

Supporting Information

Photochromic Torsional Switch (PTS): a Light-Driven Actuator for Dynamic Tuning of π -Conjugation Extension

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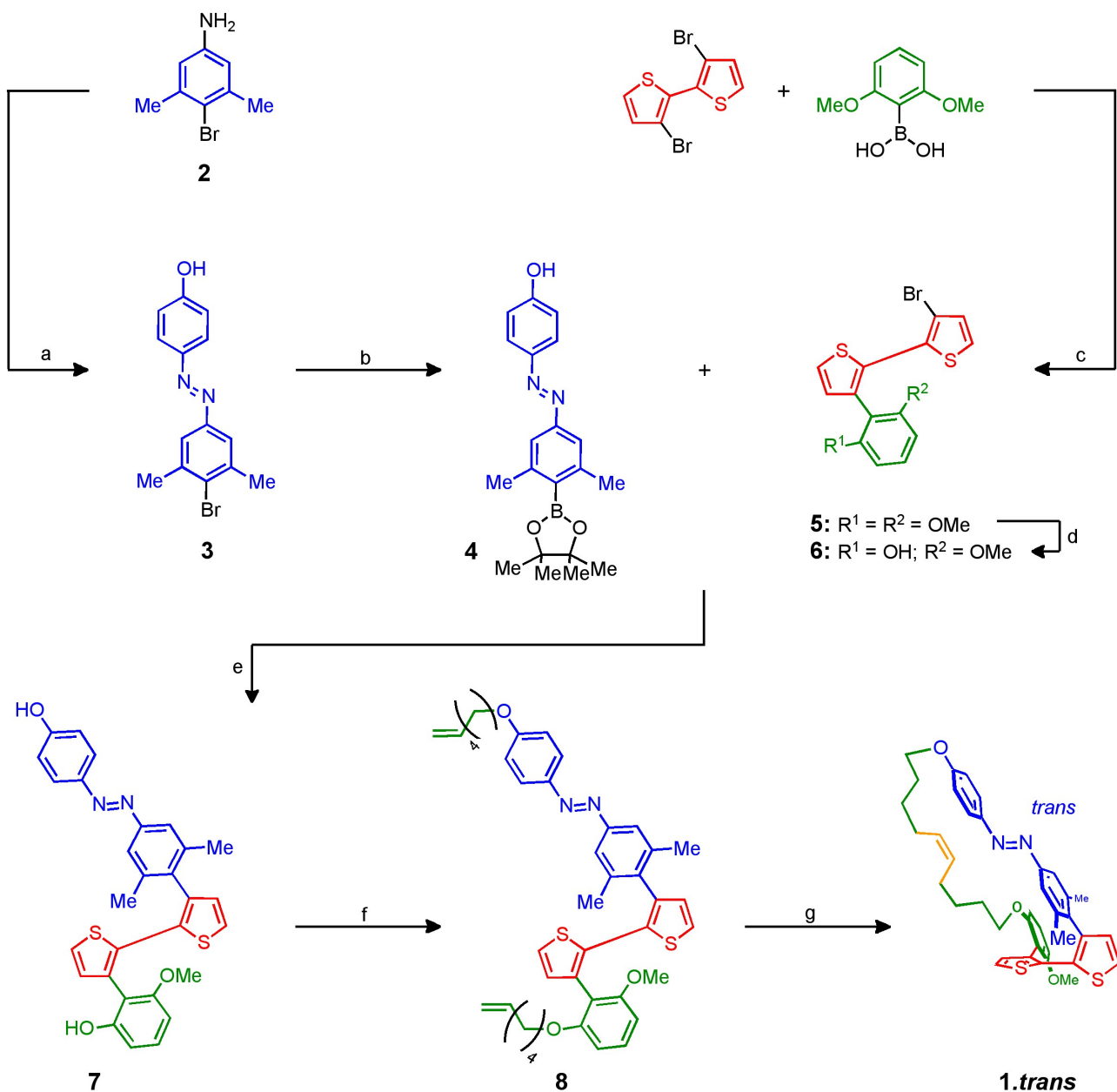
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Section 1: General Experimental Details

Manipulations of air or water sensitive compounds were performed using standard high vacuum techniques. DCM, acetone, petroleum ether, heptanes, EtOAc and toluene solvents were purchased from Reactolab SA and distilled under reduced pressure before their use. All other reagents were used as commercially supplied. Acetonitrile (99.99%) and THF (99.99%) were purchased from Fischer Scientific. NBS (99%), K₂CO₃ (99+%, anhydrous), DMF (99.8%, extra dry, acroseal), and K₃PO₄ (97%, anhydrous) were purchased from Acros organics. Pd(PPh₃)₂Cl₂ (98%), sPhos (95+%), Bis(pinacolato)diboron, 6-bromo-1-hexene, and 3,5-dimethylaniline (98%) were purchased from Fluorochem Ltd. KOAc (99%) and NaNO₂ (98%) were purchased from Abcr. Dioxane (>99.5%), Pd(PPh₃)₄, and Grubbs catalyst 2nd generation were purchased from Sigma-Aldrich. 3,3'-Dibromo-2,2'-bithiophene (>98%) was purchased from TCI. Phenol (≥99%) was purchased from SAFC. KOH pellets were purchased from Reactolab SA. Concentrated HCl (37%) was purchased from Carlo Erba Reagents. Analytical thin layer chromatography (TLC) was carried out on Merck aluminium backed silica gel 60 GF254 plates. Column chromatography was carried out on silica gel 60 GF254 (particle size 40 – 63 μm, Merck) using positive air pressure. NMR spectra were recorded at ambient probe temperature using the following Fourier transform instruments: Bruker Avance III 400 MHz (9.0 T) equipped with BBFO probe, and Bruker Avance III 600 MHz (14.1 T) equipped with TCI CryoProbe. Chemical shifts (δ_{H} and δ_{C}) are reported in parts per million (ppm) relative to the residual solvent peak. Coupling constants (J) are reported in Hertz. ¹H and ¹³C resonances were assigned with the aid of additional information from 1D & 2D NMR spectra (H,H-COSY, DEPT 135, HSQC and HMBC). Accurate mass determinations using ESI (HR ESI-MS) were performed on a Xevo G2-S QTOF mass spectrometer. UV-Vis spectra were recorded on a JASCO V-670 spectrophotometer and the absorption wavelengths (λ) are reported in nm (extinction coefficient ϵ in M⁻¹cm⁻¹). Photoisomerizations were carried using a Camag UV lamp TL 900/U.

Section 2: Synthesis and characterization

2.1. Synthesis of **1**, precursors and model compound

Scheme S1: Synthetic scheme for the preparation of the photochromic torsional switches **1**. (a) NaNO_2/HCl , phenol, water; (b) pinacolborane, $\text{Pd}(\text{dppf})\text{Cl}_2$, KOAc, dioxane; (c) $\text{Ph}(\text{PPh}_3)_4$, K_2CO_3 , dioxane/water; (d) BBr_3 , DCM; (e) $\text{Ph}(\text{PPh}_3)_4$, K_2CO_3 , DMF; (f) 6-bromo-1-hexene, K_2CO_3 , DMF; (g) Grubbs catalyst 2nd generation, toluene.

Compound 2: This compound was synthesized according to reported procedures.^[1]

[1] 'Synthesis of arylbromides from arenes and N-bromosuccinimide (NBS) in acetonitrile - A convenient method for aromatic bromination' E. Zysman-Colman, K. Arias, J. Siegel, *Can. J. Chem.*, 2009, **87**, 440-447.

Compound 3: This compound was synthesized by adapting a reported procedure.^[2] Concentrated hydrochloric acid (10 mL) was added to a suspension of 4-bromo-3,5-dimethylaniline **2** (5 g, 25.0 mmol) in water (100 mL). The mixture was cooled to 5 °C in an ice bath and stirred vigorously. A solution of NaNO₂ (1.9 g, 27.5 mmol) in water (15 mL) was then added dropwise to the cooled suspension, and the mixture was stirred for 1h. In a separate flask, NaOH 5M (25 mL) was added to a solution of phenol (2.8 g, 30.0 mmol) in water (20 mL), and cooled to 0 °C. The former mixture was then slowly transferred to the solution of phenol and vigorously stirred for 1h at 0 °C (pH = 2). The resultant precipitate was filtered. The filtrate was cooled to 5 °C in an ice bath and transferred to a new solution of phenol (2.8 g, 30.0 mmol) in water (20 mL) and NaOH 5M (25 mL) to obtain additional precipitate. The mixture was stirred for 1.5h at 0 °C (pH = 9). The obtained precipitate was filtered. The combined precipitates were purified by silica chromatography (*R_f* = 0.43, Heptane/Ethyl Acetate = 8:2) to give a bright yellow powder (6.66 g, 87.4%). ¹H NMR (400 MHz, CD₃Cl): δ = 7.86 (d, ³*J*(H,H) = 8.51 Hz, 2H), 7.60 (s, 2H), 6.94 (d, ³*J*(H,H) = 8.51 Hz, 2H), 5.08 (br, 1H, OH), 2.51 (s, 6H). ¹³C NMR (101 MHz, CD₃Cl): 158.3, 151.0, 147.4, 139.3, 130.0, 125.1, 122.1, 116.0, 24.2. HRMS (ESI, positive mode) *m/z* calculated for C₁₄H₁₃BrN₂O [M + H]⁺: 305.0290; found: 305.0292.

[2] 'Selective glucose recognition by boronic acid azoprobe/g-cyclodextrin complexes in water' C. Shimpuku, R. Ozawa, A. Sasaki, F. Sato, T. Hashimoto, A. Yamauchi, I. Suzuki, and T. Hayashita, *Chem. Commun.*, 2009, 1709-1711.

Compound 4: This compound was synthesized by adapting a reported procedure.^[3] A mixture of **3** (5.0 g, 16.4 mmol), pinacolborane (5.0 g, 19.7 mmol), Pd(dppf)Cl₂ (670.0 mg, 82.0 mmol), and potassium acetate (4.8 g, 49.1 mmol) was dissolved in dioxane (25 mL) under argon atmosphere. The mixture was heated to 80 °C and stirred until all of **3** was consumed. The reaction was monitored by TLC using DCM/EtOAc (9.5:0.5) as eluent. After 6h the heating was stopped, the reaction was allowed to reach room temperature, diluted with ethyl acetate (150 mL) and washed with water. The organic layer was dried over MgSO₄, filtered, and the solvent removed under reduced pressure. The product was purified by silica chromatography (*R_f* = 0.53, DCM/Ethyl Acetate = 9.5:0.5) to give an orange powder (5.13 g, 88.9%). ¹H NMR (400 MHz, CD₃Cl): δ = 7.84 (d, *J* = 8.7 Hz, 2H), 7.45 (s, 2H), 6.91 (d, *J* = 8.7 Hz, 2H), 5.25 (br, 1H, OH), 2.49 (s, 6H), 1.42 (s, 12H). ¹³C NMR (101 MHz, CDCl₃) δ = 158.6, 153.3, 147.1, 142.9, 124.9, 120.6, 115.9, 84.34, 84.29, 25.1, 22.3. HRMS (ESI, positive mode) *m/z* calculated for C₂₀H₂₆BN₂O₃ [M + H]⁺: 353.2040; found: 353.2039.

[3] 'Palladium(0)-Catalyzed Cross-Coupling Reaction of Alkoxydiboron with Haloarenes: A Direct Procedure for Arylboronic Esters' T. Ishiyama, M. Murata, and N. Miyaura, *J. Org. Chem.*, 1995, **60**, 7508-7510.

Compound 5: A mixture of 3,3-dibromo-2,2-bithiophene (5.0 g, 15.4 mmol), 2,6-dimethoxybenzene-boronic acid (3.37 g, 18.5 mmol), Pd(PPh₃)₄ (1.8 g, 1.54 mmol) and K₂CO₃ (8.50 g, 61.6 mmol) were dissolved in dioxane/water (95 mL/5 mL) under argon atmosphere. The mixture was heated to 80 °C and stirred for 48 hours. The reaction was allowed to reach room temperature, diluted with ethyl acetate (250 mL) and washed with water. The organic layer was dried over MgSO₄, filtered, and the solvent

removed under reduced pressure. The product was purified by silica chromatography ($R_f = 0.53$, DCM/Pet. Ether = 1:1) to give a white solid (3.87 g, 66%). ^1H NMR (400 MHz, CDCl_3): $\delta = 7.43$ (d, $J = 5.5$ Hz, 1H), 7.27 (t, $J = 8.6$ Hz, 1H), 7.10 (d, $J = 5.5$ Hz, 1H), 7.08 (d, $J = 5.5$ Hz, 1H), 6.90 (d, $J = 5.5$ Hz, 1H), 6.54 (d, $J = 8.6$ Hz, 2H), 3.53 (s, 6H). ^{13}C NMR (101 MHz, CDCl_3): $\delta = 158.4, 133.8, 132.3, 131.1, 130.5, 130.4, 129.5, 125.7, 125.0, 113.8, 109.6, 104.1, 55.8$. HRMS (ESI, positive mode) m/z calculated for $\text{C}_{16}\text{H}_{14}\text{BrO}_2\text{S}_2$ [$\text{M} + \text{H}$] $^+$: 380.9613, found: 380.9607; $\epsilon = 1.25 \times 10^4 \text{ M}^{-1}\text{cm}^{-1}$ ($\lambda_{\text{max}} = 249 \text{ nm}$).

Compound 6: This compound was synthesized by adapting a reported procedure.^[4] A solution of **5** (3.6 g, 9.44 mmol) in DCM (180 ml) was cooled to 0°C . BBr_3 1M (11.3 mL, 11.32 mmol) was slowly added and the mixture stirred for 2 hrs. MeOH (22 ml) was added and the stirred for 15 min at 0°C . The mixture was allowed to reach room temperature, and washed with water. The organic layer was dried over MgSO_4 , filtered, and the solvent removed under reduced pressure. The product was purified by silica chromatography ($R_f = 0.32$, DCM/Pet.Ether = 1:1) to give **5** as white solid (2.3 g, 68%). ^1H NMR (400 MHz, CDCl_3): $\delta = 7.56$ (d, $J = 5.0$ Hz, 1H), 7.21 (t, $J = 8.2$ Hz, 1H), 7.16 (d, $J = 5.2$ Hz, 1H), 7.08 (d, $J = 5.0$ Hz, 1H), 6.93 (d, $J = 5.2$ Hz, 1H), 6.57 (d, $J = 8.2$ Hz, 1H), 6.48 (d, $J = 8.2$ Hz, 1H), 4.94 (s, 1H, OH); 3.66 (s, 3H). ^{13}C NMR (101 MHz, CDCl_3): $\delta = 158.4, 154.5, 132.3, 131.9, 130.7, 130.5, 130.4, 130.1, 127.3, 126.7, 111.4, 110.5, 108.4, 103.1, 55.8$. HRMS (ESI, positive mode) m/z calculated for $\text{C}_{15}\text{H}_{12}\text{BrO}_2\text{S}_2$ [$\text{M} + \text{H}$] $^+$: 366.9462, found: 366.9464. $\epsilon = 1.26 \times 10^4 \text{ M}^{-1}\text{cm}^{-1}$ ($\lambda_{\text{max}} = 250 \text{ nm}$).

[4] 'A Self-Threading Polythiophene: Defect-Free Insulated Molecular Wires Endowed with Long Effective Conjugation Length' K. Sugiyasu, Y. Honsho, R. M. Harrison, A. Sato, T. Yasuda, S. Seki, M. Takeuchi, *J. Am. Chem. Soc.*, 2010, **132**, 14754–14756.

Compound 7: A solution of **6** (1.0 g, 2.72 mmol), **4** (1.92 g, 5.44 mmol), K_2CO_3 (1.88 g, 13.6 mmol), $\text{Pd}(\text{PPh}_3)_4$ (0.63 g, 0.54 mmol) and DMF (10 mL) was stirred at 95°C for 60 hrs under Argon atmosphere. The mixture was allowed to reach room temperature, diluted with ethyl acetate, transferred into a separatory funnel, and washed with water. The organic layers were collected, dried over MgSO_4 , filtered and concentrated in vacuo. The crude mixture was then purified through column chromatography ($R_f = 0.41$, DCM/Ethyl Acetate = 9.5:0.5). The fraction containing the final product was then purified through a second column chromatography ($R_f = 0.43$, Pet.Ether /Acetone = 7:3) to afford a yellow solid (640 mg, 45 %). ^1H NMR (400 MHz, CDCl_3): $\delta = 7.90$ (d, $J = 7.9$ Hz, 2H), 7.62 (s, 1H), 7.61 (s, 1H), 7.29 (t, $J = 7.9$ Hz, 1H), 7.21 (d, $J = 5.1$ Hz, 1H), 7.19 (d, $J = 5.1$ Hz, 1H), 6.96 (d, $J = 7.9$ Hz, 1H), 6.85 (d, $J = 4.9$ Hz, 1H), 6.76 (d, $J = 4.9$ Hz, 1H), 6.64 (d, $J = 8.1$ Hz, 1H), 6.52 (d, $J = 8.1$ Hz, 1H), 5.22 (s, 1H, OH), 4.86 (s, 1H, OH), 3.64 (s, 3H), 2.09 (s, 6H). ^{13}C NMR (101 MHz, CDCl_3): $\delta = 158.8, 158.3, 154.9, 152.4, 147.5, 139.4, 139.0, 138.7, 137.8, 135.0, 131.3, 130.3, 130.2, 128.8, 128.3, 126.0, 125.7, 125.1, 121.83, 121.80, 116.0, 111.9, 108.5, 103.3, 77.5, 77.2, 76.8, 55.8, 20.7, 20.6$. HRMS (ESI, positive mode) m/z calculated for $\text{C}_{29}\text{H}_{25}\text{N}_2\text{O}_3\text{S}_2$ [$\text{M} + \text{H}$] $^+$: 513.1301; found: 513.1304. $\epsilon_{\text{trans}} = 2.51 \times 10^4 \text{ M}^{-1}\text{cm}^{-1}$ ($\lambda_{\text{max}} = 357 \text{ nm}$).

Compound 8: A solution of **7** (600 mg, 1.17 mmol), 6-bromo-1-hexene (1.14 g, 7.02 mmol), K_2CO_3 (485 mg, 3.51 mmol) and dry DMF (12 mL) was stirred at 70°C for 24 hrs. The mixture was allowed to reach room temperature, diluted with ethyl acetate, transferred into a separatory funnel, and washed with water. The organic layers were collected, dried over MgSO_4 , filtered and concentrated in vacuo.

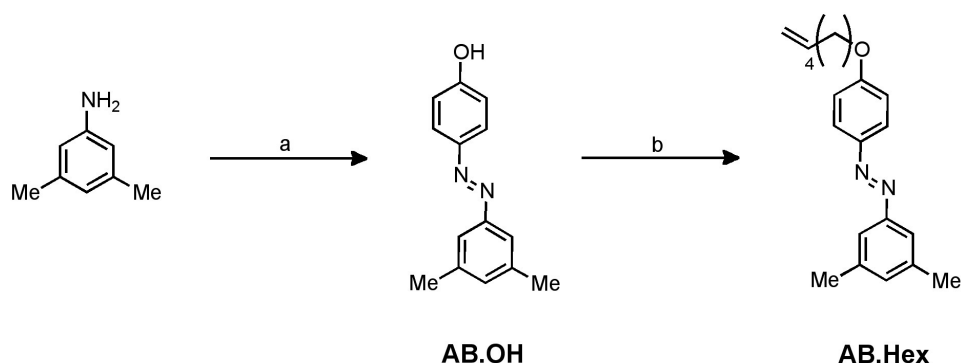
The crude product was filtered through a silica pad ($R_f = 0.32$ in DCM/Pet.Ether = 1:1; Pet.Ether = 100% \rightarrow DCM/Pet.Ether = 1:1). The filtrate was then evaporated and the product was obtained as a yellow solid (681 mg, 86%). ^1H NMR (400 MHz, CDCl_3): $\delta = 7.93$ (d, $J = 8.9$ Hz, 2H), 7.59 (s, 2H), 7.30 (t, $J = 8.3$, 1H), 7.14 (d, $J = 5.1$ Hz, 1H), 7.06 (d, $J = 5.2$ Hz, 1H), 7.02 (d, $J = 8.9$ Hz, 2H), 6.78 (d, $J = 5.2$ Hz, 1H), 6.71 (d, $J = 5.2$ Hz, 1H), 6.57 (d, $J = 8.3$ Hz, 1H), 6.56 (d, $J = 8.3$ Hz, 1H), 5.84 (dd, $J = 17.1$ Hz, $J = 10.4$ Hz, 1H), 5.70 (dd, $J = 17.1$ Hz, $J = 10.4$ Hz, 1H), 5.06 (d, $J = 17.1$ Hz, 1H), 5.00 (d, $J = 10.2$ Hz, 1H), 4.92 (d, $J = 17.1$ Hz, 1H), 4.90 (d, $J = 10.2$ Hz, 1H), 4.07 (t, $J = 6.4$ Hz, 2H), 3.83 (t, $J = 6.4$ Hz, 2H), 3.62 (s, 3H), 2.23-2.13 (m, 4H), 2.09 (s, 3H), 2.07 (s, 3H), 2.00-1.91 (m, 2H), 1.90-1.80 (m, 2H), 1.68-1.51 (m, 2H), 1.39-1.23 (m, 2H). ^{13}C NMR (101 MHz, CDCl_3): $\delta = 161.61$, 158.84, 158.59, 152.23, 147.22, 139.28, 139.14, 139.13, 138.82, 138.59, 136.57, 133.06, 132.60, 131.35, 130.75, 129.55, 128.68, 124.75, 124.42, 123.63, 121.67, 121.59, 114.99, 114.83, 114.57, 105.41, 103.98, 77.48, 77.16, 76.84, 68.34, 68.26, 55.72, 33.56, 33.37, 28.80, 28.57, 25.45, 25.18, 20.82, 20.63. HRMS (ESI, positive mode) m/z calculated for $\text{C}_{41}\text{H}_{45}\text{N}_2\text{O}_3\text{S}_2$ $[\text{M} + \text{H}]^+$: 677.2872; found: 677.2882. $\epsilon_{\text{trans}} = 2.67 \times 10^4 \text{ M}^{-1}\text{cm}^{-1}$ ($\lambda_{\text{max}} = 358 \text{ nm}$).

NOTE: Typical batches of this product result in only *trans* isomer. However, on some occasion presence of the *cis* form is observed. The later isomer is converted to its *trans* counterpart by thermal relaxation.

Compound 1.trans: A solution of **8** (100.0 mg, 0.15 mmol) and 2nd Generation Grubbs catalyst (25 mg, 0.03 mmol) in toluene (1 L) was stirred at 50°C for 18 hrs. After cooling to RT, the reaction mixture was filtered through a short silica plug to remove the catalyst. The filtrate was then concentrated under reduced pressure and the product was purified by column chromatography ($R_f = 0.58$, DCM/Pet.Ether = 7:3) followed by precipitation from methanol. The desired product **1.trans** was obtained as a yellow solid (37 mg, 38%). ^1H NMR (400 MHz, THF-d_8): $\delta = 7.90$ (d, $J = 8.9$ Hz, 2H), 7.47 (d, $J = 5.2$ Hz, 1H), 7.36 (s, 1H), 7.24 (d, $J = 5.2$ Hz, 1H), 7.20 (s, 1H), 7.10 (t, $J = 8.3$ Hz, 1H), 7.06 (d, $J = 8.9$ Hz, 2H), 6.81 (d, $J = 5.2$ Hz, 1H), 6.67 (d, $J = 5.2$ Hz, 1H), 6.36 (d, $J = 8.3$ Hz, 1H), 6.28 (d, $J = 8.3$ Hz, 1H), 4.90 (m, 2H), 4.32 (t, $J = 4.9$ Hz, 2H), 3.43 (s, 3H), 3.33 – 3.23 (m, 1H), 3.15 – 3.06 (m, 1H), 1.95 – 1.85 (m, 2H), 1.92 (s, 3H), 1.63 – 1.43 (m, 6H), 1.41 (s, 3H), 1.27 – 1.01 (m, 2H), 0.81 – 0.54 (m, 2H). ^{13}C NMR (101 MHz, THF-d_8): $\delta = 160.5$, 158.7, 158.1, 151.8, 147.9, 139.4, 138.7, 138.5, 138.2, 134.7, 133.9, 132.7, 132.6, 131.5, 131.4, 130.0, 129.4, 128.9, 125.8, 124.8, 124.1, 122.3, 121.1, 118.0, 115.3, 113.9, 104.3, 103.8, 68.2, 67.8, 55.1, 33.3, 31.5, 29.6, 26.0, 25.6, 23.9, 21.1, 20.3. HRMS (ESI, positive mode) m/z calculated for $\text{C}_{39}\text{H}_{41}\text{N}_2\text{O}_3\text{S}_2$ $[\text{M} + \text{H}]^+$: 649.2553; found: 649.2447. $\epsilon = 2.60 \times 10^4 \text{ M}^{-1}\text{cm}^{-1}$ ($\lambda_{\text{max}} = 363 \text{ nm}$).

Compound 1.cis (obtained by irradiating with 350nm light; ~14% of residual **1.trans**): ^1H NMR (400 MHz, THF-d_8): $\delta = 7.27$ (t, $J = 8.4$ Hz, 1H), 7.11 (d, $J = 5.2$ Hz, 1H), 7.11 (d, $J = 5.0$ Hz, 1H), 6.88-6.79 (m, 5H), 6.70 (d, $J = 5.2$ Hz, 1H), 6.69 (d, $J = 8.3$ Hz, 1H), 6.66 (d, $J = 5.0$ Hz, 1H), 6.58 (d, $J = 8.3$ Hz, 1H), 6.06 (s, 1H), 5.35 (m, 2H), 4.07 – 3.97 (m, 3H), 3.93-3.85 (m, 1H), 3.51 (s, 3H), 2.08 – 1.94 (m, 2H), 2.01(s, 3H), 1.93 – 1.84 (m, 2H), 1.87 (s, 3H), 1.83 – 1.70 (m, 2H), 1.65 (m, 4H), 1.38 – 1.27 (m, 2H). ^{13}C NMR (101 MHz, THF-d_8): $\delta = 159.8$, 159.3, 158.7, 156.7, 149.1, 139.7, 139.6, 136.5, 135.4, 134.1, 133.1, 131.9, 131.50, 131.4, 131.3, 130.2, 130.1, 128.3, 124.5, 123.36, 123.36 123.2, 120.9,

116.7, 114.61, 114.61, 106.1, 104.7, 68.8, 68.3, 55.3, 32.8, 32.7, 29.5, 29.2, 27.1, 27.0, 20.5, 20.4. $\epsilon = 6.08 \times 10^5 \text{ M}^{-1}\text{cm}^{-1}$ ($\lambda_{\text{max}} = 363 \text{ nm}$).



Scheme S1: Synthetic scheme for the preparation of the photochromic torsional switches **AB**. (a) NaNO_2/HCl , phenol, water; (b) 6-bromo-1-hexene, K_2CO_3 , DMF.

Compound AB.OH: This compound was synthesized as reported for compound **3**. Concentrated hydrochloric acid (2 mL) was added to a suspension of 3,5-dimethylaniline (1.0 g, 5.0 mmol) in water (20 mL). The mixture was cooled to 5 °C in an ice bath and stirred vigorously. A solution of NaNO_2 (0.38 g, 5.5 mmol) in water (3 mL) was then added dropwise to the cooled suspension, and the mixture was stirred for 1 h. In a separate flask, NaOH 5M (5 mL) was added to a solution of phenol (0.56 g, 6.0 mmol) in water (2 mL), and cooled to 0 °C. The former mixture was then slowly transferred to the solution of phenol and vigorously stirred for 1 h at 0 °C (pH = 2). The resultant precipitate was filtered. The filtrate was cooled to 5 °C in an ice bath and transferred to a new solution of phenol (0.56 g, 6.0 mmol) in water (2 mL) and NaOH 5M (5 mL) to obtain additional precipitate. The mixture was stirred for 1.5 h at 0 °C (pH = 9). The obtained precipitate was filtered. The combined precipitates were purified by silica chromatography ($R_f = 0.43$, Heptane/ Ethyl Acetate 8:2) to give a bright yellow powder (1.16 g, 76%). ^1H -NMR (400 MHz, CDCl_3): $\delta = 7.86$ (d, $J = 8.8$ Hz, 2H), 7.49 (s, 2H), 7.09 (s, 1H), 6.94 (d, $J = 8.8$ Hz, 2H), 5.28 (s, 1H, OH), 2.41 (s, 6H). ^{13}C NMR (101 MHz, CD_3Cl): $\delta = 158.2, 153.0, 147.4, 138.9, 132.4, 125.0, 120.5, 115.9, 21.4$. HRMS (ESI, positive mode) m/z calculated for $\text{C}_{14}\text{H}_{15}\text{N}_2\text{O}$ [$\text{M} + \text{H}$] $^+$: 227.1174; found: 227.1179. $\epsilon_{\text{trans}} = 2.42 \times 10^4 \text{ M}^{-1}\text{cm}^{-1}$ ($\lambda_{\text{max}} = 358 \text{ nm}$).

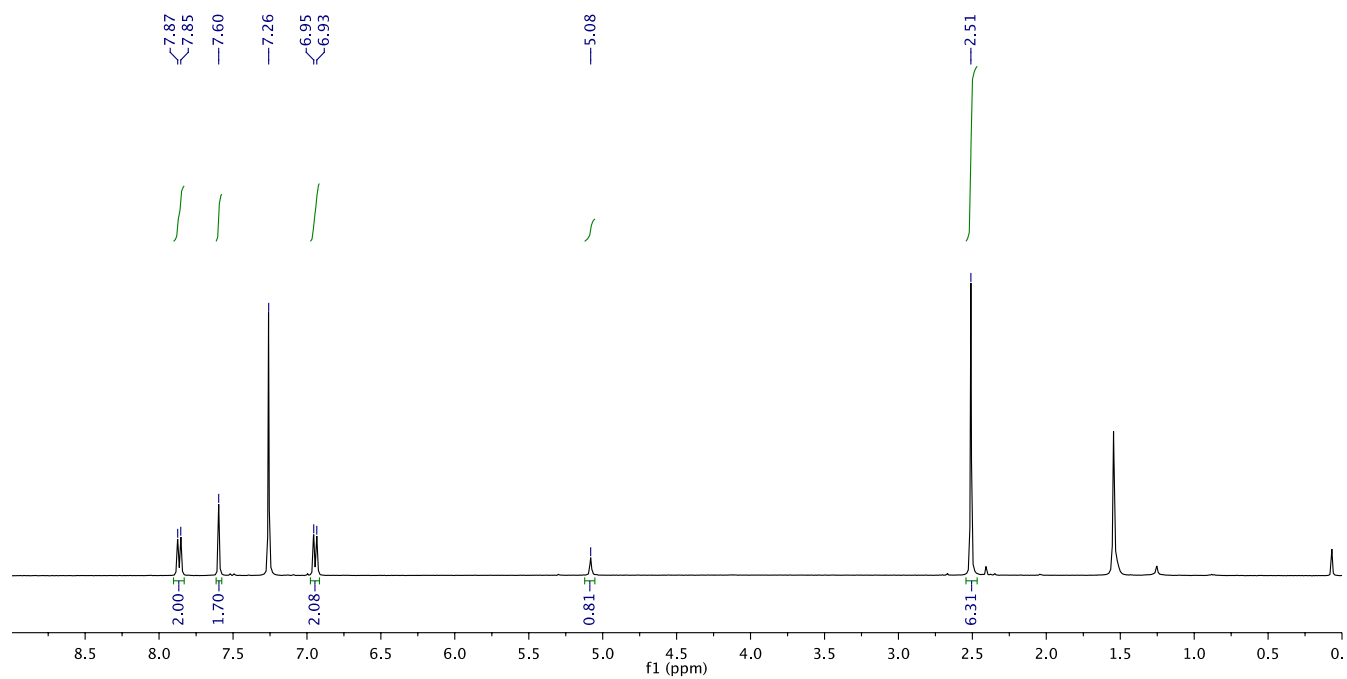
Compound AB.Hex: A solution of **AB.OH** (100 mg, 0.44 mmol), 6-bromo-1-hexene (216.2 mg, 1.32 mmol), K_2CO_3 (91.4 mg, 0.66 mmol) and dry DMF (1 mL) was stirred at 70 °C for 24 hrs. The mixture was allowed to reach room temperature, diluted with ethyl acetate, transferred in a separatory funnel, and washed with water. The organic layers were collected, dried over MgSO_4 , filtered and concentrated in vacuo. The crude product was filtered through a silica pad ($R_f = 0.43$ in PET/EtOAc = 9.5 : 0.5; PET = 100% \rightarrow PET/EtOAc = 9.5 : 0.5). The filtrate was then evaporated and the product was obtained as a yellow solid (120 mg, 88%). ^1H NMR (400 MHz, CDCl_3) (trans): $\delta = 7.89$ (d, $J = 7.9$ Hz, 2H), 7.49 (s, 2H), 7.08 (s, 1H), 6.99 (d, $J = 7.9$ Hz, 2H), 5.84 (dd, $J = 16.7, 8.9$ Hz, 1H), 5.05 (d, $J = 17.0$ Hz, 1H), 4.99 (d, $J = 9.8$ Hz, 1H), 4.05 (t, $J = 6.0$ Hz, 2H), 2.41 (s, 6H), 2.21 – 2.07 (m, 2H), 1.91 – 1.76 (m, 2H), 1.67 – 1.50 (m, 2H). ^{13}C NMR (101 MHz, CDCl_3): $\delta = 161.6, 153.1, 147.1, 138.8, 138.6, 132.2, 124.8,$

Supporting Information

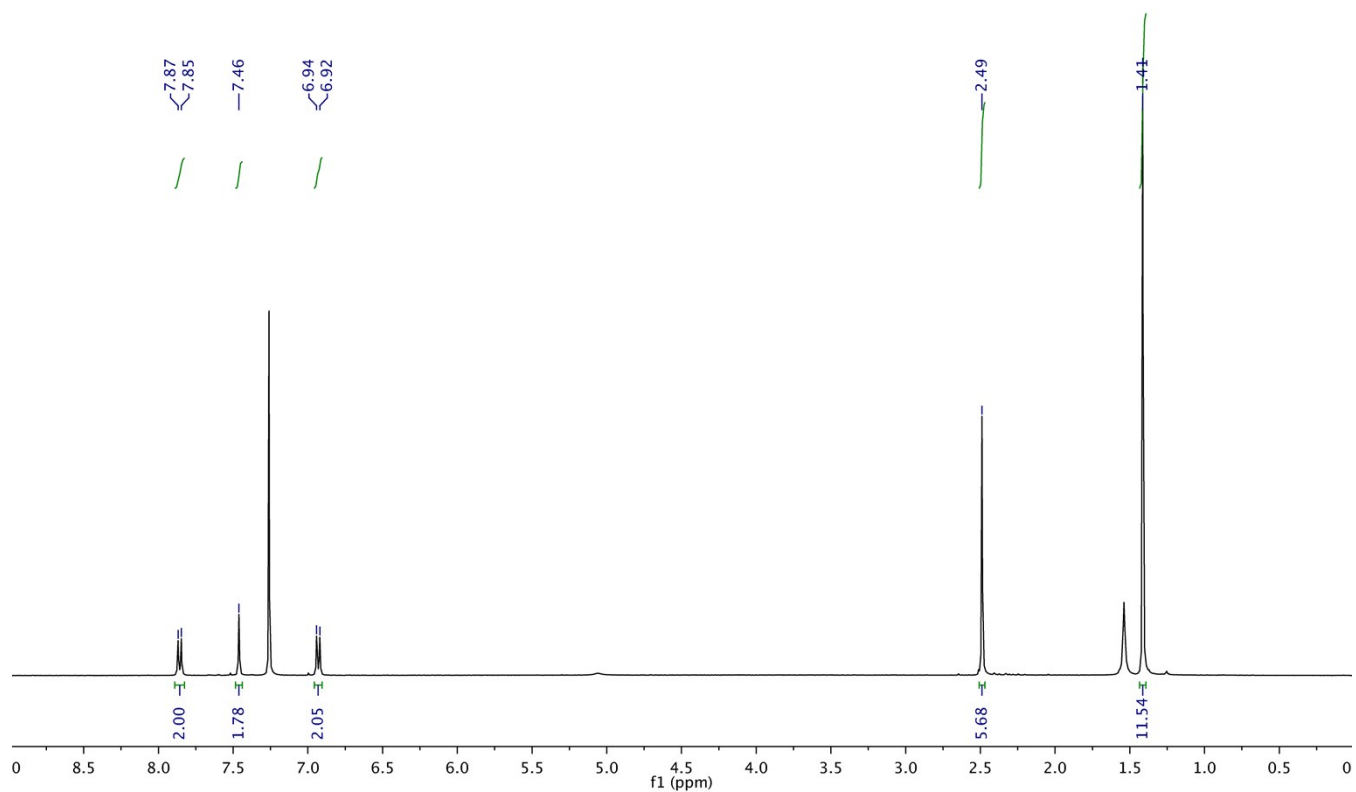
120.5, 115.0, 114.8, 68.2, 33.6, 28.8, 25.4, 21.4. HRMS (ESI, positive mode) m/z calculated for $C_{20}H_{25}N_2O$ $[M + H]^+$: 309.1961; found: 309.1954. $\epsilon_{\text{trans}} = 2.61 \times 10^4 \text{ M}^{-1}\text{cm}^{-1}$ ($\lambda_{\text{max}} = 357 \text{ nm}$).

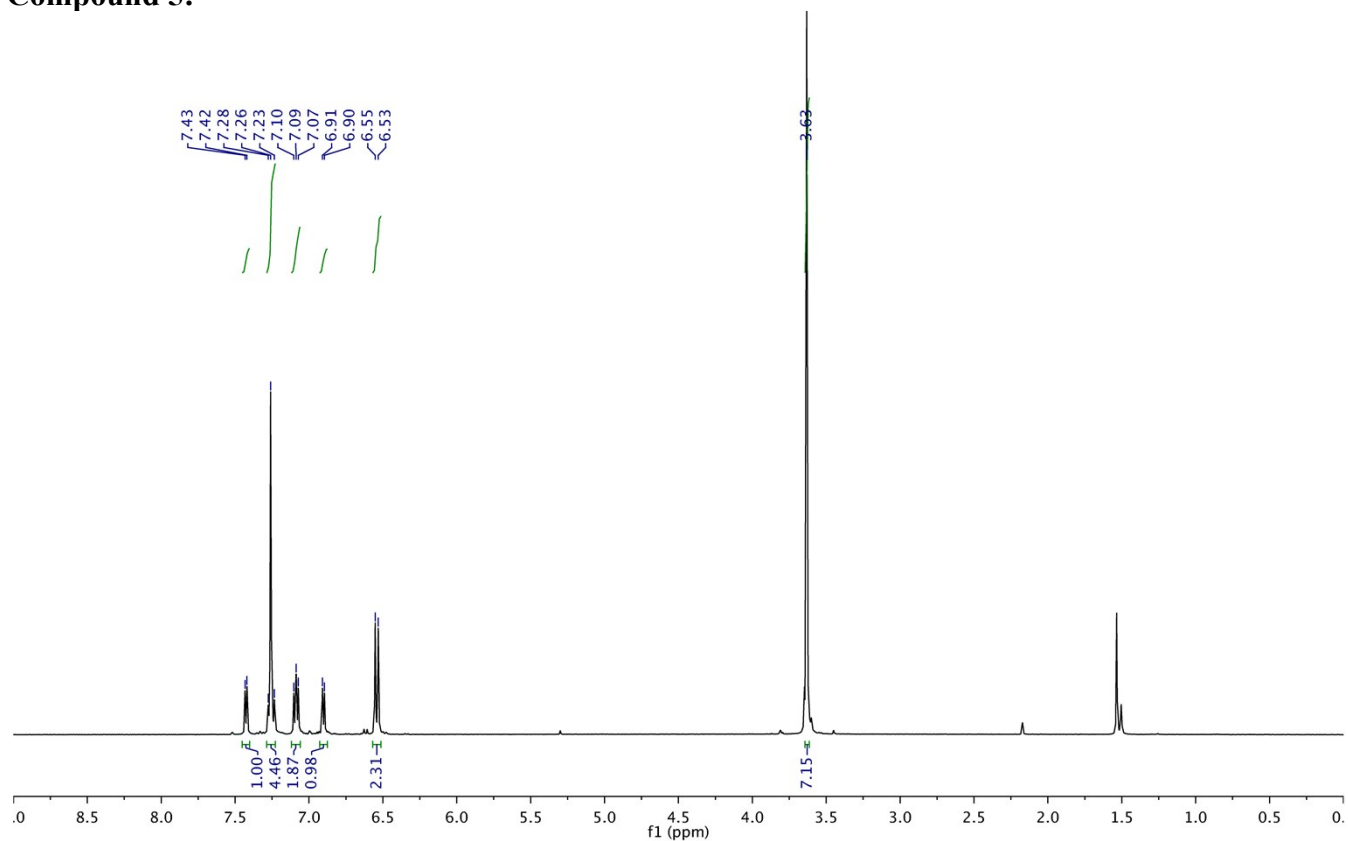
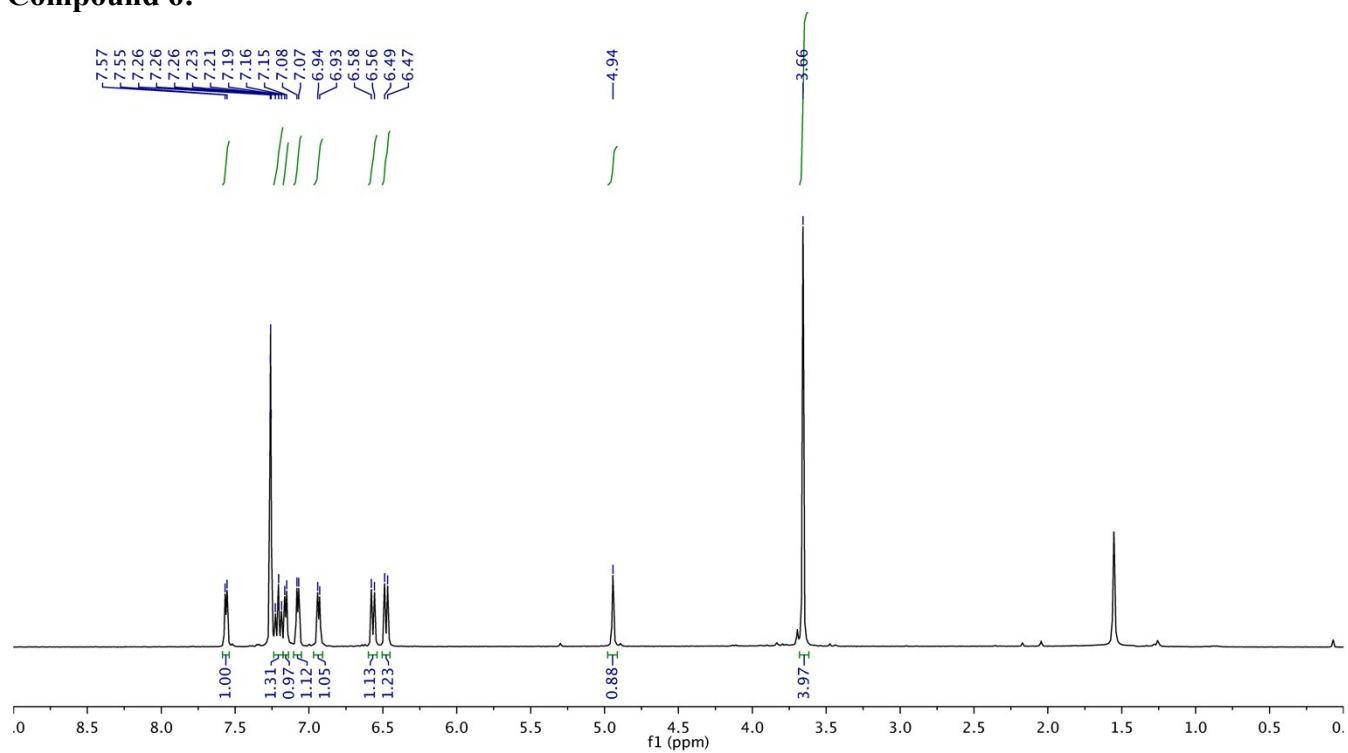
2.2. ^1H -NMR spectra of 1 and related molecules

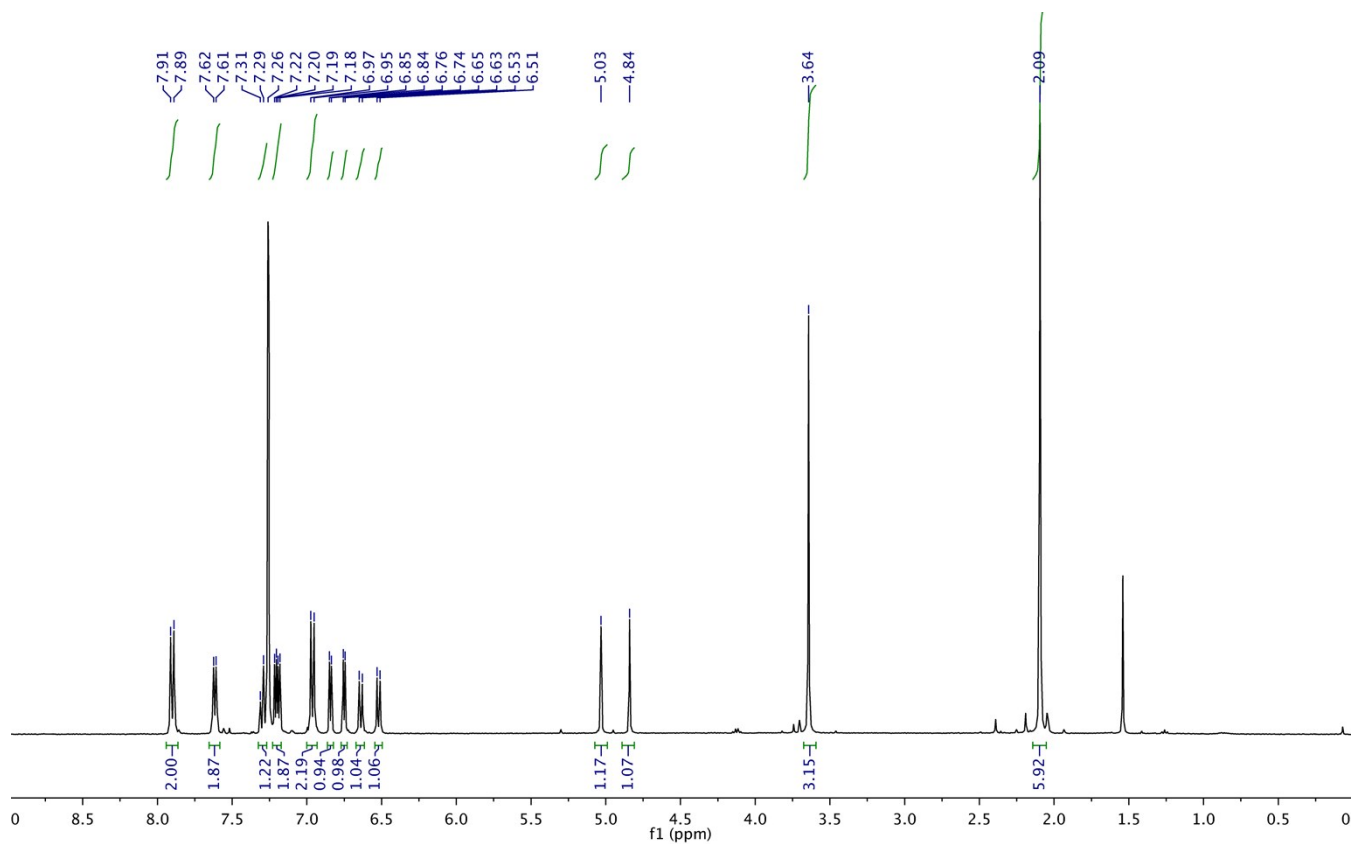
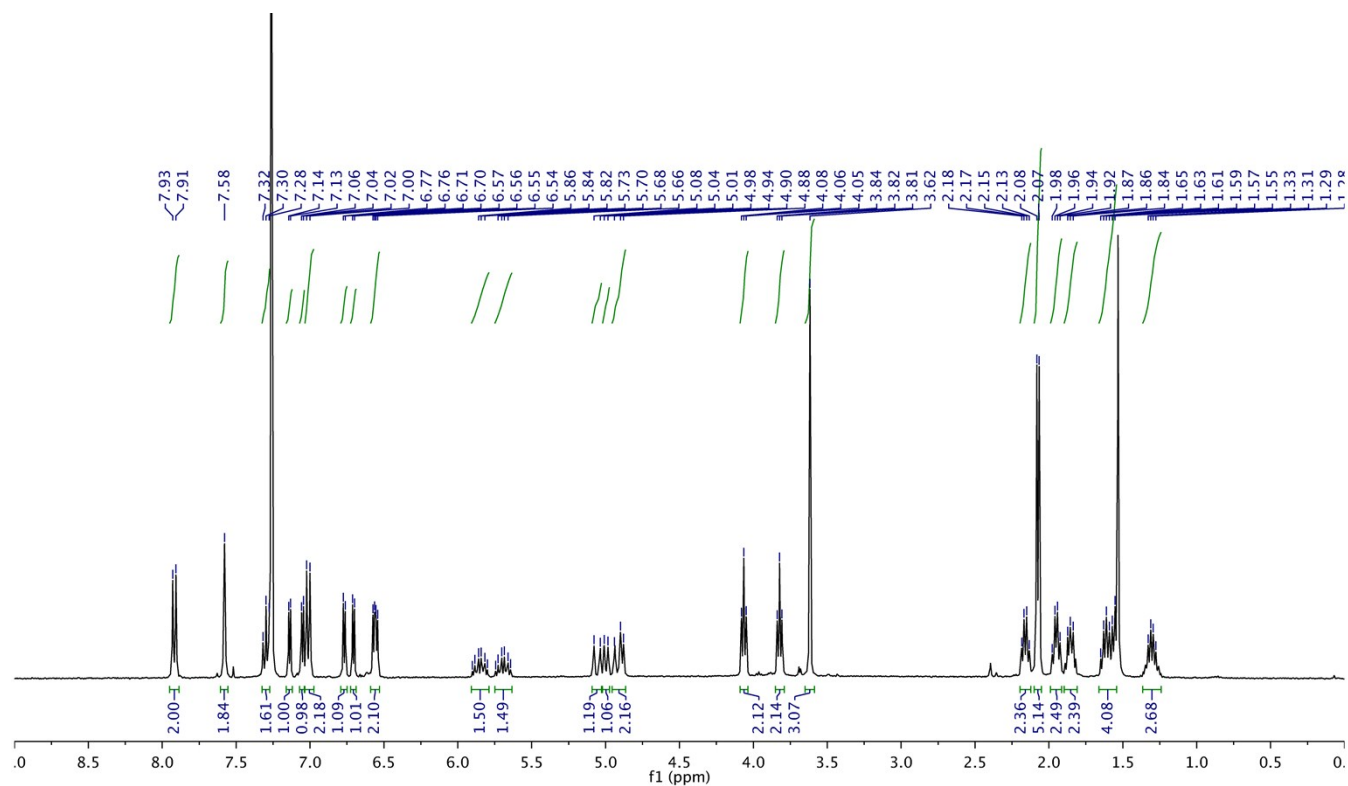
Compound 3:

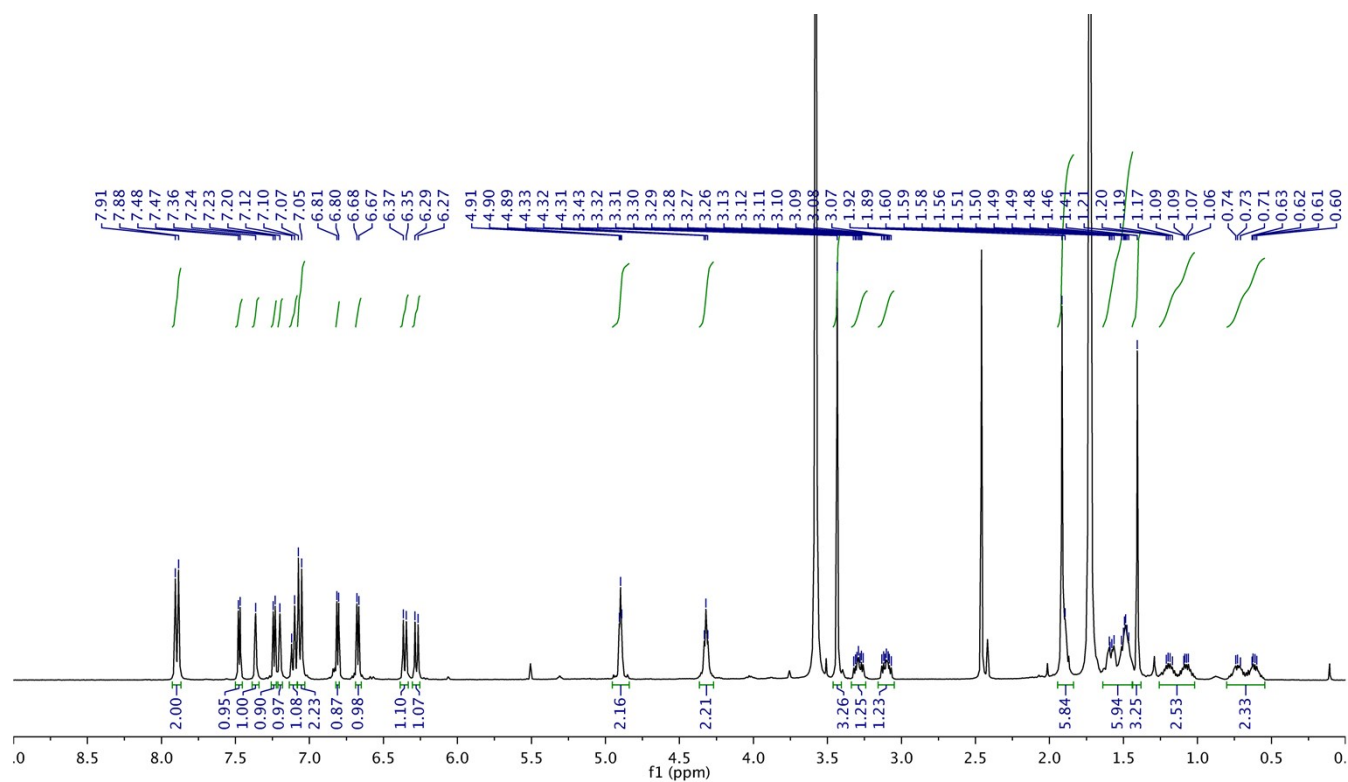
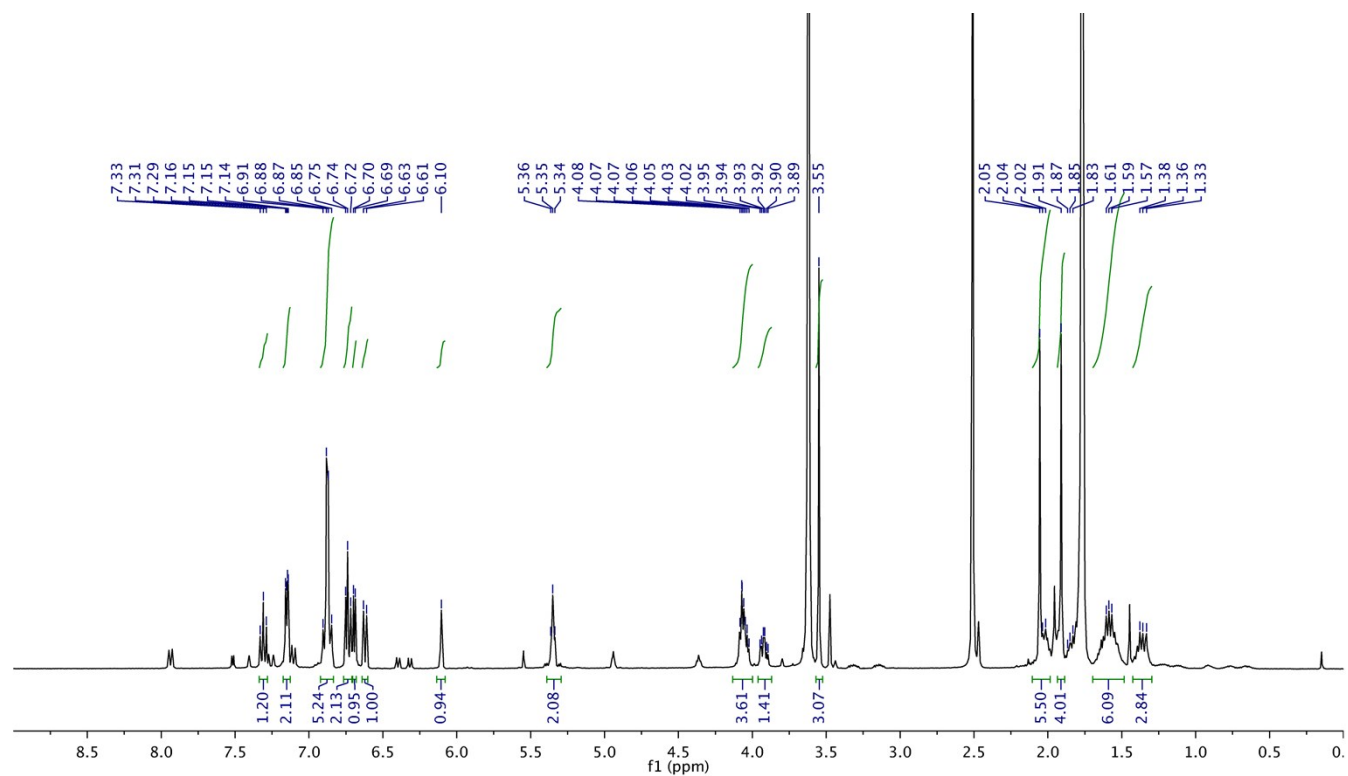


Compound 4:



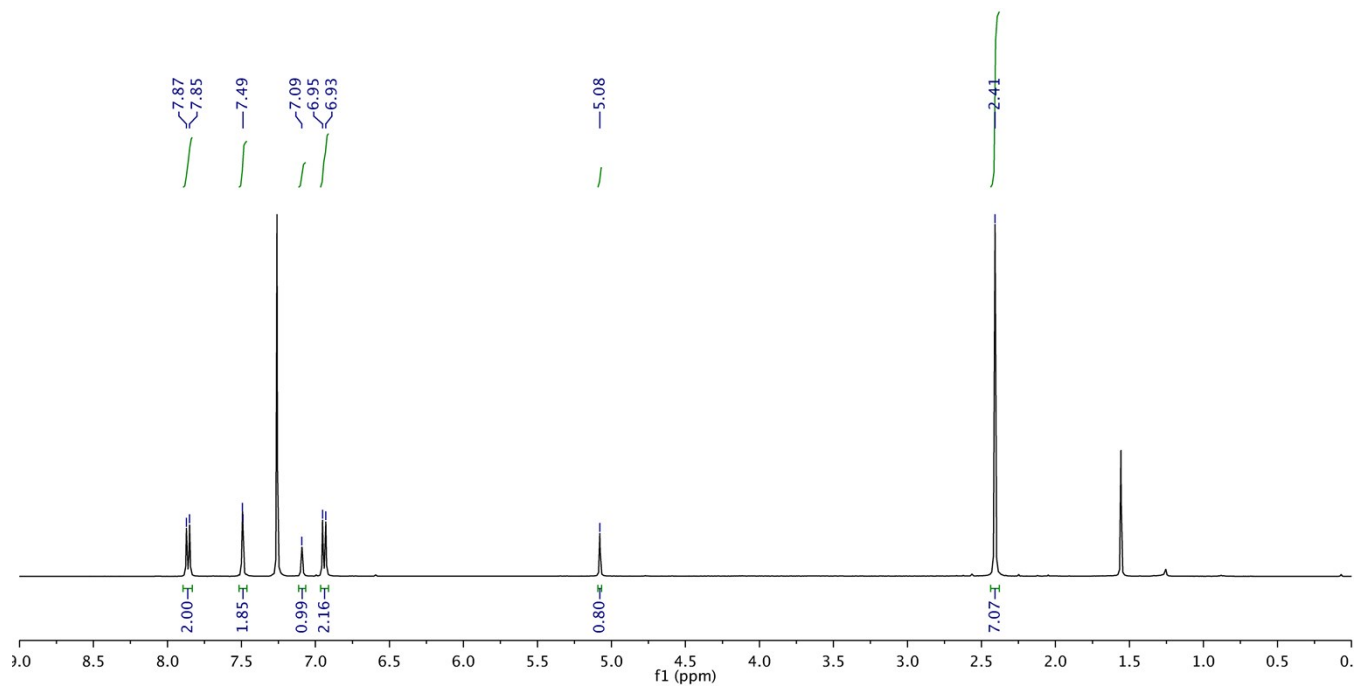
Compound 5:**Compound 6:**

Compound 7:**Compound 8:**

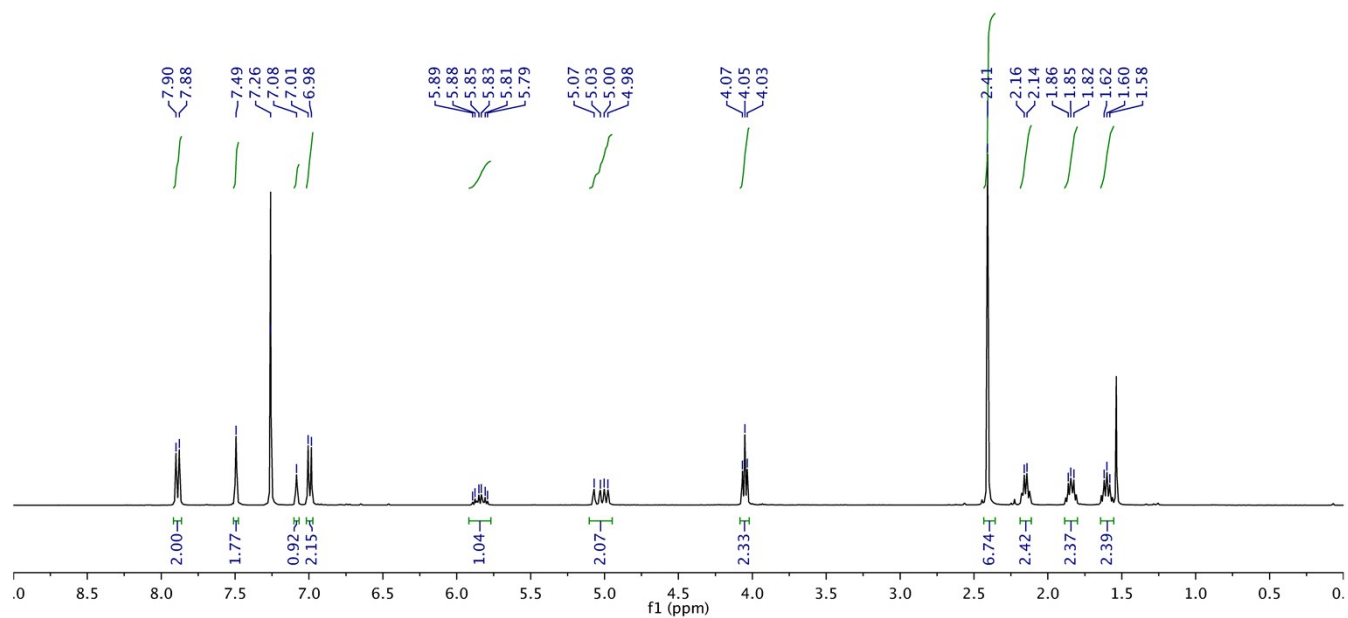
Compound 1.trans:**Compound 1.cis (upon 350 nm for 1h):**

Supporting Information

Compound AB.OH:

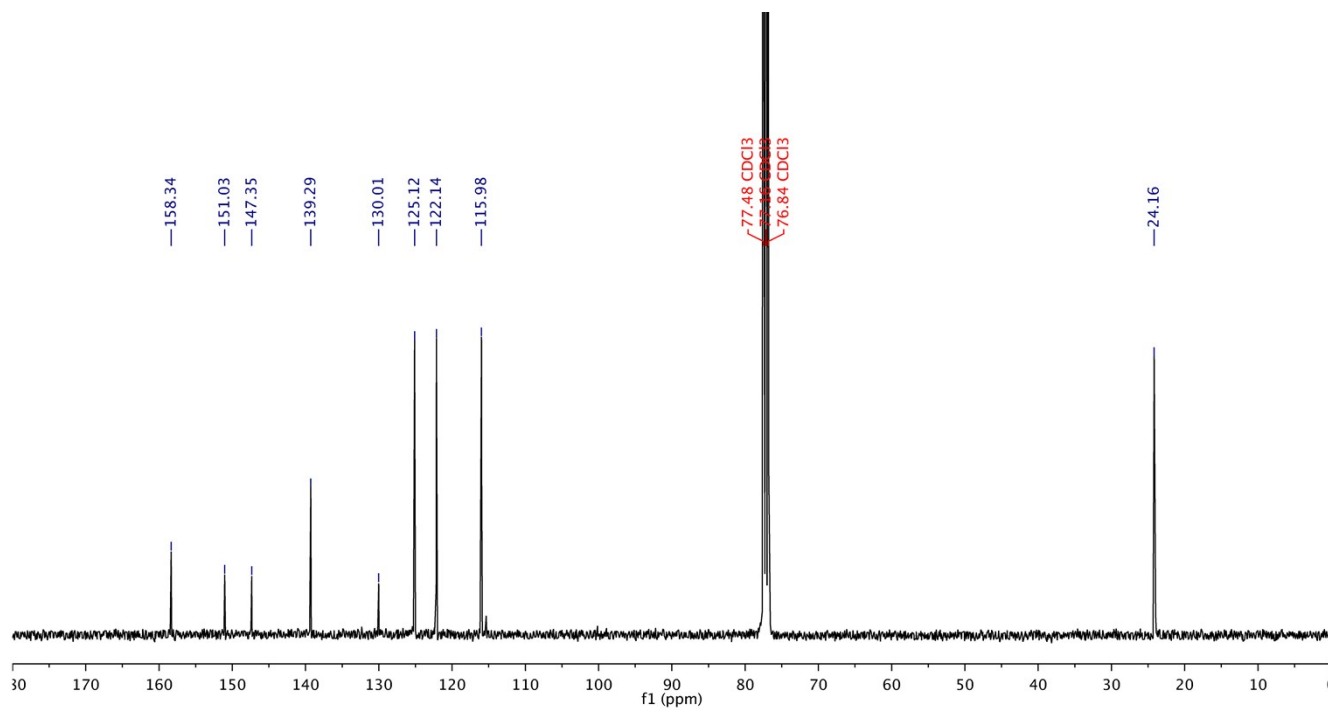


Compound AB.Hex:

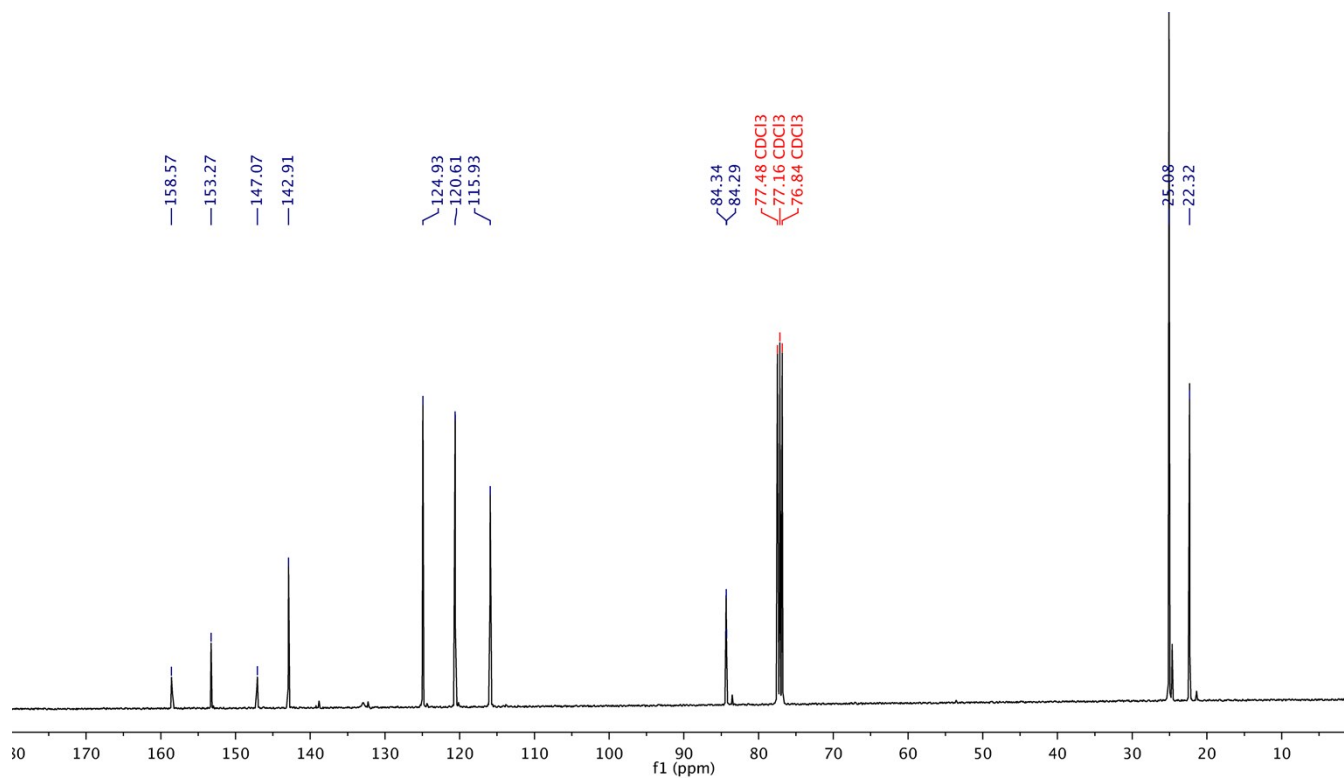


2.2. ^{13}C -NMR spectra of 1 and related molecules

Compound 3:

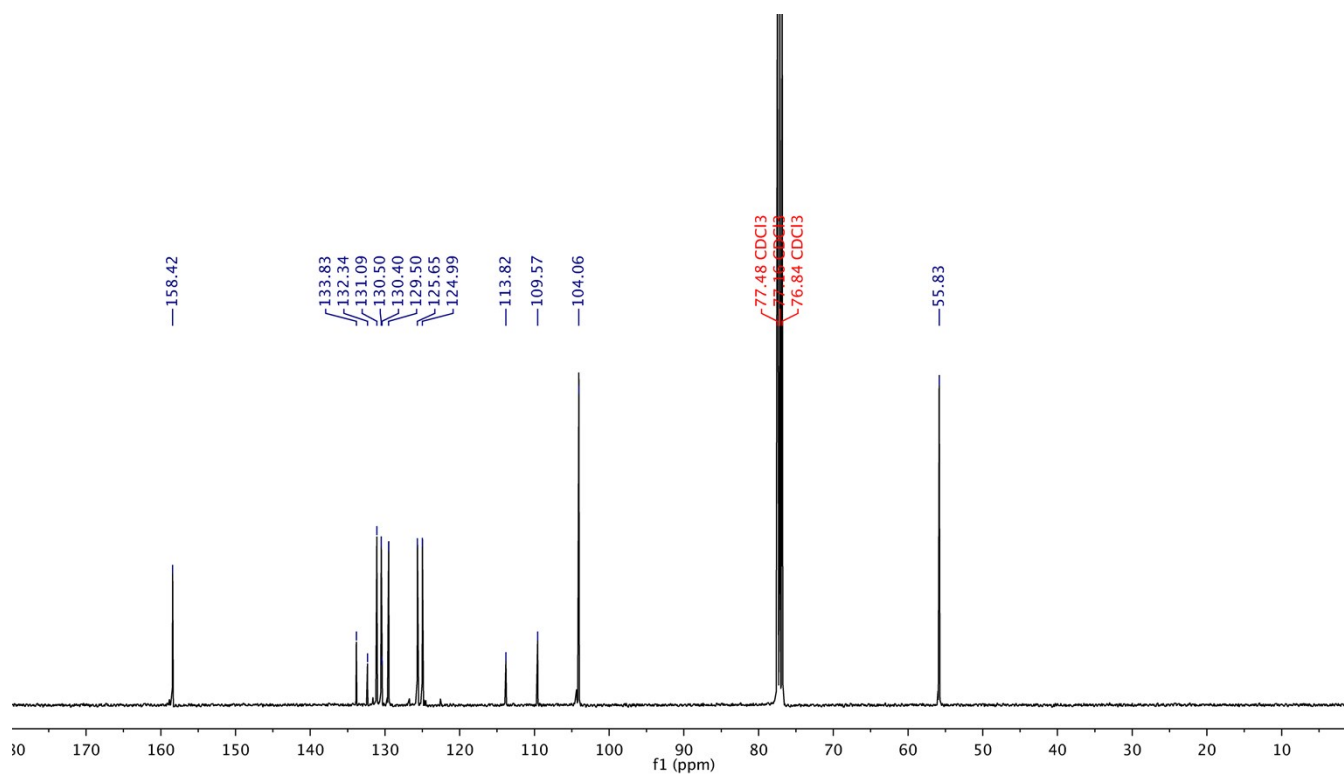


Compound 4:

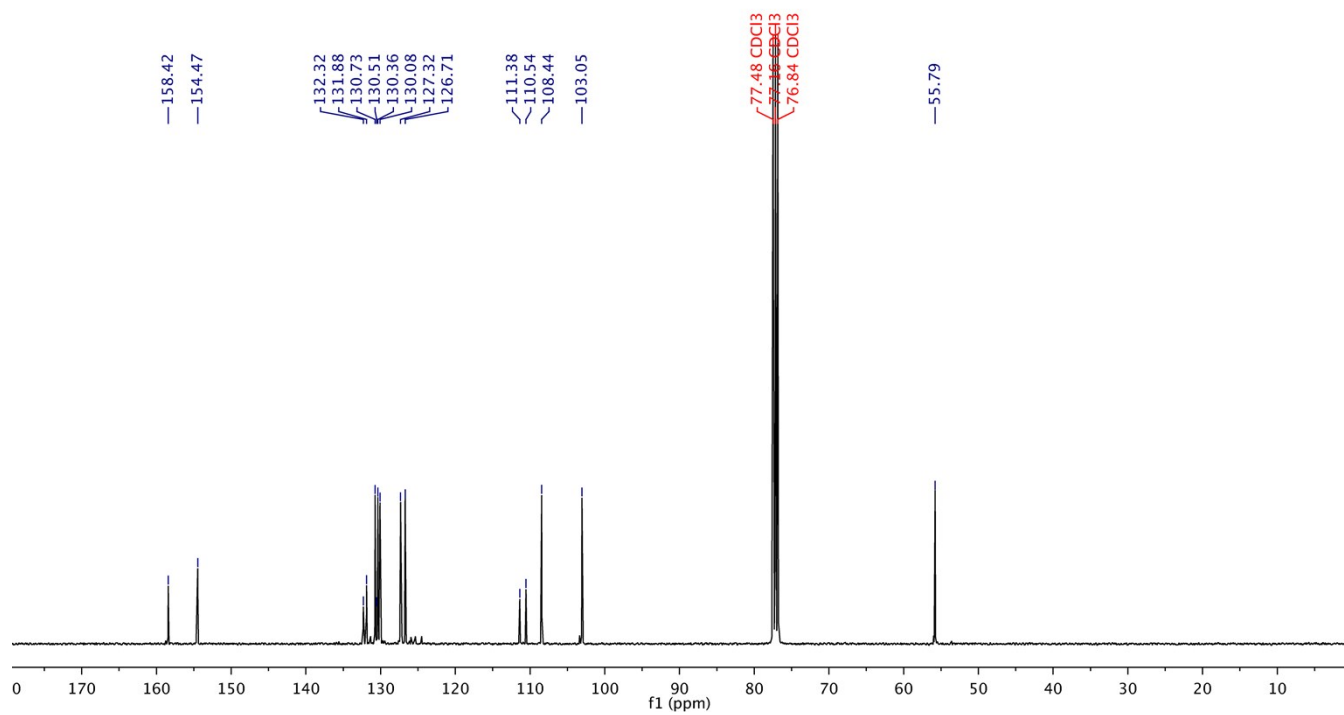


Supporting Information

Compound 5:

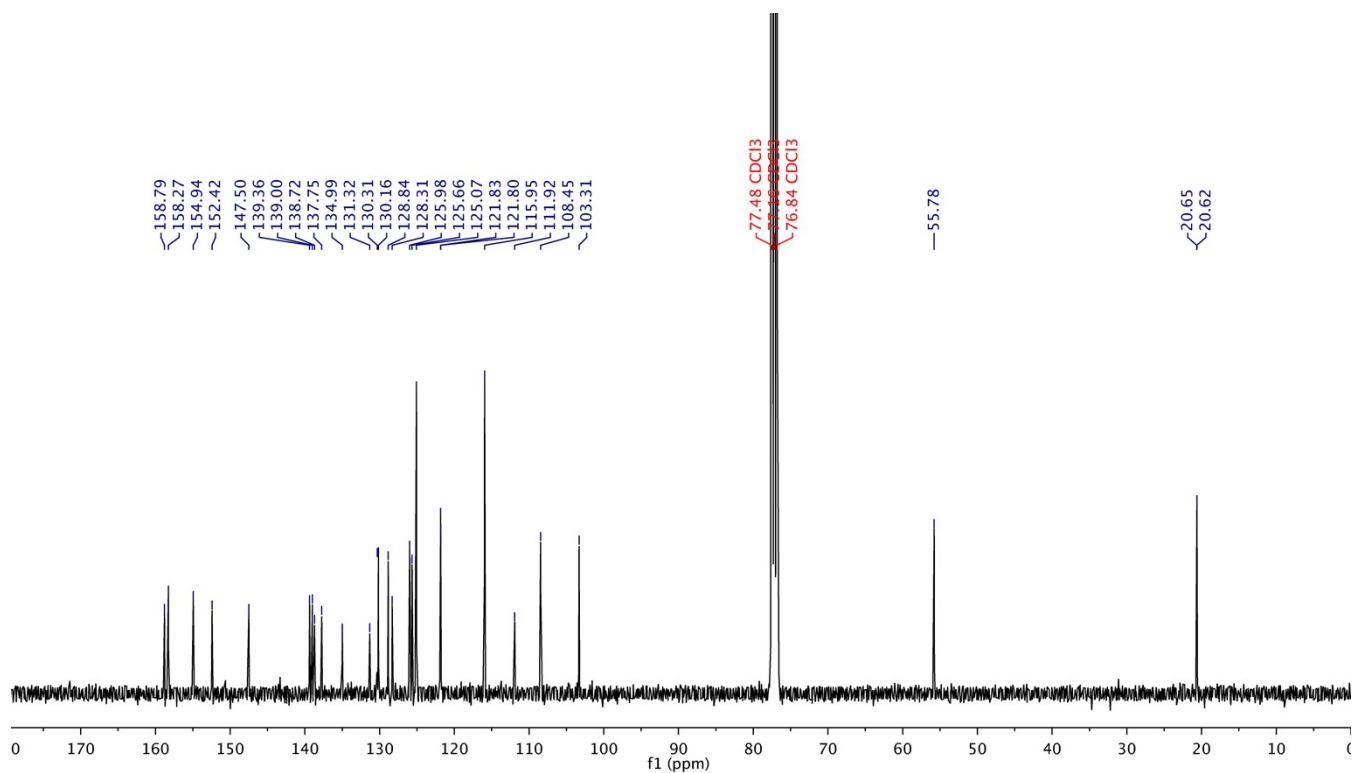


Compound 6:

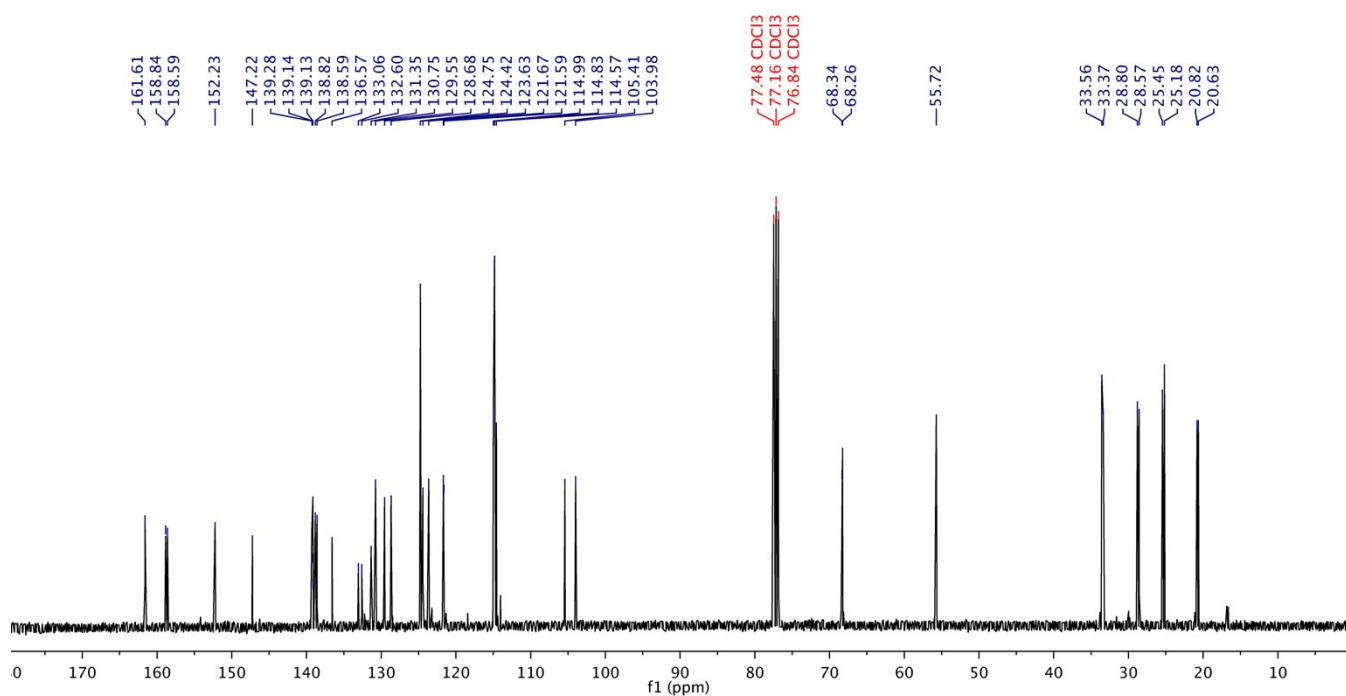


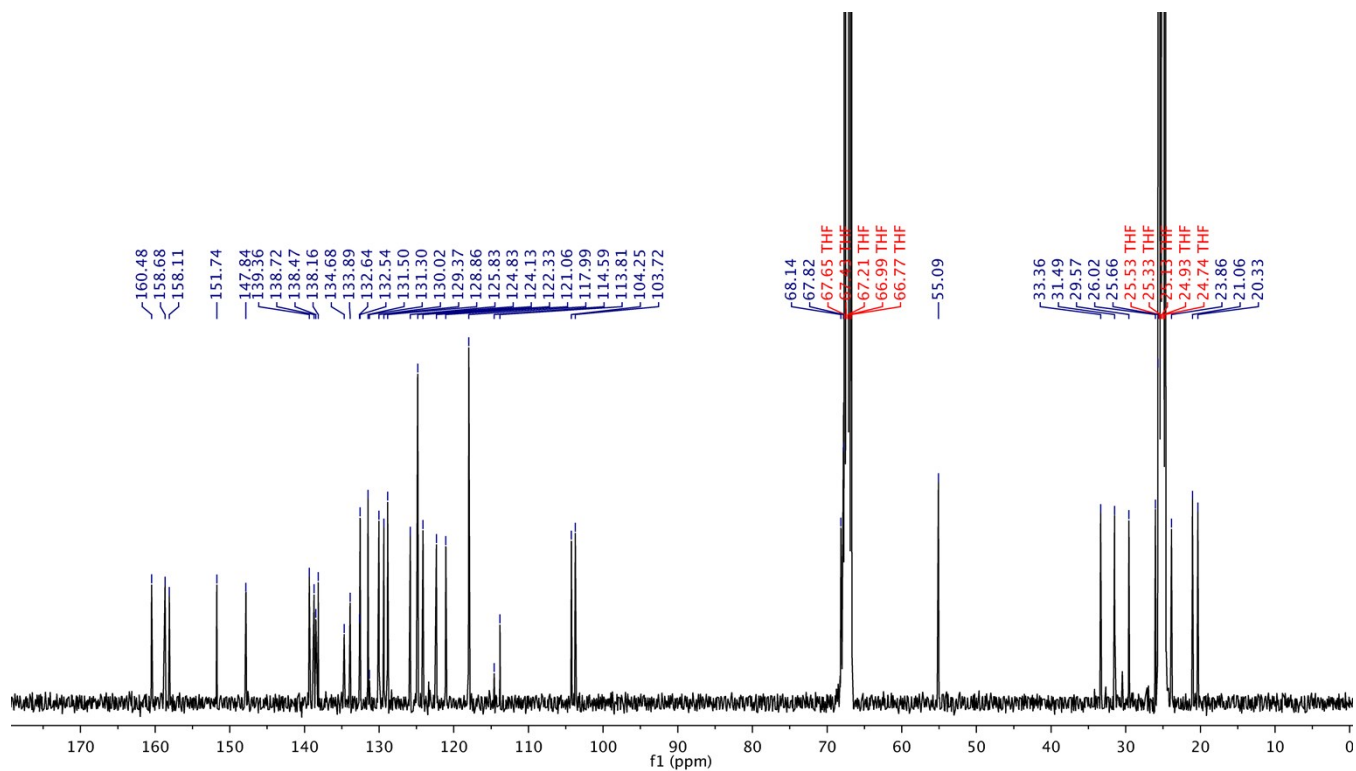
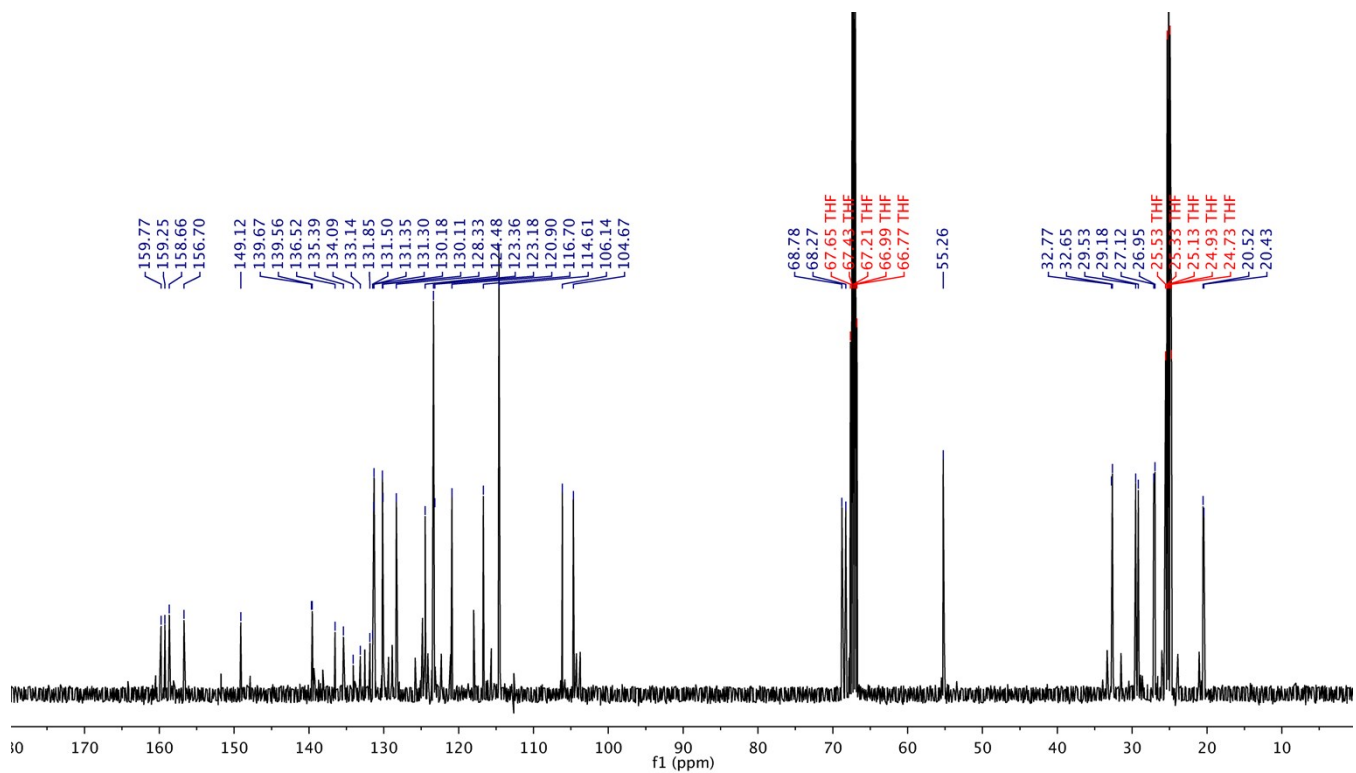
Supporting Information

Compound 7:



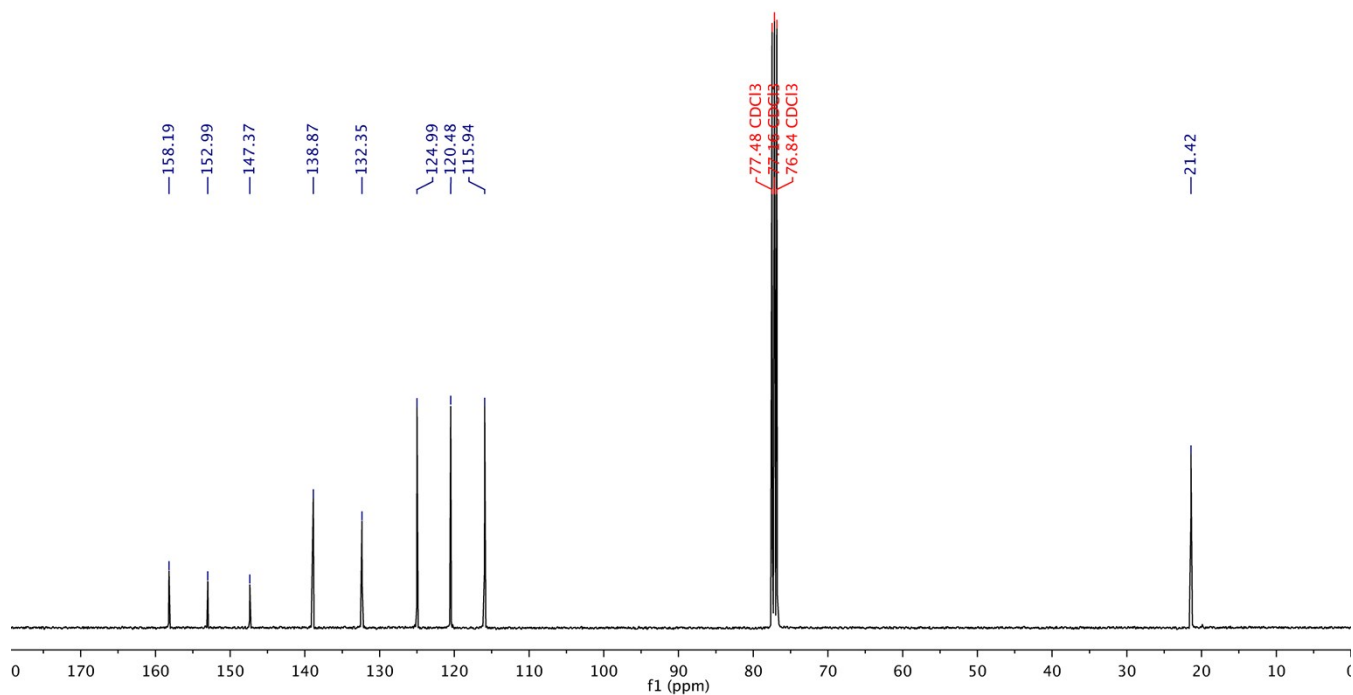
Compound 8:



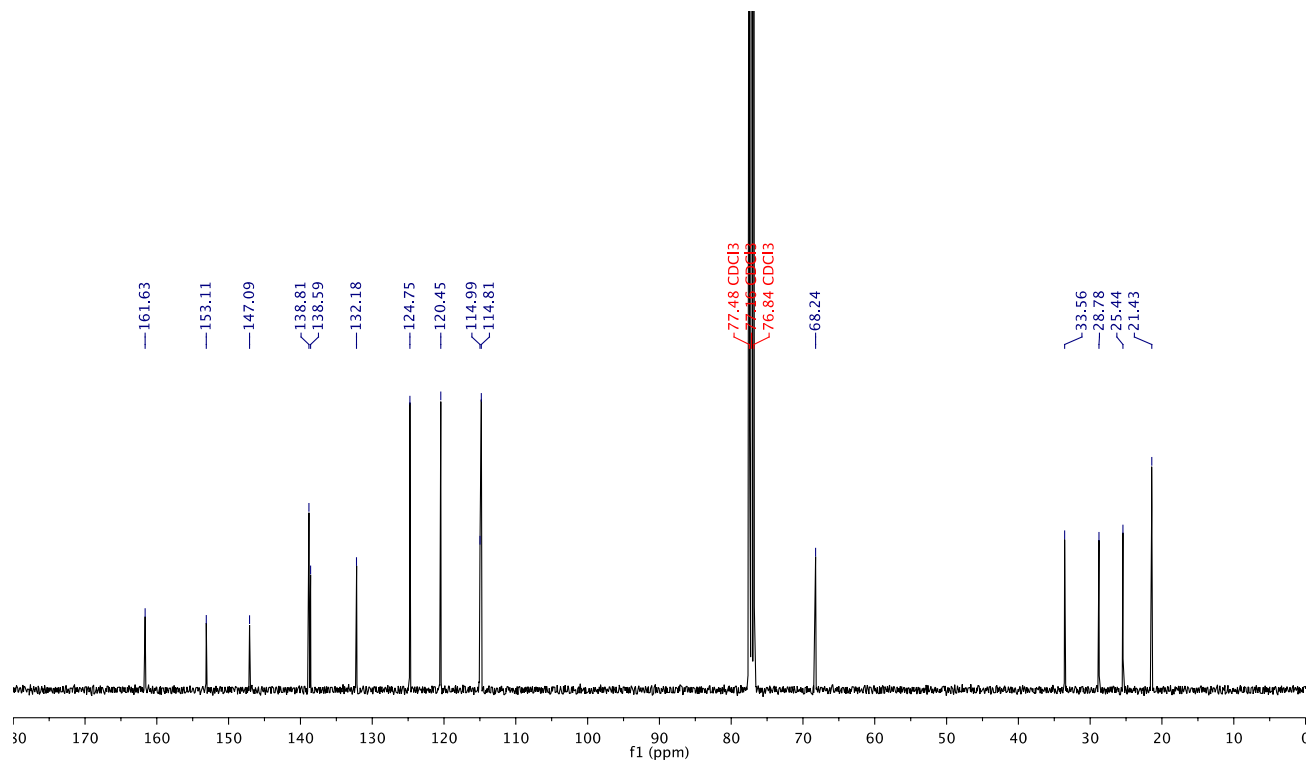
Compound 1.*trans*:**Compound 1.*cis* (upon 350 nm for 1h):**

Supporting Information

Compound AB.OH:



Compound AB.Hex:



2.3. ^1H -NMR Spectra: *trans*-to-*cis* isomerization and PSS of **1**

^1H -NMR spectroscopy shows that when **1.trans** is exposed to 350nm light, ~86% of **1.trans** is converted to **1.cis**. This process can be inverted by irradiating **1.cis** with 254nm light to reach the photostationary state consisting ~55% of **1.trans** and ~45% of **1.cis**.

After irradiation with 254nm wavelength no evidence of isomerization of the olefin double bond is observed. The retention of the *cis* configuration of the olefinic protons was confirmed by NOESY experiments.

Determination of the *cis* conformation was also assessed by the retention of the same J coupling constant on azobenzene isomerization. The J values measured before and after the irradiation with 350 nm and 254 nm wavelength is 3.3Hz, which is lower than what generally expected for *cis* isomer (6-15Hz). However, it has to be noticed that this low J value could be given either by the torsion tension induced by the macrocycle⁵ or by a partial overlap of the doublet of triplet expected by the olefinic protons. Thus, we decided to not to determine any specific structure of the peak and rather define it as a multiplet.

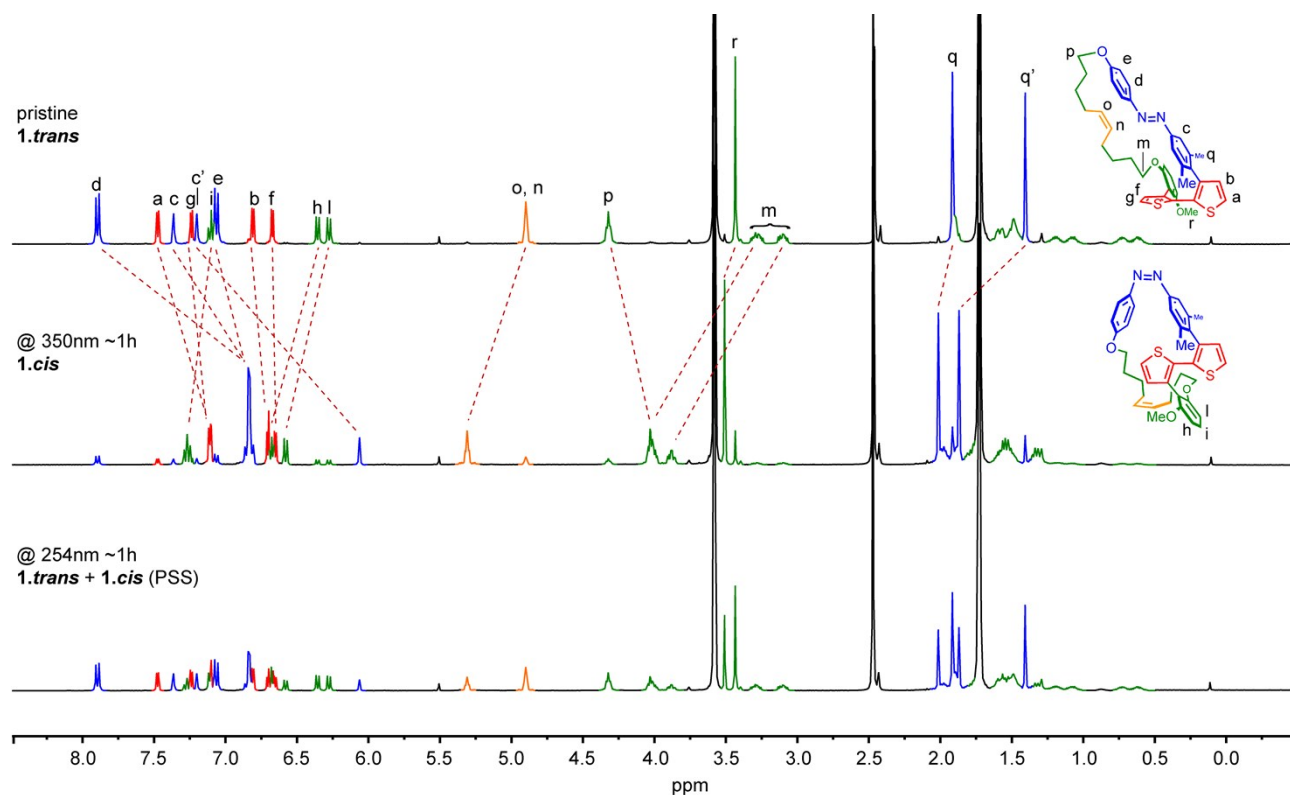


Figure S1: ^1H -NMR spectrum of compound **1** in tetrahydrofuran- d_8 . Before (top), after (middle) 1 h of irradiation at 350 nm, and after (bottom) 1 h of irradiation at 254 nm.

[5] ' ^1H Nuclear Magnetic Resonance Spectra of Cyclic Monoenes: Hydrocarbons, Ketones, Heterocycles, and Benzo Derivatives' H. Gunther, G. Jikeli *Chem. Rev.*, 1977, 77, 599-637.

Section 3: Computations of the molecular structures

3.1 Replica-Exchange Molecular Dynamic simulations (REMD)

The dynamic simulations were performed using the i-PI driver⁶ in the NVT ensemble with REMD@DFTB3⁷ for 100,000 steps. A time step of 0.25 fs ensured the stability of the dynamics at all temperatures, ranging from 300K (the target temperature) to the highest 1200K over 32 replicas that are allowed to exchange configurations every 50 steps. The GLE thermostat^{8, 9} ensures an optimal mapping of the phase space. Forces are provided to i-PI from the DFTB+ software at the DFTB3/3OB^{10, 11} level together with the UFF force field accounting for London dispersion.¹²

3.2 Static computations

Geometries of the most relevant (low-lying) conformations of PTS **1.cis** and **1.trans** were extracted from the REMD simulations prior to static optimization at the PBE0-dDsC¹³/def2SVP level using the development version of Q-Chem.¹⁴

- [6] M. Ceriotti, J. More, D. E. Manolopoulos, *Comput. Phys. Commun.*, 2014, **185**, 1019–1026.
- [7] R. Petraglia, A. Nicolai, M. D. Wodrich, M. Ceriotti, C. Corminboeuf, *J. Comput. Chem.*, 2016, **37**, 83–92.
- [8] M. Ceriotti, G. Bussi, M. Parrinello, *J. Chem. Theory Comput.*, 2010, **6**, 1170–1180.
- [9] M. Ceriotti, G. Bussi, M. Parrinello, *Phys. Rev. Lett.*, 2009, **102**, 020601
- [10] M. Gaus, Q. Cui, M. Elstner, *J. Chem. Theory Comput.*, 2011, **7**, 931–948.
- [11] M. Gaus, X. Lu, M. Elstner, Q. Cui, *J. Chem. Theory Comput.*, 2014, **10**, 1518–1537.
- [12] A. K. Rappi, C. J. Casewit, K. S. Colwell, W. A. Goddard III, W. M. Skid, *J. Am. Chem. Soc.*, 1992, **114**, 10024–10035.
- [13] S. N. Steinmann, C. Corminboeuf, *J. Chem. Theory Comput.*, 2011, **7**, 3567–3577.
- [14] Y. Shao, Z. Gan, E. Epifanovsky, A. T. B. Gilbert, M. Wormit, J. Kussmann, A. W. Lange, A. Behn, J. Deng, X. Feng, D. Ghosh, M. Goldey, P. R. Horn, L. D. Jacobson, I. Kaliman, R. Z. Khaliullin, T. Kuš, A. Landau, J. Liu, E. I. Proynov, Y. M. Rhee, R. M. Richard, M. A. Rohrdanz, R. P. Steele, E. J. Sundstrom, H. L. Woodcock, P. M. Zimmerman, D. Zuev, B. Albrecht, E. Alguire, B. Austin, G. J. O. Beran, Y. A. Bernard, E. Berquist, K. Brandhorst, K. B. Bravaya, S. T. Brown, D. Casanova, C.-M. Chang, Y. Chen, S. H. Chien, K. D. Closser, D. L. Crittenden, M. Diedenhofen, R. A. DiStasio, H. Do, A. D. Dutoi, R. G. Edgar, S. Fatehi, L. Fusti-Molnar, A. Ghysels, A. Golubeva-Zadorozhnaya, Joseph Gomes, Magnus W.D. Hanson-Heine, Philipp H.P. Harbach, Andreas W. Hauser, Edward G. Hohenstein, Z. C. Holden, T.-C. Jagau, H. Ji, B. Kaduk, K. Khistyayev, J. Kim, J. Kim, R. A. King, P. Klunzinger, D. Kosenkov, T. Kowalczyk, C. M. Krauter, K. U. Lao, A. D. Laurent, K. V. Lawler, S. V. Levchenko, C. Y. Lin, F. Liu, E. Livshits, R. C. Lochan, A. Luenser, P. Manohar, S. F. Manzer, S.-P. Mao, N. Mardirossian, A. V. Marenich, Simon A. Maurer, Nicholas J. Mayhall, Eric Neuscamman, C. Melania Oana, Roberto Olivares-Amaya, Darragh P. O'Neill, J. A. Parkhill, T. M. Perrine, R. Peverati, A. Prociuk, D. R. Rehn, E. Rosta, N. J. Russ, S. M. Sharada, S. Sharma, D. W. Small, A. Sodt, T. Stein, D. Stück, Y.-C. Su, A. J. W. Thom, T. Tsuchimochi, V. Vanovschi, L. Vogt, O. Vydrov, T. Wang, M. A. Watson, J. Wenzel, A. White, C. F. Williams, J. Yang, S. Yeganeh, S. R. Yost, Z.-Q. You, I. Y. Zhang, X. Zhang, Y. Zhao, B. R. Brooks, G. K. L. Chan, D. M. Chipman, C. J. Cramer, W. A. Goddard, M. S. Gordon, W. J. Hehre, A. Klamt, H. F. Schaefer, M. W. Schmidt, C. D. Sherrill, D. G. Truhlar, A. Warshel, X. Xu, Alán Aspuru-Guzik, Roi Baer, Alexis T. Bell, Nicholas A. Besley, Jeng-Da Chai, Andreas Dreuw, Barry D. Dunietz, T. R. Furlani, S. R. Gwaltney, C.-P. Hsu, Y. Jung, J. Kong, D. S. Lambrecht, W. Liang, C. Ochsenfeld, V. A. Rassolov, L. V. Slipchenko, J. E. Subotnik, T. V. Voorhis, J. M. Herbert, A. I. Krylov, P. M.W. Gill, M. Head-Gordon, QChem 4.0, *Mol. Phys.*, 2015, **113**, 184–215.

Section 4: Steady-state Spectroscopy

4.1 Absorption Spectra

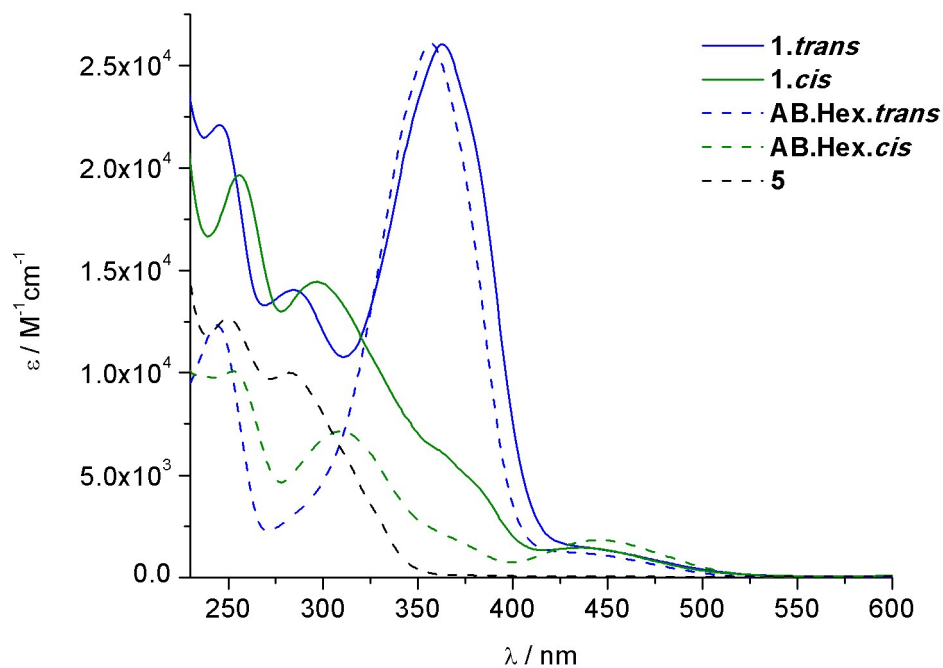


Figure S2: Absorption spectrum of **1.trans**, **8.cis**, **AB.Hex.trans**, **AB.Hex.cis**, and **5** in THF solution.

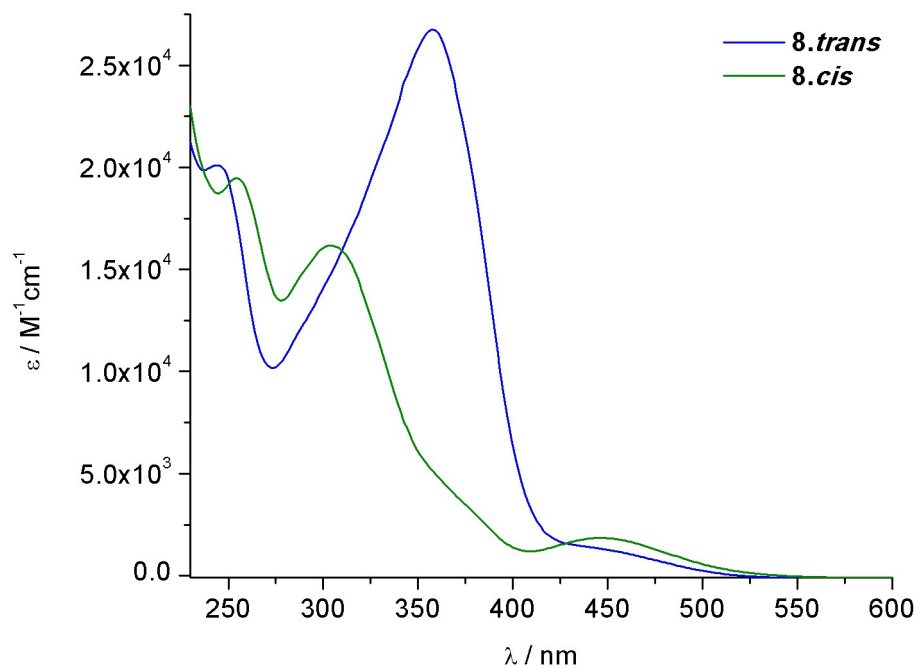


Figure S3: Absorption spectrum of **8.trans** and **8.cis** in THF solution.

4.2 Cyclability

A dilute solution of **1** ($\sim 1 \times 10^{-4}$ M) in THF was placed ~ 3.5 cm from the light source and irradiated with repeated alternating cycles of 1 min with 350 nm and 254 nm wavelengths (each 6 W).

4.3 Thermal relaxation

Dilute solutions of **1.trans**, **8.trans** and **AB.Hex.trans** ($\sim 1 \times 10^{-4}$ M) in THF were irradiated with 350 nm wavelengths (~ 1 min) to isomerize into the corresponding *cis* form. The solutions were then stored at 25°C in the dark, and absorption spectra measured every 12 h.

It was observed that compounds **8.cis** and **AB.Hex.cis** have respectively a half-life ($\tau_{1/2}$) of ~ 12 h and ~ 16 h as expected for alkoxy-azobenzene derivatives. Contrarily, **1.cis** exhibits a slower thermal relaxation with a $\tau_{1/2} = 120$ h. Given the fact that the intrinsic properties of the azobenzene in **1**, **8** and **AB.Hex** should be comparable, the slow thermal relaxation of **1.cis** can be associated to a reduced degree of freedom in the isomerization motion. Further investigations are currently ongoing to get a deeper understanding into the dynamics of this process.

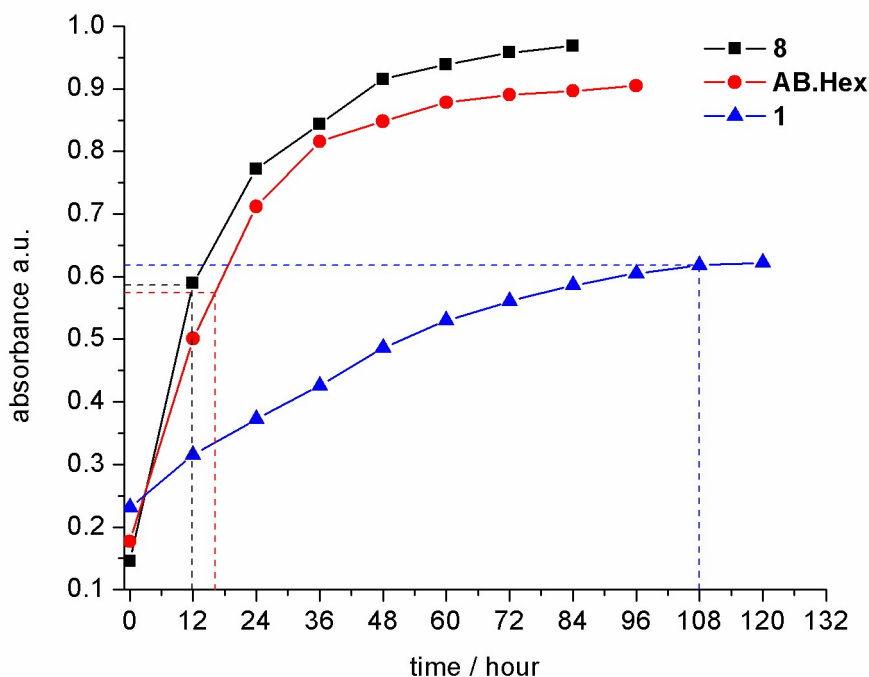


Figure S4: Measured absorbance at the corresponding λ_{\max} of **1**, **8**, and **AB.Hex** in THF solution during the thermal relaxation. Dashed lines indicate the corresponding absorbance intensity at the observed half-life.

Section 5: Time Dependent Density Functional Theory (TDDFT) calculations

5.1. Computed absorption spectra

Excited states and electronic vertical transitions were evaluated at the TDDFT level of theory (ω B96XD/6-311+G**), on top of the lowest-energy structures as derived from the REMD//DFTB study (see Section 3). Figure S5 reports the oscillator strengths and absorption spectra (as obtained from a convolution of Lorentzian functions peaked on each vertical transition, FWHM = 0.3 eV), for **1.cis** and **1.trans**. TDDFT calculations, with the use of range-separated functionals, tend to overestimate the transitions energies.^{15,16} Although in the current calculations we do not take into account the vibronic relaxations and spectral broadening effects,¹⁷ the computed transition energies and band intensity ratio are consistent and in good agreement with the experimental findings. All calculations were performed in *vacuum*; small effects on the vertical transition energies are expected to occur with the inclusion of explicit or implicit solvent.

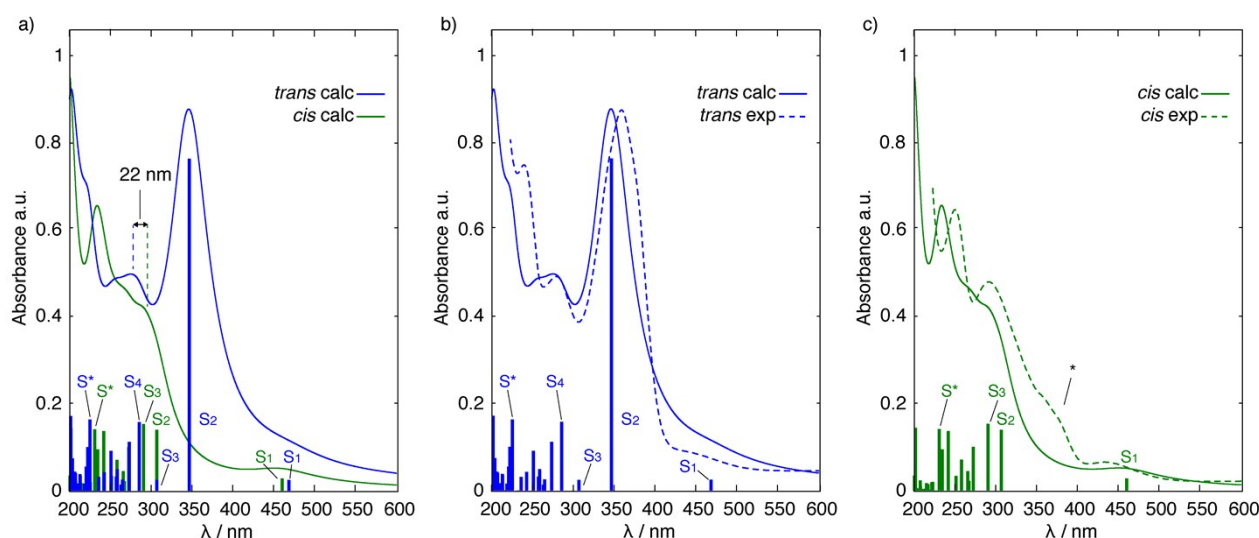


Figure S5. TDDFT (ω B97XD/6-311+G**) vertical transitions for **1.cis** (green) and **1.trans** (blue). Relevant excited states identified for the spectroscopic assignments (see manuscript) are reported. (a) Calculated absorption spectra of **1.cis** (green) and **1.trans** (blue); (b) Absorption spectra of **1.trans** calculated (blue solid) and measured in THF solution (blue dashed); (c) Absorption spectra of **1.cis** calculated (green solid) and measured in THF solution (green dashed). (*) Residual signature of **1.trans** (~14%).

[15] ‘TD-DFT benchmarks: A review’ A. D. Laurent; D. Jacquemin, *Int. J. Quantum Chem.*, 2013, **113**, 2019–2039

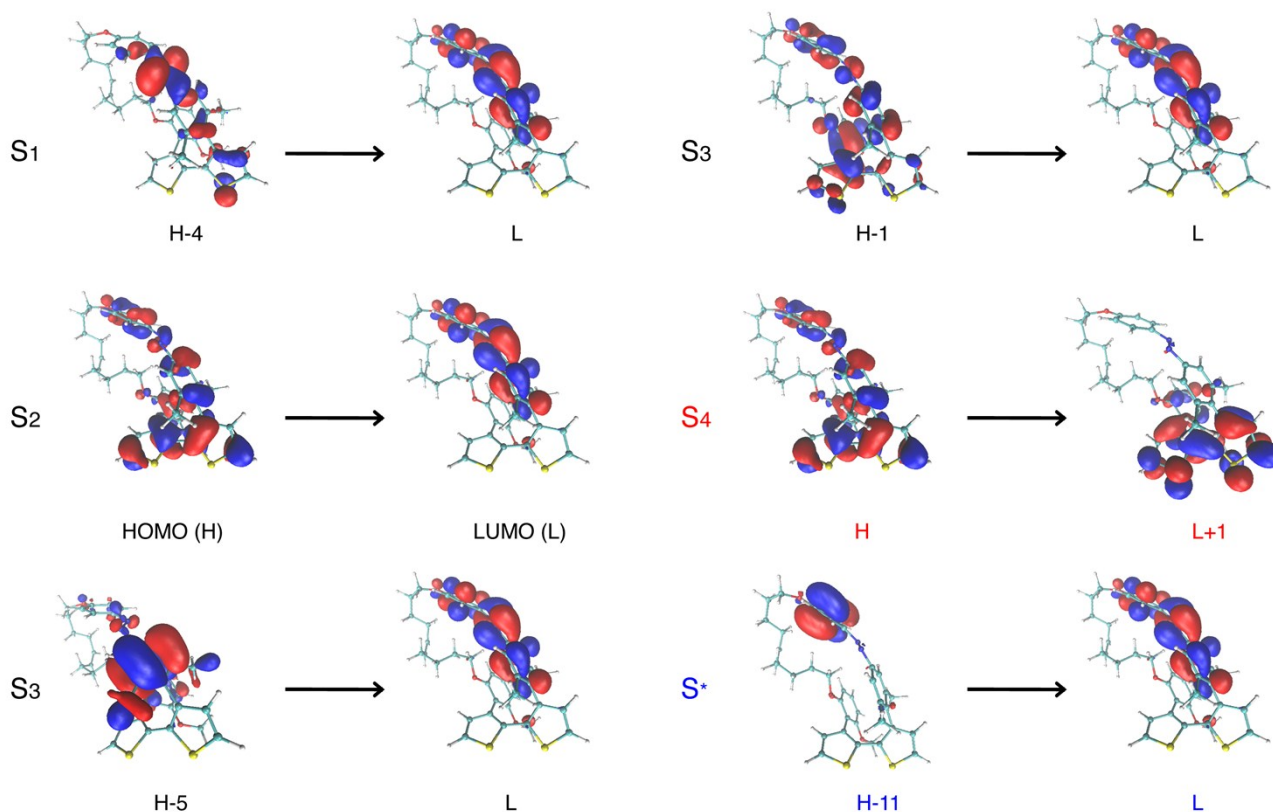
[16] ‘Electronic Energy Gaps for π -Conjugated Oligomers and Polymers Calculated with Density Functional Theory’ H. Sun, J. Autschbach, *J. Chem. Theory Comput.*, 2014, **10**, 1035–1047

[17] ‘Spectrum simulation and decomposition with nuclear ensemble: formal derivation and application to benzene, furan and 2-phenylfuran’ R. Crespo-Otero and M. Barbatti, *Theor. Chem. Acc.*, 2012, **131**, 1237

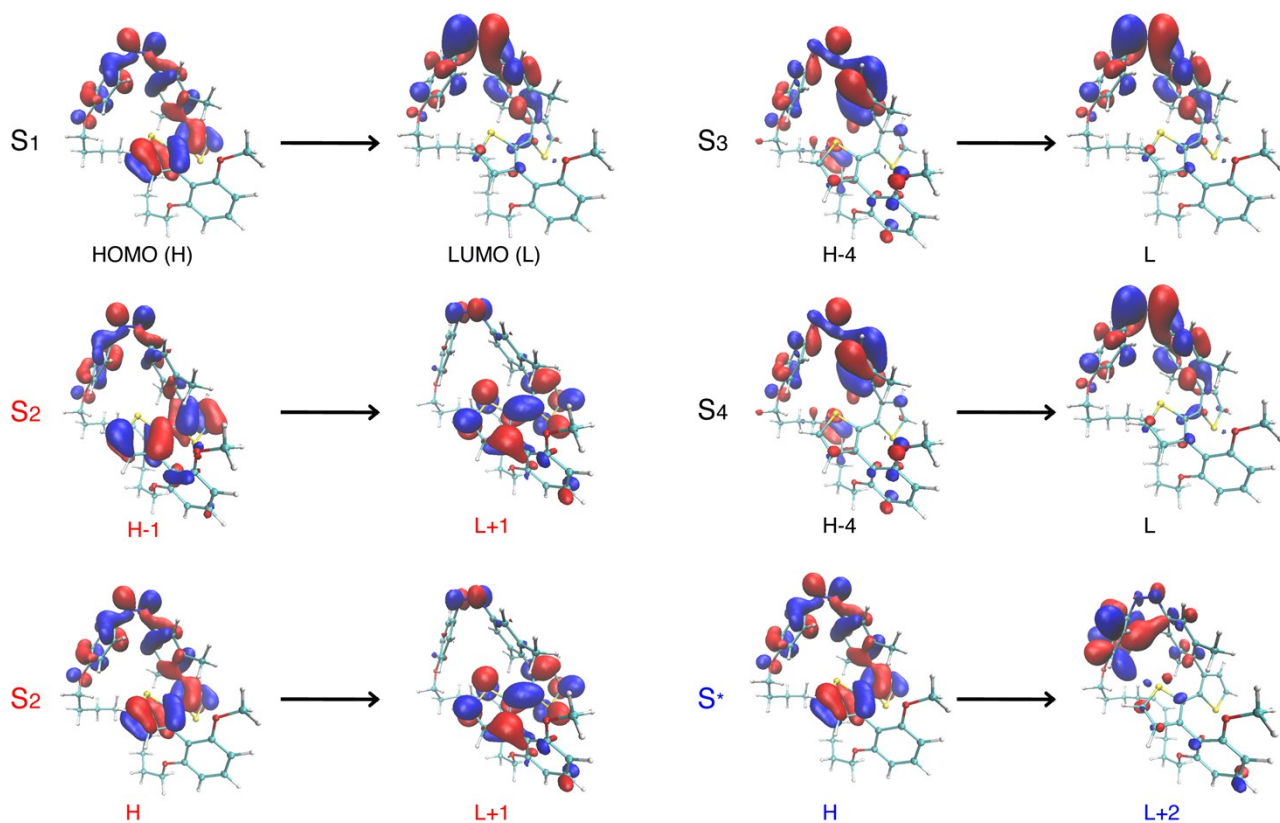
5.2 Excited states assignments: MOs picture

As discussed in the manuscript, the conformational changes of the bithiophene unit, as induced by the *trans-cis* azobenzene isomerization, can be traced by monitoring the energy shift of the electronic

transition that shows a large molecular orbital contribution localized on the thiophene segments. In the tables below we report the assignments, based on a molecular orbitals (MOs) of each electronic transition discussed in the manuscript. Only the relevant MOs contributions for each electronic transition are shown. The red entry represents the excitation mainly localized on the thiophene units, while the blue represents the transition mainly localized on the phenyls of the azobenzene moiety. For **1.trans** the electronic transition localized on the thiophene units is the $S_0 \rightarrow S_4$ (4.34 eV, 285 nm), while for **1.cis** is the $S_0 \rightarrow S_2$ (4.03 eV, 307 nm). Upon *trans-to-cis* azobenzene isomerization, the computed band shift is 22 nm, which is in close agreement with the observed bathochromic shift of 13 nm.

Electronic Transition - Molecular Orbitals **1.trans**

| | energy | oscillator strength | MO contributions |
|-----------------------|-----------------------|---------------------|--|
| $S_0 \rightarrow S_1$ | 2.6452 eV (468.71 nm) | $f = 0.0249$ | H-4 -> L |
| $S_0 \rightarrow S_2$ | 3.5753 eV (346.78 nm) | $f = 0.7630$ | H -> L H-1 -> L |
| $S_0 \rightarrow S_3$ | 4.0396 eV (306.92 nm) | $f = 0.0245$ | H-5 -> L H-1 -> L H-2 -> L |
| $S_0 \rightarrow S_4$ | 4.3410 eV (285.61 nm) | $f = 0.1579$ | H -> L+1 H-1 -> L+1 |
| $S_0 \rightarrow S^*$ | 5.5058 eV (225.19 nm) | $f = 0.1633$ | H-11 -> L |

Electronic Transition - Molecular Orbitals **1.cis**

| | <i>energy</i> | <i>oscillator strength</i> | <i>MO contributions</i> |
|-----------------------|-----------------------|----------------------------|--|
| $S_0 \rightarrow S_1$ | 2.6927 eV (460.44 nm) | $f = 0.0280$ | H -> L H-1 -> L |
| $S_0 \rightarrow S_2$ | 4.0375 eV (307.09 nm) | $f = 0.1398$ | H-1 -> L+1 H -> L+1 H -> L |
| $S_0 \rightarrow S_3$ | 4.2624 eV (290.88 nm) | $f = 0.1532$ | H-4 -> L H-1 -> L H-6 -> L H-7 -> L |
| $S_0 \rightarrow S_4$ | 4.5462 eV (272.72 nm) | $f = 0.1004$ | H-4 -> L H-5 -> L H-3 -> L |
| $S_0 \rightarrow S^*$ | 5.3706 eV (230.86 nm) | $f = 0.1413$ | H -> L+2 |