Supporting information

Asymmetrically bridged aroyl-*S,N*-ketene acetal-based multichromophores with aggregation-induced tunable emission

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1 General considerations

Reactions were carried out in dried and sintered *Schlenk* tubes or round bottom flasks under nitrogen atmosphere. Solvents were dried by a solvent purification system *MB-SPS-800* of the company *MBraun Inertgas-Systeme GmbH*.
The used chemicals which have not been synthesized were purchased at *Acros Organics BVBA, Alfa Aeser GmbH & Co KG, Fluorochem Ltd., J&K Scientific Ltd., Merck KGaA, Macherey-Nagel GmbH & Co. KG, Sigma-Aldrich Chemie GmbH* and *VWR* and have been used without further purification. The solvents ethanol and tetrahydrofuran (THF) (spectroscopic grade) were purchased from *Merck* and *Sigma-Aldrich* (Germany), respectively. Milli-Q-water was obtained from a *Millipore water purification system*. Carboxylated 8 µm-sized polystyrene particles (PSP) were obtained from *Kisker Biotech GmbH* (Germany).

Further purification of the compounds was performed by flash column chromatography (silica gel M60 pore size 0.040-0.063 nm) of the company *Macherey-Nagel*. The crude product was adsorbed on Celite®545 of the company *Carl Roth GmbH*, placed on the suspended silica gel and purified with a positive pressure of 2 bar. Distilled solvent mixtures of *n*-hexane, acetone and methanol have been used as eluents.

The control of reaction progress was done via thin layer chromatography (TLC) with silica coated aluminium plates F_{254}, of the company *Macherey-Nagel GmbH & Co. KG.*

The melting points have been measured with *Melting Point B-540* of the company *Büchi* according to the protocol of *Kofler*.[1] Several scans with increasing accuracy and decreasing increment enabled the determination of precise melting points.

^{1}H,^{13}C and DEPT 135-spectra have been measured at 298 K on an *Avance III - 300* and an *Avance III - 600* of the company *Bruker*. Chemical shifts in the ^{1}H and ^{13}C NMR are reported in ppm relative to deuterated solvents such as acetone-d_6 (δ_H 2.05, δ_C 29.84, δ_C 206.26) with CS_2 (δ_C 192.28) and DMSO-d_6 (δ_H 2.50, δ_C 39.51).[2] The multiplicity is abbreviated as followed: s = singulet; d = doublet; t = triplet; td = triplet of doublet; dd = doublet of doublet; dt = doublet of triplet, dq = doublet of $_{quat}$et; pd = pentet of doublet m = multiplet. The assignment of primary carbon centers (CH), secondary carbon centers (CH_2), tertiary carbon centers (CH_3) and quaternary carbon centers (C_{quat}) were made by using DEPT-135 spectra.
All mass spectrometry experiments have been performed by the department for mass spectrometry of the University of Düsseldorf (HHUCeMSA). EI mass spectra have been measured with Triple-Quadrupol-spectrometer *TSQ 7000* of the company *Finnigan MAT*. MALDI spectra have been measured with a *MALDI/TOF UltrafleXtreme* of the company *Bruker Daltronik*.

IR spectra were recorded with neat compounds under attenuated total reflection (ATR) with *IRAffinity-1* of the company *Shimadzu* and the intensities were characterized as strong (s), middle (m) and weak (w).

The elementary analyses have been measured with *Perkin Elmer Series II Analyser 2400* or *Vario Micro Cube* of the company *Analysensysteme GmbH* at the microanalytical laboratory of the institute for Pharmaceutical and Medicinal Chemistry of the University Düsseldorf.

UV/Vis spectra of the dye solutions were measured with a *Lambda 19* spectrometer from *Perkin Elmer*. The emission spectra of the dye solutions and the solid compounds were recorded with a *Hitachi F-7000* spectrofluorometer using the emission correction curve provided by the instrument manufacturer. Emission spectra were not corrected for the wavelength-dependent spectral responsivity of the fluorometer. All solution spectra were recorded with dyes dissolved in spectroscopic grade solvents at 298 K using 1 cm-quartz cuvettes from *Hellma GmbH*. The molar extinction coefficients of dye solutions of known dye concentration were determined by five-point regression line.

The fluorescence spectra of solutions and aggregates of selected dyes in solution and in the solid-state were also measured with a calibrated spectrofluorometer from *Edinburgh Instruments (FLS 920)* at Federal Institute for Materials Research and Testing (BAM), equipped with a xenon lamp, *Czerny−Turner* double monochromators, a reference channel, and *Glan−Thompson* polarizers. The polarizers were set to 0° and 54.7° in the excitation and emission channel, respectively (magic angle conditions). This instrument was also used for recording the fluorescence excitation and emission spectra of the dye-loaded PSP. The fluorescence excitation and emission spectra were measured with spectral bandwidths of 10 and 6 nm in excitation and emission, respectively, an integration time of 0.2 s, and a step width of 1 nm using 10 mm × 10 mm -quartz cuvettes from *Hellma GmbH*. The scan range was 400−750 nm, with three repetitive scans being performed for each sample. All spectra were subsequently corrected for the wavelength-dependent spectral responsivity of the fluorometer's detection channel determined with a calibrated spectral radiance transfer standard and a while standard.

The photoluminescence quantum yields (Φ_f) were determined absolutely with a calibrated integrating sphere setup from *Hamamatsu (Quantaurus-QY C11347-11*). All Φ_f measurements were performed at 25 °C using special 10 mm × 10 mm long neck $_{quat}$z cuvettes from *Hamamatsu*. With this setup, Φ_f values ≥ 0.01 can be reliably measured.

The fluorescence decay kinetics providing the fluorescence lifetimes (τ) of the dyes, dye aggregates, and dye-loaded particles were recorded with the calibrated fluorometer *Edinburgh Instruments* (*FLS 920*) equipped with a EPLED (ex 280 ± 10 nm, ex 330 ± 10 nm and 375 ± 10 nm) and a fast multichannel plate photomultiplier (*MCP-PMT*) as detector. All samples were

excited at the corresponding absorption maximum and the emission was always detected at the emission maximum with a spectral bandwidth of the emission monochromator of 10 nm, a 4096-channel setting, and time ranges of 20, and 50 ns. With this setup, τ values ≥ 0.2 ns can be reliably measured. The measured fluorescence decay kinetics were evaluated using the reconvolution procedure of the FAST program (Edinburgh Instruments). This procedure considers the measured instrument response function determined with a non-emissive scattering LUDOX solution (silica particle dispersion) which can influence the fluorescence decays. All photoluminescence decay profiles could be satisfactorily analyzed with mono-, bi- or tri-exponential fits with reduced χ^2 values between 0.8 and 1.2. From the multiexponential decays, subsequently, the intensity-weighted average lifetimes were calculated and provided.

2 Overview of synthesized bridged aroyl-*S,N*-ketene acetals 5

Table S1: Synthesis of bridged aroyl-*S,N*-ketene acetals **5**.

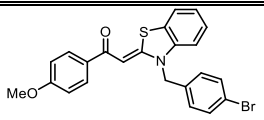
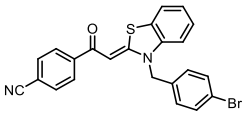
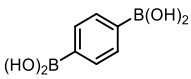
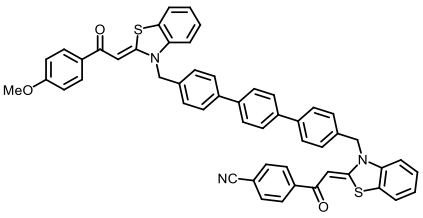
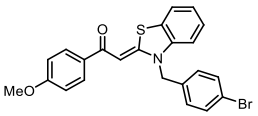
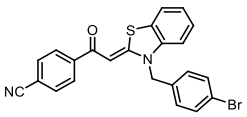
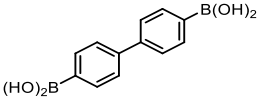
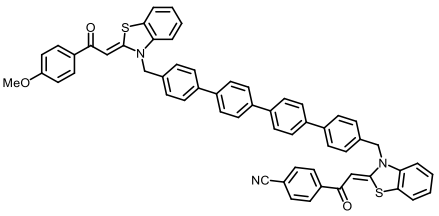
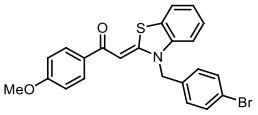
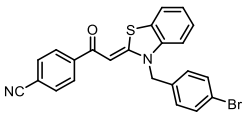
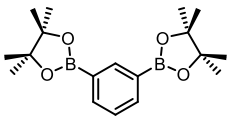
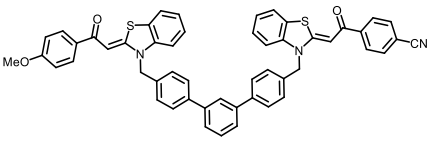
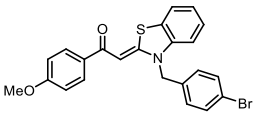
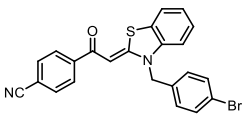
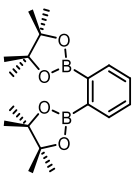
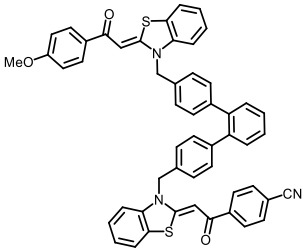
Entry	Aroyl-*S,N*-ketene acetals **3**	Boronic acid (ester) **4**	Bridged aroyl-*S,N*-ketene acetal **5** (%)
1	 **3a**  **3e**	 **4a**	 **5a** (64)
2	 **3a**  **3e**	 **4b**	 **5b** (40)
3	 **3a**  **3e**	 **4c**	 **5c** (73)
4	 **3a**  **3e**	 **4d**	 **5d** (43)

Table S2: Synthesis of bridged aroyl-*S,N*-ketene acetals **5**.

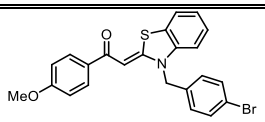
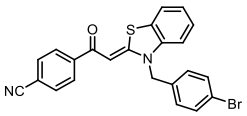
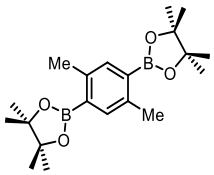
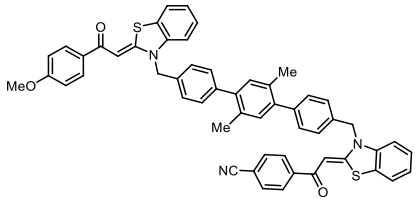
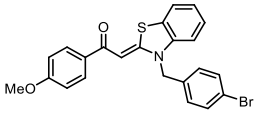
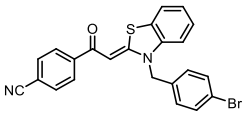
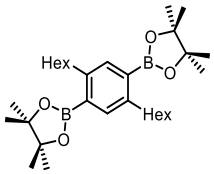
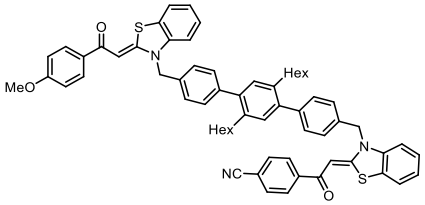
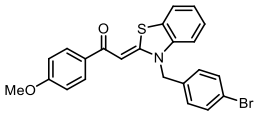
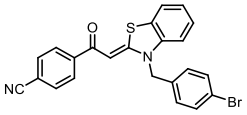
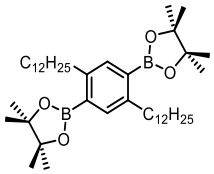
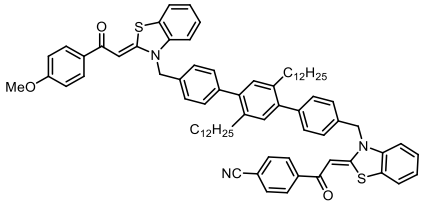
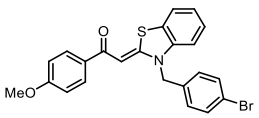
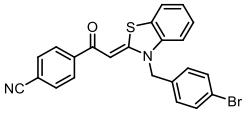
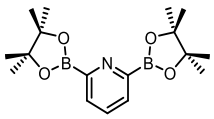
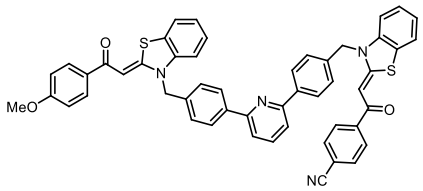
Entry	Aroyl-*S,N*-ketene acetals **3**	Boronic acid (ester) **4**	Bridged aroyl-*S,N*-ketene acetal **5** (%)
5	 **3a**  **3e**	 **4e**	 **5e** (94)
6	 **3a**  **3e**	 **4f**	 **5f** (58)
7	 **3a**  **3e**	 **4g**	 **5g** (59)
8	 **3a**  **3e**	 **4h**	 **5h** (19)

Table S3: Synthesis of bridged aroyl-*S,N*-ketene acetals **5**.

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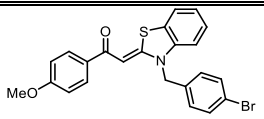
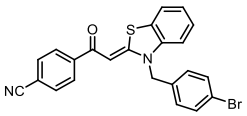
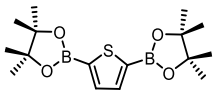
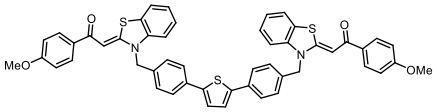
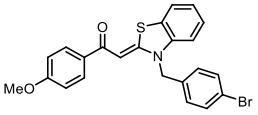
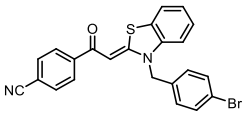
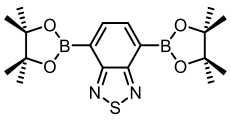
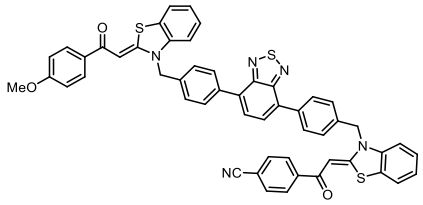
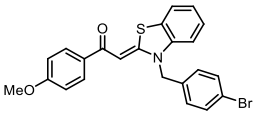
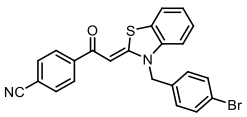
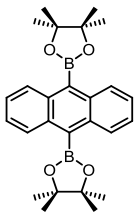
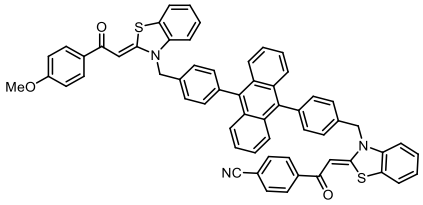
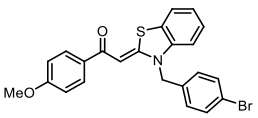
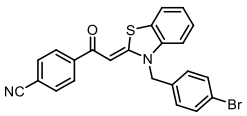
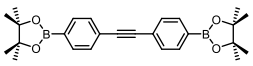
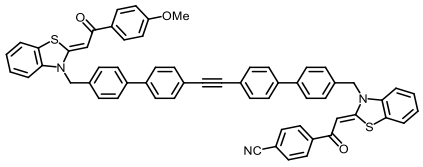
9	 **3a**  **3e**	 **4i**	 **5i** (47)
10	 **3a**  **3e**	 **4j**	 **5j** (71)
11	 **3a**  **3e**	 **4k**	 **5k** (28)
12	 **3a**  **3e**	 **4l**	 **5l** (61)

Table S4: Synthesis of bridged aroyl-*S,N*-ketene acetals **5**.

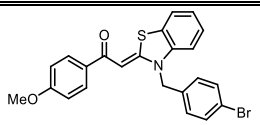
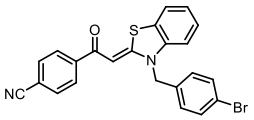
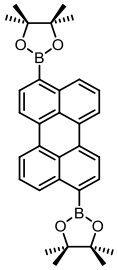
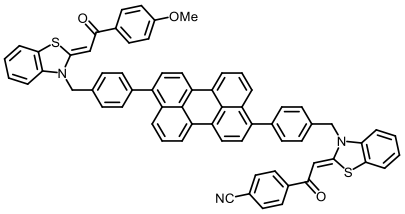
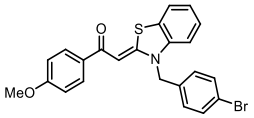
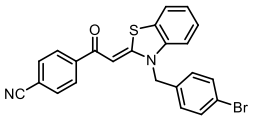
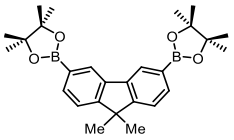
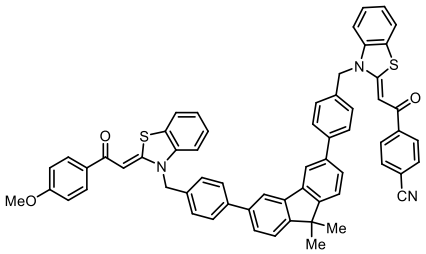
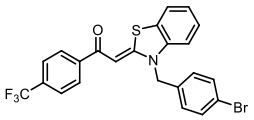
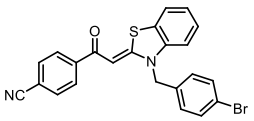
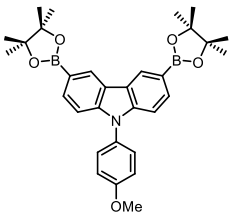
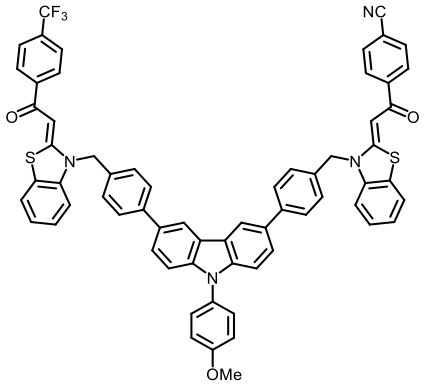
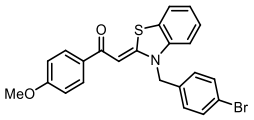
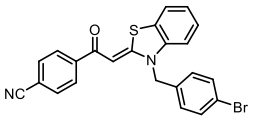
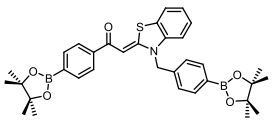
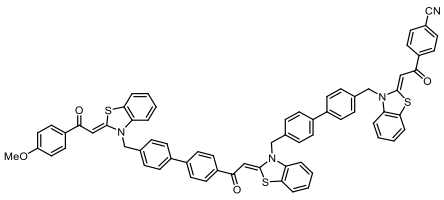
Entry	Aroyl-*S,N*-ketene acetals **3**	Boronic acid (ester) **4**	Bridged aroyl-*S,N*-ketene acetal **5** (%)
13	 **3a**  **3e**	 **4m**	 **5m** (74)
14	 **3a**  **3e**	 **4n**	 **5n** (76)
15	 **3d**  **3e**	 **4o**	 **5o** (72)
16	 **3a**  **3e**	 **4p**	 **5p** (76)

Table S5: Synthesis of bridged aroyl-*S,N*-ketene acetals **5**.

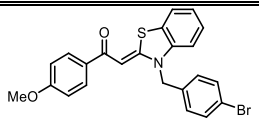
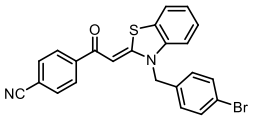
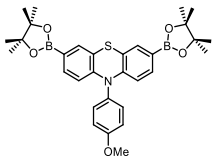
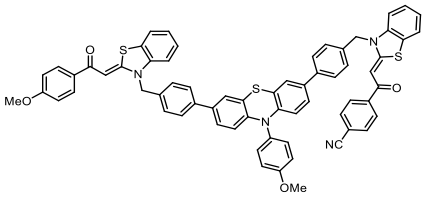
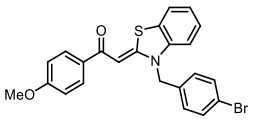
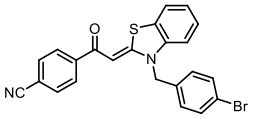
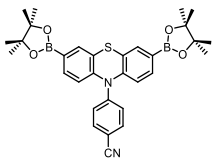
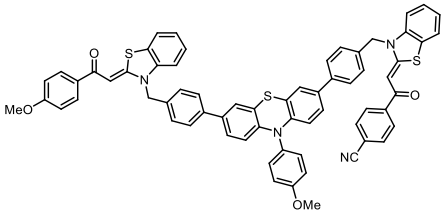
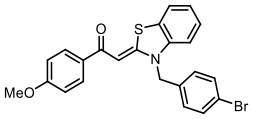
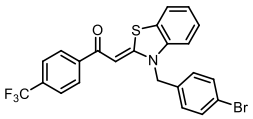
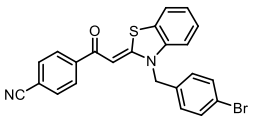
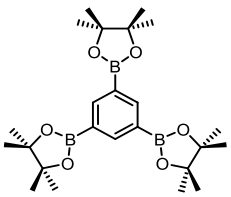
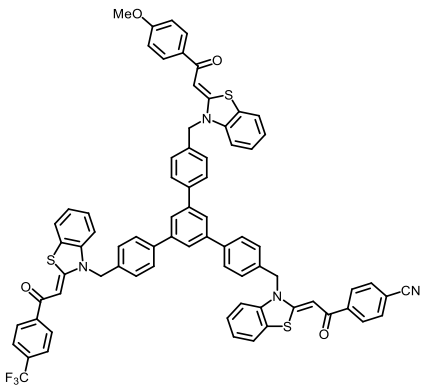
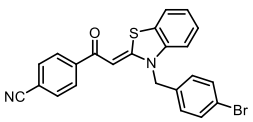
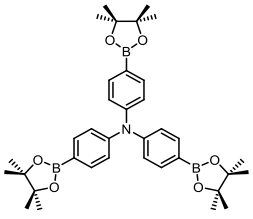
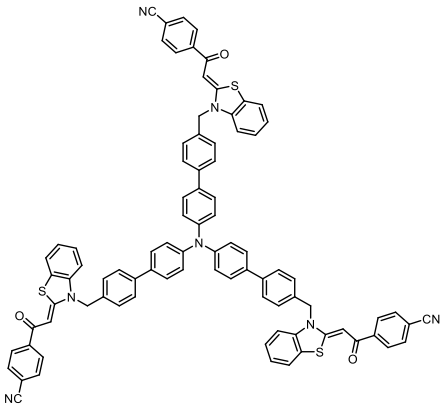
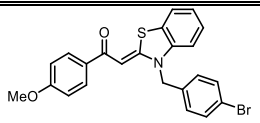
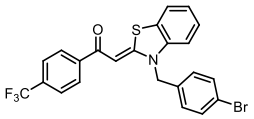
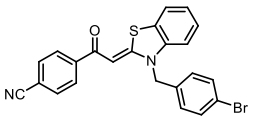
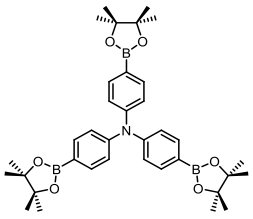
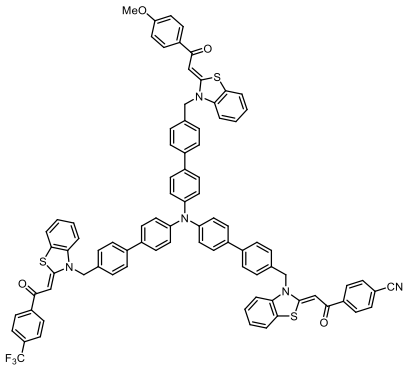
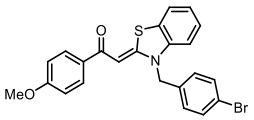
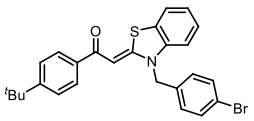
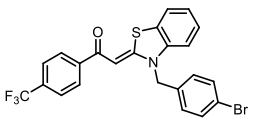
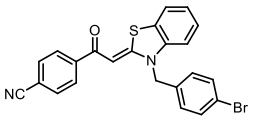
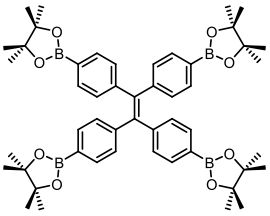
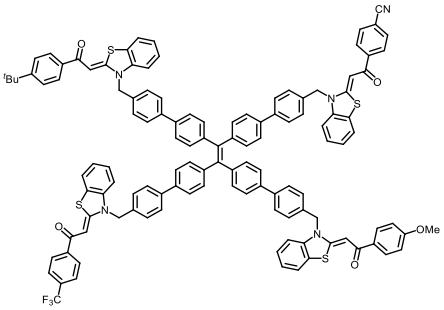
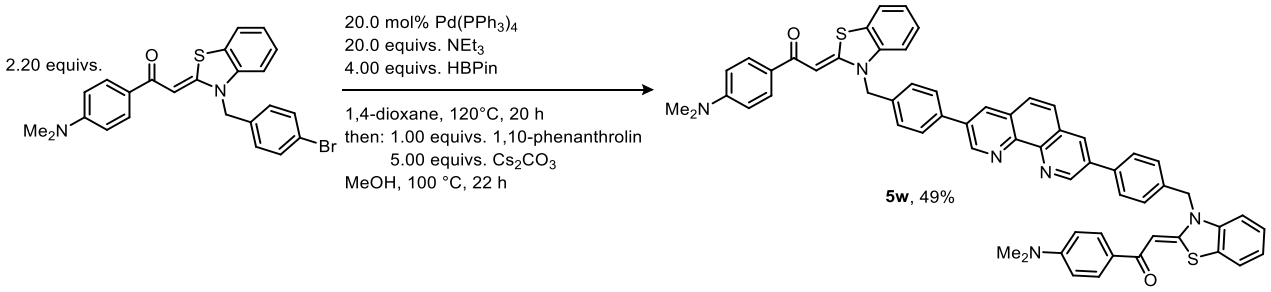
Entry	Aroyl-*S,N*-ketene acetals **3**	Boronic acid (ester) **4**	Bridged aroyl-*S,N*-ketene acetal **5** (%)
17	 **3a**  **3e**	 **4q**	 **5q** (55)
18	 **3a**  **3e**	 **4r**	 **5r** (76)
19	 **3a**  **3d**  **3e**	 **4s**	 **5s** (50)
20	 **3e**	 **4t**	 **5t** (67)

Table S6: Synthesis of bridged aroyl-*S,N*-ketene acetals **5**.

Entry	Aroyl-*S,N*-ketene acetals **3**	Boronic acid (ester) **4**	Bridged aroyl-*S,N*-ketene acetal **5** (%)
21	 **3a**  **3d**  **3e**	 **4t**	 **5u** (55)
22	 **3a**  **3b**  **3d**  **3e**	 **4u**	 **5v** (78)

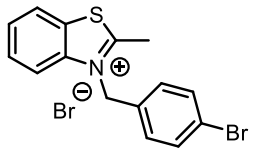


Scheme S1: Synthesis of 1,10-phenanthrolin-bridged dimethylamino-aroyl-*S,N*-ketene acetal **5w** via *Masuda* borylation-*Suzuki* coupling (MBSC) sequence.

3 Syntheses

3.1 Synthesis of starting materials

3.1.1 3-(4-Bromobenzyl)-2-methylbenzo[*d*]thiazol-3-iumbromide 2[3],[4]



$C_{15}H_{13}Br_2NS$

[396.91]

2-Methylbenzothiazole (3.73 g, 25.0 mmol) and 4-bromobenzyl bromide (7.50 g, 30.0 mmol) were placed in a round-bottom flask. The reaction mixture was stirred at 75 °C for 20 h, until the solution was completely hardened. The formed solid was filtrated via a Buechner funnel, washed with diethyl ether and dried under vacuo to give compound **2** (9.85 g,24.8 mmol, 99%) as a pink solid.

Mp: 237 °C.

R_f (*n*-hexane/acetone 4:1): 0.10.

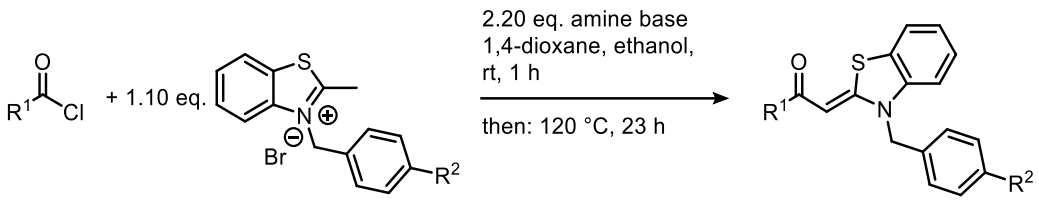
^{1}H NMR (300 MHz, DMSO-d_6): δ 3.25 (s, 3 H), 6.07 (s, 2 H), 7.29-7.32 (m, 2 H), 7.58-7.61 (m, 2 H), 7.82 (pd, ^3J = 7.5 Hz, ^4J = 1.9 Hz, 2 H), 8.18 (dd, ^3J = 7.5 Hz, ^4J = 1.5 Hz, 1 H), 8.50 (dd, ^3J = 7.4 Hz, ^4J = 1.8 Hz, 1 H).

^{13}C NMR (75 MHz, DMSO-d_6): δ 17.4 (CH_3), 51.3 (CH_2), 117.0 (CH), 121.8 (C_{quat}), 124.9 (CH), 128.2 (CH), 129.3 (CH), 129.4 (CH), 129.5 (C_{quat}), 131.9 (CH), 132.2 (C_{quat}), 140.9 (C_{quat}), 178.7 (C_{quat}).

EI + MS (70 eV, *m/z* (%)): 320 ($[C_{15}H_{13}{}^{81}BrNS]^+$, 13), 319 ($[C_{15}H_{12}{}^{81}BrNS]^+$, 69), 318 ($[C_{15}H_{13}{}^{79}BrNS^+$, 57), 317 ($[C_{15}H_{12}{}^{79}BrNS]^+$, 68), 316 (51), 238 ($[C_{15}H_{13}NS]^+$, 13), 236 (11), 223 ($[C_{14}H_9NS]^+$, 12), 171 ($[C_7H_6{}^{81}Br]^+$, 95), 169 ($[C_7H_6{}^{79}Br]^+$, 100), 162 ($[C_9H_8NS]^+$, 23), 149 ($[C_8H_6NS]^+$, 15), 148 ($[C_8H_6NS]^+$, 34), 124 (13), 119 (18), 118 (21), 108 (12), 104 ($[C_7H_6N]^+$, 12), 90 ($[C_7H_6]^+$, 43), 89 (36), 82 (14), 63 (12).

3.2 Synthesis and analytical data of aroyl-*S,N*-ketene acetals 3

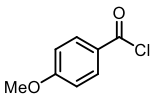
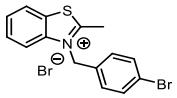
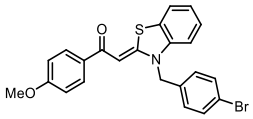
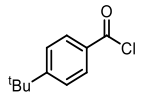
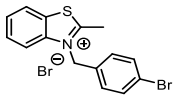
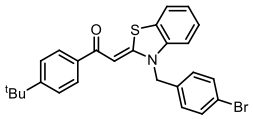
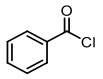
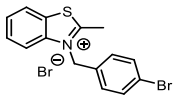
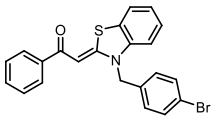
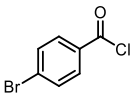
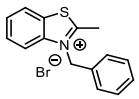
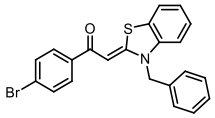
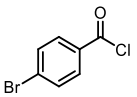
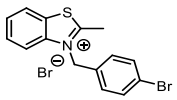
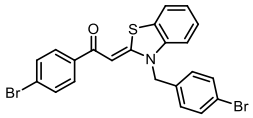
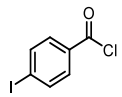
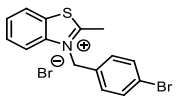
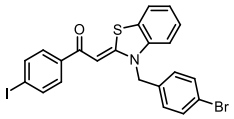
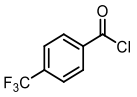
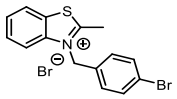
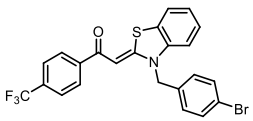
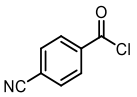
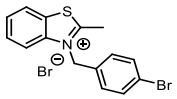
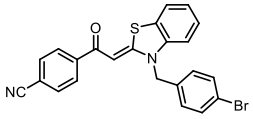
3.2.1 General procedure I (GPI) for the synthesis of aroyl-*S,N*-ketene acetals 3[4]



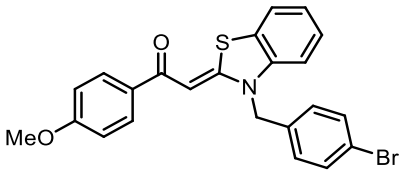
1 **2** **3**

Acid chloride **1** (1.00 equiv, 10.0 mmol) and 1.10 equiv (4.31 g, 11.0 mmol) of 3-benzyl-2-methylbenzo[*d*]thiazol-3-iumbromide **2** were placed in a sintered, dry screw-cap Schlenk-tube under nitrogen atmosphere and dissolved in 30 mL dry 1,4-dioxane and 10 mL ethanol. 2.20 equiv (22.0 mmol) amine base was added to the reaction mixture and the solution was stirred for 1 h at room temperature. Thereafter, the reaction mixture was stirred at 120 °C (oil bath) for 23 h. The crude product was absorbed onto Celite® and purified by flash chromatography on silica gel (*n*-hexane/acetone 3:1). The product was suspended in *n*-hexane, the sediment was filtrated and dried under vacuo.

Table S2: Experimental details for the synthesis of aroyl-*S,N*-ketene acetals **3**.[4]

Entry	Acid chloride **1** [g] ([mmol])	Benzylbenzo-thiazoliumbromide **2** [g] ([mmol])	Yield of product **3** [g] (%)
1	 1.70 (10.0) of **1a**	 4.31 (11.0) of **2**	 3.23 (72) of **3a**
2	 1.97 (10.0) of **1b**	 4.31 (11.0) of **2**	 3.11 (65) of **3b**
3	 1.40 (10.0) of **1c**	 4.31 (11.0) of **2**	 3.04 (72) of **3c**
4	 2.18 (10.0) of **1d**	 3.51 (11.0) of **2a**	 1.85 (44) of **3d**
5	 2.18 (10.0) of **1e**	 4.31 (11.0) of **2**	 1.99 (40) of **3e**
6	 2.66 (10.0) of **1f**	 4.31 (1.10) of **2**	 2.24 (59) of **3f**
7	 2.08 (10.0) of **1g**	 4.31 (11.0) of **2**	 1.67 (34) of **3g**
8	 1.65 (10.0) of **1h**	 4.31 (11.0) of **2**	 2.02 (45) of **3h**

(*Z*)-2-(3-(4-Bromobenzyl)benzo[*d*]thiazol-2(3*H*)-ylidene)-1-(4-(methoxyphenyl)ethan-1-one (3a)[4]



$C_{23}H_{18}BrNO_2S$

[451.02]

The synthesis was performed according to **GPI** to give compound **3a** (3.23 g, 7.16 mmol, 72%) as a yellow solid.

Mp: 169 °C.

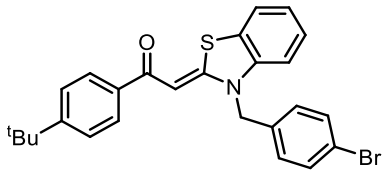
R_f (*n*-hexane/acetone 4:1): 0.18.

^{1}H NMR (600 MHz, acetone-d_6/CS_2 5:1): δ 3.83 (s, 3 H), 5.56 (s, 2 H), 6.82 (s, 1 H), 6.92 (d, ^3J = 8.8 Hz, 2 H), 7.20-7.22 (m, 1 H), 7.27 (d, ^3J = 8.1 Hz, 2 H), 7.31-7.36 (m, 2 H), 7.49-7.54 (m, 2 H), 7.72 (d, ^3J = 8.0 Hz, 1 H), 7.93 (d, ^3J = 8.1 Hz, 2 H).

^{13}C NMR (150 MHz, acetone-d_6/CS_2 5:1): δ 48.2 (CH_2), 54.9 (CH_3), 87.1 (CH), 110.4 (CH), 113.4 (CH), 121.1 (CH), 122.3 (CH), 122.9 (CH), 126.6 (CH), 127.1 (C_{quat}), 128.8 (CH), 129.0 (CH), 131.9 (CH), 132.3 (C_{quat}), 135.0 (C_{quat}), 140.0 (C_{quat}), 161.0 (C_{quat}), 162.0 (C_{quat}), 183.0 (C_{quat}).

MALDI-TOF (*m/z*): 454.1 ($C_{23}H_{18}{}^{81}BrNO_2S+H^+$), 452.1 ($C_{23}H_{18}{}^{79}BrNO_2S^+ + H^+$).

(*Z*)-2-(3-(4-Bromobenzyl)benzo[*d*]thiazol-2(3*H*)-ylidene)-1-(4-*tert*-butylphenyl)ethan-1-one (3b)[4]



$C_{26}H_{24}BrNOS$

[477.08]

The synthesis was performed according to **GPI** to give compound **3b** (3.11 g, 6.52 mmol, 65%) as a yellow solid.

Mp: 196 °C.

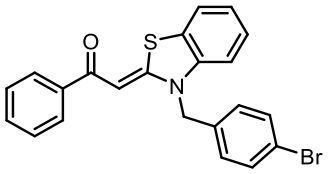
R_f (*n*-hexane/acetone 4:1): 0.35.

^{1}H NMR (600 MHz, acetone-d_6/CS_2 5:1): δ 1.34 (s, 9 H), 5.55 (s, 2 H), 6.80 (s, 1 H), 7.21-7.23 (m, 2 H), 7.27 (d, ^3J = 8.2 Hz, 2 H), 7.32-7.37 (m, 2 H), 7.43 (d, ^3J = 8.2 Hz, 2 H), 7.52 (d, ^3J = 8.5 Hz, 2 H), 7.73 (d, ^3J = 7.8 Hz, 1 H), 7.86 (d, ^3J = 7.8 Hz, 1 H).

^{13}C NMR (150 MHz, acetone-d_6/CS_2 5:1): δ 31.6 (CH_3), 35.3 (C_{quat}), 49.1 (CH_2), 88.3 (CH), 111.5 (CH), 122.2 (CH), 123.2 (CH), 123.8 (CH), 125.8 (CH), 127.4 (CH), 127.9 (C_{quat}), 128.0 (CH), 129.5 (CH), 132.7 (CH), 135.5 (C_{quat}), 137.8 (C_{quat}), 140.7 (C_{quat}), 154.6 (C_{quat}), 161.9 (C_{quat}), 184.2 (C_{quat}).

MALDI-TOF (*m/z*): 480.0 ($C_{26}H_{24}{}^{81}BrNOS+H^+$), 478.0 ($C_{26}H_{24}{}^{79}BrNOS+H^+$).

(*Z*)-2-(3-(4-Bromobenzyl)benzo[*d*]thiazol-2(3*H*)-ylidene)-1-phenylethan-1-one (3c)[4]



$C_{22}H_{16}BrNOS$

[421.01]

The synthesis was performed according to **GPI** to give compound **3c** (3.04 g, 7.22 mmol, 72%) as a yellow solid.

Mp: 176 °C (decomposition).

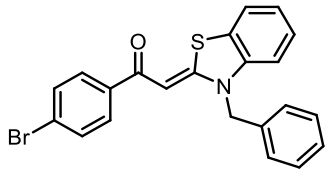
R_f (*n*-hexane/acetone 4:1): 0.18.

^{1}H NMR (300 MHz, acetone-d_6): δ 5.57 (s, 2 H), 6.83 (s, 1 H), 7.22-7.27 (m, 3 H), 7.32-7.43 (m, 5 H), 7.51 (d, ^3J = 8.3 Hz, 2 H), 7.73 (d, ^3J = 8.3 Hz, 1 H), 7.93 (d, ^3J = 8.1 Hz, 2 H).

^{13}C NMR (75 MHz, acetone-d_6): δ 49.1 (CH_2), 88.2 (CH), 111.2 (CH), 122.2 (C_{quat}), 123.2 (CH), 123.8 (CH), 127.5 (CH), 127.9 (CH), 128.0 (C_{quat}), 128.9 (CH), 129.5 (CH), 131.5 (CH), 132.7 (CH), 135.4 (C_{quat}), 140.4 (C_{quat}), 140.7 (C_{quat}), 162.3 (C_{quat}), 184.3 (C_{quat}).

EI + MS (70 eV, *m/z* (%)): 423 ($[C_{22}H_{16}{}^{81}BrNOS]^+$, 30), 421 ($[C_{22}H_{16}{}^{79}BrNOS]^+$, 30), 406 ($[C_{22}H_{15}{}^{81}BrNS]^+$, 13), 404 ($[C_{22}H_{15}{}^{79}BrNS]^+$, 12), 318 ($[C_{15}H_{11}{}^{81}BrNS]^+$, 25), 316 ($[C_{15}H_{11}{}^{79}BrNS]^+$, 27), 237 (19), 236 ($[C_{15}H_{10}N^{32}S]^+$, 28), 225 (11), 224 (40), 223 ($[C_{14}H_9NS]^+$, 49), 171 ($[C_7H_6{}^{81}Br]^+$, 61), 169 ($[C_7H_6{}^{81}Br]^+$, 62), 105 ($[C_7H_6O]^+$, 100), 90 ($[C_7H_6]^+$, 30), 89 ($[C_7H_5]^+$, 21), 77 ($[C_6H_5]^+$, 29).

(*Z*)-2-(3-Benzyl)benzo[*d*]thiazol-2(3*H*)-ylidene)-1-(4-bromophenyl)ethan-1-one (3d)[4]



$C_{22}H_{16}BrNOS$

[421.01]

The synthesis was performed according to **GPI** to give compound **3d** (1.85 g, 4.39 mmol, 44%) as a yellow solid.

Mp: 217 °C.

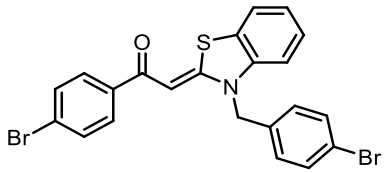
R_f (*n*-hexane/acetone 4:1): 0.20.

^{1}H NMR (600 MHz, acetone-d_6/CS_2 5:1): δ 5.60 (s, 2 H), 6.86 (s, 1 H), 7.23-7.39 (m, 8 H), 7.57 (d, ^3J = 8.6 Hz, 2 H), 7.77 (d, ^3J = 7.7 Hz, 1 H), 7.89 (d, ^3J = 8.5 Hz, 2 H).

^{13}C NMR (150 MHz, acetone-d_6/CS_2 5:1): δ 49.7 (CH_2), 88.0 (CH), 111.5 (CH), 123.2 (CH), 123.9 (CH), 124.1 (CH), 125.8 (CH), 127.4 (CH), 127.5 (CH), 128.0 (C_{quat}), 128.5 (C_{quat}), 129.7 (CH), 129.8 (CH), 132.2 (CH), 132.8 (CH), 136.0 (C_{quat}), 139.5 (C_{quat}), 140.7 (C_{quat}), 162.9 (C_{quat}), 182.8 (C_{quat}).

MALDI-TOF (*m/z*): 424.1 ($C_{22}H_{16}{}^{81}BrNOS+H^+$), 422.1 ($C_{22}H_{16}{}^{79}Br_2NOS+H^+$).

(*Z*)-2-(3-(4-Bromobenzyl)benzo[*d*]thiazol-2(3*H*)-ylidene)-1-(4-bromophenyl)ethan-1-one (3e)[4]



$C_{22}H_{15}Br_2NOS$

[500.92]

The synthesis was performed according to **GPI** to give compound **3e** (1.99 g, 3.97 mmol, 40%) as a yellow solid.

Mp: 199 °C.

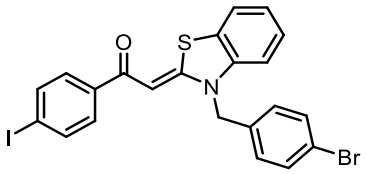
R_f (*n*-hexane/acetone 4:1): 0.30.

^{1}H NMR (500 MHz, acetone-d_6/CS_2 5:1): δ 5.59 (s, 2 H), 6.86 (s, 1 H), 7.24-7.28 (m, 3 H), 7.35-7.41 (m, 2 H), 7.48-7.52 (m, 2 H), 7.53-7.58 (m, 2 H), 7.77 (d, ^3J = 7.9 Hz, 1 H), 7.89 (d, ^3J = 8.5 Hz, 2 H).

^{13}C NMR (125 MHz, acetone-d_6/CS_2 5:1): δ 49.2 (CH_2), 88.0 (CH), 111.5 (CH), 122.2 (CH), 123.3 (CH), 124.1 (CH), 125.8 (CH), 127.6 (CH), 128.0 (C_{quat}), 129.6 (CH), 129.9 (CH), 132.2 (CH), 132.8 (CH), 135.5 (C_{quat}), 137.3 (C_{quat}), 138.2 (C_{quat}), 139.6 (C_{quat}), 140.7 (C_{quat}), 162.9 (C_{quat}), 183.1 (C_{quat}).

MALDI-TOF (*m/z*): 503.9 ($C_{22}H_{15}{}^{81}Br_2NOS+H^+$), 501.9 ($C_{22}H_{15}{}^{81}Br^{79}BrNOS+H^+$), 499.9 ($C_{22}H_{15}{}^{79}Br_2NOS+H^+$).

(*Z*)-2-(3-(4-Bromobenzyl)benzo[*d*]thiazol-2(3*H*)-ylidene)-1-(4-iodophenyl)ethan-1-one (3f)[4]



$C_{22}H_{15}BrINOS$

[546.91]

The synthesis was performed according to **GPI** to give compound **3f** (3.24 g, 5.92 mmol, 59%) as a yellow solid.

Mp: 236 °C.

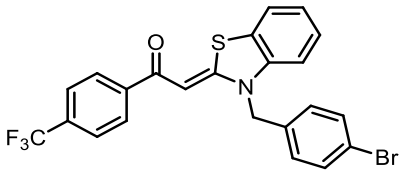
R_f (*n*-hexane/acetone 4:1): 0.43.

^{1}H NMR (600 MHz, acetone-d_6/CS_2 5:1): δ 5.51 (s, 2 H), 6.73 (s, 1 H), 7.20-7.23 (m, 3 H), 7.26-7.27 (m, 1 H), 7.32-7.35 (m, 1 H), 7.47-7.49 (m, 2 H), 7.66-7.68 (m, 2 H), 7.70 (d, ^3J = 7.9 Hz, 1 H), 7.72-7.74 (m, 2 H).

^{13}C NMR (150 MHz, acetone-d_6/CS_2 5:1): δ 49.1 (CH_2), 87.8 (CH), 98.7 (C_{quat}), 111.1 (CH), 122.4 (CH), 123.2 (CH), 123.9 (CH), 127.4 (CH), 128.0 (CH), 129.2 (CH), 129.7 (CH), 132.7 (CH), 134.9 (C_{quat}), 138.0 (C_{quat}), 139.7 (C_{quat}), 140.4 (C_{quat}), 162.5 (C_{quat}), 182.8 (C_{quat}).

MALDI-TOF (*m/z*): 549.9 ($C_{22}H_{15}{}^{81}BrOS+H^+$), 547.9 ($C_{22}H_{15}{}^{79}BrINOS+H^+$).

(*Z*)-2-(3-(4-Bromobenzyl)benzo[*d*]thiazol-2(3*H*)-ylidene)-1-(4-(trifluoromethyl)-phenyl)ethan-1-one (3g)[4]



$C_{23}H_{15}BrF_3NOS$

[489.00]

The synthesis was performed according to **GPI** to give compound **3g** (1.67 g, 3.42 mmol, 34%) as a yellow solid.

Mp: 209 °C.

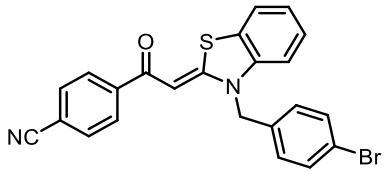
R_f (*n*-hexane/acetone 4:1): 0.26.

^{1}H NMR (600 MHz, acetone-d_6/CS_2 5:1): δ 5.63 (s, 2 H), 6.94 (s, 1 H), 7.26-7.28 (m, 3 H), 7.39-7.40 (m, 2 H), 7.51-7.53 (m, 2 H), 7.72 (d, ^3J = 8.1 Hz, 2 H), 7.79 (d, ^3J = 8.1 Hz, 1 H), 8.14 (d, ^3J = 8.1 Hz, 2 H).

^{13}C NMR (150 MHz, acetone-d_6/CS_2 5:1): δ 49.2 (CH_2), 88.3 (CH), 111.7 (CH), 122.2 (CH), 123.4 (CH), 124.2 (CH), 125.9 (CH), 126.0 (CF_3), 127.7 (CH), 127.9 (CH), 128.5 (C_{quat}), 129.5 (CH), 132.2 (CH), 132.4 (C_{quat}), 132.8 (CH), 135.4 (C_{quat}), 137.3 (C_{quat}), 138.2 (C_{quat}), 139.6 (C_{quat}), 143.8 (C_{quat}), 162.9 (C_{quat}), 183.1 (C_{quat}).

MALDI-TOF (*m/z*): 492.1 ($C_{23}H_{15}{}^{81}BrF_3NOS+H^+$), 490.1 ($C_{23}H_{15}{}^{79}BrF_3NOS^+ + H^+$).

(*Z*)-4-(2-(3-(4-Bromobenzyl)benzo[*d*]thiazol-2(3*H*)-ylidene)acetyl)benzonitrile (3h)[4]



$C_{23}H_{15}BrN_2OS$

[446.01]

The synthesis was performed according to **GPI** to give compound **3h** (2.02 g, 4.53 mmol, 45%) as an orange solid.

Mp: 250 °C (decomposition).

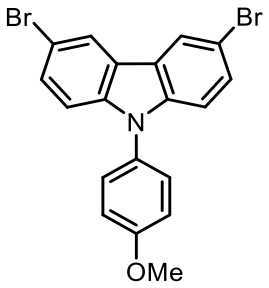
R_f (*n*-hexane/acetone 4:1): 0.20.

^{1}H NMR (300 MHz, DMSO-d_6): δ 5.67 (s, 2 H), 7.04 (s, 1 H), 7.16-7.27 (m, 3 H), 7.36-7.52 (m, 5 H), 7.85-7.91 (m, 2 H), 8.13 (d, ^3J = 8.2 Hz, 2 H).

^{13}C NMR (75 MHz, DMSO-d_6): δ 47.8 (CH_2), 87.7 (CH), 111.4 (CH), 113.0 (C_{quat}), 118.6 (C_{quat}), 120.7 (CH), 122.8 (CH), 123.4 (C_{quat}), 126.1 (CH), 127.0 (CH), 127.7 (CH), 128.9 (CH), 131.7 (CH), 134.9 (C_{quat}), 139.3 (C_{quat}), 142.6 (C_{quat}), 162.5 (C_{quat}), 181.0 (C_{quat}).

MALDI-TOF (*m/z*): 448.1 ($C_{23}H_{15}{}^{81}BrN_2OS+H^+$), 446.1 ($C_{23}H_{15}{}^{79}BrN_2OS+H^+$).

3.2.2 3,6-Dibromo-9-(4-methoxyphenyl)-9*H*-carbazol[5]



$C_{19}H_{13}Br_2NO$

[430.93]

3,6-Dibromocarbazol (0.975 g, 3.00 mmol, 1.00 equiv.), 1.50 equivs. (1.05 g, 4.50 mmol) 4-iodoanisol, 2.00 equivs. (0.828 g, 6.00 mmol) potassium carbonate and 1.20 equivs. (0.228 g, 3.60 mmol) copper powder were placed in a sintered, dry screw-cap *Schlenk*-tube under nitrogen atmosphere and dissolved in 8 mL dimethylacetamide. the reaction mixture was stirred at 180 °C (oil bath) for 40 h. After cooling to room temperature, the copper powder was filtered off and the residue washed several times with ethyl acetate. 30 mL deionized water and 30 mL ethyl acetate were added to the crude product and the mixture was transferred to a separation funnel. The organic layer was separated, and the watery layer was extracted five times with 20 mL deionized water and one time with 30 mL brine. The combined organic layers were dried with anhydrous magnesium sulfate, the drying agent was filtered off und the solvent was removed under reduced pressure. The crude product was adsorbed onto Celite® and purified by flash chromatography on silica gel (*n*-hexane/dichloromethane 2:1 to 1:1). This led to 0.789 g (1.83 mmol, 61 %) of the desired product as a colorless solid.

Mp:103 °C.

R_f (*n*-hexane/dichloromethane 2:1): 0.68.

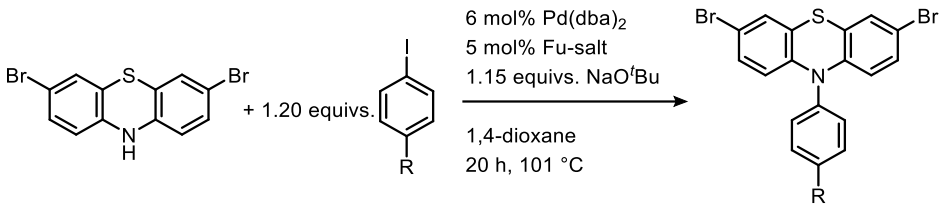
^{1}H NMR (300 MHz, acetone-d_6): δ 3.92 (s, 3 H), 7.19-7.32 (m, 4 H), 7.44-7.49 (m, 2 H), 7.52-7.62 (m, 2 H), 8.42-8.52 (m, 2 H).

^{13}C NMR (75 MHz, acetone-d_6): δ 56.0 (CH_3), 112.5 (CH) 113.3 (CH), 113.4 (CH), 116.2 (CH), 117.4 (C_{quat}), 124.3 (CH), 125.3 (C_{quat}), 129.3 (CH), 130.2 (CH), 135.9 (CH), 139.0 (C_{quat}), 141.3 (C_{quat}), 160.5 (C_{quat}).

EI + MS (70 eV, *m/z* (%)): 432 ([$C_{19}H_{13}{}^{81}Br^{81}BrNO]^+$, 17), 431 ([$C_{19}H_{13}{}^{79}Br^{81}BrNO]^+$, 90), 430 ([$C_{19}H_{13}{}^{79}Br^{79}BrNO]^+$, 42), 418 (14), 416 (32), 414 (15), 352 ([$C_{19}H_{13}{}^{81}BrNO]^+$, 11), 351 (11), 350 ([$C_{19}H_{13}{}^{79}BrNO]^+$, 10), 309 (20), 308 (18), 307 (22), 306 (15), 256 (20), 240 ([$C_{18}H_{10}N]^+$, 12), 239 (16), 234 ([$C_{16}H_{12}NO]^+$, 100), 229 (19), 228 (77), 227 (50), 226 (26), 219 (34), 201 (13), 200 (17), 191 (16), 188 (18), 186 (17), 176 (12), 175 (14), 164 (([$C_{12}H_6N]^+$, 17), 135 (22), 120 (12), 119 (17), 114 (47), 113 (20), 108 (23), 107 ([$C_7H_7O]^+$, 10), 100 (18), 92 (24), 78 (14), 77 (23), 65 (11), 64 ([$C_6H_4]^+$, 19), 63 (24), 50 (11).

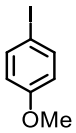
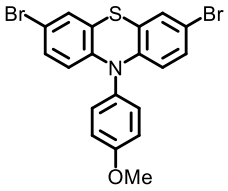
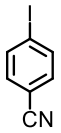
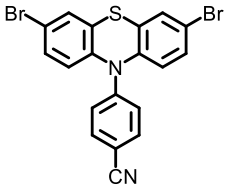
3.2.4 Synthesis and analytical data of N-arylated 3,7-dibromophenothiazines[6]

3.2.5 General procedure II (GPII) for the synthesis of N-arylated 3,7-dibromophenothiazines



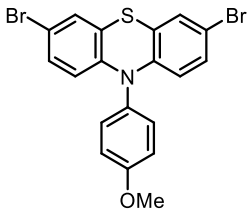
3,7-Dibromo phenothiazine (1.43 g, 4.00 mmol, 1.00 equiv.), 1.20 equivs, aryl iodide (4.80 mmol), 6 mol% (0.138 g, 0.240 mmol) dibenzylidenacetone palladium, 5 mol% (0.058 g, 0.200 mmol) *Fu*-salt and 1.15 equivs. (0.442 g, 4.60 mmol) sodium-*tert*-butoxide were placed in a sintered, dry screw-cap *Schlenk*-tube under nitrogen atmosphere and dissolved in 12 mL dry 1,4-dioxane. The reaction mixture was degased with nitrogen for 5 min and then stirred at 101 °C for 20 h. After cooling to rt, 30 mL deionized water, 15 mL saturated Na_2SO_3 solution and 50 mL dichloromethane were added to the crude product and the mixture was transferred to a separation funnel. The organic layer was separated, and the watery layer was extracted three times with 20 mL dichloromethane. The combined organic layers were dried with anhydrous magnesium sulfate, the drying agent was filtered off und the solvent was removed under reduced pressure. The crude product was adsorbed onto Celite®, purified by flash chromatography on silica gel (*n*-hexane/acetone 50:1 to 20:1 to 10:1 to 2:1) and dried under vacuo.

Table S3: Experimental details for the synthesis of *N*-arylated 3,7-dibromo phenothiazine.

Entry	Aryl iodide [g] ([mmol])	Yield of product [g] (%)
1		
	1.14 (4.80)	0.654 (35)
2		
	1.10 (4.80)	0.718 (39)

3.2.5.1 Spectroscopic data

3,7-Dibromo-10-(4-methoxyphenyl)-10*H*-phenothiazin



$C_{19}H_{13}Br_2NOS$

[462.91]

The synthesis was performed according to **GPII** to give 0.654 g (1.41 mmol, 35 %) of the desired product as a beige solid.

Mp: 77 °C.

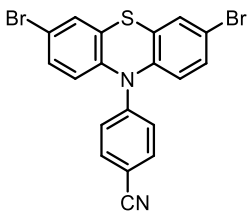
R_f (*n*-hexane/acetone 4:1): 0.43.

^{1}H NMR (300 MHz, acetone-d_6): δ 3.77 (s, 3 H), 6.79 (d, ^3J = 7.8 Hz, 2 H), 7.02-7.07 (m, 4 H), 7.15-7.20 (m, 2 H), 7.57 (d, ^3J = 2.0 Hz, 2 H).

^{13}C NMR (75 MHz, acetone-d_6): δ 55.0 (CH_3), 115.0 (CH), 118.2 (C_{quat}), 119.4 (CH), 122.1 (C_{quat}), 128.2 (CH), 128.5 (CH), 131.3 (CH), 137.4 (C_{quat}), 143.4 (C_{quat}), 158.7 (C_{quat}).

EI + MS (70 eV, *m/z* (%)): 465 ($[C_{19}H_{13}{}^{82}Br_2NOS]^+$, 2), 463 ($[C_{19}H_{13}{}^{82}Br^{79}BrNOS]^+$, 4), 461 ($[C_{19}H_{13}{}^{79}Br_2NOS]^+$, 2), 445.2 (19), 340 (24), 339 (41), 237 (23), 210 (35), 198 (19), 197 ($[C_{12}H_7NS]^+$, 100), 194 (12), 178 (14), 166 (16), 165 (57), 153 (11), 152 (13), 135 (23), 131 (18), 105 (11), 103 (17), 91 (17), 77 ($[C_6H_5]^+$, 17), 57 (14), 56 (11).

3,7-Dibromo-10-(4-cyanophenyl)-10*H*-phenothiazin



$C_{19}H_{10}Br_2N_2S$

[457.89]

The synthesis was performed according to **GPII** to give 0.718 g (1.57 mmol, 39 %) of the desired product as a yellow solid.

Mp: 80 °C.

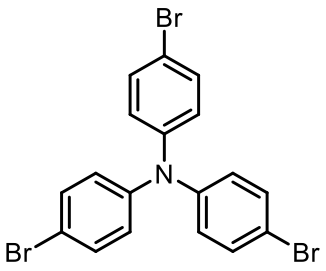
R_f (*n*-hexane/acetone 4:1): 0.38.

^{1}H NMR (300 MHz, acetone-d_6): δ 6.87 (d, ^3J = 7.8 Hz, 2 H), 7.36-7.40 (m, 4 H), 7.51 (d, ^3J = 2.3 Hz, 2 H), 7.82-7.85 (m, 2 H).

^{13}C NMR (75 MHz, acetone-d_6): δ 55.0 (CH_3), 108.8 (C_{quat}), 118.2 (C_{quat}), 119.2 (C_{quat}), 123.8 (CH), 124.7 (CH), 130.5 (C_{quat}), 131.0 (CH), 142.0 (C_{quat}), 147.6 (C_{quat}).

EI + MS (70 eV, *m/z* (%)): 460 ($[C_{19}H_{10}{}^{82}Br_2N_2S]^+$, 44), 459 (22), 458 ($[C_{19}H_{10}{}^{82}Br^{79}BrN_2S]^+$, 100), 456 ($[C_{19}H_{10}{}^{79}Br_2N_2S]^+$, 46), 380 (34), 379 ($[C_{19}H_{10}{}^{82}BrN_2S]^+$, 79), 378 (46), 377 ($[C_{19}H_{10}{}^{79}BrN_2S]^+$, 79), 358 ($[C_{12}H_6{}^{82}Br_2NS]^+$, 15), 356 ($[C_{12}H_6{}^{82}Br^{79}BrNS]^+$, 32), 354 ($[C_{12}H_6{}^{79}Br_2NS]^+$, 15), 300 (44), 299 (64), 298 ($[C_{19}H_{10}N_2S]^+$, 68), 296 (17), 278 (11), 277 (20), 276 (13), 275 (20), 268 (14), 267 (10), 266 (29), 265 (10), 253 (12), 234 (19), 233 (23), 229 (14), 199 (10), 198 (19), 197 (26), 196 ($[C_{12}H_6NS]^+$, 77), 190 (17), 189 (20), 169 (13), 164 (12), 153 (11), 152 (21), 150 (14), 148 (11), 136 (10), 135 (18), 127 (11), 103 (15), 102 ($[C_7H_4N]^+$, 33), 91 (17), 77 ($[C_6H_5]^+$, 14), 76 (14), 75 (26), 69 (15), 63 (14), 51 (15).

3.2.6 Tris(4-bromophenyl)amine[7]



$C_{18}H_{12}Br_3N$

[482.01]

Triphenylamine (1.47 g. 6.00 mmol, 1.00 equiv.) were placed in a sintered, dry screw-cap *Schlenk*-tube under nitrogen atmosphere and dissolved in 18 mL dimethyl formamide. The *Schlenk*-tube was darkened using aluminium foil and cooled to 0 °C with an ice bath. Then, *N*-bromosuccinimide (3.52 g, 19.8 mmol, 3.30 equivs.) were added in portions to the solution and was stirred at 0 °C for 1 h. The ice bath was removed, the reaction mixture warmed up to room temperature and stirred at this temperature for 5 h. 30 mL deionized water and 30 mL chloroform was added to the reaction mixture and it was transferred to a separation funnel. The organic layer was separated, and the watery layer was extracted three times with 20 mL chloroform. The organic layer was dried with anhydrous magnesium sulfate, the drying agent was filtered off und the solvent was removed under reduced pressure. The crude product was adsorbed onto Celite® and purified by flash chromatography on silica gel (*n*-hexane/acetone 100:1) to give 2.85 g (5.91 mmol, 99 %) of the desired product as a colorless solid.

Mp: 122 °C.

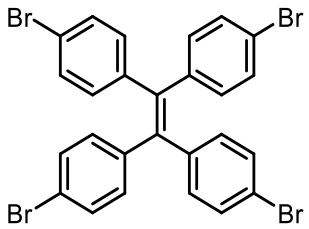
R_f (*n*-hexane/acetone 10:1): 0.70.

^{1}H NMR (300 MHz, acetone-d_6): δ 7.02-7.06 (m, 6 H), 7.63-7.67 (m, 6 H).

^{13}C NMR (75 MHz, acetone-d_6): δ 25.3 (CH_3), 84.1 (C_{quat}), 124.1 (CH), 136.8 (CH), 150.4 (C_{quat}).

EI + MS (70ev, *m/z* (%)): 485 ($[C_{18}H_{12}{}^{81}Br_3N]^+$, 16), 483 ($[C_{18}H_{12}{}^{79}Br^{81}Br_2N]^+$, 60), 481 ($[C_{18}H_{12}{}^{79}Br_2{}^{81}BrN]^+$, 56), 479 ($[C_{18}H_{12}{}^{79}Br_3N]^+$, 17), 403 ($[C_{18}H_{11}{}^{81}Br_2N]^+$, 11), 401 ($[C_{18}H_{11}{}^{79}Br^{81}BrN]^+$, 21), 399 ($[C_{18}H_{11}{}^{79}Br_2N]^+$, 11), 323 ($[C_{18}H_{12}{}^{81}BrN]^+$, 31), 322 (14), 321 ($[C_{18}H_{12}{}^{79}BrN]^+$, 39), 320 (10), 242 ($[C_{18}H_{12}N]^+$, 30), 241 (81), 240 (25), 139 (12), 166 (36), 165 (13), 164 (15), 155 (11), 140 (30), 139 (38), 121 (41), 121 (100), 119 (17), 76 (23), 75 (21).

3.2.7 1,1,2,2-Tetrakis(4-bromophenyl)ethene[8]



$C_{26}H_{16}Br_4$

[647.79]

Tetraphenylethene (2.56 g, 7.70 mmol) was placed in a sintered, dry screw-cap *Schlenk*-tube under nitrogen atmosphere and dissolved in 15 mL acetic acid. The reaction mixture was cooled to 0 °C with an ice bath and 3.0 mL (60 mmol) bromine was added over a period of 20 min. After adding 11 mL dichloromethane, the red reaction mixture was heated to 50 °C (oil bath) and stirred at this temperature for 30 min. After cooling to room temperature, the reaction mixture was poured into deionized water. The precipitated solid was filtered using a Büchner funnel and washed several times with ethanol and deionized water to give 5.01 g (7.70 mmol, 100 %) of the desired product as a colorless solid.

Mp: 246 °C.

R_f (*n*-hexane): 0.33.

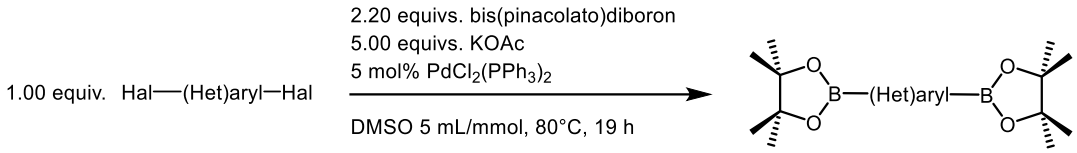
^{1}H NMR (300 MHz, $CDCl_3$): δ 6.90-6.94 (m, 8 H), 7.29-7.34 (m, 8 H).

^{13}C NMR (75 MHz, $CDCl_3$): δ 121.4 (C_{quat}), 131.5 (CH), 132.9 (CH), 139.8 (C_{quat}), 141.6 (C_{quat}).

EI + MS (70 eV, *m/z* (%)): 650 ($[C_{26}H_{16}{}^{81}Br_3{}^{79}Br]^+$, 27), 648 ($[C_{26}H_{16}{}^{81}Br_2{}^{79}Br_2]^+$, 48), 646 ($[C_{26}H_{16}{}^{81}Br{}^{79}Br_3]^+$, 30), 570 (13), 568 (16), 488 (15), 329 (15), 328 ($[C_{26}H_{16}]^+$, 44), 327 (40), 326 (37), 324 (14), 253 (14), 252 (39), 251 (10), 250 (26), 176 (11), 165 (15), 164 (74), 163 ($[C_{13}H_7]^+$, 44), 162 (52), 161 (11), 157 (60), 151 (15), 150 (35), 149 (12).

3.3 Synthesis and analytical data of pinacol boronic acid ester 4[9]

3.3.1 General procedure III (GPIII) for the synthesis of bispinacol boronic acid ester 4[9]



Dihalide (1.00 equiv.) was placed in a sintered, dry screw-cap *Schlenk*-tube under nitrogen atmosphere and dissolved in DMSO (5 mL/mmol). Potassium acetate (5.00 equivs.), bisp(pinacolato)diboron (2.20 equivs.) and bis(triphenylphosphine)palladium(II)-dichlorid (5.00 mol%) were added and the brown reaction mixture was stirred at 80 °C for 19 h. The catalysator was filtered off and 20 mL chloroform was added to the crude mixture. The mixture was transferred to a separation funnel and the organic layer was extracted five times with 50 mL deionized water. The combined organic layers were dried with anhydrous magnesium sulfate, the drying agent was filtered off und the solvent was removed under reduced pressure. The crude product was adsorbed onto Celite® and purified by flash chromatography on silica gel (*n*-hexane/acetone).

Table S4: Experimental details for the synthesis of diboronic acid esters **4**.

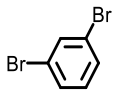
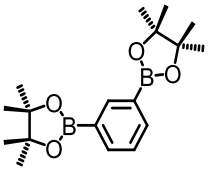
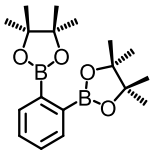
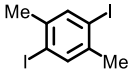
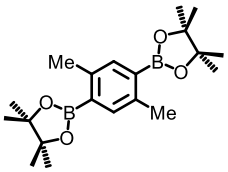
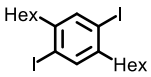
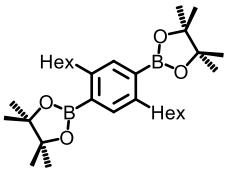
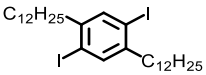
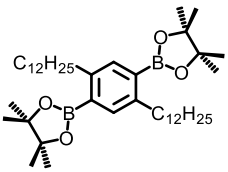
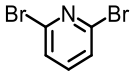
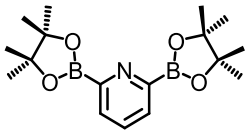
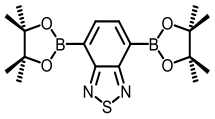
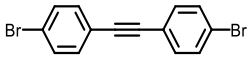
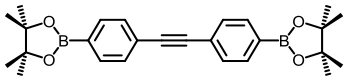
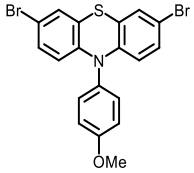
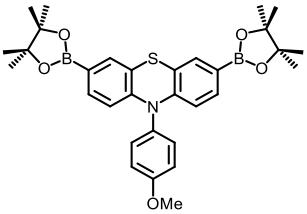
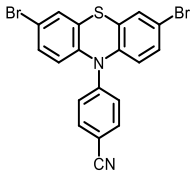
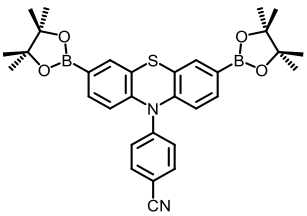
Entry	(Hetero)aryl-Br_2 [g] ([mmol])	Yield of product [g] (%)
1[(a)]		
	0.610 (2.50)	0.523 (63) of **4c**
2[(a)]		
	0.610 (2.50)	0.565 (68) of **4d**
3[(a)]		
	0.895 (2.50)	0.772 (86) of **4e**
4[(a)]		
	1.25 (2.50)	0.823 (68) of **4f**
5[(b)]		
	0.999 (1.50)	0.866 (87) of **4g**
6[(a)]		
	0.592 (2.50)	0.740 (89) of **4h**

Table S4: Experimental details for the synthesis of diboronic acid esters **4**.

Entry	(Hetero)aryl-Br_2 [g] ([mmol])	Yield of product [g] (%)
7[(c)]		
	0.588 (2.00)	0.545 (56) of **4j**
8[(a)]		
	0.840 (2.50)	0.854 (79) of **4l**
9[(b)]		
	0.694 (1.50)	0.222 (27) of **4q**
10[(d)]		
	0.458 (1.00)	0.231 (42) of **4r**

(a): KOAc: 1.30 g (12.5 mmol), Bis(pinacolato)diboron: 1.59 g (6.25 mmol), $PdCl_2(PPh_3)_2$: 0.175 g (0.250 mmol).

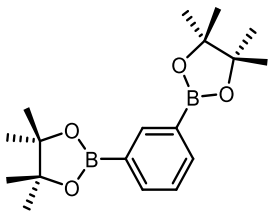
(b): KOAc: 0.768 g (7.50 mmol), Bis(pinacolato)diboron: 0.800 g (3.15 mmol), $PdCl_2(PPh_3)_2$: 0.105 g (0.150 mmol).

(c): KOAc: 0.982 g (10.0 mmol), Bis(pinacolato)diboron: 1.22 g (4.80 mmol), $PdCl_2(PPh_3)_2$: 0.351 g (0.500 mmol).

(d): KOAc: 0.512 g (5.00 mmol), Bis(pinacolato)diboron: 0.533 g (2.10 mmol), $PdCl_2(PPh_3)_2$: 0.070 g (0.100 mmol).

3.3.2 Spectroscopic Data

Benzene-1,3-diboronic acid bis(pinacol)ester (4c)



$C_{18}H_{28}B_2O_4$

[330.22]

The synthesis was performed according to **GPIII**. The purification was performed by flash chromatography on silica gel (*n*-hexane/acetone 20:1) followed by a recrystallization in methanol to give compound **4c** (0.523 g, 1.58 mmol, 63 %) as a colorless solid.

Mp: 126 °C.

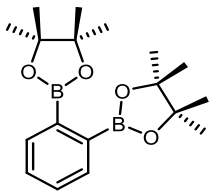
R_f (*n*-hexane): 0.32.

^{1}H NMR (300 MHz, $CDCl_3$): δ 1.34 (s, 24 H), 7.37 (td, ^1J = 7.4 Hz, ^2J = 0.7 Hz, 1 H), 7.91 (dd, ^1J = 7.4 Hz, ^2J = 1.3 Hz, 2 H), 8.28 (s, 1 H).

^{13}C NMR (75 MHz, $CDCl_3$): δ 25.0 (CH_3), 83.9 (C_{quat}), 127.8 (CH), 137.8 (CH), 141.4 (C_{quat}).

EI + MS (70 eV, *m/z* (%)): 330 ($[C_{18}H_{27}B_2O_4]^+$, 27), 315 ($[C_{17}H_{25}B_2O_4]^+$, 49), 273 ($[C_{15}H_{23}B_2O_3]^+$, 20), 244 ($[C_{12}H_{16}B_2O_4]^+$, 100), 231 ($[C_{12}H_{17}B_2O_3]^+$, 89), 215 ($[C_{12}H_{17}B_2O_2]^+$, 19), 187 (10), 158 (22), 150 (11), 144 (20), 131 (25), 101 ($[C_6H_{13}O]^+$, 17), 84 ($C_6H_{12}]^+$, 52), 59 (14), 57 (12), 43 (27).

Benzene-1,2-diboronic acid bis(pinacol)ester (4d)



$C_{18}H_{28}B_2O_4$

[330.22]

The synthesis was performed according to **GPIII**. The purification was performed by flash chromatography on silica gel (*n*-hexane/acetone 20:1) to give compound **4d** (0.565 g, 1.71 mmol, 68 %) a colorless solid.

Mp: 69 °C.

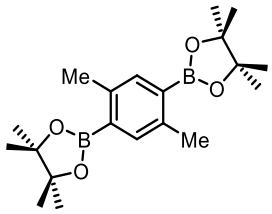
R_f (*n*-hexane/acetone 20:1): 0.31.

^{1}H NMR (300 MHz, $CDCl_3$): δ 1.37 (s, 24 H), 7.35-7.38 (m, 2 H), 7.63-7.66 (m, 2 H).

^{13}C NMR (75 MHz, $CDCl_3$): δ 25.0 (CH_3), 84.0 (C_{quat}), 129.3 (CH), 133.6 (CH).

EI + MS (70 eV, *m/z* (%)): 272 ($[C_{15}H_{22}B_2O_3]^+$, 20), 203 ($[C_{12}H_{16}BO_2]^+$, 10), 189 ($[C_{11}H_{14}BO_2]^+$, 100), 149 ($[C_5H_3B_2O_4]^+$, 21), 84 ($[C_6H_{12}]^+$, 42), 69 ($[C_5H_9]^+$, 11), 43 ($[C_2H_3O]^+$, 10), 41 ($[C_3H_5]^+$, 14).

2,2'-(2,5-Dimethyl-1,4-phenylene)bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolan) (4e)



$C_{20}H_{32}B_2O_4$

[358.25]

The synthesis was performed according to **GPIII**. The purification was performed by flash chromatography on silica gel (*n*-hexane/acetone 12:1 to 10:1 to 5:1) to give compound **4e** (0.772 g, 2.15 mmol, 86 %) as a colorless solid.

Mp: 144 °C.

R_f (*n*-hexane/acetone 10:1): 0.04.

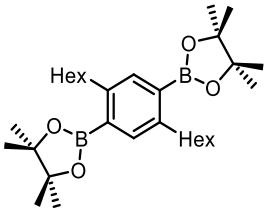
^{1}H NMR (300 MHz, $CDCl_3$): δ 1.34 (s, 24 H), 2.49 (s, 6 H), 7.54 (s, 2 H).

^{13}C NMR (75 MHz, $CDCl_3$): δ 21.6 (CH_3), 25.0 (CH_3), 83.5 (C_{quat}), 137.0 (CH), 140.7 (C_{quat}).

EI + MS (70 eV, *m/z* (%)): 358 ($[C_{20}H_{32}B_2O_4]^+$, 38), 357 (20), 301 (38), 300 (33), 299 (12), 259 ($[C_{13}H_{17}B_2O_4]^+$, 26), 258 (35), 257 ($[C_{14}H_{19}B_2O_3]^+$, 100), 256 (24), 243 ($[C_{13}H_{17}B_2O_3]^+$, 16), 243 ($[C_{12}H_{14}BO_2]^+$, 34), 200 (23), 199 (11), 159 (24), 158 (26), 157 (25), 150 (11), 131 ($[C_7H_4BO_2]^+$, 11), 101 ($[C_6H_{13}O]^+$, 18), 84 ($C_6H_{13}]^+$, 11), 83 (38), 59 (12), 57 (11), 55 (12).

*The quaternary carbon nucleus covalently bound to the boron core could not be observed in the ^{13}C NMR spectrum.

1,1'-(2,5-Bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-1,4-phenylene)bis(hexane) (4f)



$C_{30}H_{52}B_2O_4$

[498.41]

The synthesis was performed according to **GPIII**. The purification was performed by flash chromatography on silica gel (*n*-hexane/acetone 20:1) to give compound **4f** (0.823 g, 1.65 mmol, 66 %) as a colorless solid.

Mp: 90 °C.

R_f (*n*-hexane/acetone 10:1): 0.71.

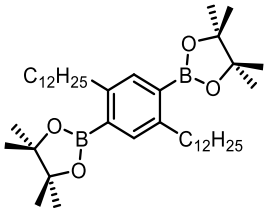
^{1}H NMR (300 MHz, $CDCl_3$): δ 0.79-0.89 (m, 6 H), 1.19-1.31 (m, 36 H), 1.41-1.47 (m, 4 H), 2.71-2.76 (m, 4 H), 7.45 (s, 2 H).

^{13}C NMR (75 MHz, $CDCl_3$): δ 14.3 (CH_3), 22.9 (CH_2), 25.0 (CH_3), 29.8 (CH_2), 32.0 (CH_2), 34.0 (CH_2), 35.7 (CH_2), 83.4 (C_{quat}), 136.6 (CH), 146.3 (C_{quat}).

EI + MS (70 eV, *m/z* (%)): 500 (11), 499 ($[C_{30}H_{52}B_2O_4]^+$, 37), 498 (19), 441 ($[C_{26}H_{43}B_2O_4]^+$, 13), 440 (21), 427 ($[C_{25}H_{41}B_2O_4]^+$, 20), 397 (11), 383 (33) 372 ($[C_{24}H_{40}BO_2]^+$, 14), 369 ($[C_{21}H_{32}B_2O_4]^+$, 12), 327 ($[C_{18}H_{25}B_2O_4]^+$, 11), 327 ($[C_{18}H_{25}B_2O_4]^+$, 11), 315 (28), 314 ($[C_{20}H_{31}BO_2]^+$, 26), 313 (14), 301 ($[C_{19}H_{29}BO_2]^+$, 13), 283 (12), 271 (21), 257 ($[C_{14}H_{19}B_2O_3]^+$, 16), 255 (10), 245 (28), 244 (59), 243 ($[C_{13}H_{17}B_2O_3]^+$, 31), 241 (11), 231 (14), 229 (12), 227 (11), 217 (10), 216 (16), 215 (38), 201 (35), 199 (12), 187 (13), 185 (10), 183 (10), 175 (13), 173 (15), 171 (15), 159 (12), 157 (21), 145 (14), 143 (18), 131 ($[C_7H_4BO_2]^+$, 31), 129 (14), 117 (15), 101 ($[C_6H_{13}O]^+$, 66), 85 (30), 84 ($[C_6H_{13}]^+$, 49), 83 ($[C_6H_{12}]^+$, 100), 59 (14), 57 (19), 55 (36).

*The quaternary carbon nucleus covalently bound to the boron core could not be observed in the ^{13}C NMR spectrum.

2,2'-(2,5-Didodecyl-1,4-phenylene)bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolan) (4g)



$C_{42}H_{76}B_2O_4$

[666.59]

The synthesis was performed according to **GPIII**. The purification was performed by flash chromatography on silica gel (*n*-hexane/acetone 100:1 to 50:1 to 5:1) to give compound **4g** (0.866 g, 1.30 mmol, 87 %) as a beige solid.

Mp: 66 °C.

R_f (*n*-hexane/acetone 10:1): 0.73.

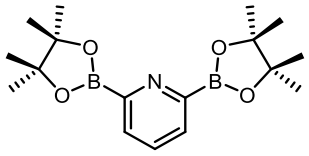
^{1}H NMR (300 MHz, $CDCl_3$): δ 0.75-0.83 (m, 6 H), 1.18-1.23 (m, 32 H), 1.26-1.29 (m, 32 H), 2.70-2.76 (m, 4 H), 7.45 (s, 2 H).

^{13}C NMR (75 MHz, $CDCl_3$): δ 14.3 (CH_3), 22.9 (CH_2), 25.0 (CH_3), 29.5 (CH_2), 29.79 (CH_2), 29.82 (CH_2), 29.9 (CH_2), 30.2 (CH_2), 32.1 (CH_2), 34.1 (CH_2), 35.7 (CH_2), 83.4 (C_{quat}), 136.6 (CH), 146.3 (C_{quat}).

EI + MS (70 eV, *m/z* (%)): 666 ($[C_{42}H_{76}B_2O_4]^+$, 24), 412 ($[C_{24}H_{38}B_2O_4]^+$, 16), 299 ($[C_{16}H_{21}B_2O_4]^+$, 29), 294 (13), 293 (12), 285 (14), 262 (11)185 (14), 183 (33), 171 (13), 157 (11), 145 (15), 131 ($[C_7H_4BO_2]^+$, 14), 105 (17), 101 ($[C_6H_{13}O]^+$, 44), 85 (33), 84 ($[C_6H_{12}]^+$, 68), 83 ($[C_6H_{11}]^+$, 100), 71 (12), 69 ($[C_5H_9]^+$, 18),57 (32), 55 ($[C_4H_7]^+$, 28).

*The quaternary carbon nucleus covalently bound to the boron core could not be observed in the ^{13}C NMR spectrum.

Pyridine-2,6-diboronic acid bis(pinacol)ester (4h)



$C_{17}H_{27}B_2O_4$

[331.21]

The synthesis was performed according to **GPIII**. The purification was performed by flash chromatography on silica gel (*n*-hexane/acetone 20:1) to give compound **4h** (0.902 g, 2.72 mmol, 89 %) as a colorless solid.

Mp: 88 °C.

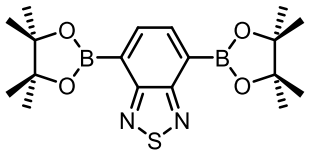
R_f (*n*-hexane/ethyl acetate): 0.32.

^{1}H NMR (300 MHz, $CDCl_3$): δ 1.26 (s, 24 H), 7.50-7.58 (m, 2 H), 7.75-7.78 (m, 1 H).

^{13}C NMR (75 MHz, $CDCl_3$): δ 25.1 (CH_3), 85.0 (C_{quat}), 130.0 (CH), 137.2 (CH), 143.4 (C_{quat}).

EI + MS (70 eV, *m/z* (%)): 239 ($[C_{12}H_{12}B_2NO_3]^+$, 20), 84 ($[C_6H_{12}]^+$, 100), 69 ($[C_5H_9]^+$, 19), 55 ($[C_4H_7]^+$, 11), 43 ($[C_2H_3O]^+$, 14), 41 ($[C_3H_5]^+$, 17).

4,7-Bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)benzo[*c*][1,2,5]thiadiazole (4j)



$C_{18}H_{26}B_2N_2O_4S$

[388.18]

The synthesis was performed according to **GPIII**. The purification was performed by flash chromatography on silica gel (*n*-hexane/acetone 5:1 to 4:1 to 2:1 to pure acetone) to give compound **4j** (0.545 g, 1.40 mmol, 56 %) as a brown solid.

Mp: 77 °C.

R_f (*n*-hexane/acetone 4:1): 0.32.

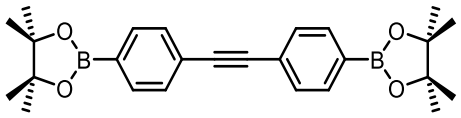
^{1}H-NMR (300 MHz, $CDCl_3$): δ 1.43 (s, 24 H), 8.12 (s, 2 H).

^{13}C-NMR (75 MHz, $CDCl_3$): δ 25.0 (CH_3), 84.6 (C_{quat}), 137.9 (CH), 157.1 (C_{quat}).

EI + MS (70 eV, *m/z* (%)): 388 ($[C_{18}H_{26}B_2N_2O_4S]^+$, 15), 332 ($[C_{18}H_{26}B_2O_4]^+$, 17), 331 ($[C_{14}H_{17}B_2N_2O_4S]^+$, 26), 330 ($[C_{14}H_{16}B_2N_2O_4S]^+$, 100), 329 (54), 289 ($[C_{15}H_{24}B_2O_4]^+$, 10), 248 (20), 247 ($[C_{11}H_{12}BN_2O_2S]^+$, 33), 247 (14), 230 ($[C_{10}H_7BN_2O_2S]^+$, 19), 229 (19), 215 (20), 207 (18), 206 (11), 189 ($[C_{11}H_{14}BO_2]^+$, 31), 188 ($[C_{11}H_{14}BO_2]^+$, 16), 185 (($[C_{11}H_{11}BO_2]^+$, 11), 183 (19), 129 (60), 128 (20), 118 (54), 105 (71), 104 (25), 103 ($[C_6H_4BO]^+$, 36), 101 (23), 85 (11), 84 ($[C_6H_{12}]^+$, 30), 83 (19), 69 ($[C_5H_9]^+$, 10), 59 ($[C_3H_7O]^+$, 15), 57 (14), 55 (12).

* The quaternary carbon nucleus covalently bound to the boron core could not be observed in the ^{13}C NMR spectrum.

1,2-Bis(4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)phenyl)ethyne (4l)



$C_{26}H_{32}B_2O_4$

[430.29]

The synthesis was performed according to **GPIII**. The purification was performed by flash chromatography on silica gel (*n*-hexane/acetone 15:1) to give compound **4l** (0.845 g, 1.98 mmol, 79 %) as a colorless solid.

Mp: 202 °C.

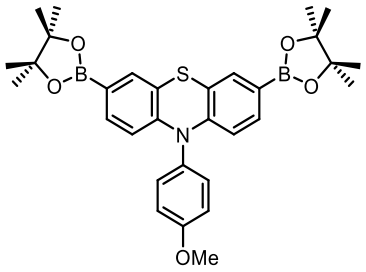
R_f (*n*-hexane/acetone 10:1): 0.29.

^{1}H-NMR (300 MHz, $CDCl_3$): δ 1.34 (s, 24 H), 7.51-7.55 (m, 4 H), 7.76-7.79 (m, 4 H).

^{13}C-NMR (75 MHz, $CDCl_3$): δ 24.9 (CH_3), 84.1 (C_{quat}), 91.0 (C_{quat}), 125.9 (C_{quat}), 129.3 (C_{quat}), 130.9 (CH), 134.7 (CH).

EI + MS (70 eV, *m/z* (%)): 430 ($[C_{26}H_{32}B_2O_4]^+$, 4), 255 (16), 229 ($[C_{14}H_{16}BO_2]^+$, 16), 204 ($[C_{12}H_{17}BO_2]^+$, 18), 189 ($[C_{11}H_{14}BO_2]^+$, 42), 188 ($[C_{11}H_{14}BO_2]^+$, 10), 185 (($[C_{11}H_{11}BO_2]^+$, 82), 184 (22), 129 (60), 128 (20), 118 (54), 105 (71), 104 (25), 103 ($[C_6H_4BO]^+$, 36), 101 (23), 85 (41), 84 ($[C_6H_{12}]^+$, 100), 83 (60), 69 ($[C_5H_9]^+$, 19), 59 ($[C_3H_7O]^+$, 11), 57 (35), 55 (29).

10-(4-Methoxyphenyl)-3,7-bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-10*H*-phenothiazin (4q)



$C_{31}H_{37}B_2NO_5S$

[557.26]

The synthesis was performed according to **GPIII**. The purification was performed by flash chromatography on silica gel (*n*-hexane/acetone 5:1 to 2:1) to give compound **4q** (0.222 g, 0.398 mmol, 27 %) as an orange solid.

Mp: 72 °C.

R_f (*n*-hexane/acetone 4:1): 0.38.

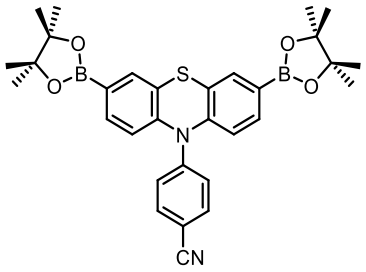
^{1}H NMR (300 MHz, acetone-d_6): δ 1.42 (s, 24 H), 3.76 (s, 3 H), 6.74 (d, ^3J = 7.8 Hz, 2 H), 7.01-7.08 (m, 4 H), 7.13-7.22 (m, 2 H), 7.55 (d, ^3J = 2.0 Hz, 2 H).

^{13}C NMR (75 MHz, acetone-d_6): δ 25.2 (CH_3), 55.1 (CH_3), 83.2 (C_{quat}), 114.7 (CH), 118.0 (C_{quat}), 119.2 (CH), 122.3 (C_{quat}), 128.4 (CH), 128.7 (CH), 131.2 (CH), 137.9 (C_{quat}), 158.7 (C_{quat}).

EI + MS (70 eV, *m/z* (%)): 557 ($[C_{31}H_{37}B_2NO_5S]^+$, 1), 445 ($[C_{24}H_{25}B_2NO_4S]^+$, 10), 255 (14), 237 ($[C_{15}H_{11}B_2NS]^+$, 46), 198 ($[C_{12}H_8NS]^+$, 19), 197 ($[C_{12}H_7NS]^+$, 100), 195 (12), 194 (12), 185 (12), 183 (13), 178 (12), 170 (15), 169 (11), 166 (52), 155 (10), 154 (10), 153 (14), 152 (14), 135 (28), 131 (16), 129 (17), 128 (14), 121 (10), 105 (12), 103 (13), 91 (14), 84 (18), 83 (18), 77 ($[C_6H_5]^+$, 12).

[*] The quaternary carbon nucleus covalently bound to the boron core could not be observed in the ^{13}C NMR spectrum.

4-(3,7-Bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-10*H*-phenothiazine-10-yl)benzonitrile (4r)



$C_{31}H_{34}B_2N_2O_4S$

[552.24]

The synthesis was performed according to **GPIII**. The purification was performed by flash chromatography on silica gel (*n*-hexane/acetone 5:1 to 4:1) to give compound **4r** (0.231 g, 0.418 mmol, 42 %) as a brown solid.

Mp: 93 °C.

R_f (*n*-hexane/acetone 4:1): 0.15.

^{1}H NMR (300 MHz, acetone-d_6): δ 1.44 (s, 24 H), 6.79 (d, ^3J = 7.8 Hz, 2 H), 7.32-7.38 (m, 4 H), 7.49 (d, ^3J = 2.3 Hz, 2 H), 7.77-7.81 (m, 2 H).

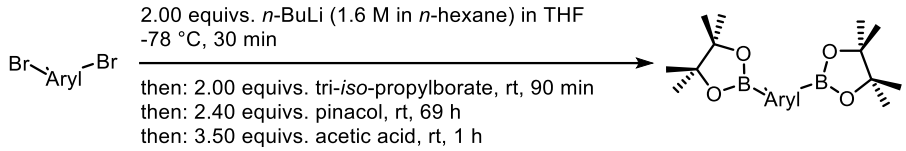
^{13}C NMR (75 MHz, acetone-d_6): δ 25.2 (CH_3), 85.3 (C_{quat}), 108.8 (C_{quat}), 118.2 (C_{quat}), 119.2 (C_{quat}), 123.8 (CH), 124.7 (CH), 130.5 (C_{quat}), 131.0 (CH), 147.6 (C_{quat}).

EI + MS (70 eV, *m/z* (%)): 552 ($[C_{31}H_{34}B_2N_2O_4S]^+$, 2), 255 (17), 229 (13), 185 ($[C_{12}H_{10}BO_2]^+$, 85), 184 (22), 128 ($[C_6H_{13}BO_2]^+$, 72), 127 (21), 115 (13), 103 (34), 101 ($[C_7H_3N]^+$, 22), 85 (21), 84 ($[C_6H_{12}]^+$, 100), 83 (52), 69 (17), 59 (36), 57 (17), 55 (18).

*The quaternary carbon nucleus covalently bound to the boron core could not be observed in the ^{13}C NMR spectrum.

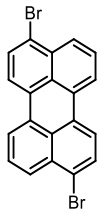
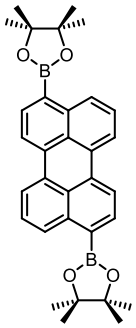
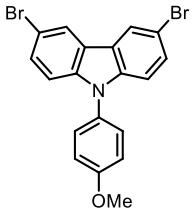
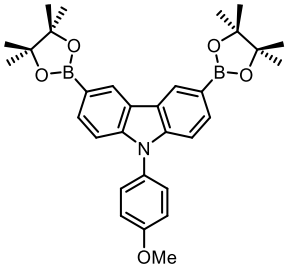
3.4 Synthesis and analytical data of carbazole and perylene pinacol boronic acid ester 4[10]

3.4.1 General procedure IV (GPIV) for the synthesis of bispinacol boronic acid ester 4[10]



Aryl bromide (1.00 equiv) was placed in a sintered, dry screw-cap *Schlenk*-tube under nitrogen atmosphere and dissolved in 3 mL/mmol dry THF. The reaction mixture was cooled to -78 °C with an acetone/dry ice bath and stirred for 10 min at this temperature. *n*-Butyllithium solution (1.00 equiv., 1.6 M in *n*-hexane) was added dropwise. After stirring the reaction mixture at -78 °C for 30 min, tri-*iso*-propylborate (1.00 equiv.) was added dropwise. After the addition, the mixture was stirred at -78 °C for 10 min and then heated to room temperature. The solution was stirred at room temperature for 30 min before adding pinacol (1.20 equivs.). The reaction mixture was stirred at room temperature for 69 h. To quench this reaction, concentrated acetic acid (1.75 equivs.) were added and the mixture was stirred at room temperature for 1 h. After the addition of 10 mL distilled water and 15 mL dichloromethane, the mixture was transferred to a separation funnel. The organic layer was removed and the watery phase was extracted three times with 10 mL dichloromethane. The combined organic layers were dried with anhydrous magnesium sulfate, the drying agent was filtered off und the solvent was removed under reduced pressure. The crude product was adsorbed onto Celite® and purified by flash chromatography on silica gel (*n*-hexane/acetone).

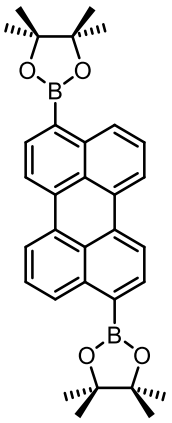
Table S5: Experimental details for the synthesis of diboronic acid esters **4**.

Entry	(Hetero)aryl-Br_2 [g] ([mmol])	Yield of product **4** [g] (%)
1[(a)]		
	0.205 (0.500)	0.205 (81) of **4m**
2[(b)]		
	0.646 (1.50)	0.376 (47) of **4o**

(a): *n*-BuLi: 0.660 mL (1.00 mmol), tri-*iso*-propylborate: 0.235 mL (1.00 mmol), pinacol: 0.142 g (1.20 mmol), acetic acid: 0.200 mL (1.75 mmol), 4 mL THF.

(b): *n*-BuLi: 1.87 mL (3.00 mmol), tri-*iso*-propylborate: 0.578 mL (3.00 mmol), pinacol: 0.426 g (3.60 mmol), acetic acid: 0.360 mL (5.25 mmol), 6 mL THF.

3,9-Bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)perylene (4m)



$C_{32}H_{34}B_2O_4$

[504.26]

The synthesis was performed according to **GPIV**. The purification was performed by flash chromatography on silica gel (*n*-hexane/acetone 30:1 to 25:1 to 10:1 to 2:1) to give compound **4m** (0.205 g, 0.407 mmol, 81 %) as a yellow solid.

Mp: 285 °C.

R_f (*n*-hexane/acetone 20:1): 0.33.

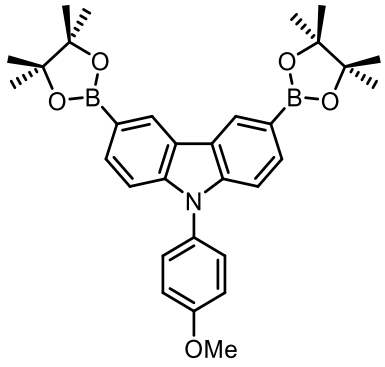
^{1}H NMR (300 MHz, acetone-d_6): δ 1.45 (s, 24 H), 7.50-7.58 (m, 2 H), 8.06-8.09 (m, 2 H), 8.27-8.37 (m, 4 H), 8.67-8.74 (m, 2 H).

^{13}C NMR (75 MHz, acetone-d_6): δ 25.4 (CH_3), 84.4 (C_{quat}), 120.5 (CH), 121.0 (CH), 121.3 (CH), 121.9 (CH), 127.6 (CH), 127.7 (CH), 128.6 (CH), 129.1 (C_{quat}), 129.5 (CH), 130.2 (C_{quat}), 131.6 (C_{quat}), 132.0 (C_{quat}), 134.6 (C_{quat}), 135.0 (C_{quat}), 137.3 (C_{quat}), 137.4 (C_{quat}), 139.2 (C_{quat}).

MALDI-TOF (*m/z*): 504.4 ($C_{32}H_{34}B_2O_4^+$).

*The quaternary carbon nucleus covalently bound to the boron core could not be observed in the ^{13}C NMR spectrum.

9-(4-Methoxyphenyl)-3,6-bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-9*H*-carbazole (4o)



$C_{31}H_{37}B_2NO_5$

[525.29]

The synthesis was performed according to **GPIV**. The purification was performed by flash chromatography on silica gel (*n*-hexane/acetone 30:1 to 20:1 to 10:1) to give compound **4o** (0.376 g, 0.706 mmol, 47 %) as a colorless solid.

Mp: 103 °C.

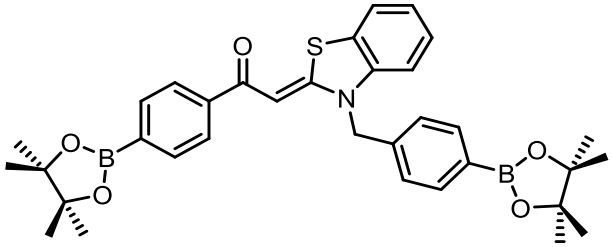
R_f (*n*-hexane/acetone 10:1): 0.24.

^{1}H NMR (300 MHz, acetone-d_6): δ 1.38 (s, 24 H), 3.94 (s, 3 H), 7.22-7.25 (m, 2 H), 7.29-7.32 (m, 2 H), 7.49-7.52 (m, 2 H), 7.82 (dd, ^3J = 8.3 Hz, ^4J = 1.1 Hz, 2 H), 8.66-8.67 (m, 2H).

^{13}C NMR (75 MHz, acetone-d_6): δ 25.0 (CH_3), 56.0 (CH_3), 84.3 (C_{quat}), 110.0 (CH), 116.2 (CH), 123.5 (C_{quat}), 128.2 (CH), 129.3 (CH), 130.4 (CH), 133.3 (CH), 144.4 (C_{quat}), 160.4 (C_{quat}).*

EI + MS (70 eV, *m/z* (%)): 526 (30), 525 ($[C_{31}H_{37}B_2NO_5]^+$, 100), 524 (54), 326 (16), 325 (16), 57 (12).

3.4.1 (*Z*)-2-(3-(4-(4,4,5,5-Tetramethyl-1,3,2-dioxaborolan-2-yl)benzyl)benzo[*d*]thiazol-2(3*H*)-ylidene)-1-(4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)phenyl)ethan-1-one (4p)



$C_{34}H_{39}B_2NO_5S$

[595.27]

Dibrominated aroyl-*S,N*-ketene acetal (**3p**) (0.501 g, 1.00 mmol, 1.00 equiv.) was placed in a sintered, dry screw-cap *Schlenk*-tube under nitrogen atmosphere and dissolved in 6 mL DMSO. Potassium acetate (0.533 g, 5.00 mmol, 5.00 equivs.), bisp(pinacolato)diboron (0.533 g, 2.10 mmol, 2.10 equivs.) and bis(triphenylphosphine)palladium(II)-dichlorid (0.070 g, 0.010 mmol, 10.0 mol%) were added and the brown reaction mixture was stirred at 80 °C for 19 h. The catalysator was filtered off and 20 mL chloroform was added to the crude mixture. The mixture was transferred to a separation funnel and the organic layer was extracted five times with 50 mL deionized water. The combined organic layers were dried with anhydrous magnesium sulfate, the drying agent was filtered off und the solvent was removed under reduced pressure. The crude product was adsorbed onto Celite® and purified by flash chromatography on silica gel (*n*-hexane/acetone 3:1 to 2:1) to give compound **4p** (0.412 g, 0.692 mmol, 69 %) as a yellow solid.

Mp:301 °C.

R_f (*n*-hexane/acetone 3:1): 0.35.

^{1}H NMR (300 MHz, acetone-d_6/CS_2 5:1): δ 1.31 (s, 12 H), 1.35 (s, 12 H), 5.58 (s, 2 H), 6.81 (s, 1 H), 7.20-7.38 (m, 5 H), 7.71-7.77 (m, 5 H), 7.87-7.90 (2 H).

^{13}C NMR (75 MHz, acetone-d_6/CS_2 5:1): δ 25.27 (CH_3), 25.31 (CH_3), 49.9 (CH_2), 84.3 (C_{quat}), 84.4 (C_{quat}), 88.5 (C_{quat}), 111.3 (CH), 123.2 (CH), 123.8 (CH), 126.6 (CH), 127.0 (CH), 127.4 (CH), 128.1 (C_{quat}), 135.3 (CH), 136.1 (CH), 139.0 (C_{quat}), 140.8 (C_{quat}), 142.6 (C_{quat}), 162.5 (C_{quat}), 184.0 (C_{quat}).

MALDI-TOF (m/z): 596 ($C_{34}H_{39}N\ B_2NO_5S$ +H^+).

IR $\tilde{\nu}$ [cm^{-1}]: 654 (m), 669 (m), 719 (m), 746 (m), 770 (m), 826 (m), 860 (m), 883 (m), 964 (m), 1020 (m), 1047 (w), 1067 (w), 1092 (m), 1144 (s), 1167 (w), 1206 (m), 1229 (w), 1267 (m), 1296 (w), 1308 (w), 1327 (m), 1360 (s), 1439 (w), 1460 (m), 1477 (s), 1510 (m), 1549 (m), 1587 (m), 1612 (w), 2930 (w), 2978 (w), 3069 (w).

UV/Vis (C_3H_6O): λ_{max} (ε) = 255 (26800), 390 (36500).

Anal calcd for $C_{34}H_{39}B_2NO_5S$ [595.3]: C 68.59, H 6.60, N 2.35, S 5.38; Found: C 68.69, H 6.86, N 2.39, S 5.17.

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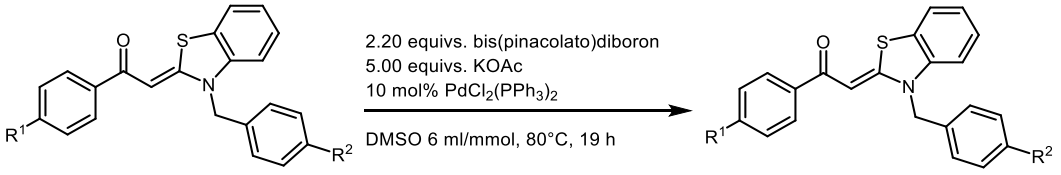
* The quaternary carbon nucleus covalently bound to the boron core could not be observed in the ^{13}C NMR spectrum.

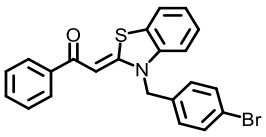
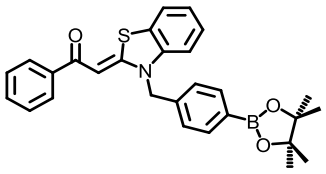
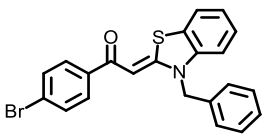
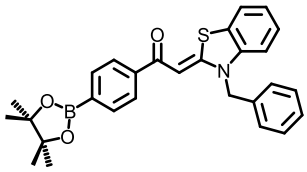
3.5 Synthesis and analytical data of mono borylated aroyl-*S,N*-ketene acetals

3.5.1 General procedure V (GPV) for the synthesis of mono borylated aroyl-*S,N*-ketene acetals



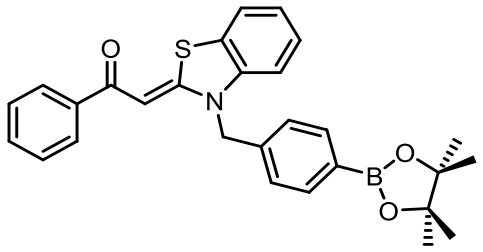
Brominated aroyl-*S,N*-ketene acetal (0.421 g, 1.00 mmol, 1.00 equiv.) was placed in a sintered, dry screw-cap *Schlenk*-tube under nitrogen atmosphere and dissolved in DMSO (6 mL). Potassium acetate (0.533 g, 5.00 mmol, 5.00 equivs.), bisp(pinacolato)diboron (0.305 g, 1.20 mmol, 1.20 equivs.) and bis(triphenylphosphane)palladium(II)-dichloride (0.070 g, 0.010 mmol, 10.0 mol%) were added and the brown reaction mixture was stirred at 80 °C for 19 h. The catalysator was filtered off and chloroform (20 mL) was added to the crude mixture. The mixture was transferred to a separation funnel and the organic layer was extracted five times with deionized water (50 mL). The combined organic layers were dried with anhydrous magnesium sulfate, the drying agent was filtered off und the solvent was removed under reduced pressure. The crude product was adsorbed onto Celite® and purified by flash chromatography on silica gel (*n*-hexane/acetone 3:1).

Table S6: Experimental details for the synthesis of mono borylated aroyl-*S,N*-ketene acetals.

Entry	Brominated aroyl-*S,N*-ketene acetal **3**	Yield of product [g] (%)
1		
	3c	0.344 (73)
2		
	3d	0.372 (79)

3.5.1.1 Spectroscopic Data

(*Z*)-1-Phenyl-2-(3-(4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)benzyl)benzo[*d*]thiazol-2(3*H*)-ylidene)ethan-1-one



$C_{28}H_{28}BNO_3S$

[469.19]

The synthesis was performed according to **GPV** to give 344 mg (0.733 mmol, 73%) of the desired product as a yellow solid.

Mp: 230 °C.

R_f (*n*-hexane/acetone 3:1): 0.32.

^{1}H NMR (300 MHz, acetone-d_6/CS_2 5:1): δ 1.31 (s, 12 H), 5.61 (s, 2 H), 6.84 (s, 1 H), 7.21-7.26 (m, 1 H), 7.30-7.44 (m, 7 H), 7.72-7.77 (m, 3 H), 7.92- 7.95 (2 H).

^{13}C NMR (75 MHz, acetone-d_6/CS_2 5:1): δ 25.2 (CH_3), 49.8 (CH_2), 84.4 (C_{quat}), 88.2 (CH), 111.4 (CH), 123.2 (CH), 123.8 (CH), 126.7 (CH), 127.5 (CH), 127.9 (CH), 131.5 (CH), 136.1 (CH), 139.2 (C_{quat}), 140.5 (C_{quat}), 140.9 (C_{quat}), 162.4 (C_{quat}), 184.3 (C_{quat}).

MALDI-TOF (m/z): 470 ($C_{28}H_{28}BNO_3S$ +H^+).

IR $\tilde{\nu}$ [cm^{-1}]: 614 (s), 652 (m), 667 (m), 698 (m), 719 (m), 731 (s), 748 (m), 783 (w), 820 (w), 831 (w), 860 (m), 881 (m), 922 (w), 935 (w), 951 (w), 962 (m), 988 (w), 1001 (w), 1020 (m), 1047 (m), 1063 (m), 1092 (m), 1115 (w), 1146 (m), 1175 (m), 1202 (m), 1231 (m), 1269 (m), 1292 (w), 1300 (m), 1325 (m), 1344 (m), 1364 (s), 1398 (m), 1439 (m), 1458 (m), 1468 (s), 1516 (w), 1558 (w), 1570 (m), 1597 (m), 1614 (w), 1699 (w), 1865 (w), 1960 (w), 1977 (w), 1992 (w), 2147 (w), 2359 (w), 2737 (w), 2847 (w), 2884 (w), 2901 (w), 2913 (w), 2928 (w), 2943 (w), 2978 (w), 3044 (w), 3055 (w), 3417 (w), 3645 (w).

UV/Vis (C_3H_6O): λ_{max} (ε) = 383 (35700).

Anal calcd for $C_{28}H_{28}BNO_3S$ [470.2]: C 71.65, H 6.01, N 2.98, S 6.83; Found: C 71.41, H 6.13, N 2.82, S 6.66.

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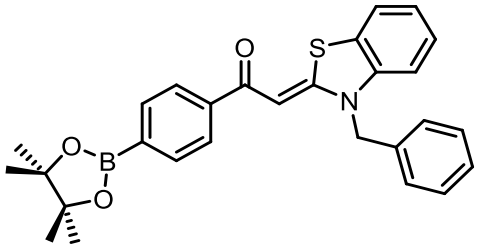
[*] The quaternary carbon nucleus covalently bound to the boron core could not be observed in the ^{13}C NMR spectrum.

(*Z*)-2-(3-Benzylbenzo[*d*]thiazol-2(3*H*)-ylidene)-1-(4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)phenyl)ethan-1-one



$C_{28}H_{28}BNO_3S$

[469.19]

The synthesis was performed according to **GPV** to give 372 mg (0.793 mmol, 79%) of the desired product as a yellow solid.

Mp: 214 °C.

R_f (*n*-hexane/acetone 3:1): 0.38.

^{1}H NMR (300 MHz, acetone-d_6/CS_2 5:1): δ 1.35 (s, 12 H), 5.60 (s, 2 H), 6.89 (s, 1 H), 7.22-7.39 (m, 8 H), 7.75-7.79 (m, 3 H), 7.92-7.95 (2 H).

^{13}C NMR (75 MHz, acetone-d_6/CS_2 5:1): δ 25.3 (CH_3), 49.7 (CH_2), 84.5 (C_{quat}), 88.5 (CH), 111.5 (CH), 123.2 (CH), 123.8 (CH), 127.1 (CH), 127.5 (CH), 128.0 (CH), 128.5 (CH), 129.7 (CH), 135.4 (CH), 136.1 (C_{quat}), 140.9 (C_{quat}), 142.8 (C_{quat}), 162.6 (C_{quat}), 184.1 (C_{quat}).

MALDI-TOF (m/z): 470 ($C_{28}H_{28}BNO_3S$ +H^+).

IR $\tilde{\nu}$ [cm^{-1}]: 650 (m), 667 (m), 694 (m), 718 (s), 743 (s), 772 (m), 795 (w), 810 (m), 822 (m), 858 (m), 870 (m), 905 (m), 924 (w), 951 (w), 962 (m), 982 (w), 1001 (w), 1016 (m), 1045 (m), 1066 (m), 1087 (s), 1109 (m), 1142 (m), 1167 (w), 1182 (m), 1200 (m), 1227 (m), 1269 (m), 1296 (m), 1327 (m), 1354 (m), 1410 (m), 1435 (m), 1447 (s), 1510 (m), 1548 (w), 1597 (m), 2868 (w), 2928 (w), 2974 (w), 3063 (w), 3385 (w), 3470 (w).

UV/Vis (C_3H_6O): λ_{max} (ε) = 261 (42300), 390 (37400).

Anal calcd for $C_{28}H_{28}BNO_3S$ [470.2]: C 71.65, H 6.01, N 2.98, S 6.83; Found: C 71.44, H 6.15, N 2.84, S 6.61.

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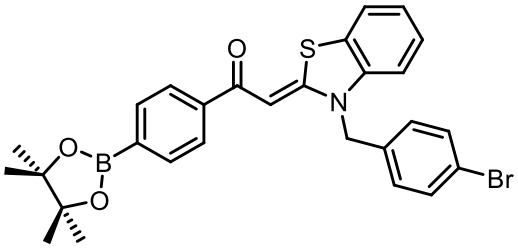
[*] The quaternary carbon nucleus covalently bound to the boron core could not be observed in the ^{13}C NMR spectrum.

(*Z*)-2-(3-(4-Bromobenzyl)benzo[*d*]thiazol-2(3*H*)-ylidene)-1-(4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)phenyl)ethan-1-one



$C_{28}H_{27}BBrNO_3S$

[547.10]

Aroyl-*S,N*-ketene acetal **3f** (0.383 g, 0.700 mmol, 1.00 equiv.) was placed in a sintered, dry screw-cap *Schlenk*-tube under nitrogen atmosphere and dissolved in 4 mL DMSO. Potassium acetate (0.358 g, 3.50 mmol, 5.00 equivs.), bisp(pinacolato)diboron (0.180 g, 0.710 mmol, 1.01 equivs.) and bis(triphenylphosphane)palladium(II)-dichloride (0.049 g, 0.007 mmol, 10.0 mol%) were added and the brown reaction mixture was stirred at 80 °C for 19 h. The catalysator was filtered off and 20 mL chloroform was added to the crude mixture. The mixture was transferred to a separation funnel and the organic layer was extracted five times with 50 mL deionized water. The combined organic layers were dried with anhydrous magnesium sulfate, the drying agent was filtered off und the solvent was removed under reduced pressure. The crude product was adsorbed onto Celite® and purified by flash chromatography on silica gel (*n*-hexane/acetone 4:1 to 3:1) to give 0.227 g (0.415 mmol, 59 %) of the desired product as a yellow solid.

Mp: 209 °C.

R_f (*n*-hexane/acetone 3:1): 0.37.

^{1}H NMR (300 MHz, acetone-d_6): δ 1.34 (s, 12 H), 5.63 (s, 2 H), 6.96 (s, 1 H), 7.24-7.32 (m, 3 H), 7.38-7.42 (m, 2 H), 7.54-7.57 (m, 2 H), 7.75-7.82 (m, 3 H), 7.97-8.02 (2 H).

^{13}C NMR (75 MHz, acetone-d_6): δ 25.2 (CH_3), 49.1 (CH_2), 84.7 (C_{quat}), 88.4 (CH), 111.5 (CH), 121.9 (CH), 123.3 (CH), 124.0 (CH), 126.9 (C_{quat}), 127.1 (CH), 127.7 (CH), 127.8 (CH), 129.7 (CH), 132.8 (CH), 135.4 (CH), 135.8 (CH), 136.1 (C_{quat}), 140.8 (C_{quat}), 142.8 (C_{quat}), 162.7 (C_{quat}), 184.4 (C_{quat}).

MALDI-TOF (m/z): 550 ($C_{28}H_{27}B^{81}BrNO_3S$ +H^+), 548 ($C_{28}H_{27}B^{79}BrNO_3S$ +H^+).

IR $\tilde{\nu}$ [cm^{-1}]: 648 (m), 689 (w), 718 (s), 739 (m), 770 (m), 787 (m), 824 (m), 858 (m), 878 (m), 924 (w), 951 (w), 962 (m), 982 (w), 993 (w), 1011 (m), 1040 (w), 1070 (m), 1090 (s), 1142 (m), 1179 (m), 1192 (m), 1225 (m), 1263 (m), 1294 (m), 1308 (w), 1327 (m), 1354 (s), 1389 (m), 1445 (m), 1460 (s), 1508 (m), 1549 (m), 1595 (m), 2845 (w), 2884 (w), 2901 (w), 2913 (w), 2974 (w).

UV/Vis (C_3H_6O): λ_{max} (ε) = 390 (32600).

Anal calcd for $C_{28}H_{27}BBrNO_3S$ [547.1]: C 61.34, H 4.96, N 2.55, S 5.85; Found: C 61.01, H 5.33, N 2.30, S 5.52.

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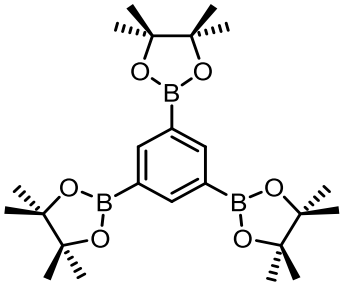
*The quaternary carbon nucleus covalently bound to the boron core could not be observed in the ^{13}C NMR spectrum.

1,3,5-Tris(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)benzene (4r)[9]



$C_{24}H_{39}B_3O_6$

[456.30]

1,3,5-Tribromobenzene (0.784 g, 2.50 mmol, 1.00 equiv.) was placed in a sintered, dry screw-cap *Schlenk*-tube under nitrogen atmosphere and dissolved in DMSO (15 mL). Potassium acetate (1.92 g, 18.8 mmol, 7.50 equivs.), bisp(pinacolato)diboron (2.03 g, 8.00 mmol, 3.20 equivs.) and bis(triphenylphosphane)palladium(II)-dichloride (0.140 g, 0.038 mmol, 15.0 mol%) were added and the brown reaction mixture was stirred at 80 °C for 19 h. The catalysator was filtered off and chloroform (20 mL) was added to the crude mixture. The mixture was transferred to a separation funnel and the organic layer was extracted five times with deionized water (50 mL). The combined organic layers were dried with anhydrous magnesium sulfate, the drying agent was filtered off und the solvent was removed under reduced pressure. The crude product was adsorbed onto Celite® and purified by flash chromatography on silica gel (*n*-hexane/acetone 15:1 to 10:1 to 5:1) to give 0.968 g (2.13 mmol, 85 %) of the desired product **4r** as a colorless solid.

Mp: 256 °C.

R_f (*n*-hexane/acetone 10:1): 0.25.

^{1}H NMR (300 MHz, $CDCl_3$): δ 1.33 (s, 36 H), 8.36 (s, 3 H).

^{13}C NMR (75 MHz, $CDCl_3$): δ 25.0 (CH_3), 83.8 (C_{quat}), 144.2 (CH).

EI + MS (70 eV, *m/z* (%)): 456 ($[C_{24}H_{39}B_3O_6]^+$, 15), 455 (14), 441 ($[C_{23}H_{36}B_3O_6]^+$, 16), 440 (16), 399 (23), 398 (20), 372 ($[C_{18}H_{28}B_3O_6]^+$, 16), 370 49), 369 (26), 357 (19), 356 ($[C_{18}H_{28}B_3O_6]^+$, 17), 355 (12), 341 (10), 312 ($[C_{17}H_{22}B_2O_4]^+$, 12), 286 (13), 285 (11), 271 (15), 270 (19), 257 (15), 256 (11), 243 (11), 213 ($[C_{12}H_{15}B_2O_2]^+$, 17) 101 ($[C_7H_3N]^+$, 12), 85 (29), 84 ($[C_6H_{12}]^+$, 68), 83 $[C_6H_{11}]^+$, 100), 59 ($[C_3H_7O]^+$, 24), 58 (16), 57 (23), 55 (28).

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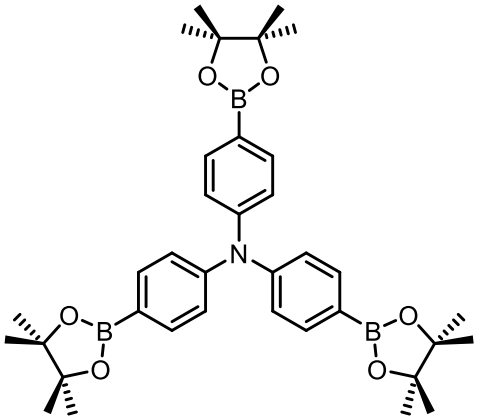
*The quaternary carbon nucleus covalently bound to the boron core could not be observed in the ^{13}C NMR spectrum.

Tris(4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)phenyl)amine (4s)[5]



$C_{36}H_{48}B_3NO_6$

[623.38]

Tris(4-bromophenyl)amine (1.92 g, 3.98 mmol, 1.00 equiv) was placed in a sintered, dry screw-cap *Schlenk*-tube under nitrogen atmosphere and dissolved in 13 mL dry THF. The reaction mixture was cooled to -78 °C with an acetone/dry ice bath and stirred for 10 min at this temperature. *n*-Butyllithium solution (8.15 mL, 13.0 mmol, 3.27 equivs., 1.6 M in *n*-hexane) was added dropwise. After stirring the reaction mixture at -78 °C for 30 min, tri-*iso*-propylborate (3.03 mL, 13.3 mmol, 3.34 equivs.) was added dropwise. After the addition, the mixture was stirred at -78 °C for 10 min and then heated to room temperature. The solution was stirred at room temperature for 30 min before adding pinacol (2.01 g, 17.0 mmol, 4.27 equivs.). The reaction mixture was stirred at room temperature for 99 h. To quench this reaction, concentrated acetic acid (0.500 mL, 8.7 mmol, 2.20 equivs.) were added and the mixture was stirred at room temperature for 1 h. After the addition of 10 mL distilled water and 15 mL dichloromethane, the mixture was transferred to a separation funnel. The organic layer was removed and the watery phase was extracted three times with 10 mL dichloromethane. The combined organic layers were dried with anhydrous magnesium sulfate, the drying agent was filtered off und the solvent was removed under reduced pressure. The crude product was adsorbed onto Celite® and purified by flash chromatography on silica gel (*n*-hexane/acetone 10:1 to 5:1 to 3:1 to 2:1). After a recrystallization in boiling ethanol compound **4s** (1.45 g, 2.32 mmol, 58 %) as a yellow solid were obtained.

Mp: 322 °C.

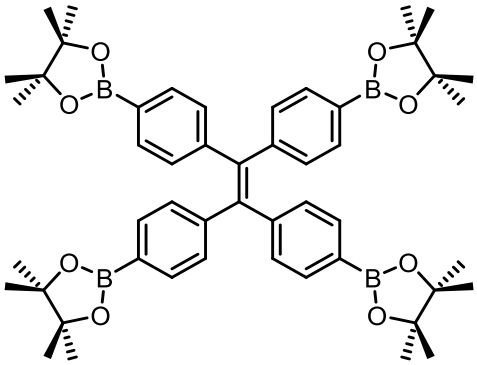
R_f (*n*-hexane/acetone 10:1): 0.55.

^{1}H NMR (300 MHz, acetone-d_6): δ 1.34 (s, 36 H), 7.02-7.06 (m, 6 H), 7.63-7.67 (m, 6 H).

^{13}C NMR (75 MHz, acetone-d_6): δ 25.3 (CH_3), 84.1 (C_{quat}), 124.1 (CH), 136.8 (CH), 150.4 (C_{quat}).

EI + MS (70ev, *m/z (%)*): 624 ($[C_{36}H_{48}{}^{11}B_3NO_6]^+ + H^+$, 32), 623 ($[C_{36}H_{48}{}^{11}B_3NO_6]^+$, 100), 622 ($[C_{36}H_{48}{}^{10}B^{11}B_2NO_6]^+$, 84), 101 ($[C_6H_{12}O + H]^+$, 16), 85 ($[C_6H_{12} + H]^+$, 14), 83 ($[C_6H_{12} - H]^+$, 23), 57 ($[C_3H_5O]^+$, 10), 55 (10).

1,1,2,2-Tetrakis(4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)phenyl)ethene (4t)[9],[11]



$C_{50}H_{64}B_4O_8$

[836.50]

Tetrabromotetraphenylethene (1.62 g, 2.50 mmol, 1.00 equiv) was placed in a sintered, dry screw-cap *Schlenk*-tube under nitrogen atmosphere and dissolved in dry THF (4.8 mL/mmol). The reaction mixture was cooled to -78 °C with an acetone/dry ice bath and stirred for 10 min at this temperature. *n*-Butyllithium solution (7.80 mL, 12.5 mmol, 5.00 equivs., 1.6 M in *n*-hexane) was added dropwise. After stirring the reaction mixture at -78 °C for 30 min, tri-*iso*-propylborate (2.4 mL, 12.5 mmol, 5.00 equivs.) was added dropwise. After the addition, the mixture was stirred at -78 °C for 10 min and then heated to room temperature. The solution was stirred at room temperature for 30 min before adding pinacol (1.63 g, 13.8 mmol, 5.52 equivs.). The reaction mixture was stirred at room temperature for 99 h. To quench this reaction, concentrated acetic acid (1.75 mL, 25.0 mmol, 10.0 equivs.) were added and the mixture was stirred at room temperature for 1 h. After the addition of distilled water (10 mL) and dichloromethane (15 mL), the mixture was transferred to a separation funnel. The organic layer was removed and the watery phase was extracted three times with dichloromethane (10 mL). The combined organic layers were dried with anhydrous magnesium sulfate, the drying agent was filtered off und the solvent was removed under reduced pressure. The crude product was adsorbed onto Celite® and purified by flash chromatography on silica gel (*n*-hexane/acetone 40:1 to 10:1 to 3:2). This gave compound **4t** (1.40 g, 1.67 mmol, 67 %) as a colorless solid.

Mp: 242 °C.

R_f (*n*-hexane/acetone 10:1): 0.48.

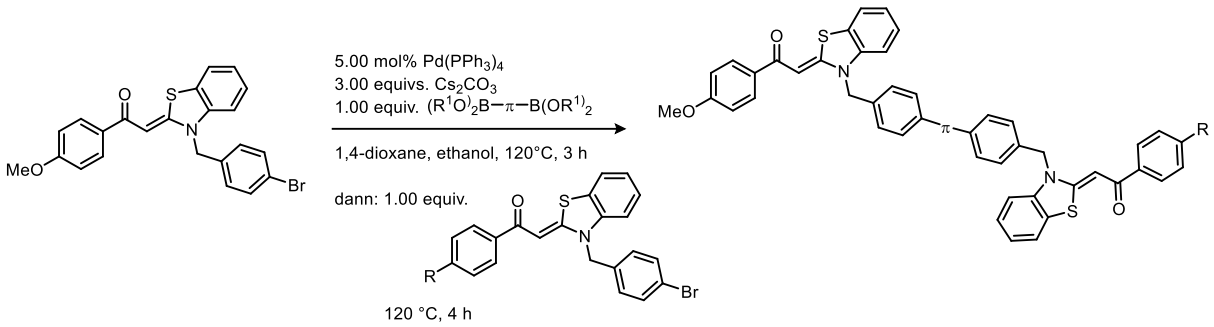
^{1}H-NMR (300 MHz, $CDCl_3$): δ 1.32 (s, 48 H), 6.98-7.09 (m, 8 H), 7.49-7.55 (m, 8 H).

^{13}C NMR (75 MHz, $CDCl_3$): δ 25.0 (CH_3), 83.8 (C_{quat}), 127.8 (C_{quat}), 130.8 (CH), 131.5 (C_{quat}), 134.3 (CH), 146.5 (C_{quat}).

EI + MS (70ev, *m/z (%)*): 854.3 ($C_{50}H_{64}B_4O_8^+ + NH_4^+$), 836.5 ($C_{50}H_{64}B_4O_8^+$).

3.6 Synthesis and analytical data of bridged aroyl-*S,N*-ketene acetals 5

3.6.1 General procedure VI (GPVI) for the synthesis of bridged aroyl-*S,N*-ketene acetals 5



Methoxy-substituted aroyl-*S,N*-ketene acetal (1.00 equiv.), tetrakis(triphenylphosphane)palladium(0) (5 mol%) and cesium carbonate (3.00 equivs.) were placed in a sintered, dry screw-cap *Schlenk*-tube under nitrogen atmosphere and dissolved in dry 1,4-dioxane (6 mL/mmol) and ethanol (2 mL/mmol). The reaction mixture was stirred at 120 °C (oil bath) for 3 h. Thereafter, a second aroyl-*S,N*-ketene acetal (1.00 equiv.) was added to the reaction mixture and the mixture was stirred at 120 °C (oil bath) for 4 h. The crude product was adsorbed onto Celite® and purified by flash chromatography on silica gel (*n*-hexane/acetone). The product was suspended in *n*-hexane, the sediment was filtrated and dried under vacuo.

Table S7: Experimental details for the synthesis bridged aroyl-*S,N*-ketene acetals **5**.

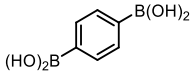
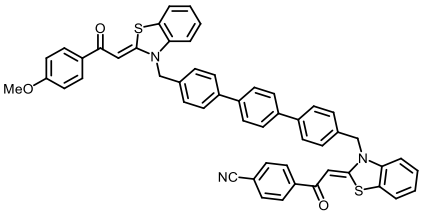
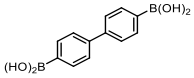
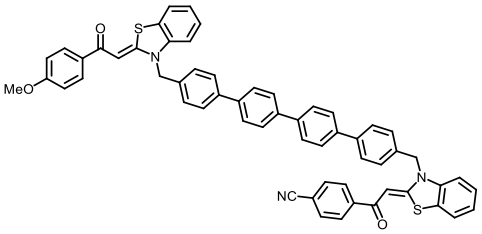
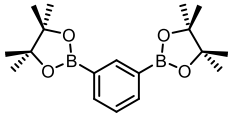
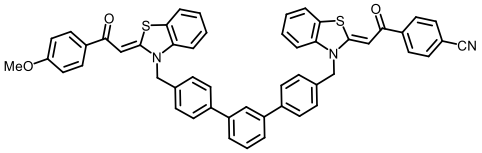
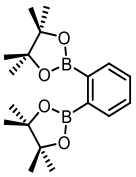
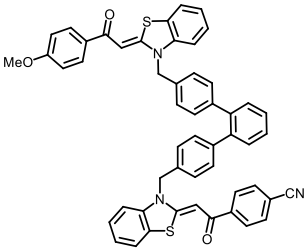
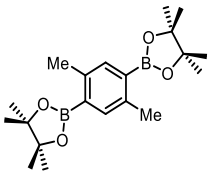
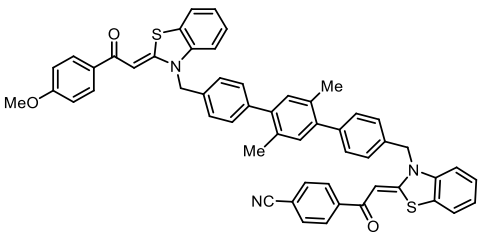
Entry	R [g] ([mmol])	Diboronic acid [g] ([mmol])	Yield of product [mg] (%)
1[(a)]	CN 0.224 (0.500) of **3h**	 0.083 (0.500) of **4a**	 0.263 (64) of **5a**
2[(a)]	CN 0.224 (0.500) of **3h**	 0.122 (0.500) of **4b**	 0.178 (40) of **5b**
3[(a)]	CN 0.224 (0.500) of **3h**	 0.116 (0.500) of **4c**	 0.296 (73) of **5c**
4[(a)]	CN 0.224 (0.500) of **3h**	 0.116 (0.500) of **4d**	 0.176 (43) of **5d**
5[(a)]	CN 0.224 (0.500) of **3h**	 0.179 (0.500) of **4e**	 0.397 (94) of **5e**

Table S7: Experimental details for the synthesis bridged aroyl-*S,N*-ketene acetals **5**.

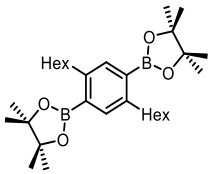
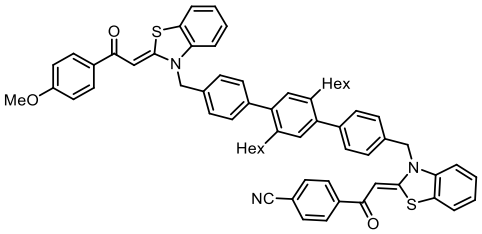
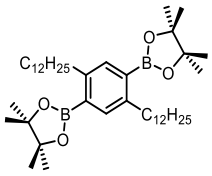
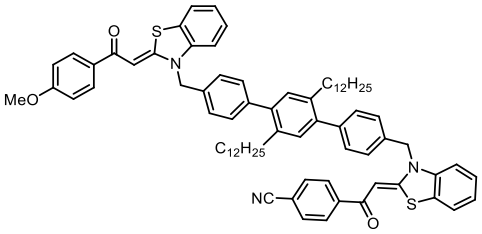
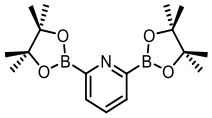
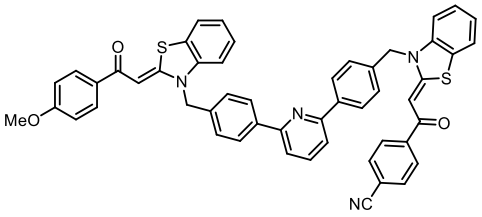
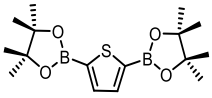
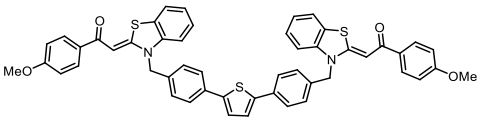
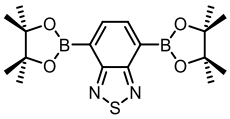
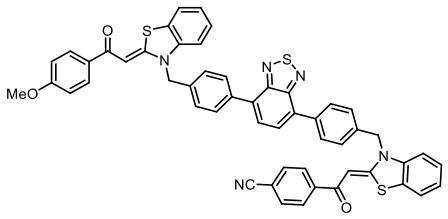
Entry	R [g] ([mmol])	Diboronic acid [g] ([mmol])	Yield of product [mg] (%)
6[(a)]	CN 0.224 (0.500) of **3h**	 0.249 (0.500) of **4f**	 0.286 (58) of **5f**
7[(b)]	CN 0.134 (0.300) of **3h**	 0.200 (0.300) of **4g**	 0.199 (59) of **5g**
8[(c)]	CN 0.224 (0.500) of **3h**	 0.132 (0.400) of **4h**	 0.062 (19) of **5h**
9[(a)]	CN 0.224 (0.500) of **3h**	 0.118 (0.500) of **4i**	 0.097 (47) of **5i**
10[(a)]	CN 0.224 (0.500) of **3h**	 0.144 (0.500) of **4j**	 0.312 (71) of **5j**

Table S7: Experimental details for the synthesis bridged aroyl-*S,N*-ketene acetals **5**.

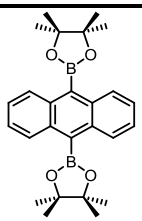
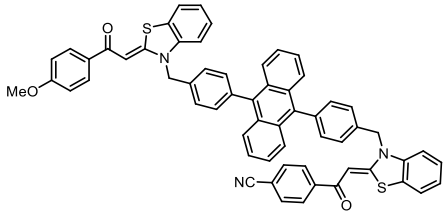
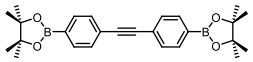
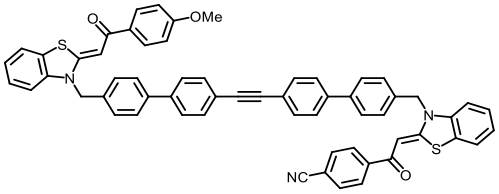
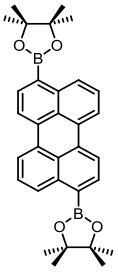
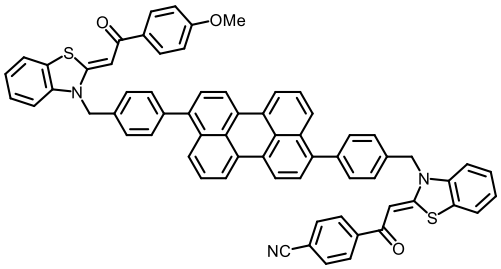
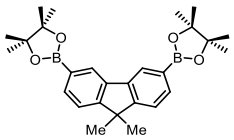
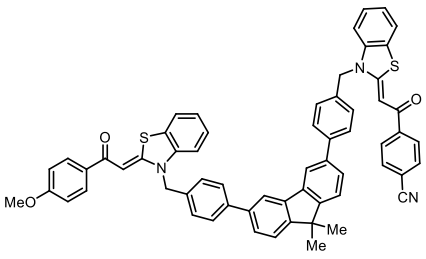
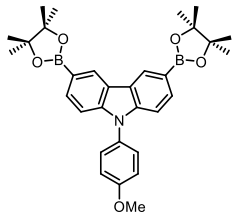
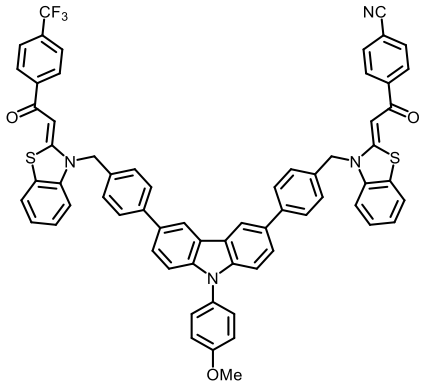
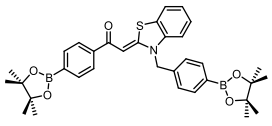
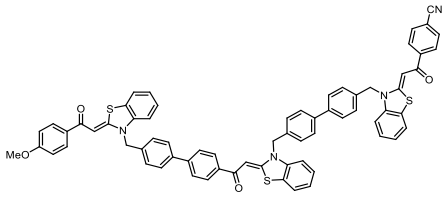
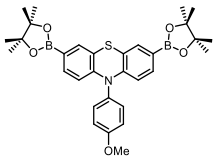
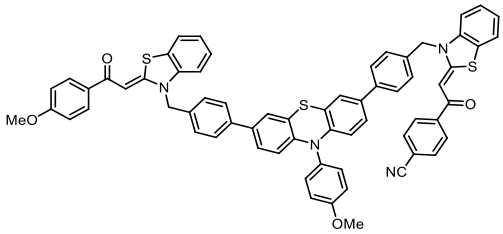
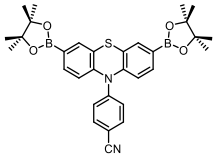
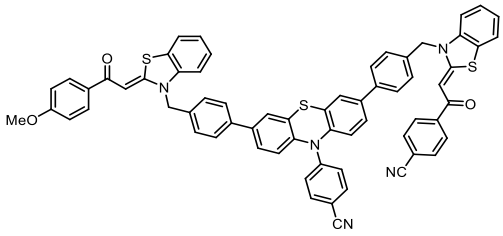
Entry	R [g] ([mmol])	Diboronic acid [g] ([mmol])	Yield of product [mg] (%)
11[(c)]	CN 0.179 (0.400) of **3h**	 0.172 (0.400) of **4k**	 0.101 (28) of **5k**
12[(a)]	CN 0.224 (0.500) of **3h**	 0.215 (0.500) of **4l**	 0.277 (61) of **5l**
13[(b)]	CN 0.134 (0.300) of **3h**	 0.151 (0.300) of **4m**	 0.219 (74) of **5m**
14[(b)]	CN 0.179 (0.400) of **3h**	 0.178 (0.400) of **4n**	 0.282 (76) of **5n**

Table S7: Experimental details for the synthesis bridged aroyl-*S,N*-ketene acetals **5**.

Entry	R [g] ([mmol])	Diboronic acid [g] ([mmol])	Yield of product [mg] (%)
15[(d)]	CF_3 0.196 (0.400) of **3h**	 0.240 (0.400) of **4o**	 0.314 (72) of **5o**
16[(a)]	CN 0.112 (0.250) of **3h**	 0.149 (0.250) of **4p**	 0.205 (76) of **5p**
17[(e)]	CN 0.112 (0.250) of **3h**	 0.139 (0.250) of **4q**	 0.143 (55) of **5q**
18[(e)]	CN 0.112 (0.250) of **3h**	 0.138 (0.250) of **4r**	 0.153 (49) of **5r**

(a): $C_{23}H_{18}BrNO_2S$ (**7c**): 226 mg (0.500 mmol), $Pd(PPh_3)_4$: 29.0 mg (0.025 mmol), Cs_2CO_3: 489 mg (1.50 mmol).

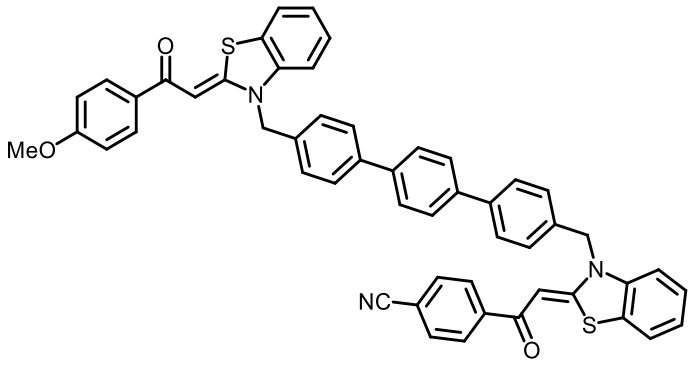
(b): $C_{23}H_{18}BrNO_2S$ (**7c**): 135 mg (0.300 mmol), $Pd(PPh_3)_4$: 17.0 mg (0.015 mmol), Cs_2CO_3: 293 mg (0.900 mmol).

(c): $C_{23}H_{18}BrNO_2S$ (**7c**): 181 mg (0.400 mmol), $Pd(PPh_3)_4$: 24.0 mg (0.020 mmol), Cs_2CO_3: 392 mg (1.20 mmol).

(d): Anstelle von Verbindung **7b** wurde **3h** verwendet. $C_{23}H_{15}BrN_2OS$ (**3h**): 178 mg (0.400 mmol), $Pd(PPh_3)_4$: 23.0 mg (0.020 mmol), Cs_2CO_3: 391 mg (1.20 mmol).

(e): $C_{23}H_{18}BrNO_2S$ (**7c**): 113 mg (0.250 mmol), $Pd(PPh_3)_4$: 15.0 mg (0.0125 mmol), Cs_2CO_3: 245 mg (0.750 mmol).

4-((*Z*)-2-(3-((4''-(((*Z*)-2-(2-(4-Methoxyphenyl)-2-oxoethylidene)benzo[*d*]thiazol-3(2*H*)-yl)methyl)-[1,1':4',1''-terphenyl]-4-yl)methyl)benzo[*d*]thiazol-2(3*H*)-ylidene)acetyl)benzonitrile (5a)



$C_{52}H_{37}N_3O_3S_2$

[815.23]

The synthesis was performed according to **GPVI**. The flash chromatography on silica gel was performed with a mixture of *n*-hexane and acetone 4:1 to 3:1 to 2:1 to 1:2 as eluent. It was possible to isolate compound **5a** (0.263 g, 0.321 mmol, 64 %) as a yellow solid.

Mp: 180 °C (decomposition).

R_f (*n*-hexane/acetone 1:1): 0.30.

^{1}H NMR (300 MHz, DMSO-d$_6$): δ 3.73 (s, 3 H), 5.61 (s, 2 H), 5.69 (s, 2 H), 6.89-6.93 (m, 3 H), 7.06 (s, 1 H), 7.13-7.66 (m, 18 H), 7.76 (d, ^{3}J = 7.8 Hz, 1 H), 7.82-7.92 (m, 5 H), 8.09-8.12 (m, 2 H).

^{13}C NMR (75 MHz, DMSO-d$_6$): δ 47.9 (CH_2), 48.2 (CH_2), 55.4 (CH_3), 87.2 (CH), 87.8 (CH), 111.0 (CH), 111.6 (CH), 113.1 (CH), 113.6 (CH), 118.7 (CH), 122.6 (C_{quat}), 122.86 (C_{quat}), 122.94 (C_{quat}), 123.5 (CH), 126.18 (CH), 126.22 (CH), 127.0 (CH), 127.05 (CH), 127.12 (CH), 127.4 (CH), 127.8 (CH), 128.7 (CH), 128.9 (CH), 129.0 (CH), 131.5 (CH), 131.6 (CH), 131.8 (CH), 132.1 (C_{quat}), 132.5 (CH), 133.4 (C_{quat}), 134.8 (C_{quat}), 135.0 (C_{quat}), 138.6 (C_{quat}), 138.66 (C_{quat}), 138.68 (C_{quat}), 138.85 (C_{quat}), 138.94 (C_{quat}), 139.6 (C_{quat}), 139.8 (C_{quat}), 142.8 (C_{quat}), 160.9 (C_{quat}), 161.6 (C_{quat}), 162.7 (C_{quat}), 164.4 (C_{quat}), 181.0 (C_{quat}), 182.5 (C_{quat}).

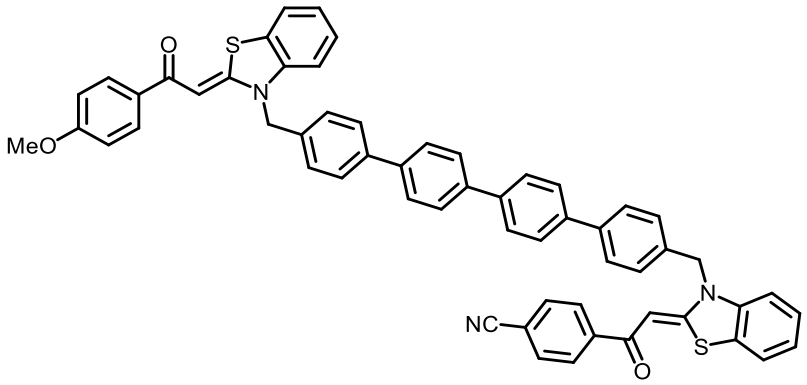
MALDI-TOF (m/z): 816.3 ($C_{52}H_{37}N_3O_3S_2$+H^+), 533.3 ($C_{36}H_{25}N_2OS$+H^+).

IR $\tilde{\nu}$ [cm^{-1}]: 635 (m), 673 (m), 689 (m), 710 (m), 719 (m), 743 (s), 764 (s), 791 (m)), 806 (m), 826 (w), 841 (w), 881 8m), 926 (w), 955 (w), 976 (w), 1005 (m), 1018 (m), 1067 (m), 1088 (m), 1113 (m), 1165 (m), 1194 (m), 1227 (m), 1254 (m), 1296 (w), 1304 (m), 1331 (m), 1354 (m), 1437 (s), 1456 (s), 1506 (m), 1558 (m), 1591 (w), 1844 (w), 3011 (w), 3107 (w9, 3200 (w), 3211 (w); 3435 (w), 3487 (w), 3547 (w), 3566 (w), 3800 (w), 3898 (w).

UV/Vis (C_3H_6O): λ_{max} (ε) = 281 (30000), 389 (31300).

Anal calcd for $C_{52}H_{37}N_3O_3S_2$ [815.2]: C 76.54, H 4.57, N 5.15, S 7.86; Found: C 76.81, H 4.76, N 4.86, S 7.66.

4-((*Z*)-2-(3-((4'''-(((*Z*)-2-(2-(4-Methoxyphenyl)-2-oxoethylidene)benzo[*d*]thiazol-3(2*H*)-yl)methyl)-[1,1':4',1'':4'',1'''-quaterphenyl]-4-yl)methyl)benzo[*d*]thiazol-2(3*H*)-ylidene)acetyl)benzonitrile (5b)



$C_{58}H_{41}N_3O_3S_2$

[891.26]

The synthesis was performed according to **GPVI**. The flash chromatography on silica gel was performed with a mixture of *n*-hexane and acetone 3:1 to 2:1 to 1:1 to 1:4 to pure acetone as eluent. It was possible to isolate compound **5b** (0.178 g, 0.199 mmol, 40 %) as a yellow solid.

Mp: 173 °C (decomposition).

R_f (*n*-hexane/acetone 1:1): 0.54.

^{1}H NMR (300 MHz, acetone-d_6/CS_2 5:1): δ 3.71 (s, 3 H), 5.57 (s, 2 H), 5.61 (s, 2 H), 6.82 (s, 1 H), 7.14-7.37 (m, 14 H), 7.40-7.68 (m, 17 H), 7.96-7.98 (m, 2 H).

^{13}C NMR (75 MHz, acetone-d_6/CS_2 5:1): δ 49.3 (CH_2), 49.5 (CH_2), 55.2 (CH_3), 88.0 (CH), 88.4 (CH), 111.2 (CH), 111.7 (CH), 114.1 (CH), 114.7 (CH), 118.9 (CH), 121.77 (C_{quat}), 121.79 (C_{quat}), 123. 4 (C_{quat}), 124.3 (CH), 127.5 (CH), 127.6 (CH), 127.7 (CH), 128.1 (CH), 128.2 (CH), 128.6 (CH), 129.2 (CH), 129.3 (CH), 129.8 (CH), 132.47 (CH), 132.54 (CH), 132.6 (CH), 132.8 (CH), 133.3 (CH), 134.0 (C_{quat}), 134.7 (C_{quat}), 135.9 (C_{quat}), 139.5 (C_{quat}), 139.96 (C_{quat}), 140.01 (C_{quat}), 141.5 (C_{quat}), 147.0 (C_{quat}), 154.5 (C_{quat}), 154.8 (C_{quat}), 166.8 (C_{quat}), 169.2 (C_{quat}), 181.4 (C_{quat}), 183.2 (C_{quat}).

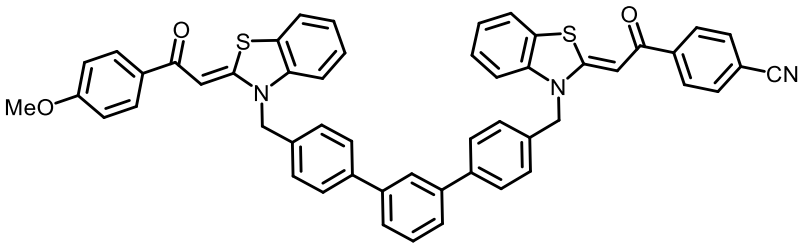
MALDI-TOF (m/z): 892.3 ($C_{58}H_{41}N_3O_3S_2$+H^+), 574.2.

IR $\tilde{\nu}$ [cm^{-1}]: 694 (s), 719 (s), 745 (m), 768 (s), 806 (s), 827 (m), 862 (m), 880 (w), 955 (m), 1003 (w), 1020 (w), 1051 (m), 1067 (w), 1082 (m), 1119 (m), 1167 (m), 1227 (w), 1246 (m), 1254 (w), 1306 (m), 1364 (w), 1379 (m), 1437 (s), 1472 (m), 1541 (m), 1580 (m), 3055 (w), 3092 (w); 3111 (w), 3298 (w), 3318 (w), 3649 (w), 3869 (w).

UV/Vis (C_3H_6O): λ_{max} (ε) = 274 (24800), 391 (15900).

Anal calcd for $C_{58}H_{41}N_3O_3S_2$ [891.3]: C 78.09, H 4.63, N 4.71, S 7.19; Found: C 78.22, H 4.81, N 4.66, S 6.88.

4-((*Z*)-2-(3-((4''-(((*Z*)-2-(2-(4-Methoxyphenyl)-2-oxoethylidene)benzo[*d*]thiazol-3(2*H*)-yl)methyl)-[1,1':3',1''-terphenyl]-4-yl)methyl)benzo[*d*]thiazol-2(3*H*)-ylidene)acetyl)benzonitrile (5c)



$C_{52}H_{37}N_3O_3S_2$

[815.23]

The synthesis was performed according to **GPVI**. The flash chromatography on silica gel was performed with a mixture of *n*-hexane and acetone 3:1 to 2:1 to 1:1 to 1:2 as eluent. It was possible isolate compound **5c** (0.296 g, 0.363 mmol, 73 %) as an orange-yellow solid.

Mp: 95 °C.

R_f (*n*-hexane/acetone 2:1): 0.18.

^{1}H NMR (300 MHz, acetone-d_6/CS_2 5:1): δ 3.83 (s, 3 H), 5.52 (s, 2 H), 5.61 (s, 2 H), 6.75 (s, 1 H), 6.88-6.98 (m, 3 H), 7.17-7.39 (m, 10 H), 7.49-7.55 (m, 7 H), 7.68-7.77 (m, 4 H), 7.86-7.98 (m, 3 H), 8.09-8.12 (m, 1 H).

^{13}C NMR (75 MHz, acetone-d_6/CS_2 5:1): δ 49.0 (CH_2), 49.2 (CH_2), 55.6 (CH_3), 87.9 (CH), 88.3 (CH), 111.0 (CH), 111.6 (CH), 114.1 (CH), 114.4 (CH), 114.7 (CH), 122.2 (C_{quat}), 122.3 (C_{quat}), 123.1 (CH), 123.3 (C_{quat}), 123.6 (CH), 123.8 (CH), 124.2 (CH), 127.3 (CH), 127.7 (CH), 128.1 (CH), 128.6 (CH), 129.4 (CH), 129.8 (CH),131.2 (CH), 132.1 (C_{quat}), 132.5 (CH), 132.70 (CH), 132.74 (C_{quat}), 132.8 (C_{quat}), 133.03 (C_{quat}), 133.04 (C_{quat}), 134.6 (CH), 135.2 (C_{quat}), 135.4 (C_{quat}), 140.5 (C_{quat}), 140.7 (C_{quat}), 143.8 (C_{quat}), 161.5 (C_{quat}), 161.6 (C_{quat}), 162.7 (C_{quat}), 163.4 (C_{quat}), 182.0 (C_{quat}), 183.5 (C_{quat}).

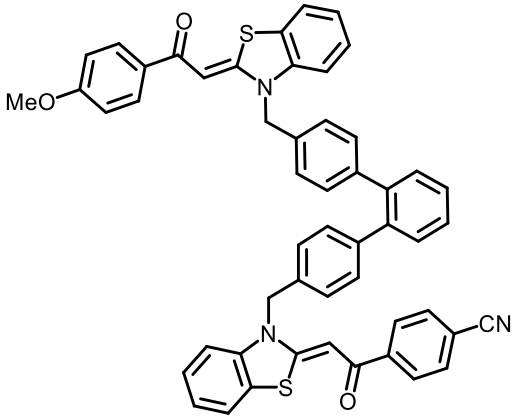
MALDI-TOF (m/z): 816.3 ($C_{52}H_{37}N_3O_3S_2$+H^+), 538.2.

IR $\tilde{\nu}$ [cm^{-1}]: 627 (w), 675 (w), 696 (m), 719 (m), 743 (m), 768 (m), 791 (w), 814 (w), 829 (w); 843 (m), 880 (s), 912 (w), 924 (w), 949 (w), 982 (w); 1024 (m), 1067 (m), 1090 (m), 1117 (m), 1144 (m), 1167 (m), 1194 (m), 1229 (m), 1254 (m), 1294 (m), 1306 (m), 1331 (m), 1379 (m), 1395 (m), 1406 (m), 1437 (s), 1452 (s), 1547 (w), 1555 (m), 1560 (m), 1591 (m), 1643 (w).

UV/Vis (C_3H_6O): λ_{max} (ε) = 255 (60700), 389 (47700).

Anal calcd for $C_{52}H_{37}N_3O_3S_2$ [815.2]: C 76.54, H 4.57, N 5.15, S 7.86; Found: C 76.38, H 4.18, N 4.78, S 7.67.

4-((*Z*)-2-(3-((4''-(((*Z*)-2-(2-(4-Methoxyphenyl)-2-oxoethylidene)benzo[*d*]thiazol-3(2*H*)-yl)methyl)-[1,1':3',1''-terphenyl]-4-yl)methyl)benzo[*d*]thiazol-2(3*H*)-ylidene)acetyl)benzonitrile (5d)



$C_{52}H_{37}N_3O_3S_2$

[815.23]

The synthesis was performed according to **GPVI**. The flash chromatography on silica gel was performed with a mixture of *n*-hexane and acetone 3:1 to 2:1 to 1:1 to pure acetone as eluent. It was possible to isolate compound **5d** (0.176 g, 0.126 mmol, 43 %) as an orange-yellow solid.

Mp: 132 °C.

R_f (*n*-hexane/acetone 3:1): 0.16.

^{1}H NMR (300 MHz, acetone-d_6/CS_2 5:1): δ 3.83 (s, 3 H), 5.51 (s, 2 H), 5.61 (s, 2 H), 6.74 (s, 1 H), 6.87-6.97 (m, 4 H), 7.17-7.38 (m, 10 H), 7.45-7.53 (m, 5 H), 7.67-7.79 (m, 5 H), 7.85-7.97 (m, 4 H), 8.07-8.11 (m, 1 H).

^{13}C NMR (75 MHz, acetone-d_6/CS_2 5:1): δ 49.0 (CH_2), 49.2 (CH_2), 55.6 (CH_3), 87.9 (CH), 88.3 (CH), 110.9 (CH), 111.6 (CH), 114.1 (CH), 114.3 (CH), 114.7 (CH), 118.8 (CH), 122.2 (C_{quat}), 122.3 (C_{quat}), 123.1 (CH), 123.3 (C_{quat}), 123.6 (CH), 124.2 (CH), 125.3 (CH), 127.3 (CH), 127.7 (CH), 127.9 (CH), 128.1 (CH), 128.6 (CH), 129.4 (CH), 129.8 (CH), 132.1 (C_{quat}), 132.7 (C_{quat}), 133.0 (C_{quat}), 134.6 (CH), 135.1 (C_{quat}), 135.4 (C_{quat}), 140.5 (C_{quat}), 140.7 (C_{quat}), 143.8 (C_{quat}), 161.6 (C_{quat}), 162.6 (C_{quat}), 163.4 (C_{quat}), 164.0 (C_{quat}), 182.0 (C_{quat}), 183.5 (C_{quat}).

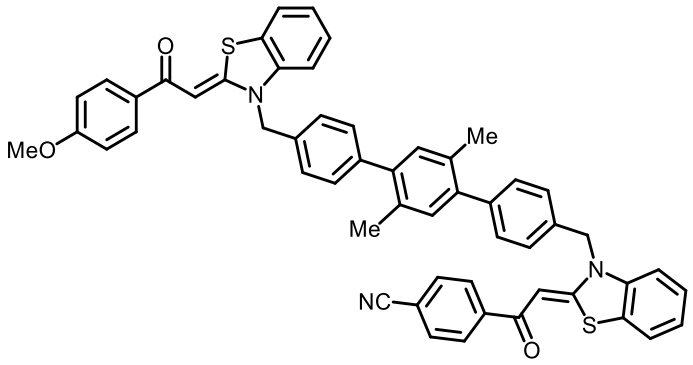
MALDI-TOF (m/z): 816.3 ($C_{52}H_{37}N_3O_3S_2$+H^+), 538.2.

IR $\tilde{\nu}$ [cm^{-1}]: 613 (m), 642 (w), 656 (w), 677 (w), 698 (m), 719 (m), 745 (s), 764 (m), 800 (w9, 822 (w), 843 (m), 861 (s), 926 (w), 949 (w), 972 (w), 984 (w), 1007 (w), 1022 (m), 1065 (m), 1090 (m), 1111 (m), 1167 (s), 1196 (m), 1229 (m), 1256 (m), 1296 (m), 1306 (m), 1331 (m), 1350 (m), 1381 (w), 1404 (m), 1454 (s), 1464 (s), 1539 (w), 1557 (m), 1564 (m), 1593 (m), 1651 (w), 1661 (w), 1711 (w), 2837 (w), 2853 (w), 2866 (w), 2926 (w), 2953 (w), 3057 (w), 3316 (w).

UV/Vis (C_3H_6O): λ_{max} (ε) = 386 (54600).

Anal calcd for $C_{52}H_{37}N_3O_3S_2$ [815.2]: C 76.54, H 4.57, N 5.15, S 7.86; Found: C 76.46, H 4.56, N 4.83, S 7.69.

4-((*Z*)-2-(3-((4''-(((*Z*)-2-(2-(4-Methoxyphenyl)-2-oxoethylidene)benzo[*d*]thiazol-3(2*H*)-yl)methyl)-2',5'-dimethyl-[1,1':4',1''-terphenyl]-4-yl)methyl)benzo[*d*]thiazol-2(3*H*)-ylidene)acetyl)benzonitrile (5e)



$C_{54}H_{41}N_3O_3S_2$

[843.26]

The synthesis was performed according to **GPVI**. The flash chromatography on silica gel was performed with a mixture of *n*-hexane and acetone 3:1 to 1:1 to 1:4 to pure acetone as eluent. It was possible to isolate compound **5e** (0.397 g, 0.471 mmol, 94 %) as a yellow solid.

Mp: 246 °C (decomposition).

R_f (*n*-hexane/acetone 3:1): 0.33.

^{1}H NMR (300 MHz, acetone-d_6/CS_2 5:1): δ 2.33 (s, 6 H), 3.79 (s, 3 H), 5.48 (s, 2 H), 5.58 (s, 2 H), 6.72 (s, 1 H), 6.84-6.94 (m, 4 H), 7.14-7.39 (m, 10 H), 7.42-7.49 (m, 4 H), 7.67-7.76 (m, 5 H), 7.82-7.92 (m, 3 H), 8.05-8.08 (m, 1 H).

^{13}C NMR (75 MHz, acetone-d_6/CS_2 5:1): δ 27.2 (CH_3), 49.0 (CH_2), 49.2 (CH_2), 55.6 (CH_3), 87.9 (CH), 88.3 (CH), 101.6 (CH), 111.0 (CH), 111.6 (CH), 114.1 (CH), 114.4 (C_{quat}), 114.6 (C_{quat}), 118.9 (CH), 122.1 (C_{quat}), 122.2 (C_{quat}), 123.1 (CH), 123.3 (CH), 123.6 (CH), 124.2 (CH), 127.3 (CH), 127.7 (CH), 127.9 (C_{quat}), 128.0 (CH), 128.6 (CH), 129.4 (CH), 129.8 (CH), 132.1 (CH), 132.69 (CH), 132.73 (CH), 132.8 (CH), 133.0 (CH), 135.2 (C_{quat}), 135.4 (CH), 140.1 (CH), 140.7 (C_{quat}), 141.5 (C_{quat}), 143.8 (C_{quat}), 161.6 (C_{quat}), 162.7 (C_{quat}), 163.4 (C_{quat}), 164.1 (C_{quat}), 182.0 (C_{quat}), 183.5 (C_{quat}).

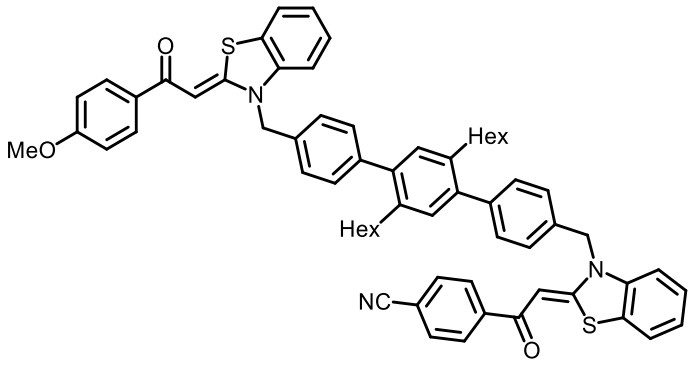
MALDI-TOF (m/z): 844.3 ($C_{54}H_{41}N_3O_3S_2$+H^+), 566.3 ($C_{38}H_{32}NO_2S^+$), 284.4 ($C_{22}H_{20}^+$).

IR $\tilde{\nu}$ [cm^{-1}]: 629 (w), 700 (m), 748 (m), 764 (m), 802 (m), 843 (m), 881 (s), 930 (w), 949 (w), 968 (w), 980 (w), 997 (w), 1018 (m), 1067 (m), 1090 (m), 1111 (m), 1167 (s), 1198 (m), 1229 (m), 1256 (m), 1277 (w), 1294 (w), 1306 (m), 1337 (m), 1408 (m), 1450 (s), 1468 (s), 1557 (m), 1593 (m), 1645 (w), 1703 (w), 2922 (w).

UV/Vis (C_3H_6O): λ_{max} (ε) = 254 (37000), 390 (24300).

Anal calcd for $C_{54}H_{41}N_3O_3S_2$ [843.3]: C 76.84, H 4.90, N 4.98, S 7.60; Found: C 76.73, H 4.82, N 4.89, S 7.74.

4-((*Z*)-2-(3-((2',5'-Dihexyl-4''-(((*Z*)-2-(2-(4-methoxyphenyl)-2-oxoethylidene)benzo[*d*]thiazol-3(2*H*)-yl)methyl)-[1,1':4',1''-terphenyl]-4-yl)methyl)benzo[*d*]thiazol-2(3*H*)-ylidene)acetyl)benzonitrile (5f)



$C_{64}H_{61}N_3O_3S_2$

[983.42]

The synthesis was performed according to **GPVI**. The flash chromatography on silica gel was performed with a mixture of *n*-hexane and acetone 2:1 to 1:1 to 1:2 to 1:4 as eluent. It was possible to isolate compound **5f** (0.286 g, 0.291 mmol, 58 %) as a yellow solid.

Mp: 55 °C.

R_f (*n*-hexane/acetone 2:1): 0.27.

^{1}H NMR (300 MHz, acetone-d_6/CS_2 5:1): δ 0.94 (t, ^3J = 7.2 Hz, 6 H), 1.34-1.46 (m, 12 H), 1.56-1.62 (m, 4 H), 2.66 (t, ^3J = 7.5 Hz, 4 H), 3.83 (s, 3 H), 5.50 (s, 2 H), 5.60 (s, 2 H), 6.72 (s, 1 H), 6.87-6.90 (m, 3 H), 7.17-7.39 (m, 12 H), 7.48-7.53 (m, 5 H), 7.66-7.70 (m, 3 H), 7.86 (d, ^3J = 9.0 Hz, 2 H), 8.09 (d, ^3J = 8.8 Hz, 2 H).

^{13}C NMR (75 MHz, acetone-d_6/CS_2 5:1): δ 14.8 (CH_3), 23.6 (CH_2), 32.6 (CH_2), 40.6 (CH_2), 49.0 (CH_2), 49.2 (CH_2), 55.6 (CH_3), 87.9 (CH), 88.3 (CH), 101.4 (CH), 110.9 (CH), 111.6 (CH), 114.1 (CH), 114.7 (CH), 118.8 (CH), 122.2 (C_{quat}), 122.4 (C_{quat}), 123.0 (CH), 123.3 (CH), 123.6 (CH), 124.2 (CH), 127.2 (CH), 127.6 (CH), 127.9 (CH), 128.1 (CH), 128.6 (CH), 129.4 (CH), 129.8 (CH), 132.69 (CH), 132.72 (CH), 132.8 (CH), 133.0 (C_{quat}), 135.1 (C_{quat}), 135.3 (C_{quat}), 140.1 (CH), 140.7 (C_{quat}), 143.8 (C_{quat}), 145.6 (C_{quat}), 161.5 (C_{quat}), 162.6 (C_{quat}), 163.4 (C_{quat}), 181.94 (C_{quat}), 183.4 (C_{quat}).

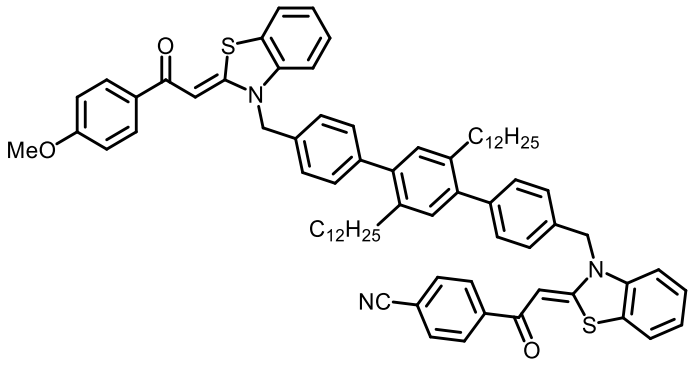
MALDI-TOF (m/z): 984.3 ($C_{64}H_{61}N_3O_3S_2$+H^+), 706.2 ($C_{48}H_{52}NO_2S^+$), 424.3 ($C_{32}H_{40}^+$), 373.3 ($C_{23}H_{18}NO_2S$+H^+).

IR $\tilde{\nu}$ [cm^{-1}]: 613 (m), 633 (m), 700 (m), 719 (m), 743 (m), 766 (m), 816 (w), 843 (m), 876 (m), 905 (w), 926 (w), 949 (w), 968 (w), 984 (w), 1022 (m), 1065 (m), 1090 (m), 1111 (m), 1165 (s), 1196 (m), 1227 (m), 1254 (m), 1296 (m), 1306 (m), 1329 (m), 1354 (m), 1377 (w), 1408 (m), 1450 (s9, 1462 (s), 1539 (w), 1554 (m), 1564 (m), 1593 (m), 1651 (w) 1665 (w), 1703 (w), 2226 (w), 2290 (w), 2725 (w), 2853 (w), 2899 (w), 2926 (w), 2953 (w), 3034 (w), 3065 (w).

UV/Vis (C_3H_6O): λ_{max} (ε) = 257 (70400), 388 (59900).

Anal calcd for $C_{64}H_{61}N_3O_3S_2$ [983.4]: C 78.09, H 6.25, N 4.27, S 6.51; Found: C 78.27, H 6.05, N 3.90, S 6.81.

4-((*Z*)-2-(3-((2',5'-Didodecyl-4''-(((*Z*)-2-(2-(4-methoxyphenyl)-2-oxoethylidene)benzo[*d*]thiazol-3(2*H*)-yl)methyl)-[1,1':4',1''-terphenyl]-4-yl)methyl)benzo[*d*]thiazol-2(3*H*)-ylidene)acetyl)benzonitrile (5g)



$C_{76}H_{85}N_3O_3S_2$

[1151.60]

The synthesis was performed according to **GPVI**. The flash chromatography on silica gel was performed with a mixture of *n*-hexane and acetone 3:1 to 2:1 to 1:1 as eluent. It was possible to isolate compound **5g** (0.199 g, 0.176 mmol, 59 %) as an orange resin.

R_f (*n*-hexane/acetone 2:1): 0.66.

^{1}H NMR (300 MHz, acetone-d_6/CS_2 5:1): δ 0.92 (t, ^3J = 7.4 Hz, 6 H), 1.32-1.43 (m, 36 H), 1.57-1.62 (m, 4 H), 2.66 (t, ^3J = 7.4 Hz, 3 H), 3.82 (s, 3H), 5.49 (s, 2 H), 5.59 (s, 2 H), 6.72 (s, 1 H), 6.86-6.90 (m, 3 H), 7.16-7.37 (m, 12 H), 7.47-7.52 (m, 5 H), 7.65-7.68 (m, 3 H), 7.71-7.77 (m, 3 H), 7.87 (d, ^3J = 8.9 Hz, 2 H).

^{13}C NMR (75 MHz, acetone-d_6/CS_2 5:1): δ 14.8 (CH_3), 23.7 (CH_2), 30.2 (CH_2), 30.3 (CH_2), 30.4 (CH_2), 30.55 (CH_2), 30.64 (CH_2), 31.1 (CH_2), 32.9 (CH_2), 40.5 (CH_2), 49.0 (CH_2), 49.2 (CH_2), 55.6 (CH_3), 87.9 (CH), 88.3 (CH), 101.4 (CH), 110.9 (CH), 111.5 (CH), 114.0 (CH), 114.6 (CH), 118.8 (CH), 122.2 (C_{quat}), 122.4 (C_{quat}), 123.0 (CH), 123.3 (CH), 123.6 (CH), 124.2 (CH), 127.2 (CH), 127.6 (CH), 127.9 (CH), 128.1 (CH), 128.5 (CH), 129.3 (CH), 129.7 (CH), 132.66 (CH), 132.69 (CH), 132.71 (CH), 135.0 (C_{quat}), 135.3 (C_{quat}), 140.1 (CH), 140.4 (C_{quat}), 140.6 (C_{quat}), 143.7 (C_{quat}), 145.5 (C_{quat}), 161.5 (C_{quat}), 162.6 (C_{quat}), 163.3 (C_{quat}), 181.9 (C_{quat}), 183.4 (C_{quat}).

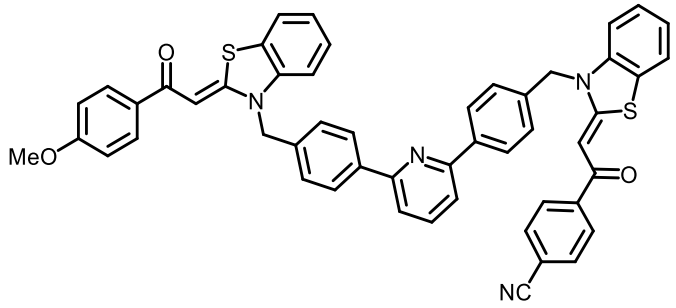
MALDI-TOF (m/z): 1152.6 ($C_{76}H_{85}N_3O_3S_2$+H^+), 874.6 ($C_{60}H_{76}NO_2S^+$).

IR $\tilde{\nu}$ [cm^{-1}]: 613 (m), 700 (m), 719 (m), 743 (m), 766 (m), 814 (w), 841 (m), 880 (m), 905 (w), 926 (w), 949 (w), 972 (w), 993 (w), 1016 (m), 1067 (m), 1090 (m), 1111 (m), 1136 (w), 1165 (s), 1196 (m), 1227 (m), 1256 (m), 1296 (m), 1306 (m), 1329 (m), 1354 (m), 1377 (w), 1408 (m), 1452 (s), 1464 (s), 1564 (m) 1593 (m), 1699 (w), 2228 (w), 2851 (w(, 2922 (m), 3065 (w).

UV/Vis (C_3H_6O): λ_{max} (ε) = 258 (74800), 389 (76200).

Anal calcd for $C_{76}H_{85}N_3O_3S_2$ [1151.6]: C 80.60, H 5.79, N 3.71, S 5.66; Found: C 80.24, H 5.99, N 3.61, S 5.97.

4-((*Z*)-2-(3-(4-(6-(4-(((*Z*)-2-(2-(4-Methoxyphenyl)-2-oxoethylidene)benzo[*d*]thiazol-3(2*H*)-yl)methyl)phenyl)pyridin-2-yl)benzyl)benzo[*d*]thiazol-2(3*H*)-ylidene)acetyl)benzonitrile (5h)



$C_{51}H_{36}N_4O_3S_2$

[816.22]

The synthesis was performed according to **GPVI**. The flash chromatography on silica gel was performed with a mixture of *n*-hexane and acetone 2:1 to 1:4 to pure acetone + 2% methanol as eluent. It was possible to isolate compound **5h** (0.062 g, 0.076 mmol, 19 %) as a yellow solid.

Mp: 69 °C.

R_f (*n*-hexane/acetone 2:1): 0.23.

^{1}H NMR (500 MHz, acetone-d_6/CS_2 5:1): δ 3.84 (s, 3 H), 5.54 (s, 2 H), 5.63 (s, 2 H), 6.77 (s, 1 H), 6.90-6.93 (m, 2 H), 7.19-7.22 (m, 1 H), 7.25-7.36 (m, 7 H), 7.39-7.40 (m, 1 H), 7.51-7.53 (m, 4 H), 7.62-7.72 (m, 6 H), 7.77-7.80 (m, 3 H), 7.91 (d, ^3J = 8.4 Hz, 2 H), 8.11 (d, ^3J = 7.7 Hz, 2 H).

^{13}C NMR (125 MHz, acetone-d_6/CS_2 5:1): δ 49.2 (CH_2), 49.4 (CH_2), 55.7 (CH_3), 88.1 (CH), 88.4 (CH), 111.1 (CH), 111.8 (CH), 114.3 (CH), 114.8 (CH), 119.0 (CH), 122.2 (C_{quat}), 122.3 (C_{quat}), 123.2 (CH), 123.4 (CH), 123.7 (CH), 124.3 (CH), 127.4 (CH), 127.8 (CH), 128.0 (C_{quat}), 128.2 (C_{quat}), 128.3 (CH), 128.7 (CH), 129.6 (CH), 129.9 (CH), 132.8 (CH), 132.86 (CH), 132.94 (CH), 133.29 (C_{quat}), 133.30 (C_{quat}), 135.4 (C_{quat}), 135.7 (C_{quat}), 140.7 (C_{quat}), 140.9 (C_{quat}), 141.3 (C_{quat}), 142.0 (CH), 144.1 (C_{quat}), 161.7 (C_{quat}), 161.8 (C_{quat}), 162.9 (C_{quat}), 163.58 (C_{quat}), 163.62 (C_{quat}), 182.3 (C_{quat}), 183.8 (C_{quat}).

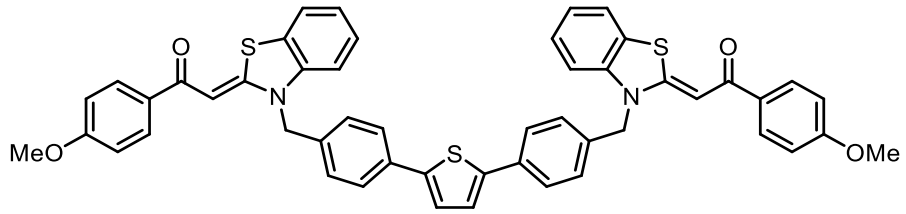
MALDI-TOF (m/z): 817.3 ($C_{51}H_{36}N_4O_3S_2$+H^+), 574.2 ($C_{34}H_{28}N_3O_2S_2^+$), 553.3 ($C_{35}H_{27}N_3S_2^+$).

IR $\tilde{\nu}$ [cm^{-1}]: 604 (w), 640 (m), 675 (m), 692 (s), 719 (s), 746 (m), 814 (w), 851 (m), 881 (m), 926 (w), 953 (w), 982 (m), 997 (w), 1018 (w), 1043 (w), 1069 (m), 1092 (m), 1117 (s), 1446 (m), 1169 (m), 1229 (m), 1258 (w), 1310 (w), 1331 (m), 1371 (m), 1389 (m), 1402 (m), 1437 (m), 1456 (m), 1471 (m), 1504 (w), 1557 (w), 1564 (w), 1591 (w), 1667 (w), 2226 (w), 2860 (w), 2926 (w), 2976 (w), 3057 (w), 3280 (w), 3343 (w), 3456 (w).

UV/Vis (C_3H_6O): λ_{max} (ε) = 267 (46000), 392 (20700).

Anal calcd for $C_{51}H_{36}N_4O_3S_2$ [816.2]: C 74.98, H 4.44, N 6.86, S 7.85; Found: C 74.97, H 4.15, N 6.62, S 7.49.

(2*Z*,2'*Z*)-2,2'-(((Thiophene-2,5-diylbis(4,1-phenylene))bis(methylene))-bis(benzo[*d*]thiazole-3(3*H*)-yl-2(3*H*)-ylidene))bis(1-(4-methoxyphenyl)ethan-1-one) (5i)



$C_{50}H_{38}N_2O_4S_3$

[826.20]

The synthesis was performed according to **GPVI**. The flash chromatography on silica gel was performed with a mixture of *n*-hexane and acetone 3:1 as eluent. It was possible to isolate compound **5i** (0.097 g, 0.117 mmol, 47 %) as a yellow solid.

Mp: 211 °C

R_f (*n*-hexane/acetone 1:1): 0.50.

^{1}H NMR (300 MHz, acetone-d_6): δ 3.82 (s, 6 H), 5.52 (s, 4 H), 6.74 (s, 2 H), 6.84-6.90 (m, 4 H), 7.16-7.22 (m, 2 H), 7.28-7.37 (m, 10 H), 7.59-7.64 (m, 4 H), 7.66-7.70 (m, 2 H), 7.80-7.90 (m, 4 H).

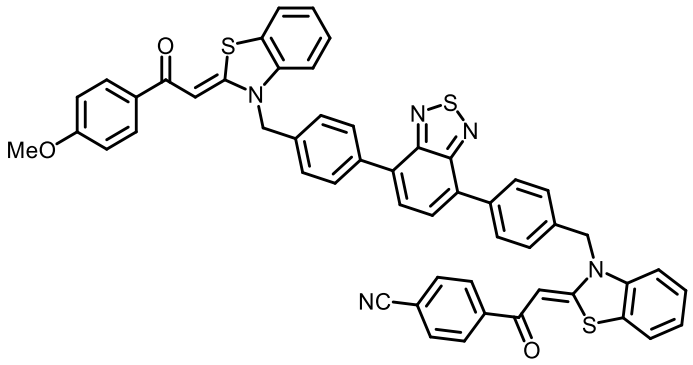
^{13}C NMR (75 MHz, acetone-d_6): δ 49.4 (CH_3), 55.6 (CH_2), 87.9 (CH), 111.0 (CH), 114.1 (CH), 123.0 (CH), 123.6 (CH), 125.4 (CH), 126.7 (CH), 127.2 (CH), 128.1 (CH), 129.8 (CH), 132.7 (C_{quat}), 133.1 (C_{quat}), 134.4 (C_{quat}), 135.4 (C_{quat}), 140.8 (C_{quat}), 143.7 (C_{quat}), 161.6 (C_{quat}), 162.6 (C_{quat}), 183.4 (C_{quat}).

MALDI-TOF (*m/z*): 827.2 ($[C_{50}H_{38}N_2O_4S_3 + H]^+$), 544.2 ($[C_{34}H_{26}NO_2S_2]^+$), 487.2 ($[C_{31}H_{22}NOS_2 - H]^+$), 262.4 ($[C_{18}H_{14}S]^+$).

IR $\tilde{\nu}$ [cm^{-1}]: 613 (m), 708 (m), 743 (s), 764 (s), 795 (m), 843 (w), 878 (s), 972 (w), 1026 (m), 1065 (w), 1088 (w), 1117 (w), 1167 (s), 1192 (m), 1223 (s), 1254 (m), 1304 (m), 1329 (w), 1350 (w), 1410 (m), 1452 (s), 1566 (m), 1595 (m), 2833 (w), 2930 (w), 3065 (w).

Anal calcd for $C_{50}H_{38}N_2O_4S_3$ [826.2]: C 72.61, H 4.63, N 3.39, S 11.63; Found: C 72.78, H 4.61, N 3.65, S 11.37.

4-((*Z*)-2-(3-(4-(7-(4-(((*Z*)-2-(2-(4-Methoxyphenyl)-2-oxoethylidene)benzo[*d*]thiazol-3(2*H*)-yl)methyl)phenyl)benzo[*c*][1,2,5]thiadiazol-4-yl)benzyl)benzo[*d*]thiazol-2(3*H*)-ylidene)acetyl)benzonitril (5j)



$C_{52}H_{35}N_5O_3S_3$

[873.19]

The synthesis was performed according to **GPVI**. The flash chromatography on silica gel was performed with a mixture of *n*-hexane and acetone 3:1 to 2:1 to 1:2 to 1:5 as eluent. It was possible to isolate compound **5j** (0.312 g, 0.357 mmol, 71 %) as an orange solid.

Mp: 149 °C.

R_f (*n*-hexane/acetone 2:1): 0.21.

^{1}H NMR (300 MHz, acetone-d_6/CS_2 5:1): δ 3.84 (s, 3 H), 5.53 (s, 2 H), 5.63 (s, 2 H), 6.76 (s, 1 H), 6.88-6.93 (m, 3 H), 7.18-7.34 (m, 8 H), 7.38-7.40 (m, 2 H), 7.50-7.53 (m, 4 H), 7.69-7.72 (m, 1 H), 7.76-7.81 (m, 3 H), 7.88-7.91 (m, 4 H), 8.09-8.12 (m, 2 H).

^{13}C NMR (75 MHz, acetone-d_6/CS_2 5:1): δ 49.0 (CH_2), 49.2 (CH_2), 55.6 (CH_3), 87.9 (CH), 88.3 (CH), 111.0 (CH), 111.7 (CH), 114.1 (CH), 114.7 (CH), 118.9 (CH), 122.1 (C_{quat}), 122.3 (C_{quat}), 123.1 (CH), 123.4 (CH), 123.6 (CH), 124.2 (CH), 125.97 (CH), 126.02 (CH), 127.3 (CH),127.7 (CH), 127.9 (C_{quat}), 128.1 (C_{quat}), 128.6 (CH), 129.5 (CH), 129.8 (CH), 132.7 (CH), 132.8 (CH), 132.9 (CH), 133.0 (C_{quat}), 133.5 (CH), 135.2 (C_{quat}), 135.5 (C_{quat}), 140.5 (C_{quat}), 140.7 (C_{quat}), 143.9 (C_{quat}), 153.7 (C_{quat}), 161.6 (C_{quat}), 162.7 (C_{quat}), 163.5 (C_{quat}), 182.1 (C_{quat}), 183.5 (C_{quat}).

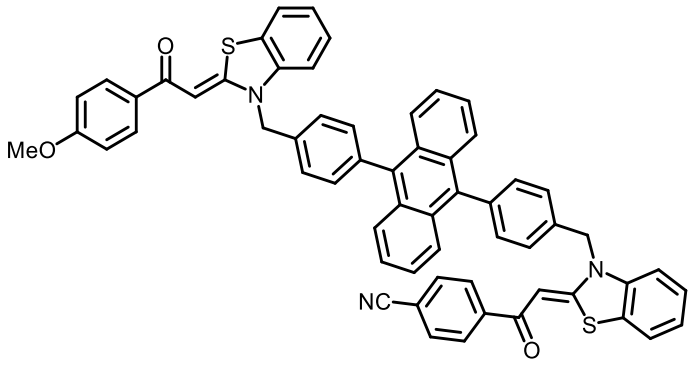
MALDI-TOF (m/z): 874.3 ($C_{52}H_{35}N_5O_3S_3$+H^+), 314.2 ($C_{20}H_{14}N_2S^+$).

IR $\tilde{\nu}$ [cm^{-1}]: 613 (m), 633 (m), 642 (m), 675 (m), 694 (s), 721 (s), 746 (s), 766 (m), 800 (w), 829 (m), 843 (m), 881 (s), 949 (m), 982 (m), 997 (w), 1022 (m), 1066 (m), 1092 (m), 1119 (m), 1167 (s), 1194 (m), 1229 (m), 1256 (m), 1308 (m), 1331 (m), 1366 (m), 1408 (m), 1439 (s), 1454 (s), 1464 (s), 1557 (m), 1593 (m), 1697 (w), 2228 (w), 2839 (w), 2934 (w), 2976 (w), 3057 (w), 3238 (w), 3257 (w), 3311 (w), 3339 (w), 3389 (w), 3402 (w).

UV/Vis (C_3H_6O): λ_{max} (ε) = 272 (51800), 387 (34400).

Anal calcd for $C_{52}H_{35}N_5O_3S_3$ [873.2]: C 71.46, H 4.04, N 8.01, S 11.00; Found: C 71.13, H 3.81, N 8.03, S 11.27.

4-((*Z*)-2-(3-(4-(10-(4-(((*Z*)-2-(2-(4-Methoxyphenyl)-2-oxoethylidene)benzo[*d*]thiazol-3(2*H*)-yl)methyl)phenyl)anthracene-9-yl)benzyl)benzo[*d*]thiazol-2(3*H*)-ylidene)acetyl)benzonitrile (5k)



$C_{60}H_{41}N_3O_3S_2$

[915.26]

The synthesis was performed according to **GPVI**. The flash chromatography on silica gel was performed with a mixture of *n*-hexane and acetone 2:1 to 1:1 to pure acetone as eluent. It was possible to isolate compound **5k** (0.101 g, 0.110 mmol, 28%) as an orange solid.

Mp: 165 °C.

R_f (*n*-hexane/acetone 2:1): 0.35.

^{1}H NMR (300 MHz, acetone-d$_6$/CS$_2$ 1:1): δ 3.58 (s, 3 H), 5.73 (s, 2 H), 5.83 (s, 2 H), 6.89-6.94 (m, 4 H), 7.02-7.07 (m, 1 H), 7.25-7.33 (m, 3 H), 7.40-7.53 (m, 10 H), 7.55-7.68 (m, 8 H), 7.72–7.81 (m, 3 H), 7.93-7.96 (m, 3 H), 8.06 (d, ^3J = 8.6 Hz, 1 H), 8.13-8.18 (m, 1 H).

^{13}C NMR (75 MHz, acetone-d$_6$/CS$_2$ 1:1): δ 50.7 (CH_2), 52.7 (CH_2), 55.2 (CH_3), 67.6 (C_{quat}), 87.0 (CH), 87.4 (CH), 111.1 (CH), 112.0 (CH), 114.1 (CH), 117.9 (CH), 120.5 (CH), 120.7 (CH), 122.2 (C_{quat}), 122.4 (C_{quat}), 123.6 (CH), 124.2 (CH), 124.7 (CH), 125.9 (CH), 125.97 (CH), 126.02 (CH), 126.3 (CH), 127.2 (CH), 127.36 (CH), 127.39 (CH), 127.7 (CH), 127.8 (CH), 128.6 (CH), 129.1 (CH), 129.3 (CH), 129.8 (CH), 130.6 (CH), 132.46 (C_{quat}), 132.53 (CH), 132.7 (CH), 132.8 (C_{quat}), 134.8 (C_{quat}), 135.1 (C_{quat}), 137.18 (C_{quat}), 137.20 (C_{quat}), 157.2 (C_{quat}), 157.7 (C_{quat}), 163.1 (C_{quat}), 163.46 (C_{quat}), 163.53 (C_{quat}), 182.6 (C_{quat}), 184.8 (C_{quat}).

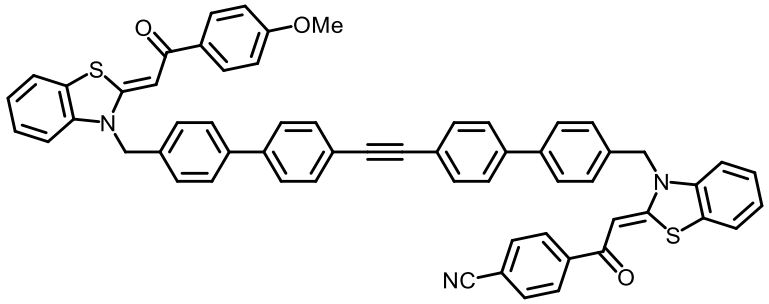
MALDI-TOF (m/z): 916.3 ($C_{60}H_{41}N_3O_3S_2$+H^+), 638.2 ($C_{44}H_{32}NO_2S^+$), 356.2 ($C_{28}H_{20}^+$).

IR $\tilde{\nu}$ [cm^{-1}]: 611 (m), 673 (m), 698 (m), 721 (m), 739 (m), 768 (s), 799 (w), 876 (m), 943 (m), 980 (w), 1022 (m), 1067 (m), 1090 (m), 1111 (m), 1169 (s), 1196 (m), 1227 (m), 1254 (m), 1294 (w), 1308 (m), 1331 (m), 1354 (w), 1393 (m), 1408 (m), 1441 (m), 1468 (s), 1564 (m), 1593 (m), 1653 (w), 1663 (w), 1699 (w), 2330 (w), 2359 (w), 2835 (w), 2893 (w), 3026 (w).

UV/Vis (C_3H_6O): λ_{max} (ε) = 257 (73000), 391 (25000).

Anal calcd for $C_{60}H_{41}N_3O_3S_2$ [915.3]: C 78.66, H 4.51, N 4.59, S 7.00; Found: C 78.42, H 4.66, N 4.34, S 7.24.

4-((*Z*)-2-(3-((4'-((4'-(((*Z*)-2-(2-(4-Methoxyphenyl)-2-oxoethylidene)benzo[*d*]thiazol-3(2*H*)-yl)methyl)-[1,1'-biphenyl]-4-yl)ethynyl)-[1,1'-biphenyl]-4-yl)methyl)benzo[*d*]thiazol-2(3*H*)-ylidene)acetyl)benzonitrile (5l)



$C_{60}H_{41}N_3O_3S_2$

[915.26]

The synthesis was performed according to **GPVI**. The flash chromatography on silica gel was performed with a mixture of *n*-hexane and acetone 2:1 to 1:1 to pure acetone as eluent. It was possible to isolate compound **5l** (0.277 g, 0.303 mmol, 61 %) as a yellow solid.

Mp: 80 °C.

R_f (*n*-hexane/acetone 1:1): 0.46.

^{1}H NMR (300 MHz, acetone-d$_6$/CS$_2$ 5:1): δ 3.83 (s, 3 H), 5.54 (s, 2 H), 5.63 (s, 2 H), 6.78 (s, 1 H), 6.89-6.94 (m, 4 H), 7.20-7.40 (m, 11 H), 7.44-7.60 (m, 12 H), 7.69-7.79 (m, 3 H), 7.89-7.96 (m, 3 H).

^{13}C NMR (75 MHz, acetone-d$_6$/CS$_2$ 5:1): δ 49.0 (CH_2), 49.2 (CH_2), 55.6 (CH_3), 60.9 (C_{quat}), 87.9 (CH), 88.3 (CH), 90.3 (C_{quat}), 111.1 (CH), 111.7 (CH), 114.1 (CH), 118.9 (CH), 122.1 (C_{quat}), 122.2 (C_{quat}), 122.8 (CH), 123.1 (C_{quat}), 123.5 (CH), 123.7 (CH), 124.3 (CH), 127.3 (CH), 127.7 (CH), 127.9 (CH), 128.0 (CH), 128.6 (CH), 129.5 (CH), 129.8 (CH), 132.1 (C_{quat}), 132.6 (CH), 132.7 (CH), 132.8 (C_{quat}), 132.9 (C_{quat}), 133.1 (C_{quat}), 134.0 (CH), 135.3 (C_{quat}), 135.6 (C_{quat}), 140.7 (C_{quat}), 143.9 (C_{quat}), 161.7 (C_{quat}), 162.7 (C_{quat}), 163.5 (C_{quat}), 182.1 (C_{quat}), 183.6 (C_{quat}).

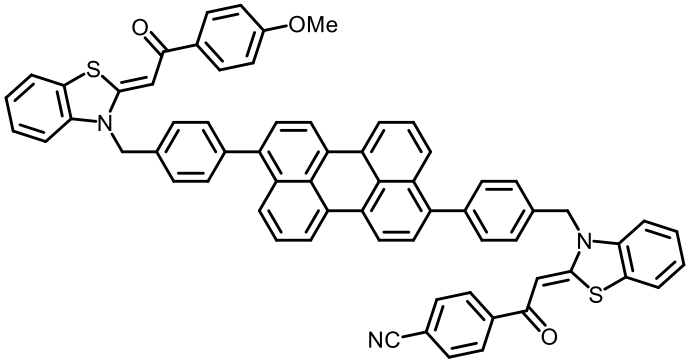
MALDI-TOF (m/z): 916 ($C_{60}H_{41}N_3O_3S+H^+$), 640 ($C_{44}H_{34}NO_2S^+$), 574 ($C_{39}H_{28}NO_2S^+$), 451, 358 ($C_{22}H_{16}NO_2S^+$).

IR $\tilde{\nu}$ [cm^{-1}]: 669 (m), 700 (m), 721 (m), 745 (m), 768 (m), 804 (m), 822 (m), 843 (m), 883 (m), 949 (m), 982 (w), 1022 (m), 1067 (m), 1092 (m), 1117 (m), 1167 (s), 1231 (m), 1256 (m), 1286 (w), 1310 (m), 1333 (m), 1348 (w), 1368 (m), 1400 (w), 1452 (s), 1468 (s), 1560 (m), 1593 (m), 3404 (w), 3420 (w).

UV/Vis (C_3H_6O): λ_{max} (ε) = 273 (21600), 388 (17700).

Anal calcd for $C_{60}H_{41}N_3O_3S_2$ [915.3]: C 78.66, H 4.51, N 4.59, S 7.00; Found: C 78.94, H 4.49, N 4.76, S 6.78.

4-((*Z*)-2-(3-(4-(9-(4-(((*Z*)-2-(2-(4-Methoxyphenyl)-2-oxoethylidene)benzo[*d*]thiazol-3(2*H*)-yl)methyl)phenyl)perylene-3-yl)benzyl)benzo[*d*]thiazol-2(3*H*)-ylidene)acetyl)benzonitrile (5m)



$C_{66}H_{43}N_3O_3S_2$

[989.27]

The synthesis was performed according to **GPVI**. The flash chromatography on silica gel was performed with a mixture of *n*-hexane and acetone 3:1 to 2:1 to 1:1 to 1:2 to pure acetone to pure acetone + 3% methanol as eluent. It was possible to isolate compound **5m** (0.219 g, 0.221 mmol, 74 %) as a yellow solid.

Mp: 165 °C (decomposition).

R_f (*n*-hexane/acetone 1:1): 0.53.

^{1}H NMR (300 MHz, acetone-d$_6$/CS$_2$ 5:1): δ 3.84 (s, 3 H), 5.53 (s, 2 H), 5.62 (s, 2 H), 6.77 (s, 1 H), 6.89-6.93 (m, 3 H), 7.18-7.40 (m, 10 H), 7.47-7.54 (m, 8 H), 7.69-7.81 (m, 7 H), 7.88-7.92 (m, 2 H), 8.09-8.13 (m, 1 H), 8.26-8.29 (m, 4 H).

^{13}C NMR (75 MHz, acetone-d$_6$/CS$_2$ 5:1): δ 49.0 (CH_2), 49.2 (CH_2), 55.7 (CH_3), 87.9 (CH), 88.3 (CH), 111.0 (CH), 111.7 (CH), 114.1 (CH), 114.7 (CH), 118.9 (CH), 121.3 (CH), 122.1 (C_{quat}), 122.3 (C_{quat}), 123.1 (C_{quat}), 123.4 (CH), 123.7 (CH), 124.3 (CH), 127.3 (CH), 127.5 (CH), 127.7 (CH), 127.9 (CH), 128.1 (CH), 128.6 (CH), 128.8 (CH), 129.5 (CH), 129.8 (CH), 131.9 (C_{quat}), 132.7 (CH), 132.9 (C_{quat}), 133.1 (C_{quat}), 135.2 (C_{quat}), 135.5 (C_{quat}), 135.7 (C_{quat}), 140.7 (C_{quat}), 143.9 (C_{quat}), 161.7 (C_{quat}), 162.7 (C_{quat}), 163.5 (C_{quat}), 182.1 (C_{quat}), 183.6 (C_{quat}).

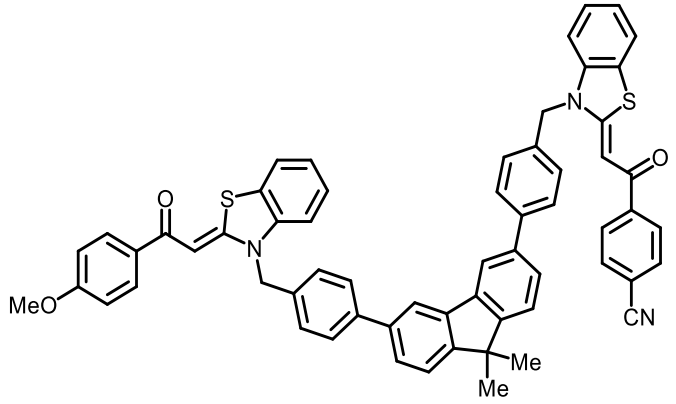
MALDI-TOF (m/z): 990 ($C_{66}H_{43}N_3O_3S_2$+H^+), 712 ($C_{50}H_{43}NO_2S^+$), 430 ($C_{34}H_{22}$), 341 ($C_{27}H_{17}$).

IR $\tilde{\nu}$ [cm^{-1}]: 606(m), 719 (m), 745 (m), 764 (s), 812 (m), 839 (m), 881 (s), 972 (w), 1022 (m), 1032 (m), 1067 (m), 1088 (m), 1111 (m), 1165 (s), 1194 (m), 1227 (m), 1254 (m), 1294 (m), 1308 (m), 1331 (m), 1350 (m), 1395 (m), 1406 (m), 1454 (s), 1466 (s), 1566 (m), 1593 (m), 2833 (w), 2872 (w), 2901 (w), 2932 (w), 2972 (w).

UV/Vis (C_3H_6O): λ_{max} (ε) = 258 (23300), 393 (18200).

Anal calcd for $C_{66}H_{43}N_3O_3S_2$ [989.3]: C 80.06, H 4.38, N 4.24, S 6.48; Found: C 80.37, H 4.71, N 3.89, S 6.20.

4-((*Z*)-2-(3-(4-(6-(4-(((*Z*)-2-(2-(4-Methoxyphenyl)-2-oxoethylidene)benzo[*d*]thiazol-3(2*H*)-yl)methyl)phenyl)-9,9-dimethyl-9*H*-fluoren-3-yl)benzyl)benzo[*d*]thiazol-2(3*H*)-ylidene)acetyl)benzonitrile (5n)



$C_{61}H_{45}N_3O_3S_2$

[931.29]

The synthesis was performed according to **GPVI**. The flash chromatography on silica gel was performed with a mixture of *n*-hexane and acetone 2:1 to 1:1 to pure acetone as eluent. It was possible to isolate compound **5n** (0.282 g, 0.303 mmol, 76 %) as an orange solid.

Mp: 115 °C.

R_f (*n*-hexane/acetone 2:1): 0.17.

^{1}H NMR (300 MHz, acetone-d$_6$/CS$_2$ 5:1): δ 3.58 (s, 6 H), 3.82 (s, 3 H), 5.59 (s, 2 H), 5.69 (s, 2 H), 6.83 (s, 1 H), 6.89-6.92 (m, 2 H), 6.99 (s, 1 H), 7.21-7.24 (m, 1 H), 7.26-7.31 (m, 1 H), 7.33-7.44 (m, 7 H), 7.48–7.61 (m, 4 H), 7.62-7.82 (m, 11 H), 7.91-7.95 (m, 2 H), 8.12-8.15 (m, 1 H).

^{13}C NMR (75 MHz, acetone-d$_6$/CS$_2$ 5:1): δ 25.3 (CH_3), 49.4 (CH_2), 49.6 (CH_2), 55.6 (CH_3), 67.6 (CH), 74.7 (CH), 88.0 (CH), 88.4 (CH), 111.2 (CH), 111.9 (CH), 114.1 (CH), 114.6 (CH), 118.9 (CH), 121.4 (CH), 122.1 (C_{quat}), 123.1 (C_{quat}), 123.4 (CH), 123.6 (CH), 124.2 (CH), 126.9 (CH), 127.0 (CH), 127.3 (CH), 127.7 (CH), 128.0 (CH), 128.1 (CH), 128.3 (CH), 128.6 (CH), 129.2 (CH), 129.3 (CH), 129.8 (CH), 132.5 (CH), 132.6 (CH), 132.7 (CH), 132.9 (C_{quat}), 133.5 (C_{quat}), 134.8 (C_{quat}), 135.0 (C_{quat}), 139.0 (C_{quat}), 140.5 (C_{quat}), 140.7 (C_{quat}), 140.9 (C_{quat}), 141.6 (C_{quat}), 144.0 (C_{quat}), 155.4 (C_{quat}), 161.8 (C_{quat}), 162.7 (C_{quat}), 163.6 (C_{quat}), 182.0 (C_{quat}), 183.5 (C_{quat}).

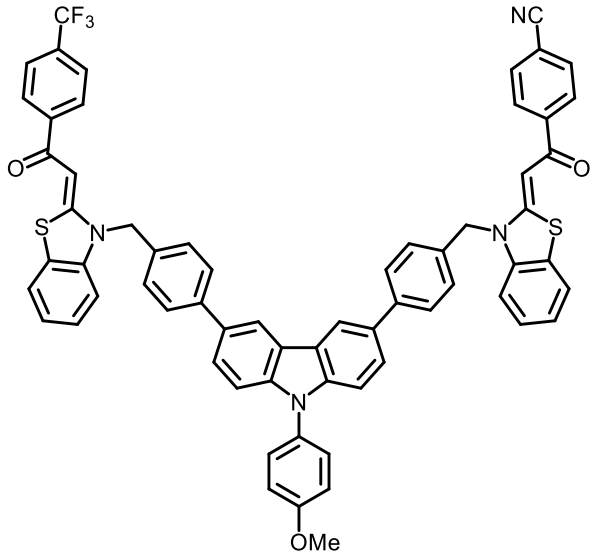
MALDI-TOF (m/z): 932.3 ($C_{61}H_{45}N_3O_3S_2$+H^+), 654.2 ($C_{45}H_{36}NO_2S^+$), 372.3 ($C_{29}H_{24}$).

IR $\tilde{\nu}$ [cm^{-1}]: 623 (m), 669 (w), 694 (m), 721 (m), 745 (m), 766 (m), 816 (m), 843 (m), 881 (s), 949 (w), 984 (w), 1016 (m), 1067 (m), 1090 (m), 1117 (m), 1142 (w), 1167 (s), 1196 (m), 1229 (m), 1256 (m), 1296 (m), 1308 (m), 1331 (m), 1358 (m), 1379 (m), 1406 (m), 1452 (s), 1560 (m), 1593 (m), 1697 (w), 2226 (w), 2839 (w), 2930 (w), 2965 (w), 3022 (w).

UV/Vis (C_3H_6O): λ_{max} (ε) = 274 (44100), 328 (28600), 388 (30900).

Anal calcd for $C_{61}H_{45}N_3O_3S_2$ [931.3]: C 78.60, H 4.87, N 4.51, S 6.88; Found: C 78.27, H 4.80, N 4.79, S 6.99.

4-((*Z*)-2-(3-(4-(9-(4-Methoxyphenyl)-6-(4-(((*Z*)-2-(2-(4-methoxyphenyl)-2-oxoethylidene)benzo[*d*]thiazol-3(2*H*)-yl)methyl)phenyl)-9*H*-carbazol-3-yl)benzyl)benzo[*d*]thiazol-2(3*H*)-ylidene)acetyl)benzonitrile (5o)



$C_{65}H_{43}F_3N_4O_3S_2$

[1048.27]

The synthesis was performed according to **GPVI**. The flash chromatography on silica gel was performed with a mixture of *n*-hexane and acetone 3:1 to 2:1 to 1:1 to pure acetone as eluent. It was possible to isolate compound **5o** (0.314 g, 0.282 mmol, 72 %) as a yellow solid.

Mp: 101 °C.

R_f (*n*-hexane/acetone 2:1): 0.19.

^{1}H NMR (300 MHz, acetone-d_6/CS_2 5:1): δ 3.93 (s, 3 H), 5.59 (s, 2 H), 5.60 (s, 2 H), 6.73-6.78 (m, 1 H), 6.88 (d, ^3J = 4.6 Hz, 1 H), 7.07-7.17 (m, 9 H), 7.22-7.28 (m, 5 H), 7.34-7.40 (m, 8 H), 7.44-7.76 (m, 6 H), 8.07-8.13 (m, 3 H), 8.32-8.42 (m, 2 H), 8.51-8.59 (m, 1 H).

^{13}C NMR (75 MHz, acetone-d_6/CS_2 5:1): δ 49.2 (CH_2), 50.6 (CH_2), 56.0 (CH_3), 88.25 (CH), 88.30 (CH), 111.5 (CH), 111.6 (CH), 112.3 (CH), 112.4 (CH), 112.8 (CH), 113.7 (CH), 114.7 (CH), 116.2 (CH), 116.3 (CH), 118.8 (CH), 122.4 (C_{quat}), 123.31 (C_{quat}), 123.34 (C_{quat}), 124.1 (CH), 124.2 (CH), 124.6 (CH), 125.8 (CH), 125.9 (CH), 126.7 (CH), 127.6 (CH), 127.7 (CH), 127.9 (CH), 128.2 (CH), 128.5 (CH), 128.6 (CH), 129.0 (CH), 129.1 (CH), 129.39 (CH), 129.40 (CH), 129.6 (C_{quat}), 130.1 (CH), 130.3 (CH), 130.8 (C_{quat}), 131.8 (CF_3), 132.75 (CH), 132.78 (CH), 135.09 (C_{quat}), 135.13 (C_{quat}), 135.7 (C_{quat}), 137.0 (C_{quat}), 137.4 (C_{quat}), 138.0 (C_{quat}), 138.9 (C_{quat}), 140.5 (C_{quat}), 141.1 (C_{quat}), 143.8 (C_{quat}), 160.2 (C_{quat}), 163.1 (C_{quat}), 163.4 (C_{quat}), 169.7 (C_{quat}), 182.0 (C_{quat}), 182.5 (C_{quat}).

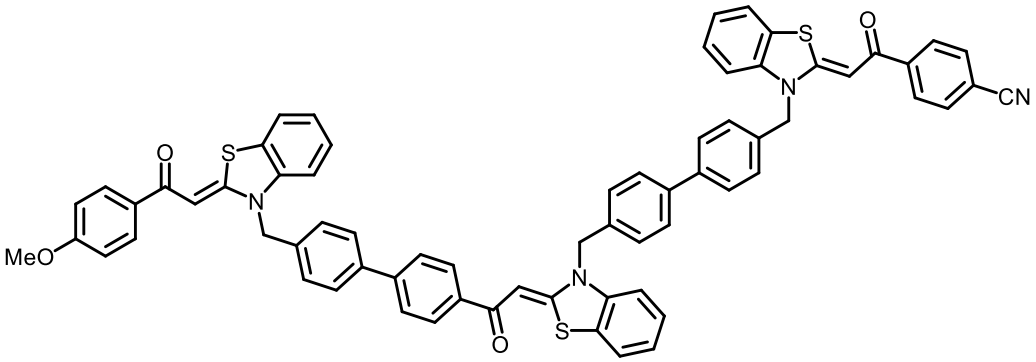
MALDI-TOF (m/z): 1048 ($C_{65}H_{43}F_3N_4O_3S_2^+$), 799 ($C_{51}H_{33}N_3O_3S_2^+$), 771 ($C_{49}H_{33}F_3N_2O_2S^+$), 728 ($C_{49}H_{34}N_3O_2S^+$), 692 ($C_{47}H_{36}N_2O_2S_2^+$), 451 ($C_{33}H_{25}NO^+$),412 ($C_{23}H_{17}F_3NOS^+$), 378 ($C_{24}H_{14}N_2OS^+$).

IR $\tilde{\nu}$ [cm^{-1}]: 654 (w), 675 (w), 698 (m), 719 (m), 745 (m), 764 (m), 804 (m), 829 (m), 854 (m), 881 (s), 947 (m), 984 (w), 1015 (m), 1065 (m), 1092 (m), 1111 (m), 1123 (m), 1157 (m), 1233 (m), 1246 (m), 1271 (w), 1281 (w), 1292 (w), 1323 (s), 1362 (w), 1368 (m), 1404 (m), 1456 (s), 1512 (m), 1558 (w), 1562 (w), 1601 (w), 2228 (w), 2320 (w9, 2359 (w), 2853 (w), 2926 (w), 2976 (w9, 3065 (w), 3217 (w), 3275 (w), 3358 (w), 3516 (w).

UV/Vis (C_3H_6O): λ_{max} (ε) = 255.5 (61200), 291.3 (44500), 395.0 (34000).

Anal calcd for $C_{65}H_{43}F_3N_4O_3S_2$ [1048.3]: C 74.41, H 4.13, N 5.34, S 6.11; Found: C 74.19, H 4.23, N 5.63, S 5.89.

4-((*Z*)-2-(3-((4'-(((*Z*)-2-(2-(4'-(((*Z*)-2-(2-(4-Methoxyphenyl)-2-oxoethylidene)benzo[*d*]thiazol-3(2*H*)-yl)methyl)-[1,1'-biphenyl]-4-yl)-2-oxoethylidene)benzo[*d*]thiazol-3(2*H*)-yl)methyl)-[1,1'-biphenyl]-4-yl)methyl)benzo[*d*]thiazol-2(3*H*)-ylidene)acetyl)benzonitrile (5p)



$C_{68}H_{48}N_4O_3S_3$

[1080.23]

The synthesis was performed according to **GPVI**. The flash chromatography on silica gel was performed with a mixture of *n*-hexane and acetone 1:1 to 1:2 to 1:4 to 1:2 to pure acetone + 2% methanol as eluent. It was possible to isolate compound **5p** 0.205 g, 0.190 mmol, 76 %) as a yellow solid.

Mp: 119 °C.

R_f (*n*-hexane/acetone 1:1): 0.34.

^{1}H NMR (300 MHz, acetone-d$_6$/CS$_2$ 5:1): δ 3.83 (s, 3 H), 5.53 (s, 2 H), 5.58 (s, 2 H), 5.63 (s, 2 H), 6.77 (s, 1 H), 6.84 (s, 1 H), 6.88-6.93 (m, 3 H), 7.20-7.40 (m, 15 H), 7.50-7.57 (m, 8 H), 7.68-7.80 (m, 5 H), 7.86-7.92 (m, 4 H), 8.09-8.13 (m, 2 H).

^{13}C NMR (75 MHz, acetone-d$_6$/CS$_2$ 5:1): δ 49.2 (CH_2), 49.3 (CH_2), 49.4 (CH_2), 55.8 (CH_3), 88.1 (CH), 88.5 (CH), 111.2 (CH), 111.6 (CH), 111.9 (CH), 114.3 (CH), 114.8 (CH), 119.1 (CH), 122.2 (C_{quat}), 122.3 (C_{quat}), 122.4 (C_{quat}), 123.2 (CH), 123.4 (CH), 123.5 (CH), 123.8 (CH), 124.2 (CH), 124.4 (CH), 126.0 (C_{quat}), 127.5 (CH), 127.7 (CH), 127.9 (CH), 128.0 (CH), 128.1 (CH), 128.2 (CH), 128.8 (CH), 129.6 (CH), 129.95 (CH), 130.00 (CH), 132.2 (CH), 132.90 (CH), 132.91 (CH), 133.0 (C_{quat}), 133.2 (C_{quat}), 135.4 (C_{quat}), 135.5 (C_{quat}), 135.7 (C_{quat}), 139.5 (C_{quat}), 140.9 (C_{quat}), 144.1 (C_{quat}), 161.8 (C_{quat}), 162.9 (C_{quat}), 163.0 (C_{quat}), 163.7 (C_{quat}), 182.3 (C_{quat}), 183.1 (C_{quat}), 183.7 (C_{quat}).

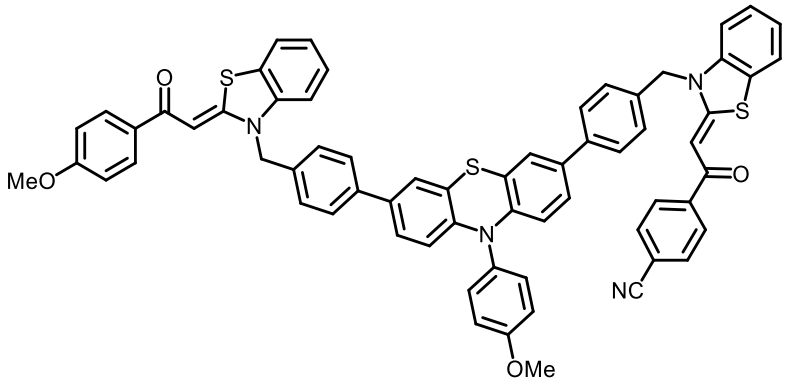
MALDI-TOF (m/z): 1081.2 ($C_{68}H_{48}N_4O_3S_3 + H^+$), 803.3 ($C_{52}H_{39}N_2O_3S_2^+$), 775.3 ($C_{50}H_{34}N_3O_2S_2^+$), 451.2 ($C_{31}H_{17}NOS^+$), 327.3 ($C_{21}H_{13}NOS^+$).

IR $\tilde{\nu}$ [cm^{-1}]: 615 (m), 644 (m), 675 (m), 696 (m), 719 (m), 745 (m), 766 (m), 802 (w), 820 (m), 843 (m), 881 (s), 928 8w), 951 (w), 984 (w), 1005 (m), 1022 (m), 1067 (m), 1090 (m), 1117 (m), 1136 (w), 1165 (m), 1194 (m), 1227 (m), 1256 (m), 1296 (m), 1308 (m), 1331 (m), 1350 (m), 1402 (m), 1423 (m), 1454 (s), 1553 (m), 1564 (m), 1593 (m), 1661 (w), 1703 (w), 2833 (w), 2856 (w), 2899 (w), 2916 (w), 2972 (w), 3026 (w), 3053 (w).

UV/Vis (C_3H_6O): λ_{max} (ε) = 272 (60000), 391 (17000).

Anal calcd for $C_{68}H_{48}N_4O_3S_3$ [1080.2]: C 75.53, H 4.85, N 4.52, S 8.89; Found: C 75.46, H 4.92, N 4.91, S 8.93.

4-((*Z*)-2-(3-(4-(10-(4-Methoxyphenyl)-7-(4-(((*Z*)-2-(2-(4-methoxyphenyl)-2-oxoethylidene)benzo[*d*]thiazol-3(2*H*)-yl)methyl)phenyl)-10*H*-phenothiazin-3-yl)benzyl)benzo[*d*]thiazol-2(3*H*)-ylidene)acetyl)benzonitrile (5q)



$C_{65}H_{46}N_4O_4S_3$

[1042.27]

The synthesis was performed according to **GPVI**. The flash chromatography on silica gel was performed with a mixture of *n*-hexane and acetone 2:1 to 1:4 to 1:1 to 1:2 to pure acetone + 2% methanol as eluent. It was possible to isolate compound **5q** (0.143 g, 0.137 mmol, 55 %) as a yellow solid.

Mp: 141 °C.

R_f (*n*-hexane/acetone 2:1): 0.15.

^{1}H NMR (300 MHz, DMSO-d$_6$): δ 2.13 (s, 3 H), 3.80 (s, 3 H), 5.65 (s, 2 H), 5.73 (s, 2 H), 6.19-6.24 (m, 1 H), 6.95-7.04 (m, 3 H), 7.10-7.45 (m, 7 H), 7.51-7.67 (m, 19 H), 7.92-8.00 (m, 4 H), 8.15-8.18 (m, 2 H).

^{13}C NMR (75 MHz, DMSO-d$_6$): δ 47.9 (CH_2), 48.5 (CH_2), 55.3 (CH_3), 55.8 (CH_3), 73.5 (CH), 81.4 (CH), 87.2 (CH), 87.8 (CH), 110.9 (CH), 111.6 (CH), 113.0 (CH), 118.6 (CH), 122.5 (C_{quat}), 122.8 (C_{quat}), 122.9 (C_{quat}), 123.4 (CH), 124.2 (CH), 126.2 (CH), 126.3 (CH), 126.7 (CH), 126.8 (CH), 127.2 (CH), 127.8 (CH), 128.7 (CH), 128.8 (CH), 129.0 (CH), 131.4 (CH), 131.6 (CH), 131.8 (C_{quat}), 132.0 (CH), 132.1 (CH), 132.5 (C_{quat}), 133.4 (CH), 134.3 (C_{quat}), 138.0 (C_{quat}), 139.7 (C_{quat}), 142.8 (C_{quat}), 143.6 (C_{quat}), 160.8 (C_{quat}), 161.5 (C_{quat}), 162.6 (C_{quat}), 180.9 (C_{quat}), 182.4 (C_{quat}).

MALDI-TOF (m/z): 1042 ($C_{65}H_{46}N_4O_4S_3^+$), 856 ($C_{53}H_{34}N_3O_3S_3^+$), 732 ($C_{47}H_{30}N_3O_2S_2^+$), 574 ($C_{37}H_{22}N_2OS_2^+$), 485 ($C_{33}H_{27}NOS^+$), 369 ($C_{23}H_{17}N_2OS^+$), 279 ($C_{16}H_{11}N_2OS^+$).

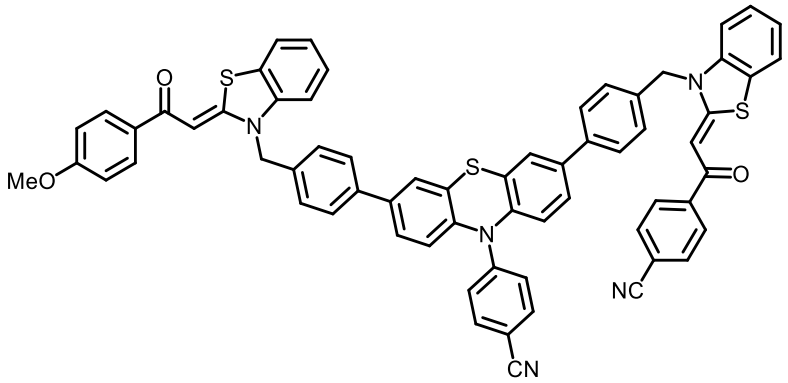
IR $\tilde{\nu}$ [cm^{-1}]: 610 (m), 694 (s), 719 (s), 745 (m), 766 (m), 810 (m), 841 (m), 880 (m), 907 (w), 924 (w), 949 (w), 982 (w), 997 (w), 1024 (m), 1067 (m), 1090 (m), 1117 (m), 1167 (m),

1192 (m), 1229 (m), 1256 (m), 1296 (m), 1306 (m), 1331 (m), 1379 (w), 1406 (w), 1437 (m), 1464 (s), 1557 (m), 1591 (m), 2224 (w), 2837 (w), 2857 (w), 2924 (w), 3223 (w).

UV/Vis (C_3H_6O): λ_{max} (ε) = 271 (68800), 388 (14000).

Anal calcd for $C_{65}H_{46}N_4O_4S_3$ [1042.3]: C 74.83, H 4.44, N 5.37, S 9.22; Found: C 75.25, H 4.40, N 5.56, S 9.23.

4-(3-(4-(((*Z*)-2-(2-(4-Cyanophenyl)-2-oxoethylidene)benzo[*d*]thiazol-3(2*H*)-yl)methyl)phenyl)-7-(4-(((*Z*)-2-(2-(4-methoxyphenyl)-2-oxoethylidene)benzo[*d*]thiazol-3(2*H*)-yl)methyl)phenyl)-10*H*-phenothiazin-10-yl)benzonitrile (5r)



$C_{71}H_{43}N_5O_3S_3$

[1038.27]

The synthesis was performed according to **GPVI**. The flash chromatography on silica gel was performed with a mixture of *n*-hexane and acetone 2:1 to 1:2 to pure as eluent. It was possible to isolate compound **5r** (0.153 g, 0.145 mmol, 58 %) as a yellow solid.

Mp: 132 °C.

R_f (*n*-hexane/acetone 1:1): 0.23.

^{1}H NMR (300 MHz, DMSO-d_6): δ 3.80 (s, 3 H), 5.68 (s, 2 H), 5.70 (s, 2 H), 6.90-6.99 (m, 7 H), 7.20-7.39 (m, 6 H), 7.49-7.66 (m, 16 H), 7.75-7.96 (m, 6 H), 8.06-8.17 (m, 1 H).

^{13}C NMR (75 MHz, DMSO-d_6): δ 55.2 (CH_2), 55.4 (CH_2), 55.9 (CH_3), 73.6 (CH), 81.4 (CH), 86.3 (CH), 87.8 (CH), 110.8 (CH), 111.0 (CH), 113.6 (CH), 114.9 (CH), 119.1 (CH), 122.6 (C_{quat}), 122.7 (C_{quat}), 123.0 (C_{quat}), 125.9 (CH), 126.2 (CH), 126.7 (CH), 127.8 (CH), 128.7 (CH), 128.9 (CH), 129.0 (CH), 131.2 (CH), 131.35 (CH), 131.44 (CH), 131.5 (CH), 131.6 (C_{quat}), 132.0 (CH), 132.06 (CH), 132.10 (C_{quat}), 132.5 (C_{quat}), 133.4 (CH), 134.3 (C_{quat}), 134.5 (C_{quat}), 135.2 (C_{quat}), 139.6 (C_{quat}), 140.7 (C_{quat}), 142.4 (C_{quat}), 142.8 (C_{quat}), 143.2 (C_{quat}), 155.8 (C_{quat}), 160.8 (C_{quat}), 161.6 (C_{quat}), 162.6 (C_{quat}), 180.0 (C_{quat}), 182.4 (C_{quat}).

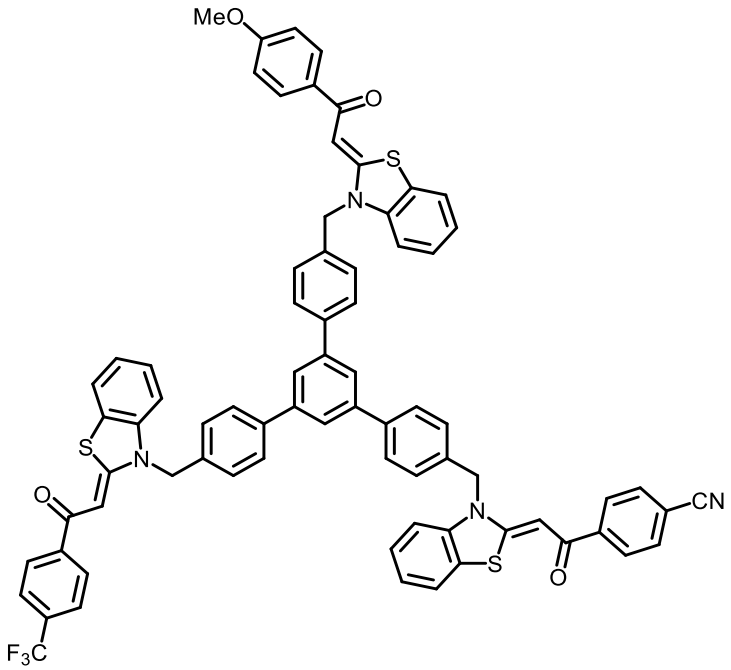
MALDI-TOF (m/z): 1038 ($C_{71}H_{43}N_5O_3S_3^+$), 985 ($C_{63}H_{43}N_3O_3S_3^+$), 703 ($C_{47}H_{31}N_2OS_2^+$), 574 ($C_{37}H_{22}N_2OS_2^+$), 374 ($C_{23}H_{19}NO_2S$.

IR $\tilde{\nu}$ [cm^{-1}]: 638 (m), 657 (w), 694 (s), 721 (s), 746 (m), 824 (m), 881 (m), 924 (w), 947 (w), 997 (w), 1024 (m), 1069 (m), 1092 (m), 1119 (m), 1169 (s), 1231 (m), 1260 (m), 1320 (m), 1362 (w), 1404 (m), 1437 (m), 1460 (s), 1504 (m), 1558 (m), 1568 (m), 1593 (m), 1699 (w), 2216 (w), 2918 (w),2930 (w), 2974 (w), 3053 (w).

UV/Vis (C_3H_6O): λ_{max} (ε) = 269 (44800), 391 (56300).

Anal calcd for $C_{71}H_{43}N_5O_3S_3$ [1038.3]: C 75.19, H 4.17, N 6.75, S 9.26; Found: C 75.27, H 4.20, N 6.60, S 9.33.

4-((*Z*)-2-(3-((4''-(((*Z*)-2-(2-(4-Methoxyphenyl)-2-oxoethylidene)benzo[*d*]thiazol-3(2*H*)-yl)methyl)-5'-(4-(((*Z*)-2-(2-oxo-2-(4-(trifluoromethyl)phenyl)ethylidene)benzo[d]thiazol-3(2*H*)-yl)methyl)phenyl)-[1,1':3',1''-terphenyl]-4-yl)methyl)benzo[*d*]thiazol-2(3*H*)-ylidene)acetyl)benzonitrile (5s)



$C_{75}H_{51}F_3N_4O_4S_3$

[1224.30]

Methoxy-substituted aroyl-*S,N*-ketene acetal **3a** (0.135 g, 0.300 mmol, 1.00 equiv.), 1,3,5-Tris(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)benzol (**4u**) (0.137 g, 0.300 mmol, 1.00 equiv.) tetrakis(triphenylphosphin)palladium(0) (0.017 g, 0.015 mmol, 20 mol%) and cesium carbonate (0.391 g, 0.900 mmol, 3.00 equivs.) were placed in a sintered, dry screw-cap *Schlenk*-tube under nitrogen atmosphere and dissolved in 3 mL dry 1,4-dioxane and 1 mL ethanol. The reaction mixture was stirred at 120 °C (oil bath) for 2 h. Thereafter, cyano-substituted aroyl-*S,N*-ketene acetal **3h** (0.134 g, 0.300 mmol, 1.00 equiv.) was added to the reaction mixture and the mixture was stirred at 120 °C (oil bath) for 3 h. Then, trifluoromethyl-substituted aroyl-*S,N*-ketene acetal **3g** (0.147 g, 0.300 mmol, 1.00 equiv.) was added to the reaction mixture and the mixture was stirred at 120 °C (oil bath) for 12 h. The crude product was adsorbed onto Celite® and purified by flash chromatography on silica gel (*n*-hexane/acetone 2:1 to 1:1 to 1:3 to pure acetone to pure acetone + 2% methanol). The product was suspended in *n*-hexane, the sediment was filtrated and dried under vacuo. After a second flash chromatography on silica gel (*n*-hexane/dichloromethane/acetone 2:1:1), compound **5s** (0.303 g, 0.247 mmol, 50%) was obtained as an orange solid.

Mp: 98 °C.

R_f (*n*-hexane/acetone 1:1): 0.50.

^{1}H NMR (300 MHz, acetone-d_6/CS_2 5:1): δ 3.83 (s, 3 H), 5.51 (s, 2 H), 5.60 (s, 2 H), 5.61 (s, 2 H), 6.74 (s, 1 H), 6.87-6.91 (m, 4 H), 7.17-7.31 (m, 11 H), 7.33-7.39 (m, 4 H), 7.49-7.52 (m, 6 H), 7.67-7.73 (m, 3 H), 7.74-7.79 (m, 8 H), 7.85-7.90 (m, 2 H), 8.08-8.13 (m, 3 H),.

^{13}C NMR (75 MHz, acetone-d_6/CS_2 5:1): δ 49.0 (CH_2), 49.1 (CH_2), 49.2 (CH_2), 55.6 (CH_3), 87.9 (CH), 88.26 (CH), 88.31 (CH), 110.9 (CH), 111.5 (CH), 111.6 (CH), 114.1 (CH), 114.7 (C_{quat}), 118.8 (CH), 122.2 (C_{quat}), 122.26 (C_{quat}), 122.31 (C_{quat}), 123.1 (CH), 123.31 (CH), 123.34 (CH), 123.6 (CH), 124.1 (CH), 124.2 (CH), 124.3 (CH), 125.8 (CH), 125.9 (CH), 126.7 (C_{quat}), 127.3 (CH), 127.6 (CH), 127.7 (CH), 127.9 (CH), 128.1 (C_{quat}), 128.5 (CH), 128.6 (CH), 129.4 (CH), 129.8 (CH), 132.1 (CF_3), 132.70 (CH), 132.74 (CH), 132.8 (CH), 133.0 (C_{quat}), 133.8 (CH), 135.1 (C_{quat}), 135.2 (C_{quat}), 135.4 (C_{quat}), 140.5 (C_{quat}), 140.7 (C_{quat}), 143.7 (C_{quat}), 143.8 (C_{quat}), 161.6 (C_{quat}), 162.6 (C_{quat}), 163.2 (C_{quat}), 163.4 (C_{quat}), 182.0 (C_{quat}), 182.5 (C_{quat}), 183.5 (C_{quat}).

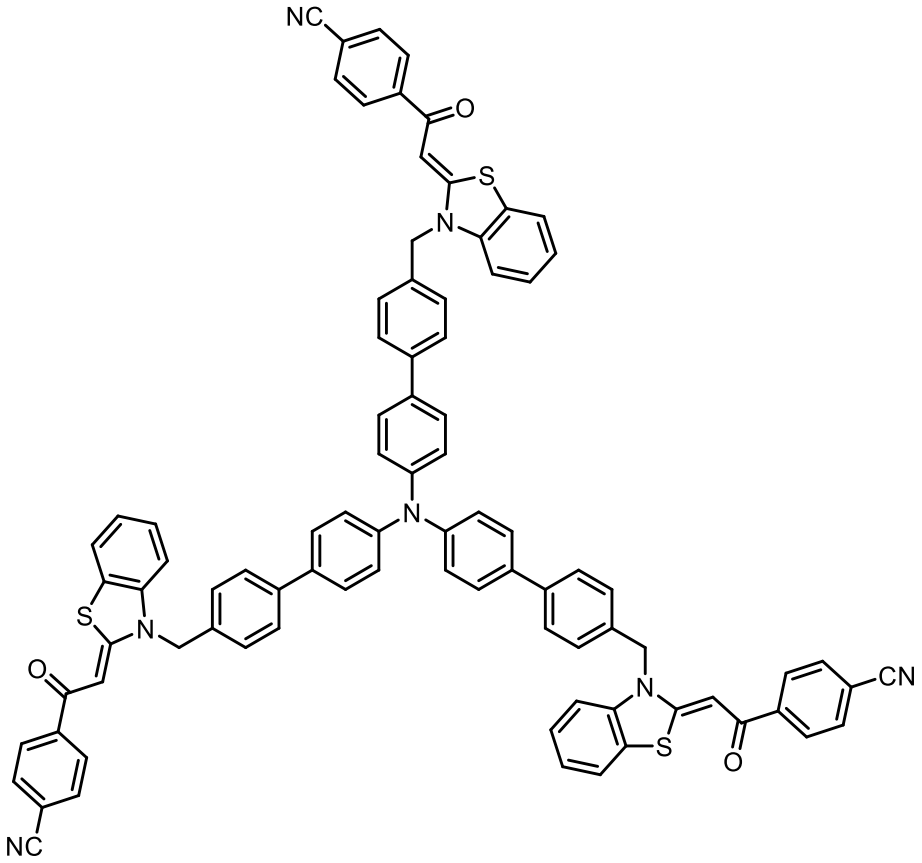
MALDI-TOF (m/z): 1225 ($C_{75}H_{51}F_3N_4O_4S_3$+H^+), 665 ($C_{43}H_{30}F_3NOS^+$), 495 ($C_{35}H_{29}NS^+$), 345 ($C_{27}H_{21}^+$).

IR $\tilde{\nu}$ [cm^{-1}]: 615 (m), 635 (m), 654 (m), 694 (m), 721 (m), 745 (m), 770 (m), 802 (m), 822 (m), 854 (m), 880 (s), 949 (m), 964 (w), 1015 (m), 1067 (s), 1092 (s), 1111 (s), 1165 (s), 1231 (m), 1258 (m), 1312 (m), 1323 (s), 1368 (m), 1454 (s), 1464 (s), 1514 (w), 1558 (w), 1593 (w), 2928 (w), 2976 (w), 3343 (w), 3368 (w), 3381 (w), 3406 (w), 3424 (w).

UV/Vis (C_3H_6O): λ_{max} (ε) = 269 (44800), 391 (56300).

Anal calcd for $C_{75}H_{51}F_3N_4O_4S_3$ [1224.3]: C 73.51, H 4.05, N 4.57, S 7.85; Found: C 73.61, H 4.05, N 4.41, S 7.63.

4,4',4''-((2*Z*,2'*Z*,2''*Z*)-2,2',2''-(((Nitrilotris([1,1'-biphenyl]-4',4-diyl))tris(methylene))-tris(benzo[*d*]thiazole-3(3*H*)-yl-2(3*H*)-ylidene))tris(acetyl))tribenzonitrile (5t)



$C_{87}H_{57}N_7O_3S_3$

[1343.37]

Cyano-substituted aroyl-*S,N*-ketene acetal **3h** (0.446 g, 1.00 mmol, 3.33 equivs.), tris(4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)phenyl)amine (**4t**) (0.187 g, 0.300 mmol, 1.00 equiv.) tetrakis(triphenylphosphane)palladium(0) (0.058 g, 0.05 mmol, 16.7 mol%) and cesium carbonate (0.391 g, 1.20 mmol, 4.00 equivs.) were placed in a sintered, dry screw-cap *Schlenk*-tube under nitrogen atmosphere and dissolved in 5 mL dry 1,4-dioxane and 2 mL ethanol. The reaction mixture was stirred at 120 °C (oil bath) for 5 h. The crude product was adsorbed onto Celite® and purified by flash chromatography on silica gel (*n*-hexane/acetone 3:1 to 2:1 to 1:1 to 1:2 to 1:2 + 7% methanol). The product was suspended in *n*-hexane, the sediment was filtrated, recrystallized from boiling *n*-hexane and dried under vacuo to give compound **57** (0.270 g, 0.201 mmol, 67%) as an orange solid.

Mp: 197 °C.

R_f (*n*-hexane/acetone 1:1): 0.50.

^{1}H NMR (300 MHz, acetone-d_6): δ 5.59 (s, 6H), 6.85-6.91 (m, 2 H), 6.97-7.03 (m, 7 H), 7.20-7.28 (m, 9 H), 7.32-7.37 (m, 6 H), 7.38-7.44 (m, 9 H), 7.47-7.52 (m, 6 H), 7.71-7.76 (m, 6 H), 8.05-8.10 (m, 6 H).

^{13}C NMR (75 MHz, acetone-d_6): δ 49.2 (CH_2), 88.3 (CH), 111.5 (CH), 114.7 (C_{quat}), 116.8 (C_{quat}), 122.4 (C_{quat}), 123.3 (CH), 124.2 (CH), 124.4 (CH), 126.5 (CH), 127.6 (CH), 128.0 (C_{quat}), 128.6 (CH), 129.3 (CH), 132.7 (CH), 133.0 (CH), 133.3 (CH), 135.0 (C_{quat}), 140.4 (C_{quat}), 143.7 (C_{quat}), 146.8 (C_{quat}), 163.3 (C_{quat}), 181.9 (C_{quat}).

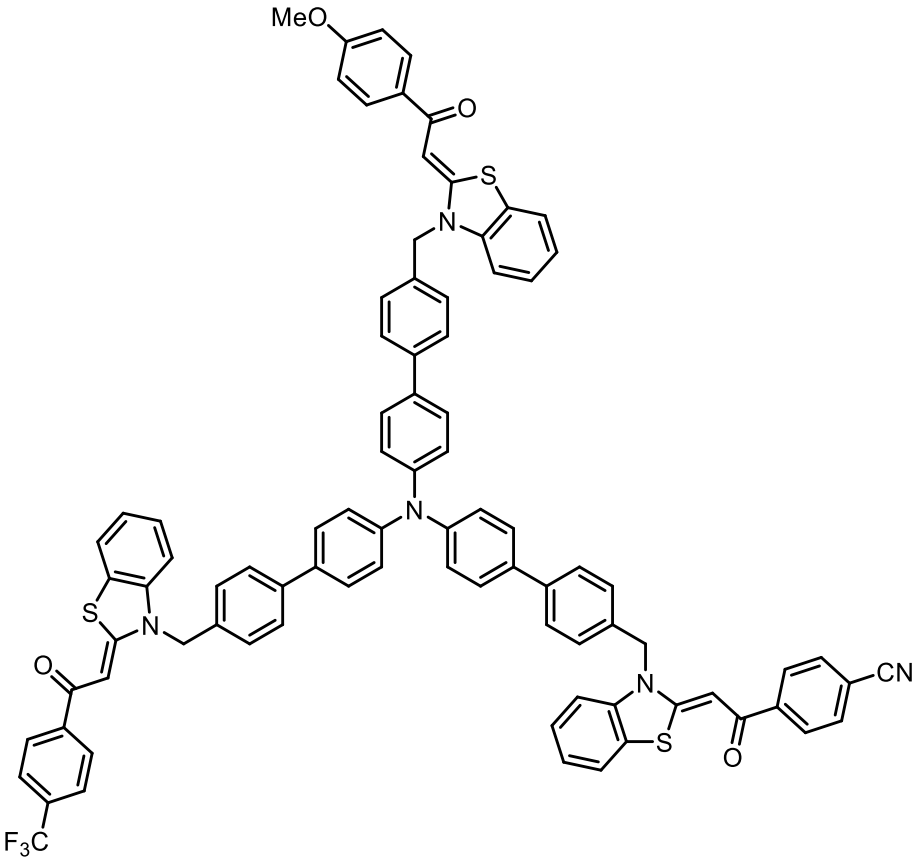
MALDI-TOF (*m/z*): 1112.4, ($[C_{72}H_{48}N_4O_3S_3]^+$), 1066.3 ($[C_{71}H_{48}N_5O_2S_2]^+$), 1014.3 ($[C_{68}H_{47}N_4O_2S_2$ - H$]^+$), 939.3 ($[C_{63}H_{44}N_3O_2S_2$ + H$]^+$), 836.0, 789.3 ($[C_{55}H_{39}N_2OS]^+$), 716.3, 638.6, 569.2, 512.3 ($[C_{39}H_{30}N]^+$).

IR $\tilde{\nu}$ [cm^{-1}]: 632 (w), 640 (w), 683 (w), 700 (m), 719 (m), 745 (m), 762 (m), 808 (w), 818 (w), 853 (w), 881 (m), 926 (w), 949 (w), 972 (w), 1005 (w), 1016 (w), 1042 (w), 1069 (w), 1092 (w), 1117 (w), 1142 (w), 1159 (w), 1177 (m), 1196 (m), 1227 (w), 1265 (w), 1294 (m), 1323 (m), 1398 (m), 1456 (s), 1558 (w), 1597 (w), 2226 (w), 3034 (w), 3115 (w).

UV/Vis (C_3H_6O): λ_{max} (ε) = 271.5, 400.7 (18400).

Anal calcd for $C_{87}H_{57}N_7O_3S_3$ [1343.4]: C 77.71, H 4.27, N 7.29, S 7.15; Found: C 77.62, H 4.02, N 7.13, S 7.26.

4-((*Z*)-2-(3-((4'-((4'-(((*Z*)-2-(2-(4-Methoxyphenyl)-2-oxoethylidene)-benzo[*d*]thiazol-3(2*H*)-yl)methyl)-[1,1'-biphenyl]-4-yl)(4'-(((*Z*)-2-(2-oxo-2-(4-(trifluoromethyl)phenyl)ethylidene)benzo[*d*]thiazol-3(2*H*)-yl)methyl)-[1,1'-biphenyl]-4-yl)amino)-[1,1'-biphenyl]-4-yl)methyl)benzo[*d*]thiazol-2(3*H*)-ylidene)acetyl)benzonitrile (5u)



$C_{87}H_{60}F_3N_5O_4S_3$

[1391.38]

Methoxy-substituted aroyl-*S,N*-ketene acetal **3a** (0.226 g, 0.500 mmol, 1.00 equiv.), tris(4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)phenyl)amine (**4t**) (0.312 g, 0.500 mmol, 1.00 equiv.) tetrakis(triphenylphosphane)palladium(0) (0.029 g, 0.025 mmol, 5 mol%) and cesium carbonate (0.544 g, 2.00 mmol, 4.00 equivs.) were placed in a sintered, dry screw-cap *Schlenk*-tube under nitrogen atmosphere and dissolved in 5 mL dry 1,4-dioxane and 2 mL ethanol. The reaction mixture was stirred at 120 °C (oil bath) for 2 h. Thereafter, cyano-substituted aroyl-*S,N*-ketene acetal **3h** (0.223 g, 0.500 mmol, 1.00 equiv.) was added to the reaction mixture and the mixture was stirred at 120 °C (oil bath) for 3 h. Then, trifluoromethyl-substituted aroyl-*S,N*-ketene acetal **3g** (0.244 g, 0.500 mmol, 1.00 equiv.) was added to the reaction mixture and the mixture was stirred at 120 °C (oil bath) for 12 h. The crude product was adsorbed onto Celite® and purified by flash chromatography on silica gel (*n*-hexane/acetone 3:1 to 2:1 to 1:1 1:1 + 5% methanol). The product was suspended in *n*-hexane,

the sediment was filtrated several times and dried under vacuo to give compound **5u** (0.381 g, 0.274 mmol, 55%) as a yellow solid.

Mp: 230 °C.

R_f (*n*-hexane/acetone 2:1): 0.37.

^{1}H NMR (300 MHz, acetone-d_6): δ 3.83 (s, 3 H), 5.52 (s, 2H), 5.59-5.63 (m, 4 H), 6.74 (s, 1 H), 6.86-6.92 (m, 5 H), 6.97-7.03 (m, 5 H), 7.19-7.39 (m, 15 H), 7.40-7.46 (m, 6 H), 7.48-7.54 (m, 6 H), 7.61 (dd, ^3J = 8.5 Hz, ^4J = 2.2 Hz, 1 H), 7.67-7.72 (m, 3 H), 7.73-7.78 (m, 3 H), 8.85-8.91 (m, 2 H), 8.07-8.14 (m, 4 H).

^{13}C NMR (75 MHz, acetone-d_6): δ 49.0 (CH_2), 49.2 (CH_2), 55.6 (CH_3), 87.9 (CH), 88.3 (CH), 111.0 (CH), 111.5 (CH), 111.6 (CH), 114.1 (CH), 114.7 (C_{quat}), 116.8 (C_{quat}), 118.8 (C_{quat}), 122.2 (C_{quat}), 122.3 (C_{quat}), 123.1 (CH), 123.3 (CH), 123.6 (CH), 124.1 (CH), 124.2 (CH), 124.5 (CH), 125.8 (CH), 125.9 (CH), 126.6 (CH), 127.3 (CH), 127.6 (CH), 127.7(CH), 127.9 (C_{quat}), 128.1 (C_{quat}), 128.5 (CH), 128.6 (CH), 129.4 (C_{quat}), 129.8 (CH), 132.7 (CH), 132.8 (CH), 132.8 (CH), 133.0 (C_{quat}), 133.1 (CH), 133.3 (CH), 135.2 (C_{quat}), 135.4 (C_{quat}), 140.5 (C_{quat}), 140.7 (C_{quat}), 143.7 (C_{quat}), 143.8 (C_{quat}), 146.1 (C_{quat}), 146.9 (C_{quat}), 161.6 (C_{quat}), 162.7 (C_{quat}), 163.2 (C_{quat}), 182.0 (C_{quat}), 182.5 (C_{quat}), 183.5 (C_{quat}).

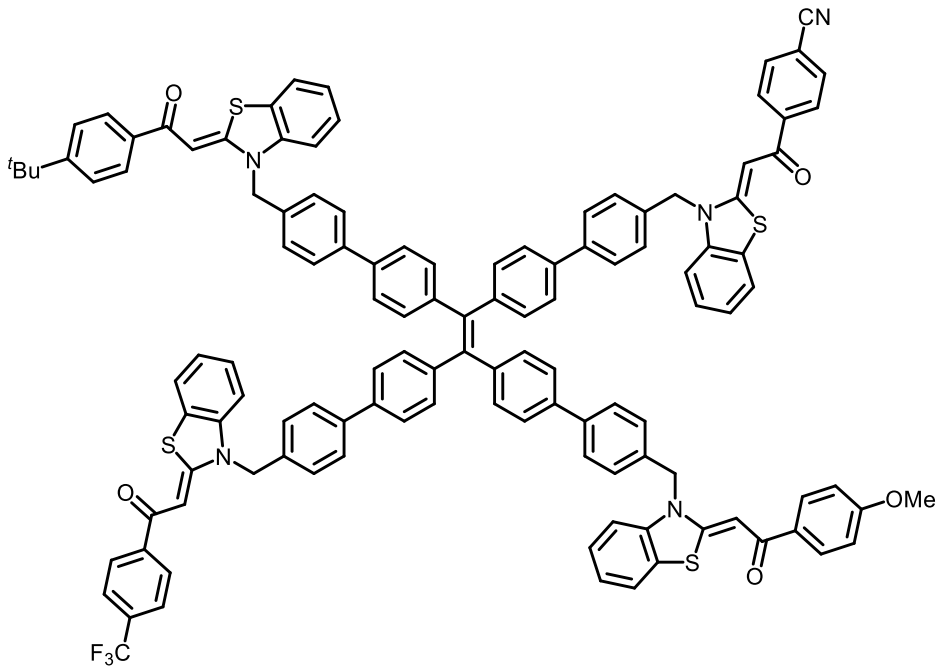
MALDI-TOF (*m/z*): 1326.5, 1152.4, 1114.4 ($[C_{71}H_{51}F_3N_3O_3S_2]^+$), 1066.4 ($[C_{69}H_{48}F_3N_5O_4$ - H$]^+$), 1014.3 ($[C_{68}H_{47}N_4O_2S_2$ - H$]^+$), 939.3 ($[C_{63}H_{44}N_3O_2S_2$ + H$]^+$), 836.1, 832.3 ($[C_{55}H_{39}F_3N_2OS]^+$), 789.3 ($[C_{55}H_{39}N_3OS]^+$), 700.3, 512.3 ($[C_{39}H_{30}N]^+$), 451.2, 406.4, 374.3 350.3.

IR $\tilde{\nu}$ [cm^{-1}]: 679 (w), 704 (m), 718 (m), 743 (s), 764 (m), 806 (m), 818 (m), 841 (m), 881 (s), 924 (w), 949 (w), 982 (w), 1005 (m), 1067 (m), 1090 (m), 1113 (m), 1165 (s), 1196 (m), 1227 (m), 1258 (m), 1294 (m), 1310 (m), 1323 (s), 1398 (m), 1454 (s), 1558 (m), 1568 (w), 1597 (m), 2226 (w), 2359 (w), 2776 (w), 2835 (w), 2874 (w), 2901 (w), 3674 (w), 3688 (w).

UV/Vis (C_3H_6O): λ_{max} (ε) = 266.5, 386.7 (8700).

Anal calcd for $C_{87}H_{60}F_3N_5O_4S_3$ [1391.4]: C 75.03, H 4.34, N 5.03, S 6.91; Found: C 74.88, H 4.41, N 5.22, S 7.02.

4-((*Z*)-2-(3-((4'-(1-(4'-(((*Z*)-2-(2-(4-(*tert*-Butyl)phenyl)-2-oxoethylidene)benzo[*d*]thiazol-3(2*H*)-yl)methyl)-[1,1'-biphenyl]-4-yl)-2-(4'-(((*Z*)-2-(2-(4-methoxyphenyl)-2-oxoethylidene)benzo[*d*]thiazol-3(2*H*)-yl)methyl)-[1,1'-biphenyl]-4-yl)-2-(4'-(((*Z*)-2-(2-oxo-2-(4-(trifluoromethyl)phenyl)ethylidene)benzo[*d*]thiazol-3(2*H*)-yl)methyl)-[1,1'-biphenyl]-4-yl)vinyl)-[1,1'-biphenyl]-4-yl)methyl)benzo[*d*]thiazol-2(3*H*)-ylidene)acetyl)benzonitrile (5v)



$C_{121}H_{88}F_3N_5O_5S_4$

[1876.57]

Methoxy-substituted aroyl-*S,N*-ketene acetal **3a** (0.226 g, 0.500 mmol, 1.00 equiv.), 1,1,2,2-tetrakis(4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)phenyl)ethene (**4u**) (0.418 g, 0.500 mmol, 1.00 equiv.) tetrakis(triphenylphosphane)palladium(0) (0.087 g, 0.075 mmol, 15 mol%) and cesium carbonate (0.544 g, 2.00 mmol, 4.00 equivs.) were placed in a sintered, dry screw-cap *Schlenk*-tube under nitrogen atmosphere and dissolved in 5 mL dry 1,4-dioxane and 2 mL ethanol. The reaction mixture was stirred at 120 °C (oil bath) for 2 h. Afterwards, *tert*-butyl-substituted aroyl-*S,N*-ketene acetal **3b** (0.239 g, 0.500 mmol, 1.00 equiv.) was added to the reaction mixture and the mixture was stirred at 120 °C (oil bath) for 2 h Thereafter, cyano-substituted aroyl-*S,N*-ketene acetal **3h** (0.223 g, 0.500 mmol, 1.00 equiv.) was added to the reaction mixture and the mixture was stirred at 120 °C (oil bath) for 3 h. Then, trifluoromethyl-substituted aroyl-*S,N*-ketene acetal **3g** (0.244 g, 0.500 mmol, 1.00 equiv.) was added to the reaction mixture and the mixture was stirred at 120 °C (oil bath) for 12 h. The crude product was adsorbed onto Celite® and purified by flash chromatography on silica gel (*n*-hexane/acetone 3:1 to 2:1 to 1:1 to pure acetone). The product was suspended in *n*-hexane,

the sediment was filtrated several times and dried under vacuo to give compound **5v** (0.735 g, 0.392 mmol, 78%) as an orange solid.

Mp: 109 °C.

R_f (*n*-hexane/acetone 1:1): 0.50.

^{1}H NMR (300 MHz, acetone-d_6/CS_2 5:1): δ 1.35 (s, 9 H), 3.84 (s, 3 H), 5.54 (s, 2 H), 5.55 (s, 2 H), 5.63 (s, 2 H), 5.64 (s, 2 H), 6.78-6.79 (m, 2 H), 6.89-6.99 (m, 9 H), 7.08-7.11 (m, 1 H), 7.23-7.47 (m, 31 H), 7.50-7.54 (m, 9 H), 7.70-7.75 (m, 4 H), 7.77-7.92 (m, 8 H), 8.10-8.15 (m, 4 H).

^{13}C NMR (75 MHz, acetone-d_6/CS_2 5:1): δ 35.3 (CH_3), 49.0 (CH_2), 49.07 (CH_2), 49.13 (CH_2), 49.2 (CH_2), 55.7 (CH_3), 87.9 (CH), 88.28 (CH), 88.29 (CH), 88.4 (CH), 111.1 (CH), 111.2 (CH), 111.6 (CH), 111.7 (CH), 114.1 (CH), 114.7 (C_{quat}), 121.9 (CH), 122.1 (CH), 122.2 (CH), 122.3 (CH), 123.1 (CH), 123.2 (CH), 123.36 (CH), 123.39 (CH), 123.7 (CH), 123.8 (CH), 124.2 (CH), 124.3 (CH), 125.8 (CH), 125.8 (C_{quat}), 126.0 (C_{quat}), 126.8 (C_{quat}), 127.35 (CH), 127.42 (CH), 127.68 (CH), 127.73 (CH), 127.86 (CH), 127.89 (CH), 128.0 (C_{quat}), 128.1 (C_{quat}), 128.3 (C_{quat}), 128.5 (CH), 128.6 (CH), 128.9 (C_{quat}), 129.50 (CH), 129.51 (CH), 129.8 (CH), 130.9 (C_{quat}), 131.7 (C_{quat}), 131.8 (C_{quat}), 131.9 (C_{quat}), 132.0 (CH), 132.4 (CH), 132.7 (CH), 132.75 (CH), 132.78 (CH), 132.9 (CH), 133.1 (C_{quat}), 137.4 (C_{quat}), 137.8 (C_{quat}), 137.8 (C_{quat}), 139.0 (C_{quat}), 139.9 (C_{quat}), 140.57 (C_{quat}), 140.59 (C_{quat}), 140.63 (C_{quat}) 140.74 (C_{quat}), 140.8 (C_{quat}), 141.9 (C_{quat}), 142.5 (C_{quat}), 143.9 (C_{quat}), 154.6 (C_{quat}), 161.7 (C_{quat}), 161.9 (C_{quat}), 162.7 (C_{quat}), 163.2 (C_{quat}), 163.3(C_{quat}), 166.8 (C_{quat}), 182.1 (C_{quat}), 182.6 (C_{quat}), 183.6 (C_{quat}), 184.2 (C_{quat}).

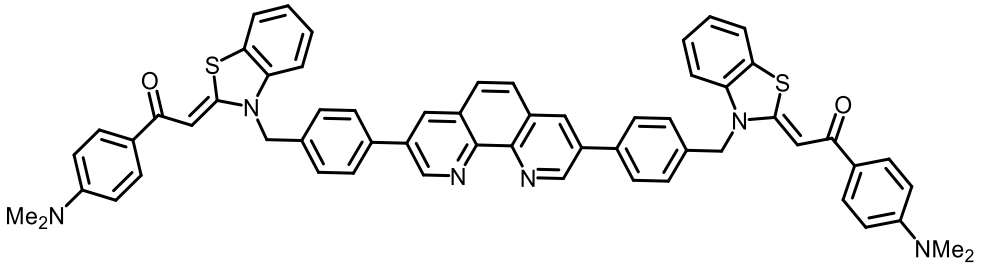
MALDI-TOF (m/z): 890 ($C_{57}H_{40}F_3N_2OS_2^+$), 746 ($C_{54}H_{36}NOS^+$), 688 ($C_{54}H_{32}^+$), 510 ($C_{40}H_{30}^+$), 451 ($C_{29}H_{24}NO_2S^+$), 400 ($C_{26}H_{28}NOS^+$), 339 ($C_{22}H_{13}NO^+$).

IR $\tilde{\nu}$ [cm^{-1}]: 657 (m), 694 (m), 721 (m), 746 (m), 768 (m), 797 (w), 822 (m), 881 (s), 926 (w), 949 (m), 982 (m), 1005 (m), 1042 (w), 1067 (m), 1092 (m), 1113 (m), 1117 (m), 1146 (m), 1167 (m), 1231 (m), 1256 (w), 1310 (m), 1325 (m), 1369 (m), 1439 (s), 1452 (s), 1557 (m), 1593 (m), 2874 (w), 2936 (w), 2974 (w), 3026 (w).

UV/Vis (C_3H_6O): λ_{max} (ε) = 384 (22500).

Anal calcd for $C_{121}H_{88}F_3N_5O_5S_4$ [1876.6]: C 77.42, H 4.73, N 3.73, S 6.83; Found: C 77.69, H 5.02, N 3.62, S 6.83.

(2*Z*,2'*Z*)-2,2'-((((1,10-Phenanthrolin-3,8-diyl)bis(4,1-phenylene))bis(methylene))bis(benzo[*d*]thiazol-3(3*H*)-yl-2(3*H*)-ylidene))bis(1-(4-(dimethylamino)phenyl)ethan-1-one) (5w)



$C_{60}H_{48}N_6O_2S_2$

[948.33]

Dimethylamino-aroyl-*S,N*-ketene acetal (0.278 g, 0.600 mmol, 1.20 equivs) and tetrakis(triphenylphosphine)-palladium(0) (0.058 g, 0.050 mmol, 20.0 mol%) were placed in a sintered, dry screw-cap *Schlenk*-tube under nitrogen atmosphere and dissolved in 3 mL dry 1,4-dioxane. 4,4,5,5-Tetramethyl-1,3,2-dioxaborolan (0.145 mL, 1.00 mmol, 4.00 equivs.) and triethylamine (0.680 mL, 5.00 mmol, 20.0 equivs.) were added to the reaction mixture and the solution was stirred at 120 °C (oil bath) for 20 h. After cooling to room temperature, 1,10-dibromophenanthrolin (0.084 g, 0.250 mmol, 1.00 mmol), cesium carbonate (0.408 g, 1.25 mmol, 2.50 equivs) and 1 mL methanol were added to the reaction mixture under nitrogen atmosphere and the mixture was stirred at 120 °C (oil bath) for 22 h. The crude product was adsorbed onto Celite® and purified by flash chromatography on silica gel (*n*-hexane/acetone 2:1 to 1:2 to 1:4 to acetone to acetone + 2 % methanol). The product was suspended in *n*-hexane, the sediment was filtrated and dried under vacuo to give compound **5w** (0.116 mg, 0.122 mmol, 49%) as an orange solid.

Mp: 166 °C.

R_f (*n*-hexane/acetone 1:1): 0.19.

^{1}H NMR (500 MHz, DMSO-d$_6$): δ 2.98 (s, 12 H), 5.54 (s, 2 H), 5.56 (s, 2 H), 6.70 (d, ^3J = 8.4 Hz, 4 H), 6.77–6.81 (m, 4 H), 7.17-7.25 (m, 5 H), 7.33-7.40 (m, 3 H), 7.54-7.55 (m, 3 H), 7.74-7.77 (m, 2 H), 7.81-7.85 (m, 5 H), 8.01 (s, 2 H), 8.83 (d, ^3J = 2.5 Hz, 2 H), 9.15 (s, 2 H).

^{13}C NMR (125 MHz, DMSO-d$_6$): δ 39.8 (CH_3), 39.9 (CH_3), 47.4 (CH_2), 87.0 (CH), 110.3 (CH), 110.7 (CH), 111.0 (CH), 113.9 (C_{quat}), 116.9 (C_{quat}), 119.5 (C_{quat}), 120.4 (C_{quat}), 122.2 (CH), 122.4 (CH), 126.2 (CH), 126.4 (C_{quat}), 126.5 (C_{quat}), 127.1 (CH), 128.6 (CH), 128.8 (CH), 129.6 (C_{quart}), 130.7 (CH), 131.6 (CH), 131.9 (CH), 135.1 (C_{quat}), 137.7 (CH),

139.6 (C_{quat}), 143.4 (C_{quat}), 150.6 (C_{quat}), 152.0 (C_{quat}), 153.0 (C_{quat}), 154.1 (C_{quat}), 159.3 (C_{quat}), 167.3 (C_{quat}), 182.6 (C_{quat}).

MALDI-TOF (m/z): 949 ($C_{60}H_{48}N_6O_2S + H^+$).

IR $\tilde{\nu}$ [cm^{-1}]: 633 (m), 696 (m), 729 (m), 770 (m), 789 (m), 827 (m), 872 (w), 881 (w), 914 (w), 945 (m), 1001 (w), 1038 (m), 1059 (m), 1119 (m), 1165 (s), 1231 (m), 1287 (m), 1317 (m), 1366 (m), 1418 (m),1470 (m), 1504 (m), 1524 (m), 1557 (m), 1595 (s), 1634 (w), 1638 (w), 1667 (w), 1703 (w), 1931 (w), 2359 (w).

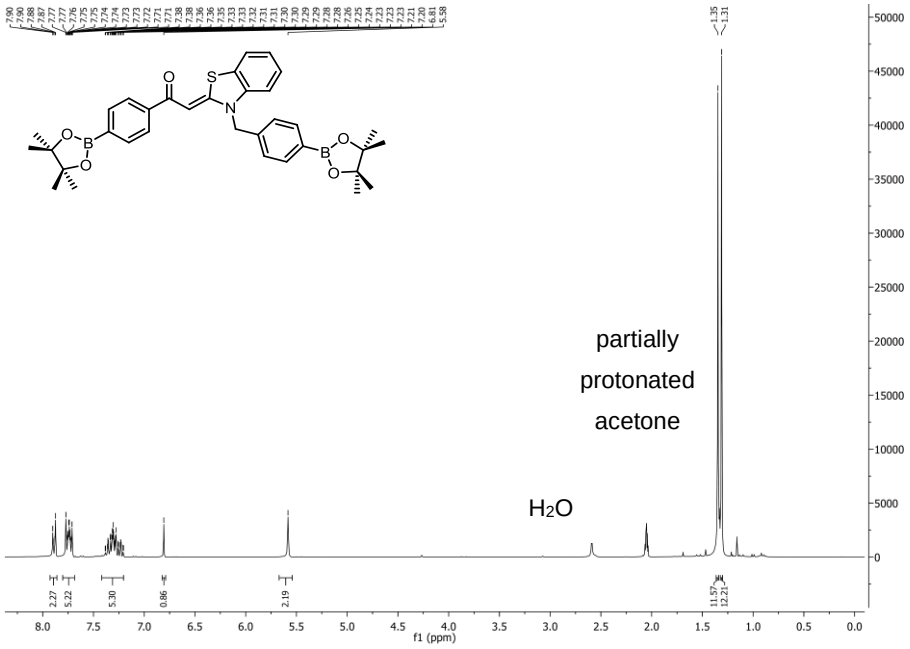
UV/Vis (C_3H_6O): λ_{max} (ε) = 373 (25400).

Anal calcd for $C_{60}H_{48}N_6O_2S_2$ [948.3]: C 75.92, H 5.10, N 8.85, S 6.76; Found: C 75.70, H 5.17, N 8.65, S 6.64.

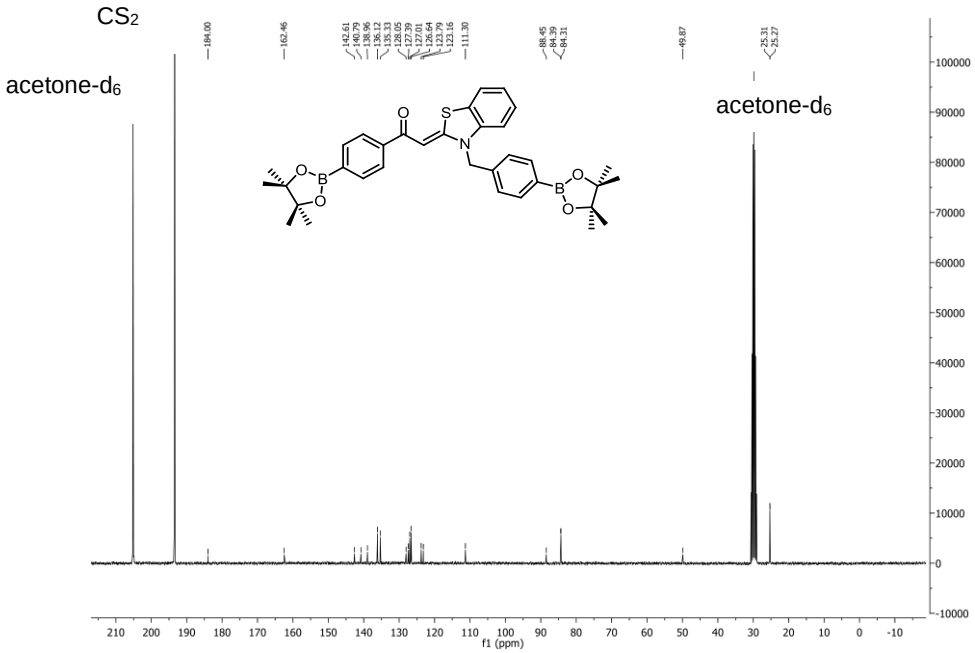
4 NMR spectra

4.1 NMR spectra of borylated aroyl-*S,N*-ketene acetals

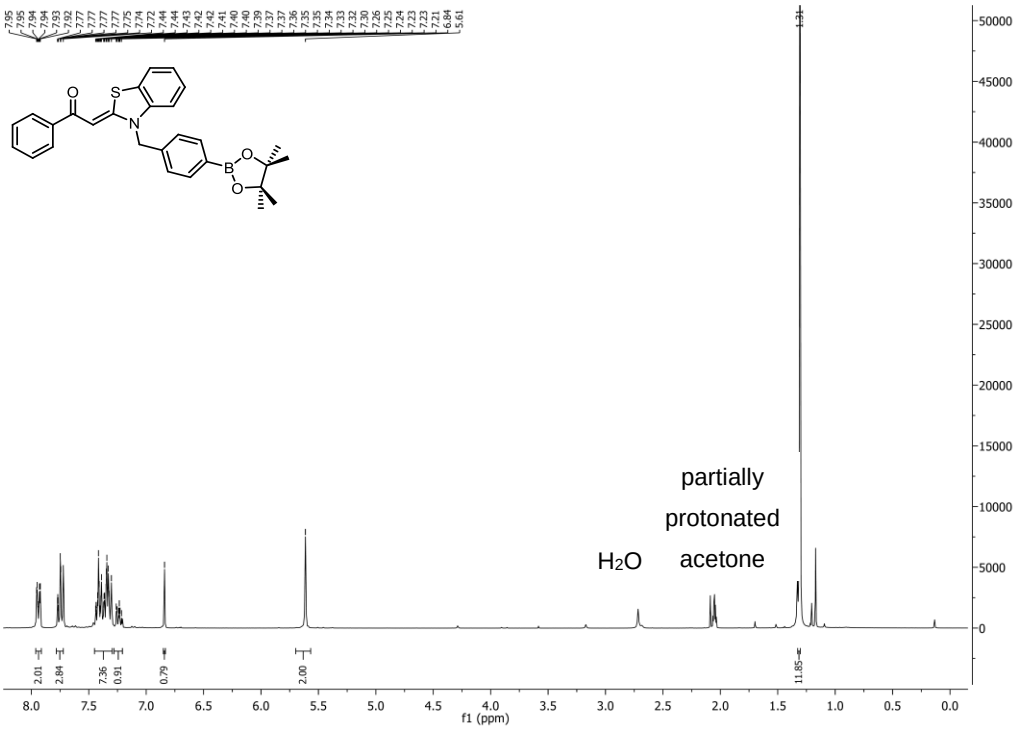
^{1}H NMR-spectrum (*Z*)-2-(3-(4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)benzyl)benzo[*d*]thiazol-2(3*H*)-ylidene)-1-(4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)phenyl)ethan-1-one (4p) (300 MHz, acetone-d_6/CS_2 5:1, 293 K)



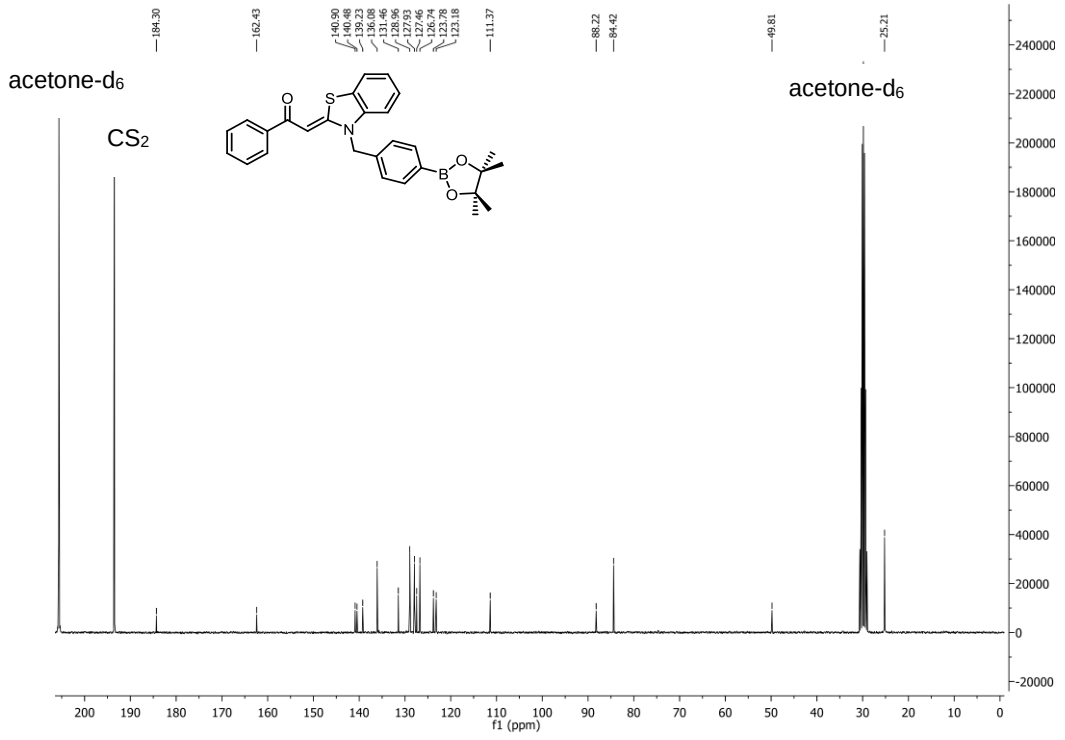
^{13}C NMR-spectrum (*Z*)-2-(3-(4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)benzyl)benzo[*d*]thiazol-2(3*H*)-ylidene)-1-(4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)phenyl)ethan-1-one (4p) (75 MHz, acetone-d_6/CS_2 5:1, 293 K)



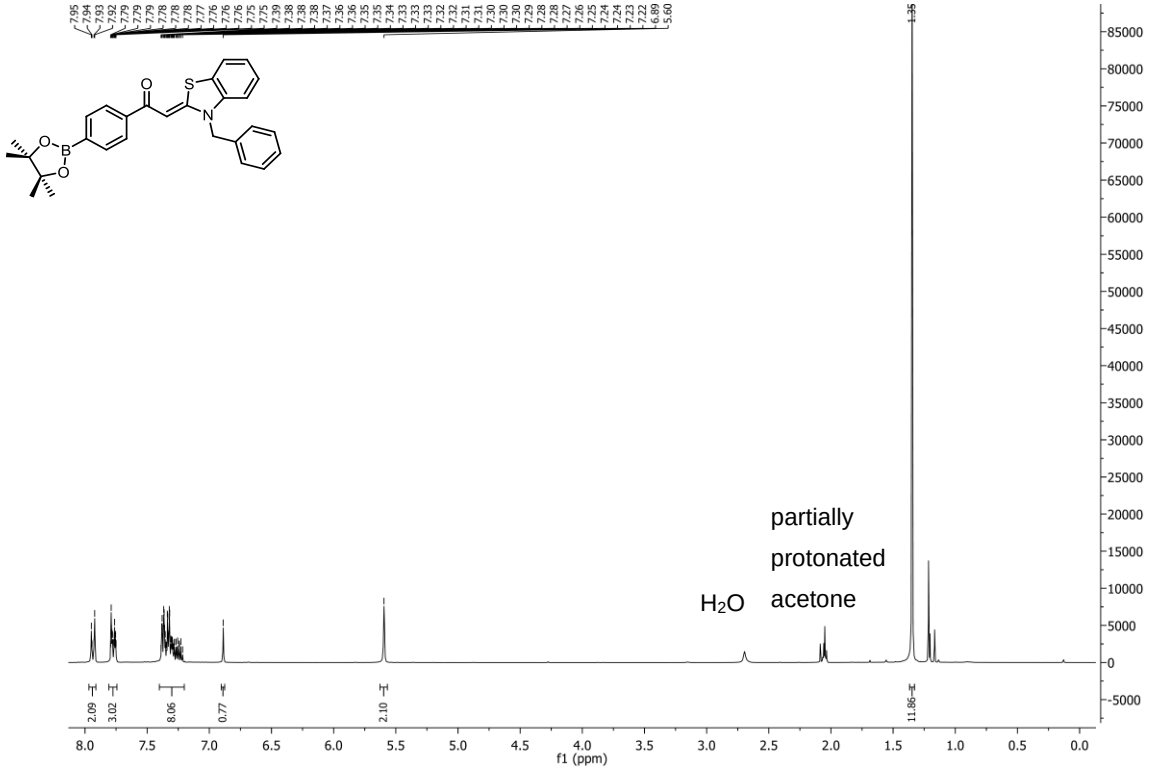
^{1}H NMR-spectrum (*Z*)-1-Phenyl-2-(3-(4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)benzyl)benzo[*d*]thiazol-2(3*H*)-ylidene)ethan-1-one (300 MHz, acetone-d_6/CS_2 5:1, 293 K)



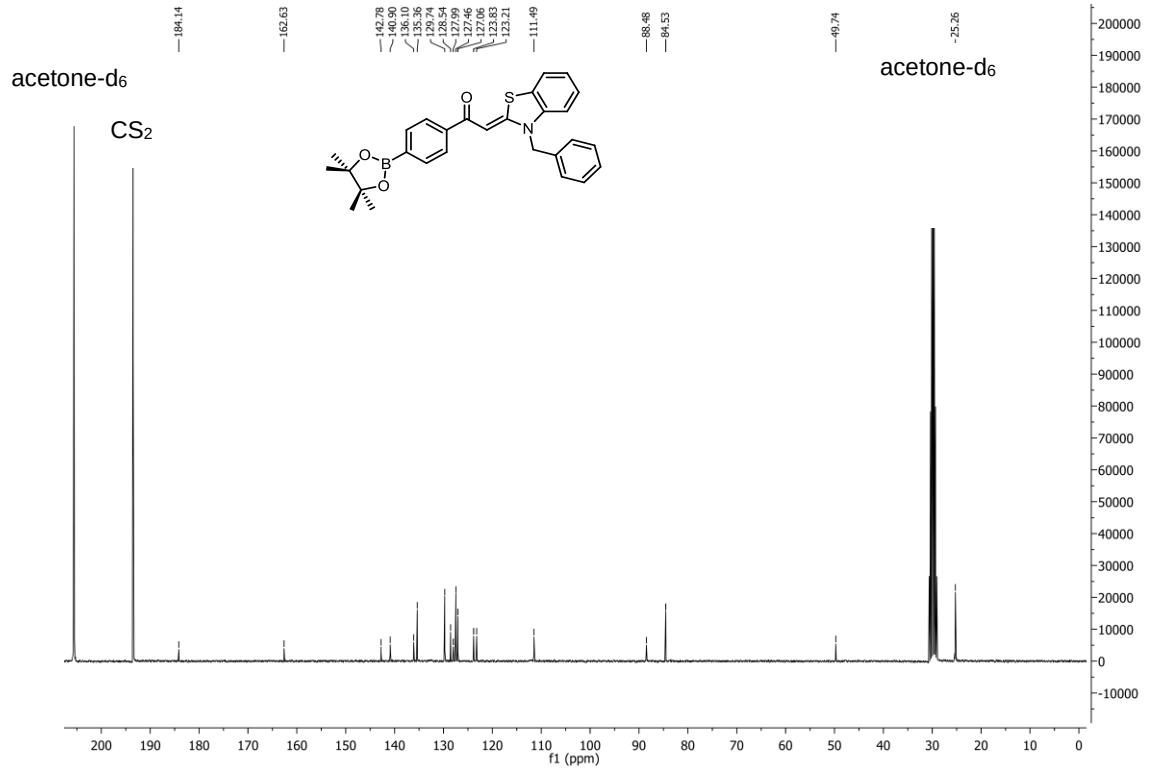
^{13}C NMR-spectrum (*Z*)-1-Phenyl-2-(3-(4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)benzyl)benzo[*d*]thiazol-2(3*H*)-ylidene)ethan-1-one (75 MHz, acetone-d_6/CS_2 5:1, 293 K)



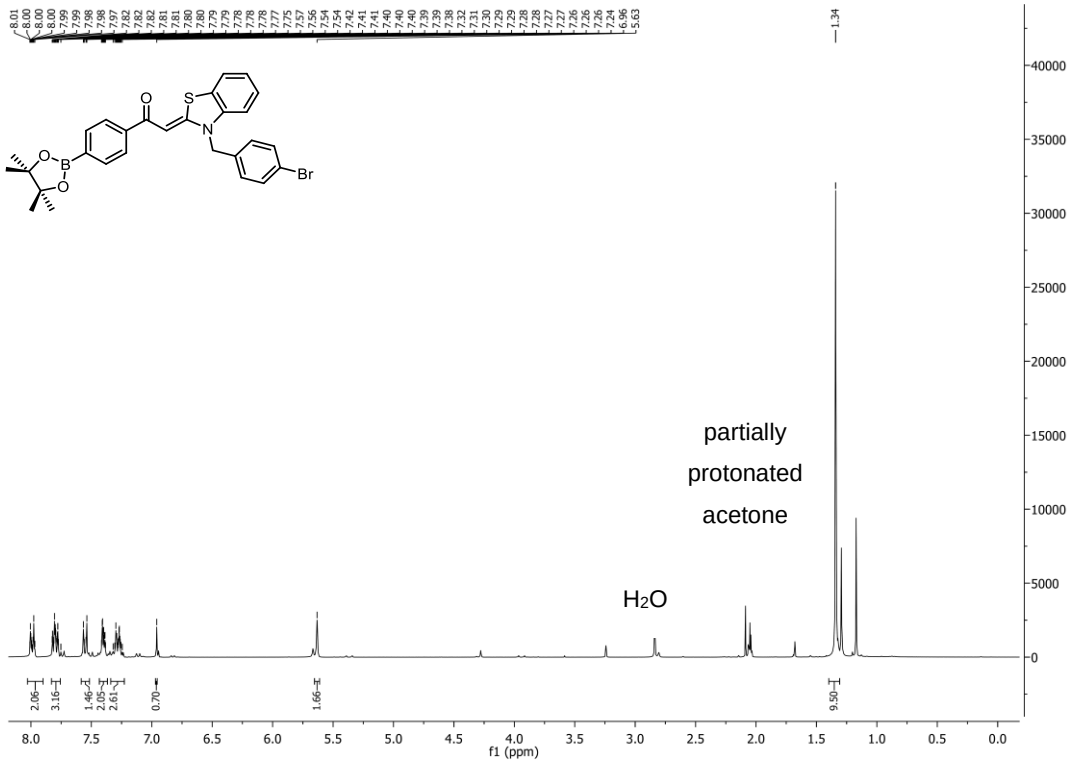
^{1}H NMR-spectrum (*Z*)-2-(3-Benzylbenzo[*d*]thiazol-2(3*H*)-ylidene)-1-(4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)phenyl)ethan-1-one (300 MHz, acetone-d_6/CS_2 5:1, 293 K)



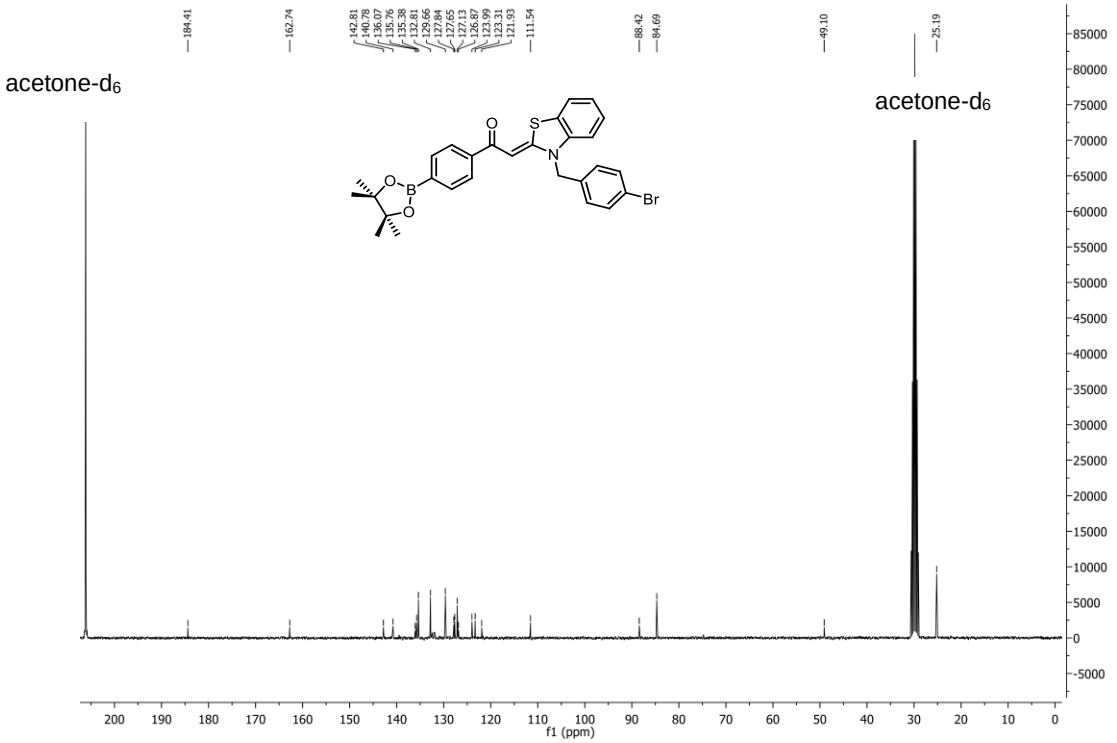
^{13}C NMR-spectrum (*Z*)-2-(3-Benzylbenzo[*d*]thiazol-2(3*H*)-ylidene)-1-(4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)phenyl)ethan-1-one (75 MHz, acetone-d_6/CS_2 5:1, 293 K)



^{1}H NMR-spectrum (*Z*)-2-(3-(4-bromobenzyl)benzo[*d*]thiazol-2(3*H*)-ylidene)-1-(4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)phenyl)ethan-1-one (300 MHz, acetone-d$_6$, 293 K)

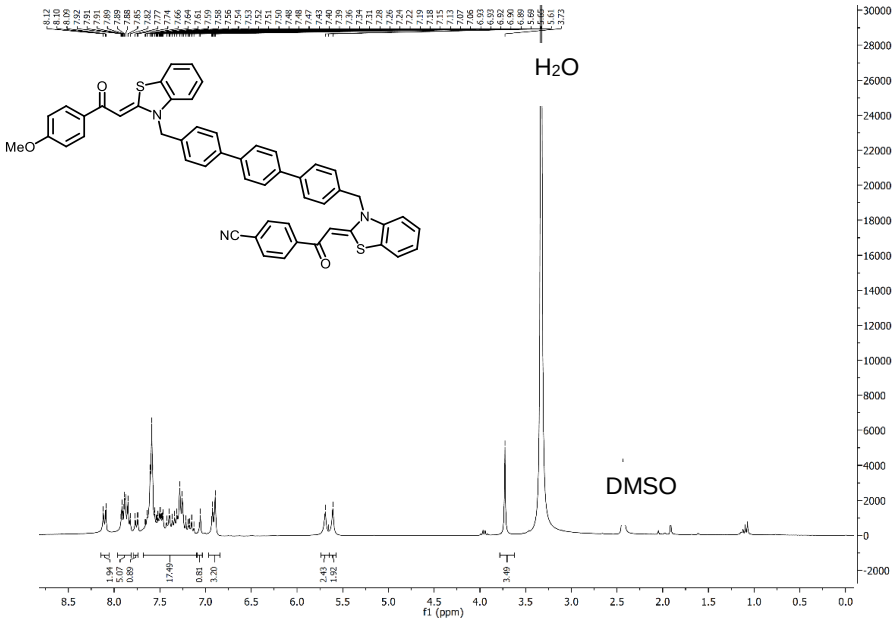


^{13}C NMR-spectrum (*Z*)-2-(3-(4-bromobenzyl)benzo[*d*]thiazol-2(3*H*)-ylidene)-1-(4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)phenyl)ethan-1-one (75 MHz, acetone-d$_6$, 293 K)

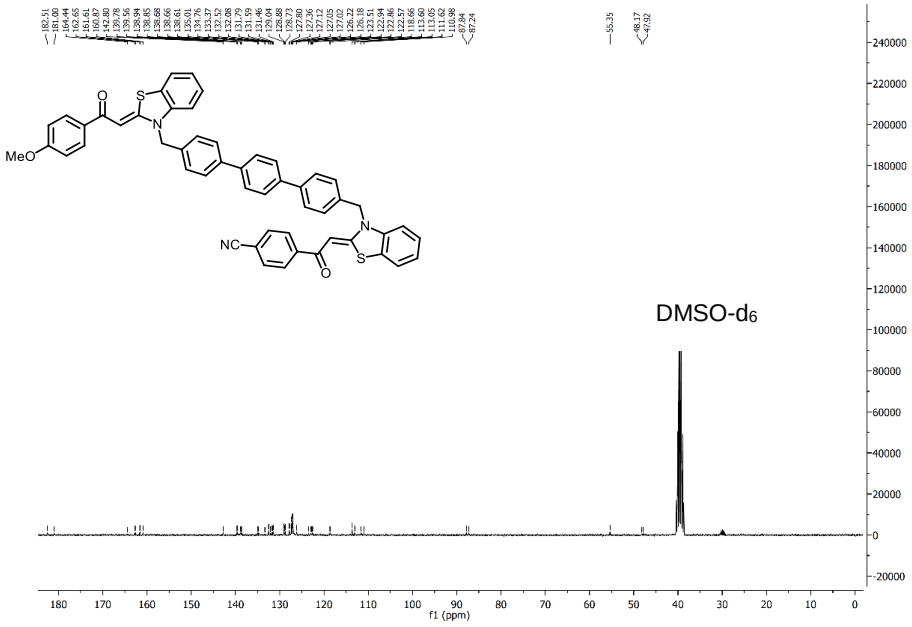


4.2 NMR spectra of bridged aroyl-*S,N*-ketene acetals 5

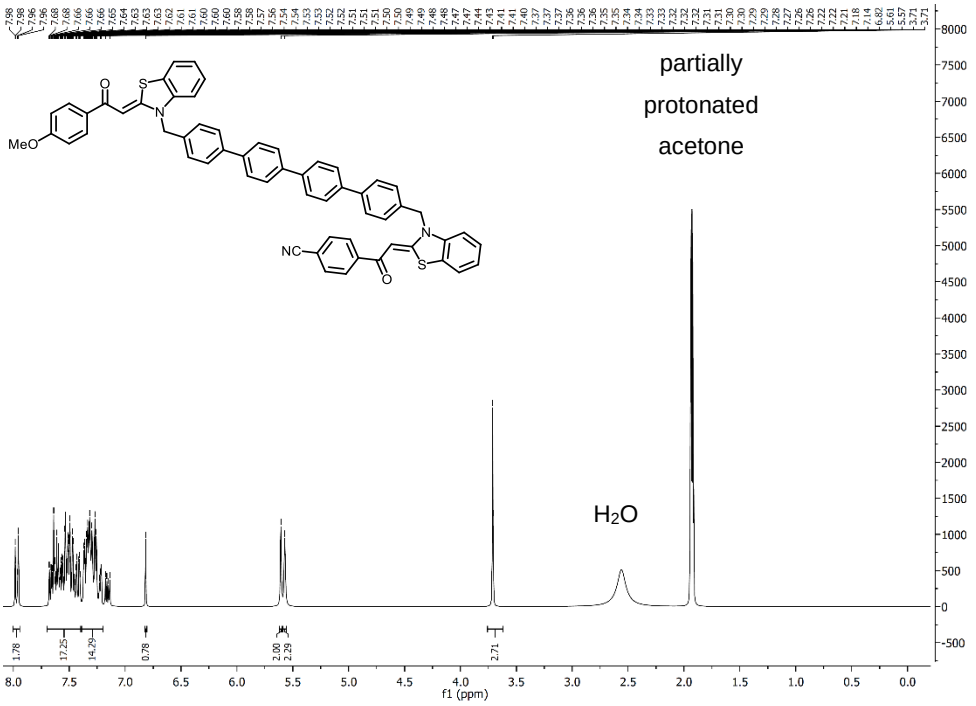
^{1}H NMR-spectrum 4-((*Z*)-2-(3-((4''-(((*Z*)-2-(2-(4-methoxyphenyl)-2-oxoethylidene)benzo[*d*]thiazol-3(2*H*)-yl)methyl)-[1,1':4',1''-terphenyl]-4-yl)methyl)benzo[*d*]thiazol-2(3*H*)-ylidene)acetyl)benzonitrile (5a) (300 MHz, DMSO-d$_6$, 293 K)



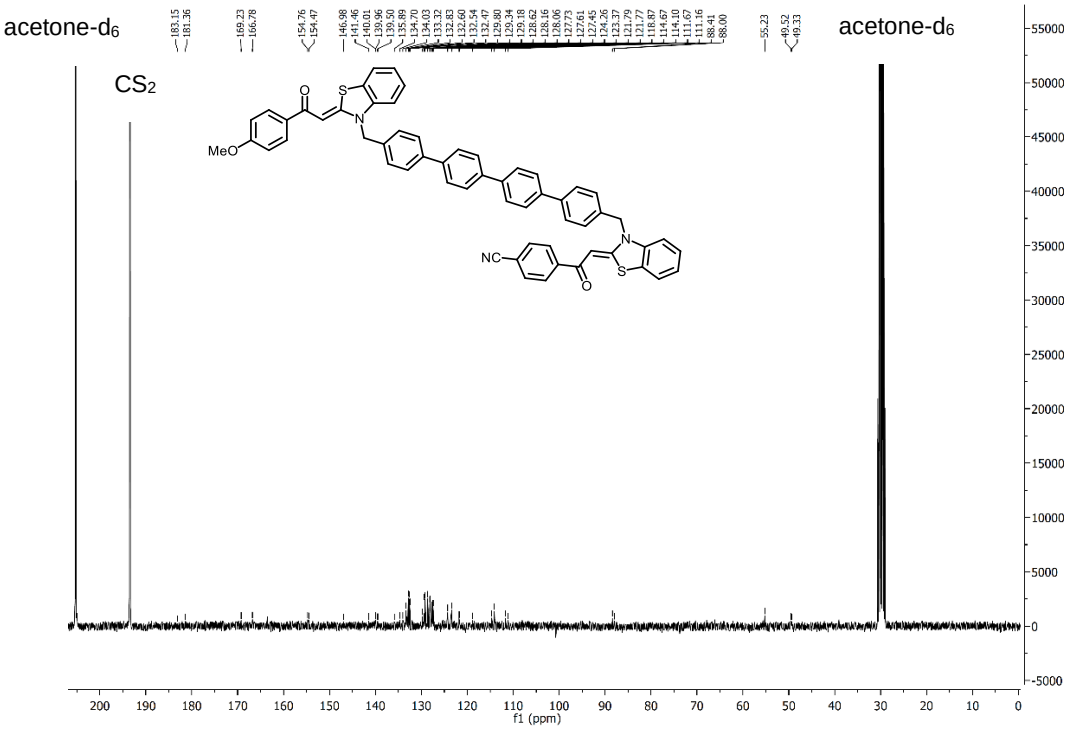
^{13}C NMR-spectrum 4-((*Z*)-2-(3-((4''-(((*Z*)-2-(2-(4-methoxyphenyl)-2-oxoethylidene)benzo[*d*]thiazol-3(2*H*)-yl)methyl)-[1,1':4',1''-terphenyl]-4-yl)methyl)benzo[*d*]thiazol-2(3*H*)-ylidene)acetyl)benzonitrile (5a) (75 MHz, DMSO-d$_6$, 293 K)



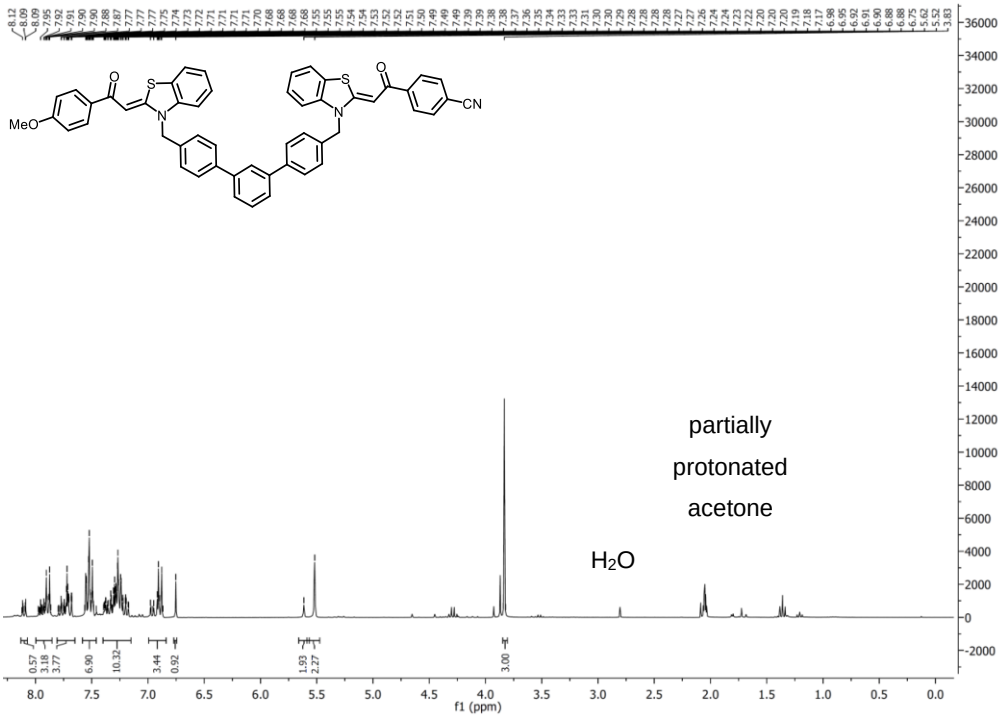
^{1}H NMR-spectrum 4-((*Z*)-2-(3-((4'''-(((*Z*)-2-(2-(4-methoxyphenyl)-2-oxoethylidene)benzo[*d*]thiazol-3(2*H*)-yl)methyl)-[1,1':4',1'':4'',1'''-quaterphenyl]-4-yl)methyl)benzo[*d*]thiazol-2(3*H*)-ylidene)acetyl)benzonitrile (5b) (300 MHz, acetone-d_6/CS_2 5:1, 293 K)



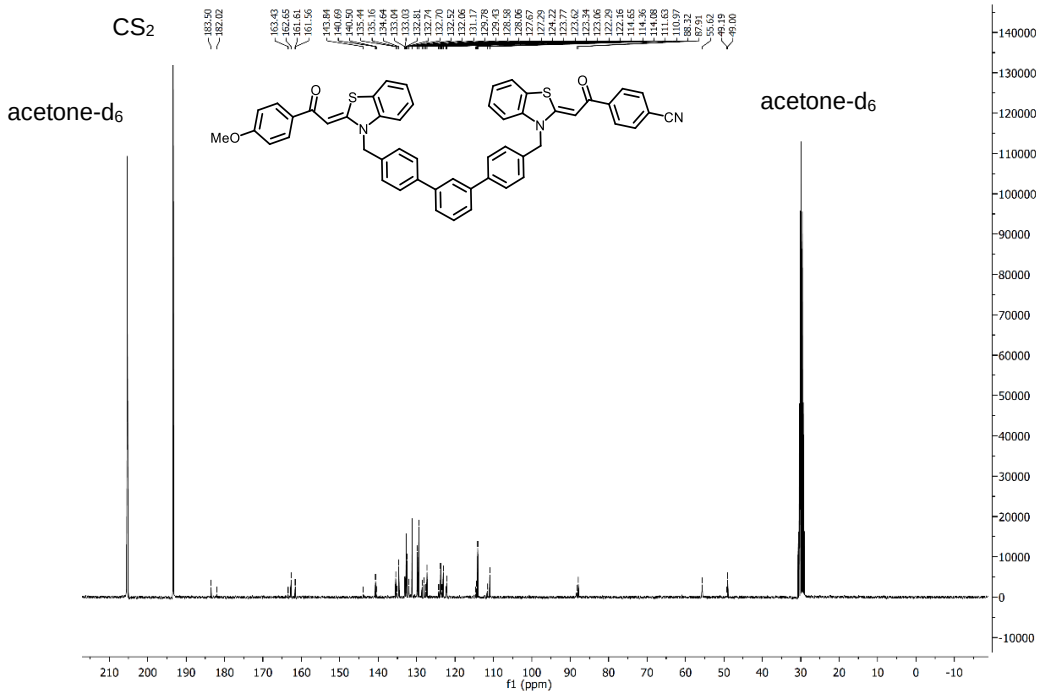
^{13}C NMR-spectrum 4-((*Z*)-2-(3-((4'''-(((*Z*)-2-(2-(4-methoxyphenyl)-2-oxoethylidene)benzo[*d*]thiazol-3(2*H*)-yl)methyl)-[1,1':4',1'':4'',1'''-quaterphenyl]-4-yl)methyl)benzo[*d*]thiazol-2(3*H*)-ylidene)acetyl)benzonitrile (5b) (75 MHz, acetone-d_6/CS_2 5:1, 293 K)



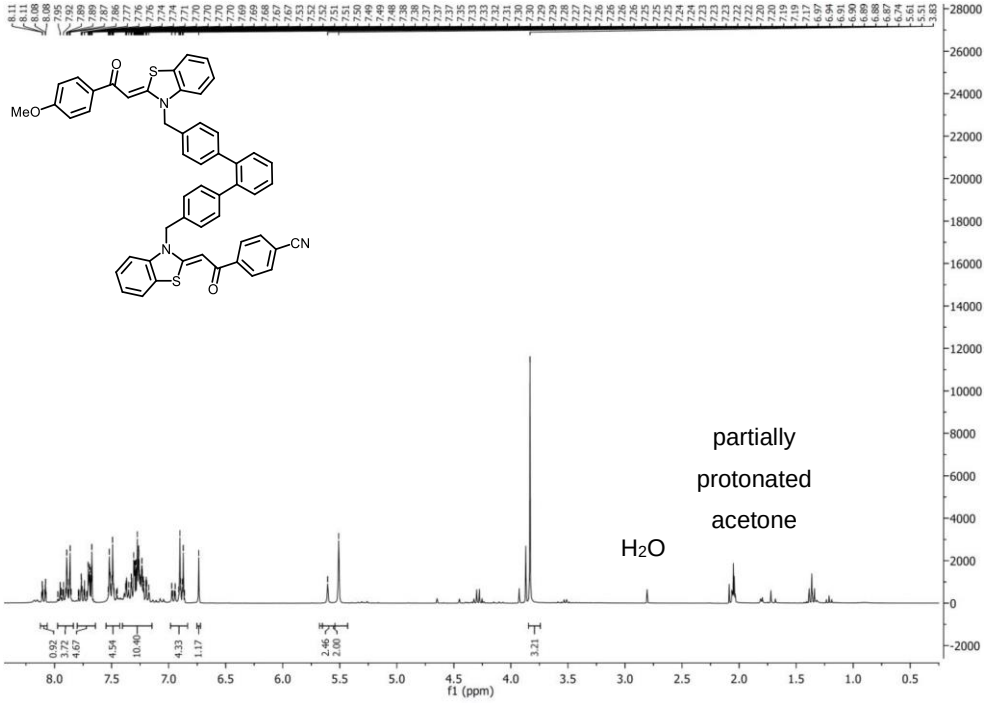
^{1}H NMR-spectrum 4-((*Z*)-2-(3-((4''-(((*Z*)-2-(2-(4-methoxyphenyl)-2-oxoethylidene)benzo[*d*]thiazol-3(2*H*)-yl)methyl)-[1,1':3',1''-terphenyl]-4-yl)methyl)benzo[*d*]thiazol-2(3*H*)-ylidene)acetyl)benzonitrile (5c) (300 MHz, acetone-d_6/CS_2 5:1, 293 K)



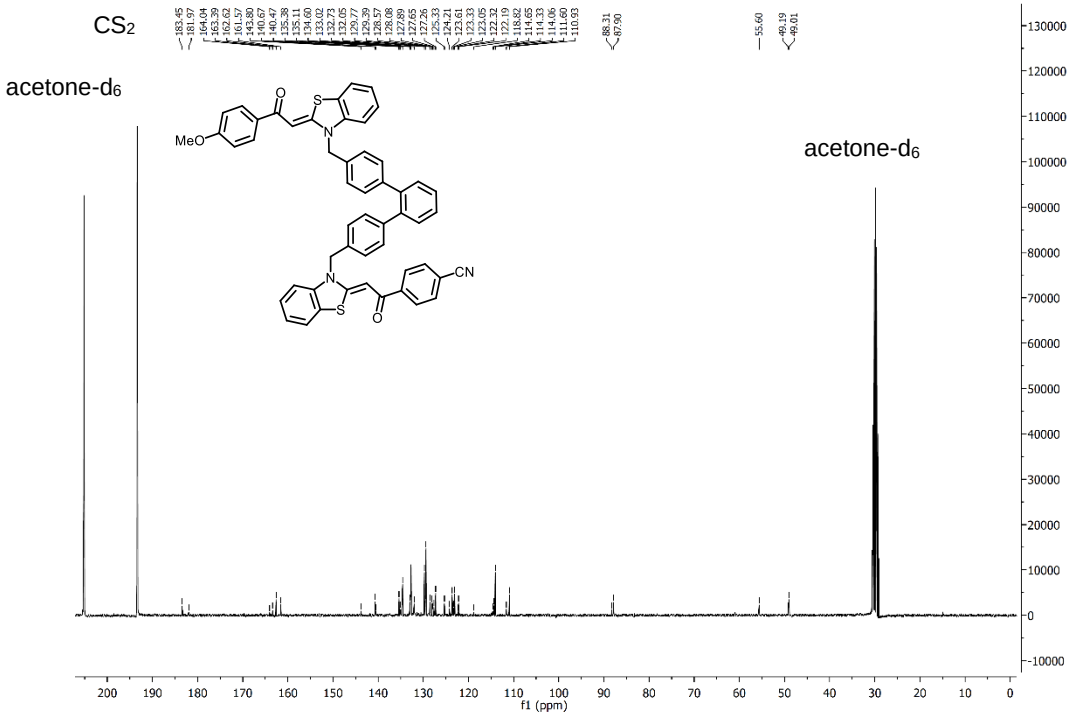
^{13}C NMR-spectrum 4-((*Z*)-2-(3-((4''-(((*Z*)-2-(2-(4-methoxyphenyl)-2-oxoethylidene)benzo[*d*]thiazol-3(2*H*)-yl)methyl)-[1,1':3',1''-terphenyl]-4-yl)methyl)benzo[*d*]thiazol-2(3*H*)-ylidene)acetyl)benzonitrile (5c) (75 MHz, acetone-d_6/CS_2 5:1, 293 K)



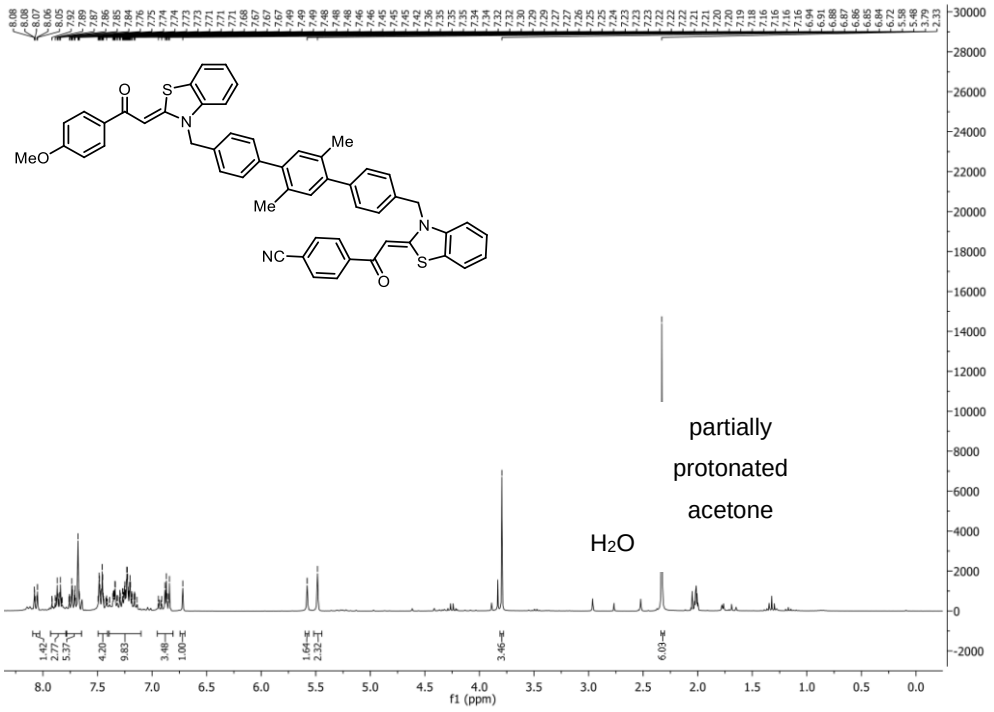
^{1}H NMR-spectrum 4-((*Z*)-2-(3-((4''-(((*Z*)-2-(2-(4-methoxyphenyl)-2-oxoethylidene)benzo[*d*]thiazol-3(2*H*)-yl)methyl)-[1,1':3',1''-terphenyl]-4-yl)methyl)benzo[*d*]thiazol-2(3*H*)-ylidene)acetyl)benzonitrile (5d) (300 MHz, acetone-d_6/CS_2 5:1, 293 K)



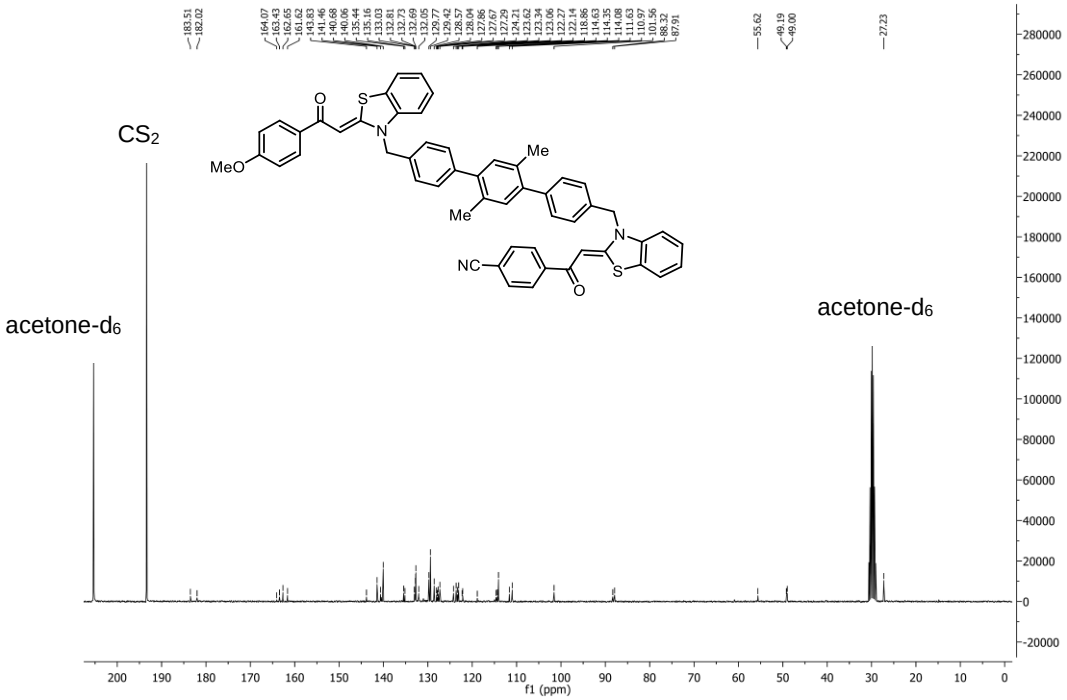
^{13}C NMR-spectrum 4-((*Z*)-2-(3-((4''-(((*Z*)-2-(2-(4-methoxyphenyl)-2-oxoethylidene)benzo[*d*]thiazol-3(2*H*)-yl)methyl)-[1,1':3',1''-terphenyl]-4-yl)methyl)benzo[*d*]thiazol-2(3*H*)-ylidene)acetyl)benzonitrile (5d) (75 MHz, acetone-d_6/CS_2 5:1, 293 K)



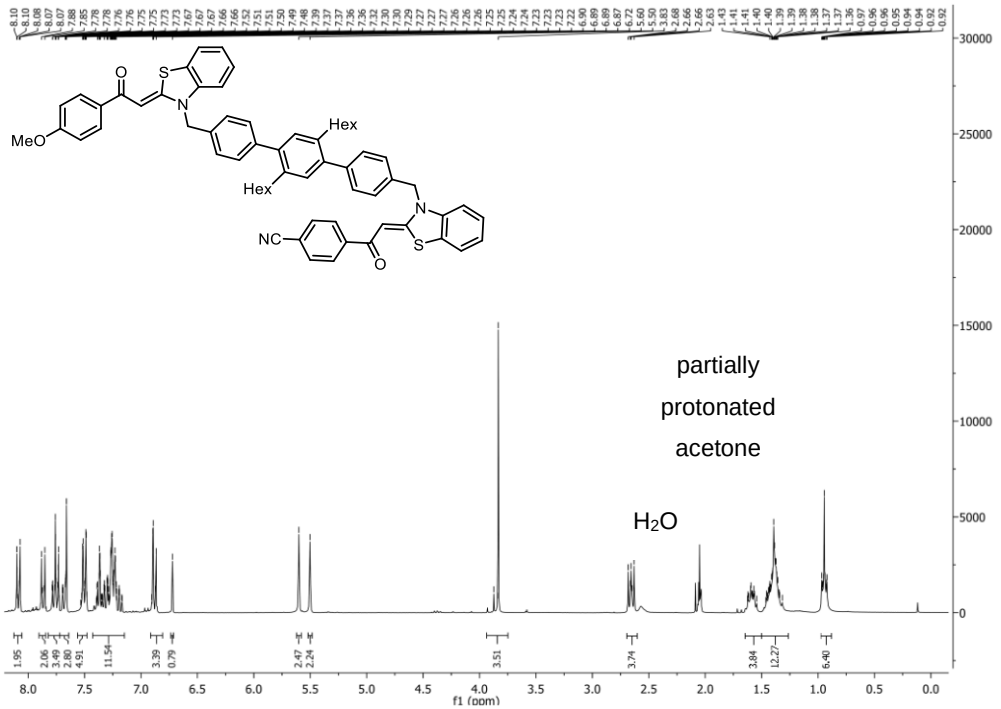
^{1}H NMR-spectrum 4-((*Z*)-2-(3-((4''-(((*Z*)-2-(2-(4-methoxyphenyl)-2-oxoethylidene)benzo[*d*]thiazol-3(2*H*)-yl)methyl)-2',5'-dimethyl-[1,1':4',1''-terphenyl]-4-yl)methyl)benzo[*d*]thiazol-2(3*H*)-ylidene)acetyl)benzonitrile (5e) (300 MHz, acetone-d_6/CS_2 5:1, 293 K)



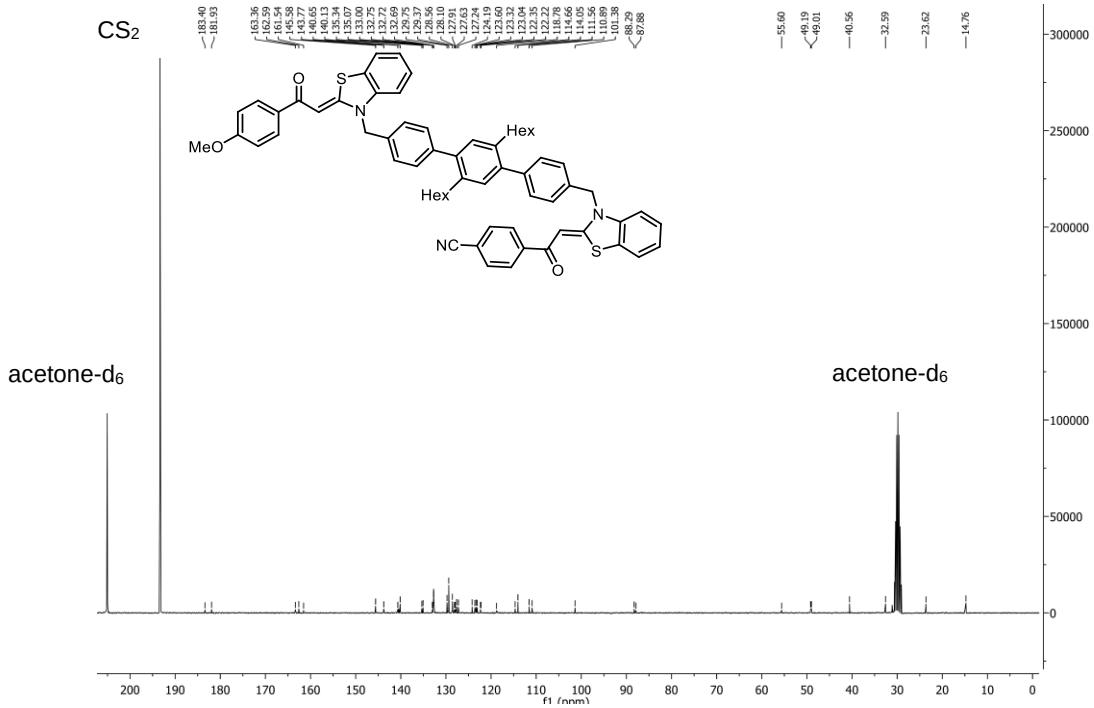
^{13}C NMR-spectrum 4-((*Z*)-2-(3-((4''-(((*Z*)-2-(2-(4-methoxyphenyl)-2-oxoethylidene)benzo[*d*]thiazol-3(2*H*)-yl)methyl)-2',5'-dimethyl-[1,1':4',1''-terphenyl]-4-yl)methyl)benzo[*d*]thiazol-2(3*H*)-ylidene)acetyl)benzonitrile (5e) (75 MHz, acetone-d_6/CS_2 5:1, 293 K)



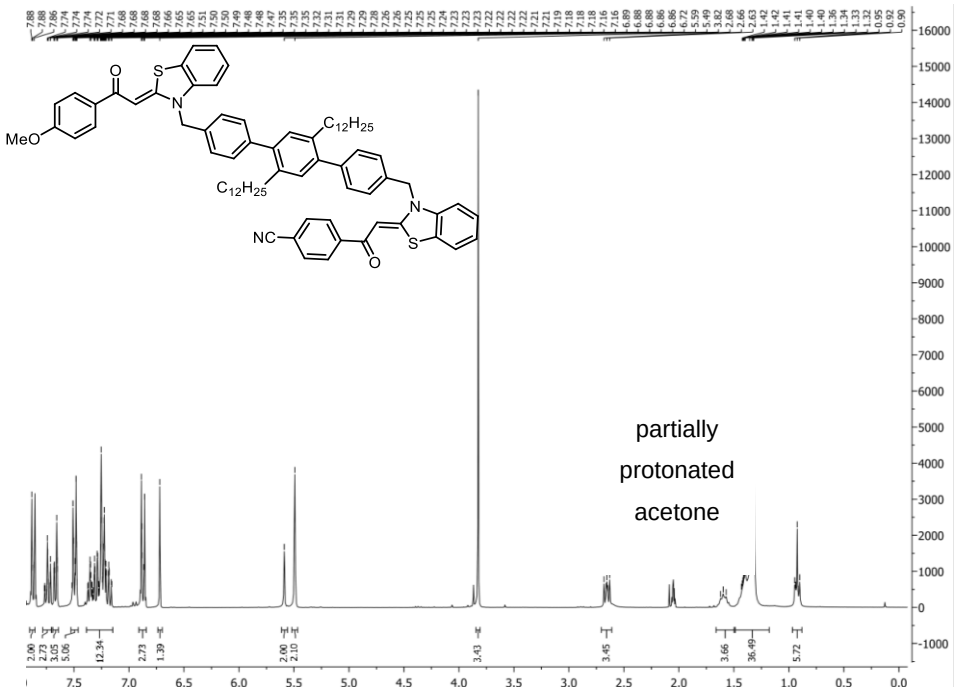
^{1}H NMR-spectrum 4-((*Z*)-2-(3-((2',5'-dihexyl-4''-(((*Z*)-2-(2-(4-methoxyphenyl)-2-oxoethylidene)benzo[*d*]thiazol-3(2*H*)-yl)methyl)-[1,1':4',1''-terphenyl]-4-yl)methyl)benzo[*d*]thiazol-2(3*H*)-ylidene)acetyl)benzonitrile (5f) (300 MHz, acetone-d_6/CS_2 5:1, 293 K)



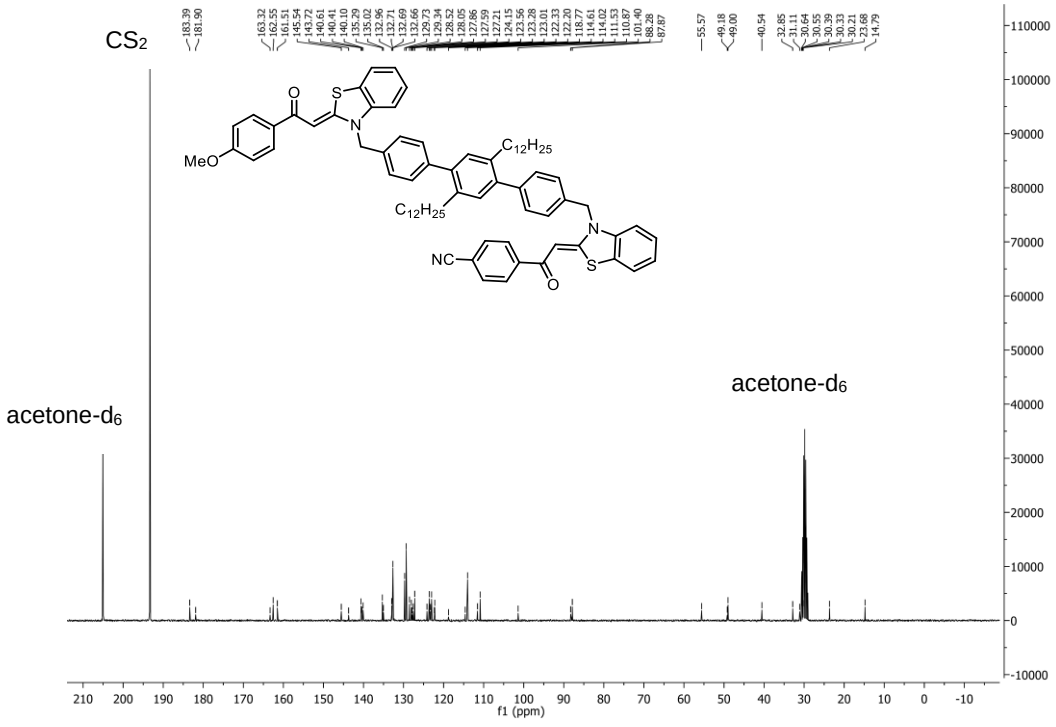
^{13}C NMR-spectrum 4-((*Z*)-2-(3-((2',5'-dihexyl-4''-(((*Z*)-2-(2-(4-methoxyphenyl)-2-oxoethylidene)benzo[*d*]thiazol-3(2*H*)-yl)methyl)-[1,1':4',1''-terphenyl]-4-yl)methyl)benzo[*d*]thiazol-2(3*H*)-ylidene)acetyl)benzonitrile (5f) (75 MHz, acetone-d_6/CS_2 5:1, 293 K)



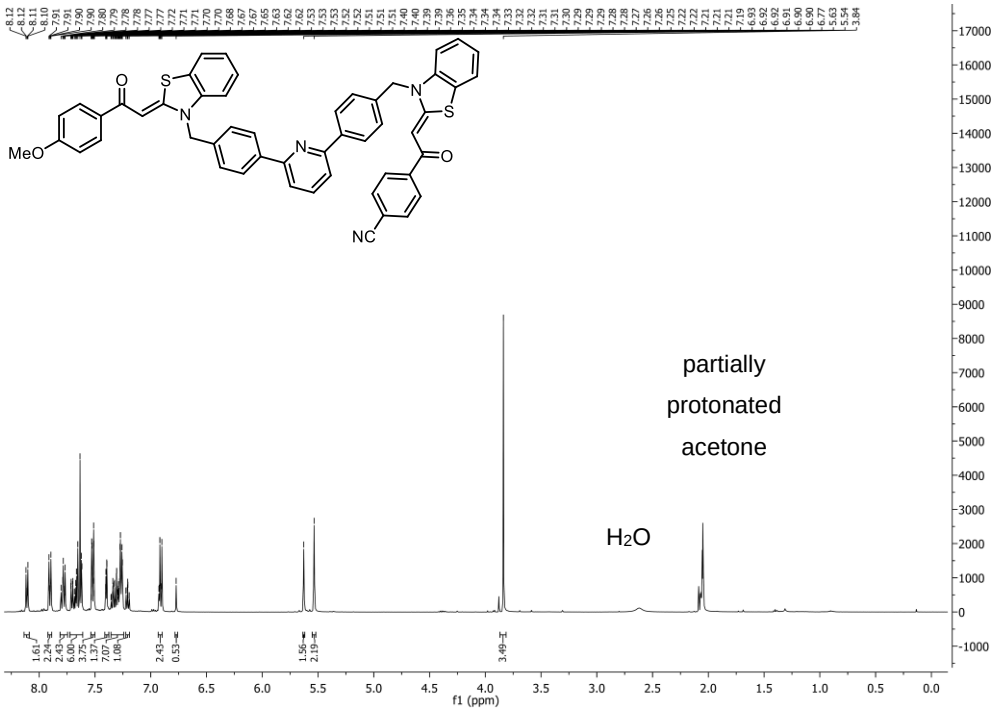
^{1}H NMR-spectrum (4-((*Z*)-2-(3-((2',5'-didodecyl-4''-(((*Z*)-2-(2-(4-methoxyphenyl)-2-oxoethylidene)benzo[*d*]thiazol-3(2*H*)-yl)methyl)-[1,1':4',1''-terphenyl]-4-yl)methyl)benzo[*d*]thiazol-2(3*H*)-ylidene)acetyl)benzonitrile (5g) (300 MHz, acetone-d_6/CS_2 5:1, 293 K)



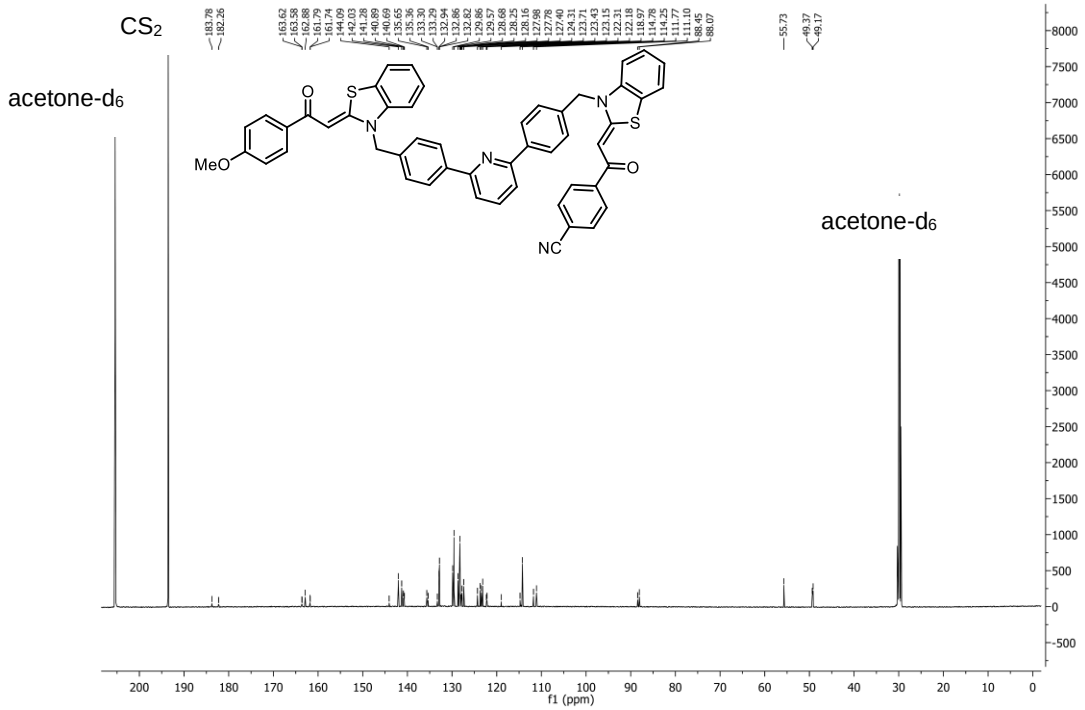
^{13}C NMR-spectrum 4-((*Z*)-2-(3-((2',5'-didodecyl-4''-(((*Z*)-2-(2-(4-methoxyphenyl)-2-oxoethylidene)benzo[*d*]thiazol-3(2*H*)-yl)methyl)-[1,1':4',1''-terphenyl]-4-yl)methyl)benzo[*d*]thiazol-2(3*H*)-ylidene)acetyl)benzonitrile (5g) (75 MHz, acetone-d_6/CS_2 5:1, 293 K)



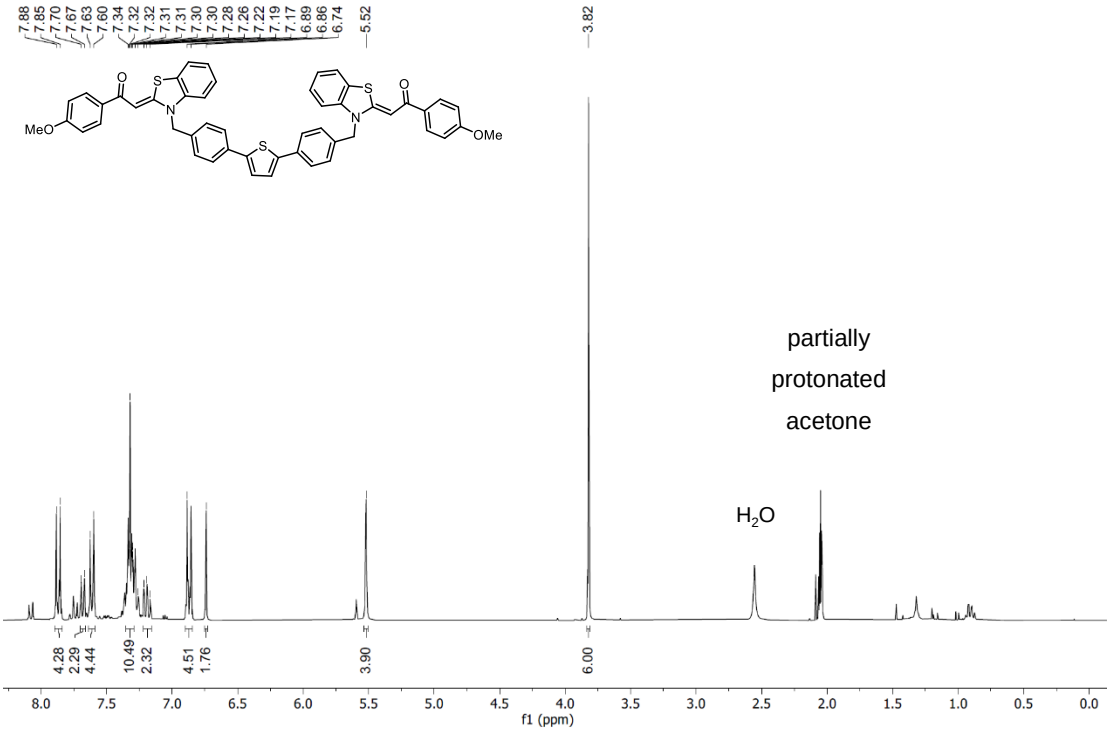
^{1}H NMR-spectrum 4-((*Z*)-2-(3-(4-(6-(4-((((*Z*)-2-(2-(4-methoxyphenyl)-2-oxoethylidene)benzo[*d*]thiazol-3(2*H*)-yl)methyl)phenyl)pyridin-2-yl)benzyl)benzo[*d*]thiazol-2(3*H*)-ylidene)acetyl)benzonitril (5h) (500 MHz, acetone-d_6/CS_2 5:1, 293 K)



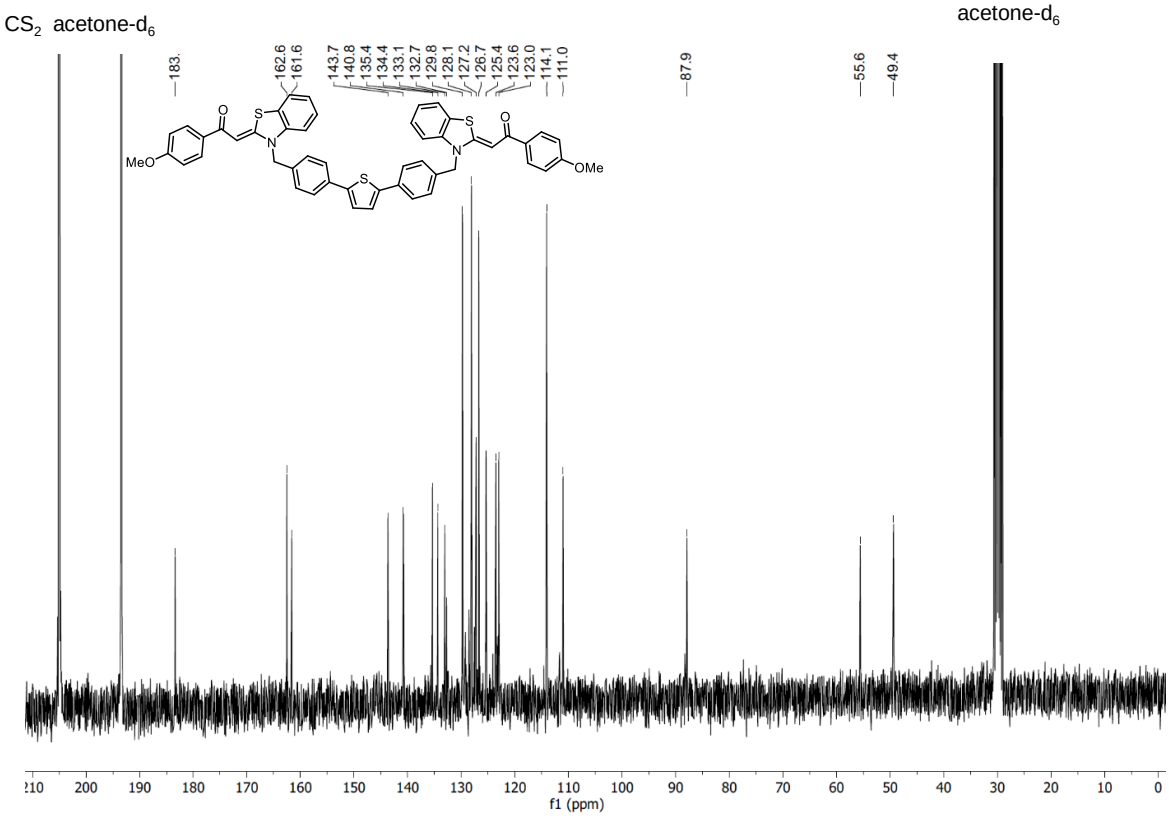
^{13}C NMR-spectrum (4-((*Z*)-2-(3-(4-(6-(4-((((*Z*)-2-(2-(4-methoxyphenyl)-2-oxoethylidene)benzo[*d*]thiazol-3(2*H*)-yl)methyl)phenyl)pyridin-2-yl)benzyl)benzo[*d*]thiazol-2(3*H*)-ylidene)acetyl)benzonitrile (5h) (125 MHz, acetone-d_6/CS_2 5:1, 293 K)



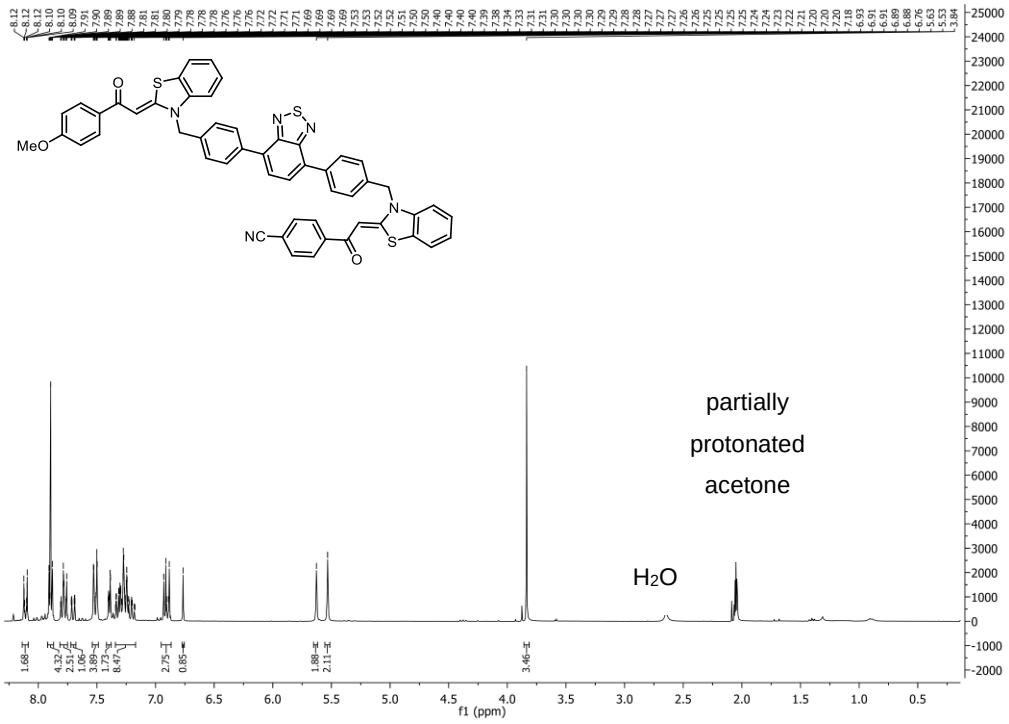
^{1}H NMR-spectrum (2*Z*,2'*Z*)-2,2'-(((thiophen-2,5-diylbis(4,1-phenylene))bis(methylene))bis(benzo[*d*]thiazol-3(3*H*)-yl-2(3*H*)-ylidene))bis(1-(4-methoxyphenyl)-ethan-1-one) (5i) (acetone-d_6/CS_2 5:1, 300 MHz, 298 K)



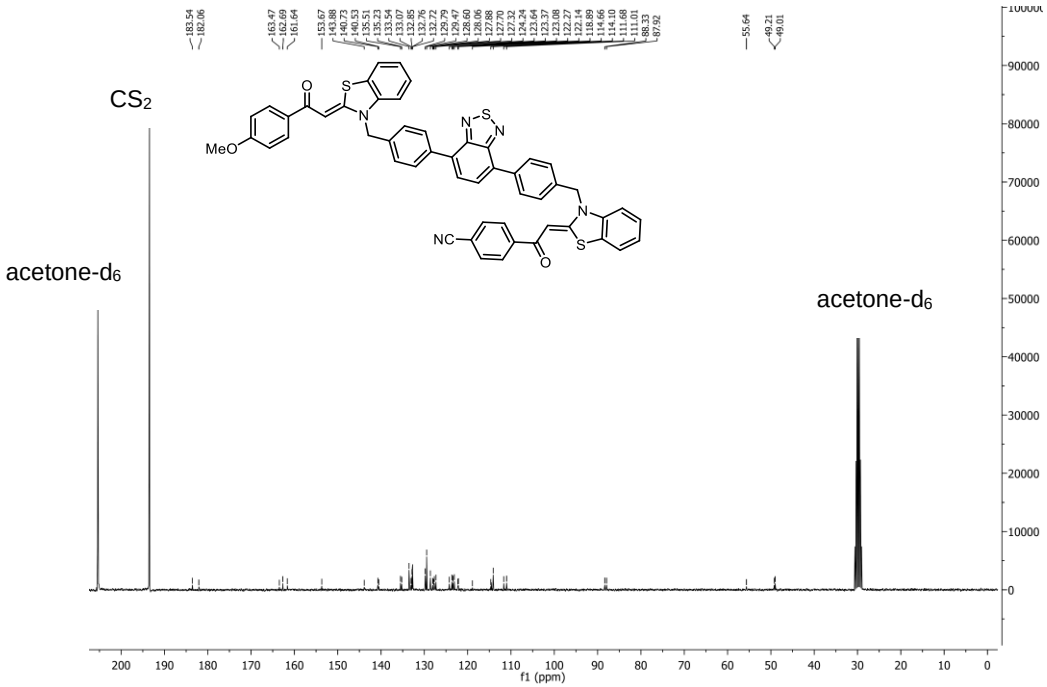
^{13}C NMR-spectrum (2Z,2'Z)-2,2'-(((thiophen-2,5-diylbis(4,1-phenylene))bis(methylene))bis(benzo[*d*]thiazol-3(3*H*)-yl-2(3*H*)-ylidene))bis(1-(4-methoxyphenyl)-ethan-1-one) (5i) (acetone-d_6/CS_2 5:1, 75 MHz, 298 K)



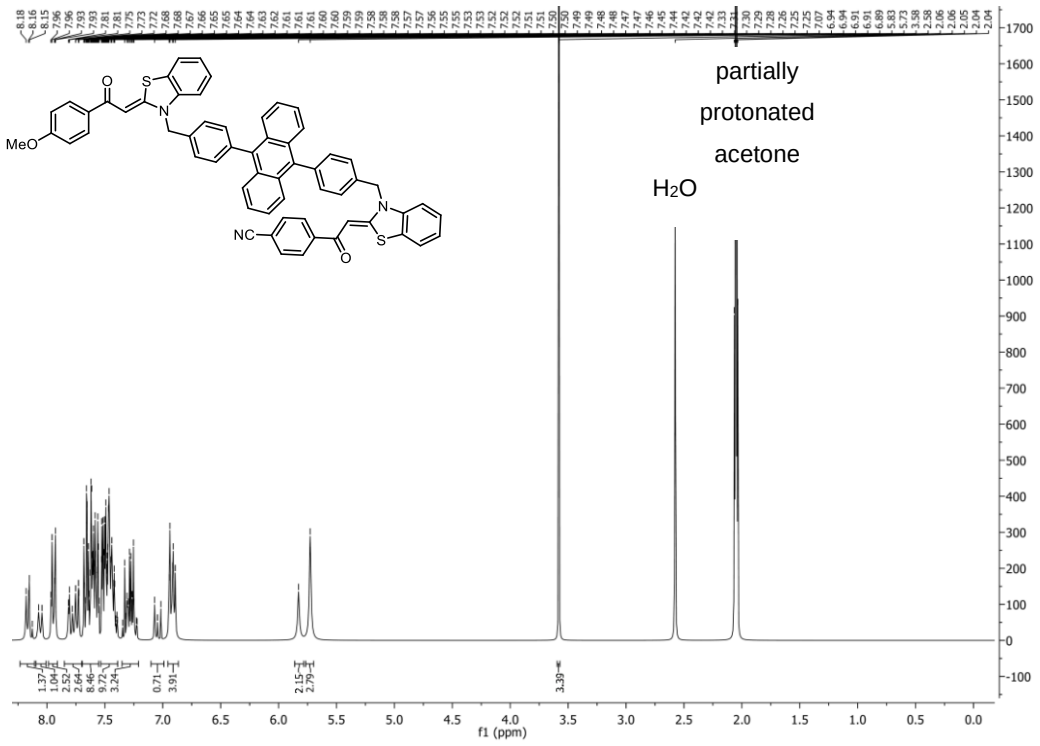
^{1}H NMR-spectrum 4-((*Z*)-2-(3-(4-(7-(4-(((*Z*)-2-(2-(4-methoxyphenyl)-2-oxoethylidene)benzo[*d*]thiazol-3(2*H*)-yl)methyl)phenyl)benzo[*c*][1,2,5]thiadiazol-4-yl)benzyl)benzo[*d*]thiazol-2(3*H*)-ylidene)acetyl)benzonitrile (5j) (300 MHz, acetone-d_6/CS_2 5:1, 293 K)



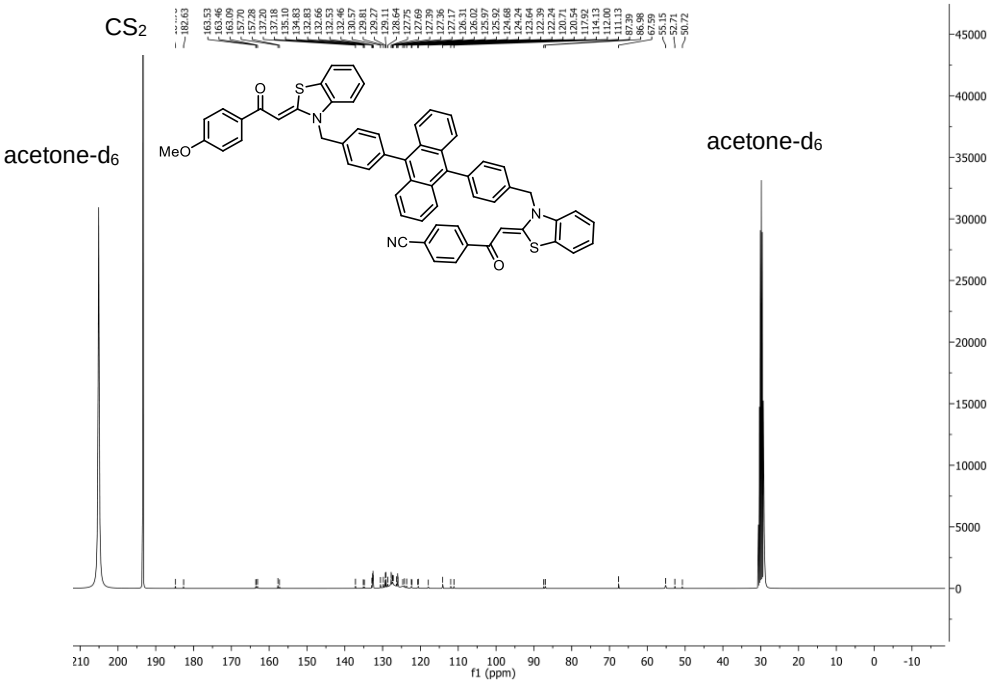
^{13}C NMR-spectrum 4-((*Z*)-2-(3-(4-(7-(4-(((*Z*)-2-(2-(4-methoxyphenyl)-2-oxoethylidene)benzo[*d*]thiazol-3(2*H*)-yl)methyl)phenyl)benzo[*c*][1,2,5]thiadiazol-4-yl)benzyl)benzo[*d*]thiazol-2(3*H*)-ylidene)acetyl)benzonitrile (5j) (75 MHz, acetone-d_6/CS_2 5:1, 293 K)



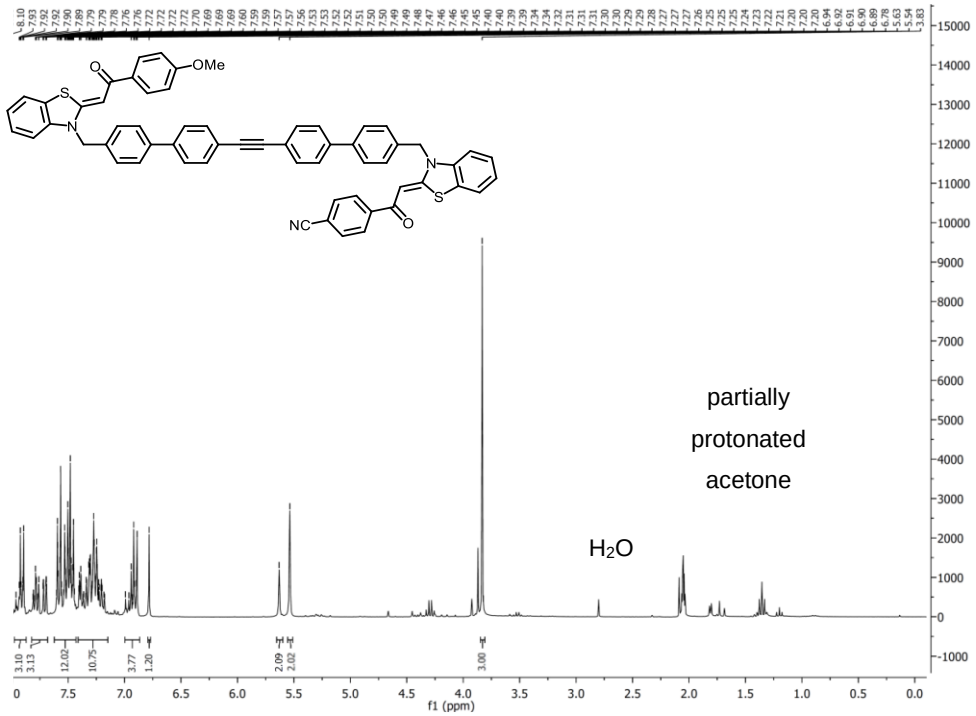
^{1}H NMR-spectrum 4-((*Z*)-2-(3-(4-(10-(4-(((*Z*)-2-(2-(4-methoxyphenyl)-2-oxoethylidene)benzo[*d*]thiazol-3(2*H*)-yl)methyl)phenyl)anthracene-9-yl)benzyl)benzo[*d*]thiazol-2(3*H*)-ylidene)acetyl)benzonitrile (5k) (300 MHz, acetone-d_6/CS_2 1:1, 293 K)



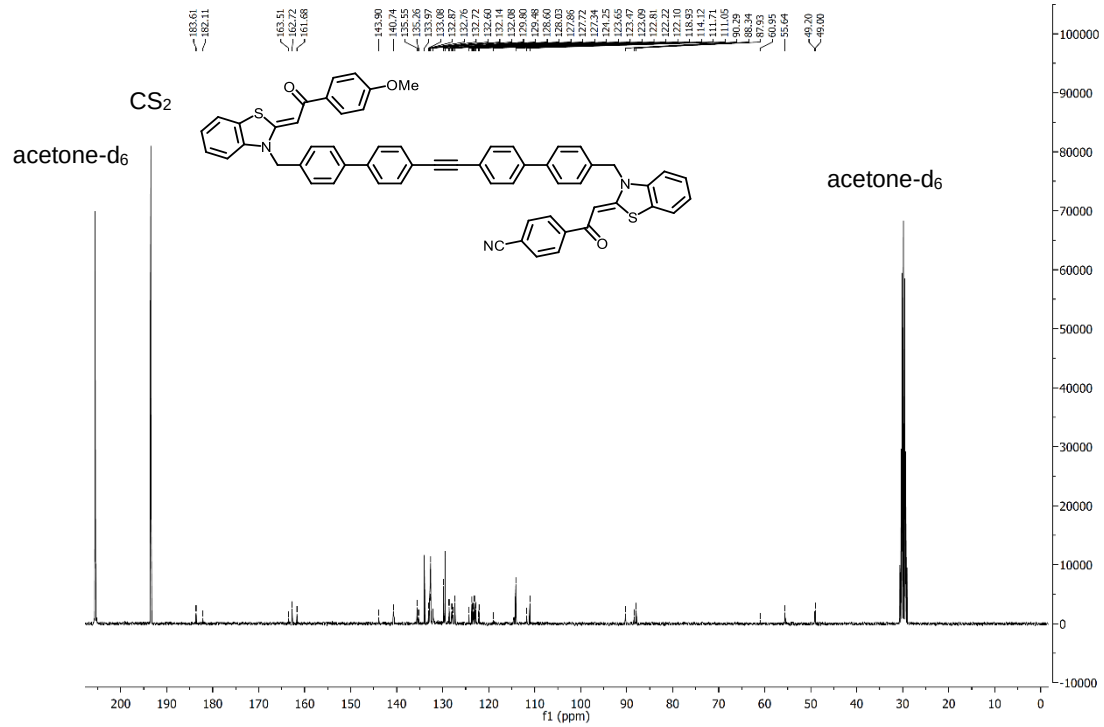
^{13}C NMR-spectrum 4-((*Z*)-2-(3-(4-(10-(4-(((*Z*)-2-(2-(4-methoxyphenyl)-2-oxoethylidene)benzo[*d*]thiazol-3(2*H*)-yl)methyl)phenyl)anthracene-9-yl)benzyl)benzo[*d*]thiazol-2(3*H*)-ylidene)acetyl)benzonitrile (5k) (75 MHz, acetone-d_6/CS_2 1:1, 293 K)



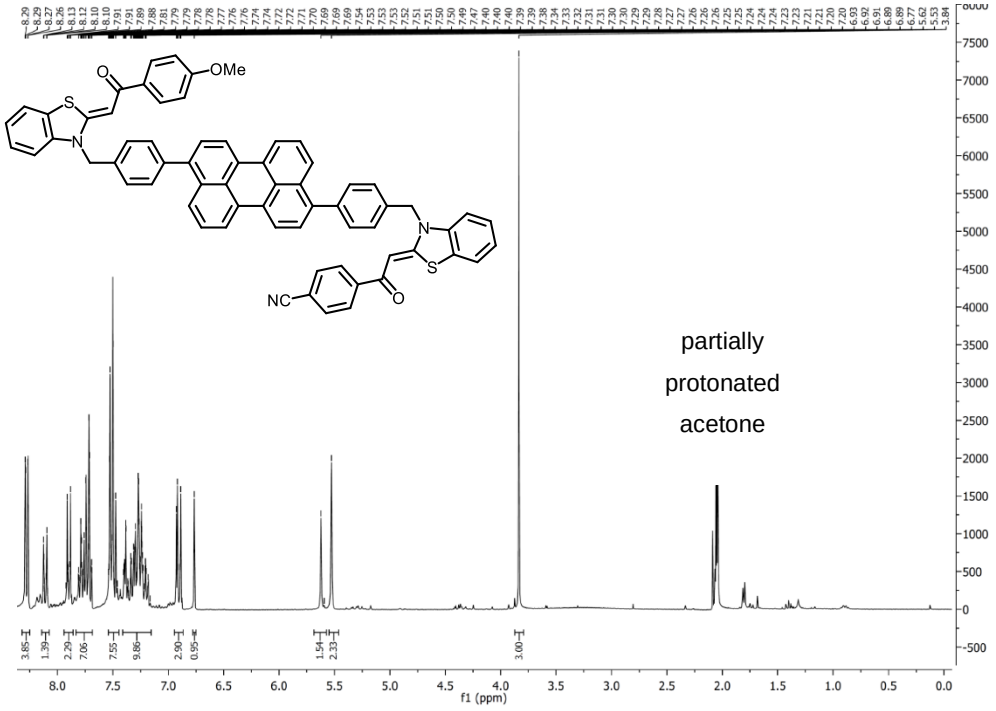
^{1}H NMR-spectrum 4-((*Z*)-2-(3-((4'-((4'-(((*Z*)-2-(2-(4-methoxyphenyl)-2-oxoethylidene)benzo[*d*]thiazol-3(2*H*)-yl)methyl)-[1,1'-biphenyl]-4-yl)ethynyl)-[1,1'-biphenyl]-4-yl)methyl)benzo[*d*]thiazol-2(3*H*)-ylidene)acetyl)benzonitrile (5l) (300 MHz, acetone-d_6/CS_2 5:1, 293 K)



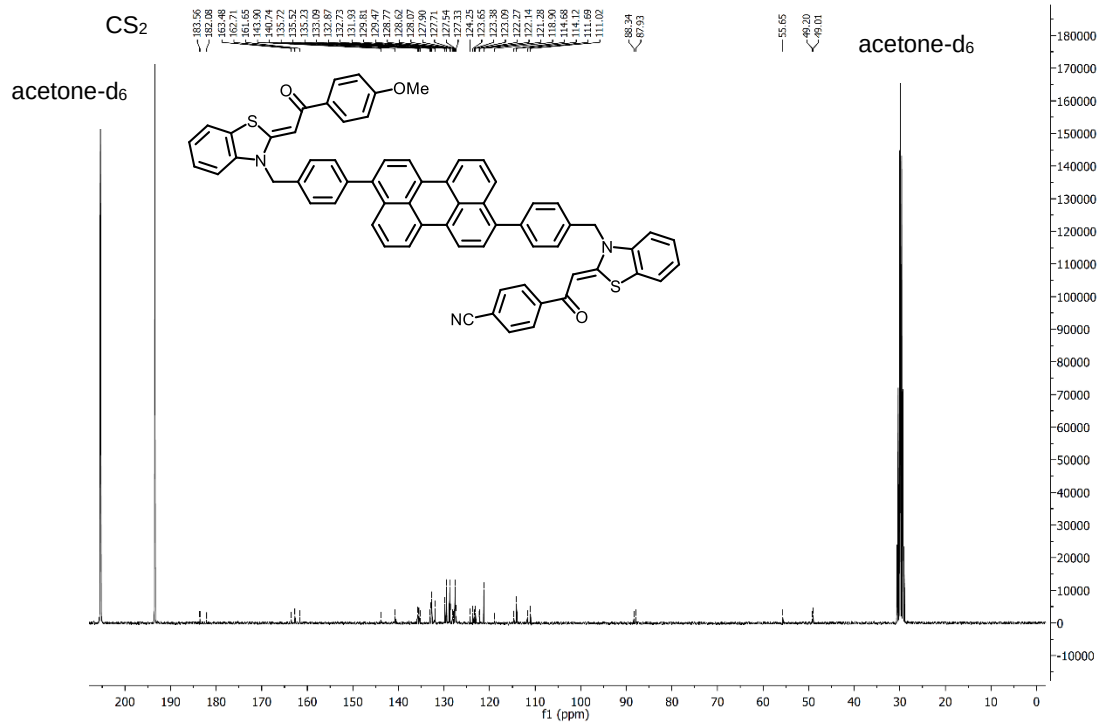
^{13}C NMR-spectrum 4-((*Z*)-2-(3-((4'-((4'-(((*Z*)-2-(2-(4-methoxyphenyl)-2-oxoethylidene)benzo[*d*]thiazol-3(2*H*)-yl)methyl)-[1,1'-biphenyl]-4-yl)ethynyl)-[1,1'-biphenyl]-4-yl)methyl)benzo[*d*]thiazol-2(3*H*)-ylidene)acetyl)benzonitrile (5l) (75 MHz, acetone-d_6/CS_2 5:1, 293 K)



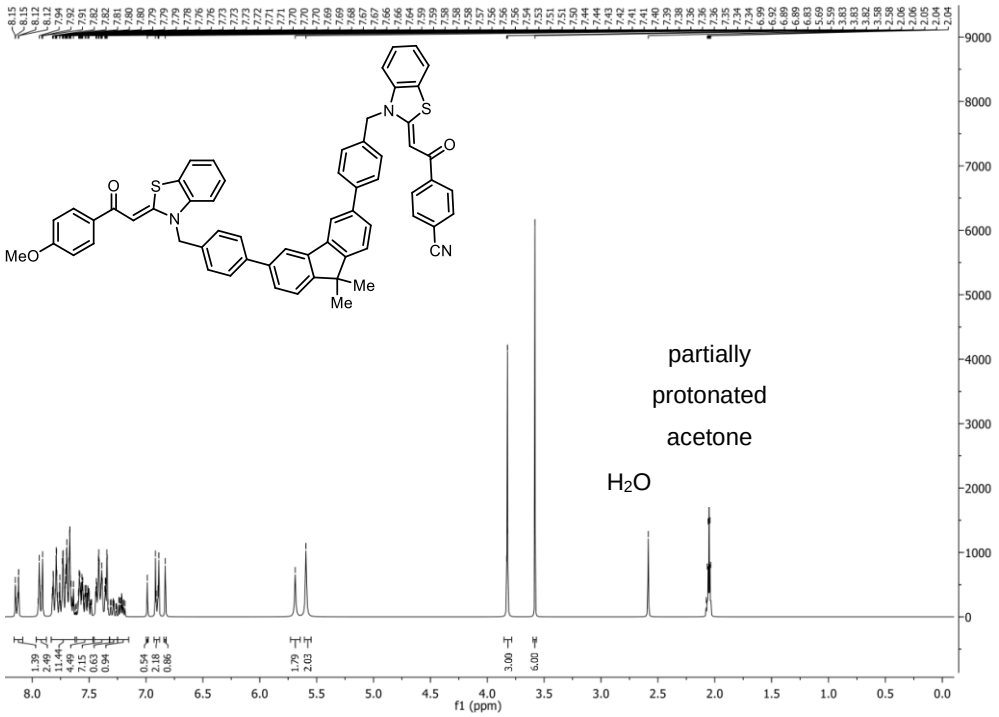
^{1}H NMR-spectrum 4-((*Z*)-2-(3-(4-(9-(4-(((*Z*)-2-(2-(4-methoxyphenyl)-2-oxoethylidene)benzo[*d*]thiazol-3(2*H*)-yl)methyl)phenyl)perylene-3-yl)benzyl)benzo[*d*]thiazol-2(3*H*)-ylidene)acetyl)benzonitrile (5m) (300 MHz, acetone-d_6/CS_2 5:1, 293 K)



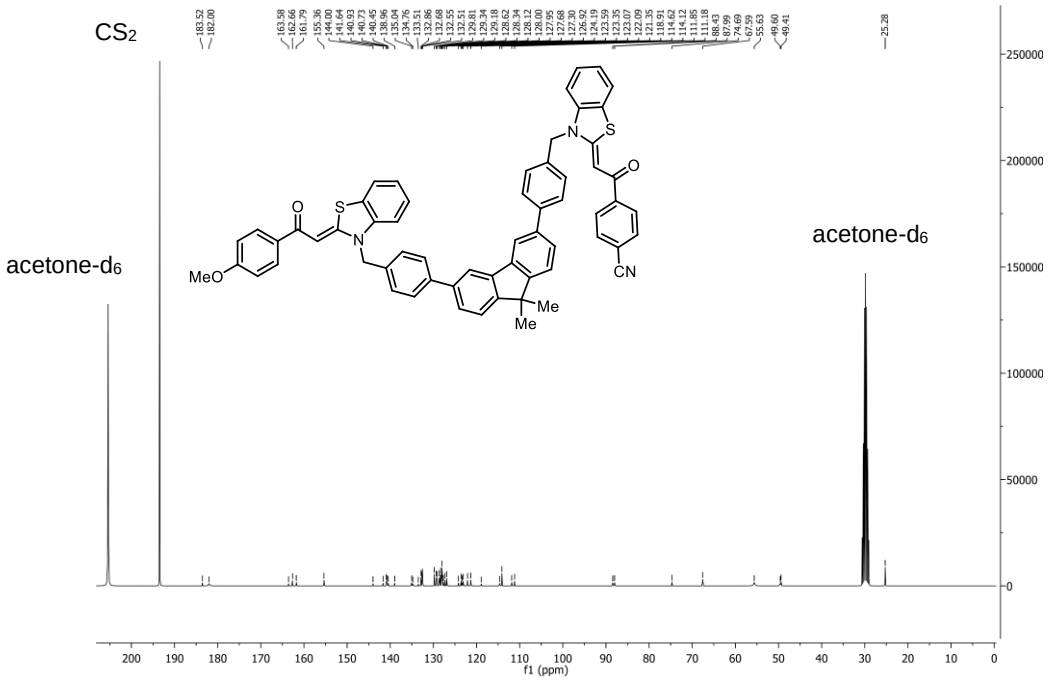
^{13}C NMR-spectrum 4-((*Z*)-2-(3-(4-(9-(4-(((*Z*)-2-(2-(4-methoxyphenyl)-2-oxoethylidene)benzo[*d*]thiazol-3(2*H*)-yl)methyl)phenyl)perylene-3-yl)benzyl)benzo[*d*]thiazol-2(3*H*)-ylidene)acetyl)benzonitrile (5m) (75 MHz, acetone-d_6/CS_2 5:1, 293 K)



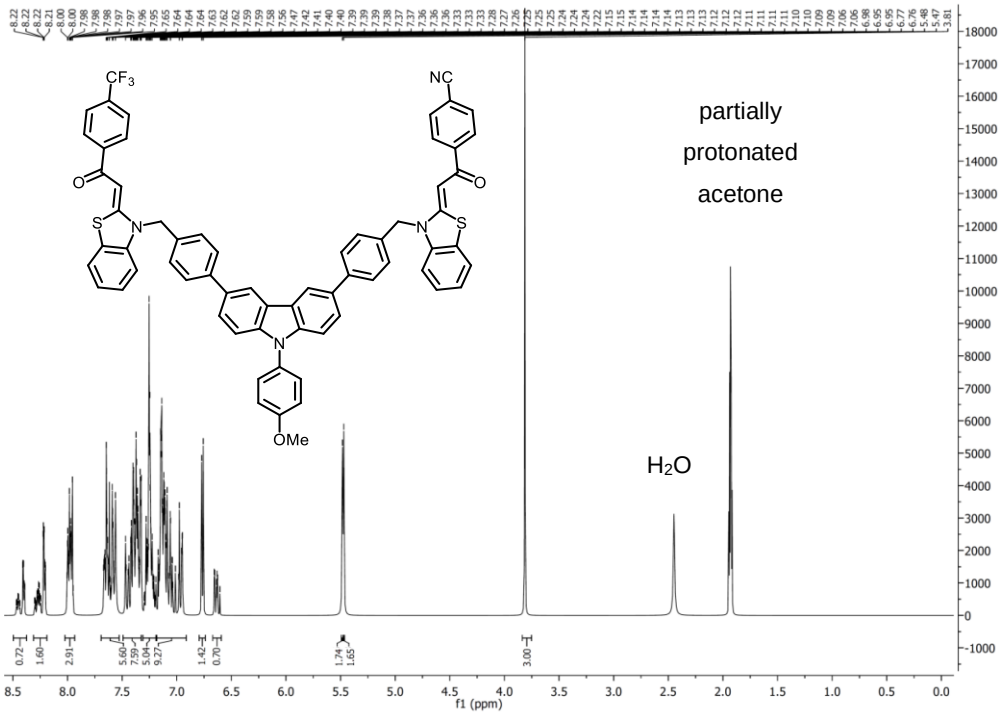
^{1}H NMR-spectrum 4-((*Z*)-2-(3-(4-(6-(4-(((*Z*)-2-(2-(4-methoxyphenyl)-2-oxoethylidene)benzo[*d*]thiazol-3(2*H*)-yl)methyl)phenyl)-9,9-dimethyl-9*H*-fluoren-3-yl)benzyl)benzo[*d*]thiazol-2(3*H*)-ylidene)acetyl)benzonitrile (5n) (300 MHz, acetone-d_6/CS_2 5:1, 293 K)



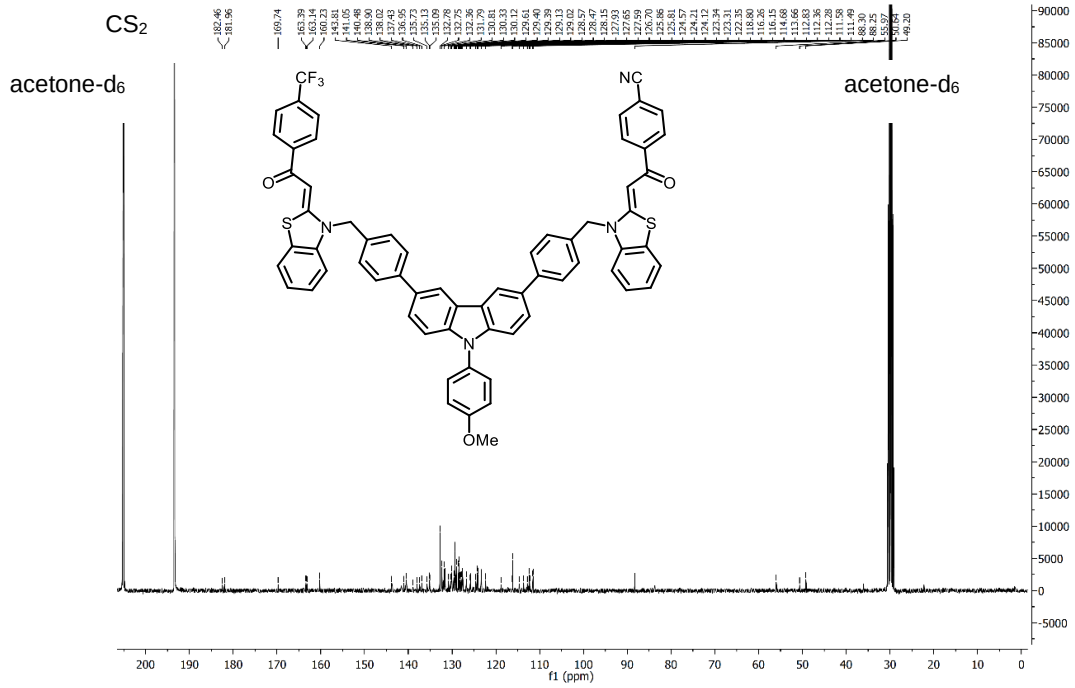
^{13}C NMR-spectrum 4-((*Z*)-2-(3-(4-(6-(4-(((*Z*)-2-(2-(4-methoxyphenyl)-2-oxoethylidene)benzo[*d*]thiazol-3(2*H*)-yl)methyl)phenyl)-9,9-dimethyl-9*H*-fluoren-3-yl)benzyl)benzo[*d*]thiazol-2(3*H*)-ylidene)acetyl)benzonitrile (5n) (75 MHz, acetone-d_6/CS_2 5:1, 293 K)



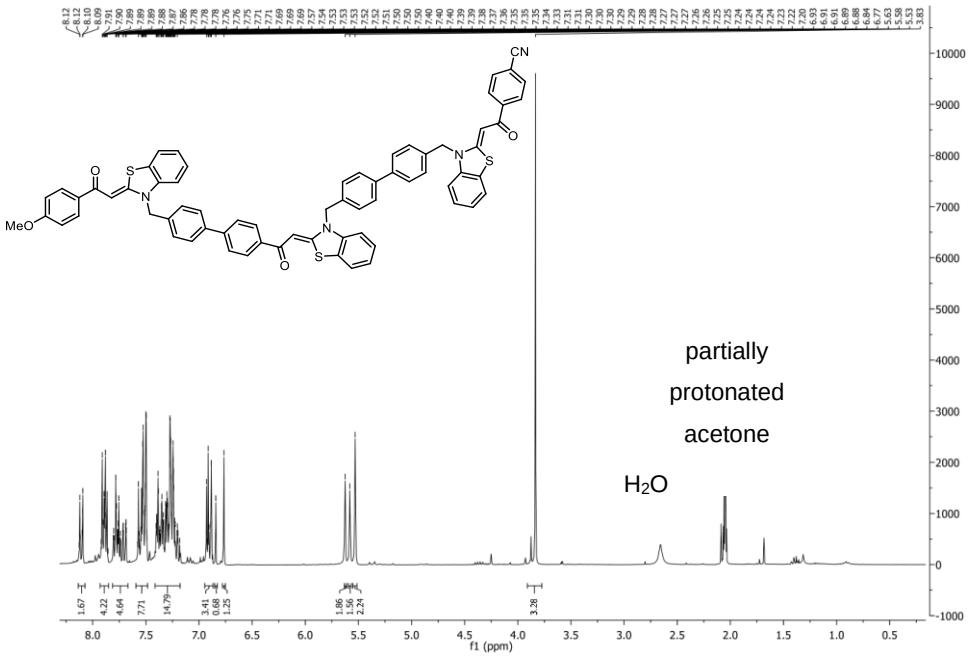
^{1}H NMR-spectrum 4-((*Z*)-2-(3-(4-(9-(4-methoxyphenyl)-6-(4-(((*Z*)-2-(2-(4-methoxyphenyl)-2-oxoethylidene)benzo[*d*]thiazol-3(2*H*)-yl)methyl)phenyl)-9*H*-carbazol-3-yl)benzyl)benzo[*d*]thiazol-2(3*H*)-ylidene)acetyl)benzonitrile (5o) (300 MHz, acetone-d_6/CS_2 5:1, 293 K)



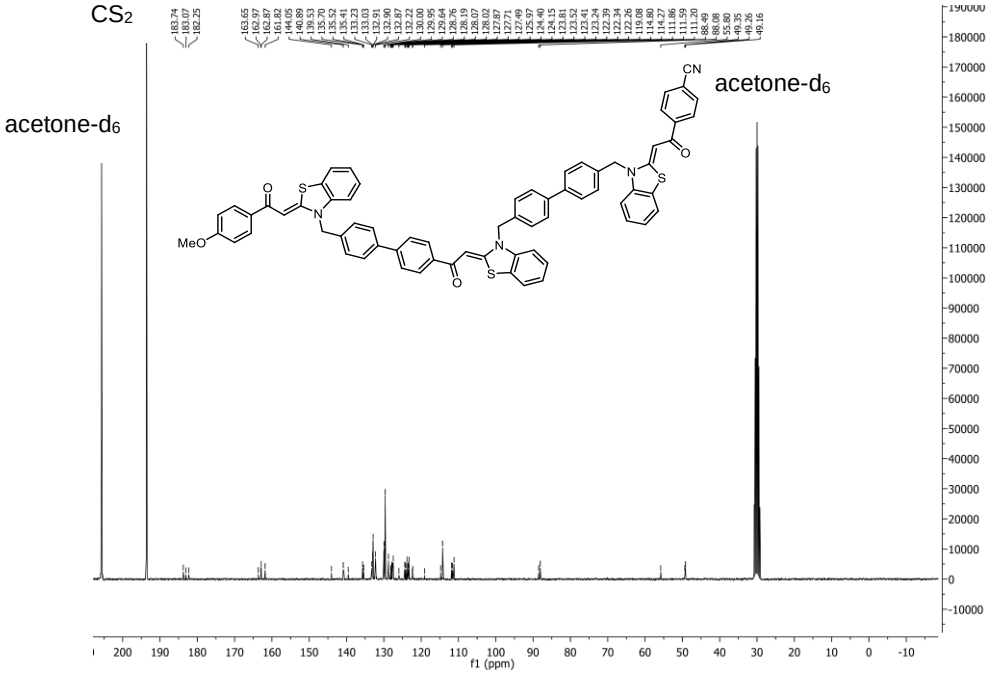
^{13}C NMR-spectrum 4-((*Z*)-2-(3-(4-(9-(4-methoxyphenyl)-6-(4-(((*Z*)-2-(2-(4-methoxyphenyl)-2-oxoethylidene)benzo[*d*]thiazol-3(2*H*)-yl)methyl)phenyl)-9*H*-carbazol-3-yl)benzyl)benzo[*d*]thiazol-2(3*H*)-ylidene)acetyl)benzonitrile (5o) (75 MHz, acetone-d_6/CS_2 5:1, 293 K)



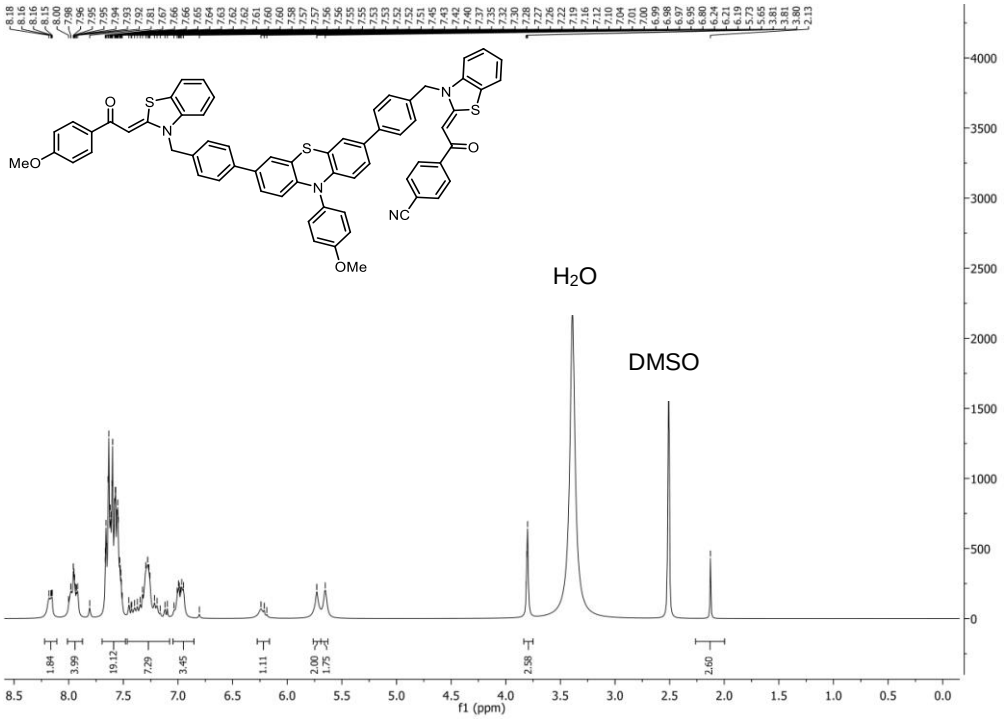
^{1}H NMR-spectrum 4-((*Z*)-2-(3-((4'-(((*Z*)-2-(2-(4'-(((*Z*)-2-(2-(4-methoxyphenyl)-2-oxoethylidene)benzo[*d*]thiazol-3(2*H*)-yl)methyl)-[1,1'-biphenyl]-4-yl)-2-oxoethylidene)benzo[*d*]thiazol-3(2*H*)-yl)methyl)-[1,1'-biphenyl]-4-yl)methyl)benzo[*d*]thiazol-2(3*H*)-ylidene)acetyl)benzonitrile (5p) (300 MHz, acetone-d_6/CS_2 5:1, 293 K)



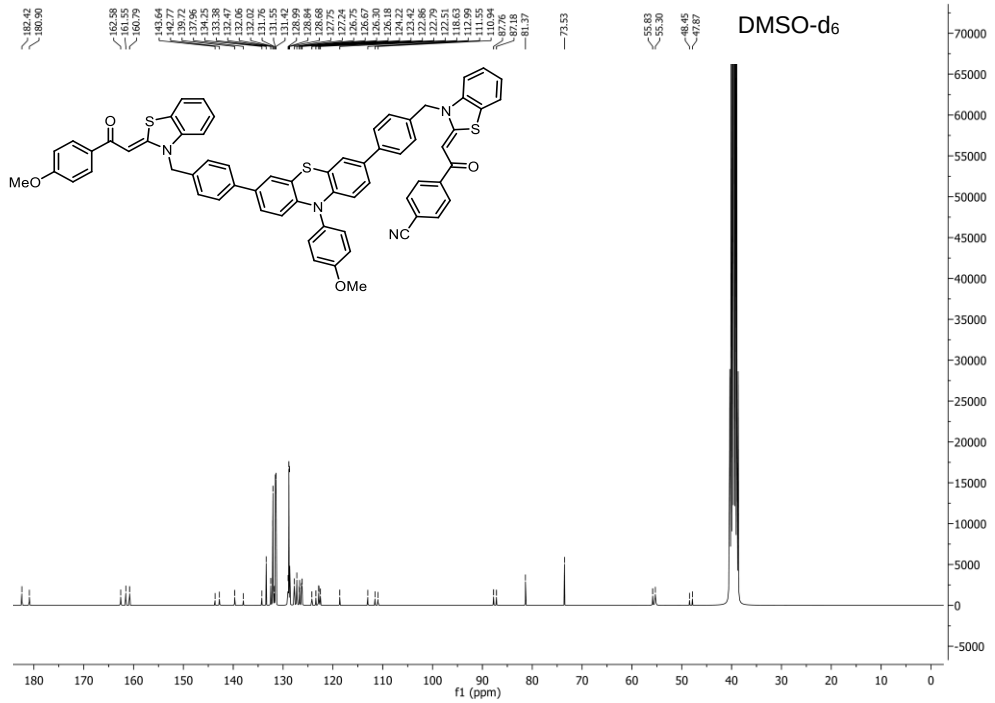
^{13}C NMR-spectrum 4-((*Z*)-2-(3-((4'-(((*Z*)-2-(2-(4'-(((*Z*)-2-(2-(4-methoxyphenyl)-2-oxoethylidene)benzo[*d*]thiazol-3(2*H*)-yl)methyl)-[1,1'-biphenyl]-4-yl)-2-oxoethylidene)benzo[*d*]thiazol-3(2*H*)-yl)methyl)-[1,1'-biphenyl]-4-yl)methyl)benzo[*d*]thiazol-2(3*H*)-ylidene)acetyl)benzonitrile (5p) (75 MHz, acetone-d_6/CS_2 5:1, 293 K)



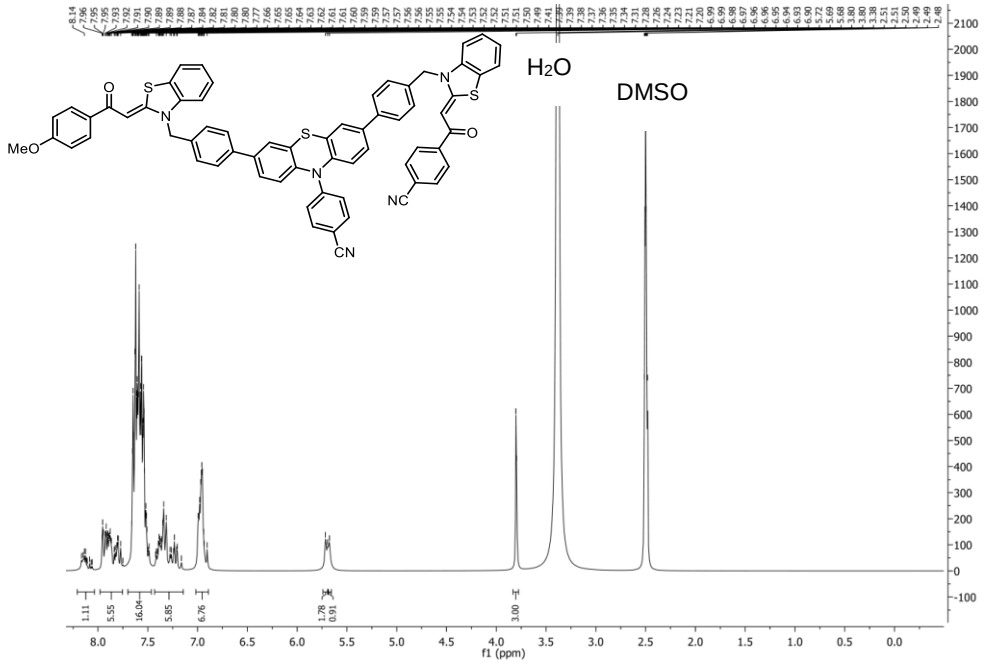
^{1}H NMR-spectrum 4-((*Z*)-2-(3-(4-(10-(4-methoxyphenyl)-7-(4-(((*Z*)-2-(2-(4-methoxyphenyl)-2-oxoethylidene)benzo[*d*]thiazol-3(2*H*)-yl)methyl)phenyl)-10*H*-phenothiazin-3-yl)benzyl)benzo[*d*]thiazol-2(3*H*)-ylidene)acetyl)benzonitrile (5q) (300 MHz, DMSO-d$_6$, 293 K)



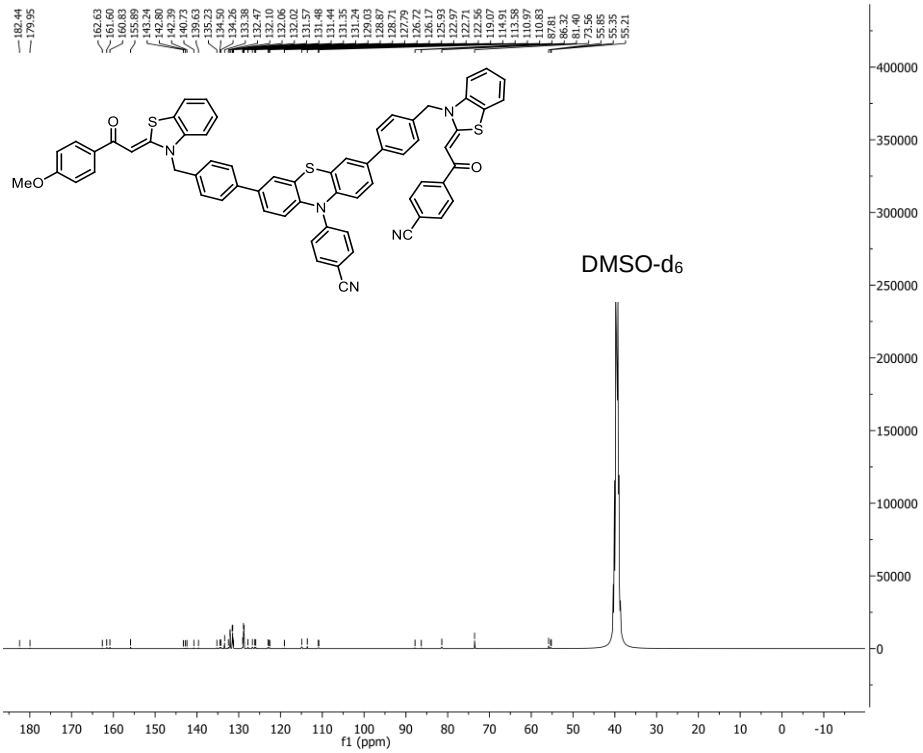
^{13}C NMR-spectrum 4-((*Z*)-2-(3-(4-(10-(4-methoxyphenyl)-7-(4-(((*Z*)-2-(2-(4-methoxyphenyl)-2-oxoethylidene)benzo[*d*]thiazol-3(2*H*)-yl)methyl)phenyl)-10*H*-phenothiazin-3-yl)benzyl)benzo[*d*]thiazol-2(3*H*)-ylidene)acetyl)benzonitrile (5q) (75 MHz, DMSO-d$_6$, 293 K)



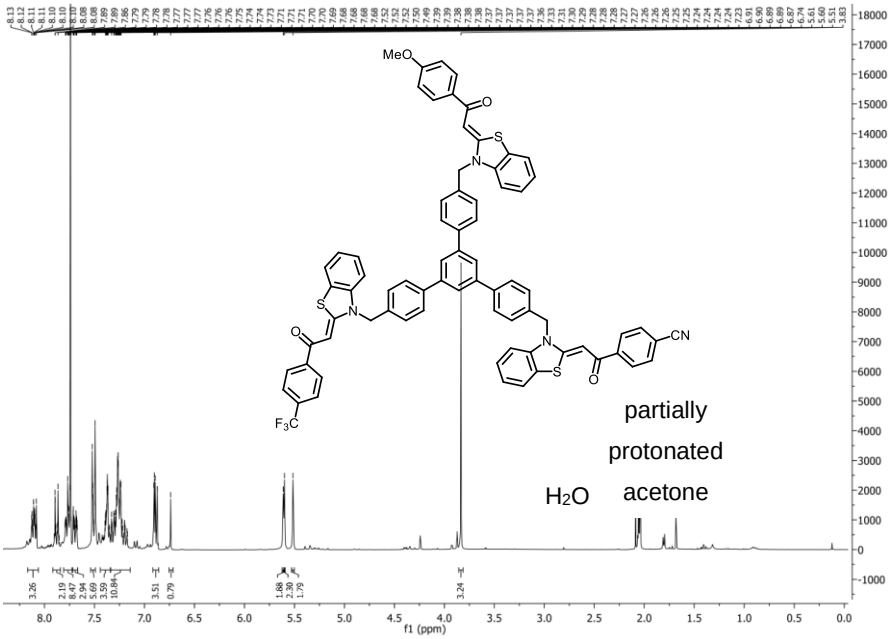
^{1}H NMR-spectrum 4-(3-(4-(((*Z*)-2-(2-(4-cyanophenyl)-2-oxoethylidene)benzo[*d*]thiazol-3(2*H*)-yl)methyl)phenyl)-7-(4-(((*Z*)-2-(2-(4-methoxyphenyl)-2-oxoethylidene)benzo[*d*]thiazol-3(2*H*)-yl)methyl)phenyl)-10*H*-phenothiazin-10-yl)benzonitrile (5r) (300 MHz, DMSO-d$_6$, 293 K)



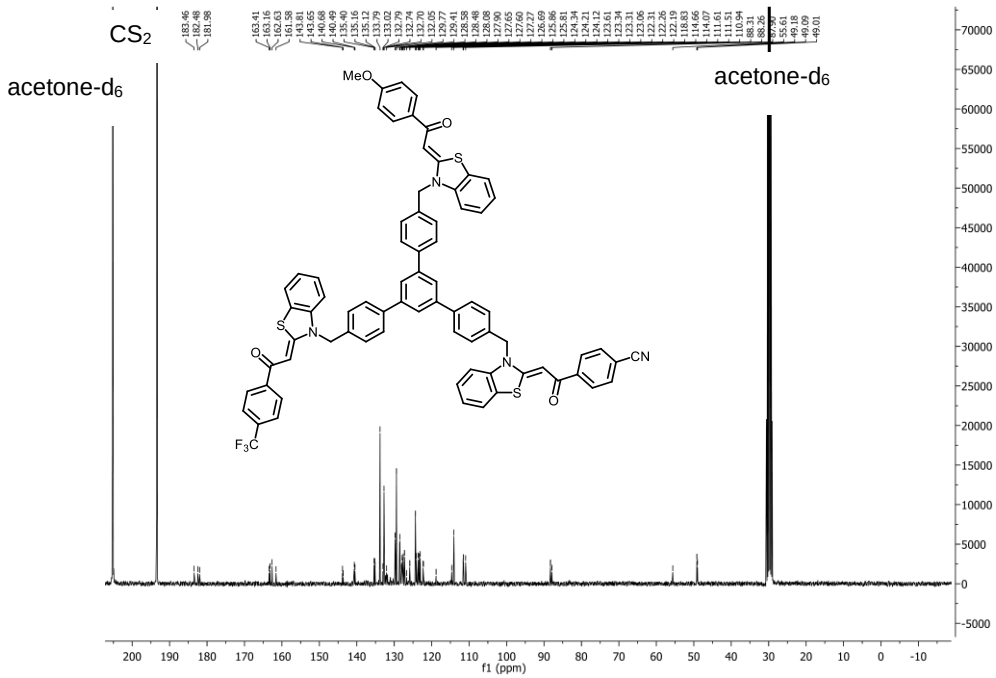
^{13}C NMR-spectrum 4-(3-(4-(((*Z*)-2-(2-(4-cyanophenyl)-2-oxoethylidene)benzo[*d*]thiazol-3(2*H*)-yl)methyl)phenyl)-7-(4-(((*Z*)-2-(2-(4-methoxyphenyl)-2-oxoethylidene)benzo[*d*]thiazol-3(2*H*)-yl)methyl)phenyl)-10*H*-phenothiazin-10-yl)benzonitrile (5r) (75 MHz, DMSO-d$_6$, 293 K)



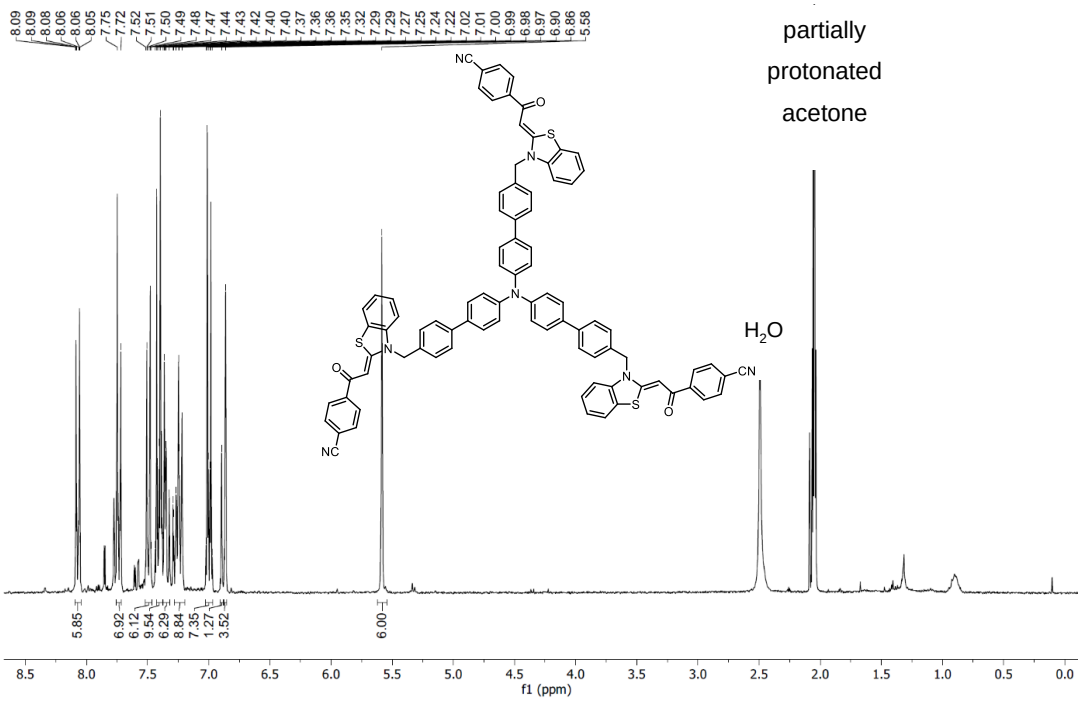
^{1}H NMR-spectrum 4-((*Z*)-2-(3-((4''-(((*Z*)-2-(2-(4-methoxyphenyl)-2-oxoethylidene)benzo[*d*]thiazol-3(2*H*)-yl)methyl)-5'-(4-(((*Z*)-2-(2-oxo-2-(4-(trifluoromethyl)phenyl)ethylidene)benzo[d]thiazol-3(2*H*)-yl)methyl)phenyl)-[1,1':3',1''-terphenyl]-4-yl)methyl)benzo[*d*]thiazol-2(3*H*)-ylidene)acetyl)benzonitrile (5s) (300 MHz, acetone-d$_6$/CS$_2$ 5:1, 293 K)



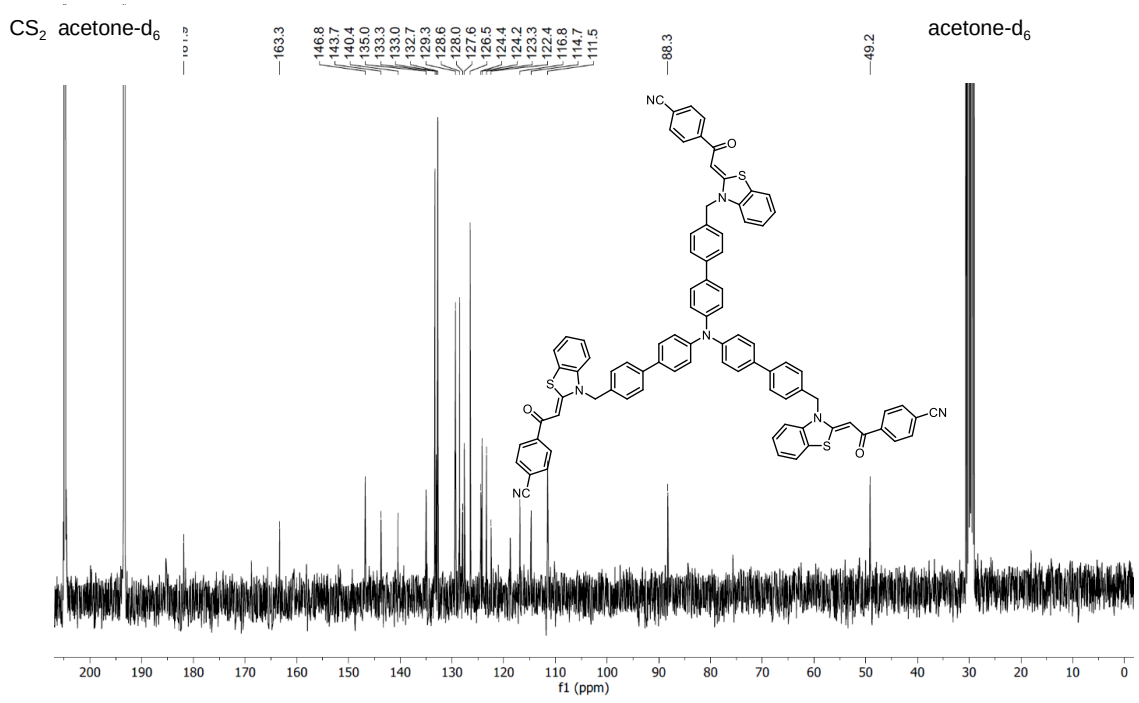
^{13}C NMR-spectrum 4-((*Z*)-2-(3-((4''-(((*Z*)-2-(2-(4-methoxyphenyl)-2-oxoethylidene)benzo[*d*]thiazol-3(2*H*)-yl)methyl)-5'-(4-(((*Z*)-2-(2-oxo-2-(4-(trifluoromethyl)phenyl)ethylidene)benzo[d]thiazol-3(2*H*)-yl)methyl)phenyl)-[1,1':3',1''-terphenyl]-4-yl)methyl)benzo[*d*]thiazol-2(3*H*)-ylidene)acetyl)benzonitrile (5s) (75 MHz, acetone-d$_6$/CS$_2$ 5:1, 293 K)



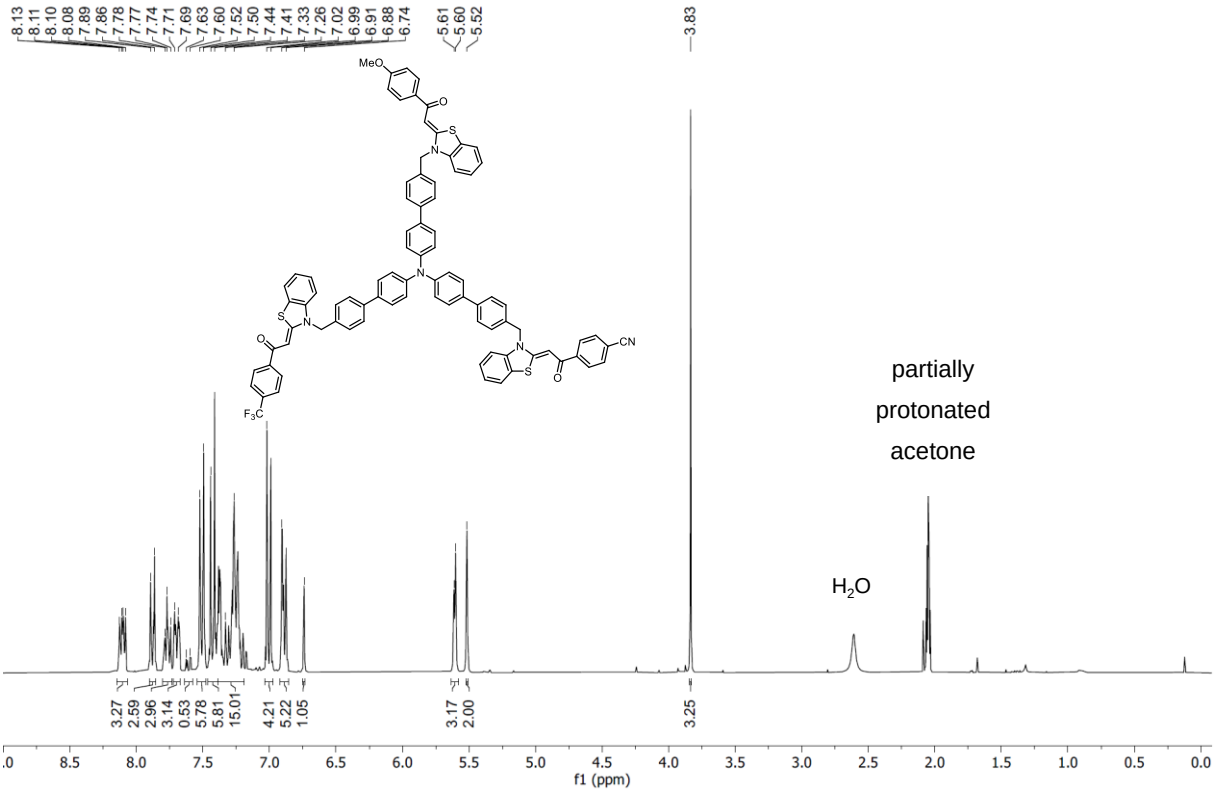
^{1}H NMR-spectrum 4,4',4''-((2*Z*,2'*Z*,2''*Z*)-2,2',2''-(((nitrilotris([1,1'-biphenyl]-4',4-diyl))tris(methylene))tris(benzo[*d*]thiazol-3(3*H*)-yl-2(3*H*)-ylidene))tris(acetyl))tribenzonitrile (5t) (acetone-d_6/CS_2 5:1, 300 MHz, 298 K)



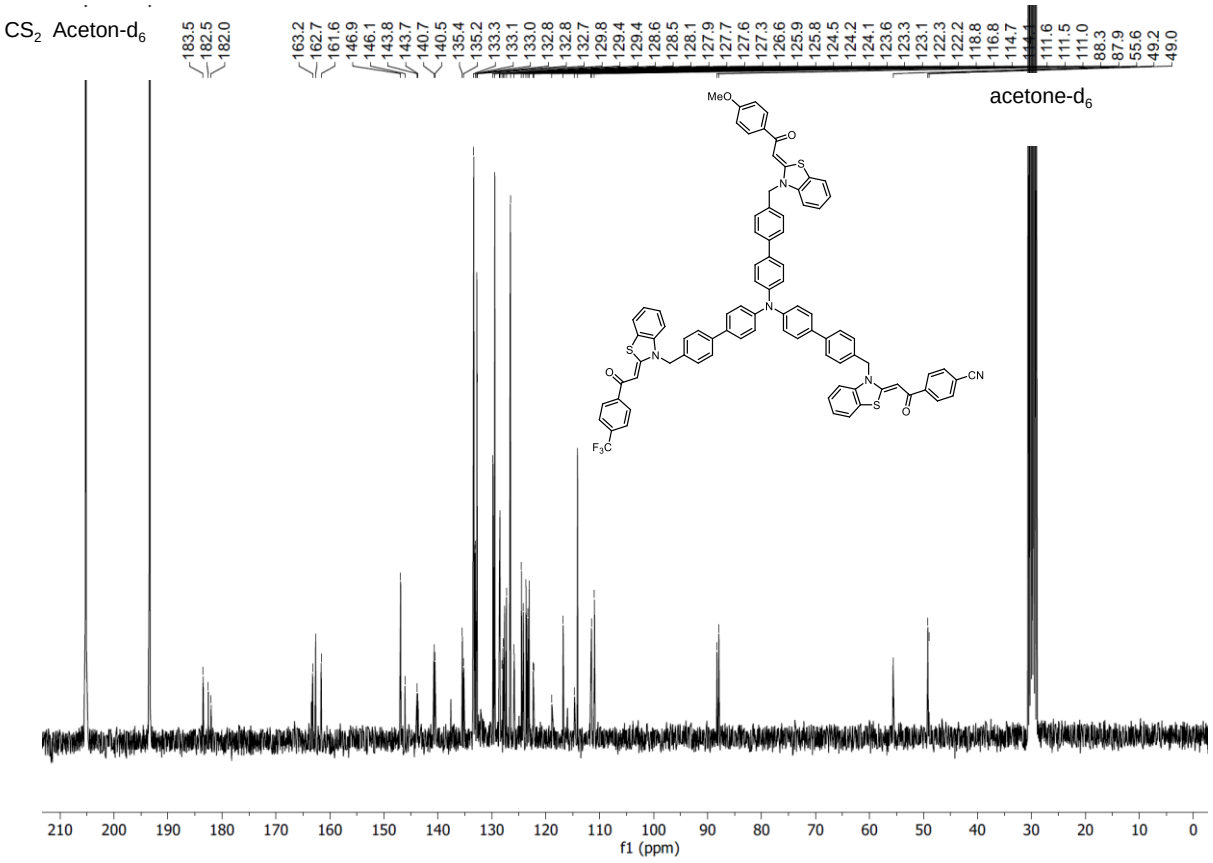
^{13}C NMR-spectrum 4,4',4''-((2*Z*,2'*Z*,2''*Z*)-2,2',2''-(((nitrilotris([1,1'-biphenyl]-4',4-diyl))tris(methylene))tris(benzo[*d*]thiazol-(3*H*)-yl-2(3H)-ylidene))tris(acetyl))tribenzonitrile (5t) (acetone-d_6/CS_2 5:1, 75 MHz, 298 K)



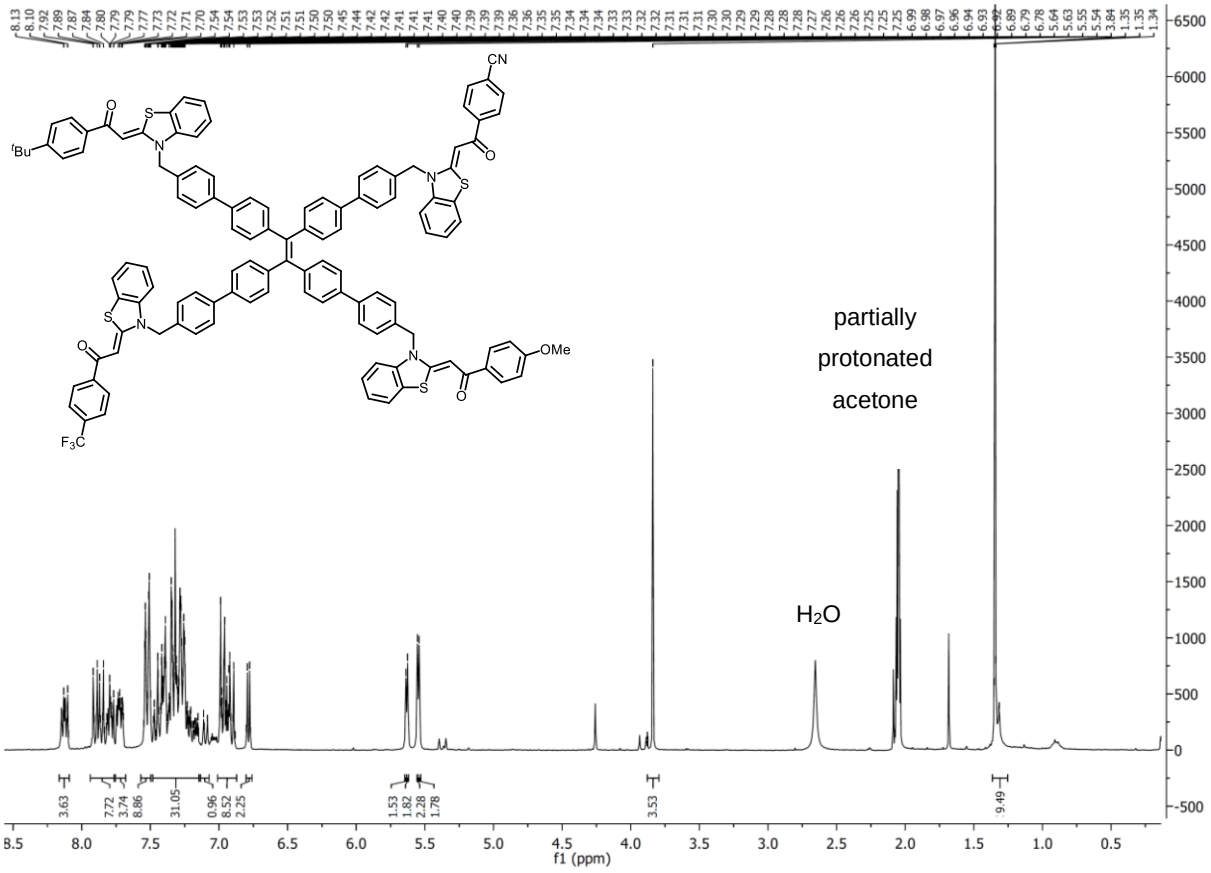
^{1}H NMR-spectrum 4-((*Z*)-2-(3-((4'-((4'-(((*Z*)-2-(2-(4-methoxyphenyl)-2-oxoethylidene)benzo[*d*]thiazol-3(2*H*)-yl)methyl)-[1,1'-biphenyl]-4-yl)(4'-(((*Z*)-2-(2-oxo-2-(4-(trifluoromethyl)phenyl)ethylidene)benzo[*d*]thiazol-3(2*H*)-yl)methyl)-[1,1'-biphenyl]-4-yl)amino)-[1,1'-biphenyl]-4-yl)methyl)benzo[*d*]thiazol-2(3*H*)-ylidene)acetyl)benzonitrile (5u) (acetone-d_6/CS_2 5:1, 300 MHz, 298 K)



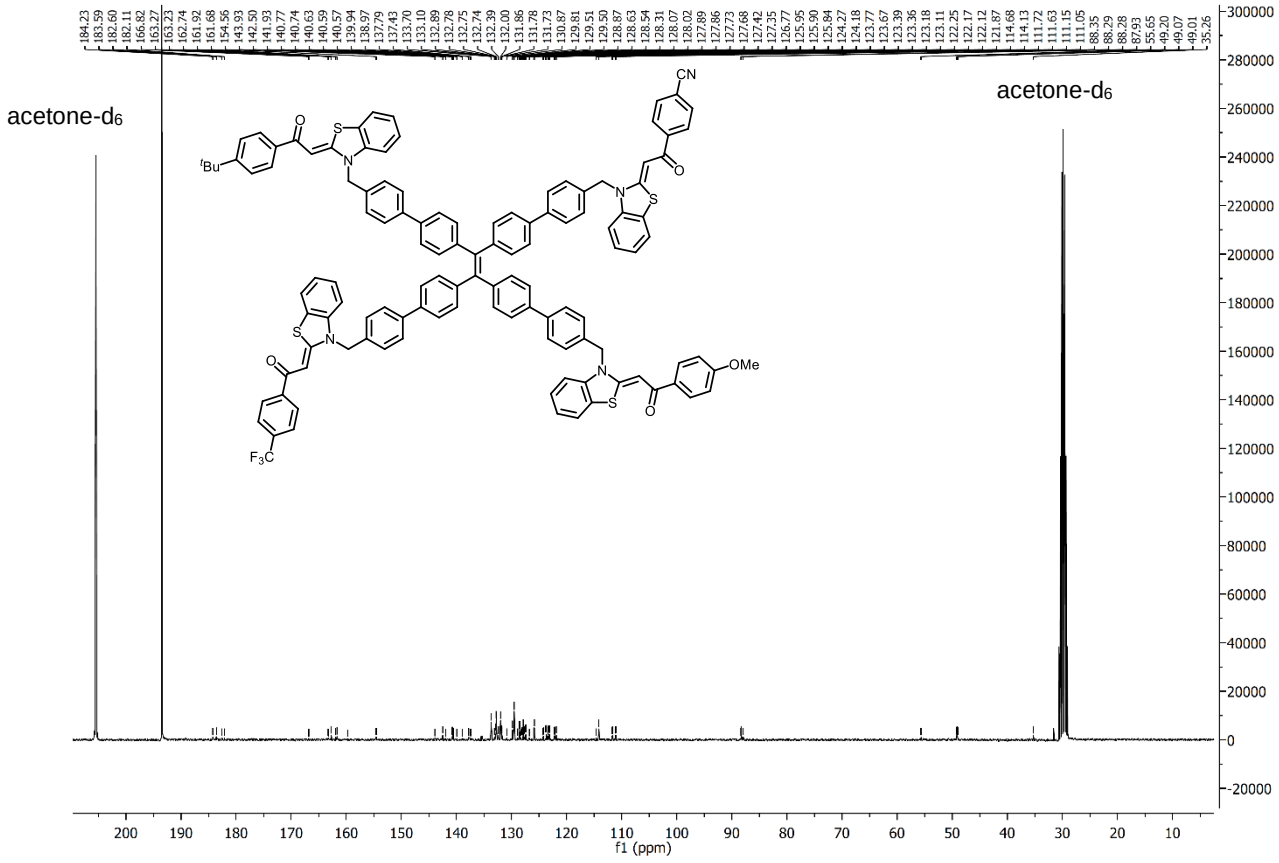
^{13}C NMR-spectrum 4-((*Z*)-2-(3-((4'-((4'-(((*Z*)-2-(2-(4-methoxyphenyl)-2-oxoethylidene)benzo[*d*]thiazol-3(2*H*)-yl)methyl)-[1,1'-biphenyl]-4-yl)(4'-(((*Z*)-2-(2-oxo-2-(4-(trifluoromethyl)phenyl)ethylidene)benzo[*d*]thiazol-3(2*H*)-yl)methyl)-[1,1'-biphenyl]-4-yl)amino)-[1,1'-biphenyl]-4-yl)methyl)benzo[*d*]thiazol-2(3*H*)-ylidene)acetyl)benzonitrile (5u) (acetone-d_6/CS_2 5:1, 75 MHz, 298 K)



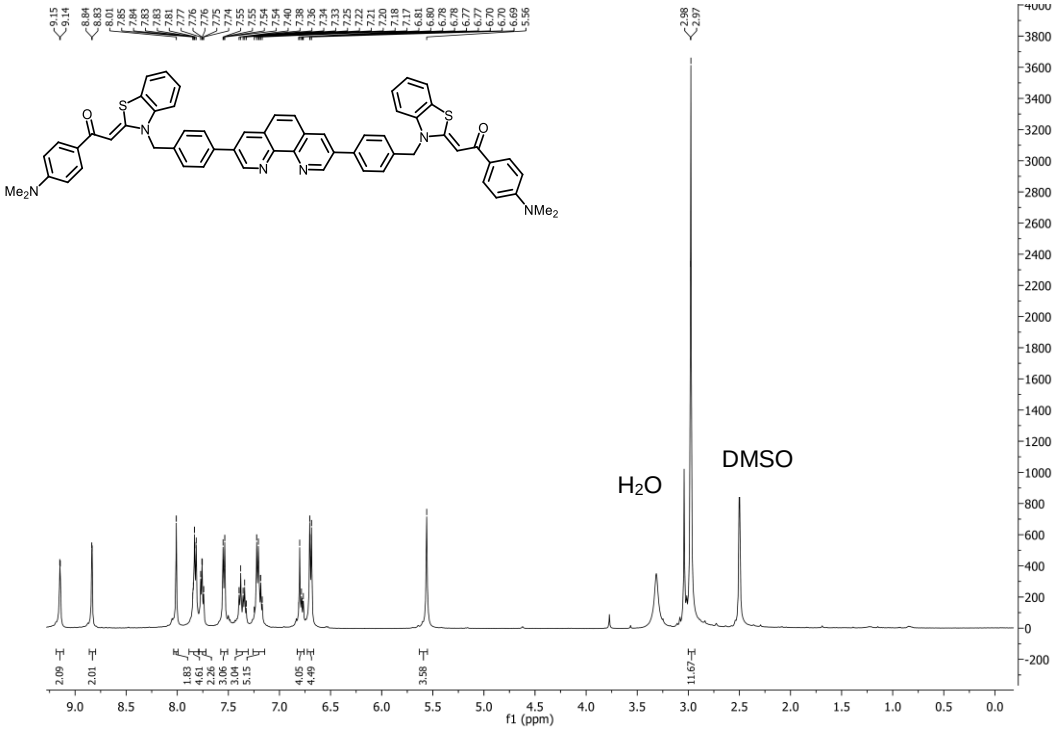
^{1}H NMR-spectrum 4-((*Z*)-2-(3-((4'-(1-(4'-(((*Z*)-2-(2-(4-(*tert*-butyl)phenyl)-2-oxoethylidene)benzo[*d*]thiazol-3(2*H*)-yl)methyl)-[1,1'-biphenyl]-4-yl)-2-(4'-(((*Z*)-2-(2-(4-methoxyphenyl)-2-oxoethylidene)benzo[*d*]thiazol-3(2*H*)-yl)methyl)-[1,1'-biphenyl]-4-yl)-2-(4'-(((*Z*)-2-(2-oxo-2-(4-(trifluoromethyl)phenyl)ethylidene)benzo[*d*]thiazol-3(2*H*)-yl)methyl)-[1,1'-biphenyl]-4-yl)vinyl)-[1,1'-biphenyl]-4-yl)methyl)benzo[*d*]thiazol-2(3*H*)-ylidene)acetyl)benzonitrile (5v) (300 MHz, acetone-d_6/CS_2 5:1, 293 K)



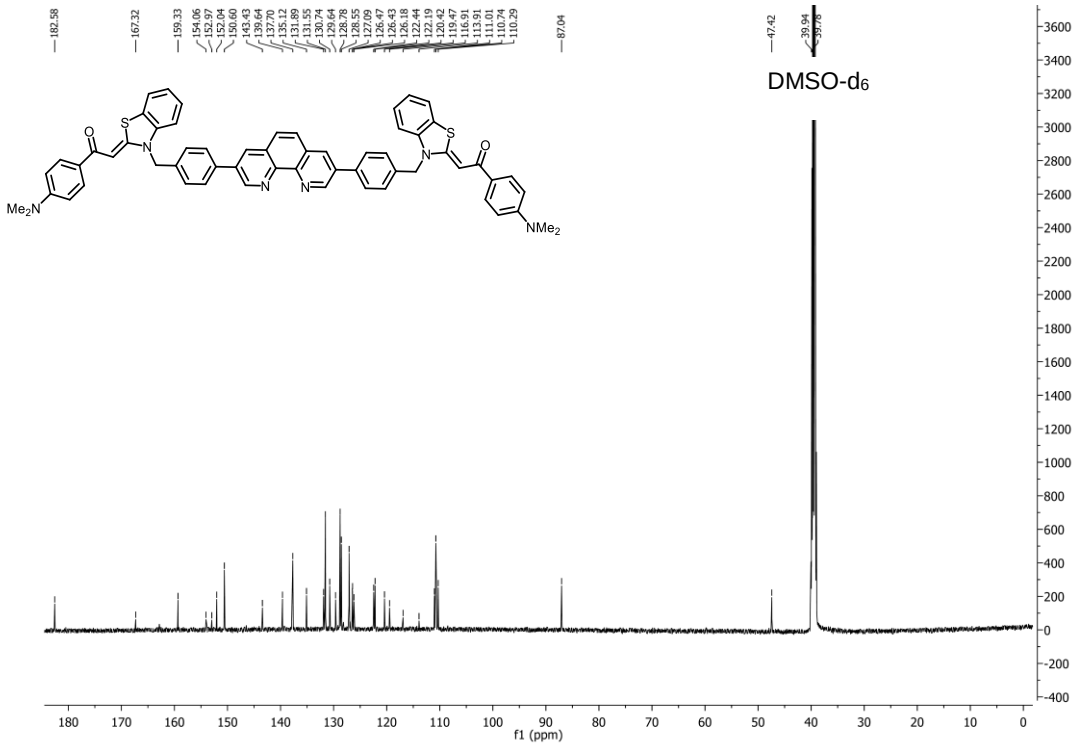
^{13}C NMR-Spektrum 4-((*Z*)-2-(3-((4'-(1-(4'-(((*Z*)-2-(2-(4-(*tert*-butyl)phenyl)-2-oxoethylidene)benzo[*d*]thiazol-3(2*H*)-yl)methyl)-[1,1'-biphenyl]-4-yl)-2-(4'-(((*Z*)-2-(2-(4-methoxyphenyl)-2-oxoethylidene)benzo[*d*]thiazol-3(2*H*)-yl)methyl)-[1,1'-biphenyl]-4-yl)-2-(4'-(((*Z*)-2-(2-oxo-2-(4-(trifluoromethyl)phenyl)ethylidene)benzo[*d*]thiazol-3(2*H*)-yl)methyl)-[1,1'-biphenyl]-4-yl)vinyl)-[1,1'-biphenyl]-4-yl)methyl)benzo[*d*]thiazol-2(3*H*)-ylidene)acetyl)benzonitrile (5v) (75 MHz, acetone-d_6/CS_2 5:1, 293 K)



^{1}H NMR spectrum (2*Z*,2'*Z*)-2,2'-((((1,10-phenanthrolin-3,8-diyl)bis(4,1-phenylene))bis(methylene))bis(benzo[*d*]thiazol-3(3*H*)-yl-2(3*H*)-ylidene))bis(1-(4-(dimethylamino)phenyl)ethan-1-one) (5w) (500 MHz, DMSO-d$_6$, 293 K)



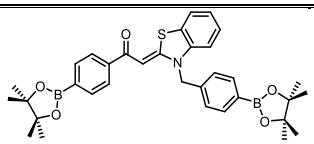
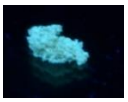
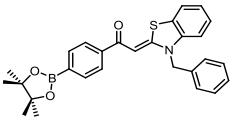
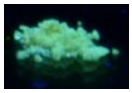
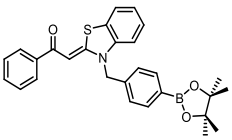
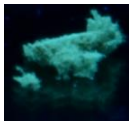
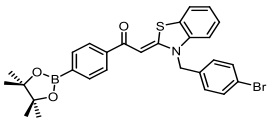
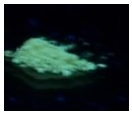
^{13}C NMR spectrum (2*Z*,2'*Z*)-2,2'-((((1,10-phenanthrolin-3,8-diyl)bis(4,1-phenylene))bis(methylene))bis(benzo[*d*]thiazol-3(3*H*)-yl-2(3*H*)-ylidene))bis(1-(4-(dimethylamino)phenyl)ethan-1-one) (5w) (125 MHz, DMSO-d$_6$, 293 K)



5 Overview of photophysical properties of borylated aroyl-*S,N*-ketene acetals

All solution spectra were recorded in ethanol or in ethanol/water mixtures at T = 298 K, the excitation wavelengths λ_{exc} for the AIE-titration studies and the emission spectra in solution were determined from the absorption maxima λ_{max} of this compound, the excitation wavelength for the solid state emission spectra was determined from solid state excitation spectra. The dye concentration of the solution for absorption measurements was $c = 10^{-5}$ M and the dye concentration of the ethanol/water mixtures for AIE measurements was $c = 10^{-7}$ M.

Table S8: Photophysical properties of borylated aroyl-*S,N*-ketene acetal.

Entry	Compound	$\lambda_{max(abs.)}$ solution [nm] (ε [L·mol^{-1}·cm^{-1}])[a]	$\lambda_{max(em.)}$ solid state [nm][b]	solid state picture[c]
1		255 (26800), 390 (36500)	489	
2		383 (35700)	455, 525	
3		261 (42300), 390 (37400)	497	
4		390 (32600)	500	

[a]: measured in ethanol, T = 298 K, $c = 10^{-5}$ M, [b]: T = 298 K, $\lambda_{exc} = \lambda_{abs,max}$, [c]: pictures taken under UV-light (λ_{exc} = 365 nm).

6 Absorption and emission spectra

6.1 Absorption and emission spectra of borylated aroyl-*S,N*-ketene acetals

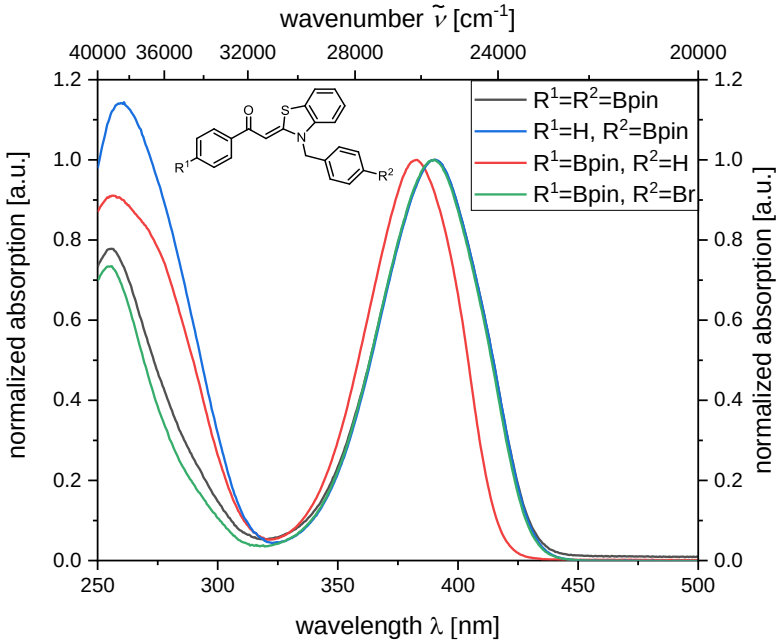


Figure S1: Normalized UV/Vis absorption bands of borylated aroyl-*S,N*-ketene acetals.

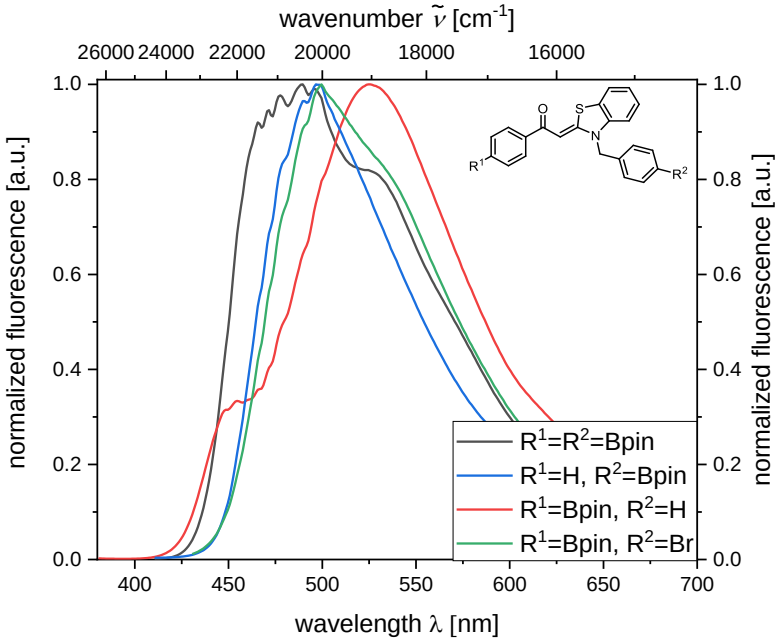


Figure S2: Normalized solid state emission bands of borylated aroyl-*S,N*-ketene acetals.

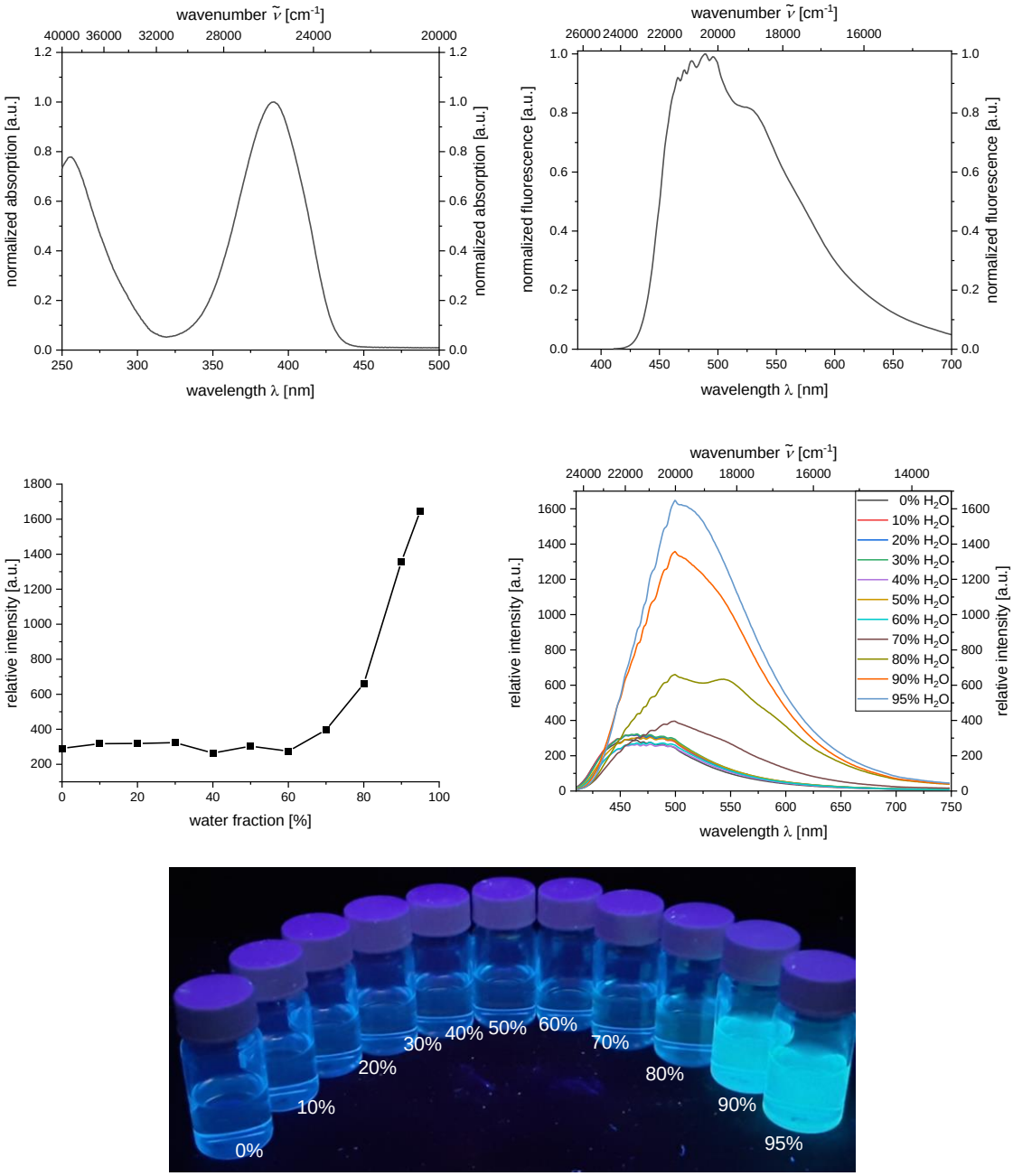


Figure S3: Absorption spectrum of compound **4p** in ethanol (top, left), solid state emission spectrum (top, right), and AIE-induced changes in emission (center, left), AIE-related emission spectra of compound **4p** (center, right) and photographs of solutions of dye **4p** in ethanol/water mixtures of increasing water content (bottom). The latter spectra were measured in ethanol/water mixtures of varying water content.

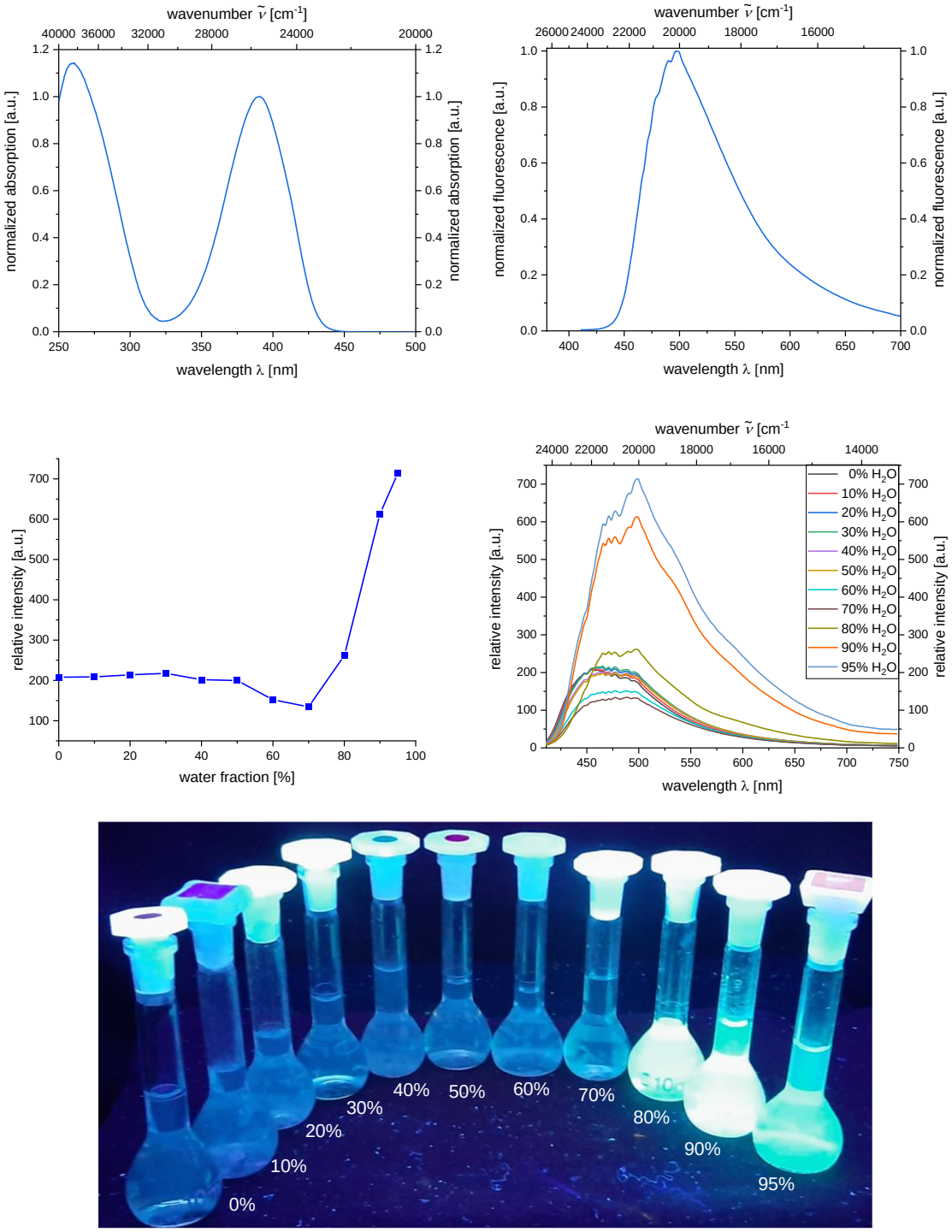


Figure S4: Absorption spectrum of compound (*Z*)-1-phenyl-2-(3-(4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)benzyl)benzo[*d*]thiazol-2(3*H*)-ylidene)ethan-1-one in ethanol (top, left), solid state emission spectrum (top, right), and AIE-induced changes in emission (center, left), AIE-related emission spectra of compound (*Z*)-1-Phenyl-2-(3-(4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)benzyl)benzo[*d*]thiazol-2(3*H*)-ylidene)ethan-1-one (center, right) and photographs of solutions of dye (*Z*)-1-Phenyl-2-(3-(4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)benzyl)benzo[*d*]thiazol-2(3*H*)-ylidene)ethan-1-one in ethanol/water mixtures of increasing

water content (bottom). The latter spectra were measured in ethanol/water mixtures of varying water content.

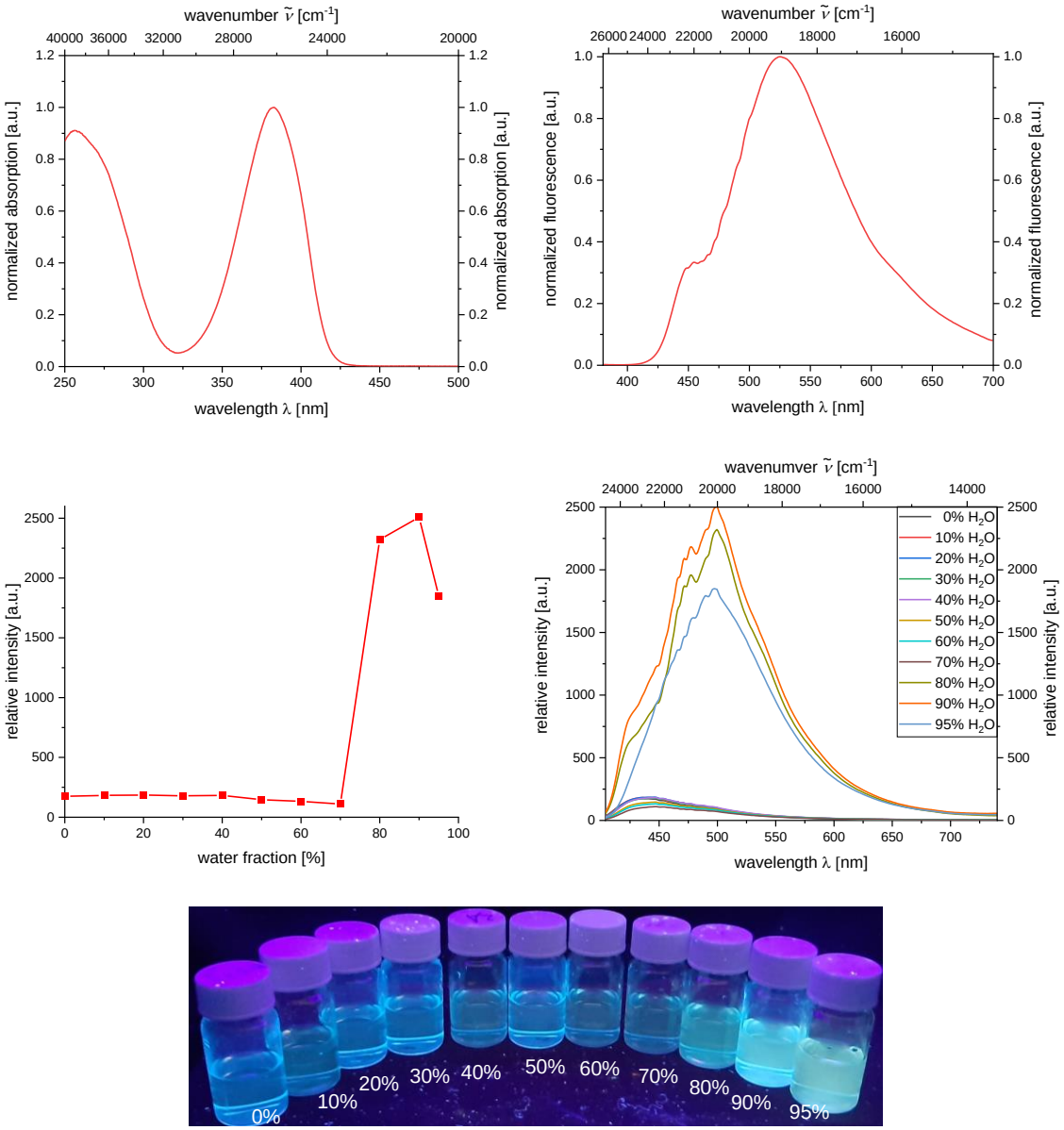


Figure S5: Absorption spectrum of compound (*Z*)-2-(3-benzylbenzo[*d*]thiazol-2(3*H*)-ylidene)-1-(4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)phenyl)ethan-1-one in ethanol (top, left), solid state emission spectrum (top, right), and AIE-induced changes in emission (center, left), AIE-related emission spectra of compound (*Z*)-2-(3-benzylbenzo[*d*]thiazol-2(3*H*)-ylidene)-1-(4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)phenyl)ethan-1-one (center, right) and photographs of solutions of dye (*Z*)-2-(3-benzylbenzo[*d*]thiazol-2(3*H*)-ylidene)-1-(4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)phenyl)ethan-1-one in ethanol/water mixtures of increasing water content (bottom). The latter spectra were measured in ethanol/water mixtures of varying water content.

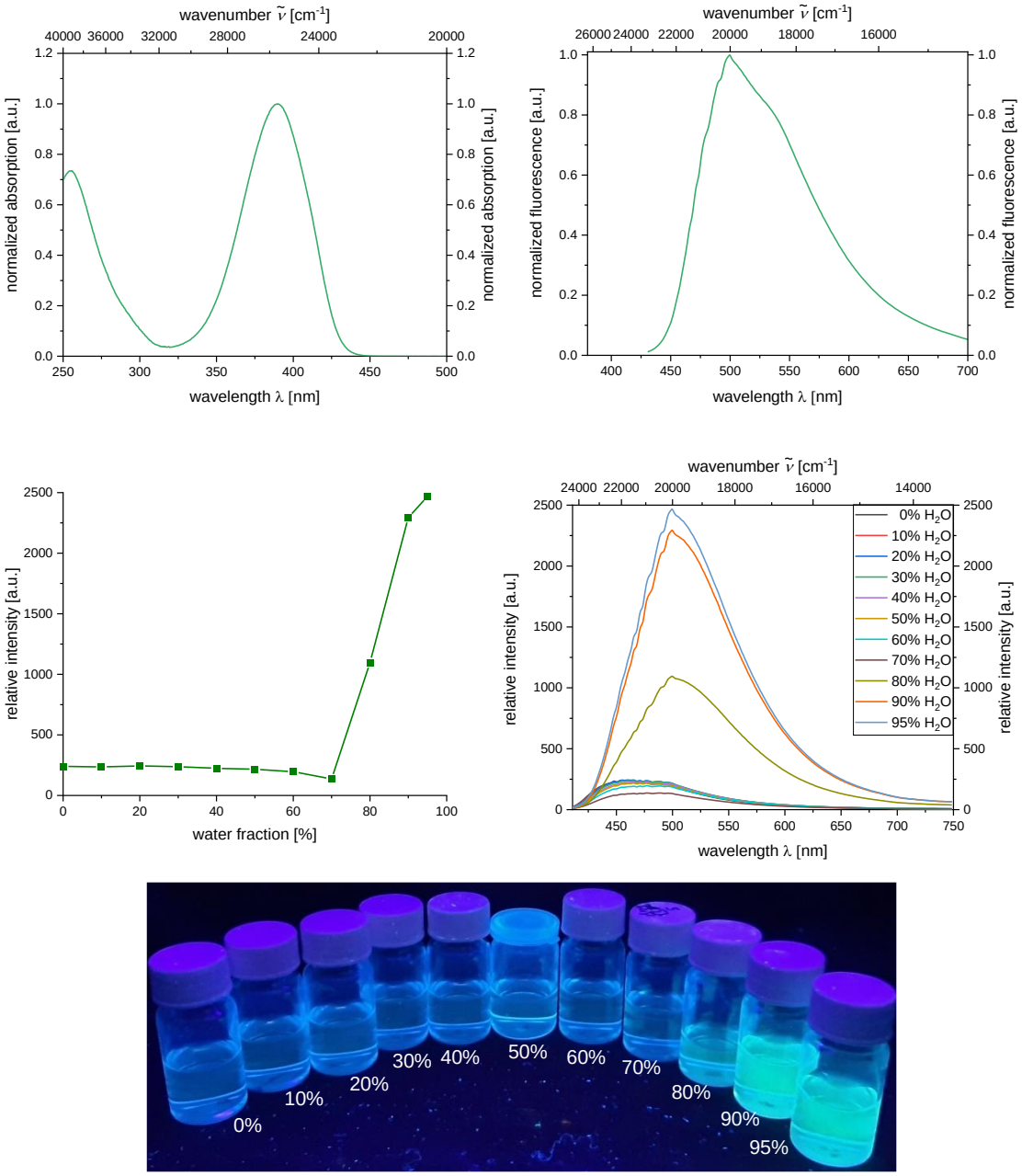


Figure S6: Absorption spectrum of compound (*Z*)-2-(3-(4-bromobenzyl)benzo[*d*]thiazol-2(3*H*)-ylidene)-1-(4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)phenyl)ethan-1-one in ethanol (top, left), solid state emission spectrum (top, right), and AIE-induced changes in emission (center, left), AIE-related emission spectra of compound (*Z*)-2-(3-(4-bromobenzyl)benzo[*d*]thiazol-2(3*H*)-ylidene)-1-(4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)phenyl)ethan-1-one (center, right) and photographs of solutions of dye (*Z*)-2-(3-(4-bromobenzyl)benzo[*d*]thiazol-2(3*H*)-ylidene)-1-(4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)phenyl)ethan-1-one in ethanol/water mixtures of increasing water content (bottom). The latter spectra were measured in ethanol/water mixtures of varying water content.

7 Overview of photophysical properties of bridged aroyl-*S,N*-ketene acetals 5

All solution spectra were recorded in ethanol or in ethanol/water mixtures at T = 298 K, the excitation wavelengths λ_{exc} for the AIE-titration studies and the emission spectra in solution were determined from the absorption maxima λ_{max} of this compound, the excitation wavelength for the solid state emission spectra was determined from solid state excitation spectra. The dye concentration of the solution for absorption measurements was $c = 10^{-5}$ M and the dye concentration of the ethanol/water mixtures for AIE measurements was $c = 10^{-7}$ M.

Table S9: Photophysical properties of bridged aroyl-*S,N*-ketene acetals **5**.

Entry	Example **5**	$\lambda_{max(abs.)}$ solution [nm] (ε [L·mol^{-1}·cm^{-1}])[a]	$\lambda_{max(em.)}$ solution [nm][b]	*Stokes*-Shift[c[$\tilde{\nu}$ [cm^{-1}]	$\lambda_{max(em.)}$ solid state [nm][d]
1	**5a**	280 (30000) 389 (31300)	-	-	536
2	**5b**	274 (24800) 391 (15900)	-	-	-
3	**5c**	254 (60700) 389 (47700)	436	2800	563
4	**5d**	386 (54600)	441	3200	559
5	**5e**	254 (37000) 390 (24300)	435	2700	533

[a]: measured in ethanol, T = 298 K, c(**5**) = 10^{-5} M, [b]: measured in ethanol, T = 298 K, c(**5**) = 10^{-7} M, $\lambda_{exc} = \lambda_{abs,max}$ if not otherwise specified, [c]: $\tilde{\nu} = \tilde{\nu}_{max(Abs.)} - \tilde{\nu}_{max(Em.)}$, [d]: T = 298 K, $\lambda_{exc} = \lambda_{abs,max}$, [e]: $\lambda_{exc} \approx$ 291 nm, [f]: $\lambda_{exc} \approx$ 395 nm.

Table S9: Photophysical properties of bridged aroyl-*S,N*-ketene acetals **5**.

Entry	Example **5**	$\lambda_{max(abs.)}$ solution [nm] (ε [L·mol^{-1}·cm^{-1}])[a]	$\lambda_{max(em.)}$ solution [nm][b]	*Stokes*-Shift[c[$\tilde{\nu}$ [cm^{-1}]	$\lambda_{max(em.)}$ solid state [nm][d]
6	**5f**	257 (70400) 388 (59900)	441	3100	-
7	**5g**	258 (74800) 389 (76200)	436	2800	-
8	**5h**	267 (46000) 392 (20651)	446	3100	-
9	**5i**	389 (26800)	439	2900	524
10	**5j**	272 (51800) 387 (34400)	500	5800	566
11	**5k**	257 (73000) 391 (25000)	430	2300	540
12	**5l**	273 (21600) 388 (17700)	437	2900	551
13	**5m**	258 (23300) 393 (18200)	479	4600	455
14	**5n**	274 (44100) 328 (28617) 388 (30900)	435	2800	570
15	**5o**	256 (61200) 291 (44500) 395 (34000)	382[e] 501[e] 520[f]	8100[e] 6100[f]	544

[a]: measured in ethanol, T = 298 K, c(**5**) = 10^{-5} M, [b]: measured in ethanol, T = 298 K, c(**5**) = 10^{-7} M, $\lambda_{exc} = \lambda_{abs,max}$ if not otherwise specified, [c]: $\tilde{\nu} = \tilde{\nu}_{max(Abs.)} - \tilde{\nu}_{max(Em.)}$, [d]: T = 298 K, $\lambda_{exc} = \lambda_{abs,max}$, [e]: $\lambda_{exc} \approx$ 291 nm, [f]: $\lambda_{exc} \approx$ 395 nm.

Table S9: Photophysical properties of bridged aroyl-*S,N*-ketene acetals **5**.

Entry	Example **5**	$\lambda_{max(abs.)}$ solution [nm] (ε [L·mol^{-1}·cm^{-1}])[a]	$\lambda_{max(em.)}$ solution [nm][b]	*Stokes*-Shift[c[$\tilde{\nu}$ [cm^{-1}]	$\lambda_{max(em.)}$ solid state [nm][d]
16	**5p**	269 (48300) 389 (28000)	465	4200	560
17	**5q**	272 (60000) 391 (17000)	448	3300	577
18	**5r**	271 (68800) 388 (14000)	437	2900	515
19	**5s**	269 (44800) 391 (56300)	455	3600	559
20	**5t**	400 (18400)	500	5000	552
21	**5u**	385 (8700)	438 498	3100	545
22	**5v**	384 (22500)	-	-	550
23	**5w**	274 (26300) 373 (25400)	455	4800	571

[a]: measured in ethanol, T = 298 K, c(**5**) = 10^{-5} M, [b]: measured in ethanol, T = 298 K, c(**5**) = 10^{-7} M, $\lambda_{exc} = \lambda_{abs,max}$ if not otherwise specified, [c]: $\tilde{\nu} = \tilde{\nu}_{max(Abs.)} - \tilde{\nu}_{max(Em.)}$, [d]: T = 298 K, $\lambda_{exc} = \lambda_{abs,max}$, [e]: $\lambda_{exc} \approx$ 291 nm, [f]: $\lambda_{exc} \approx$ 395 nm.

8 Absorption and emission spectra

All solution spectra were recorded in ethanol or in ethanol/water mixtures at T = 298 K, the excitation wavelengths λ_{exc} for the AIE-titration studies and the emission spectra in solution were determined from the absorption maxima λ_{max} of this compound, the excitation wavelength for the solid state emission spectra was determined from solid state excitation spectra. The dye concentration of the solution for absorption measurements was c(**5**) = 10^{-5} M and the dye concentration of the ethanol/water mixtures for AIE measurements was c(**5**) = 10^{-7} M.

8.1 Absorption and emission spectra of bridged aroyl-*S,N*-ketene acetals 5

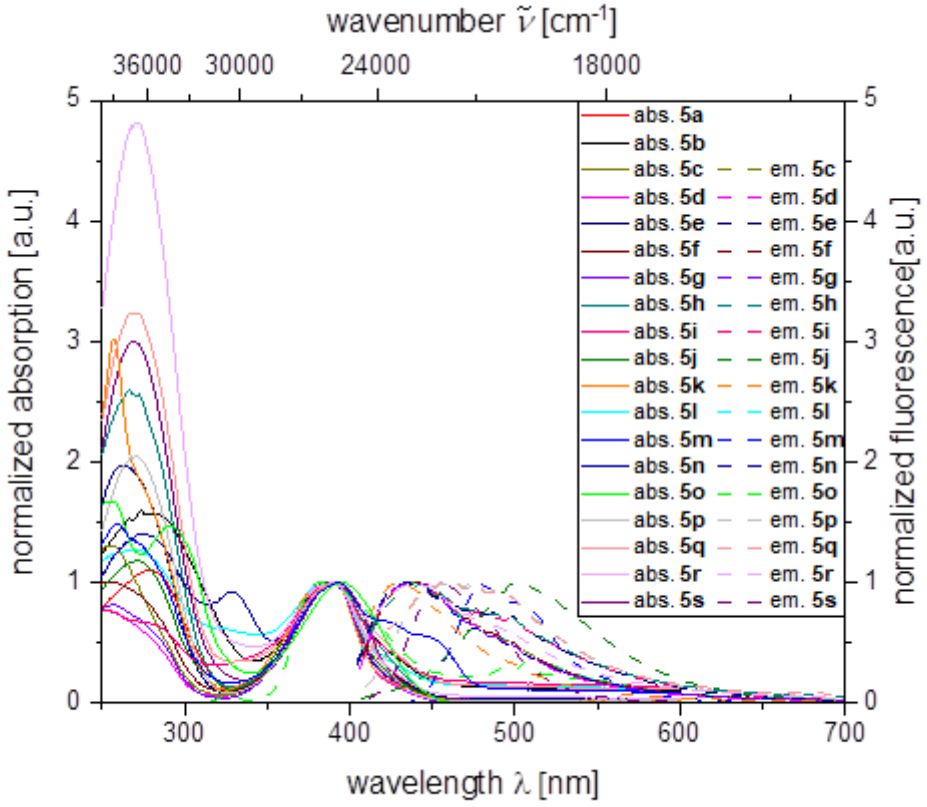


Figure S7: Selected, normalized UV/Vis absorption and emission bands of bridged aroyl-*S,N*-ketene acetals **5**.

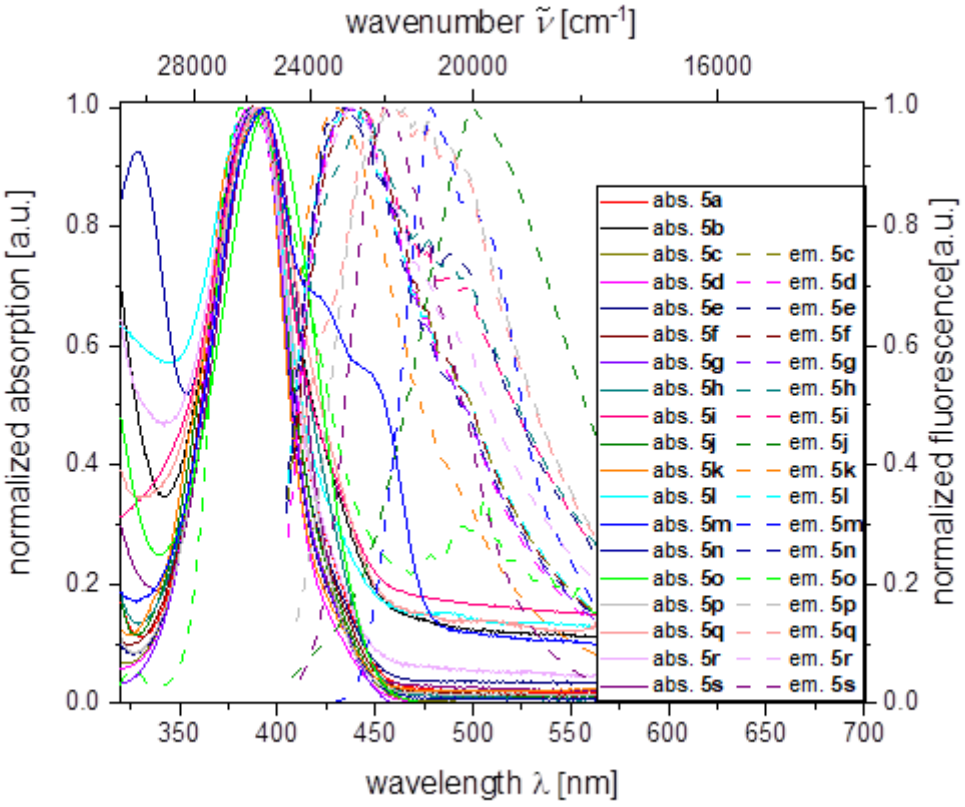


Figure S8: Selected, normalized UV/Vis absorption and emission bands of bridged aroyl-*S,N*-ketene acetals **5** (zoomed in).

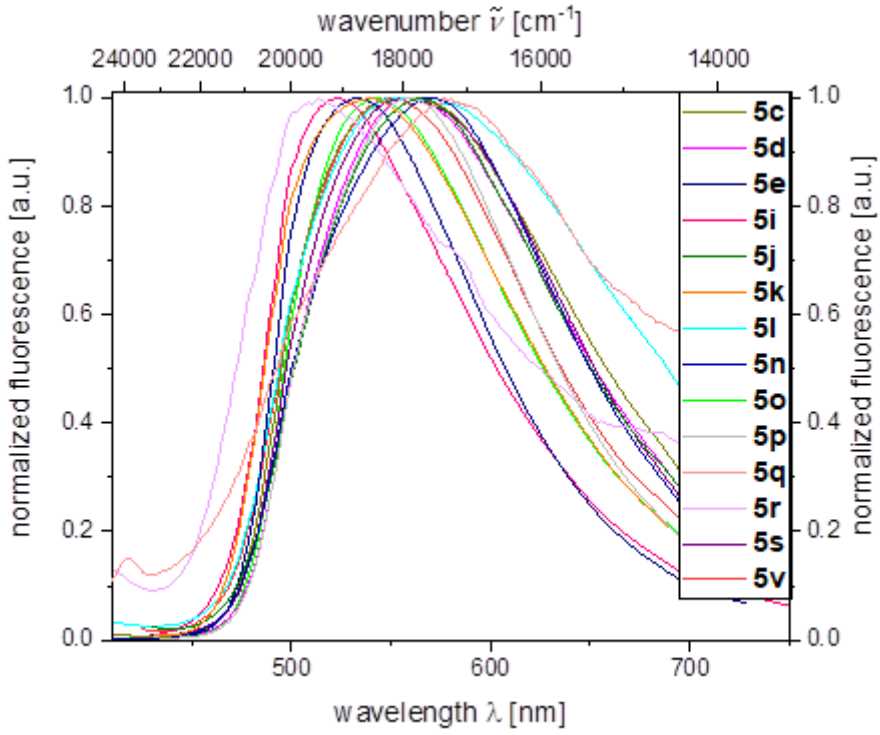


Figure S9: Selected, normalized solid-state emission bands of bridged aroyl-*S,N*-ketene acetals **5**.

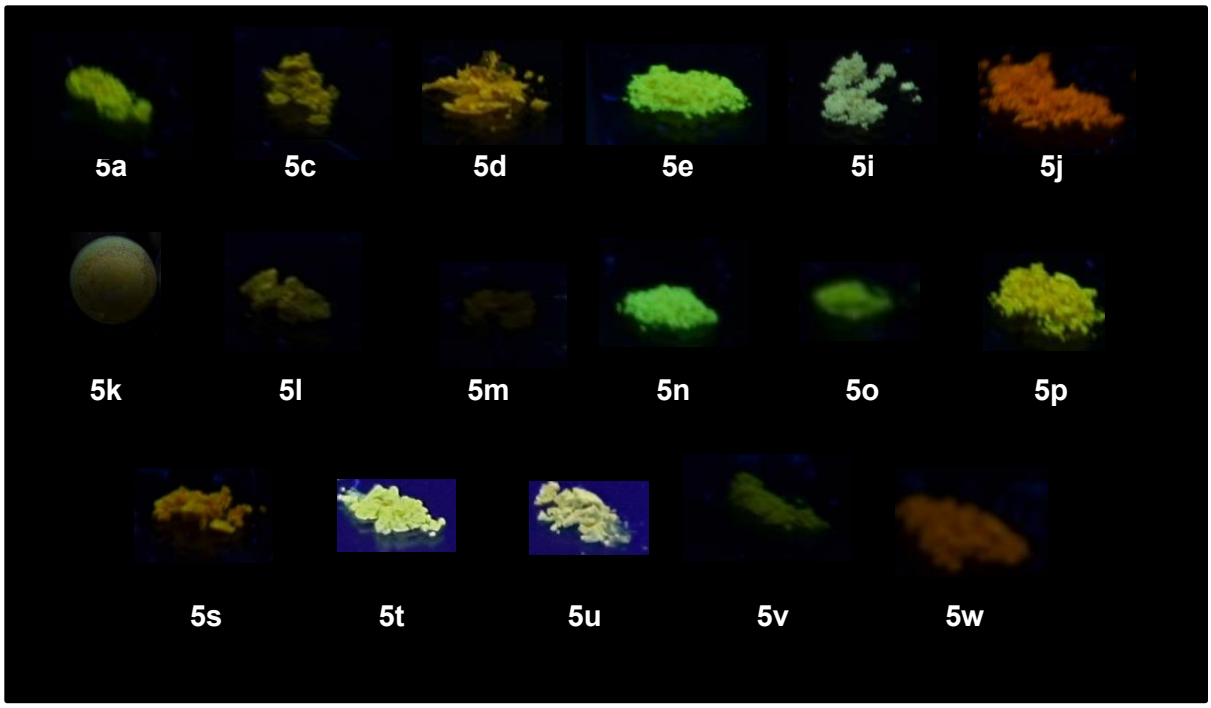
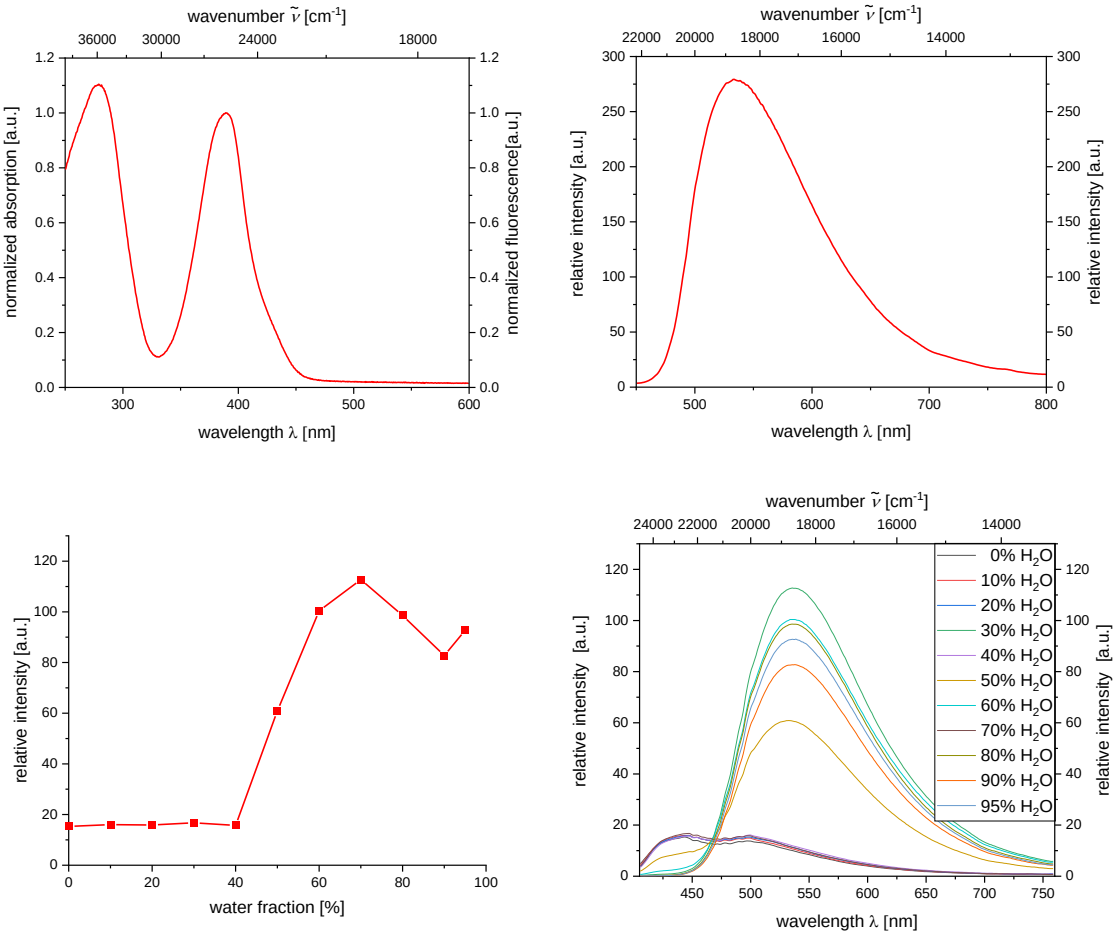


Figure S10: Photographs of solids of selected dyes **5**.



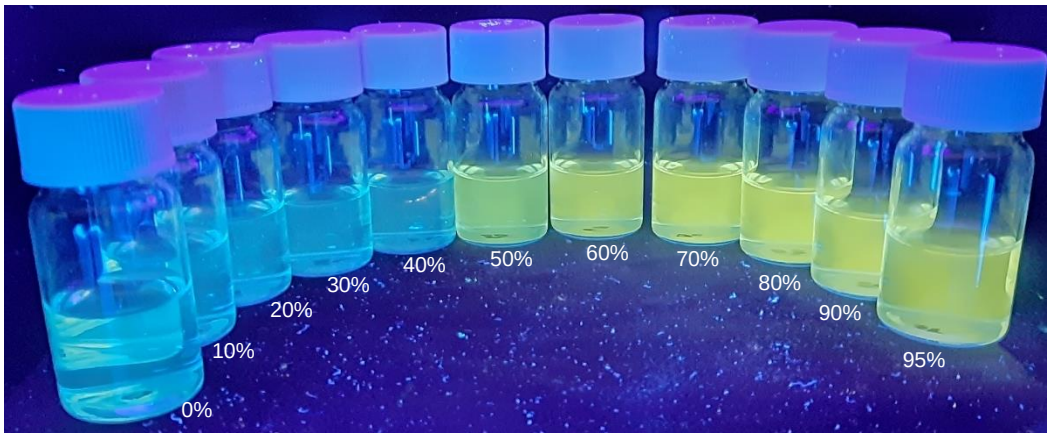


Figure S11: Absorption spectrum of **5a** in ethanol (top, left), solid state emission spectrum (top, right), and AIE-induced changes in emission (center, left), AIE-related emission spectra of compound **5a** (center, right) and photographs of solutions of dye **5a** in ethanol/water mixtures of increasing water content (bottom). The latter spectra were measured in ethanol/water mixtures of varying water content.

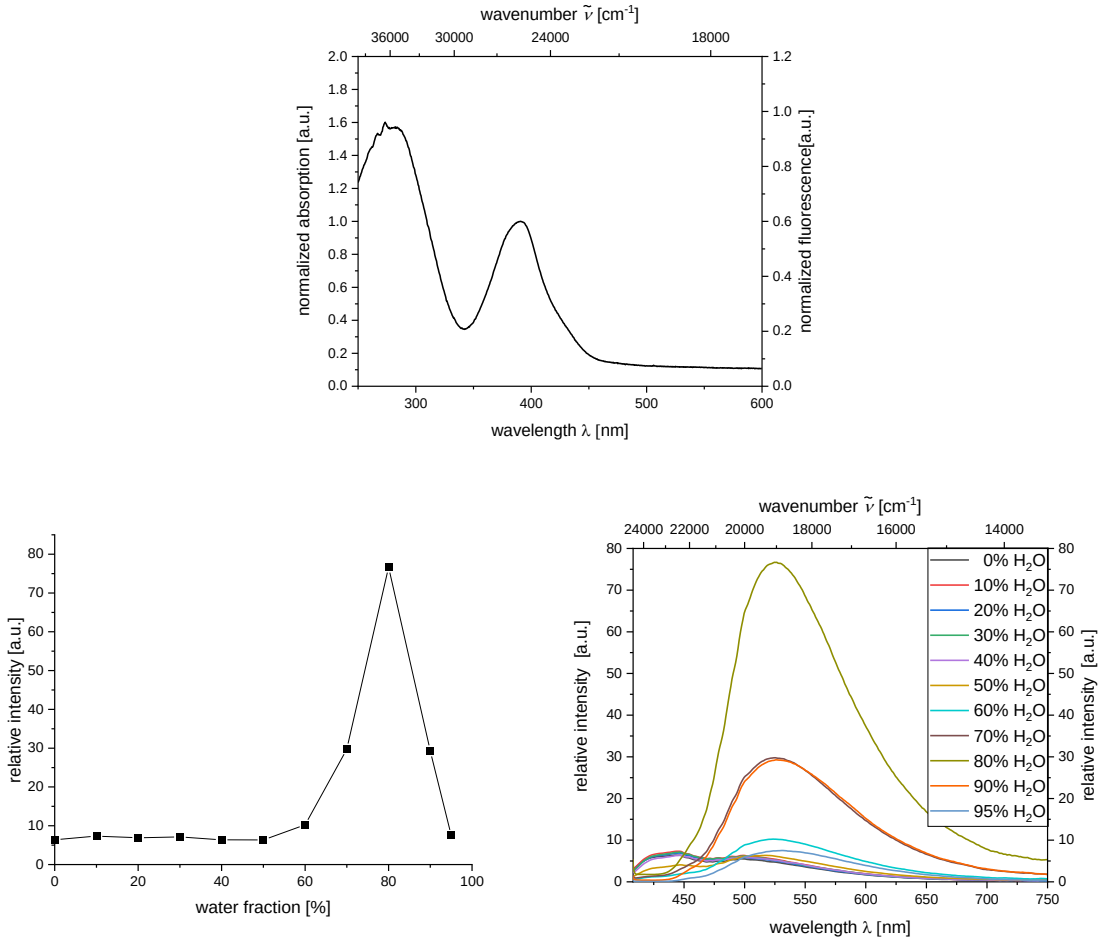


Figure S12: Absorption spectrum of **5b** in ethanol (top), and AIE-induced changes in emission (bottom, left), AIE-related emission spectra of compound **5b** (bottom, right).

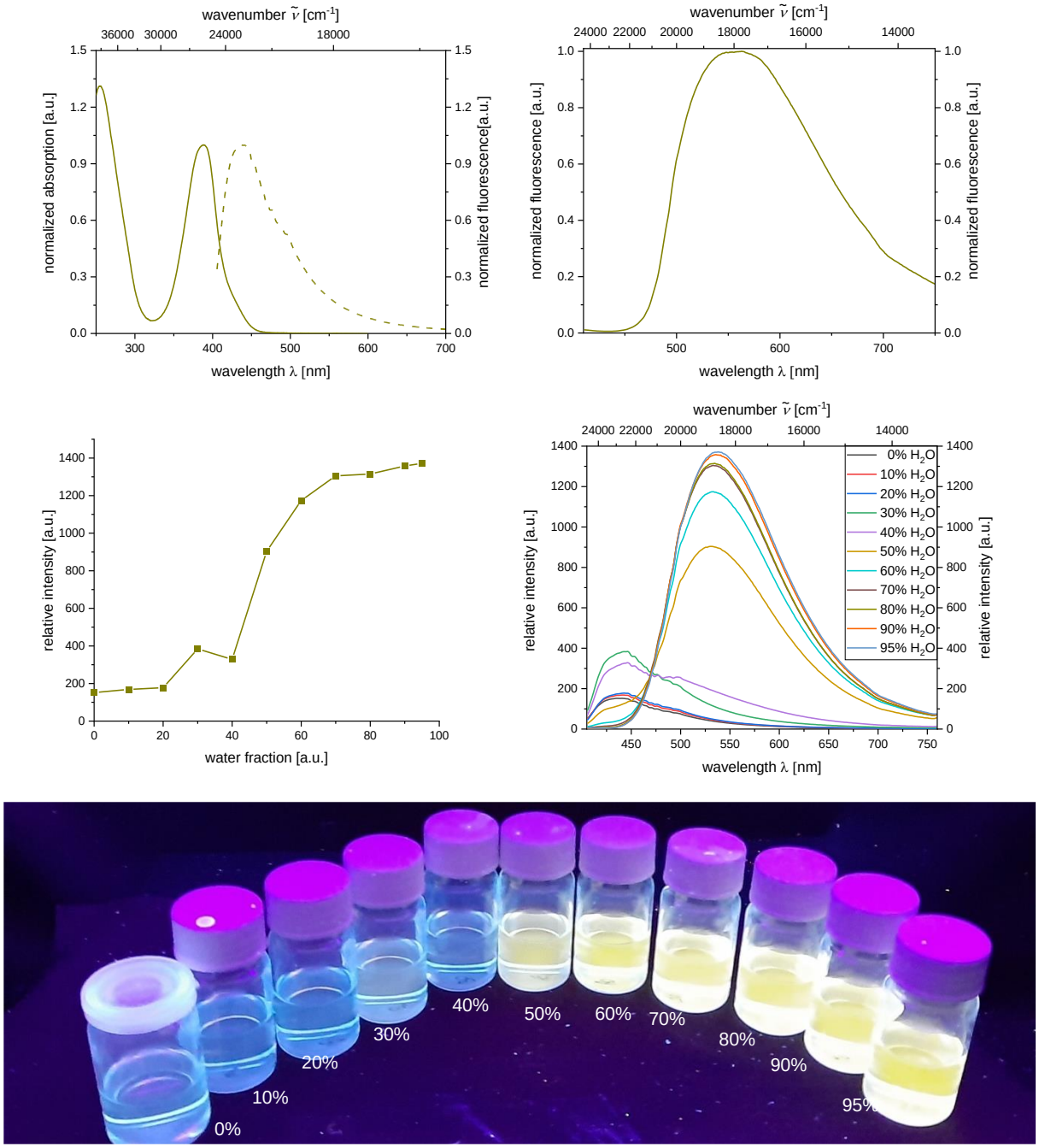
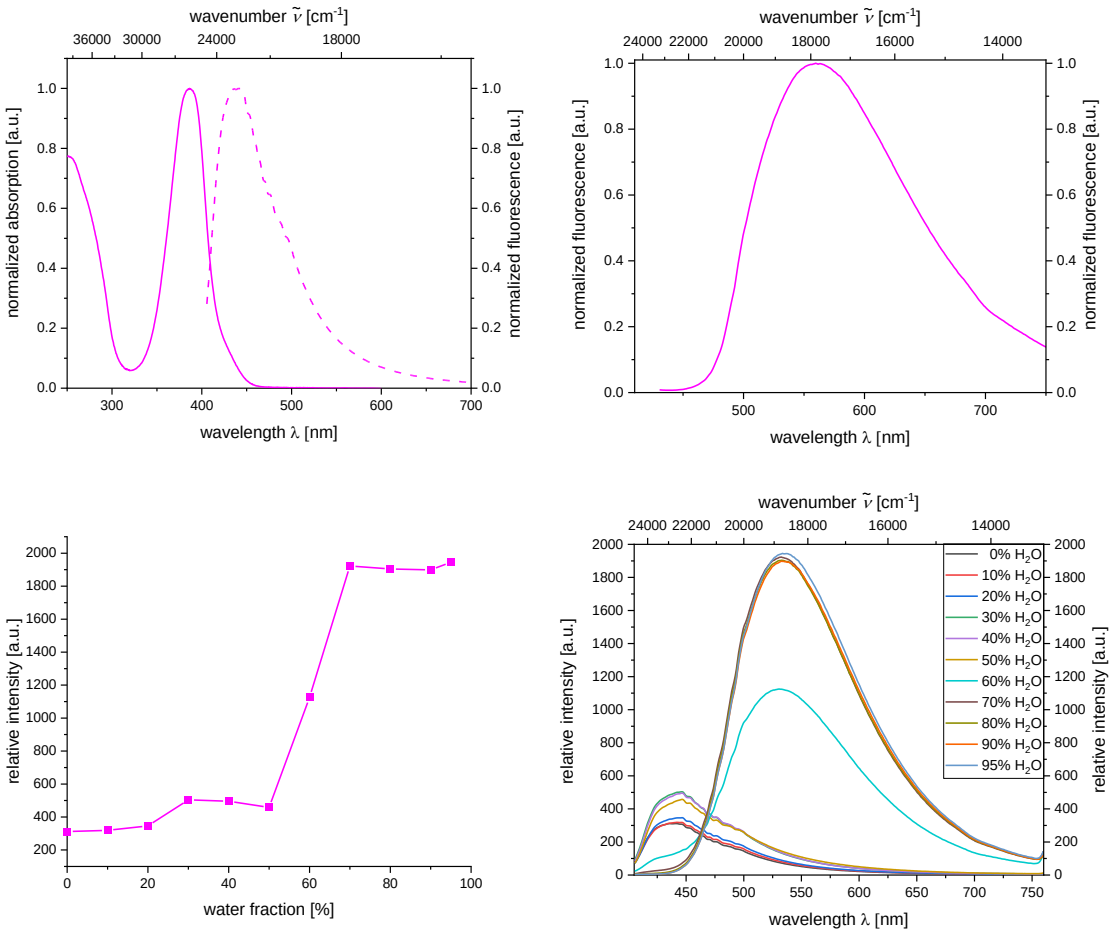


Figure S13: Absorption and emission spectrum of **5c** in ethanol (top, left), solid state emission spectrum (top, right), and AIE-induced changes in emission (center, left), AIE-related emission spectra of compound **5c** (center, right) and photographs of solutions of dye **5c** in ethanol/water mixtures of increasing water content (bottom). The latter spectra were measured in ethanol/water mixtures of varying water content.



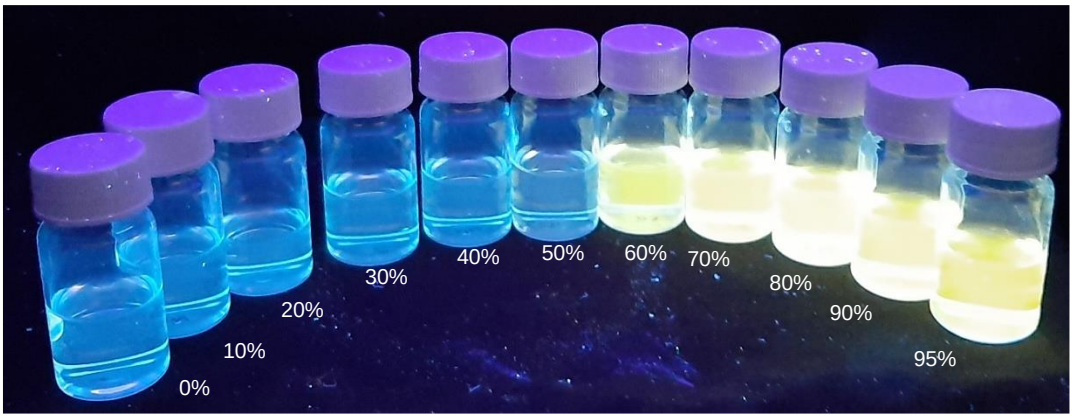


Figure S14: Absorption and emission spectrum of **5d** in ethanol (top, left), solid state emission spectrum (top, right), and AIE-induced changes in emission (center, left), AIE-related emission spectra of compound **5d** (center, right) and photographs of solutions of dye **5d** in ethanol/water mixtures of increasing water content (bottom). The latter spectra were measured in ethanol/water mixtures of varying water content.

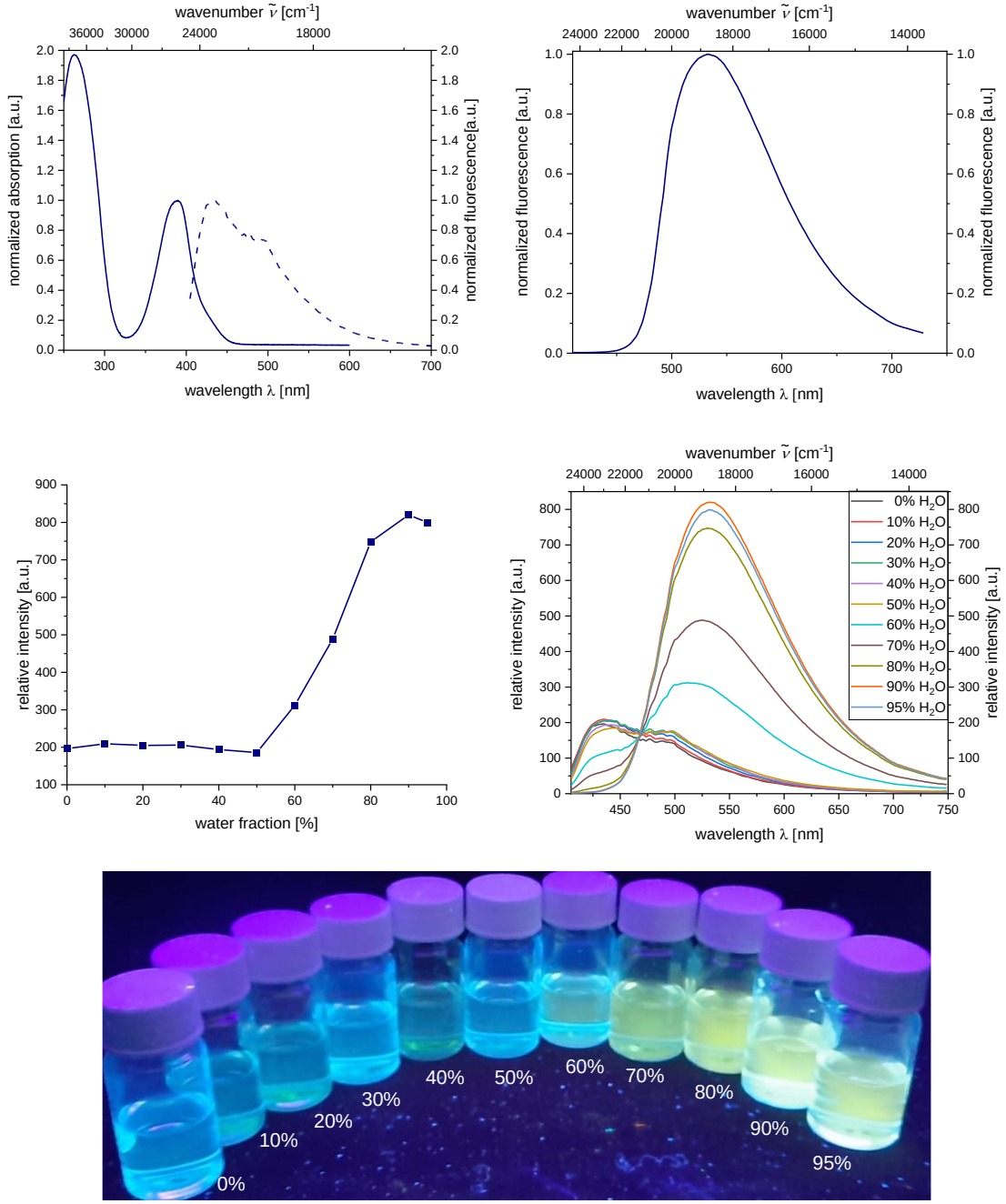


Figure S15: Absorption and emission spectrum of **5e** in ethanol (top, left), solid state emission spectrum (top, right), and AIE-induced changes in emission (center, left), AIE-related emission spectra of compound **5e** (center, right) and photographs of solutions of dye **5e** in ethanol/water mixtures of increasing water content (bottom). The latter spectra were measured in ethanol/water mixtures of varying water content.

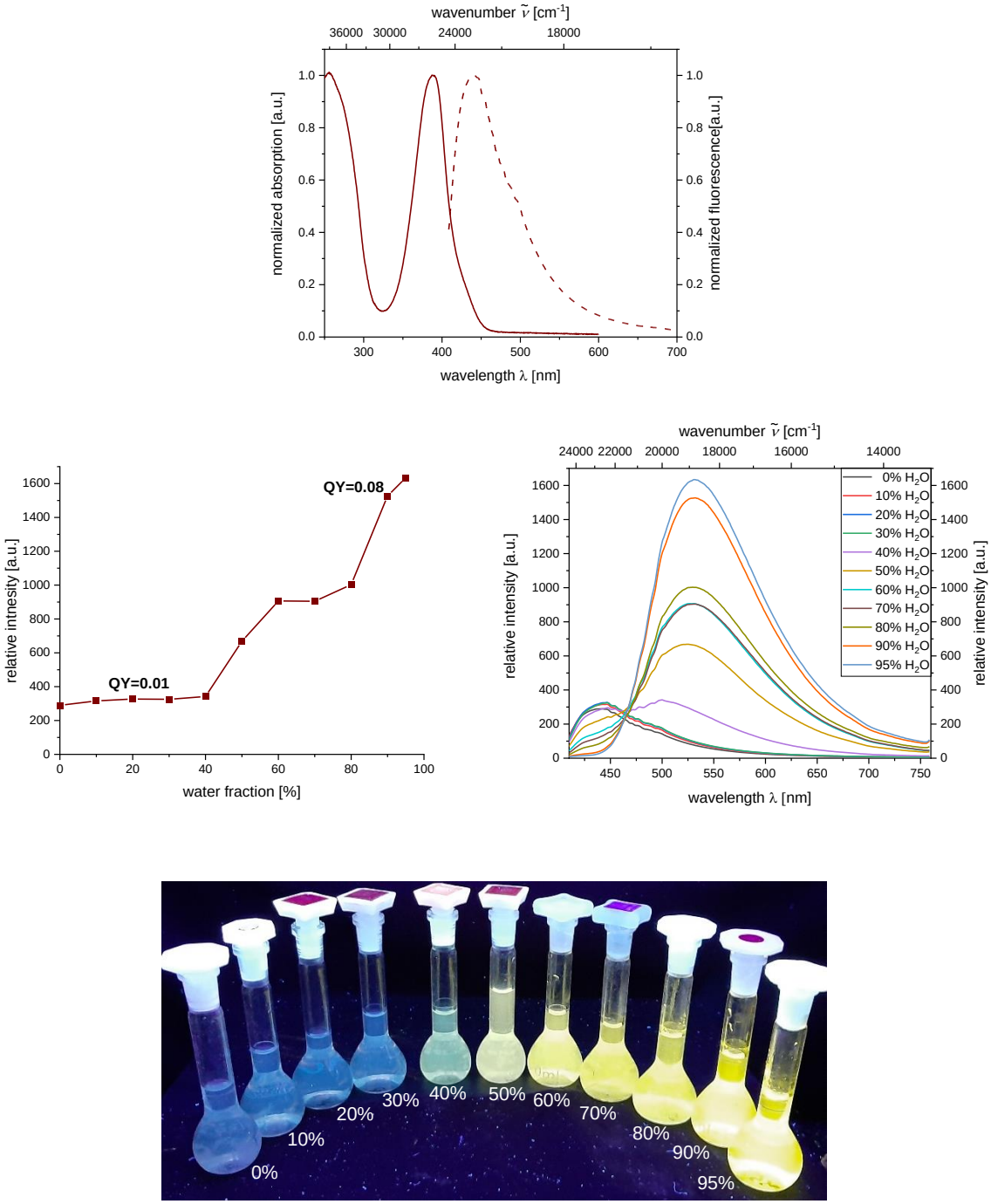


Figure S16: Absorption and emission spectrum of **5f** in ethanol (top), and AIE-induced changes in emission (center, left), AIE-related emission spectra of compound **5f** (center, right) and photographs of solutions of dye **5f** in ethanol/water mixtures of increasing water content (bottom). The latter spectra were measured in ethanol/water mixtures of varying water content.

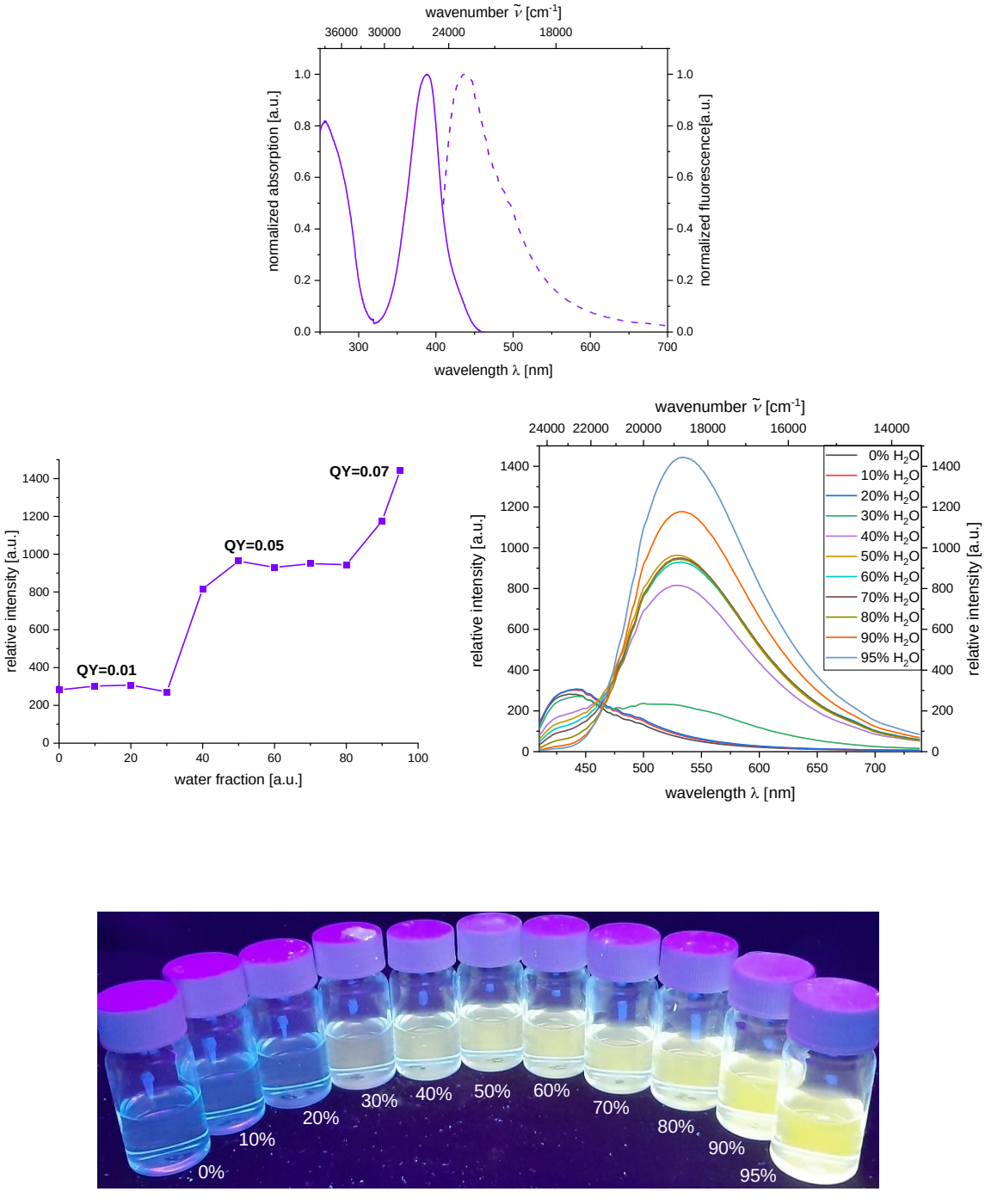


Figure S17: Absorption and emission spectrum of **5g** in ethanol (top), and AIE-induced changes in emission (center, left), AIE-related emission spectra of compound **5g** (center, right) and photographs of solutions of dye **5g** in ethanol/water mixtures of increasing water content (bottom). The latter spectra were measured in ethanol/water mixtures of varying water content.

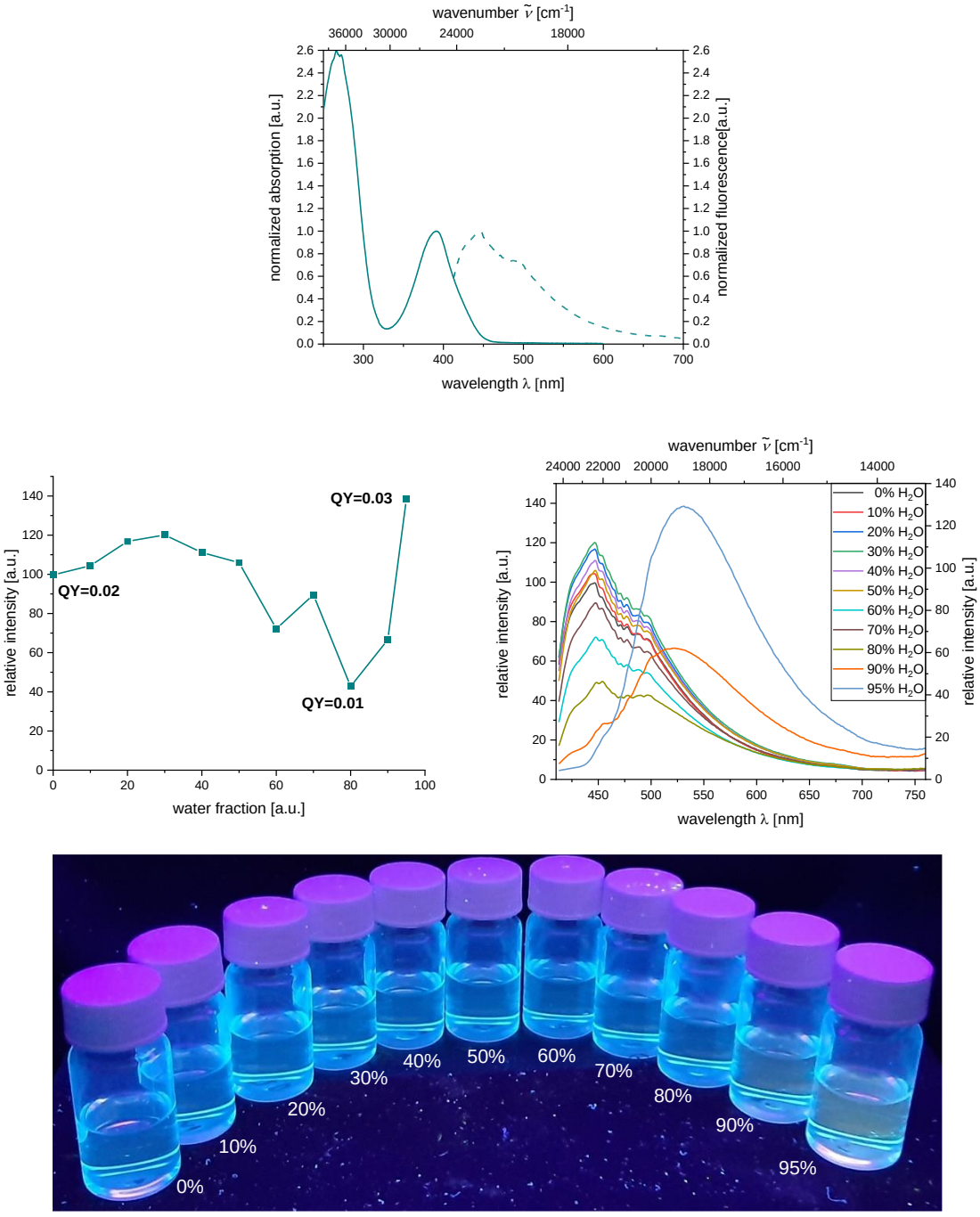
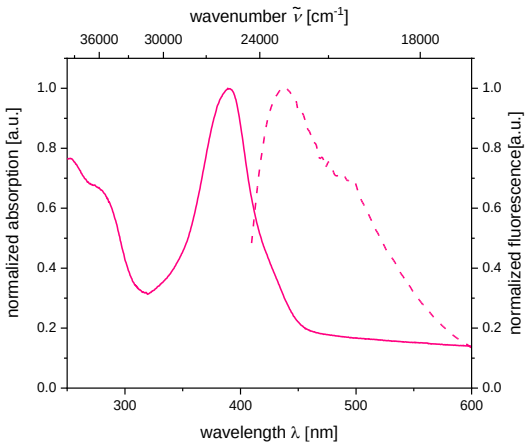


Figure S18: Absorption and emission spectrum of **5h** in ethanol (top), and AIE-induced changes in emission (center, left), AIE-related emission spectra of compound **5h** (center, right) and photographs of solutions of dye **5h** in ethanol/water mixtures of increasing water content (bottom). The latter spectra were measured in ethanol/water mixtures of varying water content.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30000
24000
18000
normalized absorption [a.u.]
normalized fluorescence[a.u.]
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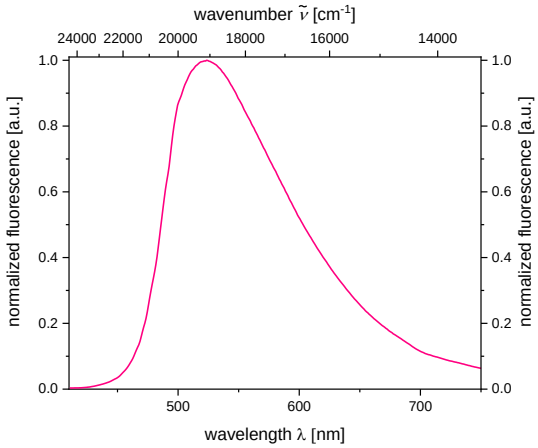
0.2
0.4
0.6
0.8
1.0
300
400
500
600
wavelength λ [nm]


wavenumber $\tilde{\nu}$ [cm^{-1}]
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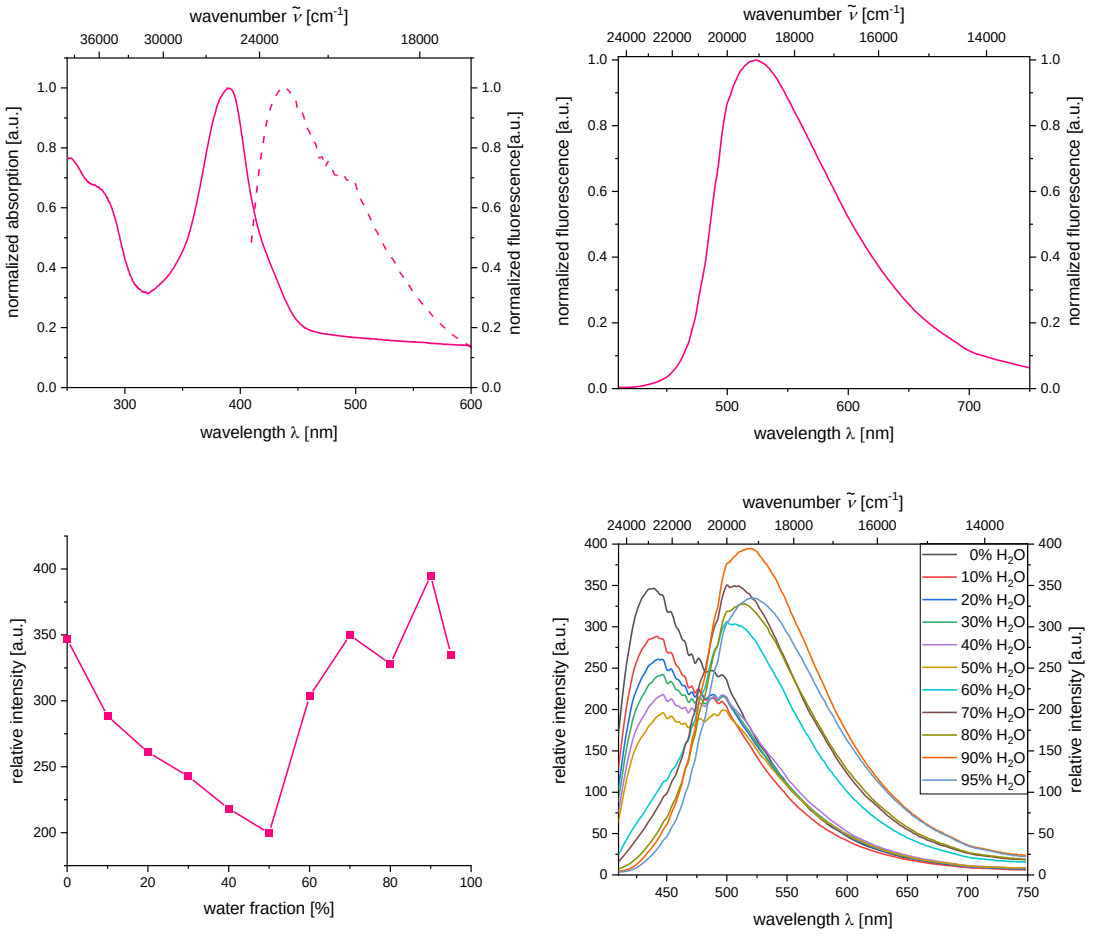
22000
20000
18000
16000
14000
normalized fluorescence [a.u.]
normalized fluorescence [a.u.]
0.0
0.2
0.4
0.6
0.8
1.0
500
600
700
wavelength λ [nm]



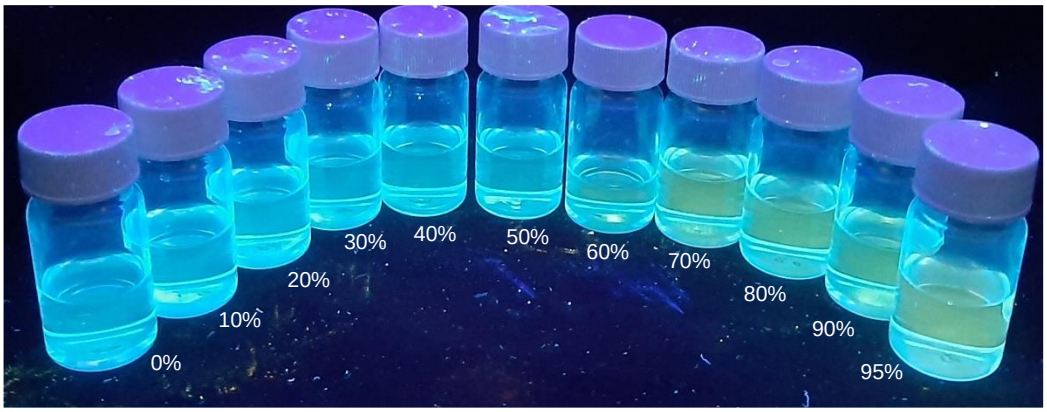
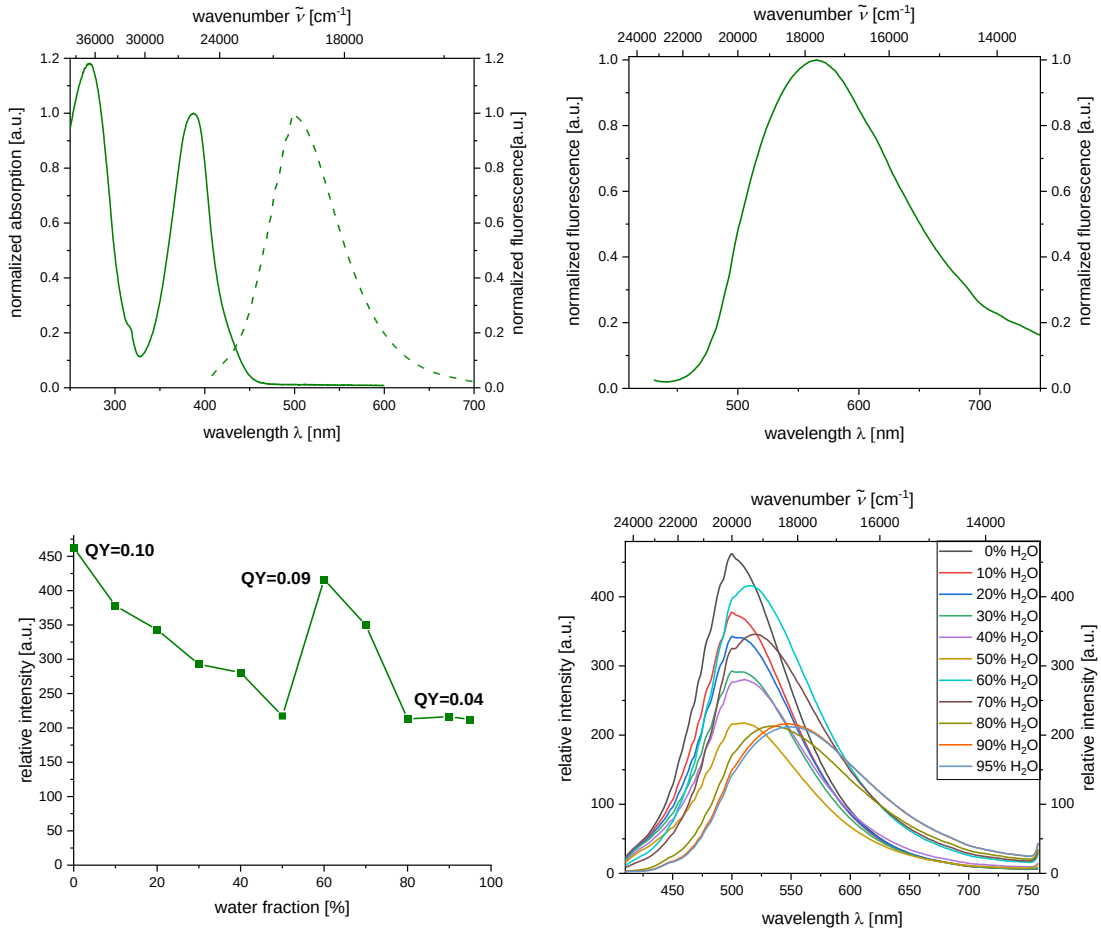


Figure S19: Absorption and emission spectrum of **5i** in ethanol (top, left), solid state emission spectrum (top, right), and AIE-induced changes in emission (center, left), AIE-related emission spectra of compound **5i** (center, right) and photographs of solutions of dye **5i** in ethanol/water mixtures of increasing water content (bottom). The latter spectra were measured in ethanol/water mixtures of varying water content.



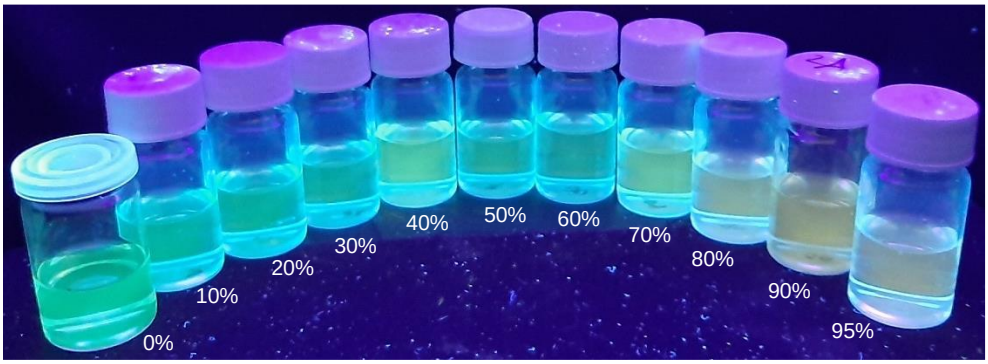


Figure S20: Absorption and emission spectrum of **5j** in ethanol (top, left), solid state emission spectrum (top, right), and AIE-induced changes in emission (center, left), AIE-related emission spectra of compound **5j** (center, right) and photographs of solutions of dye **5j** in ethanol/water mixtures of increasing water content (bottom). The latter spectra were measured in ethanol/water mixtures of varying water content.

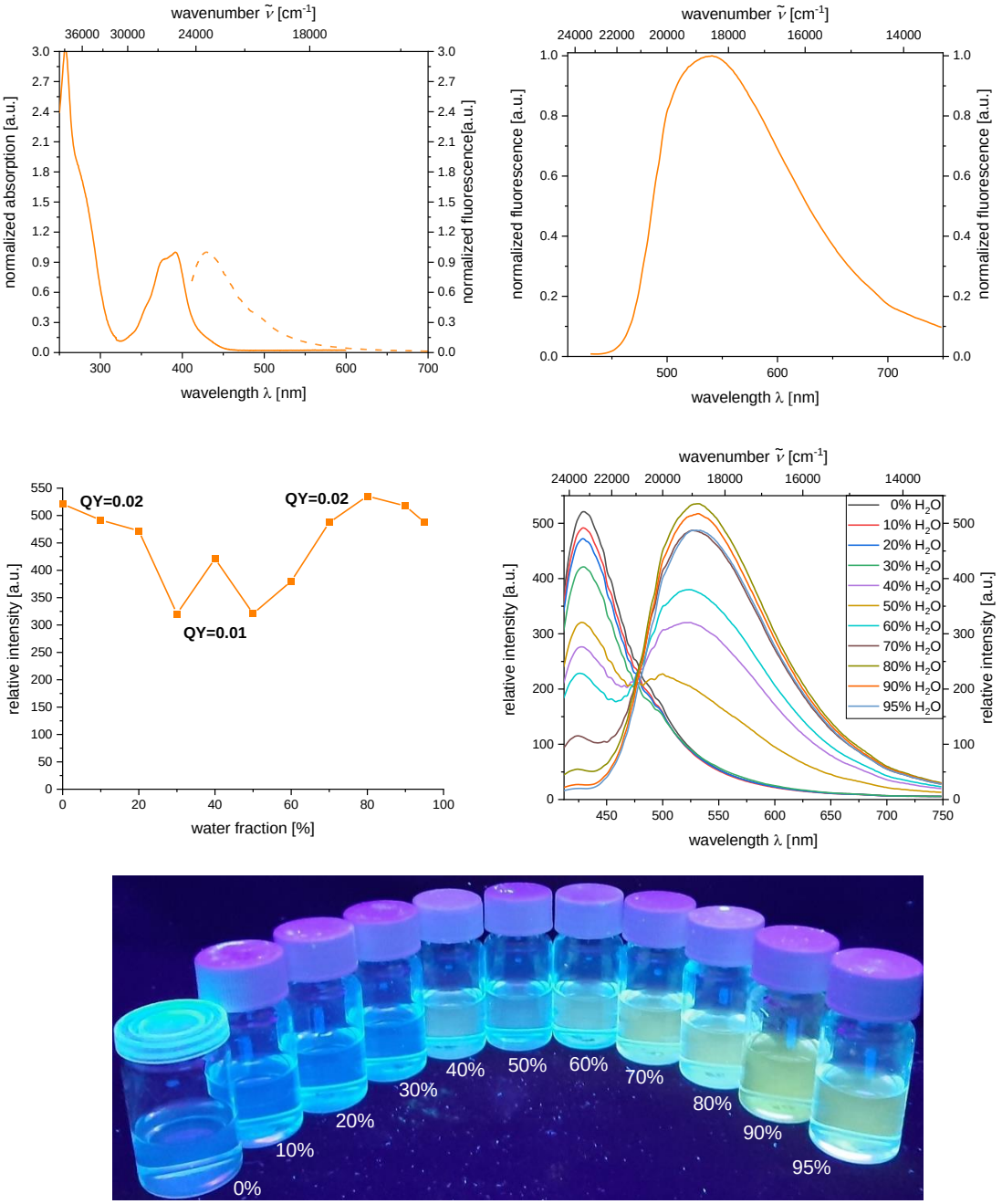


Figure S21: Absorption and emission spectrum of **5k** in ethanol (top, left), solid state emission spectrum (top, right), and AIE-induced changes in emission (center, left), AIE-related emission spectra of compound **5k** (center, right) and photographs of solutions of dye **5k** in ethanol/water mixtures of increasing water content (bottom). The latter spectra were measured in ethanol/water mixtures of varying water content.

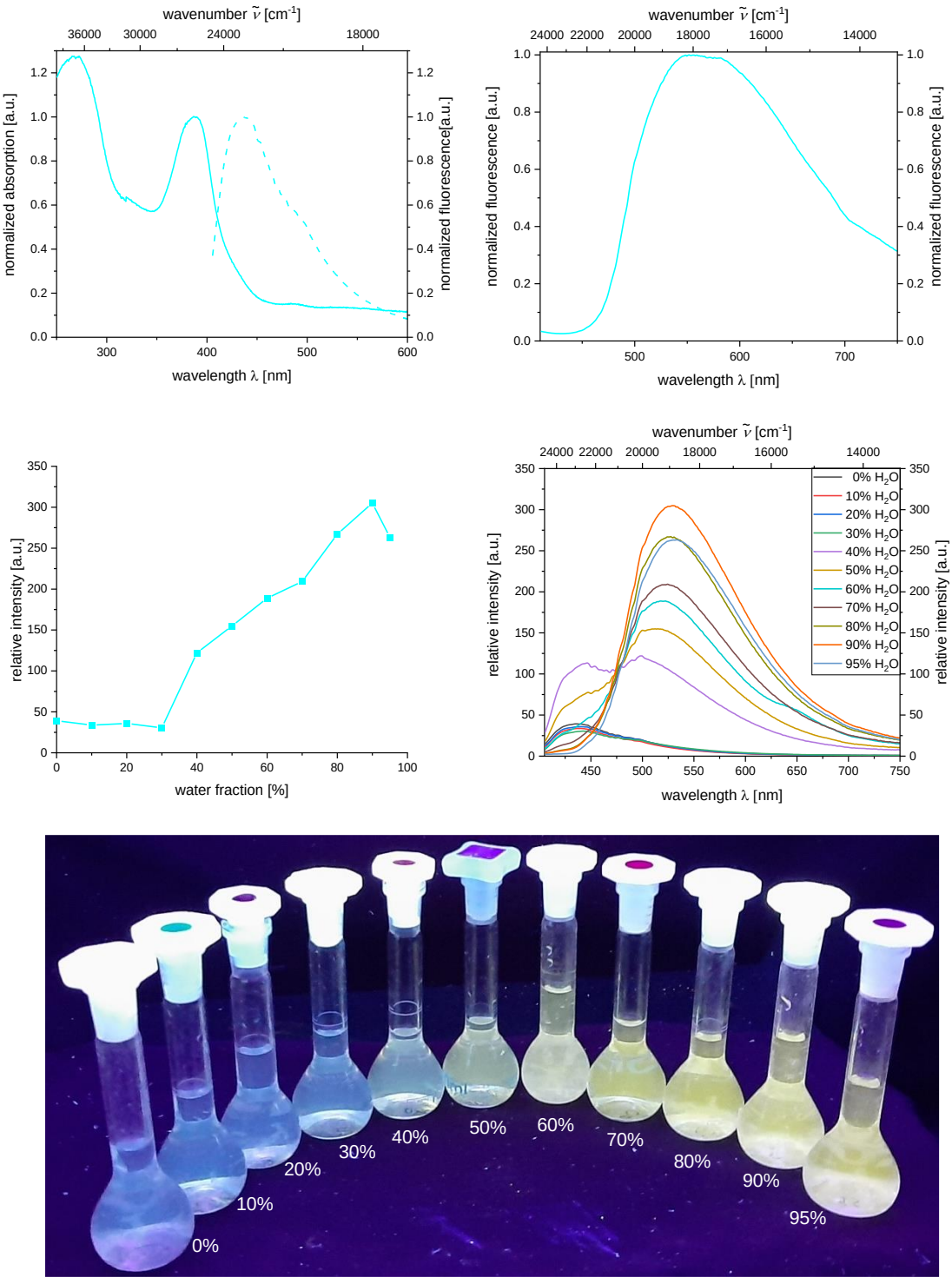


Figure S22: Absorption and emission spectrum of **5l** in ethanol (top, left), solid state emission spectrum (top, right), and AIE-induced changes in emission (center, left), AIE-related emission spectra of compound **5l** (center, right) and photographs of solutions of dye **5l** in ethanol/water mixtures of increasing water content (bottom). The latter spectra were measured in ethanol/water mixtures of varying water content.

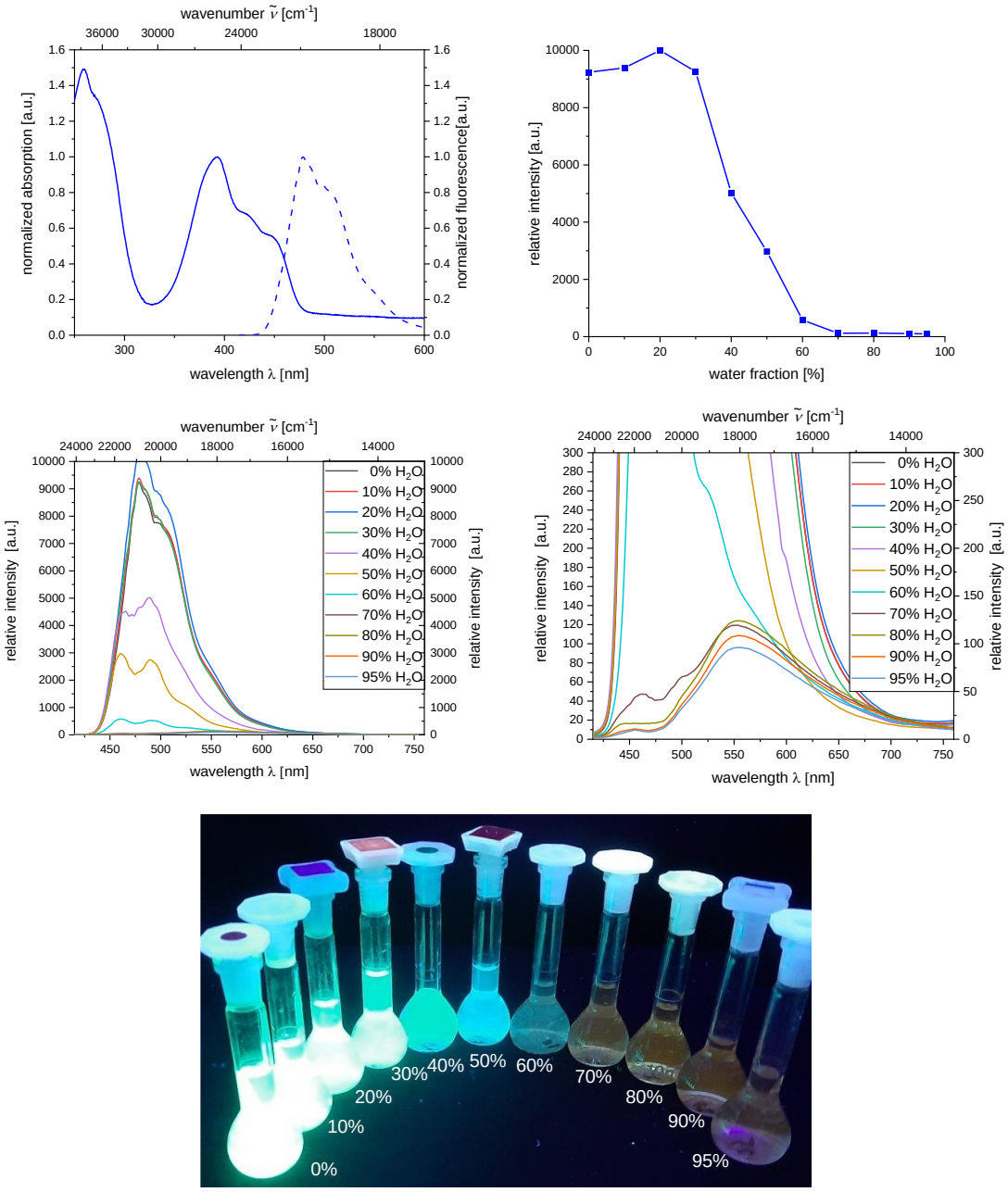


Figure S23: Absorption and emission spectrum of **5m** in ethanol (top, left), and AIE-induced changes in emission (top, right), AIE-related emission spectra of compound **5m** (center, left), zoomed-in AIE-related emission spectra of compound **5m** (center, right) and photographs of solutions of dye **5m** in ethanol/water mixtures of increasing water content (bottom). The latter spectra were measured in ethanol/water mixtures of varying water content.

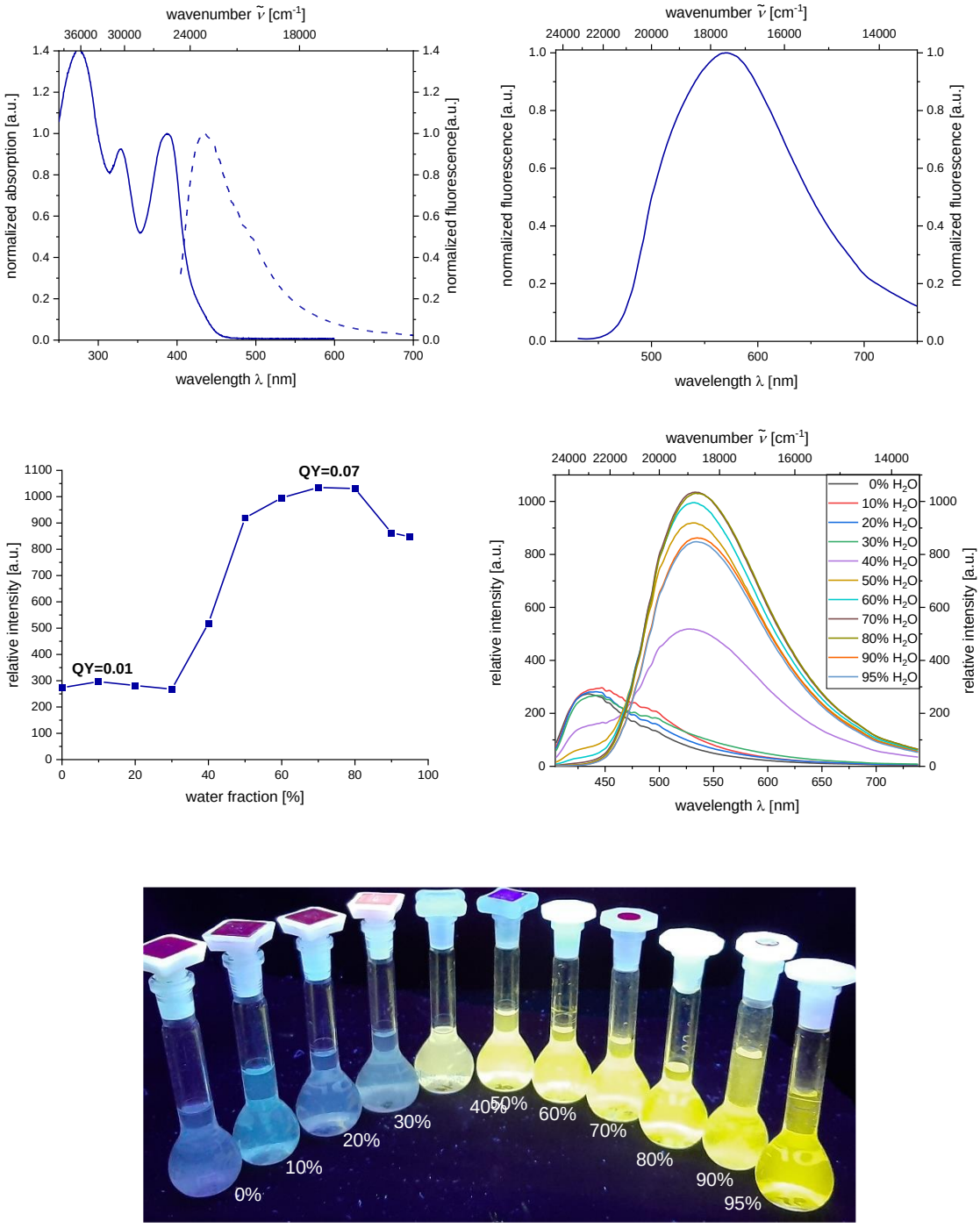
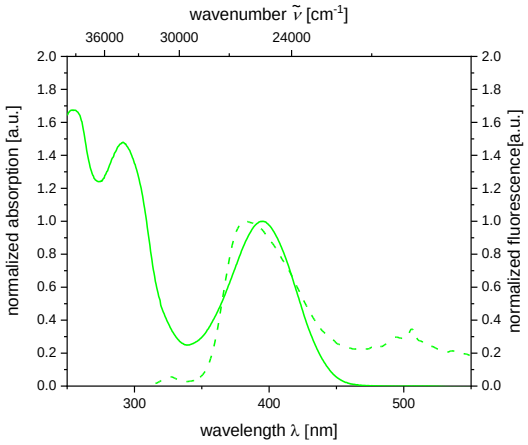


Figure S24: Absorption and emission spectrum of **5n** in ethanol (top, left), solid state emission spectrum (top, right), and AIE-induced changes in emission (center, left), AIE-related emission spectra of compound **5n** (center, right) and photographs of solutions of dye **5n** in ethanol/water mixtures of increasing water content (bottom). The latter spectra were measured in ethanol/water mixtures of varying water content.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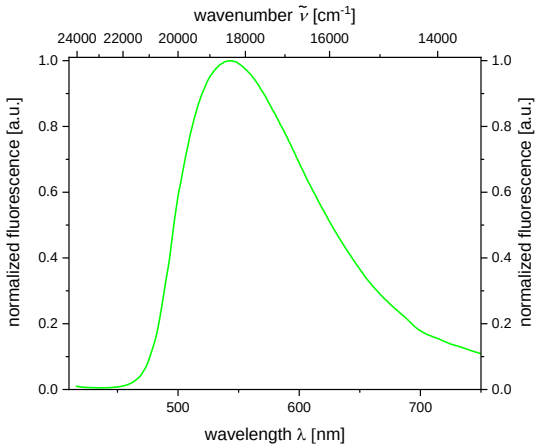
30000
24000
normalized absorption [a.u.]
normalized fluorescence[a.u.]
wavelength λ [nm]


wavenumber $\tilde{\nu}$ [cm^{-1}]
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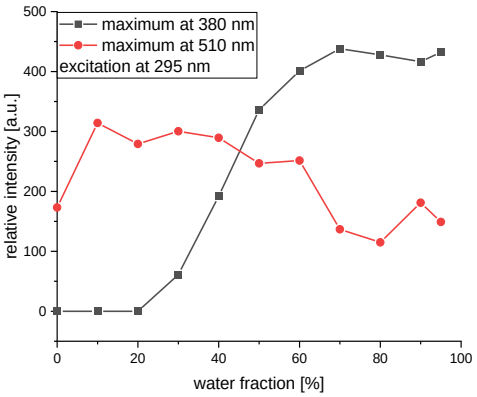
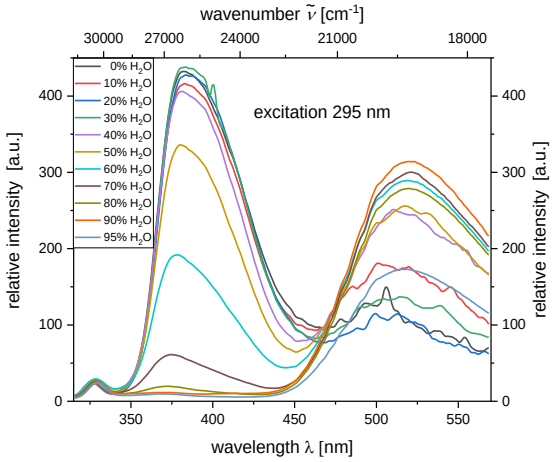
22000
20000
18000
16000
14000
normalized fluorescence [a.u.]
normalized fluorescence [a.u.]
wavelength λ [nm]


maximum at 380 nm
maximum at 510 nm
excitation at 295 nm
relative intensity [a.u.]
water fraction [%]


wavenumber $\tilde{\nu}$ [cm^{-1}]
30000
27000
24000
21000
18000
0% H2O
10% H2O
20% H2O
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40% H2O
50% H2O
60% H2O
70% H2O
80% H2O
90% H2O
95% H2O
excitation 295 nm
relative intensity [a.u.]
relative intensity [a.u.]
wavelength λ [nm]

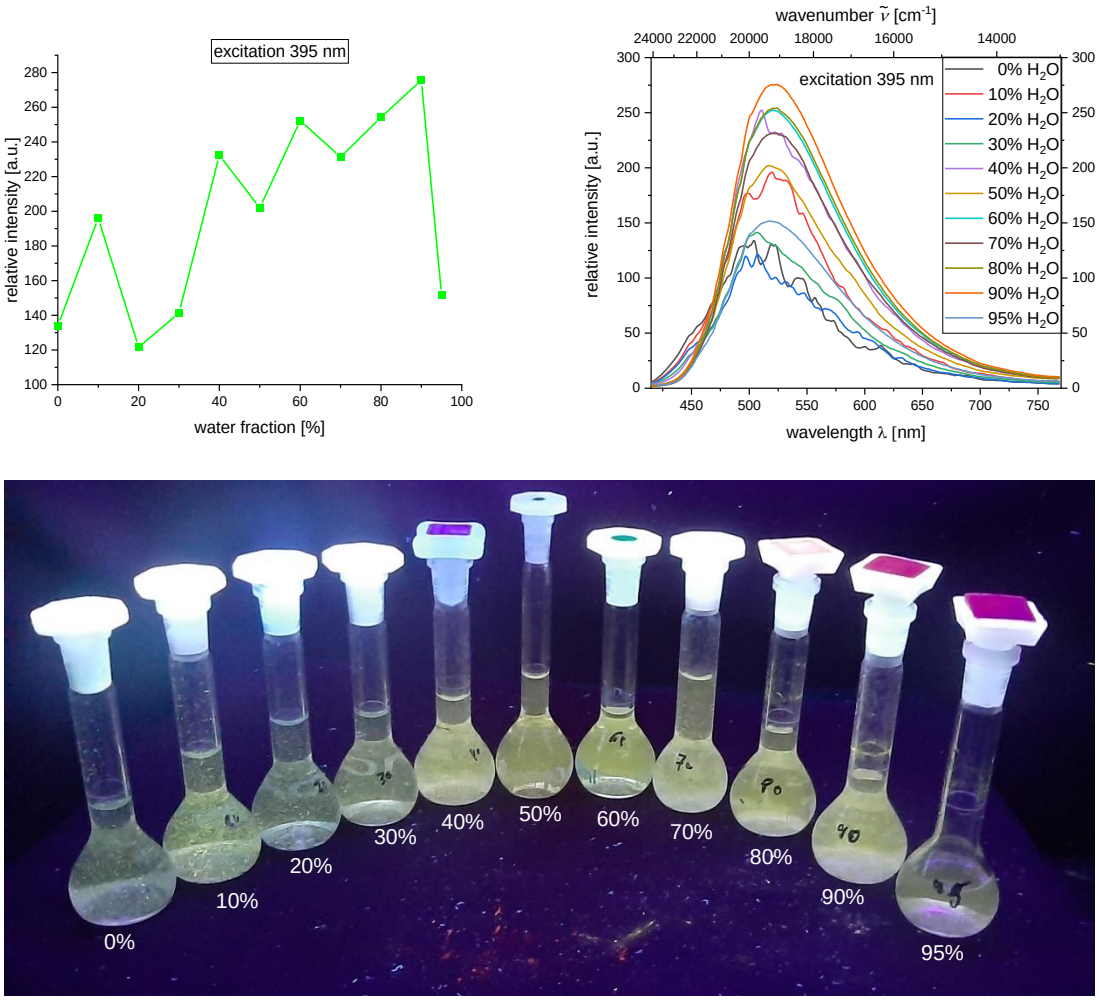


Figure S2: Absorption and emission spectrum of compound **5o** in ethanol (top, left, λ_{exc} = 295 nm), (top, left, λ_{exc} = 292 nm), solid state emission spectrum ((top, right, λ_{exc} = 395 nm), AIE-induced changes in emission (2nd row, left, λ_{exc} = 295 nm), AIE-related emission spectra of compound **5o** (2nd row, right, λ_{exc} = 295 nm), AIE-induced changes in emission (3rd row, left, λ_{exc} = 395 nm), AIE-related emission spectra of compound **5o** (3rd row, right, λ_{exc} = 395 nm) and photographs of solutions of dye **5o** in ethanol/water mixtures of increasing water content (bottom). The latter spectra were measured in ethanol/water mixtures of varying water content.

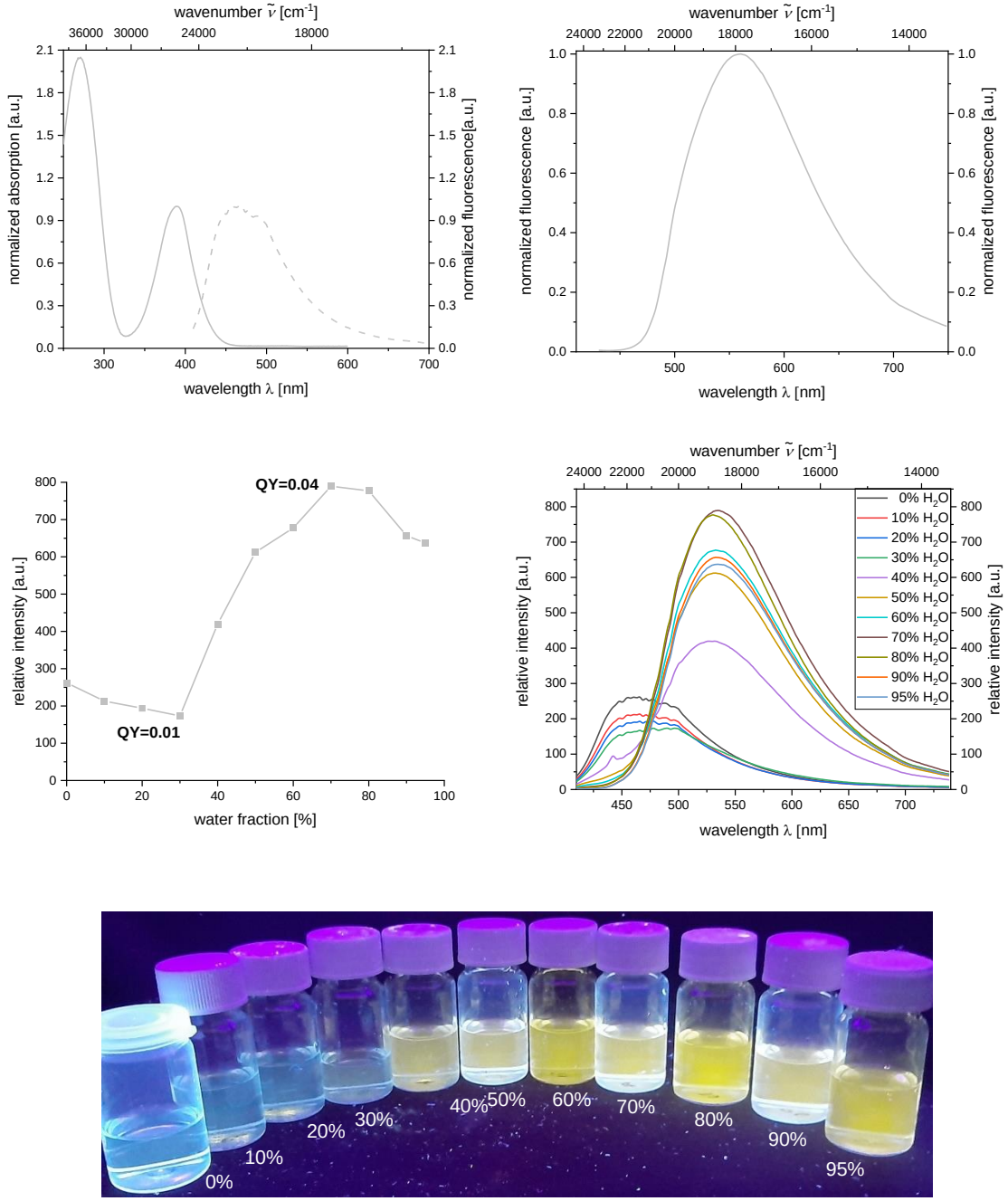
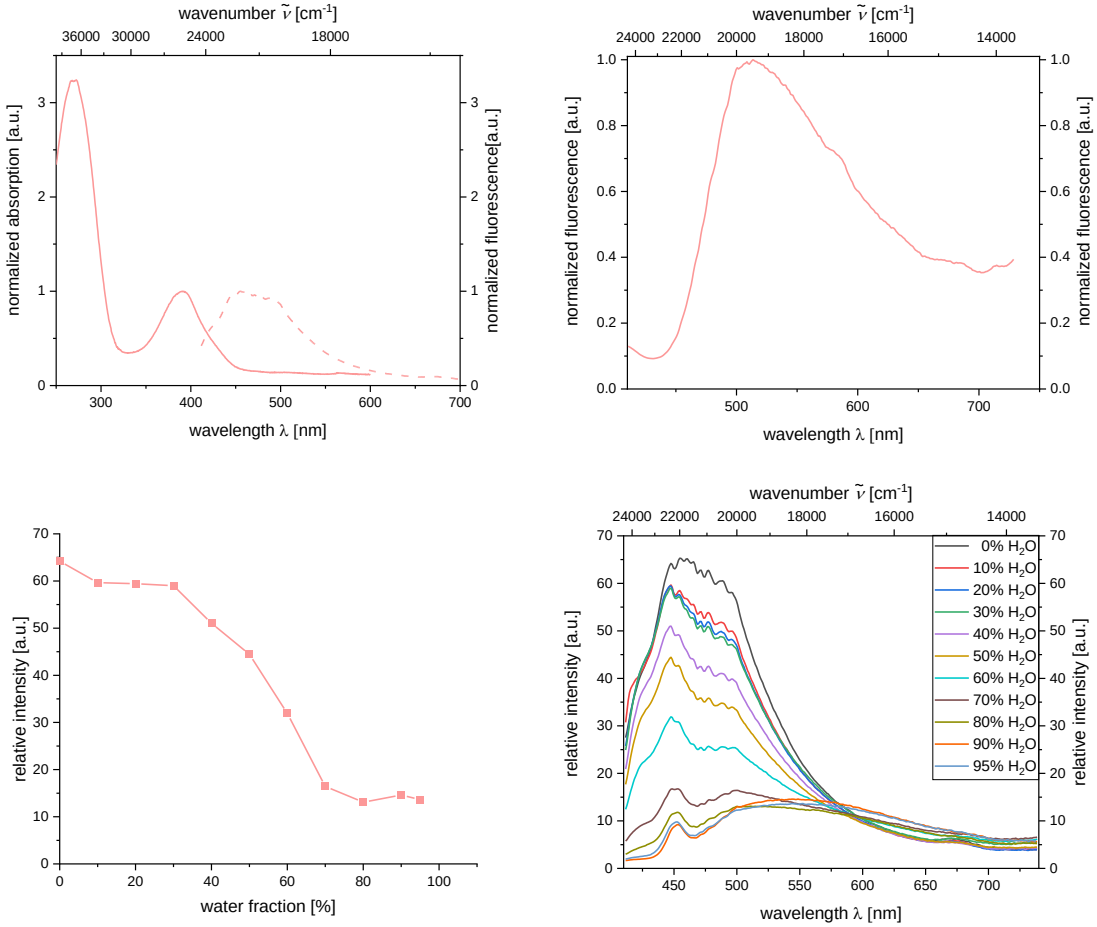


Figure S26: Absorption and emission spectrum of **5p** in ethanol (top, left), solid state emission spectrum (top, right), and AIE-induced changes in emission (center, left), AIE-related emission spectra of compound **5p** (center, right) and photographs of solutions of dye **5p** in ethanol/water mixtures of increasing water content (bottom). The latter spectra were measured in ethanol/water mixtures of varying water content.



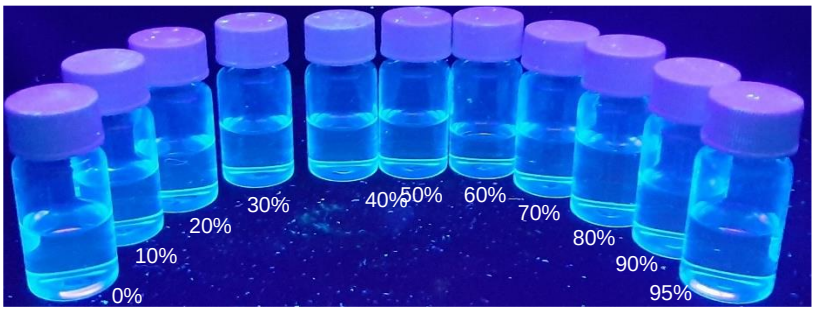


Figure S27: Absorption and emission spectrum of **5q** in ethanol (top, left), solid state emission spectrum (top, right), and AIE-induced changes in emission (center, left), AIE-related emission spectra of compound **5q** (center, right) and photographs of solutions of dye **5q** in ethanol/water mixtures of increasing water content (bottom). The latter spectra were measured in ethanol/water mixtures of varying water content.

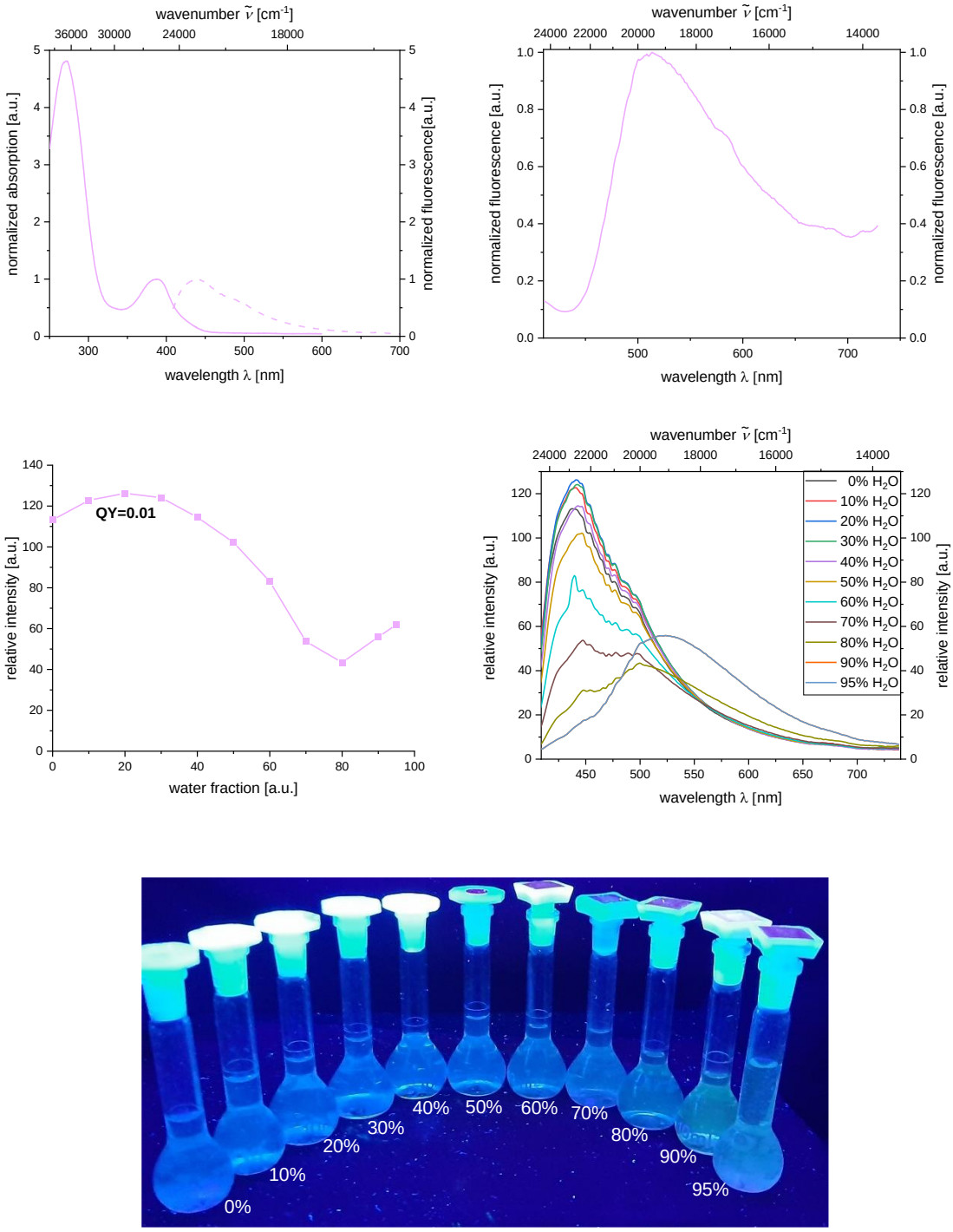


Figure S28: Absorption and emission spectrum of **5r** in ethanol (top, left), solid state emission spectrum (top, right), and AIE-induced changes in emission (center, left), AIE-related emission spectra of compound **5r** (center, right) and photographs of solutions of dye **5r** in ethanol/water mixtures of increasing water content (bottom). The latter spectra were measured in ethanol/water mixtures of varying water content.

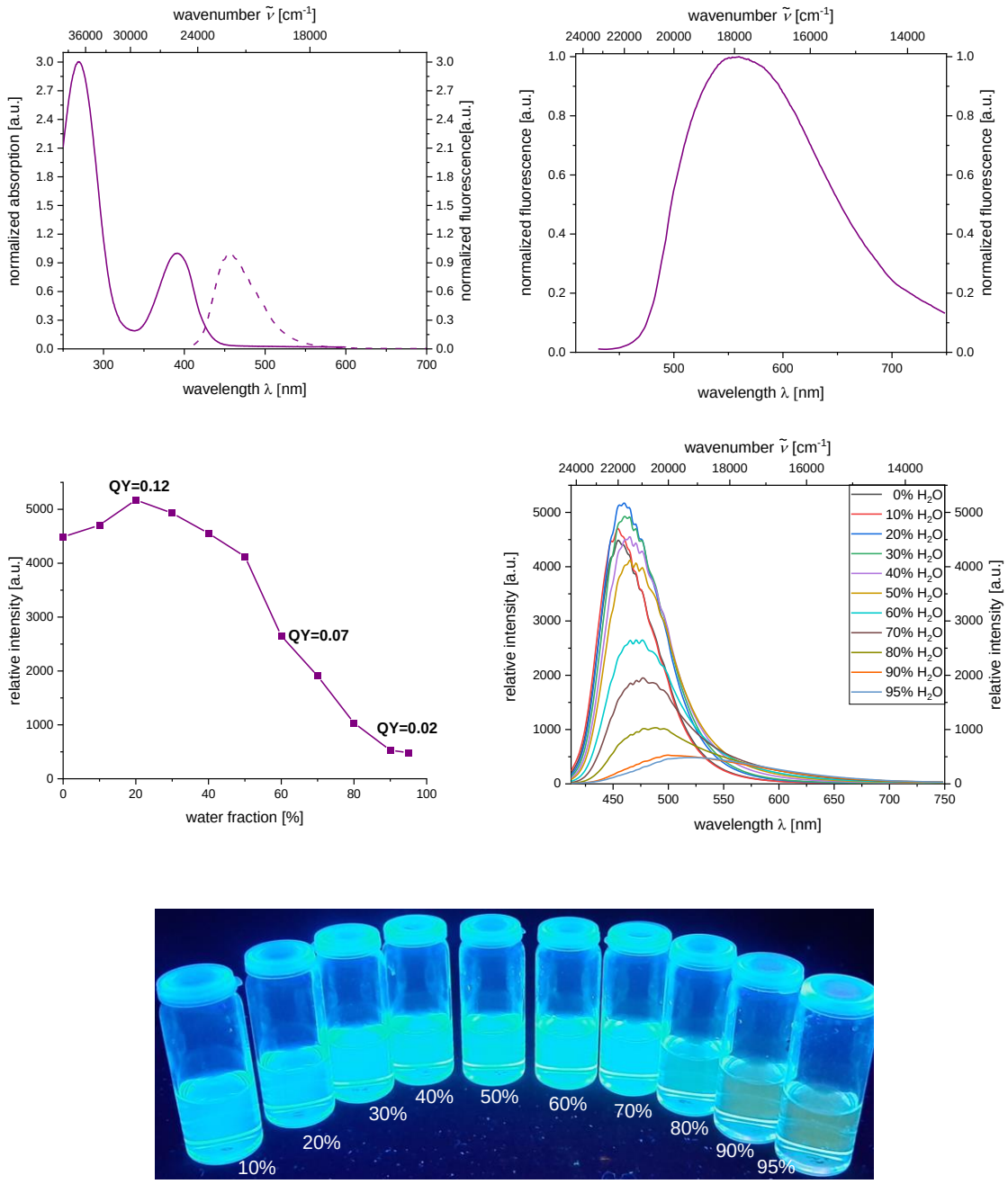


Figure S29: Absorption and emission spectrum of **5s** in ethanol (top, left), solid state emission spectrum (top, right), and AIE-induced changes in emission (center, left), AIE-related emission spectra of compound **5s** (center, right) and photographs of solutions of dye **5s** in ethanol/water mixtures of increasing water content (bottom). The latter spectra were measured in ethanol/water mixtures of varying water content.

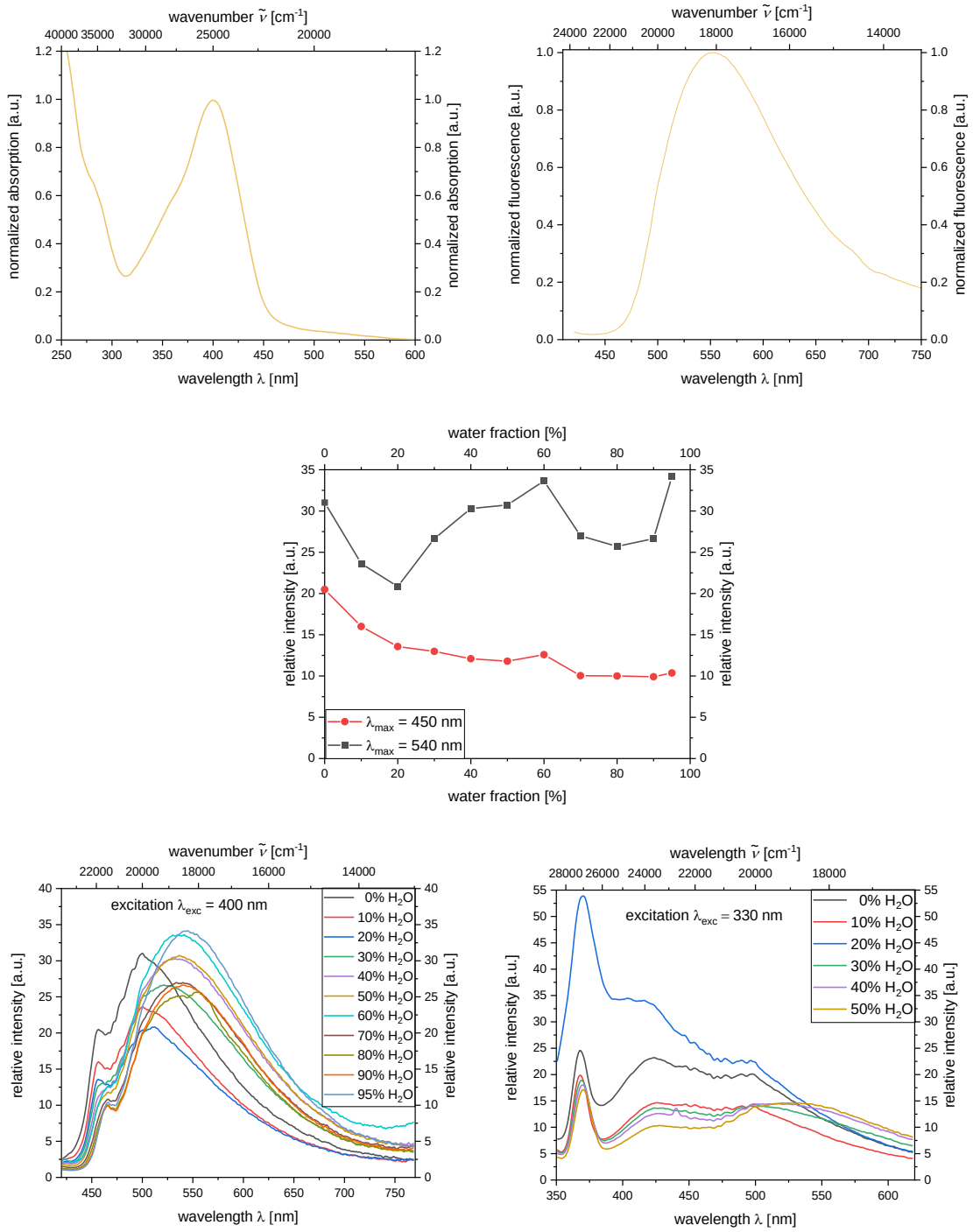


Figure S30: Absorption spectrum of **5t** in ethanol (top, left), solid state emission spectrum (top, right), and AIE-induced changes in emission (center), AIE-related emission spectra of compound **5t** (λ_{exc} = 400 nm) (bottom, left) and AIE-related emission spectra of compound **5t** (λ_{exc} = 330 nm) (bottom, right). The latter spectra were measured in ethanol/water mixtures of varying water content.

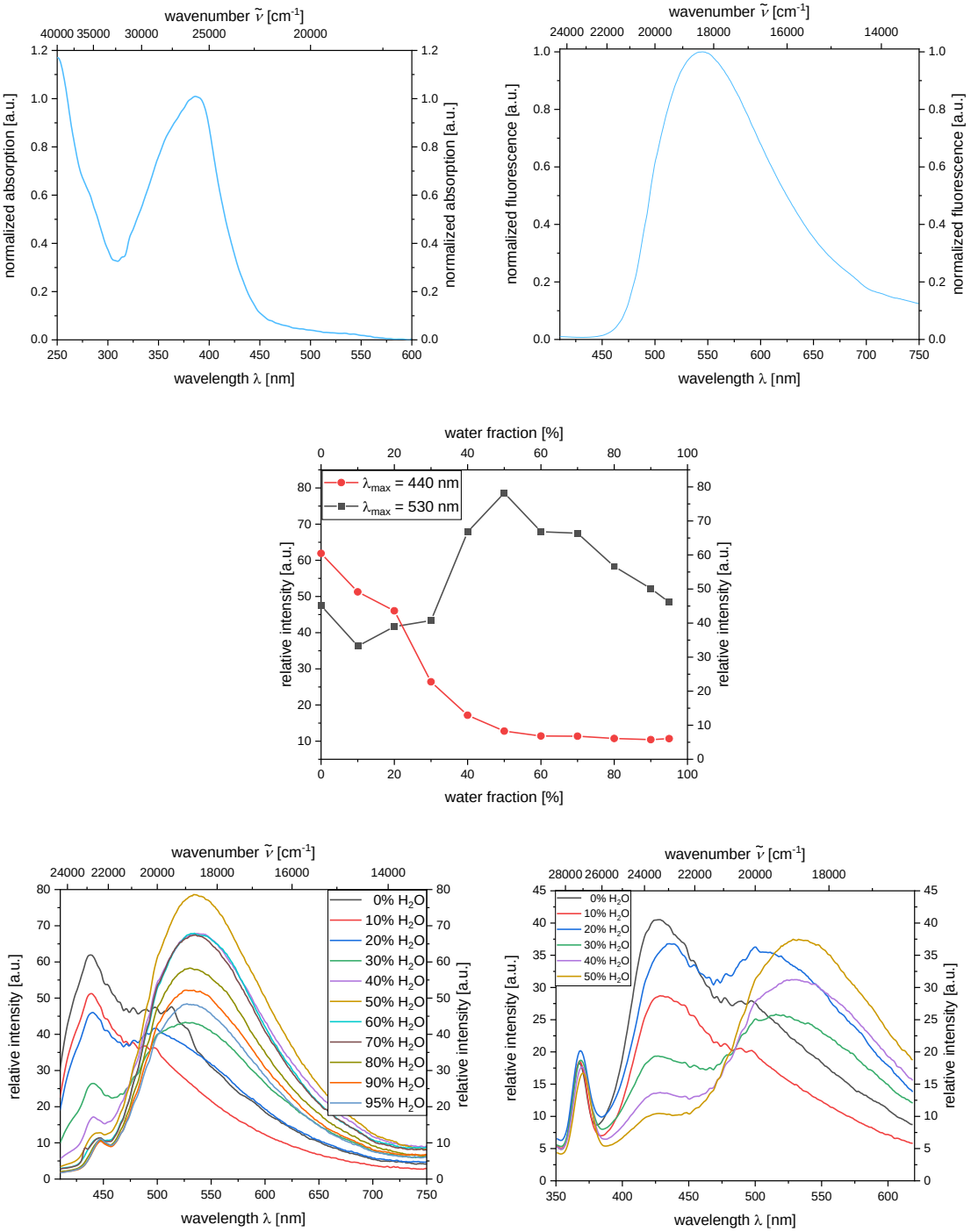


Figure S31: Absorption spectrum of **5u** in ethanol (top, left), solid state emission spectrum (top, right), and AIE-induced changes in emission (center), AIE-related emission spectra of compound **5u** (λ_{exc} = 400 nm) (bottom, left) and AIE-related emission spectra of compound **5u** (λ_{exc} = 330 nm) (bottom, right). The latter spectra were measured in ethanol/water mixtures of varying water content.

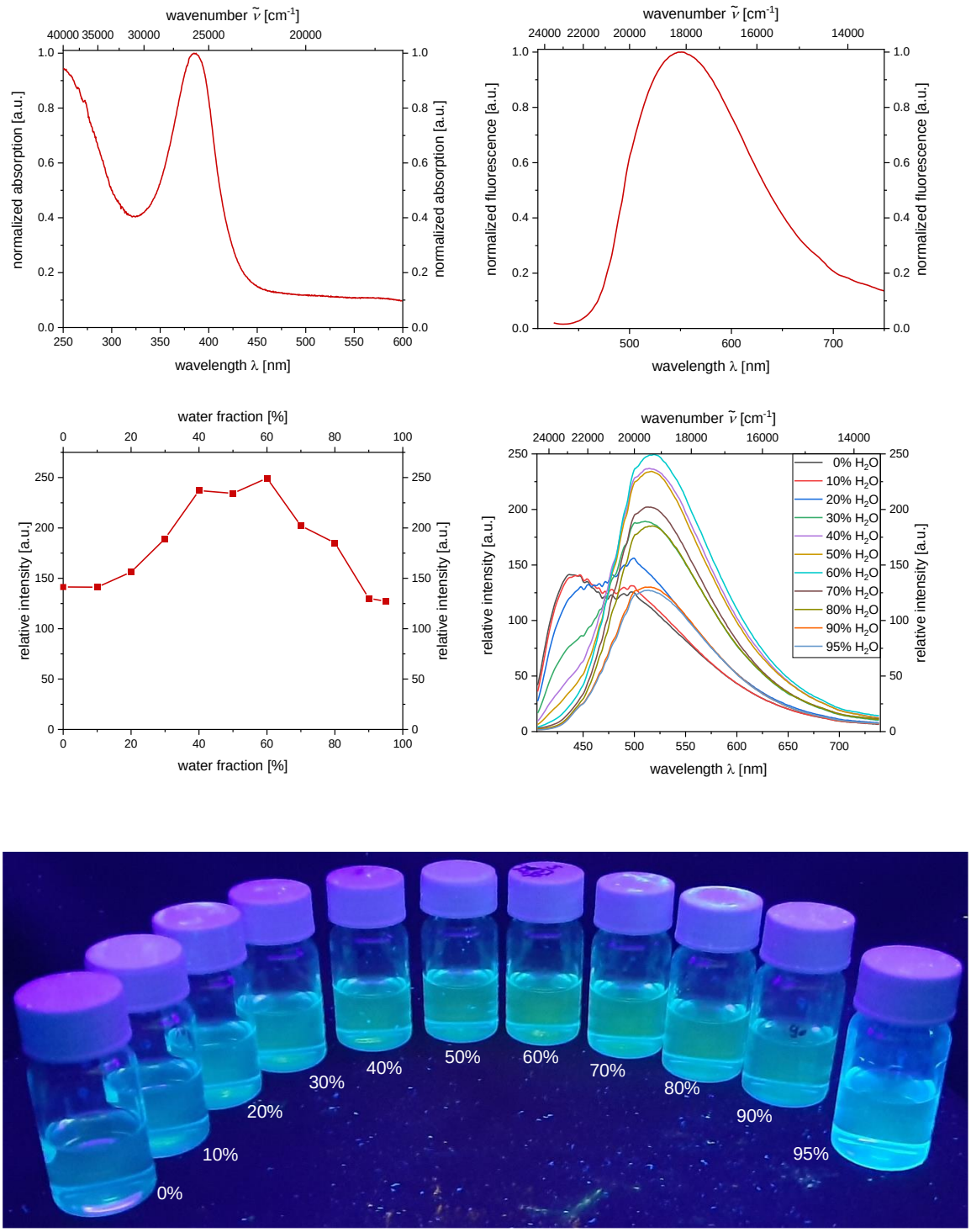
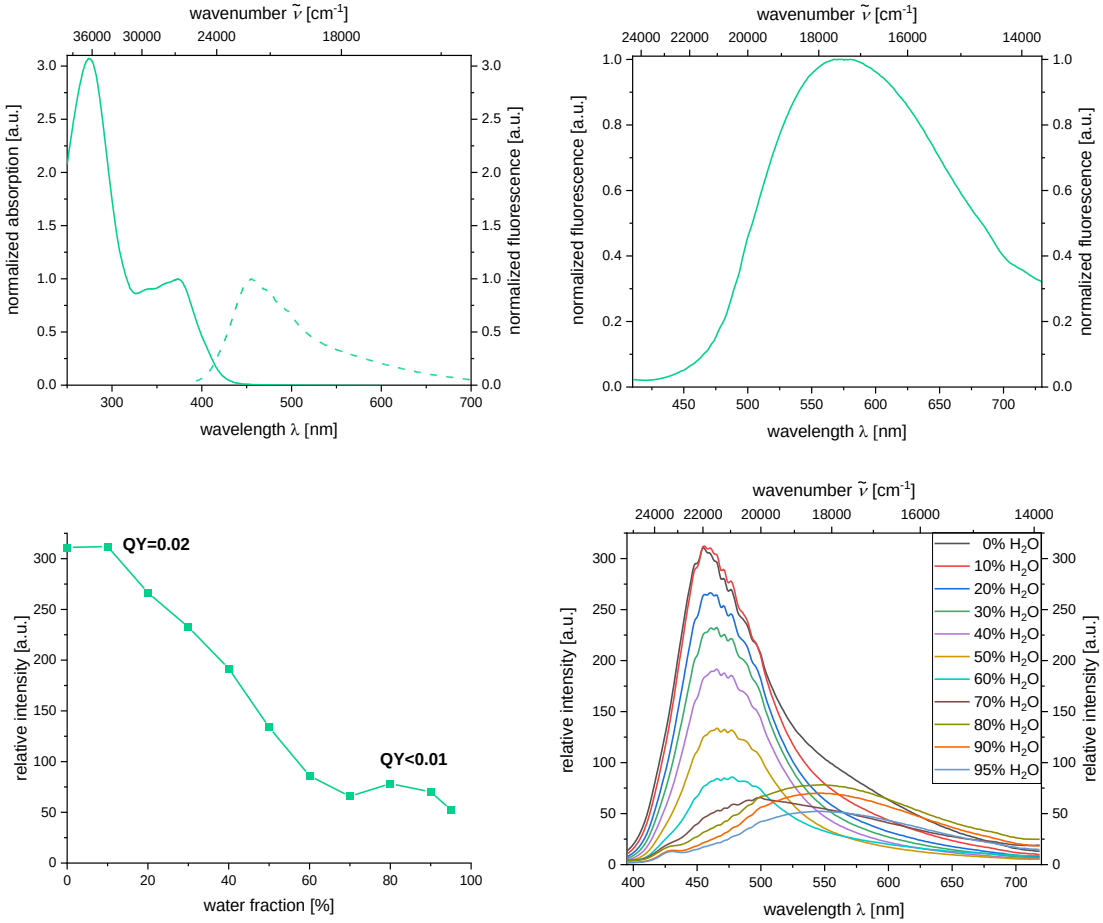


Figure S32: Absorption and emission spectrum of **5v** in ethanol (top, left), solid state emission spectrum (top, right), and AIE-induced changes in emission (center, left), AIE-related emission spectra of compound **5v** (center, right) and photographs of solutions of dye **5v** in ethanol/water mixtures of increasing water content (bottom). The latter spectra were measured in ethanol/water mixtures of varying water content.



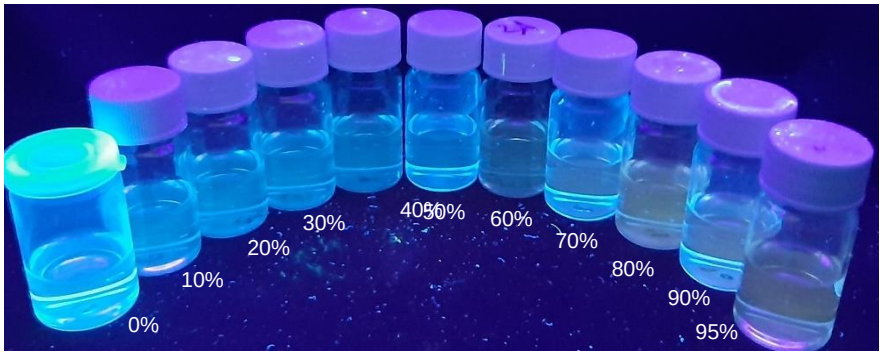


Figure S33: Absorption and emission spectrum of **5w** in ethanol (top, left), solid state emission spectrum (top, right), and AIE-induced changes in emission (center, left), AIE-related emission spectra of compound **5w** (center, right) and photographs of solutions of dye **5w** in ethanol/water mixtures of increasing water content (bottom). The latter spectra were measured in ethanol/water mixtures of varying water content.

Additional measurements of dyes **5o** and **5u** were performed at the Division Biophotonics, Bundesanstalt für Materialforschung und -prüfung (BAM) in Berlin by Dr. N. Nirmalananthan-Budau and Dr. U. Resch-Genger.

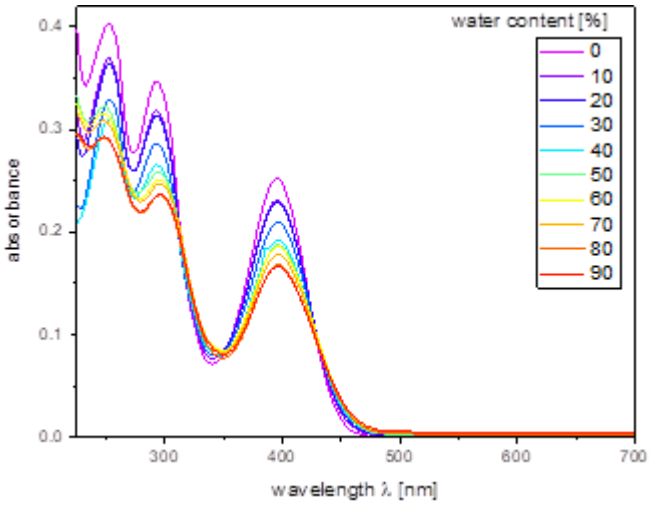


Figure S34: Absorption spectra of **5o** in ethanol/water upon increasing water content (recorded at T = 298 K, c = 10^{-5} M).

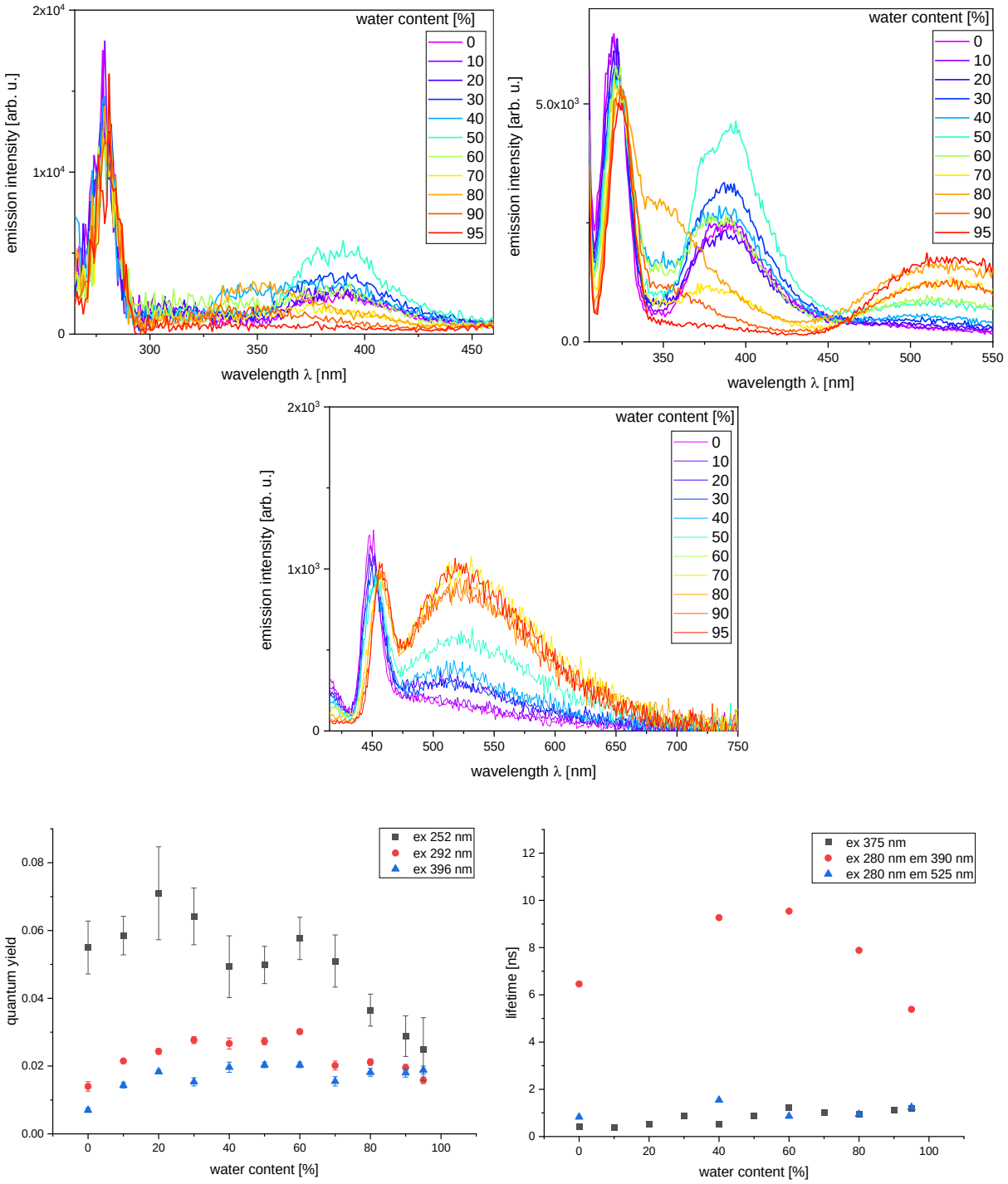


Figure S35: Emission spectra of **5o** in ethanol/water upon increasing water content (recorded at *T* = 298 K, c = 10^{-7} M) Top, left: λ_{exc} (**5o**) = 252 nm, top, right: λ_{exc} (**5o**) = 295 nm; middle λ_{exc} (**5o**) = 395 nm, bottom, left: quantum yield at different water fractions, bottom, right: fluorescence lifetimes at different water fractions.

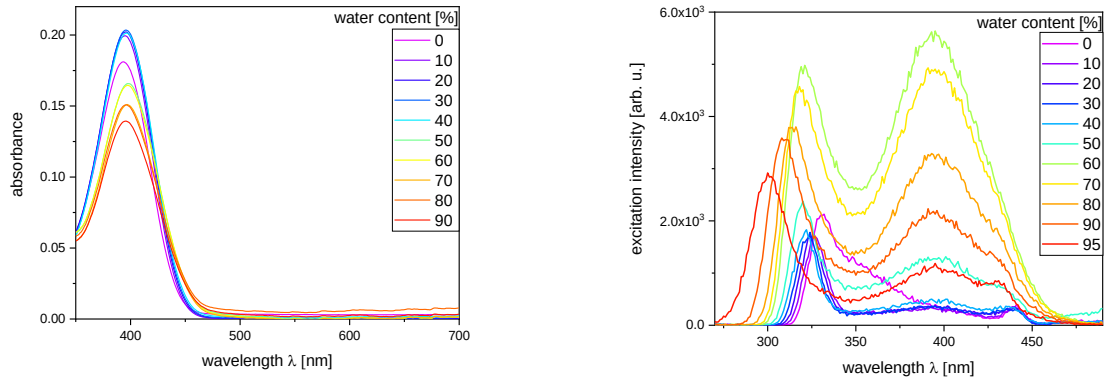


Figure S36: Left: Absorption spectra of **5o** in acetone/water upon increasing water content, right: Excitation spectra of **5o** in acetone/water upon increasing water content (recorded at T = 298 K, c = 10^{-5} M).

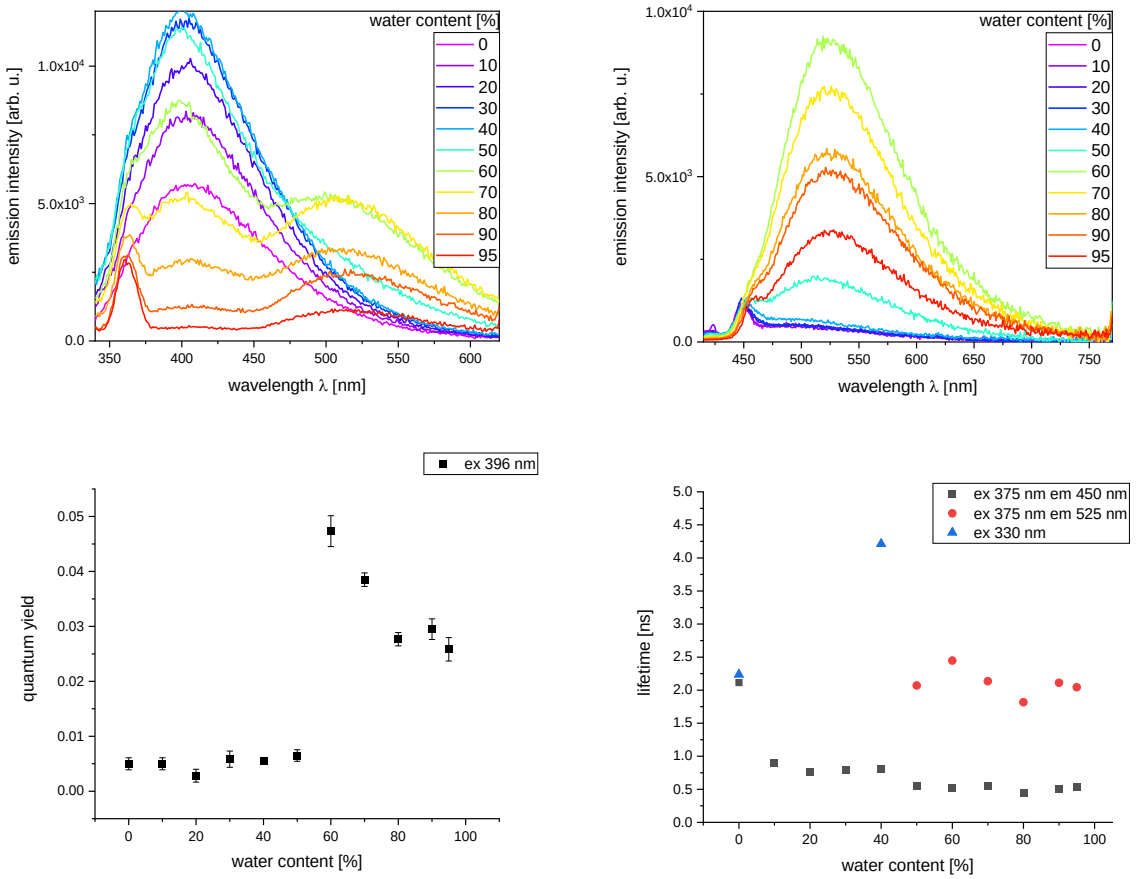


Figure S37: Emission spectra of **5o** in acetone/water upon increasing water content (recorded at T = 298 K, c = 10^{-7} M) Top, left: λ_{exc} (**5o**) = 322 nm, top, right: λ_{exc} (**5o**) = 396 nm; bottom, left: quantum yield at different water fractions, bottom, right: fluorescence lifetimes at different water fractions.

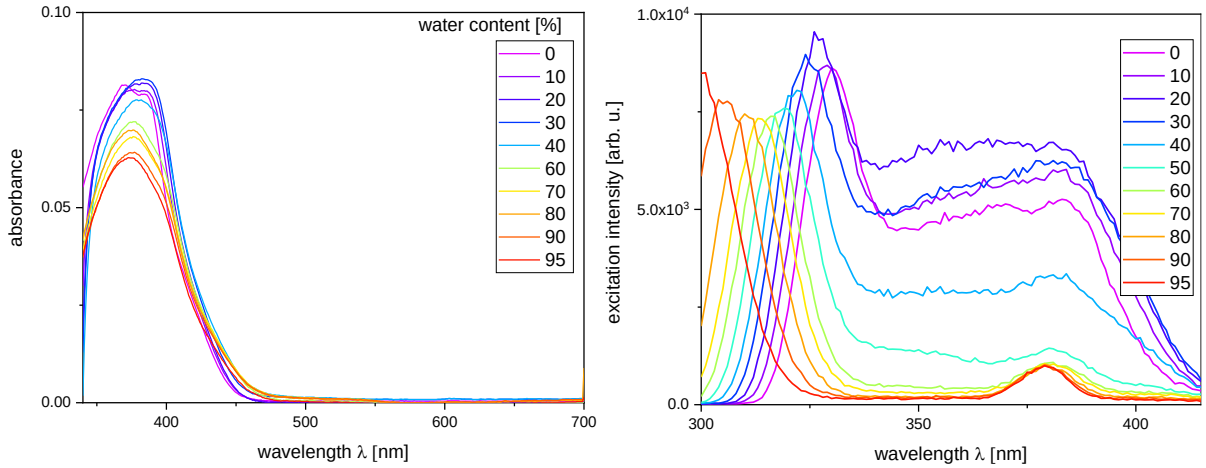


Figure S38: Left: Absorption spectra of **5u** in acetone/water upon increasing water content, right: Excitation spectra of **5u** in acetone/water upon increasing water content (recorded at T = 298 K, c = 10^{-5} M).

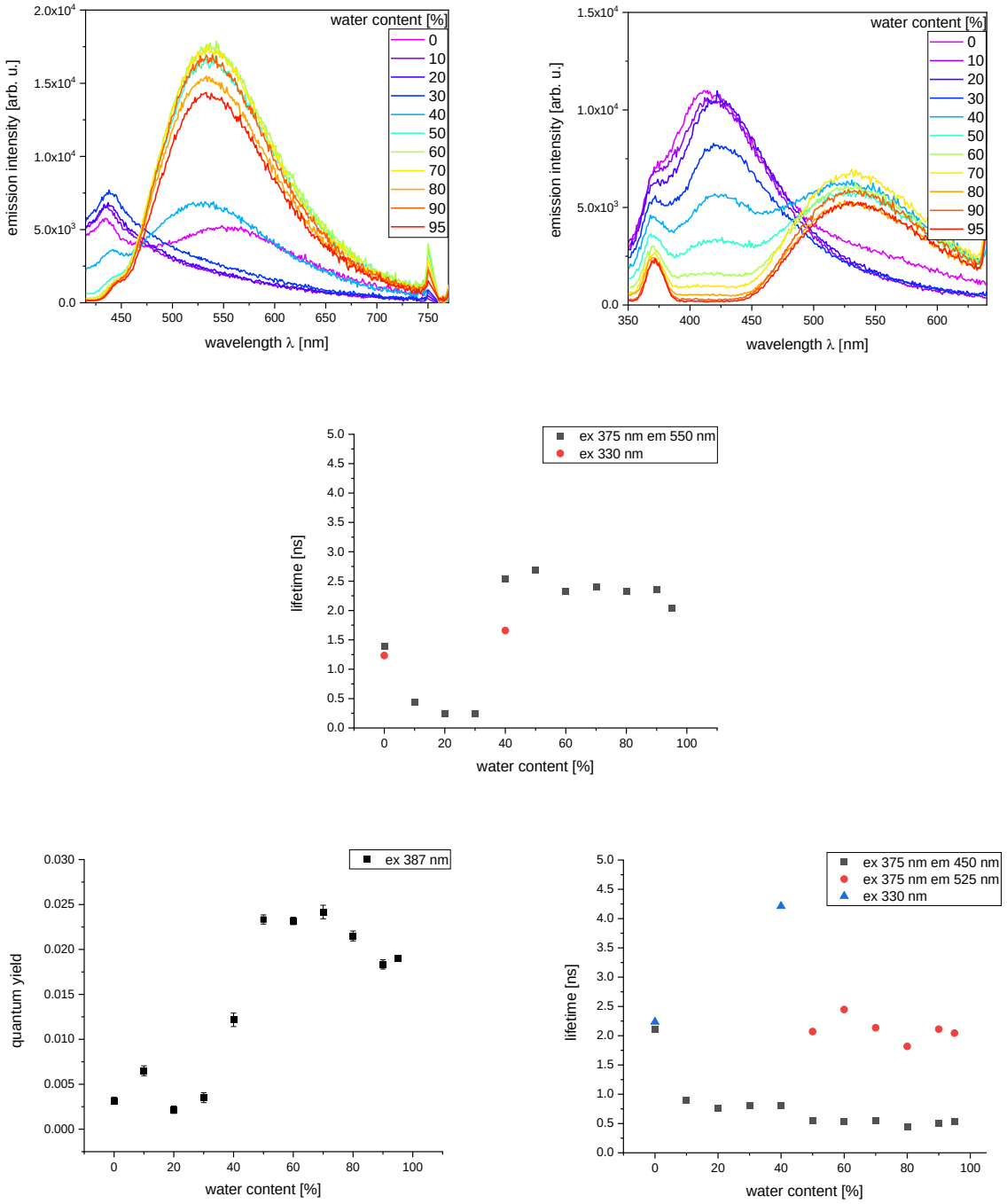


Figure S39: Emission spectra of **5u** in acetone/water upon increasing water content (recorded at *T* = 298 K, c = 10^{-7} M) Top, left: λ_{exc} (**5u**) = 330 nm, top, right: λ_{exc} (**5u**) = 387 nm; bottom, left: quantum yield at different water fractions, bottom, right: fluorescence lifetimes at different water fractions.

Bridged aroyl-*S,N*-ketene acetals **5o** and **5u** were incorporated into 8 μm-sized carboxy-functionalized polystyrene particles (PSP) from Kisker using an established straightforward swelling procedure from Behnke et al.[12]

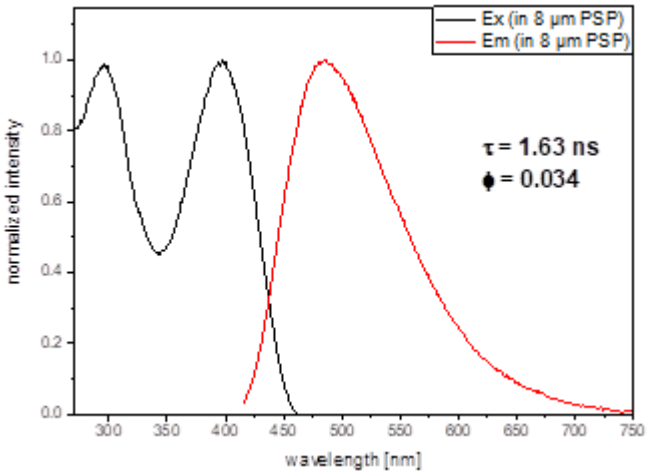


Figure S40: Normalized fluorescence excitation and emission spectra (λ_{exc} = 400 nm) of dispersed 8 µm-sized PSP loaded with dye **5o**.

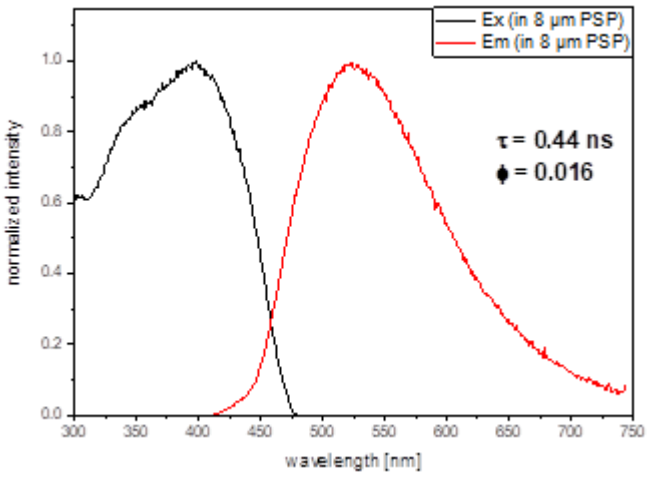


Figure S41: Normalized fluorescence excitation and emission spectra (λ_{exc} = 400 nm) of dispersed 8 µm-sized PSP loaded with dye **5u**.

9 Literature

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