Electronic Supplementary Material (ESI) for New Journal of Chemistry.

Supporting information for

Poly-halogenated aza-bodipy dyes with improved solubility as versatile synthetic platforms for the design of photonic materials

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1) General. NMR spectra (^{1}H, ^{13}C) were recorded at room temperature on a Bruker AVANCE 300 operating at 300.13 MHz, 96 MHz and 282.40 for ^{1}H, ^{11}B and ^{19}F respectively and on a Bruker AVANCE 400 operating at 400.14 MHZ and 100.62 MHz for ^{1}H and ^{13}C, respectively. Data are listed in parts per million (ppm) and are reported relative to tetramethylsilane (^{1}H, ^{13}C), residual solvent peaks being used as internal standard ($CHCl_3$ ^{1}H: 7.26 ppm, ^{13}C: 77.16 ppm). ^{1}H NMR patterns are designated as singlet (s), doublet (d), triplet (t), quartet (q), quintet (quint), multiplet (m), broad (br). High resolution mass spectrometry measurements were performed at the *Centre Commun de Spectrométrie de Masse* (Université Claude Bernard Lyon 1) with a ESI-QTOF (Bruker Daltonics MicroTOF-Q II).

2) Absorption and emission spectroscopies. UV-visible spectra and transmittance spectra were recorded on a Jasco V-550 spectrophotometer in diluted solution (*ca*. 10^{-6} mol.L^{-1}) using spectrophotometric grade solvents. The luminescence spectra were measured using a Horiba-Jobin Yvon Fluorolog-3® spectrofluorimeter, equipped with a three slits double grating excitation and emission monochromator with dispersions of 2.1 nm/mm (1200 grooves/mm). The steady-state luminescence was excited by unpolarized light from a 450 W xenon CW lamp and detected at an angle of 90° for diluted solution measurements by a R928 detector (400-845 nm), a Peltier-cooled red-sensitive Hamamatsu R2658P photomultiplier tube (300-1010 nm) or a liquid-nitrogen-cooled solid indium/gallium/arsenic NIR detector (850–1600 nm). Spectra were corrected for both excitation-source light-intensity variation and emission spectral responses. Fluorescence lifetime was measured using TC-SPC Horiba apparatus; with Ludox in distilled water to determine the instrumental response function used for deconvolution. Excitation was performed using NanoLEDs. Luminescence quantum yields were measured in diluted solutions with an absorbance lower than 0.1 using the following equation $Q_x/Q_r = [A_r(\lambda)/A_x(\lambda)][n_x^2/n_r^2][D_x/D_r]$ were A is the absorbance at the excitation wavelength (λ), n the refractive index and D the integrated luminescence intensity. “r” and “x” stand for reference and sample. Excitation of reference and sample compounds was performed at the same wavelength. For singlet oxygen quantum yield determination ϕ_Δ, the principle is exactly the same except that the singlet oxygen luminescence emission band (D) is integrated for both sample (x) and reference (r) compounds. A(λ) is the absorbance (or optical density) at the excitation wavelength. In this case it is very important that both experiments are conducted in the same solvent at exactly the same excitation wavelength ($n_x = n_r$). The reported results are the average of 4–5 independent measurements at various absorbances (comprised between 0.01–0.1) for both sample and reference. The plot of the integrated singlet oxygen luminescence intensity vs. absorbance gives straight line with excellent correlation coefficients and the slope S can be determined for both sample (x) and reference (r). In the present case, the reference is phenalenone ($\phi_{\Delta r} = 0.98$ in dichloromethane).

3) Crystallography

Single-crystal X-ray diffraction studies of molecules **1d** and **1g** were carried out with a Gemini diffractometer and the related analysis software.[1] An absorption correction based on the crystal faces was applied to the data sets (analytical).[2-3] The structures were solved by direct methods using the SIR97 program,[4] combined with Fourier difference syntheses and refined against F using reflections with [I/σ(*I*) > 3] by using the CRYSTALS program.[5] All atomic displacement parameters for non-hydrogen atoms were refined with anisotropic terms. The hydrogen atoms were theoretically located on the basis of the conformation of the supporting atom and were refined by using the riding model. X-ray diffraction crystallographic data and refinement details for both complexes are summarized in the Supporting Information, Table S1. Important bond lengths and bond angles are collated in Table S2. CCDC-1977349 (for **1d**) and -1977346 (for **1g**) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre.

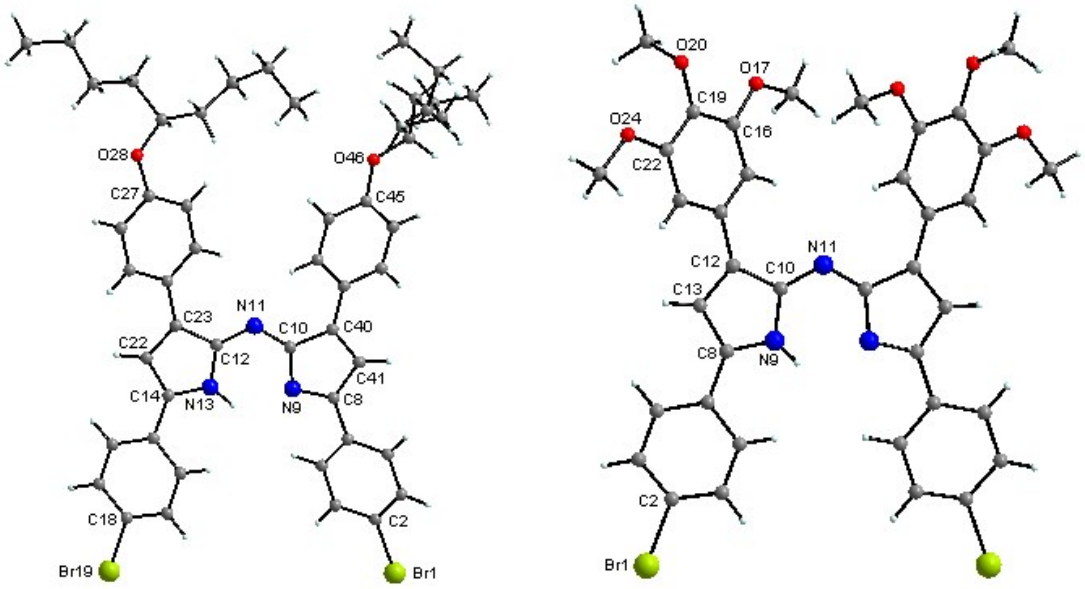


Figure S1. 1d (left) and **1g** (right) crystal structures

Table S1. Single-crystal X-ray diffraction data and crystal structure refinement results for **1d** and **1g**.

	1d	**1g**
Formula	$C_{50}H_{57}Br_2N_3O_2$	$C_{40.67}H_{38}Br_2N_3O_{6.67}$
Molecular weight (g.mol^{-1})	891.8	835.2
Temperature (K)	293	100
Crystal system	Triclinic	Monoclinic
Space group	P-1	I2/a
Crystal shape	Needle	Needle
Crystal color	Dark	Dark
Crystal size (mm^3)	0.11×0.14×0.53	0.11×0.14×0.53
Density	1.366	1.434
μ (mm^{-1})	1.913	2.147
a (Å)	9.485(1)	8.008(1)
b (Å)	11.075(1)	17.521(2)
c (Å)	22.199(2)	27.658(4)
α (deg.)	77.140(8)	90
β (deg.)	79.573(9)	94.25(1)
γ (deg.)	74.00(1)	90
V (Å^3)	2167.5(4)	3869.8(8)
Z	2	4
No. refl. / unique refl. / R_{int}	10280 / 0.050	4753 / 0.044
R(F) / R_w(F) [I > 3σ(I)]	0.0472 / 0.0434	0.0613 / 0.0902
S	1.17	1.38
No. refl. used	6970	3600
No. refined parameters	515	271
Electronic residue (e$^-$.Å^{-3})	-1.27 / +1.10	-1.03 / +1.48
Absorption correction	Analytical	Analytical

Table S2. Selected bond lengths (Å) and bond angles (°) for **1d** and **1g**.

1d					
C27-O28	1.376(4)	C45-O46	1.369(4)		
C18-Br19	1.897(3)	C2-Br1	1.887(3)		
C12-N11	1.342(4)	C10-N11	1.319(4)		
C12-N13	1.378(4)	N13-C14	1.343(4)	C14-C22	1.409(4)
C22-C23	1.394(4)	C12-C23	1.435(4)		
N9-C10	1.393(4)	C8-N9	1.326(4)	C8-C41	1.436(4)
C40-C41	1.363(4)	C10-C40	1.460(4)		
1g					
C16-O17	1.363(5)	C19-O20	1.372(5)	C22-O24	1.360(5)
C2-Br1	1.911(4)				
N9-C10	1.393(5)	C8-N9	1.342(6)	C8-C13	1.421(6)
C12-C13	1.384(6)	C10-C12	1.446(6)		

4) Solubility measurements

Protocol. The solubility of the compound was measured by UV-Vis. The general protocol is illustrated in Figure S2.

Calibration curve. The first step was the preparation of a stock solution S1 at a concentration around 5 mg.mL^{-1} in THF. For molecules **1a** and **1g**, because of their apparent low solubility, a concentration of S1' = 2.5 mg.mL^{-1} was used. These stock solutions were diluted by taking 100 µL of S1 (200 µL for S1') and completing the volume to 4 mL with THF to obtain S2 solutions. Four solutions of known concentration C1-C4 were then prepared by taking 100-400 µL of S2 and completing the volume to 4 mL with THF (Figure S2). The absorbance of the 4 solutions of known concentration were then measured. By plotting $(\lambda_{max}) = f(C)$, we get, according to the Beer-Lambert law a line with a slope corresponding to the ε value, *i.e.* extinction coefficient of the molecule (Figure S3).

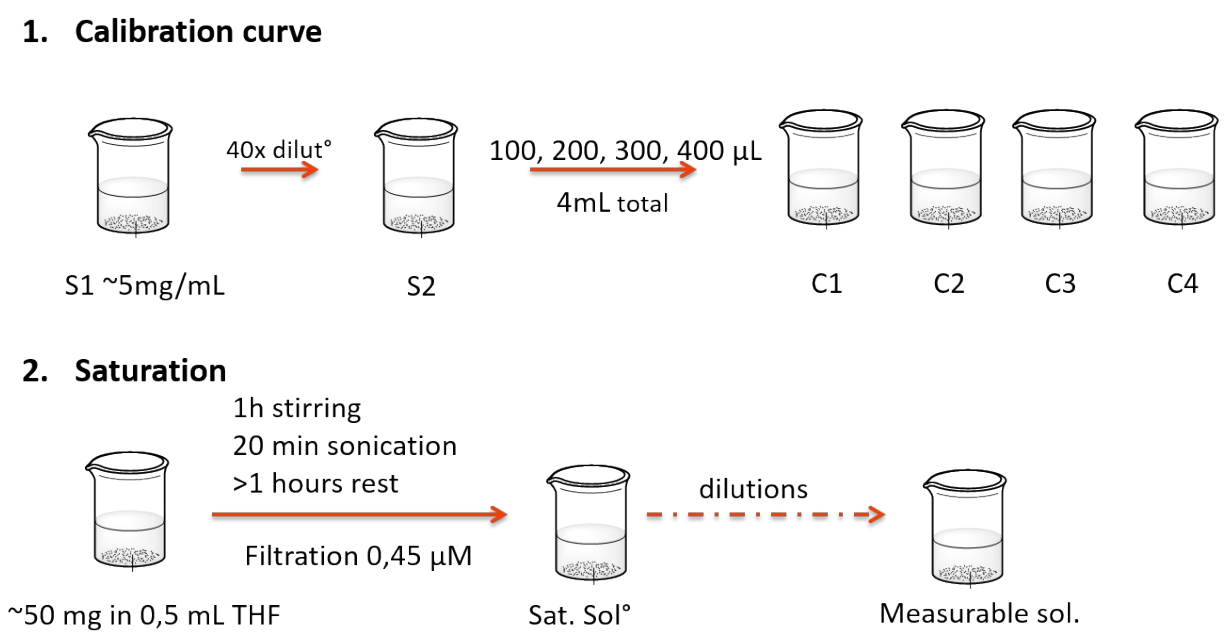
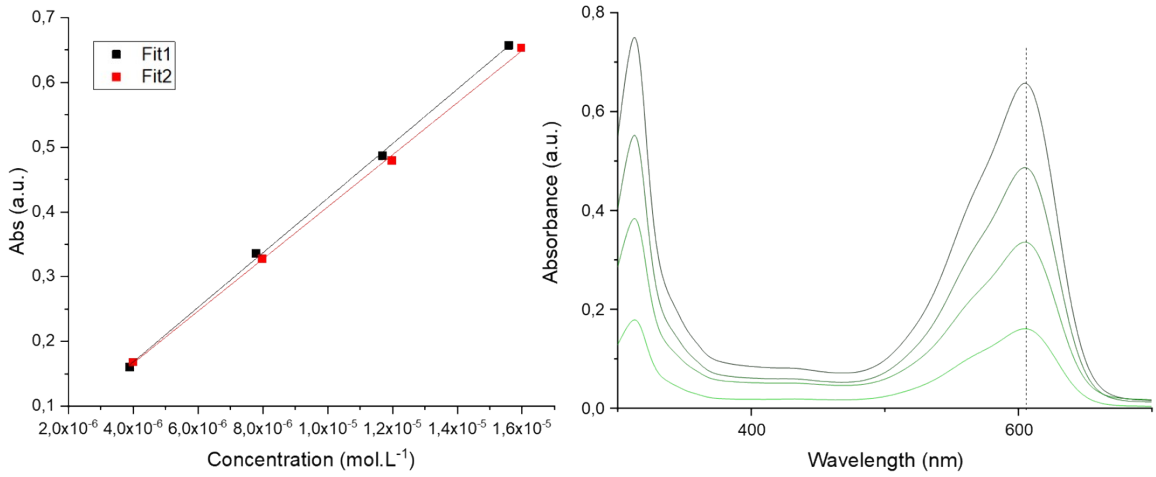


Figure S2. Solubility measurement protocol.



Curve	Slope	R^2
Fit1	42095	0.999
Fit2	40200	0.999

Figure S3. Left: comparison of the two calibration curves made for compound **1a.** Right: example of absorbance measurement made for a calibration curve on compound **1a.**

Saturated solution preparation. In a vial, approximately 50-60 mg of the dye were diluted in 500 µL of THF. The vial was hermetically closed and stirred for 1 hour. The mixture was then sonicated for 20 min and left to rest for 1 hour. This solution was filtered using 0.45 µm PTFE syringe filter. The obtained saturated solution was then diluted until reaching a sufficiently low concentration for a UV-Vis absorption measurement. The experimental protocol was tested several time on **1a** to evaluate the experimental error. The calibration was made twice. As it can be seen of Figure S2, two nearly perfect lines were obtained indicating the negligible error made on stock solutions dilutions. The difference of slope between the two curves also shows that weighing error is small and considered negligible. Five different saturated solutions were prepared for compound **1a** to test the method reliability. Saturation concentration found for each of these solutions is reported Table S3. One can observe a disparity in reported value which could be caused by small temperature variations that occurred during the several days when these experiments were done. From these data the measurement error was estimated around 10%.

Table S3. Different tries on saturation concentration for compound **1a**.

Try	Saturation concentration [mmol.L^{-1}]	Saturation concentration [mg.mL^{-1}]
1	14.5	8.8
2	13.2	8.0
3	11.1	6.7
4	11.4	6.9
5	12.5	7.6

5) Synthesis

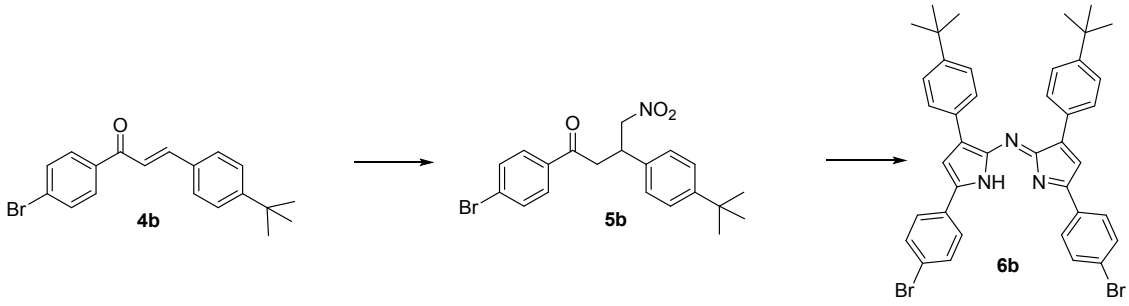
Compounds **4a, 5a** and **1a** were synthesized according to already published procedures.[6-9] Aza-dipyrromethenes **1b-h** were synthesized in the three step typical procedure described hereafter. For time efficiency, the three steps were done in a row for some compounds without isolating intermediates. Full characterizations are given otherwise.

Typical procedure. To a solution of desired substituted acetophenone (1 equiv.) in EtOH was added 4-bromobenzaldehyde (1 equiv.). The mixture was cooled to 0 °C then NaOH 2.5 M (1:1 ratio with EtOH) was added. After stirring at room temperature for one night, the reaction mixture was filtered and the solid was washed with cold ethanol. If no precipitation occurred or if the product is too soluble in EtOH, regular extraction with EtOAc and washing with water and brine was performed. The crude product was further used without purification (otherwise stated below).

The chalcone, as obtained, was dissolved in methanol. Diethylamine (5 equiv.) and nitromethane (5 equiv.) were then added. The solution was refluxed overnight. After cooling down to 0 °C, the solution was quenched with an aqueous solution of hydrochloric acid (1 M) until pH ≈ 2. The solution was extracted three times with EtOAc and the combined organic layers were washed with brine and dried over sodium sulfate. The solvent was then evaporated and the residue was either used as obtained or purified by recrystallization or by flash chromatography.

For the formation of the aza-dipyrromethene, Michael adduct was dissolved in alcohol, ammonium acetate (approx. 35 equiv.) was then added to the reaction mixture. The resulting solution was heated under reflux during 16-72h. The reaction was then cooled down to RT. The solvent was concentrated to half and filtered. The isolated solid was washed thoroughly with cold ethanol and pentane to give the desired product.

Compound 1b



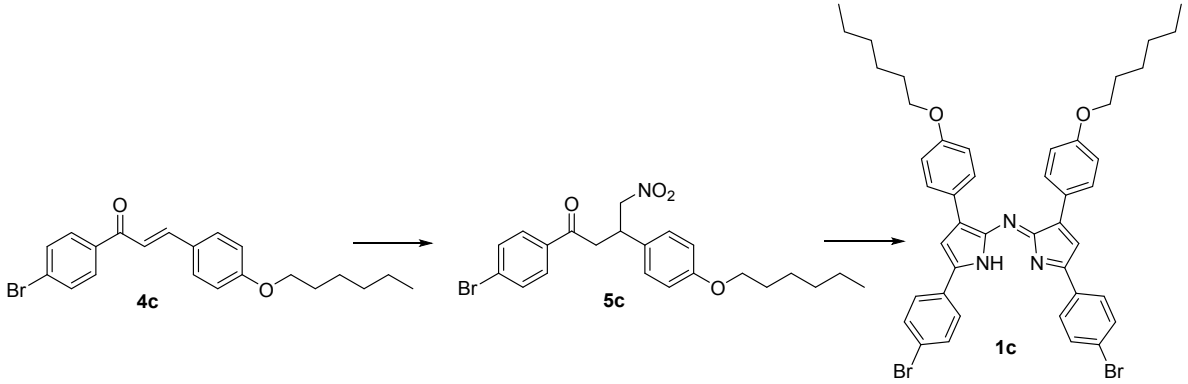
4b was prepared according to typical procedure, with 4-bromoacetophenone (2.45 g, 12.33 mmol, 1 equiv.), 4-*tert*-butylbenzaldehyde (2.00 g, 12.33 mmol, 1 equiv.) in ethanol (50 mL) and sodium hydroxide 2.5 M (50 mL). Time: 16h; temperature: RT; purification: filtration and washing with cold EtOH and pentane; product: off-white powder (3.482 g, 81%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.88 (d, *J* = 8.6 Hz, 2H), 7.81 (d, *J* = 15.6 Hz, 1H), 7.65 (d, *J* = 8.6 Hz, 2H), 7.59 (d, *J* = 8.5 Hz, 1H), 7.48 – 7.40 (m, 3H),

1.35 (s, 9H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 189.72, 154.67, 145.60, 137.26, 132.10, 132.05, 130.17, 128.57, 127.90, 126.16, 120.87, 35.14, 31.30. HRMS (ESI^+) calcd. for $[M+H]^+$: 343.0692. Found: 343.0691.

5b was prepared according to typical procedure with chalcone **4b** (3.0 g, 8.74 mmol, 1 equiv.), diethylamine (3.20 g, 43.7 mmol, 4.52 mL, 5 equiv.) and nitromethane (2.67 g, 43.7 mmol, 2.34 mL, 5 equiv.) in methanol (70 mL). Temperature: reflux; time: 4 days; purification: column chromatography using PE/EtOAC 9:1 as eluent; product: brown oil (4.221 g, 73%); purification: recrystallization from methanol; product: white solid (2.278 g, 64%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.77 (d, *J* = 8.4 Hz, 2H), 7.59 (d, *J* = 8.4 Hz, 2H), 7.34 (d, *J* = 8.1 Hz, 2H), 7.19 (d, *J* = 8.1 Hz, 2H), 4.80 (dd, *J* = 12.5, 6.9 Hz, 1H), 4.68 (dd, *J* = 12.5, 7.6 Hz, 1H), 4.23 – 4.14 (m, 1H), 3.43 – 3.37 (m, 2H), 1.29 (s, 9H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 196.18, 151.00, 135.93, 135.29, 132.19, 129.68, 128.91, 127.19, 126.16, 79.64, 41.73, 38.90, 34.65, 31.40. HRMS (ESI^+) calcd. for $[M+H]^+$: 404.0856. Found: 404.0853.

1b was prepared according to typical procedure with compound **5b** (2.00 g, 4.947 mmol, 1 equiv.), ammonium acetate (13.3 g, 173 mmol, 35 equiv.) in ethanol (20 mL). Time: overnight; temperature: reflux; purification: filtration with cold EtOH; product: purple foils, no NMR characterization was possible due to poor solubility (0.449 g). HRMS (ESI^+) calcd. for $[M+H]^+$: 718.1427. Found: 718.1434

Compound 1c



4c was prepared according to typical procedure, with 4-bromoacetophenone (3.86 g, 19.39 mmol, 1 equiv.), 4'-hexyloxybenzaldehyde (4.00 g, 19.39 mmol, 1 equiv.) in EtOH (70 mL) and sodium hydroxide 2.5 M (70 mL). Time: 19h; temperature: RT; purification: filtration and washing with cold EtOH and pentane; product: off-white powder (7.5 g, quant.). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.91 – 7.85 (m, 2H), 7.79 (d, *J* = 15.6 Hz, 1H), 7.66 – 7.61 (m, 2H), 7.61 – 7.57 (m, 2H), 7.35 (d, *J* = 15.6 Hz, 1H), 6.96 – 6.89 (m, 2H), 4.00 (t, *J* = 6.6 Hz, 2H), 1.84 – 1.76 (m, 2H), 1.51 – 1.42 (m, 2H), 1.40 – 1.31 (m, 4H), 0.94 – 0.88 (m, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 189.59, 161.63, 145.59, 137.35, 131.98, 130.52, 130.10, 127.74,

127.23, 118.97, 115.06, 68.34, 31.69, 29.23, 25.81, 22.74, 14.20. HRMS (ESI^+) calcd. for $[M+H]^+$: 387.0954. Found: 387.0950

5b was prepared according to typical procedure with chalcone **4c** (7.00 g, 18.07 mmol, 1 equiv.), $MeNO_2$ (4.8 mL, 5 equiv.), $HNEt_2$ (9.4 mL, 5 equiv.) in MeOH (140 mL) and chloroform (40 mL). Time: 15h; temperature: reflux; purification: recrystallization in MeOH; product: off-white solid (6.788 g, 84%). ^1H NMR (300 MHz, $CDCl_3$) δ 7.77 (d, *J* = 8.4 Hz, 2H), 7.59 (d, *J* = 8.4 Hz, 2H), 7.16 (d, *J* = 8.5 Hz, 2H), 6.84 (d, *J* = 8.5 Hz, 2H), 4.77 (dd, *J* = 12.3, 6.9 Hz, 1H), 4.64 (dd, *J* = 12.3, 7.7 Hz, 1H), 4.14 (quint, *J* = 7.1 Hz, 1H), 3.91 (t, *J* = 6.5 Hz, 2H), 3.38 (d, *J* = 6.8 Hz, 2H), 1.75 (quint, *J* = 6.6 Hz, 2H), 1.50 – 1.24 (m, 6H), 0.90 (t, *J* = 6.5 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 196.16, 158.82, 135.17, 132.17, 130.52, 129.65, 128.92, 128.55, 115.06, 79.89, 68.08, 41.69, 38.67, 31.69, 29.30, 25.83, 22.73, 14.19. HRMS (ESI^+) calcd. for $[M+H]^+$: 448.1118. Found: 448.1128.

1c was prepared according to typical procedure with Michael's adduct **5c** (1.500 g, 3.346 mmol, 1 equiv.), ammonium acetate (9 g, 117 mmol, 35 equiv.) in ethanol (15 mL). Time: 15 h; temperature: reflux; purification: filtration with cold EtOH; product: dark blue solid (0.634 g, 47%). ^1H NMR (400 MHz, $CDCl_3$) δ 7.97 (d, *J* = 8.2 Hz, 4H), 7.73 (d, *J* = 8.0 Hz, 4H), 7.63 (d, *J* = 8.0 Hz, 4H), 7.03 (s, 2H), 6.94 (d, *J* = 8.2 Hz, 4H), 4.03 (t, *J* = 6.5 Hz, 4H), 1.92 – 1.75 (m, 4H), 1.52 – 1.44 (m, 4H), 1.45 – 1.28 (m, 8H), 1.01 – 0.83 (m, 6H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 159.61, 154.05, 149.80, 142.85, 132.45, 131.33, 130.51, 127.90, 126.34, 124.32, 114.51, 113.48, 68.28, 31.79, 29.44, 25.93, 22.79, 14.21. HRMS (ESI^+) calcd. for $[M+H]^+$: 806.1951. Found: 806.1955.

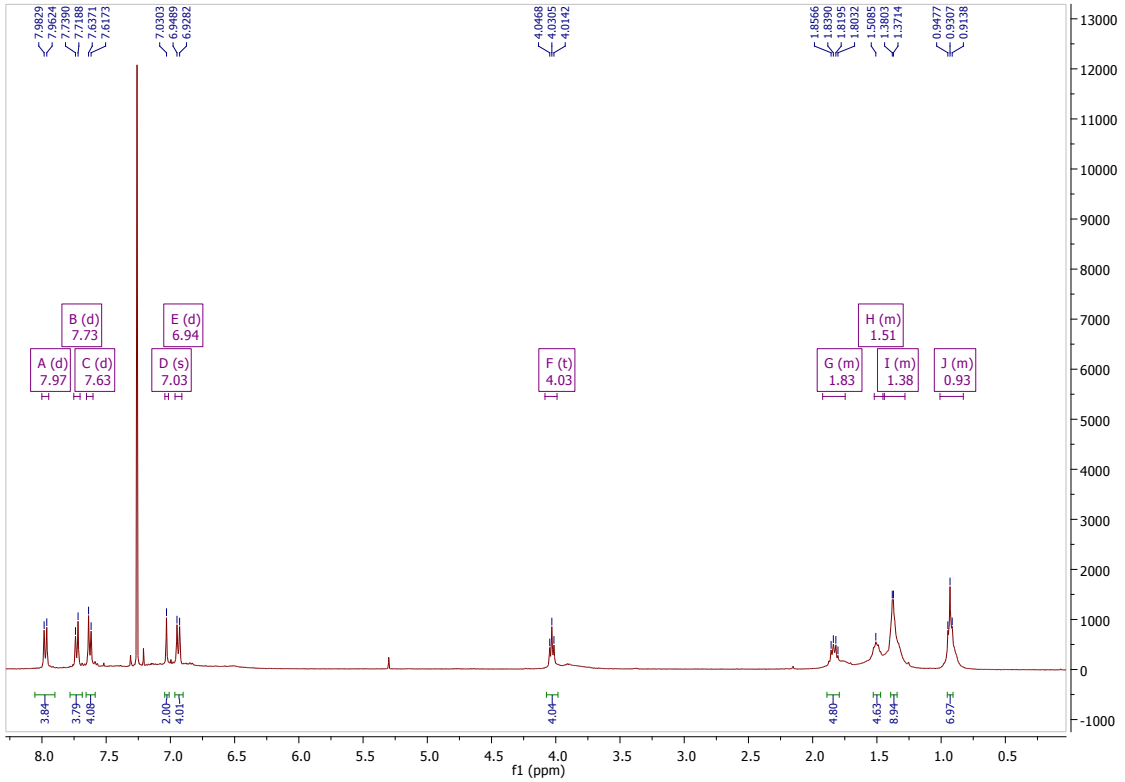


Figure S4. ^{1}H NMR spectrum ($CDCl_3$) of compound **1c**

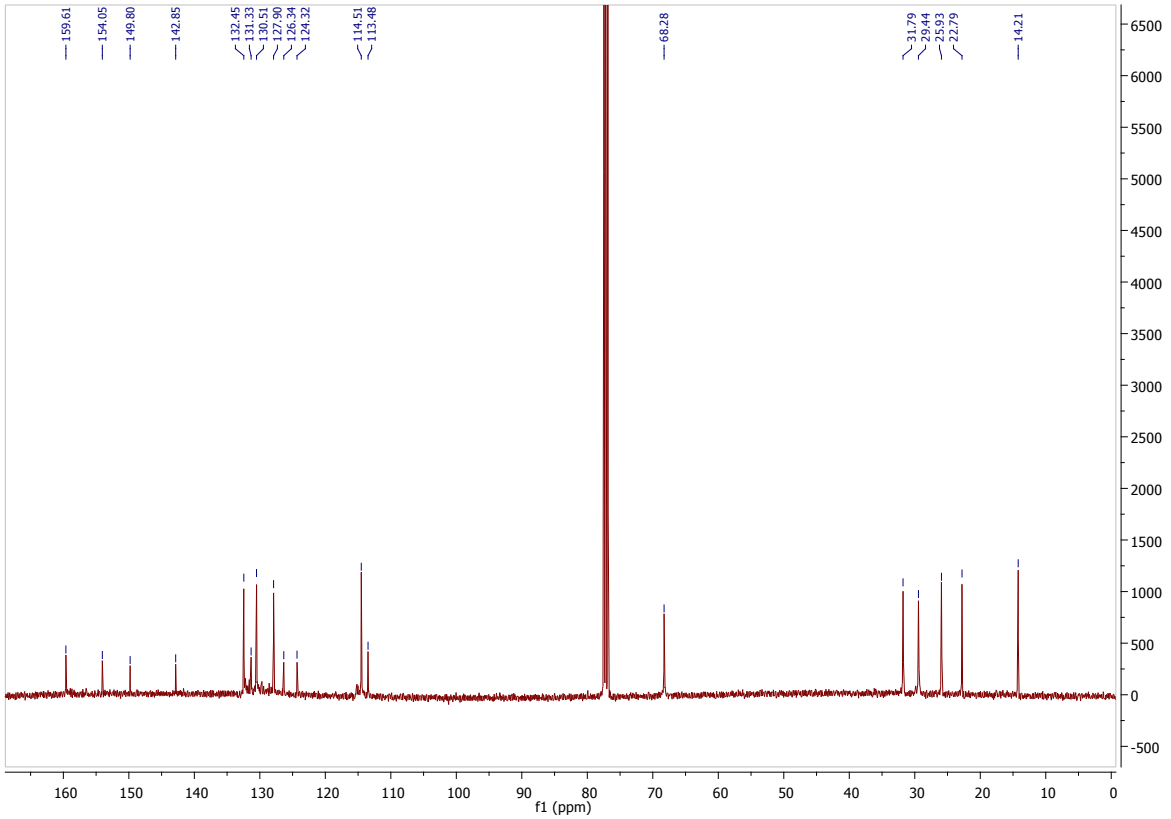
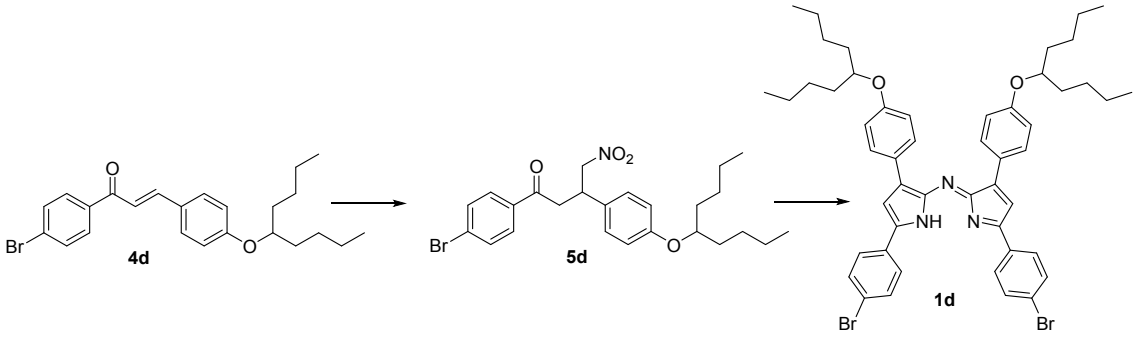


Figure S5. ^{13}C NMR spectrum ($CDCl_3$) of compound **1c**.

Compound 1d



Compound **4d** was prepared according to typical procedure, with 4-bromoacetophenone (0.978 g, 4.912 mmol, 1 equiv.), benzaldehyde **2d** (1.220 g, crude) in ethanol (20 mL) and sodium hydroxide 2.5 M (20 mL). Time: one night; temperature: RT. As there was no precipitation, the reaction mixture was extracted with EtOAc, and combined organic layers washed with water. The crude orange oil was purified by column chromatography with PE/EtOAc 98:2 – 9:1 as eluent. The product was immediately used for the next step (483 mg). ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.91 – 7.85 (m, 2H), 7.79 (d, *J* = 15.6 Hz, 1H), 7.67 – 7.61 (m, 2H), 7.58 (d, *J* = 8.8 Hz, 2H), 7.34 (d, *J* = 15.6 Hz, 1H), 6.91 (d, *J* = 8.8 Hz, 2H), 4.29 (quint, *J* = 5.9 Hz, 1H), 1.75 – 1.60 (m, 4H), 1.42 – 1.24 (m, 8H), 0.90 (t, *J* = 7.0 Hz, 6H).

Compound **5d** was prepared according to typical procedure with chalcone **4d** (483 mg, 1.125 mmol, 1 equiv.), diethylamine (411 mg, 5.624 mmol, 0.6 mL, 5 equiv) and nitromethane (343 mg, 5.624 mmol, 0.3 mL, 5 equiv) in methanol (10 mL). temperature: reflux; time: 1 night; Product used without further purification. Product: Yellow oil (535 mg, 97%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.79 – 7.75 (m, 2H), 7.62 – 7.57 (m, 2H), 7.16 – 7.12 (m, 2H), 6.84 – 6.79 (m, 2H), 4.77 (dd, *J* = 12.4, 6.9 Hz, 1H), 4.64 (dd, *J* = 12.4, 7.6 Hz, 1H), 4.19 – 4.11 (m, 2H), 3.38 (dd, *J* = 6.9, 3.4 Hz, 2H), 1.67 – 1.57 (m, 4H), 1.42 – 1.20 (m, 8H), 0.95 – 0.81 (m, 6H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 196.23, 158.47, 135.31, 132.20, 130.42, 129.68, 128.92, 128.61, 116.36, 79.87, 78.17, 41.81, 38.71, 33.72, 27.71, 22.93, 14.21.

Compound **1d** was prepared according to typical procedure with **5d** (535 mg, 1.091 mmol, 1 equiv.), ammonium acetate (approx. 3 g, approx. 35 equiv) in BuOH (10 mL). Time: 17h; temperature: reflux; product: blue powder (94 mg, 7% over 3 steps). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.95 (d, *J* = 8.7 Hz, 4H), 7.69 (d, *J* = 8.3 Hz, 4H), 7.59 (d, *J* = 8.3 Hz, 4H), 6.99 (s, 2H), 6.92 (d, *J* = 8.7 Hz, 4H), 4.32 (p, *J* = 5.9 Hz, 2H), 1.78 – 1.63 (m, 8H), 1.51 – 1.33 (m, 16H), 0.93 (t, *J* = 7.1 Hz, 12H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 159.28, 153.98, 149.79, 142.83, 132.41, 131.30, 130.54, 127.85, 126.11, 124.26, 115.67, 113.32, 78.09, 33.87, 27.77, 23.00, 14.26. HRMS (ESI^+) calcd. for $[M+H]^+$: 890.2890. Found: 890.2905.

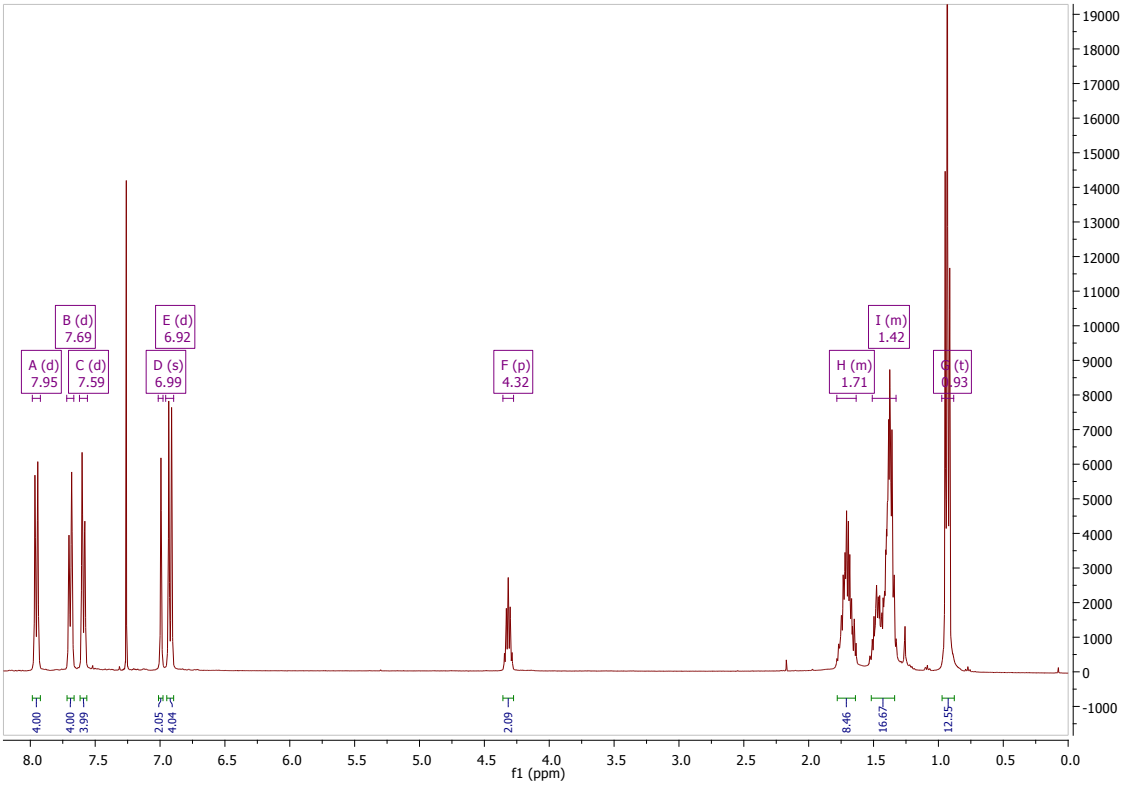


Figure S6. ^{1}H NMR spectrum ($CDCl_3$) of compound **1d**

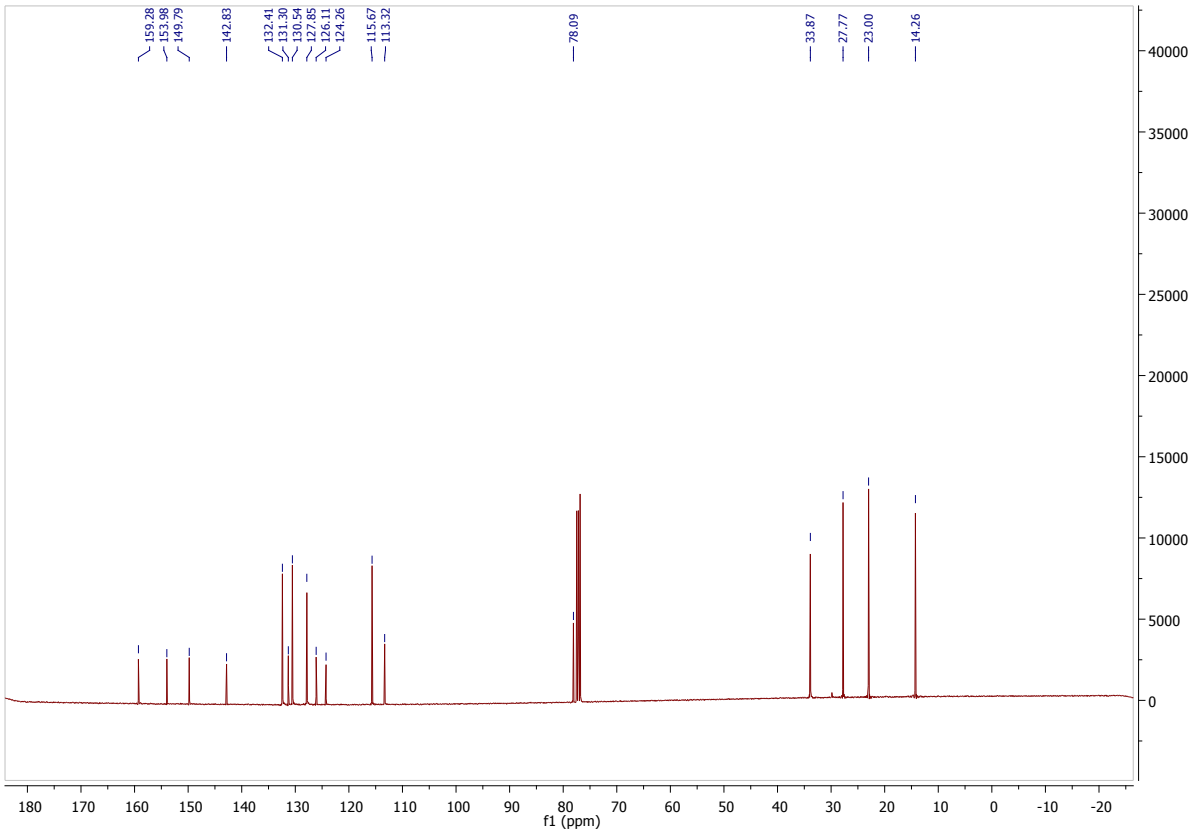
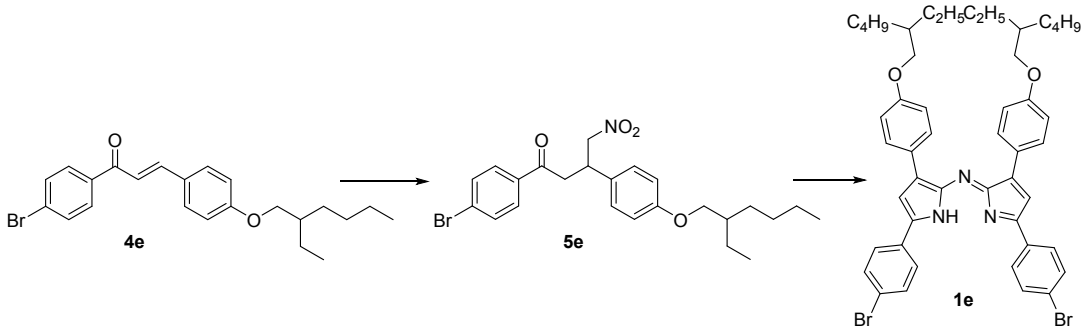


Figure S7. ^{13}C NMR spectrum ($CDCl_3$) of compound **1d**

Compounds 1e



Compound **4e** was prepared according to typical procedure, with 4-bromoacetophenone (1.73 g, 8.68 mmol, 1 equiv.), benzaldehyde **2e** (2.04 g, 8.68 mmol, 1 equiv.) in ethanol (30 mL) and sodium hydroxide 2.5 M (30 mL). Time: one night; temperature: RT; purification: filtration and washing with cold EtOH and pentane; product: off-white solid (3.52 g, 97%). Used without further purification. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.91 – 7.86 (m, 2H), 7.79 (d, *J* = 15.8 Hz, 1H), 7.67 – 7.61 (m, 2H), 7.61 – 7.57 (m, 2H), 7.35 (d, *J* = 15.6 Hz, 1H), 6.95 – 6.91 (m, 2H), 3.89 (dd, *J* = 5.7, 1.0 Hz, 2H), 1.78 – 1.70 (m, 1H), 1.59 – 1.26 (m, 8H), 0.97 – 0.87 (m, 6H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 189.59, 161.89, 145.62, 137.37, 131.98, 130.50, 130.10, 127.72, 127.17, 118.92, 115.09, 70.74, 39.39, 30.57, 29.18, 23.90, 23.18, 14.26, 11.24. HRMS (ESI^+) calcd. for $[M+H]^+$: 415.1267. Found: 415.1252.

Compound **5e** was prepared according to typical procedure with chalcone **4e** (3.48 g, 8.43 mmol, 1 equiv.), diethylamine (3.08 g, 42.1 mmol, 4.4 mL, 5 equiv.) and nitromethane (2.57 g, 42.1 mmol, 2.3 mL, 5 equiv.) in methanol (75 mL). temperature: reflux; time: 1 night. The product was quickly purified with flash chromatography (EP/EtOAc 9:1 as eluent) and immediately used for the next step (2.393 g, 60%). ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.77 (d, *J* = 8.4 Hz, 2H), 7.60 (d, *J* = 8.4 Hz, 2H), 7.16 (d, *J* = 8.5 Hz, 2H), 6.85 (d, *J* = 8.5 Hz, 2H), 4.77 (dd, *J* = 12.3, 6.9 Hz, 1H), 4.64 (dd, *J* = 12.3, 7.6 Hz, 1H), 4.20 – 4.09 (m, 1H), 3.79 (d, *J* = 5.7 Hz, 2H), 3.38 (d, *J* = 7.3 Hz, 2H), 1.75 – 1.63 (m, 1H), 1.53 – 1.23 (m, 8H), 0.97 – 0.83 (m, 6H).

Aza-dipyrromethene **1e** was prepared according to typical procedure with **5e** (2.393 g, 5.023 mmol, 1 equiv.), ammonium acetate (approx. 14 g, approx. 35 equiv) in BuOH (40 mL). Time: 2 days; temperature: reflux; product: purple powder (1.018 g, 47%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.99 – 7.94 (m, 4H), 7.71 (d, *J* = 8.6 Hz, 4H), 7.61 (d, *J* = 8.6 Hz, 4H), 7.01 (s, 2H), 6.94 (d, *J* = 8.9 Hz, 4H), 3.92 (d, *J* = 5.8 Hz, 4H), 1.82 – 1.73 (m, 2H), 1.62 – 1.29 (m, 16H), 1.01 – 0.89 (m, 12H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 159.81, 153.98, 149.75, 142.79, 132.41, 131.25, 130.45, 127.87, 126.22, 124.28, 114.49, 113.42, 70.69, 39.49, 30.65, 29.22, 23.96, 23.23, 14.29, 11.29. HRMS (ESI^+) calcd. for $[M+H]^+$: 862.2577. Found: 862.2570.

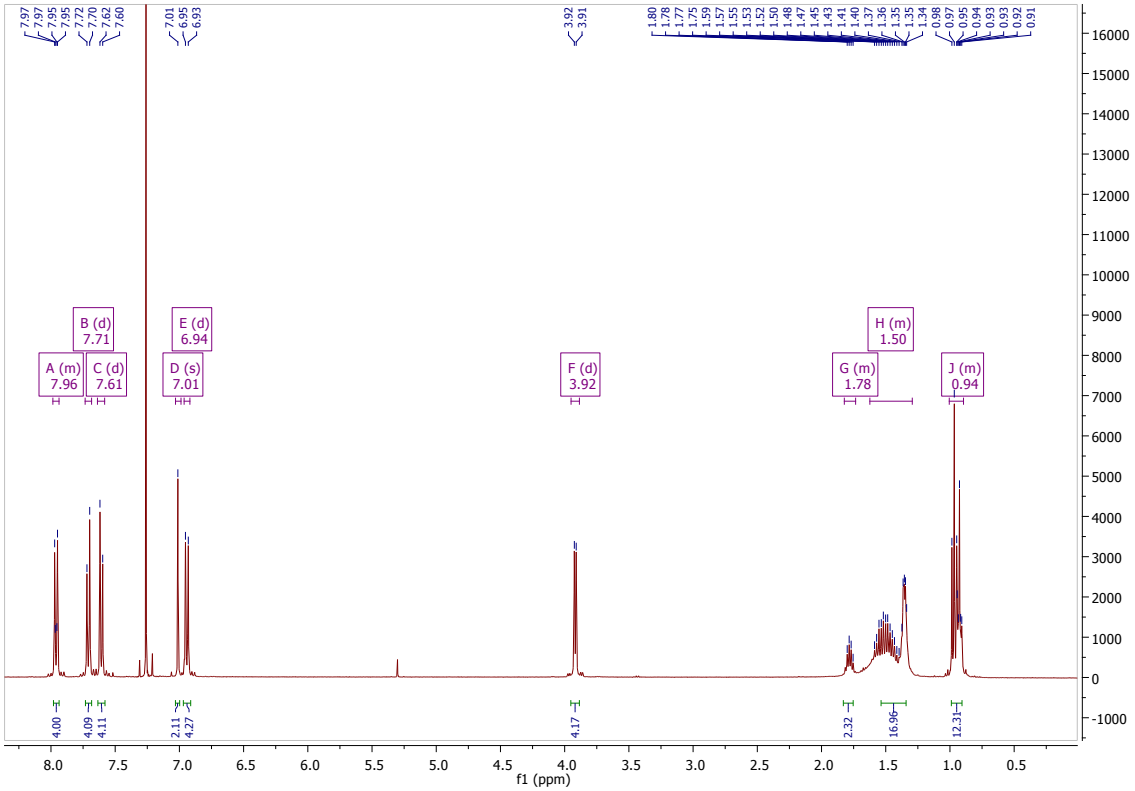


Figure S8. ^{1}H NMR spectrum ($CDCl_3$) of compound **1e**

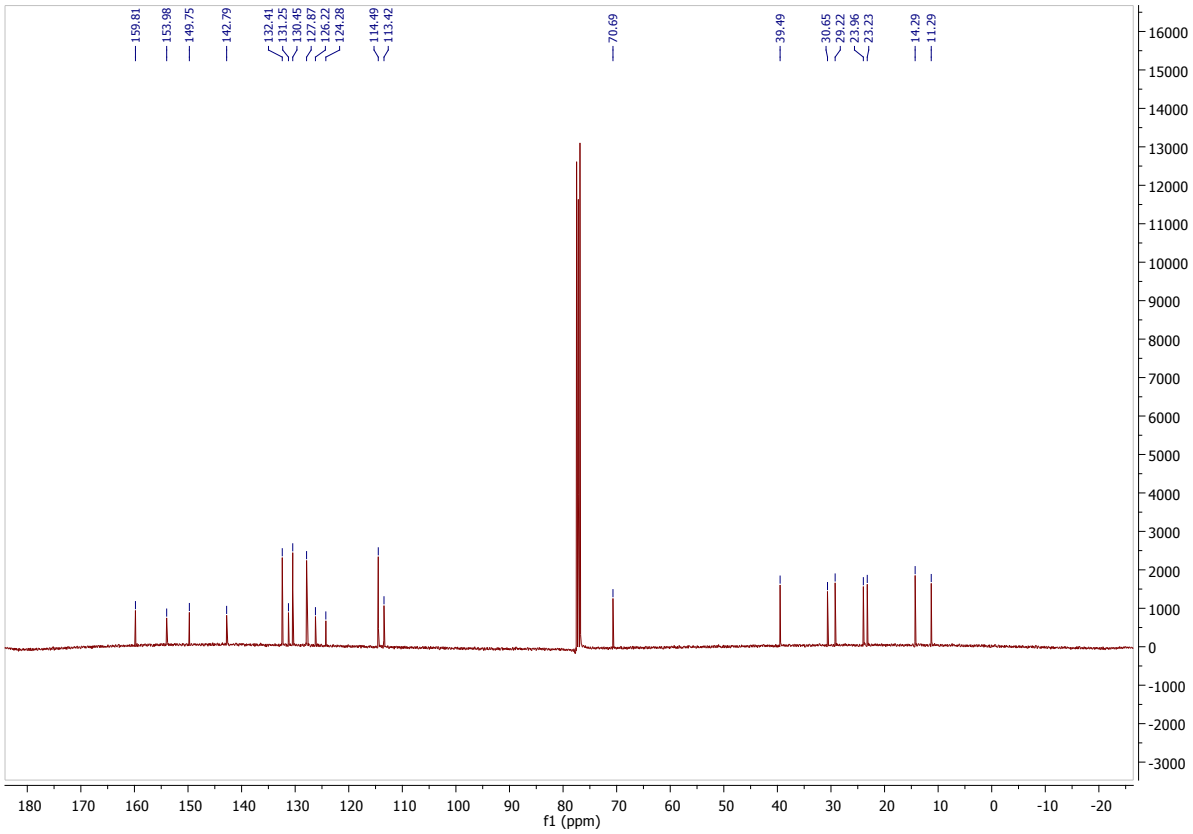
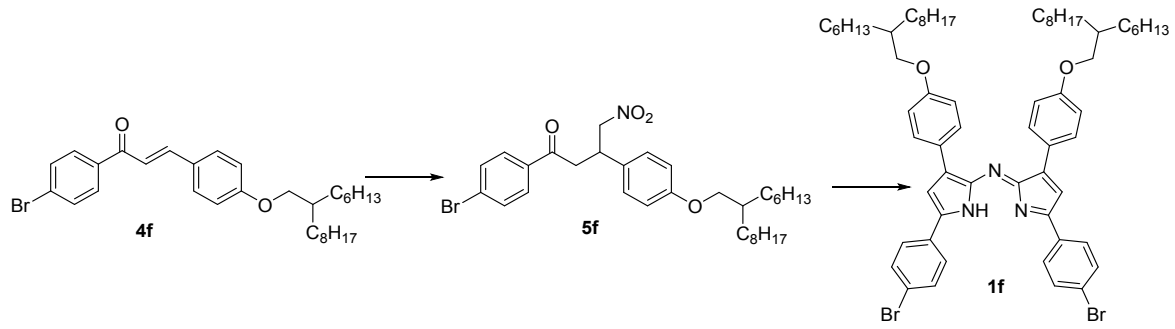


Figure S9. ^{13}C NMR spectrum ($CDCl_3$) of compound **1e**

Compounds 1f



Compound **4f** was prepared according to typical procedure, with 4-bromoacetophenone (4.933 g, 24.78 mmol, 1.1 equiv.), benzaldehyde **2f** (7.808 g, 22.53 mmol, 1 equiv.) in ethanol (90 mL) and sodium hydroxide 2.5 M (90 mL). Time: one night; temperature: RT; As there was no precipitation, the reaction mixture was extracted with EtOAc, and combined organic layers washed with water and brine. The crude yellow oil was purified by column chromatography with PE/EtOAc 95:5 – 9:1 as eluent. The product (yellow oil, 8.1 g) was immediately used for the next step. ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.90 – 7.85 (m, 2H), 7.79 (d, *J* = 15.6 Hz, 1H), 7.67 – 7.62 (m, 2H), 7.59 (d, *J* = 8.7 Hz, 2H), 7.34 (d, *J* = 15.6 Hz, 1H), 6.93 (d, *J* = 8.7 Hz, 2H), 3.88 (d, *J* = 5.7 Hz, 2H), 1.86 – 1.71 (m, 1H), 1.48 – 1.20 (m, 24H), 0.95 – 0.79 (m, 6H).

Compound **5f** was prepared according to typical procedure with chalcone **4f** (8.1 g, 15.35 mmol, 1 equiv.), diethylamine (5.61 g, 76.76 mmol, 7.9 mL, 5 equiv.) and nitromethane (4.69 g, 76.76 mmol, 4.1 mL, 5 equiv.) in methanol (110 mL). Temperature: reflux; time: 1 day; product: brown oil (8.166 g), used without further purification. ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.77 (d, *J* = 8.6 Hz, 2H), 7.60 (d, *J* = 8.6 Hz, 2H), 7.16 (d, *J* = 8.6 Hz, 2H), 6.84 (d, *J* = 8.6 Hz, 3H), 4.77 (dd, *J* = 12.4, 7.0 Hz, 1H), 4.64 (dd, *J* = 12.4, 7.6 Hz, 1H), 4.19 – 4.08 (m, 1H), 3.78 (d, *J* = 5.7 Hz, 2H), 3.38 (d, *J* = 7.4 Hz, 2H), 1.81 – 1.20 (m, 25H), 0.8 7(t, *J* = 6.6 Hz, 6H).

Compound **1f** was prepared according to typical procedure with **5f** (8.166 g, 13.87 mmol, 1 equiv.), ammonium acetate (approx. 37 g, approx. 486 mmol, approx. 35 equiv.) in BuOH (125 mL). Temperature: reflux; time: 18h; product: black powder (2.593 g, 21% over 3 steps). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.94 – 7.91 (m, 4H), 7.64 (d, *J* = 8.6 Hz, 4H), 7.55 (d, *J* = 8.6 Hz, 4H), 6.95 (s, 2H), 6.92 (d, *J* = 8.9 Hz, 4H), 3.91 (d, *J* = 5.7 Hz, 4H), 1.91 – 1.73 (m, 2H), 1.54 – 1.24 (m, 48H), 0.94 – 0.81 (m, 12H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 159.86, 153.88, 149.79, 142.70, 132.34, 131.24, 130.41, 127.84, 126.26, 124.19, 114.51, 113.32, 71.21, 38.20, 32.08, 32.05, 31.54, 30.24, 29.90, 29.80, 29.53, 27.06, 27.02, 22.85, 14.28. HRMS (ESI^+) calcd. for $[M+H]^+$: 1086.5081. Found: 1086.5103.

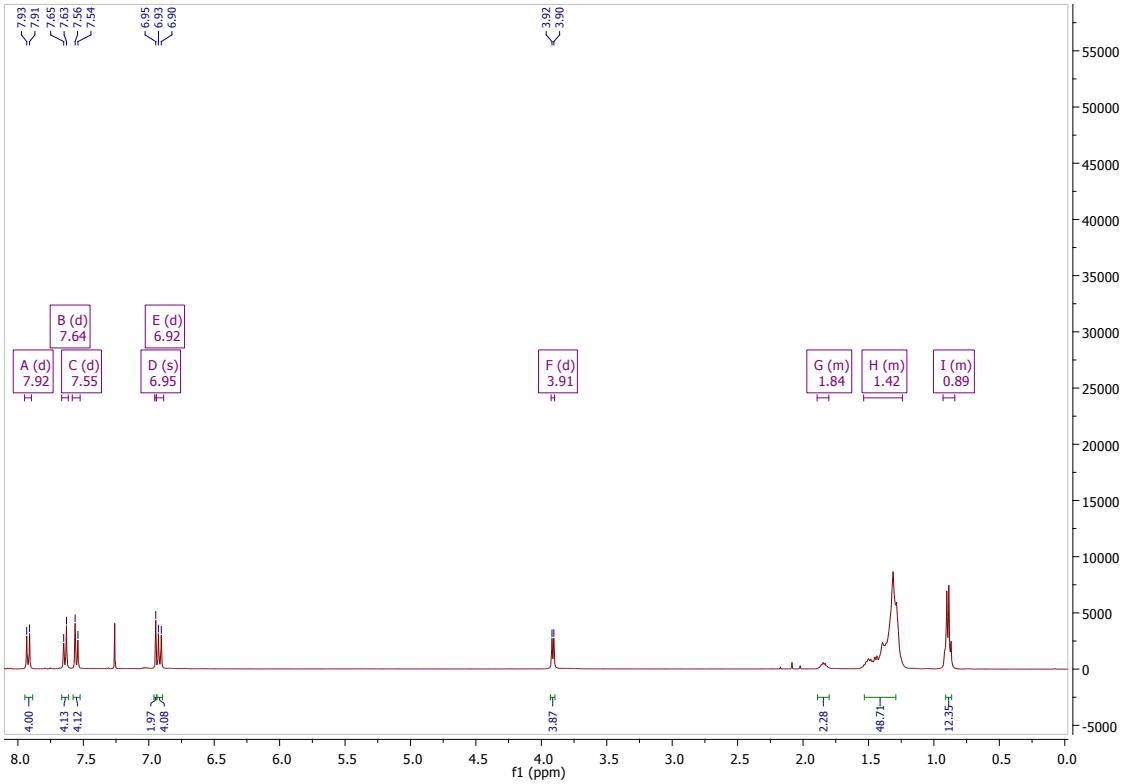


Figure S10. ^{1}H NMR spectrum ($CDCl_3$) of compound **1f**

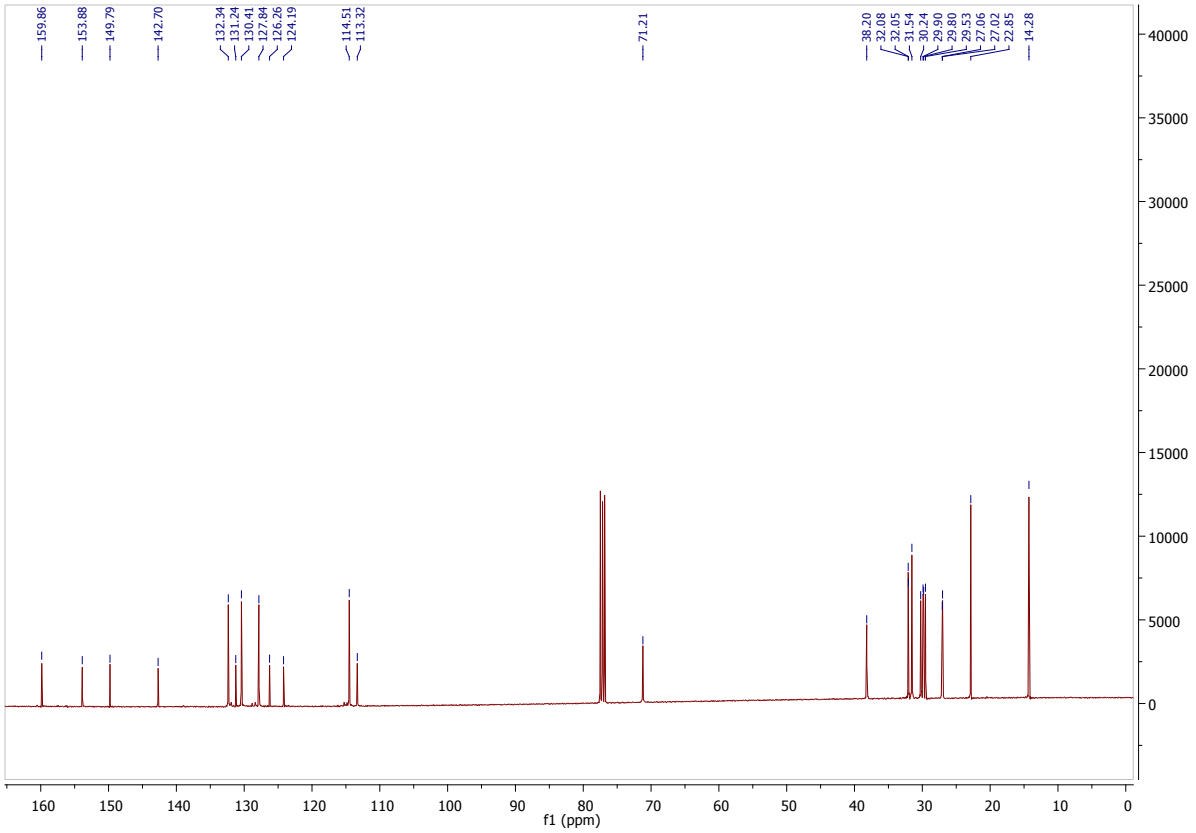
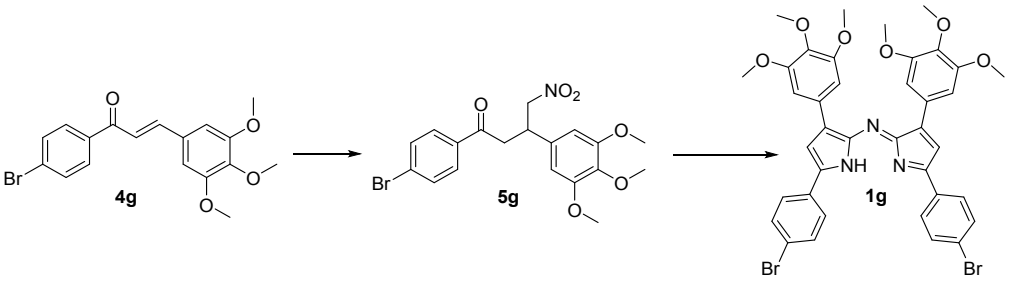


Figure S11. ^{13}C NMR spectrum ($CDCl_3$) of compound **1f**

Compound 1g



Compound **4g** was prepared according to typical procedure, with 4'-bromoacetophenone (2.00 g, 10.05 mmol, 1 equiv.), 3,4,5-trimethoxybenzaldehyde (1.97 g, 10.05 mmol, 1 equiv.) in ethanol (35 mL) and sodium hydroxide 2.5 M (35 mL). Time: one night; temperature: RT; purification: filtration and washing with cold EtOH and pentane; product: yellow solid (3.78 g, 99%). Used without further purification. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.88 (d, *J* = 8.5 Hz, 2H), 7.72 (d, *J* = 15.6 Hz, 1H), 7.65 (d, *J* = 8.5 Hz, 2H), 7.34 (d, *J* = 15.6 Hz, 1H), 6.86 (s, 2H), 3.92 (s, 6H), 3.91 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 189.59, 153.69, 145.77, 140.86, 137.17, 132.08, 130.29, 130.17, 127.96, 121.03, 105.95, 61.17, 56.42.

Compound **5g** was prepared according to typical procedure with chalcone **4g** (3.78 g, 10.02 mmol, 1 equiv.), diethylamine (3.68 g, 50.25 mmol, 5.2 mL, 5 equiv.) and nitromethane (3.07 g, 50.25 mmol, 2.7 mL, 5 equiv.) in methanol (90 mL). Temperature: reflux; time: 1 night; purification: recrystallization in MeOH. Product: off-white solid (2.741 g, 62%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.78 (d, *J* = 8.5 Hz, 2H), 7.61 (d, *J* = 8.5 Hz, 2H), 6.45 (s, 2H), 4.80 (dd, *J* = 12.5, 6.8 Hz, 1H), 4.68 (dd, *J* = 12.5, 7.8 Hz, 1H), 4.18 – 4.10 (m, 1H), 3.84 (s, 6H), 3.81 (s, 3H), 3.41 – 3.35 (m, 2H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 196.06, 153.78, 137.86, 135.25, 134.67, 132.27, 129.67, 129.07, 104.70, 79.53, 60.97, 56.40, 41.77, 39.75.

Compound **1g** was prepared according to typical procedure with compound **5g** (2.741 g, 6.254 mmol, 1 equiv.), ammonium acetate (17 g, 227 mmol, 35 equiv.) in EtOH (50 mL). Time: 17h; temperature: reflux; purification: filtration with cold EtOH; product: purple powder (584 mg, 0.699 mmol, 22%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.79 (d, *J* = 8.4 Hz, 4H), 7.67 (d, *J* = 8.4 Hz, 4H), 7.13 (s, 4H), 7.08 (s, 2H), 3.91 (s, 6H), 3.71 (s, 12H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 154.23, 153.24, 149.76, 143.52, 138.58, 132.62, 131.10, 129.28, 128.01, 124.78, 115.02, 106.54, 61.09, 56.08. HRMS (ESI^+) calcd. for $[M+H]^+$: 786.0809. Found: 786.0820.

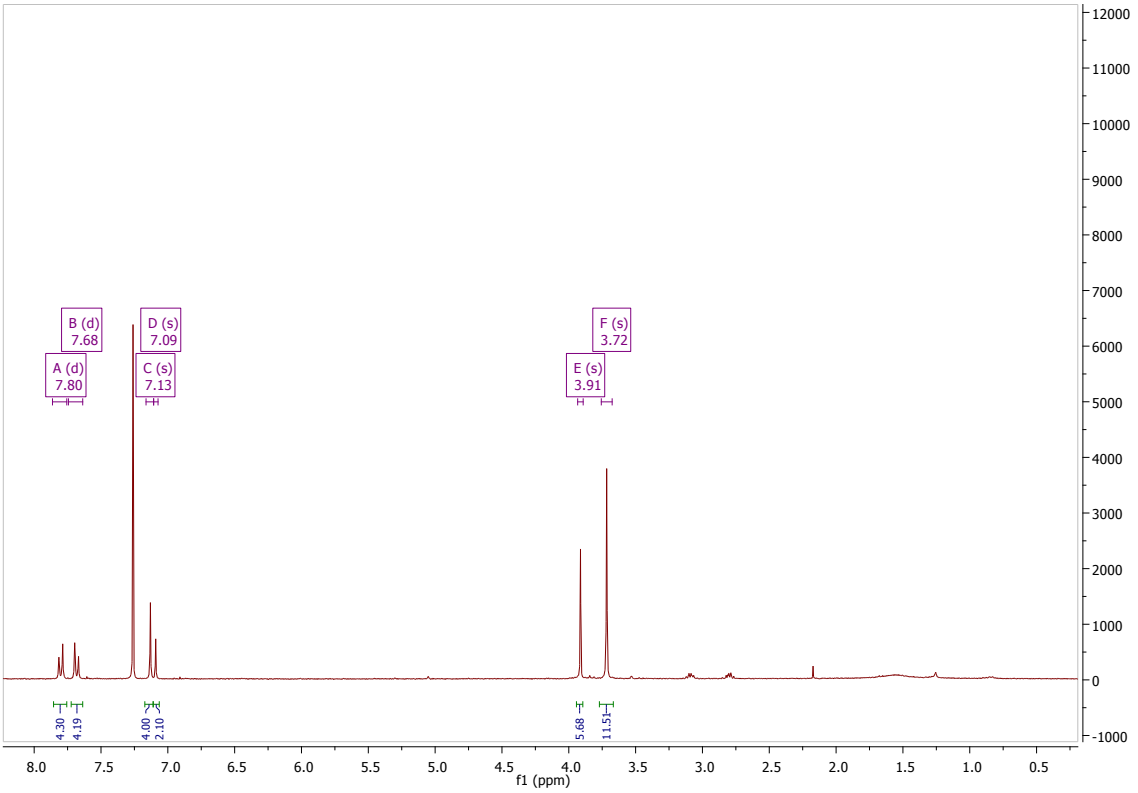


Figure S12. ^{1}H NMR spectrum ($CDCl_3$) of compound **1g**

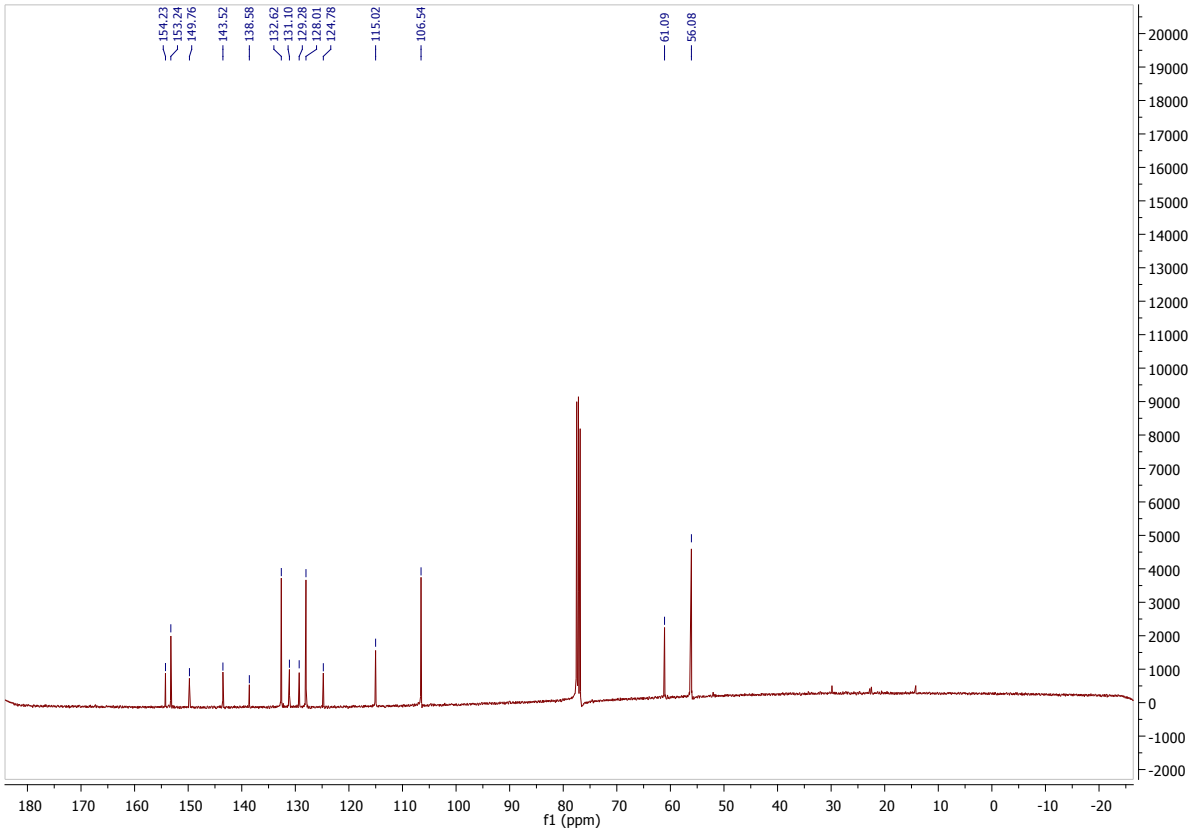
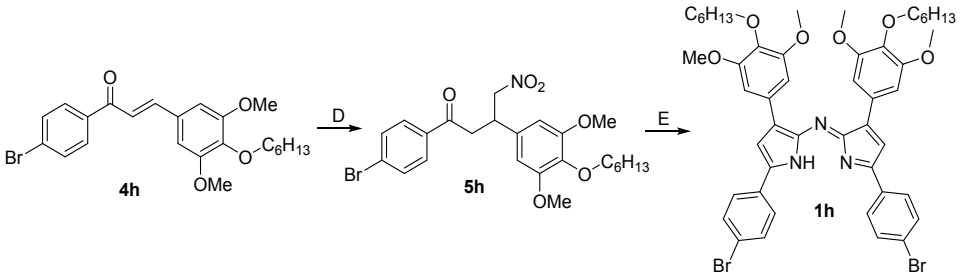


Figure S13. ^{13}C NMR spectrum ($CDCl_3$) of compound **1g**

Compound 1h



Compound **4h** was prepared according to typical procedure, with 4-bromoacetophenone (2.179 g, 10.95 mmol, 1 equiv.), benzaldehyde **2h** (2.917 g, 10.95 mmol, 1 equiv.) in ethanol (40 mL) and sodium hydroxide 2.5 M (40 mL). Time: one night; temperature: RT; As there was no precipitation, the reaction mixture was extracted with EtOAc, and combined organic layers washed with water and brine. The crude yellow oil (3.949 g) was immediately used for the next step without further purification. ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.92 – 7.85 (m, 2H), 7.72 (d, *J* = 15.6 Hz, 1H), 7.68 – 7.62 (m, 2H), 7.33 (d, *J* = 15.6 Hz, 1H), 6.85 (s, 2H), 4.04 (d, *J* = 6.8 Hz, 2H), 3.90 (s, 6H), 1.82 – 1.69 (m, 2H), 1.52 – 1.41 (m, 2H), 1.37 – 1.27 (m, 4H), 0.95 – 0.82 (m, 3H).

Compound 5**h** was prepared according to typical procedure with chalcone **4h** (3.949 g, 8.827 mmol, 1 equiv.), diethylamine (3.27 g, 44.14 mmol, 4.6 mL, 5 equiv.) and nitromethane (2.69 g, 44.14 mmol, 2.4 mL, 5 equiv.) in methanol (75 mL). temperature: reflux; time: one night; product: brown oil, used without further purification (quant.). ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.78 (d, *J* = 8.6 Hz, 2H), 7.61 (d, *J* = 8.6 Hz, 2H), 6.43 (s, 2H), 4.80 (dd, *J* = 12.5, 6.8 Hz, 1H), 4.68 (dd, *J* = 12.5, 7.7 Hz, 1H), 4.20 – 4.09 (m, 1H), 3.91 (t, *J* = 6.9 Hz, 2H), 3.82 (s, 6H), 3.39 (dd, *J* = 6.9, 3.7 Hz, 2H), 1.78 – 1.65 (m, 2H), 1.47 – 1.38 (m, 2H), 1.37 – 1.24 (m, 4H), 0.94 – 0.85 (m, 3H).

Aza-dipyrromethene **1h** was prepared according to typical procedure with **5h** (4.488 g, 8.827 mmol, 1 equiv.), ammonium acetate (approx. 24 g, approx. 309 mmol, approx. 35 equiv.) in BuOH (75 mL). The mixture was refluxed overnight. Product: blue powder (417 mg, 8% over 3 steps). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.79 (d, *J* = 8.5 Hz, 4H), 7.68 (d, *J* = 8.5 Hz, 4H), 7.13 (s, 4H), 7.08 (s, 2H), 4.02 (t, *J* = 6.8 Hz, 4H), 3.69 (s, 12H), 1.84 – 1.73 (m, 4H), 1.65 – 1.42 (m, 4H), 1.42 – 1.21 (m, 8H), 0.99 – 0.82 (m, 6H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 154.18, 153.52, 149.82, 143.64, 138.06, 132.61, 131.18, 129.01, 128.02, 124.72, 114.95, 106.63, 73.84, 56.10, 31.86, 30.30, 25.74, 22.84, 14.25. HRMS (ESI^+) calcd. for $[M+H]^+$: 926.2374. Found: 926.2387.

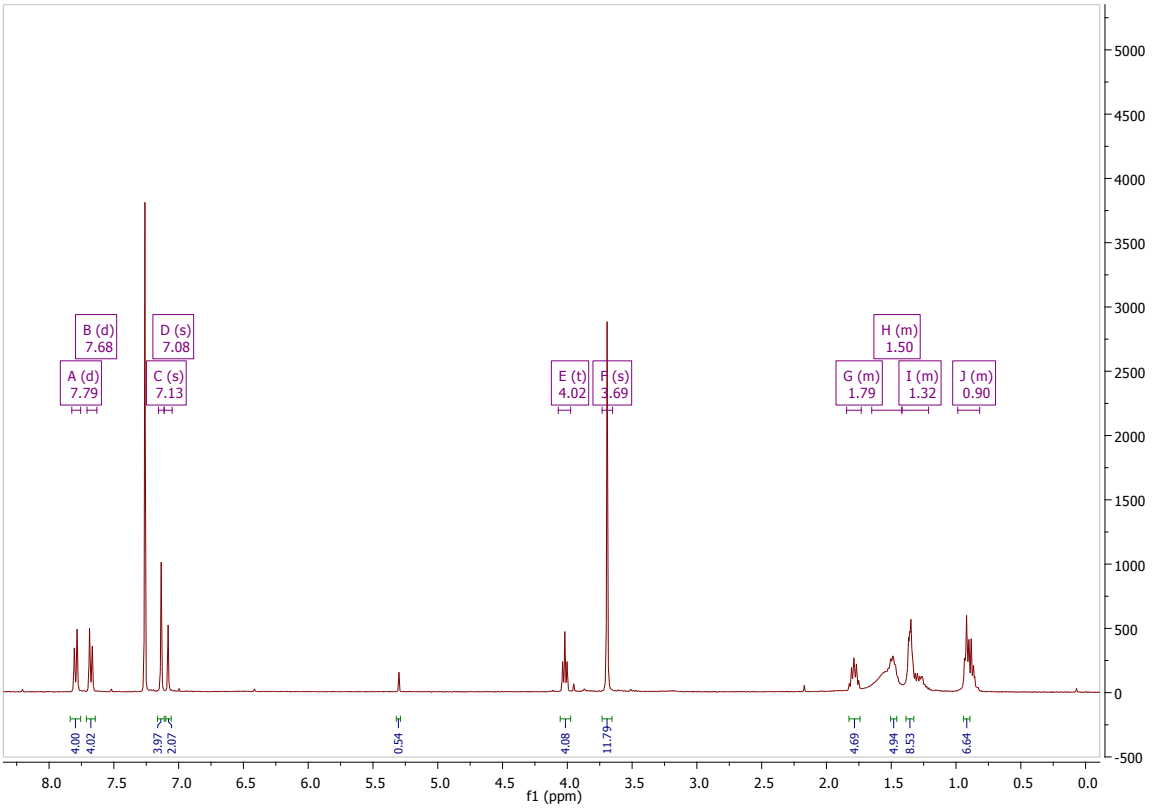


Figure S14. ^{1}H NMR spectrum ($CDCl_3$) of compound **1h**

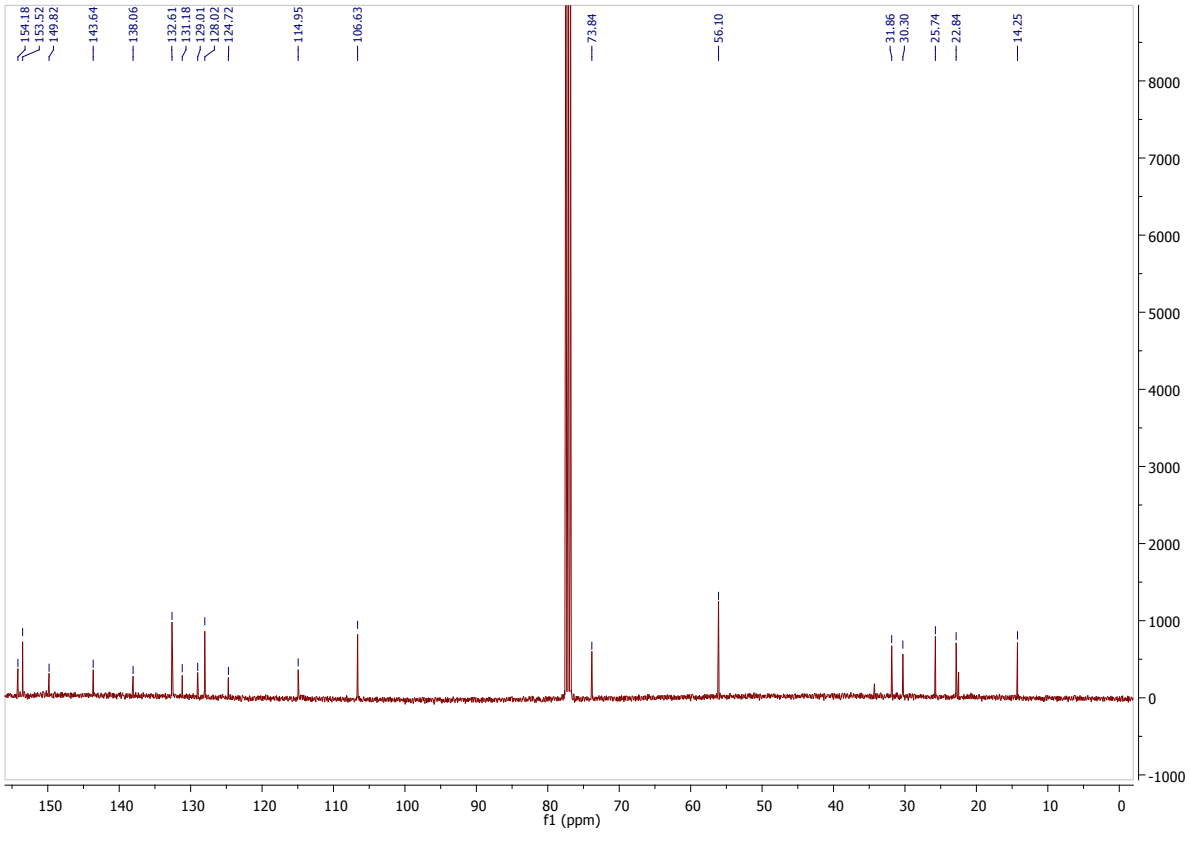
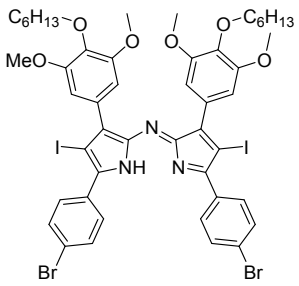


Figure S15. ^{13}C NMR spectrum ($CDCl_3$) of compound **1h**

Compound 6



Aza-dipyrromethene **1h** (150 mg, 0.162 mmol, 1 equiv.) was dissolved in a AcOH/$CHCl_3$ mixture (1:3, 10 mL). After 20 min of degassing by argon bubbling, NIS (80 mg, 0.356 mmol, 2.2 equiv.) was added and the mixture was stirred at RT under argon overnight. The mixture that has turned purple was washed with sodium thiosulfate, extracted with DCM, dries over sodium sulfate and evaporated under reduced pressure to lead to a purple solid (177 mg, 93%, used without further purification). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.80 (d, *J* = 8.4 Hz, 4H), 7.66 (d, *J* = 8.4 Hz, 4H), 6.91 (s, 4H), 4.04 (t, *J* = 6.7 Hz, 4H), 3.57 (s, 12H), 1.87 – 1.75 (m, 4H), 1.58 – 1.43 (m, 4H), 1.43 – 1.28 (m, 8H), 0.97 – 0.82 (m, 6H). ^{13}C NMR (101 MHz, CDCl3) δ 155.25, 152.71, 148.66, 146.46, 138.13, 132.04, 131.79, 130.60, 127.79, 125.10, 108.61, 73.76, 56.04, 31.92, 30.48, 25.79, 22.86, 14.27. (One carbon signal is missing). HRMS (ESI$^+$) calcd. for $[M+H]^+$: 1178.0307. Found: 1178.0349.

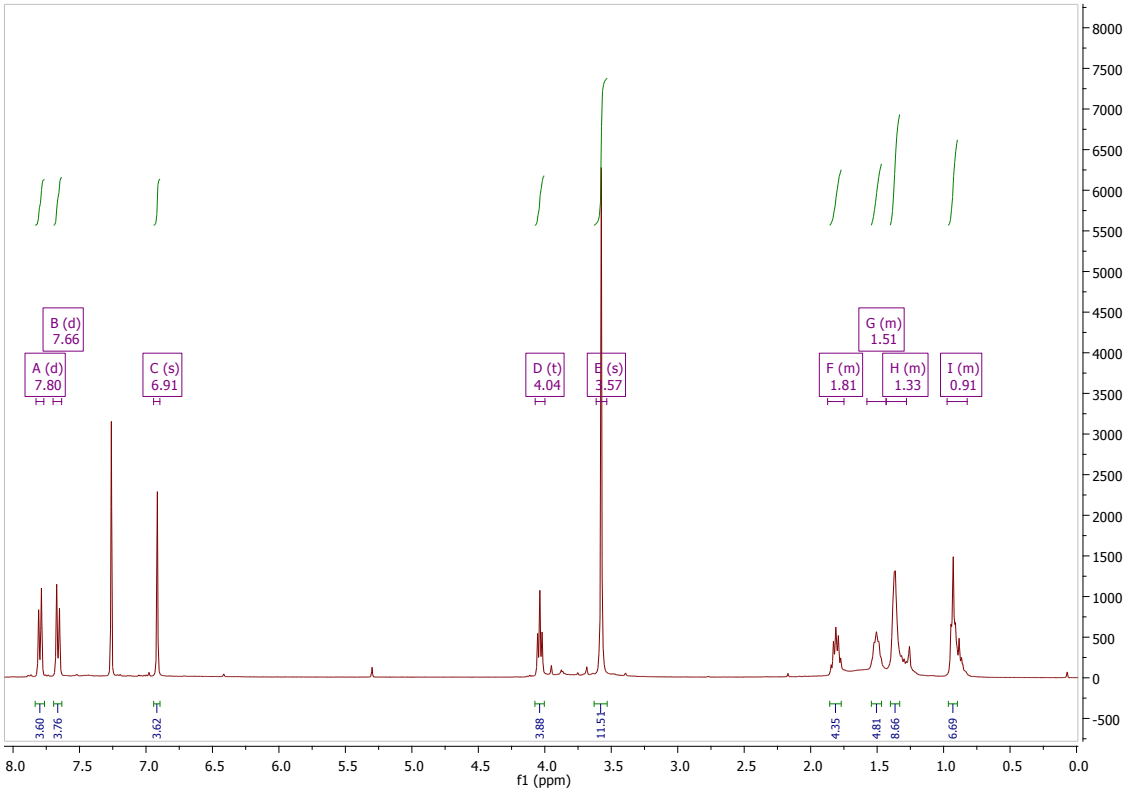


Figure S16. ^{1}H NMR spectrum ($CDCl_3$) of compound **6**

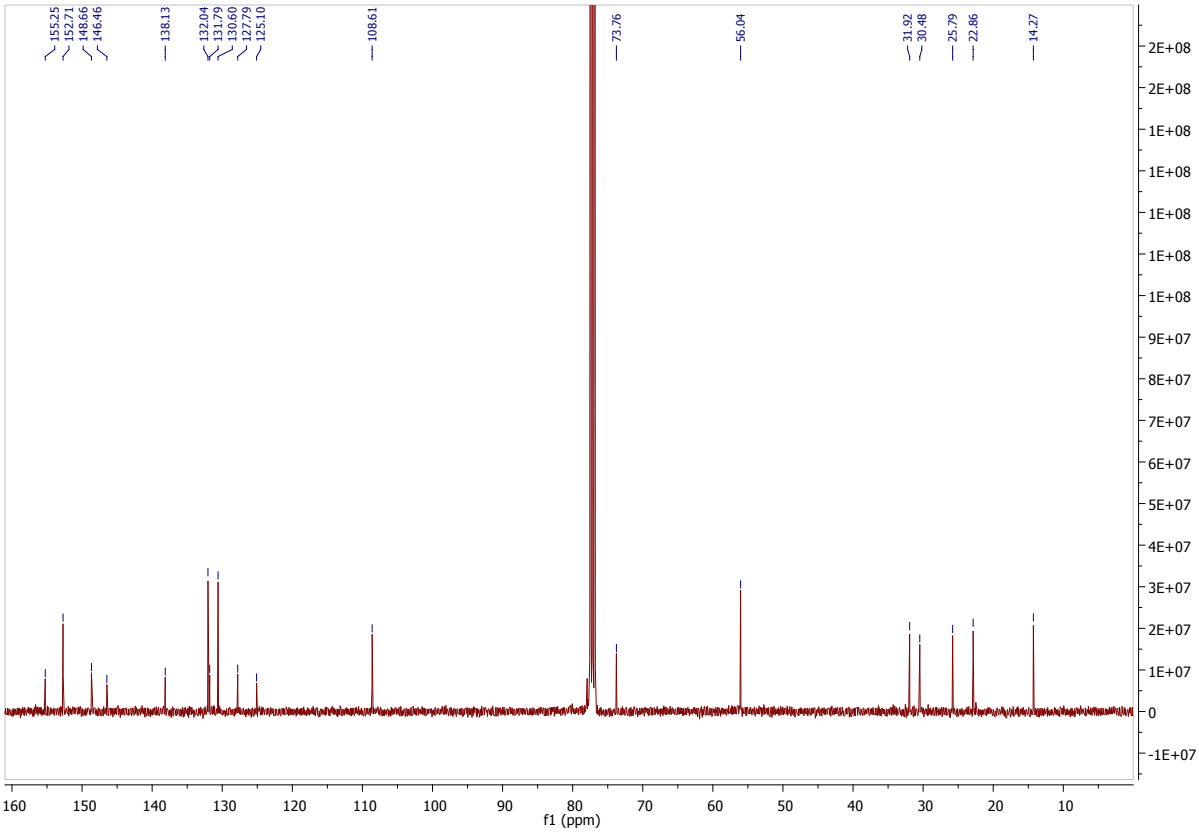
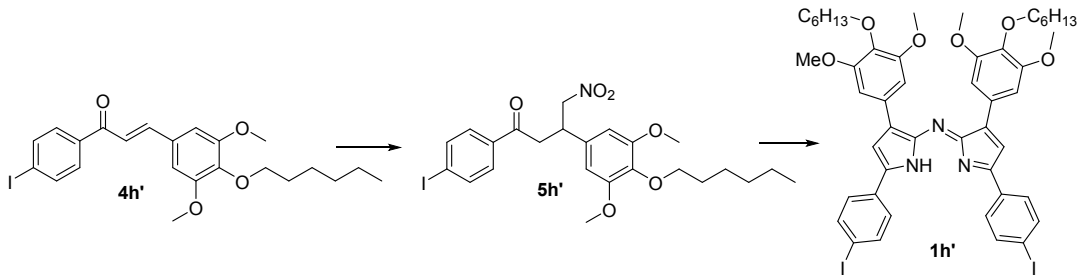


Figure S17. ^{13}C NMR spectrum ($CDCl_3$) of compound **6**

Compounds 4h', 5h', 1h'



Compound **4f'** was prepared according to typical procedure, with 4-iodoacetophenone (7.39 g, 30.04 mmol, 1 equiv.), benzaldehyde **2h** (8.00 g, 30.04 mmol, 1 equiv.) in ethanol (100 mL) and sodium hydroxide 2.5 M (100 mL). Time: one night; temperature: RT; As there was no precipitation, the reaction mixture was extracted with EtOAc, and combined organic layers washed with water. The crude orange oil (14.113 g) was used for the next step without further purification. (NMR yield 83%). ^1H NMR (300 MHz, $CDCl_3$) δ 7.87 (d, *J* = 8.0 Hz, 2H), 7.76 – 7.66 (m, 3H), 7.32 (d, *J* = 15.7 Hz, 1H), 6.85 (s, 2H), 4.03 (t, *J* = 6.8 Hz, 2H), 3.90 (s, 6H), 1.81 – 1.70 (m, 2H), 1.51 – 1.17 (m, 6H), 0.95 – 0.84 (m, 3H).

Compound **5f'** was prepared according to typical procedure with crude chalcone **4f'** (14.113 g, crude), diethylamine (2.735 g, 37.4 mmol, 5 equiv.) and nitromethane (2.283 g, 37.4 mmol, 5 equiv.) in

MeOH/CHCl3 (60 mL/20 mL). Time: one night; temperature: reflux; product (brown solid, 15.57 g) was directly used for the next step.

Aza-dipyrromethene **1f'** was prepared according to typical procedure with crude from **5f'**, ammonium acetate (approx. 67 g, 35 eq.) in 220 mL of BuOH. The mixture was refluxed for 3 days. Purification: filtration and washing with cold EtOH; product: black powder (2.421 g, 17 % over 3 steps). ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.88 (d, *J* = 8.4 Hz, 4H), 7.65 (d, *J* = 8.4 Hz, 4H), 7.13 (s, 4H), 7.08 (s, 2H), 4.02 (t, *J* = 6.9 Hz, 4H), 3.69 (s, 12H), 1.84 – 1.73 (m, 4H), 1.53 – 1.44 (m, 4H), 1.39 – 1.31 (m, 8H), 0.92 (t, *J* = 6.5 Hz, 6H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 154.28, 153.50, 149.87, 143.59, 138.53, 138.02, 131.66, 129.00, 128.04, 114.91, 106.60, 96.60, 73.83, 56.08, 31.85, 30.28, 25.73, 22.83, 14.24. HRMS (ESI$^+$) calcd. for [M+H]$^+$: 1022.2097. Found: 1022.2092.

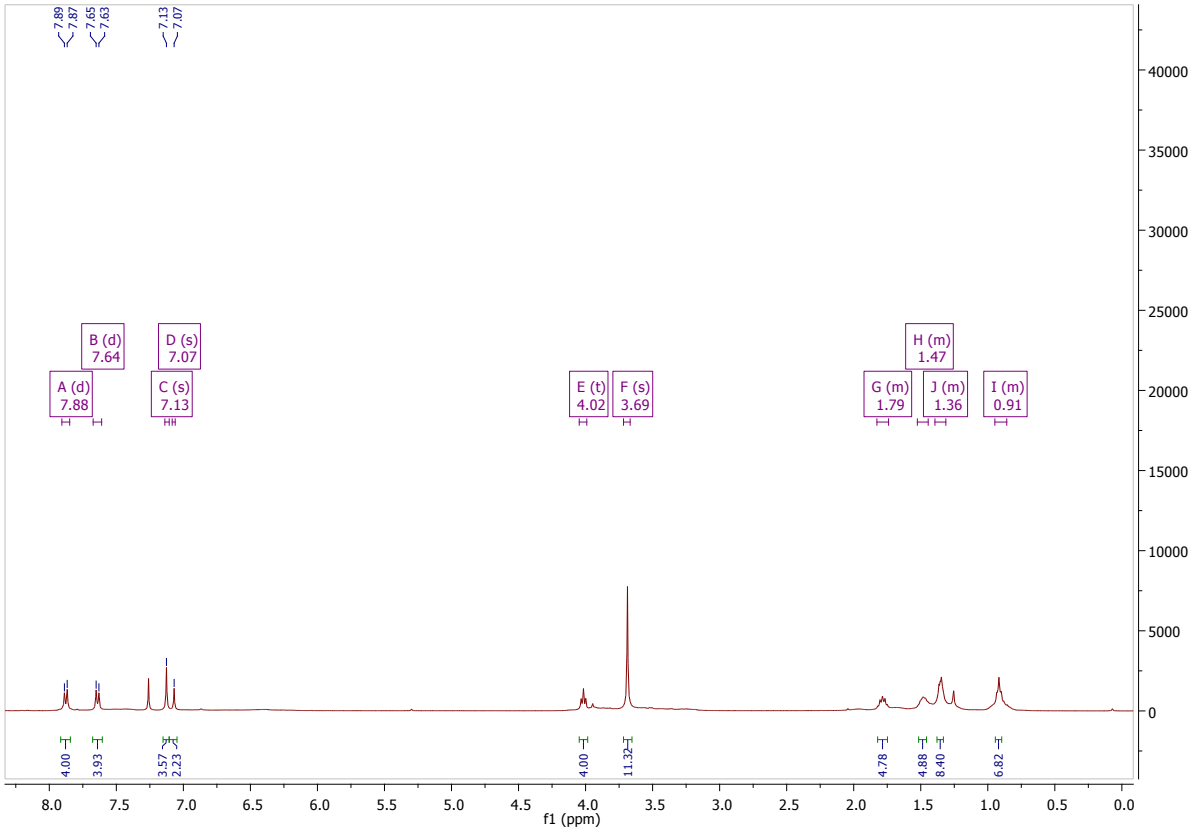


Figure S18. ^{1}H NMR spectrum ($CDCl_3$) of compound **1h'**

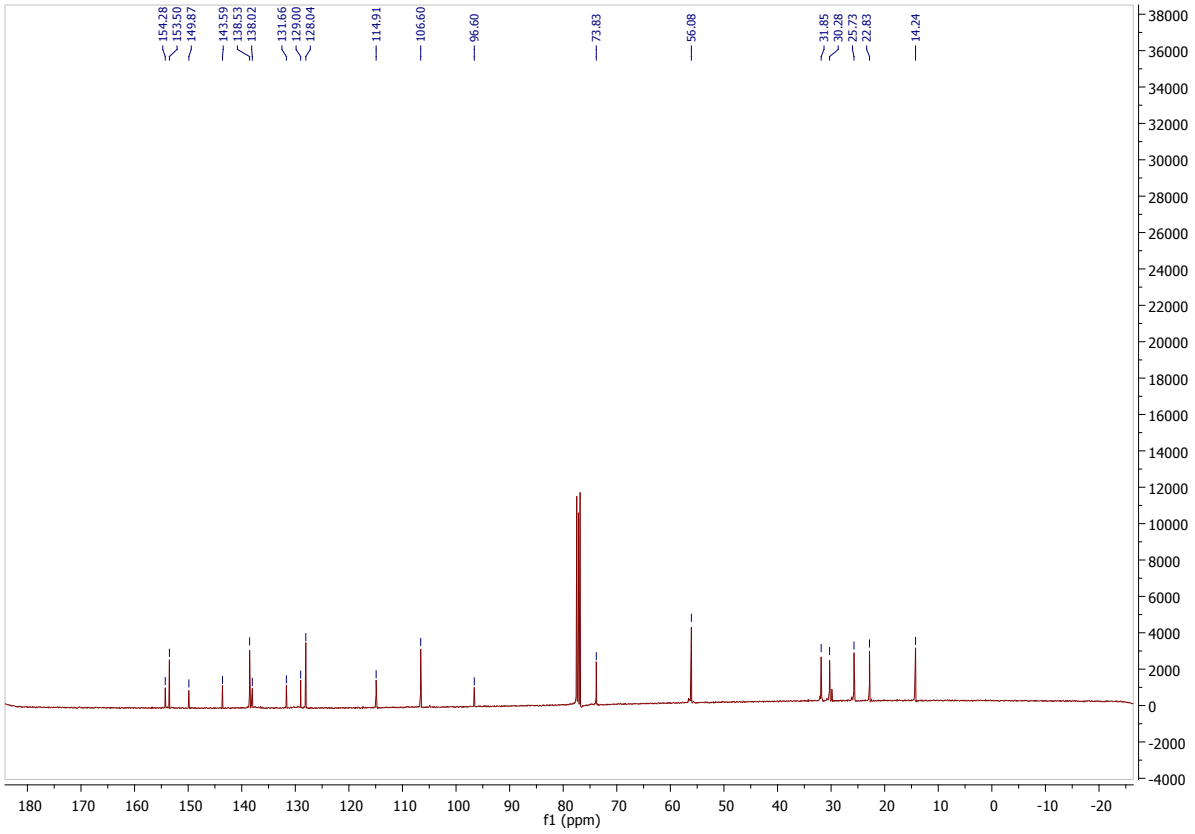
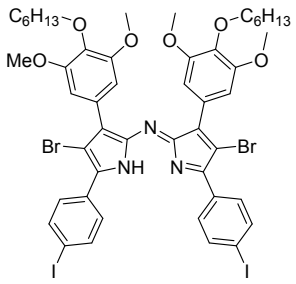


Figure S19. ^{13}C NMR spectrum ($CDCl_3$) of compound **1h'**

Compound 7



Aza-dipyrromethene **1h'** (50 mg, 0.049 mmol, 1 equiv.) was dissolved in a AcOH/$CHCl_3$ mixture (1:3, 5 mL). After 20 min of degassing by argon bubbling, NBS (19 mg, 0.108 mmol, 2.2 eq) was added and the mixture was stirred at 50 °C under argon overnight. The mixture that has turned purple, was washed with sodium thiosulfate, sodium carbonate, water brine, dried over sodium sulfate, and evaporated under reduced pressure. The crude was purified by column chromatography (DCM/EP 70:30 as eluent) to obtained the desired compound as a purple solid. (15 mg, 26%). ^1H NMR (400 MHz, $CDCl_3$) δ 7.88 (d, *J* = 8.5 Hz, 4H), 7.72 (d, *J* = 8.5 Hz, 4H), 6.97 (s, 4H), 4.03 (t, *J* = 6.8 Hz, 4H), 3.57 (s, 12H), 1.81 (quint, *J* = 7.0 Hz, 4H), 1.54 – 1.45 (m, 4H), 1.40 – 1.33 (m, 8H), 0.92 (t, *J* = 7.0 Hz, 6H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 152.85, 152.52, 148.17, 141.22, 138.17, 131.27, 130.17, 126.57, 108.52, 106.98, 97.27, 73.79, 56.02,

31.90, 30.44, 25.77, 22.85, 14.26. (One carbon signal is missing). HRMS (ESI$^+$) calcd. for $[M+H]^+$: 1178.0307. Found: 1178.0318.

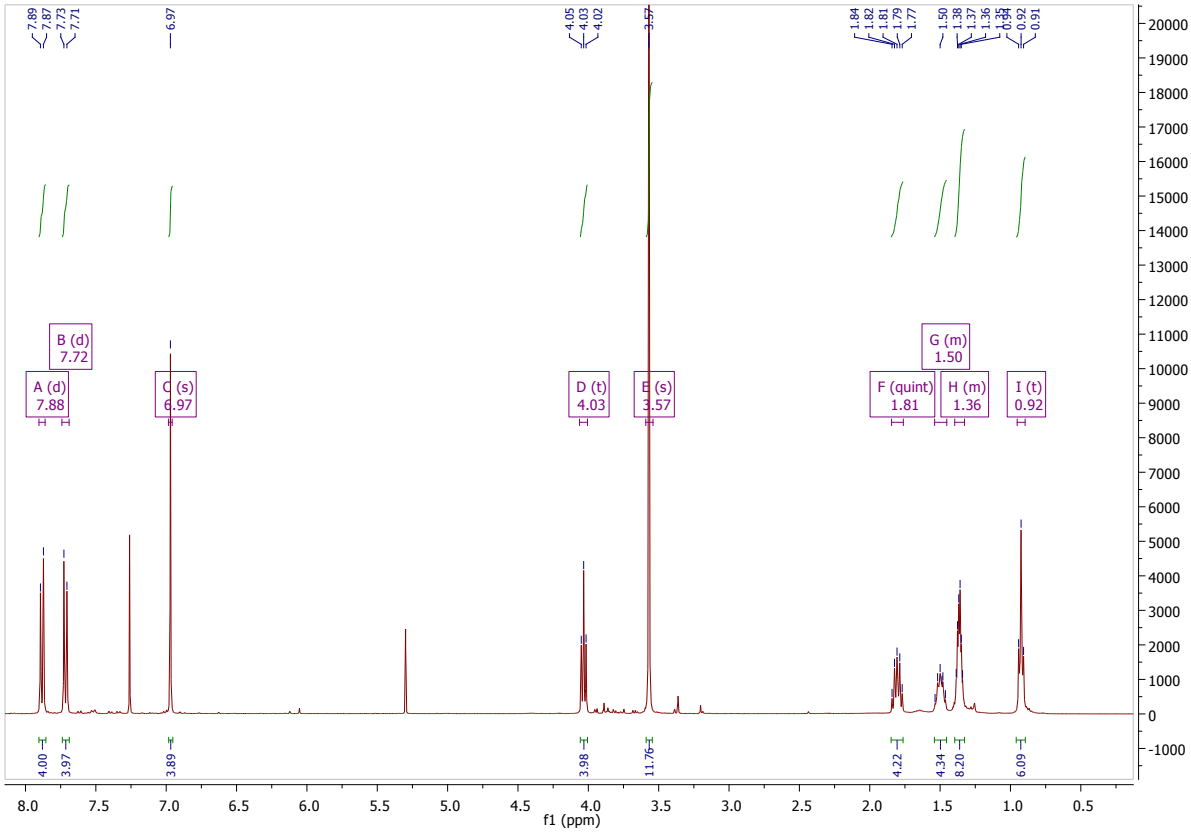


Figure S20. ^{1}H NMR spectrum ($CDCl_3$) of compound **7**

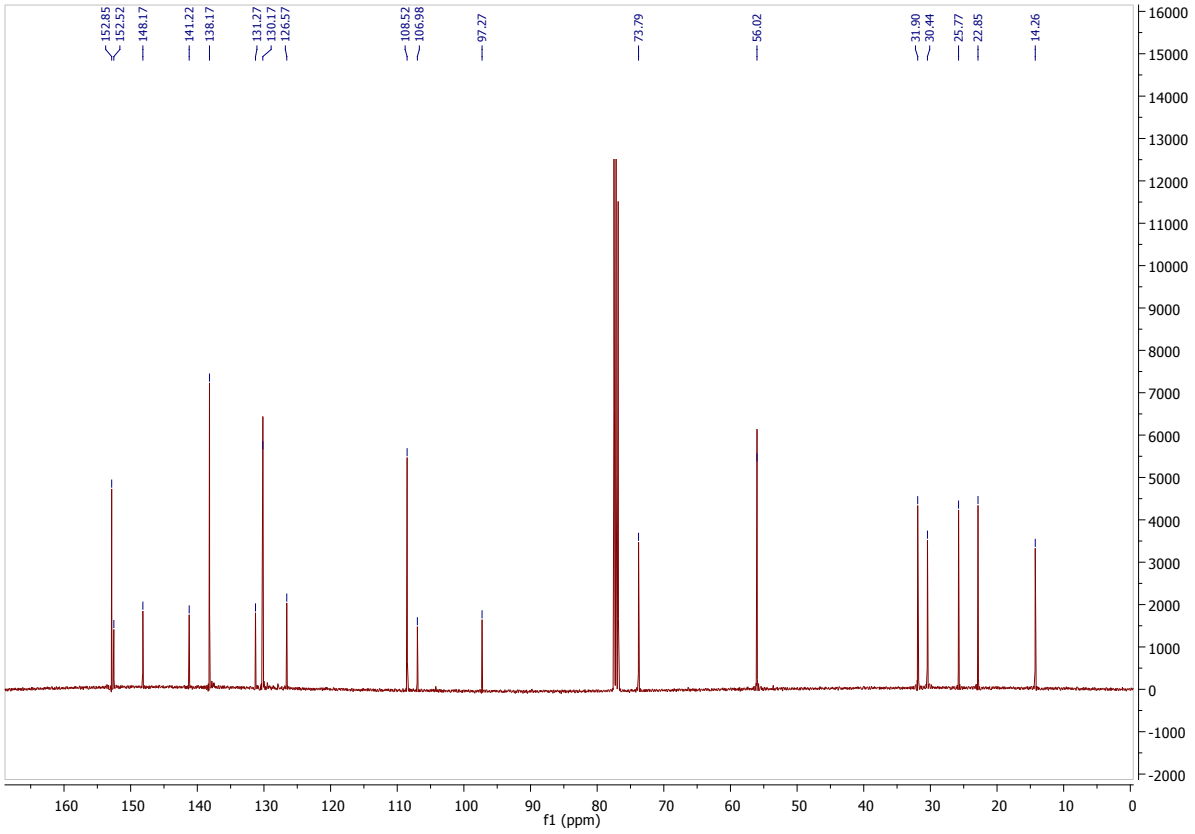
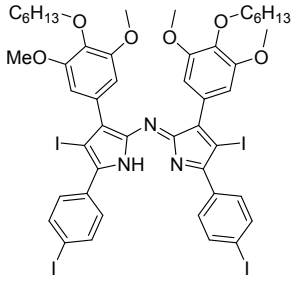


Figure S21. ^{13}C NMR spectrum ($CDCl_3$) of compound **7**

Compound 8



Aza-dipyrromethene **1h'** (100 mg, 0.098 mmol, 1 equiv.) was dissolved in a AcOH/$CHCl_3$ mixture (1:3, 5 mL). After 20 min of degassing by argon bubbling, NIS (48 mg, 0.215 mmol, 2.2 equiv.) was added and the mixture was stirred at RT under argon overnight. The mixture dissolved in DCM, washed with sodium thiosulfate, water and brine, dried over sodium sulfate, and evaporated under reduced pressure. Product was obtained as a purple solid (116 mg, 93%). ^1H NMR (400 MHz, $CDCl_3$) δ 7.87 (d, *J* = 8.5 Hz, 4H), 7.65 (d, *J* = 8.5 Hz, 4H), 6.91 (s, 4H), 4.03 (t, *J* = 6.8 Hz, 4H), 3.57 (s, 12H), 1.85 – 1.75 (m, 4H), 1.55 – 1.45 (m, 4H), 1.41 – 1.33 (m, 8H), 0.93 (t, *J* = 7.0 Hz, 6H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 155.37, 152.70, 148.70, 146.47, 138.11, 137.98, 132.33, 130.60, 127.79, 108.60, 97.16, 73.76, 56.03, 31.92,

30.48, 25.79, 22.86, 14.27. (One carbon signal is missing). HRMS (ESI$^+$) calcd. for $[M+H]^+$: 1274.0030. Found: 1274.015.

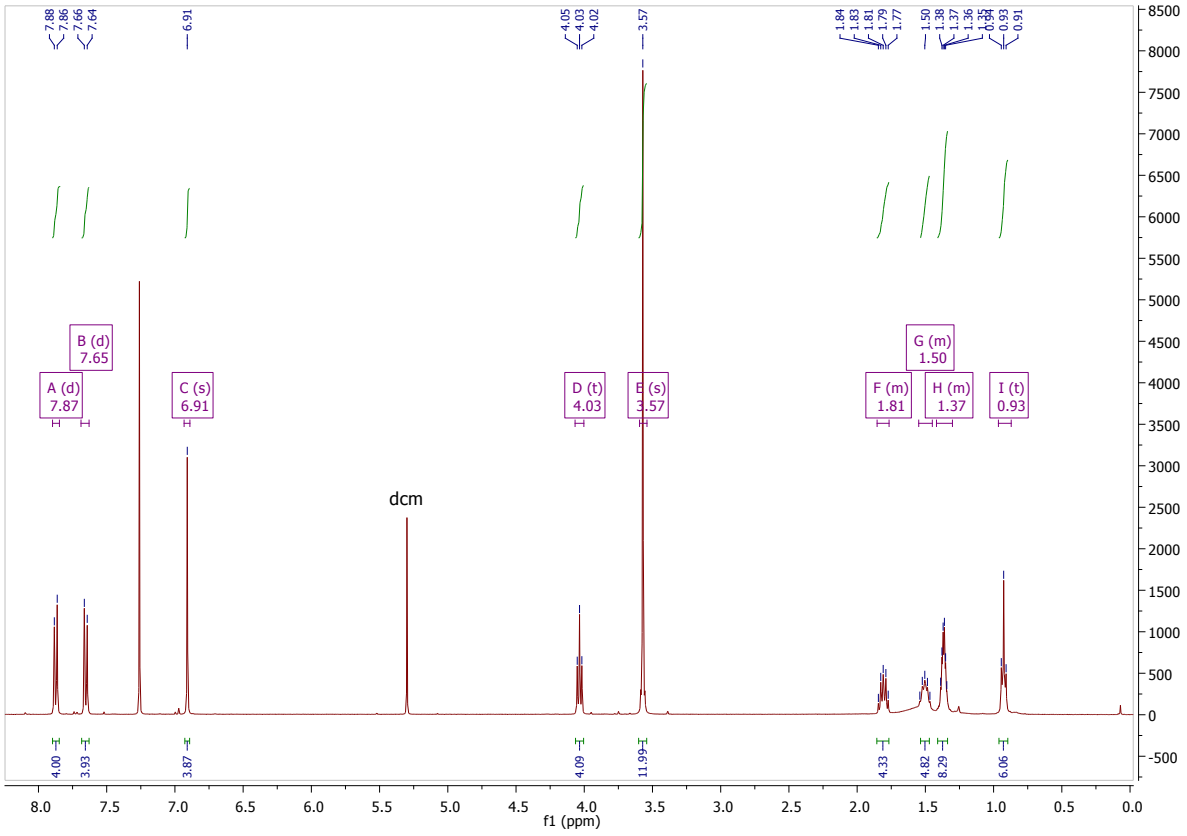


Figure S22. ^{1}H NMR spectrum ($CDCl_3$) of compound **8**

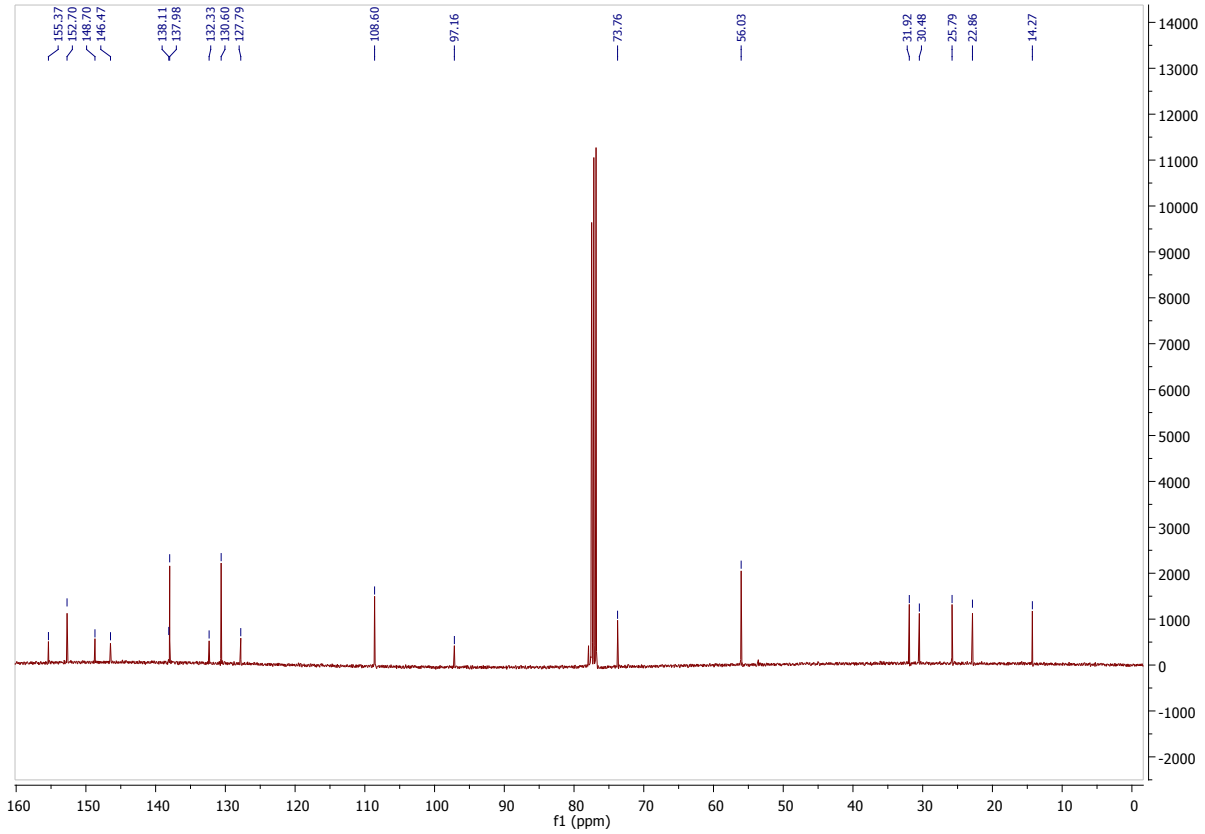
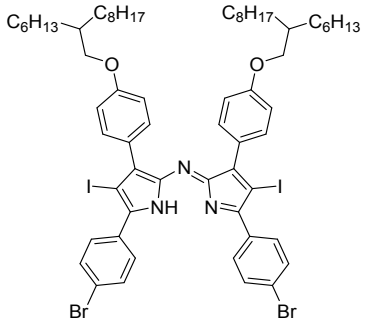


Figure S23. ^{13}C NMR spectrum ($CDCl_3$) of compound **8**

Compound 9



Aza-dipyrromethene **1f** (150 mg, 0.138 mmol, 1 eq.) was dissolved in a AcOH/$CHCl_3$ mixture (1:3, 10 mL). After 20 min of degassing by argon bubbling, NIS (68 mg, 0.303 mmol, 2.2 equiv.) was added and the mixture was stirred at RT under argon overnight. The mixture dissolved in DCM, washed with sodium thiosulfate, water and brine, dried over sodium sulfate, and evaporated under reduced pressure. Product was obtained as a purple solid (149 mg, 81%). ^1H NMR (400 MHz, $CDCl_3$) δ 7.77 (d, *J* = 8.5 Hz, 4H), 7.67 (d, *J* = 8.7 Hz, 4H), 7.62 (d, *J* = 8.5 Hz, 4H), 6.90 (d, *J* = 8.7 Hz, 4H), 3.88 (d, *J* = 5.5 Hz, 4H), 1.87 – 1.76 (m, 2H), 1.53 – 1.17 (m, 48H), 0.95 – 0.81 (m, 12H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 159.93, 154.86, 148.98, 146.64, 132.27, 131.93, 130.55, 125.19, 124.84, 113.83, 71.05, 38.20, 32.08, 32.06,

31.55, 30.25, 29.91, 29.81, 29.54, 27.08, 27.04, 22.86, 14.27. (Two carbon signals are missing). HRMS (ESI$^+$) calcd. for $[M+H]^+$: 1338.3014. Found: 1338.3059.

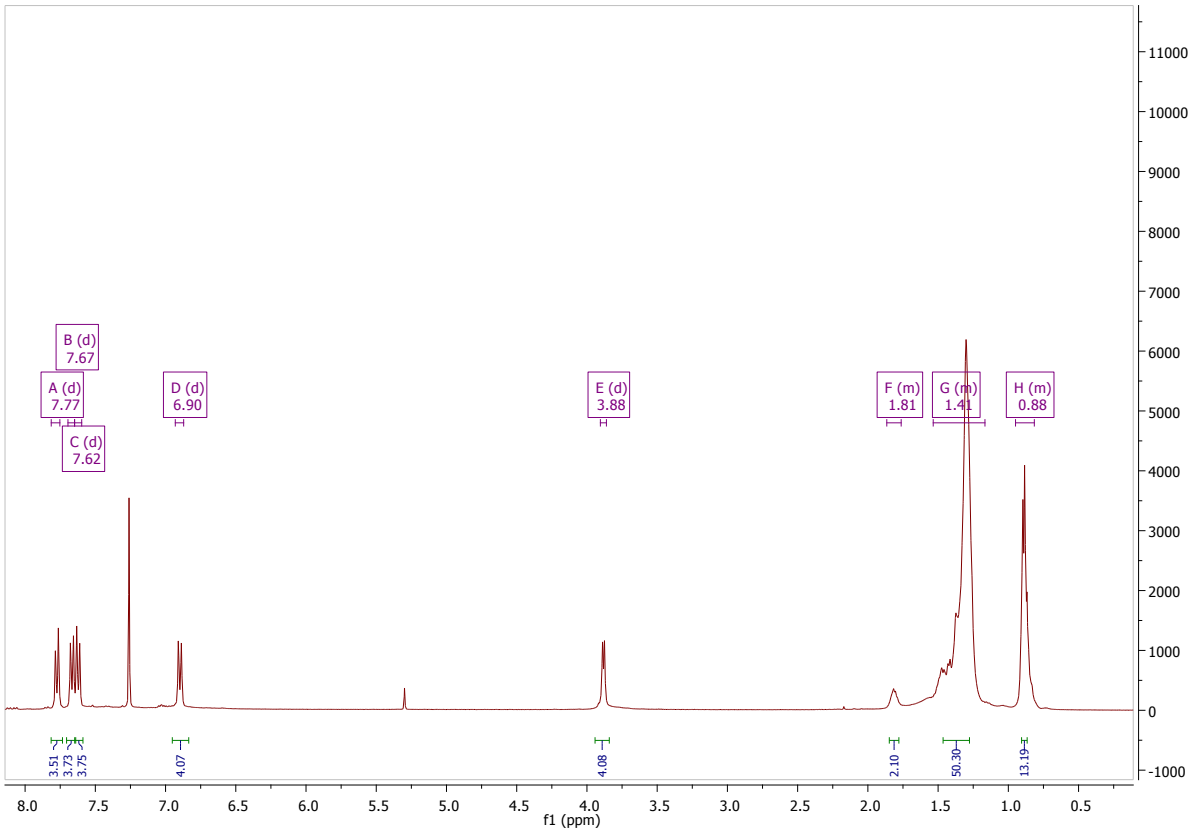


Figure S24. ^{1}H NMR spectrum ($CDCl_3$) of compound **9**

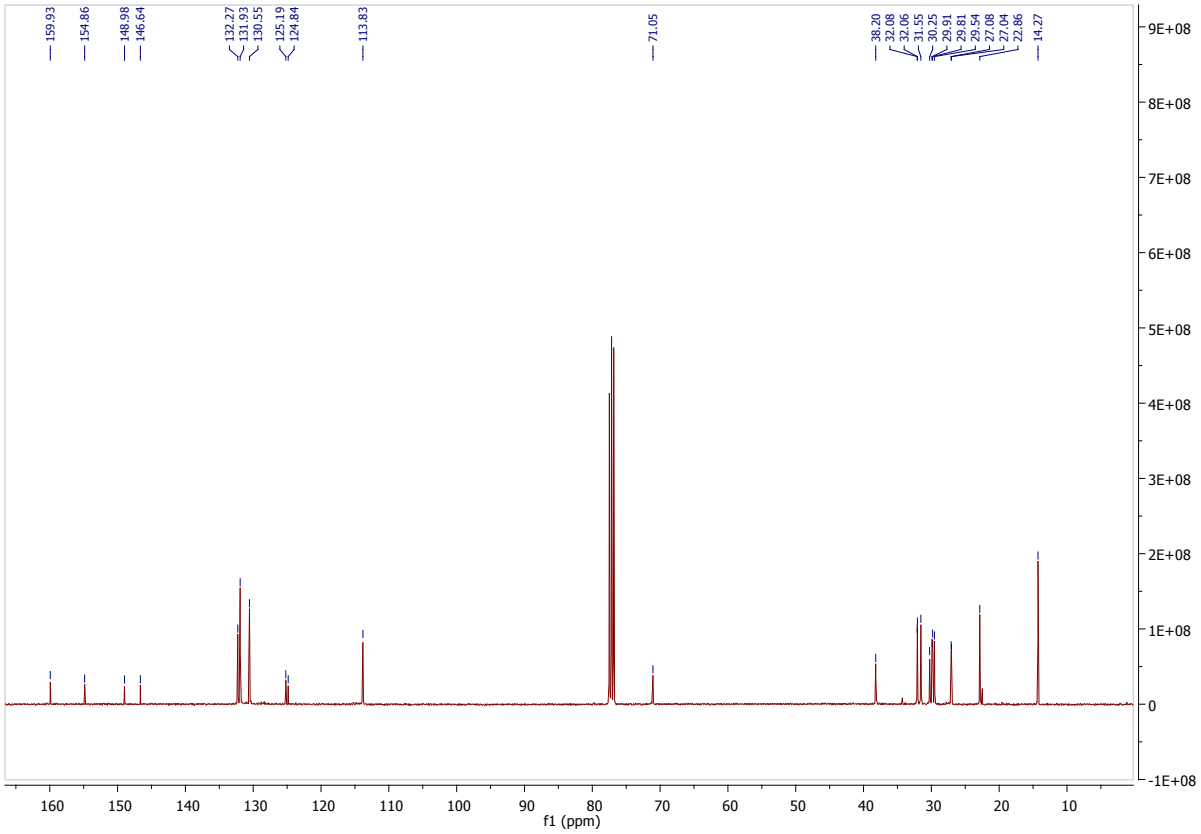
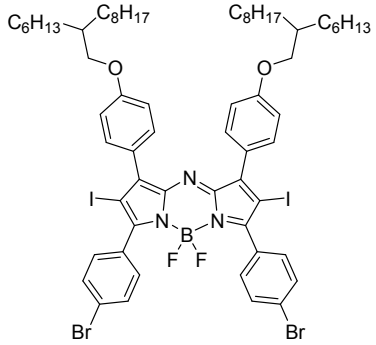


Figure S25. ^{13}C NMR spectrum ($CDCl_3$) of compound **9**

Compound 10



Aza-dipyrromethene **9** (50 mg, 0.037 mmol, 1 equiv.) was dissolved in DCM (4 mL). Diisopropylethylamine (48 mg, 0.373 mmol, 10 equiv.) was then added and the mixture stirred for 20 min under argon. $BF_3.OEt_2$ (79 mg, 0.560 mmol, 15 equiv.) was added and the mixture was stirred under argon for 17 h.

The crude mixture was washed with a saturated aqueous ammonium chloride solution, water and brine. The organic layer was dried over sodium sulfate and the solvent was evaporated to yield to compound **10** (44 mg, 86%).^{1}H NMR (400 MHz, $CDCl_3$) δ 7.83 (d, *J* = 8.8 Hz, 4H), 7.59 (d, *J* = 8.5 Hz, 4H), 7.51 (d, *J* = 8.5 Hz, 4H), 6.97 (d, *J* = 8.8 Hz, 4H), 3.90 (d, *J* = 5.5 Hz, 4H), 1.87 – 1.80 (m, *J* = 5.2 Hz, 2H), 1.50 – 1.23 (m,

48H), 0.93 – 0.85 (m, 12H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 161.21, 159.85, 148.09, 145.19, 132.56, 132.02, 131.45, 130.15, 125.61, 124.17, 114.28, 80.65, 71.25, 38.11, 32.07, 32.02, 31.50, 30.20, 29.85, 29.77, 29.51, 27.02, 26.98, 22.84, 14.26. HRMS (ESI+) calcd. for [M+Na]+: 1408.2817. Found: 1408.2838

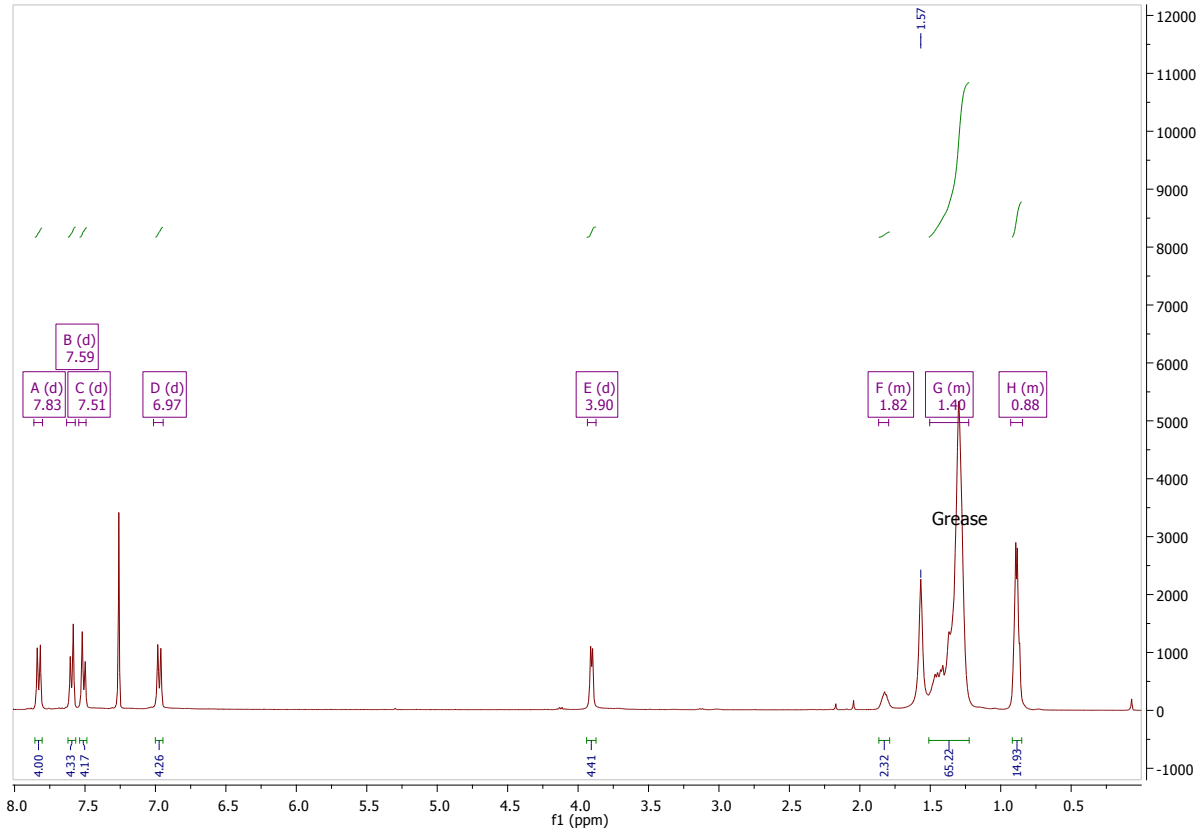


Figure S26. ^{1}H NMR spectrum ($CDCl_3$) of compound **10**

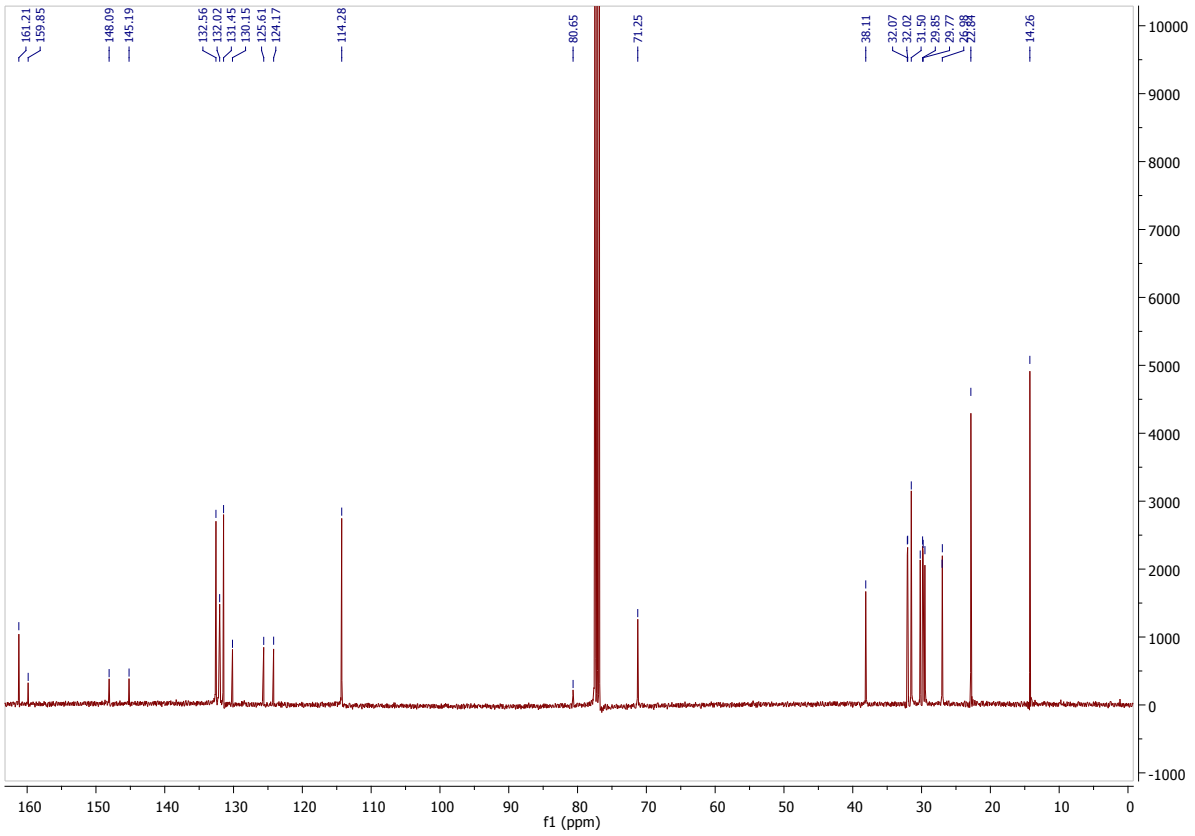
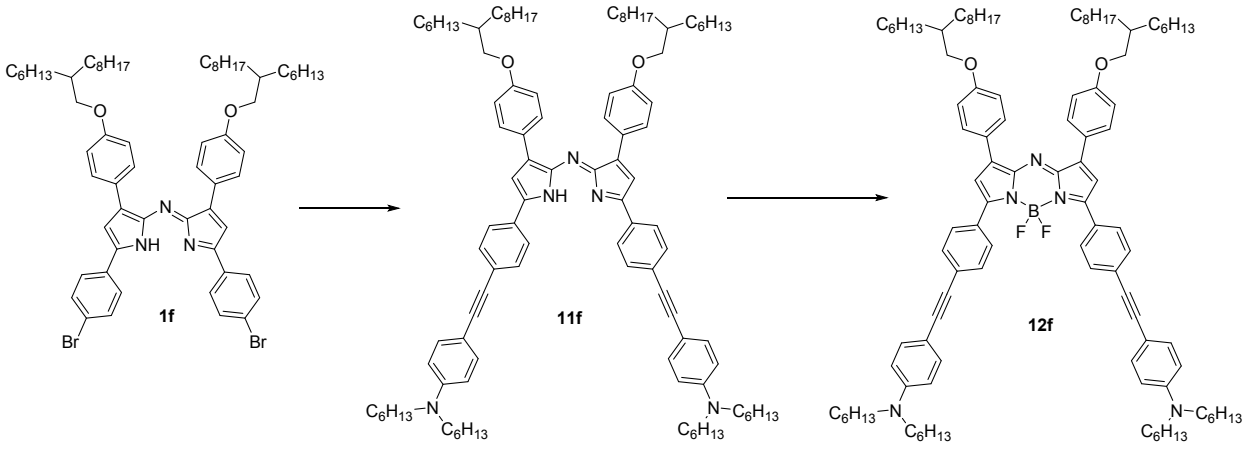


Figure S27. ^{13}C NMR spectrum ($CDCl_3$) of compound **10**

Synthesis of compounds **12f** and **12h** is done with Sonogashira coupling to form aza-dipyrromethene **11f** and **11h** followed by a borylation step to form final aza-bodipy **12**. Due to limited stability of compounds **11** over silica, only compounds **12** were totally purified and isolated.

Compound 11f-12f



Aza-dipyrromethene **1f** (1.626 g, 1.495 mmol, 1 equiv.), 4-ethynyl-N,N-dihexylaniline (0.896 g, 3.193 mmol, 2.1 equiv.), potassium carbonate (0.826 mg, 5.98 mmol, 4 equiv.) were dissolved in DMF (40

mL). The mixture was degassed 3 times by freeze-pump-thaw. $Pd(PPh_3)_4$ (173 mg, 0.150 mmol, 10 mol%) was then added and the mixture stirred under argon at 100 °C overnight. The mixture was filtered over celite, eluted with DCM and washed several times with ammonium chloride, water and brine. The organic layer was dried over sodium sulfate and evaporated under reduced pressure. The crude was triturated in EtOH to remove excess alkyne. The crude product **11f** (black wax) was directly used for the next step. ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.03 (d, *J* = 8.8 Hz, 4H), 7.90 (d, *J* = 8.4 Hz, 4H), 7.63 (d, *J* = 8.4 Hz, 4H), 7.41 (d, *J* = 8.9 Hz, 4H), 7.12 (s, 2H), 6.97 (d, *J* = 8.8 Hz, 4H), 6.60 (d, *J* = 8.9 Hz, 4H), 3.91 (d, *J* = 5.6 Hz, 4H), 3.34 – 3.23 (m, 8H), 1.84 (s, 2H), 1.65 – 1.19 (m, 80H), 0.98 – 0.77 (m, 24H).

Crude aza-dipyrromethene **11f** (2.24 g, 1.495 mmol, 1 equiv.) was dissolved in DCM (120 mL). Diisopropylethylamine (DIPEA) (1.932 mg, 14.95 mmol, 2.6 mL, 10 equiv.) was added dropwise. The solution was stirred at RT for 20 min then $BF_3.OEt_2$ (3.183 g, 22.425 mmol, 2.8 mL, 15 equiv.) was added. The solution was stirred at RT under argon overnight and the solution was washed with a saturated aqueous ammonium chloride solution, water and brine. The organic layer was dried over sodium sulfate and the solvent was evaporated. The crude product was purified by column chromatography on silica using DCM/Cyclohexane gradient 3:7 to 5:5 as eluent. Product **12f:** dark blue wax (1.386 g, 60% over two steps). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.10 – 8.03 (m, 8H), 7.57 (d, *J* = 8.5 Hz, 4H), 7.39 (d, *J* = 8.8 Hz, 4H), 7.00 (d, *J* = 8.5 Hz, 6H), 6.58 (d, *J* = 9.0 Hz, 4H), 3.93 (d, *J* = 5.7 Hz, 4H), 3.33 – 3.25 (m, 8H), 1.92 – 1.82 (m, 2H), 1.68 – 1.59 (m, 8H), 1.53 – 1.23 (m, 72H), 0.95 – 0.82 (m, 24H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 160.80, 157.73, 148.19, 145.77, 143.35, 133.16, 131.24, 130.81, 130.30, 129.50, 126.96, 125.15, 117.47, 114.79, 111.22, 108.46, 94.56, 87.81, 71.15, 51.00, 38.01, 31.92, 31.87, 31.72, 31.37, 30.05, 29.70, 29.61, 29.36, 27.21, 26.92, 26.88, 26.81, 22.69, 14.12, 14.05. ^{19}F NMR (282 MHz, $CDCl_3$) δ -130.91 (q, *J* = 31.8 Hz). HRMS (ESI^+) calcd. for $[M+H]^+$: 1545.1454. Found: 1545.1514.

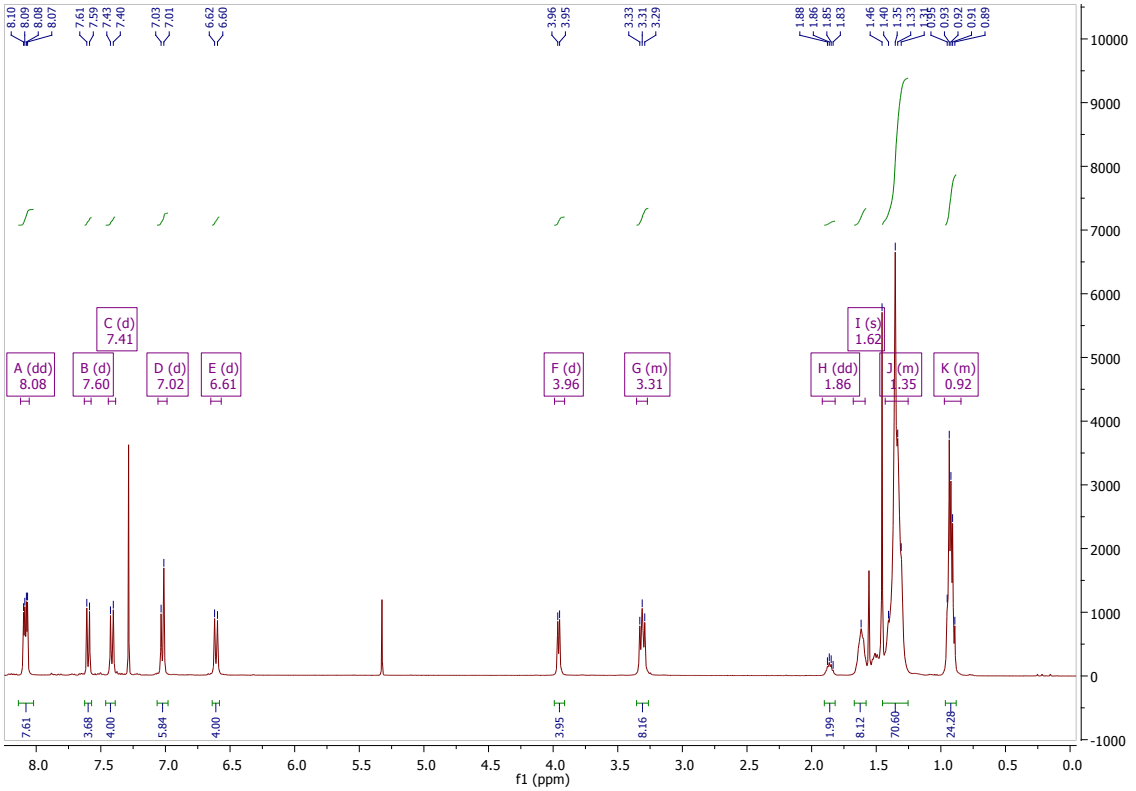


Figure S28. ^{1}H NMR spectrum ($CDCl_3$) of compound **12f**

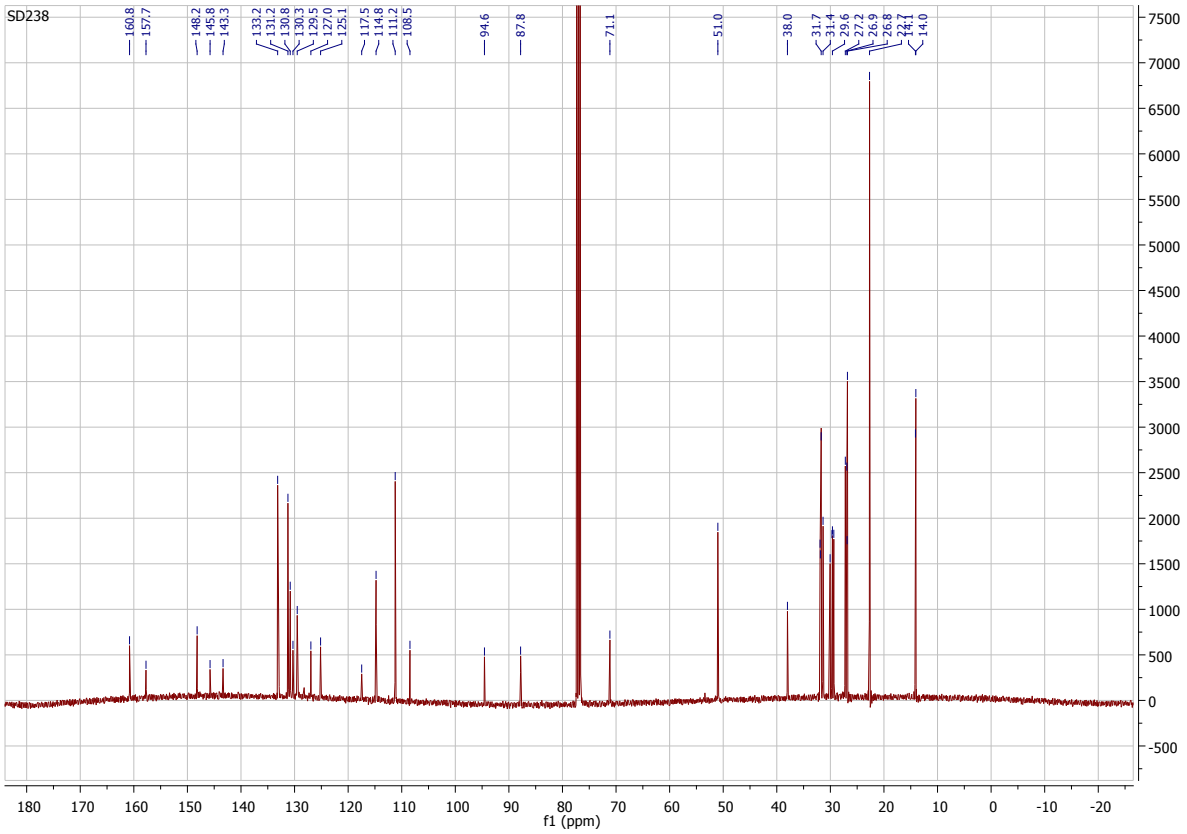
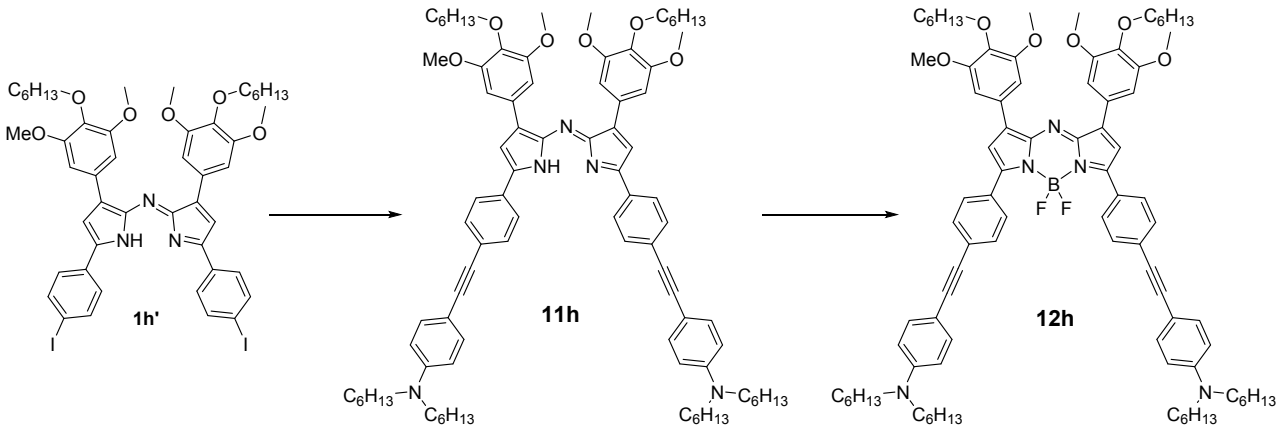


Figure S29. ^{13}C NMR spectrum ($CDCl_3$) of compound **12f**

Compound 12h



Aza-dipyrromethene **1h'** (417 mg, 0.409 mmol, 1 equiv.), 4-ethynyl-N,N-dihexylaniline (245 mg, 0.858 mmol, 2.2 equiv.), potassium carbonate (226 mg, 1.636 mmol, 4 equiv.) were dissolved in DMF (12 mL). The mixture was degassed 3 times by freeze-pump-thaw. $Pd(PPh_3)_4$ (47 mg, 0.041 mmol, 10 mol%) was then added and the mixture stirred under argon at 100 °C overnight. The blue-grey mixture was filtered over celite, eluted with DCM and washed several times with water and brine. The organic layer was dried over sodium sulfate and evaporated under reduced pressure. The greasy solid was used without further purification (total conversion). ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.91 (d, *J* = 8.4 Hz, 4H), 7.65 (d, *J* = 8.4 Hz, 4H), 7.41 (d, *J* = 8.9 Hz, 4H), 7.17 (s, 4H), 7.13 (s, 2H), 6.60 (d, *J* = 8.9 Hz, 4H), 4.02 (t, *J* = 6.8 Hz, 4H), 3.71 (s, 12H), 3.33 – 3.26 (m, 8H), 1.85 – 1.73 (m, 4H), 1.65 – 1.24 (m, 44H), 0.97 – 0.88 (m, 18H).

Crude aza-dipyrromethene **11h** (547 mg, 0.409 mmol, 1 equiv.) was dissolved in DCM (20 mL). Diisopropylethylamine (DIPEA) (529 mg, 4.09 mmol, 0.7 mL, 10 equiv.) was added dropwise. The solution was stirred at RT for 20 min then $BF_3.OEt_2$ (870 mg, 6.135 mmol, 0.8 mL, 15 equiv.) was added. The solution was stirred at RT under argon for 18h and the solution was washed with a saturated aqueous ammonium chloride solution, water and brine. The organic layer was dried over sodium sulfate and the solvent was evaporated. The crude product was purified by automatic puriflash® chromatography using DCM/EP gradient 7:3 to 1:0 as eluent. Product 1**2h**: dark blue film (324 mg, 57% over two steps). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.07 (d, *J* = 8.6 Hz, 4H), 7.58 (d, *J* = 8.6 Hz, 4H), 7.39 (d, *J* = 8.9 Hz, 4H), 7.20 (s, 4H), 7.00 (s, 2H), 6.59 (d, *J* = 9.0 Hz, 4H), 4.04 (t, *J* = 6.8 Hz, 4H), 3.76 (s, 12H), 3.29 (d, *J* = 7.5 Hz, 8H), 1.84 – 1.74 (m, 4H), 1.63 – 1.56 (m, 8 H), 1.51 – 1.45 (m, 4H), 1.38 – 1.30 (m, 32H), 0.95 – 0.87 (m, 18H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 157.99, 153.70, 148.40, 145.97, 144.07, 139.17, 133.34, 131.44, 130.12, 129.75, 127.99, 127.46, 119.01, 111.36, 108.48, 106.96, 95.13, 87.97, 73.93, 56.19, 51.15, 31.86, 30.28, 27.35, 26.96, 25.71, 22.83, 14.24, 14.19.(Two carbon signals are missing, as hexyl carbons are partially overlapping). HRMS (ESI^+) calcd. for $[M+H]^+$: 1384.8746. Found: 1384.8779.

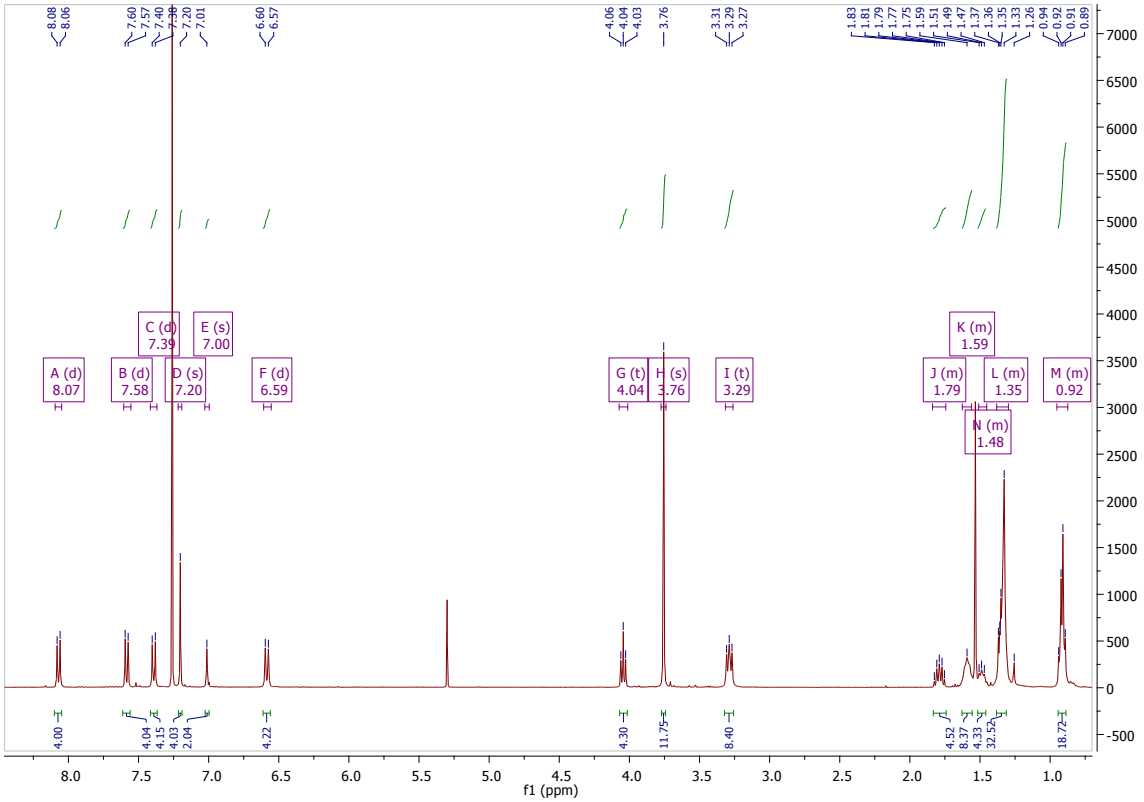


Figure S30. ^{1}H NMR spectrum ($CDCl_3$) of compound **12h**

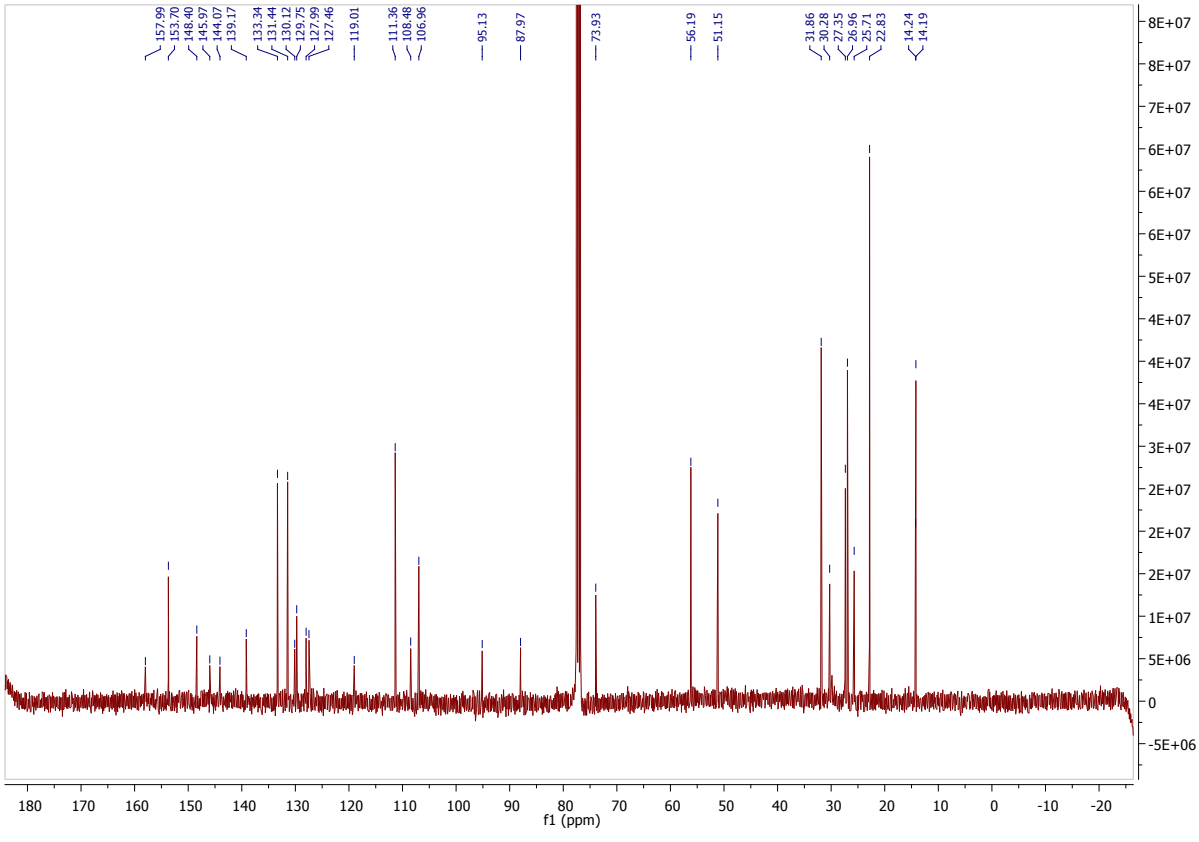


Figure S31. ^{13}C NMR spectrum ($CDCl_3$) of compound **12h**

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