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Synthesis and electronic properties of bridged [8]-, [12]- and [16]-cyclo-*para*-phenylenes

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1 General information

1.1. Synthesis

All manipulations of oxygen and moisture-sensitive materials were conducted with a standard Schlenk technique. All glassware was kept in an oven at 80 °C. Argon atmosphere was generated by three repetitive cycles of vacuum/Argon. Commercially available reagents and solvents were used without further purification other than those detailed below. THF was obtained through a PURE SOLV™ solvent purification system. Light petroleum refers to the fraction with bp 40-60°C. Analytical thin layer chromatography was carried out using aluminum backed plates coated with Merck Kieselgel 60 GF254 and visualized under UV light (at 254 and 360 nm). Flash chromatography was carried out using Teledyne Isco CombiFlash® Rf 400 (UV detection 200-360nm), over standard silica cartridges (Redisep® Isco or Puriflash® columns Interchim). In order to be purified through a recycling size exclusion chromatography apparatus, the compounds were solubilized in HPLC grade chloroform (stabilized with ethanol). Prior to injection, the solution was filtered through a 0.45 μm PTFE filter. Purification was performed on a LC-9160 II NEXT system from the Japan Analytical Industry Co., Ltd. (JAI) equipped with coupled UV-vis 4Ch NEXT through a set of two JAIGEL-2H columns at an elution rate of 10 mL.min-1 ($CHCl_3$). ^1H and ^{13}C NMR spectra were recorded using Bruker 300 MHz instruments (^1H frequency, corresponding ^{13}C frequency: 75 MHz); chemical shifts were recorded in ppm and J values in Hz. The residual signals for the NMR solvents used are 5.32 ppm (proton) and 54.00 ppm (carbon) for CD_2Cl_2, 7.26 ppm (proton) and 77.16 ppm (carbon) for $CDCl_3$ and 77.16 ppm (carbon), 2.09 ppm (proton) for toluene-d8. In the ^{13}C NMR spectra, signals corresponding to C, CH, CH_2 or CH_3 groups, assigned from DEPT experiment, are noted. The following abbreviations have been used for the NMR assignment: s for singlet, d for doublet, t for triplet, q for quadruplet and m for multiplet. High resolution mass spectra were recorded at the Centre Régional de Mesures Physiques de l'Ouest (CRMPO-Rennes) on a Thermo-Fisher Q-Exactive instrument or a Bruker MaXis 4G or a Bruker Ultraflex III.

1.2. Spectroscopic studies

Cyclohexane (99+% for spectroscopy, Acros Organics), tetrahydrofuran (THF, 99.5+% for spectroscopy, Acros Organics), dichloromethane (99.8+% for spectroscopy, Acros Organics), acetronitrile (99+% for spectroscopy, Acros Organics), toluene (99+% for spectroscopy, Acros Organics), ethyl acetate (spectroscopic grade, Merck), chloroform (spectroscopic grade, Sigma Aldrich), 1 N solution of sulfuric acid in water (Standard solution, Alfa Aesar) and quinine sulfate dihydrate (99+%, ACROS organics) were used without further purification.

UV-visible spectra were recorded using an UV-Visible spectrophotometer SHIMADZU UV-1605 or a UV-Visible spectrophotometer JASCO FS-110. Molar extinction coefficients (ε) were calculated from the gradients extracted from the plots of absorbance *vs* concentration with five solutions of different concentrations for each sample and at least two mother solutions were prepared.

$$A = \varepsilon \times l \times C$$

Above, l refers to the path length and C to the sample concentration.

Emission spectra were recorded with a HORIBA Scientific Fluoromax-4 equipped with a Xenon lamp.

Quantum yields in solution (øsol) were calculated relative to quinine sulfate (øref = 0.546 in H_2SO_4 1 N). øsol was determined according to the following equation,

$$\phi sol = \phi ref \times \frac{Grad_s}{Grad_r} \times \left(\frac{\eta_s}{\eta_r}\right)^2$$

where subscripts *s* and *r* refer respectively to the sample and reference, *Grad* is the gradient from the plot of integrated fluorescence intensity *vs* absorbance, η is the refracting index of the solvent (η_s = 1.426 for cyclohexane, η_s = 1.445 for chloroform, η_s = 1.336 for 1 N solution of sulfuric acid in water). Five solutions of different concentration (A < 0.1) of the sample and five solutions of the reference (quinine sulfate) were prepared. The integrated area of the fluorescence peak was plotted against the absorbance at the excitation wavelength for both the sample and reference. The gradients of these plots were then injected in the equation to calculate the reported quantum yield value for the sample.

Absolute quantum yields of films were recorded using a deported HORIBA Scientific Quanta-Phi integrating sphere linked to the Fluoromax-4.

Fluorescent decay measurements were carried out on the HORIBA Scientific Fluoromax-4 equipped with its TCSPC pulsed source interface.

Spin-coated film were prepared form a 1g/mL solution in THF using a Labspins Tournette from Süss Microtec.

IR spectra were recorded on a Bruker Vertex 7 0 using a diamond crystal MIRacle ATR (Pike).

1.3. Electrochemical studies

Electrochemical experiments were performed under argon atmosphere using a Pt disk electrode (diameter 1 mm). The counter electrode was a vitreous carbon rod. The reference electrode was either a silver wire in a 0.1 M $AgNO_3$ solution in CH_3CN for the studies in oxidation or a Silver wire coated by a thin film of AgI (silver(I)iodide) in a 0.1 M Bu_4NI solution in DMF for the studies in reduction. Ferrocene was added to the electrolyte solution at the end of a series of experiments. The ferrocene/ferrocenium (Fc/Fc^+) couple served as internal standard. The three electrodes cell was connected to a potentiostat/galvanostat (Autolab/PGSTAT101) monitored with the Nova 2.1 Software. Activated Al_2O_3 was added in the electrolytic solution to remove excess moisture. For a further comparison of the electrochemical and optical properties, all potentials are referred to the Fc/Fc^+ system. We estimated the electron affinity (EA) or lowest unoccupied molecular orbital (LUMO) and the ionization potential (IP) or highest occupied molecular orbital (HOMO) from the redox data. The LUMO level was calculated from: LUMO (eV) = -[E_{onset}^{red} (*vs* Fc/Fc^+) + 4.8]. Similarly the HOMO level was calculated from: HOMO (eV) = -[E_{onset}^{ox} (*vs* Fc/Fc^+) + 4.8], based on a Fc/Fc^+ energy level of 4.8 eV relative to the vacuum.

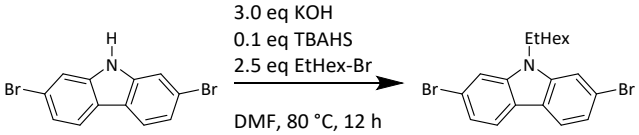
1.4. Molecular modelling

Full geometry optimization of the ground state and vibrational frequency calculation were performed with Density Functional Theory (DFT)[1,2] using the hybrid Becke-3 parameter exchange functional [3-5] and the Lee-Yang-Parr non-local correlation functional[6] (B3LYP) implemented in the Gaussian 16 program suite,[7] using the 6-31G(d) basis set and the default convergence criterion implemented in the program. All stationary points were characterized as minima by analytical frequency calculations.

This work was granted access to the HPC resources of CEA-TGCC under the allocation 2022-AD010805032R1 awarded by GENCI and of the "Mésocentre" computing center of CentraleSupélec and École Normale Supérieure Paris-Saclay supported by CNRS and Région Île-de-France (http://mesocentre.centralesupelec.fr/).

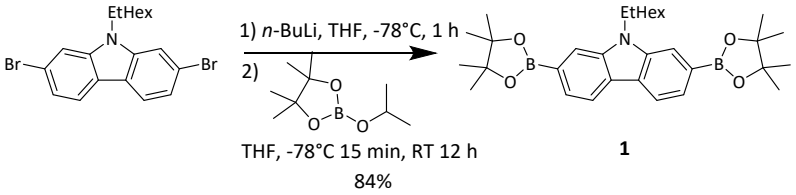
Figures were generated with GaussView 6.0.

2 Synthetic procedures



Scheme S 1. Synthesis of 2,7-dibromo-N-(2-ethylhexyl)-carbazole

2,7-dibromo-*N*-(2-ethylhexyl)-carbazole: 2,7-Dibromocarbazole (4.00 g, 12.3 mmol, 1.0 eq), KOH (2.07 g, 36.9 mmol, 3.0 eq) and tetrabutylammonium hydrogen sulfate (0.418 g, 1.23 mmol, 0.1 eq) were charged in a Schlenk tube under an argon atmosphere. Then 2-ethylhexyle bromine (5.47 mL, 30.8 mmol, 2.5 eq) and dry DMF (40 mL) were added. The resulting mixture was stirred at 80°C overnight under air. After cooling to RT, a saturated solution of ammonium chloride was added. The organic layer was extracted with CH_2Cl_2. The organic layer was then washed with water, brine, dried over $MgSO_4$, filtered and concentrated under reduced pressure. After purification with flash chromatography on silica gel [column condition: silica cartridge (40 g); solid deposit on Celite®; λdetection: (254 nm, 280 nm); CH_2Cl_2/light petroleum (5/95) at 40 mL/min], the *title compound* was obtained as a white solid (3.92 g, 8.98 mmol); yield 73 %; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.86 (d, *J* = 8.3 Hz, 2H), 7.49 (d, *J* = 1.7 Hz, 2H), 7.33 (dd, *J* = 8.3, 1.7 Hz, 2H), 4.12 – 3.93 (m, 2H), 2.11 – 1.91 (m, 1H), 1.45 – 1.21 (m, 8H), 0.93 – 0.83 (m, 6H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$) δ 142.0 (2C), 122.6 (2CH), 121.5 (2CH), 121.4 (2C), 119.8 (2C), 112.4 (2CH), 47.8 (CH_2), 39.3 (CH), 30.9 (CH_2), 28.7 (CH_2), 24.5 (CH_2), 23.2 (CH_2), 14.1 (CH_3), 11.0 (CH_3) ppm. IR (ATR platinum) 2959, 2925, 2873, 2858, 1621, 1584, 1483, 1459, 1450, 1425, 1378, 1364, 1342, 1326, 1310, 1297, 1269, 1247, 1225, 1210, 1130, 1067, 1053, 997, 967, 946, 930, 901, 883, 874, 864, 845, 821, 795, 762, 747, 723, 664, 594, 558, 548, 430 cm^{-1}. HRMS (ASAP, 130 °C): $[M+H]^+$ ($C_{20}H_{24}N^{79}Br_2$) found 436.0272, required 436.0270. m.p.: 103 °C.



*Scheme S 2. Synthesis of **1***

N-(2-ethylhexyl)-2,7-bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-carbazole **1**: 2,7-dibromo-*N*-(2-ethylhexyl)-carbazole (2.00 g, 4.58 mmol, 1.0 eq) was dissolved in anhydrous THF (340 mL) under an argon atmosphere. The reaction mixture was cooled to -78 °C. A 2.5 M solution of *n*-BuLi in hexanes (20.58 mL, 51.5 mmol, 3.3 eq) was then added dropwise to the solution at -78 °C. The solution was stirred at this temperature for an hour and 2-isopropoxy-4,4,5,5-tetramethyl-1,3,2,-dioxaborolane (11.34 mL, 55.6 mmol, 3.5 eq) was added to the mixture and stirred at -78 °C for 15 minutes. The reaction mixture was allowed to warm up to room temperature overnight under stirring. The reaction mixture was quenched with few drops of absolute ethanol and concentrated under reduced pressure. The crude product was dissolved in CH_2Cl_2. The organic layer was washed with water, brine, dried over $MgSO_4$, filtered and concentrated under reduced pressure. After flash chromatography on silica gel [column conditions: silica cartridge (40 g); solid deposit on Celite®; λdetection: (254 nm, 280 nm); CH_2Cl_2/light petroleum (3/7) at 40 mL/min], giving the *title compound* as a white solid (2.04 g, 3.84 mmol); yield 84%; ^{1}H NMR (300 MHz, $CDCl_3$): 8.12 (d, J = 7.8 Hz, 2H), 7.88 (s, 2H), 7.67 (d, J = 7.8 Hz, 2H), 4.37 – 4.16 (m, 2H), 2.29 – 1.96 (m, 1H), 1.40 – 1.22 (m, 32H), 0.90 (dt, J = 7.2, 4.1 Hz, 6H). ^{13}C NMR

(101 MHz, $CDCl_3$) δ 141.1 (2C), 125.2 (4C), 124.9 (2CH), 120.1 (2CH), 115.8 (2CH), 83.9 (4C), 47.3 (CH_2), 39.3 (CH), 30.8 (CH_2), 28.6 (CH_2), 25.1 ($8CH_3$), 24.6 (CH_2), 23.2 (CH_2), 14.3 (CH_3), 11.1 (CH_3) ppm. IR (ATR platinum): 2995, 2978, 2960, 2928, 2869, 1624, 1561, 1500, 1482, 1461, 1449, 1433, 1392, 1380, 1371, 1354, 1337, 1313, 1266, 1252, 1234, 1212, 1167, 1141, 1114, 1076, 1055, 999, 980, 964, 945, 936, 899, 880, 855, 821, 793, 766, 735, 706, 689, 671, 658, 646, 579, 557, 519, 419 cm^{-1}. HRMS (ASAP, 140 °C): $[M+H]^+$ ($C_{32}H_{48}NO_4{}^{11}B_2$) found 532.3771, required 532.3764. m.p.: 109 °C.

2,7-bis(4-bromophenyl)-*N*-(2-ethylhexyl)-carbazole **2**: *N*-(2-ethylhexyl)-2,7-bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-carbazole **1** (0.150 g, 0.282 mmol, 1.0 eq), 1-bromo-4-iodobenzene (0.240 g, 0.847 mmol, 3.0 eq), [1,1'-bis(diphenylphosphino)ferrocene]palladium(II) dichloride (0.021 g , 2.82×10^{-2} mmol, 0.1 eq) and KOH (0.079 g, 1,41 mmol, 5.0 eq) were dissolved in THF (10 mL) under an argon atmosphere. Degassed H_2O (0.5 mL, 5 %vol) was added and the resulting mixture was stirred at 50 °C for 5h. After cooling to RT, a saturated solution of NH_4Cl was added and the crude was extracted with CH_2Cl_2. The organic layer was washed with H_2O, dried over $MgSO_4$, filtered and solvent was removed under reduced pressure. The residue was further purified with flash chromatography on silica gel [column conditions: silica cartridge (40 g); solid deposit on Celite®; λdetection: (254 nm, 280 nm); CH_2Cl_2/light petroleum (5:95) at 40 mL/min], giving the *title compound* as a white solid (0.152 g, 0.258 mmol); yield 91%; ^{1}H NMR (300 MHz, CD_2Cl_2) δ 8.16 (d, *J* = 8.2 Hz, 2H), 7.63 (s, 8H), 7.59 (d, *J* = 1.5 Hz, 2H), 7.46 (dd, *J* = 8.2, 1.5 Hz, 2H), 4.28 (dd, *J* = 7.5, 2.6 Hz, 2H), 2.15 (t, *J* = 6.9 Hz, 1H), 1.48 – 1.20 (m, 8H), 0.94 (t, *J* = 7.4 Hz, 3H), 0.86 (t, *J* = 7.2 Hz, 3H) ppm. ^{13}C NMR (75 MHz, CD_2Cl_2) δ 142.7 (2C), 141.7 (2C), 138.4 (2C), 132.5 (4CH), 129.7 (4CH), 122.6 (2CH), 121.8 (2CH), 121.3 (2C), 119.0 (2C), 108.0 (2CH), 48.0 (CH_2), 40.0 (CH), 31.5 (CH_2), 29.4 (CH_2), 25.1 (CH_2), 23.6 (CH_2), 14.4 (CH_3), 11.3 (CH_3) ppm. IR (ATR, platinum): 2959, 2924, 2854, 1896, 1625, 1598, 1573, 1557, 1541, 1503, 1481, 1458, 1438, 1396, 1379, 1337, 1301, 1262, 1232, 1215, 1194, 1143, 1116, 1105, 1076, 1057, 1036, 1005, 997, 946, 914, 899, 887, 855, 832, 823, 798, 766, 748, 727, 710, 657, 645, 630, 596, 575, 546, 505, 436, 420 cm^{-1}. HRMS (MALDI, DCTB): $M^{+\cdot}$found 587.082 for $C_{32}H_{31}N^{79}Br_2$ required 587.0818. m.p.: 174 °C

N-(2-ethylhexyl)-2,7-bis(4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)phenyl)-carbazole **3**: 2,7-bis(4-bromophenyl)-*N*-(2-ethylhexyl)-carbazole **3** (3.00 g, 5.63 mmol, 1.0 eq), THF (100 mL), *n*-BuLi (6.75 mL, 16.9 mmol, 3.0 eq) and 2-isopropoxy-4,4,5,5-tetramethyl-1,3,2,-dioxaborolane (3.67 mL, 18.0 mmol, 3.2 eq). After flash chromatography on silica gel [column conditions: silica cartridge (40 g); solid deposit on Celite®; λdetection: (254 nm, 280 nm); gradient CH_2Cl_2/light petroleum from 0 % to 60 % in 80 min at 40 mL/min], giving the *title compound* as a white solid (1.85 g, 2.95 mmol); yield 52 %; ^{1}H NMR (300 MHz, CD_2Cl_2) δ 8.17 (d, *J* = 8.0 Hz, 2H), 7.89 (d, *J* = 8.2 Hz, 4H), 7.76 (d, *J* = 8.2 Hz, 4H), 7.67 (d, *J* = 1.5 Hz, 2H), 7.53 (dd, *J* = 8.1, 1.5 Hz, 2H), 4.38 – 4.23 (m, 2H), 2.17 (t, *J* = 6.5 Hz, 1H), 1.49 – 1.22 (m, 32H), 0.95 (t, *J* = 7.4 Hz, 3H), 0.87 (t, *J* = 7.1 Hz, 3H).ppm. ^{13}C NMR (75 MHz, CD_2Cl_2) δ 145.2 (2C), 142.7 (2C), 139.3 (2C), 135.8 (4CH), 127.3 (4CH), 122.6 (2C), 121.2 (2CH), 119.2 (2CH), 108.3 (2CH), 84.4 (6C), 48.0 (CH_2), 40.0 (CH), 31.6 (CH_2), 29.4 (CH_2), 25.3 ($8CH_3$), 25.1 (CH_2), 23.7 (CH_2), 14.4 (CH_3), 11.3 (CH_3) ppm. IR (ATR, platinum): 2977, 2959, 2926, 2865, 1606, 1547, 1521, 1490, 1458, 1434, 1399, 1357, 1317, 1267, 1251, 1213, 1192, 1166, 1142, 1107, 1089, 1059, 1017, 997, 962, 948, 859, 835, 805, 768, 756, 742, 725, 698, 674, 655, 629, 597, 576, 520, 446 cm^{-1}. HRMS (ESI, CH_3OH/CH_2Cl_2: 98/2): $[M+H]^+$ found 706.4227 for $C_{44}H_{56}NO_4{}^{11}B_2$ required 706.42194 m.p.: 191 °C.

[4]cyclo-*para*-9-ethylhexyl-2,7-diphenyl-carbazole **[16]CPP4N**: *N*-(2-ethylhexyl)-2,7-bis(4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)phenyl)-carbazole **3** (0.250 g, 0.366 mmol, 1.0 eq), cesium fluoride (0.333 g, 2.19 mmol, 6.0 eq) and 1,5-cyclooctadieneplatinium (II) dichloride (0.137 g, 0.366 mmol, 1.0 eq) were dissolved in extra dry DCE (15 mL) under an argon atmosphere and refluxed for 24 h. Solvent was then removed under reduced pressure and the crude product was dried under vacuum at 60°C for 24 h. Triphenylphosphine (1.43 g, 5.49 mmol, 15 eq) was then added to the crude product

and 1,2-dichlorobenzene (30 mL) was added under an argon atmosphere. The resulting mixture was stirred for one hour at room temperature and then refluxed for 48 h. Then, solvent was removed under reduced pressure. The crude product was dissolved in CH_2Cl_2. Water was added and the organic layer was extracted with CH_2Cl_2, dried over $MgSO_4$, filtered and solvent was removed under reduced pressure. The residue was first purified with flash chromatography on silica gel [column conditions: silica cartridge (40 g); solid deposit on Celite®; λdetection (254 nm, 280 nm); gradient dichloromethane/light petroleum 5% to 60 % at 40 mL/min] and second with recycling size exclusion chromatography ($CHCl_3$) to give the *title compound* as a pale yellow solid (0.029 g, 1.35×10^{-2} mmol); yield 15 %. ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.14 (d, *J* = 8.2 Hz, 8H), 7.80 (d, *J* = 8.2 Hz, 16H), 7.70 (d, *J* = 8.3 Hz, 16H), 7.60 (d, *J* = 8.1, 1.5 Hz, 8H), 7.29 (s, 8H), 4.03 (d, *J* = 7.2 Hz, 8H), 2.08 – 2.02 (m, 4H), 1.40 – 1.18 (m, 34H), 0.88 – 0.83 (m, 24H) ppm. ^{13}C NMR (126 MHz, $CDCl_3$) δ 142.4 (8C), 141.6 (8C), 139.0 (8C), 138.5 (8C), 128.3 (16 CH), 127.1 (16CH), 122.0 (8CH), 121.3 (8CH), 117.2 (8C), 110.4 (8CH), 46.9 ($4CH_2$), 39.5 (4CH), 31.0 ($4CH_2$), 28.8 ($4CH_2$), 24.5 ($4CH_2$), 23.2 ($4CH_2$), 14.2 ($4CH_3$), 11.0 ($4CH_3$) ppm. IR (ATR, platinum): 3032, 2963, 2930, 2865, 1777, 1738, 1722, 1704, 1689, 1657, 1640, 1630, 1607, 1580, 1563, 1545, 1526, 1509, 1500, 1460, 1438, 1400, 1383, 1356, 1328, 1311, 1255, 1222, 1196, 1134, 1066, 1001, 946, 859, 848, 832, 807, 767, 753, 740, 728, 702, 671, 657, 632, 601, 586, 566, 530, 464, 448, 423 cm^{-1}. HRMS (MALDI, DCTB): Found [$M^{+\cdot}$], 1716.979, $C_{128}H_{124}N_4$ required 1716.98205.

[3]cyclo-*para*-9-ethylhexyl-2,7-diphenyl-carbazole **[12]CPP3N**: The title compound was obtained through the previous synthesis as a second product as a pale yellow solid (0.005 g, 0.28×10^{-2} mmol); yield 3 %; ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.08 (d, J = 8.2 Hz, 6H), 7.82 (d, J = 8.7 Hz, 12H), 7.62 – 7.53 (m, 18H), 7.09 (s, 6H), 3.85 – 3.80 (m, 6H), 2.04 – 1.96 (m, 3H), 1.43 – 1.27 (m, 24H), 0.90 – 0.85 (m, 18H) ppm. ^{13}C NMR (126 MHz, $CDCl_3$) δ 142.8 (6C), 141.5 (6C), 139.2 (6C), 137.2 (6C), 128.3 (12CH), 126.4 (12CH), 122.1 (6CH), 121.7 (6CH), 116.9 (6C), 111.6 (6CH), 46.5 ($3CH_2$), 39.6 (3CH), 31.0 ($3CH_2$), 29.9 ($2CH_2$), 28.9 (CH_2), 24.5($3CH_2$), 23.1 ($3CH_2$), 14.2 ($3CH_3$), 11.0 ($3CH_3$) ppm. IR (ATR, platinum): 3032, 2963, 2929, 2883, 2858, 1895, 1777, 1739, 1721, 1704, 1689, 1657, 1629, 1605, 1563, 1544, 1526, 1509, 1494, 1460, 1437, 1400, 1382, 1355, 1328, 1309, 1258, 1225, 1196, 1133, 1065, 1001, 947, 863, 850, 832, 806, 772, 762, 752, 738, 725, 700, 671, 654, 630, 600, 582, 565, 523, 455 cm^{-1}. HRMS (MALDI, DCTB): Found $M^{+\cdot}$, 1287.737, $C_{96}H_{93}N_3$ required 1287.7364.

[4]cyclo-*para*-9-ethylhexyl-carbazole **[8]CPP4N**: *N*-(2-ethylhexyl)-2,7-bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-carbazole **1** (0.250 g, 0.470 mmol, 1.0 eq), cesium fluoride (0.429 g, 2.82 mmol, 6.0 eq) and 1,5-cyclooctadieneplatinium (II) dichloride (0.176 g, 0.470 mmol, 1.0 eq) were dissolved in DCE (20 mL) under an argon atmosphere and refluxed for 24 h. Solvent was then removed under reduced pressure and the crude product was dried under vacuum at 60°C for 24 h. Triphenylphosphine (1.85 g, 7.06 mmol, 15 eq) was then added to the crude product and 1,2-dichlorobenzene (30 mL) was added under an argon atmosphere. The resulting mixture was stirred for one hour at room temperature and then refluxed for 48 h. Then, solvent was removed under reduced pressure. The crude product was dissolved in CH_2Cl_2. Water was added and the organic layer was extracted with CH_2Cl_2, dried over $MgSO_4$, filtered and solvent was removed under reduced pressure. The residue was purified by flash chromatography on silica gel [column conditions: silica cartridge (40 g); solid deposit on Celite®; λdetection (254 nm, 280 nm); dichloromethane/light petroleum (5:95) at 40 mL/min] giving the *title compound* as a yellow solid (47 mg, 4.23×10^{-2} mmol); yield 36 %; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.93 (d, *J* = 8.3 Hz, 8H), 7.48 (d, *J* = 8.4 Hz, 8H), 6.53 (s, 8H), 3.43 (d, *J* = 7.1 Hz, 8H), 1.95 – 1.78 (m, 4H), 1.28 (tp, *J* = 15.1, 7.5 Hz, 32H), 0.94 – 0.81 (m, 24H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$) δ 144.2 (4C), 144.0 (4C), 141.9 (4C), 122.2 (4CH), 116.5 (4CH), 115.7 (4CH), 45.9 ($4CH_2$), 39.6 (4CH), 30.8 ($4CH_2$), 28.9 ($4CH_2$), 24.2 ($4CH_2$), 23.1 ($4CH_2$), 14.2 ($4CH_3$), 10.8 ($4CH_3$) ppm. IR (ATR platinum) 2957, 2924, 2873, 2854, 1610, 1587, 1560, 1541, 1475, 1449, 1414, 1376, 1346, 1319, 1308, 1253, 1240, 1219, 1190, 1131, 1061, 863,

849, 827, 816, 795, 758, 746, 726, 656, 621, 593, 550, 482, 456, 444 cm^{-1}. HRMS (ASAP, 300 °C): Found $[M+H]^+$, 1109.7390, $C_{80}H_{93}N_4$ required 1109.7395. m.p. > 350 °C.

3 1D and 2D (COSY and NOESY) NMR spectra

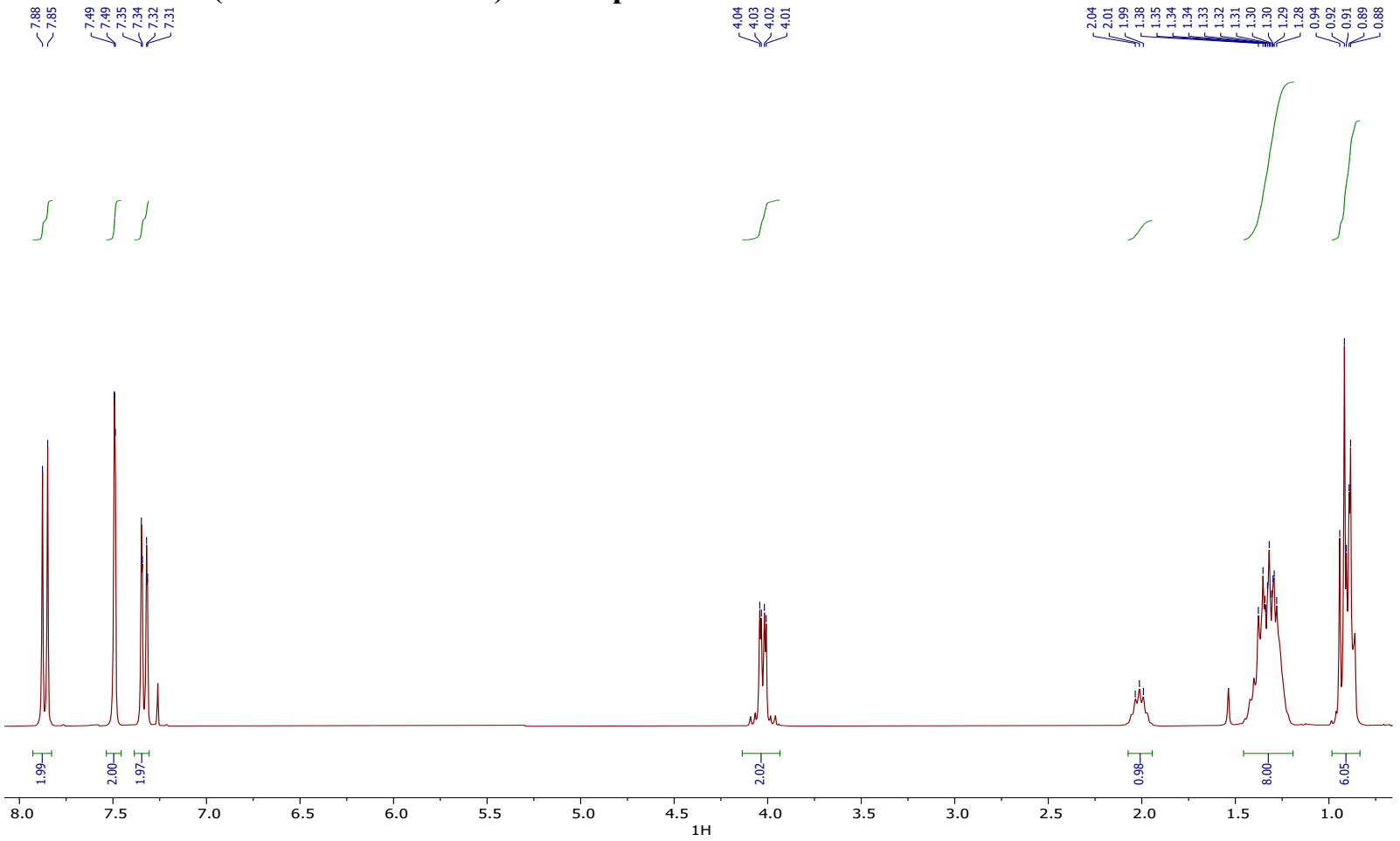


Figure S 1 1D ^{1}H NMR spectrum of 2,7-dibromo-N-(2-ethylhexyl)-carbazole in $CDCl_3$

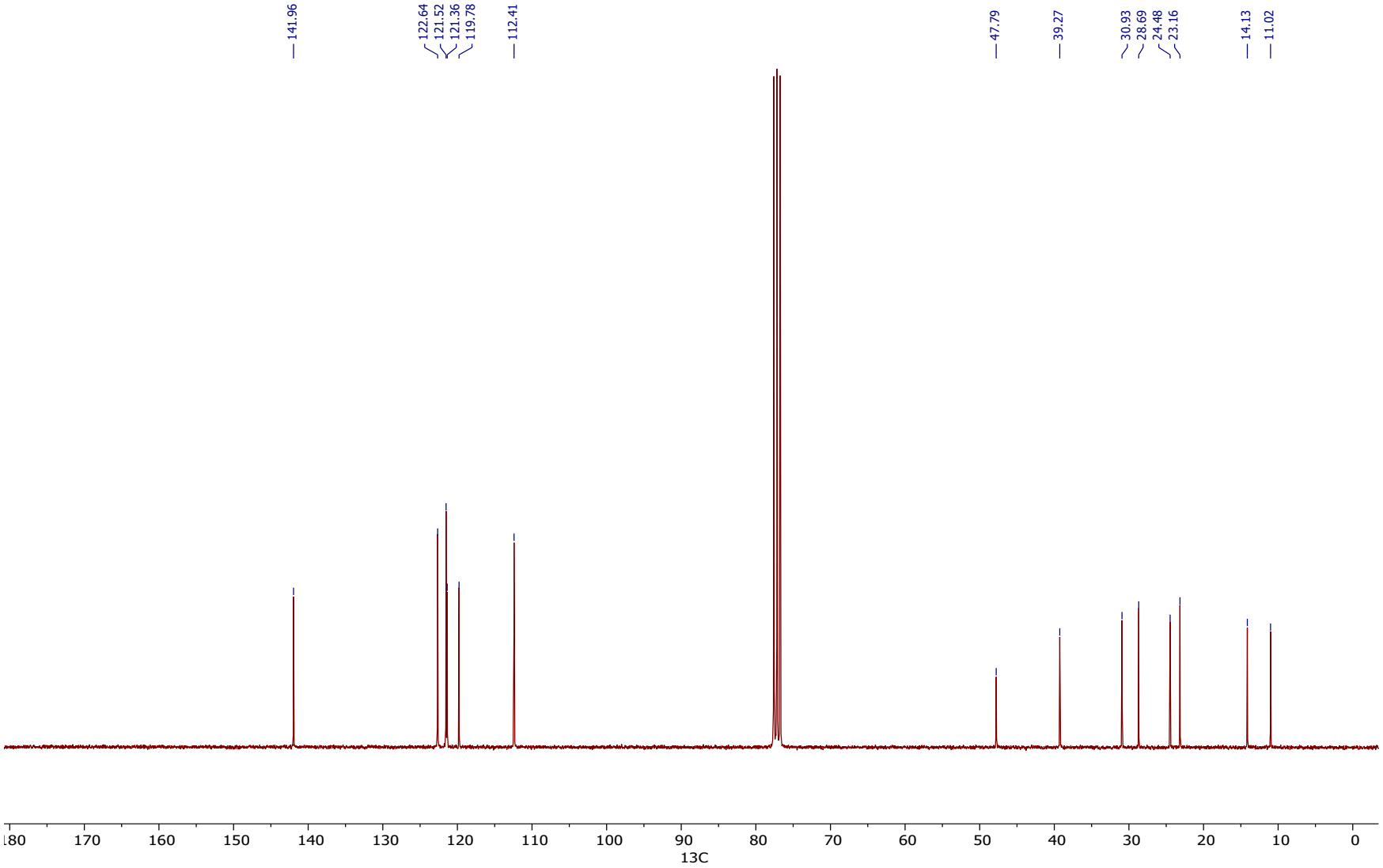


*Figure S 2 1D ^{13}C NMR spectrum of 2,7-dibromo-*N*-(2-ethylhexyl)-carbazole in $CDCl_3$*

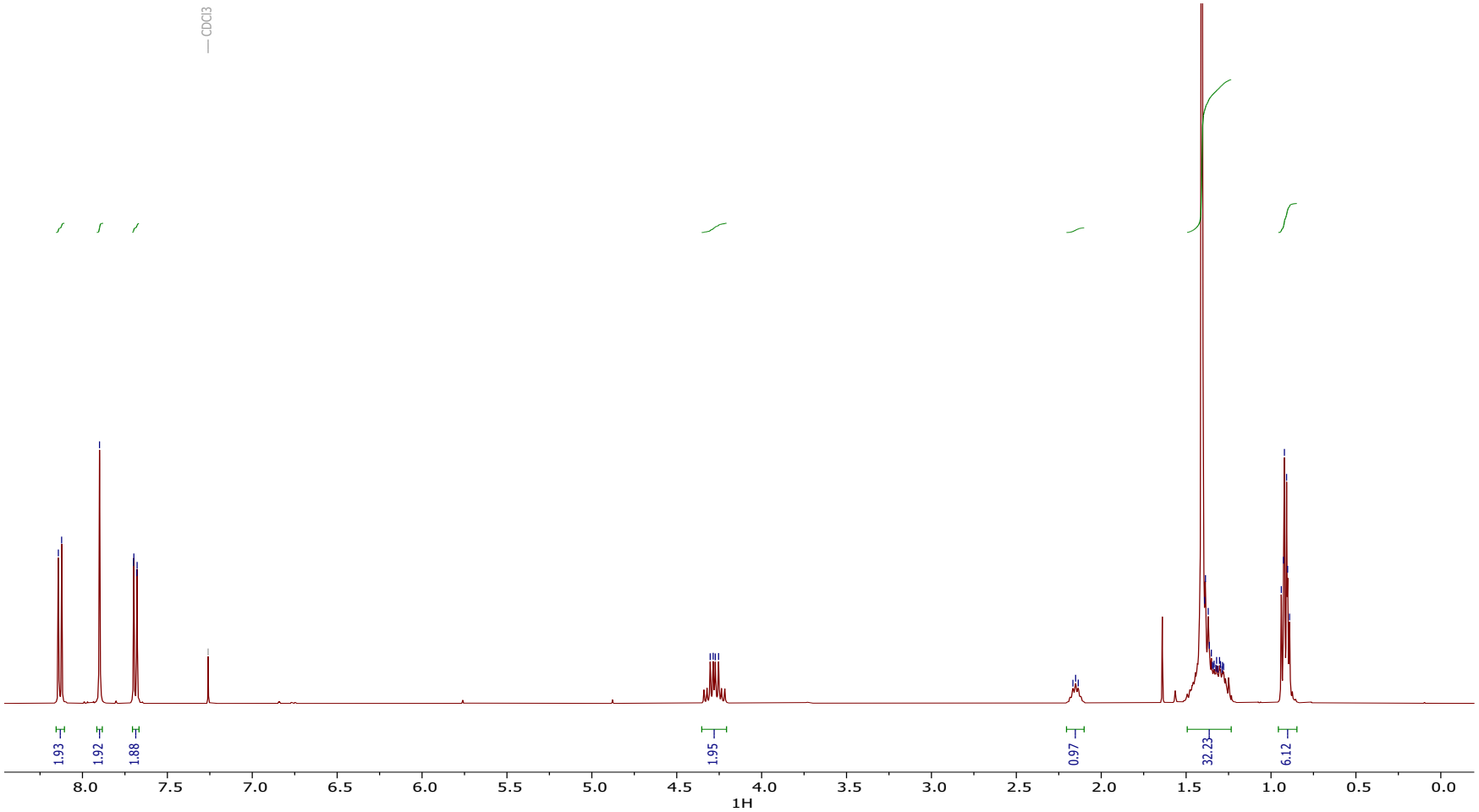


*Figure S 3 1D ^{1}H NMR spectrum of **1** in $CDCl_3$*

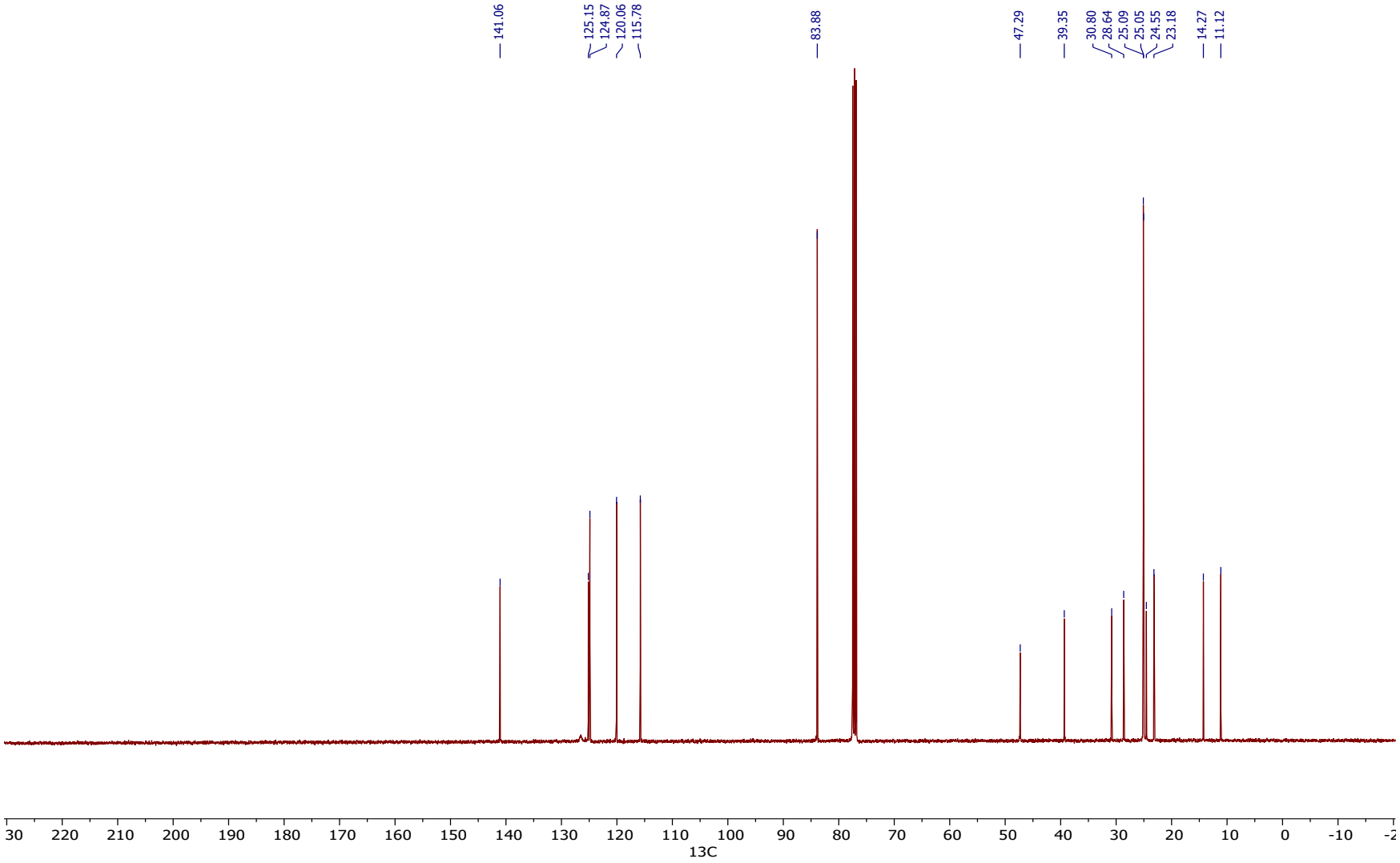


*Figure S 4 1D ^{13}C NMR spectrum of **1** in $CDCl_3$*

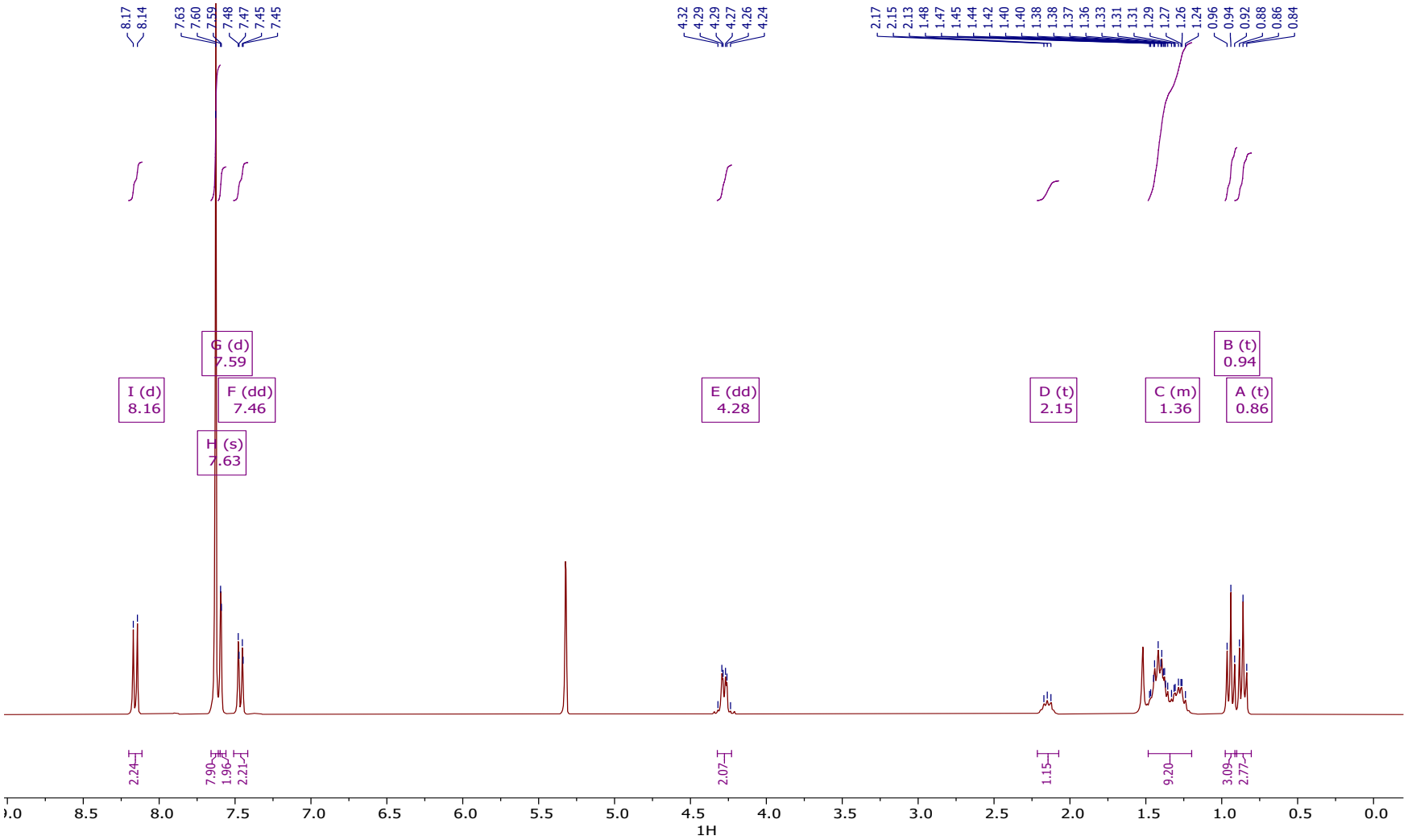


*Figure S 5 1D ^{1}H NMR spectrum of **2** in CD_2Cl_2*

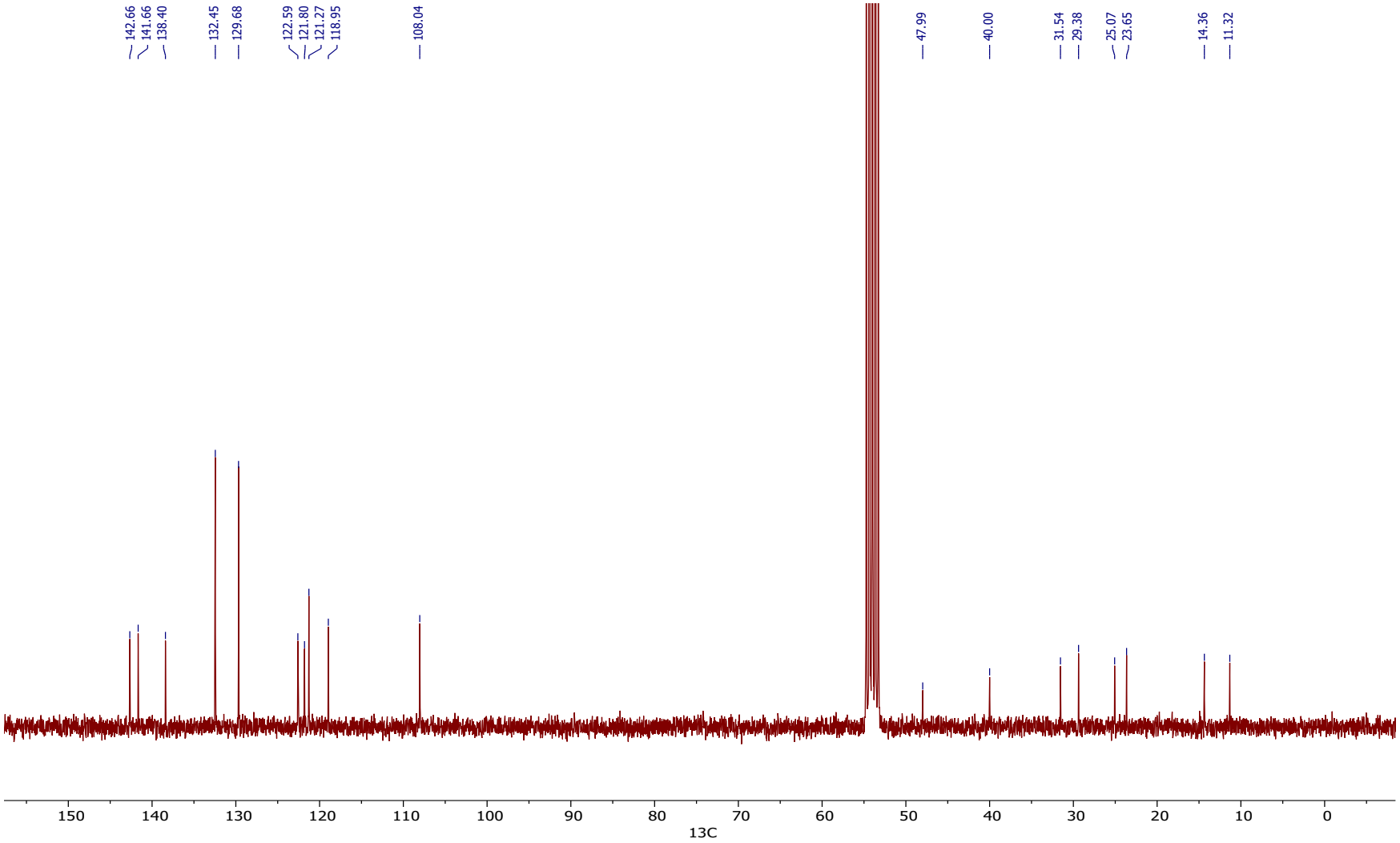


*Figure S 6 1D ^{13}C NMR spectrum of **2** in CD_2Cl_2*

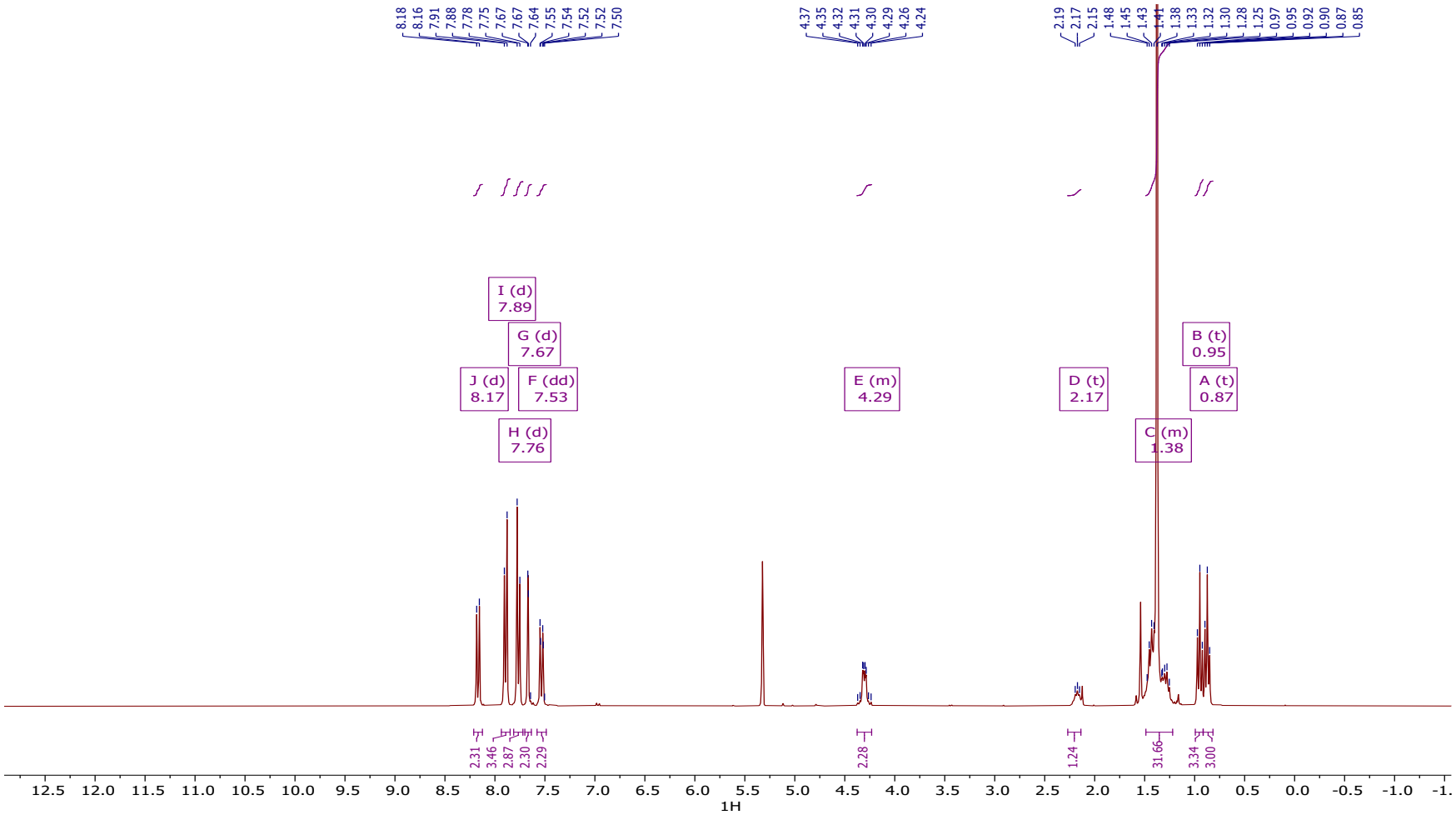


*Figure S 7 1D ^{1}H NMR spectrum of **3** in CD_2Cl_2*

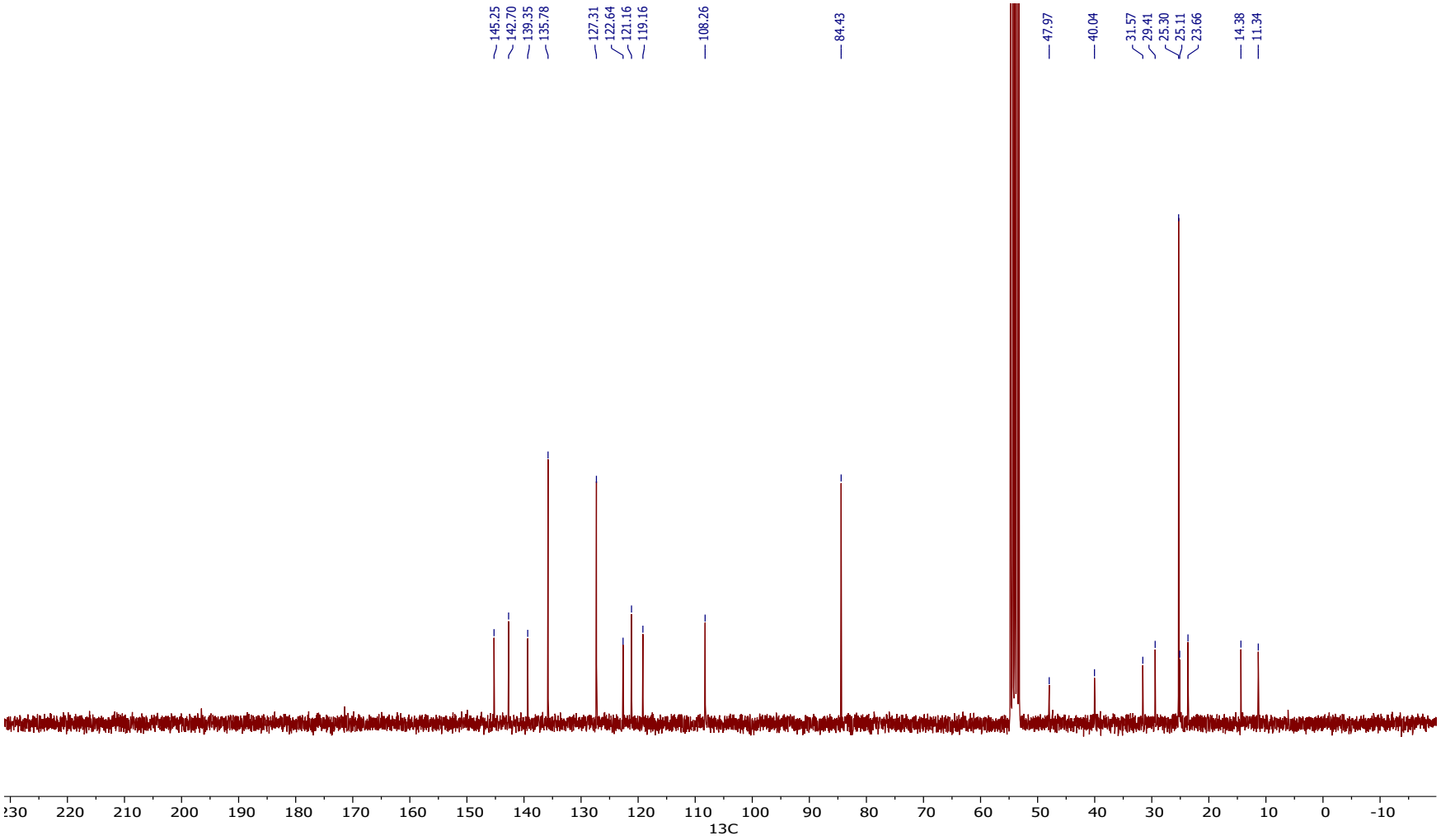


*Figure S 8 1D ^{13}C NMR spectrum of **3** in CD_2Cl_2*

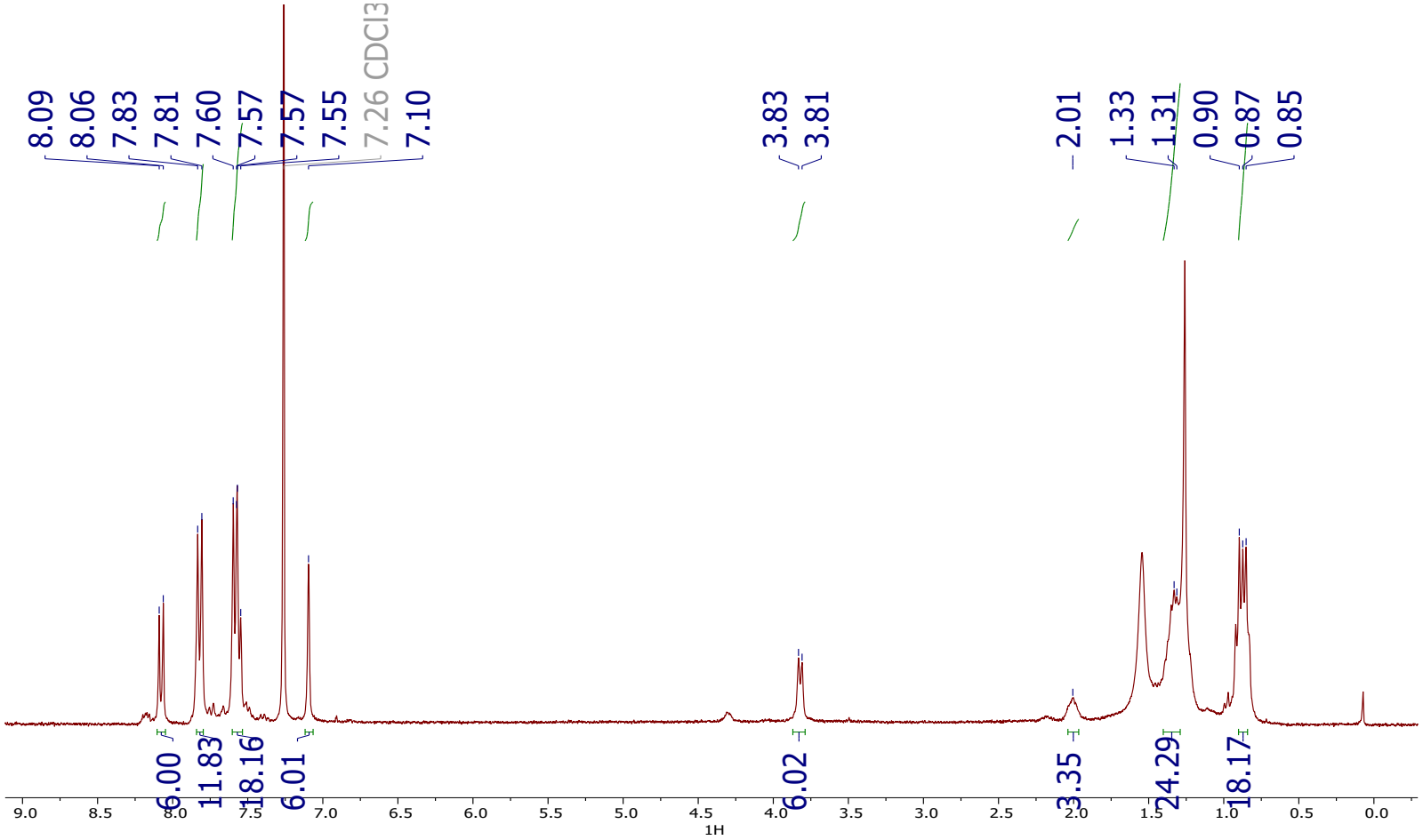


*Figure S 9 1D ^{1}H NMR spectrum of **[12]CPP3N** in $CDCl_3$*

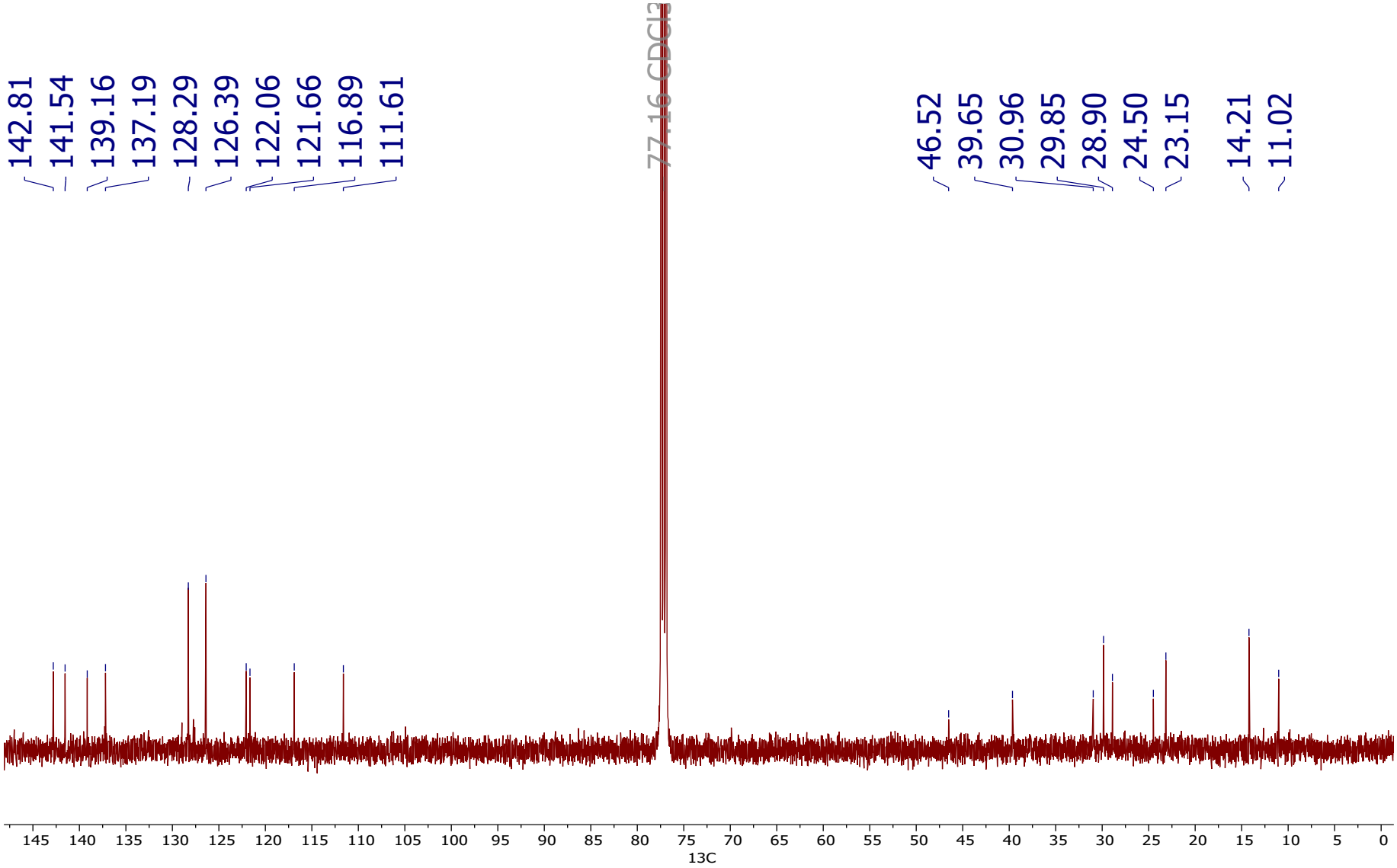


*Figure S 10 1D ^{13}C NMR spectrum of **[12]CPP3N** in $CDCl_3$*

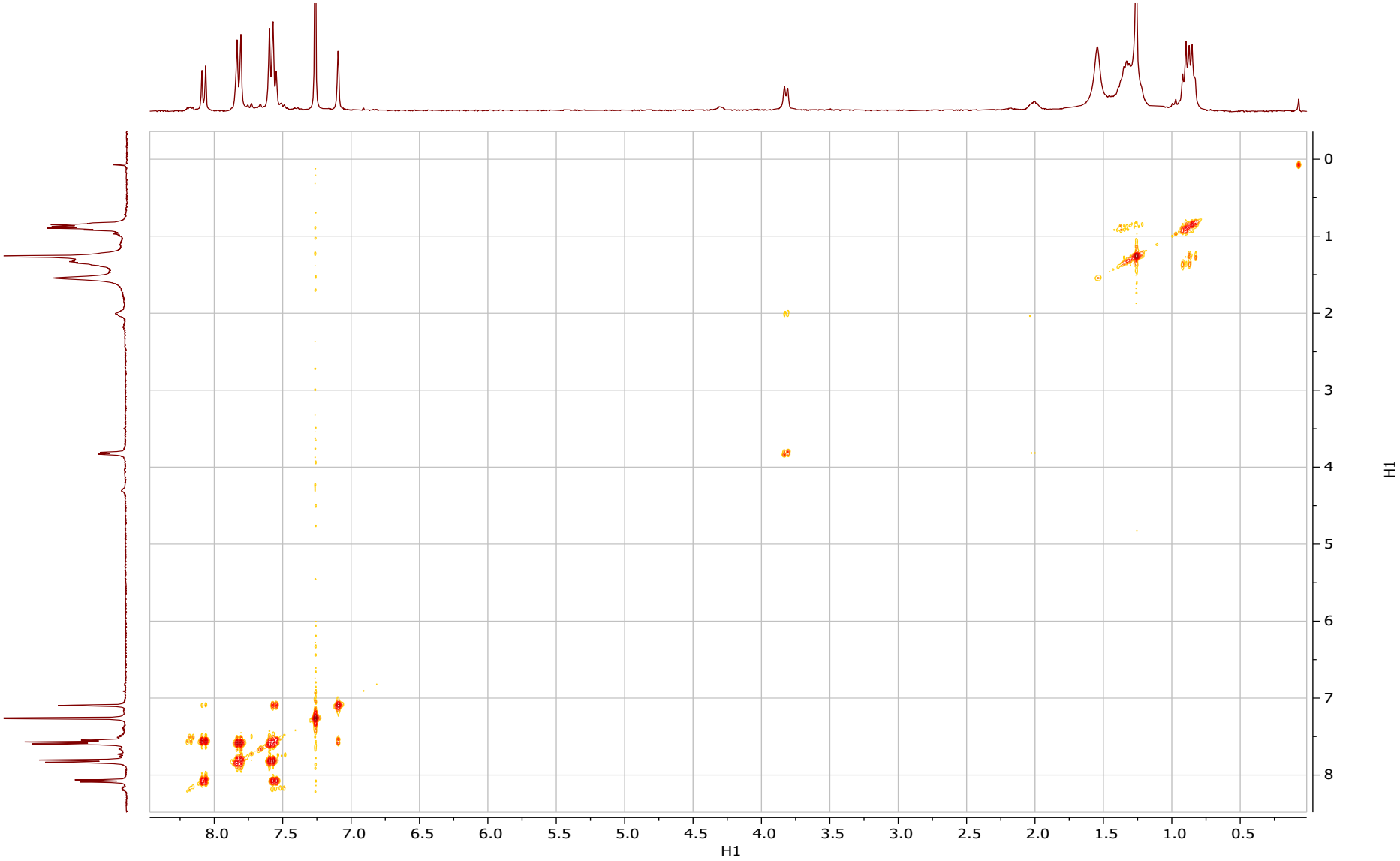


Figure S 11 2D-COSY NMR spectrum of ***[12]CPP3N*** *in* $CDCl_3$

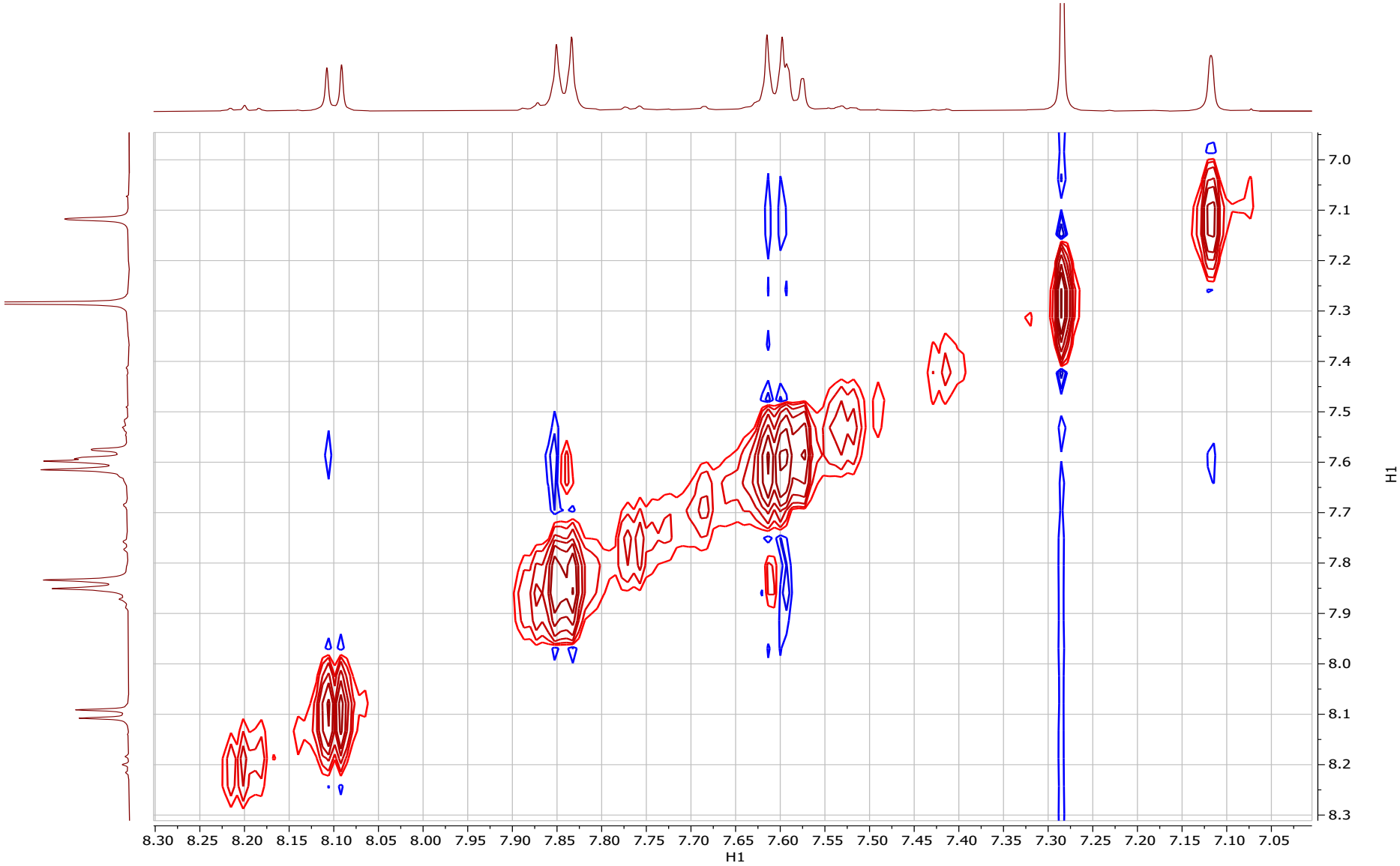


Figure S 12 2D-NOESY NMR spectrum of ***[12]CPP3N*** *in* $CDCl_3$

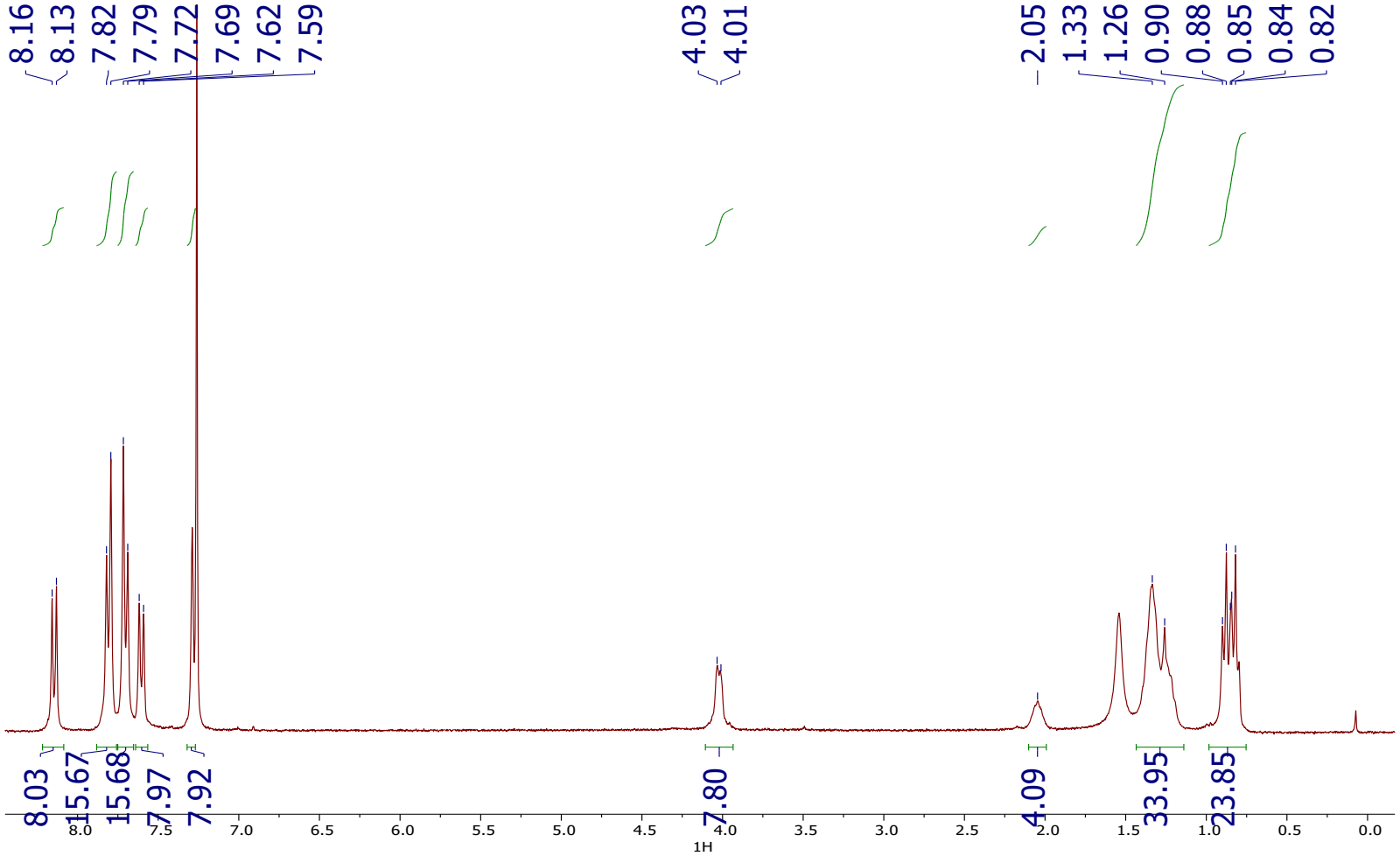


*Figure S 13 1D ^{1}H NMR spectrum of **[16]CPP4N** in $CDCl_3$*

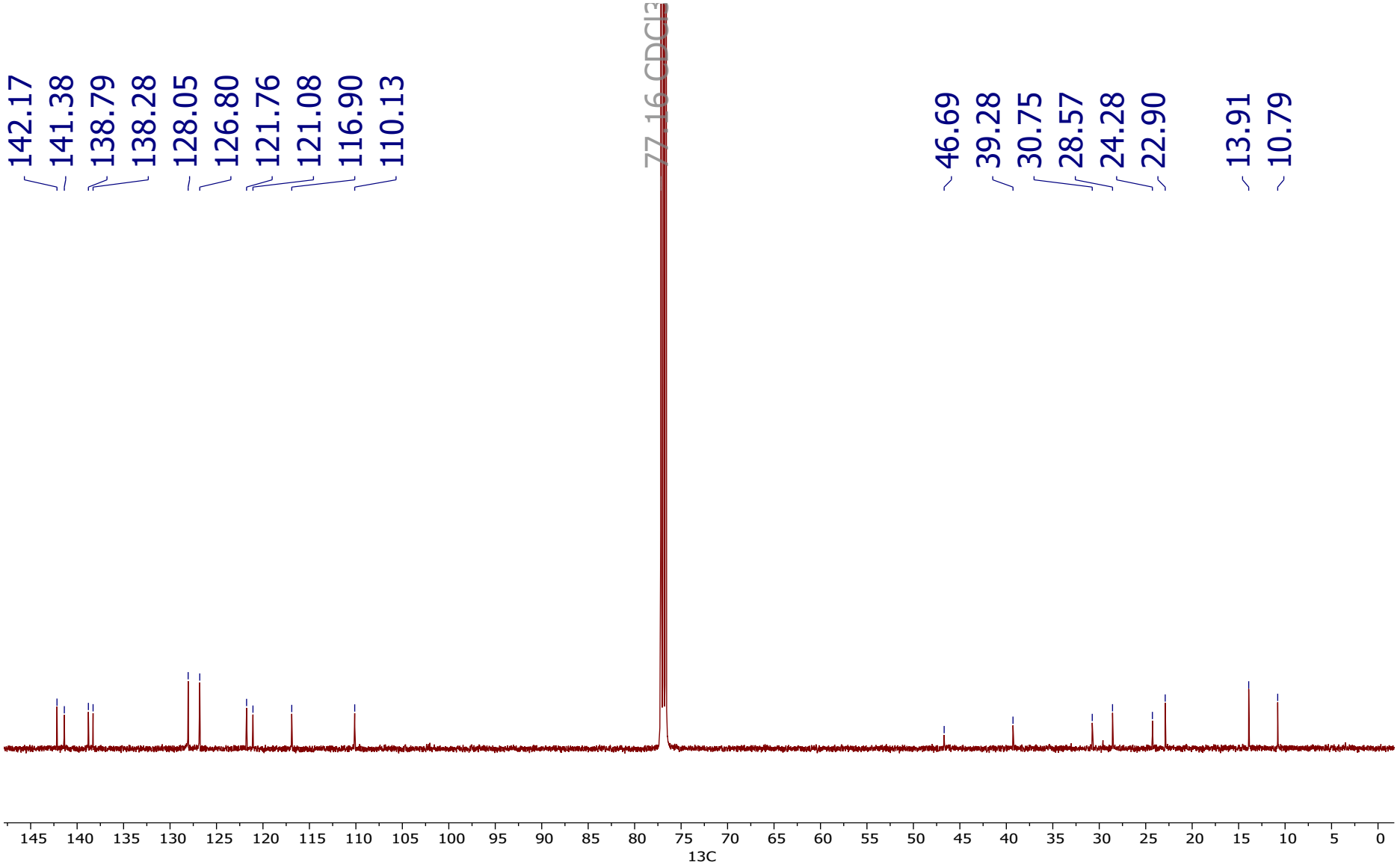


*Figure S 14 1D ^{13}C NMR spectrum of **[16]CPP4N** in $CDCl_3$*

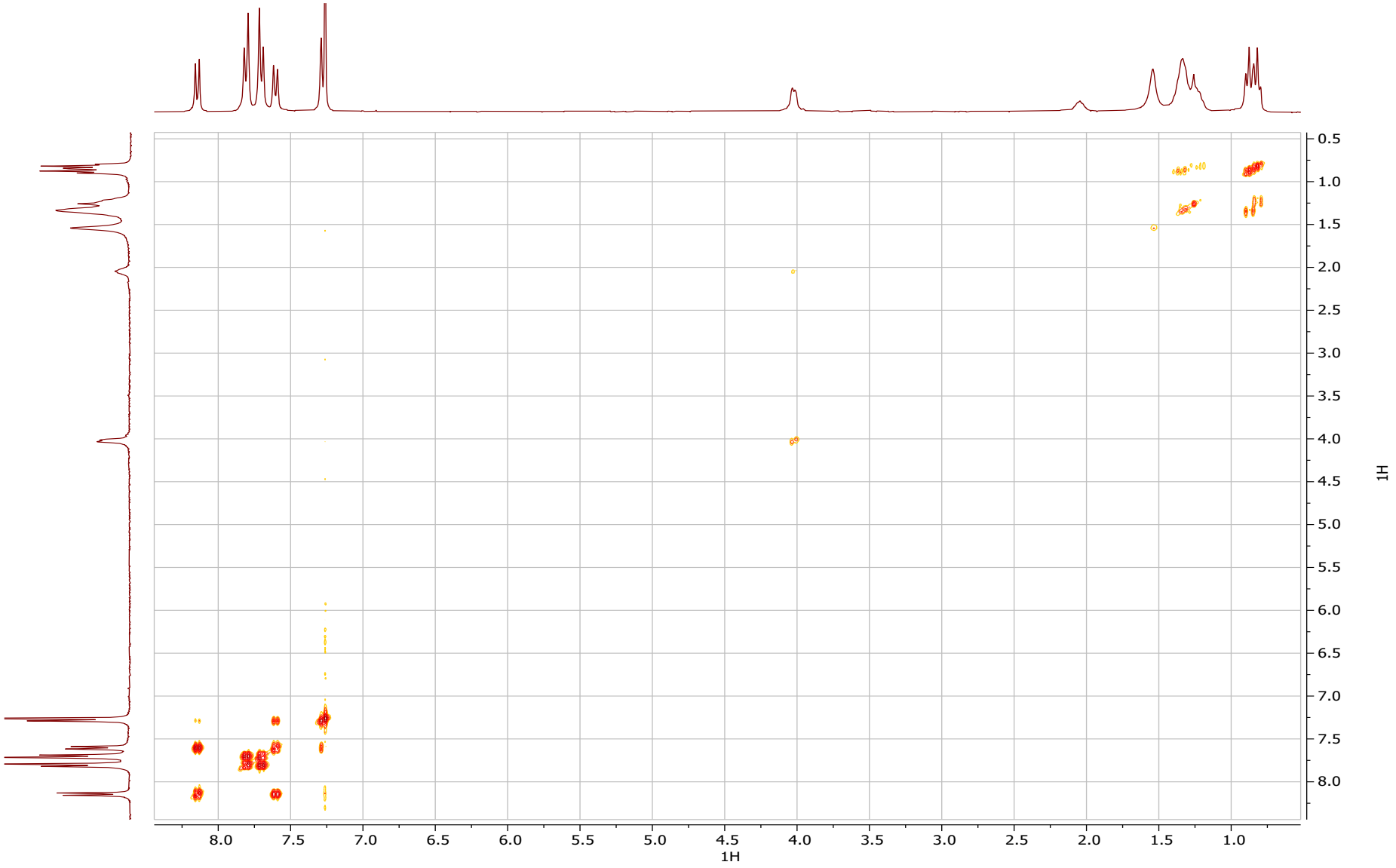


*Figure S 15 2D-COSY NMR spectrum of **[16]CPP4N** in $CDCl_3$*

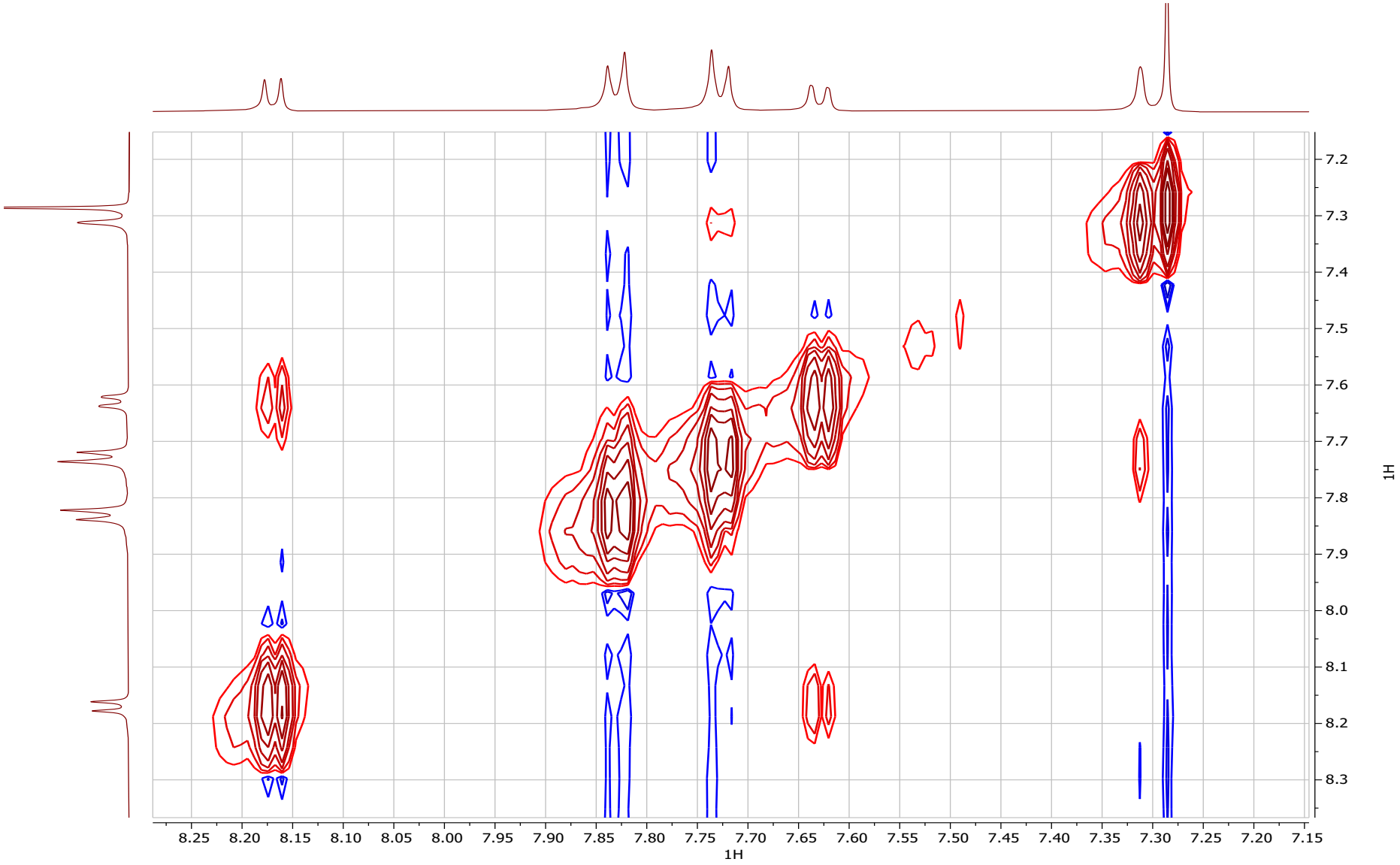


Figure S 16 2D-NOESY NMR spectrum of ***[16]CPP4N*** *in* $CDCl_3$

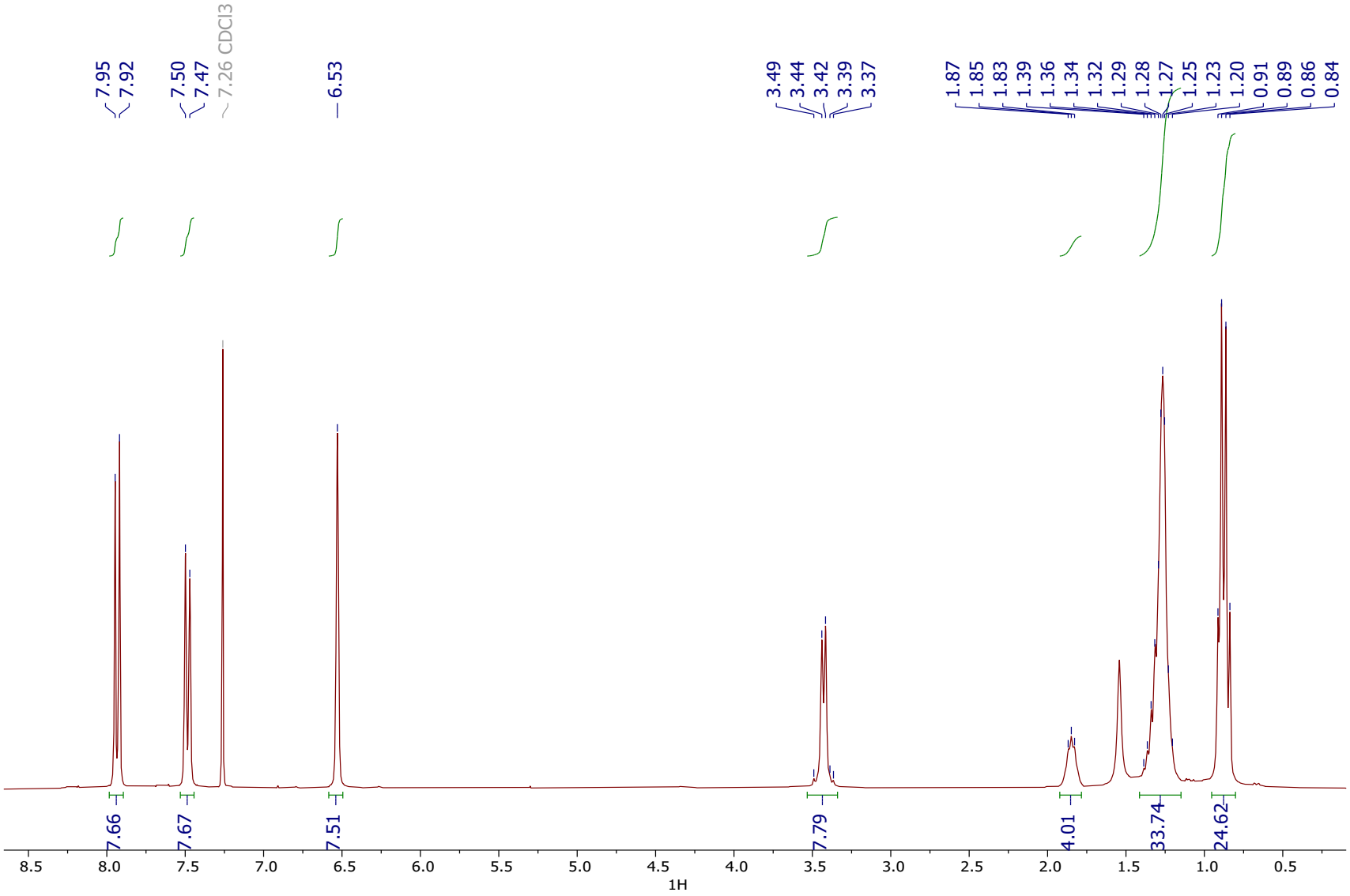


*Figure S 17 1D ^{1}H NMR spectrum of **[8]CPP4N** in $CDCl_3$*

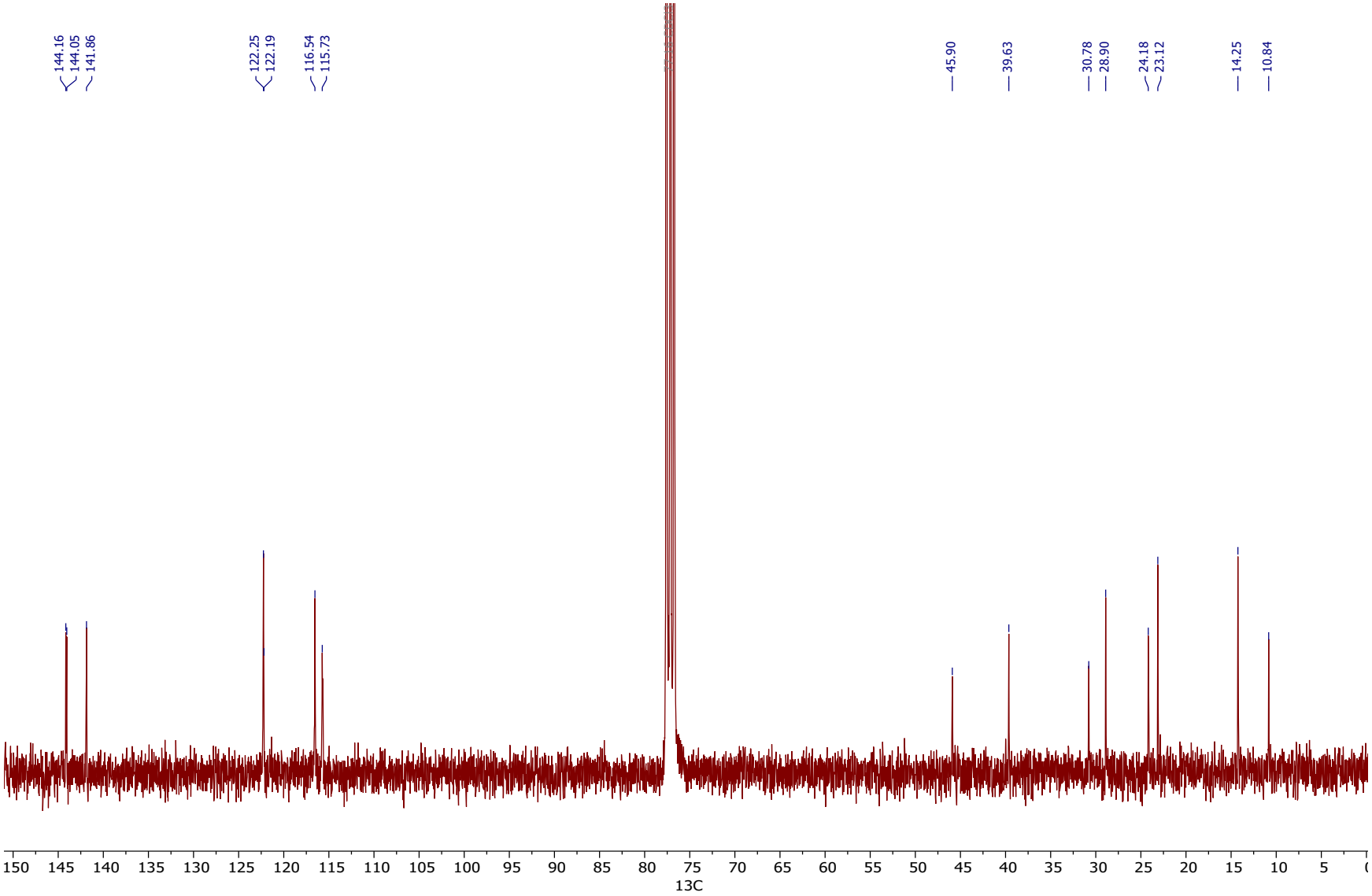


*Figure S 18 1D ^{13}C NMR spectrum of **[8]CPP4N** in $CDCl_3$*

4 IR

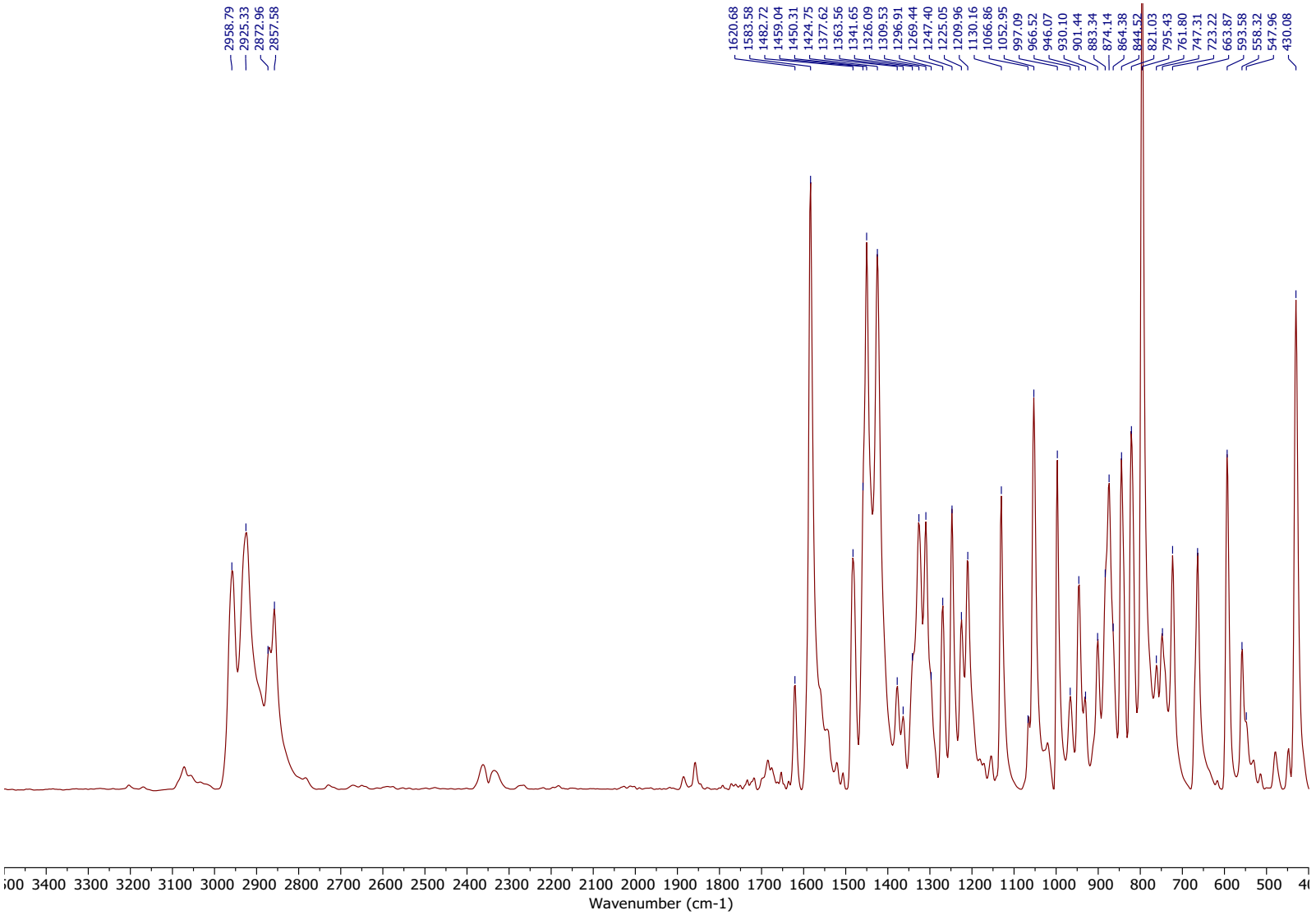


Figure S 19 IR spectrum of 2,7-dibromo-N-(2-ethylhexyl)-carbazole

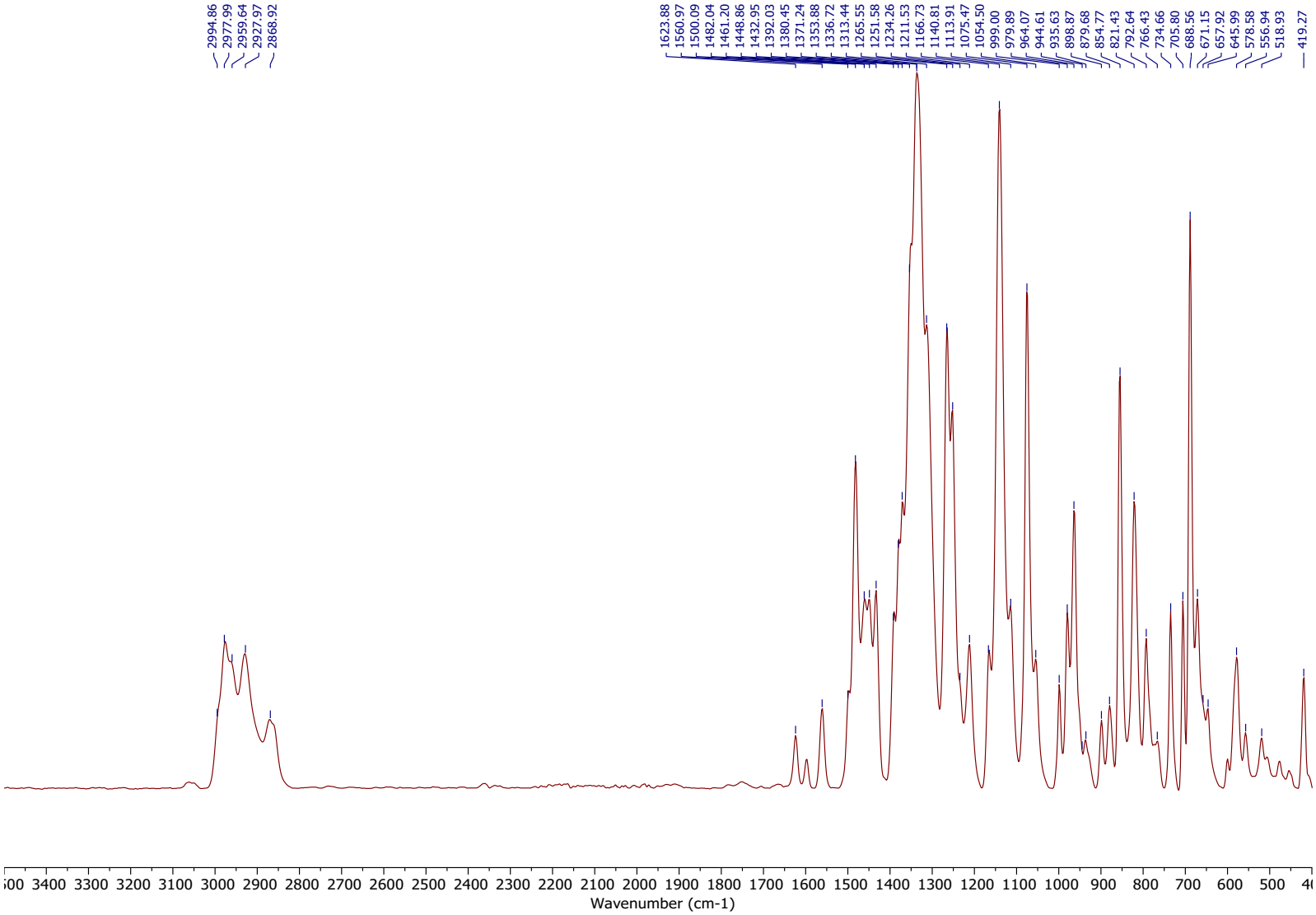


*Figure S 20 IR spectrum of **1***

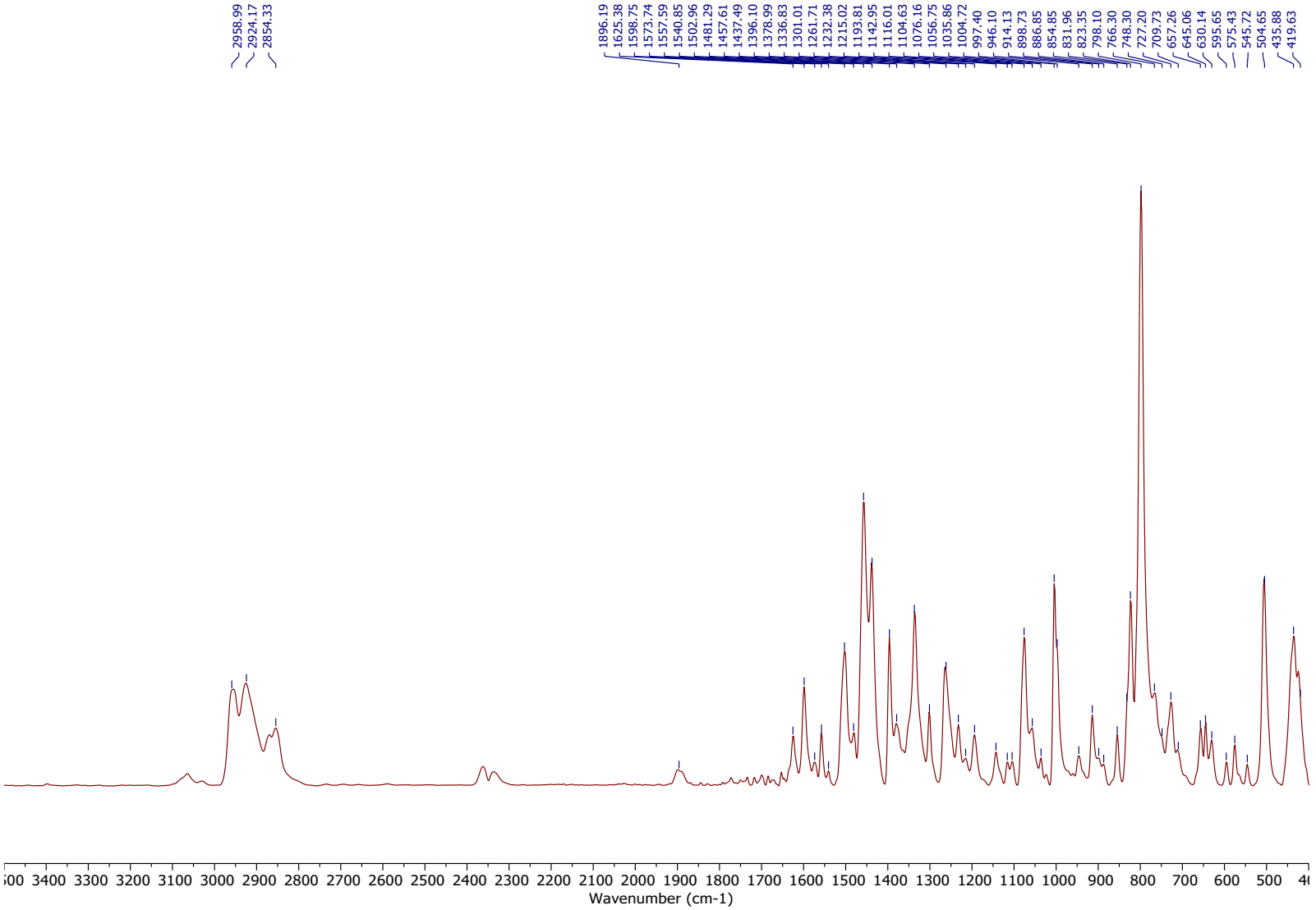


Figure S 21 IR spectrum of ***2***

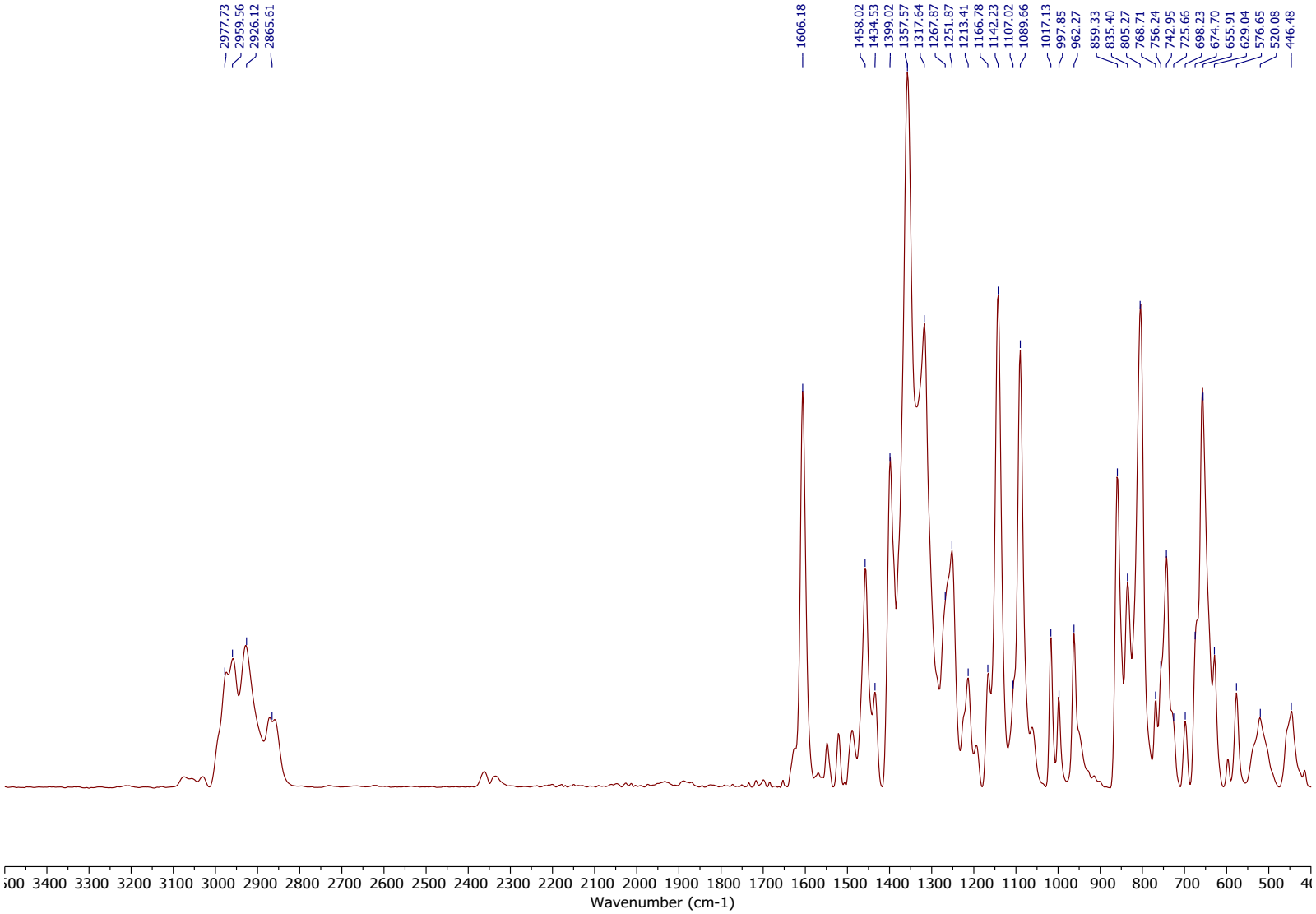


*Figure S 22 IR spectrum of **3***

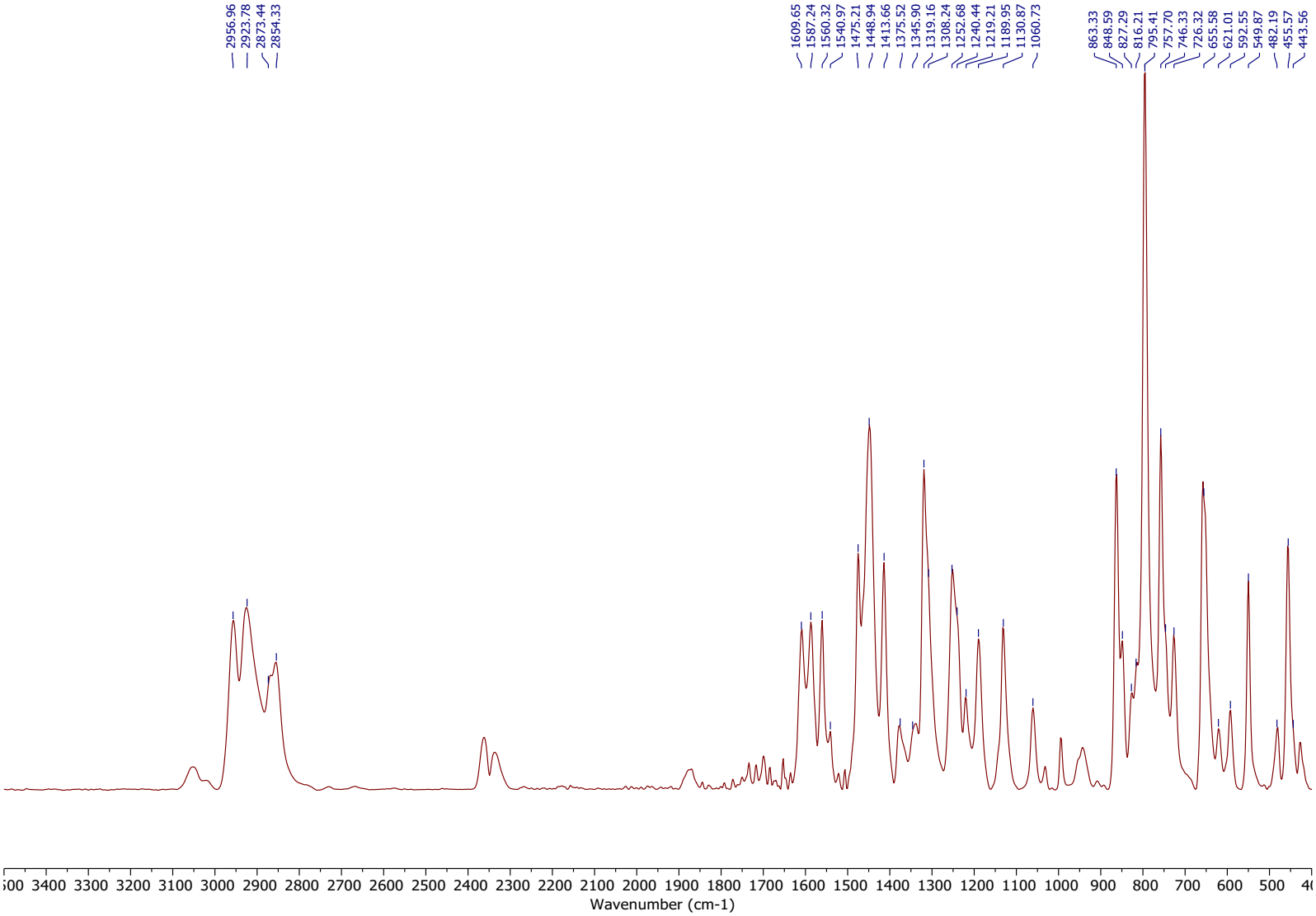


Figure S 23 IR spectrum of ***[8]CPP4N***

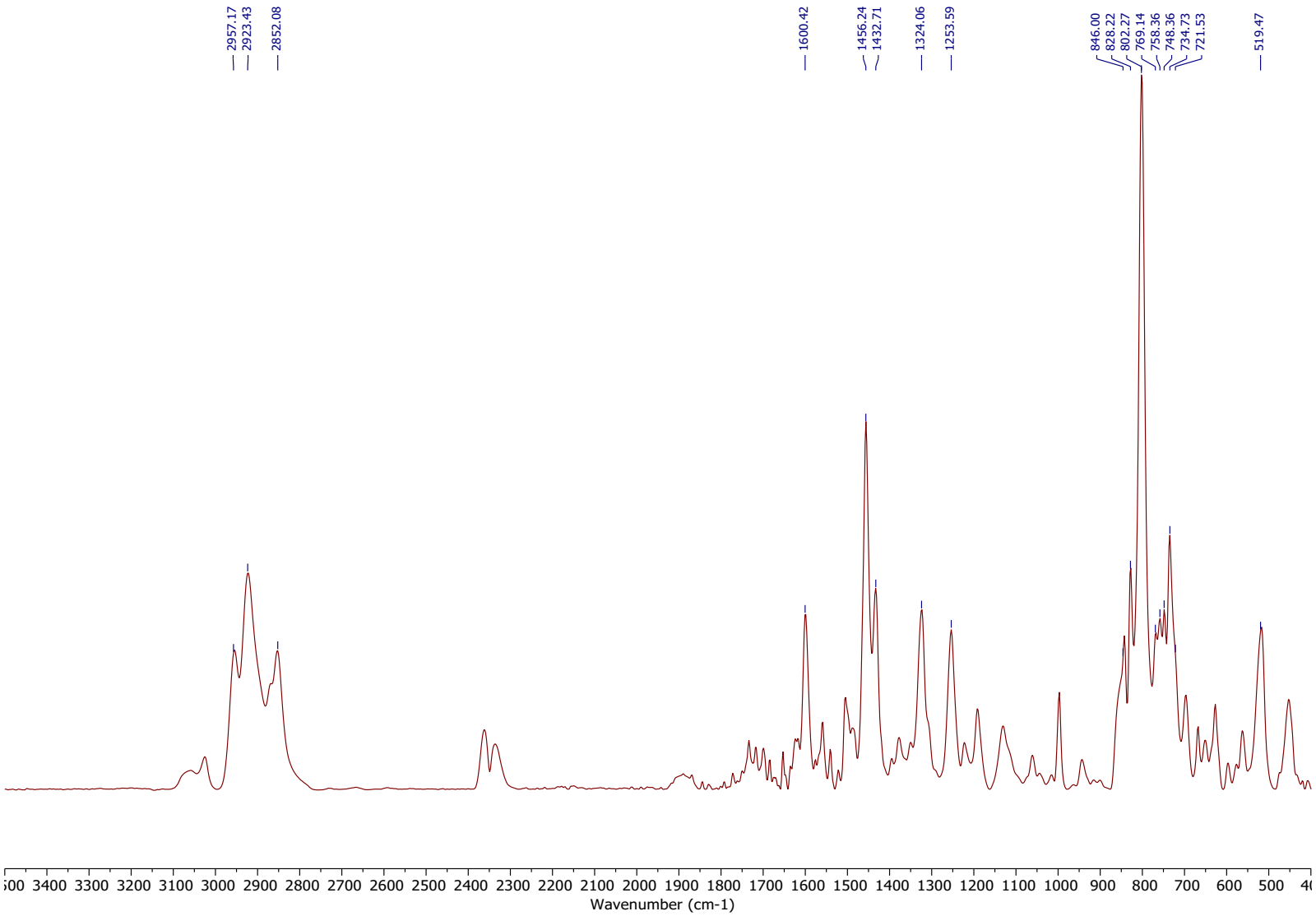


Figure S 24 IR spectrum of ***[12]CPP3N***

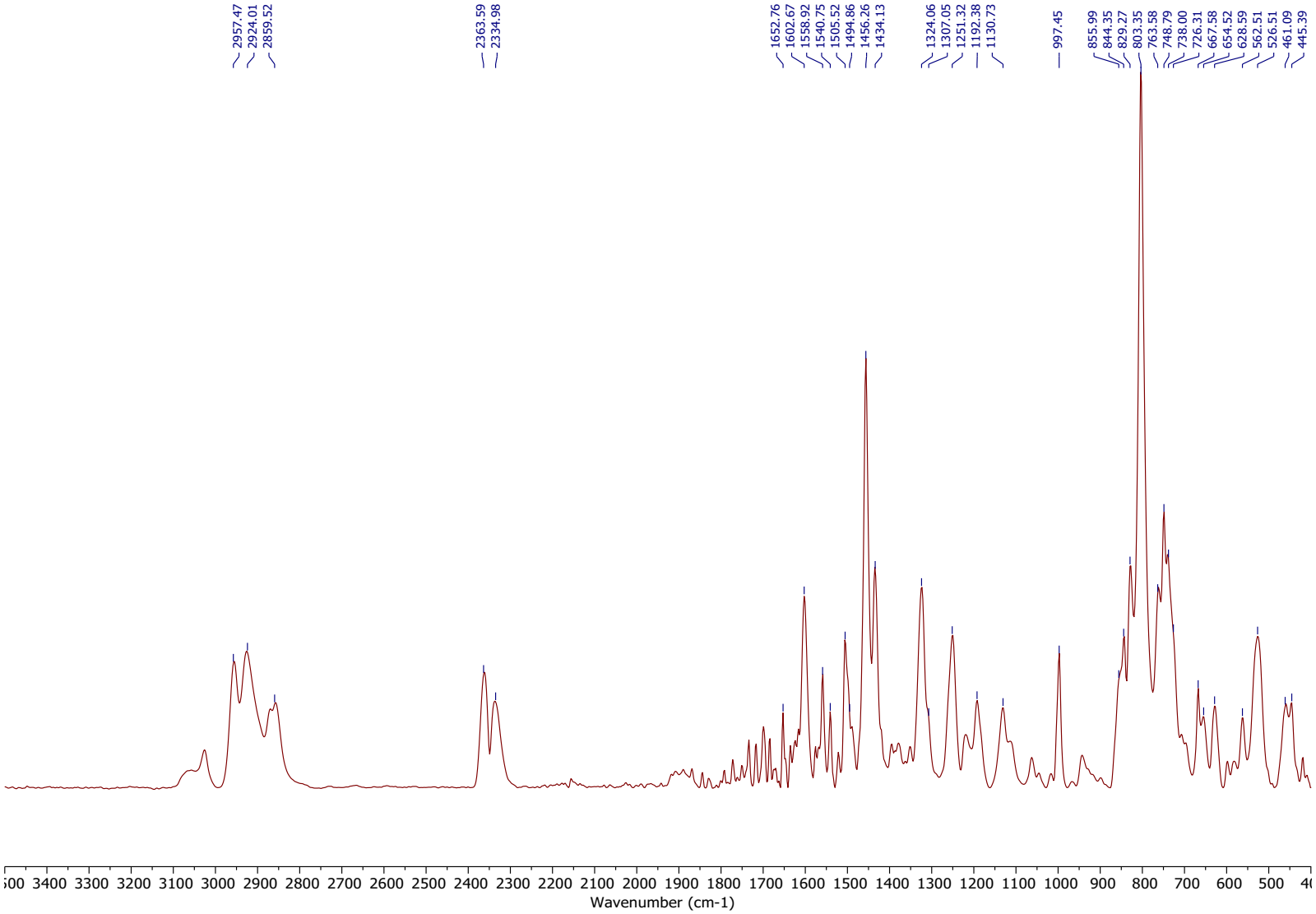


Figure S 25 IR spectrum of ***[16]CPP4N***

5 HRMS

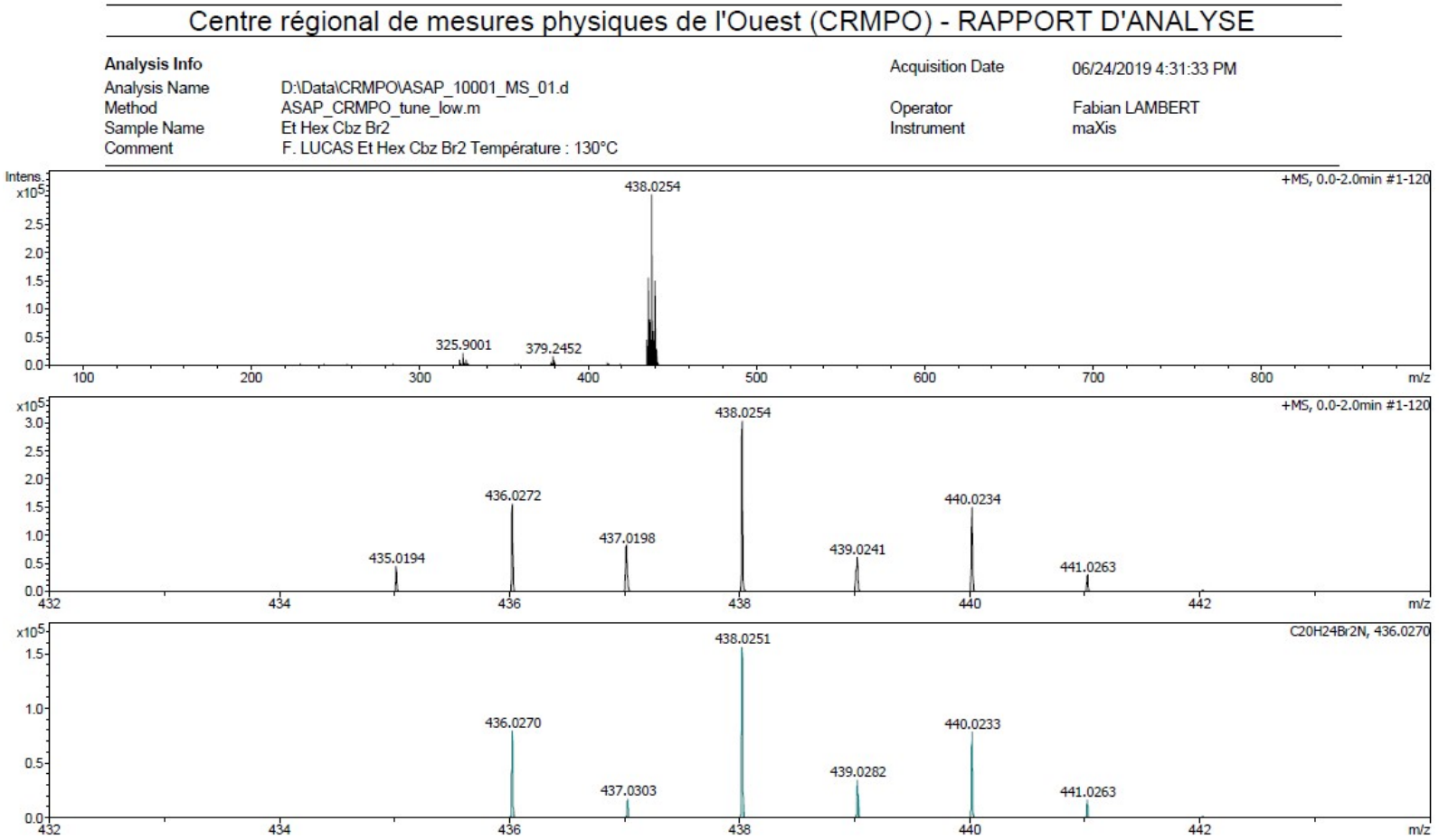


Figure S 26 HRMS of 2,7-dibromo-N-(2-ethylhexyl)-carbazole

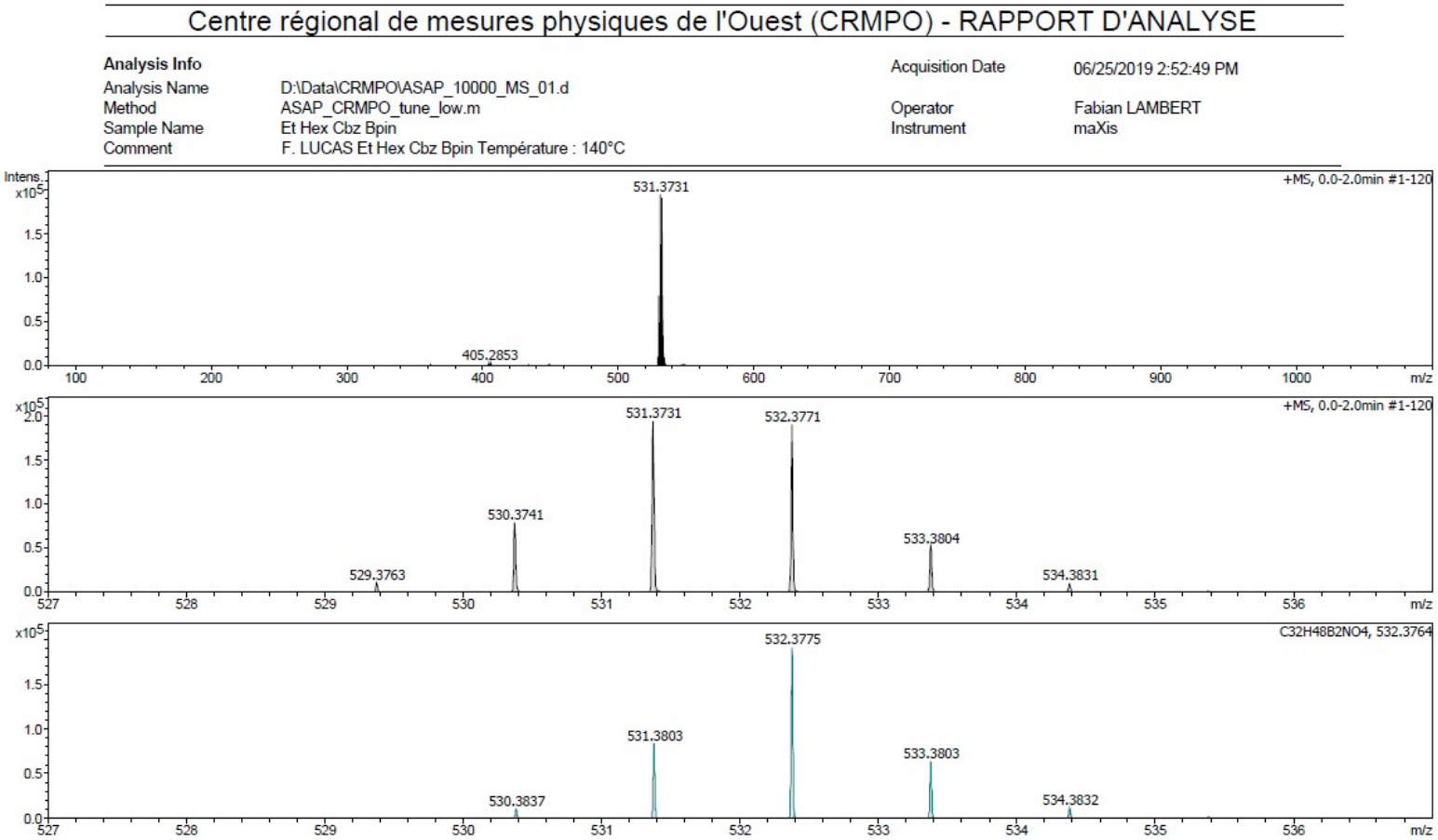


Figure S 27 HRMS of ***1***

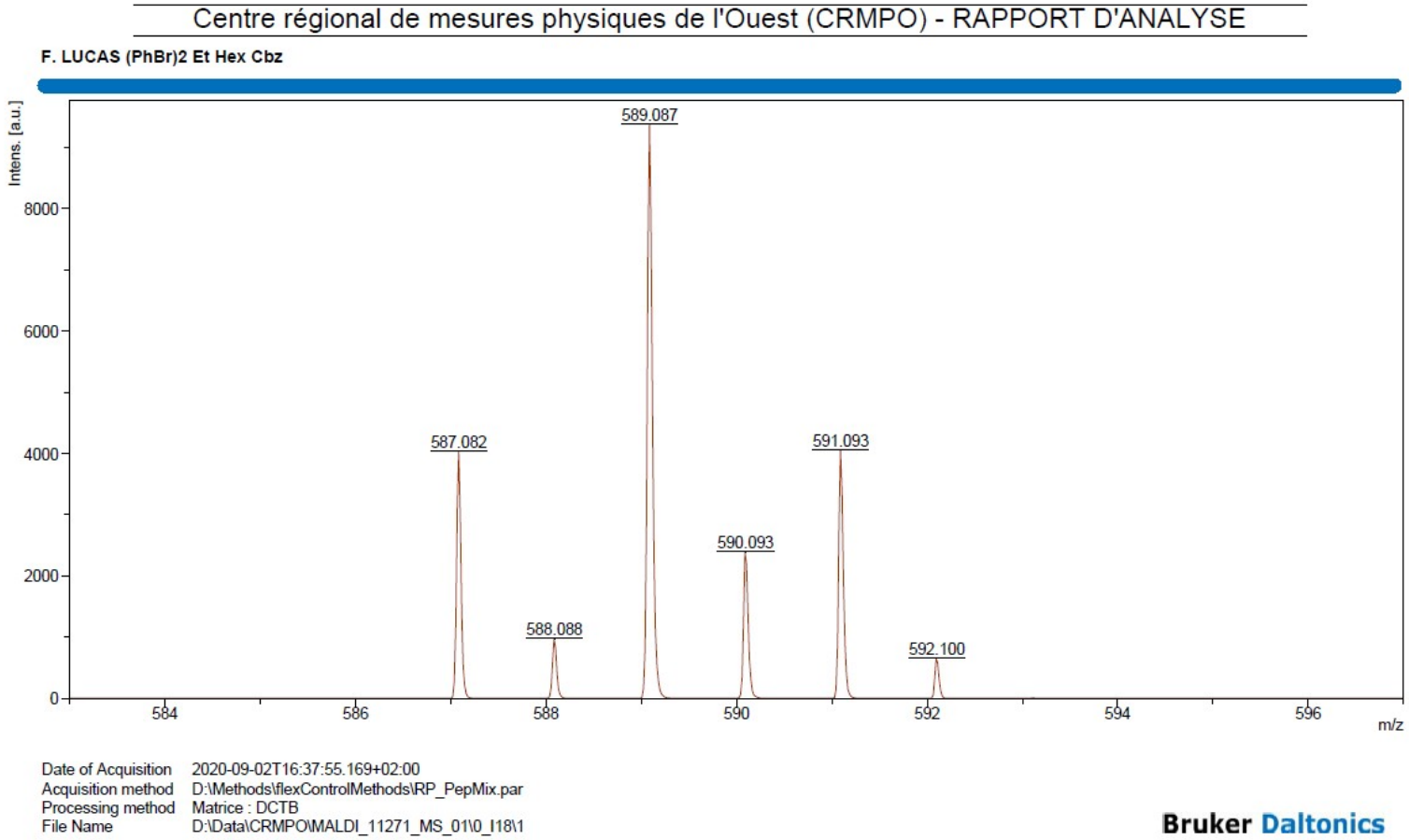


Figure S 28 HRMS of ***2***

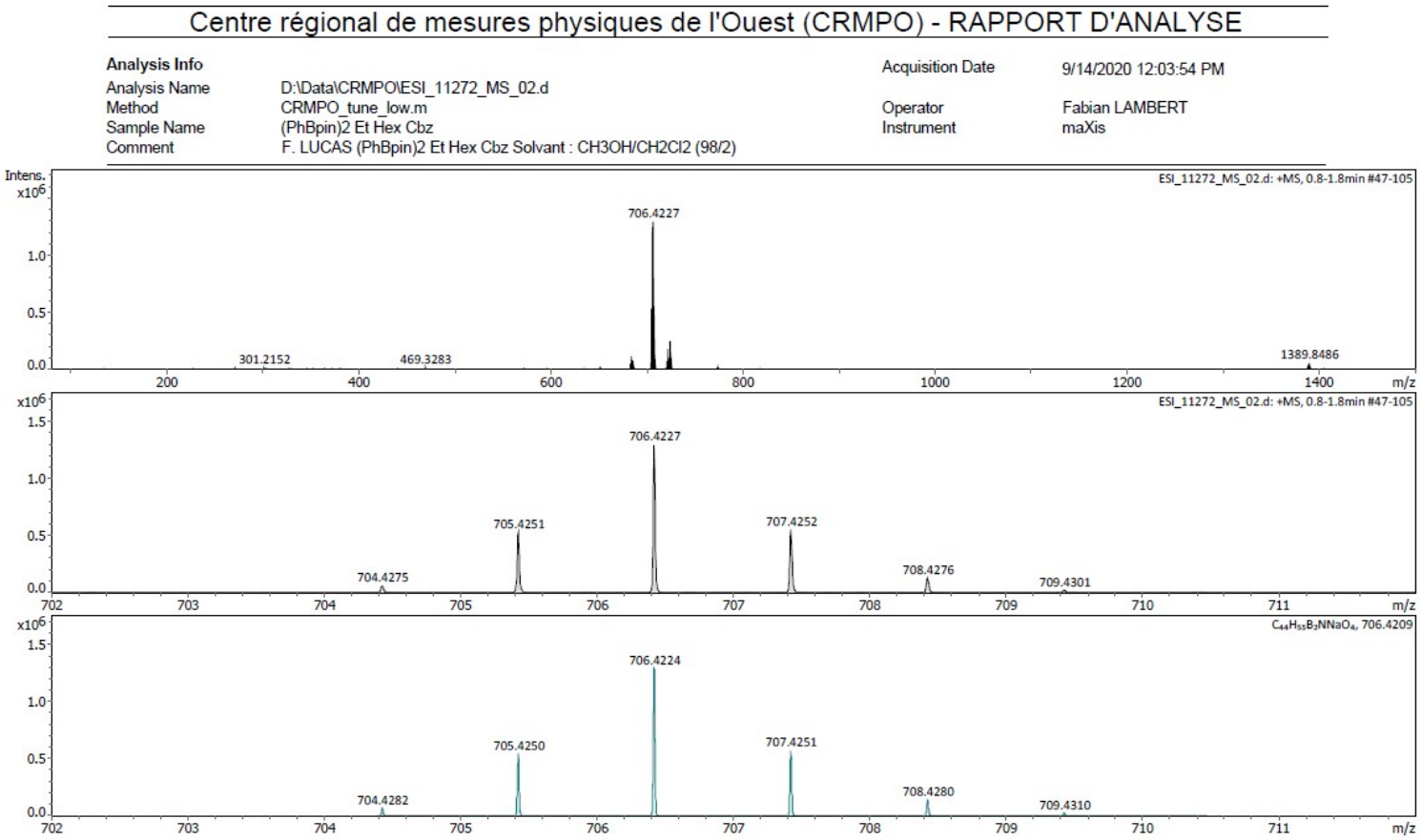


*Figure S 29 HRMS of **3***

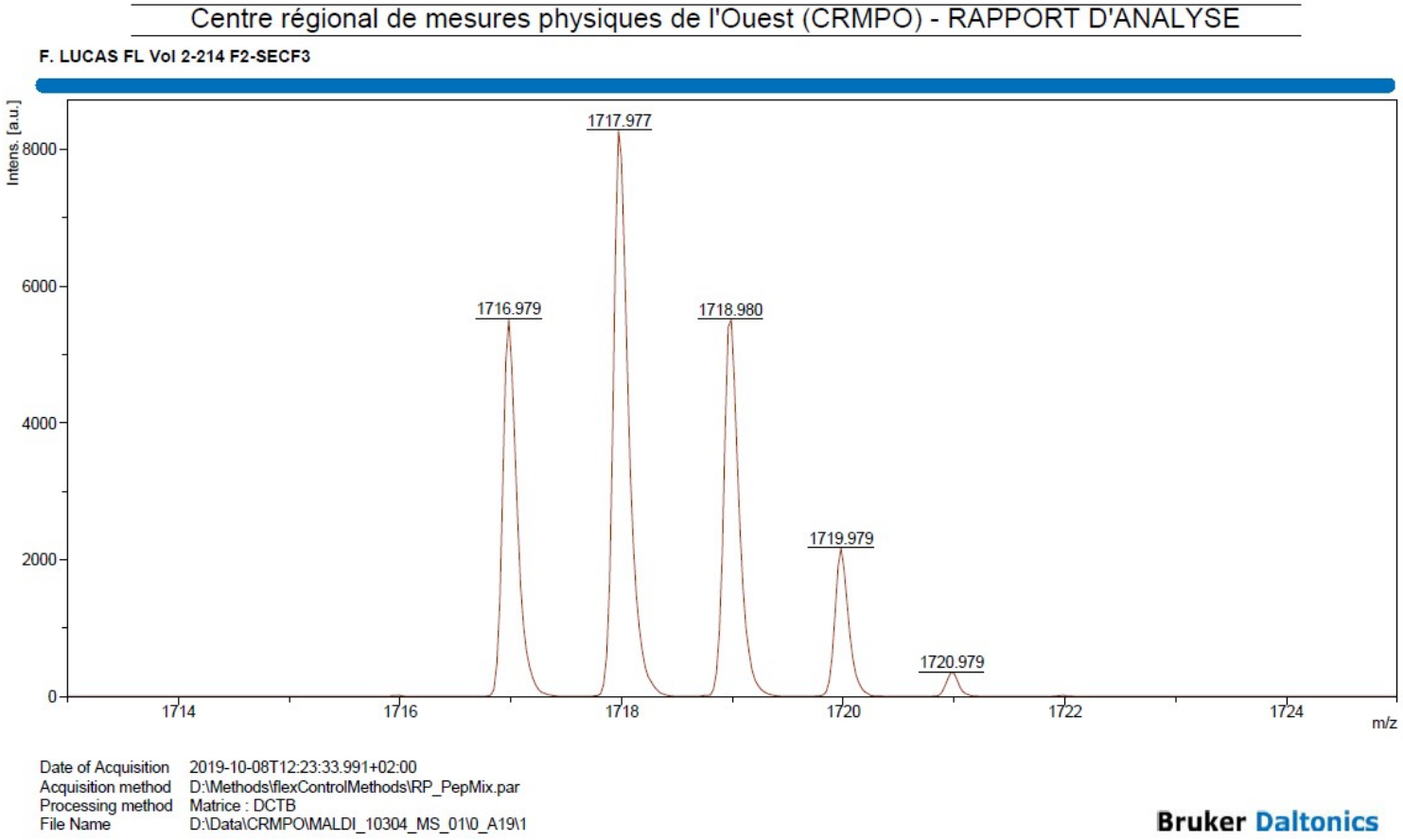


Figure S 30 HRMS of ***[16]CPP4N***

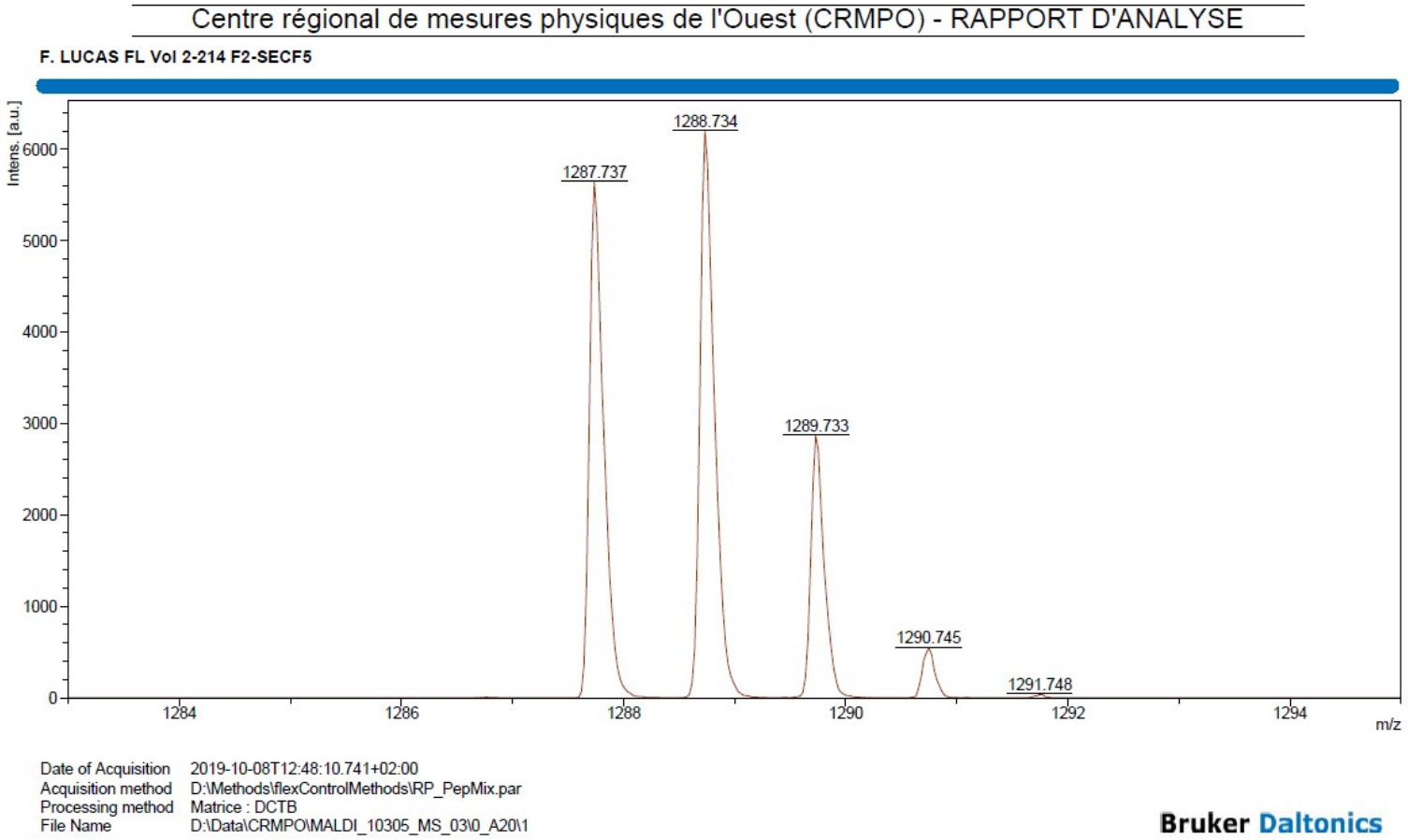


Figure S 31 HRMS of ***[12]CPP3N***

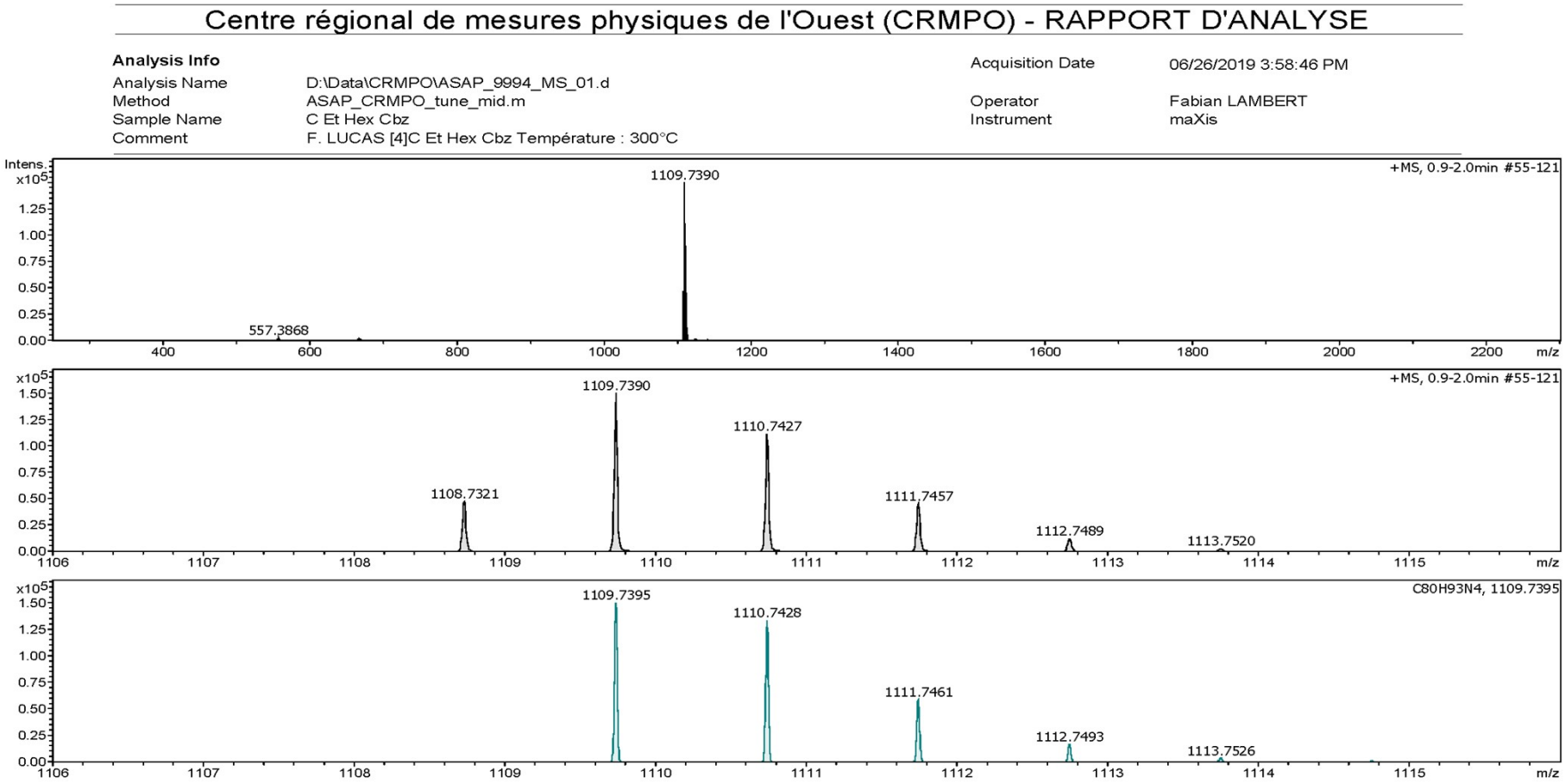


Figure S 32 HRMS of ***[8]CPP4N***

6 Electrochemical studies

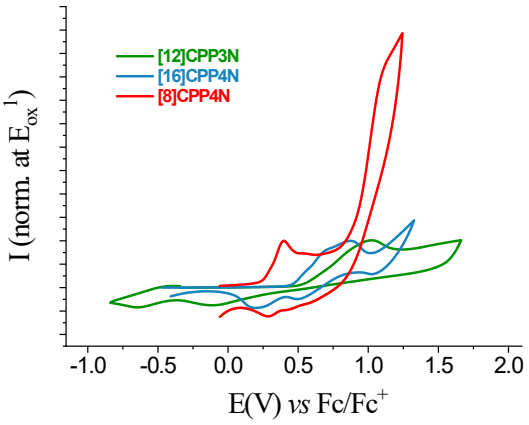


*Figure S 33. Cyclic voltammograms of **[16]CPP4N**, **[12]CPP3N** and **[8]CPP4N** in oxidation showing additional oxidation processes at high potential values, $C_2H_2Cl_4$+Bu_4NPF_6, 0.2 M, 100 mV.s^{-1}*

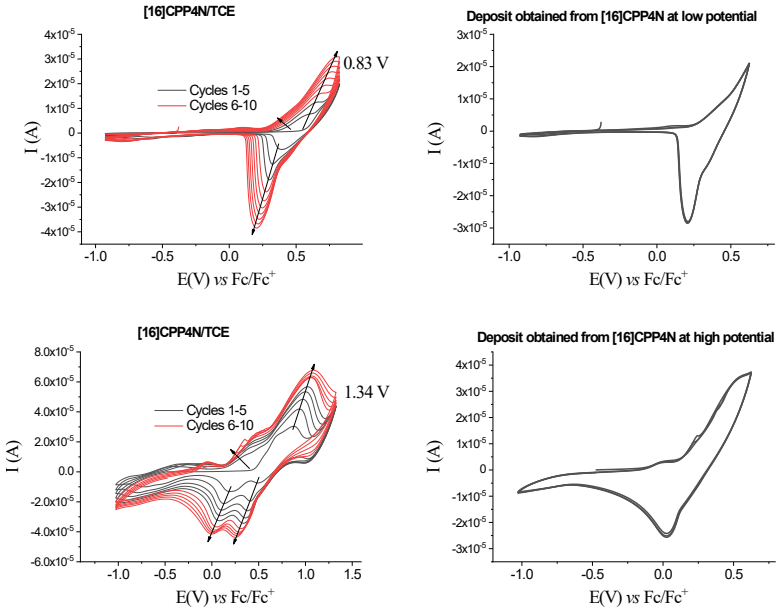
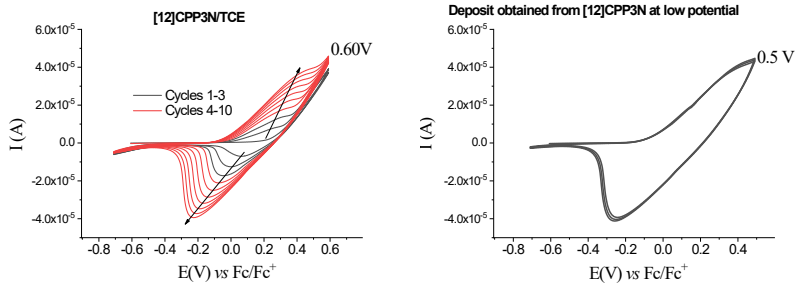


*Figure S 34. Cyclic voltammograms recorded in $C_2H_2Cl_4$+Bu_4NPF_6, 0.2 M. Left: ten cycles up to 0.85 V (top) or 1.34 V (bottom) in presence of **[16]CPP4N**. Right: electrochemical behaviour of the deposit covering the platinum after the 10 Cycles.*



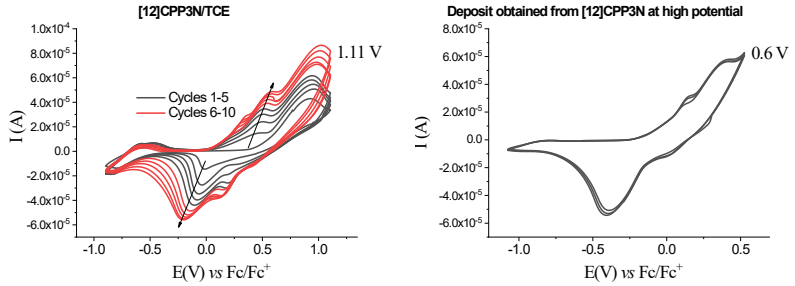


*Figure S 35. Cyclic voltammograms recorded in $C_2H_2Cl_4$+Bu_4NPF_6, 0.2 M. Left: ten cycles up to 0.6 V (top) or 1.11 V (bottom) in presence of **[12]CPP3N**. Right: electrochemical behaviour of the deposit covering the platinum after the 10 Cycles.*

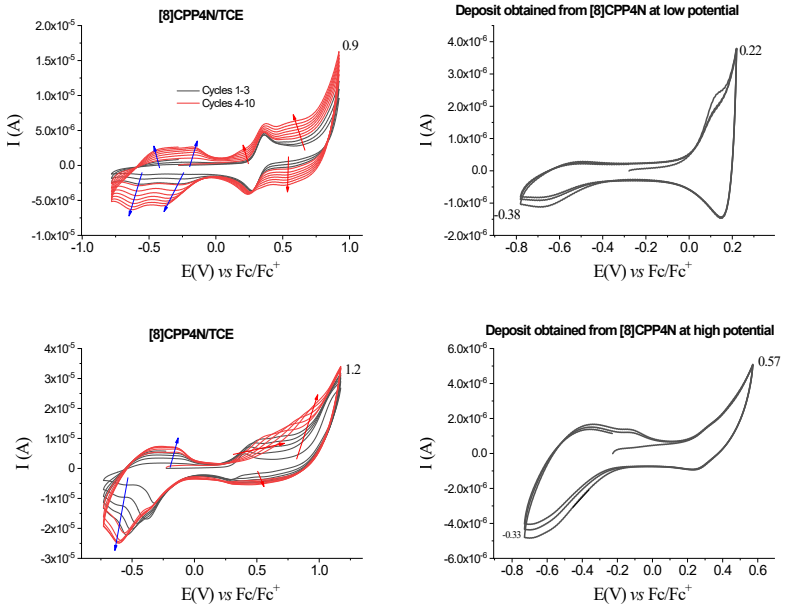


*Figure S 36. Cyclic voltammograms recorded in $C_2H_2Cl_4$+Bu_4NPF_6, 0.2 M. Left: ten cycles up to 0.9 V (top) or 1.2 V (bottom) in presence of **[8]CPP4N**. Right: electrochemical behaviour of the deposit covering the platinum after the 10 Cycles.*

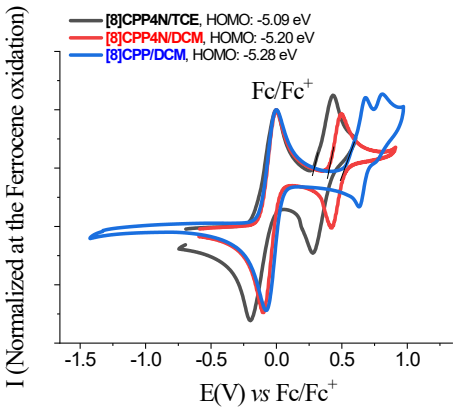


*Figure S 37. Comparison of the cyclic voltammograms of **[8]CPP4N** recorded in $C_2H_2Cl_4$+Bu_4NPF_6, 0.2 M (black line) or in CH_2Cl_2+Bu_4NPF_6, 0.2 M (red line) with that of **[8]CPP** recorded in CH_2Cl_2+Bu_4NPF_6, 0.2 M (blue line) in presence of ferrocene. Sweep-rate 100 mV.s^{-1}.*

7 Photophysical properties

The spectroscopic properties of the three nanohoops have been studied in both cyclohexane (apolar solvent usually used for spectroscopic study but in which **[8]CPP4N** and **[12]CPP3N** are only slightly soluble) and chloroform (in which the three nanohoops are soluble enough to measure a molar extinction coefficient).

*7.1. Photophysical properties of **[12]CPP3N***

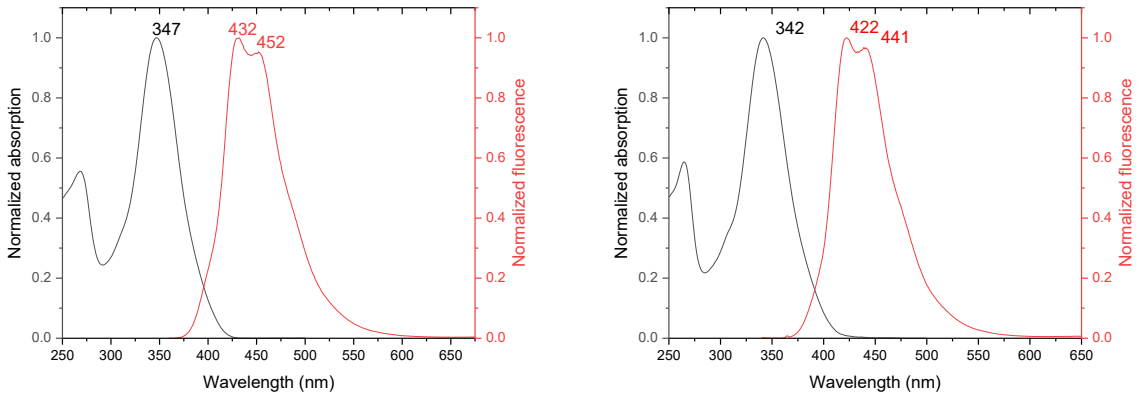
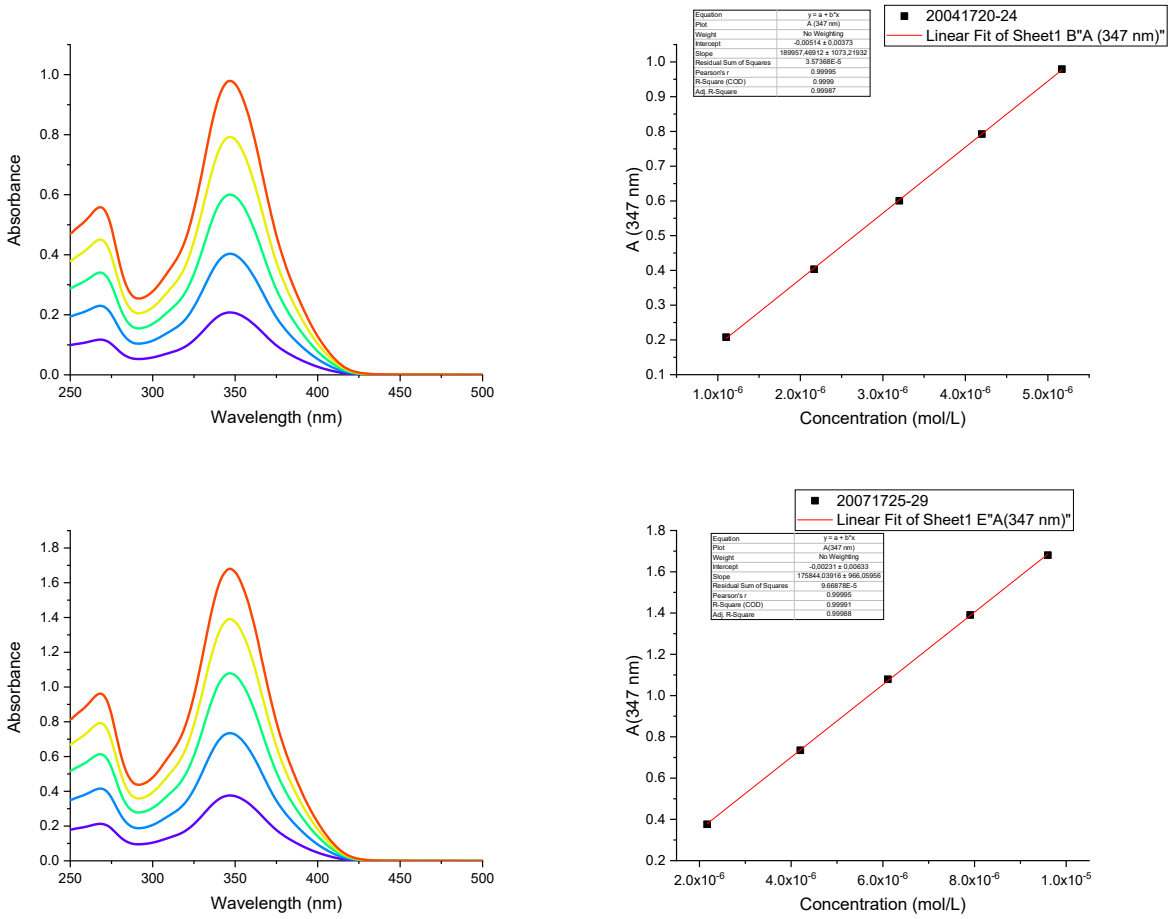


*Figure S 38. Normalized absorption and fluorescence spectra of **[12]CPP3N** in chloroform (left) and in cyclohexane (right)*



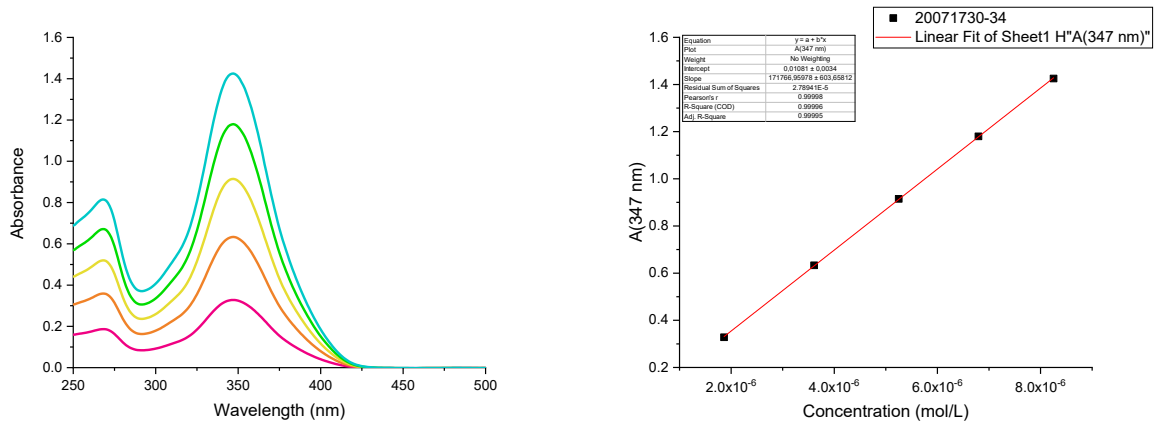
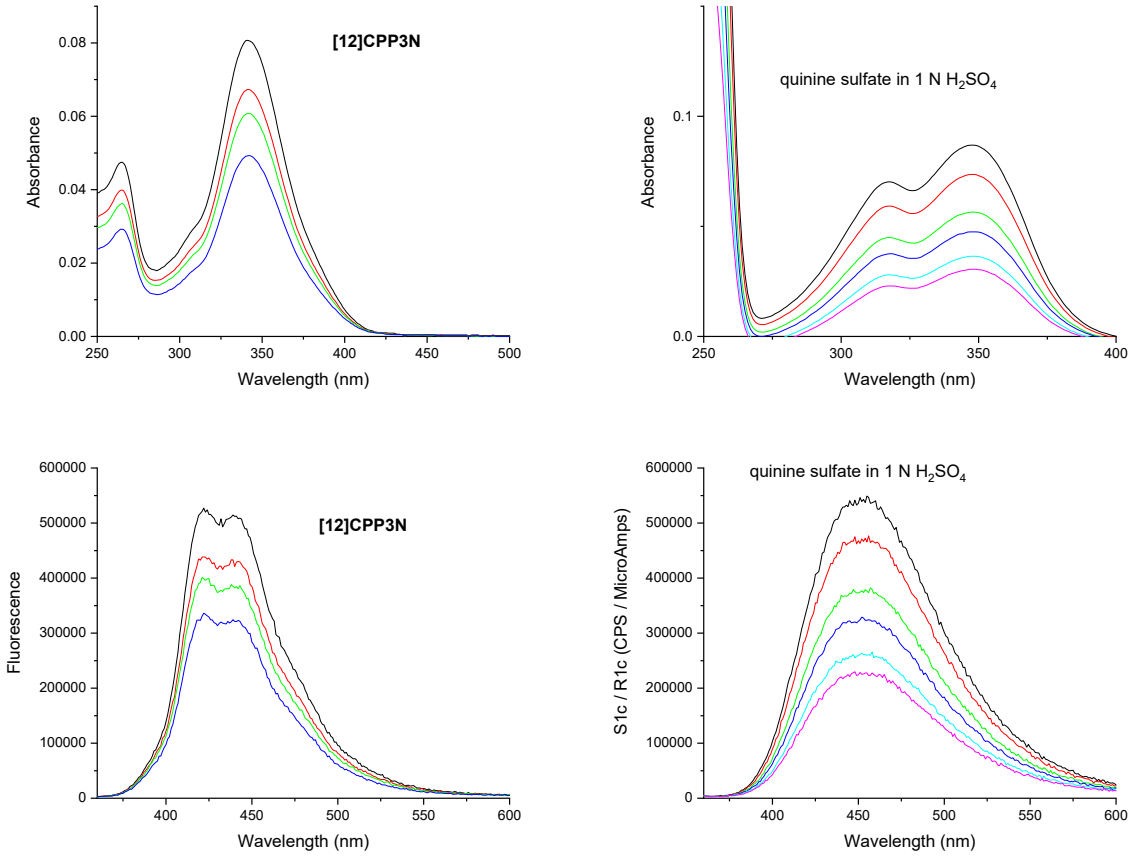
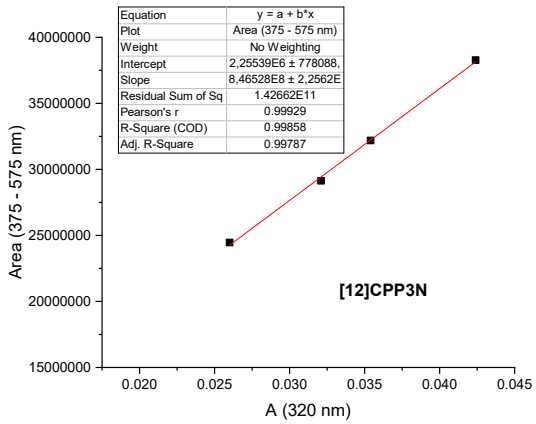
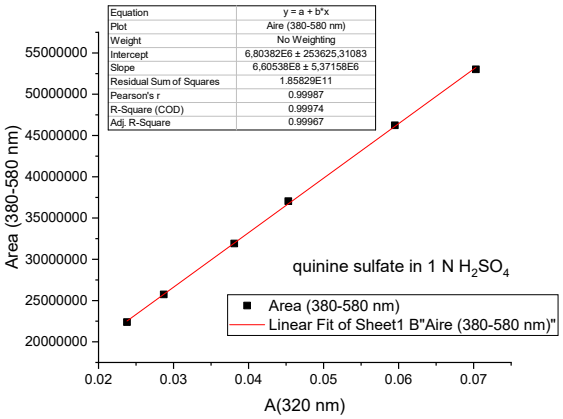


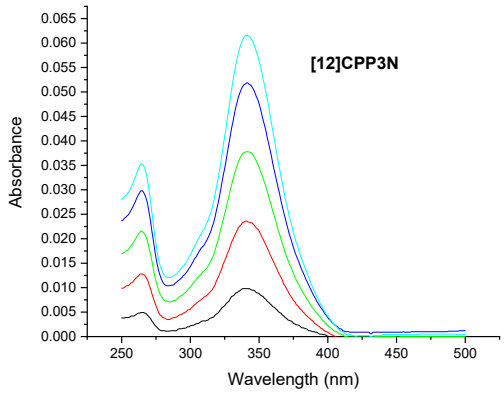
*Figure S 39. Determination of the molar extinction coefficient of **[12]CPP3N** in chloroform*

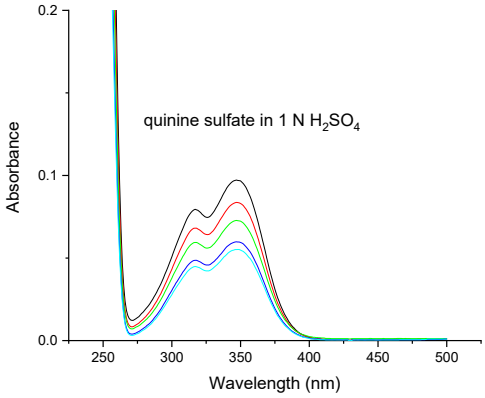


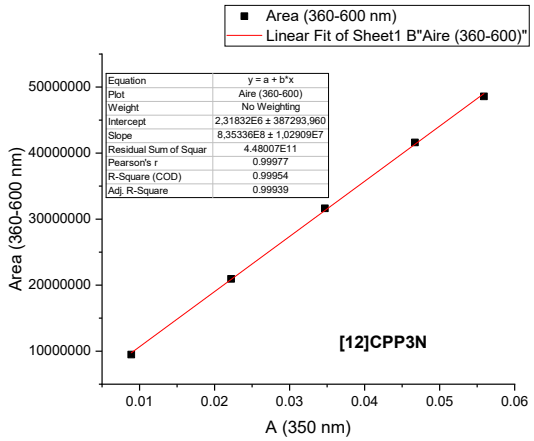


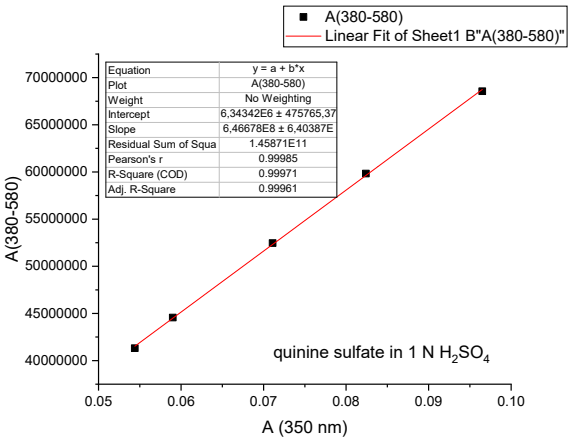


	Quinine sulfate in H_2SO_4	**[12]CPP3N**
slope	6.61E+08	8.47E+08
refracting index	1.336	1.42662
QY	0.546	7.98E-01

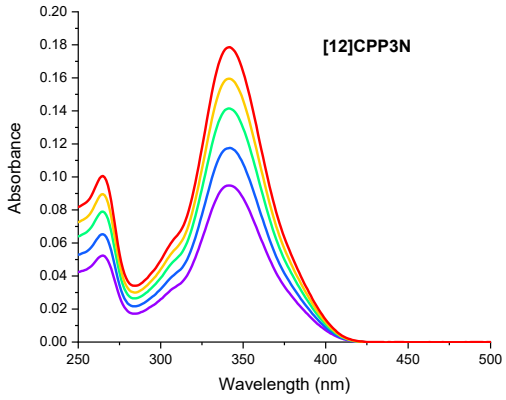


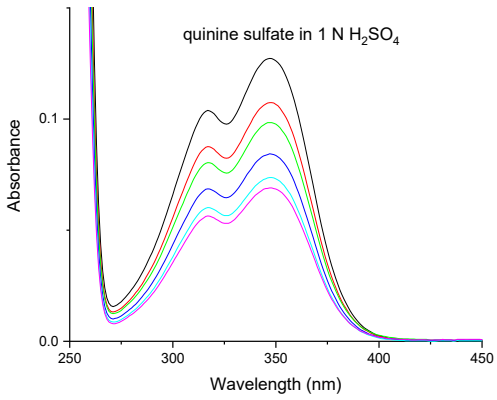


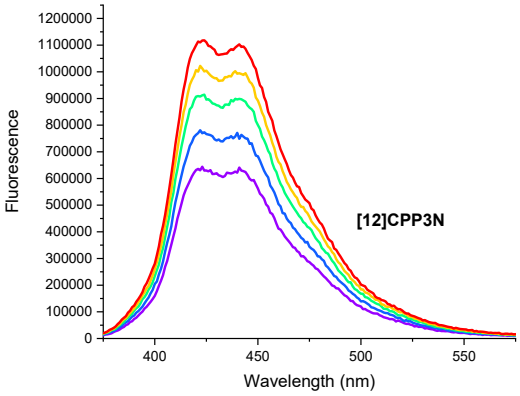


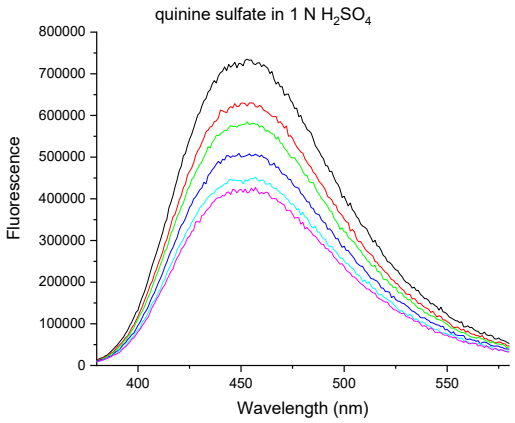


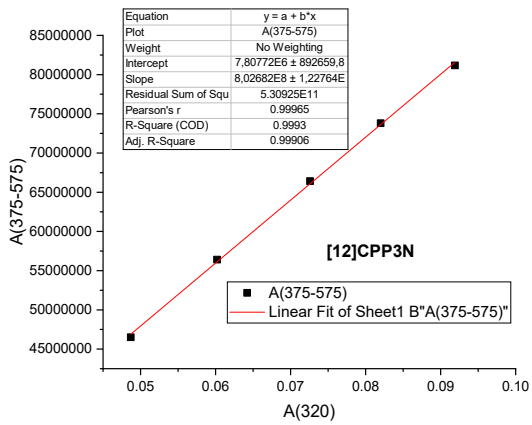
	Quinine sulfate in H_2SO_4	**[12]CPP3N**
slope	6.47E+08	8.35E+08
refracting index	1.336	1.42662
QY	0.546	8.04E-01

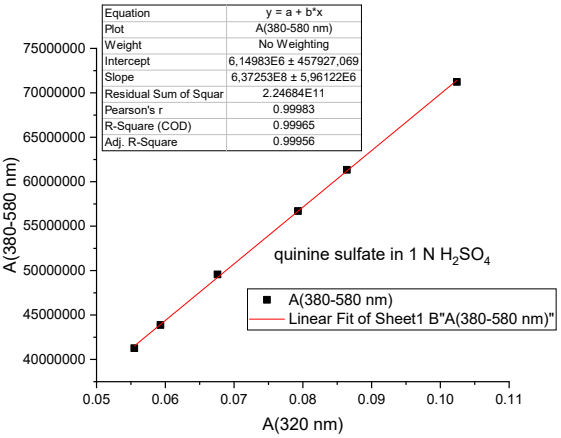




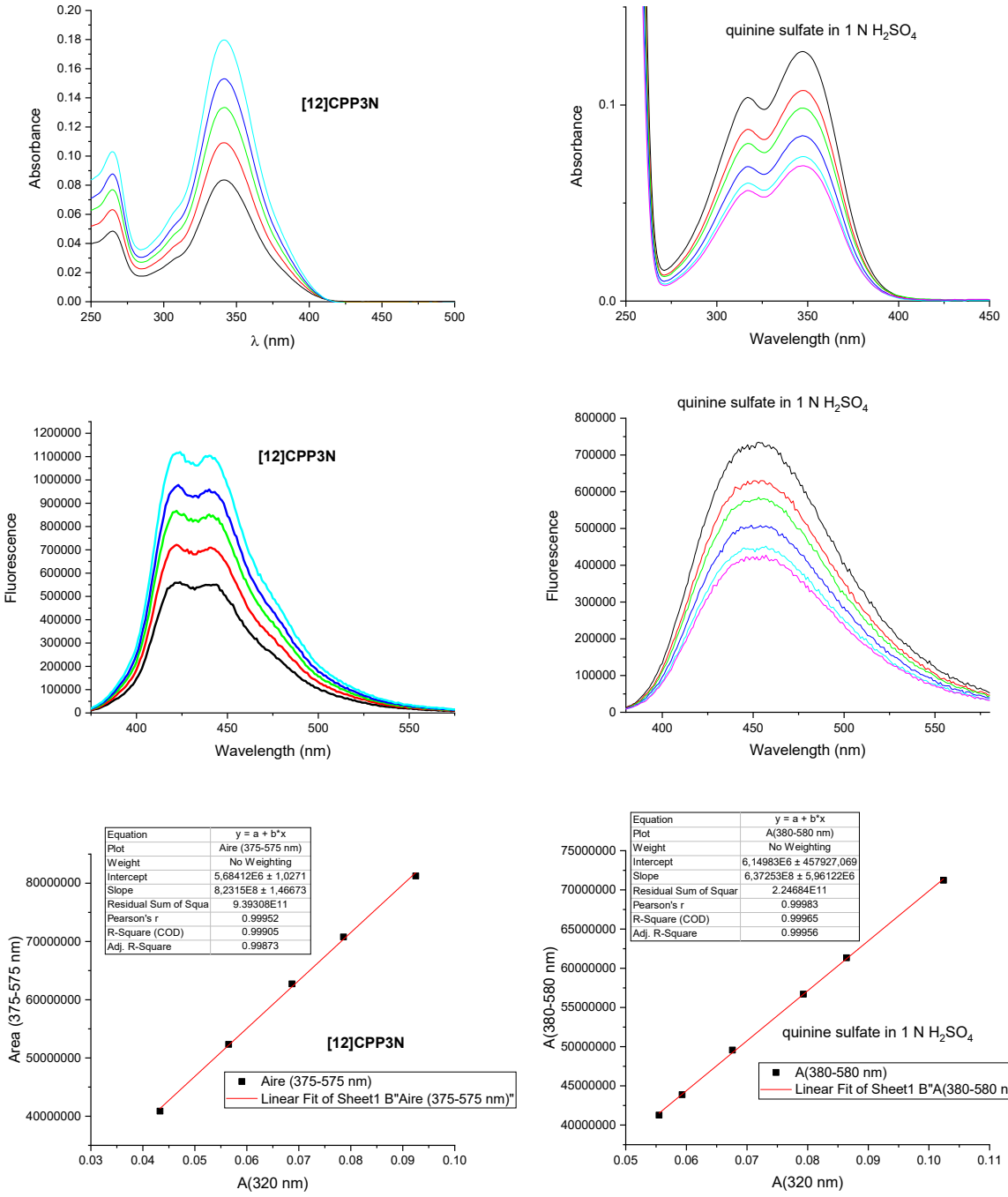






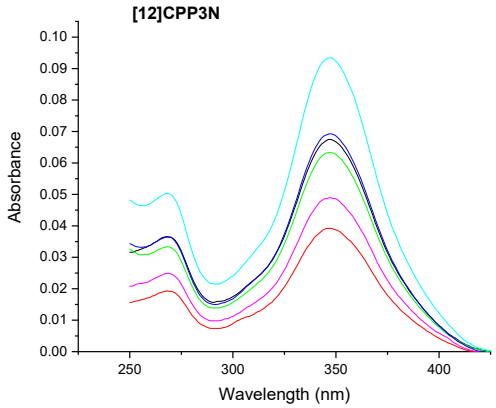


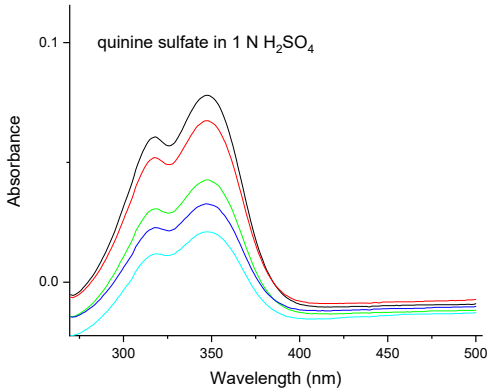
	Quinine sulfate in H_2SO_4	**[12]CPP3N**
slope	6.37E+08	8.03E+08
refracting index	1.336	1.42662
QY	0.546	7.84E-01

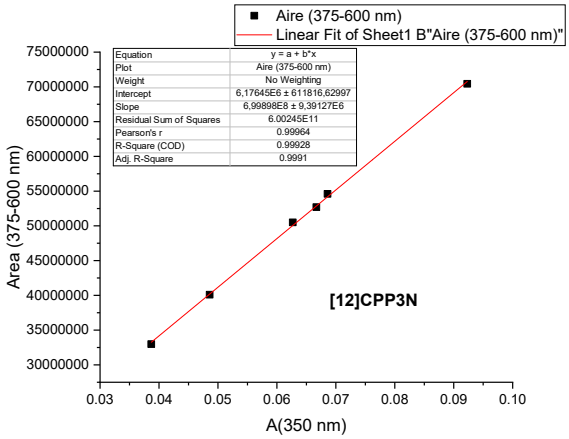


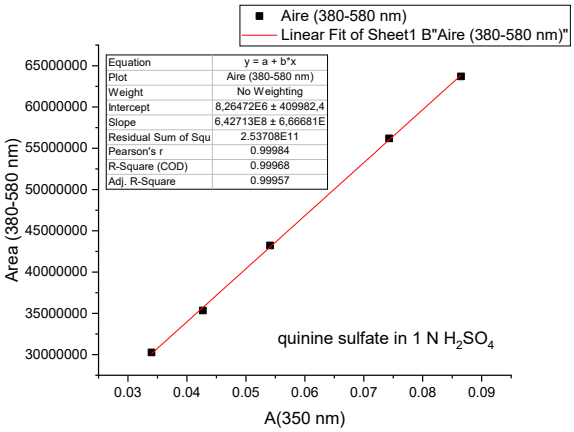
	Quinine sulfate in H_2SO_4	**[12]CPP3N**
slope	6.37E+08	8.23E+08
refracting index	1.336	1.42662
QY	0.546	8.04E-01

*Figure S 40. Determination of the quantum yield of **[12]CPP3N** in cyclohexane*

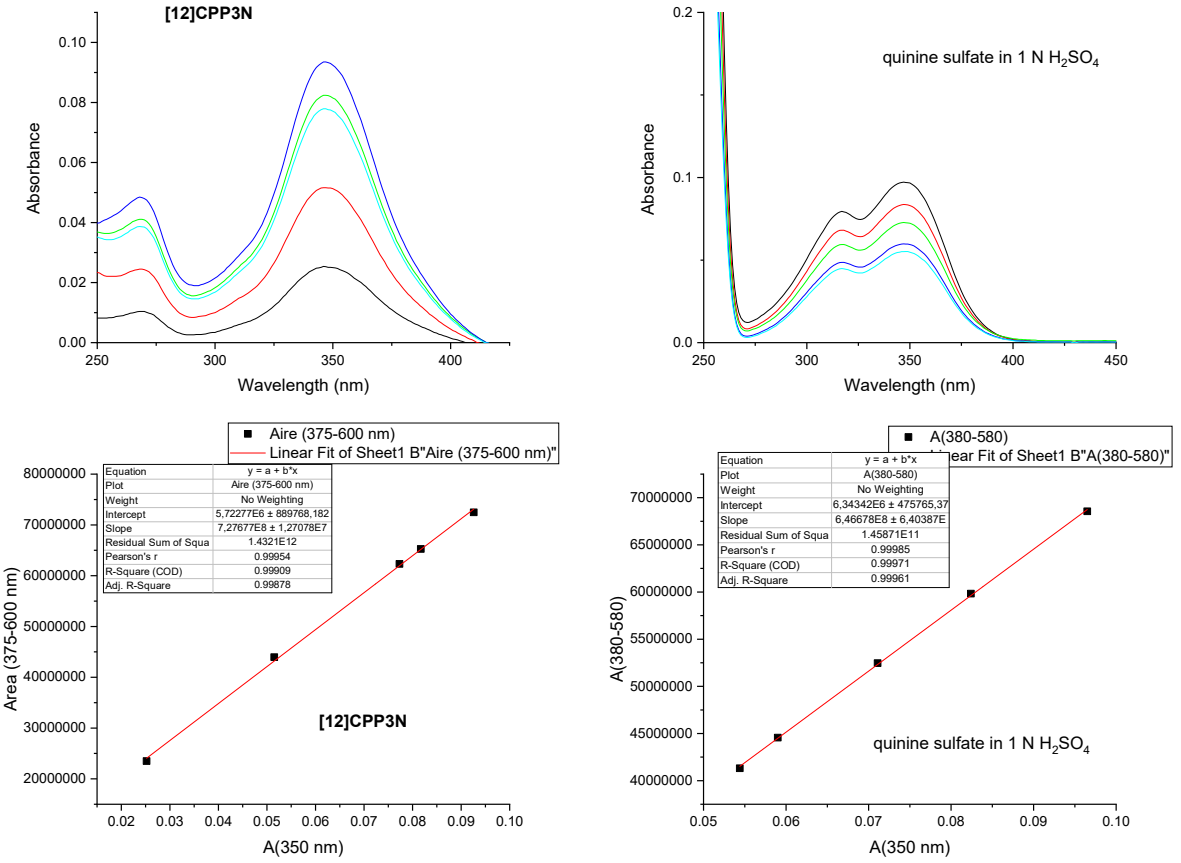








	Quinine sulfate in H_2SO_4	**[12]CPP3N**
slope	6.43E+08	7.00E+08
refracting index	1.336	1.445
QY	0.546	6.96E-01



	Quinine sulfate in H_2SO_4	**[12]CPP3N**
slope	6.47E+08	7.28E+08
refracting index	1.336	1.445
QY	0.546	7.19E-01

*Figure S 41. Determination of the quantum yield of **[12]CPP3N** in chloroform*

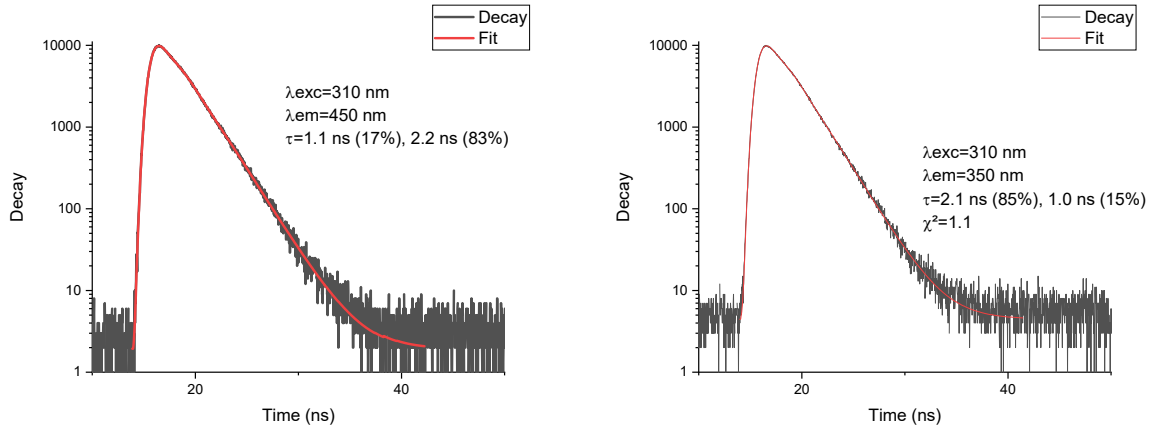


*Figure S 42. Fluorescence lifetimes of **[12]CPP3N** in chloroform (left) and in cyclohexane (right)*

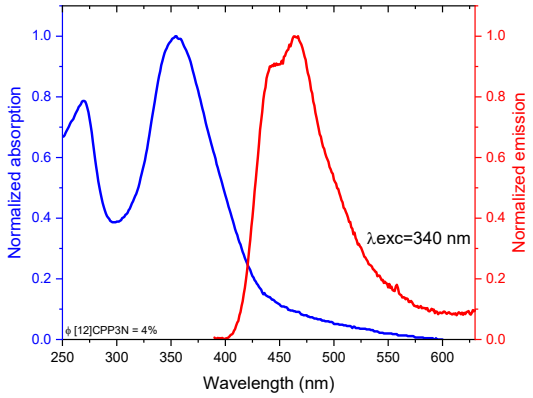


*Figure S 43. Absorption and emission spectra of **[12]CPP3N** in thin film*

*7.2. Photophysical properties of **[16]CPP4N***

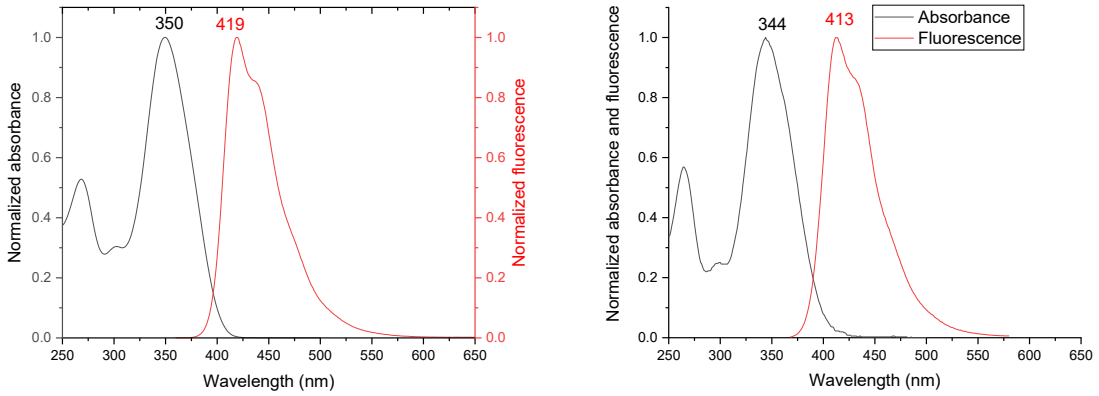
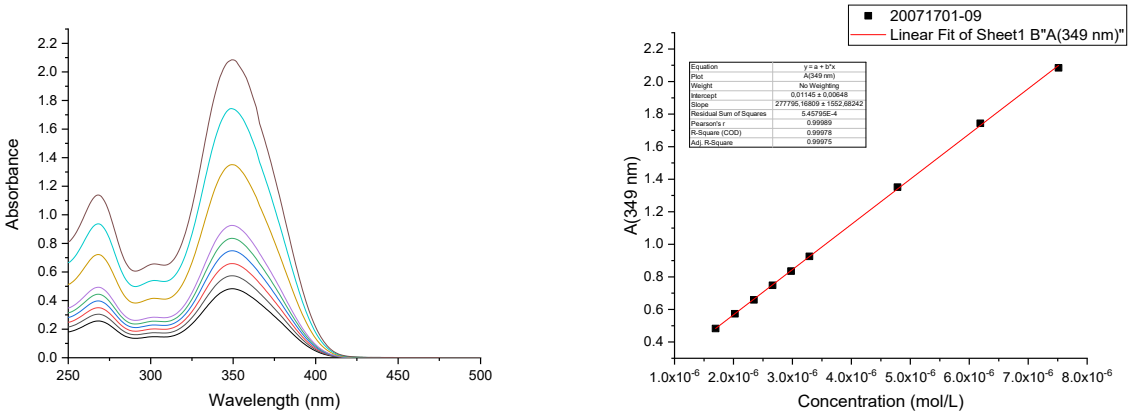


*Figure S 44. Normalized absorption and fluorescence spectra of **[16]CPP4N** in chloroform (left) and in cyclohexane (right)*



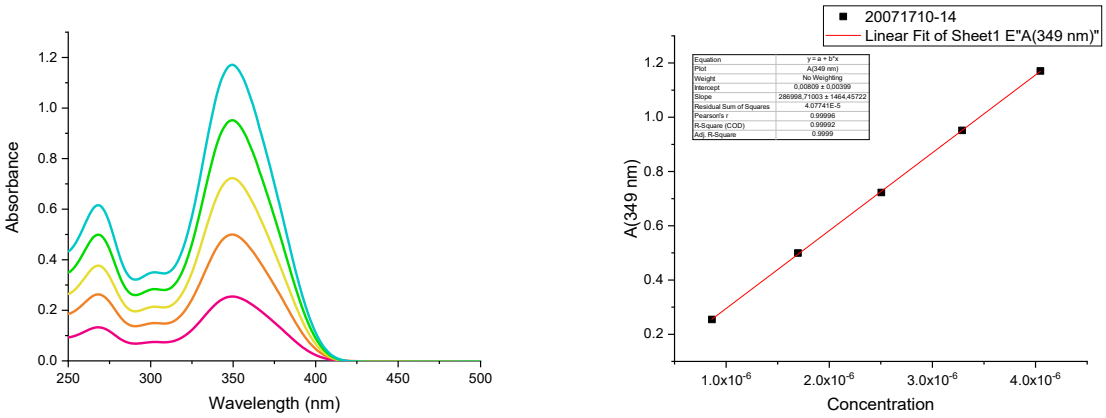
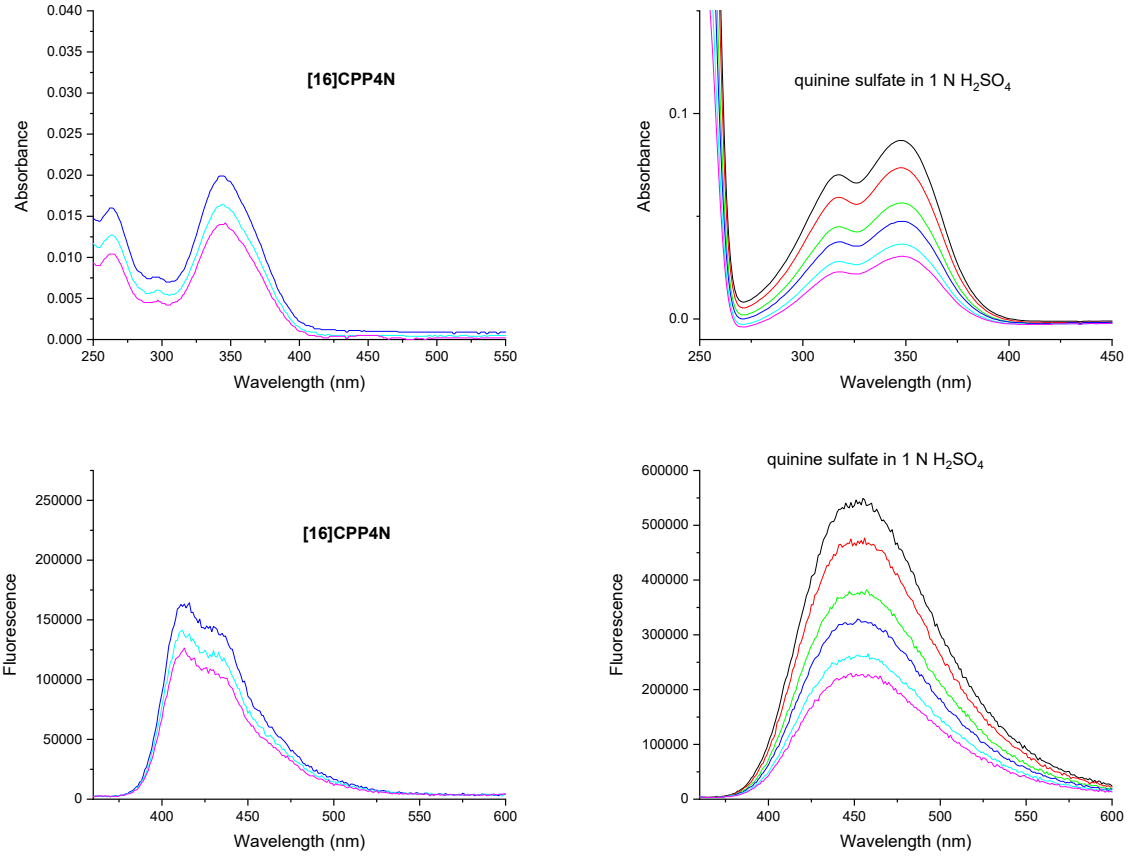
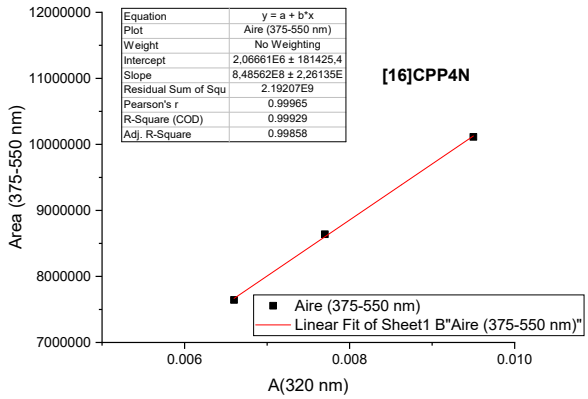
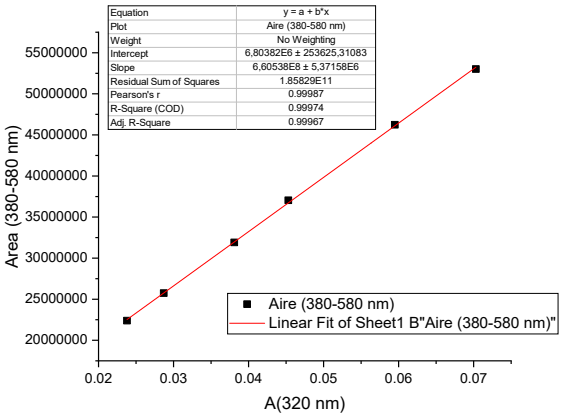


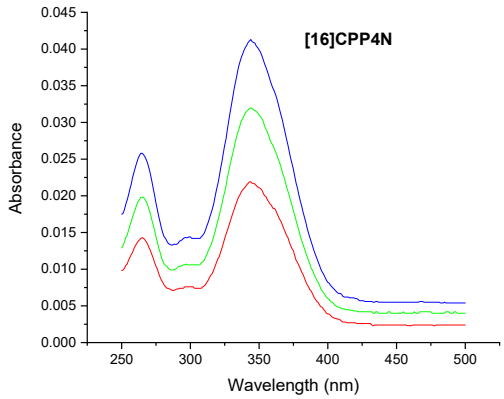
*Figure S 45. Determination of the molar extinction coefficient of **[16]CPP4N** in chloroform*

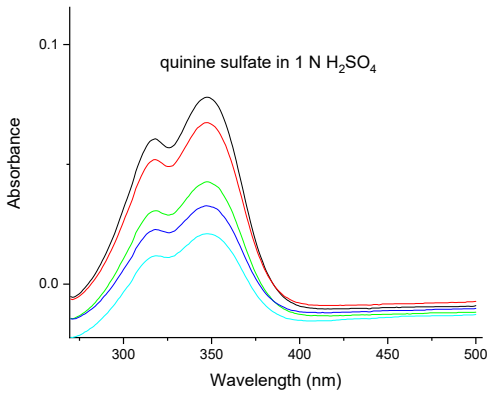


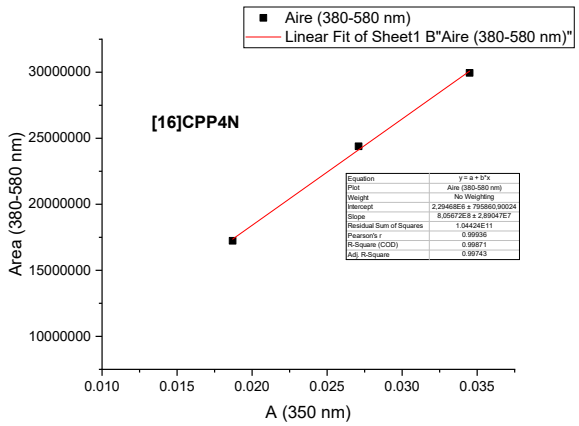


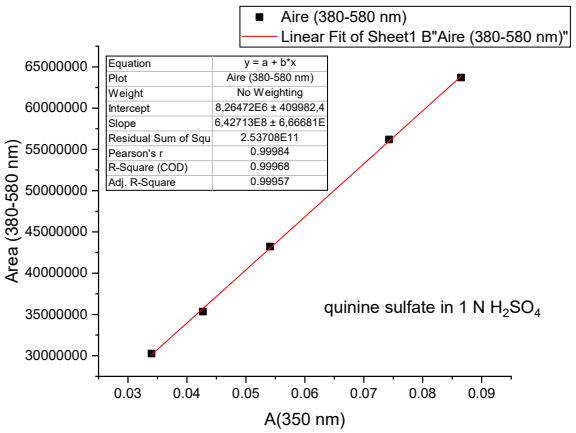


	Quinine sulfate in H_2SO_4	**[16]CPP4N**
slope	6.61E+08	8.49E+08
refracting index	1.336	1.42662
QY	0.546	8.00E-01





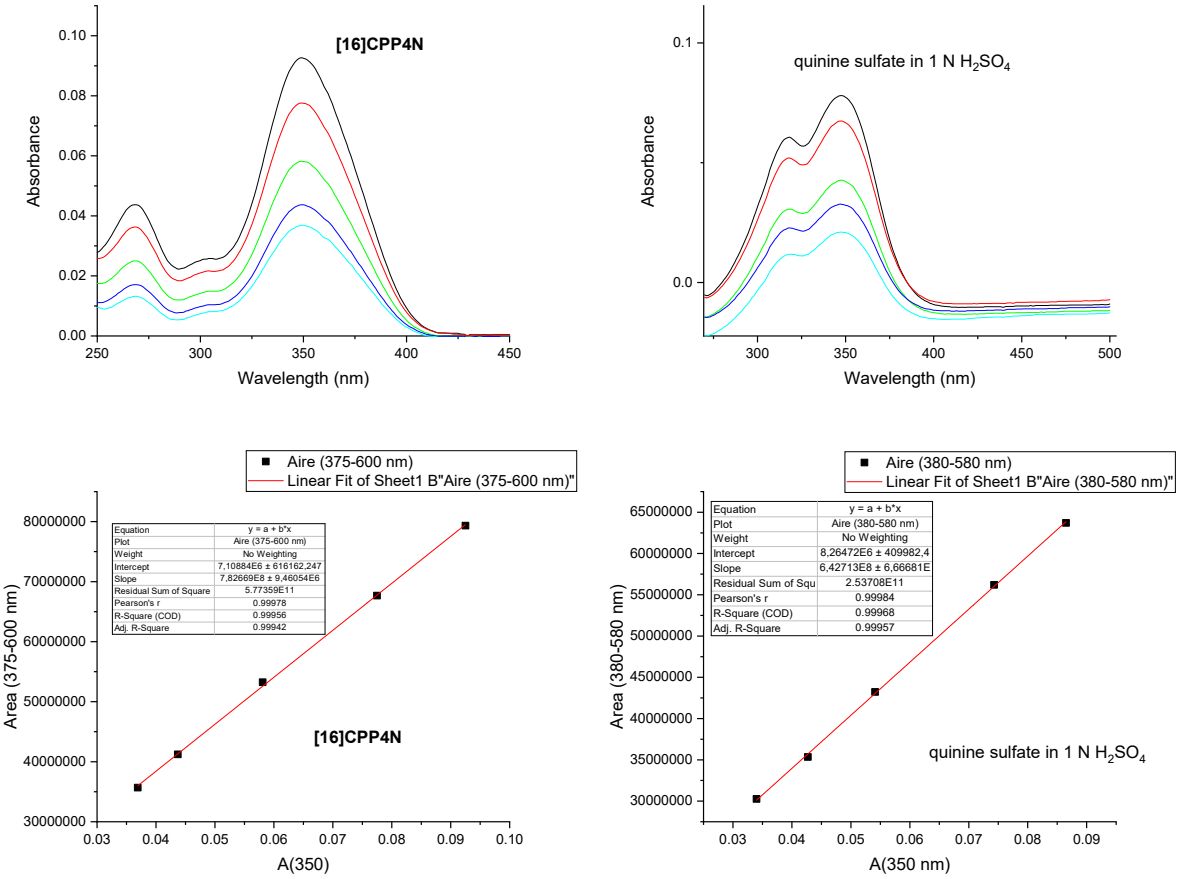




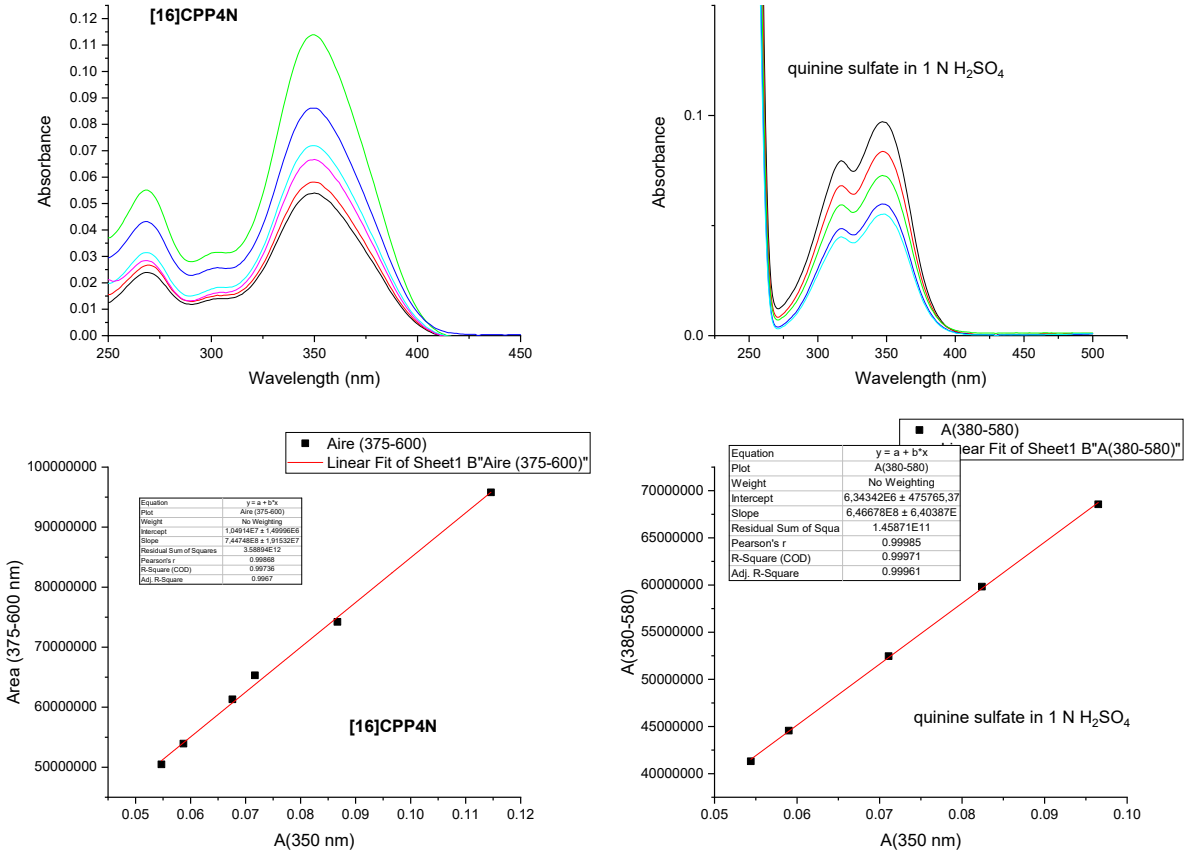
	Quinine sulfate in H_2SO_4	**[16]CPP4N**
slope	6.43E+08	8.06E+08
refracting index	1.336	1.42662

QY	0.546	7.80E-01

*Figure S 46. Determination of the quantum yield of **[16]CPP4N** in cyclohexane*



	Quinine sulfate in H_2SO_4	**[16]CPP4N**
slope	6.43E+08	7.83E+08
refracting index	1.336	1.445
QY	0.546	7.78E-01



	Quinine sulfate in H_2SO_4	**[16]CPP4N**
slope	6.47E+08	7.45E+08
refracting index	1.336	1.445
QY	0.546	7.36E-01

*Figure S 47. Determination of the quantum yield of **[16]CPP4N** in chloroform*

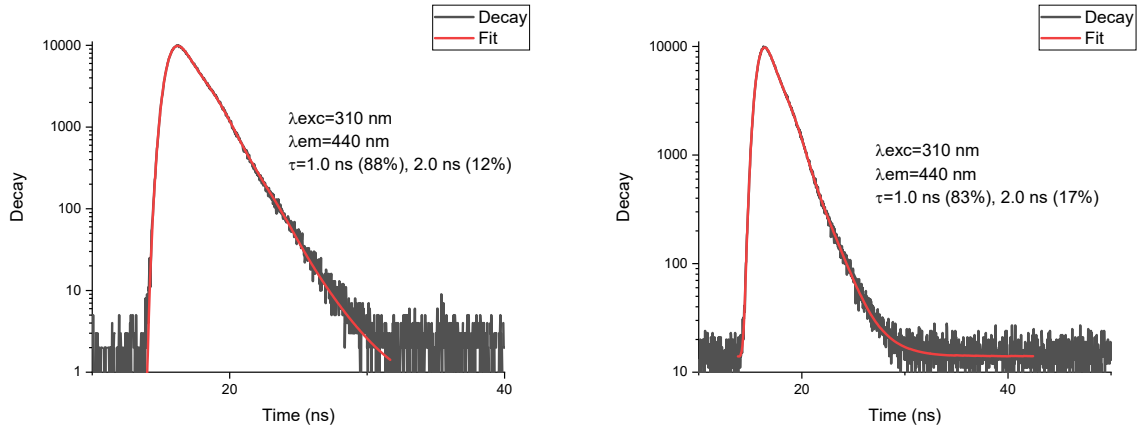


*Figure S 48. Fluorescence lifetimes of **[16]CPP4N** in chloroform (left) and in cyclohexane (right)*

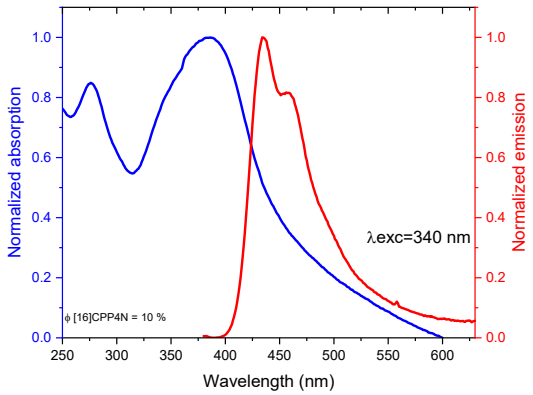


*Figure S 49. Absorption and emission spectra of **[16]CPP4N** in thin film*

*7.3. Photophysical properties of **[8]CPP4N***

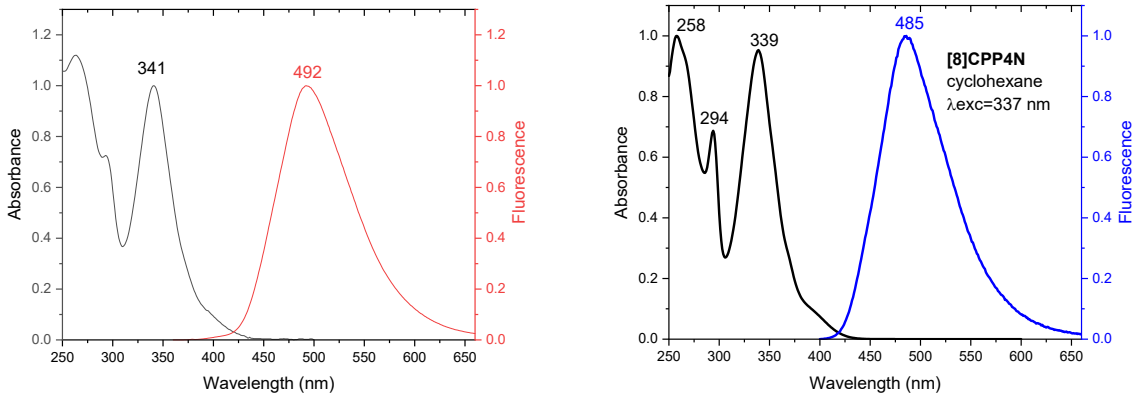


*Figure S 50. Normalized absorption and fluorescence spectra of **[8]CPP4N** in chloroform (left) and in cyclohexane (right)*

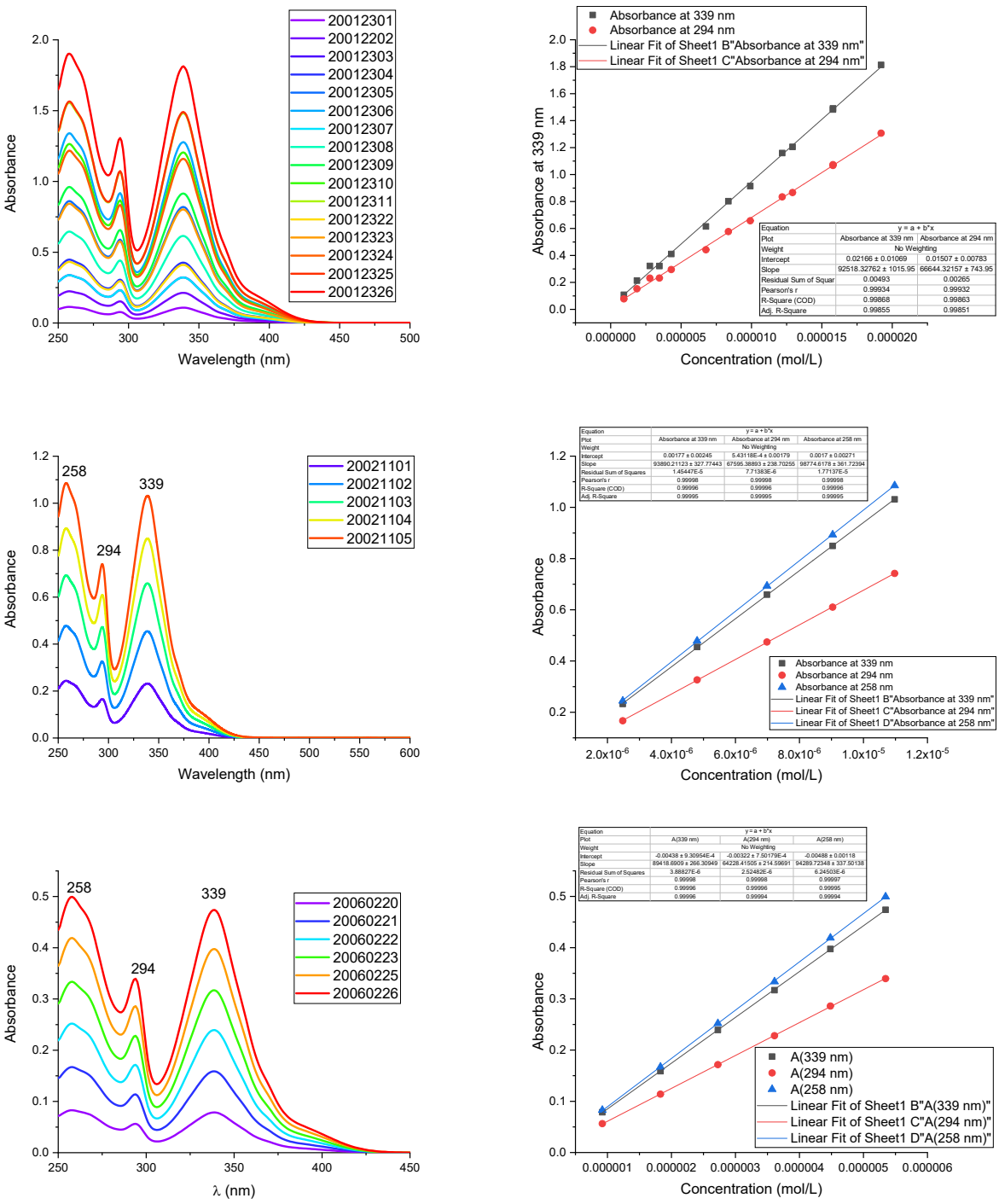


*Figure S 51. Determination of the molar extinction coefficient of **[8]CPP4N** in cyclohexane*

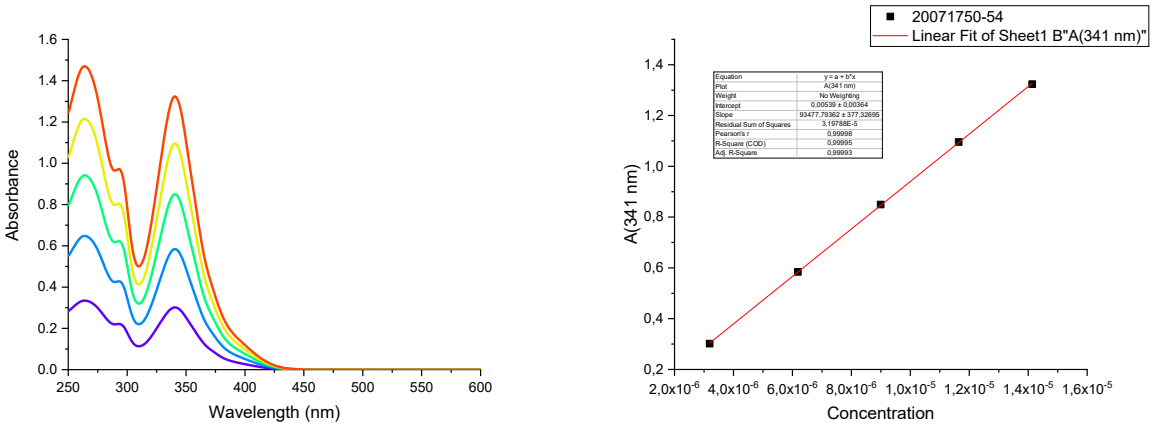
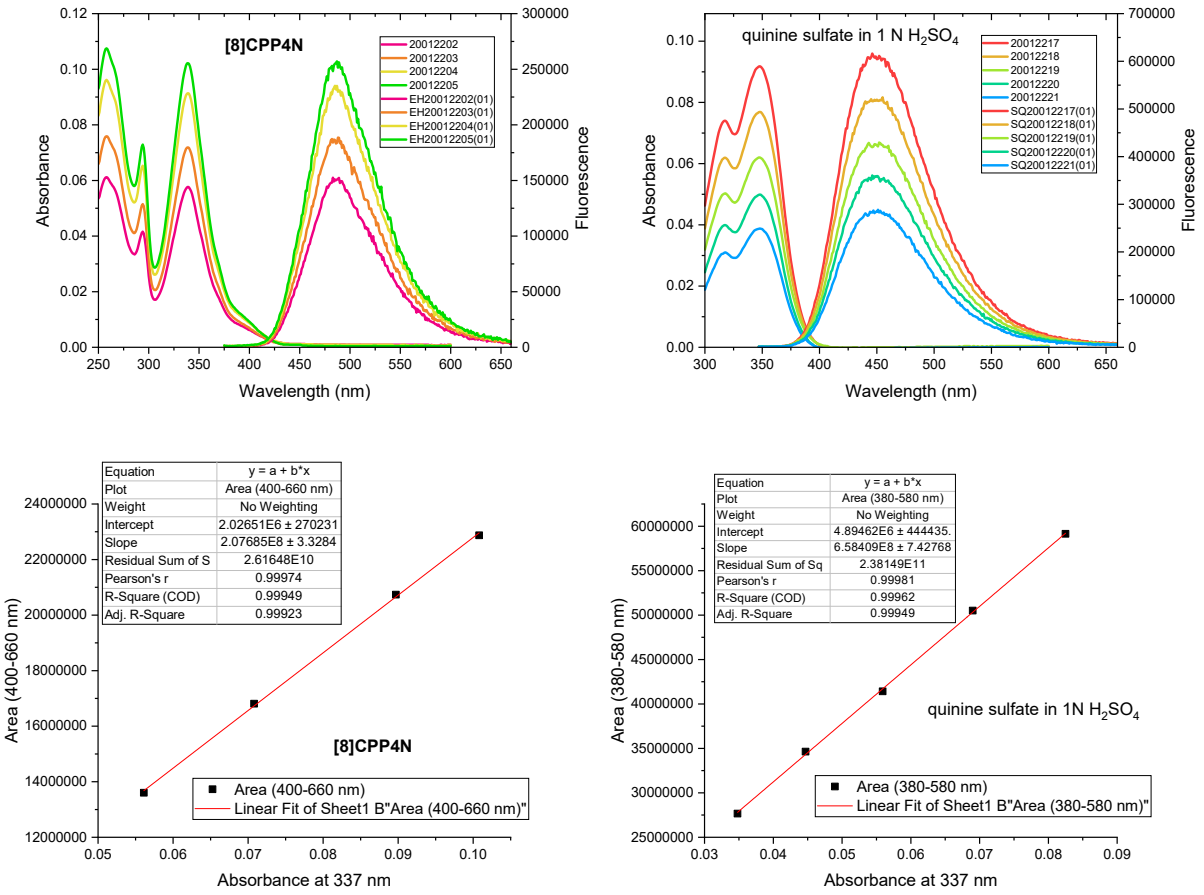
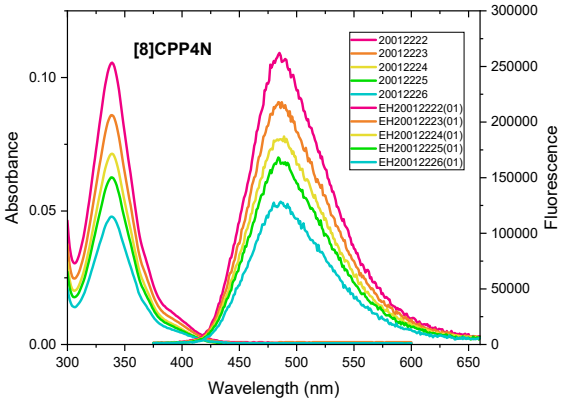
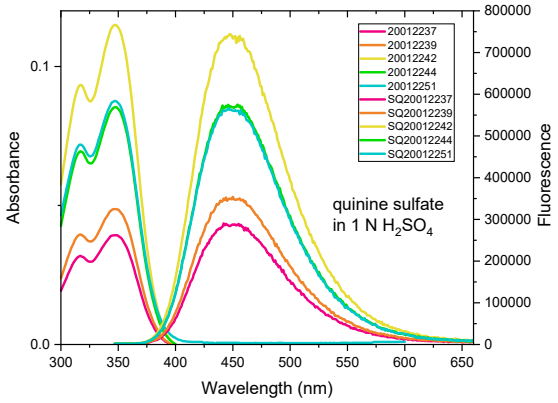


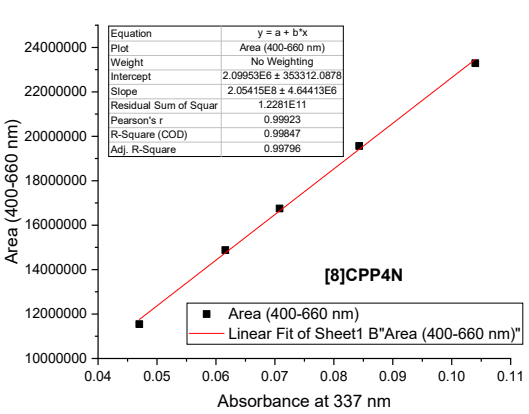
*Figure S 52. Determination of the molar extinction coefficient of **[8]CPP4N** in chloroform*

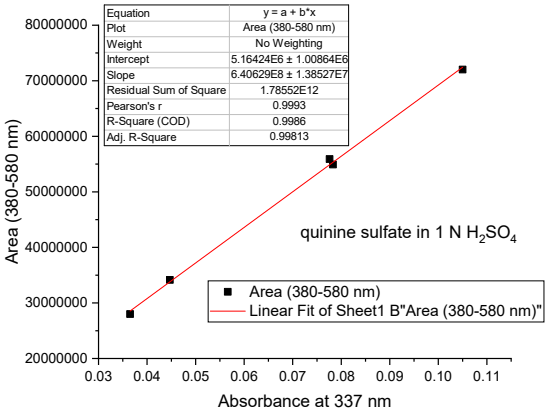


	Quinine sulfate in H_2SO_4	**[8]CPP4N**
slope	6.58E+08	2.08E+08
refracting index	1.336	1.42662
QY	0.546	1.96E-01

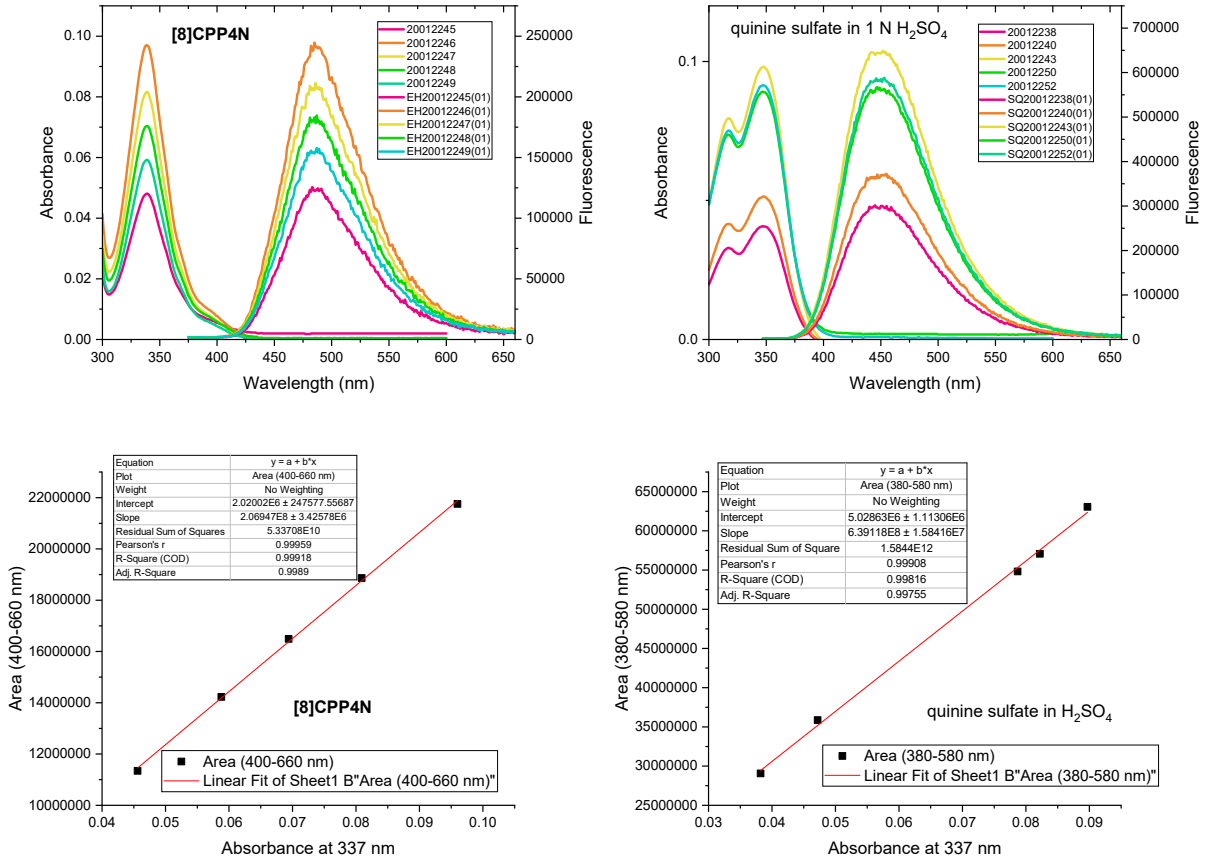






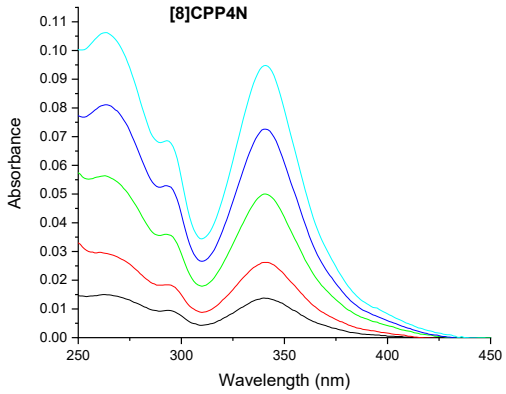


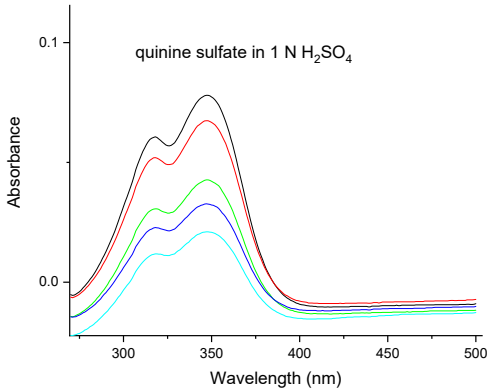
	Quinine sulfate in H_2SO_4	**[8]CPP4N**
slope	6.41E+08	2.05E+08
refracting index	1.336	1.42662
QY	0.546	2.00E-01

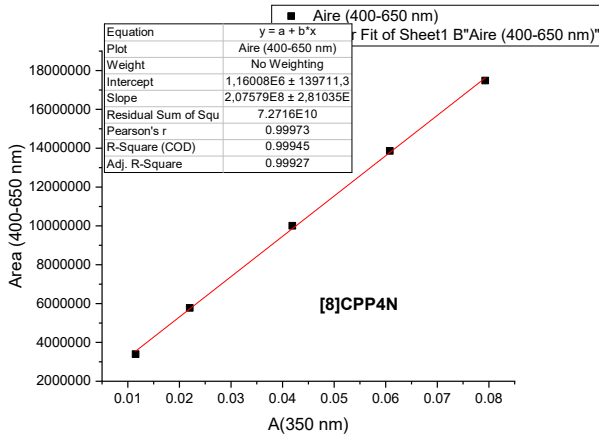


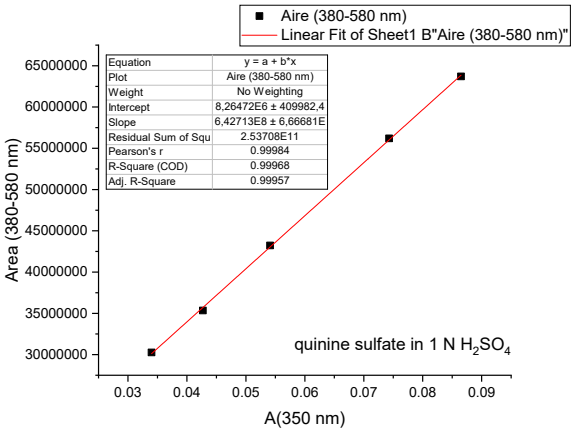
	Quinine sulfate in H_2SO_4	**[8]CPP4N**
slope	6.39E+08	2.07E+08
refracting index	1.336	1.42662
QY	0.546	2.02E-01

*Figure S 53. Determination of the quantum yield of **[8]CPP4N** in cyclohexane*

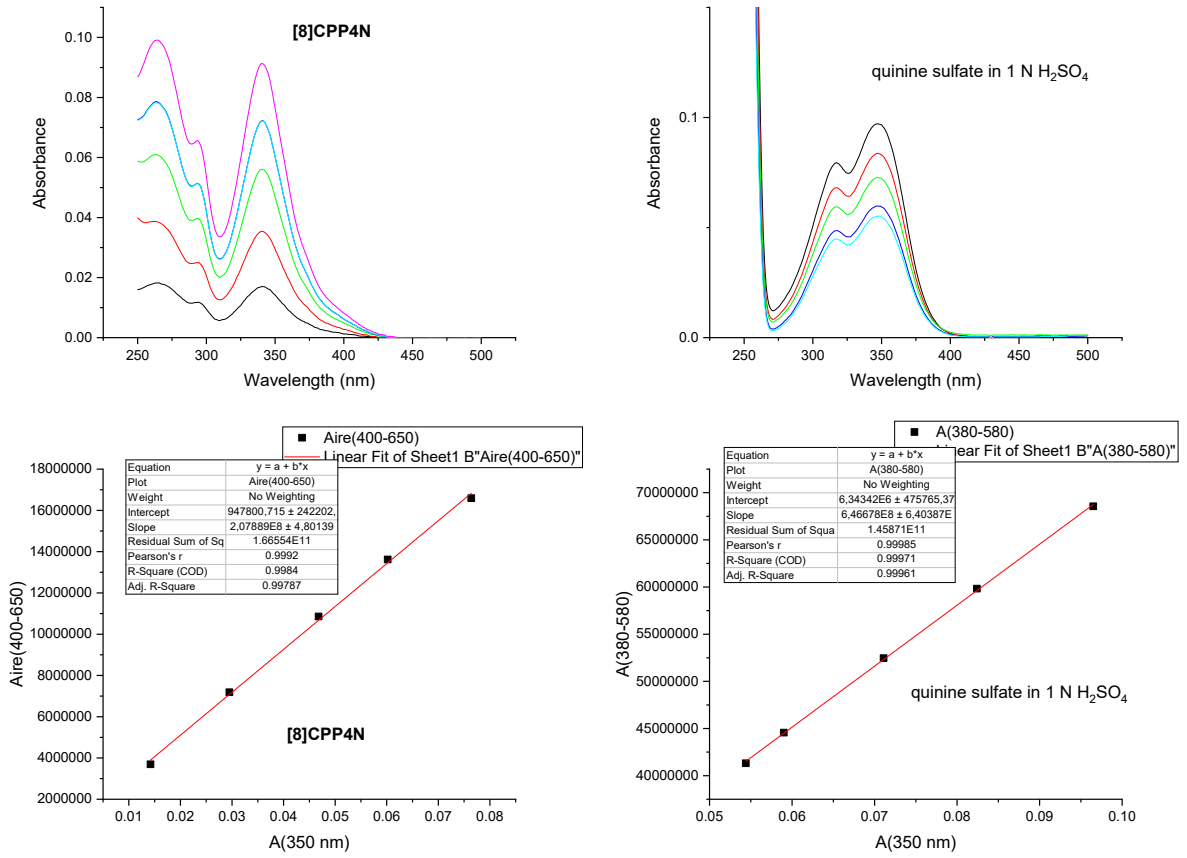








	Quinine sulfate in H_2SO_4	**[8]CPP4N**
slope	6.43E+08	2.08E+08
refracting index	1.336	1.445
QY	0.546	2.06E-01



	Quinine sulfate in H_2SO_4	**[8]CPP4N**
slope	6.47E+08	2.08E+08
refracting index	1.336	1.445
QY	0.546	2.05E-01

*Figure S 54. Determination of the quantum yield of **[8]CPP4N** in chloroform*

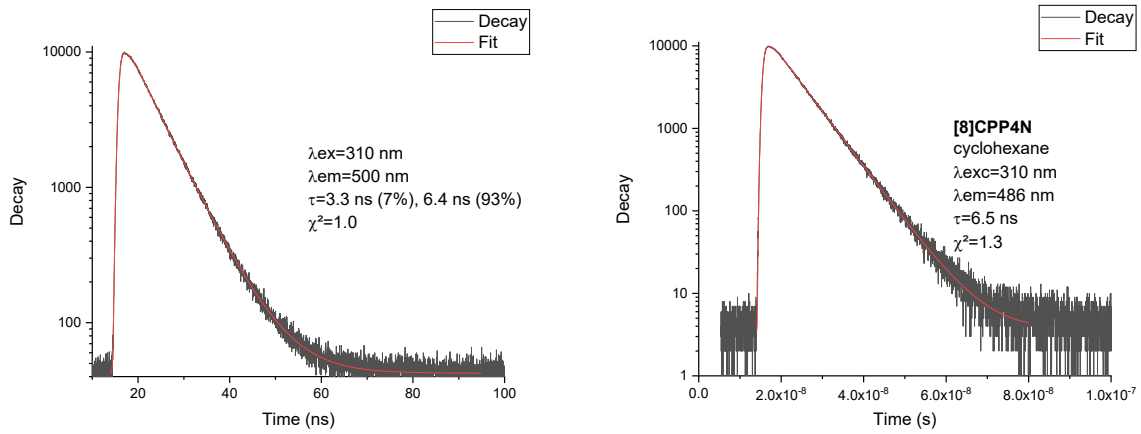


*Figure S 55. Fluorescence lifetimes of **[8]CPP4N** in chloroform (left) and in cyclohexane (right)*

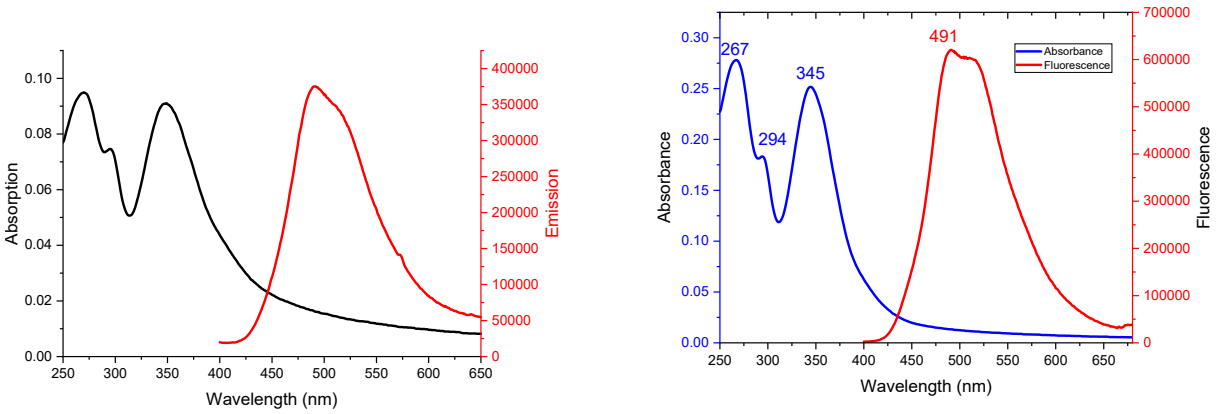


*Figure S 56. Absorption and emission spectra of **[8]CPP4N** in thin film obtained by spin coating (left) or evaporation under vacuum (right)*

7.4. Solvatochromic data

*Table S 1. Absorption and emission maxima in different solvents of **[16]CPP4N**, **[12]CPP3N** and **[8]CPP4N***

	[16]CPP4N		**[12]CPP3N**		**[8]CPP4N**	
	λ_{abs} max	λ_{em} max	λ_{abs} max	λ_{em} max	λ_{abs} max	λ_{em} max
Cyclohexane	344	412	341	422	339	486
Toluene	349	416	347	428	339	494
Chloroform	349	419	347	432	341	492
Ethyl acetate	349	416	345	427	337	482
Tetrahydrofuran	349	427	345	431	337	485
Dichloromethane	349	419	346	431	339	491
Acetonitrile	-	430	348	431	338	488

8 Theoretical properties

The ethylhexyl chains are needed to achieve the synthesis of the hybrid nanohoops but prevent the obtention of crystals suitable for X-Ray diffraction. Thus, we modelized the geometries of the three nanohoops with theoretical calculations. In the case of the large nanohoops, the conformations of carbazole may vary. Thus, optimizations of geometry and frequency calculations have been performed on the two conformations of **[12]CPP3N** (ααα and αβα) and on the four conformations of **[16]CPP4N** (αααα, αβαβ, ααββ and αβαα). The geometric parameters of all conformers are indicated in the SI whereas the ones of the most stable conformers (αβα-**[12]CPP3N** and αβαα-**[16]CPP4N**) are discussed in the article. For computing time reasons, the ethylhexyl chains were replaced by methyl groups.

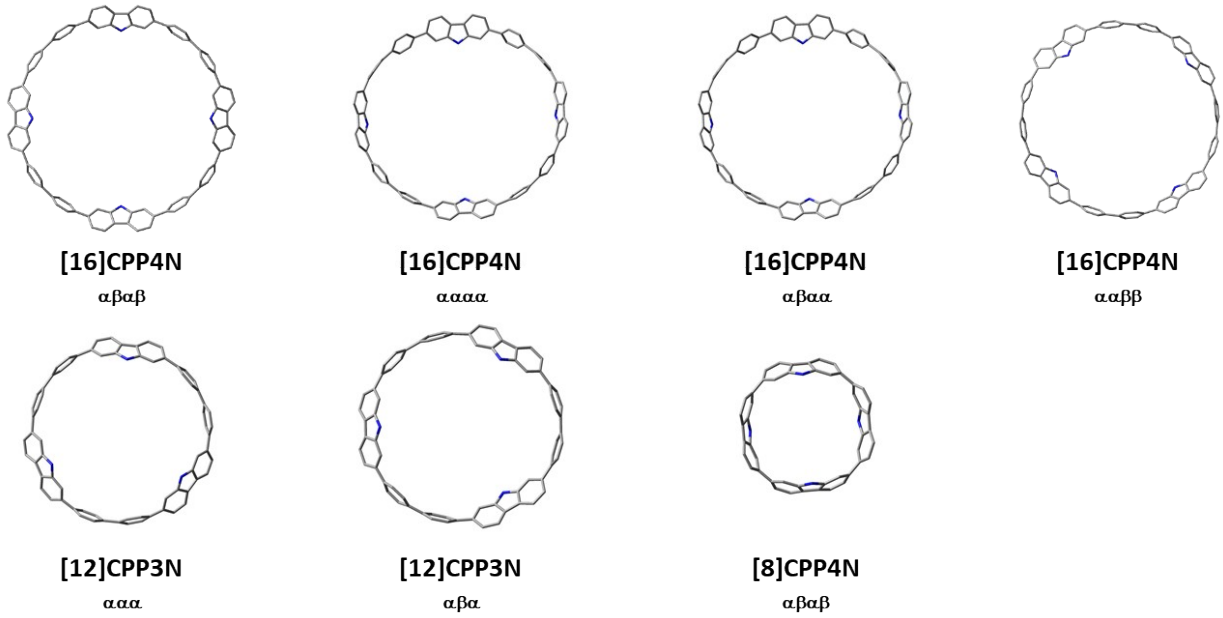


*Figure S 57. Representation of the optimized geometries of the different conformers of **[16]CPP4N**, **[12]CPP3N** and **[8]CPP4N** (for clarity reasons, hydrogen atoms and alkyl chains are removed)*

Table S 2. Angle values (definitions of torsion angle and displacement angle are respectively given in Fig. S59 and S60)

Nanohoop	**[16]CPP4N (αβαβ)**		**[16]CPP4N (αβαα)**		**[16]CPP4N (αααα)**		**[16]CPP4N (ααββ)**	
Total energy (Hartree)	-4070.77732		-4070.77815		-4070.77702		-4070.77633	
Nature of angle	Torsion angle	Displacement angle	Torsion angle	Displacement angle	Torsion angle	Displacement angle	Torsion angle	Displacement angle
Average	26.7	3.6	26.7	7.4	27.2	7.3	25.7	7.4
Value	0.00	5.09	30.19	9.32	0	2.86	0.29	4.36
	0.00	5.34	29.98	9.61	0.01	9.68	0.11	6.15
	0.02	5.37	36.59	4.13	0.02	9.83	38.65	10.1
	0.03	5.14	34.88	3.91	0.04	6.59	36.49	10.1
	0.00	2.22	0.27	10.05	0	6.51	31.78	6.14
	0.00	1.54	0.12	10.47	0	9.66	31.79	4.36
	0.02	2.23	38.83	4.78	0.02	9.49	36.49	10.09
	0.03	1.54	36.81	4.77	0.03	3.63	38.65	9.64
	38.72	5.38	32.37	10.46	40.13	3.63	0.11	3.86
	36.42	5.14	32.22	10.05	40.33	9.48	0.29	3.99
	32.07	5.33	36.03	3.91	30.95	9.67	34.19	10.71
	32.10	5.09	37.72	4.13	31.29	6.51	36.18	10.71
	36.52	2.13	0	9.62	36.44	6.59	27.14	3.99
	38.89	1.46	0.01	9.33	38.99	9.83	27.66	3.86
	36.27	2.13	37.72	6.41	36.45	9.69	43.02	9.63
	38.58	1.47	36.03	6.42	39.01	2.87	47.52	10.1
	31.85	5.02	32.22	9.32	30.94	2.86	0.93	4.36
	31.88	5.26	32.37	9.61	31.29	9.68	1.97	6.15
	37.70	5.27	36.8	4.13	40.14	9.83	29.35	10.1
	35.93	5.03	38.83	3.91	40.35	6.59	30.13	10.1
	37.70	2.40	0.12	10.05	40.44	6.51	24.16	6.14
	35.93	2.10	0.26	10.47	40.64	9.66	24.15	4.36
	31.86	2.40	34.88	4.78	30.99	9.49	30.15	10.09
	31.89	2.10	36.59	4.77	30.66	3.63	29.37	9.64
	36.27	5.26	29.98	10.46	37.82	3.63	1.99	3.86
	38.56	5.03	30.18	10.05	35.88	9.48	0.92	3.99
	36.51	5.27	40.76	3.91	37.82	9.67	47.5	10.71
	38.87	5.01	40.83	4.13	35.86	6.51	46.02	10.71
	32.06	2.13	0	9.62	30.99	6.59	27.64	3.99
	32.10	1.47	0	9.33	30.67	9.83	27.12	3.86
	36.40	1.46	40.76	6.41	40.63	9.69	36.18	9.63
	38.72	2.13	40.84	6.42	40.44	2.87	34.19	10.1

Nanohoop	**[12]CPP3N (αβα)**		**[12]CPP3N (ααα)**		**[8]CPP4N**	
Total energy (Hartree)	-3053.04493		-3053.04469		-2222.24976	
Nature of angle	Torsion angle	Displacement angle	Torsion angle	Displacement angle	Torsion angle	Displacement angle
Average	23.1	10.8	24.6	5.3	21.2	7.4
Value	27.67	14.78	0.87	7.20	0.04	8.24
	27.04	9.3	1.9	7.29	0.2	8.18
	20.56	6.8	0.86	7.03	0.52	8.26
	20.31	13.46	1.89	7.12	0.21	8.23
	35.43	13.98	0.91	6.44	0.04	6.46
	33.23	6.2	2.01	6.76	0.76	6.54

0.14	6.85	29.1	6.65	0.23	6.73
0.11	15.47	30.04	6.53	0.62	6.69
34.09	15.42	20.26	3.83	42.24	8.03
32.04	6.8	20.22	3.07	41.93	6.51
21.11	6.2	47.61	3.73	41.73	8.22
21.12	14.17	46.41	2.93	42.22	6.68
31.99	14.78	29.46	4.21	42.42	8.26
34.01	9.3	30.48	4.05	42.06	6.48
0.12	6.8	20.81	4.06	41.76	8.07
0.18	13.46	20.89	4.15	42.36	6.62
33.53	13.98	46.06	7.04		
35.69	6.2	47.14	7.20		
22.64	6.85	29.09	6.77		
22.92	15.47	30.00	6.56		
47.4	15.42	20.66	3.87		
48.81	6.8	20.7	4.16		
1.12	6.2	46.07	3.08		
2.36	14.17	47.07	4.18		

Torsion angle

Definition of a torsion angle: The external torsion angle (θ_{ext}) is the dihedral angle between two unbridged phenylenes. Two angles are measured for each C-C bound (C1-C2-C3-C4 and C5-C2-C3-C6). The internal torsion angle (θ_{int}) is the dihedral angle between two bridged phenylenes. Two angles are measured for each C-C bound (Ca-Cb-Cc-Cd and Ce-Cb-Cc-Cf).

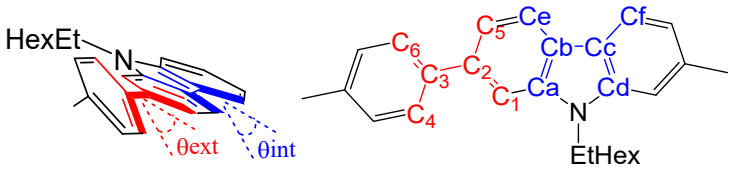


Figure S 58. Definition of a torsion angle θ

Displacement angle

Definition of a displacement angle: The mean planes passing by C1-Ca-Ce-C5 (red), C1-C2-C5 (yellow) and Ca-Cb-Ce (green) are drawn. The displacement angles (ω) are measured for the phenylene labelled C1-C2-C5-Ce-Cb-Ca between red and yellow planes on the one hand and between red and green planes on the other hand (whatever this phenylene is substituted by a nitrogen atom or not).

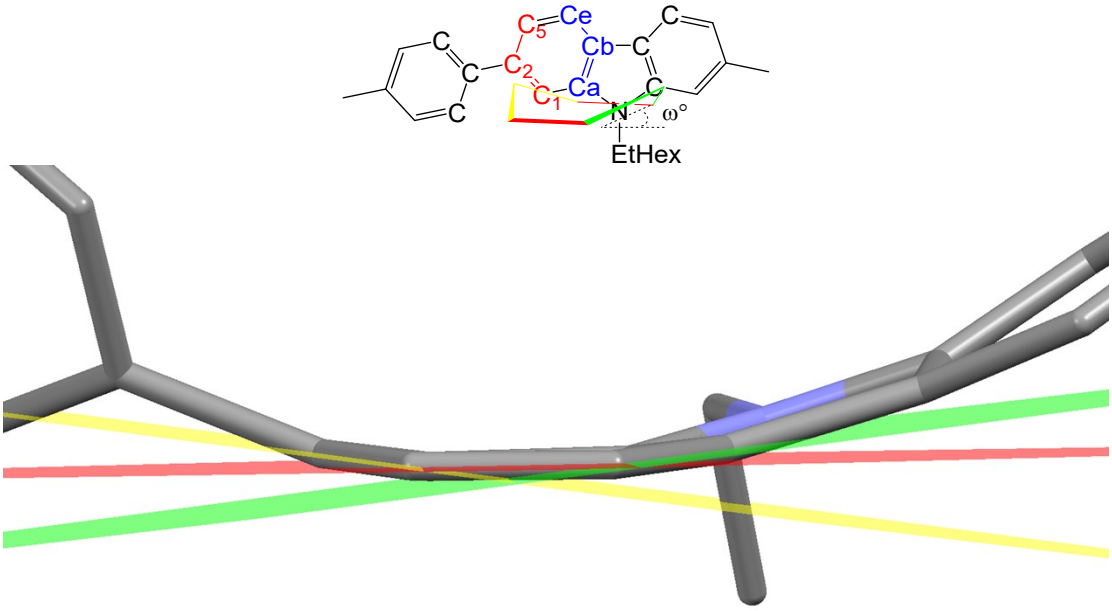
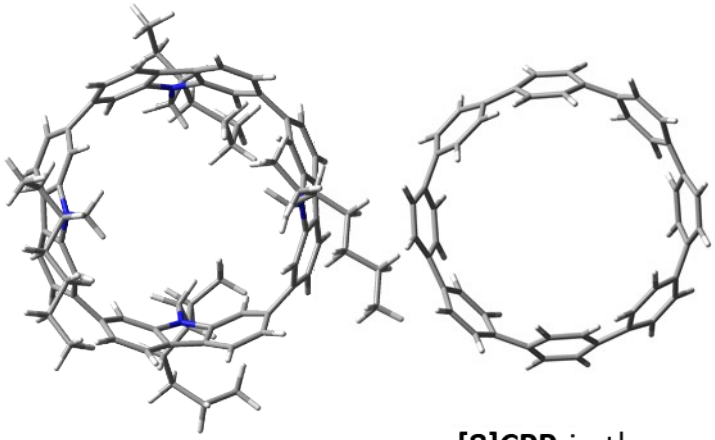


Figure S59 Measurement of a displacement angle ω



[8]CPP4N

[8]CPP in the geometry of **[8]CPP4N**

*Figure S 60. Optimized geometry of **[8]CPP4N** and structure of **[8]CPP** in the geometry optimized for **[8]CPP4N** (all the torsion angles and displacement angles have been frozen; each nitrogen bridge has been replaced by two hydrogen atoms with standard structure properties)*

*Table S 3. Calculated energy levels of the frontier orbitals of **[16]CPP4N**, **[12]CPP3N**, **[8]CPP4N*** and ***[8]CPP***

	[16]CPP4N				**[12]CPP3N**		**[8]CPP4N**		**[8]CPP**
conformation	αβαα	αααα	αβαβ	αβαβ	αβα	ααα	αβαβ		of **[8]CPP4N**
Basis set	6-31g(d)	6-31g(d)	6-31g(d)	6-31g(d)	6-31g(d)	6-31g(d)	6-31g(d)	6-311+g(d,p)	6-311+g(d,p)
Alkyl chain	methyl	methyl	methyl	methyl	methyl	methyl	methyl	2-ethex	-
LUMO (eV)	-1.55	-1.53	-1.55	-1.36	-1.63	-1.58	-1.36	-1.76	-2.27
HOMO(eV)	-5.12	-5.13	-5.12	-4.89	-5.04	-5.07	-4.89	-5.16	-5.23

*Table S 4. Atomic coordinates of αβαβ-**[16]CPP4N** after geometry optimization (b3lyp/6-31g(d), methyl chains have been used instead of ethylhexyl chains, E=-4070.77732 Hartree)*

Atoms	X (Å)	Y (Å)	Z (Å)
C	8.283604	-7.193827	-0.063462
C	8.40681	-6.501065	-1.281184
C	9.171726	-5.344947	-1.380423
C	9.843021	-4.814437	-0.264953
C	9.821859	-5.573979	0.917735
C	9.062834	-6.737522	1.014647
C	10.390428	-3.434487	-0.28735
C	9.663855	-2.452814	-0.976969
C	10.05083	-1.120649	-0.864468
C	11.157758	-0.719826	-0.068443
C	11.910192	-1.714503	0.571372
C	11.527081	-3.04891	0.462121
C	9.838315	4.823823	-0.26483
C	9.166479	5.353649	-1.380298
C	8.400449	6.509032	-1.281078
C	8.276592	7.201707	-0.063374
C	9.056264	6.746171	1.014741
H	7.833083	-6.827155	-2.143744
H	9.211893	-4.816037	-2.328676
H	10.344064	-5.207641	1.797307
H	9.039255	-7.273969	1.959309
H	8.758395	-2.724605	-1.50848
H	12.775267	-1.448169	1.173263
H	12.108798	-3.812724	0.970028
H	9.207136	4.824748	-2.328536
H	9.032177	7.282614	1.959392
C	9.816415	5.583361	0.917847
C	10.387044	3.444401	-0.287211
C	11.524078	3.059917	0.462245
C	9.661453	2.462047	-0.976892
C	11.908495	1.725882	0.571451
H	12.105056	3.824285	0.970163
C	10.049731	1.130258	-0.864431
H	8.755743	2.732975	-1.508421
C	11.157042	0.730491	-0.068409
H	12.773833	1.460375	1.173329

N	9.424624	0.004507	-1.382907
C	8.204602	0.003926	-2.159714
H	8.181451	-0.879535	-2.802992
H	7.307215	0.003482	-1.525823
H	8.180595	0.88738	-2.802969
C	-8.299569	7.216381	-0.081069
C	-9.086221	6.764848	0.993624
C	-9.836892	5.595511	0.899768
C	-9.840736	4.82525	-0.27607
C	-9.164143	5.35113	-1.390466
C	-8.408279	6.51346	-1.29435
C	-10.371724	3.438631	-0.288322
C	-11.520747	3.049883	0.440278
C	-11.895558	1.713323	0.550143
C	-11.119468	0.719582	-0.062694
C	-9.98828	1.121404	-0.823604
C	-9.620206	2.457704	-0.951027
C	-9.831447	-5.604904	0.899626
C	-9.07965	-6.773517	0.9935
C	-8.292561	-7.224304	-0.081185
C	-8.401964	-6.521517	-1.294484
C	-9.158958	-5.359924	-1.390621
H	-9.074165	7.309282	1.93395
H	-10.364822	5.232848	1.777497
H	-9.191974	4.813559	-2.334323
H	-7.828962	6.836227	-2.154433
H	-12.121958	3.813385	0.925508
H	-8.718023	2.738313	-1.483493
H	-10.359731	-5.242741	1.777348
H	-9.06706	-7.317921	1.933835
H	-7.822348	-6.843744	-2.154567
H	-9.187334	-4.822414	-2.334494
C	-9.83603	-4.834662	-0.276222
C	-10.368393	-3.448566	-0.288495
C	-9.617803	-2.466872	-0.951118
C	-11.517789	-3.060958	0.440126
C	-9.98718	-1.130937	-0.823646
H	-8.715328	-2.746575	-1.483565
C	-11.893898	-1.724767	0.55005
H	-12.118248	-3.82506	0.925342
C	-11.118769	-0.730246	-0.062735
H	7.826395	6.834543	-2.143639
C	-7.243311	-8.261421	0.081556
C	-6.532948	-8.355731	1.291711
C	-6.79012	-9.050609	-0.990576
C	-5.363615	-9.100746	1.386691
H	-6.856342	-7.773651	2.149673
C	-5.613832	-9.790613	-0.897855
H	-7.339409	-9.049317	-1.928159
C	-4.837885	-9.780503	0.274177

H	-5.251144	-10.32138	-1.773878
C	-6.540994	8.3495	1.291764
C	-5.372374	9.09564	1.386693
C	-7.251329	8.254519	0.081644
C	-4.847353	9.775915	0.274161
H	-4.829715	9.113276	2.327872
C	-6.798935	9.044134	-0.990508
C	-5.623356	9.785271	-0.897838
H	-7.348256	9.042306	-1.928073
H	-5.261213	10.316379	-1.773881
C	7.223703	8.235266	0.09795
C	6.506337	8.323802	1.304406
C	6.776697	9.029808	-0.972841
C	5.337672	9.070136	1.396925
H	6.824329	7.737255	2.161328
C	5.600848	9.770758	-0.882788
H	7.331183	9.033001	-1.907335
C	4.819036	9.756842	0.285313
H	4.790553	9.083733	2.33557
H	5.243709	10.306331	-1.758148
C	7.231703	-8.228391	0.097881
C	6.78539	-9.023317	-0.972913
C	6.514493	-8.317653	1.304375
C	5.610247	-9.765382	-0.88282
H	7.339825	-9.025947	-1.907441
C	5.346542	-9.065097	1.396936
H	6.831983	-7.73084	2.161302
C	4.828488	-9.752249	0.285327
H	5.253563	-10.30126	-1.758179
H	4.799496	-9.079252	2.335613
C	3.441025	-10.280983	0.292588
C	2.456098	-9.523354	0.94229
C	3.056878	-11.437924	-0.425869
C	1.120983	-9.895375	0.814007
H	2.733096	-8.615408	1.466791
C	1.72138	-11.816083	-0.537113
H	3.82329	-12.043427	-0.901053
C	0.724047	-11.035773	0.06435
H	1.456468	-12.70364	-1.105993
C	3.431072	10.284258	0.292507
C	3.04583	11.440742	-0.426097
C	2.44687	9.52578	0.942315
C	1.709972	11.817615	-0.537391
H	3.811666	12.046911	-0.901359
C	1.111401	9.896511	0.81398
H	2.724735	8.618169	1.466937
C	0.713382	11.036431	0.064168
H	1.444217	12.704845	-1.106387
C	-3.457702	10.298912	0.284733
C	-2.478297	9.536731	0.937448

C	-3.066027	11.453235	-0.433775
C	-1.140948	9.901504	0.811742
H	-2.761435	8.63068	1.461968
C	-1.728323	11.824583	-0.541816
H	-3.828234	12.061986	-0.911593
C	-0.736446	11.039526	0.062527
H	-1.45746	12.710367	-1.110659
C	-3.447737	-10.302178	0.284817
C	-2.469051	-9.538972	0.937415
C	-3.054967	-11.456223	-0.433538
C	-1.131358	-9.902497	0.811761
H	-2.753046	-8.633118	1.461809
C	-1.716912	-11.826325	-0.541522
H	-3.816596	-12.065759	-0.911277
C	-0.725778	-11.040248	0.062716
H	-1.445209	-12.711927	-1.110245
H	-4.82099	-9.117875	2.327899
H	-6.863778	7.767094	2.149735
H	10.338975	5.217543	1.797424
H	-12.774985	-1.456967	1.127572
H	-12.776387	1.444643	1.127651
N	-0.016714	9.229221	1.271266
N	-9.323361	-0.004434	-1.289929
N	-0.007762	-9.229107	1.271222
C	-0.020185	8.018296	2.062813
H	-0.904305	7.42265	1.821066
H	0.86143	7.418414	1.822382
H	-0.020485	8.228199	3.140504
C	-8.119826	-0.003826	-2.092697
H	-7.519405	-0.886432	-1.857311
H	-8.339805	-0.003848	-3.168359
H	-7.520205	0.87929	-1.857183
C	-0.012372	-8.018111	2.062653
H	0.868648	-7.417394	1.822118
H	-0.897084	-7.423351	1.820892
H	-0.012413	-8.227906	3.140365

No imaginary frequency

*Table S 5. Atomic coordinates of αααββ-**[16]CPP4N** after geometry optimization (b3lyp/6-31g(d), methyl chains have been used instead of ethylhexyl chains, E=-4070.77633 Hartree)*

Atoms	X (Å)	Y (Å)	Z (Å)
C	-0.671222	10.85731	0.057251
C	-1.545043	11.143326	-1.007224
C	-2.902665	10.839252	-0.93363
C	-3.456391	10.245415	0.213882
C	-2.606627	10.081406	1.321793
C	-1.250477	10.369227	1.242603
C	-4.822146	9.663795	0.214686
C	-5.013902	8.441939	0.876248
C	-6.242427	7.798097	0.768043

C	-7.310938	8.331364	-0.00239
C	-7.12432	9.574791	-0.622319
C	-5.897894	10.225934	-0.512919
C	-10.423979	3.557087	0.243001
C	-10.977256	3.006947	-0.926143
C	-11.29207	1.652529	-1.00655
C	-11.063142	0.783483	0.075285
C	-10.633281	1.362847	1.282512
H	-1.152798	11.570824	-1.925785
H	-3.528075	10.999846	-1.807499
H	-3.008253	9.680638	2.248168
H	-0.619116	10.142682	2.096191
H	-4.184172	7.968225	1.38905
H	-7.924081	10.02422	-1.205366
H	-5.76152	11.187041	-1.000152
H	-11.087808	3.630134	-1.809391
H	-10.457779	0.730644	2.147942
C	-10.327493	2.715855	1.365225
C	-9.797312	4.903073	0.245421
C	-10.314921	5.995532	-0.489805
C	-8.568153	5.04687	0.905131
C	-9.612455	7.192466	-0.608765
H	-11.280656	5.894498	-0.97668
C	-7.869811	6.244005	0.781792
H	-8.131627	4.200345	1.42378
C	-8.359465	7.328854	0.005102
H	-10.028285	8.006606	-1.19683
N	-6.612614	6.561082	1.276475
C	-5.757147	5.672255	2.031413
H	-5.093197	6.259721	2.670942
H	-5.146047	5.030942	1.381613
C	0.716798	-10.896319	0.084916
C	1.325419	-10.649017	1.328628
C	2.693033	-10.410823	1.432678
C	3.513663	-10.389045	0.293425
C	2.92898	-10.750146	-0.9322
C	1.565956	-11.009452	-1.03164
C	4.883255	-9.817565	0.365068
C	5.793687	-10.147342	1.395185
C	6.991622	-9.455285	1.5544
C	7.298664	-8.393238	0.693128
C	6.396994	-8.095104	-0.364411
C	5.209415	-8.800765	-0.543247
C	10.751406	-2.890496	1.238799
C	11.041663	-1.530408	1.188656
C	10.877201	-0.78658	0.005807
C	10.539665	-1.509603	-1.153186
C	10.273261	-2.872438	-1.10804
H	0.709291	-10.546224	2.216894
H	3.114213	-10.13778	2.396452

H	3.550117	-10.802912	-1.8227
H	1.150598	-11.274866	-1.999621
H	5.54356	-10.951709	2.081137
H	4.491619	-8.509171	-1.303039
H	10.806798	-3.402524	2.194985
H	11.358731	-1.032295	2.100201
H	10.414144	-0.988078	-2.096932
H	9.994883	-3.382538	-2.025731
C	10.301725	-3.587084	0.102901
C	9.72816	-4.952368	0.209056
C	8.655174	-5.296234	-0.627443
C	10.128347	-5.86417	1.216036
C	7.979706	-6.493532	-0.40717
H	8.296259	-4.591065	-1.3687
C	9.438954	-7.051344	1.443924
H	10.986346	-5.624612	1.836823
C	8.324737	-7.370015	0.656189
H	-11.675956	1.255577	-1.942402
C	10.883376	0.697861	-0.004753
C	10.551441	1.423689	1.154104
C	11.054414	1.440275	-1.18756
C	10.296336	2.788681	1.108837
H	10.421266	0.903253	2.097819
C	10.775422	2.802713	-1.237837
H	11.367698	0.939539	-2.098975
C	10.331111	3.503028	-0.102117
H	10.835396	3.31424	-2.194015
C	-10.644777	-1.276134	-1.281742
C	-10.350233	-2.631632	-1.36456
C	-11.069301	-0.693216	-0.074333
C	-10.453207	-3.472007	-0.242269
H	-9.985405	-3.038442	-2.303665
C	-11.304986	-1.560317	1.007605
C	-11.001433	-2.917296	0.927091
H	-11.685177	-1.160185	1.943612
H	-11.116774	-3.539546	1.810385
C	-0.760498	-10.851463	-0.058132
C	-1.33592	-10.358831	-1.24348
C	-1.636483	-11.130322	1.006462
C	-2.6897	-10.060039	-1.32253
H	-0.70284	-10.137535	-2.097166
C	-2.991603	-10.815267	0.933002
H	-1.247592	-11.560911	1.925001
C	-3.540619	-10.217052	-0.214494
H	-3.088201	-9.656114	-2.248885
H	-3.618217	-10.97071	1.806939
C	0.806352	10.890223	-0.085913
C	1.41292	10.637609	-1.329541
C	1.656436	10.996879	1.030584
C	2.77857	10.388318	-1.433544

H	0.795978	10.539464	-2.217773
C	3.017318	10.726525	0.931202
H	1.243278	11.266004	1.998488
C	3.599029	10.360255	-0.294317
H	3.197466	10.111563	-2.397257
H	3.63886	10.774588	1.821683
C	4.963929	9.77762	-0.365732
C	5.281638	8.758306	0.542778
C	5.877133	10.099794	-1.395784
C	6.463403	8.042896	0.364226
H	4.561317	8.472766	1.302474
C	7.069365	9.3979	-1.554754
H	5.633681	10.90606	-2.081909
C	7.367584	8.3335	-0.693299
H	7.745056	9.654333	-2.366684
C	-4.90161	-9.624364	-0.215137
C	-5.981778	-10.177693	0.512679
C	-5.083527	-8.401017	-0.876703
C	-7.202827	-9.516563	0.62229
H	-5.853167	-11.139876	0.999899
C	-6.306739	-7.74716	-0.768299
H	-4.250053	-7.934118	-1.38969
C	-7.379404	-8.271653	0.002385
H	-8.006108	-9.959443	1.20551
C	-9.837652	-4.823123	-0.244858
C	-8.609921	-4.977021	-0.904963
C	-10.363993	-5.911265	0.490558
C	-7.921383	-6.179836	-0.781762
H	-8.166643	-4.134135	-1.423811
C	-9.671333	-7.113921	0.609353
H	-11.32871	-5.802272	0.977739
C	-8.419699	-7.260599	-0.004895
H	-10.093645	-7.924614	1.197559
C	9.768792	4.872958	-0.208525
C	8.698643	5.225757	0.627893
C	10.176482	5.781268	-1.215654
C	8.033043	6.428514	0.407353
H	8.33395	4.523703	1.369287
C	9.496862	6.974022	-1.443782
H	11.032523	5.534577	-1.83635
C	8.385275	7.301953	-0.656134
H	9.815333	7.632245	-2.248049
H	10.021889	3.301095	2.026423
H	-10.464433	-0.645418	-2.147262
H	-9.958917	3.119603	2.304189
H	9.752001	-7.712279	2.248095
H	7.665091	-9.717401	2.366359
N	-6.666961	-6.50721	-1.276765
N	6.851571	-6.979516	-1.055485
N	6.908858	6.92375	1.055501

C	-5.804496	-5.625264	-2.03181
H	-6.411224	-4.986233	-2.678583
H	-5.188998	-4.988091	-1.382087
C	6.14115	-6.306522	-2.120613
H	6.855372	-5.78434	-2.762563
H	5.616979	-7.044313	-2.733544
C	6.193192	6.256417	2.120682
H	5.458787	5.533308	1.739855
H	6.903557	5.731139	2.764434
H	5.67242	6.998119	2.731741
H	5.410341	-5.579835	-1.739674
H	-5.144601	-6.218077	-2.670577
H	-6.368975	5.037345	2.67742

No imaginary frequency

*Table S 6. Atomic coordinates of αβαα-**[16]CPP4N** after geometry optimization (b3lyp/6-31g(d), methyl chains have been used instead of ethylhexyl chains, E=-4070.77815 Hartree)*

Atoms	X (Å)	Y (Å)	Z (Å)
C	-8.286028	-7.078357	0.090615
C	-8.482991	-6.491814	1.35333
C	-9.291037	-5.371089	1.513582
C	-9.933158	-4.773574	0.415999
C	-9.826984	-5.424011	-0.825671
C	-9.027947	-6.552551	-0.983118
C	-10.53054	-3.421089	0.553187
C	-10.226409	-2.456902	-0.418932
C	-10.563283	-1.126461	-0.174806
C	-11.212395	-0.72357	1.023086
C	-11.585505	-1.707374	1.947908
C	-11.242553	-3.035036	1.713241
C	-9.932604	4.774636	0.416202
C	-9.290385	5.372019	1.513801
C	-8.482212	6.492658	1.353586
C	-8.285222	7.079249	0.090897
C	-9.027229	6.553586	-0.982844
H	-7.921746	-6.858075	2.207795
H	-9.34624	-4.892589	2.487257
H	-10.361702	-5.025267	-1.683972
H	-8.960436	-7.01864	-1.962303
H	-9.63705	-2.734589	-1.286756
H	-12.104006	-1.434313	2.863386
H	-11.506894	-3.792906	2.444981
H	-9.345617	4.893472	2.487451
H	-8.959685	7.019718	-1.962007
C	-9.826387	5.425126	-0.825436
C	-10.530132	3.422211	0.553331
C	-11.242176	3.036189	1.713384
C	-10.226121	2.458035	-0.418824

C	-11.585278	1.708562	1.947993
H	-11.506427	3.794062	2.445152
C	-10.563141	1.12761	-0.174754
H	-9.636729	2.735677	-1.286638
C	-11.21229	0.724748	1.023126
H	-12.103816	1.435521	2.863457
N	-10.241539	0.000578	-0.922299
C	-9.461452	0.000511	-2.140401
H	-9.711347	-0.882819	-2.733809
H	-8.380424	0.000157	-1.942925
C	8.348606	7.169255	0.116246
C	9.145779	6.709213	-0.946975
C	9.917682	5.55654	-0.826422
C	9.933802	4.812252	0.366007
C	9.244739	5.349348	1.467404
C	8.467321	6.494994	1.344692
C	10.49179	3.437007	0.408334
C	11.637913	3.052524	-0.327164
C	12.027017	1.719123	-0.426549
C	11.271021	0.724514	0.209153
C	10.155923	1.124858	0.993916
C	9.763303	2.456161	1.097075
C	9.917112	-5.557688	-0.826098
C	9.145075	-6.710275	-0.946614
C	8.347784	-7.170145	0.116592
C	8.466503	-6.495805	1.344996
C	9.24406	-5.350248	1.467673
H	9.125697	7.232972	-1.89882
H	10.453675	5.184855	-1.695372
H	9.280178	4.832787	2.422655
H	7.880097	6.825692	2.196407
H	12.221207	3.816148	-0.833559
H	8.85116	2.726825	1.617634
H	10.453198	-5.186128	-1.695045
H	9.124979	-7.234096	-1.898425
H	7.879179	-6.82636	2.196697
H	9.279497	-4.833615	2.422885
C	9.933259	-4.81332	0.366279
C	10.491406	-3.438139	0.408538
C	9.763018	-2.457171	1.097208
C	11.637589	-3.053832	-0.326959
C	10.155793	-1.125919	0.993976
H	8.850839	-2.727702	1.617775
C	12.026845	-1.720481	-0.426419
H	12.220801	-3.817553	-0.833303
C	11.270948	-0.725748	0.209207
H	-7.920898	6.858806	2.208053
C	7.282886	-8.186521	-0.072231
C	6.574417	-8.240258	-1.285926
C	6.81729	-8.997024	0.978431

C	5.39815	-8.970683	-1.403748
H	6.906438	-7.638999	-2.127179
C	5.634281	-9.723113	0.862657
H	7.363513	-9.025241	1.917402
C	4.863491	-9.676288	-0.311843
H	5.263697	-10.273588	1.723085
C	6.575265	8.239499	-1.286214
C	5.399078	8.970059	-1.40399
C	7.283827	8.185757	-0.072572
C	4.864591	9.675796	-0.312087
H	4.858672	8.956992	-2.346511
C	6.818406	8.996375	0.978078
C	5.635471	9.722594	0.862354
H	7.3647	9.024575	1.917008
H	5.265013	10.273158	1.72278
C	-7.208474	8.081027	-0.108574
C	-6.466962	8.090329	-1.303569
C	-6.773585	8.935787	0.920085
C	-5.295078	8.827308	-1.42218
H	-6.77199	7.454272	-2.129223
C	-5.592398	9.664652	0.805908
H	-7.344288	9.000278	1.842379
C	-4.792906	9.581731	-0.34735
H	-4.734628	8.784037	-2.3519
H	-5.248522	10.250608	1.653761
C	-7.209393	-8.080255	-0.108869
C	-6.774651	-8.935115	0.919768
C	-6.467822	-8.089583	-1.303829
C	-5.593544	-9.664111	0.805613
H	-7.345402	-8.99958	1.842034
C	-5.296019	-8.826696	-1.422421
H	-6.772728	-7.453444	-2.129463
C	-4.793988	-9.581232	-0.347604
H	-5.249774	-10.250145	1.653456
H	-4.735514	-8.783437	-2.352108
C	-3.411662	-10.121764	-0.375146
C	-2.417089	-9.354224	-0.998796
C	-3.040445	-11.307668	0.301973
C	-1.088695	-9.756762	-0.898241
H	-2.677076	-8.413822	-1.472266
C	-1.709335	-11.704148	0.402836
H	-3.813261	-11.919811	0.75771
C	-0.703144	-10.917584	-0.174733
H	-1.455048	-12.609579	0.94788
C	-3.41052	10.122112	-0.374938
C	-3.039143	11.307965	0.30218
C	-2.416057	9.354473	-0.998646
C	-1.707986	11.704305	0.40298
H	-3.811873	11.920189	0.757956
C	-1.087616	9.756869	-0.898152

H	-2.676167	8.414102	-1.47211
C	-0.701908	10.917645	-0.174654
H	-1.453577	12.609708	0.948013
C	3.473312	10.192851	-0.347718
C	2.500726	9.40781	-0.983923
C	3.072823	11.366569	0.333259
C	1.163219	9.780838	-0.890771
H	2.78602	8.476214	-1.460419
C	1.733033	11.736478	0.421939
H	3.829482	11.989975	0.800896
C	0.748323	10.932201	-0.168328
H	1.455241	12.634134	0.968376
C	3.472159	-10.193201	-0.347553
C	2.499688	-9.408077	-0.983833
C	3.07151	-11.366861	0.333429
C	1.162138	-9.780968	-0.890751
H	2.785099	-8.476514	-1.460323
C	1.731679	-11.736636	0.422036
H	3.828078	-11.990336	0.801121
C	0.747084	-10.932274	-0.168309
H	1.453764	-12.634257	0.968468
H	4.85783	-8.957621	-2.346318
H	6.907142	7.638139	-2.127451
H	-10.361171	5.026487	-1.683744
H	12.898454	-1.454691	-1.019058
H	12.898592	1.453199	-1.019179
N	0.046375	9.108739	-1.367773
N	9.526385	-0.000481	1.507995
N	0.045387	-9.108754	-1.36781
C	0.06212	7.842242	-2.065977
H	0.948711	7.787047	-2.702965
H	0.068155	6.986785	-1.376654
C	8.296836	-0.000397	2.269741
H	8.265404	-0.883791	2.91273
H	8.265443	0.883098	2.912592
C	0.061296	-7.84226	-2.066017
H	0.067349	-6.986801	-1.376697
H	0.947942	-7.787143	-2.702934
H	-0.818912	-7.768962	-2.710057
H	7.407316	-0.000428	1.62484
H	-0.818146	7.769017	-2.709946
H	-9.710787	0.884177	-2.733541

No imaginary frequency

*Table S 7. Atomic coordinates of αααα-**[16]CPP4N** after geometry optimization (b3lyp/6-31g(d), methyl chains have been used instead of ethylhexyl chains, E=-4070.77702 Hartree)*

Atoms	X (Å)	Y (Å)	Z (Å)
C	-7.302234	-8.029537	0.098941
C	-6.863025	-8.899379	-0.915005
C	-5.661688	-9.595497	-0.80192

C	-4.84542	-9.459246	0.334168
C	-5.34798	-8.689542	1.397676
C	-6.541493	-7.987995	1.281049
C	-3.447401	-9.958664	0.35233
C	-2.463266	-9.128181	0.907202
C	-1.125952	-9.498498	0.80121
C	-0.724876	-10.705892	0.16763
C	-1.719956	-11.549565	-0.345426
C	-3.058353	-11.175287	-0.256216
C	4.845626	-9.45908	0.33379
C	5.661747	-9.59511	-0.802434
C	6.863071	-8.898978	-0.915542
C	7.302411	-8.029336	0.098518
C	6.541819	-7.988003	1.280729
H	-7.447099	-9.000977	-1.825621
H	-5.31633	-10.196309	-1.638866
H	-4.771266	-8.605923	2.314676
H	-6.849929	-7.337917	2.094459
H	-2.744796	-8.17681	1.345224
H	-1.451733	-12.487016	-0.82582
H	-3.823444	-11.833085	-0.658399
H	5.316279	-10.19576	-1.639451
H	6.850363	-7.338062	2.094206
C	5.348321	-8.689573	1.397377
C	3.447623	-9.958536	0.352064
C	3.058559	-11.175177	-0.256441
C	2.463487	-9.128094	0.907009
C	1.720169	-11.549523	-0.345566
H	3.823642	-11.832954	-0.658674
C	1.126195	-9.498508	0.801105
H	2.744935	-8.176689	1.345008
C	0.725091	-10.705895	0.167563
H	1.451968	-12.486987	-0.825947
N	0.000157	-8.783845	1.185545
C	0.00045	-7.500773	1.853519
H	-0.883527	-6.930747	1.555979
H	0.882189	-6.929139	1.552303
C	7.281923	8.014679	0.076927
C	6.533149	7.990013	1.267124
C	5.345582	8.700662	1.389173
C	4.836089	9.462535	0.323245
C	5.640141	9.579553	-0.823748
C	6.836044	8.875256	-0.942041
C	-3.444233	9.976961	0.354455
C	-3.057586	11.180582	-0.281034
C	-1.721049	11.562057	-0.368998
C	-0.725329	10.741071	0.178075
C	-1.125699	9.557118	0.854581
C	-2.459595	9.170662	0.943874
C	-5.345831	8.700515	1.38912

C	-6.53337	7.989826	1.267044
C	-7.282168	8.014544	0.076866
C	-6.836348	8.875213	-0.94205
C	-5.640475	9.579564	-0.823732
H	6.84637	7.347152	2.08441
H	4.779074	8.631133	2.313638
H	5.289497	10.172721	-1.663879
H	7.410748	8.963833	-1.859916
H	-3.822802	11.819865	-0.711744
H	-2.733532	8.218018	1.383938
H	-4.779282	8.630931	2.313556
H	-6.846545	7.346896	2.084296
H	-7.411066	8.963837	-1.859912
H	-5.289867	10.172807	-1.663824
C	-4.836398	9.462497	0.323239
C	3.443917	9.976983	0.354466
C	2.459276	9.170661	0.943851
C	3.057263	11.180622	-0.280986
C	1.125373	9.557098	0.854583
H	2.733233	8.218002	1.383869
C	1.720722	11.562072	-0.368961
H	3.822469	11.819928	-0.711677
C	0.725006	10.741067	0.178091
H	7.447043	-9.000394	-1.826245
C	-8.379483	7.036515	-0.128082
C	-9.131598	6.521457	0.943695
C	-8.586184	6.45776	-1.392724
C	-9.948568	5.406471	0.783005
H	-9.056615	6.984231	1.923942
C	-9.411307	5.349736	-1.555954
H	-8.018546	6.817658	-2.245759
C	-10.062015	4.759029	-0.459706
H	-9.472523	4.873908	-2.530585
C	9.131419	6.521699	0.943847
C	9.948437	5.406748	0.7832
C	8.3793	7.036689	-0.127962
C	10.061934	4.759277	-0.459492
H	10.490203	5.01474	1.64017
C	8.58605	6.457916	-1.392586
C	9.411232	5.349925	-1.555772
H	8.018417	6.81778	-2.245639
H	9.472495	4.874074	-2.530388
C	8.403703	-7.055689	-0.106208
C	9.149209	-6.533554	0.966735
C	8.618132	-6.485438	-1.373386
C	9.965924	-5.418707	0.803888
H	9.068276	-6.99007	1.949463
C	9.442521	-5.377126	-1.538515
H	8.056013	-6.851569	-2.227446
C	10.08507	-4.778139	-0.441922

H	10.502078	-5.020718	1.661628
H	9.508479	-4.907177	-2.515671
C	-8.403528	-7.055913	-0.105854
C	-8.618046	-6.485831	-1.373095
C	-9.148977	-6.533636	0.967057
C	-9.442435	-5.377537	-1.538321
H	-8.055993	-6.85207	-2.227151
C	-9.965704	-5.418807	0.804114
H	-9.068003	-6.990011	1.949849
C	-10.084923	-4.778401	-0.441771
H	-9.508451	-4.90772	-2.515536
H	-10.501805	-5.020711	1.661837
C	-10.689773	-3.429575	-0.582424
C	-10.390696	-2.463702	0.389587
C	-11.398708	-3.045315	-1.745039
C	-10.727316	-1.133961	0.142605
H	-9.803025	-2.738959	1.259247
C	-11.740914	-1.717902	-1.982913
H	-11.660148	-3.803927	-2.477068
C	-11.370862	-0.732197	-1.058654
H	-12.255746	-1.446507	-2.900955
C	10.689924	-3.429299	-0.582438
C	11.398996	-3.044976	-1.744949
C	10.390705	-2.46347	0.389574
C	11.74121	-1.717546	-1.982721
H	11.660547	-3.803553	-2.476974
C	10.727329	-1.133712	0.142692
H	9.802929	-2.738776	1.259147
C	11.371017	-0.731886	-1.05847
H	12.256155	-1.446103	-2.900685
C	10.671608	3.41221	-0.596068
C	10.378012	2.44886	0.380066
C	11.381272	3.02692	-1.757845
C	10.721204	1.11985	0.138165
H	9.789896	2.724901	1.249196
C	11.73074	1.700419	-1.990283
H	11.637864	3.783943	-2.493234
C	11.366804	0.71666	-1.061544
H	12.246456	1.427944	-2.907507
C	-10.671616	3.411934	-0.59632
C	-10.378116	2.448628	0.379885
C	-11.381134	3.026583	-1.758167
C	-10.72124	1.119599	0.137989
H	-9.790118	2.724715	1.249082
C	-11.730531	1.700063	-1.990603
H	-11.637663	3.78357	-2.493615
C	-11.366684	0.716348	-1.061783
H	-12.246122	1.42754	-2.907884
H	-10.490325	5.014416	1.639959
H	9.056393	6.984509	1.924071

H	4.771735	-8.606135	2.314472
H	1.45438	12.484105	-0.879303
H	-1.454721	12.48409	-0.879347
N	10.406624	-0.006284	0.889802
N	-0.000176	8.876928	1.298339
N	-10.406732	-0.006497	0.889711
C	9.630269	-0.005901	2.110234
H	9.879643	0.879234	2.701157
H	8.548617	-0.008772	1.916096
C	-0.000297	7.584194	1.946805
H	0.883626	7.494607	2.58364
H	-0.883364	7.4954	2.584964
C	-9.630549	-0.00605	2.110252
H	-8.548869	-0.008918	1.916267
H	-9.880016	0.87911	2.701099
H	-9.884145	-0.88786	2.704335
H	-0.001212	6.756248	1.224713
H	9.883791	-0.887736	2.704312
H	0.002812	-7.602864	2.946817

No imaginary frequency

*Table S 8. Atomic coordinates of ααα-**[12]CPP3N** after geometry optimization (b3lyp/6-31g(d), methyl chains have been used instead of ethylhexyl chains, E=-3053.04469 Hartree)*

Atoms	X (Å)	Y (Å)	Z (Å)
C	7.756176	-2.264725	0.867909
C	7.273198	-3.567019	0.83253
C	7.143631	-4.273027	-0.378581
C	7.681792	-3.655762	-1.52318
C	8.139337	-2.341534	-1.49304
C	6.274746	-5.47699	-0.459533
C	5.890957	-6.204438	0.683874
C	4.793115	-7.060091	0.66359
C	4.043433	-7.254373	-0.509016
C	4.53424	-6.67149	-1.688511
C	5.615135	-5.796319	-1.661234
C	2.663693	-7.808351	-0.489695
C	1.778536	-7.268307	0.453674
C	0.41257	-7.499945	0.305389
C	-0.104874	-8.303554	-0.746552
C	0.799982	-8.918838	-1.623466
C	2.163146	-8.660548	-1.501235
C	-5.785548	-5.563766	0.860547
C	-6.678095	-4.500068	0.811412
C	-7.224532	-4.051717	-0.406074
C	-6.950636	-4.836063	-1.542058
C	-6.03555	-5.884087	-1.498116
C	-7.84231	-2.702714	-0.50168
C	-8.299726	-2.003756	0.632342
C	-8.501902	-0.626776	0.601814

C	-8.285413	0.114659	-0.572235
C	-8.00624	-0.606529	-1.744423
C	-7.779497	-1.978426	-1.70683
C	-8.083193	1.587679	-0.558901
C	-7.192289	2.09506	0.397102
C	-6.707758	3.392627	0.244294
C	-7.12468	4.230725	-0.825221
C	-8.094307	3.74557	-1.714543
C	-8.553734	2.437006	-1.587282
C	-6.264256	5.397383	-0.788362
C	-5.359449	5.193055	0.28747
C	-4.250534	6.011933	0.484653
C	-4.01793	7.076887	-0.39907
C	-4.975732	7.346463	-1.407325
C	-6.079993	6.52255	-1.604661
C	-2.682475	7.727017	-0.3687
C	-1.911239	7.767418	0.806976
C	-0.541642	7.998265	0.766964
C	0.131555	8.232617	-0.447023
C	-0.674473	8.383815	-1.59074
C	-2.041652	8.125097	-1.555762
C	1.608613	8.084475	-0.530394
C	2.434613	8.133712	0.609347
C	3.727641	7.618234	0.590011
C	4.269331	7.055284	-0.578143
C	3.512653	7.168583	-1.755697
C	2.211729	7.660102	-1.729199
C	5.44666	6.147512	-0.554446
C	5.441078	5.126606	0.40615
C	6.330084	4.062986	0.263471
C	7.270256	4.005398	-0.801007
C	7.333029	5.08354	-1.695426
C	6.42294	6.131045	-1.577694
C	7.859225	2.681149	-0.754095
C	7.229761	2.001774	0.322858
C	7.39291	0.634287	0.52891
C	8.918676	0.593858	-1.357045
C	8.749574	1.960036	-1.5626
H	7.794907	-1.746154	1.821761
H	6.908249	-4.005175	1.756044
H	7.679796	-4.180844	-2.473702
H	8.434678	-1.870556	-2.426035
H	6.423102	-6.062972	1.620058
H	4.482463	-7.551243	1.582419
H	3.986459	-6.80876	-2.616786
H	5.871868	-5.270223	-2.57494
H	2.15026	-6.574804	1.200783
H	0.439853	-9.553836	-2.428887
H	2.857433	-9.097702	-2.213367
H	-5.356338	-5.844051	1.818409
H	-6.880787	-3.955621	1.728268

H	-7.403202	-4.583791	-2.496448
H	-5.76988	-6.384316	-2.424836
H	-8.450987	-2.531644	1.569462
H	-8.787389	-0.109147	1.514246
H	-7.842712	-0.067502	-2.673543
H	-7.436945	-2.466833	-2.613346
H	-6.789482	1.434118	1.157424
H	-8.449136	4.366259	-2.533365
H	-9.26573	2.046472	-2.308956
H	-3.507711	5.755198	1.231128
H	-4.829316	8.199095	-2.063726
H	-6.771259	6.732399	-2.416897
H	-2.37765	7.54743	1.76318
H	0.022866	7.90542	1.689382
H	-0.220469	8.639045	-2.543618
H	-2.599581	8.141205	-2.487412
H	2.047475	8.533516	1.542078
H	4.312423	7.610157	1.506499
H	3.903538	6.752913	-2.680341
H	1.623757	7.604415	-2.639574
H	4.663291	5.107298	1.162404
H	8.05231	5.080765	-2.510445
H	6.440053	6.939865	-2.302795
H	6.799463	0.119942	1.276004
H	9.58951	0.041138	-2.008048
H	9.27705	2.452481	-2.375544
C	8.206708	-0.099581	-0.347661
C	8.108775	-1.581473	-0.309988
C	-5.3642	-6.221553	-0.309186
C	-4.127634	-7.044466	-0.332832
C	-3.881012	-8.026094	-1.323749
C	-3.08704	-6.689867	0.539253
C	-2.613363	-8.568295	-1.514908
H	-4.693685	-8.342041	-1.971114
C	-1.82161	-7.238478	0.348241
H	-3.23751	-5.904378	1.270934
C	-1.545977	-8.144954	-0.710006
H	-2.448967	-9.286899	-2.313771
N	6.367013	2.871941	0.978633
N	-0.638562	-6.917429	1.003448
N	-5.688577	4.017882	0.952585
C	-4.912014	3.40774	2.020777
H	-5.601814	2.819971	2.634456
H	-4.536328	4.212797	2.663233
C	5.451008	2.503143	2.046872
H	5.268697	3.399285	2.648097
H	5.969338	1.792261	2.701242
C	-0.499478	-5.911168	2.044177
H	0.359389	-6.189058	2.665728
H	-1.381302	-5.975945	2.691816
C	4.128814	1.895848	1.54675

H	3.618337	2.627739	0.907081
H	4.363601	1.036332	0.906955
C	3.191057	1.449182	2.680076
H	2.355902	0.892049	2.236333
H	3.718721	0.734913	3.328869
C	2.628713	2.59545	3.53075
H	2.094852	3.323156	2.907031
H	1.922723	2.21809	4.279105
H	3.415538	3.134723	4.070849
C	-0.331356	-4.478988	1.511572
H	0.547684	-4.442652	0.855072
H	-1.19652	-4.226187	0.884834
C	-0.183786	-3.44842	2.637794
H	-1.063543	-3.497212	3.295513
H	0.679709	-3.713731	3.264559
C	-0.015095	-2.016886	2.117825
H	-0.879479	-1.709838	1.51673
H	0.088986	-1.303785	2.943687
H	0.876023	-1.928687	1.484668
C	-3.744508	2.540396	1.51902
H	-4.143116	1.735975	0.887059
H	-3.109307	3.156889	0.87112
C	-2.893121	1.941034	2.649962
H	-2.010398	1.467569	2.201277
H	-2.509906	2.751764	3.286621
C	-3.622932	0.908436	3.518895
H	-4.017409	0.087547	2.907166
H	-2.945208	0.472946	4.261781
H	-4.464198	1.348478	4.06675

No imaginary frequency

*Table S 9. Atomic coordinates of αβα-**[12]CPP3N** after geometry optimization (b3lyp/6-31g(d), methyl chains have been used instead of ethylhexyl chains, E=-3053.04493 Hartree)*

Atoms	X (Å)	Y (Å)	Z (Å)
C	-6.713149	5.377584	0.774671
C	-5.752902	6.385063	0.786412
C	-4.930427	6.625647	-0.331211
C	-5.250707	5.933235	-1.513638
C	-6.229118	4.943814	-1.534334
C	-3.646495	7.367288	-0.220856
C	-2.981354	7.438401	1.017562
C	-1.639204	7.784982	1.101806
C	-0.87944	8.05562	-0.050153
C	-1.580664	8.147468	-1.265186
C	-2.932709	7.820876	-1.345897
C	0.604592	8.005766	-0.010878
C	1.18984	7.061897	0.845987
C	2.551896	6.802159	0.741579
C	3.379095	7.459824	-0.208599
C	2.799536	8.457217	-1.006937
C	1.434605	8.720416	-0.907582

C	7.646042	2.807234	1.355055
C	8.076967	1.488562	1.286823
C	8.442924	0.896951	0.062881
C	8.524177	1.756257	-1.049527
C	8.069393	3.071076	-0.98662
C	8.471151	-0.583529	-0.069545
C	8.574362	-1.439575	1.043562
C	8.170118	-2.770603	0.976345
C	7.663318	-3.31976	-0.214666
C	7.758246	-2.521808	-1.369052
C	8.138604	-1.187897	-1.296768
C	0.911725	-7.993035	-0.072288
C	1.466936	-7.024173	-0.921273
C	2.816688	-6.711269	-0.804142
C	3.660736	-7.338284	0.151965
C	3.113889	-8.360111	0.942536
C	1.761456	-8.67696	0.830053
C	4.918472	-6.613063	0.120941
C	4.762268	-5.587457	-0.850249
C	5.700072	-4.574498	-1.017857
C	6.845626	-4.559773	-0.208281
C	7.05028	-5.624999	0.701805
C	6.106418	-6.636711	0.866867
C	-0.569296	-8.101428	-0.0469
C	-1.278347	-8.230059	1.160254
C	-2.642243	-7.954873	1.230481
C	-3.362958	-7.51761	0.102797
C	-2.683448	-7.555674	-1.129719
C	-1.328815	-7.851278	-1.203653
C	-4.672904	-6.823111	0.207997
C	-5.055503	-6.19193	1.406805
C	-6.060913	-5.232841	1.435354
C	-6.720572	-4.825455	0.261223
C	-6.458832	-5.577831	-0.89823
C	-5.472697	-6.559043	-0.919859
C	-7.457805	-3.5374	0.187895
C	-7.047229	-2.491366	1.028894
C	-7.49808	-1.198722	0.776416
C	-8.345925	-0.895972	-0.322052
C	-8.835717	-1.961021	-1.09111
C	-8.401053	-3.257566	-0.831772
C	-8.370883	0.550311	-0.432208
C	-7.557246	1.045271	0.622839
C	-7.191914	2.386596	0.707738
C	-8.473041	2.797377	-1.316598
C	-8.862784	1.461188	-1.377883
H	-7.281039	5.170352	1.678273
H	-5.606391	6.955833	1.69885
H	-4.651074	6.083931	-2.405818
H	-6.372611	4.358054	-2.438223
H	-3.492225	7.128816	1.923726

H	-1.153105	7.778294	2.073418
H	-1.041256	8.385036	-2.17798
H	-3.418508	7.854504	-2.316849
H	0.564033	6.459561	1.494627
H	3.401226	9.000762	-1.730898
H	0.992729	9.477769	-1.548821
H	7.320223	3.204913	2.312146
H	8.031644	0.88485	2.187565
H	8.874991	1.374969	-2.004042
H	8.038571	3.659932	-1.899152
H	8.901802	-1.04569	2.001282
H	8.153329	-3.360742	1.888427
H	7.456121	-2.930979	-2.329052
H	8.078583	-0.585917	-2.197799
H	0.823807	-6.444846	-1.573844
H	3.730171	-8.881652	1.670414
H	1.344386	-9.453417	1.465039
H	5.49136	-3.738311	-1.675234
H	7.953897	-5.640791	1.304453
H	6.278627	-7.418585	1.602144
H	-0.739372	-8.454734	2.07659
H	-3.133516	-8.01533	2.197254
H	-3.195026	-7.25961	-2.039668
H	-0.835266	-7.819503	-2.170961
H	-4.500114	-6.382309	2.319769
H	-6.287384	-4.742197	2.377686
H	-6.964794	-5.329094	-1.826274
H	-5.27767	-7.074264	-1.855587
H	-6.285531	-2.665016	1.78024
H	-9.518256	-1.776211	-1.916669
H	-8.767965	-4.069175	-1.452797
H	-6.485139	2.727477	1.457163
H	-8.813495	3.490455	-2.080836
H	-9.50083	1.12067	-2.189379
C	-7.60909	3.266903	-0.300733
C	-6.919374	4.583072	-0.365793
C	7.531309	3.600821	0.199449
C	6.666793	4.808591	0.184712
C	6.837732	5.8797	-0.725417
C	5.514721	4.780125	0.984628
C	5.856595	6.853532	-0.900514
H	7.74511	5.929717	-1.320481
C	4.539732	5.755599	0.807235
H	5.33303	3.937167	1.641386
C	4.664079	6.784699	-0.164774
H	6.004417	7.640213	-1.635956
N	-7.103646	-0.017974	1.393405
N	3.286184	5.825002	1.398207
N	3.517568	-5.704311	-1.452047
C	2.95388	-4.767786	-2.399427
H	2.214693	-5.27866	-3.021709

H	3.743306	-4.393722	-3.056296
C	-6.13099	0.081238	2.45949
H	-6.251618	-0.763673	3.142342
H	-6.304762	0.998542	3.027778
C	2.750782	4.86829	2.341574
H	1.988919	5.351545	2.958666
H	3.548854	4.523436	3.00394
H	2.470698	-3.914032	-1.90442
H	-5.098589	0.088261	2.082681
H	2.3029	3.997318	1.843253
C	-6.713149	5.377584	0.774671
C	-5.752902	6.385063	0.786412
C	-4.930427	6.625647	-0.331211
C	-5.250707	5.933235	-1.513638
C	-6.229118	4.943814	-1.534334
C	-3.646495	7.367288	-0.220856
C	-2.981354	7.438401	1.017562
C	-1.639204	7.784982	1.101806
C	-0.87944	8.05562	-0.050153
C	-1.580664	8.147468	-1.265186
C	-2.932709	7.820876	-1.345897
C	0.604592	8.005766	-0.010878
C	1.18984	7.061897	0.845987
C	2.551896	6.802159	0.741579
C	3.379095	7.459824	-0.208599
C	2.799536	8.457217	-1.006937
C	1.434605	8.720416	-0.907582
C	7.646042	2.807234	1.355055
C	8.076967	1.488562	1.286823
C	8.442924	0.896951	0.062881
C	8.524177	1.756257	-1.049527
C	8.069393	3.071076	-0.98662
C	8.471151	-0.583529	-0.069545
C	8.574362	-1.439575	1.043562
C	8.170118	-2.770603	0.976345
C	7.663318	-3.31976	-0.214666
C	7.758246	-2.521808	-1.369052

No imaginary frequency

*Table S 10. Atomic coordinates of **[8]CPP4N** after geometry optimization (b3lyp/6-31g(d))*

Atoms	X (Å)	Y (Å)	Z (Å)
N	3.905216	-0.58033	-2.72035
C	4.387727	0.461458	-1.928899
C	4.187643	-1.775631	-2.063766
C	3.001817	-0.46021	-3.85512
N	-0.28654	-5.136497	1.291706
C	-1.580827	-5.169568	0.771711
C	0.594622	-5.359082	0.235844
N	0.576123	4.143806	1.858547

C	-0.68163	4.498112	1.36977
C	1.497255	4.335115	0.831358
C	3.540325	-3.001827	-2.226667
C	5.03597	-1.518062	-0.954563
C	3.693405	-3.985789	-1.239229
H	2.771225	-3.120068	-2.982215
C	4.66412	-3.792164	-0.225824
C	2.563726	-4.95113	-1.094083
C	1.935768	-4.978898	0.159858
C	1.89177	-5.510761	-2.207994
C	0.562582	-5.916323	-2.123178
H	2.399577	-5.545046	-3.168136
C	-0.134384	-5.760554	-0.914726
H	0.047121	-6.264395	-3.014914
C	-1.537901	-5.641361	-0.568355
H	2.422871	-4.514151	1.009554
C	5.332943	-2.579454	-0.084842
H	4.827477	-4.579364	0.50526
H	6.013144	-2.432725	0.75054
C	5.168007	-0.076102	-0.869409
C	5.652127	0.800719	0.114576
C	5.222216	2.124125	0.1303
H	6.288941	0.430684	0.914338
C	4.308469	2.611073	-0.836
H	5.524972	2.774835	0.946236
C	3.977626	1.796159	-1.928043
C	3.37418	3.742559	-0.559392
C	2.747857	3.729921	0.695323
C	2.829164	4.549745	-1.587716
H	3.133263	3.083686	1.476417
C	0.869207	5.00785	-0.249982
C	1.597434	5.181085	-1.437694
C	-0.534731	5.11584	0.098291
H	1.166763	5.728364	-2.272585
H	3.345958	4.608393	-2.541936
H	3.238023	2.145938	-2.639831
C	3.617954	-0.93305	-5.191505
H	2.69816	0.586202	-3.935056
H	2.091497	-1.031874	-3.63648
C	4.882729	-0.134107	-5.578152
H	3.942769	-1.973577	-5.042893
C	4.681429	1.348658	-5.92729
H	5.344714	-0.636833	-6.439945
H	5.609352	-0.211042	-4.758842
C	5.994506	2.048003	-6.30611
H	3.97132	1.448337	-6.760146
H	4.235169	1.882147	-5.076316
C	5.811272	3.528336	-6.655041
H	6.706067	1.952801	-5.474166
H	6.450359	1.524007	-7.158344
H	5.128431	3.655037	-7.504454

H	6.765078	3.997341	-6.922235
H	5.392763	4.086136	-5.808123
H	0.702058	-3.676549	2.39495
H	-0.798324	-4.258149	3.09781
C	0.892909	-5.546537	3.501466
C	0.108521	-4.581611	2.579516
H	1.638043	-6.073301	2.887516
C	1.647981	-4.731329	4.57967
H	1.938234	-5.417268	5.384773
C	2.900229	-3.991123	4.083676
H	0.954377	-4.008808	5.038712
H	3.611979	-4.725394	3.677508
H	2.639701	-3.326972	3.248819
C	3.606451	-3.149013	5.160939
H	4.403117	-2.566824	4.678922
H	2.896666	-2.41351	5.566243
C	4.213156	-3.961127	6.311591
H	4.925257	-4.706465	5.935385
H	4.752334	-3.310043	7.009112
H	3.448249	-4.494265	6.887123
C	-2.734253	-4.591122	1.304392
C	-2.728339	-5.650398	-1.311971
C	-3.859687	-4.43134	0.482721
H	-2.704562	-4.079533	2.260046
C	-3.869904	-5.047399	-0.792071
H	-2.740098	-6.045311	-2.324849
C	-4.775739	-3.307396	0.838984
H	-4.762941	-4.974486	-1.406929
C	-4.955586	-2.323976	-0.143932
C	-5.133274	-3.011554	2.177079
C	-5.27647	-1.022118	0.246475
H	-4.645764	-2.533772	-1.161492
H	-5.054175	-3.791131	2.929992
C	-5.481352	-1.72065	2.561865
N	-5.16811	0.147625	-0.508955
C	-5.469609	-0.685912	1.612754
H	-5.672474	-1.502496	3.609683
C	-5.070483	1.215324	0.385478
C	-4.884492	0.207092	-1.938191
C	-5.337508	0.754772	1.70233
C	-4.513742	2.475109	0.154031
H	-4.181802	1.02843	-2.109512
H	-4.352773	-0.709925	-2.212955
C	-6.124579	0.369038	-2.852992
C	-5.173142	1.650609	2.770834
C	-4.169863	3.281612	1.248477
H	-4.156095	2.745872	-0.832616
H	-5.729204	0.305011	-3.880325
C	-6.800703	1.747574	-2.689994
H	-5.412816	1.344149	3.786067
C	-4.591933	2.894326	2.543592

C	-3.055587	4.249975	1.023194
H	-7.810729	1.706586	-3.116787
H	-6.937795	1.956382	-1.620281
C	-6.052736	2.91154	-3.356654
H	-4.380831	3.54783	3.385763
C	-1.929691	4.090263	1.843386
C	-2.935058	5.011419	-0.164983
H	-5.991216	2.726631	-4.439638
H	-5.013052	2.955187	-3.001563
C	-6.714429	4.273759	-3.110882
H	-2.007992	3.471332	2.730337
C	-1.694267	5.445549	-0.621505
H	-3.819614	5.189456	-0.770822
H	-6.762382	4.459217	-2.028717
H	-7.756348	4.237923	-3.459596
C	-5.985479	5.432926	-3.797993
H	-1.620152	5.95995	-1.57647
H	-5.951643	5.292519	-4.885542
H	-6.480898	6.390371	-3.601048
H	-4.949808	5.515637	-3.444549
C	0.853886	3.394109	3.074699
H	-0.101645	3.082451	3.506674
H	1.387816	2.476714	2.799818
C	1.653742	4.192216	4.130364
C	0.812746	5.380332	4.640956
H	-0.040065	4.976676	5.20885
H	2.548464	4.584063	3.627765
H	0.380943	5.895423	3.773187
C	1.519025	6.437452	5.512527
H	0.74153	7.142665	5.834232
H	1.900897	5.984352	6.438057
C	2.652685	7.233114	4.825549
C	4.063549	6.662617	5.024753
H	2.647221	8.259408	5.215308
H	2.437071	7.321634	3.751516
H	4.166535	5.651047	4.617543
H	4.814326	7.291975	4.53275
H	4.3182	6.615396	6.090946
C	2.555717	-0.937837	-6.31283
H	3.073976	-1.048491	-7.27489
H	2.053523	0.0389	-6.35379
C	1.501644	-2.046887	-6.195457
H	1.972331	-3.037628	-6.1792
H	0.895276	-1.953046	-5.287368
H	0.813285	-2.021676	-7.047861
C	-0.001545	-6.608646	4.178086
H	-0.761257	-6.094817	4.787071
H	0.627621	-7.15868	4.891208
C	-0.685143	-7.626597	3.256496
H	-1.170459	-8.408248	3.85279
H	-1.451456	-7.171752	2.623631

H	0.042218	-8.115096	2.597184
C	2.105562	3.262213	5.276005
H	2.476669	3.878224	6.103432
H	1.226576	2.730746	5.671322
C	3.196975	2.249677	4.903624
H	2.870366	1.542116	4.133276
H	4.093711	2.75784	4.52776
H	3.494787	1.660403	5.778331
C	-7.117688	-0.798846	-2.668836
H	-6.554008	-1.738204	-2.595035
H	-7.637925	-0.684739	-1.708878
C	-8.142889	-0.94182	-3.800411
H	-8.787466	-0.060804	-3.892359
H	-7.646498	-1.091712	-4.76745
H	-8.794858	-1.804861	-3.624808

No imaginary frequency

*Table S 11. Atomic coordinates of **[8]CPP4N** after geometry optimization (methyl chains have been used instead of ethylhexyl substituents, b3lyp/6-31g(d), E=-2222.24976 Hartree)*

Atoms	X (Å)	Y (Å)	Z (Å)
N	-0.9757	4.6138	1.6313
C	0.0867	5.0191	0.8271
C	-2.1118	4.5541	0.8278
C	-0.8267	3.9112	2.8875
N	-4.6143	-0.9757	-1.6314
C	-4.5544	-2.1117	-0.8278
C	-5.0195	0.0867	-0.8271
N	4.6143	0.9758	-1.6314
C	5.0195	-0.0867	-0.8271
C	4.5544	2.1118	-0.8279
C	-3.2593	3.7915	1.0427
C	-1.8334	5.1563	-0.4278
C	-4.1476	3.5891	-0.0242
H	-3.3594	3.1916	1.941
C	-3.9607	4.3266	-1.2184
C	-4.9613	2.3385	0.0263
C	-4.7874	1.4449	-1.0414
C	-5.5591	1.8681	1.2206
C	-5.8108	0.5132	1.4223
H	-5.7465	2.5707	2.0282
C	-5.457	-0.4124	0.4284
H	-6.1933	0.1728	2.3813
C	-5.1565	-1.8334	0.4279
H	-4.2804	1.7799	-1.94
C	-2.824	5.1053	-1.4208
H	-4.6798	4.2139	-2.0253
H	-2.6684	5.5931	-2.3799
C	-0.4124	5.4567	-0.4284
C	0.5132	5.8106	-1.4222
C	1.8681	5.559	-1.2205
H	0.1728	6.1932	-2.3812

C	2.3385	4.9611	-0.0262
H	2.5707	5.7465	-2.0281
C	1.445	4.787	1.0414
C	3.5892	4.1476	0.0242
C	3.7917	3.2593	-1.0428
C	4.3267	3.9607	1.2185
H	3.1919	3.3594	-1.9411
C	5.1565	1.8335	0.4278
C	5.1054	2.8239	1.4208
C	5.457	0.4125	0.4284
H	5.5932	2.6684	2.3799
H	4.2138	4.6797	2.0254
H	1.7799	4.28	1.9399
H	-0.0202	4.3686	3.4661
H	-0.6011	2.8442	2.7452
H	-2.8448	-0.6005	-2.7451
H	-4.003	-1.7488	-3.4666
C	-3.9116	-0.8266	-2.8875
C	-3.7917	-3.2592	-1.0427
C	-5.1054	-2.8239	1.4209
C	-3.5891	-4.1475	0.0242
H	-3.1919	-3.3594	-1.9411
C	-4.3266	-3.9606	1.2185
H	-5.5931	-2.6683	2.38
C	-2.3385	-4.9611	-0.0263
H	-4.2137	-4.6796	2.0254
C	-1.4449	-4.7869	1.0413
C	-1.8681	-5.559	-1.2206
C	-0.0867	-5.0191	0.827
H	-1.7798	-4.2797	1.9398
H	-2.5707	-5.7465	-2.0281
C	-0.5133	-5.8106	-1.4222
N	0.9757	-4.6138	1.6312
C	0.4124	-5.4567	-0.4285
H	-0.1729	-6.1932	-2.3812
C	2.1118	-4.5541	0.8278
C	0.827	-3.9117	2.8878
C	1.8335	-5.1563	-0.4279
C	3.2593	-3.7914	1.0427
H	0.6019	-2.8446	2.7461
H	0.0205	-4.3692	3.4662
C	2.824	-5.1053	-1.4209
C	4.1477	-3.589	-0.0242
H	3.3592	-3.1915	1.9409
H	2.6685	-5.5931	-2.3799
C	3.9608	-4.3266	-1.2184
C	4.9613	-2.3384	0.0262
H	4.6798	-4.2139	-2.0254
C	4.7874	-1.4449	-1.0414
C	5.5591	-1.868	1.2206
H	4.2804	-1.7799	-1.94

C	5.8107	-0.5132	1.4222
H	5.7464	-2.5706	2.0281
H	6.1932	-0.1728	2.3812
C	3.9112	0.8266	-2.8874
H	4.3688	0.0204	-3.4663
H	2.8445	0.6005	-2.7447
H	-4.3692	-0.0204	-3.4663
H	1.7492	-4.0043	3.4669
H	4.0025	1.7488	-3.4665
H	-1.7488	4.0031	3.4667

No imaginary frequency

*Table S 12. Atomic coordinates of **[8]CPP** in the geometry of **[8]CPP4N***

Atoms	X (Å)	Y (Å)	Z (Å)
C	4.38772747	-0.4614569	1.92889913
C	4.18764286	1.77563225	2.06376614
C	-1.5808285	5.16956796	-0.7717111
C	0.59462065	5.35908257	-0.235844
C	-0.6816288	-4.4981125	-1.3697701
C	1.49725629	-4.3351149	-0.8313581
C	3.54032449	3.00182817	2.22666715
C	5.03596999	1.51806346	0.95456306
C	3.69340424	3.98579028	1.23922908
H	2.77122441	3.12006897	2.98221521
C	4.66411936	3.79216552	0.22582401
C	2.5637249	4.95113105	1.09408307
C	1.93576685	4.97889888	-0.159858
C	1.89176871	5.51076191	2.20799415
C	0.5625805	5.91632357	2.12317814
H	2.39957573	5.54504704	3.16813622
C	-0.1343855	5.76055437	0.91472606
H	0.04711937	6.26439546	3.01491421
C	-1.5379026	5.641361	0.56835503
H	2.42287001	4.51415198	-1.0095541
C	5.33294274	2.57945561	0.084842
H	4.82747617	4.57936562	-0.5052601
H	6.01314385	2.43272679	-0.7505401
C	5.16800739	0.07610339	0.86940905
C	5.65212764	-0.8007175	-0.114576
C	5.22221698	-2.1241238	-0.1303
H	6.28894161	-0.4306824	-0.9143381
C	4.30847004	-2.611072	0.83600005
H	5.52497318	-2.7748337	-0.9462361
C	3.9776268	-1.7961581	1.92804313
C	3.37418127	-3.7425584	0.55939203
C	2.74785822	-3.7299205	-0.6953231
C	2.82916545	-4.5497446	1.5877161
H	3.13326408	-3.0836854	-1.4764171
C	0.86920843	-5.0078501	0.24998201
C	1.59743553	-5.1810849	1.43769409
C	-0.5347296	-5.1158405	-0.098291

H	1.16676464	-5.7283641	2.27258516
H	3.3459595	-4.6083924	2.54193617
H	3.23802384	-2.1459373	2.63983118
C	-2.7342544	4.59112161	-1.3043921
C	-2.7283407	5.65039771	1.31197108
C	-3.8596884	4.4313393	-0.482721
H	-2.7045632	4.07953258	-2.2600462
C	-3.8699056	5.04739834	0.79207105
H	-2.7400998	6.04531073	2.32484916
C	-4.7757402	3.30739498	-0.8389841
H	-4.7629426	4.9744851	1.40692909
C	-4.9555869	2.32397485	0.143932
C	-5.1332751	3.01155286	-2.1770792
C	-5.2764706	1.02211668	-0.246475
H	-4.645765	2.53377095	1.16149208
H	-5.0541763	3.79112994	-2.9299922
C	-5.4813528	1.72064868	-2.5618652
C	-5.4696095	0.6859106	-1.6127541
H	-5.6724748	1.50249461	-3.6096833
C	-5.070483	-1.2153254	-0.385478
C	-5.3375082	-0.7547735	-1.7023301
C	-4.5137416	-2.4751104	-0.154031
C	-5.1731419	-1.6506105	-2.7708342
C	-4.1698624	-3.2816133	-1.2484771
H	-4.1560945	-2.7458733	0.83261605
H	-5.412816	-1.3441505	-3.7860673
C	-4.5919325	-2.8943274	-2.5435922
C	-3.0555861	-4.2499761	-1.0231941
H	-4.3808303	-3.5478314	-3.3857633
C	-1.92969	-4.0902638	-1.8433861
C	-2.9350568	-5.0114201	0.164983
H	-2.0079912	-3.4713328	-2.7303372
C	-1.6942656	-5.4455498	0.62150504
H	-3.8196129	-5.1894574	0.77082204
H	-1.6201505	-5.9599508	1.5764701
H	4.04041547	1.00858061	2.79510456
H	4.10831011	0.17093954	2.74553903
H	-5.3789834	0.26189438	0.49948287
H	-5.3007638	-0.58367	0.44691742
H	0.99806797	-4.2908245	-1.7767413
H	0.18465314	-4.3420537	-1.9781296
H	0.10303487	5.34765495	-1.1861665
H	-0.7094341	5.25980242	-1.3860641

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