Electronic Supporting Information

Aromatic Oligoamide Foldamers as Versatile Scaffolds for Induced Circularly Polarized Luminescence at Adjustable Wavelengths

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This PDF file includes:

1. Materials and Methods

1.1 Nuclear Magnetic Resonance and High-resolution Mass spectrometry analyses

^{1}H NMR and ^{13}C NMR analyses were performed on a Bruker Avance I 300 MHz spectrometer. Chemical shift values are given in ppm with reference to solvent residual signals.

HR-MS spectra were performed by the CESAMO (Bordeaux, France) on a Qexactive mass spectrometer (Thermo). The instrument is equipped with an ESI source and spectra were recorded in the negative/positive mode. The spray voltage was maintained at 3200 V and capillary temperature set at 320°C. Samples were introduced by injection through a 20 µL sample loop into a 300 µL/min flow of methanol from the LC pump.

1.2 Molecular modeling

Molecular Models calculation were performed 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.

1.3 Crystallography

The X-ray diffraction measurements were carried out on a Rigaku FRX rotating anode (2.9 kW) diffractometer at the IECB x-ray facility (UMS 3033 – UMS001). CuKα radiation monochromated with high flux Osmic Varimax mirrors was used for data collections. The x-ray source is equipped with a Dectris Pilatus 200K detector and partial chi goniometer.

1.4 UV-visible absorption, Fluorescence emission, Circular Dichroism (CD) and Circular Polarized Luminescence (CPL)

UV-visible absorption spectra were recorded on a UV-1650PC SHIMADZU spectrophotometer using a 1 cm pathlength quartz cuvette.

Steady-state emission spectra were recorded on a spectrofluorometer fitted with a PMT detector and exciting with a 450W Xe-lamp across a double monochromator, and were corrected for instrumental response. 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 $\Phi = \Phi_r(I/I_r)(A_r/A)(\eta^2/\eta_r^2)$ in which Φ_r refers to the quantum yield reference, I is the integrated emission intensity, A is the absorbance at the excitation wavelength and η is the refractive index of the solvent.[1] Tetramers **1** and **4** : an optically dilute solution of quinine sulphate (λ_{exc} = 370 nm) in 1N sulphuric acid was used as the standard, Φ_f = 0.54. Tetramers **2** and **3**: an optically dilute solution of Fluorescein (λ_{exc} = 440 nm) in 1M NaOH was used as the standard, Φ_f = 0.95. Luminescence

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

CD spectra were recorded on a JASCO J-815 spectropolarimeter using a 1 mm pathlength quartz cuvette.

CPL spectra were recorded on a CPL-300 spectrophotometer using a 1 cm pathlength quartz cuvette.

2. Methods for chemical synthesis

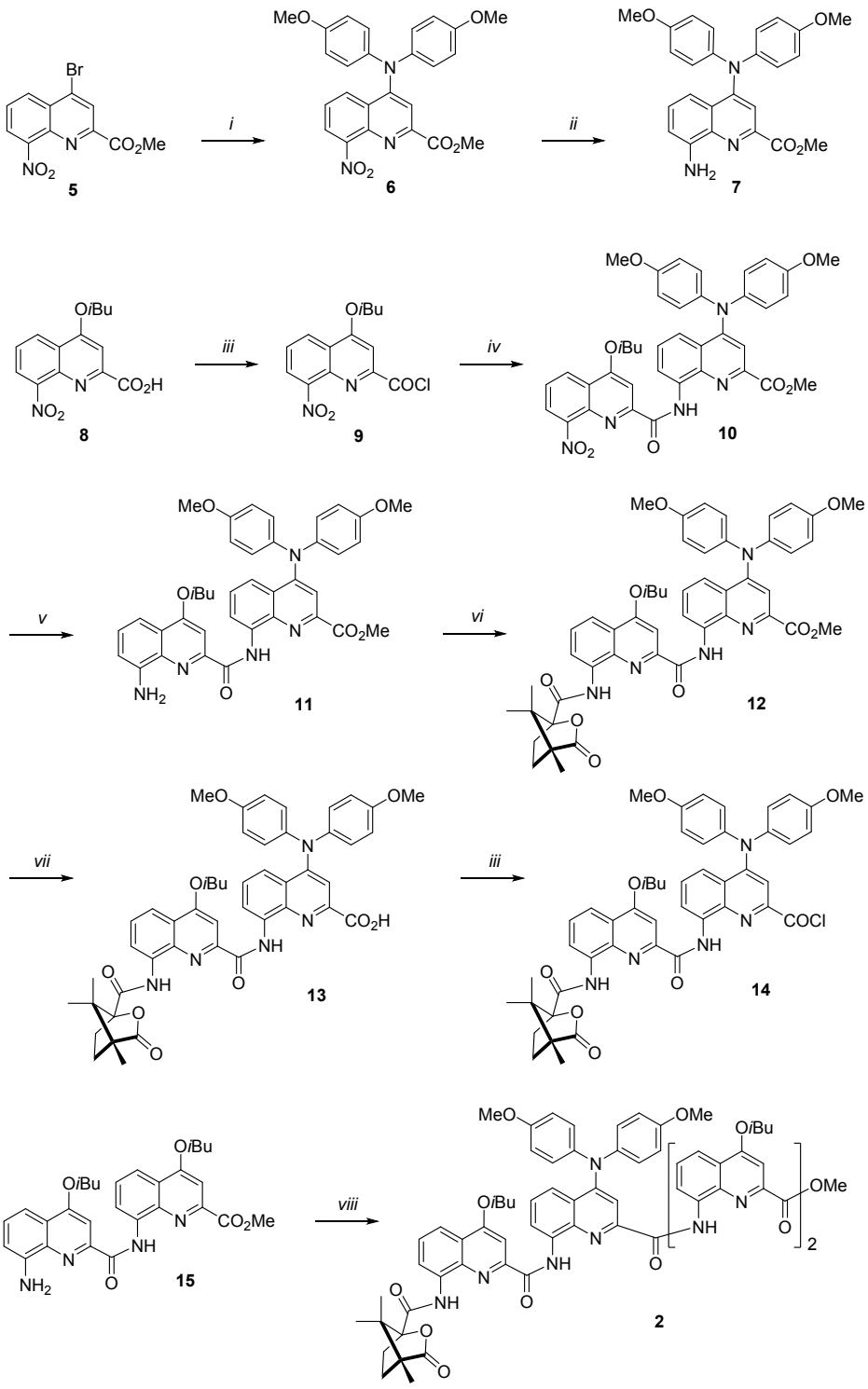
All reactions were carried out under a dry nitrogen atmosphere. Commercial reagents were purchased from Sigma-Aldrich, Alfa-Aesar or TCI and used without further purification unless otherwise specified. Chloroform ($CHCl_3$) and diisopropylethylamine (DIPEA) were dried over calcium hydride (CaH_2) and distilled prior to use. Toluene was dried over sodium and distilled prior to use.

Quinoline monomers **5** and **8**, dimer **15** and tetramer **1** were obtained as described in the literature.[2]

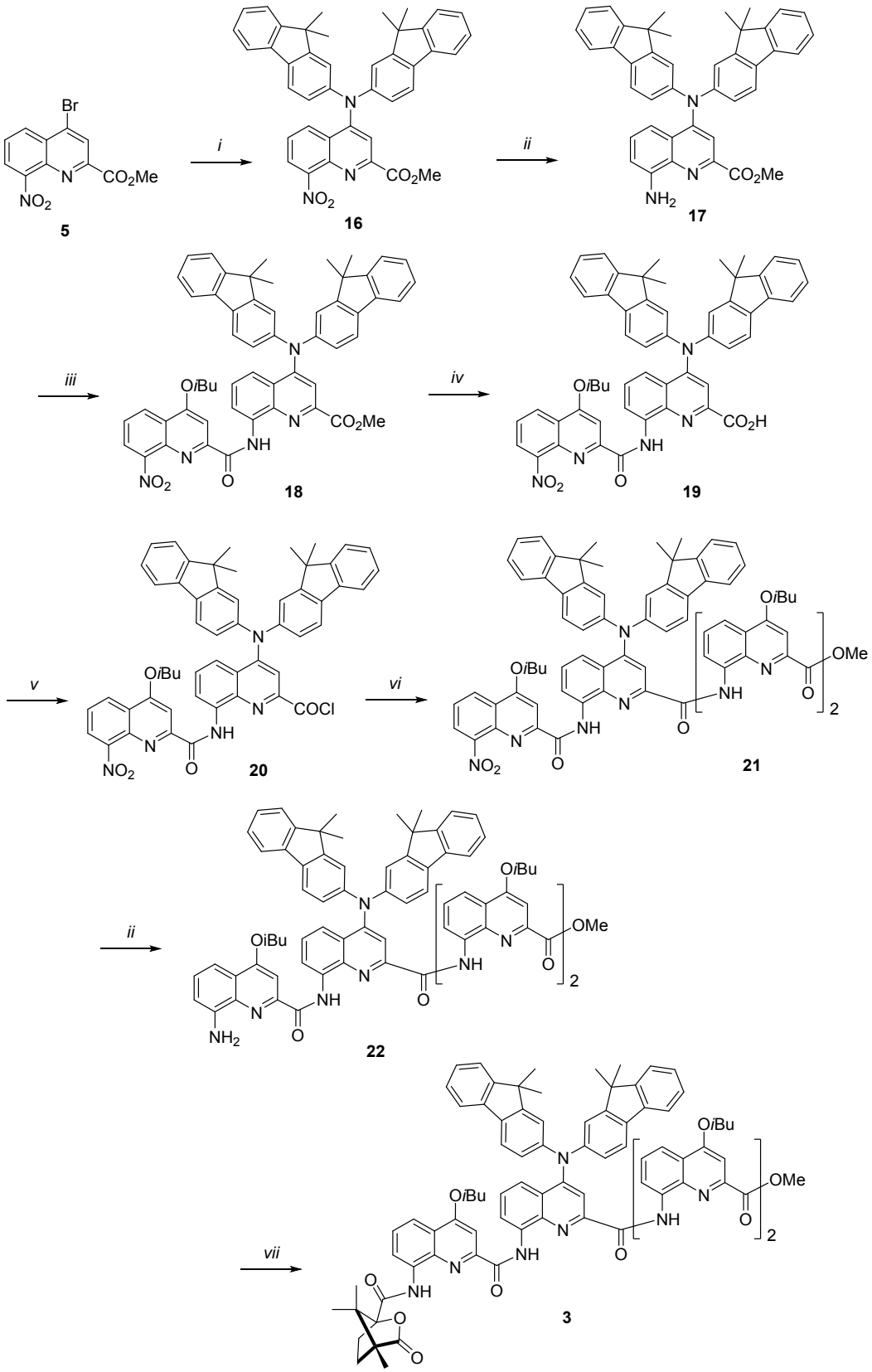
[1] Eaton, D. E. Handbook of Organic Photochemistry, Vol 1; Scaiano, J. C., Ed.; CRC : Boca Raton, FL, 1989.

[2] T. Qi, T. Deschrijver and I. Huc, *Nature Protoc.*, 2013, **8**, 693.

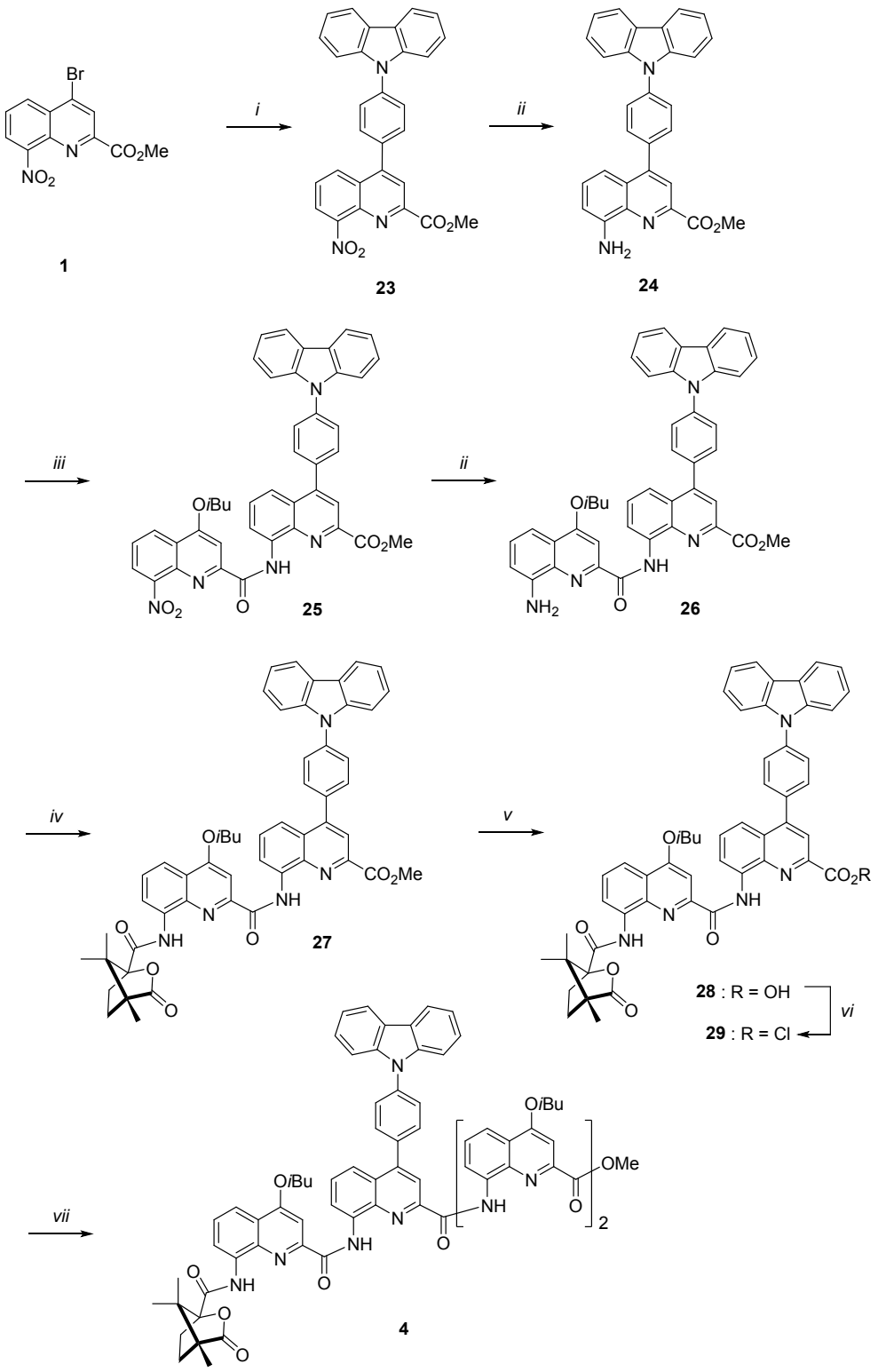
2.1 Oligomer synthesis



Scheme S1. Synthesis of **2**. *i*) *4,4'*-dimethoxydiphenylamine, $Cl_2Pd(dppf).CH_2Cl_2$, Cs_2CO_3, toluene; *ii*) H_2, Pd/C, ethyl acetate; *iii*) $(COCl)_2$, $CHCl_3$; *iv*) 7, DIPEA, $CHCl_3$; *v*) H_2, Pd/C, DMF; *vi*) (*1S*)-(−)-camphanic chloride, DIPEA, $CHCl_3$; *vii*) KOH, THF/MeOH/H_2O; *viii*) **14**, DIPEA, $CHCl_3$.

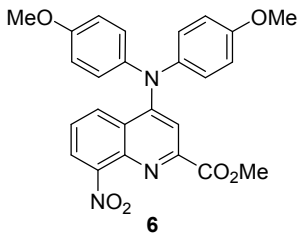


Scheme S2. Synthesis of **3**. *i*) bis(9,9-dimethyl-9H-fluoren-2-yl)amine, $Cl_2Pd(dppf).CH_2Cl_2$, Cs_2CO_3, toluene; *ii*) H_2, Pd/C, ethyl acetate; *iii*) **9**, DIPEA, $CHCl_3$; *iv*) KOH, THF/MeOH/H_2O; *v*) $(COCl)_2$, $CHCl_3$; *vi*) **15**, DIPEA, $CHCl_3$; *vii*); (*1S*)-(−)-camphanic chloride, DIPEA.



Scheme S3. Synthesis of **4**. *i*) 4-(9-carbazolyl)benzeneboronic acid pinacol ester, $Cl_2Pd(dppf).CH_2Cl_2$, K_2CO_3, toluene/dioxane/H_2O; *ii*) H_2, Pd/C, THF; *iii*) **9**, DIPEA, $CHCl_3$; *iv*) (*1S*)-(−)-camphanic chloride, DIPEA; *v*) KOH, THF/MeOH/H_2O; *vi*) $(COCl)_2$, $CHCl_3$; *vii*) **15**, DIPEA, $CHCl_3$.

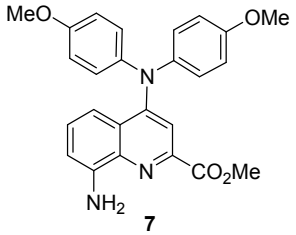
2.2 Synthetic procedures



6

Monomer 6. In a Schlenk tube under inert atmosphere were introduced bromoquinoline **5** (1.50 g, 4.8 mmol, 1 equiv.), *4,4'*-dimethoxydiphenylamine (1.65 g, 7.2 mmol, 1.5 equiv.), $Cl_2Pd(dppf).CH_2Cl_2$ (235 mg, 0.288 mmol, 6%) and Cs_2CO_3 (4.68 g, 14.4 mmol, 3 equiv.). Dry and degassed toluene (50 mL) was subsequently added and the mixture was stirred at 80°C for 20 h. The crude mixture was filtered, evaporated to dryness and the residue was purified by chromatography (silica gel) eluting with (cyclohexane/ethyl acetate 8:2, v/v) to obtain **6** as an orange powder (70 %, 1.54 g).

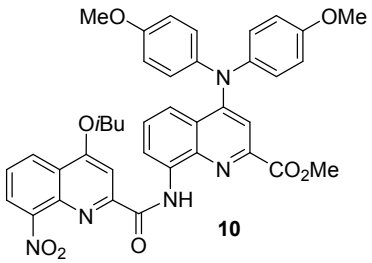
^{1}H NMR ($CDCl_3$, 300 MHz) δ 7.90 (t, 2H, $^3J_{H-H}$ = 8.5 Hz), 7.64 (s, 1H), 7.30 (dd, 1H, $^3J_{H-H}$ = 7.5 Hz), 6.96 (d, 4H, $^3J_{H-H}$ = 9.1 Hz), 6.84 (d, 4H, $^3J_{H-H}$ = 9.1 Hz), 3.95 (s, 3H), 3.80 (s, 6H). ^{13}C NMR ($CDCl_3$, 75 MHz) δ 165.7, 156.9, 154.4, 150.3, 149.3, 141.4, 140.8, 129.0, 126.1, 125.3, 124.8, 123.6, 115.9, 115.1, 55.4, 53.1. HRMS (ESI^+) m/z 460.1496 $[M+H]^+$ (calc. 460.1503 for $C_{25}H_{22}O_6N_3$)



7

Monomer 7. To a solution of **6** (500 mg, 0.33 mmol) in degassed EtOAc (25 mL), was added 10% Pd/C (10% w/w, 50 mg). The reaction mixture was stirred overnight at RT under a hydrogen atmosphere. The reaction was monitored by ^{1}H NMR until completion. The solution was filtered through celite, the solvent evaporated and the residue dried under vacuum to yield **7** as a yellow solid (420 mg, 90%).

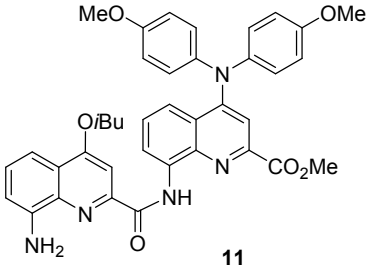
^{1}H NMR ($CDCl_3$, 300 MHz) δ 7.58 (s, 1H), 7.09 (dd, 1H, $^3J_{H-H}$ = 7.5 Hz), 6.94 (m, 5H), 6.79 (m, 5H), 5.16 (s, 2H), 3.94 (s, 3H), 3.78 (s, 6H). ^{13}C NMR ($CDCl_3$, 75 MHz) δ 166.3, 156.1, 153.7, 145.5, 145.2, 141.7, 139.7, 128.2, 125.7, 116.3, 114.7, 113.2, 109.7, 55.4, 52.6. HRMS (ESI^+) m/z 430.1752 $[M+H]^+$ (calc. 430.1761 for $C_{25}H_{24}O_4N_3$)



10

Dimer 10. Quinoline acid **8** (312 mg, 1.07 mmol, 1 equiv.) was dissolved in anhydrous $CHCl_3$ (2 mL). Oxalyl chloride (369 µL, 4.3 mmol, 4 equiv.) was added at 0°C. The reaction was allowed to stir at room temperature for 2 h. The solvent and excess reagent were removed under vacuum and the residue was dried under vacuum for 3 h to yield acid chloride **9** as a yellow solid. To a solution of amine **7** (420 mg, 0.978 mmol, 1 equiv.) and distilled DIPEA (665 µL, 3.91 mmol, 4 equiv.) in dry $CHCl_3$ (5 mL), was added dropwise at 0 °C a solution of the freshly prepared acid chloride **9** (330 mg, 0.365 mmol, 1.1 equiv.) redissolved in dry $CHCl_3$ (3 mL). The reaction was allowed to proceed overnight at RT. The volatiles were removed under reduced pressure. The residue was dissolved in CH_2Cl_2, washed with 5% NH_4Cl solution and pure water. The organic phases were dried over $MgSO_4$, filtered and the solvents were removed under reduced pressure. The residue was purified by precipitation from a dichloromethane/MeOH mixture to obtain dimer **10** as a yellow solid (454 mg, 66 %).

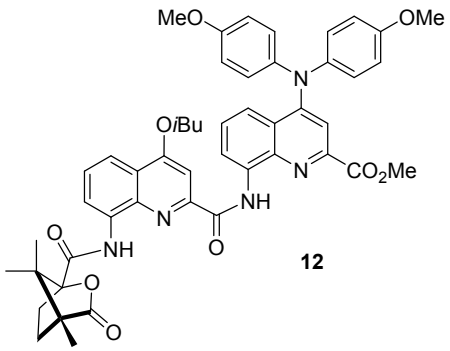
^{1}H NMR ($CDCl_3$, 300 MHz) δ 11.96 (s, 1H), 8.93 (dd, 1H, $^3J_{H\text{-}H}$ = 7.6 Hz, $^4J_{H\text{-}H}$ = 1.2 Hz), 8.53 (dd, 1H, $^3J_{H\text{-}H}$ = 8.4 Hz, $^4J_{H\text{-}H}$ = 1.4 Hz), 8.18 (dd, 1H, $^3J_{H\text{-}H}$ = 7.5 Hz, $^4J_{H\text{-}H}$ = 1.4 Hz), 7.94 (s, 1H), 7.67 (s, 1H), 7.66 (dd, 1H, $^3J_{H\text{-}H}$ = 7.6 Hz), 7.47 (dd, 1H, $^3J_{H\text{-}H}$ = 8.6 Hz, $^4J_{H\text{-}H}$ = 1.2 Hz), 7.35 (dd, 1H, $^3J_{H\text{-}H}$ = 7.7 Hz), 6.96 (d, 4H, $^3J_{H\text{-}H}$ = 9.1 Hz), 6.82 (d, 4H, $^3J_{H\text{-}H}$ = 9.1 Hz),4.18 (d, 2H, $^3J_{H\text{-}H}$ = 6.5 Hz), 4.13 (s, 3H), 3.80 (s, 6H), 2.33 (m, 1H, $^3J_{H\text{-}H}$ = 6.6 Hz), 1.16 (d, 6H, $^3J_{H\text{-}H}$ = 6.7 Hz). ^{13}C NMR ($CDCl_3$, 75 MHz) δ 166.8, 163.2, 162.4, 156.5, 154.2, 154.0, 147.9, 147.7, 141.5, 141.1, 139.4, 135.4, 127.2, 126.6, 126.0, 125.4, 124.7, 123.5, 120.1, 117.9, 116.2, 114.9, 100.2, 75.7, 55.5, 53.5, 29.7, 28.1, 19.2. HRMS (ESI$^+$) m/z 702.2548 $[M+H]^+$ (calc. 702.2558 for $C_{39}H_{36}O_8N_5$)



11

Dimer 11. To a solution of dimer **10** (454 mg, 0.650 mmol) in degassed DMF (20 mL), was added 10% Pd/C (10% w/w, 45 mg). The reaction mixture was stirred overnight at 35°C under a hydrogen atmosphere. The reaction was monitored by ^{1}H NMR until completion. The solution was filtered through celite, the solvent evaporated and the residue dried under vacuum to yield **11** as a yellow solid (310 mg, 71%).

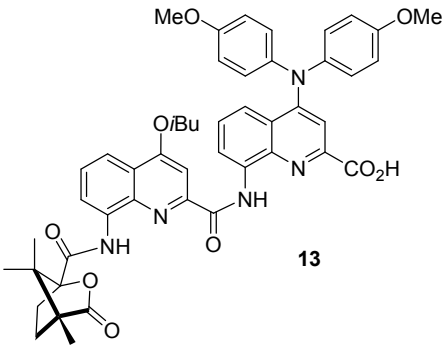
^{1}H NMR ($CDCl_3$, 300 MHz) δ 12.77 (s, 1H), 8.92 (dd, 1H, $^{3}J_{H-H}$ = 6.2 Hz, $^{4}J_{H-H}$ = 2.7 Hz), 7.75 (s, 1H), 7.61 (s, 1H), 7.54 (dd, 1H, $^{3}J_{H-H}$ = 8.3 Hz, $^{4}J_{H-H}$ = 1.2 Hz), 7.40-7.34 (m, 3H), 6.99 (d, 1H, $^{3}J_{H-H}$ = 8.3 Hz), 6.97 (d, 4H, $^{3}J_{H-H}$ = 9.0 Hz), 6.83 (d, 4H, $^{3}J_{H-H}$ = 9.0 Hz), 4.09 (d, 2H, $^{3}J_{H-H}$ = 6.5 Hz), 3.98 (s, 3H), 3.80 (s, 6H), 2.29 (m, 1H, $^{3}J_{H-H}$ = 6.6 Hz), 1.14 (d, 6H, $^{3}J_{H-H}$ = 6.7 Hz). ^{13}C NMR ($CDCl_3$, 75 MHz) δ 165.5, 163.4, 163.3, 156.4, 154.5, 148.4, 146.2, 144.9, 141.6, 141.1, 137.5, 135.9, 128.3, 128.0, 126.1, 124.8, 123.2, 119.2, 116.5, 116.1, 115.0, 110.9, 109.6, 98.4, 75.1, 55.6, 52.9, 29.8, 28.3, 19.4. HRMS (ESI^{+}) m/z 672.2806 $[M+H]^{+}$ (calc. 672.2816 for $C_{39}H_{38}O_8N_5$)



12

Dimer 12. Dimer amine **11** (150 mg, 0.223 mmol) and (*1S*)-(−)-camphanic chloride (120 mg, 0.558 mmol, 2.5 equiv.) were dissolved in dry $CHCl_3$ (1 mL) under argon. DIPEA (114 µL, 0.669 mmol, 3 equiv.) was added to the solution at 0°C and the reaction mixture was stirred at RT overnight. The volatiles were removed under reduced pressure. The residue was dissolved in CH_2Cl_2, washed with 5% NH_4Cl solution and pure water. The organic phases were dried over $MgSO_4$, filtered and the solvents were removed under reduced pressure. The residue was purified by precipitation from a CH_2Cl_2/MeOH mixture to obtain (*1S*)-(−)-camphanyl-derived dimer **12** as a light orange solid (133 mg, 70 %).

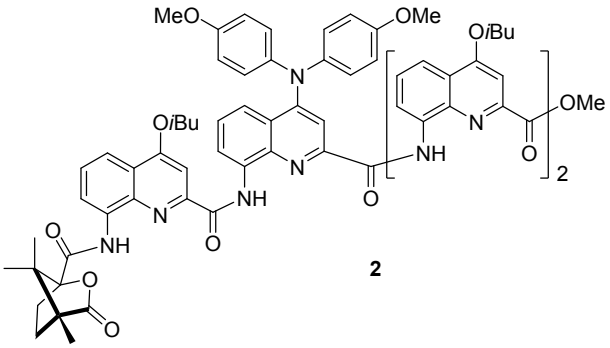
^{1}H NMR ($CDCl_3$, 300 MHz) δ 12.15 (s, 1H), 10.71 (s, 1H), 8.83 (dd, 1H, $^{3}J_{H-H}$ = 7.7 Hz, $^{4}J_{H-H}$ = 1.2 Hz), 8.76 (dd, 1H, $^{3}J_{H-H}$ = 7.4 Hz, $^{4}J_{H-H}$ = 1.3 Hz), 8.02 (dd, 1H, $^{3}J_{H-H}$ = 8.4 Hz, $^{4}J_{H-H}$ = 1.2 Hz), 7.73 (s, 1H), 7.65 (s, 1H), 7.59 (dd, 1H, $^{3}J_{H-H}$ = 8.3 Hz), 7.45 (dd, 1H, $^{3}J_{H-H}$ = 8.6 Hz, $^{4}J_{H-H}$ = 1.3 Hz), 7.36 (dd, 1H, $^{3}J_{H-H}$ = 7.4 Hz), 7.05 (d, 4H, $^{3}J_{H-H}$ = 9.0 Hz), 6.82 (d, 4H, $^{3}J_{H-H}$ = 9.0 Hz), 4.13 (d, 2H, $^{3}J_{H-H}$ = 6.5 Hz), 3.80 (s, 3H), 3.79 (s, 6H), 2.65-2.57 (m, 1H), 2.31 (m, 1H, $^{3}J_{H-H}$ = 6.6 Hz), 1.98-1.82 (m, 2H), 1.57-1.49 (m, 2H), 1.14 (d, 6H, $^{3}J_{H-H}$ = 6.7 Hz), 1.09 (s, 3H), 0.94 (s, 3H), 0.81 (s, 3H). ^{13}C NMR ($CDCl_3$, 75 MHz) δ 176.5, 166.5, 166.3, 163.8, 163.1, 156.4, 154.5, 151.4, 146.6, 141.8, 141.5, 138.7, 135.5, 133.8, 127.6, 127.5, 126.0, 125.3, 122.4, 119.8, 118.8, 118.3, 117.1, 117.0, 116.6, 114.9, 99.5, 92.2, 75.1, 55.6, 55.1, 54.3, 52.6, 30.2, 29.8, 29.2, 28.3, 19.3, 16.8, 16.6, 9.8. HRMS (ESI^{+}) m/z 852.3589 $[M+H]^{+}$ (calc. 852.3603 for $C_{49}H_{50}O_9N_5$)



13

Dimer 13. Dimer **12** (110 mg, 0.129 mmol) was dissolved in a solvent mixture of THF/MeOH/H_2O (10 mL, 3:1:1, v/v). KOH (22 mg, 0.387 mmol, 3 equiv.) was added to this mixture and the resulting slurry was vigorously stirred for 3 hours at RT. The excess of KOH was subsequently quenched by the addition of a 5% citric acid solution. After evaporation of THF under reduced pressure, the aqueous phase was extracted by CH_2Cl_2. The organic layer was then washed with water, dried over $MgSO_4$ and evaporated to dryness to obtain dimer **13** as an orange solid (100 mg, 93 %).

^{1}H NMR ($CDCl_3$, 300 MHz) δ 11.49 (s, 1H), 10.60 (s, 1H), 8.94 (dd, 1H, $^3J_{H-H}$ = 7.7 Hz, $^4J_{H-H}$ = 1.2 Hz), 8.72 (dd, 1H, $^3J_{H-H}$ = 7.6 Hz, $^4J_{H-H}$ = 1.1 Hz), 8.02 (dd, 1H, $^3J_{H-H}$ = 8.4 Hz, $^4J_{H-H}$ = 1.2 Hz), 7.79 (s, 1H), 7.68 (s, 1H), 7.61 (dd, 1H, $^3J_{H-H}$ = 8.2 Hz), 7.51 (dd, 1H, $^3J_{H-H}$ = 8.7 Hz, $^4J_{H-H}$ = 1.2 Hz), 7.37 (dd, 1H, $^3J_{H-H}$ = 7.7 Hz), 7.04 (d, 4H, $^3J_{H-H}$ = 9.0 Hz), 6.84 (d, 4H, $^3J_{H-H}$ = 9.0 Hz), 4.12 (dd, 2H, $^3J_{H-H}$ = 6.5 Hz, $^4J_{H-H}$ = 2.7 Hz), 3.81 (s, 6H), 2.61 (m, 1H), 2.36-2.27 (m, 3H), 1.91 (m, 1H), 1.62 (m, 1H), 1.16 (d, 6H, $^3J_{H-H}$ = 6.6 Hz), 1.15 (s, 3H), 0.97 (s, 3H), 0.86 (s, 3H). ^{13}C NMR ($CDCl_3$, 75 MHz) δ 176.6, 166.0, 164.6, 163.9, 162.6, 156.7, 155.8, 150.5, 145.0, 141.3, 140.1, 138.1, 134.2, 133.6, 127.8, 127.4, 126.2, 125.3, 122.3, 120.6, 118.8, 118.0, 116.8, 115.0, 113.8, 99.5, 92.7, 75.5, 55.5, 55.2, 30.3, 30.0, 29.3, 28.1, 19.2, 16.8, 16.5, 9.7. HRMS (ESI$^+$) m/z 838.3432 $[M+H]^+$ (calc. 838.3446 for $C_{48}H_{48}O_9N_5$)

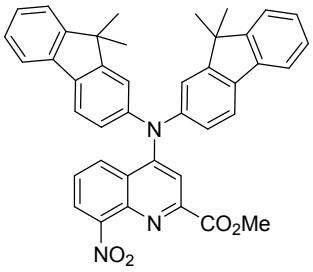


2

Tetramer 2. Dimer acid **13** (90 mg, 1.07 mmol, 1 equiv.) was dissolved in anhydrous $CHCl_3$ (1 mL). Oxalyl chloride (37 µL, 4.3 mmol, 4 equiv.) was added at 0°C. The reaction was allowed to stir at room temperature for 2 h. The solvent and excess reagent were removed under vacuum and the residue was dried under vacuum for 3 h to yield intermediate acid chloride **14** as a yellow solid. To a solution of dimer amine **15** (50.4 mg, 0.978 mmol, 1 equiv.) and distilled DIPEA (665 µL, 3.91 mmol, 4 equiv.) in dry $CHCl_3$ (1 mL) was added dropwise at 0 °C a solution of the freshly prepared acid chloride **14** (92

mg, 1.07 mmol, 1.1 equiv.) redissolved in dry $CHCl_3$ (1 mL). The reaction was allowed to proceed overnight at RT. The volatiles were removed under reduced pressure. The residue was dissolved in CH_2Cl_2, washed with 5% NH_4Cl solution and pure water. The organics were dried over $MgSO_4$, filtered and the solvents were removed under reduced pressure. The residue was purified precipitation from a dichloromethane /MeOH mixture to obtain pure (*1S*)-(−)-camphanyl-derived quinoline tetramer **2** as an orange powder (86 mg, 66 %).

^{1}H NMR ($CDCl_3$, 300 MHz) δ 12.45 (s, 1H), 11.98 (s, 1H), 11.88 (s, 1H), 10.00 (s, 1H), 8.98 (d, 1H, $^3J_{H-H}$ = 7.7 Hz), 8.61 (d, 1H, $^3J_{H-H}$ = 7.6 Hz), 8.02 (dd, 1H, $^3J_{H-H}$ = 8.4 Hz, $^4J_{H-H}$ = 1.2 Hz), 7.94 (dd, 1H, $^3J_{H-H}$ = 8.4 Hz, $^4J_{H-H}$ = 1.2 Hz), 7.92 (dd, 1H, $^3J_{H-H}$ = 8.4 Hz, $^4J_{H-H}$ = 1.2 Hz), 7.87 (dd, 1H, $^3J_{H-H}$ = 7.7 Hz, $^4J_{H-H}$ = 1.1 Hz), 7.78 (dd, 1H, $^3J_{H-H}$ = 7.6 Hz, $^4J_{H-H}$ = 1.1 Hz), 7.78 (s, 1H), 7.69 (dd, 1H, $^3J_{H-H}$ = 8.1 Hz), 7.61 (dd, 1H, $^3J_{H-H}$ = 8.1 Hz), 7.37 (s, 1H), 7.34 (dd, 1H, $^3J_{H-H}$ = 8.6 Hz, $^4J_{H-H}$ = 1.1 Hz), 7.27 (d, 4H, $^3J_{H-H}$ = 9.0 Hz), 7.21 (dd, 1H, $^3J_{H-H}$ = 8.1 Hz), 6.95 (dd, 1H, $^3J_{H-H}$ = 8.5 Hz), 6.88 (d, 4H, $^3J_{H-H}$ = 9.0 Hz), 6.80 (s, 1H), 6.79 (s, 1H), 4.42 (dd, 1H, $^3J_{H-H}$ = 6.2 Hz), 4.18 (dd, 1H, $^3J_{H-H}$ = 7.1 Hz), 3.89 (dd, 2H, $^3J_{H-H}$ = 6.1 Hz), 3.82 (m, 2H), 3.81 (s, 6H), 3.49 (s, 3H), 2.50 (m, 1H, $^3J_{H-H}$ = 6.6 Hz), 2.31-2.23 (m, 4H), 1.75 (m, 1H), 1.31-1.15 (m, 18H), 0.82 (s, 3H), 0.81 (s, 3H), 0.37 (s, 3H). ^{13}C NMR ($CDCl_3$, 75 MHz) δ 176.2, 165.1, 165.0, 164.3, 164.2, 163.7, 163.1, 162.5, 161.1, 161.0, 156.5, 155.4, 150.8, 149.6, 148.8, 145.8, 142.2, 139.5, 139.3, 138.3, 137.5, 134.7, 134.2, 134.1, 132.7, 127.8, 127.6, 126.5, 126.2, 124.7, 122.2, 122.1, 122.0, 119.4, 117.0, 116.6, 116.4, 116.3, 114.8, 114.6, 113.5, 100.5, 99.6, 98.0, 92.0, 75.6, 75.1, 55.6, 54.7, 54.3, 52.7, 29.8, 29.1, 29.0, 28.4, 28.3, 19.5, 19.4, 19.3, 16.4, 16.2, 9.8. HRMS (ESI$^+$) m/z 1336.5717 $[M+H]^+$ (calc. 1336.5719 for $C_{77}H_{78}O_{13}N_9$); 1358.5535 $[M+Na]^+$ (calc. 1358.5533 for $C_{77}H_{77}O_{13}N_9Na$).

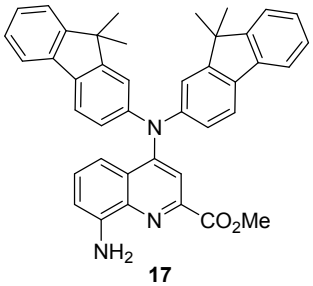


16

Monomer 16. In a Schlenk tube under inert atmosphere were introduced 4-bromoquinoline **5** (500 mg, 1.6 mmol), bis(9,9-dimethyl-9H-fluoren-2-yl)amine (1 g, 2.5 mmol, 1.5 equiv.), $Cl_2Pd(dppf).CH_2Cl_2$ (78 mg, 0.096 mmol, 6%) and Cs_2CO_3 (1.6 g, 1.8 mmol, 3 equiv.). Dry and degassed toluene (25 mL) was added subsequently and the mixture was stirred at 80°C for 20 hours. The crude mixture was filtered, evaporated to dryness and the residue was purified by chromatography (silica gel) eluting with cyclohexane/ethyl acetate (80:20, v/v) to obtain **16** as a deep orange powder (710 mg, 70 %).

^{1}H NMR ($CDCl_3$, 300 MHz) δ 7.98 (dd, 1H, $^3J_{H-H}$ = 8.7 Hz, $^4J_{H-H}$ = 1.2 Hz), 7.93 (dd, 1H, $^3J_{H-H}$ = 8.7 Hz, $^4J_{H-H}$ = 1.2 Hz), 7.92 (s, 1H), 7.68 (dd, 2H, $^3J_{H-H}$ = 8.1 Hz, $^4J_{H-H}$ = 2.0 Hz), 7.64 (d, 2H, $^3J_{H-H}$ = 8.1 Hz),

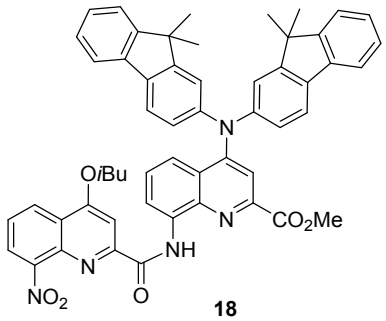
7.41-7.28 (m, 7H), 7.13 (d, 2H, $^4J_{H-H}$ = 2.0 Hz), 7.03 (dd, 2H, $^3J_{H-H}$ = 8.1 Hz, $^4J_{H-H}$ = 2.0 Hz), 3.96 (s, 3H), 1.38 (s, 12H). ^{13}C NMR ($CDCl_3$, 75 MHz) δ 165.5, 155.7, 154.2, 153.6, 150.7, 149.4, 146.8, 141.6, 138.3, 136.3, 129.06, 127.3, 127.2, 126.1, 125.3, 124.0, 123.6, 122.6, 121.2, 119.8, 118.9, 118.2, 53.2, 47.0, 26.9. HRMS (ESI$^+$) m/z 632.2537 $[M+H]^+$ (calc. 632.2543 for $C_{41}H_{34}O_4N_3$)



17

Monomer 17. To a solution of **16** (210 mg, 0.33 mmol) in degassed EtOAc (15 mL), 10% Pd/C (10% w/w, 21 mg) was added at RT. The flask was evacuated, filled with hydrogen (1 atm) and the resulting mixture was stirred overnight at RT. The reaction was monitored by ^{1}H NMR until completion. The solution was filtered through celite and washed with CH_2Cl_2. The filtrate was evaporated under reduced pressure and the residue dried under vacuum to yield **17** as a yellow solid (198 mg, 99%).

^{1}H NMR ($CDCl_3$, 300 MHz) δ 7.84 (s, 1H), 7.65 (dd, 2H, $^3J_{H-H}$ = 6.4 Hz, $^4J_{H-H}$ = 1.2 Hz), 7.59 (d, 2H, $^3J_{H-H}$ = 8.2 Hz), 7.39 (dd, 2H, $^3J_{H-H}$ = 6.4 Hz, $^4J_{H-H}$ = 1.3 Hz), 7.34-7.25 (m, 4H), 7.14 (d, 2H, $^4J_{H-H}$ = 2.0 Hz), 7.09 (d, 1H, $^3J_{H-H}$ = 7.4 Hz), 7.03-6.97 (m, 3H), 6.83 (dd, 1H, $^3J_{H-H}$ = 7.4 Hz, $^4J_{H-H}$ = 1.2 Hz), 5.23 (s, 2H), 3.95 (s, 3H), 1.37 (s, 12H). ^{13}C NMR ($CDCl_3$, 75 MHz) δ 166.1, 155.2, 153.6, 153.3, 147.4, 145.6, 145.4, 139.9, 138.8, 135.0, 128.8, 127.1, 126.8, 126.5, 123.0, 122.6, 120.8, 119.6, 118.4, 113.1, 110.1, 52.8, 46.9, 27.0. HRMS (ESI$^+$) m/z 602.2786 $[M+H]^+$ (calc. 602.2802 for $C_{41}H_{36}O_2N_3$).

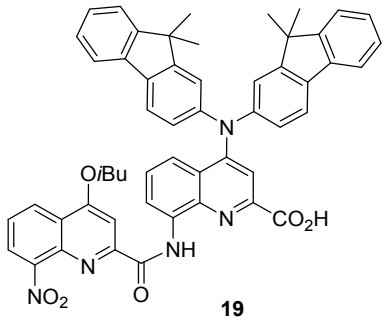


18

Dimer 18. Quinoline acid **8** (106 mg, 0.365 mmol, 1 eq.) was dissolved in anhydrous $CHCl_3$ (2 mL). Oxalyl chloride (125 µL, 1.46 mmol, 4 equiv.) was added at 0°C. The reaction was allowed to stir at room temperature for 2 h. The solvent and excess reagent were removed under vacuum and the residue was dried under vacuum for 3 h to yield acid chloride **9** as a pale yellow solid. To a solution of monomer amine **17** (200 mg, 0.332 mmol, 1 equiv.) and distilled DIPEA (226 µL, 1.32 mmol, 4 equiv.) in dry $CHCl_3$ (2 mL) was added dropwise at 0 °C a solution of the freshly prepared acid chloride **9** (112.6 mg, 0.365 mmol, 1.1 equiv.) dissolved in dry $CHCl_3$ (2 mL). The reaction was allowed to proceed overnight

at RT. The volatiles were removed under reduced pressure. The residue was dissolved in CH_2Cl_2, washed with 5% NH_4Cl solution then water. The organic phases were dried over $MgSO_4$, filtered and the solvents were removed under reduced pressure. The residue was purified by chromatography (silica gel) eluting with cyclohexane/EtOAc (75:25, v/v) to obtain the dimer **18** as a yellow solid (240 mg, 83 %).

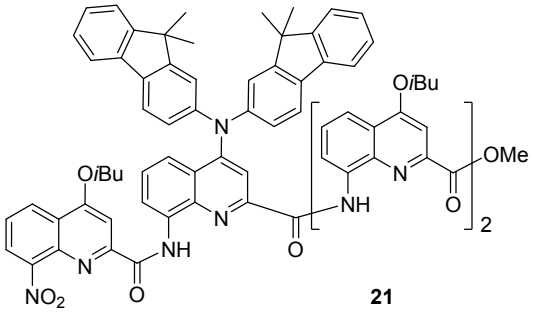
^{1}H NMR ($CDCl_3$, 300 MHz) δ 12.02 (s, 1H), 8.97 (dd, 1H, $^3J_{H-H}$ = 7.5 Hz, $^4J_{H-H}$ = 1.2 Hz), 8.54 (dd, 1H, $^3J_{H-H}$ = 8.6 Hz, $^4J_{H-H}$ = 1.4 Hz), 8.19 (dd, 1H, $^3J_{H-H}$ = 7.5 Hz, $^4J_{H-H}$ = 1.4 Hz), 7.95 (s, 1H), 7.94 (s, 1H), 7.70-7.65 (m, 3H), 7.62 (d, 2H, $^3J_{H-H}$ = 8.1 Hz), 7.52 (dd, 1H, $^3J_{H-H}$ = 8.6 Hz, $^4J_{H-H}$ = 1.2 Hz), 7.40-7.27 (m, 7H), 7.14 (d, 2H, $^4J_{H-H}$ = 2.0 Hz), 7.03 (dd, 2H, $^3J_{H-H}$ = 8.1 Hz, $^4J_{H-H}$ = 2.0 Hz), 4.18 (d, 2H, $^3J_{H-H}$ = 6.5 Hz), 4.15 (s, 3H), 2.34 (m, 1H, $^3J_{H-H}$ = 6.6 Hz), 1.38 (s, 12H), 1.17 (d, 6H, $^3J_{H-H}$ = 6.7 Hz). ^{13}C NMR ($CDCl_3$, 75 MHz) δ 166.8, 163.4, 162.7, 155.5, 154.7, 154.0, 153.8, 148.1, 147.4, 141.4, 139.6, 138.8, 135.7, 135.6, 127.9, 127.2, 127.0, 126.8, 125.6, 125.5, 123.7, 123.4, 122.7, 121.1, 120.1, 119.8, 118.8, 118.5, 118.2, 100.4, 75.5, 53.7, 47.1, 28.3, 27.1, 19.4. HRMS (ESI$^+$) m/z 874.3595 $[M+H]^+$ (calc. 874.3599 for $C_{55}H_{48}O_6N_5$)



19

Dimer 19. Dimer **18** (230 mg, 0.26 mmol, 1 equiv.) was dissolved in a solvent mixture of THF/MeOH/H_2O (10 mL, 3:1:1, v:v). KOH (44 mg, 0.78 mmol, 3 equiv.) was added to this mixture and the resulting slurry was vigorously stirred for 3 hours at RT. The excess of KOH was subsequently quenched by the addition of a 5% citric acid solution. After evaporation of THF under reduced pressure, the aqueous phase was extracted by CH_2Cl_2. Then the organic layers was washed with water, dried over $MgSO_4$ and evaporated to dryness to obtain dimer **19** as an orange solid (200 mg, 88 %).

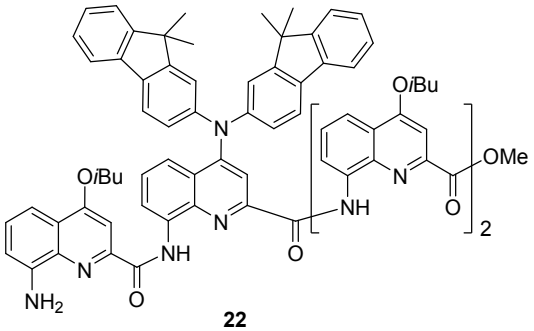
^{1}H NMR ($CDCl_3$, 300 MHz) δ 11.81 (s, 1H), 9.00 (dd, 1H, $^3J_{H-H}$ = 7.7 Hz, $^4J_{H-H}$ = 1.2 Hz), 8.56 (dd, 1H, $^3J_{H-H}$ = 8.5 Hz, $^4J_{H-H}$ = 1.4 Hz), 8.26 (dd, 1H, $^3J_{H-H}$ = 7.5 Hz, $^4J_{H-H}$ = 1.4 Hz), 8.09 (s, 1H), 7.93 (s, 1H), 7.71-7.65 (m, 3H), 7.62 (d, 2H, $^3J_{H-H}$ = 8.1 Hz), 7.57 (dd, 1H, $^3J_{H-H}$ = 8.6 Hz, $^4J_{H-H}$ = 1.2 Hz), 7.41-7.28 (m, 7H), 7.14 (d, 2H, $^4J_{H-H}$ = 2.0 Hz), 7.03 (dd, 2H, $^3J_{H-H}$ = 8.1 Hz, $^4J_{H-H}$ = 2.0 Hz), 4.18 (d, 2H, $^3J_{H-H}$ = 6.5 Hz), 2.34 (m, 1H, $^3J_{H-H}$ = 6.4 Hz), 1.38 (s, 12H), 1.17 (d, 6H, $^3J_{H-H}$ = 6.7 Hz). ^{13}C NMR ($CDCl_3$, 75 MHz) δ 164.7, 163.8, 162.4, 155.7, 155.4, 153.9, 153.7, 147.7, 147.3, 146.1, 140.4, 139.5, 138.7, 136.2, 134.9, 129.3, 128.4, 128.2, 127.4, 127.3, 127.3, 126.2, 126.0, 125.9, 123.8, 123.7, 122.8, 121.3, 120.8, 120.0, 119.2, 116.7, 100.3, 75.5, 47.2, 28.4, 27.2, 19.4. HRMS (ESI$^+$) m/z 860.3439 $[M+H]^+$ (calc. 860.3442 for $C_{54}H_{46}O_6N_5$)



21

Tetramer 21. Dimer **19** (190 mg, 0.222 mmol) was dissolved in anhydrous $CHCl_3$ (2 mL). Oxalyl chloride (76 µL, 0.888 mmol, 4 equiv.) was added at 0°C. The reaction was allowed to stir at room temperature for 2 hours. The solvent and excess reagent were removed under vacuum and the residue was dried under vacuum for 3 hours to yield the corresponding acid chloride dimer **20** as a yellow solid. To a solution of dimer amine **15** (103 mg, 0.200 mmol) and distilled DIPEA (136 µL, 0.76 mmol, 4 equiv.) in dry $CHCl_3$ (2 mL) was added dropwise at 0 °C a solution of the freshly prepared acid chloride dimer **20** (195 mg, 0.222 mmol, 1.1 equiv.) dissolved in dry $CHCl_3$ (2 mL). The reaction was allowed to proceed overnight at RT. The volatiles were removed under reduced pressure. The residue was dissolved in CH_2Cl_2, washed with 5% NH_4Cl solution then water. The organics were dried over $MgSO_4$, filtered and the solvents were removed under reduced pressure. The residue was purified by chromatography (silica gel) eluting with cyclohexane/EtOAc (85:15, v:v) to obtain tetramer **21** as a yellow solid (236 mg, 87 %).

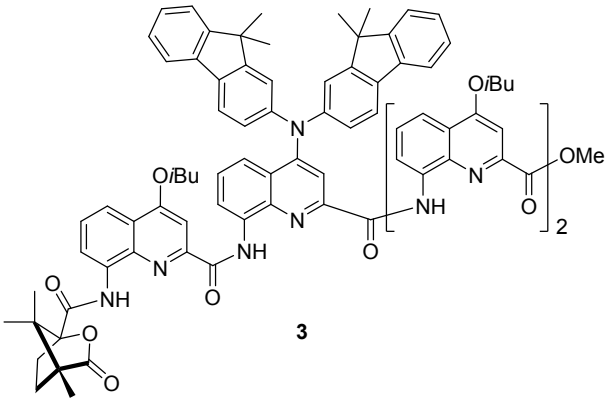
^{1}H NMR ($CDCl_3$, 300 MHz) δ 12.27 (s, 1H), 12.06 (s, 1H), 11.76 (s, 1H), 9.12 (dd, 1H, $^3J_{H-H}$ = 7.6 Hz, $^4J_{H-H}$ = 1.1 Hz), 8.58 (dd, 1H, $^3J_{H-H}$ = 8.3 Hz, $^4J_{H-H}$ = 1.4 Hz), 8.40 (dd, 1H, $^3J_{H-H}$ = 7.6 Hz, $^4J_{H-H}$ = 1.1 Hz), 8.15 (s, 1H), 8.06-7.97 (m, 3H), 7.73-7.57 (m, 7H), 7.47 (s, 1H), 7.42-7.27 (m, 12H), 6.96 (dd, 1H, $^3J_{H-H}$ = 8.3 Hz), 6.88 (s, 1H), 6.82 (s, 1H), 4.35 (m, 1H), 4.20 (m, 1H), 3.92-3.82 (m, 4H), 3.48 (s, 3H), 2.49 (m, 1H, $^3J_{H-H}$ = 6.4 Hz), 2.30 (m, 2H, $^3J_{H-H}$ = 6.4 Hz), 1.34-1.15 (m, 30H). ^{13}C NMR ($CDCl_3$, 75 MHz) δ 164.9, 163.2, 163.1, 163.0, 162.5, 161.5, 160.6, 155.3, 154.3, 153.8, 153.6, 149.9, 149.0, 147.7, 145.8, 145.2, 139.5, 139.1, 139.0, 138.7, 135.7, 135.3, 134.4, 134.0, 128.1, 127.9, 127.4, 127.0, 126.9, 126.2, 125.8, 124.5, 124.4, 124.2, 123.8, 122.5, 122.1, 122.0, 120.9, 119.8, 119.7, 119.4, 117.7, 116.9, 116.7, 115.9, 115.6, 114.3, 100.5, 100.2, 97.6, 75.8, 75.2, 75.1, 52.8, 47.0, 29.7, 28.2, 28.2, 28.1, 26.9, 19.4, 19.3. HRMS (ESI$^+$) m/z 1358.5711 $[M+H]^+$ (calc. 1358.5709 for $C_{83}H_{76}O_{10}N_9$)



22

Tetramer 22. To a solution of **21** (180 mg, 0.132 mmol) in degassed THF/MeOH (15 mL, 1:1, v:v) mixture, 20% Pd/C (10% w/w, 36 mg) was added at RT. The flask was evacuated, filled with hydrogen (1 atm) and the resulting mixture was stirred overnight at RT. The reaction was monitored by ^{1}H NMR until completion. The solution was filtered through celite and washed with CH_2Cl_2. The filtrate was evaporated under reduced pressure and the residue dried under vacuum to yield tetramer amine **22** as a yellow solid (156 mg, 89 %).

^{1}H NMR ($CDCl_3$, 300 MHz) δ 12.42 (s, 1H), 12.09 (s, 1H), 11.90 (s, 1H), 9.03 (dd, 1H, $^{3}J_{H\text{-}H}$ = 7.6 Hz, $^{4}J_{H\text{-}H}$ = 1.2 Hz), 8.46 (dd, 1H, $^{3}J_{H\text{-}H}$ = 7.6 Hz, $^{4}J_{H\text{-}H}$ = 1.1 Hz), 8.05 (s, 1H), 8.02 (d, 1H, $^{3}J_{H\text{-}H}$ = 7.2 Hz), 8.01 (dd, 1H, $^{3}J_{H\text{-}H}$ = 8.4 Hz, $^{4}J_{H\text{-}H}$ = 1.2 Hz), 7.89 (dd, 1H, $^{3}J_{H\text{-}H}$ = 7.6 Hz, $^{4}J_{H\text{-}H}$ = 1.1 Hz), 7.71-7.65 (m, 6H), 7.55 (dd, 1H, $^{3}J_{H\text{-}H}$ = 8.3 Hz, $^{4}J_{H\text{-}H}$ = 1.1 Hz), 7.42-7.27 (m, 12H), 7.05-6.92 (m, 3H), 6.82 (s, 1H), 5.96 (dd, 1H, $^{3}J_{H\text{-}H}$ = 7.5 Hz, $^{4}J_{H\text{-}H}$ = 1.1 Hz), 4.30 (m, 1H), 4.12 (m, 1H), 3.85 (m, 4H), 3.53 (s, 3H), 2.46 (m, 1H, $^{3}J_{H\text{-}H}$ = 6.4 Hz), 2.30 (m, 2H, $^{3}J_{H\text{-}H}$ = 6.4 Hz), 1.52-1.14 (m, 30H). ^{13}C NMR ($CDCl_3$, 75 MHz) δ 165.0, 163.8, 163.2, 163.1, 162.5, 161.7, 160.8, 155.4, 154.7, 153.8, 149.7, 149.6, 148.7, 147.7, 145.6, 143.2, 139.3, 139.2, 139.0, 138.7, 136.5, 136.0, 134.8, 134.5, 134.1, 127.9, 127.5, 127.1, 127.0, 126.7, 125.6, 124.5, 124.4, 123.0, 122.6, 122.0, 121.9, 121.0, 119.8, 119.2, 117.2, 116.6, 116.5, 116.4, 115.0, 113.7, 110.1, 109.7, 100.4, 99.7, 98.1, 75.3, 75.2, 75.1, 52.9, 47.0, 30.4, 29.7, 28.3, 28.3, 28.2, 27.0, 19.5, 19.3. HRMS (ESI^{+}) m/z 1328.5974 $[M+H]^{+}$ (calc. 1328.5967 for $C_{83}H_{78}O_8N_9$)

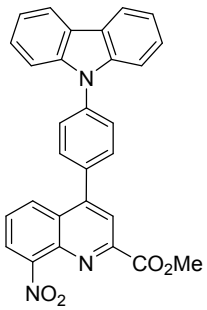


3

Tetramer 3. Tetramer amine **22** (50 mg, 0.036 mmol) and (*1S*)-(−)-camphanic chloride (35 mg, 0.09 mmol, 2.5 equiv.) were dissolved in dry $CHCl_3$ (1 mL) under argon. DIPEA (20 µL, 0.11 mmol, 3 equiv.) was added to the solution at 0°C and the reaction mixture was stirred at RT overnight. The

volatiles were removed under reduced pressure. The residue was dissolved in CH_2Cl_2, washed with 5% NH_4Cl solution and pure water. The organics were dried over $MgSO_4$, filtered and the solvents were removed under reduced pressure. The residue was purified by precipitation from a CH_2Cl_2/MeOH mixture to give pure (*1S*)-(−)-camphanyl-derived tetramer **3** as a yellow solid (32 mg, 58 %).

^{1}H NMR ($CDCl_3$, 300 MHz) δ 12.45 (s, 1H), 12.02 (s, 1H), 11.91 (s, 1H), 10.04 (s, 1H), 9.02 (dd, 1H, $^3J_{H-H}$ = 7.6 Hz, $^4J_{H-H}$ = 1.1 Hz), 8.60 (dd, 1H, $^3J_{H-H}$ = 7.6 Hz, $^4J_{H-H}$ = 1.1 Hz), 8.07 (s, 1H), 8.03 (dd, 1H, $^3J_{H-H}$ = 8.4 Hz, $^4J_{H-H}$ = 1.2 Hz), 7.96 (dd, 1H, $^3J_{H-H}$ = 8.4 Hz, $^4J_{H-H}$ = 1.1 Hz), 7.94 (dd, 1H, $^3J_{H-H}$ = 8.4 Hz, $^4J_{H-H}$ = 1.1 Hz), 7.86 (dd, 1H, $^3J_{H-H}$ = 7.6 Hz, $^4J_{H-H}$ = 1.1 Hz), 7.81 (dd, 1H, $^3J_{H-H}$ = 7.6 Hz, $^4J_{H-H}$ = 1.1 Hz), 7.71-7.58 (m, 7H), 7.41-7.19 (m, 12H), 6.94 (m, 1H), 6.82 (s, 1H), 6.81 (s, 1H), 4.42 (m, 1H), 4.17 (m, 1H), 3.92-3.78 (m, 4H), 3.52 (s, 3H), 2.51 (m, 1H, $^3J_{H-H}$ = 6.5 Hz), 2.31 (m, 4H, $^3J_{H-H}$ = 6.6 Hz), 1.52-1.13 (m, 32H), 0.86 (s, 3H), 0.82 (s, 3H), 0.39 (s, 3H). ^{13}C NMR ($CDCl_3$, 75 MHz) δ 176.2, 165.1, 165.0, 164.2, 163.7, 163.1, 162.6, 161.3, 161.0, 155.4, 154.9, 153.9, 150.7, 149.7, 148.9, 148.2, 145.9, 139.6, 139.3, 139.0, 138.4, 137.5, 135.3, 134.7, 134.2, 132.7, 127.7, 127.6, 127.1, 126.8, 126.5, 126.4, 125.4, 124.3, 122.6, 122.2, 122.1, 120.8, 119.7, 119.6, 117.1, 116.7, 116.4, 116.3, 114.9, 114.7, 100.5, 99.6, 98.1, 92.0, 75.6, 75.2, 54.8, 54.3, 53.0, 47.1, 29.8, 29.0, 28.4, 27.0, 19.5, 19.4, 19.3, 16.4, 16.3, 10.0. HRMS (ESI$^+$) m/z 1508.6752 $[M+H]^+$ (calc. 1508.6760 for $C_{93}H_{89}O_{90}N_9$); 1531.6607 $[M+Na]^+$ (calc. 1531.6606 for $C_{93}H_{89}O_{11}N_9Na$)

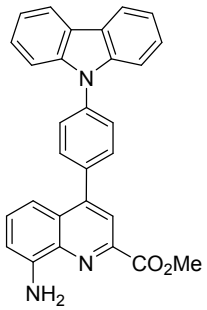


23

Monomer 23. In a Schlenk tube under inert atmosphere were introduced **5** (200 mg, 0.64 mmol), 4-(9-carbazolyl)benzeneboronic acid pinacol ester (285 mg, 0.77 mmol, 1.2 equiv.), $Cl_2Pd(dppf).CH_2Cl_2$ (52 mg, 0.064 mmol, 10%) and K_2CO_3 (178 mg, 1.28 mmol, 2 equiv.). Degassed toluene (10 mL), 1,4-dioxane (10 mL) and water (300 µL) were added subsequently and the mixture was stirred at 90°C for 20 hours. The crude mixture was filtered and the volatiles were evaporated. The residue was dissolved in CH_2Cl_2 and washed with water. The organics were dried over $MgSO_4$, filtered and the solvents were removed under reduced pressure. The residue was purified by chromatography (silica gel) eluting with CH_2Cl_2 to give **23** as a yellow powder (77 %, 233 mg).

^{1}H NMR (DMF-d7, 300 MHz) δ 8.52 (d, 2H, $^3J_{H-H}$ = 8.0 Hz), 8.36 (s, 1H), 8.35 (d, 2H, $^3J_{H-H}$ = 6.6 Hz), 8.11-8.00 (m, 5H), 7.65 (d, 2H, $^3J_{H-H}$ = 8.2 Hz), 7.54 (t, 2H, $^3J_{H-H}$ = 8.2 Hz), 7.38 (t, 2H, $^3J_{H-H}$ = 7.3 Hz), 4.06 (s, 3H). ^{13}C NMR (DMF-d7, 75 MHz) δ 166.0, 150.7, 150.5, 141.6, 140.1, 139.6, 136.5, 132.8,

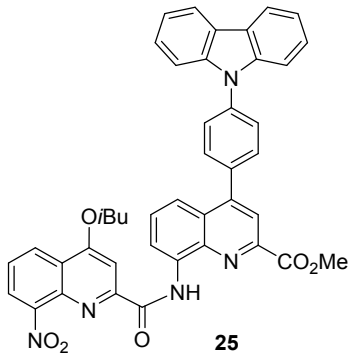
130.7, 129.5, 129.2, 128.4, 127.5, 125.2, 124.6, 123.9, 121.6, 121.5, 110.9, 53.8. HRMS (ESI^+) m/z 474.1436 $[M+H]^+$ (calc. 474.1448 for $C_{29}H_{20}O_4N_3$)



24

Monomer 24. To a solution of **23** (450 mg, 0.95 mmol) in degassed DMF (20 mL), was added 10% Pd/C (10% w/w, 45 mg). The reaction mixture was stirred overnight at 35°C under a hydrogen atmosphere. The reaction was monitored by ^1H NMR until completion. The solution was filtered through celite, the solvent evaporated and the residue dried under vacuum to yield **24** as a yellow solid (200 mg, 51%).

^1H NMR ($CDCl_3$, 300 MHz) δ 8.19 (s, 1H), 8.18 (d, 2H, $^3J_{H-H}$ = 6.5 Hz), 7.77 (m, 4H), 7.54 (d, 2H, $^3J_{H-H}$ = 8.2 Hz), 7.46 (t, 3H, $^3J_{H-H}$ = 7.2 Hz), 7.33 (m, 3H, $^3J_{H-H}$ = 6.9 Hz), 7.01 (dd, 1H, $^3J_{H-H}$ = 7.4 Hz, $^4J_{H-H}$ = 1.2 Hz), 5.30 (s, 2H), 4.08 (s, 3H). ^{13}C NMR ($CDCl_3$, 75 MHz) δ 166.1, 145.7, 144.3, 140.8, 138.3, 138.2, 137.2, 131.2, 130.2, 128.6, 127.1, 126.2, 123.7, 121.7, 120.5, 120.3, 113.4, 110.3, 109.9, 52.9. HRMS (ESI^+) m/z 444.1693 $[M+H]^+$ (calc. 444.1706 for $C_{29}H_{22}O_2N_3$)

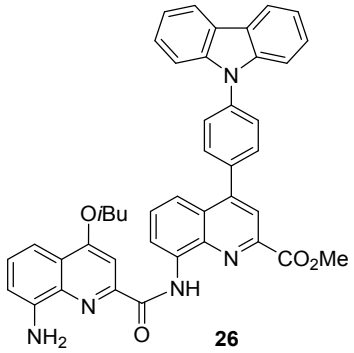


25

Dimer 25. Quinoline monomer **8** (136 mg, 0.47 mmol, 1 eq.) was dissolved in anhydrous $CHCl_3$ (2 mL). Oxalyl chloride (152 µL, 1.72 mmol, 4 equiv.) was added and the reaction was allowed to stir at room temperature for 2 hours. The solvent and excess reagent were removed under vacuum and the residue was dried under vacuum for 3 hours to yield acid chloride **9** as a pale yellow solid. To a solution of amine **24** (186 mg, 0.42 mmol) and distilled DIPEA (300 µL, 1.68 mmol, 4 equiv.) in dry $CHCl_3$ (2 mL) was added dropwise at 0 °C a solution of the freshly prepared acid chloride **9** (145 mg, 0.47 mmol, 1.2 equiv.) dissolved in dry $CHCl_3$ (2 mL). The reaction was allowed to proceed overnight at RT. The volatiles were removed under reduced pressure. The residue was dissolved in CH_2Cl_2, washed with 5%

NH_4Cl solution and pure water. The organics were dried over $MgSO_4$, filtered and the solvents were removed under reduced pressure. The residue was purified by chromatography (silica gel) eluting with cyclohexane/EtOAc (75:25, v/v) to give dimer **25** as a yellow solid (270 mg, 88 %).

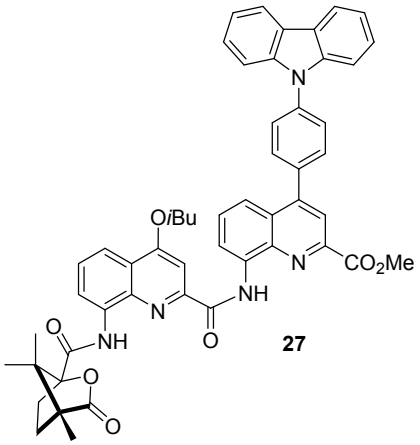
^{1}H NMR ($CDCl_3$, 300 MHz) δ 12.06 (s, 1H), 9.18 (dd, 1H, $^3J_{H-H}$ = 7.6 Hz, $^4J_{H-H}$ = 1.2 Hz), 8.56 (dd, 1H, $^3J_{H-H}$ = 7.6 Hz, $^4J_{H-H}$ = 1.4 Hz), 8.34 (s, 1H), 8.22 (dd, 1H, $^3J_{H-H}$ = 7.5 Hz, $^4J_{H-H}$ = 1.4 Hz), 8.18 (d, 2H, $^3J_{H-H}$ = 7.5 Hz), 7.98 (s, 1H), 7.89 (dd, 1H, $^3J_{H-H}$ = 8.5 Hz, $^4J_{H-H}$ = 1.3 Hz), 7.80 (m, 5H), 7.69 (dd, 1H, $^3J_{H-H}$ = 7.5 Hz), 7.57 (d, 2H, $^3J_{H-H}$ = 8.1 Hz), 7.48 (t, 2H, $^3J_{H-H}$ = 7.0 Hz), 7.34 (t, 2H, $^3J_{H-H}$ = 6.9 Hz), 4.27 (s, 3H), 4.20 (d, 2H, $^3J_{H-H}$ = 6.5 Hz), 2.36 (m, 1H, $^3J_{H-H}$ = 6.5 Hz), 1.20 (s, 3H), 1.17 (s, 3H). ^{13}C NMR ($CDCl_3$, 75 MHz) δ 166.7, 163.5, 162.8, 154.0, 149.1, 148.1, 146.8, 140.8, 139.6, 139.5, 138.5, 136.5, 135.7, 131.4, 129.5, 127.8, 127.2, 126.8, 126.2, 125.6, 123.7, 123.6, 122.3, 120.5, 120.4, 118.5, 109.9, 100.4, 75.9, 53.8, 29.8, 28.3, 19.3. HRMS (ESI$^+$) m/z 738.2302 $[M+Na]^+$ (calc. 738.2323 for $C_{43}H_{33}O_6N_5Na$)



26

Dimer 26. To a solution of **25** (150 mg, 0.2 mmol) in degassed THF (40 mL) and MeOH (2 mL), was added 10% Pd/C (15% w/w, 22 mg). The reaction mixture was stirred overnight at 35°C under a hydrogen atmosphere. The reaction was monitored by ^{1}H NMR until completion. The solution was filtered through celite, the solvent evaporated and the residue dried under vacuum to yield **26** as a yellow solid (130 mg, 90%).

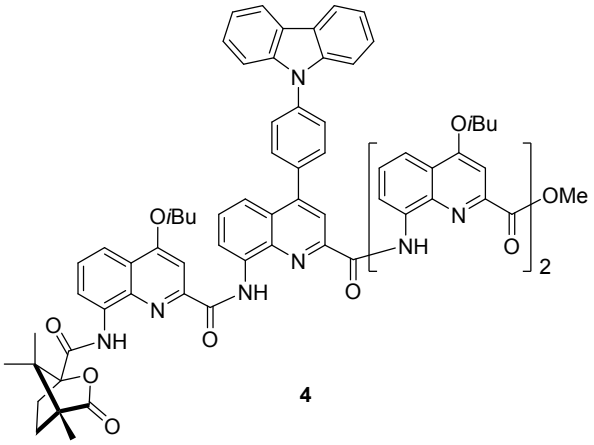
^{1}H NMR ($CDCl_3$, 300 MHz) δ 12.89 (s, 1H), 9.16 (dd, 1H, $^3J_{H-H}$ = 7.3 Hz, $^4J_{H-H}$ = 1.5 Hz), 8.29 (s, 1H), 8.19 (d, 2H, $^3J_{H-H}$ = 7.7 Hz), 7.82-7.78 (m, 8H), 7.59-7.32 (m, 11H), 7.04 (d, 1H, $^3J_{H-H}$ = 6.9 Hz), 4.15 (s, 3H), 5.63 (m, 2H), 4.13 (d, 2H, $^3J_{H-H}$ = 6.5 Hz), 2.31 (m, 1H, $^3J_{H-H}$ = 6.5 Hz), 1.18 (s, 3H), 1.16 (s, 3H). ^{13}C NMR ($CDCl_3$, 75 MHz) δ 166.2, 165.2, 163.5, 149.3, 148.6, 145.7, 144.4, 140.9, 140.8, 138.3, 138.2, 137.3, 131.4, 131.3, 130.3, 128.6, 127.3, 127.2, 126.3, 123.7, 121.8, 120.6, 120.4, 113.5, 110.4, 109.9, 75.2, 53.0, 29.9, 28.4, 19.5. HRMS (ESI$^+$) m/z 686.2745 $[M+H]^+$ (calc. 686.2761 for $C_{43}H_{36}O_4N_5$)



27

Dimer 27. Dimer amine **26** (60 mg, 0.11 mmol) and (*1S*)-(−)-camphanyl chloride (60 mg, 0.28 mmol, 2.5 equiv.) were dissolved in dry $CHCl_3$ (1 mL) under argon. DIPEA (45 µL, 0.33 mmol, 3 equiv.) was added to the solution and the reaction mixture was stirred at RT overnight. The volatiles were removed under reduced pressure. The residue was dissolved in CH_2Cl_2, washed with 5% NH_4Cl solution and pure water. The organic phases were dried over $MgSO_4$, filtered and the solvents were removed under reduced pressure. The residue was purified by precipitation from a CH_2Cl_2/MeOH mixture to give (*1S*)-(−)-camphanyl-derived dimer **27** as a light yellow solid (23 mg, 30 %).

^{1}H NMR ($CDCl_3$, 300 MHz) δ 12.23 (s, 1H), 10.69 (s, 1H), 8.91 (dd, 1H, $^3J_{H-H}$ = 7.6 Hz, $^4J_{H-H}$ = 1.2 Hz), 8.87 (dd, 1H, $^3J_{H-H}$ = 7.7 Hz, $^4J_{H-H}$ = 1.2 Hz), 8.28 (s, 1H), 8.19 (d, 2H, $^3J_{H-H}$ = 7.6 Hz), 8.06 (dd, 1H, $^3J_{H-H}$ = 8.4 Hz, $^4J_{H-H}$ = 1.2 Hz), 7.90-7.86 (m, 3H), 7.80-7.73 (m, 4H), 7.63 (t, 1H, 8.2), 7.57 (d, 2H, $^3J_{H-H}$ = 8.1 Hz), 7.48 (t, 2H, $^3J_{H-H}$ = 8.2 Hz), 7.34 (t, 2H, $^3J_{H-H}$ = 7.9 Hz), 4.15 (d, 2H, $^3J_{H-H}$ = 6.5 Hz), 3.94 (s, 3H), 2.66 (m, 1H), 2.33 (m, 1H, $^3J_{H-H}$ = 6.6 Hz), 2.05 (m, 1H), 1.90 (m, 1H), 1.18 (s, 3H), 1.15 (s, 3H), 1.11 (s, 3H), 0.93 (s, 3H), 0.86 (s, 3H). ^{13}C NMR ($CDCl_3$, 75 MHz) δ 176.9, 166.3, 166.0, 163.8, 163.4, 151.3, 149.0, 145.9, 140.8, 139.8, 138.9, 138.4, 136.7, 135.6, 133.8, 131.5, 129.6, 127.8, 127.6, 127.0, 126.2, 123.7, 122.5, 122.1, 120.5, 120.4, 120.2, 118,8, 117,8, 117.2, 109.9, 99.6, 92.3, 75.6, 55.2, 54.4, 52.8, 30.3, 29.8, 28.3, 28.0, 19.3, 16.8, 16.7, 9.8. HRMS (ESI$^+$) m/z 888.3344 $[M+Na]^+$ (calc. 888.3367 for $C_{25}H_{24}O_4N_3Na$)



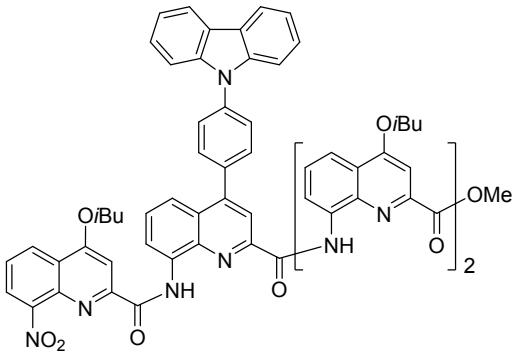
4

Tetramer 4. Dimer **27** (23 mg, 0.026 mmol, 1 equiv.) was dissolved in a mixture of THF/MeOH/H_2O (5 mL, 3:1:1, v:v). KOH (4.4 mg, 0.078 mmol, 3 equiv.) was added to this mixture and the resulting slurry was vigorously stirred for 3 hours at RT. The excess of KOH was subsequently quenched by the addition of a 5% citric acid solution. After evaporation of THF under reduced pressure, the aqueous phase was extracted by CH_2Cl_2. Then the organic layers was washed with water, dried over $MgSO_4$ and evaporated to dryness to obtain dimer acid **28** ready to be used in the subsequent coupling reaction. Dimer acid **28** (22 mg, 0.021 mmol, 1 equiv.) was then dissolved in anhydrous $CHCl_3$ (0.5 mL). Oxalyl chloride (10 µL, 0.1 mmol, 5 equiv.) was added and the reaction was allowed to stir at room temperature for 2 h. The solvent and excess reagent were removed under vacuum and the residue was dried under vacuum for 3 h to yield intermediate acid chloride **29** as a yellow solid. To a solution of dimer amine **15** (16 mg, 0.031 mmol, 1 equiv.) and distilled DIPEA (11 µL, 3.91 mmol, 3 equiv.) in dry $CHCl_3$ (0.25 mL) was added dropwise at 0 °C a solution of the freshly prepared acid chloride **29** (18.4 mg, 0.032 mmol, 1.1 equiv.) dissolved in dry $CHCl_3$ (0.25 mL). The reaction was allowed to proceed overnight at RT. The volatiles were removed under reduced pressure. The residue was dissolved in CH_2Cl_2, washed with 5% NH_4Cl solution and pure water. The organics were dried over $MgSO_4$, filtered and the solvents were removed under reduced pressure. The residue was purified by precipitation from a dichloromethane/MeOH mixture to give pure (*1S*)-(−)-camphanyl-derived tetramer **4** as a pale yellow powder (16 mg, 60 %).

^{1}H NMR ($CDCl_3$, 300 MHz) δ 12.51 (s, 1H), 11.98 (s, 1H), 11.93 (s, 1H), 9.97 (s, 1H), 9.11 (dd, 1H, $^3J_{H\text{-}H}$ = 7.6 Hz, $^4J_{H\text{-}H}$ = 1.1 Hz), 8.63 (dd, 1H, $^3J_{H\text{-}H}$ = 7.6 Hz, $^4J_{H\text{-}H}$ = 1.1 Hz), 8.42 (s, 1H), 8.22 (d, 2H, $^3J_{H\text{-}H}$ = 7.6 Hz), 8.08-7.93 (m, 8H), 7.88 (d, 2H, $^3J_{H\text{-}H}$ = 8.4 Hz), 7.77-7.64 (m, 6H), 7.54-7.49 (m, 2H), 7.45 (s, 1H), 7.39-7.34 (m, 3H), 7.27 (m, 1H, $^3J_{H\text{-}H}$ = 8.1 Hz), 6.83 (s, 1H), 6.74 (s, 1H), 4.45 (m, 1H), 4.20 (m, 1H), 3.92 (d, 2H, $^3J_{H\text{-}H}$ = 6.2 Hz), 3.97 (d, 2H, $^3J_{H\text{-}H}$ = 6.3 Hz), 3.59 (s, 3H), 2.53 (m, 1H), 2.36-2.29 (m, 4H), 1.80 (m, 1H), 1.68 (m, 1H), 1.33-1.18 (m, 18H), 0.82 (s, 3H), 0.79 (s, 3H), 0.40 (s, 3H).

^{13}C NMR ($CDCl_3$, 75 MHz) δ 176.6, 164.9, 164.6, 164.0, 163.7, 163.2, 162.5, 161.5, 161.0, 150.7, 149.8, 149.1, 149.0, 145.6, 140.9, 139.2, 138.4, 138.3, 137.8, 137.6, 137.1, 134.6, 134.3, 134.2, 132.7, 131.6, 128.3, 127.8, 127.6, 127.5, 127.1, 126.6, 126.2, 123.7, 122.3, 122.1, 122.0, 120.5, 120.3, 119.7,

119.4, 117.2, 116.8, 116.7, 116.6, 115.5, 110.0, 100.5, 99.8, 98.2, 92.1, 75.6, 75.3, 75.2, 54.9, 54.4, 52.8, 30.3, 29.8, 29.3, 28.9, 28.4, 28.3, 27.0, 19.6, 19.6, 19.5, 19.5, 19.5, 19.4, 19.4, 16.4, 16.3, 9.8. HRMS (ESI$^+$) m/z 1350.5653 $[M+H]^+$ (calc. 1350.5658 for $C_{81}H_{76}N_9O_{11}$)



Tetramer 30 (prepared for the purpose of growing single crystals). Dimer **25** (350 mg, 0.49 mmol, 1 equiv.) was dissolved in a mixture of THF (9 mL) and MeOH (3 mL). NaOH (59 mg, 1.47 mmol, 3 equiv.) was added to this mixture and the resulting slurry was vigorously stirred for 12 hours at RT. The excess of NaOH was subsequently quenched by the addition of a 5% citric acid solution. After evaporation of THF under reduced pressure, the aqueous phase was extracted by CH_2Cl_2. Then the organic layers was washed with water, dried over $MgSO_4$ and evaporated to dryness to obtain in a quantitative yield the corresponding dimer acid $Q^{O\mathit{i}Bu}Q^{Cz}COOH$ ready to use in subsequent coupling reaction. Dimer acid $Q^{O\mathit{i}Bu}Q^{Cz}COOH$ (160 mg, 0.228 mmol, 1 equiv.) was then dissolved in anhydrous $CHCl_3$ (3 mL). Oxalyl chloride (100 µL, 1.14 mmol, 5 equiv.) was added and the reaction was allowed to stir at room temperature for 4 h. The solvent and excess reagent were removed under vacuum and the residue was dried under vacuum for 3 h to yield intermediate acid chloride $Q^{O\mathit{i}Bu}Q^{Cz}COCl$ as a yellow solid. To a solution of dimer amine **15** (107 mg, 0.207 mmol, 1 equiv.) and distilled DIPEA (200 µL, 1.14 mmol, 5 equiv.) in dry $CHCl_3$ (3 mL) was added dropwise at 0 °C a solution of the freshly prepared acid chloride $Q^{O\mathit{i}Bu}Q^{Cz}COCl$ (164 mg, 0.228 mmol, 1.1 equiv.) dissolved in dry $CHCl_3$ (7 mL). The reaction was allowed to proceed 48H at RT. The volatiles were removed under reduced pressure. The residue was dissolved in CH_2Cl_2, washed with 5% NH_4Cl solution and pure water. The organics were dried over $MgSO_4$, filtered and the solvents were removed under reduced pressure. The residue was purified by precipitation from a dichloromethane/MeOH mixture to give pure tetramer **30** as pale yellow powder (183 mg, 73 %).

^{1}H NMR (300 MHz, $CDCl_3$) δ 12.34 (s, 1H), 11.94 (s, 1H), 11.86 (s, 1H), 9.19 (d, 1H, $^3J_{H\text{-}H}$ = 7.6 Hz), 8.58 (dd, 1H, $^3J_{H\text{-}H}$ = 6.6 Hz, $^4J_{H\text{-}H}$ = 1.4 Hz), 8.57 (s, 1H), 8.45 (dd, 1H, $^3J_{H\text{-}H}$ = 7.6 Hz, $^4J_{H\text{-}H}$ = 1.2 Hz), 8.23 (dd, 1H, $^3J_{H\text{-}H}$ = 8.1 Hz, $^4J_{H\text{-}H}$ = 1.0 Hz), 8.20 (d, 2H, $^3J_{H\text{-}H}$ = 7.7 Hz), 8.06 (dd, 1H, $^3J_{H\text{-}H}$ = 8.4 Hz, $^4J_{H\text{-}H}$ = 1.2 Hz), 8.02 (dd, 1H, $^3J_{H\text{-}H}$ = 8.4 Hz, $^4J_{H\text{-}H}$ = 1.2 Hz), 7.97 (d, 2H, $^3J_{H\text{-}H}$ = 8.3 Hz), 7.86 (d, 2H, $^3J_{H\text{-}H}$ = 8.3 Hz), 7.80–7.73 (m, 2H), 7.67–7.59 (m, 4H), 7.53–7.48 (m, 3H), 7.42–7.33 (m, 4H), 6. 89 (s, 1H), 6.73 (s, 1H), 4.30 (s, 2H), 3.90 (d, 2H, $^3J_{H\text{-}H}$ = 6.3 Hz), 3.86 (d, 2H, $^3J_{H\text{-}H}$ = 6.3 Hz), 3.53 (s, 3H),

2.50 (m, 1H), 2.31 (m, 2H), 1.31 (d, 6H, $^{3}J_{H-H}$ = 6.7 Hz), 1.21 (m, 12H). ^{13}C NMR (76 MHz, $CDCl_3$) δ 164.5, 163.2, 163.1, 162.8, 162.4, 161.6, 160.8, 153.4, 149.9, 149.0, 149.0, 145.6, 145.1, 140.7, 139.1, 139.0, 138.3, 137.7, 136.7, 135.1, 134.4, 134.1, 131.2, 128.3, 128.1, 128.0, 127.6, 127.5, 127.1, 126.1, 126.0, 124.3, 123.8, 123.6, 122.1, 122.0, 120.4, 120.2, 119.9, 119.5, 117.8, 117.1, 116.8, 116.2, 116.1, 109.9, 100.4, 100.2, 97.6, 75.8, 75.2, 75.1, 52.7, 28.2, 28.1, 19.4, 19.3, 19.3. HRMS (ESI^+) m/z 1222.4437 $[M+Na]^+$ (calc. 1222.4433 for $C_{71}H_{61}O_{10}N_9Na$)

3. Solution studies

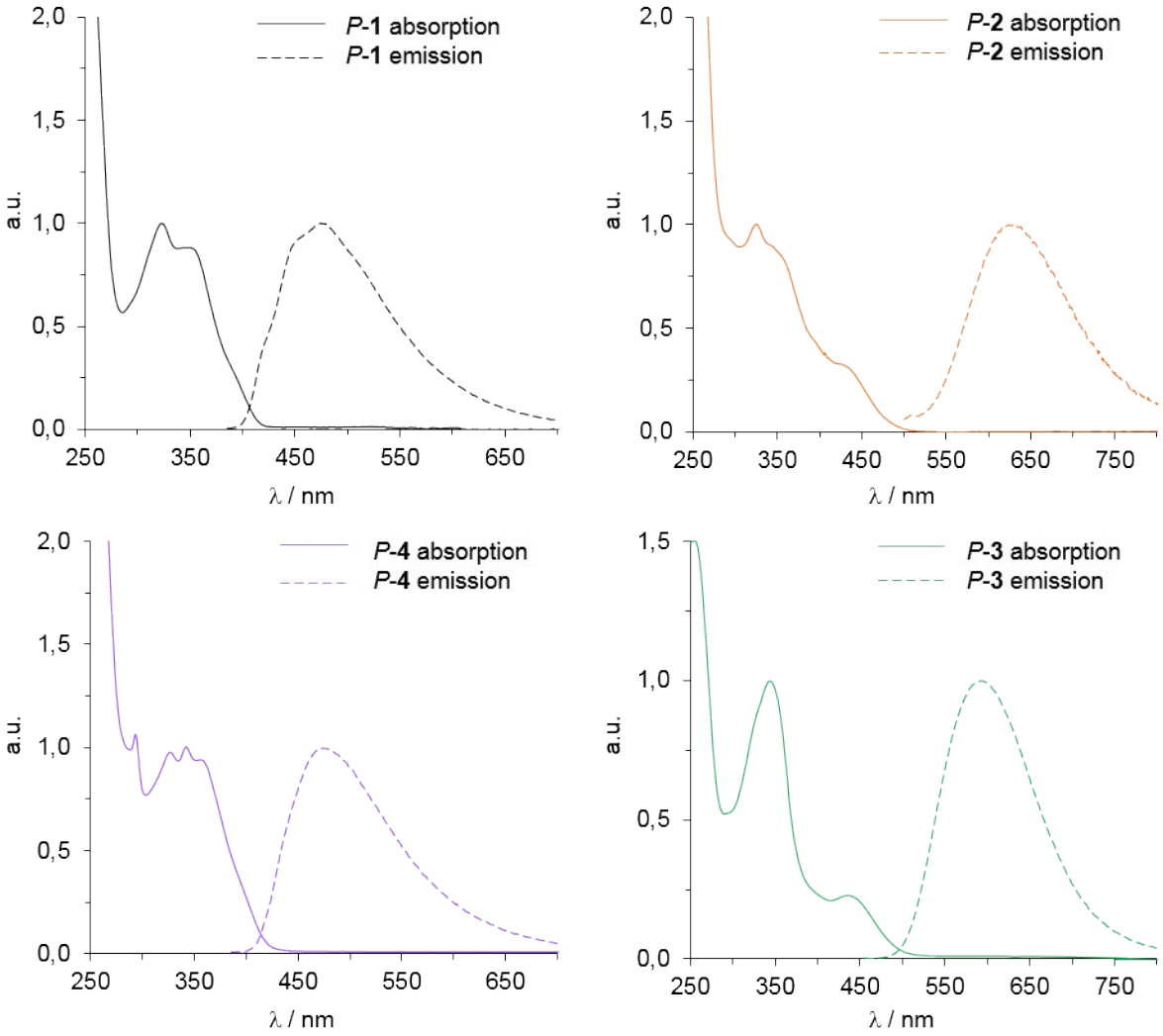


Figure S1. Normalized absorption (plain) and emission spectra (dashed) of *P*-**1** (black), *P*-**2** (orange), *P*-**3** (green) and *P*-**4** (purple) in $CHCl_3$. (**1** and **4** : λ_{exc} = 370 nm; **2** and **3** : λ_{exc} = 440 nm).

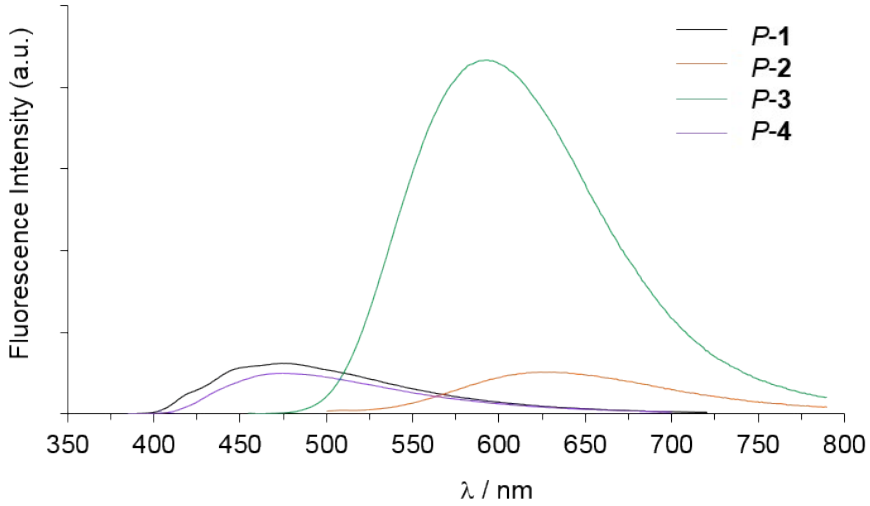


Figure S2. Fluorescence emission of *P*-**1** (black, λ_{exc} = 370 nm), *P*-**2** (orange, λ_{exc} = 440 nm), *P*-**3** (green, λ_{exc} = 440 nm) and *P*-**4** (purple, λ_{exc} = 370 nm) in CH_2Cl_2. Comparison for optically dilute isosbestic solutions.

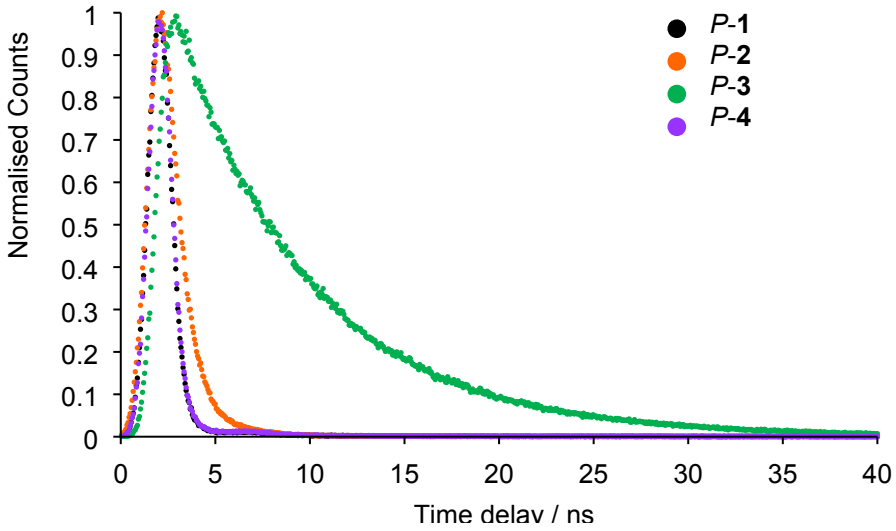


Figure S3. Time-resolved fluorescence decay of *P*-**1** (black, λ_{em} = 460 nm), *P*-**2** (orange, λ_{em} = 550 nm), *P*-**3** (green, λ_{em} = 550 nm) and *P*-**4** (purple, λ_{em} = 460 nm) in CH_2Cl_2 (λ_{ex}= 371 nm).

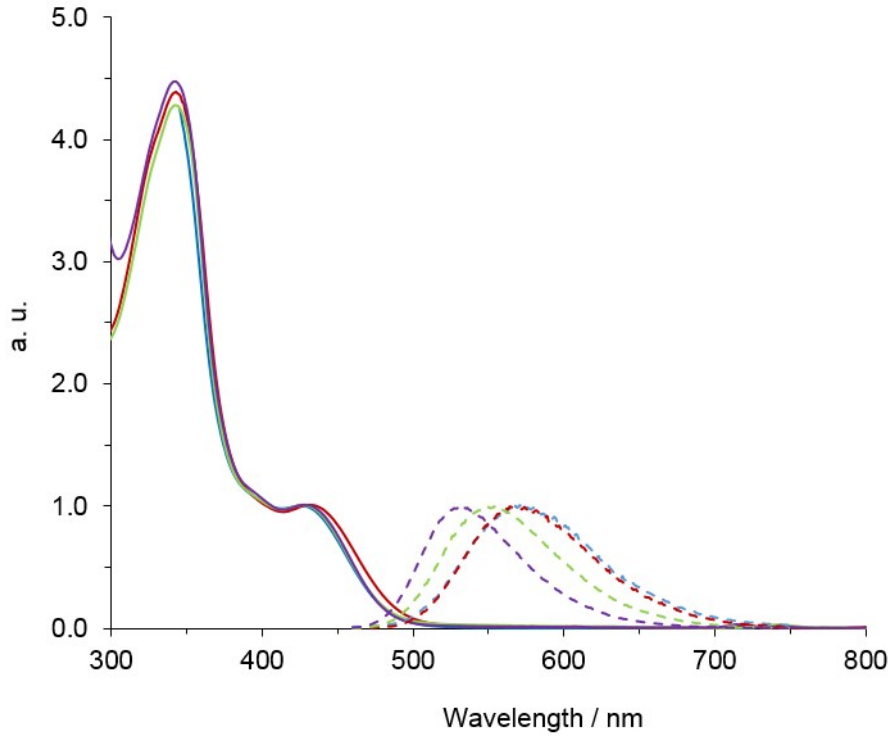


Figure S4. Normalized absorption (plain) and emission (dashed) spectra of *P*-**3** in different solvants: acetone (blue), dichloromethane (red), THF (green) and toluene (purple). λ_{exc} = 440 nm.

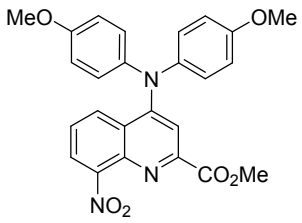
4. X-ray crystallography

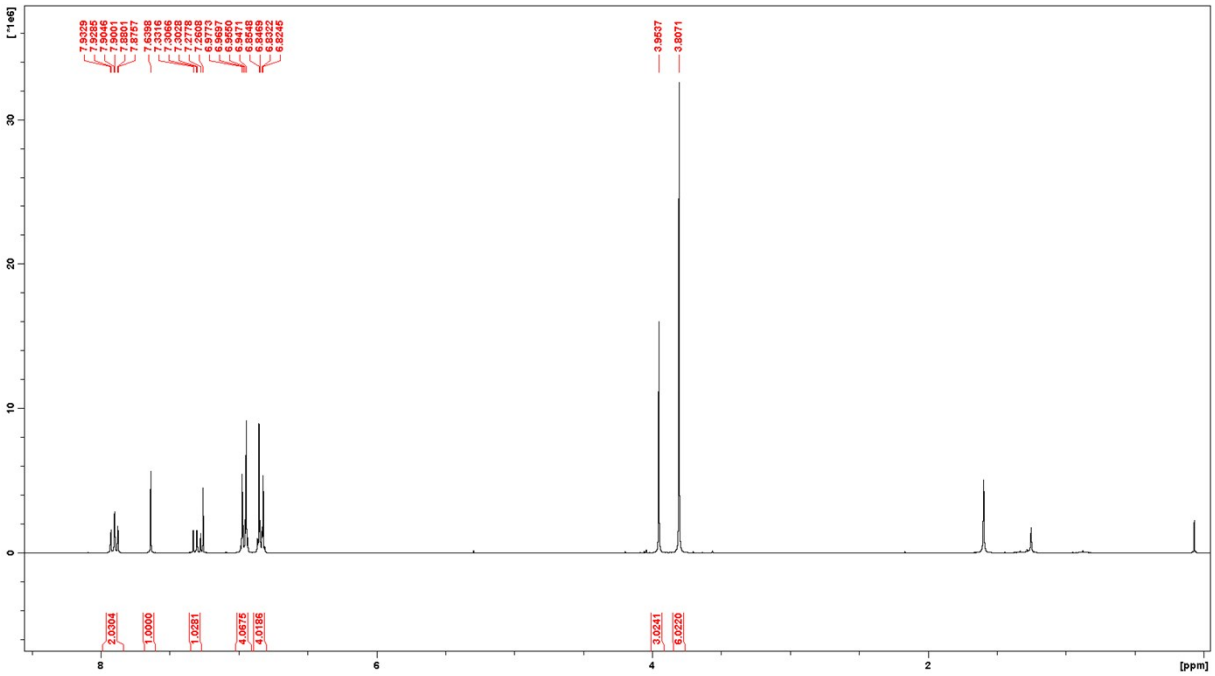
Table S1. Crystallographic data for **21** and **30**.

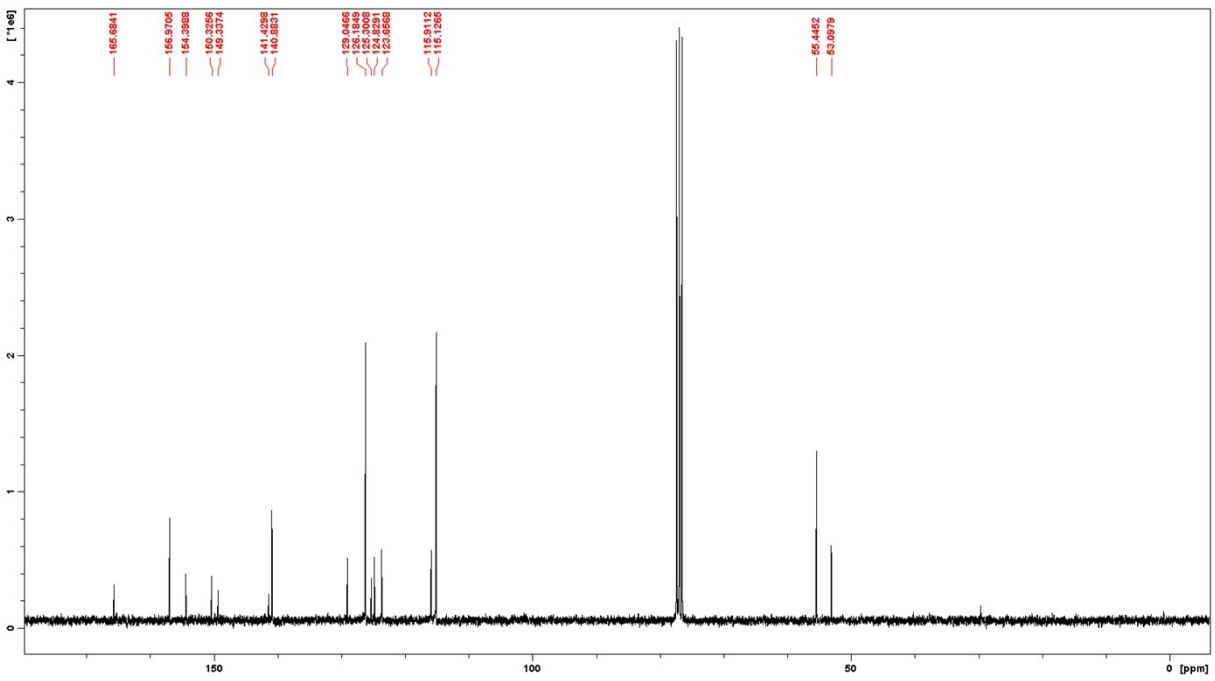
Compound	**21**	**30**
Chemical formula	$C_{85}H_{77}Cl_6N_9O_{10}$	$C_{80}H_{78}Cl_9N_9O_{10}$
Formula weight, g/mol	1597.25	1644.56
Temperature, K	150	100
Crystal system	triclinic	triclinic
Space group	P-1	P-1
a, Å	13.2948(5)	13.4624(3)
b, Å	18.1431(10)	17.3266(2)
c, Å	20.1869(9)	17.4125(3)
α, °	109.695(5)	78.3760(10)
β, °	98.506(4)	82.129(2)
γ, °	100.557(4)	88.2630(10)
V, Å^3	4389.7(4)	3940.80(12)
Z	2	2
$\rho_{calc,}$ g/cm^3	1.208	1.386
μ, mm^{-1}	2.266	3.451
F(000)	1664.0	1708.0
Crystal size, mm^3	0.2 × 0.2 × 0.01	0.4 × 0.02 × 0.02
Radiation	CuKα (λ = 1.54184)	CuKα (λ = 1.54184)
2Θ range for data collection, °	4.774 to 147.058	5.208 to 146.984
Index ranges	-15 ≤ h ≤ 16, -22 ≤ k ≤ 22, -24 ≤ l ≤ 25	-16 ≤ h ≤ 16, -21 ≤ k ≤ 21, -21 ≤ l ≤ 21
Reflections collected	62904	52189
Independent reflections	17124 [R_{int} = 0.0760, R_{sigma} = 0.0562]	15424 [R_{int} = 0.0461, R_{sigma} = 0.0244]
Data/restraints/parameters	17124/0/1003	15424/1/995
Goodness-of-fit on F^2	1.172	1.054
Final R indexes [I>=2σ (I)]	R_1 = 0.1084, wR_2 = 0.3137	R_1 = 0.0780, wR_2 = 0.2233
Final R indexes [all data]	R_1 = 0.1404, wR_2 = 0.3534	R_1 = 0.0791, wR_2 = 0.2247
Largest diff. peak/hole / e Å^{-3}	1.22/-1.15	1.64/-1.25
CCDC #	1934790	1934840

5. NMR spectra

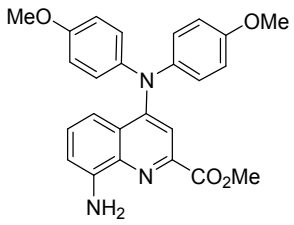
Monomer **6**







Monomer **7**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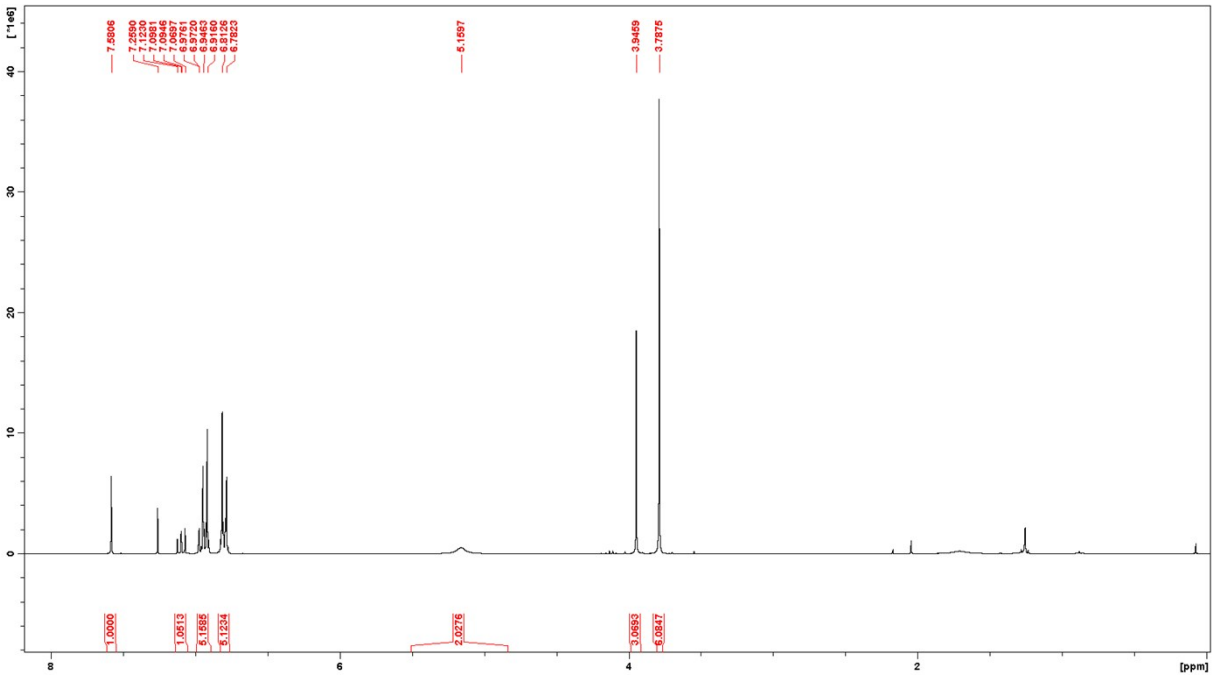
N
CO2Me
NH2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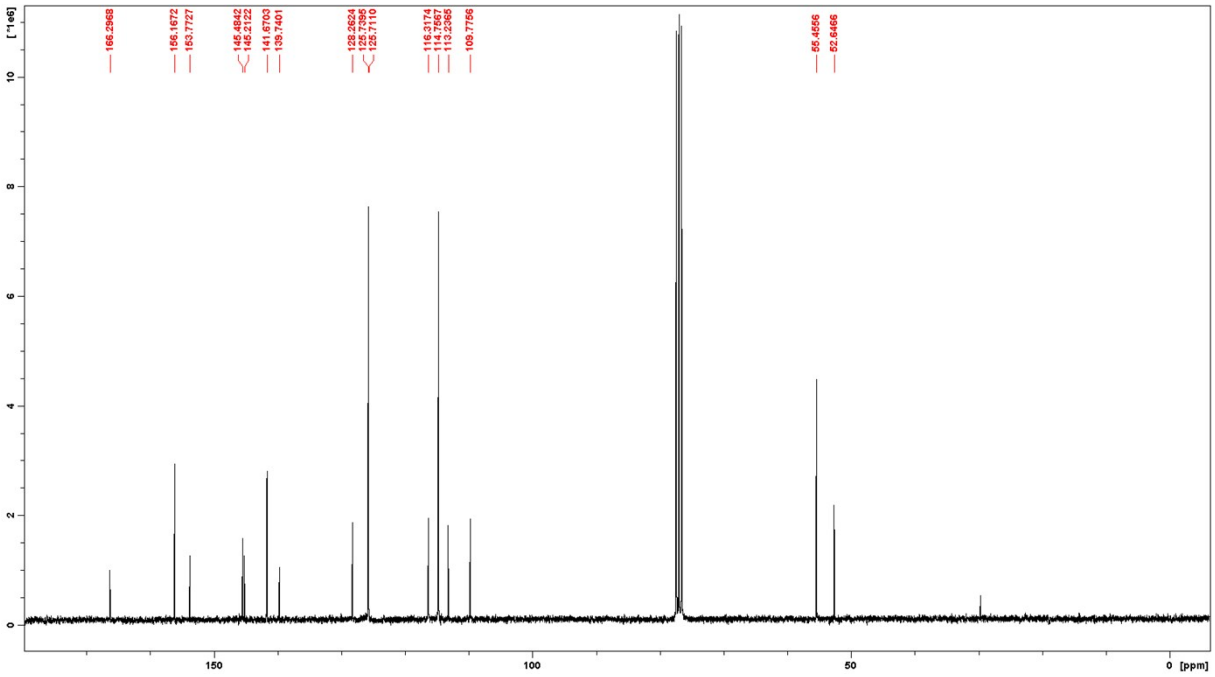
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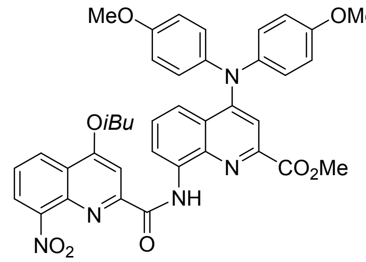

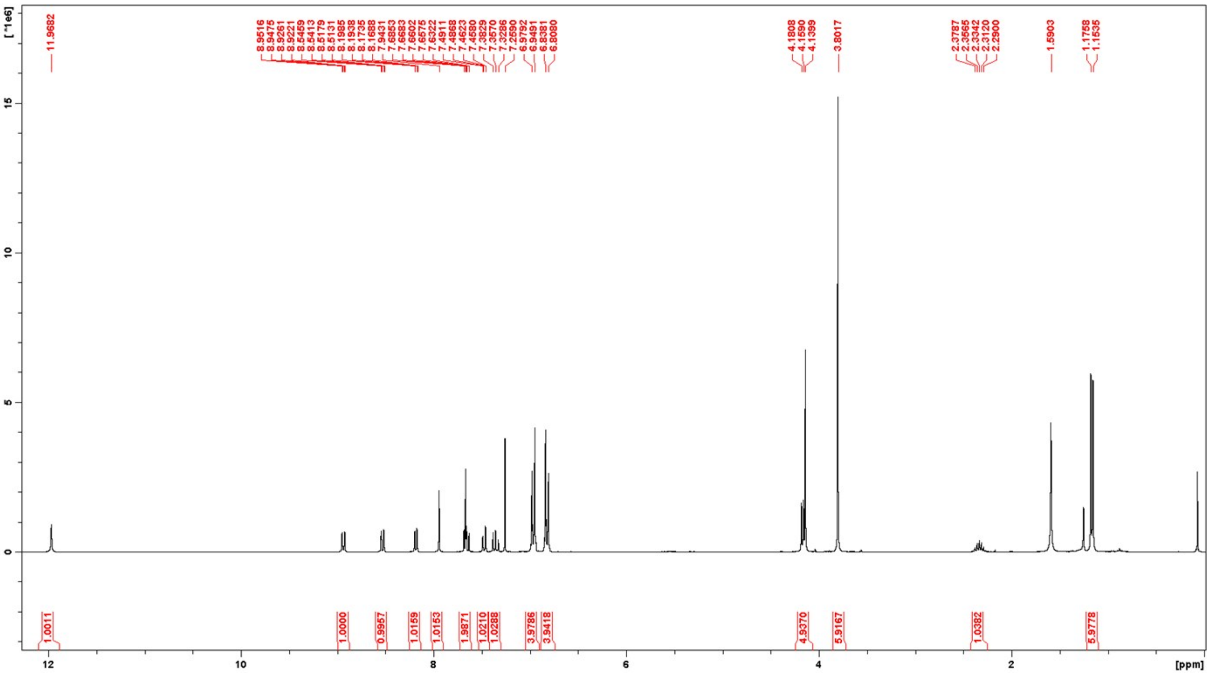

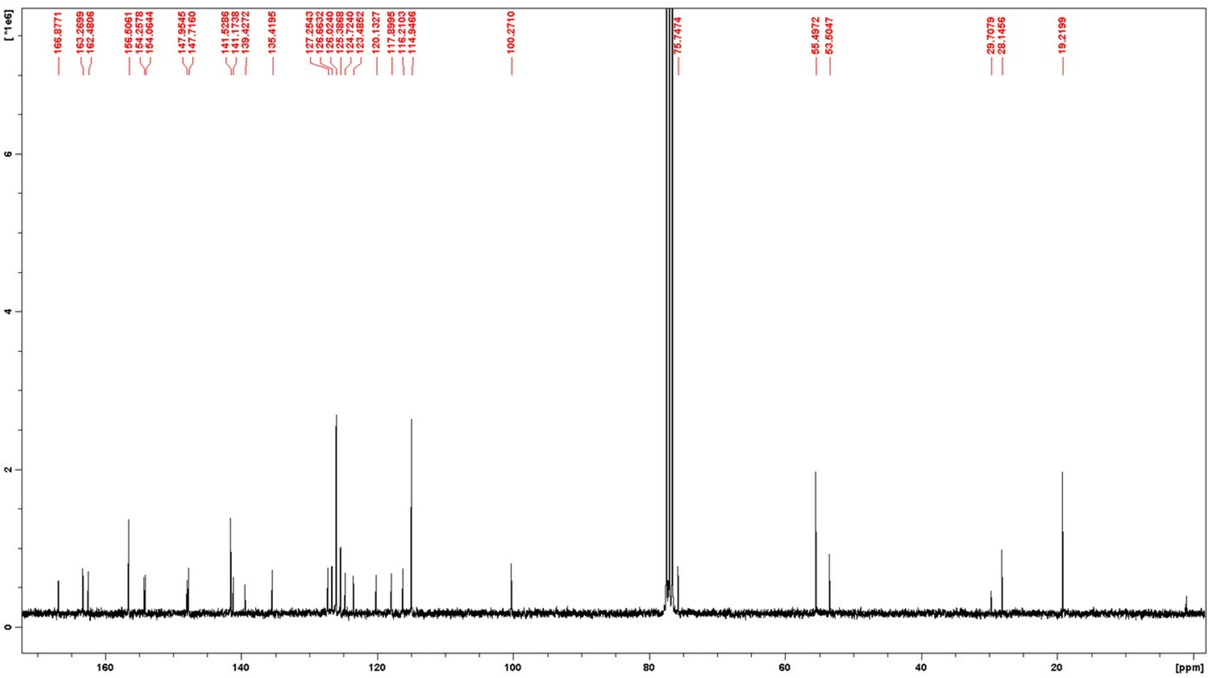

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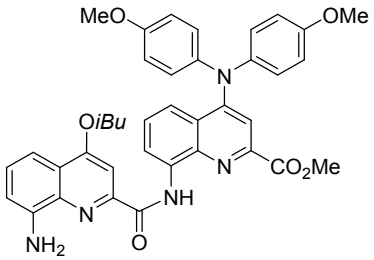

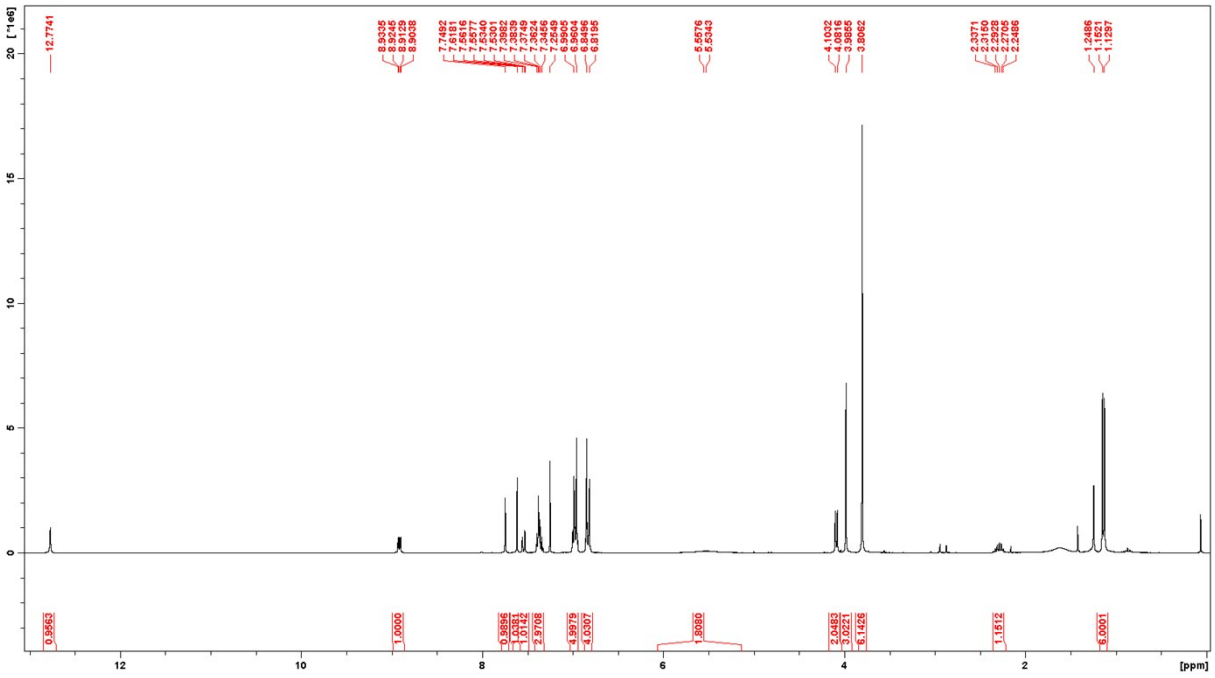

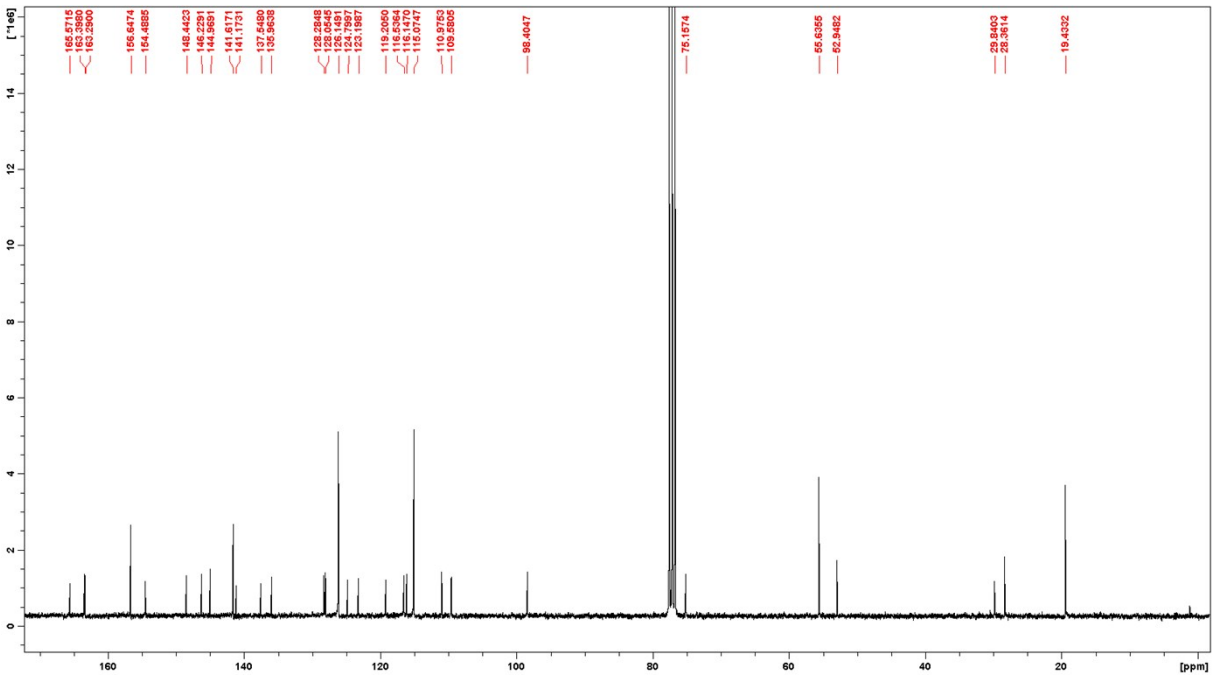

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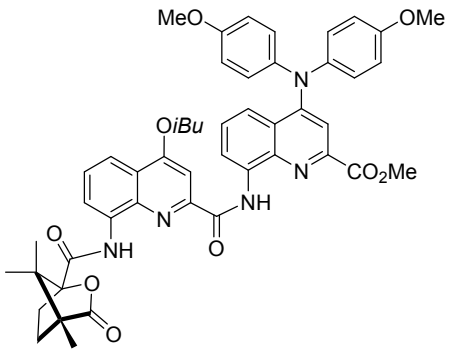

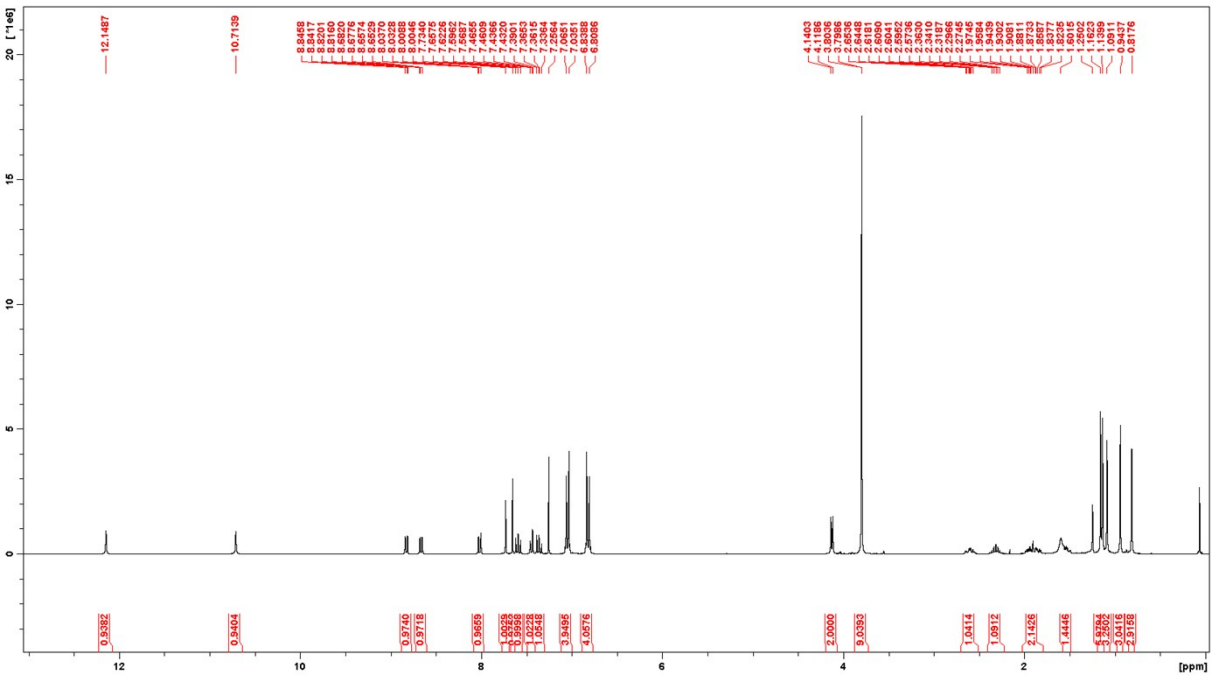

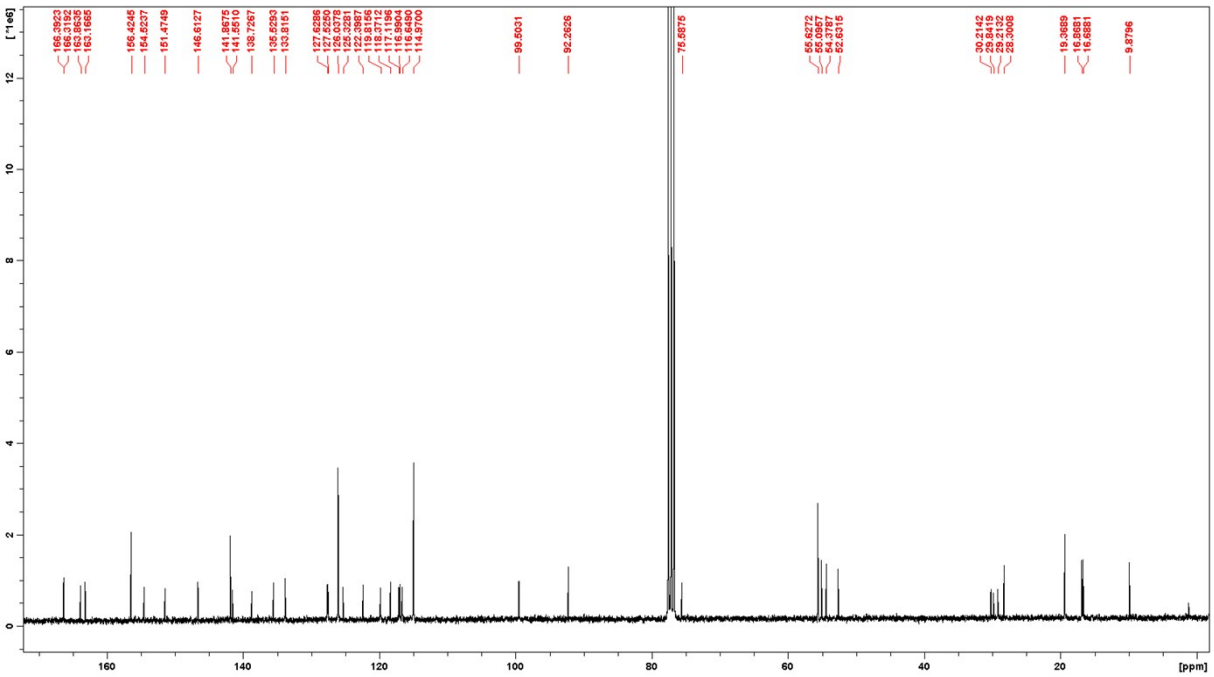

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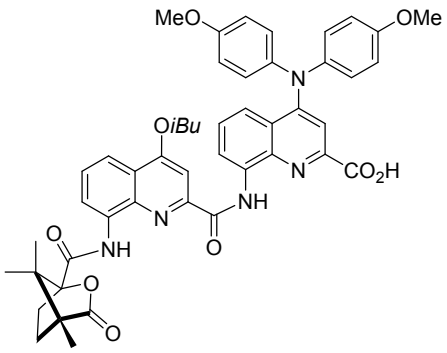

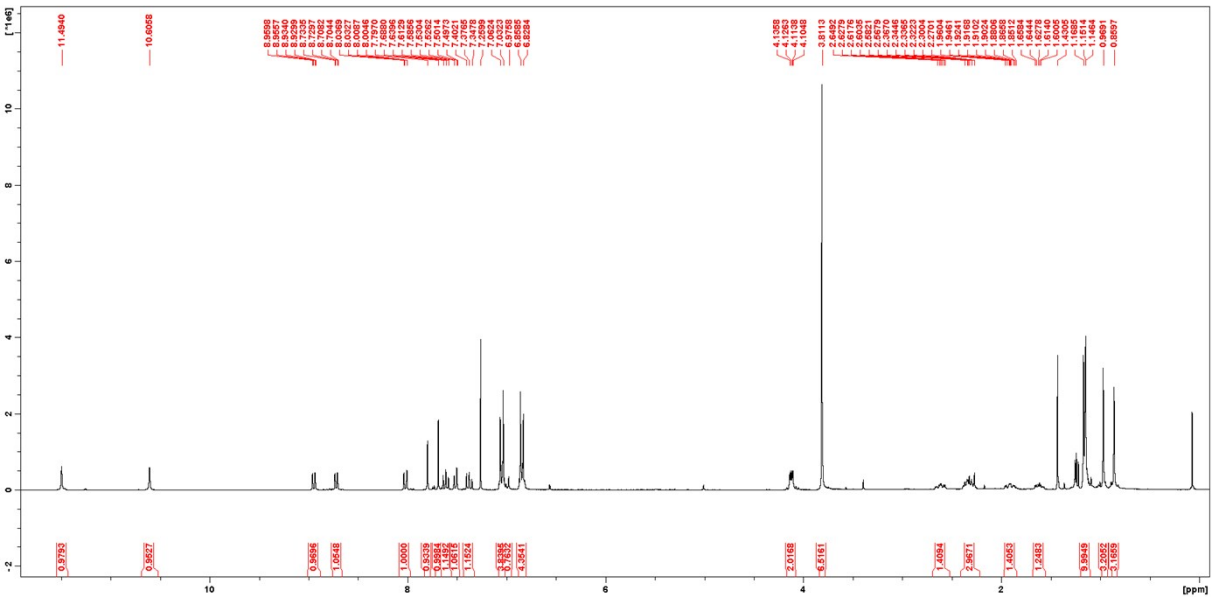

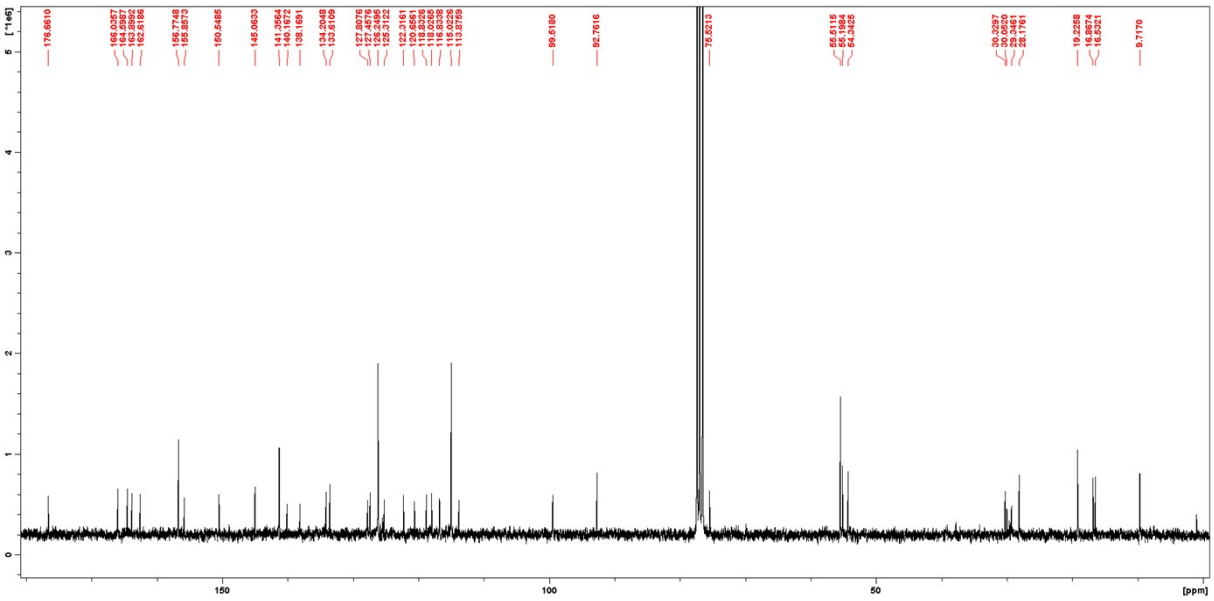

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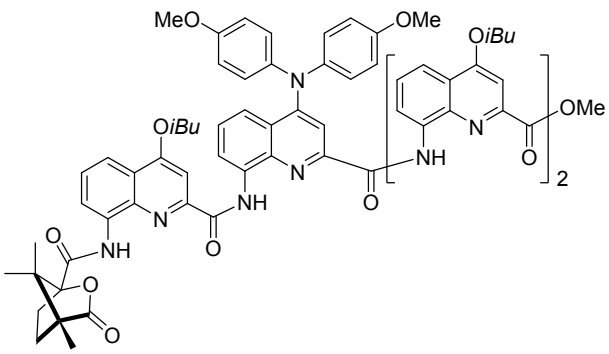
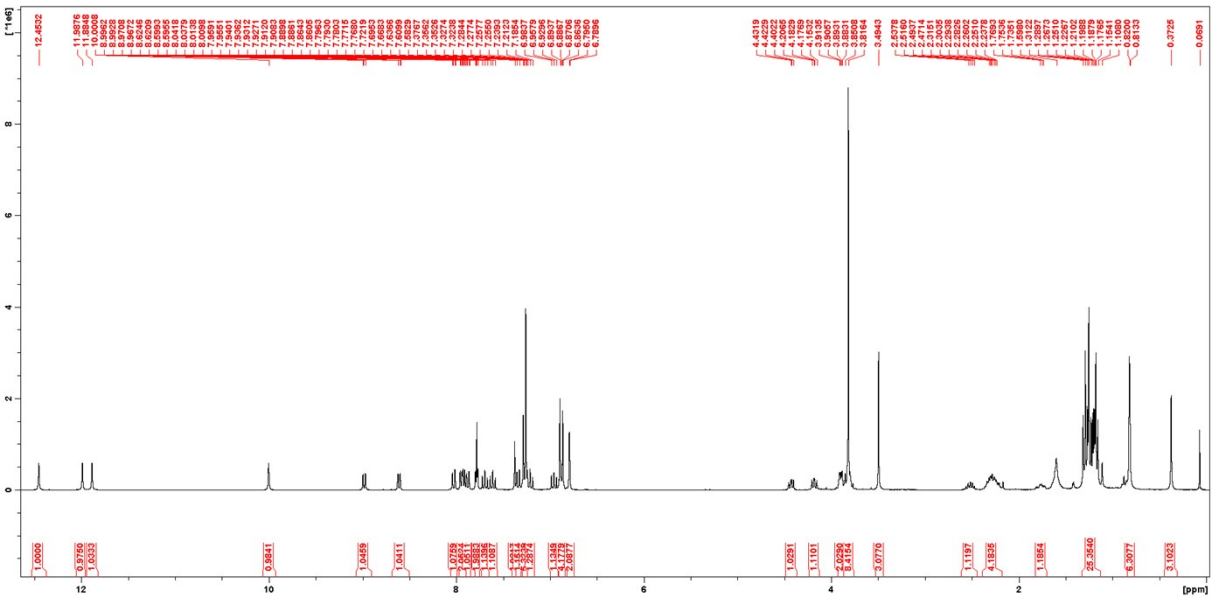
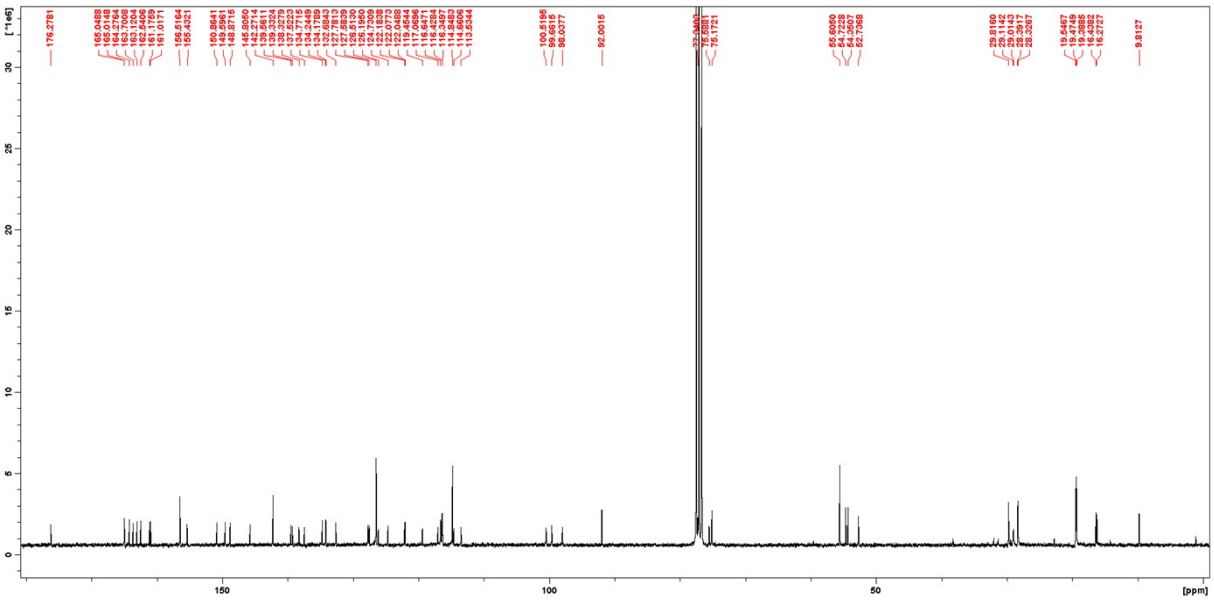
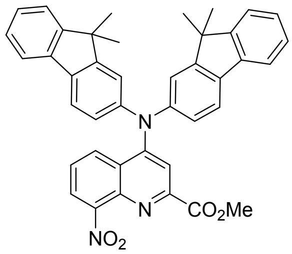






Monomer **16**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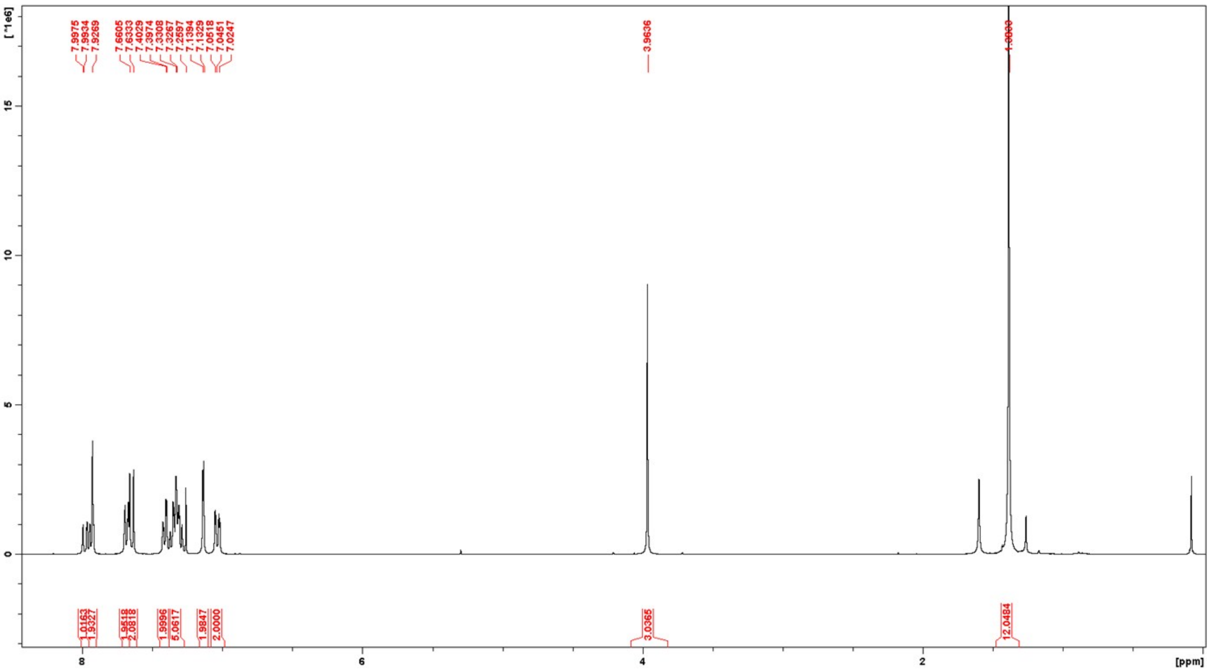
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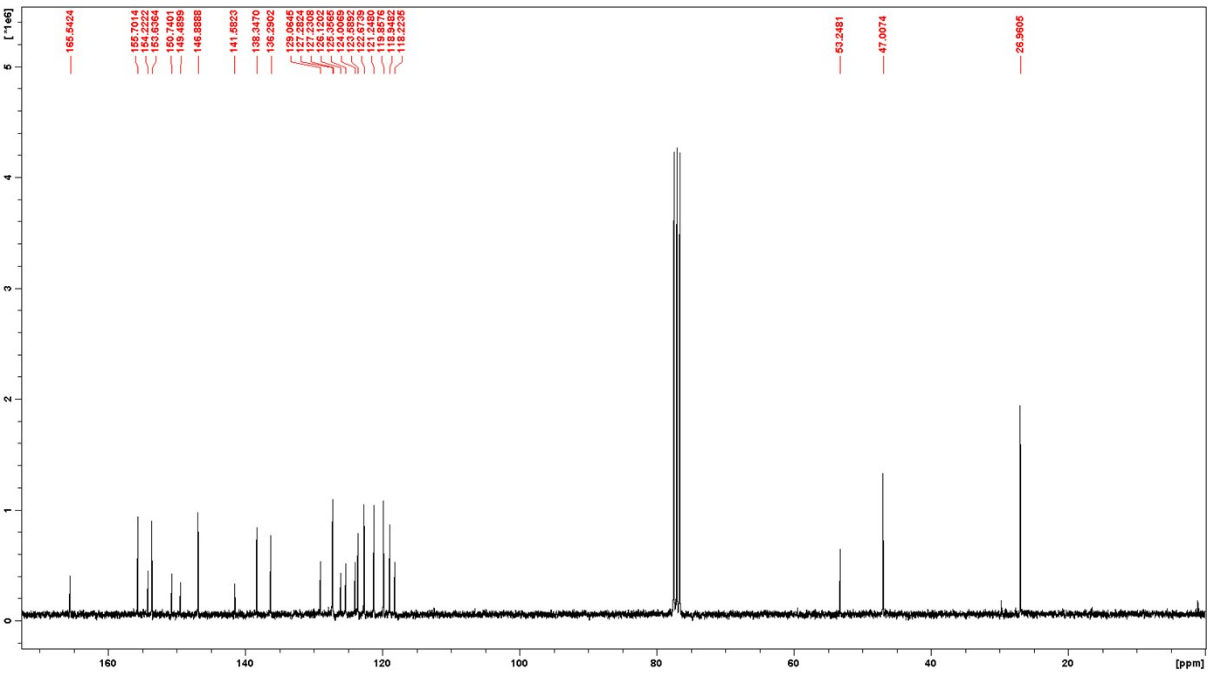
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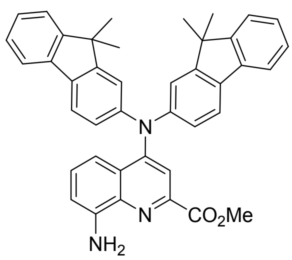
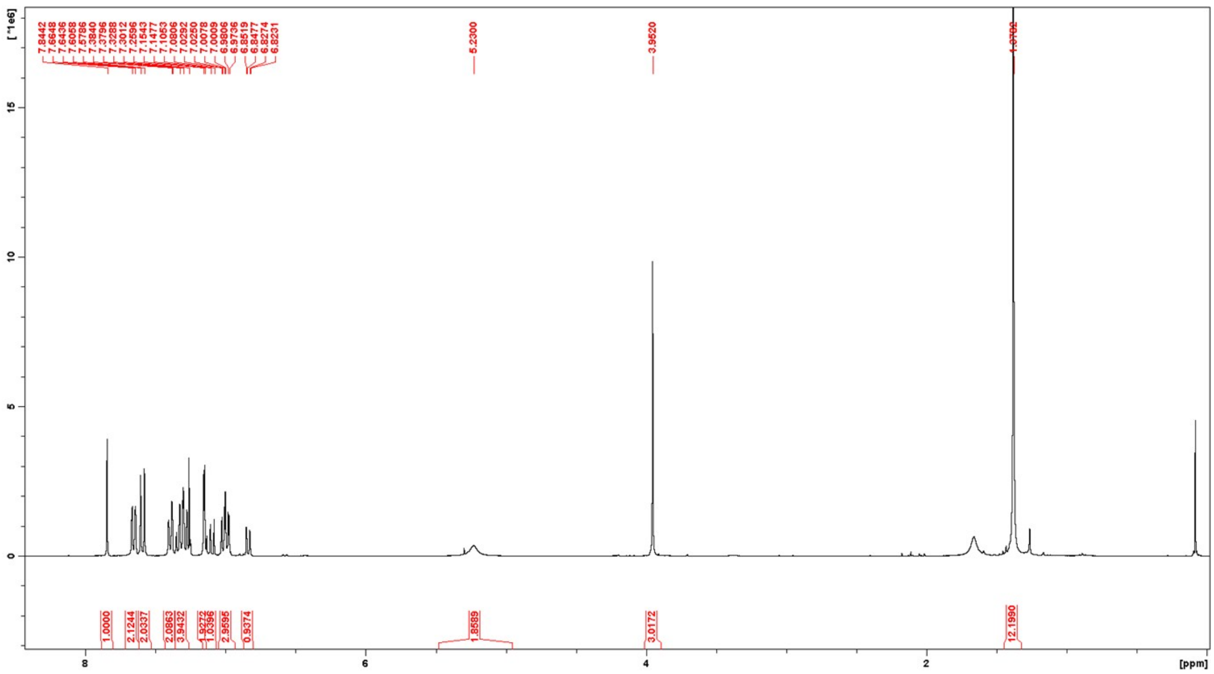
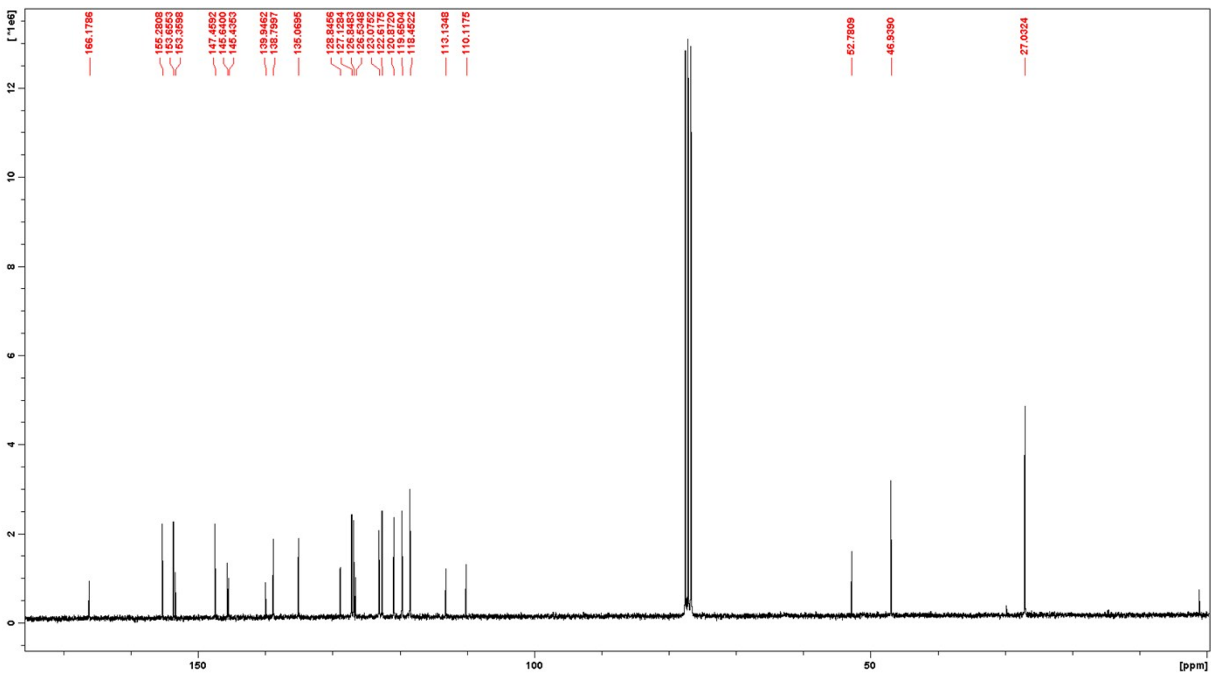
Monomer **17**







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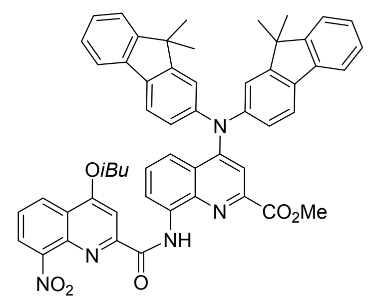

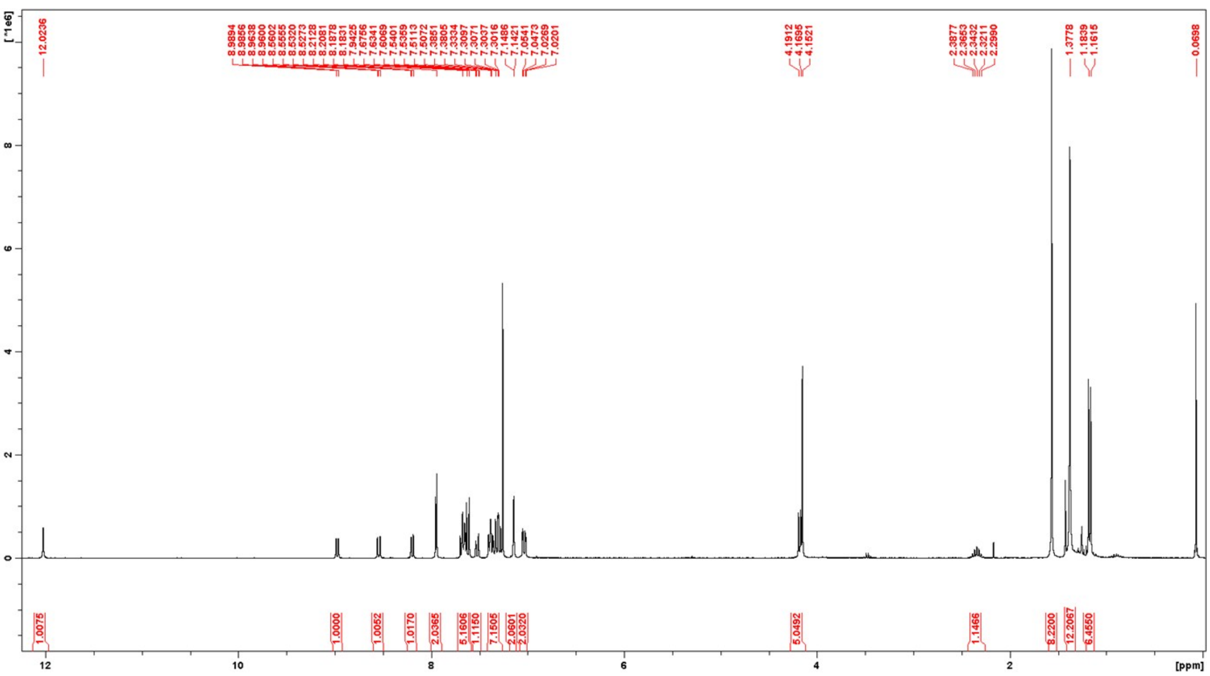

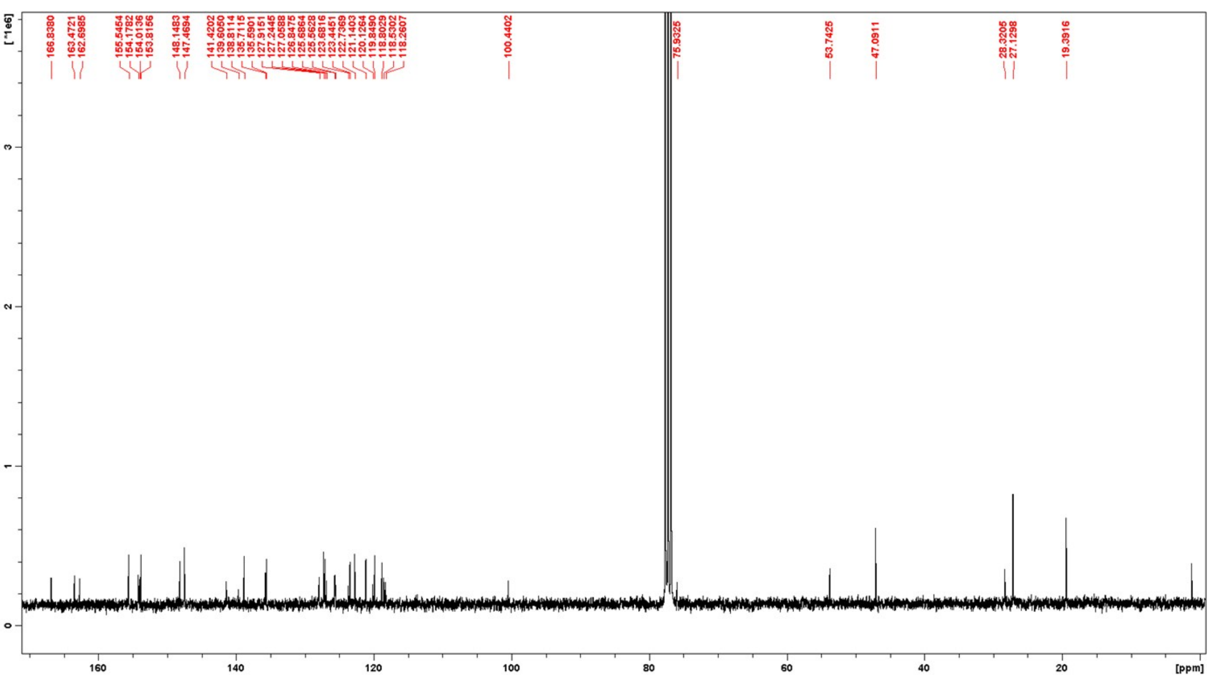

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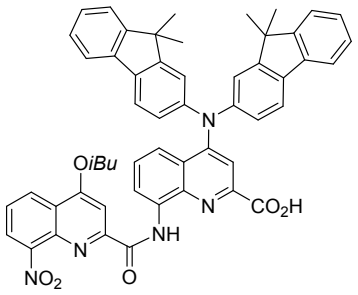

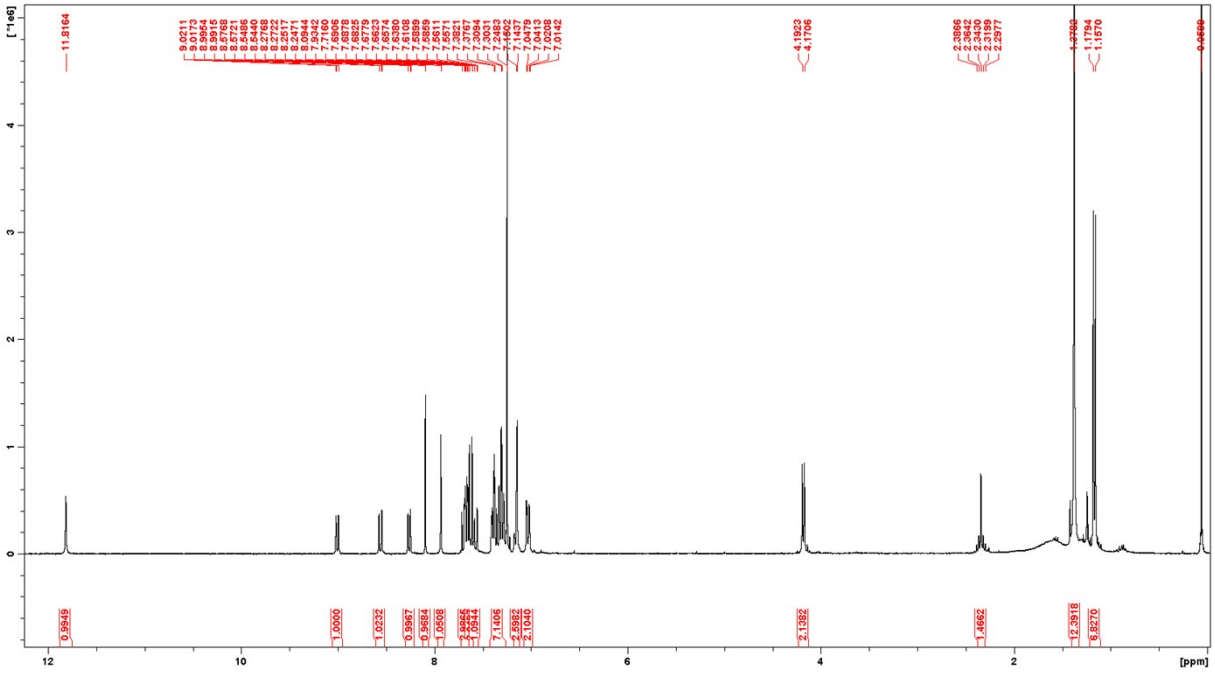

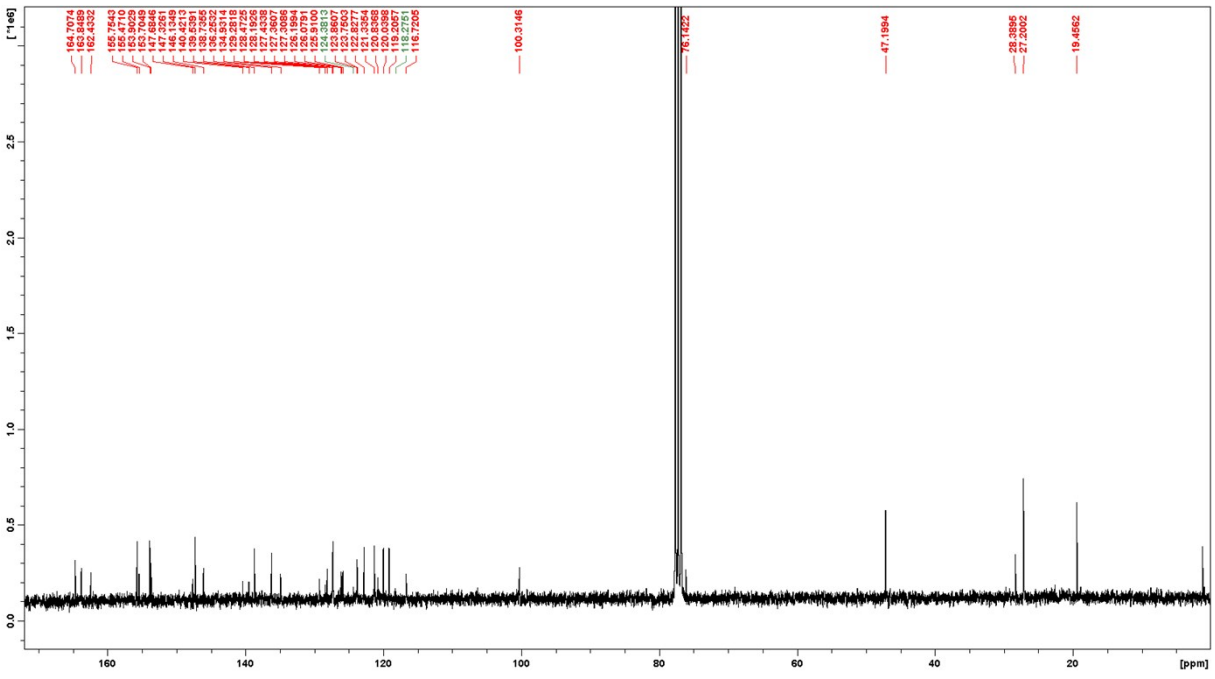

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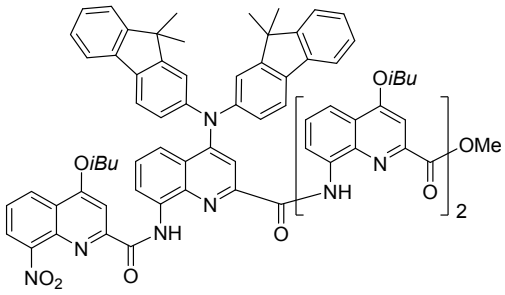

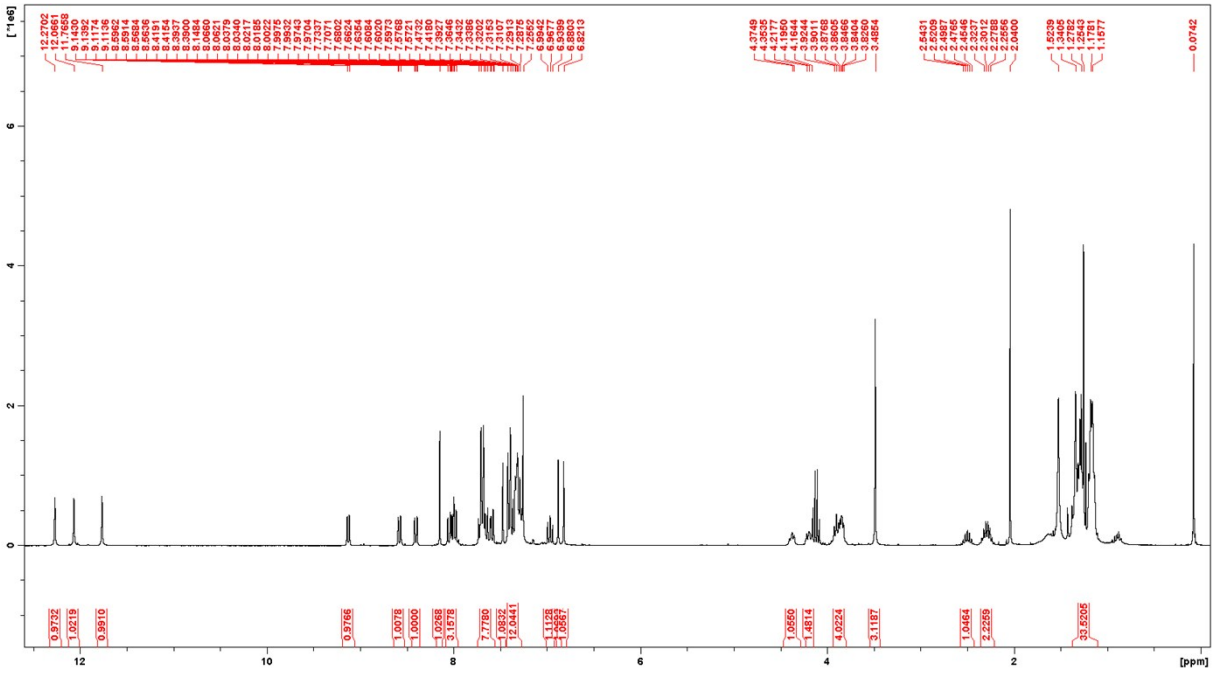

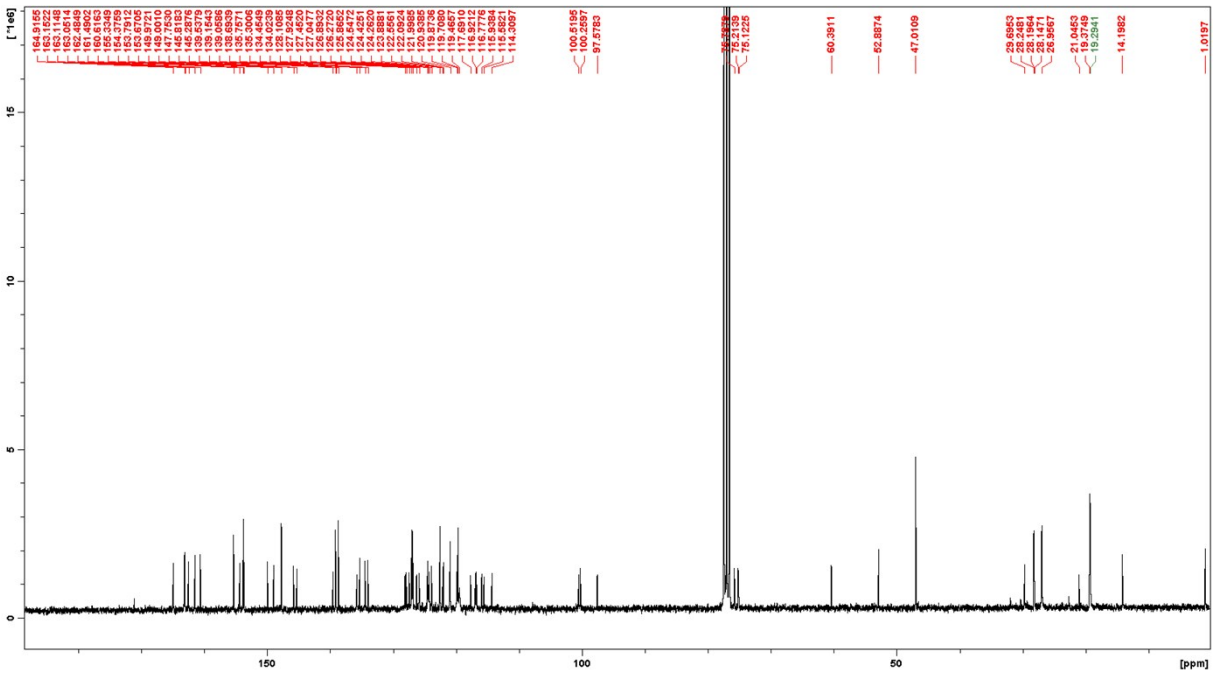

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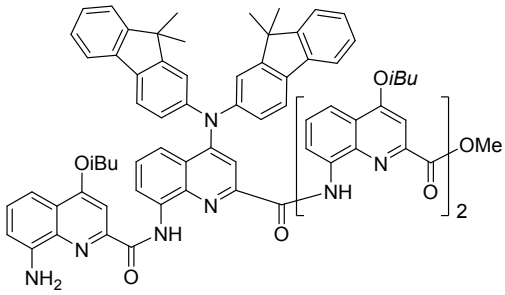

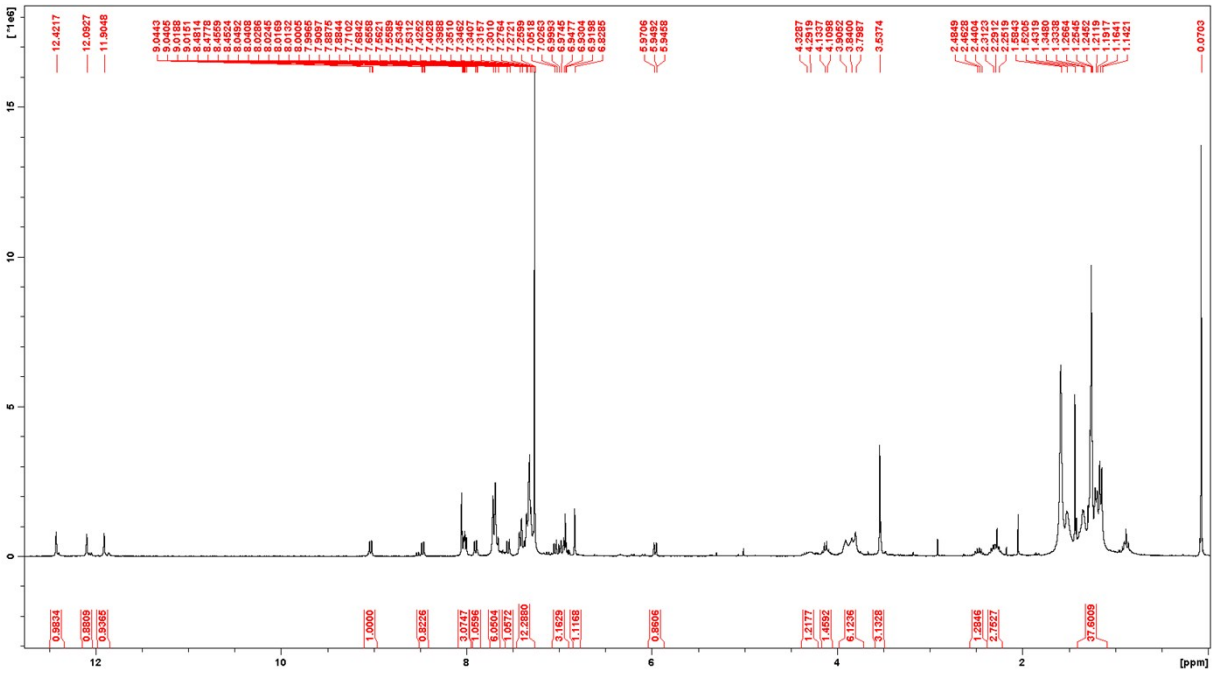

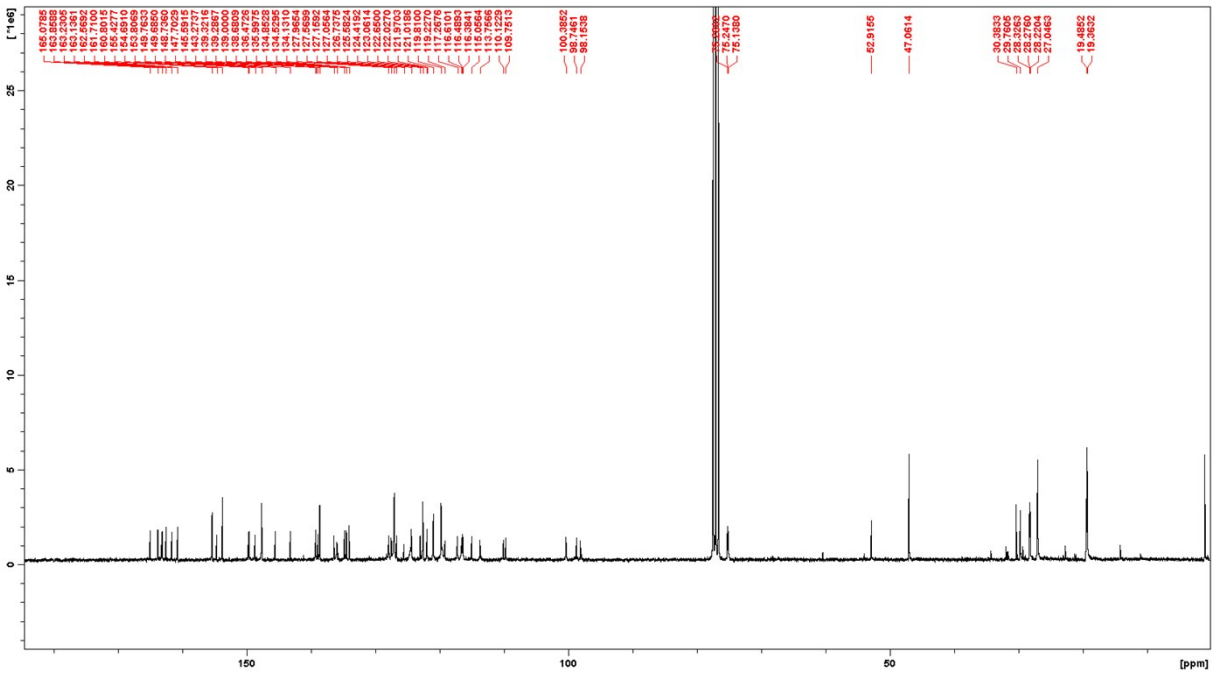

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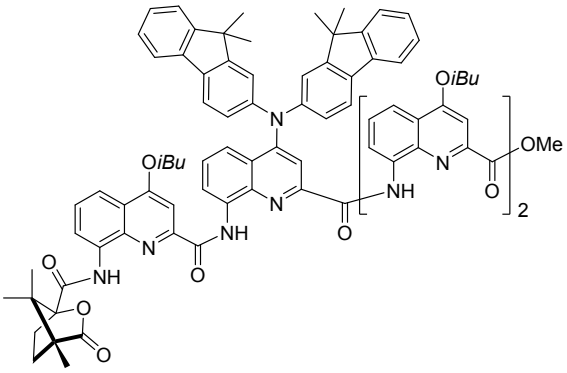
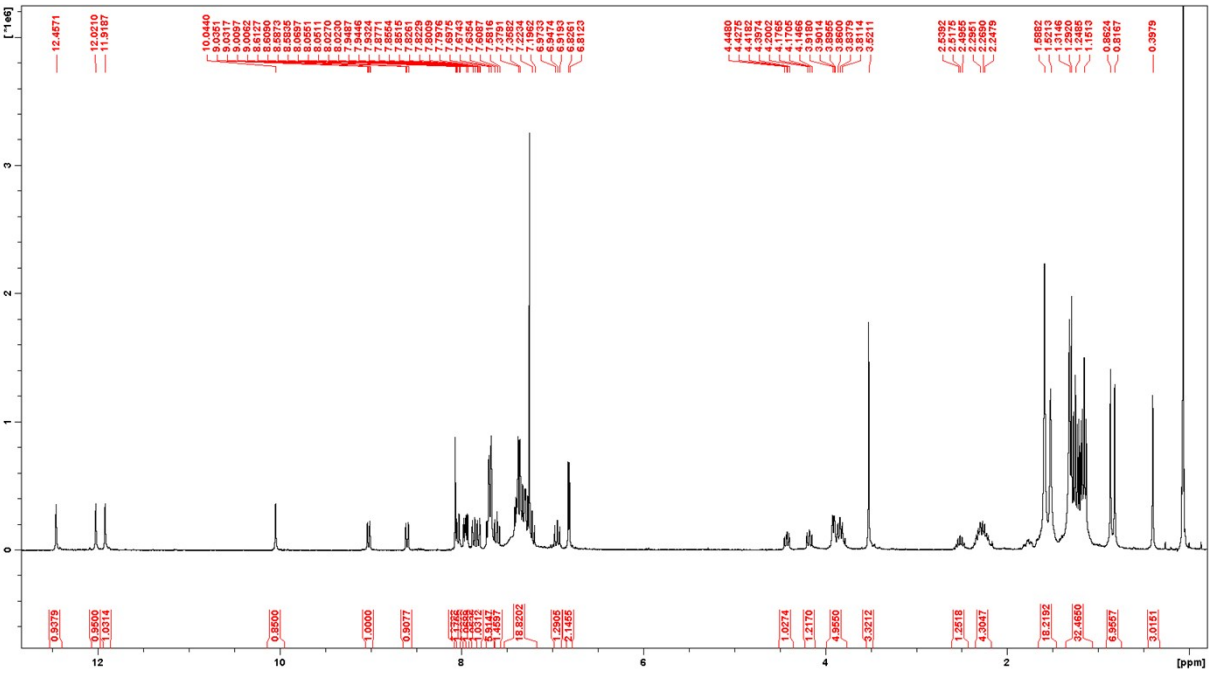
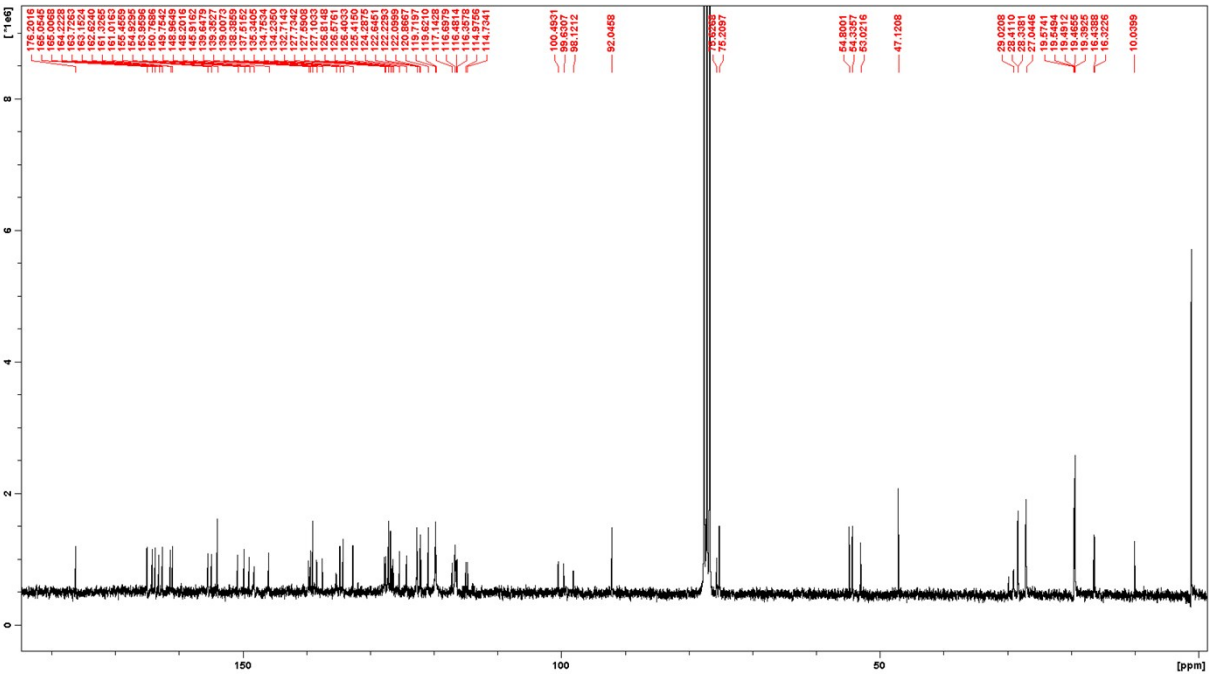
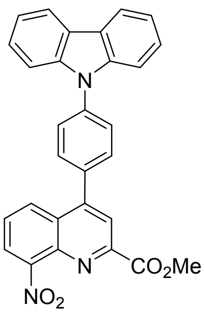






Monomer **23**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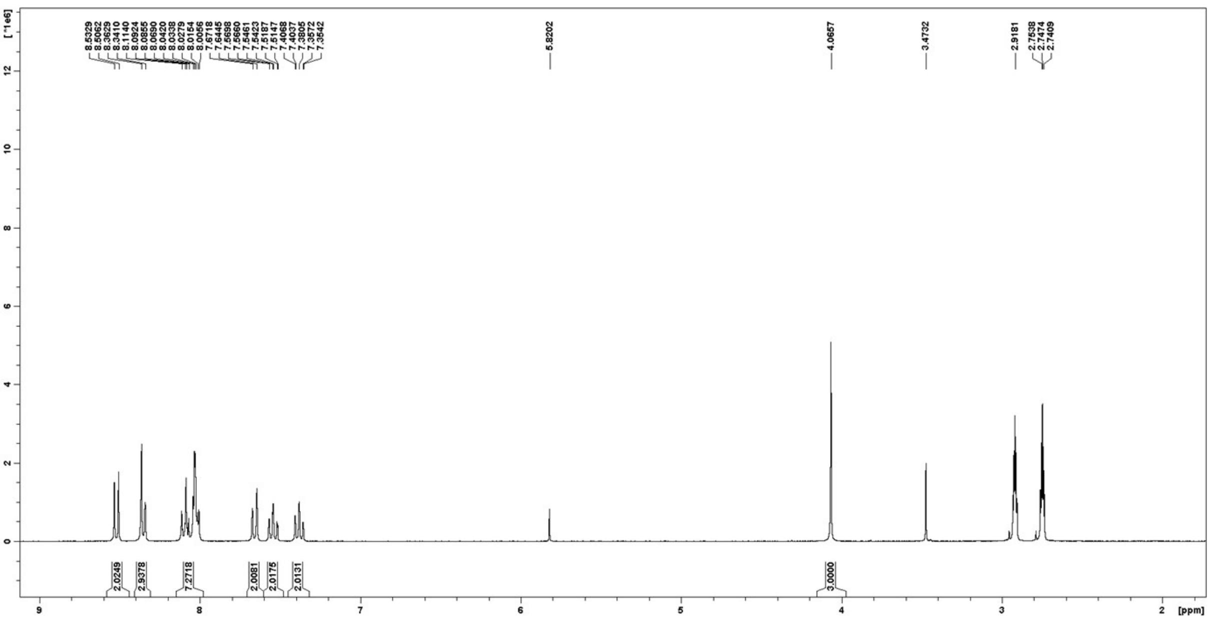
NO2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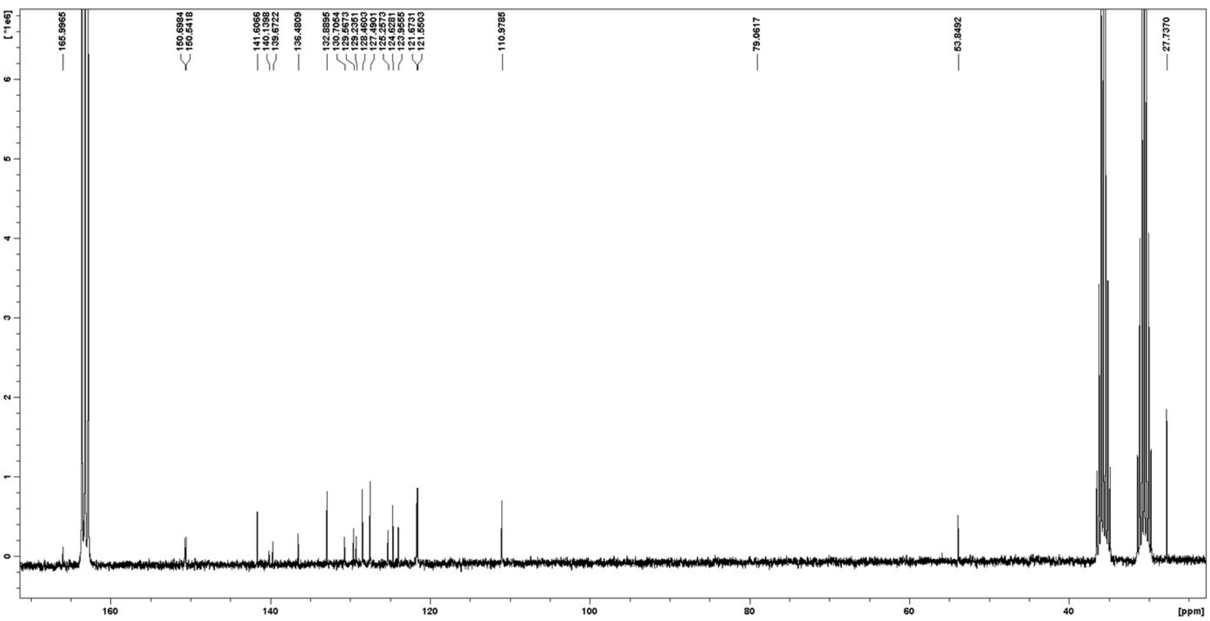
[*1e6]
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150.5984
150.5418
141.6066
140.1398
139.6722
136.4809
132.8895
130.7054
129.5673
129.2351
128.4603
127.4901
125.2573
124.6281
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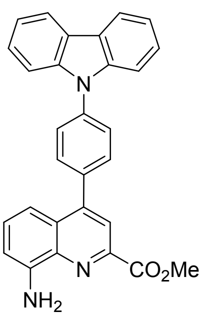
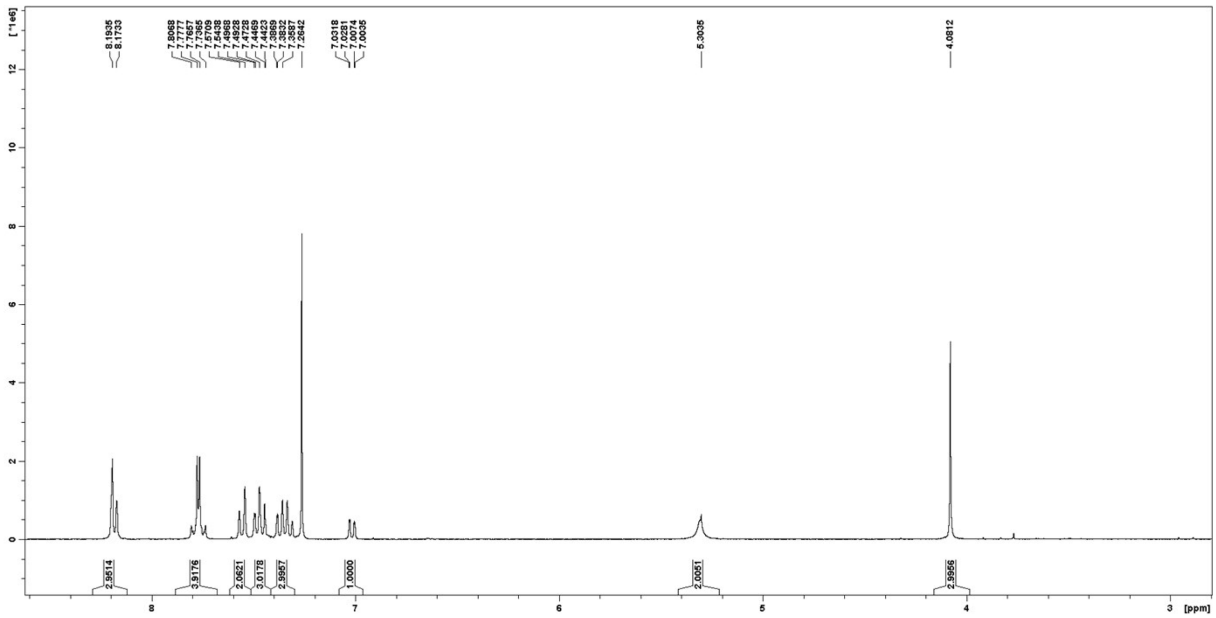
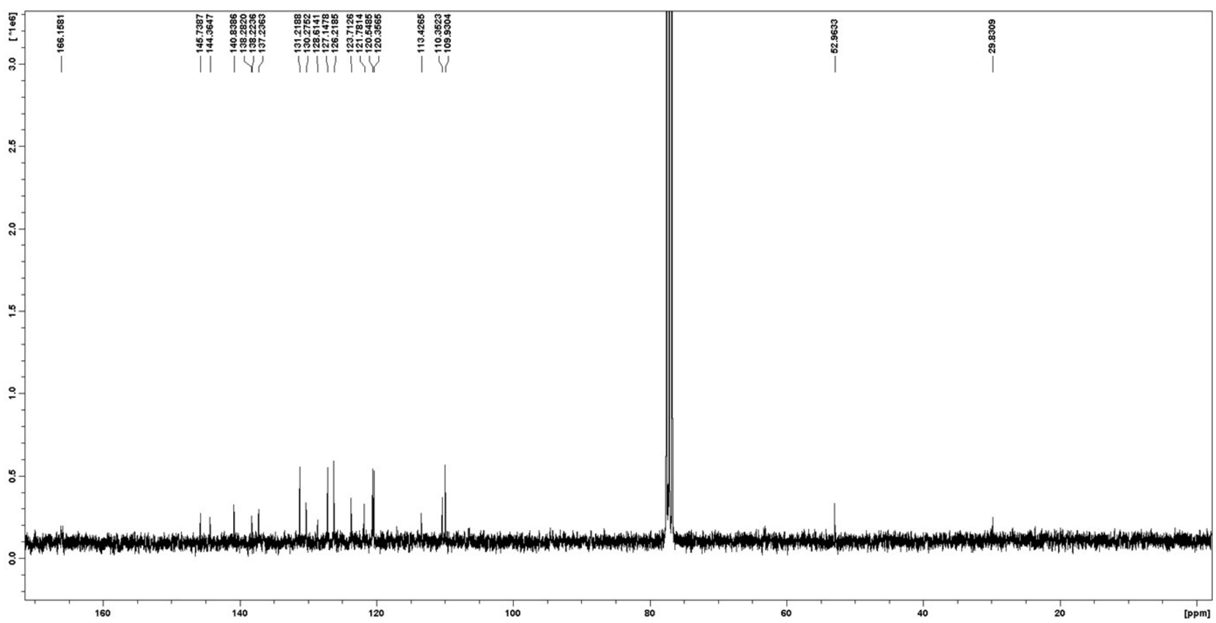
121.6731
121.5503
110.9785
79.0617
53.8492
27.7370
[ppm]

Monomer **24**







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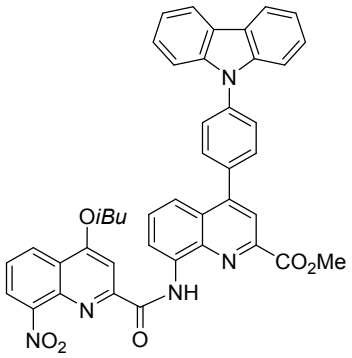
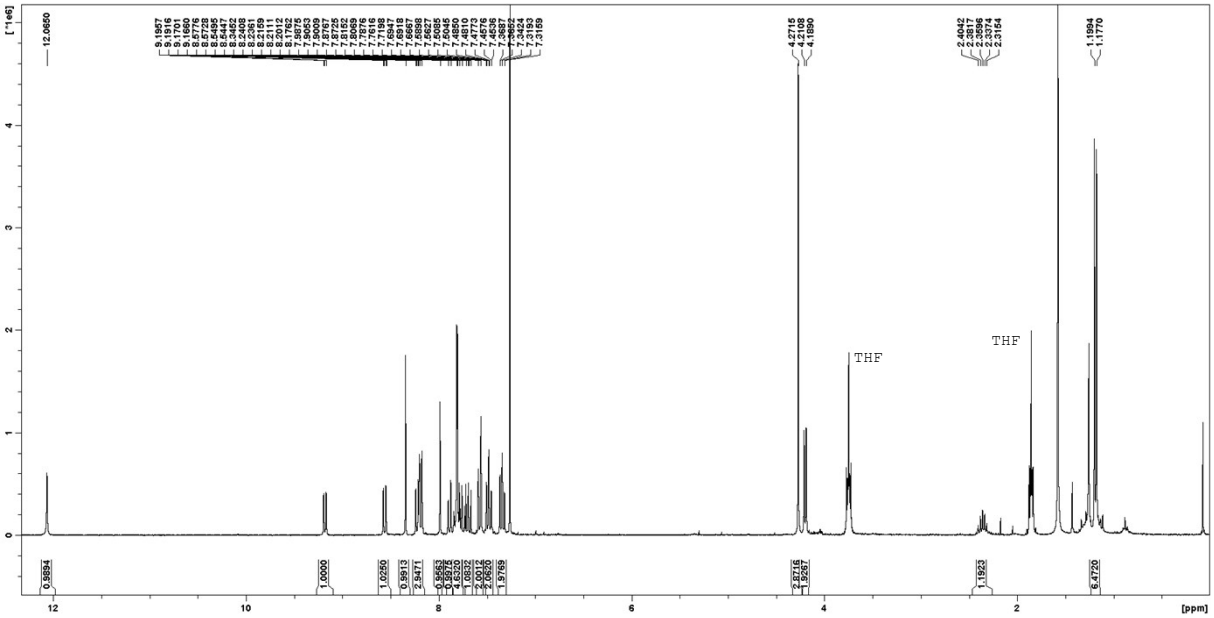
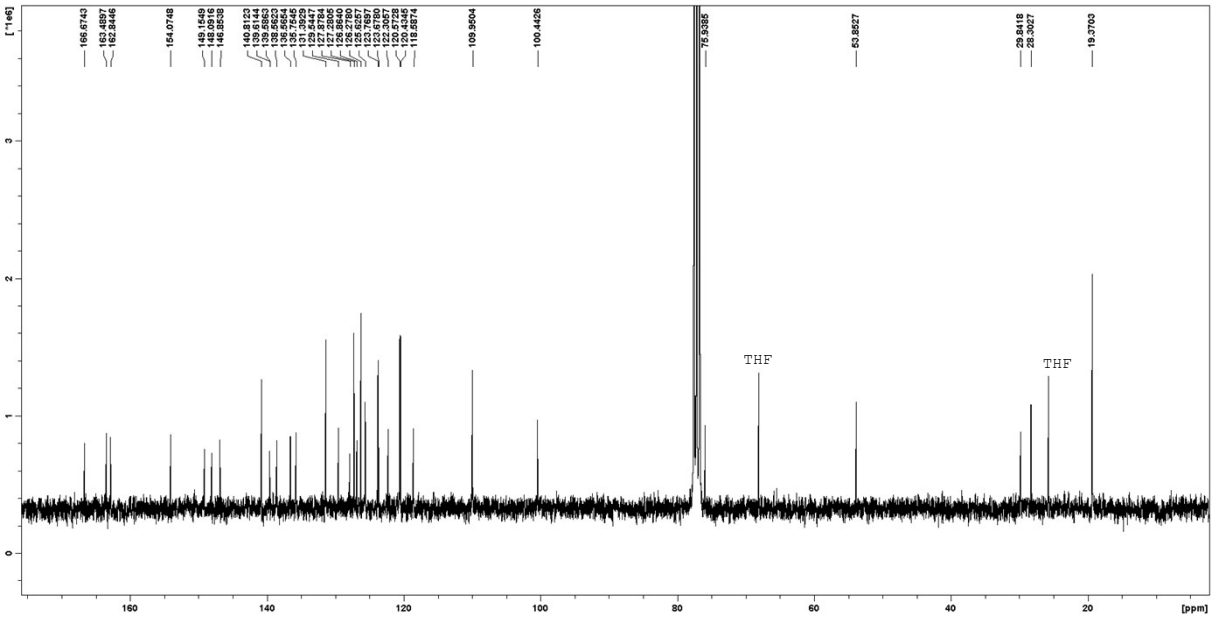
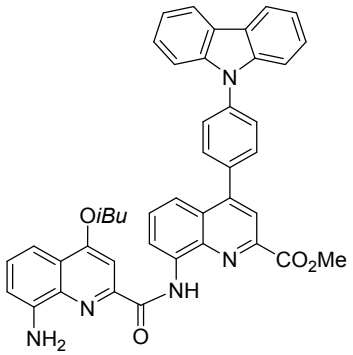
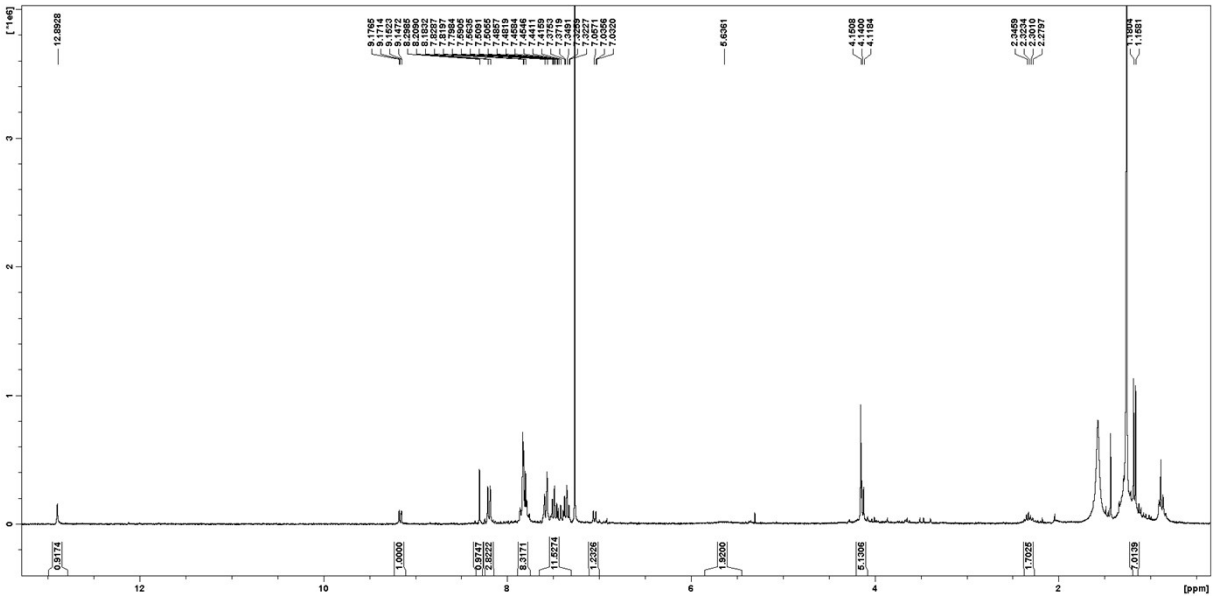


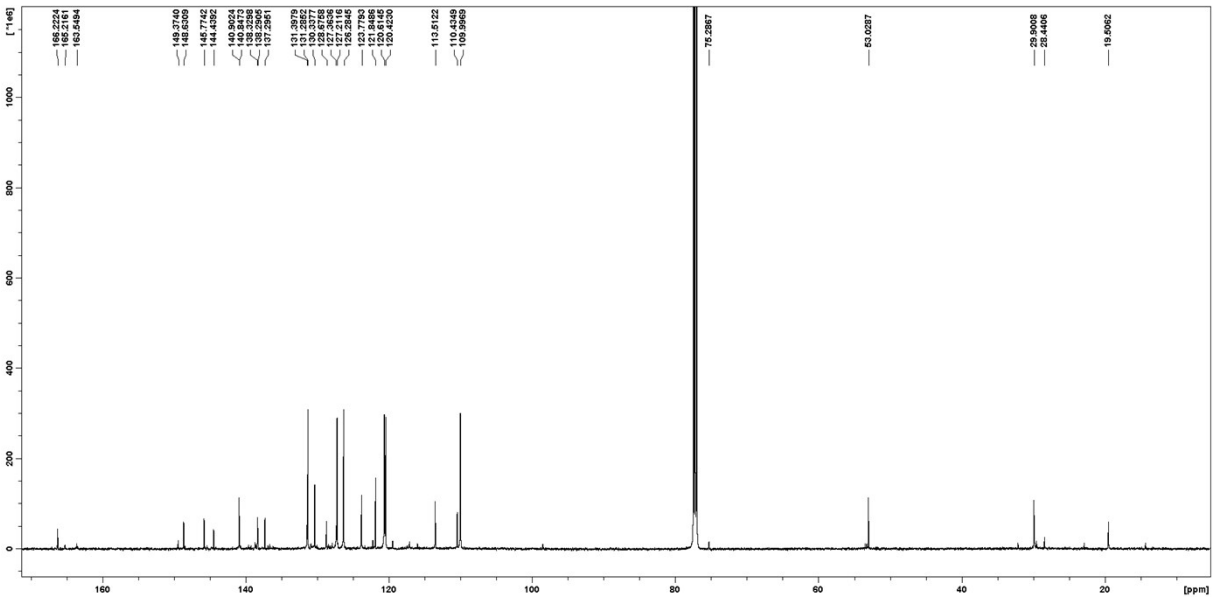




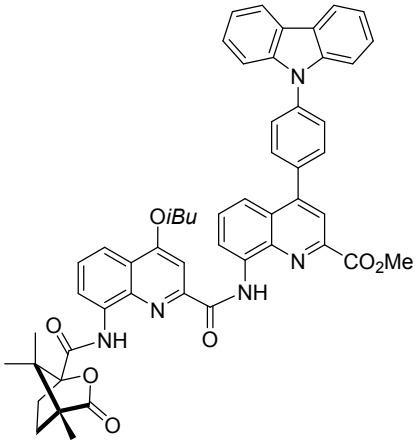
Dimer **26**

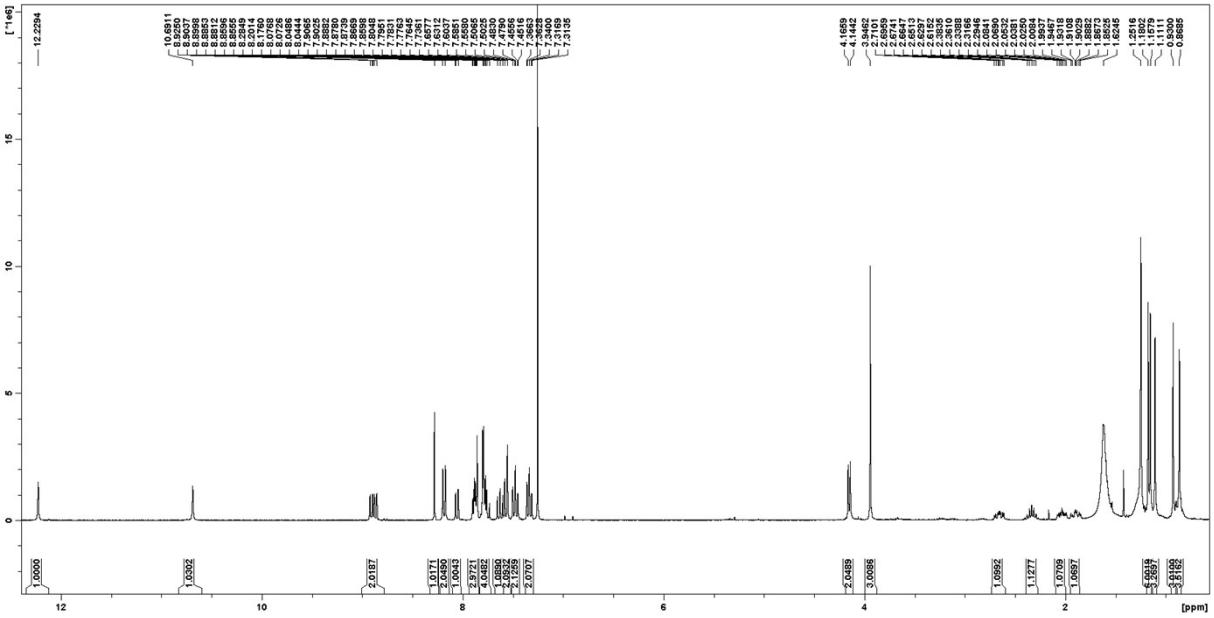


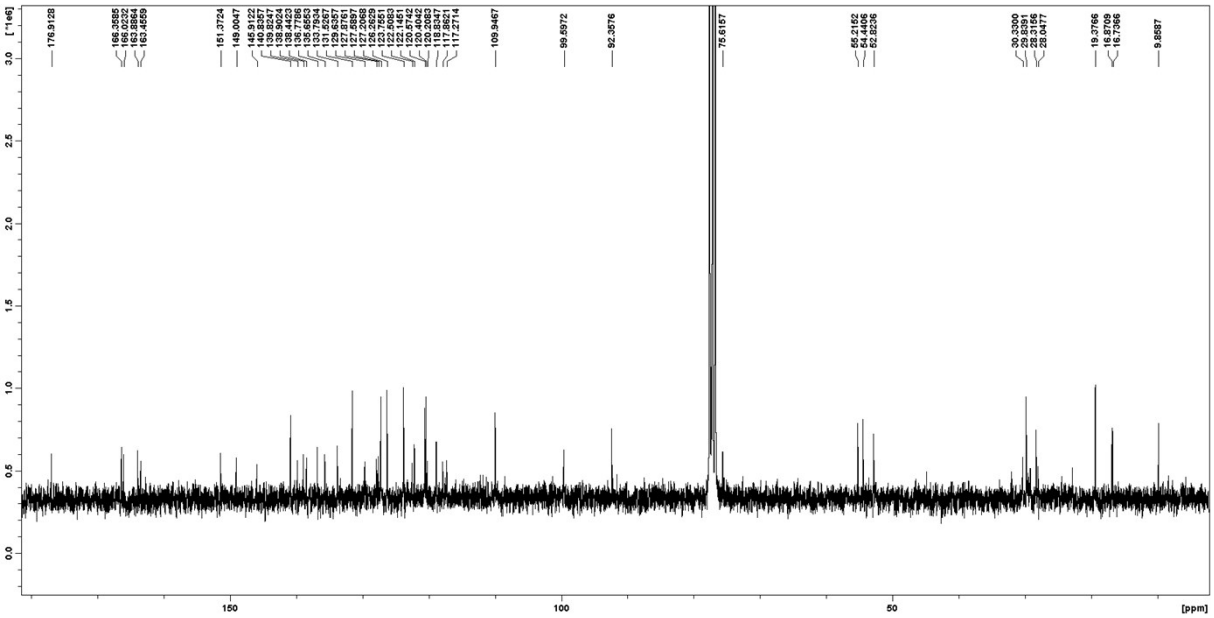




Dimer **27**







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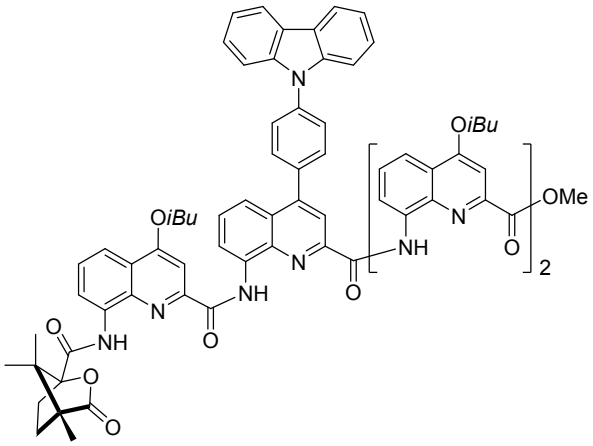

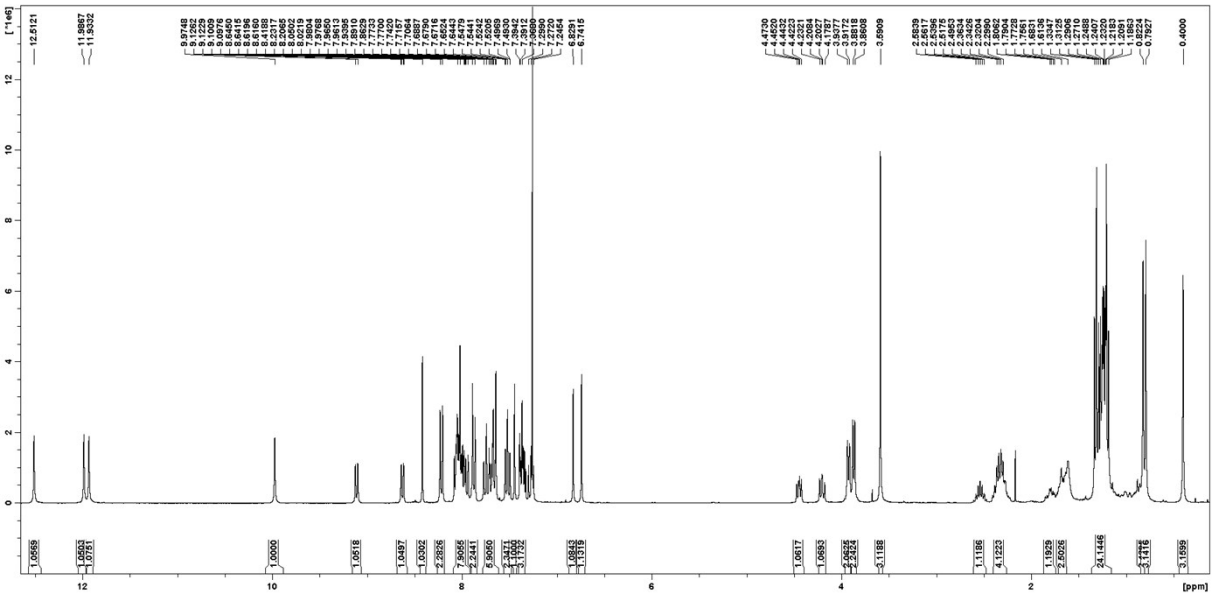

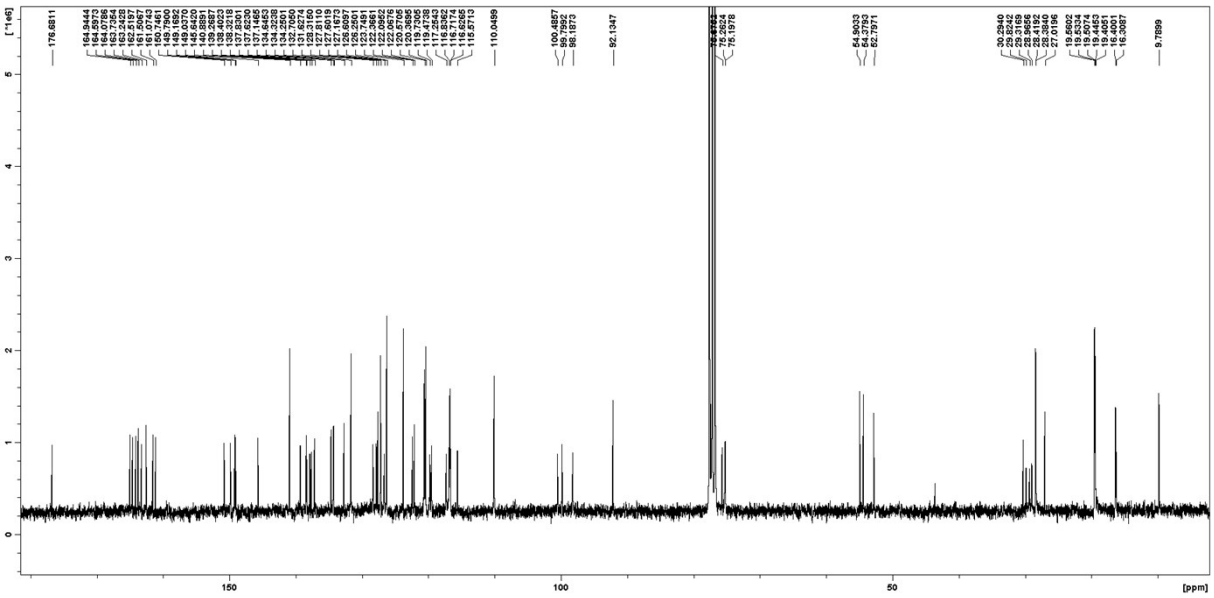

Tetramer **30**