Supporting Information for:

Synthesis of a double-stranded spiroborate helicate bearing stilbene units and its photoresponsive behaviour

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Table S1 Gibbs free energies and energy differences calculated for optimized geometries of helicates in CH_3CN at the HF/6-31G* level to theory

	Gibbs free energies / Ha			Relative Gibbs free energies / kcal mol^{-1}	
Dianion	*meso-cis*-$\mathbf{3_E}$	*cis*-$\mathbf{3_E}$	*trans*-$\mathbf{3_E}$	Δ (*meso-cis*-$\mathbf{3_E}$ – *cis*-$\mathbf{3_E}$)	Δ (*cis*-$\mathbf{3_E}$ – *trans*-$\mathbf{3_E}$)
	–3553.8516	–3553.8473	–3553.8538	–2.7	+4.1
Monoanion	*cis*-$\mathbf{3_C}$	[*cis*-$\mathbf{3_E}$ + Na^+]		Δ (*cis*-$\mathbf{3_C}$ – [*cis*-$\mathbf{3_E}$ + Na^+])	
	–3715.6775	–3715.6778		+0.2	

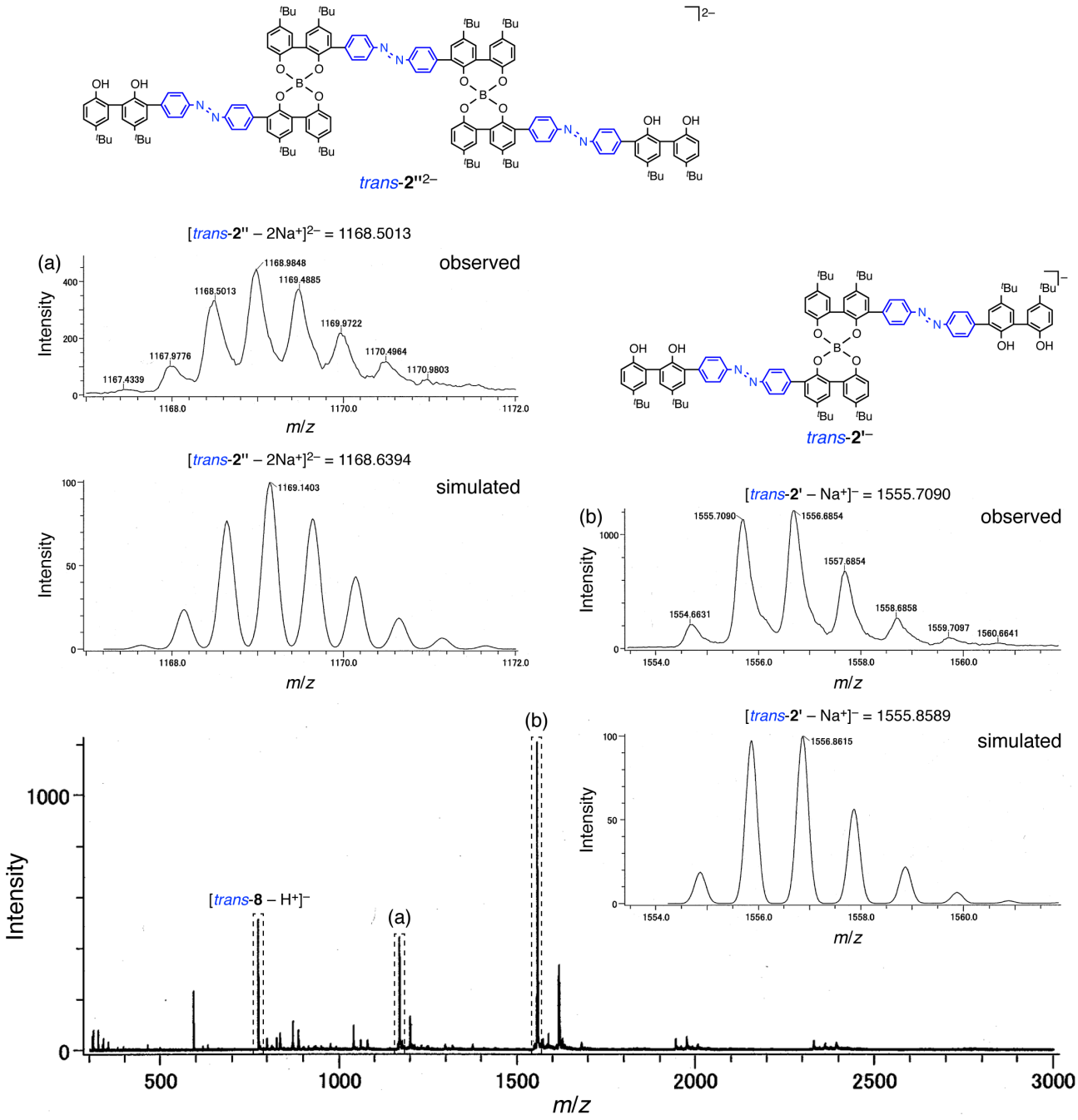

Fig. S1 Negative mode ESI-MS spectrum of the product obtained by the reaction of *trans*-**8** with $NaBH_4$ using CH_3CN as the eluent.

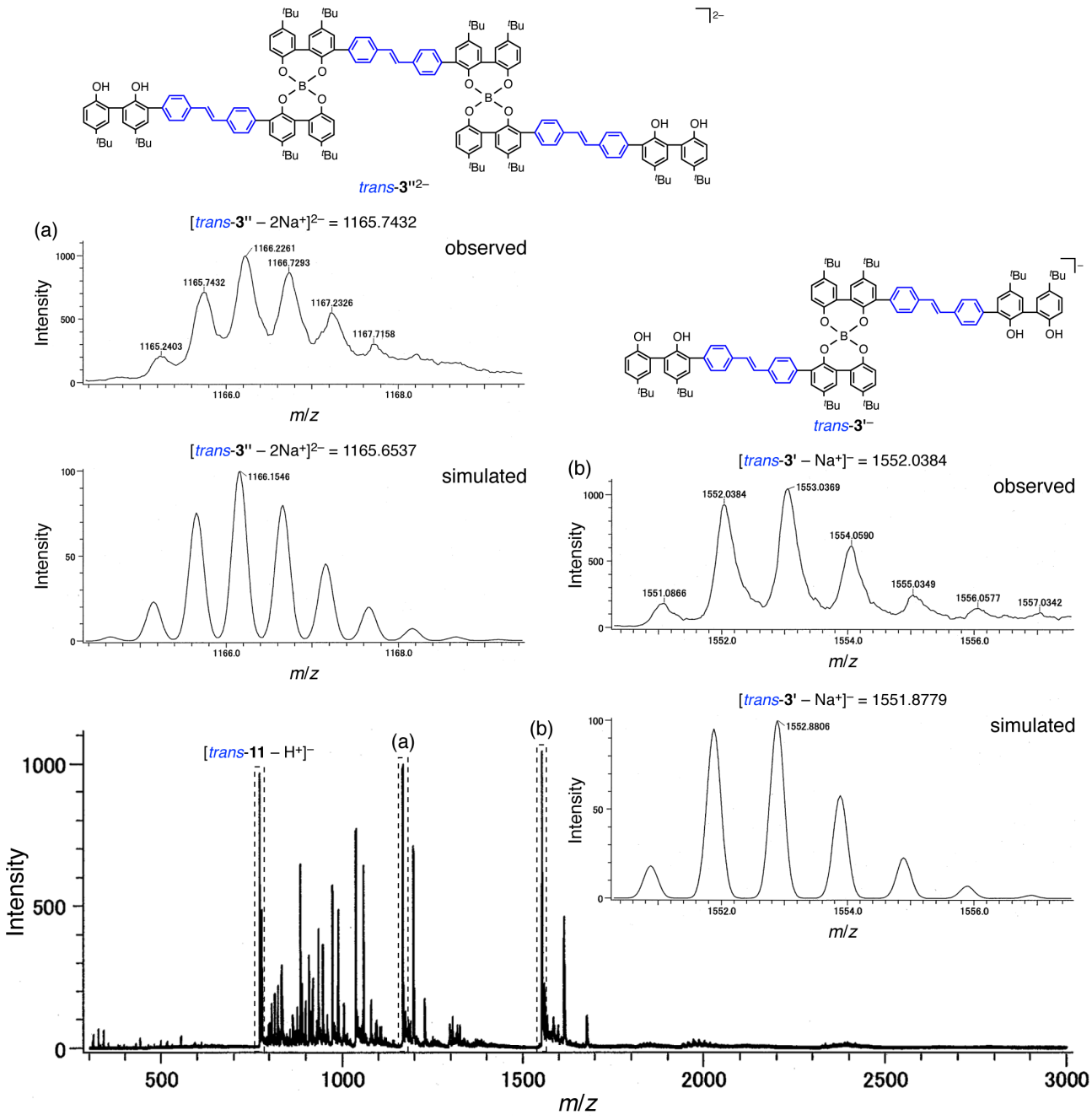

Fig. S2 Negative mode ESI-MS spectrum of the product obtained by the reaction of *trans*-**11** with $NaBH_4$ using CH_3CN as the eluent.

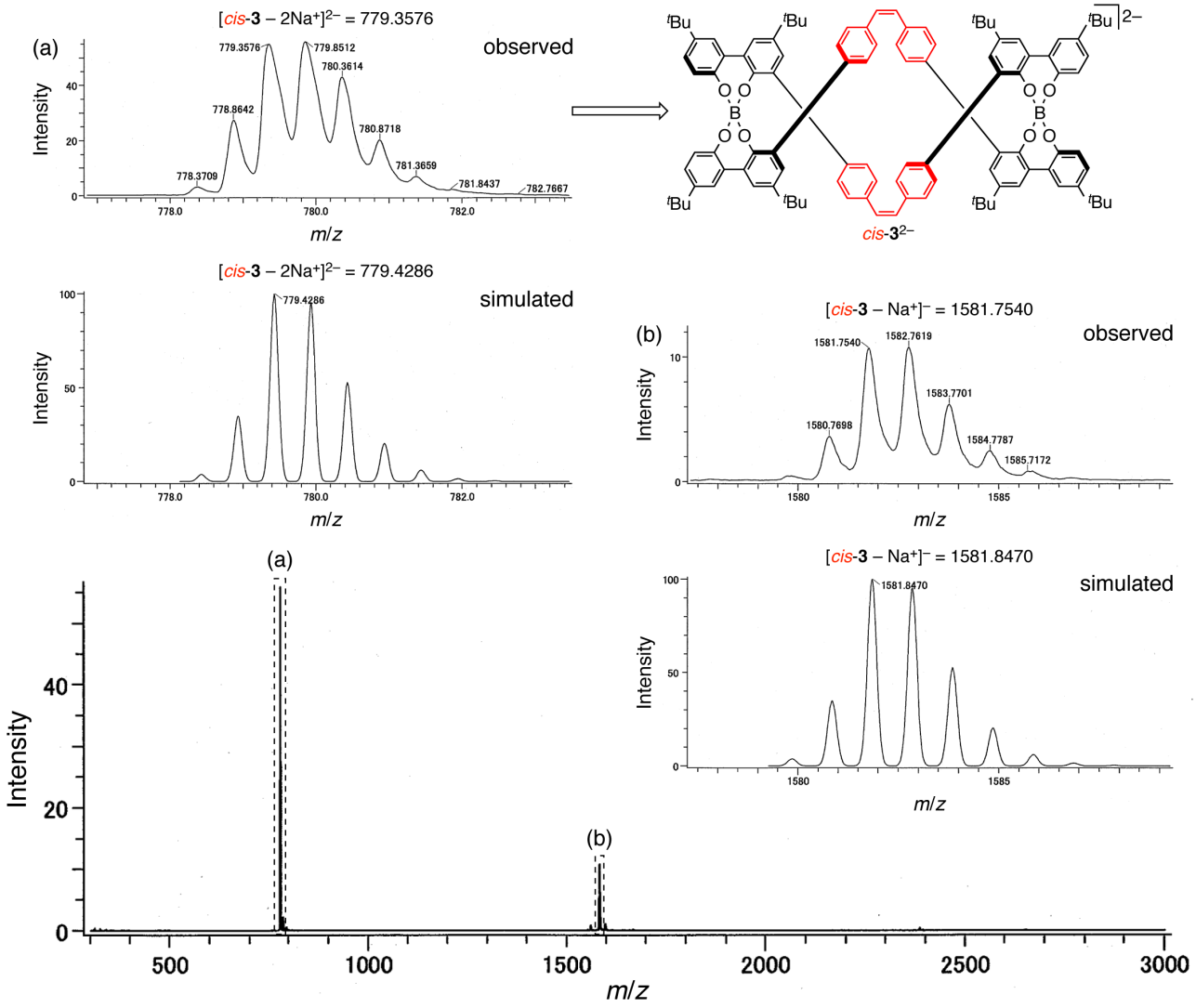

Fig. S3 Negative mode ESI-MS spectrum of *cis*-**3** using CH_3CN as the eluent.

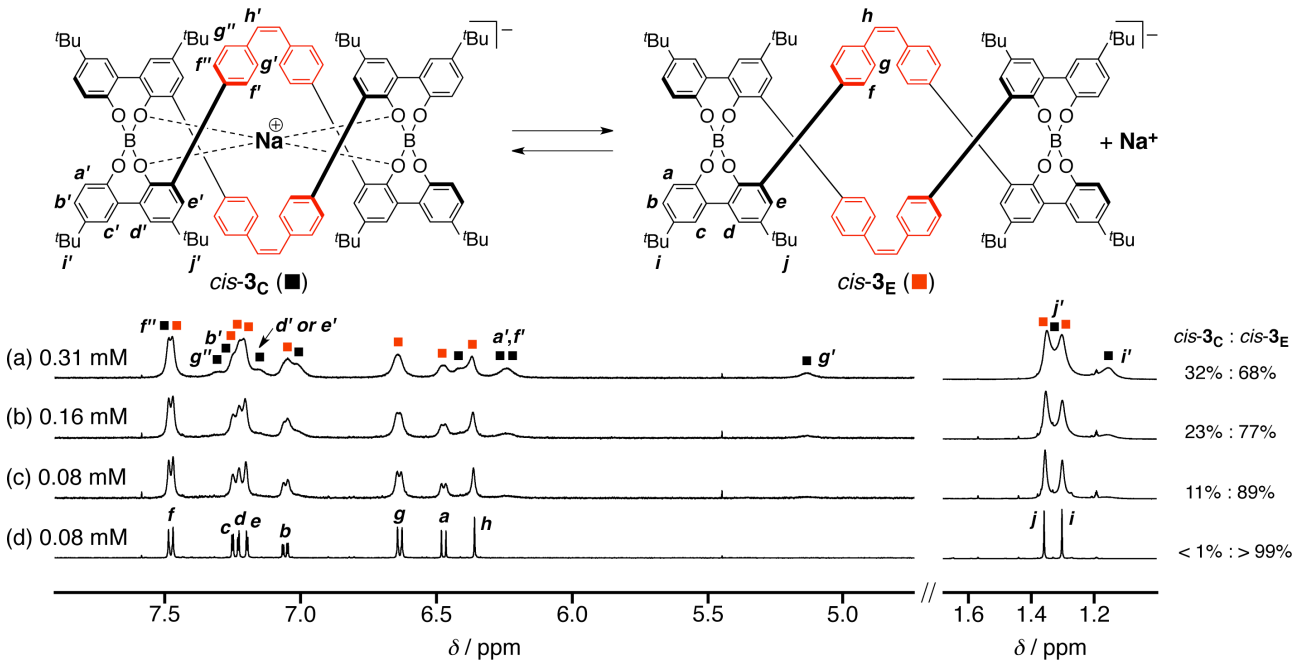

Fig. S4 ^{1}H NMR spectra (500 MHz, CD_3CN, 25 °C) of *cis*-**3** at various concentrations: 0.31 (a), 0.16 (b), 0.080 mM (c), and (c) + 6 equiv. [2.2.1] (d). ■ and ■ denote the signals due to the contracted (*cis*-$\mathbf{3_C}$) and extended (*cis*-$\mathbf{3_E}$) forms, respectively.

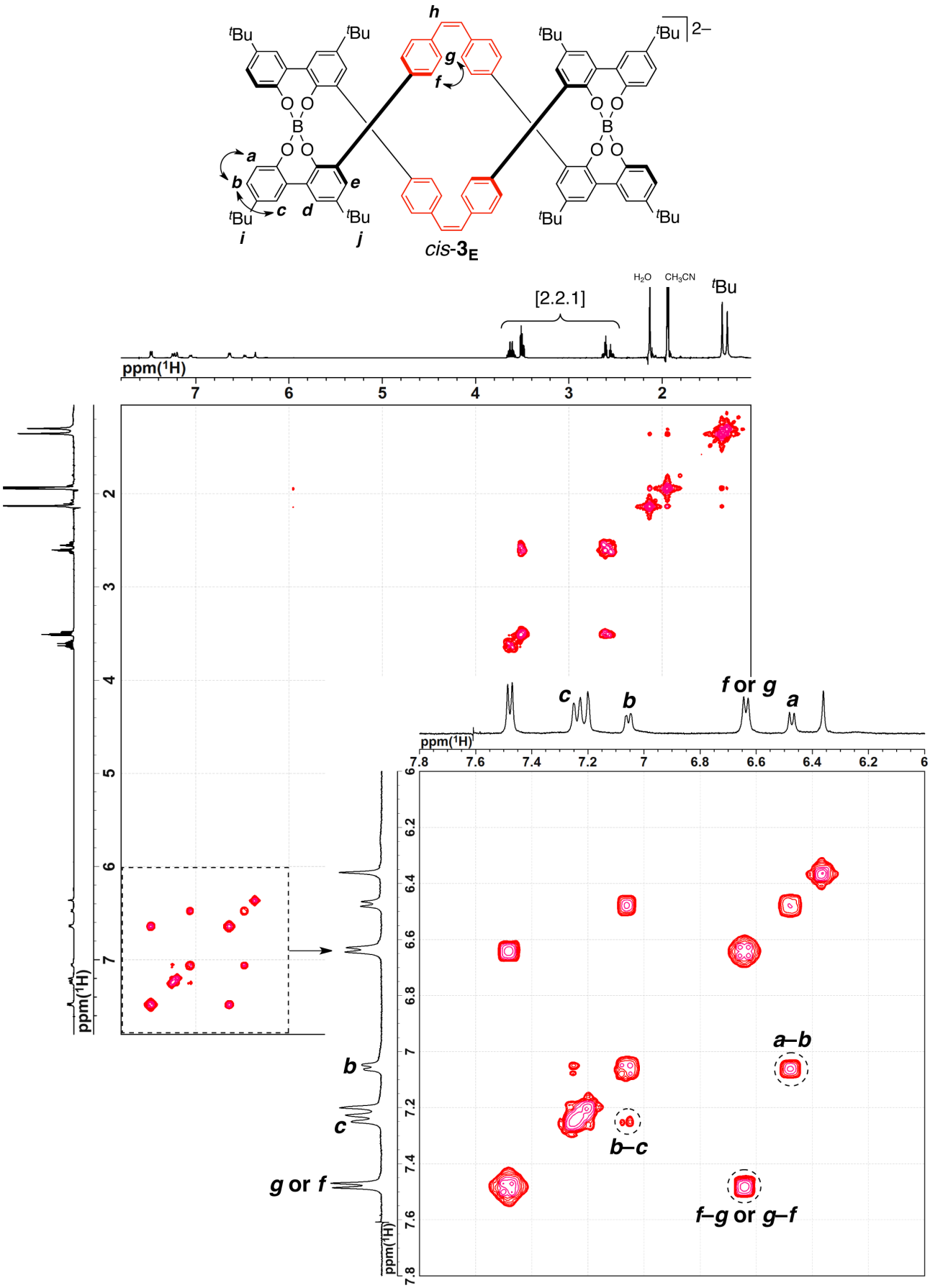

Fig. S5 gCOSY spectrum of *cis*-**3** (*cis*-$\mathbf{3_C}$: *cis*-$\mathbf{3_E}$ = 10 : 90) (500 MHz, CD_3CN, 25 °C, 0.30 mM) in the presence of 2 equiv. [2.2.1].

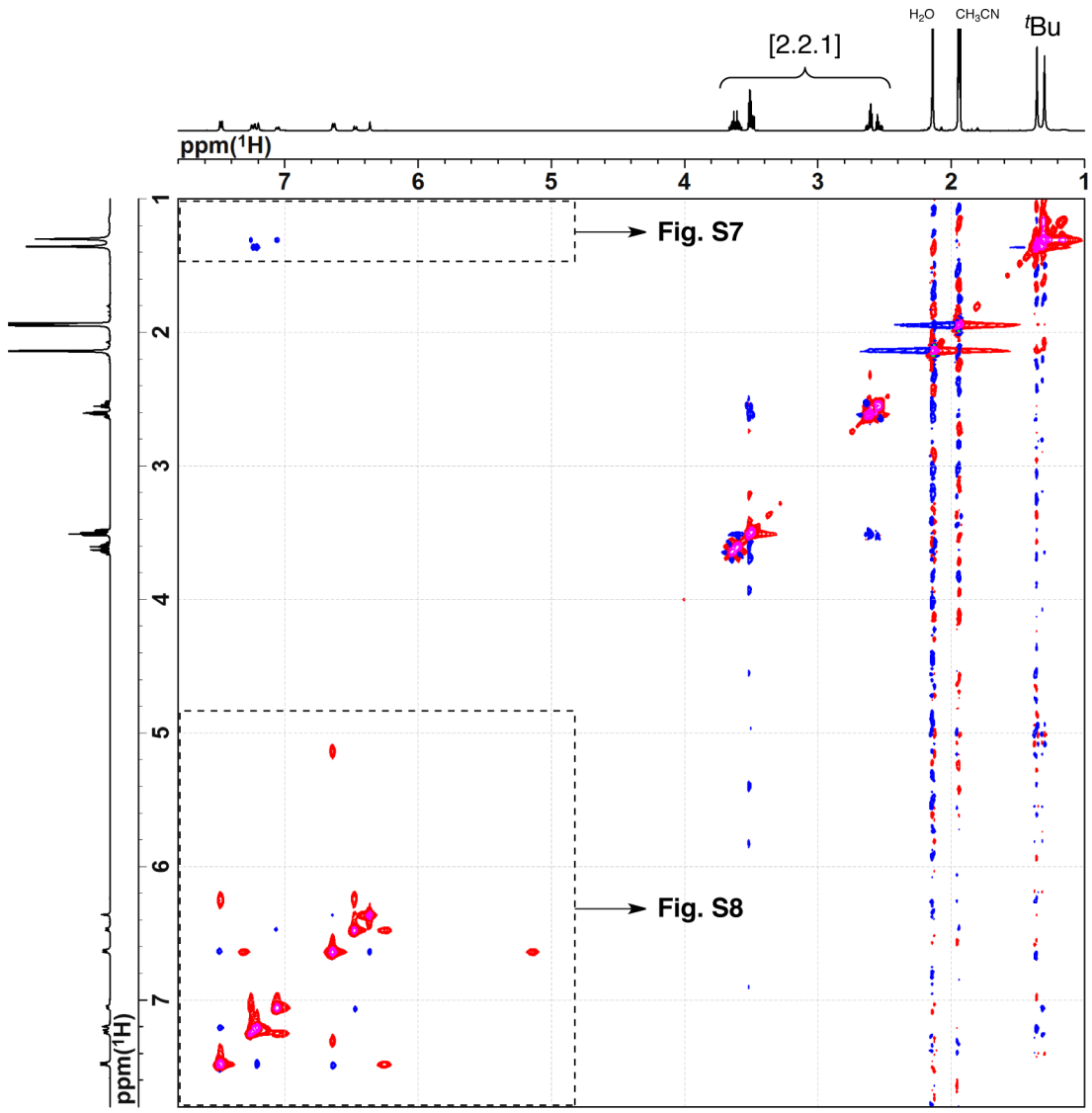

Fig. S6 NOESY spectrum of *cis*-**3** (*cis*-$\mathbf{3_C}$: *cis*-$\mathbf{3_E}$ = 10 : 90) (500 MHz, CD_3CN, 25 °C, 0.30 mM, mixing time = 500 ms) in the presence of 2 equiv. [2.2.1]. Red and blue cross-peaks denote the exchange ones between contracted *cis*-$\mathbf{3_C}$ and extended *cis*-$\mathbf{3_E}$ forms, and the intrastrand NOE ones for *cis*-$\mathbf{3_E}$, respectively.

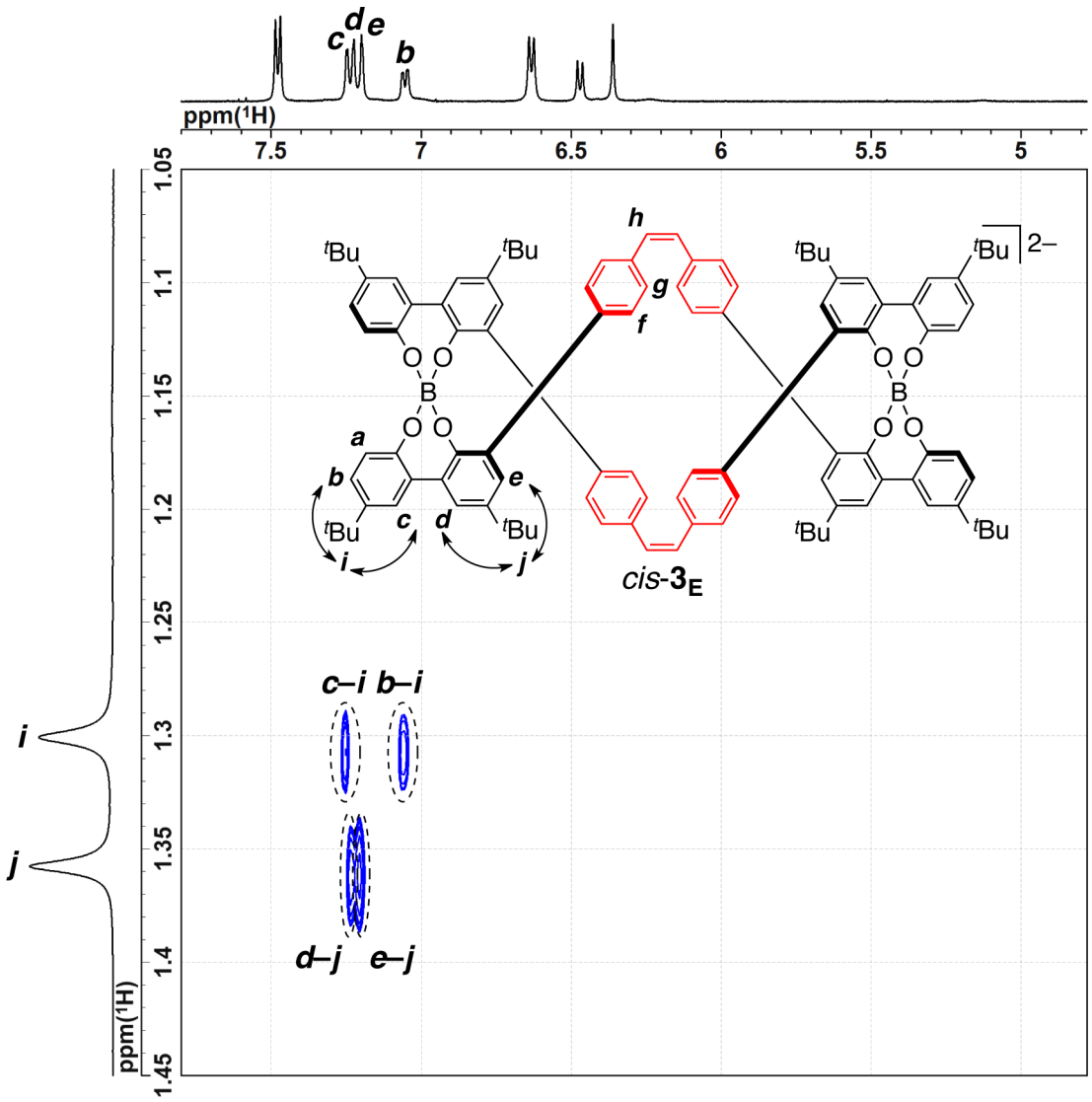

Fig. S7 Partial NOESY spectrum of *cis*-**3** (*cis*-$\mathbf{3_C}$: *cis*-$\mathbf{3_E}$ = 10 : 90) (500 MHz, CD_3CN, 25 °C, 0.30 mM, mixing time = 500 ms) in the presence of 2 equiv. [2.2.1].

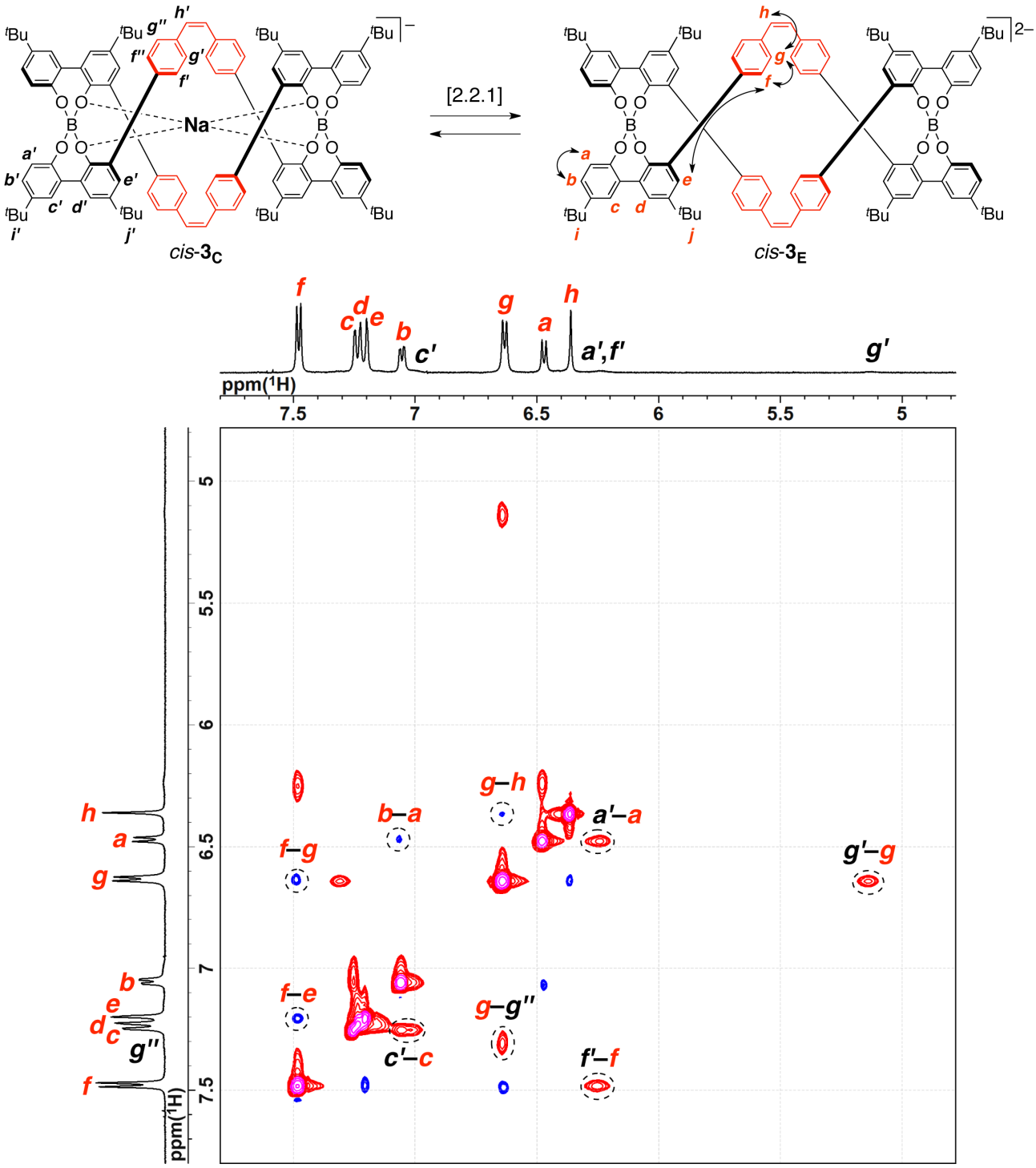

Fig. S8 Partial NOESY spectrum of *cis*-**3** (*cis*-$\mathbf{3_C}$: *cis*-$\mathbf{3_E}$ = 10 : 90) (500 MHz, CD_3CN, 25 °C, 0.30 mM, mixing time = 500 ms) in the presence of 2 equiv. [2.2.1]. Red and blue cross-peaks denote the exchange ones between contracted *cis*-$\mathbf{3_C}$ and extended *cis*-$\mathbf{3_E}$ forms, and the intrastrand NOE ones for *cis*-$\mathbf{3_E}$, respectively.

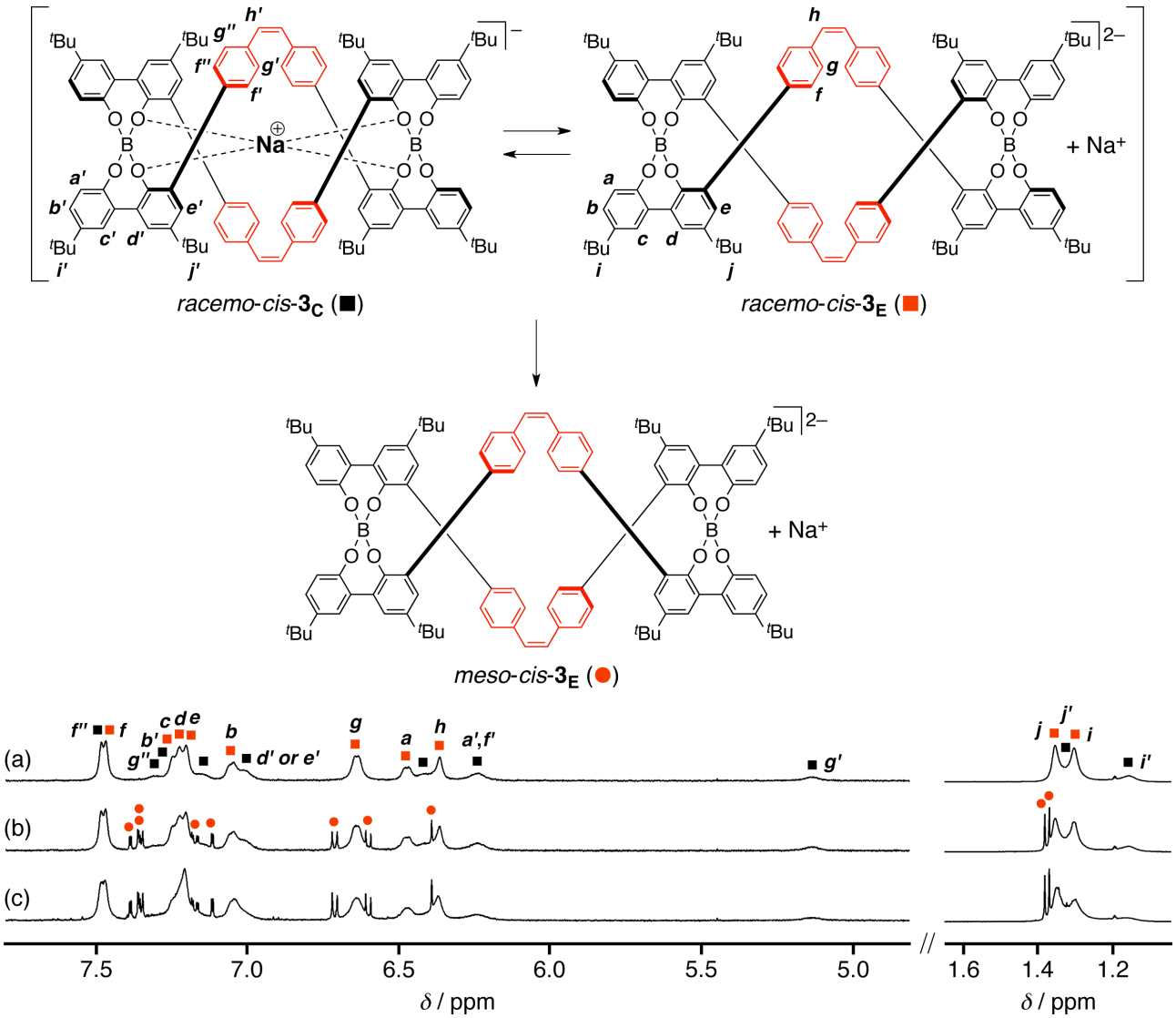

Fig. S9A Time-dependent ^{1}H NMR spectral changes of *cis*-**3** (500 MHz, CD_3CN, 25 °C, 0.31 mM) (a) after standing in CD_3CN for ca. 12 h (b) and 11.5 d (c). ■ and ■ denote the signals due to the contracted (*cis*-$\mathbf{3_C}$) and extended (*cis*-$\mathbf{3_E}$) forms, respectively. ● denotes the signals tentatively assigned to *meso*-*cis*-$\mathbf{3_E}$ (see Fig. S9B) whose contents for (b) and (c) were estimated to be ca. 10 and 12%, respectively, by the integral ratios of their ^{1}H NMR spectra (b and c in Fig. S9A).

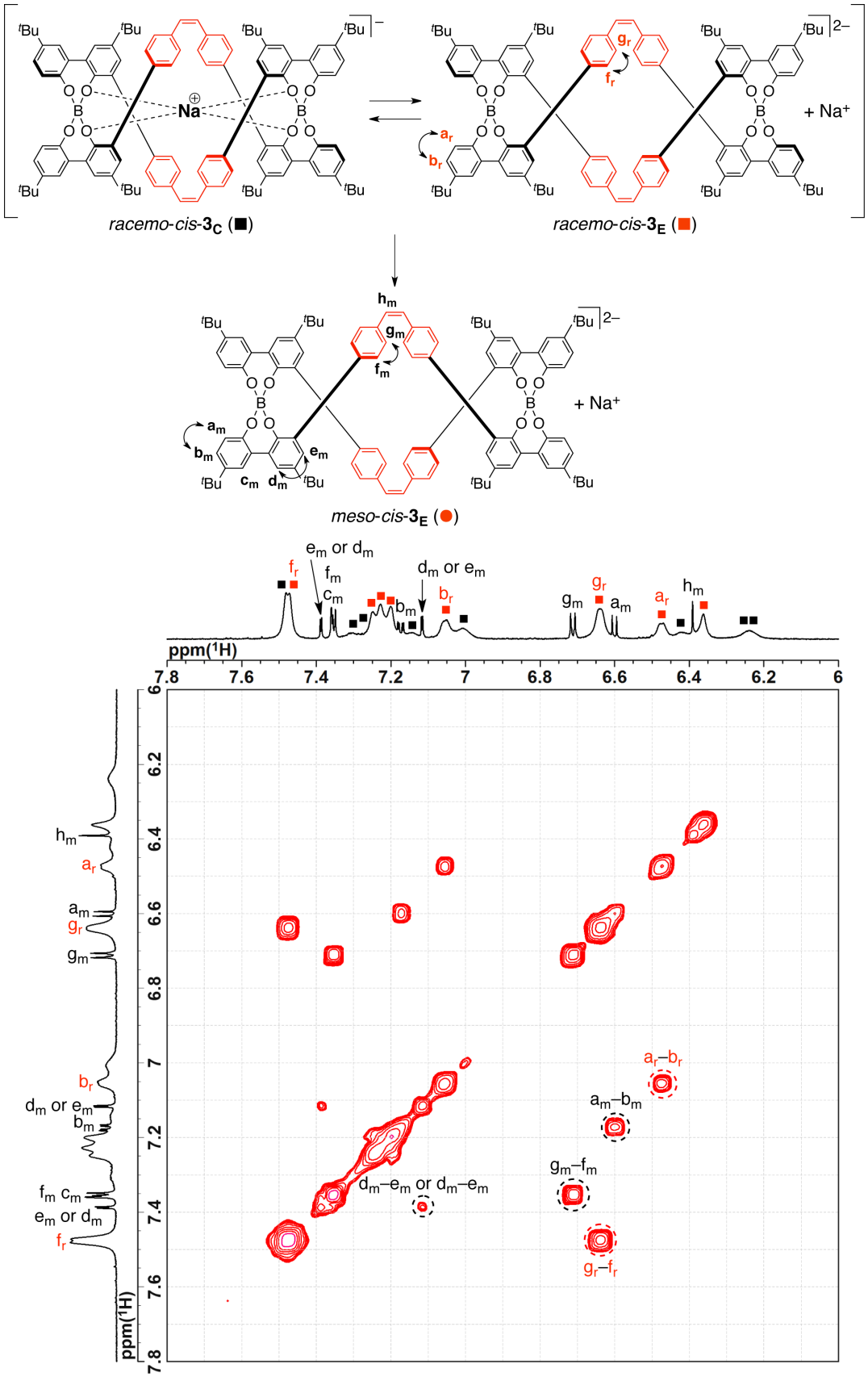

Fig. S9B Partial gCOSY spectrum of *cis*-**3** (700 MHz, CD_3CN, 25 °C, 0.31 mM) after standing in CD_3CN for ca. 36 h. ■ and ■ denote the signals due to the contracted (*cis*-$\mathbf{3_C}$) and extended (*cis*-$\mathbf{3_E}$) forms, respectively, and the signals due to *meso-cis*-$\mathbf{3_E}$ (ca. 12%) are tentatively assigned.

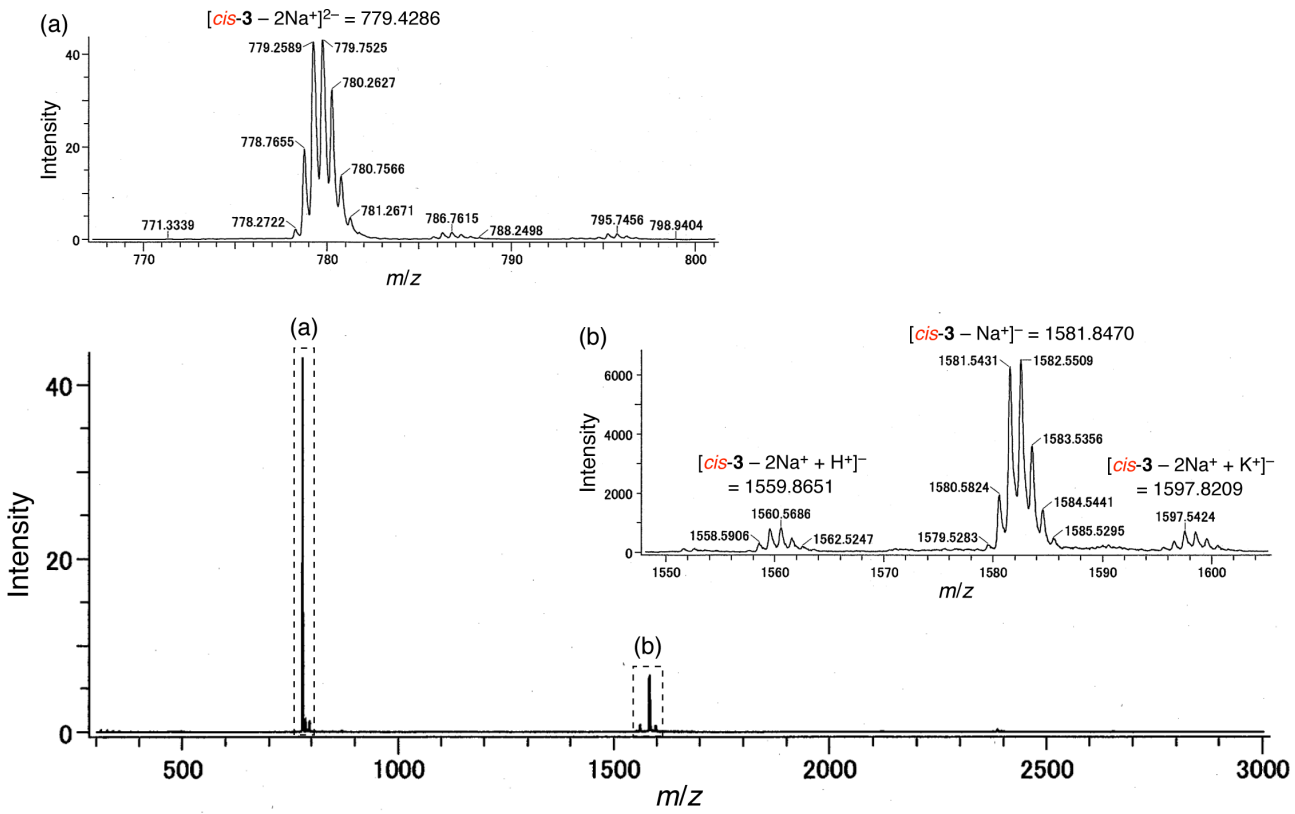

Fig. S10 Negative mode ESI-MS spectrum of *cis*-**3** (*racemo-cis*-$\mathbf{3_C}$: *racemo-cis*-$\mathbf{3_E}$: *meso-cis*-$\mathbf{3_E}$ = 21 : 67 : 12) (see Fig. S9Ac) measured after standing in CD_3CN for ca. 11.5 d at ambient temperature using CH_3CN as the eluent.

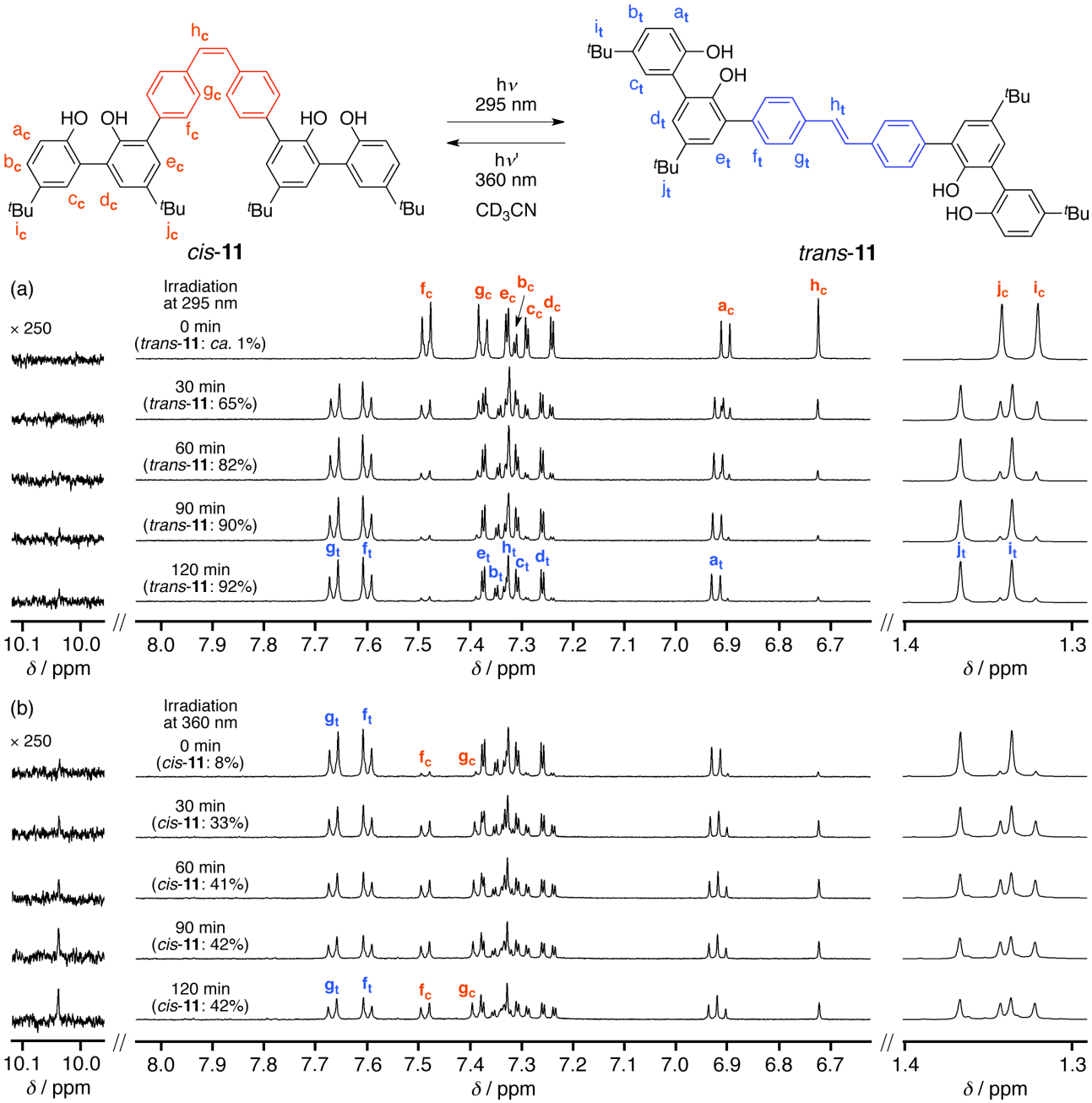

Fig. S11 (a) Time-dependent ^{1}H NMR spectral changes of *cis*-**11** (0.65 mM) in CD_3CN at 25 °C during the *cis*-to-*trans* isomerisation upon irradiation of UV light at 295 nm. (b) Time-dependent ^{1}H NMR spectral changes of 92% *trans*-**11** obtained from *cis*-**11** (a) in CD_3CN at 25 °C during the *trans*-to-*cis* isomerisation upon irradiation of UV light at 360 nm under air. A trace amount of photooxidised aldehydes (ca. 2%) was produced after irradiation of UV light at 360 nm for 120 min.

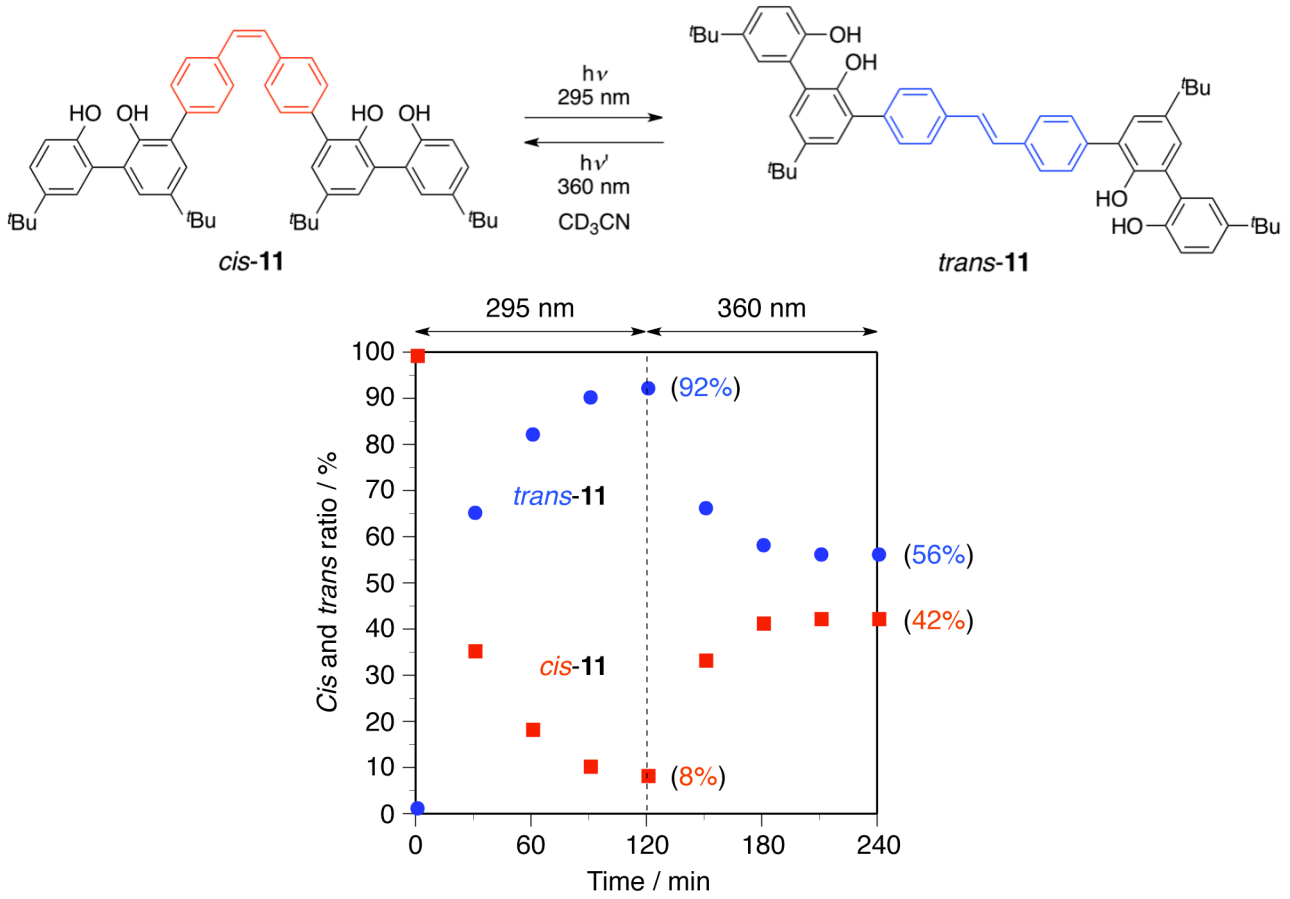

Fig. S12 Time-dependent changes in the *cis* and *trans* ratio determined by ^{1}H NMR (see Fig. S11) during the photoisomerisation of *cis*-**11** (0.65 mM) in CD_3CN at ambient temperature upon irradiation of UV light at 295 nm, followed by irradiation at 360 nm under air.

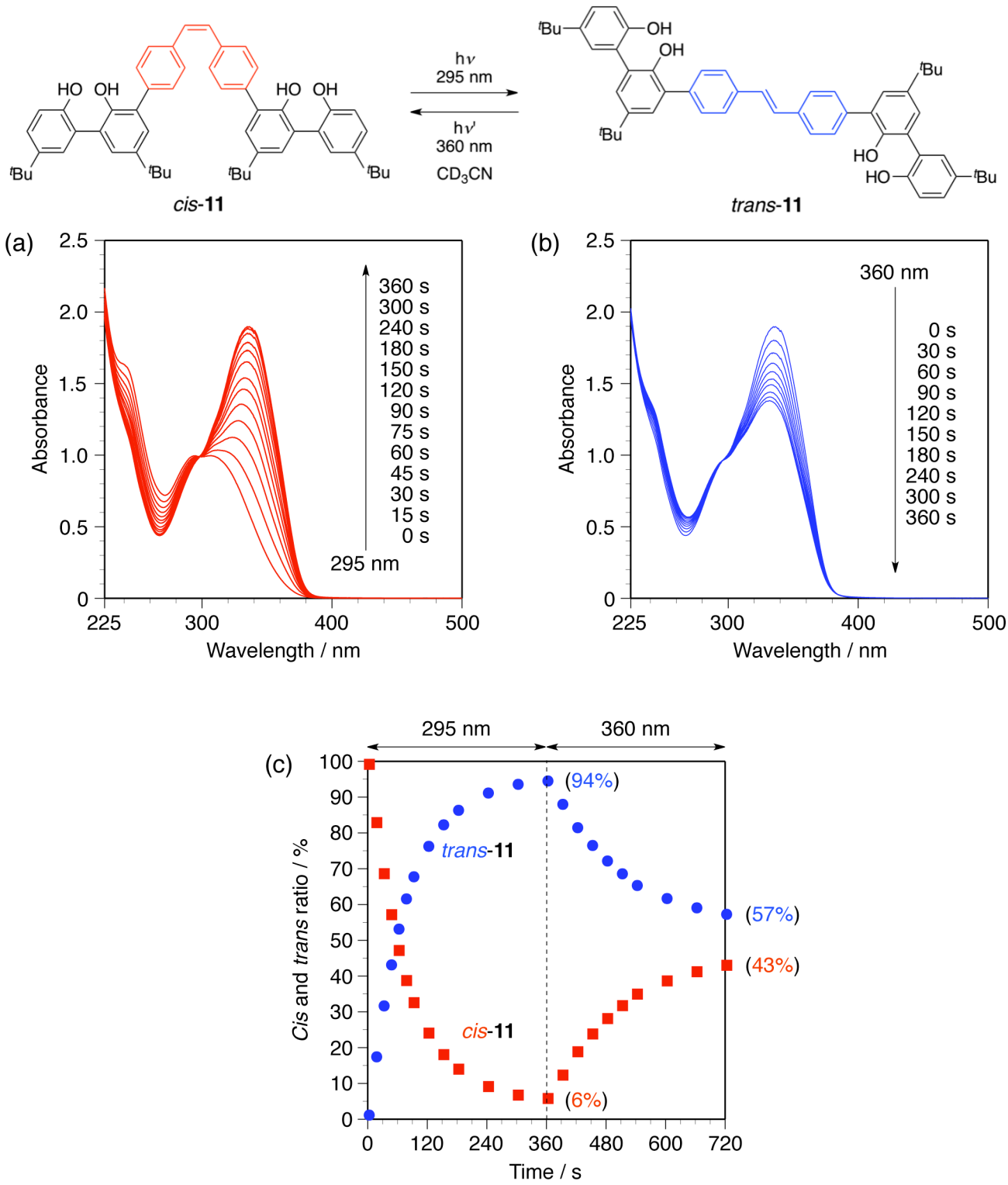

Fig. S13 (a) Time-dependent absorption spectral changes of *cis*-**11** (0.037 mM) in CD_3CN at ambient temperature during the *cis*-to-*trans* isomerisation upon irradiation of UV light at 295 nm. (b) Time-dependent absorption spectral changes of *trans*-**11** (94%) obtained from *cis*-**11** (a) in CD_3CN at ambient temperature during the *trans*-to-*cis* isomerisation upon irradiation of UV light at 360 nm. (c) Changes in the *cis* and *trans* ratio during the photoisomerisation of *cis*-**11** (0.037 mM) in CD_3CN at ambient temperature upon irradiation of UV light at 295 nm, followed by irradiation at 360 nm under air (see (a) and (b)).

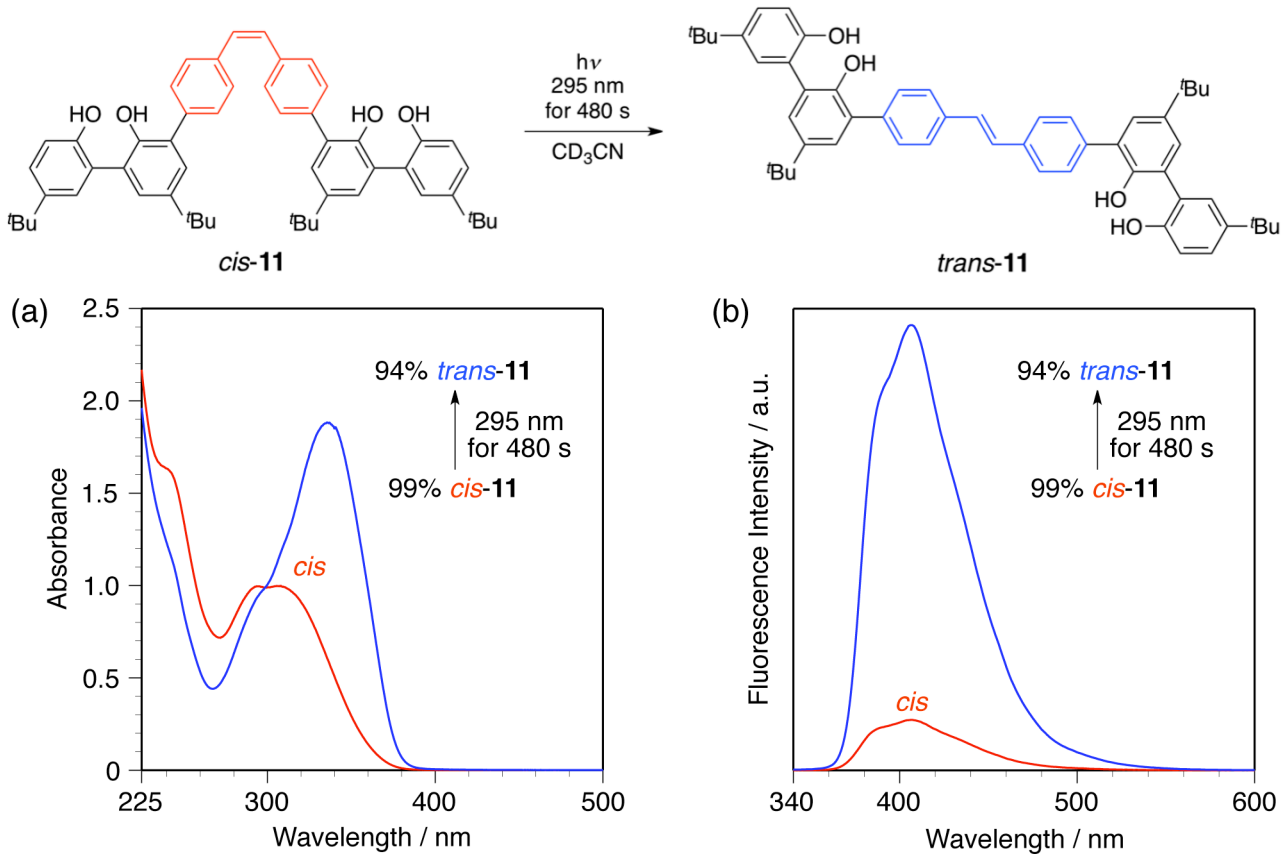

Fig. S14 Absorption (a) and fluorescence (b) spectra of *cis*-**11** (0.037 mM) in CD_3CN at ambient temperature before (red) and after (blue) irradiation of UV light at 295 nm for 480 s. Excited wavelength: 335 nm.

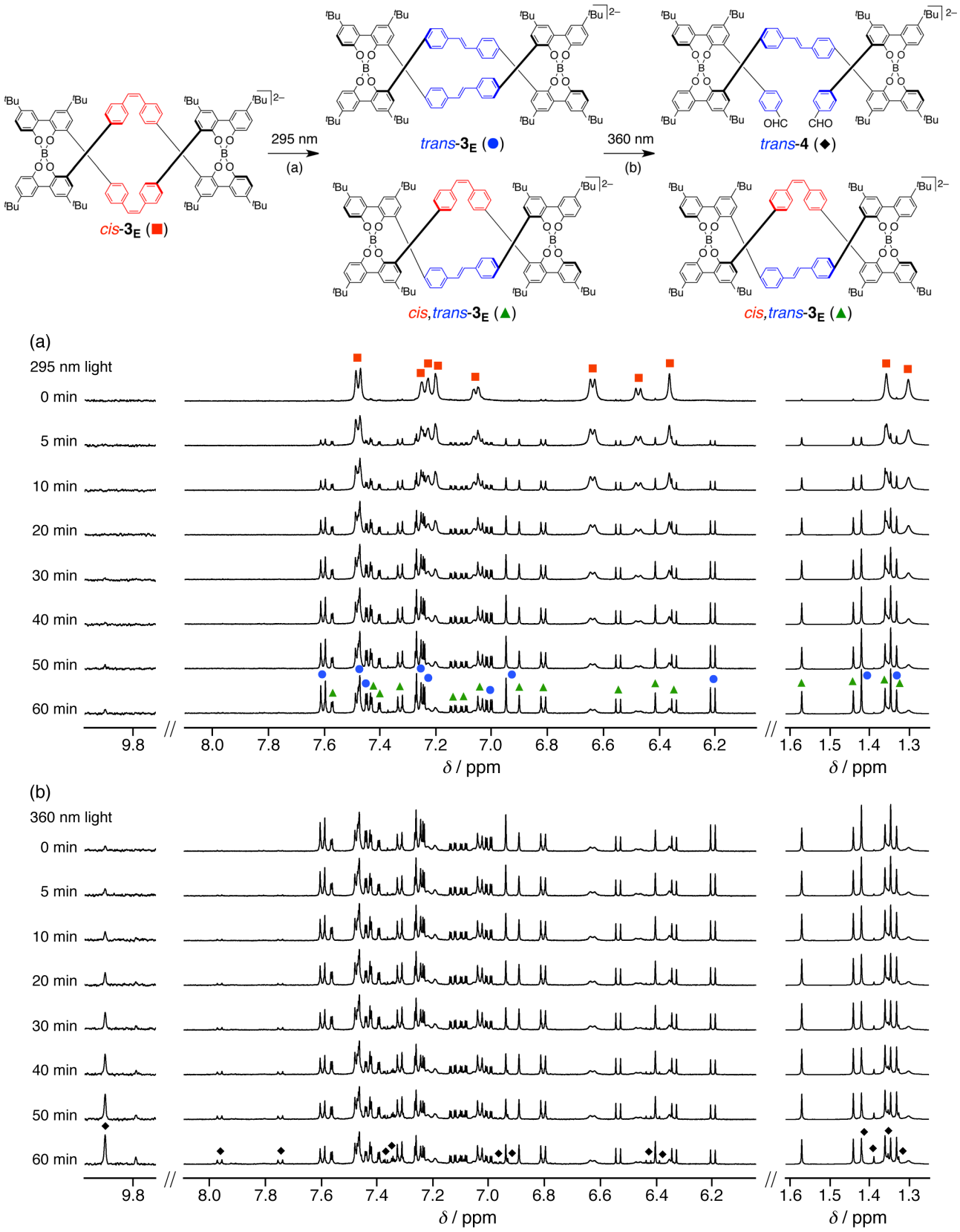

Fig. S15 (a) Time-dependent ^{1}H NMR spectral changes of *cis*-**3** (500 MHz, CD_3CN, 25 °C, 0.25 mM) in the presence of 2 equiv. [2.2.1] upon irradiation of UV light at 295 nm for 60 min, (b) followed by irradiation of UV light at 360 nm for 60 min under argon. The peak assignments were done on the basis of gCOSY and NOESY spectra (Figs. S17–S19).

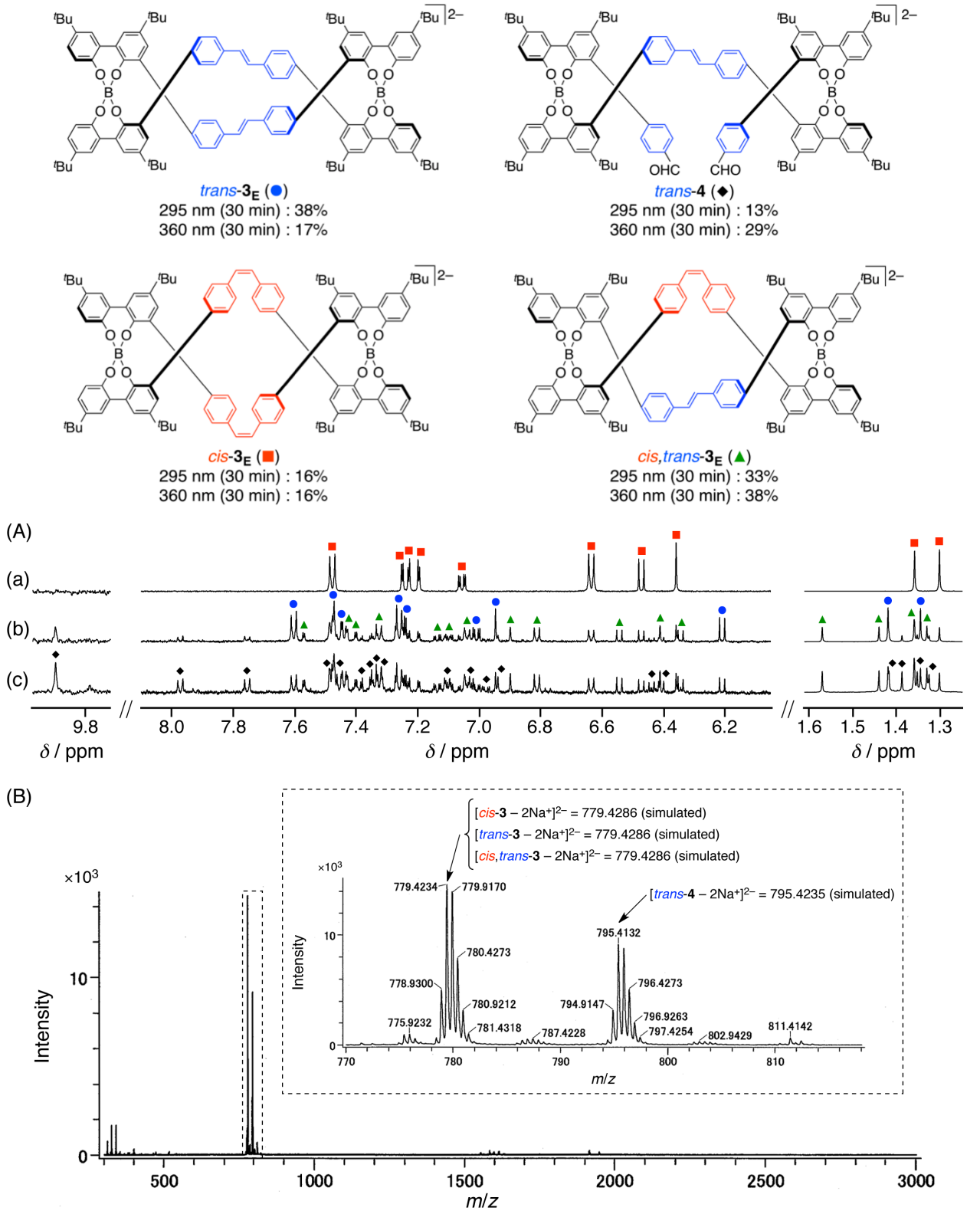

Fig. S16 (A) ^{1}H NMR spectra of *cis*-**3**$_E$ (0.17 mM) in the presence of 3 equiv. [2.2.1] in CD_3CN at 25 °C before (a) and after (b) irradiation of UV light at 295 nm for 30 min, followed by irradiation at 360 nm for 30 min under air (c). (B) Negative mode ESI-MS spectrum of the sample (c) using CH_3CN as the eluent. ■, ▲, ●, and ◆ denote the signals due to *cis*-**3**$_E$, *cis*,*trans*-**3**$_E$, *trans*-**3**$_E$, and *trans*-**4**, respectively. We note that photoirradiation of *cis*-**3** in air produced a larger amount of the photooxidised *trans*-**4**.

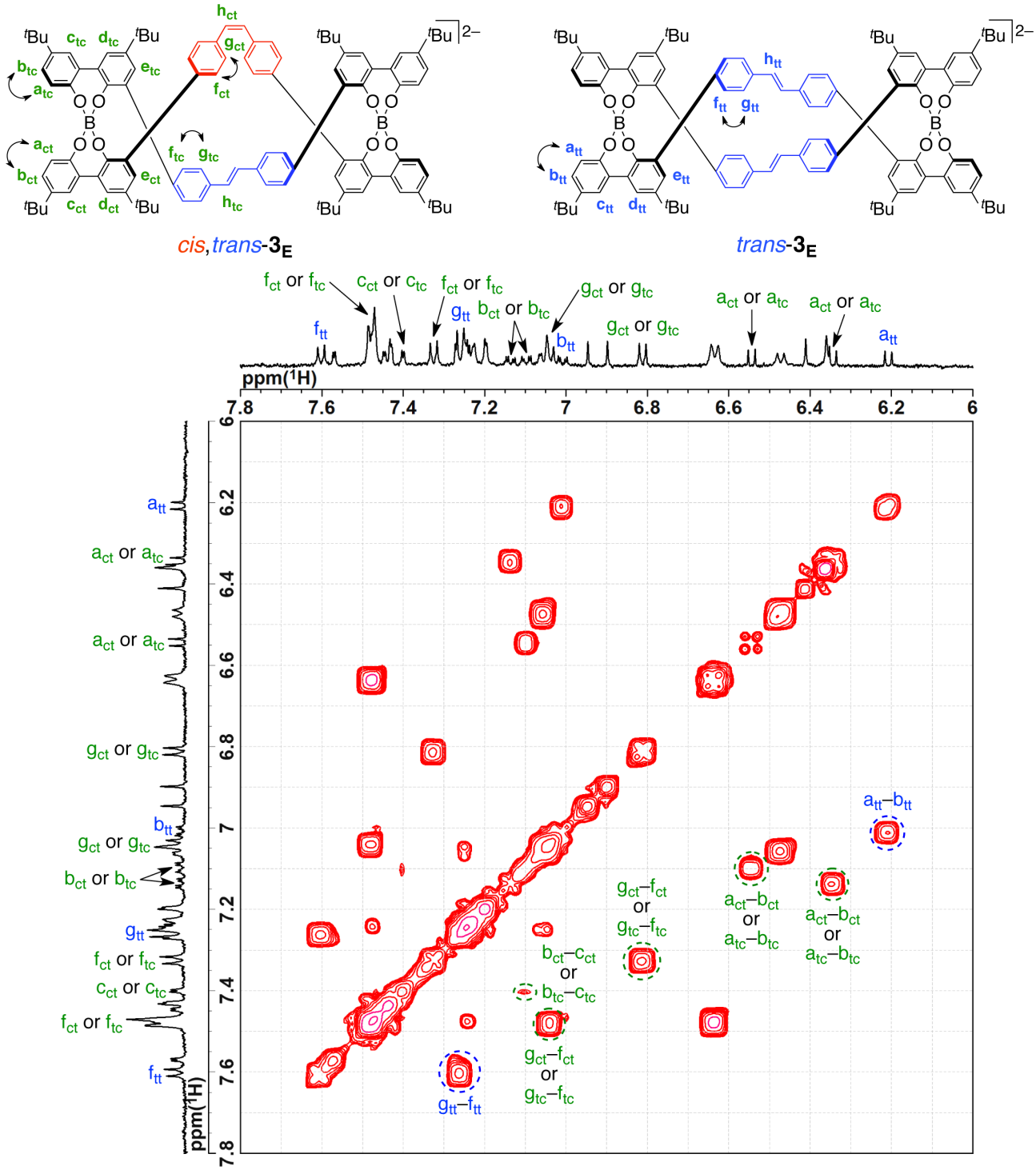

Fig. S17 gCOSY spectrum of *cis*-**3** (500 MHz, CD_3CN, 25 °C, 0.1 mM) in the presence of 2 equiv. [2.2.1] after irradiation of UV light at 295 nm for 180 min. The product contents were estimated to be 41 and 18% for *cis*,*trans*-$\mathbf{3_E}$ and *trans*-$\mathbf{3_E}$ on the basis of its ^{1}H NMR spectrum.

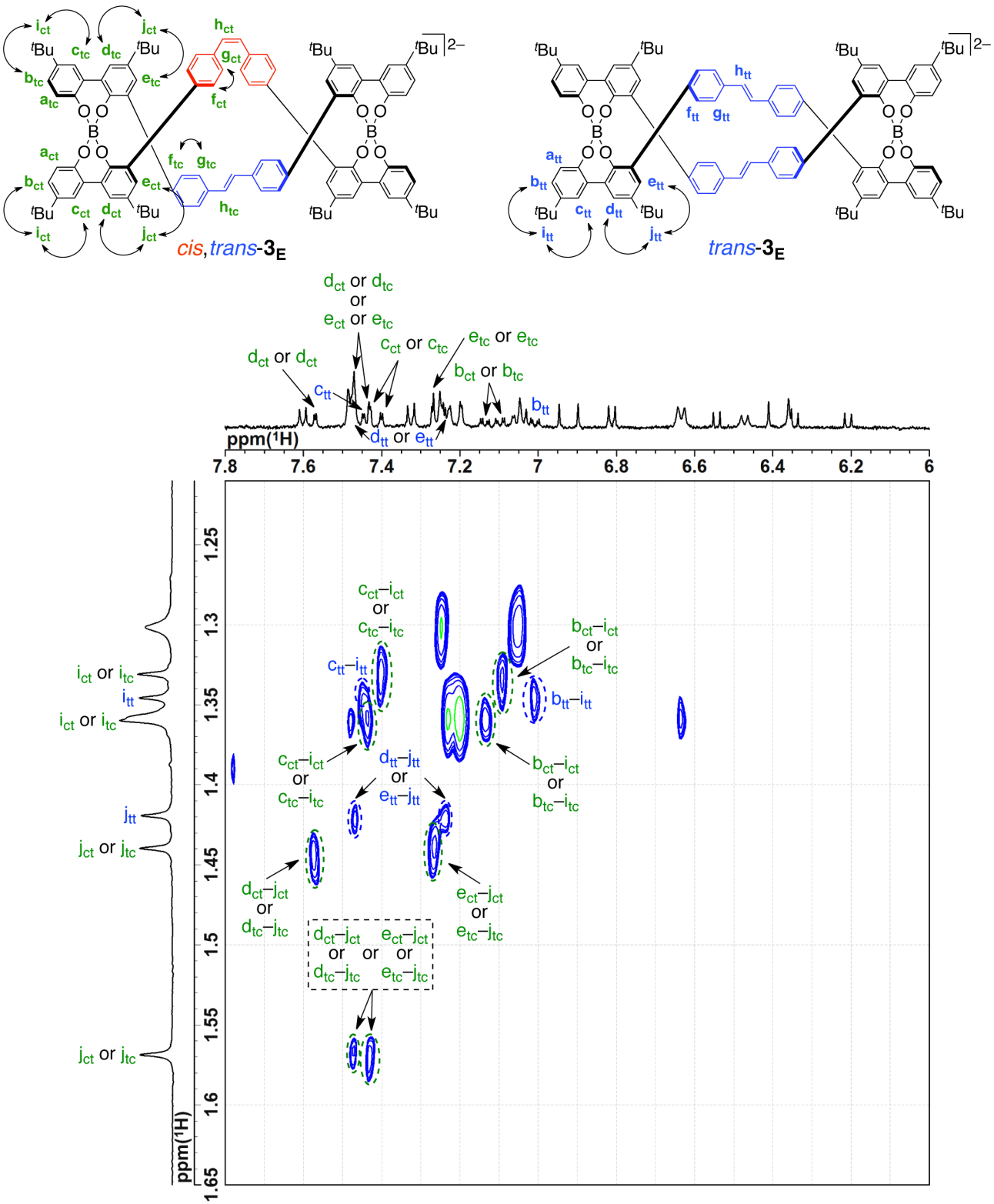

Fig. S18 Partial NOESY spectrum of *cis*-**3** (500 MHz, CD_3CN, 25 °C, 0.1 mM, mixing time = 500 ms) in the presence of 2 equiv. [2.2.1] after irradiation of UV light at 295 nm for 180 min. The product contents were estimated to be 41 and 18% for *cis*,*trans*-$\mathbf{3_E}$ and *trans*-$\mathbf{3_E}$ on the basis of its ^{1}H NMR spectrum.

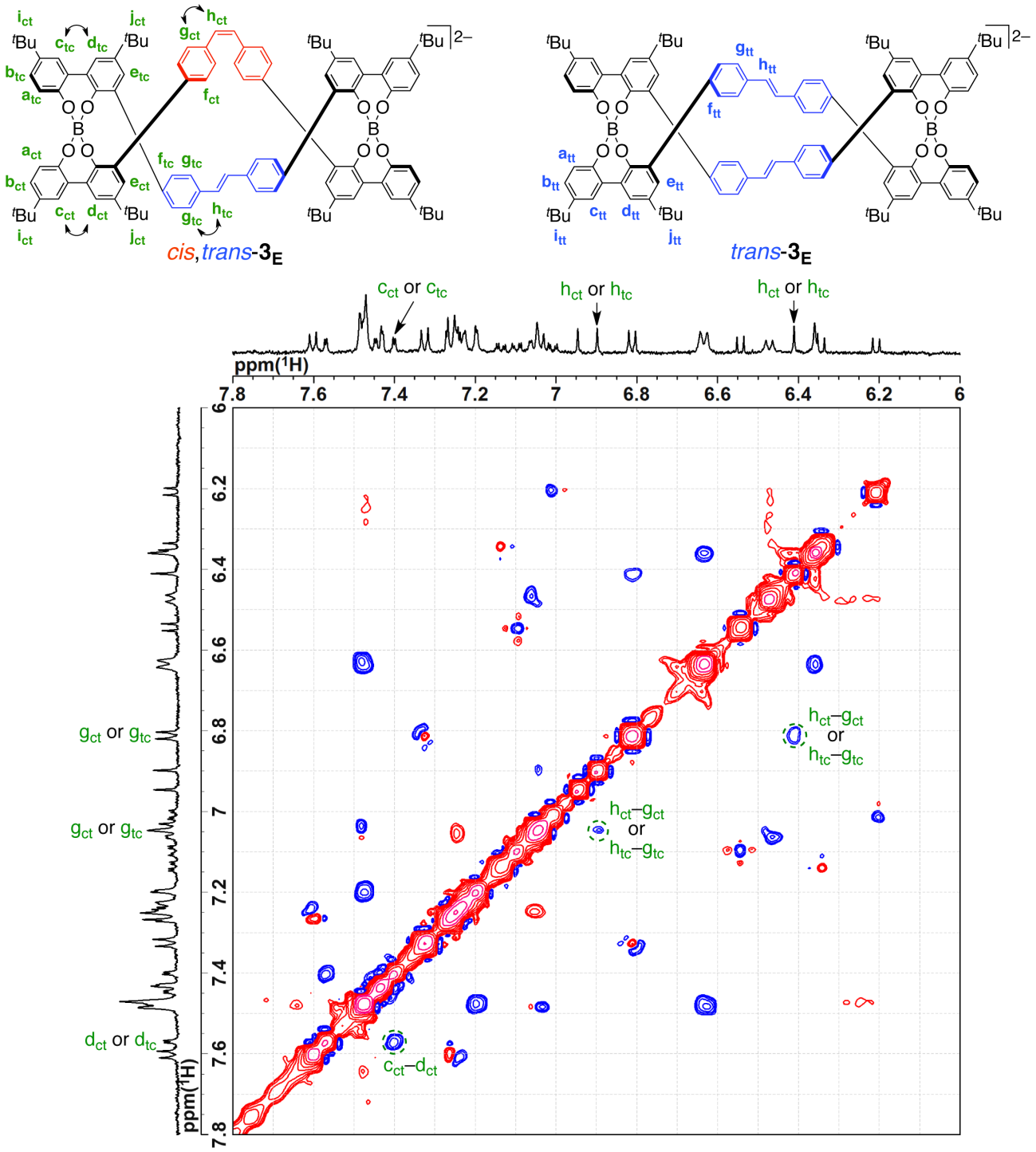

Fig. S19 Partial NOESY spectrum of *cis*-**3** (500 MHz, CD_3CN, 25 °C, 0.1 mM, mixing time = 500 ms) in the presence of 2 equiv. [2.2.1] after irradiation of UV light at 295 nm for 180 min. The product contents were estimated to be 41 and 18% for *cis*,*trans*-$\mathbf{3_E}$ and *trans*-$\mathbf{3_E}$ on the basis of its ^{1}H NMR spectrum.

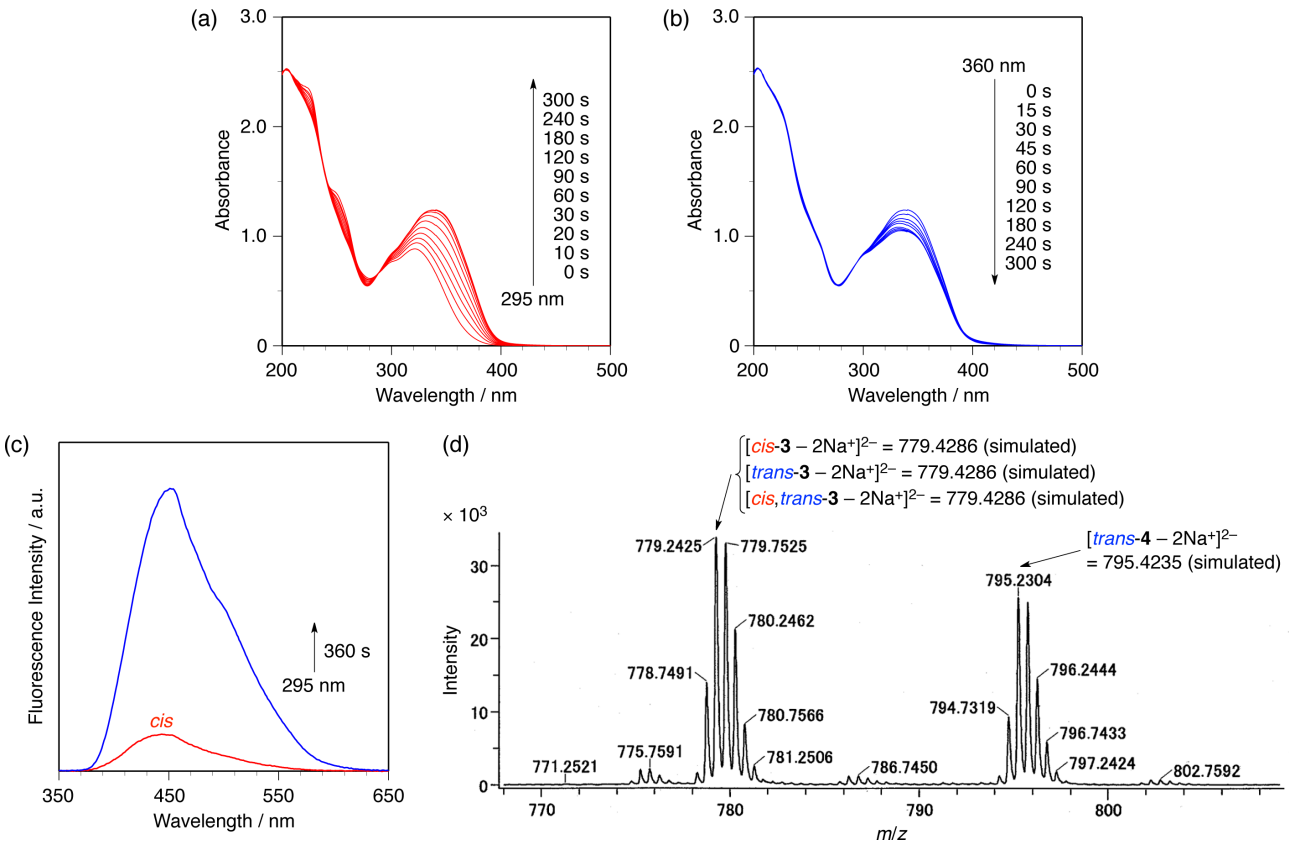

Fig. S20 (a) Time-dependent absorption spectral changes of *cis*-**3** (0.016 mM) in the presence of 3 equiv. [2.2.1] in CH_3CN at ambient temperature during the *cis*-to-*trans* isomerisation upon irradiation of UV light at 295 nm. (b) Time-dependent absorption spectral changes of the sample after irradiation at 295 nm for 300 s in CH_3CN at ambient temperature during the *trans*-to-*cis* isomerisation upon irradiation of UV light at 360 nm. (c) Fluorescence spectra of *cis*-**3** (0.016 mM) in the presence of 3 equiv. [2.2.1] in CH_3CN at 25 °C before (red) and after (blue) irradiation of UV light at 295 nm for 360 s. Excited wavelength: 340 nm. (d) Negative ESI-MS spectrum of the sample (b) after irradiation of UV light at 360 nm for 300 s.

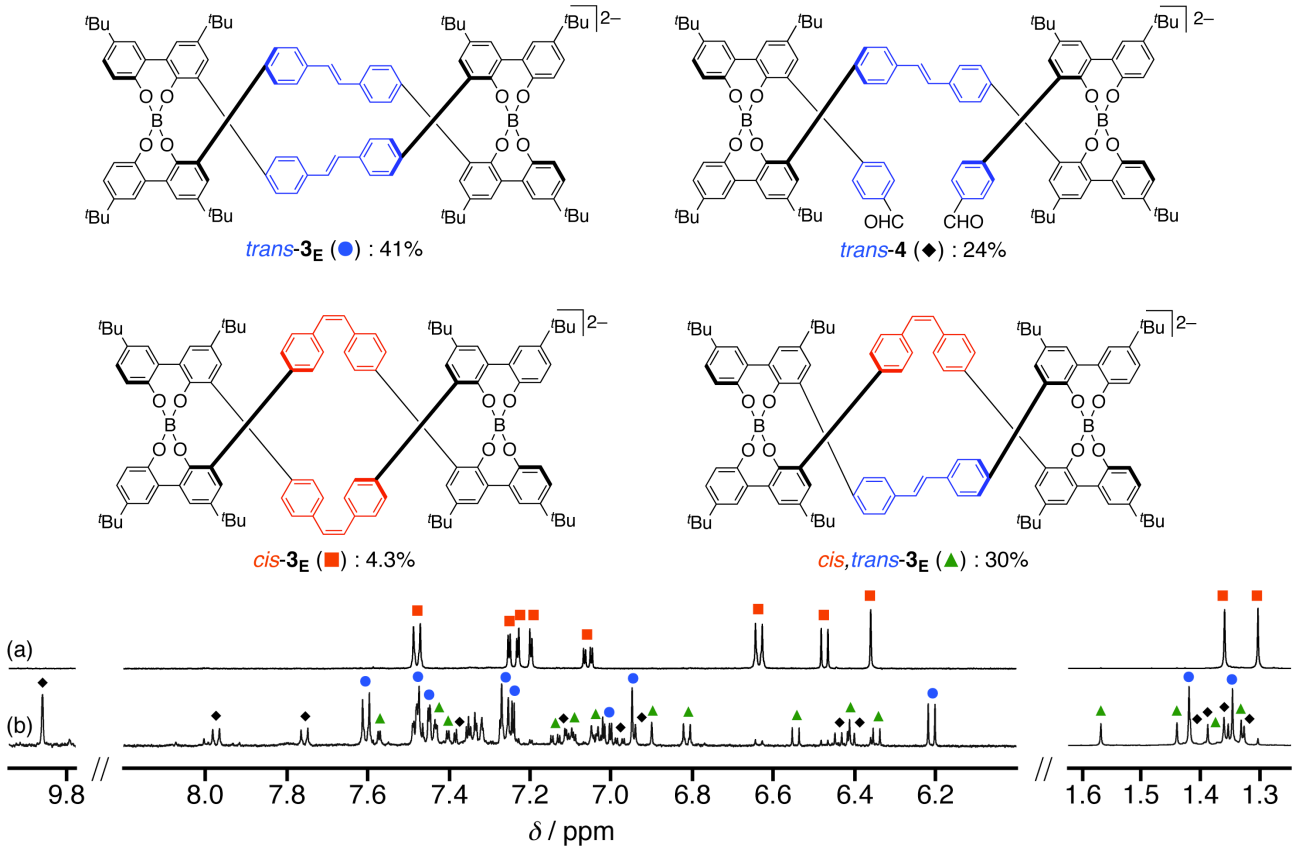

Fig. S21 ^{1}H NMR spectra (CD_3CN, 25 °C, 0.20 mM) of *racemo-cis*-$\mathbf{3_E}$ in the presence of 7 equiv. [2.2.1] before (a) and after (b) irradiation of UV light at 295 nm for 90 min under air. We note that photoirradiation of *cis*-**3** in air produced a larger amount of the photooxidised *trans*-**4**. The sample (b) was further subjected to chiral HPLC analysis (see Fig. 4). The product ratio determined by ^{1}H NMR (b) is also shown.