

Supporting Information

Sensitive Assays by Nucleophile-Induced Rearrangement of Photoactivated Diarylethenes

Sebastian Fredrich, Aurelio Bonasera, Virginia Valderrey, and Stefan Hecht*

Department of Chemistry & IRIS Adlershof, Humboldt-Universität zu Berlin,

Brook-Taylor-Str. 2, 12489 Berlin, Germany

sh@chemie.hu-berlin.de

Table of Contents:

1. General Methods	S2
1.1. Synthetic and analytical methods	S2
2. Synthesis	S3
2.1. Synthetic procedures	S3
2.2. ¹ H NMR spectra	S44
3. Photochemistry of Diarylethenes 1 - 18	S55
3.1. Determination of the photostationary state	S55
3.2. Thermal decays	S65
3.3. Switching cycles	S66
3.4. Determination of quantum yields and actinometry	S72
3.5. Determination of fluorescence quantum yields	S74
3.6. Fluorescence spectra	S76
4. UV/vis Absorption Spectroscopy of the Rearrangement Products and the Imines	S83
5. Kinetic Measurements and Analysis	S85
6. Computational Models	S98
References	S102

1. General Methods

1.1. Synthetic and analytical methods

Chemicals were purchased at *Sigma-Aldrich* or *ABCR* and used without further purification. Solvents were distilled and dried or degassed (if necessary) before use. For spectroscopy experiments, solvents of spectroscopic grade were used. For column chromatography, silica gel (0.035-0.070 mm, 60 Å) was used if not differently specified.

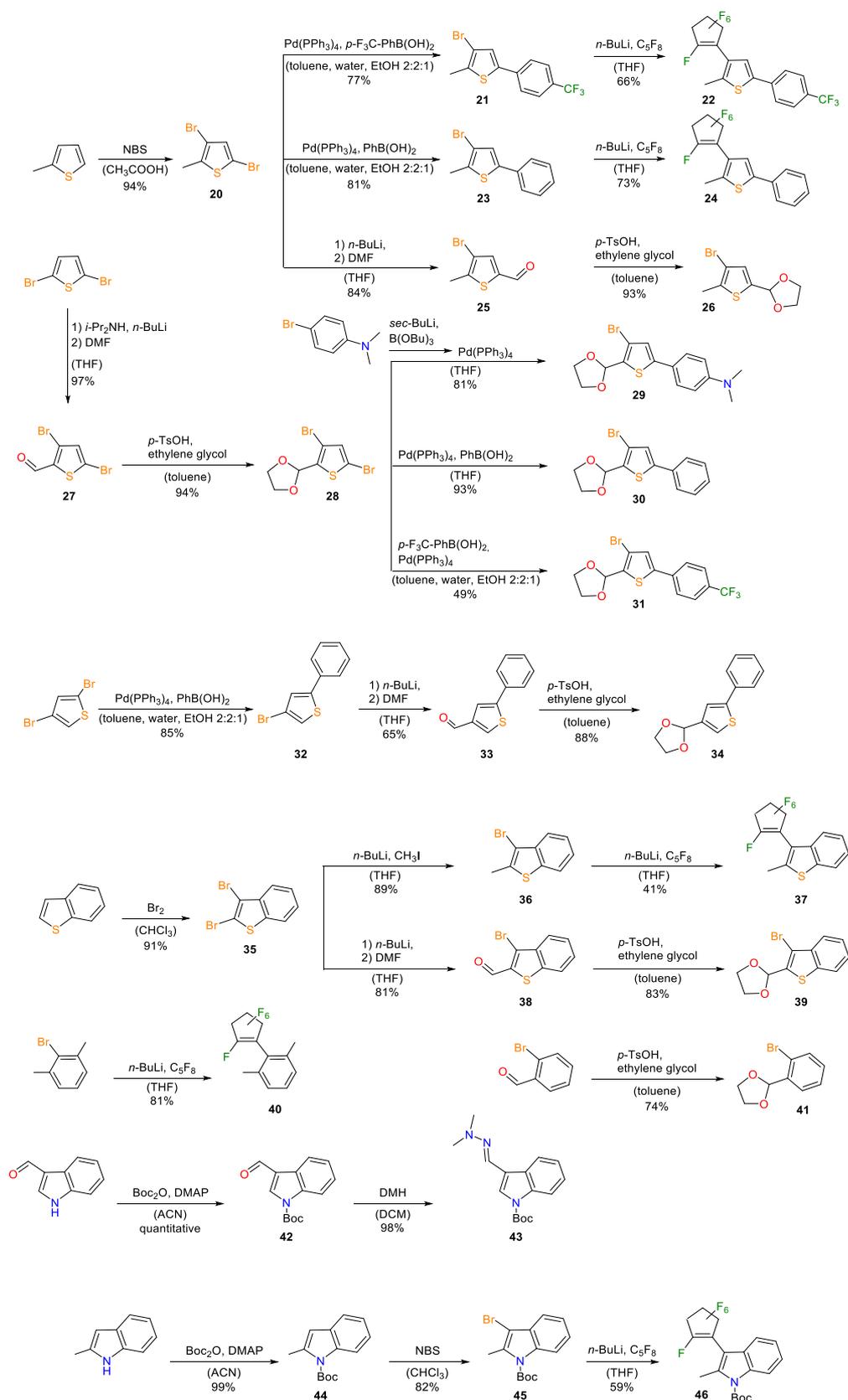
NMR spectra were recorded at a *Bruker AVANCE 300* (^1H : 300 MHz, ^{13}C : 75 MHz, ^{19}F : 282 MHz) or at a 500 MHz *Bruker AVANCE 500* (^1H : 500 MHz, ^{13}C : 125 MHz, ^{19}F : 470 MHz). Samples were dissolved in deuterated solvent (CDCl_3), using residual proton signals as standard (^1H : $\delta = 7.26$ ppm; ^{13}C : $\delta = 77.16$ ppm). Chemical shifts are denoted in δ (ppm), coupling constants J in Hz. The splitting patterns are designated as: s (singlet); d (doublet); t (triplet); q (quartet); quin (quintet); m (multiplet). Ultra-high performance liquid chromatography electro-spray ionization mass spectrometry (UPLC-ESI-MS) was performed on a *Waters Acquity UPLC* (gradient mixtures of acetonitrile/water) with a *Waters LCT Premier XE* mass detector. Additionally, a *Waters Alliance System* with *Waters Separations Module 2695*, a *Waters Diode Array Detector 996* and a *Waters Mass Detector ZQ 2000* were used. For the diarylethene samples, chromatographic separations were performed with a gradient acetonitrile in water with 0.1% formic acid. To determine the compounds' purity, the integration of UV/vis-trace from 210 nm to 800 nm was used.

UV/vis spectra were recorded using quartz cuvettes on a *Varian Cary 50* or a *Varian Cary 60* spectrophotometer equipped with a Peltier thermostated cell holder at 25 ± 0.1 °C.

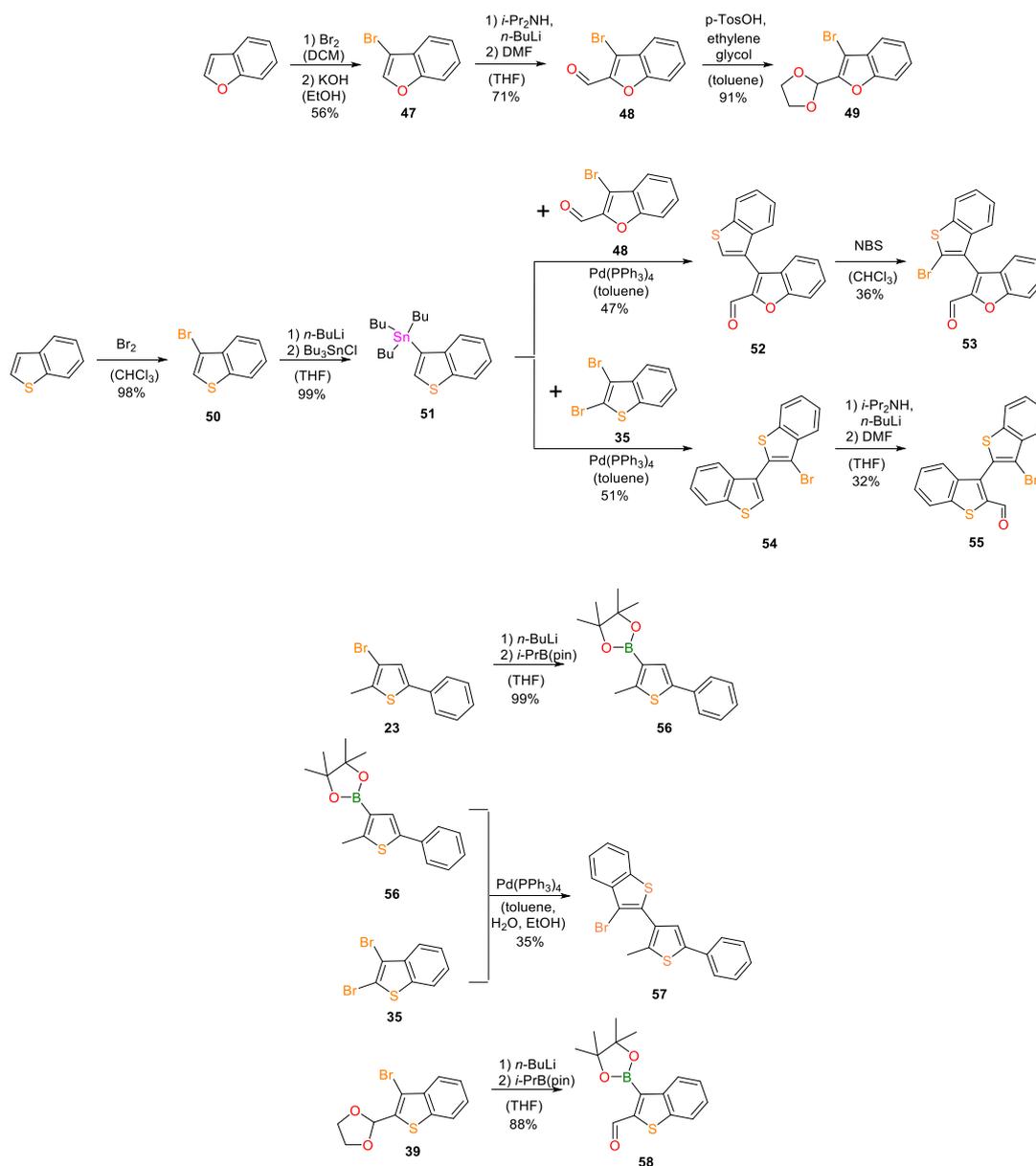
For quantitative irradiation, *ThorLabs* LEDs (various wavelengths) were used, coupled with an optical fiber in order to direct light to the sample solution. For quantum yield (ϕ) determination experiments, an *Oriel 500 W Hg(Xe)*-short-arc lamp model *LSB740* in an *Oriel* arc lamp box *LSH302* was used. It was equipped with an *Oriel* 300 mm grating monochromator model *MSH-300*, a shutter and a light guide by *Oriel*. Light intensities were usually between 5×10^9 and 1×10^{11} photons $\text{s}^{-1}\text{cm}^{-1}$.

2. Synthesis

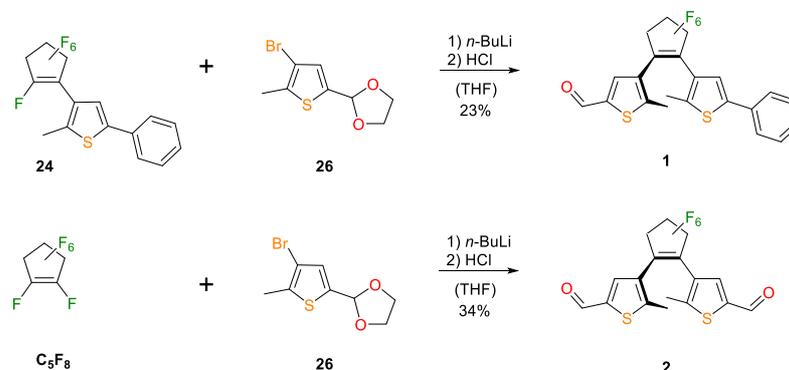
2.1. Synthetic procedures



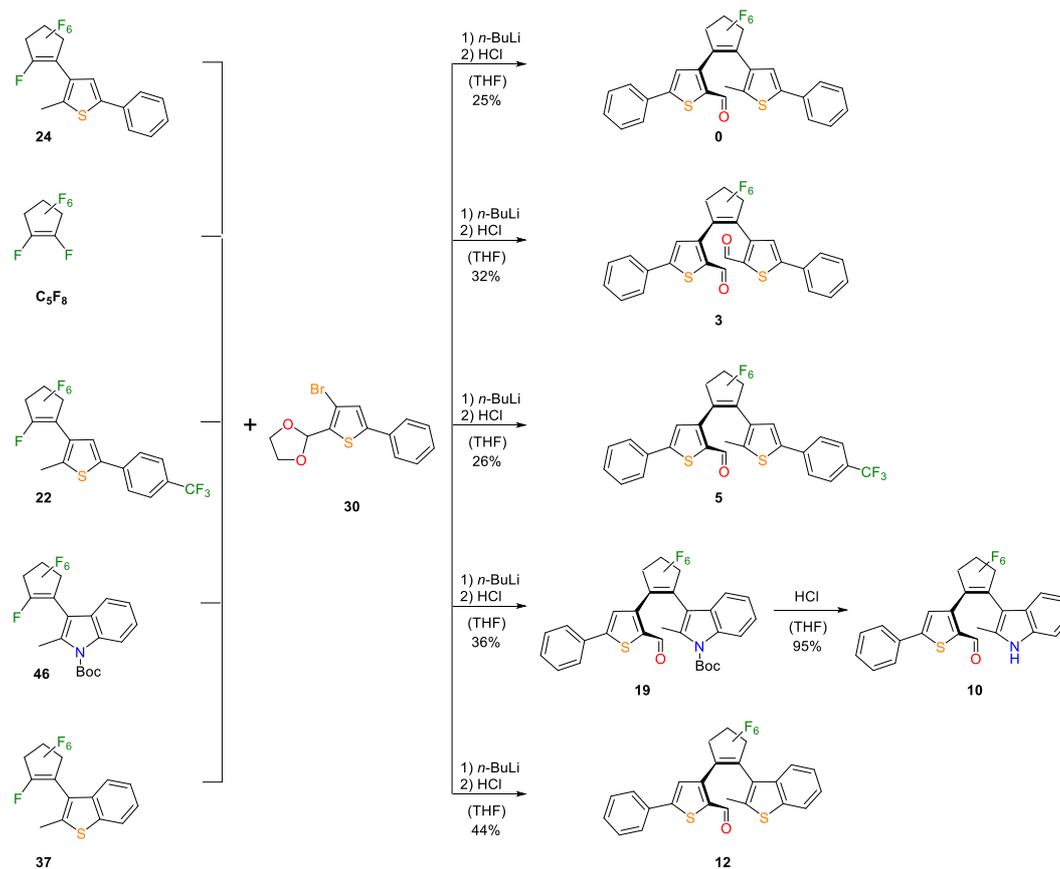
Scheme S1: General route for the synthesis of the precursor molecules.



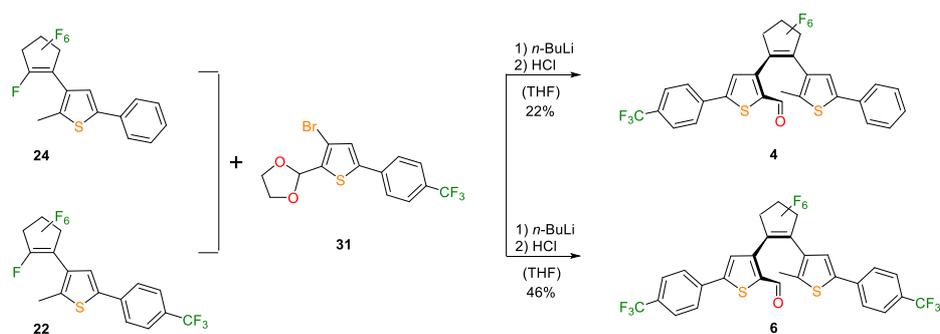
Scheme S2: General route for the synthesis of the precursor molecules.



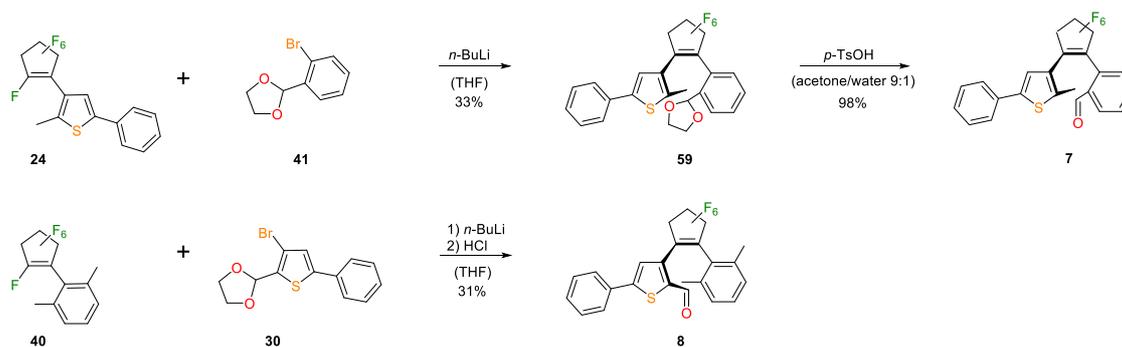
Scheme S3: General route for the synthesis of the diarylethenes switches **1** and **2** with the aldehyde function at the periphery of the molecular scaffold.



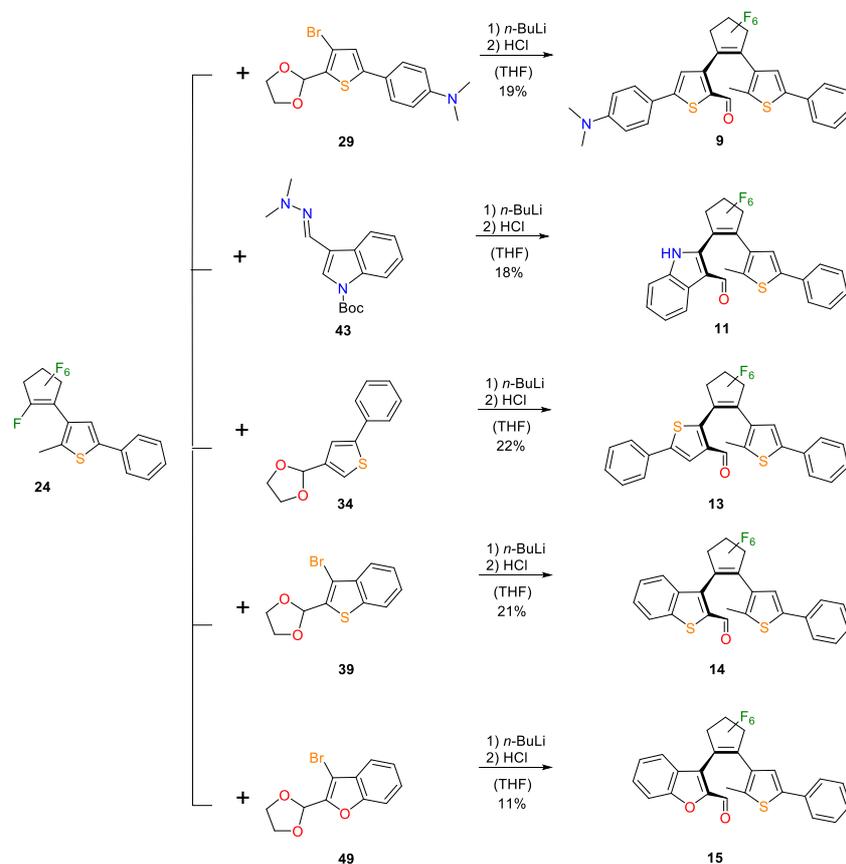
Scheme S4: General route for the synthesis of the diarylethene switches from the common aldehyde precursor **30**.



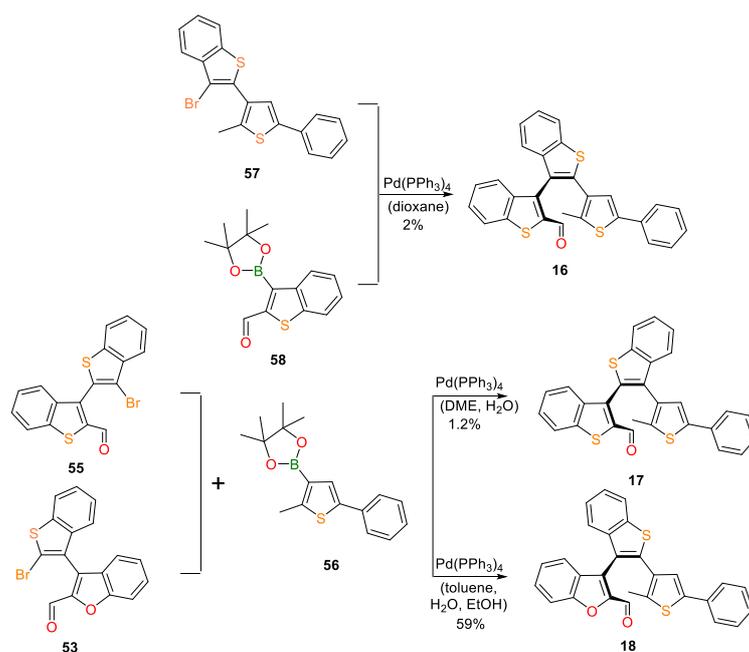
Scheme S5: General route for the synthesis of the diarylethene switches from the common aldehyde precursor **31**.



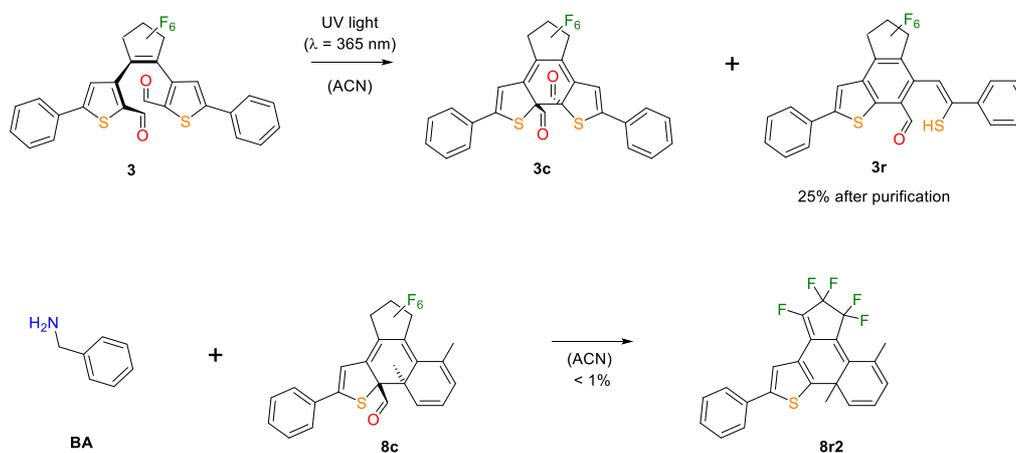
Scheme S6: General route for the synthesis of the diarylethene switches **7** and **8** with phenyl fragments in the molecule core.



Scheme S7: General route for the synthesis of diarylethene switches with different designs compared with the other previously mentioned molecules.

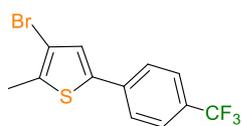


Scheme S8: General route for the synthesis of diarylethene switches with benzothiophene bridges.



Scheme S9: Synthetic route for the isolation of the rearrangement products for the diarylethenes **3** and **8**.

The synthesis of compounds **0**, **20**, **23**, **24**, **27**, **28** and **30** was already reported from us in a previous communication.¹

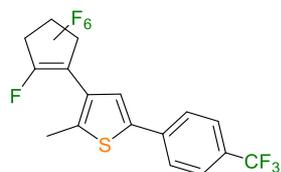
3-Bromo-2-methyl-5-(4-(trifluoromethyl)phenyl)thiophene (21)²

20 (1.03 g, 4.0 mmol, 1.0 equiv.) was dissolved in a mixture of 6 ml toluene and 6 ml of 2 M Na₂CO₃ aqueous solution. The mixture was degassed bubbling argon through it for 10 min. *p*-Trifluoromethylphenyl boronic acid (0.77 g, 4.0 mmol, 1.0 equiv.) was dissolved in 3 ml EtOH and added to the first mixture. The flask was degassed with argon for further 5 min. Pd(PPh₃)₄ (40 mg, 0.26 mmol, 0.009 equiv.) was added and the mixture was heated to reflux for 17 h. After cooling to room temperature, the organic phase was extracted twice with ethyl acetate and was washed with brine, dried over MgSO₄ and evaporated. The product was purified by column chromatography (silica, petroleum ether 100%) to yield compound **21** (0.98 g, 3.06 mmol, 77%) as white solid.

¹H NMR (300 MHz, CDCl₃): δ (ppm) = 7.60 (s, 4H), 7.19 (s, 1H), 2.43 (s, 3H).

¹³C NMR (75 MHz, CDCl₃): δ (ppm) = 139.4, 136.9, 135.5, 127.1, 126.2, 126.1, 126.0, 125.5, 110.5, 15.1.

¹⁹F NMR (282 MHz, CDCl₃): δ (ppm) = -62.0 (s, 3F).

2-Methyl-3-(perfluorocyclopent-1-en-1-yl)-5-(4-(trifluoromethyl)phenyl)thiophene (22)²

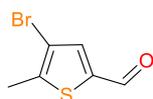
21 (0.51 g, 1.6 mmol, 1.0 equiv.) was dissolved in 10 ml dry THF and cooled to -78°C before *n*-butyllithium (900 μl, 2.0 mmol, 2.3 M in hexane, 1.2 equiv.) was added. After 30 min of stirring, octafluorocyclopentene (C₅F₈, 250 μl, 1.8 mmol, 1.1 equiv.) was added at once. The mixture was further stirred for 1 h at -78°C, allowed to warm to room temperature and stirred for another 1 h. It was hydrolysed by addition of 5 ml 1 M HCl, the organic phase extracted with ethyl acetate and washed with brine. The crude product was purified by column chromatography (silica, petroleum ether 100%) to yield a white solid (0.46 g, 1.05 mmol, 66%).

¹H NMR (300 MHz, CDCl₃): δ (ppm) = 7.65 (br, 4H), 7.32 (s, 1H), 2.50 (d, 3H, $^3J(\text{H},\text{F}) = 3.2$ Hz).

¹³C NMR (75 MHz, CDCl₃): δ (ppm) = 140.9, 136.6, 129.8, 126.7, 126.3, 126.2, 126.1, 126.0, 125.3, 123.8, 122.3, 14.9.

¹⁹F NMR (282 MHz, CDCl₃): δ (ppm) = -62.0 (s, 3F), -107.8 (s, 2F), -117.5 (s, 2F), -126.2 (s, 1F), -129.3 (s, 2F).

4-Bromo-5-methylthiophene-2-carbaldehyde (**25**)³

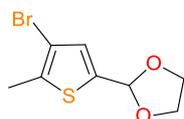


20 (1.99 g, 7.6 mmol, 1.0 equiv.) was dissolved in 5 ml dry degassed THF under argon. The solution was cooled to -78°C before *n*-butyllithium (3.8 ml, 8.3 mmol, 2.3 M in hexane, 1.1 equiv.) was added at -78°C; then, the mixture was stirred for 20 min before dry DMF (0.64 ml, 8.3 mmol, 1.1 equiv.) was added. The mixture was allowed to warm to 0°C, and afterwards 5 ml 1 M HCl were added. It was extracted with MTBE, the organic phase was washed with water and dried over MgSO₄. After column chromatography (silica, petroleum ether/ethyl acetate 10:1) a yellowish solid was isolated (1.29 g, 6.93 mmol, 84%).

¹H NMR (300 MHz, CDCl₃): δ (ppm) = 9.77 (s, 1H), 7.58 (s, 1H), 2.48 (s, 3H).

¹³C NMR (75 MHz, CDCl₃): δ (ppm) = 181.7, 146.0, 140.2, 138.9, 111.4, 16.1.

2-(4-Bromo-5-methylthiophen-2-yl)-1,3-dioxolane (**26**)⁴

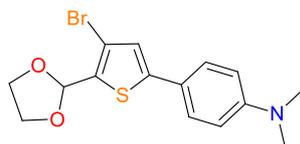


25 (2.00 g, 9.9 mmol, 1.0 equiv.), *p*-toluene sulfonic acid monohydrate (95 mg, 0.49 mmol, 0.05 equiv.) and ethylene glycol (8 ml, 143 mmol, 14.3 equiv.) were added to 50 ml toluene. The mixture was refluxed using a Dean-Stark-Trap for 2 h. Water was added to the cooled solution, then the organic phase was extracted with ethyl acetate and washed with water. The collected organic phases were dried over MgSO₄ and evaporated under reduced pressure to give the compound as a yellow oil (2.31 g, 9.3 mmol, 93%).

¹H NMR (300 MHz, CDCl₃): δ (ppm) = 6.96 (s, 1H), 6.00 (s, 1H), 4.11-3.97 (m, 4H), 2.38 (s, 3H).

¹³C NMR (75 MHz, CDCl₃): δ (ppm) = 135.5, 128.9, 128.4, 108.6, 99.8, 65.3, 15.0.

4-(4-Bromo-5-(1,3-dioxolan-2-yl)thiophen-2-yl)-*N,N*-dimethylaniline (29)

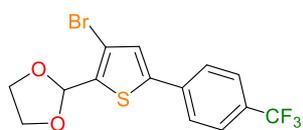


p-Bromo-*N,N*-dimethylaniline (1.54 g, 7.64 mmol, 1.2 equiv.) was dissolved in 10 ml of dry degassed THF under argon. The solution was cooled to -78°C before *sec*-butyllithium (3.6 ml, 8.3 mmol, 1.3 M in hexane, 1.3 equiv.) was added. The solution was stirred for 1 h at -78°C. Afterwards, tributyl borate (2.58 g, 9.56 mmol, 1.5 equiv.) is added and the mixture stirred for another 1 h at room temperature. **28** (2.00 g, 6.37 mmol, 1.0 equiv.) was dissolved in a mixture of 10 ml THF and 5 ml of 2 M Na₂CO₃ solution. This mixture was degassed by bubbling argon through the solution for 10 min. To this solution Pd(PPh₃)₄ (0.37 g, 319 μmol, 0.05 equiv.) was added. The first solution was then given to the second without isolation and purification. The mixture was heated to reflux for 18 h. After cooling down the solution, it was extracted with MTBE, the organic phase was washed with water and brine, and dried over MgSO₄. After column chromatography (silica, petroleum ether/ethyl acetate 10:1) a yellowish solid was isolated (2.19 g, 6.19 mmol, 81%).

¹H NMR (300 MHz, CDCl₃): δ (ppm) = 7.44 (d, 2H, ⁴J(H,H) = 9.0 Hz), 7.00 (s, 1H), 6.72 (d, 2H, ³J(H,H) = 8.7 Hz), 6.14 (s, 1H), 4.23-4.03 (m, 4H), 3.01 (s, 6H).

HRMS (ESI⁺): *m/z* = 354.0125 (calcd: 354.0158 for [C₁₅H₁₇BrNO₂S]⁺).

UPLC: *t_R* = 4.20 min (100% peak area).

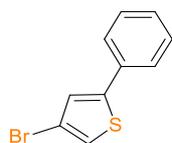
2-(3-Bromo-5-(4-(trifluoromethyl)phenyl)thiophen-2-yl)-1,3-dioxolane (31)

28 (1.51 g, 4.8 mmol, 1.1 equiv.) was dissolved in 8 ml toluene and 8 ml of 2 M Na₂CO₃ aqueous solution and degassed by bubbling argon through it for 10 min. *p*-Trifluoromethylphenyl boronic acid (0.83 g, 4.4 mmol, 1.0 equiv.) was dissolved in 4 ml EtOH and added to the first solution. It was further degassed for 5 min, before Pd(PPh₃)₄ (0.17 g, 0.15 mmol, 0.03 equiv.) was added and the mixture was refluxed for 16 h. After cooling to room temperature, it was extracted with ethyl acetate and washed with brine. The solvent was dried over MgSO₄ and evaporated under reduced pressure. Column chromatography (silica, petroleum ether/ethyl acetate 10:1) gave the product as viscous colorless oil (0.82 g, 2.1 mmol, 49%).

¹H NMR (500 MHz, CDCl₃): δ (ppm) = 7.64 (s, 4H), 7.23 (s, 1H), 6.14 (s, 1H), 4.19 (m, 2H), 4.07 (m, 2H).

¹³C NMR (126 MHz, CDCl₃): δ (ppm) = 143.1, 136.8, 127.5, 126.2, 126.1, 126.0, 125.9, 111.0, 99.6, 65.7.

¹⁹F NMR (471 MHz, CDCl₃): δ (ppm) = -62.9 (s, 3F).

4-Bromo-2-phenylthiophene (32)⁵

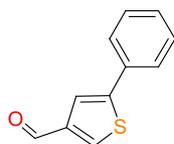
2,4-dibromo-thiophene (1.1 ml, 9.9 mmol, 1.0 equiv.) was dissolved in a mixture of 8 ml toluene and 8 ml of 2 M Na₂CO₃ aqueous solution, and degassed by bubbling argon through it for 10 min. Phenyl boronic acid (1.20 g, 9.9 mmol, 1.0 equiv.) was dissolved in 4 ml EtOH and added to the first solution. It was further degassed for 5 min. Then, Pd(PPh₃)₄ (0.11 g, 0.9 mmol, 0.01 equiv.) was added and the mixture was refluxed for 17 h. After cooling to room temperature, it was extracted with ethyl acetate and the organic phase was washed with brine. The organic phase

was dried over MgSO_4 and further purified by column chromatography (silica, petroleum ether 100%) to give the product (2.03 g, 8.48 mmol, 85%) as white solid.

$^1\text{H NMR}$ (300 MHz, CDCl_3): δ (ppm) = 7.56 (m, 2H), 7.43-7.29 (m, 3H), 7.21 (d, 1H, $^4J(\text{H,H}) = 1.5$ Hz), 7.18 (d, 1H, $^4J(\text{H,H}) = 1.5$ Hz).

$^{13}\text{C NMR}$ (75 MHz, CDCl_3): δ (ppm) = 129.2, 128.4, 125.9, 125.8, 122.1, 110.6.

5-phenylthiophene-3-carbaldehyde (33)

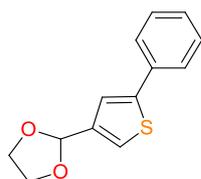


32 (1.19 g, 5.0 mmol, 1.0 equiv.) was dissolved in 5 ml dry, degassed THF under argon. The solution was cooled to -78°C , then *n*-butyllithium (2.4 ml, 5.5 mmol, 2.3 M in hexane, 1.1 equiv.) was added. The mixture was stirred for 30 min at low temperature before dry DMF (420 μl , 5.5 mmol, 1.1 equiv.) was added. It was allowed to warm to 0°C and 5 ml of 1 M HCl were added. It was extracted with ethyl acetate, the organic phase was washed with water and dried over MgSO_4 . Column chromatography (silica, petroleum ether/ethyl acetate 12:1) gave the product (0.61 g, 0.32 mmol, 65%) as a slightly yellowish solid.

$^1\text{H NMR}$ (300 MHz, CDCl_3): δ (ppm) = 9.89 (s, 1H), 8.04 (d, 1H, $^4J(\text{H,H}) = 1.3$ Hz), 7.71 (d, 1H, $^4J(\text{H,H}) = 1.2$ Hz), 7.61 (dt, 2H, $^3J(\text{H,H}) = 6.9$ Hz, $^4J(\text{H,H}) = 1.4$ Hz), 7.50-7.31 (m, 3H).

$^{13}\text{C NMR}$ (75 MHz, CDCl_3): δ (ppm) = 185.26, 146.6, 143.9, 136.2, 133.2, 129.2, 128.6, 126.2, 120.5.

2-(5-phenylthiophen-3-yl)-1,3-dioxolane (34)



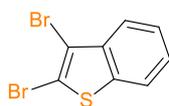
33 (0.61 g, 3.2 mmol, 1.0 equiv.), *p*-toluene sulfonic acid monohydrate (30 mg, 0.16 mmol, 0.05 equiv.), and ethylene glycol (1.8 ml, 32 mmol, 10 equiv.) were added to 50 ml toluene. The

mixture was refluxed using a Dean-Stark-Trap for 2 h. To the cooled solution, 5 ml 1 M NaOH aqueous solution were added, then the organic phase was extracted with ethyl acetate and washed with water. The collected organic phases were dried over MgSO₄ and evaporated under reduced pressure to give the compound as a yellowish oil (0.65 g, 2.8 mmol, 88%).

¹H NMR (300 MHz, CDCl₃): δ (ppm) = 7.58 (m, 2H), 7.35 (m, 4H), 7.26 (tt, 1H, ³J (H,H) = 7.4 Hz, ⁴J (H,H) = 6.9 Hz), 5.86 (s, 1H), 4.00 (m, 4H).

¹³C NMR (75 MHz, CDCl₃): δ (ppm) = 145.5, 140.9, 134.3, 129.0, 127.8, 126.0, 123.0, 121.6, 100.6, 65.2.

2,3-Dibromobenzo[*b*]thiophene (35)⁶

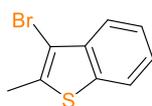


To a stirred solution of 2,3-benzo[*b*]thiophene (1.01 g, 7.5 mmol, 1.0 equiv.) in 20 ml CHCl₃, bromine (0.8 ml, 15 mmol, 2.0 equiv.) in 20 ml CHCl₃ was added dropwise at room temperature over 1 h. After stirring for 18 h in the dark, solid NaHCO₃ was added to neutralize the hydrobromic acid until gas evolution ceased. The organic phase was washed with water and 10% aqueous Na₂S₂O₃ solution, extracted with CHCl₃, and dried over MgSO₄. After evaporation of the solvent, crystallization from methanol gave 2,3-dibromobenzo[*b*]thiophene (2.03 g, 7.0 mmol, 91%) as a white solid.

¹H NMR (300 MHz, CDCl₃): δ (ppm) = 7.73 (m, 2H), 7.40 (m, 2H).

¹³C NMR (75 MHz, CDCl₃): δ (ppm) = 139.0, 137.6, 125.8, 125.7, 123.5, 122.0, 114.4, 111.8.

3-Bromo-2-methylbenzo[*b*]thiophene (36)



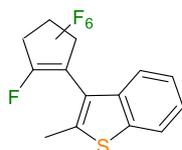
35 (2.04 g, 7.0 mmol, 1.0 equiv.) was dissolved in 10 ml dry degassed THF under argon. The solution was cooled to -78°C before *n*-butyllithium (3.3 ml, 7.7 mmol, 2.3 M in hexane, 1.1 equiv.) was added, and the mixture was stirred for 30 min before iodomethane (0.5 ml, 7.9 mmol,

1.1 equiv.) was added. The mixture was allowed to warm to room temperature, washed with water, extracted with ethyl acetate and dried over MgSO_4 . A short column chromatography (silica, petroleum ether 100%) gave the product as white solid (1.41 g, 6.23 mmol, 89%).

$^1\text{H NMR}$ (300 MHz, CDCl_3): δ (ppm) = 7.73 (m, 2H), 7.38 (m, 2H), 2.57 (s, 3H).

$^{13}\text{C NMR}$ (75 MHz, CDCl_3): δ (ppm) = 138.6, 137.3, 135.3, 125.0, 124.9, 122.7, 122.3, 106.7, 15.6.

2-Methyl-3-(perfluorocyclopent-1-en-1-yl)benzo[b]thiophene (37)⁷



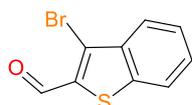
36 (1.25 g, 5.6 mmol, 1.0 equiv.) was dissolved in 15 ml dry THF and cooled to -78°C . To this solution, *n*-butyllithium (2.8 μl , 6.4 mmol, 2.3 M in hexane, 1.15 equiv.) was added. The mixture was stirred for 30 min before it was added to a cooled stirred solution of C_5F_8 (0.940 ml, 7.0 mmol, 1.25 equiv.) in 20 ml dry THF. The mixture was further stirred for 1 h at -78°C , allowed to warm to room temperature and stirred for another 1 h. It was hydrolysed by addition of 5 ml 1 M HCl and water, extracted with ethyl acetate and washed with brine. The organic phase was dried over MgSO_4 . Purification by column chromatography (silica, petroleum ether 100%) gave the product as white crystals (0.78 g, 2.8 mmol, 41%).

$^1\text{H NMR}$ (300 MHz, CDCl_3): δ (ppm) = 7.80 (m, 1H), 7.48 (m, 1H), 7.38 (m, 2H), 2.53 (s, 3H).

$^{13}\text{C NMR}$ (75 MHz, CDCl_3): δ (ppm) = 144.3, 138.4, 125.3, 124.9, 122.3, 121.7, 114.5, 14.8.

$^{19}\text{F NMR}$ (282 MHz, CDCl_3): δ (ppm) = -107.10 (d, 2F, $^3J(\text{F},\text{F}) = 10$ Hz), -118.2 (m, 2F), -124.5 (m, 1F), -129.7 (quin, 2F, $^3J(\text{F},\text{F}) = 3$ Hz).

3-Bromobenzo[b]thiophene-2-carbaldehyde (38)⁸



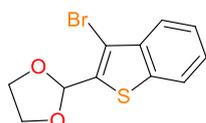
35 (2.03 g, 7.0 mmol, 1.0 equiv.) was dissolved in 5 ml dry degassed THF under argon. The solution was cooled to -78°C before *n*-butyllithium (3.3 ml, 7.7 mmol, 1.1 equiv.) was added. The

mixture was stirred at -78°C for 20 min before dry DMF (0.6 ml, 7.7 mmol, 1.1 equiv.) was added. The mixture was allowed to warm to 0°C , then 5 ml 1 M HCl were added. It was extracted with MTBE, the organic phase was washed with water and dried over MgSO_4 . The residue was recrystallized from methanol to obtain the product (1.36 g, 5.5 mmol, 81%) as a slightly yellowish white solid.

$^1\text{H NMR}$ (300 MHz, CDCl_3): δ (ppm) = 10.28 (s, 1H), 8.01 (m, 1H), 7.86 (m, 1H), 7.54 (m, 2H).

$^{13}\text{C NMR}$ (75 MHz, CDCl_3): δ (ppm) = 184.9, 140.6, 138.2, 136.6, 129.4, 126.1, 125.1, 123.5, 119.0.

2-(3-Bromobenzo[b]thiophen-2-yl)-1,3-dioxolane (39)



38 (1.82 g, 7.5 mmol, 1.0 equiv.), *p*-toluene sulfonic acid monohydrate (70 mg, 0.36 mmol, 0.05 equiv.) and ethylene glycol (6 ml, 107 mmol, 14.3 equiv.) were added to 50 ml toluene. The mixture was refluxed using a Dean-Stark-Trap for 2 h. Water was added to the cooled solution, then it was extracted with ethyl acetate and the organic phase was washed with water. The collected organic phases were dried over MgSO_4 and evaporated under reduced pressure. Filtration through a plug of silica gave the compound as a yellow oil (1.77 g, 6.2 mmol, 83%).

$^1\text{H NMR}$ (300 MHz, CDCl_3): δ (ppm) = 7.82 (m, 2H), 7.43 (m, 2H), 6.35 (s, 1H), 4.24-4.06 (m, 4H).

$^{13}\text{C NMR}$ (75 MHz, CDCl_3): δ (ppm) = 138.2, 137.8, 137.1, 129.2, 128.4, 126.1, 125.4, 125.2, 123.3, 122.8, 107.9, 100.0, 65.8.

1,3-Dimethyl-2-(perfluorocyclopent-1-en-1-yl)benzene (40)



2-Bromoxylene (1.05 g, 8.0 mmol, 1.0 equiv.) was dissolved in 15 ml dry THF and cooled to -78°C . Then, *n*-butyllithium (2.0 ml, 4.6 mmol, 2.3 M in hexane, 2.3 equiv.) was added slowly, and

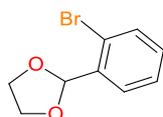
the mixture was allowed to warm to 0°C for 5 min before it was cooled again to -78°C and stirred for 30 min. The mixture was slowly transferred to a stirred solution of C₅F₈ (1.0 ml, 8.0 mmol, 1.0 equiv.) kept at the same temperature in 5 ml dry THF. The new mixture was further stirred for 1 h at -78°C, allowed to warm to room temperature and stirred overnight. It was hydrolysed with water, extracted with ethyl acetate and purified by column chromatography (silica, petroleum ether 100%) to give a colorless volatile liquid (1.92 g, 0.64 mmol, 81%).

¹H NMR (300 MHz, CDCl₃): δ (ppm) = 7.29 (dd, 1H, ³J(H,H) = 7.2 Hz, ³J(H,H) = 8.5 Hz), 7.14 (d, 2H, ³J(H,H) = 7.8 Hz), 2.23 (s, 6H).

¹³C NMR (75 MHz, CDCl₃): δ (ppm) = 137.7, 130.5, 128.1, 121.9, 20.0.

¹⁹F NMR (282 MHz, CDCl₃): δ (ppm) = -108.1 (d, 2F, ³J(F,F) = 12 Hz), -118.7 (d, 2F, ³J(F,F) = 14 Hz), 127.4 (m, 1F), -129.9 (d, 2F, ³J(F,F) = 3 Hz).

2-(2-Bromophenyl)-1,3-dioxolane (41)⁹



2-Bromobenzaldehyde (0.47 g, 2.5 mmol, 1.0 equiv.), *p*-toluene sulfonic acid monohydrate (0.02 g, 0.13 mmol, 0.05 equiv.) and ethylene glycol (0.55 ml, 38.1 mmol, 15.0 equiv.) were dissolved in 25 ml of toluene. The mixture was refluxed using a Dean-Stark trap for 2 h. Water was added to the cooled solution, and the organic phase was washed with water and Na₂CO₃ aq. solution. The organic phase was dried over MgSO₄ and concentrated in vacuum to obtain a colorless oil that was used in the next reaction step without further purification (0.80 g, 3.49 mmol, 74%).

¹H NMR (300 MHz, CDCl₃): δ (ppm) = 7.58 (m, 2H), 7.34 (m, 1H), 7.22 (m, 1H), 6.11 (s, 1H), 4.12 (m, 4H).

¹³C NMR (75 MHz, CDCl₃): δ (ppm) = 179.9, 136.5, 132.8, 130.5, 127.7, 127.3, 122.8, 102.5, 65.4.

1-Boc-3-formylindole (42)¹⁰

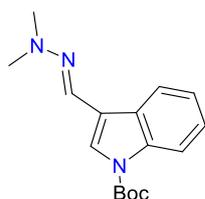


Indol-3-carbaldehyde (1.44 g, 10 mmol, 1.0 equiv.) and Boc₂O (2.40 g, 11 mmol, 1.1 equiv.) were added to 15 ml of CH₃CN, before DMAP (0.12 g, 1.0 mmol, 0.1 equiv.) was added. The resulting solution was stirred overnight, and then the solvent was removed under reduced pressure. The solid residue was dissolved in DCM and washed with saturated NaHCO₃ solution and water. Concentration *in vacuo* yielded the desired product as white solid (2.45 g, 10 mmol, quantitative).

¹H NMR (300 MHz, CDCl₃): δ (ppm) = 10.10 (s, 1H), 8.29 (m, 1H), 8.23 (s, 1H), 8.15 (m, 1H), 7.39 (m, 2H), 1.71 (s, 9H).

¹³C NMR (75 MHz, CDCl₃): δ (ppm) = 186.0, 148.9, 136.7, 136.1, 126.2, 124.7, 124.4, 122.2, 121.7, 115.3, 85.8, 28.2.

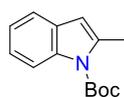
1-Boc- (E)-3-((2,2-dimethylhydrazono)methyl)-1H-indole-1-carboxylate (43)



42 (0.98, 4.0 mmol, 1.0 equiv.) was dissolved in 5 ml DCM, then dimethylhydrazone (0.45 g, 5.9 mmol, 1.5 equiv.) was slowly added. To this mixture, *p*-toluene sulfonic acid monohydrate (25 mg, 0.1 mmol, 0.04 equiv.) was added and the solution was stirred for 1 h at room temperature. The mixture was washed with water, extracted with ethyl acetate, and the organic phase was washed with brine and dried over MgSO₄. No further purification was necessary to yield the product as brownish oil (1.11 g, 4.0 mmol, 98%).

¹H NMR (300 MHz, CDCl₃): δ (ppm) = 8.36 (d, 1H, ³J(H,H) = 7.9 Hz), 8.17 (d, 1H, ³J(H,H) = 7.9 Hz), 7.66 (s, 1H), 7.50 (s, 1H), 7.40-7.25 (m, 2H), 2.99 (s, 6H), 1.69 (s, 9H).

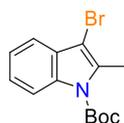
¹³C NMR (75 MHz, CDCl₃): δ (ppm) = 149.7, 136.1, 128.3, 128.0, 125.0, 124.4, 123.1, 122.7, 118.8, 114.9, 83.7, 43.0, 28.2.

1-Boc-2-methylindole (44)

2-Methylindole (1.65 g, 11.3 mmol, 1.0 equiv.) and Boc₂O (2.412 g, 11.0 mmol, 1.0 equiv.) were added to 15 ml of acetonitrile, before DMAP (0.13 g, 1.1 mmol, 1.1 equiv.) was added. The resulting solution was stirred overnight and then the solvent was removed under reduced pressure. The solid residue was dissolved in DCM and washed with sat. NaHCO₃-solution and water. It was dried over MgSO₄ and concentrated *in vacuo* to yield the desired product (2.62 g, 11.3 mmol, 99%) as white solid.

¹H NMR (300 MHz, CDCl₃): δ (ppm) = 8.12 (m, 1H, ³J(H,H) = 8.1 Hz), 7.44 (m, 1H), 7.29-7.16 (m, 2H), 6.33 (quin, 1H, ³J(H,H) = 1.1 Hz), 2.61 (d, 3H, 3J = 1.1 Hz), 1.70 (s, 9H).

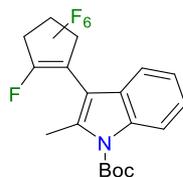
¹³C NMR (75 MHz, CDCl₃): δ (ppm) = 150.8, 137.9, 136.6, 129.5, 123.2, 122.7, 119.6, 115.6, 108.1, 83.7, 28.4, 17.3.

1-Boc-3-bromo-2-methylindole (45)

44 (2.33 g, 10 mmol) and NBS (1.99 g, 11 mmol) were dissolved in 15 ml CHCl₃ and stirred at room temperature for 16 h in the dark. The organic phase was washed with water, dried over MgSO₄ and evaporated under reduced pressure. Purification via column chromatography (silica, petroleum ether/ethyl acetate 20:1) gave the product (2.56 g, 8.2 mmol, 82%) as white solid.

¹H NMR (300 MHz, CDCl₃): δ (ppm) = 8.11 (m, 1H), 7.46 (m, 1H), 7.29 (m, 2H), 2.65 (s, 3H), 1.69 (s, 9H).

¹³C NMR (75 MHz, CDCl₃): δ (ppm) = 150.6, 135.3, 134.8, 128.7, 124.6, 123.3, 128.8, 115.6, 99.8, 84.5, 28.4, 15.4.

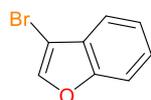
1-Boc-2-methyl-3-(perfluorocyclopent-1-en-1-yl)-1H-indole (46)

45 (1.09 g, 3.5 mmol, 1.0 equiv.) was dissolved in 10 ml dry THF under argon and cooled to -78°C, before n-butyllithium (1.8 ml, 4.2 mmol, 1.2 equiv., 2.3 M in hexane) was added. After 30 min of stirring at low temperature, C_5F_8 (0.50 ml, 3.7 mmol, 1.0 equiv.) was added in one shot. It was further stirred for 1 h at -78°C, allowed to warm to room temperature and stirred for another 1 h. The mixture was hydrolyzed with water and extracted with ethyl acetate that was evaporated subsequently. It was further purified by column chromatography (silica, petroleum ether/ethyl acetate 20:1) to give a white solid (0.88 g, 2.1 mmol, 59%).

1H NMR (300 MHz, $CDCl_3$): δ (ppm) = 8.15 (m, 1H), 7.43 (d, 1H, $^3J(H,H) = 7.7$ Hz), 7.37-7.24 (m, 2H), 2.55 (d, 3H, $^3J(H,H) = 1.5$ Hz), 1.71 (s, 9H).

^{13}C NMR (75 MHz, $CDCl_3$): δ (ppm) = 150.0, 139.5, 136.0, 127.2, 124.7, 123.7, 128.9, 115.7, 110.1, 85.3, 28.3, 15.8.

^{19}F NMR (282 MHz, $CDCl_3$): δ (ppm) = -107.0 (d, 2F, $^3J(F,F) = 12$ Hz), -118.0 (m, 2F), -125.6 (m, 1F), -129.7 (m, 2F).

3-Bromobenzofuran (47)¹¹

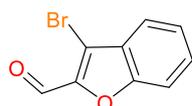
Benzofuran (2.211 g, 20.0 mmol, 1.0 equiv.) was dissolved in 20 ml of DCM and cooled to -10 °C in an ice-salt-mixture. Bromine (1.1 ml, 21.2 mmol, 1.1 equiv.), dissolved in 5 ml DCM, was slowly added at -10 °C. The reaction mixture was stirred for 1 h before 1 ml of 1 M aqueous NaOH-solution was added. It was washed with water, $Na_2S_2O_3$ -solution and extracted with DCM. After evaporation of the solvent, 20 ml ethanol were saturated with KOH and cooled to 0 °C. The intermediate was dissolved in 20 ml ethanol and was added dropwise to the first solution at 0 °C. After refluxing for 2 h, water was added and the EtOH was evaporated. The residue was

extracted with ethyl acetate and washed with brine. After drying and evaporation of the solvent, the wanted product was obtained as a yellowish oil (2.190 g, 11.2 mmol, 56%).

¹H-NMR (300 MHz, CDCl₃): δ (ppm) = 7.66 (s, 1H), 7.58-7.46 (m, 2H), 7.39-7.27 (m, 2H).

¹³C-NMR (75 MHz, CDCl₃): δ (ppm) = 142.7, 130.8, 125.6, 123.6, 119.9, 111.9, 98.1, 64.8.

3-Bromobenzofuran-2-carbaldehyde (**48**)¹²

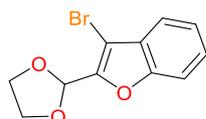


LDA was prepared in 5 ml dry, degassed THF from diisopropylamine (1.8 ml, 12.8 mmol, 1.3 equiv.) and *n*-butyllithium (4.8 ml, 11 mmol, 2.3 M in hexane, 1.1 equiv.) at -78 °C. **47** (2.007 g, 10.2 mmol, 10 equiv.) was slowly added. The mixture was stirred for 20 min at low temperature before dry DMF (850 μ l, 11 mmol, 1.1 equiv.) was added. It was allowed to warm to 0 °C and 5 ml of 1 M HCl were added. It was extracted with ethyl acetate, washed with water and the organic phase was dried over MgSO₄. Recrystallization from MeOH gave the product (1.602 g, 7.1 mmol, 71%) as a slightly yellowish solid.

¹H-NMR (300 MHz, CDCl₃): δ (ppm) = 10.00 (s, 1H), 7.71 (dt, 1H, ³*J*(H,H) = 7.9 Hz, ³*J*(H,H) = 1.0 Hz), 7.60 (d, 1H, ³*J*(H,H) = 1.1 Hz), 7.58 (dd, 1H, ³*J*(H,H) = 0.9 Hz, ³*J*(H,H) = 1.7 Hz), 7.42 (m, 1H).

¹³C-NMR (75 MHz, CDCl₃): δ (ppm) = 178.3, 155.0, 147.5, 130.7, 127.4, 124.9, 122.2, 113.1, 110.5.

3-Bromo-2-(1,3-dioxolan-2-yl)benzofuran (**49**)¹²



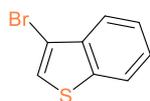
48 (270 mg, 1.2 mmol, 1.0 equiv.), *p*-toluene sulfonic acid monohydrate (29 mg, 0.06 mmol, 0.05 equiv.) and ethylene glycol (1 ml, 13 mmol, 10.8 equiv.) were added to 50 mL toluene. The mixture was refluxed using a Dean-Stark-Trap for 2 h. Water was added to the cooled solution, then the organic phase was extracted with ethyl acetate and washed with water. The collected

organic phases were dried over MgSO_4 and evaporated under reduced pressure. Filtration through a plug of silica gave the compound as a yellow oil (295 mg, 1.10 mmol, 91%).

$^1\text{H-NMR}$ (300 MHz, CDCl_3): δ (ppm) = 7.52 (m, 2H), 7.41-7.28 (m, 2H), 6.22 (s, 1H), 4.20 (m, 4H).

$^{13}\text{C-NMR}$ (75 MHz, CDCl_3): δ (ppm) = 153.9, 148.9, 127.7, 126.5, 123.7, 120.3, 112.1, 98.0, 96.7, 65.9.

3-Bromobenzo[b]thiophene (**50**)¹³

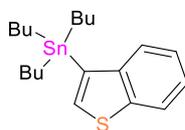


Benzo[b]thiophene (3.460 g, 26.0 mmol, 1.0 equiv.) was dissolved in 20 ml of chloroform. Bromine (1.35 ml, 26.0 mmol, 1.0 equiv.), dissolved in 20 ml chloroform was slowly added over 1 h at room temperature. The reaction mixture was stirred for 18 h before solid NaHCO_3 was added. The organic layer was washed with water, $\text{Na}_2\text{S}_2\text{O}_3$ -solution and extracted with chloroform. After drying over MgSO_4 , evaporation of the solvent, and recrystallization from MeOH, the wanted product was obtained as a colorless oil (5.451 g, 25.6 mmol, 98%).

$^1\text{H-NMR}$ (300 MHz, CDCl_3): δ (ppm) = 7.85 (m, 2H), 7.53-7.38 (m, 3H).

$^{13}\text{C-NMR}$ (75 MHz, CDCl_3): δ (ppm) = 138.7, 137.6, 125.4, 125.1, 123.6, 123.2, 122.8, 107.8.

Benzo[b]thiophen-3-yltributylstannane (**51**)¹⁴



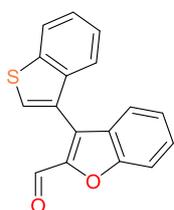
50 (3.012 g, 14.1 mmol, 1.0 equiv.) was dissolved in 5 ml dry degassed THF under argon. To this solution *n*-butyllithium (7 ml, 16.1 mmol, 2.3 M in hexane, 1.15 equiv.) was added at $-78\text{ }^\circ\text{C}$ and it was stirred for 30 min at low temperature. Now tributyl tin chloride (4.2 ml, 15.5 mmol, 1.1 eq.) was added. The mixture was further stirred at $-78\text{ }^\circ\text{C}$ for 1 h and then allowed to warm to room temperature and stirred for 2 h. Water was added and it was extracted with ethyl acetate and

washed with saturated NaCl-solution. The organic phases were dried over MgSO₄. Filtration through a plug of silica gave the product as brownish liquid (5.998 g, 14 mmol, 99%).

¹H-NMR (500 MHz, CDCl₃): δ (ppm) = 7.97-7.73 (m, 2H), 7.41-7.27 (m, 3H), 1.64-1.15 (m, 18H), 0.94-0.87 (m, 12H).

¹³C-NMR (126 MHz, CDCl₃): δ (ppm) = 132.2, 124.6, 124.3, 123.8, 123.4, 122.8, 122.0, 121.9, 29.4, 27.5, 13.8, 11.3, 10.9, 8.9.

3-(Benzo[b]thiophen-3-yl)benzofuran-2-carbaldehyde (52)

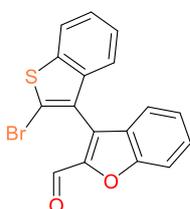


48 (680 mg, 3.1 mmol, 1.0 equiv.) and **51** (1.415 g, 3.3 mmol, 1.1 equiv.) were dissolved in 10 ml of degassed, dry toluene. To this solution Pd(PPh₃)₄ (92 mg, 0.08 mmol, 0.025 equiv.) was added. The mixture was heated to reflux over night. After cooling to room temperature, water was added and the product was extracted with ethyl acetate and washed with water. The combined organic phases were dried over MgSO₄ and the solvent was evaporated under reduced pressure. Column chromatography (silica, petroleum ether/ethyl acetate 10:1) yields a yellowish solid (389 mg, 1.40 mmol, 47%).

¹H-NMR (300 MHz, CDCl₃): δ (ppm) = 10.19 (s, 1H), 8.04 (dt, 1H, ³J(H,H) = 8.7 Hz, ⁴J(H,H) = 0.9 Hz), 7.93 (m, 2H), 7.75 (s, 1H), 7.71-7.57 (m, 3H), 7.49-7.41 (m, 3H).

¹³C-NMR (75 MHz, CDCl₃): δ (ppm) = 179.7, 155.6, 148.2, 140.9, 139.8, 130.1, 126.9, 126.8, 126.5, 125.7, 125.3, 124.8, 124.4, 123.2, 122.4, 113.1.

3-(2-bromobenzo[b]thiophen-3-yl)benzofuran-2-carbaldehyde (53)

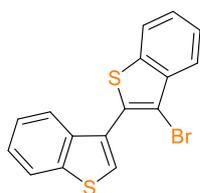


52 (397 mg, 1.4 mmol, 1.0 equiv.) was dissolved in chloroform. NBS (384 mg, 2.1 mmol, 1.5 equiv.) was added and the mixture was stirred at room temperature for 10 h. Water was added to the mixture and it was extracted with DCM and washed with aqueous Na₂S₂O₃-solution. The organic phases were dried over MgSO₄ and the solvent was removed under reduced pressure. Column chromatography (silica, petroleum ether/ethyl acetate 10:1) gave the desired product (182 mg, 0.51 mmol, 36%) as yellow solid.

¹H-NMR (300 MHz, CDCl₃): δ (ppm) = 9.97 (s, 1H), 7.94 (m, 2H), 7.78 (dt, 7.70 (dt, 1H, ³J(H,H) = 8.3 Hz, ⁴J(H,H) = 0.9 Hz), 7.64-7.50 (m, 3H), 7.41 (m, 1H).

¹³C-NMR (75 MHz, CDCl₃): δ (ppm) = 179.7, 155.6, 148.4, 139.1, 138.5, 130.0, 127.0, 126.7, 126.0, 125.5, 124.7, 124.6, 124.3, 123.3, 122.5, 113.1, 110.8.

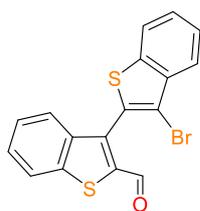
3-Bromo-2,3'-bibenzo[b]thiophene (**54**)



2,3-dibromobenzo[*b*]thiophene **35** (1.413 g, 5.0 mmol, 1.0 equiv.) was dissolved in 10 ml toluene. To this solution 10 ml of 2 M aqueous Na₂CO₃-solution and **51** (2.5 g, 6.0 mmol, 1.2 equiv.) were added and the mixture was degassed by bubbling argon through it. Then, Pd(PPh₃)₄ (132 mg, 0.11 mmol, 0.023 equiv.) was added. The mixture is heated to reflux for 18 h. After cooling to room temperature, it was extracted with ethyl acetate and washed with water. The combined organic phases were dried over MgSO₄ and the solvent evaporated under reduced pressure. Column chromatography (silica, petroleum ether) gave the desired product (0.886 g, 2.56 mmol, 51%) as a white solid.

¹H-NMR (300 MHz, CDCl₃): δ (ppm) = 7.95-7.76 (m, 5H), 7.53-7.37 (m, 4H).

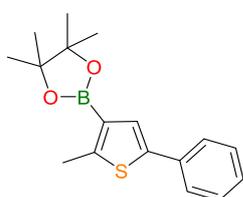
¹³C-NMR (75 MHz, CDCl₃): δ (ppm) = 140.4, 139.3, 137.3, 134.8, 132.2, 126.5, 126.2, 125.6, 125.3, 125.0, 124.7, 124.1, 123.9, 122.2, 122.1, 106.4.

3-Bromo-[2,3'-bibenzo[b]thiophene]-2'--carbaldehyde (55)

Diisopropylamine (0.5 ml, 3.5 mmol, 1.2 equiv.) was dissolved in 10 ml dry, degassed THF under argon. The solution was cooled to -78 °C and *n*-butyllithium (1.4 ml, 3.2 mmol, 2.3 M in hexane, 1.2 equiv.) was added. **54** (928 mg, 2.7 mmol, 1.0 eq.) was added as solid, the mixture allowed to warm up until the solid was completely dissolved and then re-cooled to -78 °C for 30 min before DMF (250 μ l, 3.2 mmol, 1.2 equiv.) was added. It was allowed to warm to 0 °C and 5 ml 1 M aqueous HCl was added. The mixture was extracted with ethyl acetate and washed with saturated NaCl-solution. Column chromatography (silica, petroleum ether/ethyl acetate 10:1) gave the product as yellowish solid (260 mg, 0.7 mmol, 32%).

¹H-NMR (300 MHz, CDCl₃): δ (ppm) = 10.43 (s, 1H), 8.78 (m, 1H), 7.91-7.82 (m, 3H), 7.61 (s, 1H), 7.59-7.41 (m, 4H).

¹³C-NMR (75 MHz, CDCl₃): δ (ppm) = 186.4, 151.9, 141.4, 139.7, 138.4, 137.3, 132.6, 131.1, 127.6, 126.7, 126.5, 125.7, 125.5, 125.4, 124.7, 122.3, 121.7.

4,4,5,5-tetramethyl-2-(2-methyl-5-phenylthiophen-3-yl)-1,3,2-dioxaborolane (56)⁶

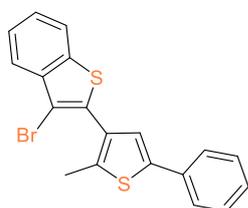
23 (2.441 g, 7.7 mmol, 1.0 equiv.) was dissolved in 25 ml dry degassed THF under argon. To this mixture, *n*-butyllithium (5.0 ml, 11.4 mmol, 2.3 M in hexane, 1.2 equiv.) was added and it was stirred for 1 h. Then isopropoxyboronic acid pinacol ester (2.6 ml, 12.6 mmol, 1.3 equiv.) was added at -78 °C, it was allowed to warm to room temperature and it was further stirred for 1 h. Water was added and the mixture was extracted with ethyl acetate and neutralized with saturated aqueous NH₄Cl-solution. The organic phases were dried over MgSO₄. The solvent was

removed under reduced pressure and the residue was purified by column chromatography (silica, petroleum ether). The product (2.9 g, 9.6 mmol, 99%) was obtained as a yellow oil.

¹H-NMR (300 MHz, CDCl₃): δ (ppm) = 7.57 (m, 2H), 7.43 (s, 1H), 7.33 (7.22 (tt, 1H, ³J(H,H) = 7.4 Hz, ⁴J(H,H) = 1.3 Hz), 2.70 (s, 3H), 1.34 (s, 12H).

¹³C-NMR (75 MHz, CDCl₃): δ (ppm) = 152.5, 141.0, 134.6, 129.0, 128.8, 127.0, 125.8, 83.4, 83.0, 25.0, 24.9, 16.1.

3-Bromo-2-(2-methyl-5-phenylthiophen-3-yl)benzo[b]thiophene (57)⁶

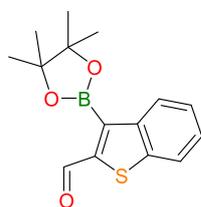


56 (0.288 g, 1.0 mmol, 2.0 equiv.) and **35** (0.888 g, 3.1 mmol, 1.0 equiv.) were dissolved in 3 ml toluene, 3 ml 2 M aqueous Na₂CO₃-solution, and 2 ml EtOH. It was degassed by bubbling argon through the solution. Then, Pd(PPh₃)₄ (71 mg, 0.12 mmol, 0.06 equiv.) and PPh₃ (22 mg, 0.1 mmol, 0.2 equiv.) were added and the suspension was refluxed for 18 h. The cooled solution was extracted with MTBE and washed with water. The organic phases were dried over MgSO₄ and evaporated under reduced pressure. Column chromatography (silica, petroleum ether/ethyl acetate 10:1) gave the product as yellowish solid (0.402 g, 1.04 mmol, 35%).

¹H-NMR (300 MHz, CDCl₃): δ (ppm) = 7.82 (m, 2H), 7.60 (m, 2H), 7.44-7.27 (m, 6H), 2.69 (s, 3H).

¹³C-NMR (75 MHz, CDCl₃): δ (ppm) = 138.9, 133.9, 133.6, 128.9, 128.8, 128.6, 128.5, 127.5, 125.6, 125.5, 125.3, 125.2, 123.5, 122.2, 14.9.

3-(4,4,5,5-Tetramethyl-1,3,2-dioxaborolan-2-yl)benzo[b]thiophene-2-carbaldehyde (58)

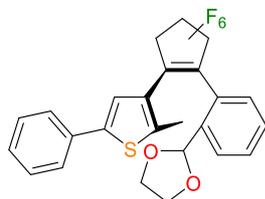


39 (1.439 g, 5.2 mmol, 1.0 equiv.) was dissolved in 15 ml dry degassed THF under argon. *n*-Butyllithium (2.7 ml, 6.2 mmol, 2.3 M in hexane, 1.2 equiv.) was added at -78 °C and the mixture was stirred for 1 h. Then, isopropoxyboronic acid pinacol ester (1.7 ml, 8.3 mmol, 1.6 equiv.) was added at -78 °C and it was stirred for 1 h at room temperature. Water was added to the reaction, it was extracted with ethyl acetate and washed with saturated aqueous NH₄Cl-solution. After drying with MgSO₄ and evaporation of the solvent, the product was purified by column chromatography (silica, petroleum ether/ethyl acetate 10:1) and obtained as a yellow oil (1.524 g, 4.59 mmol, 88%).

¹H-NMR (300 MHz, CDCl₃): δ (ppm) = 8.33 (m, 1H), 7.81 (m, 1H), 7.34 (m, 2H), 6.75 (s, 1H), 4.13 (m, 4H), 1.39 (s, 12H).

¹³C-NMR (75 MHz, CDCl₃): δ (ppm) = 155.5, 143.8, 140.0, 126.0, 124.7, 124.4, 122.1, 100.0, 83.8, 75.4, 65.8, 60.5, 25.0.

3-(2-(2-Methyl-5-phenylthiophen-3-yl)perfluorocyclopent-1-en-1-yl)-2-phenyl)-1,3-dioxolane (59)



41 (0.73 g, 3.2 mmol, 1.0 equiv.) was dissolved in 15 mL dry degassed THF and cooled to -78 °C. *n*-Butyllithium (2.3 M in hexane, 1.7 mL, 3.8 mmol, 1.2 equiv.) was added. After 30 min of stirring, **24** (0.77 g, 2.3 mmol, 0.7 equiv.) was dissolved in 5 mL of dry degassed THF and slowly added to the reaction mixture. The reaction mixture was stirred for 1 h at -78 °C, then allowed to warm to room temperature and stirred for further 16 h. The reaction mixture was hydrolyzed with water and extracted with diethylether. The organic phase was evaporated and dried over MgSO₄. Column chromatography (silica, petroleum ether) gave the desired product as a colorless oil (0.52 g, 1.05 mmol, 33%).

¹H NMR (300 MHz, CDCl₃): δ (ppm) = 7.62 (m, 1H), 7.46 (m, 4H), 7.42-7.23 (m, 4H), 7.14 (m, 1H), 5.49 (s, 1H), 3.90 (m, 4H), 2.02 (s, 3H).

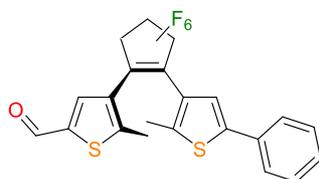
¹³C NMR (75 MHz, CDCl₃): δ (ppm) = 137.5, 133.5, 130.1, 129.2, 128.9, 127.7, 127.5, 125.5, 123.1, 100.8, 65.0, 14.7.

¹⁹F NMR (282 MHz, CDCl₃): δ (ppm) = -110.3 (m, 4F, ³J(F,F) 5Hz), -131.5 (m, 2F, ³J(F,F) 5Hz).

HRMS (ESI⁻): m/z = 495.084 (calcd: 495.0853 for [C₂₅H₁₇F₆O₂S]⁻).

UPLC: t_R = 4.09 min (100 % peak area).

4-(Perfluoro-2-(2-methyl-5-phenylthiophen-3-yl)cyclopent-1-en-1-yl)-5-methylthiophene-2-carbaldehyde (1)¹⁵



26 (0.80 g, 3.2 mmol, 1.1 equiv.) was dissolved in 10 ml dry THF and cooled to -78°C, before *n*-butyllithium (1.6 ml, 3.7 mmol, 2.3 M in hexane, 1.2 equiv.) was added. After 1 h of stirring, **24** (1.06 g, 3.0 mmol, 1.0 equiv.) in 5 ml of dry degassed THF was added. It was further stirred for 1 h at -78°C, and another 1 h at room temperature. The mixture was hydrolysed with 5 ml concentrated HCl. The mixture was washed with water and extracted with ethyl acetate. Purification via column chromatography (silica, petroleum ether/ethyl acetate 20:1) and recrystallization from heptane gave the product as yellowish white solid (0.33 g, 0.7 mmol, 23%).

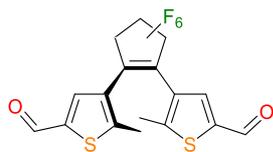
¹H NMR (300 MHz, CDCl₃): δ (ppm) = 9.86 (s, 1H), 7.77 (s, 1H), 7.52 (m, 2H), 7.43-7.27 (m, 3H), 7.24 (m, 1H), 2.05 (s, 3H), 1.93 (s, 3H). (for spectrum see Figure S1, page 44)

¹³C NMR (75 MHz, CDCl₃): δ (ppm) = 182.3, 143.1, 141.9, 136.4, 133.1, 129.2, 128.3, 125.8, 122.1, 15.6, 14.7.

¹⁹F NMR (282 MHz, CDCl₃): δ (ppm) = -109.4 (s, 2F), -109.7 (s, 2F), -131.2 (quin, 2F, ³J(F,F) = 5 Hz).

HRMS (ESI⁺): m/z = 473.0475 (calcd: 473.0463 for [C₂₂H₁₅F₆OS₂]⁺).

UPLC: t_R = 5.64 min (98% peak area).

4,4'-(Perfluorocyclopent-1-ene-1,2-diyl)bis(5-methylthiophene-2-carbaldehyde) (2)⁴

26 (2.11 g, 8.5 mmol, 2.1 equiv.) was dissolved in 10 ml dry THF and cooled to -78°C. Then *n*-butyllithium (4.0 ml, 9.2 mmol, 2.3 M in hexane, 2.3 equiv.) was added slowly. After 1 h of stirring, C₅F₈ (0.540 ml, 4.0 mmol, 1.0 equiv.) was added. The mixture was further stirred for 1 h at -78°C, allowed to warm to room temperature and stirred for another 1 h. Subsequently, the mixture was hydrolysed with 5 ml concentrated HCl, extracted with ethyl acetate, washed with water and dried over MgSO₄. Purification by column chromatography (silica, petroleum ether/ethyl acetate 10:1) yielded the product as white solid that was further recrystallized from heptane (0.57 g, 1.35 mmol, 34%).

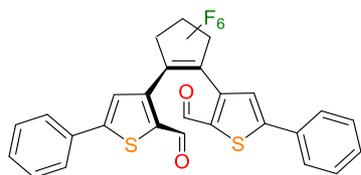
¹H NMR (300 MHz, CDCl₃): δ (ppm) = 9.85 (s, 2H), 7.73 (s, 2H), 2.03 (s, 6H). (for spectrum see Figure S2, page 44)

¹³C NMR (75 MHz, CDCl₃): δ (ppm) = 182.1, 151.8, 142.4, 135.8, 126.0, 15.6.

¹⁹F NMR (282 MHz, CDCl₃): δ (ppm) = -109.7 (t, 4F, ³J(F,F) = 5 Hz), -131.2 (quin, 2F, ³J(F,F) = 5 Hz).

HRMS (ESI): m/z = 422.9962 (calcd: 422.9954 for [C₁₇H₉F₆O₂S₂]⁻)

UPLC: t_R = 4.65 min (100% peak area).

3,3'-(Perfluorocyclopent-1-ene-1,2-diyl)bis(5-phenylthiophene-2-carbaldehyde) (3)

30 (1.32 g, 4.3 mmol, 2.1 equiv.) was dissolved in 10 ml dry THF and cooled to -78°C. Then, *n* butyllithium (2.0 ml, 4.6 mmol, 2.3 M in hexane, 2.3 equiv.) was added slowly. After 1 h of stirring, C₅F₈ (0.27 ml, 2.0 mmol, 1.0 equiv.) was added. It was further stirred for 1 h at -78°C, allowed to warm to room temperature and stirred for other 18 h. The mixture was then

hydrolysed with 3 ml concentrated HCl, washed with water, extracted with ethyl acetate and dried over MgSO₄. Purification via column chromatography (silica, petroleum ether/ethyl acetate 20:1) and further recrystallization from heptane gave the product as yellow solid (50 mg, 0.36 mmol, 32%).

¹H NMR (300 MHz, CDCl₃): δ (ppm) = 9.61 (s, 2H), 7.62 (m, 4H), 7.45 (m, 6H), 7.41 (s, 2H). (for spectrum see Figure S3, page 45)

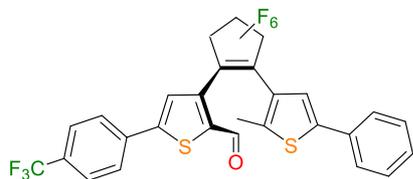
¹³C NMR (75 MHz, CDCl₃): δ (ppm) = 180.3, 155.1, 140.0, 132.9, 131.8, 130.4, 129.6, 126.7, 124.8.

¹⁹F NMR (282 MHz, CDCl₃): δ (ppm) = -110.0 (t, 4F, ³J(F,F) = 5 Hz), -130.7 (quin, 2F, ³J(F,F) = 5 Hz).

HRMS (ESI⁺): m/z = 549.0475 (calcd: 549.0412 for [C₂₇H₁₅F₆O₂S₂]⁺).

UPLC: t_R = 5.78 min (100% peak area).

3-(Perfluoro-2-(2-methyl-5-phenylthiophen-3-yl)cyclopent-1-en-1-yl)-5-(4-(trifluoromethyl)phenyl)thiophene-2-carbaldehyde (**4**)



31 (0.50 g, 1.4 mmol, 1.4 equiv.) was dissolved in 10 ml dry, degassed THF under argon and cooled to -78°C. Then, *n*-butyllithium (0.70 ml, 1.5 mmol, 2.3 M in hexane, 1.6 equiv.) was added to the solution. After 1 h of stirring, **24** (0.35 g, 1.0 mmol, 1.0 equiv.) dissolved in 5 ml dry, degassed THF was added. It was further stirred for 30 min at -78°C, allowed to warm to room temperature and stirred for another 1 h. It was hydrolyzed by addition of 5 ml concentrated HCl and stirred for 30 min at room temperature, extracted with ethyl acetate and washed with water. The solvent was evaporated and the residue purified by column chromatography (silica, petroleum ether/ethyl acetate 20:1) and recrystallized from heptane to give a slightly yellowish solid (0.12 g, 0.21 mmol, 22%).

¹H NMR (500 MHz, CDCl₃): δ (ppm) = 9.59 (s, 1H), 7.75 (dd, 4H, ³J(H,H) = 25.7 Hz, ³J(H,H) = 8.5 Hz), 7.51 (m, 3H), 7.38 (m, 2H), 7.31 (tt, 1H, ³J(H,H) = 7.3 Hz, ⁴J(H,H) = 1.2 Hz), 7.22 (s, 1H), 2.04 (s, 3H). (for spectrum see Figure S4, page 45)

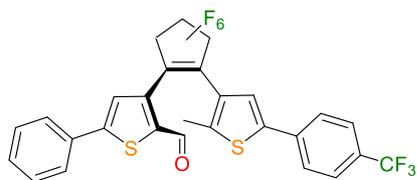
¹³C NMR (126 MHz, CDCl₃): δ (ppm) = 180.8, 151.9, 143.8, 141.7, 141.3, 135.4, 135.0, 133.0, 132.0, 131.8, 129.2, 128.4, 126.9, 126.6, 126.5, 125.9, 125.7, 123.9, 122.7, 122.4, 14.7.

¹⁹F NMR (471 MHz, CDCl₃): δ (ppm) = -63.1 (s, 3F), -109.8 (s, 2F), -111.2 (s, 2F), -131.9 (s, 2F).

HRMS (ESI⁺): m/z = 603.0497 (calcd: 603.0493 for [C₂₈H₁₆F₉OS₂]⁺).

UPLC: t_R = 5.76 min (100% peak area).

3-(Perfluoro-2-(2-methyl-5-(4-(trifluoromethyl)phenyl)thiophen-3-yl)cyclopent-1-en-1-yl)-5-phenylthiophene-2-carbaldehyde (5)



30 (0.35 g, 1.1 mmol, 1.1 equiv.) was dissolved in 5 ml dry THF and cooled to -78°C before *n*-butyllithium (0.60 ml, 1.4 mmol, 2.3 M in hexane, 1.4 equiv.) was added. After 1 h of stirring, a solution of **22** (0.44 g, 1.0 mmol, 1.0 equiv.) in 5 ml dry THF was added. The mixture was further stirred for 1 h at -78°C, allowed to warm to room temperature and stirred for other 16 h. The mixture was then hydrolysed with 3 ml concentrated HCl, washed with water and brine and extracted with ethyl acetate. Purification via column chromatography (silica, cHex/DCM 10:1) and recrystallization from cyclohexane gave the product as yellowish white solid (0.17 g, 0.26 mmol, 26%).

¹H NMR (300 MHz, CDCl₃): δ (ppm) = 9.54 (s, 1H), 7.66 (m, 2H), 7.61 (m, 4H), 7.46 (m, 4H), 7.30 (s, 1H), 2.06 (s, 3H). (for spectrum see Figure S5, page 46)

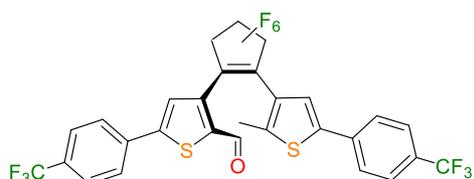
¹³C NMR (75 MHz, CDCl₃): δ (ppm) = 180.7, 154.6, 140.0, 132.0, 130.4, 129.6, 126.6, 126.5, 126.2, 126.1, 124.4, 124.0, 14.7.

¹⁹F NMR (282 MHz, CDCl₃): δ (ppm) = -62.0 (s, 3F), -109.2 (s, 2F), -110.2 (s, 2F), -131.1 (quin, 2F, ³J(F,F) = 5 Hz).

HRMS (ESI⁺): $m/z = 603.0493$ (calcd: 603.0493 for [C₂₈H₁₆F₉OS₂]⁺).

UPLC: $t_R = 5.72$ min (88% peak area).

3-(Perfluoro-2-(2-methyl-5-(4-(trifluoromethyl)phenyl)thiophen-3-yl)cyclopent-1-en-1-yl)-5-(4-(trifluoromethyl)phenyl)thiophene-2-carbaldehyde (6)



31 (0.58 g, 1.5 mmol, 2.2 equiv.) was dissolved in 10 ml dry, degassed THF under argon and cooled to -78°C before *n*-butyllithium (0.8 ml, 1.8 mmol, 2.3 M in hexane, 2.6 equiv.) was added. After 30 min of stirring at low temperature, **22** (0.30 g, 0.7 mmol, 1.0 equiv.) dissolved in 5 ml dry, degassed THF was added. It was further stirred for 30 min at -78°C, allowed to warm to room temperature and stirred for another 1 h. The mixture was hydrolyzed by addition of 5 ml concentrated HCl and stirred for 2 h, before it was washed with water and extracted with ethyl acetate. The solvent was evaporated under reduced pressure and the residue was purified by column chromatography (silica, petroleum ether/ethyl acetate 20:1) and recrystallized from heptane to give a slightly yellowish solid (0.22 g, 0.32 mmol, 46%).

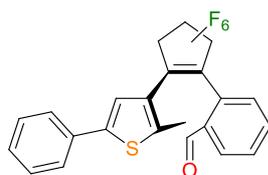
¹H NMR (500 MHz, CDCl₃): δ (ppm) = 9.57 (s, 1H), 7.75 (dd, 4H, ³J(H,H) = 25.1 Hz, ³J(H,H) = 8.1 Hz), 7.62 (dd, 4H, ³J(H,H) = 15.5 Hz, 3J = 8.6 Hz), 7.54 (s, 1H), 7.30 (s, 1H), 2.05 (s, 3H). (for spectrum see Figure S6, page 46)

¹³C NMR (126 MHz, CDCl₃): δ (ppm) = 180.6, 152.1, 143.0, 141.9, 141.2, 136.3, 135.3, 134.8, 132.2, 131.8, 130.3, 130.0, 126.9, 126.6, 126.2, 126.0, 125.6, 125.4, 125.1, 124.3, 123.8, 14.7.

¹⁹F NMR (471 MHz, CDCl₃): δ (ppm) = -62.9 (s, 3F), -63.1 (s, 3F), -109.9 (s, 2F), -111.1 (s, 2F), -131.9 (s, 2F).

HRMS (ESI⁺): $m/z = 671.0379$ (calcd: 671.0367 for [C₂₉H₁₅F₁₂OS₂]⁺).

UPLC: $t_R = 5.88$ min (100% peak area).

2-(Perfluoro-2-(2-methyl-5-phenylthiophen-3-yl)cyclopent-1-en-1-yl)benzaldehyde (7)

59 (0.52 g, 1.05 mmol, 1.0 equiv.) was dissolved in 20 ml acetone/water 9:1 mixture. Then, *p*-toluene sulfonic acid monohydrate (0.99 g, 5.20 mmol, 5.0 equiv) was added and the reaction mixture was refluxed for 1 h. The reaction mixture was concentrated under vacuum, then 20 ml DCM were added. The organic phase was separated and washed with water (3 x 20 ml), dried over MgSO₄ and concentrated to afford light pink crystals (0.47 g, 1.05 mmol, 98%).

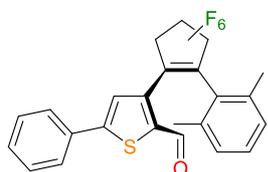
¹H NMR (300 MHz, CDCl₃): δ (ppm) = 9.90 (s, 1H), 7.91 (dd, 1H, ³*J*(H,H) = 7.6 Hz, ⁴*J*(H,H) = 1.3 Hz), 7.63-7.58 (m, 2H), 7.48 (d, 1H, ³*J*(H,H) = 7.6 Hz), 7.44 (m, 2H), 7.38-7.26 (m, 3H), 7.05 (s, 1H), 1.99 (s, 3H). (for spectrum see Figure S7, page 47)

¹³C NMR (75 MHz, CDCl₃): δ (ppm) = 189.4, 142.6, 141.2, 134.4, 134.2, 133.3, 130.8, 130.4, 129.7, 129.1, 128.1, 125.8, 124.0, 123.0, 14.6.

¹⁹F NMR (282 MHz, CDCl₃): δ (ppm) = -110.4 (m, 4H), -131.6 (m, 2H).

HRMS (ESI⁺): *m/z* = 453.0768 (calcd: 453.0742 for [C₂₃H₁₅F₆OS]⁺).

UPLC: *t_R* = 3.78 min (97 % peak area).

3-(2-(2,6-Dimethylphenyl)-perfluorocyclopent-1-en-1-yl)-5-phenylthiophene-2-carbaldehyde (8)

30 (3.44 g, 11.0 mmol, 1.1 equiv.) was dissolved in 20 ml dry THF and cooled to -78°C. Then *n*-butyllithium (5.9 ml, 13 mmol, 2.2 M in hexane, 1.3 equiv.) was added slowly. After 1 h of stirring, a solution of **40** (3.00 g, 10.1 mmol, 1.0 equiv.) in 10 ml of dry THF was added. The mixture was further stirred for 1 h at -78°C, allowed to warm to room temperature and stirred for another 16 h. It was then hydrolysed with 8 ml of concentrated HCl, extracted with ethyl

acetate, washed with water, dried over MgSO_4 and purified by column chromatography (silica, petroleum ether/ethyl acetate 20:1). The slightly reddish product was further recrystallized from heptane to yield the pure product (1.44 g, 3.09 mmol, 31%).

^1H NMR (300 MHz, CDCl_3): δ (ppm) = 9.75 (s, 1H), 7.52 (m, 2H), 7.41 (m, 3H), 7.21 (m, 2H), 7.06 (d, 2H, $^3J(\text{H,H}) = 7.7$ Hz), 2.24 (s, 6H). (for spectrum see Figure S8, page 47)

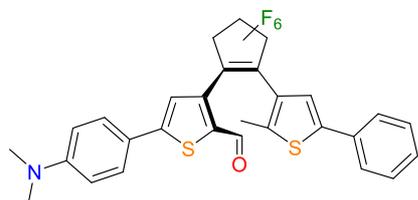
^{13}C NMR (75 MHz, CDCl_3): δ (ppm) = 181.4, 153.8, 141.1, 136.9, 134.3, 132.1, 130.2, 130.1, 129.5, 128.4, 126.5, 125.5, 124.5, 20.5.

^{19}F NMR (282 MHz, CDCl_3): δ (ppm) = -110.0 (t, 2F, $^3J(\text{F,F}) = 8$ Hz), -110.8 (s, 2F), -132.1 (quin, 2F, $^3J(\text{F,F}) = 6$ Hz).

HRMS (ESI⁺): $m/z = 467.0897$ (calcd: 467.0899 for $[\text{C}_{24}\text{H}_{17}\text{F}_6\text{OS}]^+$).

UPLC: $t_{\text{R}} = 5.21$ min (100% peak area).

5-(4-(Dimethylamino)phenyl)-3-(perfluoro-2-(2-methyl-5-phenylthiophen-3-yl)cyclopent-1-en-1-yl)thiophene-2-carbaldehyde (9)



29 (0.19 g, 0.53 mmol, 1.3 equiv.) was dissolved in 5 ml dry THF and cooled to -78°C . To this solution, *n*-butyllithium (0.30 ml, 1.1 mmol, 2.3 M in hexane, 2.8 equiv.) was added. After 1 h of stirring, a solution of **24** (0.15 g, 0.41 mmol, 1.0 equiv.) in 5 ml dry THF was added. The mixture was further stirred for 1 h at -78°C , allowed to warm to room temperature and stirred for other 16 h. It was hydrolysed with water, extracted with ethyl acetate, the organic phase dried over MgSO_4 and purified by column chromatography (silica, petroleum ether/ethyl acetate 10:1) to give the product as red solid (46 mg, 79 μmol , 19%).

^1H NMR (300 MHz, CDCl_3): δ (ppm) = 9.48 (s, 1H), 7.54 (m, 2H), 7.50 (m, 2H), 7.37 (m, 2H), 7.28 (m, 2H), 7.21 (s, 1H), 6.71 (m, 2H), 3.04 (s, 6H), 2.04 (s, 3H). (for spectrum see Figure S9, page 48)

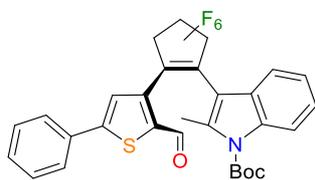
¹³C NMR (75 MHz, CDCl₃): δ (ppm) = 180.6, 156.0, 151.7, 143.3, 137.3, 135.6, 133.2, 129.1, 128.2, 127.7, 127.4, 125.9, 124.2, 122.6, 121.7, 119.7, 112.2, 40.4, 29.8, 14.7.

¹⁹F NMR (282 MHz, CDCl₃): δ (ppm) = -109.1 (s, 2F), -110.2 (s, 2F), -131.2 (quin, 2F, ³J(F,F) = 5 Hz).

HRMS (ESI⁺): m/z = 578.1101 (calcd: 578.1042 for [C₂₉H₂₂F₆NOS₂]⁺).

UPLC: t_R = 5.15 min (100% peak area).

3-(2-(*N*-Boc-2-methyl-1*H*-indol-3-yl)-perfluorocyclopent-1-en-1-yl)-5-phenylthiophene-2-carbaldehyde (**19**)



30 (0.57 g, 1.8 mmol, 1.2 equiv.) was dissolved in 20 ml dry THF under argon and cooled to -78°C. To this solution, *n*-butyllithium (0.85 ml, 2.0 mmol, 1.3 equiv., 2.3 M in hexane) was added. After 1 h of stirring, **46** (0.62 g, 1.5 mmol, 1.0 equiv.) was added. It was further stirred for 1 h at -78°C, allowed to warm to room temperature and stirred for another 1 h. It was hydrolyzed by addition of 5 ml concentrated HCl and extracted with ethyl acetate. It was dried over MgSO₄ and evaporated under reduced pressure. The mixture was separated via column chromatography (silica, petroleum ether/ethyl acetate 10:1) and the yellow product was further recrystallized from heptane to yield the pure product (0.32 g, 0.53 mmol, 36%).

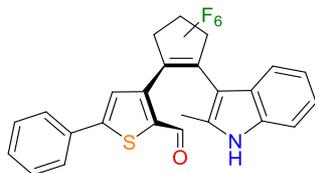
¹H NMR (300 MHz, CDCl₃): δ (ppm) = 9.59 (s, 1H), 8.05 (m, 1H), 7.59 (m, 2H), 7.43 (m, 4H), 7.36 (d, 1H, ³J(H,H) = 7.4 Hz), 7.31-7.20 (m, 2H), 2.38 (s, 3H), 1.66 (s, 9H).

¹³C NMR (75 MHz, CDCl₃): δ (ppm) = 180.8, 154.1, 149.9, 140.5, 138.5, 135.9, 134.9, 132.1, 129.5, 127.4, 126.6, 124.8, 124.5, 123.9, 118.4, 115.9, 106.3, 85.3, 28.3, 15.3.

¹⁹F NMR (282 MHz, CDCl₃): δ (ppm) = -109.8 (m, 4F), 131.6 (dquin, 2F, ²J(F,F) = 58 Hz, ³J(F,F) = 5 Hz).

HRMS (ESI⁺): m/z = 592.1404 (calcd: 592.1376 for [C₃₀H₂₄F₆NO₃S]⁺)

UPLC: t_R = 6.15 min (100% peak area).

3-(2-(2-Methyl-1H-indol-3-yl)-perfluorocyclopent-1-en-1-yl)-5-phenylthiophene-2-carbaldehyde (10)

19 (0.15 g, 250 μmol) was dissolved in a mixture of 20 ml THF and 20 ml 1 M aqueous HCl. The solution was heated to reflux for 4 h and subsequently extracted with ethyl acetate. It was washed with brine, dried over MgSO_4 and the solvent was evaporated under reduced pressure. The pure product (0.12 g, 236 μmol , 95%) was obtained as yellow solid.

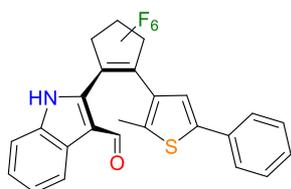
^1H NMR (300 MHz, CDCl_3): δ (ppm) = 9.50 (s, 1H), 8.27 (s, 1H), 7.64 (m, 2H), 7.55 (t, 1H, $^3\text{J}(\text{H,H}) = 1.2$ Hz), 7.50-7.41 (m, 3H), 7.40 (d, 1H, $^3\text{J}(\text{H,H}) = 8.1$ Hz), 7.23 (m, 1H), 7.18-7.04 (m, 2H), 2.17 (s, 3H). (for spectrum see Figure S10, page 48)

^{13}C NMR (75 MHz, CDCl_3): δ (ppm) = 181.3, 154.0, 140.0, 137.1, 136.4, 135.5, 132.3, 130.1, 129.5, 126.5, 124.7, 123.0, 121.7, 119.0, 111.0, 100.3, 13.3.

^{19}F NMR (282 MHz, CDCl_3): δ (ppm) = -108.7 (s, 2F), -109.1 (s, 2F), -131.8 (quin, 2F, $^3\text{J}(\text{F,F}) = 6$ Hz).

HRMS (ESI⁺): $m/z = 492.0876$ (calcd: 492.0851 for $[\text{C}_{25}\text{H}_{16}\text{F}_6\text{NOS}]^+$)

UPLC: $t_{\text{R}} = 5.14$ min (93% peak area).

2-(Perfluoro-2-(2-methyl-5-phenylthiophen-3-yl)cyclopent-1-en-1-yl)-1H-indole-3-carbaldehyde (11)

43 (0.60 g, 2.1 mmol, 1.5 equiv.) was dissolved in 4 ml dry THF and cooled to -78°C . To this solution, *n*-butyllithium (1.0 ml, 2.3 mmol, 2.3 M in hexane, 1.6 equiv.) was added. The mixture was heated to 0°C for 15 min accompanied by a color change from green to brown. After cooling again to -78°C , a solution of **24** (0.50 g, 1.4 mmol, 1.0 equiv.) in 4 ml dry THF was added. It was

further stirred for 1 h at room temperature, before 5 ml concentrated HCl were added and the mixture was stirred for another 1 h at room temperature. Water was added and the mixture was extracted with ethyl acetate. The organic phase was dried over MgSO₄ and further purified by column chromatography (silica, petroleum ether/ethyl acetate 10:1) to yield the product as yellow solid (0.13 g, 256 μmol, 18%).

¹H NMR (300 MHz, CDCl₃): δ (ppm) = 10.14 (s, 1H), 8.32 (d, 1H, ³J(H,H) = 7.9 Hz), 7.96 (s, 1H), 7.53 (m, 2H), 7.47-7.27 (m, 5H), 7.15 (m, 1H), 6.88 (d, 1H, ³J(H,H) = 8.3 Hz), 1.64 (s, 3H). (for spectrum see Figure S11, page 49)

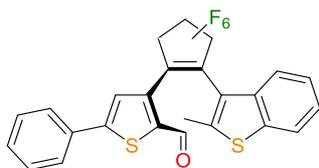
¹³C NMR (75 MHz, CDCl₃): δ (ppm) = 185.1, 135.3, 129.2, 128.4, 125.9, 125.7, 124.8, 122.7, 111.7, 14.2.

¹⁹F NMR (282 MHz, CDCl₃): δ (ppm) = -108.3 (s, 2F), -110.5 (s, 2F), -130.5 (quin, 2F, ³J(F,F) = 5 Hz).

HRMS (ESI⁺): m/z = 492.0879 (calcd: 492.0851 for [C₂₅H₁₆F₆NOS]⁺).

UPLC: t_R = 5.55 min (92% peak area).

3-(Perfluoro-2-(2-methylbenzo[b]thiophen-3-yl)cyclopent-1-en-1-yl)-5-phenyl-4,5-dihydrothiophene-2-carbaldehyde (12)



30 (0.69 g, 2.2 mmol, 1.1 equiv.) was dissolved in 10 ml dry THF and cooled to -78°C. *N*-butyllithium (1.25 ml, 2.8 mmol, 2.3 M in hexane, 1.4 equiv.) was added. After 1 h of stirring, **37** (0.664 g, 1.9 mmol, 1.0 equiv.) was dissolved in 5 ml of THF and added to the first solution. It was further stirred for 30 min at -78°C, allowed to warm to room temperature and stirred for another 1 h. The mixture was hydrolyzed by addition of 5 ml concentrated HCl, extracted with ethyl acetate and washed with water. The organic phase was dried over MgSO₄ and purified by column chromatography (silica, cHex/DCM 3:1). The product was isolated as a yellow solid (0.43 g, 0.85 mmol, 44%).

¹H NMR (300 MHz, CDCl₃): δ (ppm) = 9.60 (s, 1H), 7.72 (m, 2H), 7.54 (m, 2H), 7.49-7.27 (m, 6H), 2.39 (s, 3H). (for spectrum see Figure S12, page 49)

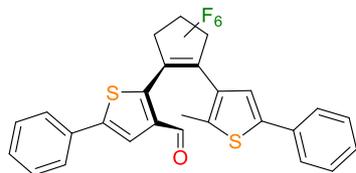
¹³C NMR (75 MHz, CDCl₃): δ (ppm) = 180.5, 154.0, 143.3, 140.8, 138.5, 132.0, 130.2, 129.5, 126.5, 125.4, 125.0, 124.4, 122.5, 121.5, 110.1, 15.1.

¹⁹F NMR (282 MHz, CDCl₃): δ (ppm) = -109.8 (m, 4F), -131.6 (m, 2F).

HRMS (ESI⁺): m/z = 509.0453 (calcd: 509.0463 for [C₂₅H₁₅F₆OS₂]⁺).

UPLC: t_R = 5.83 min (100% peak area).

2-(Perfluoro-2-(2-methyl-5-phenylthiophen-3-yl)cyclopent-1-en-1-yl)-5-phenylthiophene-3-carbaldehyde (13)



34 (0.65 g, 2.7 mmol, 1.3 equiv.) was dissolved in 10 ml dry THF and cooled to -78°C, before *n*-butyllithium (1.4 ml, 3.3 mmol, 2.3 M in hexane, 1.5 equiv.) was added. After 30 min of stirring, a solution of **24** (0.80 g, 2.2 mmol, 1.0 equiv.) dissolved in 5 ml dry THF was added. The mixture was further stirred for 30 min at -78°C, allowed to warm to room temperature and stirred for another 1 h. It was hydrolyzed by addition of 5 ml concentrated HCl, extracted with ethyl acetate and washed with water. The organic phase was dried over MgSO₄ and purified by column chromatography (silica, petroleum ether/ethyl acetate 20:1). The slightly reddish product was further recrystallized from heptane to yield the spectroscopy pure product as yellow solid (0.26 g, 22.4 mmol, 22%).

¹H NMR (300 MHz, CDCl₃): δ (ppm) = 9.60 (s, 1H), 7.67 (s, 1H), 7.61 (m, 2H), 7.51 (m, 2H), 7.47-7.27 (m, 6H), 7.21 (s, 1H), 2.07 (s, 3H). (for spectrum see Figure S13, page 50)

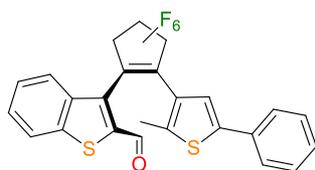
¹³C NMR (75 MHz, CDCl₃): δ (ppm) = 183.0, 149.1, 143.7, 141.4, 133.1, 132.0, 129.6, 129.4, 129.1, 128.3, 126.3, 125.9, 122.5, 122.3, 14.7.

¹⁹F NMR (282 MHz, CDCl₃): δ (ppm) = 108.9 (m, 2F), 110.0 (m, 2F), 130.9 (quin, 2F, ³J(F,F) = 5 Hz).

HRMS (ESI⁺): $m/z = 535.0635$ (calcd: 535.0620 for [C₂₇H₁₇F₆OS₂]⁺).

UPLC: $t_R = 6.11$ min (98% peak area).

3-(Perfluoro-2-(2-methylbenzo[b]thiophen-3-yl)cyclopent-1-en-1-yl)-5-phenylthiophene-2-carbaldehyde (14)



39 (0.92 g, 3.2 mmol, 1.1 equiv.) was dissolved in 10 ml dry, degassed THF and cooled to -78°C. To this solution, *n*-butyllithium (1.6 ml, 3.7 mmol, 2.3 M in hexane, 1.2 equiv.) was added. After 1 h of stirring, a solution of **24** (1.07 g, 3.0 mmol, 1.0 equiv.) in 5 ml of dry, degassed THF was added. The mixture was further stirred for 1 h at -78°C, allowed to warm to room temperature and stirred for another 1 h. It was hydrolysed with 5 ml concentrated HCl and washed with water; the organic phase was extracted with MTBE and dried over MgSO₄. Further purification via column chromatography (silica, petroleum ether/DCM 1:1) and recrystallization from heptane gave the product as white solid (0.32 g, 0.6 mmol, 21%).

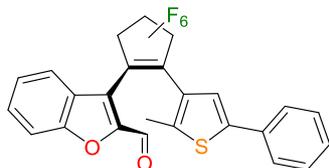
¹H NMR (300 MHz, CDCl₃): δ (ppm) = 9.96 (s, 1H), 7.91 (d, 1H, ³*J*(H,H) = 8.2 Hz), 7.76 (d, 1H, ³*J*(H,H) = 8.3 Hz), 7.58-7.44 (m, 2H), 7.40-7.27 (m, 5H), 7.07 (s, 1H), 2.03 (s, 3H). (for spectrum see Figure S14, page 50)

¹³C NMR (75 MHz, CDCl₃): δ (ppm) = 183.2, 142.9, 142.2, 141.8, 137.6, 133.0, 131.1, 129.1, 128.2, 126.3, 125.8, 124.7, 124.6, 124.0, 123.6, 122.5, 15.1.

¹⁹F NMR (282 MHz, CDCl₃): δ (ppm) = -109.1 (d, 2F, ³*J*(F,F) = 68 Hz), -110.3 (s, 2F), -131.7 (quin, 2F, ³*J*(F,F) = 6 Hz).

HRMS (ESI⁺): $m/z = 509.0498$ (calcd: 509.0463 for [C₂₅H₁₅F₆OS₂]⁺).

UPLC: $t_R = 5.80$ min (98% peak area).

3-(Perfluoro-2-(2-methylbenzofuran-3-yl)cyclopent-1-en-1-yl)-5-phenylthiophene-2-carbaldehyde (15)

49 (301 mg, 1.1 mmol, 1.1 equiv.) was dissolved in 10 ml dry THF and cooled to -78 °C. To this solution *n*-butyllithium (530 μ l, 1.2 mmol, 2.3 M in hexane, 1.2 equiv.) was added. After 1 h of stirring, **24** (372 mg, 1.0 mmol, 1.0 equiv.) in 5 ml of dry degassed THF was added. It was further stirred for 1 h at -78 °C, allowed to warm to room temperature and stirred for another 1 h. It was hydrolysed by addition of 5 ml concentrated HCl, washed with water, and extracted with ethyl acetate. Further purification by column chromatography (silica, petroleum ether/DCM 1:1) gave the title compound (53 mg, 108 μ mol, 11%) as yellowish solid.

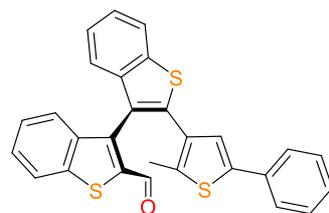
¹H-NMR (300 MHz, CDCl₃): δ (ppm) = 9.76 (s, 1H), 7.68-7.54 (m, 3H), 7.44 (m, 3H), 7.40-7.26 (m, 4H), 7.21 (s, 1H), 1.99 (s, 3H). (for spectrum see Figure S15, page 51)

¹³C-NMR (75 MHz, CDCl₃): δ (ppm) = 178.6, 155.5, 148.8, 143.1, 141.7, 133.1, 130.2, 129.1, 128.2, 125.8, 125.6, 125.5, 124.3, 122.6, 122.5, 117.6, 113.2, 14.9.

¹⁹F-NMR (282 MHz, CDCl₃): δ (ppm) = -108.7 (br, 2H), -110.6 (s, 2H), -131.3 (quin, $^3J(\text{F,F}) = 5$ Hz, 2F).

HRMS (ESI⁺): $m/z = 493.0694$ (calcd: 493.0691 for [C₂₅H₁₅F₆O₂S]⁺)

UPLC: $t_{\text{R}} = 5.18$ min (100% peak area).

2'-(2-Methyl-5-phenylthiophen-3-yl)-[3,3'-bibenzo[*b*]thiophene]-2-carbaldehyde (16)

57 (1.202 g, 3.6 mmol, 1.3 equiv.) and **58** (1.098 g, 2.8 mmol, 1.0 equiv.), as well as PPh₃ (355 mg, 1.4 mmol, 0.5 equiv.), and K₃PO₄ (4.808 g, 22.6 mmol, 8.0 equiv.) were dissolved in

10 ml water and 15 ml dioxane. It was degassed for 5 min by bubbling argon through the solution, before Pd(PPh₃)₄ (1.58 mg, 0.14 mmol, 0.05 equiv.) was added to the solution and the mixture was stirred at 100 °C for 18 h. After cooling to room temperature, it was extracted with ethyl acetate and washed with water. The organic phases were dried over MgSO₄ and the solvent was evaporated. Column chromatography (silica, petroleum ether) gave the product (23 mg, 0.05 mmol, 2%) as white crystals.

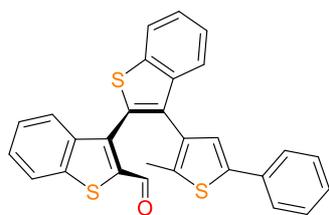
¹H-NMR (500 MHz, CDCl₃): δ (ppm) = 9.78 (s, 1H), 7.96 (m, 2H), 7.88 (t, 1H, ³J(H,H) = 8.5 Hz), 7.61 (d, 1H, ³J(H,H) = 8.3 Hz), 7.52 (m, 1H), 7.48-7.27 (m, 8H), 7.22 (tt, 1H, ³J(H,H) = 7.2 Hz, ⁴J(H,H) = 1.6 Hz), (6.93 (s, 1H), 2.14 (s, 3H). (for spectrum see Figure S16, page 51)

¹³C-NMR (125 MHz, CDCl₃): δ (ppm) = 185.2, 141.3, 140.6, 140.0, 139.9, 139.2, 139.1, 139.0, 133.7, 130.4, 128.9, 128.8, 128.5, 127.7, 127.4, 126.0, 125.7, 125.6, 125.3, 125.2, 125.1, 123.5, 123.4, 123.1, 122.4, 14.7.

HRMS (ESI+): m/z = 467.0594 (calcd: 467.0593 for [C₂₈H₁₉OS₃]⁺)

UPLC: t_R = 6.26 min (99% peak area).

3-(2-Methyl-5-phenylthiophen-3-yl)-[2,3'-bibenzo[b]thiophene]-2'-carbaldehyde (17)



A mixture of **55** (265 mg, 0.7 mmol, 1.0 equiv.), **56** (532 mg, 1.8 mmol, 2.5 equiv.), barium hydroxide octahydrate (894 mg, 2.8 mmol, 4.0 equiv.), 5 ml dimethoxyethanol and 2 ml water was degassed via bubbling argon through it for 5 min. Then, Pd(PPh₃)₄ (78 mg, 0.07 mmol, 0.1 equiv.) and PPh₃ (42 mg, 0.2 mmol, 0.1 equiv.) were added and the suspension was refluxed for 2 days. The mixture was extracted with ethyl acetate, washed with water, and the organic phases dried over MgSO₄. The mixture was purified by column chromatography (silica, petroleum ether/ethyl acetate 20:1) to give a white solid (5 mg, 9 μmol, 1.2%).

¹H-NMR (300 MHz, CDCl₃): δ (ppm) = 10.19 (s, 1H), 8.68 (d, 1H, ³J(H,H) = 8.3 Hz), 7.94 (d, 1H, ³J(H,H) = 8.1 Hz), 7.78 (d, 1H, ³J(H,H) = 8.1 Hz), 7.70 (d, 1H, ³J(H,H) = 7.9 Hz), 7.55-7.40 (m, 6H),

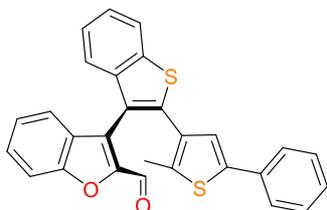
7.35 (t, 2H, $^3J(\text{H,H}) = 7.8$ Hz), 7.26 (m, 1H), 7.20 (s, 1H), 2.13 (s, 3H). (for spectrum see Figure S17, page 52)

$^{13}\text{C-NMR}$ (75 MHz, CDCl_3): δ (ppm) = 186.1, 151.0, 141.7, 140.5, 139.9, 139.4, 138.3, 136.5, 134.3, 134.1, 131.4, 131.1, 129.0, 127.6, 126.4, 126.3, 125.7, 125.6, 125.5, 125.0, 124.6, 122.3, 121.7, 14.4.

HRMS (ESI+): $m/z = 467.0619$ (calcd: 467.0593 for $[\text{C}_{28}\text{H}_{19}\text{OS}_3]^+$)

UPLC: $t_{\text{R}} = 6.45$ min (99% peak area).

3-(2-(2-Methyl-5-phenylthiophen-3-yl)benzo[b]thiophen-3-yl)benzofuran-2-carbaldehyde (18)



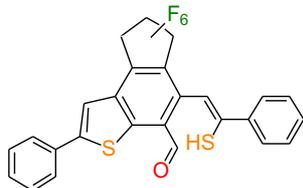
A mixture of **53** (183 mg, 0.5 mmol, 1.0 equiv.), **56** (0.298 g, 1.0 mmol, 2.0 equiv.), 3 ml toluene, 3 ml 2 M aqueous Na_2CO_3 -solution and 2 ml EtOH was degassed by bubbling argon through the solution. Then, $\text{Pd}(\text{PPh}_3)_4$ (71 mg, 0.12 mmol, 0.06 equiv.) and PPh_3 (22 mg, 0.1 mmol, 0.2 equiv.) were added and the suspension was refluxed for 18 h. After cooling to room temperature, it was extracted with ethyl acetate, washed with brine and the combined organic phase were dried over MgSO_4 . The mixture was purified via column chromatography (silica, petroleum ether/ethyl acetate 10:1) to give the product (137.1 mg, 0.29 mmol, 59%) as yellowish solid.

$^1\text{H-NMR}$ (300 MHz, CDCl_3): δ (ppm) = 9.80 (s, 1H), 7.97 (m, 1H), 7.75 (m, 1H), 7.68 (dt, 1H, $^3J(\text{H,H}) = 8.5$ Hz, $^4J(\text{H,H}) = 1.0$ Hz), 7.61 (dt, 1H, $^3J(\text{H,H}) = 8.5$ Hz, $^4J(\text{H,H}) = 1.0$ Hz), 7.55-7.45 (m, 6H), 7.38-7.22 (m, 3H), 7.20 (s, 1H), 2.02 (s, 3H). (for spectrum see Figure S18, page 52)

$^{13}\text{C-NMR}$ (75 MHz, CDCl_3): δ (ppm) = 179.4, 155.6, 148.0, 141.9, 140.2, 139.9, 137.5, 134.1, 133.3, 131.5, 129.8, 129.0, 127.6, 127.0, 126.6, 126.3, 125.9, 125.7, 125.3, 124.7, 124.6, 124.4, 122.9, 122.5, 112.9, 29.2.

HRMS (ESI+): $m/z = 451.0822$ (calcd: 451.0821 for $[\text{C}_{28}\text{H}_{19}\text{O}_2\text{S}_2]^+$)

UPLC: $t_{\text{R}} = 6.07$ min (98% peak area).

2-(6,6,7,7,8,8-Hexafluoro-4-methyl-2-phenyl-7,8-dihydro-6H-indeno[5,4-b]thiophen-5-yl)-1-phenylethene-1-thiol (3r)

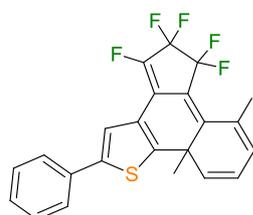
3 (5.5 mg, 10.0 μmol) was dissolved in 20 ml of dry CH_3CN and irradiated with a common laboratory UV-lamp for 1 h. The solution was concentrated under vacuum, then the crude mixture was purified by means of preparative TLC, using petroleum ether/ethyl acetate 10:1 mixture as mobile phase. The **3r** layer was scratched out, redissolved in DCM, filtered, dried over MgSO_4 and concentrated in order to afford the compound as a yellow solid (1.3 mg, 2.50 μmol , 25%).

^1H NMR (300 MHz, CDCl_3): δ (ppm) = 10.58 (s, 1H), 7.71 (m, 3H), 7.66 (d, 1H, $^3J(\text{H,H}) = 2.9$ Hz), 7.64-7.54 (m, 4H), 7.46 (m, 3H), 6.14 (bd, 1H). (for spectrum see Figure S19, page 53)

^{19}F NMR (282 MHz, CDCl_3): δ (ppm) = -103.6 (q, 2F, $^3J(\text{H,H}) = 250$ Hz), -106.2 (q, 2F, $^2J(\text{F,F}) = 250$ Hz), -127.6 (q, 2F, $^2J(\text{F,F}) = 250$ Hz).

HRMS (ESI): $m/z = 519.0283$ (calcd: 519.0317 for $[\text{C}_{26}\text{H}_{13}\text{F}_6\text{OS}_2]^-$).

UPLC: $t_{\text{R}} = 5.96$ min (100% peak area).

4,5,5,6,6-Pentafluoro-7,10a-dimethyl-2-phenyl-6,10a-dihydro-5H-cyclopenta[3,4]naphtha[1,2-b]thiophene (8r)

6 (0.70 g, 1.5 mmol, 1.0 equiv.) was dissolved in 18 ml of CH_3CN . The colorless solution was irradiated in a photoreactor ($\lambda_{\text{irr.}} = 350$ nm) for 30 min until the photo-stationary state was reached and the solution turned to violet color. After that, benzylamine (0.04 mL, 0.34 mmol, 0.23 equiv.) was added and the reaction stirred at room temperature until complete

decoloration was observed. The reaction mixture was concentrated and the desired compound was recovered as yellow oil (5.0 mg, 11.9 μmol , < 1%) after purification by column chromatography (silica, hexane, 2 times) and size-exclusion column chromatography (silica, THF).

^1H NMR (300 MHz, CDCl_3): δ (ppm) = 7.61 (m, 2H), 7.49 (d, 1H), 7.44-7.30 (m, 3H), 6.24 (m, 1H), 6.03 (m, 2H), 2.28 (d, 3H), 1.61 (s, 3H). (for 1D- and 2D-spectra see Figures S20-22, pages 53,54)

^{13}C -NMR (75 MHz, CDCl_3): δ (ppm) = 133.6, 131.9, 129.5, 129.3, 129.1, 128.4, 126.9, 126.0, 122.6, 117.4, 116.9, 17.6.

^{19}F NMR (282 MHz, CDCl_3): δ (ppm) = -103.1 (d, 1F, $^2J(\text{F},\text{F}) = 254$ Hz), -109.7 (d, 1F, $^2J(\text{F},\text{F}) = 253$ Hz), -116.8 (m, 2F), -147.9 (t, 1F, $^3J(\text{F},\text{F}) = 16$ Hz).

HRMS (ESI+): $m/z = 419.0895$ (calcd: 419.0887 for $[\text{C}_{23}\text{H}_{16}\text{F}_5\text{S}]^+$)

UPLC: $t_{\text{R}} = 4.89$ min (92% peak area).

2.2. ^1H NMR spectra

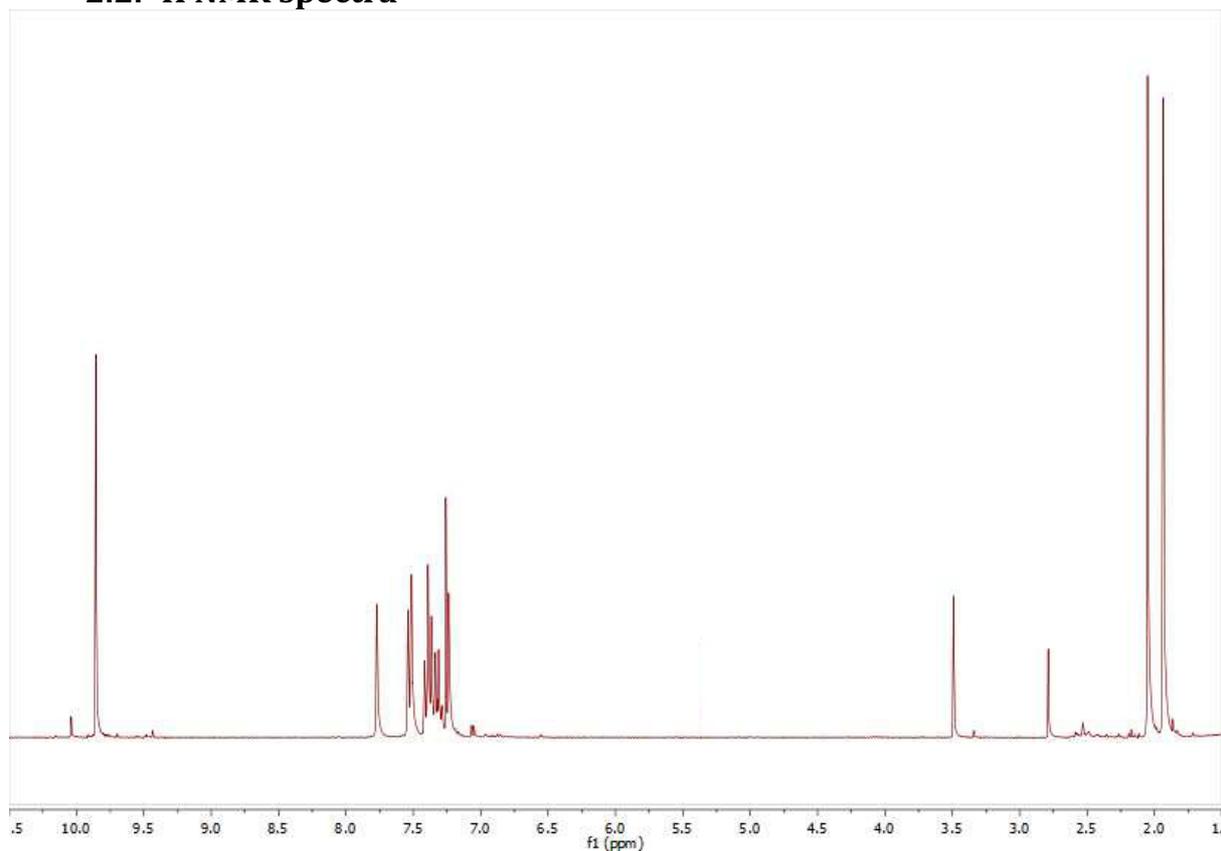


Figure S1: ^1H NMR spectrum (300 MHz, 298 K, CDCl_3) of **1**.

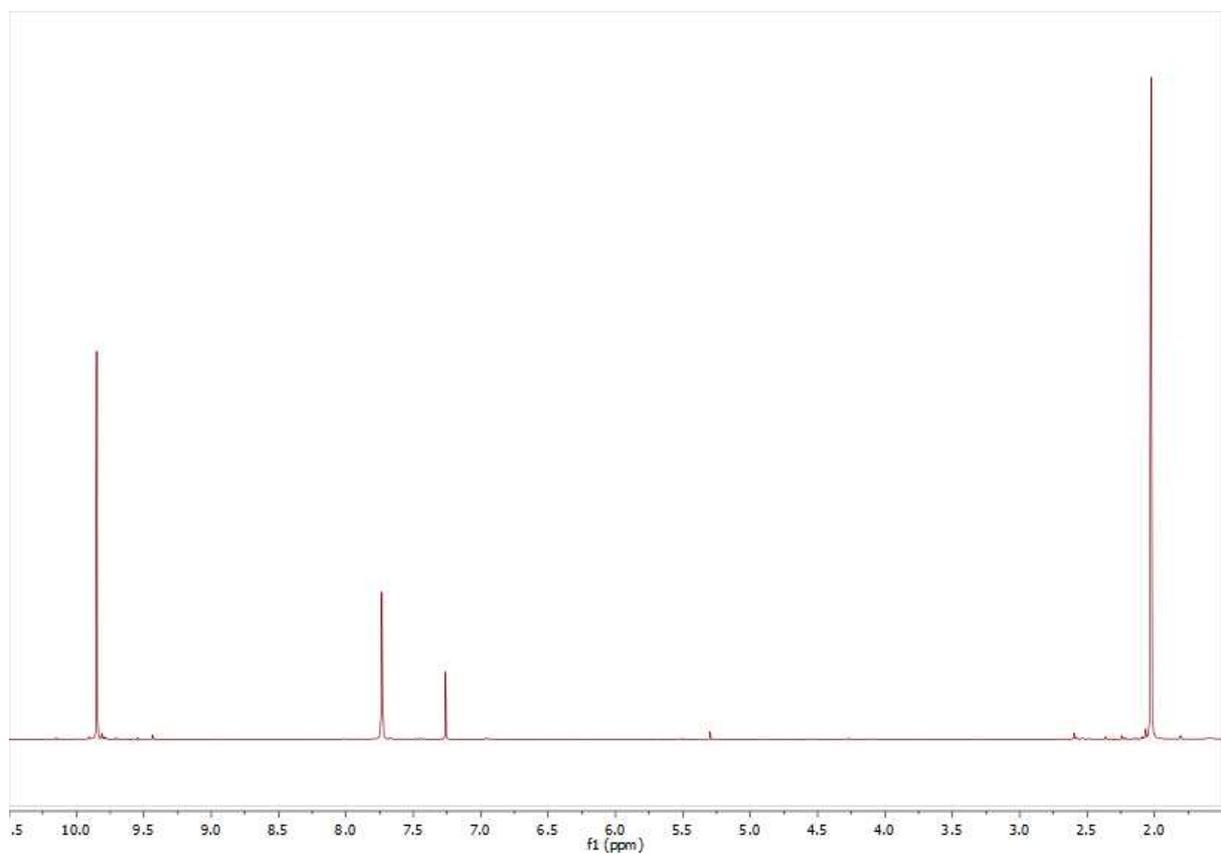


Figure S2: ^1H NMR spectrum (300 MHz, 298 K, CDCl_3) of **2**.

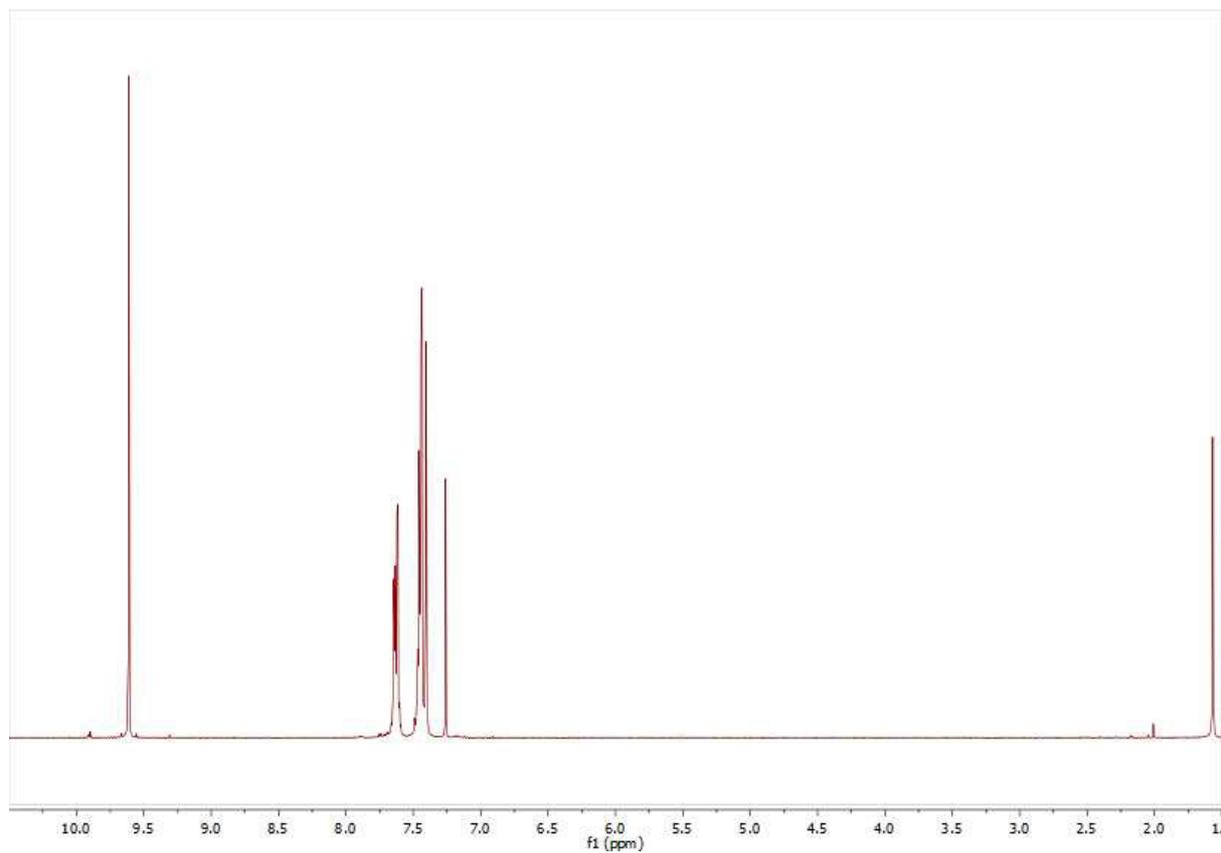


Figure S3: ^1H NMR spectrum (300 MHz, 298 K, CDCl_3) of **3**.

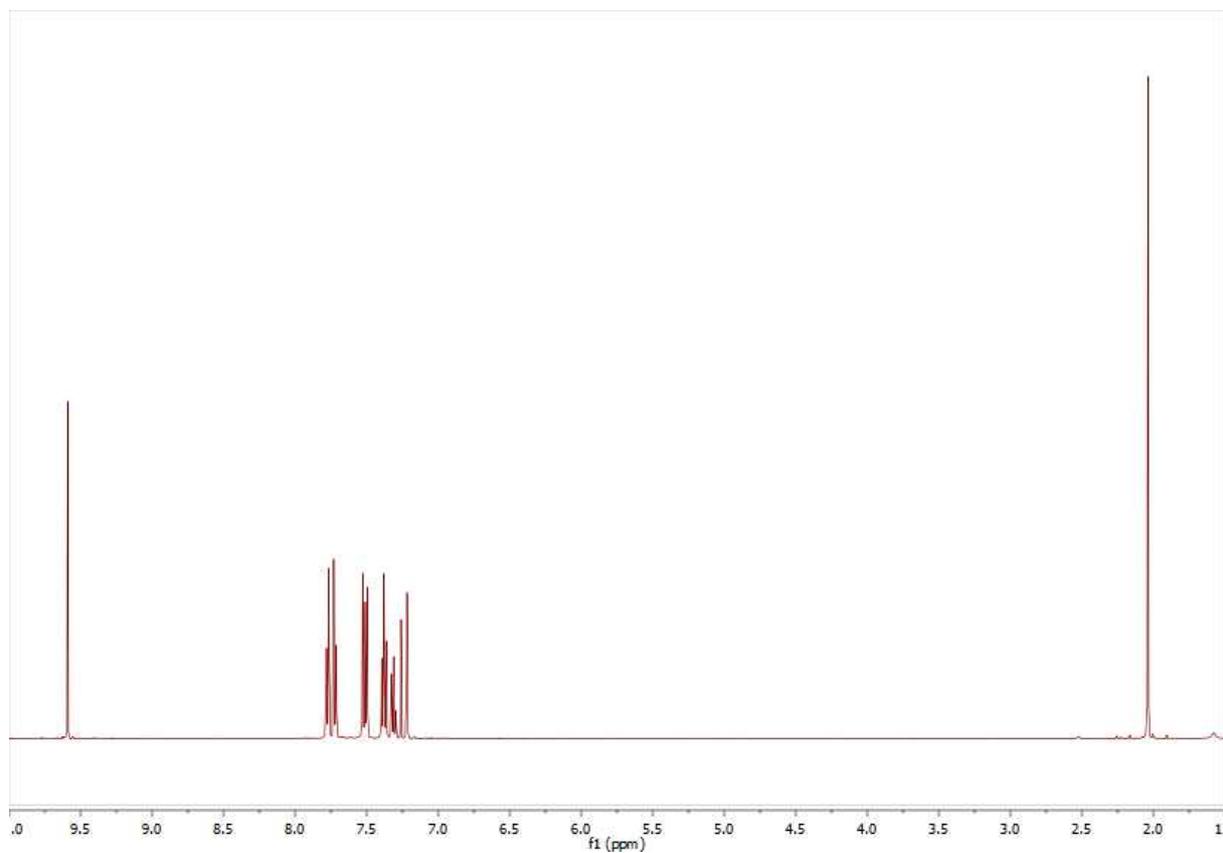


Figure S4: ^1H NMR spectrum (500 MHz, 298 K, CDCl_3) of **4**.

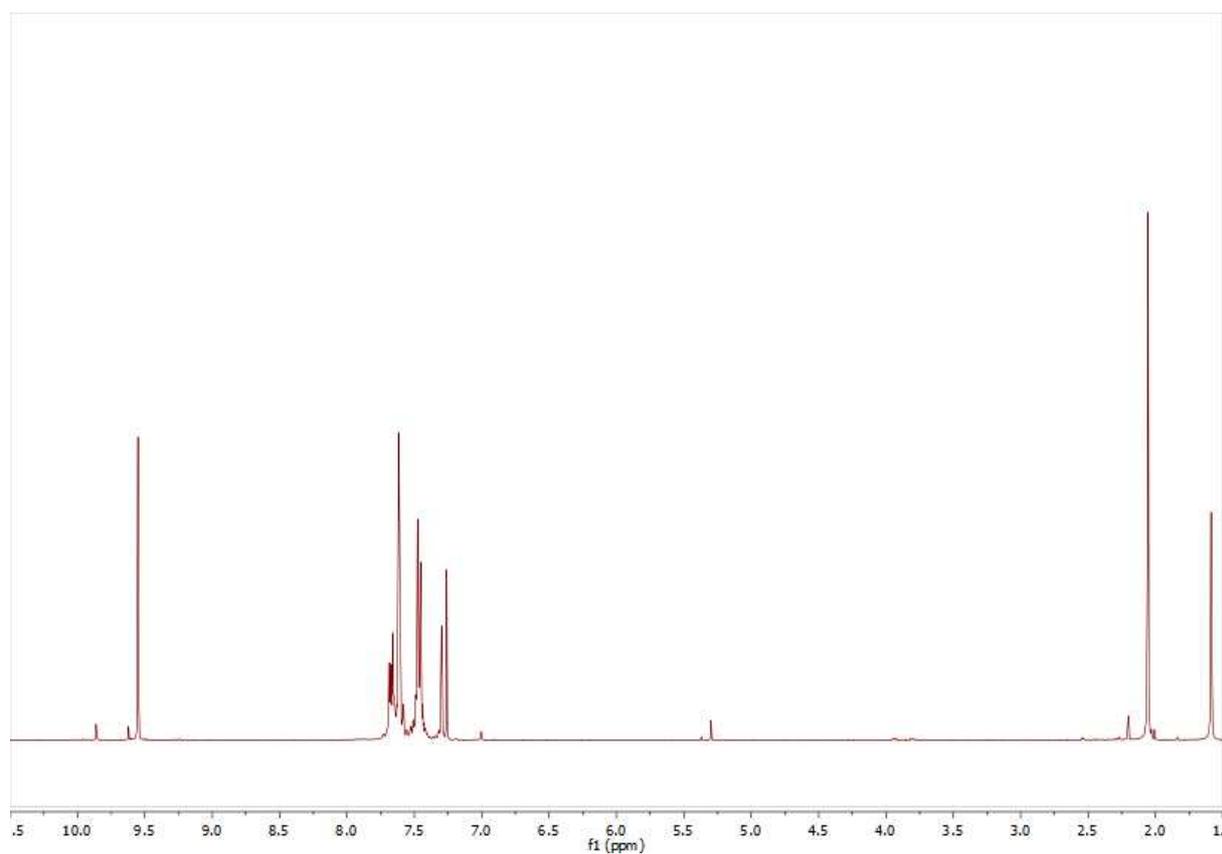


Figure S5: ^1H NMR spectrum (300 MHz, 298 K, CDCl_3) of **5**.

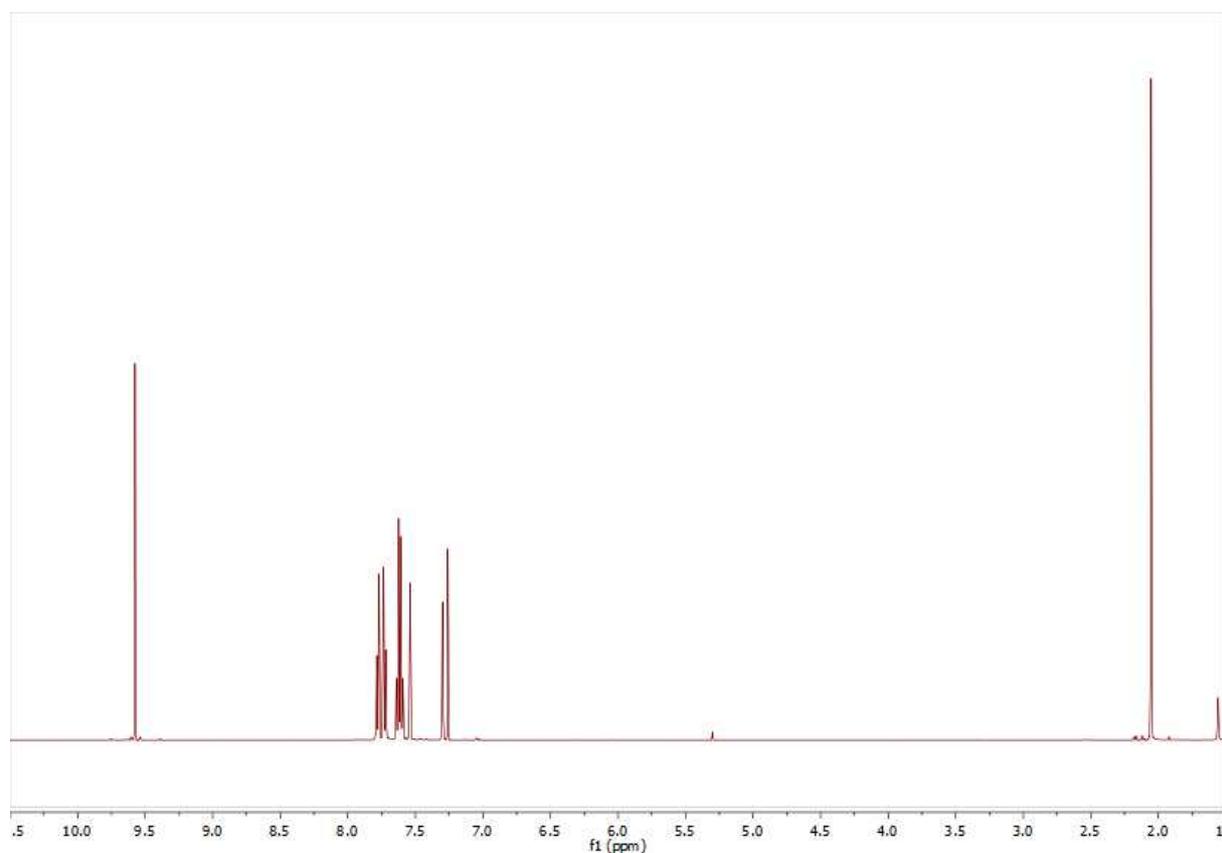


Figure S6: ^1H NMR spectrum (500 MHz, 298 K, CDCl_3) of **6**.

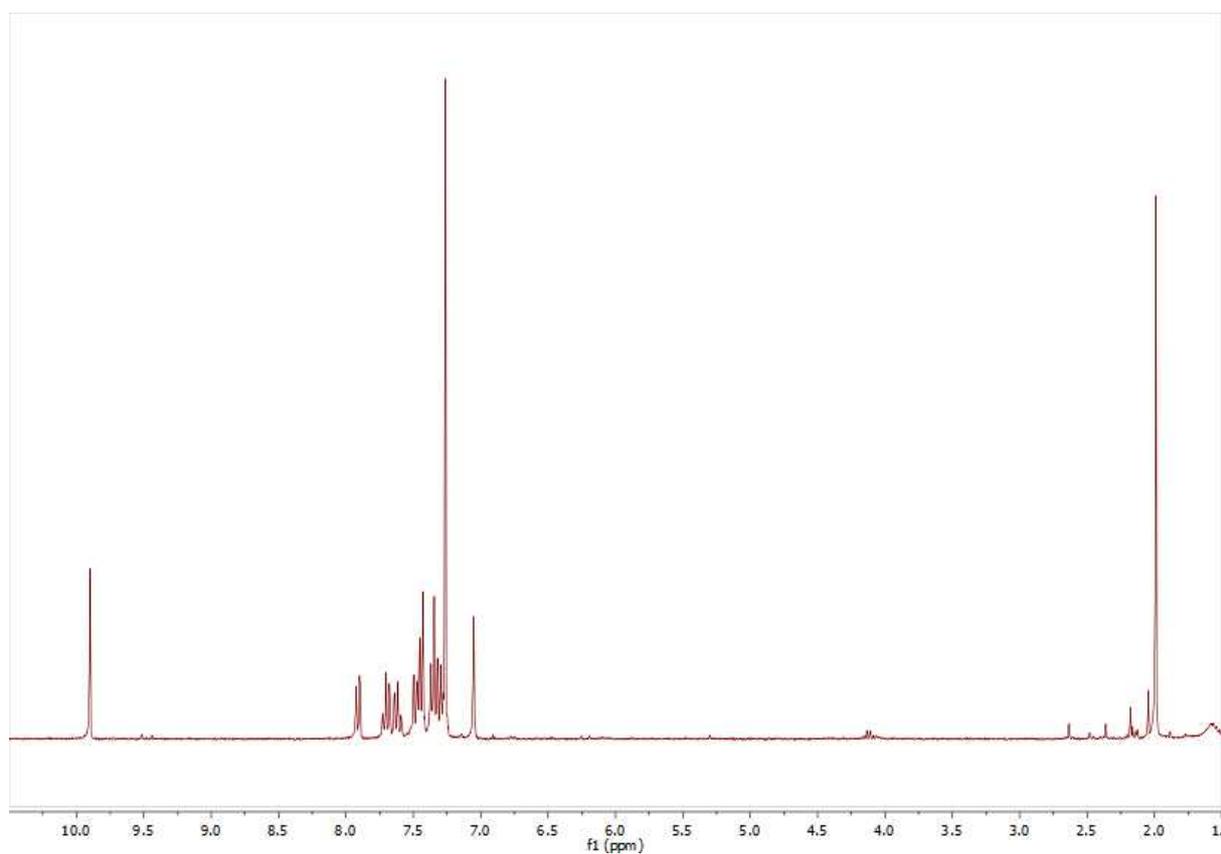


Figure S7: ¹H NMR spectrum (300 MHz, 298 K, CDCl₃) of **7**.

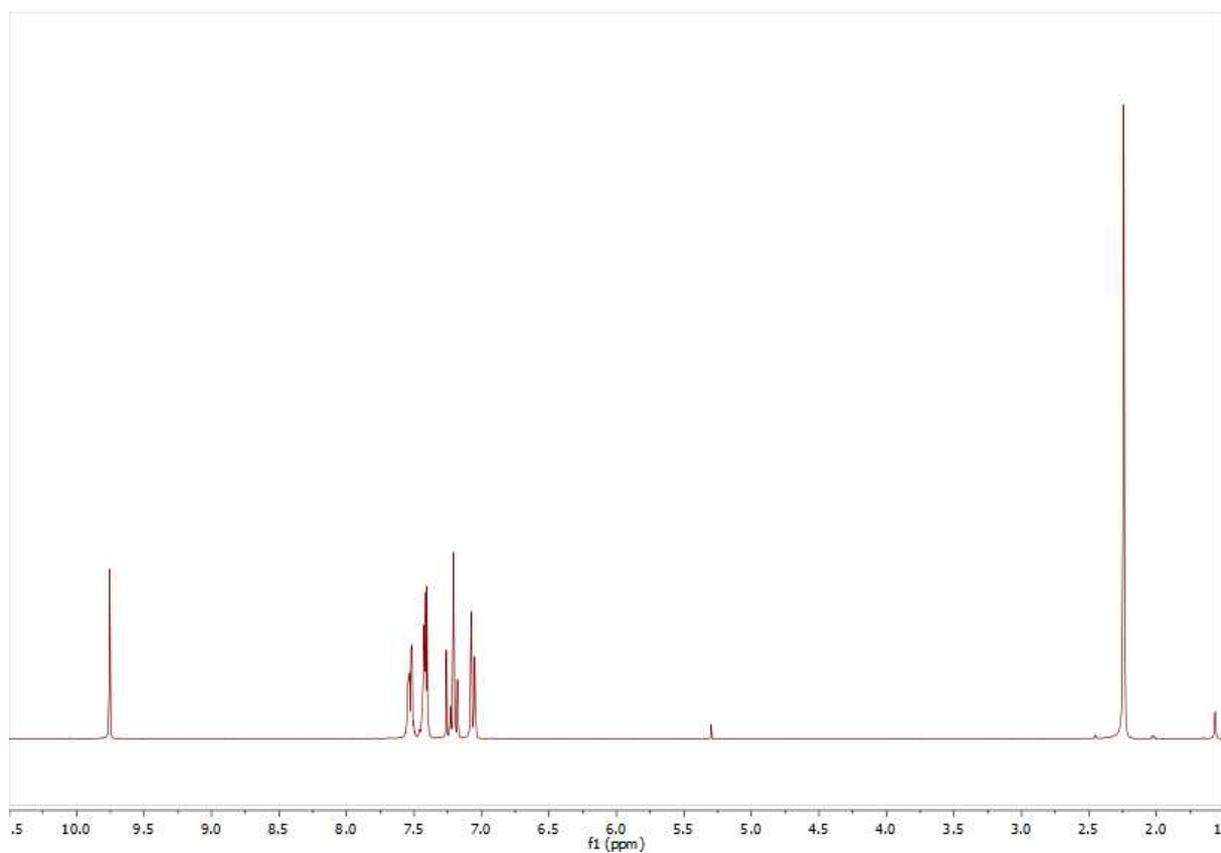


Figure S8: ¹H NMR spectrum (300 MHz, 298 K, CDCl₃) of **8**.

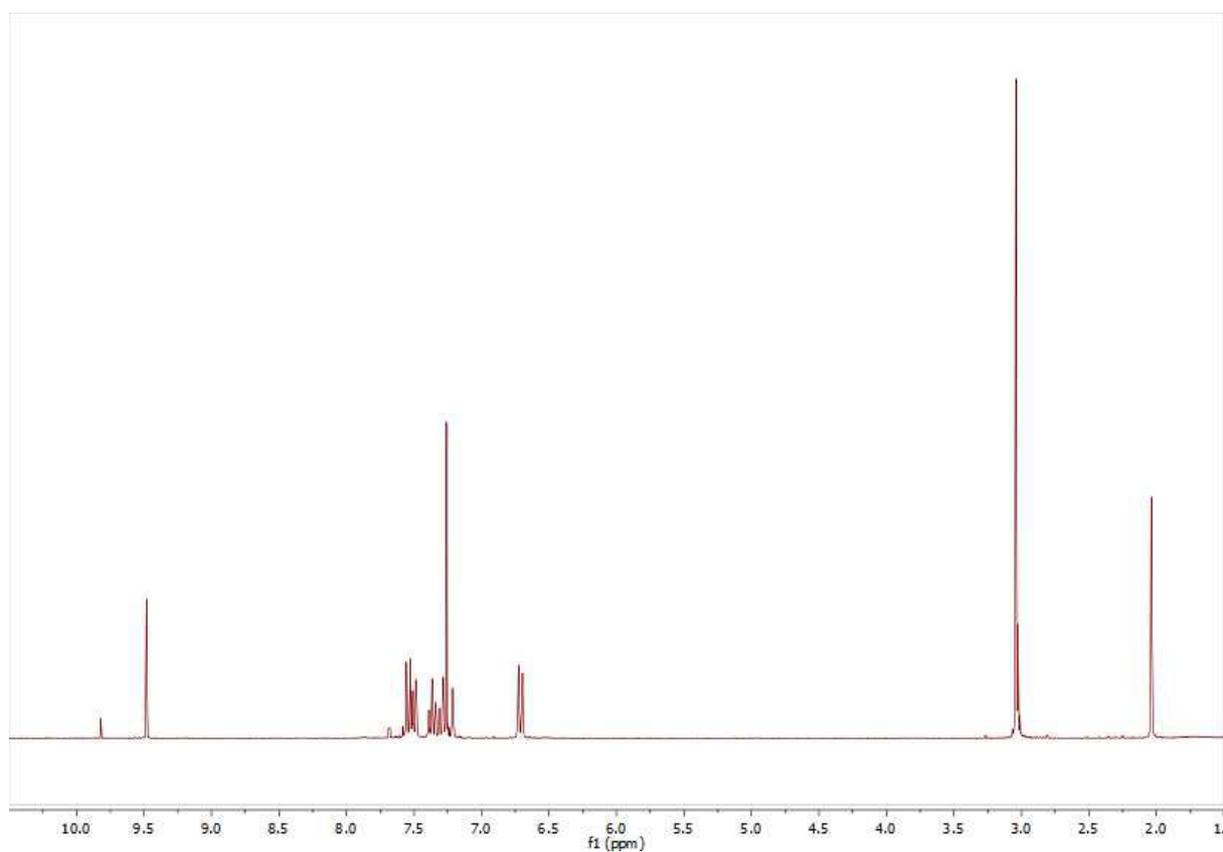


Figure S9: ^1H NMR spectrum (300 MHz, 298 K, CDCl_3) of **9**.

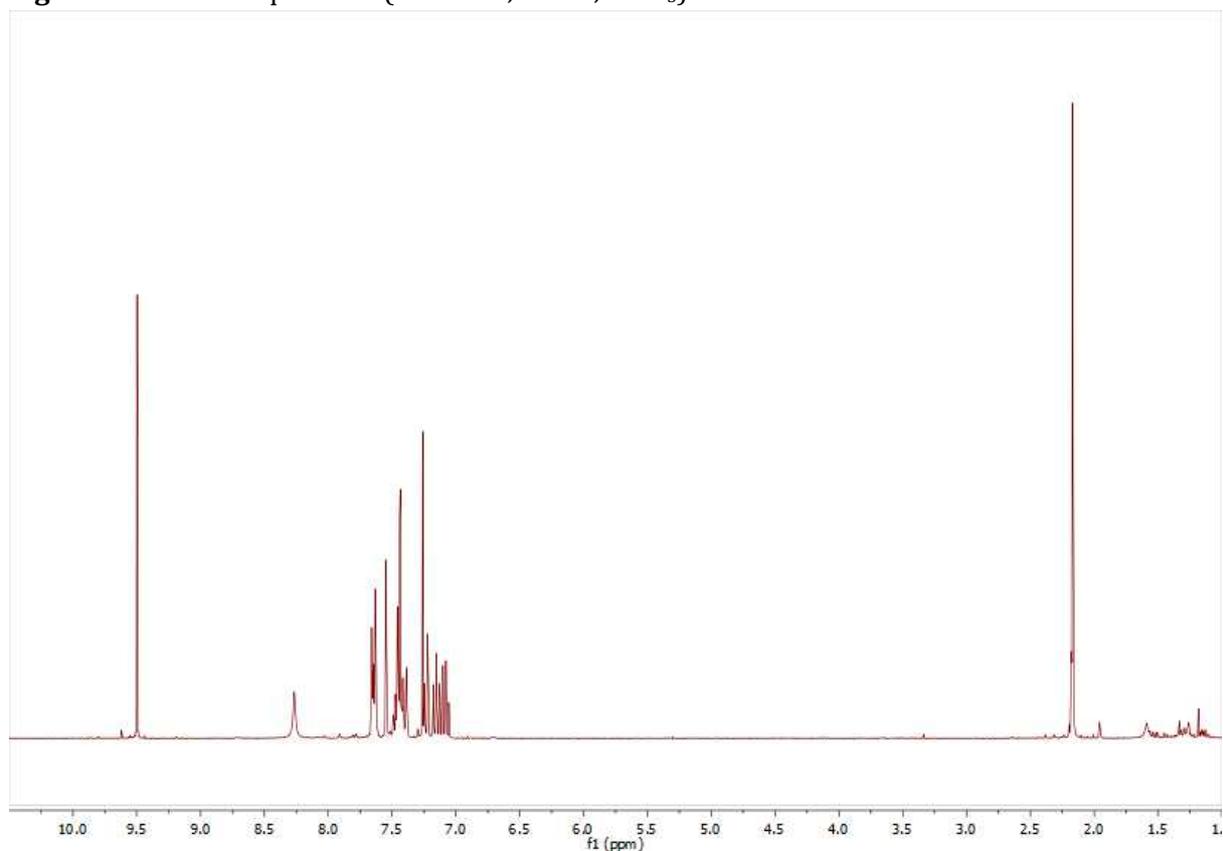


Figure S10: ^1H NMR spectrum (300 MHz, 298 K, CDCl_3) of **10**.

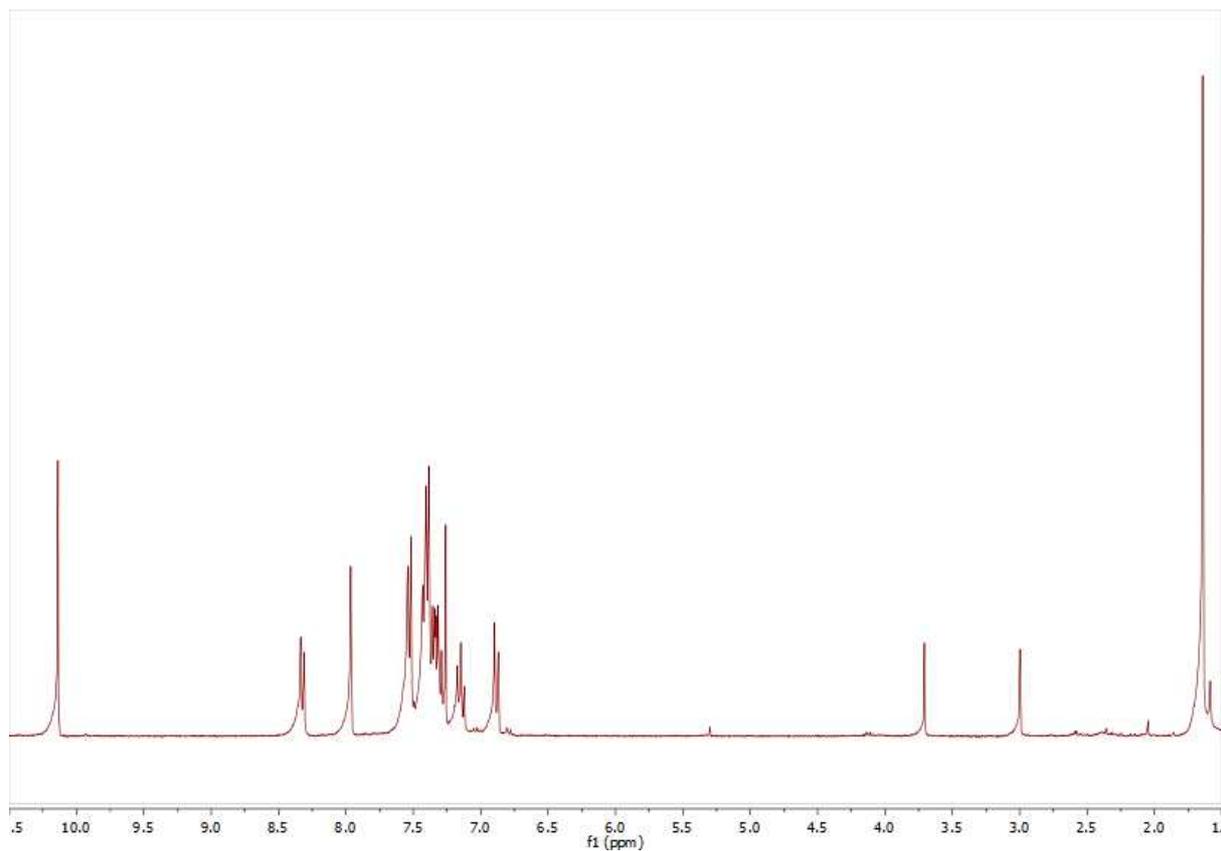


Figure S11: ¹H NMR spectrum (300 MHz, 298 K, CDCl₃) of **11**.

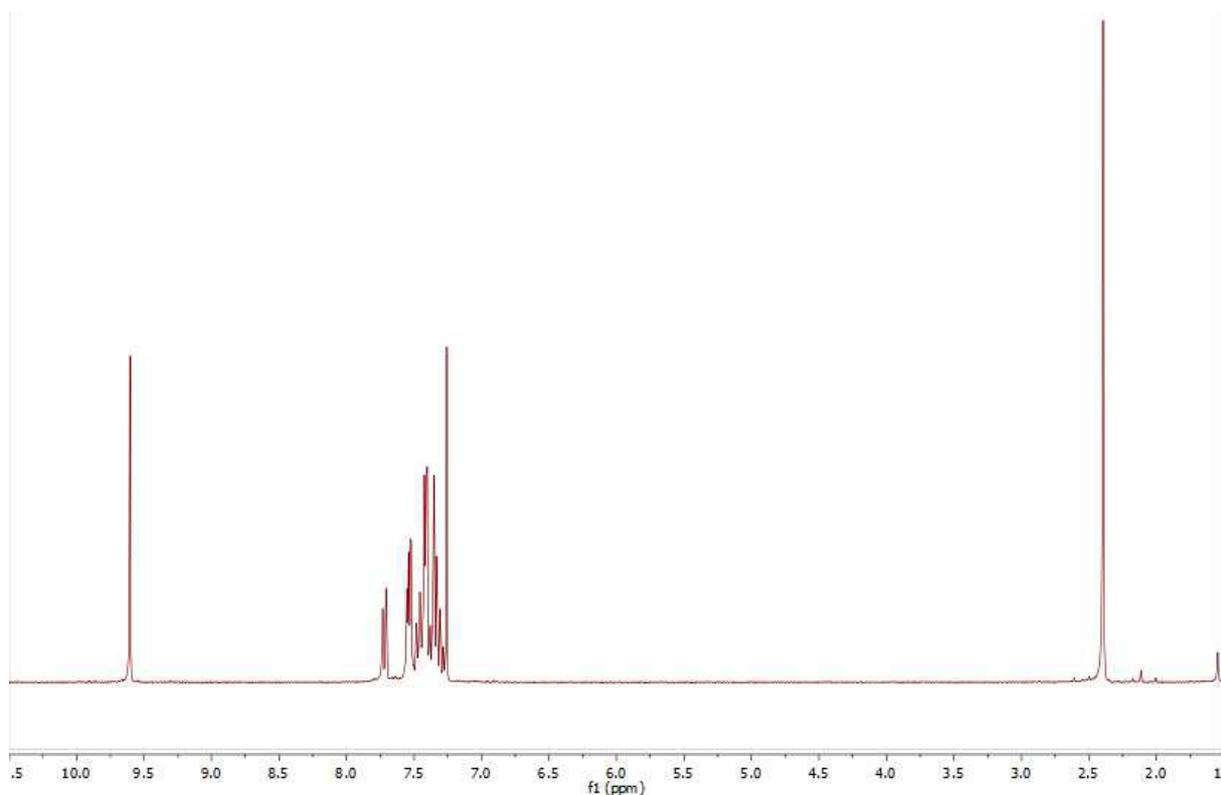


Figure S12: ¹H NMR spectrum (300 MHz, 298 K, CDCl₃) of **12**.

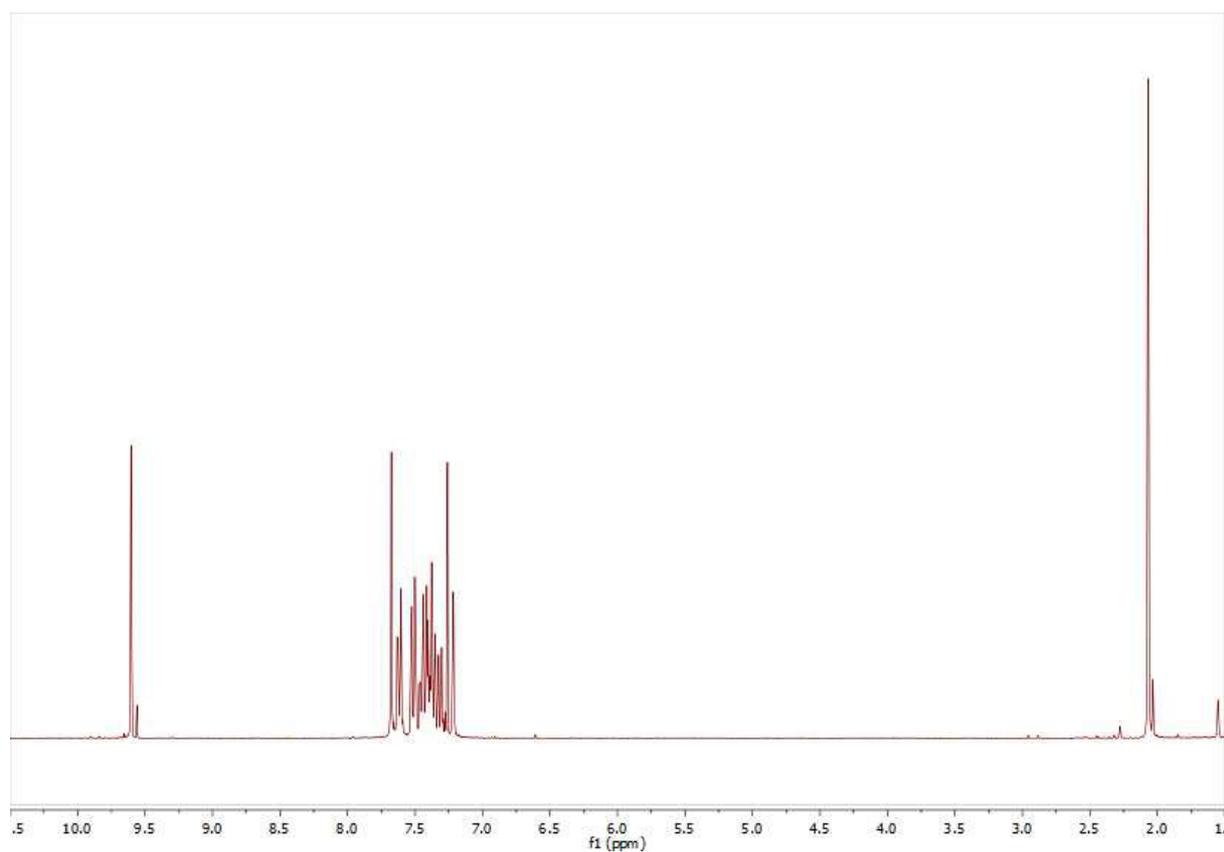


Figure S13: ^1H NMR spectrum (300 MHz, 298 K, CDCl_3) of **13**.

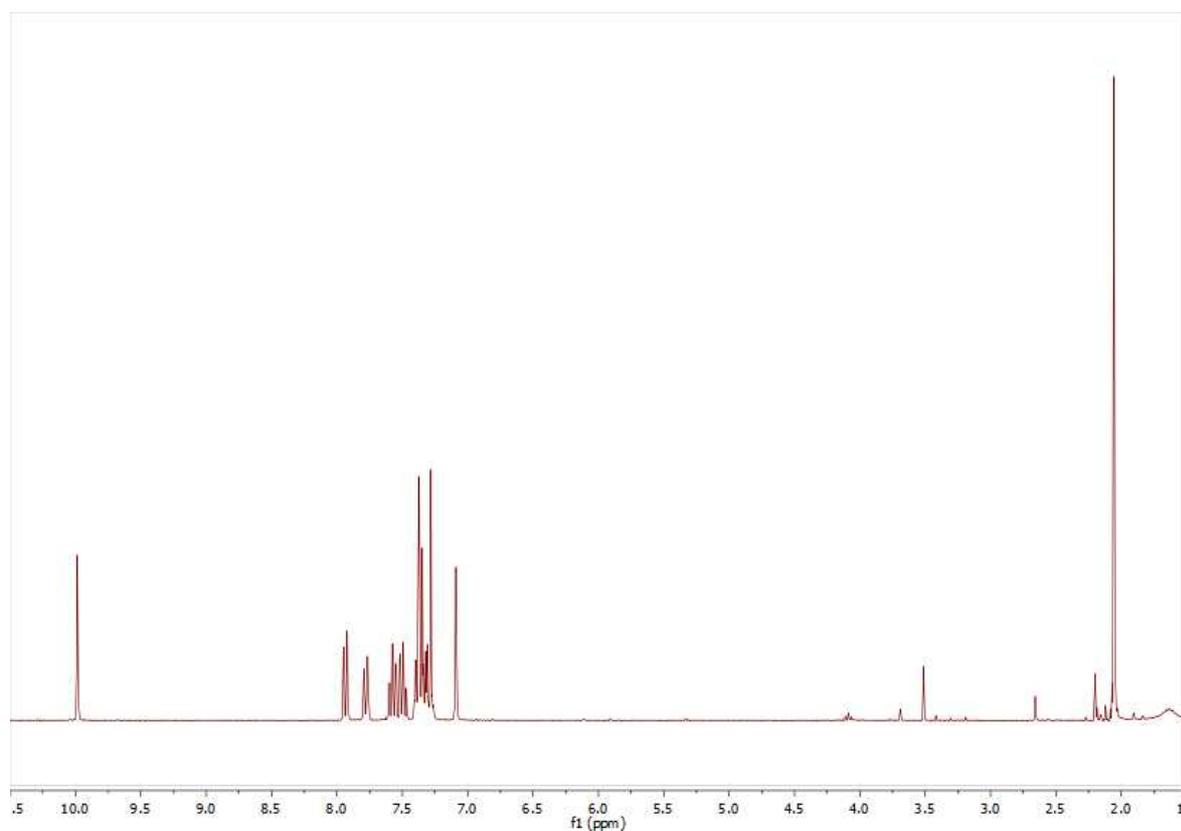


Figure S14: ^1H NMR spectrum (300 MHz, 298 K, CDCl_3) of **14**.

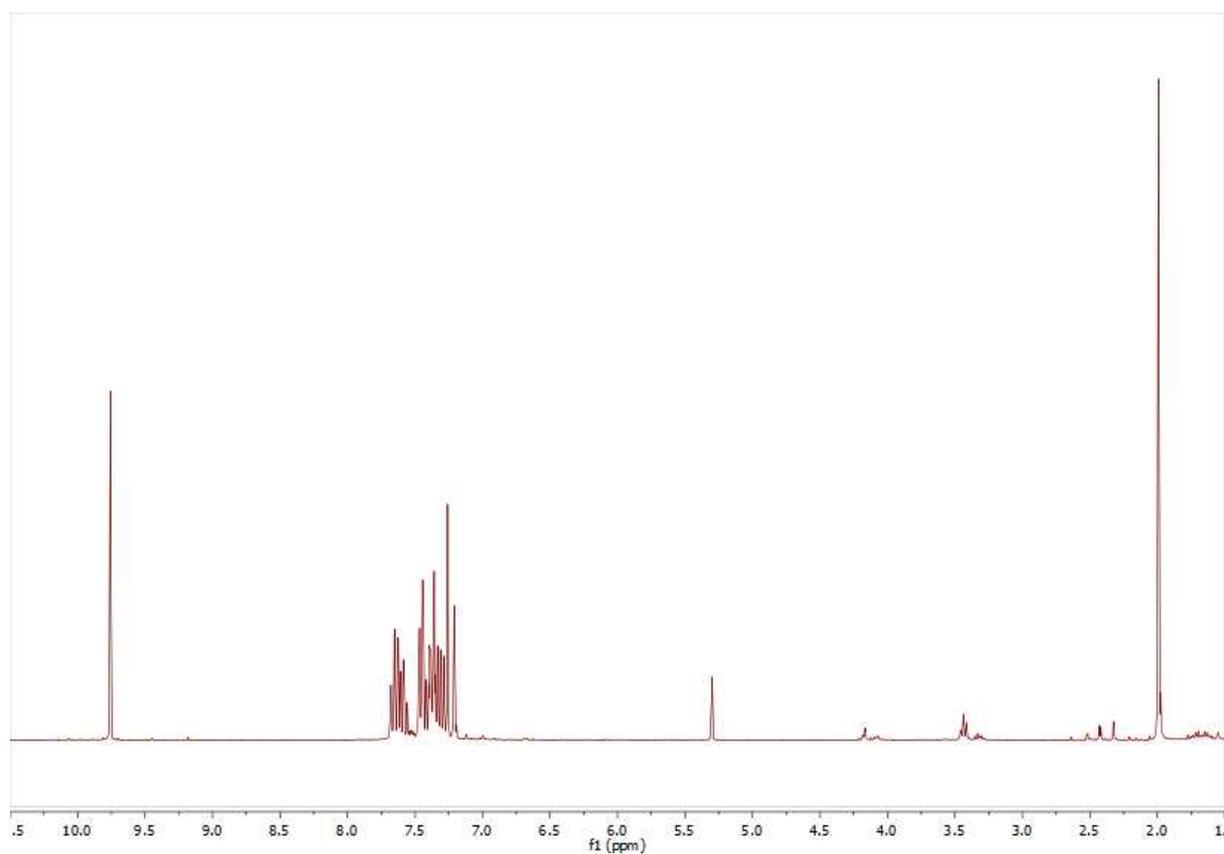


Figure S15: ^1H NMR spectrum (500 MHz, 298 K, CDCl_3) of **15**.

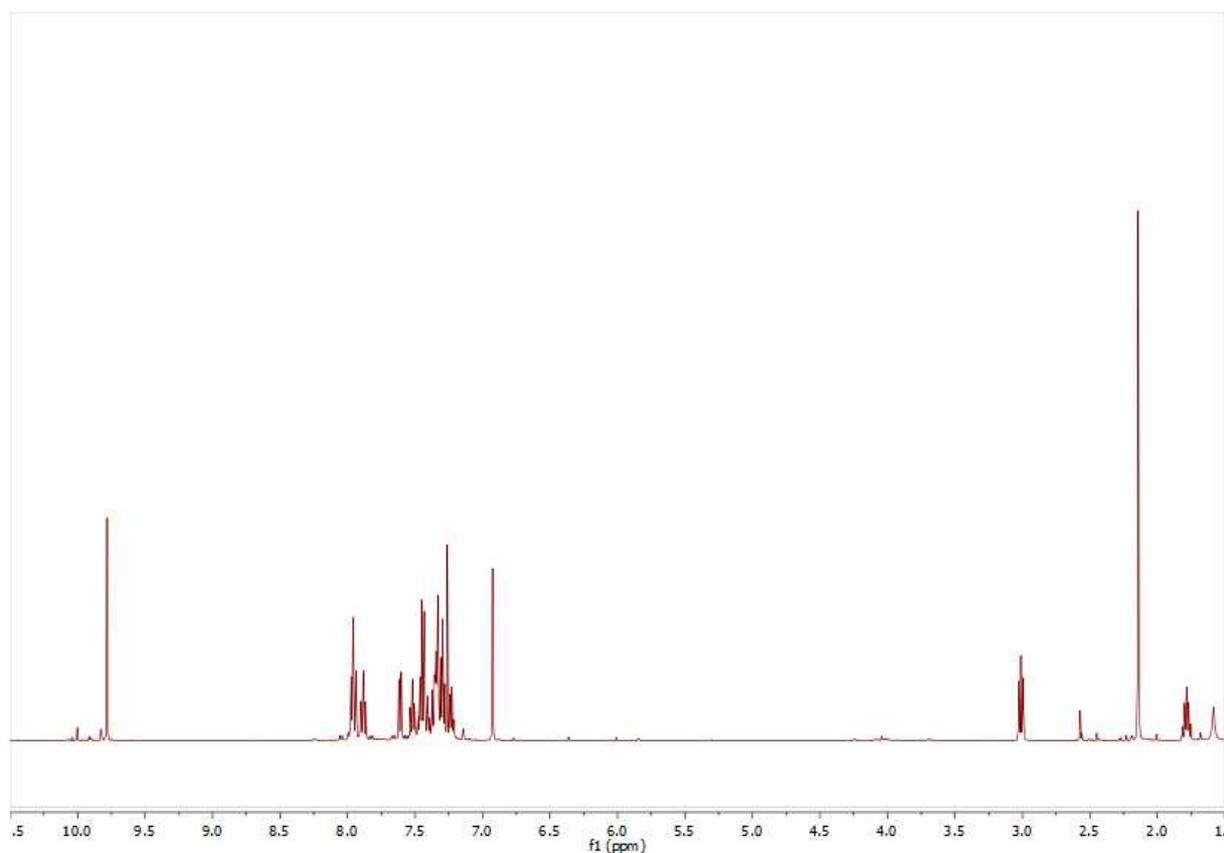


Figure S16: ^1H NMR spectrum (500 MHz, 298 K, CDCl_3) of **16**.

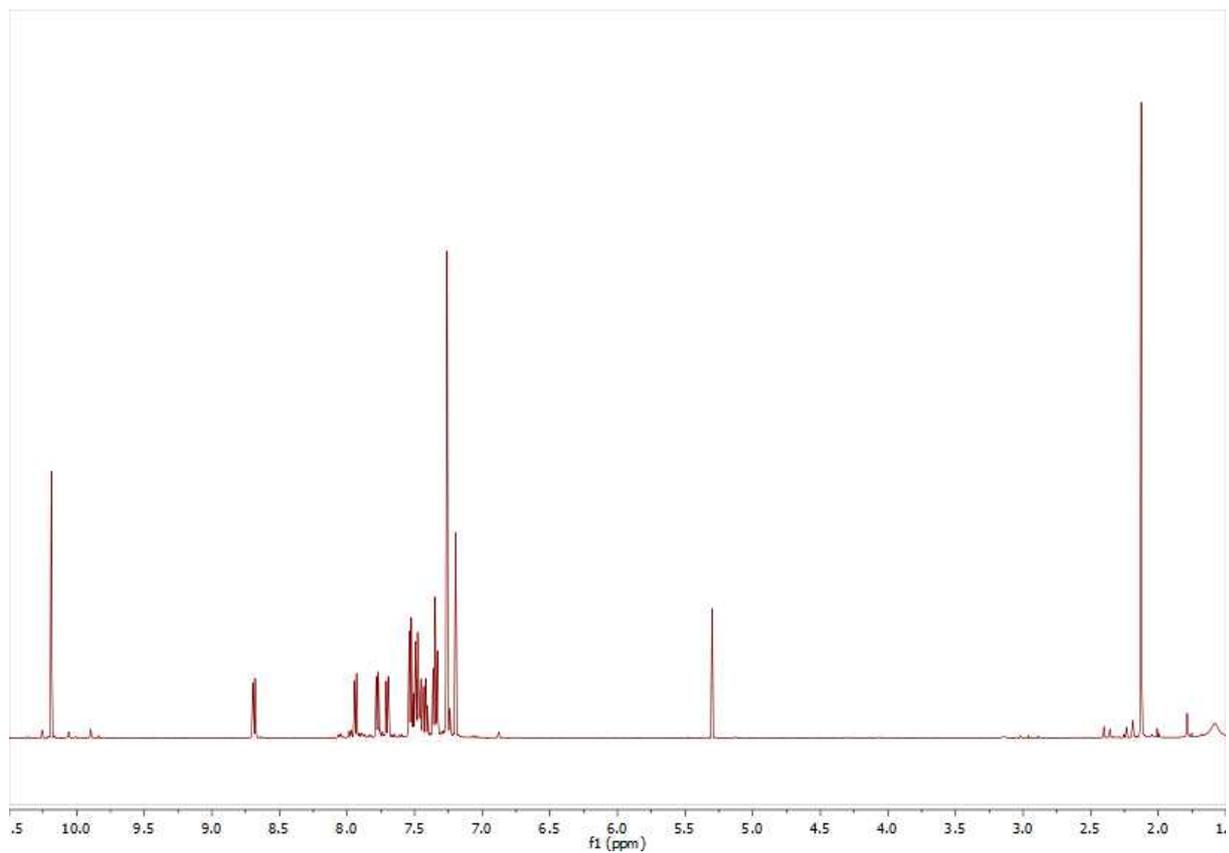


Figure S17: ^1H NMR spectrum (500 MHz, 298 K, CDCl_3) of **17**.

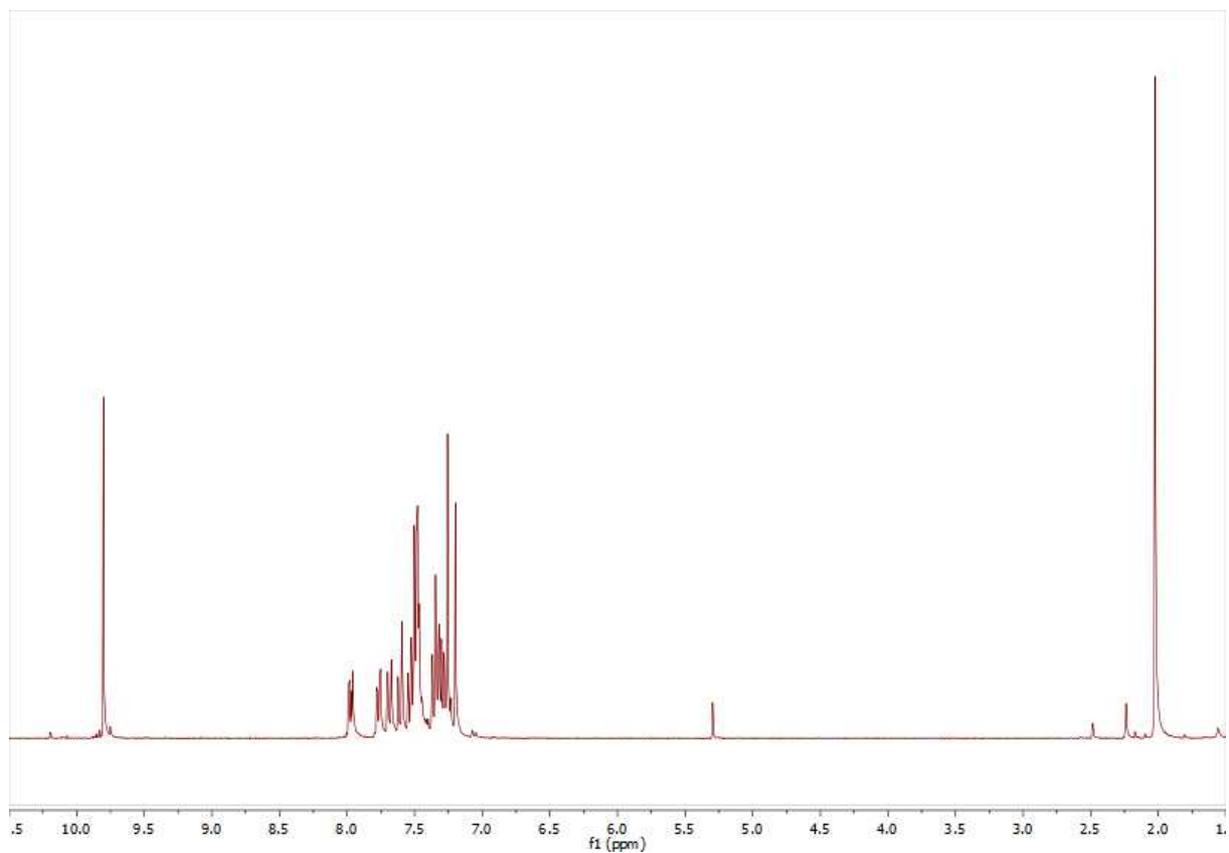


Figure S18: ^1H NMR spectrum (500 MHz, 298 K, CDCl_3) of **18**.

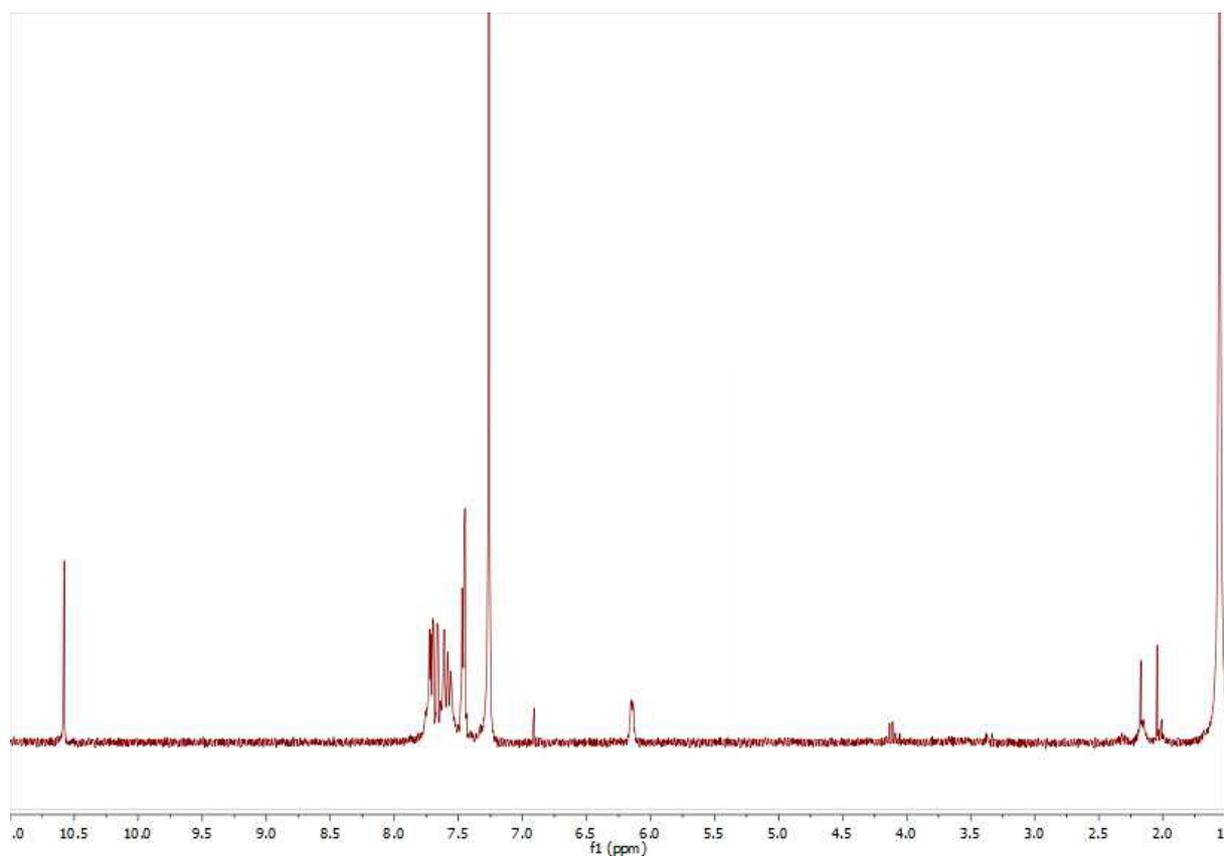


Figure S19: ^1H NMR spectrum (300 MHz, 298 K, CDCl_3) of **3r**.

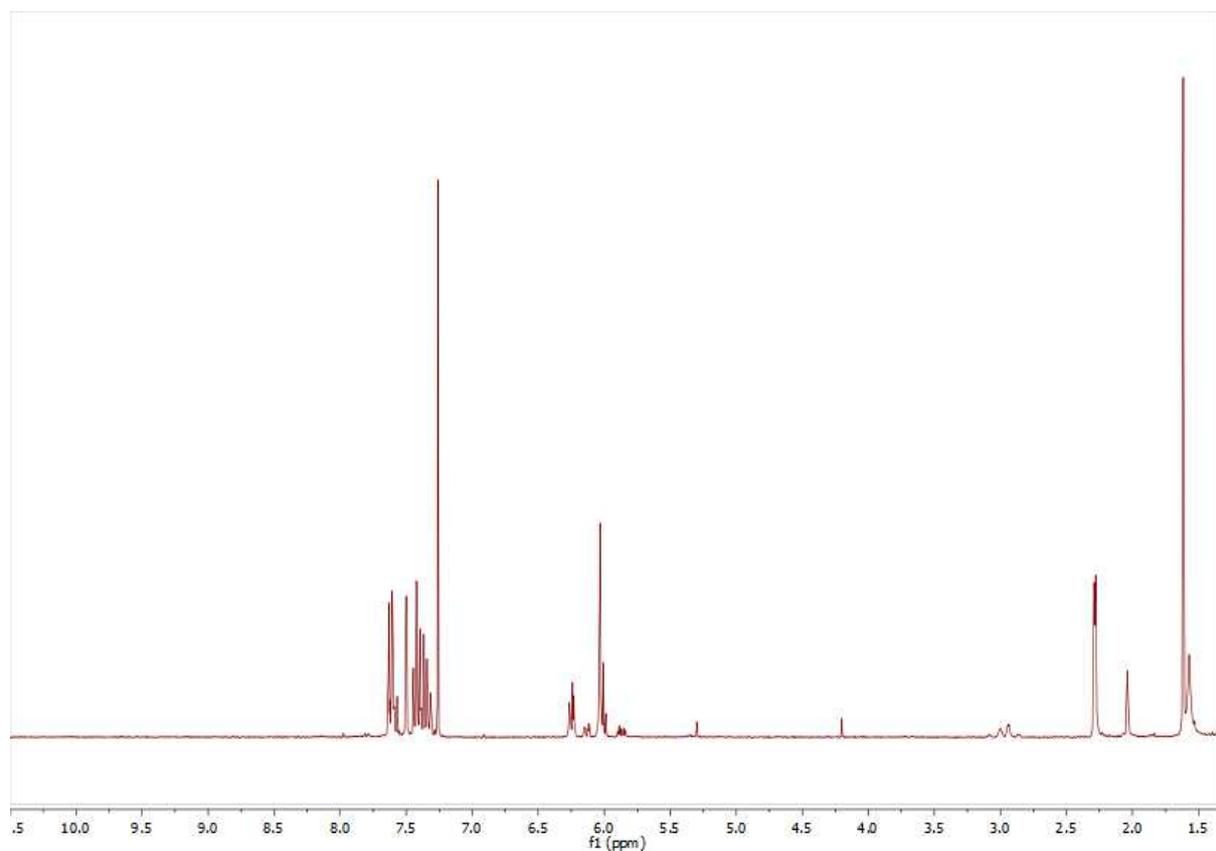


Figure S20: ^1H NMR spectrum (300 MHz, 298 K, CDCl_3) of **8r**.

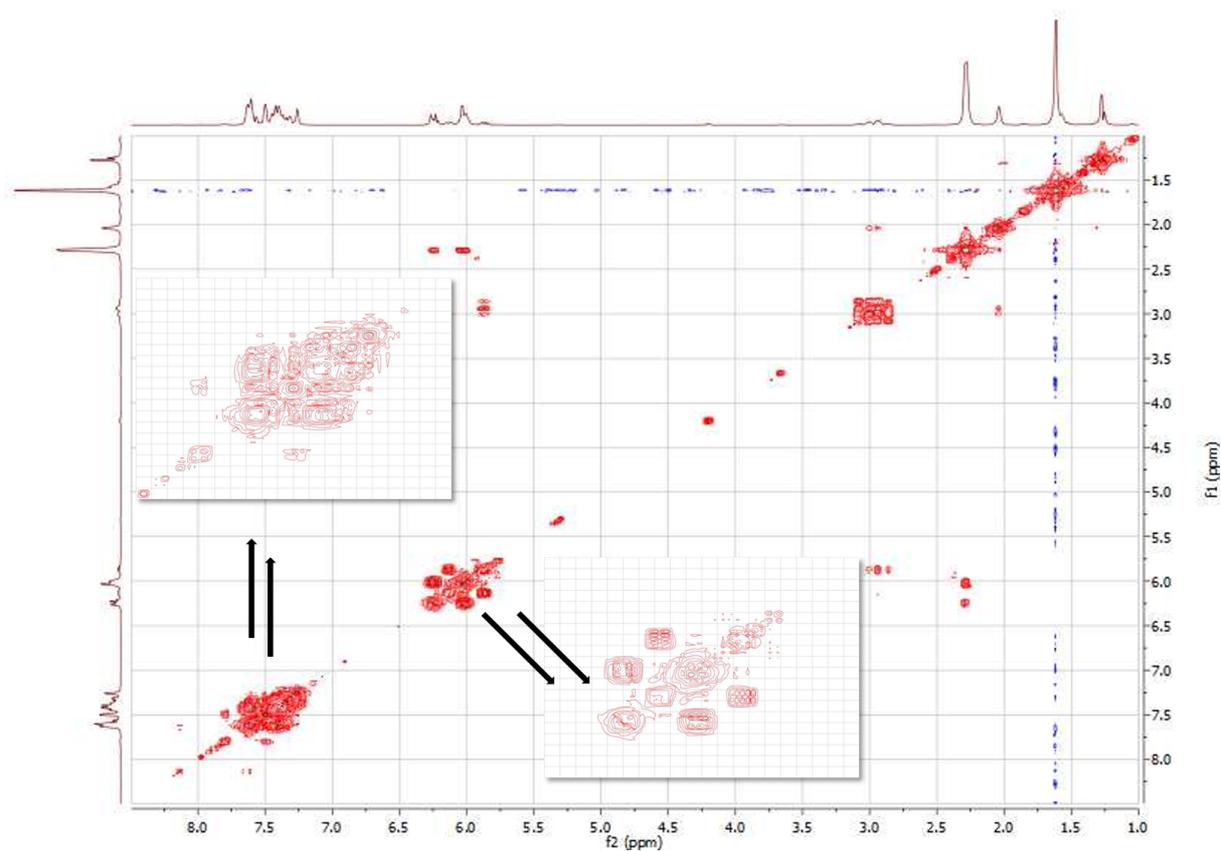


Figure S21: ^1H - ^1H COSY-NMR spectrum (300 MHz, 298 K, CDCl_3) of **8r**.

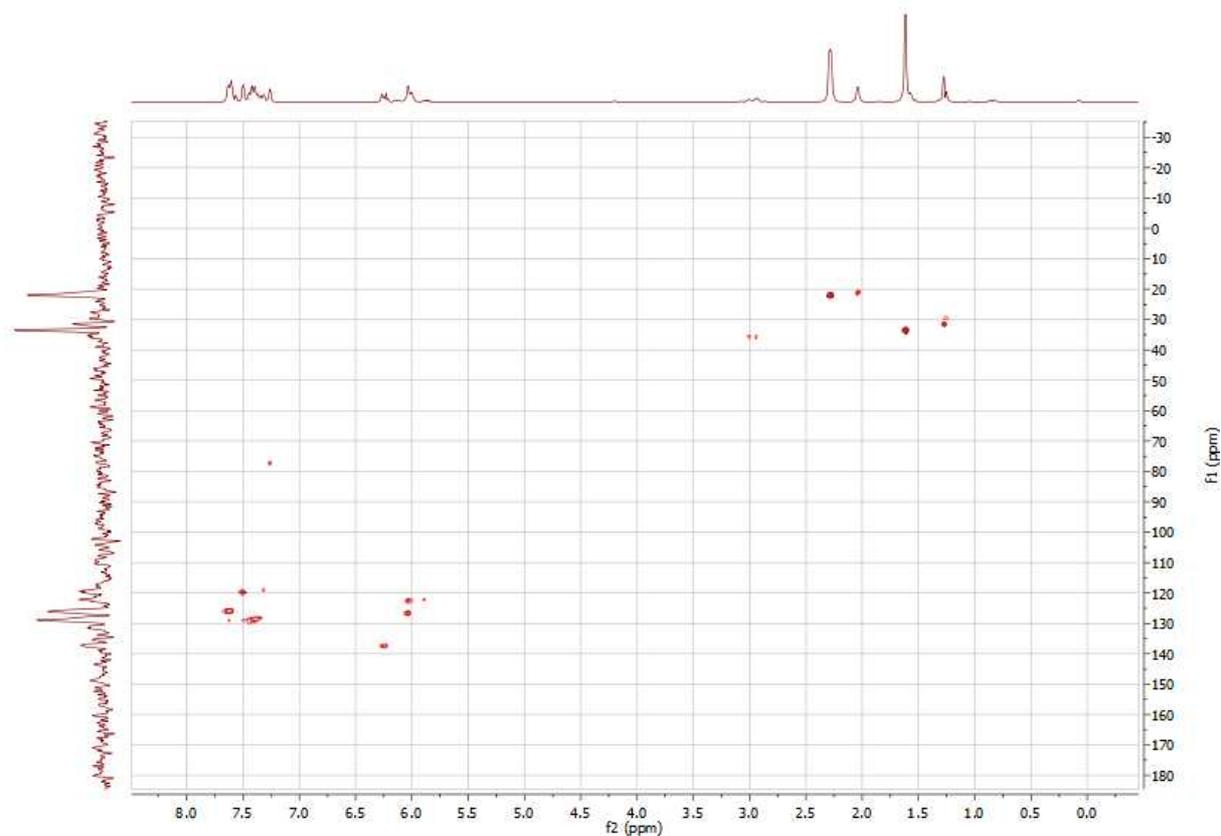


Figure S22: ^1H - ^{13}C HMQC NMR spectrum (300 MHz, 298 K, CDCl_3) of **8r**.

3. Photochemistry of Diarylethenes 1 - 18.

3.1. Determination of the photostationary state

The extinction coefficients of the open diarylethene isomers were determined upon precise preparation of stock solutions with defined concentrations and subsequent measurement of the absorption spectra. The molar absorptivity of the closed form was determined equally with respect to the ratio of isomers in the photostationary state (PSS) via UPLC using UV/vis-detection.

The ratio of open and closed isomer in the PSS was determined by injection of irradiated samples into a UPLC and detection with and UV/vis diode array integrated at the isosbestic point of the corresponding irradiation spectrum. The different ratio of water and CH₃CN caused by the gradient in the UPLC was disregarded as no significant shift of the spectra compared to the pure acetonitrile solutions was observed.

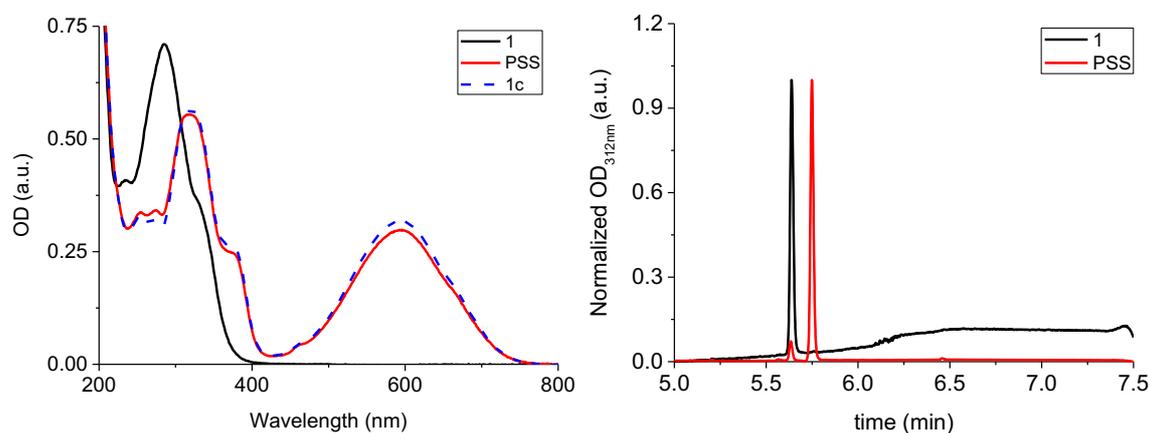


Figure S23: Left: Absorption spectra of **1** (1.93×10^{-5} M in aerated CH₃CN, **black**), the **PSS** reached upon irradiation at 365 nm (**red**), and the calculated spectrum for the pure closed isomer **1c** (**dashed blue**). Right: UPLC traces of compound **1** upon irradiation at 302 nm detected at the isosbestic point for the open form (**black**) and the photostationary state (**red**) (1.93×10^{-5} M in aerated CH₃CN).

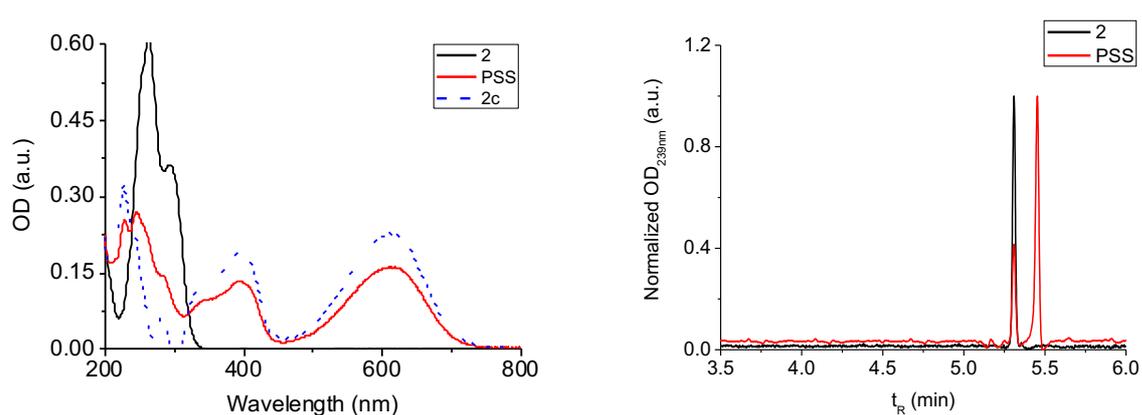


Figure S24: Left: Absorption spectra of **2** (1.93×10^{-5} M in aerated CH₃CN, **black**), the **PSS** reached upon irradiation at 365 nm (**red**), and the calculated spectrum for the pure closed isomer **2c** (**dashed blue**). Right: UPLC traces of compound **2** upon irradiation at 302 nm detected at the isosbestic point for the open form (**black**) and the photostationary state (**red**) (1.93×10^{-5} M in aerated CH₃CN).

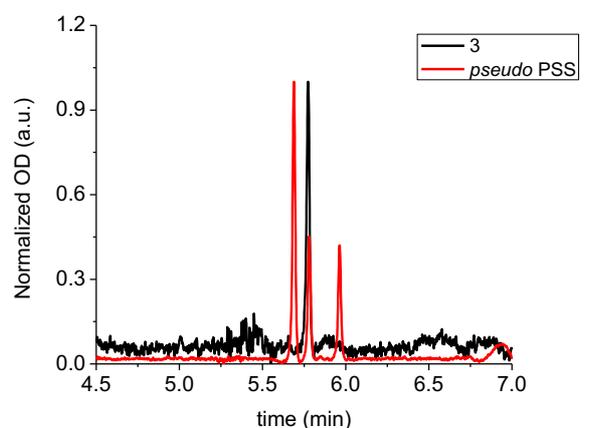


Figure S25: Comparison between the UPLC traces recorded for of **3** (2.45×10^{-5} M in aerated CH₃CN, **black**) and the *pseudo*PSS reached upon irradiation at 365 nm (**red**); from left to right the peaks belong to the closed isomer **3c** ($t_R = 5.69$ min), the open isomer **3o** ($t_R = 5.78$ min), and the rearrangement product **3r** ($t_R = 5.96$ min).

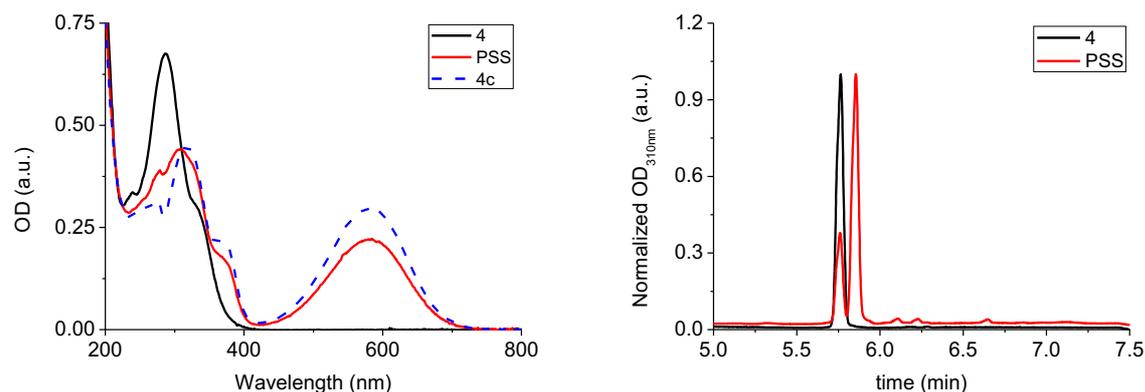


Figure S26: Left: Absorption spectra of **4** (1.93×10^{-5} M in aerated CH_3CN , **black**), the **PSS** reached upon irradiation at 365 nm (**red**), and the calculated spectrum for the pure closed isomer **4c** (**dashed blue**). Right: UPLC traces of compound **4** upon irradiation at 365 nm detected at the isosbestic point for the open form (**black**) and the photostationary state (**red**) (1.93×10^{-5} M in aerated CH_3CN).

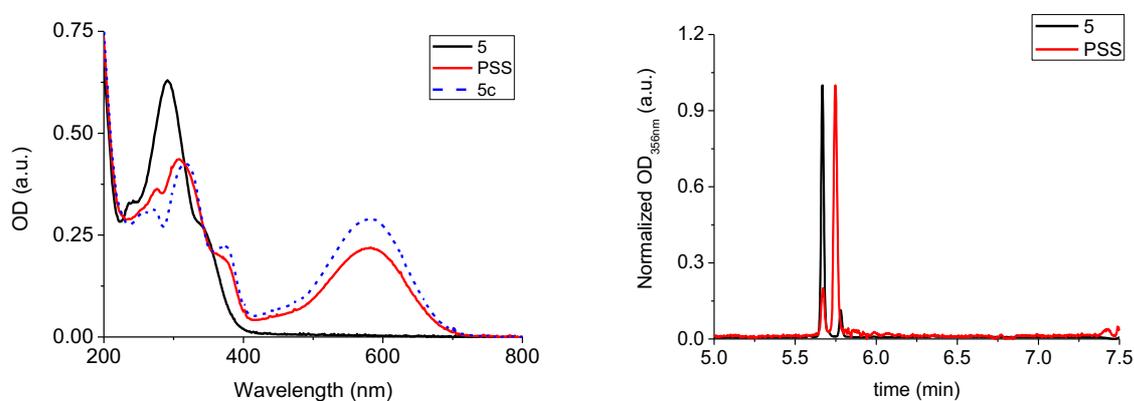


Figure S27: Left: Absorption spectra of **5** (1.93×10^{-5} M in aerated CH_3CN , **black**), the **PSS** reached upon irradiation at 365 nm (**red**), and the calculated spectrum for the pure closed isomer **5c** (**dashed blue**). Right: UPLC traces of compound **5** upon irradiation at 365 nm detected at the isosbestic point for the open form (**black**) and the photostationary state (**red**) (1.93×10^{-5} M in aerated CH_3CN).

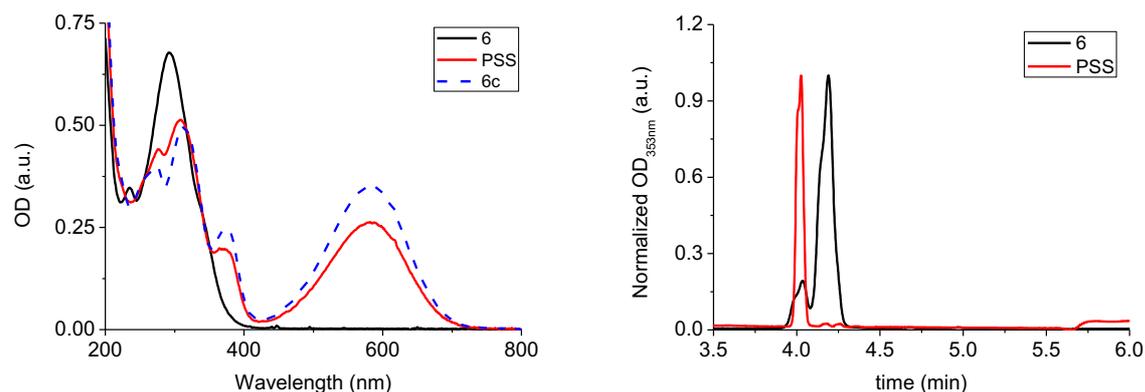


Figure S28: Left: Absorption spectra of **6** (1.93×10^{-5} M in aerated CH_3CN , **black**), the **PSS** reached upon irradiation at 365 nm (**red**), and the calculated spectrum for the pure closed isomer **6c** (**dashed blue**). Right: UPLC traces of compound **6** upon irradiation at 365 nm detected at the isosbestic point for the open form (**black**) and the photostationary state (**red**) (1.93×10^{-5} M in aerated CH_3CN).

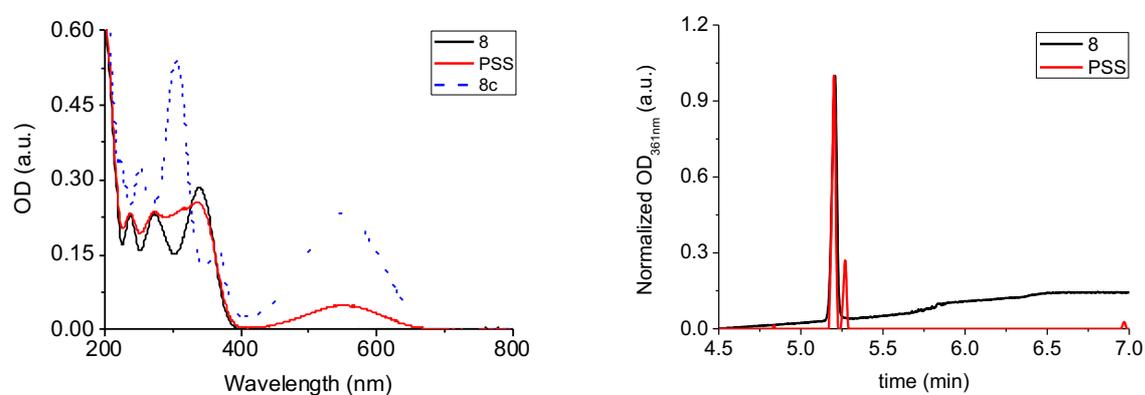


Figure S29: Left: Absorption spectra of **8** (1.98×10^{-5} M in aerated CH_3CN , **black**), the **PSS** reached upon irradiation at 365 nm (**red**), and the calculated spectrum for the pure closed isomer **8c** (**dashed blue**). Right: UPLC traces of compound **8** upon irradiation at 365 nm detected at the isosbestic point for the open form (**black**) and the photostationary state (**red**) (1.98×10^{-5} M in aerated CH_3CN).

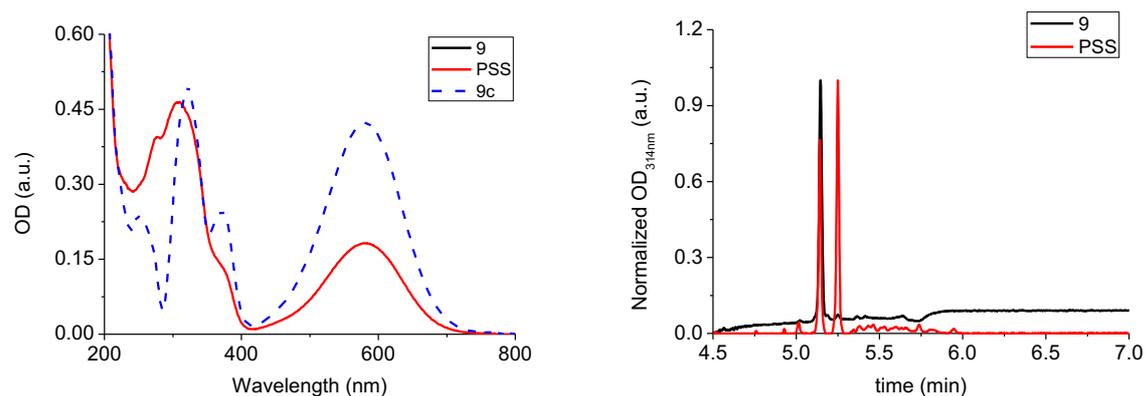


Figure S30: Left: Absorption spectra of **9** (1.92×10^{-5} M in aerated CH_3CN , **black**), in acidic conditions ($[\text{MsOH}] = 1.02 \times 10^{-4}$ M), the **PSS** reached upon irradiation at 365 nm (**red**), and the calculated spectrum for the pure closed isomer **9c** (**dashed blue**). Right: UPLC traces of compound **9** upon irradiation at 365 nm detected at the isosbestic point for the open form (**black**) and the photostationary state (**red**) (1.92×10^{-5} M in aerated CH_3CN).

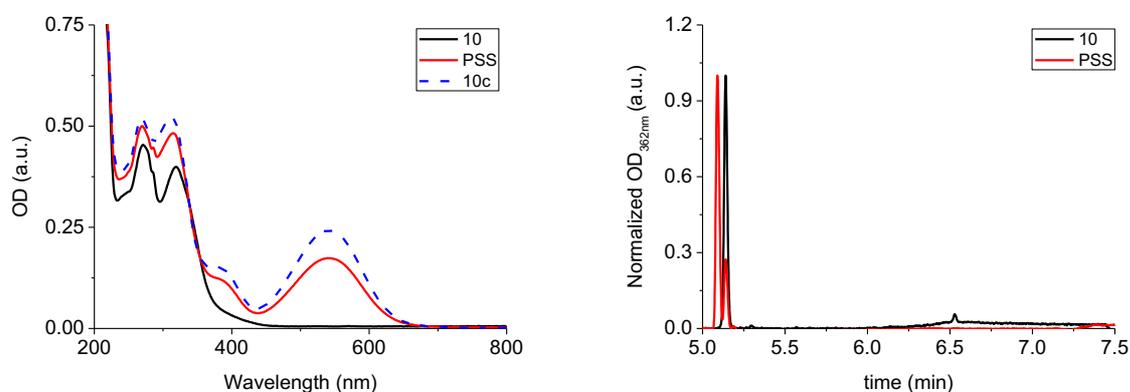


Figure S31: Left: Absorption spectra of **10** (4×10^{-5} M in aerated *n*-hexane, **black**), the **PSS** reached upon irradiation at 365 nm (**red**), and the calculated spectrum for the pure closed isomer **10c** (**dashed blue**). Right: UPLC traces of compound **10** upon irradiation at 365 nm detected at the isosbestic point for the open form (**black**) and the photostationary state (**red**) (4×10^{-5} M in aerated *n*-hexane).

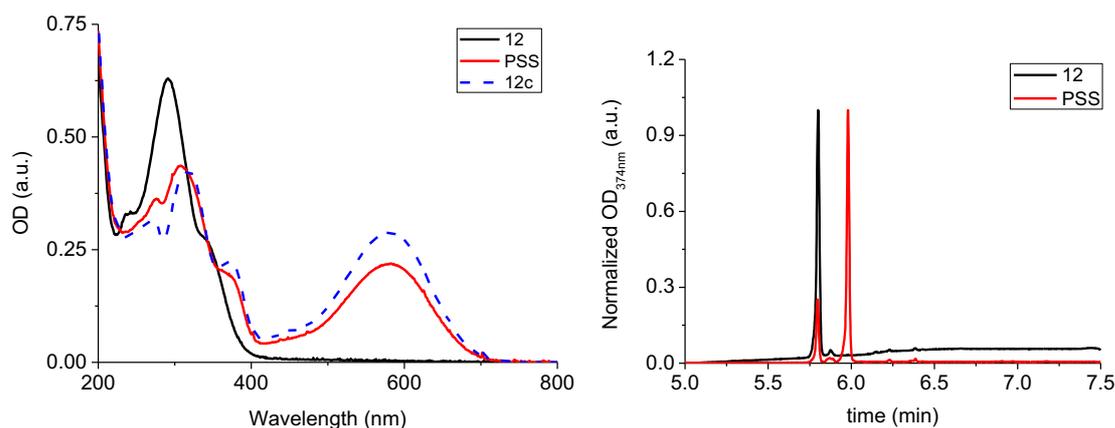


Figure S32: Left: Absorption spectra of **12** (1.93×10^{-5} M in aerated CH_3CN , **black**), the **PSS** reached upon irradiation at 365 nm (**red**), and the calculated spectrum for the pure closed isomer **12c** (**dashed blue**). Right: UPLC traces of compound **12** upon irradiation at 365 nm detected at the isosbestic point for the open form (**black**) and the photostationary state (**red**) (1.93×10^{-5} M in aerated CH_3CN).

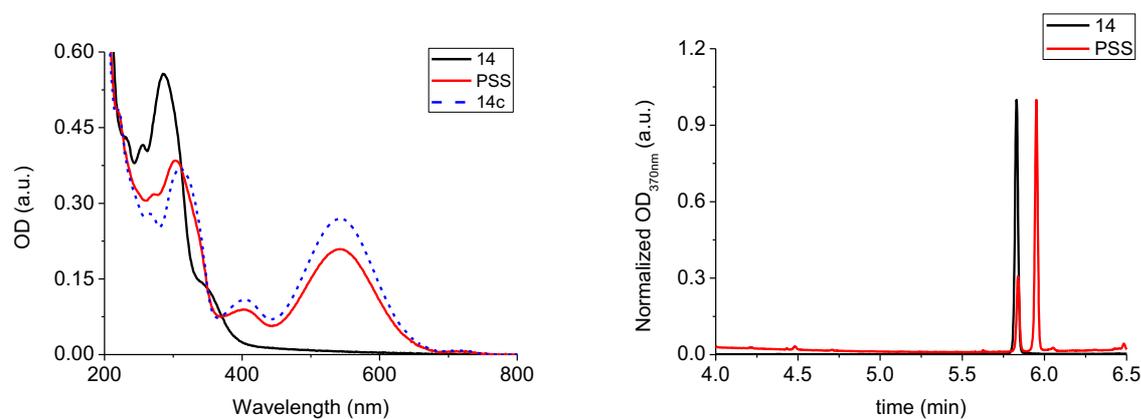


Figure S33: Left: Absorption spectra of **14** (1.93×10^{-5} M in aerated CH_3CN , **black**), the **PSS** reached upon irradiation at 365 nm (**red**), and the calculated spectrum for the pure closed isomer **14c** (**dashed blue**). Right: UPLC traces of compound **14** upon irradiation at 365 nm detected at the isosbestic point for the open form (**black**) and the photostationary state (**red**) (1.93×10^{-5} M in aerated CH_3CN).

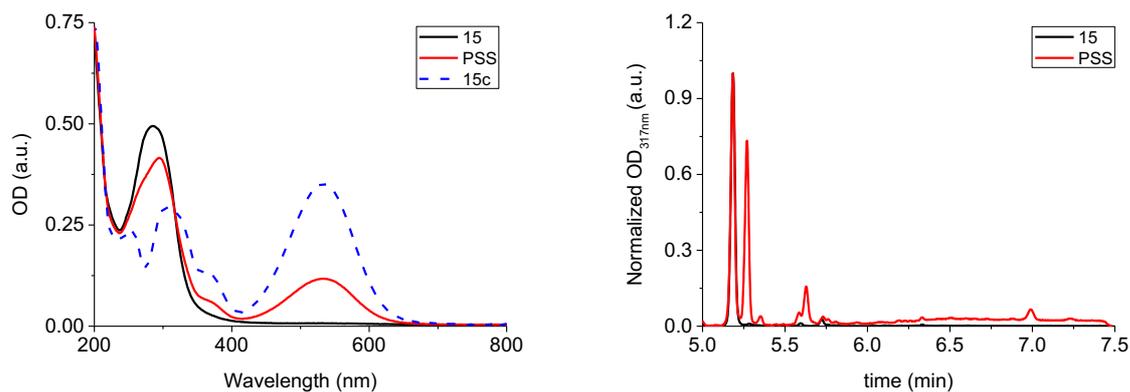


Figure S34: Left: Absorption spectra of **15** (4×10^{-5} M in aerated CH_3CN , **black**), the **PSS** reached upon irradiation at 365 nm (**red**), and the calculated spectrum for the pure closed isomer **15c** (**dashed blue**). Right: UPLC traces of compound **15** upon irradiation at 365 nm detected at the isosbestic point for the open form (**black**) and the photostationary state (**red**) (4×10^{-5} M in aerated CH_3CN).

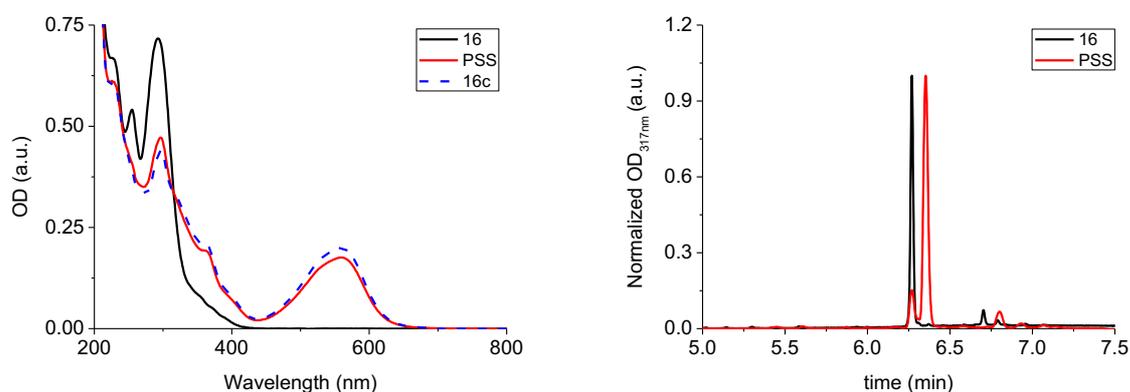


Figure S35: Left: Absorption spectra of **16** (4×10^{-5} M in aerated CH_3CN , **black**), the **PSS** reached upon irradiation at 365 nm (**red**), and the calculated spectrum for the pure closed isomer **16c** (**dashed blue**). Right: UPLC traces of compound **16** upon irradiation at 365 nm detected at the isosbestic point for the open form (**black**) and the photostationary state (**red**) (4×10^{-5} M in aerated CH_3CN).

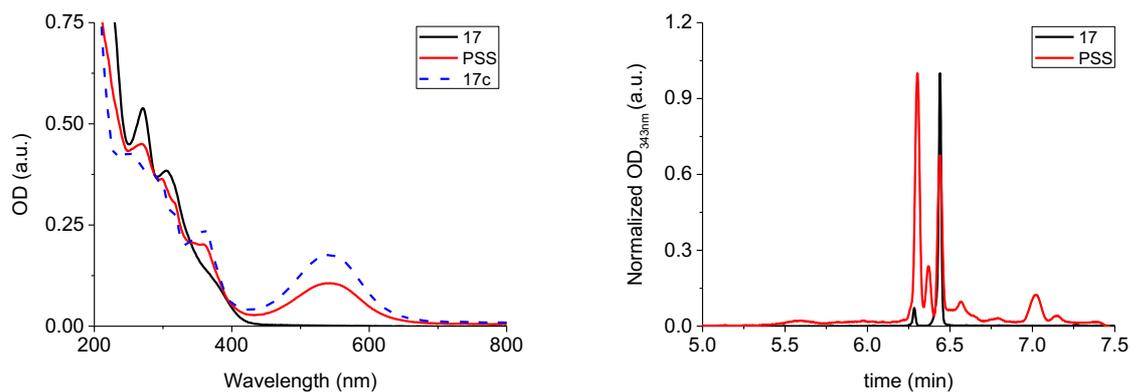


Figure S36: Left: Absorption spectra of **17** (4×10^{-5} M in aerated CH_3CN , **black**), the **PSS** reached upon irradiation at 365 nm (**red**), and the calculated spectrum for the pure closed isomer **17c** (**dashed blue**). Right: UPLC traces of compound **17** upon irradiation at 365 nm detected at the isosbestic point for the open form (**black**) and the photostationary state (**red**) (4×10^{-5} M in aerated CH_3CN).

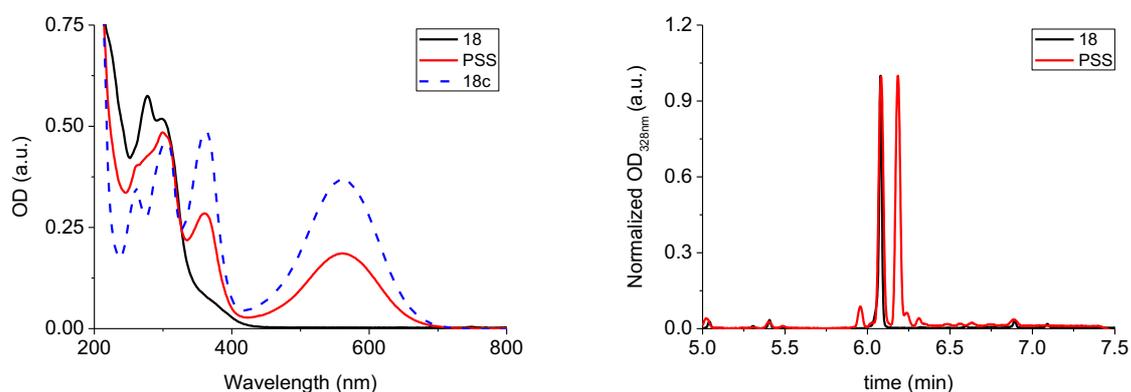


Figure S37: Left: Absorption spectra of **18** (4×10^{-5} M in aerated CH_3CN , **black**), the **PSS** reached upon irradiation at 365 nm (**red**), and the calculated spectrum for the pure closed isomer **18c** (**dashed blue**). Right: UPLC traces of compound **18** upon irradiation at 365 nm detected at the isosbestic point for the open form (**black**) and the photostationary state (**red**) (4×10^{-5} M in aerated CH_3CN).

Table S1: Absorption maxima and corresponding extinction coefficients of the investigated diarylethenes as open and closed isomers in CH₃CN.

Compound	UV-band	visible band
	λ_{\max} [nm], $\epsilon(\lambda_{\max})$ [L mol ⁻¹ cm ⁻¹]	
1o	268, 28300	
1c	327, 15700	607, 12000
2o	263, 31800	
2c	227, 16800	615, 11800
3o	331, 27900	
3c	/(a)	/(a)
4o	286, 34900	
4c	308, 30600	582, 15400
5o	288, 32200	
5c	319, 22100	581, 14300
6o	291, 35300	
6c	309, 29400	585, 15200
7o	284, 18200	
7c	/(a)	/(a)
8o	339, 14400	
8c	305, 27200	552, 10200
9o	288, 34300 ^(b)	
9c	319, 24600 ^(b)	583, 20600 ^(b)
10o	271, 15300 ^(c)	
10c	269, 16700 ^(c)	541, 5800 ^(c)
11o	277, 26100	
11c	/(d)	/(d)
12o	335, 15700	
12c	310, 19300	533, 16200
13o	266, 30700	
13c	/(a)	/(a)
14o	286, 27400	
14c	309, 19200	542, 14000
15o	284, 12400	
15c	302, 7400	535, 20300
16o	292, 18000	
16c	297, 11000	560, 9100
17o	271, 13500	
17c	254, 10700	543, 7800
18o	274, 14000	
18c	362, 12200	561, 12000

^(a) decomposition occurring before reaching the PSS^(b) evaluated in acidic conditions ([MsOH] = 1.02 x 10⁻⁴ M)^(c) data evaluated in *n*-hexane^(d) no switching behavior revealed

Table S2: Open/closed isomers ratio of the different DAEs the photostationary state determined from the analysis of UPLC peak area at the given isosbestic point.

Compound	λ_{irr} (nm)	λ_{iso} (nm)	o/c ratio (%)
1	302	312	13/87
2	302	239	29/71
3	365	/(a)	/(a)
4	365	310	25/75
5	365	356	25/75
6	365	353	11/89
7	365	/(a)	/(a)
8	365	361	79/21
9	365	314 ^(b)	57/43 ^(b)
10	313	362 ^(c)	29/71 ^(c)
11	365	/(d)	/(d)
12	365	374	19/81
13	365	/(a)	/(a)
14	365	370	23/77
15	365	317	68/32
16	365	317	12/88
17	365	343	50/50
18	365	328	40/60

^(a) decomposition occurring before reaching the PSS

^(b) evaluated in acidic conditions ($[MsOH] = 1.02 \times 10^{-4} M$)

^(c) data evaluated in *n*-hexane

^(d) no switching behavior revealed

3.2. Thermal decays

Table S3: Monitoring the thermal decay for a solution of DAE after reaching the PSS, for two hours at 25 °C in the dark. (Percentages are referred to the quantity of closed switch present at the PSS).

Compound	λ_{\max} (nm)	DAE-c (%)
1	607	98
2	615	100
3	/(a)	96(a)
4	582	99
5	581	98
6	585	99
7	/(a)	/(a)
8	552	78
9	583(b)	27(b)
10	541(c)	97(c)
11	/(d)	/(d)
12	533	96
13	/(a)	/(a)
14	542	100
15	535	98
16	560	71
17	543	93
18	561	95

(a) decomposition occurring before reaching the PSS

(b) evaluated in acidic conditions ($[MsOH] = 1.02 \times 10^{-4} M$)

(c) data evaluated in *n*-hexane

(d) no switching behavior revealed

3.3. Switching cycles

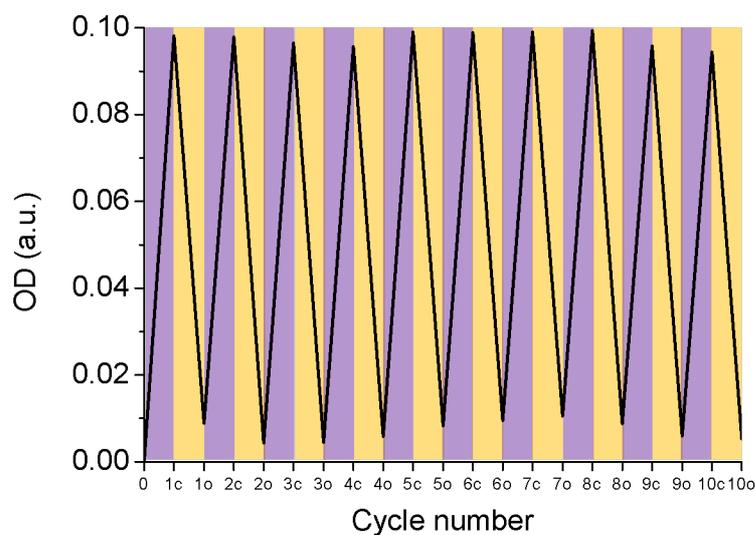


Figure S38: Switching cycles consisting of alternate irradiation with UV light until reaching the PSS and visible light until no further spectral changes can be detected of **1** ($c = 0.94 \times 10^{-5}$ M in CH_3CN , $\lambda_{irr1} = 365$ nm, $\lambda_{irr2} > 440$ nm); evolution of the OD at 607 nm.

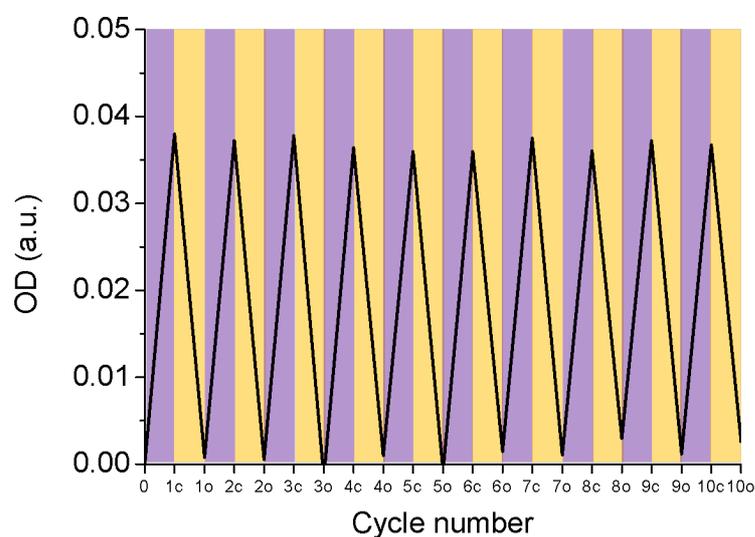


Figure S39: Switching cycles consisting of alternate irradiation with UV light until reaching the PSS and visible light until no further spectral changes can be detected of **2** ($c = 0.50 \times 10^{-5}$ M in CH_3CN , $\lambda_{irr1} = 365$ nm, $\lambda_{irr2} > 440$ nm); evolution of the OD at 615 nm.

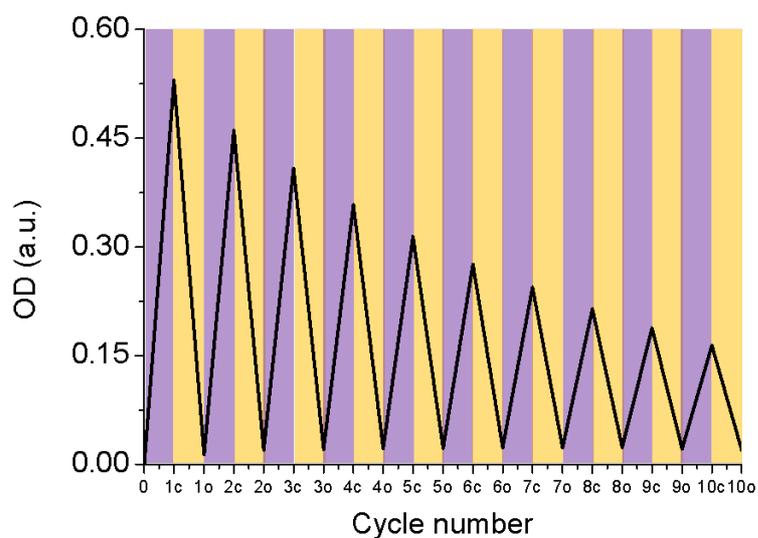


Figure S40: Switching cycles consisting of alternate irradiation with UV light until reaching the PSS and visible light until no further spectral changes can be detected of **4** ($c = 4.61 \times 10^{-5}$ M in CH_3CN , $\lambda_{\text{irr}1} = 365$ nm, $\lambda_{\text{irr}2} > 440$ nm); evolution of the OD at 582 nm.

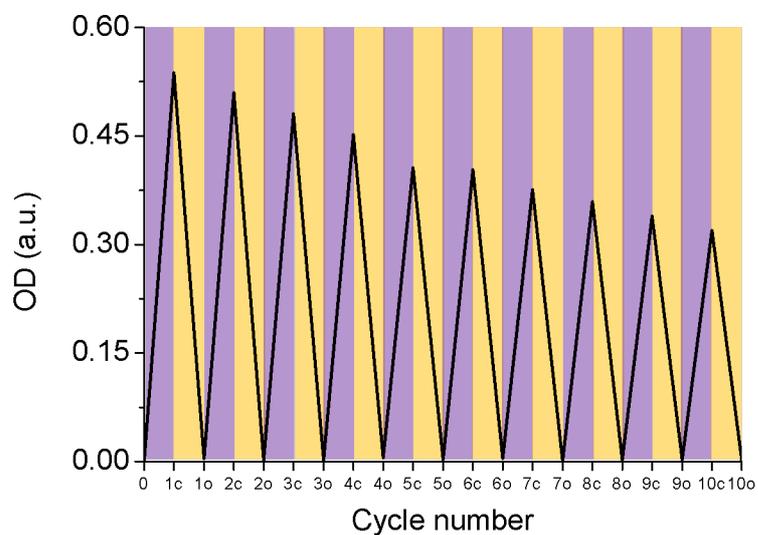


Figure S41: Switching cycles consisting of alternate irradiation with UV light until reaching the PSS and visible light until no further spectral changes can be detected of **5** ($c = 5.01 \times 10^{-5}$ M in CH_3CN , $\lambda_{\text{irr}1} = 365$ nm, $\lambda_{\text{irr}2} > 440$ nm); evolution of the OD at 581 nm.

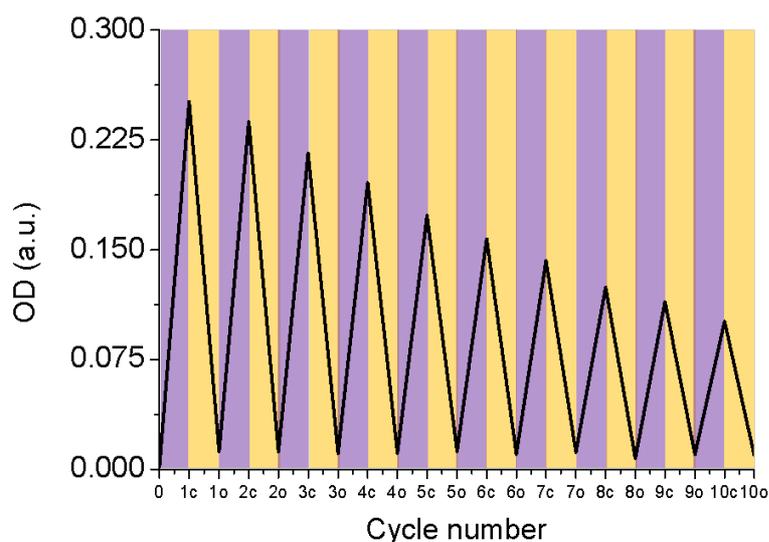


Figure S42: Switching cycles consisting of alternate irradiation with UV light until reaching the PSS and visible light until no further spectral changes can be detected of **6** ($c = 1.86 \times 10^{-5}$ M in CH_3CN , $\lambda_{irr1} = 365$ nm, $\lambda_{irr2} > 440$ nm); evolution of the OD at 585 nm.

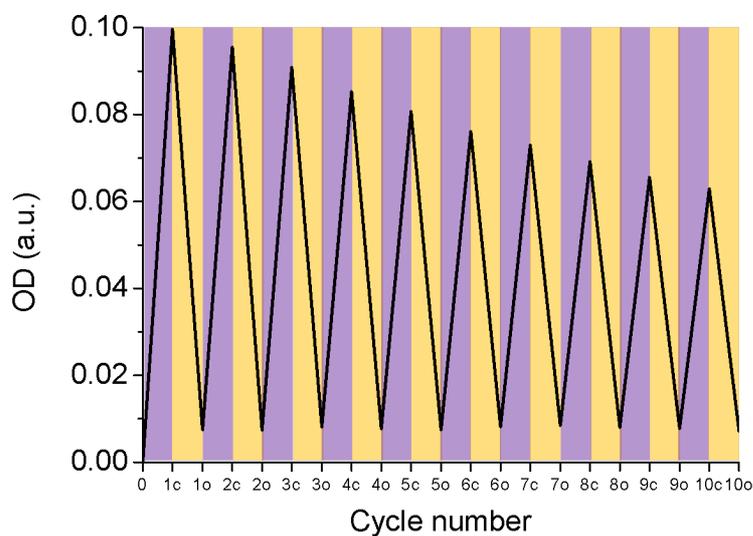


Figure S43: Switching cycles consisting of alternate irradiation with UV light until reaching the PSS and visible light until no further spectral changes can be detected of **8** ($c = 4.65 \times 10^{-5}$ M in CH_3CN , $\lambda_{irr1} = 365$ nm, $\lambda_{irr2} > 440$ nm); evolution of the OD at 552 nm.

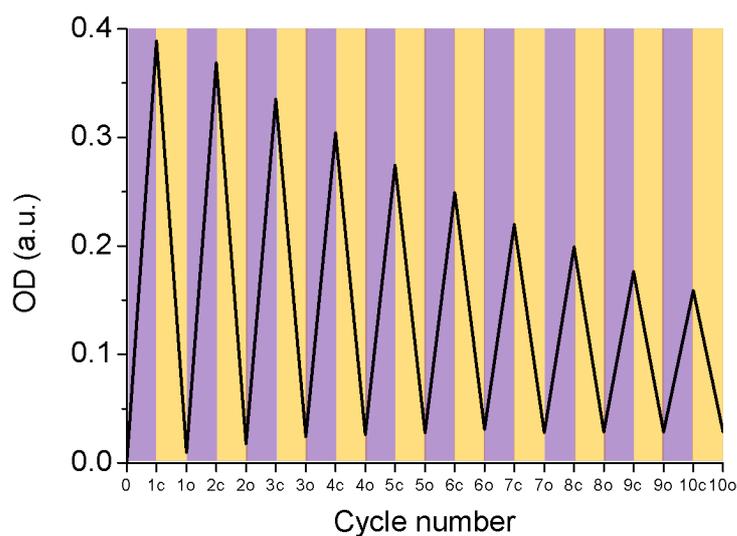


Figure S44: Switching cycles consisting of alternate irradiation with UV light until reaching the PSS and visible light until no further spectral changes can be detected of **9** ($c = 4.39 \times 10^{-5}$ M in CH_3CN , $[\text{MsOH}] = 1.02 \times 10^{-4}$ M, $\lambda_{\text{irr1}} = 365$ nm, $\lambda_{\text{irr2}} > 440$ nm); evolution of the OD at 583 nm.

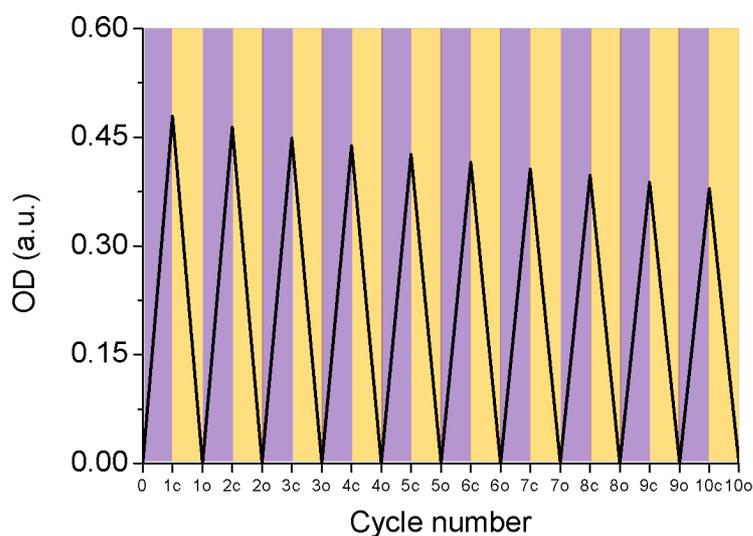


Figure S45: Switching cycles consisting of alternate irradiation with UV light until reaching the PSS and visible light until no further spectral changes can be detected of **12** ($c = 3.65 \times 10^{-5}$ M in CH_3CN , $\lambda_{\text{irr1}} = 365$ nm, $\lambda_{\text{irr2}} > 440$ nm); evolution of the OD at 533 nm.

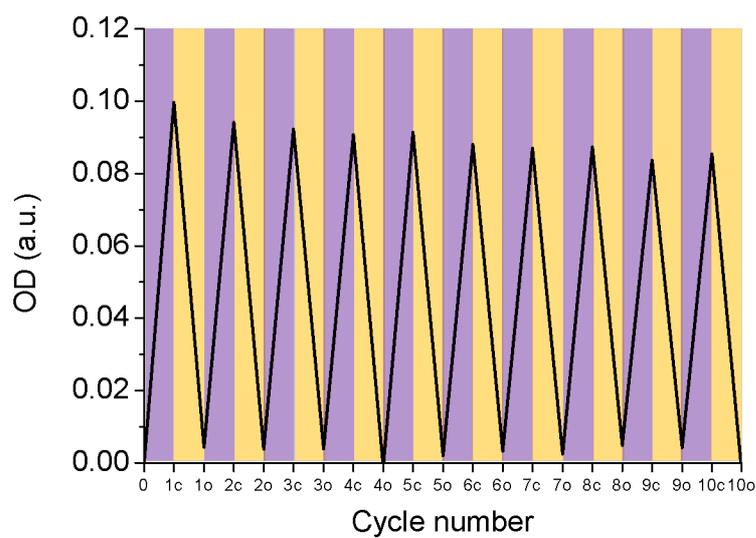


Figure S46: Switching cycles consisting of alternate irradiation with UV light until reaching the PSS and visible light until no further spectral changes can be detected of **14** ($c = 0.92 \times 10^{-5}$ M in CH_3CN , $\lambda_{\text{irr1}} = 365$ nm, $\lambda_{\text{irr2}} > 440$ nm); evolution of the OD at 542 nm.

Table S4: Percentage loss of OD after irradiating the solution of DAEs at the PSS at the given wavelength λ_{irr} , and then prolonging the irradiation for 1 h ($\text{Fatigue}_{\text{irrad}}$) or cycling the switch between open and closed state for 10 times ($\text{Fatigue}_{\text{cycle}}$). OD changes are followed at the λ_{max} of the specific DAE-c.

Compound	λ_{irr} (nm)	λ_{max} (nm)	$\text{Fatigue}_{\text{irrad}}$ (%)	$\text{Fatigue}_{\text{cycle}}$ (%)
1	302	607	0	4
2	302	615	2	3
3	365	/(a)	/(a)	/(a)
4	365	582	24	73
5	365	581	39	41
6	365	585	39	63
7	365	/(a)	/(a)	/(a)
8	365	552	36	37
9	365	583(b)	9(b)	59(b)
10	313	541(c)	36(c)	45(c)
11	365	/(d)	/(d)	/(d)
12	365	533	9	21
13	365	/(a)	/(a)	/(a)
14	365	542	1	14

(a) decomposition occurring before reaching the PSS

(b) evaluated in acidic conditions ($[\text{MsOH}] = 1.02 \times 10^{-4} \text{ M}$)

(c) data evaluated in *n*-hexane

(d) no switching behavior revealed

3.4. Determination of quantum yields and actinometry

Quantum yields for ring-closure reactions with UV-light were determined using the initial slope method. Light intensity at 302, 313 and 365 nm was determined by using ferrioxalate actinometry.¹⁶⁻¹⁷ For this purpose, 3 ml of a 0.006 M solution in 0.05 M H₂SO₄ was irradiated and 0.5 ml of phenanthroline (0.1 wt% in 0.5 M H₂SO₄/1.6 M NaOAc) were added subsequently. The resulting absorbance at 510 nm was used to calculate the light intensity via Formula S1.

$$I_0 = \frac{\Delta A_{510nm}}{\Delta t * \varepsilon_{510nm} * \Phi_{irr} * 1000} * \frac{3.5mL}{3mL} \quad (S1)$$

Thereby ΔA_{510nm} is the difference of the absorption at 510 nm for an irradiated versus a non-irradiated solution, Δt is the irradiation time, ε_{510nm} is 11100 M⁻¹ cm⁻¹ and Φ_{irr} is the quantum yield at the used irradiation wavelength (1.24 for 280 nm, 1.23 for 313 nm, 1.21 for 365 nm).¹⁷

For the determination of the quantum yield Formula S2 was used:

$$\Phi = \frac{\Delta A / \Delta t}{(1 - 10^{-A'}) * \varepsilon * I_0 * 1000} \quad (S2)$$

for which $\Delta A / \Delta t$ is the change of absorbance at a wavelength, which changes upon irradiation within the time. $1 - 10^{-A'}$ is the percentage of the absorbed photons by the solution at irradiation wavelength, ε is the extinction coefficient at observed wavelength and I_0 the light intensity. This method of calculating the quantum yield was applied for the initial stages of the reaction (maximum 5% of photochemical conversion).

The spectroscopic setup for the measurement of irradiation spectra as well as all procedures for the determination of spectra of pure ring-closed isomers and quantum yields for the isomerization reactions have been described in detail previously.⁷

Table S5: Quantum yields (ϕ) for the photocyclization process of the investigated DAE switches in CH₃CN solution at the given wavelengths (λ_{irr}).

Compound	λ_{irr} (nm)	ϕ
1	302	0.55
2	302	0.45
3	/(a)	/(a)
4	365	0.25
5	365	0.48
6	365	0.39
7	/(a)	/(a)
8	365	0.03
9	365	0.09(b)
10	313(c)	0.49(c)
11	/(d)	/(d)
12	365	0.50
13	/(a)	/(a)
14	365	0.12
15	365	0.16
16	365	1.00
17	365	0.41
18	365	0.57

(a) decomposition occurring before reaching the PSS

(b) evaluated in acidic conditions ($[MsOH] = 1.02 \times 10^{-4}$ M)

(c) data evaluated in *n*-hexane

(d) no switching behavior revealed

3.5. Determination of fluorescence quantum yields

For the evaluation of the emission of the different forms of the DAEs, 4×10^{-5} M solutions were prepared. The solutions were irradiated until the PSS, followed by subsequent addition of an excess of octylamine. Excitation spectra of all three steps (pure open isomer solution, PSS mixture, and rearranged form together with open form according to the PSS ratio) were measured in order to find the excitation wavelength, giving the highest fluorescence signal.

The determination of the fluorescence quantum yields of the rearrangement products afforded first the dilution of the initial mixtures in order to have an absorbance at excitation wavelength of below 0.1. At this absorbance the reabsorption of the emission light can be neglected and the emission can be considered linear dependent on the concentration and therefore also on the absorbance. The emission signal was determined from additional 10 nm to the excitation wavelength (to avoid scattered light of the irradiation beam) until 700 nm and the emission was integrated.

The same procedure was also done with reference compounds (anthracene in the excitation range of 240 nm to 380 nm and 9,10-diphenylanthracene for 320 nm to 380 nm).

The integrated fluorescence values of compounds and references were now inserted in equation S 3 to calculate the quantum yields. The absorbance of remaining open form in the mixture was considered and subtracted before.

$$\Phi_F = \Phi_{F_{ref}} \frac{I * A_{ref} * n^2}{I_{ref} * A * n_{ref}^2} \quad (\text{S3})$$

Thereby Φ_F is the fluorescence quantum yield, I is the integrated emission intensity, A is the absorbance and n is the refractive index of the solvent. The index labels the corresponding values for the reference compound. For anthracene Φ_F was 0.27 and for 9,10 diphenylanthracene it was 0.95.

Table S6: Fluorescence quantum yields (Φ_F) of the rearranged forms of the investigated DAE switches in CH₃CN solution at the given excitation wavelengths (λ_{exc}). The maximum of the emission band is given as well.

Compound	λ_{exc} (nm)	$\lambda_{em\ max}$ (nm)	Φ_F (%)
10	380(a)	480(a)	3.0(a)
14	250	366	0.7
15	400	475	1.7
16	335	395	2.4
17	240	355	0.8
18	370	490	2.5
19	320	440	2.2

(a) data evaluated in *n*-hexane

3.6. Fluorescence spectra

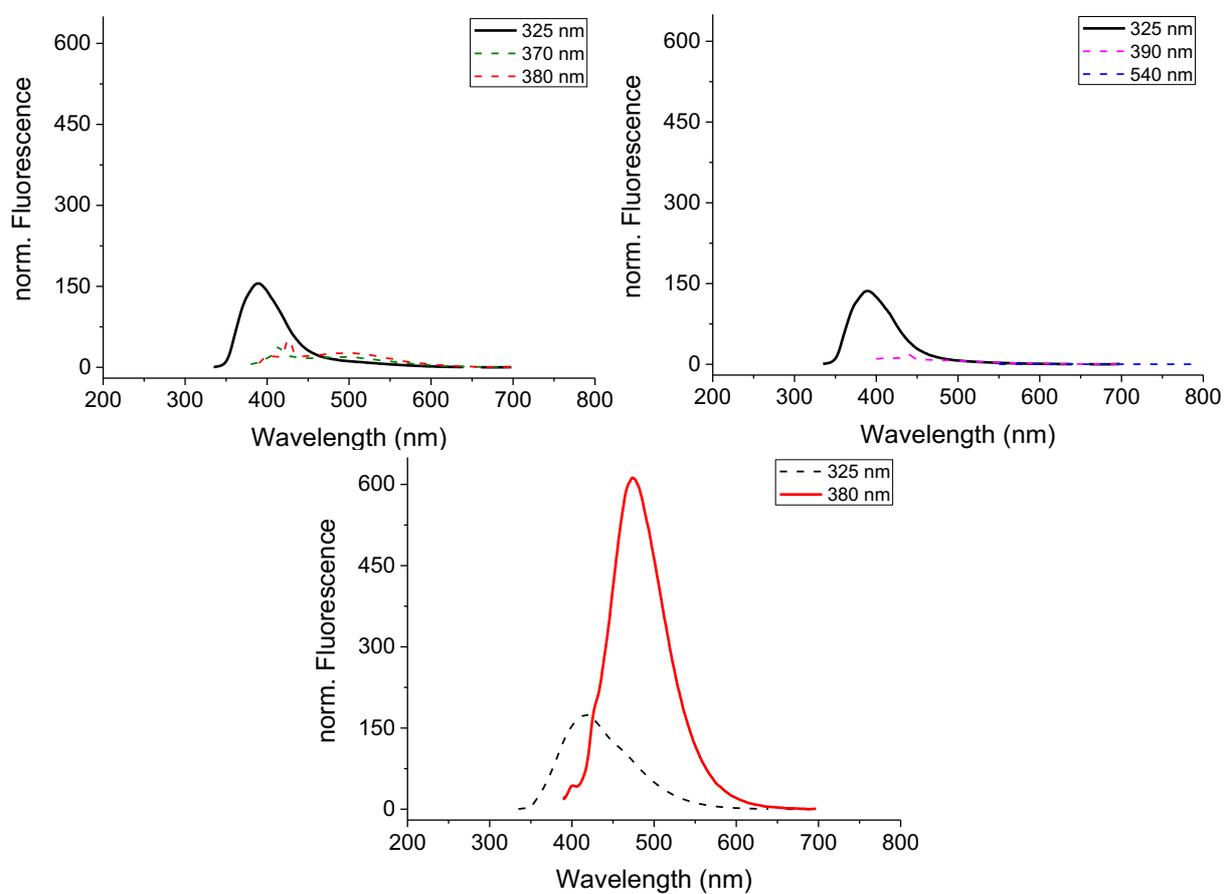


Figure S47: Emission spectra of **10** (4×10^{-5} M in aerated *n*-hexane) corrected for the absorbance at given excitation wavelengths. Left: pure open form **10o**. Right: the PSS reached upon irradiation at 365 nm (**10o** and **10c**). Bottom: PSS mixture after addition of OA in excess, spectra were obtained after completion of rearrangement (**10o** and **10r**).

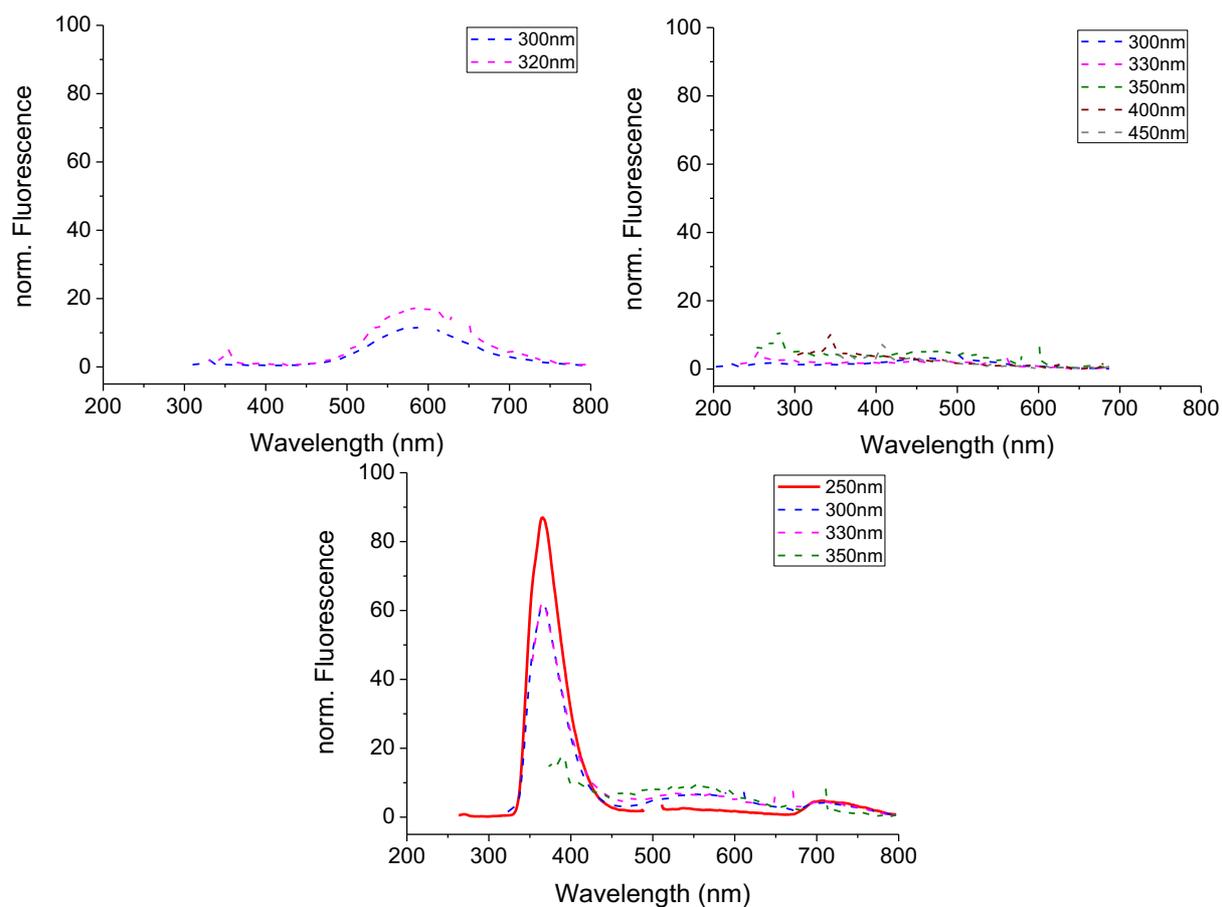


Figure S48: Emission spectra of **14** (4×10^{-5} M in aerated CH_3CN) corrected for the absorbance at given excitation wavelengths. Left: pure open form **14o**. Right: the PSS reached upon irradiation at 365 nm (**14o** and **14c**). Bottom: PSS mixture after addition of OA in excess, spectra were obtained after completion of rearrangement (**14o** and **14r**).

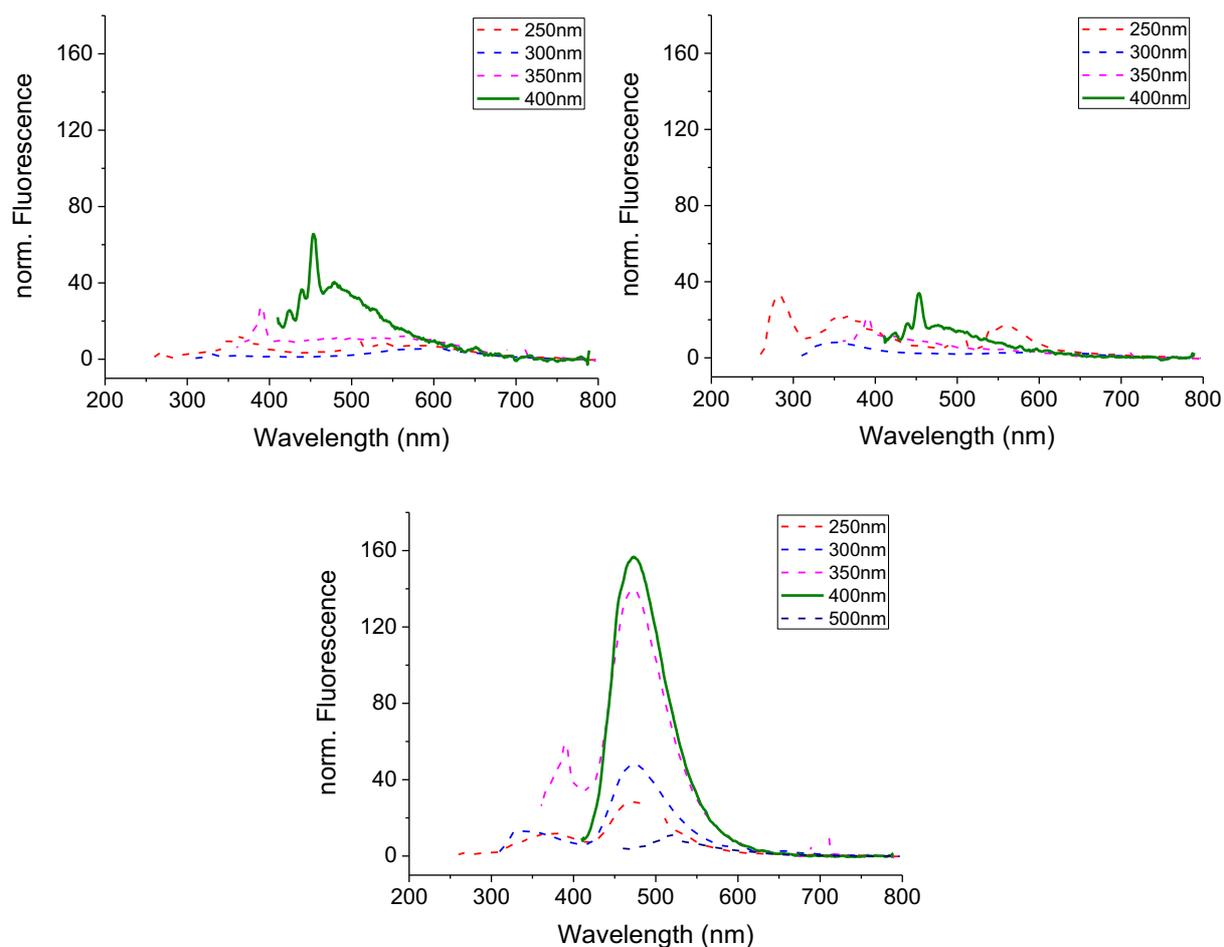


Figure S49: Emission spectra of **15** (4×10^{-5} M in aerated CH₃CN) corrected for the absorbance at given excitation wavelengths. Left: pure open form **15o**. Right: the PSS reached upon irradiation at 365 nm (**15o** and **15c**). Bottom: PSS mixture after addition of OA in excess, spectra were obtained after completion of rearrangement (**15o** and **15r**).

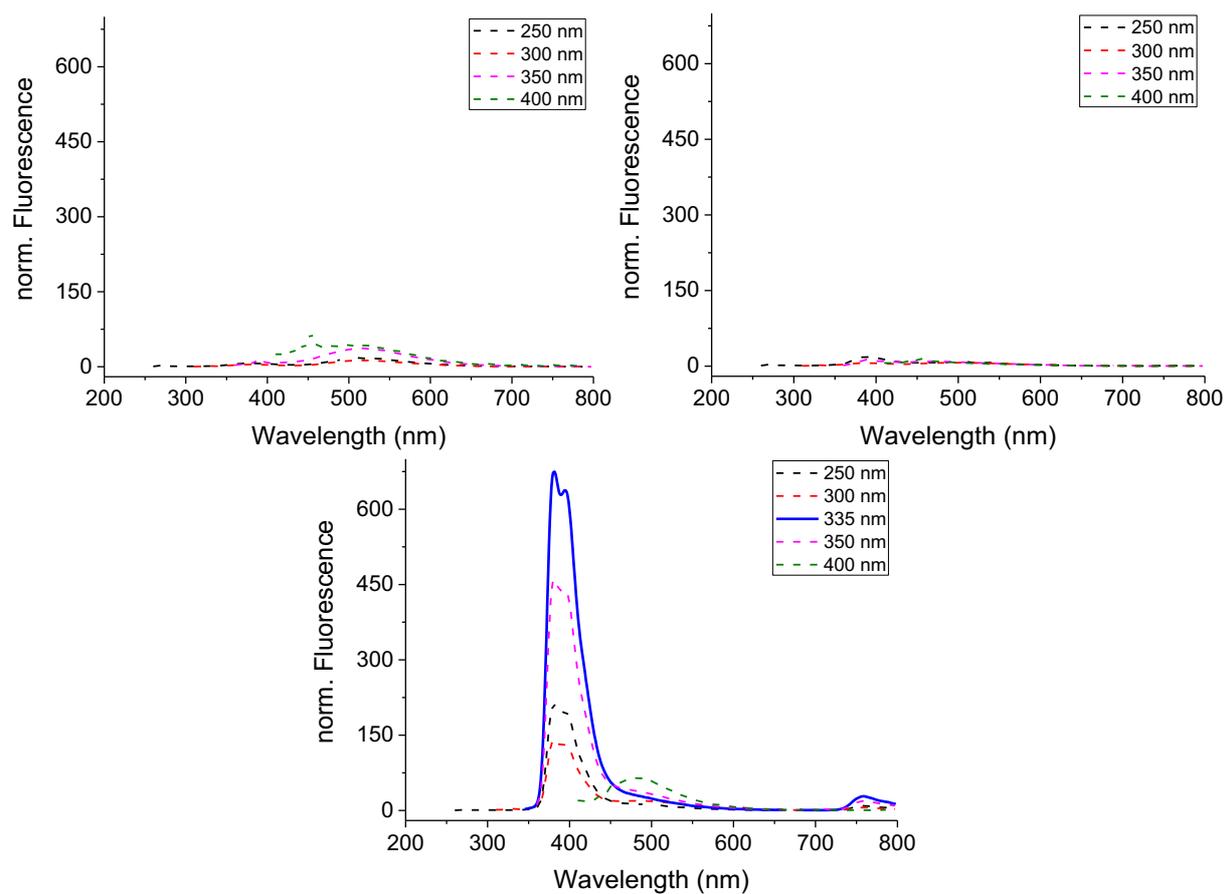


Figure S50: Emission spectra of **16** (4×10^{-5} M in aerated CH_3CN) corrected for the absorbance at given excitation wavelengths. Left: pure open form **16o**. Right: the PSS reached upon irradiation at 365 nm (**16o** and **16c**). Bottom: PSS mixture after addition of OA in excess, spectra were obtained after completion of rearrangement (**16o** and **16r**).

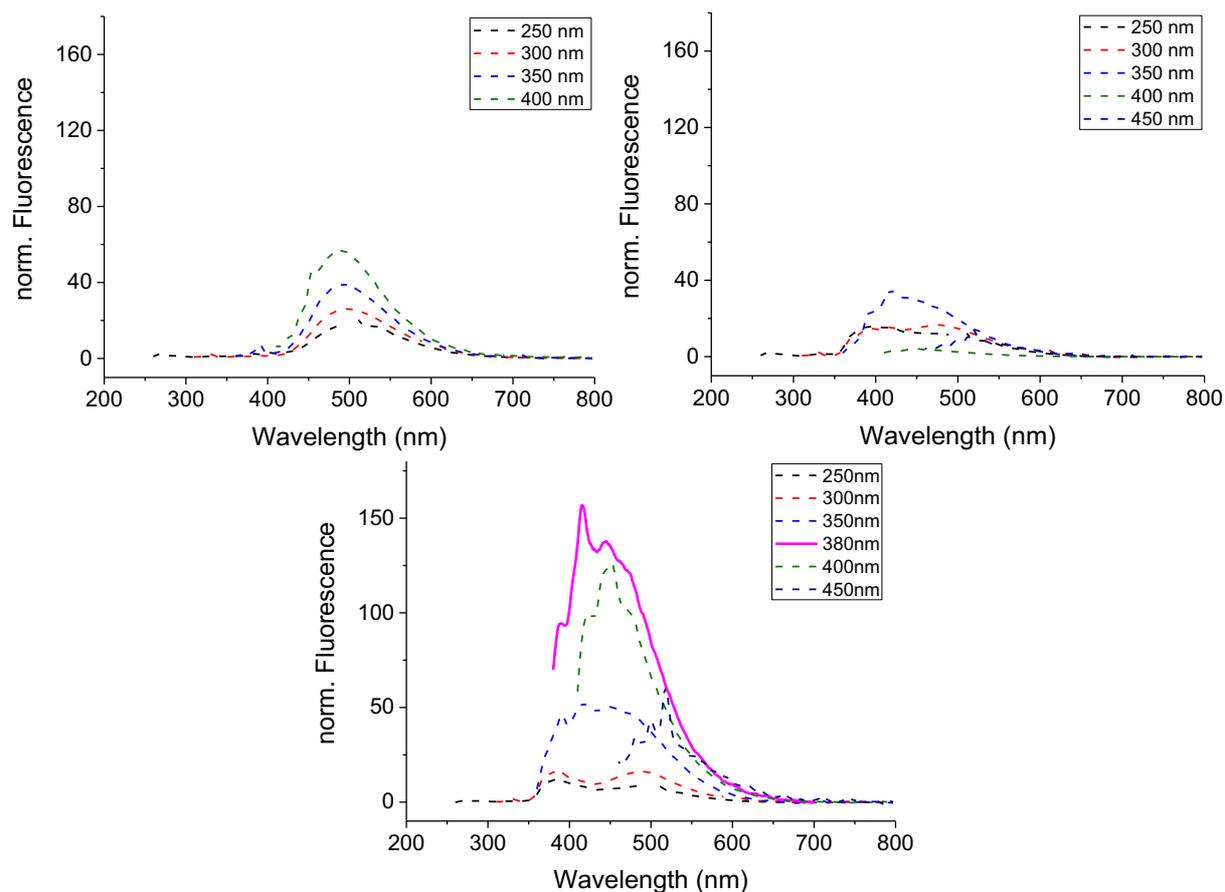


Figure S51: Emission spectra of **17** (4×10^{-5} M in aerated CH_3CN) corrected for the absorbance at given excitation wavelengths. Left: pure open form **17o**. Right: the PSS reached upon irradiation at 365 nm (**17o** and **17c**). Bottom: PSS mixture after addition of OA in excess, spectra were obtained after completion of rearrangement (**17o** and **17r**).

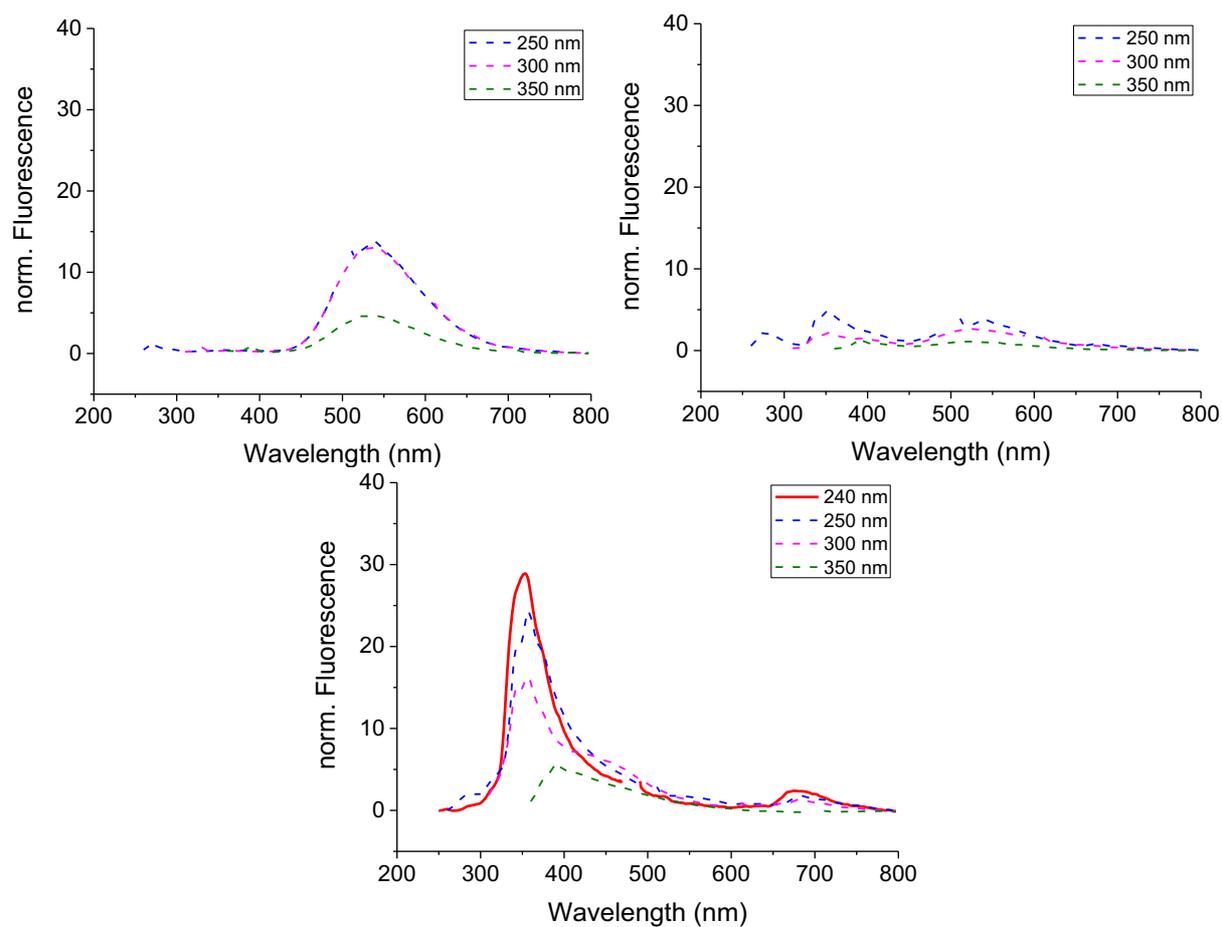


Figure S52: Emission spectra of **18** (4×10^{-5} M in aerated CH_3CN) corrected for the absorbance at given excitation wavelengths. Left: pure open form **18o**. Right: the PSS reached upon irradiation at 365 nm (**18o** and **18c**). Bottom: PSS mixture after addition of OA in excess, spectra were obtained after completion of rearrangement (**18o** and **18r**).

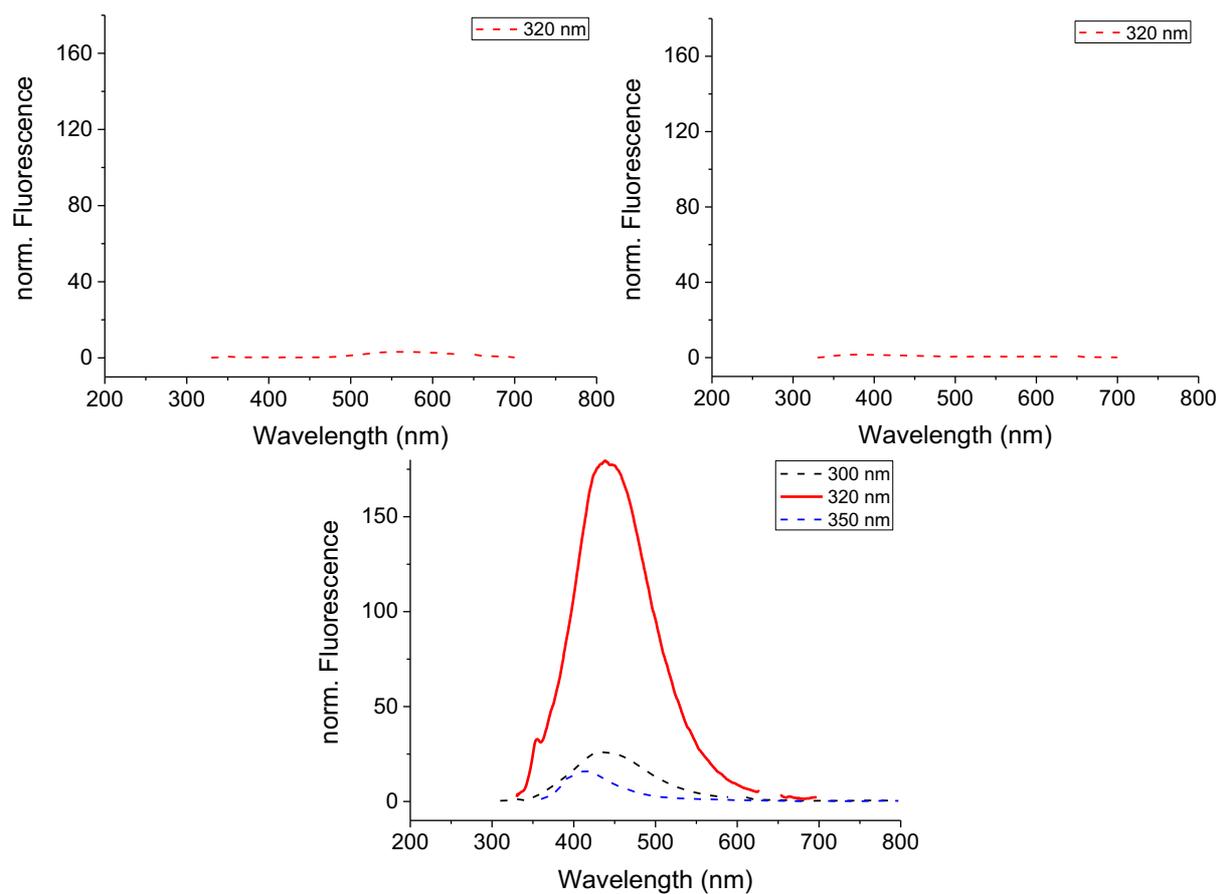


Figure S53: Emission spectra of **19** (4×10^{-5} M in aerated CH_3CN) corrected for the absorbance at given excitation wavelengths. Left: pure open form **19o**. Right: the PSS reached upon irradiation at 365 nm (**19o** and **19c**). Bottom: PSS mixture after addition of OA in excess, spectra were obtained after completion of rearrangement (**19o** and **19r**).

4. UV/vis Absorption Spectroscopy of the Rearrangement Products and the Imines

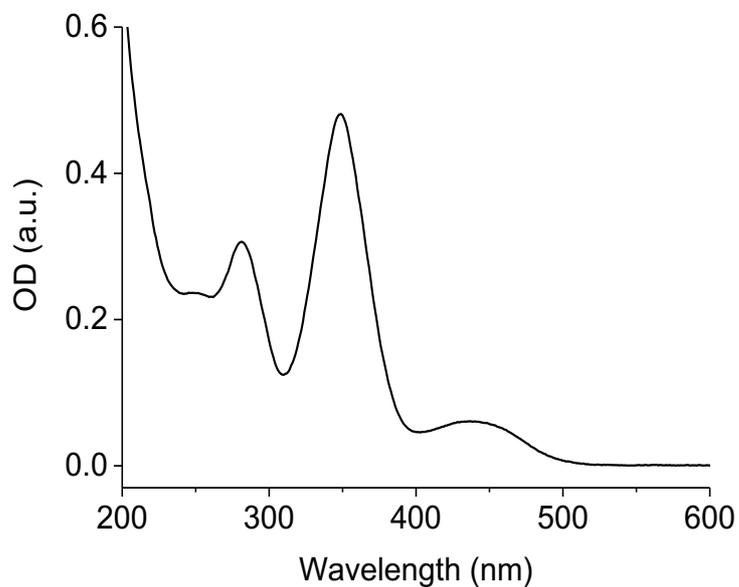


Figure S54: Absorption spectrum of **3r** (4.00×10^{-5} M in aerated CH_3CN) at 25 °C.

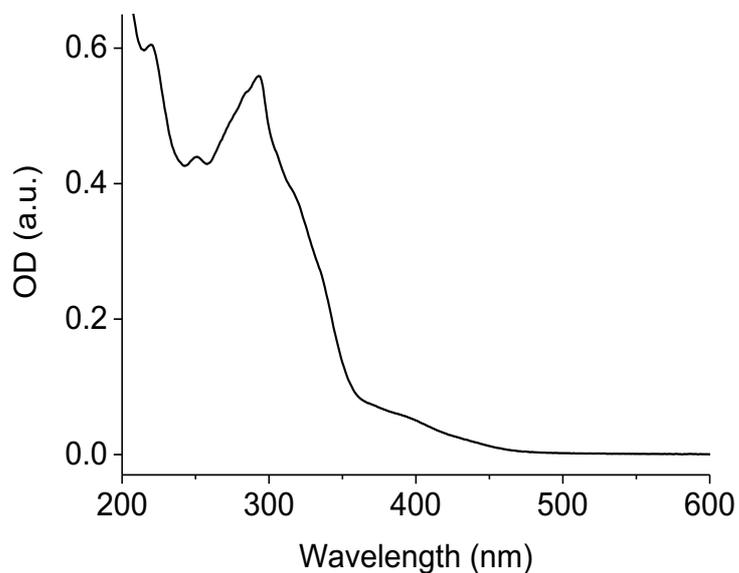


Figure S55: Absorption spectrum of **8r** (4.00×10^{-5} M in aerated CH_3CN) at 25 °C.

Table S7: Absorption maxima and corresponding extinction coefficients of the investigated rearrangement compounds in CH₃CN.

Compound	λ_{\max} [nm], $\epsilon(\lambda_{\max})$ [L mol ⁻¹ cm ⁻¹]
3r	349, 12000
8r	293, 14000

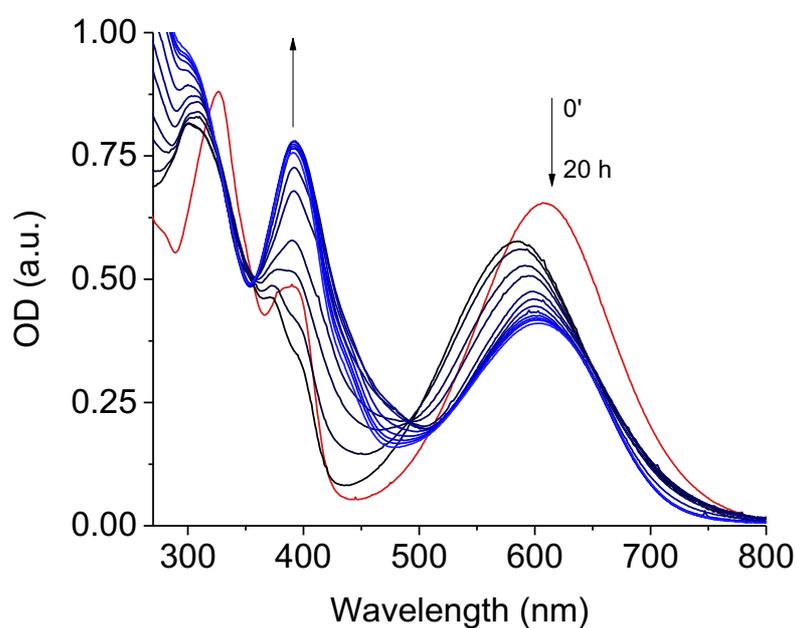


Figure S56: Evolution of the absorption spectrum of a solution of **1c** (5.46×10^{-5} M in aerated CH₃CN) in the presence of octylamine (OA, 4.00×10^{-2} M).

5. Kinetic Measurements and Analysis

In a typical experiment for amine sensing, if not differently specified, a solution of DAE (2×10^{-5} M in aerated CH_3CN) was prepared in a quartz cuvette and irradiated with UV light until reaching the PSS. Then, a precise amount of amine is added to the solution; the bleaching of the typical band from the closed DAE in the visible region was monitored by means of a spectrophotometer. In a typical experiment for thiols sensing, if not differently specified, the working conditions remained unchanged except for the addition of a precise amount of thiol instead of amine and, after homogeneously stirring the mixture, the subsequent addition of DMBA (4.93×10^{-2} M) in order to generate the reactive thiolate.

For the determination of the kinetic constant k , data were corrected taking into account the quantity of closed DAE formed in the PSS and the volume changes due to the addition of amine in the cuvette. The kinetic constant was evaluated with the Formula S4 considering the variation of absorbance at the maximum peak of the closed DAE.

$$\ln[A]_t = -kt + \ln[A]_0 \quad (\text{S4})$$

Values for k were determined using the initial slope method and considering only the data until the visible band intensity diminished up to the 50%, in order to avoid significant errors due to deviation of the data when signal/noise ratio is increasing at the end of the kinetic measurement.

List of the sampled nucleophiles and the given acronyms:

benzylamine (BA), cadaverine (CAD), 1,3-diaminopropane (DAP), *N,N*-dimethylbenzylamine (DMBA), *n*-octylamine (OA), spermidine (SPER), *p*-*tert*-butylbenzyl mercaptan (*t*BBM), thiophenol (TP).

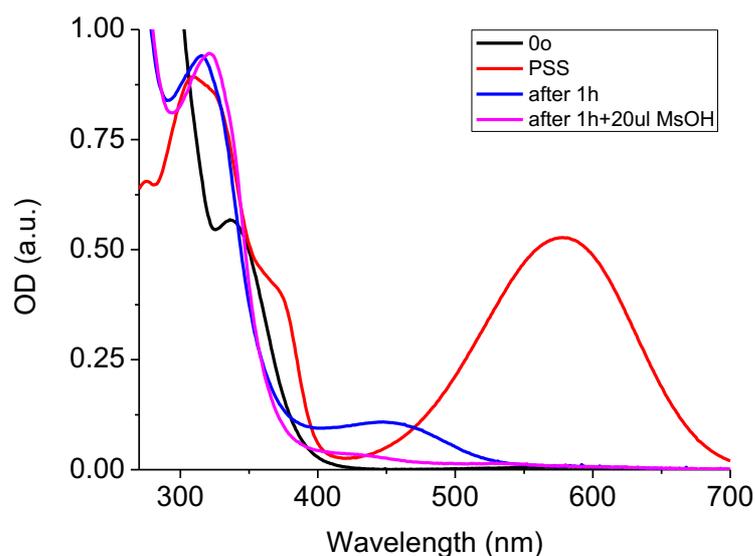


Figure S57: Evolution of the absorption spectrum of a solution of **0c** (3.59×10^{-5} M in aerated CH_3CN) in the presence of OA (1.00×10^{-2} M); in evidence, the spectra of only **0c** (**black**), the PSS (starting point of the spectra in the left figure, **red**), the final point of the kinetic evolution (**blue**) and the evolution of the last spectrum in presence of methanesulphonic acid (1.01×10^{-4} , **pink**).

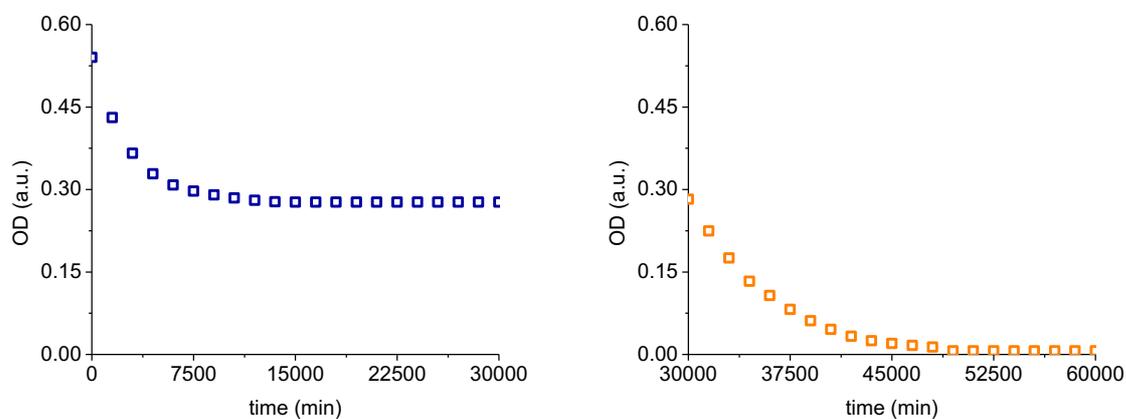


Figure S58: Left: Evolution of the absorption spectrum of a solution of **0** after reaching the PSS under UV-light irradiation (conc. **DAE-c** = 3.68×10^{-5} M in aerated CH_3CN) in the presence of OA (1.99×10^{-5} M) followed at 580 nm. Right: subsequent rearrangement of the remaining amount of **0c** upon addition of DMBA (4.44×10^{-2} M) to the mixture.

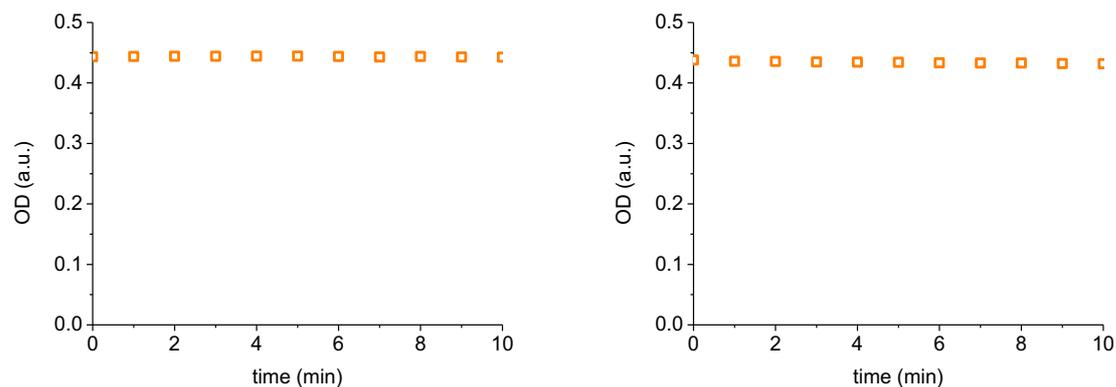


Figure S59: Evolution of the absorption spectrum of a solution of **6** after reaching the PSS under UV-light irradiation (conc. **DAE-c** = 3.07×10^{-5} M in aerated CH_3CN) in the presence of **ONLY** the thiol *t*BBM (3.94×10^{-5} M, left) and of **ONLY** DMBA (4.93×10^{-2} M, right) followed at 580 nm.

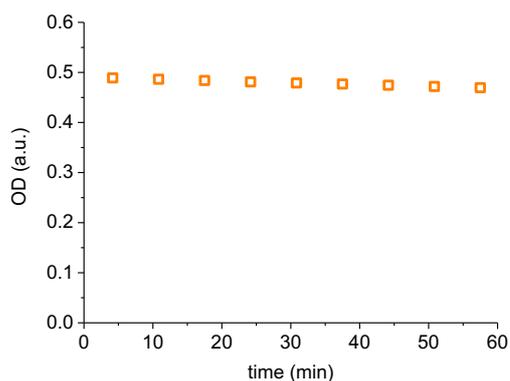


Figure S60: Evolution of the absorption spectrum of a solution of **5** after reaching the PSS under UV-light irradiation (conc. **DAE-c** = 3.02×10^{-5} M in aerated CH_3CN) in the presence S-ethyl acetate (7.59×10^{-2} M, left) and DMBA (5.42×10^{-2} M) followed at 580 nm.

Conc. BA (M)	k (min ⁻¹)
3.98 x 10 ⁻²	0.92
1.99 x 10 ⁻²	0.22
9.96 x 10 ⁻³	0.063
4.98 x 10 ⁻³	0.0022
2.49 x 10 ⁻³	0.0049
1.24 x 10 ⁻³	0.0012
0.62 x 10 ⁻³	0.00055

Conc. OA (M)	k (min ⁻¹)
4.00 x 10 ⁻²	3.74
2.00 x 10 ⁻²	0.69
1.00 x 10 ⁻²	0.16
5.00 x 10 ⁻³	0.050
2.50 x 10 ⁻³	0.018
1.25 x 10 ⁻³	0.0066
0.63 x 10 ⁻³	0.0024

Conc. CAD (M)	k (min ⁻¹)
4.00 x 10 ⁻²	4.07
2.00 x 10 ⁻²	2.35
1.00 x 10 ⁻²	0.61
5.00 x 10 ⁻³	0.27
2.50 x 10 ⁻³	0.094
1.25 x 10 ⁻³	0.053
0.63 x 10 ⁻³	0.034

Conc. DAP (M)	k (min ⁻¹)
4.00 x 10 ⁻²	5.00
2.00 x 10 ⁻²	4.22
1.00 x 10 ⁻²	3.00
5.00 x 10 ⁻³	1.51
2.50 x 10 ⁻³	0.75
1.25 x 10 ⁻³	0.35
0.63 x 10 ⁻³	0.30

Conc. SPER (M)	k (min ⁻¹)
4.01 x 10 ⁻²	n.d.
2.01 x 10 ⁻²	6.09
1.00 x 10 ⁻²	3.36
5.02 x 10 ⁻³	1.77
2.51 x 10 ⁻³	0.96
1.25 x 10 ⁻³	0.47

Figure S61: Determined k values for the reaction of **4** after reaching the PSS under UV-light irradiation (conc. **DAE-c** = 2.00x 10⁻⁵ M in aerated CH₃CN) in presence of different quantities of amines.

Conc. BA (M)	k (min ⁻¹)
3.98 x 10 ⁻²	0.29
1.99 x 10 ⁻²	0.050
9.96 x 10 ⁻³	0.035
4.98 x 10 ⁻³	0.010
2.49 x 10 ⁻³	0.0080
1.24 x 10 ⁻³	0.0017
0.62 x 10 ⁻³	0.0011

Conc. OA (M)	k (min ⁻¹)
4.00 x 10 ⁻²	2.12
2.00 x 10 ⁻²	0.39
1.00 x 10 ⁻²	0.19
5.00 x 10 ⁻³	0.042
2.50 x 10 ⁻³	0.0056
1.25 x 10 ⁻³	0.0025
0.63 x 10 ⁻³	0.0012

Conc. CAD (M)	k (min ⁻¹)
4.00 x 10 ⁻²	3.33
2.00 x 10 ⁻²	2.08
1.00 x 10 ⁻²	0.89
5.00 x 10 ⁻³	0.25
2.50 x 10 ⁻³	0.15
1.25 x 10 ⁻³	0.045
0.63 x 10 ⁻³	0.024

Conc. DAP (M)	k (min ⁻¹)
4.00 x 10 ⁻²	7.68
2.00 x 10 ⁻²	4.61
1.00 x 10 ⁻²	2.20
5.00 x 10 ⁻³	1.20
2.50 x 10 ⁻³	0.61
1.25 x 10 ⁻³	0.31
0.63 x 10 ⁻³	0.079

Conc. SPER (M)	k (min ⁻¹)
4.01 x 10 ⁻²	n.m.
2.01 x 10 ⁻²	7.89
1.00 x 10 ⁻²	2.77
5.02 x 10 ⁻³	1.54
2.51 x 10 ⁻³	0.89
1.25 x 10 ⁻³	0.47
0.63 x 10 ⁻³	0.20

Figure S62: Determined *k* values for the reaction of **5** after reaching the PSS under UV-light irradiation (conc. **DAE-c** = 2.00x 10⁻⁵ M in aerated CH₃CN) in presence of different quantities of amines.

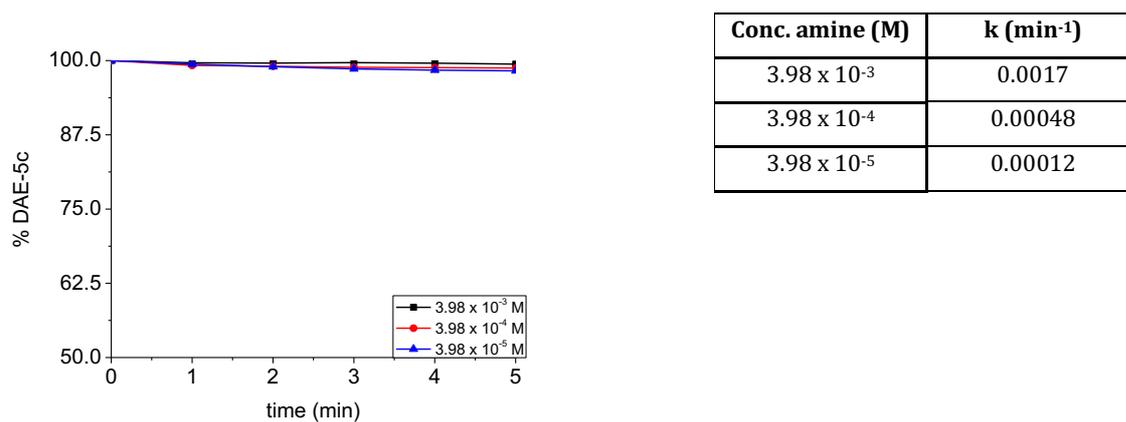


Figure S63: Left: kinetics for the reaction of a solution of **5** after reaching the PSS under UV-light irradiation (conc. **DAE-c** = 2.00x 10⁻⁵ M in aerated CH₃CN) in the presence of different aliquotes of a dry solution of ammonia in methanol. Right: Determined *k* values for the reaction of **5c** in presence of different aliquotes of a dry solution of ammonia in methanol.

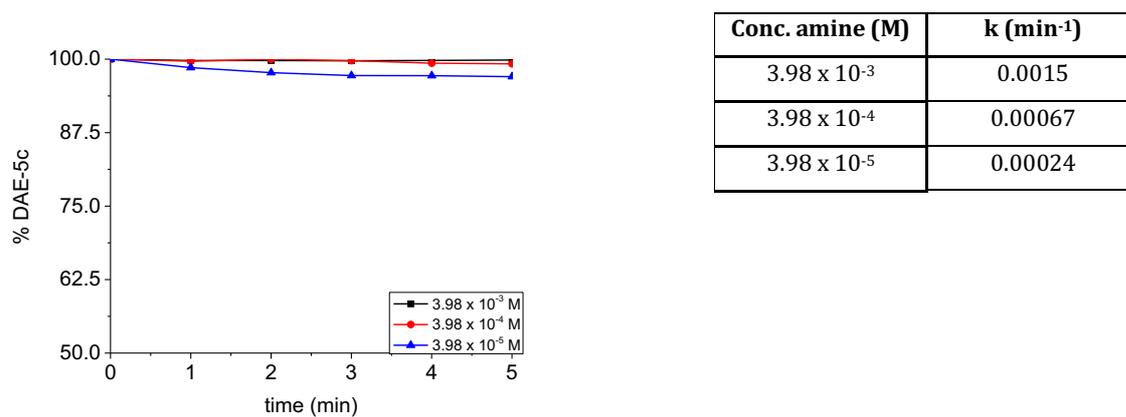


Figure S64: Left: kinetics for the reaction of a solution of **5** after reaching the PSS under UV-light irradiation (conc. **DAE-c** = 2.00x 10⁻⁵ M in aerated CH₃CN) in the presence of different aliquotes of 25% aq. solution ammonia. Right: Determined *k* values for the reaction of **5c** in presence of different aliquotes of 25% aq. solution ammonia.

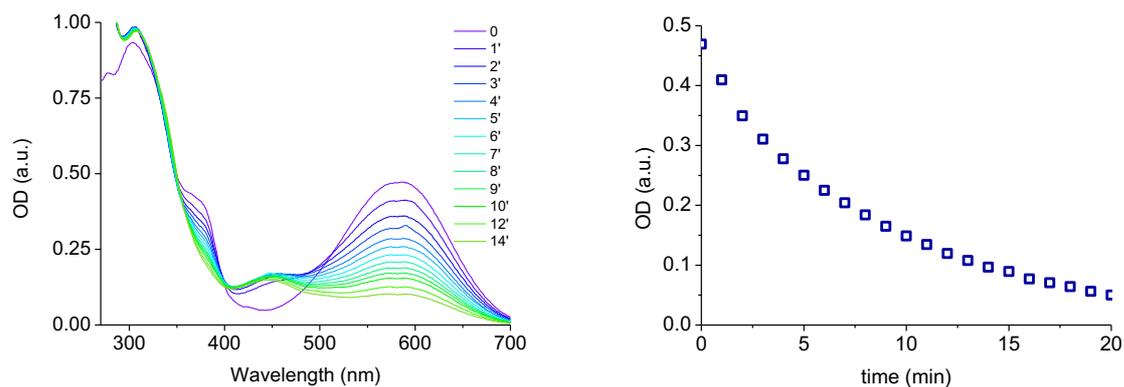


Figure S65: Left: Evolution of the absorption spectrum of a solution of **5** after reaching the PSS under UV-light irradiation (conc. **DAE-c** = 4.37×10^{-5} M in aerated CH_3CN) in the presence of *t*BBM (1.99×10^{-2} M) and DMBA (4.93×10^{-2} M). Right: Related kinetic profile followed at 581 nm.

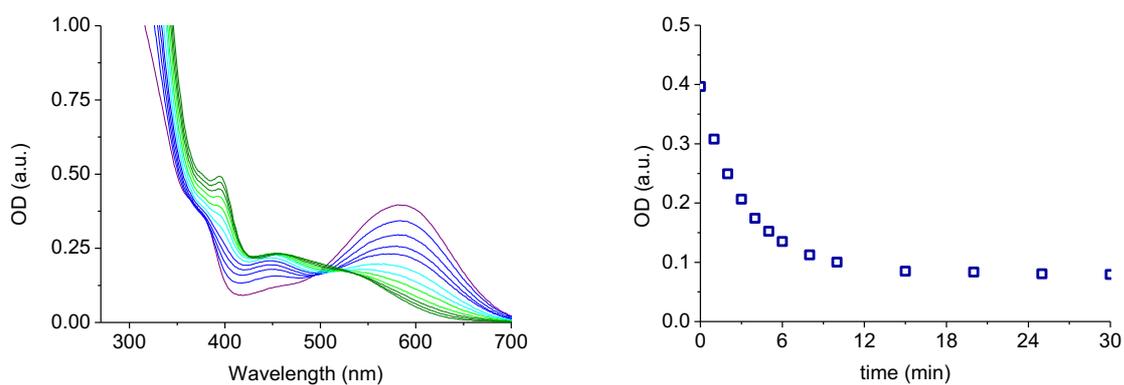
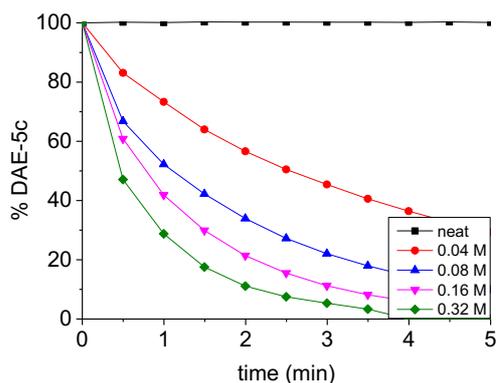


Figure S66: Left: Evolution of the absorption spectrum of a solution of **5** after reaching the PSS under UV-light irradiation (conc. **DAE-c** = 2.77×10^{-5} M in aerated CH_3CN) in the presence of TP (1.99×10^{-2} M) and DMBA (4.93×10^{-2} M). Right: Related kinetic profile followed at 581 nm.

Conc. tBBM (M)	k (min ⁻¹)
3.98 x 10 ⁻²	0.17
1.99 x 10 ⁻²	0.07
0.97 x 10 ⁻²	0.047
4.98 x 10 ⁻³	0.030
2.49 x 10 ⁻³	0.015
1.24 x 10 ⁻³	0.0088
0.62 x 10 ⁻³	0.0053

Conc. TP (M)	k (min ⁻¹)
3.98 x 10 ⁻²	0.24
1.99 x 10 ⁻²	0.11
0.97 x 10 ⁻²	0.10
4.98 x 10 ⁻³	0.067
2.49 x 10 ⁻³	0.031
1.24 x 10 ⁻³	0.014
0.62 x 10 ⁻³	0.009

Figure S67: Determined k values for the reaction of **5** after reaching the PSS under UV-light irradiation (conc. **DAE-c** = 2.00 x 10⁻⁵ M in aerated CH₃CN) in presence of different quantities of thiols.



Conc. DMBA (M)	k (min ⁻¹)
0	0.00032
0.04	0.17
0.08	0.38
0.16	0.54
0.32	0.95

Figure S68: Left: kinetics for the reaction of a solution of **5** after reaching the PSS under UV-light irradiation (conc. **DAE-c** = 2.00 x 10⁻⁵ M in aerated CH₃CN) in the presence of tBBM (3.94 x 10⁻⁵ M) and different amounts of DMBA. Right: Determined k values for the reaction of **5c** in presence of different quantities of tBBM.

Conc. BA (M)	k (min ⁻¹)
3.98 x 10 ⁻²	1.01
1.99 x 10 ⁻²	0.23
9.96 x 10 ⁻³	0.065
4.98 x 10 ⁻³	0.015
2.49 x 10 ⁻³	0.0067
1.24 x 10 ⁻³	0.0023
6.22 x 10 ⁻⁴	0.0015

Conc. OA (M)	k (min ⁻¹)
4.00 x 10 ⁻²	3.08
2.00 x 10 ⁻²	0.74
1.00 x 10 ⁻²	0.20
5.00 x 10 ⁻³	0.082
2.50 x 10 ⁻³	0.032
1.25 x 10 ⁻³	0.0082
0.63 x 10 ⁻³	0.0072

Conc. CAD (M)	k (min ⁻¹)
4.00 x 10 ⁻²	5.82
2.00 x 10 ⁻²	2.92
1.00 x 10 ⁻²	1.30
5.00 x 10 ⁻³	0.34
2.50 x 10 ⁻³	0.12
1.25 x 10 ⁻³	0.057
0.63 x 10 ⁻³	0.024

Conc. DAP (M)	k (min ⁻¹)
4.00 x 10 ⁻²	13.38
2.00 x 10 ⁻²	8.57
1.00 x 10 ⁻²	4.93
5.00 x 10 ⁻³	3.40
2.50 x 10 ⁻³	2.09
1.25 x 10 ⁻³	0.91
0.63 x 10 ⁻³	0.40

Conc. SPER (M)	k (min ⁻¹)
4.01 x 10 ⁻²	n.m.
2.01 x 10 ⁻²	10.20
1.00 x 10 ⁻²	5.68
5.02 x 10 ⁻³	2.63
2.51 x 10 ⁻³	1.42
1.25 x 10 ⁻³	0.53
0.63 x 10 ⁻³	0.30

Figure S69: Determined k values for the reaction of **6** after reaching the PSS under UV-light irradiation (conc. **DAE-c** = 2.00x 10⁻⁵ M in aerated CH₃CN) in presence of different quantities of amines.

Conc. BA (M)	k (min ⁻¹)
3.98 x 10 ⁻²	0.40
1.99 x 10 ⁻²	0.13
9.96 x 10 ⁻³	0.095
4.98 x 10 ⁻³	0.024
2.49 x 10 ⁻³	0.0079
1.24 x 10 ⁻³	0.0061
0.62 x 10 ⁻³	0.0041

Conc. OA (M)	k (min ⁻¹)
4.00 x 10 ⁻²	1.44
2.00 x 10 ⁻²	0.57
1.00 x 10 ⁻²	0.16
5.00 x 10 ⁻³	0.066
2.50 x 10 ⁻³	0.031
1.25 x 10 ⁻³	0.018
0.63 x 10 ⁻³	0.0085

Conc. CAD (M)	k (min ⁻¹)
4.00 x 10 ⁻²	2.36
2.00 x 10 ⁻²	0.90
1.00 x 10 ⁻²	0.55
5.00 x 10 ⁻³	0.14
2.50 x 10 ⁻³	0.079
1.25 x 10 ⁻³	0.0054
0.63 x 10 ⁻³	0.0041

Conc. DAP (M)	k (min ⁻¹)
4.00 x 10 ⁻²	4.00
2.00 x 10 ⁻²	2.59
1.00 x 10 ⁻²	1.42
5.00 x 10 ⁻³	0.59
2.50 x 10 ⁻³	0.30
1.25 x 10 ⁻³	0.12
0.63 x 10 ⁻³	0.082

Conc. SPER (M)	k (min ⁻¹)
4.01 x 10 ⁻²	n.m.
2.01 x 10 ⁻²	6.14
1.00 x 10 ⁻²	2.85
5.02 x 10 ⁻³	1.60
2.51 x 10 ⁻³	0.86
1.25 x 10 ⁻³	0.32
0.63 x 10 ⁻³	0.25

Figure S70: Determined k values for the reaction of **8** after reaching the PSS under UV-light irradiation (conc. **DAE-c** = 2.00x 10⁻⁵ M in aerated CH₃CN) in presence of different quantities of amines.

Conc. BA (M)	k (min ⁻¹)
3.98 x 10 ⁻²	0.38
1.99 x 10 ⁻²	0.10
9.96 x 10 ⁻³	0.032
4.98 x 10 ⁻³	0.0080
2.49 x 10 ⁻³	0.0064
1.24 x 10 ⁻³	0.0051
0.62 x 10 ⁻³	0.0013

Conc. OA (M)	k (min ⁻¹)
4.00 x 10 ⁻²	1.11
2.00 x 10 ⁻²	0.39
1.00 x 10 ⁻²	0.12
5.00 x 10 ⁻³	0.065
2.50 x 10 ⁻³	0.025
1.25 x 10 ⁻³	0.0069
0.63 x 10 ⁻³	0.0043

Conc. CAD (M)	k (min ⁻¹)
4.00 x 10 ⁻²	3.75
2.00 x 10 ⁻²	1.21
1.00 x 10 ⁻²	0.61
5.00 x 10 ⁻³	0.22
2.50 x 10 ⁻³	0.076
1.25 x 10 ⁻³	0.033
0.63 x 10 ⁻³	0.0015

Conc. DAP (M)	k (min ⁻¹)
4.00 x 10 ⁻²	4.71
2.00 x 10 ⁻²	1.80
1.00 x 10 ⁻²	1.24
5.00 x 10 ⁻³	0.60
2.50 x 10 ⁻³	0.21
1.25 x 10 ⁻³	0.14
0.63 x 10 ⁻³	0.060

Conc. SPER (M)	k (min ⁻¹)
4.01 x 10 ⁻²	n.m.
2.01 x 10 ⁻²	7.47
1.00 x 10 ⁻²	3.71
5.02 x 10 ⁻³	0.91
2.51 x 10 ⁻³	0.77
1.25 x 10 ⁻³	0.41
0.63 x 10 ⁻³	0.20

Figure S71: Determined *k* values for the reaction of **12** after reaching the PSS under UV-light irradiation (conc. **DAE-c** = 2.00 x 10⁻⁵ M in aerated CH₃CN) in presence of different quantities of amines.

Conc. BA (M)	k (min ⁻¹)
3.98 x 10 ⁻²	0.22
1.99 x 10 ⁻²	0.09
9.96 x 10 ⁻³	0.028
4.98 x 10 ⁻³	0.0075
2.49 x 10 ⁻³	0.0025
1.24 x 10 ⁻³	0.0016
0.62 x 10 ⁻³	0.0015

Conc. OA (M)	k (min ⁻¹)
4.00 x 10 ⁻²	0.78
2.00 x 10 ⁻²	0.24
1.00 x 10 ⁻²	0.079
5.00 x 10 ⁻³	0.034
2.50 x 10 ⁻³	0.011
1.25 x 10 ⁻³	0.0024
0.63 x 10 ⁻³	0.00019

Conc. CAD (M)	k (min ⁻¹)
4.00 x 10 ⁻²	3.30
2.00 x 10 ⁻²	1.01
1.00 x 10 ⁻²	0.52
5.00 x 10 ⁻³	0.14
2.50 x 10 ⁻³	0.095
1.25 x 10 ⁻³	0.033
0.63 x 10 ⁻³	0.013

Conc. DAP (M)	k (min ⁻¹)
4.00 x 10 ⁻²	4.85
2.00 x 10 ⁻²	2.25
1.00 x 10 ⁻²	1.10
5.00 x 10 ⁻³	0.39
2.50 x 10 ⁻³	0.26
1.25 x 10 ⁻³	0.17
0.63 x 10 ⁻³	0.096

Conc. SPER (M)	k (min ⁻¹)
4.01 x 10 ⁻²	4.83
2.01 x 10 ⁻²	2.41
1.00 x 10 ⁻²	1.49
5.02 x 10 ⁻³	0.91
2.51 x 10 ⁻³	0.33
1.25 x 10 ⁻³	0.26
0.63 x 10 ⁻³	0.13

Figure S72: Determined k values for the reaction of **14** after reaching the PSS under UV-light irradiation (conc. **DAE-c** = 2.00x 10⁻⁵ M in aerated CH₃CN) in presence of different quantities of amines.

compound	Conc. OA (M)	k (min ⁻¹)
19	4.95 x 10 ⁻³	0.065
10(a)	4.95 x 10 ⁻³	0.001
15	9.90 x 10 ⁻²	0.466
16	4.95 x 10 ⁻³	0.008
17	9.90 x 10 ⁻²	0.001
18	9.90 x 10 ⁻²	0.013

Figure S73: Determined *k* values for the reaction of diverse DAEs after reaching the PSS under UV-light irradiation (conc. **DAE-o** = 4.00 x 10⁻⁵ M in aerated CH₃CN) in presence of octylamine. (a) in *n*-hexane.

Conc. <i>t</i> BBM (M)	k (min ⁻¹)
3.98 x 10 ⁻²	0.71
1.99 x 10 ⁻²	0.43
0.97 x 10 ⁻²	0.26
4.98 x 10 ⁻³	0.077
2.49 x 10 ⁻³	0.037
1.24 x 10 ⁻³	0.023
0.62 x 10 ⁻³	0.012

Conc. TP (M)	k (min ⁻¹)
1.99 x 10 ⁻²	1.07
0.97 x 10 ⁻²	0.64
4.98 x 10 ⁻³	0.43
2.49 x 10 ⁻³	0.30
1.24 x 10 ⁻³	0.25
0.62 x 10 ⁻³	0.15

Figure S74: Determined *k* values for the reaction of **4** after reaching the PSS under UV-light irradiation (conc. **DAE-c** = 2.00x 10⁻⁵ M in aerated CH₃CN) in presence of different quantities of thiols.

Conc. <i>t</i> BBM (M)	k (min ⁻¹)
3.98 x 10 ⁻²	1.79
1.99 x 10 ⁻²	0.94
0.97 x 10 ⁻²	0.64
4.98 x 10 ⁻³	0.30
2.49 x 10 ⁻³	0.18
1.24 x 10 ⁻³	0.11
0.62 x 10 ⁻³	0.06

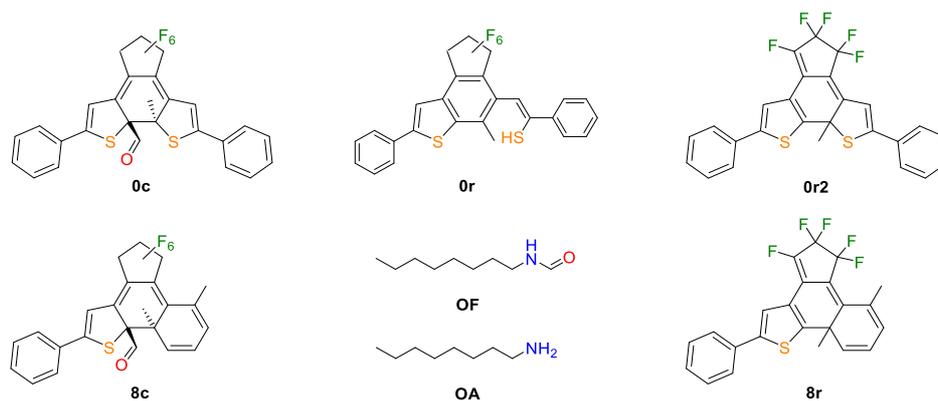
Conc. TP (M)	k (min ⁻¹)
3.98 x 10 ⁻²	1.41
1.99 x 10 ⁻²	0.89
0.97 x 10 ⁻²	0.66
4.98 x 10 ⁻³	0.42
2.49 x 10 ⁻³	0.23
1.24 x 10 ⁻³	0.18
0.62 x 10 ⁻³	0.12

Figure S75: Determined *k* values for the reaction of **6** after reaching the PSS under UV-light irradiation (conc. **DAE-c** = 2.00x 10⁻⁵ M in aerated CH₃CN) in presence of different quantities of thiols.

6. Computational Methods

Calculations were performed using Gaussian 09 suite of programs (Rev. C01), and GaussView v.5.0.8 for the graphic representation of the molecules.¹⁸ Geometry optimization of the target structures was performed by means of *Density Functional Theory* (DFT); B3LYP functional,¹⁹⁻²⁰ 6-311+G(d,p) Pople basis set²¹ were used for all the calculations. The nature of the critical points was checked by vibrational analysis; the enthalpic and entropic corrections to the absolute energy values were evaluated at 298.15 K. Solvent effects (acetonitrile) were taken into account by using the *Polarizable Continuum Model* (IEF-PCM).²²⁻²³

The relative thermodynamic stability of the closed and rearranged forms of DAE-**O** and DAE-**8** were calculated by comparing the sum of energies. In our simplified method, we labelled as starting point SP the sum of the energies of the closed switches and the amine used for inducing their rearrangement. In order to overlap with the experimental work, OA was chosen. The second stage, final point FP was the sum of the energies related to the rearranged products, formamide, and in the case of DAE-**8** we considered a molecule of HF. Calculations showed in both the two cases that the different reactions are thermodynamically allowed, with a ΔG of ca. -48 and -44 kcal/mol for DAE-**O** and DAE-**8**, respectively (Table S8). This justifies our experimental findings of a similar observed rate of DAE-**8** and the other tested switches. Once clarified the mechanism of **8c** to rearrange, it was interesting to evaluate a similar mechanism for the decomposition of typical thiophene based DAEs. Again, we considered structure **Oc** and simulated the potential by-product generated by HF release from the bridge, which will be referred as structure **Or2**. Calculations showed that the pathway is still thermodynamically allowed, but the smaller ΔG (-41 kcal/mol) is consistent with our findings. The optimization of **Oc** also provided another little detail to be reported: the bond length of the C-S bond destroyed after the rearrangement is longer than the corresponding C-S bond on the other thiophene ring that is not affected from the rearrangement (1.87 Å vs 1.85 Å). Thus, we got once again a confirmation of the lability of such C-S bond.



Scheme S10: Structures investigated with computational methods.

Table S8: Summary of the findings obtained with the computational investigation.

molecule	G (hartree)	state	G (hartree)	ΔG (hartree)	ΔG (kcal/mol)
0c	-2509.35	SP_0(0c+OA)	-2880.29		
0r	-2396.05	FP_0(0r+OF)	-2880.37	-0.077	-48.15
0r2	-2295.54	FP_02(0r2+OF+HF)	-2880.36	-0.066	-41.49
8c	-1996.77	SP_8(8c+OA)	-2367.72		
8r	-1782.97	FP_8(8r+OF+HF)	-2367.79	-0.070	-43.70
OA	-370.95				
OF	-484.33				
HF	-100.50				

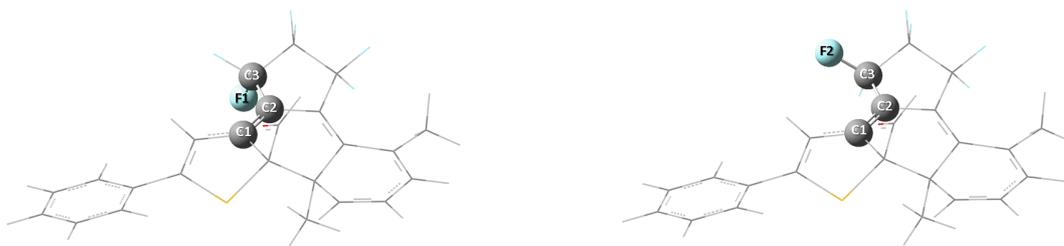


Figure S76: Dihedral angles described from the fluorine substituents involved in the rearrangement from **8c** to **8r**. Left, the angle involving F1, which is released during the rearrangement ($d_{C1=C2-C3-F1} = -86.8^\circ$). Right, the angle involving F2, which will remain connected to C3-atom after the rearrangement and the change of hybridization ($d_{C1=C2-C3-F2} = 34.6^\circ$). To be noticed, F2 is almost coplanar to the rest of the structure even before the rearrangement, while F1 is ready to be released.

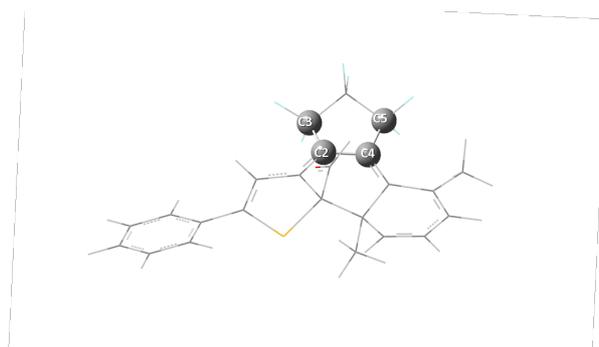


Figure S77: In evidence, the bonds of the bridging unit show already a different length, with $d_{C2=C3} < d_{C4=C5}$ (data are reported in Table S8). As discussed before for the dihedral angles involving fluorines F1 and F2, the closed isomer **8c** resembles the structure of **8r**: in **8c**, the shorter $d_{C2=C3}$ resembles what it will be a double bond in **8r**.

Table S9: Bond length values for the investigated bonds in structure **8c**.

Bond	bond length (Å)
C3-F1	1.38
C3-F2	1.36
C2-C3	1.50
C4-C5	1.52

Table S10: atomic coordinates for the optimized structure of **8r**.

	X	Y	Z		X	Y	Z
H	1.925390	-1.960518	0.044770	C	1.756072	-0.891833	0.029381
H	0.540128	2.404839	-2.276484	C	2.770006	0.026255	-0.046633
H	-0.340343	0.866290	-2.376349	C	-2.024975	1.256018	-0.246314
H	-1.218345	2.403890	-2.512629	C	-0.635144	1.933807	-0.466054
H	4.834351	1.630893	0.709802	C	-3.192612	2.133073	-0.382457
H	3.942096	-2.216085	-1.018257	C	-0.389218	1.896899	-2.013521
H	7.247155	1.135346	0.555158	C	4.206841	-0.257449	-0.135451
H	6.351079	-2.718588	-1.139009	C	5.162657	0.684715	0.291125
H	-0.756836	0.928761	2.182866	C	4.659258	-1.487930	-0.653875
H	8.022026	-1.045648	-0.360030	C	6.525437	0.399934	0.212597
H	0.355854	3.843775	0.145293	C	6.021216	-1.767761	-0.731226
H	-1.718585	5.162020	0.298079	C	6.960443	-0.825930	-0.297378
H	-3.890006	4.125383	-0.322723	C	0.223870	1.324508	1.859187
H	-4.599486	0.956668	-1.540303	C	-0.613988	3.386319	-0.030719
H	-5.026701	1.092808	0.160703	C	-3.018218	3.482119	-0.239858
H	-5.236794	2.480920	-0.908015	C	-1.744059	4.106588	0.043063
C	-2.529553	-2.458567	0.402257	O	-4.587432	1.631835	-0.681143
C	-1.077289	-2.353358	-0.122807	F	1.016605	1.765516	2.655024
C	-0.784702	-0.889393	-0.029778	F	-4.106781	-0.758451	0.969606
C	-2.018274	-0.112096	-0.086553	F	-3.852613	-1.251642	-1.161369
C	-31.758.31	-10.865.13	0.023188	F	-3.211716	-3.511876	-0.090918
H	19.253.90	-19.605.18	0.044770	F	-2.491735	-2.570968	1.758413
C	0.449749	-0.317780	0.067149	F	-0.227190	-3.150805	0.586099
C	0.473311	11.79858	0.319927	S	-1.040053	-2.809991	-1.424171

References:

- (1) Valderrey, V.; Bonasera, A.; Fredrich, S.; Hecht, S., *Angew. Chem. Int. Ed.* **2017**, *56*, 1914-1918.
- (2) Liu, H.; Pu, S.; Liu, G.; Chen, B., *Dyes Pigm.* **2014**, *102*, 159-168.
- (3) Jeong, W.; Khazi, M. I.; Park, D.-H.; Jung, Y.-S.; Kim, J.-M., *Adv. Funct. Mater.* **2016**, *26*, 5230-5238.
- (4) Fan, C.; Yang, P.; Wang, X.; Liu, G.; Jiang, X.; Chen, H.; Tao, X.; Wang, M.; Jiang, M., *Sol. Energy Mater. Sol. Cells* **2011**, *95*, 992-1000.
- (5) Cai, J.; Farhat, A.; Tsitovitch, P. B.; Bodani, V.; Toogood, R. D.; Murphy, R. S., *J. Photoch. Photobio. A* **2010**, *212*, 176-182.
- (6) Li, R.; Nakashima, T.; Galangau, O.; Iijima, S.; Kanazawa, R.; Kawai, T., *Chem.-Asian J.* **2015**, *10*, 1725-1730.
- (7) Moreno, J.; Schweighöfer, F.; Wachtveitl, J.; Hecht, S., *Chem. Eur. J.* **2016**, *22*, 1070-1075.
- (8) Lyaskovskyy, V.; Fröhlich, R.; Würthwein, E.-U., *Synthesis* **2007**, *2007*, 2135-2144.
- (9) Li, Z.; Kumar, A.; Vachhani, D. D.; Sharma, S. K.; Parmar, V. S.; Van der Eycken, E. V., *Eur. J. Org. Chem.* **2014**, *2014*, 2084-2091.
- (10) Avendaño, C.; Sánchez, J. D.; Menéndez, J. C., *Synlett* **2005**, *2005*, 107-110.
- (11) Baciocchi, E.; Ruzziconi, R.; Sebastiani, G. V., *J. Am. Chem. Soc.* **1983**, *105*, 6114-6120.
- (12) Sevrécourt, M.; Robba, M., *B. Soc. Chim. Fr. II-Ch.* **1977**, 142-144.
- (13) Berens, U.; Englert, U.; Geysler, S.; Runsink, J.; Salzer, A., *Eur. J. Org. Chem.* **2006**, *2006*, 2100-2109.
- (14) Ren, L.; Liu, C.; Wang, Z.; Zhu, X., *J. Mater. Chem. C* **2016**, *4*, 5202-5206.
- (15) Aubert, V.; Guerschais, V.; Ishow, E.; Hoang-Thi, K.; Ledoux, I.; Nakatani, K.; Le Bozec, H., *Angew. Chem. Int. Ed.* **2008**, *47*, 577-580.
- (16) Hatchard, C. G.; Parker, C. A., *P. Roy. Soc. Lond. A Mat.* **1956**, *235*, 518-536.
- (17) Montalti, M.; Credi, A.; Prodi, L.; Gandolfi, M. T., *Handbook of Photochemistry, Third Edition*. CRC Press: Boca Raton: **2006**; 601-616.
- (18) Frisch, M. J.; Trucks, G. W.; Schlegel, H. B.; Scuseria, G. E.; Robb, M. A.; Cheeseman, J. R.; Scalmani, G.; Barone, V.; Mennucci, B.; Petersson, G. A.; Nakatsuji, H.; Caricato, M.; Li, X.; Hratchian, H. P.; Izmaylov, A. F.; Bloino, J.; Zheng, G.; Sonnenberg, J. L.; Hada, M.; Ehara, M.; Toyota, K.; Fukuda, R.; Hasegawa, J.; Ishida, M.; Nakajima, T.; Honda, Y.; Kitao, O.; Nakai, H.; Vreven, T.; Montgomery, J. A.; Peralta, J. E.; Ogliaro, F.; Bearpark, M.; Heyd, J. J.; Brothers, E.; Kudin, K. N.; Staroverov, V. N.; Kobayashi, R.; Normand, J.; Raghavachari, K.; Rendell, A.; Burant, J. C.; Iyengar, S. S.; Tomasi, J.; Cossi, M.; Rega, N.; Millam, J. M.; Klene, M.; Knox, J. E.; Cross, J. B.; Bakken, V.; Adamo, C.; Jaramillo, J.; Gomperts, R.; Stratmann, R. E.; Yazyev, O.; Austin, A. J.; Cammi, R.; Pomelli, C.; Ochterski, J. W.; Martin, R. L.; Morokuma, K.; Zakrzewski, V. G.; Voth, G. A.; Salvador, P.; Dannenberg, J. J.; Dapprich, S.; Daniels, A. D.; Farkas; Foresman, J. B.; Ortiz, J. V.; Cioslowski, J.; Fox, D. J., Wallingford CT, 2009.
- (19) Becke, A. D., *J. Chem. Phys.* **1993**, *98*, 5648-5652.
- (20) Stephens, P. J.; Devlin, F. J.; Chabalowski, C. F.; Frisch, M. J., *J. Phys. Chem.* **1994**, *98*, 11623-11627.
- (21) Ditchfield, R.; Hehre, W. J.; Pople, J. A., *J. Chem. Phys.* **1971**, *54*, 724-728.
- (22) Miertuš, S.; Scrocco, E.; Tomasi, J., *Chem. Phys.* **1981**, *55*, 117-129.
- (23) Tomasi, J.; Mennucci, B.; Cancès, E., *J. Mol. Struct.-Theochem* **1999**, *464*, 211-226.