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All-Visible-Light-Driven Stiff-stilbene Photoswitches

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1. General methods and materials.

All commercial reagents from Acros, Aldrich, TCI and Merck were used as received. All dry solvents used in the reactions were from an MBraun SPS-800 solvent purification system or purchased from Acros. Analytical TLCs were performed on Merck silica gel 60 F254 plates, and visualization was accomplished by UV light. Solvents used for irradiation experiments were degassed by purging with argon for 2 min prior to use. Column chromatography was performed on a Reveleris X2 Flash Chromatography system. Supercritical fluid chromatography (SFC) was carried out on the TharSFC system with a Chiralpak® ID column (4.6×250 mm, particle size: 5 µm). NMR spectra were recorded at 25 °C on Varian AMX400 (^{1}H: 400 MHz, ^{13}C: 101 MHz) and Varian Unity Plus (^{1}H: 500 MHz, ^{13}C: 126 MHz) spectrometers. Chemical shifts (δ) are expressed relative to the resonances of the residual non-deuterated solvent for ^{1}H NMR [$CDCl_3$: ^{1}H(δ) = 7.26 ppm, CD_2Cl_2: ^{1}H(δ) = 5.32 ppm] and ^{13}C NMR [$CDCl_3$: ^{13}C(δ) = 77.2 ppm, CD_2Cl_2: ^{13}C (δ) = 53.5 ppm]. Absolute values of the coupling constants are given in Hertz (Hz), regardless of their sign. Multiplicities are abbreviated as singlet (s), doublet (d), doublet of doublets (dd), triplet (t), triplet of doublets (td), quartet (q), multiplet (m), and broad (br). High-resolution mass spectrometry (HRMS) was performed on an LTQ Orbitrap XL spectrometer with ESI or APCI ionization. All reactions were performed under anhydrous conditions under N_2 atmosphere. UV-vis spectra were recorded on a Hewlett-Packard HP 8543 Diode Array in a 1 cm path length. Irradiation of samples was carried out at 298 K using the Thorlabs model M365F1, M395F1, 405FP1, 420 F1, 455F1 LED positioned at a distance of 1 cm from the samples. Large-scale photoisomerizations were performed in an Acceled Photoreactor m2.

X-ray analysis

Stiff-stilbenes **S1**, **S5** and **S6** were crystallized by slow evaporation of a concentrated solution of the compounds in CH_2Cl_2. A single crystal was mounted on a cryoloop and analyzed on a Bruker-AXS D8 Venture diffractometer. The data collection was done at room temperature under ambient conditions. The Bruker APEX4 software suite was used for data collection and processing, and the structure was solved using SHELXT.[1] Refinement was performed using SHELXL[2] in the OLEX2[3] software package. No A- or B- level alerts were raised by CheckCIF for the fully refined structures.

Nanosecond transient absorption spectroscopy

Nanosecond transient absorption spectra were recorded with an in-house assembled setup. A flow setup was used in which the the solution was passed through a flow cuvette during the measurements. A different excitation wavelength (340 - 455 nm) was used depending on the absorption spectrum of the sample. The excitation wavelength was generated using a tunable Nd:YAG-laser system (NT342B, Ekspla) comprising the pump laser (NL300) with harmonics generators (SHG, THG) producing 355 nm to pump an optical parametric oscillator (OPO) with SHG connected in a single device. The laser system was operated at a repetition rate of 10 Hz with a pulse length of 5 ns. The probe light running at 20 Hz was generated by a high-stability short arc xenon flash lamp (FX-1160, Excelitas Technologies) using a modified PS302 controller (EG&G). Using a 50/50 beam splitter, the probe light was split equally into a signal beam and a reference beam and focused (bi-convex lens 75mm) on the entrance slit of a spectrograph (SpectraPro-150, Princeton Instruments) with a grating of 150 ln/mm and blazed at 500 nm. The probe beam (A = 1 mm^2) was passed through the sample cell and orthogonally overlapped with the excitation beam on a 1 mm × 1 cm area. In order to correct for fluctuations in the flash lamp spectral intensity, the reference was used to normalize the signal. Both beams were recorded simultaneously using a gated intensified CCD camera (PI-MAX3, Princeton Instruments) which has an adjustable gate of minimal 2.9 ns. Normally a gate of 20 ns and software binning are used to improve the dynamic range and signal-to-noise ratio. Two delay generators (DG535 and DG645, Stanford Research Systems, Inc.) were used to trigger the excitation and to change the delay of the flash lamp together with the gate of the camera during the experiment. The setup was controlled by an in-house written Labview program. The data was fitted via global analysis using the Glotaran 1.5.1 software package.[4]

2. Synthesis.

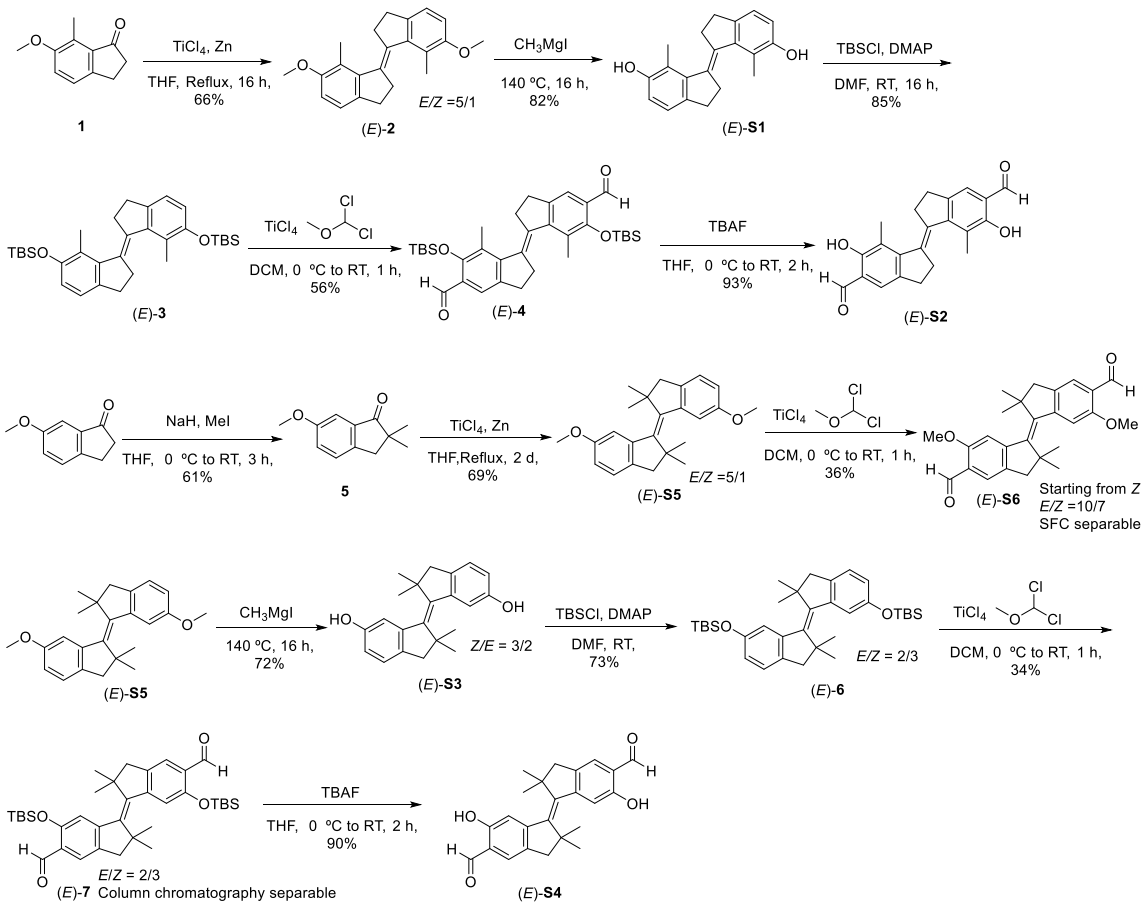
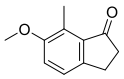


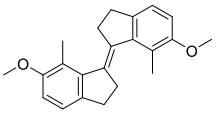
Figure S1. Synthesis of stiff-stilbene derivatives **S1-6**.

6-methoxy-7-methyl-2,3-dihydro-1H-inden-1-one (1)



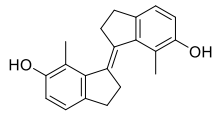
Compound **1** was synthesized as described in the literature.[5] ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.23 (d, *J* = 8.2 Hz, 1H), 7.08 (d, *J* = 8.2 Hz, 1H), 3.86 (s, 3H), 3.05 – 2.97 (m, 2H), 2.73 – 2.64 (m, 2H), 2.54 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 208.5, 157.0, 147.5, 135.3, 127.0, 124.0, 117.0, 56.5, 37.9, 24.5, 10.1. HRMS (APCI) calcd. for $[M+H]^+$: 178.0944, found: 178.0952.

(E)/(Z)-6,6'-dimethoxy-7,7'-dimethyl-2,2',3,3'-tetrahydro-1,1'-biindenylidene ((*E*)/(*Z*)-2)



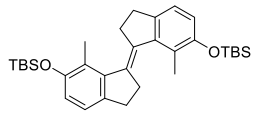
To a suspension of Zn powder (5.5 g, 84.0 mmol) in anhydrous THF (120 mL) was added $TiCl_4$ (4.6 mL, 42. mmol). After heating at reflux for 2 h, compound **1** (3.5 g, 20.0 mmol) was added to the reaction mixture, and the mixture was heated at reflux for 16 h. After cooling to room temperature, the reaction mixture was treated with a saturated aqueous solution of NH_4Cl, followed by extraction with EtOAc. The organic layer was washed with brine and dried over Na_2SO_4. The solution was concentrated *in vacuo* and purified by column chromatography (SiO_2, pentane/EtOAc = 19/1) to afford **2** as an *E/Z* mixture with a ratio of 5:1 (2.1 g, 66%) as a white solid. *E*-**2** (1.7 g, 53%) was obtained by crystalizing in a pentane/CH_2Cl_2 (10/1) mixture. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.09 (d, J = 8.0 Hz, 2H), 6.78 (d, J = 8.0 Hz, 2H), 3.88 (s, 6H), 2.87-2.53 (m, 8H), 2.24 (s, 6H). 13C NMR (101 MHz, CDCl3) δ 157.4, 144.1, 138.4, 137.6, 122.3, 121.7, 109.2, 56.1, 38.5, 31.8, 15.7. HRMS (APCI) calcd. for $[M+H]^+$: 321.1849, found: 321.1865.

(*E*)-7,7'-dimethyl-2,2',3,3'-tetrahydro-[1,1'-biindenylidene]-6,6'-diol ((*E*)/(*Z*)-S1)



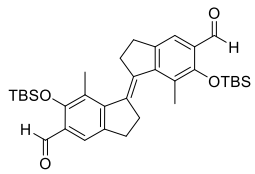
To (*E*)-**2** (1.3 g, 4.0 mmol) was added a solution of CH_3MgI (3 M in Et_2O, 8.0 mL, 24.0 mmol). The mixture was heated to 140 °C, while the solvent was evaporated via a needle in the septum. Once the solvent completely evaporated, the needle was removed, and the mixture was heated at 140 °C for 16 h. After cooling to room temperature, the spongy solid was quenched with ice and a saturated aqueous solution of NH_4Cl, followed by extraction with EtOAc. The organic layer was washed with brine and dried over anhydrous Na_2SO_4. The solution was concentrated *in vacuo* and purified by column chromatography (SiO_2, pentane/EtOAc = 4/1) to afford (*E*)-**S1** (960.0 mg, 82%) as a white solid. ^{1}H NMR (400 MHz, DMSO-d_6) δ 9.11(s, 2H), 6.89 (d, J = 7.9 Hz, 2H), 6.70 (d, J = 7.9 Hz, 2H), 2.72-2.33 (t, J = 5.9 Hz, 8H, overlap with DMSO-d_6), 2.09 (s, 6H).^{13}C NMR (151 MHz, DMSO-d_6) δ 154.6, 143.1, 136.6, 135.8, 121.6, 119.3, 113.6, 37.8, 31.1, 15.5. HRMS (APCI) calcd. for $[M+H]^+$: 294.1570, found: 294.1588.

(*E*)-((7,7'-dimethyl-2,2',3,3'-tetrahydro-[1,1'-biindenylidene]-6,6'-diyl)bis(oxy))bis(tert-butyldimethylsilane) ((*E*)-3)



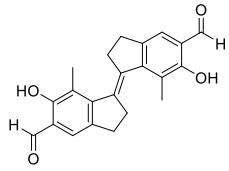
To a DMF (20 mL) solution of (*E*)-**S1** (584.0 mg, 2.0 mmol) was added 4-dimethylaminopyridine (586 mg, 4.8 mmol) and *tert*-butyldimethylsilyl chloride (664.0 mg, 4.4 mmol), and the mixture was stirred overnight at room temperature. After the reaction was complete, a saturated aqueous solution of NH_4Cl was added, and the aqueous phase was extracted with EtOAc. The organic layer was washed with brine, dried over Na_2SO_4, and concentrated *in vacuo*. The crude product was purified by column chromatography (SiO_2, pentane) to afford compound (*E*)-**3** (883 mg, 85% yield) as a white solid. ^{1}H NMR (400 MHz, $CDCl_3$) δ 6.97 (d, *J* = 7.9 Hz, 2H), 6.69 (d, *J* = 7.9 Hz, 2H), 2.75 (s, 8H), 2.19 (s, 6H), 1.04 (s, 18H), 0.24 (s, 12H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 153.3, 144.4, 138.9, 137.6, 124.7, 121.7, 117.4, 38.5, 32.0, 26.0, 18.5, 16.6, -4.0. HRMS (ESI^+) calcd. for $[M]^+$: 521.3221, found: 521.3261.

(*E*)-6,6'-bis((tert-butyldimethylsilyl)oxy)-7,7'-dimethyl-2,2',3,3'-tetrahydro-[1,1'-biindenylidene]-5,5'-dicarbaldehyde ((*E*)-4)



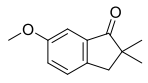
To a CH_2Cl_2 (10 mL) solution of (*E*)-**3** (104 mg, 0.2 mmol) was added $TiCl_4$ (132 µL, 1.2 mmol) at 0 °C, and the mixture was stirred for 20 min. Then the dichloro(methoxy)methane (180 µL, 2.0 mmol) was added to the mixture, which was stirred at room temperature for 30 min. After the reaction was complete, a saturated aqueous solution of NH_4Cl was added, and the aqueous phase was extracted with CH_2Cl_2. The organic layer was washed with brine, dried over Na_2SO_4, and concentrated *in vacuo*. The crude product was purified by (SiO_2, pentane/EtOAc = 19/1) to afford compound (*E*)-**4** (65 mg, 112 µmol, 56% yield) as a yellow solid**.** ^{1}H NMR (400 MHz, $CDCl_3$) δ 10.32 (s, 2H), 7.57 (s, 2H), 2.69 (d, *J* = 141.9 Hz, 8H), 2.21 (s, 6H), 1.09 (s, 18H), 0.22 (s, 12H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 190.6, 157.4, 150.1, 140.2, 140.0, 126.99, 126.4, 120.5, 38.3, 31.8, 26.1, 18.8, 16.9, -3.6.

(*E*)-6,6'-dihydroxy-7,7'-dimethyl-2,2',3,3'-tetrahydro-[1,1'-biindenylidene]-5,5'-dicarbaldehyde ((*E*)-S2)



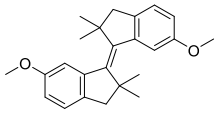
To a THF (5 mL) solution of (*E*)-**4** (60 mg, 104 µmol) was added a TBAF solution (1 M in THF, 0.3 mL, 0.3 mmol) at 0 °C. After stirring at room temperature for 2 h, the mixture was quenched with water and extracted with CH_2Cl_2. The organic layer was washed with brine, dried over Na_2SO_4, and concentrated *in vacuo*. The crude product was purified by column chromatography (SiO_2, pentane/EtOAc = 9/1) to afford compound (*E*)-**S2** (34 mg, 97 µmol, 93% yield) as a yellow solid**.** ^{1}H NMR (500 MHz, CD_2Cl_2) δ 11.53 (s, 2H), 9.82 (s, 2H), 7.28 (s, 2H), 2.98-2.46 (m, 8H), 2.23 (s, 6H).^{13}C NMR (126 MHz, $CDCl_3$) δ 196.17, 160.4, 140.8, 137.2, 125.6, 122.4, 119.1, 38.2, 31.4, 14.9. HRMS (ESI+) calcd. for $[M]^+$: 350.1468, found: 350.1477.

6-methoxy-2,2-dimethyl-2,3-dihydro-1H-inden-1-one (5)[6]



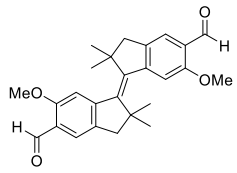
To a THF (300 mL) solution of NaH (60% in mineral oil, 4.1 g, 110.0 mmol) was added 6-methoxy-2,3-dihydro-1H-inden-1-one (8.1 g, 50.0 mmol) and methyl iodide (6.9 mL, 110.0 mmol) at 0 °C. After stirring at room temperature for 2 h, the mixture was quenched with water and extracted with EtOAc. The organic layer was washed with brine, dried over Na_2SO_4 and concentrated *in vacuo*. The crude product was purified by column chromatography (SiO_2, pentane/EtOAc = 9/1) to afford compound **5** (5.8, 30.6 mmol, 61% yield) as a yellow solid. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.30 (d, J = 9.2 Hz, 1H), 7.23 – 7.14 (m, 2H), 3.82 (s, 3H), 2.91 (s, 2H), 1.22 (s, 6H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 211.6, 159.6, 145.1, 136.6, 127.5, 124.4, 105.7, 55.7, 46.5, 42.4, 25.5. HRMS (APCI) calcd. for $[M+H]^+$: 192.1100, found: 192.1094.

(*E*)/(*Z*)-6,6'-dimethoxy-2,2,2',2'-tetramethyl-2,2',3,3'-tetrahydro-1,1'-biindenylidene ((*E*)/(*Z*)-S5)



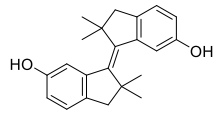
To a suspension of Zn powder (5.5 g, 84.0 mmol) in anhydrous THF (120 mL) was added $TiCl_4$ (4.6 mL, 42.0 mmol). After heating at reflux for 2 h, compound **5** (3.8 g, 20.0 mmol) was added to the reaction mixture, and the mixture was heated at reflux for 16 h. After cooling to room temperature, the reaction mixture was treated with a saturated aqueous solution of NH_4Cl, and extracted with EtOAc. The organic layer was washed with brine and dried over Na_2SO_4. The solution was concentrated *in vacuo* and purified by column chromatography (SiO_2, pentane/CH_2Cl_2= 50/1) to afford an *E/Z* mixture with a ratio of 5:1 (2.4 g, 69%) as a white solid. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.16 – 7.02 (m, 24H), 6.75 (dd, *J* = 8.1, 2.4 Hz, 10H), 6.65 (dd, *J* = 8.2, 2.4 Hz, 2H), 3.82 (s, 30H), 3.56 (s, 6H), 3.07 (d, *J* = 14.2 Hz, 2H), 2.73 (s, 20H), 2.47 (d, *J* = 14.2 Hz, 2H), 1.63 (s, 6H), 1.35 (s, 60H), 1.21 (s, 6H). *E*-**S5** (2.0 g, 57%) was obtained by crystalizing in pentane/CH_2Cl_2 (20/1) mixture. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.12 – 7.06 (m, 4H), 6.75 (dd, *J* = 8.0, 2.6 Hz, 2H), 3.82 (s, 6H), 2.72 (s, 4H), 1.34 (s, 12H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 157.5, 146.6, 144.2, 137.8, 124.7, 113.7, 113.2, 55.6, 51.5, 51.3, 28.0. A part of the *E*/*Z* mixture (200 mg) was photochemically switched in 13 mL CH_2Cl_2 to the PSS with 365 nm light in a benchtop photoreactor and subsequently purified by flash column chromatography (0-10% CH_2Cl_2 in pentane) to obtain pure *Z*-**S5** (60 mg, 30% yield). ^{1}H NMR (400 MHz, cdcl3) δ 7.13 (d, J = 2.4 Hz, 2H), 7.05 (d, J = 8.1 Hz, 2H), 6.65 (dd, J = 8.2, 2.4 Hz, 2H), 3.56 (s, 6H), 3.07 (d, J = 14.2 Hz, 2H), 2.47 (d, J = 14.2 Hz, 2H), 1.63 (s, 6H), 1.21 (s, 6H). ^{13}C NMR (101 MHz, cdcl3) δ 157.00, 145.25, 144.49, 137.65, 125.12, 114.83, 111.53, 55.42, 51.95, 50.52, 29.02, 26.63. HRMS (APCI) calcd. for $[M+H]^+$: 350.2196, found: 350.2186.

(*E*)/(*Z*)-6,6'-dimethoxy-2,2,2',2'-tetramethyl-2,2',3,3'-tetrahydro-[1,1'-biindenylidene]-5,5'-dicarbaldehyde ((*E*)/(*Z*)-S6)



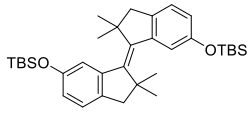
To a CH_2Cl_2 (10 mL) solution of *E*-**S5** (140 mg, 0.4 mmol) was added $TiCl_4$ (145 µL, 1.3 mmol) at 0 °C, and the mixture was stirred for 20 min. Then dichloro(methoxy)methane (180 µL, 2.0 mmol) was added to the mixture, which was stirred at room temperature for 30 min. After the reaction was complete, a saturated aqueous solution of NH_4Cl was added and the aqueous phase was extracted with CH_2Cl_2. The organic layer was washed with brine, dried over Na_2SO_4 and concentrated *in vacuo*. The crude product was purified by column chromatography (SiO_2, pentane/EtOAc = 10/1) to afford compound (*E*)/(*Z*)-**S6** with a molar ratio of 10/7 (56 mg, 36% yield) as a yellow solid. ^{1}H NMR (400 MHz, $CDCl_3$) δ 10.45 (s, 2H), 10.37 (s, 1H), 7.66 (s, 3H), 7.15 (s, 2H), 7.12 (s, 1H), 3.95 (s, 6H), 3.59 (s, 4H), 3.11 (d, *J* = 14.4 Hz, 2H), 2.79 (s, 4H), 2.58 (d, *J* = 14.5 Hz, 2H), 1.66 (s, 5H), 1.36 (s, 12H), 1.21 (s, 5H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 189.7, 189.6, 160.3, 159.6, 150.8, 150.1, 149.7, 148.9, 138.1, 137.8, 124.8, 124.5, 124.4, 123.6, 111.3, 110.4, 55.9, 55.8, 51.7, 51.4, 51.1, 51.0, 28.9, 28.0, 26.5. (*E*)- and (*Z*)-**S6** were seperated by SFC (Chiralpak® ID, Isopropanol/CO_2= 1/10) (*E*)-**S6** ^{1}H NMR (400 MHz, $CDCl_3$) 10.44 (s, 2H), 7.66 (s, 2H), 7.15 (s, 2H), 3.94 (s, 6H), 2.79 (s, 4H), 1.36 (s, 12H).^{13}C NMR (101 MHz, $CDCl_3$) δ 189.7, 160.3, 150.1, 149.7, 137.8, 124.4, 123.6, 111.3, 55.9, 51.7, 51.0, 29.9, 28.0. (*Z*)-**S6** ^{1}H NMR (400 MHz, $CDCl_3$) δ 10.37 (s, 2H), 7.67 (s, 2H), 7.12 (s, 2H), 3.59 (s, 6H), 3.10 (d, *J* = 14.5 Hz, 3H), 2.57 (d, *J* = 14.7 Hz, 3H), 1.66 (s, 6H), 1.21 (s, 6H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 189.6, 159.6, 150.8, 148.9, 138.1, 124.8, 124.5, 110.4, 55.8, 51.4, 51.1, 28.9, 26.5. HRMS (ESI+) calcd. for $[M]^+$: 406.2094, found: 406.2091.

(*E*)/(*Z*)-2,2,2',2'-tetramethyl-2,2',3,3'-tetrahydro-[1,1'-biindenylidene]-6,6'-diol ((*E*)/(*Z*)-**S3**)



To ***E*-S3** (480 mg, 1.4 mmol) was added a solution of CH_3MgI (3 M in Et_2O, 2.8 mL, 8.4 mmol). The mixture was heated to 140 °C, while the solvent was evaporated via a needle in the septum. Once the solvent completely evaporated, the needle was removed, and the mixture was heated at 140 °C for 16 h. After cooling to room temperature, the spongy solid was quenched with ice and a saturated aqueous solution of NH_4Cl, then extracted with EtOAc. The organic layer was washed with brine and dried over anhydrous Na_2SO_4. The solution was concentrated *in vacuo* and purified by column chromatography (SiO_2, pentane/EtOAc = 9/1) to afford (*E*)/(*Z*)-**S3** (324 mg, 72%) as a white solid with a ratio of 2/3. ^{1}H NMR (400 MHz, DMSO-d_6) δ 9.12 (s, 2H), 8.85 (s, 4H), 6.99 (dd, *J* = 7.9, 4.3 Hz, 6H), 6.93 (d, *J* = 2.3 Hz, 2H), 6.90 (d, *J* = 2.2 Hz, 4H), 6.57 (dd, *J* = 8.0, 2.3 Hz, 2H), 6.49 (dd, *J* = 8.0, 2.4 Hz, 3H), 2.94 (d, *J* = 14.2 Hz, 3H), 2.62 (s, 4H), 2.40 (d, *J* = 14.2 Hz, 4H), 1.55 (s, 10H), 1.26 (s, 12H), 1.10 (s, 11H). ^{13}C NMR (151 MHz, DMSO-d_6) δ 154.7, 154.5, 145.5, 144.4, 143.9, 143.2, 135.1, 135.0, 124.8, 124.4, 115.0, 114.4, 114.4, 112.8, 51.2, 50.8, 50.4, 50.0, 28.5, 27.3, 26.2. HRMS (ESI) calcd. for [M]: 320.1737, found: 320.1735.

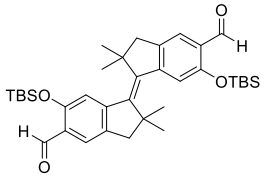
(*E*)/(*Z*)-((2,2,2',2'-tetramethyl-2,2',3,3'-tetrahydro-[1,1'-biindenylidene]-6,6'-diyl)bis(oxy))bis(tert-butyldimethylsilane) ((*E*)/(*Z*)-6)



To a DMF (10 mL) solution of (*E*)/(*Z*)-**S3** (160.0 mg, 0.5 mmol) was added 4-dimethylaminopyridine (586 mg, 4.8 mmol) and *tert*-butyldimethylsilyl chloride (664.0 mg, 4.4 mmol), and the mixture was stirred overnight at room temperature. After the reaction was complete, a saturated aqueous solution of NH_4Cl was added and the aqueous phase was extracted with EtOAc. The organic layer was washed with brine,

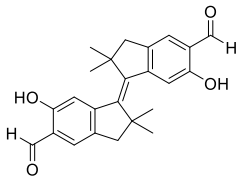
dried over Na_2SO_4 and concentrated *in vacuo*. The crude product was purified by column chromatography (SiO_2, pentane) to afford compound (*E*)/(*Z*)-**6** (213 mg, 73%) as a white solid. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.05 – 6.95 (m, 11H), 6.67 (dd, *J* = 8.0, 2.3 Hz, 2H), 6.54 (dd, *J* = 8.0, 2.4 Hz, 3H), 3.06 (d, *J* = 14.1 Hz, 3H), 2.70 (s, 4H), 2.42 (d, *J* = 14.1 Hz, 3H), 1.60 (s, 10H), 1.32 (s, 13H), 1.16 (s, 10H), 1.00 (s, 19H), 0.90 (s, 30H), 0.21 (s, 12H), 0.06 (d, *J* = 4.8 Hz, 20H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 153.16, 153.07, 146.41, 145.15, 145.06, 144.31, 138.39, 138.07, 124.90, 124.67, 119.67, 119.34, 119.27, 118.18, 77.52, 77.20, 76.88, 52.04, 51.59, 51.27, 50.72, 29.49, 27.74, 26.53, 25.89, 18.35, 18.23, -4.07, -4.21, -4.26. HRMS (ESI+) calcd. for $[M]^+$: 550.3612, found: 550.3608.

6,6'-bis((tert-butyldimethylsilyl)oxy)-2,2,2',2'-tetramethyl-2,2',3,3'-tetrahydro-[1,1'-biindenylidene]-5,5'-dicarbaldehyde ((*E*)-7)



To a CH_2Cl_2 (10 mL) solution of (*E*)/(*Z*)-**6** (220 mg, 0.4 mmol) was added $TiCl_4$ (145 µL, 1.2 mmol) at 0 °C, and the mixture was stirred for 20 min. Then the dichloro(methoxy)methane (180 µL, 2.0 mmol) was added to the mixture and stirred at room temperature for 30 min. After the reaction was complete, a saturated aqueous solution of NH_4Cl was added and the aqueous phase was extracted with CH_2Cl_2. The organic layer was washed with brine, dried over Na_2SO_4 and concentrated *in vacuo*. The crude product was purified by column chromatography (SiO_2, pentane/EtOAc = 19/1) to afford compound (*E*)/(*Z*)-**7** (81 mg, 34% yield) as a yellow solid. (*E*)-**7** was separated by column chromatography (SiO_2, pentane/EtOAc = 19/1). ^{1}H NMR (400 MHz, $CDCl_3$) δ 10.44 (s, 1H), 7.63 (s, 1H), 7.02 (s, 1H), 2.75 (s, 2H), 1.33 (s, 6H), 1.03 (s, 9H), 0.31 (s, 6H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 190.1, 157.1, 150.2, 149.5, 138.7, 126.6, 123.3, 119.4, 51.5, 50.9, 27.7, 25.9, 18.5, -3.9.

(*E*)-6,6'-dihydroxy-7,7'-dimethyl-2,2',3,3'-tetrahydro-[1,1'-biindenylidene]-5,5'-dicarbaldehyde ((*E*)-**S4**)



To a THF (5 mL) solution of **7** (30 mg, 50.0 µmol) was added a TBAF solution (1 M in THF, 0.3 mL, 0.3 mmol) at 0 °C. After stirring of reaction mixture at room temperature for 2 h, the mixture was quenched by water and extracted with CH_2Cl_2. The organic layer was washed with brine, dried over Na_2SO_4 and concentrated *in vacuo*. The crude product was purified by column chromatography (SiO_2, pentane/EtOAc = 9/1) to afford (*E*)-**S4** (17 mg, 90%) as a yellow solid**.** ^{1}H NMR (400 MHz, $CDCl_3$) δ 11.11 (s, 2H), 9.90 (s, 2H), 7.43 (s, 2H), 7.12 (s, 2H), 2.83 (s, 4H), 1.37 (s, 12H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 11.53 (s, 2H), 9.82 (s, 2H), 7.28 (s, 2H), 2.98-2.46 (m, 8H), 2.23 (s, 6H). HRMS (ESI+) calcd. for $[M]^+$: 376.1635, found: 376.1629.

3. UV-vis study of photo-switching behavior

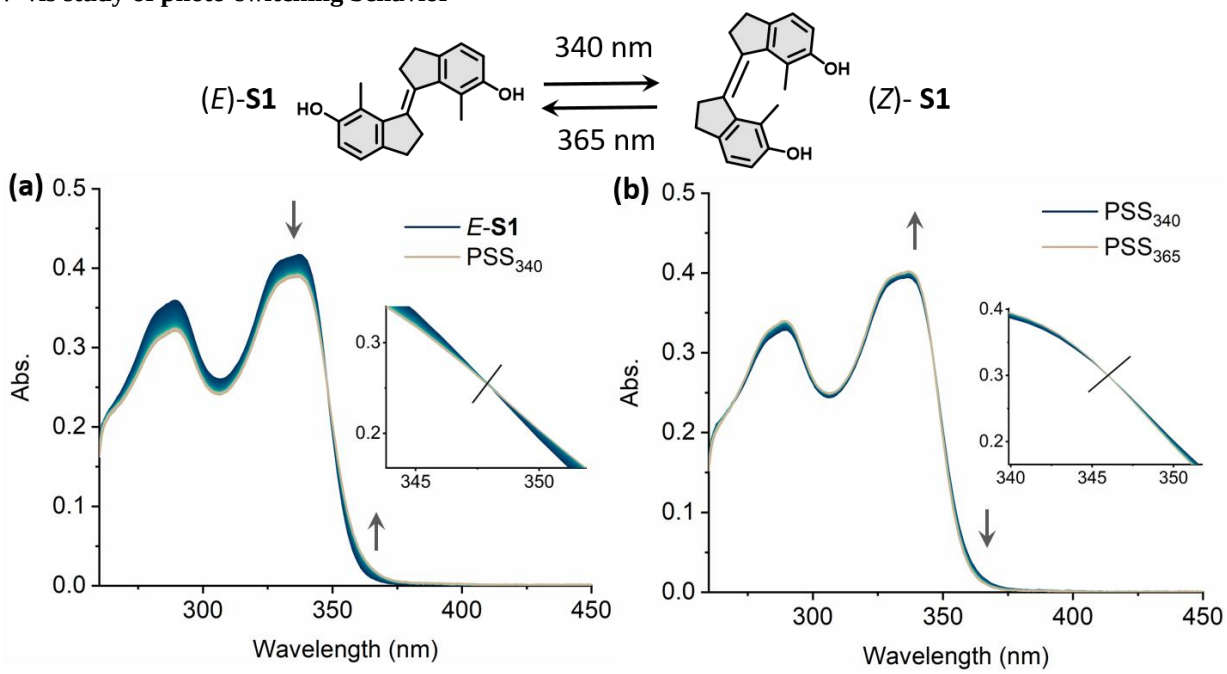


Figure S2. Changes in the UV−Vis absorption spectra starting from (*E*)-**S1** (15 µM in DMSO, 298 K) (a) upon irradiation with 340 nm light to PSS_{340}, (b) upon subsequent irradiation with 365 nm light to PSS_{365}. Inserts: isosbestic point of each process.

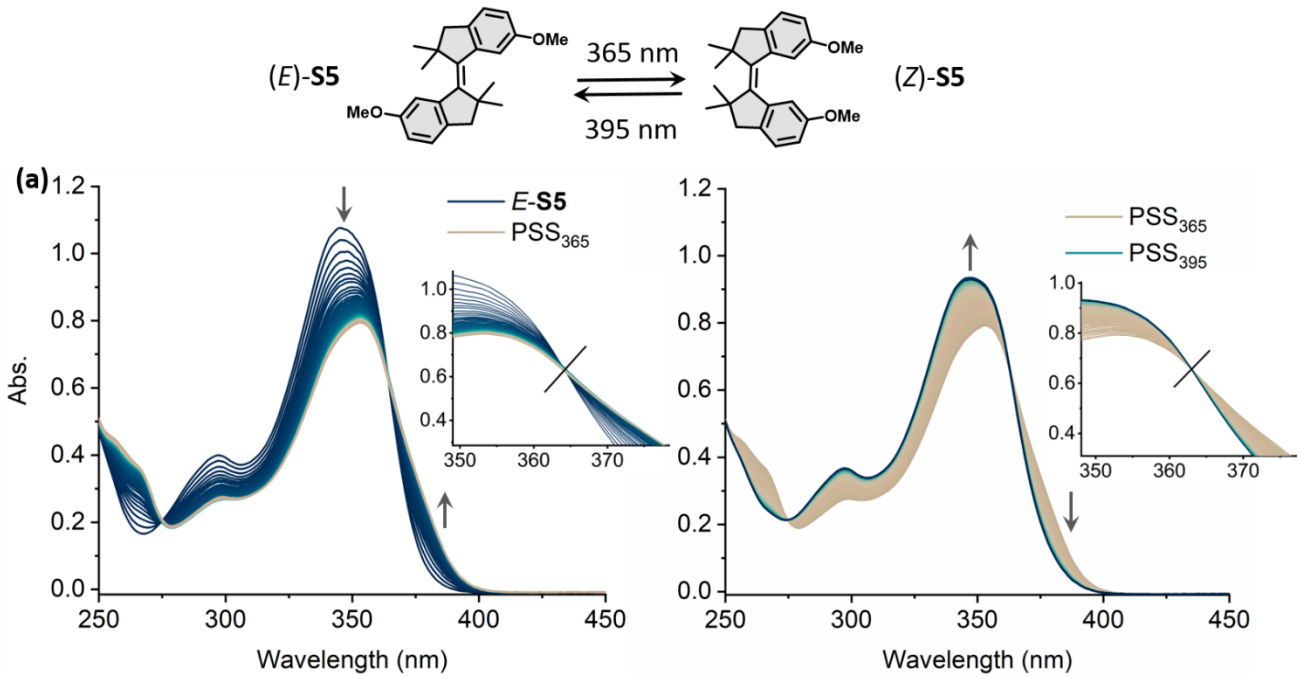


Figure S3. Changes in the UV−Vis absorption spectra starting from (*E*)-**S5** (38 µM in CH_2Cl_2, 298 K) (a) upon irradiation with 365 nm light to PSS_{365}, (b) upon subsequent irradiation with 395 nm light to PSS_{395}. Inserts: isosbestic point of each process.

4. NMR study of photo-switching behavior

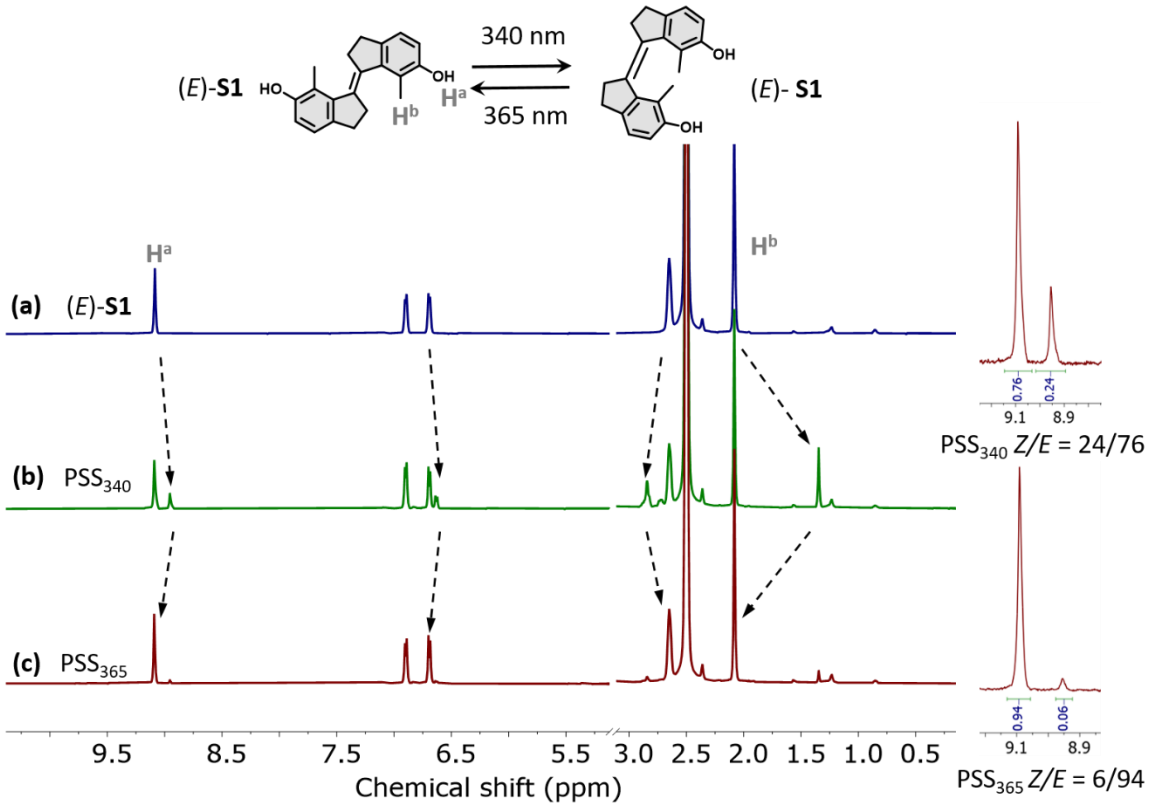


Figure S4. Changes in ^{1}H NMR spectra of (a) (*E*)-**S1** (3.4 mM in DMSO-d_6, 298 K, 500 MHz) (b) upon irradiation with 340 nm light to PSS_{340}, (c) upon subsequent irradiation with 365 nm light to PSS_{365}. Inserts: the integration of the corresponding signal of (*E*)- and (*Z*)-**S1**.

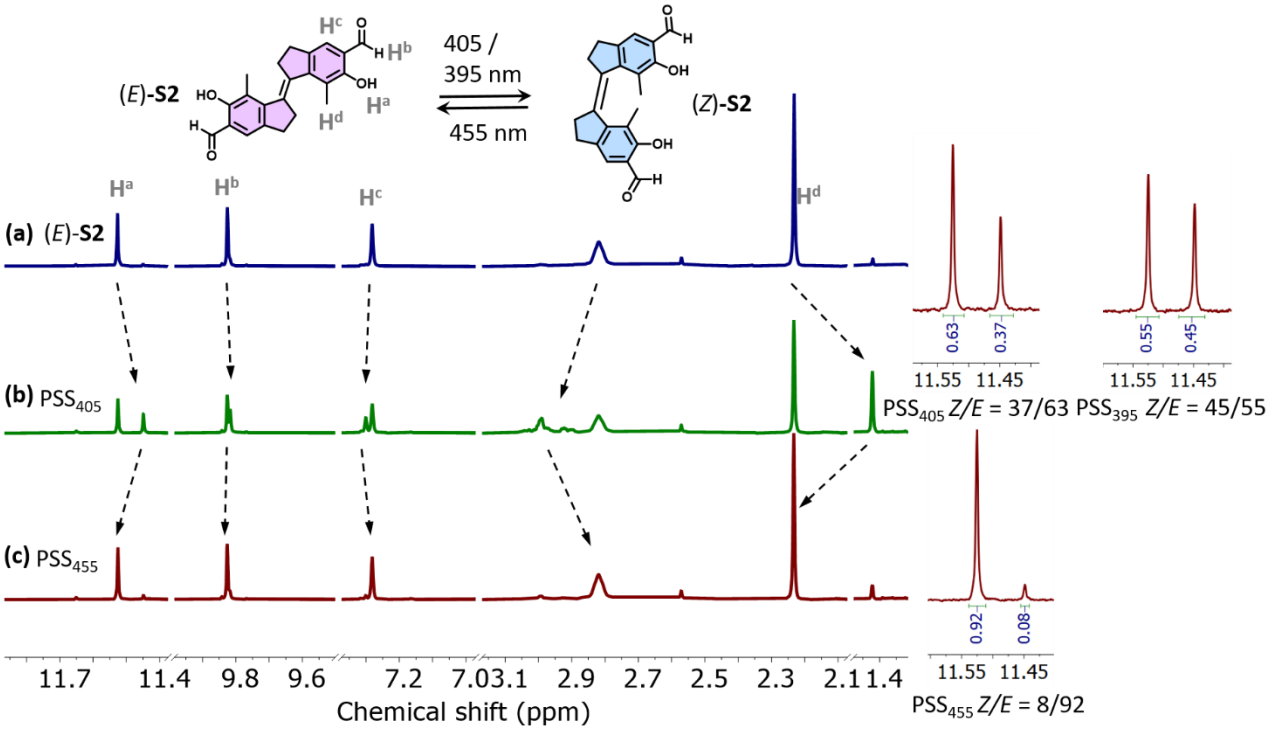


Figure S5. Changes in ^{1}H NMR spectra of (a) (*E*)-**S2** (2.9 mM in CD_2Cl_2, 298 K, 500 MHz) (b) upon irradiation with 405 nm light to PSS_{405}, (c) upon subsequent irradiation with 455 nm light to PSS_{455}. Insert: the integration of the corresponding signal of (*E*)- and (*Z*)-**S2**.

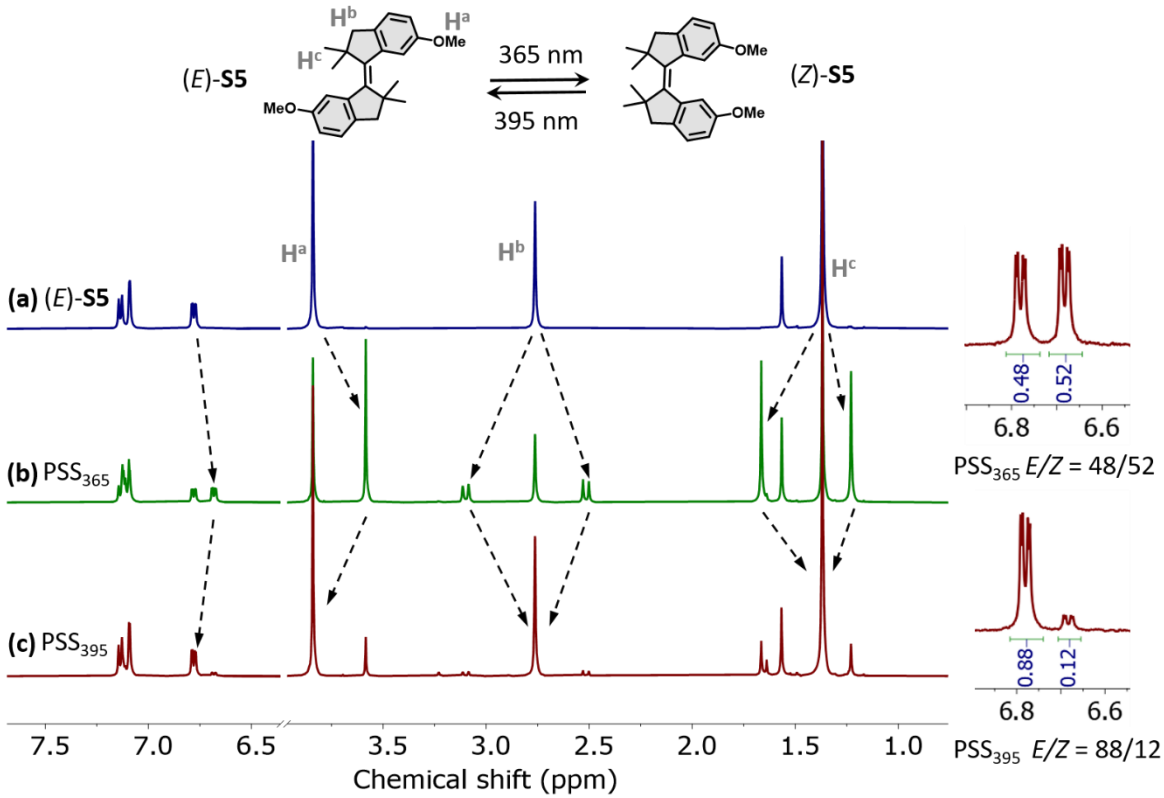


Figure S6. Changes in ^{1}H NMR spectra of (a) (*E*)-**S5** (2.9 mM in CD_2Cl_2, 298 K, 500 MHz) (b) upon irradiation with 365 nm light to PSS_{365}, (c) upon subsequent irradiation with 395 nm light to PSS_{395}. Insert: the integration of the corresponding signal of (*E*)- and (*Z*)-**S5**.

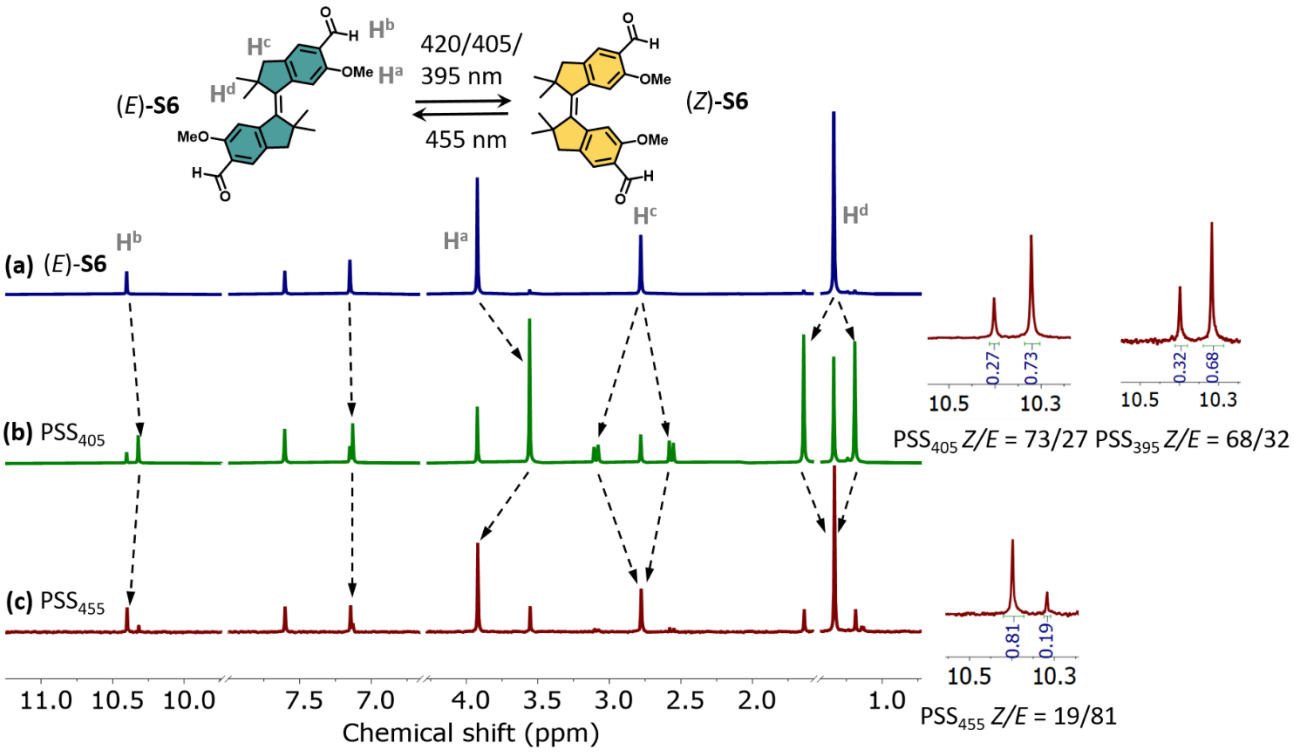


Figure S7. Changes in ^{1}H NMR spectrum of (a) (*E*)-**S6** (2.5 mM in CD_2Cl_2, 298 K, 500 MHz) (b) upon irradiation with 405 nm light to PSS_{405}, (c) upon subsequent irradiating with 455 nm light to PSS_{455}. Insert: the integration of the corresponding signal of (*E*)- and (*Z*)-**S6**.

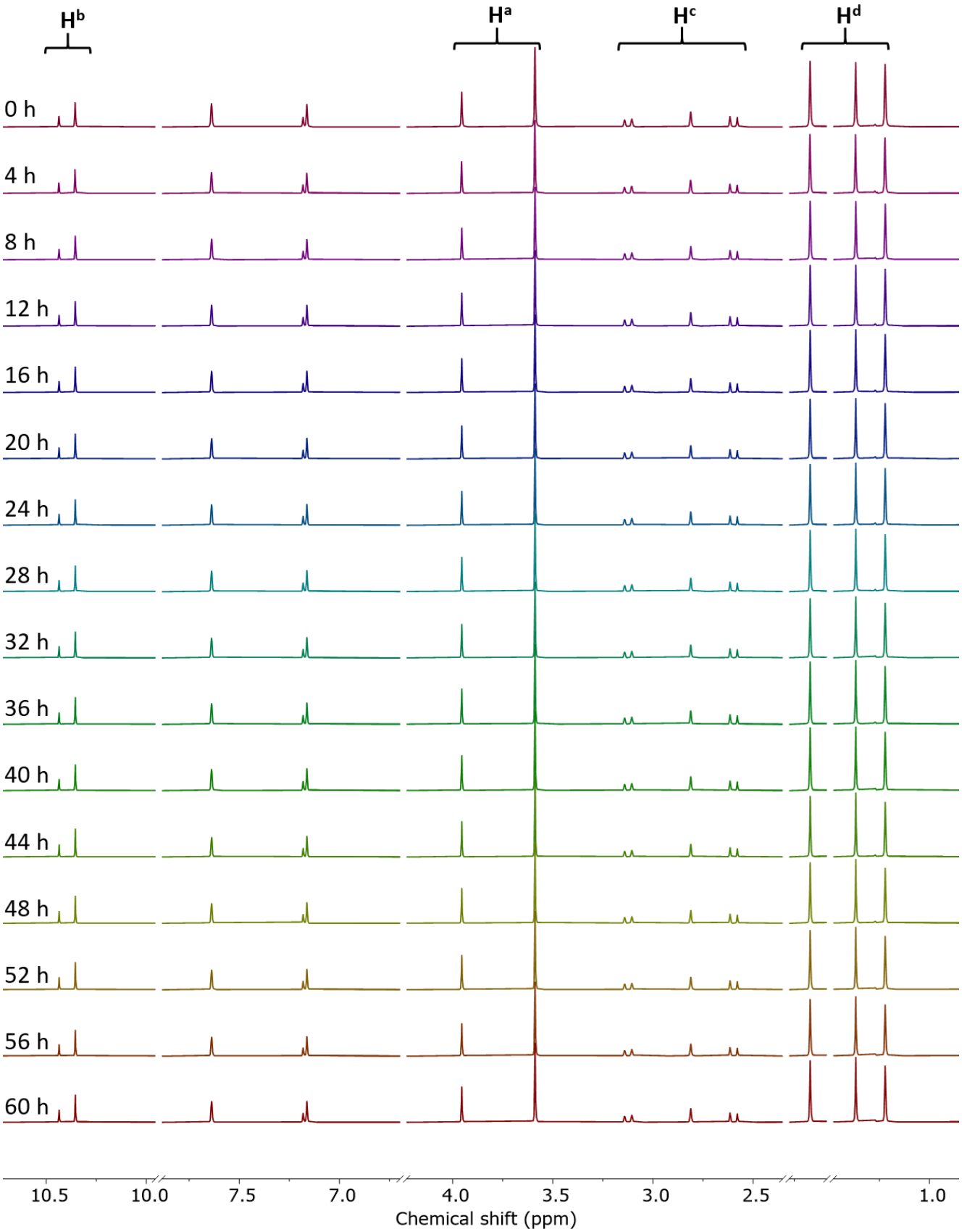


Figure S8. Time-dependent ^{1}H NMR spectra of ***Z*-S6** at PSS_{405} (2.5 mM in CD_2Cl_2, 298 K, 400 MHz).

5.Quantum Yields determination

Photon fluxes for light sources at 390 nm and 365 nm were determined using standard ferrioxolate actinometry which provided values $3.16 \cdot 10^{-5}$ mmol s^{-1} and $3.95 \cdot 10^{-5}$ mmol s^{-1}, respectively. Evolution of the UV-Vis electronic absorption spectra upon irradiation at specific wavelength with pre-determined photon flux was followed over time. Spectra were processed in SpectraGryph software using the simple baseline correction to account for the baseline drift throughout the acquisition. Molar attenuation coefficients of the *Z* diastereomers of the stilbenes S2, S5 and S6 were determined by recording absorbance for the series of solutions (solvent) at known concentration and least-square fitting these data to the Beer-Lamber law (Table S1). Molar attenuation coefficients of the corresponding *E* diastereomers were calculated from Beer-Lamber law using photostationary state distributions which were established by ^{1}H NMR spectroscopy (Table S1). Quantum yields were determined following the approach developed by Stranius and Börjesson.[7] Time-dependent evolution of the absorbance at the irradiation wavelength was fitted using COPASI 4.30 software to the kinetic equation:

$$\frac{d[E]}{dt} = -\frac{QY_{EZ} \cdot I \cdot \beta_E(t)}{N_A \cdot V} + \frac{QY_{ZE} \cdot I \cdot \beta_Z(t)}{N_A \cdot V} \qquad [1]$$

Where, QY_{EZ} is quantum yield of the isomerization of the *E* diastereomer, QY_{ZE} is the quantum yield of the isomerization of the *Z* diastereomer at the selected wavelength, *I* is the photon flux, previously determined with ferrioxalate actinometry, N_A the Avogadro number, *V* the total volume of the irradiated solution (2 mL) and β the fractions of photons absorbed by either the *Z* or the *E* diastereomer. All measurements were performed at least in duplicates. Fors stilbenes S2 and S6 changes in total absorbance at the irradiation wavelength (395 nm) were fitted to equation 1. In case of stilbene S1 difference in the UV/Vis spectra between *E* and *Z* diastereomers were too small to determine of QYs with a reasonable error margin. For stilbene S5 the irradiation wavelength was located close to the isosbestic point, therefore the transient concentrations of E and Z diastereomers were calculated (Eq. 2) from UV-Vis electronic absorption spectra (using the known initial concentration of *E* diastereomer and molar absorptivity coefficients) and fitted to the same equation.

$$[E] = \frac{\frac{A}{l} - c_0\varepsilon_Z}{\varepsilon_E - \varepsilon_Z} \qquad [2]$$

Photostationary state distributions (PSD) of diastereomers were calculated (Eq. 3) using the determined values of QYs and compared with the distributions derived from ^{1}H NMR spectra to validate the values.

$$\frac{[Z]}{[E]} = \frac{QY_{EZ}\varepsilon_E}{QY_{ZE}\varepsilon_Z} \qquad [3]$$

Table S1. Photochemical and photophysical parameters of stiff-stilbene derivatives.

Stilbene	Wavelength (nm)	ε_E ($M^{-1}\cdot cm$)	ε_Z ($M^{-1}\cdot cm$)	QY_{EZ}	QY_{ZE}	PSD_{NMR} (*Z*:*E*)	PSD_{cld} (*Z*:*E*)
S2	390	2.8×10^4	2.4×10^4	0.31	0.50	45:55[a]	43:57
S5	365	1.6×10^4	1.2×10^4	0.34	0.42	52:48	51:49
S6	390	4.4×10^4	2.5×10^4	0.27	0.11	73:27[b]	81:19

[a] upon irradiation with 395 nm LED light.
[b] upon irradiation with 405 nm LED light.

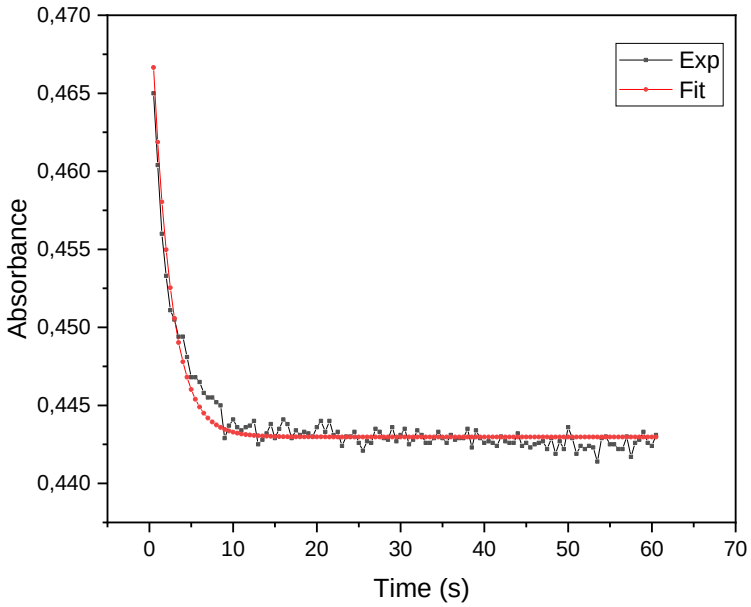


Figure S9. Evolution of the absorbance at 395 nm during the irradiation of (*E*)-**S2** in CH_2Cl_2 at 395 nm (black line). The red line represents the fit obtained with the ODE solver from COPASI.

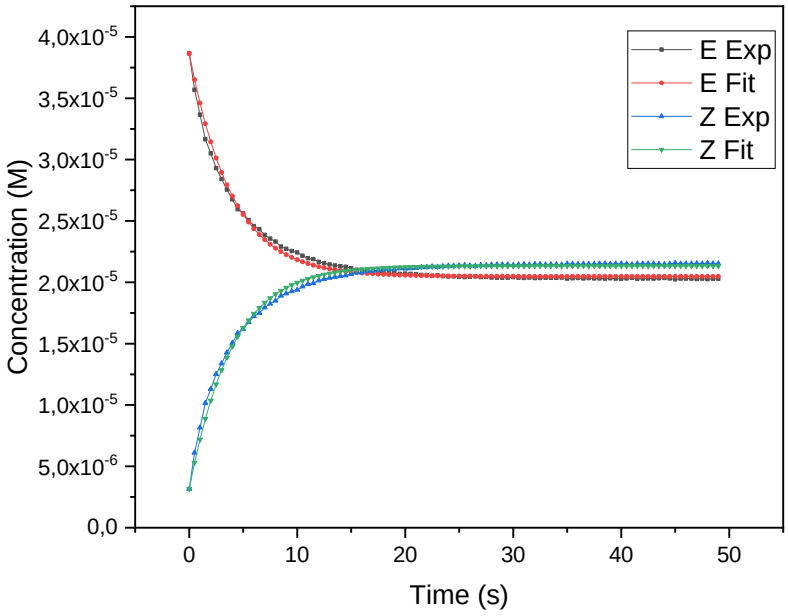


Figure S10. Evolution of the concentrations of (*E*)-**S5** and (*Z*)-**S5** in solvent during the irradiation at 365 nm (black and blue lines, respectively) as calculated from UV-Vis spectra. The red and blue data sets represents the fit obtained with the ODE solver from COPASI

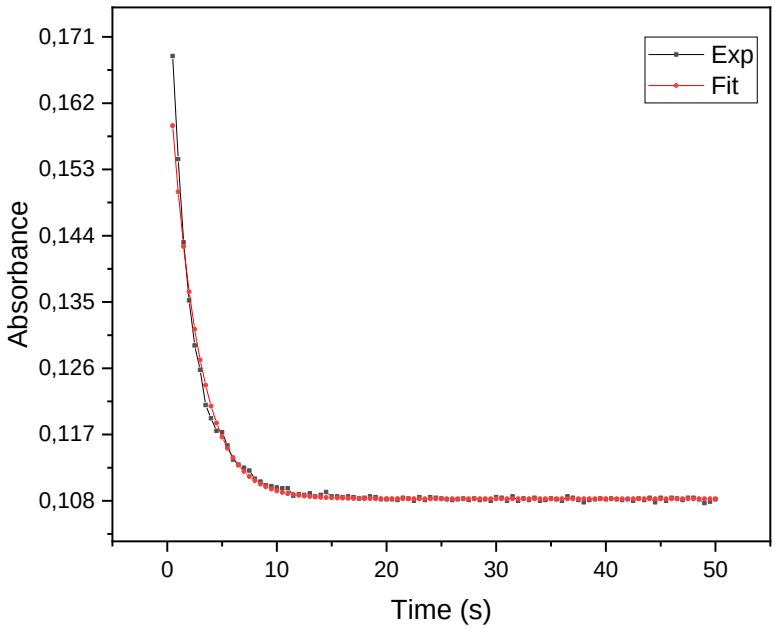


Figure S11. Evolution of the absorbance at 395 nm during the irradiation of (*E*)-**S6** in CH_2Cl_2 at 395 nm (black line). The red line represents the fit obtained with the ODE solver from COPASI.

6. Nanosecond transient absorption spectroscopy

Figures S12-S15 show the ns transient absorption spectra of **(*E*)-S5**, **(*Z*)-S5**, **(*E*)-S6**, and **(*Z*)-S5** in CH_2Cl_2. In each case a bleach is observed in the absorption band of the initial isomer as well as an – on the time scale of the experiment – instantaneous appearance of an induced absorption band corresponding to the absorption of the generated photoisomer. Figures S12-S15 show spectra for delays up to 10 or 20 ns. Spectra recorded for longer delay times show that both bleaching and induced absorption bands are permanent on the time scale accessible in the experiment. Note that the spectra of **(*E*)-S5** and **(*Z*)-S5** show a very small induced absorption band around 500 nm that could not unambiguously be assigned. However, as this absorption band was also permanent on the time scale accessible in the experiment, we conclude that it cannot be attributed to a triplet state.

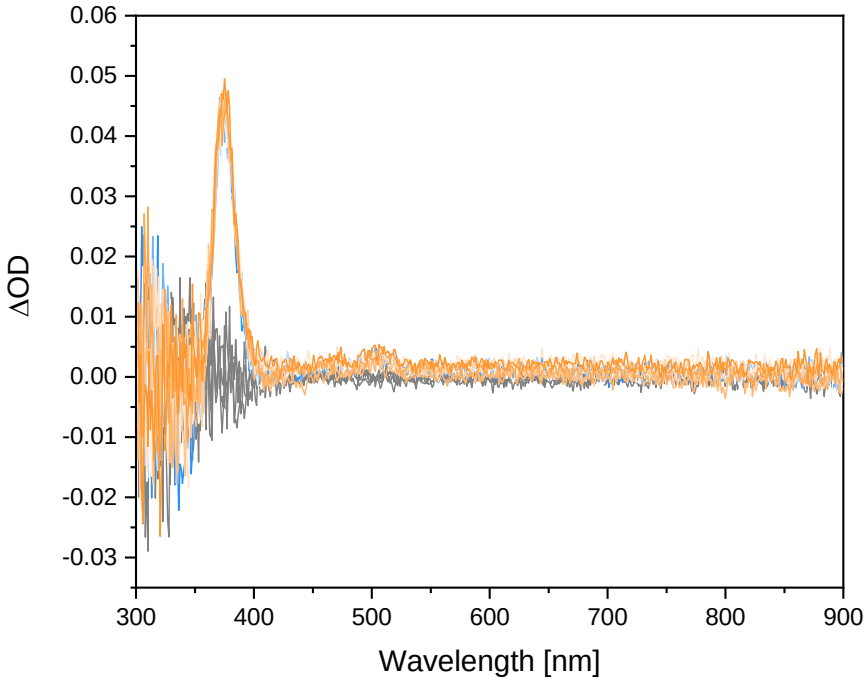


Figure S12. Transient absorption of **(*E*)-S5** in CH_2Cl_2 at room temperature. The sample was irradiated with a 340 nm light pulse upon which the spectrum was recorded in steps of 2 ns increasing delay until 20 ns. Baseline spectra before the laser pulse are shown in grey, and spectra after the laser pulse start from blue progressing to orange.

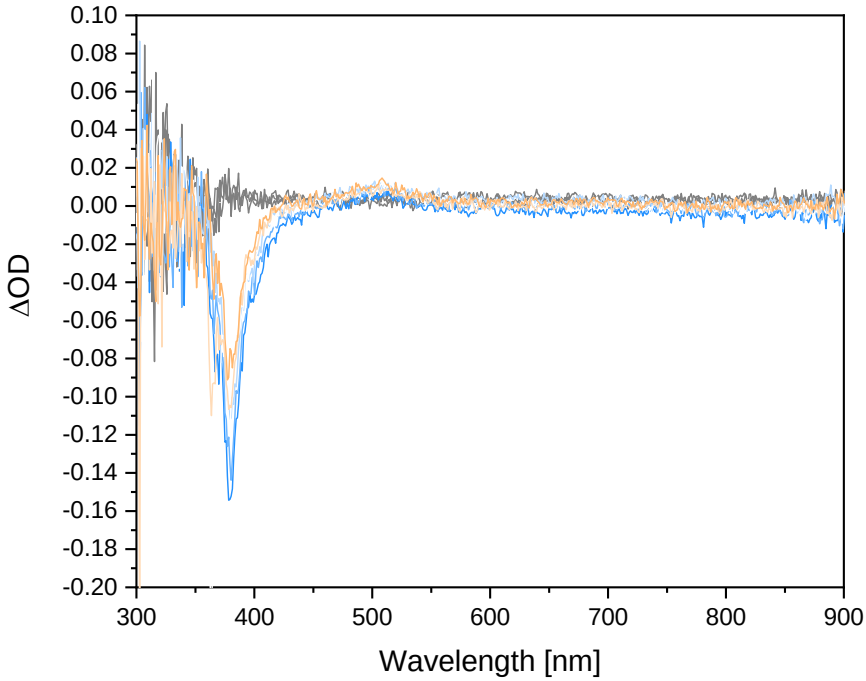


Figure S13. Transient absorption of **(*Z*)-S5** in CH_2Cl_2 at room temperature. The sample was irradiated with a 365 nm light pulse upon which the spectrum was recorded in steps of 2 ns increasing delay until 10 ns. Baseline spectra before the laser pulse are shown in grey, and spectra after the laser pulse start from blue progressing to orange.

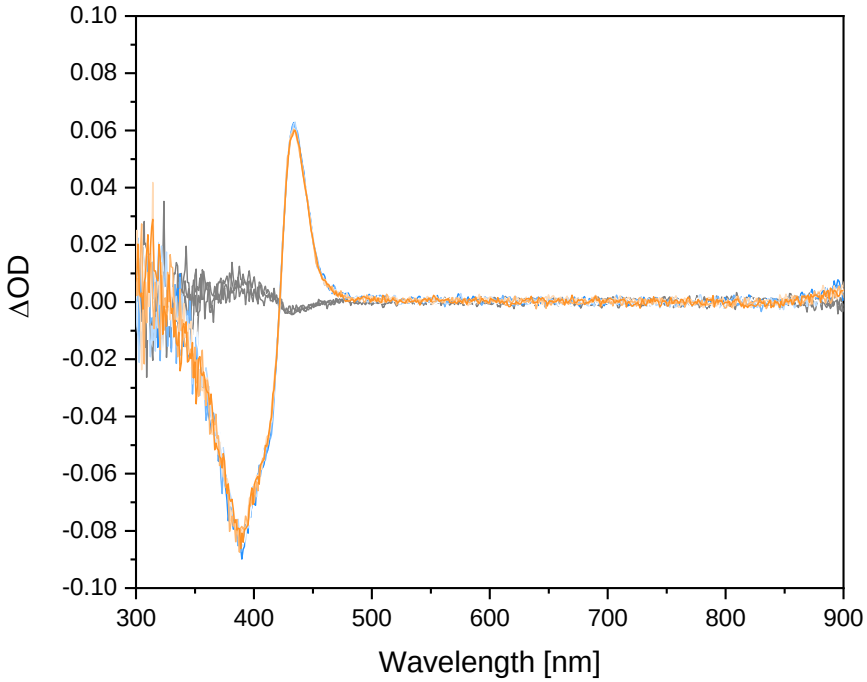


Figure S14. Transient absorption of **(*E*)-S6** in CH_2Cl_2 at room temperature. The sample was irradiated with a 340 nm light pulse upon which the spectrum was recorded in steps of 2 ns increasing delay until 10 ns. Baseline spectra before the laser pulse are shown in grey, and spectra after the laser pulse start from blue progressing to orange.

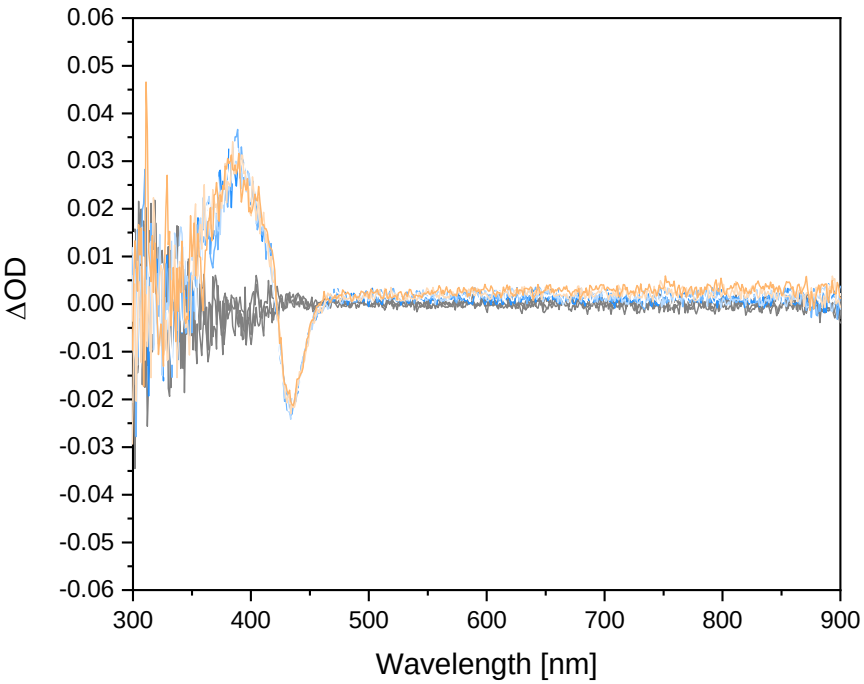
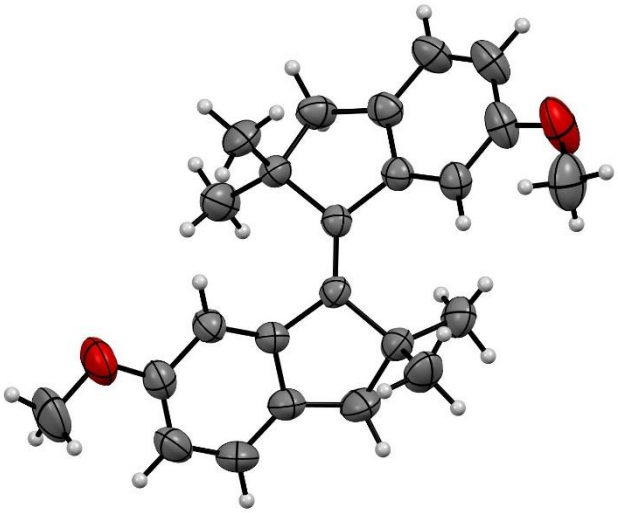


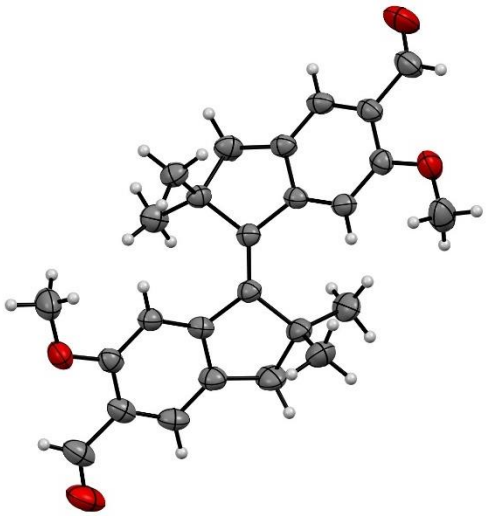
Figure S15. Transient absorption of **(*Z*)-S6** in CH_2Cl_2 at room temperature. The sample was irradiated with a 455 nm light pulse upon which the spectrum was recorded in steps of 2 ns increasing delay until 10 ns. Baseline spectra before the laser pulse are shown in grey, and spectra after the laser pulse start from blue progressing to orange.

7. X-ray structural analysis



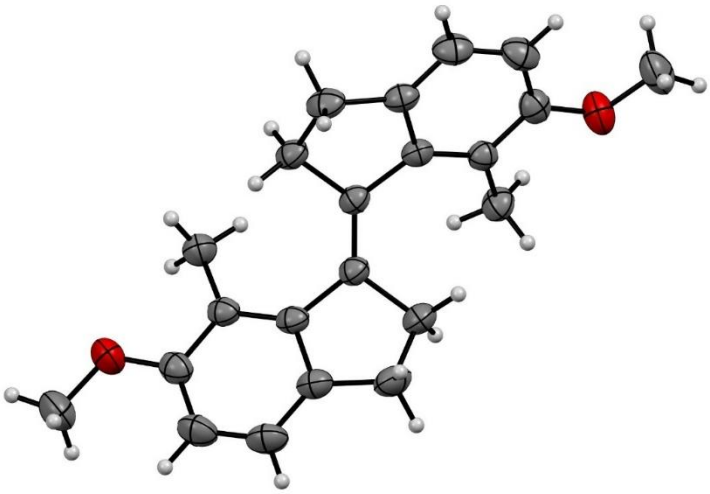
Crystal data and structure refinement for (*E*)-S5.

Identification code	mo_CNS_JS_186_0m_a
Empirical formula	$C_{24}H_{28}O_2$
Formula weight	348.46
Temperature/K	293
Crystal system	monoclinic
Space group	Cc
a/Å	11.361(4)
b/Å	20.063(7)
c/Å	9.862(4)
α/°	90
β/°	116.079(16)
γ/°	90
Volume/Å^3	2019.1(13)
Z	4
ρ_{calc}g/cm^3	1.146
μ/mm^{-1}	0.071
F(000)	752.0
Crystal size/mm^3	0.355 × 0.156 × 0.139
Radiation	MoKα (λ = 0.71073)
2Θ range for data collection/°	7.286 to 59.122
Index ranges	-15 ≤ h ≤ 15, -27 ≤ k ≤ 27, -13 ≤ l ≤ 13
Reflections collected	55231
Independent reflections	5625 [R_{int} = 0.1198, R_{sigma} = 0.0542]
Data/restraints/parameters	5625/2/241
Goodness-of-fit on F^2	1.026
Final R indexes [I>=2σ (I)]	R_1 = 0.0547, wR_2 = 0.1097
Final R indexes [all data]	R_1 = 0.0843, wR_2 = 0.1258
Largest diff. peak/hole / e Å^{-3}	0.15/-0.14
Flack parameter	-0.1(9)



Crystal data and structure refinement for (*E*)-S6.

Identification code	mo_CNS_Jin_12_0m_a
Empirical formula	$C_{26}H_{28}O_4$
Formula weight	404.48
Temperature/K	293
Crystal system	orthorhombic
Space group	$P2_12_12_1$
a/Å	9.6167(8)
b/Å	12.0209(10)
c/Å	18.8367(16)
α/°	90
β/°	90
γ/°	90
Volume/Å^3	2177.5(3)
Z	4
ρ_{calc}g/cm^3	1.234
μ/mm^{-1}	0.082
F(000)	864.0
Crystal size/mm^3	0.175 × 0.137 × 0.117
Radiation	MoKα (λ = 0.71073)
2Θ range for data collection/°	4.756 to 59.168
Index ranges	$-13 \le h \le 13$, $-16 \le k \le 16$, $-26 \le l \le 26$
Reflections collected	111523
Independent reflections	6111 [R_{int} = 0.1663, R_{sigma} = 0.0594]
Data/restraints/parameters	6111/0/277
Goodness-of-fit on F^2	1.025
Final R indexes [I>=2σ (I)]	R_1 = 0.0545, wR_2 = 0.1163
Final R indexes [all data]	R_1 = 0.0766, wR_2 = 0.1297
Largest diff. peak/hole / e Å^{-3}	0.16/-0.19
Flack parameter	0.3(7)



Crystal data and structure refinement for (*E*)-S1.

Identification code	mo_CNSJIN_22_0ma_a
Empirical formula	$C_{22}H_{24}O_2$
Formula weight	320.41
Temperature/K	293
Crystal system	monoclinic
Space group	$P2_1/c$
a/Å	13.2599(18)
b/Å	8.8008(13)
c/Å	15.7527(19)
α/°	90
β/°	110.535(5)
γ/°	90
Volume/Å^3	1721.5(4)
Z	4
ρ_{calc}g/cm^3	1.236
μ/mm^{-1}	0.077
F(000)	688.0
Crystal size/mm^3	0.415 × 0.218 × 0.19
Radiation	MoKα (λ = 0.71073)
2Θ range for data collection/°	6.796 to 59.166
Index ranges	$-18 \leq h \leq 18$, $-12 \leq k \leq 12$, $-21 \leq l \leq 21$
Reflections collected	91760
Independent reflections	4809 [R_{int} = 0.1109, R_{sigma} = 0.0352]
Data/restraints/parameters	4809/0/221
Goodness-of-fit on F^2	1.061
Final R indexes [I>=2σ (I)]	R_1 = 0.0612, wR_2 = 0.1238
Final R indexes [all data]	R_1 = 0.0971, wR_2 = 0.1476
Largest diff. peak/hole / e Å^{-3}	0.26/-0.19

8. Computational analysis

Computational analysis was employed to optimize the structures of differently substituted stiff stilbenes, and compare the effect of the substituent themselves on the electronic characteristics of the molecular switches. All the geometries were optimized at the r^{2}SCAN-3c level of theory[8] as implemented in the ORCA 5.0.2 software.[9] The nature of the stationary point was confirmed by means of frequency calculations. The electronic energy of all stationary points was refined at the PW6B95-D4/def2-QZVP level.[10–14] The cartesian coordinates of the optimized structures follow.

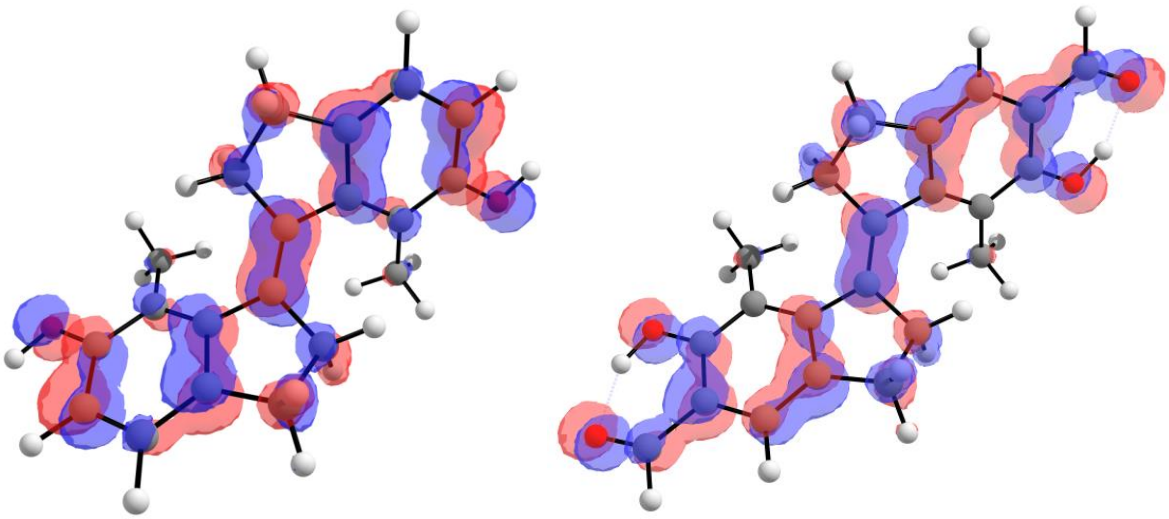


Figure S16. HOMO of (*E*)-**S1** (on the left) and of (*E*)-**S2** computed at the the PW6B95-D4/def2-QZVP//r^{2}SCAN-3c level of theory.

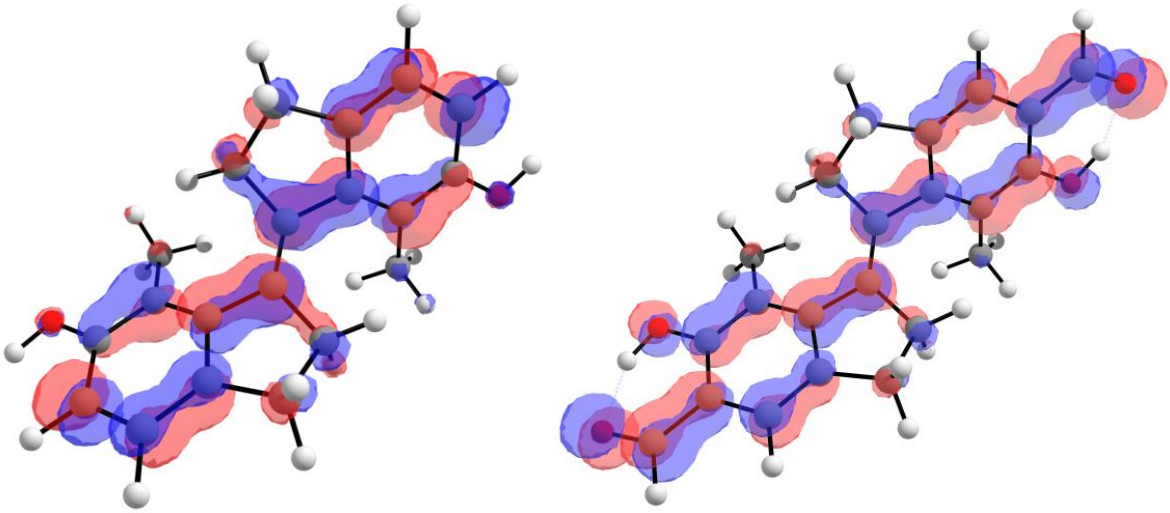


Figure S17. LUMO of (*E*)-**S1** (on the left) and of (*E*)-**S2** computed at the the PW6B95-D4/def2-QZVP//r^{2}SCAN-3c level of theory.

(*E*)-**S1**

Electronic energy (PW6B95/def2-QZVP): -926.252833694405 Hartree

Gibbs free energy correction: 0.30491837 Hartree

C	2.90068327383148	4.91010109548314	-4.87047245624815
C	3.59789897057321	3.87796043554367	-4.24670871570043
C	2.94647807334747	2.77534808512792	-3.67093443394754
C	1.54522545604782	2.78476131151474	-3.70830507823622
C	0.83992942518903	3.79302494274631	-4.39400848442791
C	1.50953423895057	4.85936240956474	-4.96275179377345
C	0.57474037032860	1.81311092926910	-3.18332459974808
C	-0.68393455072473	1.99263473753762	-4.01161884077046
C	-0.63687198264335	3.49539035077420	-4.38329191542133
C	3.76556206553793	1.62015885389618	-3.17272713050051
C	0.64900081575702	1.13931326467183	-2.01133897959736
C	1.63904001416077	1.42675156034351	-0.89760637070148
C	0.75083319340732	1.38231012888112	0.37045743698063
C	-0.34833057521531	0.42983512707048	-0.02157286138531
C	-0.38238867645364	0.27373188316434	-1.42100511231850
C	-1.24309393661297	-0.24673132110239	0.78512635306110
C	-2.16656291180556	-1.10955238775669	0.19435492148388
C	-2.15360571334775	-1.30935616054085	-1.18430488672208
C	-1.24847591108612	-0.64621348259578	-2.02836404094081
C	-1.17519009090540	-1.04005586517885	-3.47509367481539
O	4.97117856178568	3.86884835827377	-4.19295239636107
O	-3.00926014535668	-2.19862449323926	-1.78917974053973
H	0.97061008890986	5.64612803266592	-5.48448245952292
H	-1.58647706890279	1.71227265241625	-3.46248868896786
H	-1.14447598871282	4.08606127446391	-3.60748052899463
H	-1.12370896507035	3.71697000035315	-5.33879030635015

H	4.58271290627907	1.41568619493365	-3.87097642839799
H	3.14688042438833	0.72552565097399	-3.07624080739378
H	4.22875104809465	1.82493135869673	-2.20011034763427
H	2.14997091242085	2.38372475430136	-1.03174385244473
H	0.34187965556703	2.38235495880994	0.57330347741831
H	1.29509970416966	1.06062594865926	1.26454252941868
H	-1.22932768527600	-0.12273850271501	1.86499075160926
H	-1.24896426217446	-2.12773534394019	-3.56835678923803
H	-0.23250030741833	-0.70811505737279	-3.91504375305188
H	-1.99781267013232	-0.61897739553427	-4.06537649956985
H	2.40082939585941	0.63871487117505	-0.82656415055001
H	-0.64439356341742	1.39696991927331	-4.93372990271994
H	-3.54265428400275	-2.62665028295318	-1.11047643463136
H	5.30508926430550	4.64283154085117	-4.65965848560299
H	3.44855527048771	5.73855050151819	-5.31568743220784
H	-2.87727193255824	-1.65595815412433	0.81169028320334

(*Z*)-**S1**

Electronic energy (PW6B95/def2-QZVP): -926.250107018078 Hartree

Gibbs free energy correction: 0.30455323 Hartree

C	-2.08198180379283	2.04450024506970	-6.56400769268458
C	-2.69673838399990	1.96719683957330	-5.31660907596811
C	-1.96352108290531	1.87866130549227	-4.12182832952132
C	-0.56745630771221	1.81438003131841	-4.24696124011384
C	0.05824556555919	1.97488636472414	-5.50019170009958
C	-0.69033420476627	2.07449475529292	-6.65663219443039

C	0.47195899084816	1.74842006903193	-3.21333242264391
C	1.70247111294489	2.39731904791773	-3.82923059170558
C	1.55350877094139	2.05376271985579	-5.33089989626784
C	-2.68650134948117	1.96406180544491	-2.81162972172790
C	0.48884610184688	1.16530247307595	-1.99197901450954
C	1.54302357760402	1.48883803913901	-0.94373391270969
C	0.74021363044245	1.42581487297760	0.37804372392884
C	-0.32965320077029	0.41323535376162	0.06143915595647
C	-0.45513538759990	0.25465861607280	-1.33383114466335
C	-1.10045235170664	-0.33397255570152	0.93030368862117
C	-1.98790690423778	-1.27413841449837	0.40641772284377
C	-2.05062300772425	-1.48394296816074	-0.96913368680463
C	-1.26971522178378	-0.75040920163862	-1.87742748781111
C	-1.26997908436086	-1.14110607753908	-3.32447299783766
O	-4.06494121187750	1.99956403392580	-5.18991782481570
O	-2.86983379082115	-2.44653363717951	-1.50910790409013
H	-0.21211592884869	2.18880956360946	-7.62608997010756
H	2.63840215138835	2.03223398903596	-3.39790859108090
H	2.02242888310588	1.08036983822054	-5.53556955692574
H	2.01891442520540	2.79119507383573	-5.99296875870638
H	-3.51031655725093	2.67929838775306	-2.88744900694544
H	-2.00678973030319	2.27619672446122	-2.01653535624873
H	-3.12219545846008	1.00372900424907	-2.50949573552637
H	2.02372671201587	2.45728133743047	-1.10595907936929
H	0.29827767042498	2.41026391159211	0.58985853967657
H	1.35044157764649	1.14472038992587	1.24260724727235
H	-1.01390658760891	-0.20853934945509	2.00657211402227

H	-1.32818806991806	-2.22931420634063	-3.41593279074740
H	-0.36585756878998	-0.78303213898326	-3.82056626637704
H	-2.12680039612086	-0.72705298784400	-3.87015301742008
H	2.32418468461512	0.71473361048315	-0.92894623665319
H	1.66825594374514	3.48940849933690	-3.70283495190391
H	-3.30988692451914	-2.91588736490904	-0.79192366043249
H	-4.45419361663519	2.11524013757954	-6.06365545597196
H	-2.69190804536376	2.12198365733193	-7.46214694710583
H	-2.60513985156247	-1.87445789688473	1.07223789064494

(*E*)-**S2**

Electronic energy (PW6B95/def2-QZVP): -1153.301062315707 Hartree

Gibbs free energy correction: 0.32100994 Hartree

C	2.90170202023285	4.90527066653361	-4.86956417930148
C	3.61289176671208	3.85118819561217	-4.24114897455829
C	2.94422328745162	2.74968749001215	-3.67323604458391
C	1.54654316353385	2.77237447948651	-3.71037754795359
C	0.83092256317725	3.78991531438119	-4.39308784337113
C	1.49510852853357	4.84876085932858	-4.95424590163320
C	0.57716271940895	1.80386146714367	-3.18886587978669
C	-0.68476206636452	1.98295317311986	-4.01121165153873
C	-0.64432116589670	3.48749371663126	-4.37430965492256
C	3.61841958770000	6.00512494545419	-5.46539603971012
H	2.99661776046330	6.78421520497527	-5.95266559026930
O	4.84931815543125	6.12118663285338	-5.46288328780000
C	3.76236758015346	1.59237643342351	-3.18295431453548

C	0.65868497667424	1.13097756588817	-2.01362888222308
C	1.64855682422019	1.42390734121911	-0.90199594437569
C	0.75982673624438	1.38826318457146	0.36540338252038
C	-0.33821225888192	0.43220880264718	-0.01918855840184
C	-0.37089350228816	0.26692158645610	-1.42804273420942
C	-1.22837696083836	-0.23678255406993	0.77921327075867
C	-2.16257026884971	-1.11311171403189	0.18919761683509
C	-2.14463192647439	-1.32177726797500	-1.21367704645917
C	-1.22558981255104	-0.65247969668441	-2.04442305616743
C	-3.09935082491762	-1.83417466195995	1.01427170398006
H	-3.04438032804969	-1.63185712199655	2.10378585499230
O	-3.93188239622441	-2.64166229085260	0.58564358401578
C	-1.14659494291984	-1.05073014120908	-3.48810931093826
O	4.95287902032220	3.85924678267617	-4.19827928726794
O	-2.98770090267631	-2.19223313515597	-1.78735671457527
H	0.96230586277138	5.64396024533633	-5.47295740394012
H	-1.58485805523888	1.69596102814516	-3.46250113630802
H	-1.14753664658012	4.07112663190563	-3.59113111698750
H	-1.13790402941324	3.71269138123141	-5.32474806663897
H	4.57637113864037	1.39462312613725	-3.88654555124286
H	3.14707815457539	0.69569725933637	-3.08666012659296
H	4.23306432201571	1.79701696793528	-2.21418819793616
H	2.16216272295052	2.37827205352893	-1.04043211208963
H	0.34966866407019	2.38907734638478	0.55882789868413
H	1.30394717901621	1.07424823340657	1.26152178529501
H	-1.22565647404663	-0.11432552370903	1.86103298574256
H	-1.21978809265015	-2.13898759009383	-3.57305145492648

H	-0.20480769816586	-0.72038985483591	-3.93054646991200
H	-1.97250891483837	-0.63784592776656	-4.07912401797006
H	2.40784618581256	0.63414827822790	-0.82900398945694
H	-0.64329769345909	1.39122216142055	-4.93531080376917
H	-3.54289317391632	-2.57240876839269	-1.05476101155903
H	5.24542528972250	4.69374342595332	-4.65373096429330

(*Z*)-**S2**

Electronic energy (PW6B95/def2-QZVP): -1153.298173428632 Hartree

Gibbs free energy correction: 0.32061310 Hartree

C	3.00892347917713	4.80525344883368	-4.99970950969723
C	3.66591748033900	3.77486668605732	-4.28073925649869
C	2.94479571783136	2.76166843282663	-3.61790492462878
C	1.54833679818155	2.85602976883169	-3.65204579712977
C	0.88694458665663	3.83745825407256	-4.43861724445163
C	1.60153832161453	4.80685035914980	-5.08994738064119
C	0.53481866933116	1.96342033570692	-3.09102716308708
C	-0.69466746197473	2.11721449443904	-3.97262839753685
C	-0.59879108795459	3.58877229804416	-4.43945841913704
C	3.77806953254161	5.81407471954487	-5.68427054829059
H	3.19366775351202	6.57754373657223	-6.23824310217889
O	5.01309599148924	5.87089398153542	-5.68769312347527
C	3.70761344815807	1.62210943914358	-3.01694470084904
C	0.53883819132791	1.18997263644533	-1.97690762095197
C	-0.47144359972211	0.07538851323476	-1.75451130091102
C	0.35990021684317	-0.99710459159338	-1.01206904075700

C	1.38117575586746	-0.16964189545591	-0.27594773178106
C	1.46268704062390	1.12995432112467	-0.84487237185560
C	2.14491270851739	-0.50451374700795	0.80991470708989
C	2.99455305358856	0.46489448058450	1.38199293597086
C	3.00850685829275	1.78313843106361	0.86033986408801
C	2.21625491722887	2.14724753993478	-0.24683597209816
C	3.80238343163573	0.13180283181228	2.52851165709408
H	3.72498380064402	-0.91450394625308	2.88980228887483
O	4.54959482235076	0.92474014556872	3.11282304365387
C	2.16175677998112	3.59102296711546	-0.63931100688893
O	5.00448525901724	3.72431860250360	-4.23017147375092
O	3.76633785066201	2.73321785235599	1.42584714457880
H	1.10865582286991	5.57129669908784	-5.68826947381509
H	-1.62581329640330	1.89581700698491	-3.44498253675341
H	-1.10400869045122	4.23989780408570	-3.71236550085454
H	-1.05818494548268	3.76414457237630	-5.41699031468439
H	4.55859602370184	1.37103461251848	-3.65593791969641
H	3.06913026940486	0.74445193601364	-2.89918589712921
H	4.11547261031851	1.86897999171231	-2.02891455045908
H	-0.90983996110657	-0.29227611783238	-2.68574782975266
H	0.84704883949755	-1.65739887766906	-1.74313030466877
H	-0.23886239233793	-1.62456631766782	-0.34498307633186
H	2.10179479226153	-1.49896245778839	1.25099540176934
H	2.18852536371253	4.21683048546057	0.25685312869254
H	1.25468300247558	3.80642904879701	-1.20720547533814
H	3.01745730343315	3.88740463141158	-1.25848684494683
H	-1.28826162694929	0.42059431551899	-1.10420957932498

H	-0.62855833182571	1.45172730268279	-4.84554837040956
H	4.24039035744455	2.30255678869385	2.18668817929050
H	5.33769703675351	4.50122099541842	-4.75399151752627

(*E*)-**S3**

Electronic energy (PW6B95/def2-QZVP): -847.489129915378 Hartree

Gibbs free energy correction: 0.25110485 Hartree

C	2.94251795236087	4.79277994485789	-5.07398876390537
C	3.52360133168526	4.05488595600861	-4.04052002075179
C	2.78113588096399	3.13298182255710	-3.30696100378015
C	1.42968016133455	2.95423456599401	-3.61577965085946
C	0.84923446270711	3.68309596597580	-4.67158076542708
C	1.59862352137440	4.59842077707720	-5.39056875478876
C	0.43667804659118	2.04629206627652	-3.03966042667372
C	-0.76087698551259	2.05045394645256	-3.97529916584423
C	-0.60264070300472	3.32573291630025	-4.83349755631155
C	0.51712083507957	1.37356134744332	-1.86695462212781
C	1.63417125157377	1.51066362589704	-0.84566108572766
C	1.03338148538830	1.00553574595477	0.48531375088397
C	-0.16293091396969	0.20379292317375	0.05181091171843
C	-0.46368962117975	0.44524962627049	-1.30245467427926
C	-0.94083321480862	-0.66133558759733	0.80194378309977
C	-2.02457038374596	-1.30768883693945	0.20884257623349
C	-2.31000075114164	-1.08438879474570	-1.13985547009338
C	-1.53817472964511	-0.21437399091227	-1.90561632109164
O	4.84626351102766	4.18917386516313	-3.70441999188408

O	-3.34833357597731	-1.71306280442189	-1.77804721544012
H	1.15010877835366	5.16491641730781	-6.20307158451979
H	-1.70834936272659	2.03088867392485	-3.42855943758390
H	-1.23913564374163	4.13156795573687	-4.44283011370816
H	-0.88652621199304	3.17061946216702	-5.87990256724256
H	1.99984179579303	2.53936224710454	-0.77416745048736
H	0.71824458562634	1.85304427201769	1.10938884629278
H	1.74487484654015	0.41860287188332	1.07600343233741
H	-0.71217554020023	-0.84507575294328	1.84893215487008
H	2.48712834686794	0.87912352043431	-1.13131849347077
H	-0.73767936786470	1.16276983662567	-4.62296604078327
H	-3.78804267380015	-2.30288949898944	-1.15578327697397
H	5.25561733711396	4.83306132578891	-4.29287113741143
H	3.28861973198528	2.55875537839177	-2.54242298862448
H	-1.77720862525549	-0.10560069992247	-2.95576961208151
H	3.54105258521142	5.50498888505520	-5.63837809288512
H	-2.63740096801204	-1.99458305136956	0.78905312432231

(*Z*)-**S3**

Electronic energy (PW6B95/def2-QZVP): -847.483667836053 Hartree

Gibbs free energy correction: 0.25103704 Hartree

C	-1.22148960185738	1.11332416574128	-7.02497908834157
C	-1.99496573932159	0.84438092563363	-5.89205723645677
C	-1.45908650205375	0.95208775746273	-4.61219015231279
C	-0.12318827152756	1.33029974229145	-4.47109257716919
C	0.64394119658664	1.64592876354106	-5.60842131942955

C	0.10086309727224	1.52744126912004	-6.87697824968022
C	0.65957011059235	1.61011408438563	-3.26366257333390
C	1.84359179857563	2.45466151463114	-3.71161795151452
C	2.01674915819864	2.11728695670869	-5.20957932828764
C	0.47460301383940	1.25240167557246	-1.97329398493169
C	1.29726560477118	1.84686732420923	-0.83927130254044
C	0.41333304316117	1.67078215365878	0.41577334319309
C	-0.47794982961076	0.51747087944849	0.03971441965355
C	-0.45391516065528	0.30360390898164	-1.35150822852975
C	-1.23510223554541	-0.29936500581006	0.86291389898716
C	-1.96082102220795	-1.35282626553164	0.31026211496614
C	-1.89967346450702	-1.59035211278873	-1.06600579615033
C	-1.14858178411362	-0.77266426755789	-1.90510649795149
O	-3.31269061740505	0.47827903074834	-5.98292340322483
O	-2.55857429301928	-2.63996750990429	-1.65155513179305
H	0.69227420727021	1.76596444095172	-7.75759853164346
H	2.74552189416665	2.25783644574849	-3.12426552905598
H	2.75252270510598	1.31014982552632	-5.33212662529604
H	2.36434526494223	2.96842697673167	-5.80440532174790
H	1.57201671095413	2.88994686162279	-1.02285135358029
H	-0.18230996891090	2.57815039204341	0.58813717452405
H	0.99202451083905	1.48286385738418	1.32616586329073
H	-1.25925208172866	-0.13404736003521	1.93727638514257
H	2.23025991343416	1.27732963407039	-0.71561990496225
H	1.60470146318405	3.52273697058265	-3.59988135266006
H	-3.01798944821546	-3.14185355103606	-0.96929597535134
H	-3.57099469233301	0.46393093608934	-6.91109491893385

H	-2.10330802780433	0.77618100522096	-3.75841159156920
H	-1.09231107958220	-1.01576289836159	-2.95991496393743
H	-1.65942345279582	1.02275251192069	-8.01697676134509
H	-2.55406863969660	-2.00384744100278	0.94917426297208

(*E*)-**S4**

Electronic energy (PW6B95/def2-QZVP): -1074.536236389157 Hartree

Gibbs free energy correction: 0.26738196 Hartree

C	2.95137973736086	4.82438197085015	-5.02472870606258
C	3.53510469531889	4.06113047395613	-3.97675943646067
C	2.76494304915229	3.14430971293648	-3.25993026010241
C	1.41594895980614	2.99024045634656	-3.57893128443093
C	0.83607212409087	3.73595582405574	-4.63634870730647
C	1.59117455504083	4.64024697000203	-5.34168342718241
C	0.41485070324415	2.08896914783489	-3.01668898252679
C	-0.78098093549789	2.10590038548489	-3.95245076348609
C	-0.61763360107319	3.38826325320058	-4.79774678213682
C	3.75177656209138	5.76491022979066	-5.76971681385829
H	3.22868649403515	6.32018577146368	-6.57578499176863
O	4.95117002109056	5.97634948118983	-5.56227187048804
C	0.49123560766841	1.41253212231173	-1.84080974246532
C	1.59852078902079	1.55072775633737	-0.81082911112988
C	0.98417367653954	1.05341120065213	0.51603008035911
C	-0.20643604515547	0.24824640530093	0.07519247669062
C	-0.49614000211272	0.48814155070836	-1.29189343759407
C	-0.98585599105658	-0.61308851315137	0.80725764816405
C	-2.07277329664763	-1.27206285172989	0.19995177189070

C	-2.34916432569667	-1.04414660381885	-1.17598551441905
C	-1.55686143945660	-0.16661666251263	-1.91729152374612
C	-2.88653358098752	-2.18745413683325	0.96177607135484
H	-2.60564119544565	-2.31870368250419	2.02743620518025
O	-3.84845229138279	-2.81186093143363	0.50265680402111
O	4.83003156867077	4.19212631011411	-3.66217723370190
O	-3.35940548364582	-1.66985930275402	-1.79333402548342
H	1.15739638274312	5.22250546046735	-6.15337171423671
H	-1.72918446407357	2.08323549873284	-3.40782605450726
H	-1.24820770622860	4.19242119272700	-4.39575782368965
H	-0.90475110771265	3.24541650645577	-5.84434561925755
H	1.96793233417626	2.57779396545860	-0.74057318775258
H	0.66166863789625	1.90513699821751	1.12951278618630
H	1.68929889837217	0.47095618672704	1.11748832475719
H	-0.77707066514186	-0.80393227040555	1.85891010230824
H	2.45073781625767	0.91449003477989	-1.08724365834981
H	-0.75811338790594	1.22420516649850	-4.60787534091849
H	-3.79517846509395	-2.24704695643356	-1.11419243743608
H	5.20437300460581	4.87610093843939	-4.27581526630084
H	3.26104967412099	2.55559199776593	-2.49942926869850
H	-1.77743710698507	-0.05556663023291	-2.97090076141304

(*Z*)-**S4**

Electronic energy (PW6B95/def2-QZVP): -1074.530466021287 Hartree

Gibbs free energy correction: 0.26722621 Hartree

C	-1.62540429328800	1.33492377587749	-6.90986143727807

C	-2.35466170992829	1.10500266446712	-5.70964393157891
C	-1.70486679004714	1.13455277657628	-4.47543863036011
C	-0.33555801683734	1.38400137158940	-4.43464858607404
C	0.38671508383443	1.65545566047687	-5.62408607338230
C	-0.24838705575006	1.62046717876162	-6.84140170197696
C	0.55131723839247	1.56658205877286	-3.28714181014911
C	1.77885951102971	2.30332417481623	-3.79896023602342
C	1.82084034959149	1.98442752065642	-5.30959666404223
C	-2.29892693296560	1.31341759978790	-8.18534998513670
H	-1.66313006680470	1.50931018788774	-9.07397922725177
O	-3.50505681601970	1.09400113280203	-8.33337370659480
C	0.41564923333086	1.21101154863117	-1.98609953168418
C	1.35282806718782	1.72669419782616	-0.90571160571458
C	0.54262622727418	1.60086059308079	0.40328908047867
C	-0.45616126779566	0.52326312595021	0.07871404284590
C	-0.54072623111413	0.32692245187082	-1.32277177475501
C	-1.21088519991781	-0.24553739920461	0.93059668843341
C	-2.05578774391010	-1.24686718893371	0.41476992200532
C	-2.10389272957762	-1.46898561331568	-0.99006317587119
C	-1.34146347673831	-0.68127553082848	-1.85280198533136
C	-2.83779566527648	-2.06676357582385	1.30786686595160
H	-2.73931327437832	-1.83745258702166	2.38956559069064
O	-3.58372069356227	-2.98036593416745	0.94230775348591
O	-3.67250281858389	0.87318855825385	-5.73443474628836
O	-2.86238458134171	-2.44047472925493	-1.51158088399696
H	0.29292492040583	1.82410244064790	-7.76413790580296
H	2.69233858930350	2.00698629671897	-3.27511152338901

H	2.46401455765893	1.11270124840109	-5.49144196382946
H	2.21003501863917	2.81034664180496	-5.91292126528203
H	1.69276632429904	2.74806398293816	-1.10049974997281
H	0.03032026179696	2.54789486343756	0.62068180980559
H	1.16347407211234	1.35776101505283	1.27111781058897
H	-1.15934114564940	-0.10545454327579	2.00933759228073
H	2.24644557633839	1.08760644905314	-0.85132949527482
H	1.65194171004812	3.38600010730653	-3.65210921977238
H	-3.31899178688226	-2.88581969249587	-0.75289271255830
H	-3.94916806760475	0.89523049886248	-6.68608405884614
H	-2.29722573181530	0.99809085465524	-3.57811920493512
H	-1.36784749146039	-0.90407651963694	-2.91316209541370

(*E*)-**S5**

Electronic energy (PW6B95/def2-QZVP): -1083.732023387843 Hartree

Gibbs free energy correction: 0.41030014 Hartree

C	2.80459144497576	4.44719313292705	-5.53919982746105
C	3.26250700160033	3.15749154750579	-5.25521233354343
C	2.57449222364851	2.33604526298434	-4.35806204614627
C	1.43704298356826	2.82160527191500	-3.72441696691544
C	0.95029387804779	4.10077646733006	-4.04416773264739
C	1.63014267971445	4.90800971271786	-4.93533205608522
C	0.49101507236854	2.13485160473166	-2.83134442074071
C	-0.85602340428086	2.87753881370040	-3.02765245085907
C	-0.34622075244461	4.32466717267315	-3.33117667264795
C	0.78004721345303	1.16700274313003	-1.92311488136062

C	2.15777307741502	0.84221818182217	-1.29122115147605
C	1.73117464346473	0.51487434854457	0.17774792051630
C	0.37211534340965	-0.09235910650362	0.02466432694912
C	-0.17912134908159	0.31625921909917	-1.20180507814937
C	-0.31479257276831	-0.96391946514854	0.84723198600782
C	-1.56292961659035	-1.45800400467525	0.45405284139455
C	-2.08918409494416	-1.08616564695649	-0.78625427460165
C	-1.39368133111072	-0.21041714923507	-1.62419600284719
O	4.37283292980159	2.59254979182296	-5.82179257338217
C	5.08461930691725	3.36064386739069	-6.78326596952773
O	-3.27967430233708	-1.54134728092542	-1.28507154385354
C	-4.01599259355756	-2.46284225833144	-0.49138354290645
H	1.25526924323623	5.89796430477416	-5.18413160331078
H	-0.18374297678630	4.85758904559559	-2.38270299929502
H	-1.07811732753235	4.89640030428780	-3.91425047400175
H	1.67727895099929	1.44994716324517	0.75455234478120
H	2.45652108393343	-0.14206589657784	0.67257028722222
H	0.10979097024461	-1.28130870379681	1.79666923013757
H	4.45054056267542	3.61461154700299	-7.64393104939350
H	5.91061905589240	2.73010700992969	-7.11720447609823
H	5.48864898335511	4.28302732824924	-6.34357854448773
H	-4.91440508416144	-2.69950653576801	-1.06419668504247
H	-4.30616032663632	-2.02142428239703	0.47204609427681
H	-3.44574386038578	-3.38490040359082	-0.31269290288466
H	2.93069349326474	1.32398692305192	-4.20901827923338
H	-1.80853346211847	0.00788607762416	-2.60067853452289
C	-1.59294432879834	2.37168821723027	-4.28091124392176

H	-0.95208365325090	2.45356856645808	-5.16532631351527
H	-1.89327261080764	1.32551599076447	-4.17994504753622
H	-2.49707009128686	2.96783761482830	-4.45263325467471
C	-1.79882137776720	2.93138321625621	-1.82609664373450
H	-2.51450016395883	3.74888802851444	-1.97656073119353
H	-2.37411246463910	2.01582344556298	-1.68348019717718
H	-1.24518010154381	3.12789804876773	-0.90185730375346
C	3.18931701700067	1.96950510804227	-1.26260413931898
H	3.95082640920178	1.73037713602352	-0.51037020030993
H	3.70267935714317	2.11326200419533	-2.21408202224942
H	2.72186920677749	2.92047061670089	-0.98575167142269
C	2.76070337678751	-0.43787631273348	-1.89746567248786
H	3.69019318957751	-0.69877639975997	-1.37760884304980
H	2.06380361180463	-1.27729232535149	-1.80106897068378
H	2.99098622984742	-0.31411616500429	-2.95882418382830
H	3.32693966705325	5.08594654109905	-6.24151260697781
H	-2.09120196435876	-2.14529895082566	1.10416938394533

(*Z*)-**S5**

Electronic energy (PW6B95/def2-QZVP): -1083.729624290188 Hartree

Gibbs free energy correction: 0.41098709 Hartree

C	2.88862197808001	4.52245796832088	-5.16841773223082
C	3.34056151041057	3.23312201202258	-4.86160159102314
C	2.57044841153598	2.37150421007464	-4.07991617043797
C	1.34839264786148	2.81393340803950	-3.58315431978906
C	0.87469537475613	4.08919670031010	-3.92550998143020

C	1.63959056601115	4.93918377737901	-4.70385859615866
C	0.30649584062824	2.06205083722142	-2.85110884377237
C	-1.01466569757393	2.80752215254443	-3.16211118148317
C	-0.50220274421168	4.27020600343709	-3.37239510899300
C	0.55704514570384	0.98461560961831	-2.05949971088243
C	-0.36838890672843	-0.16332340334004	-1.58650004188007
C	0.64215613862888	-1.35204644616618	-1.47732784449079
C	1.93531172782989	-0.69134173276962	-1.12271827499630
C	1.88634463807220	0.65887718647122	-1.49988327765108
C	3.04929269637449	-1.20415222115206	-0.48255780328339
C	4.13078460534617	-0.37015477292910	-0.19262095647247
C	4.06160409213152	0.98716394146873	-0.53009278197124
C	2.93855700879934	1.50884584852422	-1.17276038573226
O	4.52864326480320	2.71420878672920	-5.29938667371709
C	5.35104853791205	3.54221132358866	-6.11014578910814
O	5.04709687548479	1.89562845655599	-0.25473482937098
C	6.20910804632907	1.42533925478487	0.41459002417538
H	1.27292697926999	5.92795449773402	-4.96906590149148
H	-0.46788149628892	4.78708984896434	-2.40197605367139
H	-1.17139388738404	4.83966272230469	-4.02823549215164
H	0.71767982292526	-1.85784236942184	-2.45127251711702
H	0.31032906958551	-2.09552752291312	-0.74289730738314
H	3.08810856638224	-2.25097406663198	-0.19089367329913
H	4.84494175941547	3.82313793520944	-7.04430676497037
H	6.23505735086099	2.94652595597403	-6.34492756933078
H	5.65889931973271	4.45132795627190	-5.57510880871428
H	6.85531643850456	2.29630064078562	0.53828769666368

H	6.73602324887815	0.66530716690208	-0.17892698744577
H	5.96551177126409	1.01134746170313	1.40300286058182
H	2.94594551537919	1.37390013366449	-3.88036296450639
H	2.91456598022167	2.56896375620207	-1.39977739737938
C	-1.62183244893596	2.33260045241459	-4.49469726561428
H	-0.88815588555158	2.42681918244850	-5.30255604857441
H	-1.94039864693397	1.28966397217940	-4.44577401199979
H	-2.49512181651068	2.94485180374245	-4.75040855441630
C	-2.06724345924493	2.83072103137979	-2.05465717512954
H	-2.81904907896778	3.59241429337998	-2.29524675988349
H	-2.59759220166912	1.88557737854029	-1.93605478732250
H	-1.61258765741186	3.09715189444040	-1.09513700490295
C	-1.48518680752519	-0.57926006998219	-2.54301129402704
H	-1.89116615931772	-1.54419717922224	-2.21554504396419
H	-2.31753726099347	0.12407151476209	-2.57447482095305
H	-1.09716980161734	-0.70402090232950	-3.55901162113808
C	-0.91928097713437	0.10884730088412	-0.17511643182366
H	-1.47464298545758	-0.76529015083297	0.18571810603080
H	-0.09849652860609	0.30633114251049	0.52288095162689
H	-1.59192930193236	0.96844840055333	-0.16150562486995
H	3.47943439762985	5.19339335773245	-5.78057962579731
H	4.99795033424909	-0.77904853407993	0.31226297566763

(*E*)-**S6**

Electronic energy (PW6B95/def2-QZVP): -1310.745124779810 Hartree

Gibbs free energy correction: 0.42163420 Hartree

C	2.89901273161899	4.61201811325300	-5.30753573573436

C	3.33334524828330	3.30853194428373	-5.00643878892362
C	2.62850591522550	2.49855104232940	-4.12449990869592
C	1.48034572557820	2.99954373066015	-3.51160939386561
C	1.01571521064560	4.28694274066492	-3.84714534727311
C	1.71533549185048	5.08996647458163	-4.71960282991755
C	0.51644445515327	2.33262794416067	-2.63184661867957
C	-0.81756346286518	3.09683339970063	-2.83801070125496
C	-0.28178768744553	4.53315981225057	-3.14393437216244
C	3.65325333561699	5.47024824695264	-6.23623956123695
H	4.59909243793262	5.03998336587336	-6.62363582002134
O	3.29012666092332	6.58482681474120	-6.56689557660452
C	0.78554709764952	1.35989548234596	-1.71779003365214
C	2.15096757277058	1.02456059410740	-1.06395454416244
C	1.69755411254713	0.69918019581182	0.39657468186425
C	0.33596903187612	0.10398758455026	0.22270652522921
C	-0.19218251120878	0.52560901282643	-1.01371101567680
C	-0.37025824817429	-0.74548379888677	1.04439382529394
C	-1.62717958673242	-1.22314335268151	0.63537668888393
C	-2.12821738504666	-0.83874562803571	-0.62148048206621
C	-1.41633787221634	0.01984653528838	-1.45008089729194
C	-2.38905291244273	-2.12493210519601	1.51534484540854
H	-3.38974844849458	-2.42376100482056	1.14240471296497
O	-1.97582402355897	-2.52382638183707	2.58942423859423
O	4.49013451613958	2.82215996553213	-5.57846183645345
C	4.26270015870401	2.06281937063729	-6.77240078803287
O	-3.35814094196585	-1.30108839585027	-1.04012735639307
C	-3.28200242580266	-2.48223842686497	-1.84814773371834

H	1.38147320781011	6.09094560255593	-4.98133567236613
H	-0.10931194732898	5.06617122550619	-2.19793952010690
H	-0.99680850518396	5.11852415090480	-3.73253732112337
H	1.63487607846355	1.63304114590410	0.97337720134176
H	2.40600537245659	0.03693634897138	0.90640679402454
H	0.01231398548434	-1.07084194883840	2.00861814357943
H	3.62361014490769	1.19256768419454	-6.57041047134135
H	5.24230800110245	1.72650920017139	-7.11807466657086
H	3.79008511697855	2.68323876890478	-7.54687206079260
H	-4.30737230118532	-2.73619805979764	-2.12447681618535
H	-2.83404415236098	-3.31324722898540	-1.28532412851030
H	-2.68891716992653	-2.30174532817780	-2.75485367823856
H	2.97767406712189	1.48730349786717	-3.95197655822543
H	-1.82173706519991	0.25883235382949	-2.42622550866065
C	-1.55490412754906	2.59998612682341	-4.09525522254096
H	-0.91025572124196	2.67049830426002	-4.97784135303742
H	-1.87459861646954	1.55947098697113	-3.99544179311827
H	-2.44760715119234	3.21086942852931	-4.27128803157621
C	-1.76501797234415	3.16768506787218	-1.64107705003591
H	-2.46707446664153	3.99514468059952	-1.79723706275041
H	-2.35805735593404	2.26328717153597	-1.50006584389488
H	-1.21440709876069	3.35915877250169	-0.71409235890623
C	3.18961011764539	2.14472098310461	-1.01949345098323
H	3.93659671900777	1.90001296648795	-0.25536597426686
H	3.72294152256924	2.28315333729628	-1.96070852627528
H	2.72627131530745	3.09950409338837	-0.74941927764202
C	2.75270601915974	-0.26124465820104	-1.66059795896200

H	3.67191735892860	-0.52699934301632	-1.12628066242050
H	2.05050615377485	-1.09720753240544	-1.57348892920314
H	3.00143172605281	-0.14191080008031	-2.71831268163571

(*Z*)-**S6**

Electronic energy (PW6B95/def2-QZVP): -1310.756512952932 Hartree

Gibbs free energy correction: 0.42484547 Hartree

C	3.09332267719618	4.83596360748015	-4.71222510227195
C	3.41498913889725	3.45504790353839	-4.74559082349818
C	2.60965412741049	2.52249344775435	-4.09899883475190
C	1.49334193207197	2.96779830173394	-3.38519089291504
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C	0.45161515234411	2.17577874228351	-2.71097206690494
C	-0.79983839539169	3.08592526630387	-2.69274043223203
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C	3.93001218211819	5.83935815256016	-5.38863703705577
H	4.82343811514728	5.45262090840307	-5.91578900346009
O	3.68000632165385	7.03309704736383	-5.38313392637344
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C	-0.32645972667462	-0.22382835759928	-1.89049297272359
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C	1.94858795164130	-1.01496009590089	-1.82543868497793
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C	3.06988540460993	-1.73500067608039	-1.46900492543164
C	4.26104128668690	-1.07043647027487	-1.15142362347938
C	4.28644685250910	0.34755683039801	-1.16906458884977

C	3.15246064111816	1.07379669804959	-1.51950427209591
C	5.44814396751075	-1.85829730001029	-0.78432639836445
H	6.35791353045183	-1.27947082031622	-0.53345013698919
O	5.45893046646811	-3.07746777318976	-0.75336683618696
O	4.53289615511870	3.11757719264827	-5.44362793734542
C	4.90976008433796	1.74170415884145	-5.47788970122508
O	5.46571686498075	0.92913987492535	-0.82030773332833
C	5.54344570962466	2.35376466066218	-0.85033139743100
H	1.69762531844312	6.31054795806030	-4.05561272791124
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H	0.49646073497629	-1.76431053306790	-3.21500465349736
H	0.23920447357781	-2.34067575656844	-1.55991368526087
H	3.07006816887197	-2.82089743202269	-1.41790082501091
H	5.08137163320857	1.34894396045954	-4.46647929267658
H	5.84007097318854	1.70527351060942	-6.04633353597870
H	4.14906990598275	1.13262998784363	-5.98273527719472
H	6.57180208622334	2.59834443165680	-0.58104333649657
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H	5.32300922459006	2.74466158613598	-1.85286063548240
H	2.83455732890794	1.46513842252179	-4.14268211247428
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H	-2.41019301203249	3.69748855225946	-4.01664564144834
C	-1.72141495807417	2.95015755014661	-1.48183881668827

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H	-2.03312045869443	-1.29815402164829	-2.63543550258017
H	-2.32070830238969	0.43376138788765	-2.54954437813354
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C	-0.71204671997815	-0.23415492716677	-0.39993481701221
H	-1.33920674610534	-1.10687269053936	-0.18437307420708
H	0.18335341666926	-0.29297670319580	0.22828630384494
H	-1.26749537070243	0.66202042343931	-0.11826989011130

9. ^{1}H NMR and ^{13}C NMR spectra

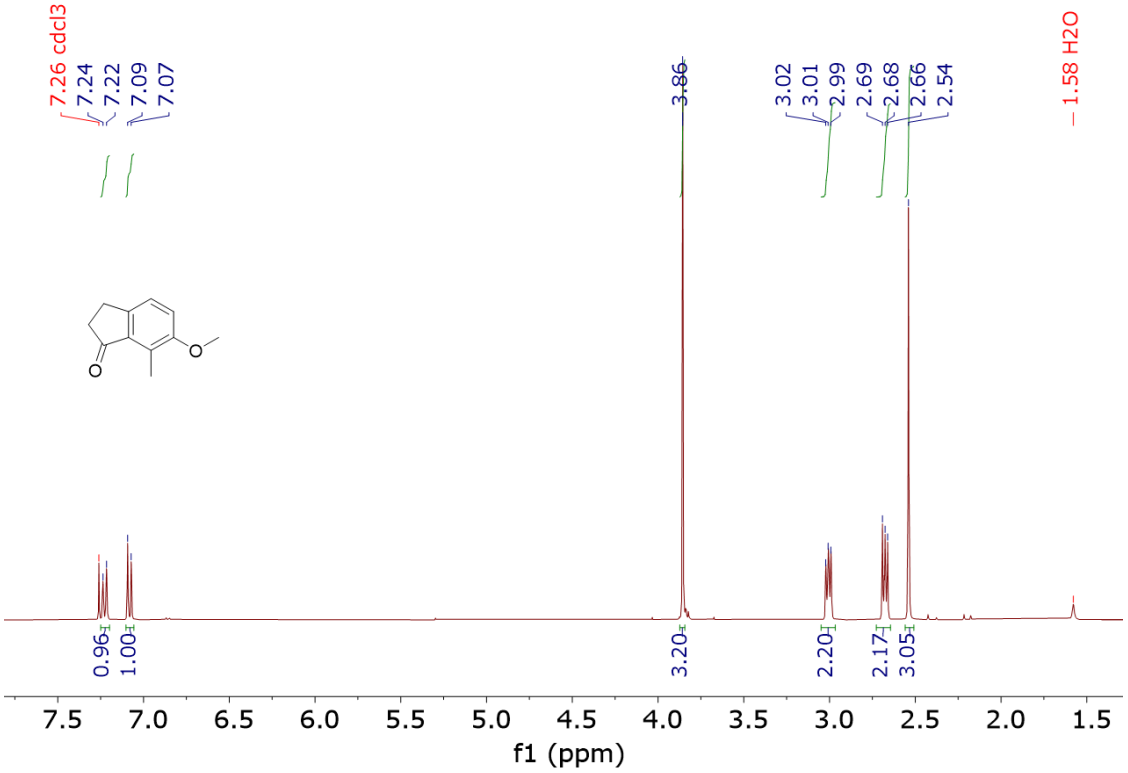

Figure S18. ^{1}H NMR spectrum of compound **1** ($CDCl_3$, 298 K, 400 MHz)**.**

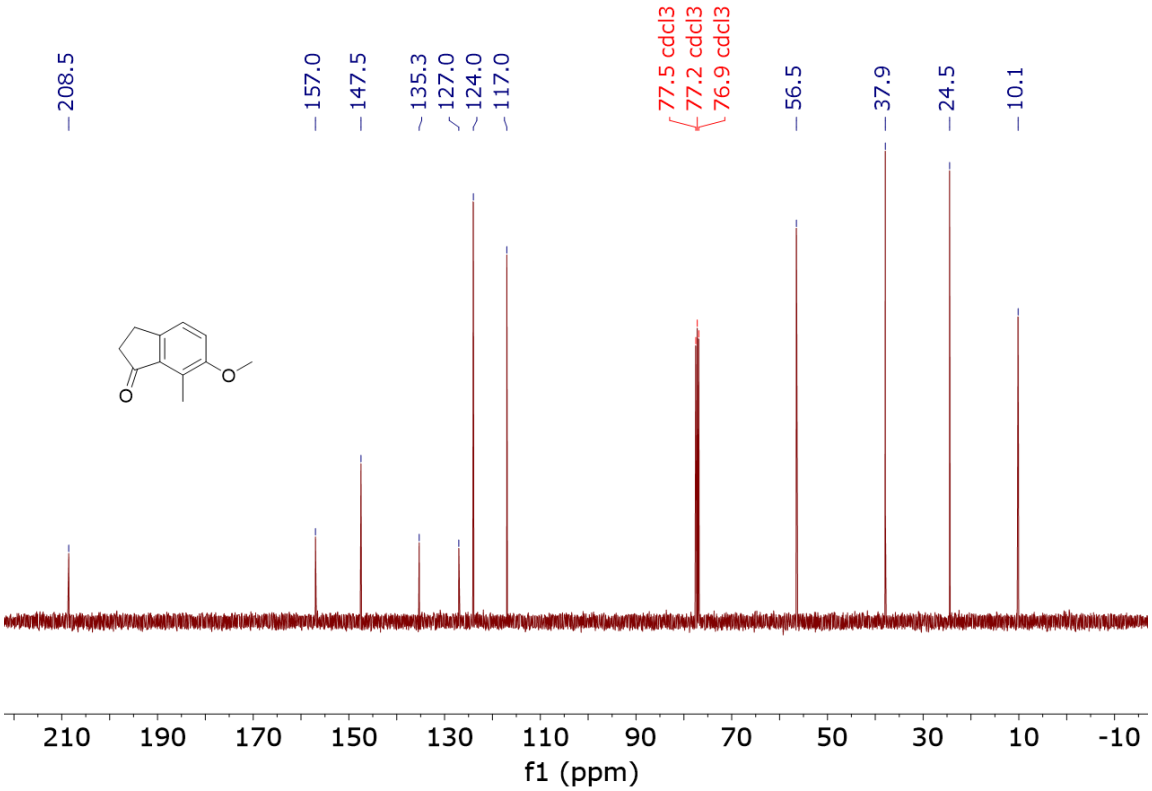

Figure S19. ^{13}C NMR spectrum of compound **1** ($CDCl_3$, 298 K, 400 MHz)**.**

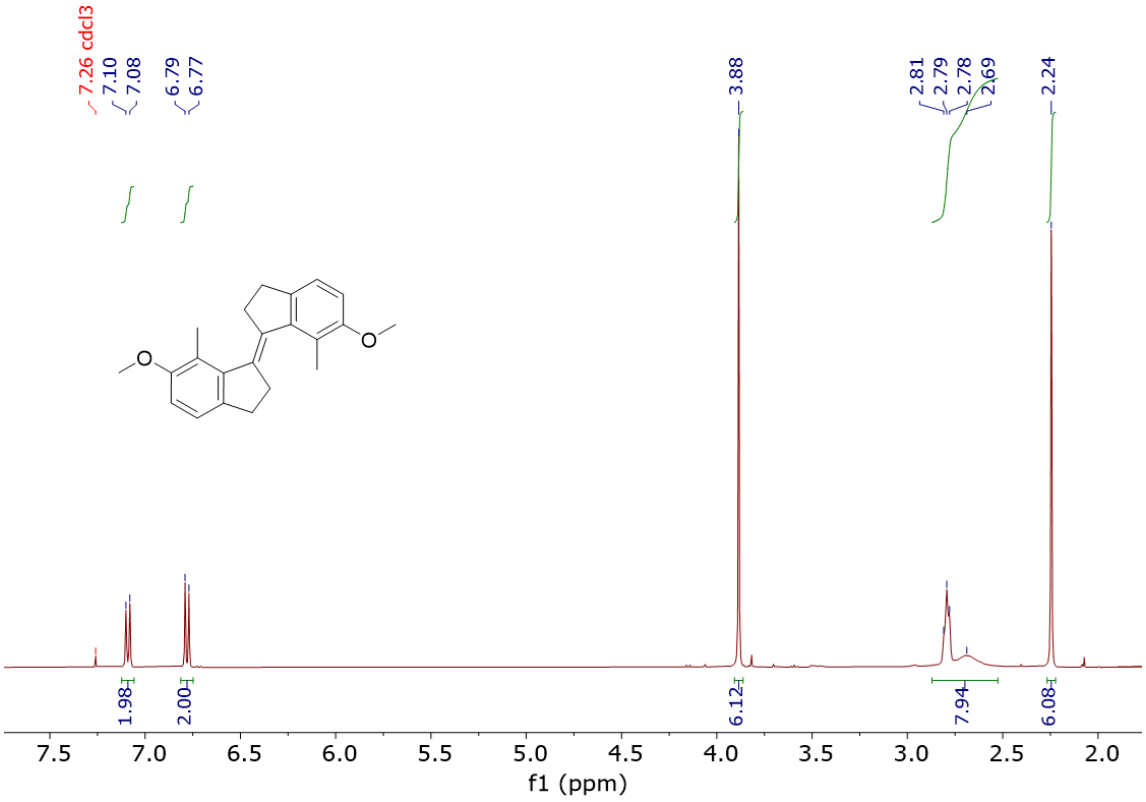

Figure S20. ^{1}H NMR spectrum of (*E*)-**2** ($CDCl_3$, 298 K, 400 MHz)**.**

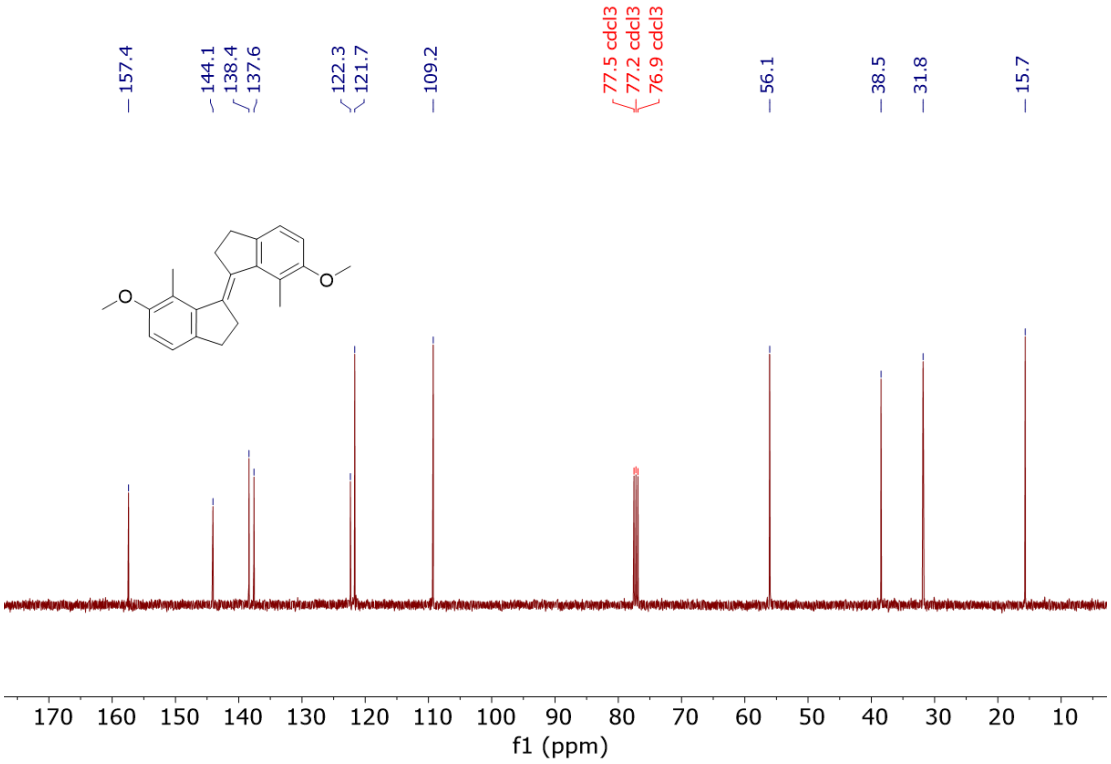

Figure S21. ^{13}C NMR spectrum of (*E*)-**2** ($CDCl_3$, 298 K, 400 MHz)**.**

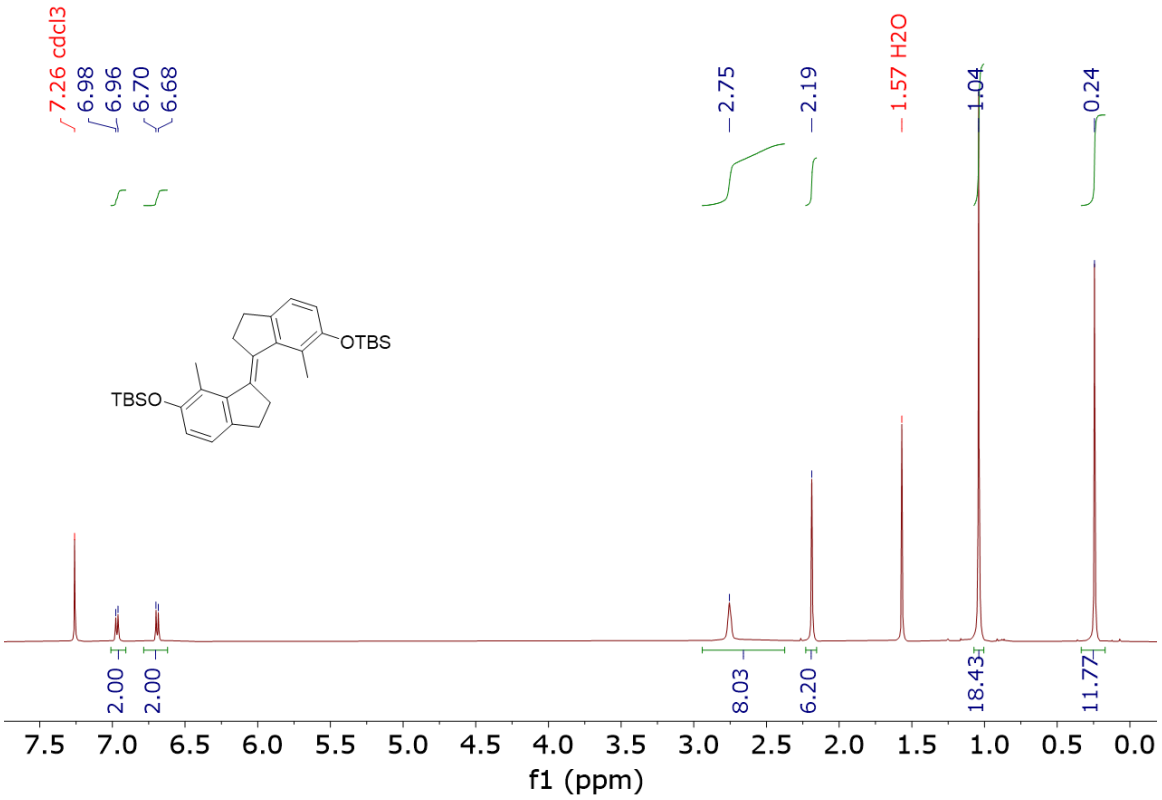

Figure S22. ^{1}H NMR spectrum of (*E*)-**3** ($CDCl_3$, 298 K, 400 MHz)**.**

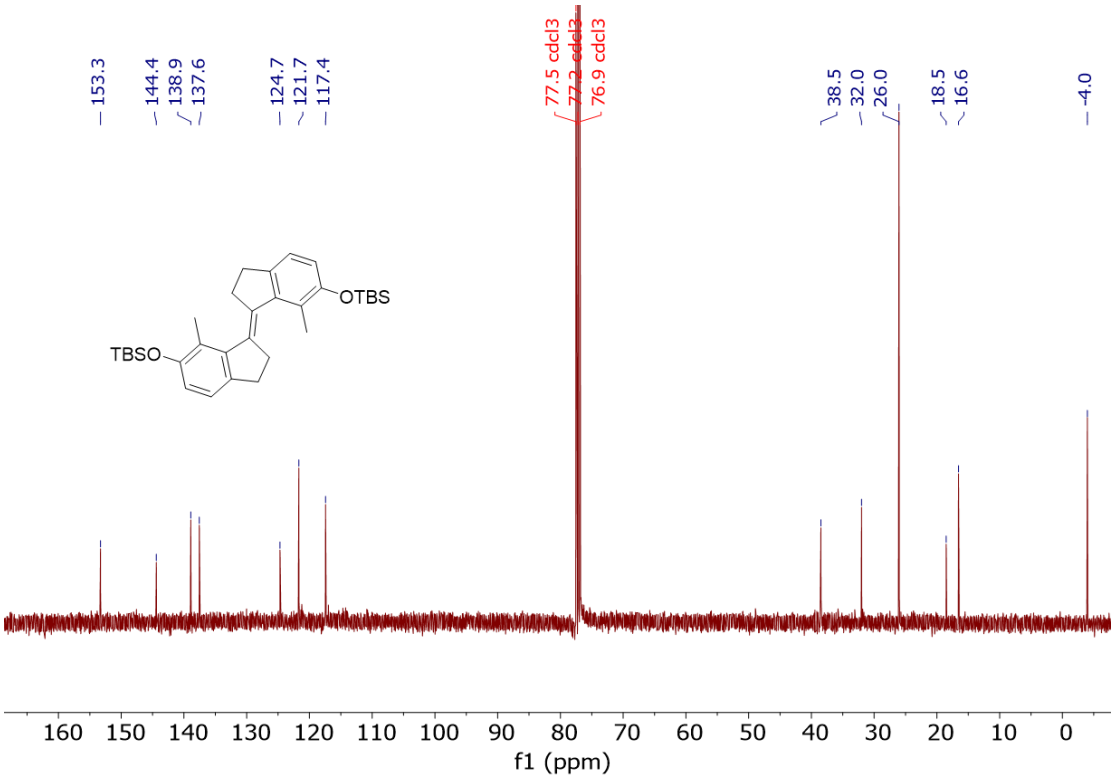

Figure S23. ^{13}C NMR spectrum of (*E*)-**3** ($CDCl_3$, 298 K, 400 MHz)**.**

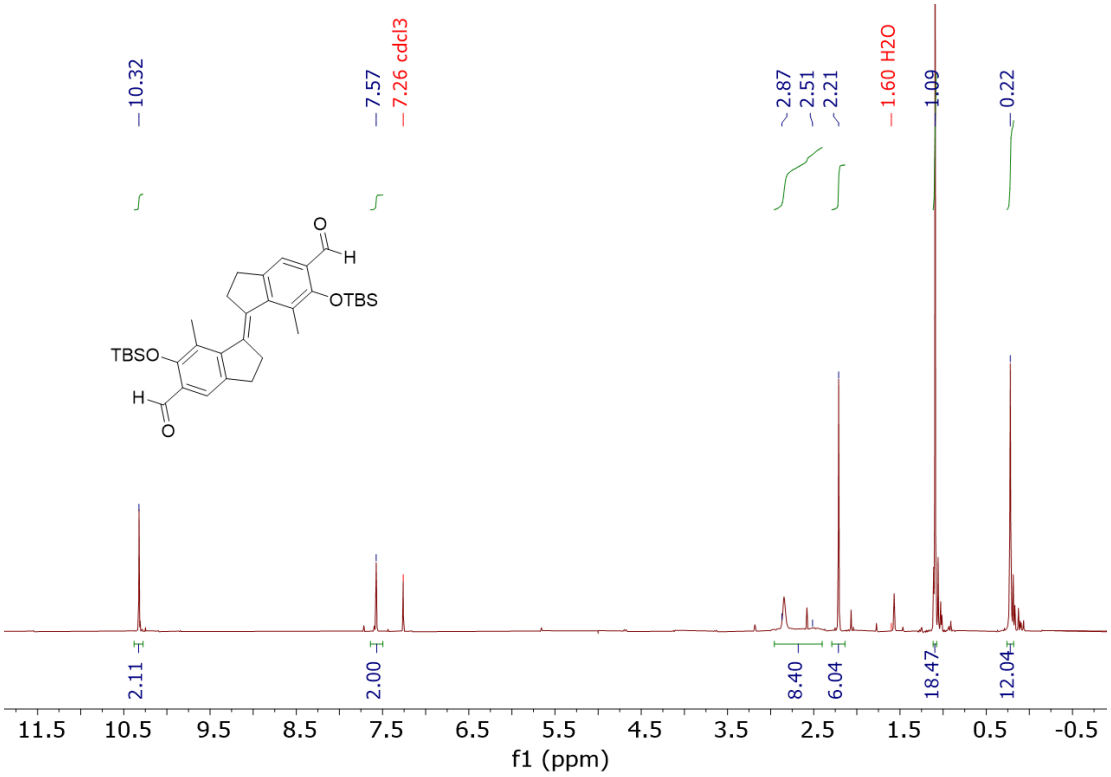

Figure S24. ^{1}H NMR spectrum of (*E*)-**4** ($CDCl_3$, 298 K, 400 MHz)**.**

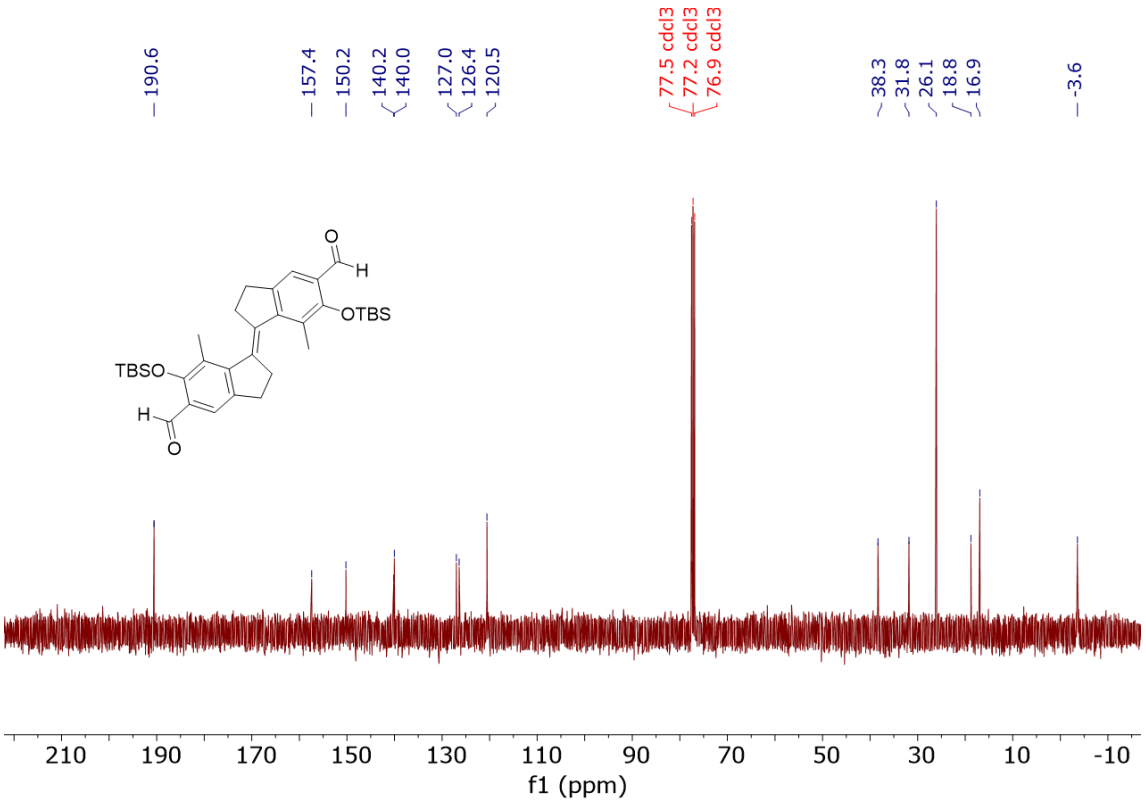

Figure S25. ^{13}C NMR spectrum of (*E*)-**4** ($CDCl_3$, 298 K, 400 MHz)**.**

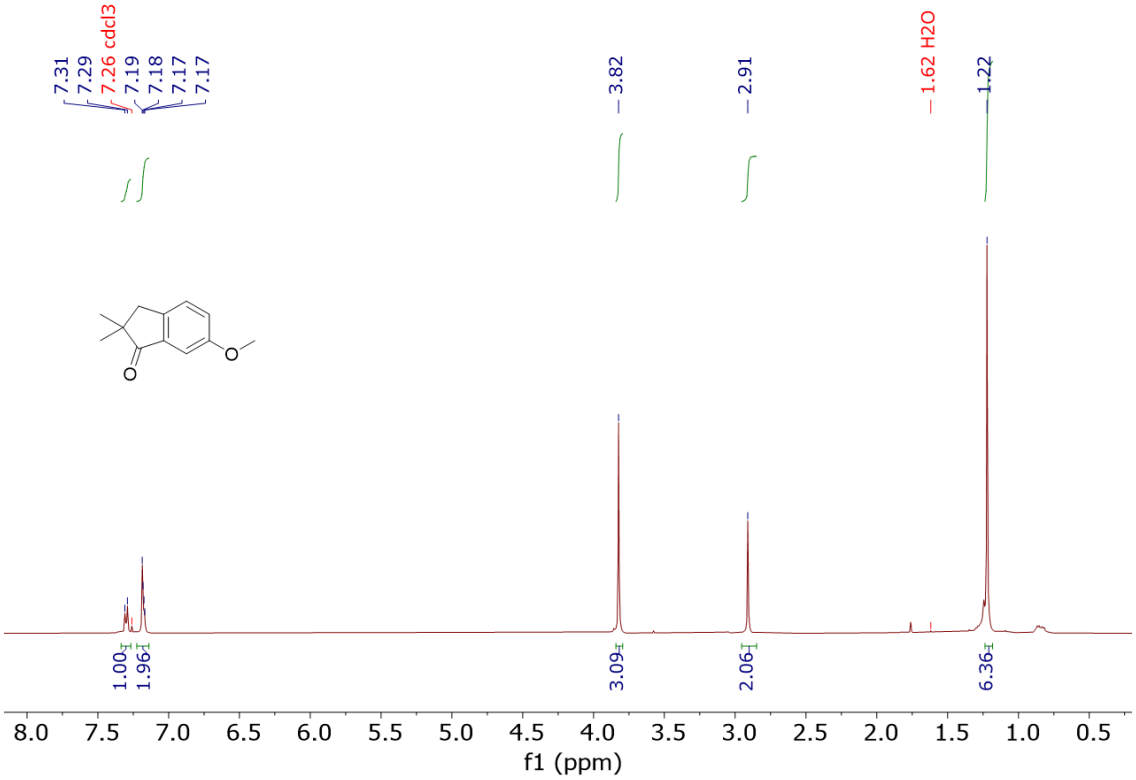

Figure S26. ^{1}H NMR spectrum of compound **5** ($CDCl_3$, 298 K, 400 MHz)**.**

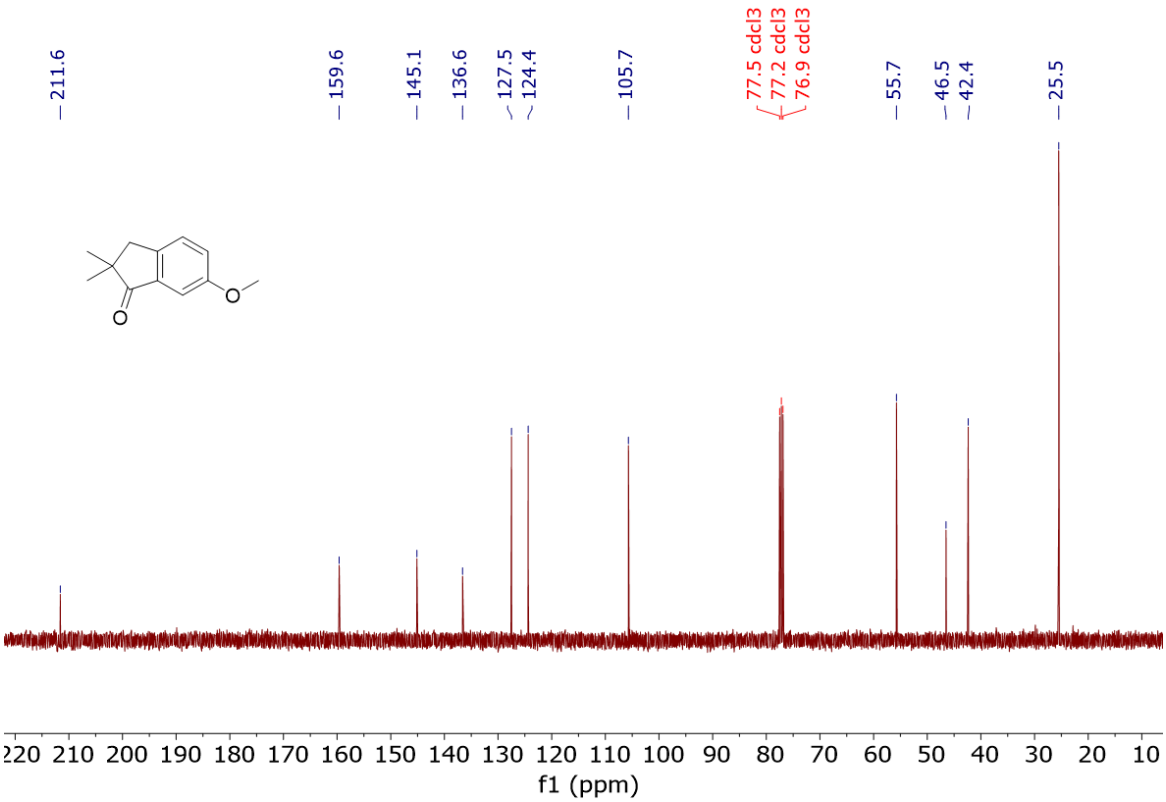

Figure S27. ^{13}C NMR spectrum of compound **5** ($CDCl_3$, 298 K, 400 MHz)**.**

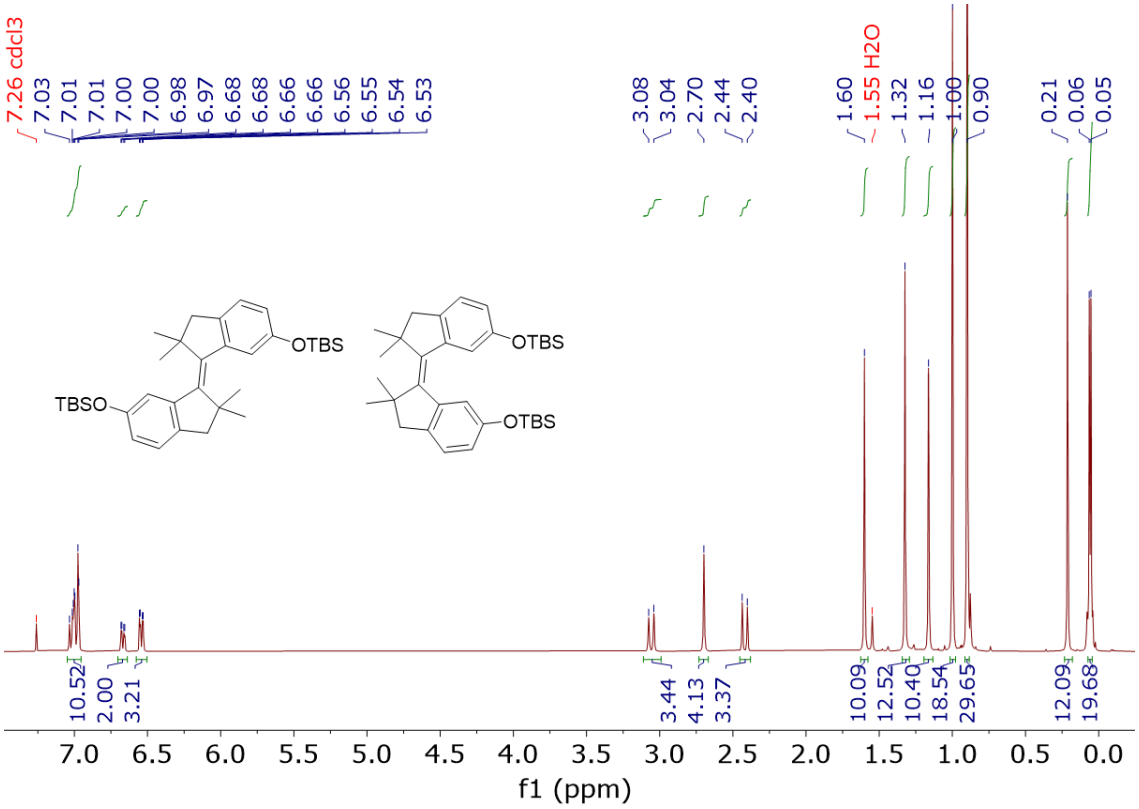

Figure S28. ^{1}H NMR spectrum of (*E*)/(*Z*)-**6** ($CDCl_3$, 298 K, 400 MHz)**.**

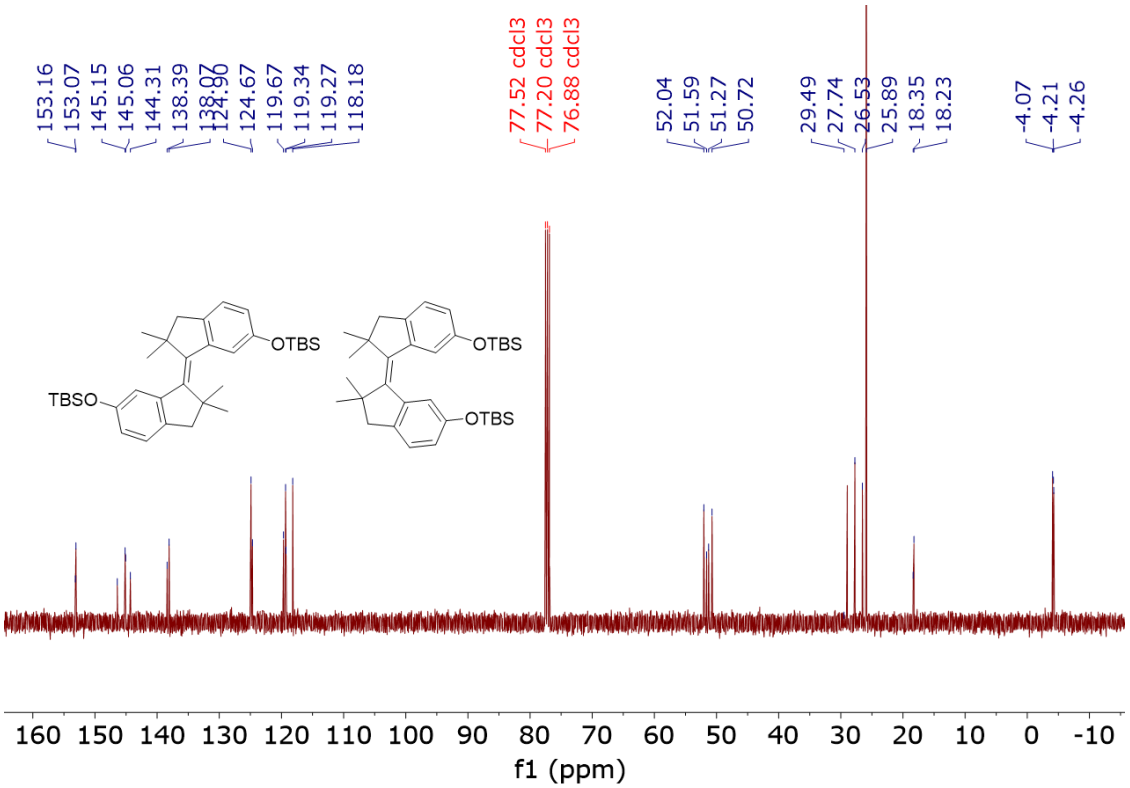

Figure S29. ^{13}C NMR spectrum of (*E*)/(*Z*)-**6** ($CDCl_3$, 298 K, 400 MHz)**.**

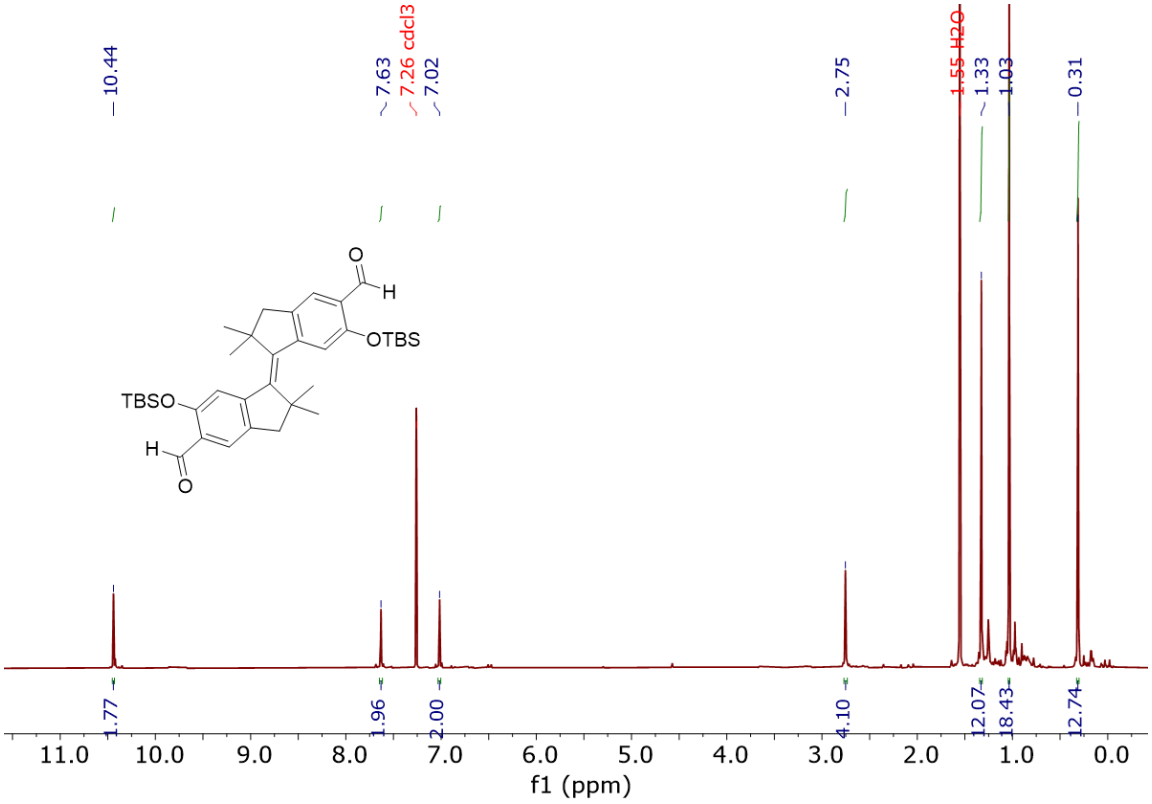

Figure S30. ^{1}H NMR spectrum of (*E*)-**7** ($CDCl_3$, 298 K, 400 MHz)**.**

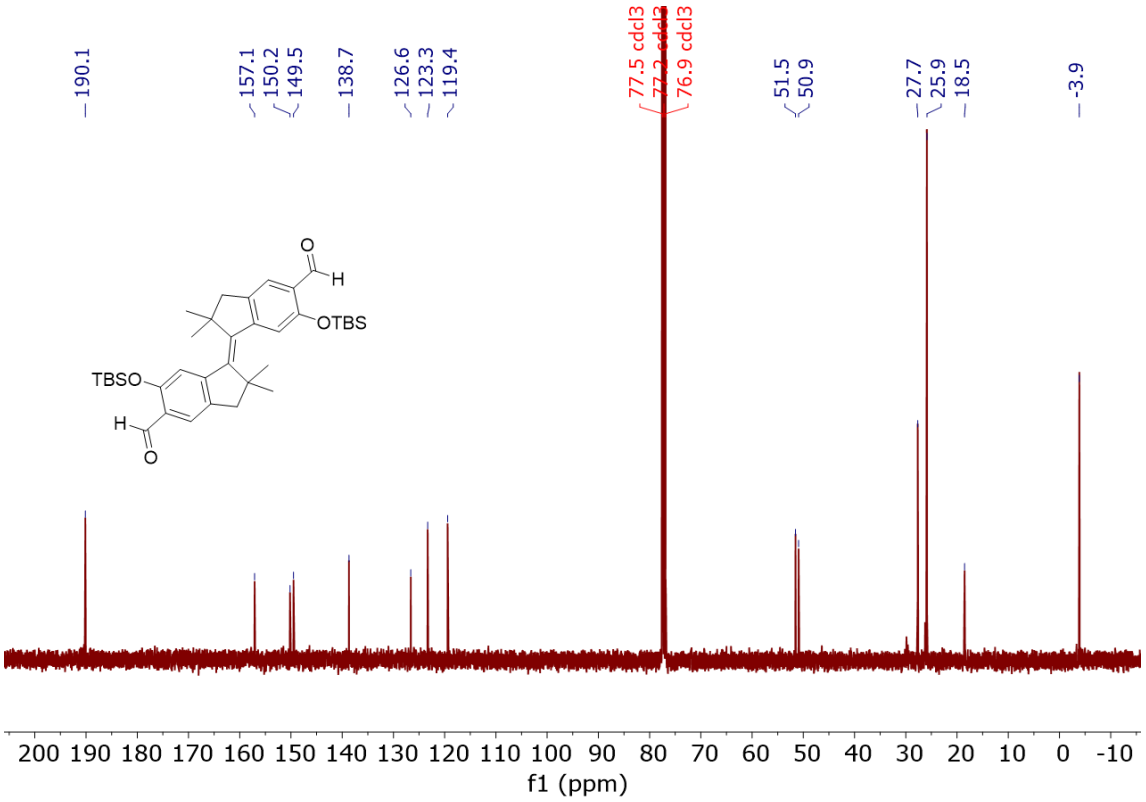

Figure S31. ^{13}C NMR spectrum of (*E*)-**7** ($CDCl_3$, 298 K, 400 MHz)**.**

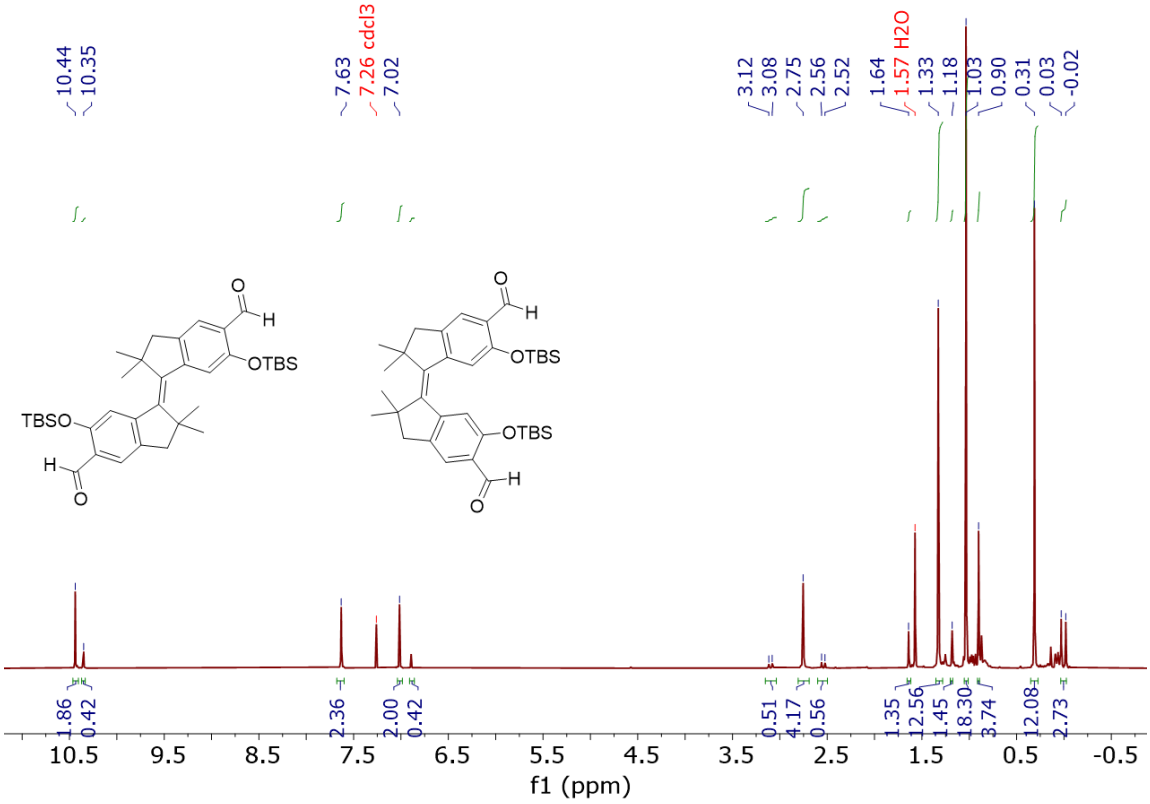

Figure S32. ^{1}H NMR spectrum of (*E*)/(*Z*)-**7** ($CDCl_3$, 298 K, 400 MHz)**.**

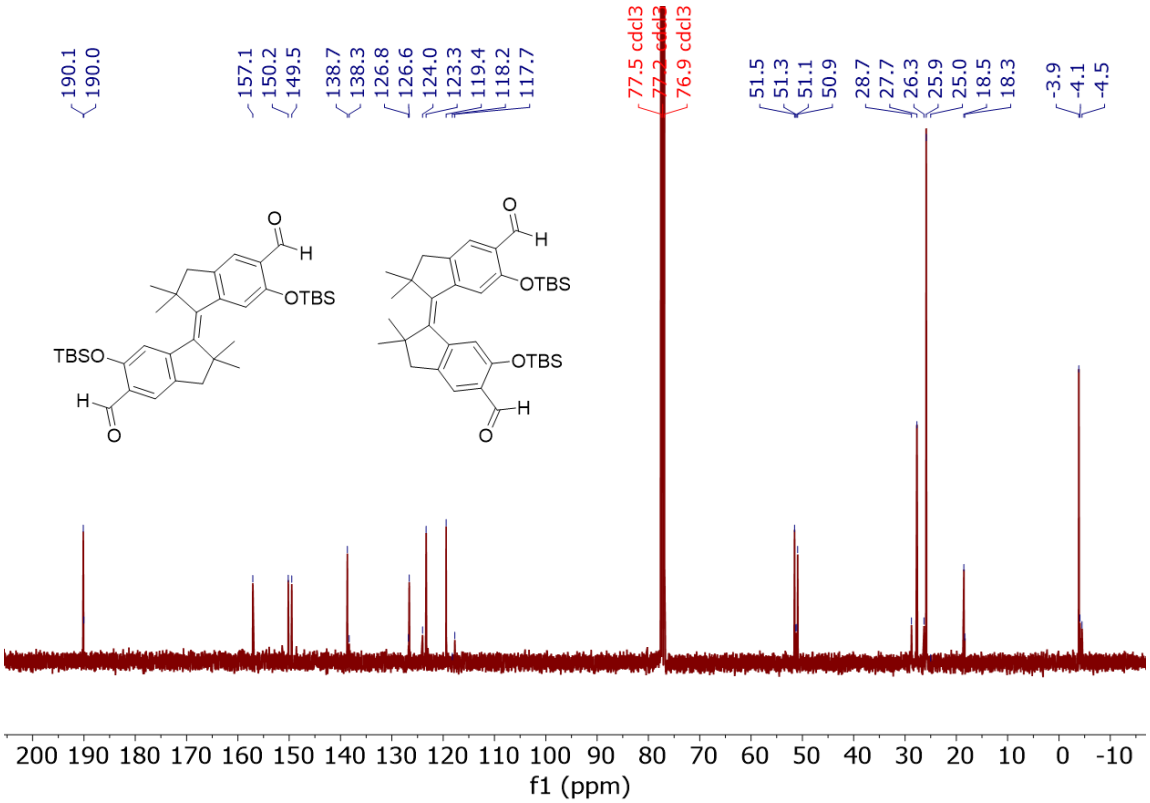

Figure S33. ^{13}C NMR spectrum of (*E*)/(*Z*)-**7** ($CDCl_3$, 298 K, 400 MHz)**.**

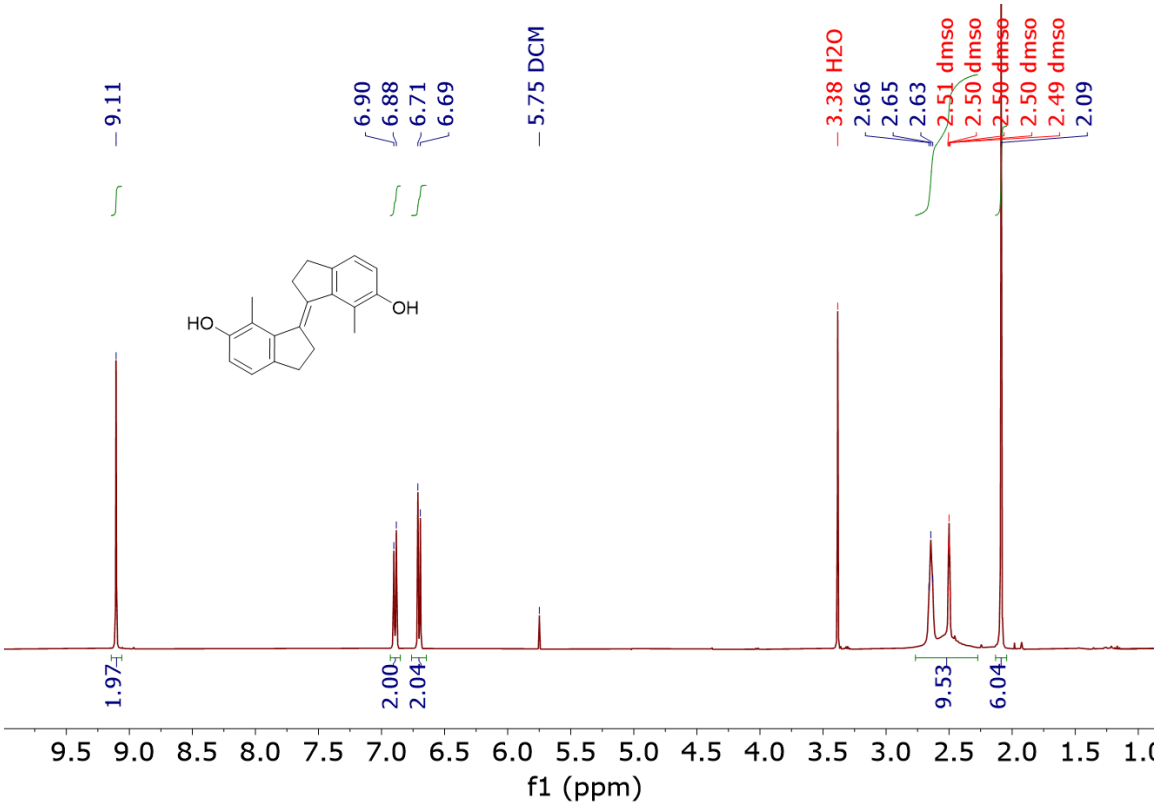

Figure S34. [1]H NMR spectrum of (*E*)-**S1** (DMSO-d_6, 298 K, 400 MHz)**.**

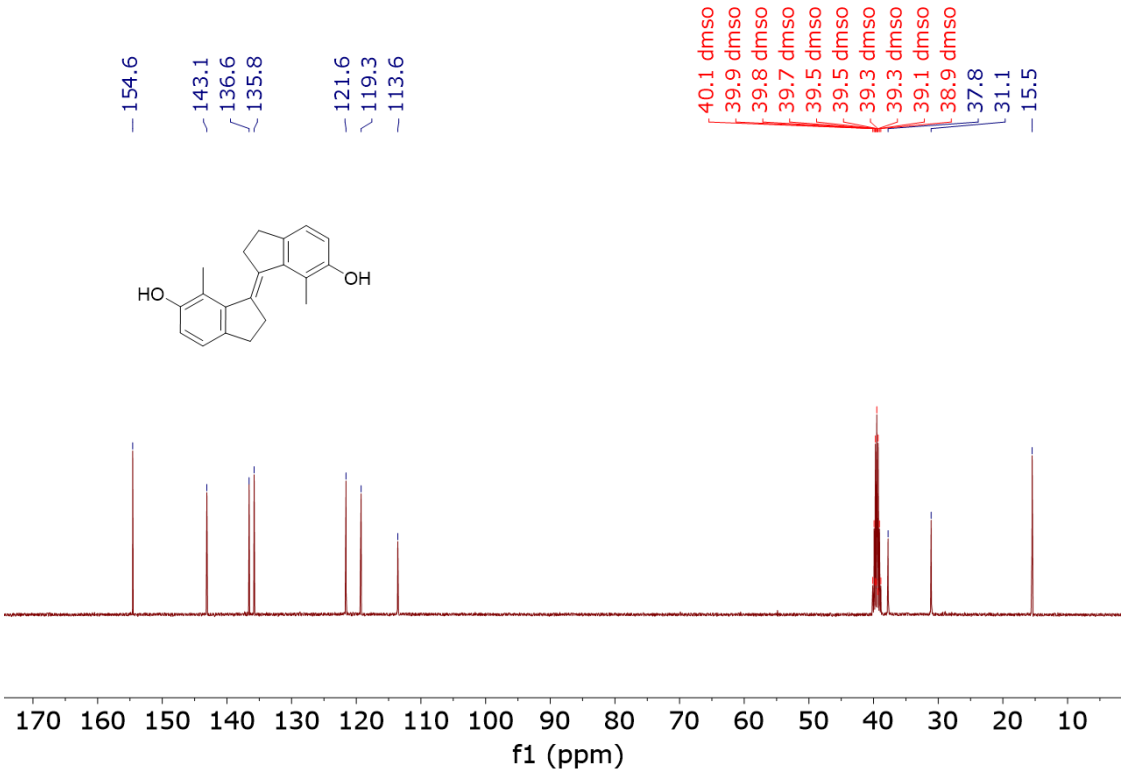

Figure S35. [13]C NMR spectrum of (*E*)-**S1** (DMSO-d_6, 298 K, 400 MHz)**.**

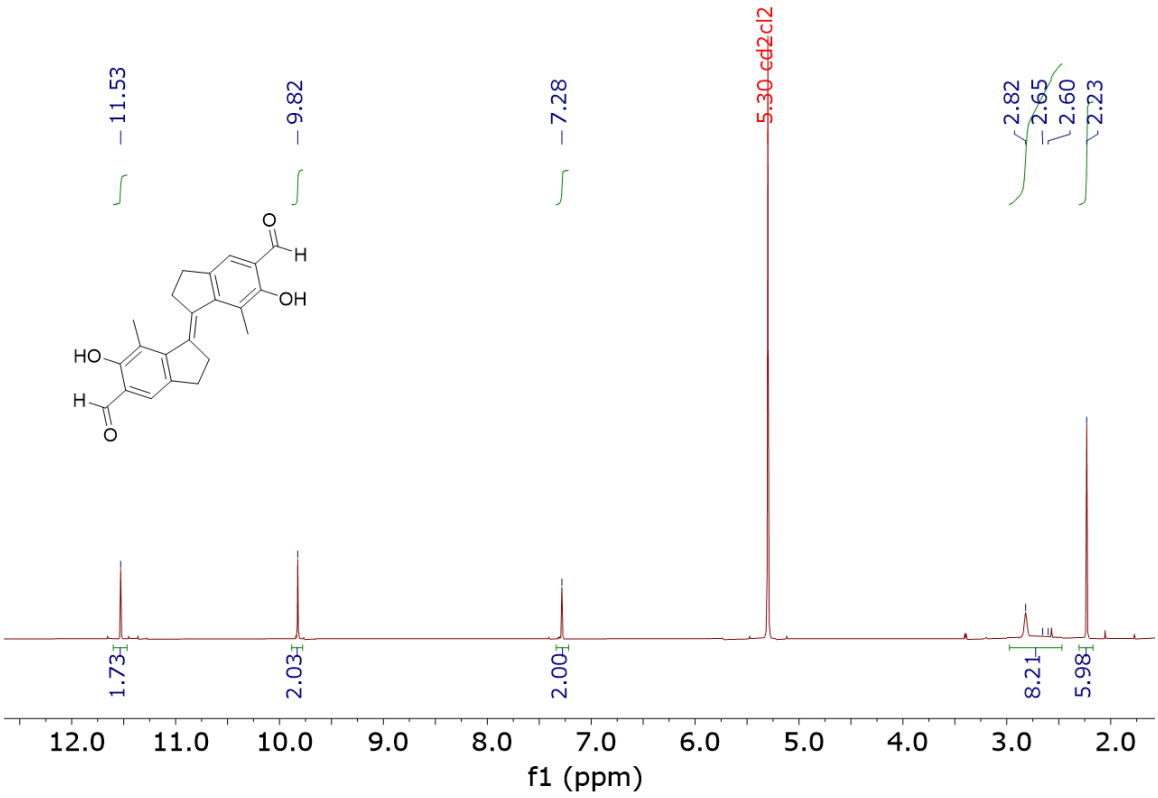

Figure S36. ^{1}H NMR spectrum of (*E*)-**S2** (CD_2Cl_2, 298 K, 500 MHz)**.**

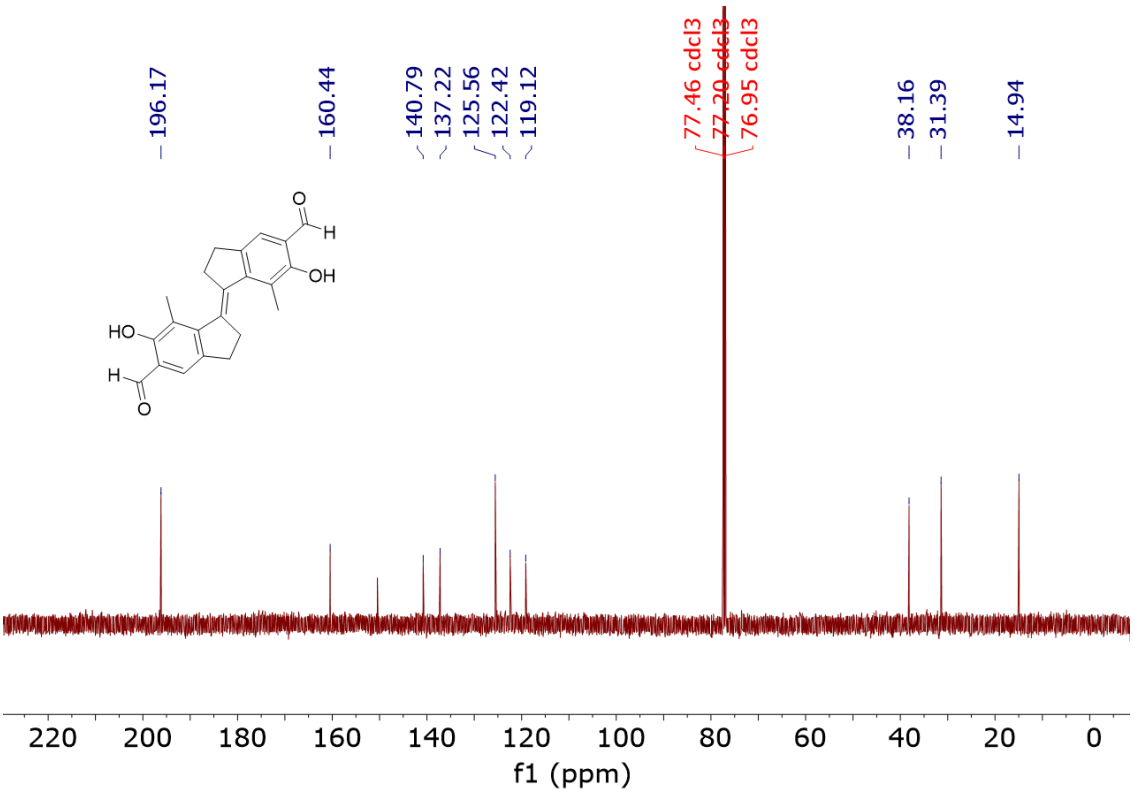

Figure S37. ^{1}H NMR spectrum of (*E*)-**S2** ($CDCl_3$, 298 K, 500 MHz)**.**

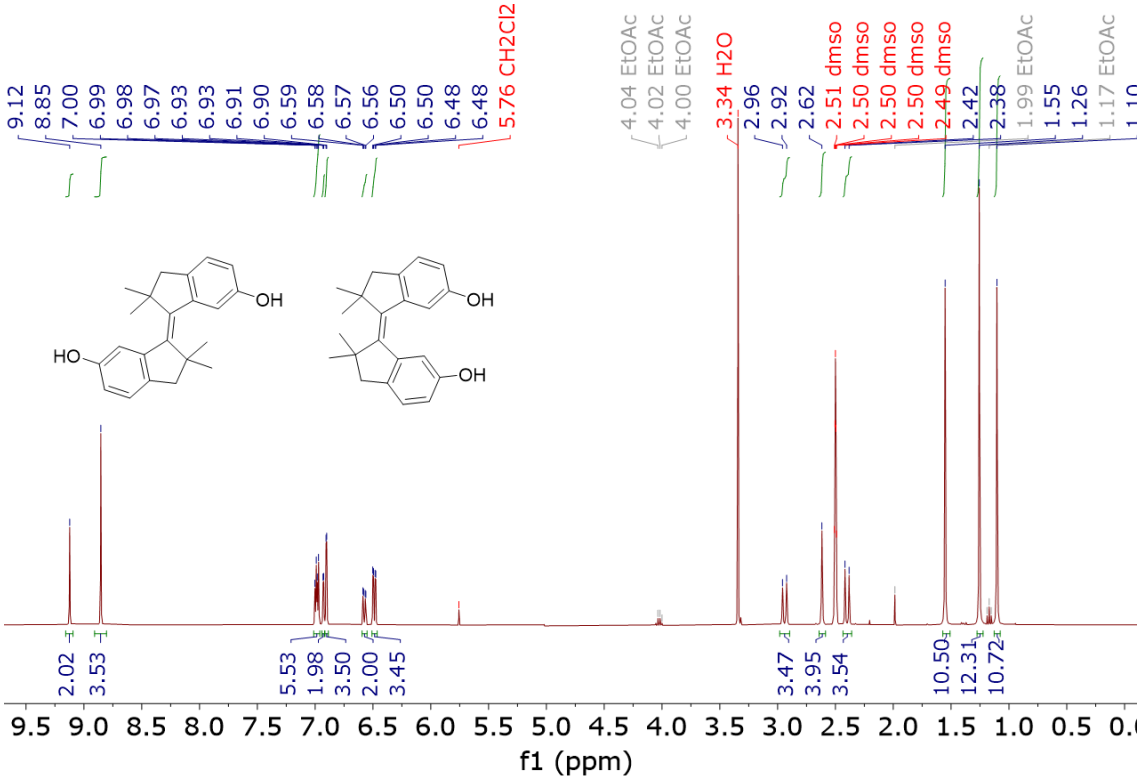

Figure 38. [1]H NMR spectrum of (*E*)/(*Z*)-**S3** (DMSO-d_6, 298 K, 400 MHz)**.**

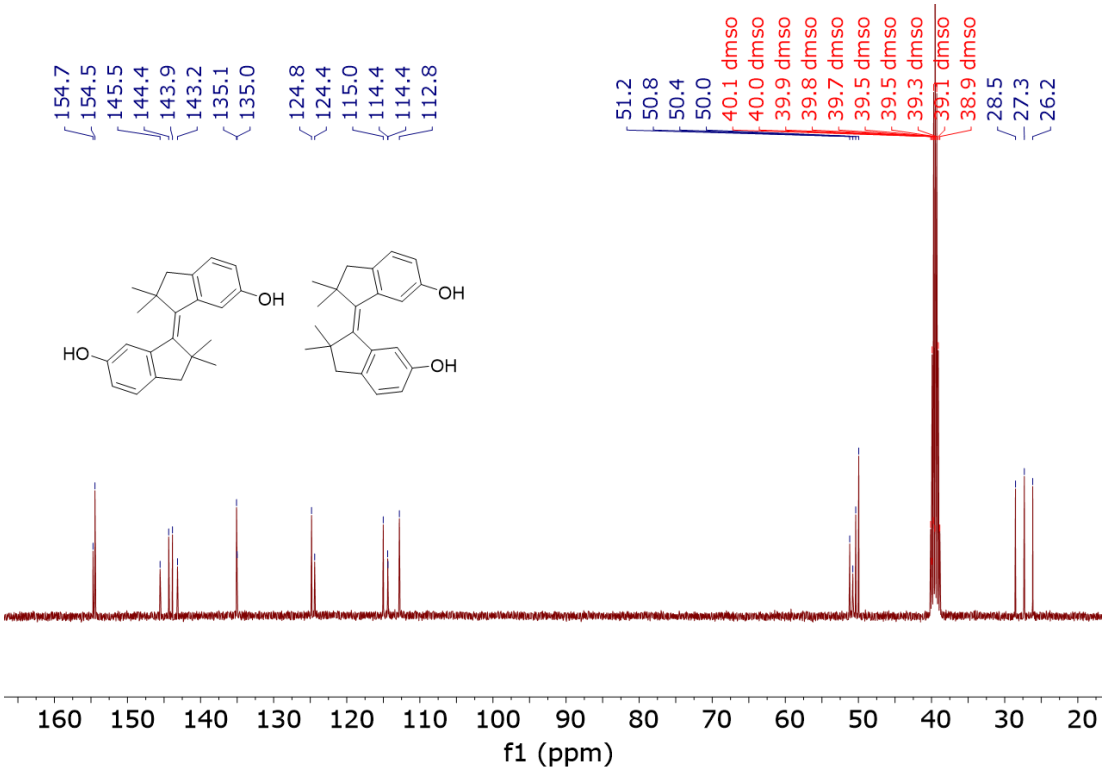

Figure S39. [13]C NMR spectrum of (*E*)/(*Z*)-**S3** (DMSO-d_6, 298 K, 400 MHz)**.**

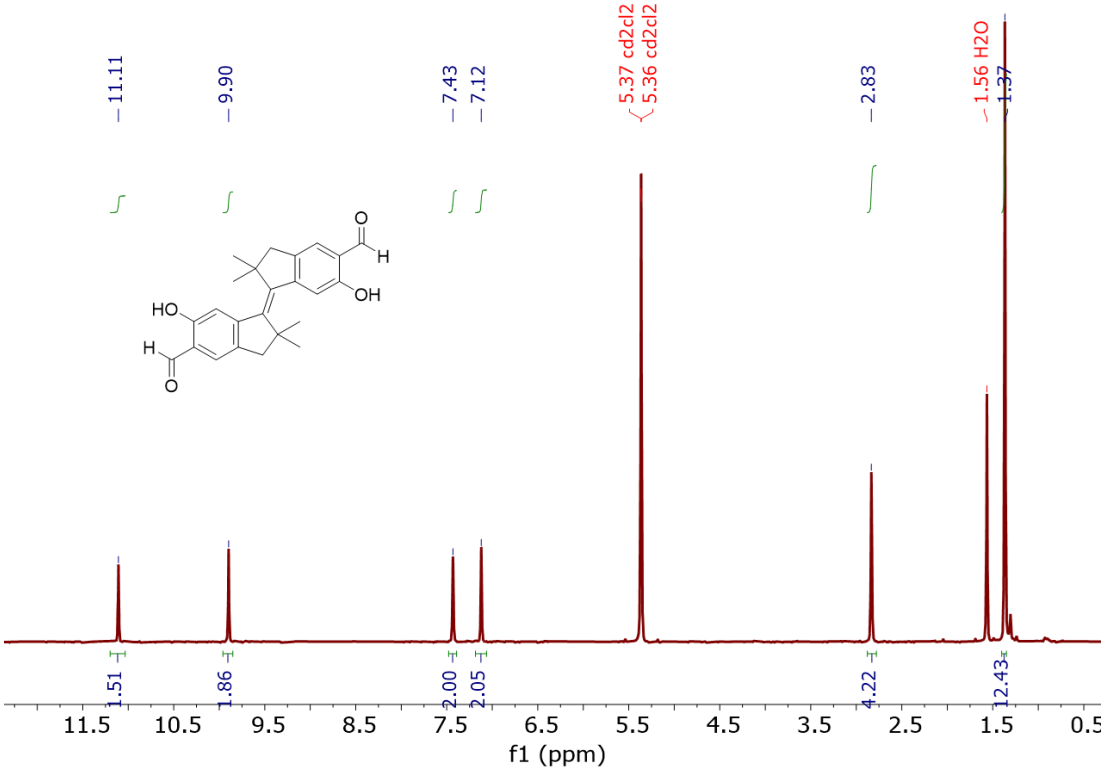

Figure S40. ^{1}H NMR spectrum of (*E*)-**S4** (CD_2Cl_2, 298 K, 400 MHz)**.**

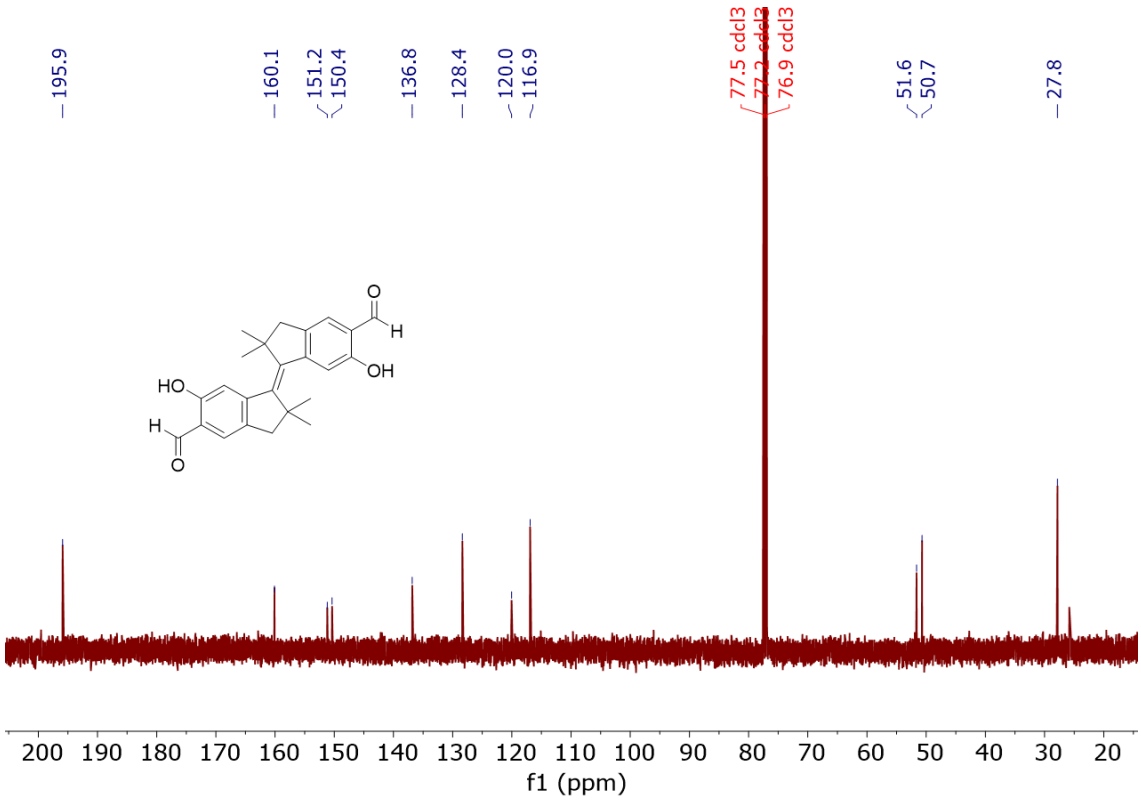

Figure S41. ^{13}C NMR spectrum of (*E*)-**S4** ($CDCl_3$, 298 K, 400 MHz)**.**

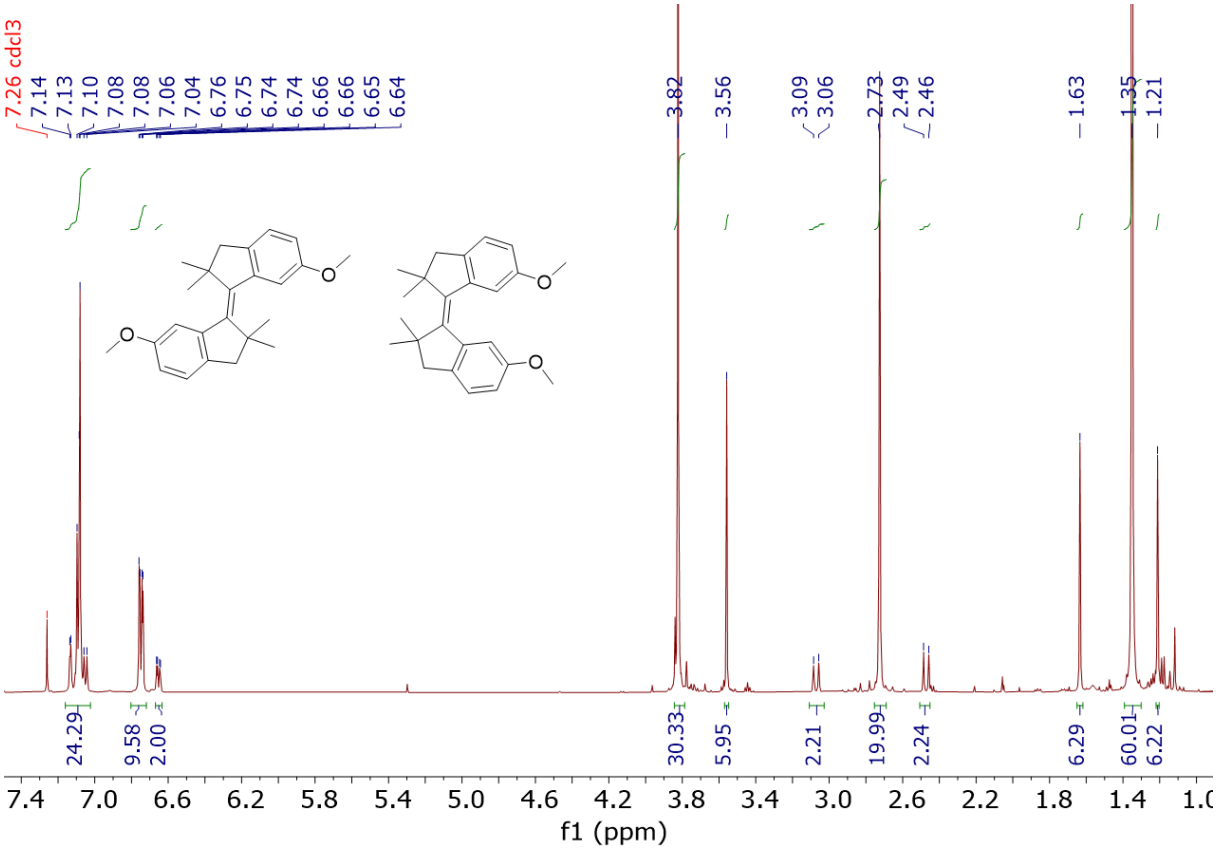

Figure S42. ^{1}H NMR spectrum of (*E*)/(*Z*)-**S5** ($CDCl_3$, 298 K, 400 MHz)**.**

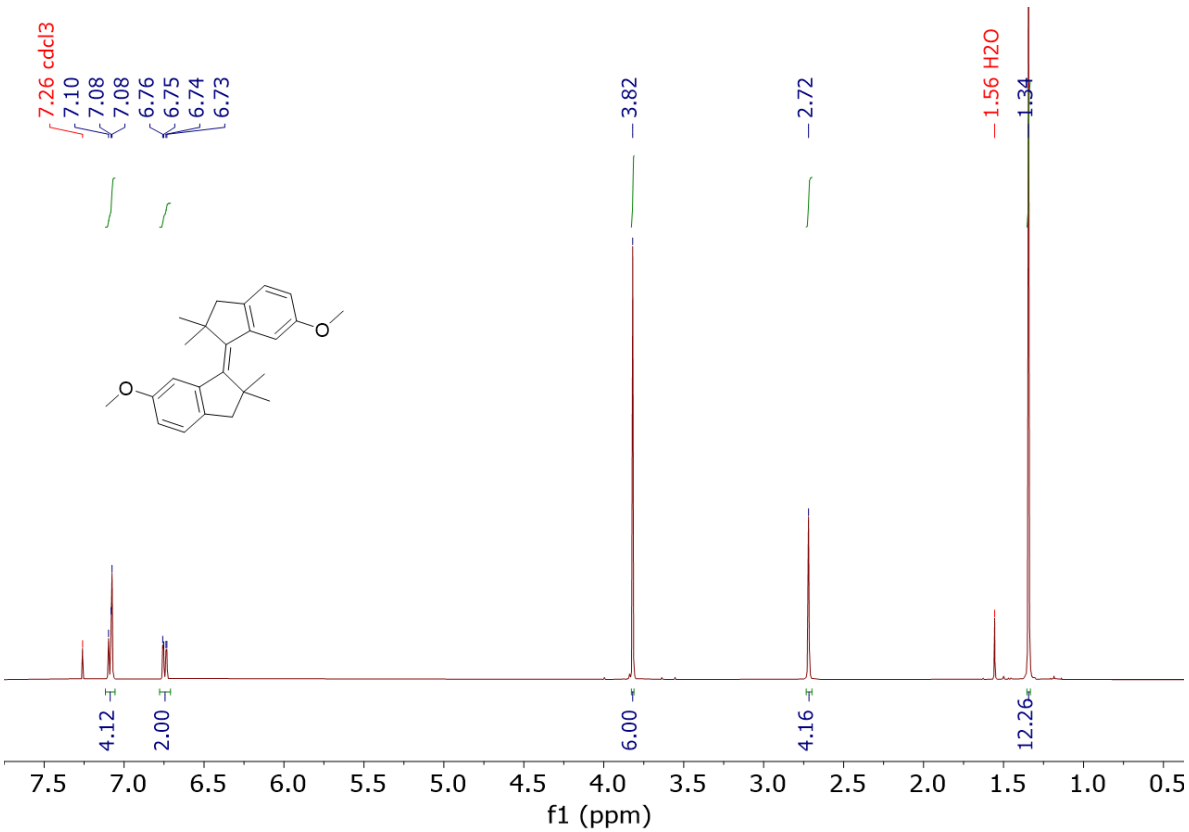

Figure S43. ^{1}H NMR spectrum of (*E*)-**S5** ($CDCl_3$, 298 K, 400 MHz)**.**

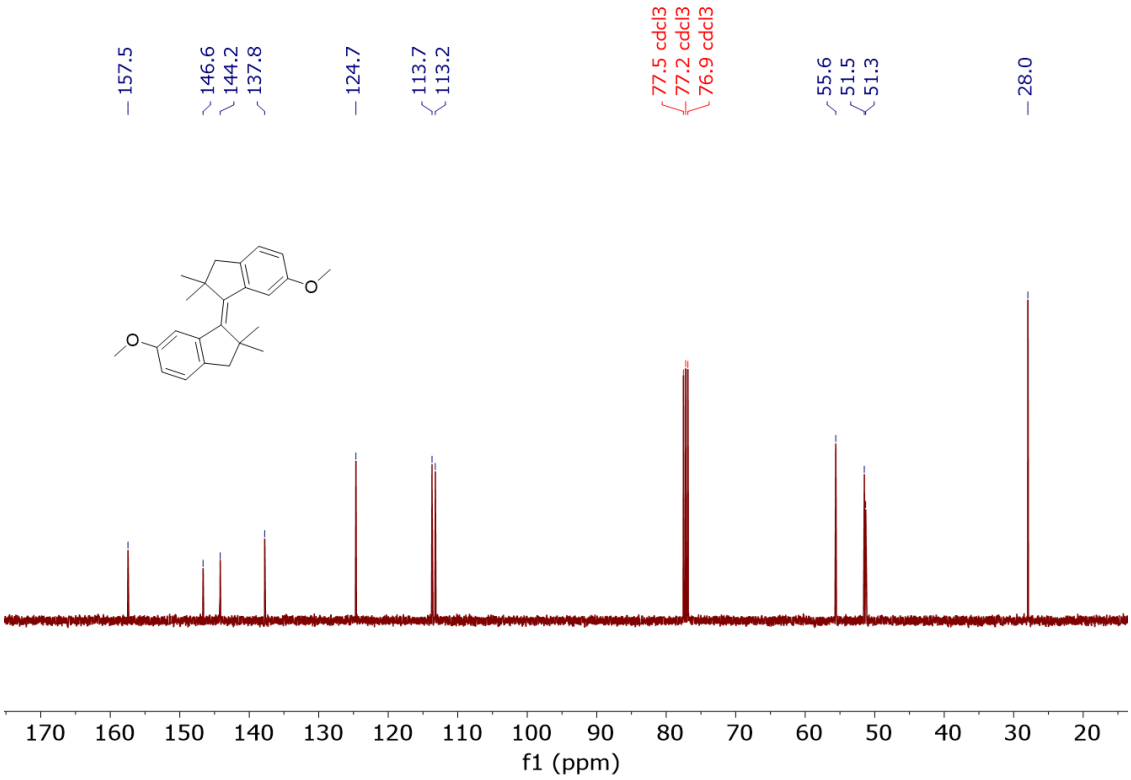

Figure S44. ^{13}C NMR spectrum of (*E*)-**S5** ($CDCl_3$, 298 K, 400 MHz)**.**

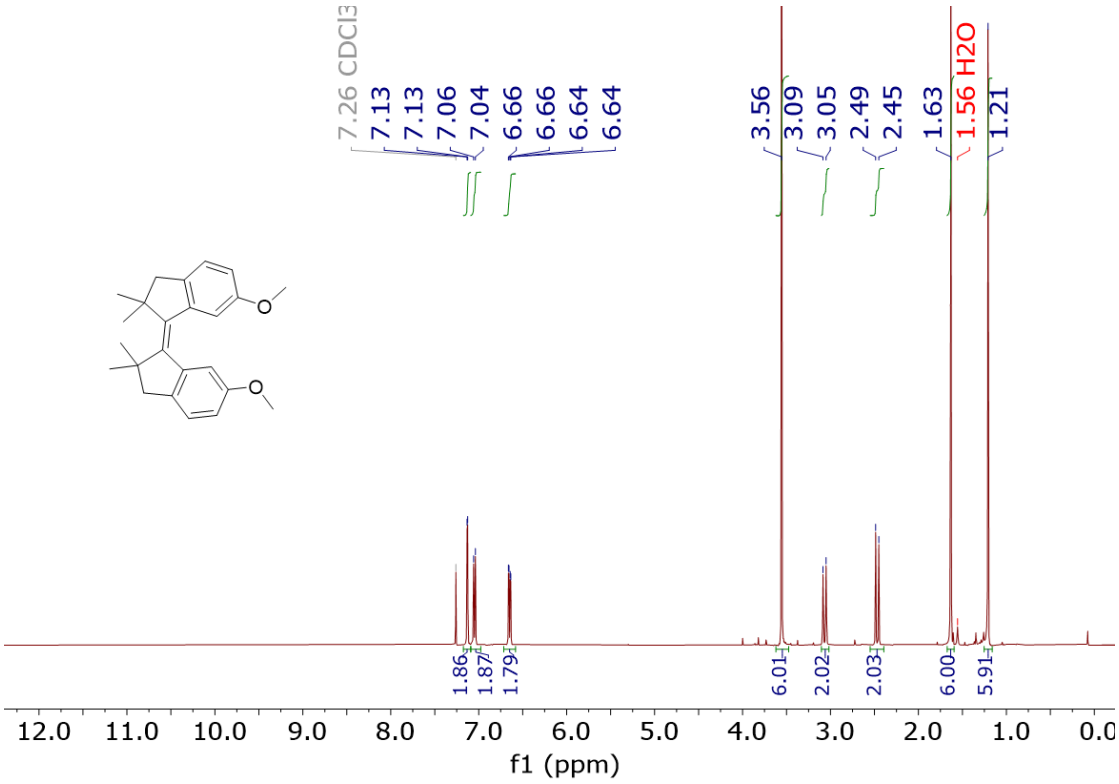

Figure S45. ^{1}H NMR spectrum of (*Z*)-**S5** ($CDCl_3$, 298 K, 400 MHz)**.**

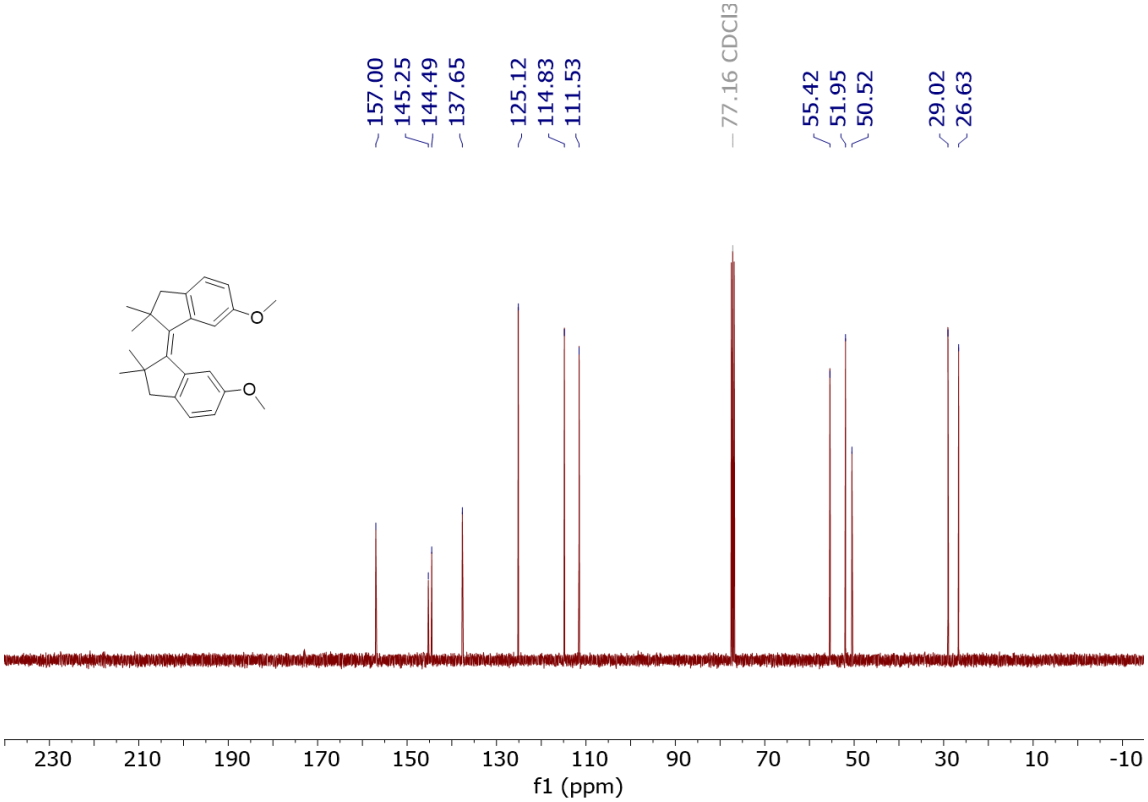

Figure S46. ^{13}C NMR spectrum of (*Z*)-**S5** ($CDCl_3$, 298 K, 400 MHz).

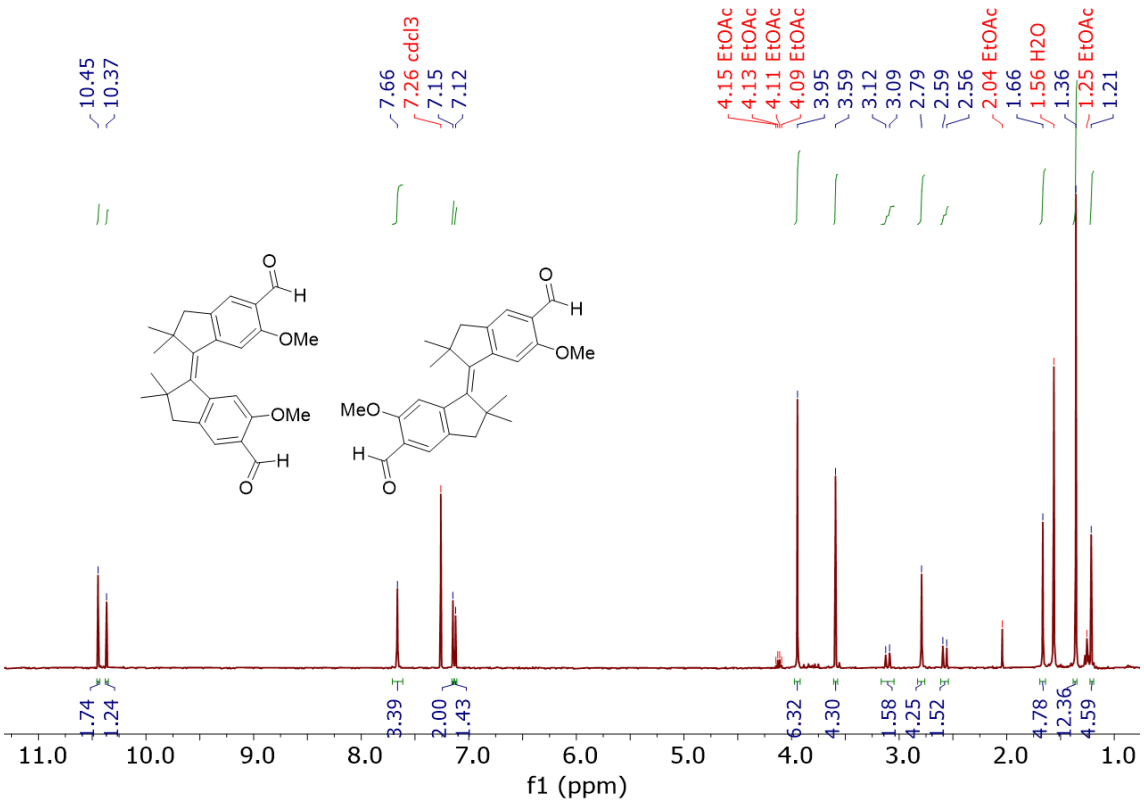

Figure S47. ^{1}H NMR spectrum of (*E*)/(*Z*)-**S6** ($CDCl_3$, 298 K, 400 MHz)**.**

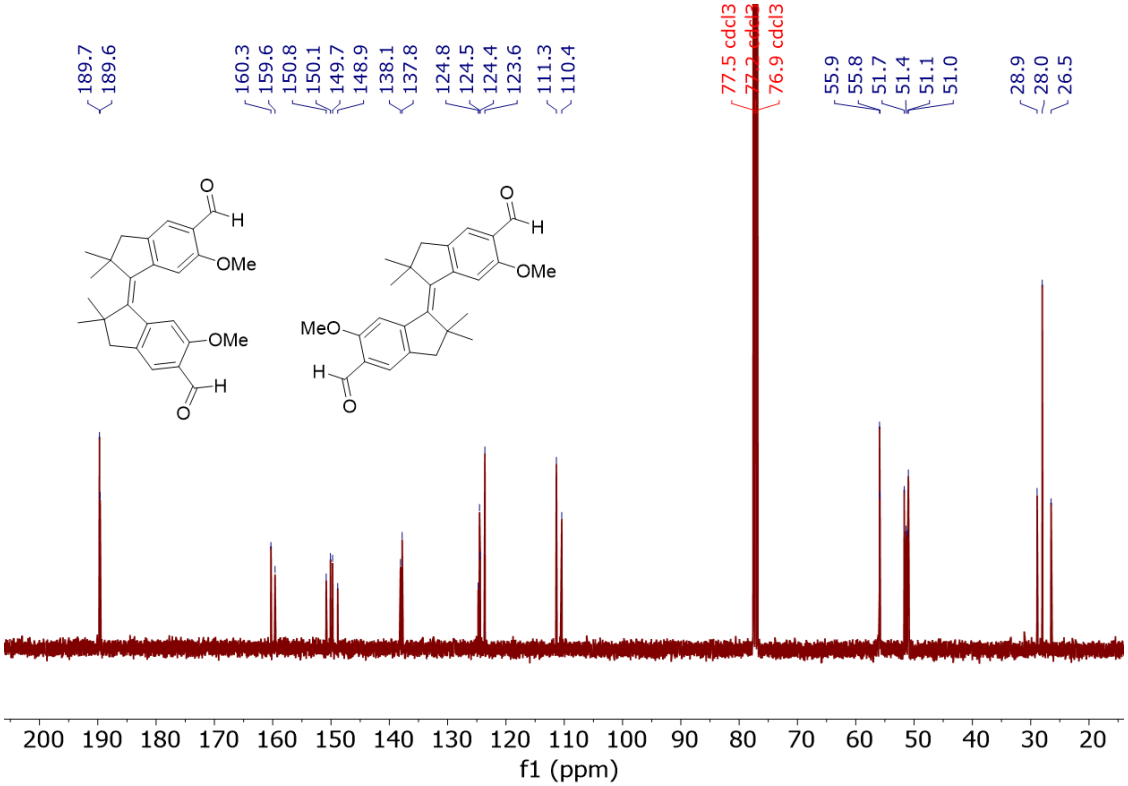

Figure S48. ^{13}C NMR spectrum of (*E*)/(*Z*)-**S6** ($CDCl_3$, 298 K, 400 MHz)**.**

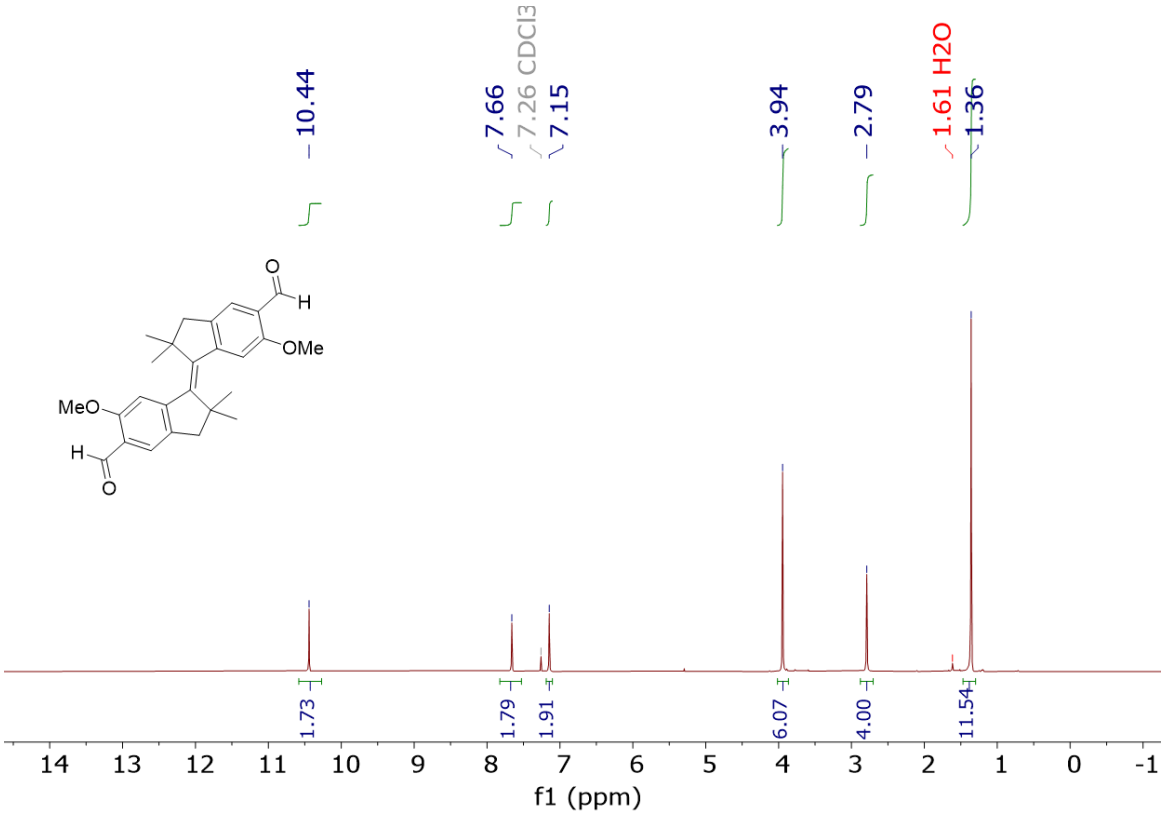

Figure S49. ^{1}H NMR spectrum of (*E*)-**S6** ($CDCl_3$, 298 K, 400 MHz)**.**

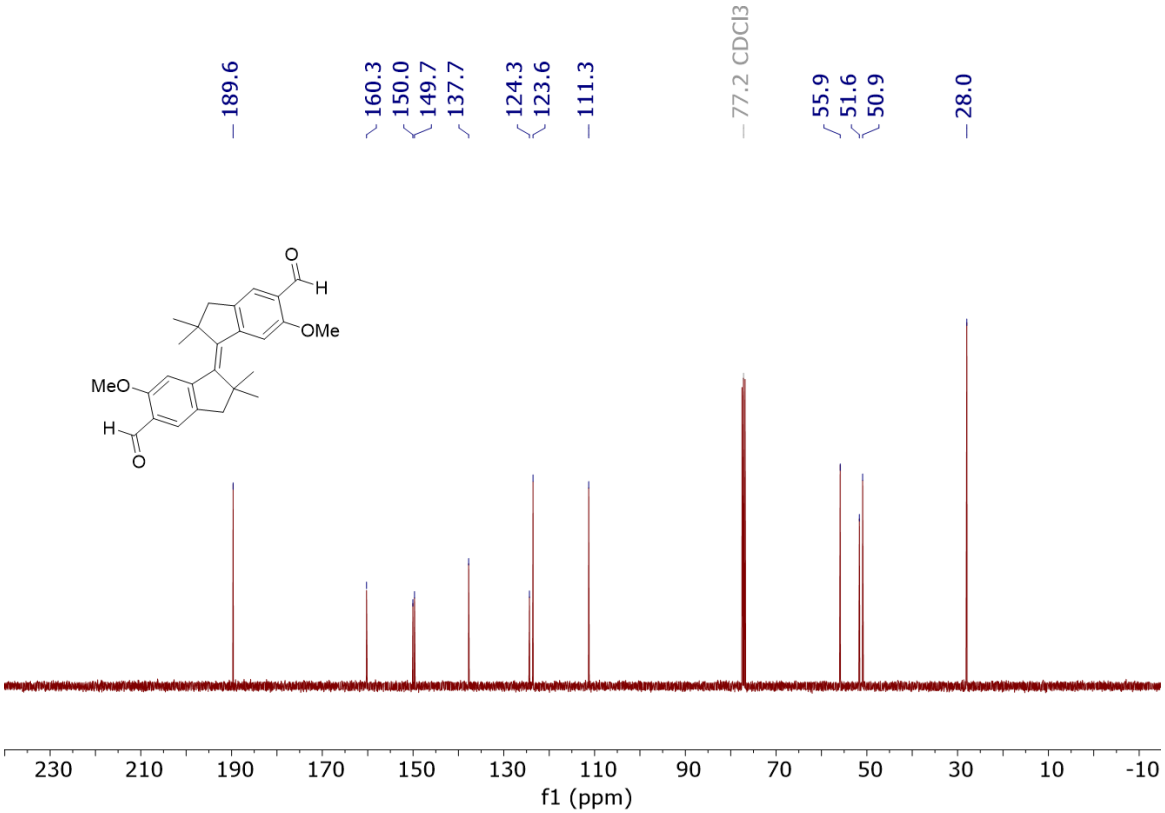

Figure S50. ^{13}C NMR spectrum of (*E*)-**S6** ($CDCl_3$, 298 K, 400 MHz)**.**

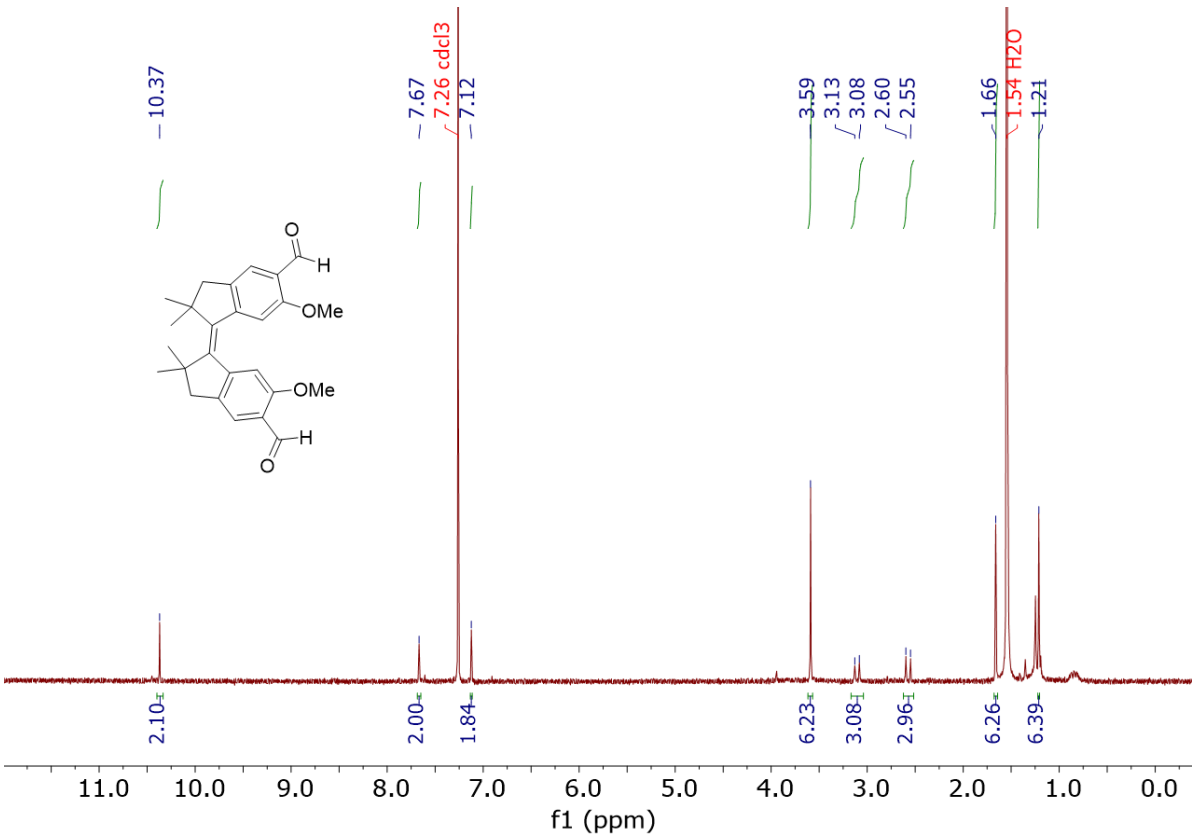

Figure S51. ^{1}H NMR spectrum of (*Z*)-**S6** ($CDCl_3$, 298 K, 400 MHz).

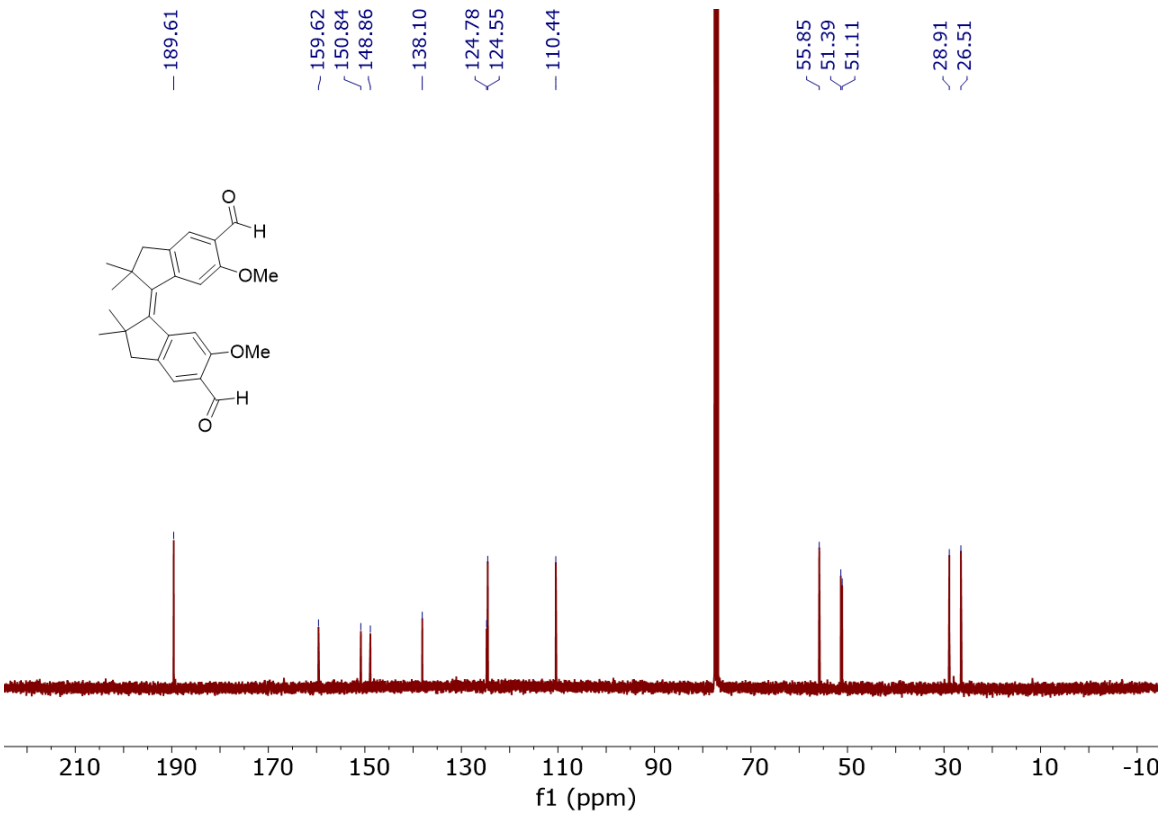

Figure S52. ^{13}C NMR spectrum of (*Z*)-**S6** ($CDCl_3$, 298 K, 400 MHz)**.**

References

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