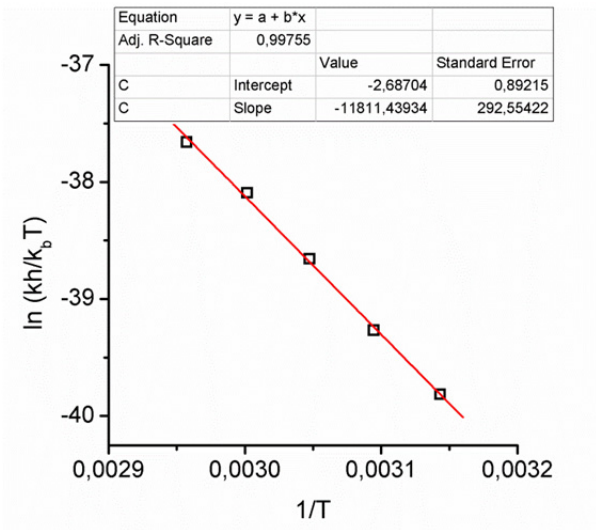


Figure S11. Eyring plot analysis of the thermal isomerization step from unstable to stable *cis*-**1** monitored by the decrease in absorption at 365 nm in DMSO/0.5%H_2O. The rate constants (k) of the first order decay at five temperatures (45, 50, 55, 60 and 65 °C) were obtained by fitting to the equation $A=A_0e^{-kt}$ using Origin software. $\Delta H^{\ddagger} = 98.2$ kJ mol^{-1}, $\Delta S^{\ddagger} = -22.3$ J K^{-1} mol^{-1} , $\Delta G^{\ddagger}$(20 °C) = 105 kJ mol^{-1}, k(20 °C) = 1.31×10^{-6} s^{-1}, $t_{1/2}$(20 °C) = 147 h.

^{1}H NMR titrations and data analysis

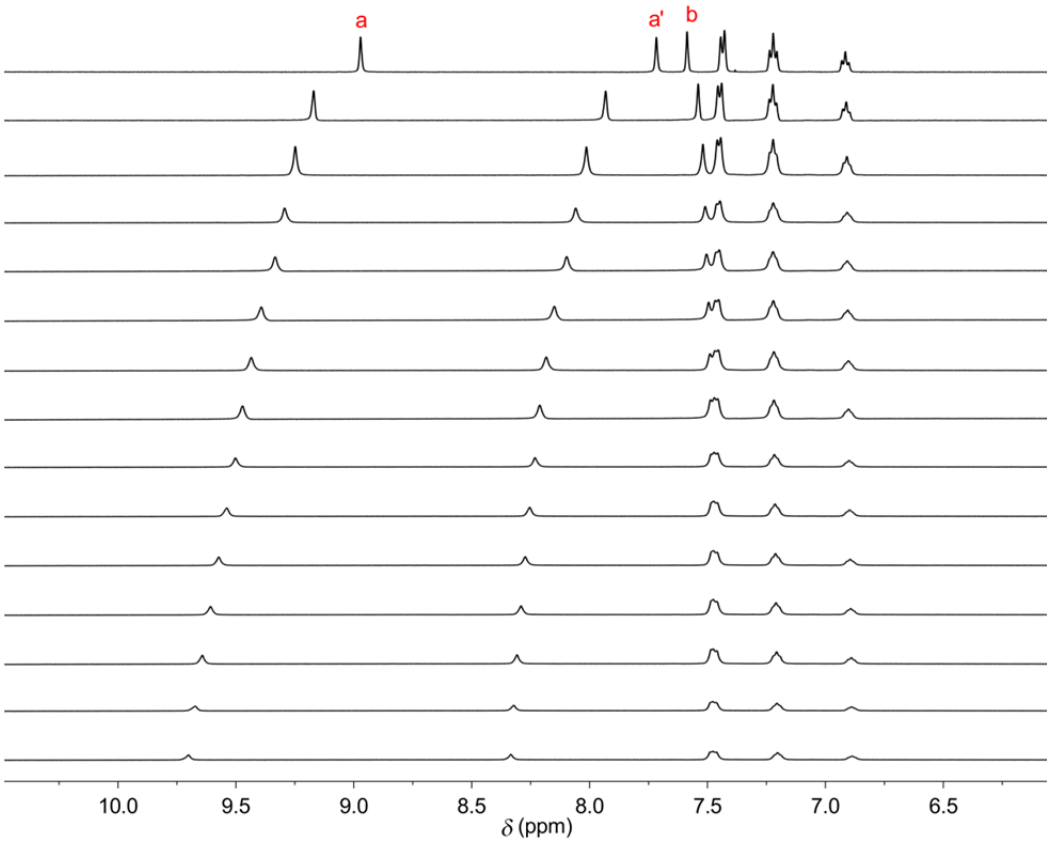


Figure S12. ^{1}H NMR spectral changes in the aromatic region of stable *cis*-**1** (5×10^{-3} M in DMSO-d_6/0.5%H_2O) upon the stepwise addition of $[Bu_4N]^+[Cl]^-$ (from top to bottom: 0.0, 2.9, 5.0, 6.9, 8.7, 12.0, 15.2, 18.1, 20.8, 24.6, 28.0, 32.1, 35.8, 39.9, 43.5 equivalents).

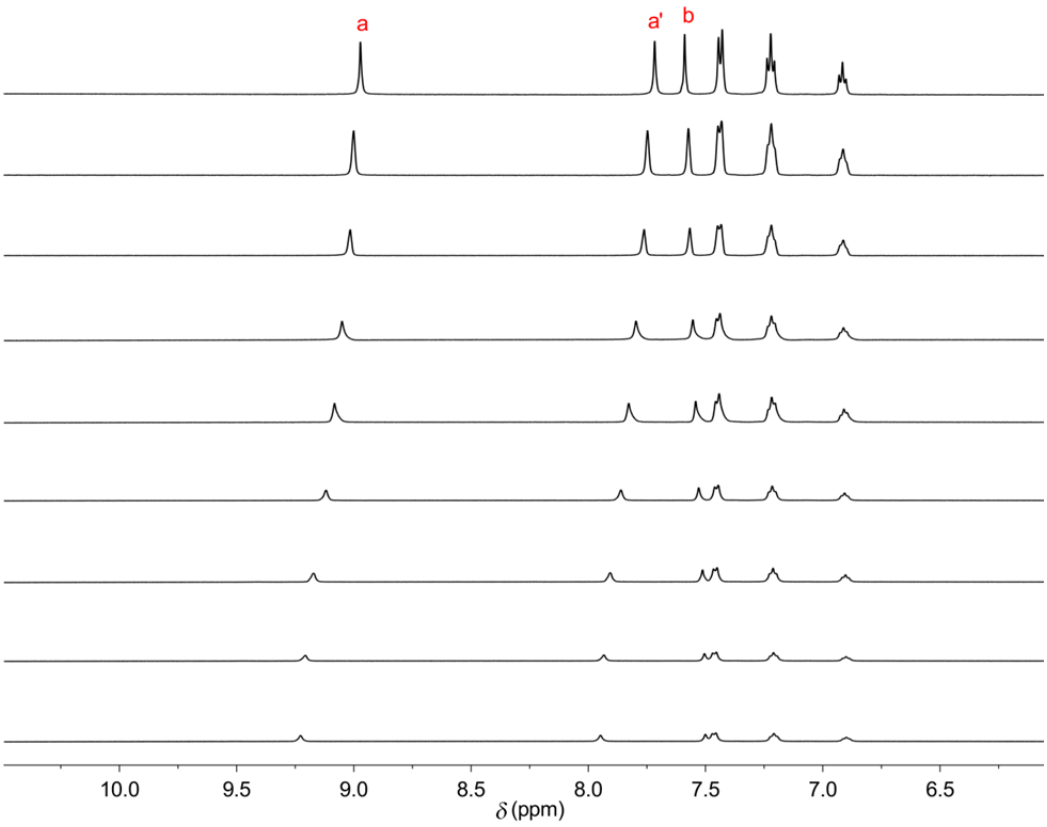


Figure S13. ^{1}H NMR spectral changes in the aromatic region of stable *cis*-**1** (5×10^{-3} M in DMSO-d_6/0.5%H_2O) upon the stepwise addition of $[Bu_4N]^+[Br]^-$ (from top to bottom: 0.0, 2.9, 4.4, 8.7, 13.6, 20.8, 32.1, 40.6, 47.2 equivalents).

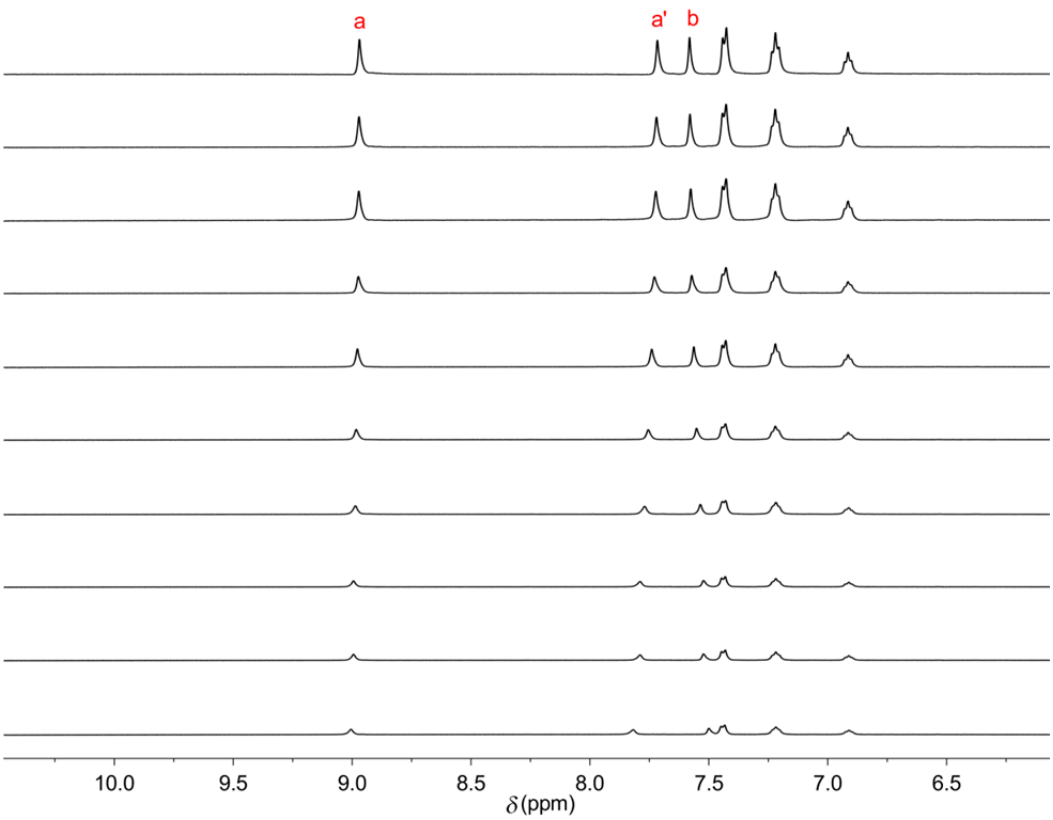


Figure S14. ^{1}H NMR spectral changes in the aromatic region of stable *cis*-**1** (5×10^{-3} M in DMSO-d_6/0.5%H_2O) upon the stepwise addition of $[Bu_4N]^+[NO_3]^-$ (from top to bottom: 0.0, 1.0, 2.0, 3.9, 7.4, 12.3, 19.4, 28.6, 37.5, 50.0 equivalents).

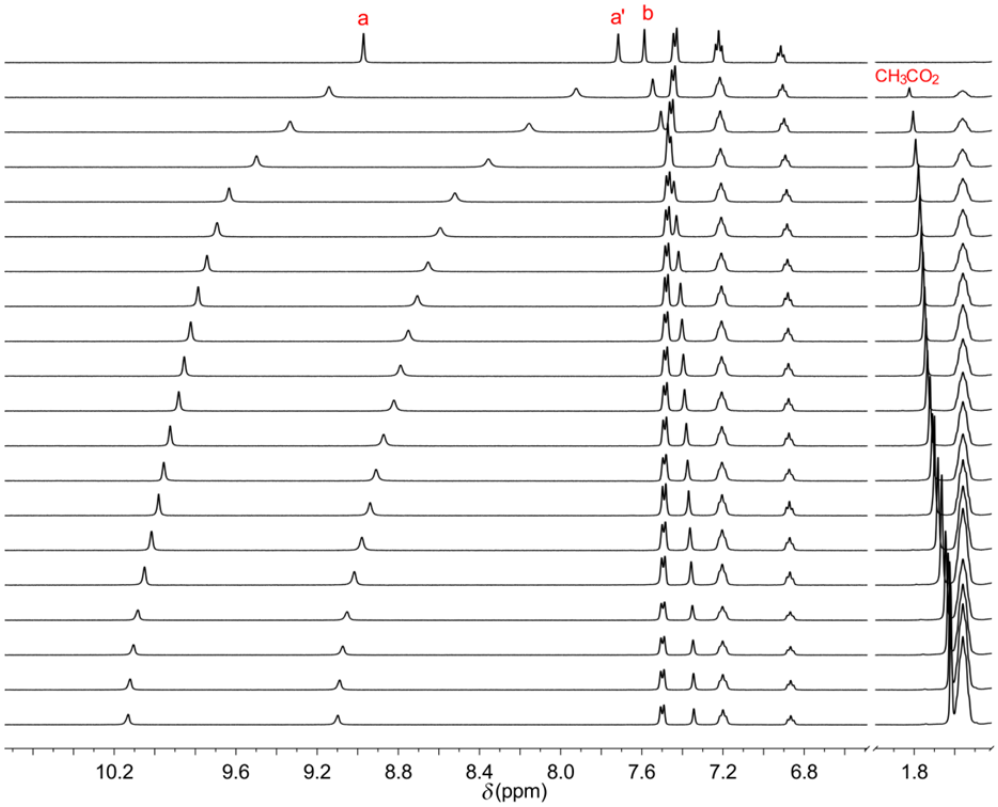


Figure S15. ^{1}H NMR spectral changes in the aromatic and aliphatic region of stable *cis*-**1** (5×10^{-3} M in DMSO-d_6/0.5%H_2O) upon the stepwise addition of $[Bu_4N]^+[CH_3CO_2]^-$ (from top to bottom: 0.00, 0.20, 0.38, 0.57, 0.74, 0.83, 0.91, 0.99, 1.07, 1.15, 1.23, 1.38, 1.53, 1.67, 1.94, 2.31, 2.86, 3.33, 3.75, 4.12 equivalents).

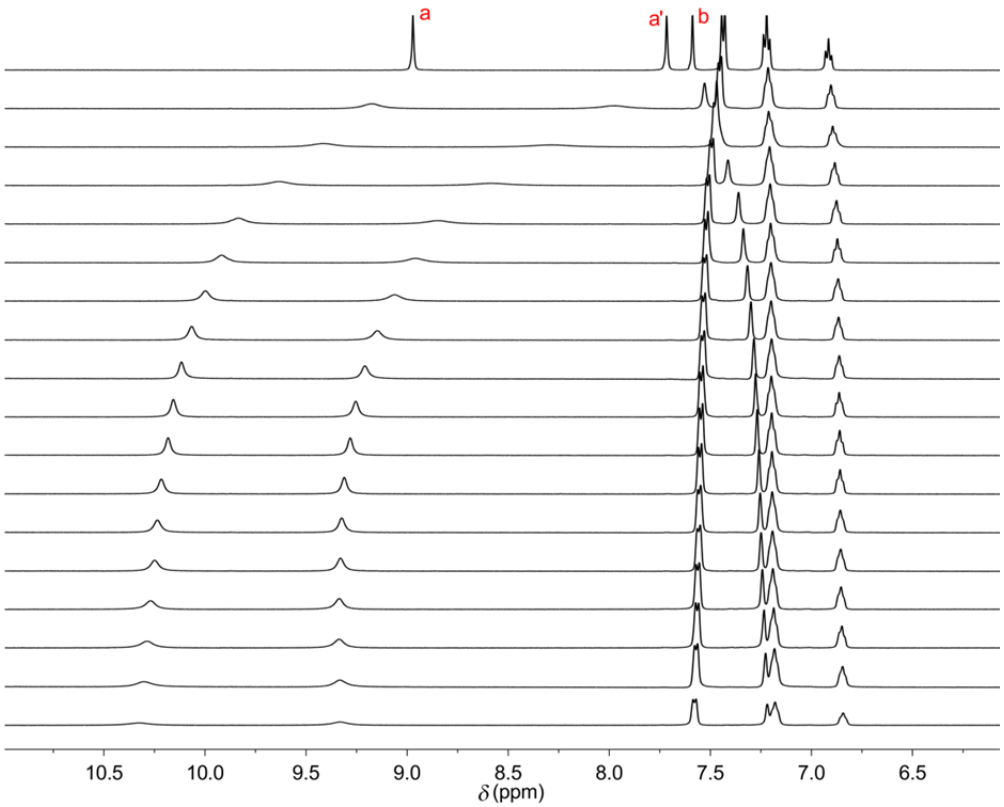


Figure S16. ^{1}H NMR spectral changes in the aromatic region of stable *cis*-**1** (5×10^{-3} M in DMSO-d_6/0.5%H_2O) upon the stepwise addition of $[Bu_4N]^+[H_2PO_4]^-$ (from top to bottom: 0.00, 0.20, 0.38, 0.57, 0.74, 0.83, 0.91, 0.99, 1.07, 1.15, 1.23, 1.38, 1.53, 1.67, 1.94, 2.31, 2.86, 3.33, 3.75 equivalents).

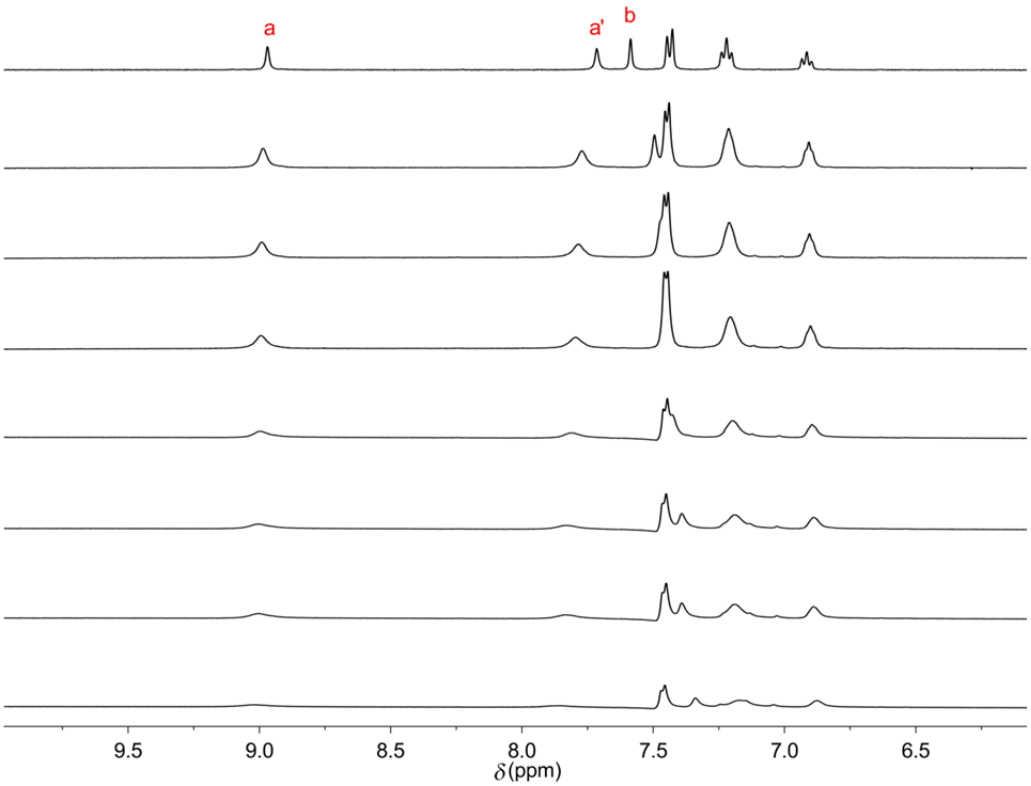


Figure S17. ^{1}H NMR spectral changes in the aromatic region of stable *cis*-**1** (5×10^{-3} M in DMSO-d_6/0.5%H_2O) upon the stepwise addition of $[Bu_4N]^+[H_2SO_4]^-$ (from top to bottom: 0.0, 5.0, 6.9, 8.7, 12.0, 16.7, 20.8, 26.9 equivalents).

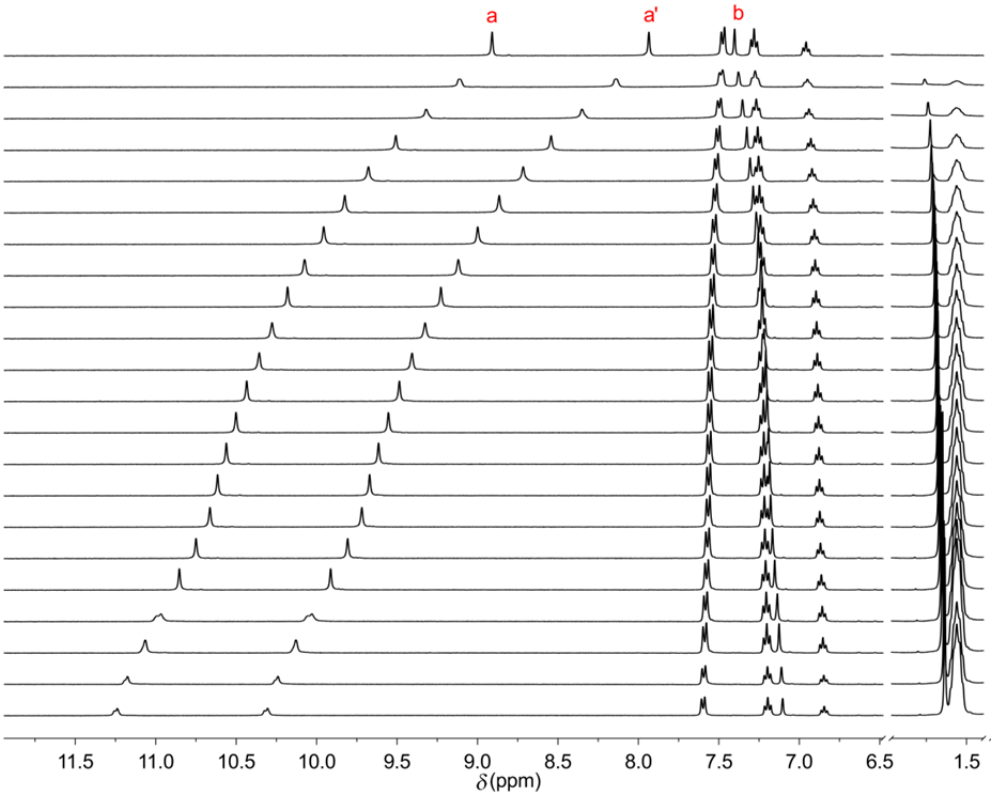


Figure S18. ^{1}H NMR spectral changes in the aromatic and aliphatic region of stable *trans*-**1** (5×10^{-3} M in DMSO-d_6/0.5%H_2O) upon the stepwise addition of $[Bu_4N]^+[CH_3CO_2]^-$ (from top to bottom: 0.00, 0.20, 0.38, 0.57, 0.74, 0.91, 1.07, 1.23, 1.38, 1.53, 1.67, 1.80, 1.94, 2.06, 2.19, 2.31, 2.54, 2.86, 3.33, 3.75, 4.44, 5.00 equivalents).

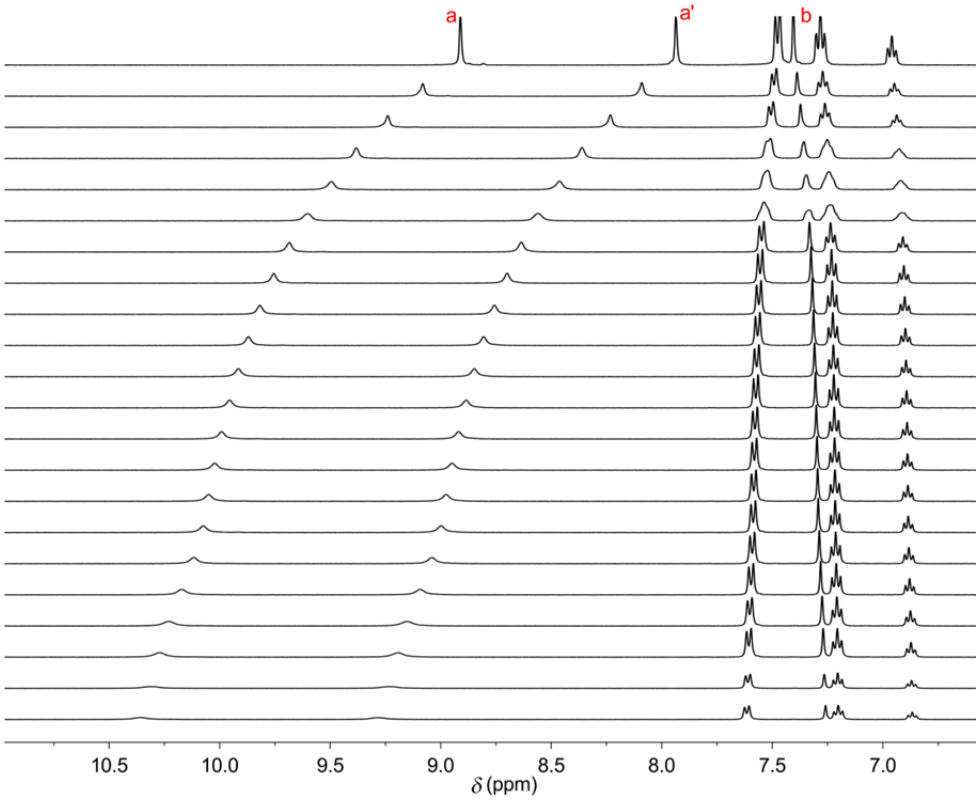


Figure S19. ^{1}H NMR spectral changes in the aromatic region of stable *trans*-**1** (5×10^{-3} M in DMSO-d_6/0.5%H_2O) upon the stepwise addition of $[Bu_4N]^+[H_2PO_4]^-$ (from top to bottom: 0.00, 0.20, 0.38, 0.57, 0.74, 0.91, 1.07, 1.23, 1.38, 1.53, 1.67, 1.80, 1.94, 2.06, 2.19, 2.31, 2.54, 2.86, 3.33, 3.75, 4.44, 5.00 equivalents).

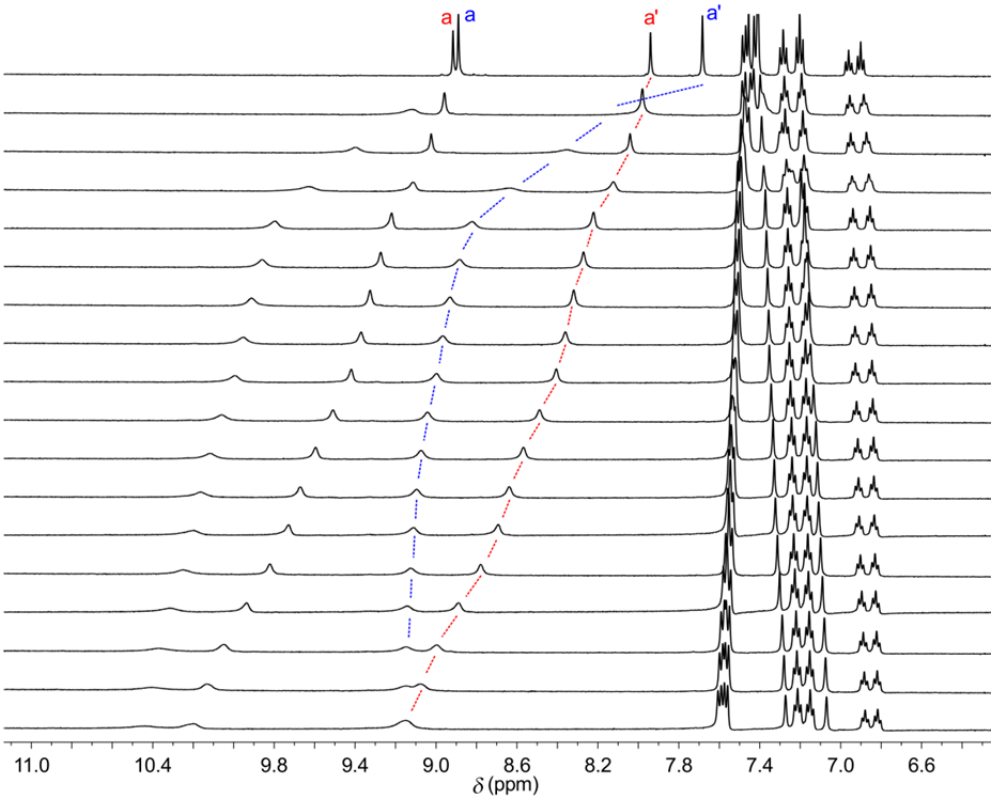


Figure S20. ^{1}H NMR spectral changes in the aromatic region of a stable *trans*-**1** (red)/ unstable *cis*-**1** (blue) mixture (5×10^{-3} M in DMSO-d_6/0.5%H_2O, *cis*/*trans* = 57:43) upon the stepwise addition of $[Bu_4N]^+[H_2PO_4]^-$ (from top to bottom: 0.00, 0.20, 0.38, 0.57, 0.74, 0.91, 1.07, 1.23, 1.38, 1.53, 1.67, 1.80, 1.94, 2.06, 2.19, 2.31, 2.54, 2.86, 3.33, 3.75, 4.44, 5.00 equivalents).

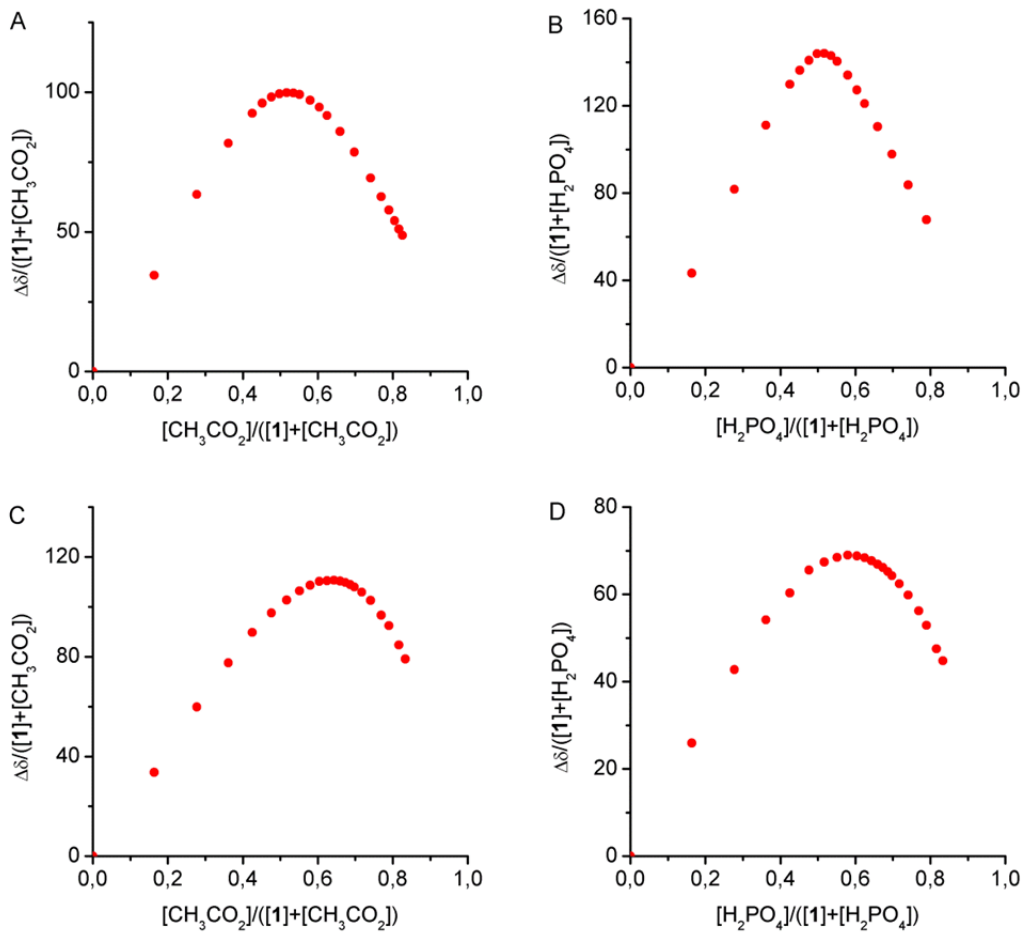


Figure S21. Job plot analyses generated from the titration data of $[Bu_4N]^+[CH_3CO_2]^-$ and $[Bu_4N]^+[H_2PO_4]^-$ to stable *cis*-**1** (A-B) and stable *trans*-**1** (C-D). The position of the maxima's reveal 1:1 and 2:1 anion/**1** binding stoichiometries, respectively.

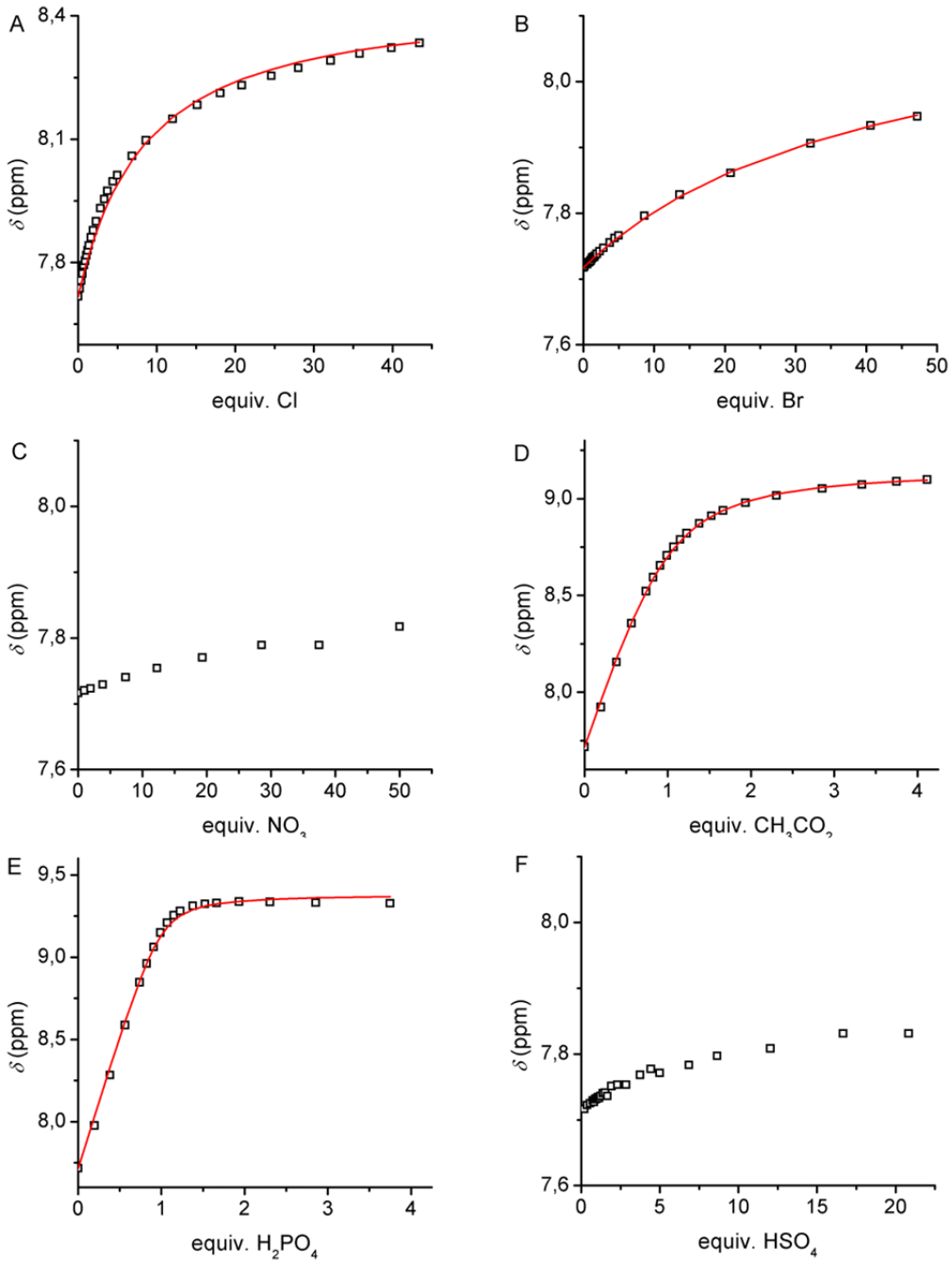
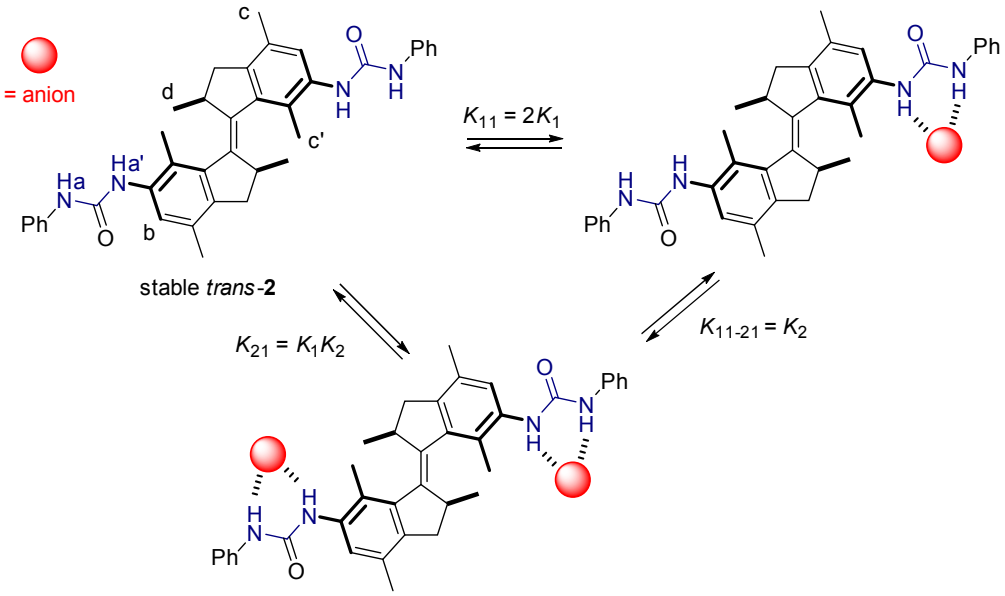


Figure S22. Titration curves for stable *cis*-**1** obtained upon addition of tetrabutyl ammonium anions carried out at 5×10^{-3} M in DMSO-d_6/0.5%H_2O. Data fits (red line) were obtained by simultaneous analysis of H_a, $H_{a'}$, H_b (for the lettering assignment see Scheme 1 and S3) and CH_3CO_2 chemical shift changes considering a 1:1 binding model using HypNMR software.[4] The data for the Br^- ion (B) were fitted manually and the ^1H chemical shift changes induced by NO_3^- (C) and HSO_4^- (F) were insignificant to derive a stability constant. Note that only the data points and data fit of the inmost urea chemical shift (H_a') is depicted here for clarity.



Scheme S3. Involved species in the titration of $CH_3CO_2^-$ and $H_2PO_4^-$ to stable *trans*-**1**. K_{11} is the stability constant of the 1:1 complex, K_{21} that of the 2:1 complex and $K_{11\text{-}21}$ the stepwise constant. Binding of the first (K_1) anion is assumed to be identical to that of the (K_2) second (cf. cooperativity factor: α = 1) and is subjected to a statistical correction factor.

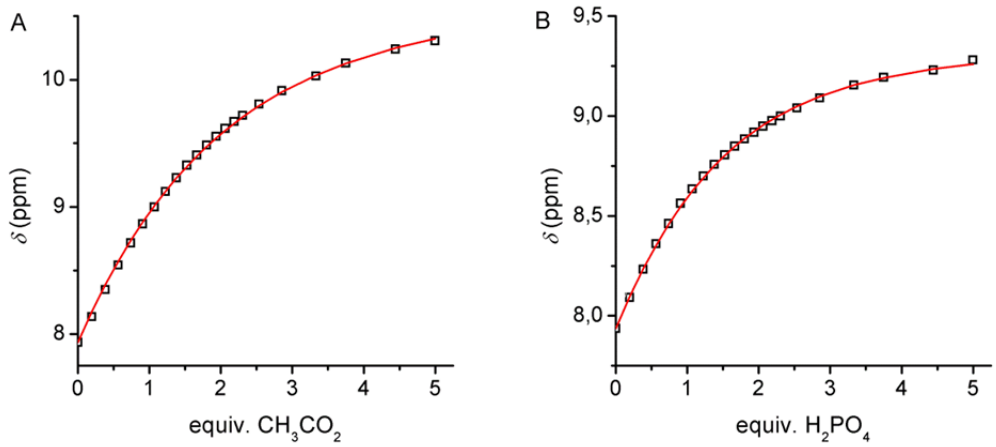


Figure S23. Titration curves for stable *trans*-**1** obtained upon addition of $[Bu_4N]^+[CH_3CO_2]^-$ (A) and $[Bu_4N]^+[H_2PO_4]^-$ (B) carried out at 5×10^{-3} M in DMSO-d_6/0.5%H_2O. The data was initially fitted to a 1:1 binding model by simultaneous analysis of H_a, $H_{a'}$, H_b and CH_3CO_2 chemical shifts, after which the 2:1 species were included assuming $K_1 = K_2$. Again, only the data points and data fit of the inmost urea chemical shift (H_a') is depicted for clarity.

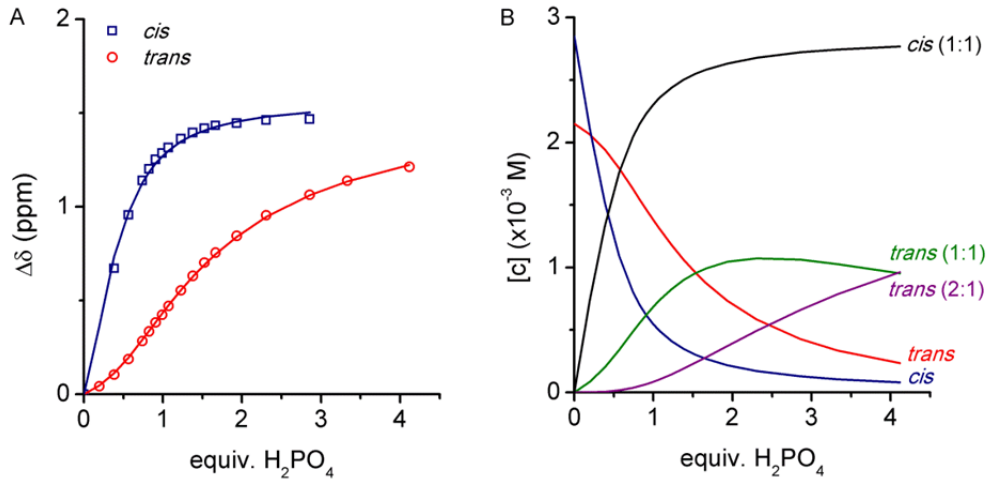


Figure S24. (A) Competitive titration curves (Δδ $H_{a'}$) for the addition of $[Bu_4N]^+[H_2PO_4]^-$ to a mixture of unstable *cis*-**1** and stable *trans*-**1** (*cis*/*trans* = 57:43) obtained after irradiation of the latter with 312 nm light for 2 h ([**1**] = 5×10^{-3} M in DMSO-d_6/0.5%H_2O). The data was analyzed by considering free, 1:1 and 2:1 anion/*trans*-**1** species, in addition to free and 1:1 anion/*cis*-**1** species, and by using the known values of the 1:1 and 2:1 *trans*-complexes. At the right (B) are the simulated concentration profiles of all the complexes involved upon the addition of $H_2PO_4^-$.

^{31}P NMR reversible switching studies

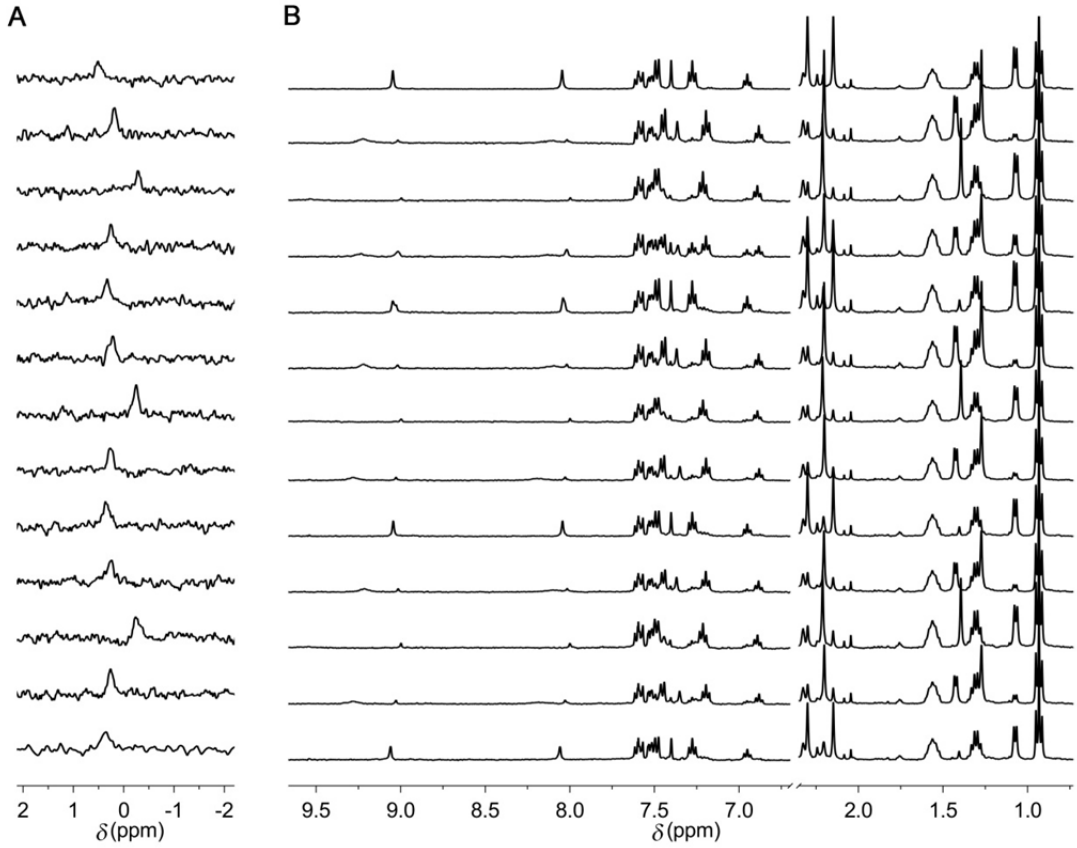
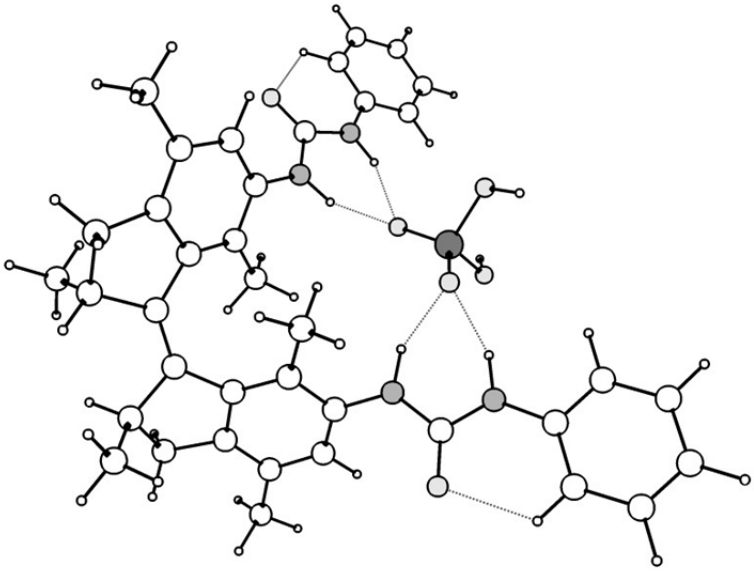


Figure S25. ^{31}P (A) and ^{1}H NMR (B) spectral changes starting with a solution of stable *trans*-**1**⊃$H_2PO_4^-$ (1×10^{-3} M in DMSO-d_6) upon the following switching cycle (from top to bottom): (i) irradiation with 312 nm light for 2 h at 20 °C, (ii) heating at 60 °C for 16 h, (iii) irradiation with 312 nm light for 2 h at 20 °C, (iv)) irradiation with 365 nm light for 1.5 h at 20 °C.

DFT Calculations

The Gaussian 09 program[5] was used for geometry optimizations and the calculation of energies. Initially, different input geometries were optimized at the semi-empirical PM6 level to find the global minima. Further geometry optimizations were performed at the DFT B3LYP/6-31G++(d,p) level with tight convergence criteria and using an IEFPCM DMSO solvation model. All the DFT geometries were found to have zero imaginary frequencies.

Table S1. Cartesian coordinates of stable *cis*-**1**⊃$H_2PO_4^-$.



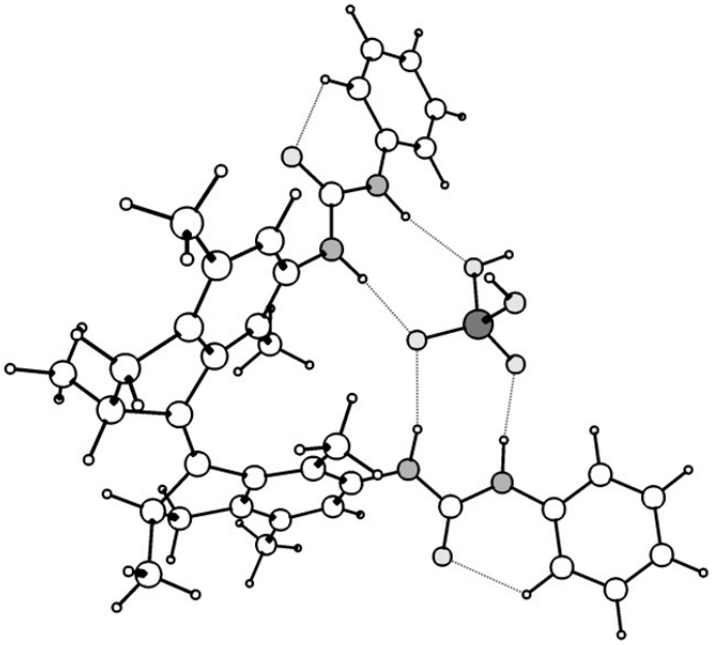
atom	X	Y	Z
C	-0.277198000	0.621091000	-4.189312000
C	0.277198000	-0.621091000	-4.189313000
C	0.653779000	-1.542877000	-3.088711000
C	1.746093000	-2.325489000	-3.522853000
C	2.082347000	-2.004056000	-4.961408000
C	0.797726000	-1.290523000	-5.470390000
C	-0.653779000	1.542877000	-3.088711000
C	-1.746093000	2.325489000	-3.522852000
C	-2.082348000	2.004056000	-4.961408000
C	-0.797726000	1.290523000	-5.470390000
C	-0.201392000	-2.299222000	-6.069987000
C	0.031627000	-1.800934000	-1.848826000
C	0.657068000	-2.747117000	-1.004617000
C	1.802524000	-3.445513000	-1.412078000
C	2.346316000	-3.274748000	-2.692017000
C	-0.031627000	1.800934000	-1.848826000
C	-0.657067000	2.747117000	-1.004617000

C	-1.802523000	3.445513000	-1.412077000
C	-2.346316000	3.274748000	-2.692016000
C	0.201392000	2.299222000	-6.069987000
C	1.294155000	1.200649000	-1.450722000
C	-3.535184000	4.088254000	-3.149035000
C	-1.294154000	-1.200649000	-1.450722000
C	3.535184000	-4.088253000	-3.149036000
H	0.224353000	-2.778206000	-6.959235000
H	-1.135290000	-1.808857000	-6.363748000
H	2.252153000	-4.156335000	-0.727676000
H	-2.252152000	4.156335000	-0.727675000
H	2.328780000	-2.895413000	-5.549585000
H	2.946069000	-1.326440000	-5.027391000
H	1.045699000	-0.547811000	-6.232873000
H	-2.328781000	2.895413000	-5.549584000
H	-2.946069000	1.326440000	-5.027391000
H	-0.446460000	-3.084203000	-5.345843000
H	-1.045700000	0.547811000	-6.232873000
H	1.135289000	1.808857000	-6.363748000
H	0.446460000	3.084204000	-5.345843000
H	-0.224353000	2.778207000	-6.959235000
H	-1.820977000	-0.811983000	-2.323553000
H	-1.195249000	-0.373654000	-0.738077000
H	-1.920676000	-1.961572000	-0.973867000
H	3.912840000	-4.721808000	-2.341665000
H	4.356541000	-3.446177000	-3.488077000
H	3.273152000	-4.740449000	-3.991550000
H	1.195249000	0.373653000	-0.738077000
H	1.920676000	1.961571000	-0.973866000
H	1.820977000	0.811983000	-2.323553000
H	-4.356541000	3.446177000	-3.488076000
H	-3.273152000	4.740449000	-3.991549000
H	-3.912839000	4.721808000	-2.341664000
C	0.034788000	4.156404000	0.931103000
N	0.478591000	4.002357000	2.232489000
O	-0.190089000	5.251829000	0.398679000
C	0.824174000	4.992971000	3.164162000
C	0.736532000	6.377499000	2.924959000
C	1.109159000	7.280430000	3.925905000
C	1.568788000	6.839255000	5.169583000
C	1.654770000	5.462310000	5.407119000
C	1.288266000	4.549596000	4.420094000
C	-0.034787000	-4.156404000	0.931103000
N	-0.478590000	-4.002357000	2.232489000
O	0.190091000	-5.251829000	0.398679000
C	-0.824173000	-4.992971000	3.164162000
C	-0.736530000	-6.377499000	2.924960000
C	-1.109157000	-7.280430000	3.925906000
C	-1.568786000	-6.839255000	5.169584000
C	-1.654770000	-5.462310000	5.407119000

C	-1.288266000	-4.549595000	4.420093000
N	-0.117398000	2.944918000	0.292684000
N	0.117398000	-2.944918000	0.292684000
O	-0.696759000	-1.122785000	2.404510000
P	-0.000002000	0.000000000	3.146762000
O	0.696757000	1.122785000	2.404512000
O	1.065449000	-0.735856000	4.159230000
H	0.598557000	3.034163000	2.541359000
H	0.381677000	6.730979000	1.967578000
H	1.035397000	8.345388000	3.722256000
H	1.854340000	7.550911000	5.938156000
H	2.009241000	5.093380000	6.365555000
H	1.360301000	3.483079000	4.615607000
H	-0.598557000	-3.034164000	2.541358000
H	-0.381674000	-6.730980000	1.967579000
H	-1.035394000	-8.345388000	3.722258000
H	-1.854338000	-7.550910000	5.938157000
H	-2.009241000	-5.093379000	6.365555000
H	-1.360302000	-3.483079000	4.615606000
H	0.164240000	2.116634000	0.820752000
H	-0.164240000	-2.116634000	0.820751000
H	1.678302000	-0.099842000	4.558447000
O	-1.065456000	0.735856000	4.159227000
H	-1.678311000	0.099842000	4.558442000

Sum of electronic and zero-point Energies= –2484.853563

Table S2. Cartesian coordinates of stable *cis*-**1**⊃$H_2PO_4^-$ (alternative binding mode).

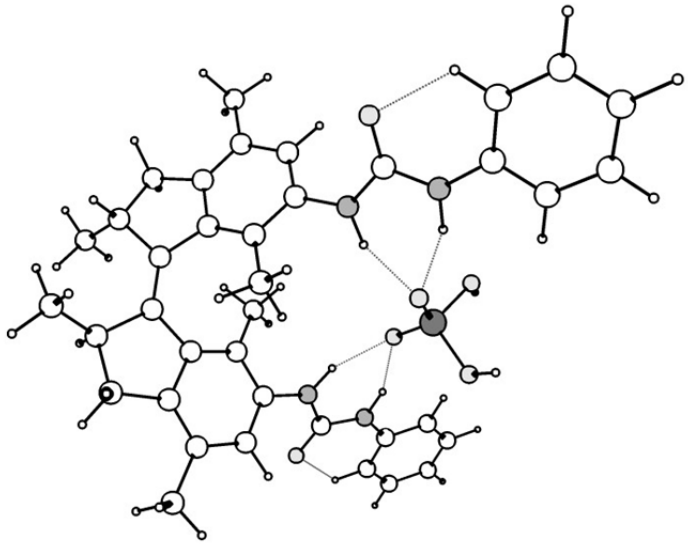


atom	X	Y	Z
C	-0.323995000	0.635312000	-4.313675000
C	0.243534000	-0.600326000	-4.324584000
C	0.637832000	-1.505292000	-3.218778000
C	1.741284000	-2.274824000	-3.646110000
C	2.060500000	-1.971824000	-5.093354000
C	0.770364000	-1.266053000	-5.603414000
C	-0.711023000	1.523993000	-3.191786000
C	-1.832689000	2.280004000	-3.593539000
C	-2.165480000	1.994064000	-5.041250000
C	-0.872379000	1.312670000	-5.576961000
C	-0.221086000	-2.280428000	-6.206111000
C	0.033770000	-1.748783000	-1.967157000
C	0.706021000	-2.636135000	-1.100471000
C	1.858381000	-3.323326000	-1.502532000
C	2.374531000	-3.189076000	-2.798846000
C	-0.089554000	1.762133000	-1.947378000
C	-0.762243000	2.627044000	-1.057928000
C	-1.936900000	3.293261000	-1.432719000
C	-2.470629000	3.167924000	-2.722353000
C	0.100346000	2.346837000	-6.176184000
C	1.273135000	1.224378000	-1.586331000
C	-3.689744000	3.954221000	-3.145638000
C	-1.313895000	-1.196900000	-1.572668000
C	3.571189000	-3.992378000	-3.253070000
C	0.001971000	3.999673000	0.856973000
N	0.385284000	3.898036000	2.179451000
O	-0.109362000	5.076058000	0.251854000
C	0.796150000	4.931467000	3.041360000
C	0.911323000	6.285028000	2.671153000
C	1.337074000	7.229445000	3.611372000
C	1.651992000	6.860752000	4.921642000
C	1.537789000	5.514421000	5.288438000
C	1.117607000	4.559728000	4.364213000
C	-0.117505000	-3.978095000	0.809142000
N	-0.505669000	-3.857505000	2.134008000
O	-0.078325000	-5.059944000	0.206584000
C	-0.987930000	-4.863446000	2.992534000
C	-0.911660000	-6.241611000	2.718654000
C	-1.404629000	-7.162766000	3.648404000
C	-1.970224000	-6.745044000	4.855971000
C	-2.042611000	-5.374299000	5.128767000
C	-1.562211000	-4.443341000	4.209245000
N	-0.246206000	2.781224000	0.260723000
N	0.213619000	-2.778476000	0.229124000
O	0.302424000	1.381449000	3.623478000
P	0.553030000	0.075096000	2.907363000
O	0.165712000	-0.090214000	1.451782000

O	-0.204162000	-1.173093000	3.683974000
O	2.147514000	-0.261607000	3.125568000
H	0.210427000	-2.757589000	-7.093585000
H	-1.156181000	-1.794569000	-6.503461000
H	2.339878000	-3.992506000	-0.796134000
H	-2.419469000	3.944526000	-0.711029000
H	2.302386000	-2.871012000	-5.671382000
H	2.923996000	-1.295842000	-5.175872000
H	1.014065000	-0.520653000	-6.365148000
H	-2.425686000	2.898733000	-5.602679000
H	-3.020968000	1.308034000	-5.124584000
H	-0.465698000	-3.066828000	-5.483160000
H	-1.115891000	0.575649000	-6.346720000
H	1.036948000	1.875290000	-6.491562000
H	0.345119000	3.125354000	-5.444839000
H	-0.346757000	2.831909000	-7.051555000
H	-1.854569000	-0.829019000	-2.445964000
H	-1.241041000	-0.374758000	-0.854097000
H	-1.909214000	-1.984381000	-1.098204000
H	3.969138000	-4.602523000	-2.437406000
H	4.377738000	-3.344157000	-3.615464000
H	3.310082000	-4.666222000	-4.078544000
H	1.226017000	0.402027000	-0.865880000
H	1.870930000	2.018278000	-1.124902000
H	1.796633000	0.865223000	-2.473717000
H	-4.487914000	3.296050000	-3.508658000
H	-3.453941000	4.647816000	-3.962383000
H	-4.088587000	4.541602000	-2.313858000
H	0.352768000	2.969158000	2.616662000
H	0.666832000	6.584586000	1.662561000
H	1.419718000	8.269269000	3.306125000
H	1.979421000	7.604093000	5.642207000
H	1.778085000	5.201690000	6.300983000
H	1.034522000	3.515932000	4.651438000
H	-0.480506000	-2.927536000	2.544951000
H	-0.474537000	-6.576761000	1.789278000
H	-1.337821000	-8.222894000	3.419138000
H	-2.347328000	-7.470549000	5.570217000
H	-2.480192000	-5.023474000	6.059170000
H	-1.633911000	-3.381647000	4.426285000
H	-0.006603000	1.917887000	0.749328000
H	0.065191000	-1.901328000	0.738328000
H	-0.059484000	-1.155315000	4.642608000
H	2.437843000	-1.010767000	2.583065000

Sum of electronic and zero-point Energies= −2484.848190

Table S3. Cartesian coordinates of unstable *cis*-**1**⊃$H_2PO_4^-$.



atom	X	Y	Z
C	0.469163000	-0.499980000	-4.146636000
C	1.292462000	-1.015195000	-3.027691000
C	1.801786000	-2.287640000	-3.366439000
C	1.344880000	-2.687703000	-4.740249000
C	0.819189000	-1.368083000	-5.376974000
C	-1.292462000	1.015194000	-3.027691000
C	-1.801786000	2.287640000	-3.366439000
C	-1.344879000	2.687703000	-4.740249000
C	-0.819189000	1.368083000	-5.376974000
C	-0.321841000	-1.678157000	-6.356072000
C	1.727426000	-0.373861000	-1.840629000
C	2.523216000	-1.135726000	-0.955368000
C	2.946957000	-2.432220000	-1.276021000
C	2.626933000	-3.016764000	-2.506738000
C	-1.727427000	0.373861000	-1.840629000
C	-2.523216000	1.135726000	-0.955368000
C	-2.946957000	2.432220000	-1.276021000
C	-2.626933000	3.016764000	-2.506738000
C	0.321842000	1.678156000	-6.356072000
C	-0.469164000	0.499979000	-4.146636000
C	-1.467472000	-1.078801000	-1.530310000
C	-3.141398000	4.387605000	-2.880246000
C	1.467471000	1.078801000	-1.530310000
C	3.141400000	-4.387604000	-2.880246000
N	-2.848751000	0.573537000	0.308291000
N	2.848751000	-0.573536000	0.308291000
H	0.011507000	-2.434142000	-7.076526000
H	-0.661928000	-0.813524000	-6.927554000

H	3.553923000	-2.975790000	-0.559846000
H	-3.553923000	2.975791000	-0.559846000
H	0.526926000	-3.421930000	-4.683061000
H	2.137484000	-3.149339000	-5.339249000
H	1.656192000	-0.914338000	-5.927360000
H	-0.526925000	3.421930000	-4.683060000
H	-2.137483000	3.149340000	-5.339249000
H	-1.185114000	-2.086976000	-5.818466000
H	-1.656192000	0.914338000	-5.927361000
H	0.661929000	0.813523000	-6.927553000
H	1.185115000	2.086975000	-5.818466000
H	-0.011506000	2.434141000	-7.076526000
H	1.289015000	1.644315000	-2.447018000
H	2.329666000	1.508711000	-1.011982000
H	0.592840000	1.230992000	-0.887259000
H	2.087461000	-0.164675000	0.854693000
H	3.723373000	-4.825897000	-2.064753000
H	3.786433000	-4.344572000	-3.766688000
H	2.321019000	-5.075080000	-3.118215000
H	-0.592841000	-1.230992000	-0.887259000
H	-1.289018000	-1.644316000	-2.447017000
H	-2.329666000	-1.508710000	-1.011980000
H	-2.087461000	0.164676000	0.854693000
H	-3.786432000	4.344573000	-3.766688000
H	-2.321017000	5.075080000	-3.118214000
H	-3.723371000	4.825898000	-2.064753000
C	4.086030000	-0.604766000	0.909385000
N	4.044325000	-0.116308000	2.204041000
C	5.105889000	0.093470000	3.097082000
C	4.774040000	0.596464000	4.372215000
C	5.764264000	0.841024000	5.321593000
C	7.109614000	0.590689000	5.026405000
C	7.440376000	0.092603000	3.763369000
C	6.458604000	-0.158709000	2.799519000
O	5.115672000	-1.011317000	0.353108000
C	-4.086030000	0.604766000	0.909385000
N	-4.044325000	0.116308000	2.204041000
O	-5.115672000	1.011318000	0.353108000
C	-5.105890000	-0.093470000	3.097082000
C	-6.458604000	0.158709000	2.799520000
C	-7.440377000	-0.092603000	3.763370000
C	-7.109614000	-0.590690000	5.026406000
C	-5.764263000	-0.841025000	5.321593000
C	-4.774040000	-0.596465000	4.372215000
O	1.214333000	0.523463000	2.434938000
O	-1.214333000	-0.523463000	2.434938000
H	3.115119000	0.145509000	2.541686000
H	3.733125000	0.795772000	4.612550000
H	5.480675000	1.228674000	6.296093000
H	7.881590000	0.780606000	5.765794000

H	8.479294000	-0.107385000	3.514951000
H	6.726686000	-0.545178000	1.826615000
H	-3.115119000	-0.145509000	2.541686000
H	-6.726686000	0.545179000	1.826616000
H	-8.479294000	0.107385000	3.514952000
H	-7.881590000	-0.780607000	5.765794000
H	-5.480674000	-1.228675000	6.296093000
H	-3.733125000	-0.795772000	4.612549000
P	0.000000000	0.000000000	3.176327000
O	0.570370000	-1.162700000	4.188594000
H	-0.148928000	-1.677987000	4.584222000
O	-0.570371000	1.162700000	4.188594000
H	0.148928000	1.677988000	4.584222000

Sum of electronic and zero-point Energies= −2484.843042

References and notes

(1) M. Vlatković, L. Bernardi, E. Otten, B. L. Feringa, *Chem. Commun.* **2014**, *50*, 7773-7775.

(2) J. Wang, A. Kulago, W. R. Browne, B. L. Feringa, *J. Am. Chem. Soc.* **2010**, *132*, 4191-4196.

(3) Upon longer irradiation time some thermal isomerization to stable *cis*-**1** was noted in the ^{1}H NMR spectrum. Therefore irradiation was not prolonged till the photostationary state (PSS) was reached, but stopped after 2 h. Please note that the used solvent mixture does not allow for cooling of the solution (m.p. DMSO: 19 °C).

(4) C. Frassineti, S. Ghelli, P. Gans, A. Sabatini, M. S. Moruzzi and A. Vacca, *Anal. Biochem.* **1995**, *231*, 374-382.

(5) Gaussian 09, Revision B.01, M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, G. Scalmani, V. Barone, B. Mennucci, G. A. Petersson, H. Nakatsuji, M. Caricato, X. Li, H. P. Hratchian, A. F. Izmaylov, J. Bloino, G. Zheng, J. L. Sonnenberg, M. Hada, M. Ehara, K. Toyota, R. Fukuda, J. Hasegawa, M. Ishida, T. Nakajima, Y. Honda, O. Kitao, H. Nakai, T. Vreven, J. A. Montgomery, Jr., J. E. Peralta, F. Ogliaro, M. Bearpark, J. J. Heyd, E. Brothers, K. N. Kudin, V. N. Staroverov, R. Kobayashi, J. Normand, K. Raghavachari, A. Rendell, J. C. Burant, S. S. Iyengar, J. Tomasi, M. Cossi, N. Rega, J. M. Millam, M. Klene, J. E. Knox, J. B. Cross, V. Bakken, C. Adamo, J. Jaramillo, R. Gomperts, R. E. Stratmann, O. Yazyev, A. J. Austin, R. Cammi, C. Pomelli, J. W. Ochterski, R. L. Martin, K. Morokuma, V. G. Zakrzewski, G. A. Voth, P. Salvador, J. J. Dannenberg, S. Dapprich, A. D. Daniels, Ö. Farkas, J. B. Foresman, J. V. Ortiz, J. Cioslowski, D. J. Fox, Gaussian, Inc., Wallingford CT, **2009**.