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Synthesis and spontaneous self-assembly of non-planar aromatic macrocycles

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Supporting Information

Content

1. Material and methods

1.1 General information

All Solvents and chemicals were purchased from Finar, Rankem, Sigma-Aldrich, TCI Chemicals, Alfa-Aesar or BLD Chemicals and were used without further purification. The phenanthroline derivatives were prepared considering reported procedures for similar derivatives.[1] 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 performed using silica gel (100-200 mess). Preparative recycling GPC (gel permeation chromatography) was performed on the Japan Analytical Industry (JAI) LaboACE LC-5060 instrument using JAIGEL-2HR and JAIGEL-2.5HR (20×600 mm) columns at a flow rate of 7 mL/min with a mobile phase composed of 1% (vol/vol) ethanol and 0.5% (vol/vol) Et_3N in chloroform. Monitoring was carried out by UV detector at 254 nm, 300 nm, 400 nm, and 500 nm.

1.2 Nuclear Magnetic Resonance

NMR spectra were recorded on a Bruker Avance III HD 400 NMR spectrometer operating at 400 MHz for ^1H spectra and 100MHz for ^{13}C spectra. Chemical shifts are reported in parts per million (ppm, δ) relative to the ^1H residual signal of the deuterated solvent used. ^1H NMR splitting patterns with observed first-order coupling are designated as singlet (s), doublet (d), triplet (t), or quartet (q). Coupling constants (J) are reported in hertz. Samples were not degassed otherwise, it is specified. Data processing was performed with Topspin 3.6.4 software.

1.3 Mass Spectroscopy

High-resolution ESI mass spectra (HR-MS) were recorded using Agilent 6540 UHD Accurate-Mass Q-TOF LC/MS system under the following operation parameters: temperature 350 °C, dry nitrogen gas flow rate 10 L/min, nebulizer pressure 30 psi, Vcap 4000 and fragmentor voltage 100 V. Mass spectra were acquired either in the positive ion mode or in negative ion mode. Accurate mass analysis calibration was carried out by ESI-low concentration tuning mix solution provided by Agilent technologies, U.S.A. The accuracy error threshold was set at 5 ppm.

MALDI-TOF mass spectra were recorded using Bruker Autoflex maX MALDI TOF/TOF instrument. The matrix used was α-Cyano-4-hydroxycinnamic acid (CHCA).

1.4 Spectroscopic studies

Electronic absorption spectra were measured on Agilent Technologies Cary 8454 UV-Vis spectrophotometer. Variable temperature UV-Vis was carried out using Peltier temperature control. Steady-state emission spectra were recorded on an Edinburgh Instruments spectrophotometer equipped with standard cuvette holder SC-05 (Model: FS5) fitted with a PMT-900 detector and excited with a 150W CW Ozone-free xenon arc lamp. All solvents used for spectrophotometric analysis were of analytical grade.

1.5 Dynamic Light Scattering (DLS)

Dynamic Light Scattering (DLS) was measured using a HORIBA Ltd. made SZ-100-Z model instrument.

1.6 Microscopic studies

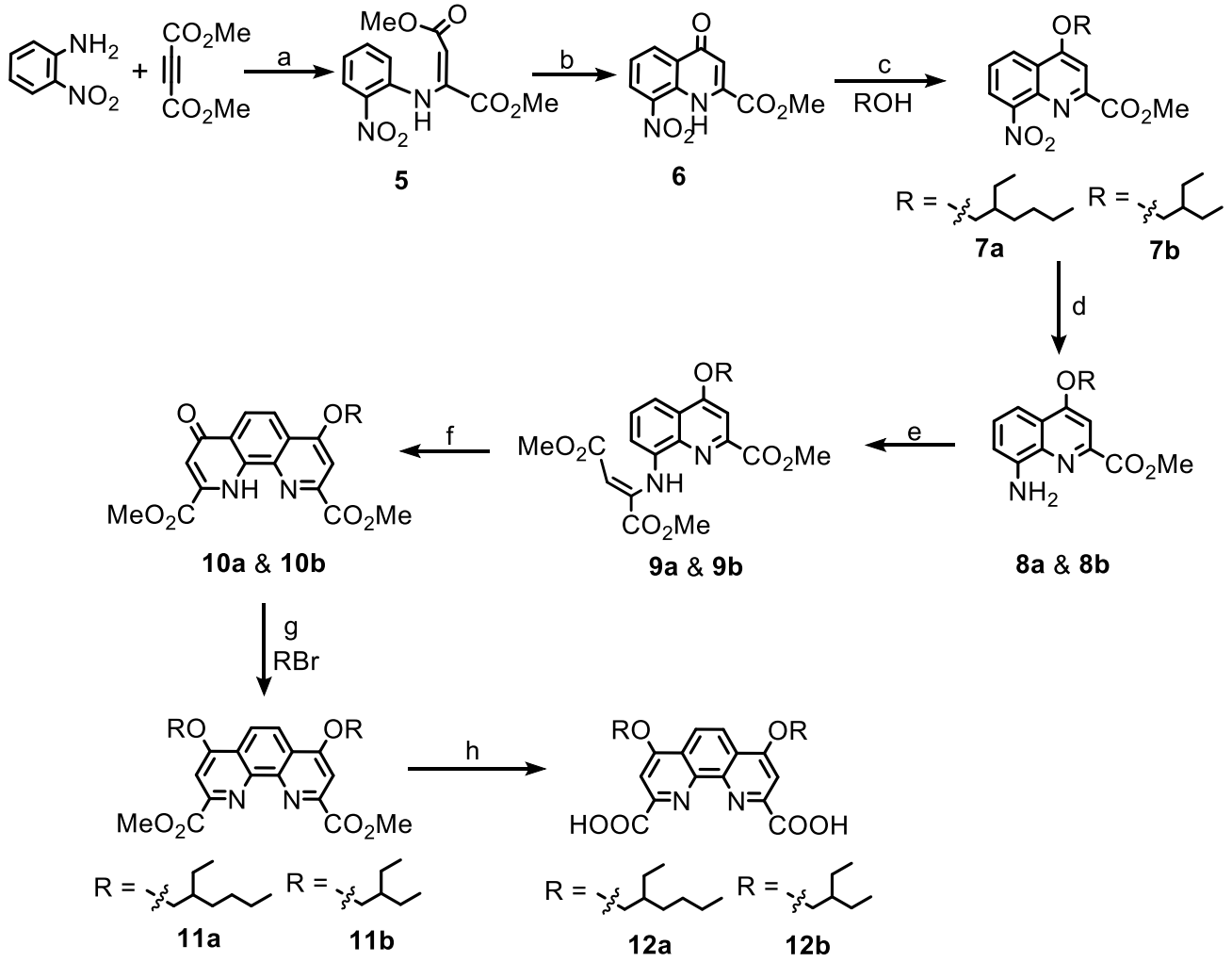
FESEM imaging was performed using a JEOL JSM-7610F PLUS instrument.

1.7 Sample preparation

The UV-vis spectroscopic measurements were carried out using ca. 10^{-6} M solutions of the macrocycles in tetrachloroethane (TCE) in a 1 cm and 0.1 cm quartz cuvette. Emission spectra were measured using 10^{-6} M solutions in TCE and a 0.5 cm quartz cuvette on a specified excitation wavelength. DLS measurements were carried out using 10^{-6} M solutions in TCE and a 1 cm quartz cuvette.

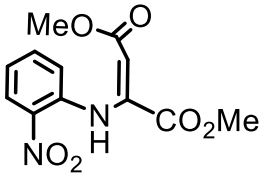
The samples for FESEM were prepared on a glass surface as follows: a typical concentration of 5 mM in chloroform was kept for 2 h to appear turbidity. Then one drop of each sample was deposited on the glass surface. The solvent was immediately blotted off the surface with tissue paper. After drying under vacuum, the samples were used for imaging.

2. Synthetic procedure



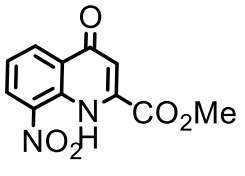
Scheme S1. Synthesis of **5** to **12**. a: MeOH, reflux, 12 hours; b: Diphenyl ether, 260 ˚C, 15 minutes; c: 2-ethylhexan-1-ol or 2-ethylbutane-1-ol, Diisopropyl azodicarboxylate, PPh_3, dry THF, room temperature, 12 hours; d: H_2, Pd/C, ethyl acetate, room temperature, 14 hours; e: Dimethyl acetylene dicarboxylate, MeOH, room temperature, 12 hours; f: Diphenyl ether, 260 ˚C, 20 min; g: 1-bromo-2-ethyl hexane or 1-bromo-2-ethyl butane, Dry DMF, K_2CO_3, 80 ˚C, 12 hours; h: KOH, MeOH, room temperature, 12 hours.

Dimethyl 2-((2-nitrophenyl)amino)fumarate, 5: In 250 round bottomed flask, 2-nitroaniline (14 gm, 101.34 mmol, 1 eq) was suspended in 200 ml of dry methanol, then dimethyl acetylene dicarboxylate (15.72gm, 110.61 mmol, 13.6 ml, 1.09 eq) was added dropwise under nitrogen atmosphere. The mixture was refluxed for 12 hours. After completion, the reaction mixture was allowed to cool down to room temperature, and then keep at -20 °C for few hours. Yellow crystalline precipitate formed was filtered and dried under vacuum (19 gm, 67% yield). ^{1}H NMR (400 MHz, $CDCl_3$, 298 K) δ ppm: 11.12 (s, 1H), 8.14 (d, J = 8.4, 1.6 Hz, 1H), 7.46 (t, J = 8.5, 7.1, 1.6 Hz, 1H), 7.08 (t, J = 8.4, 7.3, 1.2 Hz, 1H), 6.76 (d, J = 8.3, 1.2 Hz, 1H), 5.83 (s, 1H), 3.81 (s, 3H), 3.74 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$, 298 K) δ ppm: 168.13, 164.51, 143.63, 138.24, 137.04, 134.36, 126.37, 122.21, 120.54, 103.14, 53.22, 52.00. HRMS (ESI): m/z calcd for $C_{12}H_{12}N_2O_6$ $[M+H]^+$ 281.0768, Found 281.0723.



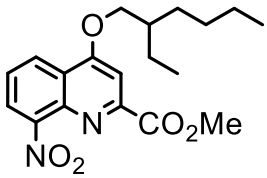
5

Methyl 8-nitro-4-oxo-1,4-dihydroquinoline-2-carboxylate, 6: In 500 ml round bottomed flask, diphenyl ether (350 ml) was taken and heated to 260 °C. After that, **5** (18 gm, 64.27 mmol, 1 eq) was added slowly and heated at same temperature for another 15 minutes. After that reaction mixture was then allowed to cool down to room temperature and hexane (2 lit) added. A brown precipitate formed was filtered and washed with more hexane until all diphenyl ether was completely removed. Then washed with cold methanol (-20 °C) obtained as reddish-brown coloured compound **6** (10 gm, 63 %). ^{1}H NMR (400 MHz, $CDCl_3$, 298 K) δ ppm: 11.78 (s, 1H), 8.73 (m, *J* = 7.2 Hz, 2H), 7.49 (t, *J* = 8.0 Hz, 1H), 7.07 (s, 1H), 4.09 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$, 298 K) δ ppm: 178.09, 162.41, 137.49, 136.08, 135.35, 134.38, 131.29, 128.40, 122.92, 113.64, 54.29. HRMS (ESI): m/z calcd for $C_{11}H_8N_2O_5$ $[M+H]^+$ 249.0506, Found 249.0490.



6

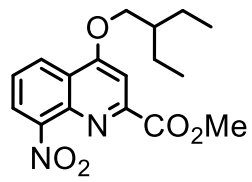
Methyl 4-((2-ethylhexyl)oxy)-8-nitroquinoline-2-carboxylate, 7a: In a dry 100 ml round bottomed flask, **6** (6 gm, 24.17 mmol, 1 eq), triphenyl phosphine (7 gm, 26.68 mmol, 1.1 eq) were taken, vacuum was applied and the mixture was degassed for 10 minutes, then filled with nitrogen gas. The mixture was added with 70 ml dry THF. The reaction mixture was cooled to 0 °C and diisopropyl azodicarboxylate (6.18 gm, 30.56 mmol, 6 ml, 1.26 eq) was added dropwise and stirred at 0 °C along with addition of 2-ethylhexan-1-ol (3.79 gm, 29.10 mmol, 4.55 ml, 1.2 eq). The reaction mixture was allowed to stir at room temperature for 12 hours. The progress of the reaction was monitored by



7a

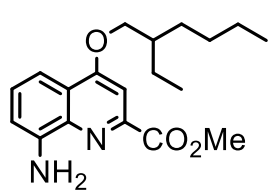
thin layer chromatography (TLC). After completion of reaction, solvent was removed under reduced pressure and crude redissolved in DCM:MeOH (1:3) at kept at -20 °C. The brown precipitate formed was filtered and was washed with cold methanol and dried under high vacuum to get compound **7a** (5 gm, 57% yield). ^{1}H NMR (400 MHz, $CDCl_3$, 298 K) δ ppm: δ 8.45 (d, J = 8.4, 1.4 Hz, 1H), 8.11 (d, J = 7.5, 1.5 Hz, 1H), 7.69 (m, 2H), 4.22 (d, J = 5.6, 1.6 Hz, 2H), 4.04 (s, 3H), 1.94 (p, J = 6.1 Hz, 1H), 1.66 (m, 4H), 1.44 (m, 4H), 1.00 (t, J = 7.5 Hz, 3H), 0.96 (m, 3H). ^{13}C NMR (100 MHz, $CDCl_3$, 298 K) δ ppm: 165.92, 163.07, 151.50, 148.57, 140.20, 126.50, 126.07, 125.22, 123.57, 102.34, 72.17, 53.54, 39.33, 30.74, 29.19, 24.17, 23.12, 14.18, 11.31. HRMS (ESI): m/z calcd for $C_{19}H_{24}N_2O_5$ $[M+H]^+$ 361.1758, Found 361.1738.

Methyl 4-(2-ethylbutoxy)-8-nitroquinoline-2-carboxylate, 7b: In a dry 100 ml round bottomed flask, **6** (4.5 gm, 18.14 mmol, 1 eq), triphenyl phosphine (7.13 gm, 27.21 mmol, 1.49 eq) were taken, vacuum was applied, and the mixture was degassed for 10 minutes, then filled with nitrogen gas. The mixture was added with 70 ml dry THF. The reaction mixture was cooled to 0 °C and diisopropyl azodicarboxylate (6.18 gm, 30.56 mmol, 6 ml, 1.68 eq) was added dropwise and stirred at 0 °C along with addition of 2-ethylbutane-1-ol (2.324 gm, 22.75mmol, 2.8 ml, 1.25 eq). The reaction mixture was allowed to stir at room temperature for 12 hours. The progress of the reaction was monitored by thin layer chromatography (TLC). After completion of reaction, solvent was removed under reduced pressure and crude redissolved in DCM: MeOH (1:3) at kept at -20 °C. The brown precipitate formed was filtered, washed with cold methanol, and dried under high vacuum to get compound **7b** (4 gm, 66.5%). ^{1}H NMR (400 MHz, $CDCl_3$, 298 K) δ ppm: 8.45 (d, J = 8.4, 1.5 Hz, 1H), 8.11 (d, J = 7.5, 1.5 Hz, 1H), 7.71 (m, 2H), 4.23 (d, J = 5.6 Hz, 2H), 4.04 (s, 3H), 1.88 (p, J = 6.1 Hz, 1H), 1.66 (m, 4H), 1.00 (t, J = 7.5 Hz, 6H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 165.90, 163.05, 151.48, 148.54, 140.18, 126.50, 126.05, 125.22, 123.54, 102.32, 71.80, 53.53, 40.84, 23.65, 11.32. HRMS (ESI): m/z calcd for $C_{17}H_{20}N_2O_5$ $[M+H]^+$ 333.1445, Found 333.1448.



7b

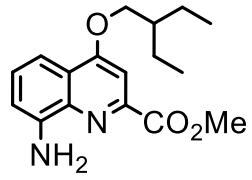
Methyl 8-amino-4-((2-ethylhexyl)oxy)quinoline-2-carboxylate, 8a: In a 250 mL round bottomed flask, **7a** (4.5 gm, 12.48 mmol, 1 eq) and Pd/C (531.49 mg) were taken and vacuum was applied. The mixture was suspended in 60 ml ethyl acetate and purged with nitrogen gas for 30 minutes. After that the round bottomed flask was connected with the hydrogen balloon. The reaction mixture was allowed to stir vigorously at room temperature for 12 hours. After completion, the



8a

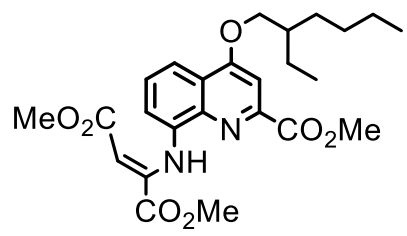
reaction mixture was filtered through celite, washed with ethyl acetate. The filtrate evaporated under reduced pressure and dried to get yellow coloured product **8a** (4 gm, 97 %). ^{1}H NMR (400 MHz, $CDCl_3$, 298 K) δ ppm: 7.51 (m, 2H), 7.36 (t, *J* = 8.3, 7.5 Hz, 1H), 6.93 (d, *J* = 7.5, 1.3 Hz, 1H), 5.11 (s, 2H), 4.14 (dd, *J* = 5.6, 1.6 Hz, 2H), 4.03 (s, 3H), 1.89 (p, *J* = 6.1 Hz, 1H), 1.66 (m, 4H), 1.41 (m, 4H), 0.98 (t, *J* = 7.5 Hz, 3H), 0.94 (t, J = 6.9 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$, 298 K) δ 166.57, 162.88, 145.99, 145.02, 138.48, 128.70, 123.19, 110.94, 109.77, 100.88, 71.24, 52.93, 39.42, 30.80, 29.23, 24.20, 23.13, 14.19, 11.34. HRMS (ESI): m/z calcd for $C_{19}H_{26}N_2O_3$ $[M+H]^+$ 331.2016, Found 331.1976.

Methyl 8-amino-4-(2-ethylbutoxy)quinoline-2-carboxylate, 8b: In a 250 mL round bottomed flask, **7b** (4 gm, 12.03 mmol, 1 eq) and Pd/C (513 mg) were taken and vacuum was applied. The mixture was suspended in 60 ml ethyl acetate and purged with nitrogen gas for 30 minutes. After that the round bottomed flask was connected with the hydrogen balloon. The reaction mixture was allowed to stir vigorously at room temperature for 12 hours. After completion, the reaction mixture was filtered through celite, washed with ethyl acetate. The filtrate evaporated under reduced pressure and dried to get yellow coloured product **8b** (3.5 gm, 96% yield). ^{1}H NMR (400 MHz, $CDCl_3$, 298 K) δ ppm: 7.52 (m, 2H), 7.39 (m, J = 8.32, 1H), 6.94 (d, J = 7.5, 1.2 Hz, 1H), 5.09 (s, 2H), 4.15 (d, J = 5.5 Hz, 2H), 4.03 (s, 3H), 1.83 (p, J = 6.1 Hz, 1H), 1.66 (m, 4H), 0.98 (t, J = 7.5 Hz, 6H). ^{13}C NMR (100 MHz, $CDCl_3$, 298 K) δ ppm: 166.55, 162.85, 145.95, 138.45, 128.69, 123.17, 110.93, 109.72, 109.69, 100.85, 70.85, 52.90, 40.94, 23.69, 11.34. HRMS (ESI): m/z calcd for $C_{17}H_{22}N_2O_3$ $[M+H]^+$ 303.1703, Found 303.1707.



8b

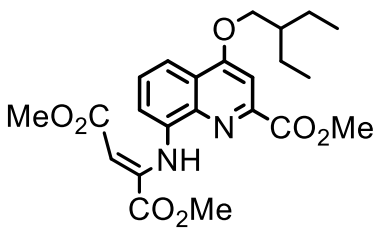
Dimethyl 2-((4-((2-ethylhexyl)oxy)-2-(methoxycarbonyl)quinolin-8-yl)amino)fumarate, 9a: : In a 250 mL round bottom flask, **8a** (3.1 gm, 9.38 mmol, 1eq) was dissolved in dry 100 mL methanol under the nitrogen atmosphere. After complete dissolution of the compound, dimethyl acetylene dicarboxylate (1.965 gm, 13.827 mmol, 1.7 mL, 1.47 eq) was added dropwise and reaction mixture was stirred at room temperature for 12 hours. After completion, the crude mixture was kept at -20 ˚C for few hours. The yellow precipitate formed was filtered and washed will cold methanol to obtain the product **9a** (3.7 gm, 83%). ^{1}H NMR (400 MHz, $CDCl_3$, 298 K) δ ppm: 11.14 (s, 1H), 7.80 (d, J = 8.3, 1.2 Hz, 1H), 7.58 (s, 1H), 7.46 (t, J = 8.0, 1H), 6.93 (d, J = 7.8, 1.2 Hz, 1H), 5.57 (s, 1H), 4.17 (d, J =



9a

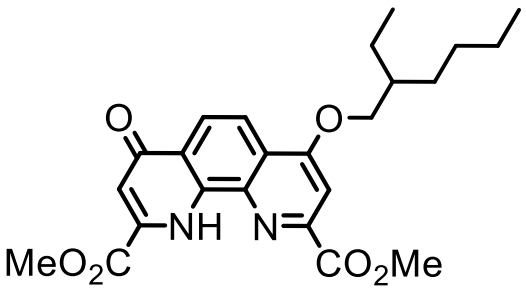
5.5, 1.5 Hz, 2H), 4.08 (s, 3H), 3.82 (s, 3H), 3.77 (s, 3H), 1.91 (p, J = 6.1 Hz, 1H), 1.65 (m, 4H), 1.36 (m, 4H), 0.99 (t, J = 7.5 Hz, 3H), 0.95 (t, J= 6.9 Hz, 3H).^{13}C NMR (100 MHz, $CDCl_3$). ^{13}C NMR (100 MHz, $CDCl_3$, 298 K) δ ppm: 169.14, 166.29, 165.31, 163.14, 147.54, 145.54, 139.94, 137.56, 127.51, 123.08, 115.23, 114.78, 101.40, 96.78, 71.55, 53.22, 52.91, 51.52, 39.41, 30.80, 29.23, 24.21, 23.14, 14.20, 11.35. HRMS (ESI): m/z calcd for $C_{25}H_{32}N_2O_7$ $[M+H]^+$473.2282, Found 473.2226.

Dimethyl 2-((4-(2-ethylbutoxy)-2-(methoxycarbonyl)quinolin-8-yl)amino)fumarate, 9b: In a 250 mL round bottom flask, **8b** (3.8 gm, 12.58 mmol, 1 eq) was dissolved in dry 120 mL methanol under the nitrogen atmosphere. After complete dissolution of the compound, dimethyl acetylene dicarboxylate (2.65 gm,, 18.65 mmol, 2.3 mL, 1.48 eq) was added dropwise. The reaction mixture was stirred at room temperature for 12 hours during which a yellow precipitate started to appear. After completion, the crude mixture was kept at -20 ˚C for few hours. The yellow precipitate formed was filtered and washed will cold methanol to obtain the product **9b** (4.5 gm, 81%). ^{1}H NMR (400 MHz, $CDCl_3$, 298 K) δ ppm: 11.14 (s, 1H), 7.81 (d, J = 8.4, 1.2 Hz, 1H), 7.59 (s, 1H), 7.46 (t, J = 7.8 Hz, 1H), 6.93 (d, J = 7.7, 1.1 Hz, 1H), 5.57 (s, 1H), 4.18 (d, J = 5.5 Hz, 2H), 4.08 (s, 3H), 3.82 (s, 3H), 3.77 (s, 3H), 1.85 (p, J = 6.1 Hz, 1H), 1.64 (m, 4H), 0.99 (t, J = 7.5 Hz, 6H). ^{13}C NMR (100 MHz, $CDCl_3$, 298 K) δ ppm: 169.12, 166.27, 165.29, 163.12, 147.52, 145.52, 139.91, 137.54, 127.49, 123.05, 115.22, 114.77, 101.37, 96.77, 71.17, 53.20, 52.89, 51.51, 40.93, 23.69, 11.35. HRMS (ESI): m/z calcd for $C_{23}H_{28}N_2O_7$ $[M+H]^+$ 445.1969, Found 445.1969.



9b

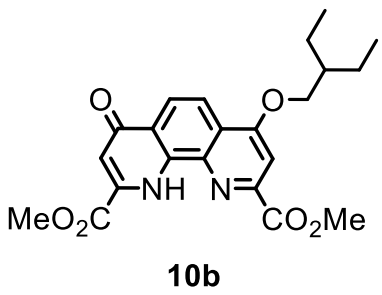
Dimethyl 7-((2-ethylhexyl)oxy)-4-oxo-1,4-dihydro-1,10-phenanthroline-2,9-dicarboxylate, 10a: In 500 ml round bottomed flask, diphenyl ether (150 ml) was taken and heated to 260 ˚C. When the temperature reached 260 °C, **9a** (5.1 gm, 10.79 mmol, 1 eq) was poured slowly and heated for another 15 minutes. reaction mixture was then allowed to cool down to room temperature and hexane was added (around 1 lit). The gel type precipitate formed was washed with more hexane to remove diphenyl ether completely and light-yellow coloured product **10a** was obtained (3.2 gm, 67%). ^{1}H NMR (400 MHz, $CDCl_3$, 298 K) δ ppm: 11.00 (s, 1H), 8.37 (d, J = 9.0 Hz, 1H), 8.02 (d, J = 9.0 Hz, 1H), 7.75 (s, 1H), 7.20 (s, 1H), 4.22 (d, J = 5.6 Hz, 2H), 4.10 (s, 6H), 1.95 (p, J = 6.2 Hz, 1H), 1.59 (m, 4H), 1.46 (m, 4H), 1.00 (t, J = 7.4 Hz, 3H), 0.93 (t, J = 6.9 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$, 298 K) δ ppm:



10a

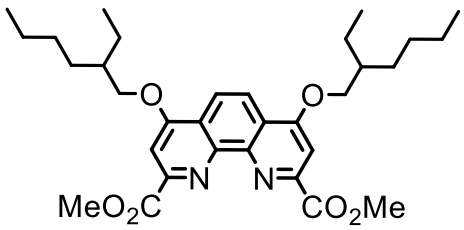
179.03, 165.75, 163.40, 163.01, 148.42, 139.64, 137.20, 135.99, 125.85, 123.92, 123.76, 117.07, 114.97, 104.34, 72.12, 53.95, 53.35, 39.38, 30.74, 29.23, 24.16, 23.13, 14.20, 11.32. HRMS (ESI): m/z calcd for $C_{24}H_{28}N_2O_6$ $[M+H]^+$ 441.2020, Found 441.1987.

Dimethyl 7-(2-ethylbutoxy)-4-oxo-1,4-dihydro-1,10-phenanthroline-2,9-dicarboxylate, 10b: In 500 ml round bottomed flask, diphenyl ether (200 ml) was taken and heated to 260 ˚C. When the temperature reached 260 °C, **9b** (6 gm, 13.50 mmol, 1 eq) was poured slowly and heated for another 15 minutes. reaction mixture was then allowed to cool down to room temperature and hexane was added (around 1 lit). The gel type precipitate formed was washed with more hexane to remove diphenyl ether completely and light-yellow coloured product **10b** was obtained (4.5 gm, 81%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 10.99 (s, 1H), 8.36 (d, J = 9.0 Hz, 1H), 8.02 (d, J = 9.0 Hz, 1H), 7.75 (s, 1H), 7.20 (s, 1H), 4.23 (d, J = 5.5 Hz, 2H), 4.10 (s, 6H), 1.94 (m, 1H), 1.61 (m, 4H), 1.01 (t, J = 7.4 Hz, 6H). ^{13}C NMR (100 MHz, $CDCl_3$) δ ppm: 178.92, 165.65, 163.30, 162.93, 148.31, 139.52, 137.10, 135.96, 125.75, 123.80, 123.64, 116.99, 114.88, 104.27, 71.72, 53.91, 53.30, 40.88, 23.61, 11.31. HRMS (ESI): m/z calcd for $C_{22}H_{24}N_2O_6$ $[M+H]^+$ 413.1707, Found 413.1692.



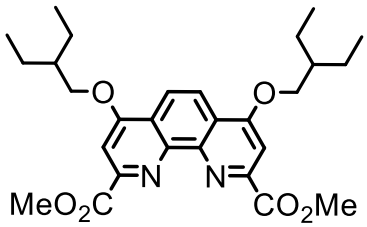
10b

Dimethyl 4,7-bis((2-ethylhexyl)oxy)-1,10-phenanthroline-2,9-dicarboxylate, 11a: In 100 ml round bottomed flask, **10a** (2.5 gm, 5.67 mmol, 1 eq) and K_2CO_3 (5.6 gm, 40.52 mmol, 6 eq) were taken. To the mixture, 40 ml dry DMF was added under nitrogen gas. Subsequently, 1-Bromo-2-ethylhexane (1.568 gm, 8.11 mmol, 1.4 mL, 1.2 eq) was added dropwise with constant stirring. Reaction mixture was heated at 80 ˚C for 12 hours. After completion, solvent was removed under reduced pressure, redissolved in chloroform, washed with water, brine solution and dried over anhydrous sodium sulphate. Purification of crude mixture was done by column chromatography in petroleum ether/ethyl acetate (70:30), yielding product **11a** as white solid (1.1 gm, 35%). ^{1}H NMR (400 MHz, $CDCl_3$, 298 K) δ ppm: 8.30 (s, 2H), 7.87 (s, 2H), 4.24 (d, J = 5.6, 1.9 Hz, 4H), 4.10 (s, 6H), 1.95 (p, J = 5.9 Hz, 2H), 1.59 (m, 8H), 1.45 (m, 8H), 1.01 (t, J = 7.5 Hz, 6H), 0.96 (t, J = 6.8 Hz, 6H). ^{13}C NMR (100 MHz, $CDCl_3$, 298 K) δ ppm: 166.70, 163.04, 149.36, 146.36, 123.08, 121.07, 104.20, 71.82, 53.16, 39.46, 30.80, 29.23, 24.22, 23.14, 14.19, 11.38.HRMS (ESI): m/z calcd for $C_{32}H_{44}N_2O_6$ $[M+H]^+$ 553.3272, Found 553.3230.



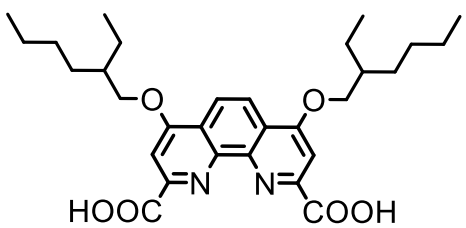
11a

Dimethyl 4,7-bis(2-ethylbutoxy)-1,10-phenanthroline-2,9-dicarboxylate, 11b: In 100 ml round bottomed flask, **10b** (2.2 gm, 5.33 mmol, 1 eq) and K_2CO_3 (2.94 gm, 21.27 mmol, 4 eq) were taken. To the mixture, 40 ml dry DMF was added under nitrogen gas. Subsequently, 1-Bromo-2-ethylbutane (969.13 mg, 5.87 mmol, 0.822 mL, 1.1 eq) was added dropwise with constant stirring. Reaction mixture was heated at 80 °C for 12 hours. After completion, solvent was removed under reduced pressure, redissolved in chloroform, washed with water, brine solution and dried over anhydrous sodium sulphate. Purification of crude mixture was done by column chromatography in petroleum ether/ethyl acetate (70:30), yielding product **11b** as white solid (1.3 gm, 49%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.30 (s, 2H), 7.88 (s, 2H), 4.25 (d, J = 5.6 Hz, 4H), 4.10 (s, 6H), 1.88 (m, 2H), 1.68 (m, 8H), 1.02 (t, J = 7.5 Hz, 12H). ^{13}C NMR (100 MHz, $CDCl_3$, 298 K) δ ppm: 166.70, 163.02, 149.38, 146.35, 123.07, 121.06, 104.17, 71.47, 53.14, 41.00, 23.73, 11.37. HRMS (ESI): m/z calcd for $C_{28}H_{36}N_2O_6$ $[M+H]^+$ 497.2646, Found 497.2646.



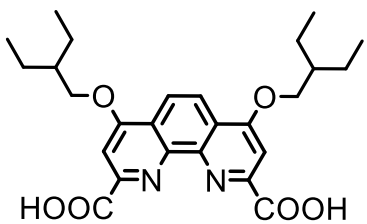
11b

4,7-bis((2-ethylhexyl)oxy)-1,10-phenanthroline-2,9-dicarboxylic acid, 12a: In a 25 ml round bottom flask, **11a** (350 mg, 0.63 m mol) was dissolved in 5 ml THF under inert condition. After that KOH (207 mg, 3.86 mmol, 6 eq) dissolved in 3 ml of methanol was added dropwise with constant stirring. The reaction mixture stirred at room temperature for 12 hours. After completion solvent was evaporate, redissolved into chloroform, washed with water, brine solution and dried over sodium sulphate, solvent evaporated under reduced pressure to get light brown powder as the product **12a** (310 mg, 93%). ^{1}H NMR (400 MHz, $CDCl_3$, 298 K) δ ppm: 8.51 (s, 2H), 8.12 (s, 2H), 4.48 (d, J = 5.5, 1.8 Hz, 4H), 2.04 (p, J = 6.1 Hz, 2H), 1.69 (m, 8H), 1.40 (m, 8H), 1.03 (t, J = 7.5 Hz, 6H), 0.93 (t, J = 6.9 Hz, 6H). HRMS (ESI): m/z calcd for $C_{30}H_{40}N_2O_6$ $[M+H]^+$ 525.2959, Found 525.2897.



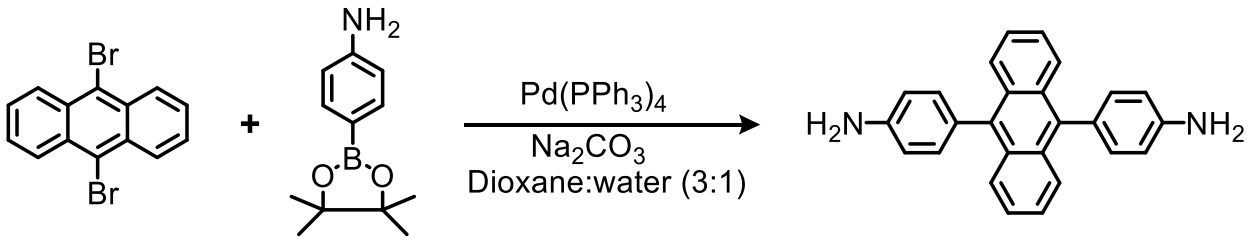
12a

4,7-bis(2-ethylbutoxy)-1,10-phenanthroline-2,9-dicarboxylic acid, 12b: In a 25 ml round bottom flask, **11b** (200 mg, 0.4 mmol, 1 eq) was dissolved in 5 ml THF under inert condition. After that KOH (160 mg, 2,85 mmol, 7.125 eq) dissolved in 3 ml of methanol was added drop wise with constant stirring. The reaction mixture stirred at room temperature for 12 hours. After completion, solvent was evaporated, redissolved into chloroform,



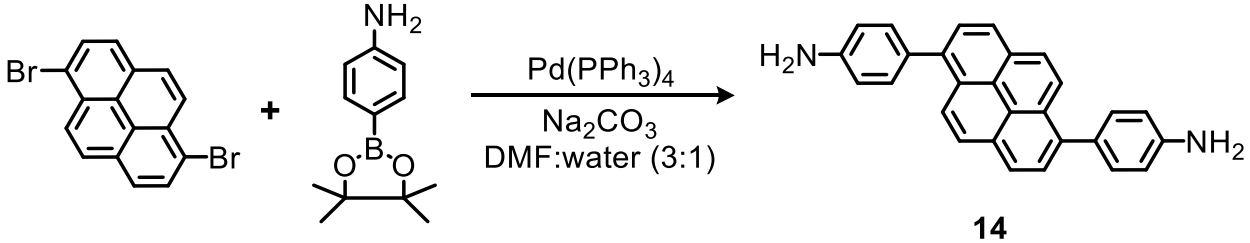
12b

washed with water, brine solution, and dried over sodium sulphate, solvent evaporated under reduced pressure to get light brown powder as the product **12b** (180 mg, 95%). ^{1}H NMR (400 MHz, $CDCl_3$, 298 K) δ ppm: 8.51 (s, 2H), 8.13 (s, 2H), 4.49 (d, J = 5.6 Hz, 4H), 2.03 (m, 2H), 1.64 (m, 8H), 1.04 (t, J = 7.5 Hz, 12H). HRMS (ESI): m/z calcd for $C_{26}H_{32}N_2O_6$ $[M+H]^+$ 469.2333, Found 469.2279.



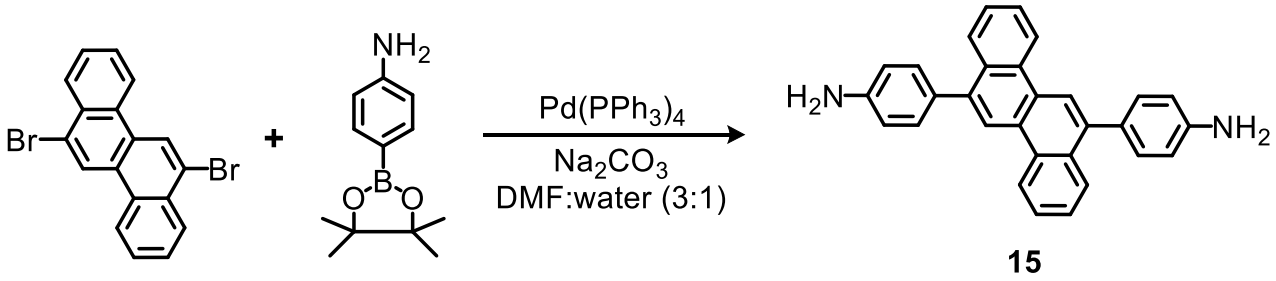
13

4,4'-(anthracene-9,10-diyl)di-aniline: 4,4'-(anthracene-9,10-diyl)dianiline was synthesized according to modified literature procedure.[2] In a 100 ml two neck round bottomed flask, 9,10-dibromoanthracene (300 mg, 0.892 mmol, 1 eq), 4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl) aniline (410.8 mg, 1.87 mmol, 2.1 eq), sodium carbonate (378.19 mg, 3.57 mmol, 4 eq) and Pd(PPh3)4 (102.84 mg, 0.089 mmol, 0.1 eq) were taken and a reflux condenser connected subsequently. The flux was purged with nitrogen gas. The mixture was added with a degassed solution of 1,4 dioxane and water (3:1, 32 ml) and refluxed at 100 °C for 48 hours under the nitrogen atmosphere. Thereafter, the reaction mixture was filtered through celite, diluted with chloroform. The organic fraction was separated, washed with water, brine solution and dried over anhydrous sodium sulphate. The crude product was purified by column chromatography using silica gel and eluting with chloroform/petroleum ether (1:1). The pure product collected as yellow solid (170 mg, 52% yield). ^{1}H NMR (400 MHz, $CDCl_3$, 298 K) δ ppm: 7.80 (dd, *J* = 6.8, 3.3 Hz, 4H), 7.31 (dd, *J* = 6.9, 3.2 Hz, 4H), 7.24 (d, *J* = 8.3 Hz, 4H), 6.92 (d, *J* = 8.3 Hz, 4H), 3.85 (s, 4H). ^{13}C NMR (100 MHz, $CDCl_3$, 298 K) δ ppm: 145.76, 137.15, 132.41, 130.52, 129.17, 127.31, 124.81, 115.18. HRMS (ESI): m/z calcd for $C_{26}H_{20}N_2$ $[M+H]^+$ 361.1699, Found : 361.1655.



14

4,4'-(pyrene-1,6-diyl) dianiline: 4,4'-(pyrene-1,6-diyl) dianiline was prepared by modified literature procedure.[3] In a 100 mL two neck round bottom flask, 1,6-dibromopyrene (262 mg, 0.727 mmol, 1eq), 4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl) aniline (326 mg, 1.48 mmol, 2.05 eq), $Pd(PPh_3)_4$ (80 mg, 0.069 mmol, 0.094 eq) and sodium carbonate (154 mg, 1.45 mmol, 2 eq)) were taken and connected with a refluxing condenser. The mixture was purged with nitrogen gas and a degassed solution of dimethylformamide (DMF) and water mixture (3:1, 32 ml) was added. The reaction mixture was then heated to 110°C for 24 hours. The hot suspension was filtered through celite to remove the catalyst and insoluble. The filtrate was concentrated under vacuum. Then, it was kept at -20 ^{0}C and the brown colour precipitate obtained was filtered and washed several times with diethyl ether to remove excess DMF. Yield (160 mg, 58%). ^{1}H NMR (400 MHz, $CDCl_3$, 298 K) δ ppm: 8.23 (d, *J* = 9.3 Hz, 2H), 8.15 (d, *J* = 7.8 Hz, 2H), 8.01 (d, *J* = 9.3 Hz, 2H), 7.95 (d, *J* = 7.8 Hz, 2H), 7.45 (d, *J* = 8.4 Hz, 4H), 6.89 (d, *J* = 8.4 Hz, 4H), 3.83 (s, 4H). ^{13}C NMR (100 MHz, $CDCl_3$, 298 K) δ ppm: 145.79, 137.97, 131.71, 130.20, 129.09, 127.89, 127.30, 125.54, 125.37, 124.42, 115.16. HRMS (ESI): m/z calcd for $C_{28}H_{20}N_2$ $[M+H]^+$ 385.1699, Found 385.1646.

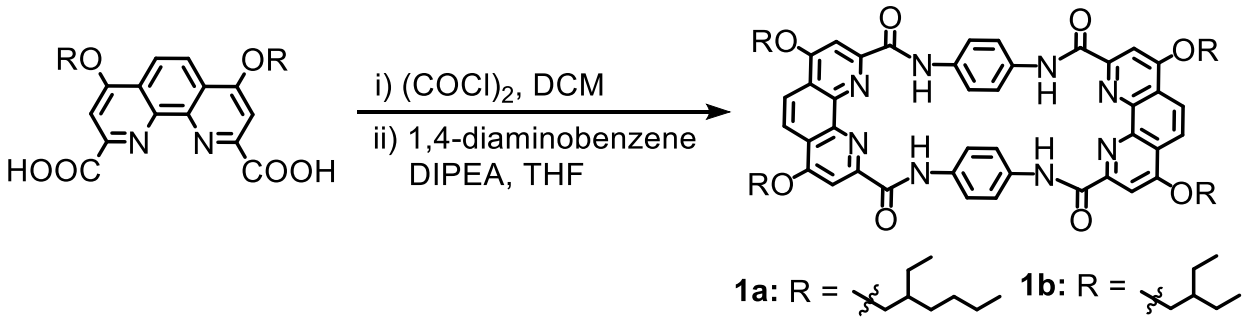


15

4,4'-(chrysene-6,12-diyl) dianiline4,4'-(chrysene-6,12-diyl)dianiline: The synthesis of 6,12-bis(4-aminophenyl)chrysene has been carried out following literature procedure with slight modification.[4] In a 100 ml two neck round button flask, 6,12-dibromochrysene (562 mg, 1.45 mmol, 1 eq), 4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl) aniline (644.03 mg, 2.94 mmol, 2.03 eq), sodium carbonate (800 mg, 7.55 mmol, 5.2 eq), $Pd(PPh_3)_4$ (167.56 mg, 0.145 mmol, 0.1 eq) were taken and connected with a refluxing condenser. The flask was purged with nitrogen gas and the mixture was added with degassed mixture of DMF:H_2O (3:1, 50 ml). The reaction mixture was refluxed at 100 °C for 24 hours under nitrogen atmosphere. The hot suspension was filtered through celite and diluted with water, extracted with dichloromethane. The organic part was washed with water, brine and dried over sodium sulphate. The residual solid obtained was recrystalised with DCM and petroleum ether. The recrystallised product collected as brown solid (400 mg, 67%). ^{1}H NMR (400 MHz, DMSO, 298 K) δ ppm: 8.98 (d, *J* = 8.5 Hz, 2H), 8.63 (s, 2H), 8.08 (d, *J* = 8.3 Hz, 2H), 7.72 (t, *J* = 7.6 Hz, 2H), 7.63 (t, *J* = 7.6 Hz, 2H), 7.32 (d, *J* = 7.9 Hz, 4H), 6.79 (d, *J* = 7.9 Hz, 4H), 5.32 (s, 4H). ^{13}C NMR (100 MHz, DMSO, 298

K) δ ppm: 148.33, 139.07, 130.84, 130.72, 130.36, 127.48, 126.62, 126.41, 126.38, 123.81, 121.14, 113.79. HRMS (ESI): m/z calcd for $C_{30}H_{22}N_2$ $[M+H]^+$ 411.1856, Found 411.1812.

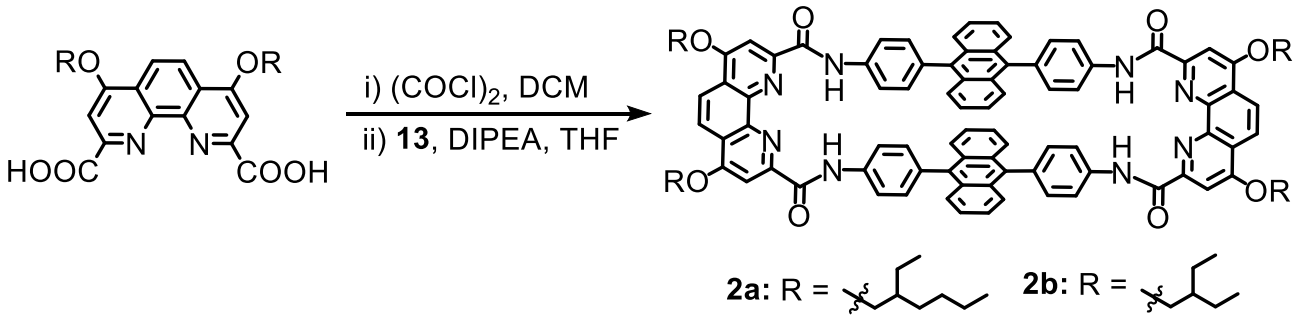
Synthesis of macrocycle:



Macrocycle 1a: In a 10 ml round button flask, **12a** (100 mg, 0.190 mmol, 1 eq) was dissolved into dry DCM (2 ml) and oxalyl chloride (239.2 mg, 1.9 mmol, 0.162 mL, 10 eq) was added dropwise at 0 °C. After the reaction mixture was stirred for 2 hours at room temperature under inert condition, solvent was evaporated under high vacuum and dried for 3 hours. The acid chloride formed was used as it is without further purification for the macrocyclization reaction. In the same flask 5 ml dry THF was used to dissolve acid chloride. Subsequently, 1,4-diaminobenzene (19.89 mg, mg, 0.184 mmol, 0.96 eq), dissolved in 5 ml dry THF and DIPEA (193.28 mg, 1.49 mmol, 0.256 mL, 7.84 eq) in another 10 ml round bottom, was added dropwise at 0 °C. The crude mixture was stirred for 12 hrs at room temperature. After completion of reaction solvent was evaporated under vacuum, redissolved in chloroform. The organic part was washed with 5% citric acid, water and then saturated brine solution. The combined organic layer was dried with sodium sulphate and concentrated by under reduced pressure. The crude mixture obtained was purified by gel permeation chromatography (GPC) to yield macrocycle as light-yellow product (13 mg, 6%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 11.28 (s, 4H), 8.29 (s, 4H), 7.98 (s, 4H), 7.82 (s, 8H), 4.32 (d, J = 5.6 Hz, 8H), 2.00 (m, 4H), 1.60 (m, 16), 1.41 (m, 16H), 1.05 (t, J = 7.4 Hz, 12H), 0.95 (t, J = 6.9 Hz, 12H). MALDI-TOF Mass: m/z calcd for $C_{72}H_{88}N_8O_8$ $[M+H]^+$ 1193.679, Found 1193.576.

Macrocycle 1b: In a 10 ml round button flask, **12b** (100 mg, 0.213 mmol, 1 eq) was dissolved into dry DCM (2 ml) and oxalyl chloride (268.64 mg,, 2.13 mmol, 0.183 mL, s10 eq) was added dropwise at 0 °C. After the reaction mixture was stirred for 2 hours at room temperature under inert condition, solvent was evaporated under high vacuum and dried for 3 hours. The acid chloride formed was used as it is without further purification for the macrocyclization reaction. In the same flask 2 ml dry THF

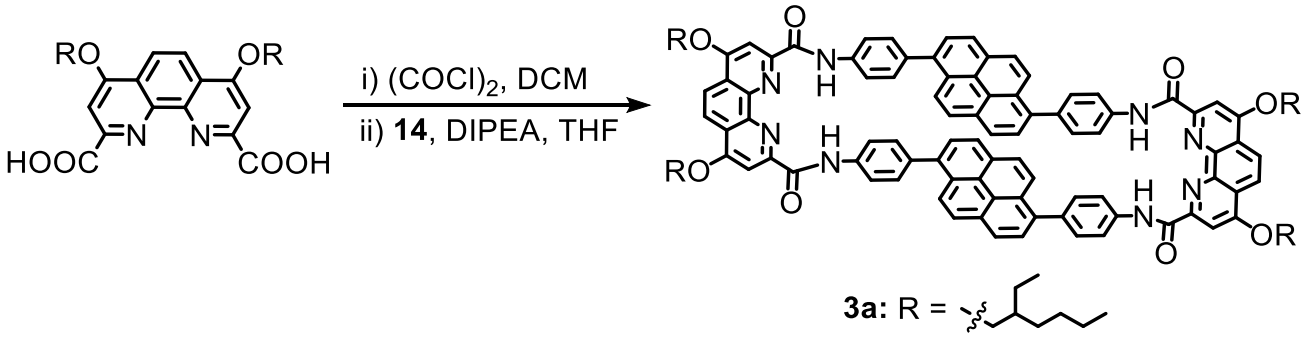
was used to dissolve acid chloride. Subsequently, 1,4-diaminobenzene (23.03 mg, 0.213 mmol, 1 eq), dissolved in 5 ml dry THF and DIPEA (220.24 mg, 1.704 mmol, 0.29 mL, 8 eq), in another 10 ml round bottom, was added dropwise at 0 °C. The crude mixture was stirred for 12 hrs at room temperature. After completion of reaction, solvent was evaporated under vacuum, redissolved in chloroform. The organic part was washed with 5% citric acid, water and then saturated brine solution. The combined organic layer was dried with sodium sulphate and concentrated by under reduced pressure. The crude mixture obtained was purified by gel permeation chromatography (GPC) to yield macrocycle as light-yellow product (12 mg, 6%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 11.27 (s, 4H), 8.28 (s, 4H), 7.97 (s, 4H), 7.81 (s, 8H), 4.32 (d, *J* = 5.7 Hz, 8H), 1.97 – 1.90 (m, 4H), 1.65 (d, *J* = 9.9 Hz, 16H), 1.05 (t, *J* = 7.5 Hz, 24H). MALDI-TOF Mass: m/z calcd for $C_{64}H_{72}N_8O_8$ $[M+H]^+$ 1081.554, Found 1081.664.



Macrocycle 2a: In a 10 ml round button flask, **12a** (100 mg, 0.190 m mol, 1 eq) was dissolved into dry DCM (3 ml) and oxalyl chloride (293.6 mg, 2.33 mmol, 0.2 mL, 12 eq) was added dropwise at 0 °C. After stirring the reaction mixture for 2 hours at room temperature under inert condition, solvent was evaporated under high vacuum and dried for 3 hours. The acid chloride formed was used insitu without further purification for the macrocyclization reaction. In the same flask 5 ml dry THF was used to dissolve acid chloride. Subsequently, **13** (70 mg, 0.194 mmol, 1.02 eq), dissolved 5 ml dry THF and DIPEA (203.85 mg, 1.57 mmol, 0.27 mL, 8 eq) in another 10 ml round bottom, was added dropwise at 0 °C. The crude mixture was stirred for 12 hrs at room temperature. After completion of reaction solvent was evaporated under vacuum, crude redissolved in chloroform. The organic part was washed with 5% citric acid, water and then saturated brine solution. The combined organic layer was dried with sodium sulphate and concentrated by under reduced pressure. The crude mixture obtained was purified by gel permeation chromatography (GPC) to yield macrocycle as light-yellow product **2a** (30 mg, 9%). ^{1}H NMR (400 MHz, $CDCl_3$, 298K) δ ppm: 11.25 (s, 4H), 8.38 (s, 4H), 8.20 (d, J = 7.9 Hz, 8H), 8.14 (s, 4H), 7.61 (dd, J = 6.9, 3.3 Hz, 8H), 7.44 (d, J = 8.0 Hz, 8H), 7.05 (dd, J = 7.0, 3.2 Hz, 8H), 4.38 (dd, J = 5.7, 2.3 Hz, 8H), 2.02 (q, J = 6.1 Hz, 4H), 1.63 (m, 16H), 1.50 (m, 16H), 1.07

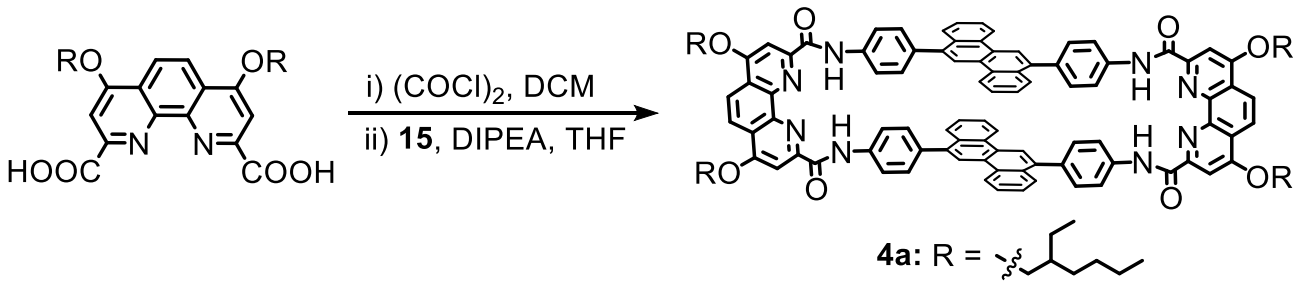
(t, J = 7.4 Hz, 12H), 0.97 (t, J = 7.0 Hz, 12H). MALDI-TOF Mass: m/z calcd for $C_{112}H_{112}N_8O_8$ $[M+H]^+$ 1698.871, Found 1698.869.

Macrocycle 2b: In a 10 ml round button flask, **12b** (81 mg, 0.172 mmol, 1 eq) was dissolved into dry DCM (4 ml) and oxalyl chloride (215.72 mg, 1.71 mmol, 0.147 mL, 9.9 eq) was added dropwise at 0 °C. After stirring the reaction mixture for 2 hours at room temperature under inert condition, solvent was evaporated under high vacuum and dried for 3 hours. The acid chloride formed was used insitu without further purification for the macrocyclization reaction. In the same flask 6 ml dry THF was used to dissolve acid chloride. Subsequently, **13** (61.92 mg, 0.171 mmol, 1 eq), dissolved 5 ml dry THF and DIPEA (180.44 mg, 1.39 mmol, 0.239 mL, 8 eq) in another 10 ml round bottom, was added dropwise at 0 °C. The crude mixture was stirred for 12 hrs at room temperature. After completion of reaction solvent was evaporated under vacuum, crude redissolved in chloroform. The organic part was washed with 5% citric acid, water and then saturated brine solution. The combined organic layer was dried with sodium sulphate and concentrated by under reduced pressure. The crude mixture obtained was purified by gel permeation chromatography (GPC) to yield macrocycle as light-yellow product **2b** (14 mg, 5%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 11.25 (s, 4H), 8.38 (s, 4H), 8.20 (d, *J* = 7.9, Hz, 8H), 8.15 (s, 4H), 7.61 (dd, *J* = 6.9, 3.3 Hz, 8H), 7.44 (d, *J* = 7.9 Hz, 8H), 7.05 (dd, *J* = 6.9, 3.3 Hz, 10H), 4.39 (d, *J* = 5.6 Hz, 8H), 2.02 – 1.93 (m, 4H), 1.67 (dt, *J* = 13.7, 7.1 Hz, 16H), 1.07 (t, *J* = 7.5 Hz, 24H). MALDI-TOF Mass: m/z calcd for $C_{104}H_{96}N_8O_8$ $[M+H]^+$ 1586.745, Found 1586.572.



Macrocycle 3a: In a 10 ml round button flask, **12a** (80 mg, 0.152 mmol, 1 eq) was dissolved into dry DCM (3 ml) and oxalyl chloride (239.26 mg, 1.9 mmol, 0.162 mL, 12.5 eq) was added dropwise at 0 °C. After the reaction mixture was stirred for 2 hours at room temperature under inert condition, solvent was reduced under high vacuum and dried for 3 hours. The acid chloride formed was used insitu without further purification for the macrocyclization reaction. In the same flask 6 ml dry THF was used to dissolve acid chloride. Subsequently, **14** (58.44 mg, 0.152 mmol, 1eq), dissolved 5 ml dry

THF and DIPEA (159.305 mg, 1.23 mmol, 0.21 mL, 8 eq) in another 10 ml round bottom, was added dropwise at 0 °C. The crude mixture was stirred for 12 hrs at room temperature. After completion of reaction solvent was evaporated under vacuum, redissolved in chloroform. The organic part was washed with 5% citric acid, water and then saturated brine solution. The combined organic layer was dried with sodium sulphate and concentrated by under reduced pressure. The crude mixture obtained was purified by gel permeation chromatography (GPC) to yield macrocycle as light-yellow product **3a** (12 mg, 4.5%). ^{1}H NMR (400 MHz, $CDCl_3$, 328K) δ ppm: 11.15 (s, 4H), 8.35 (s, 4H), 8.18 (m, 16H), 7.76 (d, J = 7.7 Hz, 4H), 7.69 (m, 12H), 7.59 (d, J = 7.8 Hz, 4H), 4.38 (d, J = 5.7 Hz, 8H), 2.08 (m, 4H), 1.68 (m, 16H), 1.49 (m, 16H), 1.09 (t, J = 7.4 Hz, 12H), 0.98 (t, J = 6.9 Hz, 12H). MALDI-TOF Mass: m/z calcd for $C_{116}H_{112}N_8O_8$ $[M+H]^+$ 1746.870, Found 1746.858.



Macrocycle 4a: In a 10 ml round button flask, **12a** (80 mg, 0.152 mmol, 1 eq) was dissolved into dry DCM (4 ml) and oxalyl chloride (176.16 mg, 1.39 mmol, 0.12 ml, 9 eq) was added dropwise at 0 °C. After stirring the reaction mixturefor 2 hours at room temperature under inert condition, solvent was reduced under high vacuum and dried for 3 hours. The acid chloride formed was used insitu without further purification for the macrocyclization reaction. In the same flask 6 ml dry THF was used to dissolve acid chloride. Subsequently, **15** (61.57 mg, 0.149 mmol, 0.98 eq), dissolved 5 ml dry THF and DIPEA (158.55 mg, 1.22 mmol, 0.21 ml, 8eq) in another 10 ml round bottom, was added dropwise at 0 °C. The crude mixture was stirred for 12 hrs at room temperature. After completion of the reaction solvent was evaporated under vacuum, redissolved in chloroform. The organic part was washed with 5% citric acid, water and then saturated brine solution. The combined organic layer was dried with sodium sulphate and concentrated by under reduced pressure. The crude mixture obtained was purified by gel permeation chromatography (GPC) to yield macrocycle as light-yellow product (15 mg, 5.5%). (^{1}H NMR (400 MHz, $C_2D_2Cl_4$, 353K) δ ppm: 10.47 (s, 4H), 7.75 (m, 4H), 7.71 (s, 8H), 7.50 (d, J = 7.9 Hz, 8H), 7.44 (s, 4H), 7.24 (m, 4H), 7.02 (d, J = 8.0 Hz, 8H), 6.55 (m, 8H), 3.71 (d, J = 5.9 Hz, 8H), 1.43 (m, 4H), 1.01 (m, 16H), 0.84 (m, 16H), 0.44 (t, J = 7.3 Hz, 12H), 0.34 (t, J = 7.0 Hz, 12H). MALDI-TOF Mass: m/z calcd for $C_{120}H_{116}N_8O_8$ $[M+H]^+$ 1798.902, Found 1798.934.

3. Characterization

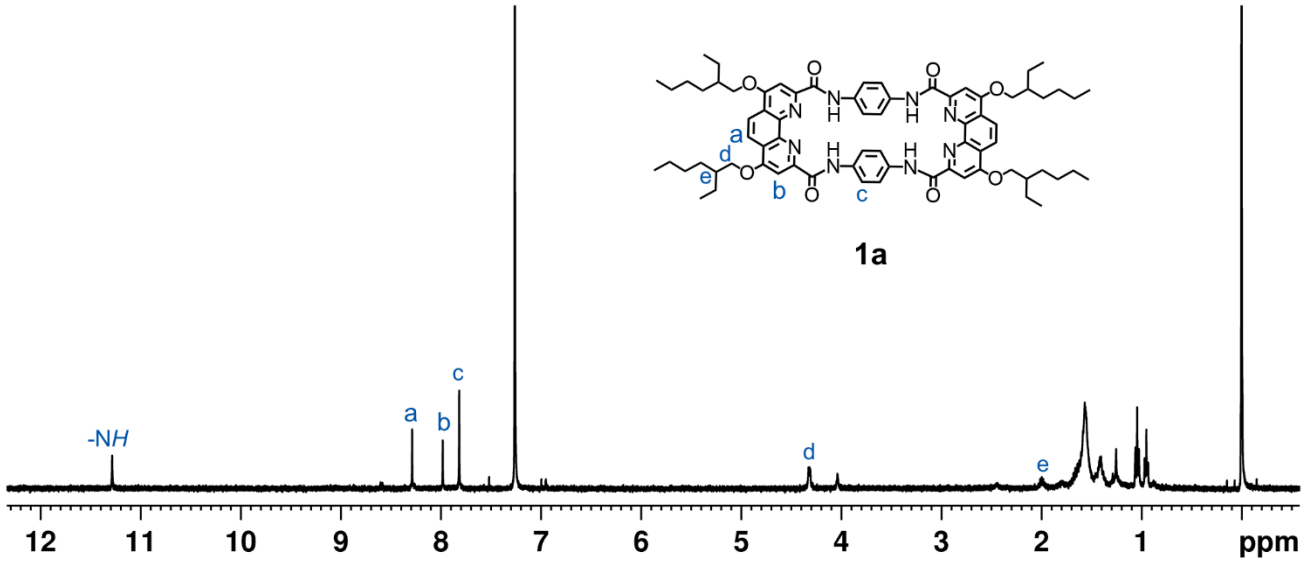


Fig. S1 ^{1}H-NMR spectra of macrocycle **1a** in $CDCl_3$ at 298 K.

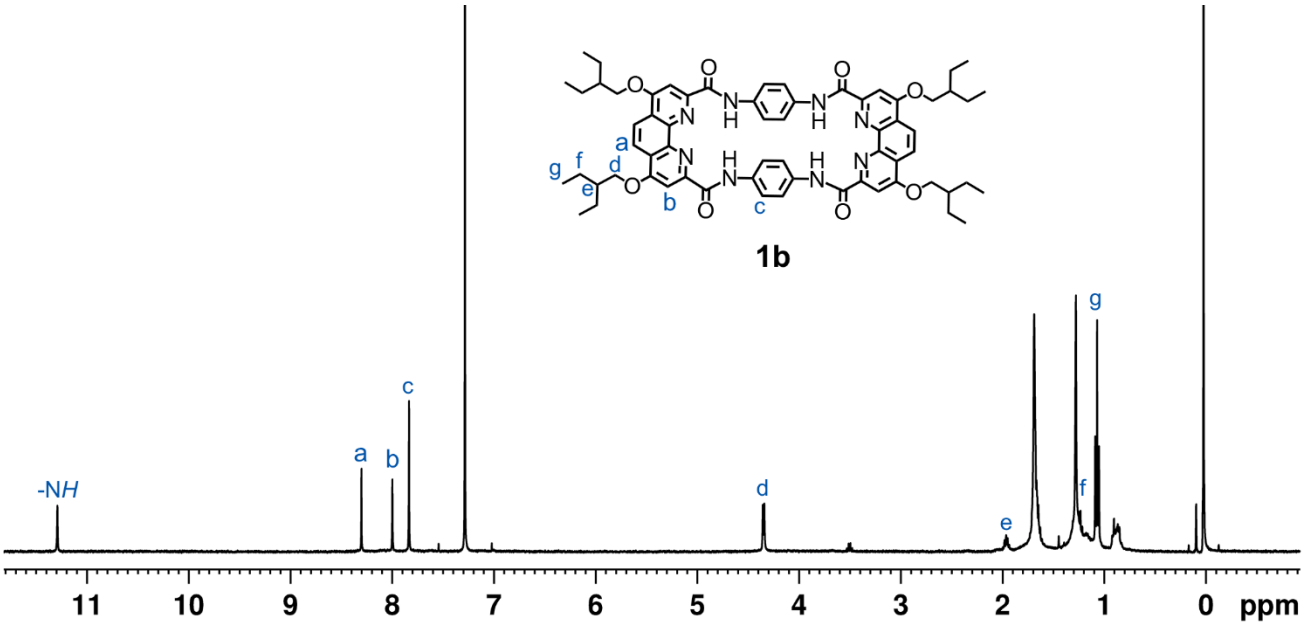


Fig. S2 ^{1}H-NMR spectra of macrocycle **1b** in $CDCl_3$ at 298 K.

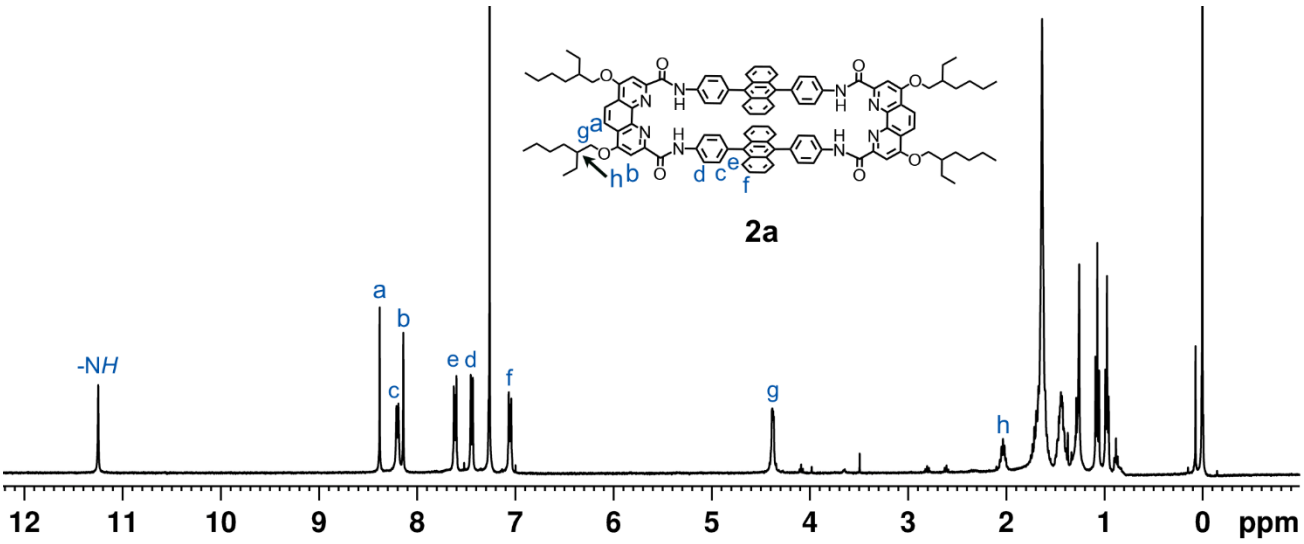


Fig. S3 ^{1}H-NMR spectra of macrocycle **2a** in $CDCl_3$ at 298 K.

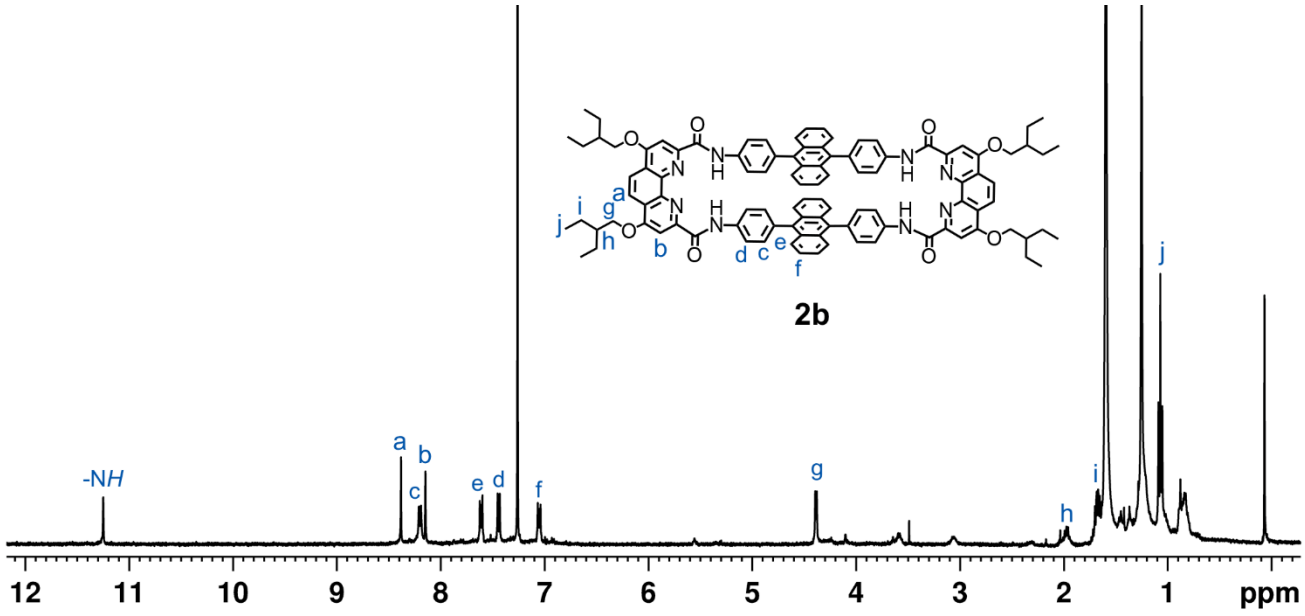


Fig. S4 ^{1}H-NMR spectra of macrocycle **2b** in $CDCl_3$ at 298 K.

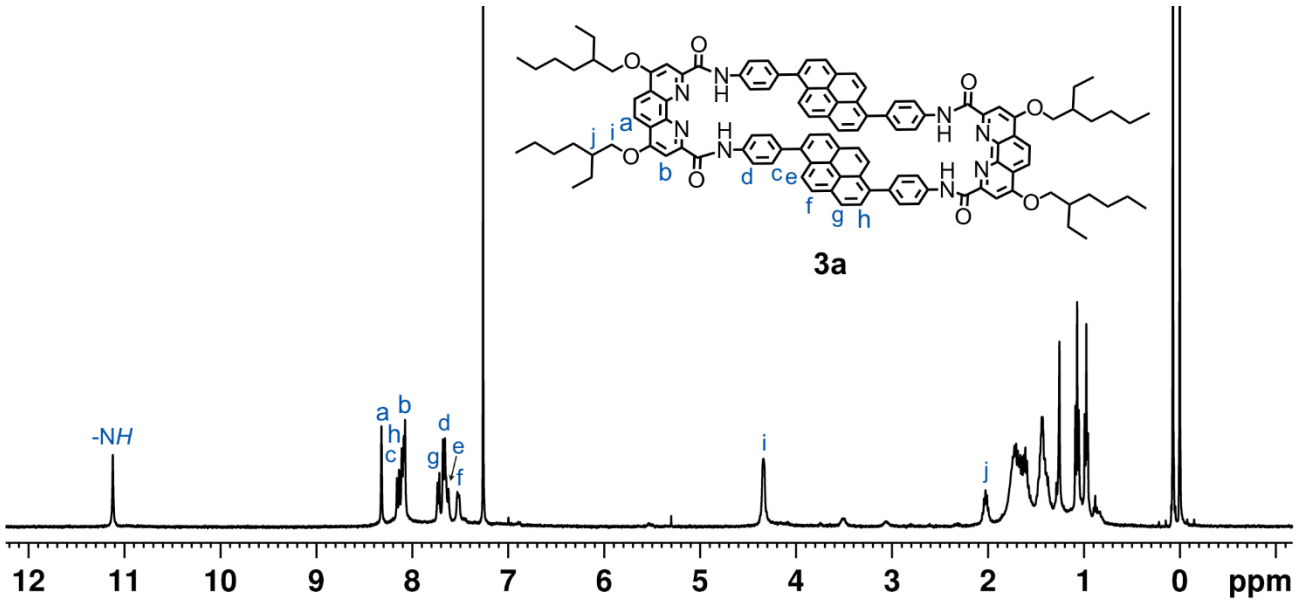


Fig. S5 ^{1}H-NMR spectra of macrocycle **3a** in $CDCl_3$ at 328 K.

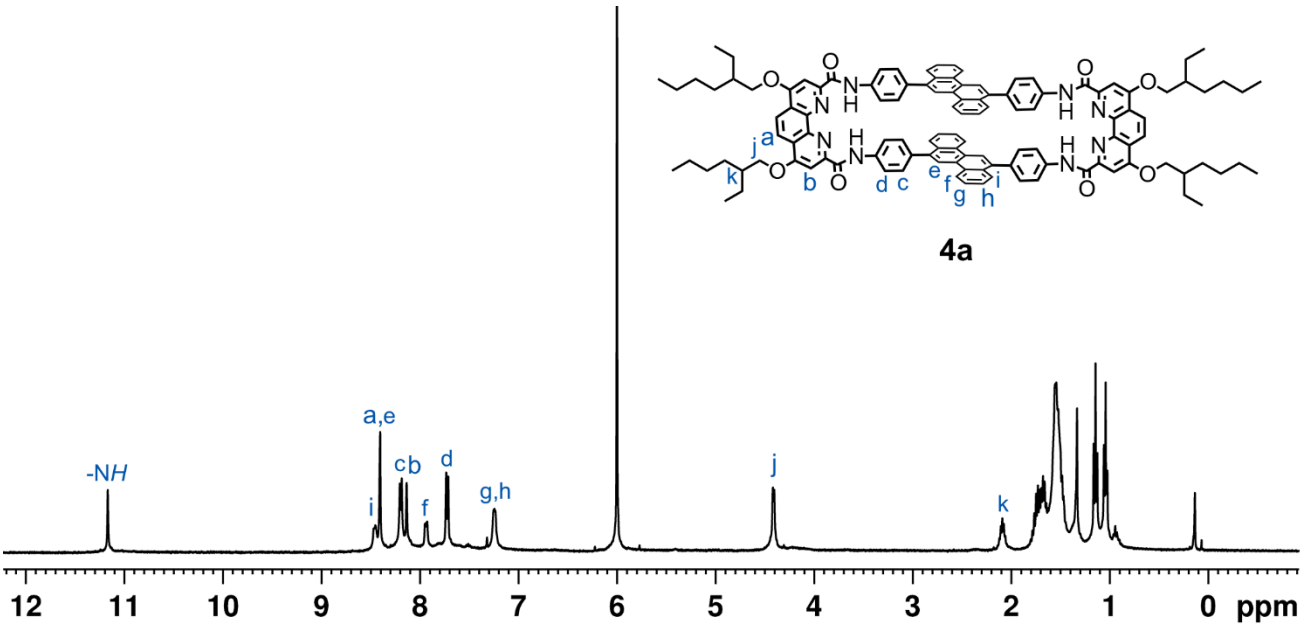


Fig. S6 ^{1}H-NMR spectra of macrocycle **4a** in $C_2D_2Cl_4$ at 353 K.

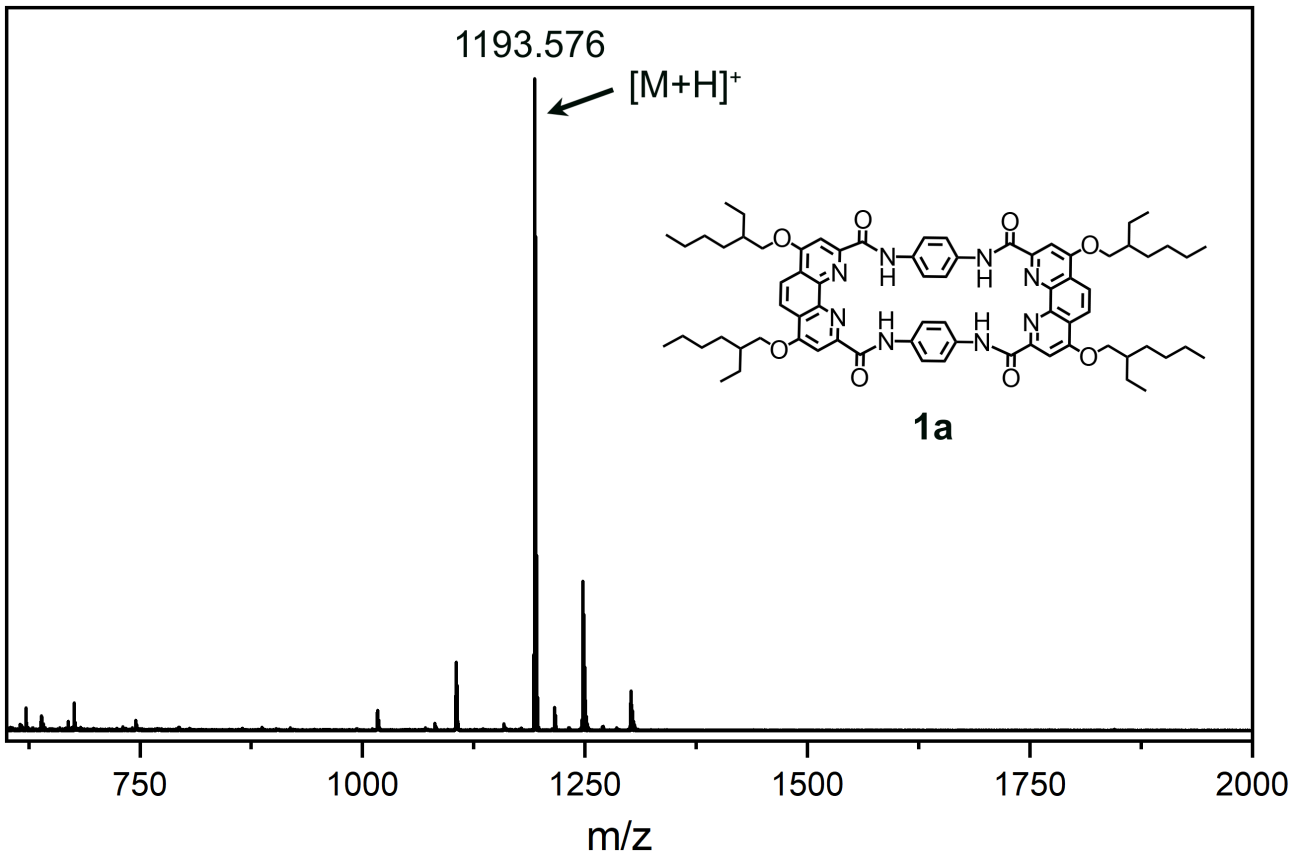


Fig. S7 MALDI-TOF mass spectra of **1a**.

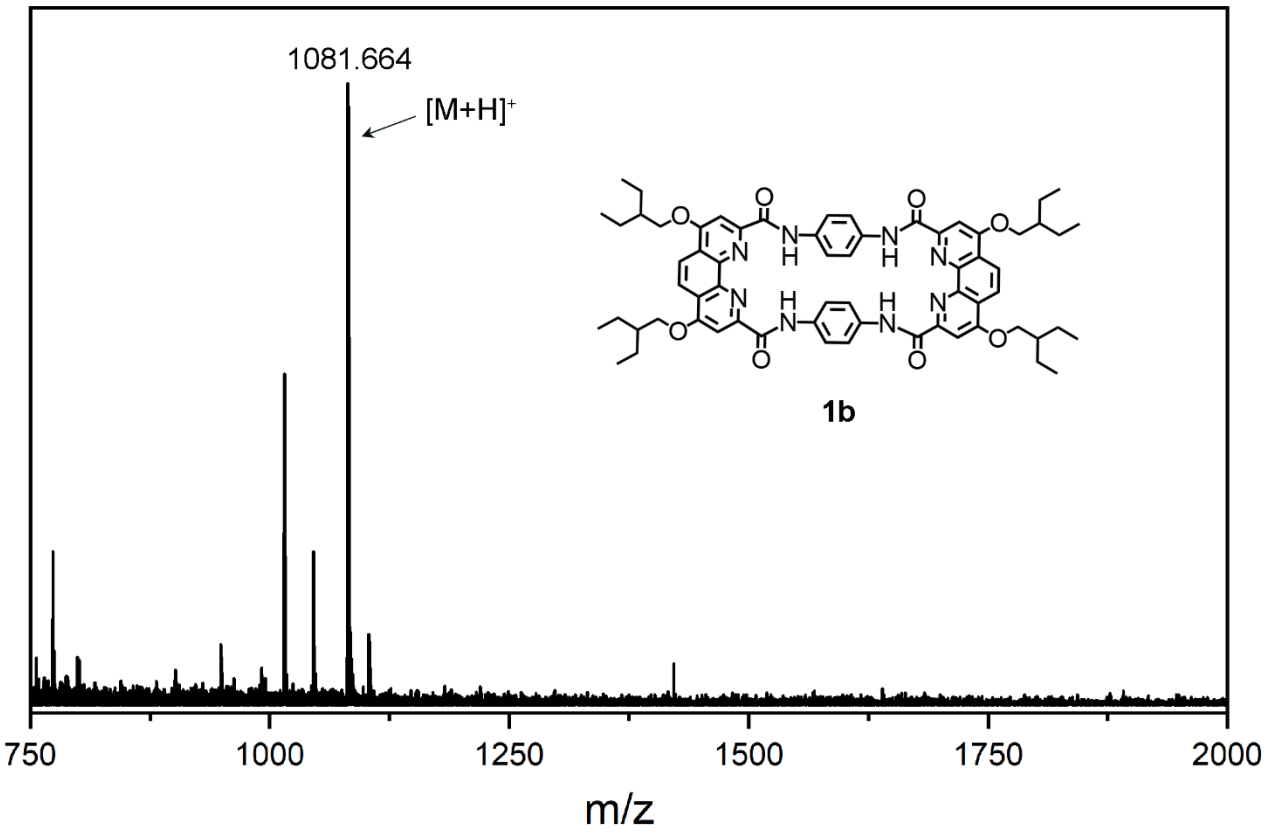


Fig. S8 MALDI-TOF mass spectra of **1b**.

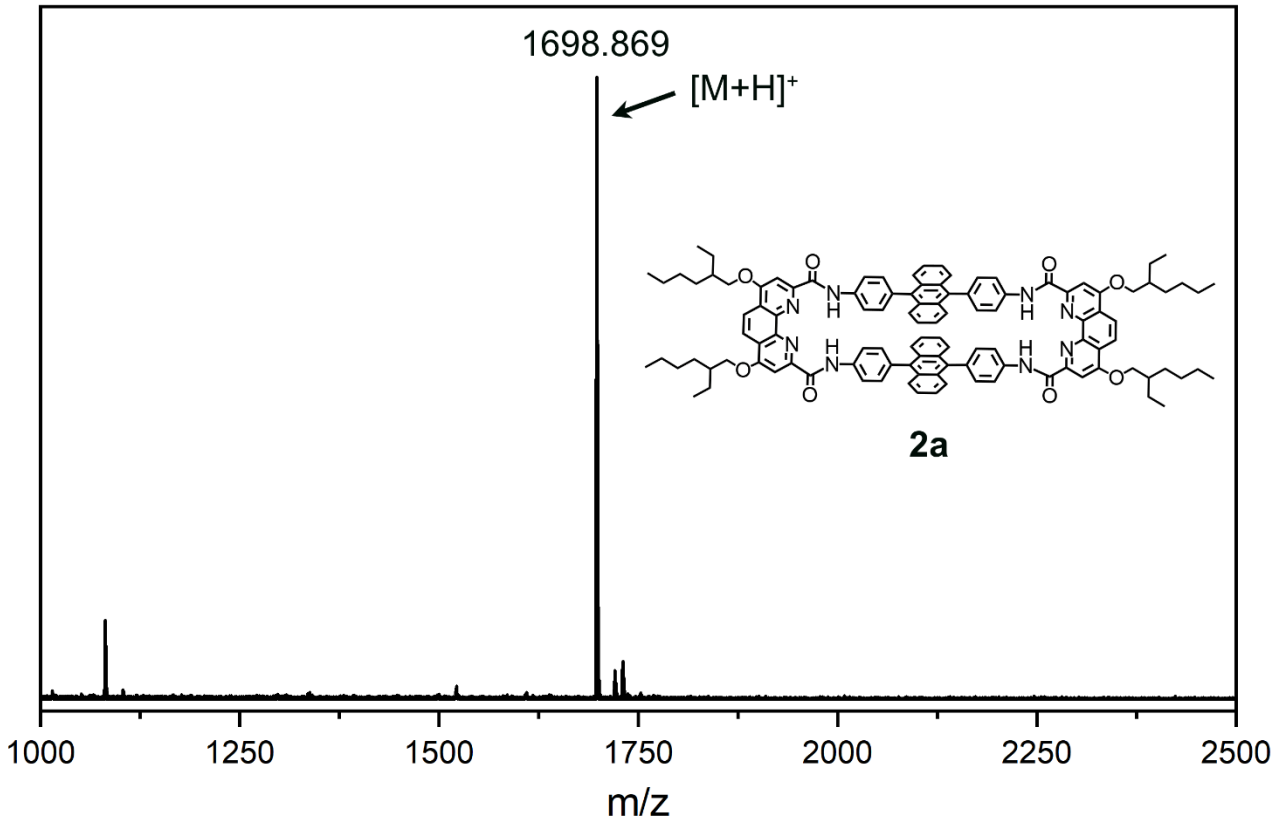


Fig. S9 MALDI-TOF mass spectra of **2a**.

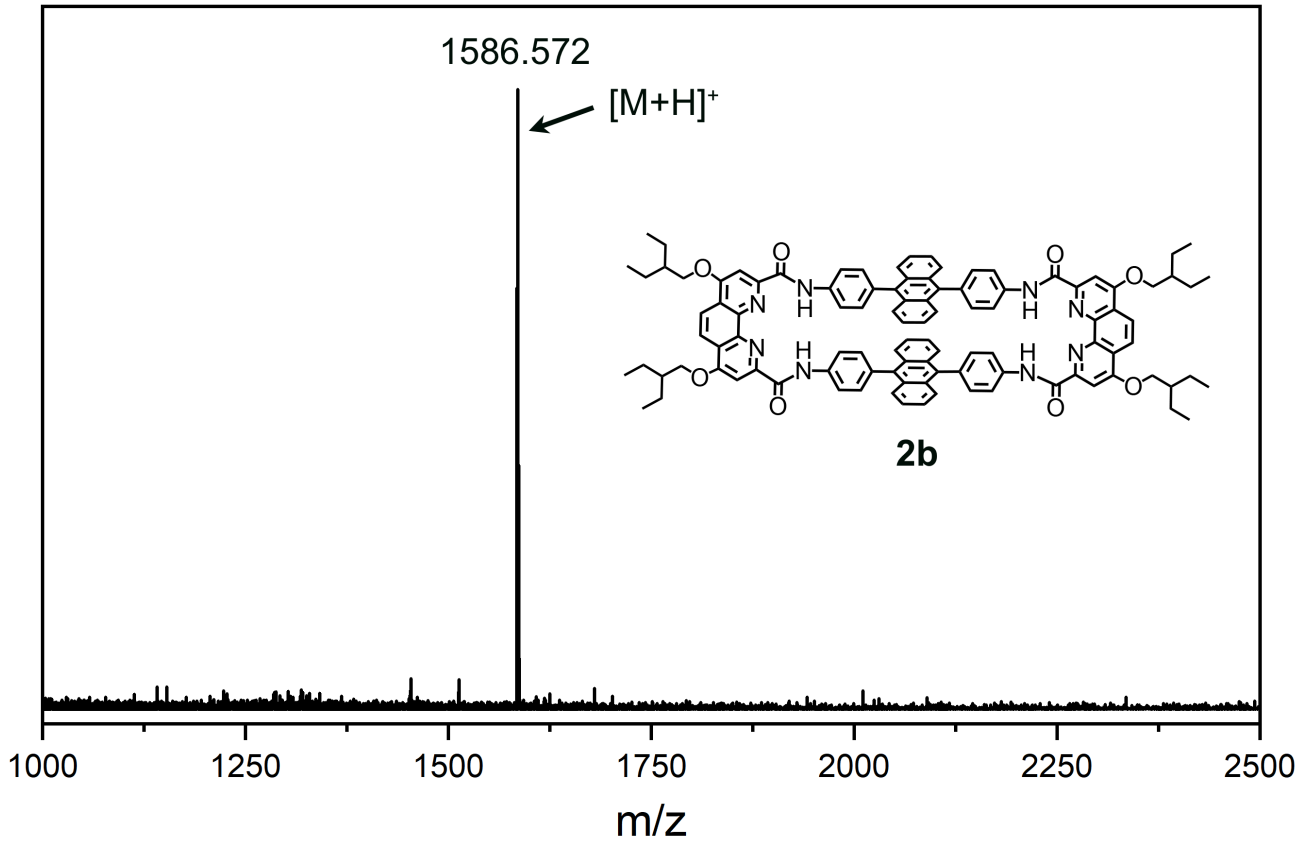


Fig. S10 MALDI-TOF mass spectra of **2b**.

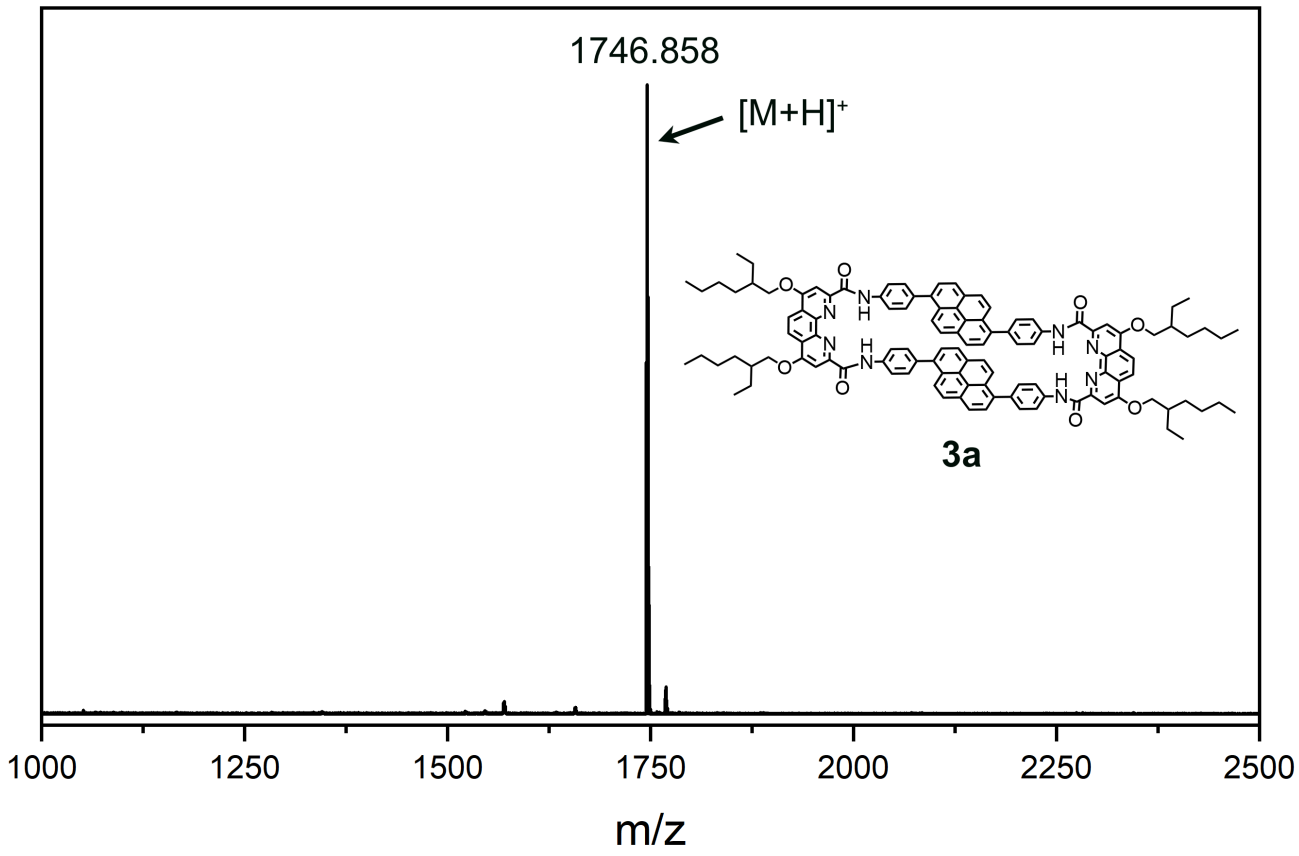


Fig. S11 MALDI-TOF mass spectra of **3a**.

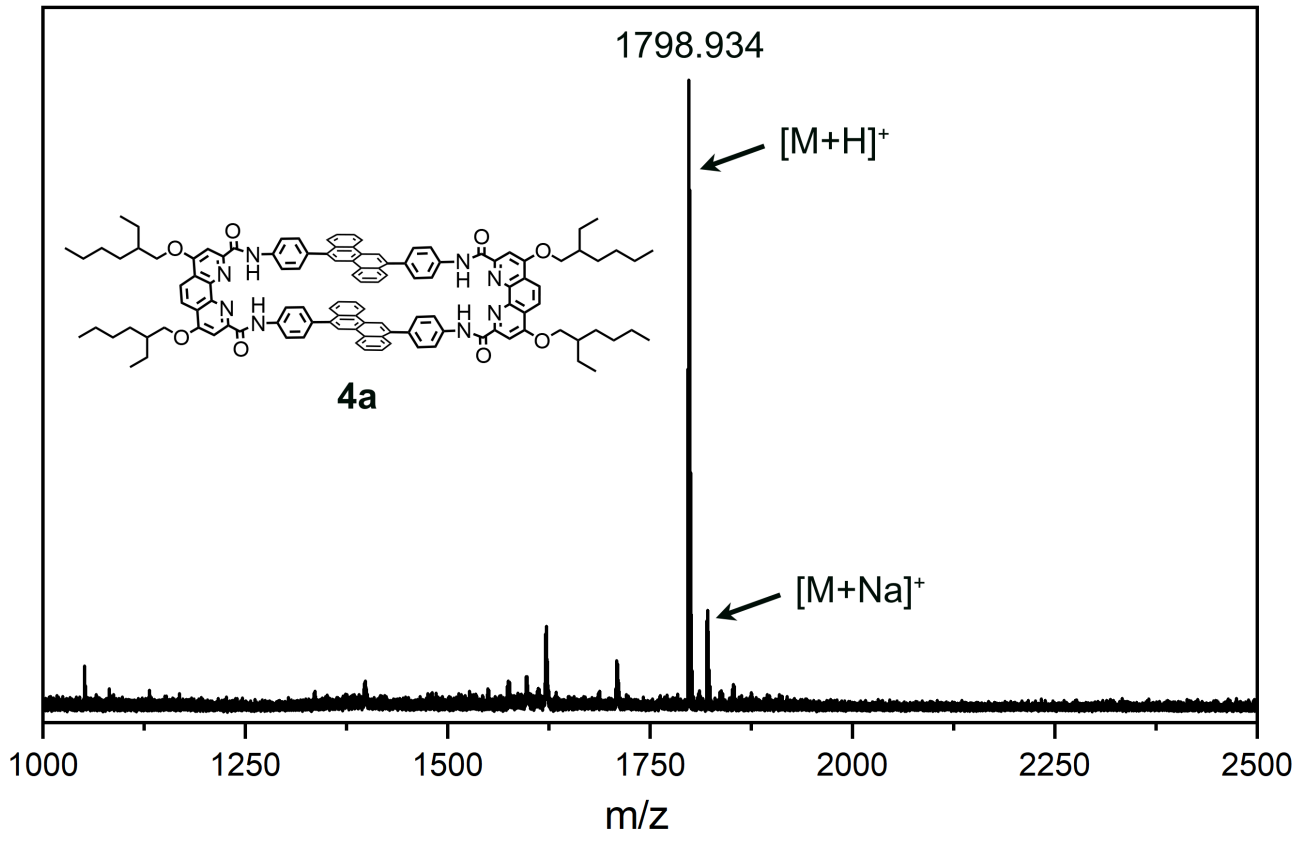


Fig. S12 MALDI-TOF mass spectra of **4a**.

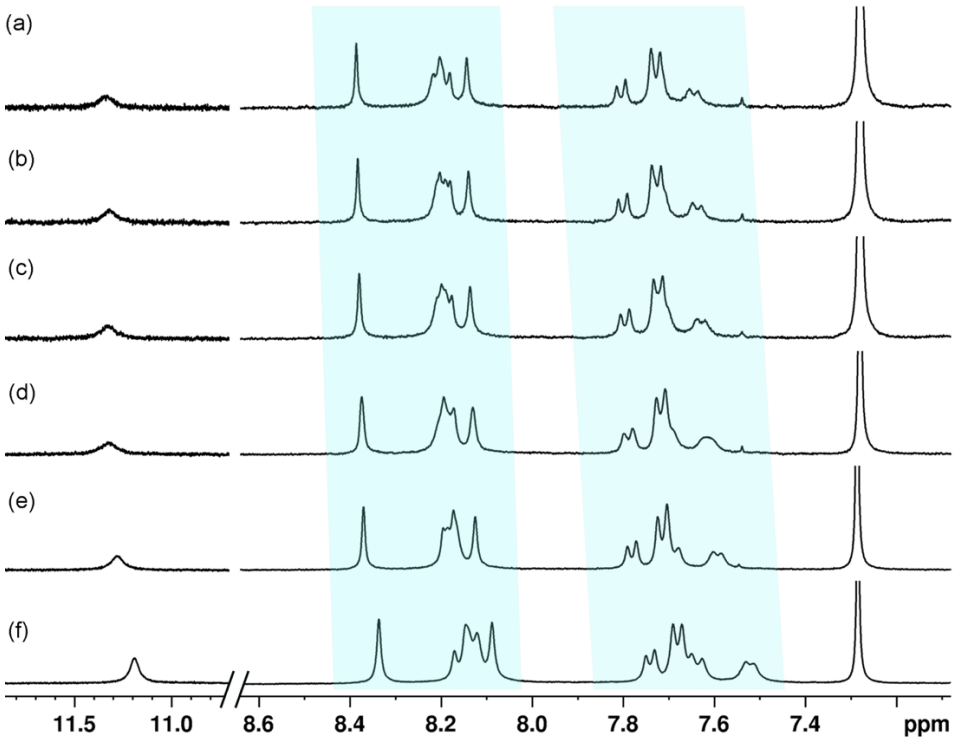


Fig. S13 Part of the ^{1}H NMR spectra of **3a** in $CDCl_3$ at 298 K in concentrations (a) 0.40 mM, (b) 0.48 mM, (c) 0.61 mM, (d) 0.81 mM, (e) 1.22 mM, and (f) 2.44 mM. The upfield shift of the signals indicated self-assembly of the macrocycle **3a**.

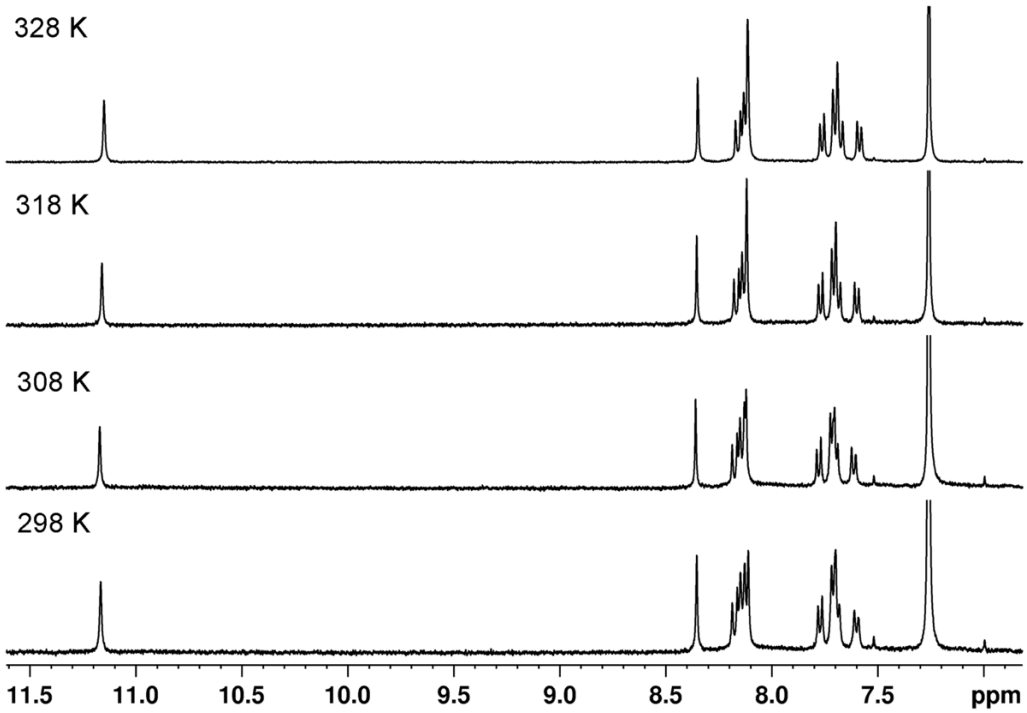


Fig. S14 Part of the variable temperature ^{1}H NMR spectra of **3a** (2 mM) in $CDCl_3$ in the temperature range 298 K to 328 K.

UV-Vis absorption and emission spectra

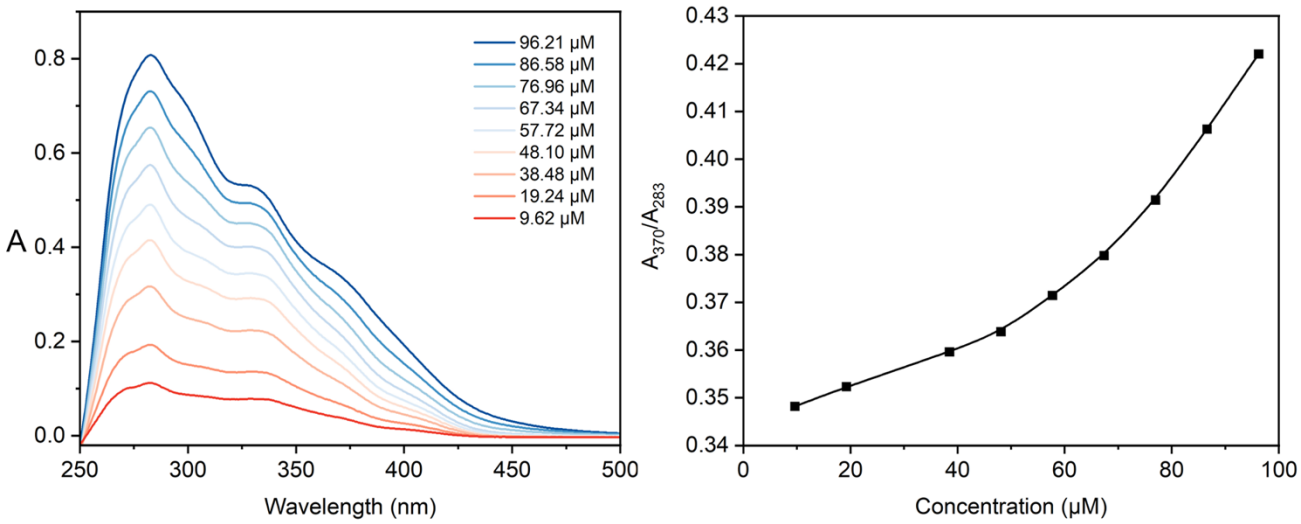


Fig S15 Concentration-dependent UV-vis spectra of **3a**. Absorbance ratio (A_{370}/A_{283}) vs concentration plot of **3a** at 298 K. Increasing intensity of the band at 370 nm with respect to the band at 283 nm signifies self-assembly at higher concentration.

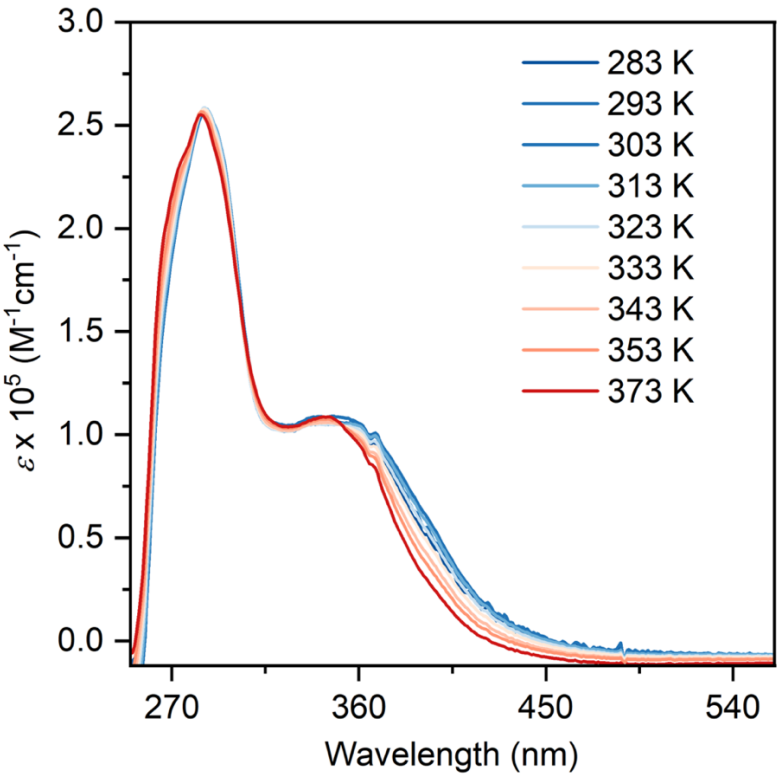


Fig S16 Variable temperature UV-Vis absorption spectra of **4a** in $C_2H_2Cl_4$ (3 μM) in the temperature range 283 K to 373 K.

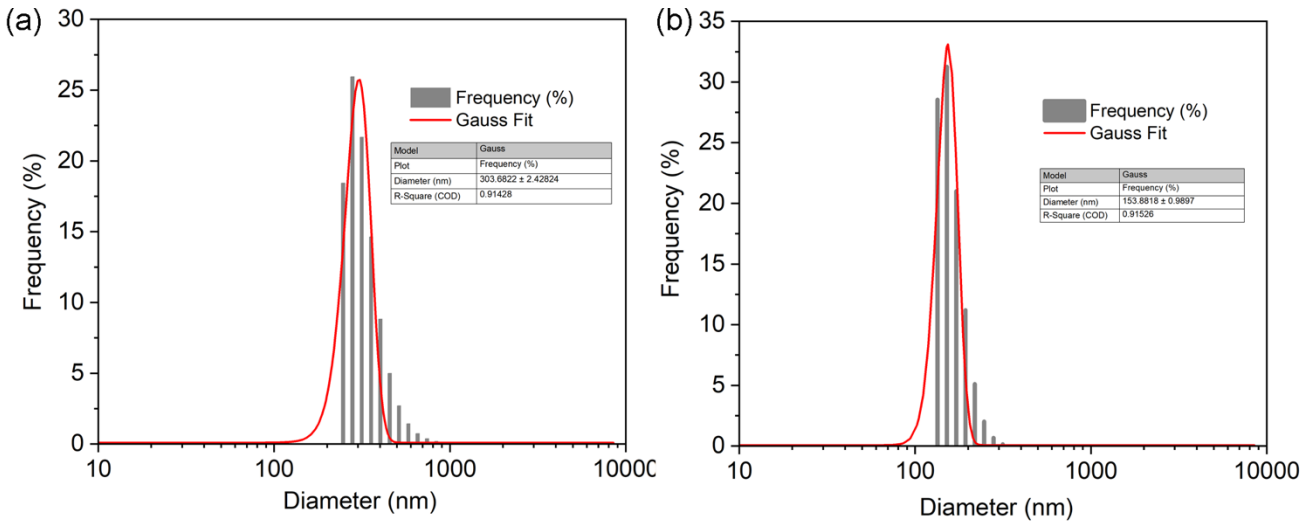


Fig. S17 Particle size distribution obtained from the Dynamic Light Scattering (DLS) experiment for 6 µM solution of **3a** (a) and **4a** (b) in tetrachloroethane ($C_2H_2Cl_4$). The data was fitted using the Gaussian function to get the mean particle diameter. The mean diameters obtained are 303 nm and 153 nm for **3a** and **4a**, respectively.

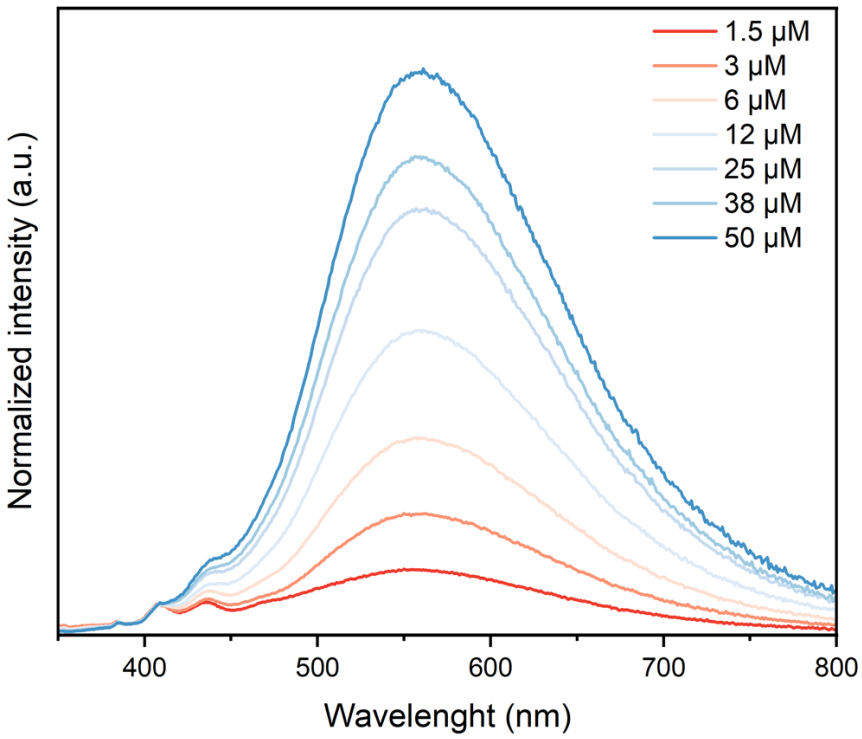


Fig. S18 Concentration-dependent steady-state emission spectra of **2a** in $C_2H_2Cl_4$ at 298 K in the concentration range 1.5 µM to 50 µM when excited at 345 nm. The spectra were normalized against the monomeric band at 408 nm.

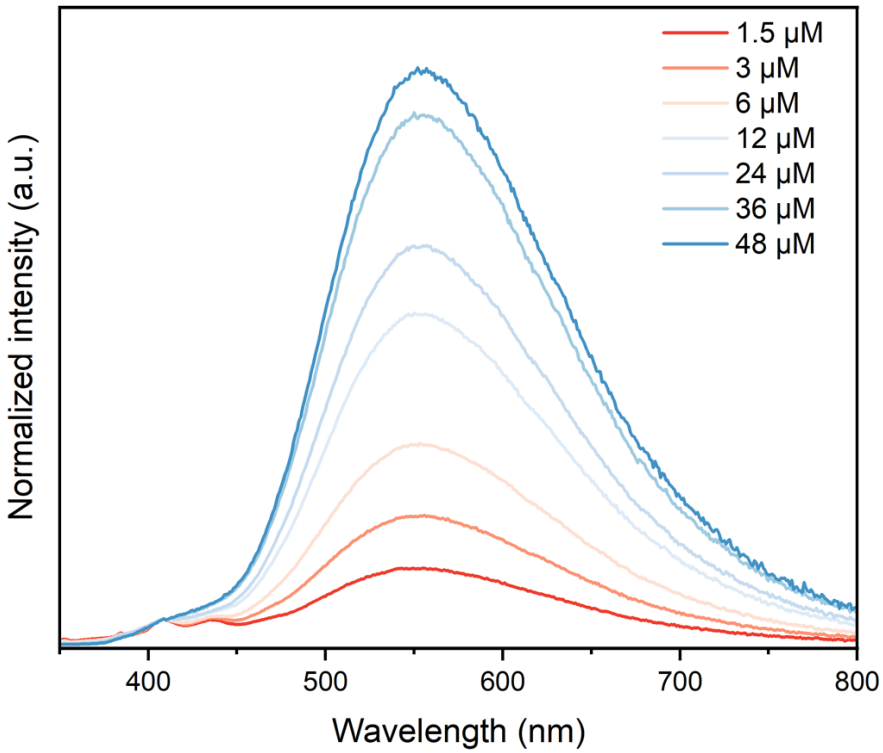


Fig. S19 Concentration-dependent steady-state emission spectra of **3a** in $C_2H_2Cl_4$ at 298 K in the concentration range 1.5 µM to 48 µM when excited at 345 nm. The spectra were normalized against the monomeric band at 408 nm.

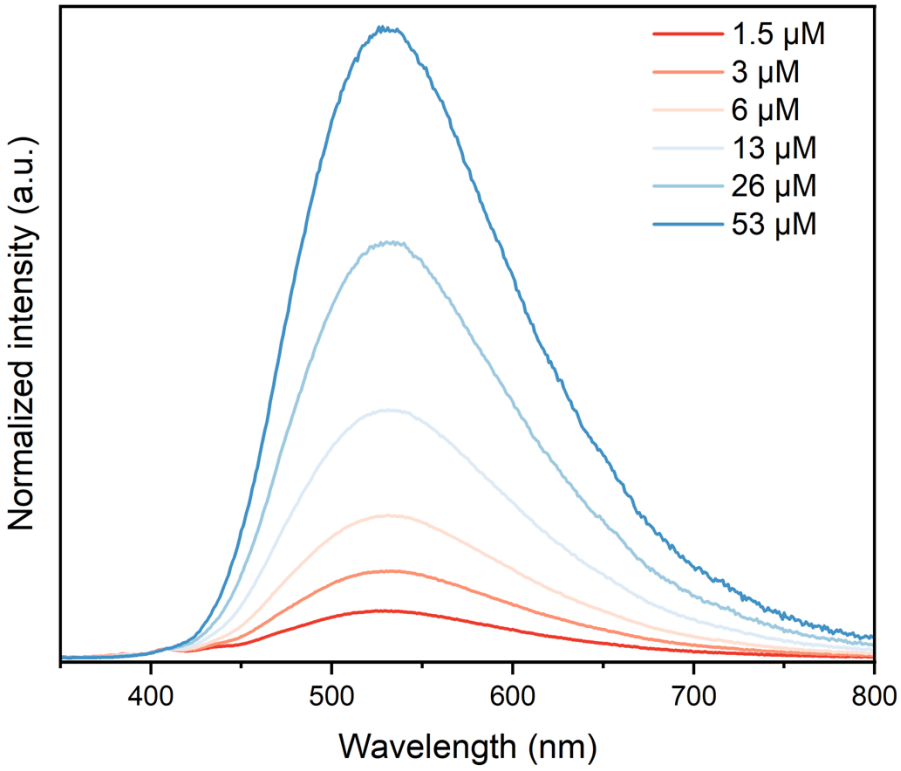


Fig. S20 Concentration-dependent steady-state emission spectra of **4a** in $C_2H_2Cl_4$ at 298 K in the concentration range 1.5 µM to 53 µM when excited at 345 nm. The spectra were normalized against the monomeric band at 408 nm.

Additional FESEM images

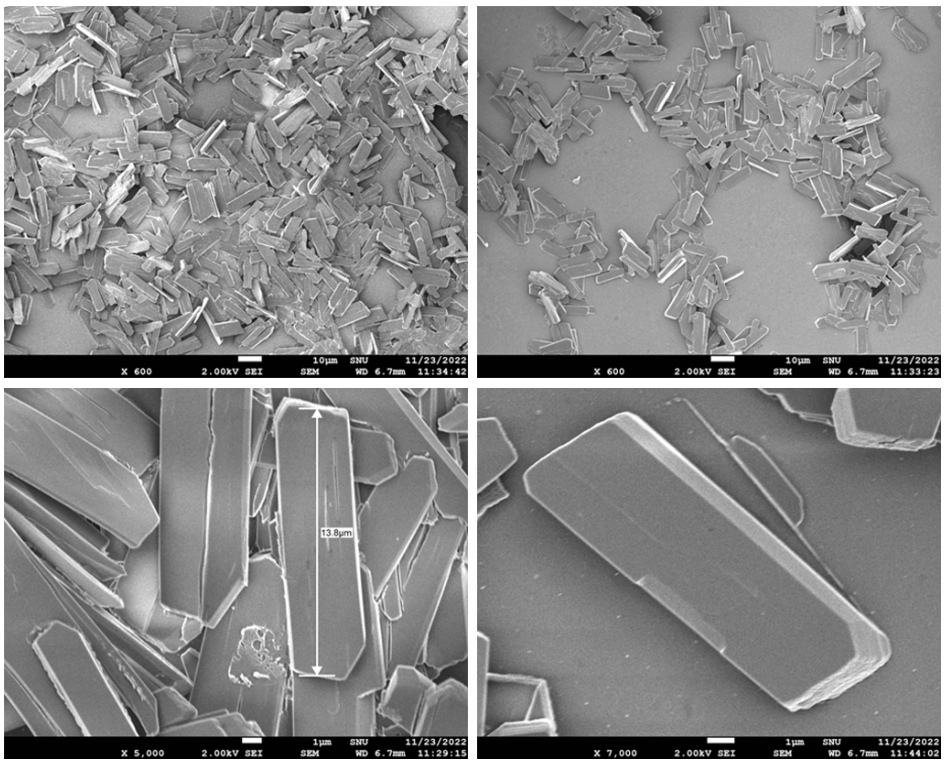


Fig. S21 FESEM images of **1b**.

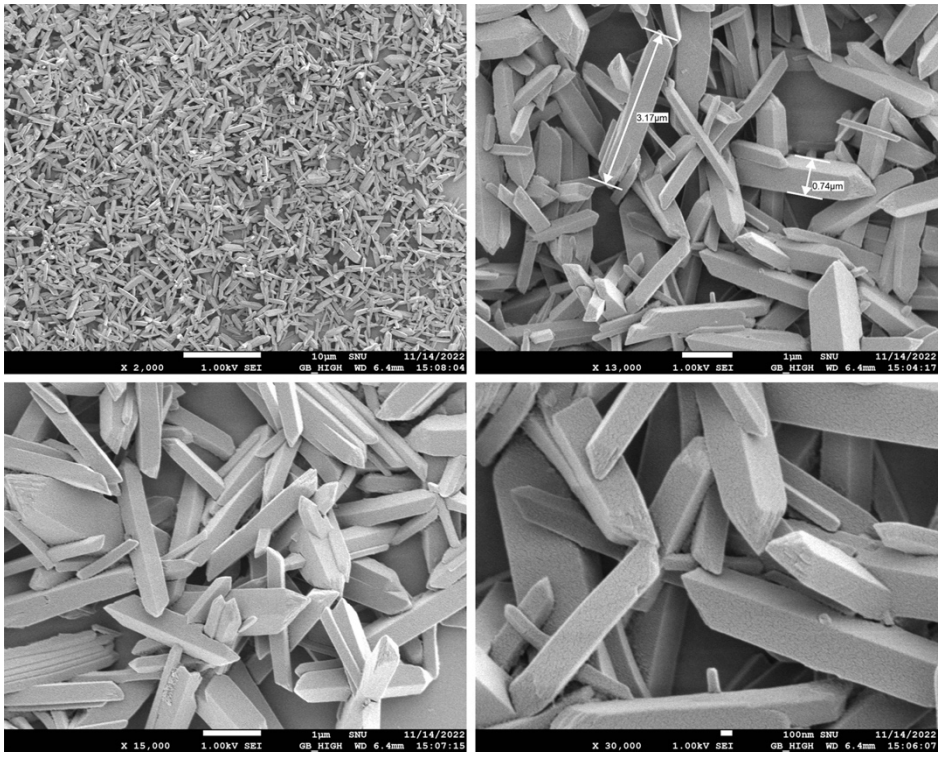


Fig. S22 FESEM images of **2a**.

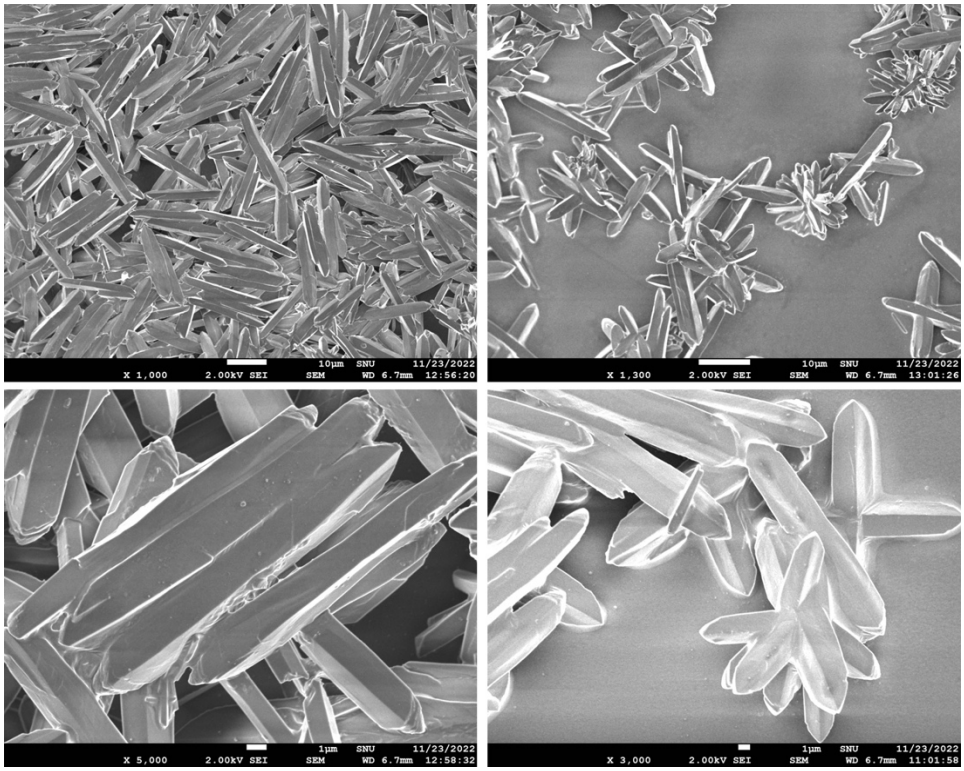


Fig. S23 FESEM images of **3a**.

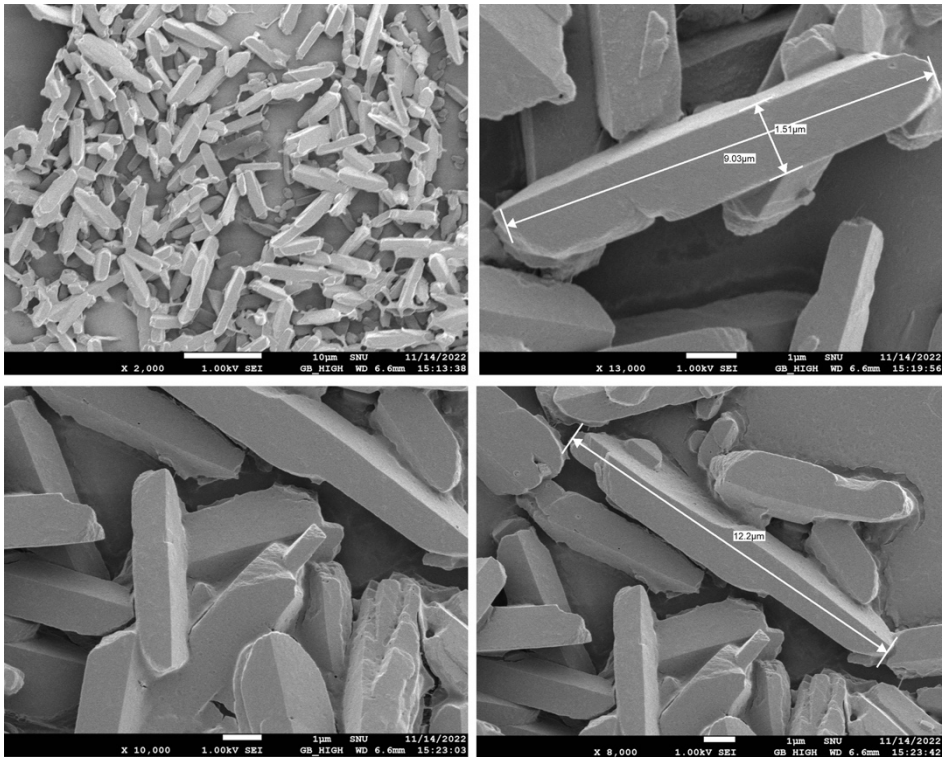


Fig. S24 FESEM images of **4a**.

4. Computational Methods and Details

The geometry optimizations of the monomeric units are done by using hybrid DFT functional, B3LYP as implemented in the Gaussian 09 suite of package, with 6-31G basis set.[5-11] The optimized ground state structures of the monomeric units **1b**, **2a**, **3a** and **4a** are given below in Fig. S25. Frequency calculations are done to estimate the ground state of these monomeric units. The absence of negative frequencies indicates minimum energy structures for these molecules.

Using the monomeric units, we have built dimeric units only with the **1b** and **3a*** (the solubilizing side chain ethyl butyl group changed to ethyl group to reduce computational time). We considered two arrangements for the dimeric units, denoted as the AA and AB-stacking. For the dimeric units, the computations are done with Vienna ab initio simulation package (VASP).[12-14] The Generalized Gradient Approximation (GGA) with Perdew Burke Ernzerhof (PBE) functional is used to incorporate the electron exchange in the calculations[15] and the electron-ion interaction is treated by employing PAW pseudopotentials and plane-wave basis set.[16] The energy cut-off of 400 eV is used for the plane wave basis set with k point mesh of (1x1x1). The electronic convergence threshold for the electronic energy is set to 10^{-6} eV in energy and the force convergence threshold is set to 10^{-3} eV/Å. A vacuum distance of 8 Å is taken between the periodic images in the adjacent cells, to ensure the absence of any inter-molecular interactions between the images in the adjacent cells. The van-der-Waals corrections[17] are done to the energy values to account for the correction due to the weak interactions between the two sub-units of the dimeric structure.

The optimized geometries of the dimeric units are given below (Fig. S26 and S27). The AB-stacking is found to be the most stable arrangement for both the dimeric units. The corresponding energy differences of 11.53 and 13.83 kcal/mol are obtained for the **1b** and **3a*,** respectively, as given below. In the AB stacking, the intermolecular distances between the aromatic units in the two monomeric subunits are 5.5 Å and 4.1 Å, respectively, for the **1b** and **3a***. The van-der-Waals stacking interactions should be weak due to the inter-molecular steric interactions between the monomeric subunits, particularly solubilizing groups, in the AA-stacking arrangements. This results in lower stability compared to the AB-stacking dimers.

Having determined the most stable dimeric arrangements, in the next step, we have optimized the intermolecular distance of the dimeric units of the AB-stacking arrangements, imposing the periodic boundary conditions. The z-axis of the simulation box is further optimized to obtain the periodic arrangement of the AB-stacked dimeric units. A similar calculation setup, as mentioned earlier, for the dimeric units is used here. However, the k-point mesh of (1×1×3) is considered to incorporate the

periodic effects along the z-direction. The vacuum distance of 8 Å is maintained between the periodic images along the x- and y-directions. The Fig. S28 shows the periodic AB-stacked polymeric units. The optimized inter-molecular distance is found to be 3.9 Å and 3.8 Å for **1b** and **3a***, respectively.

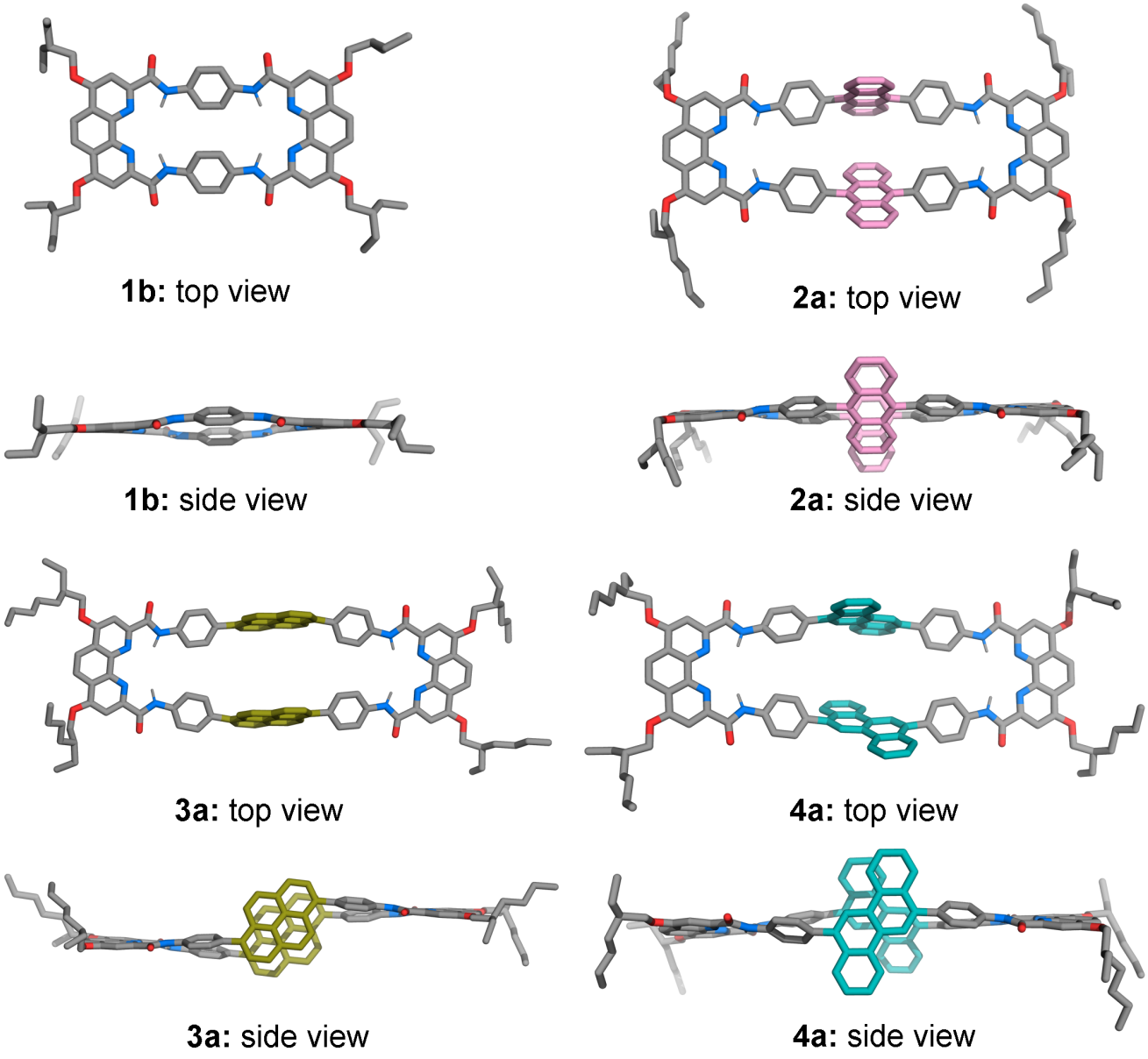


Fig. S25 Top and side views of DFT optimized geometry of the macrocycles **1b**, **2a**, **3a** and **4a**.

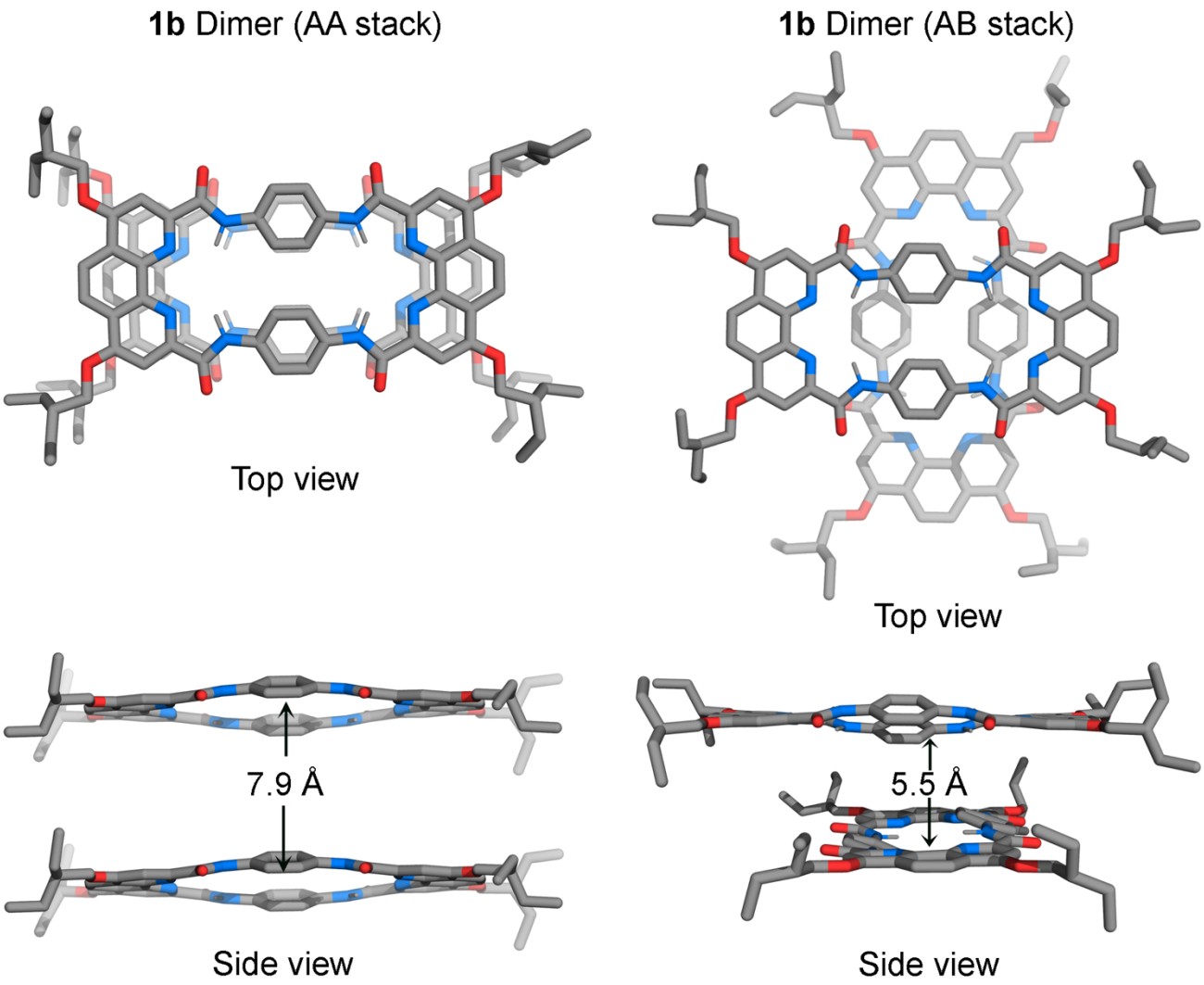


Fig. S26 Top and side views of DFT optimized geometry of the **1b** dimer in two different stacking modes, AA and AB. The AB stack was found to be 11.53 kcal/mol more stable than the AA stack. Presumably, due to the AA mode involves the larger steric repulsion between the side chains.

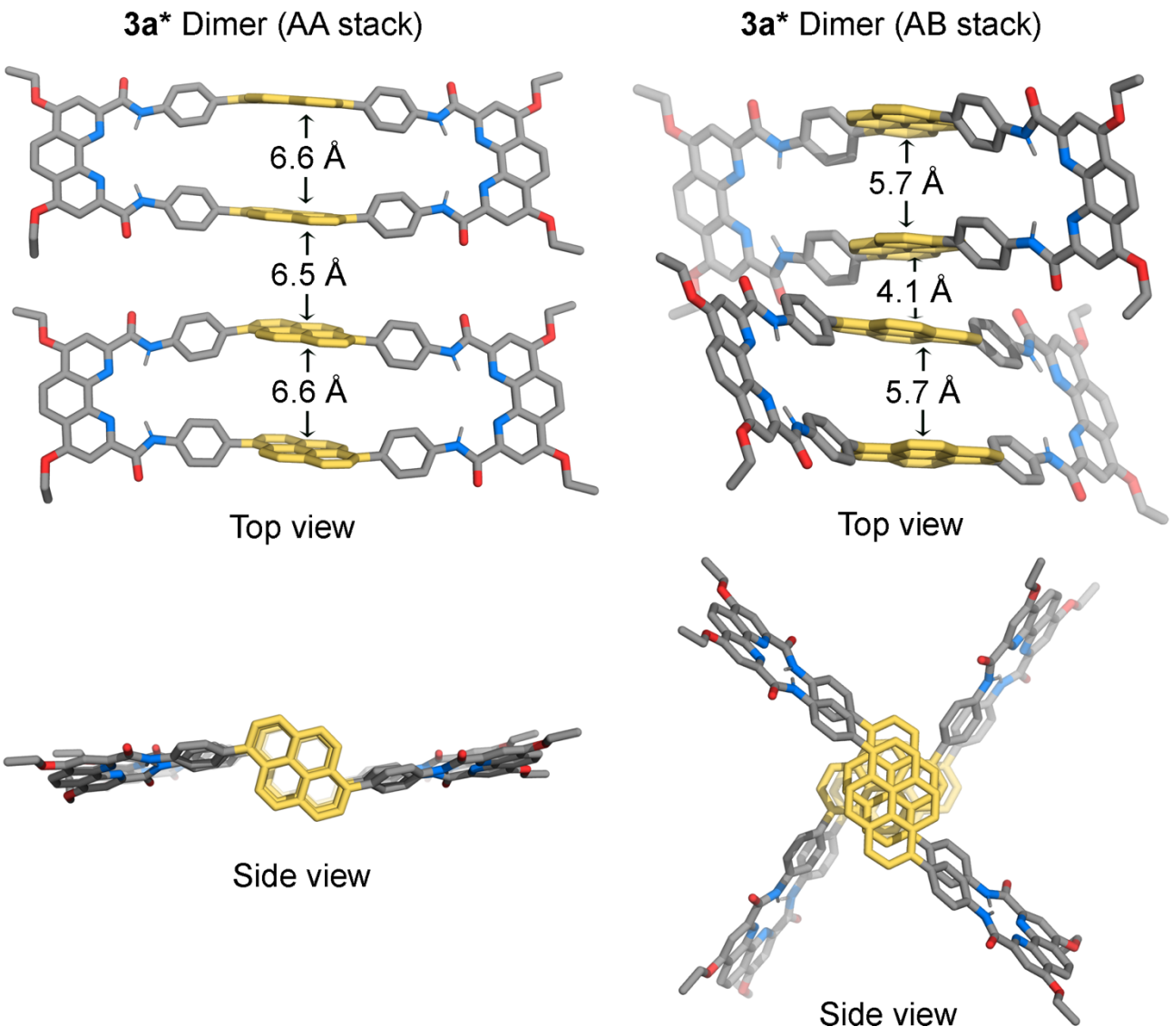


Fig. S27 Top and side views of DFT optimized geometry of the **3a*** dimer (*the solubilizing side chain ethylhexyl group changed to ethyl group to reduce computational time) in two different stacking modes AA and AB. The AB stack was found to be 13.83 kcal/mol more stable than the AA stack. The AB stack is mostly stabilized by the extensive π-π interaction between the pyrene moieties.

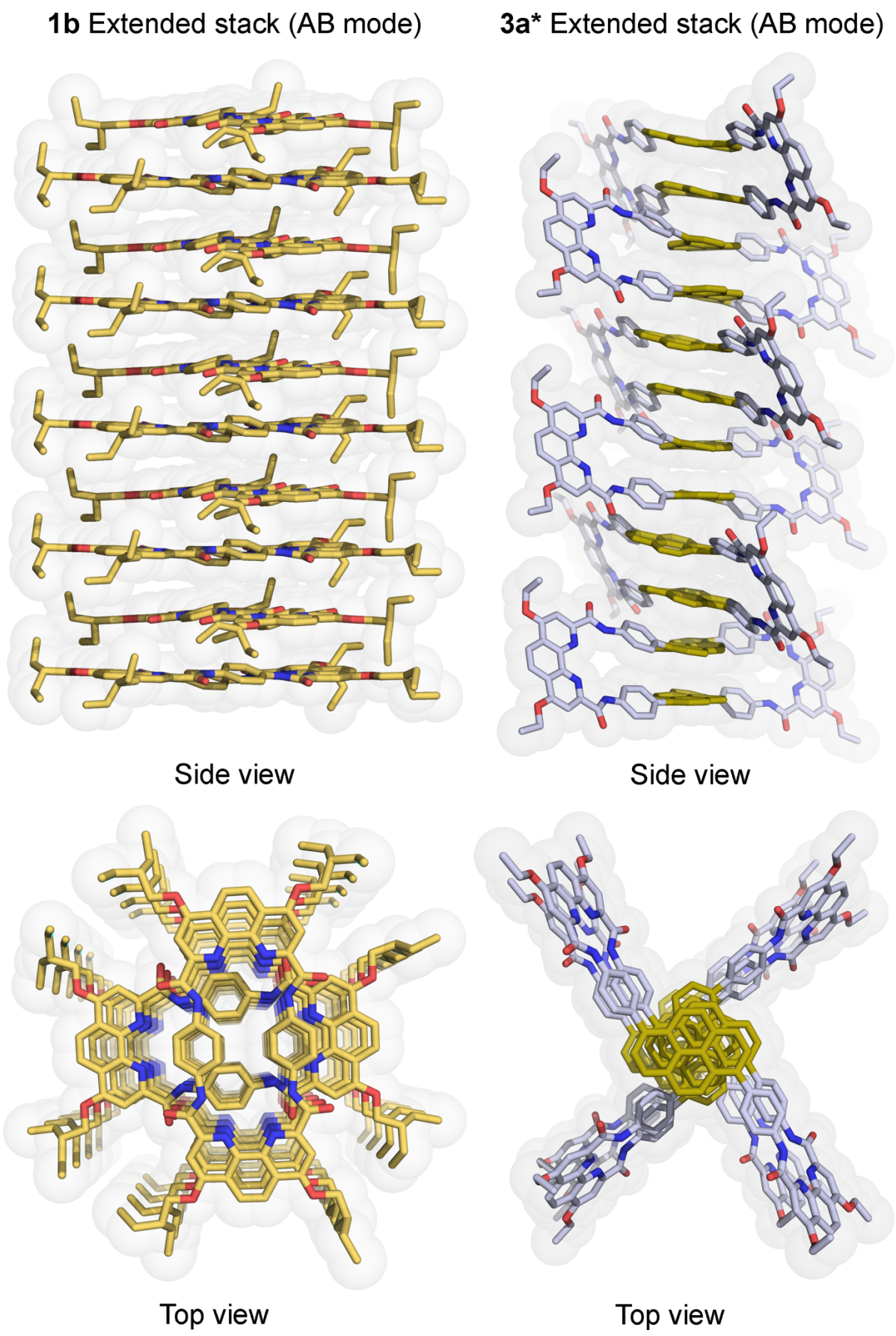
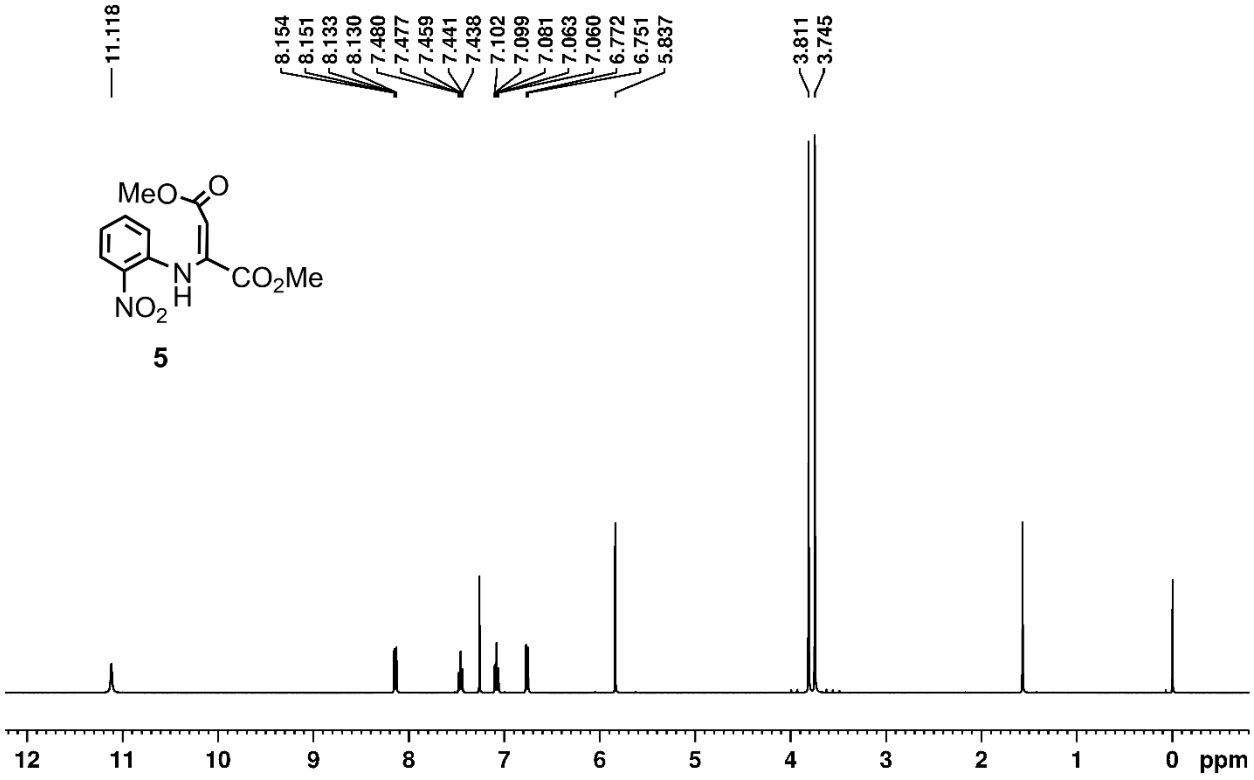
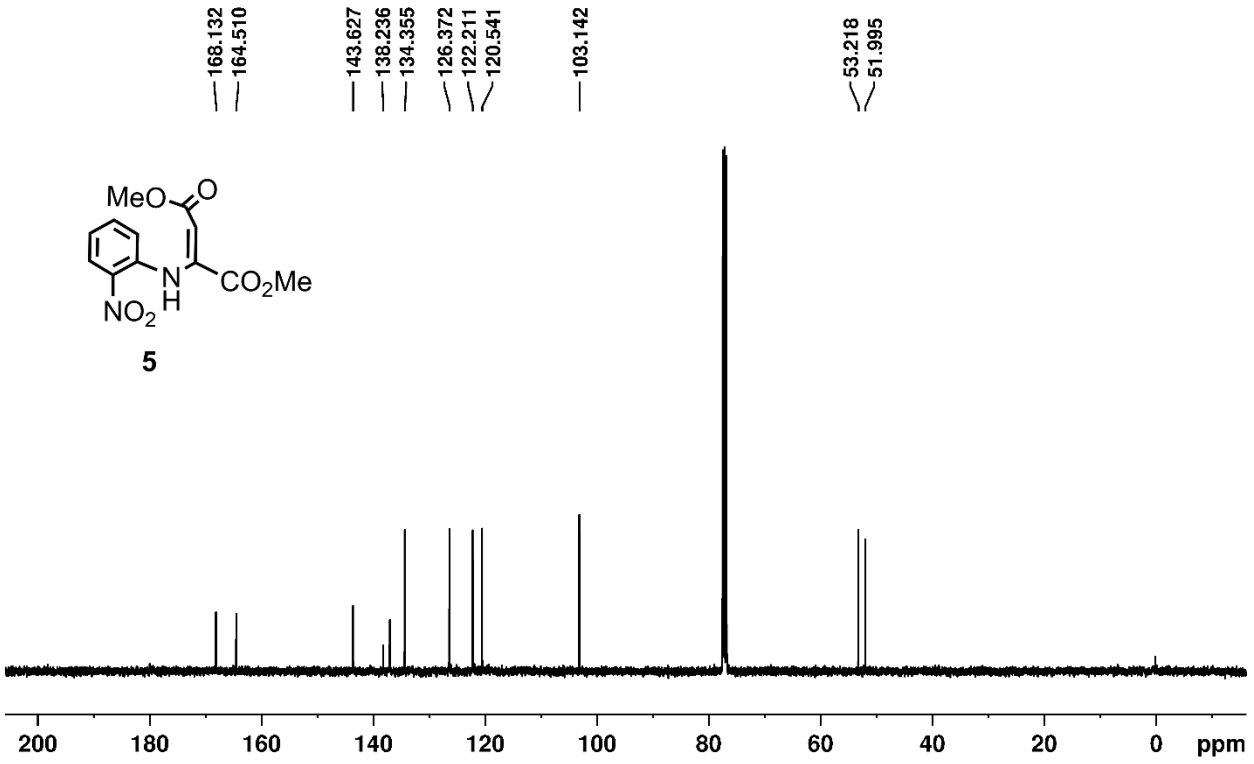
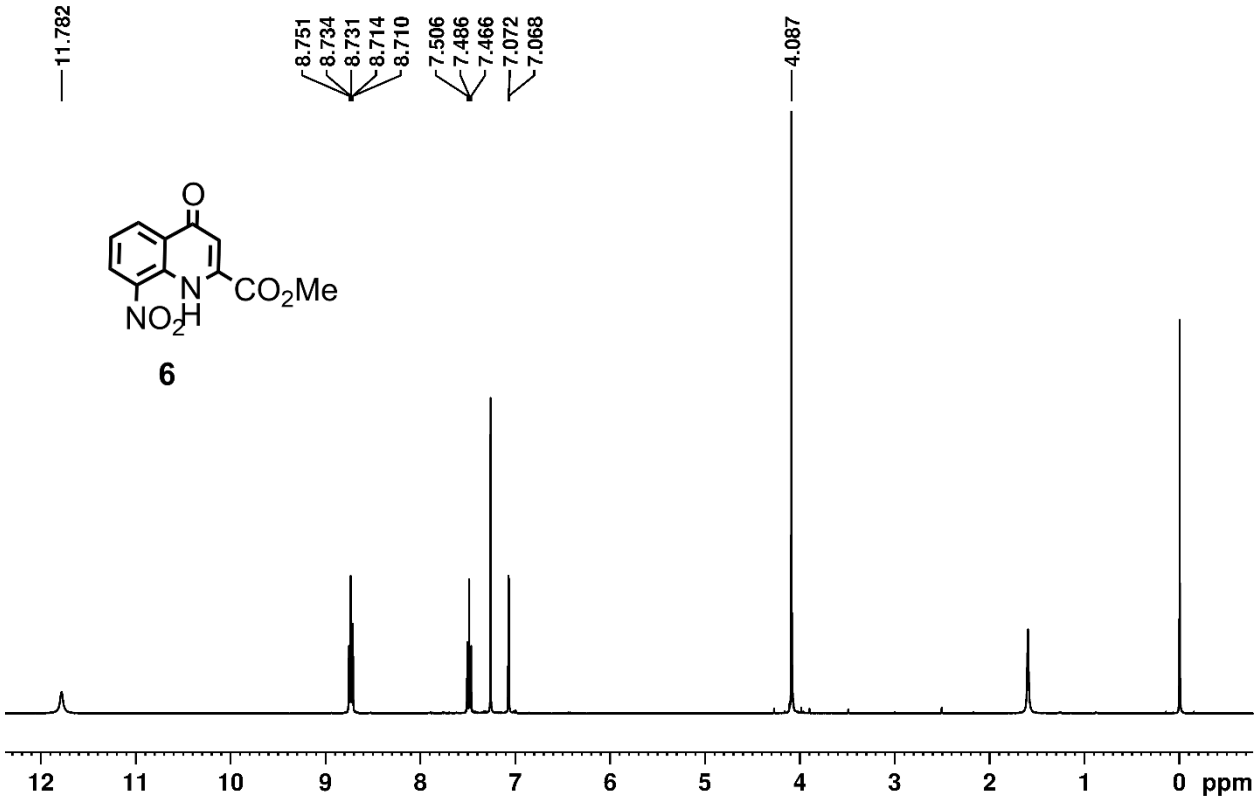


Fig. S28 Top and side views showing DFT calculated (with periodic boundary conditions) extended one-dimensional stack of **1b** and **3a*** in AB mode.

5. NMR spectra of the synthesized compounds



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8.710
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7.486
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7.072
7.068
4.087
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N
H
NO2
CO2Me
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11
10
9
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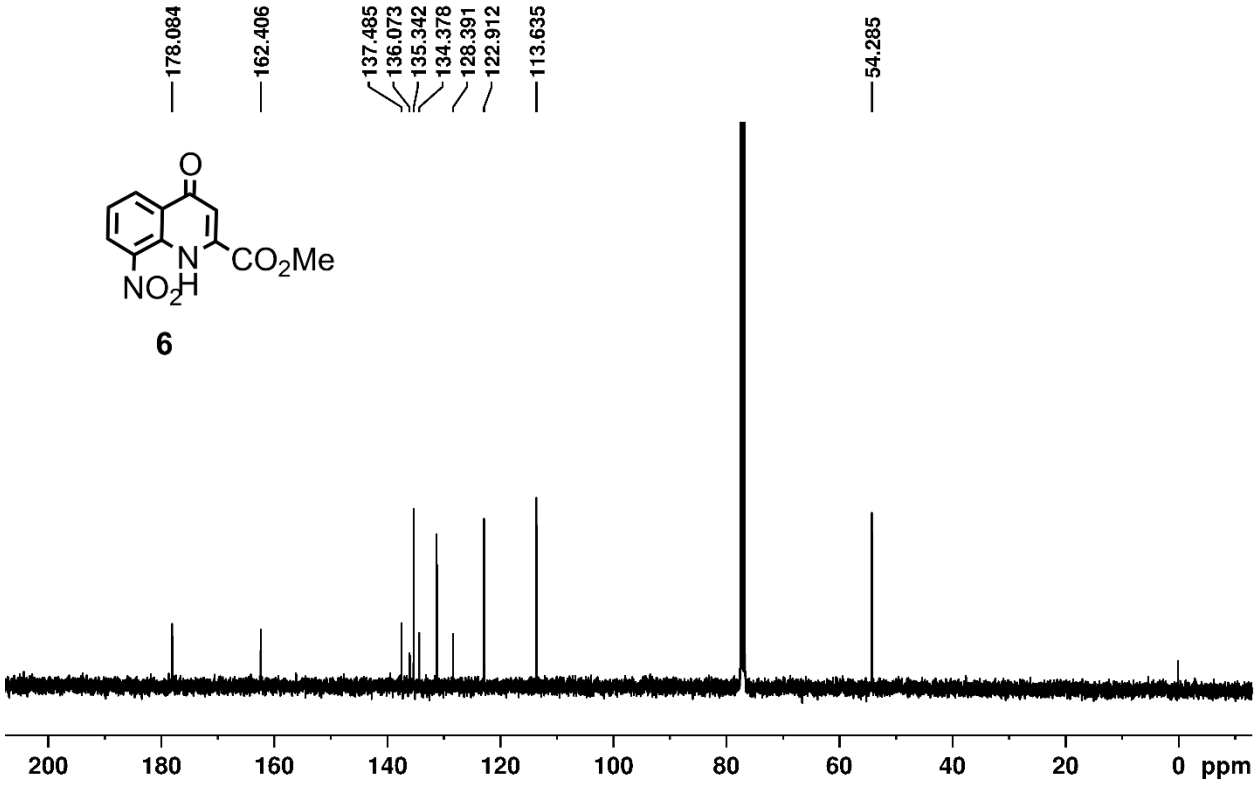
7
6
5
4
3
2
1
0 ppm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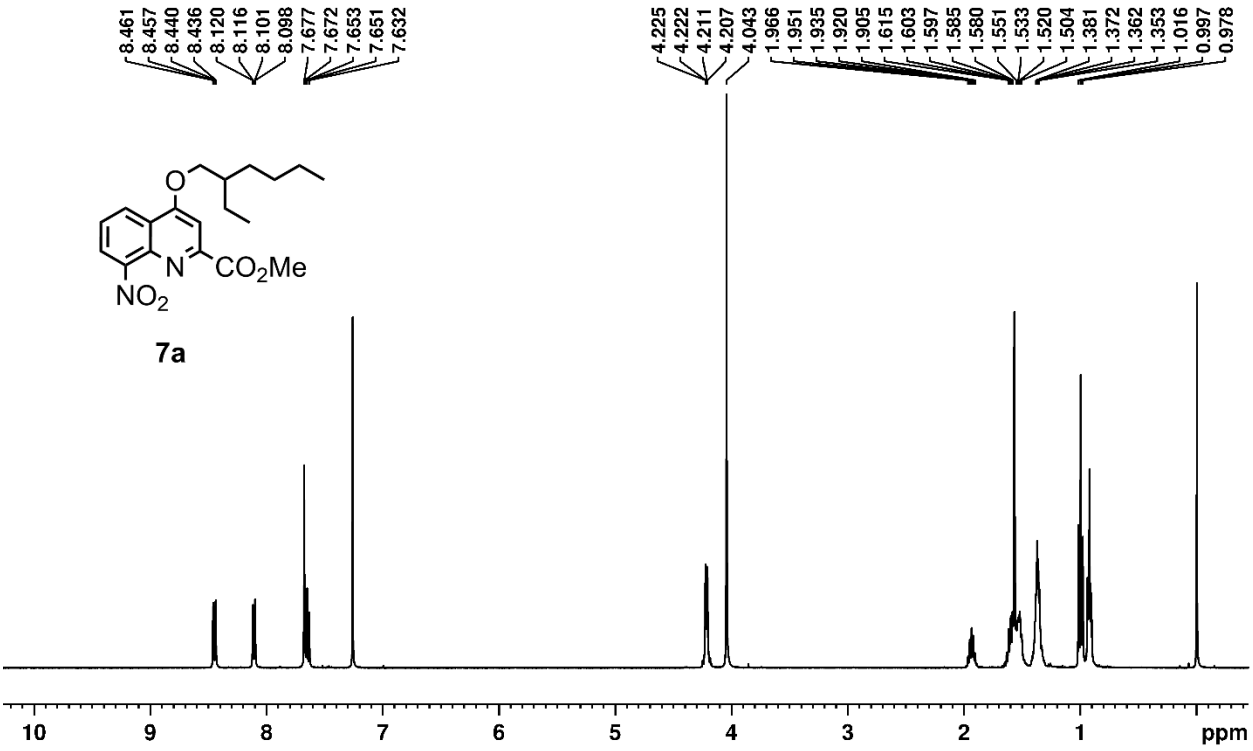
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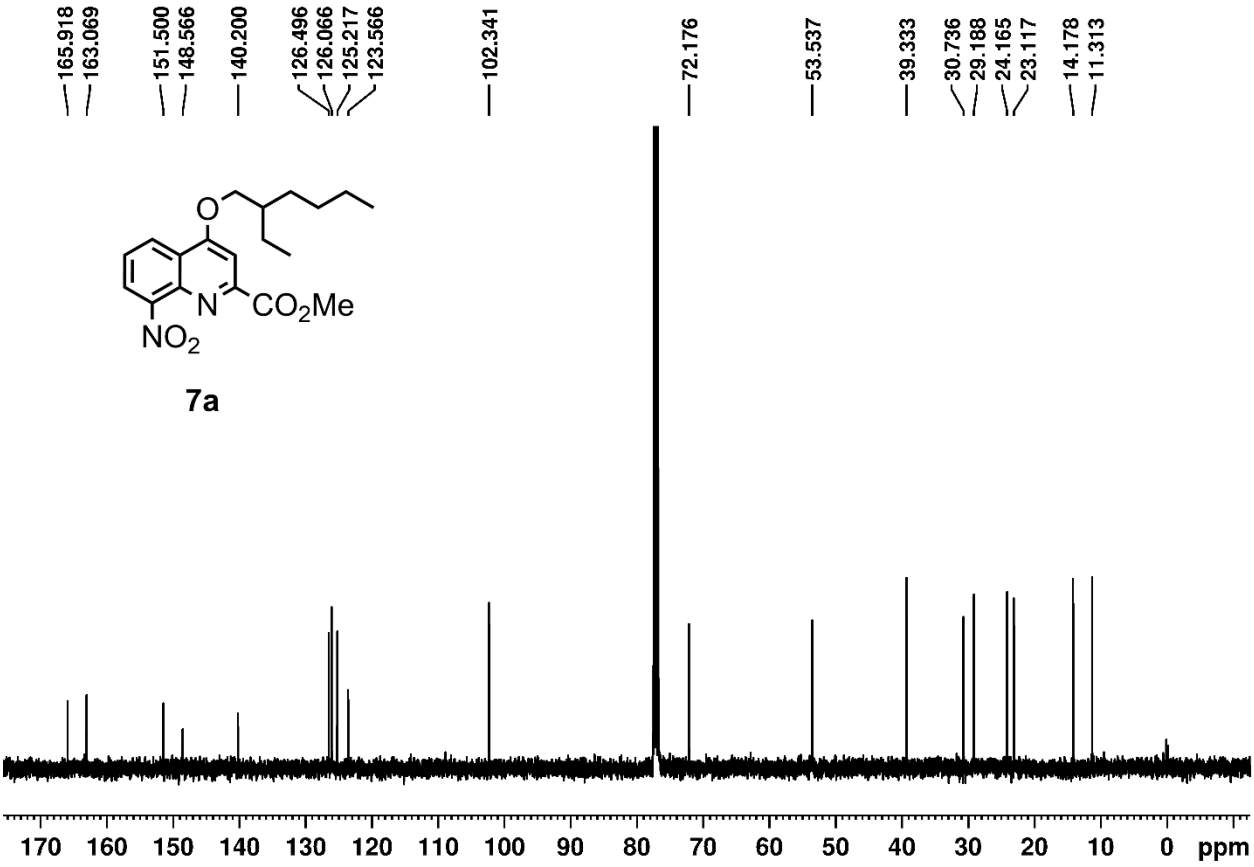
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29.188
24.165
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NO2
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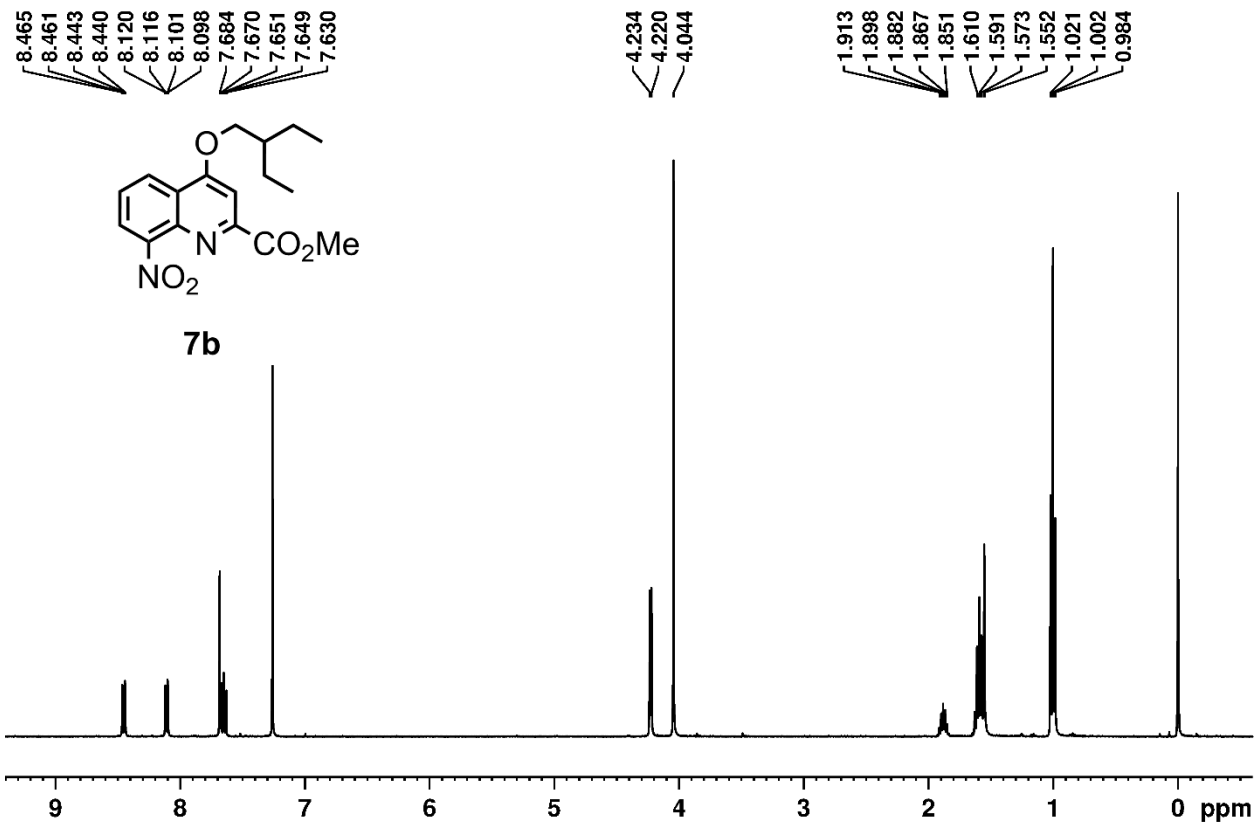
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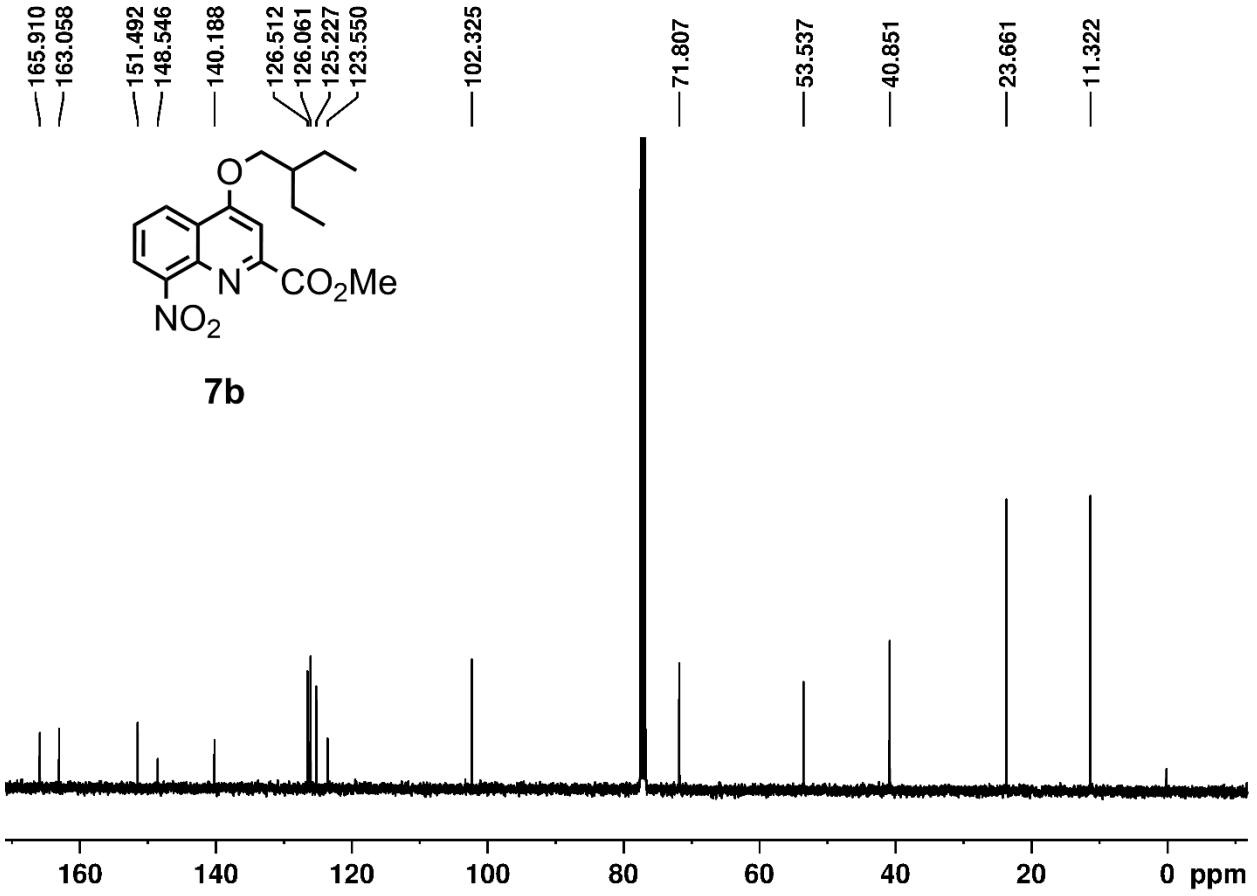
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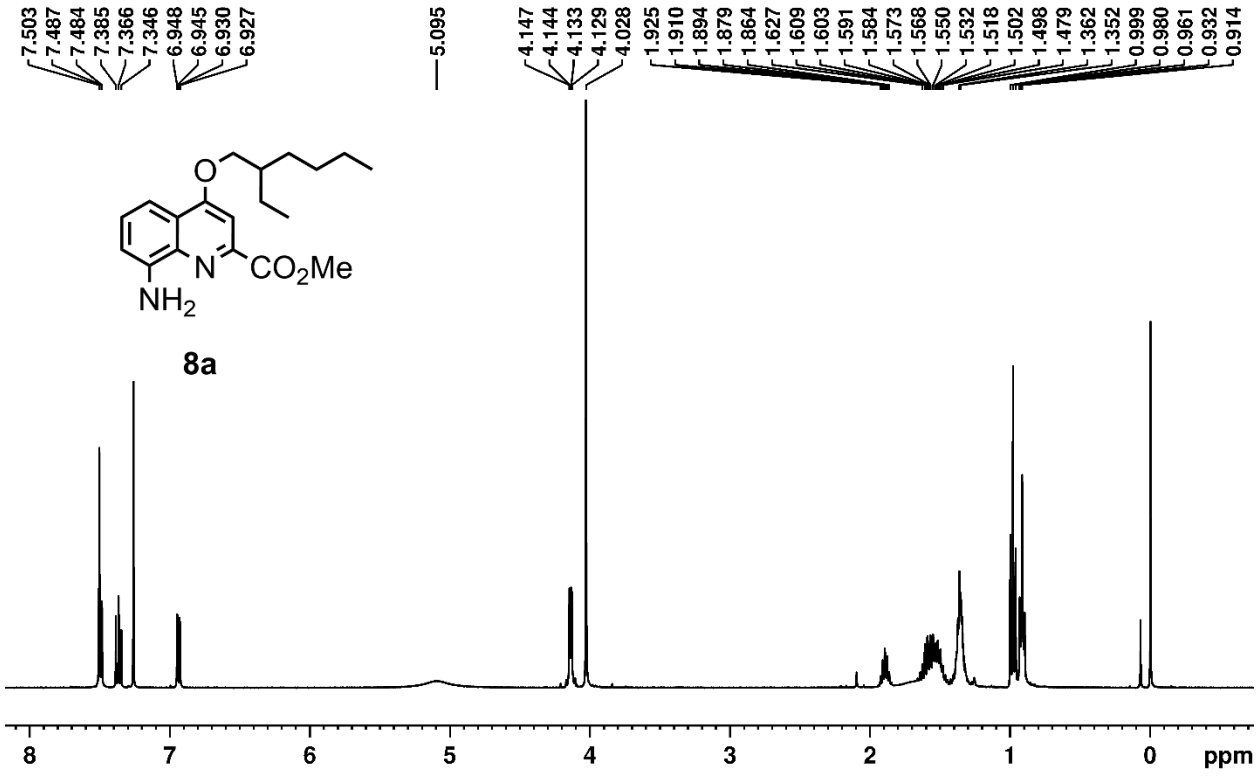
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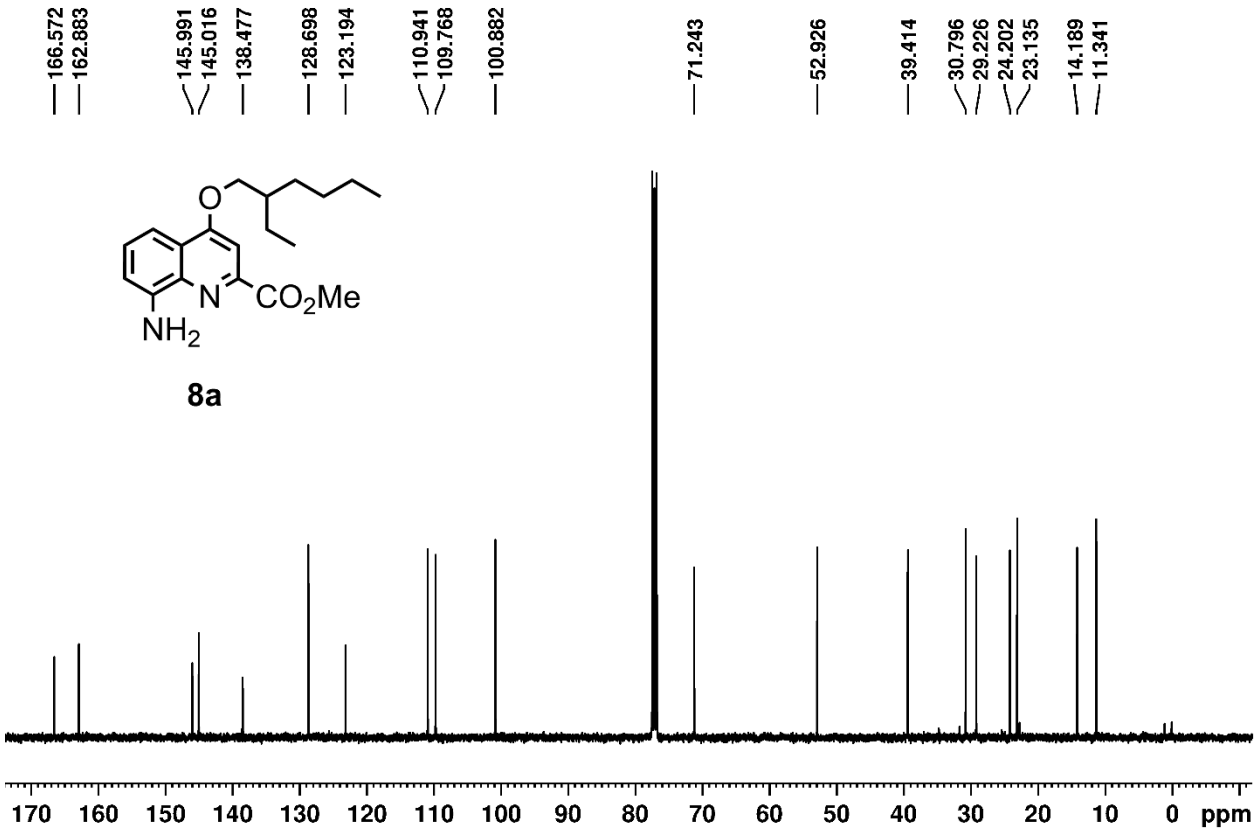
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110.941
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52.926
39.414
30.796
29.226
24.202
23.135
14.189
11.341
O
N
CO2Me
NH2
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140
130
120
110
100
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80
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60
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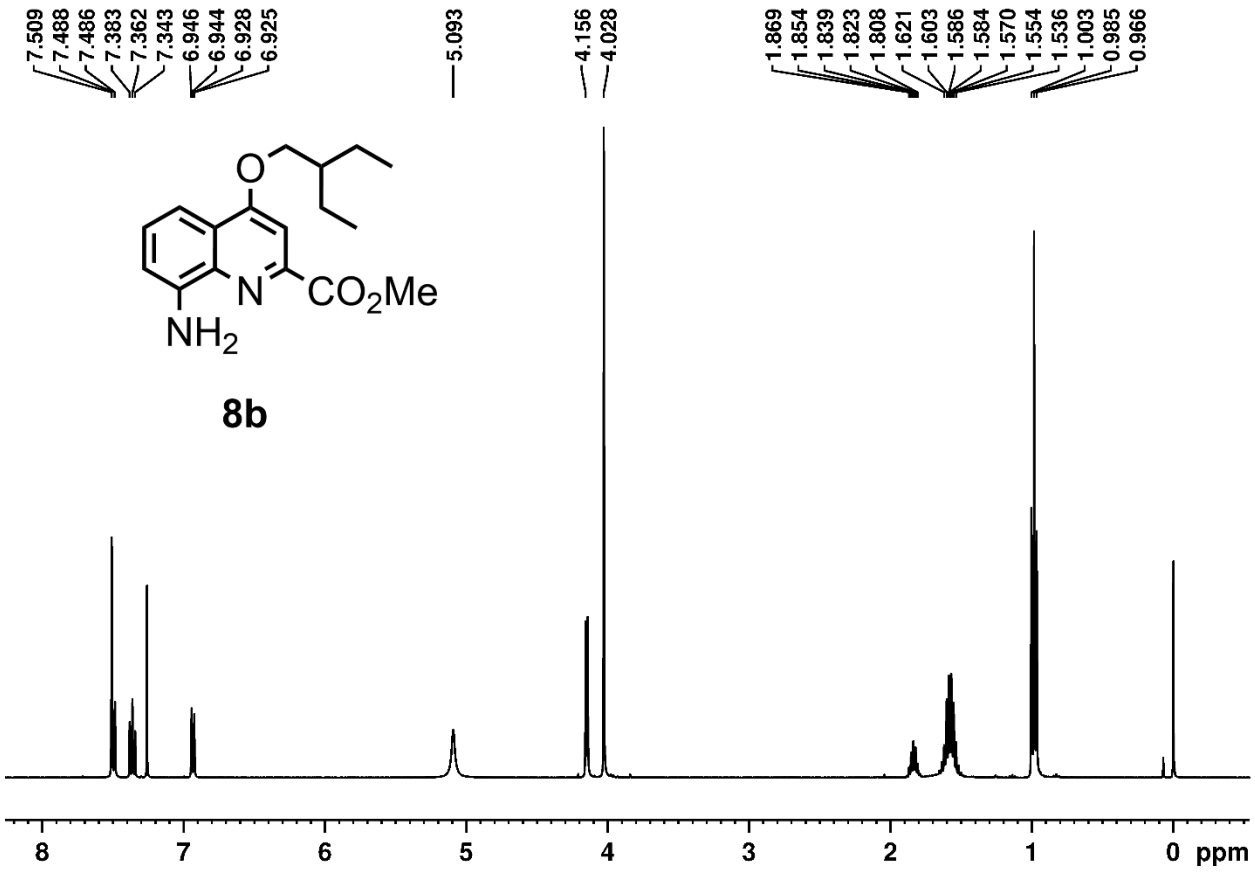
ppm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7.343
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6.944
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4.156
4.028
1.869
1.854
1.839
1.823
1.808
1.621
1.603
1.586
1.584
1.570
1.554
1.536
1.003
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CO2Me
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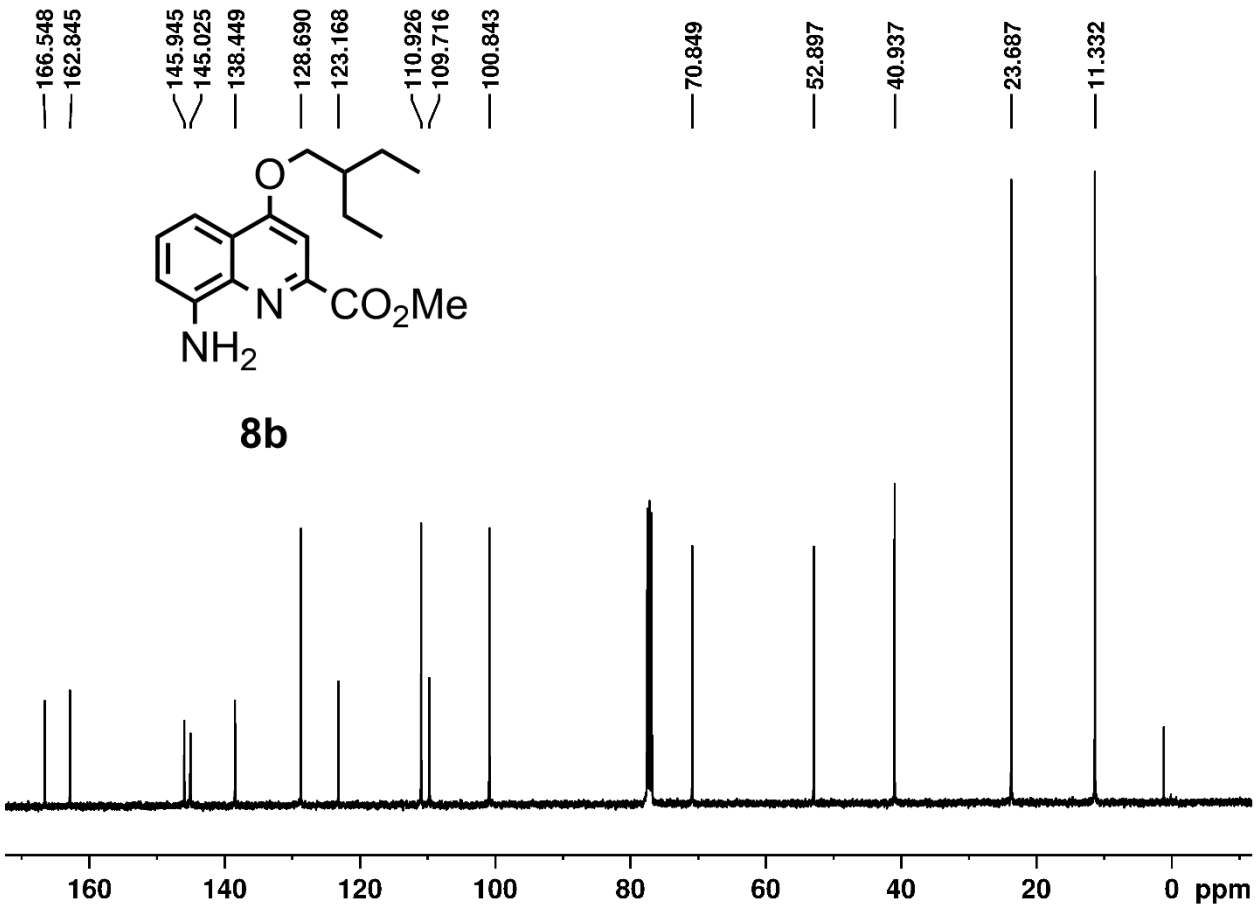
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20
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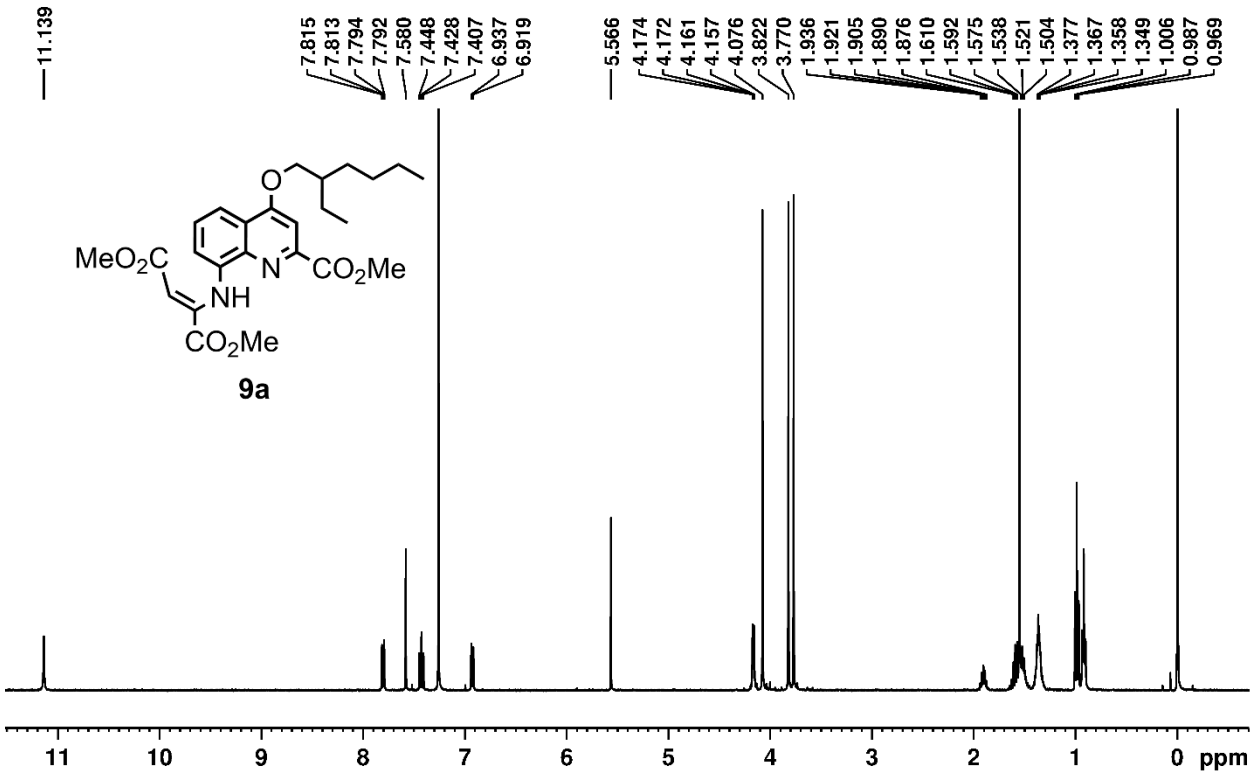
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7.813
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7.792
7.580
7.448
7.428
7.407
6.937
6.919
5.566
4.174
4.172
4.161
4.157
4.076
3.822
3.770
1.936
1.921
1.905
1.890
1.876
1.610
1.592
1.575
1.538
1.521
1.504
1.377
1.367
1.358
1.349
1.006
0.987
0.969
MeO2C
NH
CO2Me
N
CO2Me
O
CO2Me
9a
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10
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6
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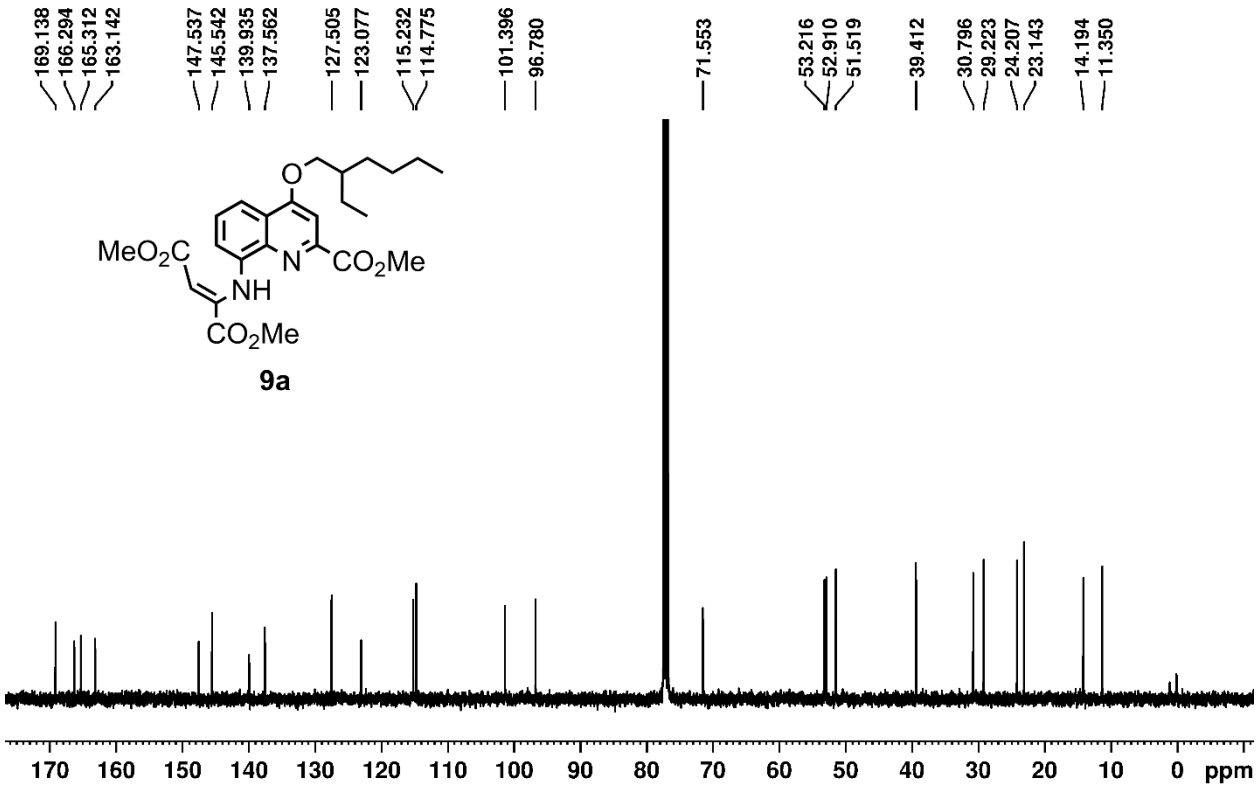
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137.562
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114.775
101.396
96.780
71.553
53.216
52.910
51.519
39.412
30.796
29.223
24.207
23.143
14.194
11.350
MeO2C
NH
CO2Me
N
CO2Me
O
CO2Me
9a
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140
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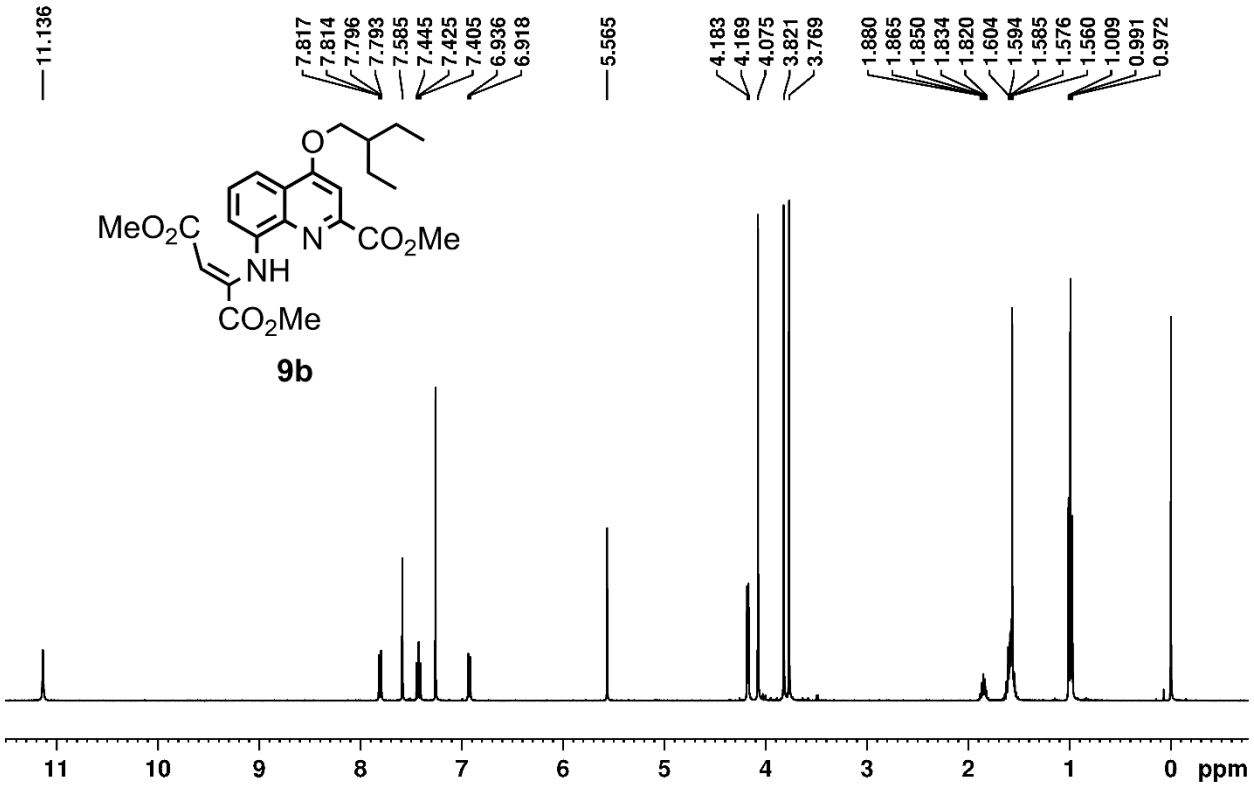
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7.814
7.796
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7.585
7.445
7.425
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6.918
5.565
4.183
4.169
4.075
3.821
3.769
1.880
1.865
1.850
1.834
1.820
1.604
1.594
1.585
1.576
1.560
1.009
0.991
0.972
MeO2C
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O
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9b
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6
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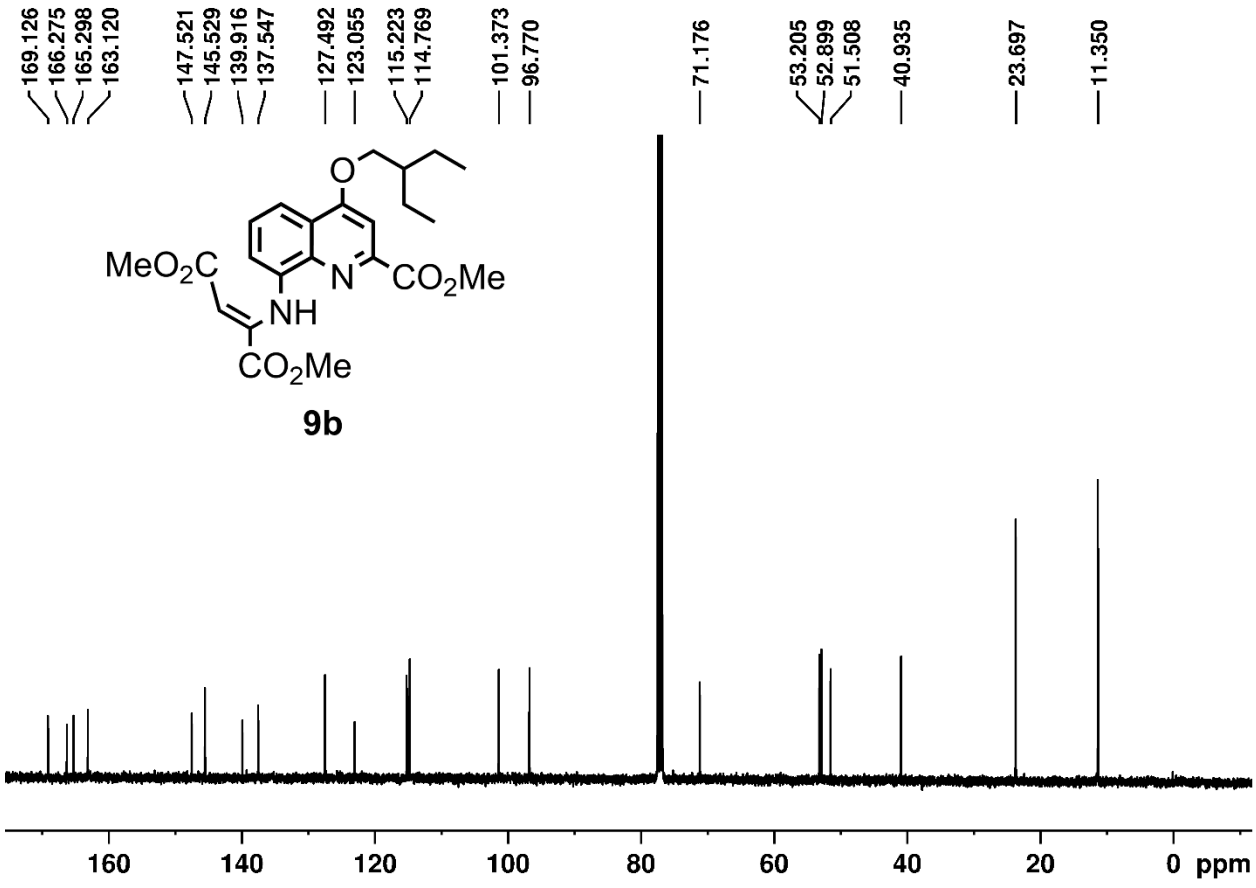
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165.298
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145.529
139.916
137.547
127.492
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115.223
114.769
101.373
96.770
71.176
53.205
52.899
51.508
40.935
23.697
11.350
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CO2Me
NH
CO2Me
O
N
9b
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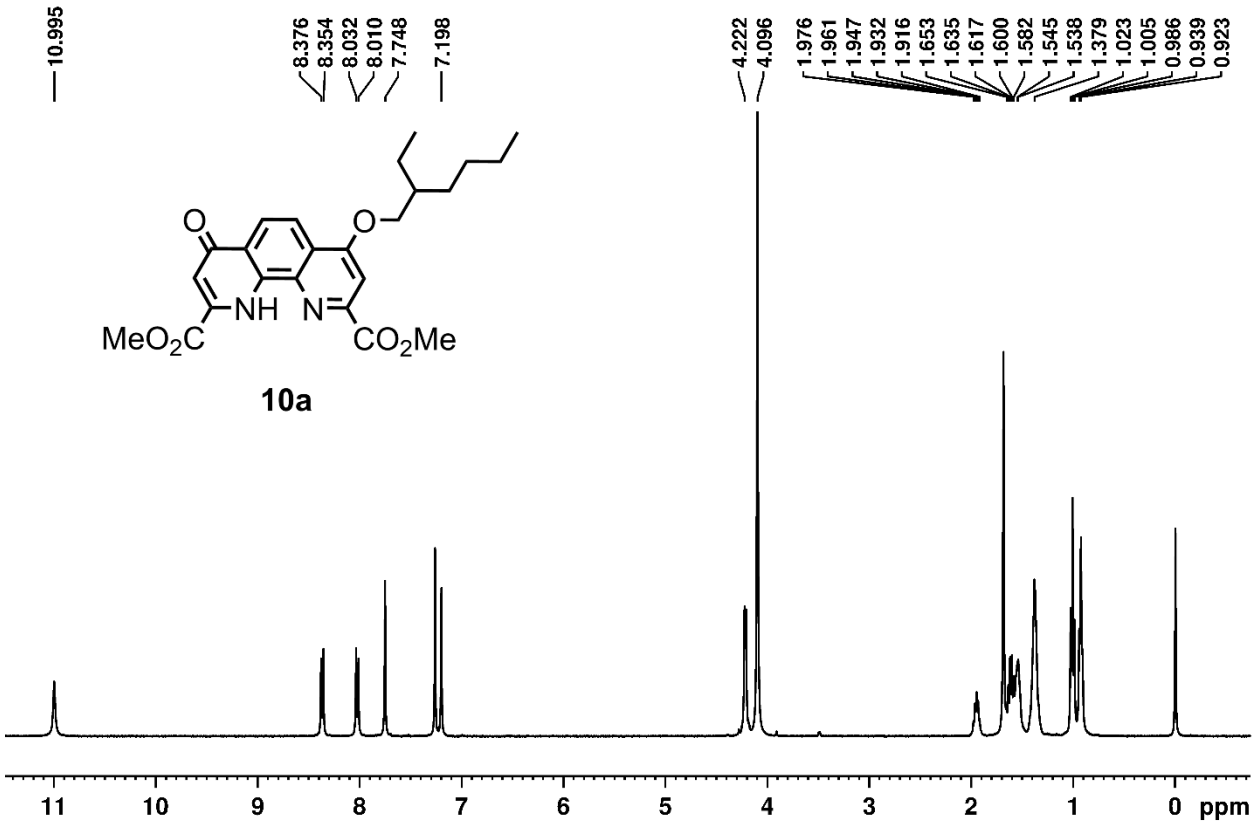
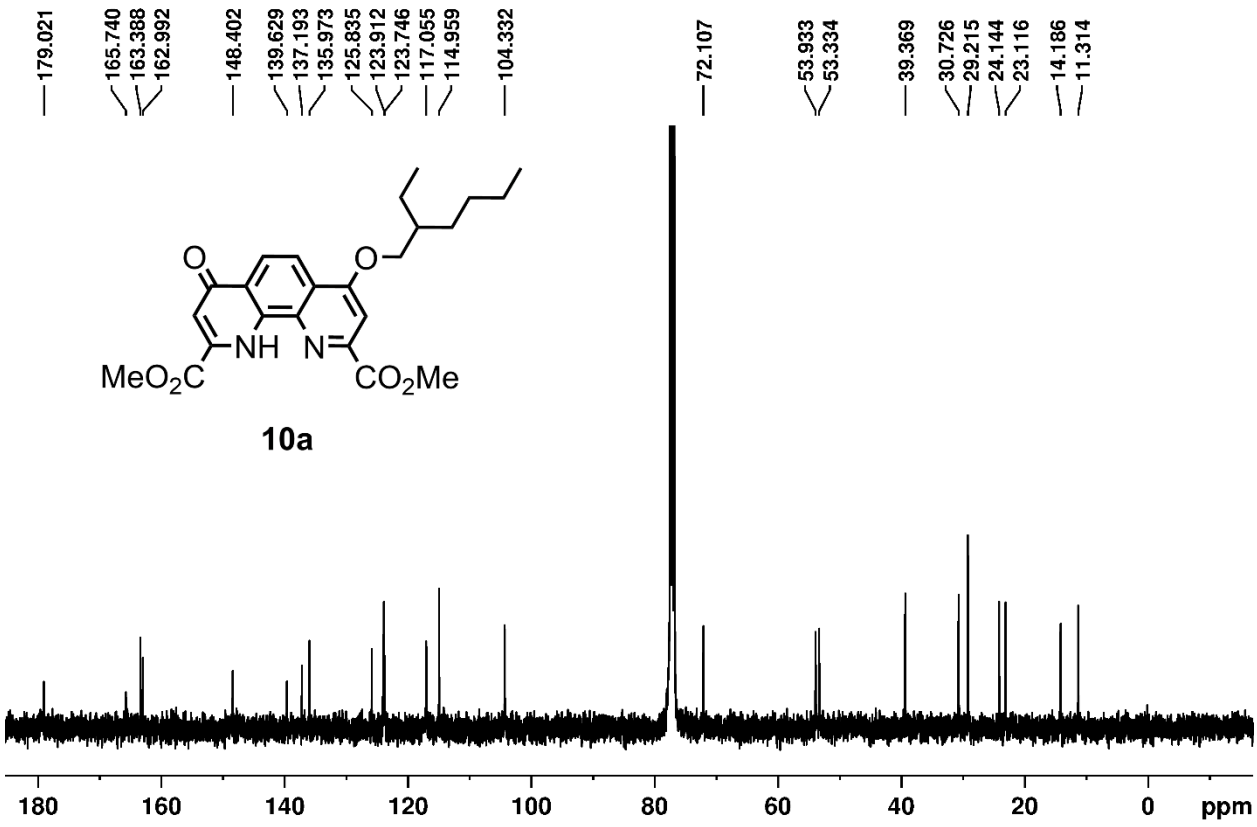
120
100
80
60
40
20
0
ppm


10.995
8.376
8.354
8.032
8.010
7.748
7.198
4.222
4.096
1.976
1.961
1.947
1.932
1.916
1.653
1.635
1.617
1.600
1.582
1.545
1.538
1.379
1.023
1.005
0.986
0.939
0.923
O
O
NH
N
MeO2C
CO2Me
10a
11
10
9
8
7
6
5
4
3
2
1
0
ppm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163.388
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148.402
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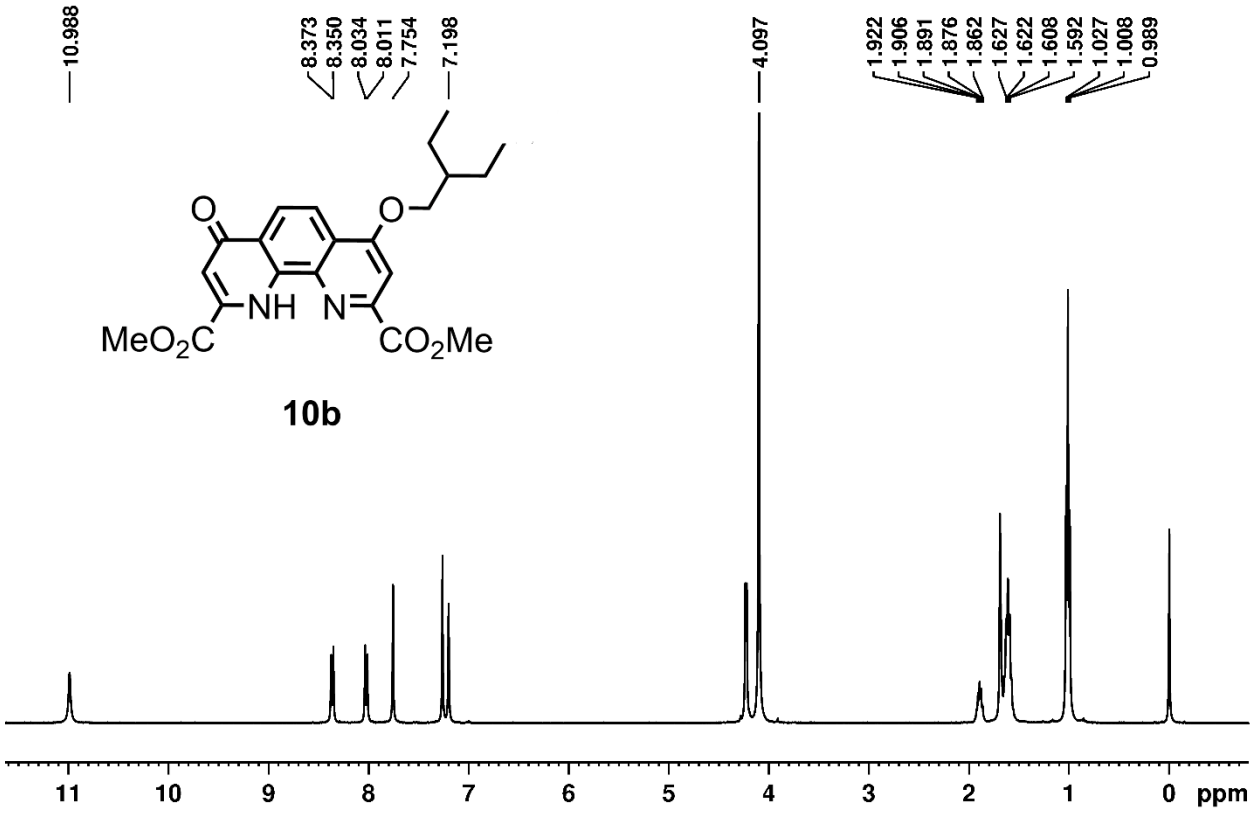
137.193
135.973
125.835
123.912
123.746
117.055
114.959
104.332
72.107
53.933
53.334
39.369
30.726
29.215
24.144
23.116
14.186
11.314
O
O
NH
N
MeO2C
CO2Me
10a
180
160
140
120
100
80
60
40
20
0
ppm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8.373
8.350
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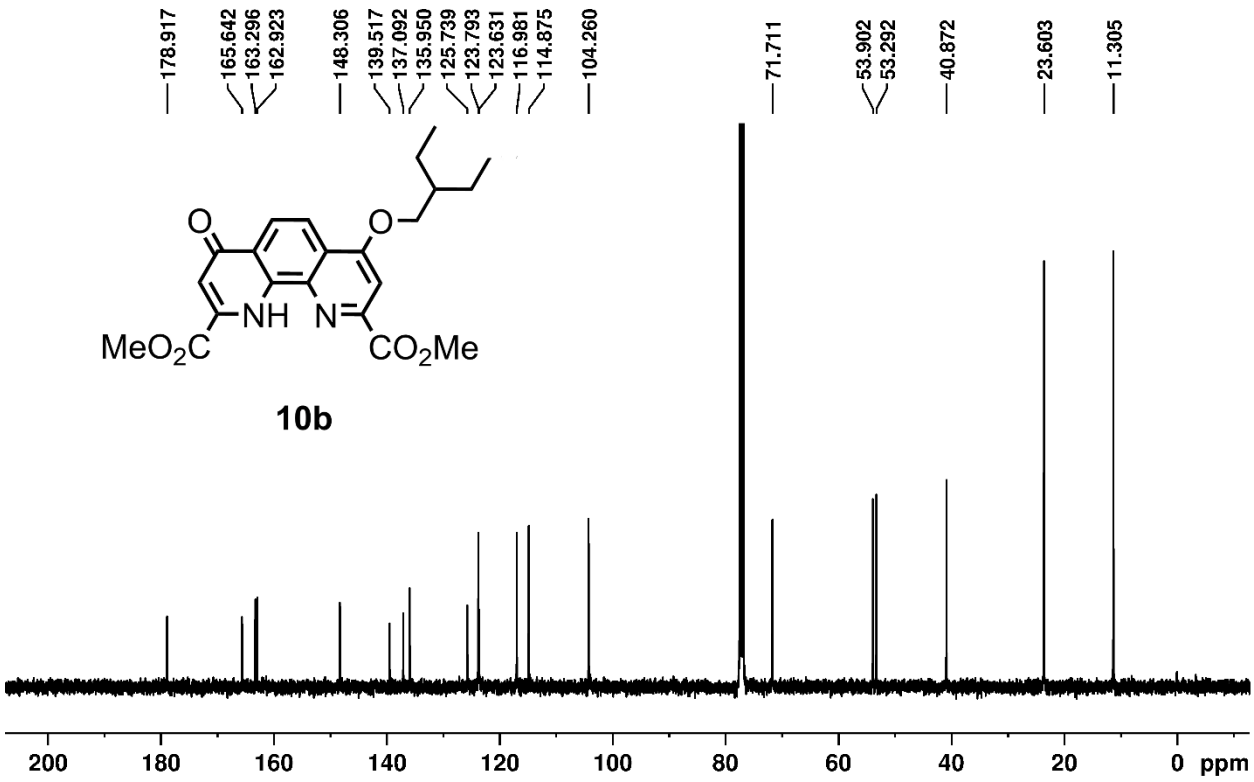
8.011
7.754
7.198
4.097
1.922
1.906
1.891
1.876
1.862
1.627
1.622
1.608
1.592
1.027
1.008
0.989
O
O
NH
N
MeO2C
CO2Me
10b
11
10
9
8
7
6
5
4
3
2
1
0
ppm


178.917
165.642
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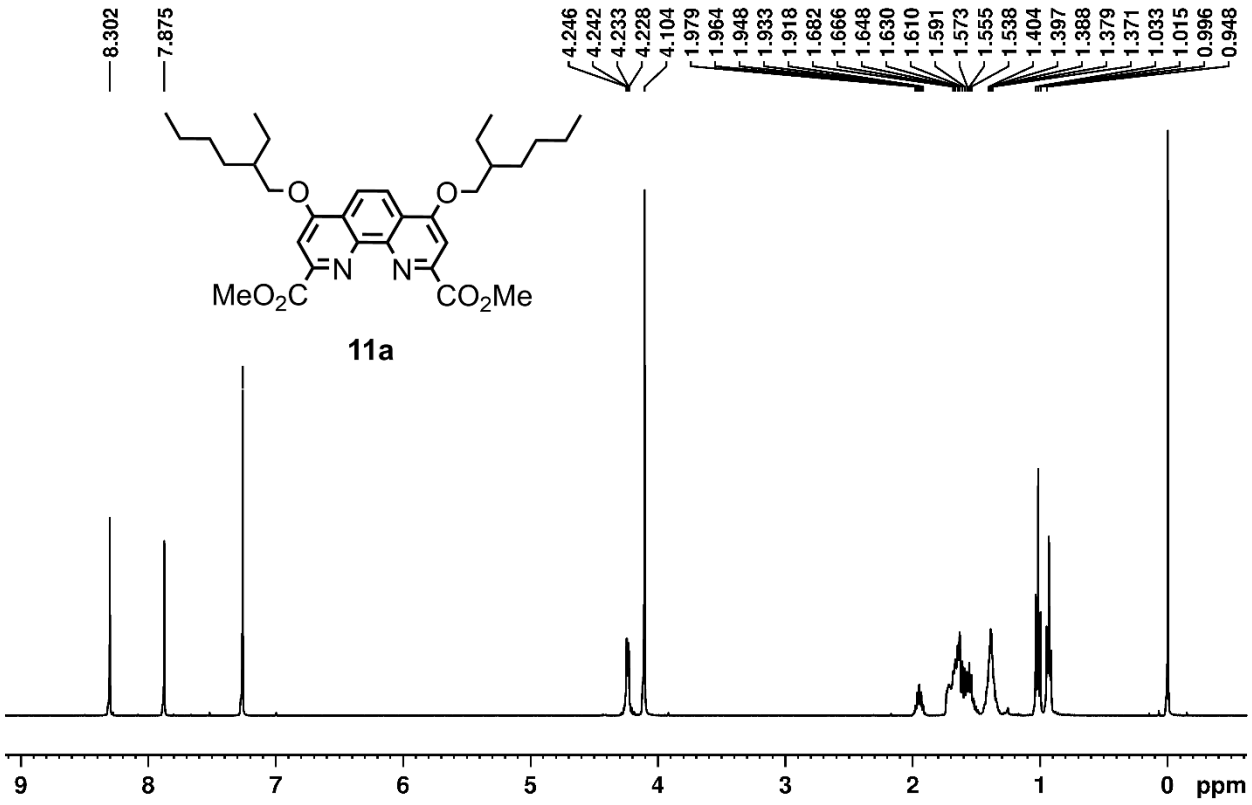
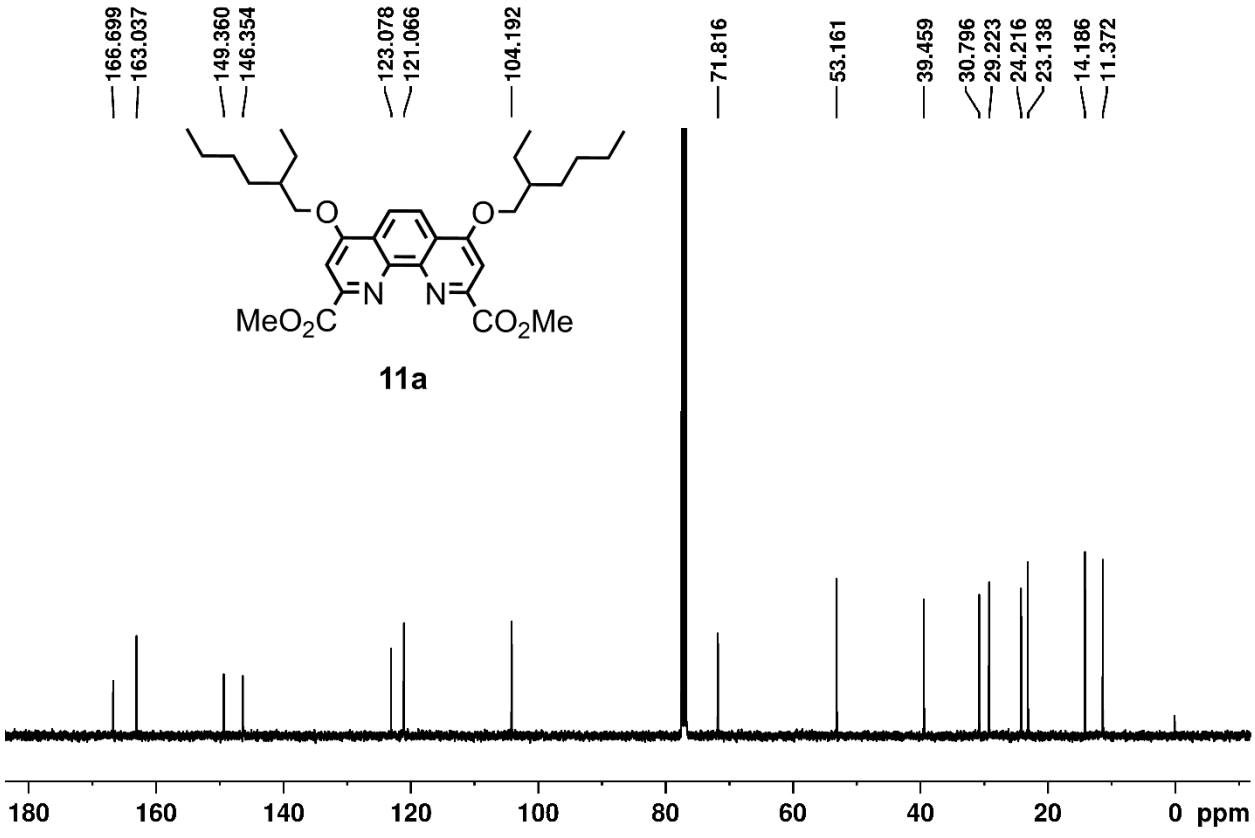
162.923
148.306
139.517
137.092
135.950
125.739
123.793
123.631
116.981
114.875
104.260
71.711
53.902
53.292
40.872
23.603
11.305
O
O
NH
N
MeO2C
CO2Me
10b
200
180
160
140
120
100
80
60
40
20
0
ppm


8.302
7.875
4.246
4.242
4.233
4.228
4.104
1.979
1.964
1.948
1.933
1.918
1.682
1.666
1.648
1.630
1.610
1.591
1.573
1.555
1.538
1.404
1.397
1.388
1.379
1.371
1.033
1.015
0.996
0.948
MeO2C
CO2Me
11a
9
8
7
6
5
4
3
2
1
0
ppm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71.816
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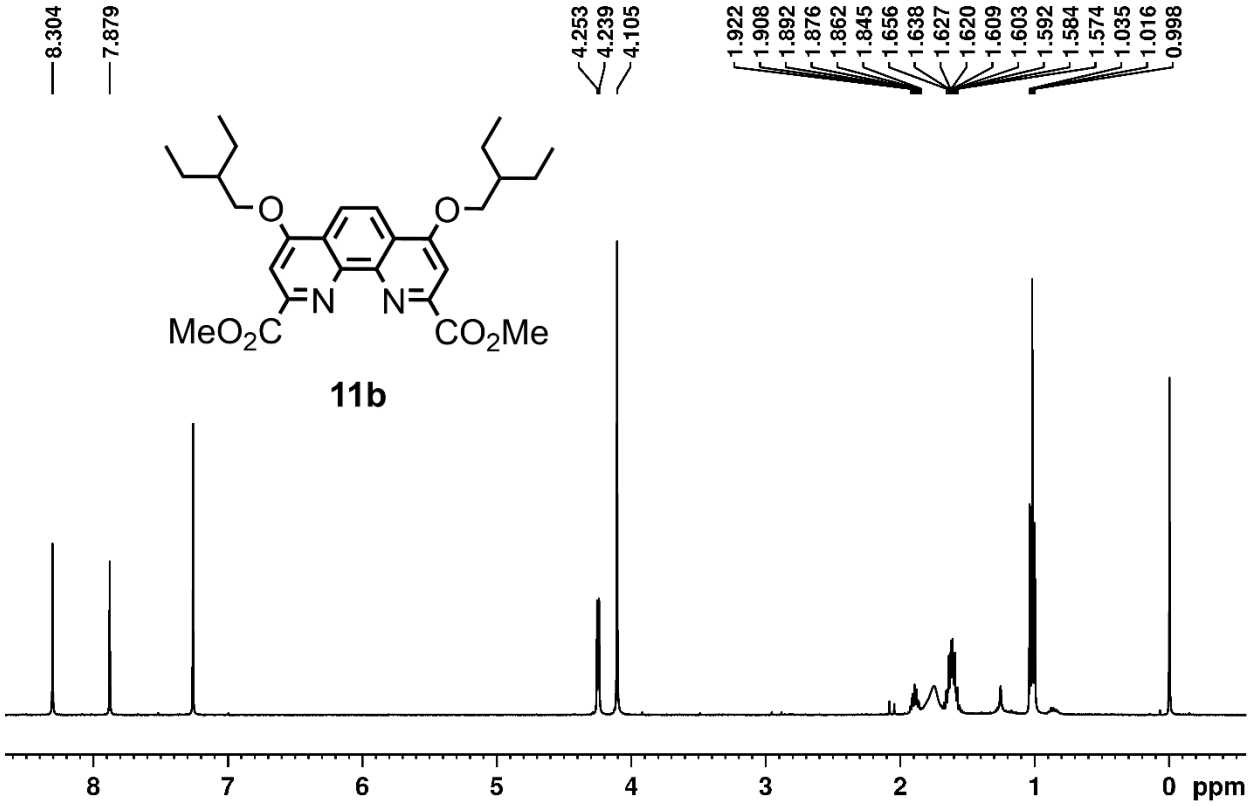
39.459
30.796
29.223
24.216
23.138
14.186
11.372
MeO2C
CO2Me
11a
180
160
140
120
100
80
60
40
20
0
ppm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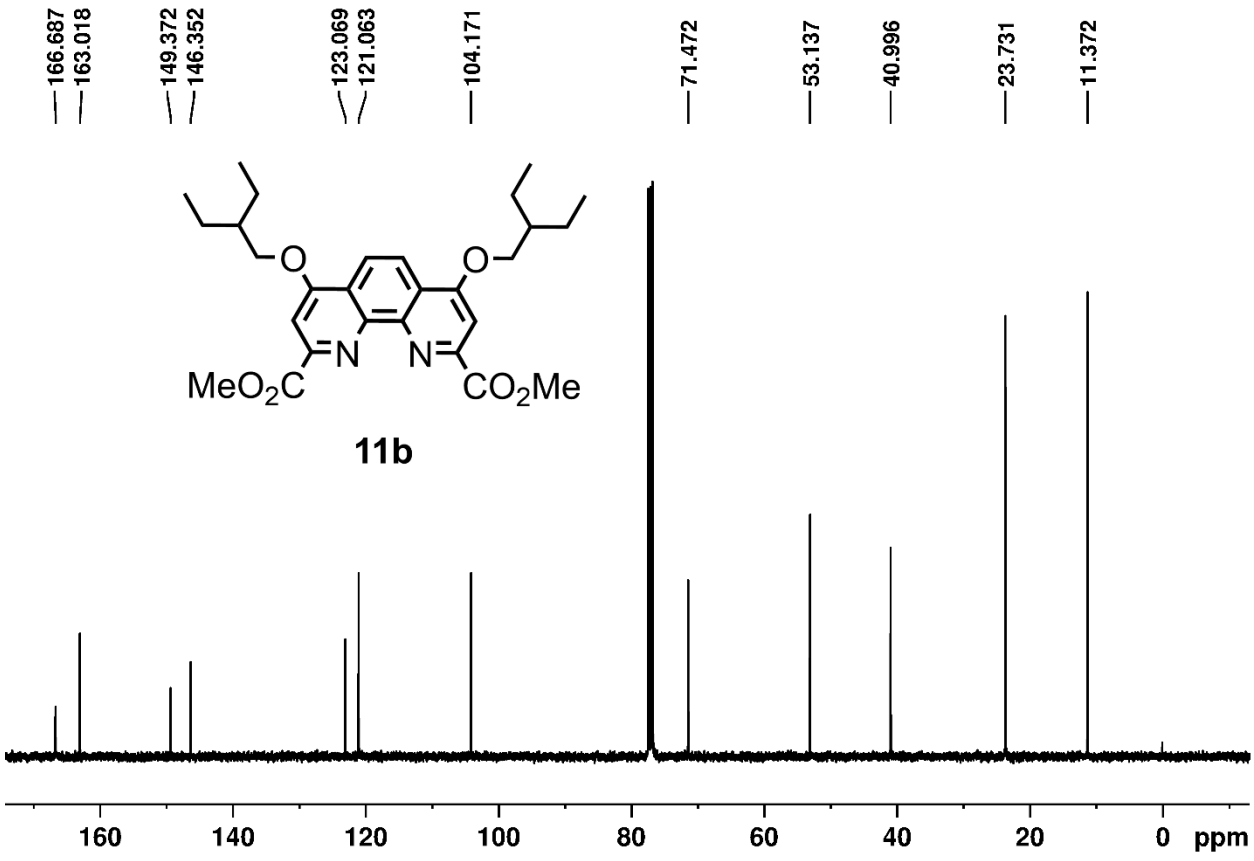
7.879
4.253
4.239
4.105
1.922
1.908
1.892
1.876
1.862
1.845
1.656
1.638
1.627
1.620
1.609
1.603
1.592
1.584
1.574
1.035
1.016
0.998
MeO2C
CO2Me
11b
8
7
6
5
4
3
2
1
0
ppm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149.372
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121.063
104.171
71.472
53.137
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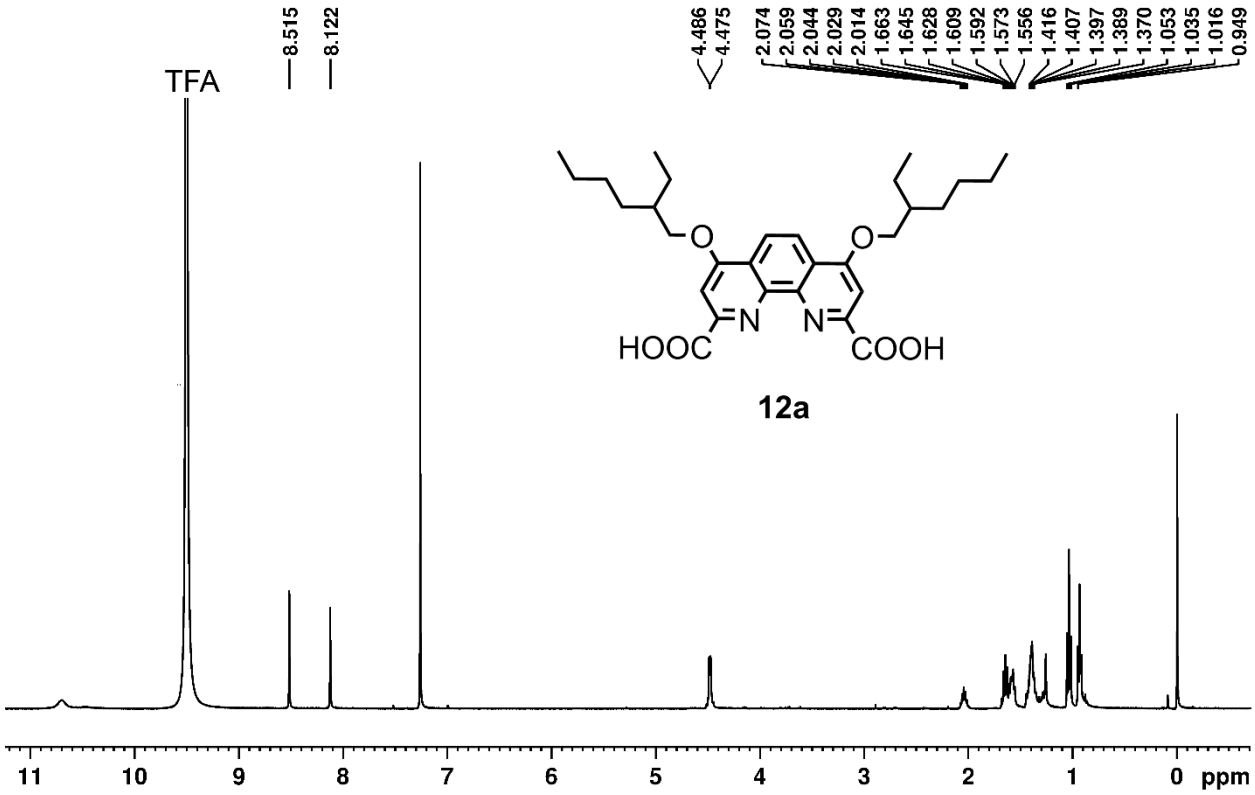
23.731
11.372
MeO2C
CO2Me
11b
160
140
120
100
80
60
40
20
0
ppm


TFA
8.515
8.122
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4.475
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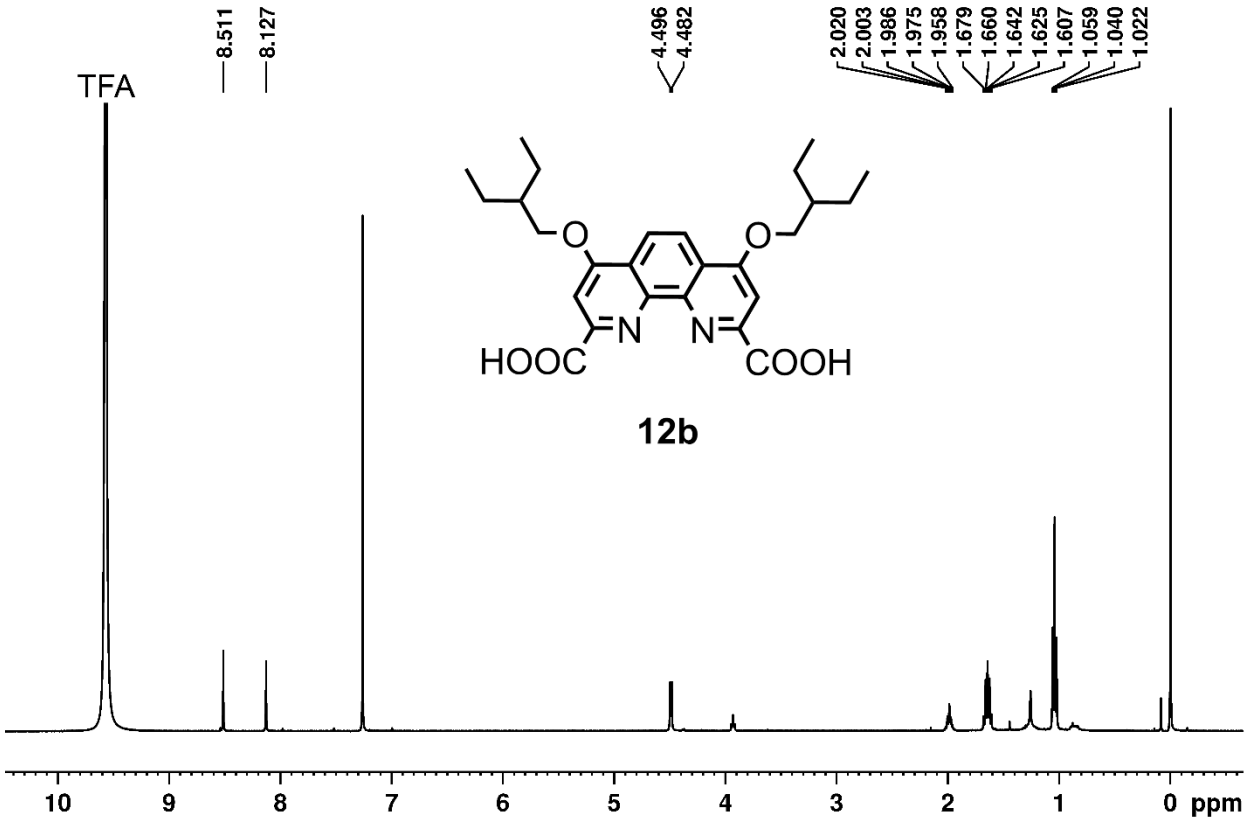
2.059
2.044
2.029
2.014
1.663
1.645
1.628
1.609
1.592
1.573
1.556
1.416
1.407
1.397
1.389
1.370
1.053
1.035
1.016
0.949
O
O
N
N
HOOC
COOH
11
10
9
8
7
6
5
4
3
2
1
0
ppm

12a


TFA
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8.127
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4.482
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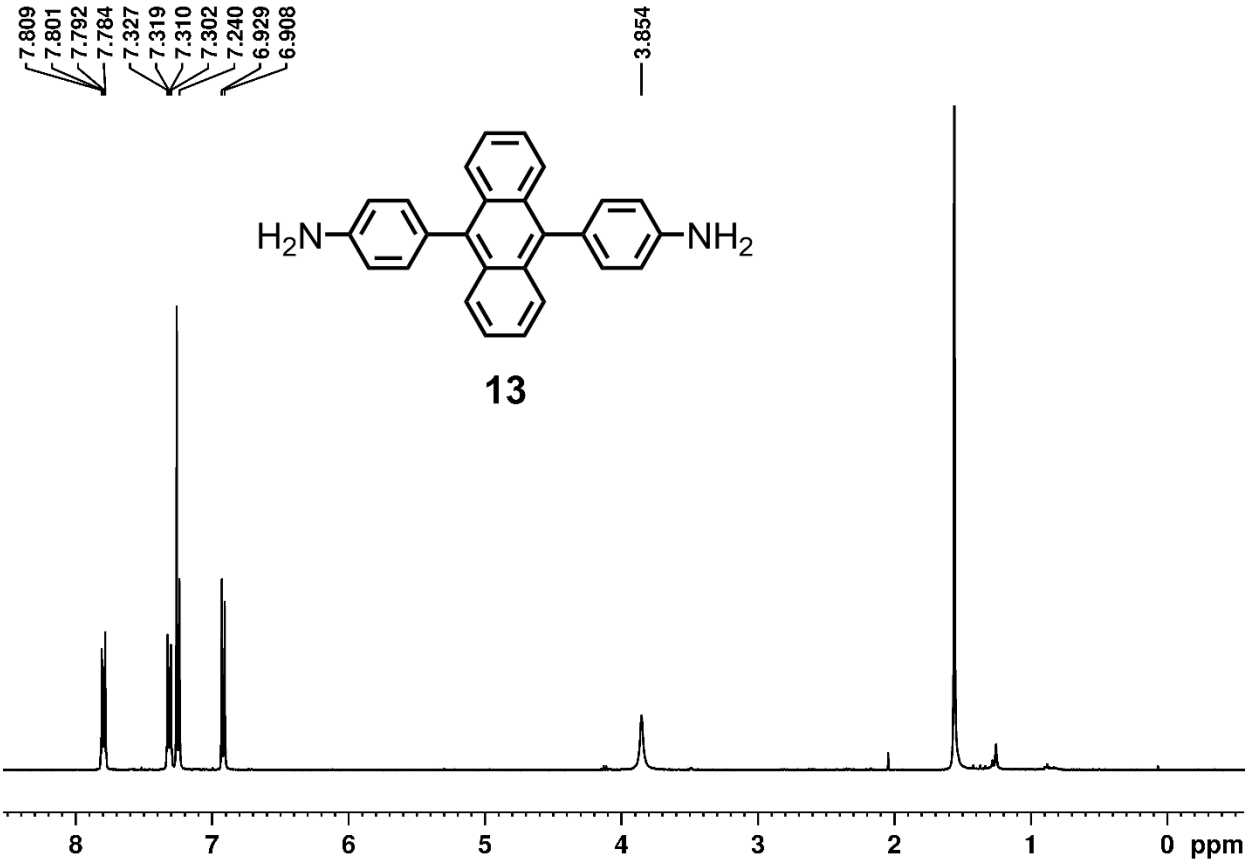
2.003
1.986
1.975
1.958
1.679
1.660
1.642
1.625
1.607
1.059
1.040
1.022
O
O
N
N
HOOC
COOH
10
9
8
7
6
5
4
3
2
1
0
ppm

12b


7.809
7.801
7.792
7.784
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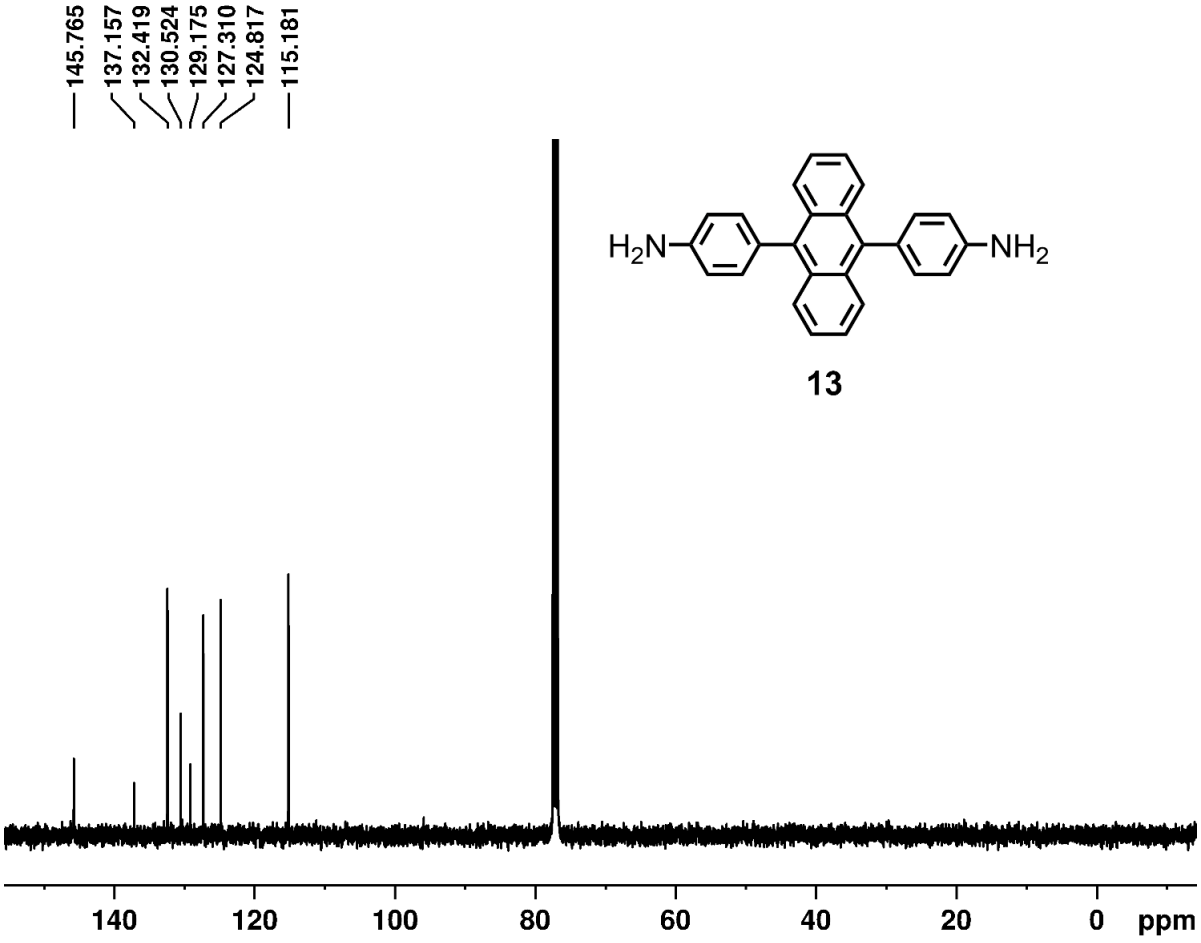
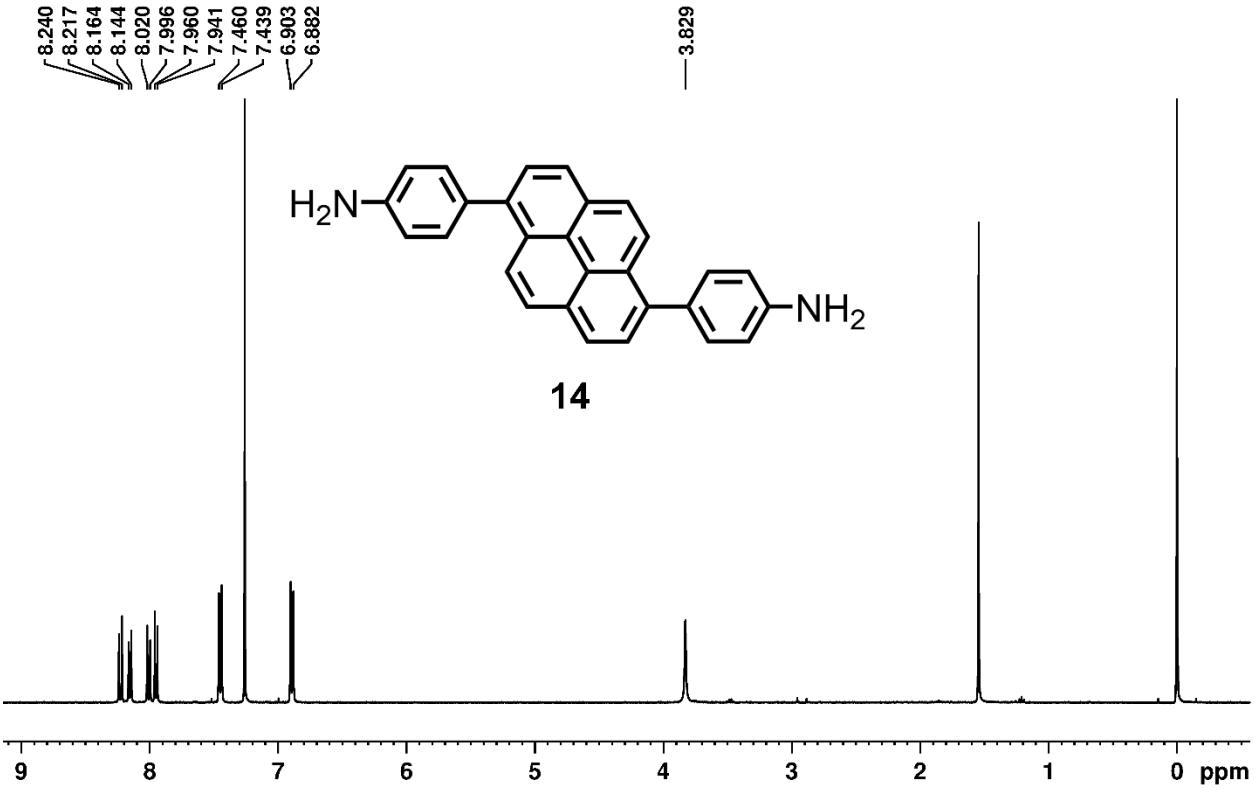
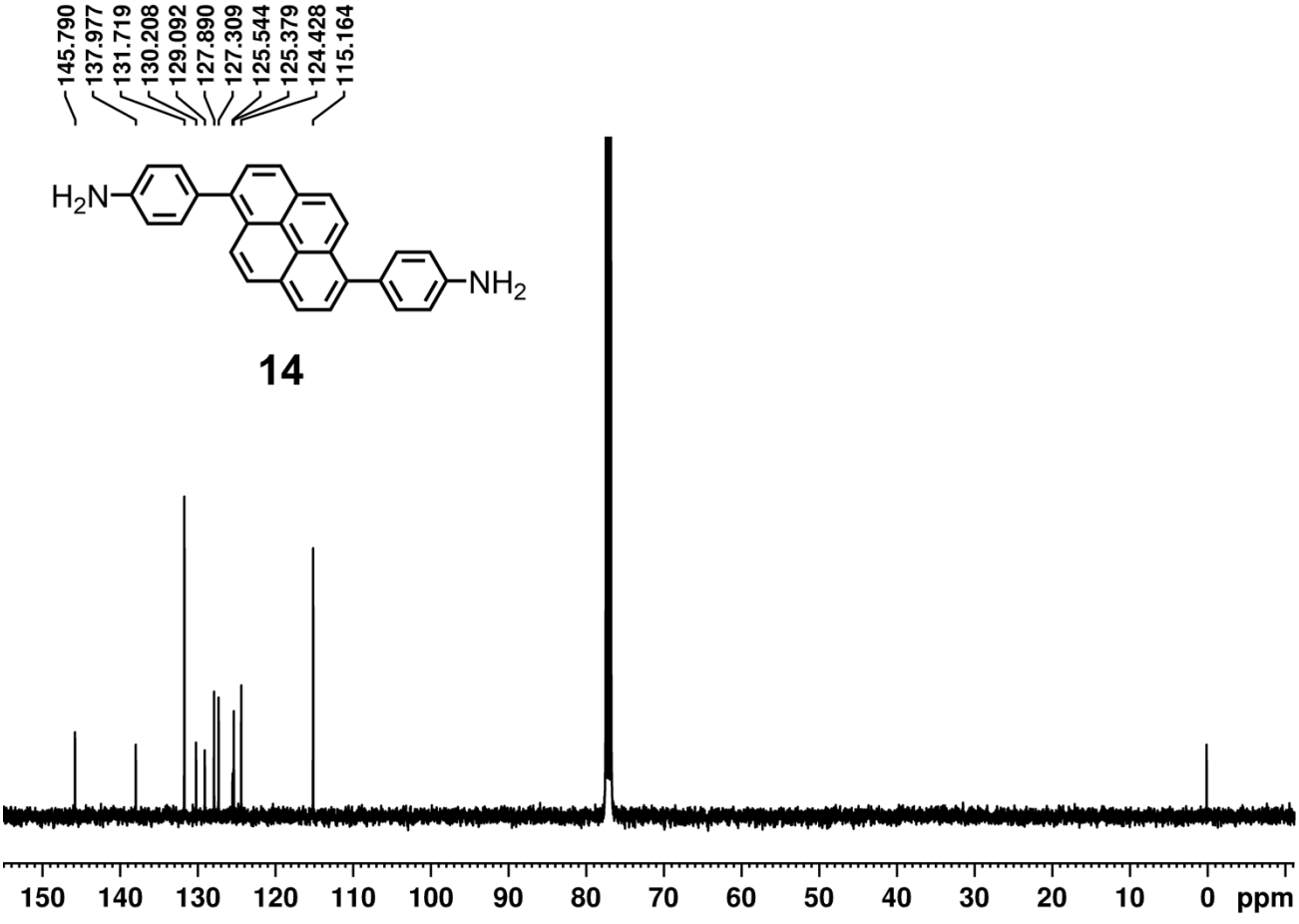
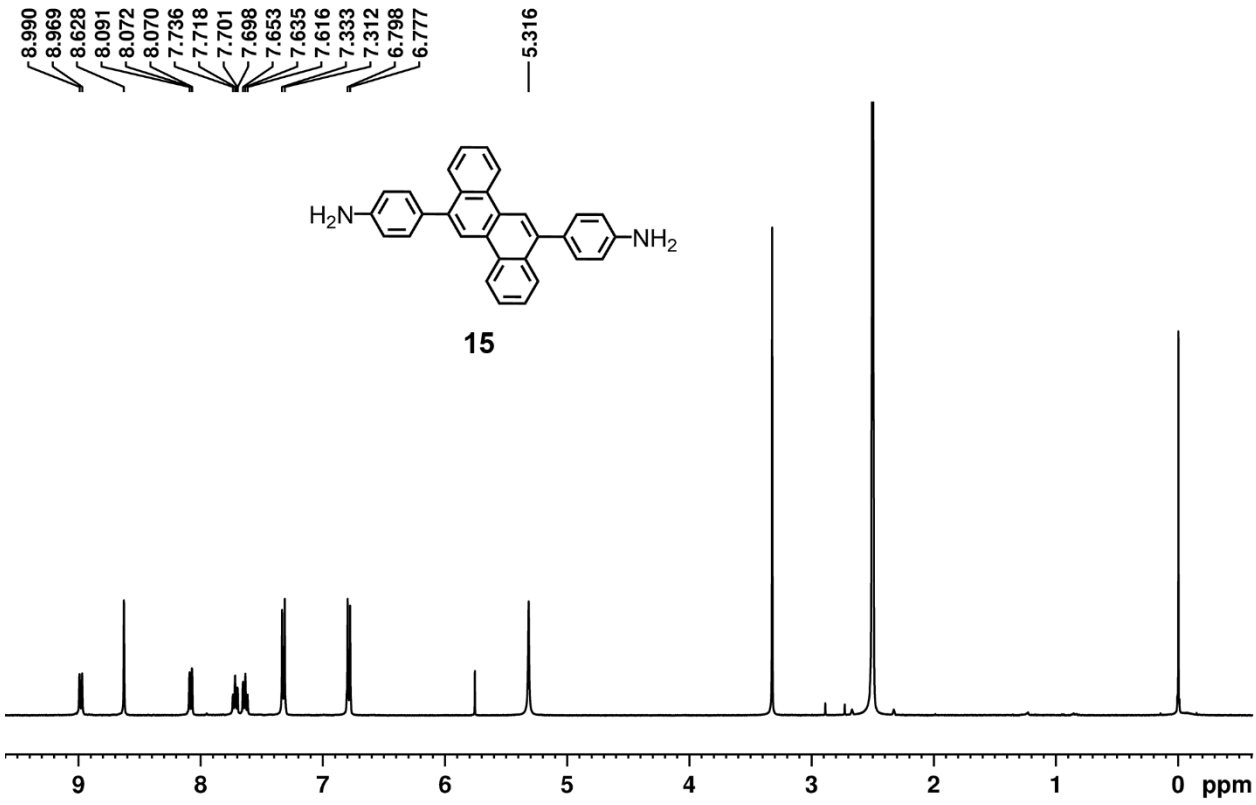
7.319
7.310
7.302
7.240
6.929
6.908
3.854
H2N
NH2
13
8
7
6
5
4
3
2
1
0 ppm


145.765
137.157
132.419
130.524
129.175
127.310
124.817
115.181
H2N
NH2
13
140
120
100
80
60
40
20
0 ppm


8.240
8.217
8.164
8.144
8.020
7.996
7.960
7.941
7.460
7.439
6.903
6.882
3.829
H2N
NH2
14
9
8
7
6
5
4
3
2
1
0 ppm


145.790
137.977
131.719
130.208
129.092
127.890
127.309
125.544
125.379
124.428
115.164
H2N
NH2
14
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0 ppm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8.969
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7.718
7.701
7.698
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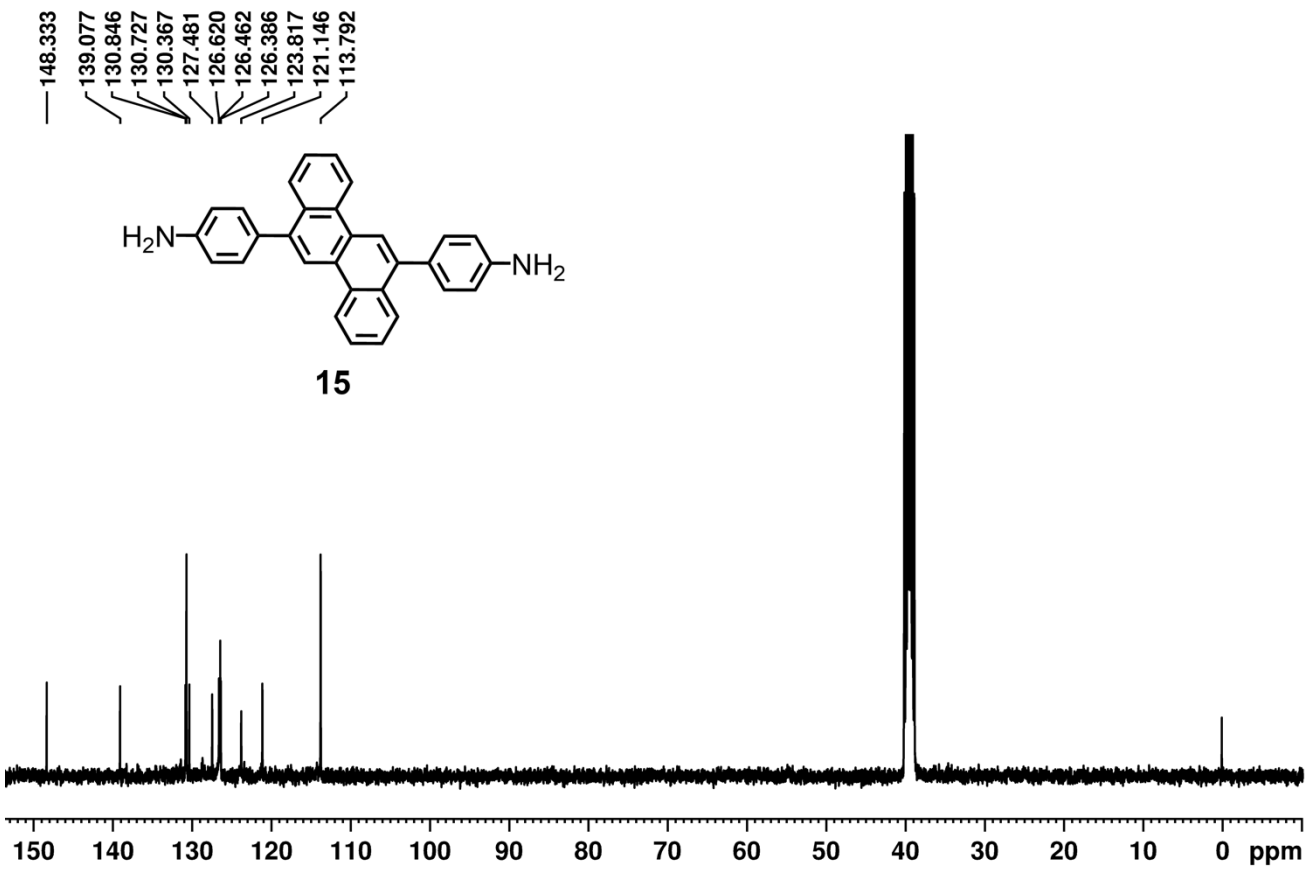
7.616
7.333
7.312
6.798
6.777
5.316
H2N
NH2
15
9
8
7
6
5
4
3
2
1
0 ppm


148.333
139.077
130.846
130.727
130.367
127.481
126.620
126.462
126.386
123.817
121.146
113.792
H2N
NH2
15
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0 ppm

6. References

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