

Supporting Information

General

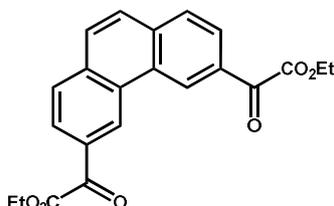
All chemicals were of the best commercially available grade and used without further purification. Thin layer chromatography was carried out using aluminium sheets of silica gel (Merck, 60 F254). Column chromatography was carried out using silica gel (Merck, silica gel 60, 35-75 μm). Mass spectrometry analyses (electrospray (ESI)) were performed by the CESAMO (ISM, Bordeaux, France). HRMS ESI spectra were obtained on a QExactiveTM benchtop Orbitrap mass spectrometer coupled to a Vanquish UHPLC system (Thermo Scientific, San Jose, USA) using electrospray ionization mode. Nuclear Magnetic Resonance spectra were acquired on a JEOL ECS-40 spectrometer. ¹H and ¹³C spectra were referenced to residual solvent peaks (chloroform: 7.26 and 77.16 ppm; dichloromethane: 5.32 and 53.84 ppm; DMSO: 2.50 and 39.52 ppm). UV-visible spectra were recorded on a JASCO-730 spectrometer at 21 °C with 1 cm wide quartz cells. Emission and excitation spectra were recorded on a JASCO-FP8300 spectrometer at 21 °C using 1 cm wide quartz cells. Quantum yields were measured as described in the literature,¹ using Coumarin 153 in EtOH as a standard, with 1.5 nm slits for excitation and 2 nm slits for emission. All compounds were excited with 450 nm light. The crystallographic data were collected with a Bruker APEX II Quasar diffractometer, equipped with a graphite monochromator centred on the path of MoK α radiation. Single crystals of **5** were obtained by slow diffusion of a dichloromethane solution of **5** into butanol, whereas single crystals of **10** were obtained by recrystallisation in ethanol. The selected single crystals were coated with CargilleTM NHV immersion oil and mounted on a fiber loop, followed by data collection at 120 K for **10**, and 298 K for **5**. At 120 K, the single crystals of **5** break into a microcrystalline powder so that the structure was not determined at low temperature. The program SAINT was used to integrate the data, which was thereafter corrected using SADABS.² The structure was solved using SHELXT³ and refined by a full-matrix least-squares method on F² using SHELXL-2019.⁴ All non-hydrogen atoms were refined with anisotropic displacement parameters, whereas hydrogen atoms were assigned to ideal positions and refined isotropically using suitable riding models.

The crystals of coronene tetraester **5** were weakly diffracting. Therefore, the data were cut at 0.90 Å, as there is no diffraction above and R_{int} becomes larger. The result is a quite low Θ_{max} value and data/parameters ratio. DFIX constraint was used between C26 and C27.

The CIF files have been deposited at the Cambridge Crystallographic Data Centre as supplementary publication no. CCDC 2335164-2335165.

Synthetic procedures

3,6-dibromophenanthrene-9,10-quinone⁵ and 3,6-dibromo-9,10-bisbutyloxyphenanthrene⁶ **6** were synthesized using published procedures.

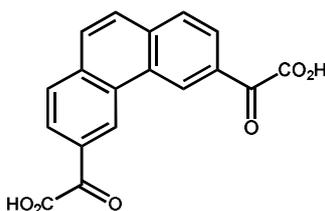


Diethyl phenanthrene-3,6-diglyoxylate **2**

3,6-Dibromophenanthrene (2.50 g, 7.4 mmol, 1 eq.) was dissolved in dry THF (200 mL). The solution was cooled down to -94 °C and *t*BuLi (1.7 M in pentane, 13.2 mL, 22.4 mmol, 4 eq.) was slowly added. The mixture was stirred under argon at -94 °C for 1 h followed by 2 more hours of stirring while the reaction was allowed to warm up to room temperature. The solution was cooled down again to -94 °C and a solution of diethyl oxalate (10.2 mL, 75.1 mmol, 10.1 eq.) was quickly added. The reaction was stirred at -94°C for 30 min, then the cooling bath was removed and the solution stirred for another 30 min at room temperature. The reaction was stopped by addition of HCl (10 %w in water, 100 mL), the phases were separated, the aqueous phase was extracted with DCM, and the combined organic phases were dried with MgSO₄. The solvent was removed under vacuum and the yellow solid obtained was recrystallized in ethanol. Yield: 1.52 g (57%).

¹H NMR (400 MHz, CD₂Cl₂, δ in ppm): 9.45 (d, ⁴J = 2 Hz, 2H), 8.24 (dd, ³J = 8 Hz, ⁴J = 2 Hz, 2H), 8.09 (d, ³J = 8 Hz, 2H), 8.00 (s, 2H), 4.56 (q, ³J = 7 Hz, 4H), 1.51 (t, ³J = 7 Hz, 6H).

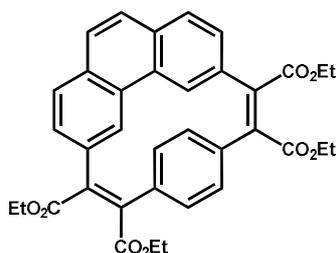
¹³C NMR (100 MHz, CDCl₃, δ in ppm): 186.1, 163.8, 136.2, 131.1, 130.2, 130.1, 129.7, 127.2, 126.4, 62.8, 14.34.



Phenanthrene-3,6-diglyoxylic acid **3**

Diethyl phenanthrene-3,6-diglyoxylate **2** (1.52 g, 4.2 mmol, 1 eq.) was dissolved in ethanol (100 mL). A solution of NaHCO₃ in water (10 g in 200 mL) and was added, and the mixture was stirred at reflux overnight. After cooling down to room temperature, HCl (10 %w in water) was added and a precipitate appears. The solid is filtered off and dried, Yield: 1.17 g, 91%.

¹H NMR (400 MHz, DMSO-d₆, δ in ppm): 9.35 (d, ⁴J = 2 Hz, 2H), 8.29 (d, ³J = 8 Hz, 2H), 8.23 – 8.18 (m, 4H).



Flexible coronene tetraester precursor **4**

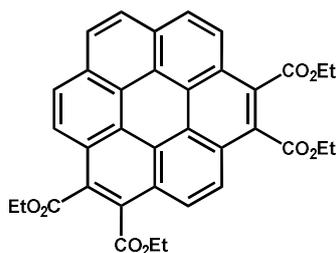
Phenanthrene-3,6-diglyoxylic acid **3** (620 mg, 1.9 mmol, 1 eq.) and 1,4-phenylenediacetic acid (373 mg, 1.9 mmol, 1 eq.) were dissolved in dry THF (50 mL). This solution was added dropwise over 24 h to a refluxing mixture of Ac₂O (11.3 mL, 102 mmol) and NEt₃ (8.3 mL, 60 mmol) in THF (1 L) under argon. After the addition, the reaction was stirred at reflux under argon for 2 more days. The solvent was then partially removed and DBU (10 mL, 67 mmol), EtOH (12 mL, 205 mmol) and EtBr (10 mL, 135 mmol) were added. The solution was stirred at reflux overnight. After being cooled down to room temperature, HCl (10%w in water, 100 mL) was added the phases were separated, the aqueous phase was extracted with DCM, and the combined organic phases were dried with MgSO₄ and concentrated. The resulting oil was purified by column chromatography in DCM on silica gel and recrystallization in EtOH to yield the product as a pale yellow solid (73 mg, 6%).

¹H NMR (400 MHz, CDCl₃, δ in ppm): 7.74 (d, ³J = 8 Hz, 2H), 7.69 (s, 2H), 7.46 – 7.39 (m, 4H), 7.23 (s, 4H), 4.54 (q, ³J = 7 Hz, 4H), 4.34 (q, ³J = 7 Hz, 4H), 1.47 (t, ³J = 7 Hz, 6H), 1.33 (t, ³J = 7 Hz, 6H).

¹³C NMR (100 MHz, CDCl₃, δ in ppm): 169.0, 166.8, 142.5, 137.6, 133.1, 132.1, 129.7, 128.6, 128.18, 127.9, 127.6, 126.3, 62.2, 62.1, 14.31, 14.27.

ESI-HRMS: m/z calcd for C₃₆H₃₂O₈²³Na [M+Na]: 615.20004, found 615.19928.

UV-vis (CH₂Cl₂) λ_{max} (ε L.mol⁻¹.cm⁻¹): 290 (3.71^{E4}), 325 (1.78^{E4}), 365 (1.15^{E4}).



Coronene tetraester **5**

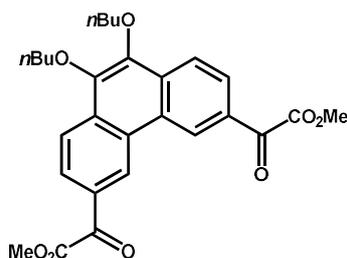
The flexible precursor **4** (37 mg, 0.06 mmol, 1 eq) was dissolved in AcOEt (400 mL). The solution was stirred for 2 days at room temperature under air in a Peschl photoreactor with irradiation from a medium pressure 150 W mercury immersion lamp inside a borosilicate immersion tube in which cooling water circulated. The solvent was evaporated and the crude product was washed with an aqueous solution of Na₂SO₃. The phases were separated, the aqueous phase was extracted with DCM, and the combined organic phases were dried with MgSO₄ and concentrated to yield the coronene tetraester in a quantitative yield (35 mg).

^1H NMR (400 MHz, CD_2Cl_2 , δ in ppm): 9.12 (s, 2H), 8.77 (d, $^3\text{J} = 9$ Hz, 2H), 8.41 (d, $^3\text{J} = 9$ Hz, 2H), 8.21 (s, 2H), 4.74 (q, $^3\text{J} = 7$ Hz, 4H), 4.73 (q, $^3\text{J} = 7$ Hz, 4H), 1.69 (t, $^3\text{J} = 7$ Hz, 12H).

^{13}C NMR (100 MHz, CD_2Cl_2 , δ in ppm): 168.8, 168.6, 130.0, 128.9, 128.6, 127.6, 127.0, 125.2, 125.0, 124.1, 122.0, 121.9, 120.1, 62.9, 14.7.

ESI-HRMS: m/z calcd for $\text{C}_{36}\text{H}_{28}\text{O}_8^{23}\text{Na}$ [$\text{M}+\text{Na}$]: 611.16764, found 611.16841.

UV-vis (CH_2Cl_2) λ_{max} (ϵ $\text{L}\cdot\text{mol}^{-1}\cdot\text{cm}^{-1}$): 310 ($4.76^{\text{E}4}$), 330 ($4.36^{\text{E}4}$), 355 ($1.59^{\text{E}4}$), 420 ($1.20^{\text{E}4}$), 440 ($1.1^{\text{E}3}$).

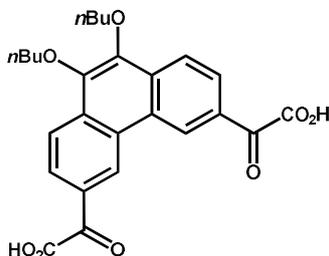


Dimethyl 9,10-bis(butyloxy)phenanthrene-3,6-diglyoxylate 7

3,6-dibromo-9,10-bis(butyloxy)phenanthrene **6** (2.740 g, 5.7 mmol, 1 eq.) was dissolved in dry THF (60 mL). The solution was cooled down to -94 °C and $t\text{BuLi}$ (1.6 M in pentane, 14.3 mL, 22.8 mmol, 4 eq.) was slowly added. The mixture was stirred under argon at -94 °C for 1 h followed by 2 more hours of stirring while the reaction was allowed to warm up to room temperature. The solution was cooled down again to -94 °C and a solution of dimethyl oxalate (4.910 g, 41.6 mmol, 7.3 eq.) in dry THF (15 mL) was added quickly. The reaction medium was stirred at -94 °C for 30 min, then the cooling bath was removed and the solution stirred for another 90 min at room temperature. The reaction was stopped by addition of HCl (10 %w in water, 100 mL) and the phases were separated, the aqueous phase was extracted with DCM, and the combined organic phases were dried with MgSO_4 . The solvent was removed under vacuum and the yellow solid obtained was washed with MeOH. Yield: 1.236 g (44 %).

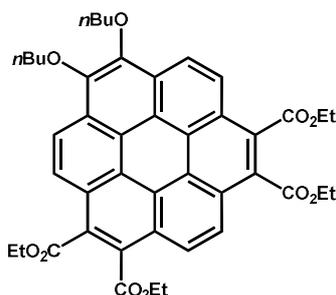
^1H NMR (400 MHz, CDCl_3 , δ in ppm): 9.39 (s, 2H), 8.37 (d, $^3\text{J} = 9$ Hz, 2H), 8.24 (dd, $^3\text{J} = 9$ Hz, $^4\text{J} = 1$ Hz, 2H), 4.26 (t, $^3\text{J} = 7$ Hz, 4H), 4.08 (s, 6H), 1.92-1.85 (m, 4H), 1.61 (sextuplet, $^3\text{J} = 7$ Hz, 4H), 1.02 (t, $^3\text{J} = 7$ Hz, 6H).

^{13}C NMR (100 MHz, CDCl_3 , δ in ppm): 185.5, 164.0, 145.8, 134.4, 130.2, 128.4, 127.3, 126.5, 123.5, 73.8, 53.1, 32.5, 19.5, 14.1.



9,10-bis(butyloxy)phenanthrene-3,6-diglyoxylic acid 8

Dimethyl 9,10-bis(butyloxy)phenanthrene-3,6-diglyoxylate **7** (1.81 g, 3.5 mmol, 1 eq.) was dissolved in THF (15 mL). A solution of NaOH (2 g) in a mixture of water (200 mL) and MeOH (20 mL) was added, and



Bis(butyloxy)coronene tetraester 10

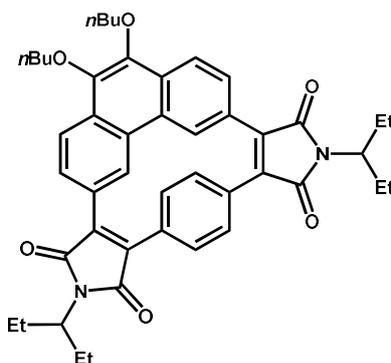
The flexible coronene precursor **9** (80 mg, 0.11 mmol, 1 eq.) and iodine (300 mg) were dissolved in PhMe/AcOEt (3:1, 800 mL). The solution was stirred overnight at room temperature under air in a Peschl photoreactor with irradiation from a medium pressure 150 W mercury immersion lamp inside a borosilicate immersion tube in which cooling water circulated. The solvent was then removed and the crude product was purified by column chromatography in chloroform on silica gel and recrystallisation in EtOH to yield the final product as yellow crystals (52 mg, 65%).

$^1\text{H NMR}$ (400 MHz, CD_2Cl_2 , δ in ppm): 9.37 (d, $^3J = 9$ Hz, 2H), 9.29 (s, 2H), 9.22 (d, $^3J = 9$ Hz, 2H), 4.74 (q, $^3J = 7$ Hz, 4H), 4.73 (q, $^3J = 7$ Hz, 4H), 4.62 (t, $^3J = 7$ Hz, 4H), 2.17 – 2.07 (m, 4H), 1.84 – 1.72 (m, 4H), 1.60 (t, $^3J = 7$ Hz, 6H), 1.599 (t, $^3J = 7$ Hz, H), 1.12 (t, $^3J = 7$ Hz, 6H).

$^{13}\text{C NMR}$ (100 MHz, CD_2Cl_2 , δ in ppm): 68.8, 168.7, 146.6, 130.6, 128.8, 127.1, 125.7, 125.6, 124.7, 124.6, 123.7, 123.1, 122.7, 119.9, 75.0, 63.0, 33.2, 20.0, 14.5, 14.3.

ESI-HRMS: m/z calcd for $\text{C}_{44}\text{H}_{48}\text{O}_{10}^{23}\text{Na}$ [M+Na]: 755.28377, found 755.28484.

UV-vis (CH_2Cl_2) λ_{max} (ϵ L.mol $^{-1}$.cm $^{-1}$): 280 ($2.36^{\text{E}4}$), 320 ($6.76^{\text{E}4}$), 335 ($8.15^{\text{E}4}$), 365 ($2.44^{\text{E}4}$), 430 ($1.96^{\text{E}3}$), 450 ($3.65^{\text{E}3}$).



Flexible bis(butyloxy)coronene diimide precursor 11

9,10-Bis(butyloxy)phenanthrenediglyoxylic acid **8** (477 mg, 1.0 mmol, 1 eq.) and 1,4-phenylenediacetic acid (194 mg, 1.0 mmol, 1 eq.) were dissolved in dry THF (50 mL). This solution was added dropwise over 24 h to a refluxing mixture of Ac_2O (14 mL, 148 mmol) and NEt_3 (16 mL, 118 mmol) in THF (1 L) under argon. After the addition ended, the reaction media was heated under argon for 2 more days. The solvent was then removed until ca. 150 mL remained and 3-aminopentane (20 mL, 171 mmol) was added. The

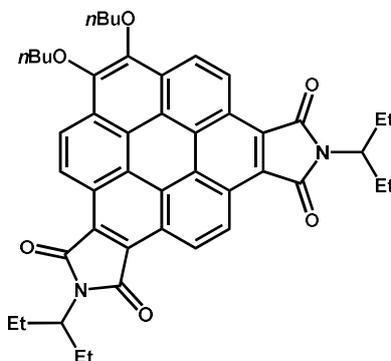
solution was stirred at reflux for another 2 days. After being cooled down to room temperature, excess HCl (10%w in water) was added and the phases were separated, the aqueous phase was extracted with DCM, and the combined organic phases were dried with MgSO₄ and the solvent removed under reduced pressure. The resulting oil was purified by column chromatography in DCM on silica gel and recrystallization in EtOH to yield the product as a yellow solid (254 mg, 35%).

¹H NMR (400 MHz, CD₂Cl₂, δ in ppm): 8.41 (dd, ³J = 9 Hz, ⁴J = 2 Hz, 2H), 8.20 (d, ³J = 9 Hz, 2H), 7.26 (s, 4H), 7.05 (d, ⁴J = 2 Hz, 2H), 4.25 (t, ³J = 7 Hz, 4H), 4.07 (m, 2H), 2.11 (m, 4H), 1.95 – 1.78 (m, 8H), 1.61 (m, 6H), 1.03 (t, ³J = 7 Hz, 6H), 0.99 (t, ³J = 7 Hz, 12H).

¹³C NMR (100 MHz, CD₂Cl₂, δ in ppm): 171.3, 170.8, 145.3, 137.4, 137.3, 133.7, 130.8, 130.2, 127.5, 127.5, 126.6, 125.7, 122.7, 74.2, 56.5, 32.9, 25.9, 19.8, 14.2, 11.5.

ESI-HRMS: m/z calcd for C₄₆H₅₀O₆²³Na [M+Na]: 749.35721, found 749.35782.

UV-vis (CH₂Cl₂) λ_{max} (ε L.mol⁻¹.cm⁻¹): 250 (7.3^{E4}), 310 (1.9^{E4}), 385 (1.5^{E4}), 450 (1.2^{E4}).



Bis(butyloxy)coronene diimide **12**

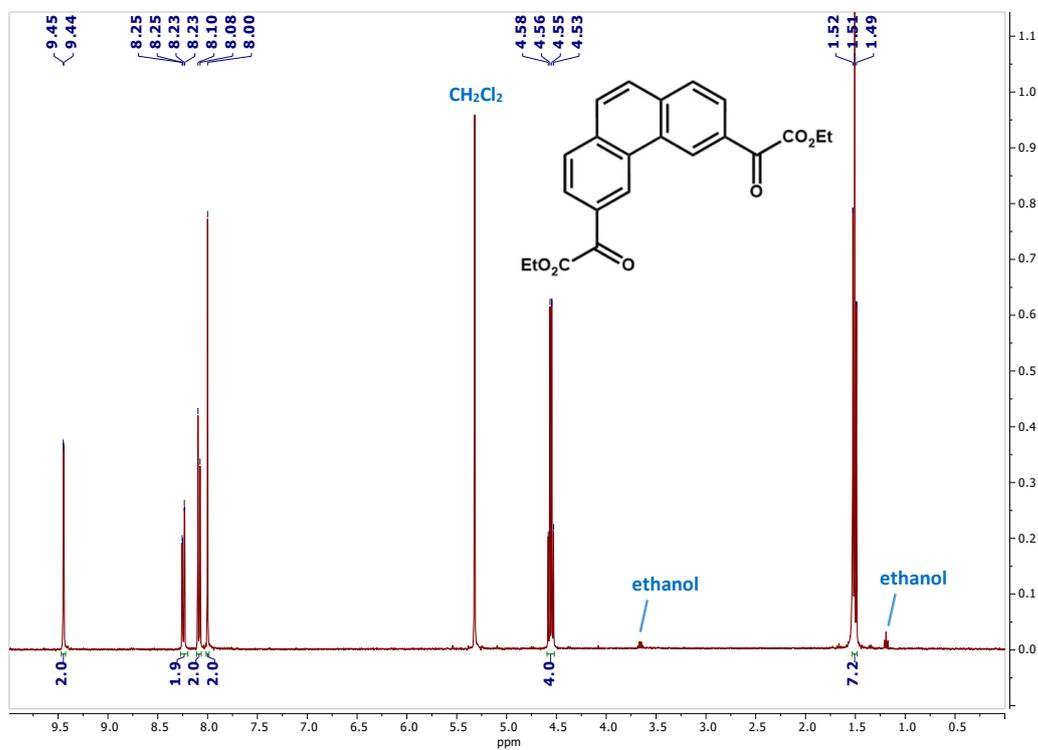
The flexible coronene precursor **11** (253 mg, 0.35 mmol, 1 eq.) and iodine (300 mg) were dissolved in PhMe/AcOEt (3:1, 800 mL). The solution was stirred overnight at room temperature under air in a Peschl photoreactor with irradiation from a medium pressure 150 W mercury immersion lamp inside a borosilicate immersion tube in which cooling water circulated. The solvent was then removed and the crude product was purified by column chromatography in CHCl₃ on silica gel and recrystallized in EtOH to yield the final product as yellow crystals (76 mg, 30%).

¹H NMR (400 MHz, CD₂Cl₂, δ in ppm): 9.71 (d, ³J = 9 Hz, 2H), 9.33 (s, 2H), 9.16 (d, ³J = 9 Hz, 2H), 4.71 (t, ³J = 7 Hz, 4H), 4.37 (m, 2H), 2.50 – 2.33 (m, 4H), 2.25 – 2.10 (m, 8H), 1.89 (h, ³J = 7 Hz, 4H), 1.23 (t, ³J = 7 Hz, 6H), 1.19 (t, ³J = 7 Hz, 12H).

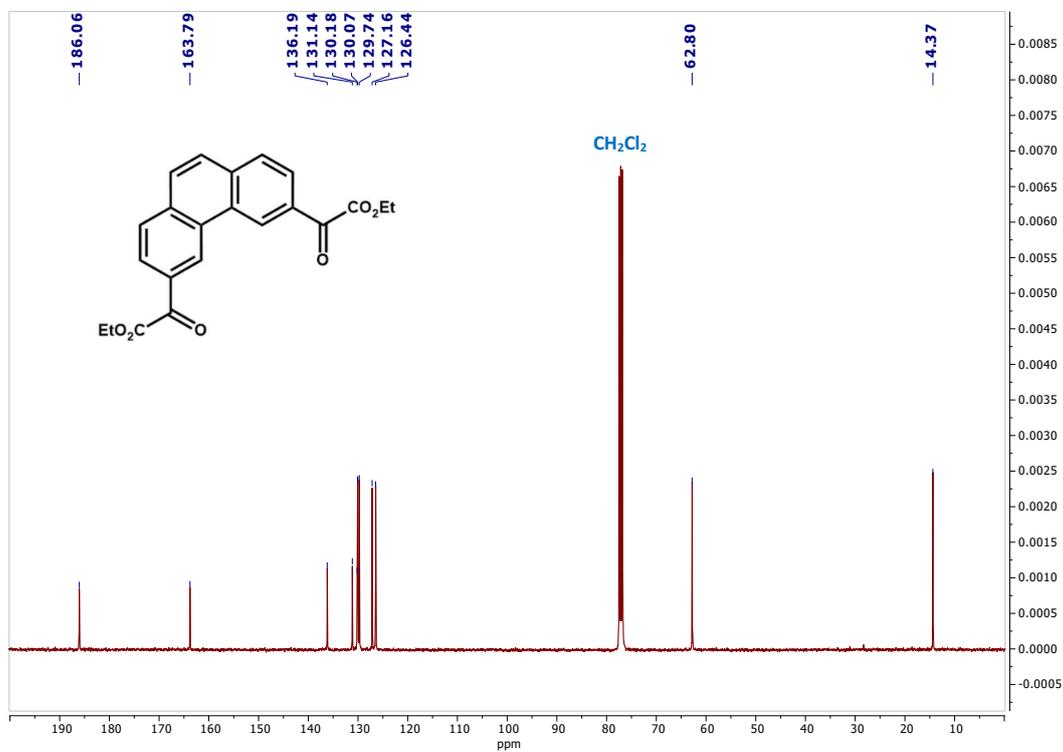
¹³C NMR (100 MHz, CD₂Cl₂, δ in ppm): 170.4, 170.3, 146.8, 126.7, 125.4, 124.1, 123.9, 123.3, 122.9, 122.8, 122.0, 118.3, 74.9, 56.0, 33.2, 25.7, 19.8, 14.3, 11.8.

UV-vis (CH₂Cl₂) λ_{max} (ε L.mol⁻¹.cm⁻¹): 265 (4.5^{E4}), 295 (5.0^{E4}), 315 (5.6^{E4}), 390 (7.2^{E4}), 475 (7.3^{E3}), 505 (1.1^{E4}).

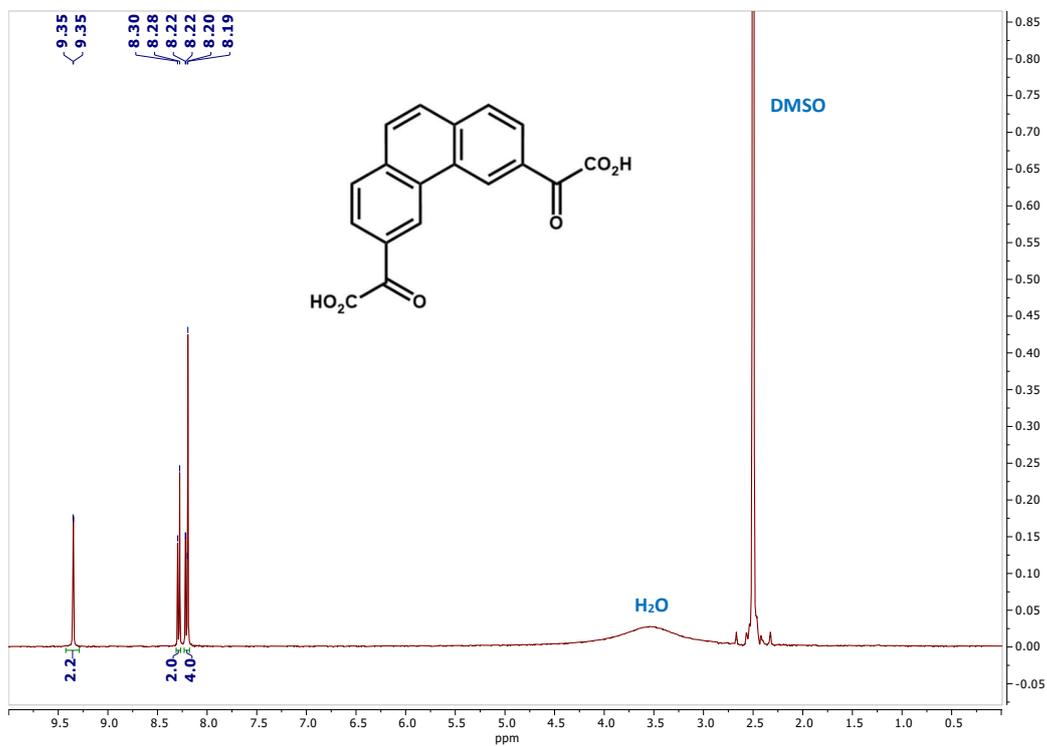
NMR spectra



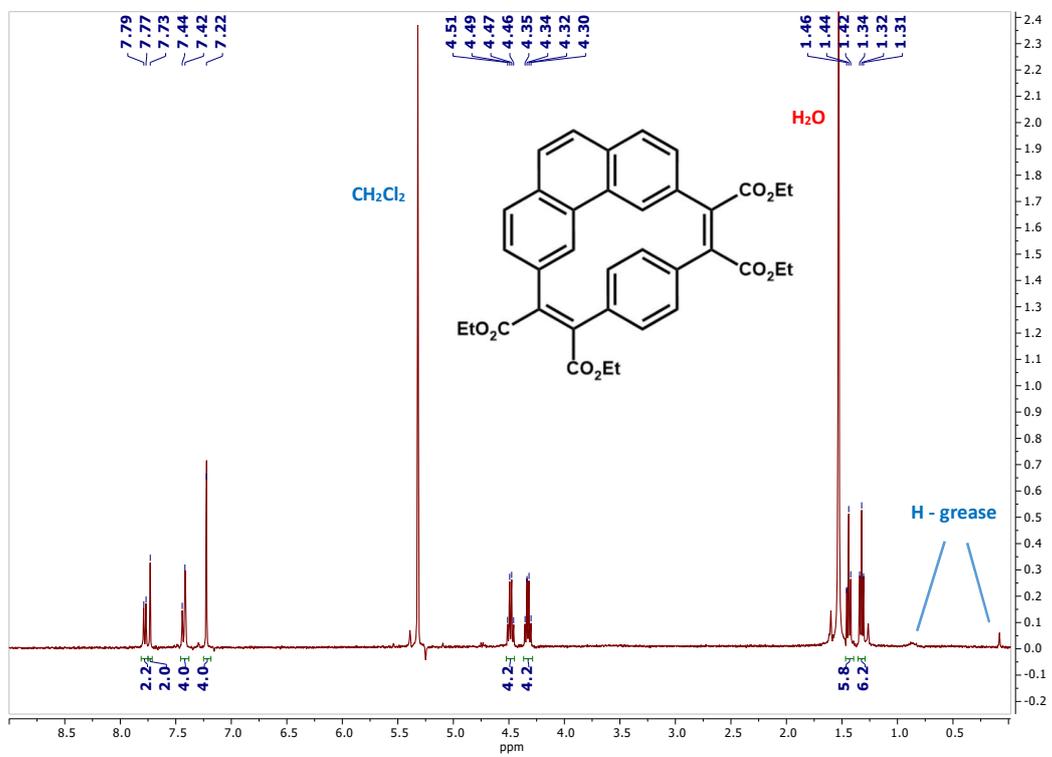
¹H NMR spectrum of 3,6-diethyl-phenanthrenediglyoxylate 2 (CD₂Cl₂, 400 MHz, 298 K)



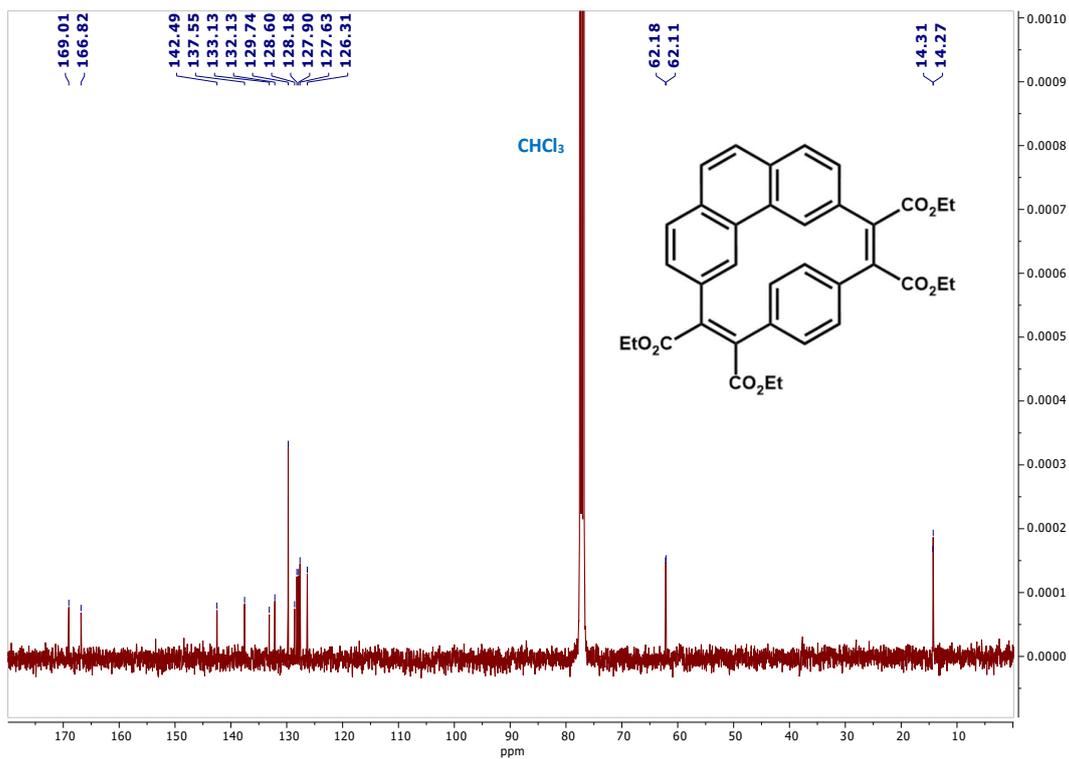
¹³C NMR spectrum of 3,6-diethyl-phenanthrenediglyoxylate 2 (CDCl₃, 100 MHz, 298 K)



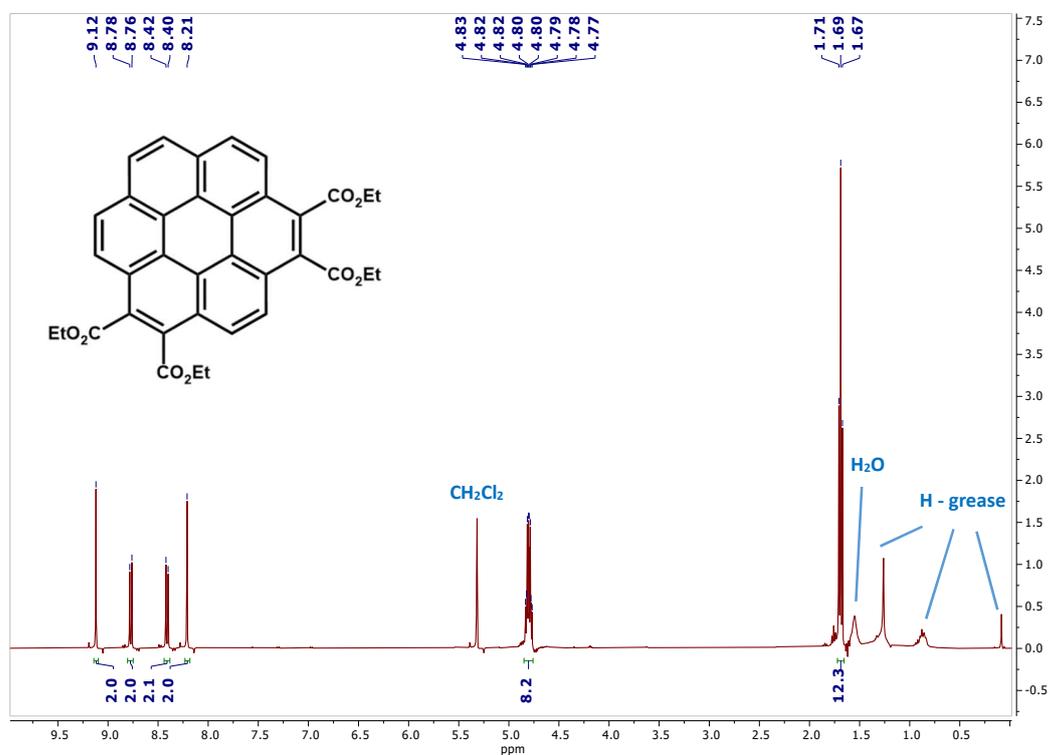
¹H NMR spectrum of phenanthrene-3,6-diglyoxylic acid **3** (DMSO-*d*₆, 400 MHz, 298 K)



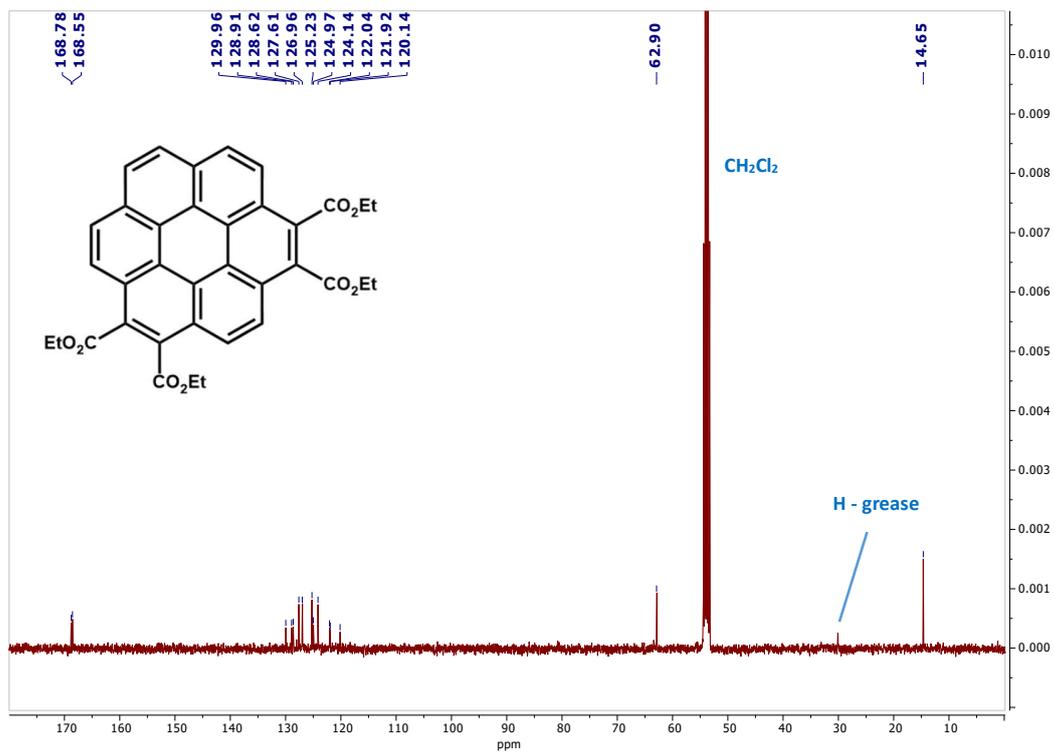
¹H NMR spectrum of the flexible coronene tetraester precursor **4** (CD₂Cl₂, 400 MHz, 298 K)



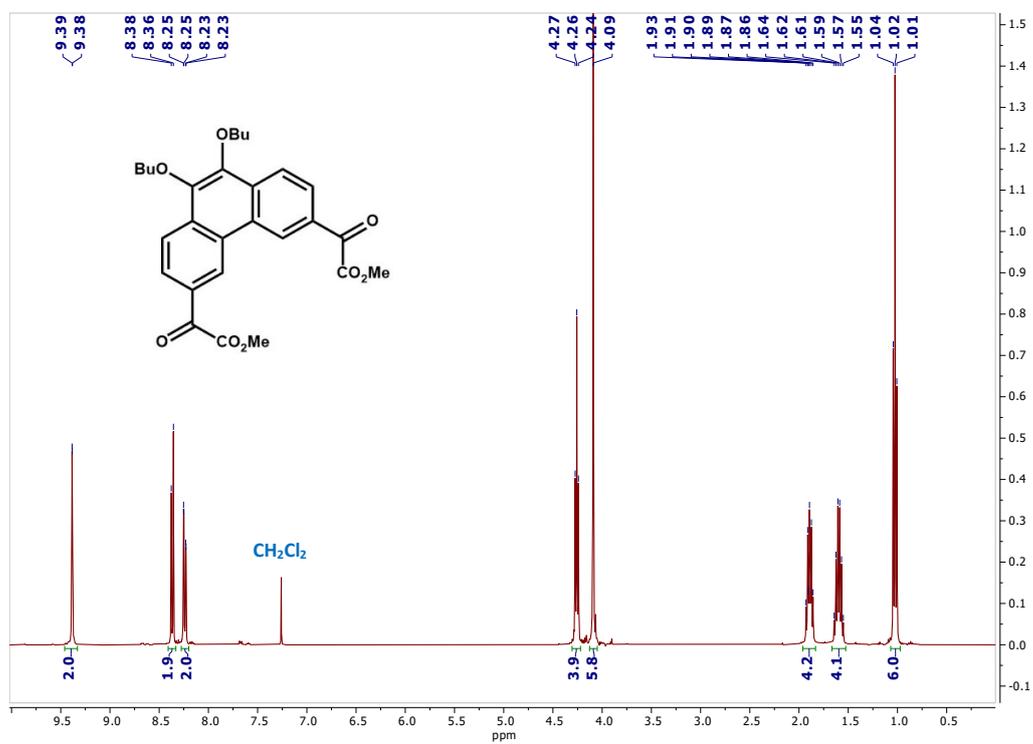
¹³C NMR spectrum of the flexible coronene tetraester precursor **4** (CDCl₃, 100 MHz, 298 K)



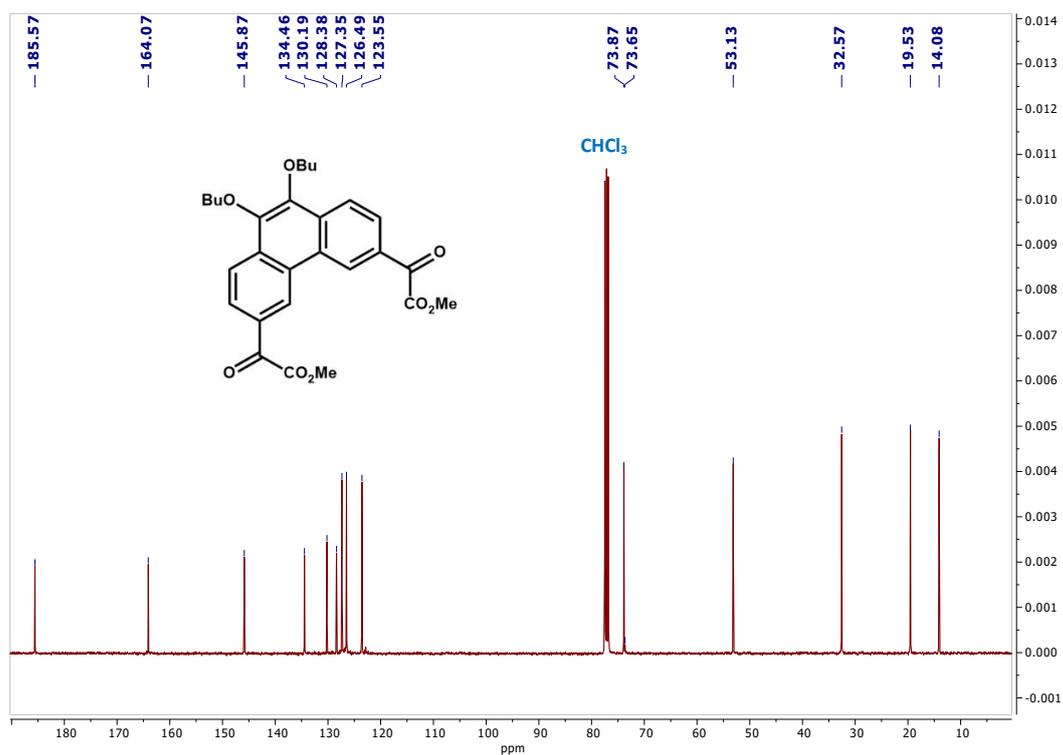
¹H NMR spectrum of coronene tetraester **5** (CD₂Cl₂, 400 MHz, 298 K)



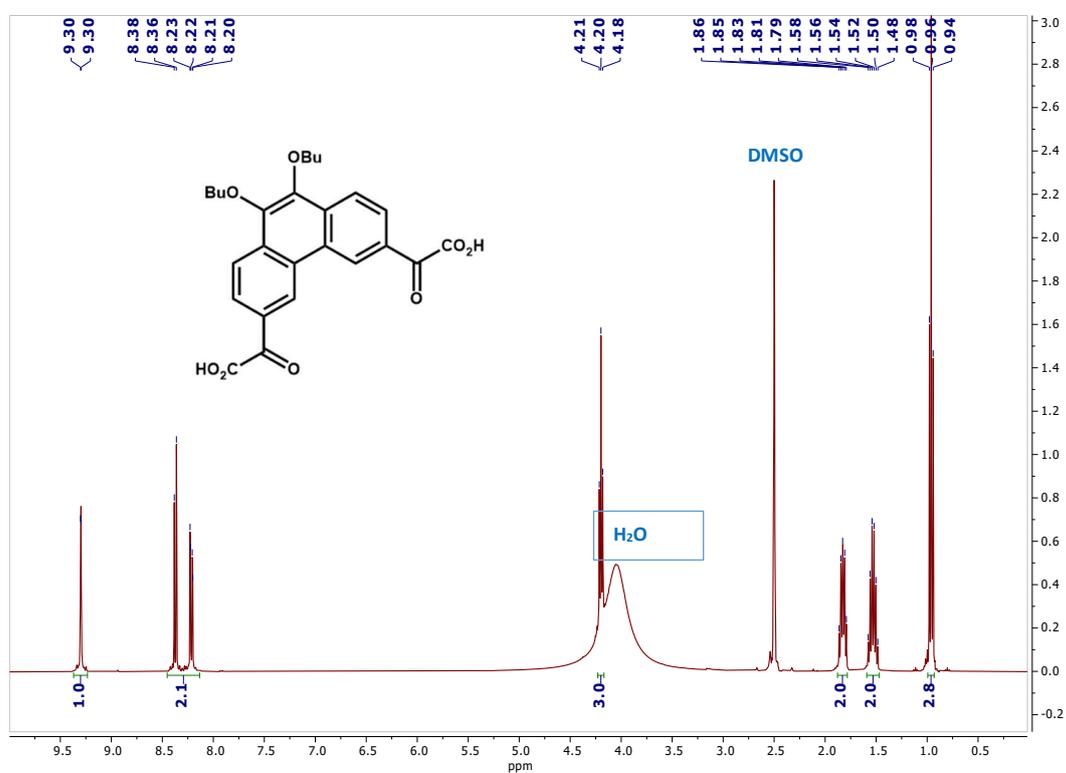
¹³C NMR spectrum of coronene tetraester **5** (CD₂Cl₂, 100 MHz, 298 K)



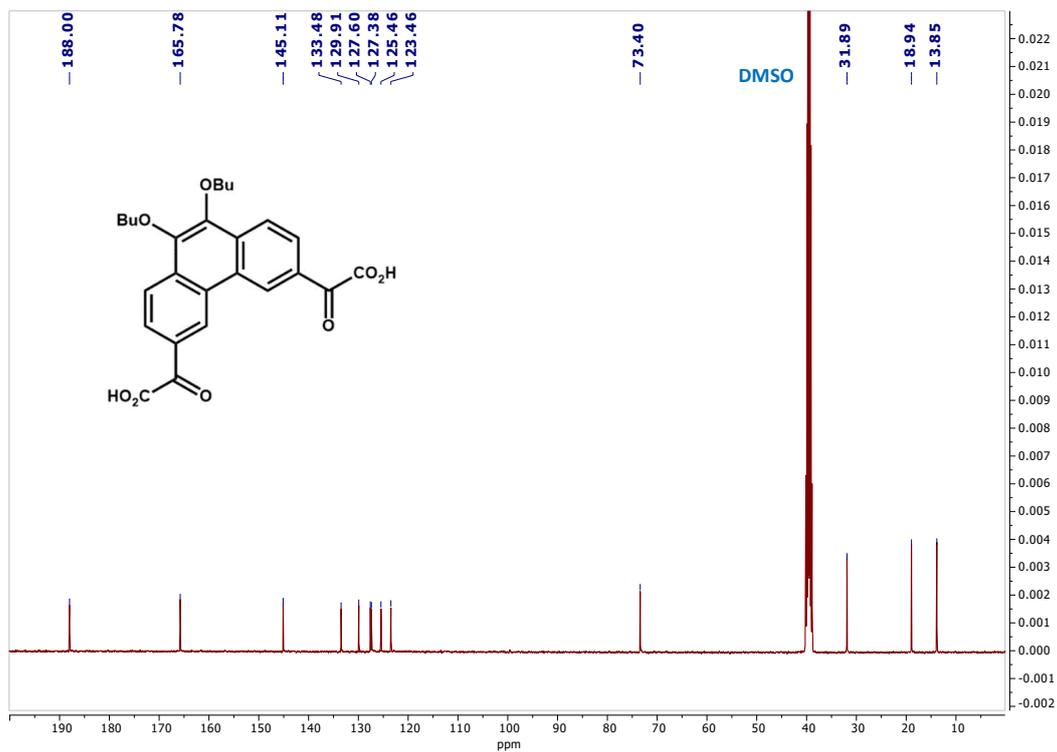
¹H NMR spectrum of 3,6-dimethyl-9,10-bisbutyloxyphenanthrediglyoxylate **6** (CDCl₃, 400 MHz, 298 K)



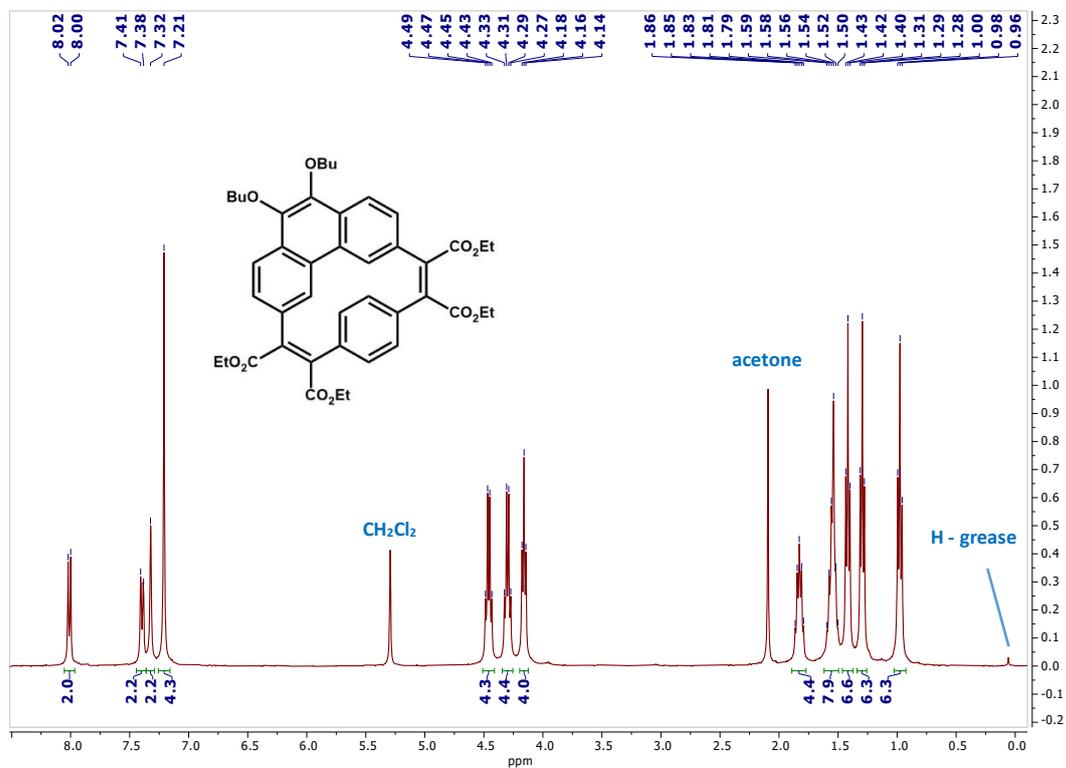
¹³C NMR spectrum of 3,6-dimethyl-9,10-bisbutyloxyphenanthrenediglyoxylate **6** (CDCl₃, 100 MHz, 298 K)



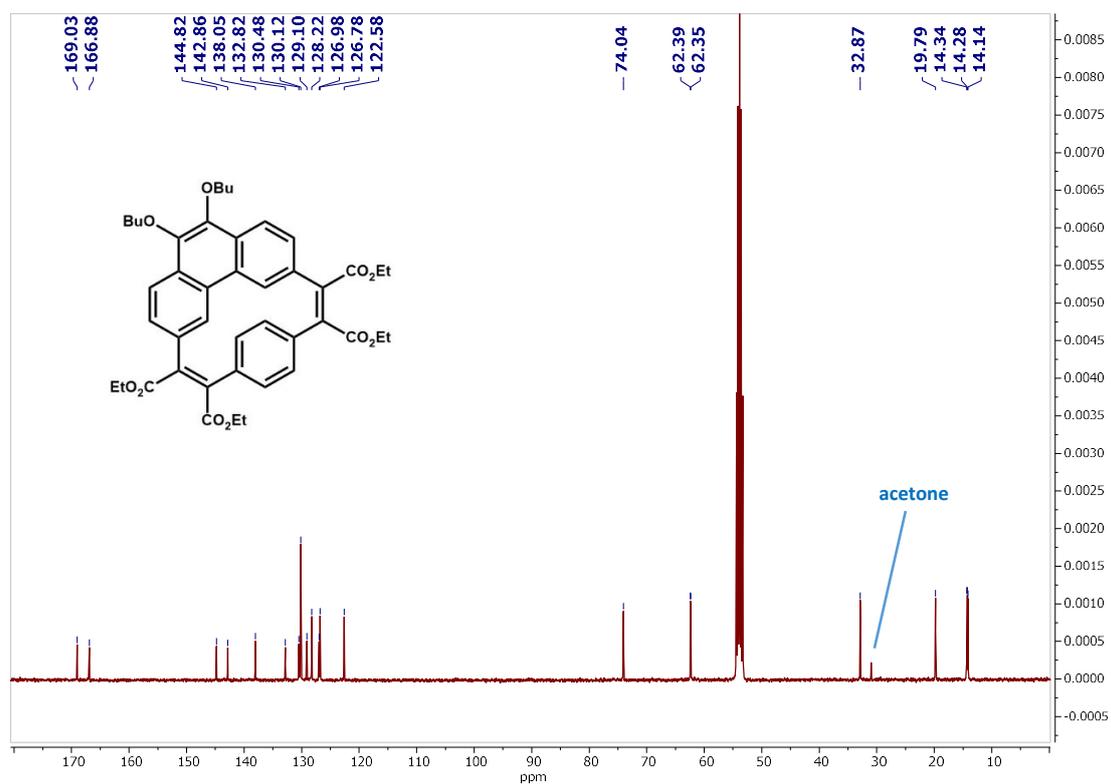
¹H NMR spectrum of acid 9,10-bisbutyloxyphenanthrene-3,6-diglyoxylic **8** (DMSO-*d*₆, 400 MHz, 298 K)



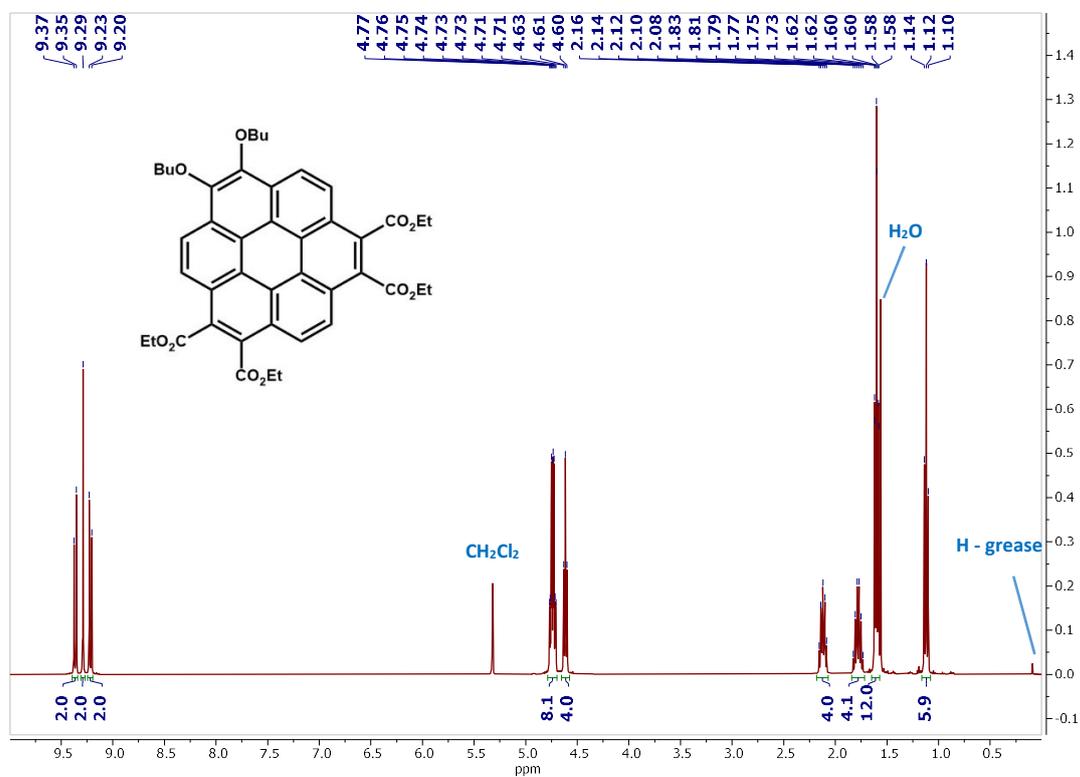
¹³C NMR spectrum of acid 9,10-bis(butyloxy)phenanthrene-3,6-diglyoxylic 8 (DMSO-*d*₆, 100 MHz, 298 K)



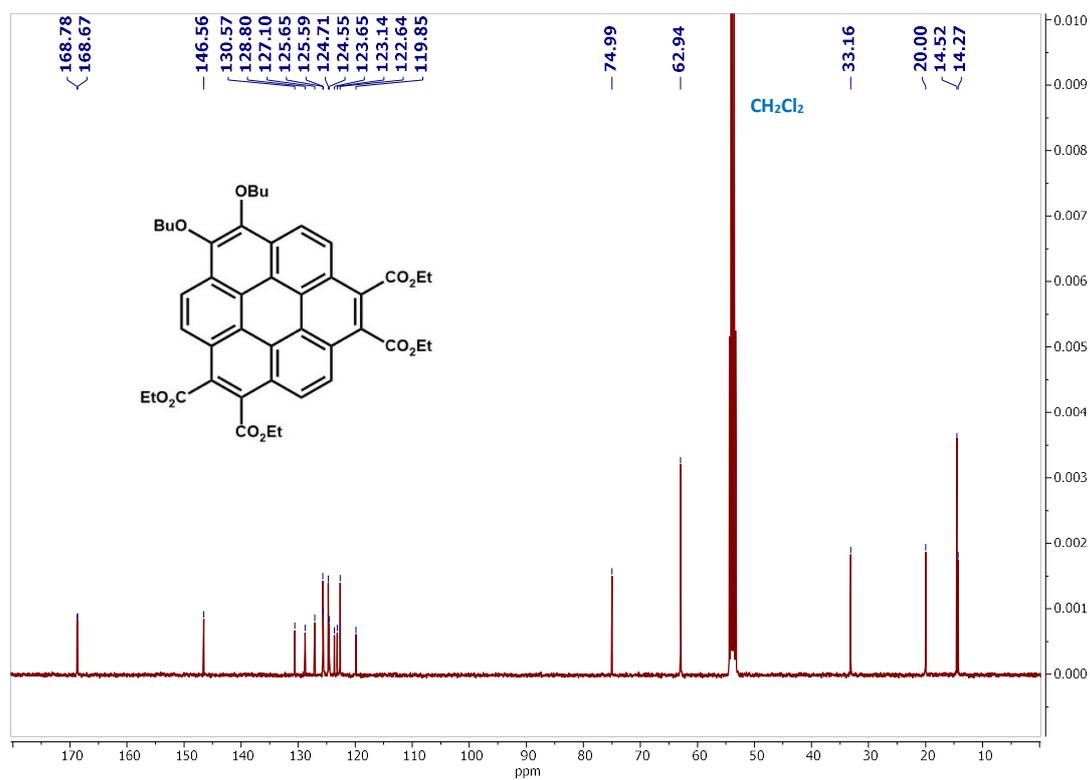
¹H NMR spectrum of the flexible bis(butyloxy)coronene tetraester precursor 9 (CD₂Cl₂, 400 MHz, 298 K)



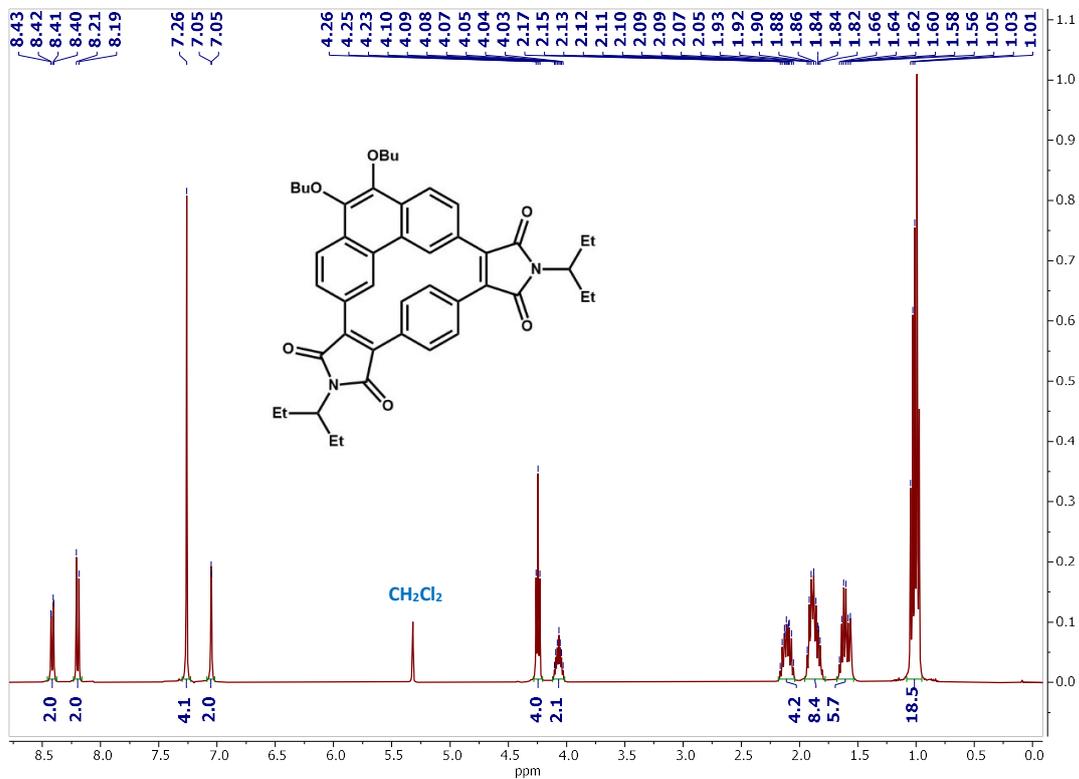
¹³C NMR spectrum of the flexible bis(butyloxy)coronene tetraester precursor 9 (CD₂Cl₂, 100 MHz, 298 K)



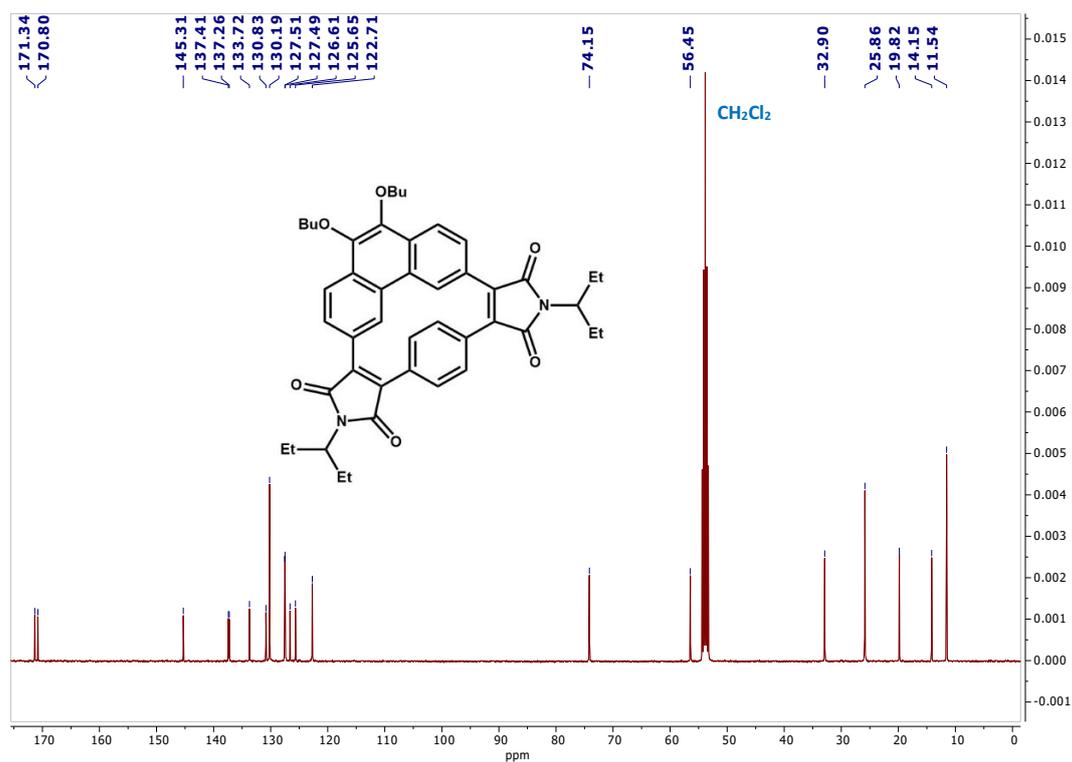
¹H NMR spectrum of bis(butyloxy)coronene tetraester 10 (CD₂Cl₂, 400 MHz, 298 K)



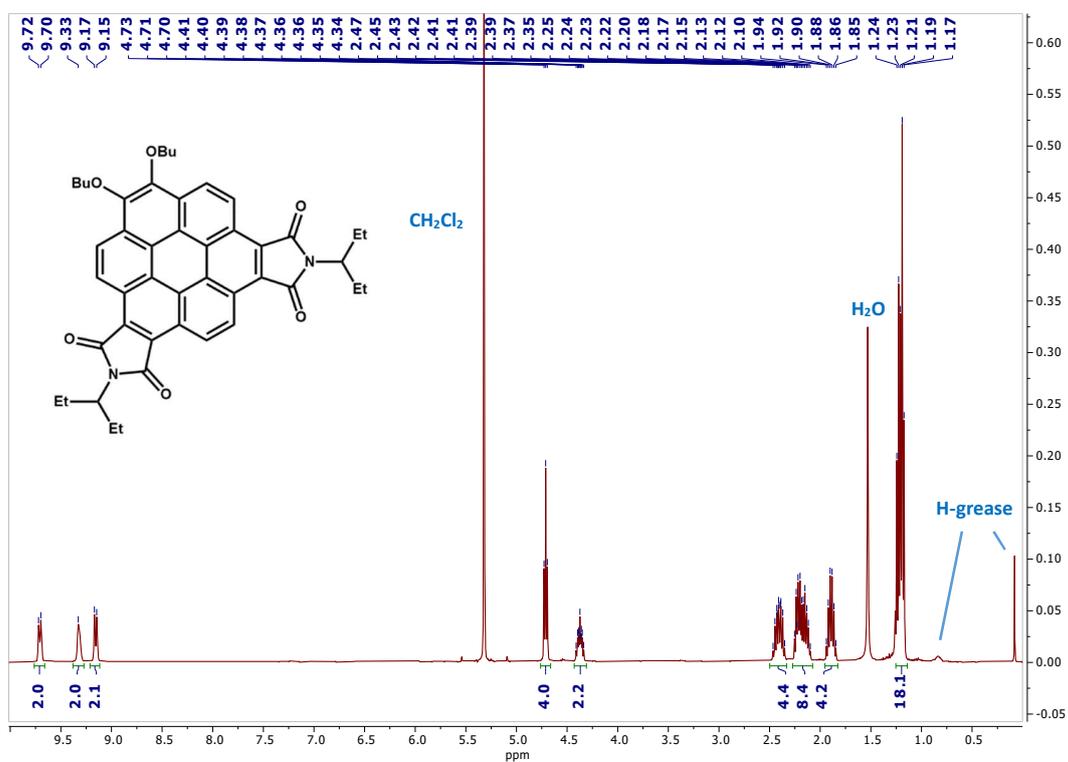
¹³C NMR spectrum of bis(butyloxy)coronene tetraester **10 (CD₂Cl₂, 100 MHz, 298 K)**



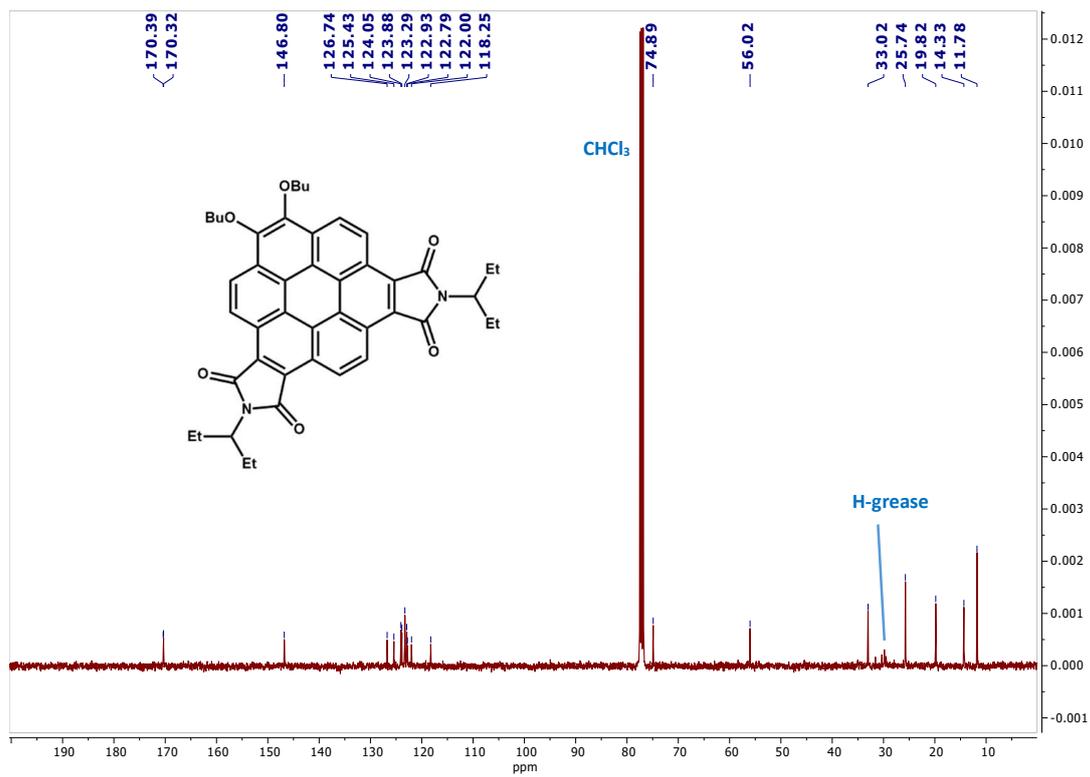
¹H NMR spectrum of the flexible bis(butyloxy)coronene diimide precursor **11 (CD₂Cl₂, 400 MHz, 298 K)**



¹³C NMR spectrum of the flexible bis(butyloxy)coronene diimide precursor **11** (CD₂Cl₂, 100 MHz, 298K)



¹H NMR spectrum of bis(butyloxy)coronene diimide **12** (CD₂Cl₂, 400 MHz, 298 K)



^{13}C NMR spectrum of bis(butyloxy)coronene diimide **12** (CDCl₃, 100 MHz, 298 K)

Single crystal X-ray diffraction

Table : crystallographic data

Compound	coronene tetraester 5	bisbutyloxycoronene tetraester 10
Formula	C ₃₆ H ₂₈ O ₈	C ₄₄ H ₄₄ O ₁₀
FW (g·mol ⁻¹)	588.58	732.79
Crystal color	yellow	yellow
Crystal size (mm)	0.40 x 0.10 x 0.03	0.30 x 0.22 x 0.11
Crystal system	triclinic	triclinic
Space group	P-1	P-1
Temperature	298 K	120 K
<i>a</i> (Å)	6.9314(5)	15.186(2)
<i>b</i> (Å)	13.7810(9)	15.823(2)
<i>c</i> (Å)	16.0680(12)	16.474(2)
α (°)	86.662(4)	69.815(5)
β (°)	82.997(4)	88.884(6)
γ (°)	76.021(3)	81.886(6)
<i>V</i> (Å ³)	1477.62(18)	3676.6(9)
<i>Z</i>	2	4
<i>d</i> _{calc}	1.323	1.324
μ (mm ⁻¹)	0.094	0.093
θ_{\min} - θ_{\max}	1.959° - 23.412°	1.318° - 24.499°
Refl. coll. / unique	109471 / 4305	43227 / 12032
Completeness to 2 θ	0.994	0.982
<i>R</i> _{int}	0.1040	0.0806
Refined param./restr.	401 / 1	985 / 0
^a <i>R</i> ₁ (<i>I</i> > 2 σ (<i>I</i>))	0.0620	0.0844
^b w <i>R</i> ₂ (all data)	0.2076	0.2602
Goodness of fit	1.097	1.059
CCDC number	2335165	2335164

$$^a R_1 = \sum ||F_o| - |F_c|| / \sum |F_o| \text{ and } ^b wR_2 = [\sum w(F_o^2 - F_c^2)^2 / \sum w(F_o^2)^2]^{1/2}$$

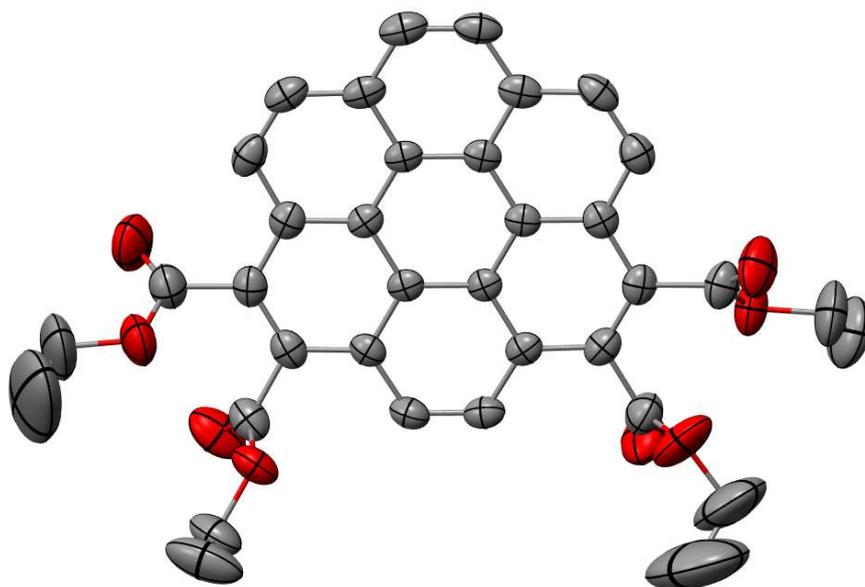


Figure S1: ORTEP-type view of the coronene tetraester **5** in the crystal at 298 K. Thermal ellipsoids are depicted at a 50 % probability level. Hydrogen atoms are omitted, for clarity. C: grey, O: red.

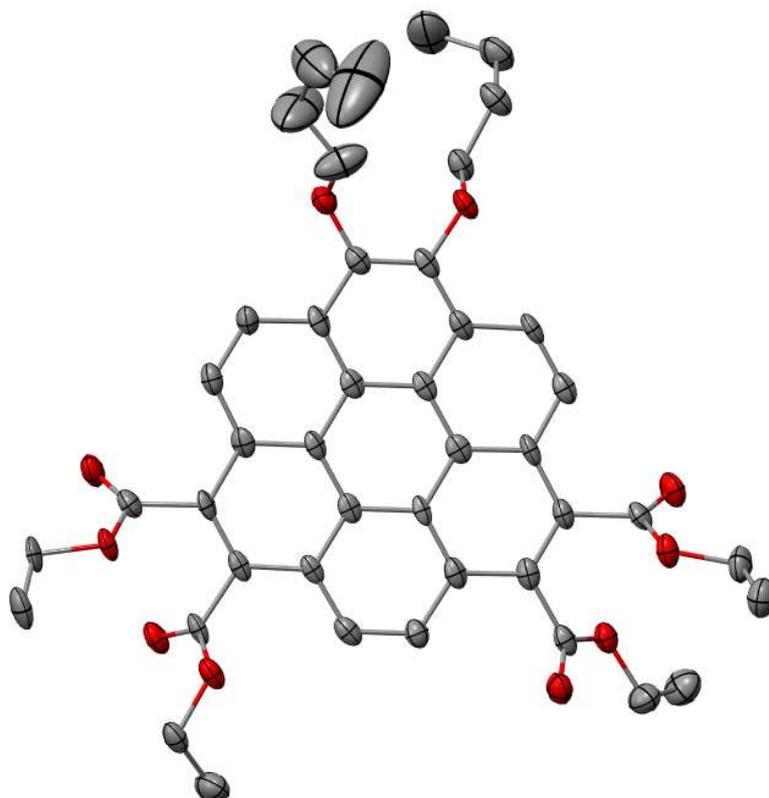


Figure S2: ORTEP-type view of bisbutyloxycoronene tetraester **10** in the crystal at 120 K. Thermal ellipsoids are depicted at a 50 % probability level. Only one of the two molecule of the asymmetric unit is depicted, and hydrogen atoms are omitted, for clarity. C: grey, O: red.

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