# ELECTRONIC SUPPORTING INFORMATION

# Anion-tunable control of the thermal *Z*→*E* isomerisation of the basic azobenzene receptors

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# 1. Synthetic Procedures and Structural Analysis

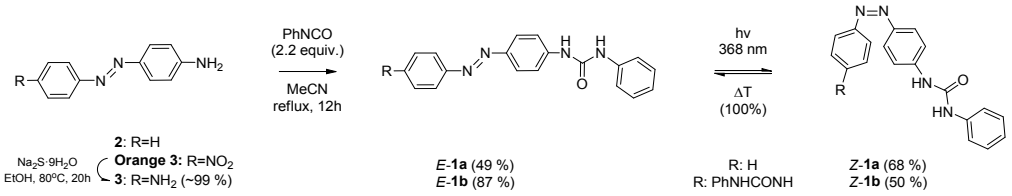
## 1.1 General Remarks

All solvents were of reagent grade quality. All reagents were purchased from Sigma-Aldrich and TCI Chemicals and used without further purification. Column chromatography was carried out using Merck Kieselgel 60 (63–100 μm mesh size), TLC was carried out on Merck Kieselgel F254 plates. Melting points were determined using a Boëtius M HMK hot-stage apparatus and were uncorrected. The NMR spectra were recorded on a Varian Gemini 2000, Mercury 400, or Varian S600 instruments. Chemical shifts are reported in ppm and are set to solvent residue peak. The splitting pattern of multiplets is described by abbreviations (s – singlet, d – doublet, t – triplet, q – quartet, dd – doublet of doublets, m –multiplet, c – covered signal, b – broad peak). *J* coupling constants values are reported in Hz. Mass spectral analyses were performed with the ESI-TOF technique on a Mariner mass spectrometer from PerSeptive Biosystem. The UV-Vis spectra were recorded using Agilent Technologies Cary 60 spectrophotometer equipped with a Peltier thermostated cell holder (temperature accuracy ± 0.1 °C).

## 1.2 Photoisomerisation

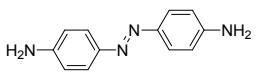
UV irradiation experiments were carried with a self-constructed Rayonet type photoreactor, equipped with eight UVA lamps (GE® F9BX BL G23 9W, $\lambda_{max}$ = 368 nm) and with an effective air cooling system to maintain fixed temperature (≤ 26°C) inside photoreactor chamber. To ensure homogenous irradiation, sample was spinned at 4 rpm. Photoisomerisation of the studied compounds was carried out in quartz cuvette (Hellma Analytics Quartz Suprasil 100-QS V = 3.5 ml, l = 10 mm) or in quartz NMR tube (Wilmad 535-PP-7QTZ, ϕ = 5 mm, limit 600 MHz). Time required to reach photostationary state (PSS) was found to be *ca.* 30 s for diluted receptor solution (c ~ $10^{-5}$ M) and 10-30 min for concentrated receptor solution (c ~ $10^{-2}$ M). Blue light irradiation experiments were carried out with SMD Power-LED bulb (3.3 W, $\lambda_{max}$ = 410 nm). UVA light intensity inside photoreactor chamber was measured by ferrioxalate actinometry[1] to be 2.3±0.1·$10^{20}$ (quanta/L·s).

## 1.3 Synthetic pathway and substance analysis




**Scheme S1.** Synthesis of receptors **1a** and **1b**

### Compound **3**



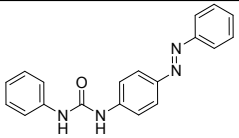
$M_w$ = 212.25 g/mol

A solution of Disperse Orange 3 (10.0 g, 37 mmol, 90% purity) and sodium sulfide nonahydrate (19.50 g, 74 mmol, 2 equiv) in ethanol (600 ml) was refluxed for 20h. The solvent was evaporated under vacuum and resulting brown oil was redissolved in a mixture of water (500 ml) and brine (30 ml), extracted with ethyl acetate (3 x 300 ml), dried ($MgSO_4$), concentrated (~100 ml), and passed through short pad of silica gel (~50 g) to afford **3** (7.82 g, ~99%) as a reddish solid (mp. 244°C, lit. 238-241).
$R_{f,3}$ = 0.55, $R_{f,2\ (Disperse\ Orange\ 3)}$ = 0.74 (hexanes - ethyl acetate 1:1 v/v)

**$^1$H NMR** (400 MHz, DMSO) δ 7.55 (d, *J* = 8.8 Hz, 4H), 6.65 (d, *J* = 8.8 Hz, 4H), 5.73 (s, 4H).

**$^{13}$C NMR** (100 MHz, DMSO) δ 151.0, 143.2, 123.9, 113.6.

### Host *E*-**1a**



$M_w$ = 316.37 g/mol

The mixture of 4-aminoazobenzene **3** (1.0 g, 5.1 mmol) and phenyl isocyanate (0.60 mL, 5.6 mmol, 1.1 equiv) was refluxed in anhydrous acetonitrile (20 mL) overnight under argon atmosphere. Then the orange product was filtered off, washed with cold acetonitrile (10 mL) and diethyl ether (20 mL), and dried at high vacuum to give host *E*-**1a** (0.72 g, 44 %) as yellowish solid (mp 228-229 °C).

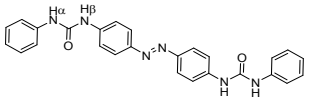
**$^1$H NMR** (200 MHz, DMSO) δ 9.14 (s, 1H), 8.82 (s, 1H), 7.86 (m, 4H), 7.69 (d, *J* = 8.9 Hz, 2H), 7.52 (m, 5H), 7.30 (t, *J* = 7.8 Hz, 2H), 7.00 (t, *J* = 7.3 Hz, 1H).
(for detailed assignments of peaks see scans of NMR spectra).

**$^{13}$C NMR** (50 MHz, DMSO) δ 152.15, 152.02, 146.58, 143.10, 139.28, 130.75, 129.34, 128.80, 123.89, 122.20, 118.38, 118.06.
(for detailed assignments of peaks see scans of NMR spectra).

**HRMS ESI** (m/z) Calc. for $C_{19}H_{17}NO_4$ $[M+H]^+$: 317.1398, found: 317.1402.

**Anal** (%) Calc. for **1a** ($C_{19}H_{16}N_4O_1$): C 72.14, H 5.10, N 17.71, found: C 72.17, H 5.15, N 17.43.

## Host *E*-**1b**



$M_w$ = 450.18 g/mol

The mixture of 4,4'-*di*aminoazobenzene **3** (1.0 g, 4.7 mmol) and phenyl isocyanate (1.12 mL, 10.3 mmol, 2.2 equiv) was refluxed in anhydrous acetonitrile (20 mL) overnight under argon atmosphere. Then the orange product was filtered off, washed with hot acetonitrile (50 mL) and suspended in diethyl ether (20 mL). After 30 minutes of vigorous stirring the product was filtered off and dried at high vacuum to give receptor *E*-**1b** (1.77 g, 87 %) as orange powder (mp > 300 °C).

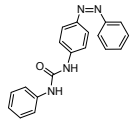
**$^1$H NMR** (500 MHz, DMSO) δ 9.07 (s, 2H), 8.79 (s, 2H), 7.83 (d, *J* = 9.0 Hz, 4H), 7.66 (d, 2H), 7.49 (dd, *J* = 8.6, 1.0 Hz, 3H), 7.30 (dd, *J* = 8.5, 7.5 Hz, 2H), 7.01 (td, *J* = 7.4, 1.1 Hz, 2H)
(for detailed assignments of peaks see scans of NMR spectra).

**$^{13}$C NMR** (125 MHz, DMSO) δ 152.2, 146.8, 142.4, 139.4, 128.8, 123.5, 122.1, 118.4, 118.1
(for detailed assignments of peaks see scans of NMR spectra).

**HRMS ESI** (m/z) Calc. for $C_{26}H_{22}N_6O_4Na$ $[M+Na]^+$: 473.1702, found: 473.1701.

**Anal** (%) Calc. for **1b** ($C_{26}H_{22}N_6O_4$): C 69.32, H 4.92, N 18.66, found: C 69.27, H 4.86, N 18.88.

## Host *Z*-**1a**



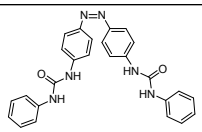
$M_w$ = 316.37 g/mol

The ~0.01 M solution of isomer *E*-**1a** in DMSO was irradiated with UV light (368 nm) over a period of 60 min to give *Z*-**1a** in 68% yield.

**$^1$H NMR** (200 MHz, DMSO) δ 8.83 (s, 1H), 8.70 (s, 1H), 7.29 (m, 10H), 6.96 (t, *J* = 7.2 Hz, 1H), 6.84 (dd, *J* = 9.2, 2.0 Hz, 4H) (for detailed assignments of peaks see scans of NMR spectra).

**$^{13}$C NMR** (50 MHz, DMSO) δ 180.34, 154.03, 152.23, 146.92, 139.34, 129.04, 128.75, 126.82, 122.00, 119.34, 118.26, 117.61. (for detailed assignments of peaks see scans of NMR spectra).

## Host *Z*-**1b**



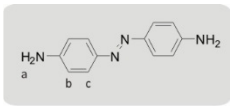
$M_w$ = 450.18 g/mol

The ~0.01 M solution of isomer *E*-**1b** in DMSO was irradiated with UV light (368 nm) over a period of 66 min to give *Z*-**1b** in 50% yield.

**$^1$H NMR** (400 MHz, DMSO) δ 8.82 (s, 2H), 8.69 (s, 2H), 7.45 – 7.39 (m, 8H), 7.29 – 7.24 (m, 4H), 6.99 – 6.93 (m, 2H), 6.86 (d, *J* = 8.7 Hz, 4H) (for detailed assignments of peaks see scans of NMR spectra).

**$^{13}$C NMR** (100 MHz, DMSO) δ 152.22, 146.83, 142.42, 139.37, 128.79, 123.44, 122.10, 118.37, 118.12
(for detailed assignments of peaks see scans of NMR spectra).

## 1.4 Copies of $^{1}H$ and $^{13}C$ NMR spectra





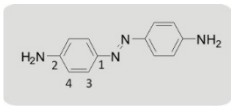






**Fig. S1** NMR spectra of compound **3** in DMSO-$d_6$ (400MHz).

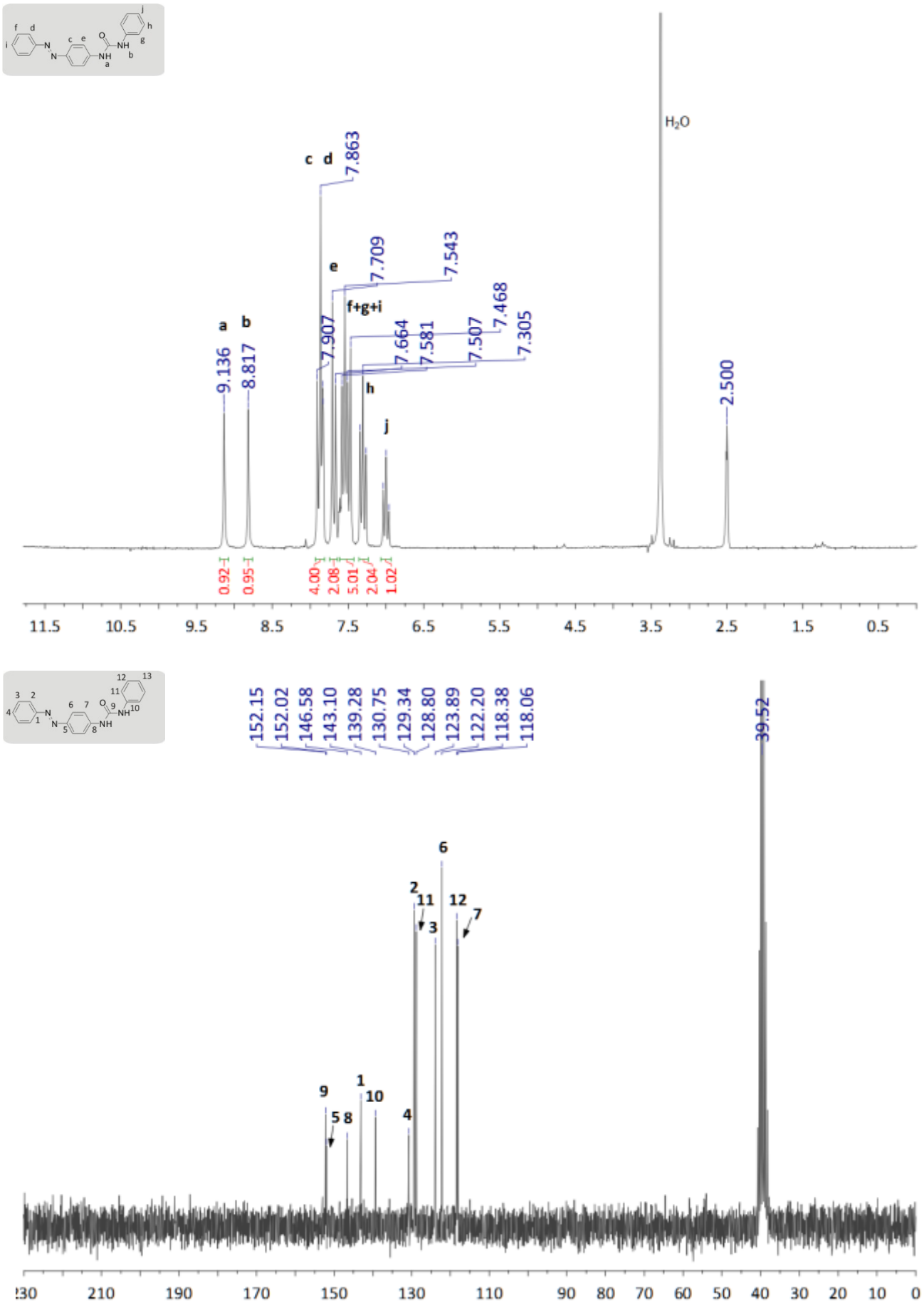
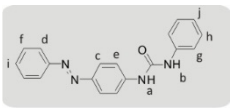



**Fig. S2** NMR spectra of compound *E*-**1a** in DMSO-$d_6$ (200MHz).





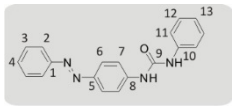






**Fig. S3** NMR spectra of a mixture of the *E*- and *Z*-**1a** in DMSO-$d_6$ (200MHz), only peak labels of *Z*-**1a** are shown (top) or labeled (bottom).

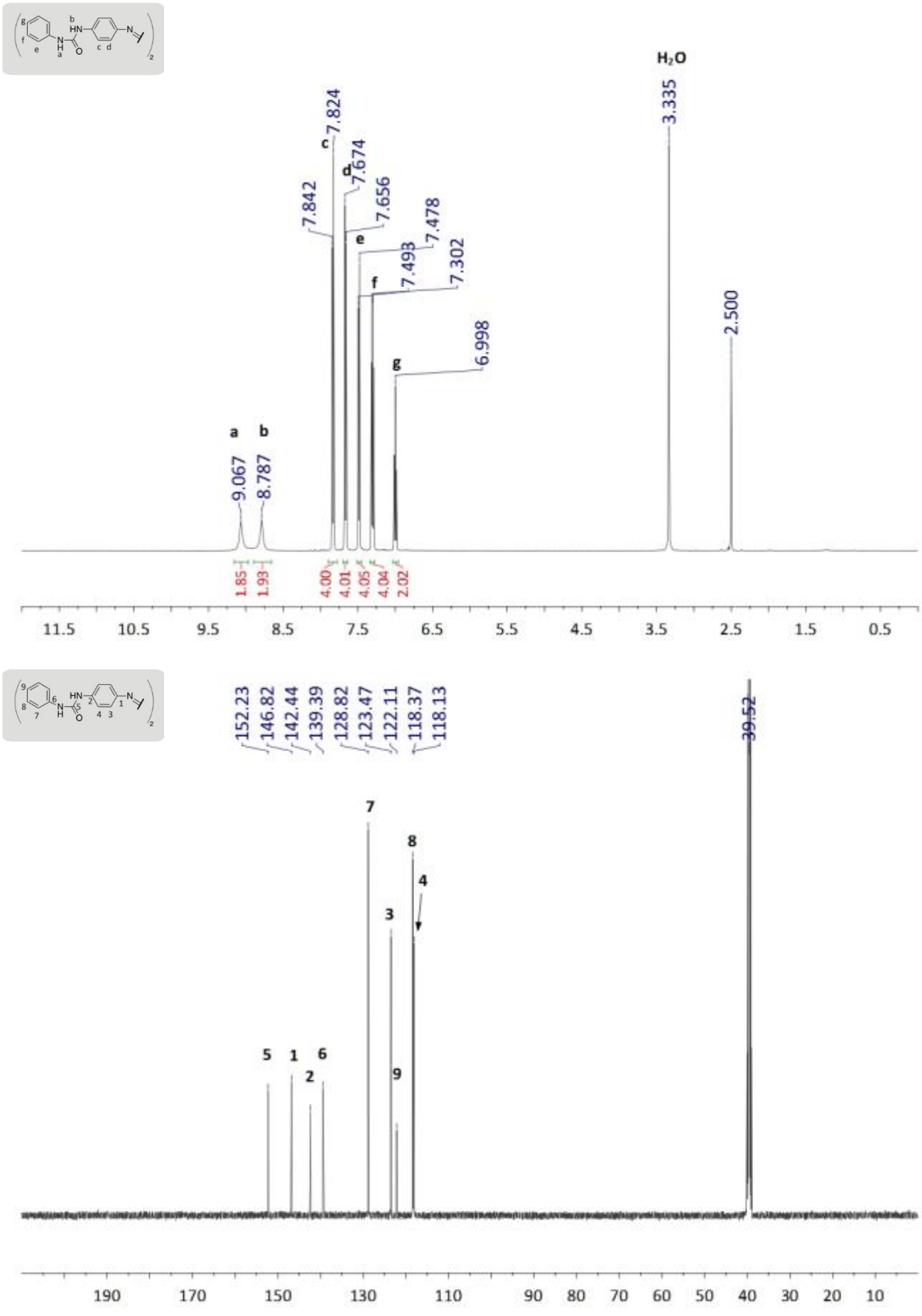
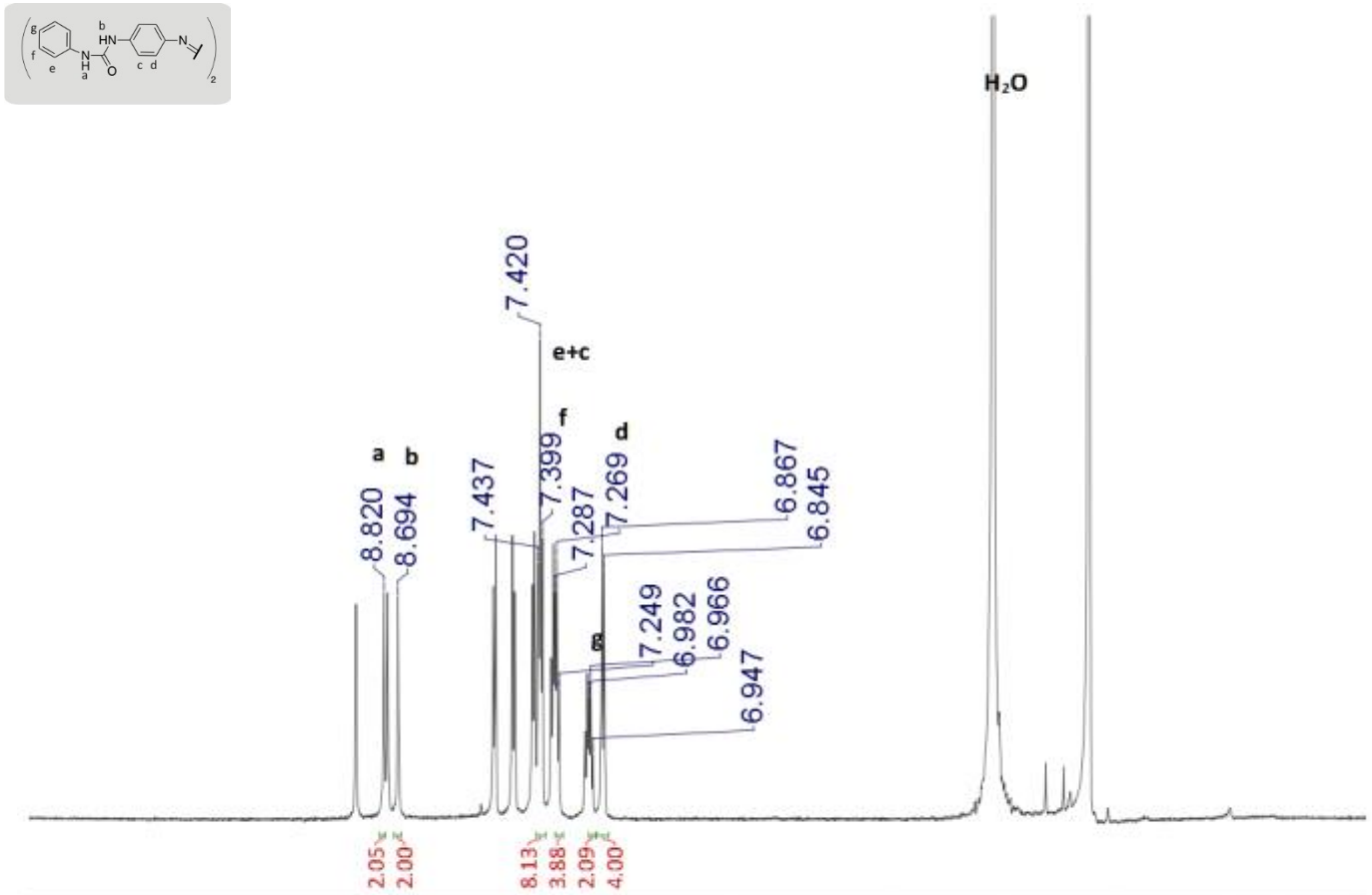



**Fig. S4** NMR spectra of compound *E*-**1b** in DMSO-*d6* (500MHz).



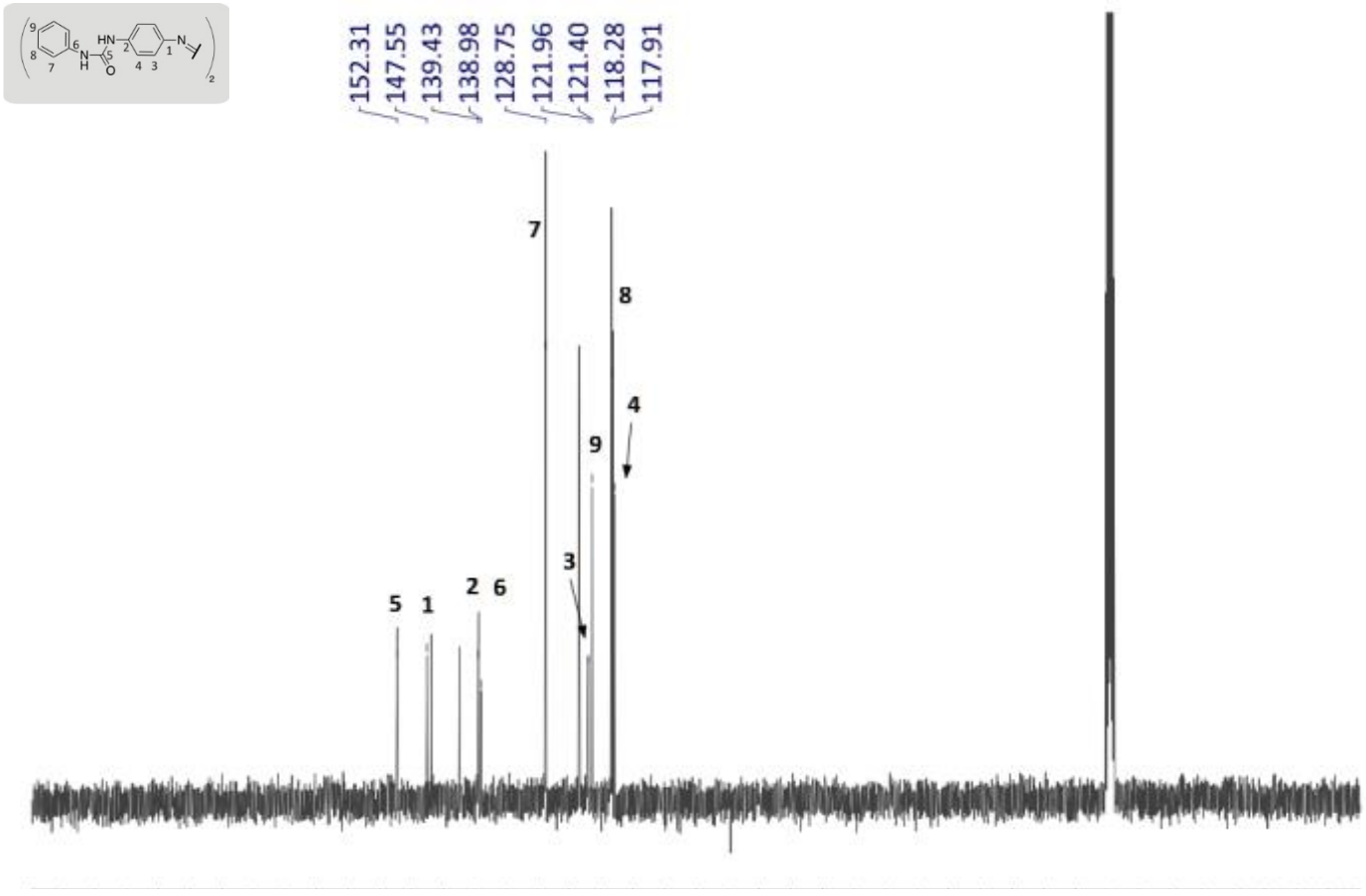




**Fig. S5** NMR spectra of a mixture of the *E*- and *Z*-**1b** in DMSO-$d_6$ (400MHz), only peak labels of *Z*-**1b** are shown.

# 2. Binding Studies

## 2.1 General remarks

Commercially available tetrabutylammonium salts were used as a source of anions. Prior to the use, salts were dried for 2 days under high vacuum at 60°C and kept in vacuum over solid tetraphosphorous decoxide ($P_4O_{10}$). HPLC grade water (purchased from Carl Roth GmbH) was added to the commercially available DMSO-$d_6$ of 99.80% isotopic purity (purchased from Euriso-Top, PN D010ES) to obtain the appropriate water concentration.

## 2.2 $^1$H NMR titration experiments

The DMSO solution of a receptor (ca. $10^{-2}$ M) was titrated in an NMR tube with the 0.1-0.2 M solution of a respective tetrabuthylammonium salt. The solution of the salt contained a certain amount of the receptor in order to keep receptor concentration constant during the titration; 16 to 19 data points were recorded, depending on the shape of the titration curve. However, it was important to choose such volumes of aliquots so that most of the data points could occur in close proximity of the inflection point of the respective titration curve. Such a procedure allows for more precise calculation of the binding constants. Moreover, we took into account the shift changes of all protons present in the receptor and guest molecules. In all cases DMSO-$d_6$ + 0.5% $H_2O$ was used as a solvent mixture. Titration of pure *E*-**1** was conducted in the amber NMR tube (Wilmad 527-PP-7, 5 mm diameter, limit 400 MHz) and titration of a mixture of *E*- and Z-**1** was conducted in the quartz NMR tube (Wilmad 535-PP-7QTZ, 5 mm diameter, limit 600 MHz). In the latter case photoisomerisation of *E*-**1** was carried out before anion was added. A nonlinear curve fitting for 1:1 or 1:2 binding model was carried out with the HypNMR 2008 Software[2,3] and allow the determination of global association constant.[4,5] Importantly, the data analysis for individual proton signals of the molecule reveal the same value of $K_a$ (in the experimental error), which suggests that the 1:2 (host:guest) model is correct. Additionally to acknowledge complexation stoichiometry, the Job experiments were also conducted.[6,7] Determination of association constants for Z-**1** was carried out using fixed values of association constant for *E*-**1** obtained during titration of pure E-**1** in darkness. Possible self-association for the host *E*-**1b** was excluded by additional dilution experiments (data not included), however, for the host *E*-**1a** weak dimerization was observed, which value ($K_{dimer.}$ 3.3 ± 1.6 $M^{-1}$) was included in the subsequent determination of the association constants $K_a$.

**Table S1.** The details of $^1$H NMR titration experiments for complexes of receptor **1** with TBA-benzoate[a]

| Host | $c_{Host}$ (M) | $c_{Guest}$ (M) | $K_{a,1}$ ($M^{-1}$) | $K_{a,2}$ ($M^{-1}$) | $\Delta\delta_{max}$ (ppm) | | | | |
|---|---|---|---|---|---|---|---|---|---|
| | | | | | NH▲ | NH■ | Ar▲ | Ar■ | Ar▲ |
| *E*-**1a** | 0.01197 | 0.21045 | 1287 ± 14 | - | 3.52 | 3.44 | -0.01 | 0.27 | 0.26 |
| *Z*-**1a** | 0.01197[b] | 0.21045 | 1127 ± 11 | - | 3.53 | 3.38 | -0.01 | -[c] | -[c] |
| *E*-**1b** | 0.01079 | 0.13922 | 989 ± 90 | 341 ± 29 | 3.45 | 3.40 | -0.04 | 0.28 | 0.26 |
| *Z*-**1b** | 0.01337[b] | 0.27825 | 231 ± 7 | - | 3.65 | 3.51 | -[d] | 0.29 | -[d] |

[a] Titration conducted in DMSO-$d_6$ + 0.5% $H_2O$ at 298 K; [b] the total host concentration is given for a mixture of *E*- and *Z*-**1**; [c] overlapping of the $^1$H signals upon titration precludes determination of the $\delta_{max}$.

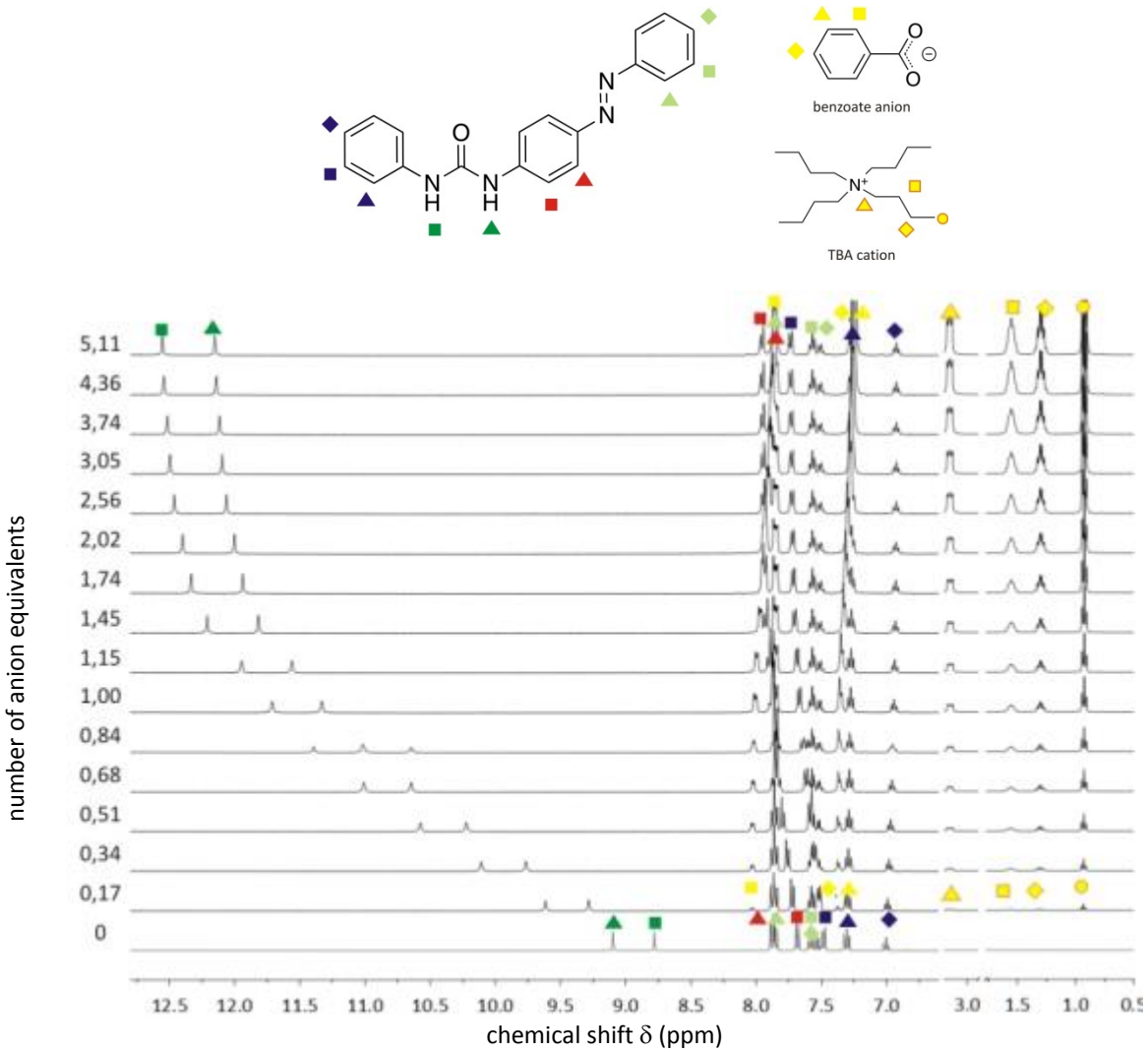



**Fig. S6** 1H NMR spectra of *E*-**1a** with increasing amount of TBA-$PhCO_2$

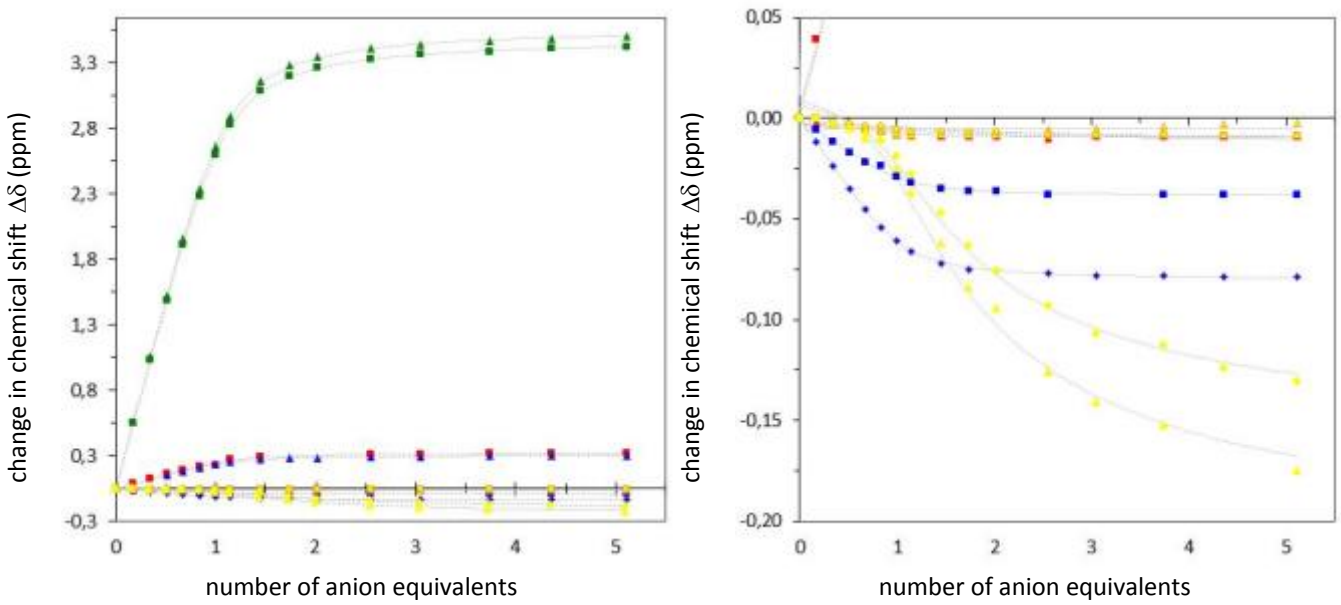



**Fig. S7** Changes in chemical shifts and calculated binding isotherms for titration of *E*-**1a** + TBA- $PhCO_2$, magnification of the plot in the range of the small chemical shift changes (right).

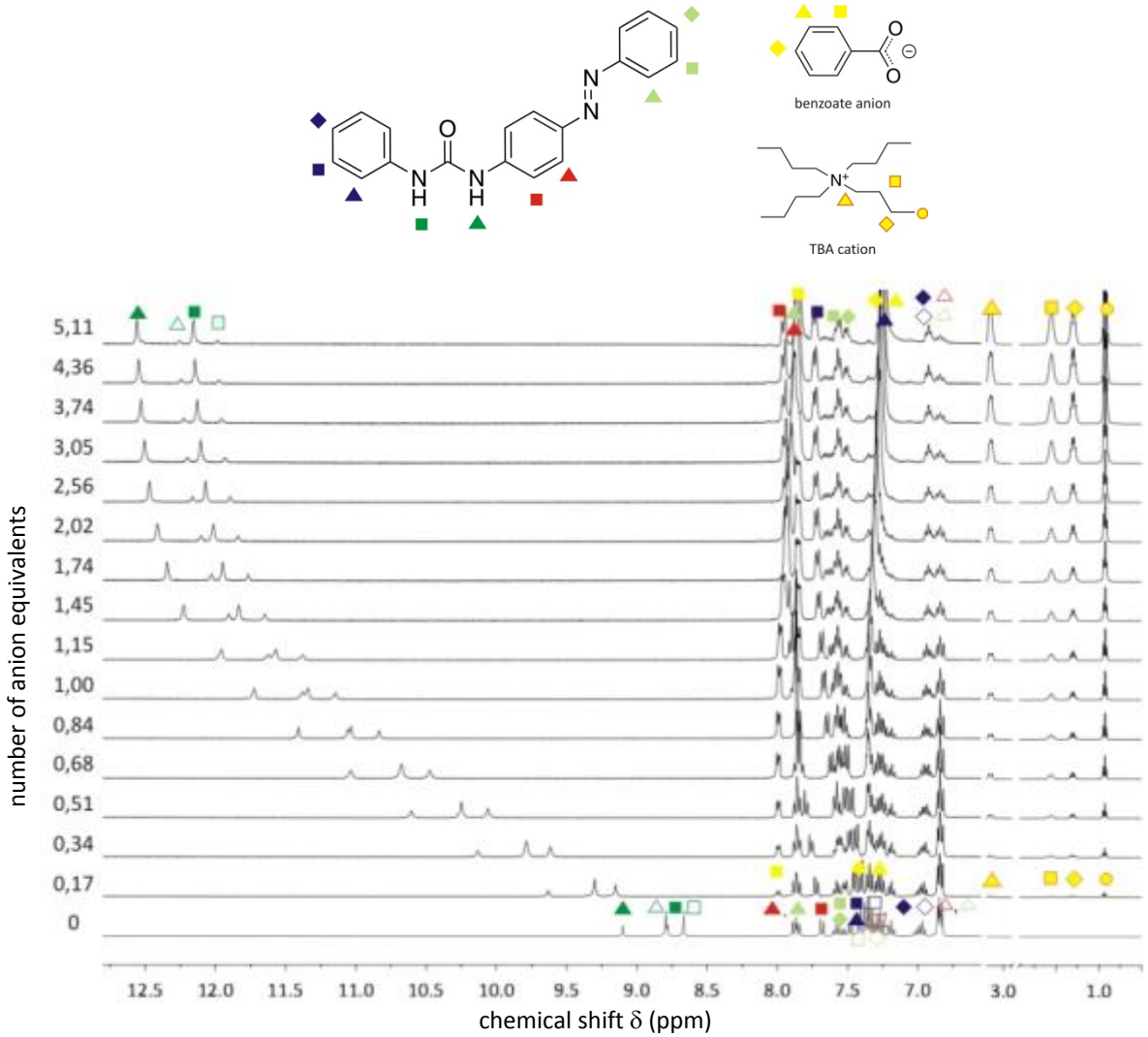



**Fig. S8** 1H NMR spectra of *EZ*-**1a** with increasing amount of TBA- $PhCO_2$

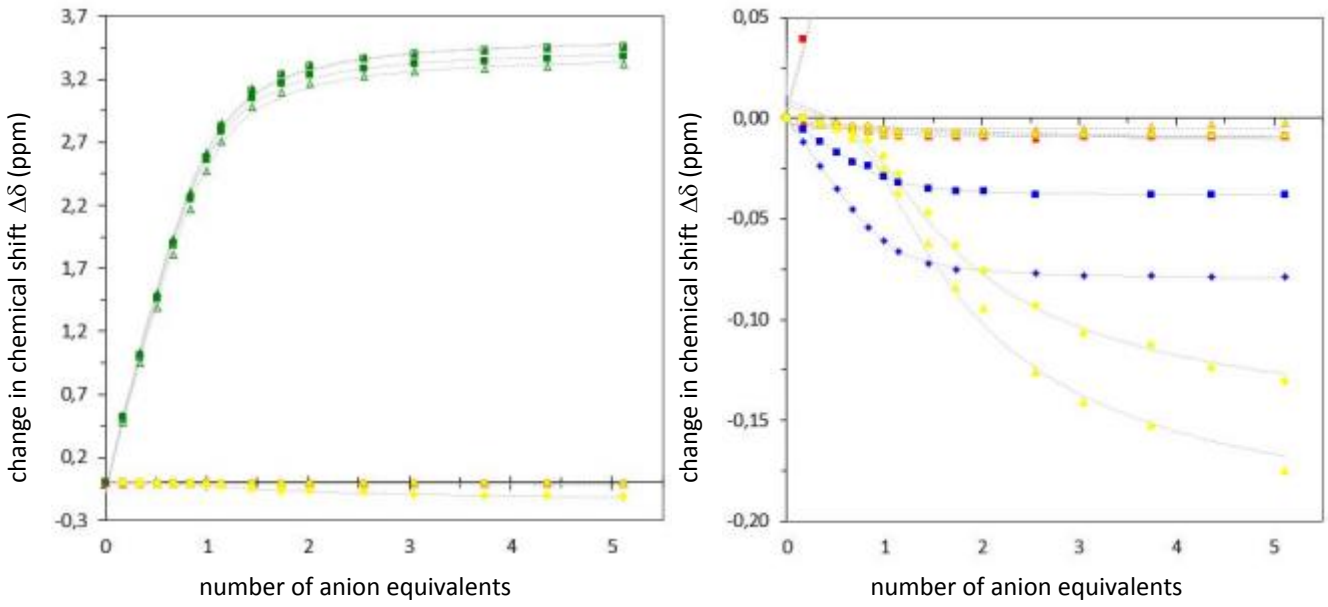



**Fig. S9** Changes in chemical shifts and calculated binding isotherms for titration of *EZ*-**1a** + TBA- $PhCO_2$, magnification of the plot in the range of the small chemical shift changes (right).

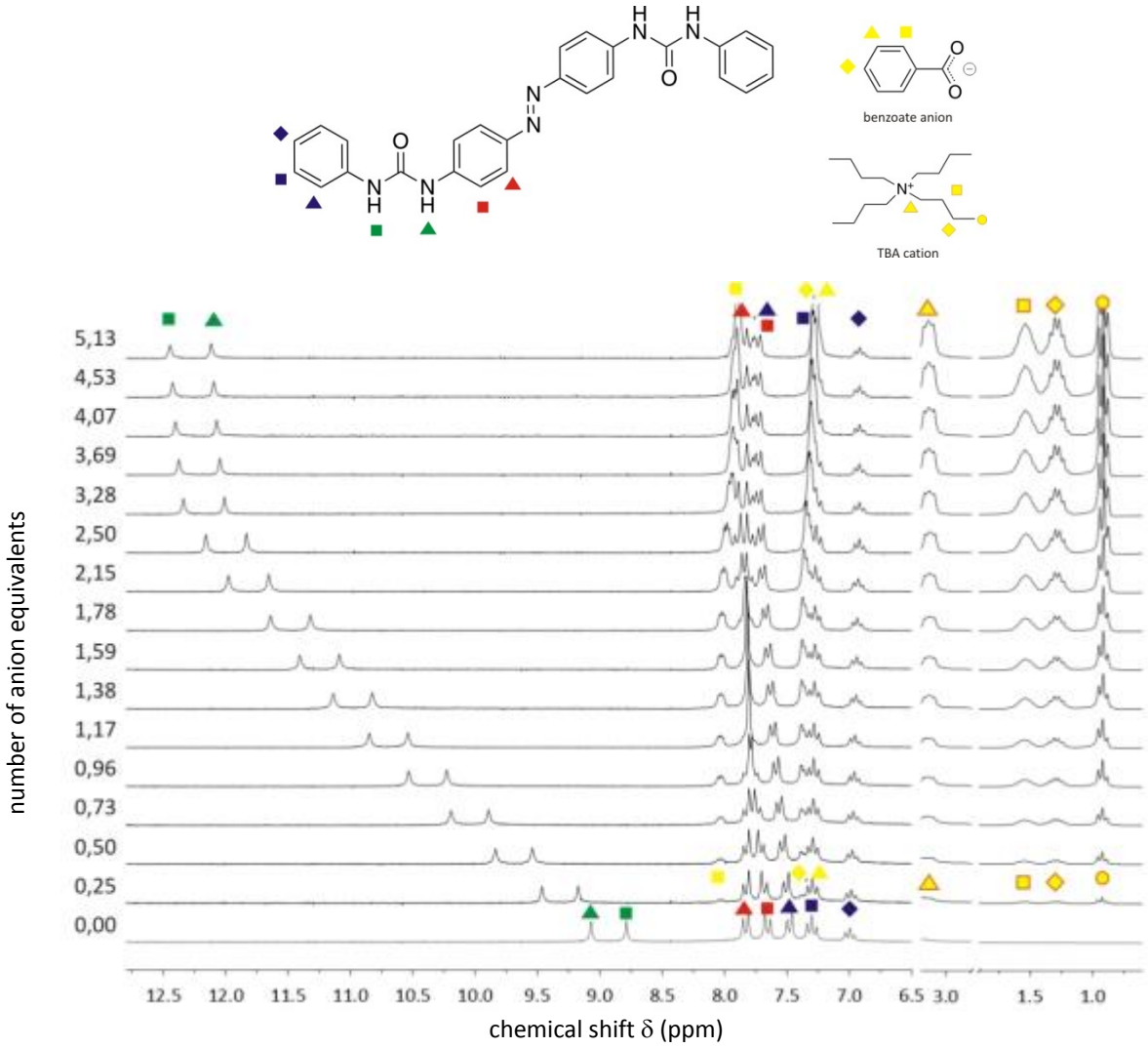



**Fig. S10** 1H NMR spectra of *E*-**1b** with increasing amount of TBA-$PhCO_2$

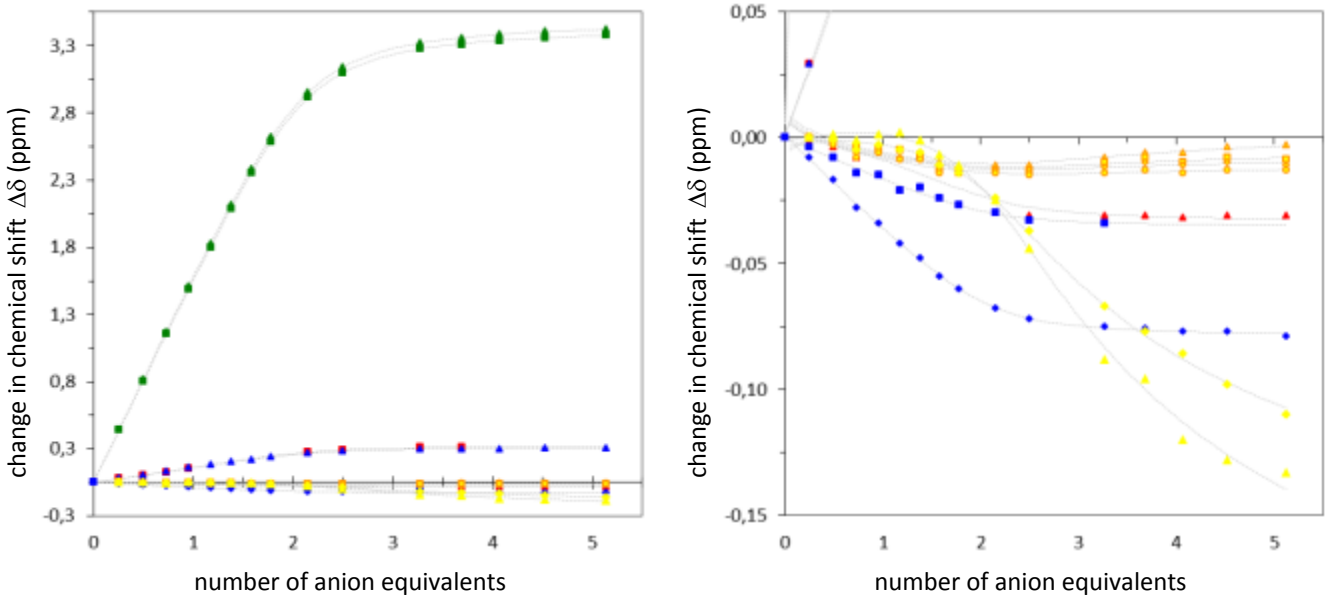



**Fig. S11** Changes in chemical shifts and calculated binding isotherms for titration of *E*-**1b** + TBA- $PhCO_2$, magnification of the plot in the range of the small chemical shift changes (right).

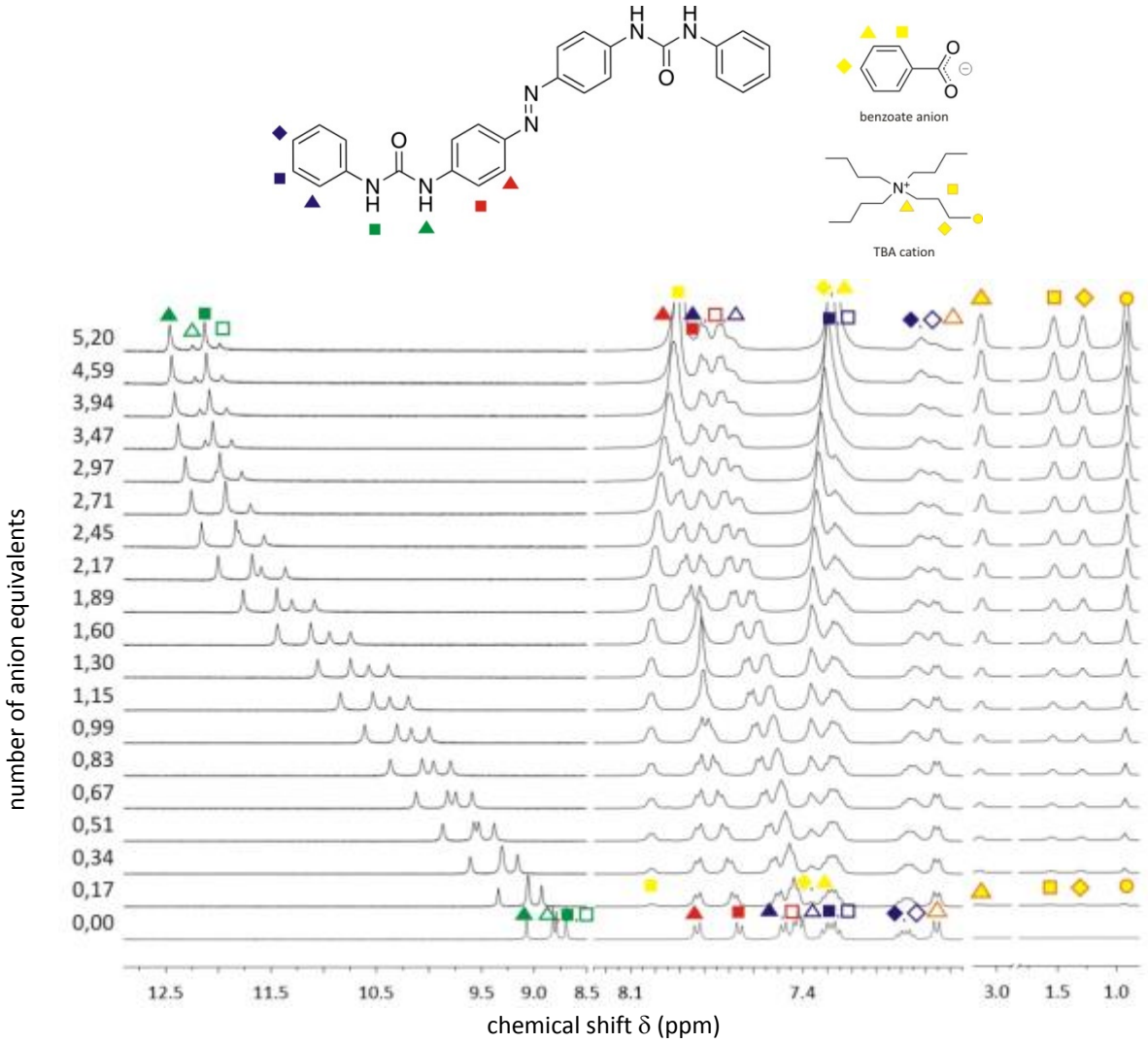



**Fig. S12** 1H NMR spectra of *EZ*-**1b** with increasing amount of TBA- $PhCO_2$

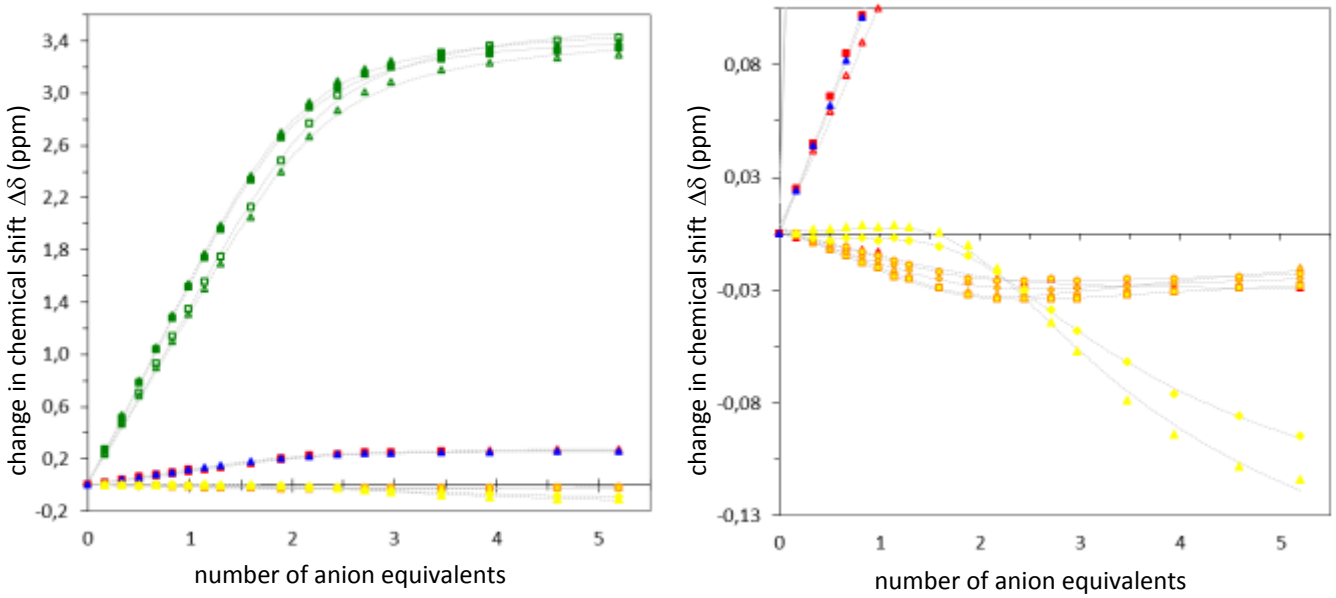



**Fig. S13** Changes in chemical shifts and calculated binding isotherms for titration of *EZ*-**1b** + TBA- $PhCO_2$, magnification of the plot in the range of the small chemical shift changes (right).

## 2.3 $^1$H NMR Job plot experiments

0.40 mL of the $2 \cdot 10^{-2}$ M receptor solution was titrated in the NMR tubes with 50µl aliquots of the equimolar solution of the respective tetrabutylammonium salt, to the point of 1:1 receptor:anion ratio. Similarly, the anion solution was titrated with the receptor solution. Approximately 16-17 data points were recorded to obtain respective Job plots.

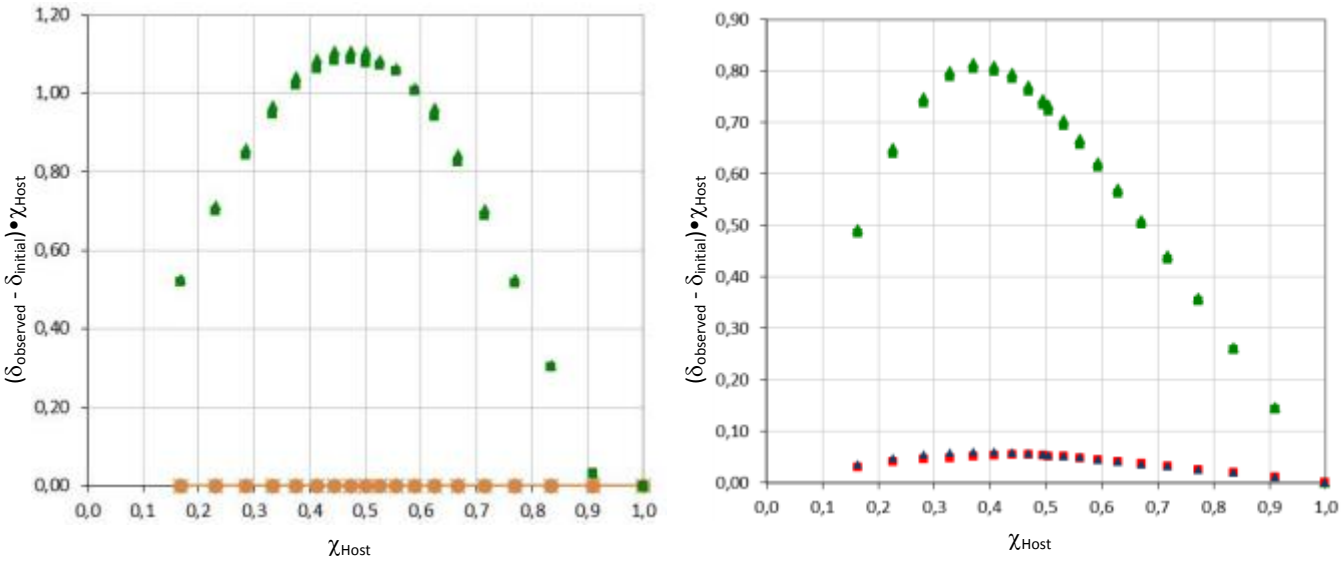



**Fig. S14** Job Plots for hosts *E*-**1a** (left) and *E*-**1b** (right) upon decreasing molar fraction of TBA-BzO.

## 2.4 DFT Calculations

All calculations were performed in the gas-phase and DMSO (employing implicit SM8 solvation model)[8] using Spartan'10 Parallel for Windows software package.[9] Commonly used exchange-correlation functional B3LYP[10] with proved to be reasonably-well in calculations of many neutral azobenzene derivatives[11] due to the lack of the dispersion component is inadequate to properly describe the hydrogen bonds and London dispersion forces associated with anion binding. Therefore, in order to improve the accuracy of calculations while remaining within acceptable computational cost, we used the density functional theory (DFT) method with long-range dispersion corrected hybrid functional ωb97x-d,[12,13] combined with the 6-31+G* basis set.[14] This functional proved to be robust and accurate in describing noncovalent supramolecular complexes.[15-20] Initial accuracy test for ωb97x-d, B3LYP, and EDF2[20,21] functionals in comparison to available X-ray structures of the *E*- and *Z*-isomers of an azobenzene (AB) clearly demonstrate that ωb97x-d functional gave results very similar to X-ray data (at least for *E*-AB), whereas B3LYP and EDF2 functionals slightly overestimate the bond distance between azo nitrogen atoms (Table S2). Nevertheless, contrary to X-ray data all studied functionals predicted shorter distance of the azo linkage for *Z*-AB than for *E*-AB. Disruption of the system π-electron conjugation in the *Z* isomer should increase the double bond character of the N=N bond and observed elongation of this bond in the solid state could be attributed to crystal packing forces.

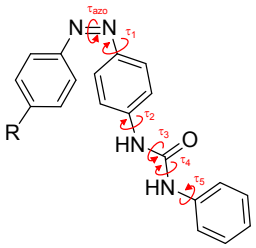
Analysis of the values of the HOMO-LUMO gap (associated with absorption frequency of the n-π* transition) in Table S2 demonstrate that ωb97x-d functional is unable to correctly predict these properties (although graphical representation of MOs and trend of their energies changes upon anion binding are correct, see section 2.5). Moreover, subsequent attemps to calculate transient spectra for a more complex molecules (e.g. hosts *E*-**1**) do not converge (in a reasonable time). Therefore, we decided to carry out additional calculations at the DFT/EDF2/6-31G* level of theory which successfully predict these properties for comparable minimum energy geometries (B3LYP gave comparable results, however, the parameterized EDF2 functional is significantly faster in calculations of transient spectra).

**Tab. S2** Accuracy test for various DFT functionals in comparison with X-ray structures for azobenzene (AB)[a]

| No. | Compound | Level of theory | $\Delta E_{Z,E}$ (kJ·mol$^{-1}$) | $d_{N=N}$ (Å) | $<_{dih,C-N=N-C}$ (°) | μ (D) | HOMO-LUMO gap (eV) |
|---|---|---|---|---|---|---|---|
| 1 | *E*-AB [b] | n.a. | n.a. | 1.247(2) | 180.0(2) | n.a. | n.a. |
| 2 | *Z*-AB [c] | | | 1.253(4) | 53.0(3) | | |
| 3 | *E*-AB | ωb97x-d/6-31G* | 50.4 | 1.249 | -180.0 | 0.00 | -7.8 |
| 4 | *Z*-AB | | | 1.242 | -6.4 | 3.37 | -7.9 |
| 5 | *E*-AB | ωb97x-d/6-31+G* | 52.3 | 1.246 | -180.0 | 0.00 | -7.7 |
| 6 | *Z*-AB | | | 1.242 | -6.2 | 3.50 | -7.8 |
| 7 | *E*-AB | EDF2/6-31G* | 63.8 | 1.257 | 180.0 | 0.00 | -3.6 |
| 8 | *Z*-AB | | | 1.246 | -10.4 | 3.24 | -3.5 |
| 9 | *E*-AB | EDF2/6-31+G* | 66.0 | 1.255 | 180.0 | 0.00 | -3.6 |
| 10 | *Z*-AB | | | 1.246 | -9.9 | 3.41 | -3.4 |
| 11 | *E*-AB | B3LYP/6-31G* | 64.2 | 1.260 | 180.0 | 0.00 | -4.0 |
| 12 | *Z*-AB | | | 1.250 | -9.5 | 3.22 | -3.8 |
| 13 | *E*-AB | B3LYP/6-31+G* | 66.6 | 1.258 | 180.0 | 0.00 | -3.9 |
| 14 | *Z*-AB | | | 1.249 | -9.3 | 3.40 | -3.7 |

[a] All calculations were performed in the gas-phase, all values are given for the lowest energy structures, n.a. – not applicable; [b] X-ray structure, data from ref. [21,22]; [c] X-ray structure, data from ref. [23]

To find lowest-energy structures of both free receptors and their complexes with anions conformational analysis as implemented in Spartan was performed. Briefly, fast semi-empirical model PM6 was used to find 64 lowest-energy conformers of both *E*- and *Z*-isomers of the corresponding compound from the set of ~20000 conformers generated for the given torsion angles (Fig. S15).




| Torsion | Variance |
|---|---|
| $\tau_{azo}$ | 12 |
| $\tau_1$ | 8 |
| $\tau_2$ - $\tau_5$ | 2 |

**Fig S15** Torsions and variances of the torsion angles used to generate conformers (**1a**: R=H, **1b**: R=PhNHCONH)

Energies of the remaining conformers were corrected at the DFT/ωb97x-d/6-31G*/SM8-DMSO level of theory and duplicates and nearly identical rotamers were removed. The geometry of the 3-4 best conformers were then optimized without any restraints at the DFT/ωb97x-d/6-31+G*/SM8-DMSO level of theory (Tab. S3). The harmonic vibrational frequencies were calculated using DFT/EDF2/6-31G*/SM8-DMSO level of theory in order to confirm whether the obtained geometries corresponded to the true energetic minima (no imaginary frequencies). Initial trials demonstrate that BSSE error is relatively small (< 8 kJ•mol$^{-1}$), at least in the gas-phase, for all compound studied.

The calculations predicts that *Z*-**1a** isomer is higher in energy by 60 kJ/mol than *E*-**1a**, whereas for *Z*-**1b** vs *E*-**1b** the difference is slightly lower (58 kJ/mol). The binding energy $\Delta E_{bind.}$ between complexes of *E*-**1a** and *Z*-**1a** with a benzoate anion is predicted to be similar; however, for *Z*-**1b** host it is much lower than for *E*-**1b**. Both isomers of **1a** as well as *E*-**1b** bind the benzoate anion with two strong hydrogen bonds derived from the urea groups and two weaker C-H···π bonds orginating from the aromatic substituents. In the case of *Z*-**1b**, the anion is bound exclusively by the four adjacent urea protons in the cavity formed between the benzene rings. However, the interaction energy for the structure where the benzoate anion is bound outside the cavity is only slightly smaller, which indicates the high deformation energy of the latter conformation.

Nonetheless, in constrast to free hosts **1**, complexes of *Z*-**1** with benzoate exhibit a reduced dipole moment compared with the corresponding *E* isomers. As has been mentioned above, ωb97x-d functional failed to predict reliable energies for MOs, however, trend in changes of their energies is similar to that predicted by EDF2 functional, i.e. anion binding raise the energy of the n and π MOs, and decrease the energy of π* MOs. As a consequence, the corresponding n-π* and π-π* bands are blue and red shifted, respectively, however, this effect is more pronounced for host **1a** than for **1b** (Tab. S4).

**Tab. S3** Energy difference between *Z* and *E* isomer, geometrical data, dipole moments, and interaction energy ($\Delta E_{int.}$) for structures of hosts **1** and their benzoate complexes calculated at different DFT level of theory[a]

| No. | Compound | $\Delta E_{Z,E}$ (kJ·mol$^{-1}$) | $d_{N=N}$ (Å) | $<_{dih,C-N=N-C}$ (°) | $d_{urea\text{-}centroids}$ (Å) | μ (D) | $\Delta E_{int.}$ (kJ·mol$^{-1}$) |
|---|---|---|---|---|---|---|---|
| Level of theory: ωb97x-d/6-31+G*/SM8-DMSO | | | | | | | |
| 1 | *E*-**1a** | 59.8 | 1.250 | -179.79 | n.a. | 5.91 | n.a. |
| 2 | *Z*-**1a** | | 1.245 | -7.76 | | 7.20 | |
| 3 | *E*-**1a**⊃$PhCO_2^-$ | 72.8 | 1.254 | -179.75 | n.a. | 8.76 | -105 |
| 4 | *Z*-**1a**⊃$PhCO_2^-$ | | 1.247 | -8.22 | | 7.66 | -106 |
| 5 | *E*-**1b** | 58.5 | 1.250 | -179.64 | 13.97 | 1.62 | n.a. |
| 6 | *Z*-**1b** | | 1.243 | -8.22 | 7.78 | 8.34 | |
| 7 | *E*-**1b**⊃$PhCO_2^-$ | 54.3 | 1.252 | -179.57 | 13.74 | 27.67 | -96 |
| 8 | *Z*-**1b**⊃$PhCO_2^-$ [b] | | 1.250 | -3.56 | 7.62 | 10.09 | -100 |
| 9 | *Z*-**1b**⊃$PhCO_2^-$ [c] | 59.5 | 1.246 | -6.83 | 7.58 | 7.88 | -95 |
| Level of theory: EDF2/6-31G*/SM8-DMSO | | | | | | | |
| 10 | *E*-**1a** | 72.9 | 1.266 | 179.94 | n.a. | 6.61 | n.a. |
| 11 | *Z*-**1a** | | 1.256 | -11.91 | | 10.08 | |
| 12 | *E*-**1a**⊃$PhCO_2^-$ | 72.8 | 1.266 | -179.90 | n.a. | 7.09 | -104 |
| 13 | *Z*-**1a**⊃$PhCO_2^-$ | | 1.257 | -11.83 | | 7.36 | -104 |
| 14 | *E*-**1b** | 75.7 | 1.268 | -179.77 | 13.70 | 11.12 | n.a. |
| 15 | *Z*-**1b** | | 1.259 | -13.72 | 11.22 | 13.50 | |
| 16 | *E*-**1b**⊃$PhCO_2^-$ | 109.6 | 1.269 | 179.54 | 13.94 | 26.62 | -103 |
| 17 | *Z*-**1b**⊃$PhCO_2^-$ [b] | | 1.261 | -6.96 | 7.86 | 9.97 | -70 |
| 18 | *Z*-**1b**⊃$PhCO_2^-$ [c] | 77.8 | 1.260 | 13.79 | 11.17 | 19.97 | -101 |

[a] Values for energy minimized structures in the SM8 DMSO solvent model, $d_{urea}$ reflects the distance between centroids of the two adjacent urea groups, n.a. – not applicable; [b] anion bound by both urea group; [c] anion bound exclusively by one urea group

**Tab. S4** Energy levels of the MOs orbitals calculated at DFT/EDF2/6-31G*/SM8-DMSO level of theory.

| No. | Compound | Molecular orbital (eV) | | | Transition | | | |
|---|---|---|---|---|---|---|---|---|
| | | n | π | π* | n-π*(eV) | n-π* (nm) | π-π* (eV) | π-π* (nm) |
| 1 | *E*-**1a** | -6.12 | -5.38 | -2.38 | 3.74 | 332 | 3.00 | 413 |
| 2 | *E*-**1a**⊃$PhCO_2^-$ | -6.00 | -5.17 | -2.28 | 3.72 | 333 | 2.89 | 429 |
| 3 | *Z*-**1a** | -5.31 | -5.75 | -2.22 | 3.09 | 401 | 3.53 | 351 |
| 4 | *Z*-**1a**⊃$PhCO_2^-$ | -5.58 | -5.13 | -2.13 | 3.45 | 359 | 3.00 | 413 |
| 5 | *E*-**1b** | -6.02 | -5.12 | -2.25 | 3.77 | 329 | 2.87 | 432 |
| 6 | *E*-**1b**⊃$PhCO_2^-$ | -5.93 | -4.97 | -2.15 | 3.78 | 328 | 2.82 | 440 |
| 7 | *Z*-**1b** | -6.33 | -5.01 | -2.19 | 4.14 | 300 | 2.82 | 440 |
| 8 | *Z*-**1b**⊃$PhCO_2^-$ [a] | -6.26 | -4.89 | -2.10 | 4.16 | 298 | 2.79 | 444 |
| 9 | *Z*-**1b**⊃$PhCO_2^-$ [b] | -6.44 | -4.99 | -2.02 | 4.42 | 280 | 2.97 | 418 |

[a] anion bound exclusively by one urea group; [b] anion bound by both urea group.

## 2.5 Visualization of the DFT calculated structures

The location of $\pi$, n, and $\pi^*$ orbitals, for both *E* and *Z* isomers, were supported by the mapping of the corresponding molecular orbital (MO) onto molecule electronic density ($p$ = 0.001 au). However, in several cases the exact position of the n MO of the corresponding *Z*-isomer could not be unambiguously distinguished due to mixing with other basic orbital from phenylurea and/or benzoate moieties.

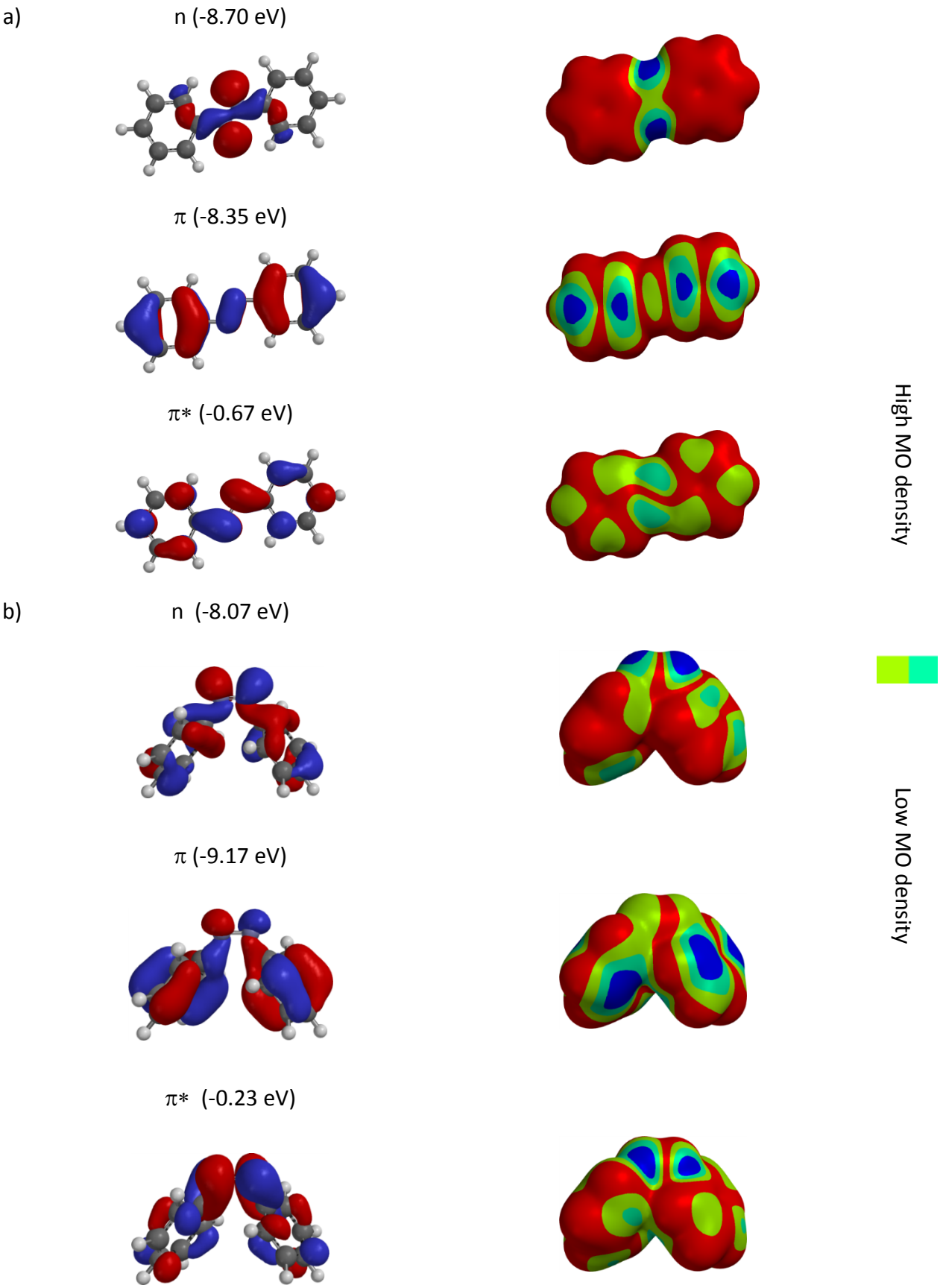



**Fig. S16** Representation of the HOMOs (n, π) and LUMO (π*) orbitals of the *E*- (a) and *Z*-isomer (b) of the parent AB calculated at the DFT/ωb97x-d/6-31+G* level of theory, the energy of the corresponding MO is given in parentheses.

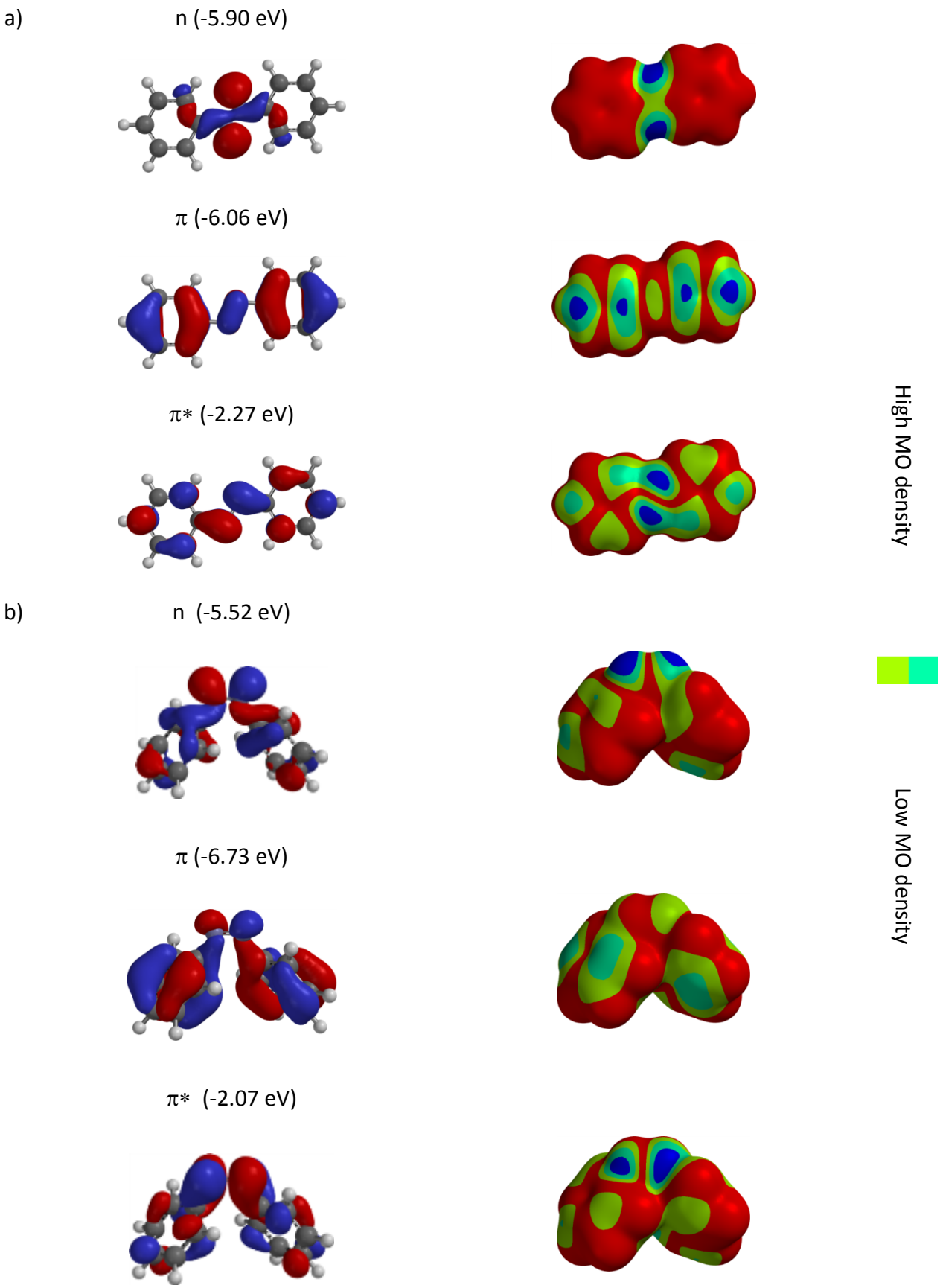



**Fig. S17** Representation of the HOMOs (n, π) and LUMO (π*) orbitals of the *E*- (a) and *Z*-isomer (b) of the parent AB calculated at the DFT/EDF2/6-31G*level of theory, the energy of the corresponding MO is given in parentheses.

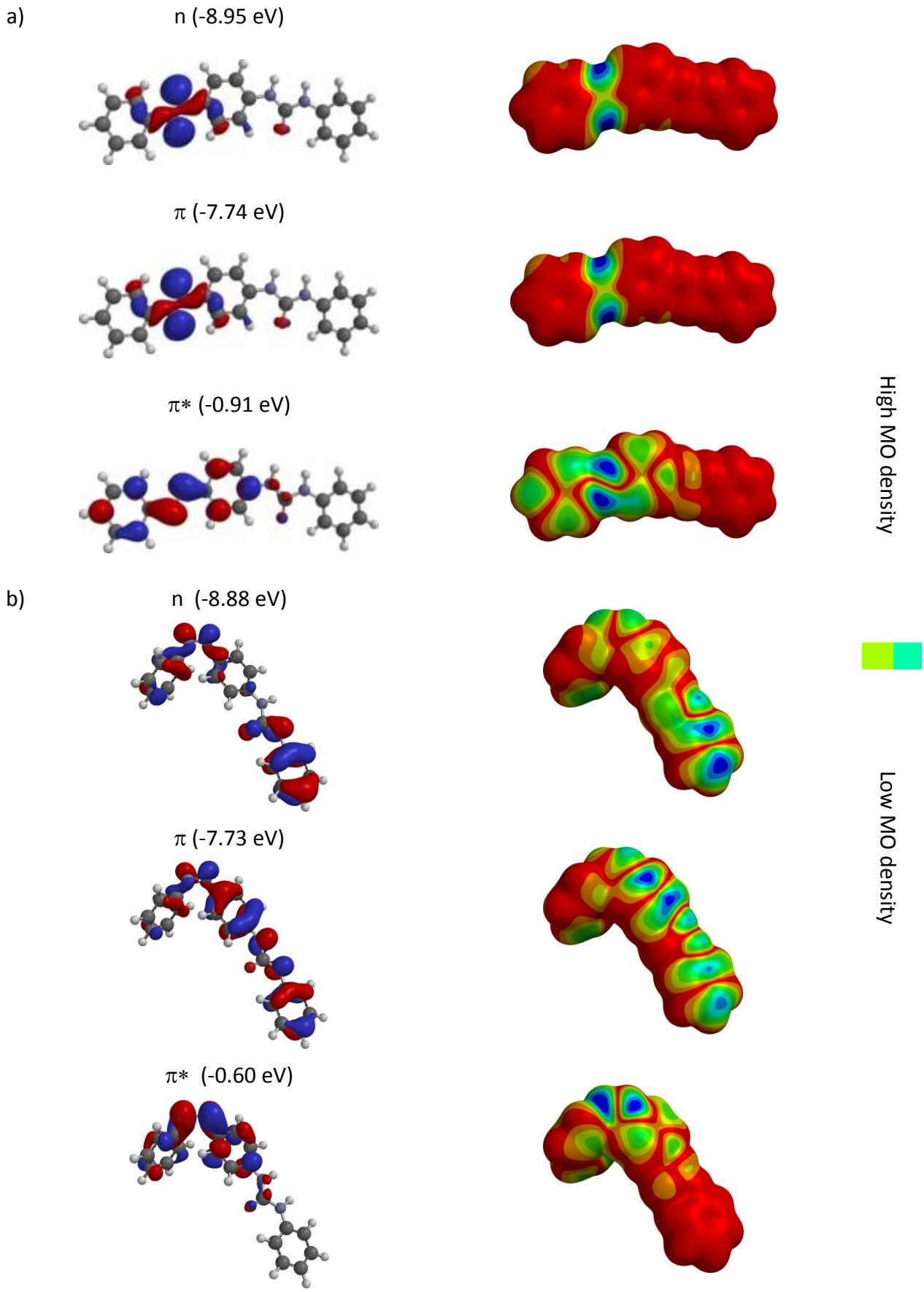



**Fig. S18** Representation of the HOMOs (n, π) and LUMO (π*) orbitals of the *E*- (a) and *Z*-isomer (b) of the host **1a** calculated at the DFT/ωb97x-d/6-31+G*/SM8-DMSO level of theory, the energy of the corresponding MO is given in parentheses.

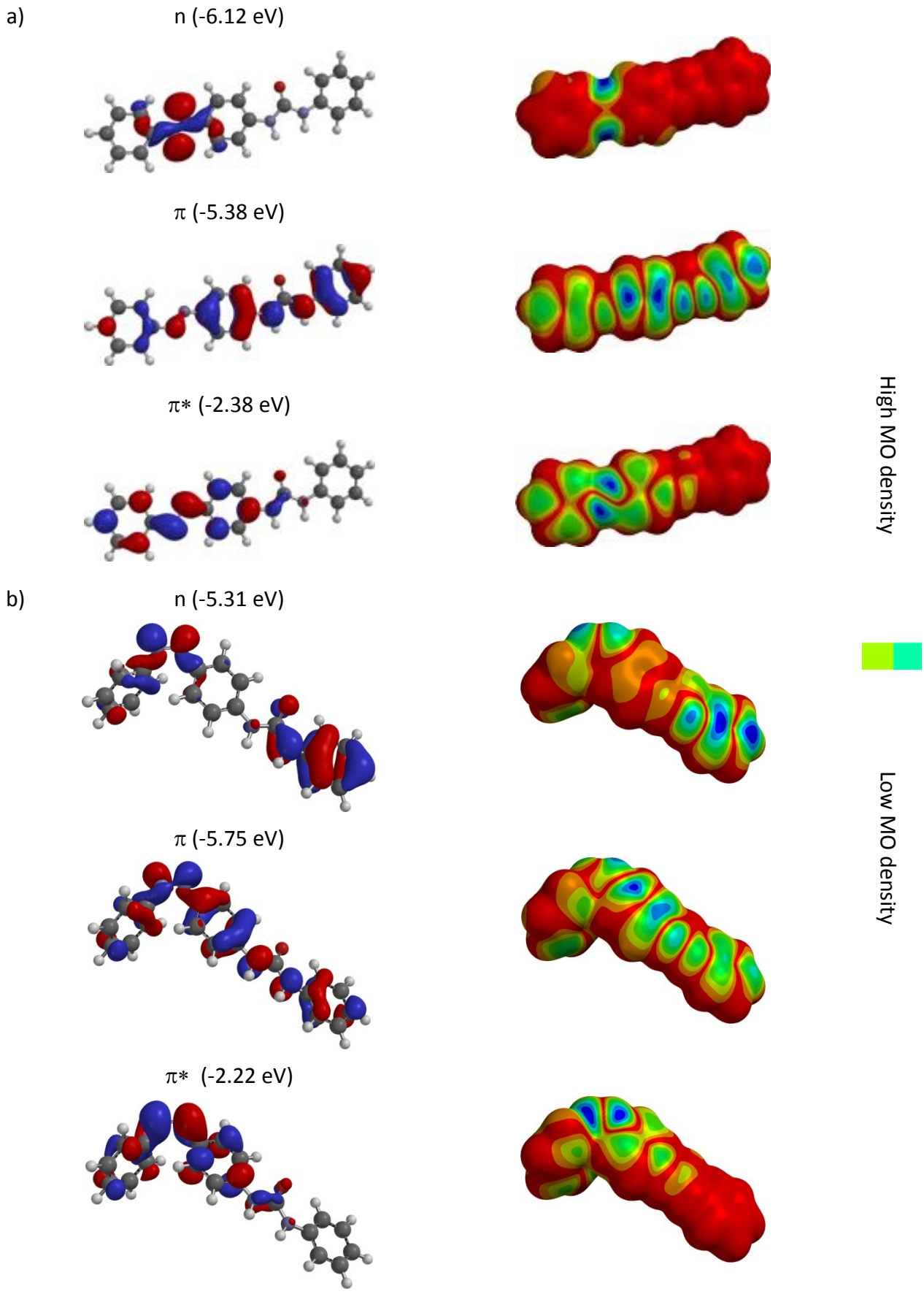



**Fig. S19** Representation of the HOMOs (n, π) and LUMO (π*) orbitals of the *E*- (a) and *Z*-isomer (b) of the host **1a** calculated at the DFT/EDF2/6-31G*/SM8-DMSO level of theory, the energy of the corresponding MO is given in parentheses.

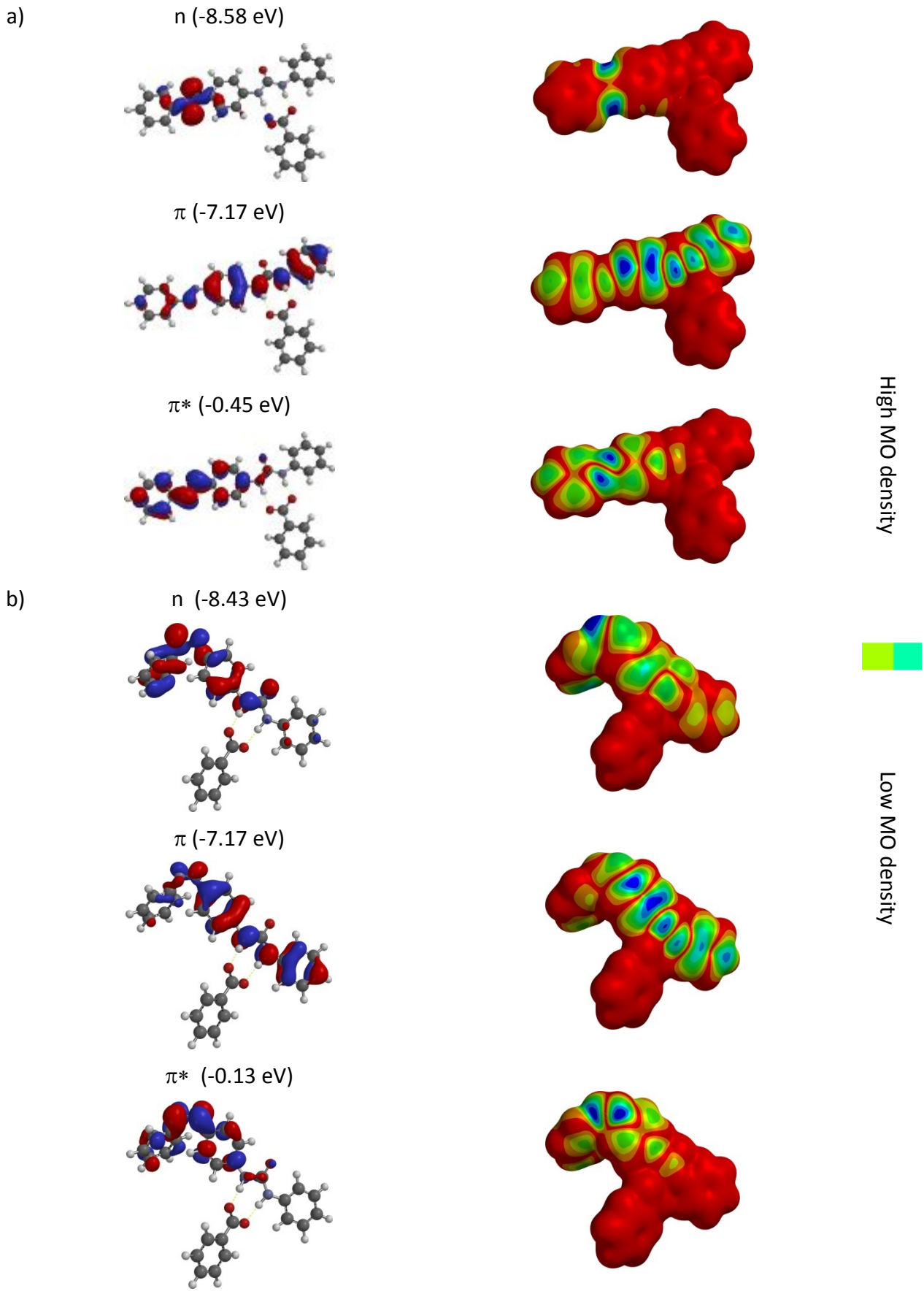



**Fig. S20** Representation of the HOMOs (n, π) and LUMO (π*) orbitals of the *E*- (a) and *Z*-isomer (b) of the benzoate complex of the host **1a** calculated at the DFT/ωb97x-d/6-31+G*/SM8-DMSO level of theory, the energy of the corresponding MO is given in parentheses.

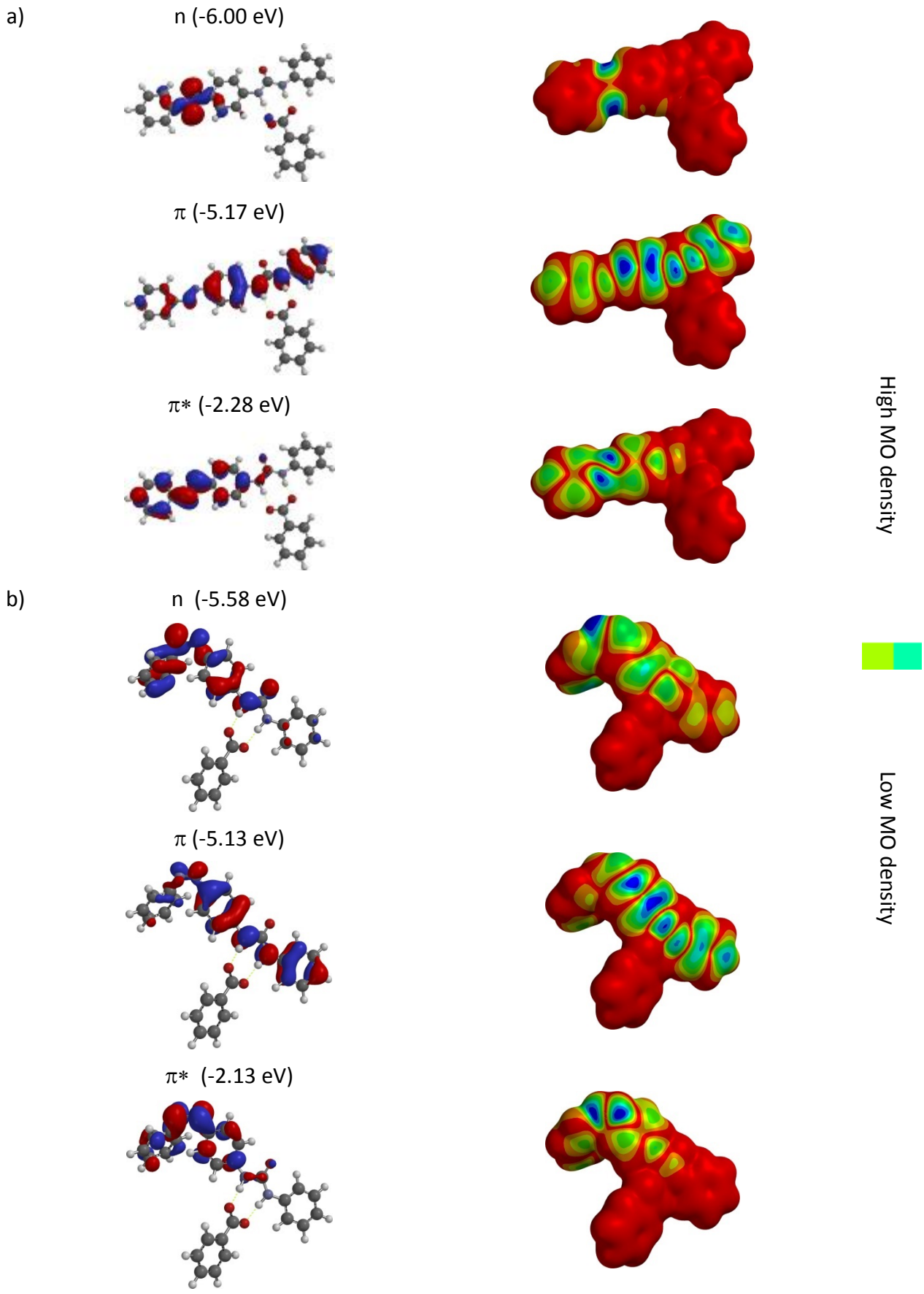



**Fig. S21** Representation of the HOMOs (n, π) and LUMO (π*) orbitals of the *E*- (a) and *Z*-isomer (b) of the benzoate complex of the host **1a** calculated at the DFT/EDF2/6-31G*/SM8-DMSO level of theory, the energy of the corresponding MO is given in parentheses.

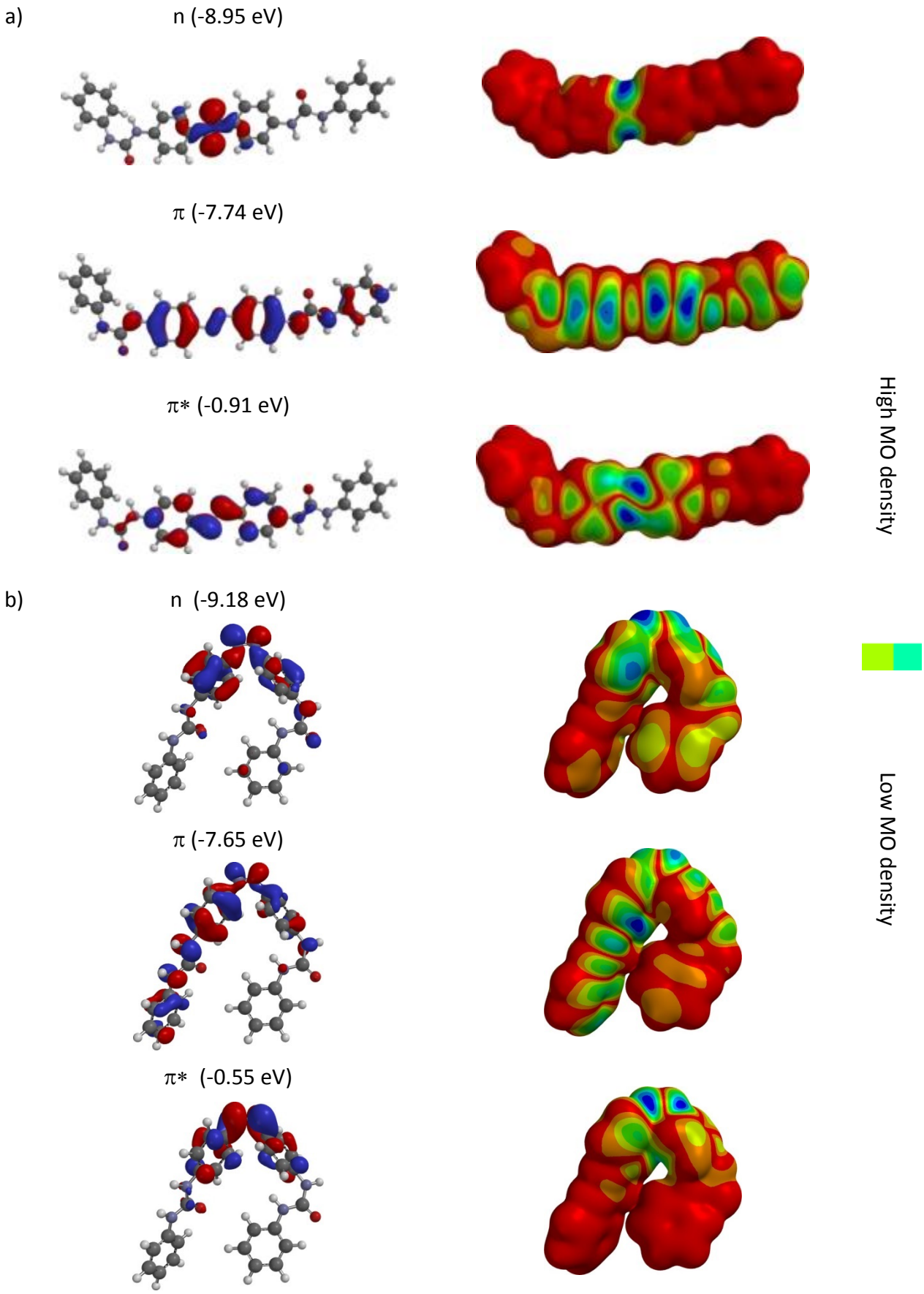



**Fig. S22** Representation of the HOMOs (n, π) and LUMO (π*) orbitals of the *E*- (a) and *Z*-isomer (b) of the host **1b** calculated at the DFT/ωb97x-d/6-31+G*/SM8-DMSO level of theory, the energy of the corresponding MO is given in parentheses.

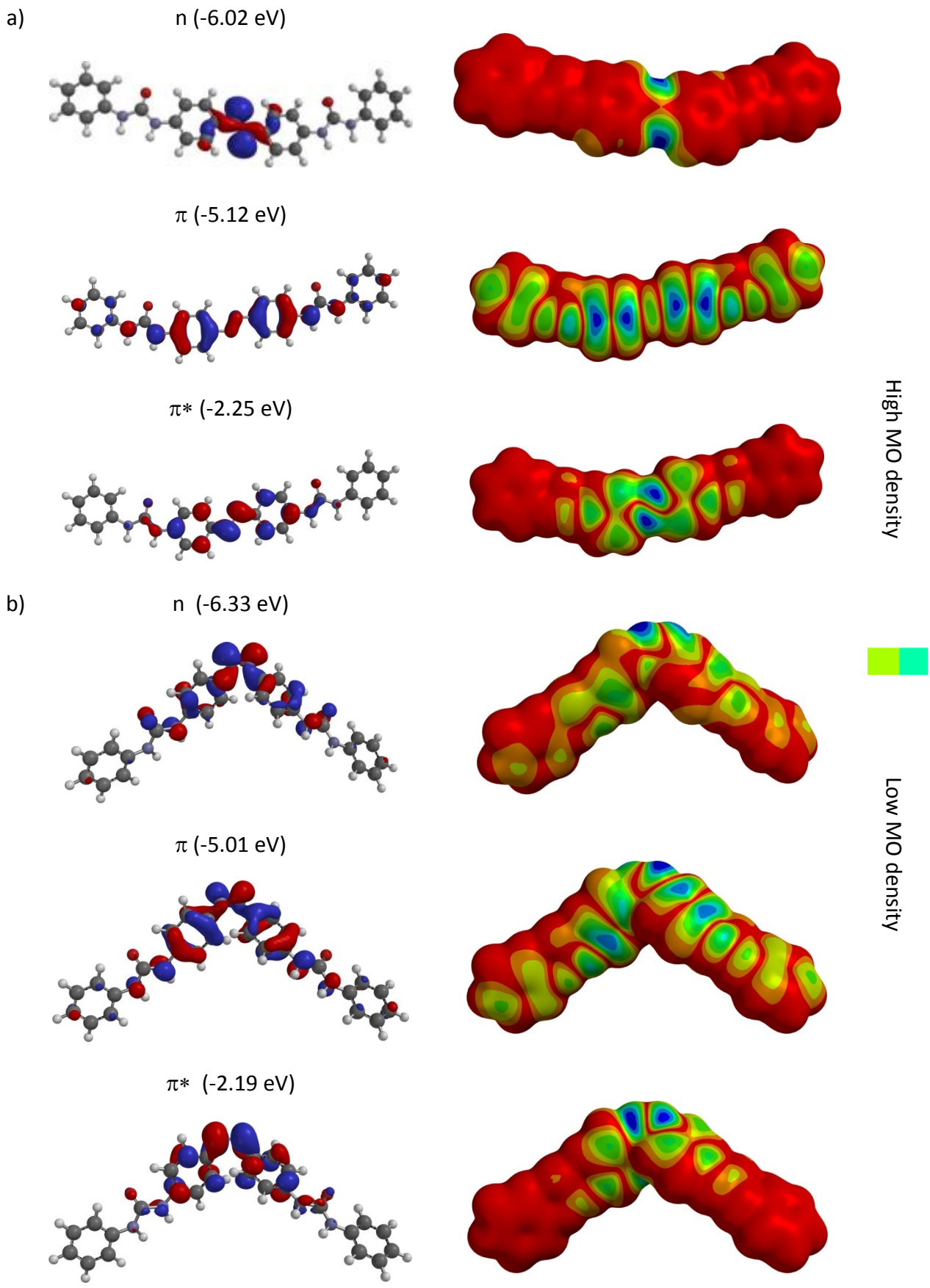



**Fig. S23** Representation of the HOMOs (n, π) and LUMO (π*) orbitals of the *E*- (a) and *Z*-isomer (b) of the host **1b** calculated at the DFT/EDF2/6-31G*/SM8-DMSO level of theory, the energy of the corresponding MO is given in parentheses.

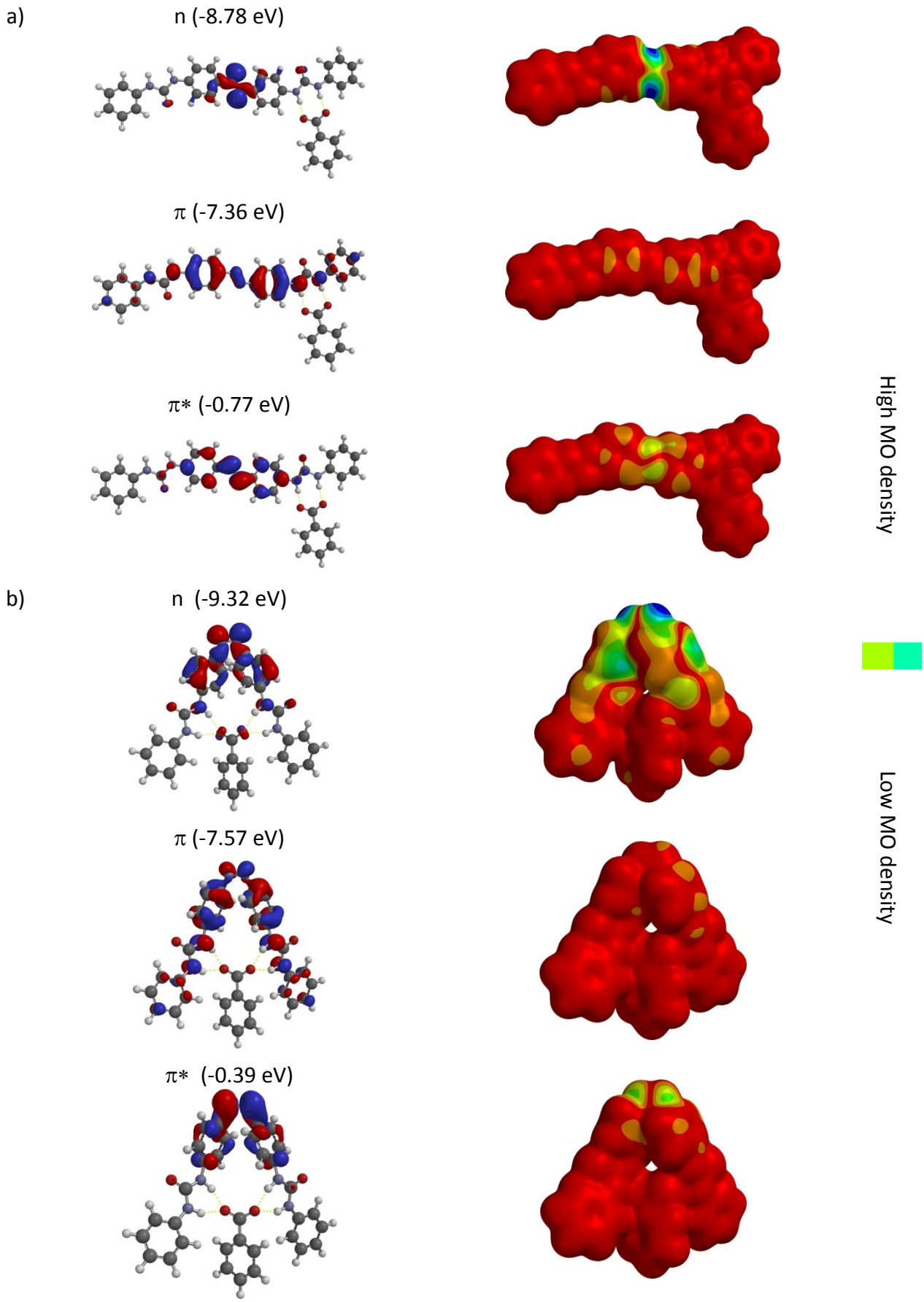



**Fig. S24** Representation of the HOMOs (n, π) and LUMO (π*) orbitals of the *E*- (a) and *Z*-isomer (b) of the benzoate complex of the host **1b** calculated at the DFT/ωb97x-d/6-31+G*/SM8-DMSO level of theory, the energy of the corresponding MO is given in parentheses.

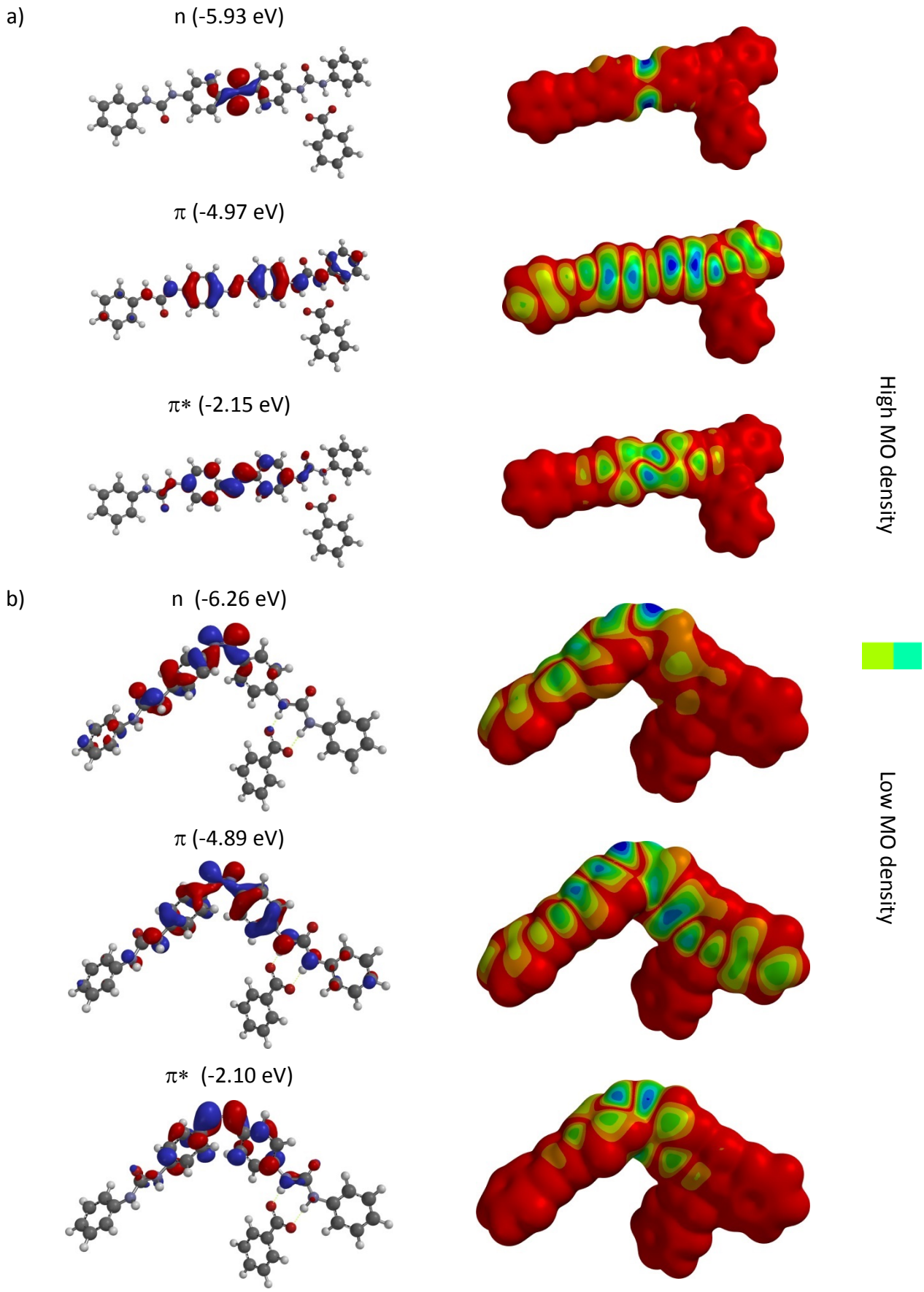



**Fig. S25** Representation of the HOMOs (n, π) and LUMO (π*) orbitals of the *E*- (a) and *Z*-isomer (b) of the benzoate complex of the host **1b** calculated at the DFT/EDF2/6-31G*/SM8-DMSO level of theory, the energy of the corresponding MO is given in parentheses.

## 2.6 Determination of the first-order rate constant $\kappa_{obs.}$ using UV-Vis spectroscopy

The rate of thermal *Z*→*E* isomerization of receptors *Z*-**1** were calculated by monitoring the absorption change of *Z* and *E* isomers in darkness at 298.0±0.1 K. The observed first-order rate $\kappa_{obs.}$ is an average of the $\kappa$ determined by Marquard non-linear technique[24] at four different wavelengths as implemented in Cary WinUV Software 5.0.0.999. In all cases, practically linear Arrhenius and Eyring plots indicate that during *Z*→*E* isomerization only one mechanism occurs (Fig. S26 and Tab. S4).

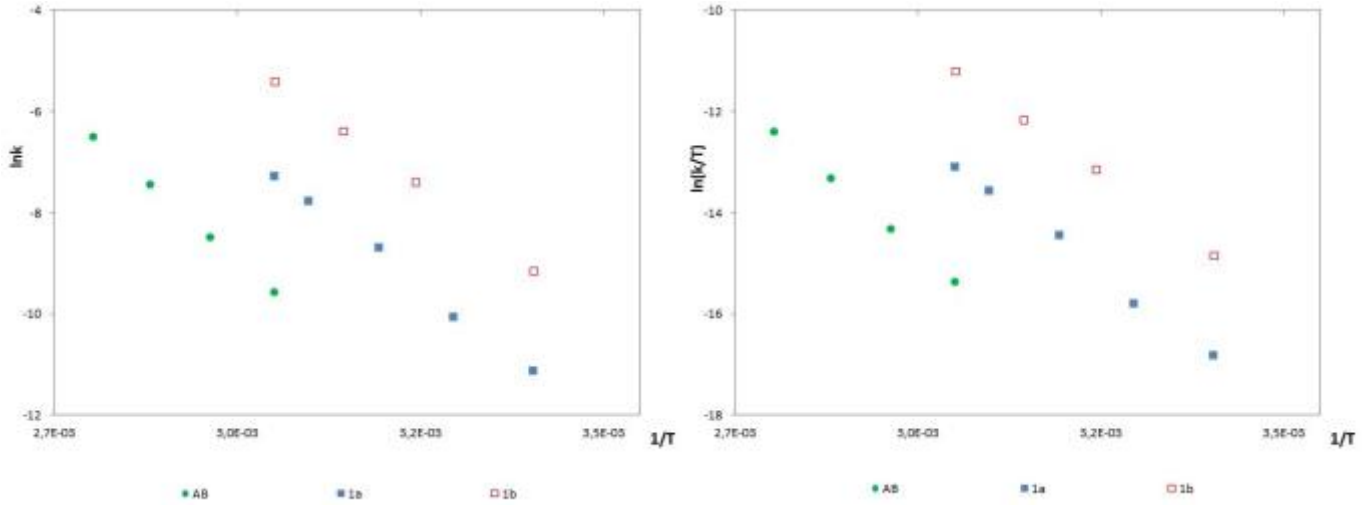



**Fig. S26** Arrhenius (left) and van't Hoff (right) plots of the thermal *Z*-**1**→*E*-**1** isomerization.

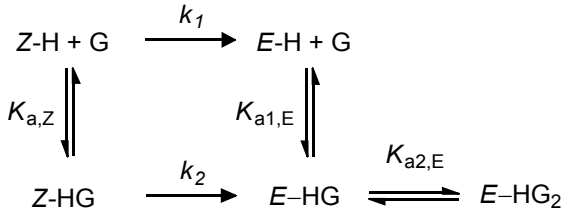
**Tab. S4** Results of the fitting the experimental data for *Z*-AB and *Z*-**1**[a]

| Host | Guest | Y=Ax+B (Arrhenius plot) | | | Y=Ax+B (van't Hoff plot) | | | $\Delta E_a$ | $\Delta H^{\ddagger}$ | $T\Delta S^{\ddagger}$ | $\Delta G^{\ddagger}$ |
|---|---|---|---|---|---|---|---|---|---|---|---|
| | | A | B | $R^2$ | A | B | $R^2$ | | | | |
| AB | none | -12342.17±58.59 | 27.48±0.17 | 1.000 | -11994.53±60.19 | 20.63±0.17 | 1.000 | 103 | 100 | -7.8 | 107 |
| **1a** | none | -11062.84±25,95 | 366.16±1.16 | 0.997 | -10747.71±19.19 | 366.62±1.16 | 0.997 | 92.0±3.0 | 89.4±3.0 | -11.3±0.7 | 100.7±3.7 |
| **1b** | none | -10632.96±26.53 | 117.80±0.37 | 1.000 | -10318.42±19.78 | 120.90±0.38 | 1.000 | 88.4±1.0 | 85.8±1.0 | -9.9±0.2 | 95.7±1.2 |

[a] values for $E_a$, $\Delta H^{\ddagger}$, $T\Delta S^{\ddagger}$, and $\Delta G^{\ddagger}$ are given in kJ·mol$^{-1}$.

## 2.7 Procedure for the determination of association constant $K_{a,Z}$ and first-order rate constant $k_2$ from "*Z*→*E* thermal titration" experiment

Assuming that receptor having two binding pockets is able to bind two anions in one form (*E*-H) and one anion in another form (*Z*-H), and additionally that anion influences the irreversible transformation of *Z*-H into *E*-H, we can describe the solution equilibria as shown in Scheme S2.




**Scheme S2**. Equilibria describing anion complexation and *Z*→*E* isomerisation, H – host, G – guest.

We can express above relations using kinetic and thermodynamic eqn S1-5:

$$\frac{d([Z-HG])}{dt} = -k_2[Z-HG] \quad \text{(S1)}$$

$$\frac{d([Z-H])}{dt} = -k_1[Z-H] \quad \text{(S2)}$$

$$K_{a,Z} = \frac{[Z-HG]}{[Z-H][G]} \quad \text{(S3)}$$

$$K_{a,E} = \frac{[E-HG]}{[E-H][G]} \quad \text{(S4)}$$

$$K_{a2,E} = \frac{[E-HG_2]}{[E-HG][G]} \quad \text{(S5)}$$

Concentration of *Z*-H does not depend on the concentration of E-H and so equilibria described by eqn (S4) and eqn (S5) are irrelevant for the *Z*→*E* transformation. Therefore one can conclude that the observed kinetic rate constant describing *Z*→*E* isomerisation depends on three parameters, namely the association constant of the *Z*- isomer with guest ($K_{a,Z}$) and two first-order rate constants for free *Z*-H ($k_1$) and its saturated complex with the corresponding guest ($k_2$). When the total concentration of the guest is much larger than the concentration of the host ($[G]_0 >> [H]$), which is generally true for UV-Vis titration experiments, one can assume that $[G] \cong [G]_0$. Then, after inserting concentration of the HG complex from eqn (S3) to the eqn (S1) and adding eqn (S1) to the eqn (S2), we arrive at eqn (S6) which after simple rearrangements gave eqn (S7) and eqn (S8):

$$\frac{d([Z-HG])}{dt}\left(1+\frac{1}{K_{a,Z}[G]_0}\right) = -[Z-HG]\left(k_2+\frac{k_1}{K_{a,Z}[G]_0}\right) \quad \text{(S6)}$$

$$\frac{d([Z-HG])}{dt} = -[Z-HG]\left(\frac{k_1+k_2K_{a,Z}[G]_0}{1+K_{a,Z}[G]_0}\right) = -[Z-HG]\kappa_{obs.} \quad \text{(S7)}$$

$$\kappa_{obs.} \equiv f_H k_1 + f_{HG}k_1 = \frac{k_1(1+k_{enh.}K_{a,Z}[G]_0)}{1+K_{a,Z}[G]_0} \quad \text{(S8)}$$

Constant $\kappa_{obs.}$ depends only on initial guest concentration ($[G]_0$) and is determined by fitting of the experimental data to the first-order kinetics using the Marquard non-linear technique. Therefore, parameters of interest ($K_{a,Z}$ and $k_2$) could be determined using a nonlinear regression technique with experimentally determined rate constants ($\kappa_{obs.}$) for various amounts of guest added. During fitting we have noticed that in case when the absolute value of $k_2$ is very small (in comparison to other variables in eqn (S6) and eqn (S7)), it is better to use the enhancement of the rate constant $k_{enh.}$ ($k_2/k_1$) for achieving good fit with the experimental data (eqn (S8)). Finally, eqn (S7) after rearrangement of variables followed by integration could be transformed into eqn (S9) which express the concentration of Z-H at any time of the experiment.

$$[Z-HG]_t = [Z-HG]_0 e^{-\kappa_{obs.}t} \quad \text{(S9)}$$

Experimental data and results of fitting for the "*Z*→*E* thermal titration" of the mixture of *EZ*-**1** with TBA-benzoate are given in Tables S5 and S6, respectively.

**Tab. S5** Experimental data for titration of the *Z*-**1** with TBA-benzoate at 298.0±0.1 K

| Exp. | *Z*-**1a** | | *Z*-**1b** | |
|---|---|---|---|---|
| no. | $[G]_0$ | $\kappa_{obs.}$ | $[G]_0$ | $\kappa_{obs.}$ |
| 1 | 0,000E+00 | 1,467E-05 | 0,000E+00 | 1,314E-04 |
| 2 | 2,495E-04 | 2,466E-04 | 2,499E-04 | 2,255E-04 |
| 3 | 4,980E-04 | 3,862E-04 | 4,997E-04 | 3,018E-04 |
| 4 | 7,454E-04 | 4,786E-04 | 7,494E-04 | 3,747E-04 |

| | | | | |
|---|---|---|---|---|
| 5 | 9,919E-04 | 5,367E-04 | 1,248E-03 | 4,915E-04 |
| 6 | 1,237E-03 | 6,051E-04 | 1,747E-03 | 5,838E-04 |
| 7 | 1,725E-03 | 6,957E-04 | 2,742E-03 | 7,275E-04 |
| 8 | 1,968E-03 | 6,868E-04 | 3,736E-03 | 8,360E-04 |
| 9 | - | - | 4,727E-03 | 9,250E-04 |
| 10 | - | - | 6,211E-03 | 1,020E-03 |
| 11 | - | - | 7,690E-03 | 1,093E-03 |
| 12 | - | - | 9,655E-03 | 1,170E-03 |
| 13 | - | - | 1,161E-02 | 1,221E-03 |
| 14 | - | - | 1,405E-02 | 1,273E-03 |
| 15 | - | - | 1,647E-02 | 1,322E-03 |
| 16 | - | - | 1,936E-02 | 1,368E-03 |
| 17 | - | - | 2,224E-02 | 1,383E-03 |
| 18 | - | - | 2,699E-02 | 1,411E-03 |

**Tab. S6** Results of the fitting the experimental data for titration of the *Z*-**1** with TBA-benzoate

| Parameter | *Z*-**1a** | | *Z*-**1b** | |
|---|---|---|---|---|
| | Value | Error | Value | Error |
| $Chi^2$ | 1.9533E-10 | - | 5.5459E-11 | - |
| $R^2$ | 0.9970 | - | 0.9997 | - |
| $K_{a,Z}$ | 1342.46 | 97.16 | 249.53 | 3.48 |
| $k_{enh}$ | 64.60 | 1.69 | 12.21 | 0.05 |
| $k_1$ | 1,467E-05 | Fixed | 1,314E-04 | Fixed |

## 2.8 Cartesian coordinates of calculated DFT structures

### DFT/ωb97x-d/6-31G*

*E*-**AB** (E = -572.558882 au)

| | | | |
|---|---|---|---|
| N | 0.377439 | 0.497301 | 0.000068 |
| N | -0.377439 | -0.497301 | 0.000068 |
| C | 1.765280 | 0.184607 | 0.000037 |
| C | 4.520131 | -0.198065 | -0.000042 |
| C | 2.285375 | -1.114088 | -0.000204 |
| C | 2.622949 | 1.283630 | 0.000230 |
| C | 4.000725 | 1.092914 | 0.000198 |
| C | 3.660299 | -1.298120 | -0.000242 |
| H | 1.601728 | -1.955309 | -0.000360 |
| H | 2.188499 | 2.278177 | 0.000406 |
| H | 4.666721 | 1.950183 | 0.000351 |
| H | 4.068437 | -2.304373 | -0.000437 |
| H | 5.595129 | -0.351346 | -0.000078 |
| C | -1.765280 | -0.184607 | 0.000037 |
| C | -4.520131 | 0.198065 | -0.000042 |
| C | -2.285375 | 1.114088 | -0.000204 |
| C | -2.622949 | -1.283630 | 0.000230 |
| C | -4.000725 | -1.092914 | 0.000198 |
| C | -3.660299 | 1.298120 | -0.000242 |
| H | -1.601728 | 1.955309 | -0.000360 |
| H | -2.188499 | -2.278177 | 0.000406 |
| H | -4.666721 | -1.950183 | 0.000351 |
| H | -4.068437 | 2.304373 | -0.000437 |
| H | -5.595129 | 0.351346 | -0.000078 |

*Z*-**AB** (E = -572.539703 au)

| | | | |
|---|---|---|---|
| H | 0.381571 | 1.813677 | 0.045075 |
| C | 1.200568 | 1.111476 | 0.159529 |
| C | 3.308304 | -0.695563 | 0.436393 |
| C | 1.394944 | 0.104876 | -0.788040 |
| C | 2.064863 | 1.205212 | 1.244151 |
| C | 3.109736 | 0.296143 | 1.394102 |
| C | 2.468615 | -0.776378 | -0.668586 |
| H | 1.916885 | 1.990387 | 1.979349 |
| H | 3.775550 | 0.369339 | 2.248333 |
| H | 2.627041 | -1.521390 | -1.442251 |
| H | 4.129988 | -1.397454 | 0.540492 |
| N | 0.620780 | 0.016567 | -1.994643 |
| N | -0.620780 | -0.016567 | -1.994643 |
| C | -1.394944 | -0.104876 | -0.788040 |
| C | -3.109736 | -0.296143 | 1.394102 |
| C | -1.200568 | -1.111476 | 0.159529 |
| C | -2.468615 | 0.776378 | -0.668586 |
| C | -3.308304 | 0.695563 | 0.436393 |
| C | -2.064863 | -1.205212 | 1.244151 |
| H | -0.381571 | -1.813677 | 0.045075 |
| H | -2.627041 | 1.521390 | -1.442251 |
| H | -4.129988 | 1.397454 | 0.540492 |
| H | -1.916885 | -1.990387 | 1.979349 |
| H | -3.775550 | -0.369339 | 2.248333 |

### DFT/ωb97x-d/6-31+G*

*E*-**AB** (E = -572.575815 au)

| | | | |
|---|---|---|---|
| N | 0.379963 | 0.493752 | 0.000034 |
| N | -0.379963 | -0.493752 | 0.000034 |
| C | 1.768606 | 0.182169 | 0.000017 |
| C | 4.526683 | -0.198082 | -0.000023 |
| C | 2.289743 | -1.117370 | -0.000167 |
| C | 2.625604 | 1.283087 | 0.000173 |
| C | 4.005123 | 1.093334 | 0.000160 |
| C | 3.666543 | -1.299655 | -0.000186 |
| H | 1.611471 | -1.963446 | -0.000296 |
| H | 2.193543 | 2.279289 | 0.000310 |
| H | 4.670191 | 1.951784 | 0.000284 |
| H | 4.075516 | -2.305953 | -0.000336 |
| H | 5.602127 | -0.350561 | -0.000041 |
| C | -1.768606 | -0.182169 | 0.000017 |
| C | -4.526683 | 0.198082 | -0.000023 |
| C | -2.289743 | 1.117370 | -0.000167 |
| C | -2.625604 | -1.283087 | 0.000173 |
| C | -4.005123 | -1.093334 | 0.000160 |
| C | -3.666543 | 1.299655 | -0.000186 |
| H | -1.611471 | 1.963446 | -0.000296 |
| H | -2.193543 | -2.279289 | 0.000310 |
| H | -4.670191 | -1.951784 | 0.000284 |
| H | -4.075516 | 2.305953 | -0.000336 |
| H | -5.602127 | 0.350561 | -0.000041 |

*Z*-**AB** (E = -572.555898 au)

| | | | |
|---|---|---|---|
| H | 0.387260 | 1.833621 | 0.025536 |
| C | 1.199056 | 1.123751 | 0.147564 |
| C | 3.293218 | -0.698975 | 0.446805 |
| C | 1.392663 | 0.110528 | -0.793929 |
| C | 2.056136 | 1.214905 | 1.239762 |
| C | 3.093964 | 0.297590 | 1.401309 |
| C | 2.460485 | -0.777196 | -0.665440 |
| H | 1.908515 | 2.004327 | 1.970972 |
| H | 3.753783 | 0.368614 | 2.260824 |
| H | 2.621672 | -1.525814 | -1.435836 |
| H | 4.110157 | -1.405782 | 0.558598 |
| N | 0.620523 | 0.020162 | -2.002261 |
| N | -0.620523 | -0.020162 | -2.002261 |
| C | -1.392663 | -0.110528 | -0.793929 |
| C | -3.093964 | -0.297590 | 1.401309 |
| C | -1.199056 | -1.123751 | 0.147564 |
| C | -2.460485 | 0.777196 | -0.665440 |
| C | -3.293218 | 0.698975 | 0.446805 |
| C | -2.056136 | -1.214905 | 1.239762 |
| H | -0.387260 | -1.833621 | 0.025536 |
| H | -2.621672 | 1.525814 | -1.435836 |
| H | -4.110157 | 1.405782 | 0.558598 |
| H | -1.908515 | -2.004327 | 1.970972 |
| H | -3.753783 | -0.368614 | 2.260824 |

### DFT/EDF2/6-31G*

*E*-**AB** (E = -572.325223 au)

| | | | |
|---|---|---|---|
| N | 0.383054 | 0.498401 | -0.000015 |
| N | -0.383054 | -0.498401 | -0.000015 |
| C | 1.758859 | 0.188072 | -0.000011 |
| C | 4.516316 | -0.198004 | -0.000002 |
| C | 2.282055 | -1.111618 | 0.000027 |
| C | 2.622157 | 1.286078 | -0.000043 |
| C | 3.997974 | 1.093315 | -0.000040 |
| C | 3.654633 | -1.297170 | 0.000032 |
| H | 1.593432 | -1.947963 | 0.000053 |
| H | 2.186832 | 2.279632 | -0.000071 |
| H | 4.665213 | 1.949238 | -0.000066 |
| H | 4.062247 | -2.303453 | 0.000062 |
| H | 5.590836 | -0.351995 | 0.000001 |
| C | -1.758859 | -0.188072 | -0.000011 |
| C | -4.516316 | 0.198004 | -0.000002 |
| C | -2.282055 | 1.111618 | 0.000027 |
| C | -2.622157 | -1.286078 | -0.000043 |
| C | -3.997974 | -1.093315 | -0.000040 |
| C | -3.654633 | 1.297170 | 0.000032 |
| H | -1.593432 | 1.947963 | 0.000053 |
| H | -2.186832 | -2.279632 | -0.000071 |
| H | -4.665213 | -1.949238 | -0.000066 |
| H | -4.062247 | 2.303453 | 0.000062 |
| H | -5.590836 | 0.351995 | 0.000001 |

*Z*-**AB** (E = -572.300913 au)

| | | | |
|---|---|---|---|
| H | 0.396444 | 1.712916 | 0.192369 |
| C | 1.245560 | 1.041540 | 0.246773 |
| C | 3.445444 | -0.671090 | 0.356241 |
| C | 1.426660 | 0.066614 | -0.739762 |
| C | 2.168331 | 1.152819 | 1.278615 |
| C | 3.259456 | 0.289396 | 1.347654 |
| C | 2.549790 | -0.763125 | -0.700546 |
| H | 2.032405 | 1.918050 | 2.036405 |
| H | 3.971374 | 0.377100 | 2.161909 |
| H | 2.698310 | -1.475813 | -1.504958 |
| H | 4.303017 | -1.335233 | 0.394418 |
| N | 0.622852 | -0.016007 | -1.915214 |
| N | -0.622852 | 0.016007 | -1.915214 |
| C | -1.426660 | -0.066614 | -0.739762 |
| C | -3.259456 | -0.289396 | 1.347654 |
| C | -1.245560 | -1.041540 | 0.246773 |
| C | -2.549790 | 0.763125 | -0.700546 |
| C | -3.445444 | 0.671090 | 0.356241 |
| C | -2.168331 | -1.152819 | 1.278615 |
| H | -0.396444 | -1.712916 | 0.192369 |
| H | -2.698310 | 1.475813 | -1.504958 |
| H | -4.303017 | 1.335233 | 0.394418 |
| H | -2.032405 | -1.918050 | 2.036405 |
| H | -3.971374 | -0.377100 | 2.161909 |

### DFT/EDF2/6-31+G*

*E*-**AB** (E = -572.346555 au)

| | | | |
|---|---|---|---|
| N | 0.385714 | 0.494640 | -0.000018 |
| N | -0.385714 | -0.494640 | -0.000018 |
| C | 1.762893 | 0.185662 | -0.000012 |
| C | 4.524526 | -0.198077 | -0.000002 |
| C | 2.287490 | -1.114876 | 0.000046 |
| C | 2.625867 | 1.285592 | -0.000062 |
| C | 4.003717 | 1.093725 | -0.000059 |
| C | 3.662237 | -1.298753 | 0.000051 |
| H | 1.605182 | -1.956764 | 0.000088 |
| H | 2.194076 | 2.281271 | -0.000103 |
| H | 4.669856 | 1.950982 | -0.000100 |
| H | 4.070518 | -2.305154 | 0.000097 |
| H | 5.599507 | -0.351246 | 0.000003 |
| C | -1.762893 | -0.185662 | -0.000012 |
| C | -4.524526 | 0.198077 | -0.000002 |
| C | -2.287490 | 1.114876 | 0.000046 |
| C | -2.625867 | -1.285592 | -0.000062 |
| C | -4.003717 | -1.093725 | -0.000059 |
| C | -3.662237 | 1.298753 | 0.000051 |
| H | -1.605182 | 1.956764 | 0.000088 |
| H | -2.194076 | -2.281271 | -0.000103 |
| H | -4.669856 | -1.950982 | -0.000100 |
| H | -4.070518 | 2.305154 | 0.000097 |
| H | -5.599507 | 0.351246 | 0.000003 |

*Z*-**AB** (E = -572.321418 au)

| | | | |
|---|---|---|---|
| H | 0.396312 | 1.714210 | 0.195456 |
| C | 1.245047 | 1.041501 | 0.246866 |
| C | 3.447797 | -0.672243 | 0.354689 |
| C | 1.427986 | 0.068171 | -0.742019 |
| C | 2.166221 | 1.149096 | 1.282574 |
| C | 3.258981 | 0.284711 | 1.351079 |
| C | 2.553076 | -0.760351 | -0.705534 |
| H | 2.028477 | 1.912059 | 2.042840 |
| H | 3.969314 | 0.369503 | 2.167521 |
| H | 2.706742 | -1.469083 | -1.513233 |
| H | 4.306831 | -1.335203 | 0.390735 |
| N | 0.622718 | -0.014470 | -1.917069 |
| N | -0.622718 | 0.014470 | -1.917069 |
| C | -1.427986 | -0.068171 | -0.742019 |
| C | -3.258981 | -0.284711 | 1.351079 |
| C | -1.245047 | -1.041501 | 0.246866 |
| C | -2.553076 | 0.760351 | -0.705534 |
| C | -3.447797 | 0.672243 | 0.354689 |
| C | -2.166221 | -1.149096 | 1.282574 |
| H | -0.396312 | -1.714210 | 0.195456 |
| H | -2.706742 | 1.469083 | -1.513233 |
| H | -4.306831 | 1.335203 | 0.390735 |
| H | -2.028477 | -1.912059 | 2.042840 |
| H | -3.969314 | -0.369503 | 2.167521 |

### DFT/B3LYP/6-31G*

*E*-**AB** (E = -572.762035 au)

| | | | |
|---|---|---|---|
| N | 0.384399 | 0.499343 | -0.000058 |
| N | -0.384399 | -0.499343 | -0.000058 |
| C | 1.768336 | 0.185218 | -0.000036 |
| C | 4.535572 | -0.200470 | 0.000008 |
| C | 2.294164 | -1.118229 | 0.000166 |
| C | 2.633841 | 1.286903 | -0.000206 |
| C | 4.014506 | 1.094445 | -0.000191 |
| C | 3.671629 | -1.303394 | 0.000187 |
| H | 1.608516 | -1.958121 | 0.000306 |
| H | 2.199350 | 2.282036 | -0.000356 |
| H | 4.681730 | 1.951964 | -0.000327 |
| H | 4.080024 | -2.310689 | 0.000350 |
| H | 5.611411 | -0.354036 | 0.000029 |
| C | -1.768336 | -0.185218 | -0.000036 |
| C | -4.535572 | 0.200470 | 0.000008 |
| C | -2.294164 | 1.118229 | 0.000166 |
| C | -2.633841 | -1.286903 | -0.000206 |
| C | -4.014506 | -1.094445 | -0.000191 |
| C | -3.671629 | 1.303394 | 0.000187 |
| H | -1.608516 | 1.958121 | 0.000306 |
| H | -2.199350 | -2.282036 | -0.000356 |
| H | -4.681730 | -1.951964 | -0.000327 |
| H | -4.080024 | 2.310689 | 0.000350 |
| H | -5.611411 | 0.354036 | 0.000029 |

*Z*-**AB** (E = -572.737601 au)

| | | | |
|---|---|---|---|
| H | 0.414453 | 1.733450 | 0.183685 |
| C | 1.258953 | 1.054920 | 0.240890 |
| C | 3.454200 | -0.677090 | 0.359477 |
| C | 1.433505 | 0.070416 | -0.743109 |
| C | 2.185429 | 1.165439 | 1.275930 |
| C | 3.274395 | 0.292749 | 1.349202 |
| C | 2.554282 | -0.769502 | -0.699720 |
| H | 2.054136 | 1.936028 | 2.030879 |
| H | 3.987826 | 0.379760 | 2.163887 |
| H | 2.698869 | -1.489430 | -1.499943 |
| H | 4.308273 | -1.347566 | 0.400933 |
| N | 0.624640 | -0.012305 | -1.926654 |
| N | -0.624640 | 0.012305 | -1.926654 |
| C | -1.433505 | -0.070416 | -0.743109 |
| C | -3.274395 | -0.292749 | 1.349202 |
| C | -1.258953 | -1.054920 | 0.240890 |
| C | -2.554282 | 0.769502 | -0.699720 |
| C | -3.454200 | 0.677090 | 0.359477 |
| C | -2.185429 | -1.165439 | 1.275930 |
| H | -0.414453 | -1.733450 | 0.183685 |
| H | -2.698869 | 1.489430 | -1.499943 |
| H | -4.308273 | 1.347566 | 0.400933 |
| H | -2.054136 | -1.936028 | 2.030879 |
| H | -3.987826 | -0.379760 | 2.163887 |

### DFT/B3LYP/6-31+G*

*E*-**AB** (E = -572.784075 au)

| | | | |
|---|---|---|---|
| N | 0.386836 | 0.495836 | -0.000053 |
| N | -0.386836 | -0.495836 | -0.000053 |
| C | 1.772089 | 0.183750 | -0.000031 |
| C | 4.543704 | -0.198774 | 0.000011 |
| C | 2.299706 | -1.120455 | 0.000196 |
| C | 2.636928 | 1.287731 | -0.000226 |
| C | 4.019761 | 1.096555 | -0.000213 |
| C | 3.679447 | -1.303590 | 0.000216 |
| H | 1.620095 | -1.965632 | 0.000360 |
| H | 2.205581 | 2.284766 | -0.000392 |
| H | 4.685603 | 1.955580 | -0.000369 |
| H | 4.088818 | -2.310838 | 0.000399 |
| H | 5.620010 | -0.351176 | 0.000030 |
| C | -1.772089 | -0.183750 | -0.000031 |
| C | -4.543704 | 0.198774 | 0.000011 |
| C | -2.299706 | 1.120455 | 0.000196 |
| C | -2.636928 | -1.287731 | -0.000226 |
| C | -4.019761 | -1.096555 | -0.000213 |
| C | -3.679447 | 1.303590 | 0.000216 |
| H | -1.620095 | 1.965632 | 0.000360 |
| H | -2.205581 | -2.284766 | -0.000392 |
| H | -4.685603 | -1.955580 | -0.000369 |
| H | -4.088818 | 2.310838 | 0.000399 |
| H | -5.620010 | 0.351176 | 0.000030 |

*Z*-**AB** (E = -572.758717 au)

| | | | |
|---|---|---|---|
| H | 0.415195 | 1.731135 | 0.193365 |
| C | 1.259819 | 1.051754 | 0.245195 |
| C | 3.459459 | -0.679993 | 0.356078 |
| C | 1.435630 | 0.070778 | -0.743368 |
| C | 2.186155 | 1.157471 | 1.283161 |
| C | 3.277504 | 0.284487 | 1.352915 |
| C | 2.559014 | -0.767223 | -0.705637 |
| H | 2.053527 | 1.924362 | 2.042102 |
| H | 3.990420 | 0.367755 | 2.168874 |
| H | 2.708257 | -1.481339 | -1.510899 |
| H | 4.315587 | -1.348660 | 0.392940 |
| N | 0.624544 | -0.010969 | -1.925993 |
| N | -0.624544 | 0.010969 | -1.925993 |
| C | -1.435630 | -0.070778 | -0.743368 |
| C | -3.277504 | -0.284487 | 1.352915 |
| C | -1.259819 | -1.051754 | 0.245195 |
| C | -2.559014 | 0.767223 | -0.705637 |
| C | -3.459459 | 0.679993 | 0.356078 |
| C | -2.186155 | -1.157471 | 1.283161 |
| H | -0.415195 | -1.731135 | 0.193365 |
| H | -2.708257 | 1.481339 | -1.510899 |
| H | -4.315587 | 1.348660 | 0.392940 |
| H | -2.053527 | -1.924362 | 2.042102 |
| H | -3.990420 | -0.367755 | 2.168874 |

| DFT/ωb97x-d/6-31+G*/SM8-DMSO | | | | | | | DFT/EDF2/6-31G*/SM8-DMSO | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| *E*-**1a** (E = -1027.59375 au) | | | | *Z*-**1a** (E = -1027.57069 au) | | | | *E*-**1a** (E = -1027.17562 au) | | | | *Z*-**1a** (E = -1027.14787 au) | | | |
| H | -2.193192 | -2.843452 | 0.047909 | H | 4.008583 | -0.218111 | -1.847030 | H | 2.390617 | -2.087078 | 0.000091 | H | -6.479670 | 0.086419 | 1.583340 |
| C | -1.563169 | -1.956425 | 0.029603 | C | 4.347686 | 0.583336 | -1.197459 | C | 1.673009 | -1.275303 | -0.000500 | C | -6.072116 | -0.435155 | 0.723689 |
| C | 0.012574 | 0.344140 | -0.015426 | C | 5.229760 | 2.628759 | 0.483943 | C | -0.143872 | 0.857362 | -0.001874 | C | -5.056519 | -1.696138 | -1.538703 |
| C | -2.170906 | -0.698332 | 0.007042 | C | 4.860416 | 0.284685 | 0.067143 | C | 2.146681 | 0.046986 | 0.000021 | C | -5.142014 | 0.225302 | -0.083515 |
| C | -0.182943 | -2.068866 | 0.028286 | C | 4.274687 | 1.908560 | -1.611779 | C | 0.320278 | -1.521499 | -0.001594 | C | -6.450981 | -1.737917 | 0.424281 |
| C | 0.624073 | -0.920660 | 0.005605 | C | 4.699876 | 2.935385 | -0.768347 | C | -0.614512 | -0.464685 | -0.002345 | C | -5.946671 | -2.372384 | -0.707442 |
| C | -1.367855 | 0.446661 | -0.015070 | C | 5.334252 | 1.302150 | 0.893159 | C | 1.218293 | 1.094358 | -0.000692 | C | -4.645536 | -0.406732 | -1.230042 |
| H | 0.273154 | -3.061849 | 0.046417 | H | 3.877082 | 2.140422 | -2.598423 | H | -0.034396 | -2.547794 | -0.001737 | H | -7.155719 | -2.251215 | 1.069654 |
| H | -1.836734 | 1.423907 | -0.032342 | H | 5.772061 | 1.044870 | 1.853857 | H | 1.600494 | 2.109592 | -0.000332 | H | -3.951715 | 0.120893 | -1.875005 |
| H | 0.626659 | 1.229269 | -0.030056 | H | 5.578404 | 3.423606 | 1.141016 | H | -0.850981 | 1.671914 | -0.002479 | H | -4.675563 | -2.176081 | -2.434015 |
| N | -3.584089 | -0.696207 | 0.010663 | N | 5.066644 | -1.067042 | 0.500637 | N | 3.491603 | 0.422641 | 0.001016 | N | -4.888502 | 1.601122 | 0.191699 |
| N | -4.124708 | 0.430110 | -0.022559 | N | 4.160196 | -1.919920 | 0.545951 | N | 4.329192 | -0.526031 | 0.001607 | N | -3.744728 | 2.117477 | 0.249686 |
| C | -5.545282 | 0.418411 | -0.013697 | C | 2.772135 | -1.649085 | 0.331152 | C | 5.680238 | -0.129493 | 0.001167 | C | -2.519756 | 1.413729 | 0.291972 |
| C | -8.322778 | 0.627269 | -0.003540 | C | -0.007647 | -1.439635 | -0.016187 | C | 8.411531 | 0.428370 | 0.000343 | C | 0.091614 | 0.370735 | 0.429608 |
| C | -6.329099 | -0.740277 | 0.050851 | C | 2.047804 | -2.698917 | -0.242560 | C | 6.613705 | -1.170401 | 0.001270 | C | -1.412914 | 2.160714 | -0.133954 |
| C | -6.152931 | 1.673042 | -0.071791 | C | 2.082576 | -0.515640 | 0.771301 | C | 6.124041 | 1.200317 | 0.000664 | C | -2.291558 | 0.140284 | 0.841756 |
| C | -7.541090 | 1.778718 | -0.067783 | C | 0.708659 | -0.411166 | 0.611866 | C | 7.482341 | 1.470587 | 0.000275 | C | -1.009074 | -0.356962 | 0.919671 |
| C | -7.713150 | -0.629403 | 0.055742 | C | 0.683033 | -2.585033 | -0.442970 | C | 7.974284 | -0.892245 | 0.000841 | C | -0.129291 | 1.650220 | -0.103625 |
| H | -5.842738 | -1.709507 | 0.096666 | H | 2.575667 | -3.603867 | -0.536518 | H | 6.239969 | -2.188748 | 0.001713 | H | -1.594611 | 3.163361 | -0.505999 |
| H | -5.519333 | 2.554581 | -0.120233 | H | 2.608744 | 0.294717 | 1.259979 | H | 5.386087 | 1.994009 | 0.000545 | H | -3.111756 | -0.446986 | 1.232444 |
| H | -8.010749 | 2.759707 | -0.113698 | H | 0.186164 | 0.462608 | 0.965730 | H | 7.824041 | 2.500414 | -0.000045 | H | -0.848471 | -1.333023 | 1.367236 |
| H | -8.325260 | -1.528640 | 0.107160 | H | 0.143496 | -3.410418 | -0.914502 | H | 8.691418 | -1.705823 | 0.000898 | H | 0.707045 | 2.228625 | -0.463607 |
| N | 2.007378 | -1.114680 | -0.000515 | N | -1.388396 | -1.413047 | -0.229408 | N | -1.950807 | -0.813085 | -0.003924 | N | 1.333141 | -0.226650 | 0.532242 |
| H | 2.292689 | -2.096492 | -0.006737 | H | -1.756840 | -2.250255 | -0.685684 | H | -2.122776 | -1.819948 | -0.006413 | H | 1.320528 | -1.144821 | 0.979657 |
| C | 3.009789 | -0.163711 | 0.014883 | C | -2.289306 | -0.415548 | 0.087870 | C | -3.059750 | 0.008309 | -0.002368 | C | 2.556425 | 0.243578 | 0.102508 |
| N | 4.265874 | -0.716746 | -0.017913 | N | -3.580494 | -0.745013 | -0.241996 | N | -4.227290 | -0.704437 | -0.000581 | N | 3.572384 | -0.627329 | 0.387347 |
| H | 4.329410 | -1.734248 | -0.077403 | H | -3.739529 | -1.670528 | -0.642793 | H | -4.147118 | -1.721927 | 0.001805 | H | 3.321041 | -1.482069 | 0.885220 |
| O | 2.794183 | 1.045617 | 0.055054 | O | -1.963774 | 0.649341 | 0.608115 | O | -2.996414 | 1.238094 | -0.000967 | O | 2.706548 | 1.322714 | -0.471891 |
| C | 5.511443 | -0.060983 | -0.009849 | C | -4.747772 | 0.027345 | -0.096773 | C | -5.540822 | -0.234629 | 0.000546 | C | 4.933004 | -0.507560 | 0.103602 |
| C | 8.072354 | 1.084858 | 0.000953 | C | -7.167726 | 1.430135 | 0.107233 | C | -8.239532 | 0.526754 | 0.002107 | C | 7.693645 | -0.432523 | -0.387470 |
| C | 5.659942 | 1.325426 | 0.081128 | C | -5.953592 | -0.568460 | -0.488407 | C | -5.889388 | 1.121045 | 0.000074 | C | 5.765855 | -1.549497 | 0.530739 |
| C | 6.654516 | -0.866485 | -0.094855 | C | -4.761500 | 1.332643 | 0.401271 | C | -6.557790 | -1.197906 | 0.001795 | C | 5.498552 | 0.577749 | -0.575441 |
| C | 7.921497 | -0.297607 | -0.089217 | C | -5.969648 | 2.018319 | 0.497121 | C | -7.890858 | -0.820219 | 0.002627 | C | 6.867934 | 0.601886 | -0.811840 |
| C | 6.936166 | 1.881839 | 0.085504 | C | -7.150857 | 0.127384 | -0.387178 | C | -7.231253 | 1.483533 | 0.000808 | C | 7.129462 | -1.510637 | 0.287334 |
| H | 4.786106 | 1.951273 | 0.145188 | H | -5.958200 | -1.588216 | -0.877159 | H | -5.111869 | 1.869721 | -0.000811 | H | 5.339213 | -2.397165 | 1.058702 |
| H | 6.555108 | -1.950916 | -0.167164 | H | -3.837883 | 1.794971 | 0.706657 | H | -6.297658 | -2.252505 | 0.002002 | H | 4.863533 | 1.384982 | -0.906822 |
| H | 8.795545 | -0.941657 | -0.156859 | H | -5.963362 | 3.033033 | 0.885187 | H | -8.660961 | -1.584192 | 0.003590 | H | 7.290212 | 1.451308 | -1.339449 |
| H | 7.032989 | 2.961487 | 0.156762 | H | -8.075745 | -0.353787 | -0.697444 | H | -7.486002 | 2.538727 | 0.000394 | H | 7.754256 | -2.329257 | 0.628273 |
| H | 9.062075 | 1.533618 | 0.004869 | H | -8.102699 | 1.978018 | 0.186952 | H | -9.281425 | 0.827541 | 0.002674 | H | 8.760263 | -0.398655 | -0.579881 |
| H | -9.409281 | 0.704948 | 0.001145 | H | 4.631583 | 3.972067 | -1.093417 | H | 9.473228 | 0.650290 | 0.000035 | H | -6.257391 | -3.382509 | -0.950219 |
| *E*-**1a**⊃$PhCO_2^-$ (E = -1447.81568 au) | | | | *Z*-**1a**⊃$PhCO_2^-$ (E = -1447.79252 au) | | | | *E*-**1a**⊃$PhCO_2^-$ (E = -1447.28224 au) | | | | *Z*-**1a**⊃$PhCO_2^-$ (E = -1447.25451 au) | | | |
| N | 5.336748 | -0.254953 | 0.003143 | O | -1.490086 | -3.356101 | 0.135494 | N | 5.586418 | -0.489273 | 0.052093 | O | -1.578700 | -3.346368 | 0.115353 |
| C | 9.536974 | -0.369828 | -0.082186 | N | -2.760143 | -1.440846 | -0.056598 | C | 9.641456 | 0.583501 | 0.098616 | N | -2.845965 | -1.428436 | -0.066191 |
| C | 8.905000 | 0.874944 | -0.101625 | N | -0.544875 | -1.270138 | 0.411503 | C | 8.683709 | 1.597455 | 0.032648 | N | -0.602896 | -1.260433 | 0.287092 |
| H | 9.496594 | 1.784299 | -0.135730 | N | 4.934025 | -2.372840 | 1.041569 | H | 8.995892 | 2.636024 | -0.004679 | N | 4.836227 | -2.497621 | 0.844384 |
| C | 7.520781 | 0.960244 | -0.075703 | C | -6.694345 | -2.820214 | -0.632878 | C | 7.333519 | 1.289308 | 0.014564 | C | -6.787338 | -2.828860 | -0.505349 |
| H | 7.010230 | 1.917029 | -0.089697 | H | -7.716471 | -3.152627 | -0.780909 | H | 6.573199 | 2.060179 | -0.036003 | H | -7.811343 | -3.167473 | -0.618415 |
| C | 6.758370 | -0.212660 | -0.029655 | C | -5.676910 | -3.740763 | -0.410306 | C | 6.925743 | -0.051562 | 0.063300 | C | -5.755563 | -3.743729 | -0.330082 |
| C | 8.778230 | -1.535156 | -0.036244 | H | -5.901079 | -4.803265 | -0.383602 | C | 9.240385 | -0.747811 | 0.147068 | H | -5.970941 | -4.807664 | -0.306088 |
| H | 9.263722 | -2.505303 | -0.020558 | C | -4.359199 | -3.332758 | -0.220043 | H | 9.978250 | -1.541044 | 0.198124 | C | -4.436201 | -3.328514 | -0.184620 |
| C | 7.390175 | -1.456459 | -0.008703 | H | -3.570191 | -4.052506 | -0.055164 | C | 7.888284 | -1.064008 | 0.129953 | H | -3.634350 | -4.040118 | -0.055084 |
| H | 6.769193 | -2.346071 | 0.027774 | C | -4.042970 | -1.968502 | -0.249725 | H | 7.540182 | -2.090892 | 0.166623 | C | -4.129811 | -1.960549 | -0.211887 |
| O | -1.306473 | 3.269242 | 0.069933 | C | -1.594166 | -2.130196 | 0.160057 | O | -0.854210 | -3.076207 | -0.092308 | C | -1.675698 | -2.117333 | 0.110938 |
| N | -2.989466 | 1.696110 | -0.009157 | C | 0.799027 | -1.594686 | 0.561425 | N | -2.760618 | -1.782833 | 0.021504 | C | 0.728862 | -1.604488 | 0.413251 |
| N | -0.822266 | 1.014059 | 0.075252 | C | 1.331552 | -2.888227 | 0.453916 | N | -0.727084 | -0.769323 | -0.084512 | C | 1.229893 | -2.918538 | 0.381538 |
| N | 4.776868 | 0.865781 | -0.045006 | H | 0.667863 | -3.719216 | 0.265536 | N | 4.723361 | 0.434497 | -0.021732 | H | 0.537348 | -3.738529 | 0.269333 |
| C | -6.539465 | 3.957394 | 0.066420 | C | 2.694344 | -3.087478 | 0.622030 | C | -5.907154 | -4.572241 | -0.050701 | C | 2.586543 | -3.137620 | 0.527079 |
| H | -7.467049 | 4.519908 | 0.085398 | H | 3.106263 | -4.090966 | 0.572336 | H | -6.734017 | -5.273646 | -0.068924 | H | 2.978750 | -4.149249 | 0.539615 |
| C | -5.316060 | 4.607172 | 0.180353 | C | 3.565426 | -2.019903 | 0.837344 | C | -4.597223 | -5.019629 | -0.178259 | C | 3.503936 | -2.083770 | 0.646824 |
| H | -5.281149 | 5.687276 | 0.290101 | C | -5.071359 | -1.038744 | -0.474119 | H | -4.393695 | -6.079386 | -0.298274 | C | -5.173450 | -1.036752 | -0.388976 |
| C | -4.116057 | 3.901549 | 0.155703 | H | -4.819345 | 0.017746 | -0.497258 | C | -3.524562 | -4.134752 | -0.155245 | H | -4.929091 | 0.020491 | -0.409744 |
| H | -3.167484 | 4.412116 | 0.238034 | C | -6.377751 | -1.463837 | -0.664121 | H | -2.506790 | -4.483514 | -0.247546 | C | -6.481774 | -1.470534 | -0.534555 |
| C | -4.131279 | 2.507971 | 0.015446 | H | -7.152886 | -0.722886 | -0.835975 | C | -3.758033 | -2.760797 | -0.002517 | H | -7.267944 | -0.734582 | -0.670521 |
| C | -1.678944 | 2.096980 | 0.046760 | C | 1.672815 | -0.526095 | 0.843301 | C | -1.406312 | -1.974374 | -0.054031 | C | 1.642165 | -0.542158 | 0.598080 |
| C | 0.566207 | 1.034573 | 0.050732 | H | 1.254588 | 0.469812 | 0.955284 | C | 0.639534 | -0.571917 | -0.071922 | H | 1.251371 | 0.468025 | 0.657560 |
| C | 1.210381 | -0.220999 | 0.123442 | C | 3.032835 | -0.730490 | 0.969120 | C | 1.600309 | -1.603952 | 0.018993 | C | 2.996697 | -0.771312 | 0.698938 |
| H | 0.595248 | -1.112283 | 0.204662 | H | 3.676729 | 0.114735 | 1.185001 | H | 1.256521 | -2.626404 | 0.066038 | H | 3.659505 | 0.071390 | 0.845807 |
| C | 2.584706 | -0.316186 | 0.095024 | H | -2.693753 | -0.411462 | -0.174156 | C | 2.945648 | -1.301358 | 0.038144 | H | -2.795368 | -0.390027 | -0.163515 |
| H | 3.071717 | -1.283512 | 0.152532 | H | -0.770817 | -0.270429 | 0.584260 | H | 3.684663 | -2.091609 | 0.106718 | H | -0.801520 | -0.238126 | 0.397529 |
| C | 3.369066 | 0.842708 | -0.008009 | N | 5.898465 | -1.684946 | 0.650913 | C | 3.391279 | 0.028595 | -0.032322 | N | 5.865686 | -1.809010 | 0.627779 |
| C | -5.367435 | 1.851299 | -0.097854 | C | 5.772693 | 1.675483 | -1.888265 | C | -5.082293 | -2.309498 | 0.125340 | C | 6.287494 | 1.787369 | -1.517288 |
| H | -5.372438 | 0.770484 | -0.206180 | C | 6.447006 | 1.724065 | -0.671438 | H | -5.255908 | -1.244705 | 0.243975 | C | 6.802112 | 1.658496 | -0.230567 |
| C | -6.552886 | 2.571243 | -0.073540 | H | 6.976000 | 2.623802 | -0.374815 | C | -6.138165 | -3.207494 | 0.101976 | H | 7.356424 | 2.474228 | 0.221065 |
| H | -7.494408 | 2.037858 | -0.164619 | C | 6.463139 | 0.611278 | 0.162484 | H | -7.151145 | -2.830793 | 0.203242 | C | 6.626617 | 0.476171 | 0.477560 |
| C | 1.352098 | 2.192866 | -0.051424 | H | 7.007712 | 0.618252 | 1.101456 | C | 1.087134 | 0.763069 | -0.142006 | H | 7.048784 | 0.345065 | 1.468430 |
| H | 0.868192 | 3.156878 | -0.101286 | C | 5.761104 | -0.536966 | -0.201661 | H | 0.347287 | 1.553323 | -0.212327 | C | 5.888779 | -0.572113 | -0.079240 |
| C | 2.734691 | 2.082786 | -0.079335 | C | 5.111623 | 0.509684 | -2.268730 | C | 2.435123 | 1.050222 | -0.122390 | C | 5.590671 | 0.725894 | -2.090106 |
| H | 3.352197 | 2.972646 | -0.156272 | H | 4.594569 | 0.460546 | -3.221451 | H | 2.786587 | 2.075284 | -0.175724 | H | 5.199757 | 0.811338 | -3.098635 |
| H | -3.181248 | 0.688446 | -0.167164 | C | 5.097368 | -0.596977 | -1.429354 | H | -3.110271 | -0.811408 | 0.178931 | C | 5.382261 | -0.447361 | -1.378657 |
| H | -1.240279 | 0.071525 | 0.211576 | H | 4.571991 | -1.501946 | -1.715959 | H | -1.291795 | 0.105025 | -0.204965 | H | 4.836082 | -1.272512 | -1.822170 |
| O | -1.761271 | -1.545185 | 0.525661 | O | -0.992850 | 1.409919 | 0.957062 | O | -3.849935 | 0.709702 | 0.495329 | O | -0.929831 | 1.438798 | 0.668608 |
| O | -3.674028 | -0.961044 | -0.489337 | O | -2.717687 | 1.304904 | -0.473420 | O | -2.034924 | 1.604107 | -0.478201 | O | -2.909184 | 1.308178 | -0.383135 |
| C | -4.123318 | -5.933872 | 0.000420 | C | -2.238544 | 6.228869 | 0.344069 | C | -5.084425 | 5.545453 | 0.027674 | C | -2.322434 | 6.237727 | 0.297132 |
| H | -4.434677 | -6.974089 | -0.003687 | H | -2.325202 | 7.310933 | 0.368210 | H | -5.561003 | 6.520335 | 0.031257 | H | -2.412839 | 7.318546 | 0.333088 |
| C | -4.961007 | -4.951938 | -0.523389 | C | -3.117050 | 5.474844 | -0.430531 | C | -3.800518 | 5.396560 | -0.490332 | C | -3.340147 | 5.470088 | -0.263053 |
| H | -5.927221 | -5.223093 | -0.937988 | H | -3.891058 | 5.965987 | -1.012532 | H | -3.270796 | 6.254001 | -0.892951 | H | -4.226357 | 5.949710 | -0.666276 |
| C | -4.560537 | -3.619853 | -0.517462 | C | -3.005167 | 4.088823 | -0.459213 | C | -3.193194 | 4.146639 | -0.493203 | C | -3.222910 | 4.086145 | -0.308320 |
| H | -5.195412 | -2.837801 | -0.920692 | H | -3.677745 | 3.480195 | -1.054717 | H | -2.194169 | 4.002791 | -0.889398 | H | -4.000442 | 3.466271 | -0.740674 |
| C | -3.321914 | -3.254297 | 0.010764 | C | -2.016526 | 3.441439 | 0.282830 | C | -3.859195 | 3.032195 | 0.018429 | C | -2.090797 | 3.452713 | 0.206121 |
| C | -2.884906 | -1.802647 | 0.015517 | C | -1.899187 | 1.930156 | 0.252289 | C | -3.197749 | 1.677021 | 0.012224 | C | -1.967303 | 1.950220 | 0.159724 |
| C | -2.885200 | -5.576966 | 0.529702 | C | -1.248360 | 5.590288 | 1.087133 | C | -5.755724 | 4.438764 | 0.541100 | C | -1.188653 | 5.613941 | 0.811344 |
| H | -2.226249 | -6.336381 | 0.939615 | H | -0.560234 | 6.171912 | 1.693104 | H | -6.756530 | 4.548139 | 0.946783 | H | -0.391594 | 6.205964 | 1.249677 |
| C | -2.488774 | -4.243944 | 0.533943 | C | -1.139715 | 4.204027 | 1.055425 | C | -5.145603 | 3.190135 | 0.535684 | C | -1.075455 | 4.229607 | 0.765478 |
| H | -1.529646 | -3.941082 | 0.940755 | H | -0.377125 | 3.684179 | 1.626032 | H | -5.646524 | 2.313015 | 0.930093 | H | -0.204407 | 3.718618 | 1.160200 |
| H | 10.620522 | -0.427038 | -0.102441 | H | 5.769624 | 2.539288 | -2.544624 | H | 10.696256 | 0.835834 | 0.112259 | H | 6.437543 | 2.703839 | -2.077080 |

| DFT/ωb97x-d/6-31+G*/SM8-DMSO | | | | | | | DFT/EDF2/6-31G*/SM8-DMSO | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| *E*-**1b** (E = -1482.59403 au) | | | | *Z*-**1b** (E = -1482.57174 au) | | | | *E*-**1b** (E = -1482.01083 au) | | | | *Z*-**1b** (E = -1481.98201 au) | | | |
| H | -1.432472 | -2.525647 | 0.197493 | H | -3.410489 | -1.641379 | 1.738150 | H | -2.050504 | -3.317427 | 0.048691 | H | -0.306893 | -1.775799 | 1.482354 |
| C | -2.056091 | -1.640510 | 0.117997 | C | -3.816077 | -1.105192 | 0.886027 | C | -2.559462 | -2.359981 | 0.034555 | C | -1.238232 | -1.867053 | 0.937525 |
| C | -3.652454 | 0.651575 | -0.091355 | C | -4.888346 | 0.282327 | -1.286651 | C | -3.805935 | 0.131447 | -0.005501 | C | -3.675696 | -2.096368 | -0.415553 |
| C | -1.456692 | -0.381332 | -0.025210 | C | -4.353045 | -1.801407 | -0.194013 | C | -1.779218 | -1.198257 | 0.001974 | C | -1.465536 | -2.973899 | 0.104257 |
| C | -3.432856 | -1.745171 | 0.157024 | C | -3.824713 | 0.280383 | 0.881464 | C | -3.937139 | -2.284980 | 0.049721 | C | -2.213403 | -0.903779 | 1.091803 |
| C | -4.252064 | -0.604243 | 0.054369 | C | -4.329046 | 0.984360 | -0.220838 | C | -4.585972 | -1.040410 | 0.029702 | C | -3.438750 | -0.984494 | 0.406218 |
| C | -2.267071 | 0.747886 | -0.127200 | C | -4.934926 | -1.105515 | -1.254436 | C | -2.428972 | 0.045575 | -0.017929 | C | -2.709956 | -3.080260 | -0.528665 |
| H | -3.886321 | -2.732846 | 0.271146 | H | -3.446580 | 0.821670 | 1.741106 | H | -4.523350 | -3.198111 | 0.076344 | H | -2.025323 | -0.067131 | 1.757935 |
| H | -1.793426 | 1.719609 | -0.237707 | H | -5.396327 | -1.659301 | -2.065793 | H | -1.823236 | 0.944156 | -0.044119 | H | -2.899728 | -3.964393 | -1.128479 |
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| C | 2.047745 | -0.944974 | -0.037379 | C | -2.158495 | -3.532308 | 0.119076 | C | 1.687466 | -0.513302 | -0.033324 | C | 1.465518 | -2.973870 | -0.104408 |
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| H | 2.031988 | 1.208170 | -0.155657 | H | -2.144418 | -2.165851 | -1.552206 | H | 1.941790 | 1.603518 | 0.011404 | H | 2.899942 | -3.964745 | 1.127745 |
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| O | 7.038182 | -2.677294 | -0.186847 | O | 2.299752 | -0.950267 | -0.974570 | O | 6.618592 | 1.381909 | 0.039170 | O | 6.138586 | -0.622862 | 0.667917 |
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| C | -9.148127 | 0.200167 | 0.059062 | C | -0.793406 | 3.273456 | 0.276502 | C | -9.306292 | 0.400379 | 0.034626 | C | -7.480122 | 1.839677 | 0.209134 |
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| H | 7.853448 | 0.784391 | 1.896508 | H | 4.190253 | -0.117491 | -1.853932 | H | 8.615029 | 2.296091 | 0.135228 | H | 8.117116 | 0.245190 | 1.078287 |
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| *E*-**1b**⊃$PhCO_2^-$ (E = -1902.87627 au) | | | | *Z*-**1b**⊃$PhCO_2^-$ (E = -1902.85557 au) | | | | *E*-**1b**⊃$PhCO_2^-$ (E = -1902.11742 au) | | | | *Z*-**1b**⊃$PhCO_2^-$ (E = -1902.07566 au) | | | |
| O | 8.226584 | -1.072951 | 0.028661 | O | 4.892111 | -1.026230 | -0.127130 | O | 8.347335 | -1.155190 | 0.360897 | O | 4.930568 | -1.298701 | -0.311258 |
| N | 9.928405 | 0.467834 | -0.051460 | N | 3.624416 | 0.897205 | -0.295836 | N | 9.813232 | 0.512698 | -0.237942 | N | 3.802126 | 0.719830 | -0.294353 |
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| O | -4.639052 | 3.077902 | 0.068585 | O | -4.749135 | -1.497487 | 0.185002 | O | -4.984550 | 3.200460 | 0.069945 | O | -4.932044 | -1.299858 | 0.310925 |
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| H | -4.812513 | -4.195497 | 0.768195 |
| C | -6.663420 | -3.482230 | -0.019168 |
| C | -6.222880 | -2.034181 | -0.017199 |
| C | -8.345040 | -5.166985 | -0.468785 |
| H | -9.344271 | -5.427870 | -0.824098 |
| C | -7.938498 | -3.834924 | -0.466131 |
| H | -8.599504 | -3.046749 | -0.810521 |

| | | | |
|---|---|---|---|
| C | -4.709742 | 1.451691 | 0.015455 |
| C | -3.743547 | -0.824512 | 0.406900 |
| C | -2.145182 | -2.700240 | 0.783378 |
| C | -2.764755 | -3.704271 | 0.031785 |
| H | -3.683358 | -3.489879 | -0.499396 |
| C | -2.169930 | -4.961461 | -0.067917 |
| H | -2.621884 | -5.726704 | -0.699098 |
| C | -0.946071 | -5.211362 | 0.545610 |
| C | -6.060078 | 1.101937 | -0.091551 |
| H | -6.355301 | 0.070875 | 0.039380 |
| C | -7.006948 | 2.086277 | -0.371214 |
| H | -8.054608 | 1.794522 | -0.449751 |
| C | -1.005550 | -3.021478 | 1.535241 |
| H | -0.559715 | -2.264224 | 2.173926 |
| C | -0.404410 | -4.260775 | 1.414381 |
| H | 0.515738 | -4.467428 | 1.953464 |
| H | -2.753345 | 0.950116 | 0.453489 |
| H | -1.763256 | -0.682304 | 0.874830 |
| O | -0.897682 | 0.934552 | 0.701339 |
| O | 0.815649 | 0.991434 | -0.748618 |
| C | -0.296737 | 5.842507 | -0.140756 |
| H | -0.353056 | 6.932628 | -0.166413 |
| C | 0.424392 | 5.155882 | -1.118680 |
| H | 0.931671 | 5.703006 | -1.913946 |
| C | 0.500128 | 3.765695 | -1.080082 |
| H | 1.062376 | 3.219620 | -1.830212 |
| C | -0.152877 | 3.046978 | -0.075146 |
| C | -0.072421 | 1.537662 | -0.038433 |
| C | -0.945591 | 5.131985 | 0.870036 |
| H | -1.507590 | 5.660714 | 1.640492 |
| C | -0.877660 | 3.740993 | 0.897079 |
| H | -1.380981 | 3.176639 | 1.675036 |

| | | | |
|---|---|---|---|
| C | -7.705347 | 2.131036 | 0.108597 |
| C | -5.228852 | 1.991872 | 0.075647 |
| C | -2.886696 | 1.182188 | 0.047317 |
| C | -2.097449 | 0.015684 | 0.177511 |
| H | -2.605925 | -0.931650 | 0.327156 |
| C | -0.724197 | 0.076678 | 0.116333 |
| H | -0.123150 | -0.819363 | 0.220969 |
| C | -0.073815 | 1.306792 | -0.085229 |
| C | -8.868676 | 1.346270 | 0.043169 |
| H | -8.761571 | 0.271336 | -0.062497 |
| C | -10.121587 | 1.935879 | 0.111139 |
| H | -11.003283 | 1.304936 | 0.057665 |
| C | -2.238849 | 2.413096 | -0.155767 |
| H | -2.835237 | 3.307758 | -0.251703 |
| C | -0.857389 | 2.457730 | -0.223040 |
| H | -0.345902 | 3.401721 | -0.381476 |
| H | -6.571483 | 0.419905 | -0.097972 |
| H | -4.568353 | 0.024920 | 0.282403 |
| O | -4.894819 | -1.621765 | 0.587730 |
| O | -6.864835 | -1.250229 | -0.425856 |
| C | -6.657320 | -6.251019 | -0.165196 |
| H | -6.827652 | -7.321154 | -0.223763 |
| C | -7.597628 | -5.364573 | -0.683945 |
| H | -8.503310 | -5.740572 | -1.149115 |
| C | -7.377810 | -3.994386 | -0.608348 |
| H | -8.093005 | -3.282480 | -1.005417 |
| C | -6.217625 | -3.493379 | -0.016503 |
| C | -5.974899 | -2.006054 | 0.054803 |
| C | -5.497813 | -5.759471 | 0.428706 |
| H | -4.760109 | -6.443855 | 0.835438 |
| C | -5.280516 | -4.388734 | 0.500581 |
| H | -4.384551 | -3.980292 | 0.954671 |

| | | | |
|---|---|---|---|
| C | -4.812727 | 1.616574 | -0.056093 |
| C | -3.902118 | -0.643094 | 0.467266 |
| C | -2.348325 | -2.531912 | 0.889108 |
| C | -3.074642 | -3.569553 | 0.288789 |
| H | -4.050579 | -3.361274 | -0.125622 |
| C | -2.505304 | -4.833275 | 0.176887 |
| H | -3.033053 | -5.621651 | -0.350007 |
| C | -1.205460 | -5.072881 | 0.621276 |
| C | -6.157526 | 1.261404 | -0.225916 |
| H | -6.447080 | 0.229792 | -0.091450 |
| C | -7.090228 | 2.233851 | -0.568104 |
| H | -8.126504 | 1.936098 | -0.695064 |
| C | -1.131405 | -2.841545 | 1.518546 |
| H | -0.607199 | -2.063119 | 2.063187 |
| C | -0.560290 | -4.087559 | 1.378319 |
| H | 0.417718 | -4.281202 | 1.802455 |
| H | -2.858108 | 1.106949 | 0.385535 |
| H | -1.901333 | -0.533510 | 0.881144 |
| O | -0.968199 | 1.007880 | 0.579614 |
| O | 0.965643 | 1.006922 | -0.578941 |
| C | 0.000904 | 5.887031 | -0.001928 |
| H | 0.001528 | 6.972072 | -0.002381 |
| C | 0.796874 | 5.187207 | -0.904447 |
| H | 1.417394 | 5.723336 | -1.615242 |
| C | 0.799618 | 3.796743 | -0.898365 |
| H | 1.412522 | 3.237280 | -1.596681 |
| C | -0.000704 | 3.087206 | -0.000713 |
| C | -0.001162 | 1.577255 | 0.000036 |
| C | -0.795916 | 5.188885 | 0.901167 |
| H | -1.415810 | 5.726356 | 1.611493 |
| C | -0.800230 | 3.798410 | 0.896315 |
| H | -1.413592 | 3.240206 | 1.595229 |

*Z*-**1b**⊃$PhCO_2^-$ (anion outside cavity)
(E = -1902.85362 au)

| | | | |
|---|---|---|---|
| O | -6.123436 | 2.292388 | 2.115229 |
| N | -4.172782 | 1.446774 | 1.220680 |
| N | -6.105367 | 0.171508 | 1.314926 |
| N | -3.949736 | -4.391194 | -1.210023 |
| C | -1.332687 | 4.523660 | 1.657209 |
| H | -0.580091 | 5.303039 | 1.760573 |
| C | -1.072501 | 3.394019 | 0.884415 |
| H | -0.122032 | 3.282373 | 0.375709 |
| C | -2.031836 | 2.399509 | 0.751594 |
| H | -1.814469 | 1.527312 | 0.142313 |
| C | -3.272616 | 2.514758 | 1.390196 |
| C | -5.496605 | 1.375413 | 1.585834 |
| C | -5.546572 | -0.972208 | 0.687315 |
| C | -6.145551 | -1.502360 | -0.459098 |
| H | -7.032818 | -1.025145 | -0.878103 |
| C | -5.614983 | -2.641075 | -1.056925 |
| H | -6.090246 | -3.080773 | -1.932712 |
| C | -4.438496 | -3.205033 | -0.561082 |
| C | -3.539286 | 3.648122 | 2.165331 |
| H | -4.497461 | 3.747396 | 2.652665 |
| C | -2.567070 | 4.638948 | 2.290752 |
| H | -2.788406 | 5.516317 | 2.898735 |
| C | -4.421533 | -1.601699 | 1.234702 |
| H | -3.990626 | -1.229459 | 2.160541 |
| C | -3.853325 | -2.698175 | 0.601002 |
| H | -2.963526 | -3.163142 | 1.014570 |
| H | -3.808996 | 0.667793 | 0.685235 |
| H | -7.115994 | 0.197489 | 1.428305 |
| O | 0.396447 | 1.241086 | -2.284677 |
| N | 2.475828 | 1.329945 | -1.298041 |
| N | 1.274288 | -0.609063 | -1.240507 |
| N | -2.763211 | -4.523587 | -1.567133 |
| C | 3.745463 | 5.311889 | -1.871644 |
| H | 4.095411 | 6.336760 | -2.006077 |
| C | 2.580335 | 4.871424 | -2.494181 |
| H | 2.005155 | 5.551104 | -3.124604 |
| C | 2.122002 | 3.563784 | -2.332796 |
| H | 1.215090 | 3.233922 | -2.817416 |
| C | 2.836548 | 2.669409 | -1.525434 |
| C | 1.313356 | 0.701272 | -1.662679 |
| C | 0.220852 | -1.515272 | -1.381087 |
| C | 0.450737 | -2.823756 | -0.919981 |
| H | 1.422611 | -3.068755 | -0.505512 |
| C | -0.539397 | -3.788444 | -1.007906 |
| H | -0.342757 | -4.805688 | -0.672498 |
| C | -1.805957 | -3.462166 | -1.497386 |
| C | 4.012448 | 3.112768 | -0.898758 |
| H | 4.567039 | 2.415677 | -0.279998 |
| C | 4.458832 | 4.416966 | -1.072733 |
| H | 5.375144 | 4.733253 | -0.573019 |
| C | -1.028796 | -1.211777 | -1.946302 |
| H | -1.205401 | -0.223446 | -2.347330 |
| C | -2.029377 | -2.174460 | -1.988734 |
| H | -2.990273 | -1.908785 | -2.421414 |
| H | 3.155840 | 0.798668 | -0.727941 |
| H | 2.115551 | -1.002220 | -0.784464 |
| O | 4.429114 | 0.092153 | 0.267315 |
| O | 3.413426 | -1.885384 | 0.009065 |
| C | 7.555099 | -3.087804 | 2.583468 |
| H | 8.365211 | -3.577453 | 3.128252 |
| C | 7.594963 | -1.711990 | 2.352903 |
| H | 8.435727 | -1.118469 | 2.714700 |
| C | 6.559409 | -1.091005 | 1.658460 |
| H | 6.571208 | -0.022465 | 1.470067 |
| C | 5.475474 | -1.834029 | 1.186315 |
| C | 4.353977 | -1.156387 | 0.429082 |

*Z*-**1b**⊃$PhCO_2^-$ (anion outside cavity)
(E = -1902.08778 au)

| | | | |
|---|---|---|---|
| O | 5.369955 | -2.419215 | -0.621877 |
| N | 5.546560 | -0.123559 | -0.471261 |
| N | 3.613516 | -1.142825 | 0.163109 |
| N | -0.388239 | -4.961831 | 1.114187 |
| C | 9.508016 | 0.687312 | -1.628415 |
| H | 10.525595 | 0.920290 | -1.922291 |
| C | 9.073264 | -0.631558 | -1.564740 |
| H | 9.753643 | -1.441243 | -1.810372 |
| C | 7.771186 | -0.946983 | -1.191605 |
| H | 7.431862 | -1.971157 | -1.146989 |
| C | 6.869961 | 0.077762 | -0.869514 |
| C | 4.889669 | -1.319462 | -0.336899 |
| C | 2.645940 | -2.113767 | 0.356276 |
| C | 2.793825 | -3.475828 | 0.041995 |
| H | 3.731746 | -3.819281 | -0.367386 |
| C | 1.757412 | -4.356147 | 0.297417 |
| H | 1.881160 | -5.415595 | 0.096885 |
| C | 0.524956 | -3.927732 | 0.807400 |
| C | 7.310799 | 1.410169 | -0.933833 |
| H | 6.608974 | 2.199353 | -0.683687 |
| C | 8.612149 | 1.704705 | -1.309824 |
| H | 8.925640 | 2.743164 | -1.351563 |
| C | 1.426279 | -1.686160 | 0.924214 |
| H | 1.325200 | -0.640367 | 1.196044 |
| C | 0.386425 | -2.566825 | 1.134690 |
| H | -0.530258 | -2.200684 | 1.580274 |
| H | 4.997723 | 0.752642 | -0.324865 |
| H | 3.352082 | -0.191826 | 0.512039 |
| O | -6.752367 | -0.768422 | 0.691100 |
| N | -6.777914 | 0.576829 | -1.173954 |
| N | -5.069131 | -0.903097 | -0.872022 |
| N | -1.642703 | -4.854889 | 1.158800 |
| C | -10.237343 | 2.925078 | -0.786869 |
| H | -11.125339 | 3.541645 | -0.702097 |
| C | -9.944039 | 1.974045 | 0.183432 |
| H | -10.606622 | 1.843644 | 1.033304 |
| C | -8.810430 | 1.174620 | 0.094202 |
| H | -8.586860 | 0.439528 | 0.852225 |
| C | -7.941372 | 1.325795 | -0.992538 |
| C | -6.244173 | -0.392801 | -0.366784 |
| C | -4.235278 | -1.865725 | -0.324756 |
| C | -3.070278 | -2.188453 | -1.041671 |
| H | -2.869914 | -1.698765 | -1.990062 |
| C | -2.163247 | -3.110585 | -0.561438 |
| H | -1.271166 | -3.331903 | -1.134700 |
| C | -2.404115 | -3.771606 | 0.652447 |
| C | -8.238534 | 2.283741 | -1.970643 |
| H | -7.569764 | 2.410644 | -2.816945 |
| C | -9.372833 | 3.073068 | -1.867016 |
| H | -9.580518 | 3.808539 | -2.636956 |
| C | -4.490043 | -2.539425 | 0.877750 |
| H | -5.390770 | -2.318008 | 1.428803 |
| C | -3.597150 | -3.495774 | 1.329705 |
| H | -3.804911 | -4.049702 | 2.239349 |
| H | -6.259266 | 0.810254 | -2.020523 |
| H | -4.739213 | -0.515897 | -1.756628 |
| O | 2.775659 | 1.268167 | 1.191262 |
| O | 4.227857 | 2.284829 | -0.187387 |
| C | 1.544878 | 6.107829 | 1.628161 |
| H | 1.109411 | 7.069838 | 1.877858 |
| C | 1.049297 | 4.944617 | 2.211535 |
| H | 0.226694 | 4.995923 | 2.917787 |
| C | 1.607493 | 3.712919 | 1.890714 |
| H | 1.240061 | 2.792678 | 2.331174 |
| C | 2.666368 | 3.627650 | 0.985705 |
| C | 3.270266 | 2.289928 | 0.635751 |

| | | | |
|---|---|---|---|
| C | 6.474166 | -3.835895 | 2.115385 |
| H | 6.433879 | -4.911546 | 2.291766 |
| C | 5.441914 | -3.210247 | 1.420253 |
| H | 4.593767 | -3.775340 | 1.047957 |

| | | | |
|---|---|---|---|
| C | 2.601270 | 6.031718 | 0.724106 |
| H | 2.993393 | 6.933762 | 0.265133 |
| C | 3.157397 | 4.798444 | 0.406413 |
| H | 3.979877 | 4.711830 | -0.294828 |

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