

Supporting Information

Strongly emitting, centrosymmetric, ladder-type bis-coumarins with crankshaft architecture

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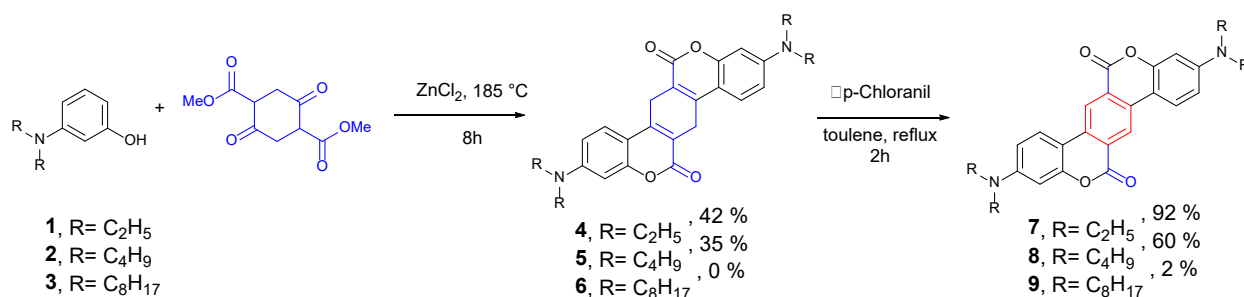
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Section S1: General Information

All reagents and solvents were purchased from commercial sources and were used as received unless otherwise noted. The reaction progress was monitored by means of thin-layer chromatography (TLC), which was performed on Kieselgel 60. The identity and purity of prepared compounds were proved by ^1H NMR and ^{13}C NMR as well as by mass spectrometry (via EI-MS or ESI-MS). HRMS (ESI-TOF) and HRMS (EI): double-focusing magnetic sector instruments with EBE geometry were utilized. NMR spectra were measured on 400 or 500 or 600 MHz instruments. Chemical shifts (δ , ppm) were determined with tetramethylsilane (TMS) as the internal reference; J values are given in Hz. All melting points for crystalline products were measured with an automated melting point apparatus and are given without correction.

Section S2: Experimental part

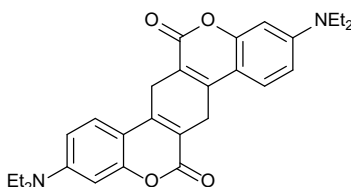


Scheme S1: Synthetic route for bis-coumarins **4-9** from 3-dialkylamino phenols **1-3**.

General Procedure for double pechmann reaction of **4-5**:

A mixture of appropriate 3-dialkyl aminophenol (10 mmol), dimethyl 2,5-dioxocyclohexane-1,4-dicarboxylate (4 mmol), ZnCl₂ (10 mmol) were placed in ace pressure tube under nitrogen at room temperature. The mixture was heated at 185 °C for 8 h and cooled at room temperature. The crude product was purified by recrystallization from chloroform/methanol yielded the desired product.

3,10-BIS(DIETHYLAMINO)-7,14-DIHYDROBENZO[1,2-*c*:4,5-*c'*]DICHROMENE-6,13-DIONE (4**):**

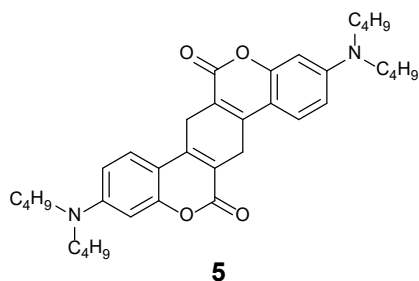


4

3-(diethylamino)phenol **1** (1.65 g, 10 mmol) and dimethyl 2,5-dioxocyclohexane-1,4-dicarboxylate (0.91 g, 4 mmol), ZnCl₂ (1.36 g, 10 mmol) were used to produce **4** as light yellow crystals with 42 % yield, 0.78

g. m.p. = 325-326 °C. ^1H NMR (500 MHz, CDCl_3) δ 7.54 (d, $J = 9.0$ Hz, 2H), 6.64 (dd, $J = 9.0$ Hz, 2H), 6.55 (d, $J = 2.3$ Hz, 2H), 3.89 (s, 4H), 3.42 (quartet, $J = 7.0$ Hz, 8H), 1.22 (t, $J = 7.1$ Hz, 12H). ^{13}C NMR (126 MHz, CDCl_3) δ 154.8, 150.2, 144.7, 124.9, 111.4, 109.0, 107.8, 97.5, 44.7, 25.6, 12.5. HRMS (ESI, m/z): $[\text{M}+\text{H}]^+$ Calcd. for $\text{C}_{28}\text{H}_{31}\text{N}_2\text{O}_4$: 459.2284; found, 459.2281.

3,10-BIS(DIBUTYLAMINO)-7,14-DIHYDROBENZO[1,2-*c*:4,5-*c'*]DICHROMENE-6,13-DIONE (5):

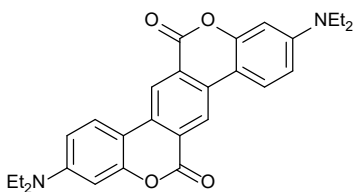


3-(dibutylamino) phenol **2** (0.5 g, 2.25 mmol) and dimethyl 2,5-dioxocyclohexane-1,4-dicarboxylate (0.21 g, 0.9 mmol), ZnCl_2 (0.31 g, 2.25 mmol) were used to produce **5** as light yellow crystals with 35 % yield, 0.45 g. m.p. = 317-318 °C. ^1H NMR (500 MHz, CDCl_3) δ 7.52 (d, $J = 9.0$ Hz, 2H), 6.64 (d, $J = 7.9$ Hz, 2H), 6.53 (s, 2H), 3.88 (s, 4H), 3.33 (t, $J = 8.0$ Hz, 8H), 1.64 (quint, $J = 8.2$ Hz, 8H), 1.40 (quint, $J = 7.4$ Hz, 8H), 0.98 (t, $J = 7.4$ Hz, 12H). ^{13}C NMR (126 MHz, CDCl_3) δ 162.0, 154.7, 150.4, 144.7, 124.8, 111.4, 109.2, 97.9, 51.1, 29.2, 25.6, 20.3, 13.9. HRMS (ESI, m/z): $[\text{M}+\text{H}]^+$ Calcd. for $\text{C}_{36}\text{H}_{46}\text{N}_2\text{O}_4$: 571.3536; found, 571.3563.

General procedure for oxidation of bis-coumarins 7-9:

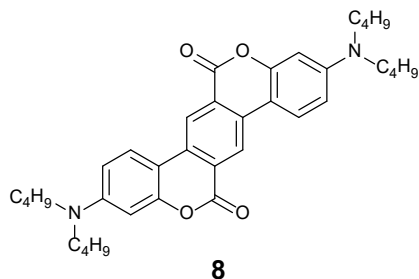
Appropriate reduced compound (1.0 eq.) and *p*-chloranil (1.0 eq) were placed in dry toluene (10 mL) under argon atmosphere and the reaction mixture was refluxed for 2 hours (TLC analysis) and the solvent was concentrated under vacuum. The crude product purified by column chromatography (DCM: Hexane =5:1) and crystallization from DCM/hexanes allowed to obtain the desired product.

3,10-BIS(DIETHYLAMINO)BENZO[1,2-*c*:4,5-*c'*]DICHROMENE-6,13-DIONE (7):



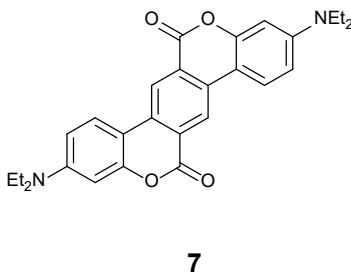
A solution of compound **4** (0.46 g, 1.0 mmol) and *p*-chloranil (0.25 g, 1.0 mmol) were used to obtain the **7** as orange crystals with a yield of 92 %, 0.42 g. m.p. = 340-341 °C. ^1H NMR (500 MHz, CDCl_3) δ 8.8 (s, 2H), 7.92 (d, $J = 9.0$ Hz, 2H), 6.68 (dd, $J = 9.0$ Hz, 2H), 6.55 (d, $J = 2.6$ Hz, 8H), 3.43 (quartet, $J = 7.1$ Hz, 8H), 1.23 (t, $J = 7.1$ Hz, 12H). ^{13}C NMR (126 MHz, CDCl_3) δ 161.6, 152.9, 149.7, 133.0, 124.0, 123.9, 122.8, 109.3, 105.5, 98.5, 44.7, 12.5. HRMS (ESI, m/z): $[\text{M}+\text{H}]^+$ Calcd. for $\text{C}_{28}\text{H}_{29}\text{N}_2\text{O}_4$: 457.2127; found, 457.2131.

3,10-BIS(DIBUTYLAMINO)BENZO[1,2-*c*:4,5-*c'*]DICHROMENE-6,13-DIONE (8):



A solution of compound **5** (0.05 g, 0.088 mmol) and *p*-chloranil (0.022 g, 0.088 mmol) were used to obtain the **8** as red crystals with a yield of 60 %, 30 mg. m.p. = 273-274 °C. ¹H NMR (500 MHz, CDCl₃) δ 8.79 (s, 2H), 7.88 (d, *J* = 10 Hz, 2H), 6.64 (dd, *J* = 9.0 Hz, 2H), 6.50 (d, *J* = 5 Hz, 2H), 3.33 (t, *J* = 7.8 Hz, 8H), 1.65-1.57 (m, 8H), 1.40 (m, 8H), 0.98 (t, *J* = 7.3 Hz, 12H). ¹³C NMR (126 MHz, CDCl₃) δ 161.7, 152.7, 150.0, 132.9, 123.9, 123.8, 122.8, 109.3, 105.2, 98.4, 50.9, 29.3, 20.3, 14.0. HRMS (EI, *m/z*): [M⁺] Calcd. for C₃₆H₄₄N₂O₄: 568.3301; found, 568.3306.

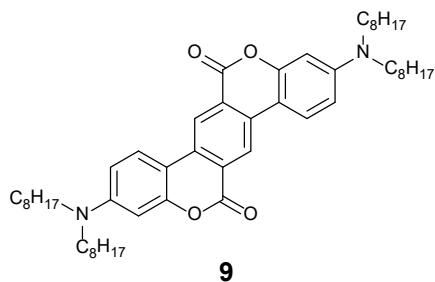
Synthesis of compound 7 via one-pot synthesis



3-(diethylamino)phenol **1** (1.65 g, 10 mmol), dimethyl 2,5-dioxocyclohexane-1,4-dicarboxylate (1.02 g, 4 mmol) and ZnCl₂ (1.36 g, 10 mmol) were placed in Ace pressure tube under nitrogen at room temperature. The mixture was heated at 185 °C for 8 hours and cooled at room temperature. A solution of *p*-chloranil (0.98 g, 4 mmol) in dry toluene was added in the crude product under nitrogen and refluxed for 2 hours (TLC analysis). The solvent was concentrated under a vacuum and the crude product purified by column chromatography (DCM: Hexane =5:1) yielded the product **7** as orange crystals with an overall yield of 28%.

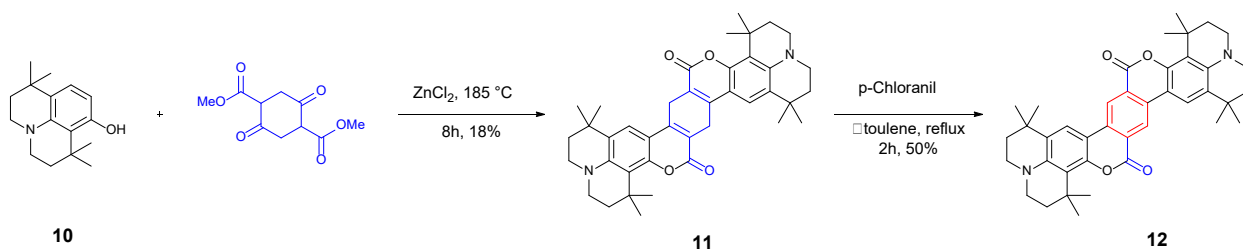
Synthesis of Compound 9 via one-pot synthesis:

3,10-BIS(DIOCTYLAMINO)BENZO[1,2-*c*:4,5-*c'*]DICHROMENE-6,13-DIONE (9)



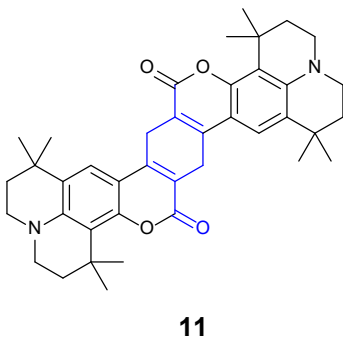
3-(diethylamino) phenol (2.5 g, 7.4 mmol) and dimethyl 2,5-dioxocyclohexane-1,4-dicarboxylate (0.69 g, 2.99 mmol), ZnCl₂ (1.02 g, 7.4 mmol) and *p*-chloranil (0.74 g, 2.99 mmol) were used to produce **9** as a light yellow crystals with 02 % yield. m.p. = 181-182 °C. ¹H NMR (500 MHz, CDCl₃) δ 8.79 (s, 2H), 7.59 (d, *J* = 8.3 Hz, 2H), 6.65 (s, 2H), 6.50 (s, 2H), 3.32 (s, 8H), 1.62 (s, 8H), 1.34-1.30 (m, 40H), 0.90 (s, 12H). ¹³C NMR (126 MHz, CDCl₃) δ 167.0, 161.6, 152.8, 150.1, 133.0, 123.9, 123.8, 122.8, 109.4, 105.4, 98.6, 51.3, 31.8, 29.5, 29.3, 27.2, 27.1, 22.6, 14.1. HRMS (ESI, *m/z*): [M+H]⁺ Calcd. for C₅₂H₇₇N₂O₄: 793.5883; found, 793.5901.

Synthesis of Julolidine bis-coumarins **11** and **12**



Scheme S3: Synthetic route for bis-coumarins **11** & **12** from phenol **10**.

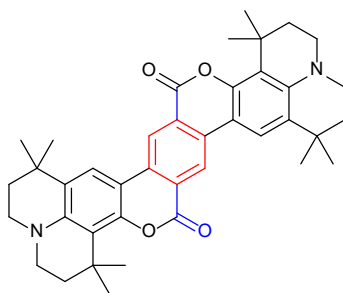
SYNTHESIS OF BIS-COUMARIN **11**:



2,3,6,7-tetrahydro-1,1,7,7-tetramethyl-1*H*,5*H*-Benzo[*ij*]quinolizin-8-ol **10** (0.5 g, 2.0 mmol), dimethyl 2,5-dioxocyclohexane-1,4-dicarboxylate (0.2 g, 0.8 mmol) and ZnCl₂ (0.28 g, 2.0 mmol) were placed in Ace

pressure tube under nitrogen at room temperature. The mixture was heated at 185 °C for 8 hours and cooled at room temperature. The crude product was purified by recrystallization from chloroform/methanol yielded the product **11** as orange crystal with 18 % yield, 0.23 g. m.p. = 356-357 °C. ¹H NMR (500 MHz, CDCl₃) δ 7.39 (s, 2H), 3.88 (s, 4H), 3.28 (t, *J* = 6.0 Hz, 4H), 3.20 (t, *J* = 5.6 Hz, 4H), 1.84 (t, *J* = 5.5 Hz, 4H), 1.70 (t, *J* = 5.9 Hz, 4H), 1.59 (s, 12H), 1.35 (s, 12H). ¹³C NMR (126 MHz, CDCl₃) δ 161.5, 151.0, 144.8, 144.7, 128.4, 119.3, 115.5, 111.1, 108.4, 47.3, 46.9, 39.8, 36.3, 32.5, 32.4, 31.2, 29.2, 25.6. HRMS (ESI, *m/z*): [M+H]⁺ Calcd. for C₄₀H₄₇N₂O₄: 619.3536; found, 619.3529.

SYNTHESIS OF BIS-COUMARIN **12**:



12

A solution of compound **11** (0.12 g, 0.19 mmol) and *p*-chloranil (0.048 g, 0.19 mmol) in dry toluene (10 mL) was refluxed for 2 hours (TLC analysis) and the solvent was concentrated under vacuum. The crude product purified by column chromatography (DCM: Hexane =5:1) and crystallization from DCM/hexanes allowed to obtain the desired product **12** as red crystals with a yield of 50 %, 60 mg. m.p. = 360-361 °C. ¹H NMR (500 MHz, CDCl₃) δ 8.84 (s, 2H), 7.81 (s, 2H), 3.28 (m, 8H), 1.86-1.82 (m, 8H), 1.61 (s, 12H), 1.40 (s, 12H). ¹³C NMR (126 MHz, CDCl₃) δ 161.2, 149.2, 144.2, 133.3, 128.8, 123.3, 122.6, 118.5, 116.5, 106.1, 47.3, 46.9, 40.0, 36.4, 32.6, 31.4, 29.4. HRMS (ESI, *m/z*): [M+H]⁺ Calcd. for C₄₀H₄₅N₂O₄: 617.3379; found, 617.3376.

Section S3: Photophysical studies

All photophysical measurements in this study were performed at RT (298 K). UV-visible spectra were recorded on HITACHI UH5700. The steady-state emission spectra and lifetime were measured with an Edinburgh FL 980 instrument. Both the wavelength-dependent excitation and emission response of the spectrofluorimeter have been calibrated. The excitation and emission spectra were corrected using the standard corrections supplied by the manufacturer for the spectral power of the excitation source and the sensitivity of the detector. The quantum yields in solution at 297K were measured by use of an integrating sphere (N-M01) with an Edinburgh Instrument FLSP1000 spectrometer. The quantum yields of the solid samples were measured by use of integrating cryosphere (Oxford Instruments Microstat N2). Fluoracle and FAST spectrometer operating software and Origin Pro 2019 9.6.0 were used for data analysis and processing.

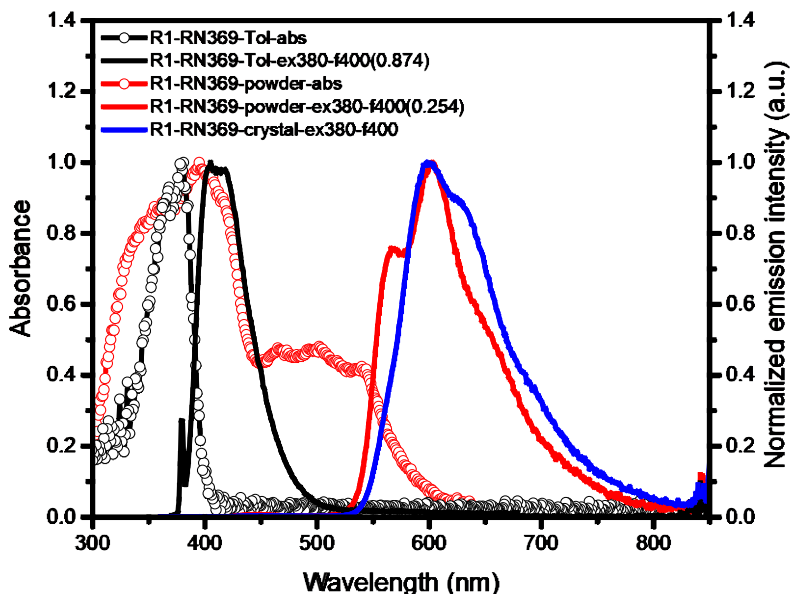


Figure S1. Absorption (dotted) and emission (solid) of compound **4** in solution (toluene) and solid state.

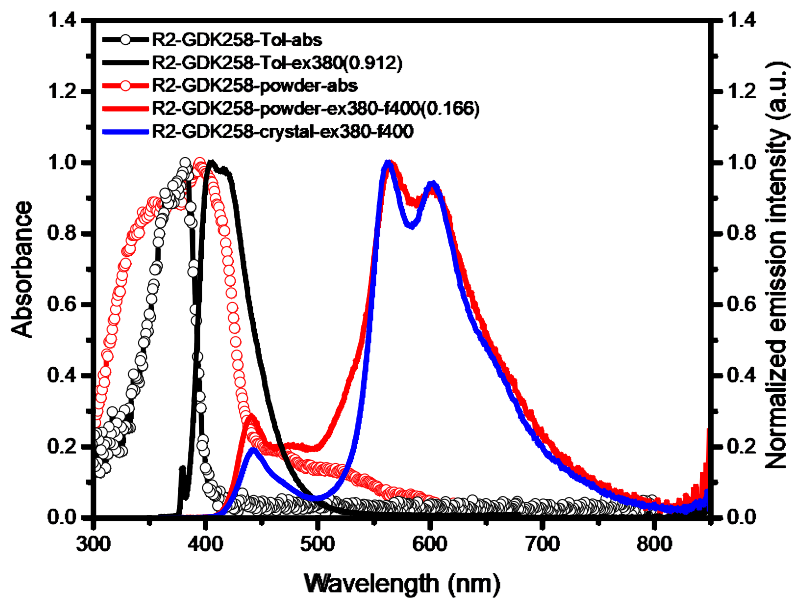


Figure S2. Absorption (dotted) and emission (solid) of compound 5 in solution (toluene) and solid state.

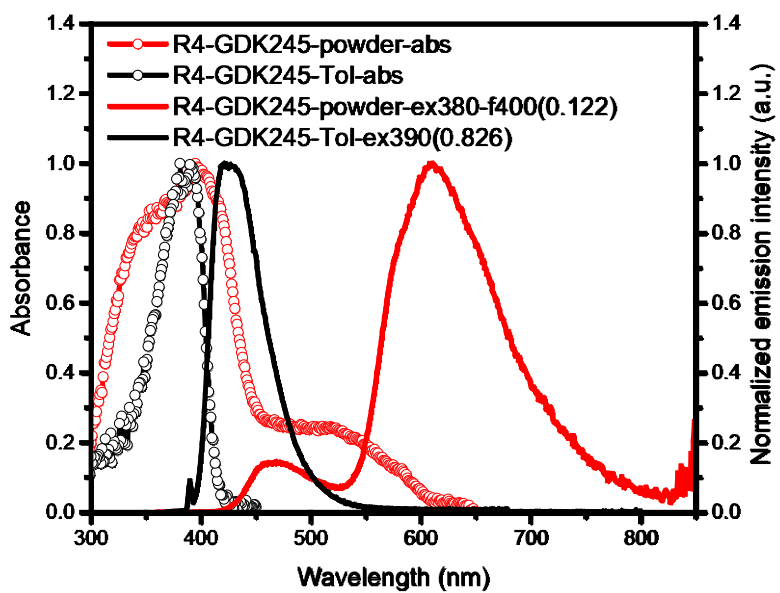


Figure S3. Absorption (dotted) and emission (solid) of compound 11 in solution (toluene) and solid state.

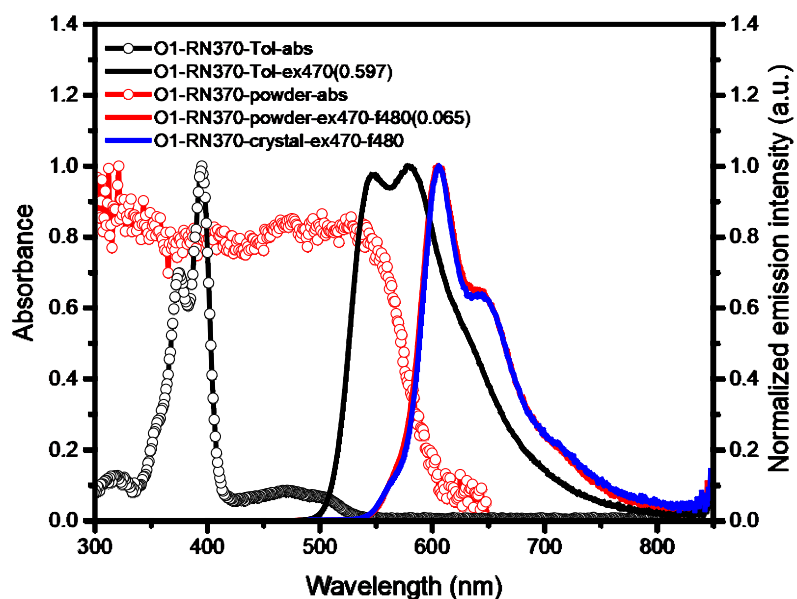


Figure S5. Absorption (dotted) and emission (solid) of compound 7 in solution (toluene) and solid state.

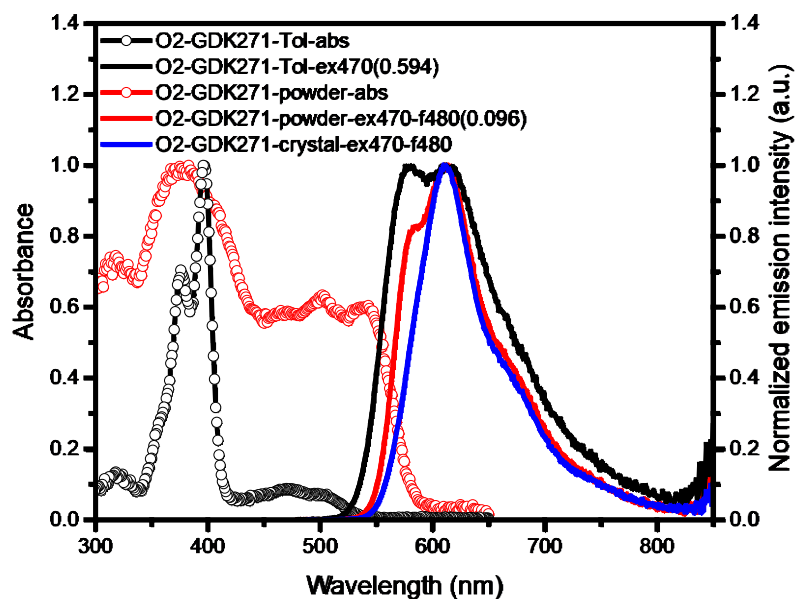


Figure S6. Absorption (dotted) and emission (solid) of compound 8 in solution (toluene) and solid state.

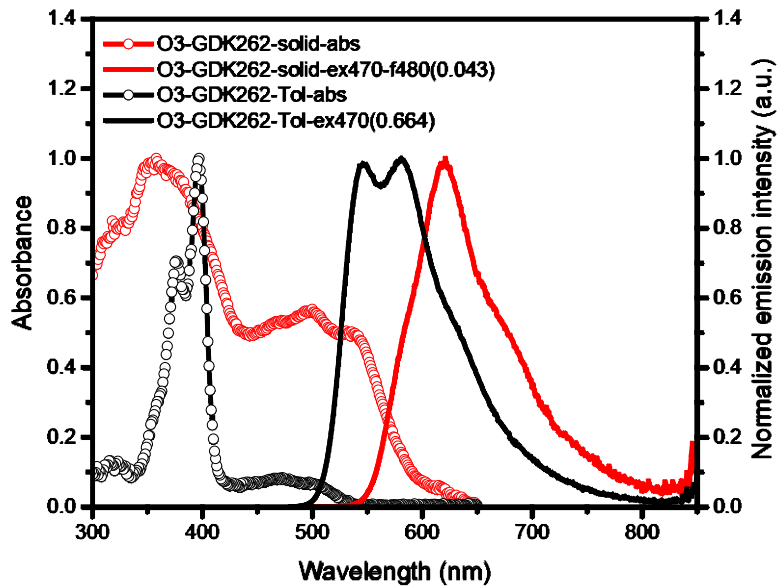


Figure S7. Absorption (dotted) and emission (solid) of compound 9 in solution (toluene) and solid state.

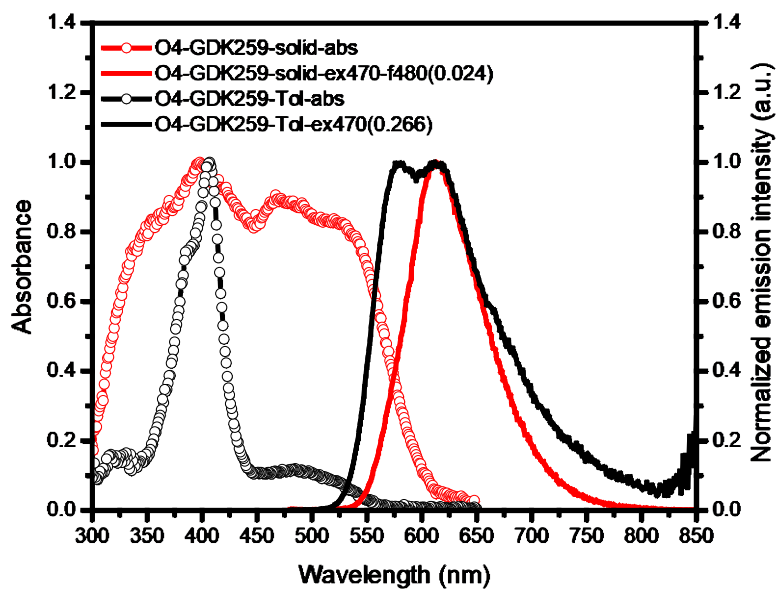


Figure S8. Absorption (dotted) and emission (solid) of compound 12 in solution (toluene) and solid state.

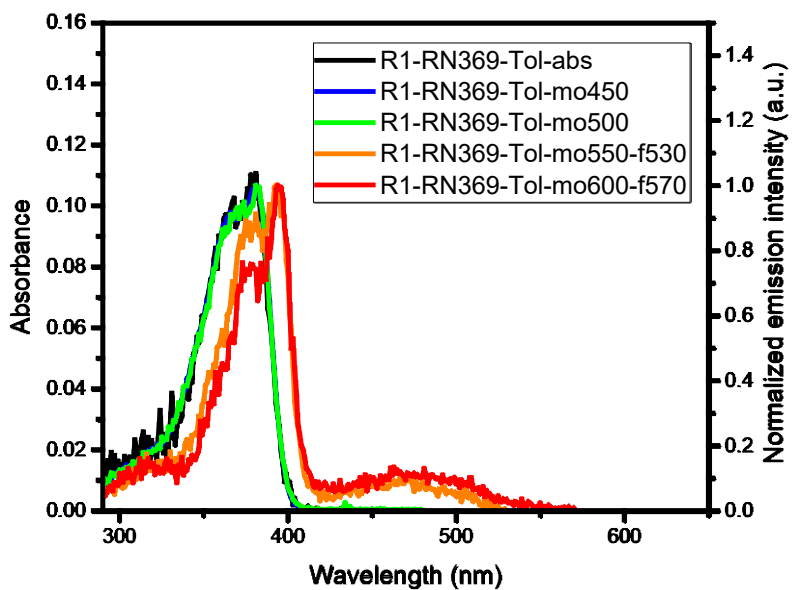


Figure S9. Excitation spectra of compound 4 in solution (toluene).

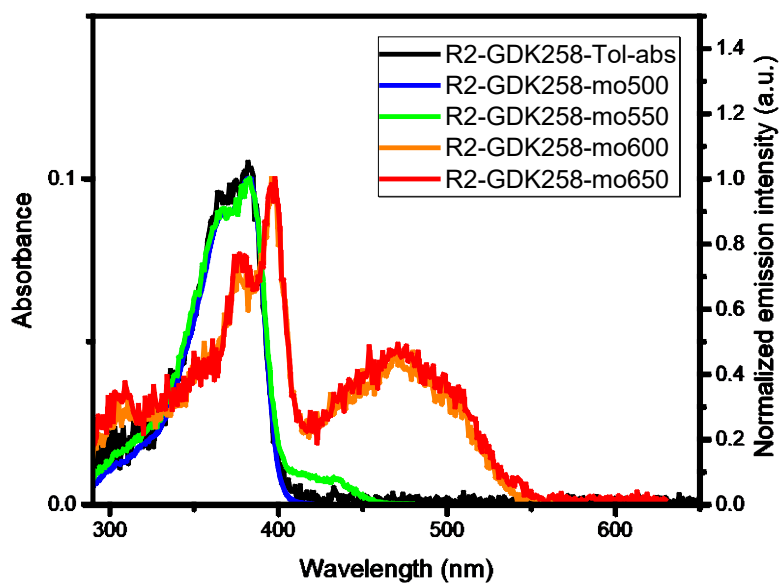


Figure S10. Excitation spectra of compound 5 in solution (toluene).

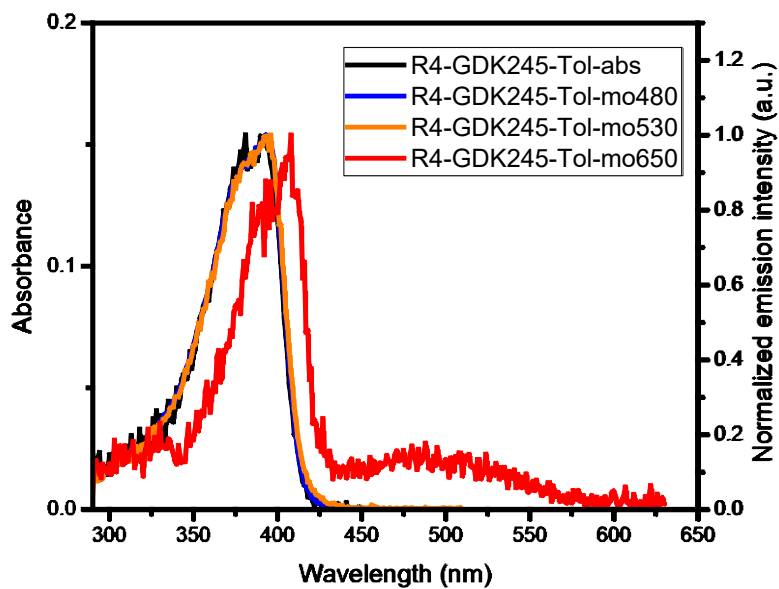


Figure S11. Excitation spectra of compound 11 in solution (toluene).

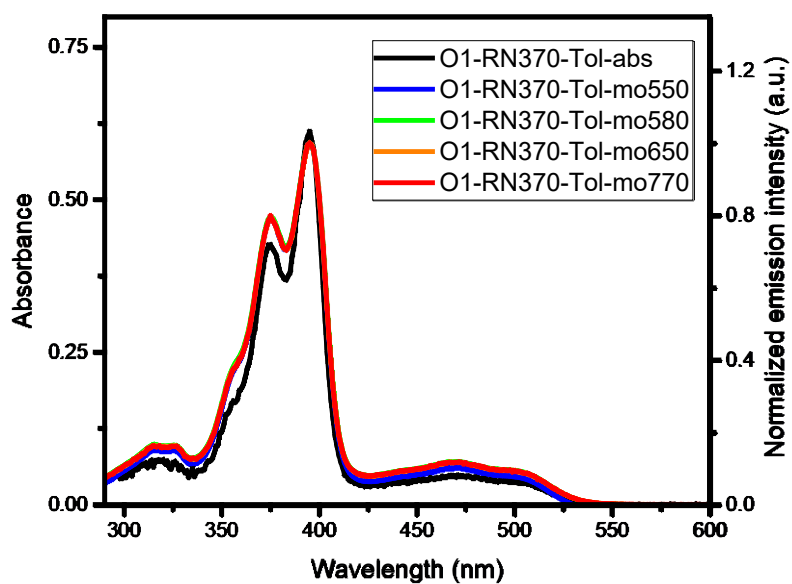


Figure S13. Excitation spectra of compound 7 in solution (toluene).

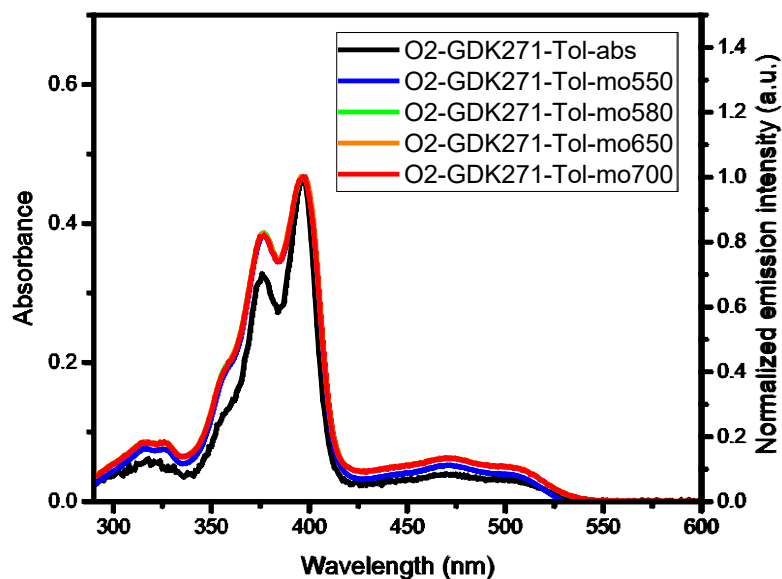


Figure S14. Excitation spectra of compound **8** in solution (toluene).

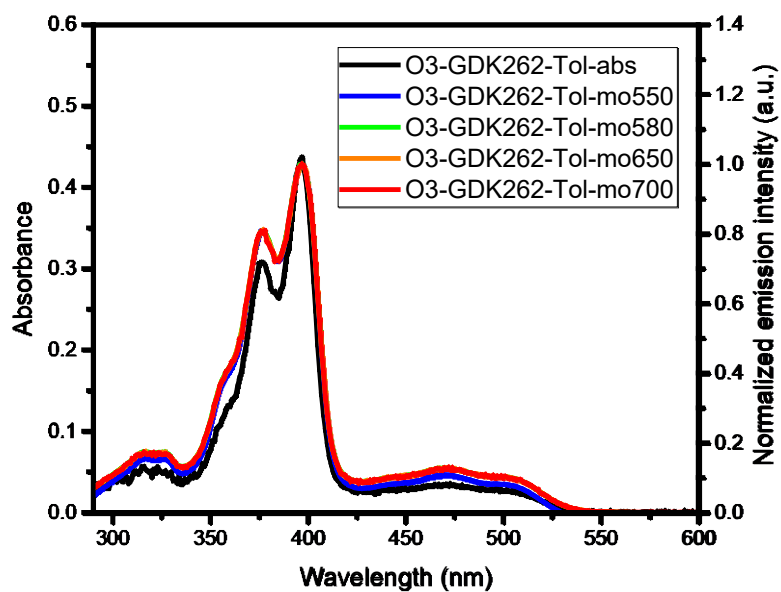


Figure S15. Excitation spectra of compound **9** in solution (toluene).

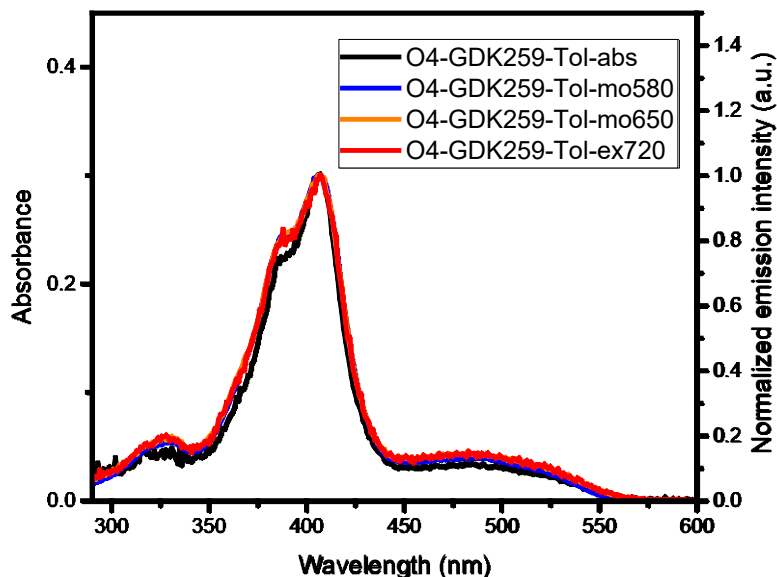


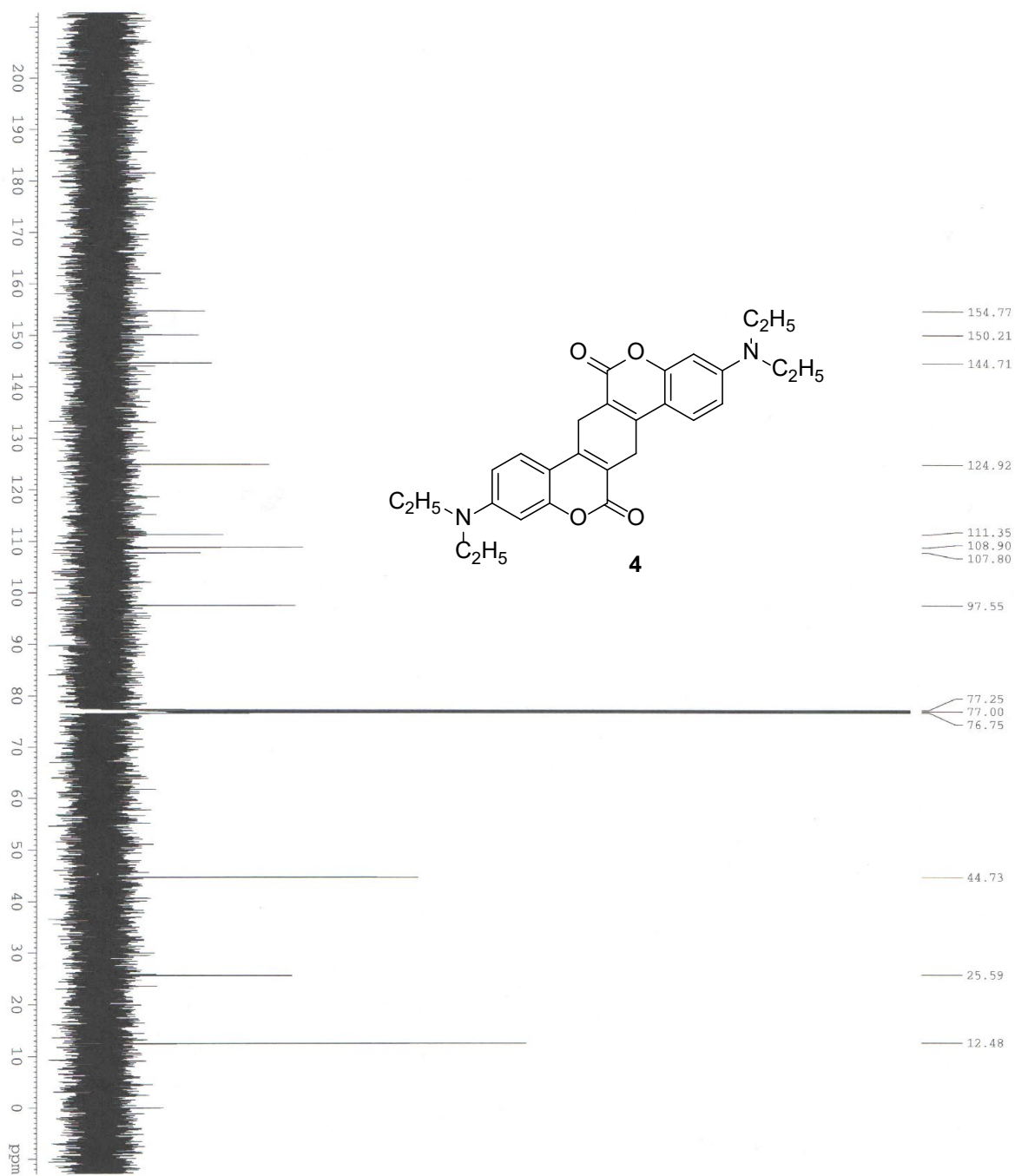
Figure S16. Excitation spectra of compound **12** in solution (toluene).

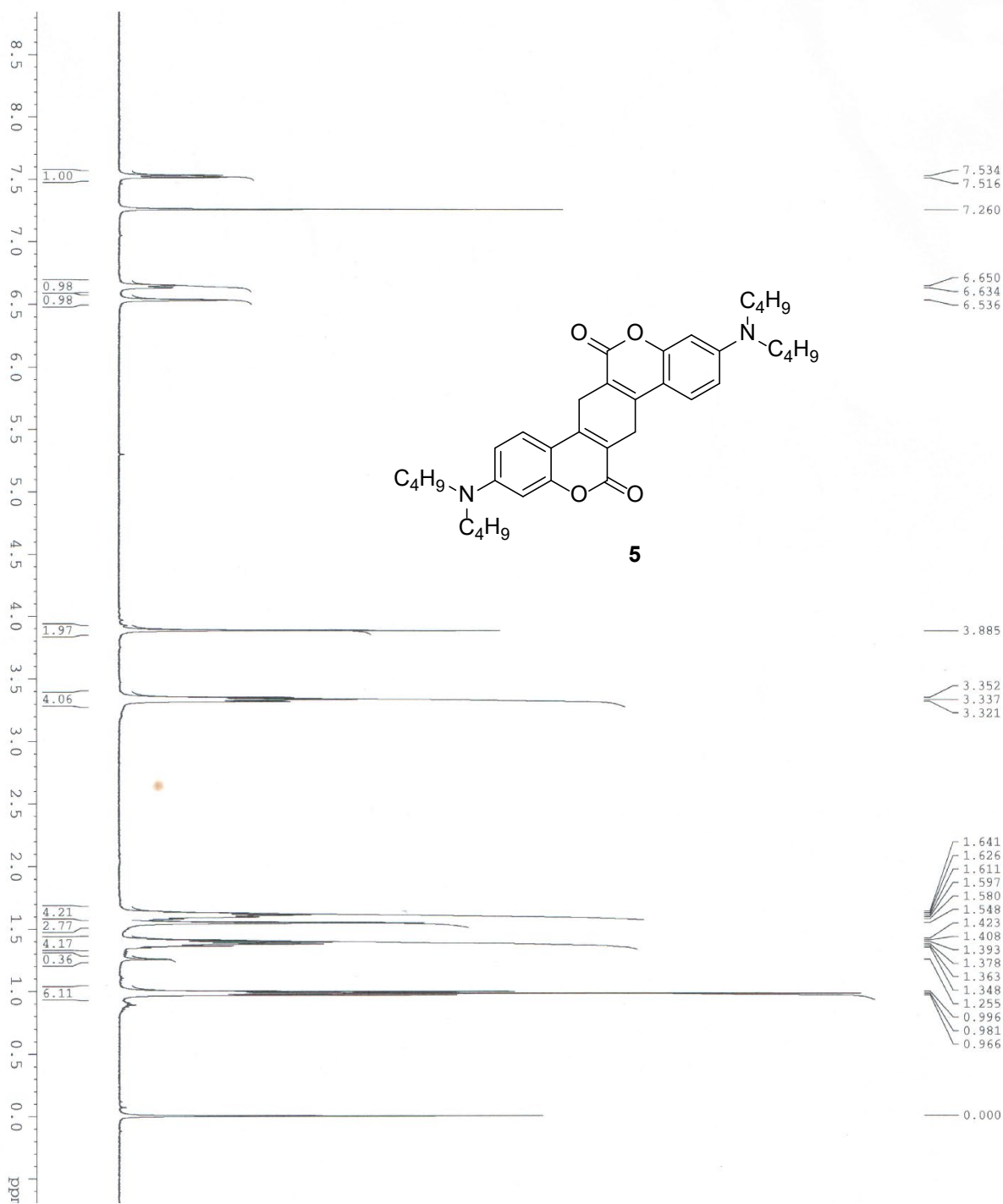
Section S4: Computational details

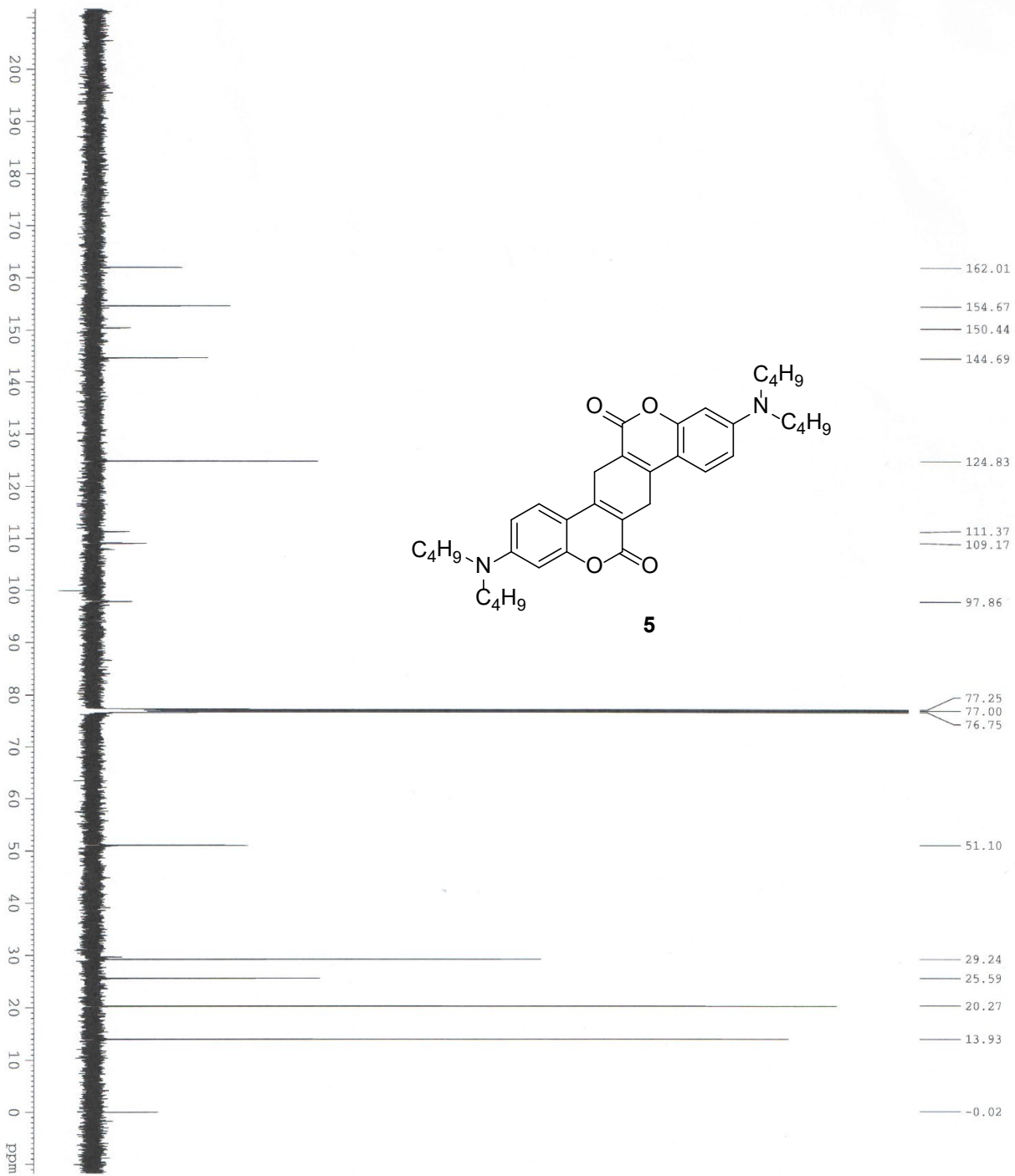
Molecular optimizations and DFT calculations were carried out at the B3LYP/6-311+G(d) level of theory using the PCM model and toluene as solvent with the GAUSSIAN 16 suite of programs.¹ The optimized structures were then used to calculate lowest energy singlet ($S_0 \rightarrow S_1$) and triplet electronic transitions ($S_0 \rightarrow T_1$) using the time-dependent density functional theory (TD-DFT) method. The solvent effect was based on the polarizable continuum model (PCM), which was implemented in the Gaussian 16 program. The optimization of the lowest energy singlet (S_1) and triplet (T_1) excited states were also simulated.

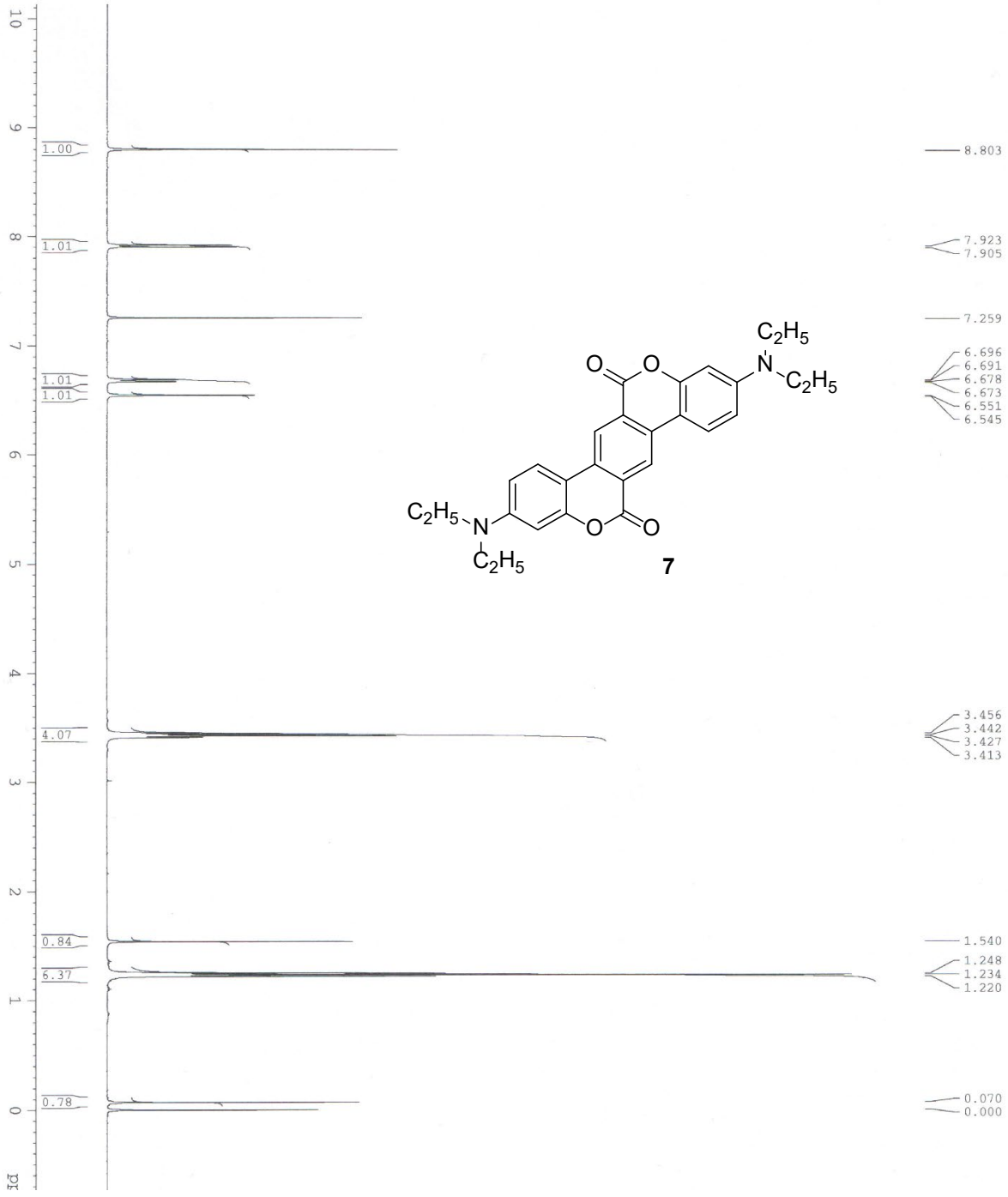
Section S5: ^1H , ^{13}C and MS spectra

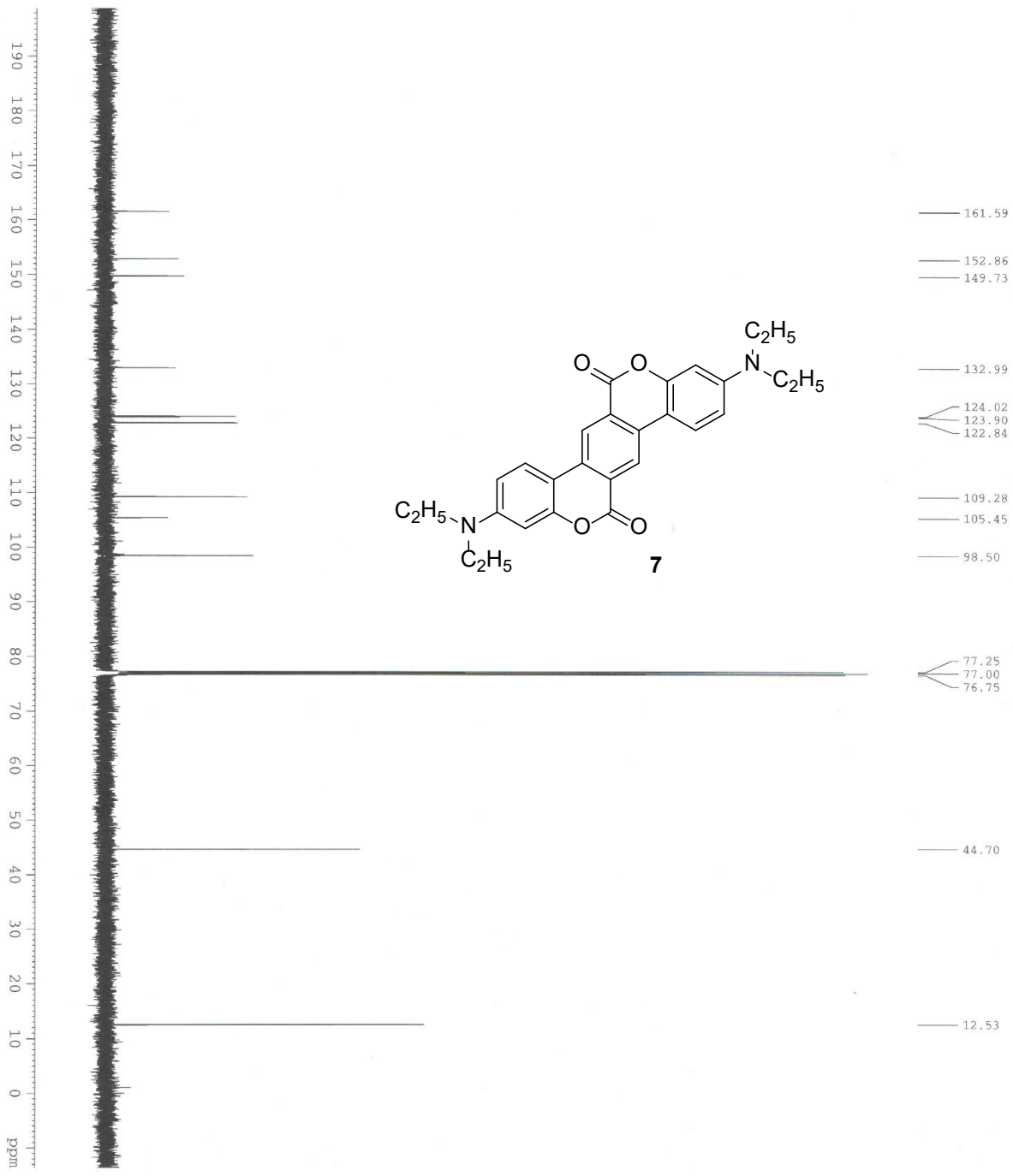


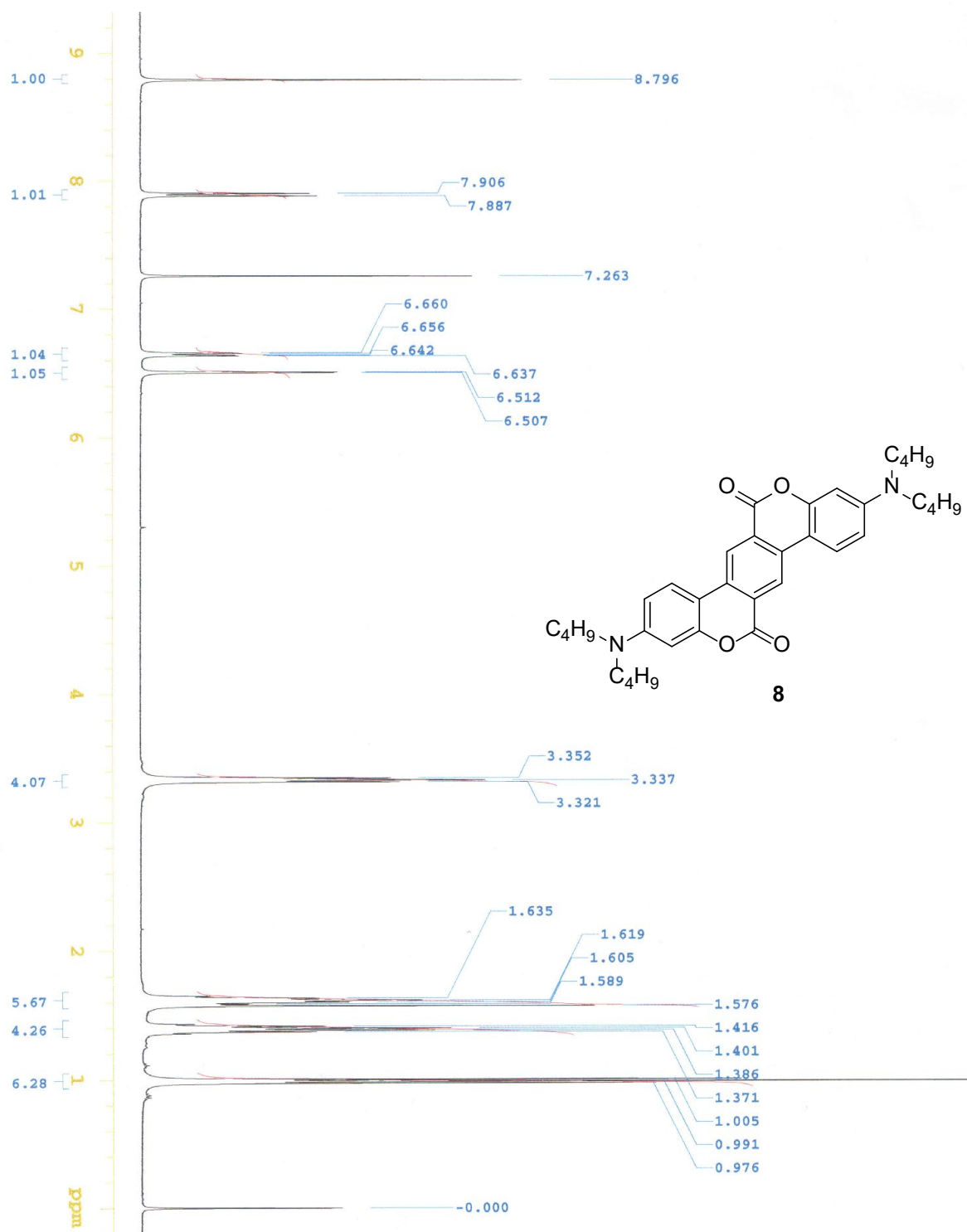


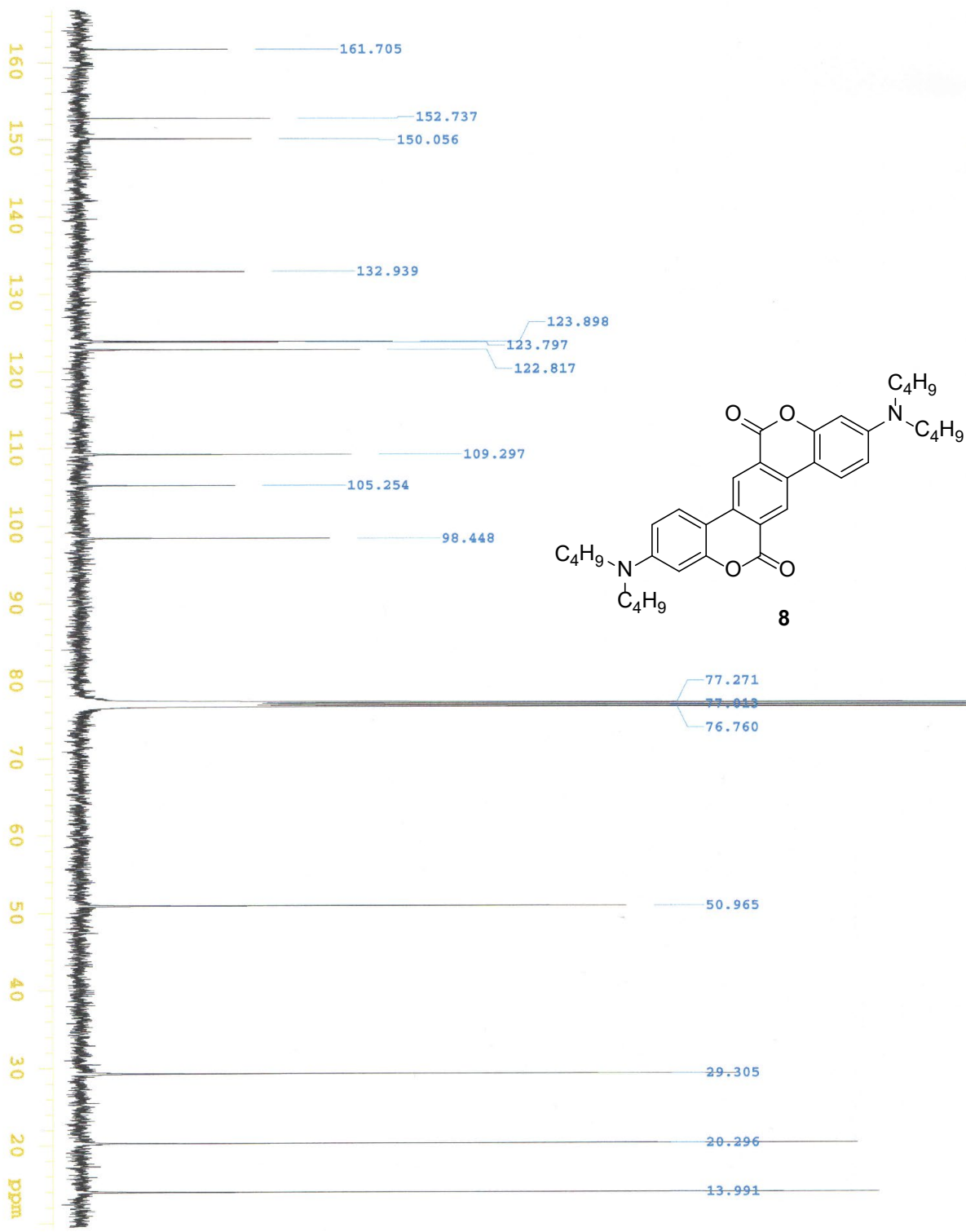


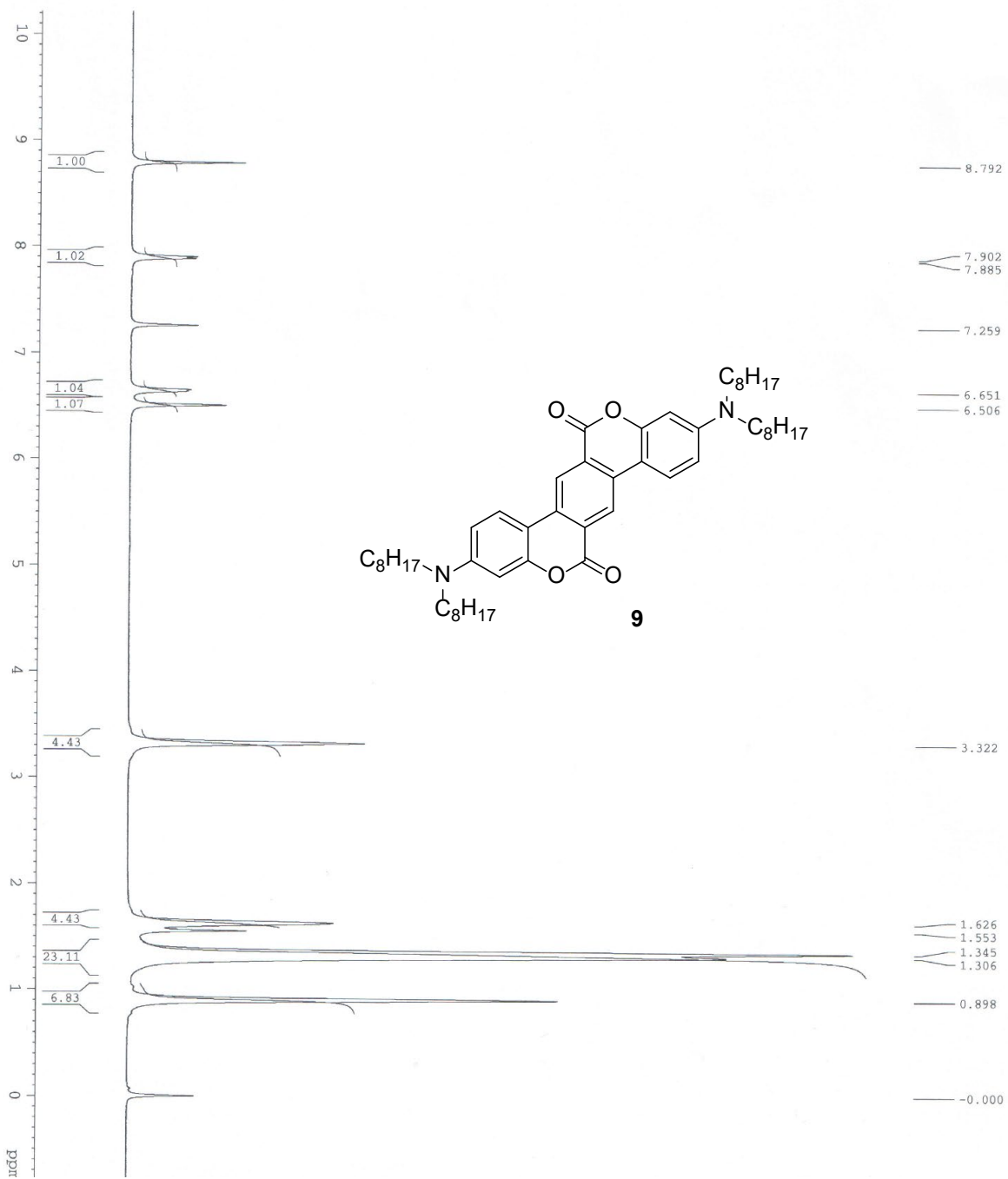




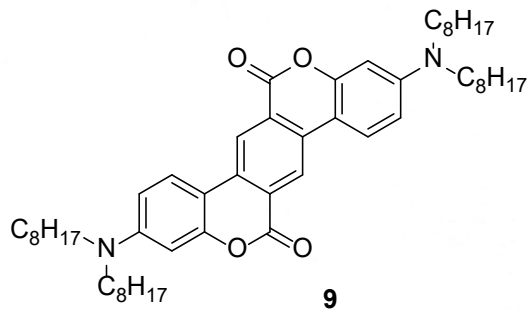






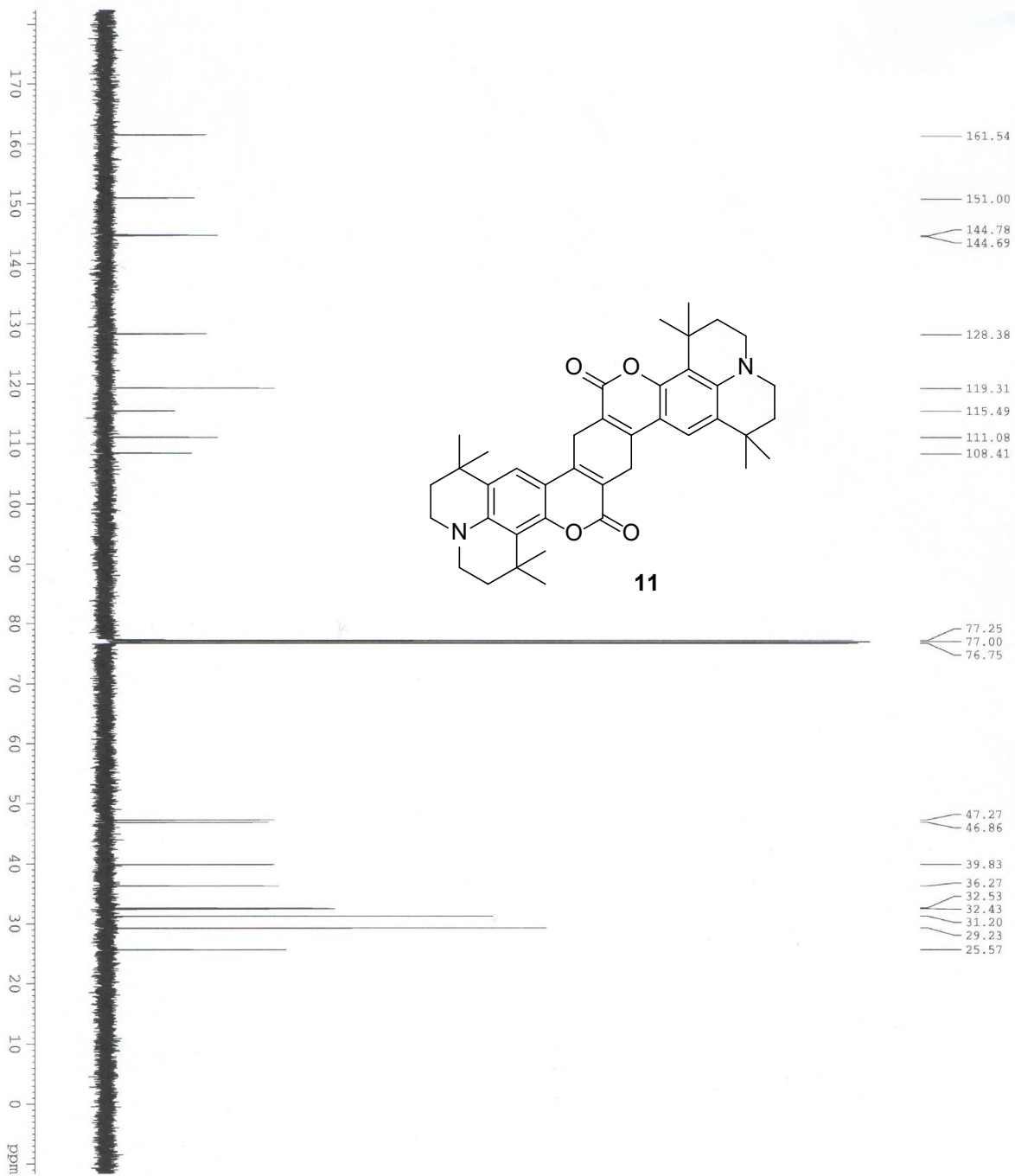


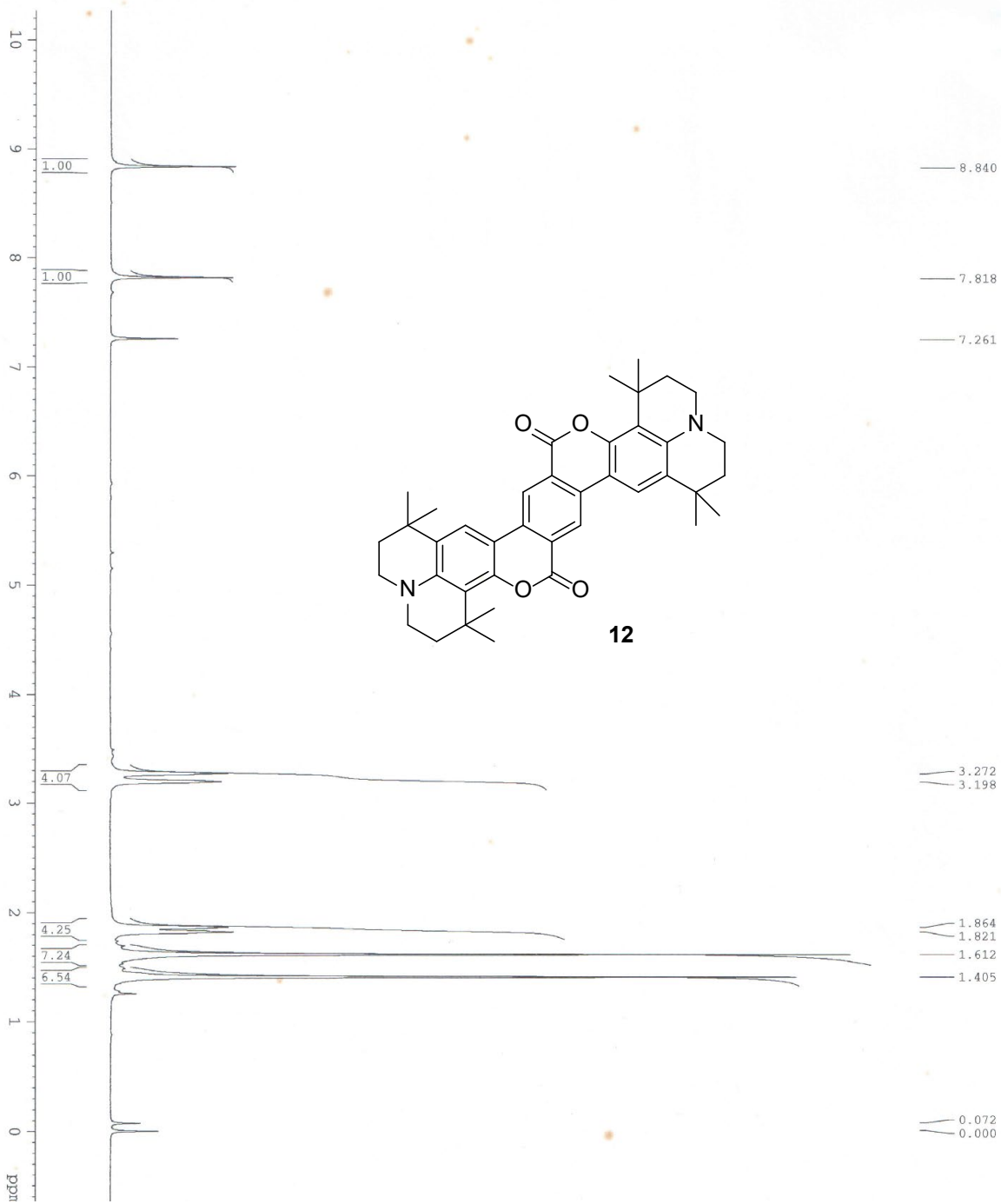
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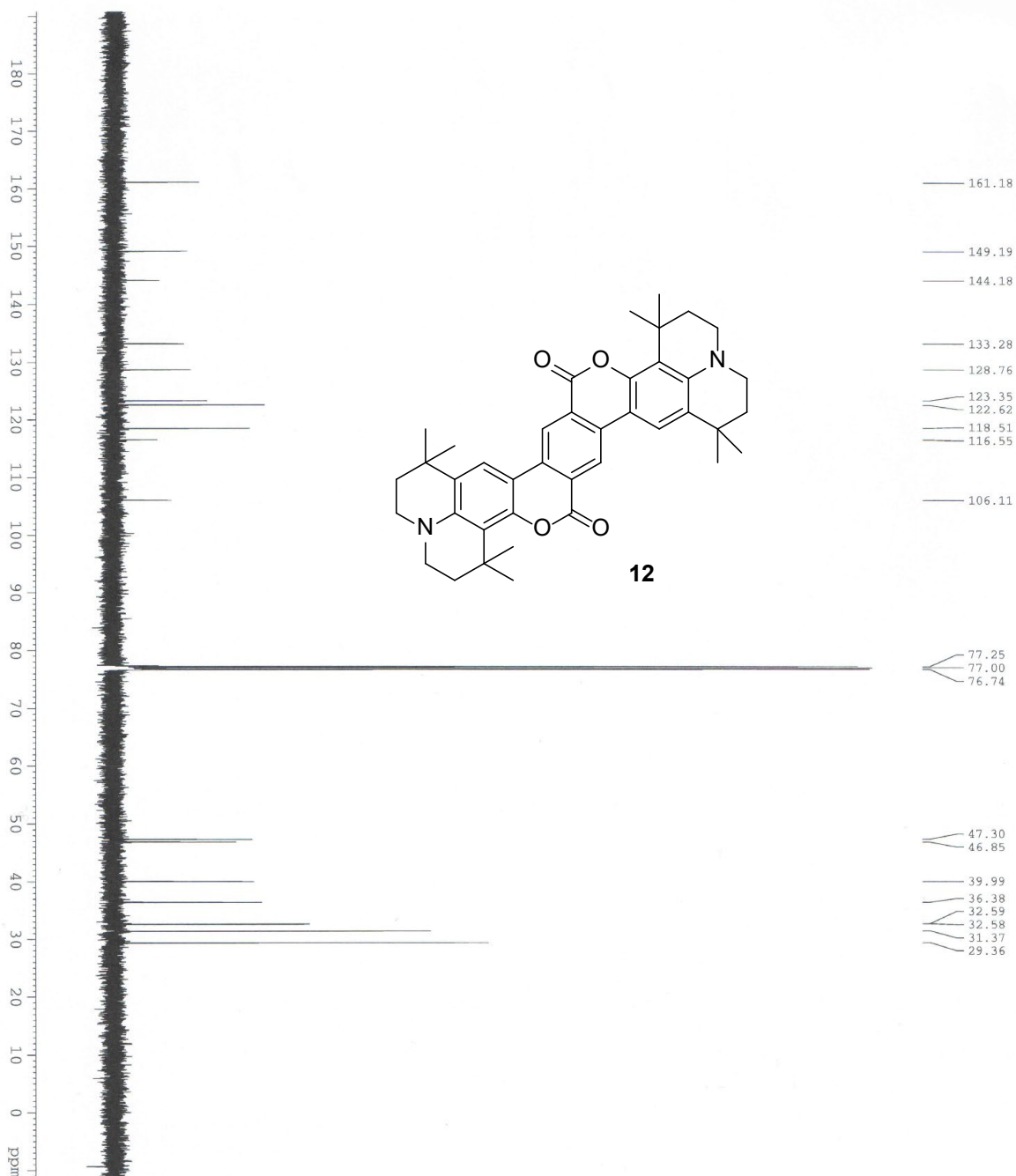


- 167.00
- 161.64
- 152.78
- 150.08
- 132.96
- 123.91
- 123.85
- 122.82
- 109.39
- 105.36
- 98.58
- 77.25
- 77.00
- 76.75
- 51.28
- 31.81
- 29.46
- 29.30
- 27.22
- 27.11
- 22.64
- 14.07









Section S7: References

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K. Throssell, J. A. Montgomery Jr., J. E. Peralta, F. Ogliaro, M. J. Bearpark, J. J. Heyd, E. N. Brothers, K. N. Kudin, V. N. Staroverov, T. A. Keith, R. Kobayashi, J. Normand, K. Raghavachari, A. P. Rendell, J. C. Burant, S. S. Iyengar, J. Tomasi, M. Cossi, J. M. Millam, M. Klene, C. Adamo, R. Cammi, J. W. Ochterski, R. L. Martin, K. Morokuma, O. Farkas, J. B. Foresman and D. J. Fox, *Gaussian 16 Rev. B.01*, Wallingford, CT, 2016.