Supplementary Information

Selective and Cooperative Photocycloadditions within Multistranded Aromatic Sheets

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1. Materials and methods

1.1 Nuclear Magnetic Resonance

NMR spectra were recorded on 3 different NMR spectrometers: (1) an Avance II NMR spectrometer (Bruker Biospin, Wissembourg, France) with a vertical 7.05 T narrow-bore/ultrashield magnet operating at 300 MHz for ^{1}H spectra and 75 MHz for ^{13}C spectra by means of a 5mm BBFO ^{1}H/^{15}N-^{31}P-^{19}F probe with Z gradient capabilities; (2) a Avance III HD 400 NMR spectrometer (Bruker Biospin, Wissembourg, France) with a vertical 9.4 T narrow-bore/ultrashield magnet operating at 400 MHz for ^{1}H spectra and 100MHz for ^{13}C spectra by means of a 5mm Smartprobe BBFO ^{1}H/^{15}N-^{31}P-^{19}F probe with Z gradient capabilities; (3) an Avance NEO NMR spectrometer (Bruker Biospin, Wissembourg, France) with a vertical 16.45 T narrowbore/ultrashield magnet operating at 700 MHz for ^{1}H spectra by means of a 5mm TXI ^{1}H/^{13}C/^{15}N probe with Z gradient capabilities. Chemical shifts are reported in parts per million (ppm, δ) relative to the ^{1}H residual signal of the deuterated solvent used. ^{1}H NMR splitting patterns with observed first-order coupling are designated as singlet (s), doublet (d), triplet (t), or quartet (q). Coupling constants (J) are reported in hertz. Samples were not degassed otherwise it is specified. Data processing was performed with Topspin 4.0 software.

The assignment of NMR of the parallel aromatic sheets **1-7** and their respective photoproducts **1a-7a** and of remarkable resonances was performed using the following bi-dimensional NMR experiments.

TOCSY. Total Correlation Spectroscopy (TOCSY) experiments were recorded at 400 MHz. They were used to identify protons of oligomer that belong to the same spin system (e.g. aromatic ring) regardless of the exact topology with the following acquisition parameters: the acquisition was performed with 2048(t 2) × 256(t 1) data points, relaxation delay of 2 s, and 32 scans per increment. Processing was done after a sine-bell multiplication in both dimensions and Fourier transformation in 1K x 1K real points.

HSQC. Heteronuclear Single-Quantum Correlation spectroscopy (HSQC) experiments were recorded at 400 MHz. They were used to observe correlations between nuclei of two different types which are separated by one bond with the following acquisition parameters: the acquisition was performed with 2048(t 2) × 256(t 1) data points, relaxation delay of 2 s, and 64 scans per increment. Processing was done after a sine-bell multiplication in both dimensions and Fourier transformation in 1K x 1K real points.

HMBC. Heteronuclear Multiple Bond Correlation spectroscopy (HMBC) experiments were recorded at 400 MHz. They were used to detect heteronuclear correlations over longer ranges of about 2–4 bonds with the following acquisition parameters: the acquisition was performed with 2048(t 2) × 256(t 1) data points, relaxation delay of 2 s, and 64 scans per increment. Processing was done after a sine-bell multiplication in both dimensions and Fourier transformation in 1K x 1K real points.

1.2 Photochemistry

Electronic absorption spectra were measured on a Cary 5000 UV-vis-NIR spectrophotometer. Steady-state emission spectra were recorded on a Horiba Jobin-Yvon Fluorlog-3 spectrofluorometer fitted with a Hamamatsu R928P PMT detector and exciting with a 450W Xe-lamp across a double monochromator and were corrected for instrumental response.

Photoirradiation experiments were carried out on solution samples in NMR tubes. Respective compounds were placed in NMR tubes, degassed and filled with argon. Subsequently, argon purged deuterated solvents were used to dissolve the compounds. The solutions were then subjected to irradiation by EXFO Lite (Model No. E3000-01) portable device having light source of 320 - 390 nm with 50 W mercury lamp. NMR were checked at different time intervals to follow the photoproduct formation. The experiments were repeated several times to establish reproducibility. Thermal reversibility experiments were performed in NMR tubes. The anthracene derivatives were dissolved in the appropriate deuterated solvent ($C_2D_2Cl_4$ or $CDCl_3$). The tube was heated to 393K or 333K for $C_2D_2Cl_4$ or $CDCl_3$, respectively. The kinetic reversibility was followed by ^{1}H NMR.

1.3 Molecular mechanics

Molecular Models calculation were done using MacroModel version 8.6 (Schrödinger Inc.) with the Merck Molecular Force Field static (MMFFs) as implemented in this software. Energy minimized structures were obtained using 500 steps of Truncated Newton Conjugate Gradient (TNCG), chloroform as implicit solvent and the extended Cutoff option.

1.4 Crystallography

The diffraction data for compounds **8**, **10** and **13**-*sym* were collected at the IECB X-ray facility (CNRS UMS 3033 – INSERM US001, University of Bordeaux) with a Rigaku FRX rotating anode (2.9 kW) diffractometer using CuKα wavelength with a partial chi goniometer (AFC11). The X-ray source is equipped with high flux Osmic Varimax mirrors and a Dectris Pilatus 200K detector. Data were processed with the Rigaku Oxford Diffraction CrysalisPro software (version1.171.40.69a). [1]

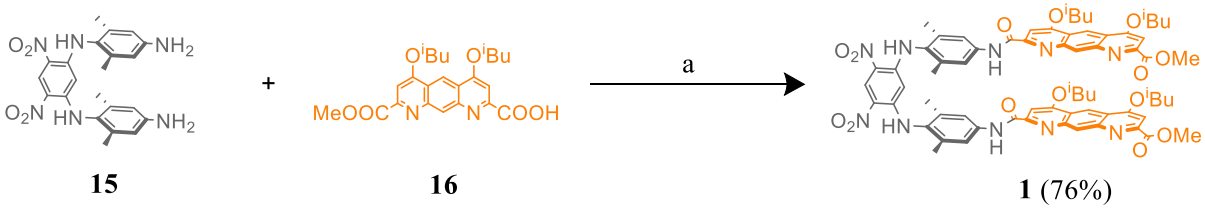
Data for compound **14**-*asym* were collected on a MetalJet (Excillium) X-ray source at the GaKα wavelength with a STOE Stadivari goniometer and a Dectris Eiger 1M detector. Data were processed with X-area version 1.87.

All structures were solved with Shelxt[2] and refined by full-matrix least-squares method on F2 with Shelxl-2014[2] within Olex2. [3] Only non-H atoms of the backbones and side chains observable in the electron density maps were refined with anisotropic displacement parameters. H-atoms were refined in the riding-model approximation, with Uiso(H)=1.2Ueq (CH, CH2, NH). DFIX, AFIX, RIGU and SIMU restraints were applied to model geometry of the molecules and thermal motion parameters.

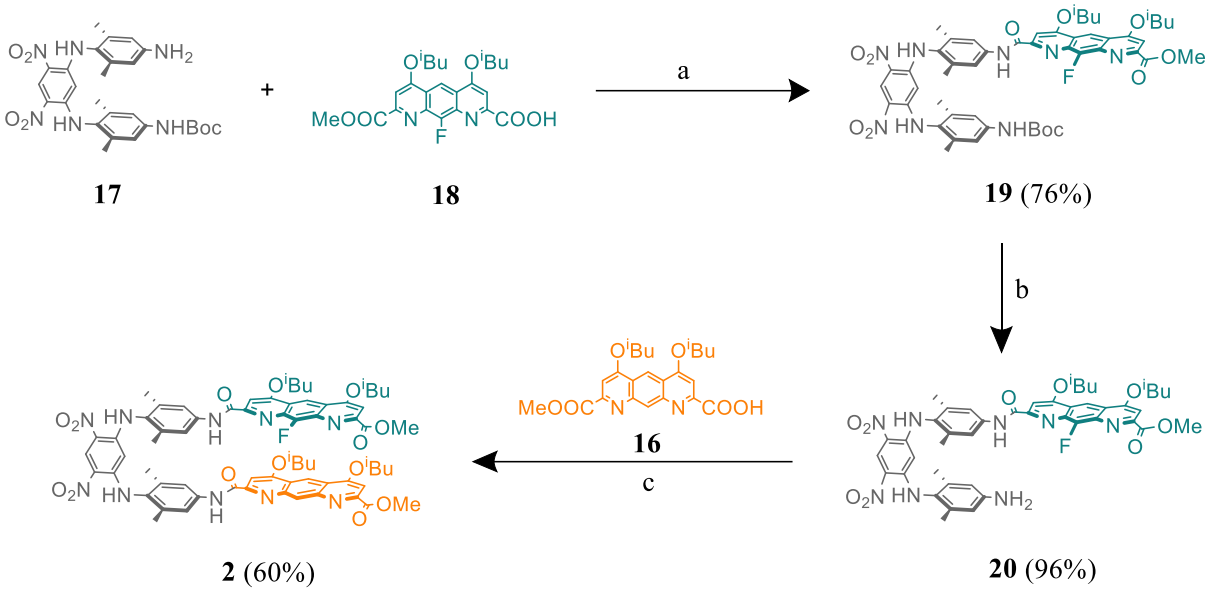
2. Methods for chemical synthesis

All reactions were carried out under a dry inert atmosphere, it is specified otherwise. Commercial reagents were purchased from Sigma Aldrich, TCI Chemicals or Alfa-Aesar and were used without further purification. Tetrahydrofuran (THF) and dichloromethane (CH_2Cl_2) were dried over alumina columns (MBRAUN SPS-800 solvent purification system); chloroform ($CHCl_3$) and diisopropylethylamine (DIPEA) were distilled over P_2O_5 and calcium hydride (CaH_2) respectively prior to use. Reactions were monitored by thin layer chromatography (TLC) on Merck silica gel 60-F254 plates and observed under UV light. Column chromatography purifications were carried out on Merck GEDURAN Si60 (40-63 µm). Preparative recycling GPC (gel permeation chromatography) were performed on JAIGEL 20*600 mm columns (Japan Analytical Industry) at a flow rate of 7 mL min^{-1} with a mobile phase composed of 1% (vol/vol) ethanol and 0.5% (vol/vol) Et_3N in chloroform. Monitoring was carried out by a UV detector at 254 nm, 280 nm, 300 nm and 360 nm. ESI mass spectra were obtained from the Mass Spectrometry Laboratory at the European Institute of Chemistry and Biology (UMS 3033 & US01 - IECB), Pessac, France.

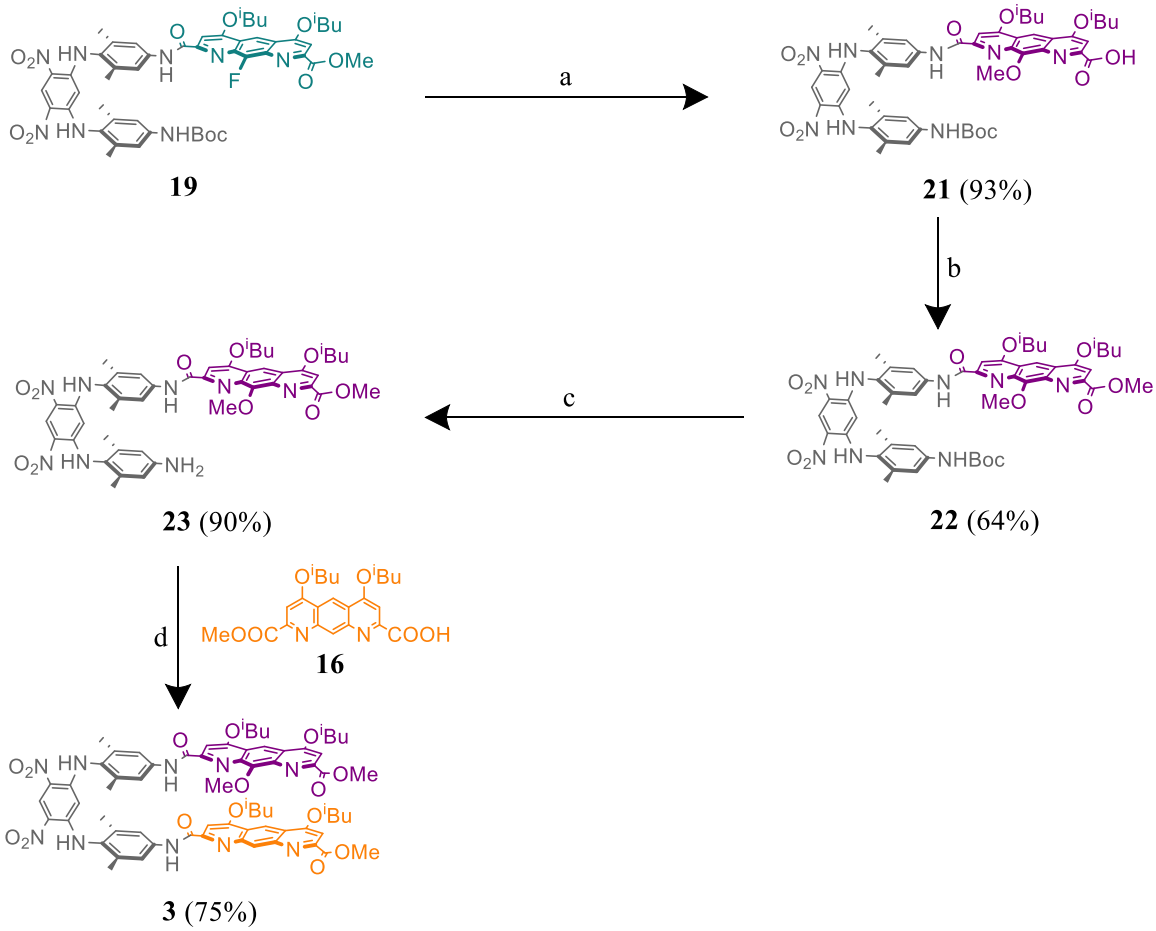
2.1 Synthesis of oligomers



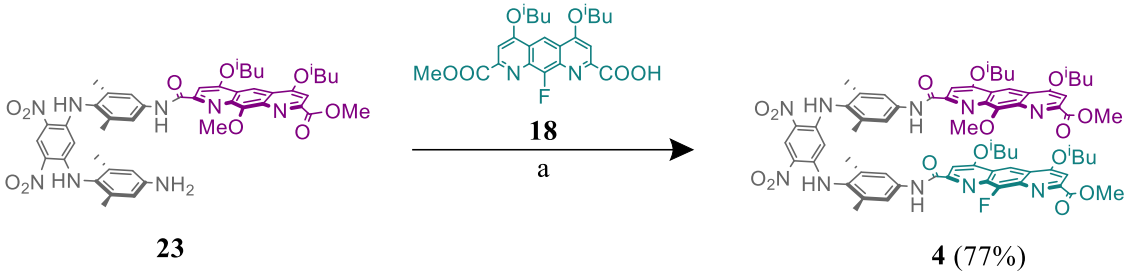
Scheme S1. Synthesis of **1**. (a) PyBOP, DIPEA, $CHCl_3$, 16 hours, room temperature.[4]



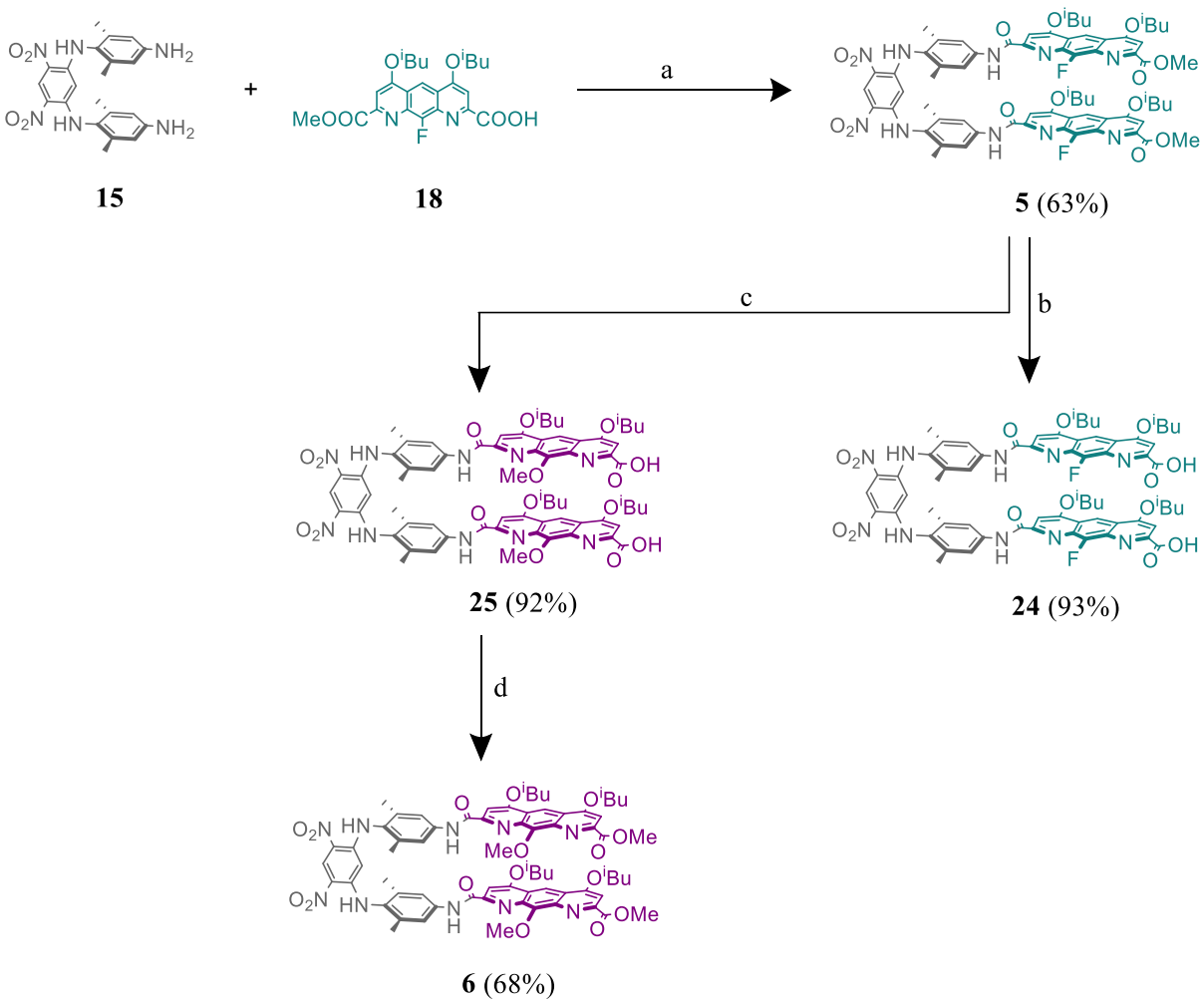
Scheme S2. Synthesis of **2**. (a) PyBOP, DIPEA, $CHCl_3$, 16 hours, room temperature. (b) TFA, $CHCl_3$, 4 hours, room temperature. (c) PyBOP, DIPEA, $CHCl_3$, 16 hours, room temperature.



Scheme S3. Synthesis of **3**. (a) (i) NaOH, MeOH, THF, 12 hours, room temperature. (ii) Citric acid. (b) (i) 1-Chloro-*N*,*N*,2-trimethyl-1-propenylamine, $CHCl_3$, 2 hours, room temperature. (ii) MeOH, DIPEA, $CHCl_3$, overnight, room temperature. (c) TFA, DCM, 3 hours, room temperature. (d) PyBOP, DIPEA, $CHCl_3$, 16 hours, room temperature.

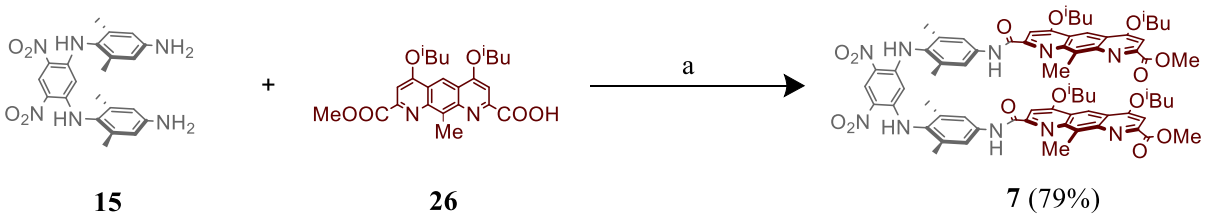


Scheme S4. Synthesis of **4**. (a) PyBOP, DIPEA, $CHCl_3$, 16 hours, room temperature.



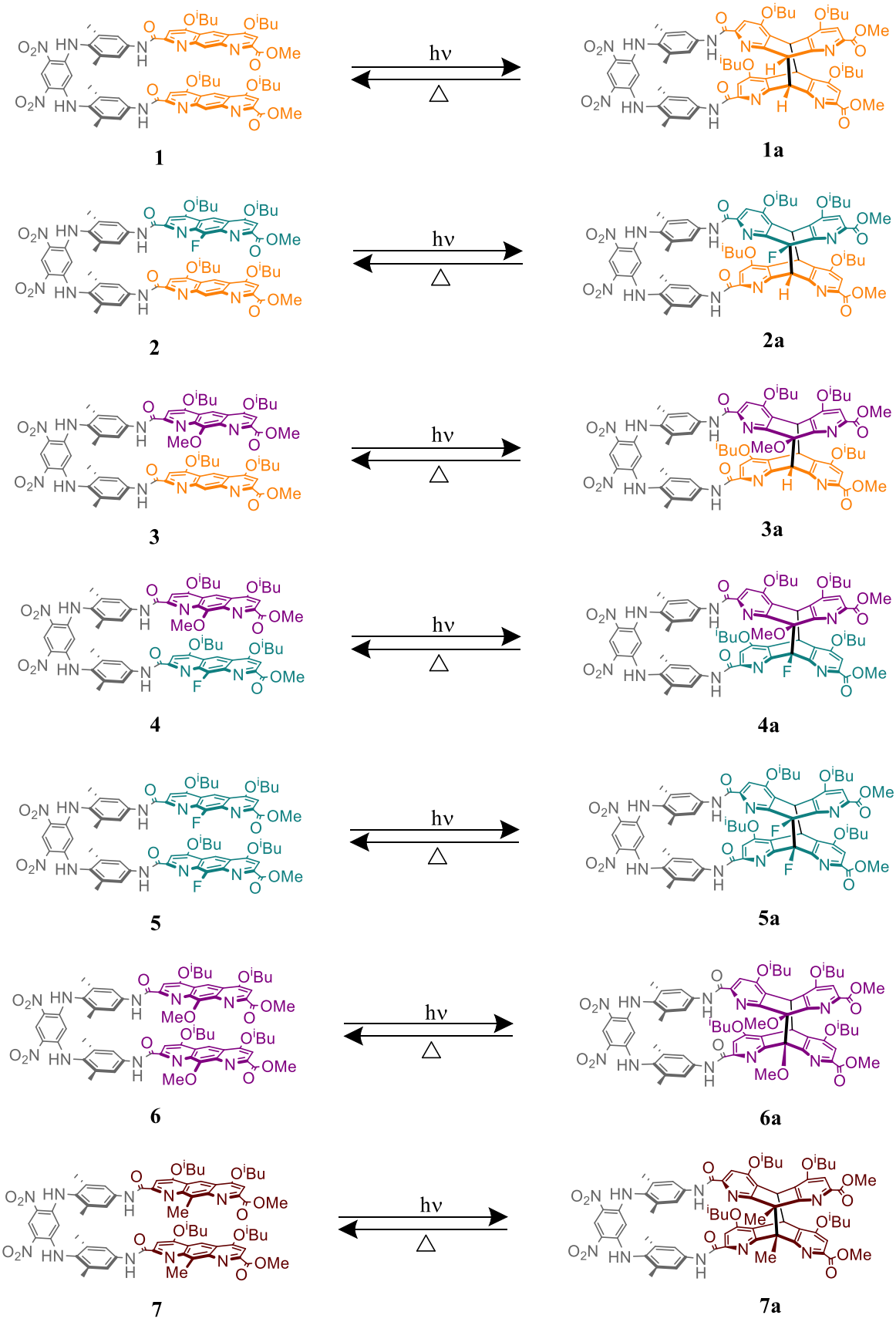
Scheme S5. Synthesis of **5** and **6**. (a) PyBOP, DIPEA, $CHCl_3$, 16 hours, room temperature. (b) (i) LiI, ethyl acetate, 3 hours, 351 K. (ii) Citric acid. (c) (i) NaOH, MeOH, THF, 12 hours, room temperature.

(ii) Citric acid. (d) $(COCl)_2$, $CHCl_3$, 2 hours, room temperature. (ii) MeOH, DIPEA, $CHCl_3$, overnight, room temperature.

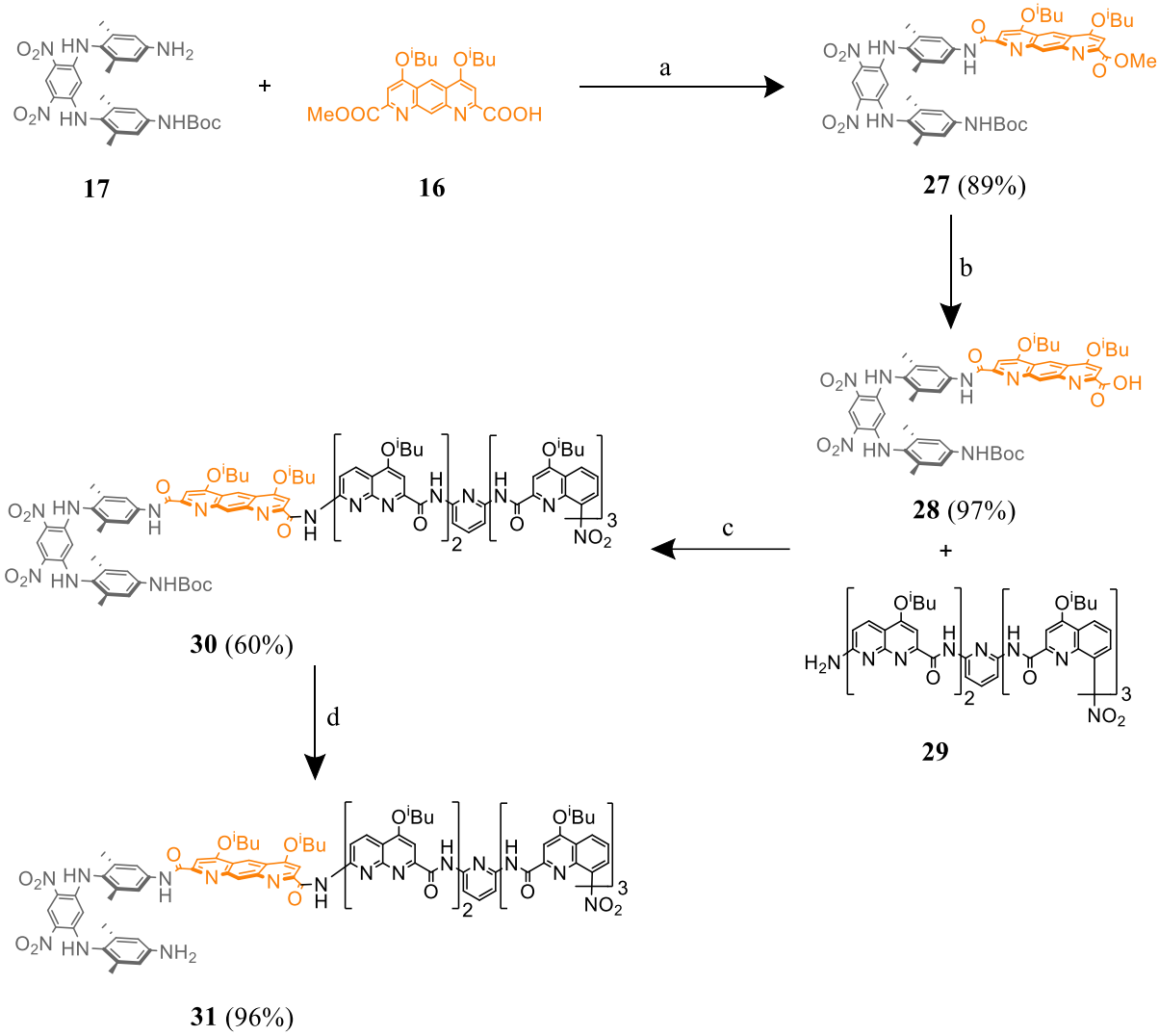


15 **26** **7** (79%)

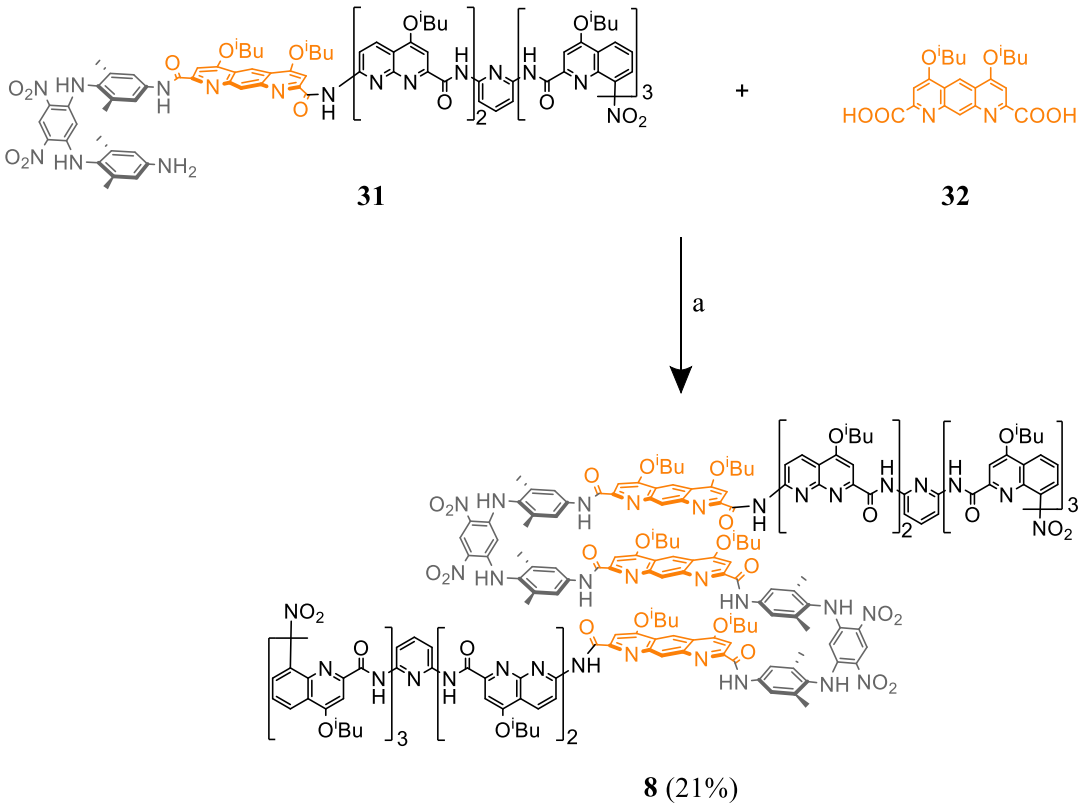
Scheme S6. Synthesis of **7**. (a) PyBOP, DIPEA, $CHCl_3$, 16 hours, room temperature.



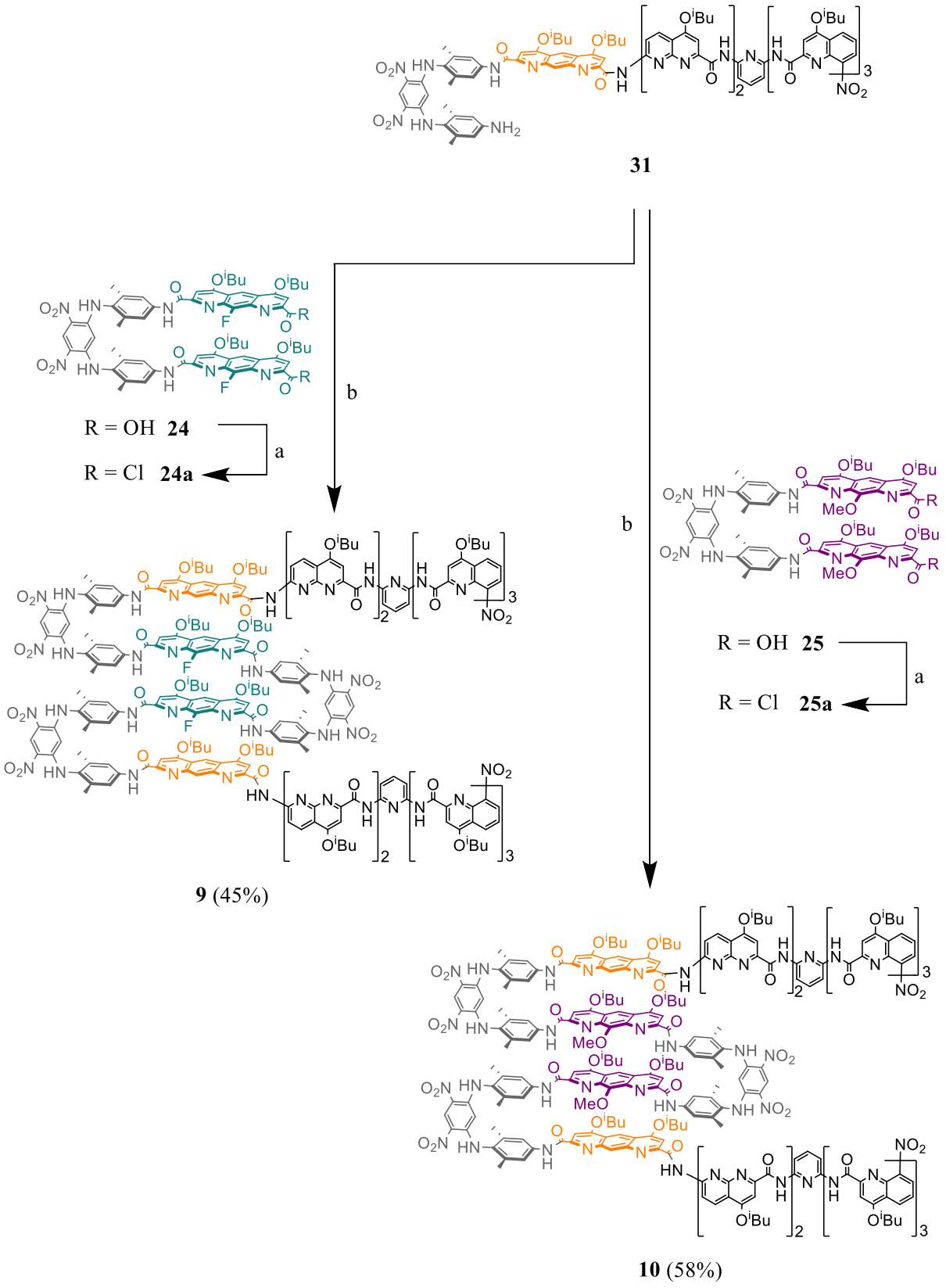
Scheme S7. Photoirradiation of **1-7** with a light source of 320 - 390 nm followed by the thermolysis at 393 K for 15 hours in tetrachloroethane-d_2.



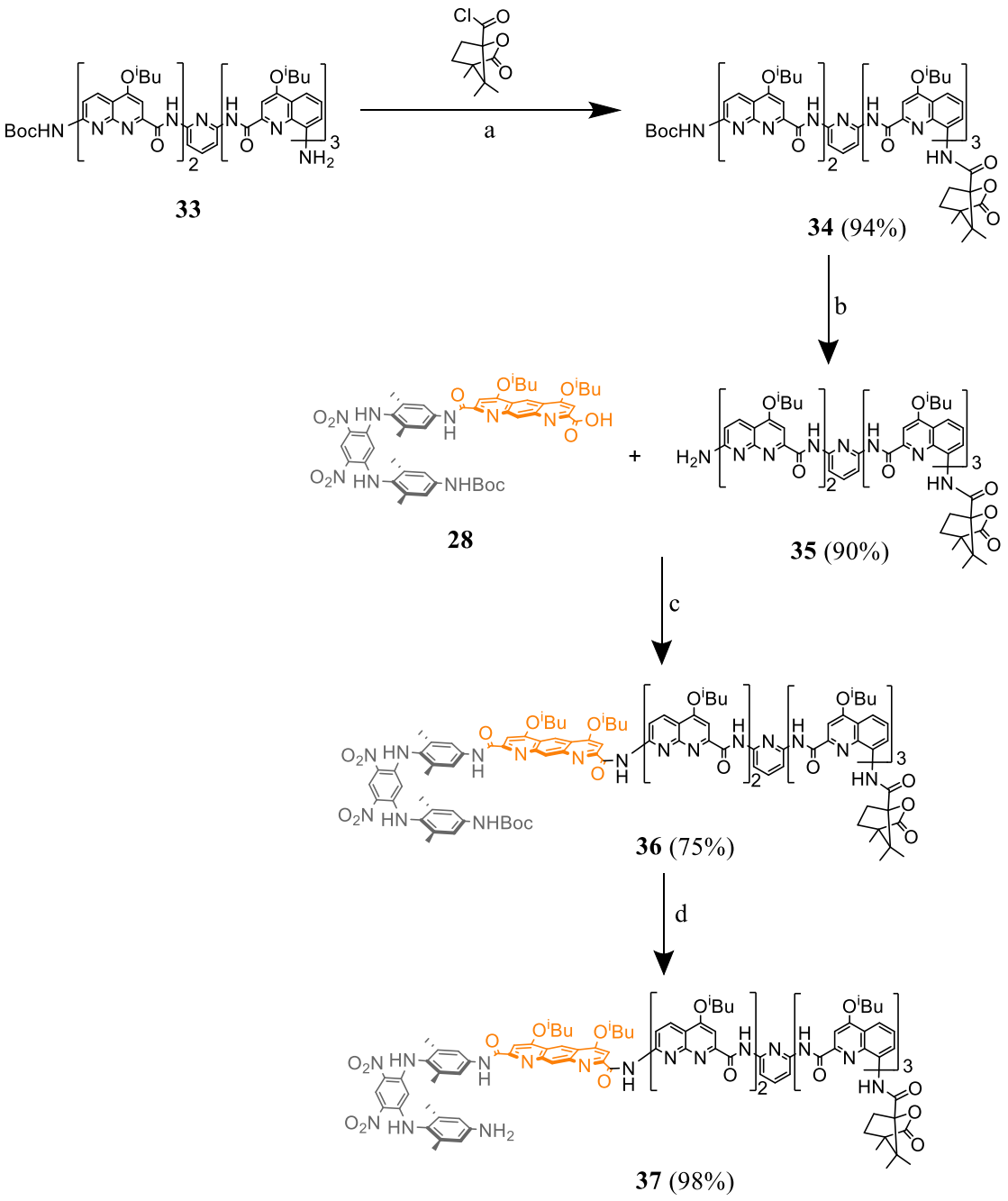
Scheme S8. Synthesis of **31**. (a) PyBOP, DIPEA, $CHCl_3$, 16 hours, room temperature. (b) (i) NaOH, MeOH, THF, 12 hours, room temperature. (ii) Citric acid. (c) PyBOP, DIPEA, $CHCl_3$, 16 hours, room temperature. (d) HCl (4M in dioxane), room temperature.



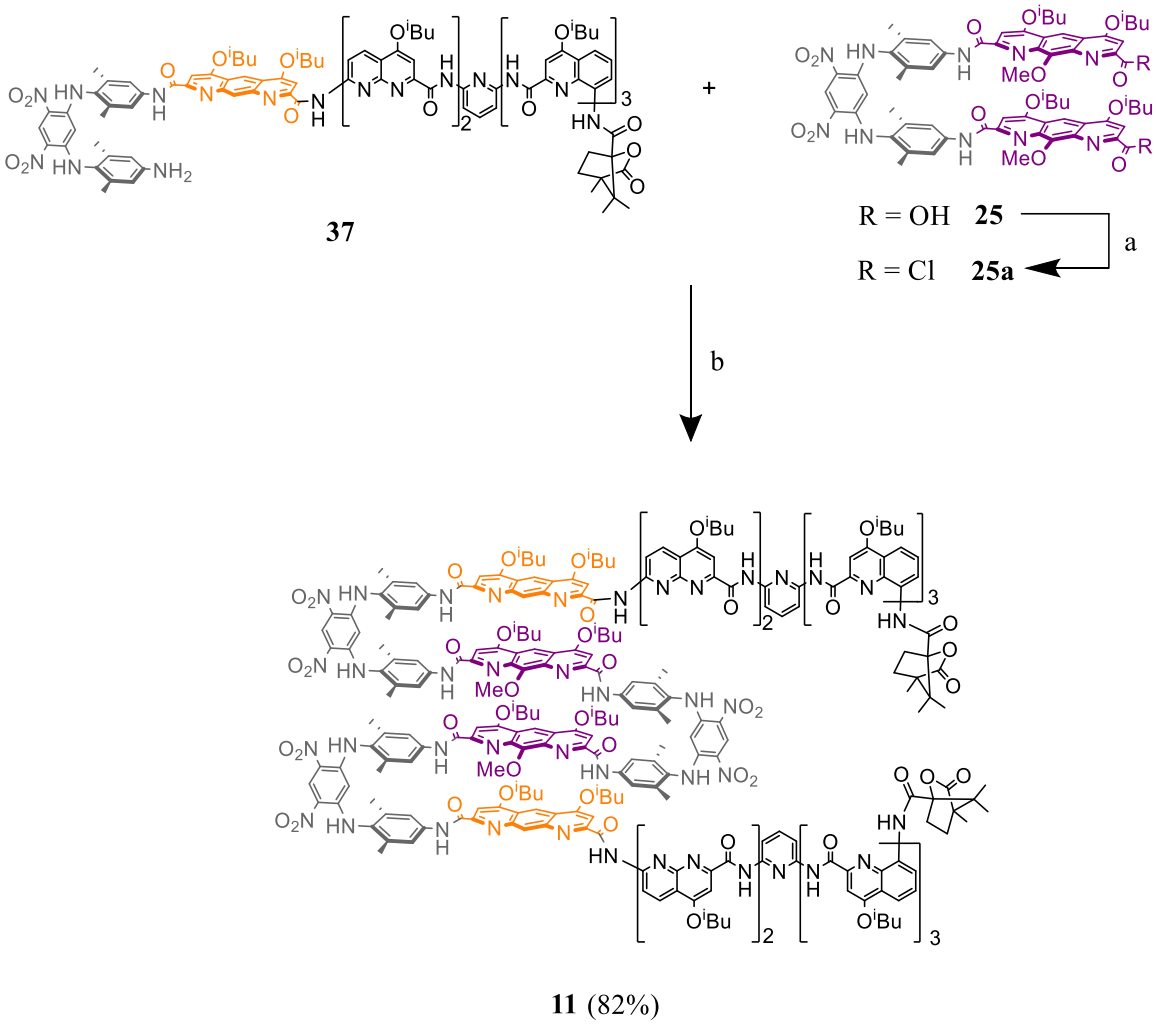
Scheme S9. Synthesis of **8**. (a) PyBOP, DIPEA, $CHCl_3$, 2 days, 318 K.



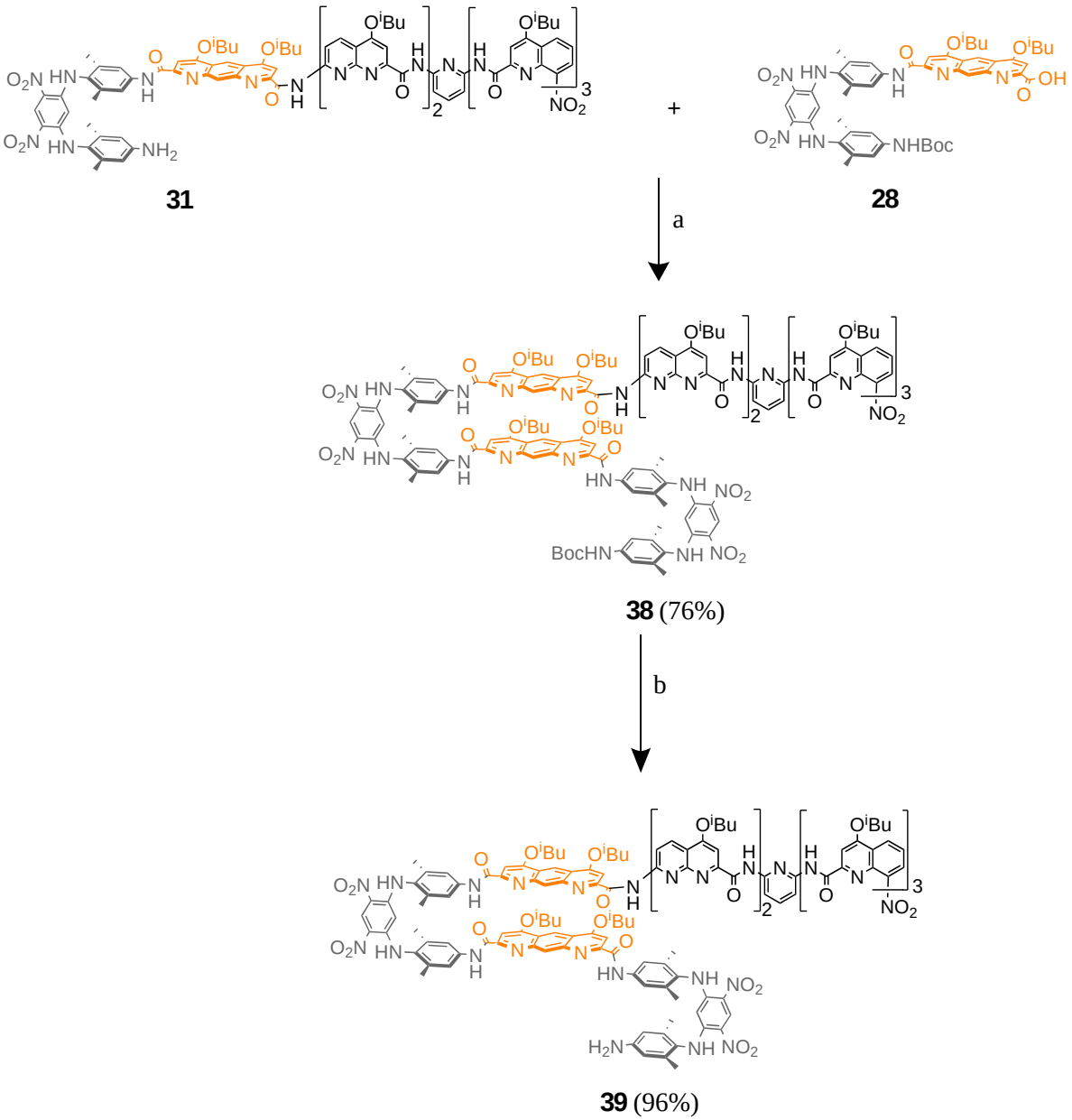
Scheme S10. Synthesis of **9** and **10**. (a) $(COCl)_2$, $CHCl_3$, 3 hours, room temperature. (b) DIPEA, $CHCl_3$, 16 hours, room temperature.



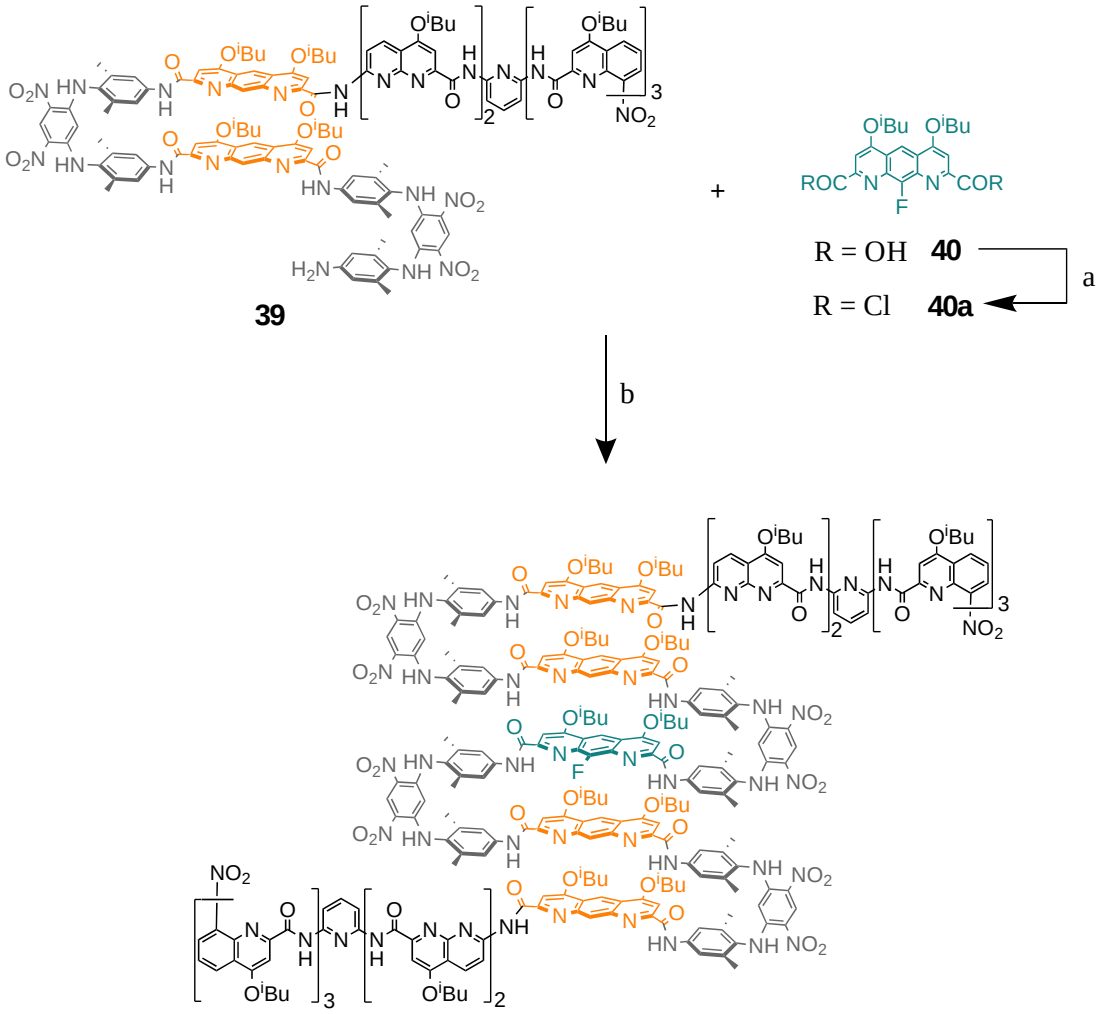
Scheme S11. Synthesis of **37**. (a) DIPEA, $CHCl_3$, 12 hours, room temperature. (b) TFA, $CHCl_3$, 4 hours, room temperature. (c) PyBOP, DIPEA, $CHCl_3$, 36 hours, room temperature. (d) HCl (4M in dioxane), room temperature.



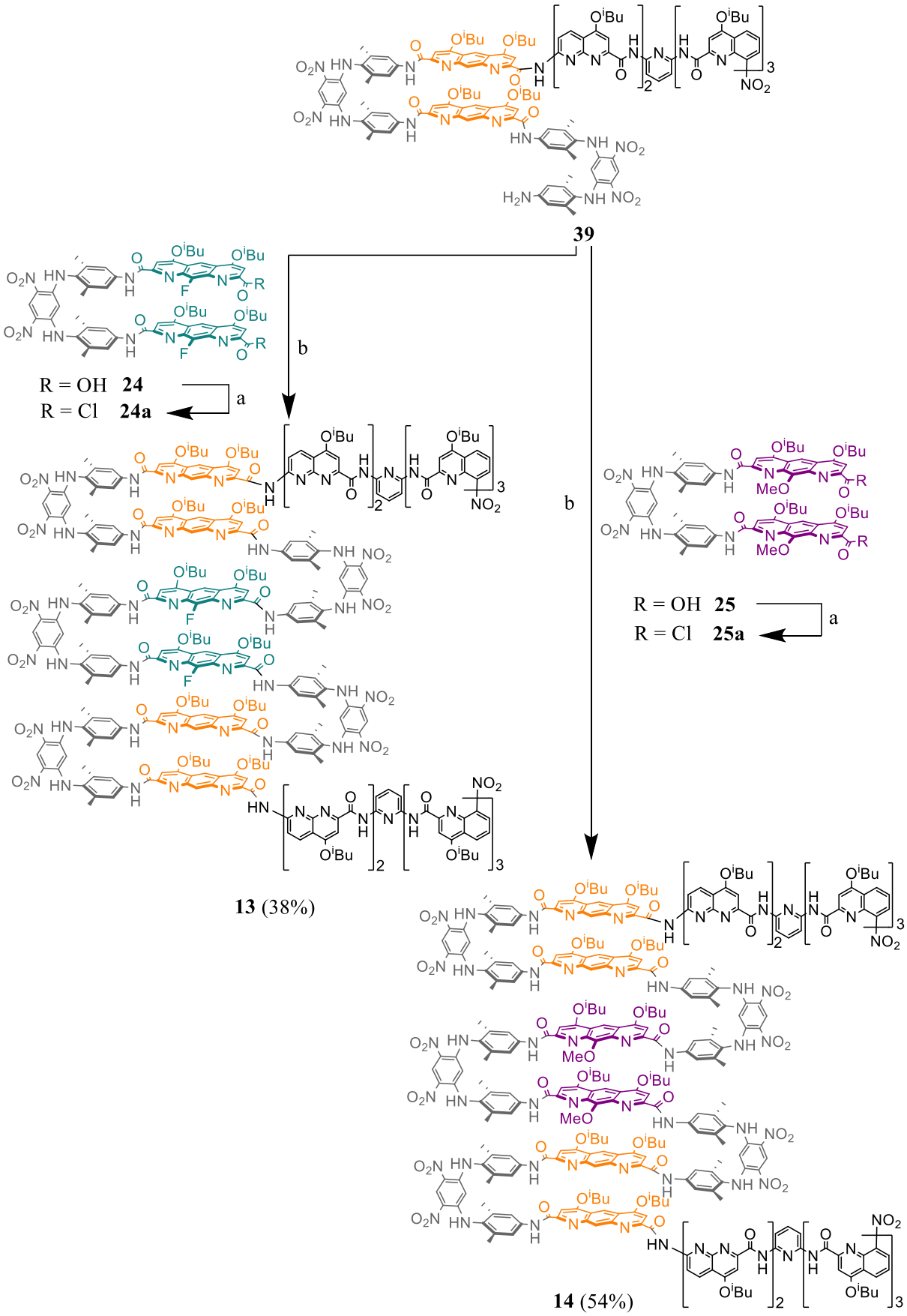
Scheme S12. Synthesis of **31**. (a) $(COCl)_2$, $CHCl_3$, 3 hours, room temperature. (b) DIPEA, $CHCl_3$, 16 hours, room temperature.



Scheme S13. Synthesis of **39**. (a) PyBOP, DIPEA, $CHCl_3$, 16 hours, room temperature. (b) HCl (4M in dioxane), room temperature.

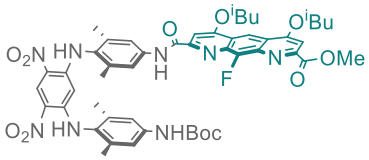


Scheme S14. Synthesis of **12**. (a) $(COCl)_2$, $CHCl_3$, 3 hours, room temperature. (b) DIPEA, $CHCl_3$, 16 hours, room temperature.



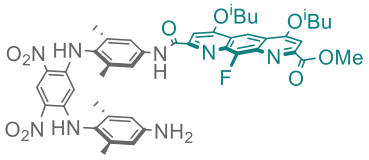
Scheme S15. Synthesis of **13** and **14**. (a) $(COCl)_2$, $CHCl_3$, 3 hours, room temperature. (b) DIPEA, $CHCl_3$, 16 hours, room temperature.

2.3 **Synthetic procedures**



19

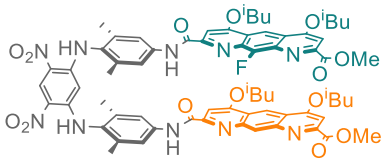
Tetramer 19. Monoamine turn **17**[5] (0.097 g, 0.18 mmol), 9-fluorodiazaanthracene **18**[6] (0.089 g, 0.2 mmol), and PyBOP (0.187 g, 0.36 mmol) were placed in a 5 mL round bottom flask then dissolved in freshly distilled $CHCl_3$ (2 mL) and DIPEA (63 µL, 0.36 mmol) was added under nitrogen atmosphere. The reaction mixture was allowed to stir at room temperature for 16 hours. The solvent was removed under reduced pressure and the residue was dissolved in dichloromethane. The solution was then washed successively with 5% NH_4Cl, water and brine. Finally, the organic layer was dried over Na_2SO_4, filtered and evaporated. The residue was purified by recycling GPC and product **19** was obtained as a yellow solid (0.132 g, 76% yield). ^{1}H NMR (300 MHz, $CDCl_3$, 298 K, δ ppm): 10.19 (s, 1H), 9.35 (s, 1H), 9.16 (s, 1H), 9.12 (s, 1H), 9.06 (d, *J* = *2.2*, 1H), 7.82 (s, 1H), 7.58 (s, 1H), 7.47 (s, 2H), 7.04 (s, 2H), 6.72 (s, 1H), 4.90 (s, 1H), 4.25 (d, *J* = 6.4 Hz, 2H), 4.19 (d, *J* = 6.4 Hz, 2H), 4.13 (s, 3H), 2.41 (m, 2H), 2.09 (s, 6H), 2.01 (s, 6H), 1.23 (d, *J* = 6.7 Hz, 12H), 1.15 (s, 9H). ^{13}C NMR (75 MHz, $CDCl_3$, 298 K, δ ppm): 165.9, 163.8, 163.7, 163.3, 163.2, 162.1, 155.5, 153.3, 153.2, 152.7, 151.9, 151.6, 151.6, 148.4, 148.1, 138.0, 137.0, 136.6, 136.5, 136.3, 136.2, 135.2, 135.1, 130.9, 129.4, 129.2, 124.9, 124.9, 122.4, 122.1, 120.6, 118.9, 111.2, 111.1, 99.7, 97.5, 93.9, 80.0, 77.2, 75.6, 75.5, 53.6, 28.3, 28.3, 28.0, 19.2, 19.1, 18.1, 17.9. ^{19}F NMR (282 MHz, $CDCl_3$, 298 K, δ ppm): -128.1. HRMS (ESI): m/z calcd for $C_{50}H_{56}FN_8O_{11}$ $[M+H]^+$ 963.4047, Found 963.4115.



20

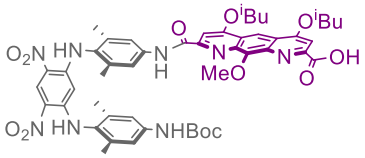
Tetramer amine 20. In a round-bottom flask, compound **19** (0.075 g, 0.078 mmol) was dissolved in 2 mL chloroform and subsequently, 2 mL TFA was added dropwise. The mixture was allowed to stir for 3 hours at room temperature. A saturated aqueous solution of $NaHCO_3$ was added to quench the excess acid. Then, the solution was extracted with CH_2Cl_2, washed with water, dried over Na_2SO_4 and evaporated. Product **19** was obtained without any further purification as a yellow solid (65 mg, 96% yield). ^{1}H NMR (300 MHz, $CDCl_3$, 298 K, δ ppm): 10.44 (s, 1H), 9.31 (s, 1H), 9.15 – 8.98 (m, 2H), 8.91 (s, 1H), 7.80 (s, 1H), 7.58 (s, 1H), 7.46 (s, 2H), 6.29 (s, 2H), 4.75 (s, 1H), 4.23 (d, *J* = 6.4 Hz, 2H), 4.19 (d, *J* = 6.4 Hz, 2H), 4.14 (s, 3H), 3.94 (s, 2H), 2.39 (m, 2H), 2.07 (s, 6H), 1.90 (s, 6H), 1.22 (d, *J* =

6.7 Hz, 12H). ^{13}C NMR (75 MHz, $CDCl_3$, 298 K, δ ppm): 165.5, 163.5, 163.53, 163.1, 163.0, 161.9, 154.6, 153.5, 153.5, 151.9, 151.4, 151.3, 148.8, 147.7, 146.2, 136.8, 136.8, 136.8, 136.6, 135.97, 135.9, 135.0, 134.9, 131.1, 128.9, 125.0, 124.8, 124.6, 122.2, 121.8, 120.6, 114.5, 111.2, 111.1, 99.5, 97.4, 94.3, 77.2, 77.0, 76.8, 76.5, 75.4, 75.3, 53.4, 29.5, 28.1, 28.0, 18.9, 17.7, 17.6, 17.5. HRMS (ESI): m/z calcd for $C_{45}H_{48}FN_8O_9$ $[M+H]^+$ 863.3528, Found 863.3587.



2

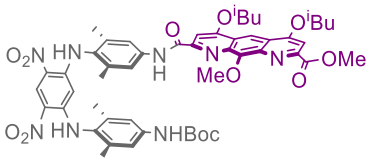
Sequence 2. Tetramer amine **20** (0.040 g, 0.046 mmol), monoacid **16**[4] (0.02 g, 0.046 mmol) and PyBOP (0.120 g, 0.23 mmol) were placed in a 5 mL round-bottom flask filled with argon. Freshly distilled $CHCl_3$ (1 mL) and DIPEA (16 µL, 0.1 mmol) were then successively added. The solution was stirred at room temperature for 16 hours. The solvent was removed under reduced pressure and the residue was dissolved in dichloromethane, washed with 5% NH_4Cl, distilled water and brine. The organic layer was dried over Na_2SO_4, filtered and concentrated under reduced pressure. The crude product was purified by recycling GPC and oligomer **2** was obtained as a yellow solid (0.095 g, 60% yield). ^{1}H NMR (300 MHz, $CDCl_3$, 298 K, δ ppm): 10.08 (s, 1H), 10.04 (s, 1H), 9.35 (s, 1H), 9.02 (d, *J* = 2.2 Hz, 2H), 8.58 (d, *J* = 0.9 Hz, 1H), 8.54 (d, *J* = 0.9 Hz, 1H), 8.23 (d, *J* = 2.0 Hz, 1H), 7.59 (d, *J* = 4.1 Hz, 4H), 7.40 (s, 1H), 7.36 (s, 1H), 7.31 (s, 1H), 7.18 (s, 1H), 4.76 (s, 1H), 4.09 (m, 10H), 3.82 (d, *J* = 6.7 Hz, 2H), 3.71 (d, *J* = 6.7 Hz, 2H), 2.33 (m, 2H), 2.12 (m, 14H), 1.20 (dd, *J* = 6.7, 1.1 Hz, 12H), 1.12 – 0.99 (m, 12H). ^{19}F NMR (282 MHz, $CDCl_3$, 298 K, δ ppm): -127.2. ^{13}C NMR (75 MHz, $CDCl_3$, 298 K, δ ppm): 166.0, 165.9, 162.9, 162.8, 162.6, 161.7, 161.4, 153.2, 152.8, 151.0, 150.8, 148.4, 148.3, 147.1, 145.9, 137.6, 137.4, 137.3, 130.6, 130.6, 129.4, 125.0, 121.6, 121.4, 121.2, 121.1, 119.6, 119.5, 116.1, 110.1, 99.3, 98.8, 96.9, 96.5, 94.5, 75.4, 75.3, 75.1, 53.5, 53.5, 28.5, 28.3, 28.2, 19.3, 19.1, 19.1, 18.1. HRMS (ESI): m/z calcd for $C_{68}H_{72}FN_{10}O_{14}$ $[M+H]^+$ 1271.5214, Found 1271.5286.



21

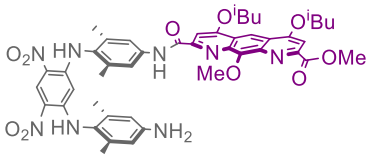
Tetramer acid 21. In a round bottom flask, compound **19** (0.096 g, 0.1 mmol) was dissolved in THF (4 mL). Sodium hydroxide (0.020 g, 0.5 mmol) dissolved in 1 mL methanol was then added dropwise. The reaction mixture was allowed to proceed at room temperature for 16 hours. Solvents were removed

under reduced pressure and the residue was suspended in water and acidified by 5% citric acid aqueous solution. The solid precipitate obtained was filtered and washed with water several times. Finally, dried over reduced pressure to get compound **21** as light brown solid which was used without further purification (0.89 g, 93% yield). ^{1}H NMR (300 MHz, $CDCl_3$, 298 K, δ ppm): 10.21 (s, 1H), 9.36 (s, 1H), 9.18 (s, 1H), 9.14 (s, 1H), 9.06 (s, 1H), 7.81 (s, 1H), 7.65 (s, 1H), 7.44 (s, 2H), 7.04 (s, 2H), 6.75 (s, 1H), 4.92 (s, 1H), 4.57 (s, 3H), 4.23 (dd, *J* = 6.4, 3.7 Hz, 4H), 2.52 – 2.31 (m, 2H), 2.10 (s, 6H), 2.02 (s, 6H), 1.25 – 1.19 (m, 12H), 1.17 (s, 9H). ^{13}C NMR (75 MHz, $CDCl_3$, 298 K, δ ppm): 165.9, 164.5, 163.9, 162.3, 152.9, 152.8, 149.7, 148.5, 148.2, 140.2, 138.1, 137.3, 136.7, 136.7, 131.1, 129.6, 129.3, 125.1, 125.0, 123.2, 122.3, 120.5, 119.0, 111.7, 97.6, 94.0, 80.2, 77.4, 76.3, 75.8, 64.7, 28.4, 28.4, 28.2, 19.3, 19.2, 18.2, 18.1. HRMS (ESI): m/z calcd for $C_{50}H_{57}N_8O_{12}$ $[M+H]^+$ 961.4096, Found 961.4161.



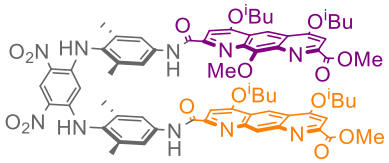
22

Tetramer 22. Tetramer acid **21** (0.085 gm, 0.088 mmol) was dissolved in anhydrous $CHCl_3$ (1 mL), then 1-Chloro-N,N,2-trimethyl-1-propenylamine (60 µL, 0.47 mmol) was added and the reaction was allowed to stir at room temperature for 2 hours under argon. The solvent and excess reagent were removed under reduced pressure and the residue was dried under high vacuum for at least 3 hours to yield the corresponding acid chloride as a yellow solid. The residue was dissolved in 1 mL of dry chloroform and 1 mL freshly dried methanol was added dropwise. Finally, distilled DIPEA (80 µL, 0.47 mmol) was added. The reaction was allowed to stir at room temperature for 12 hours. Solvents were removed under reduced pressure and the residue was dissolved in CH_2Cl_2 before being washed with a saturated solution of NH_4Cl, water and brine. The organic layer was dried over Na_2SO_4, filtered and evaporated. The crude product was purified by column chromatography using silica gel as stationary phase and DCM:MeOH (99:1) as eluent to obtain **22** as yellow powder (55 mg, 64% yield). ^{1}H NMR (300 MHz, $CDCl_3$, 298 K, δ ppm): 10.28 (s, 1H), 9.34 (s, 1H), 9.14 (s, 1H), 9.10 (s, 1H), 8.97 (s, 1H), 7.75 (s, 1H), 7.51 (s, 1H), 7.42 (s, 2H), 7.05 (s, 2H), 6.90 (s, 1H), 4.88 (s, 1H), 4.69 (s, 3H), 4.18 (dd, *J* = 16.6, 6.3 Hz, 4H), 4.09 (s, 3H), 2.38 (m, 2H), 2.08 (s, 6H), 2.01 (s, 6H), 1.21 (d, *J* = 6.7 Hz, 12H), 1.11 (s, 9H). ^{13}C NMR (75 MHz, $CDCl_3$, 298 K, δ ppm): 166.4, 164.2, 163.6, 162.8, 153.5, 152.9, 152.0, 149.9, 148.5, 148.2, 140.6, 139.6, 138.2, 137.1, 136.9, 136.6, 131.0, 129.5, 129.2, 125.1, 125.0, 122.8, 122.6, 120.7, 119.0, 110.1, 99.3, 97.1, 94.1, 80.0, 75.5, 75.4, 64.7, 53.4, 28.4, 28.4, 28.1, 19.3, 19.3, 18.2, 18.1. HRMS (ESI): m/z calcd for $C_{51}H_{59}N_8O_{12}$ $[M+H]^+$ 975.4247, Found 975.4317.



23

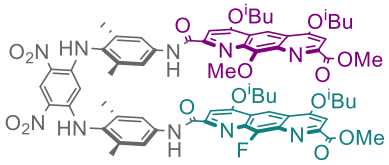
Tetramer amine 11. In a round-bottom flask, compound **22** (0.055 g, 0.056 mmol) was dissolved in 2 mL chloroform and subsequently, 2 mL TFA was added dropwise. The mixture was allowed to stir for 3 hours at room temperature. A saturated aqueous solution of $NaHCO_3$ was added to quench the excess acid. Then, the solution was extracted with CH_2Cl_2, washed with water, dried over Na_2SO_4 and evaporated. Product **23** was obtained without any further purification as a yellow solid (43 mg, 90% yield). ^{1}H NMR (300 MHz, $CDCl_3$, 298 K, δ ppm): 10.52 (s, 1H), 9.31 (s, 1H), 9.07 (s, 1H), 9.01 (s, 1H), 8.92 (s, 1H), 7.74 (s, 1H), 7.51 (s, 1H), 7.45 (s, 2H), 6.29 (s, 2H), 4.77 (s, 1H), 4.67 (s, 3H), 4.21 (d, *J* = 6.4 Hz, 2H), 4.16 (d, *J* = 6.3 Hz, 2H), 4.10 (s, 3H), 2.38 (m, 2H), 2.07 (s, 6H), 1.90 (s, 6H), 1.29 – 1.17 (m, 12H). ^{13}C NMR (75 MHz, $CDCl_3$, 298 K, δ ppm): 166.4, 164.3, 163.7, 162.8, 153.5, 152.6, 150.1, 149.1, 148.1, 146.6, 140.7, 139.8, 137.2, 137.1, 131.3, 129.3, 125.4, 125.1, 124.9, 122.8, 122.6, 120.6, 114.8, 110.6, 99.3, 97.2, 94.6, 75.6, 75.4, 64.7, 53.4, 28.4, 28.4, 19.3, 18.1, 17.9. HRMS (ESI): m/z calcd for $C_{46}H_{51}N_8O_{10}$ $[M+H]^+$ 875.3723, Found 875.3784.



3

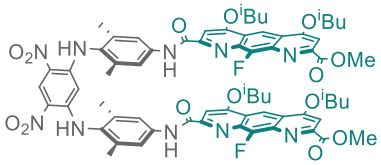
Sequence 3. Tetramer amine **23** (0.025 g, 0.028 mmol), monoacid **16**[4] (0.02 g, 0.046 mmol) and PyBOP (0.075 g, 0.143 mmol) were placed in a 5 mL round-bottom flask filled with argon. Freshly distilled $CHCl_3$ (1 mL) and DIPEA (10 µL, 0.06 mmol) were then successively added. The solution was stirred at room temperature for 16 hours. The solvent was removed under reduced pressure and the residue was dissolved in dichloromethane, washed with 5% NH_4Cl, distilled water and brine. The organic layer was dried over Na_2SO_4, filtered and concentrated under reduced pressure. The crude product was purified by recycling GPC and sequence **3** was obtained as a yellow solid (0.028 g, 75% yield). ^{1}H NMR (300 MHz, $CDCl_3$, 298 K, δ ppm): 10.29 (s, 1H), 10.05 (s, 1H), 9.34 (s, 1H), 9.02 (s, 2H), 8.77 (s, 1H), 8.55 (s, 1H), 8.20 (s, 1H), 7.57 (s, 4H), 7.37 (s, 1H), 7.35 (s, 1H), 7.21 (s, 1H), 6.94 (s, 1H), 4.77 (s, 4H), 4.09 (m, 10H), 3.63 (d, *J* = 6.7 Hz, 2H), 3.46 (d, *J* = 6.7 Hz, 2H), 2.34 (m, 2H), 2.11 (d, *J* = 2.1 Hz, 12H), 2.07 – 1.92 (m, 2H), 1.21 (dd, *J* = 6.7, 5.0 Hz, 12H), 0.99 (dd, *J* = 9.6, 6.7 Hz, 12H). ^{13}C NMR (75 MHz, $CDCl_3$, 298 K, δ ppm): 166.3, 165.9, 163.0, 163.0, 162.9, 162.8, 161.9, 161.7, 153.1, 152.9, 151.3, 150.9, 149.2, 148.4, 147.0, 146.0, 139.9, 138.7, 137.7, 137.6, 137.3, 137.2, 130.5, 130.3, 129.4, 129.3, 125.0, 121.9, 121.7, 121.4, 121.2, 119.3, 119.3, 116.4, 108.8, 98.9, 98.8,

96.4, 96.2, 94.5, 77.4, 75.3, 75.2, 75.0, 74.7, 64.5, 53.4, 53.3, 28.5, 28.5, 28.2, 28.2, 19.3, 19.3, 19.1, 19.0, 18.1, 18.1. HRMS (ESI): m/z calcd for $C_{69}H_{75}N_{10}O_{15}$ $[M+H]^+$ 1283.5408, Found 1283.5504.



4

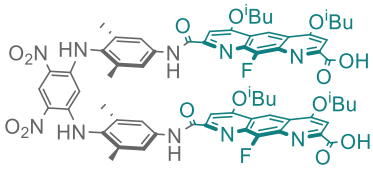
Sequence 4. Tetramer amine **23** (0.015 g, 0.017 mmol), monoacid **18**[6] (0.015 g, 0.034 mmol) and PyBOP (0.044 g, 0.085 mmol) were placed in a 5 mL round-bottom flask filled with argon. Freshly distilled $CHCl_3$ (1 mL) and DIPEA (6 µL, 0.034 mmol) were then successively added. The solution was stirred at room temperature for 16 hours. The solvent was removed under reduced pressure and the residue was dissolved in dichloromethane, washed with 5% NH_4Cl, distilled water and brine. The organic layer was dried over Na_2SO_4, filtered and concentrated under reduced pressure. The crude product was purified by recycling GPC and sequencer **4** was obtained as a yellow solid (0.017 g, 77% yield). ^{1}H NMR (300 MHz, $CDCl_3$, 298 K, δ ppm): 10.22 (s, 1H), 10.07 (s, 1H), 9.03 (s, 2H), 8.46 (d, *J* = 2.1 Hz, 1H), 8.12 (s, 1H), 7.58 (s, 2H), 7.56 (s, 2H), 7.38 (s, 2H), 7.35 (d, *J* = 1.0 Hz, 2H), 7.05 (s, 1H), 4.78 (m, 4H), 4.15 – 3.99 (m, 10H), 3.80 (d, *J* = 6.7 Hz, 2H), 3.67 (d, *J* = 6.7 Hz, 2H), 2.32 (m, 2H), 2.12 (m, 14H), 1.20 (t, *J* = 6.8 Hz, 12H), 1.05 (dd, *J* = 6.7, 5.3 Hz, 12H). ^{13}C NMR (75 MHz, $CDCl_3$, 298 K, δ ppm): 166.3, 165.7, 162.9, 162.7, 161.9, 161.5, 153.1, 152.9, 151.3, 150.7, 149.0, 148.4, 139.9, 138.6, 137.7, 137.5, 137.3, 137.2, 130.6, 130.4, 129.4, 125.0, 121.8, 121.5, 119.6, 119.4, 110.4, 110.3, 108.4, 99.2, 98.9, 97.0, 96.1, 94.5, 75.4, 75.3, 75.2, 74.8, 64.5, 53.4, 53.2, 28.5, 28.5, 28.3, 28.2, 19.3, 19.3, 19.1, 18.1, 18.1. HRMS (ESI): m/z calcd for $C_{69}H_{74}FN_{10}O_{15}$ $[M+H]^+$ 1301.5314, Found 1301.5408.



5

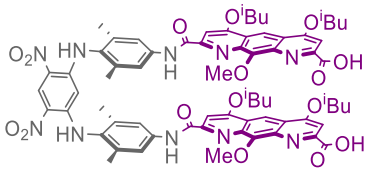
Sequence 5. Diamino turn **15**[5] (0.1 g, 0.23 mmol), 9-fluorodiazaanthracene **18**[6] (0.214 g, 0.48 mmol), and PyBOP (0.598 g, 1.15 mmol) were placed in a 5 mL round bottom flask then dissolved in freshly distilled $CHCl_3$ (2 mL) and DIPEA (0.2 mL, 1.15 mmol) was added under nitrogen atmosphere. The reaction mixture was allowed to stir at room temperature for 16 hours. The solvent was removed under reduced pressure and the residue was dissolved in dichloromethane. The solution was then washed successively with 5% NH_4Cl, water and brine. Finally, the organic layer was dried over Na_2SO_4, filtered, and evaporated. The residue was purified by recycling GPC and product **5** was obtained as a yellow

solid (0.187 g, 63% yield). ^{1}H NMR (300 MHz, $CDCl_3$, 298 K, δ ppm): 10.02 (s, 2H), 9.35 (s, 1H), 9.02 (s, 2H), 8.20 (d, *J* = 2.0 Hz, 2H), 7.58 (s, 4H), 7.42 (s, 2H), 7.37 (s, 2H), 4.76 (s, 1H), 4.15 – 4.01 (m, 10H), 3.86 (d, *J* = 6.7 Hz, 4H), 2.42 – 2.24 (m, 2H), 2.12 (m, 14H), 1.18 (d, *J* = 6.7 Hz, 12H), 1.08 (d, *J* = 6.7 Hz, 12H). ^{13}C NMR (75 MHz, $CDCl_3$, 298 K, δ ppm): 165.8, 162.6, 162.5, 162.5, 162.4, 161.4, 154.9, 152.8, 152.8, 151.3, 150.8, 150.7, 148.3, 137.2, 137.1, 135.7, 135.6, 134.4, 134.3, 130.6, 129.2, 124.9, 121.5, 121.3, 119.8, 109.9, 109.8, 99.2, 96.9, 94.5, 77.3, 75.3, 75.2, 53.4, 28.4, 28.1, 19.1, 19.0, 17.9. ^{19}F NMR (282 MHz, $CDCl_3$, 298 K, δ ppm): -127.2. HRMS (ESI): m/z calcd for $C_{68}H_{71}F_2N_{10}O_{14}$ $[M+H]^+$ 1289.5114, Found 1289.5202.



24

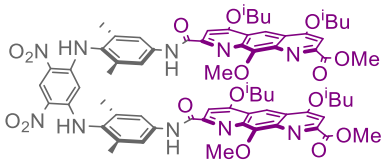
Pentamer diacid 24. In a round bottom flask, compound **5** (0.03 g, 0.023 mmol) was taken along with lithium iodide (0.025 g, 0.184 mmol) and freshly dried ethyl acetate (2 mL) was added under nitrogen atmosphere. The mixture was refluxed at 351 K for 3 hours before it cooled down to room temperature. Solvent was removed under reduced pressure, followed by diethyl ether was added to obtained precipitate. The precipitate was filtered, and 5% aqueous citric acid solution was added. Finally, the precipitate was washed with water (three times) and cold methanol followed by dried under vacuum to obtain yellow powder which was used without further purification (0.027 g, 93% yield). ^{1}H NMR (300 MHz, DMSO-d_6, 298 K, δ ppm): 10.14 (s, 2H), 9.43 (s, 2H), 9.06 (s, 1H), 8.20 (s, 2H), 7.65 (s, 4H), 7.26 (s, 2H), 7.10 (s, 2H), 4.63 (s, 1H), 4.11 (d, *J* = 6.3 Hz, 4H), 3.76 (s, 4H), 2.33 – 2.16 (m, 4H), 2.03 (s, 12H), 1.14 (d, *J* = 6.6 Hz, 12H), 1.04 (d, *J* = 6.6 Hz, 12H). ^{19}F NMR (282 MHz, $CDCl_3$, 298 K, δ ppm): -129.7. HRMS (ESI): m/z calcd for $C_{66}H_{65}F_2N_{10}O_{14}$ $[M-H]^{1-}$ 1259.4655, Found 1259.4611.



25

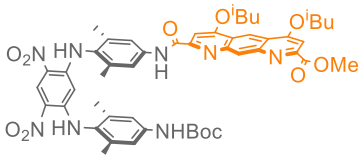
Pentamer diacid 25. In a round bottom flask, compound **5** (0.187 g, 0.145 mmol) was dissolved in THF (4 mL). Sodium hydroxide (0.035 g, 0.87 mmol) dissolved in 1 mL methanol was then added dropwise. The reaction mixture was allowed to proceed at room temperature for 16 hours. Solvents were removed under reduced pressure and the residue was suspended in water and acidified by 5% citric acid aqueous solution. The solid precipitate obtained was filtered, washed with water and diethyl ether several times and finally, dried over reduced pressure to get compound **25** as light brown solid which was used without

further purification (0.172 g, 92% yield). ^{1}H NMR (300 MHz, DMSO-d_6, 298 K, δ ppm): 10.19 (s, 2H), 9.43 (s, 2H), 9.06 (s, 1H), 8.37 (s, 2H), 7.56 (s, 4H), 7.42 (s, 2H), 6.77 (s, 2H), 4.61 (m, 7H), 4.17 (d, *J* = 6.2 Hz, 4H), 3.16 (s, 4H), 2.38 – 2.19 (m, 4H), 2.03 (s, 12H), 1.16 (d, *J* = 6.6 Hz, 12H), 0.80 (d, *J* = 6.6 Hz, 12H). ^{13}C NMR (75 MHz, DMSO-d_6, 298 K, δ ppm): 166.3, 162.4, 162.1, 160.8, 152.6, 150.5, 150.4, 147.4, 139.4, 138.0, 136.8, 136.6, 131.2, 124.0, 121.3, 121.0, 118.3, 108.2, 99.0, 95.3, 93.9, 74.6, 73.6, 64.9, 63.9, 27.8, 27.4, 18.8, 18.2, 17.6, 15.2. HRMS (ESI): m/z calcd for $C_{68}H_{73}N_{10}O_{16}$ $[M+H]^+$ 1285.5201, Found 1285.5295.



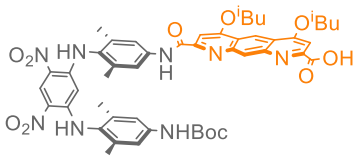
6

Sequence 6. Diacid **25** (0.025 g, 0.02 mmol) was dissolved in anhydrous $CHCl_3$ (1 mL), then oxalyl chloride (17 µL, 0.2 mmol) was added and the reaction was allowed to stir at room temperature for 3 hours under nitrogen atmosphere. The solvent and excess oxalyl chloride were removed under reduced pressure and the residue was dried under high vacuum for at least 2 hours to yield the corresponding acid chloride as a yellow solid. The residue was dissolved in 1 mL of dry chloroform and 1 mL freshly dried methanol was added dropwise. Finally, distilled DIPEA (14 µL, 0.08 mmol) was added. The reaction was allowed to stir at room temperature for 12 hours. Solvents were removed under reduced pressure and the residue was dissolved in CH_2Cl_2 before being washed with a saturated solution of NH_4Cl, water and brine. The organic layer was dried over Na_2SO_4, filtered, and evaporated. The crude product was purified by recycling GPC and the sequence **6** was obtained as a yellow powder (19 mg, 68% yield). ^{1}H NMR (300 MHz, $CDCl_3$, 298 K, δ ppm): 10.20 (s, 2H), 9.35 (s, 1H), 9.04 (s, 2H), 8.40 (s, 2H), 7.53 (s, 4H), 7.40 (s, 2H), 7.01 (s, 2H), 4.79 (s, 1H), 4.76 (s, 6H), 4.11 (d, *J* = 6.4 Hz, 4H), 4.05 (s, 6H), 3.42 (d, *J* = 6.6 Hz, 4H), 2.35 (m, 2H), 2.12 (s, 12H), 1.95 (m, 2H), 1.21 (d, *J* = 6.7 Hz, 12H), 0.93 (d, *J* = 6.7 Hz, 12H). ^{13}C NMR (75 MHz, $CDCl_3$, 298 K, δ ppm): 166.1, 163.0, 162.8, 161.8, 152.7, 151.1, 149.0, 148.3, 139.7, 138.4, 137.7, 137.1, 130.2, 129.3, 124.9, 121.9, 121.8, 119.1, 108.7, 98.8, 96.1, 94.3, 77.3, 75.1, 74.6, 64.4, 53.2, 28.4, 28.0, 19.2, 18.9, 18.0. HRMS (ESI): m/z calcd for $C_{70}H_{77}N_{10}O_{16}$ $[M+H]^+$ 1313.5514, Found 1313.5614.



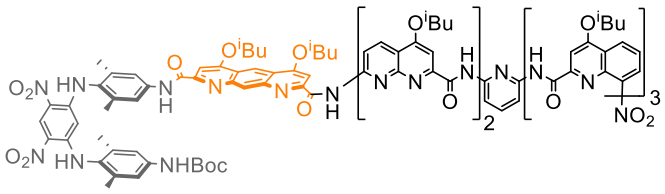
27

Tetramer 27. Monoamine turn **17**[5] (0.2 g, 0.37 mmol), diazaanthracene monoacid **16**[4] (0.19 g, 0.444 mmol), and PyBOP (0.481 g, 0.925 mmol) were placed in a 5 mL round bottom flask then dissolved in freshly distilled $CHCl_3$ (2 mL) and DIPEA (130 μL, 0.74 mmol) was added under nitrogen atmosphere. The reaction mixture was allowed to stir at room temperature for 48 hours. The mixture was dissolved in dichloromethane. The solution was then washed successively with 5% NH_4Cl, water and brine. Finally, the organic layer was dried over Na_2SO_4, filtered and evaporated. The crude product was subjected to column chromatography with silica gel as stationary phase and methanol/DCM (1:99) as eluent to obtain **27** as a yellow solid (0.313 g, 89% yield). ^{1}H NMR (300 MHz, $CDCl_3$, 298 K, δ ppm): 10.18 (s, 1H), 9.35 (s, 1H), 9.31 (d, *J* = 0.8 Hz, 1H), 9.15 (s, 1H), 9.12 (s, 1H), 9.07 (d, *J* = 0.9 Hz, 1H), 7.78 (s, 1H), 7.54 (s, 1H), 7.48 (s, 2H), 7.03 (s, 2H), 6.68 (s, 1H), 4.91 (s, 1H), 4.23 (d, *J* = 6.4 Hz, 2H), 4.18 (d, *J* = 6.4 Hz, 2H), 4.14 (s, 3H), 2.40 (m, 2H), 2.09 (s, 6H), 2.01 (s, 6H), 1.23 (d, *J* = 6.7 Hz, 12H), 1.14 (s, 9H). ^{13}C NMR (75 MHz, $CDCl_3$, 298 K, δ ppm): 166.1, 163.9, 163.4, 162.3, 153.4, 152.7, 151.7, 148.4, 148.1, 147.7, 146.7, 138.0, 136.9, 136.7, 136.5, 130.7, 129.6, 129.4, 129.1, 124.9, 124.9, 122.0, 121.8, 120.3, 118.9, 117.2, 99.1, 96.9, 93.9, 80.0, 77.5, 77.3, 77.1, 76.6, 75.4, 75.3, 53.5, 28.3, 28.23, 28.0, 19.4, 19.2, 19.2, 18.0, 17.9. HRMS (ESI): m/z calcd for $C_{50}H_{57}N_8O_{11}$ $[M+H]^+$ 945.4141, Found 945.4211.



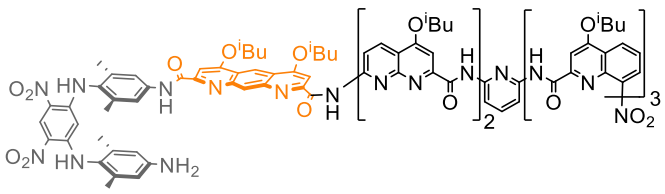
28

Tetramer acid 28. In a round bottom flask, compound **27** (0.2 g, 0.21 mmol) was dissolved in THF (3 mL). Sodium hydroxide (0.042 g, 1.05 mmol) dissolved in 1 mL methanol was then added dropwise. The reaction mixture was allowed to proceed at room temperature for 16 hours. Solvents were removed under reduced pressure and the residue was suspended in water and acidified by 5% citric acid aqueous solution. The solid precipitate obtained was filtered, washed with water and diethyl ether several times and finally, dried over reduced pressure to get compound **28** as brown solid which was used without further purification (0.190 g, 97% yield). ^{1}H NMR (300 MHz, DMSO-d_6, 298 K, δ ppm): 10.22 (s, 1H), 9.35 (d, *J* = 2.8 Hz, 2H), 9.17 (s, 1H), 9.13 (s, 1H), 9.03 (s, 1H), 7.81 (s, 1H), 7.65 (s, 1H), 7.50 (s, 2H), 7.05 (s, 2H), 6.75 (s, 1H), 4.93 (s, 1H), 4.23 (dd, *J* = 6.4, 4.9 Hz, 4H), 2.54 – 2.33 (m, 2H), 2.10 (s, 6H), 2.02 (s, 6H), 1.23 (dd, *J* = 6.7, 2.1 Hz, 12H), 1.16 (s, 9H). ^{13}C NMR (75 MHz, DMSO-d_6, 298 K, δ ppm): 164.1, 163.3, 162.1, 154.5, 152.9, 151.8, 148.5, 148.2, 147.3, 138.2, 137.1, 136.8, 136.7, 131.0, 129.6, 129.3, 126.0, 125.1, 125.0, 122.5, 121.3, 120.4, 119.0, 118.4, 98.0, 97.6, 94.0, 80.1, 76.5, 74.6, 28.4, 28.4, 28.1, 19.3, 19.2, 18.2, 18.1. HRMS (ESI): m/z calcd for $C_{49}H_{55}N_8O_{11}$ $[M+H]^+$ 931.3985, Found 931.4059.



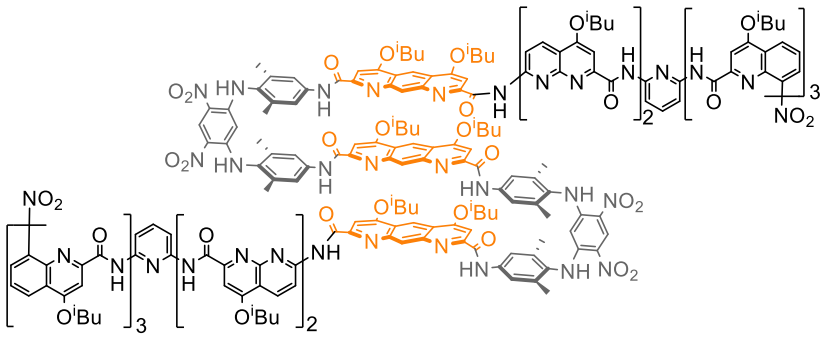
30

Oligomer 30. Monoacid **28** (0.072 g, 0.077 mmol), amino hexamer **29**[7] (0.095 g, 0.07 mmol) and PyBOP (0.182 g, 0.35 mmol) were placed in a 5 mL round-bottom flask filled with argon. Freshly distilled $CHCl_3$ (1 mL) and DIPEA (60 µL, 0.35 mmol) were then successively added. The solution was stirred at room temperature for 16 hours. The solvent was removed under reduced pressure and the residue was dissolved in dichloromethane, washed with 5% NH_4Cl, distilled water and brine. The organic layer was dried over Na_2SO_4, filtered and concentrated under reduced pressure. The crude product was purified by recycling GPC and oligomer **30** was obtained as a yellow solid (0.095 g, 60% yield). ^{1}H NMR (300 MHz, $CDCl_3$, 298 K, δ ppm): 11.90 (s, 1H), 11.85 (s, 1H), 11.61 (s, 1H), 11.59 (s, 1H), 9.99 (s, 1H), 9.76 (s, 1H), 9.60 (s, 1H), 9.30 (s, 1H), 8.99 (s, 1H), 8.98 (s, 1H), 8.92 (s, 1H), 8.90 – 8.76 (m, 4H), 8.63 (d, *J* = 0.9 Hz, 1H), 8.46 (dd, *J* = 7.7, 1.3 Hz, 1H), 8.36 (ddd, *J* = 7.1, 5.6, 1.5 Hz, 2H), 7.97 (d, *J* = 7.8 Hz, 1H), 7.87 (s, 1H), 7.86 (s, 1H), 7.84 (s, 1H), 7.79 (s, 1H), 7.71 (s, 1H), 7.32 (s, 1H), 7.31 – 7.28 (m, 1H), 7.24 – 7.16 (m, 2H), 7.11 (d, *J* = 7.9 Hz, 1H), 7.05 (s, 1H), 6.99 (dd, *J* = 8.3, 1.3 Hz, 1H), 6.79 (s, 1H), 6.76 – 6.66 (m, 2H), 6.50 (s, 1H), 6.41 – 6.32 (m, 2H), 6.23 (s, 1H), 4.43 – 4.14 (m, 7H), 3.94 (m, 4H), 3.70 (d, *J* = 7.9 Hz, 1H), 3.30 (d, *J* = 8.6 Hz, 2H), 2.40 (m, 7H), 1.71 (s, 4H), 1.46 (s, 4H), 1.33 (d, *J* = 6.8, 6H), 1.30 – 1.13 (m, 36H), 0.99 (s, 9H), 0.75 (d, *J* = 6.6 Hz, 3H), 0.51 (d, *J* = 6.7 Hz, 3H). ^{13}C NMR (75 MHz, $CDCl_3$, 298 K, δ ppm): 164.6, 163.9, 163.6, 163.4, 162.8, 162.2, 161.8, 161.3, 160.9, 160.1, 154.7, 154.6, 154.1, 153.9, 153.7, 152.6, 152.6, 151.8, 151.7, 151.2, 149.2, 148.2, 148.0, 146.9, 145.7, 145.3, 144.6, 138.9, 138.8, 138.6, 138.0, 137.6, 136.5, 136.3, 136.2, 135.9, 134.6, 134.5, 134.4, 134.4, 129.6, 129.4, 129.1, 128.1, 126.4, 126.1, 125.7, 124.8, 124.8, 124.0, 123.4, 122.7, 121.5, 120.9, 120.7, 119.1, 118.9, 118.8, 118.8, 118.7, 118.6, 117.7, 117.0, 116.2, 115.6, 115.0, 115.0, 114.5, 114.4, 109.0, 108.4, 101.3, 99.3, 98.8, 98.1, 96.9, 96.1, 95.7, 93.8, 79.8, 77.5, 77.3, 77.1, 76.6, 76.0, 75.8, 75.4, 75.2, 74.9, 29.7, 28.4, 28.4, 28.3, 28.2, 28.2, 27.9, 27.8, 19.5, 19.3, 19.3, 19.2, 18.4, 18.2, 17.9, 17.7, 17.0. HRMS (ESI$^+$): calcd. for $C_{122}H_{127}N_{23}O_{22}$ $[M + 2H]^{2+}$ 1133.4774, found 1133.4861.



31

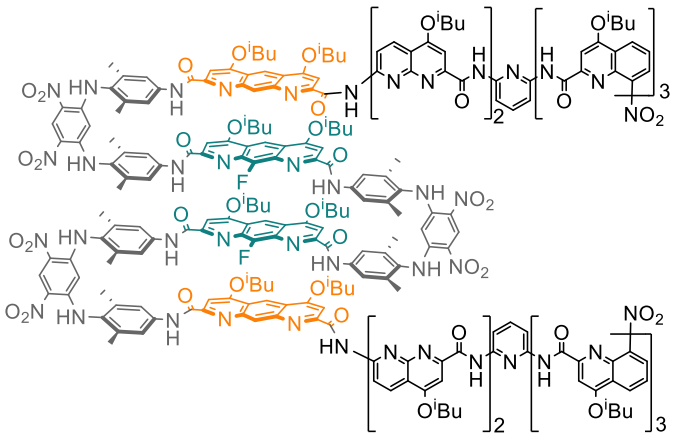
Oligomer 31. In a round-bottom flask, compound **30** (0.052 g, 0.023 mmol) was dissolved in HCl in dioxane (4M, 2mL) and chloroform (0.3 mL). The mixture was allowed to stir for 7 hours at room temperature. The reaction was quenched with saturated solution of $NaHCO_3$, and the solution was extracted three times with CH_2Cl_2, washed with water, dried over Na_2SO_4 and evaporated. Compound **31** was obtained as yellow solid which was used without any further purification (0.048 g, 96% yield). ^{1}H NMR (300 MHz, $CDCl_3$, 298 K, δ ppm): 11.92 (s, 1H), 11.82 (s, 1H), 11.65 (s, 1H), 11.60 (s, 1H), 10.04 (s, 1H), 9.75 (s, 1H), 9.69 (s, 1H), 9.24 (s, 1H), 8.95 – 8.87 (m, 2H), 8.87 – 8.77 (m, 4H), 8.75 (s, 1H), 8.62 (s, 1H), 8.47 (d, *J* = 7.6 Hz, 1H), 8.42 (d, *J* = 7.7 Hz, 1H), 8.37 (dd, *J* = 8.0, 1.7 Hz, 1H), 7.93 (s, 1H), 7.90 (s, 1H), 7.87 (s, 1H), 7.85 (s, 1H), 7.83 (s, 1H), 7.69 (s, 1H), 7.37 (s, 1H), 7.21 (ddd, *J* = 11.4, 5.6, 2.8 Hz, 4H), 7.04 (s, 1H), 6.97 (d, *J* = 8.3 Hz, 1H), 6.77 (t, *J* = 8.0 Hz, 1H), 6.45 (s, 1H), 6.37 (t, *J* = 8.0 Hz, 1H), 6.08 (s, 1H), 5.97 – 5.85 (m, 2H), 4.44 – 4.14 (m, 6H), 4.07 – 3.60 (m, 8H), 3.37 – 3.17 (m, 4H), 2.40 (m, 4H), 1.99 (s, 3H), 1.57 (d, *J* = 8.2 Hz, 4H), 1.44 (s, 4H), 1.33 (dd, *J* = 6.7, 3.8 Hz, 4H), 1.29 – 1.08 (m, 36H), 0.77 (d, *J* = 6.5 Hz, 3H), 0.55 (d, *J* = 6.7 Hz, 3H). ^{13}C NMR (75 MHz, $CDCl_3$, 298 K, δ ppm): 165.6, 164.7, 164.0, 163.7, 163.4, 162.9, 162.2, 161.9, 161.5, 160.9, 160.1, 154.6, 154.2, 154.0, 153.7, 152.6, 152.2, 151.9, 151.3, 149.3, 148.8, 148.2, 148.0, 146.9, 146.1, 145.7, 145.4, 144.7, 139.1, 139.0, 138.9, 138.0, 136.8, 136.4, 136.2, 134.7, 134.6, 134.3, 130.0, 129.8, 129.3, 128.8, 128.2, 126.5, 126.2, 125.8, 124.8, 124.1, 123.5, 1222.8, 121.5, 120.9, 120.7, 118.6, 118.3, 117.8, 117.1, 116.5, 115.6, 115.1, 114.5, 109.2, 108.5, 101.4, 99.3, 98.8, 98.0, 96.8, 96.3, 95.9, 94.2, 77.4, 76.1, 75.9, 75.5, 74.9, 30.2, 29.8, 28.5, 28.4, 28.3, 28.2, 27.9, 19.8, 19.4, 19.2, 18.6, 18.3, 14.3. HRMS (ES+): m/z calcd for $C_{117}H_{119}N_{23}O_{20}$ $[M+2H]^{2+}$ 1083.4512 Found 1083.4587.



8

Oligomer 8. 1,8-diaza-4,5-diisobutoxy-2,7-anthracene dicarboxylate **32** (4.54 mg, 0.011 mmol), oligomer **31** (50 mg, 0.023 mmol) and PyBOP (172 mg, 0.33 mmol) were placed in a 5 mL round-bottom flask filled with argon. Freshly distilled $CHCl_3$ (1 mL) and DIPEA (11 µL, 0.066 mmol) were then successively added. The solution was stirred at 318 K for two days. The solvent was removed under reduced pressure and the residue was dissolved in dichloromethane, washed with 5% NH_4Cl, distilled water and brine. The organic layer was dried over Na_2SO_4, filtered, and concentrated under reduced pressure. The crude product was purified by recycling GPC and oligomer **8** was obtained as a yellow

solid (11 mg, 21% yield). ^{1}H NMR (700 MHz, $CDCl_3$, 298 K, δ ppm): 11.54 (s, 2H), 10.97 (s, 2H), 10.90 (s, 2H), 10.00 (s, 2H), 9.89 (s, 2H), 9.85 (s, 2H), 9.27 (s, 2H), 9.05 (d, *J* = 11.8 Hz, 4H), 8.89 (d, *J* = 8.3 Hz, 2H), 8.85 (s, 2H), 8.74 (d, *J* = 8.3 Hz, 2H), 8.64 (s, 1H), 8.58 (d, *J* = 7.5 Hz, 4H), 8.47 – 8.39 (m, 3H), 8.22 (d, *J* = 6.9 Hz, 2H), 8.19 (d, *J* = 6.9 Hz, 2H), 8.04 (s, 2H), 7.95 (d, *J* = 7.1 Hz, 2H), 7.74 (s, 2H), 7.57 (d, *J* = 6.9 Hz, 2H), 7.34 (s, 2H), 7.18 (s, 2H), 7.15 (t, *J* = 7.1 Hz, 2H), 7.09 – 7.01 (m, 5H), 6.91 – 6.85 (m, 5H), 6.83 (s, 2H), 6.74 (d, *J* = 7.6 Hz, 2H), 6.39 (s, 1H), 6.27 (d, *J* = 5.3 Hz, 3H), 6.23 (s, 2H), 6.06 (t, *J* = 7.3 Hz, 2H), 5.80 (s, 2H), 5.64 (s, 2H), 4.28 (t, *J* = 5.5 Hz, 3H), 4.23 (s, 3H), 4.18 (t, *J* = 6.2 Hz, 3H), 4.15 (t, *J* = 5.7 Hz, 2H), 4.10 (q, *J* = 5.8, 5.3 Hz, 4H), 4.05 (t, *J* = 6.5 Hz, 3H), 3.99 (t, *J* = 6.8 Hz, 2H), 3.92 (t, *J* = 6.5 Hz, 2H), 3.85 (m, 4H), 3.77 (t, *J* = 6.1 Hz, 3H), 3.66 (t, *J* = 5.6 Hz, 2H), 3.48 (t, *J* = 7.2 Hz, 2H), 3.25 (d, *J* = 5.5 Hz, 2H), 3.17 (q, *J* = 3.2 Hz, 2H), 2.78 – 2.71 (m, 2H), 2.43 (m, 7H), 2.37 – 2.27 (m, 7H), 2.27 – 2.16 (m, 6H), 1.97 (s, 6H), 1.81 (d, *J* = 8.3 Hz, 7H), 1.40 (d, *J* = 7.0 Hz, 8H), 1.34 (m, 16H), 1.32 – 1.23 (m, 24H), 1.19 (m, 20H), 1.16 – 1.04 (m, 20H), 0.91 – 0.78 (m, 6H), 0.47 (d, *J* = 7.0 Hz, 6H), 0.25 (d, *J* = 6.5 Hz, 6H). HRMS (ES+): m/z calcd for $C_{256}H_{257}N_{48}O_{44}$ $[M+3H]^{3+}$ 1569.6466 Found 1569.6572.

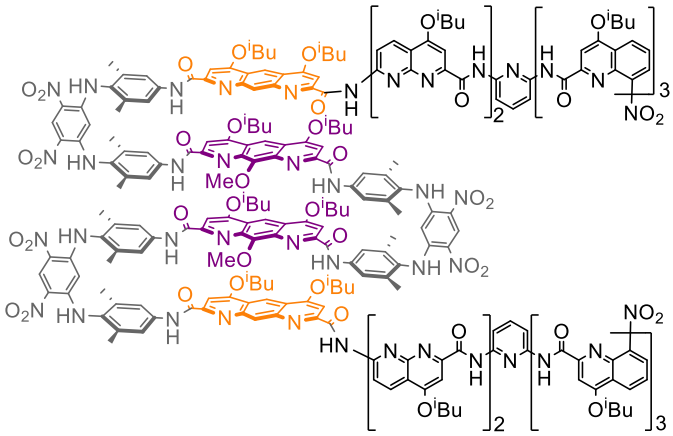


9

Oligomer 9. Dicarboxylate **24** (10.1 mg, 8 µmol) was suspended in anhydrous $CHCl_3$ (1 mL), then oxalyl chloride (7 µL, 80 µmol) was added and the reaction was allowed to stir at room temperature for 2 hours. The solvent and excess oxalyl chloride were removed under reduced pressure and the residue was dried under high vacuum for 3 hours to yield the corresponding acid chloride **24a** as a yellow solid. The solution of amine **31** (38 mg, 17 µmol) and distilled DIPEA (7 µL, 40 µmol) in anhydrous $CHCl_3$ (1 mL) was added dropwise via a syringe to solution of the freshly prepared **24a** dissolved in anhydrous $CHCl_3$ (0.5 mL). The reaction was allowed to proceed at room temperature for 16 hours. After evaporation of the solvents, the crude product was purified by recycling GPC. Oligomer **9** was obtained as a yellow product (20 mg, 45% yield). ^{1}H NMR (700 MHz, Acetone-d_6, 258 K, δ ppm; only peaks are given due to the presence of two conformers): 11.61, 11.48, 11.32, 11.18, 11.11, 10.47, 10.28, 10.05, 9.93, 9.81, 9.73, 9.51, 9.47, 9.46, 9.45, 9.38, 9.29, 9.26, 9.21, 9.20, 9.11, 9.06, 9.03, 8.98, 8.95, 8.94, 8.91, 8.90, 8.85, 8.84, 8.76, 8.75, 8.75, 8.74, 8.73, 8.60, 8.59, 8.57, 8.53, 8.52, 8.47, 8.35, 8.29, 8.28,

8.27, 8.23, 8.22, 8.21, 8.19, 8.18, 8.01, 7.93, 7.92, 7.90, 7.89, 7.89, 7.88, 7.87, 7.75, 7.74, 7.72, 7.69, 7.68, 7.63, 7.62, 7.56, 7.43, 7.36, 7.35, 7.34, 7.31, 7.27, 7.26, 7.25, 7.24, 7.16, 7.14, 7.13, 7.11, 7.11, 7.09, 7.07, 7.07, 7.07, 7.01, 7.01, 6.98, 6.96, 6.94, 6.92, 6.90, 6.89, 6.88, 6.88, 6.87, 6.82, 6.79, 6.69, 6.66, 6.65, 6.63, 6.62, 6.61, 6.57, 6.56, 6.55, 6.54, 6.32, 6.22, 6.20, 6.19, 6.18, 6.17, 6.16, 6.15, 6.11, 6.03, 5.91, 5.76, 5.69, 5.69, 5.66, 5.56, 5.34, 4.64, 4.51, 4.49, 4.47, 4.47, 4.42, 4.41, 4.40, 4.38, 4.37, 4.35, 4.34, 4.33, 4.32, 4.32, 4.31, 4.30, 4.29, 4.25, 4.24, 4.23, 4.23, 4.22, 4.16, 4.16, 4.13, 4.10, 4.07, 4.06, 4.05, 3.98, 3.98, 3.97, 3.95, 3.94, 3.93, 3.92, 3.91, 3.89, 3.88, 3.82, 3.70, 3.66, 3.61, 3.59, 3.56, 3.50, 3.49, 3.48, 3.47, 3.37, 3.34, 3.33, 3.32, 3.32, 3.31, 3.16, 3.14, 3.12, 3.11, 2.86, 2.84, 2.79, 2.79, 2.78, 2.61, 2.60, 2.59, 2.57, 2.50, 2.49, 2.48, 2.47, 2.46, 2.45, 2.44, 2.43, 2.42, 2.41, 2.40, 2.39, 2.35, 2.34, 2.33, 2.32, 2.32, 2.31, 2.30, 2.27, 2.26, 2.25, 2.24, 2.23, 2.22, 2.21, 2.20, 2.17, 2.17, 2.16, 2.15, 2.09, 2.08, 2.07, 2.07, 2.06, 2.06, 2.05, 2.05, 2.05, 2.04, 2.03, 2.01, 1.98, 1.97, 1.95, 1.95, 1.83, 1.69, 1.58, 1.56, 1.54, 1.53, 1.51, 1.51, 1.44, 1.43, 1.43, 1.42, 1.41, 1.38, 1.37, 1.36, 1.35, 1.33, 1.32, 1.31, 1.29, 1.28, 1.27, 1.26, 1.26, 1.26, 1.25, 1.25, 1.24, 1.23, 1.22, 1.22, 1.21, 1.20, 1.20, 1.19, 1.19, 1.18, 1.17, 1.15, 1.14, 1.13, 1.12, 1.12, 1.11, 1.11, 1.10, 1.10, 1.09, 1.04, 1.03, 1.03, 1.00, 0.93, 0.89, 0.88, 0.87, 0.86, 0.85, 0.85, 0.83, 0.83, 0.73, 0.69, 0.68, 0.68, 0.67, 0.63, 0.62, 0.56, 0.55, 0.19, 0.14, 0.11, 0.11, 0.08, 0.07, 0.04, 0.03. ^{19}F NMR (376 MHz, Acetone-d_6, 258 K, δ ppm): -130.3, -131.8.

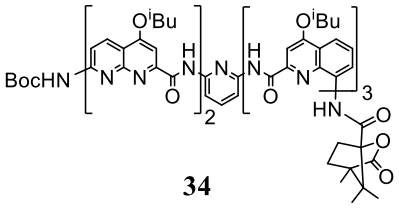
HRMS (ES+): m/z calcd for $C_{300}H_{299}F_2N_{56}O_{52}$ $[M+3H]^{3+}$: 1852.7509 found 1852.7653.



10

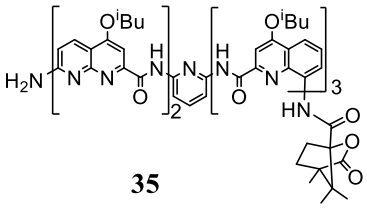
Oligomer 10. Dicarboxylate **25** (10.1 mg, 7.8 µmol) was suspended in anhydrous $CHCl_3$ (1 mL), then oxalyl chloride (7 µL, 78 µmol) was added and the reaction was allowed to stir at room temperature for 2 hours. The solvent and excess oxalyl chloride were removed under reduced pressure and the residue was dried under high vacuum for 3 hours to yield the corresponding acid chloride **25a** as a yellow solid. The solution of amine **31** (37 mg, 17 µmol) and distilled DIPEA (7 µL, 40 µmol) in anhydrous $CHCl_3$ (1 mL) was added dropwise via a syringe to solution of the freshly prepared **25a** dissolved in anhydrous $CHCl_3$ (0.5 mL). The reaction was allowed to proceed at room temperature for 16 hours. After evaporation of the solvents, the crude product was purified by recycling GPC. Oligomer **10** was obtained as a yellow product (26 mg, 58% yield). ^{1}H NMR (700 MHz, $CDCl_3$, 238 K, δ ppm): 11.76 (s, 2H),

11.02 (s, 2H), 10.55 (s, 2H), 10.50 (s, 2H), 10.37 (s, 2H), 10.21 (s, 2H), 9.88 (s, 2H), 9.46 – 9.29 (m, 5H), 9.14 (d, *J* = 7.9 Hz, 3H), 9.08 – 8.91 (m, 7H), 8.85 (d, *J* = 7.9 Hz, 3H), 8.57 (d, *J* = 14.5 Hz, 5H), 8.46 (d, *J* = 7.7 Hz, 3H), 8.44 – 8.36 (m, 5H), 8.31 (dd, *J* = 10.0, 6.6 Hz, 5H), 8.06 (s, 2H), 7.92 (s, 3H), 7.75 (s, 2H), 7.45 (d, *J* = 4.9 Hz, 5H), 7.31 (d, *J* = 6.5 Hz, 4H), 7.18 (d, *J* = 12.7 Hz, 6H), 7.12 (d, *J* = 13.7 Hz, 3H), 7.11 – 7.00 (m, 8H), 6.92 (d, *J* = 6.9 Hz, 5H), 6.87 (s, 3H), 6.78 (s, 3H), 6.67 (d, *J* = 13.7 Hz, 5H), 6.49 (s, 2H), 6.39 (s, 3H), 6.18 (t, *J* = 6.8 Hz, 3H), 6.11 (t, *J* = 6.8 Hz, 3H), 5.92 (s, 2H), 5.66 (s, 3H), 4.99 (s, 6H), 4.40 (s, 3H), 4.35 (s, 2H), 4.22 (s, 6H), 4.16 (s, 3H), 4.07 (s, 6H), 3.97 (d, *J* = 17.8 Hz, 4H), 3.92 – 3.71 (m, 8H), 3.57 (s, 6H), 2.78 (d, *J* = 10.2 Hz, 3H), 2.64 (s, 3H), 2.48 (s, 3H), 2.43 – 2.34 (m, 4H), 2.34 – 2.16 (m, 8H), 2.07 (s, 8H), 1.94 (s, 6H), 1.43 (dd, *J* = 24.7, 6.9 Hz, 9H), 1.36 – 1.00 (m, 66H), 0.90 – 0.67 (m, 9H), 0.63 – 0.48 (m, 6H), 0.41 (d, *J* = 7.2 Hz, 6H), -0.05 (d, *J* = 6.2 Hz, 6H), -0.12 (d, *J* = 6.4 Hz, 6H). HRMS (ES+): m/z calcd for $C_{302}H_{305}N_{56}O_{54}$ $[M+3H]^{3+}$: 1860.7642 found 1860.7791.



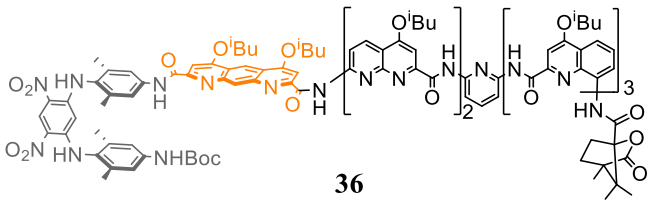
34

Heptamer 34. Amino oligomer **33**[7] (57 mg, 0.04 mmol) was dissolved in dry chloroform (2 mL) containing DIPEA (0.04 mL, 0.226 mmol), then commercially available 1*S*-(-)-camphanic chloride (43 mg, 0.2 mmol) was added as a solid to the solution. The reaction mixture was stirred at room temperature overnight and the solvents were removed under reduced pressure. The residue was purified by recycling GPC to obtain **34** as a pale-yellow solid (60 mg, 94%). ^{1}H NMR (300 MHz, $CDCl_3$, 298 K, δ ppm): 12.31 (s, 1H), 12.18 (s, 1H), 10.98 (s, 1H), 10.13 (s, 1H), 9.90 (s, 1H), 9.83 (s, 1H), 9.78 (s, 1H), 9.45 (dd, *J* = 7.7, 1.3 Hz, 1H), 8.82 – 8.68 (m, 2H), 8.65 (s, 1H), 8.61 (dd, *J* = 7.7, 1.3 Hz, 1H), 8.58 (s, 2H), 8.16 (dd, *J* = 7.6, 1.1 Hz, 1H), 8.04 (dd, *J* = 8.4, 1.3 Hz, 1H), 7.98 (dd, *J* = 8.4, 1.3 Hz, 1H), 7.88 (dd, *J* = 7.7, 1.3 Hz, 1H), 7.82 (t, *J* = 7.8 Hz, 1H), 7.77 (d, *J* = 3.0 Hz, 2H), 7.75 – 7.65 (m, 2H), 7.29 (s, 1H), 7.23 (d, *J* = 2.9 Hz, 1H), 6.95 (s, 1H), 6.89 (dd, *J* = 8.4, 1.3 Hz, 1H), 6.58 (t, *J* = 8.0 Hz, 1H), 4.68 (dd, *J* = 9.0, 5.8 Hz, 1H), 4.33 – 4.01 (m, 7H), 3.96 (d, *J* = 6.4 Hz, 2H), 2.36 (m, 6H), 2.10 – 1.94 (m, 1H), 1.86 (q, *J* = 6.8 Hz, 2H), 1.77 (s, 10H), 1.35 – 1.12 (m, 22H), 0.79 (t, *J* = 7.6 Hz, 10H), 0.52 (d, *J* = 6.7 Hz, 3H), 0.44 (s, 3H). ^{13}C NMR (75 MHz, $CDCl_3$, 298 K, δ ppm): 176.3, 164.9, 164.6, 164.2, 164.1, 163.9, 163.8, 163.5, 163.2, 162.0, 161.8, 160.5, 156.7, 155.1, 154.5, 153.9, 153.6, 153.4, 152.3, 151.5, 151.1, 149.6, 148.7, 147.9, 140.0, 138.9, 138.5, 137.7, 134.9, 134.4, 134.3, 133.4, 132.7, 127.5, 126.5, 126.0, 122.9, 122.3, 122.2, 117.7, 117.0, 116.8, 116.7, 116.5, 116.2, 115.0, 114.9, 114.8, 114.2, 109.6, 108.7, 102.2, 99.5, 98.5, 98.4, 98.3, 91.8, 81.6, 77.6, 77.4, 77.2, 76.7, 75.9, 75.8, 75.5, 75.4, 75.3, 54.9, 54.2, 29.7, 28.9, 28.8, 28.4, 28.3, 28.3, 19.6, 19.5, 19.4, 19.4, 19.4, 18.8, 16.4, 16.4, 9.8. HRMS (ES+): m/z calcd for $C_{88}H_{96}N_{15}O_{15}$ $[M+H]^{+}$ 1602.7205 Found 1602.7341.



35

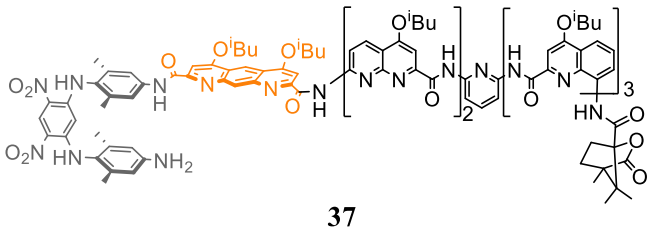
Heptamer amine 35. In a round-bottom flask, heptamer **34** (60 mg, 0.037 mmol) was dissolved in 2 mL chloroform and subsequently, 2 mL TFA was added dropwise. The mixture was allowed to stir for 3 hours at room temperature. A saturated aqueous solution of $NaHCO_3$ was added to quench the excess acid. Then, the solution was extracted with CH_2Cl_2, washed with water, dried over Na_2SO_4, and evaporated. Heptamer amine **35** was obtained without any further purification as a yellow solid (50 mg, 90% yield). ^{1}H NMR (300 MHz, $CDCl_3$, 298 K, δ ppm): 12.34 (s, 1H), 12.18 (s, 1H), 11.35 (s, 1H), 10.03 (s, 1H), 9.81 (s, 1H), 9.75 (s, 1H), 9.13 (d, *J* = 7.6 Hz, 1H), 8.74 (s, 2H), 8.59 (d, *J* = 7.5 Hz, 1H), 8.43 (s, 1H), 8.27 (d, *J* = 9.1 Hz, 1H), 8.20 (d, *J* = 7.0 Hz, 1H), 8.05 – 7.93 (m, 2H), 7.88 (t, *J* = 7.3 Hz, 1H), 7.80 (dd, *J* = 9.6, 7.8 Hz, 3H), 7.66 (t, *J* = 8.0 Hz, 1H), 7.54 (s, 1H), 7.28 (d, *J* = 3.1 Hz, 2H), 7.24 (d, *J* = 8.0 Hz, 2H), 6.99 (d, *J* = 8.4 Hz, 1H), 6.91 (s, 1H), 6.85 (d, *J* = 9.0 Hz, 1H), 6.67 (t, *J* = 8.0 Hz, 1H), 6.21 (s, 2H), 4.53 (s, 1H), 4.34 – 4.13 (m, 4H), 4.13 – 3.81 (m, 4H), 2.36 (dddd, *J* = 35.6, 29.1, 13.3, 6.7 Hz, 4H), 1.77 (dd, *J* = 14.0, 5.5 Hz, 2H), 1.39 – 1.01 (m, 24H), 0.76 (dd, *J* = 13.5, 8.5 Hz, 9H), 0.57 – 0.37 (m, 6H). ^{13}C NMR (75 MHz, $CDCl_3$, 298 K, δ ppm): 176.4, 164.8, 164.6, 164.0, 163.9, 163.7, 163.5, 163.1, 162.4, 161.8, 161.5, 160.6, 156.4, 154.7, 154.1, 153.6, 151.5, 151.1, 150.8, 149.7, 148.8, 147.8, 140.0, 138.8, 138.3, 137.7, 134.8, 134.3, 132.7, 132.4, 127.5, 126.5, 126.1, 122.7, 122.2, 117.3, 116.9, 116.8, 116.7, 116.5, 116.2, 114.8, 114.5, 113.5, 111.0, 110.0, 108.9, 101.5, 99.5, 98.6, 98.2, 96.6, 91.9, 91.6, 77.4, 75.9, 75.5, 75.4, 75.3, 75.2, 54.8, 54.2, 29.8, 29.3, 28.8, 28.4, 28.4, 28.2, 28.1, 19.6, 19.5, 19.5, 19.4, 19.3, 18.6, 16.4, 16.4, 9.8. HRMS (ESI): m/z calcd for $C_{83}H_{88}N_{15}O_{13}$ $[M+H]^+$ 1502.6681, Found 1502.6788.



36

Oligomer 36. Amino heptamer **35** (50 mg, 0.033 mmol), tetramer acid **28** (37 g, 0.04 mmol), and PyBOP (86 mg, 0.165 mmol) were placed in a 5 mL round bottom flask then dissolved in freshly distilled $CHCl_3$ (1 mL) and DIPEA (30 µL, 0.165 mmol) was added under nitrogen atmosphere. The reaction mixture was allowed to stir at room temperature for 36 hours. The solvent was removed under reduced pressure and the residue was dissolved in dichloromethane. The solution was then washed successively with 5% NH_4Cl, water and brine. Finally, the organic layer was dried over Na_2SO_4, filtered, and evaporated. The

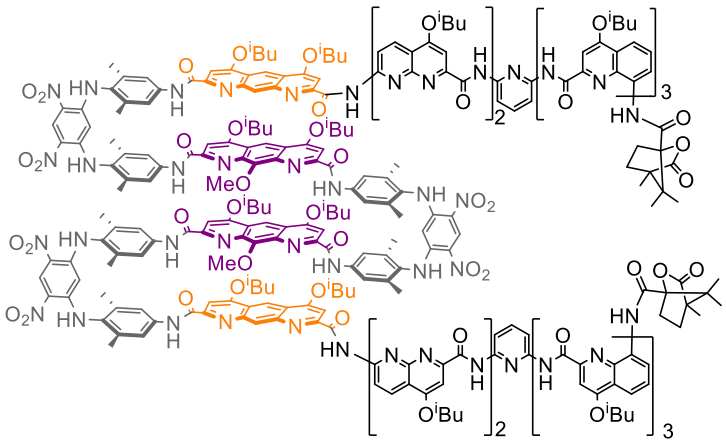
residue was purified by recycling GPC and product **36** was obtained as a yellow solid (60 mg, 75% yield). ^{1}H NMR (300 MHz, $CDCl_3$, 298 K, δ ppm): 11.94 (s, 2H), 11.85 (s, 1H), 11.76 (s, 1H), 9.79 (s, 1H), 9.75 (s, 1H), 9.61 (d, *J* = 5.2 Hz, 2H), 9.30 (s, 1H), 9.06 – 8.97 (m, 2H), 8.92 (s, 1H), 8.88 – 8.74 (m, 4H), 8.62 (s, 1H), 8.47 (dd, *J* = 7.6, 1.3 Hz, 1H), 8.22 (d, *J* = 7.5 Hz, 1H), 7.92 (d, *J* = 7.5 Hz, 1H), 7.83 (s, 2H), 7.81 – 7.72 (m, 3H), 7.68 (s, 1H), 7.56 (dd, *J* = 7.7, 1.3 Hz, 1H), 7.31 (d, *J* = 10.0 Hz, 2H), 7.24 – 7.15 (m, 2H), 7.08 – 6.97 (m, 2H), 6.86 (dd, *J* = 8.4, 1.3 Hz, 1H), 6.79 (s, 1H), 6.73 – 6.61 (m, 2H), 6.47 (t, *J* = 8.0 Hz, 1H), 6.42 (s, 1H), 6.30 (s, 1H), 6.24 (s, 1H), 4.75 (s, 1H), 4.41 – 4.12 (m, 8H), 4.01 (m, 2H), 3.88 (t, *J* = 8.0 Hz, 1H), 3.78 (t, *J* = 7.5 Hz, 1H), 3.67 (t, *J* = 8.0 Hz, 1H), 3.62 – 3.50 (m, 1H), 3.38 (t, *J* = 8.9 Hz, 1H), 2.57 – 2.23 (m, 6H), 1.96 (d, *J* = 14.4 Hz, 7H), 1.71 (s, 4H), 1.46 (s, 4H), 1.39 – 1.10 (m, 36H), 0.99 (s, 10H), 0.77 (d, *J* = 6.5 Hz, 3H), 0.60 (s, 6H), 0.52 (d, *J* = 6.7 Hz, 3H), 0.21 (s, 3H). ^{13}C NMR (75 MHz, $CDCl_3$, 298 K, δ ppm): 176.1, 164.7, 164.5, 164.1, 164.0, 163.9, 163.8, 163.4, 163.4, 163.2, 162.1, 161.8, 161.7, 160.9, 159.6, 154.8, 154.7, 154.6, 154.1, 153.8, 152.7, 152.1, 151.7, 151.3, 151.2, 149.1, 148.3, 148.1, 147.0, 145.6, 145.4, 138.8, 138.8, 137.7, 137.4, 137.1, 136.6, 136.4, 136.2, 135.9, 134.6, 134.5, 134.4, 134.2, 132.4, 129.7, 129.4, 129.2, 129.0, 126.1, 125.8, 124.9, 124.8, 122.7, 121.9, 121.4, 121.0, 120.5, 119.4, 119.1, 118.8, 116.8, 116.6, 116.3, 116.2, 115.8, 115.2, 115.1, 114.9, 114.4, 108.9, 108.7, 101.1, 99.3, 98.9, 98.1, 97.3, 96.1, 96.0, 93.9, 91.5, 79.9, 77.4, 76.1, 76.0, 75.5, 75.3, 74.9, 54.6, 54.0, 46.4, 46.4, 45.9, 29.8, 29.5, 29.0, 28.7, 28.5, 28.5, 28.3, 28.3, 28.0, 27.9, 27.0, 26.6, 26.5, 19.6, 19.5, 19.5, 19.4, 19.2, 18.6, 18.3, 18.1, 17.8, 17.1, 16.2, 16.2, 9.7. HRMS (ESI): m/z calcd for $C_{132}H_{141}N_{23}O_{23}$ $[M+2H]^{2+}$ 1208.5297, Found 1208.5390.



37

Oligomer 37. In a round-bottom flask, oligomer **36** (60 mg, 0.025 mmol) was dissolved in HCl in dioxane (4M, 2mL) and chloroform (0.5 mL). The mixture was allowed to stir for 4 hours at room temperature. The reaction was quenched with saturated solution of $NaHCO_3$, and the solution was extracted three times with CH_2Cl_2, washed with water, dried over Na_2SO_4, and evaporated. Compound **37** was obtained as yellow solid which was used without any further purification (57 mg, 98% yield). ^{1}H NMR (300 MHz, $CDCl_3$, 298 K, δ ppm): 11.96 (s, 1H), 11.93 (s, 1H), 11.82 (s, 2H), 9.85 (s, 1H), 9.73 (s, 1H), 9.70 (s, 1H), 9.60 (s, 1H), 9.23 (s, 1H), 8.99 – 8.88 (m, 2H), 8.88 – 8.71 (m, 5H), 8.61 (s, 1H), 8.48 (d, *J* = 7.5 Hz, 1H), 8.30 (d, *J* = 7.5 Hz, 1H), 7.96 – 7.85 (m, 2H), 7.84 – 7.77 (m, 3H), 7.75 (d, *J* = 5.3 Hz, 2H), 7.66 (s, 1H), 7.56 (d, *J* = 7.6 Hz, 1H), 7.38 (s, 1H), 7.36 – 7.28 (m, 3H), 7.21 (d, *J* = 8.2 Hz, 1H), 7.04 (t, *J* = 8.0 Hz, 1H), 6.99 (s, 1H), 6.84 (d, *J* = 8.3 Hz, 1H), 6.71 (t, *J* = 8.0 Hz, 1H), 6.47 (t, *J* = 8.0 Hz, 1H), 6.25 (s, 1H), 6.08 (s, 1H), 5.95 (s, 1H), 5.90 (s, 1H), 4.52 (s, 1H), 4.26 (m, 8H), 4.01 (m, 2H), 3.86 (t, *J* = 8.0 Hz, 1H), 3.73 (d, *J* = 6.8 Hz, 1H), 3.67 (d, *J* = 7.7 Hz, 1H), 3.51 (t, *J* = 7.4

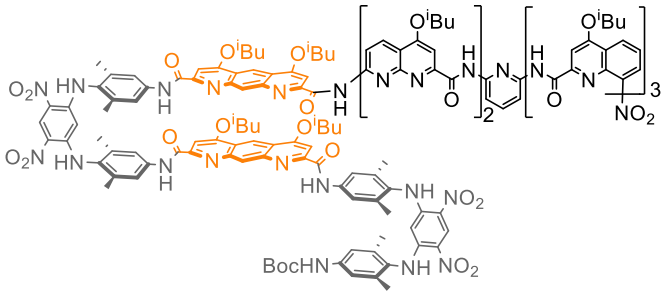
Hz, 1H), 3.37 (t, *J* = 9.0 Hz, 2H), 2.43 (m, 6H), 2.00 (s, 3H), 1.70 (s, 4H), 1.43 (s, 5H), 1.39 – 1.06 (m, 36H), 0.79 (d, *J* = 6.6 Hz, 4H), 0.58 (d, *J* = 12.6 Hz, 9H), 0.21 (s, 3H). ^{13}C NMR (75 MHz, $CDCl_3$, 298 K, δ ppm): 176.1, 164.8, 164.5, 164.1, 163.9, 163.8, 163.6, 163.3, 163.3, 162.0, 161.8, 160.9, 159.6, 154.8, 154.6, 154.0, 153.8, 152.6, 152.4, 151.9, 151.3, 151.3, 149.1, 148.8, 148.4, 148.0, 147.0, 146.2, 145.6, 145.4, 139.3, 138.8, 137.4, 137.1, 136.9, 136.8, 136.4, 136.2, 134.6, 134.4, 134.2, 132.4, 130.0, 129.3, 128.6, 126.2, 126.1, 125.8, 124.9, 124.8, 122.8, 121.9, 121.4, 120.9, 120.5, 118.6, 118.4, 116.8, 116.6, 116.4, 115.4, 115.2, 115.1, 115.0, 114.6, 114.6, 114.3, 109.1, 108.8, 101.1, 99.2, 98.8, 98.1, 97.2, 96.2, 96.1, 94.2, 91.5, 77.6, 77.4, 77.2, 76.7, 76.1, 76.0, 75.5, 75.4, 74.9, 54.6, 54.0, 29.8, 29.4, 28.9, 28.7, 28.5, 28.4, 28.4, 28.3, 27.9, 19.5, 19.5, 19.5, 19.4, 19.4, 19.4, 19.2, 18.7, 18.3, 17.7, 17.0, 16.2, 16.2, 9.7, 1.2. HRMS (ESI): m/z calcd for $C_{254}H_{264}N_{46}O_{42}$ $[2M+2H]^{2+}$ 2315.9996, Found 2316.0141.



11

Oligomer 11. Dicarboxylate **25** (6.43 mg, 5 µmol) was suspended in anhydrous $CHCl_3$ (1 mL), then oxalyl chloride (4.3 µL, 50 µmol) was added and the reaction was allowed to stir at room temperature for 2 hours. The solvent and excess oxalyl chloride were removed under reduced pressure and the residue was dried under high vacuum for 3 hours to yield the corresponding acid chloride **25a** as a yellow solid. The solution of amine **37** (37 mg, 17 µmol) and distilled DIPEA (7 µL, 40 µmol) in anhydrous $CHCl_3$ (1 mL) was added dropwise via a syringe to solution of the freshly prepared **25a** dissolved in anhydrous $CHCl_3$ (0.5 mL). The reaction was allowed to proceed at room temperature for 16 hours. After evaporation of the solvents, the crude product was purified by recycling GPC. Oligomer **11** was obtained as a yellow product (24 mg, 82% yield). ^{1}H NMR (700 MHz, $CDCl_3$, 238 K, δ ppm): 11.68 (s, 2H), 11.38 (s, 2H), 10.83 (s, 2H), 10.26 (s, 2H), 10.19 (s, 2H), 10.05 (s, 2H), 9.64 (s, 2H), 9.33 (m, 4H), 9.13 (s, 2H), 9.06 (d, *J* = 8.1 Hz, 2H), 8.96 (s, 2H), 8.90 – 8.74 (m, 3H), 8.66 (s, 2H), 8.48 (m, 4H), 8.33 (d, *J* = 6.7 Hz, 2H), 8.18 (d, *J* = 7.1 Hz, 2H), 8.10 (s, 2H), 7.86 (s, 2H), 7.76 (d, *J* = 7.5 Hz, 3H), 7.47 (d, *J* = 6.1 Hz, 5H), 7.21 – 7.05 (m, 7H), 7.00 (s, 2H), 6.95 – 6.78 (m, 7H), 6.71 (s, 2H), 6.51 (s, 2H), 6.45 – 6.18 (m, 5H), 6.18 – 5.98 (m, 4H), 5.93 (s, 2H), 4.88 (s, 4H), 4.44 (s, 2H), 4.24 (d, *J* = 6.1 Hz, 4H), 4.18 (m, 3H), 4.11 – 3.84 (m, 13H), 3.80 (t, *J* = 6.3 Hz, 2H), 3.69 – 3.56 (m, 4H), 3.49 (s, 2H), 3.06 (s, 2H),

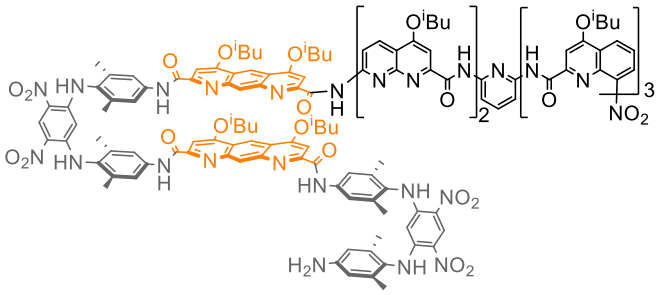
2.87 (s, 2H), 2.65 (m, 2H), 2.40 (m, 4H), 2.26 (m, 8H), 2.06 (s, 10H), 1.96 (s, 6H), 1.49 – 0.99 (m, 128H), 0.99 – 0.76 (m, 12H), 0.61 (s, 6H), 0.46 (d, *J* = 7.1 Hz, 6H), 0.39 (d, *J* = 17.1 Hz, 12H), 0.18 (s, 6H), 0.13 – 0.05 (m, 6H), 0.01 (s, 6H). ^{13}H NMR (75 MHz, $CDCl_3$, 238 K, δ ppm): 175.6, 164.3, 163.9, 163.9, 163.6, 163.5, 163.3, 163.2, 163.1, 163.1, 162.4, 162.3, 162.3, 162.1, 161.7, 161.7, 161.6, 160.5, 160.1, 159.9, 159.5, 154.7, 154.2, 153.9, 153.7, 153.5, 151.5, 151.4, 151.2, 150.6, 150.6, 150.3, 149.2, 148.6, 148.6, 148.3, 148.1, 147.4, 144.4, 143.7, 138.6, 138.5, 138.3, 138.2, 137.3, 137.2, 137.0, 136.9, 136.9, 136.9, 136.8, 136.6, 136.4, 136.1, 134.9, 134.2, 134.1, 133.6, 132.3, 130.7, 130.1, 129.4, 129.2, 129.1, 127.4, 126.4, 125.3, 125.1, 125.0, 124.7, 122.5, 122.0, 120.7, 120.6, 120.5, 120.3, 119.7, 119.5, 119.5, 119.4, 119.2, 118.2, 117.4, 117.4, 116.9, 116.4, 116.2, 115.9, 115.0, 114.4, 114.2, 109.2, 108.8, 108.4, 100.6, 99.0, 99.0, 98.3, 97.8, 95.8, 94.9, 94.4, 94.3, 91.2, 77.6, 77.4, 77.2, 76.7, 76.0, 75.3, 75.0, 74.1, 65.7, 54.3, 53.8, 29.8, 28.7, 28.5, 28.4, 28.4, 28.3, 28.3, 28.2, 27.6, 27.4, 19.7, 19.6, 19.5, 19.4, 19.4, 19.3, 19.2, 19.1, 18.4, 18.2, 17.9, 17.9, 17.7, 17.0, 16.7, 16.0, 16.0, 9.44, 1.2. HRMS (ES+): m/z calcd for $C_{322}H_{333}N_{56}O_{56}$ $[M+3H]^{3+}$: 1960.8338 found 1960.8502.



38

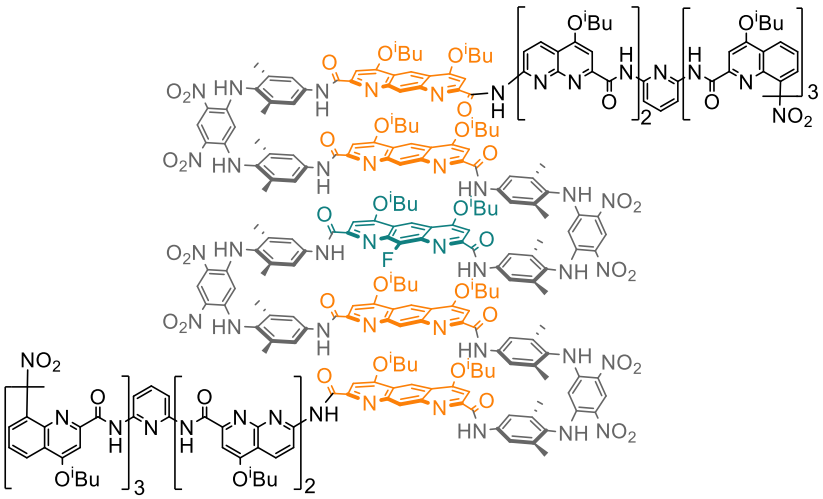
Oligomer 38. Amino oligomer **31** (61 mg, 0.028 mmol), tetramer acid **28** (31 mg, 0.034 mmol), and PyBOP (73 mg, 0.14 mmol) were placed in a 5 mL round bottom flask then dissolved in freshly distilled $CHCl_3$ (1 mL) and DIPEA (15 µL, 0.084 mmol) was added under nitrogen atmosphere. The reaction mixture was allowed to stir at room temperature for 16 hours. The solvent was removed under reduced pressure and the residue was dissolved in dichloromethane. The solution was then washed successively with 5% NH_4Cl, water and brine. Finally, the organic layer was dried over Na_2SO_4, filtered and evaporated. The residue was purified by recycling GPC and product **38** was obtained as a yellow solid (65 mg, 76% yield). ^{1}H NMR (300 MHz, $CDCl_3$, 298 K, δ ppm): 11.79 (s, 1H), 11.33 (s, 1H), 11.22 (s, 1H), 10.61 (s, 1H), 10.10 (s, 1H), 9.99 (s, 1H), 9.48 (s, 1H), 9.39 (s, 1H), 9.27 (d, *J* = 8.4 Hz, 2H), 9.06 (s, 1H), 8.99 (s, 1H), 8.84 (t, *J* = 10.8 Hz, 4H), 8.73 (s, 1H), 8.55 (s, 1H), 8.38 (d, *J* = 7.6 Hz, 1H), 8.32 (d, *J* = 8.1 Hz, 1H), 8.18 (s, 1H), 8.07 (s, 1H), 7.90 (d, *J* = 11.4 Hz, 3H), 7.80 (s, 1H), 7.58 (d, *J* = 12.9 Hz, 2H), 7.36 (d, *J* = 21.0 Hz, 3H), 7.22 – 7.07 (m, 2H), 7.02 (d, *J* = 8.2 Hz, 2H), 6.91 (s, 3H), 6.58 (d, *J* = 18.7 Hz, 2H), 6.41 (s, 3H), 6.26 (s, 1H), 6.06 (s, 1H), 4.77 (s, 1H), 4.41 (s, 1H), 4.39 – 3.73 (m, 14H), 3.56 (s, 3H), 2.98 (s, 1H), 2.66 (m, 1H), 2.60 – 2.11 (m, 9H), 2.11 – 1.88 (m, 12H), 1.81 (s, 6H),

1.48 – 1.01 (m, 58H), 0.90 (s, 9H), 0.63 (d, *J* = 6.4 Hz, 6H), 0.42 (s, 3H). HRMS (ESI): m/z calcd for $C_{166}H_{171}N_{31}O_{30}$ $[M+2H]^{2+}$ 1539.6415, Found 1539.6097.



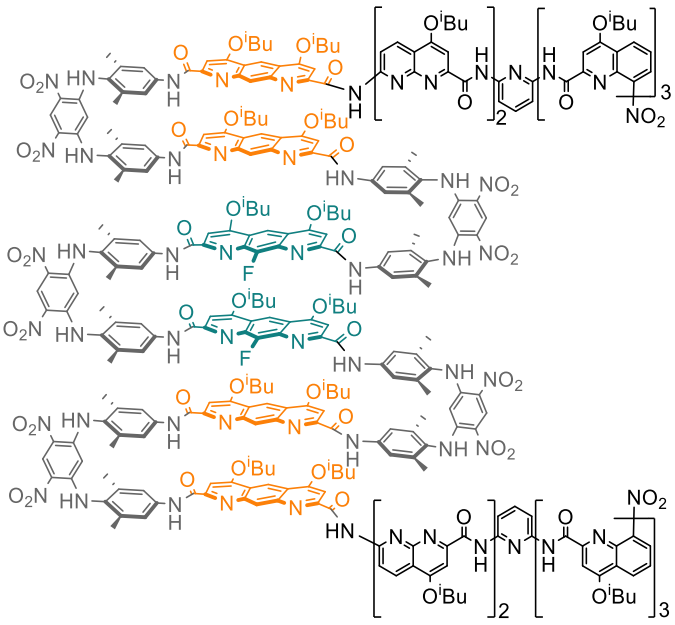
39

Oligomer 39. In a round-bottom flask, oligomer **38** (65 mg, 0.021 mmol) was dissolved in HCl in dioxane (4M, 2mL) and chloroform (0.8 mL). The mixture was allowed to stir for 5 hours at room temperature. The reaction was quenched with saturated solution of $NaHCO_3$, and the solution was extracted three times with CH_2Cl_2, washed with water, dried over Na_2SO_4, and evaporated. Compound **39** was obtained as yellow solid which was used without any further purification (60 mg, 96% yield). ^{1}H NMR (300 MHz, $CDCl_3$, 298 K, δ ppm): 11.78 (s, 1H), 11.33 (s, 2H), 10.63 (s, 1H), 10.08 (s, 1H), 9.96 (s, 2H), 9.48 (s, 1H), 9.40 (s, 1H), 9.33 (s, 1H), 9.28 (s, 1H), 9.09 (s, 1H), 8.97 (s, 1H), 8.93 – 8.66 (m, 7H), 8.52 (s, 1H), 8.38 (d, *J* = 7.6 Hz, 1H), 8.31 (dd, *J* = 7.8, 1.9 Hz, 1H), 8.18 (s, 1H), 8.00 (d, *J* = 19.2 Hz, 3H), 7.88 (s, 1H), 7.82 (s, 1H), 7.48 (d, *J* = 38.0 Hz, 5H), 7.28 (d, *J* = 3.2 Hz, 1H), 7.23 (s, 1H), 7.21 – 7.09 (m, 2H), 7.04 (s, 1H), 7.00 (d, *J* = 3.6 Hz, 2H), 6.91 (s, 2H), 6.68 – 6.16 (m, 6H), 5.98 (d, *J* = 12.7 Hz, 3H), 4.64 (s, 1H), 4.41 (d, *J* = 7.7 Hz, 2H), 4.38 – 3.72 (m, 12H), 3.69 – 3.44 (m, 3H), 3.27 (s, 2H), 2.60 – 2.14 (m, 9H), 2.00 (d, *J* = 23.9 Hz, 9H), 1.80 (d, *J* = 10.0 Hz, 6H), 1.70 (s, 3H), 1.58 (d, *J* = 19.0 Hz, 9H), 1.49 – 1.02 (m, 43H), 0.87 (d, *J* = 7.1 Hz, 2H), 0.64 (d, *J* = 6.4 Hz, 3H), 0.43 (s, 3H). ^{13}C NMR (75 MHz, $CDCl_3$, 298 K, δ ppm): 164.3, 164.1, 163.5, 163.3, 162.8, 162.3, 162.1, 161.6, 161.3, 160.9, 160.7, 160.0, 154.8, 154.4, 154.0, 153.9, 152.3, 151.9, 150.9, 149.2, 148.9, 148.3, 148.2, 148.1, 147.0, 146.0, 144.7, 144.5, 138.9, 138.8, 137.8, 137.4, 137.2, 136.6, 136.4, 134.7, 134.5, 134.4, 130.9, 129.5, 129.5, 129.1, 128.2, 126.3, 125.8, 124.9, 124.9, 124.0, 123.4, 122.6, 120.8, 120.5, 120.4, 120.3, 119.1, 118.9, 117.1, 115.5, 115.2, 115.1, 115.0, 114.7, 114.4, 114.2, 109.1, 99.5, 98.9, 97.8, 95.9, 95.7, 94.8, 93.9, 90.5, 77.4, 76.0, 75.5, 75.4, 75.2, 75.0, 71.4, 70.6, 68.9, 67.0, 59.6, 42.8, 29.8, 28.6, 28.6, 28.4, 28.4, 28.2, 28.2, 27.6, 19.5, 19.4, 19.4, 19.2, 18.4, 17.8, 17.7, 14.2. HRMS (ESI): m/z calcd for $C_{161}H_{163}N_{31}O_{28}$ $[M+2H]^{2+}$ 1489.6153, Found 1489.5822.



12

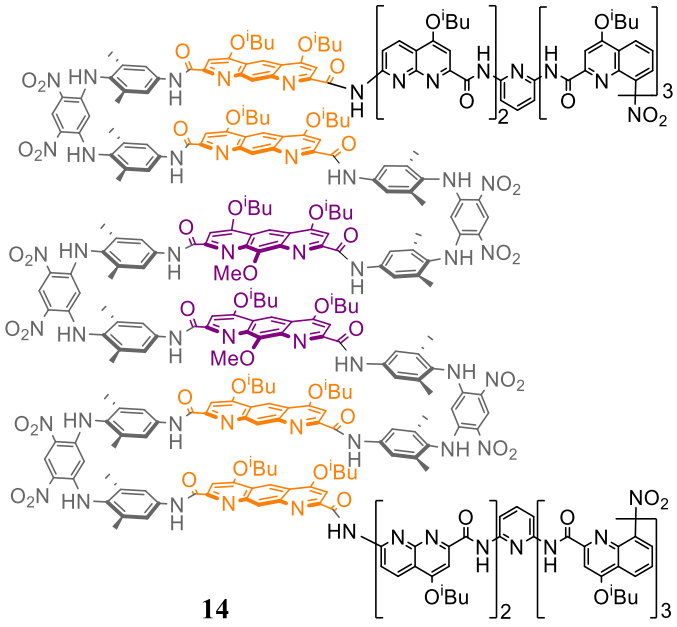
Oligomer 12. Dicarboxylic acid **40** (3 mg, 7 µmol) was suspended in anhydrous $CHCl_3$ (1 mL), then oxalyl chloride (6 µL, 68 µmol) was added and the reaction was allowed to stir at room temperature for 2 hours. The solvent and excess oxalyl chloride were removed under reduced pressure and the residue was dried under high vacuum for 3 hours to yield the corresponding acid chloride **40a** as a pale yellow solid. The solution of amine **39** (45 mg, 15 µmol) and distilled DIPEA (5 µL, 27 µmol) in anhydrous $CHCl_3$ (1 mL) was added dropwise via a syringe to solution of the freshly prepared **40a** dissolved in anhydrous $CHCl_3$ (0.5 mL). The reaction was allowed to proceed at room temperature for 16 hours. After evaporation of the solvents, the crude product was purified by recycling GPC. Oligomer **12** was obtained as a yellow product (20 mg, 46% yield). ^{1}H NMR (700 MHz, Acetone-d_6, 298 K, δ ppm): 11.45 (s, 2H), 11.14 (s, 2H), 10.87 (s, 1H), 10.11 (s, 1H), 9.69 (s, 1H), 9.39 (d, *J* = 6.5 Hz, 2H), 9.34 (s, 2H), 9.29 (s, 2H), 9.14 (d, *J* = 4.0 Hz, 2H), 9.02 (s, 1H), 8.91 (s, 1H), 8.86 (d, *J* = 8.1 Hz, 1H), 8.73 (d, *J* = 8.1 Hz, 1H), 8.59 (d, *J* = 7.9 Hz, 1H), 8.51 (d, *J* = 10.7 Hz, 3H), 8.43 (d, *J* = 7.9 Hz, 1H), 8.27 (s, 1H), 8.26 – 8.21 (m, 2H), 8.19 (d, *J* = 6.6 Hz, 1H), 7.83 (d, *J* = 8.0 Hz, 2H), 7.75 (d, *J* = 6.8 Hz, 1H), 7.67 (s, 2H), 7.40 (d, *J* = 5.5 Hz, 4H), 7.35 (s, 1H), 7.26 (t, *J* = 6.8 Hz, 1H), 7.23 (s, 2H), 7.14 (t, *J* = 6.9 Hz, 1H), 7.06 (s, 2H), 7.01 (d, *J* = 6.5 Hz, 1H), 6.93 (d, *J* = 6.8 Hz, 1H), 6.83 – 6.77 (m, 3H), 6.72 (s, 2H), 6.68 (s, 1H), 6.51 (h, *J* = 7.3 Hz, 5H), 6.42 (s, 1H), 6.16 (m, 3H), 5.95 (s, 2H), 5.69 (s, 3H), 5.62 (s, 1H), 5.34 (s, 2H), 4.47 (s, 1H), 4.42 (m, 5H), 4.36 (t, *J* = 5.9 Hz, 4H), 4.33 – 4.18 (m, 15H), 4.12 (t, *J* = 5.9 Hz, 2H), 4.05 (m, 3H), 3.95 (m, 5H), 3.83 – 3.71 (m, 2H), 3.64 (d, *J* = 5.7 Hz, 2H), 3.53 – 3.45 (m, 2H), 3.41 (m, *J* = 20.6, 5.1 Hz, 4H), 3.21 (s, 1H), 2.54 (m, 5H), 2.36 (m, 7H), 2.27 (m, 2H), 2.24 – 2.13 (m, 7H), 2.09 (d, *J* = 7.6 Hz, 5H), 1.78 (s, 4H), 1.73 (s, 4H), 1.62 (s, 7H), 1.52 (s, 5H), 1.49 – 1.04 (m, 161H), 0.87 (m, 8H), 0.64 (d, *J* = 7.3 Hz, 6H), 0.58 (d, *J* = 6.4 Hz, 5H). ^{19}F NMR (376 MHz, Acetone-d_6, 298 K, δ ppm): -131.8. HRMS (ESI): m/z calcd for $C_{344}H_{344}FN_{64}O_{60}$ $[M+3H]^{3+}$ 2117.8645, Found 2117.8780.



13

Oligomer 13. Dicarboxylic acid **24** (6.5 mg, 5.2 µmol) was suspended in anhydrous $CHCl_3$ (1 mL), then oxalyl chloride (5 µL, 52 µmol) was added and the reaction was allowed to stir at room temperature for 2 hours. The solvent and excess oxalyl chloride were removed under reduced pressure and the residue was dried under high vacuum for 3 hours to yield the corresponding acid chloride **24a** as a pale yellow solid. The solution of amine **39** (34 mg, 11.4 µmol) and distilled DIPEA (5 µL, 26 µmol) in anhydrous $CHCl_3$ (1 mL) was added dropwise via a syringe to solution of the freshly prepared **24a** dissolved in anhydrous $CHCl_3$ (0.5 mL). The reaction was allowed to proceed at room temperature for 16 hours. After evaporation of the solvents, the crude product was purified by recycling GPC. Oligomer **13** was obtained as a yellow solid (14 mg, 38% yield). ^{1}H NMR (700 MHz, Acetone-d_6, 248 K, δ ppm; only peaks are given due to the presence of two conformers): 11.60, 11.49, 11.47, 11.28, 11.18, 11.14, 11.07, 11.02, 10.93, 10.64, 10.32, 10.21, 10.09, 10.08, 9.84, 9.83, 9.72, 9.62, 9.61, 9.51, 9.48, 9.43, 9.33, 9.29, 9.27, 9.22, 9.20, 9.19, 9.18, 9.16, 9.15, 9.13, 9.07, 9.07, 9.03, 9.02, 8.96, 8.95, 8.94, 8.94, 8.93, 8.92, 8.76, 8.75, 8.74, 8.72, 8.71, 8.67, 8.62, 8.61, 8.60, 8.56, 8.54, 8.53, 8.50, 8.45, 8.43, 8.41, 8.39, 8.31, 8.30, 8.29, 8.25, 8.24, 8.24, 8.21, 8.20, 8.19, 8.18, 8.08, 8.03, 7.93, 7.92, 7.90, 7.89, 7.87, 7.86, 7.85, 7.80, 7.74, 7.74, 7.72, 7.71, 7.69, 7.68, 7.66, 7.63, 7.62, 7.53, 7.47, 7.42, 7.37, 7.36, 7.35, 7.34, 7.33, 7.32, 7.31, 7.28, 7.27, 7.26, 7.23, 7.23, 7.22, 7.20, 7.18, 7.15, 7.11, 7.10, 7.10, 7.08, 7.07, 7.06, 7.03, 7.02, 7.01, 7.01, 6.96, 6.95, 6.95, 6.94, 6.88, 6.87, 6.86, 6.83, 6.83, 6.82, 6.78, 6.70, 6.69, 6.66, 6.66, 6.64, 6.63, 6.62, 6.58, 6.56, 6.54, 6.53, 6.52, 6.48, 6.47, 6.46, 6.37, 6.31, 6.20, 6.19, 6.18, 6.18, 6.15, 6.14, 6.13, 6.12, 6.03, 5.97, 5.88, 5.75, 5.73, 5.71, 5.68, 5.64, 5.62, 5.58, 5.55, 5.53, 5.32, 5.23, 4.58, 4.50, 4.48, 4.47, 4.45, 4.42, 4.40, 4.37, 4.35, 4.31, 4.25, 4.20, 4.18, 4.10, 4.04, 4.03, 4.03, 4.02, 4.02, 4.01, 4.01, 3.98, 3.97, 3.96, 3.95, 3.93, 3.90, 3.82, 3.80, 3.68, 3.63, 3.60, 3.56, 3.47, 3.42, 3.36, 3.32, 3.32, 3.31, 3.30, 3.25, 3.24, 3.23, 3.23, 3.21, 3.20, 3.19, 3.17, 3.14, 3.13, 3.13, 3.12, 3.11, 3.11, 3.10,

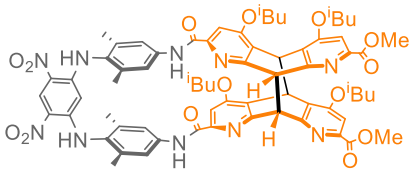
3.09, 3.08, 3.06, 3.02, 3.01, 2.83, 2.76, 2.75, 2.68, 2.61, 2.61, 2.60, 2.59, 2.53, 2.48, 2.47, 2.46, 2.45, 2.40, 2.39, 2.38, 2.38, 2.37, 2.36, 2.35, 2.34, 2.33, 2.29, 2.28, 2.27, 2.26, 2.25, 2.23, 2.22, 2.20, 2.17, 2.15, 2.14, 2.14, 2.14, 2.13, 2.13, 2.13, 2.08, 2.08, 2.07, 2.07, 2.06, 2.06, 2.05, 2.05, 2.05, 2.04, 2.03, 1.99, 1.99, 1.98, 1.97, 1.96, 1.96, 1.96, 1.96, 1.95, 1.93, 1.90, 1.89, 1.86, 1.80, 1.79, 1.78, 1.74, 1.70, 1.69, 1.66, 1.64, 1.63, 1.63, 1.61, 1.59, 1.58, 1.53, 1.51, 1.50, 1.49, 1.48, 1.47, 1.47, 1.46, 1.44, 1.43, 1.42, 1.40, 1.39, 1.38, 1.36, 1.35, 1.34, 1.33, 1.32, 1.31, 1.31, 1.30, 1.30, 1.29, 1.28, 1.25, 1.24, 1.23, 1.23, 1.22, 1.22, 1.21, 1.20, 1.20, 1.19, 1.19, 1.18, 1.18, 1.17, 1.17, 1.16, 1.15, 1.14, 1.12, 1.12, 1.12, 1.11, 1.11, 1.10, 1.10, 1.09, 1.08, 1.08, 1.06, 1.05, 1.04, 1.03, 1.03, 1.02, 1.02, 1.01, 1.00, 1.00, 0.99, 0.99, 0.98, 0.97, 0.95, 0.94, 0.93, 0.92, 0.88, 0.88, 0.87, 0.87, 0.86, 0.85, 0.84, 0.84, 0.83, 0.83, 0.82, 0.82, 0.81, 0.81, 0.80, 0.80, 0.79, 0.78, 0.70, 0.69, 0.68, 0.67, 0.66, 0.65, 0.63, 0.62, 0.58, 0.57, 0.16, 0.11, 0.09, 0.08, 0.07, 0.06, 0.05, 0.04, -0.01, -0.22, -0.23. ^{19}F NMR (376 MHz, Acetone-d_6, 248 K, δ ppm): -130.9, 131.2, -132.8. HRMS (ESI): m/z calcd for $C_{388}H_{384}F_2N_{72}O_{68}$ $[M+3H]^{3+}$ 2394.63746, Found 2394.65375.



14

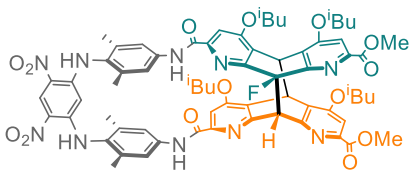
Oligomer 14. Dicarboxylic acid **25** (12.8 mg, 10 µmol) was suspended in anhydrous $CHCl_3$ (1 mL), then oxalyl chloride (20 µL, 200 µmol) was added and the reaction was allowed to stir at room temperature for 2 hours. The solvent and excess oxalyl chloride were removed under reduced pressure and the residue was dried under high vacuum for 3 hours to yield the corresponding acid chloride **25a** as a pale yellow solid. The solution of amine **39** (65.5 mg, 22 µmol) and distilled DIPEA (10 µL, 60 µmol) in anhydrous $CHCl_3$ (1 mL) was added dropwise via a syringe to solution of the freshly prepared **25a** dissolved in anhydrous $CHCl_3$ (0.5 mL). The reaction was allowed to proceed at room temperature for 16 hours. After evaporation of the solvents, the crude product was purified by recycling GPC. Oligomer **14** was obtained as a yellow product (38 mg, 54% yield). ^{1}H NMR (700 MHz, Acetone-d_6,

253 K, δ ppm; only peaks are given due to the presence of two conformers): 11.60, 11.50, 11.48, 11.28, 11.20, 11.14, 11.03, 10.92, 10.62, 10.33, 10.23, 10.19, 10.09, 9.99, 9.84, 9.64, 9.62, 9.59, 9.51, 9.47, 9.45, 9.38, 9.36, 9.32, 9.29, 9.27, 9.20, 9.18, 9.17, 9.12, 9.09, 9.05, 9.04, 9.01, 8.95, 8.92, 8.91, 8.88, 8.84, 8.72, 8.65, 8.54, 8.50, 8.45, 8.35, 8.30, 8.26, 8.25, 8.24, 8.21, 8.20, 8.19, 8.19, 8.17, 8.15, 8.04, 7.93, 7.87, 7.74, 7.71, 7.67, 7.64, 7.61, 7.56, 7.52, 7.49, 7.43, 7.41, 7.35, 7.31, 7.24, 7.22, 7.20, 7.15, 7.11, 7.07, 7.06, 7.03, 7.02, 6.94, 6.89, 6.84, 6.80, 6.77, 6.71, 6.66, 6.64, 6.61, 6.57, 6.45, 6.35, 6.24, 6.13, 6.10, 6.03, 6.01, 5.92, 5.89, 5.86, 5.71, 5.69, 5.65, 5.62, 5.57, 5.55, 5.41, 5.33, 4.59, 4.47, 4.40, 4.37, 4.35, 4.29, 4.26, 4.21, 4.16, 4.13, 4.09, 4.04, 4.03, 4.02, 4.01, 4.00, 3.96, 3.93, 3.90, 3.83, 3.70, 3.62, 3.55, 3.52, 3.44, 3.37, 3.18, 3.15, 2.93, 2.84, 2.78, 2.66, 2.60, 2.59, 2.54, 2.45, 2.40, 2.30, 2.23, 2.08, 2.07, 2.06, 2.05, 2.05, 2.05, 2.04, 2.02, 1.98, 1.96, 1.90, 1.89, 1.86, 1.82, 1.80, 1.71, 1.65, 1.64, 1.62, 1.60, 1.51, 1.50, 1.47, 1.47, 1.45, 1.43, 1.42, 1.41, 1.38, 1.36, 1.35, 1.34, 1.34, 1.33, 1.32, 1.30, 1.29, 1.27, 1.26, 1.25, 1.24, 1.21, 1.21, 1.20, 1.17, 1.17, 1.16, 1.15, 1.14, 1.13, 1.10, 1.09, 1.05, 1.05, 1.04, 1.01, 1.00, 1.00, 0.99, 0.96, 0.95, 0.94, 0.86, 0.85, 0.84, 0.83, 0.83, 0.82, 0.73, 0.71, 0.70, 0.69, 0.68, 0.66, 0.65, 0.61, 0.60, 0.57, 0.56, 0.14, 0.11, 0.07, 0.04, -0.29. HRMS (ESI): m/z calcd for $C_{390}H_{390}N_{72}O_{70}$ $[M+3H]^{3+}$ 2402.65079, Found 2402.65405.



1a

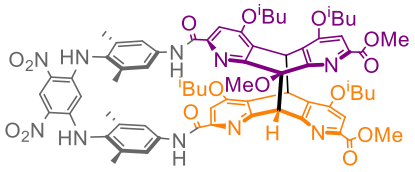
Photoproduct 1a. Compound **1** was irradiated in $CDCl_3$ as described above and the progress was followed by ^1H NMR spectroscopy. After 60 min photoirradiation, 99% of photoproduct formation was observed. ^1H NMR (300 MHz, $CDCl_3$, 298 K, δ ppm): 9.75 (s, 2H), 9.36 (s, 1H), 9.14 (s, 2H), 8.01 (s, 2H), 7.34 (s, 2H), 7.32 (s, 2H), 6.79 (s, 2H), 5.69 (s, 2H), 5.31 (s, 2H), 4.77 (s, 1H), 3.95 (s, 6H), 3.90 – 3.71 (m, 8H), 2.16 (m, 4H), 2.11 (s, 6H), 2.07 (s, 6H), 1.10 (m, 24H). ^{13}C NMR (75 MHz, $CDCl_3$, 298 K, δ ppm): 165.7, 163.5, 162.9, 161.9, 161.3, 148.9, 148.3, 147.3, 137.3, 137.0, 136.6, 130.0, 129.5, 128.1, 127.3, 124.8, 119.5, 118.9, 107.4, 103.9, 93.2, 93.2, 77.2, 75.1, 75.0, 56.1, 53.0, 33.2, 28.3, 28.3, 19.3, 19.0, 18.1, 17.8. HRMS (ESI): m/z calcd for $C_{68}H_{73}N_{10}O_{14}$ $[M+H]^+$ 1253.5302, found 1253.5358



2a

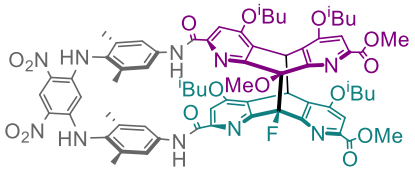
Photoproduct 2a. Compound **2** was irradiated in $CDCl_3$ as described above and the progress was followed by ^1H NMR spectroscopy. After 60 min photoirradiation, 99% of photoproduct formation was

observed. ^{1}H NMR (300 MHz, $CDCl_3$, 298 K, δ ppm): 9.93 (s, 1H), 9.75 (s, 1H), 9.14 (s, 1H), 8.00 (dd, *J* = 6.7, 2.4 Hz, 2H), 7.41 (s, 1H), 7.40 (s, 1H), 7.38 (s, 1H), 7.35 (s, 1H), 6.77 (t, *J* = 2.7 Hz, 2H), 5.81 – 5.67 (m, 2H), 5.39 (d, *J* = 28.7 Hz, 1H), 4.76 (s, 1H), 3.95 (s, 6H), 3.93 – 3.68 (m, 8H), 2.27 – 2.00 (m, 16H), 1.16 – 1.00 (m, 24H). ^{19}F NMR (282 MHz, $CDCl_3$, 298 K, δ ppm): -159.2 (d, *J* = 28.5 Hz). ^{19}F{^{1}H} NMR (282 MHz, $CDCl_3$, 298 K, δ ppm): -159.2. ^{13}C NMR (75 MHz, $CDCl_3$, 298 K, δ ppm): 165.8, 162.1, 161.5, 161.3, 160.5, 160.2, 159.9, 149.5, 149.3, 148.4, 148.4, 148.1, 147.9, 137.4, 137.1, 137.0, 136.8, 136.8, 130.3, 129.8, 127.8, 127.2, 124.9, 124.5, 119.7, 119.6, 119.3, 108.2, 107.7, 104.8, 104.4, 93.3, 75.5, 75.4, 75.3, 53.2, 53.1, 33.0, 32.8, 28.4, 19.4, 19.1, 18.2, 17.9. HRMS (ESI): m/z calcd for $C_{68}H_{72}FN_{10}O_{14}$ $[M+H]^+$ 1271.5208, Found 1271.5283.



3a

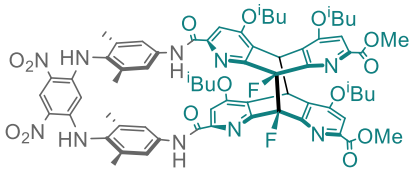
Photoproduct 3a. Compound **3** was irradiated in $CDCl_3$ as described above and the progress was followed by ^{1}H NMR spectroscopy. After 60 min photoirradiation, 99% of photoproduct formation was observed. ^{1}H NMR (300 MHz, $CDCl_3$, 298 K, δ ppm): 10.10 (s, 1H), 9.91 (s, 1H), 9.11 (s, 2H), 8.09 – 7.95 (m, 2H), 7.39 (s, 1H), 7.34 (s, 1H), 7.33 (s, 1H), 7.27 (s, 1H), 6.83 (d, *J* = 2.4 Hz, 1H), 6.77 (d, *J* = 2.4 Hz, 1H), 5.77 (d, *J* = 10.9 Hz, 1H), 5.64 (d, *J* = 10.9 Hz, 1H), 5.20 (s, 1H), 4.74 (s, 1H), 3.94 (s, 3H), 3.92 (s, 3H), 3.91 – 3.65 (m, 12H), 2.18 (m, 4H), 2.11 (d, *J* = 1.4 Hz, 6H), 2.07 (d, *J* = 4.6 Hz, 6H), 1.16 – 1.03 (m, 24H). ^{13}C NMR (75 MHz, $CDCl_3$, 298 K, δ ppm): 166.1, 166.0, 163.1, 162.6, 162.4, 161.9, 161.8, 161.7, 161.5, 161.4, 161.3, 149.2, 149.1, 148.5, 148.4, 147.8, 147.7, 137.4, 137.3, 137.3, 137.2, 136.7, 136.7, 130.3, 130.2, 129.6, 127.8, 127.2, 126.2, 126.1, 125.0, 124.9, 120.1, 119.9, 119.7, 119.6, 107.5, 107.3, 104.2, 104.1, 93.5, 88.9, 75.4, 75.2, 75.1, 67.3, 56.4, 53.1, 52.9, 33.4, 32.3, 28.4, 19.4, 19.4, 19.2, 19.1, 18.2, 17.9. HRMS (ESI): m/z calcd for $C_{69}H_{75}N_{10}O_{15}$ $[M+H]^+$ 1283.5408, Found 1283.5484.



4a

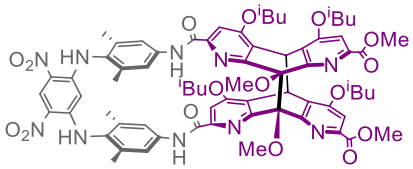
Photoproduct 4a. Compound **4** was irradiated in $CDCl_3$ as described above and the progress was followed by ^{1}H NMR spectroscopy. After 60 min photoirradiation, 99% of photoproduct formation was observed. ^{1}H NMR (300 MHz, $CDCl_3$, 298 K, δ ppm): 10.13 (s, 1H), 10.09 (s, 1H), 9.10 (s, 2H), 8.02 (d, *J* = 2.4 Hz, 1H), 7.97 (d, *J* = 2.4 Hz, 1H), 7.42 (s, 1H), 7.39 (s, 1H), 7.33 (d, *J* = 1.8 Hz, 2H), 6.88

(d, *J* = 2.4 Hz, 1H), 6.81 (d, *J* = 2.4 Hz, 1H), 5.82 (d, *J* = 10.9 Hz, 1H), 5.74 (d, *J* = 10.8 Hz, 1H), 4.73 (s, 1H), 3.93 (s, 3H), 3.91 (s, 3H), 3.90 – 3.69 (m, 12H), 2.27 – 2.12 (m, 4H), 2.10 (d, *J* = 2.4 Hz, 6H), 2.06 (d, *J* = 4.1 Hz, 6H), 1.16 – 1.04 (m, 24H). ^{19}F NMR (282 MHz, $CDCl_3$, 298 K, δ ppm): -175.4. ^{13}C NMR (75 MHz, $CDCl_3$, 298 K, δ ppm): 166.1, 165.9, 162.3, 161.6, 161.5, 161.4, 160.6, 160.4, 149.6, 149.5, 148.5, 148.4, 148.2, 148.1, 137.2, 137.2, 137.1, 136.7, 136.6, 130.4, 130.2, 129.6, 126.4, 125.0, 124.9, 124.3, 120.4, 120.0, 119.9, 108.0, 107.6, 104.6, 93.5, 75.5, 75.4, 56.7, 53.0, 52.9, 33.6, 32.2, 28.4, 19.4, 19.4, 19.1, 18.2, 17.9. HRMS (ESI): m/z calcd for $C_{69}H_{74}FN_{10}O_{15}$ $[M+H]^+$ 1301.5314, Found 1301.5402.



5a

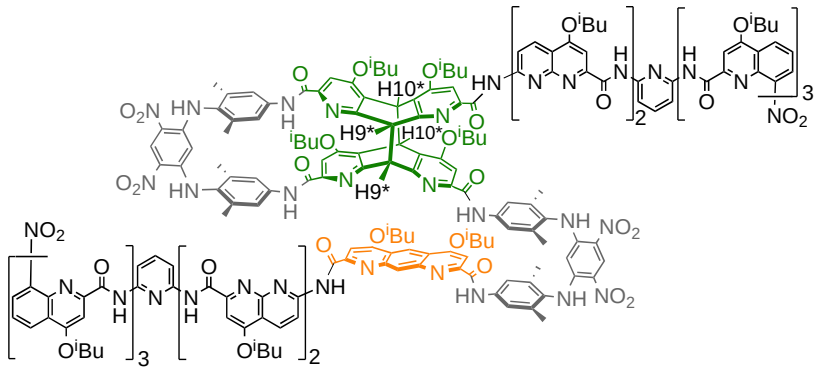
Photoproduct 5a. Compound **5** was irradiated in $CDCl_3$ as described above and the progress was followed by ^{1}H NMR spectroscopy. After 60 min photoirradiation, 99% of photoproduct formation was observed. ^{1}H NMR (300 MHz, $CDCl_3$, 298 K, δ ppm): 9.94 (s, 2H), 9.36 (s, 1H), 9.14 (s, 2H), 7.99 (d, *J* = 2.4 Hz, 2H), 7.44 (s, 2H), 7.41 (s, 2H), 6.81 (d, *J* = 2.4 Hz, 2H), 5.81 (s, 2H), 4.76 (s, 1H), 3.95 (s, 6H), 3.93 – 3.71 (m, 8H), 2.18 (m, 4H), 2.12 (s, 6H), 2.07 (s, 6H), 1.15 – 1.03 (m, 24H). ^{19}F NMR (282 MHz, $CDCl_3$, 298 K, δ ppm): -178.0. ^{13}C NMR (75 MHz, $CDCl_3$, 298 K, δ ppm): 165.7, 161.9, 161.3, 161.1, 149.7, 148.4, 137.3, 136.9, 136.8, 130.3, 129.7, 124.9, 124.7, 119.7, 108.4, 105.1, 93.3, 75.6, 75.5, 53.2, 32.9, 28.4, 19.4, 19.1, 18.2, 17.9. HRMS (ESI): m/z calcd for $C_{68}H_{71}F_2N_{10}O_{14}$ $[M+H]^+$ 1289.5114, found 1289.5207.



6a

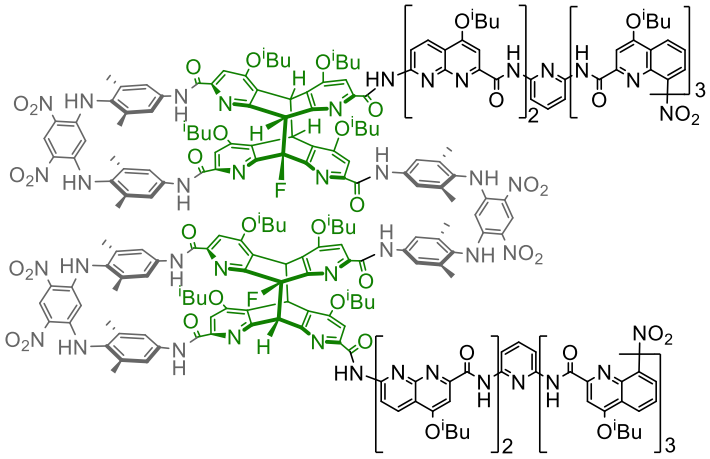
Photoproduct 6a. Compound **7** was irradiated in $CDCl_3$ as described above and the progress was followed by ^{1}H NMR spectroscopy. After 60 min photoirradiation, 99% of photoproduct formation was observed. ^{1}H NMR (300 MHz, $CDCl_3$, 298 K, δ ppm): 10.38 (s, 2H), 9.34 (s, 1H), 9.06 (s, 2H), 8.02 (d, *J* = 2.4 Hz, 2H), 7.37 (s, 2H), 7.23 (s, 2H), 6.91 (d, *J* = 2.4 Hz, 2H), 5.74 (s, 2H), 4.71 (s, 1H), 3.90 (s, 6H), 3.88 – 3.67 (m, 8H), 3.59 (s, 6H), 2.22 – 2.13 (m, 4H), 2.10 (s, 6H), 2.06 (s, 6H), 1.17 – 1.03 (m, 24H). ^{13}C NMR (75 MHz, $CDCl_3$, 298 K, δ ppm): 166.4, 162.2, 162.1, 161.6, 161.5, 161.2, 149.3, 148.4, 147.8, 137.5, 137.1, 136.5, 130.3, 129.5, 126.3, 124.9, 120.5, 107.1, 104.2, 93.8, 89.5, 75.4, 75.2, 56.6,

52.8, 33.0, 28.5, 28.4, 19.4, 19.4, 19.1, 18.2, 18.0. HRMS (ESI): m/z calcd for $C_{70}H_{77}N_{10}O_{16}$ $[M+H]^+$ 1313.5514, Found 1313.5618.



8a

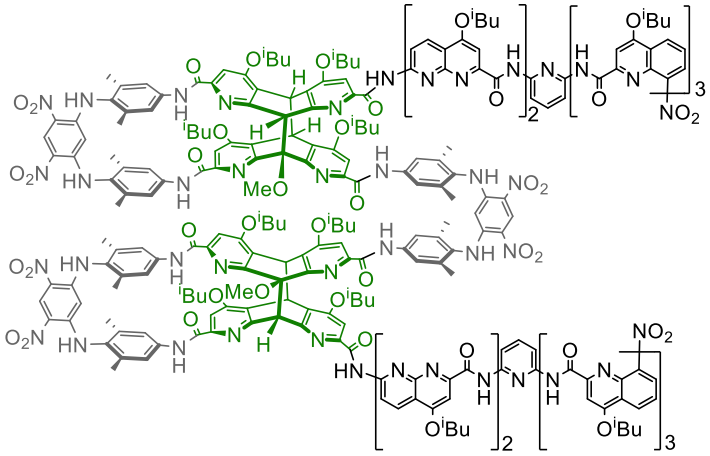
Photoproduct 8a. Compound **8** was irradiated in $CDCl_3$ as described above and the progress was followed by ^1H NMR spectroscopy. After 90 min photoirradiation, photoproduct **8a** was obtained. ^1H NMR (700 MHz, $CDCl_3$, 298 K, δ ppm): 11.81, 11.71, 11.69, 11.60, 11.58, 11.54, 11.45, 11.28, 11.21, 11.01, 10.99, 10.97, 10.90, 10.80, 10.26, 9.98, 9.89, 9.86, 9.53, 9.44, 9.37, 9.20, 9.15, 9.07, 9.05, 9.02, 8.94, 8.93, 8.90, 8.86, 8.85, 8.83, 8.81, 8.80, 8.75, 8.74, 8.73, 8.67, 8.66, 8.57, 8.48, 8.42, 8.36, 8.33, 8.32, 8.31, 8.28, 8.27, 8.26, 8.22, 8.21, 8.19, 8.15, 8.14, 8.12, 8.08, 8.05, 8.04, 7.94, 7.86, 7.83, 7.81, 7.75, 7.74, 7.73, 7.66, 7.59, 7.57, 7.51, 7.47, 7.46, 7.45, 7.41, 7.40, 7.28, 7.26, 7.22, 7.20, 7.19, 7.18, 7.15, 7.14, 7.12, 7.10, 7.08, 7.04, 7.02, 7.01, 7.00, 6.99, 6.97, 6.97, 6.96, 6.96, 6.93, 6.93, 6.89, 6.88, 6.87, 6.85, 6.84, 6.79, 6.78, 6.70, 6.57, 6.52, 6.39, 6.27, 6.24, 6.23, 6.22, 6.19, 6.18, 6.17, 6.13, 6.05, 6.00, 5.88, 5.80, 5.71, 5.64, 5.35, 5.19, 5.18, 5.06, 5.04, 4.68, 4.32, 4.31, 4.28, 4.27, 4.22, 4.21, 4.20, 4.19, 4.19, 4.18, 4.17, 4.16, 4.15, 4.13, 4.12, 4.11, 4.11, 4.10, 4.09, 4.08, 3.96, 3.95, 3.91, 3.90, 3.89, 3.88, 3.87, 3.85, 3.83, 3.82, 3.80, 3.75, 3.75, 3.74, 3.74, 3.73, 3.66, 3.65, 3.64, 3.63, 3.61, 3.54, 3.53, 3.48, 3.45, 3.27, 3.24, 3.03, 3.01, 3.00, 2.82, 2.74, 2.46, 2.45, 2.44, 2.43, 2.42, 2.41, 2.40, 2.39, 2.39, 2.35, 2.34, 2.33, 2.32, 2.31, 2.27, 2.26, 2.25, 2.24, 2.23, 2.22, 2.21, 2.13, 2.12, 2.12, 2.01, 2.00, 1.97, 1.96, 1.91, 1.86, 1.86, 1.85, 1.85, 1.84, 1.82, 1.82, 1.80, 1.75, 1.60, 1.45, 1.44, 1.43, 1.41, 1.40, 1.39, 1.35, 1.34, 1.34, 1.33, 1.33, 1.32, 1.31, 1.30, 1.29, 1.26, 1.25, 1.24, 1.24, 1.23, 1.22, 1.22, 1.21, 1.21, 1.21, 1.20, 1.19, 1.17, 1.17, 1.16, 1.15, 1.14, 1.14, 1.13, 1.11, 1.11, 1.10, 1.10, 0.99, 0.89, 0.89, 0.88, 0.88, 0.87, 0.87, 0.86, 0.85, 0.84, 0.78, 0.77, 0.69, 0.57, 0.54, 0.53, 0.53, 0.52, 0.48, 0.47, 0.42, 0.34, 0.33, 0.29, 0.28, 0.25, 0.24, 0.07. HRMS (ES+): m/z calcd for $C_{256}H_{257}N_{48}O_{44}$ $[M+3H]^{3+}$ 1569.6466 Found 1569.6514.



9a

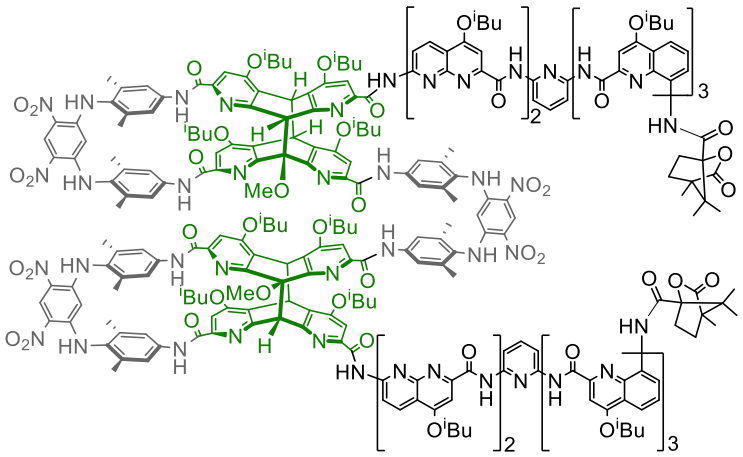
Photoproduct 9a. Compound **9** was irradiated in acetone-d_6 as described above and the progress was followed by ^{1}H NMR spectroscopy. After 5 hours of photoirradiation, 98% of photoproduct formation was observed. ^{1}H NMR (700 MHz, Acetone-d_6, 298 K, δ ppm; only peaks are given due to the presence of two conformers): 11.76, 11.67, 11.61, 11.54, 11.49, 11.48, 11.26, 11.02, 10.97, 10.85, 10.73, 10.62, 10.51, 10.11, 9.95, 9.90, 9.86, 9.84, 9.82, 9.77, 9.75, 9.70, 9.54, 9.51, 9.50, 9.47, 9.41, 9.31, 9.26, 9.25, 9.23, 9.23, 9.21, 9.18, 9.12, 9.08, 9.06, 9.05, 9.00, 8.98, 8.94, 8.92, 8.90, 8.89, 8.87, 8.86, 8.85, 8.84, 8.84, 8.82, 8.80, 8.77, 8.76, 8.67, 8.66, 8.65, 8.60, 8.58, 8.55, 8.46, 8.46, 8.45, 8.44, 8.44, 8.42, 8.41, 8.40, 8.39, 8.38, 8.37, 8.34, 8.32, 8.31, 8.29, 8.27, 8.26, 8.25, 8.23, 8.20, 8.18, 8.17, 8.13, 8.11, 7.92, 7.90, 7.87, 7.83, 7.82, 7.80, 7.78, 7.77, 7.76, 7.74, 7.71, 7.70, 7.69, 7.67, 7.64, 7.60, 7.56, 7.54, 7.52, 7.49, 7.48, 7.47, 7.44, 7.43, 7.42, 7.41, 7.38, 7.32, 7.31, 7.29, 7.27, 7.26, 7.25, 7.25, 7.23, 7.20, 7.19, 7.13, 7.10, 7.05, 7.04, 7.02, 7.00, 6.99, 6.97, 6.96, 6.95, 6.91, 6.90, 6.88, 6.87, 6.86, 6.82, 6.79, 6.76, 6.75, 6.72, 6.65, 6.62, 6.59, 6.56, 6.53, 6.51, 6.49, 6.44, 6.43, 6.42, 6.38, 6.37, 6.36, 6.33, 6.30, 6.25, 6.24, 6.23, 6.21, 6.16, 6.12, 6.10, 6.06, 6.01, 5.98, 5.76, 5.67, 5.62, 5.51, 5.49, 5.45, 5.45, 5.43, 5.42, 5.40, 5.39, 5.37, 5.35, 5.35, 5.34, 5.28, 5.27, 5.07, 4.85, 4.79, 4.75, 4.69, 4.68, 4.68, 4.67, 4.66, 4.59, 4.58, 4.55, 4.52, 4.50, 4.40, 4.39, 4.38, 4.37, 4.36, 4.35, 4.34, 4.33, 4.32, 4.31, 4.28, 4.27, 4.27, 4.26, 4.25, 4.23, 4.22, 4.21, 4.20, 4.19, 4.16, 4.15, 4.14, 4.13, 4.12, 4.11, 4.10, 4.09, 4.07, 4.06, 4.05, 4.04, 4.04, 4.03, 4.02, 4.01, 3.99, 3.98, 3.97, 3.96, 3.96, 3.92, 3.91, 3.90, 3.88, 3.87, 3.86, 3.83, 3.82, 3.81, 3.76, 3.75, 3.73, 3.72, 3.71, 3.65, 3.64, 3.61, 3.58, 3.44, 3.38, 3.30, 3.28, 3.27, 3.25, 3.24, 3.24, 3.23, 3.23, 3.22, 3.22, 3.16, 3.15, 3.14, 3.11, 2.97, 2.92, 2.91, 2.90, 2.81, 2.43, 2.42, 2.41, 2.40, 2.39, 2.38, 2.37, 2.36, 2.35, 2.34, 2.33, 2.32, 2.31, 2.30, 2.29, 2.29, 2.28, 2.26, 2.25, 2.24, 2.22, 2.17, 2.16, 2.15, 2.14, 2.14, 2.14, 2.13, 2.13, 2.12, 2.11, 2.10, 2.08, 2.07, 2.07, 2.06, 2.06, 2.05, 2.05, 2.05, 2.04, 2.02, 1.99, 1.99, 1.98, 1.97, 1.96, 1.96, 1.96, 1.95, 1.95, 1.93, 1.88, 1.86, 1.84, 1.82, 1.78, 1.74, 1.70, 1.67, 1.64, 1.63, 1.62, 1.61, 1.60, 1.59, 1.57, 1.56, 1.54, 1.48, 1.47, 1.45, 1.44, 1.42, 1.41, 1.40, 1.38, 1.37, 1.37, 1.36, 1.36, 1.35, 1.35, 1.34, 1.32, 1.31, 1.30, 1.30, 1.29, 1.27, 1.26, 1.25, 1.25, 1.24, 1.24, 1.23, 1.22, 1.21, 1.21, 1.20, 1.19, 1.17, 1.16, 1.15, 1.14, 1.13, 1.13, 1.12, 1.10, 1.03, 1.02, 1.00, 0.97, 0.96,

0.95, 0.93, 0.92, 0.91, 0.90, 0.89, 0.88, 0.87, 0.86, 0.85, 0.85, 0.83, 0.82, 0.77, 0.76, 0.69, 0.68, 0.67, 0.63, 0.60, 0.59, 0.58, 0.56, 0.56, 0.47, 0.46, 0.45, 0.44, 0.21, 0.17, 0.15, 0.13, 0.12, 0.10, 0.09, 0.09, 0.08, 0.07, 0.04. HRMS (ES+): m/z calcd for $C_{300}H_{299}F_2N_{56}O_{52}$ $[M+3H]^{3+}$: 1852.7509 found 1852.7573.



10a

Photoproduct 10a. Compound **10** was irradiated in $CDCl_3$ as described above and the progress was followed by ^1H NMR spectroscopy. After 60 min of photoirradiation, 99% of photoproduct formation was observed. ^1H NMR (700 MHz, $CDCl_3$, 298 K, δ ppm; only peaks are given due to the presence of two conformers): 11.82, 11.75, 11.60, 11.53, 11.00, 10.87, 10.83, 10.72, 9.83, 9.81, 9.75, 9.37, 9.35, 9.31, 9.24, 9.14, 8.94, 8.91, 8.86, 8.79, 8.78, 8.74, 8.73, 8.63, 8.58, 8.50, 8.45, 8.44, 8.40, 8.39, 8.39, 8.38, 8.36, 8.35, 8.33, 8.32, 8.25, 8.17, 8.08, 8.00, 7.96, 7.85, 7.79, 7.77, 7.70, 7.64, 7.63, 7.61, 7.61, 7.59, 7.50, 7.48, 7.45, 7.41, 7.31, 7.30, 7.26, 7.24, 7.23, 7.22, 7.21, 7.20, 7.19, 7.18, 7.15, 7.14, 7.11, 7.09, 7.06, 7.03, 6.99, 6.98, 6.95, 6.94, 6.91, 6.84, 6.79, 6.77, 6.74, 6.70, 6.55, 6.43, 6.33, 6.32, 6.31, 6.27, 6.22, 6.17, 5.97, 5.92, 5.37, 5.36, 5.32, 5.30, 5.23, 4.70, 4.60, 4.51, 4.42, 4.26, 4.25, 4.24, 4.21, 4.20, 4.19, 4.18, 4.17, 4.13, 4.11, 4.10, 4.09, 4.03, 4.02, 4.01, 3.99, 3.98, 3.97, 3.94, 3.93, 3.92, 3.89, 3.88, 3.81, 3.75, 3.73, 3.72, 3.71, 3.70, 3.69, 3.68, 3.65, 3.57, 3.56, 3.55, 3.50, 3.49, 3.48, 3.39, 3.31, 3.30, 3.29, 3.05, 2.99, 2.65, 2.55, 2.41, 2.40, 2.39, 2.38, 2.37, 2.37, 2.36, 2.35, 2.34, 2.33, 2.32, 2.31, 2.30, 2.29, 2.24, 2.23, 2.22, 2.21, 2.20, 2.19, 2.18, 2.17, 2.13, 2.12, 2.11, 2.10, 2.03, 2.02, 2.01, 2.00, 1.99, 1.95, 1.92, 1.88, 1.85, 1.82, 1.80, 1.61, 1.56, 1.53, 1.40, 1.33, 1.31, 1.30, 1.29, 1.28, 1.26, 1.25, 1.24, 1.23, 1.22, 1.20, 1.19, 1.19, 1.18, 1.18, 1.17, 1.16, 1.15, 1.15, 1.15, 1.14, 1.12, 1.11, 1.10, 1.09, 1.08, 1.05, 1.02, 1.01, 0.97, 0.95, 0.94, 0.93, 0.92, 0.89, 0.88, 0.87, 0.85, 0.84, 0.84, 0.76, 0.75, 0.74, 0.73, 0.59, 0.58, 0.56, 0.42, 0.15, 0.09, 0.07, 0.04, -0.02. HRMS (ES+): m/z calcd for $C_{302}H_{302}N_{56}O_{54}$ $[M+3H]^{3+}$: 1860.7642 found 1860.7721.



11a

Photoproduct 11a. Compound **11** was irradiated in $CDCl_3$ as described above and the progress was followed by ^1H NMR spectroscopy. After 40 min of photoirradiation, a quantitative photoproduct formation was observed. ^1H NMR (700 MHz, $CDCl_3$, 298 K, δ ppm): 11.89, 11.82, 11.13, 10.88, 9.86, 9.77, 9.65, 9.60, 9.39, 9.37, 8.93, 8.78, 8.75, 8.46, 8.38, 8.24, 7.97, 7.88 - 7.76, 7.70, 7.68, 7.58, 7.49, 7.36, 7.31, 7.11 - 7.01, 6.95, 6.89, 6.74, 6.62, 6.42, 6.39, 6.29, 6.15, 5.32, 5.26, 4.54, 4.43, 4.24, 4.18, 4.09, 4.03, 3.89, 3.70, 3.66, 3.61, 3.53, 3.47, 3.27, 3.06, 2.78, 2.36, 2.19, 2.05 - 1.94, 1.92, 1.80, 1.50, 1.45, 1.40, 1.37 - 1.12, 1.09, 0.92, 0.89 - 0.78, 0.72, 0.63 - 0.55, 0.53, 0.41, 0.15, 0.07. HRMS (ES+): m/z calcd for $C_{322}H_{333}N_{56}O_{56}$ $[M+3H]^{3+}$: 1960.8338 found 1960.8473.

3. Photoirradiation of aromatic sheets and thermal reversibility

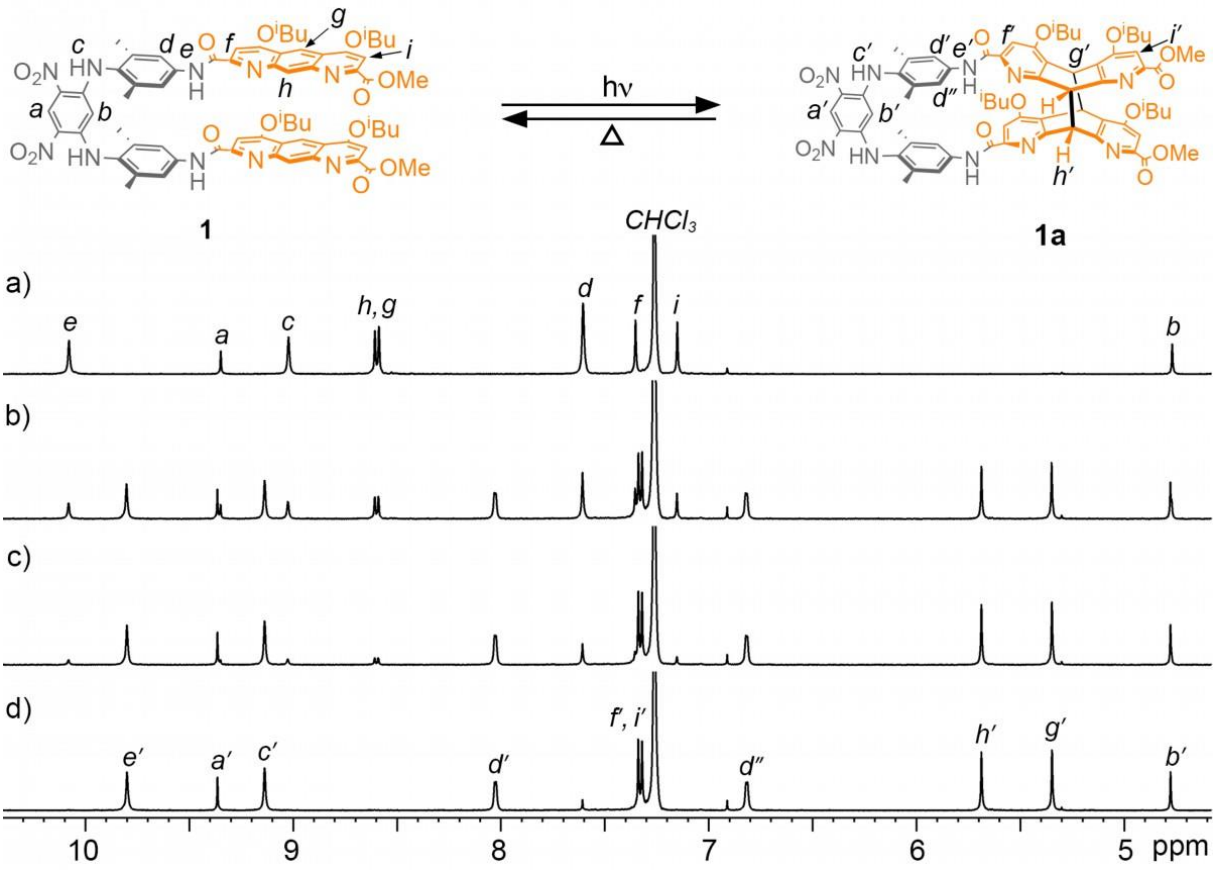


Figure S1. Excerpts from the ^{1}H NMR spectra (300 MHz, 298K) in $CDCl_3$ showing the photoproduct formation of **1** (5 mM): (a) before irradiation and after (b): 5 min; (c) 10 min; (d) 20 min of irradiation with assignment of proton resonances.

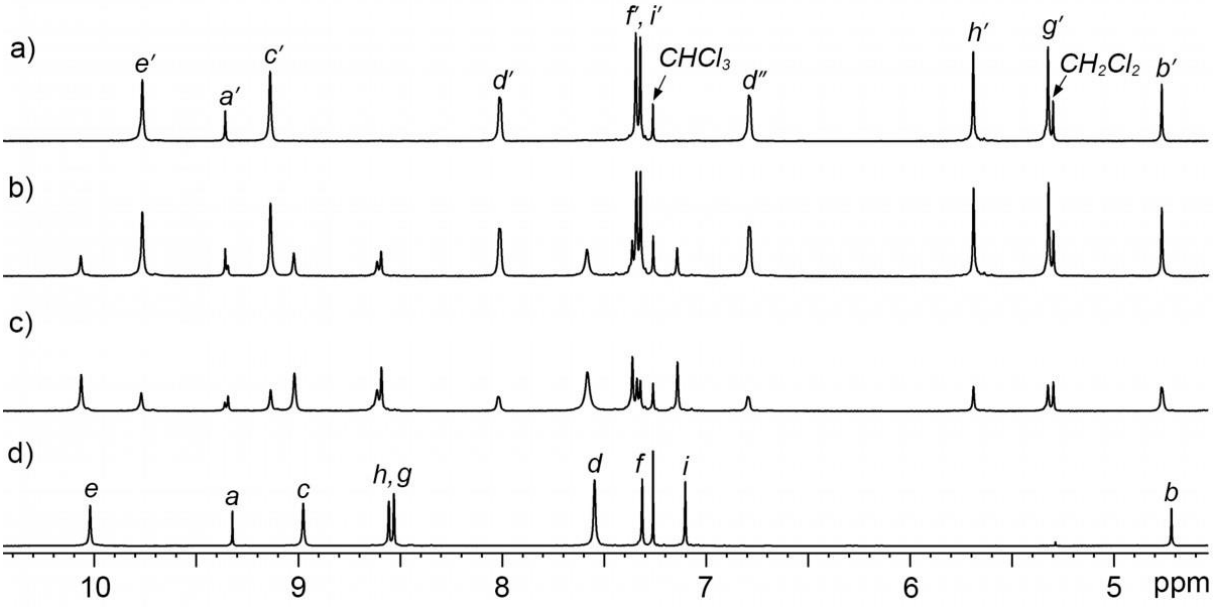


Figure S2. Excerpts from the ^{1}H NMR spectra (300 MHz, 298K) of **1a** (5 mM) in (a) $CDCl_3$ and after heating it for (b) 5 h; (c) 15 h; and (d) 30 h in $CDCl_3$ at 333 K.

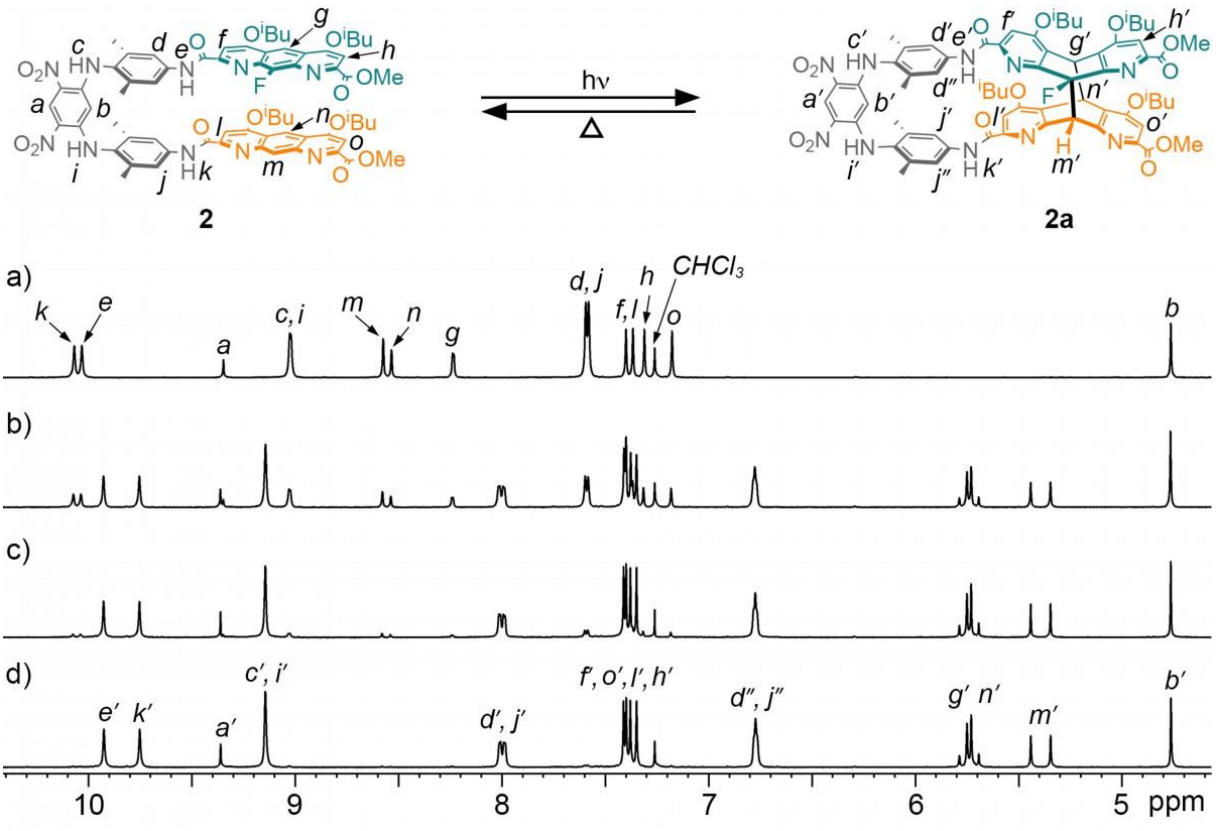


Figure S3. Excerpts from the ^{1}H NMR spectra (300 MHz, 298K) in $CDCl_3$ showing the photoproduct formation of **2** (5 mM): (a) before irradiation and after (b): 20 min; (c) 40 min; (d) 60 min of irradiation with assignment of proton resonances.

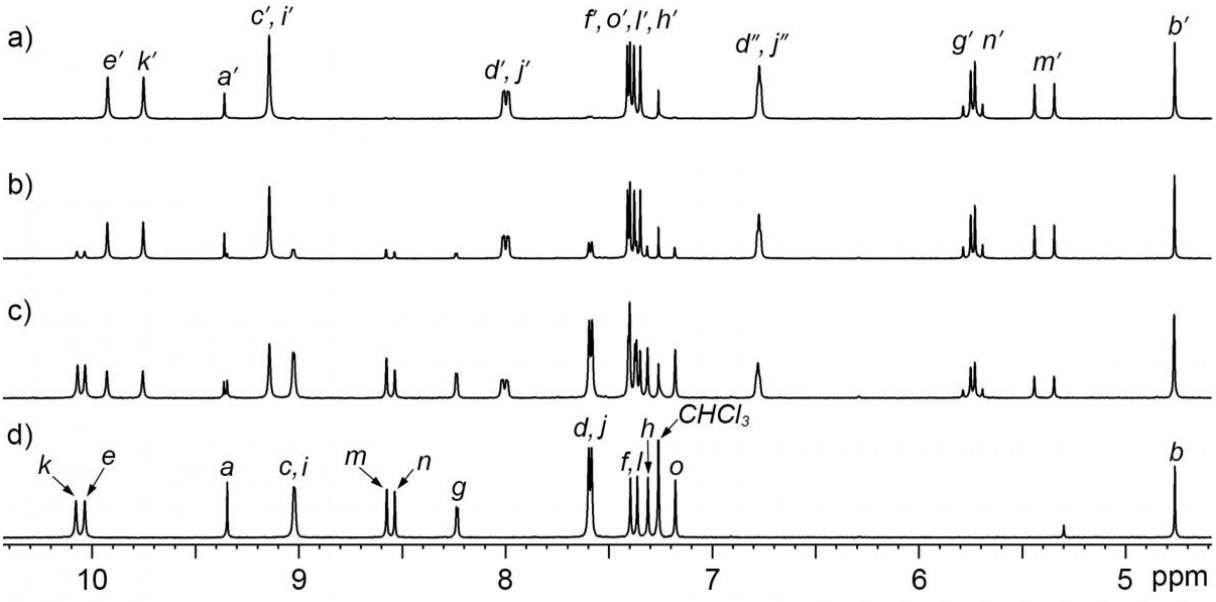


Figure S4. Excerpts from the ^{1}H NMR spectra (300 MHz, 298K) of **2a** (5 mM) in (a) $CDCl_3$ and after heating it for (b) 5 h; (c) 15 h; and (d) 30 h in $CDCl_3$ at 333 K.

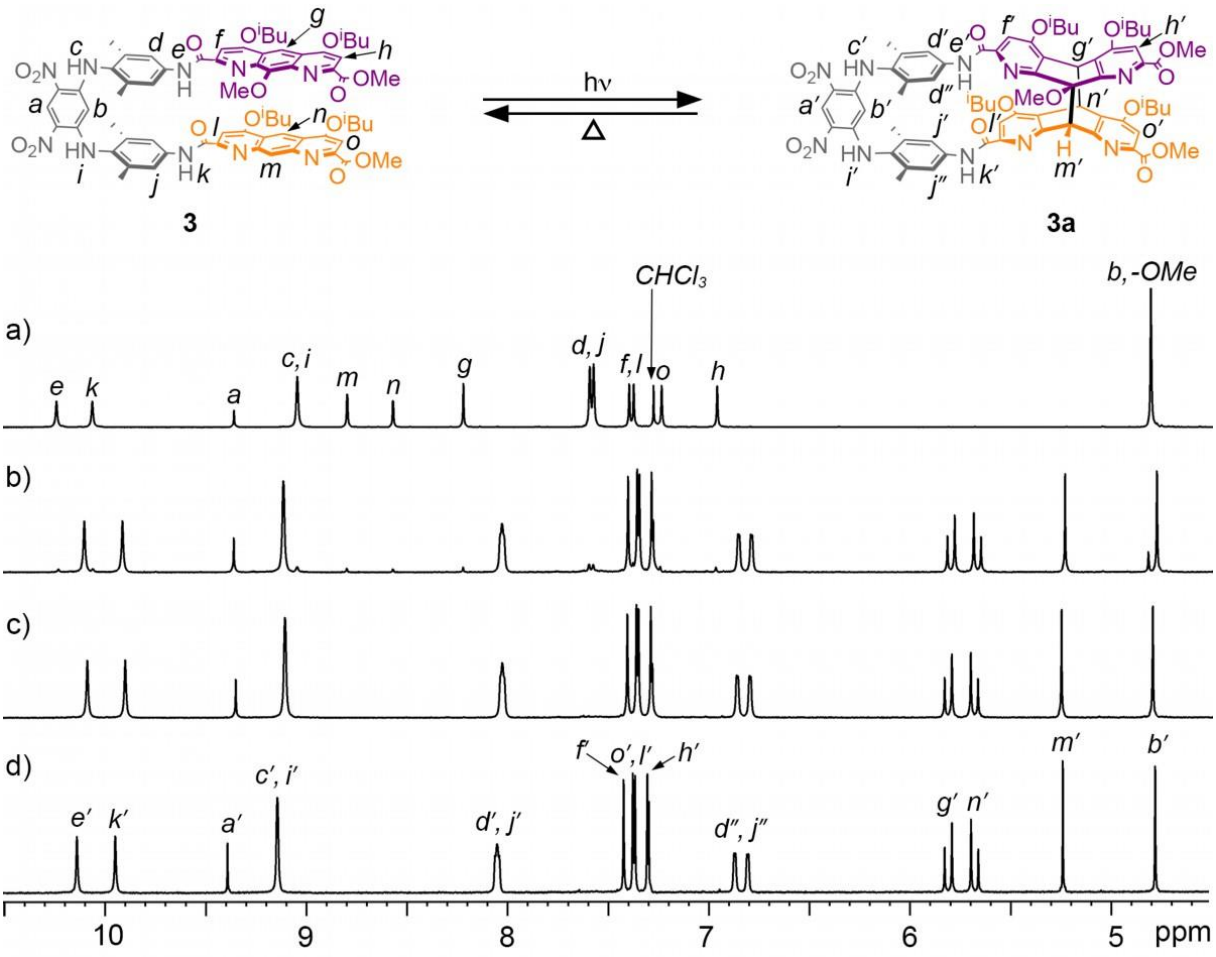


Figure S5. Excerpts from the ^{1}H NMR spectra (300 MHz, 298K) in $CDCl_3$ showing the photoproduct formation of **3** (5 mM): (a) before irradiation and after (b): 20 min.; (c) 40 min.; (d) 60 min of irradiation with assignment of proton resonances.

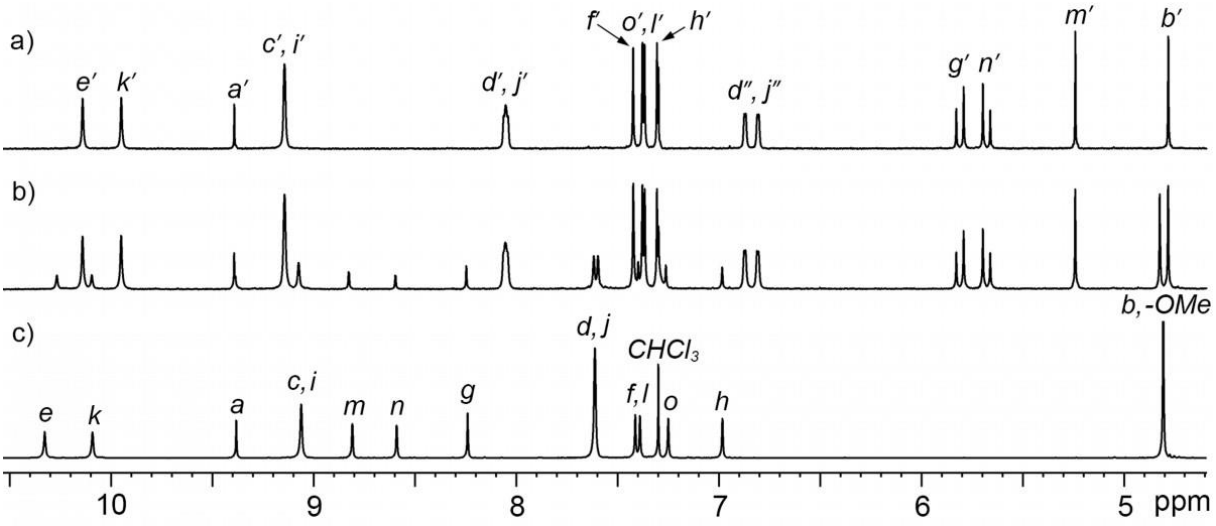


Figure S6. Excerpts from the ^{1}H NMR spectra (300 MHz, 298K) of **3a** (5 mM) in (a) $CDCl_3$ and after heating it for (b) 5 h; and (c) 30 h in $CDCl_3$ at 333 K.

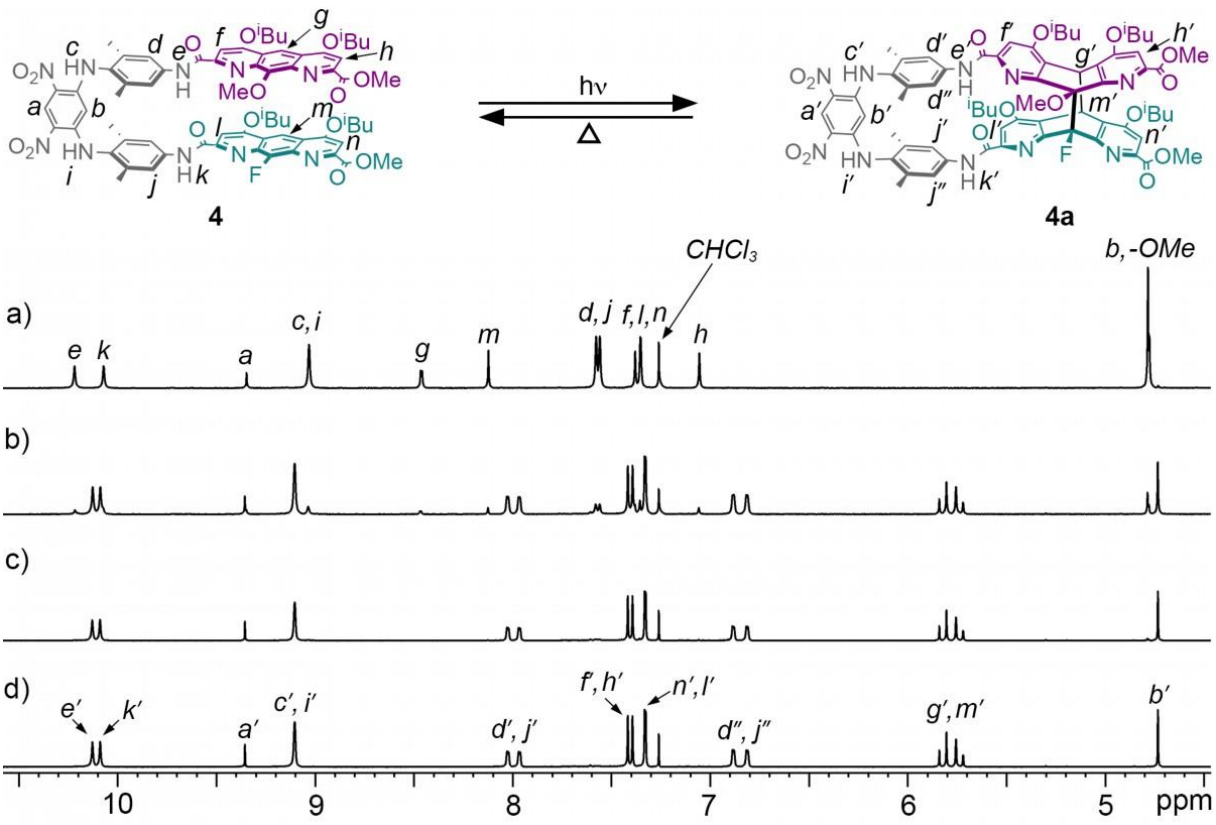


Figure S7. Excerpts from the ^{1}H NMR spectra (300 MHz, 298K) in $CDCl_3$ showing the photoproduct formation of **4** (5 mM): (a) before irradiation and after (b): 20 min.; (c) 40 min.; (d) 60 min of irradiation with assignment of proton resonances.

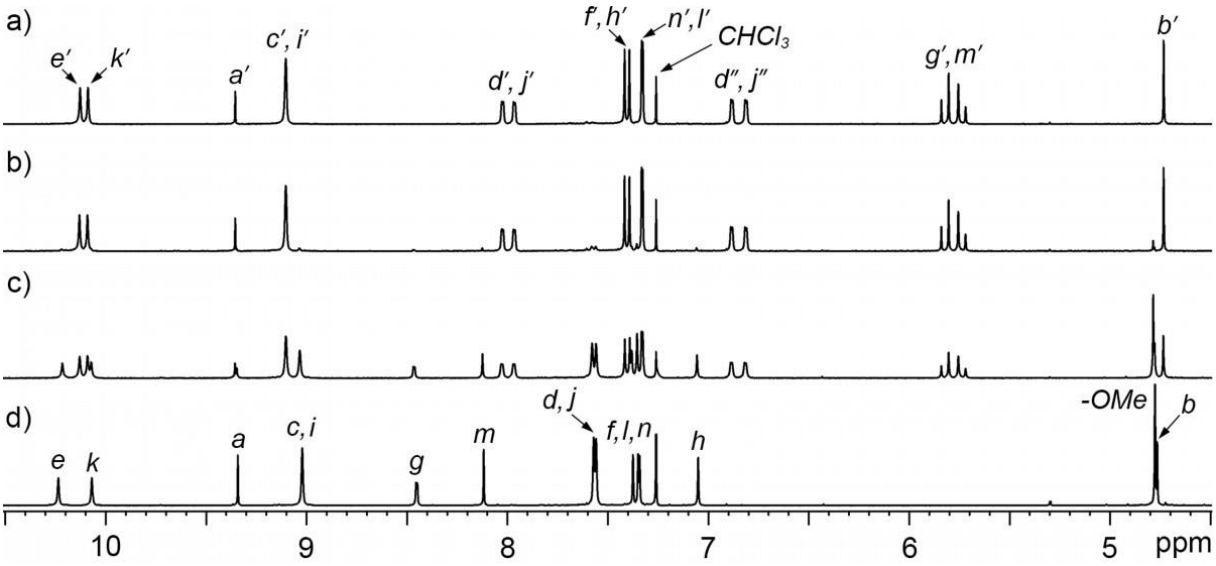


Figure S8. Excerpts from the ^{1}H NMR spectra (300 MHz, 298K) of **4a** (5 mM) in (a) $CDCl_3$ and after heating it for (b) 5 h; (c) 15 h; and (d) 30 h in $CDCl_3$ at 333 K.

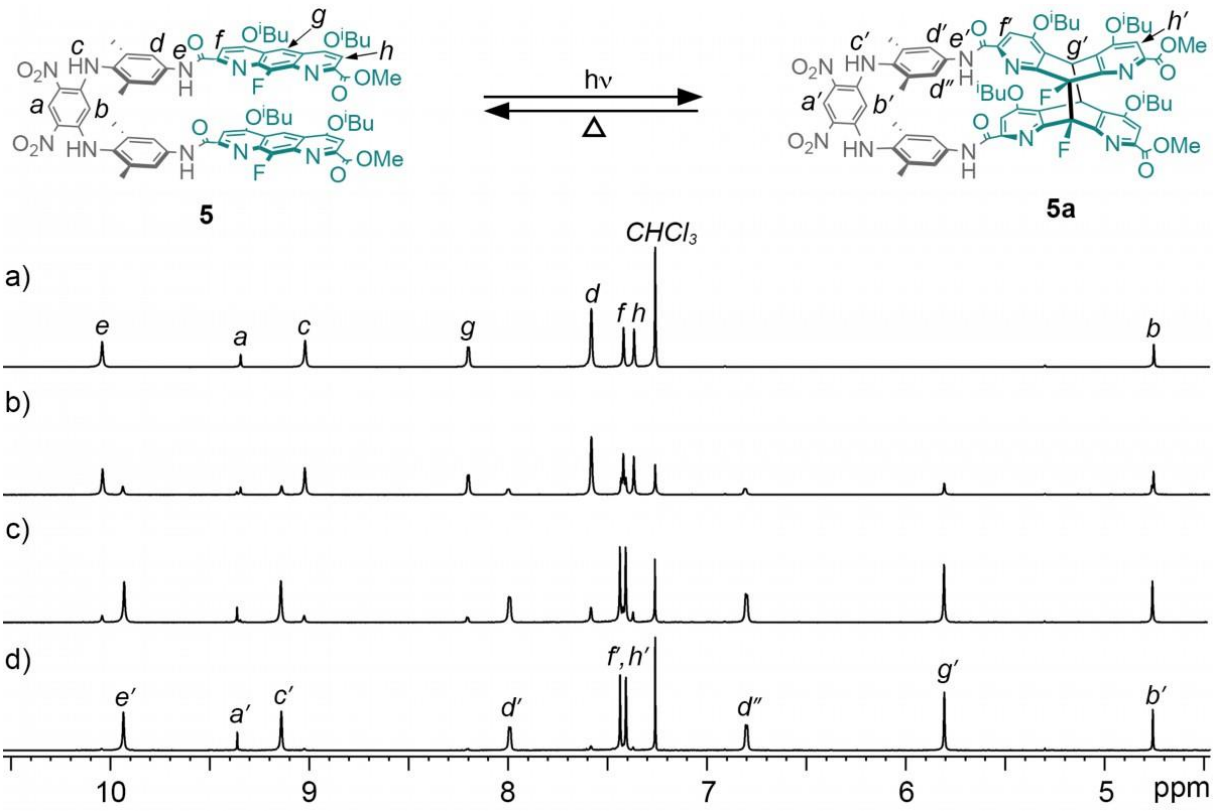


Figure S9. Excerpts from the ^{1}H NMR spectra (300 MHz, 298K) in $CDCl_3$ showing the photoproduct formation of **5** (5 mM): (a) before irradiation and after (b): 1 hour; (c) 4 hours; (d) 8 hours of irradiation with assignment of proton resonances.

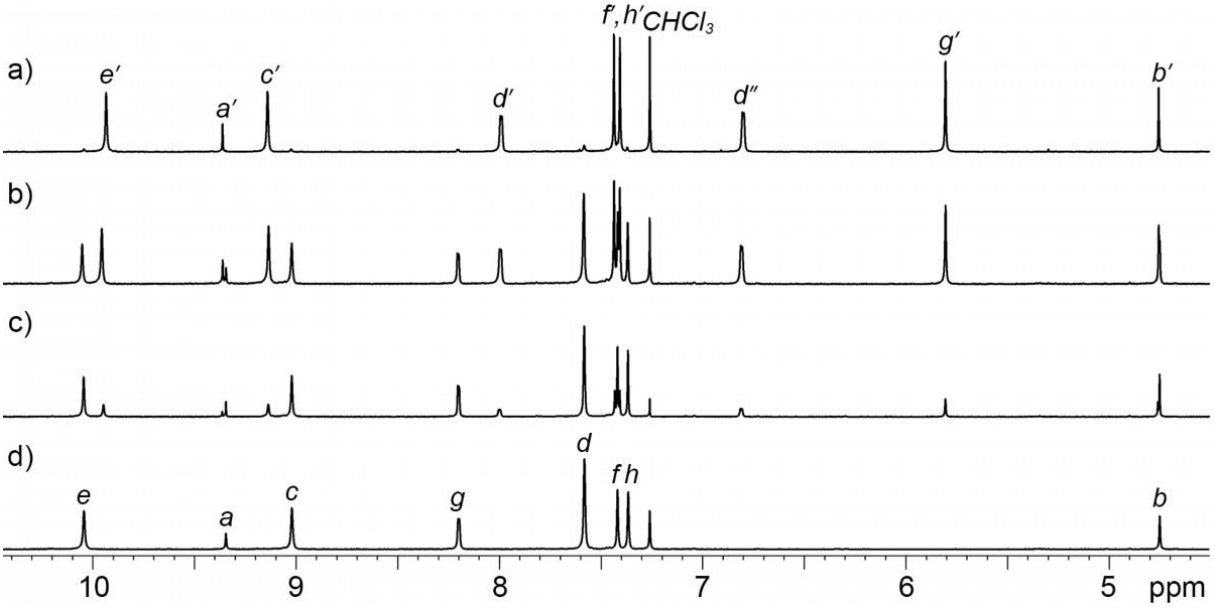


Figure S10. Excerpts from the ^{1}H NMR spectra (300 MHz, 298K) of **5a** (5 mM) in (a) $CDCl_3$ and after heating it for (b) 5 h; (c) 15 h; and (d) 30 h in $CDCl_3$ at 333 K.

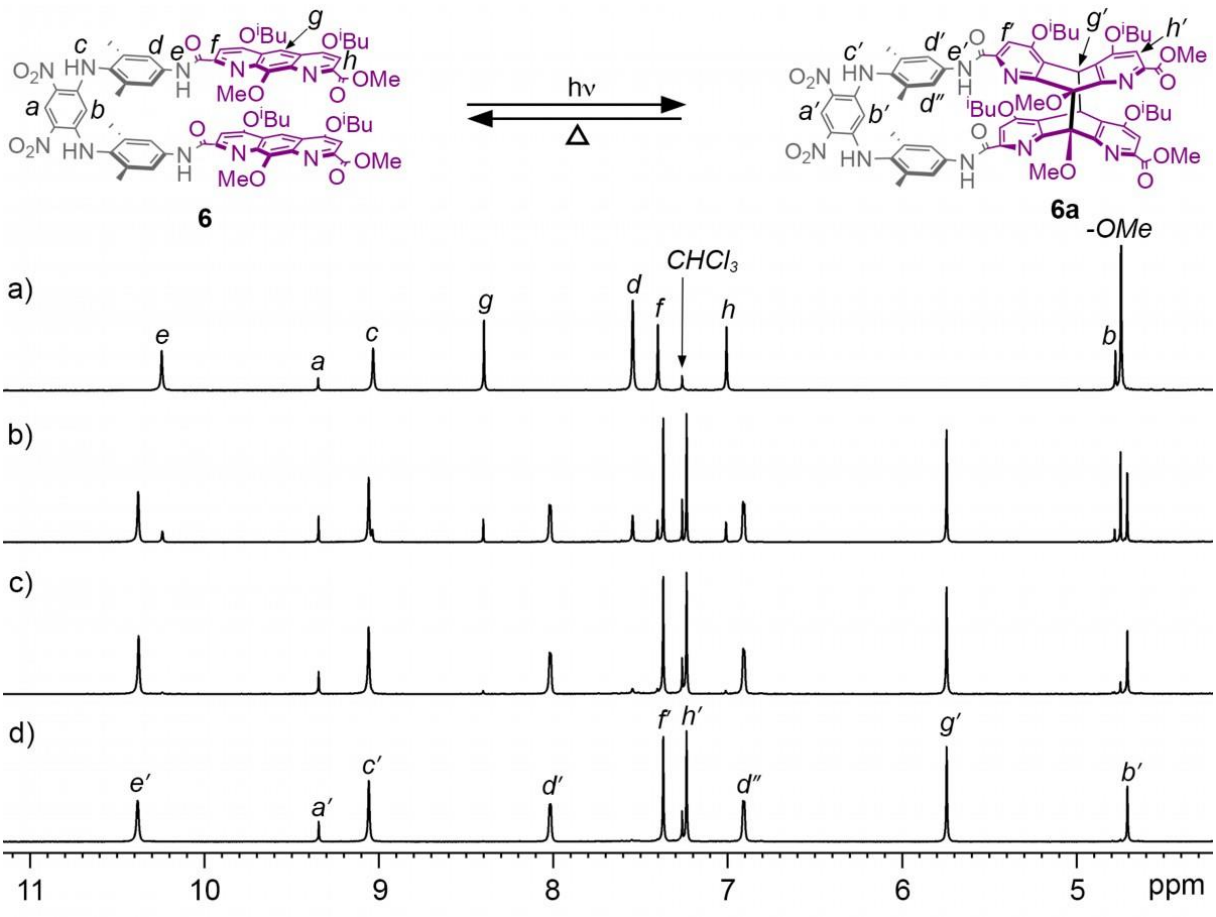


Figure S11. Excerpts from the ^{1}H NMR spectra (300 MHz, 298K) in $CDCl_3$ showing the photoproduct formation of **6** (5 mM): (a) before irradiation and after (b): 20 min.; (c) 40 min.; (d) 60 min of irradiation with assignment of proton resonances.

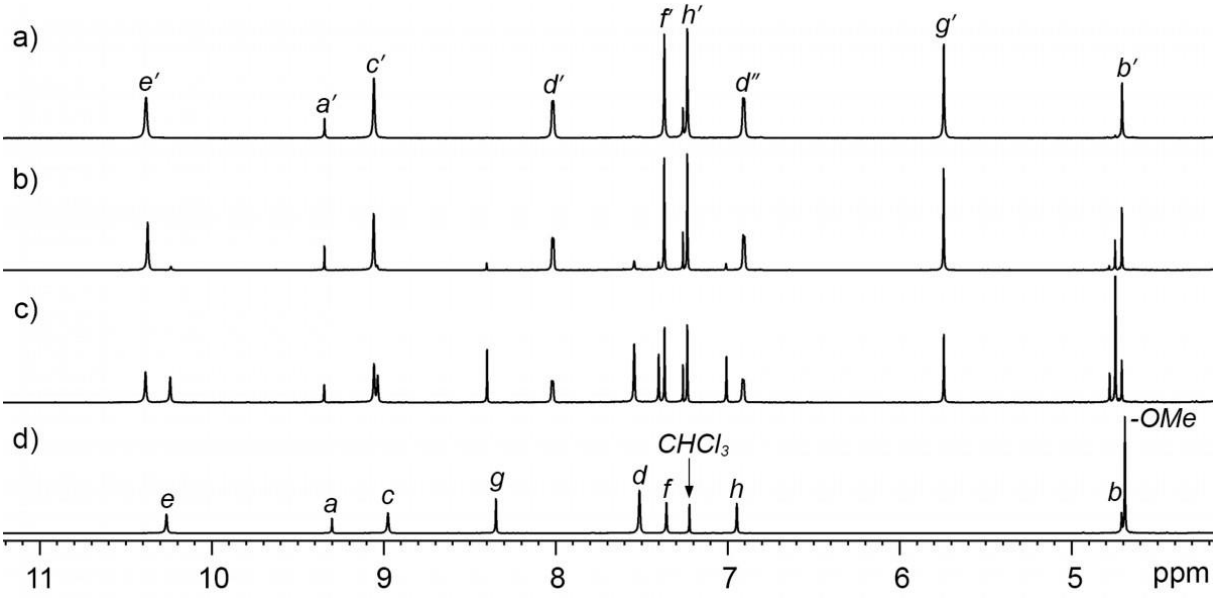


Figure S12. Excerpts from the ^{1}H NMR spectra (300 MHz, 298K) of **6a** (5 mM) in (a) $CDCl_3$ and after heating it for (b) 5 h; (c) 15 h; and (d) 30 h in $CDCl_3$ at 333 K.

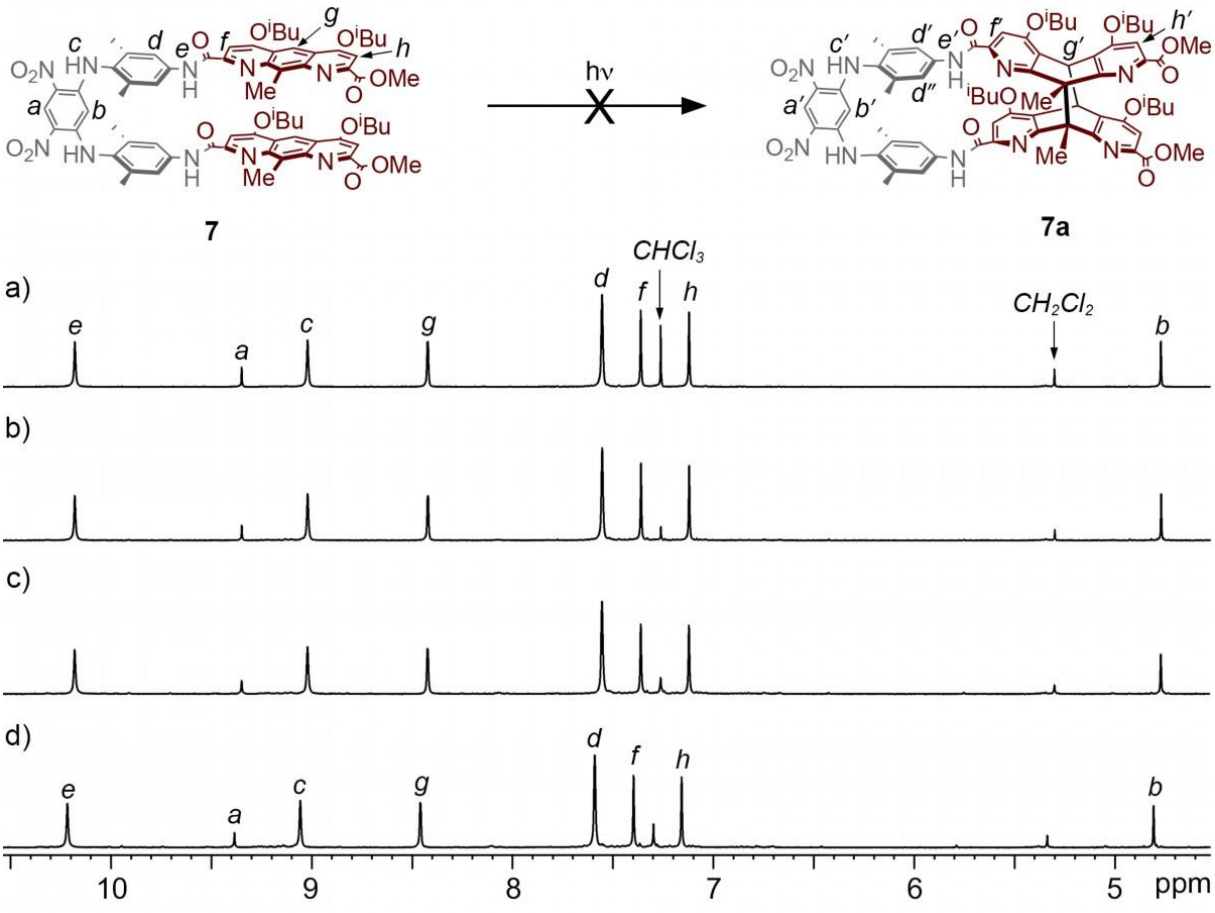


Figure S13. Excerpts from the ^{1}H NMR spectra (300 MHz, 298K) in $CDCl_3$ showing the photoirradiation process of **7** (5 mM): (a) before irradiation and after (b): 20 min; (c) 35 min; (d) 50 min of irradiation with assignment of proton resonances.

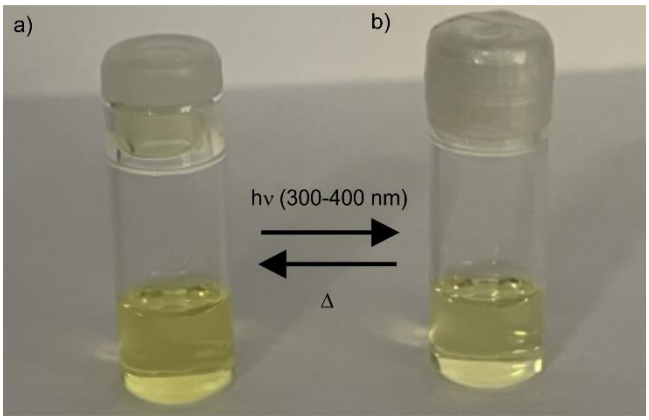


Figure S14. Photography illustrating the slight color change of a solution of **6** (0.5 mM) after irradiation and yielding the corresponding photoproduct **6a** which is less yellow.

5. Photochemistry

4.1 Fluorescence Quantum Yield

The fluorescence and reaction quantum yield were determined in degassed dichloromethane and air-equilibrated solutions as follows. The luminescence quantum yield (Φ) was calculated by using the equation $\Phi_{LUM} = \Phi_r(I/I_r)(A_r/A)(\eta^2/\eta_r^2)$ in which Φr refers to the quantum yield of the reference, I is the integrated emission intensity, A is the absorbance at the excitation wavelength and η is the refractive index of the solvent. An optically dilute solution of quinine sulphate (λ_{exc} = 370 nm) in 1N sulphuric acid was used as the reference, $\Phi_f = 0.54$.

4.2 Luminescence Decay

Luminescence lifetimes were measured via time-correlated single photon counting spectrometry on a Horiba Jobin-Yvon Fluorolog-3 spectrofluorometer, exciting with a 371 nm NanoLED (FWHM = ca. 1 ns).

4.3 Photoreaction quantum yields

Photoreaction quantum yields were determined upon excitation at 405 nm using the couple potassium ferrioxalate-phenanthroline as a chemical actinometer[8] on an optical bench equipped with a 150 W Hg-Xe lamp and a monochromator. Samples (1.09-1.52 mM for intermolecular photodimérisation in 1 mm cell and 0.022-0.027 mM for intramolecular photodimérisation in 10 mm cell) were stirred during the irradiation and the amount of converted material was determined at 2 min intervals by UV-vis following the disappearance of the absorption band of the diaazanthracene moieties at 400 nm. The error in photodimerisation quantum yield determination was estimated at ± 10%.

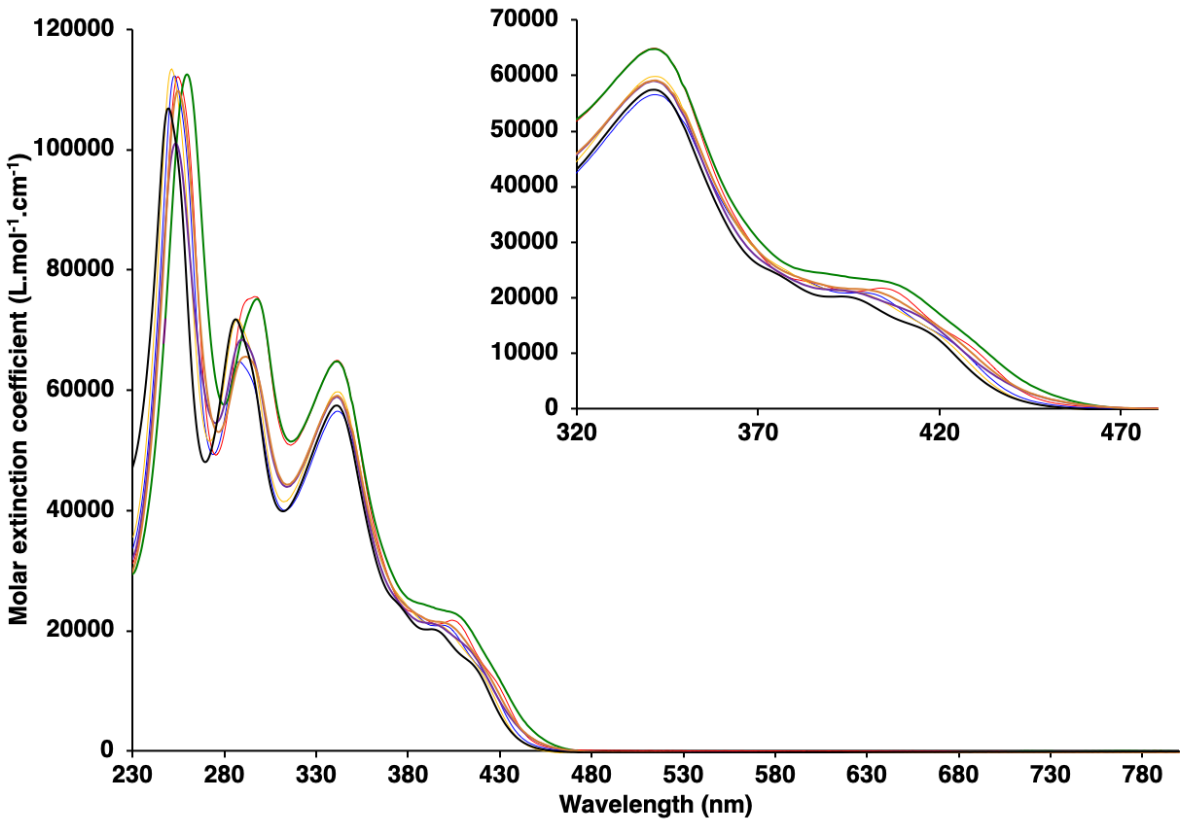


Figure S15: Electronic absorption spectra of a degassed solution of **1** (black), **2** (yellow), **3** (purple), **4** (orange), **5** (blue), **6** (green), and **7** (red) in CH_2Cl_2.

6. Nuclear Magnetic Resonance

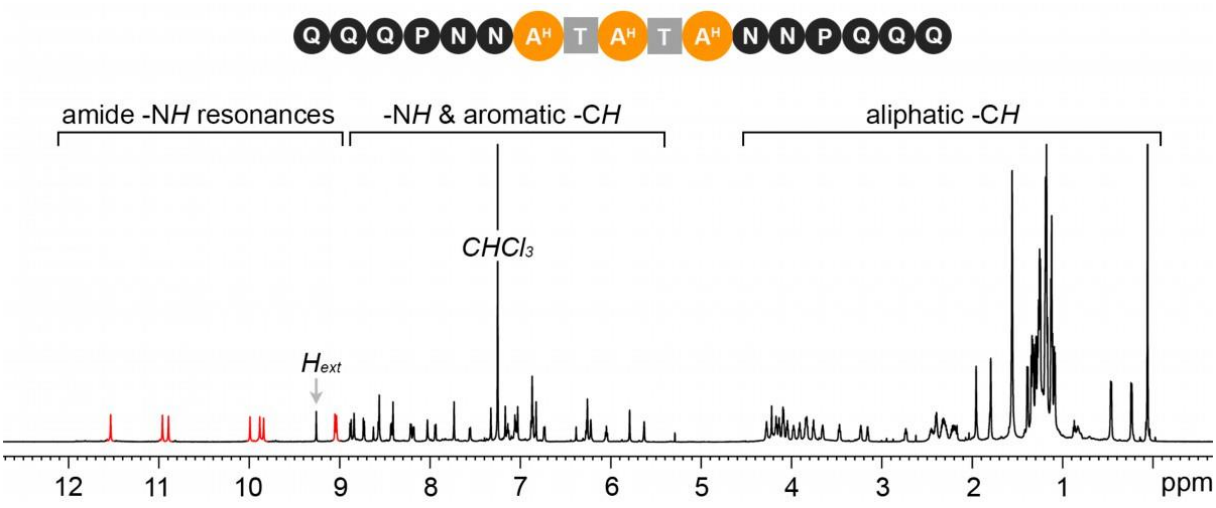


Figure S16. 700 MHz ^{1}H NMR spectra at 298 K of oligomer **8** in $CDCl_3$. The amide -N*H* signals are highlighted in red.

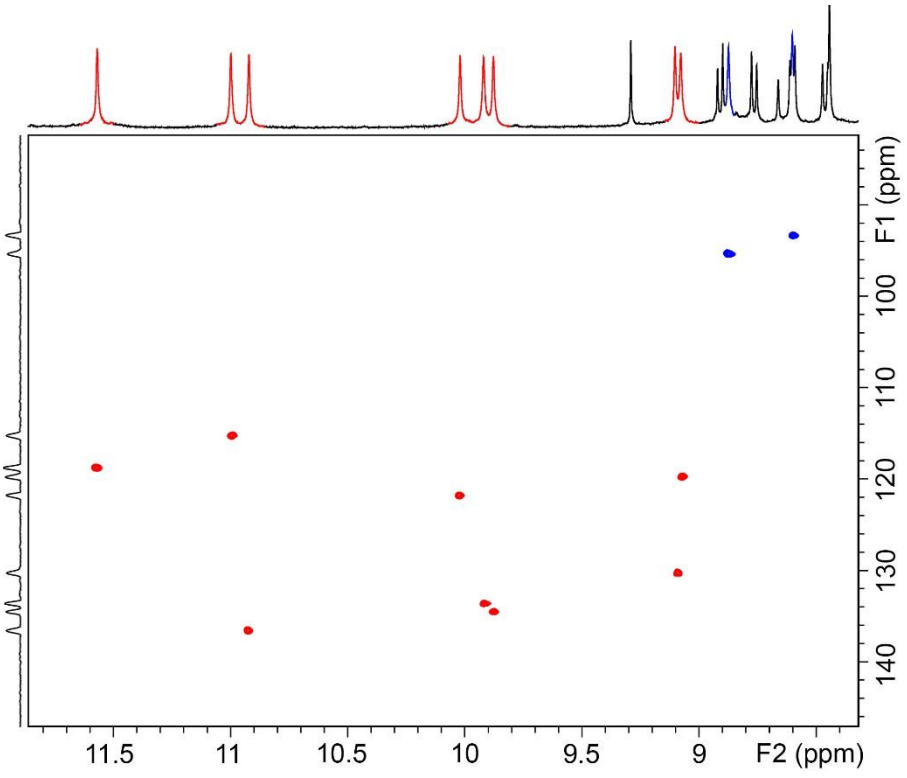


Figure S17. ^{1}H-^{15}N HSQC spectrum (400 MHz, $CDCl_3$) of **8** (1 mM) at 298K. The amide and amine -N*H* signals are highlighted in red and blue colors, respectively.

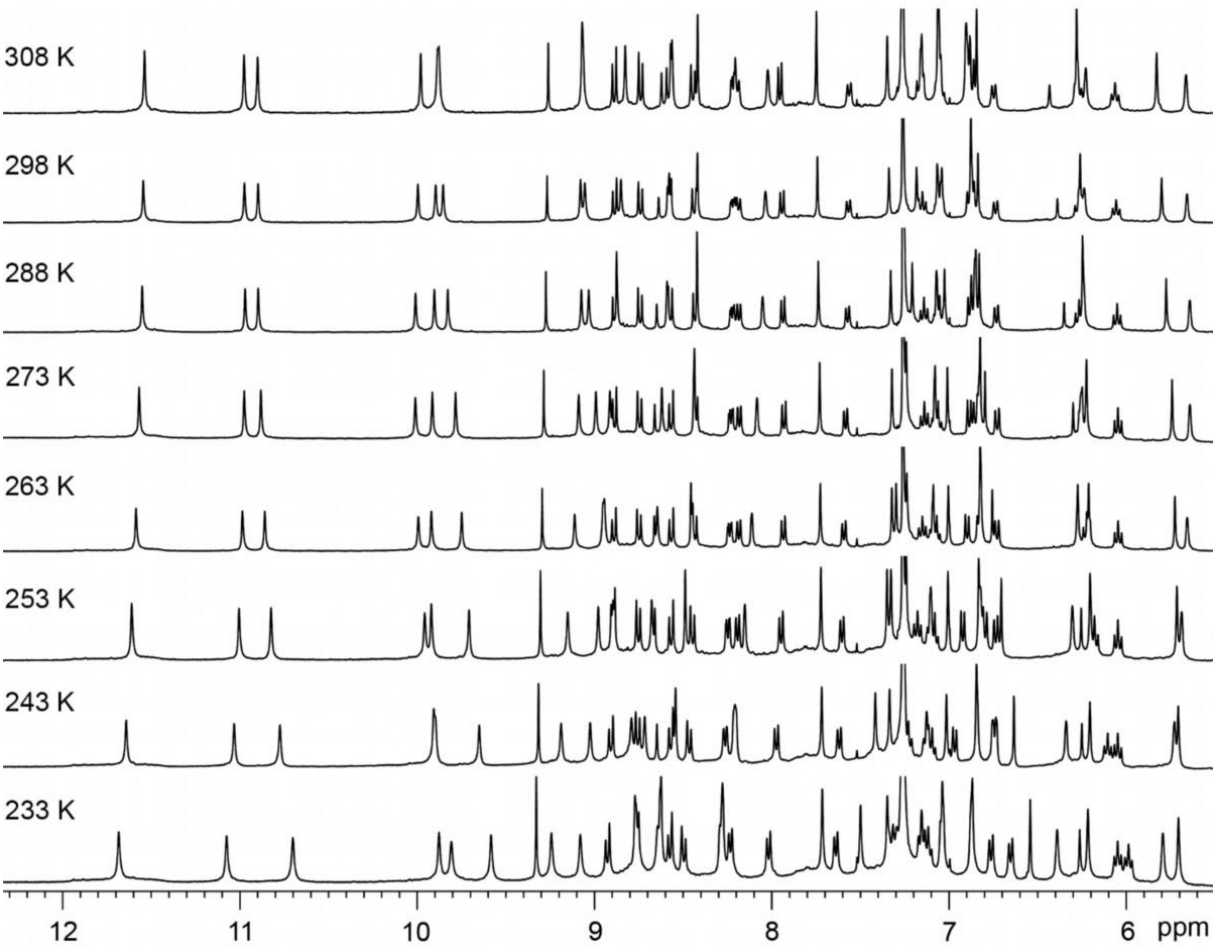


Figure S18. Part of the variable temperature ^{1}H NMR spectra (400 MHz, $CDCl_3$) of **8** (1 mM) from 308 K to 233 K.

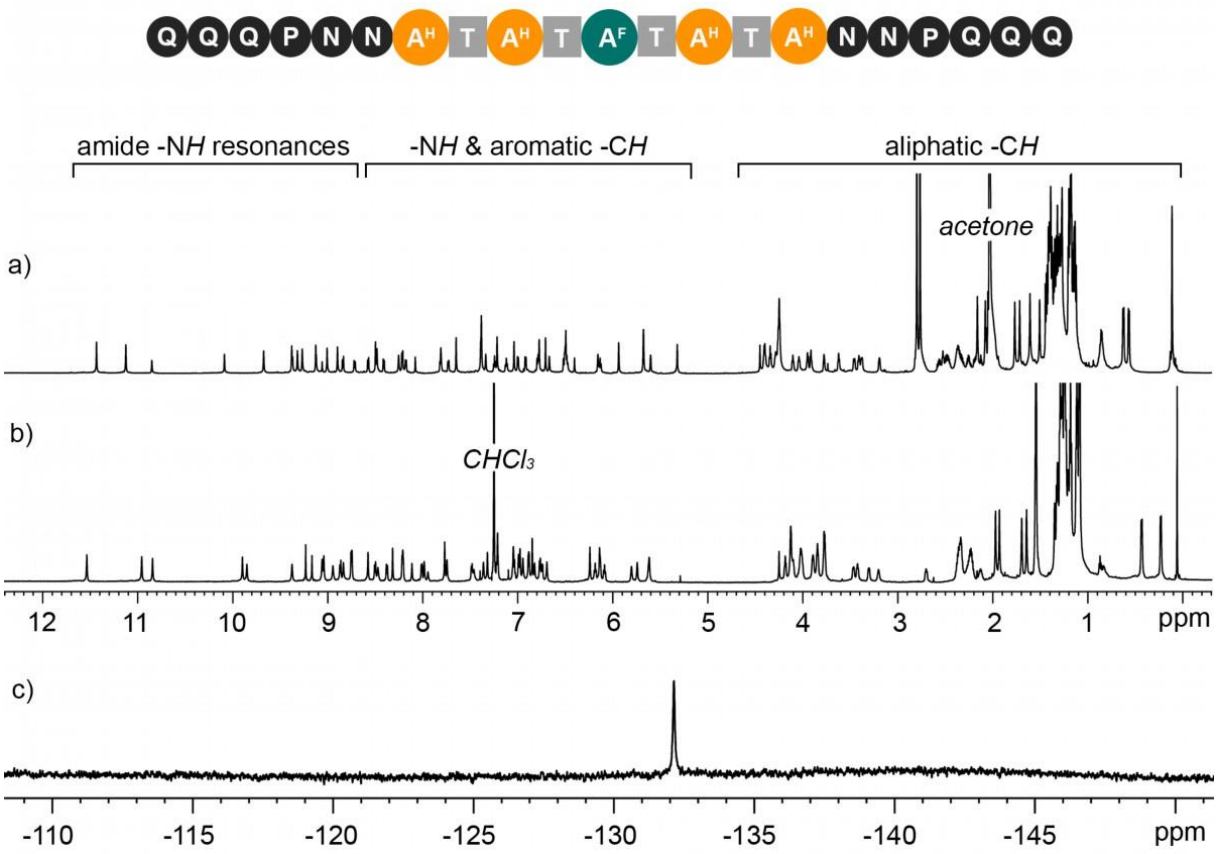


Figure S19. 700 MHz ^{1}H NMR spectra at 298 K of oligomer **12** in: (a) acetone-d_6; and (b) $CDCl_3$. (c) 376 MHz ^{19}F NMR spectra at 298 K of oligomer **12** in $CDCl_3$.

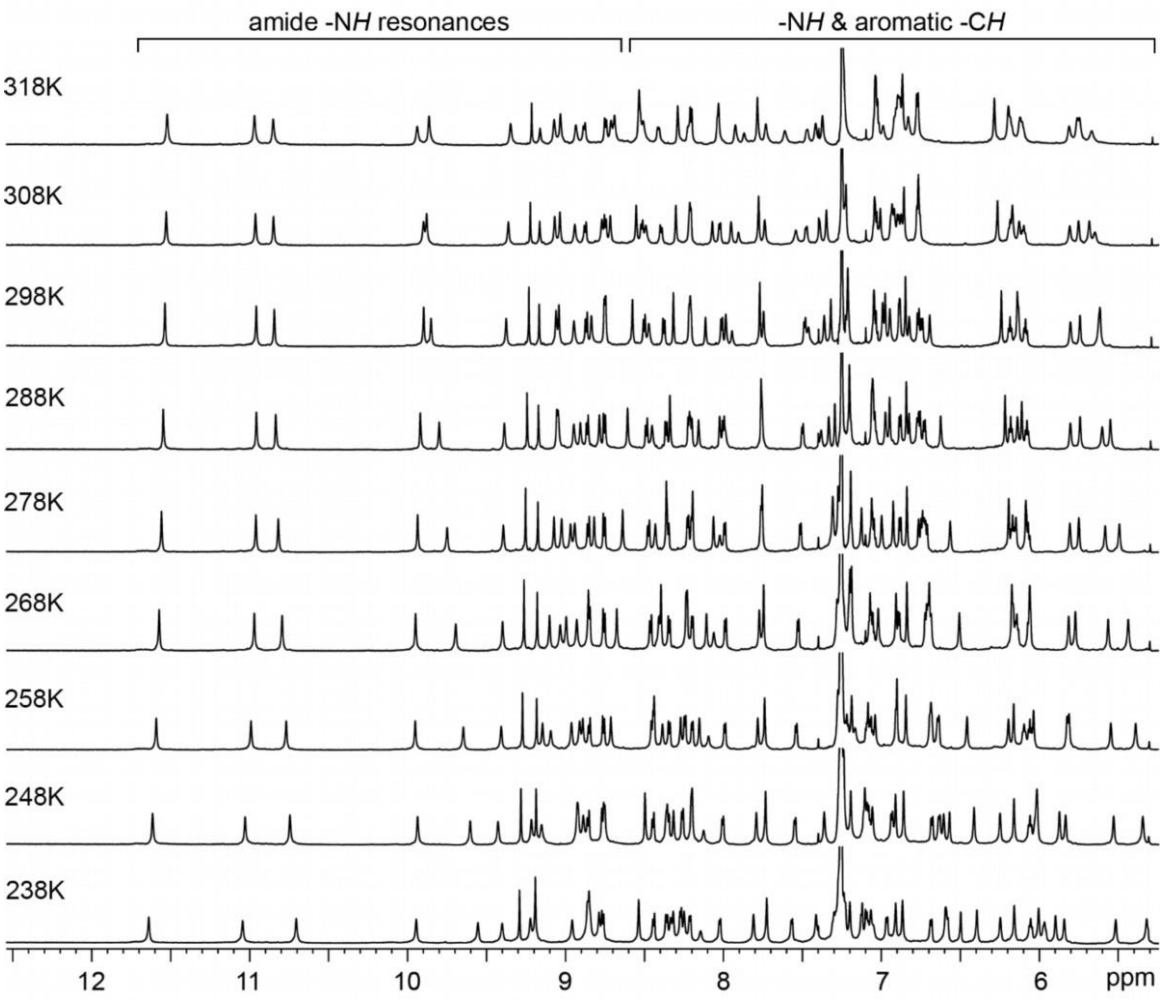


Figure S20. Part of the variable temperature ^{1}H NMR spectra (700 MHz, $CDCl_3$) of **12** (1 mM) from 318K to 238K.

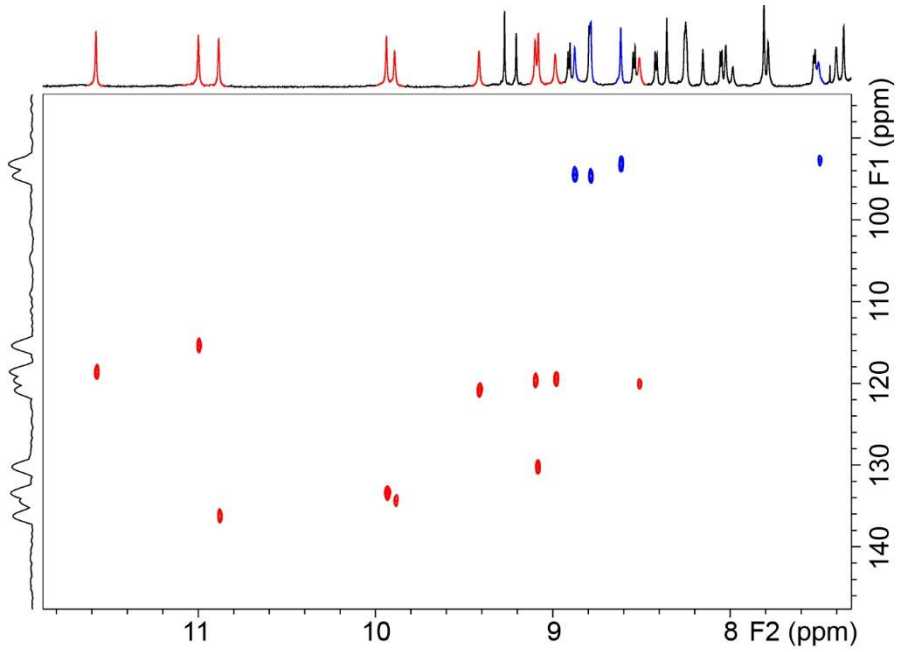


Figure S21. ^{1}H-^{15}N HSQC spectrum (400 MHz, $CDCl_3$) of **12** (1 mM) at 298K. The -N*H* amide signals are depicted in red and turn unit amine protons are shown in blue colors.

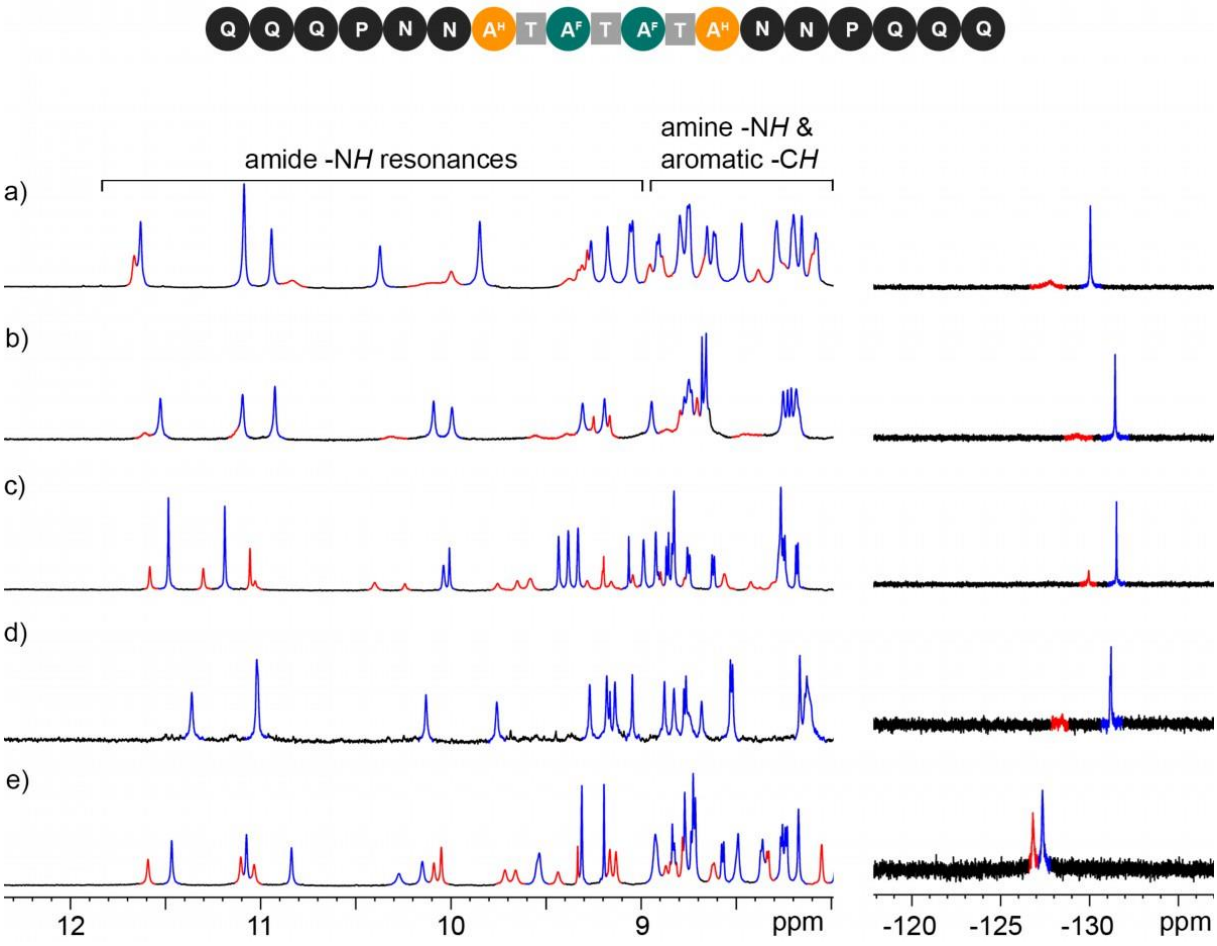


Figure S22. Part of 700 MHz ^{1}H NMR spectra at 298 K of oligomer **9** in: (a) $CDCl_3$, (b) CD_2Cl_2, (c) acetone-d_6, (d) CD_3CN, and (e) d_2-tetrachloroethane. The corresponding ^{19}F NMR in respective solvents are given in right side. Existence of two conformers has been represented by highlighting signals corresponding to those by red and blue respectively.

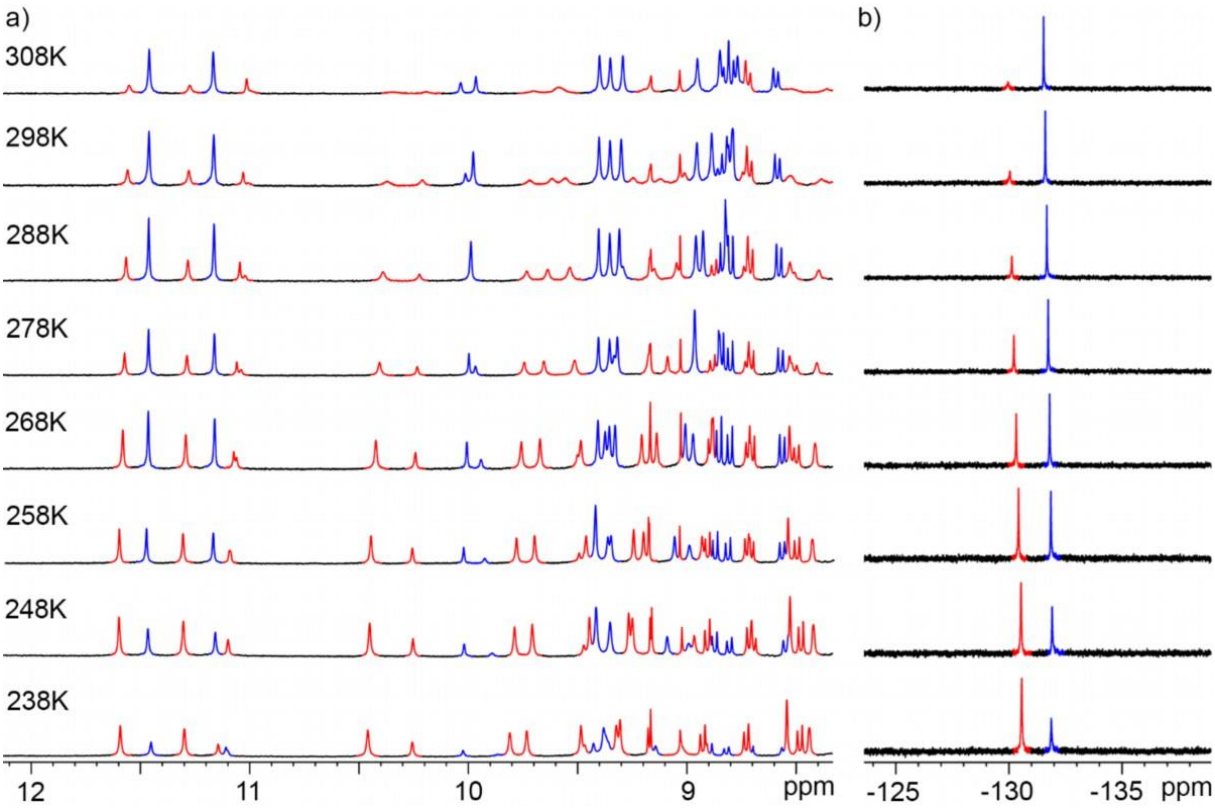


Figure S23. Part of the variable temperature (a) ^{1}H NMR spectra (400 MHz) and (b) ^{19}F-NMR in acetone-d_6 of **9** (1 mM) from 308 K to 238 K. Two conformers present at room temperature are in slow exchange at the NMR time scale are highlighted in red and blue, respectively.

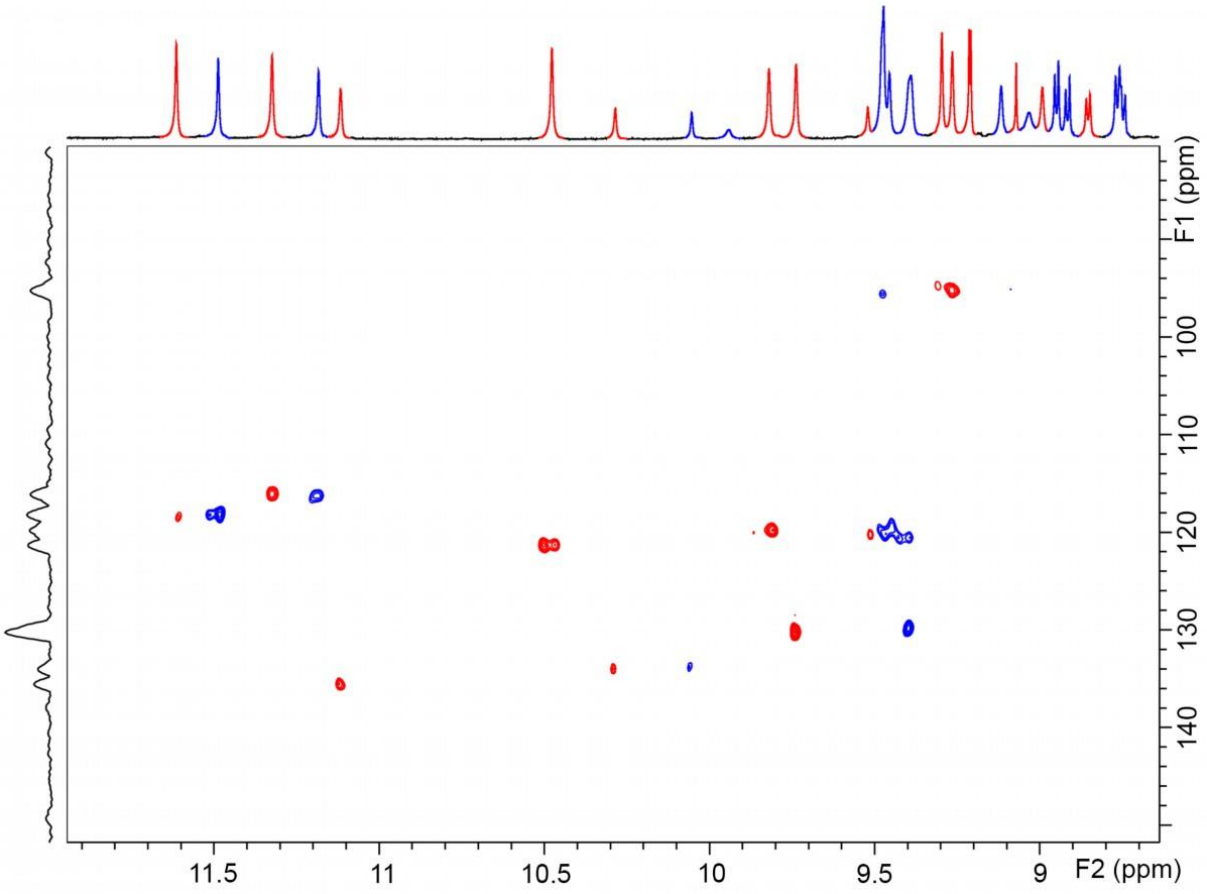


Figure S24. ^{1}H-^{15}N HSQC spectrum (700 MHz, acetone-d_6) of **9** (1 mM) at 258K. Signals correspond to two conformers are shown in red and blue colors respectively.

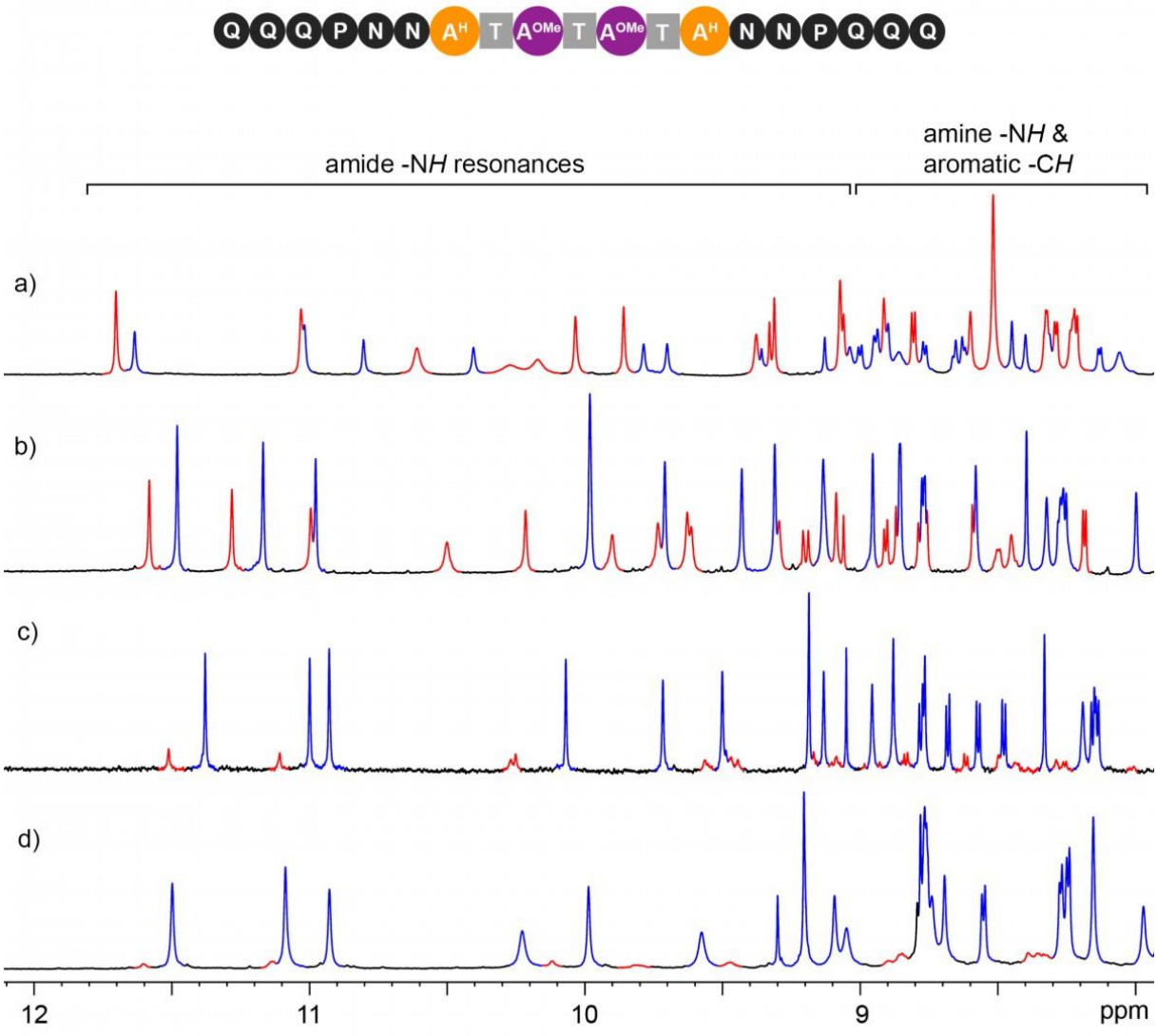


Figure S25. Part of 700 MHz ^{1}H NMR spectra at 298 K of oligomer **10** (1mM) in: (a) $CDCl_3$, (b) d_6-acetone, (c) CD_3CN, and (d) d_2-tetrachloroethane. Two conformers present at room temperature are in slow exchange at the NMR time scale are highlighted in red and blue, respectively.

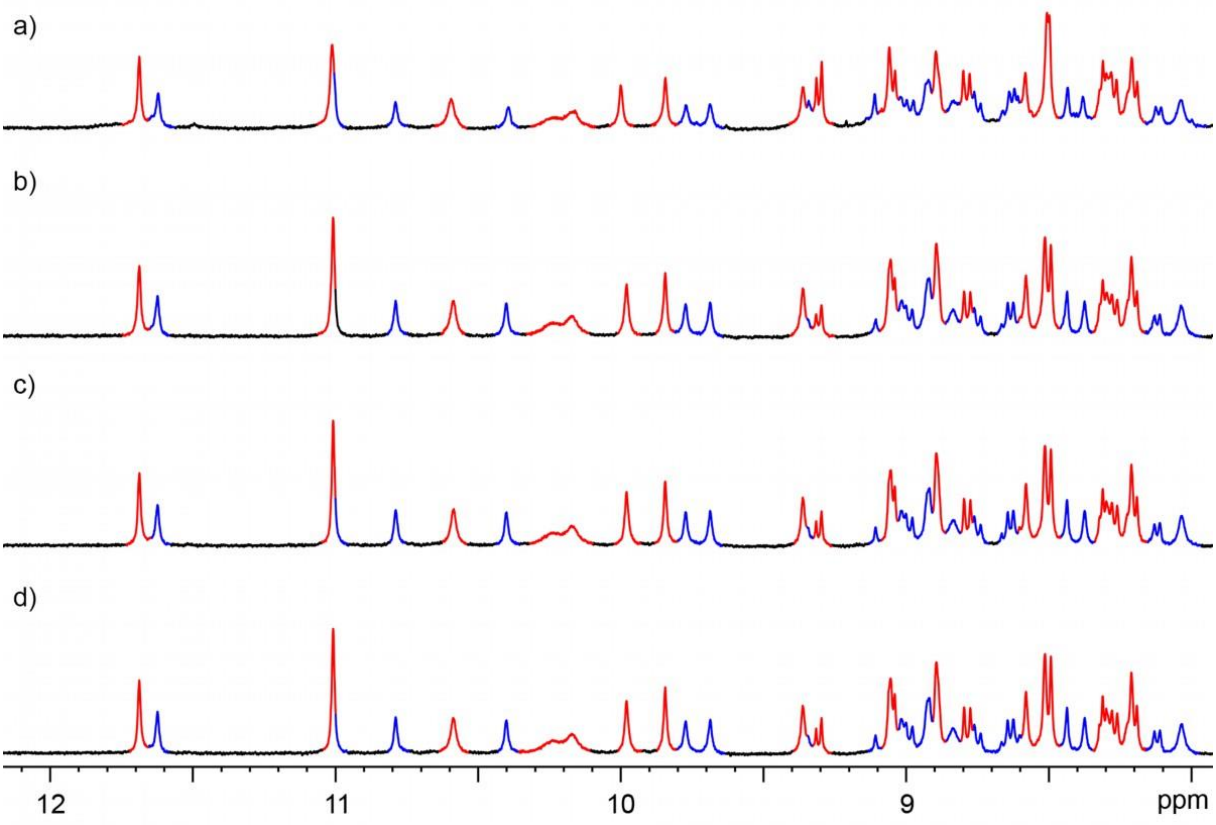


Figure S26. Part of 400 MHz ^{1}H NMR spectra at 298 K of oligomer **10**; a) in $CDCl_3$, (b) Freshly dissolved crystals after 5 min, (c) after 25 min and (d) 50 min. Signals corresponds to two conformers are highlighted in red and blue, respectively. No difference in their proportion after freshly dissolution of crystals compared to reference NMR as well as no change of it over time indicating significantly fast dynamics among the conformers.

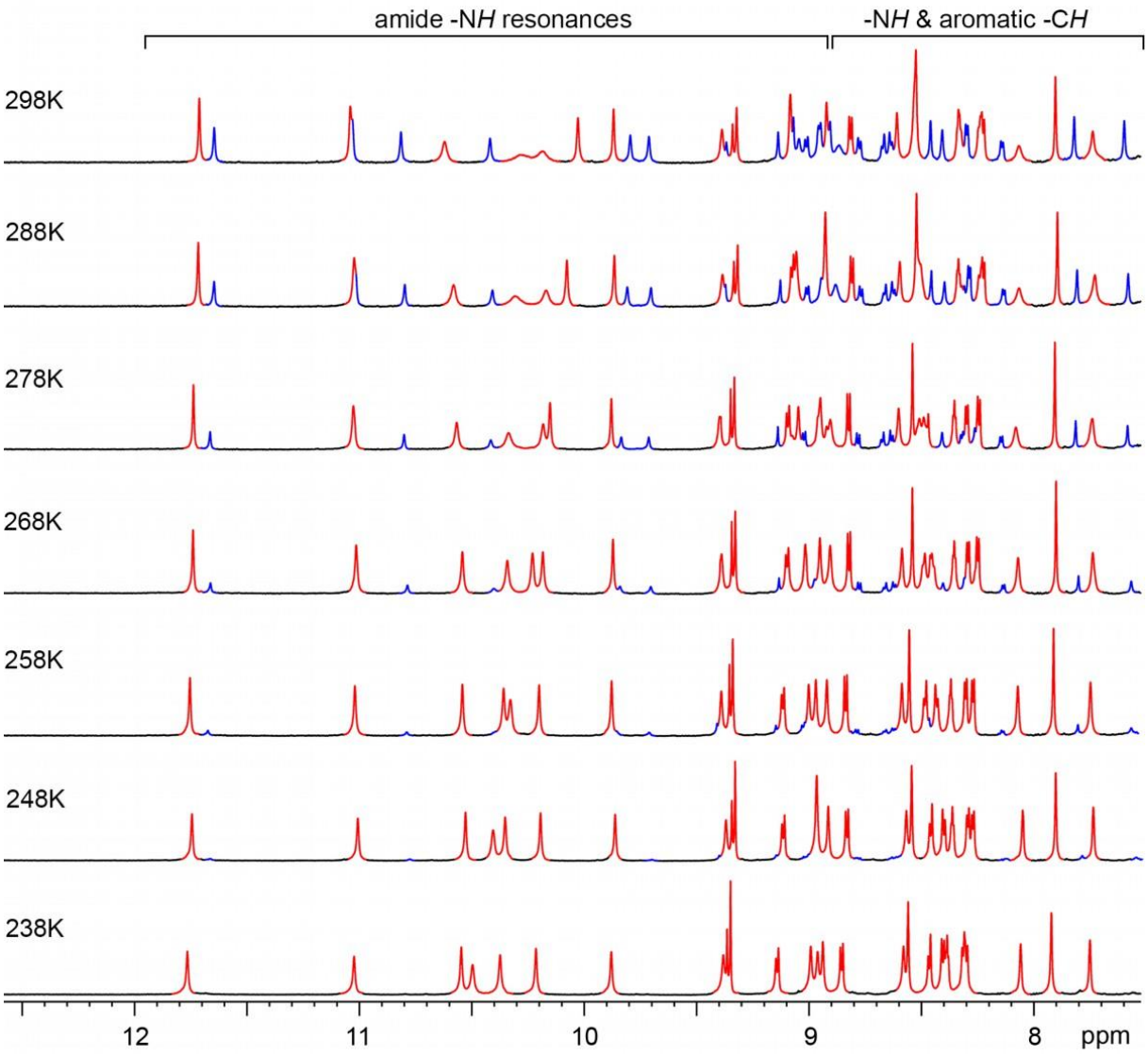


Figure S27. Part of the variable temperature ^{1}H NMR spectra (700 MHz, $CDCl_3$) of **10** (1 mM) from 298 K to 238 K. Two conformers present at room temperature are in slow exchange at the NMR time scale are highlighted in red and blue peaks, respectively. One of the conformers highlighted in blue disappear at 238 K.

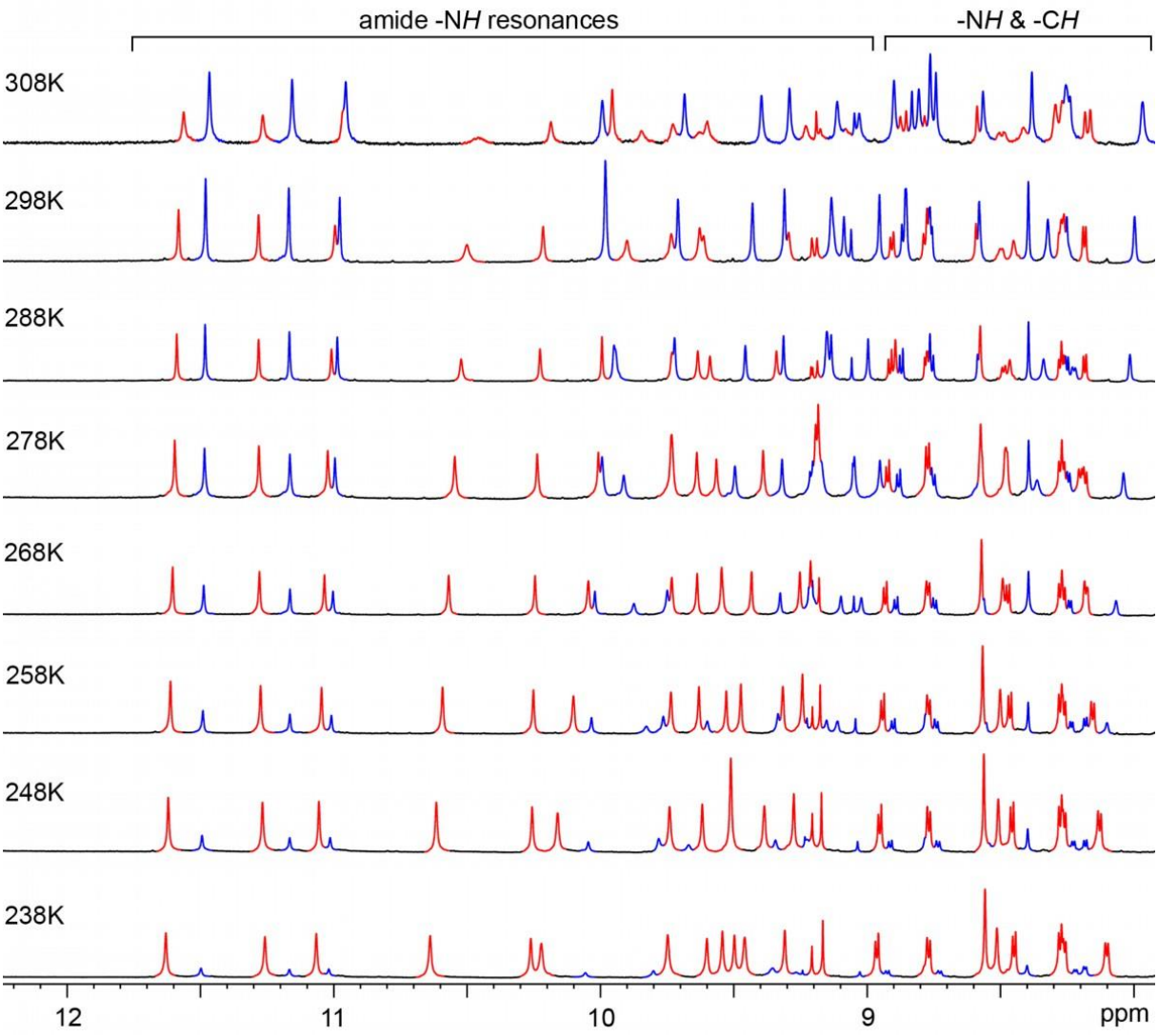


Figure S28. Part of the variable temperature ^{1}H NMR spectra (700 MHz, acetone-d_6) of **10** (1 mM) from 308K to 238K. The peaks highlighted in red and blue are corresponding to two conformers present at room temperature. Those are in slow exchange at the NMR time scale. Proportion of two conformers changes with temperature variation.

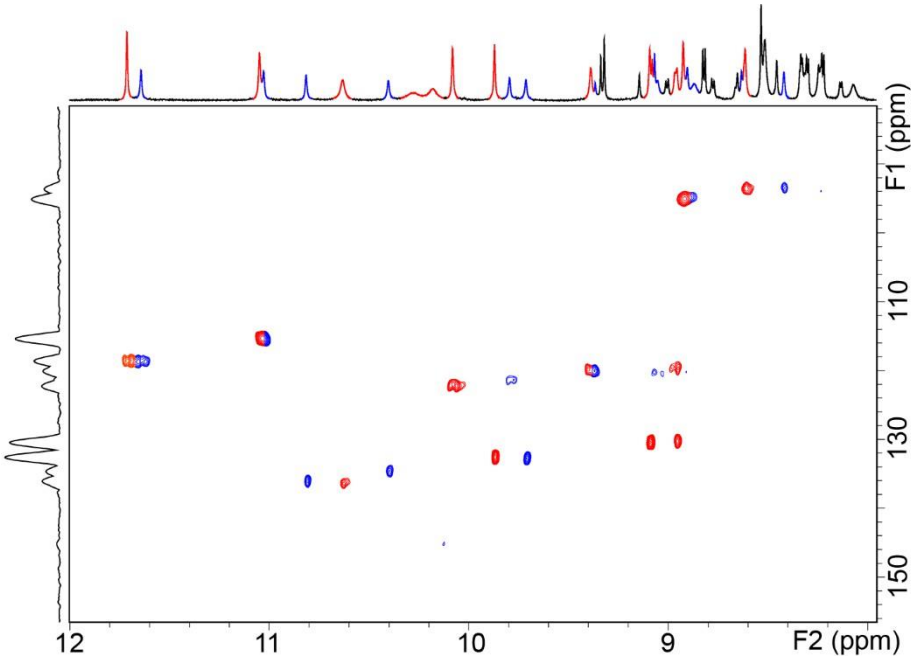


Figure S29. ^{1}H-^{15}N HSQC spectrum (700 MHz, $CDCl_3$) of **10** (1 mM) at 298K. The -N*H* signals present in two conformers are shown in red and blue colors. Two *NH* correlations could be detected due to resonance broadness.

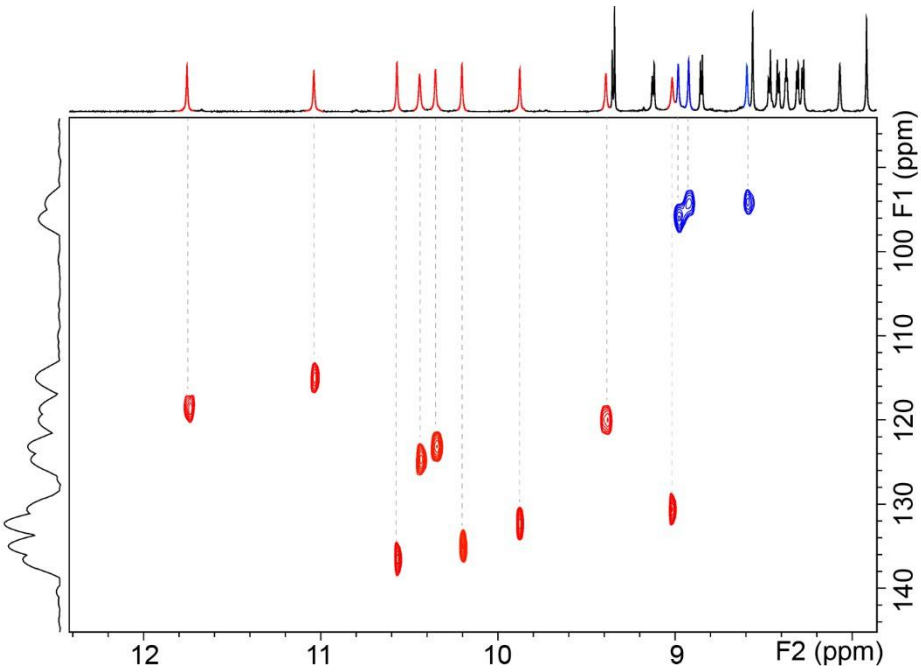


Figure S30. ^{1}H-^{15}N HSQC spectrum (700 MHz, $CDCl_3$) of **10** (1 mM) at 248K. At this temperature only one conformer was observed. The N*H* amide signals are depicted in red and turn unit amine protons are shown in blue colors.

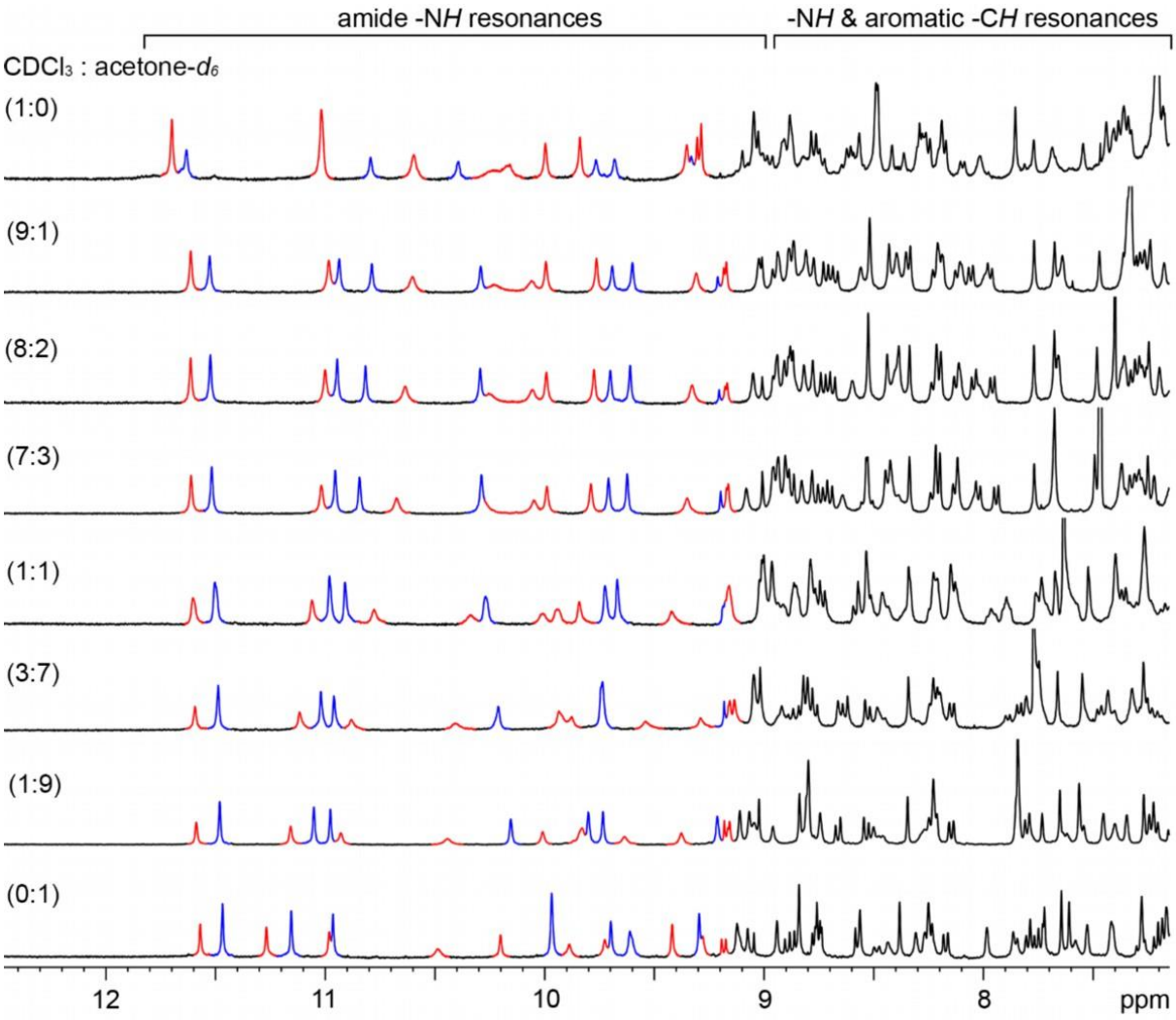


Figure S31. Part of ^{1}H NMR spectra (400 MHz) of **10** (1 mM) in varying $CDCl_3$/acetone-d_6 mixtures at 298K. Proportion of the two conformers, highlighted with red and blue peaks, can be seen changes from $CDCl_3$ to acetone-d_6.

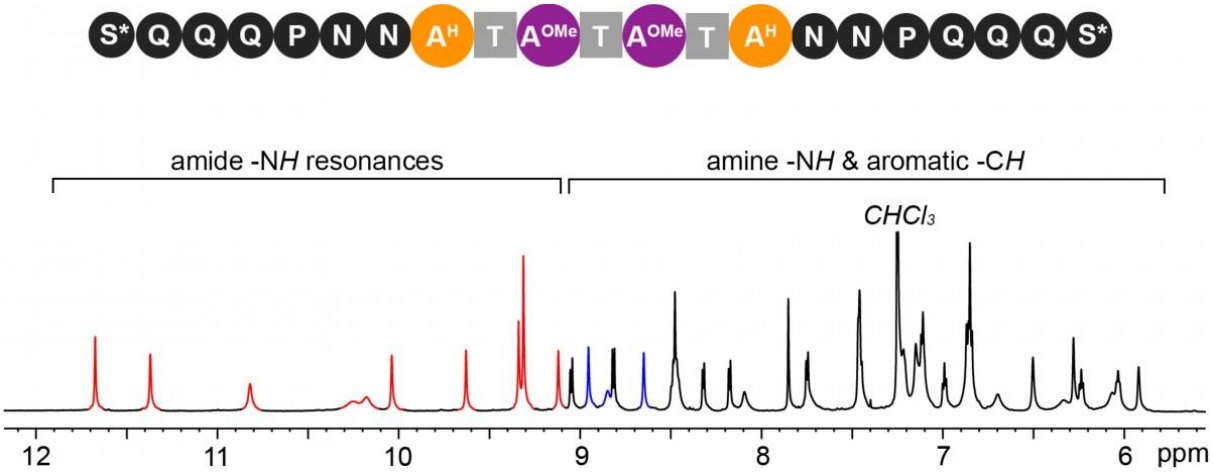


Figure S32. Part of 700 MHz ^{1}H NMR spectra at 298 K of oligomer **11** (1mM) in $CDCl_3$, showing presence of single conformer. Peaks highlighted in red and blue corresponds to the amide and amine proton signals respectively.

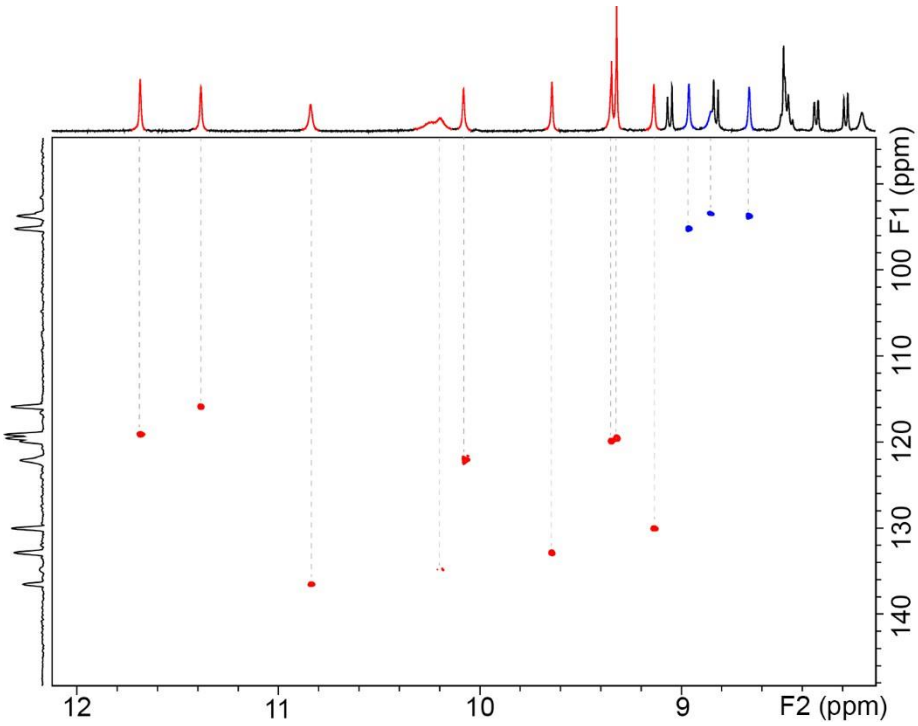


Figure S33. ^{1}H-^{15}N HSQC spectrum (700 MHz, $CDCl_3$) of **11** (1 mM) at 298K. The N*H* amide signals are depicted in red and turn unit amine protons are shown in blue colors.

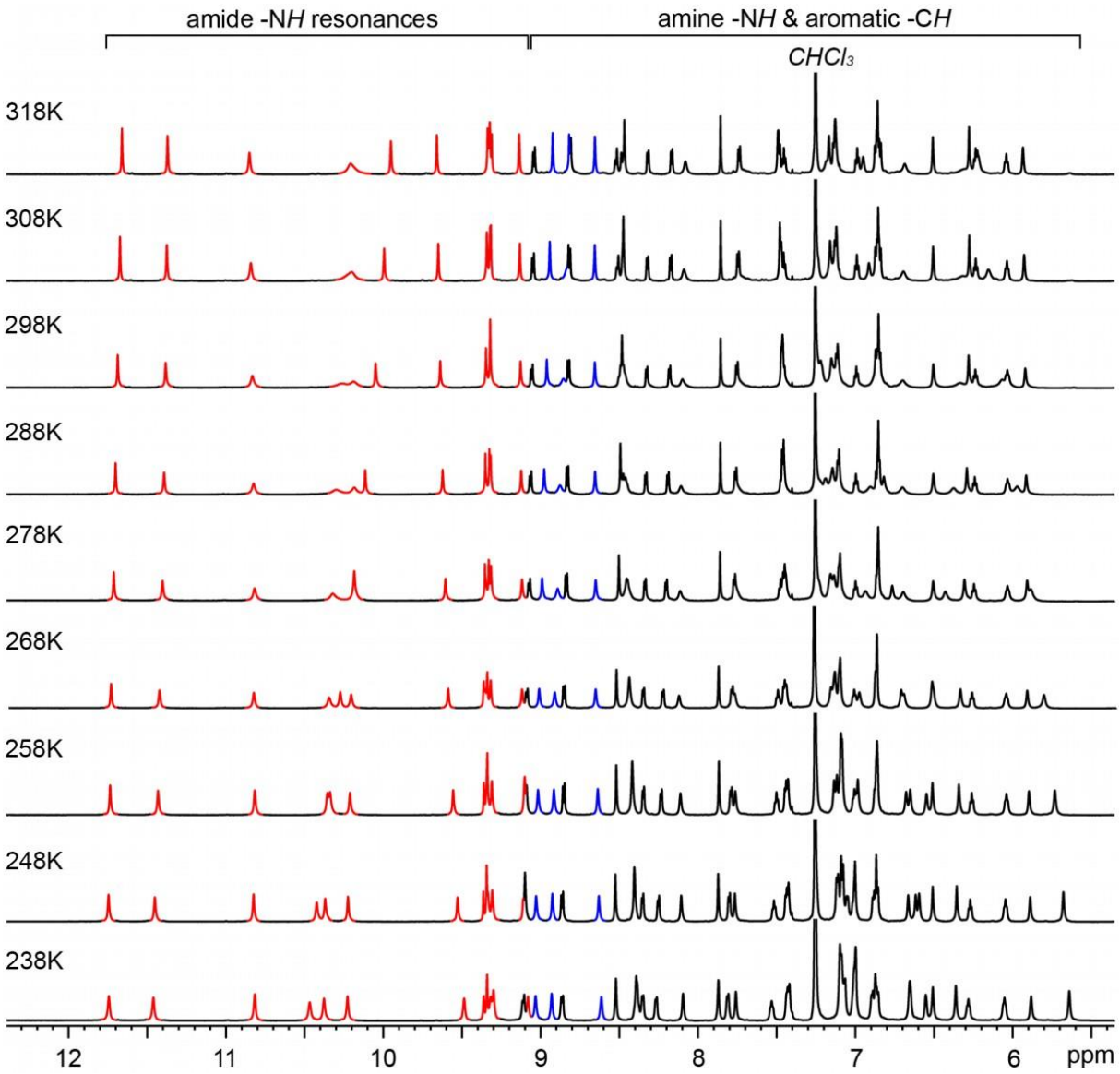


Figure S34. Part of the variable temperature ^{1}H NMR spectra (700 MHz, $CDCl_3$) of **11** (1 mM) from 318K to 238K. Peaks highlighted in red and blue corresponds to the amide and amine proton signals respectively.

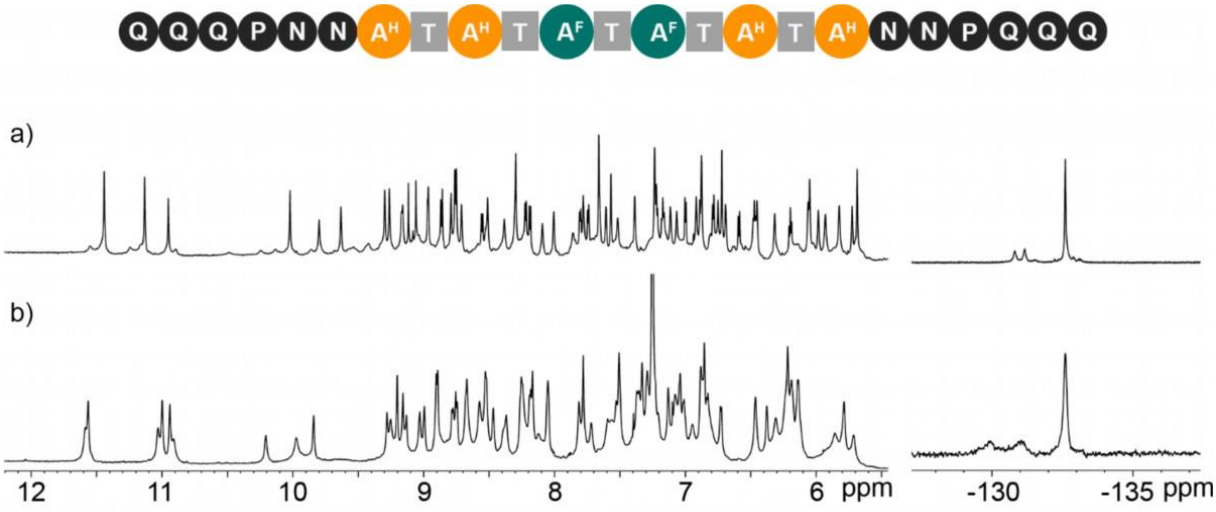


Figure S35. Part of 700 MHz ^{1}H NMR spectra at 298 K of oligomer **13** (1mM) in: (a) acetone-d_6, (b) $CDCl_3$ and corresponding 19F-NMR in respective solvents are given at right side.

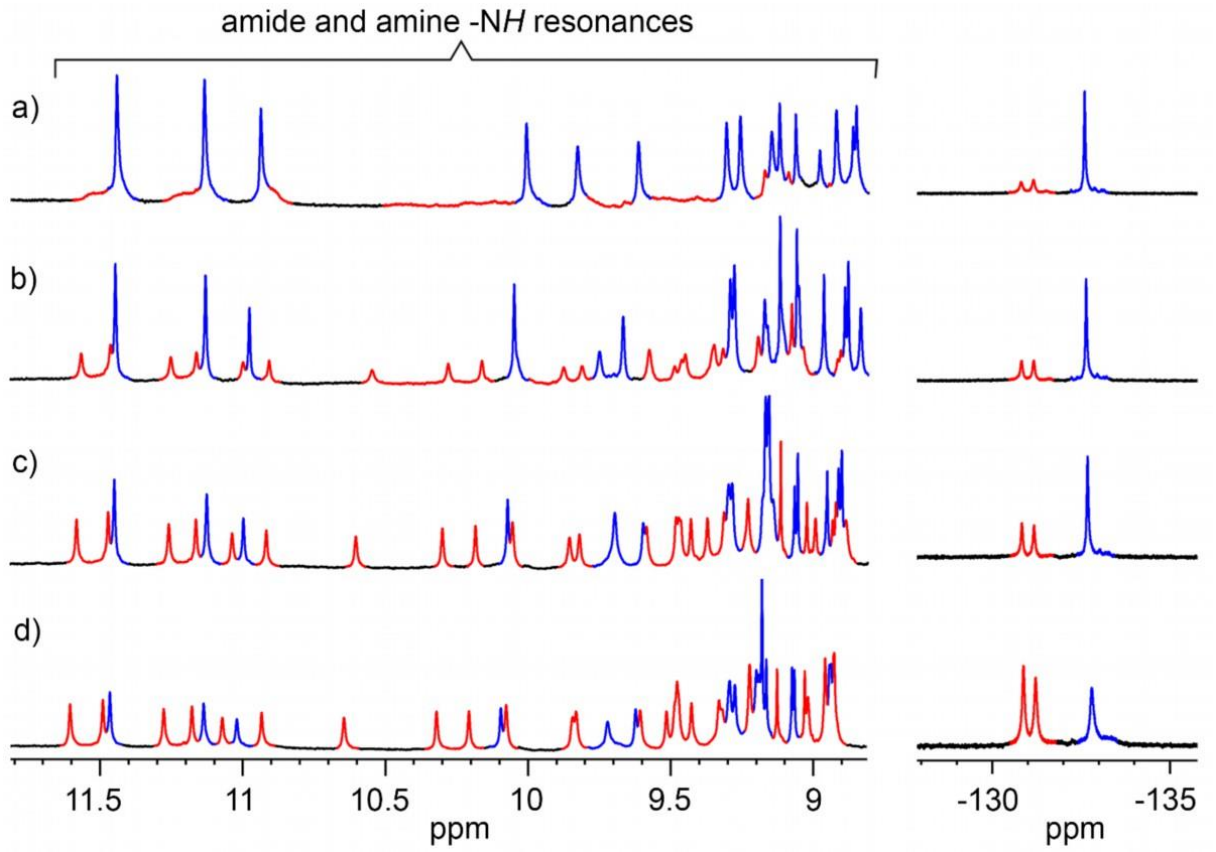


Figure S36. The 400 MHz ^{1}H-NMR (left) and side by side 376 MHz ^{19}F NMR (right) spectra of **13** (1 mm) at: a) 298 K and; b) 278 K; c) 258 K; and d) 248 K in acetone-d_6. Signals assigned to two different conformers **13**-*sym* and **13**-*asym* are highlighted in blue and red, respectively.

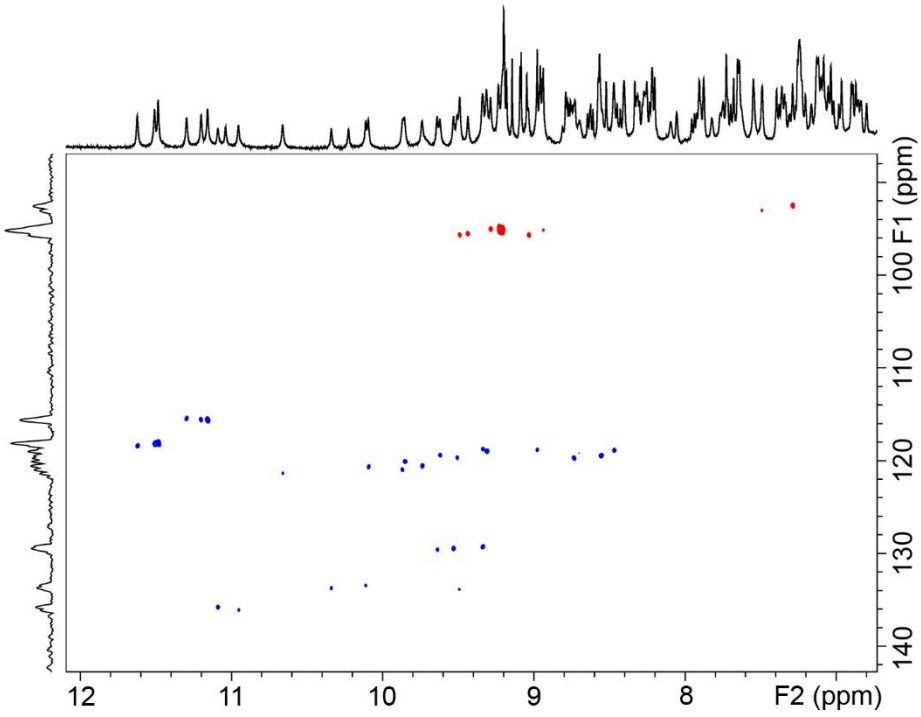


Figure S37. ^{1}H-^{15}N HSQC spectrum (700 MHz, acetone-d_6) of **13** (1 mM) at 258K. The -N*H* amide signals are depicted in blue and turn unit amine protons are shown in red colors.

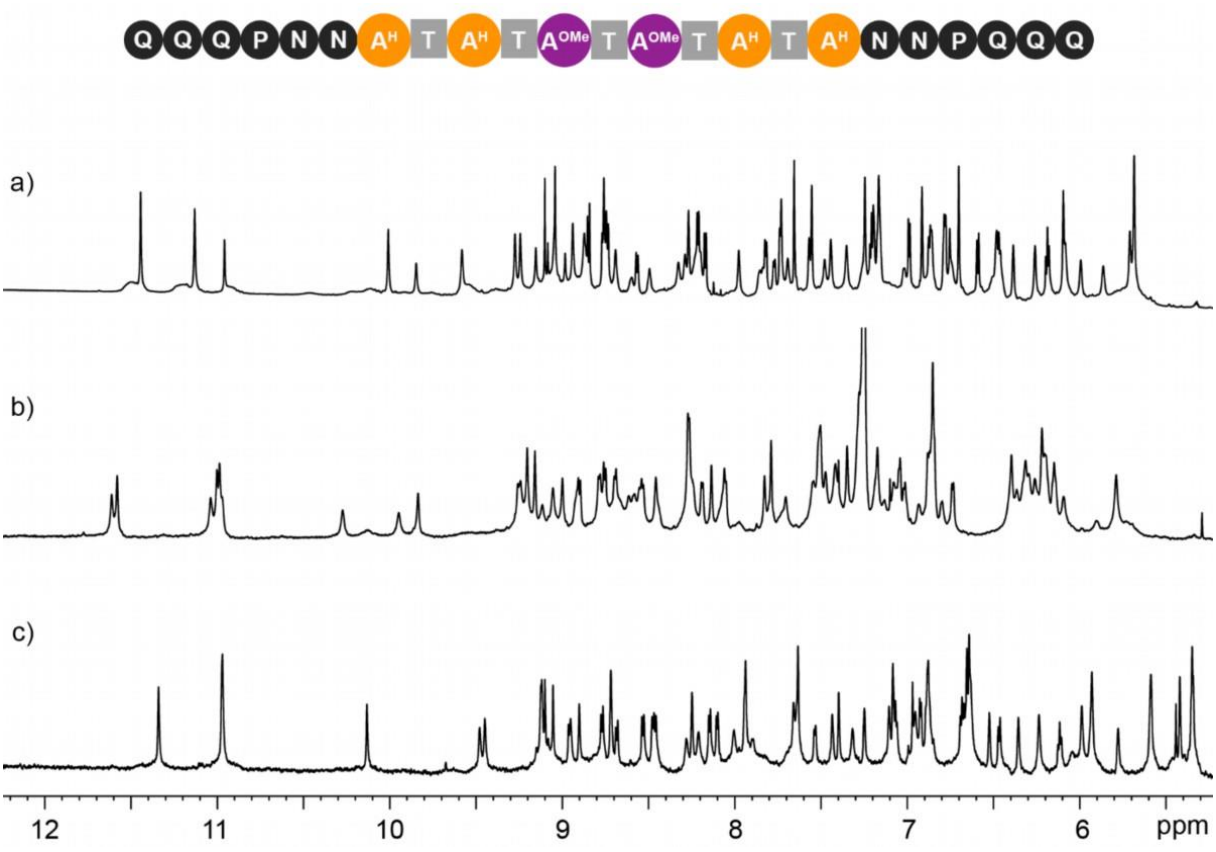


Figure S38. Part of 700 MHz ^{1}H NMR spectra at 298 K of oligomer **14** (1mM) in: (a) acetone-d_6, (b) $CDCl_3$, and (c) CD_3CN.

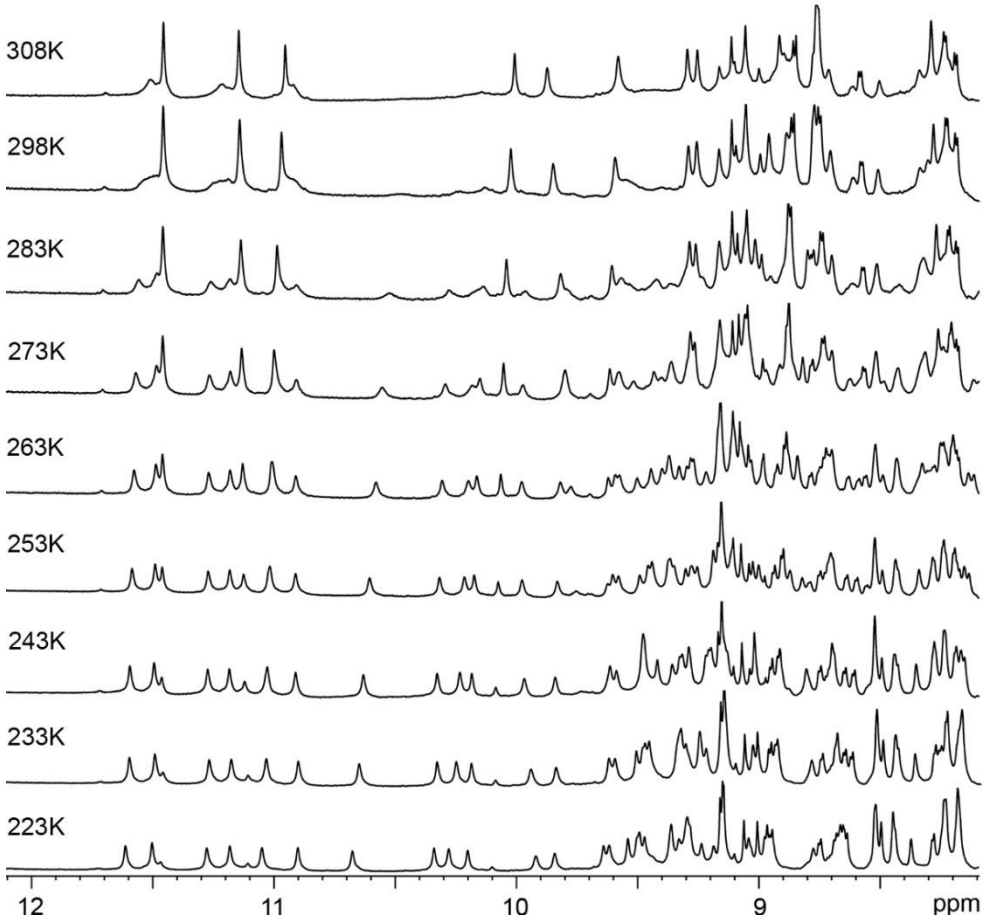


Figure S39. Part of the variable temperature ^{1}H NMR spectra (700 MHz, acetone-d_6) of **14** (1 mM) from 308K to 223K.

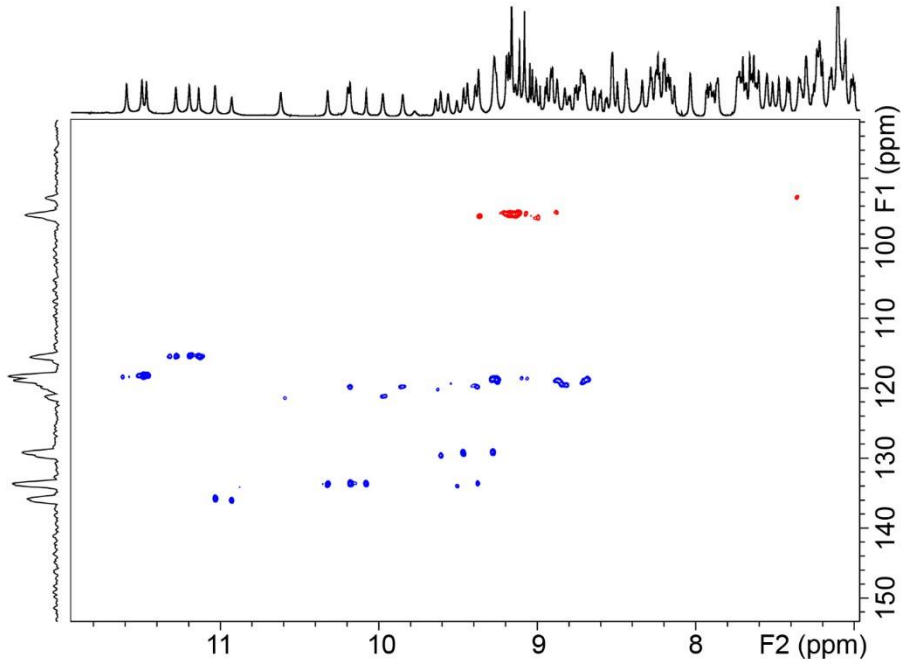


Figure S40. ^{1}H-^{15}N HSQC spectrum (700 MHz, acetone-d_6) of **14** (1 mM) at 258K. The N*H* amide signals are depicted in blue and turn unit amine protons are shown in red colors.

7. Photoirradiation of oligomers

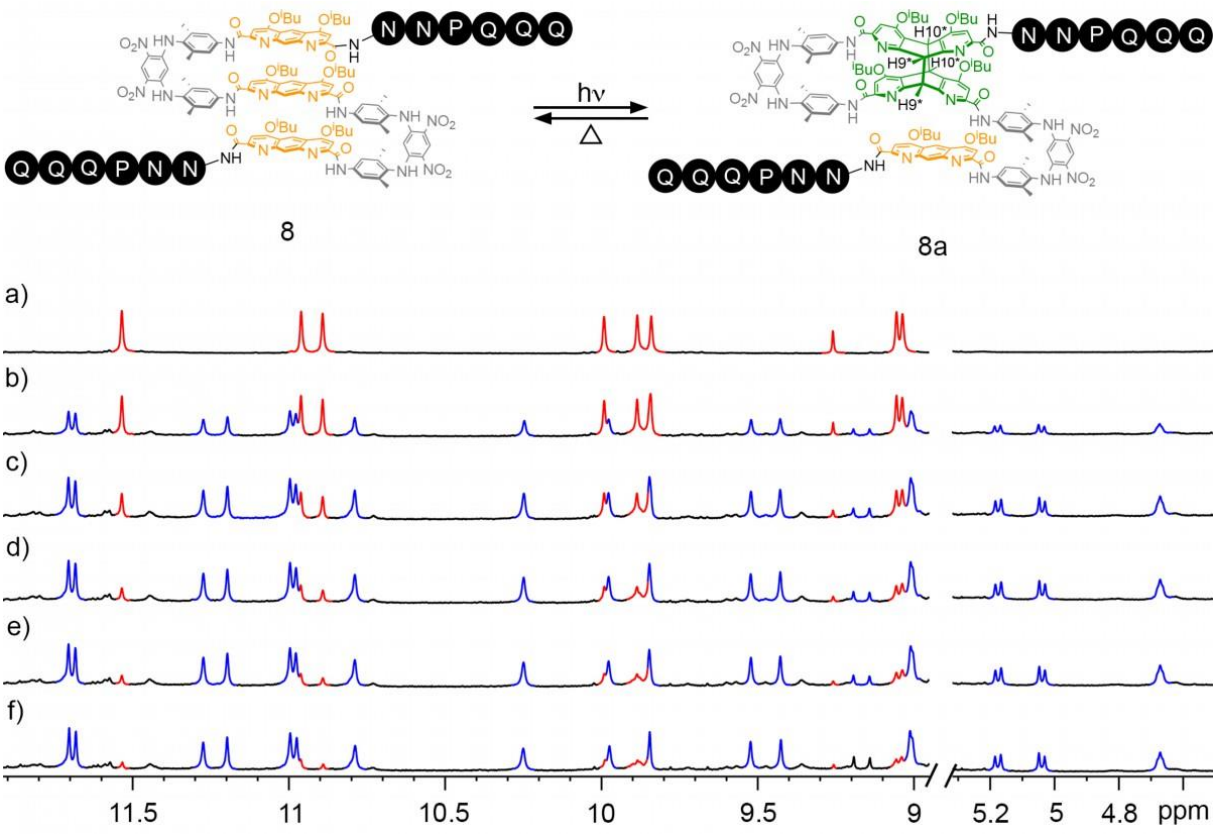


Figure S41. Part of the 700 MHz ^{1}H NMR spectra of **8** at 298K (1 mM in acetone-d_6) under photoirradiation after (a) 0 min; (b) 15 min.; (c) 30 min; (d) 45 min; (e) 60 min; and f) 90 min. The signals correspond to the starting material are shown in red and for photoproducts, **8a,** in blue. The presence of negligible amount of non identified byproduct cannot be assigned.

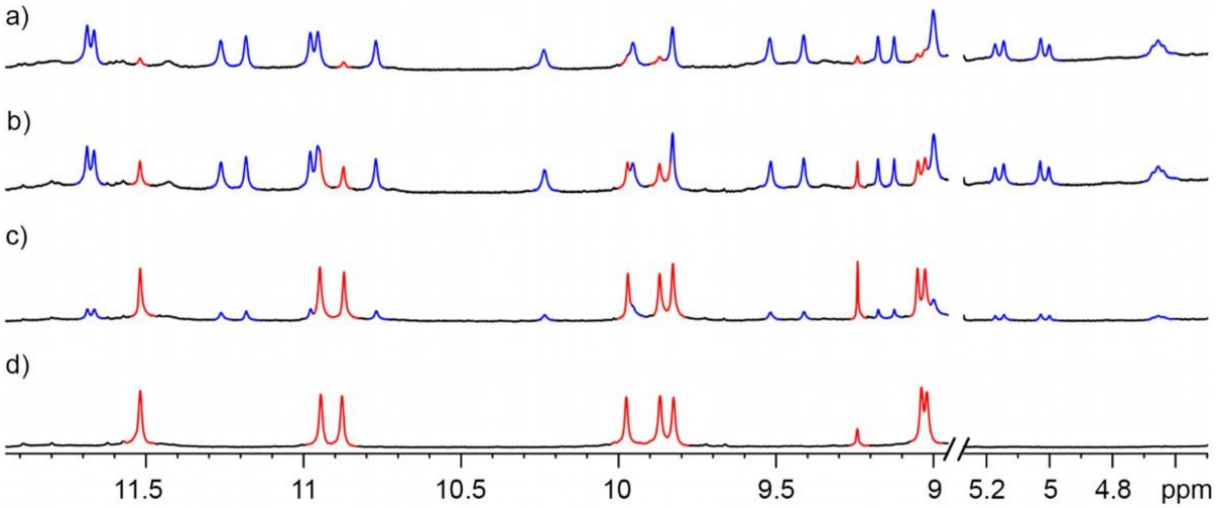


Figure S42. Part of the 400 MHz ^{1}H NMR spectra of **8a** at 298K after (a) 0 min; (b) 3 h; (c) 15 h; and (d) 36 h of heating in $CDCl_3$ at 333 K. The signals correspond to the **8a** and **8** are shown in blue and red respectively.

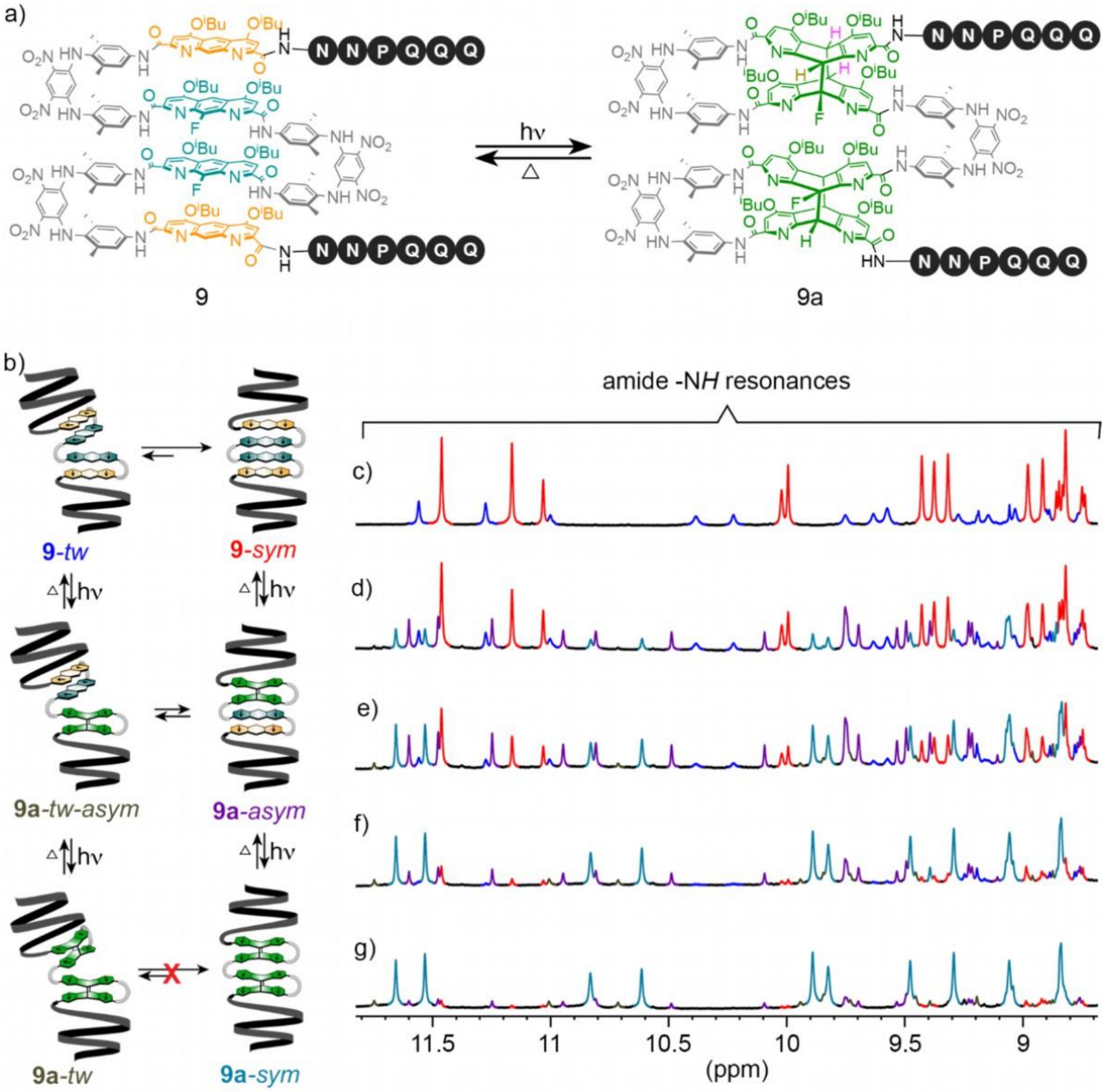


Figure S43. a) Photoproduct formation of **9** and thermal reversibility. b) Schematic illustration of stepwise photoadduct formation of different conformers of **9**. Initially two conformers, **9**-*tw* and **9**-*sym*, are present in an equilibrium at 298 K. Both have equal possibility to undergo stepwise photoadduct formation to final photoproduct **9a**-*tw* and **9a**-*sym* through intermediate monoadducts **9a**-*tw*-*asym* and **9a**-*asym*, respectively. Part of the 700 MHz ^{1}H NMR spectra of at 298K of **9** (1 mM in acetone-d_6) under photoirradiation after (b) 0 min; (c) 30 min.; (d) 1 h.; (e) 2 h.; and (f) 5 h. The signals corresponding to the starting two conformers **9**-*tw* and **9**-*sym* are shown in blue and red respectively. Signals in the photoirradiation steps are assigned to individual species are in accordance with color as depicted in (a).

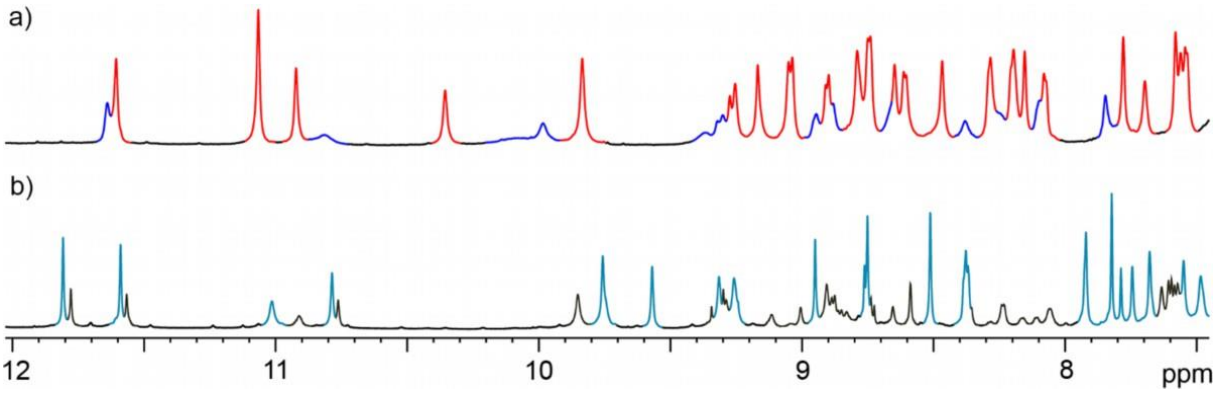


Figure S44. Part of the 700 MHz ^{1}H NMR spectra of at 298K of **9** (1 mM in $CDCl_3$) under photoirradiation. (a) before irradiation; and (b) after 5 h irradiation. The signals corresponding to the starting two conformers **9**-*tw* and **9**-*sym* are shown in blue and red respectively and signals corresponds to their respective photoproducts, **9a**-*tw* and **9a**-*sym*, are shown in grey and cyan.

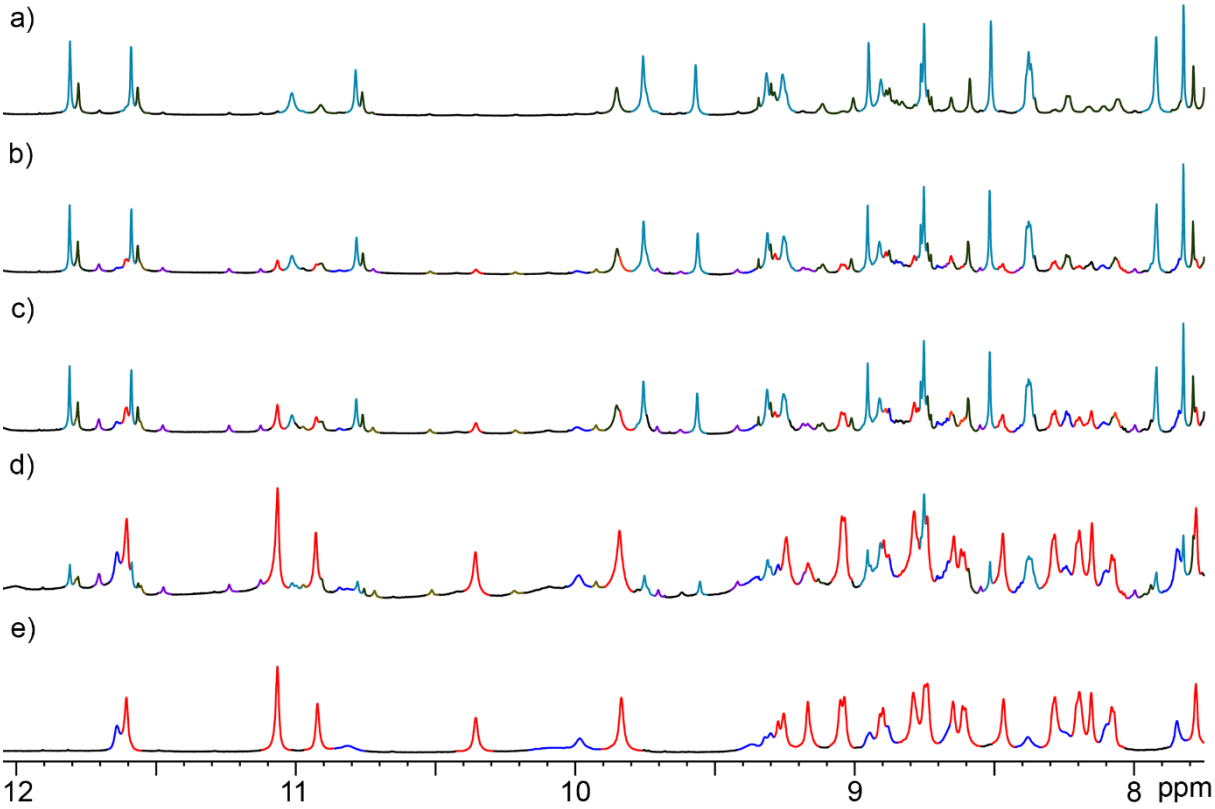


Figure S45. Thermal degradation of photoproduct **9a**. Part of the 400 MHz ^{1}H NMR spectra of **9a** at 298K (a) in $CDCl_3$; and after heating the solution for (b) 3 h; (c) 10 h; (d) 20 h; and (e) 48 h of heating in $CDCl_3$ at 333 K. The starting signals corresponding to two photoproduct conformers **9***a*-*tw* and **9a**-*sym*, shown in brown and cyan respectively. After 48 h of heating at 333 K, the photoproducts are converted back to the initial products **9**-*tw* and **9**-*sym*. Their signals are shown in blue and red respectively. In between, intermediates are observed which are the monoadducts and their color code is maintained according to Figure S43b.

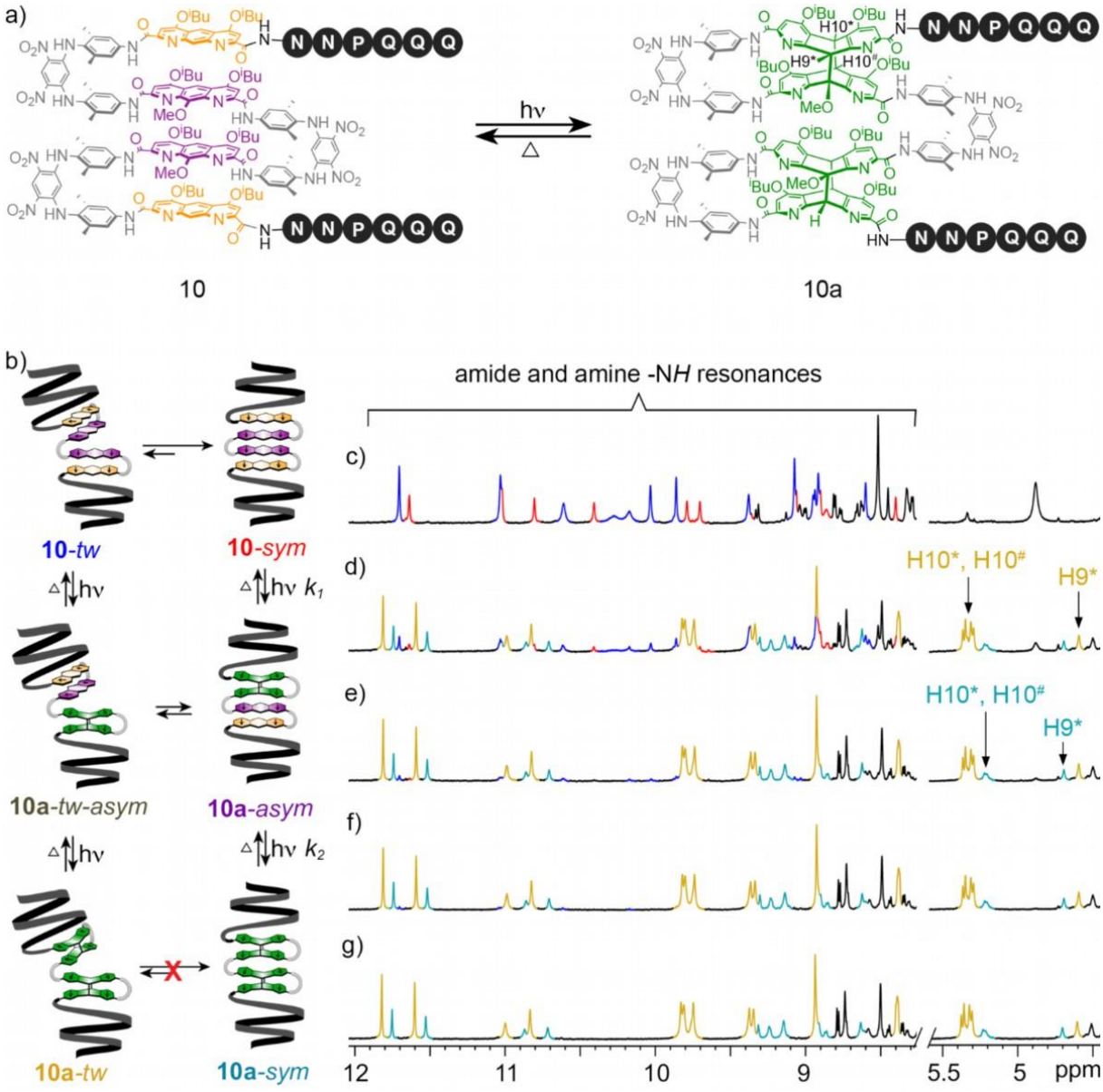


Figure S46. (a) Photoproduct formation of **10** and thermal reversibility. (b) Schematic illustration of stepwise photoadduct formation of different conformers of **10**. Initially two conformers, **10**-*tw* and **10**-*sym*, are present in an equilibrium at 298 K. Both have equal possibility to undergo stepwise photoadduct formation to final photoproduct **10a**-*tw* and **10a**-*sym* through intermediate monoadducts **10a**-*tw*-*asym* and **10a**-*asym*, respectively. Part of the 700 MHz ^{1}H NMR spectra at 298K of **10** (1 mM in $CDCl_3$) under photoirradiation after (c) 0 min; (d) 10 min; (e) 20 min; (f) 30 min; and (g) 60 min. The signals corresponding to the starting two conformers **10**-*tw* and **10**-*sym* are shown in blue and red respectively. Signals corresponding to photoproducts, **10a**-*tw* and **10a**-*sym*, are shown in olive and cyan respectively. The terms k_1 and k_2 are represent respective formation rate constants with respect to time of irradiation for monoadduct and di-adducts. Clearly, a cooperativity in the second photoadduct was observed with $k_2 >> k_1$.

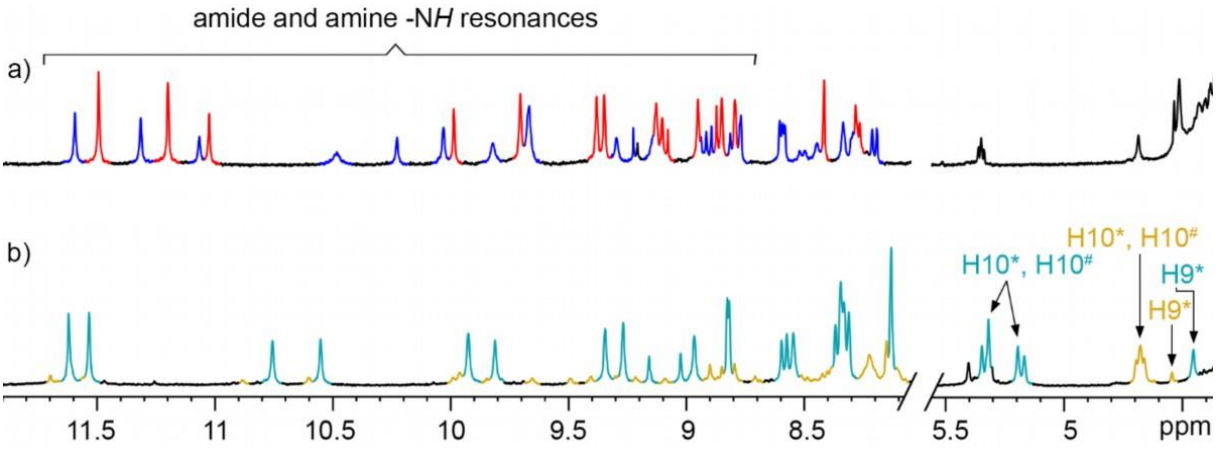


Figure S47. Part of the 400 MHz ^{1}H NMR spectra at 298K of **10** (1 mM in acetone-d_6) under photoirradiation after (a) 0 min; and (b) 60 min. The signals corresponding to the starting two conformers **10**-*tw* and **10**-*sym* are shown in blue and red respectively. Signals corresponding to photoproducts, **10a**-*tw* and **10a**-*sym*, are shown in olive and cyan respectively. Note that proportion of two photoproduct conformers, **10a**-*tw* and **10a**-*sym*, is different than that of their parent conformers.

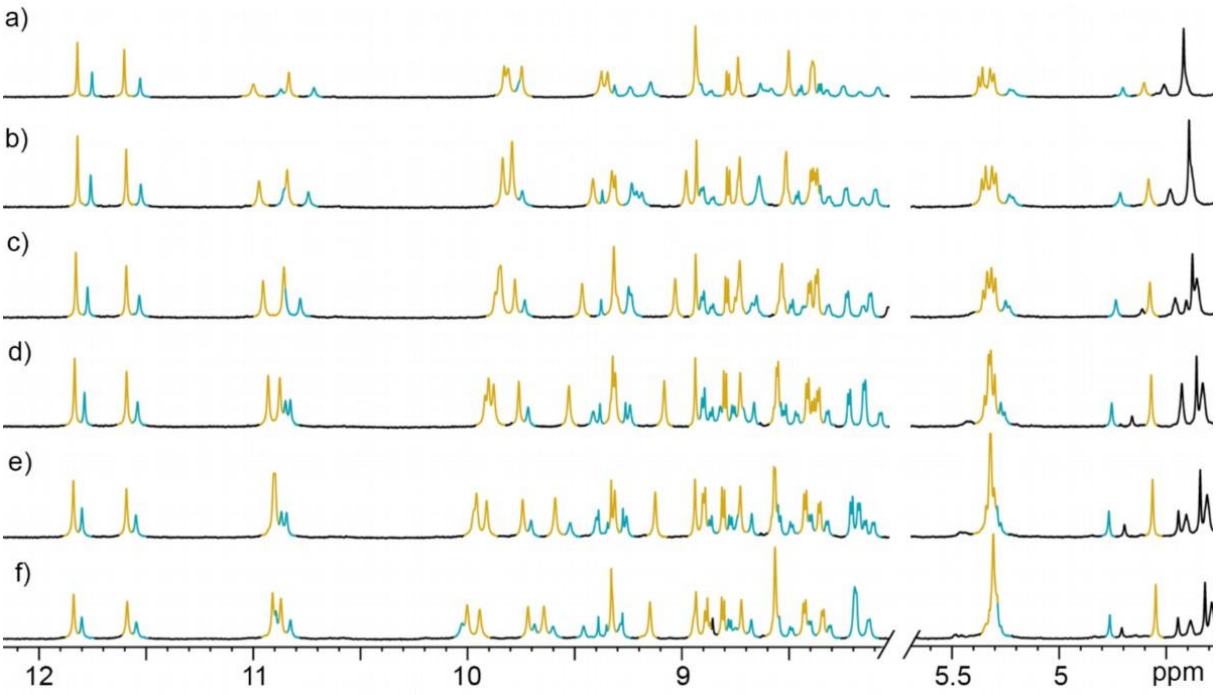


Figure S48. Part of the variable temperature ^{1}H NMR spectra (700 MHz, $CDCl_3$) of **10a** (1 mM) at different temperature. a) 298K; b) 288K; c) 278K; d) 268K; e)258K; and f) 248K. Peaks highlighted in olive and cyan corresponds to the **10a**-*tw* and **10a**-*sym* respectively. After photoproduct formation conformers have negligible influence of temperature variation.

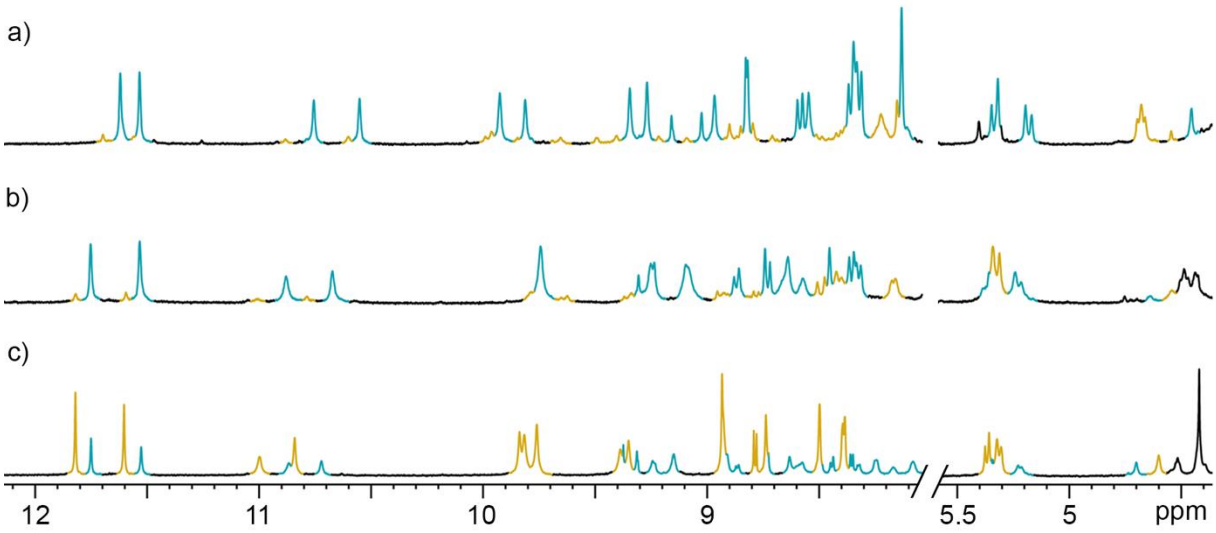


Figure S49. (a) Part of the 400 MHz ^{1}H NMR spectra of **10a** at 298K in acetone-d_6. (b) The ^{1}H NMR spectra of **10a** was recorded in $CDCl_3$ after 60 min photoirradiation in acetone. (c) In comparison, the ^{1}H NMR spectra was recorded in $CDCl_3$ after 60 min irradiation in $CDCl_3$. The signals correspond to two conformers, **10a**-*tw* and **10a**-*sym*, are shown in olive and cyan, respectively. The proportion of two photoproducts has significant difference when their starting conformers were irradiated in acetone-d_6 and $CDCl_3$. It is also evident that the photoproducts have no solvent effects.

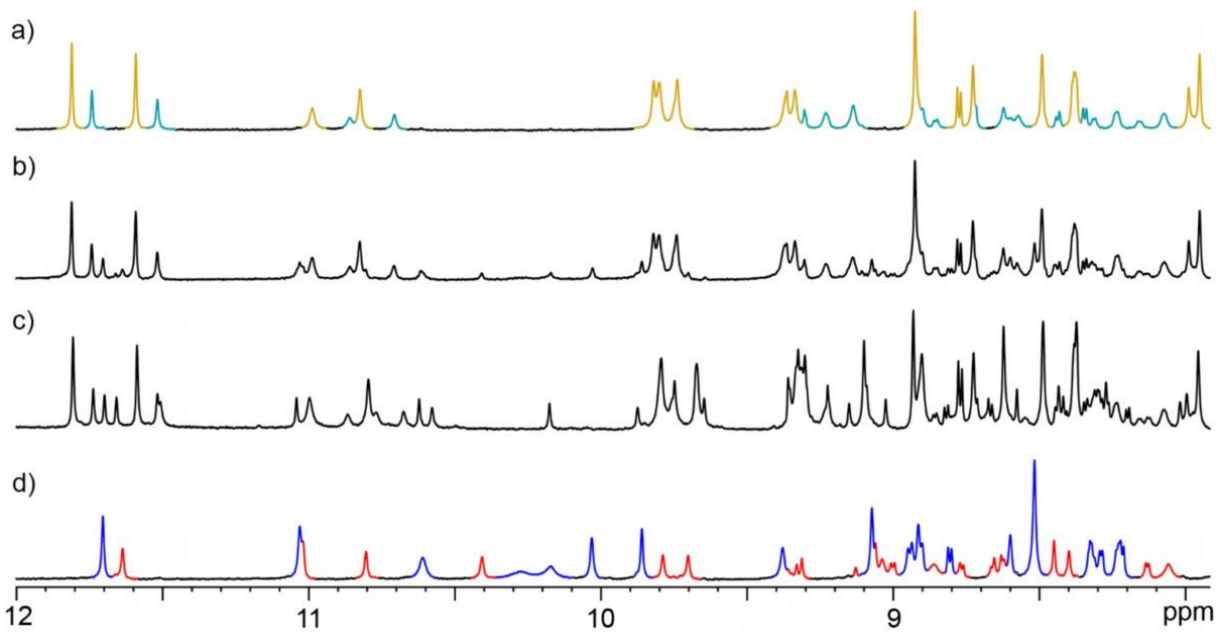


Figure S50. Part of the 700 MHz ^{1}H NMR spectra of **10a** at 298K (a) in $CDCl_3$; and after (b) 3 h; (c) 10 h; and (e) 48 h of heating in $CDCl_3$ at 333 K. The signals corresponding to the starting two conformers **10**-*tw* and **10**-*sym* are shown in blue and red respectively and signals corresponds to their respective photoproducts, **10a**-*tw* and **10a**-*sym*, are shown in olive and cyan.

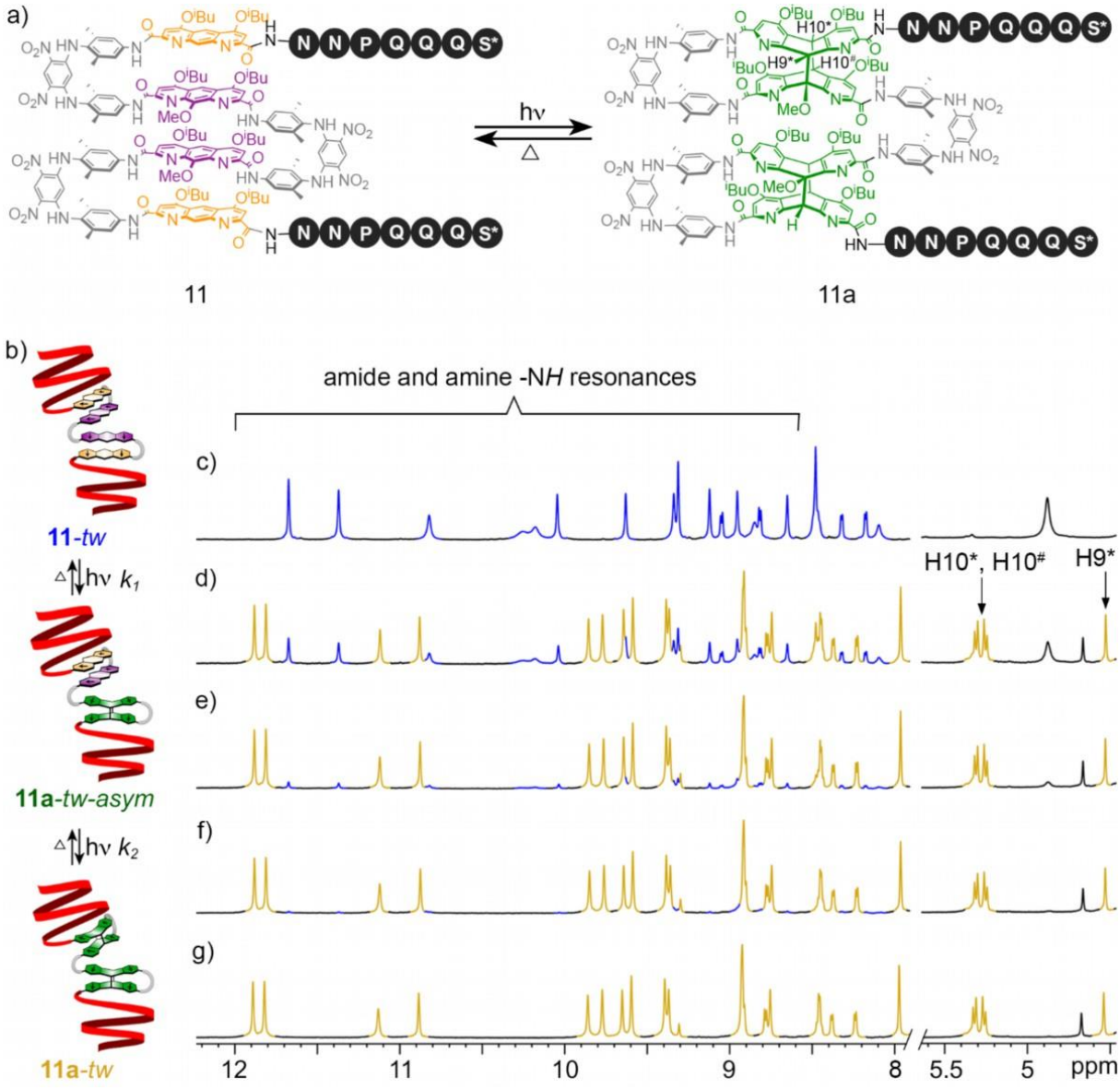


Figure S51. (a) Photoproduct formation of **11** and thermal reversibility. (b) Schematic illustration of stepwise photoadduct formation of **11**. Initially, conformer **11**-*tw* was present in the solution at 298 K. It can undergo stepwise photoadduct formation to final photoproduct **11a**-*tw* through intermediate monoadducts **11a**-*tw-asym.* Part of the 700 MHz ^{1}H NMR spectra at 298K of **11** (1 mM in $CDCl_3$) under photoirradiation after (c) 0 min; (d) 10 min; (e) 20 min; (f) 30 min; and (g) 40 min. The signals corresponding to the starting compound, **11**-*tw*, have been shown in blue and signals corresponding to photoproduct, **11a**-*tw*, are shown in olive. The terms k_1 and k_2 are represent respective formation rate constants with respect to time of irradiation for monoadduct and di-adducts. Interestingly, no monoadduct, **11a**-*tw-asym*, was identified which is indicating a high cooperativity in the second photoadduct.

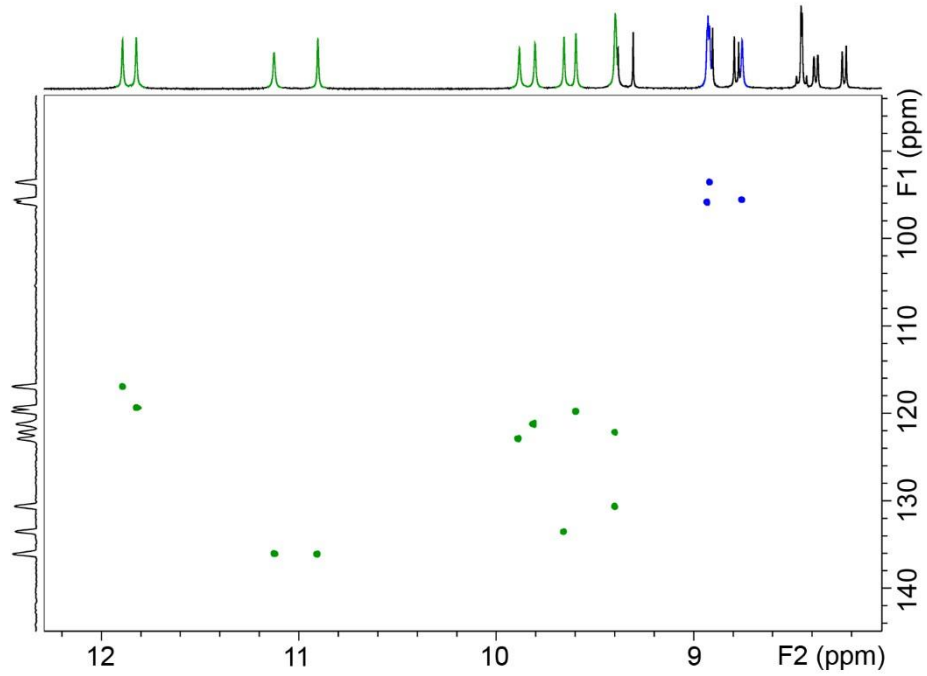


Figure S52. ^{1}H-^{15}N HSQC spectrum (400 MHz, $CDCl_3$) of photoproduct **11a** (1 mM) at 298K. The -N*H* amide signals are depicted in green and amine protons from turn units are shown in blue colors.

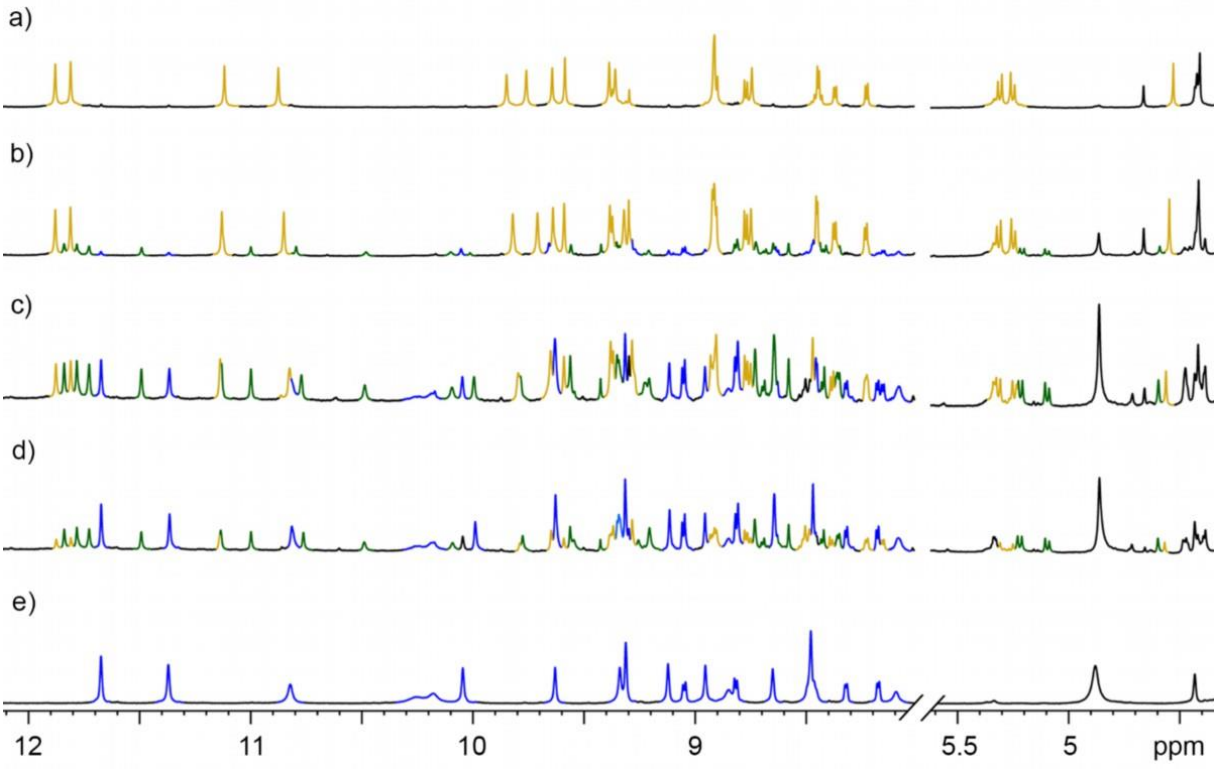


Figure S53. Part of the 700 MHz ^{1}H NMR spectra of **11a** at 298K (a) in $CDCl_3$; and after (b) 3 h; (c) 10 h; (e) 20 h; and (e) 48 h of heating in $CDCl_3$ at 333 K. The signals corresponding to the **11a** and **11** are showing in olive and blue respectively. In addition, signals correspond to monoadduct, **11a**-*tw*-*asym*, are shown in green.

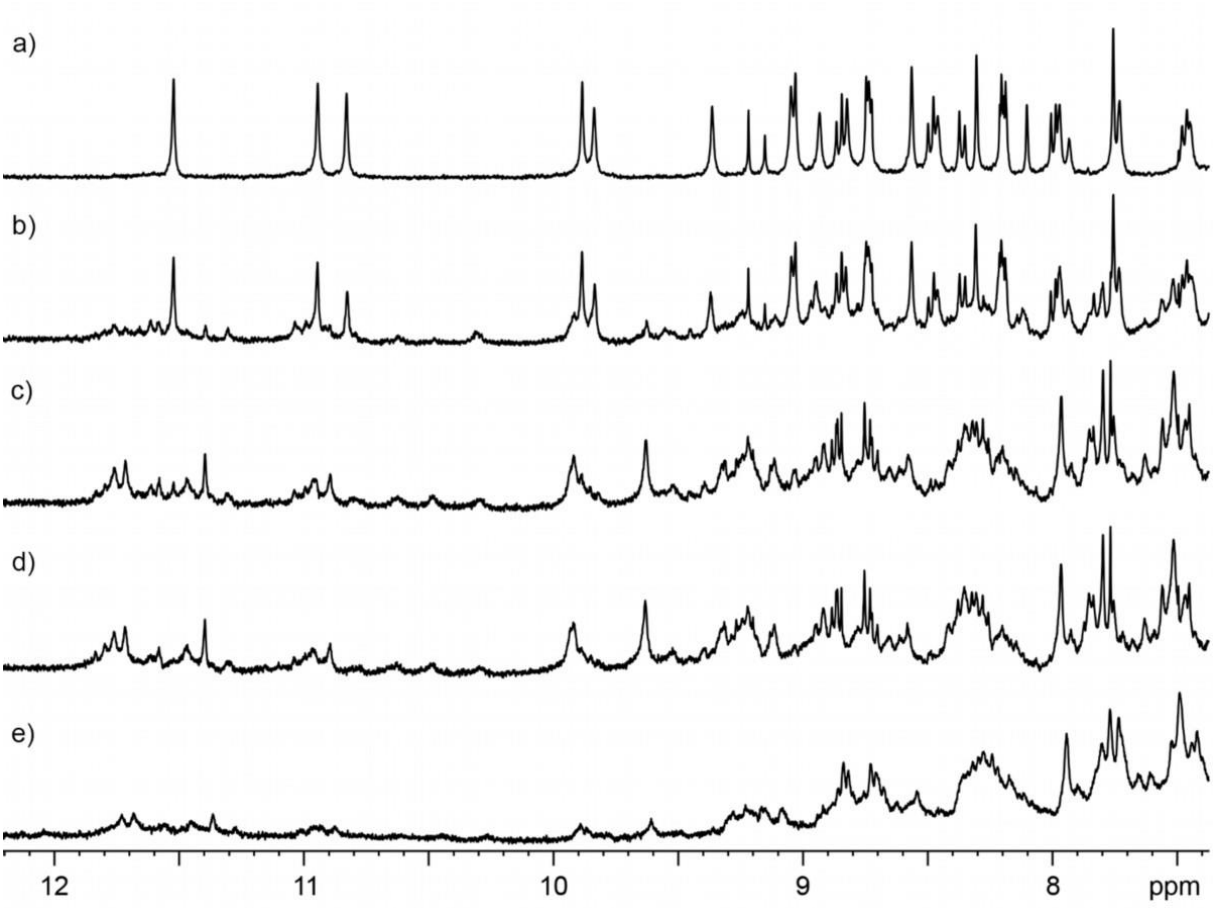


Figure S54. Part of the 700 MHz ^{1}H NMR spectra at 298K of **12** (1 mM in $CDCl_3$) under photoirradiation after (c) 0 min; (d) 30 min; (e) 2 h; (f) 3 h; and (g) 5 h. The signals corresponding to the photoproducts become significantly broad which makes difficult to monitor photoirradiation process.

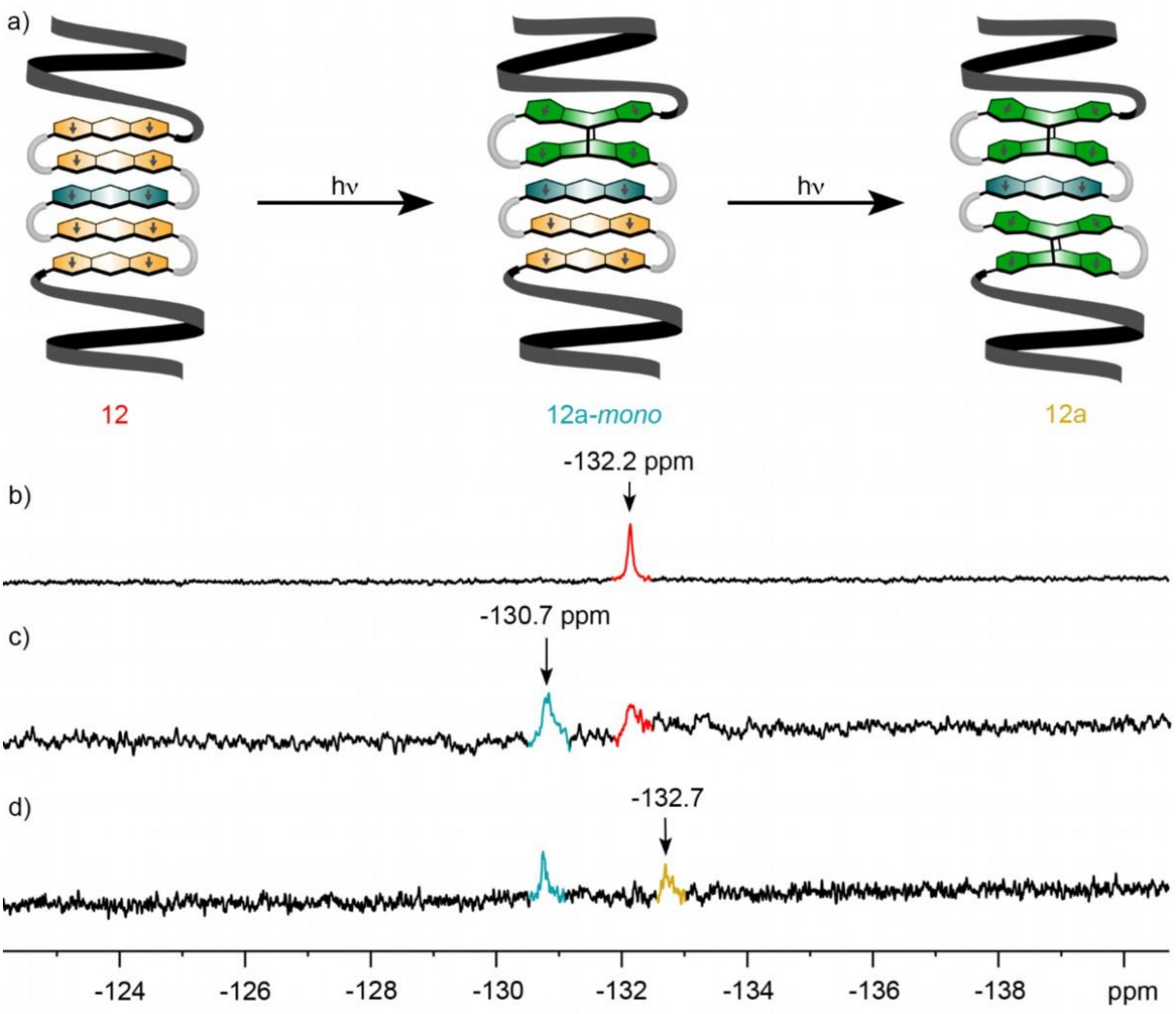


Figure S55. (a) Schematic illustration of stepwise photoadduct formation of **12**. It can undergo stepwise photoadduct formation to final photoproduct **12a** through intermediate monoadducts **12**-*mono*. Part of the 376 MHz ^{19}F NMR spectra at 298K of **12** (1 mM in $CDCl_3$) under photoirradiation after (b) 0 min; (c) 1 h; and (d) 5 h. The signals corresponding to the starting compound, **12**, have been shown in red and signals corresponding to photoproduct, **12a**-*mono* and **12a** are shown in cyan and olive respectively.

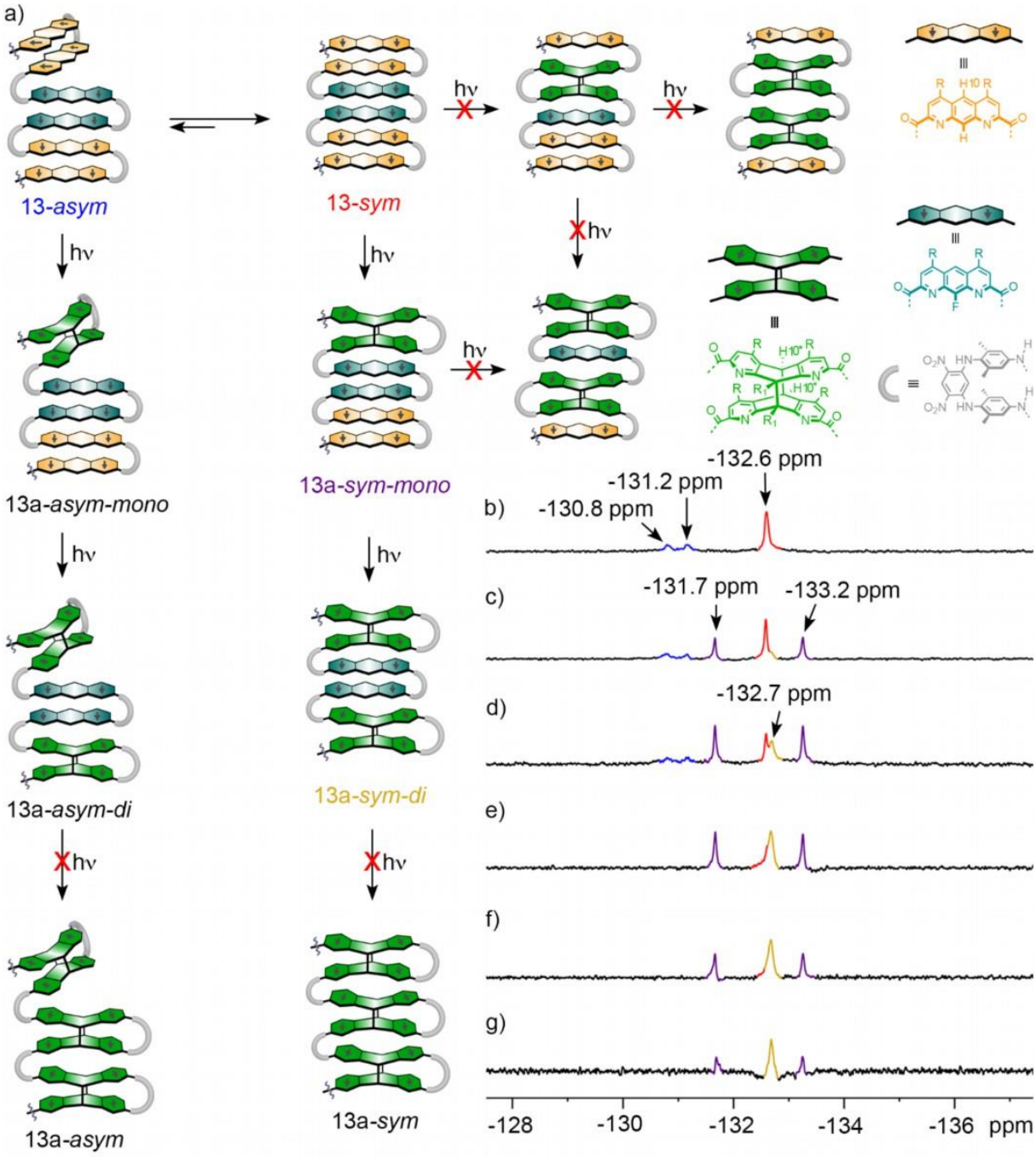


Figure S56. a) Schematic illustration of stepwise photoadduct formation of **13**. Initially two conformers, **13**-*asym* and **13**-*sym*, are present in an equilibrium at room temperature. Both have equal possibility to undergo stepwise photoadduct formation to final photoproduct **13a**-*asym* and **13a**-*sym* respectively. However, other uncontrolled photoadduct formation can be ruled out based on the design principle. In the illustration, helices are omitted for clarity. Chemical formula of each abbreviation given in the top right corner. Part of the 376 MHz ^{19}F NMR spectra of **13** (1 mm in acetone-d_6) at 298 K under photoirradiation after b) 0 min; c) 1 h; d) 2 h; e) 4 h; f) 6 h; and g) 12 h. Signals correspond to **13a**-*asym* and **13a**-*sym* are shown in blue and red respectively. Signals assigned to photoproducts **13a**-*sym-mono* and **13a**-*sym-di* are highlighted in purple and olive respectively. Note that final desired photoproducts **13a**-*asym* and **13a**-*sym* were not formed due to the low reactivity among two central A^F units.

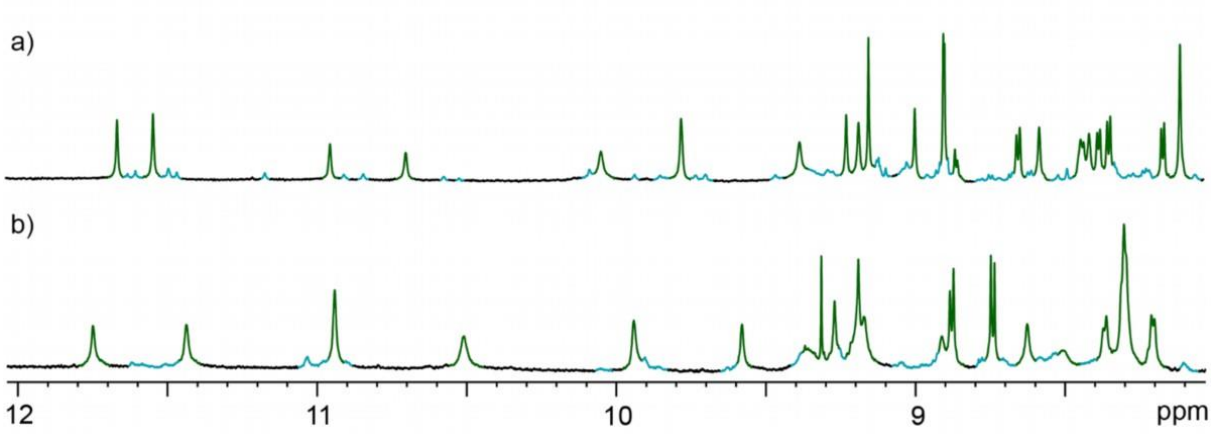


Figure S57. Part of the 700 MHz ^{1}H NMR spectra at 298K of **14a** (obtained from photoirradiation of **14** in acetone-d_6) in (a) acetone-d_6; and (c) $CDCl_3$. The signals corresponding to conformers **14a**-*sym* and **14a**-*asym* have been shown in green and cyan respectively.

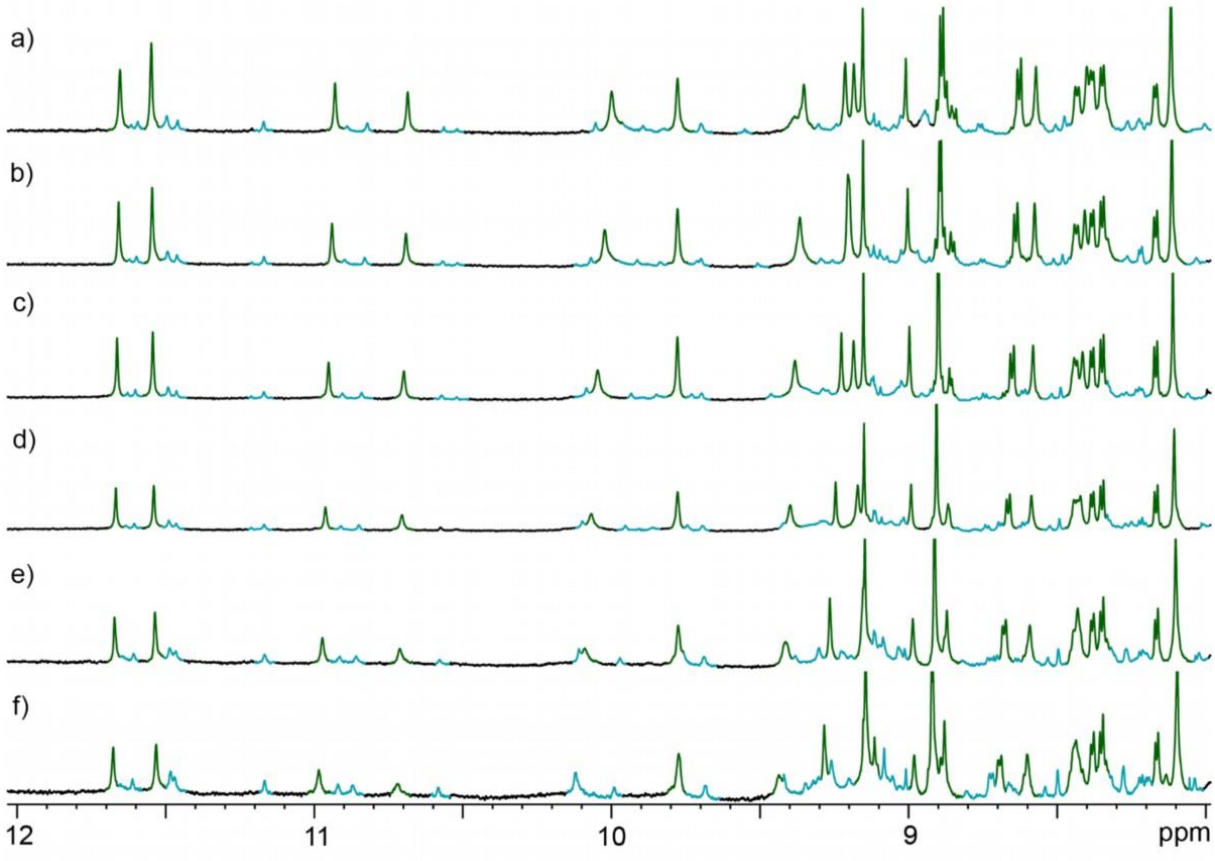


Figure S58. Part of the variable temperature ^{1}H NMR spectra (700 MHz, acetone-d_6) of **14a** at different temperature. a) 318K; b) 308K; c) 298K; d) 288K; e)278K; and f) 258K. The signals corresponding to conformers **14a**-*sym* and **14a**-*asym* have been shown in green and cyan respectively. After photoproduct formation conformers have negligible influence of temperature variation.

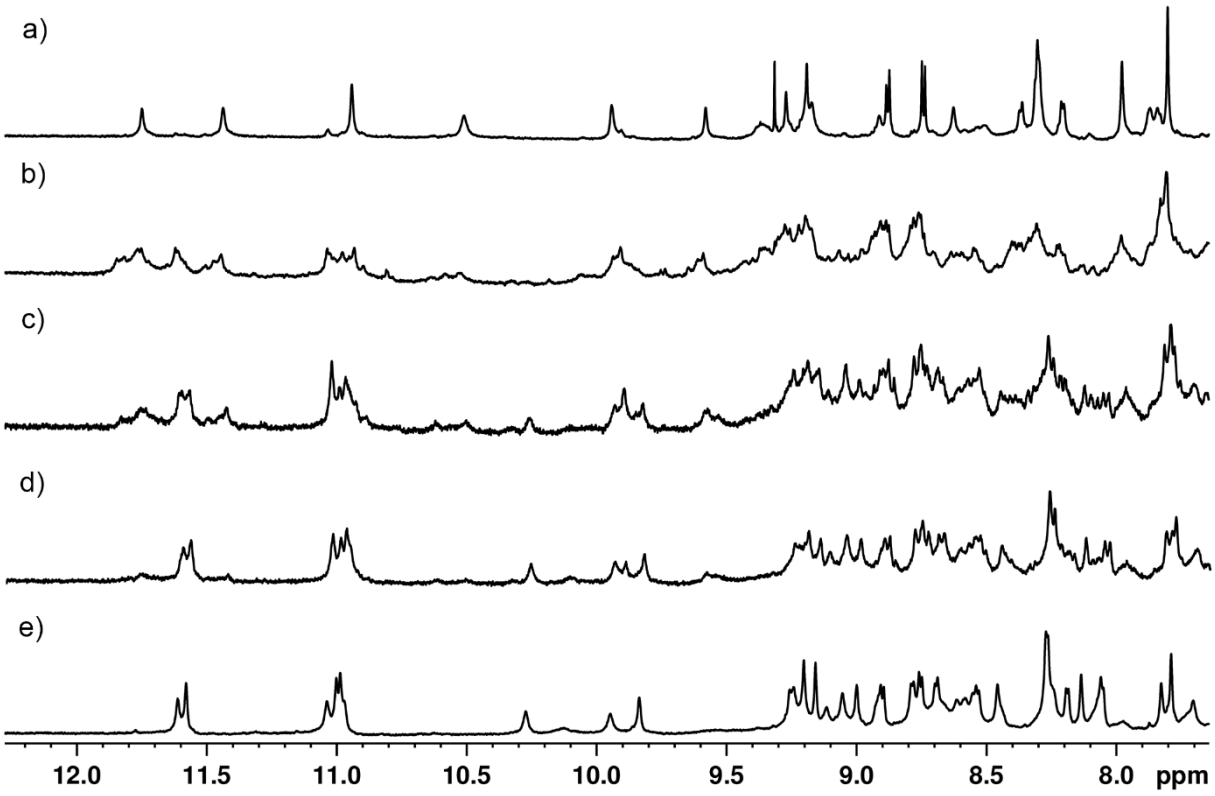


Figure S59. Part of the 400 MHz ^{1}H NMR spectra of **14a** at 298K (a) in $CDCl_3$; and after (b) 10 h; (c) 30 h; and (d) 60 h of heating in $CDCl_3$ at 333 K; e) Reference spectrum of **14**. The signals of the intermediate compounds are broad and correspond to photoproducts **14a**-*sym*-*mono*, **14a**-*sym*-*di*.

6. X-ray crystallography

Table S1. Crystal data and structure refinement for **8**.

Identification code	**8**
Empirical formula	$C_{259}H_{257}Cl_9N_{48}O_{44}$
Formula weight	5065.16
Temperature/K	130
Crystal system	monoclinic
Space group	$P2_1/n$
a/Å	24.5746(6)
b/Å	49.5101(11)
c/Å	27.7011(6)
α/°	90
β/°	102.621(2)
γ/°	90
Volume/Å^3	32889.3(13)
Z	4
ρ_{calc}g/cm^3	1.023
μ/mm^{-1}	1.232
F(000)	10608.0
Crystal size/mm^3	0.05 × 0.05 × 0.05
Radiation	CuKα (λ = 1.54184)
2Θ range for data collection/°	3.57 to 111.084
Reflections collected	135800
Independent reflections	41120 [R_{int} = 0.0594, R_{sigma} = 0.0530]
Data/restraints/parameters	41120/111/3281
Goodness-of-fit on F^2	1.396
Final R indexes [I>=2σ (I)]	R_1 = 0.1378, wR_2 = 0.3880
Final R indexes [all data]	R_1 = 0.1857, wR_2 = 0.4189
CCDC #	2144662

Table S2. Crystal data and structure refinement for **10**

Identification code	**10**
Empirical formula	$C_{292.5}H_{275}Cl_{12}N_{56}O_{54}$
Formula weight	5864.07
Temperature/K	130
Crystal system	triclinic
Space group	P-1
a/Å	24.1819(8)
b/Å	28.1154(8)
c/Å	41.6885(7)
α/°	103.493(2)
β/°	91.075(2)
γ/°	114.626(2)
Volume/Å^3	24837.6(12)
Z	2
ρ_{calc}g/cm^3	0.784
μ/mm^{-1}	1.026
F(000)	6116.0
Crystal size/mm^3	0.02 × 0.02 × 0.02
Radiation	CuKα (λ = 1.54178)
2Θ range for data collection/°	3.586 to 95.304
Reflections collected	80745
Independent reflections	41817 [R_{int} = 0.0667, R_{sigma} = 0.0900]
Data/restraints/parameters	41817/17375/3693
Goodness-of-fit on F^2	1.843
Final R indexes [I>=2σ (I)]	R_1 = 0.1995, wR_2 = 0.5081
Final R indexes [all data]	R_1 = 0.2369, wR_2 = 0.5345
CCDC #	2144663

Table S3. Crystal data and structure refinement for **13**-*sym*.

Identification code	**13**-*sym*
Empirical formula	$C_{352}H_{275}F_2N_{72}O_{68}$
Formula weight	6639.42
Temperature/K	130
Crystal system	orthorhombic
Space group	Pbca
a/Å	45.2959(12)
b/Å	40.8492(8)
c/Å	61.6329(12)
α/°	90
β/°	90
γ/°	90
Volume/Å^3	114039(4)
Z	8
ρ_{calc}g/cm^3	0.773
μ/mm^{-1}	0.463
F(000)	27624.0
Crystal size/mm^3	0.05 × 0.05 × 0.05
Radiation	CuKα (λ = 1.54178)
2Θ range for data collection/°	4.088 to 89.078
Reflections collected	345597
Independent reflections	44023 [R_{int} = 0.1821, R_{sigma} = 0.0816]
Data/restraints/parameters	44023/29266/4339
Goodness-of-fit on F^2	1.767
Final R indexes [I>=2σ (I)]	R_1 = 0.2454, wR_2 = 0.5257
Final R indexes [all data]	R_1 = 0.2877, wR_2 = 0.5581
CCDC #	2144666

Table S4. Crystal data and structure refinement for **14**-*asym*

Identification code	**14**-*asym*
Empirical formula	$C_{411}H_{438}N_{72}O_{81}$
Formula weight	7682.31
Temperature/K	120
Crystal system	triclinic
Space group	P-1
a/Å	21.130(4)
b/Å	34.790(7)
c/Å	39.590(8)
α/°	69.20(3)
β/°	77.70(3)
γ/°	86.10(3)
Volume/Å^3	26581(11)
Z	2
ρ_{calc}g/cm^3	0.960
μ/mm^{-1}	0.358
F(000)	8112.0
Crystal size/mm^3	0.05 × 0.05 × 0.05
Radiation	Ga (λ = 1.340)
2Θ range for data collection/°	4.066 to 85.182
Reflections collected	157328
Independent reflections	54334 [R_{int} = 0.1338, R_{sigma} = 0.1068]
Data/restraints/parameters	54334/4510/4942
Goodness-of-fit on F^2	1.202
Final R indexes [I>=2σ (I)]	R_1 = 0.1266, wR_2 = 0.3449
Final R indexes [all data]	R_1 = 0.1886, wR_2 = 0.3828
CCDC #	2144667

8. Molecular mechanics

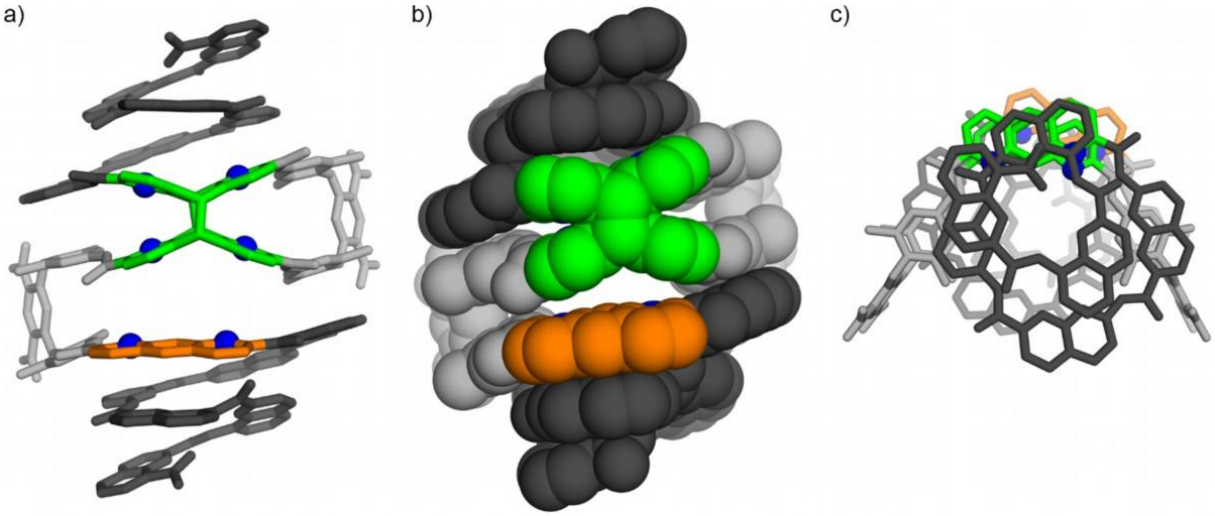


Figure S60. (a) Back view of the energy-minimized molecular model of **8a** using the Merck Molecular Force Field static (MMFFs) shown in tube representation. (b) and (c) Back and top view of the same in space filling and tube representation, respectively. (The structures are shown with color-coded monomers as defined earlier. Blue balls depicting endocyclic nitrogen atoms. Hydrogen atoms and side chains are omitted for clarity.

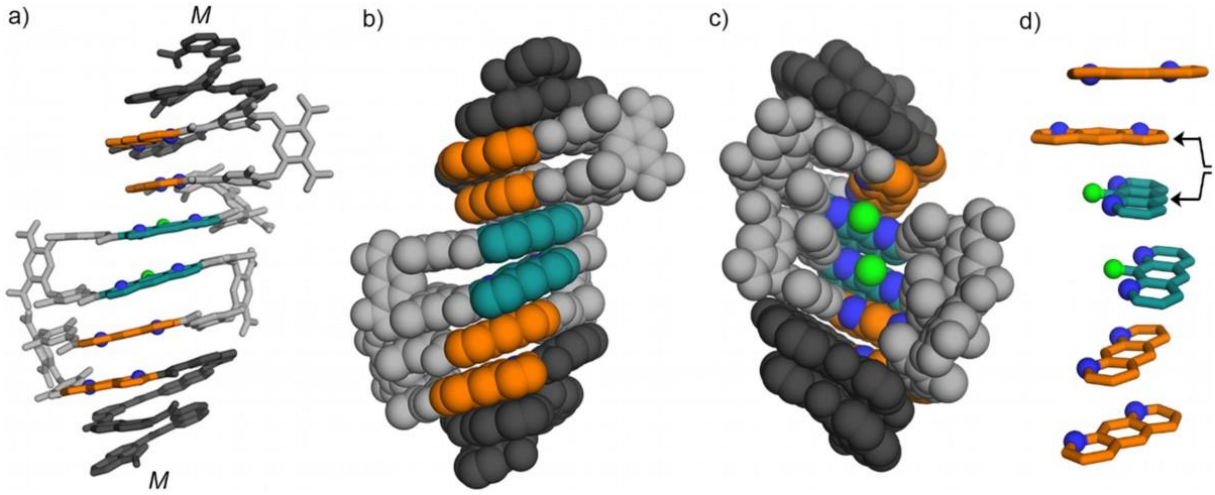


Figure S61. (a) Back view of the energy-minimized molecular model of **13**-*asym* using the Merck Molecular Force Field static (MMFFs) shown in tube representation. (b) and (c) Back and front view of the same in space filling representation, respectively. (d) Orientation of the diazaanthracene units. Arrows indicate the only pair of antiparallel diazaanthracene units. The structures are shown with color-coded monomers as defined earlier. Blue balls depicting endocyclic nitrogen atoms. Hydrogen atoms and side chains are omitted for clarity.

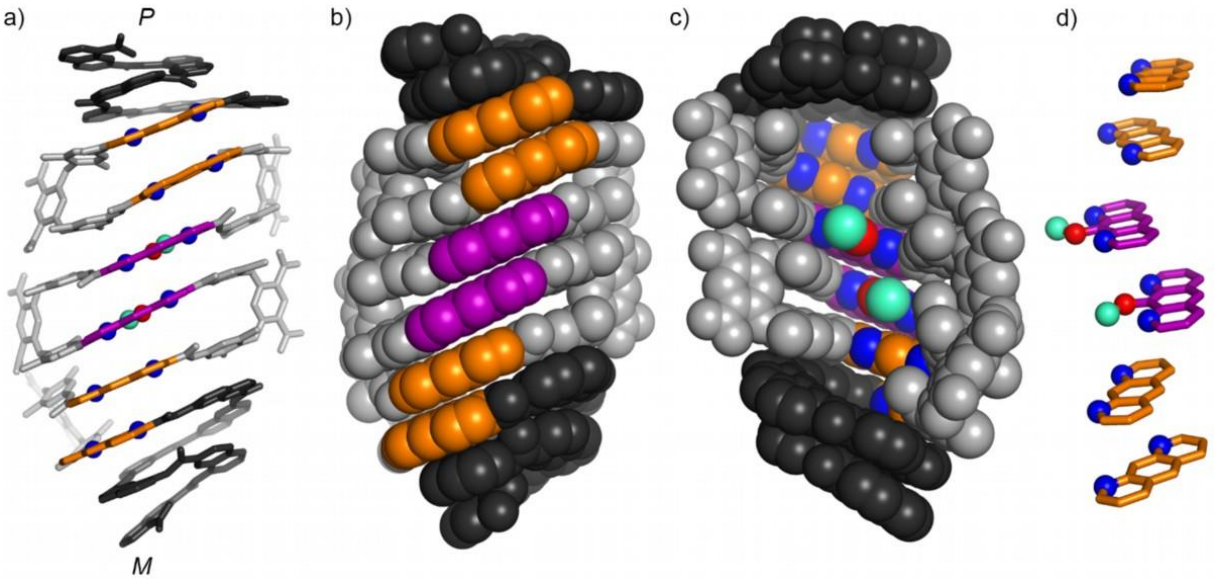


Figure S62. (a) Back view of the energy-minimized molecular model of **14**-*sym* using the Merck Molecular Force Field static (MMFFs) shown in tube representation. (b) and (c) Back and front view of the same in space filling representation, respectively. (d) Parallel orientation of the diazaanthracene units. The structures are shown with color-coded monomers as defined earlier. Blue balls depicting endocyclic nitrogen atoms. Hydrogen atoms and side chains are omitted for clarity.

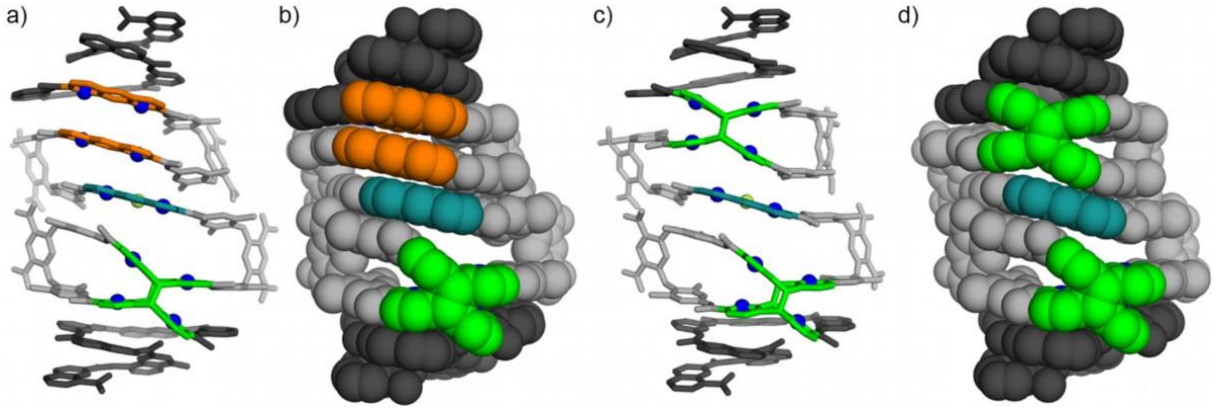


Figure S63. (a) and (b) Back view of the energy-minimized molecular model of mono (**12a**-*mono*) and di-photoadduct (**12a**) products of **12**, respectively, using the Merck Molecular Force Field static (MMFFs) shown in tube representation. (b) and (d) Back view of the same in space filling representation, respectively. The structures are shown with color-coded representation as defined earlier. Blue balls depicting endocyclic nitrogen atoms. Hydrogen atoms and side chains are omitted for clarity.

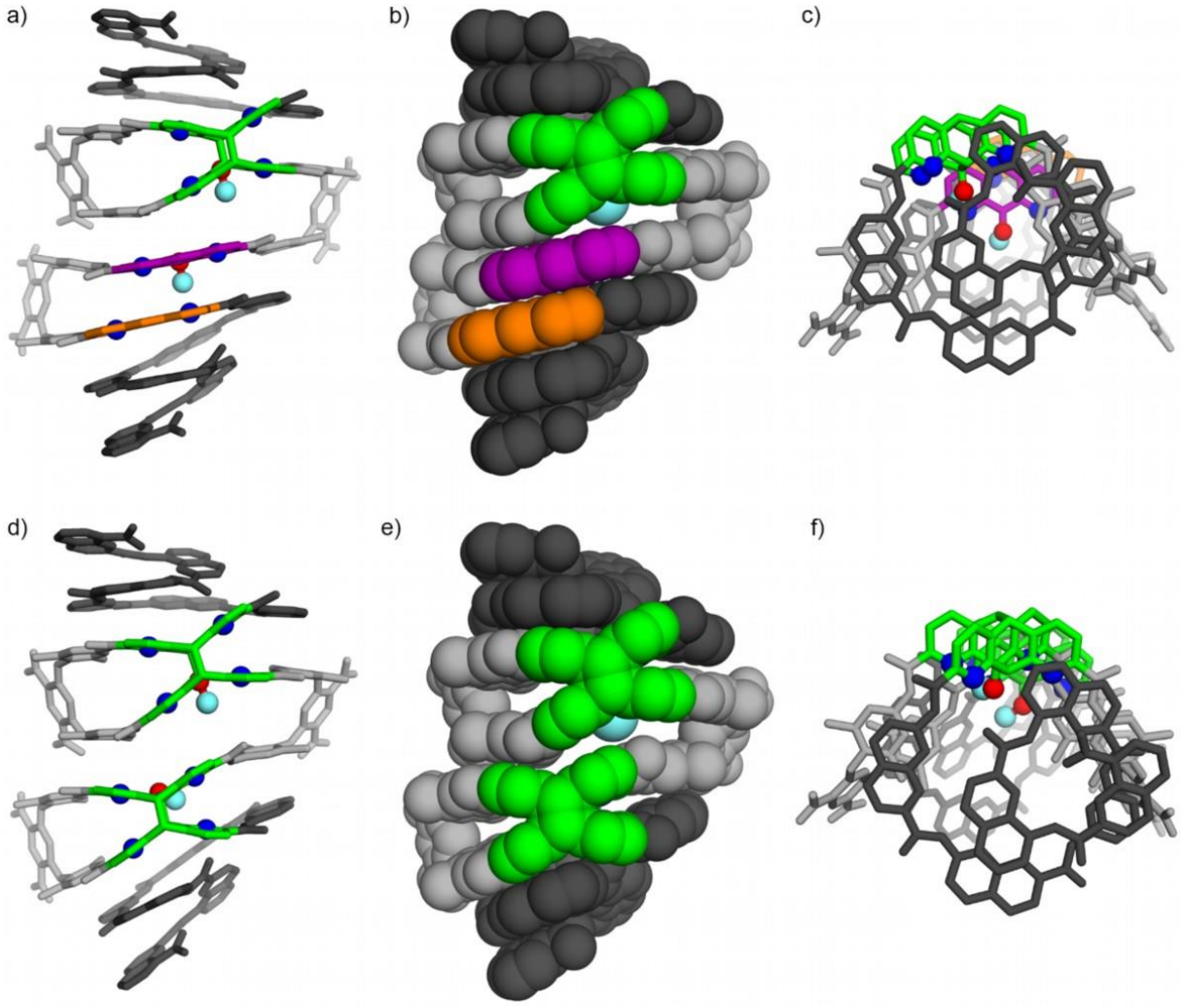


Figure S64. (a) and (d) Back view of the energy-minimized molecular model of mono (**10a**-*asym*) and di-photoadduct (**10a**-*sym*) products of **10**-*sym*, respectively, using the Merck Molecular Force Field static (MMFFs) shown in tube representation. (b) and (e) Back view of the same in space filling representation, respectively. (c) and (f) Represents the respective top views. The structures are shown with color-coded representation as defined earlier. Blue balls depicting endocyclic nitrogen atoms. Hydrogen atoms and side chains are omitted for clarity.

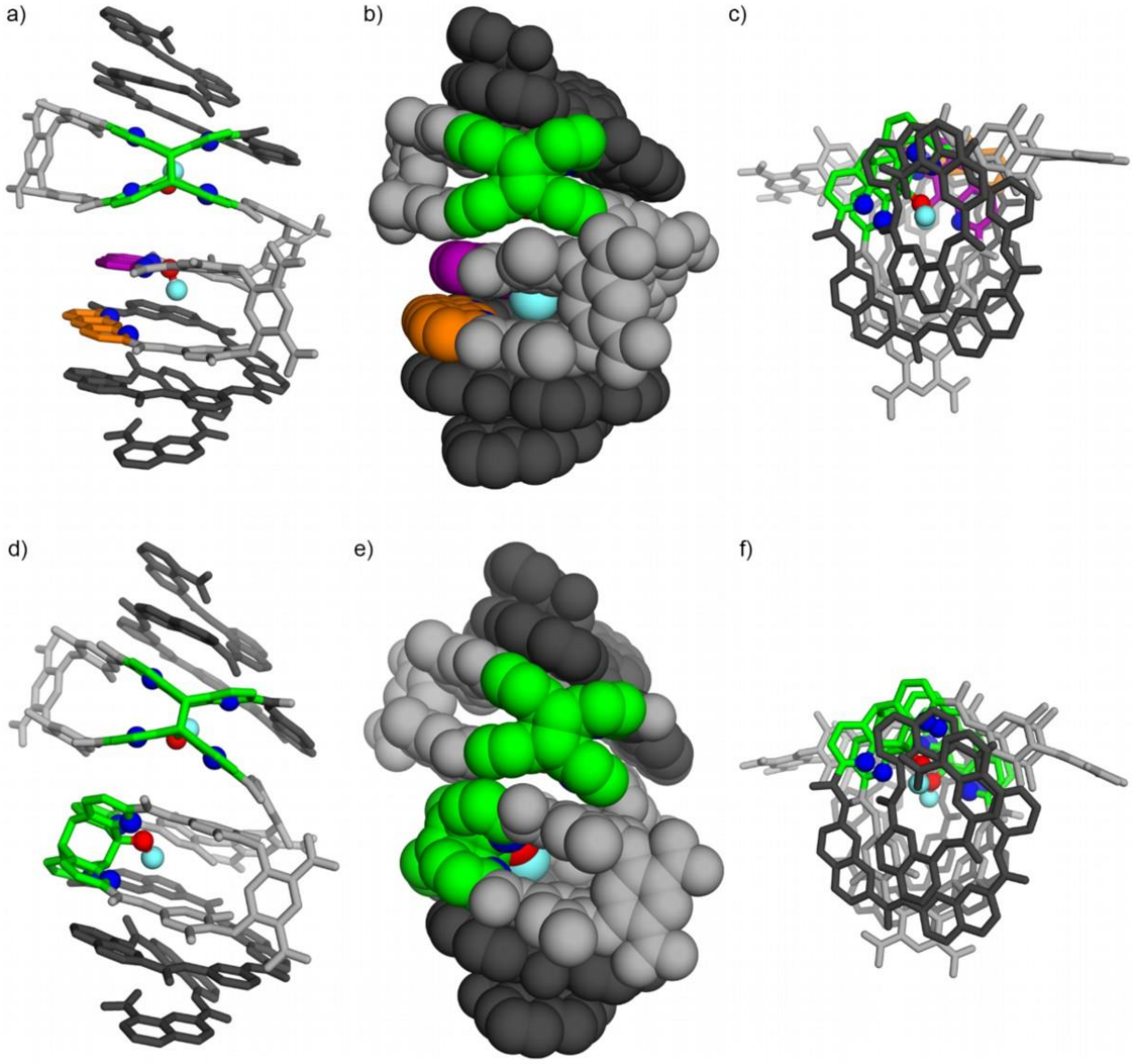


Figure S65. (a) and (d) Back view of the energy-minimized molecular model of mono (**10a**-*tw*-*asym*) and di-photoadduct (**10a**-*tw*) products of **10**-*tw*, respectively, using the Merck Molecular Force Field static (MMFFs) shown in tube representation. (b) and (e) Back view of the same in space filling representation, respectively. (c) and (f) Represents the respective top views. The structures are shown with color-coded representation as defined earlier. Blue balls depicting endocyclic nitrogen atoms. Hydrogen atoms and side chains are omitted for clarity.

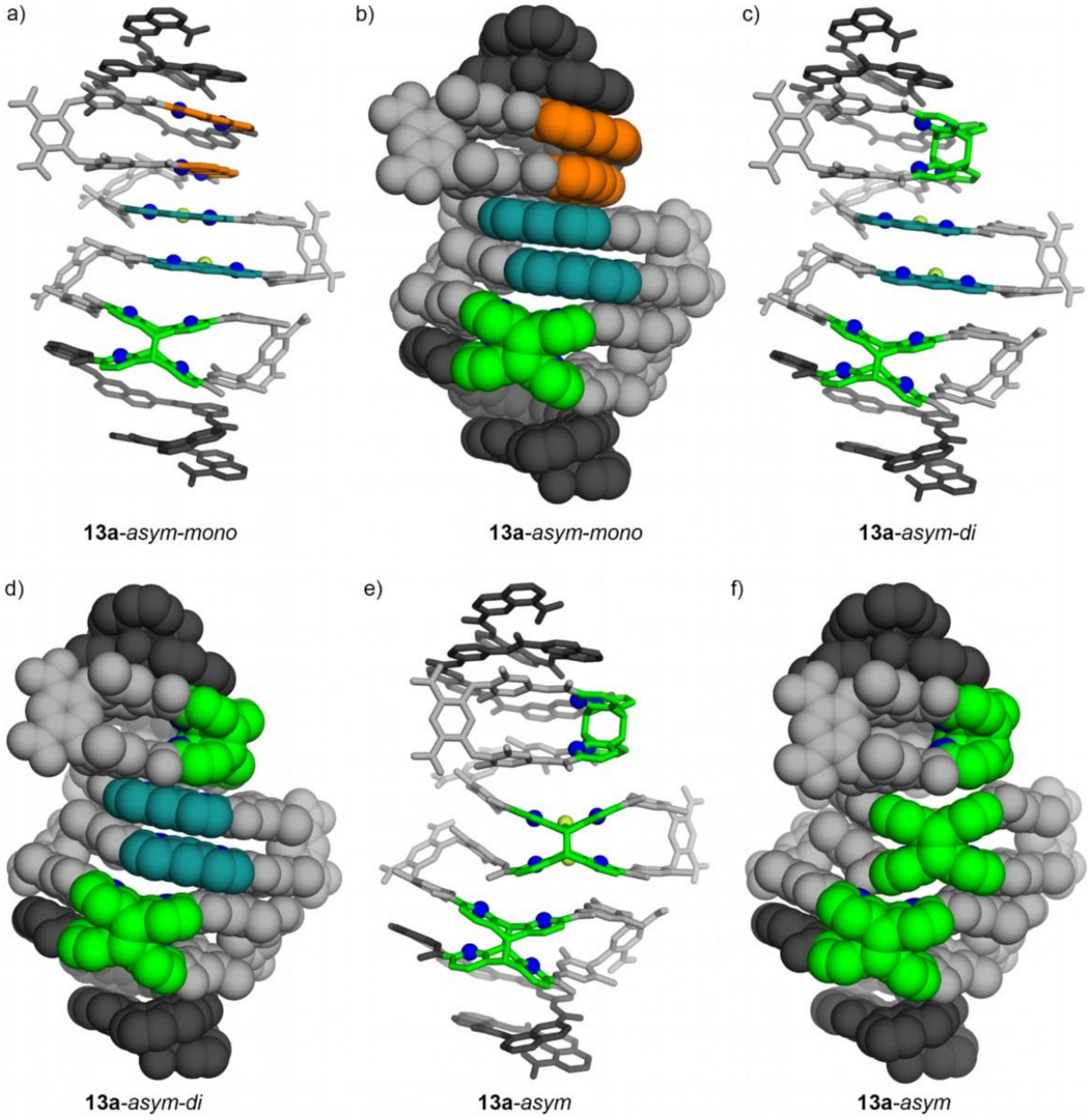


Figure S66. Stepwise photoadduct formation in **13**-*asym*. (a), (c) and (e) Back view of the energy-minimized molecular model of *mono*- (**13a**-*asym*-*mono*), *di*- (**13a**-*asym*-*di*) and *tri*- (**13a**-*asym*) photoadduct products of **13**-*asym*, respectively, using the Merck Molecular Force Field static (MMFFs) shown in tube representation. (b), (d) and (f) Back view of the same in space filling representation, respectively. The structures are shown with color-coded representation as defined earlier. Blue balls depicting endocyclic nitrogen atoms. Hydrogen atoms and side chains are omitted for clarity.

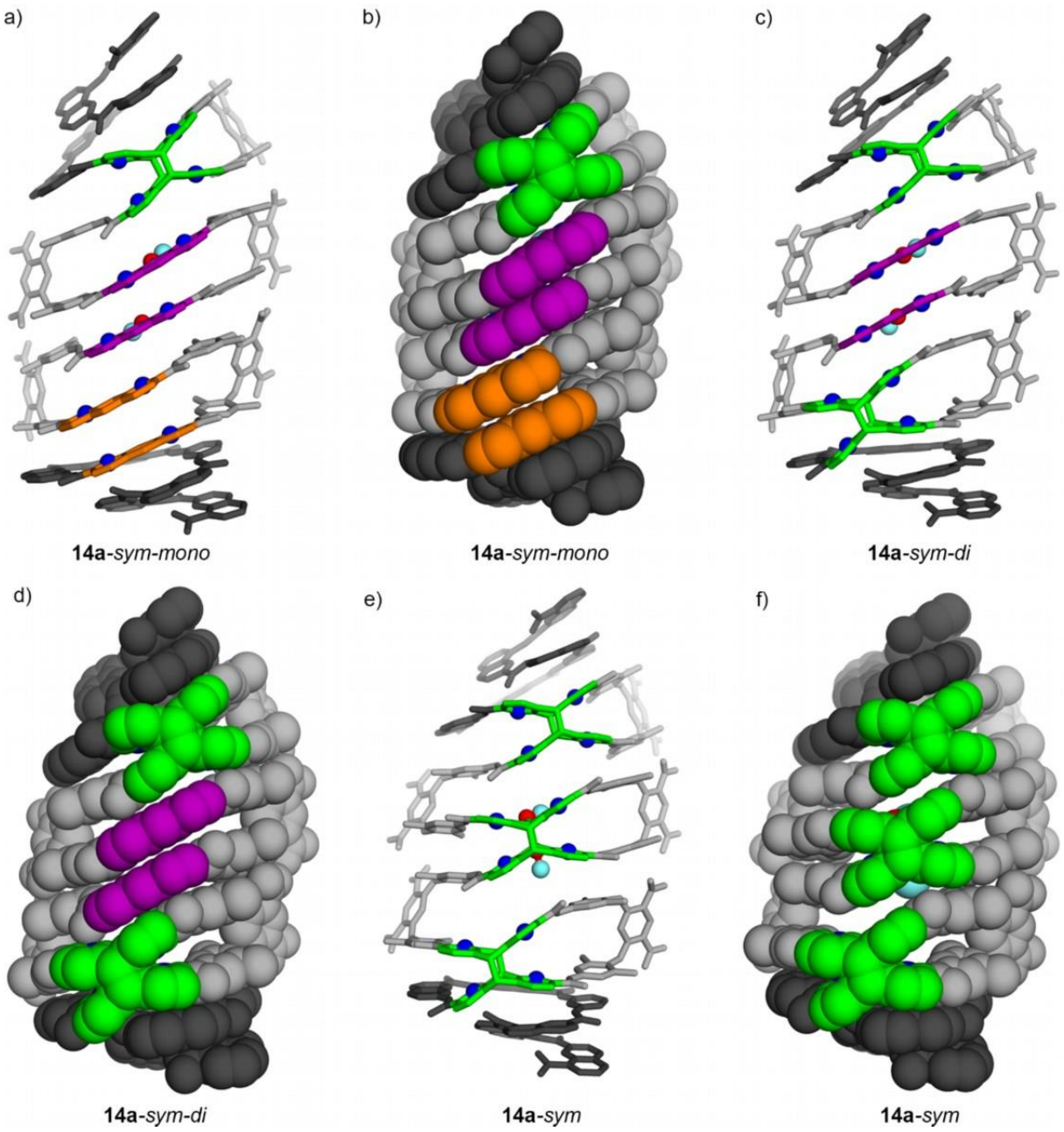
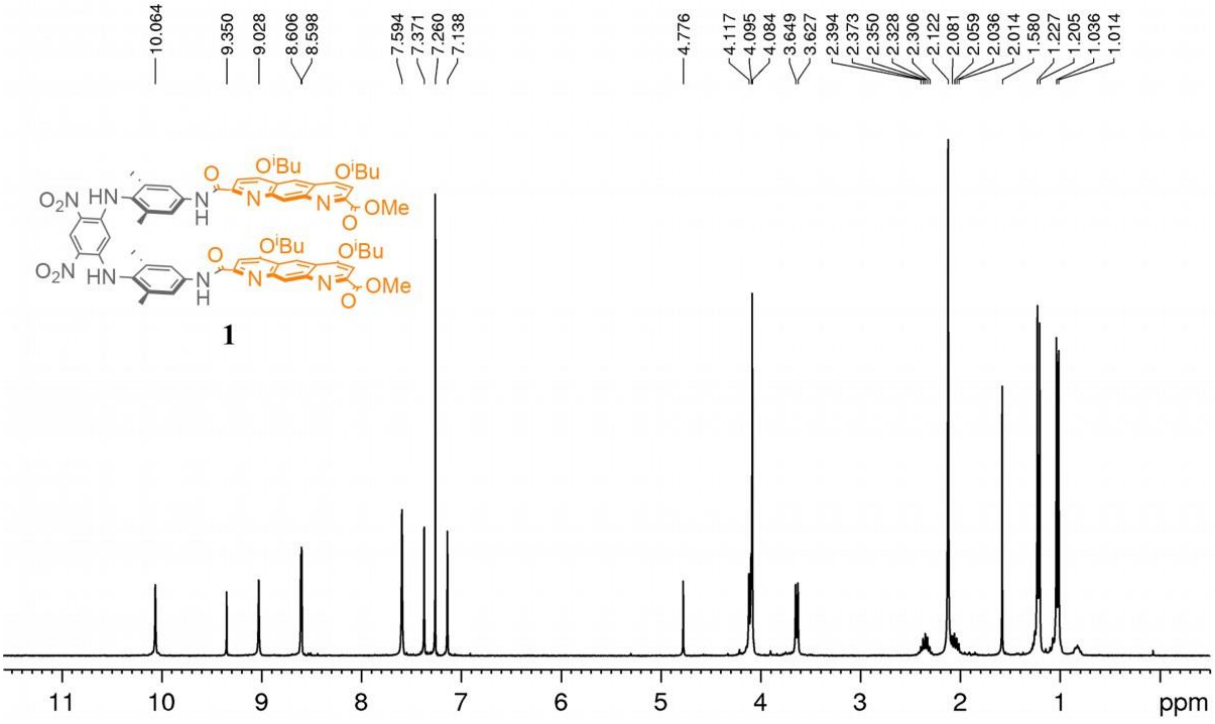


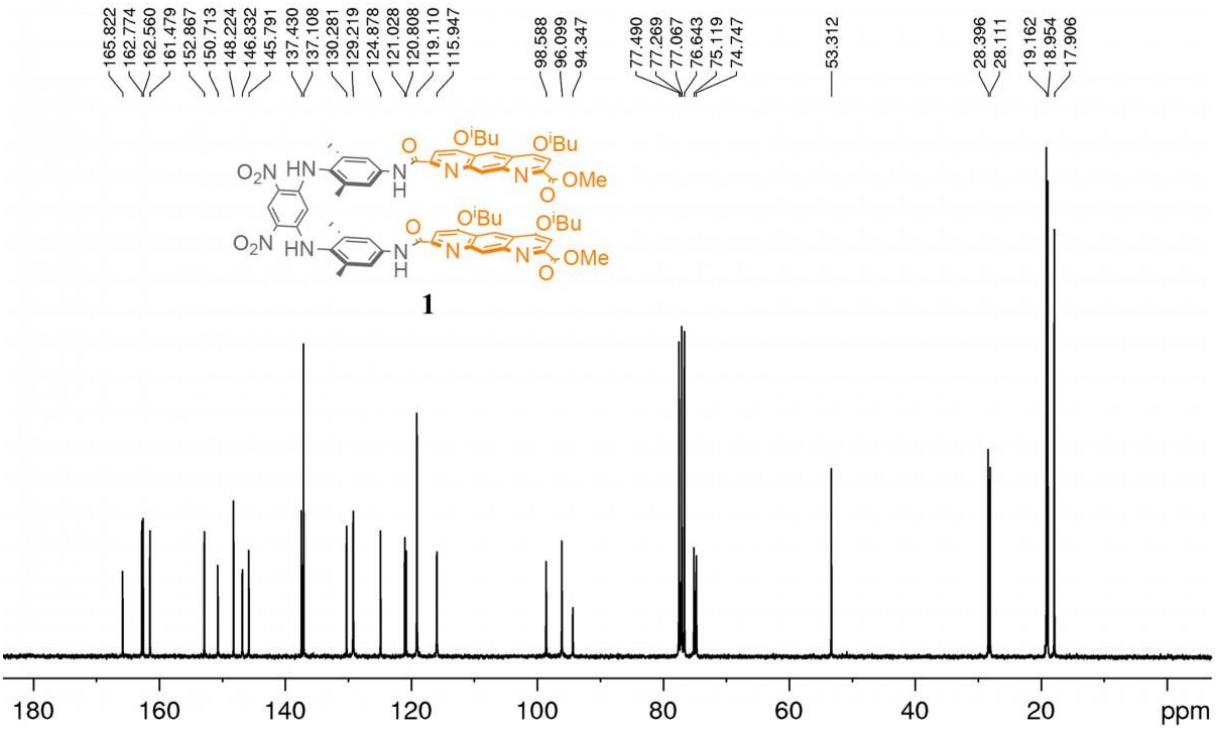
Figure S67. Stepwise photoadduct formation in **14**-*sym*. (a), (c) and (e) Back view of the energy-minimized molecular model of *mono*- (**14a**-*sym-mono*), *di*- (**14a**-*sym-di*) and *tri*- (**14a**-*sym*) photoadduct products of **14**-*sym*, respectively, using the Merck Molecular Force Field static (MMFFs) shown in tube representation. (b), (d) and (f) Back view of the same in space filling representation, respectively. The structures are shown with color-coded representation as defined earlier. Blue balls depicting endocyclic nitrogen atoms. Hydrogen atoms and side chains are omitted for clarity.

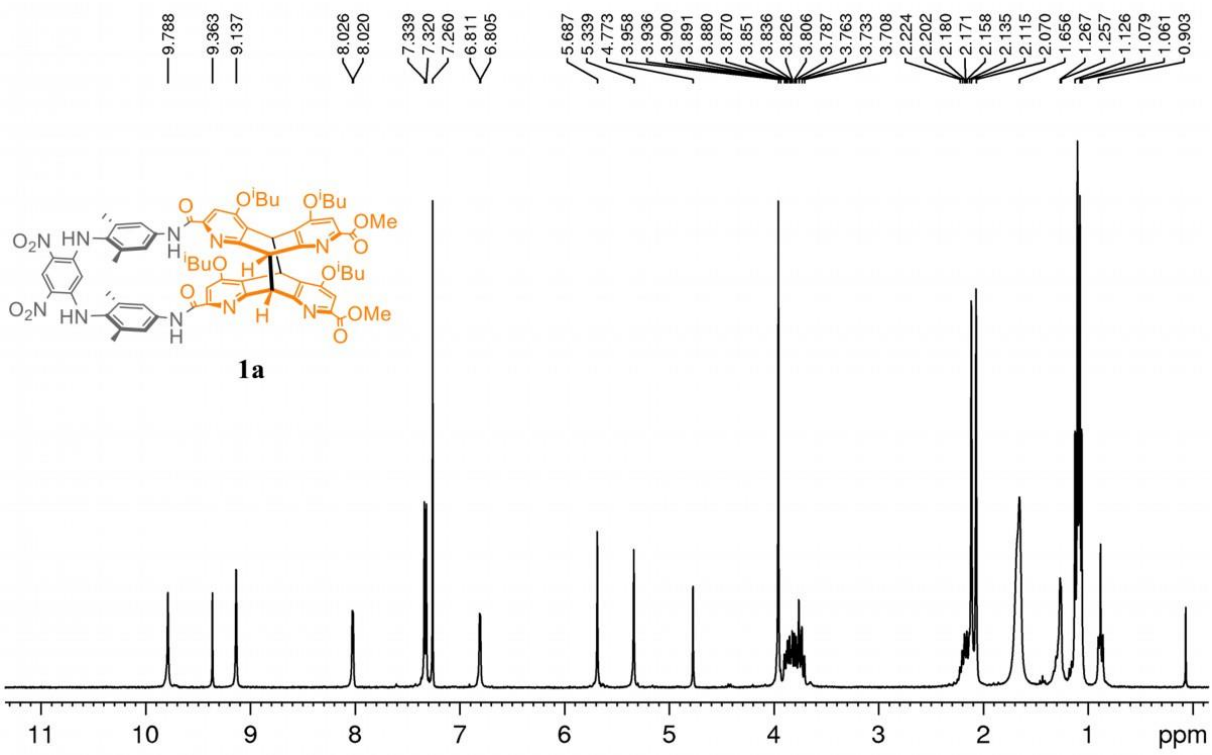
9. References

1. CrysAlisPRO : CrysAlisPRO, Oxford Diffraction /Agilent Technologies UK Ltd, Yarnton, England.
2. Sheldrick, G. M. *Acta Cryst*. **2015**, *A71*, 3–8.
3. Dolomanov, O. V.; Bourhis, L. J.; Gildea, R. J.; Howard, J. A. K.; Puschmann. H. *J. Appl. Cryst.* **2009**, *42*, 339–341.
4. Gole, B.; Kauffmann, B.; Maurizot, V.; Huc, I.; Ferrand, Y. *Angew. Chem. Int. Ed.* **2019**, *58*, 8063–8067.
5. Lamouroux, A.; Sebaoun, L.; Wicher, B.; Kauffmann, B.; Ferrand, Y.; Maurizot, V.; Huc, I. *J. Am. Chem. Soc.* **2017**, *139*, 14668–14675.
6. Wang, X.; Gan, Q.; Wicher, B.; Ferrand, Y.; Huc, I. *Angew. Chem. Int. Ed.* **2019**, *58*, 4205–4209.
7. Chandramouli, N.; Ferrand, Y.; Lautrette, G.; Kauffmann, B.; Mackereth, C. D.; Laguerre, M.; Dubreuil, D.; Huc, I. *Nat. Chem.* **2015**, *7*, 334–341.
8. Montalti, M.; Credi, A.; Prodi, L.; Gandolfi, M. T. Handbook of Photochemistry 3rd Ed. **2006**. Taylor & Francis, 601-604.

10. NMR Spectra



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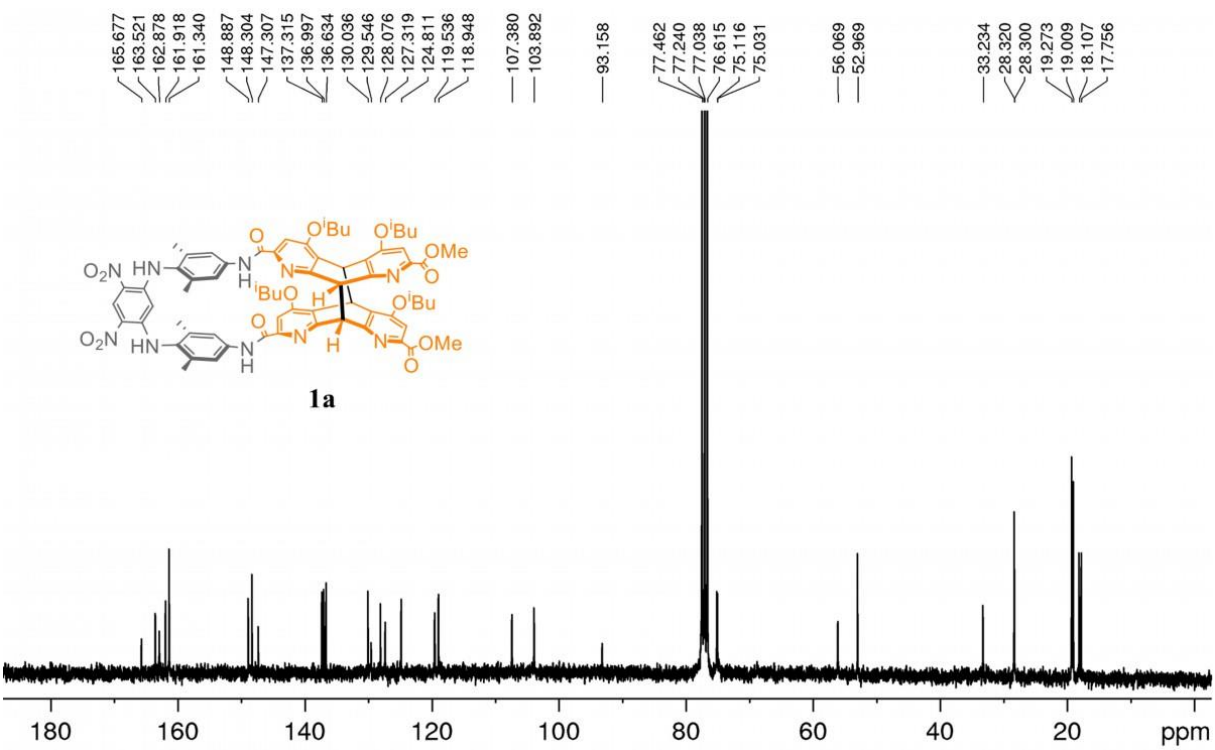
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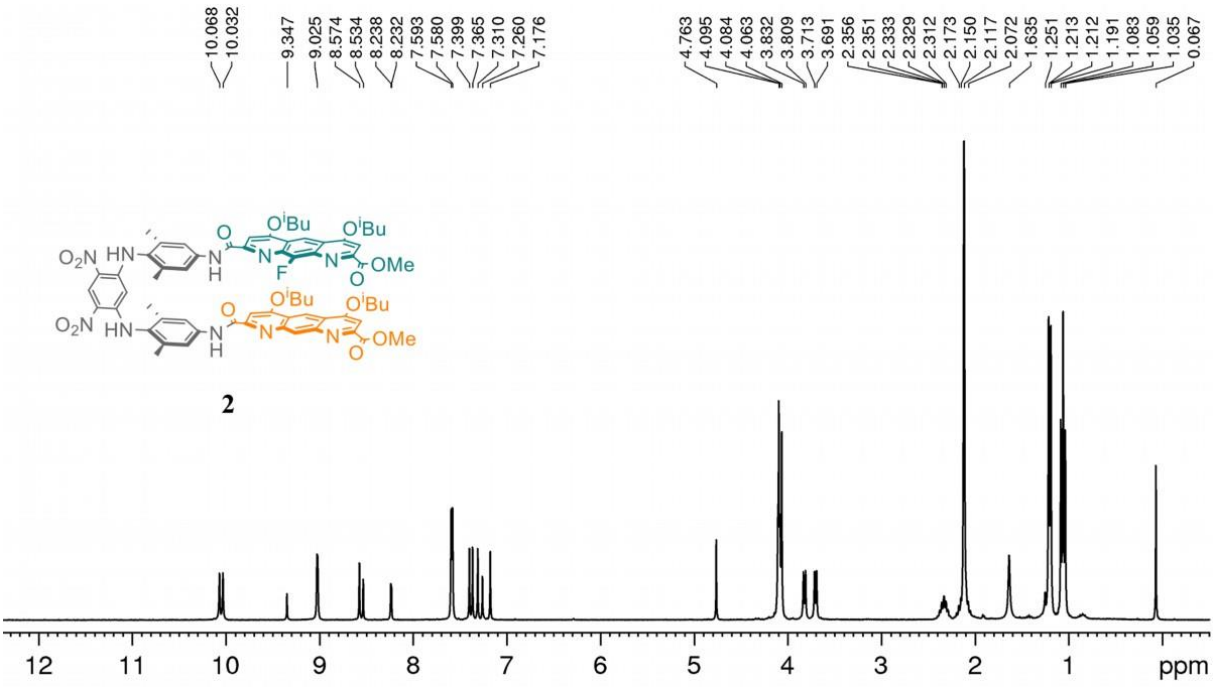
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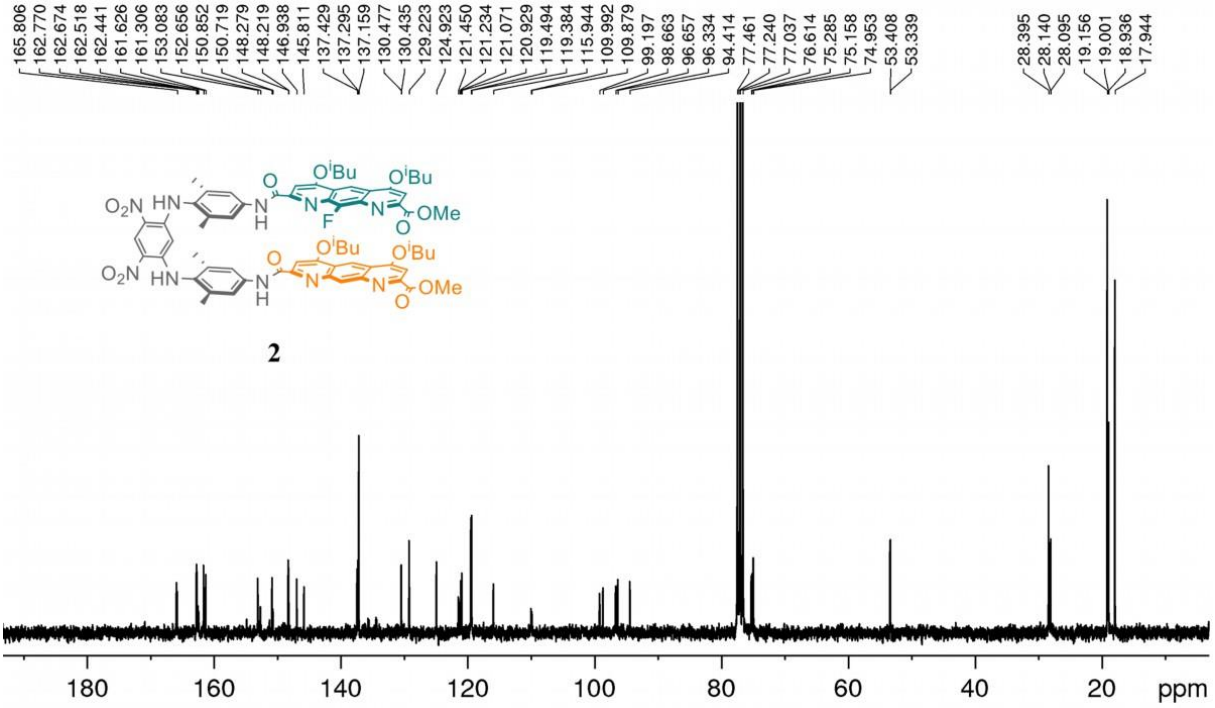
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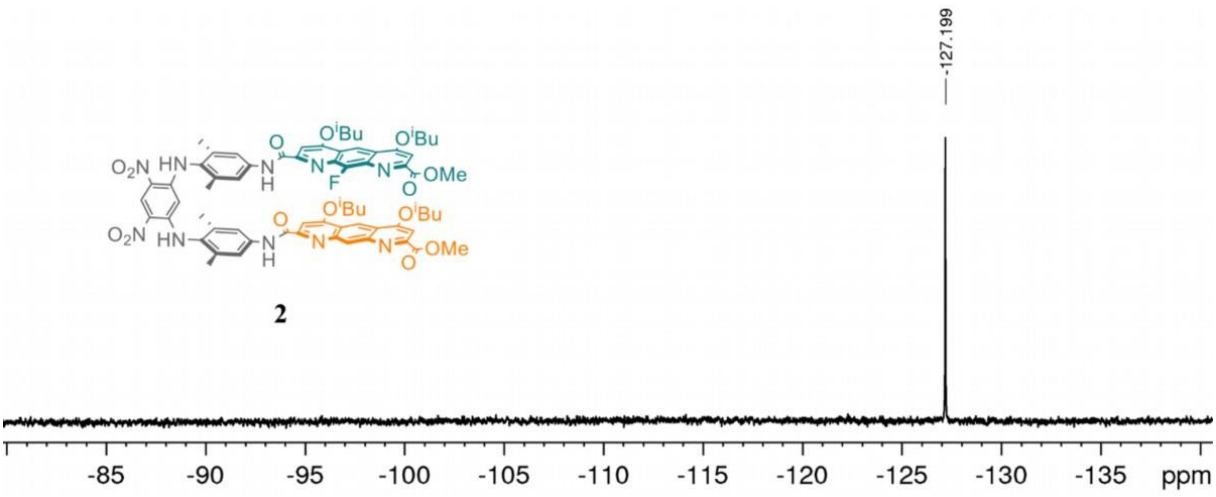
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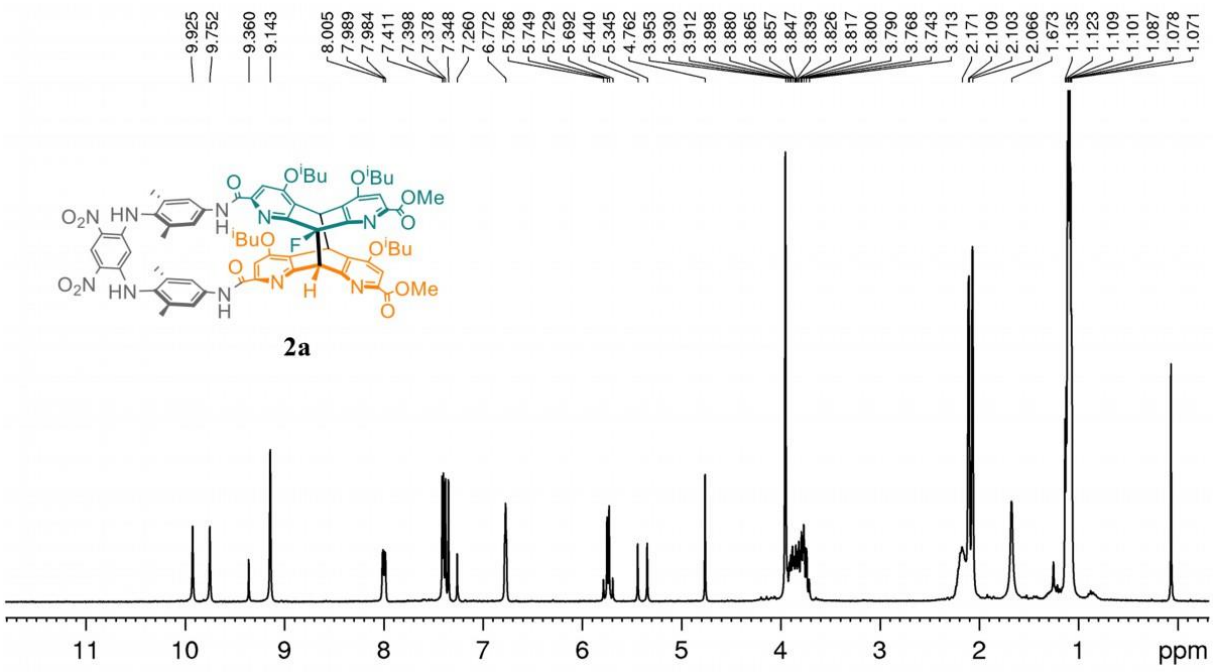
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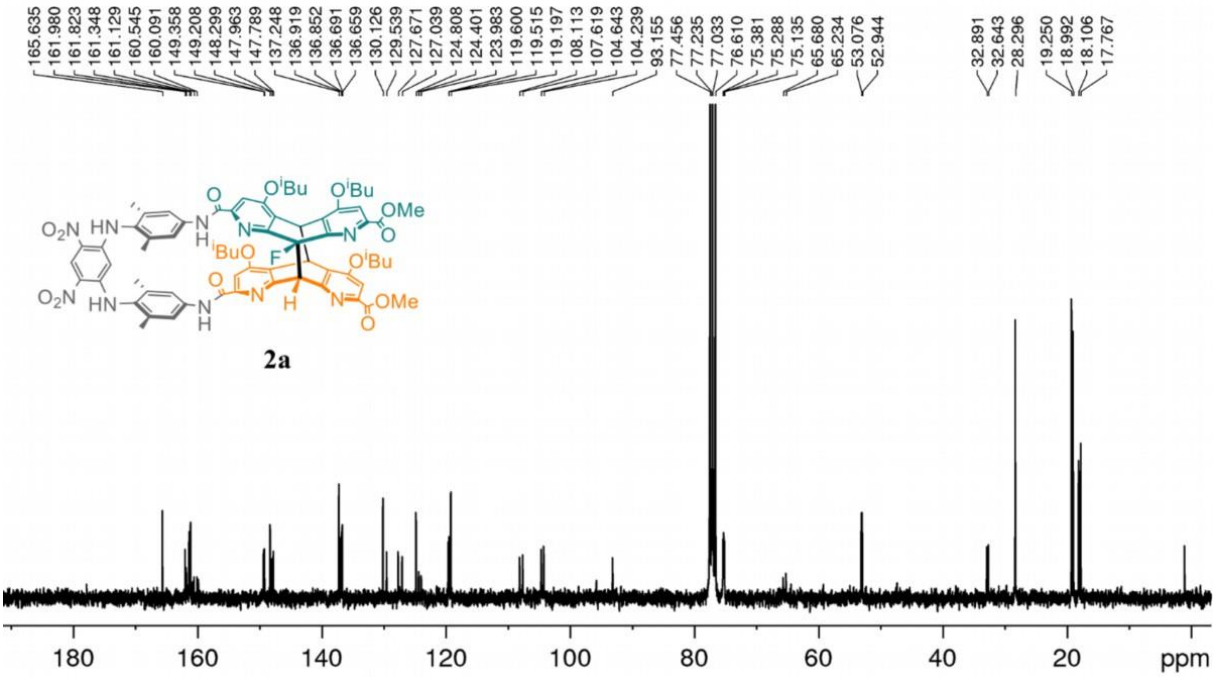
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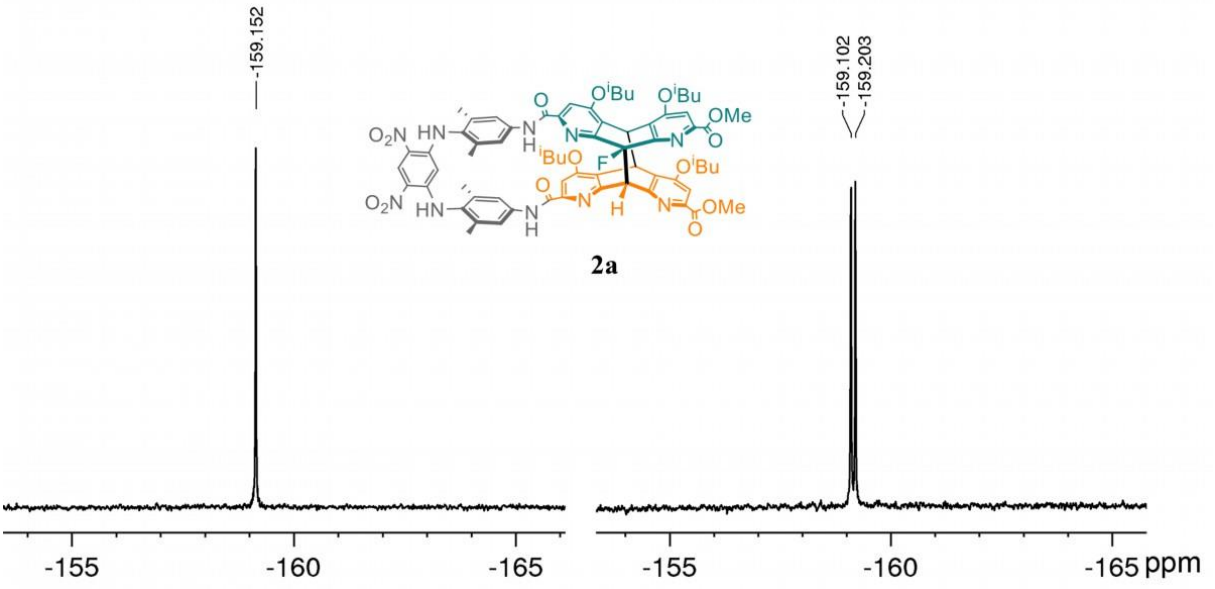
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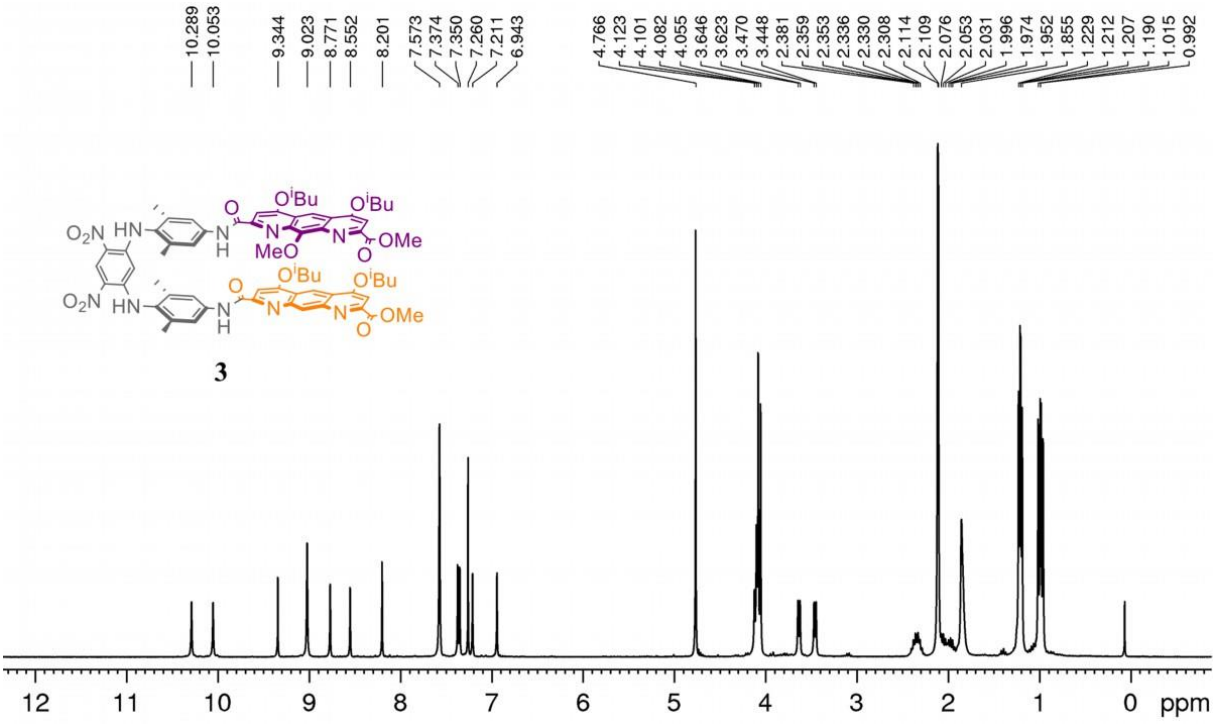
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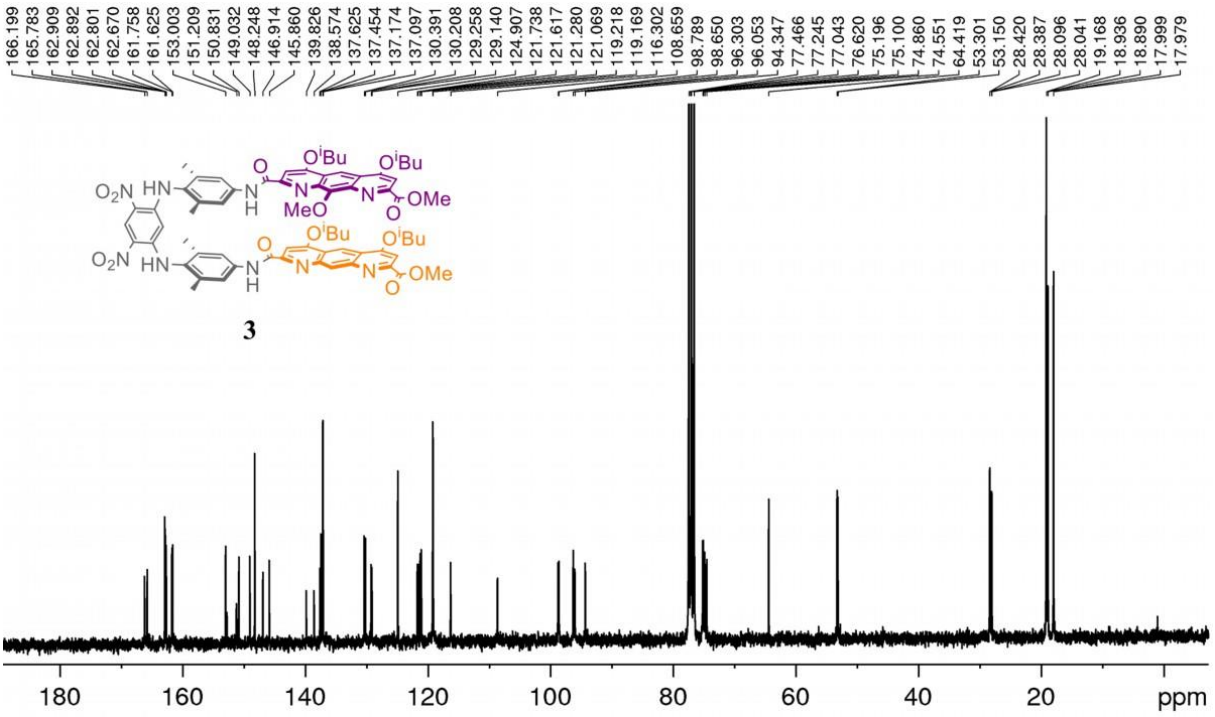
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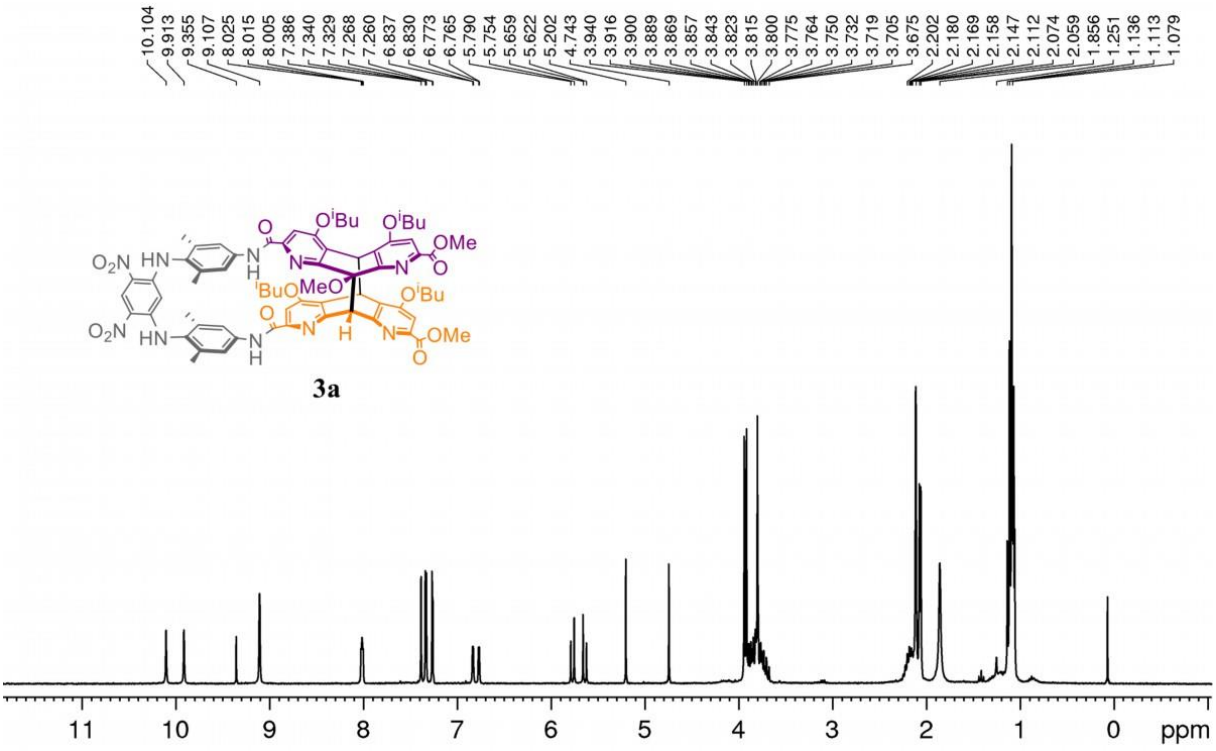
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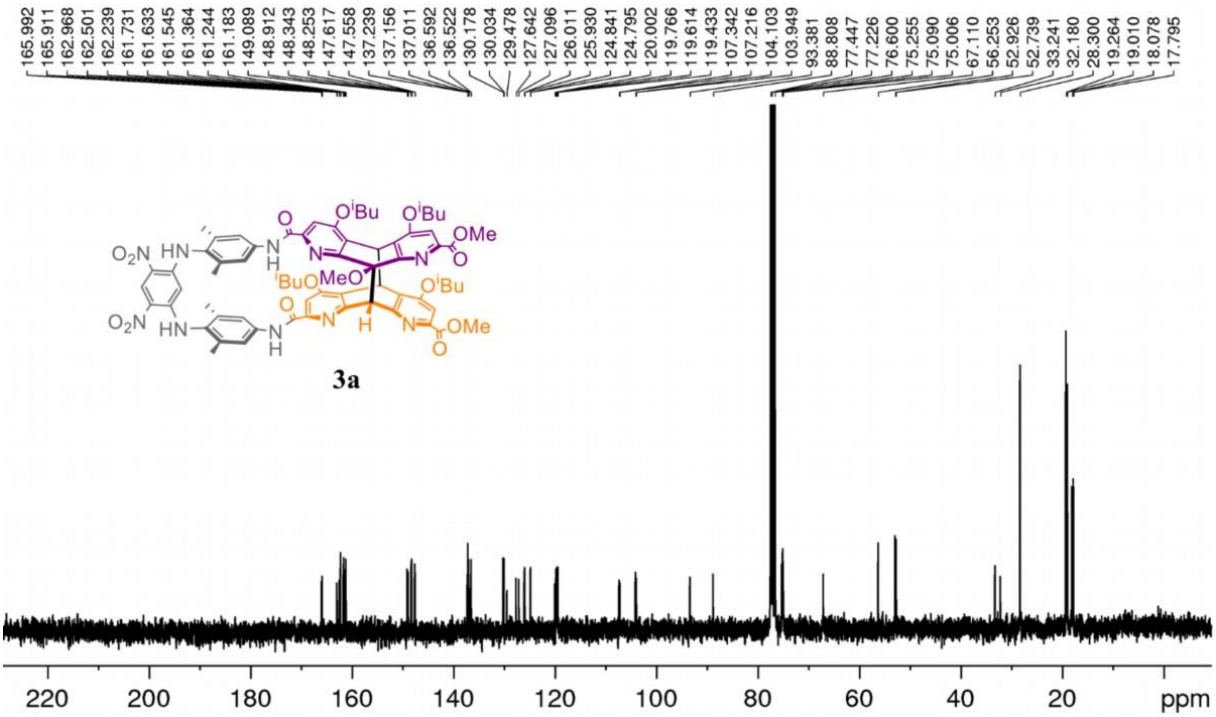
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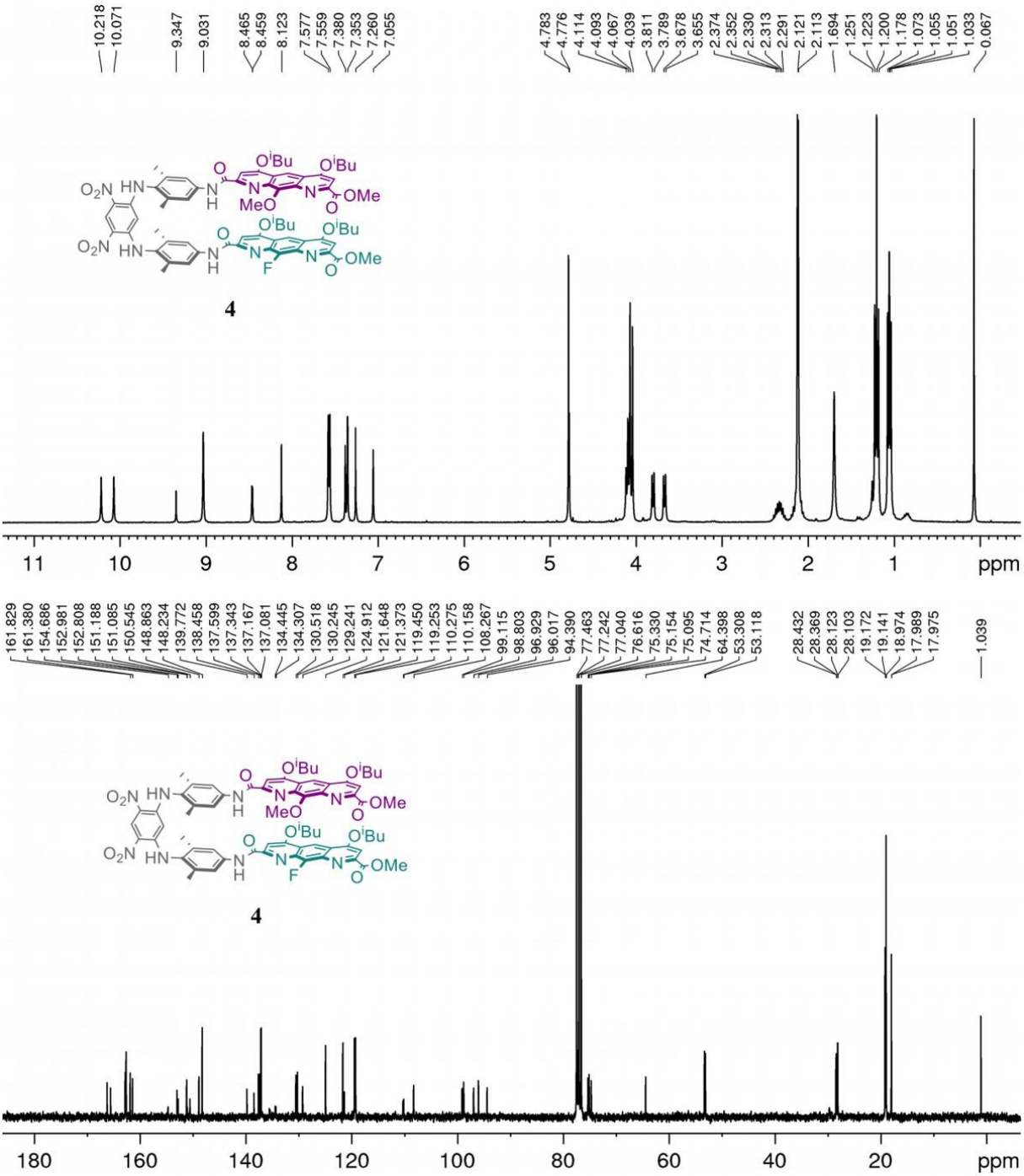
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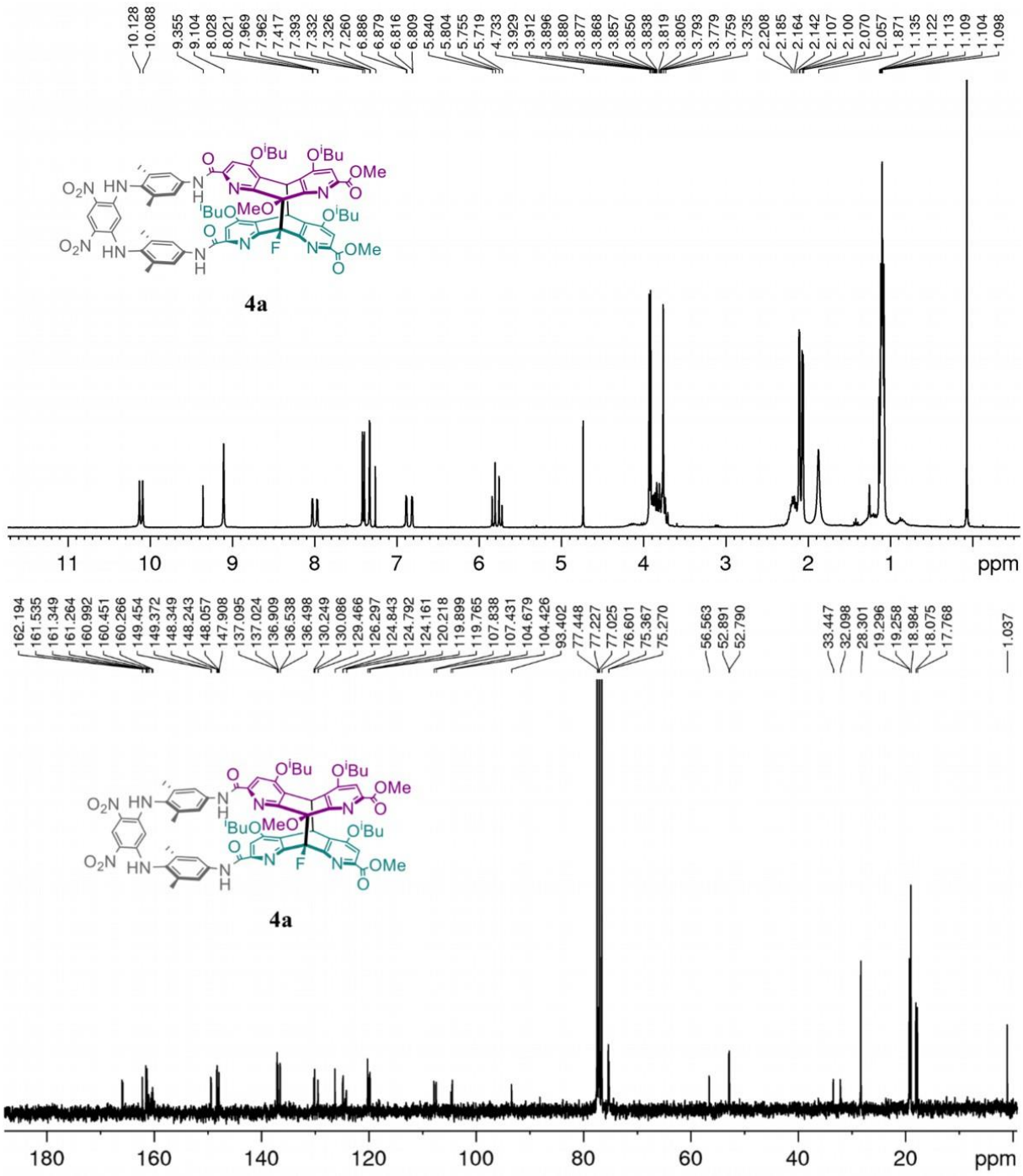
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136.498
130.249
130.086
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104.679
104.426
93.402
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77.227
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75.367
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32.098
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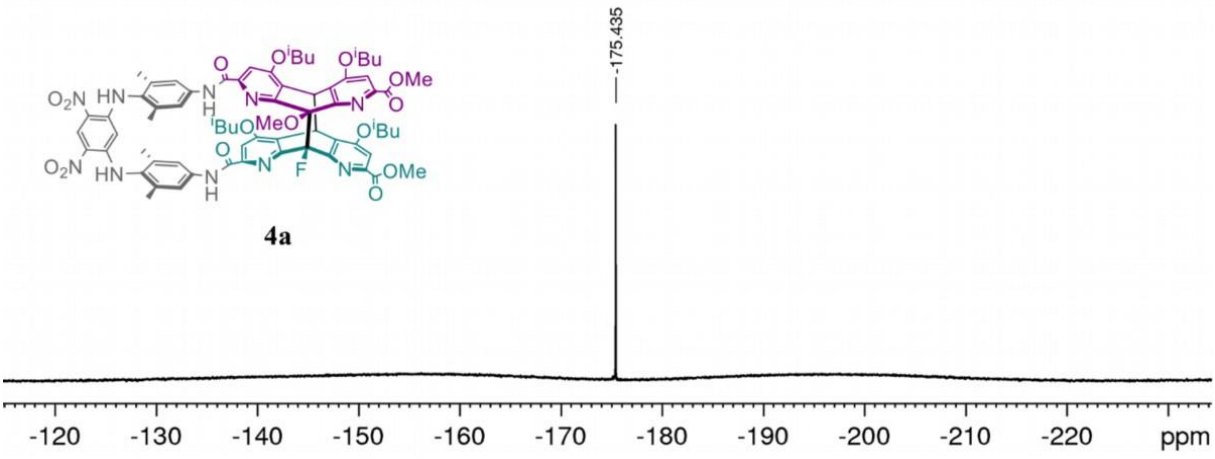
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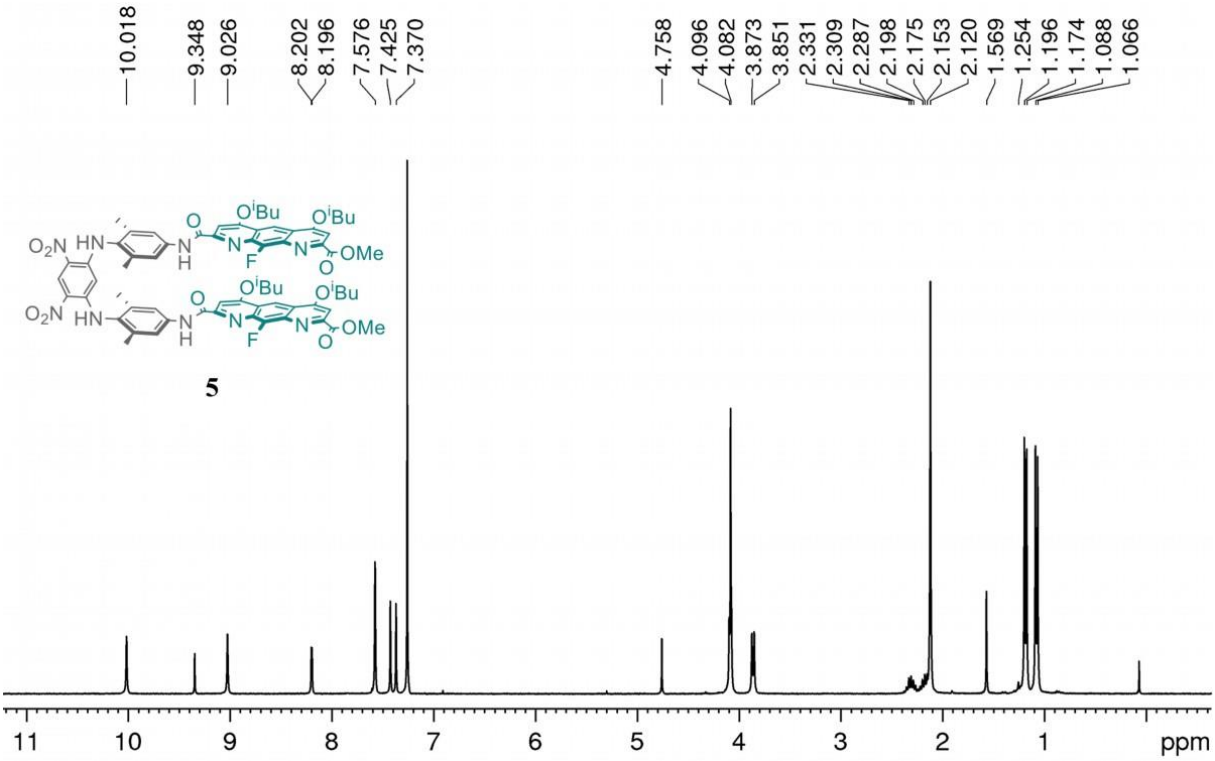
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2.309
2.287
2.198
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2.153
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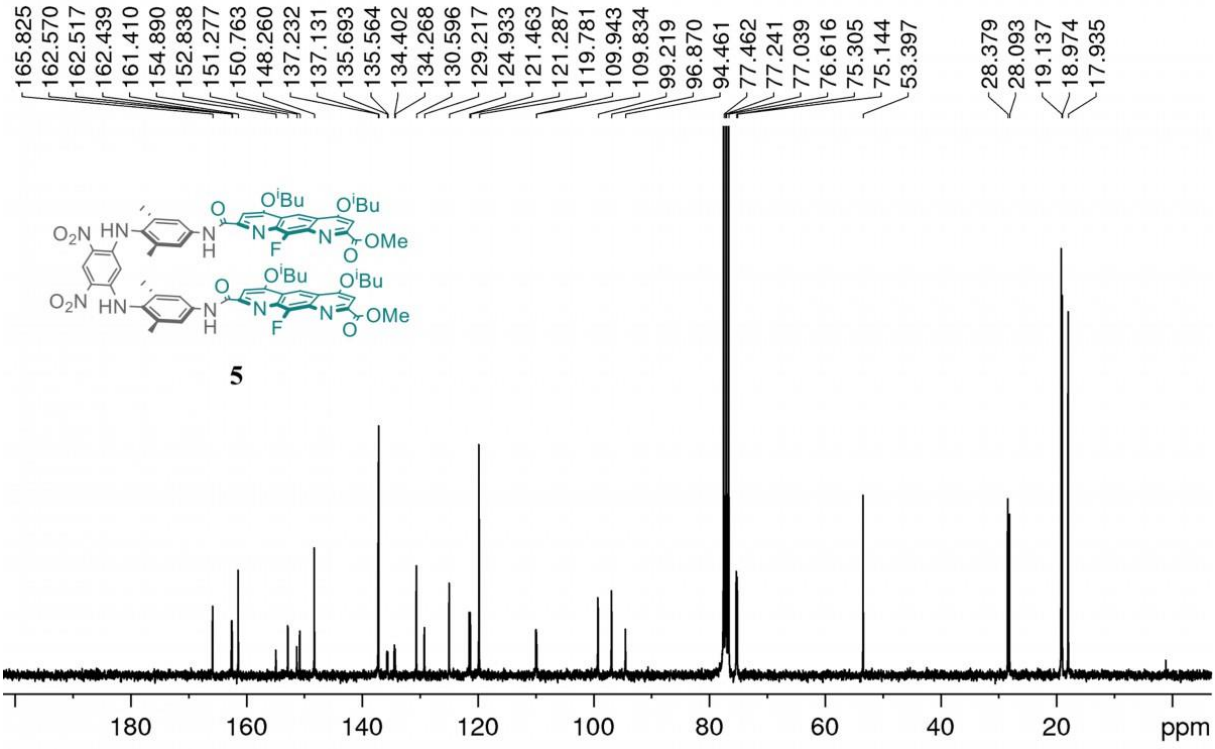
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129.217
124.933
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121.287
119.781
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77.241
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75.144
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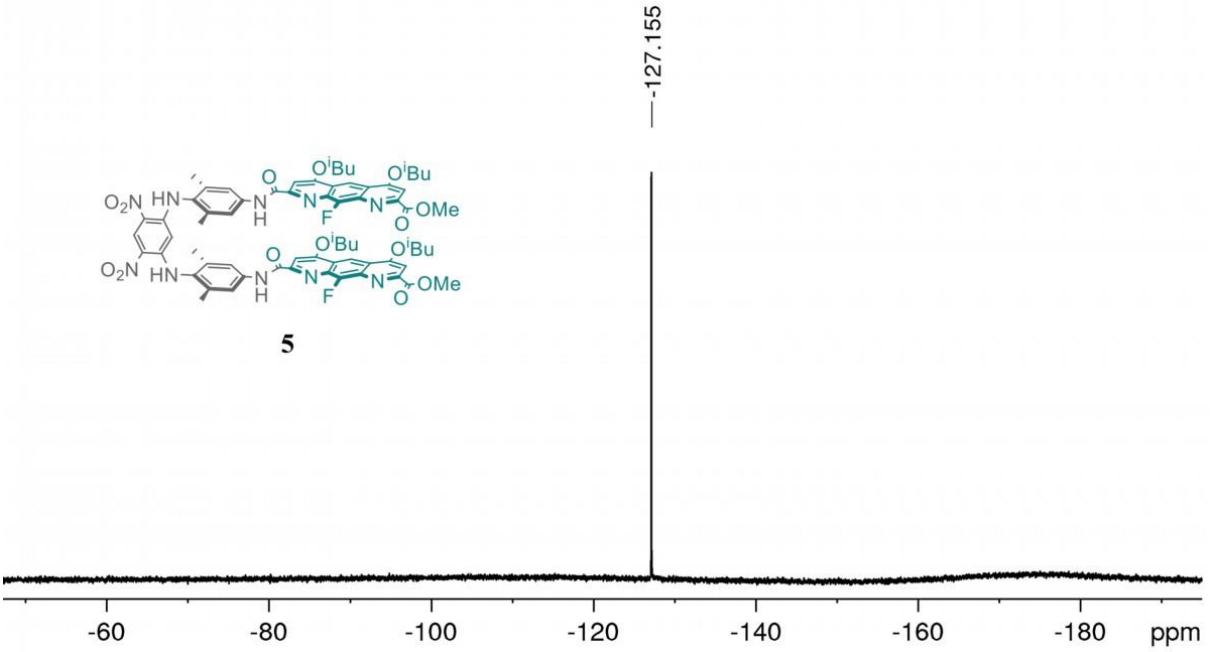
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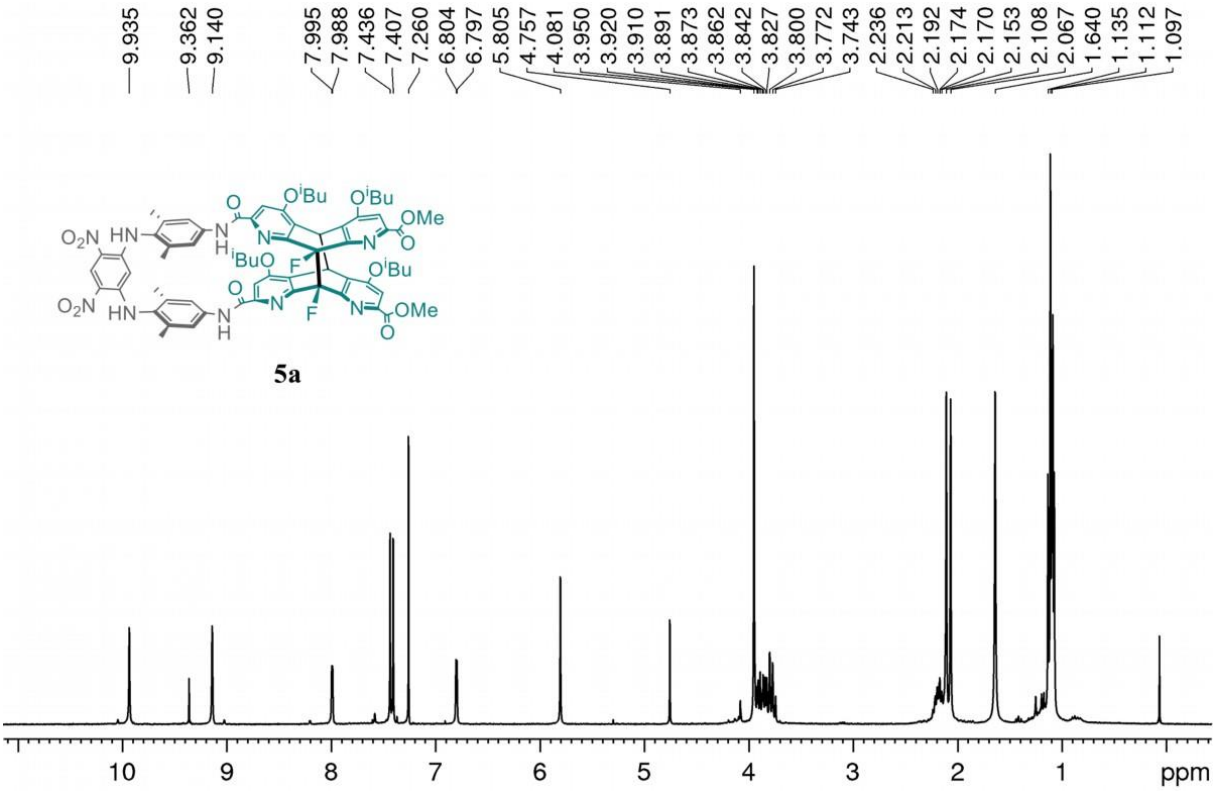
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4.081
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3.920
3.910
3.891
3.873
3.862
3.842
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3.772
3.743
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2.192
2.174
2.170
2.153
2.108
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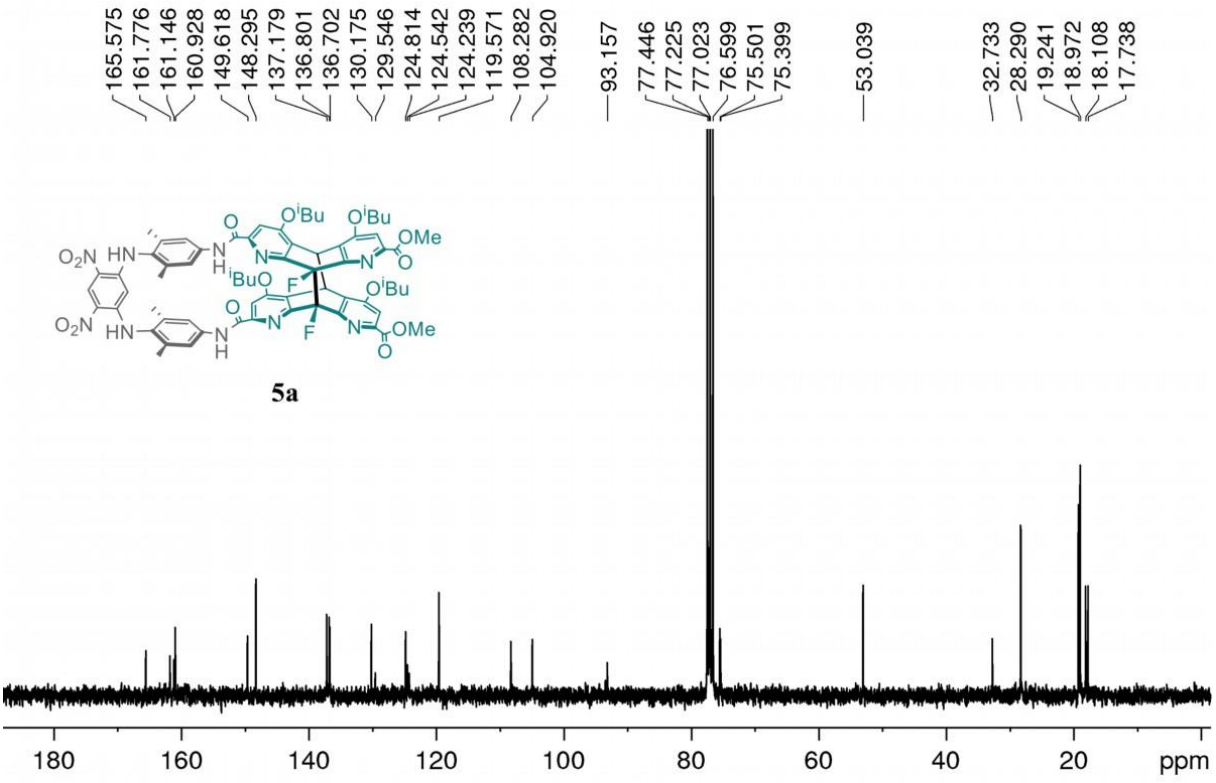
5a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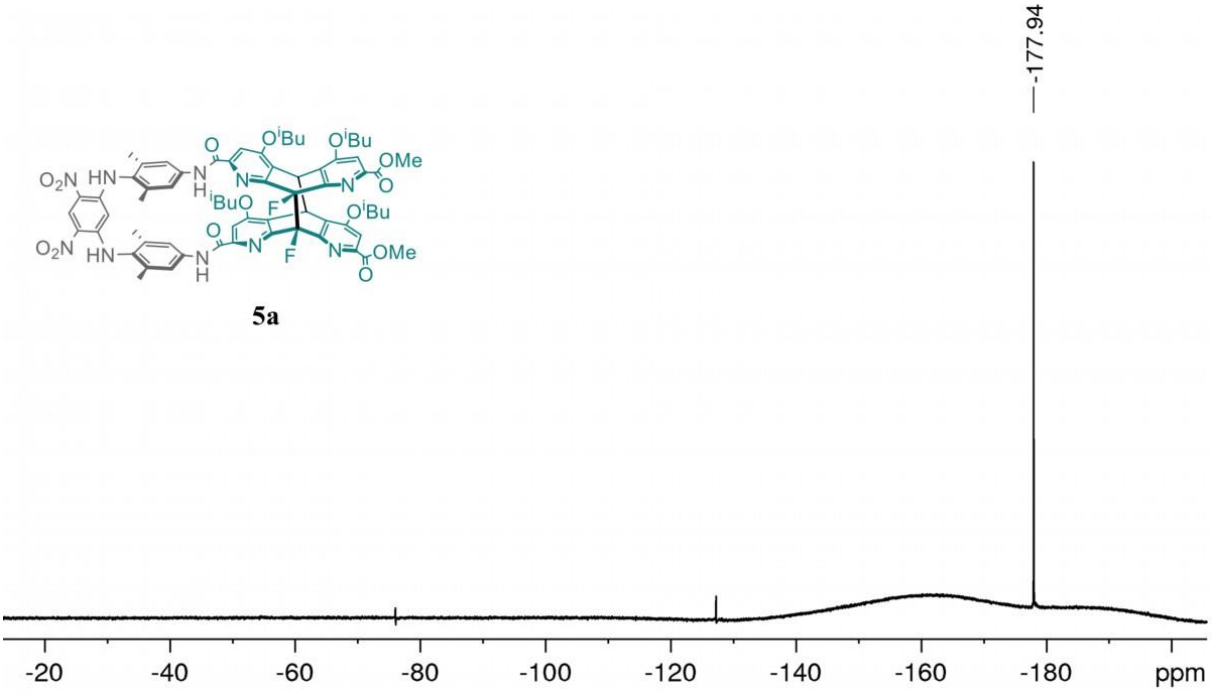
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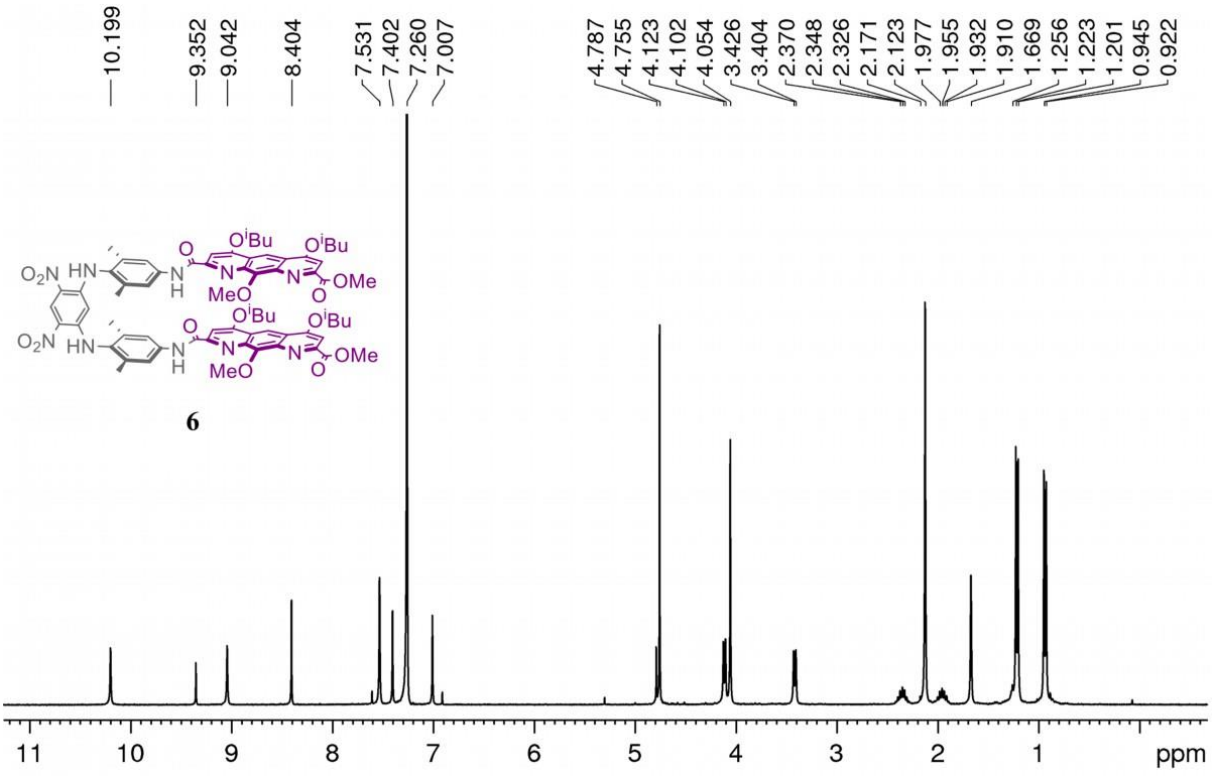
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3.404
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2.326
2.171
2.123
1.977
1.955
1.932
1.910
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1.256
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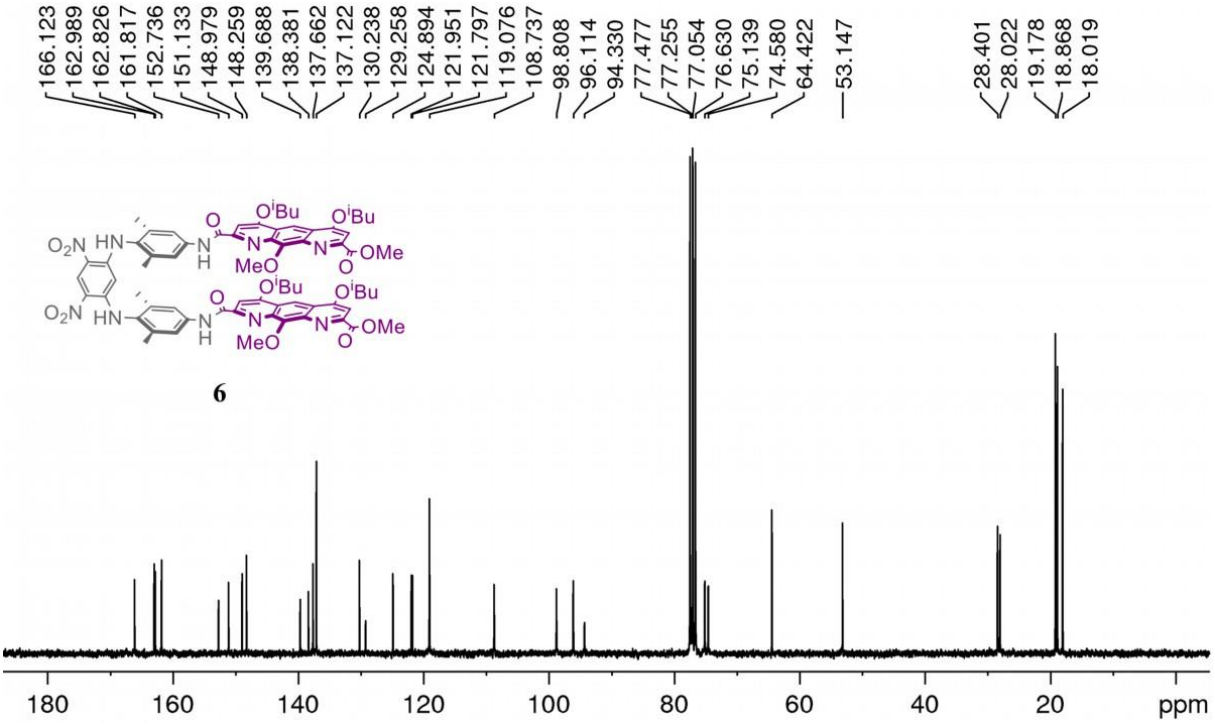
ppm

6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121.797
119.076
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98.808
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77.255
77.054
76.630
75.139
74.580
64.422
53.147
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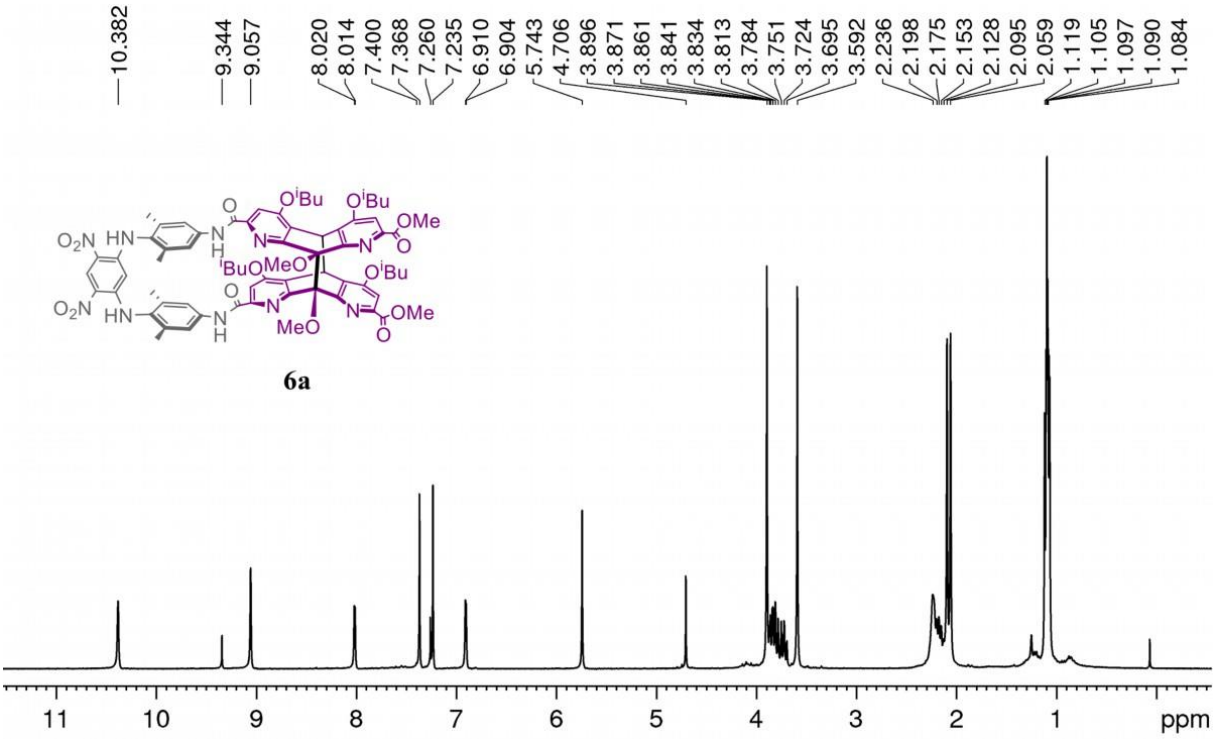
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3.841
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2.236
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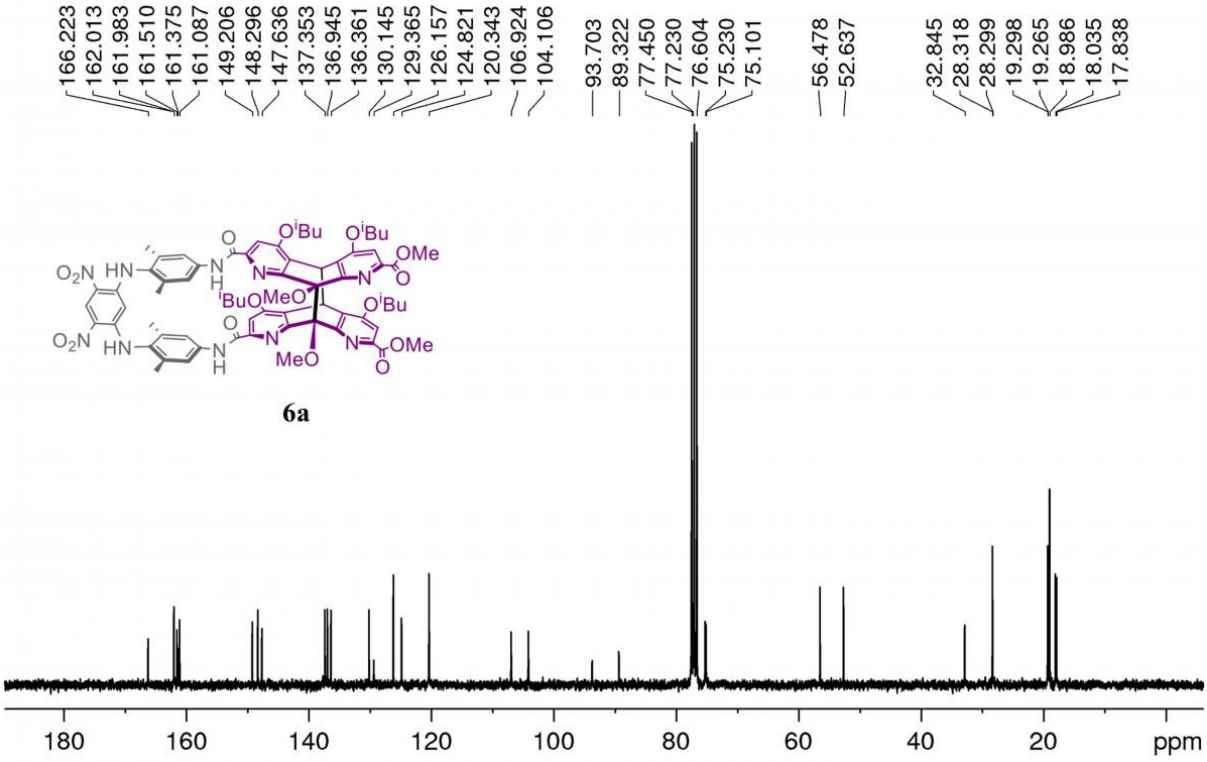
6a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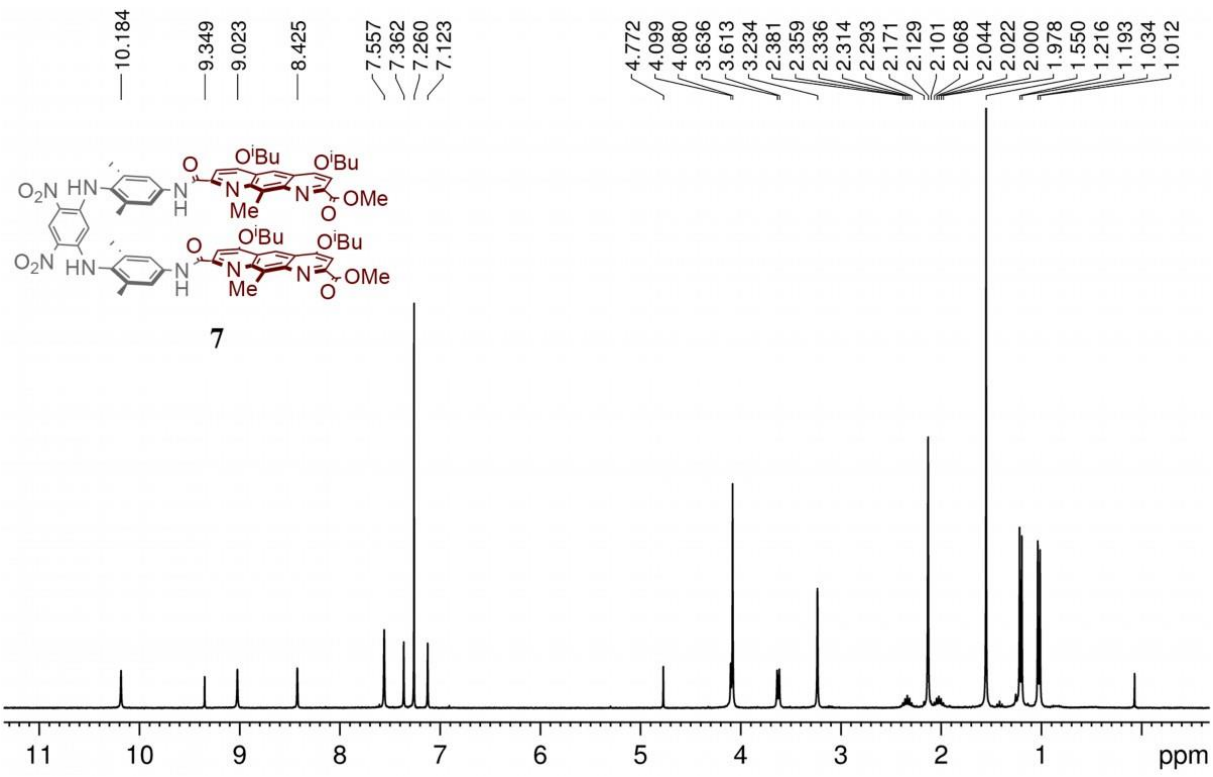
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2.381
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2.336
2.314
2.293
2.171
2.129
2.101
2.068
2.044
2.022
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1.978
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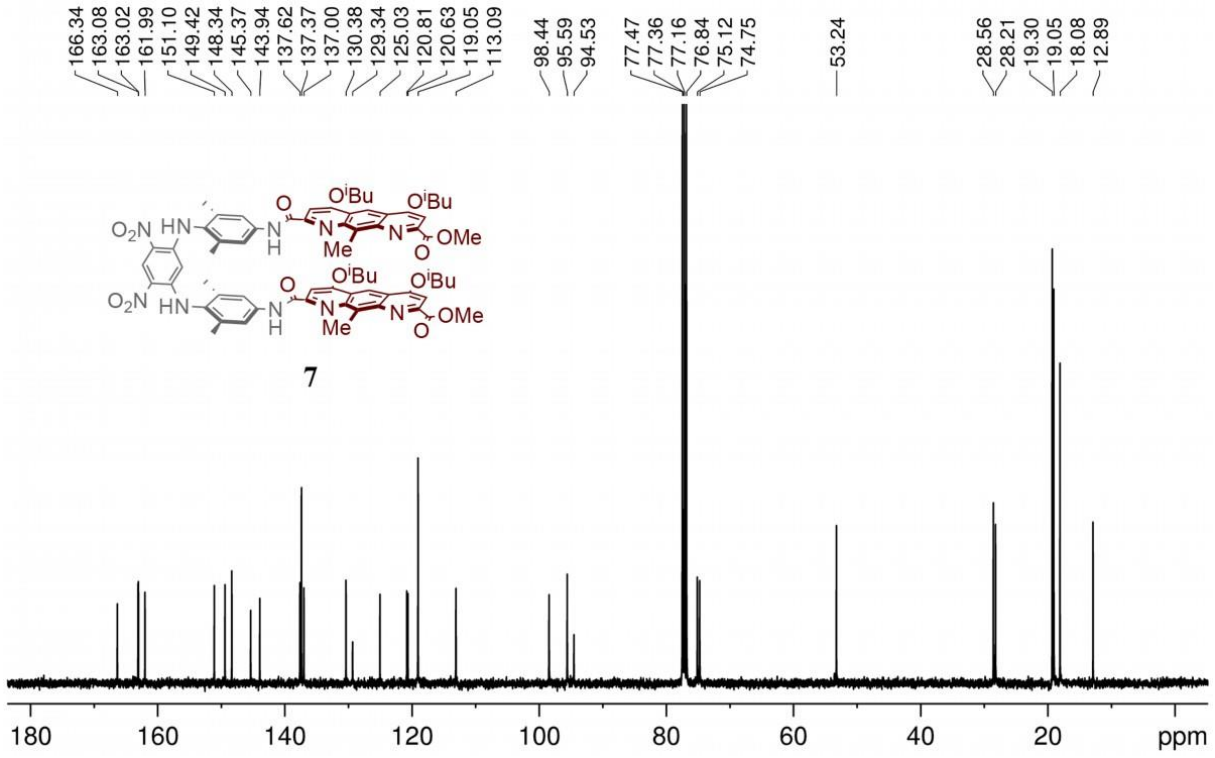
7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130.38
129.34
125.03
120.81
120.63
119.05
113.09
98.44
95.59
94.53
77.47
77.36
77.16
76.84
75.12
74.75
53.24
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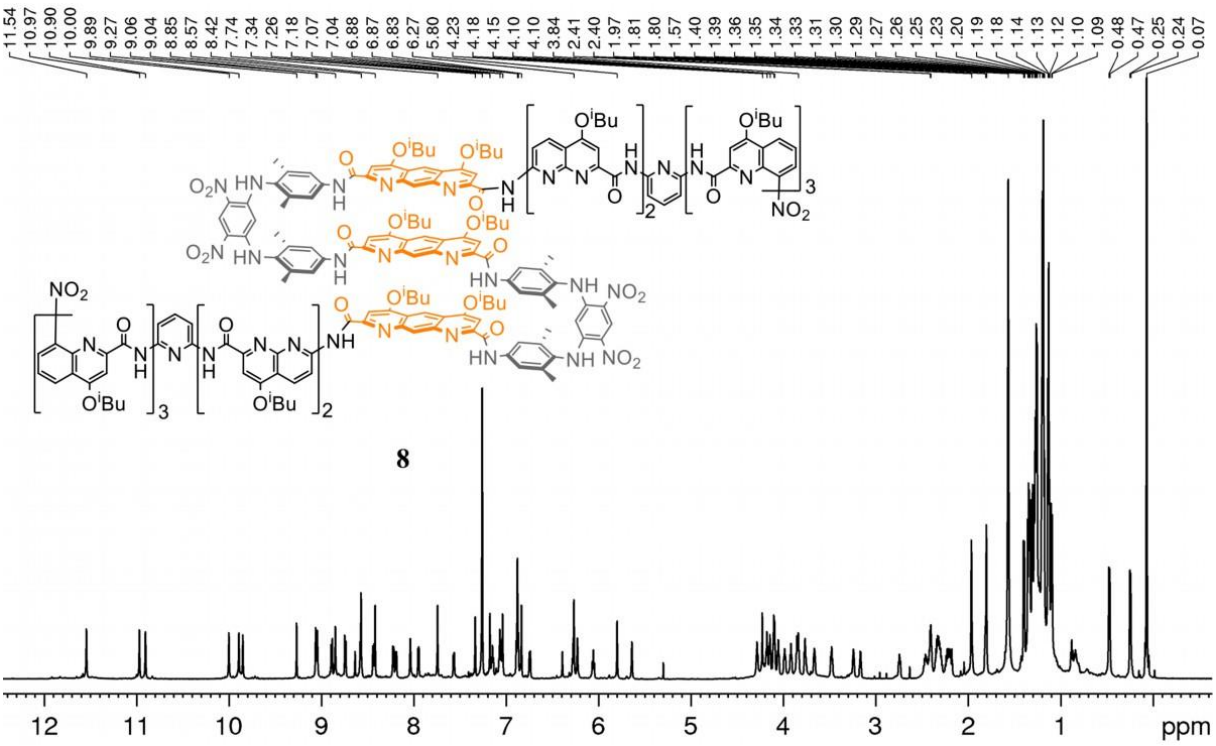
ppm

7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7.26
7.18
7.07
7.04
6.88
6.87
6.83
6.27
5.80
4.23
4.18
4.15
4.10
4.10
3.84
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1.29
1.27
1.26
1.25
1.23
1.20
1.19
1.18
1.14
1.13
1.12
1.10
1.09
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0.07
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10
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2
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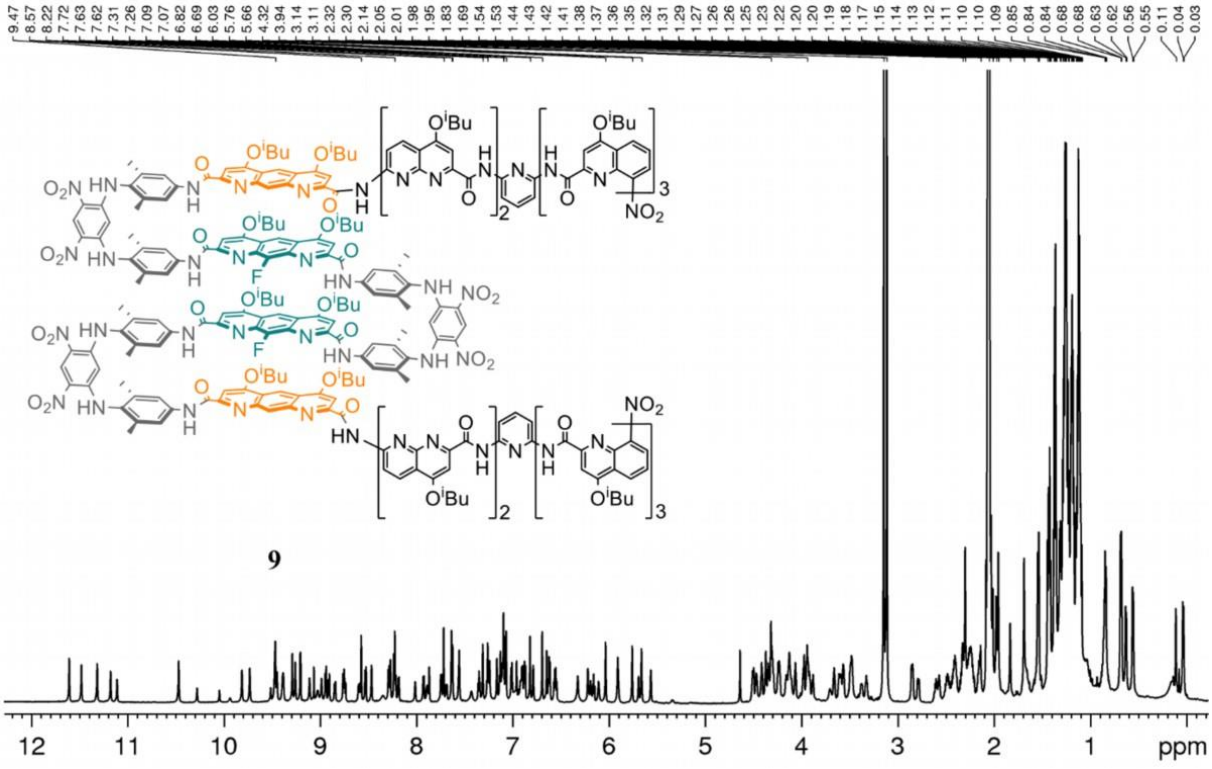
ppm

8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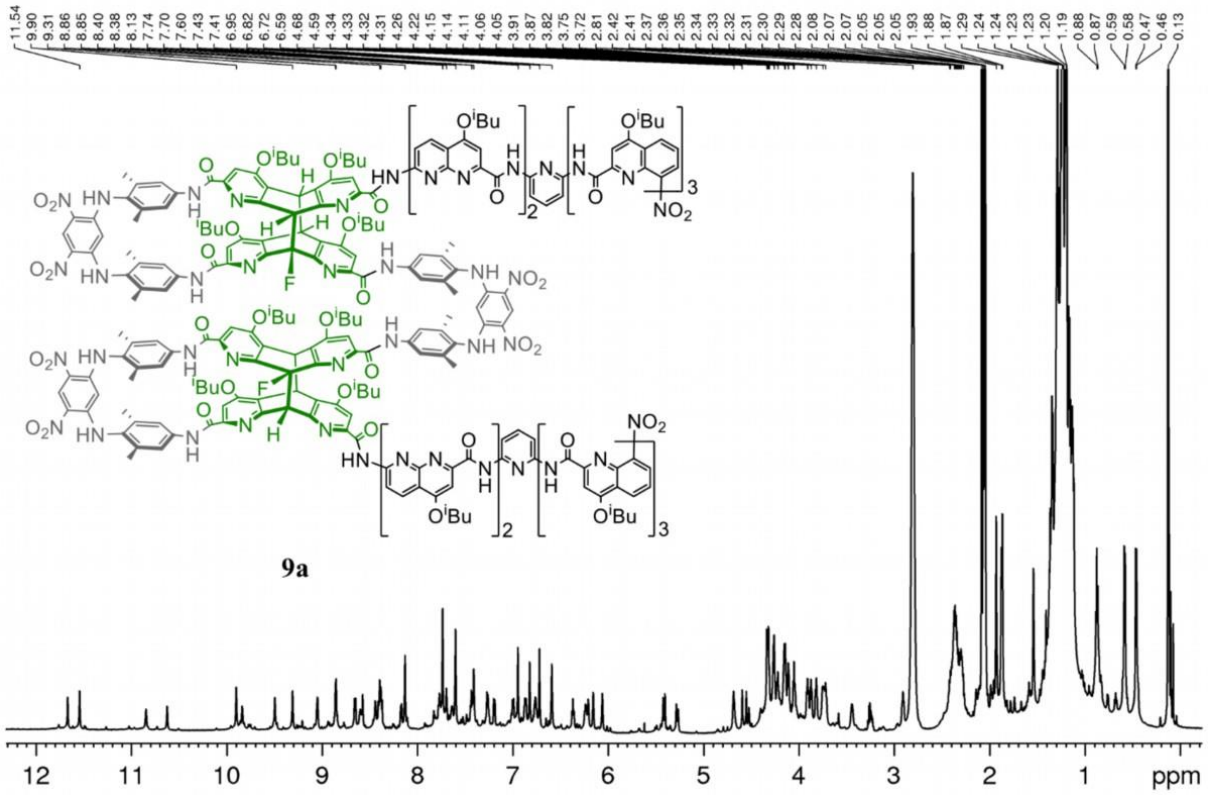
9
12 11 10 9 8 7 6 5 4 3 2 1 ppm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9a
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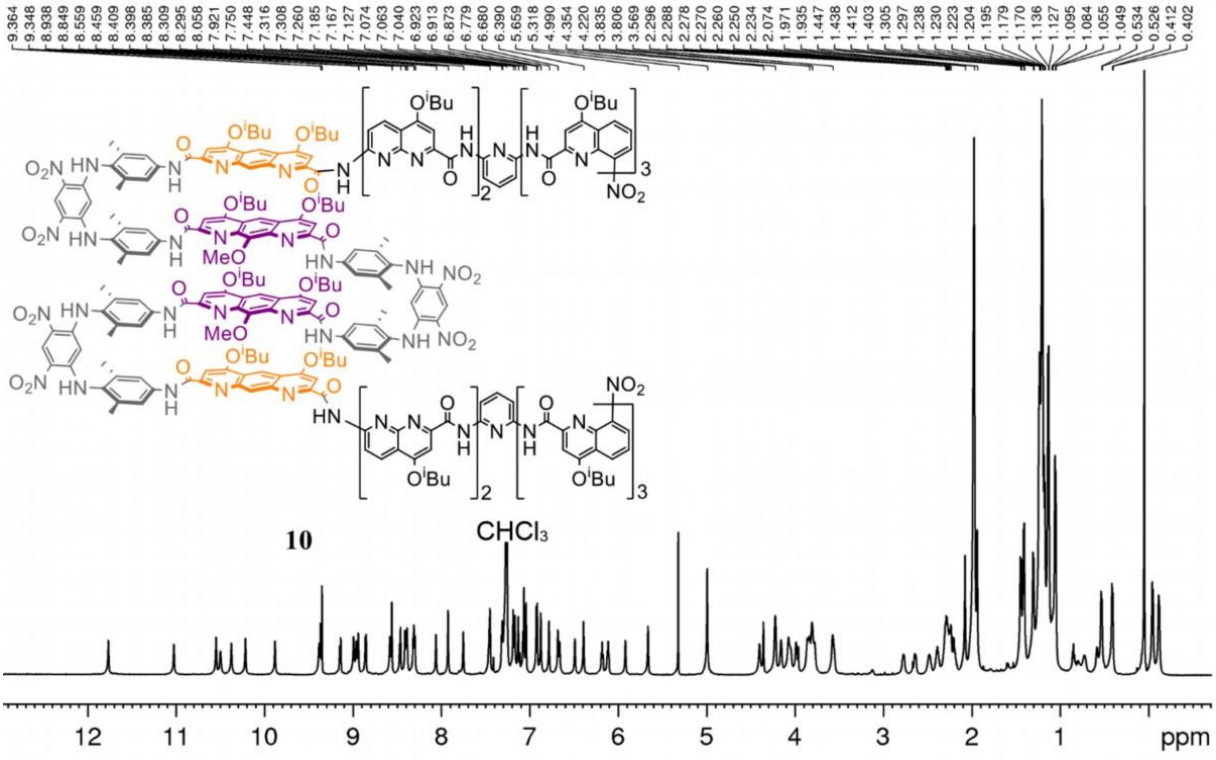
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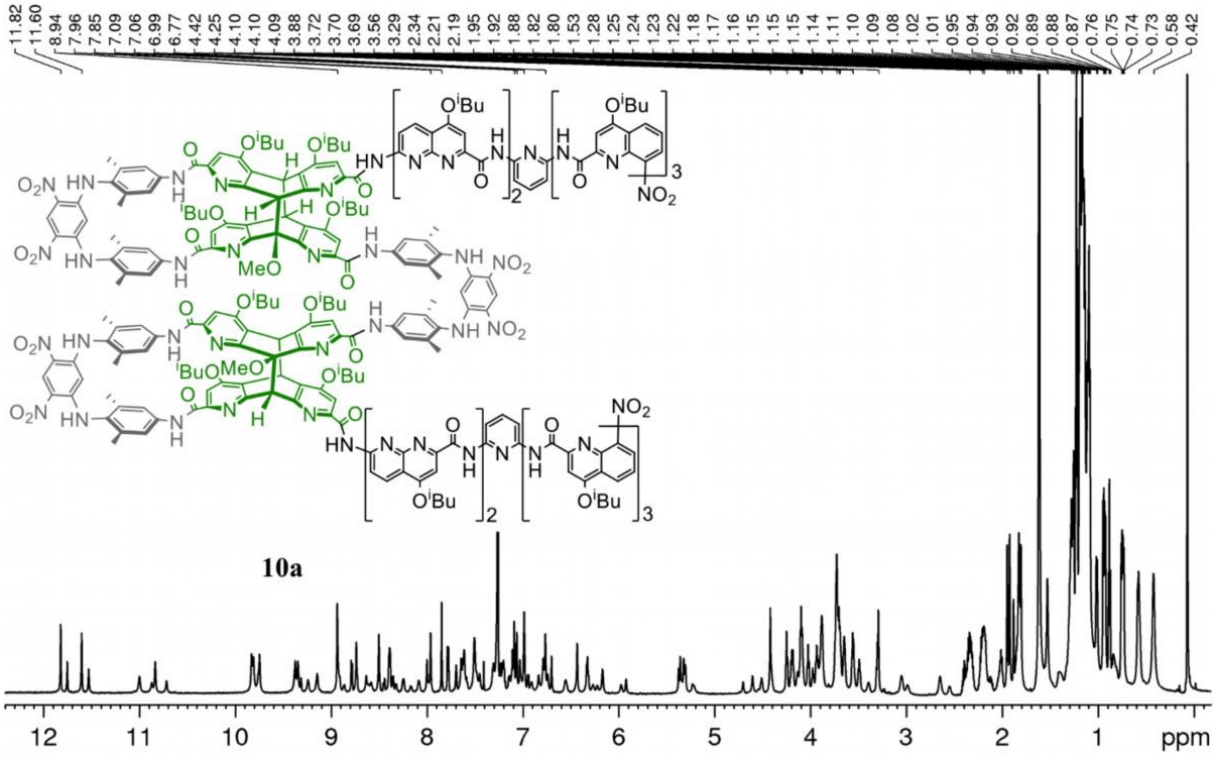
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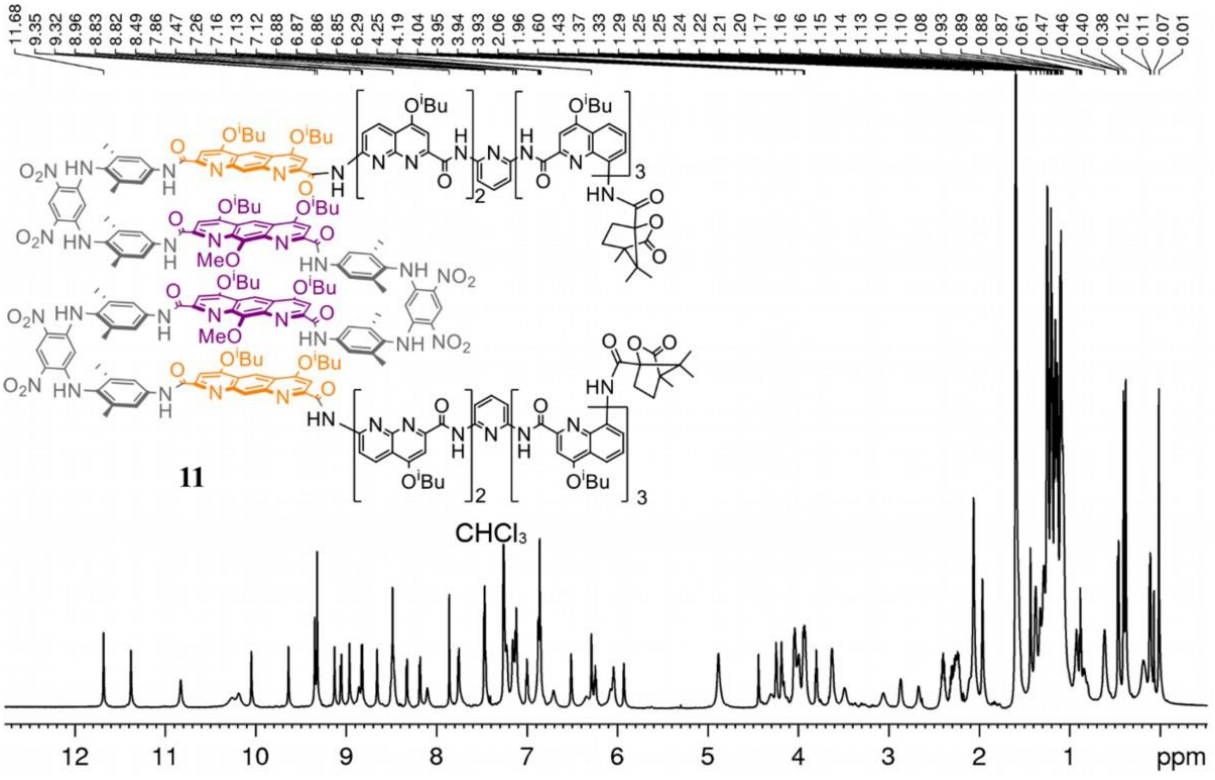
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6.29
4.25
4.19
4.04
3.95
3.94
3.93
2.06
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1.37
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1.25
1.24
1.22
1.21
1.20
1.17
1.16
1.16
1.15
1.14
1.13
1.10
1.10
1.08
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0.87
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0.40
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CHCl3
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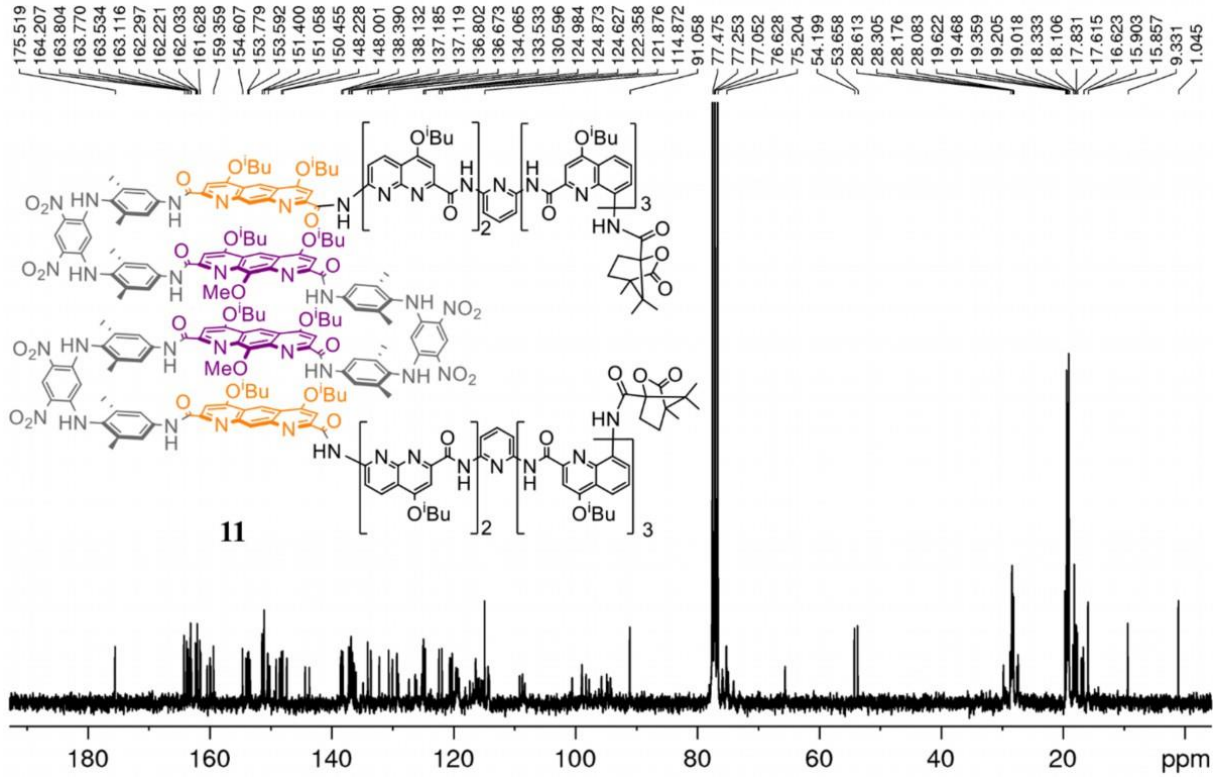
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153.592
151.400
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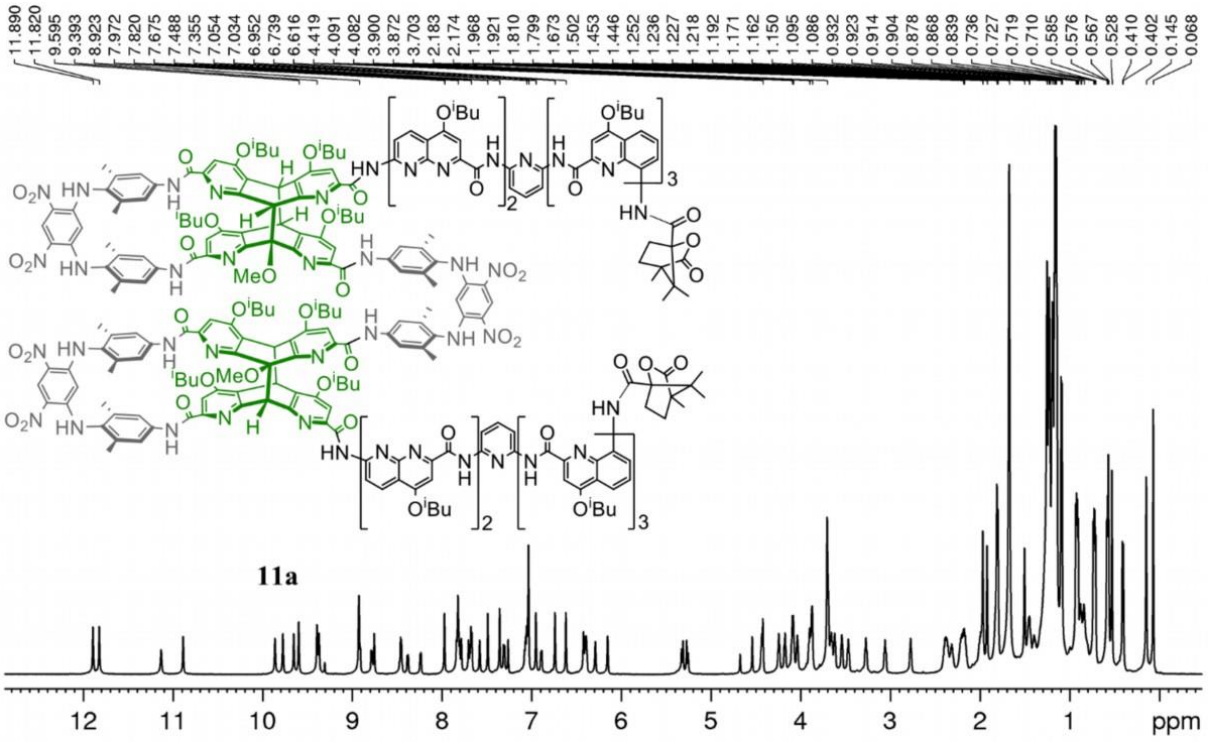
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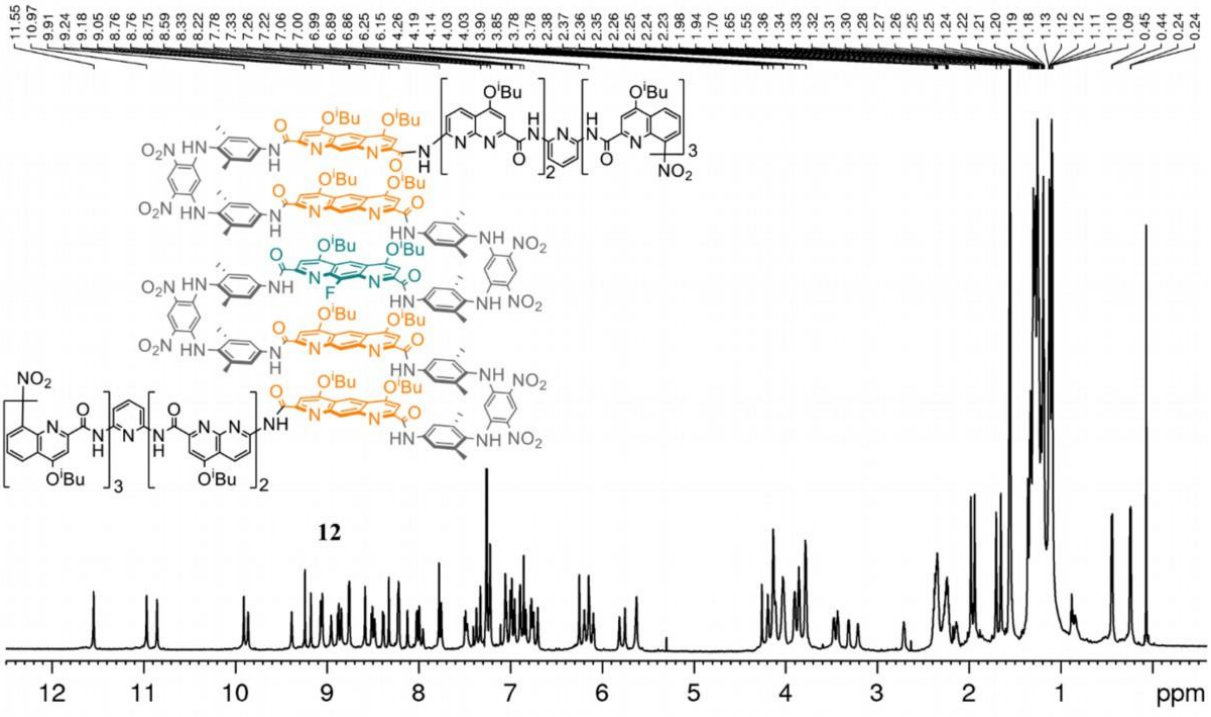
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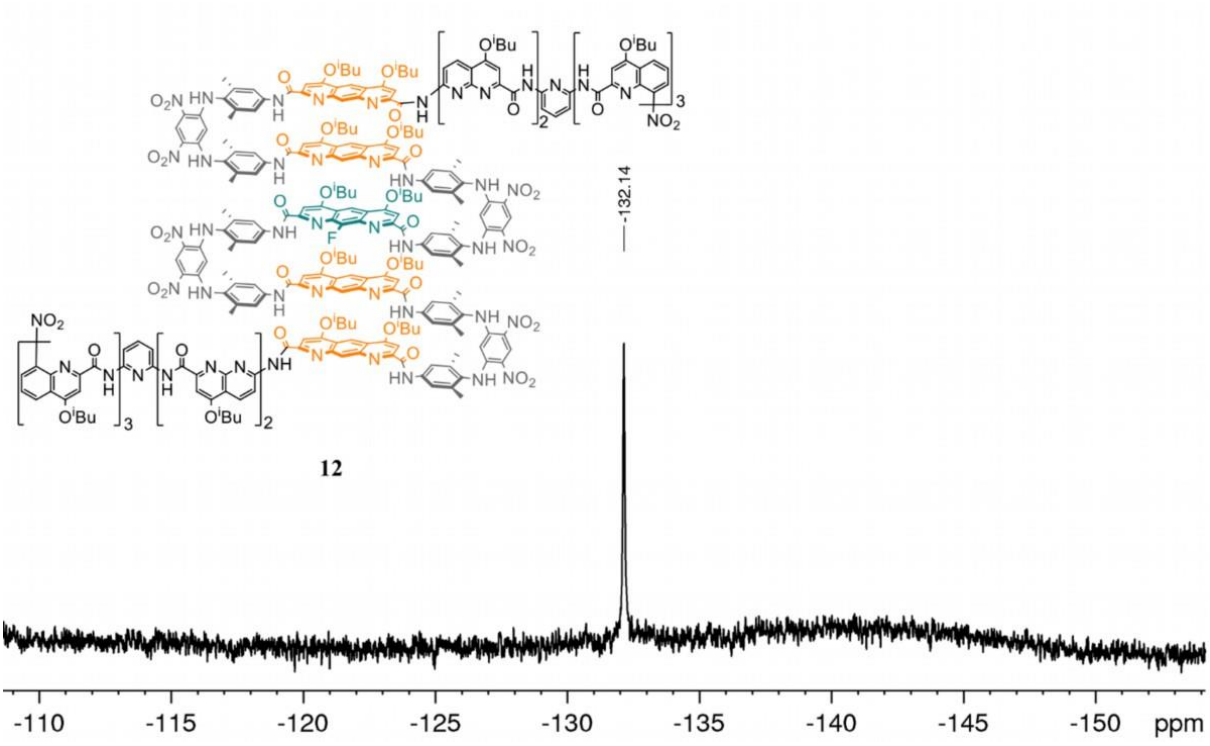
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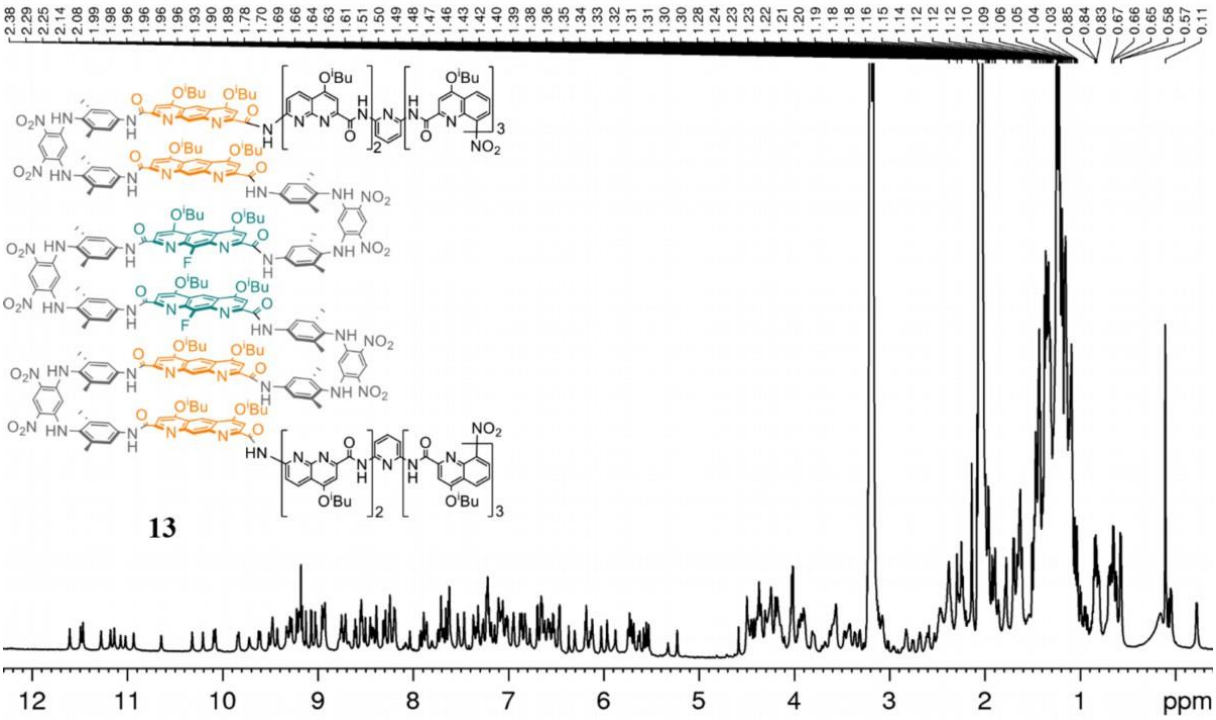
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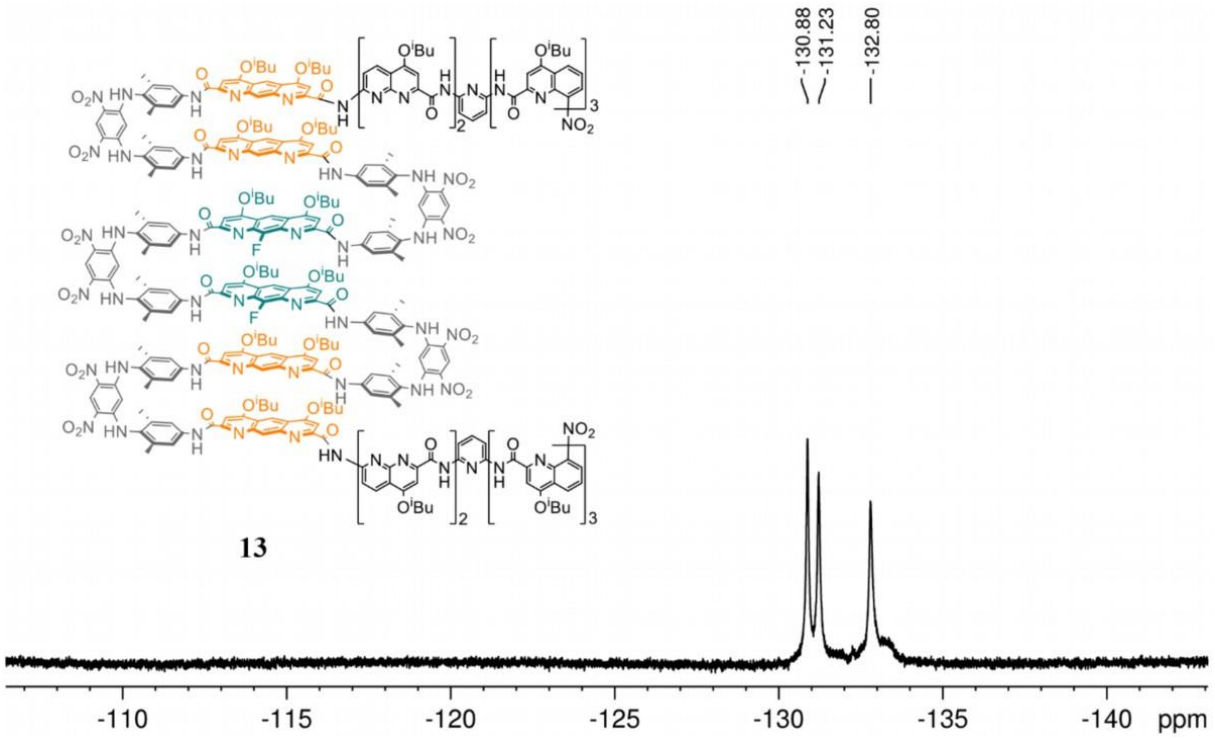
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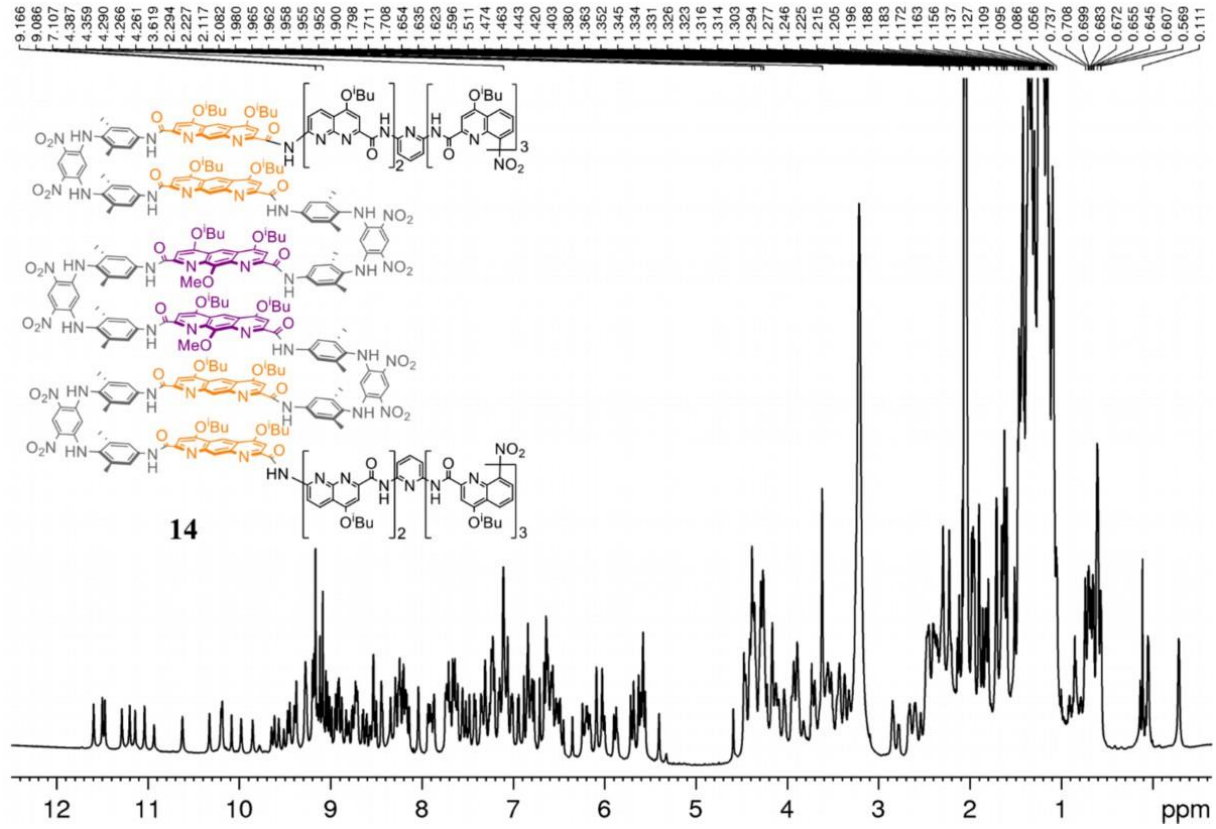
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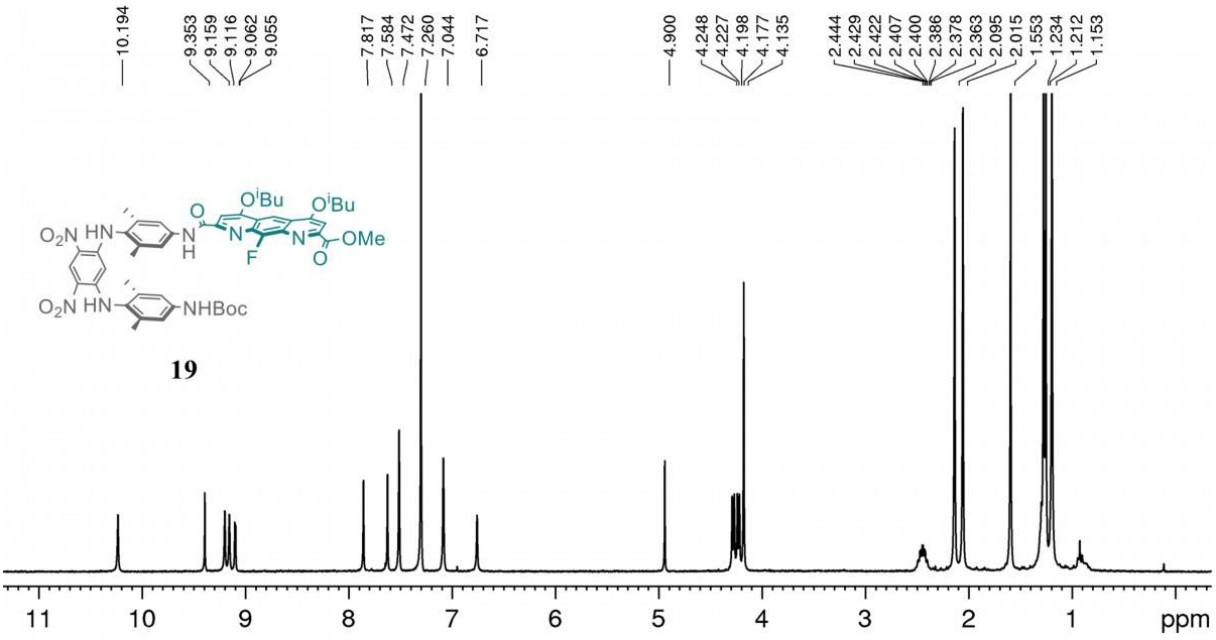
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1.212
1.153
11
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9
8
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4
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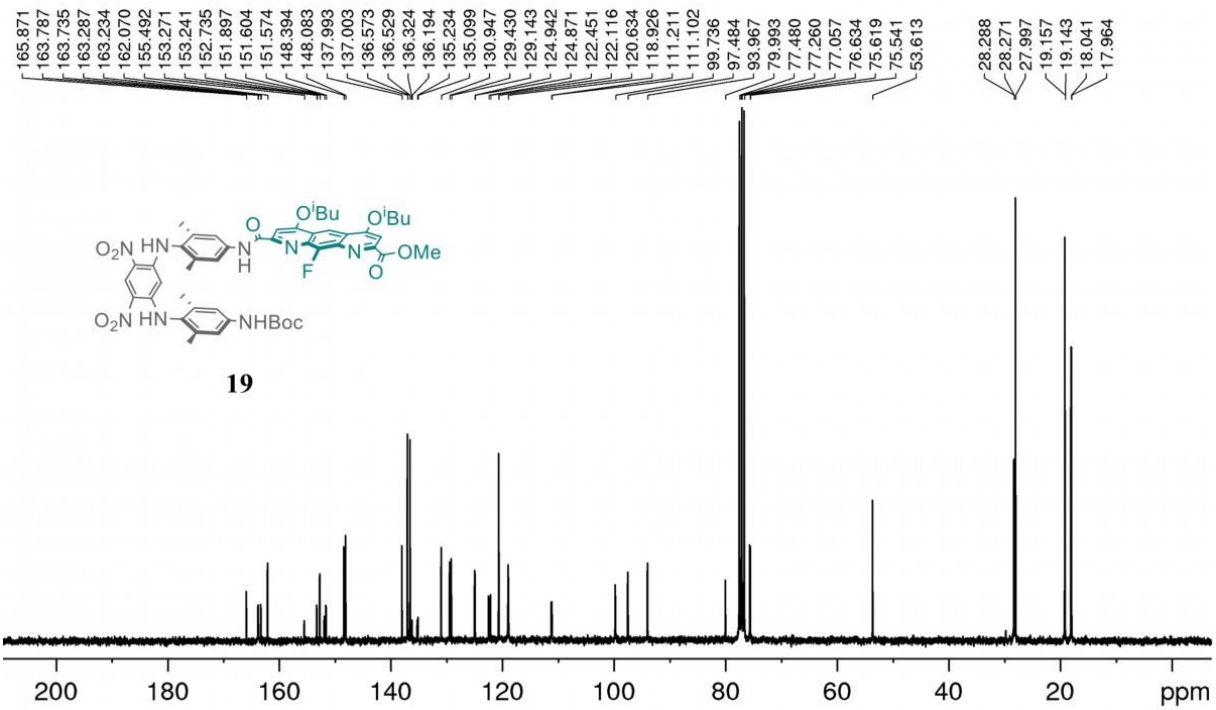
1
ppm

O2N HN
O2N HN
NHBoc
O
N
H
O
iBu
O
iBu
N
F
N
OMe
O

19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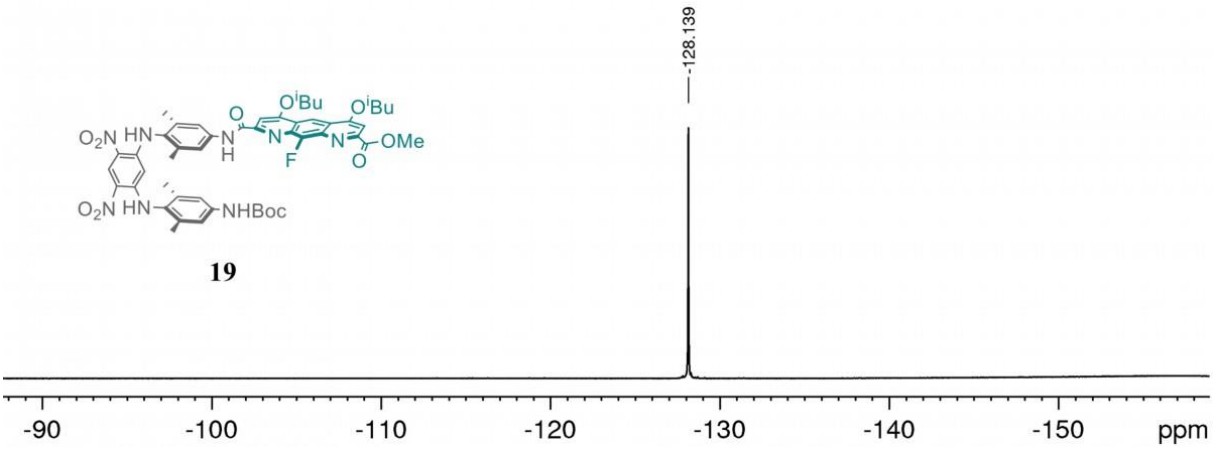
153.241
152.735
151.897
151.604
151.574
148.394
148.083
137.993
137.003
136.573
136.529
136.324
136.194
135.234
135.099
130.947
129.430
129.143
124.942
124.871
122.451
122.116
120.634
118.926
111.211
111.102
99.736
97.484
93.967
79.993
77.480
77.260
77.057
76.634
75.619
75.541
53.613
28.288
28.271
27.997
19.157
19.143
18.041
17.964
200
180
160
140
120
100
80
60
40
20
ppm

O2N HN
O2N HN
NHBoc
O
N
H
O
iBu
O
iBu
N
F
N
OMe
O

19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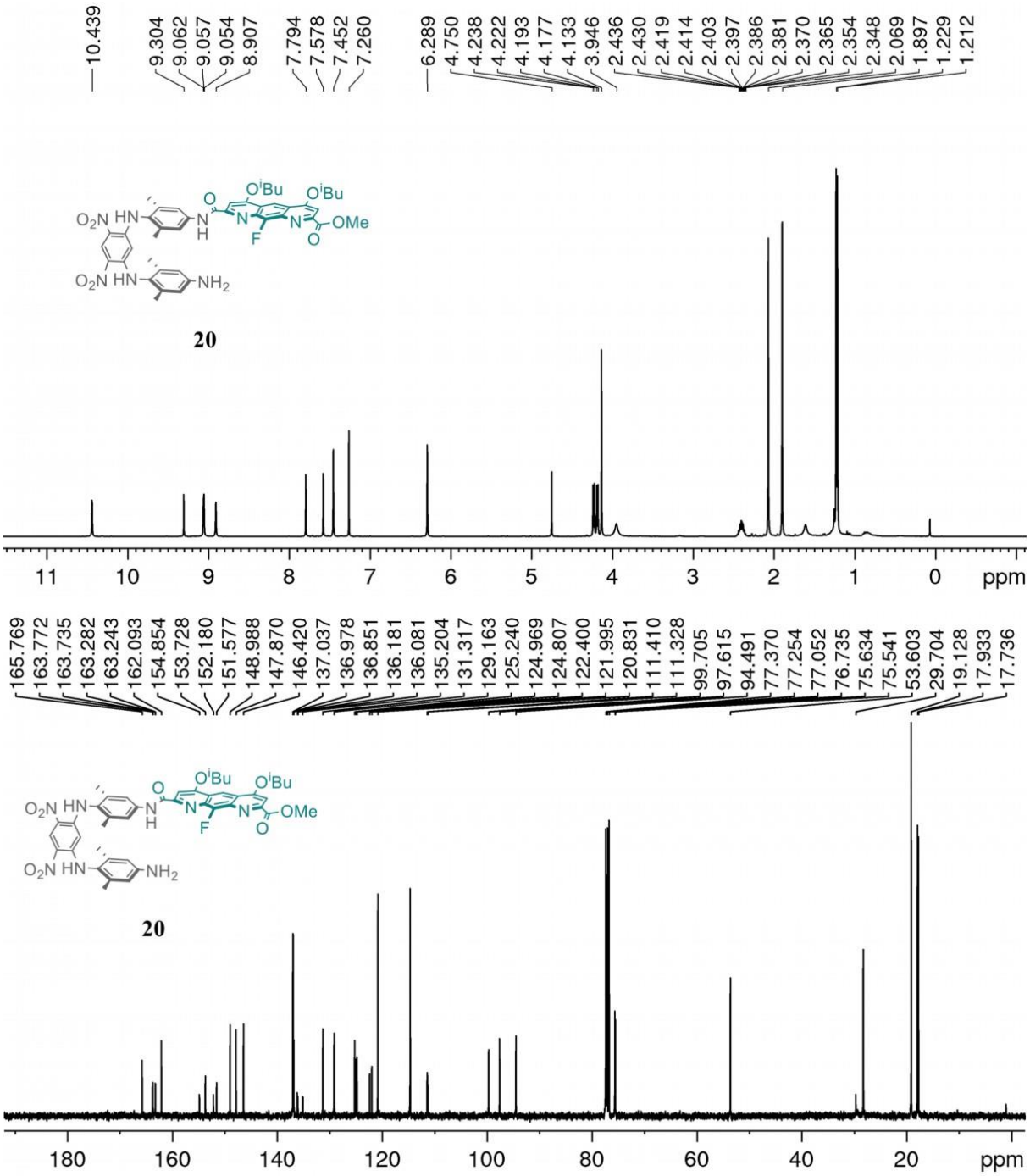
-140
-150
ppm

O2N HN
O2N HN
NHBoc
O
N
H
O
iBu
O
iBu
N
F
N
OMe
O

19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4.750
4.238
4.222
4.193
4.177
4.133
3.946
2.436
2.430
2.419
2.414
2.403
2.397
2.386
2.381
2.370
2.365
2.354
2.348
2.069
1.897
1.229
1.212
O2N HN
NH2
O
N
H
F
OiBu
OiBu
OMe
20
11
10
9
8
7
6
5
4
3
2
1
0
ppm
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163.735
163.282
163.243
162.093
154.854
153.728
152.180
151.577
148.988
147.870
146.420
137.037
136.978
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136.181
136.081
135.204
131.317
129.163
125.240
124.969
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122.400
121.995
120.831
111.410
111.328
99.705
97.615
94.491
77.370
77.254
77.052
76.735
75.634
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17.933
17.736
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140
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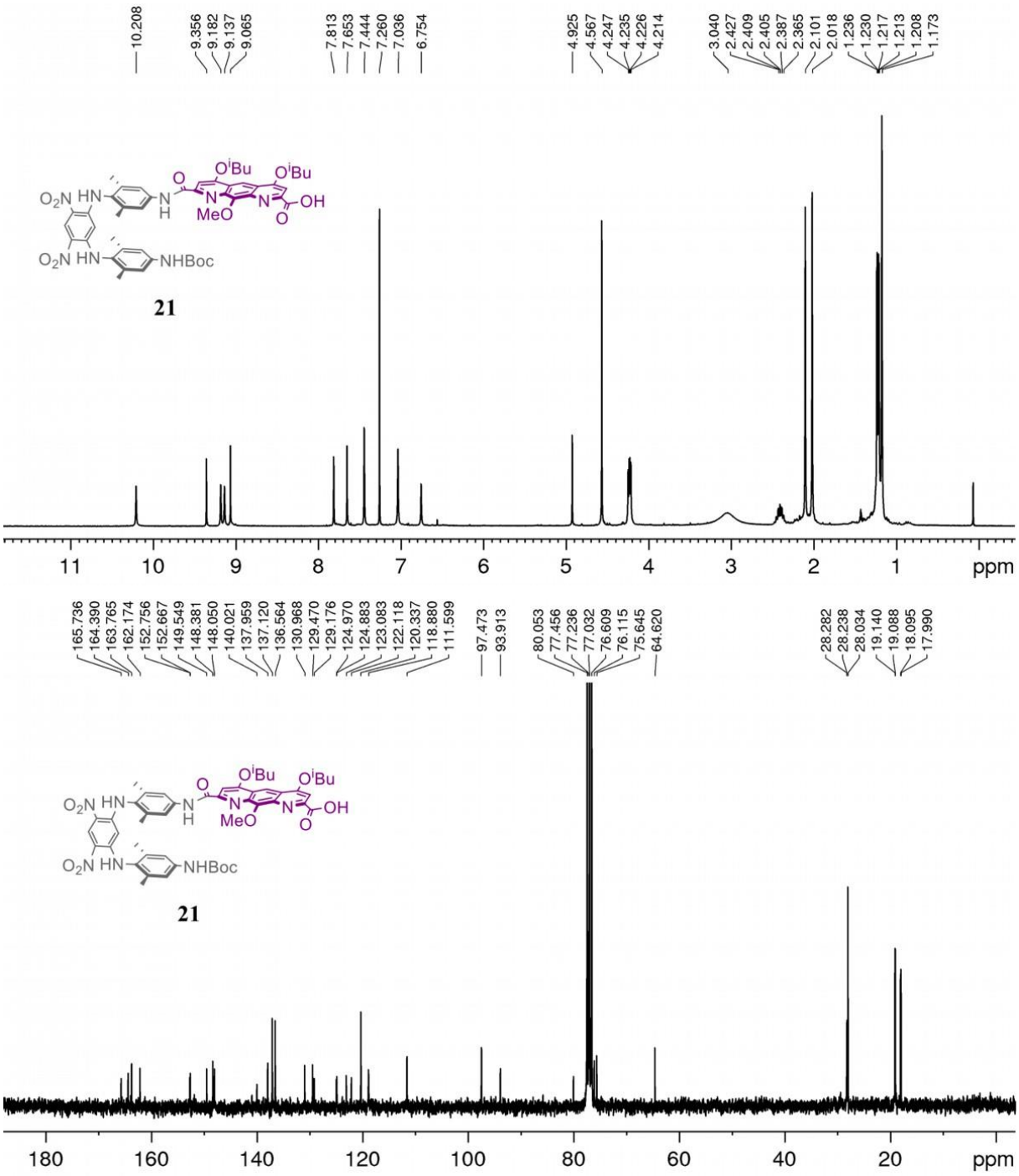
60
40
20
ppm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6.754
4.925
4.567
4.247
4.235
4.226
4.214
3.040
2.427
2.409
2.405
2.387
2.365
2.101
2.018
1.236
1.230
1.217
1.213
1.208
1.173
O2N HN
NH
O
OiBu
OiBu
N
N
MeO
OH
O
O2N HN
NHBoc
21
11
10
9
8
7
6
5
4
3
2
1
ppm
165.736
164.390
163.765
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152.667
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148.050
140.021
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137.120
136.564
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122.118
120.337
118.880
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93.913
80.053
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77.032
76.609
76.115
75.645
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28.238
28.034
19.140
19.088
18.095
17.990
O2N HN
NH
O
OiBu
OiBu
N
N
MeO
OH
O
O2N HN
NHBoc
21
180
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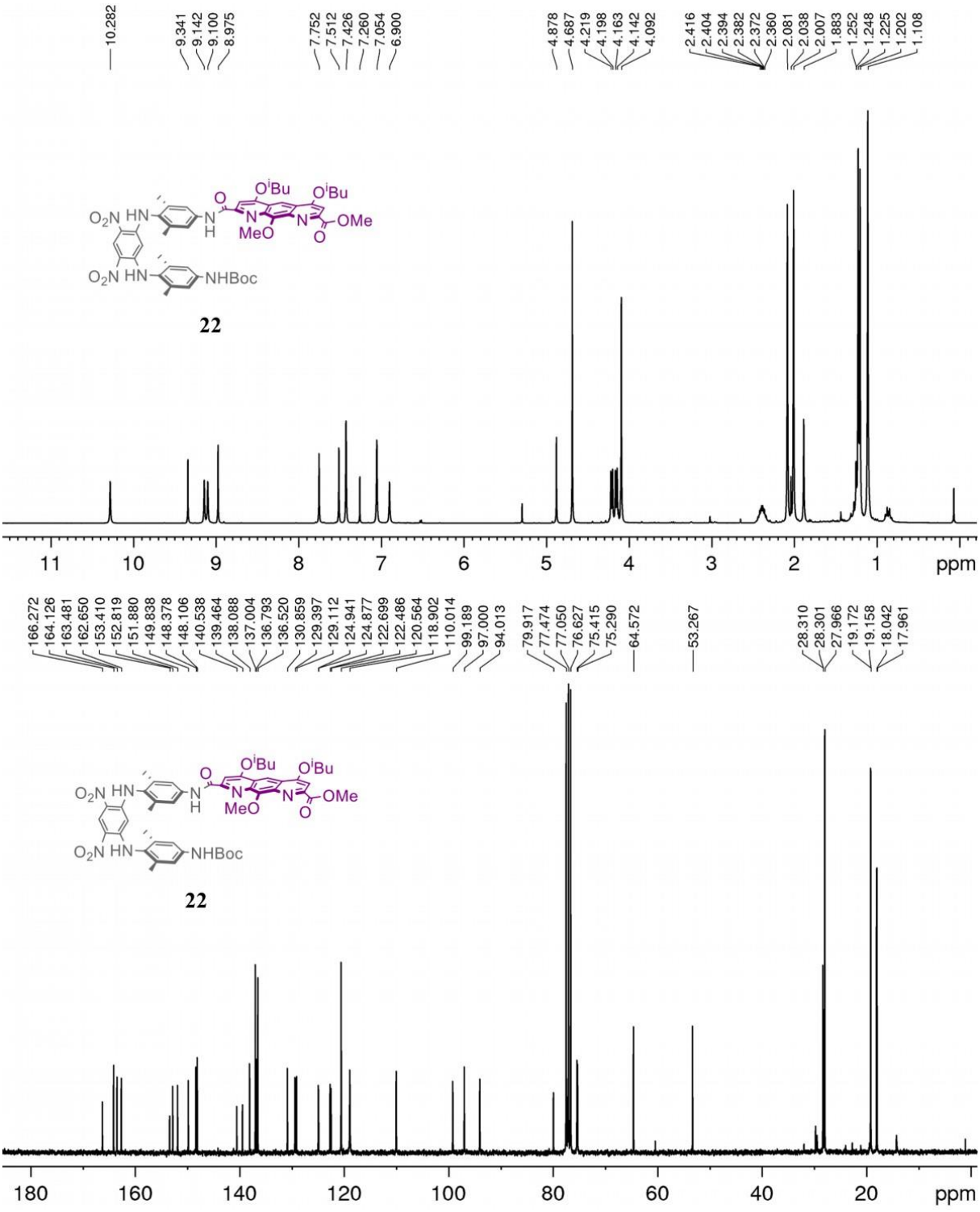
140
120
100
80
60
40
20
ppm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4.687
4.219
4.198
4.163
4.142
4.092
2.416
2.404
2.394
2.382
2.372
2.360
2.081
2.038
2.007
1.883
1.252
1.248
1.225
1.202
1.108
O2N HN
NHBoc
O2N HN
O
N
H
OiBu
OiBu
N
N
MeO
OMe
O
22
11
10
9
8
7
6
5
4
3
2
1
ppm
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164.126
163.481
162.650
153.410
152.819
151.880
149.838
148.378
148.106
140.538
139.464
138.088
137.004
136.793
136.520
130.859
129.397
129.112
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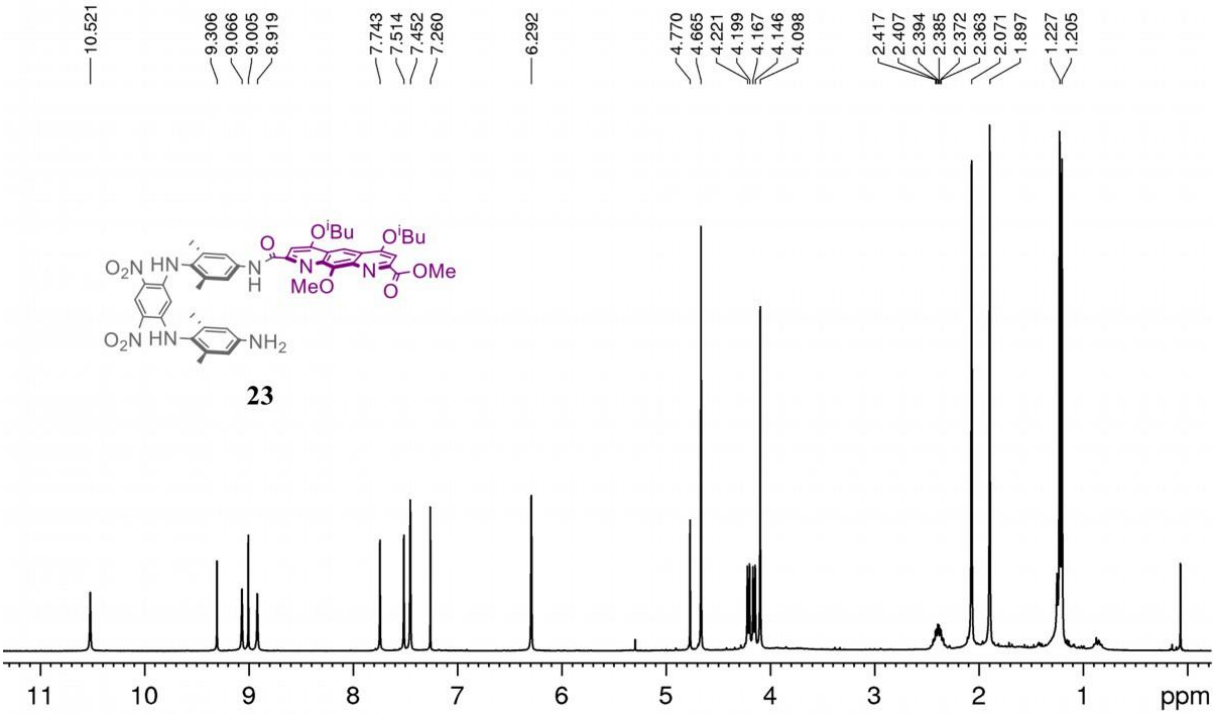
122.699
122.486
120.564
118.902
110.014
99.189
97.000
94.013
79.917
77.474
77.050
76.627
75.415
75.290
64.572
53.267
28.310
28.301
27.966
19.172
19.158
18.042
17.961
O2N HN
NHBoc
O2N HN
O
N
H
OiBu
OiBu
N
N
MeO
OMe
O
22
180
160
140
120
100
80
60
40
20
ppm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9.005
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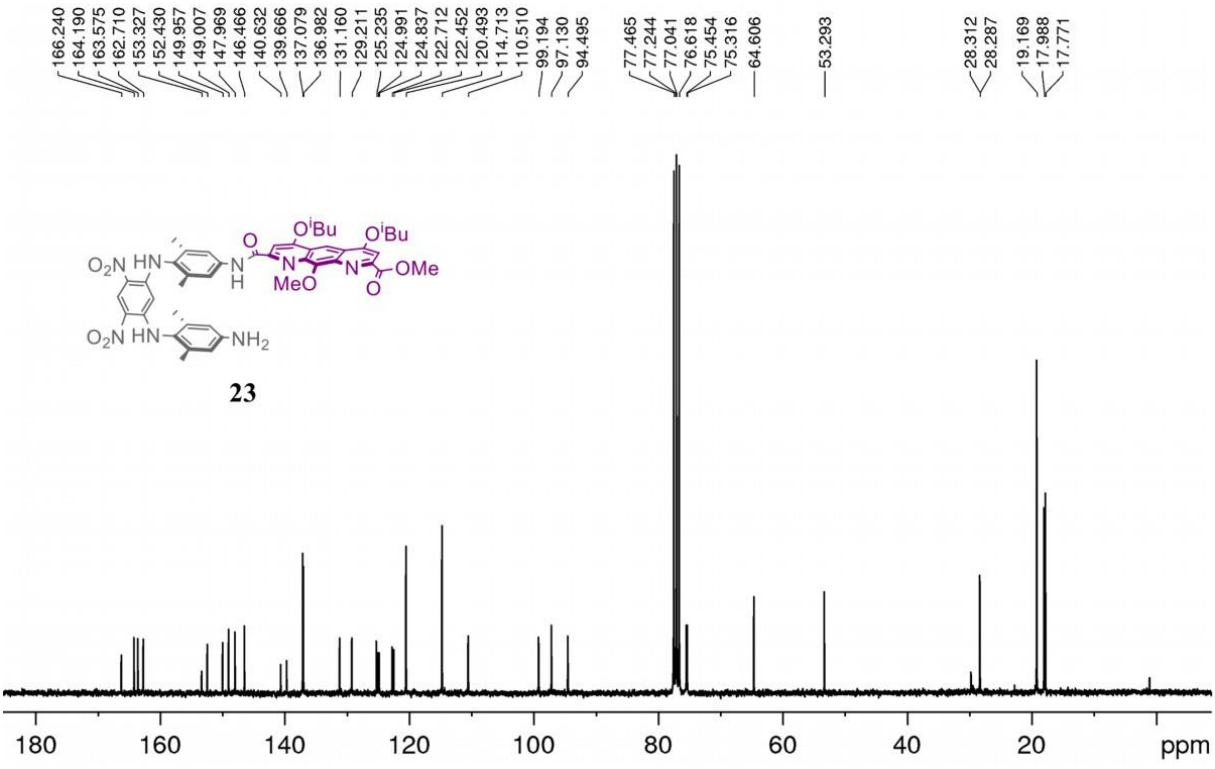
7.514
7.452
7.260
6.292
4.770
4.665
4.221
4.199
4.167
4.146
4.098
2.417
2.407
2.394
2.385
2.372
2.363
2.071
1.897
1.227
1.205
O2N HN
NH2
O
N
H
O
iBu
O
iBu
N
MeO
N
OMe
O
11
10
9
8
7
6
5
4
3
2
1
ppm

23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152.430
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149.007
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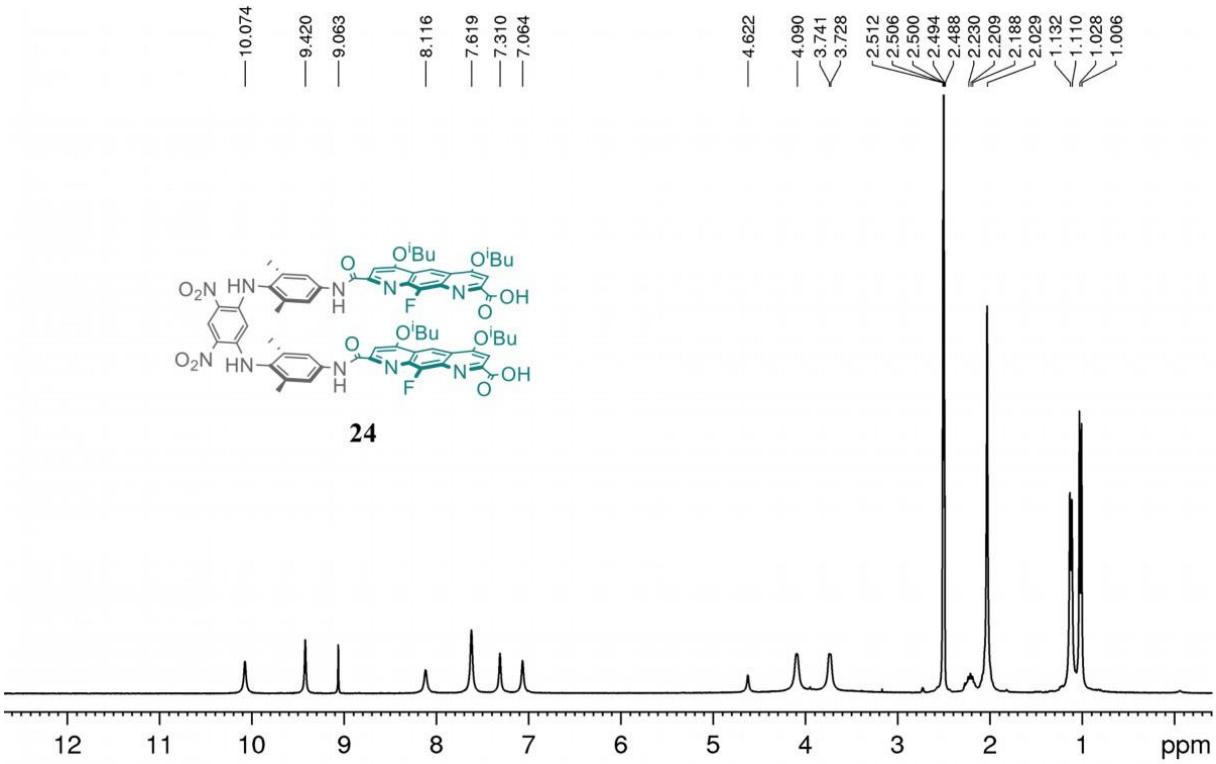
146.466
140.632
139.666
137.079
136.982
131.160
129.211
125.235
124.991
124.837
122.712
122.452
120.493
114.713
110.510
99.194
97.130
94.495
77.465
77.244
77.041
76.618
75.454
75.316
64.606
53.293
28.312
28.287
19.169
17.988
17.771
O2N HN
NH2
O
N
H
O
iBu
O
iBu
N
MeO
N
OMe
O
180
160
140
120
100
80
60
40
20
ppm

23


10.074
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9.063
8.116
7.619
7.310
7.064
4.622
4.090
3.741
3.728
2.512
2.506
2.500
2.494
2.488
2.230
2.209
2.188
2.029
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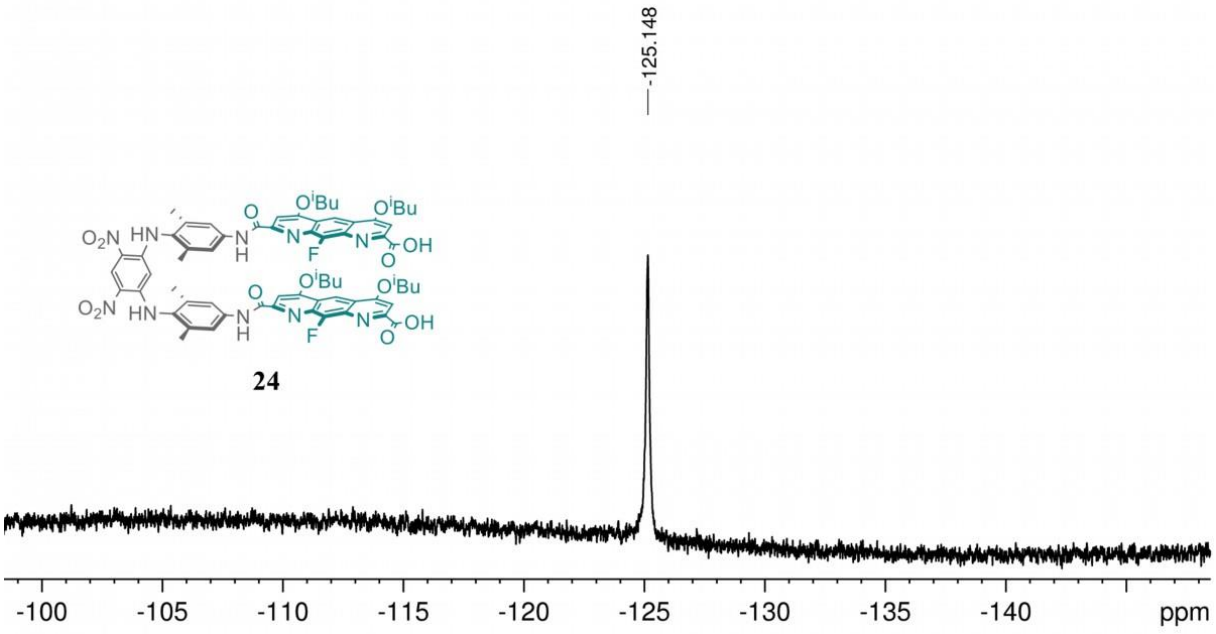
1.110
1.028
1.006
12
11
10
9
8
7
6
5
4
3
2
1
ppm

24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-125
-130
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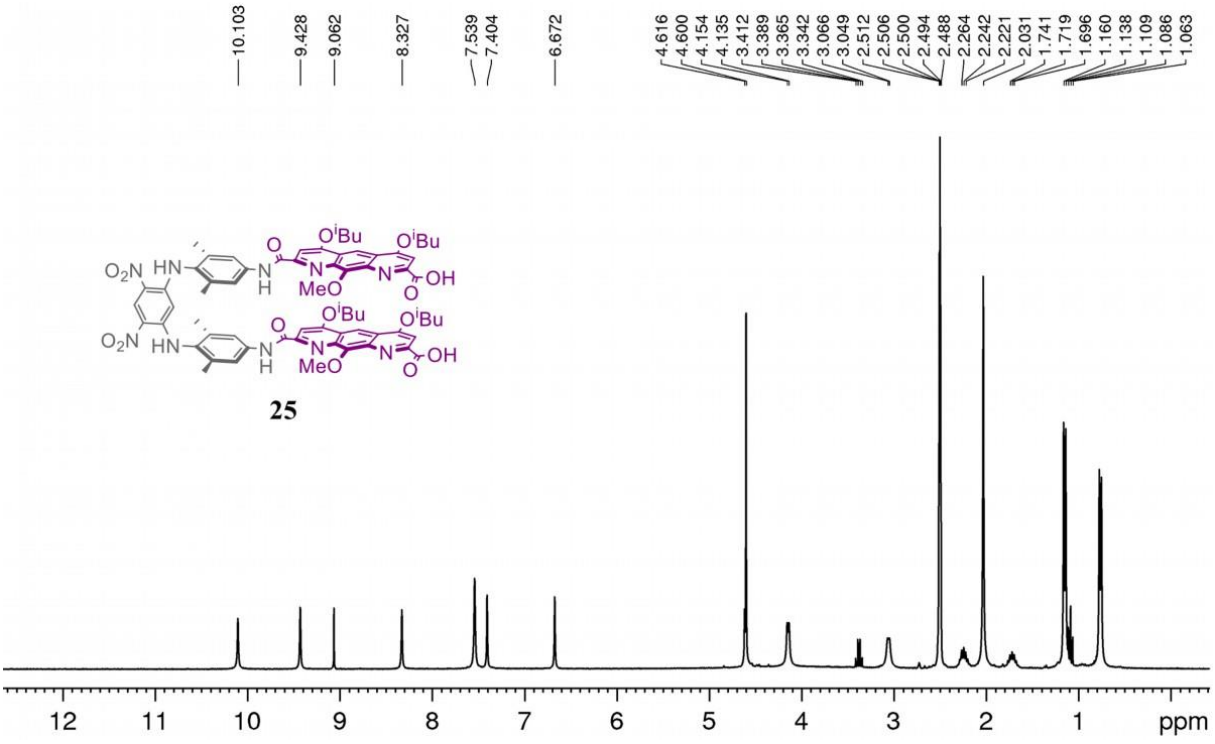
-140
ppm

24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4.616
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4.154
4.135
3.412
3.389
3.365
3.342
3.066
3.049
2.512
2.506
2.500
2.494
2.488
2.264
2.242
2.221
2.031
1.741
1.719
1.696
1.160
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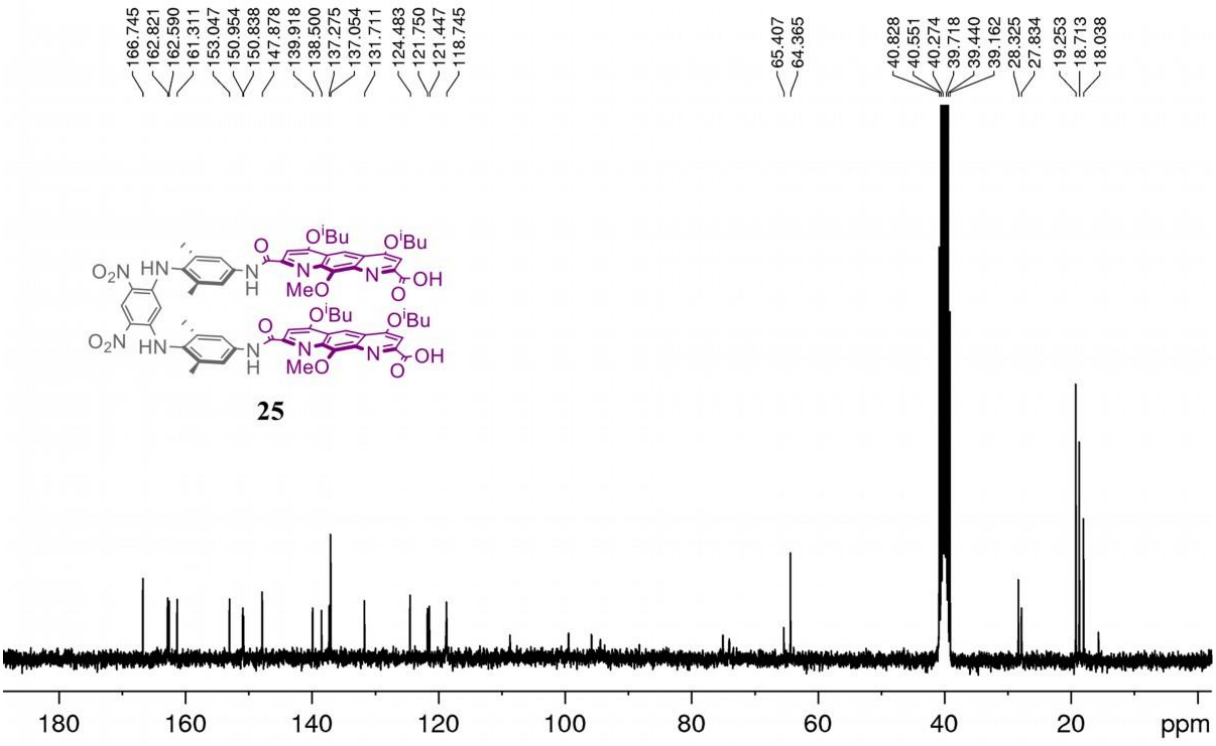
1.063
12
11
10
9
8
7
6
5
4
3
2
1
ppm

25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124.483
121.750
121.447
118.745
65.407
64.365
40.828
40.551
40.274
39.718
39.440
39.162
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19.253
18.713
18.038
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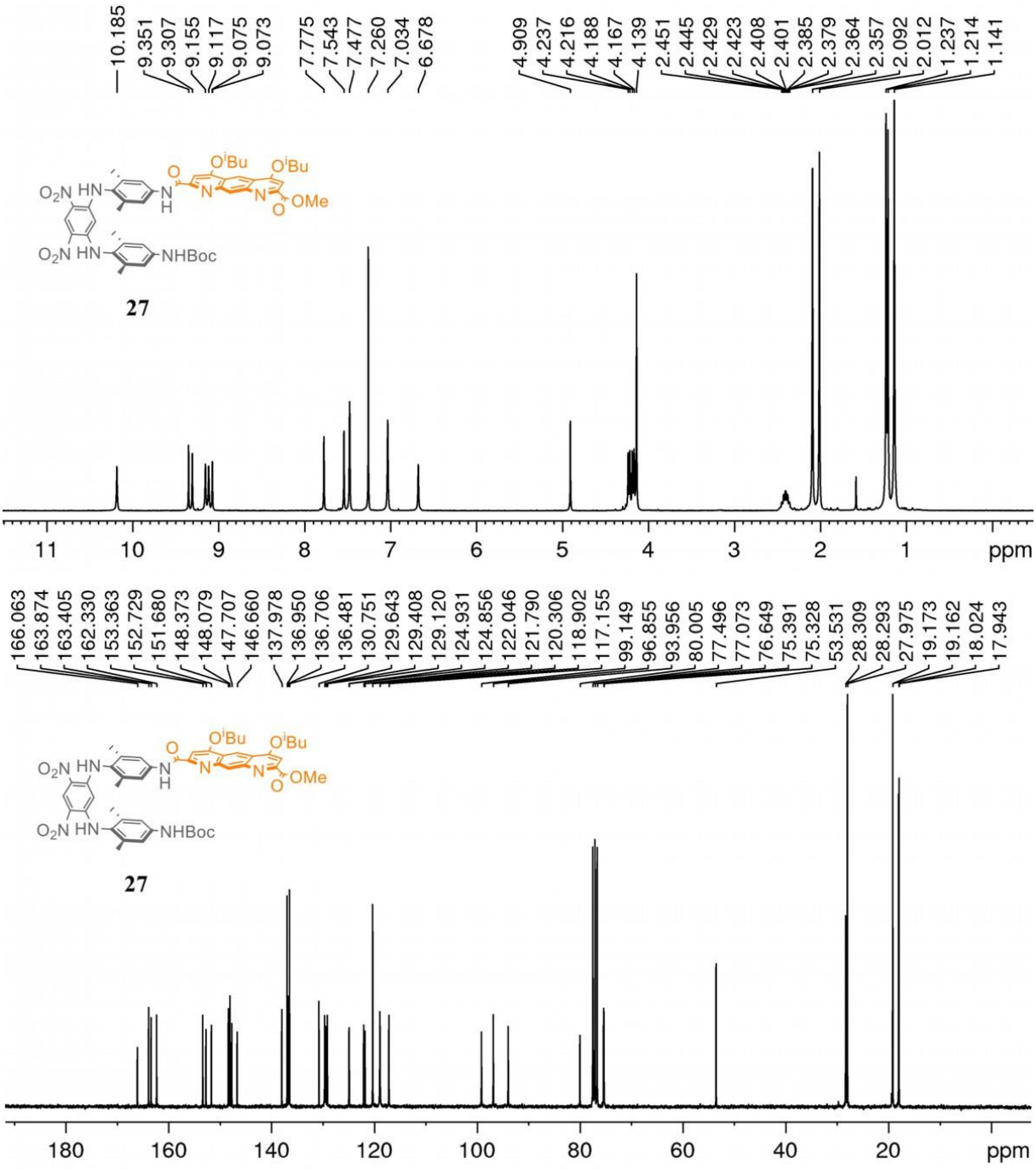
160
140
120
100
80
60
40
20
ppm

25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7.543
7.477
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7.034
6.678
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4.237
4.216
4.188
4.167
4.139
2.451
2.445
2.429
2.423
2.408
2.401
2.385
2.379
2.364
2.357
2.092
2.012
1.237
1.214
1.141
O2N HN
NHBoc
O2N HN
O
N
H
O
N
N
O
OiBu
OiBu
OMe
27
11
10
9
8
7
6
5
4
3
2
1
ppm
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163.405
162.330
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151.680
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146.660
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136.950
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75.328
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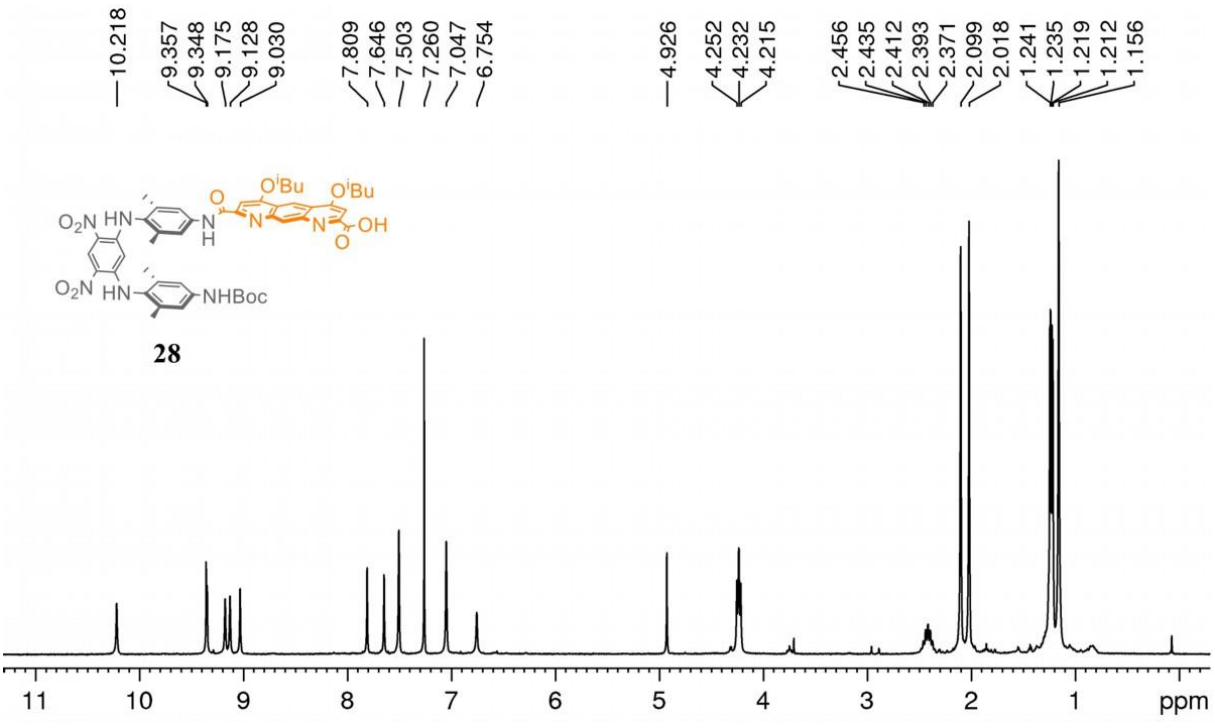
20
ppm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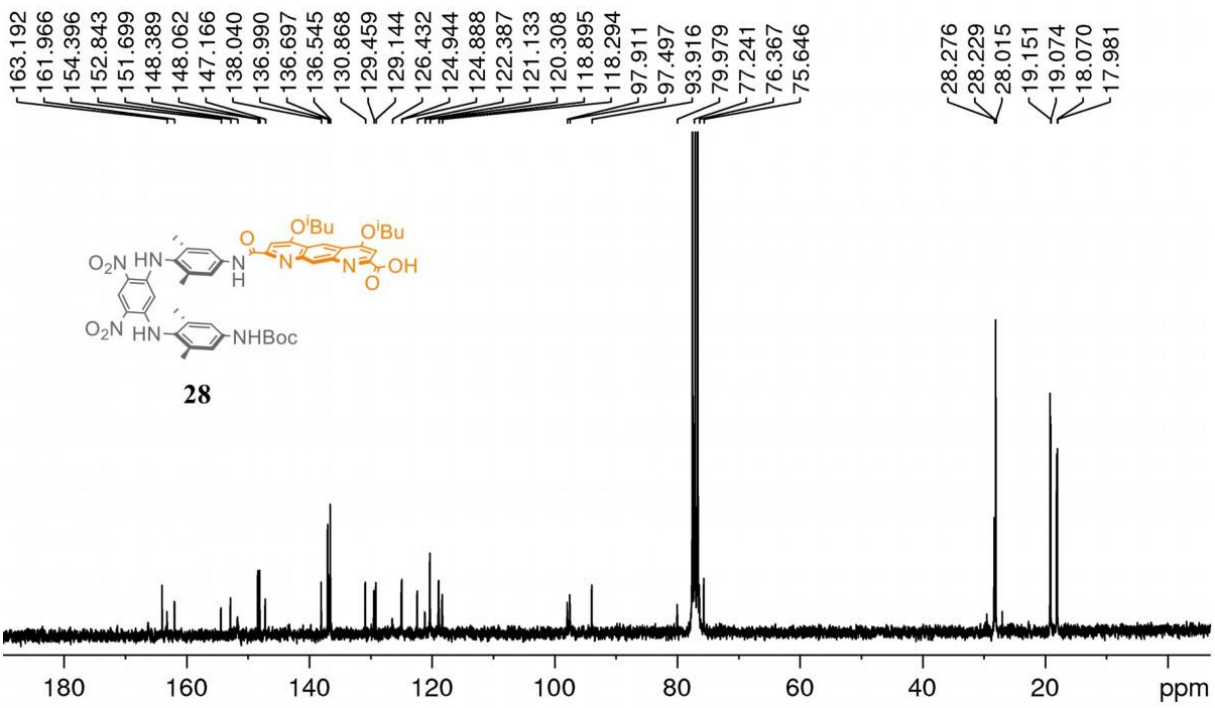
7.260
7.047
6.754
4.926
4.252
4.232
4.215
2.456
2.435
2.412
2.393
2.371
2.099
2.018
1.241
1.235
1.219
1.212
1.156
O2N HN
O2N HN
NHBoc
O
N
H
N
N
O
OH
O
iBu
O
iBu
11
10
9
8
7
6
5
4
3
2
1
ppm

28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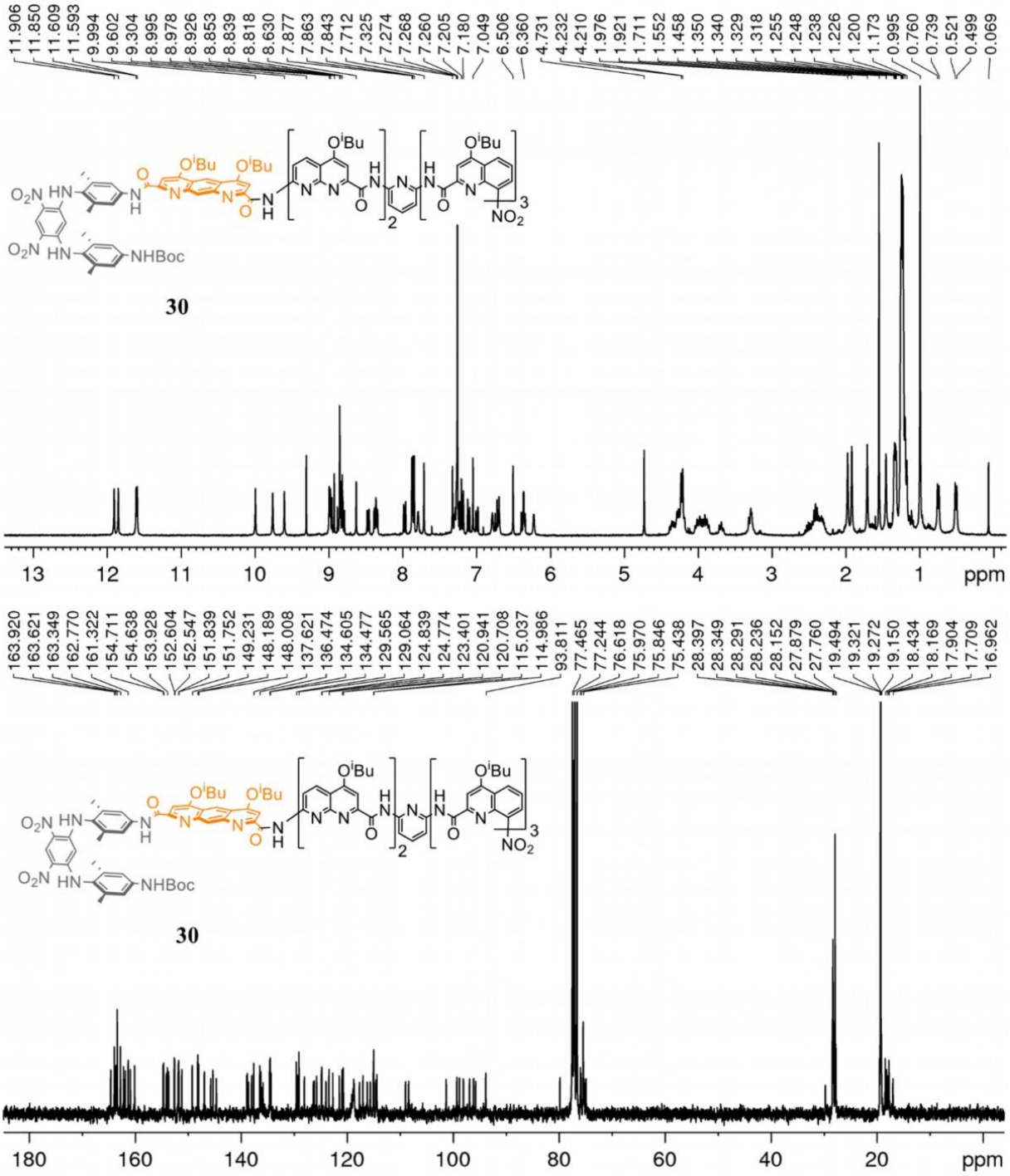
136.990
136.697
136.545
130.868
129.459
129.144
126.432
124.944
124.888
122.387
121.133
120.308
118.895
118.294
97.911
97.497
93.916
79.979
77.241
76.367
75.646
28.276
28.229
28.015
19.151
19.074
18.070
17.981
O2N HN
O2N HN
NHBoc
O
N
H
N
N
O
OH
O
iBu
O
iBu
180
160
140
120
100
80
60
40
20
ppm

28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8.926
8.853
8.839
8.818
8.630
7.877
7.863
7.843
7.712
7.325
7.274
7.268
7.260
7.205
7.180
7.049
6.506
6.360
4.731
4.232
4.210
1.976
1.921
1.711
1.552
1.458
1.350
1.340
1.329
1.318
1.255
1.248
1.238
1.226
1.200
1.173
0.995
0.760
0.739
0.521
0.499
0.069
30
13
12
11
10
9
8
7
6
5
4
3
2
1
ppm
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152.547
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151.752
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123.401
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77.465
77.244
76.618
75.970
75.846
75.438
28.397
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27.879
27.760
19.494
19.321
19.272
19.150
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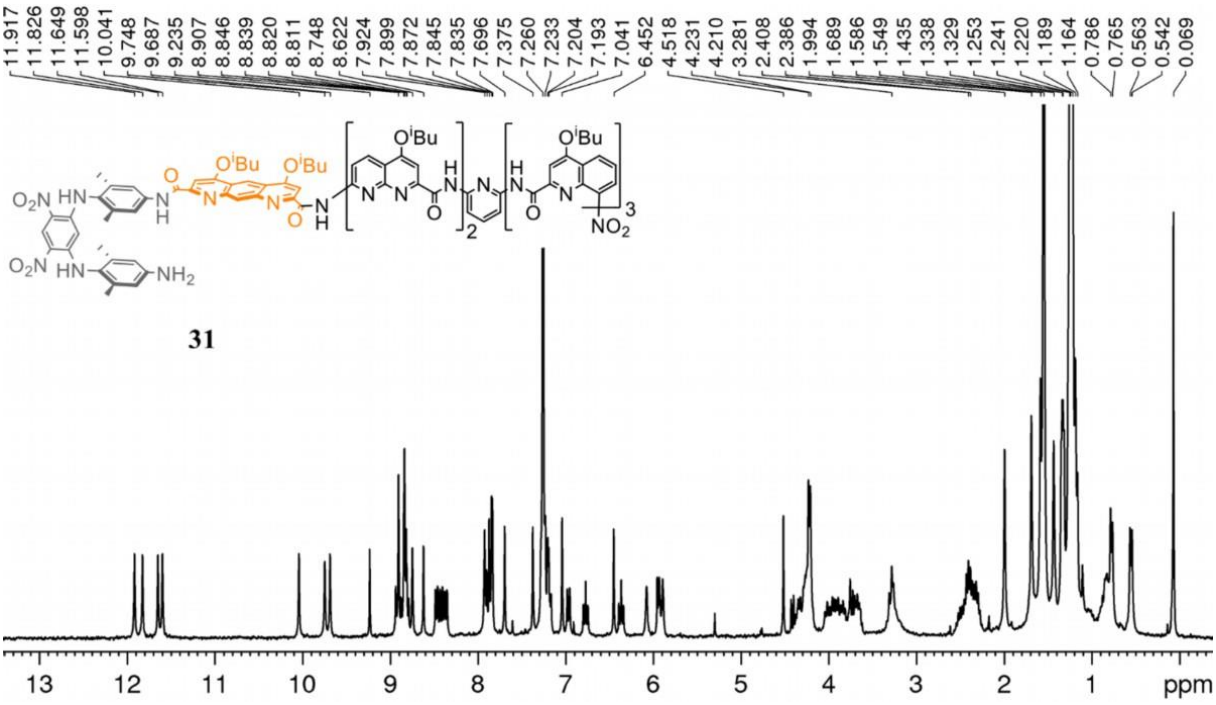
40
20
ppm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7.193
7.041
6.452
4.518
4.231
4.210
3.281
2.408
2.386
1.994
1.689
1.586
1.549
1.435
1.338
1.329
1.253
1.241
1.220
1.189
1.164
0.786
0.765
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12
11
10
9
8
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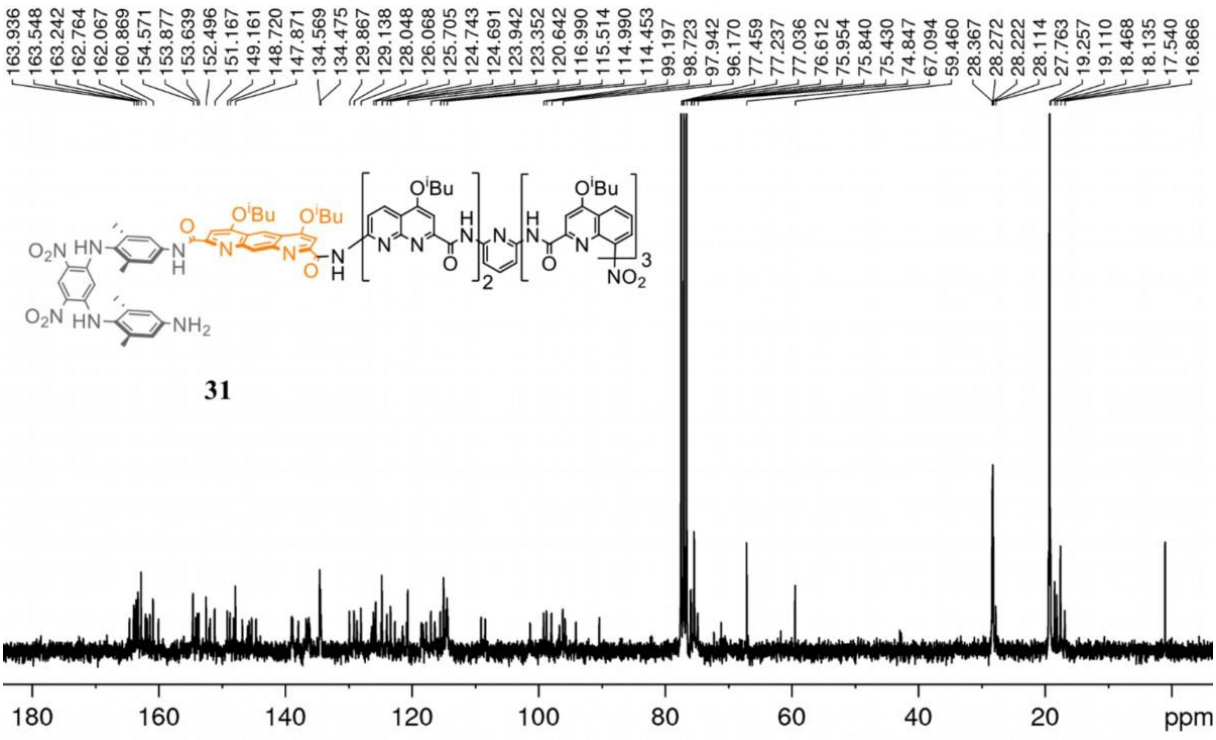
6
5
4
3
2
1
ppm

31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123.352
120.642
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114.990
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77.237
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76.612
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74.847
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59.460
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28.272
28.222
28.114
27.763
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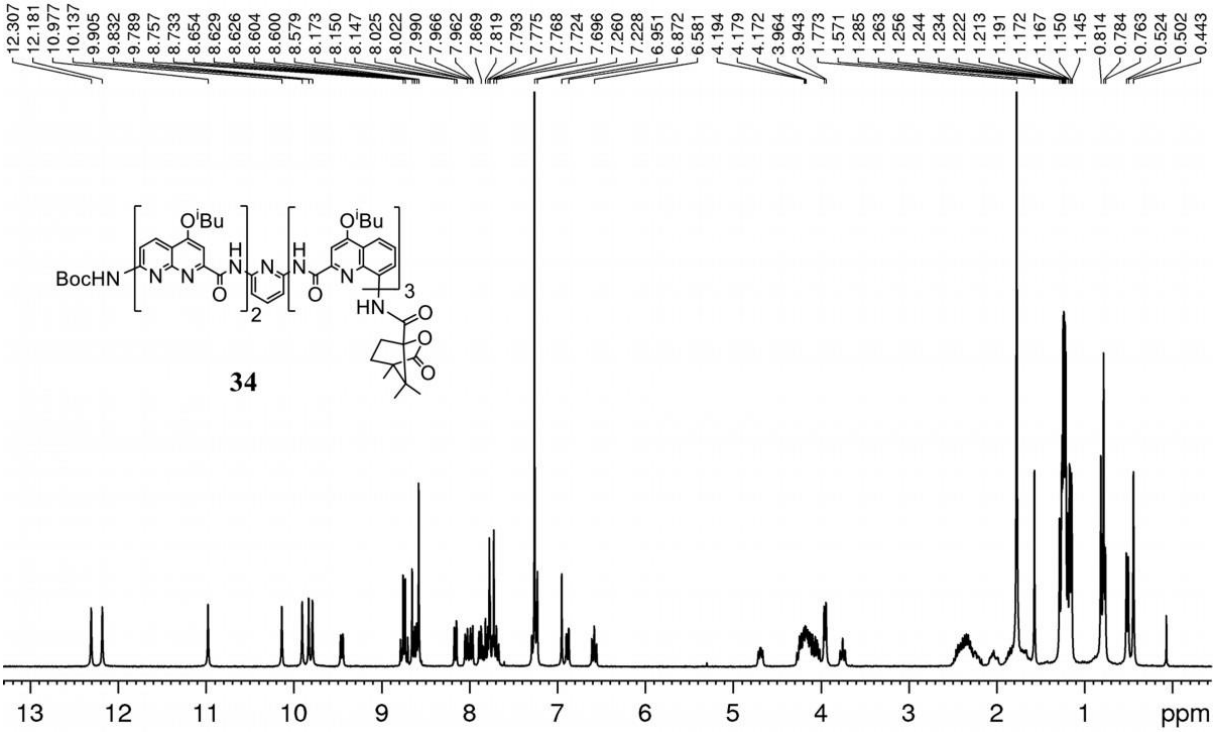
120
100
80
60
40
20
ppm

31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8.733
8.654
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8.626
8.604
8.600
8.579
8.173
8.150
8.147
8.025
8.022
7.990
7.966
7.962
7.869
7.819
7.793
7.775
7.768
7.724
7.696
7.260
7.228
6.951
6.872
6.581
4.194
4.179
4.172
3.964
3.943
1.773
1.571
1.285
1.263
1.256
1.244
1.234
1.222
1.213
1.191
1.172
1.167
1.150
1.145
0.814
0.784
0.763
0.524
0.502
0.443
BocHN
O^{i}Bu
HN
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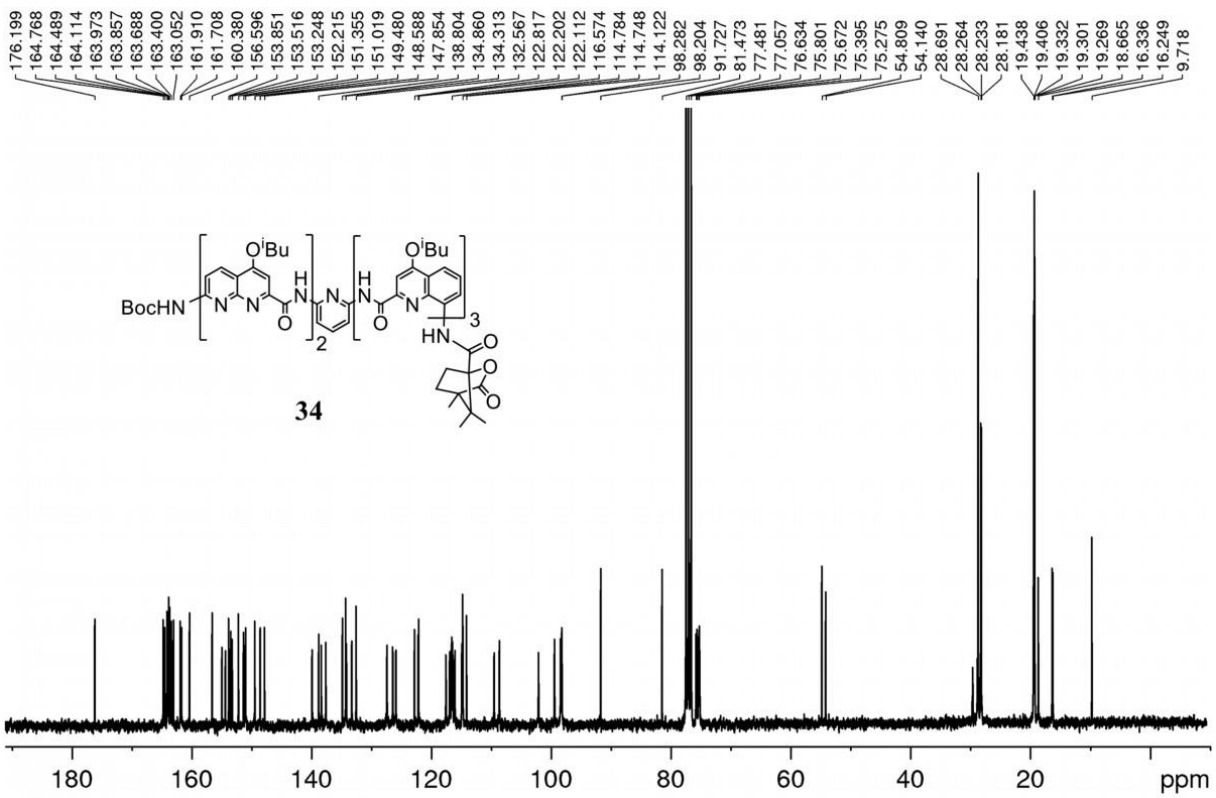
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O^{i}Bu
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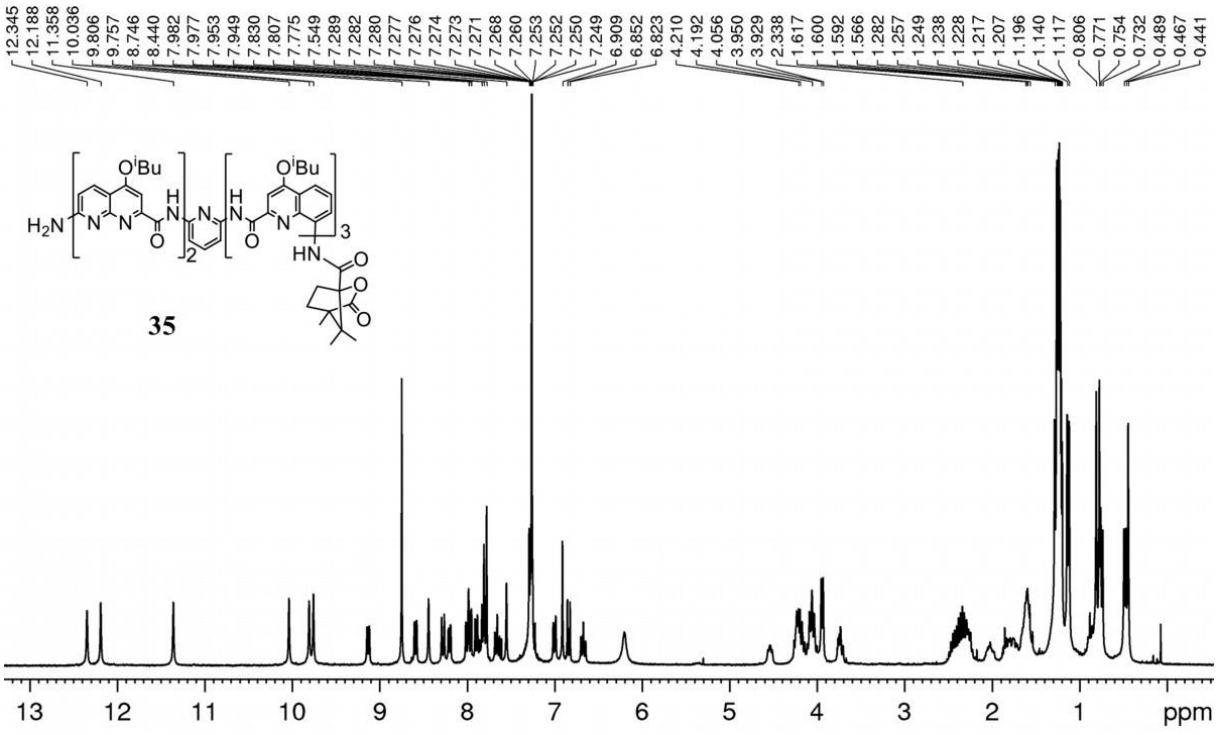
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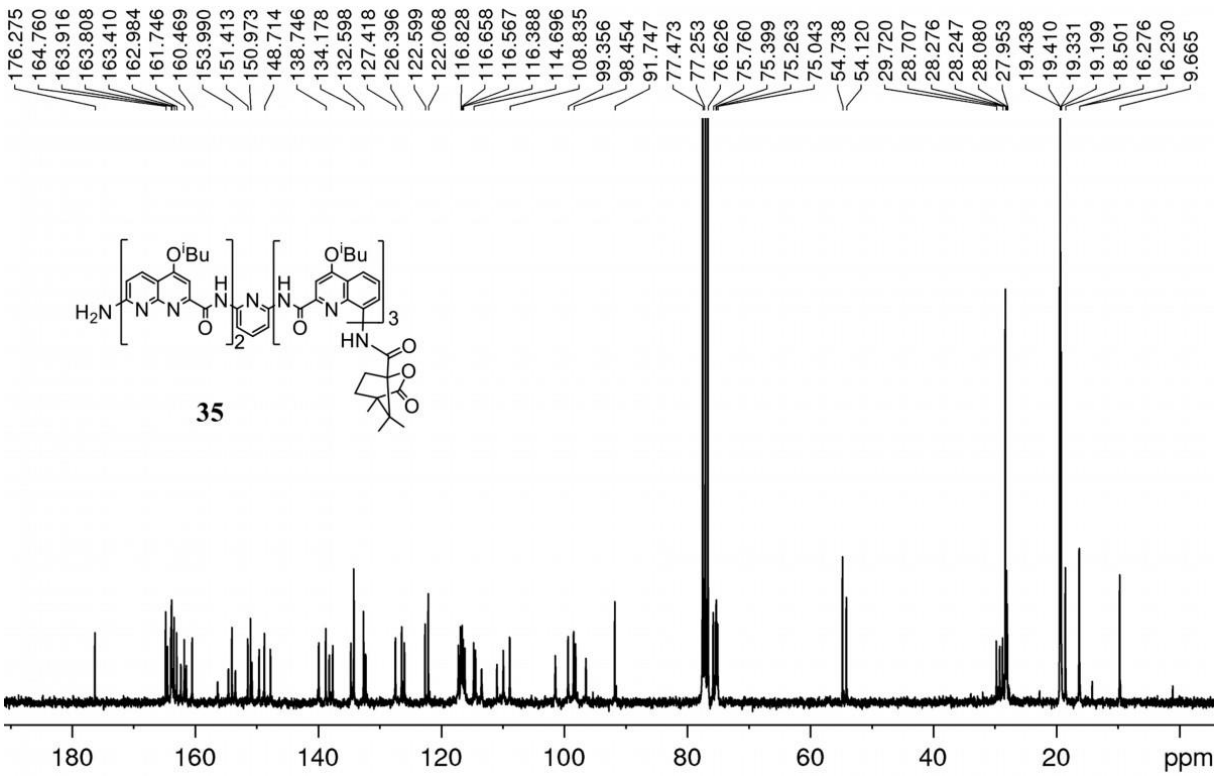
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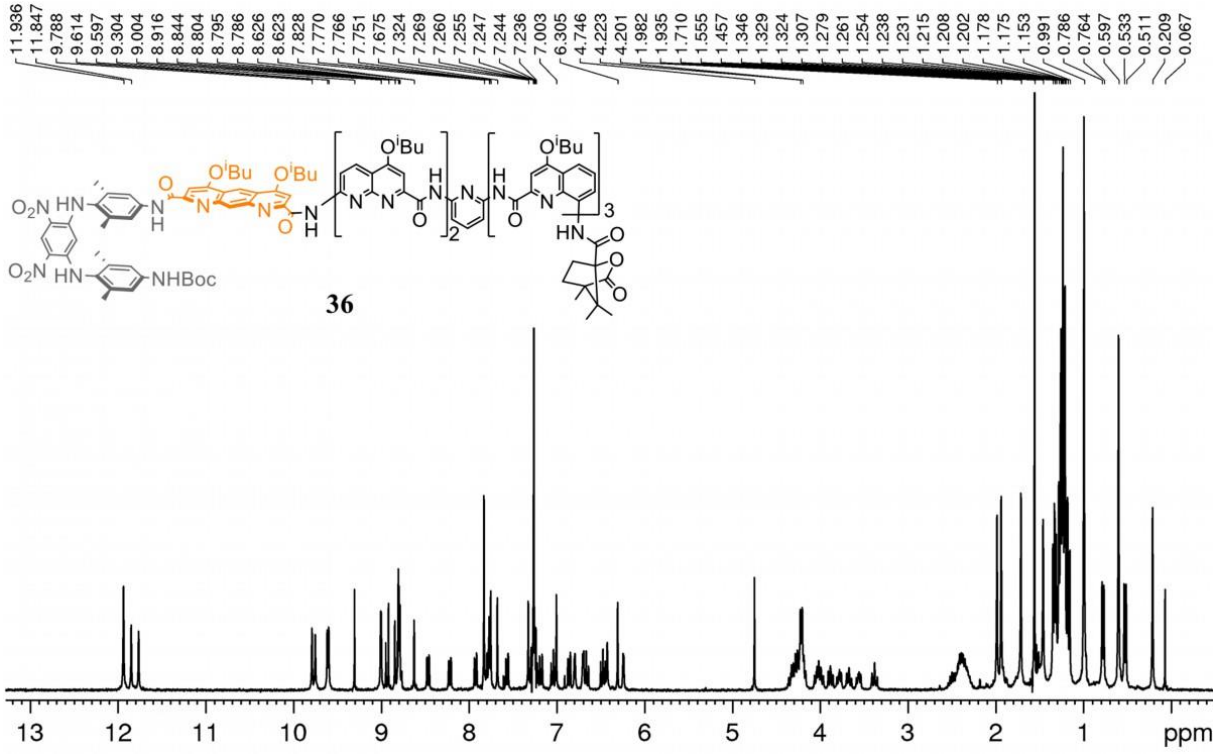
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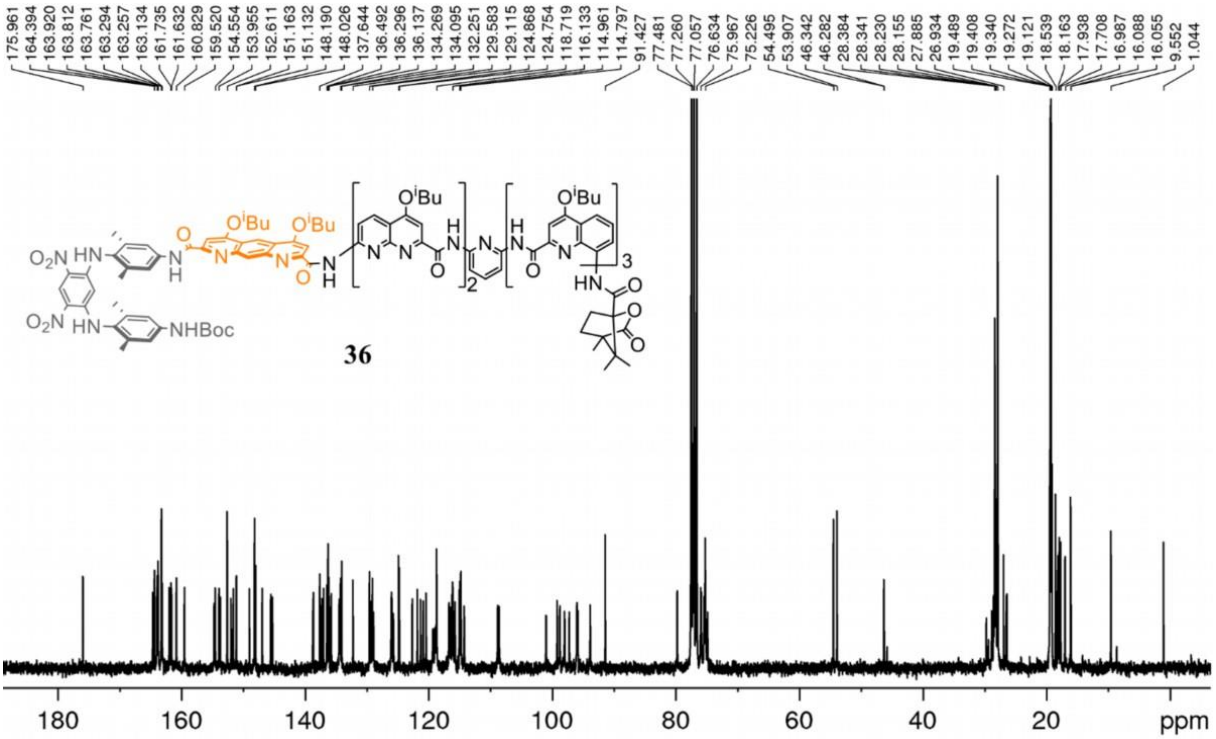
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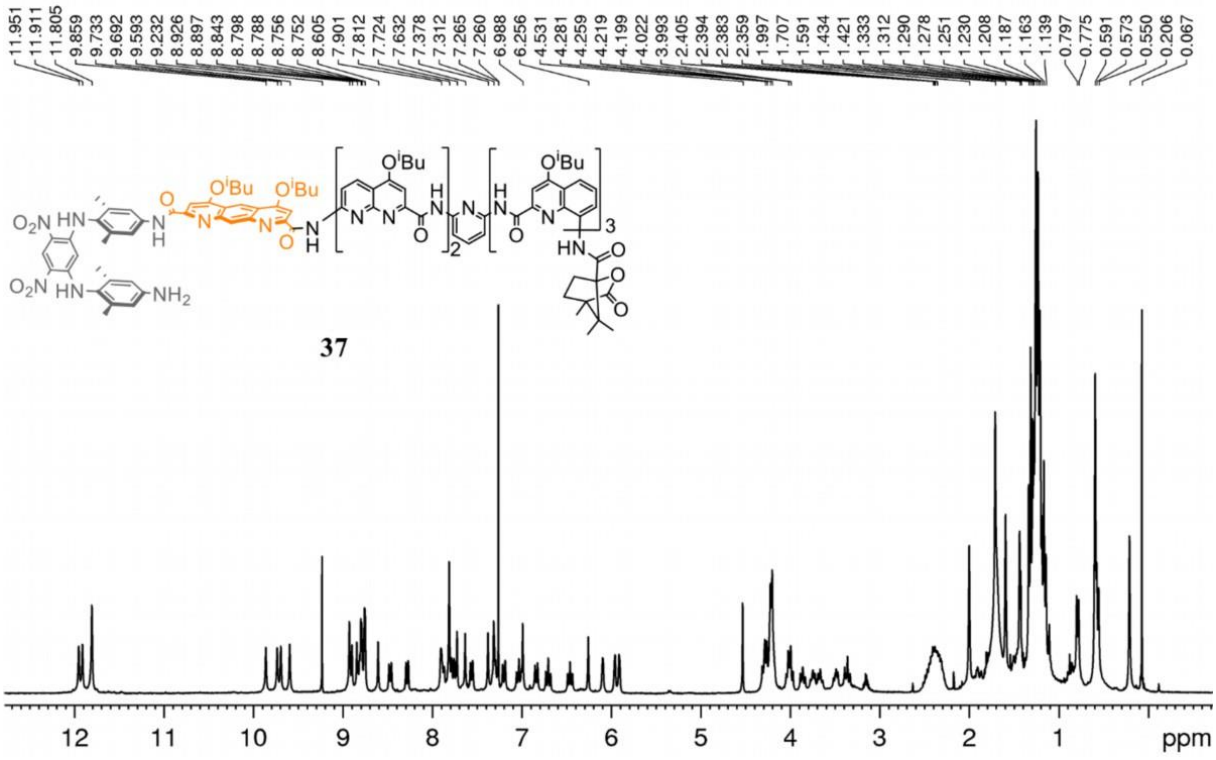
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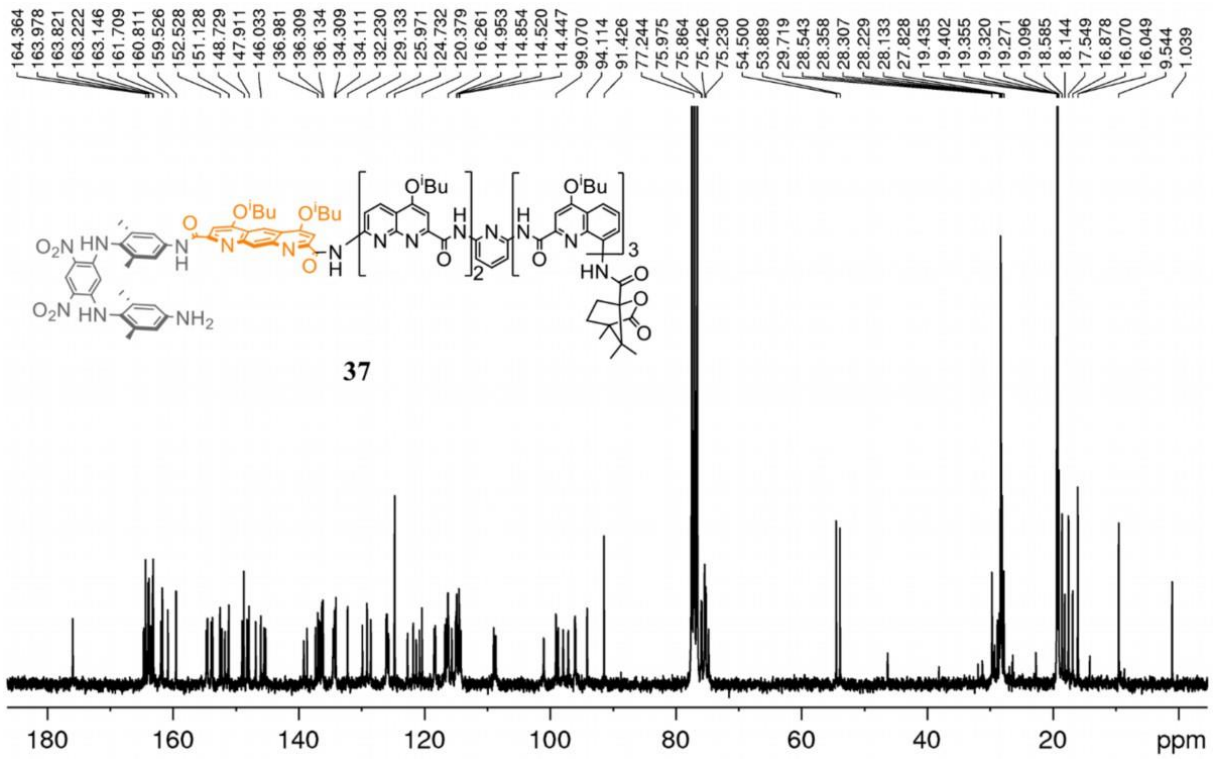
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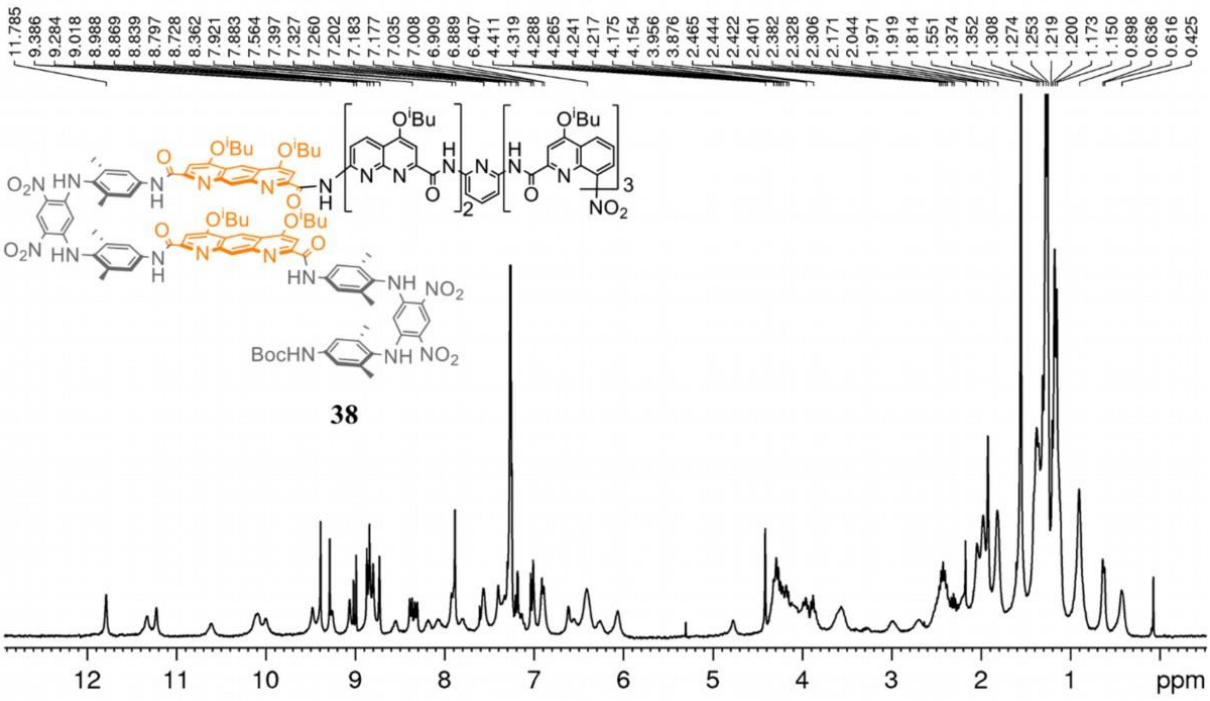
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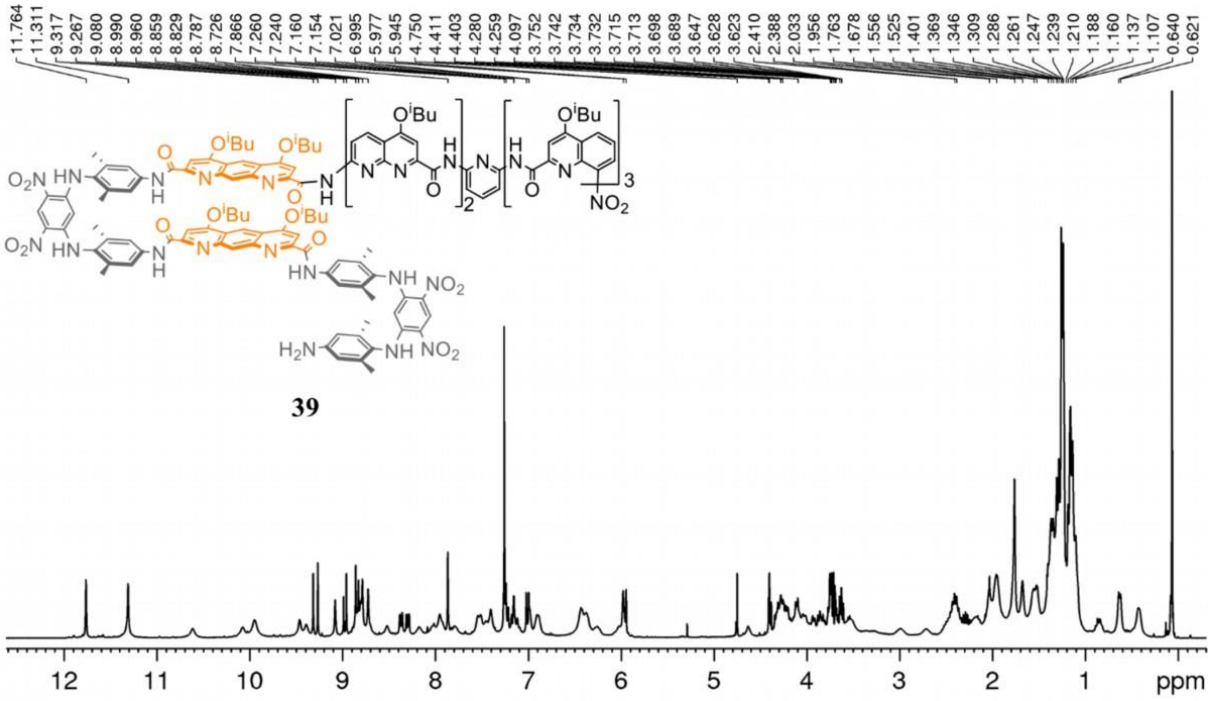
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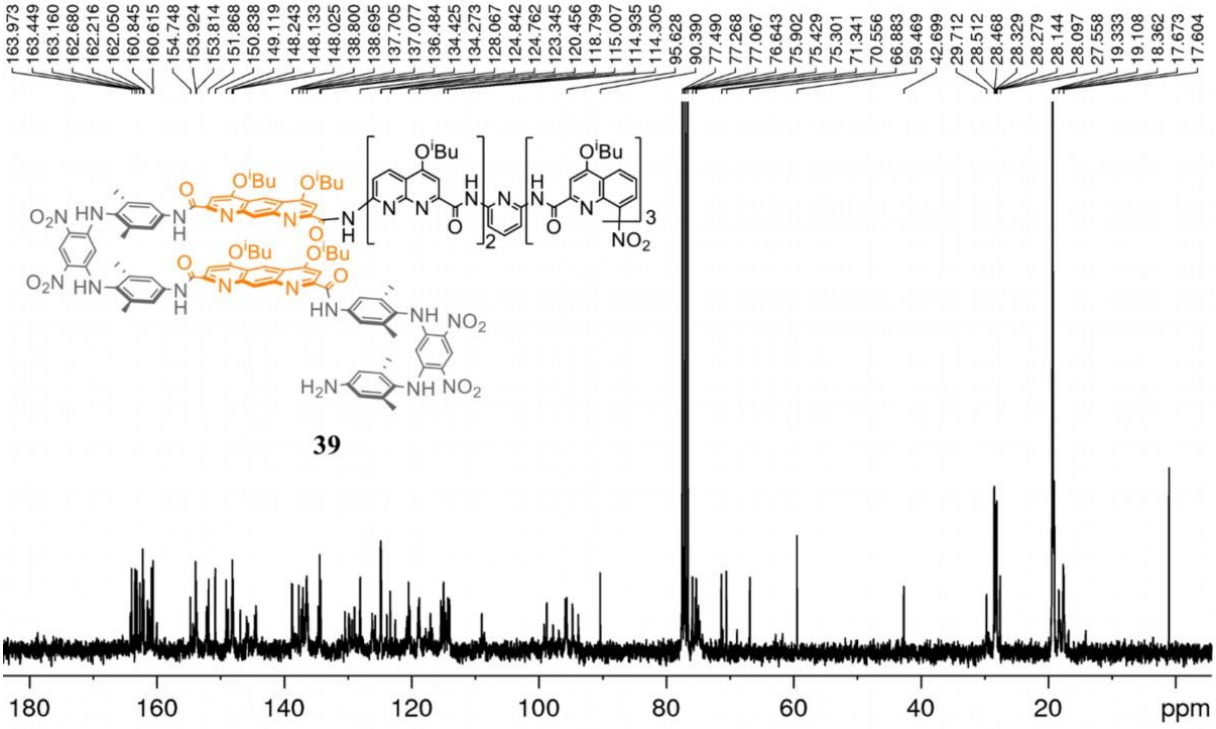
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80
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40
20
ppm

39