Supporting Information

Photon-gated Foldaxane Assembly/Disassembly

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1. Supplementary figures

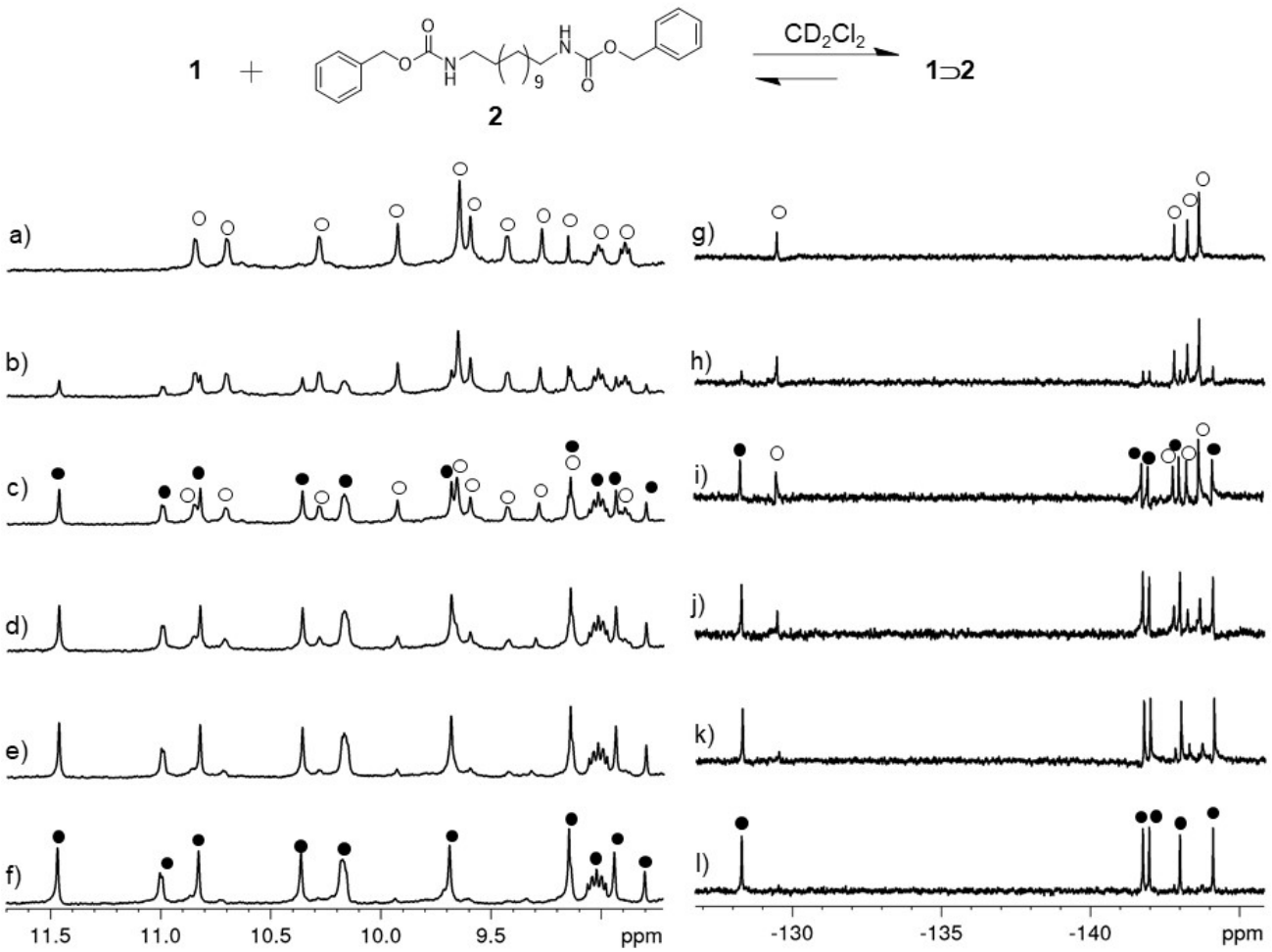


Figure S1. Schematic illustration showing encapsulation of guest **2** within foldamer **1**. Part of the 400 MHz ^{1}H NMR spectra of **1** (0.5 mM) at 298 K in CD_2Cl_2 (a), and after addition of aliquots of **2** (5 mM in CD_2Cl_2): (b) 0.2 equiv.; (c) 0.5 equiv.; (d) 1.0 equiv.; (e) 2.0 equiv. and (f) 5.0 equiv. The corresponding 376 MHz ^{19}F NMR spectra are given in (g) to (l), respectively. The signals corresponding to the starting oligomer **1** are labelled with empty circles and for the host-guest complex, **1⊃2**, are marked as black circles. The apparent K_a of the single helix of **1** for **2** was estimated by integration of the amide peaks of the empty host vs. the peaks of **1⊃2**. $K_a = 6.47 \times 10^4$ L.mol^{-1}.

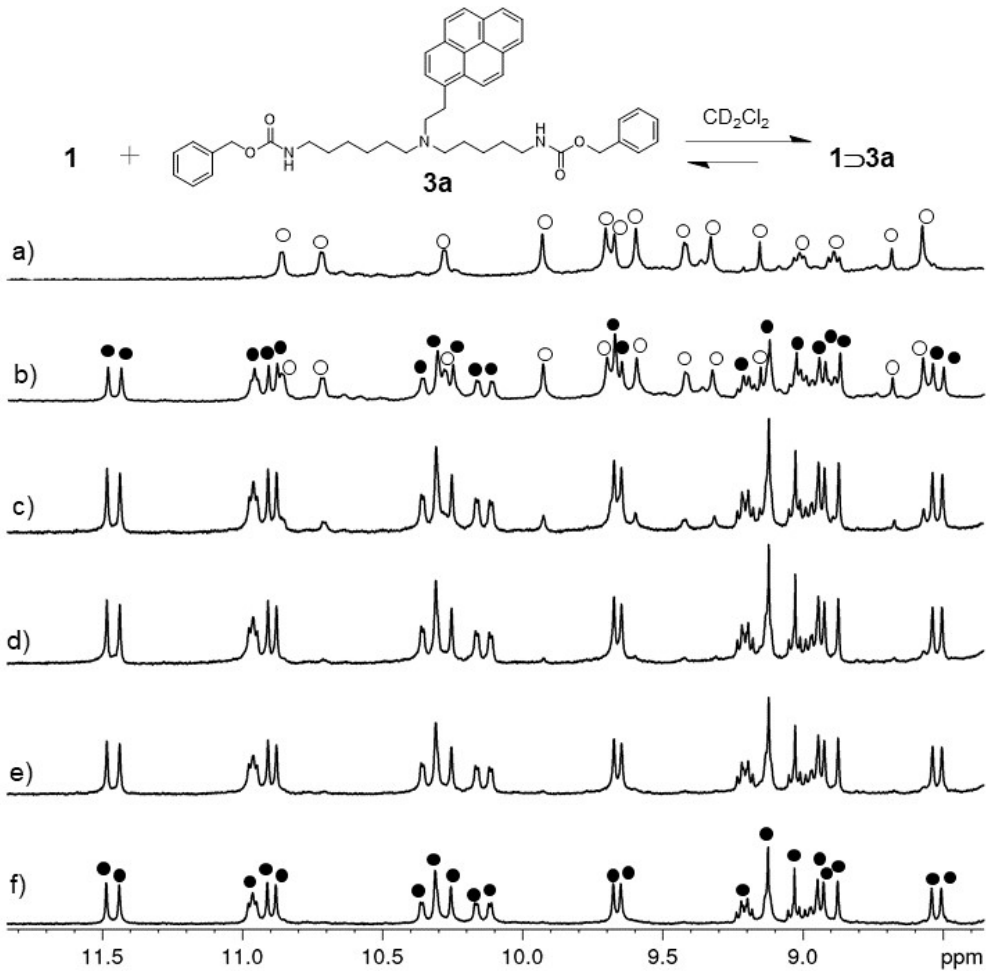


Figure S2. Schematic illustration showing encapsulation of guest **3a** within foldamer **1**. Part of the 400 MHz ^{1}H NMR spectra of **1** (1 mM) at 298 K in CD_2Cl_2 (a), and after addition of aliquots of **3a** (5 mM in CD_2Cl_2):- (b) 0.50 equiv.; (c) 1.0 equiv.; (d) 1.5 equiv.; (e) 2.0 equiv. and (f) 2.5 equiv. The signals corresponding to the starting oligomer **1** are labelled with empty circles and for the host-guest complex, **1⊃3a**, in black circles. The apparent K_a of the single helix of **1** for **3a** was estimated by integration of the amide peaks of the empty host vs. the peaks of **1⊃3a**. $K_a = 2.63 \times 10^4$ L.mol^{-1}.

For the equilibrium shown in Eq. 1, the association constant K_a of the receptor is given by Eq. 2.

(1) $H + T \rightleftharpoons HT$

(2) $K_a = [HT] / [H][T]$

where: [HT] = foldamer host-thread concentration; [H] = foldamer-host concentration; [G] = thread concentration

Alternatively, (3) $K_a = (n_{HT} * V_t) / (n_H * n_T)$

where: V_T = total volume of the sample; n_H = number of moles of host (etc.)

From mass balance, (4) $n_{H0} = n_H + n_{HT}$

(5) $n_{G0} = n_T + n_{HT}$

where: n_{H0} = initial number of moles of host; n_{T0} = number of moles of guest added to the sample

Substituting equations (4) and (5) into (3), (6) $K_a = (n_{HT} * V_t) / [(n_{H0} - n_{HT}) * (n_{G0} - n_{HT})]$

From integration of the amide signal of the amide resonances of NMR spectrum (free foldamer host and host-thread complex) it is possible to obtain the fraction of bound host molecules, X (Eq. 7).

(7) $X = n_{HT} / n_{H0}$

Using Eq. 7 to eliminate n_{HG} from Eq. 6, (8) $K_a = (X * V_T) / [n_{T0} - (X * n_{H0}) - (X * n_{T0}) + (X^2 * n_{H0})$

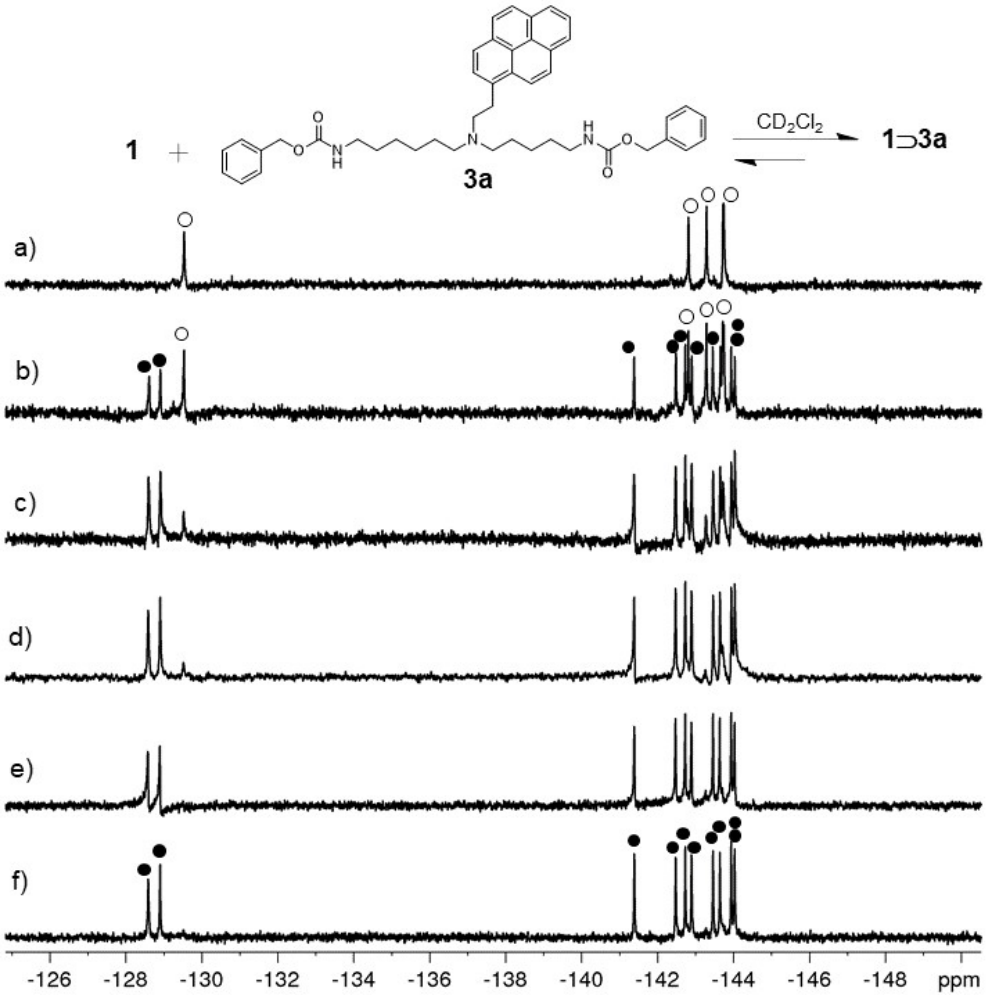


Figure S3. Schematic illustration showing encapsulation of guest **3a** within foldamer **1**. Part of the 376 MHz ^{19}F NMR spectra of **1** (1 mM) at 298 K in CD_2Cl_2 (a), and after addition of aliquots of **3a** (5 mM in CD_2Cl_2):- (b) 0.50 equiv.; (c) 1.0 equiv.; (d) 1.5 equiv.; (e) 2.0 equiv. and (f) 2.5 equiv. The signals corresponding to the starting oligomer **1** are labelled with empty circles and for the host-guest complex, **1⊃3a**, in black circles. Note: the number of signals is doubled after guest binding due to the non-symmetrical nature of the guest.

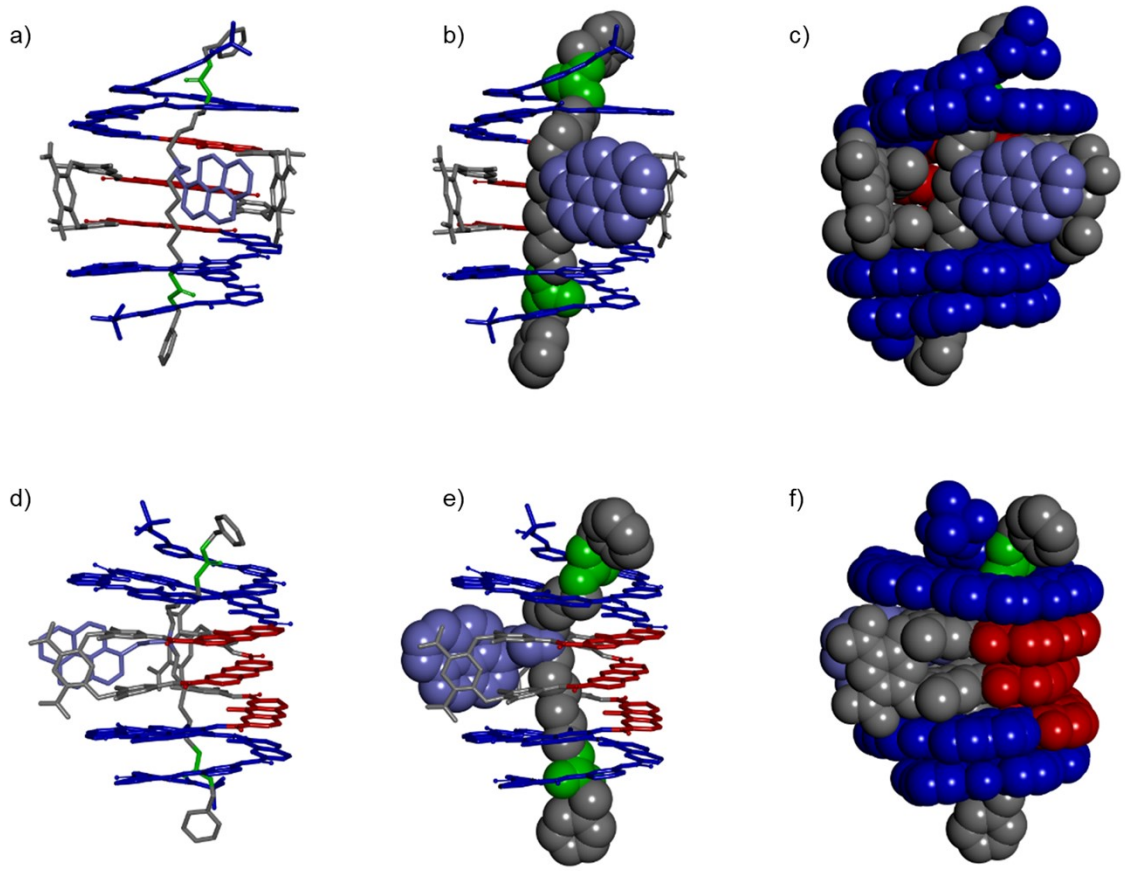


Figure S4. The X-ray structure of the complex **1⊃3a**, side view of complex **1⊃3a** is presented as : a) Stick mode; b) the rod in CPK representation and the foldamer in stick mode; c) CPK mode, different segments were marked as corresponding colour: helices (blue), sheets (red), turns (grey), alkyl chain and stopper in rod (grey), and carbamate groups (green). Front view of complex **1⊃3a** is presented as: d) Stick mode; e) the rod in CPK representation and the foldamer in stick mode; f) CPK mode. Side chains (O*i*Bu groups) and included solvent molecules have been removed for clarity.

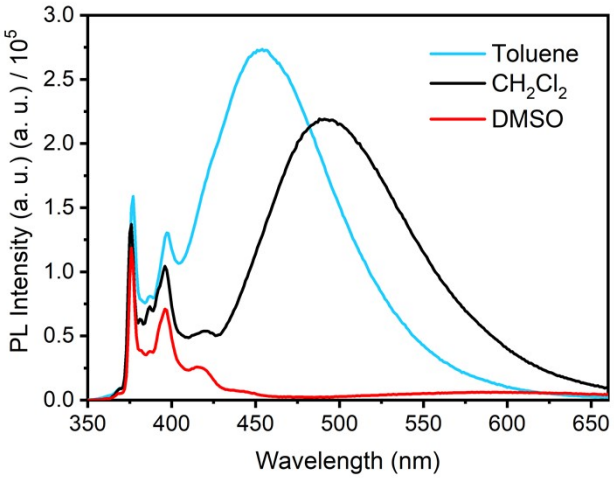


Figure S5. Photoluminescence spectra of optically matched solutions of **3a** in toluene, CH_2Cl_2 and DMSO measured at λ_{exc} = 335 nm. Considering a quantum yield of fluorescence of 0.26 in CH_2Cl_2, values of Φ_F = 0.30 and 0.033 were found in toluene and DMSO, respectively.

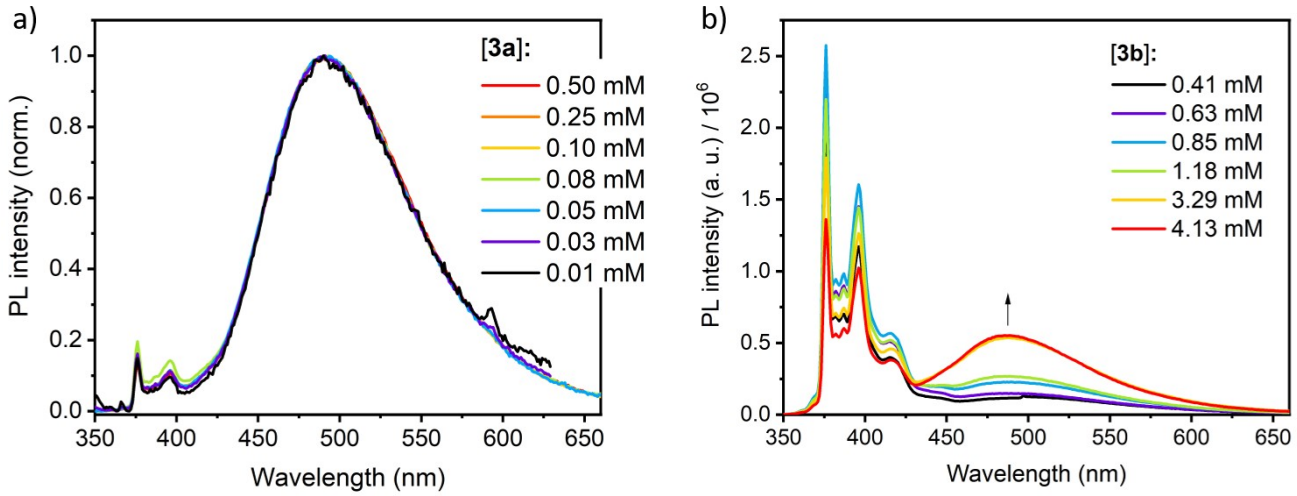


Figure S6. Concentration effects on the photoluminescence of pyrene guests **3a** and **3b**, studied as CH_2Cl_2 (1.5 mM Et_3N) solutions in 1 mm cuvettes in front-face geometry (λ_{exc} = 335 nm). a) Normalized photoluminescence spectra of **3a**: dilution does not decrease the broad exciplex emission band; b) photoluminescence spectra of **3b**: the excimer emission, comparably weak in similar solutions (~5×10^{-4} M), increases at higher concentrations.

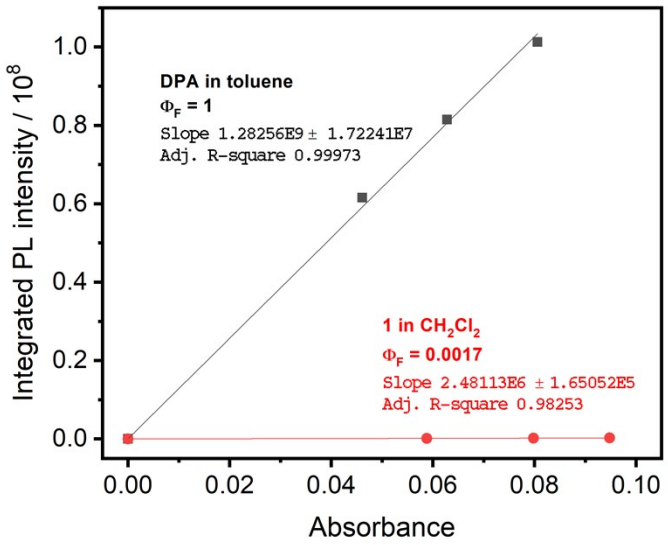


Figure S7. Linear plots for the determination of the fluorescence quantum yield of **1** using 9,10-diphenylanthracene (DPA) in toluene as a reference ($\Phi = 1$).

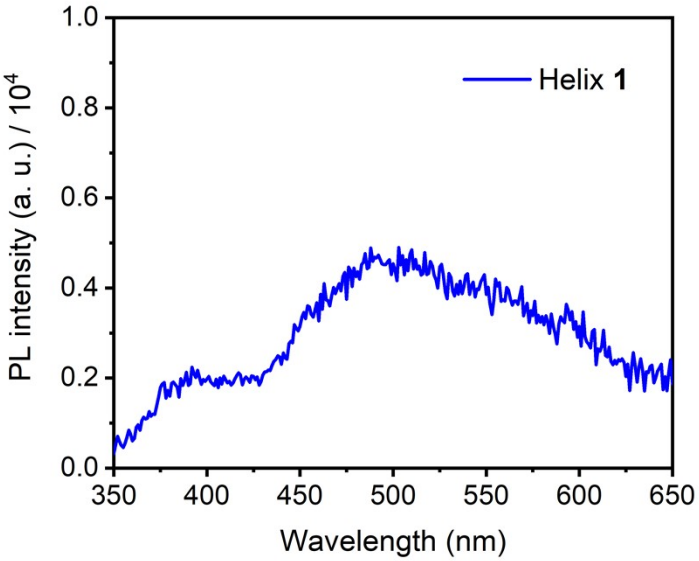


Figure S8. Photoluminescence spectrum of a 0.5 mM solution of host **1** in CH_2Cl_2 (λ_{exc} = 335 nm, 1 mm cuvette in front-face geometry).

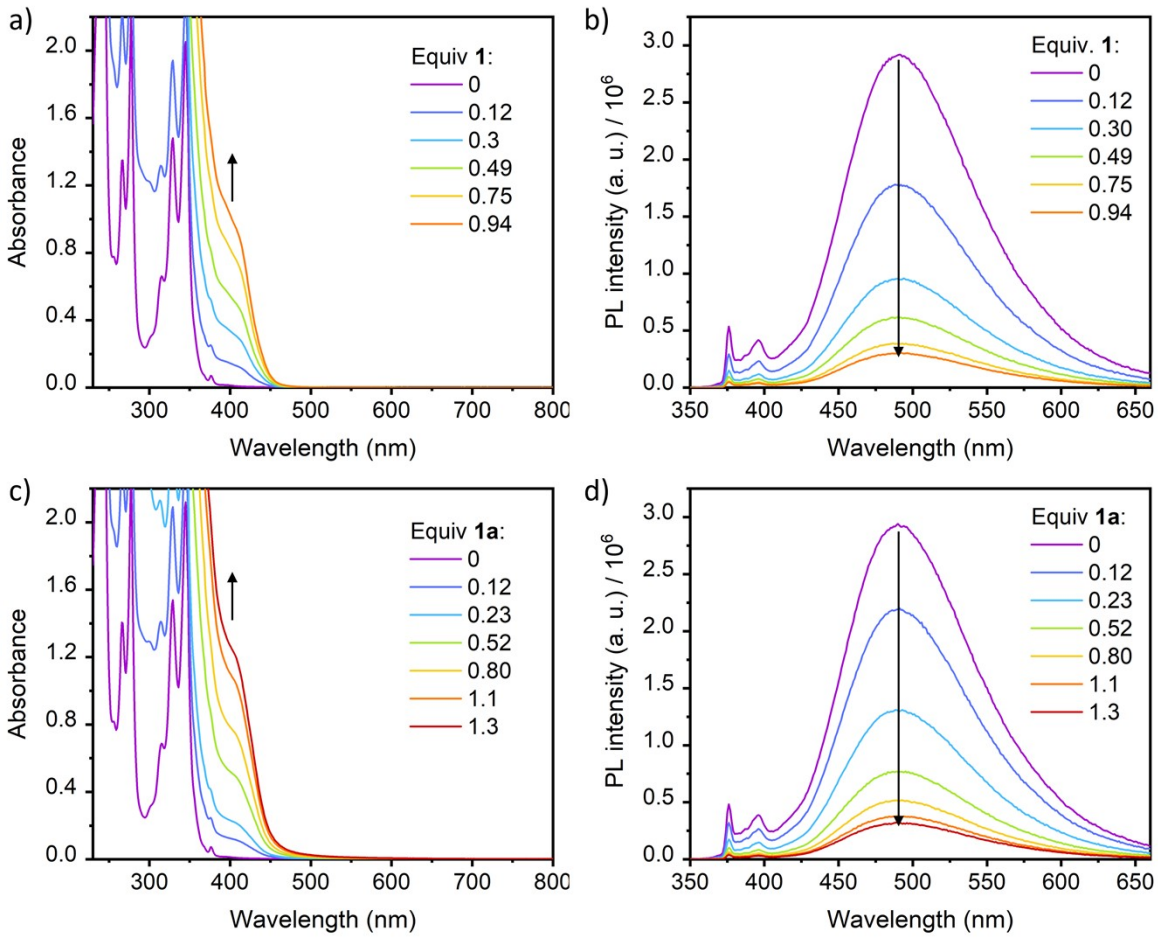


Figure S9. UV-vis and fluorescence spectra obtained upon titration of 0.5 mM solutions of **3a** in CH_2Cl_2 (in presence of Et_3N 1.5 mM): a) and b) with host **1**; c) and d) with photoproduct **1a**.

To compensate for the variations in the inner filter effect due to the increased absorption of the host, fluorescence spectra presented in Fig. S24 were then divided by $f = \frac{A_{3a}}{A_{tot}}\left(1 - 10^{-A_{tot}}\right)$, the contribution of **3a** to the total fraction of light absorbed at excitation wavelength (335 nm), assuming no intercomponent electronic interactions in the ground-state. A_{3a} is the absorbance of rod **3a**, and A_{tot} is the total absorbance, extrapolated from linear combinations of UV-vis spectra of rod **3a** and compound **1** or **1a**. Integrals of the resulting plots (on the 490–660 nm range, where reabsorption is negligible), *F*, could then be used to assess quenching effects.

Determination of the fluorescence quantum yield of 3a within 1 ⊃ 3a

The ratio of photoluminescence measured experimentally in the presence and in the absence of helix is:

$$\frac{PL}{PL_0} = \frac{\Phi_{3a}^{cplx}\left(A_{3a}^{cplx}/A\right) + \Phi_{3a}\left(A_{3a}^{free}/A\right)}{\Phi_{3a}\left(1 - 10^{-A_{3a}}\right)}\left(1 - 10^{-A}\right) \quad (1)$$

where:

- Φ_{3a}, Φ_{3a}^{cplx} : fluorescence quantum yield of **3a** in free and complexed form, respectively

- A_{3a}^{free}, A_{3a}^{cplx}, A_{3a}, A : absorbance of **3a** in free and complexed form, respectively, and total absorbance of **3a** and of the whole solution at the excitation wavelength, which gives:

$$\frac{PL}{PL_0} = \frac{x^{cplx}\Phi_{3a}^{cplx} + (1 - x^{cplx})\Phi_{3a}}{\Phi_{3a}} \times \frac{A_{3a}}{A} \times \frac{\left(1 - 10^{-A}\right)}{\left(1 - 10^{-A_{3a}}\right)} \quad (2)$$

with x^{cplx} the fraction of **3a** in complexed form. Equation 2 can be rewritten as:-

$$\Phi_{3a}^{cplx} = \frac{\Phi_{3a}}{x^{cplx}}\left(\frac{PL}{PL_0} \times \frac{A}{A_{3a}} \times \frac{\left(1 - 10^{-A_{3a}}\right)}{\left(1 - 10^{-A}\right)} - (1 - x^{cplx})\right) \quad (3)$$

Considering an association constant K_a = 2.63 × 10^4 L mol^{-1}, the ratios of complex **1⊃3a** and free rod **3a** were determined to be 73% and 27% respectively at [**3a**] = 0.5 mM and [**1**] = 0.94×[**3a**] = 4.7 mM. Thus, since the fluorescence quantum yield of free rod **3a** Φ_{3a} was found to be 0.26, the fluorescence quantum yield of **3a** inside host **1a** is $\Phi_{3a}^{cplx} = 0.06$.

Quantum yields of photoconversion of 1 and 1⊃3a

The number of moles of **1a** produced after irradiating a solution for a time t is:

$$n_{1a} = N_{h\nu/t} \times F \times \Phi_{PC} \times t \quad (4)$$

where $N_{h\nu/t}$ is the photon flux, F is the mean fraction of light absorbed by helix **1**, and Φ_{PC} is the quantum yield of photoconversion. Since both **1** and **1a** absorb at the excitation wavelength, and absorption changes over time, $F \times t$ was calculated instead as:

$$f(t) = \int_0^t \frac{A_1}{A}\left(1 - 10^{-A}\right) dt \quad (5)$$

where A_1 is the absorbance of host **1** at excitation wavelength. Using ^{1}H NMR to determine the concentrations of the different species i, $f(t)$ can be determined using:

$$f(t) = \int_0^t \frac{\varepsilon_1[1]}{\sum_i \varepsilon_i[i]}\left(1 - 10^{-\sum_i \varepsilon_i \times [i]}\right) dt \quad (6)$$

Irradiation of 200 µL of 1.0 mM solutions of host **1** in CD_2Cl_2 + Et_3N (9.0 mM) — alone or in the presence of **3a** (3 mM) — was performed with a 427 nm Kessil LED lamp. The photon flux in this experiment was found to be 5.49×10^{-7} mol.s^{-1}. Given these different parameters, the quantum yields of photoconversion could be determined by linear regression using the combination of equation (4) and equation (6) (Fig. S10).

The values found were $\Phi_{PC} = 8.3\times10^{-4}$ for host **1**, and 2.8×10^{-4} for complex **1⊃3a**.

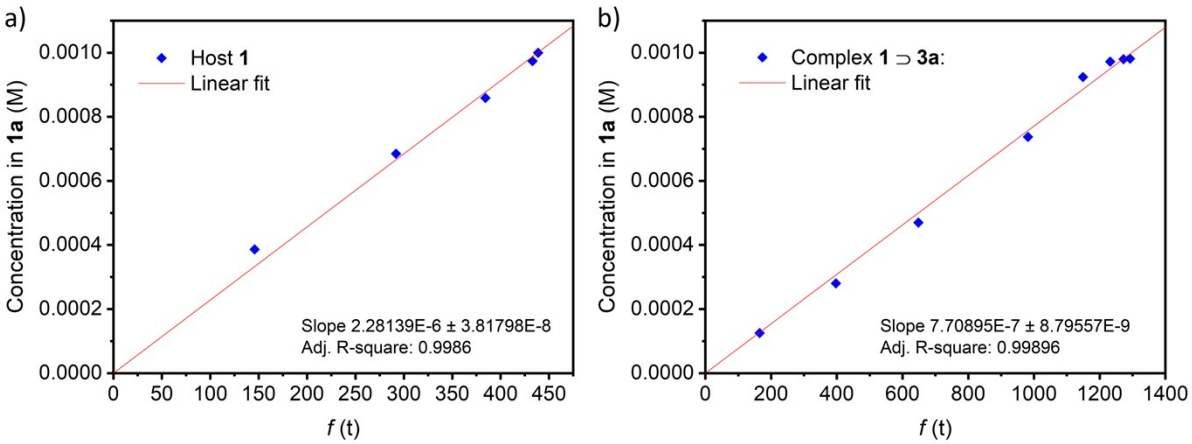


Figure S10. Linear regressions used for the calculation of Φ_{PC} : a) with host **1**, and b) with the complex **1⊃3a**.

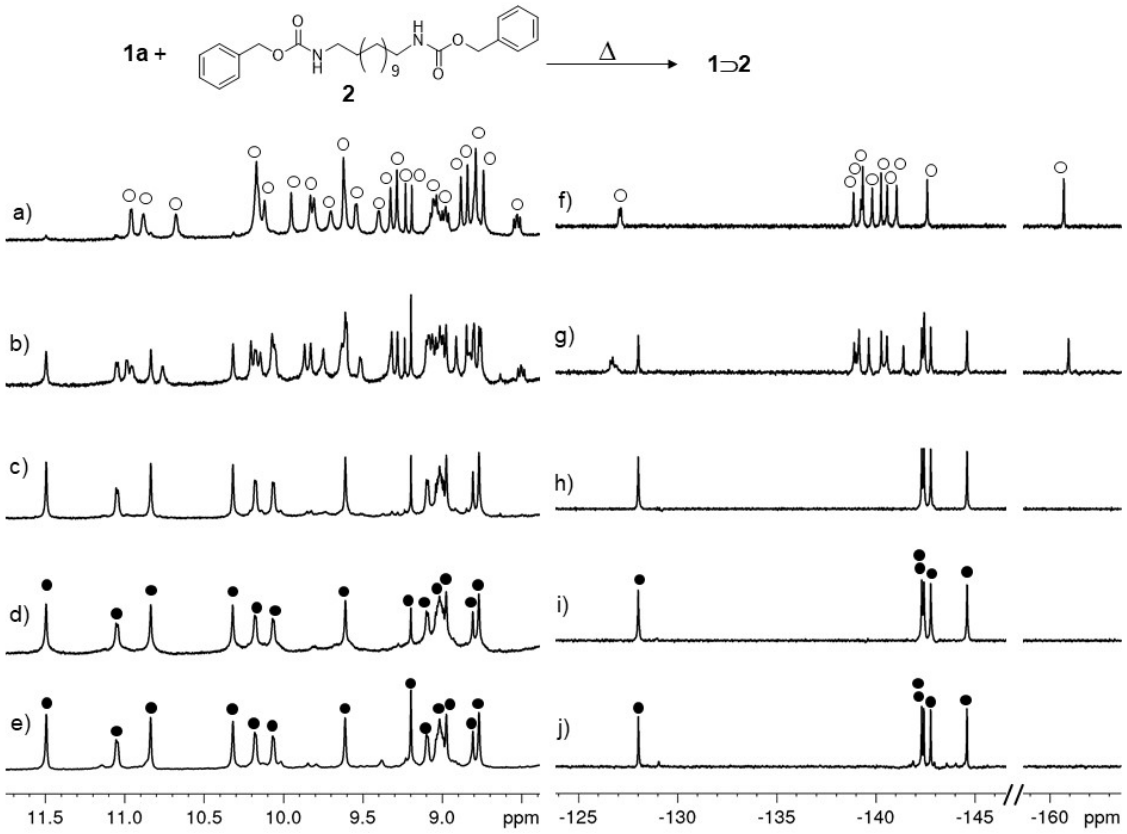


Figure S11. Schematic representation showing thermally activated cleavage of photoproduct **1a** to **1** and subsequent binding of **2**, when present in the medium. Part of the 400 MHz ^{1}H NMR spectra at 298 K in $CDCl_3$ of :- (a) **1a** (1 mM) in the presence of 5 equivalent of **2,** and after heating the mixture at 333 K for (b) 3 hours; (c) 20 hours; and (d) 24 hours. (e) The 400 MHz ^{1}H NMR spectra of **1⊃2**, obtained from different experiments are given for comparison. (f-j) The

corresponding 376 MHz ^{19}F NMR spectra. The signals are marked with empty circles and black circles corresponding to **1a** and **1⊃2**, respectively.

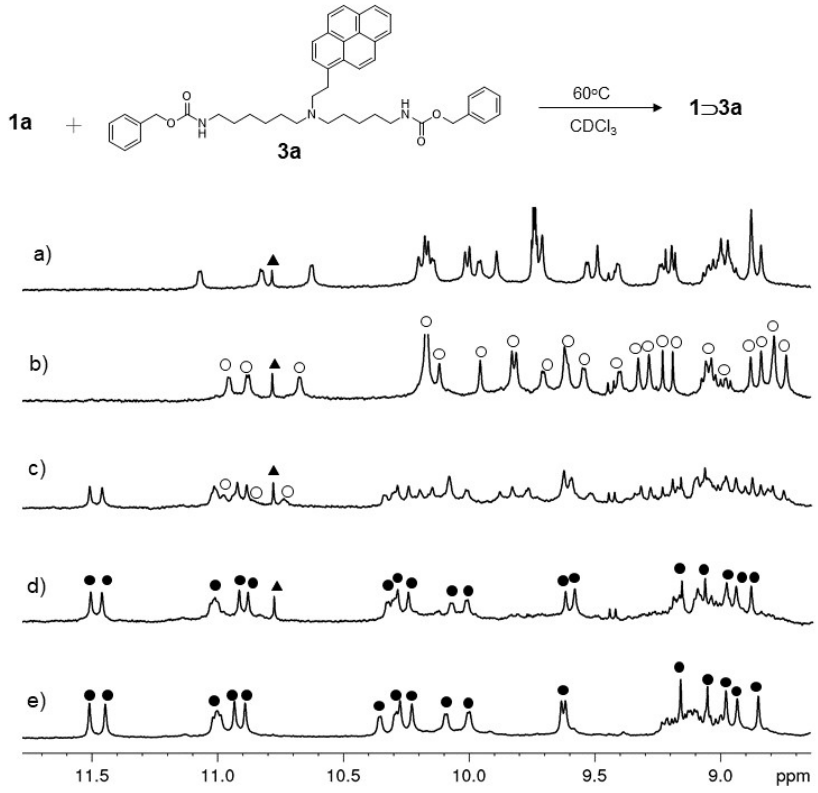


Figure S12. Part of the 400 MHz ^1H NMR spectra at 298 K of **1a** (0.5 mM) in the presence of 2.5mM of **3a** in CD_2Cl_2 (a); in $CDCl_3$ (b); and after heating the mixture at 333 K in $CDCl_3$ for (c) 15 h; (d) 24 h; (e) spectra of **1⊃3a** in $CDCl_3$, obtained from different experiments, given for comparison. The signals marked with empty circles and black circles correspond to **1a** and **1⊃3a**, respectively. Side product is marked with black triangles.

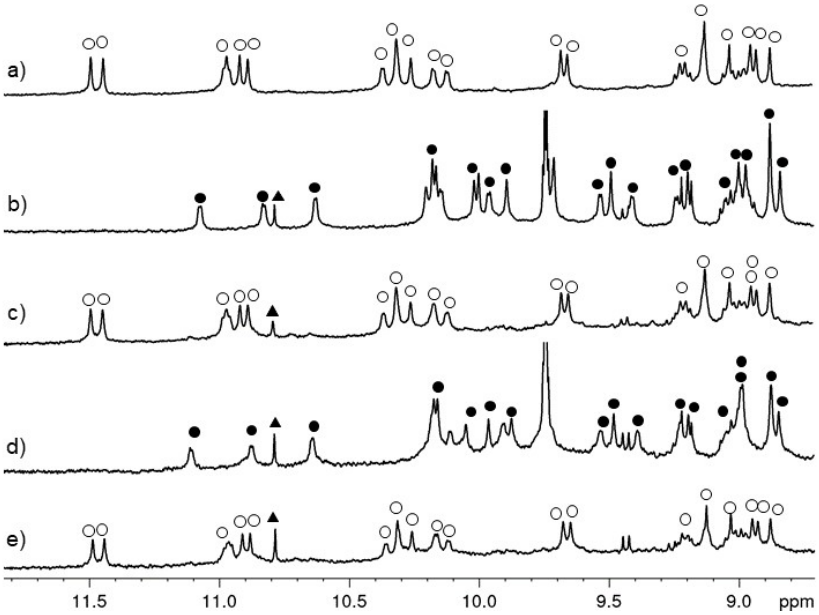
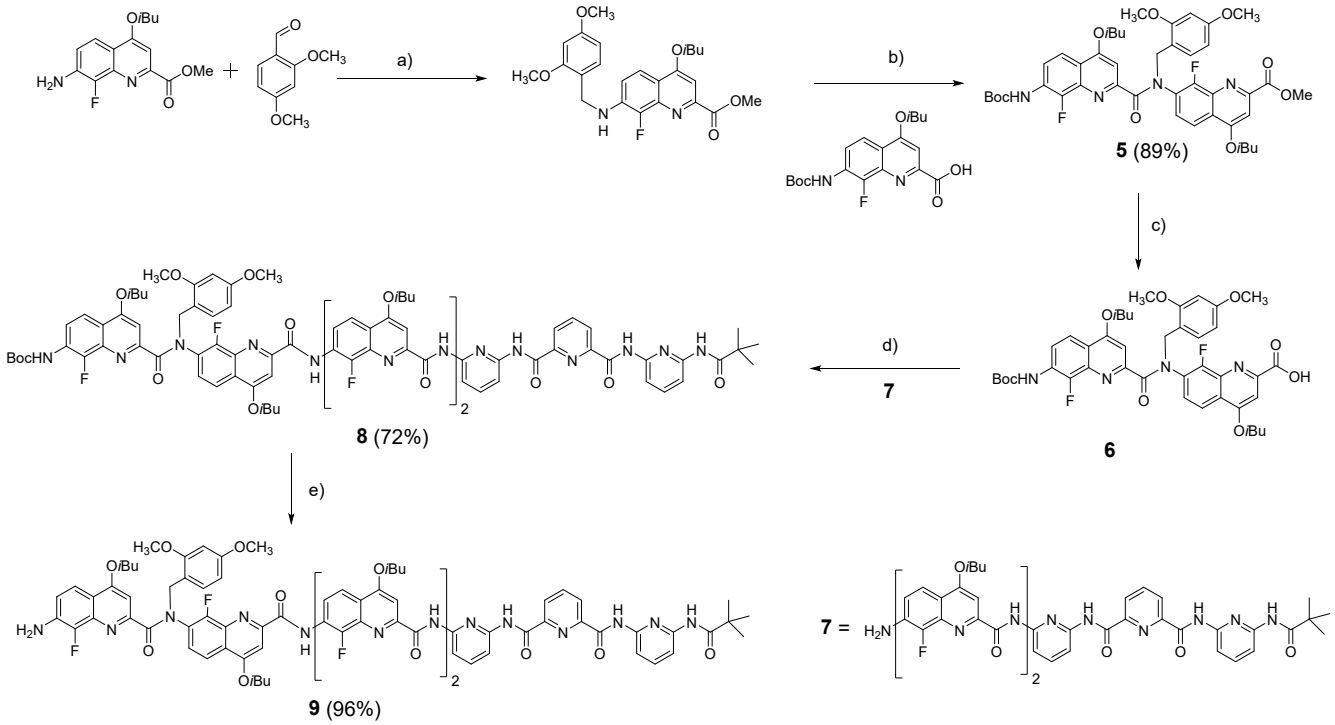
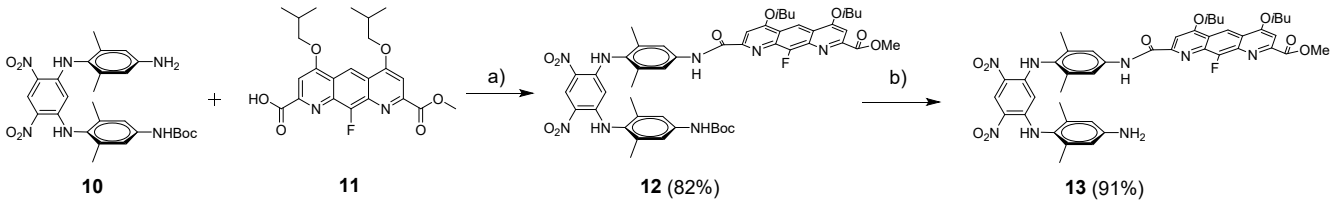


Figure S13. Part of the 400 MHz ^{1}H NMR spectra at 298 K of **1a** (0.5 mM) in CD_2Cl_2 : (a) with 2.5 mM of **3a**; b) after irradiation; (c) after thermal treatment; (d) after second irradiation; (e) followed by second thermal treatment. The signals marked with black circles and empty circles correspond to **1a** and **1⊃3a**, respectively. Side product is marked as dark triangles.

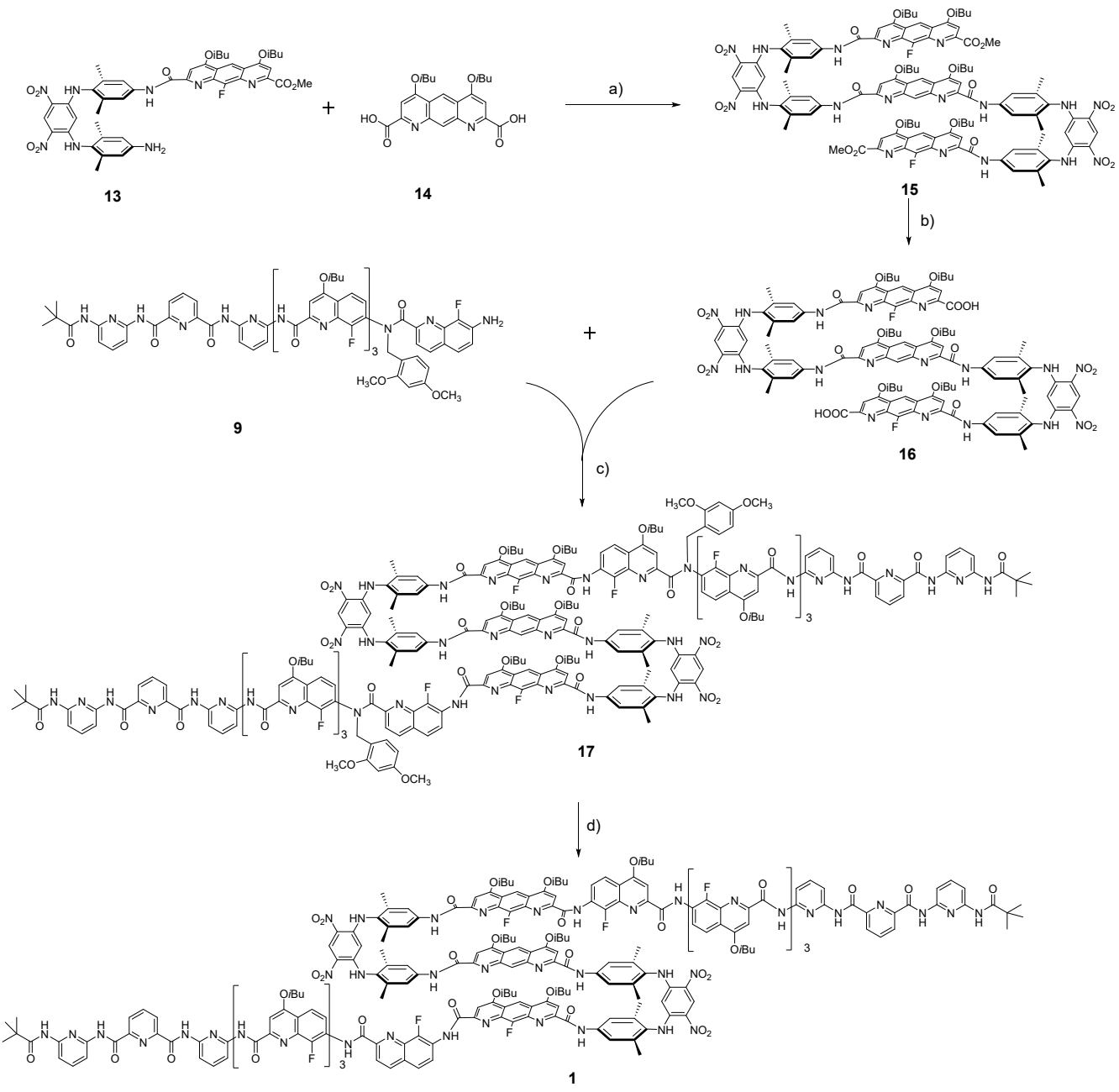
2. Supplementary schemes



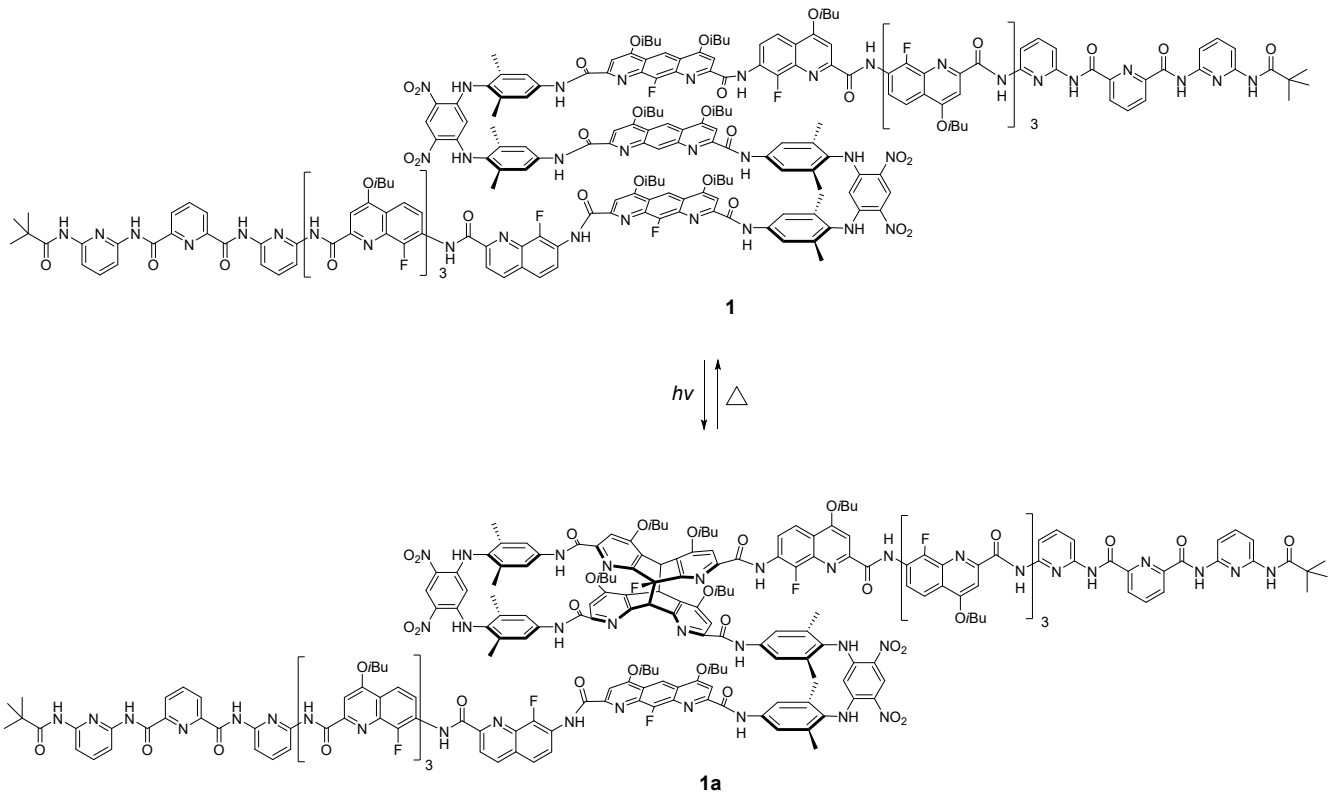
Scheme S1. Synthetic pathway of oligomer **9**. Reagents and conditions: (a) Sodium triacetoxyborohydride, 1,2-dichloroethane, 18 hours; (b) (i) 1-Chloro-*N,N,*2-trimethyl-1-propenylamine, dry $CHCl_3$, 2 hours, room temperature; (ii) Dry DIPEA, dry $CHCl_3$, 12 hours, room temperature; (c) NaOH, MeOH/H_2O/THF, 3 hours, room temperature; (d) (i) 1-Chloro-*N,N,*2-trimethyl-1-propenylamine, dry CH_2Cl_2, 2 hours, room temperature; (ii) Dry DIPEA, dry CH_2Cl_2, 12 hours, room temperature; (e) Dioxane, 4M HCl in dioxane, 3 hours, room temperature.



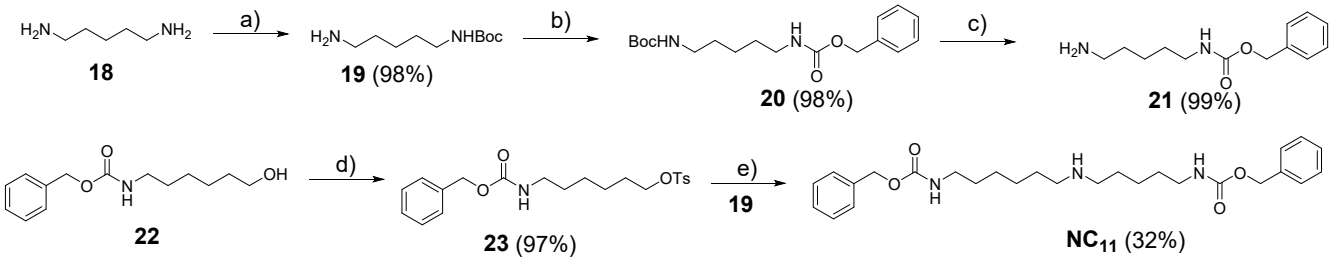
Scheme S2. Synthetic pathway of turn **13**. Reagents and conditions: (a) PyBOP, DIPEA, $CHCl_3$, 2 days, 45 °C. (b) Trifluoroacetic acid, $CHCl_3$, 3 hours, room temperature.



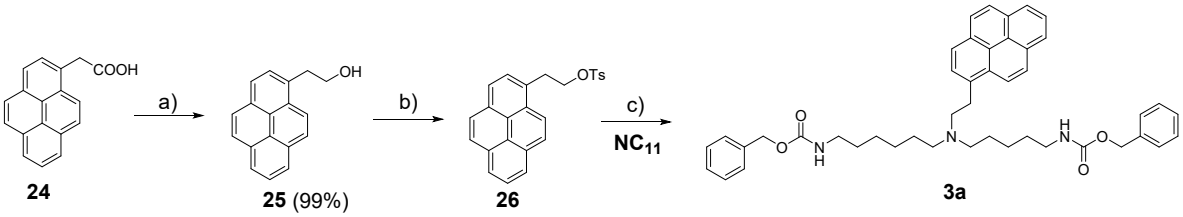
Scheme S3. Synthesis of oligomer **1**. Reagents and conditions: (a) PyBOP, DIPEA, $CHCl_3$, 2 days, 45 °C. (b) LiI, ethyl acetate, 12 hours, 78 °C; (c) (i) $(COCl)_2$, $CHCl_3$, 2 hours, room temperature. (ii) DIPEA, $CHCl_3$, 16 hours, room temperature; (d) Dioxane, 4M HCl in dioxane, 3 hours, room temperature.



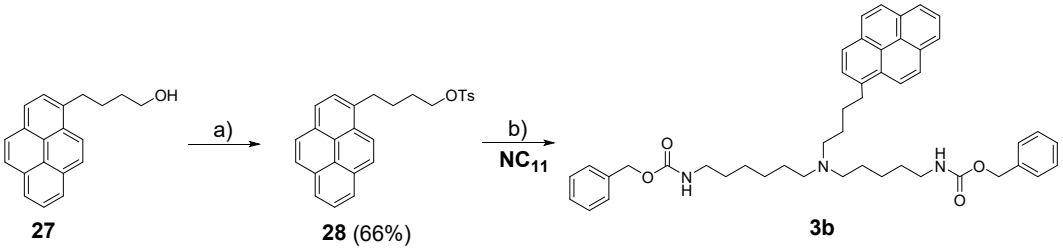
Scheme S4. Photoirradiation of **1** with a light source of 320 - 390 nm followed by the thermolysis at 333 K for 24 hours in $CDCl_3$.



Scheme S5. Synthetic pathway of $\mathbf{NC_{11}}$ rod. Reagents and conditions: (a) Di-tert-butyl-dicarbonate, dry $CHCl_3$, 5 hours, room temperature; (b) Benzyl chloroformate, NaOH (4M aqueous), 16 hours, room temperature; (c) Trifluoroacetic acid, dichloromethane, 3 hours, room temperature; (d) TsOCl, *N*,*N*-dimethylpyridin-4-amine, NEt_3, DCM, 6 hours; (e) Dry DMF, NEt_3, 16 hours, 80 °C.



Scheme S6. Synthetic pathway of **3a** rod. Reagents and conditions: (a) $LiAlH_4$, dry THF, 12 hours, room temperature; (b) TsOCl, *N*,*N*-dimethylpyridin-4-amine, NEt_3, DCM, 6 hours; (c) K_2CO_3, dry acetonitrile, reflux, 24 hours.



Scheme S7. Synthetic pathway of **3b** rod. Reagents and conditions: (a) TsOCl, *N*,*N*-dimethylpyridin-4-amine, NEt_3, DCM, 6 hours; (b) K_2CO_3, dry acetonitrile, reflux, 24 hours.

3. Supplementary methods

3.1 Nuclear Magnetic Resonance spectroscopy

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) an 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 unless specified otherwise. Data processing was performed with Topspin 3.5 software.

1.2 UV-vis Spectroscopy

Electronic absorption spectra were measured on a UV-vis-NIR spectrophotometer. Steady-state emission spectra were recorded on a Hobin-Yvon Horiba Fluorolog-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.

1.3 Photochemistry

Photoirradiation experiments were carried out 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 UV sources, namely an EXFO Lite (Model No. E3000-01) portable device having light source of 320 - 390 nm with a 50 W Hg lamp, Kessil science (PR160L) LED photoreaction lighting 370 nm (43 W) and 427 nm (45 W). 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 diazaanthracene derivatives were dissolved in the appropriate deuterated solvent ($CDCl_3$). The tube was heated to 333K for $CDCl_3$. The kinetic reversibility was followed by ^{1}H NMR.

1.4 Molecular modelling

Molecular Models calculations 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.

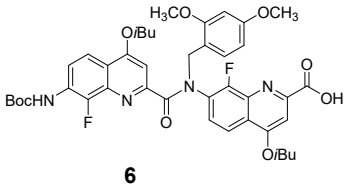
1.5 Crystallography

The diffraction data for **1⊃3a** 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 Pixel Hybrid Dectris Eiger1M detector. Data were processed with the Rigaku Oxford Diffraction CrysalisPro software (version1.171.41.118a).

The crystal structure of **1⊃3a** was solved by direct-methods combined with dual-space recycling implemented in Shelxd. The structure was refined by full-matrix least-squares method on F2 with Shelxl-2014[2] within Olex2. 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 molecular and thermal motion parameters. The PLATON/SQUEEZE procedure was applied for solvent flattening (mainly $CHCl_3$ molecules).

4. Experimental procedures for chemical synthesis

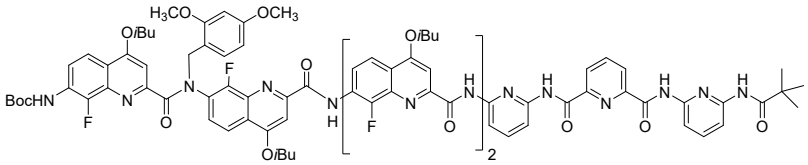
All reactions were carried out under a dry inert atmosphere unless otherwise specified. Commercial reagents were purchased from Sigma Aldrich, TCI Chemicals or Alfa-Aesar and were used without further purification. Tetrahydrofuran (THF) and dichloromethane (CH_2Cl_2) were dried over alumina columns (MBRAUN 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 photodiode detection 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.



6

Synthesis of dimer acid 6: Compound **5**[1] (0.60 g, 0.74 mmol) was dissolved in a mixture of THF (10 mL) and H_2O (2 mL). To this solution, LiOH (60 mg, 2.0 equiv.) dissolved in MeOH was added dropwise. The solution was stirred at room temperature for 3 h. Then solution was neutralized with 1N HCl to pH = 4 – 5 and concentrated under reduced pressure to remove THF. Some more H_2O (30 mL) was added to the residue. The aqueous phase was extracted with CH_2Cl_2 (3×20 mL). The combined organic phases were dried over Na_2SO_4, filtered, then evaporated to give dimer acid **6** as a yellow solid. ^{1}H NMR (400 MHz, $CDCl_3$, 298 K, δ ppm): 8.16 (t, *J* = 7.9, 1H), 7.79 – 7.75 (m, 2H), 7.52 (s, 1H), 7.48 – 7.42 (m, 2H), 7.24 (s, 1H), 6.67 (s, 1H), 6.42 (d, 1H), 6.24 (s, 1H), 5.19 (dd, *J* = 14.5, 2H), 4.02 – 3.98 (m, 6H), 3.73 (s, 4H), 2.28 – 2.17 (m, 2H), 1.47 (s, 9H), 1.08 – 1.05 (m, 12H). ^{13}C NMR (100 MHz, $CDCl_3$, 298 K, δ ppm): 168.3, 164.2, 163.7, 162.1, 160.5, 158.5, 154.4, 153.6, 152.1, 151.0, 147.6, 146.6, 144.1, 137.1, 131.8, 129.6, 122.4, 119.2, 117.8, 117.1, 116.8, 116.4, 81.5, 75.6, 75.1, 55.3, 47.7, 38.6, 37.0, 35.5, 30.3, 28.2, 28.0, 19.1. HRMS (ESI): m/z calcd. for $C_{42}H_{47}F_2N_4O_9$ $[M+H]^+$ 789.3306, found 789.3299.

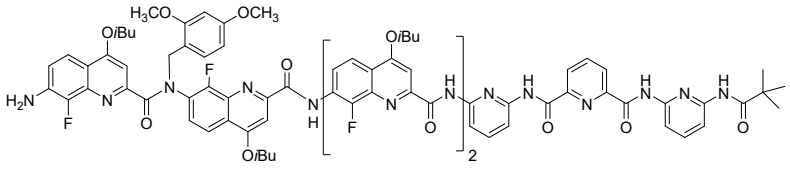
(1) Yao, C.; Kauffmann, B.; Huc, I.; Ferrand, Y. *Chem. Commun.* **2022**, *58*, 5789-5792.



8

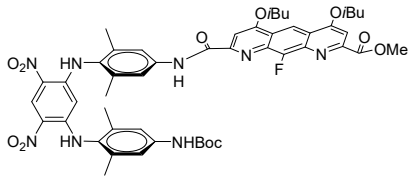
Synthesis of oligomer 8: Dimer acid **6** (100 mg, 0.126 mmol) was dried in vacuo, and then dissolved in dry CH_2Cl_2 (4 mL) in a 10 mL round bottom flask. To this 1-chloro-N,N,2-trimethylpropenylamine (32 μL, 1.5 equiv.) was added. The reaction mixture was stirred at room temperature for 2 h resulting in a homogeneous solution, and then evaporated to provide the corresponding acid chloride. To a solution of the amine **7**[2] (120 mg, 0.126 mmol) in CH_2Cl_2 (2 mL) containing DIEA (65 μL, 0.37 mmol) was added a solution of acid chloride in CH_2Cl_2 (2 mL) via syringe. The reaction mixture was stirred at room temperature for 12 h. The solution was evaporated, and the product was purified by chromatography (silica gel, ethyl acetate and cyclohexane 1:2) to get yellow solid (145 mg, 72 %). ^{1}H NMR (400 MHz, $CDCl_3$, 298 K, δ ppm): 10.77 (s, 1H), 10.68 (s, 2H), 10.16 (s, 1H), 10.06 (s, 1H), 8.78 (t, *J* = 5.2, 2H), 8.39 (d, *J* = 7.6, 1H), 8.23 (t, *J* = 6.7, 2H), 8.11 – 8.05 (m, 4H), 7.96 – 7.86 (m, 4H), 7.74 – 7.65 (m, 4H), 7.44 – 7.36 (m, 2H), 7.32 – 7.28 (m, 1H), 7.13 (s, 1H), 6.74 (s, 1H), 6.39 (d, 1H), 6.16 (s, 1H), 5.01 (dd, *J* = 13.9, 2H), 4.18 (d, *J* = 6.3, 4H), 4.10 (d, *J* = 6.1, 2H), 3.93 (d, *J* = 5.8, 2H), 3.73 (s, 3H), 3.32 (s, 3H), 2.35 – 2.22 (m, 3H), 2.18 – 2.09 (m, 1H), 1.45 (s, 9H), 0.88 (s, 9H). ^{13}C NMR (100 MHz, $CDCl_3$, 298 K, δ ppm): δ175.8, 167.1, 162.1, 161.4, 161.2, 160.9, 160.7, 160.3, 159.4, 157.4, 153.6, 152.9, 151.1, 150.2, 150.1, 149.6, 148.8, 148.6, 148.3, 147.9, 147.5, 147.2, 145.6, 144.6, 144.4, 143.1, 139.7, 139.3, 138.0, 136.9, 136.5, 136.1 136.0, 130.8, 130.4, 128.3, 125.7, 125.6, 124.6, 124.4, 121.3, 120.6, 119.9, 118.7, 118.0, 116.7, 116.0, 109.5, 109.1, 108.7, 103.0, 99.0, 98.0, 97.2, 97.0, 80.3, 74.4, 73.9, 54.2, 53.8, 46.6, 38.3. HRMS (ESI): m/z calcd. for Chemical Formula: $C_{92}H_{94}F_4N_{15}O_{15}$ $[M+H]^+$ 1725.7018, found 1725.7174.

(2) Bao, C.; Gan, Q.; Kauffmann, B.; Jiang, H.; Huc, I. *Chem. Eur. J.* **2009**, *15*, 11530-11536



9

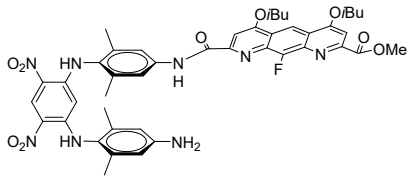
Synthesis of oligomer amine 9: Oligomer **8** (0.42 g, 0.24 mmol) was dissolved in dioxane (2 mL), and HCl (4M in dioxane, 5 mL) was added. The mixture was stirred at room temperature for 3 h. The solvent was evaporated, and the residue was dissolved in CH_2Cl_2 (20 mL), washed with saturated $NaHCO_3$, dried over Na_2SO_4 and then evaporated to give amine **9** as a yellow solid (375 mg, 96%). It was dried in vacuum and used without further purification. ^{1}H NMR (400 MHz, $CDCl_3$, 298 K, δ ppm): 10.77 (s, 1H), 10.67 (s, 2H), 10.19 (s, 1H), 10.09 (s, 1H), 8.79 – 8.73 (m, 2H), 8.36 (d, *J* = 7.5, 1H), 8.20 (t, *J* = 7.1, 2H), 8.09 (d, *J* = 9.0, 2H), 8.02 (d, *J* = 7.6, 1H), 7.94 – 7.87 (m, 4H), 7.75 – 7.67 (m, 5H), 7.53 (d, *J* = 8.8, 1H), 7.43 (t, *J* = 7.7, 1H), 7.38 (d, *J* = 8.2, 1H), 7.33 (t, *J* = 7.3, 1H), 7.02 (s, 1H), 6.79 (t, *J* = 8.1, 1H), 6.39 (d, *J* = 7.6, 1H), 6.16 (s, 1H), 5.01 (dd, *J* = 13.9, 2H), 4.12 – 4.02 (m, 8H), 3.93 (d, *J* = 5.8, 2H), 3.73 (s, 3H), 3.32 (s, 3H), 2.34 – 2.22 (m, 3H), 2.07 – 2.01 (m, 1H), 0.88 (s, 9H). ^{13}C NMR (100 MHz, $CDCl_3$, 298 K, δ ppm): 176.8, 168.3, 163.2, 162.5, 162.4, 161.9, 161.8, 161.2, 160.4, 158.4, 154.4, 154.1, 151.5, 151.1, 150.6, 149.9, 149.5, 149.3, 148.9, 148.6, 148.3, 145.6, 144.9, 142.5, 140.6, 139.1, 138.2, 138.1, 137.5, 134.1, 134.0, 131.8, 129.4, 126.8, 126.7, 126.6, 125.7, 125.5, 122.3, 121.1, 119.9, 119.8, 118.2, 117.6, 117.1, 116.1, 114.9, 110.5, 110.2, 109.8, 109.7, 104.0, 98.9, 98.6, 98.0, 75.4, 74.7, 55.3, 54.8, 47.5, 39.3. HRMS (ESI): m/z calcd. for $C_{87}H_{86}F_4N_{15}O_{13}$ $[M+H]^+$ 1625.6494, found 1625.6615.



12

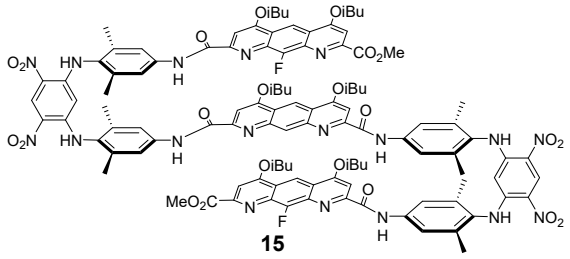
Synthesis of 12: Amine **10** (0.096 g, 0.179 mmol), acid **11** (0.080 g, 0.179 mmol) and PyBOP (0.465 g, 0.895 mmol) were placed in a 10 mL round-bottom flask filled with argon. Freshly distilled $CHCl_3$ (2.0 mL) and DIPEA (0.145 mL, 0.895 mmol) were then successively added. The solution was stirred at 318 K for 24 h. 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 **12** was obtained as a light yellow solid (0.138 g, 82% yield). ^{1}H NMR (400 MHz, $CDCl_3$, 298 K) δ 10.20 (s, 1H), 9.35 (s, 1H), 9.16 (s, 1H), 9.11 (s, 1H), 9.05 (d, *J*(H, H) = 2.0, 1H), 7.81 (s, 1H), 7.58 (s, 1H), 7.47 (s, 2H), 7.04 (s, 2H), 6.73 (s, 1H), 4.89 (s, 1H), 4.23 (d, *J*(H, H) = 6.3, 2H), 4.18 (d, *J*(H, H) = 6.3, 2H), 4.13 (s, 3H), 2.44-2.36 (m, 2H), 2.09 (s, 6H), 2.01 (s, 6H), 1.23 (s, 6H), 1.20 (s, 6H), 1.14 (s, 9H). ^{13}C NMR (100 MHz, $CDCl_3$) 165.8, 163.7, 163.3, 162.0, 155.4, 153.2, 152.7, 151.8, 151.5, 148.3, 148.0, 137.9, 137.0, 136.5, 130.9, 129.4, 129.1, 124.9, 122.4, 122.1, 120.6,

118.9, 111.1, 99.7, 97.4, 93.9, 80.0, 75.5, 53.6, 28.2, 28.0, 19.1, 18.0, 17.9. HRMS (ESI): m/z calcd. for $C_{50}H_{56}FN_8O_{11}$ $[M+H]^+$ 963.4047 found 963.4284.



13

Synthesis of 13: Oligomer **12** (0.100 g, 0.105mmol) was dissolved in $CHCl_3$ (2.0 mL), then trifluoroacetic acid (1 mL) was successively added, and the reaction was stirred at room temperature for 3 h. The reaction mixture was quenched by adding sat. $NaHCO_3$(aq.) and extracted with chloroform. The organic layer was washed with brine, and dried over Na_2SO_4. After the solvent was removed under reduced pressure and **13** was given as yellow solid (82 mg, 91%).^{1}H NMR (400 MHz, $CDCl_3$, 298 K) δ 10.44 (s, 1H), 9.30 (s, 1H), 9.06 (d, J(H, H) = 2.0, 1H), 9.05 (s, 1H), 8.90 (s, 1H), 7.79 (s, 1H), 7.57 (s, 1H), 7.45 (s, 2H), 6.28 (s, 3H), 4.74 (s, 1H), 4.22 (d, J(H, H) = 6.4, 2H), 4.18 (d, J(H, H) = 6.3, 2H), 4.13 (s, 3H), 2.43-2.35 (m, 2H), 2.06 (s, 6H), 1.89 (s, 6H), 1.22 (s, 6H), 1.20 (s, 6H). ^{13}C NMR (100 MHz, $CDCl_3$) 163.8, 162.1, 149.0, 147.8, 146.3, 137.0, 136.8, 131.3, 129.1, 125.2, 124.9, 124.8, 120.8, 114.6, 99.7, 97.6, 94.5, 75.5, 53.6, 28.2, 19.1, 17.9, 17.7. HRMS (ESI): m/z calcd. for $C_{45}H_{48}FN_8O_9$ $[M+H]^+$ 863.3523 found 863.3719.

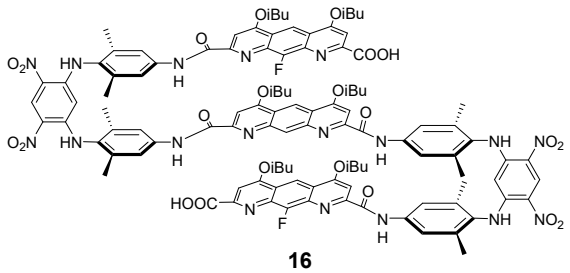


15

Oligomer 15. Tetramer amine **15** (0.185 g, 0.214 mmol), diacid **14**[3] (0.04 g, 0.1 mmol) and PyBOP (0.208 g, 0.4 mmol) were placed in a 5 mL round-bottom flask filled with argon. Freshly distilled $CHCl_3$ (2 mL) and DIPEA (70 μL, 0.4 mmol) were then successively added. The solution was stirred at 45 °C 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

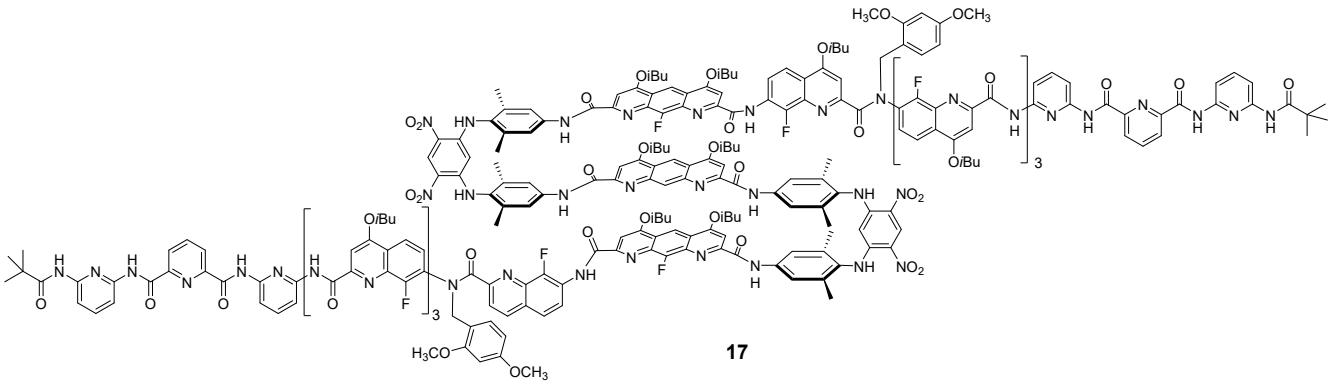
(3) Bao, C.; Kauffmann, B.; Gan, Q.; Srinivas, K.; Jiang, H.; Huc, I. *Angew. Chem. Int. Ed.* **2008**, *47*, 4153-4156.

pressure. The crude product was purified by recycling GPC and compound **15** was obtained as a yellow solid (0.087 g, 42% yield). ^{1}H NMR (300 MHz, $CDCl_3$, 298 K, δ ppm): 9.99 (s, 2H), 9.38 (s, 2H), 9.35 (s, 2H), 9.07 (s, 2H), 8.99 (s, 2H), 8.45 (s, 1H), 7.88 (d, *J* = 1.9 Hz, 2H), 7.53 – 7.29 (m, 11H), 7.16 (s, 2H), 6.57 (s, 2H), 4.77 (s, 2H), 4.02 (t, *J* = 6.7 Hz, 8H), 3.83 (s, 6H), 3.21 (d, *J* = 6.8 Hz, 4H), 2.34 – 2.25 (m, 3H), 2.14 (s, 12H), 2.05 (s, 12H), 1.99 – 1.75 (m, 3H), 1.27 – 1.19 (m, 12H), 1.16 (m, 12H), 0.90 (d, *J* = 6.7 Hz, 12H). ^{13}C NMR (75 MHz, $CDCl_3$, 298 K, δ ppm): 165.18, 162.62, 162.17, 161.02, 160.91, 152.78, 152.40, 151.18, 150.69, 148.36, 148.16, 145.19, 137.28, 137.23, 137.20, 135.64, 134.30, 134.17, 130.49, 130.47, 129.34, 127.43, 125.07, 125.03, 121.23, 121.16, 120.41, 119.10, 118.99, 115.35, 109.78, 99.52, 96.16, 94.65, 77.36, 75.21, 74.67, 53.27, 28.45, 28.43, 27.96, 19.28, 19.26, 18.88, 18.05, 18.03. ^{19}F NMR (282 MHz, $CDCl_3$, 298 K, δ ppm): -128.15. HRMS (ESI): m/z calcd. for $C_{112}H_{115}F_2N_{18}O_{22}$ $[M+H]^+$ 2102.8435, Found 2102.8297.



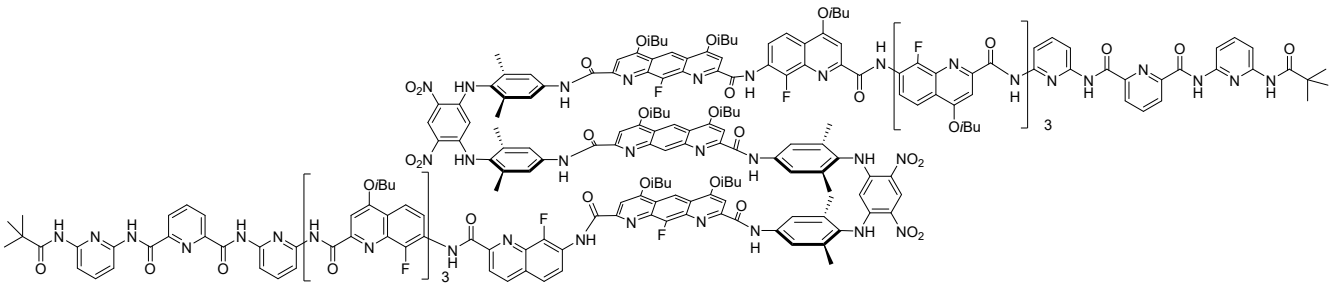
16

Oligomer diacid 16. Oligomer **15** (0.08 g, 0.038 mmol) and lithium iodide (0.05 g, 0.38 mmol) were placed in a round bottom flask, and freshly dried ethyl acetate (2 mL) was added under nitrogen atmosphere. The mixture was refluxed at 78 °C for 5 h 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 (0.074 g, 95% yield). ^{1}H NMR (400 MHz, $CDCl_3$, 298 K, δ ppm): 9.91 (s, 2H), 9.39 (s, 2H), 9.33 (s, 2H), 9.18 (s, 2H), 9.08 (s, 2H), 8.68 (s, 1H), 7.83 (s, 2H), 7.47 (s, 11H), 6.34 (s, 2H), 4.91 (s, 2H), 4.12 (d, *J* = 6.6 Hz, 8H), 3.26 (d, *J* = 6.6 Hz, 4H), 2.40 – 2.26 (m, 3H), 2.18 (s, 12H), 2.11 (s, 12H), 2.02 – 1.89 (m, 3H), 1.25 (d, *J* = 6.6 Hz, 12H), 1.21 (d, *J* = 6.6 Hz, 12H), 0.97 (d, *J* = 6.6 Hz, 12H). ^{19}F NMR (376 MHz, $CDCl_3$, 298 K, δ ppm): -129.85. HRMS (ESI): m/z calcd. for $C_{110}H_{111}F_2N_{18}O_{22}$ $[M+H]^+$ 2074.8122, Found 2074.7951.



17

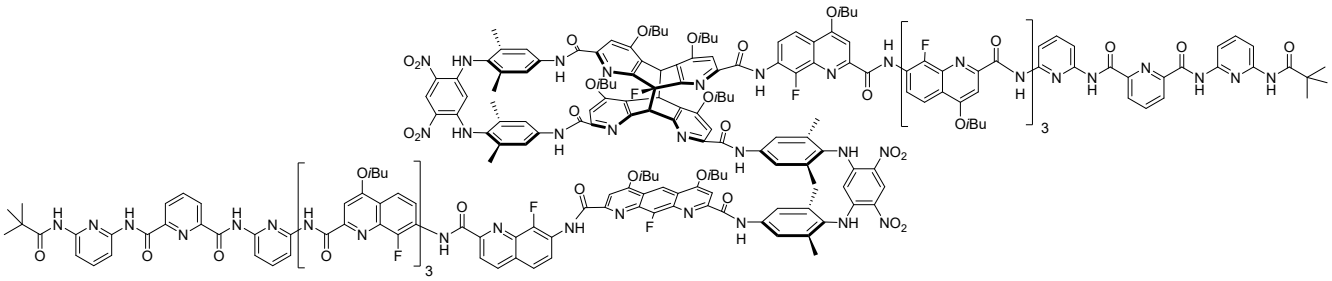
Oligomer 17. Diacid **16** (67 mg, 0.032 mmol) was suspended in anhydrous $CHCl_3$ (1 mL), then oxalyl chloride (27 µL, 0.32 mmol) was added and the reaction was allowed to stir at room temperature for 2 hours. The solvent and excess oxalyl chloride were removed under reduced pressure and the residue was dried under high vacuum for 3 hours to yield the corresponding acid chloride as a yellow solid. The solution of amine **9** (109 mg, 0.067 mmol) and distilled DIPEA (17 µL, 0.096 mmol) in anhydrous $CHCl_3$ (1 mL) was added dropwise via a syringe to solution of the freshly prepared acid chloride 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 **17** was obtained as a yellow product (64 mg, 38% yield). ^{1}H NMR (300 MHz, CDCl3, 298 K, δ ppm): 10.91 (s, 2H), 10.39 (s, 2H), 10.18 (s, 2H), 9.92 (s, 2H), 9.83 (s, 2H), 9.74 (s, 2H), 9.18-9.13 (m, 3H), 9.02 (s, 2H), 8.92 (s, 2H), 8.84 - 8.77 (m, 5H), 8.38-8.31 (m, 4H), 8.23-8.18 (m, 4H), 8.01-7.98 (m, 4H), 7.89-7.87 (m, 4H), 7.83 - 7.79 (m, 4H), 7.69 (s, 3H), 7.60 - 7.55 (m, 6H), 7.44 - 7.32 (m, 8H), 7.16 (s, 3H), 7.10 – 6.95 (m, 3H), 6.90 (s, 1H), 6.74 – 6.65 (m, 2H), 6.49 – 6.46 (m, 2H), 6.29 – 6.20 (m, 6H), 6.12 – 5.94 (m, 4H), 5.84 – 5.71 (m, 5H), 4.61 – 4.03 (m, 24H), 3.87 – 2.80 (m, 30H), 2.58 – 2.09 (m, 14H), 1.93 – 1.70 (m, 10H), 1.50 – 0.74 (m, 86H), 0.63 – 0.48 (m, 18H).^{19}F NMR (282 MHz, $CDCl_3$, 298 K, δ ppm): -129.89, -130.59, -141.37, -141.80, -142.56. HRMS (ES+): m/z calcd. for $C_{284}H_{278}F_{10}N_{48}O_{46}$ $[M+2H]^{2+}$ 2644.5410, found 2644.5188.



1

Oligomer 1. Dimethoxybenzyl-protected oligomer **17** was placed in a 5 mL round bottom flask. To that, $CHCl_3$ (1 mL) and trifluoroacetic acid (1 mL) were sequentially added under an argon atmosphere. The mixture was stirred for 36 h at room temperature. The solution was neutralized by pouring into a saturated aqueous solution

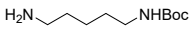
of $NaHCO_3$ and extracted with DCM. The organic layer was washed with water then brine and dried over anhydrous Na_2SO_4. Evaporation of solvent resulted in a yellow solid, which was further purified by recycling GPC. Oligomer **1** was obtained as a yellow product (49 mg, 87% yield). ^{1}H NMR (400 MHz, $CDCl_3$, 298 K, δ ppm): 11.17 (s, 2H), 10.87 (s, 2H), 10.16 (s, 2H), 10.04 (s, 2H), 9.84 (s, 2H), 9.69 (s, 2H), 9.40 (s, 2H), 9.28 (s, 2H), 9.25 (s, 2H), 9.21 (s, 2H), 9.07 (s, 1H), 8.96 (q, *J* = 6.3 Hz, 4H), 8.84 (s, 2H), 8.37 (s, 2H), 8.29 – 8.22 (m, 2H), 8.17 (d, *J* = 6.8 Hz, 5H), 8.11 (d, *J* = 13.0 Hz, 4H), 8.05 (d, *J* = 8.8 Hz, 3H), 7.78 (s, 3H), 7.76 (s, 4H), 7.69 (t, *J* = 7.5 Hz, 2H), 7.56 (s, 2H), 7.54 (s, 2H), 7.52 (s, 2H), 7.43 (s, 1H), 7.41 (s, 1H), 7.34 (s, 3H), 7.31 (s, 1H), 7.30 (s, 2H), 7.28 (s, 2H), 7.22 (s, 2H), 7.17 (s, 1H), 7.15 (s, 1H), 7.12 (s, 2H), 7.06 (s, 1H), 7.04 (s, 3H), 6.95 (s, 1H), 6.93 (s, 1H), 6.83 (t, *J* = 7.8 Hz, 2H), 6.69 (s, 2H), 6.63 (s, 2H), 6.21 (s, 1H), 6.14 (s, 2H), 5.75 (s, 2H), 5.67 (s, 2H), 4.36 (t, *J* = 7.6 Hz, 2H), 4.15 (dd, *J* = 15.6, 8.1 Hz, 10H), 4.05 (q, *J* = 7.1 Hz, 11H), 3.98 – 3.81 (m, 8H), 3.63 (t, *J* = 7.9 Hz, 3H), 3.49 (d, *J* = 7.7 Hz, 3H), 3.38 (dt, *J* = 14.7, 7.7 Hz, 1H), 3.28 (q, *J* = 7.5 Hz, 1H), 3.20 – 3.06 (m, 3H), 2.98 (t, *J* = 6.9 Hz, 2H), 2.38 (tq, *J* = 13.8, 7.4 Hz, 14H), 2.24 – 2.07 (m, 6H), 1.97 (s, 8H), 1.67 (s, 8H), 1.41 (t, *J* = 7.3 Hz, 5H), 1.35 – 1.15 (m, 84H), 1.11 (td, *J* = 7.2, 5.1 Hz, 9H), 1.04 (dd, *J* = 14.3, 6.7 Hz, 18H), 0.65 (s, 7H), 0.27 (s, 18H). ^{19}F NMR (376 MHz, $CDCl_3$, 298 K, δ ppm): -128.95, -141.78, -142.88, -143.34, -143.92. HRMS (ES+): m/z calcd. for $C_{266}H_{259}F_{10}N_{48}O_{42}$ $[M+3H]^{3+}$ 1663.3177, found 1663.3151.



1a

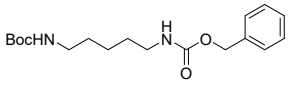
Photoproduct 1a. Oligomer **1** was irradiated in $CDCl_3$ as described above and the reaction progress was followed by ^{1}H NMR spectroscopy. After 2 hours of photoirradiation, 98% of photoproduct formation was observed. ^{1}H NMR (400 MHz, $CDCl_3$, 298 K, δ ppm): 10.95 (s, 1H), 10.86 (s, 1H), 10.65 (s, 1H), 10.21 (s, 3H), 10.17 (s, 3H), 10.03 (s, 1H), 9.84 (s, 3H), 9.78 (s, 2H), 9.66 (s, 1H), 9.63 (s, 1H), 9.58 (s, 2H), 9.47 (s, 1H), 9.35 (s, 1H), 9.31 (s, 1H), 9.25 (s, 1H), 9.21 (s, 1H), 9.11 – 8.95 (m, 4H), 8.89 (s, 1H), 8.86 (s, 2H), 8.81 (s, 3H), 8.76 (s, 2H), 8.61 – 8.51 (m, 1H), 8.32 – 8.20 (m, 3H), 8.20 – 7.98 (m, 12H), 7.96 (s, 1H), 7.93 (s, 3H), 7.81 (s, 2H), 7.78 (s, 1H), 7.76 (s, 1H), 7.72 (s, 2H), 7.67 (s, 3H), 7.55 (s, 3H), 7.52 (s, 1H), 7.42 (d, *J* = 7.0 Hz, 4H), 7.34 (s, 1H), 7.32 (s, 1H), 7.22 (s, 2H), 7.20 (s, 1H), 7.16 (s, 3H), 7.14 (s, 3H), 7.07 (s, 4H), 7.03 (s, 1H), 7.00 (s, 2H), 6.98 (s, 1H), 6.95 (s, 1H), 6.93 (s, 2H), 6.90 (s, 2H), 6.88 (s, 1H), 6.85 (d, *J* = 2.8 Hz, 3H), 6.83 (s, 2H), 6.79 (s, 1H), 6.77 (s, 1H), 6.75 (s, 2H), 6.73 (s, 2H), 6.70 (s, 1H), 6.68 (s, 2H), 6.65 (s, 4H), 6.61 (s, 3H), 6.55 (s, 2H), 6.44 (d, *J* = 7.9 Hz, 3H), 6.26 (d, *J* = 7.8 Hz, 1H), 6.20 (s, 2H), 6.12 (s, 1H), 6.10 (s, 1H), 5.48 (s, 1H), 5.34 (s, 1H), 5.30 (s, 1H), 5.27 (s, 1H), 5.24 (s, 1H), 5.07 (s, 1H), 5.06 (s, 2H), 5.03 (s, 1H), 5.00 (s, 2H), 4.86 (s, 1H),

4.37 – 4.06 (m, 24H), 3.86 – 3.05 (m, 35H), 2.77 – 2.58 (m, 3H), 2.46 (dq, *J* = 12.9, 6.7 Hz, 13H), 2.35 (t, *J* = 7.5 Hz, 4H), 2.30 – 2.14 (m, 11H), 2.02 (s, 22H), 1.91 (s, 8H), 1.88 (s, 7H), 1.80 (s, 10H), 1.44 (d, *J* = 6.7 Hz, 84H), 1.38 – 0.72 (m, 18H), 0.43 (s, 7H), 0.33 (s, 18H). ^{19}F NMR (376 MHz, $CDCl_3$, 298 K, δ ppm): -127.07, -127.17, -138.88, -139.25, -139.35, -139.83, -140.27, -140.58, -141.03, -142.60, -160.68. ^{19}F NMR (376 MHz, Proton coupled, $CDCl_3$, 298 K, δ ppm): -127.17, -138.89, -139.25, -139.36, -139.83, -140.27, -140.58, -141.04, -142.60, -160.71 (d, *J* = 37.6 Hz). HRMS (ES+): m/z calcd. for $C_{266}H_{258}F_{10}N_{48}O_{42}$ $[M+2H]^{2+}$ 2494.4729, found 2494.4624.



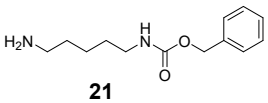
19

Synthesis of 19. 1,5-Pentanediamine **18** (3.1 gm, 30 mmol) was added to a 100 mL round bottom flask, degassed and placed under argon. Dry chloroform (50 mL) was added followed by a solution of di-tert-butyl-dicarbonate (1.31 gm, 6 mmol) in dry chloroform (20 mL), which was added dropwise via a dropping funnel over a period of 3 h at room temperature. The mixture was allowed to stir for another 2 h. Then the organic mixture was washed with water (3 × 100 mL), dried over anhydrous Na_2SO_4 and solvent was evaporated to obtain **19** (1.2 g, 98%) as a colourless oil. The ^{1}H NMR indicated that the resulting product was of sufficiently high purity and therefore no further purification was performed. ^{1}H NMR (300 MHz, $CDCl_3$, 298 K, δ ppm): 4.53 (s, br, 1H), 3.11 (q, *J* = 6.6 Hz, 2H), 2.68 (t, *J* = 6.8 Hz, 2H), 1.62 – 1.07 (m, 15H).



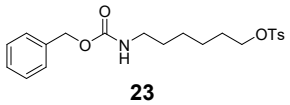
20

Synthesis of 20. Boc-protected amine **19** (1.1 g, 5.4 mmol) was added to a 25 mL round bottom flask, followed by aqueous NaOH (4M, 16 mL) and benzyl chloroformate (0.85 mL, 6.5 mmol). The mixture was stirred at room temperature for 16 h. The crude product was extracted with ethyl acetate. The organic layer was washed with brine and dried over anhydrous Na_2SO_4. After solvent was removed in vacuo, the residue was purified by column chromatography (silica gel, ethyl acetate and cyclohexane as eluent) to get **20** as a colourless liquid (1.8 g, 98%). ^{1}H NMR (300 MHz, $CDCl_3$, 298 K, δ ppm): 7.40 – 7.28 (m, 5H), 5.09 (s, 2H), 4.78 (s, 1H), 4.53 (s, 1H), 3.28 – 2.99 (m, 4H), 1.56 – 1.19 (m, 15H). ^{13}C NMR (75 MHz, $CDCl_3$, 298 K, δ ppm): 156.59, 156.19, 136.75, 128.70, 128.65, 128.27, 128.23, 127.78, 127.12, 66.75, 41.00, 40.43, 29.84, 29.69, 28.56, 23.92. HRMS (ESI): m/z calcd. for $C_{18}H_{28}N_2O_4Na$ $[M+Na]^+$ 359.1941, found 359.2114.



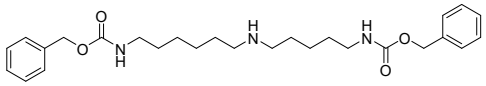
21

Synthesis of 21. In a 10 mL round-bottom flask, **20** (1.6 gm, 4.75 mmol) was dissolved in dichloromethane (3 mL) and subsequently, TFA (3 mL) was added dropwise. The mixture was allowed to stir for 3 h 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. Amine **21** was obtained without any further purification as a colourless liquid (1.1 g, 99% yield). ^{1}H NMR (300 MHz, $CDCl_3$, 298 K, δ ppm): 7.40 – 7.28 (m, 5H), 5.09 (s, 2H), 4.76 (s, 1H), 3.20 (q, *J* = 6.7 Hz, 2H), 2.68 (t, *J* = 6.8 Hz, 2H), 1.73 – 1.21 (m, 6H). ^{13}C NMR (75 MHz, $CDCl_3$, 298 K, δ ppm): 156.57, 136.75, 128.61, 128.25, 128.19, 127.58, 127.02, 66.68, 41.71, 41.02, 39.85, 32.59, 29.81, 29.71, 24.00. HRMS (ESI): m/z calcd. for $C_{26}H_{41}N_4O_4$ $[2M+H]^+$ 473.3122, found 473.3176.



23

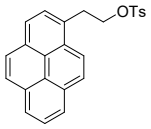
Synthesis of 23. 22 (1 g, 3.98 mmol), 4-toluenesulfonyl chloride (1.14 g, 6 mmol), and *N*,*N*-dimethylpyridin-4-amine (49 mg, 0.4 mmol) were added to a 50 mL round bottom flask. The mixture was degassed and placed under an argon atmosphere. Subsequently, dry dichloromethane (20 mL) was added, followed by triethylamine (2.78 mL, 20 mmol) while the reaction temperature was maintained at 0 °C by an iced water bath. The mixture was stirred at 0 °C for 1 h and then raised to room temperature where it was stirred for another 5 h. The mixture was neutralized by adding 2M aqueous HCl solution and extracted with dichloromethane. The organic layer was washed with 5% aqueous $NaHCO_3$, brine and dried over anhydrous Na_2SO_4. After the solvent was removed in vacuo, the residue was purified by column chromatography (silica gel, dichloromethane and cyclohexane as eluent) to give **23** as white solid (1.56 g, 97%). ^{1}H NMR (300 MHz, $CDCl_3$, 298 K, δ ppm): 7.83 – 7.74 (m, 2H), 7.40 – 7.28 (m, 7H), 5.09 (s, 2H), 4.70 (s, 1H), 4.01 (t, *J* = 6.4 Hz, 2H), 3.15 (q, *J* = 6.7 Hz, 2H), 2.45 (s, 3H), 1.63 (t, *J* = 7.1 Hz, 2H), 1.44 (d, *J* = 8.0 Hz, 2H), 1.29 (dtd, *J* = 14.3, 7.1, 3.7 Hz, 4H). ^{13}C NMR (75 MHz, $CDCl_3$, 298 K, δ ppm): 156.50, 144.84, 136.74, 133.31, 129.97, 128.67, 128.26, 128.02, 70.54, 66.77, 40.99, 29.91, 28.86, 26.16, 25.17, 21.78. HRMS (ESI): m/z calcd.. for $C_{21}H_{27}NNaO_5S$ $[M+Na]^+$ 428.1502, found 428.1596.



NC_{11}

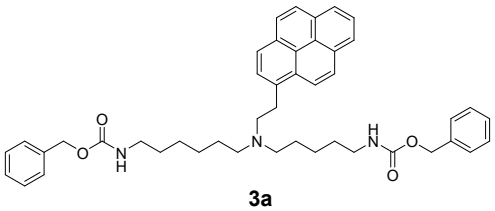
Synthesis of NC_{11}. To a 10 mL round bottom flask, compounds **21** (709 mg, 3 mmol) and **23** (1.216 gm, 3 mmol) were added. The mixture was degassed and the flask was filled with argon. To that, dry dimethylformamide (DMF, 5 mL) was added followed by triethylamine (1.25 mL, 9 mmol). The mixture was stirred at 80 °C for 16 h. Solvent was removed under vacuum. The mixture was neutralized with 5% citric acid (aqueous) giving some white precipitate. This was filtered off and neutralized by aqueous NaOH solution (4M) to obtain **NC_{11}** (450 mg,

32%) as a pure white solid, as indicated by the ^{1}H-NMR. ^{1}H NMR (300 MHz, $CDCl_3$, 298 K, δ ppm): 7.43 – 7.29 (m, 10H), 5.09 (s, 4H), 4.76 (s, 2H), 3.26 – 3.09 (m, 4H), 2.57 (td, *J* = 7.1, 3.0 Hz, 4H), 1.62 – 1.4 (m, 8H), 1.41 – 1.20 (m, 6H). ^{13}C NMR (75 MHz, $CDCl_3$, 298 K, δ ppm): 156.54, 136.79, 128.66, 128.26, 128.23, 66.73, 50.07, 50.00, 41.15, 30.16, 30.03, 29.91, 27.13, 26.75, 24.65. HRMS (ESI): m/z calcd. for $C_{27}H_{40}N_3O_4$ $[M+H]^+$ 470.3013, found 470.3098.



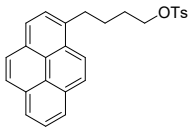
26

Synthesis of 26. 25[4] (900 mg, 3.65 mmol), 4-toluenesulfonyl chloride (1 g, 5.5 mmol) and *N*,*N*-dimethylpyridin-4-amine (45 mg, 0.4 mmol) were added to a 50 mL round bottom flask. The mixture was degassed and the flask was filled with argon. Subsequently, dry dichloromethane (20 mL) and then triethylamine (2.5 mL, 18 mmol) were added while maintaining the reaction temperature at 0 °C by an iced water bath. The mixture was stirred at 0 °C for 1 h and then raised to room temperature and stirred for another 5 h. The mixture was neutralized by 2M aqueous HCl solution and extracted with dichloromethane. The organic layer was washed with brine and dried over anhydrous Na_2SO_4. After the solvent was removed in vacuo, the residue was purified by column chromatography (silica gel, dichloromethane and cyclohexane as eluent) to get **26** as a pale yellow solid (875 mg, 60%). ^{1}H NMR (300 MHz, $CDCl_3$, 298 K, δ ppm): 8.19 (td, *J* = 7.3, 1.2 Hz, 2H), 8.10 – 7.97 (m, 6H), 7.80 (d, *J* = 7.8 Hz, 1H), 7.36 – 7.29 (m, 2H), 6.73 – 6.66 (m, 2H), 4.45 (t, *J* = 6.8 Hz, 2H), 3.68 (t, *J* = 6.9 Hz, 2H), 1.87 (s, 3H). HRMS (ESI): m/z calcd. for $C_{25}H_{20}NaO_3S$ $[M+Na]^+$ 423.1025, found 423.1111.



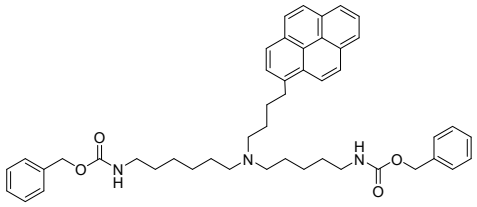
3a

Synthesis of 3a. NC$_{11}$ (70 mg, 0.15 mmol), **26** (72 mg, 0.18 mmol) and K_2CO_3 (124 mg, 0.9 mmol) were added to a 10 mL round bottom flask. The mixture was degassed and the flask was filled with argon. Subsequently, dry acetonitrile (5 mL) was added. The mixture was refluxed for 1 d and then brought to room temperature. The solvent was removed under vacuum. The crude product was purified by column chromatography (silica gel, dichloromethane and methanol as eluent) to get **3a** as a pale yellow solid (54 mg, 52%). ^{1}H NMR (300 MHz, $CDCl_3$, 298 K, δ ppm): 8.29 (d, *J* = 9.2 Hz, 1H), 8.21 – 8.07 (m, 4H), 8.05 – 7.96 (m, 3H), 7.87 (d, *J* = 7.8 Hz, 1H), 7.41 – 7.27 (m, 10H), 5.08 (s, 4H), 4.75 (br, 2H), 3.51 (br, 2H), 3.27 – 3.03 (m, 4H), 2.93 (br, 2H), 2.61 (br, 4H), 1.82 – 1.10 (m, 14H). HRMS (ESI): m/z calcd. for $C_{45}H_{52}N_3O_4$ $[M+H]^+$ 698.3952, found 698.3975.



28

Synthesis of 28. 27 (549 mg, 2 mmol), 4-toluenesulfonyl chloride (572 mg, 3 mmol) and *N*,*N*-dimethylpyridin-4-amine (24 mg, 0.2 mmol) were added to a 50 mL round bottom flask, The mixture was degassed and filled with argon. Subsequently, dry dichloromethane (15 mL) and then triethylamine (1.4 mL, 10 mmol) was added while the temperature was maintained at 0 °C by an iced water bath. The mixture was stirred at 0 °C for 1 hour and then brought to room temperature where it was stirred for another 5 h. The mixture was neutralized by 2M aqueous HCl solution and extracted with dichloromethane. The organic layer was washed with brine and dried over anhydrous Na_2SO_4. After the solvent was removed in vacuo, the residue was purified by column chromatography (silica gel, dichloromethane and cyclohexane as eluent) to get **28** as a pale yellow solid (565 mg, 66%). ^{1}H NMR (300 MHz, $CDCl_3$, 298 K, δ ppm): 8.23 – 7.96 (m, 6H), 7.82 – 7.70 (m, 2H), 7.26 – 7.20 (m, 1H), 4.08 (t, J = 6.0 Hz, 2H), 3.31 (t, J = 7.3 Hz, 2H), 2.35 (s, 3H), 1.96 – 1.73 (m, 4H). ^{13}C NMR (75 MHz, $CDCl_3$, 298 K, δ ppm): 144.81, 135.95, 133.24, 131.56, 131.00, 130.06, 129.92, 128.72, 127.98, 127.62, 127.51, 127.33, 126.86, 126.02, 125.22, 125.10, 124.92, 123.32, 70.50, 32.83, 28.89, 27.61, 27.06, 21.69. HRMS (ESI): m/z calcd. for $C_{27}H_{25}N_3S_1$ $[M+H]^+$ 429.5535, found 429.5571.



3b

Synthesis of 3b. NC$_{11}$ (70 mg, 0.15 mmol), **28** (77 mg, 0.18 mmol) and K_2CO_3 (124 mg, 0.9 mmol) were placed in a 10 mL round bottom flask. The mixture was degassed and filled with argon. Subsequently, dry acetonitrile (5 mL) was added. The mixture was refluxed for 1 d and then brought to room temperature. The solvent was removed under vacuum. The crude product was purified by column chromatography (silica gel, dichloromethane and methanol as eluent) to get **3b** as a pale yellow solid (75 mg, 69%). ^{1}H NMR (300 MHz, $CDCl_3$, 298 K, δ ppm): 8.25 (d, J = 9.3 Hz, 1H), 8.20 – 8.06 (m, 4H), 8.01 (d, J = 10.2 Hz, 3H), 7.86 (d, J = 7.8 Hz, 1H), 7.34 (m, J = 2.8 Hz, 10H), 5.08 (s, 4H), 4.78 (br, 2H), 3.40 (s, 2H), 3.21 – 2.99 (m, 4H), 2.80 (s, 6H), 1.91 (s, 4H), 1.40 (br, J = 7.4 Hz, 6H), 1.24 (d, J = 7.2 Hz, 8H). ^{13}C NMR (75 MHz, $CDCl_3$, 298 K, δ ppm): 156.49, 137.12, 136.79, 131.53, 131.03, 129.83, 128.73, 128.60, 128.20, 128.16, 127.64, 127.40, 127.21, 126.61, 125.89, 125.18, 125.14, 124.90, 124.88, 123.64, 66.66, 54.12, 54.04, 41.14, 33.56, 30.01, 29.94, 29.85, 27.27, 27.05, 26.83. HRMS

(ESI): m/z calcd. for $C_{47}H_{56}N_3O_4$ $[M+H]^+$ 726.9815, found 726.9782. m/z calcd. for $C_{47}H_{56}N_3O_4$ $[M]^+$ 726.4265, found 726.4254 (100%); $[M+H]^+$ 727.4288 (52%).

5. Additional supplementary figures

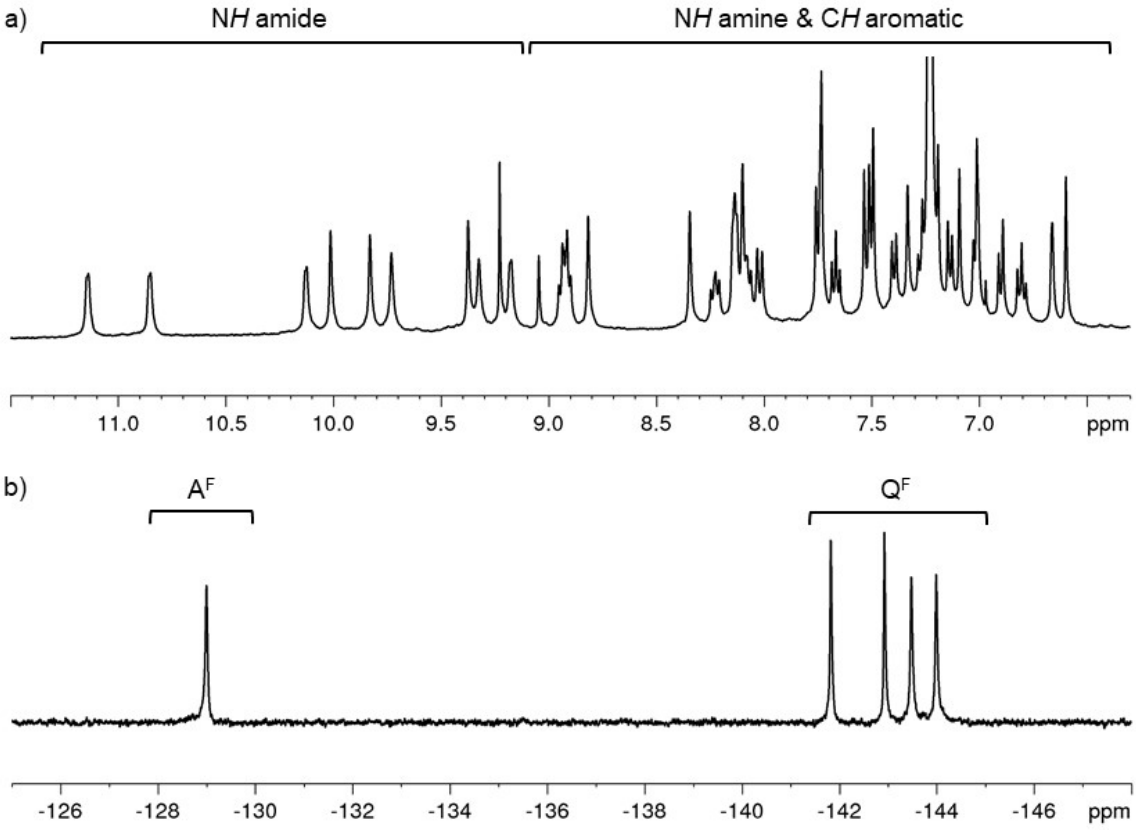


Figure S14. (a) 400 MHz ^{1}H NMR spectra at 298 K of oligomer **1** in $CDCl_3$. (b) 376 MHz ^{19}F NMR spectra at 298 K of oligomer **1** in $CDCl_3$. Four signals arise from the quinoline (Q_F) monomer and one signal arises from the diazaanthracene (A_F) monomer.

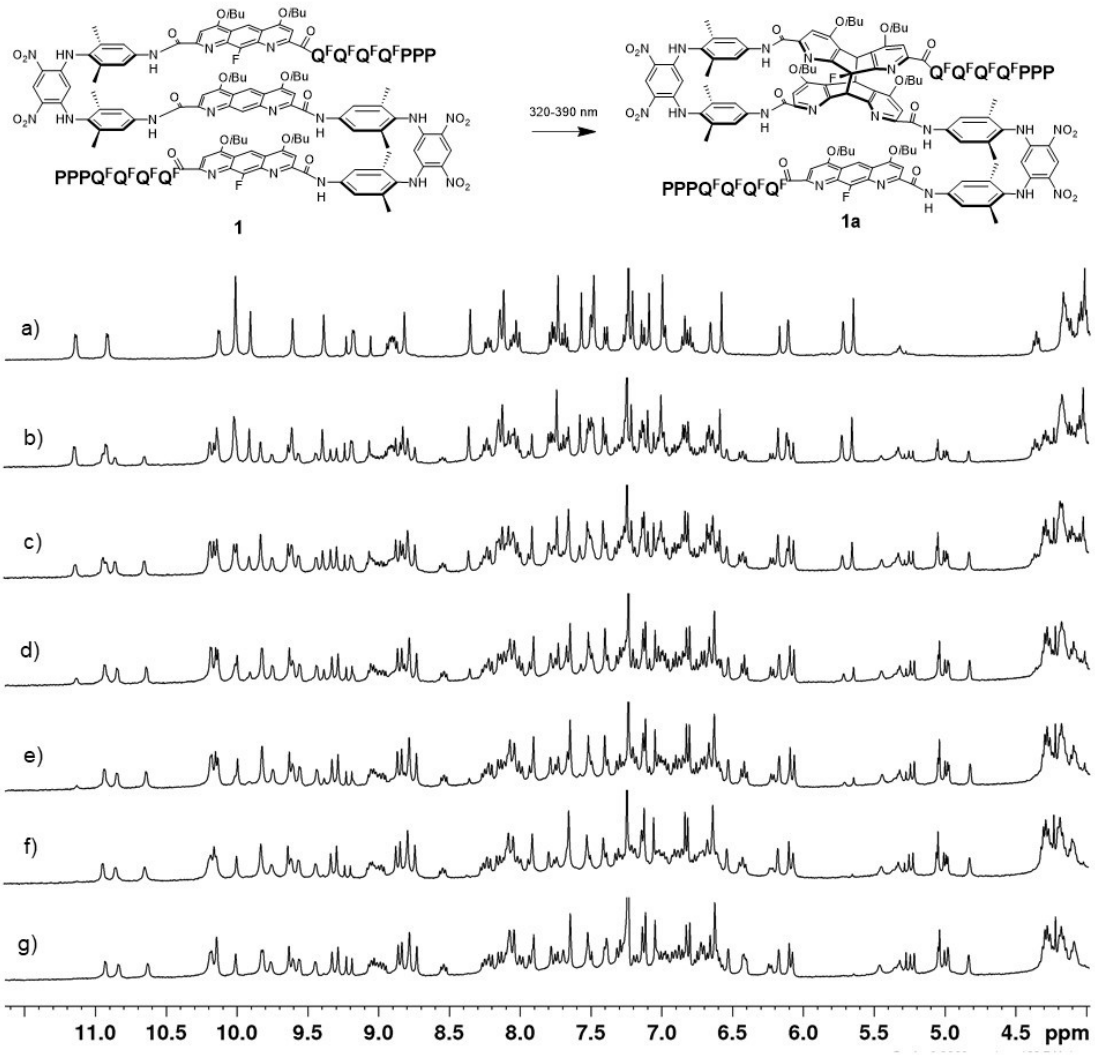


Figure S15. Schematic representation of photoirradiation (320 nm – 390 nm)-induced adduct formation between two diazaanthracene (A_F and A_H) units in **1** to **1a**. Part of the 400 MHz ^{1}H NMR spectra of **1** at 298 K (1 mM in $CDCl_3$) under photoirradiation after : (a) 0 min; (b) 15 min.; (c) 30 min; (d) 45 min; (e) 60 min; (f) 90 min; and (g) 120 min. The signals corresponding to the starting oligomer **1** are labelled with empty circles and for photoproduct **1a,** in black circles.

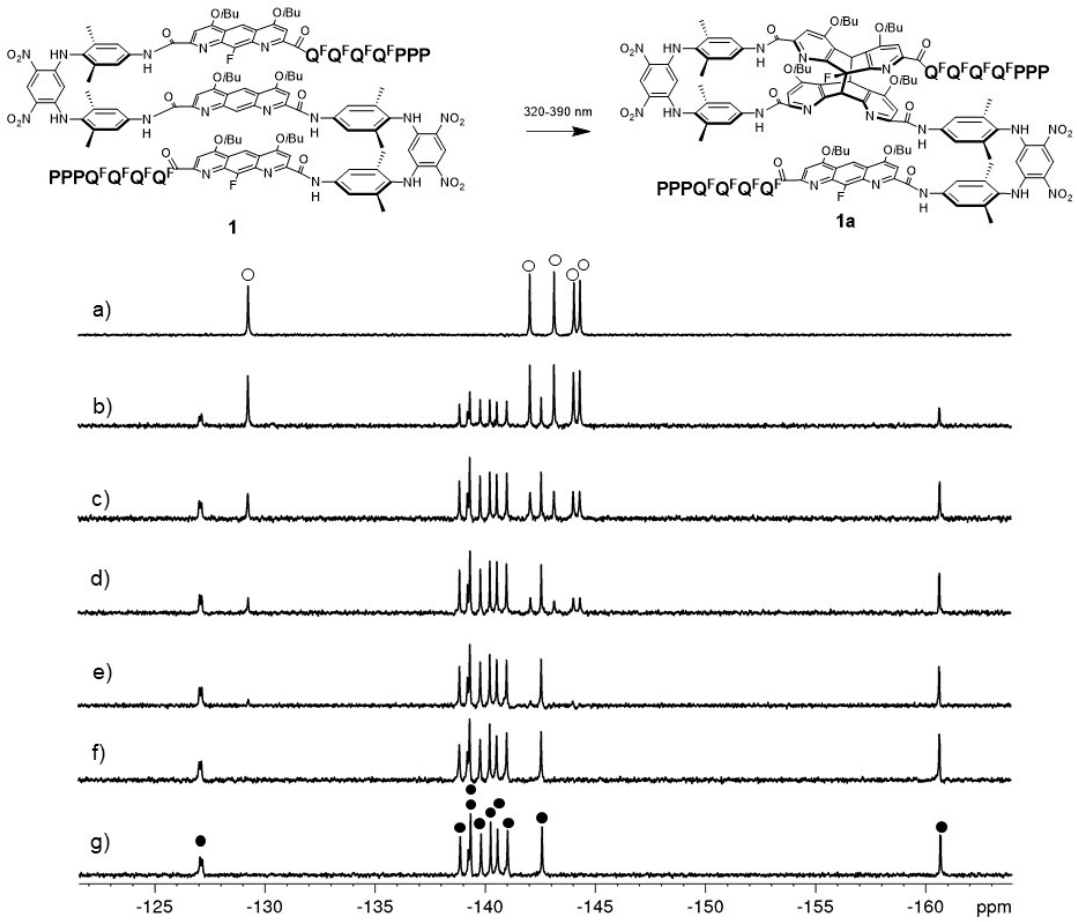


Figure S16. Schematic representation of photoirradiation (320 nm – 390 nm)-induced adduct formation between two diazaanthracene (A_F and A_H) units in **1** to **1a**. Part of the 376 MHz ^{19}F NMR spectra of **1** at 298K (1 mM in $CDCl_3$) under photoirradiation after (a) 0 min; (b) 15 min.; (c) 30 min; (d) 45 min; (e) 60 min; (f) 90 min; and (g) 120 min. The signals correspond to the starting oligomer **1** are labelled with empty circles and for photoproduct, **1a,** in black circles.

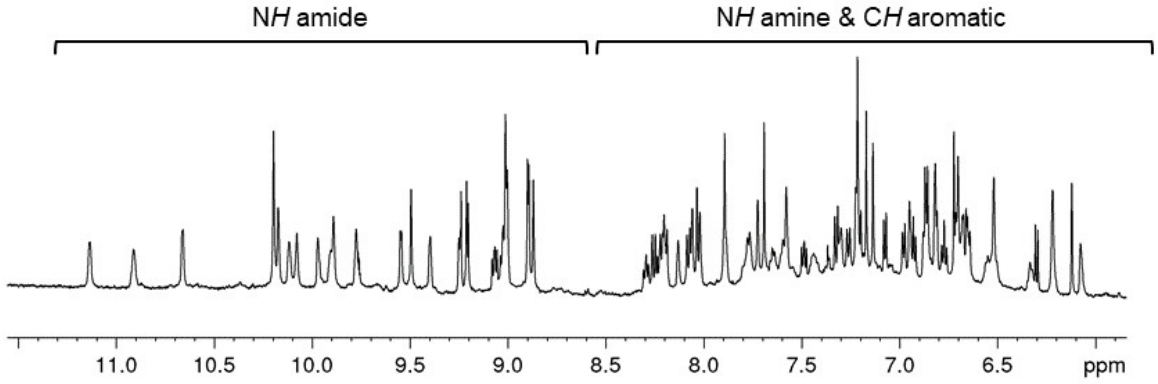


Figure S17. (a) 400 MHz ^1H NMR spectra at 298 K of oligomer **1a** in CD_2Cl_2.

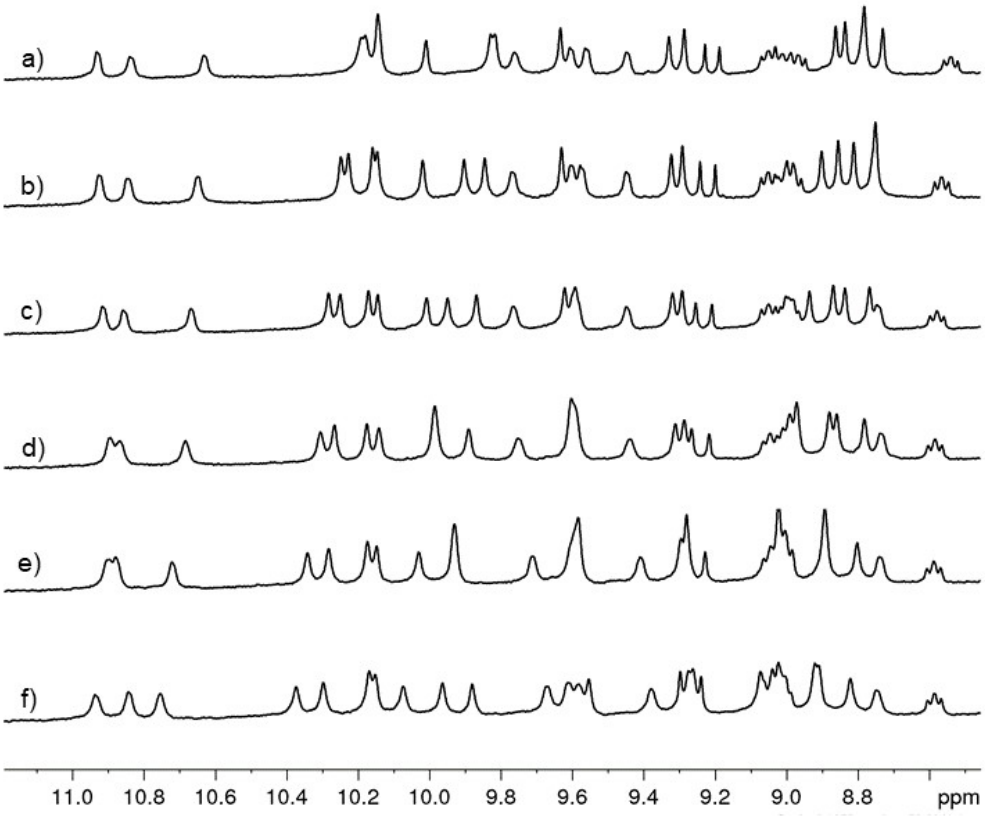


Figure S18. Part of the variable temperature ^{1}H NMR spectra (400 MHz, $CDCl_3$) of **1a** (1 mM) at different temperatures:- (a) 298 K; (b) 283 K; (c) 273 K; (d) 263 K; (e) 253 K and (f) 243 K.

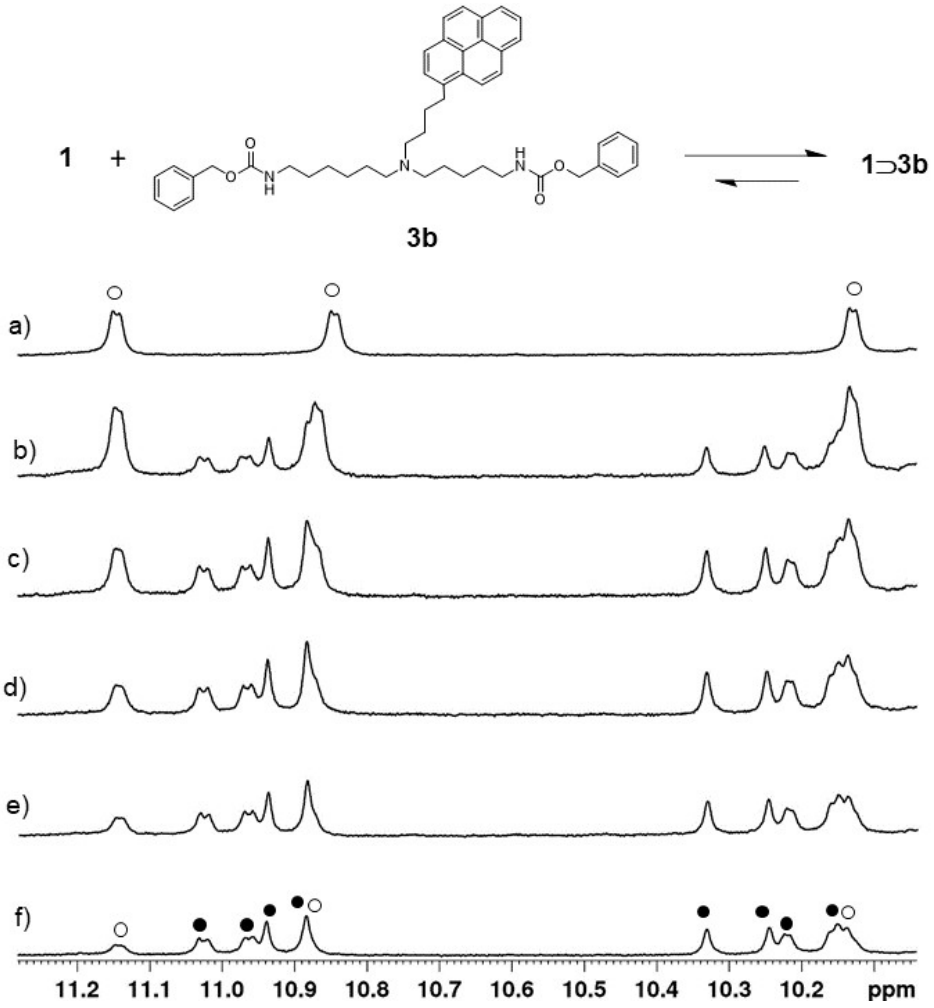


Figure S19. Schematic illustration showing the binding of guest **3b** within foldamer **1**. Part of the 400 MHz ^{1}H NMR spectra of **1** (1 mM) at 298 K in $CDCl_3$ (a) and after addition of aliquots of **3b** (5 mM in $CDCl_3$):- (b) 0.50 equiv.; (c) 1.0 equiv.; (d) 1.5 equiv.; (e) 2.0 equiv and (f) 3.0 equiv. The signals correspond to the starting oligomer **1** are labelled with empty circles and for the host-guest complex, **1⊃3b**, in black circles. The apparent K_a of the single helix of **1** for **4** was estimated by integration of the amide peaks of the empty host vs the peaks of **1⊃3b**.

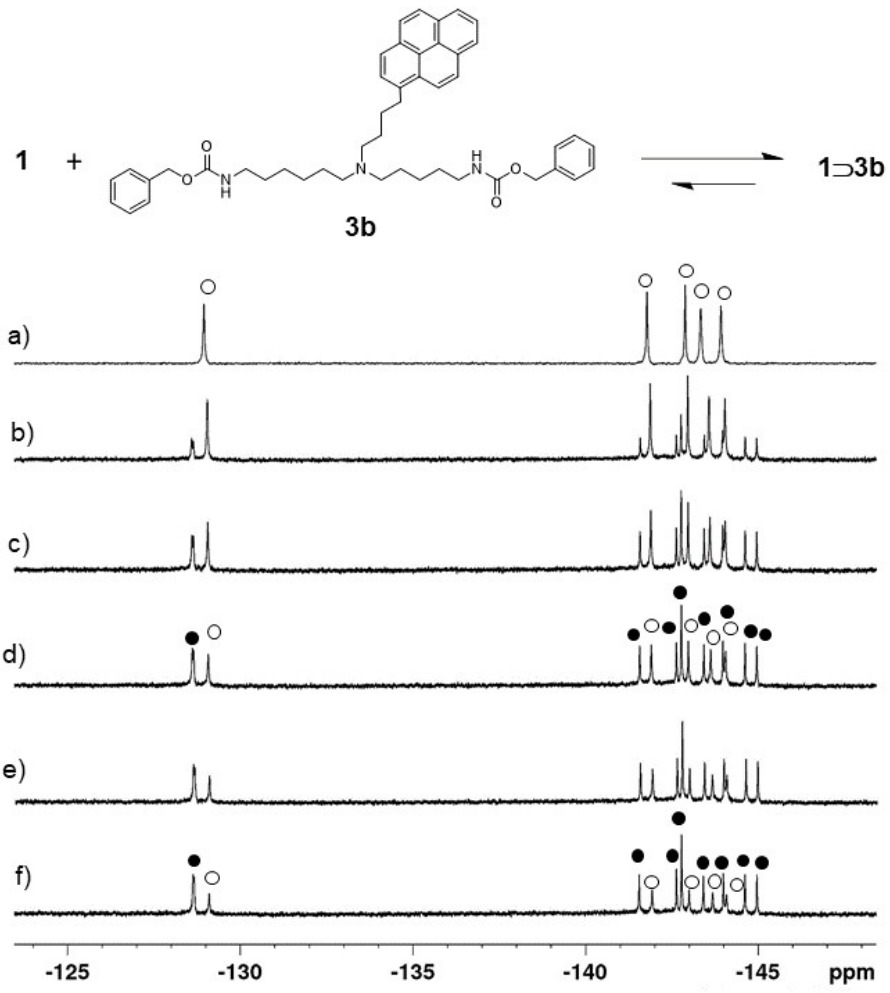


Figure S20. Schematic illustration showing encapsulation of guest **3b** within foldamer **1**. Part of the 376 MHz ^{19}F NMR spectra of **1** (1 mM) at 298 K in $CDCl_3$ (a), and after addition of aliquots of **3b** (5 mM in $CDCl_3$):- (b) 0.50 equiv.; (c) 1.0 equiv.; (d) 1.5 equiv.; (e) 2.0 equiv. and (f) 3.0 equiv. The signals corresponding to the starting oligomer **1** are labelled with empty circles and for the host-guest complex, **1⊃3b,** in black circles. Note: the number of signals is doubled after guest binding due to the non-symmetrical nature of the guest.

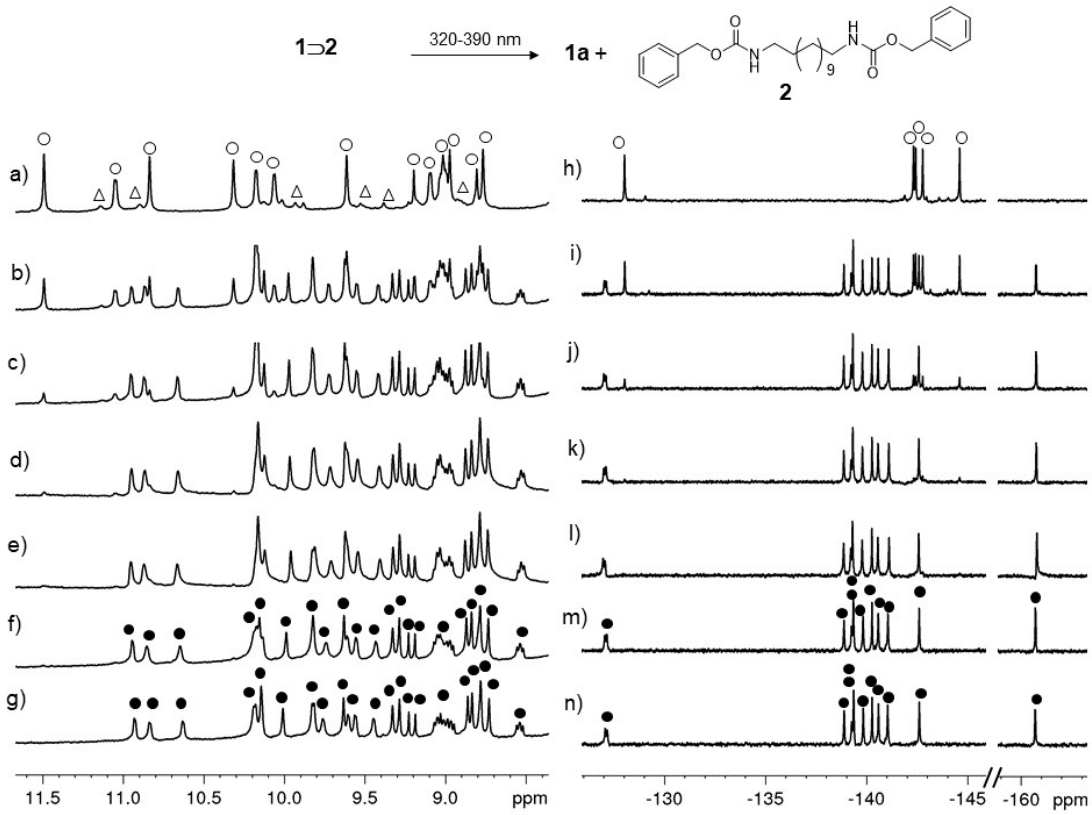


Figure S21. Schematic illustration of photoirradiation (320 nm – 390 nm)-induced guest (**2**), release from host-guest complex, **1⊃2**, upon photoadduct formation between two diazaanthracene (A_F and A_H) units. Part of the 400 MHz ^{1}H NMR spectra of (a) host-guest complex, **1⊃2**, at 298 K in $CDCl_3$ and after:- (b) 30 min; (c) 60 min.; (d) 90 min; (e) 120 min; and (f) 150 min. (g) The 400 MHz ^{1}H NMR spectra of **1a**, when produced by irradiation of **1**, given for comparison. (h-n) The corresponding 376 MHz ^{19}F NMR signals, marked with empty circles, empty triangles and dark circles corresponding to **1⊃2**, free **1** and **1a**, respectively.

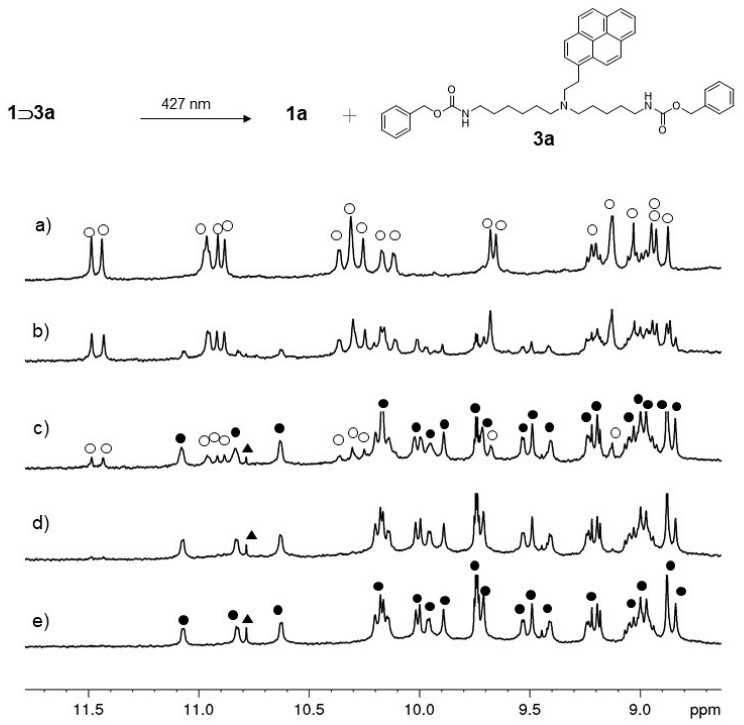


Figure S22. Schematic illustration of photoirradiation (427 nm)-induced guest **3a**, release from a host-guest complex, **1⊃3a**, upon photoadduct formation between two diazaanthracene (A_F and A_H) units. Part of the 600 MHz ^{1}H NMR spectra of : (a) host-guest complex **1⊃3a** at 298 K in CD_2Cl_2 and after irradiation for :- (b) 8 min; (c) 15 min; (d) 30 min; (e) 60 min. The signals are marked with empty circles and filled circles, corresponding to **1⊃3a** and **1a**, respectively. Side product is marked with black triangles.

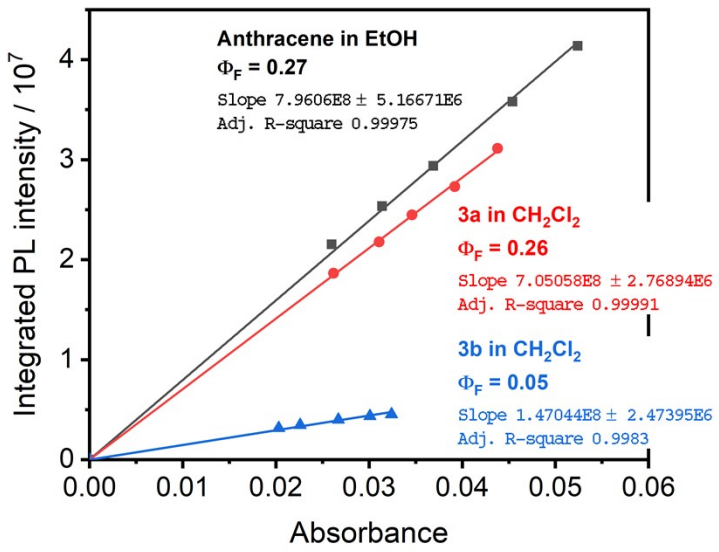


Figure S23. Linear plots for the determination of the fluorescence quantum yields of **3a** and **3b** using anthracene in ethanol as a reference (Φ = 0.27).

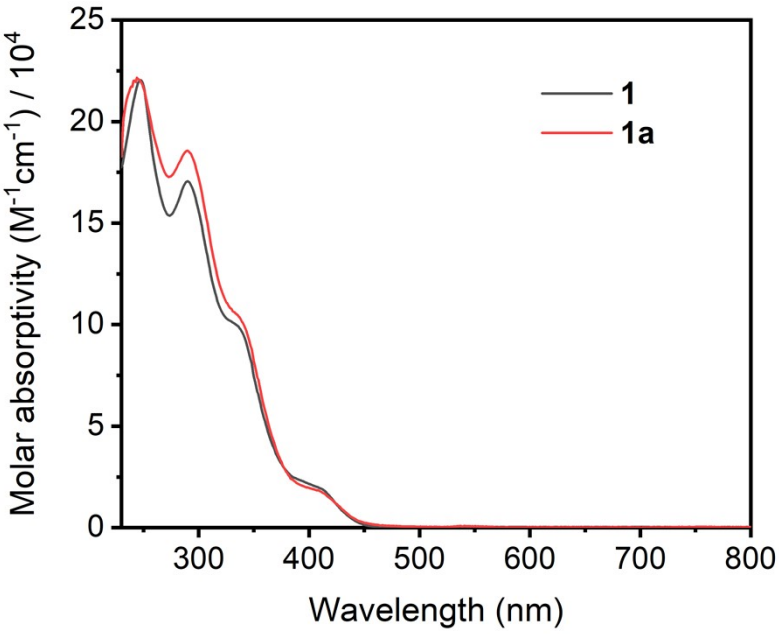


Figure S24. UV-vis spectra of **1** and **1a** in CH_2Cl_2.

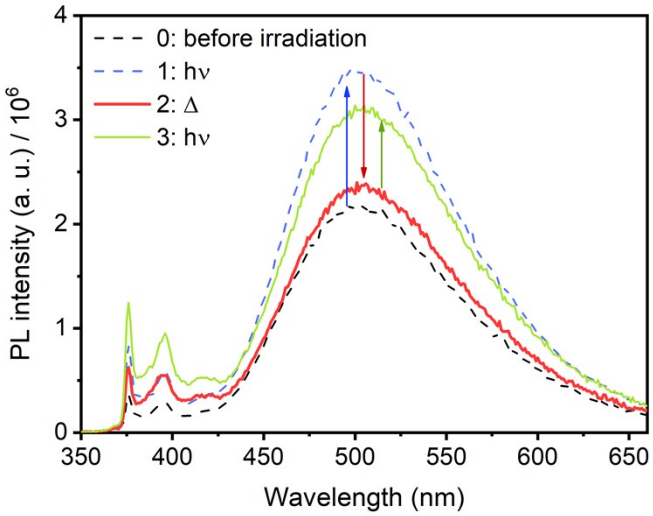


Figure S25. Changes in fluorescence spectra in dichloroethane upon photorelease of **3a** (λ_{irr} = 427 nm) and thermally-induced reassembly into **1⊃3a**.

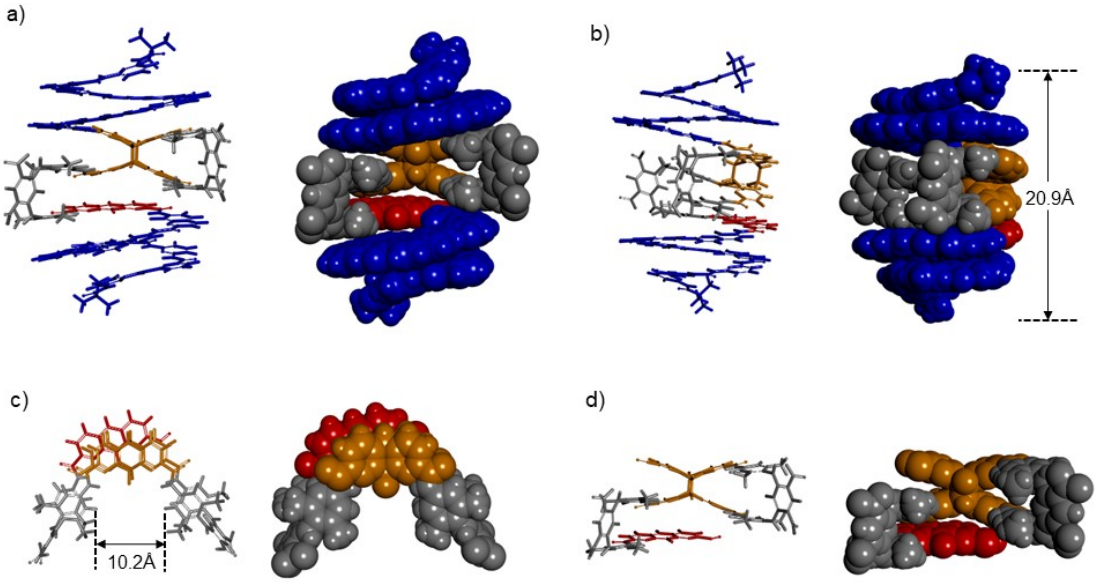
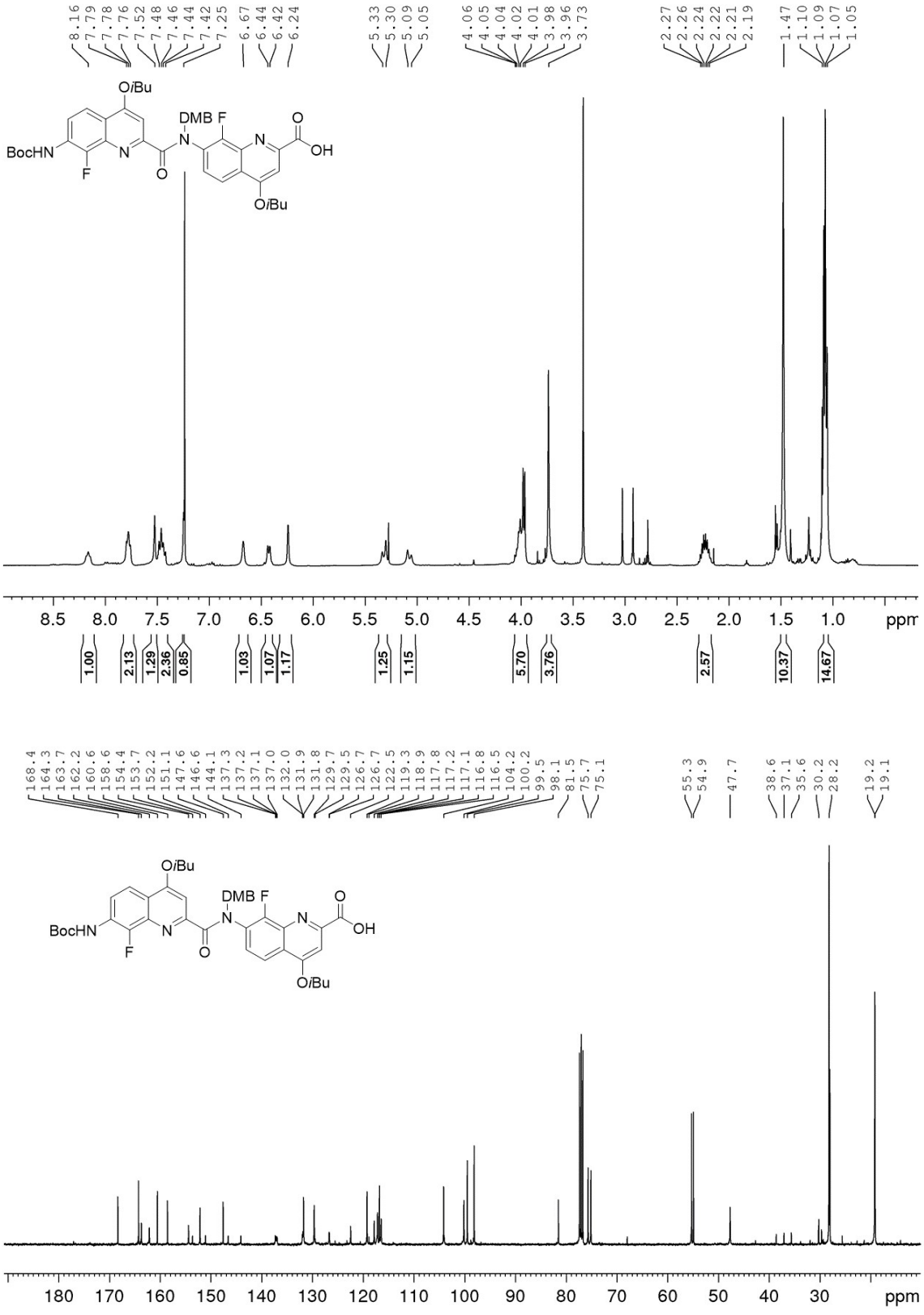


Figure S26. Energy minimized molecular models of the photoproduct **1a:** a) Side view and b) front view of **1a**, helical segments, diazaanthracene units and turns were marked as blue, red and grey, respectively; c) top view and d) side view of turn and sheets segments of **1a**. The models were produced with Maestro software package, using MMFFs force field, chloroform as solvent and TNCG as minimization method.

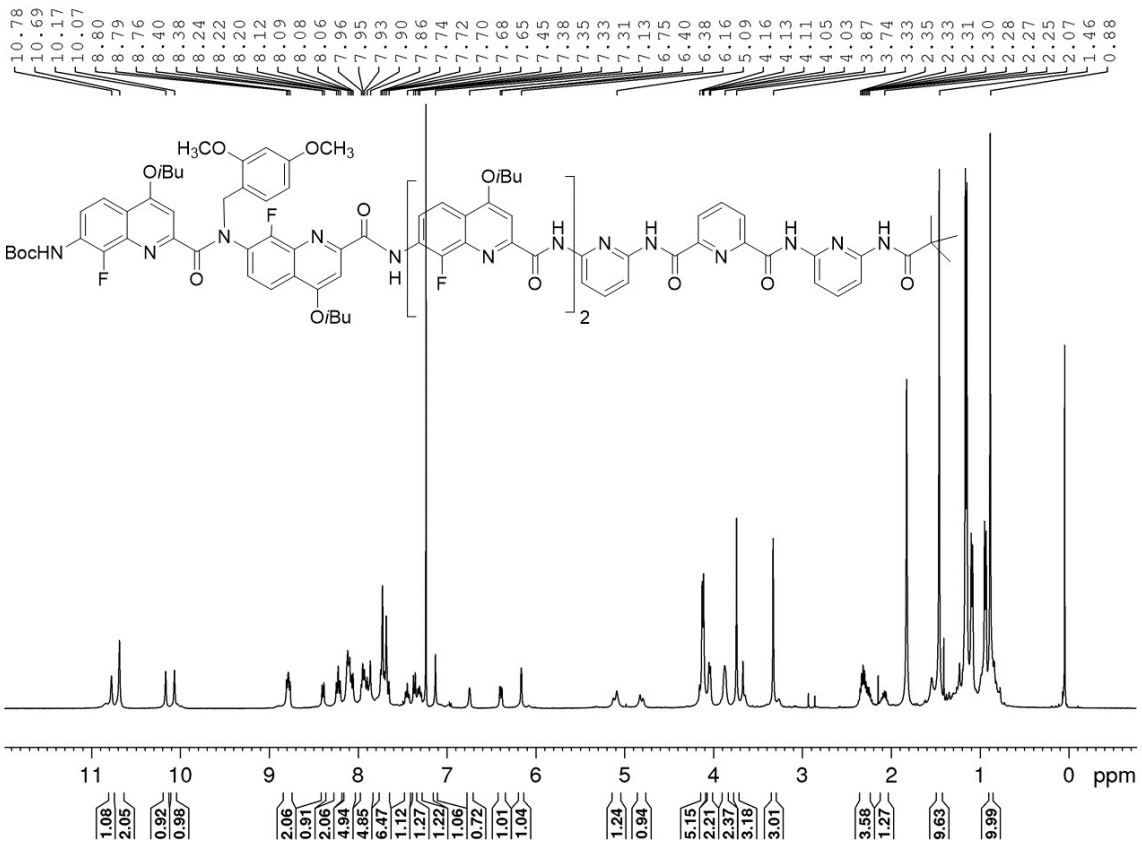
Table S1: crystal data and structure refinement for the foldaxane 1 ⊃ 3a

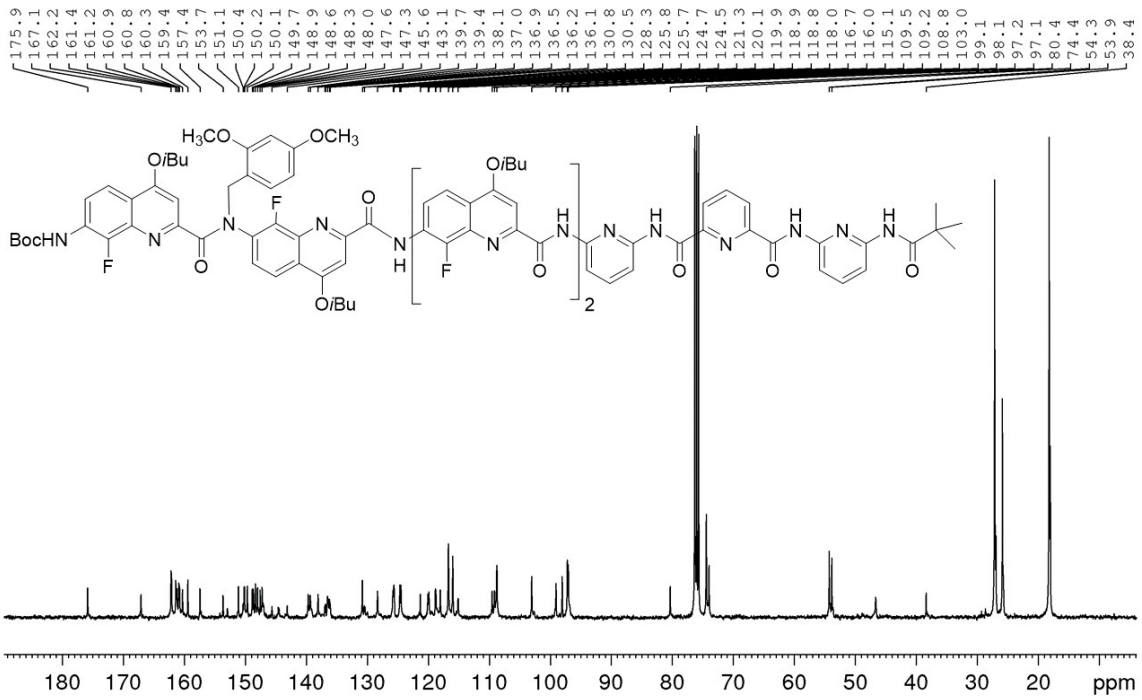
CCDC code	2162063
Empirical formula	$C_{314}H_{312}Cl_3F_{10}N_{49}O_{47}$
Formula weight	5820.46
Temperature/K	135
Crystal system	triclinic
Space group	P-1
a/Å	23.7615(4)
b/Å	24.0825(4)
c/Å	35.9358(6)
α/°	101.2045(15)
β/°	91.4858(14)
γ/°	111.9064(18)
Volume/Å³	18605.6(6)
Z	2
ρcalcg/cm³	1.039
μ/mm-1	0.805
F(000)	6112.0
Crystal size/mm³	0.05 × 0.05 × 0.05
Radiation	Cu Kα (λ = 1.54178)
2Θ range for data collection/°	5.734 to 102.778
Index ranges	$-23 \leq h \leq 18$, $-22 \leq k \leq 23$, $-35 \leq l \leq 36$
Reflections collected	122926
Independent reflections	39846 [R_{int} = 0.0379, R_{sigma} = 0.0419]
Data/restraints/parameters	39846/263/3853
Goodness-of-fit on F2	1.313
Final R indexes [I>=2σ (I)]	R1 = 0.1015, wR2 = 0.3192
Final R indexes [all data]	R1 = 0.1303, wR2 = 0.3510

6. NMR spectra

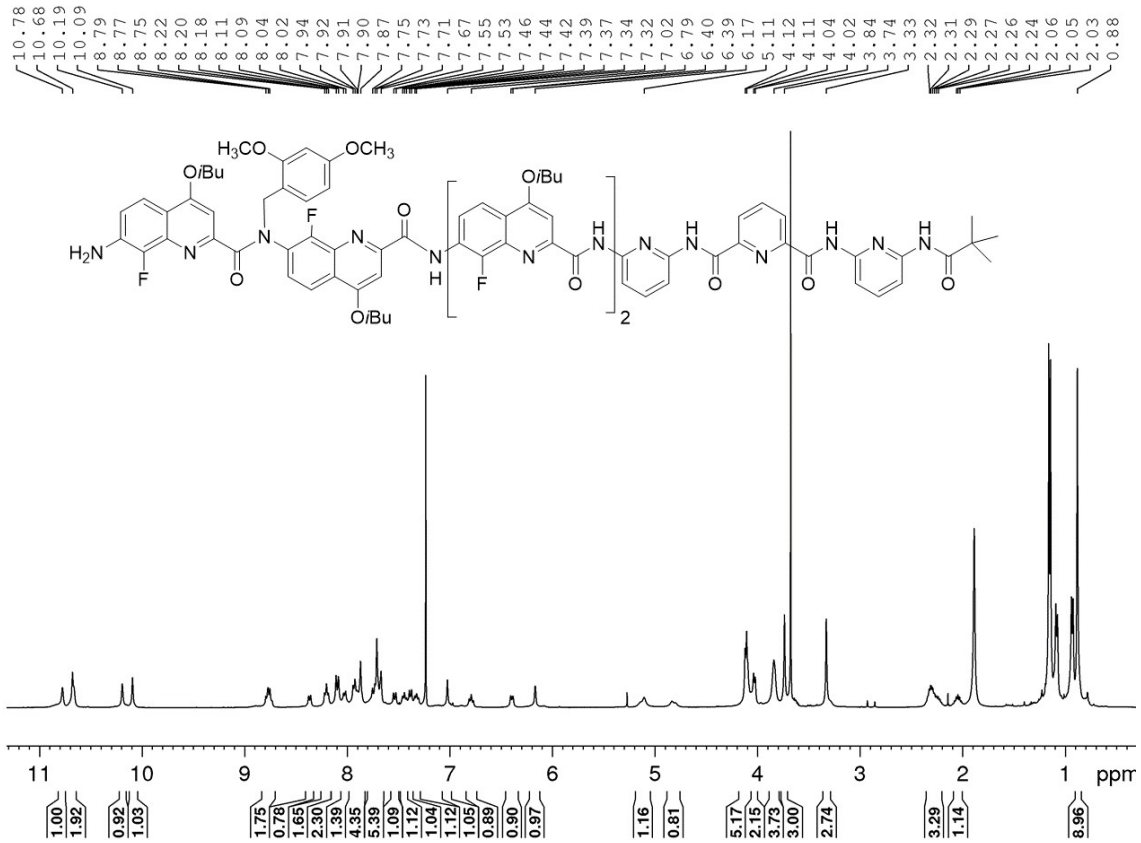


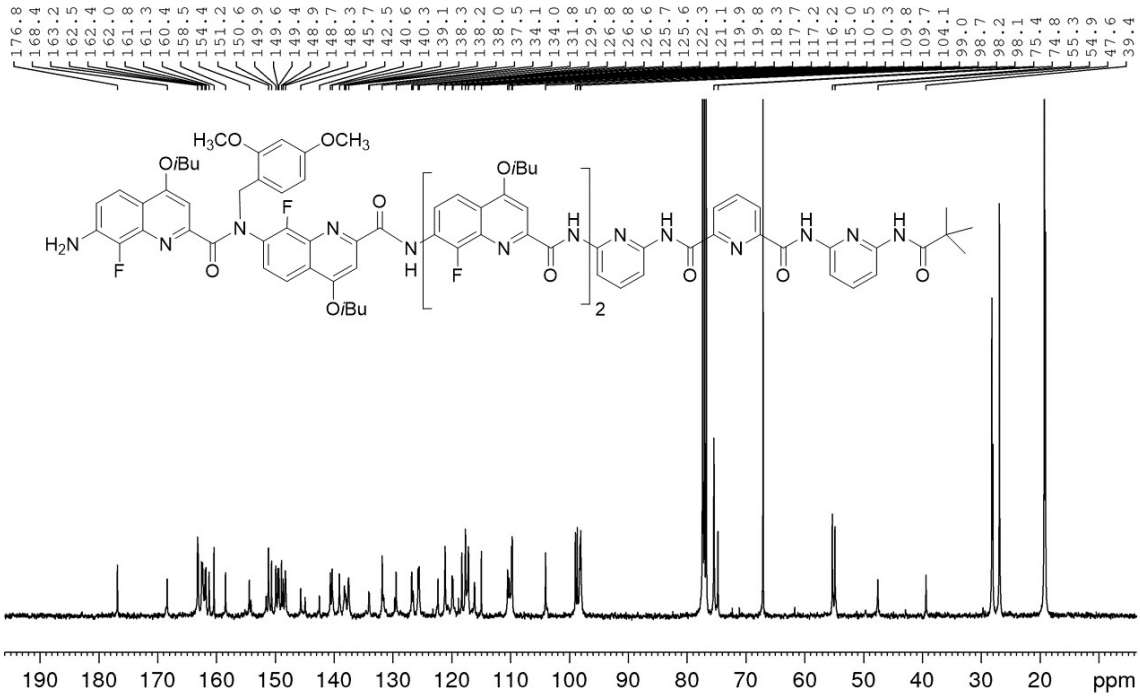
^{1}H (400 MHz, $CDCl_3$, 298 K) and ^{13}C (126 MHz, $CDCl_3$, 298 K) NMR spectra of compound **6**.



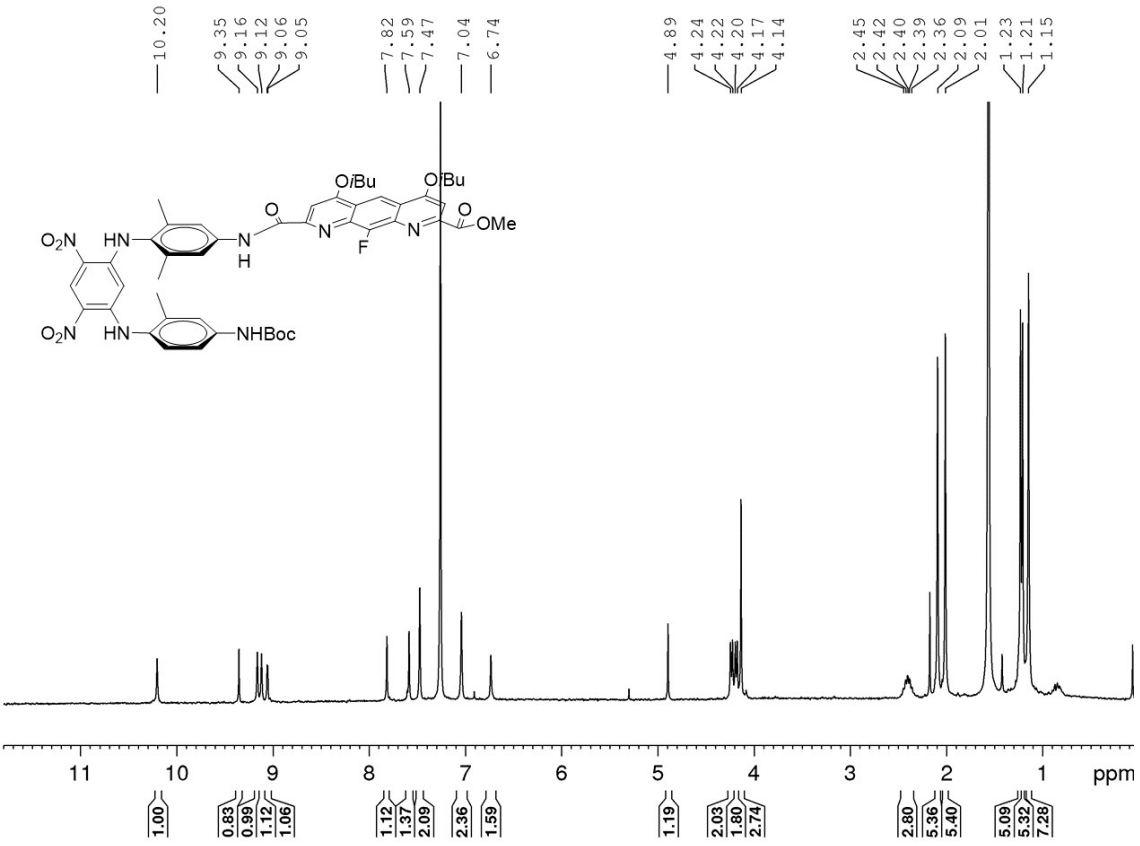


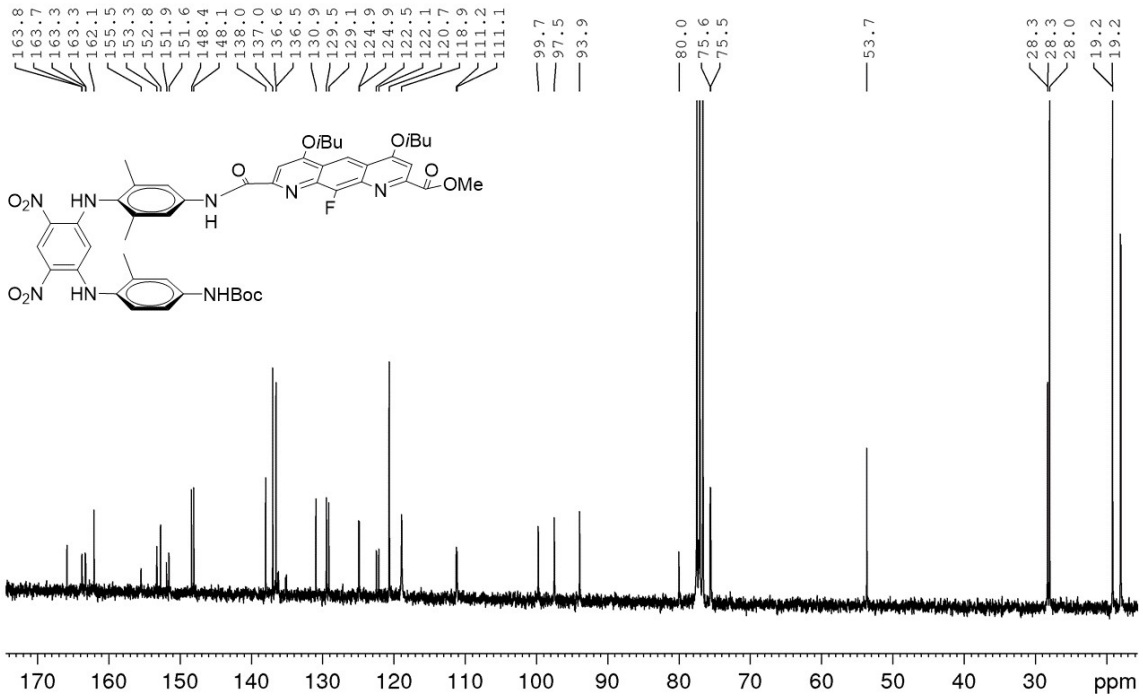
^{1}H (400 MHz, $CDCl_3$, 298 K) and ^{13}C (126 MHz, $CDCl_3$, 298 K) NMR spectra of compound **8**.



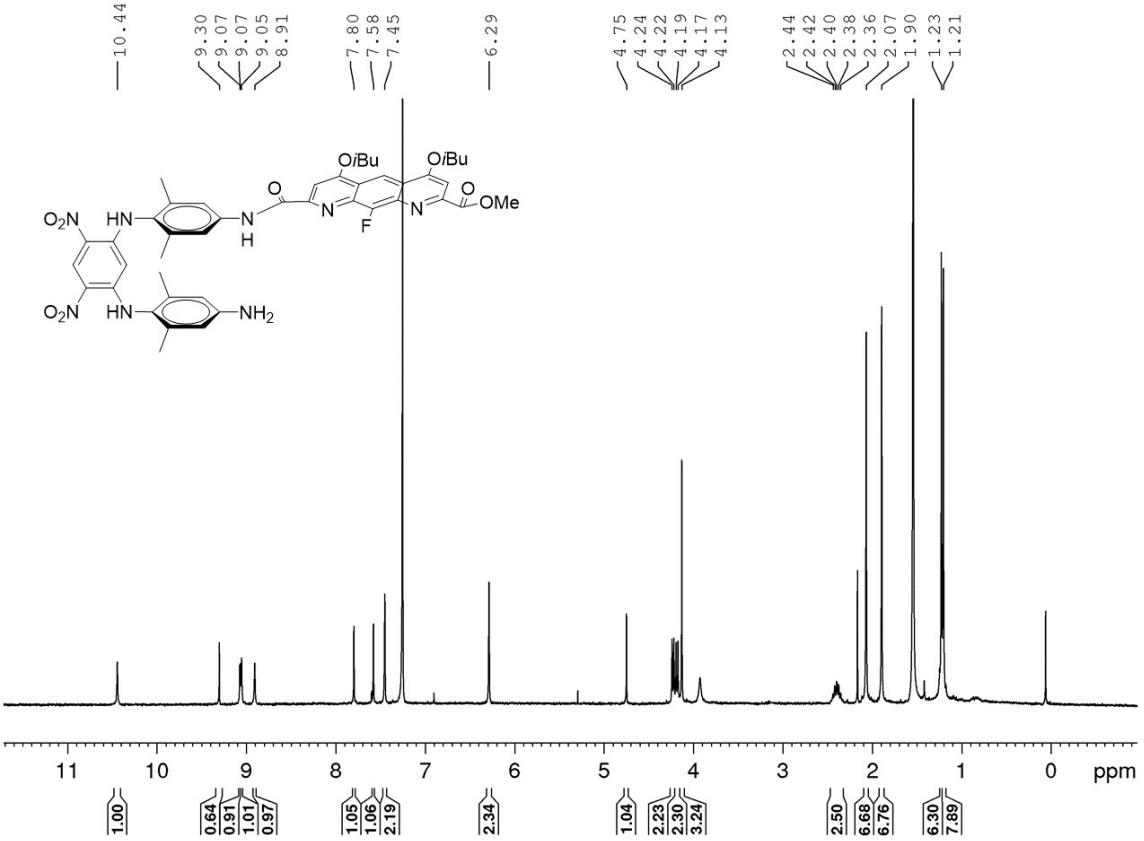


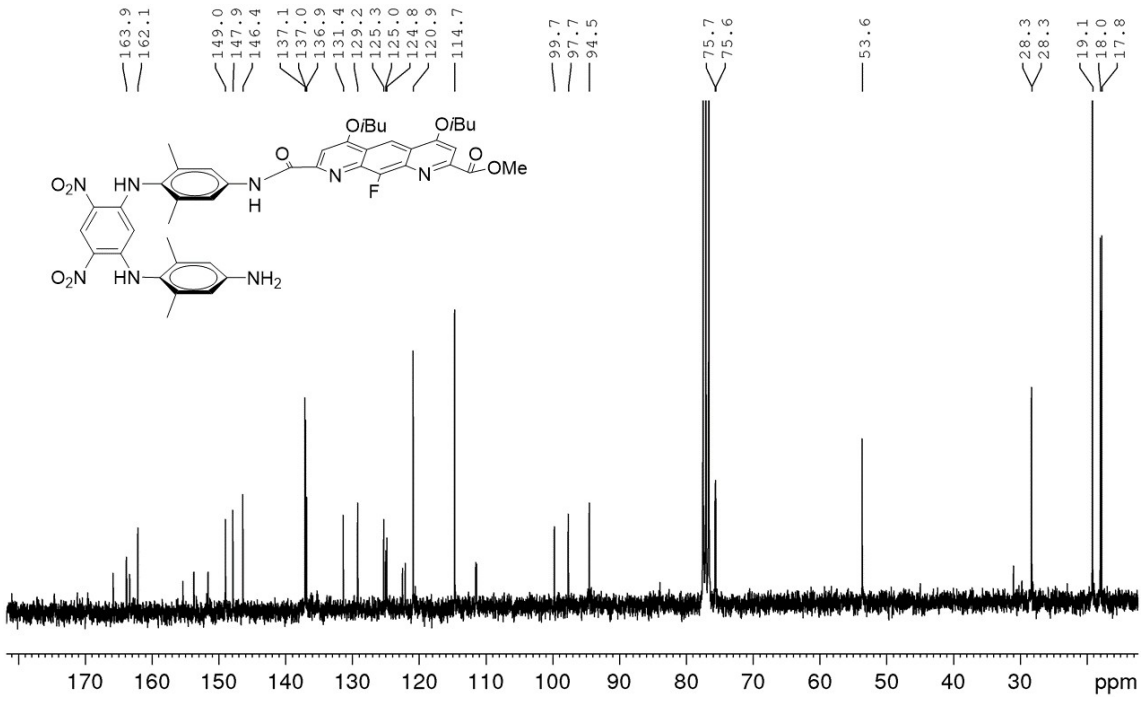
^{1}H (400 MHz, $CDCl_3$, 298 K) and ^{13}C (126 MHz, $CDCl_3$, 298 K) NMR spectra of compound **9**.



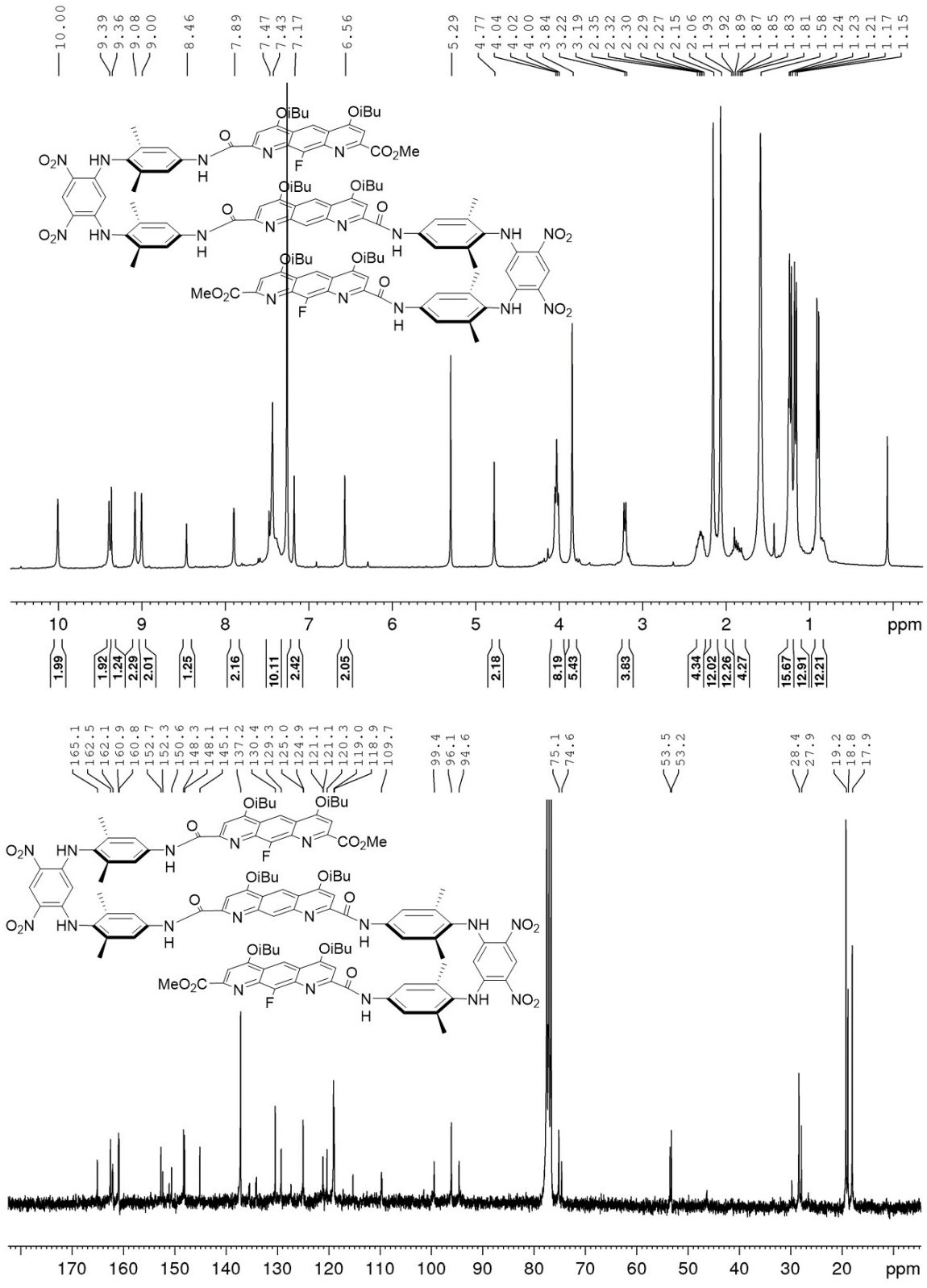


^{1}H (400 MHz, $CDCl_3$, 298 K) and ^{13}C (126 MHz, $CDCl_3$, 298 K) NMR spectra of compound **12**.

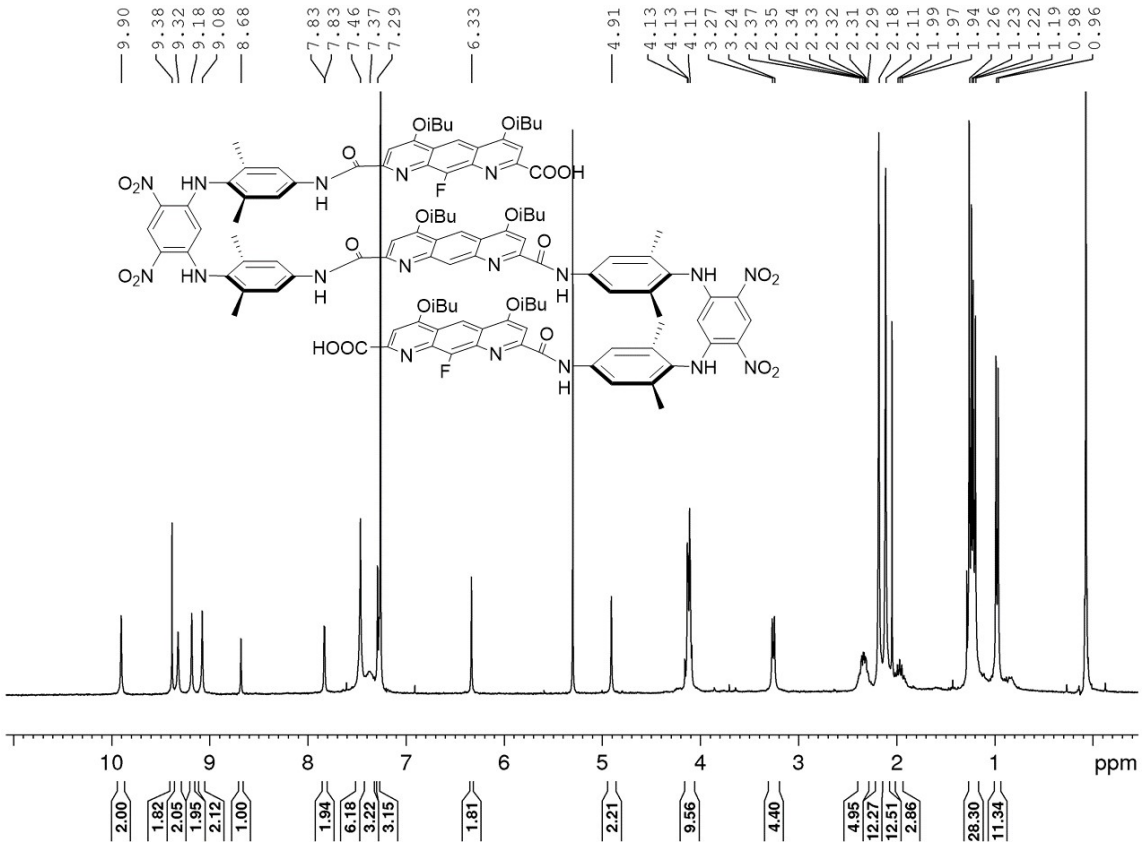




^{1}H (400 MHz, $CDCl_3$, 298 K) and ^{13}C (126 MHz, $CDCl_3$, 298 K) NMR spectra of compound **13**.



^{1}H (400 MHz, $CDCl_3$, 298 K) and ^{13}C (126 MHz, $CDCl_3$, 298 K) NMR spectra of compound **15.**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7.37
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4.11
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2.31
2.29
2.18
2.11
1.99
1.97
1.94
1.26
1.23
1.22
1.19
0.98
0.96
OiBu
OiBu
COOH
F
HN
O2N
NH
NO2
HOOC
10
9
8
7
6
5
4
3
2
1
ppm
2.00
1.82
2.05
1.95
2.12
1.00
1.94
6.18
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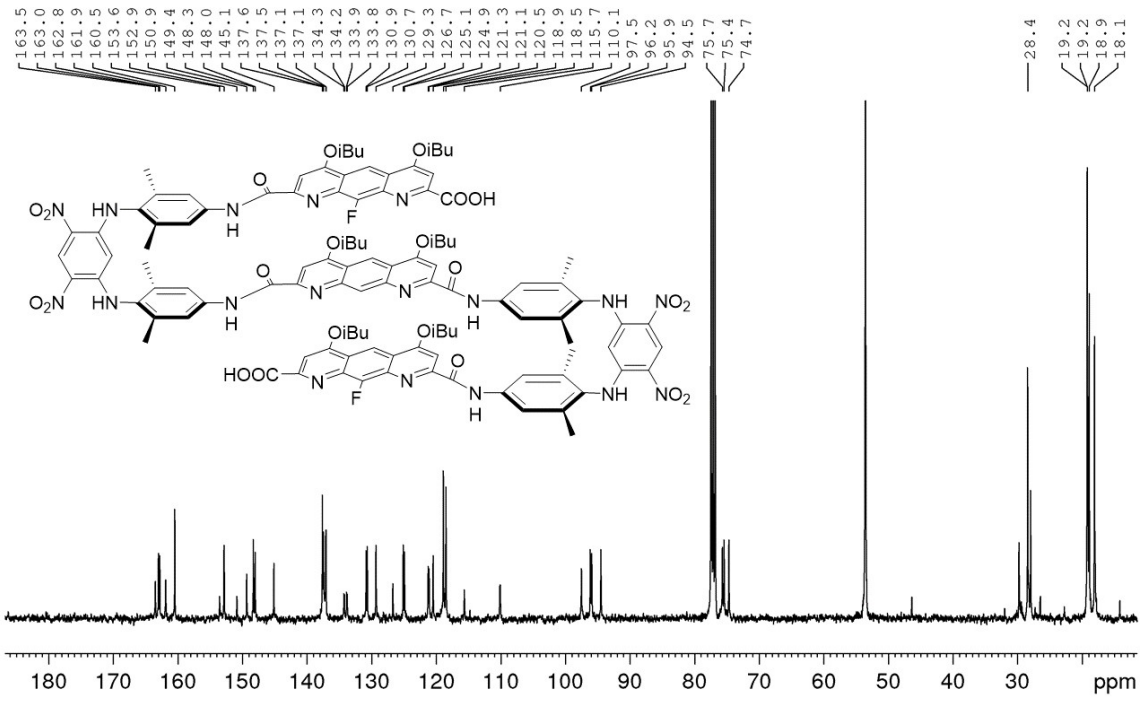
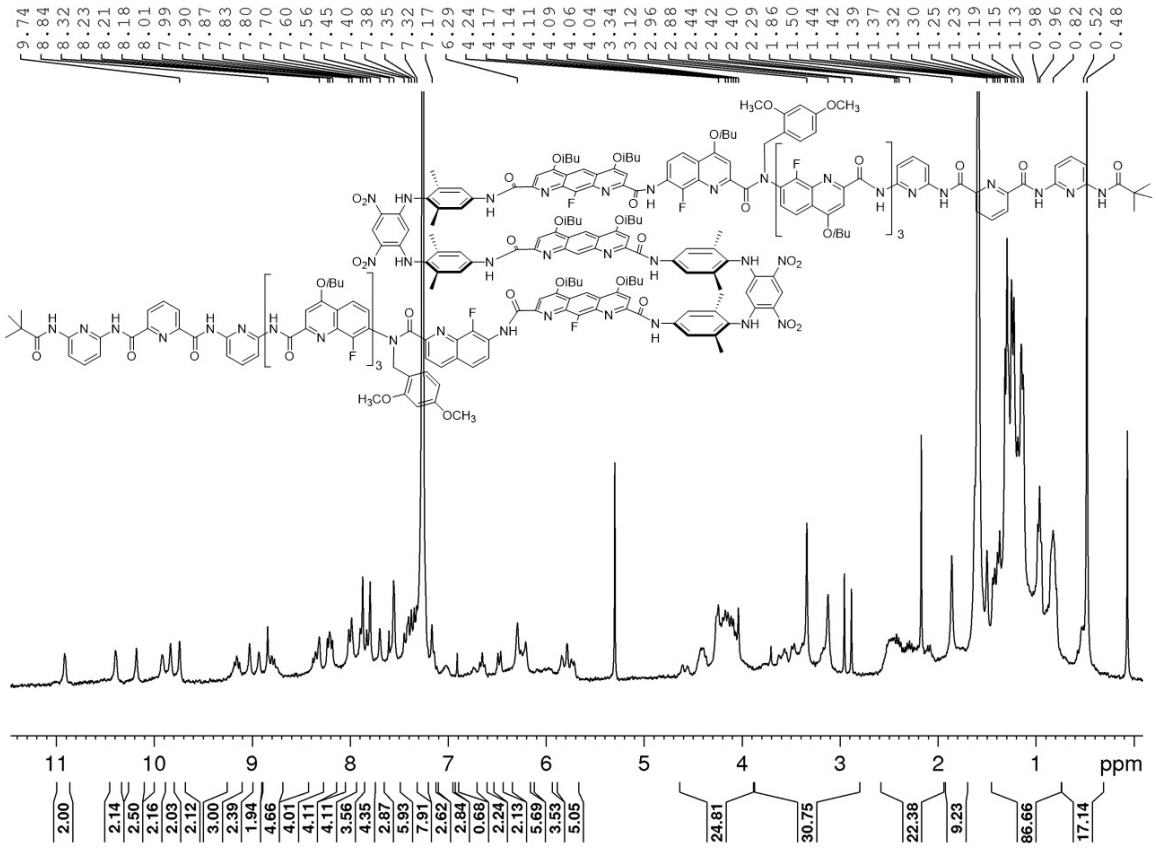
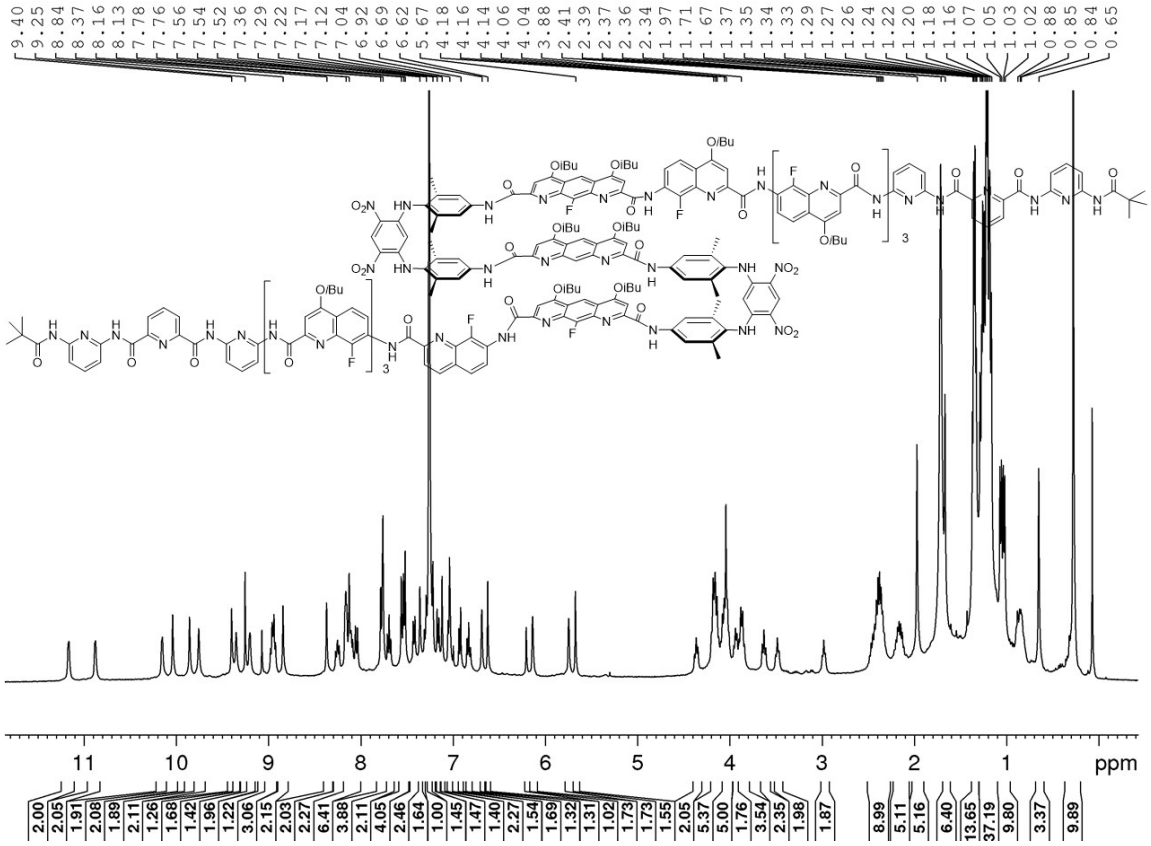
2.86
28.30
11.34



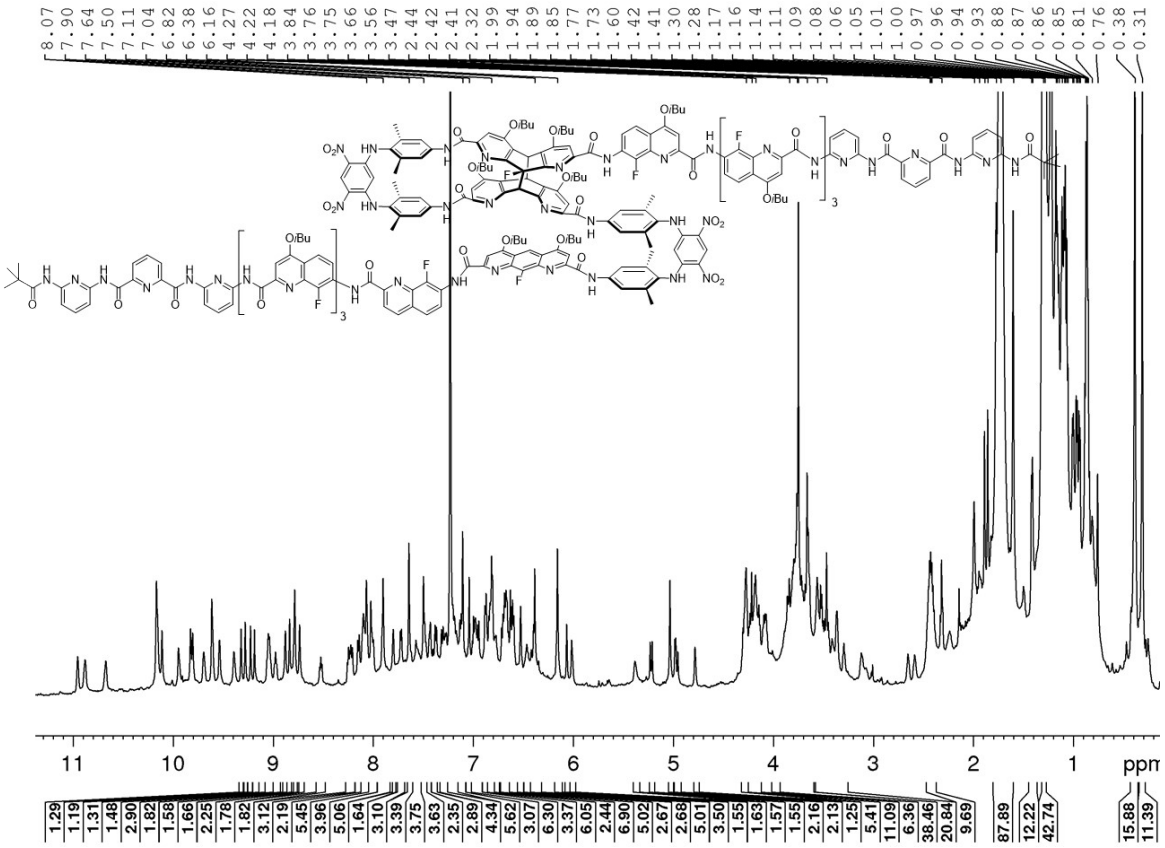
^{1}H (400 MHz, $CDCl_3$, 298 K) and ^{13}C (126 MHz, $CDCl_3$, 298 K) NMR spectra of compound **16**.



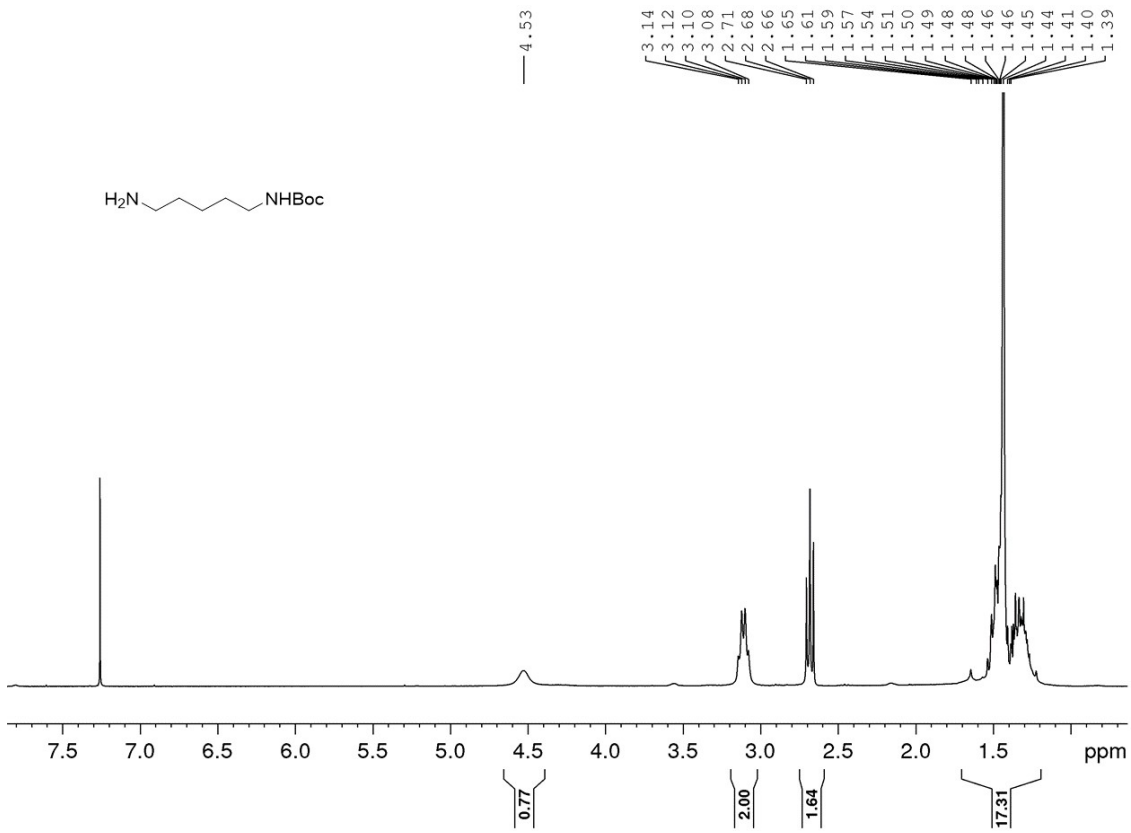
^{1}H (400 MHz, $CDCl_3$, 298 K) NMR spectrum of compound **17**.



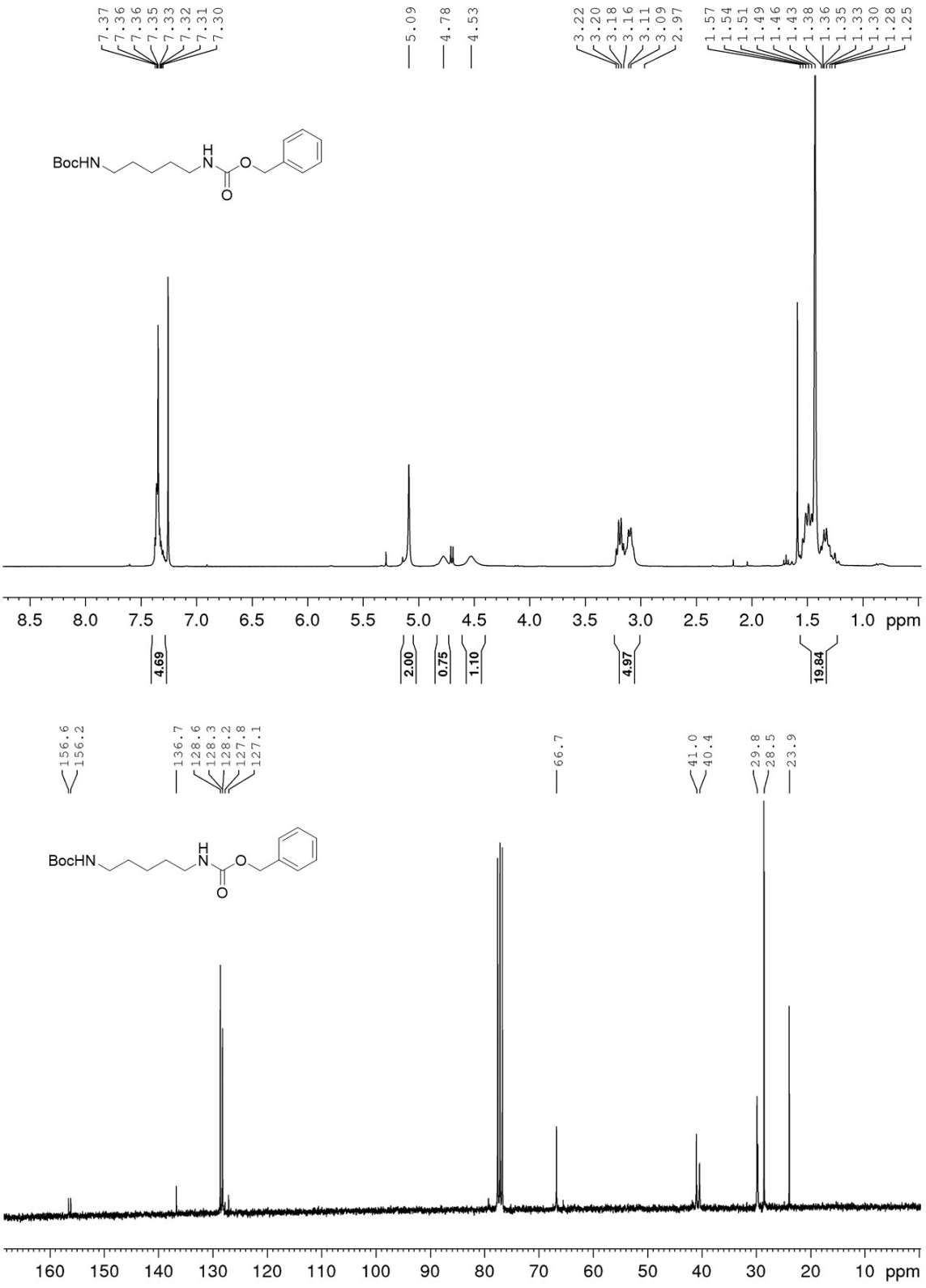
^{1}H (400 MHz, $CDCl_3$, 298 K) spectrum of compound **1**.



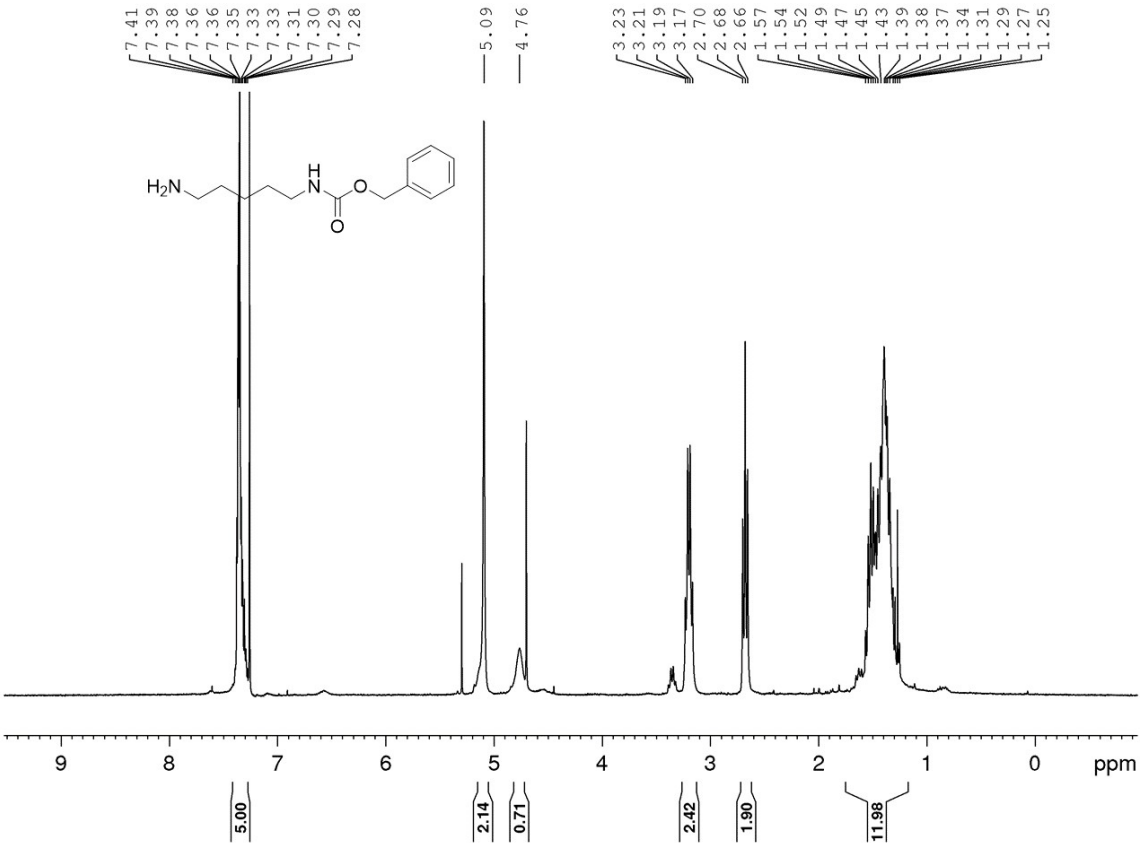
^{1}H (400 MHz, $CDCl_3$, 298 K) NMR spectrum of compound **1a**.



^{1}H (400 MHz, $CDCl_3$, 298 K) NMR spectrum of compound **19**.



^{1}H (400 MHz, $CDCl_3$, 298 K) and ^{13}C (126 MHz, $CDCl_3$, 298 K) NMR spectra of compound **20**.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3.21
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3.17
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2.68
2.66
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1.54
1.52
1.49
1.47
1.45
1.43
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1.29
1.27
1.25
H2N
H
N
O
O
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8
7
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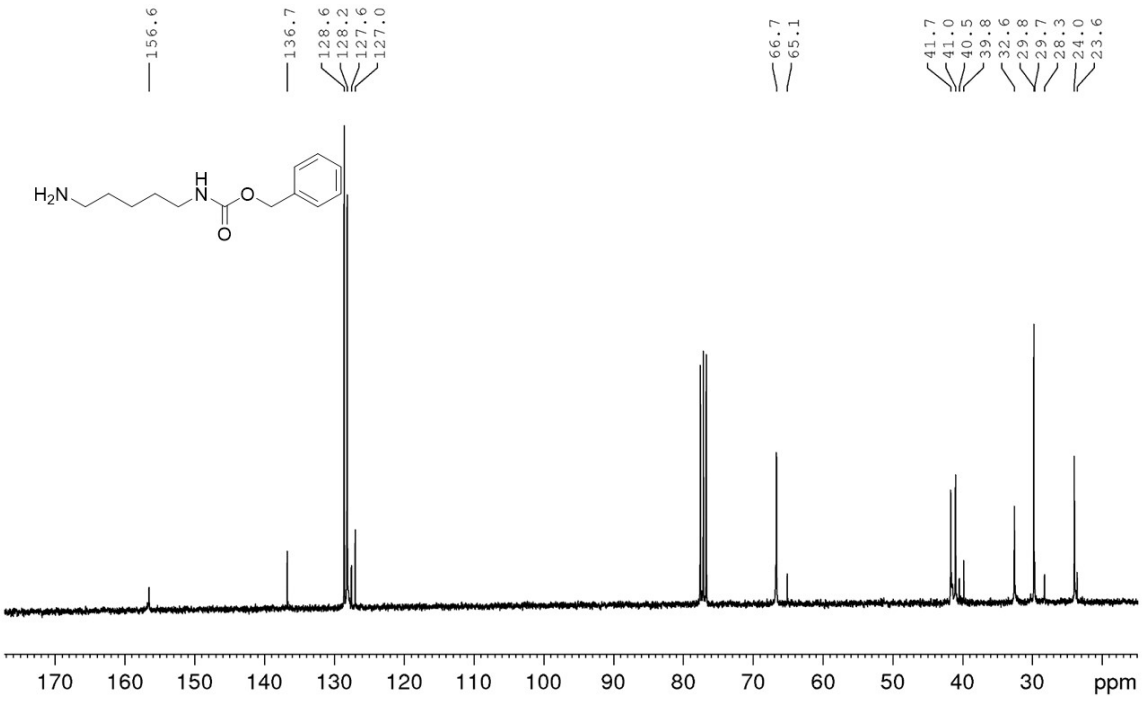
11.98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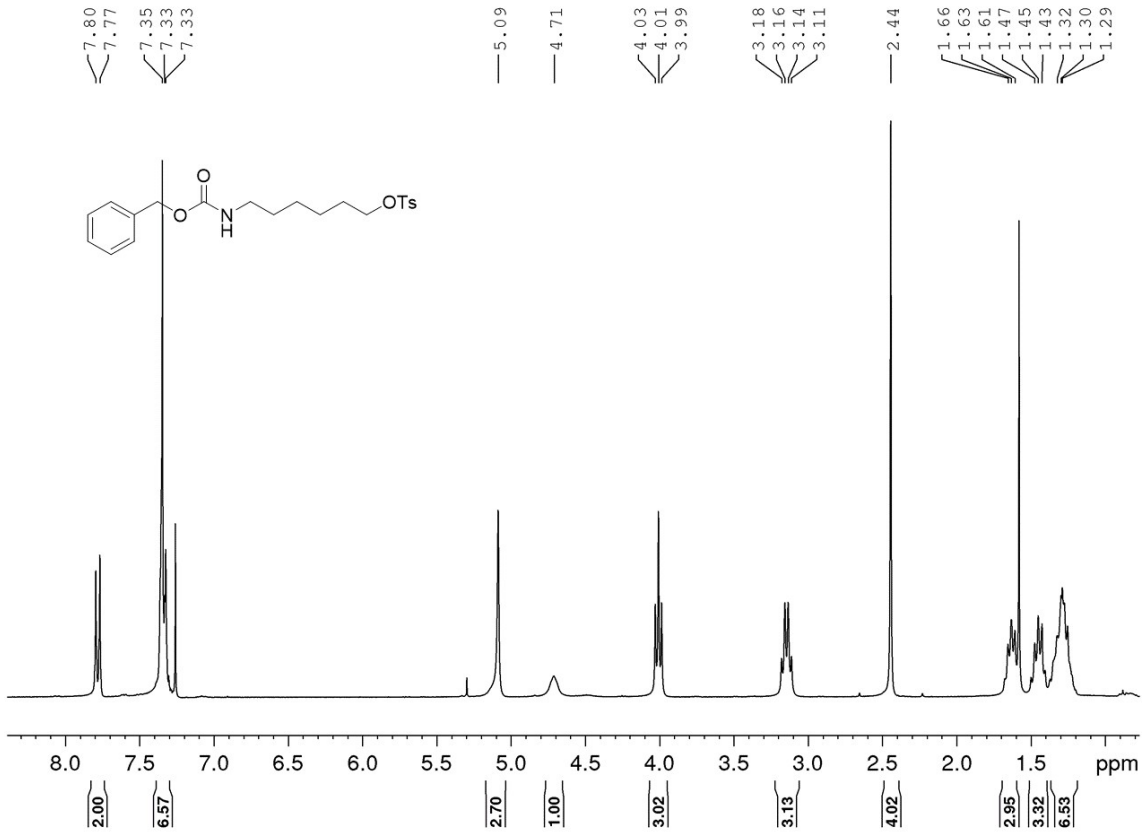
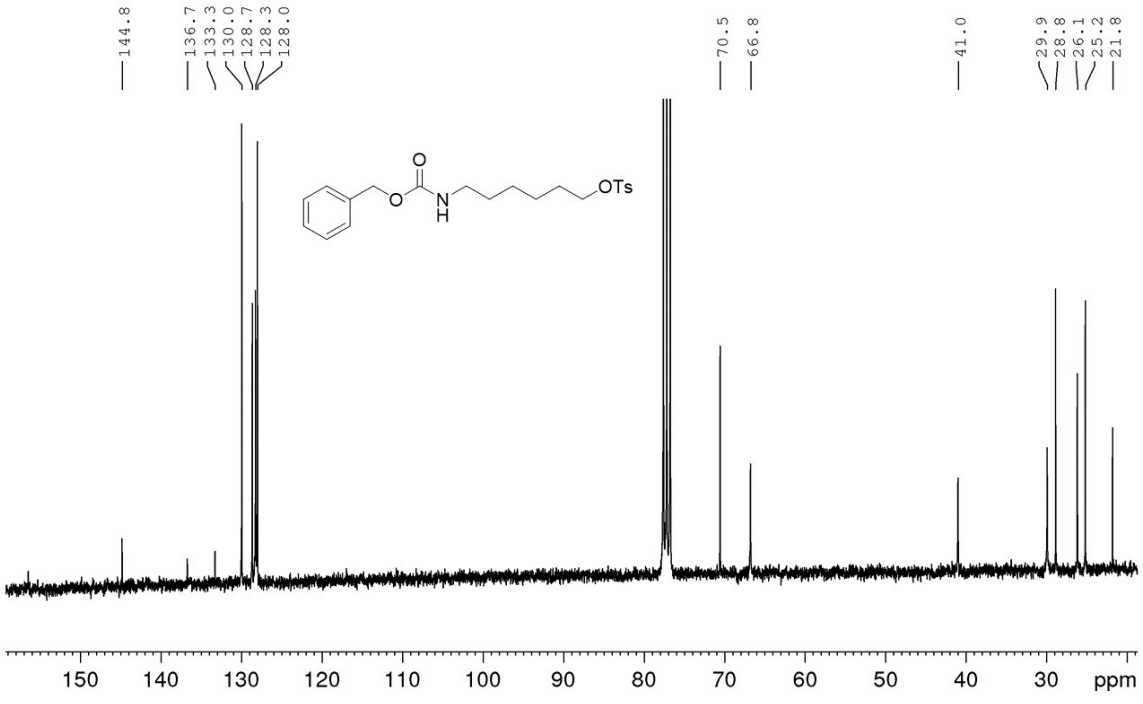
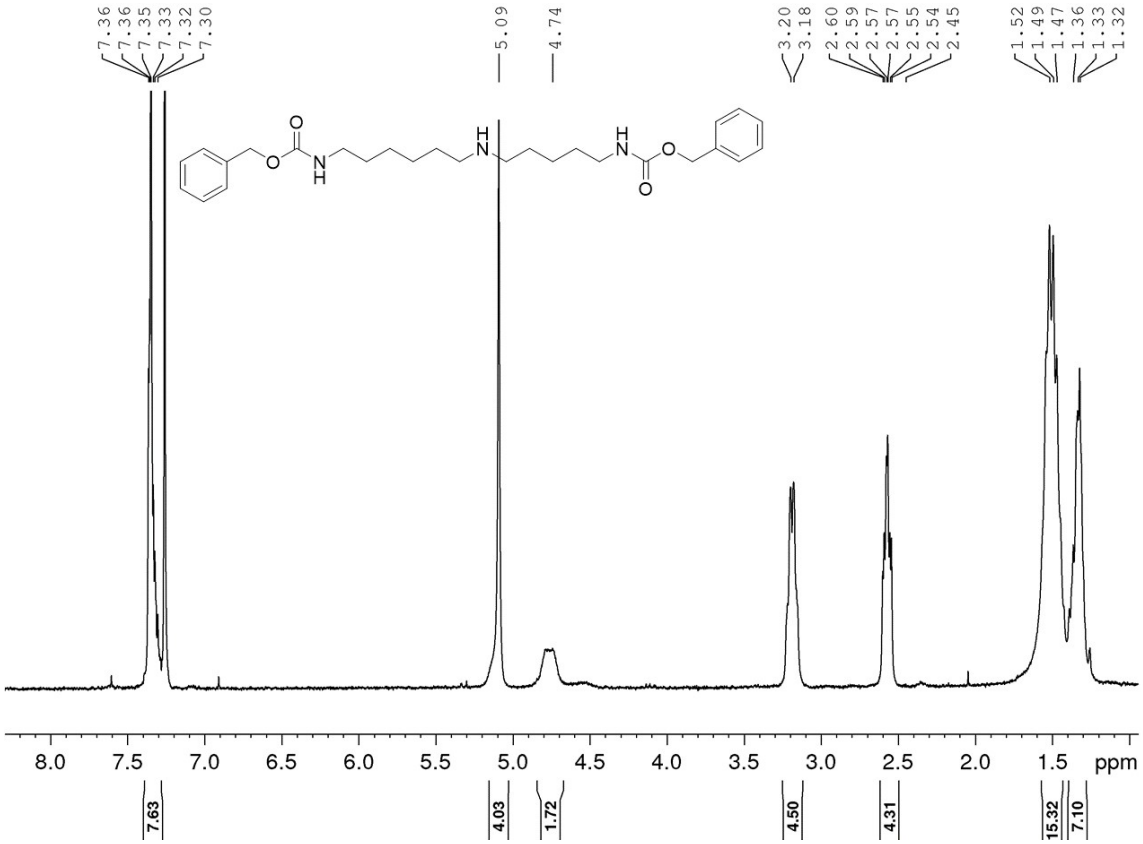
29.8
29.7
28.3
24.0
23.6
H2N
H
N
O
O
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
ppm

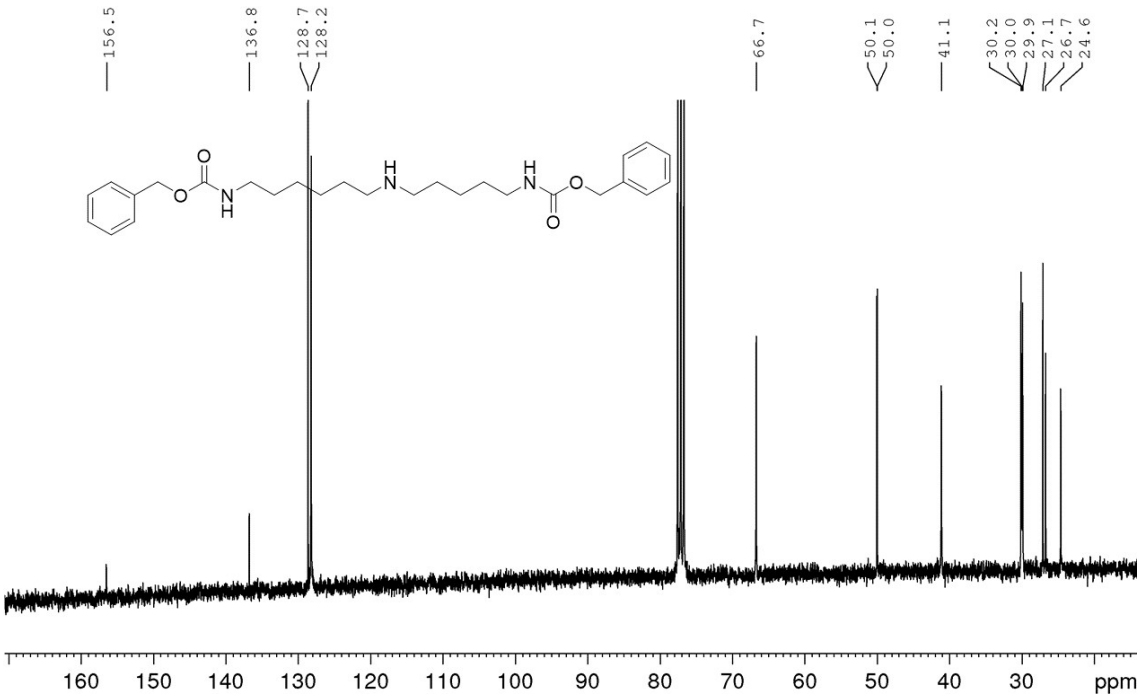
^{1}H (400 MHz, $CDCl_3$, 298 K) and ^{13}C (126 MHz, $CDCl_3$, 298 K) NMR spectra of compound **21**.



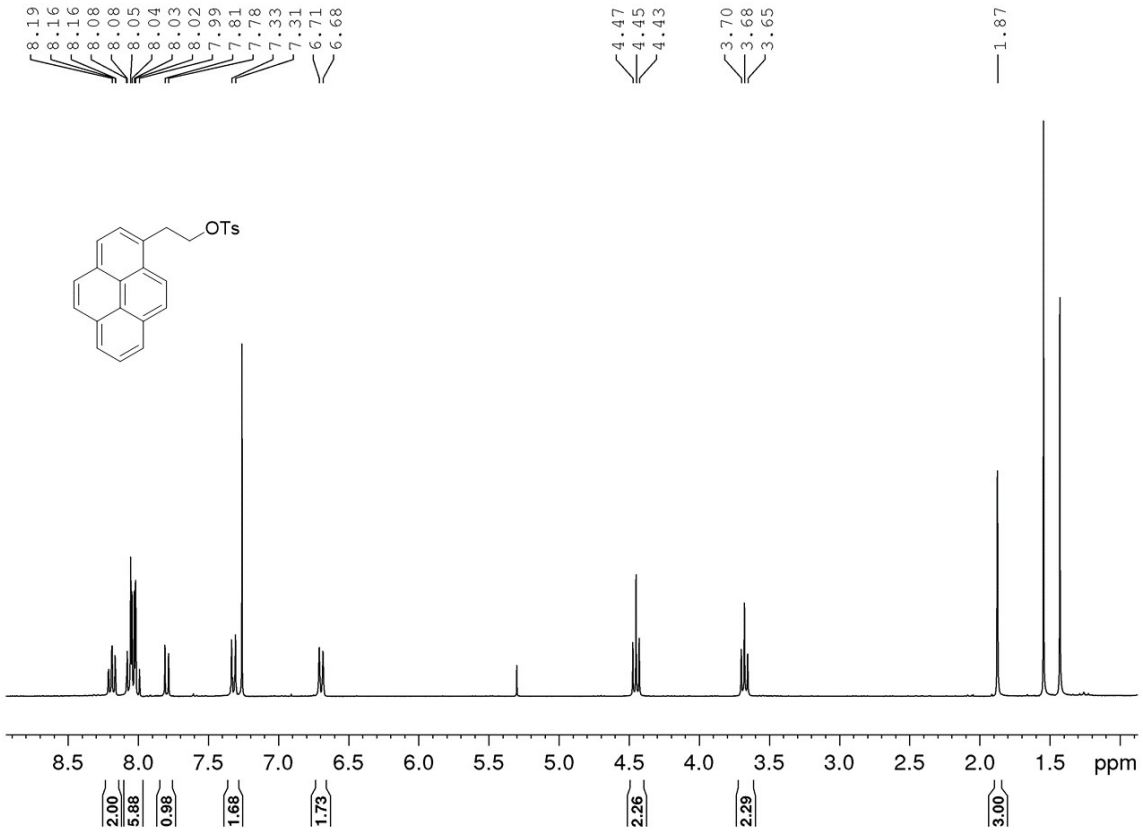


^{1}H (400 MHz, $CDCl_3$, 298 K) and ^{13}C (126 MHz, $CDCl_3$, 298 K) NMR spectra of compound **23**.

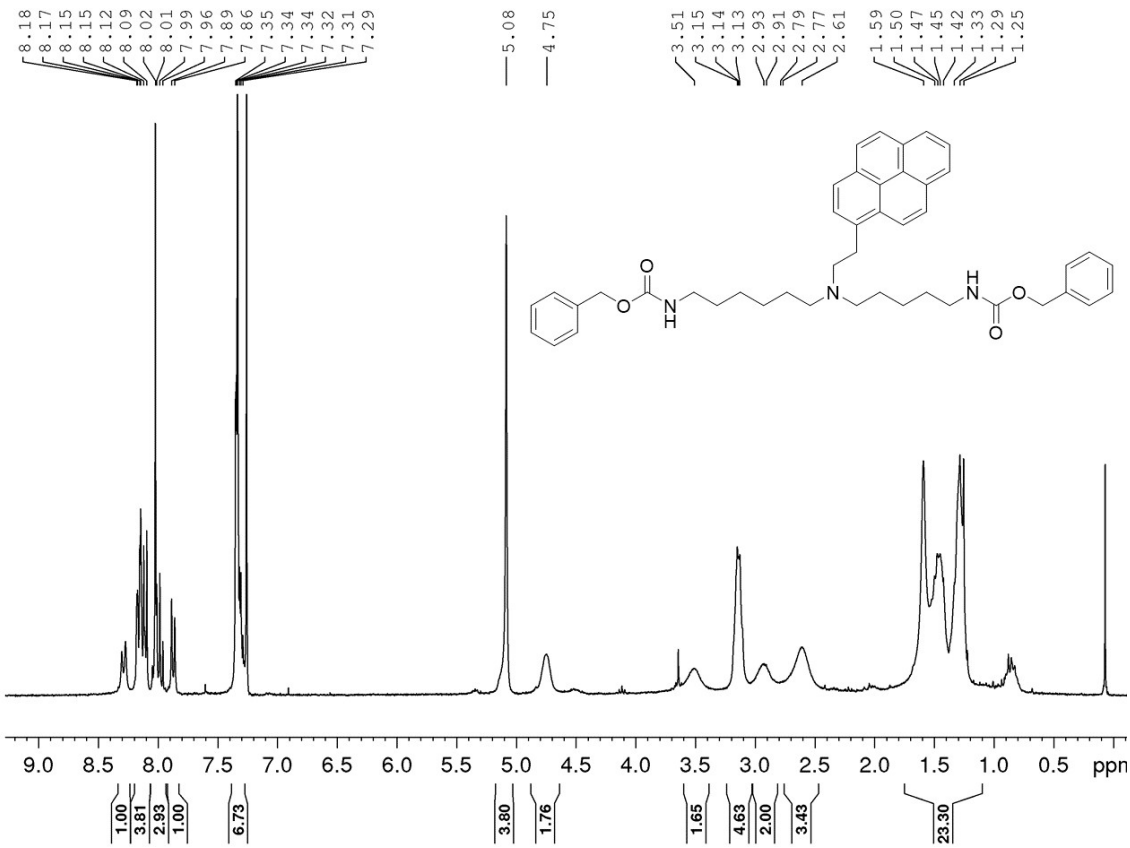




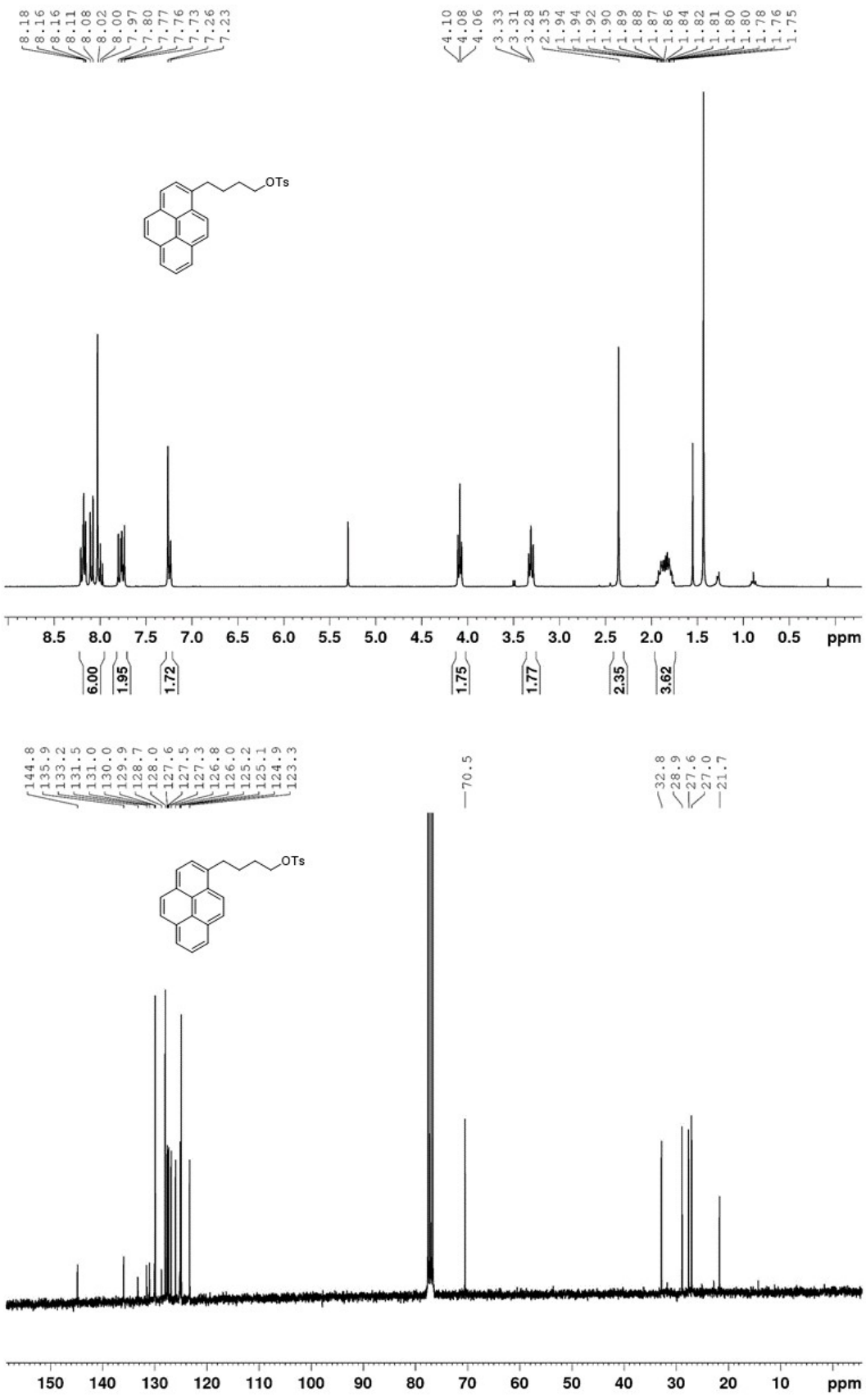
^{1}H (400 MHz, $CDCl_3$, 298 K) and ^{13}C (126 MHz, $CDCl_3$, 298 K) NMR spectra of compound **4**.



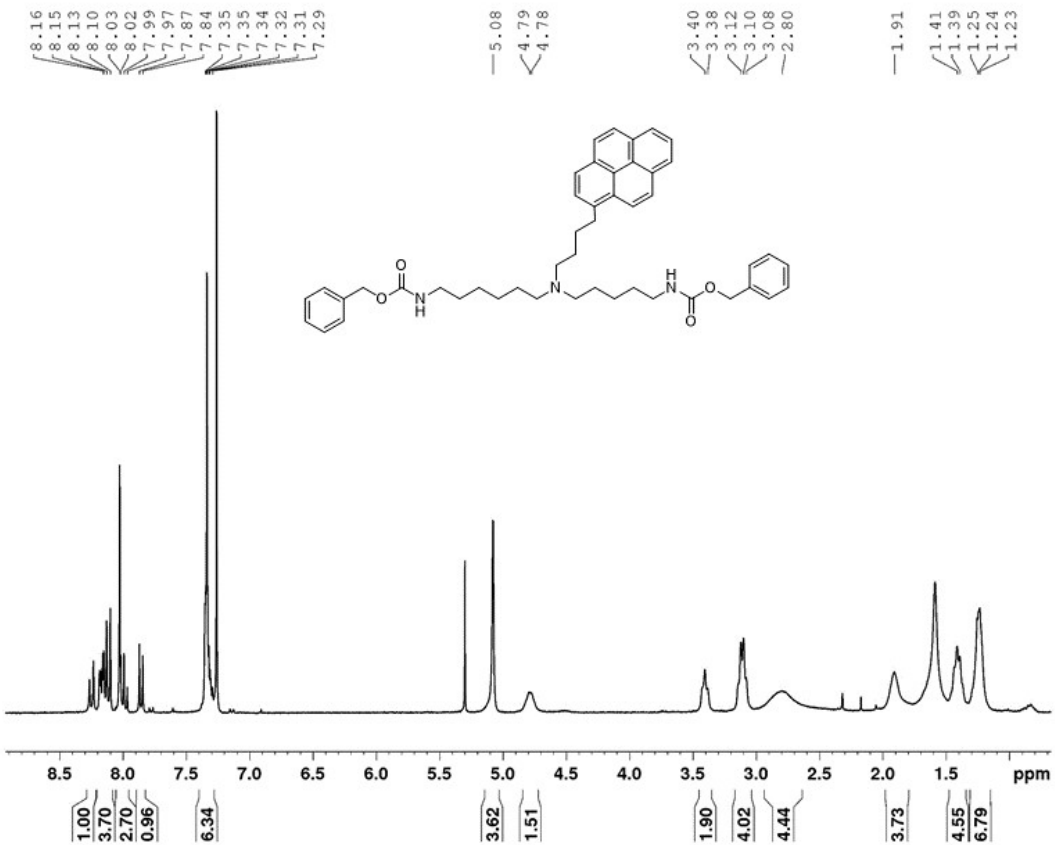
^{1}H (400 MHz, $CDCl_3$, 298 K) NMR spectrum of compound **26**.

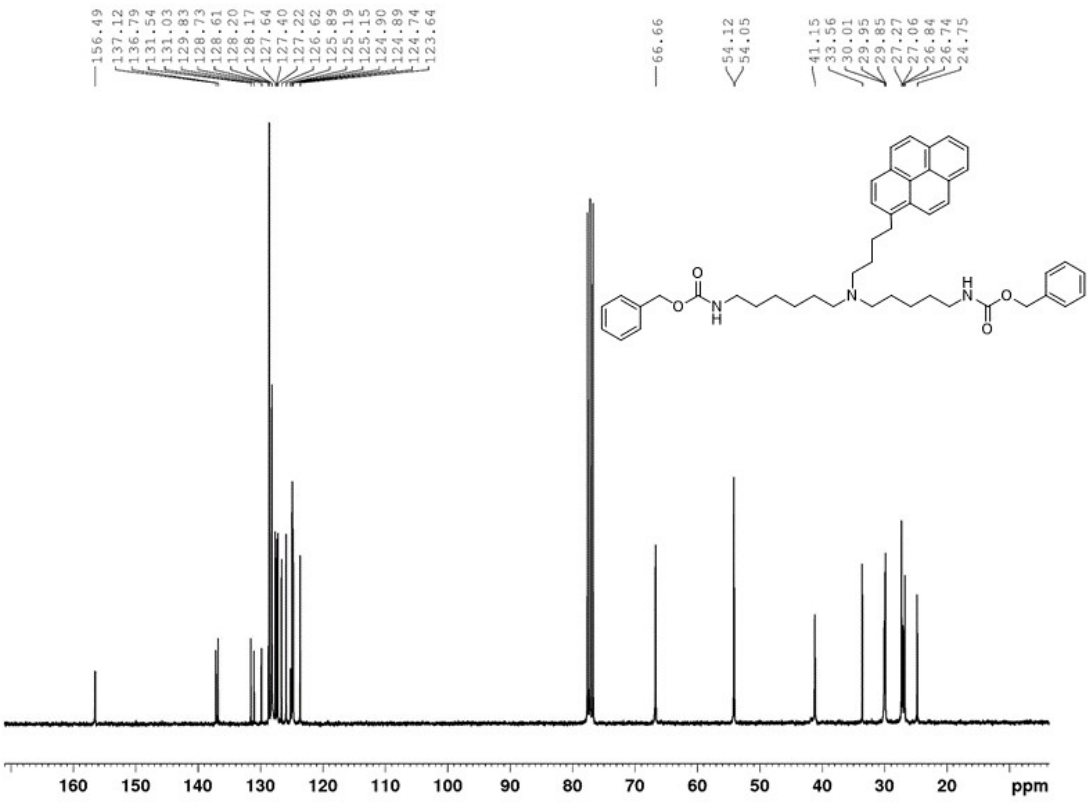


^{1}H (400 MHz, $CDCl_3$, 298 K) NMR spectrum of compound **3a**.


8.18
8.16
8.16
8.11
8.08
8.02
8.00
7.97
7.80
7.77
7.76
7.73
7.26
7.23
4.10
4.08
4.06
3.33
3.31
3.28
2.35
1.94
1.94
1.92
1.90
1.89
1.88
1.87
1.86
1.84
1.82
1.81
1.80
1.80
1.78
1.76
1.75
OTs
8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 ppm
6.00
1.95
1.72
1.75
1.77
2.35
3.62
144.8
135.9
133.2
131.5
131.0
130.0
129.9
128.7
128.0
127.6
127.5
127.3
126.8
126.0
125.2
125.1
124.9
123.3
70.5
32.8
28.9
27.6
27.0
21.7
OTs
150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 ppm

^{1}H (400 MHz, $CDCl_3$, 298 K) and ^{13}C (126 MHz, $CDCl_3$, 298 K) NMR spectra of compound **28**.





^{1}H (400 MHz, $CDCl_3$, 298 K) and ^{13}C (75 MHz, $CDCl_3$, 298 K) NMR spectra of compound **3b**.