Electronic Supplementary Material (ESI) for Chemical Communications

Supporting Information

The Right Way to Self-fuse Bi- and Terpyrenyls to Afford Graphenic Cutouts

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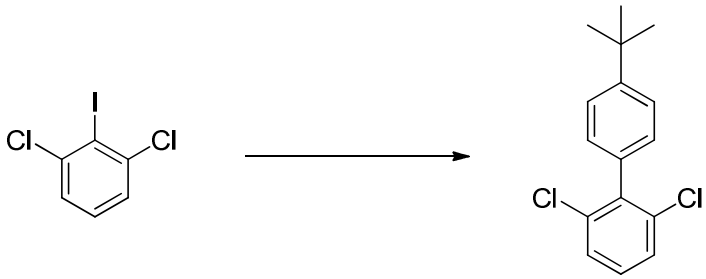
S1. Experimental Details

Commercially available reagents were used without further purification unless otherwise stated. Melting points were determined on a Büchi hot stage apparatus and are uncorrected. Fielddesorption mass spectra were obtained on a VG Instruments ZAB 2-SE-FPD spectrometer. ^{1}H-NMR and ^{13}C-NMR experiments were recorded in the listed deuterated solvents on a Bruker AVANCE 300, a Bruker AVANCE 500 or a Bruker AVANCE 700 spectrometer. The deuterated solvent was used as an internal standard. Mass spectra were obtained using FD on a VG Instruments ZAB 2 SE-FPD. High resolution MALDI mass spectrometry measurements were performed on a Solarix ESI-/MALDI-ICR (9.4T) system (Bruker Daltonics, Germany), with a SmartBeam laser II. The system was internally calibrated in positive mode using sodium trifluoroacetate (Fluka, >99%) or sodium perfluoroheptanoate (Fluka, >99%) on quadratic calibration mode. A total of 10-100 shots were accumulated for each mass spectra. The results were calculated using Data Analysis software (Bruker Daltonics, Germany). The samples were prepared with trans-2-[3-(4-*tert*-butylphenyl)-2-methyl-2-propenylidene]-malononitrile (DCTB; Aldrich, >99%), 3-hydroxypicolinic acid (3-HPA; Aldrich, >99%) or alpha-cyano-4-hydroxycinnamic acid (CCA; Aldrich, >99%) as matrix.

Elemental analysis of solid samples was carried out on a Foss Heraeus Vario EL.

S2. Synthesis

4'-(*Tert*-butyl)-2,6-dichloro-1,1'-biphenyl (7)



6 **7**

A solution of 2-(4-(*tert*-butyl)phenyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (1.00 g, 3.85 mmol, 1.05 equiv.), 1,3-dichloro-2-iodobenzene (**6**, 1.00 g, 3.66 mmol, 1 equiv.) and K_2CO_3 (0.64 g, 4.66 mmol, 1.27 equiv.) in 20 mL dry dimethylformamide was degassed for 30 min. Then 149 mg $Pd(dppf)Cl_2$ (0.183 mmol) were added and the resulting mixture was heated to 60°C for 16 h. dichloromethane was added, the organic phase was extracted, washed with water, dried over $MgSO_4$ and the organic solvent were removed under vacuum. Column chromatography on silica with petroleum ether (PE) gave **5** (0.73 g, 2.63 mmol) as colorless oil in 71 % yield.

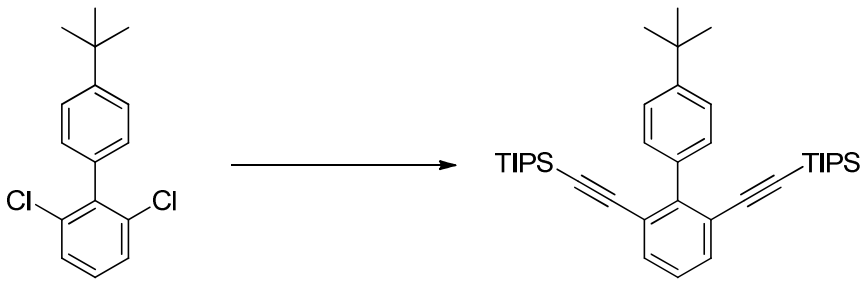
^{1}H NMR (700 MHz, 293K, CD_2Cl_2) δ/ppm 7.52 (d, *J* = 8.1 Hz, 2H), 7.43 (d, *J* = 8.2 Hz, 2H), 7.24 (m, 3H), 1.40 (s, 9H).

^{13}C NMR (176 MHz, 293K, CD_2Cl_2) δ/ppm 151.64, 139.99, 135.54, 134.59, 129.78, 129.56, 128.69, 125.68, 35.18, 31.71.

HRMS (MALDI, matrix: 3-HPA): m/z for $[C_{16}H_{16}Cl_2]^+$: 278.0623 – calculated: 278.0624.

R_f = 0.73 (petroleum ether)

4'-(*Tert*-butyl)-[1,1'-biphenyl]-2,6-diyl)bis(ethyne-2,1-diyl))bis(triisopropylsilane) (8)



7 **8**

A dry Schlenck tube was charged with 382 mg of 10 % Pd/C (0.294 mmol Pd, 0.05 equiv.), 182 mg XPhos (2-Dicyclohexylphosphino-2',4',6'-triisopropylbiphenyl, 0.38 mmol, 0.06 equiv.) and 2.64 g K_2CO_3 (19.13 mmol, 3 equiv.). The vial was purged with argon, then 30 mL dimethylformamide was added followed by 1.78 g of **7** (6.38 mmol, 1 equiv.) and 4.29 mL ethynyltriisopropylsilane (19.13 mmol, 3 equiv.). The reaction mixture was placed into an oil bath at 110 °C and was stirred for 24 h. After the mixture was cooled to ambient temperature, the charcoal was filtered off and water was added. The aqueous phase was extracted with dichloromethane, dried over $MgSO_4$ and the organic solvents were removed under vacuum. Column chromatography on silica with petroleum ether gave **8** (2.25 g, 3.96 mmol) as colorless oil in 62 % yield.

^{1}H-NMR (300 MHz, 293K, CD_2Cl_2) δ/ppm 7.53 (d, *J*=7Hz, 2H), 7.35 (m, 4H), 7.23 (t, *J*=7Hz, 1H), 1.32 (s, 9H), 0.94 (s, 42H).

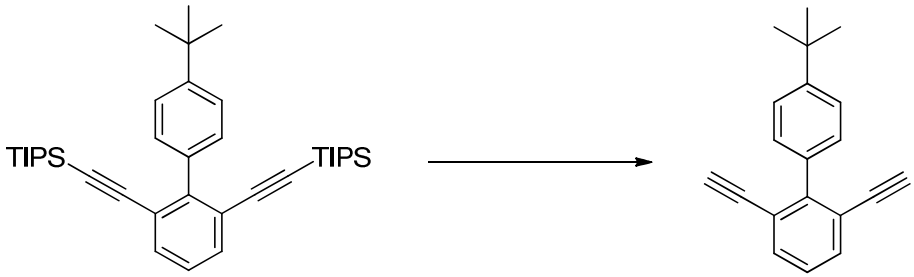
^{13}C NMR (75 MHz, 293K, CD_2Cl_2) δ/ppm 150.51, 147.92, 136.69, 133.25, 131.87, 130.05, 129.95, 128.56, 127.22, 125.44, 125.17, 124.08, 106.25, 94.97, 34.96, 31.70, 18.90, 11.79.

MS (FD, 8 kV) m/z = 570.4 g/mol – calculated: 571.4 g/mol for $C_{38}H_{58}Si_2$.

HRMS (MALDI, matrix: DCTB): m/z for $[C_{38}H_{58}Si_2+H]^+$: 571.3937 – calculated: 571.4104.

R_f = 0.48 (petroleum ether)

4'-(*Tert*-butyl)-2,6-diethynyl-1,1'-biphenyl (9)



8 **9**

A solution of 2.6 g ((4'-(*tert*-butyl)-[1,1'-biphenyl]-2,6-diyl)bis(ethyne-2,1-diyl))bis(triisopropylsilane) (**8**, 4.55 mmol, 1 equiv.) and 280 mL THF was placed in a Schlenck tube and purged with argon for 30 min. Then 45.5 mL TBAF (1 M in THF, 45.5 mmol, 10 equiv.) were added and the reaction mixture was stirred at room temperature for 4 h. It was diluted with H_2O and the crude was taken up in CH_2Cl_2. The organic phase was washed three times with H_2O, dried over Mg_2SO_4, filtered and evaporated to dryness. Without further purification **9** was afforded in 99% yield (1.18 g, 4.55 mmol) as white solid.

^{1}H NMR (300 MHz, 293K, CD_2Cl_2) δ/ppm 7.60 (d, *J* = 7.8 Hz, 2H), 7.51 – 7.37 (m, 4H), 7.28 (t, *J* = 7.8 Hz, 1H), 3.04 (s, 2H), 1.38 (s, 9H).

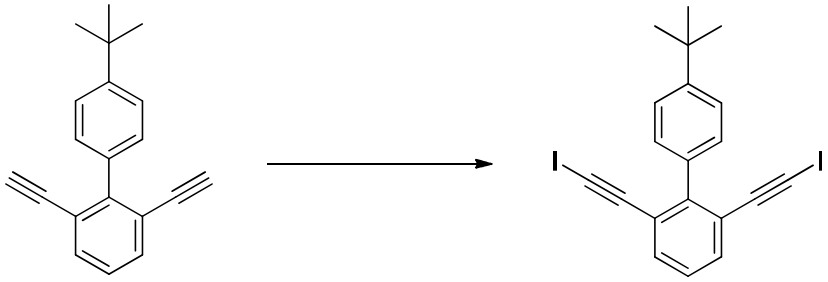
^{13}C NMR (75 MHz, 293K, CD_2Cl_2) δ/ppm 151.48, 147.32, 135.79, 134.53, 130.26, 127.51, 125.10, 122.76, 82.97, 81.15, 31.71, 30.29.

HRMS (MALDI, matrix: 3-HPA): m/z for $[C_{20}H_{18}+H]^+$: 259.1481 - calculated: 259.1442.

Elemental analysis (%) found: C, 90.81; H, 6.58; Calculated $C_{20}H_{18}$: C, 92.98; H, 7.02.

R_f = 0.31 (petroleum ether)

4'-(*Tert*-butyl)-2,6-bis(iodoethynyl)-1,1'-biphenyl (10)



9 **10**

To a solution of 116 mg 4'-(*tert*-butyl)-2,6-diethynyl-1,1'-biphenyl (**9**, 0.45 mmol, 1 equiv.) dissolved in 4 mL anhydrous dichloromethane was added 250 mg I_2 (0.99 mmol, 2.2 equiv.) and 121 mg DMAP (dimethylaminopyridine, 0.99 mmol, 2.2 equiv.). The reaction mixture was heated to 40 °C for 6h and the excess of I_2 was neutralized with $Na_2S_2O_3$ solution. The organic layer was washed with NaCl saturated solution, after H_2O, dried over $MgSO_4$, filtered and evaporated to dryness. Purification by column chromatography (SiO_2, 100% petroleum ether) followed by recycling GPC afforded **10** in 68% yield (155 mg, 0.31 mmol) as yellow oil.

^{1}H NMR (700 MHz, 293K, CD_2Cl_2) δ/ppm 7.50 (d, *J* = 7.8 Hz, 2H), 7.48 – 7.41 (m, 4H), 7.24 (t, *J* = 7.8 Hz, 1H), 1.38 (s, 9H).

^{13}C NMR (176 MHz, 293K, CD_2Cl_2) δ/ppm 151.48, 147.89, 135.13, 134.57, 134.51, 130.28, 130.25, 127.30, 125.00, 123.66, 93.56, 81.11, 35.11, 31.63.

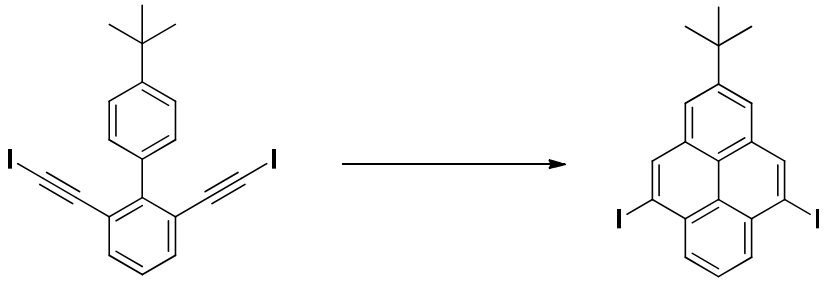
MS (FD, 8 kV) m/z = 510.4 g/mol – calculated: 509.9 g/mol for $C_{20}H_{16}I_2$.

HRMS (MALDI, matrix: DCTP): m/z for $[C_{20}H_{16}I_2]^+$: 509.9336 - calculated: 509.9341.

Elemental analysis (%) found: C, 47.30; H, 2.98; Calculated $C_{20}H_{16}I_2$: C, 47.09; H, 3.16.

R_f = 0.23 (petroleum ether)

2-(*Tert*-butyl)-5,9-diiodopyrene (11)



10 **11**

To a solution of 210 mg 4'-(*tert*-butyl)-2,6-bis(iodoethynyl)-1,1'-biphenyl (**10**, 0.41 mmol, 1 equiv.) in 15 mL anhydrous toluene 38 mg Au(I)Cl (0.16 mmol, 0.4 equiv.) was added and the mixture was degassed with argon for 30 min. After stirring at 60 °C for 16 h the reaction mixture was concentrated under reduced preassure. Purification by column chromatography (SiO_2, 100% petroleum ether) followed by recycling GPC afforded **11** in 45 % yield (94 mg, 0.18 mmol) as yellow solid.

^{1}H NMR (700 MHz, 293K, CD_2Cl_2) δ/ppm 8.76 (s, 1H), 8.49 (d, *J* = 7.9 Hz, 2H), 8.14 (s, 2H), 8.07 (t, *J* = 8.0 Hz, 1H), 1.57 (s, 8H).

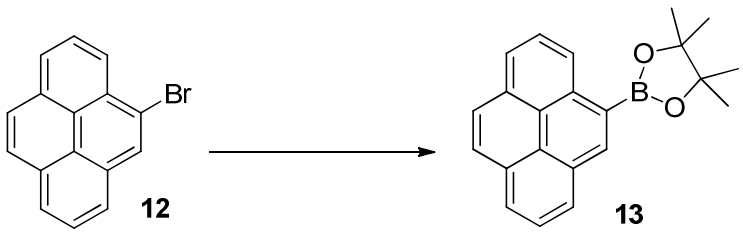
^{13}C NMR (126 MHz, CD_2Cl_2) δ/ppm 150.79, 139.85, 132.36, 131.73, 131.64, 127.60, 124.77, 123.19, 122.51, 98.90, 35.80, 32.06.

HRMS (MALDI, matrix: 3-HPA): m/z for $[C_{20}H_{16}I_2]^+$: 509.9336 - calculated: 509.9341.

Elemental analysis (%) found: C, 47.29; H, 3.01; Calculated $C_{20}H_{16}I_2$: C, 47.09; H, 3.16.

R_f = 0.26 (petroleum ether)

4,4,5,5-Tetramethyl-2-(pyren-4-yl)-1,3,2-dioxaborolane (13)



12 **13**

$Pd(dppf)Cl_2$ (21 mg, 0.03 mmol) was added to a well degassed solution of 4-bromopyrene (500 mg, 1.78 mmol), bis(pinacolato)diboron (677 mg, 2.67 mmol) and KOAc (384 mg, 3.91 mmol) in anhydrous 1,4-dioxane (4 mL). The resulting mixture was stirred at 90 °C for 4 h under argon atmosphere. After cooling, the mixture was evaporated to dryness and taken up with

dichloromethane. The organic layer was washed with H_2O, dried over $MgSO_4$, filtered and evaporated to dryness. Column chromatography (SiO2, petroleum ether/CH2Cl2 9:1) gave compound **13** (501 mg, 1.51 mmol) as a white solid in 85% yield.

^{1}H NMR (300 MHz, 293K, CD_2Cl_2) δ/ppm 9.16 (d, *J* = 7.6 Hz, 1H), 8.78 (s, 1H), 8.32 – 8.19 (m, 3H), 8.14 – 8.00 (m, 4H), 1.53 (s, 12H).

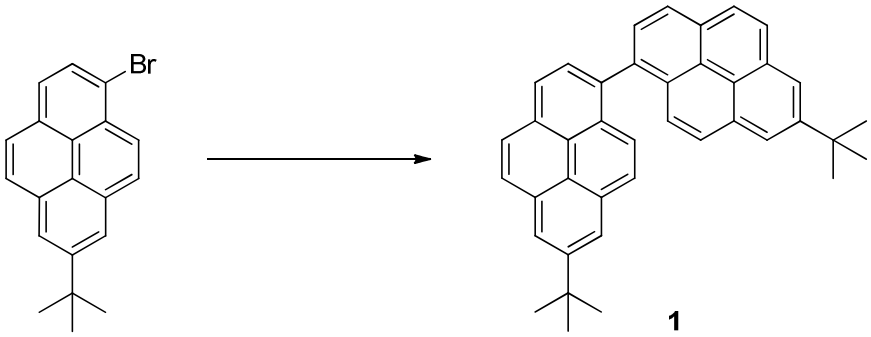
^{13}C NMR (75 MHz, 293K, CD_2Cl_2) δ/ppm 139.02, 134.05, 131.75, 131.64, 130.83, 128.42, 127.27, 126.81, 126.53, 126.42, 126.25, 126.21, 125.49, 125.07, 84.59, 25.43.

HRMS (MALDI, matrix: 3-HPA): m/z for $[C_{22}H_{21}BO_2]^+$: 328.1629 - calculated: 328.1639.

Elemantal analysis (%) found: C, 78.06; H, 6.76; Calculated $C_{22}H_{21}BO_2$: C, 80.51; H, 6.45.

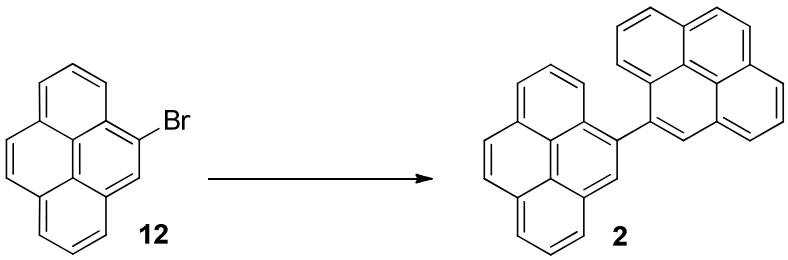
R_f = 0.16 (petroleum ether / dichloromethane; 7:3).

7,7'-Di-*tert*-butyl-1,1'-bipyrenyl (1)



Synthesis of **1** was performed according to literature.[1] Spectroscopic datas fully agreed with the already reported ones.

4,4'-Bipyrenyl (2)



Ni(COD)2 (79 mg, 0.31 mmol), 1,5-cyclooctadiene (0.037 mL, 0.31 mmol), and 2,2´-bipyridyl (49 mg, 0.31 mmol) were dissolved in dry toluene (1 mL) and dry N,N-dimethylformamide (2 mL) in a Schlenk flask within a glovebox. The reaction mixture was heated at 60 °C with stirring under argon for 20 min to generate the catalyst, and then a solution of 4-bromopyrene **12** (50 mg, 0.12 mmol) in dry toluene (4 mL) was slowly added. The reaction was heated at 80 °C for 24 h and quenched by adding

HCl_{aq} (2 M). The resulting product was participated by adding MeOH and column chromatography (SiO2, petroleum ether/CH_2Cl_2 1:1) gave compound **2** (39 mg, 0.097 mmol) as a yellow powder in 81% yield.

^{1}H NMR (700 MHz, 293K, CD_2Cl_2) δ/ppm 8.33 (s, 2H), 8.32 (d, *J* = 7.6 Hz, 2H), 8.29 (d, *J* = 7.6 Hz, 2H), 8.22 (d, *J* = 7.6 Hz, 2H), 8.21 (d, *J* = 8.9 Hz, 2H), 8.20 (d, *J* = 8.9 Hz, 2H), 8.12 (t, *J* = 7.6 Hz, 2H), 7.82 (d, *J* = 7.7 Hz, 2H), 7.78 (t, *J* = 7.6 Hz, 2H).

^{13}C NMR (176 MHz, 293K, CD_2Cl_2) δ/ppm 138.51, 132.02, 131.95, 131.78, 131.54, 129.47, 128.21, 127.89, 126.86, 126.40, 125.84, 125.78, 125.76, 125.36, 125.03.

HRMS (MALDI, matrix: DCTB): m/z for $[C_{32}H_{18}]^+$: 402.1401 - calculated: 402.1409.

Elemental analysis (%) found: C, 95.03; H, 4.72; Calculated $C_{32}H_{18}$: C, 95.49; H, 4.51.

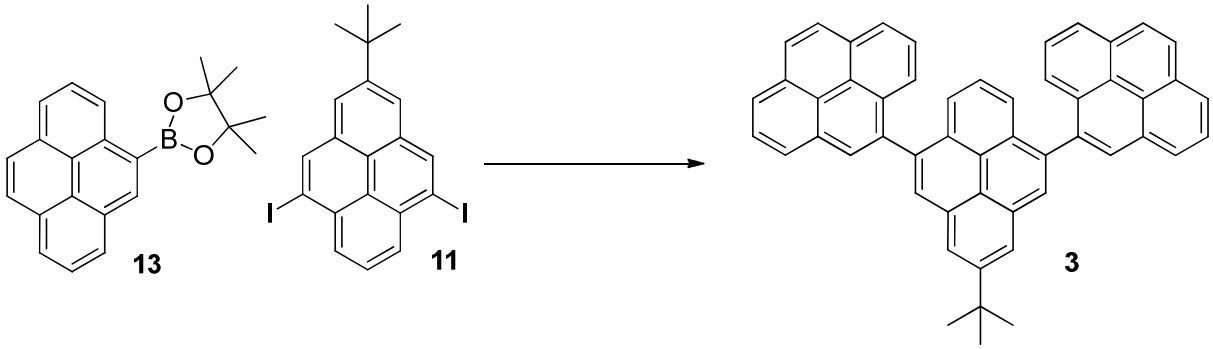
R_f = 0.21 (petroleum ether)

General procedure for Suzuki reaction:

$Pd(PPh_3)_4$ (0.05 equiv.) was added to a degassed solution of boronic acid /-ester and the halogenated compound, K_2CO_3 (6 equiv.) and Aliquat 336 (2 drops) in toluene / H_2O (2 / 1). The reaction mixture was stirred at 80 °C for 24 h under argon. The reaction was allowed to cool down to room temperature and toluene was evaporated. The crude was taken up in CH_2Cl_2. The organic phase was washed with HCl solution and H_2O, dried over Mg_2SO_4, filtered and evaporated to dryness. Purification by column chromatography (SiO_2) afforded the corresponding product.

Compounds which were prepared using this procedure:

7'-(Tert-butyl)-4,4':10',4''-terpyrenyl (3)



51 mg 2-(*tert*-Butyl)-5,9-diiodopyren **11** (0,1 mmol, 1 equiv.), 66 mg 4,4,5,5-tetramethyl-2-(pyren-4-yl)-1,3,2-dioxaborolane **13** (0.2 mmol, 2 equiv.). Pale yellow powder, yield 41 mg (62%, 0.06 mmol) of **3**.

^{1}H NMR (700 MHz, 293K, CD_2Cl_2) δ/ppm 8.44 (s, 2H), 8.44 (s, 2H), 8.40 (s, 2H), 8.40 (s, 2H), 8.38 (s, 2H), 8.36 (s, 2H) 3 singuletts from each isomer, 8.32 – 8.29 (4xd, 8H), 8.24 (d, *J* = 7.2 Hz, 2H), 8.23 (d, *J* = 7.2 Hz, 2H), 8.20 (d, *J* = 9.4 Hz, 4H), 8.19 (d, *J* = 9.4 Hz, 4H), 8.12 (t, *J* = 7.6 Hz, 2H), 8.11 (t, *J* = 7.6 Hz, 2H), 7.96 (d, *J* = 7.7 Hz, 2H), 7.88 (d, *J* = 7.7 Hz, 2H), 7.85 (t, *J* = 7.6 Hz, 2H), 7.81 (t, *J* = 7.6 Hz, 2H), 7.78 (d, *J* = 7.6 Hz, 4H), 7.47 (t, *J* = 7.7 Hz, 1H), 7.46 (t, *J* = 7.7 Hz, 1H), 1.65 (s, 9H), 1.65 (s, 9H) 1 singulett for each isomer.

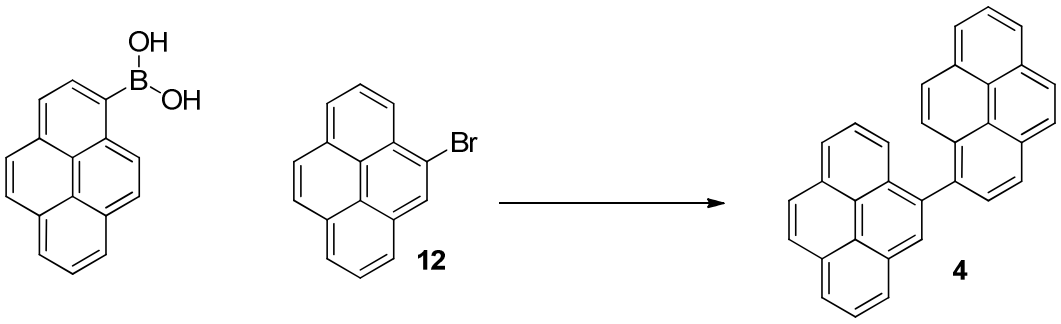
^{13}C NMR (176 MHz, 293K, CD_2Cl_2) δ/ppm 150.60, 150.58, 138.73, 138.71, 138.61, 138.60, 132.13, 132.10, 132.07, 131.97, 131.78, 131.59, 131.38, 129.68, 129.67, 129.49, 129.48, 128.21, 127.89, 126.86, 126.43, 125.92, 125.88, 125.86, 125.81, 125.80, 125.75, 125.55, 125.51, 125.39, 125.10, 125.07, 125.05, 125.04, 123.47, 123.43, 123.19, 123.18, 35.87, 32.26.

The NMR spectra are representing a mixture of two atropisomers.

HRMS (MALDI, matrix: DCTB): m/z for $[C_{52}H_{34}]^{+}$: 658.2654 - calculated: 658.2661.

R_f = 0.14 (petroleum ether / dichloromethane; 9:1)

1,4'-Bipyrenyl (4)



50 mg pyren-1-ylboronic acid (0.20 mmol), 51.4 mg 4-bromopyrene **12** (0.18 mmol). Pale yellow powder, yield 60 mg (82 %, 0.15 mmol) of **4**.

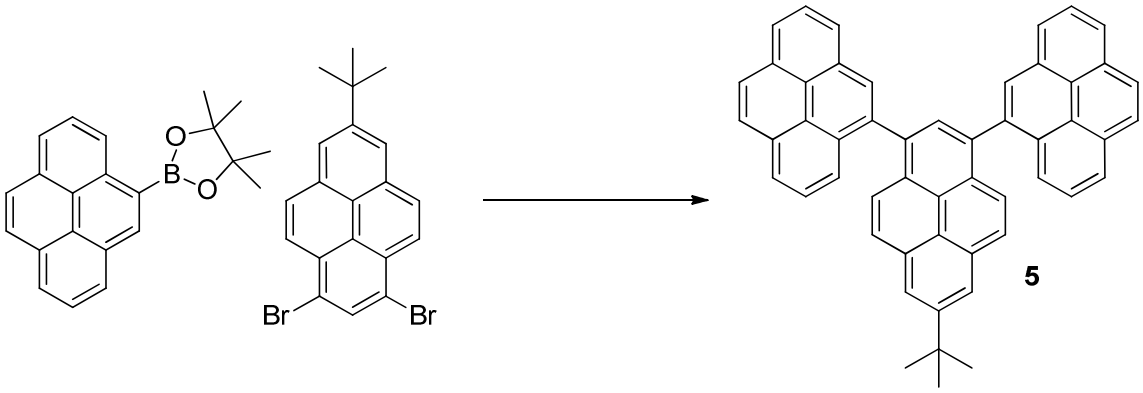
^{1}H NMR (700 MHz, 293K, THF-d8) δ/ppm 8.40 (d, *J* = 7.6 Hz, 1H), 8.30 (d, *J* = 7.8 Hz, 1H), 8.29 (d, *J* = 7.8 Hz, 1H), 8.27 (s, 1H), 8.26 (d, *J* = 7.7 Hz, 1H), 8.24 (d, *J* = 9 Hz, 1H), 8.22 (d, *J* = 7.4 Hz, 1H), 8.21-8.18 (m, 4H), 8.16 (d, *J* = 7.8 Hz, 1H), 8.08 (t, *J* = 7.8 Hz, 1H), 8.02 (t, *J* = 7.8 Hz, 1H), 7.88 (d, *J* = 9.0 Hz, 1H), 7.78 (t, *J* = 7.7 Hz, 1H), 7.76 (d, *J* = 9.4 Hz, 1H), 7.63 (d, *J* = 7.9 Hz, 1H).

^{13}C NMR (176 MHz, 293K, THF) δ/ppm 139.47, 137.01, 132.76, 132.71, 132.65, 132.45, 132.37, 132.27, 132.06, 131.26, 130.31, 129.39, 128.60, 128.58, 128.47, 128.45, 128.33, 127.26, 127.10, 126.87, 126.69, 126.32, 126.26, 126.23, 126.17, 126.11, 125.95, 125.91, 125.90, 125.76, 125.53.

HRMS (MALDI, matrix: DCTB): m/z for $[C_{32}H_{18}]^{+}$: 402.1401 - calculated: 402.1409.

R_f = 0.19 (petroleum ether)

7'-(*Tert*-butyl)-4,1':3',4''-terpyrenyl (5)



30.19 mg 1,3-Dibromo-7-(*tert*-butyl)pyren (0,059 mmol, 1 equiv.), 39 mg 4,4,5,5-tetramethyl-2-(pyren-4-yl)-1,3,2-dioxaborolane (0.118 mmol, 2 equiv.). Pale yellow powder, yield 22 mg (56%, 0.03 mmol) of **5**.

^{1}H NMR (700 MHz, 293K, CD_2Cl_2) δ/ppm 8.40-8.37 (m, 3H), 8.30-8.27 (m, 5H), 8.26 (d, J = 7.8 Hz, 1H) 8.24 (d, J = 7.5 Hz, 1H), 8.22 (d, J = 7.5 Hz, 1H), 8.18 (d, *J* = 6.3 Hz, 4H), 8.09 (t, *J* = 7.6 Hz, 1H), 8.07 (t, *J* = 7.7 Hz, 1H), 7.97 – 7.93 (m, 3H), 7.92 – 7.86 (m, 5H), 1.59 (s, 9H).

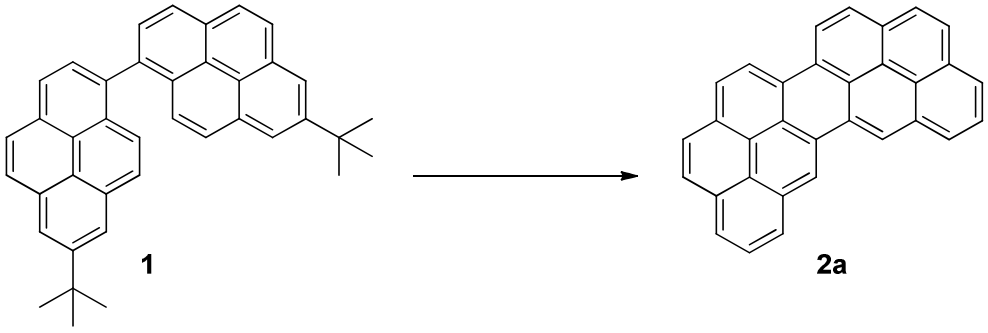
^{13}C NMR (176 MHz, 293K, CD_2Cl_2) δ/ppm 150.24, 138.74, 138.71, 136.04, 135.93, 132.25, 132.21, 131.94, 131.93, 131.74, 131.70, 131.44, 131.42, 131.05, 130.93, 130.46, 130.45, 130.09, 130.04, 128.36, 128.34, 128.17, 127.88, 126.85, 126.52, 126.50, 126.27, 126.24, 125.81, 125.79, 125.71, 125.65, 125.59, 125.34, 125.21, 125.14, 124.94, 123.71, 123.34, 32.18, 30.28.

The NMR spectra are representing a mixture of two atropisomers.

HRMS (MALDI, matrix: DCTB): m/z for $[C_{52}H_{34}]^{+}$: 658.2654 - calculated: 658.2661.

R_f = 0.17 (petroleum ether / dichloromethane; 9:1)

Dinaphtho[2,1,8,7-defg:2',1',8',7'-ijkl]pentaphene (2a)



10 mg 7,7'-di-*tert*-butyl-1,1'-bipyrene (**1**, 0.02 mmol) was added to a melt of 7 mg NaCl (0.12 mmol, 6 equiv.) and 31 mg $AlCl_3$ (0.24 mmol, 12 equiv.). After 20 minutes at 120 °C 20 mL of diluted HCl (aq., 2M) was added and heated to 80 °C for 15 minutes. The mixture was filtered and washed with diluted NH_3 (aq.). Compound **2a** (5 mg, 0.013 mmol) was afforded in 65 % yield as poorly soluble red powder.

Cyclodehydrogenation under harsh conditions (ref 10) led to depletion of *tert*-butyl groups.

^{1}H NMR (500 MHz, at 393K, in $C_2D_2Cl_4$) δ/ppm 9.06 (d, J = 9.07, 2H), 9.06 (s, assumed due to signal integration, 2H) 8.77 (d, J = 7.7 Hz, 2H), 8.37-8.31 (m, 4H), 8.16 (d, J = 8.6 Hz, 2H), 8.10 (d, J = 8.6 Hz, 2H), 7.93 (t, J = 7.7 Hz, 2H).

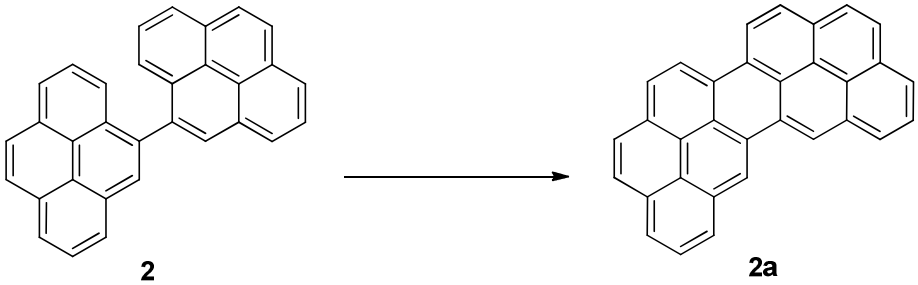
HRMS (MALDI, matrix: DCTB): m/z for $[C_{32}H_{16}]^+$: 400.1247 - calculated: 400.1252.

General procedure for "soft" cyclodehydrogenation:

10 mg of precursor (**2**, **3**, **4**, **5**) were dissolved in 10 mL freshly destilled dichloromethane and purged by a continuous and gentle argon flow for 15 minutes. Then a solution of 3 equiv. $FeCl_3$ per reacting hydrogen in nitromethane (300 mg $FeCl_3$ / mL) was added dropwise. After 1 h the argon flow was stopped, the flask was sealed with a septum and the reaction was stirred at room temperature for appropriate time. The reaction was stopped by adding 50 mL of methanol, which led to the precipitation of the products (**2a**, **3a**, **4a**, **5a**).

Compounds which were prepared using this procedure:

Dinaphtho[2,1,8,7-defg:2',1',8',7'-ijkl]pentaphene (2a)



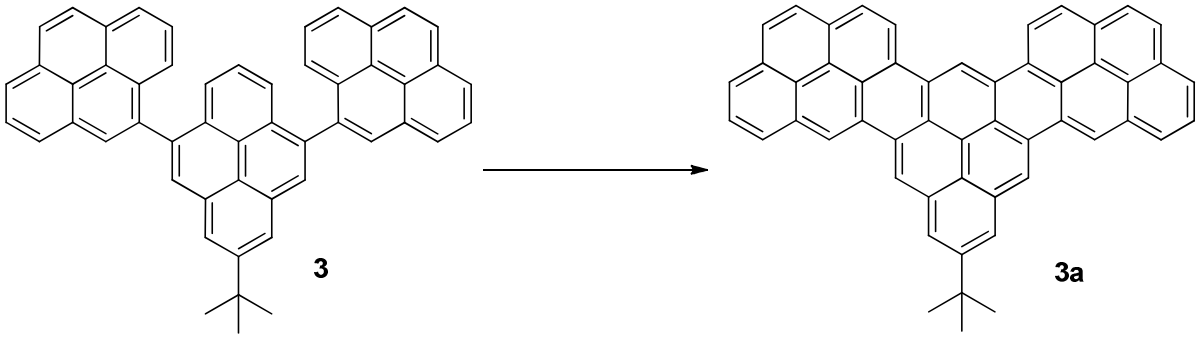
2 **2a**

Reaction was stopped after 1h. Compound **2a** (4 mg, 0.010 mmol) was afforded in 40 % yield as poorly soluble red powder.

^{1}H NMR (500 MHz, at 393K, in $C_2D_2Cl_4$) δ/ppm 9.06 (d, J = 9.07, 2H), 9.06 (s, assumed due to signal integration, 2H) 8.77 (d, J = 7.7 Hz, 2H), 8.37-8.31 (m, 4H), 8.16 (d, J = 8.6 Hz, 2H), 8.10 (d, J = 8.6 Hz, 2H), 7.93 (t, J = 7.7 Hz, 2H).

HRMS (MALDI, matrix: DCTB): m/z for $[C_{32}H_{16}]^+$: 400.1247 - calculated: 400.1252.

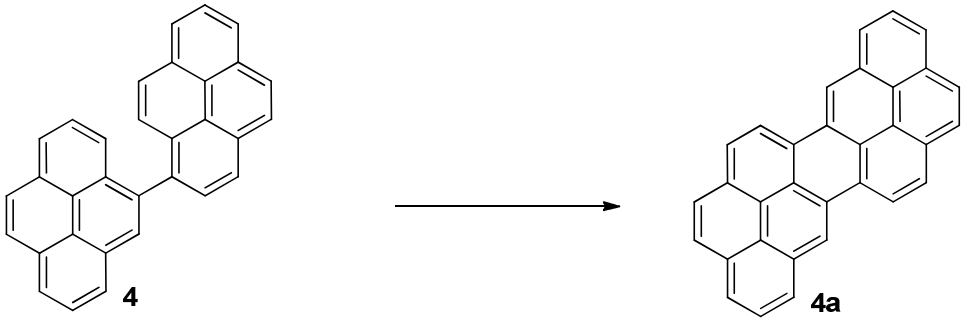
Dinaphtho[2,1,8,7-ABCD:2',1',8',7'-stuv]-5-(*tert*-butyl)phenaleno[2,1,9,8-hijk]heptacene (3a)



Reaction was stopped after 2h. Compound **3a** (3 mg, 0.005 mmol) was afforded in 30 % yield as nearly insoluble red powder.

HRMS (MALDI, matrix: DCTB): m/z for $[C_{52}H_{30}]^+$: 654.2342 - calculated: 654.2348.

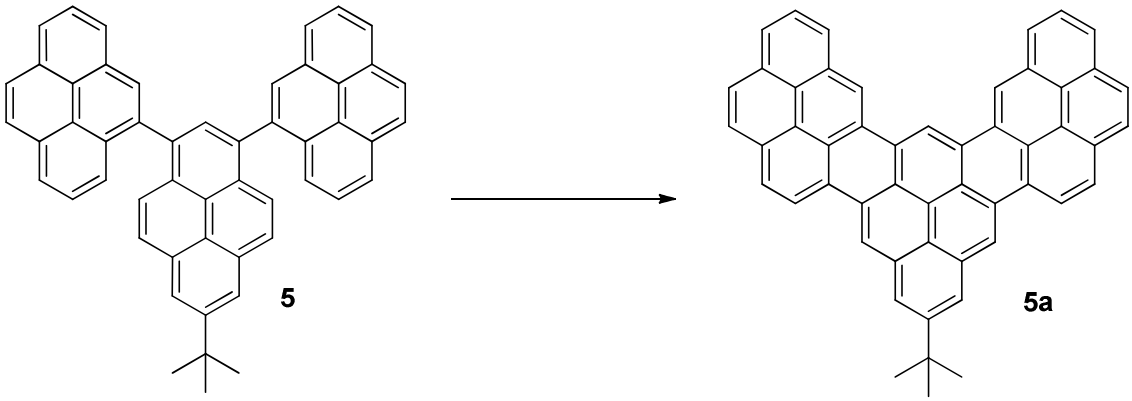
Dinaphtho[2,1,8,7-defg:2',1',8',7'-opqr]pentacene (4a)



Reaction was stopped after 2h. Compound **4a** (3 mg, 0.007 mmol) was afforded in 30 % yield as nearly insoluble red powder.

HRMS (MALDI, matrix: DCTB): m/z for $[C_{32}H_{16}]^+$: 400.1247 - calculated: 400.1252.

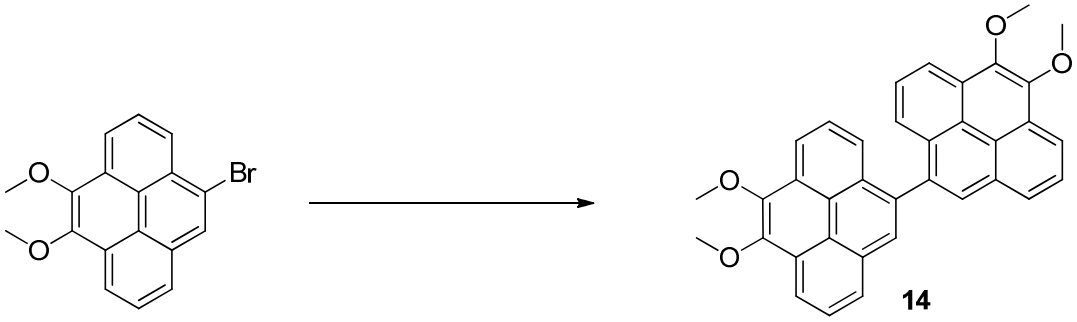
Naphtho[2,1,8,7-defg]-5-*tert*-butylphenaleno[2,1,9,8-ijkl]-phenaleno[9',1',2'-qrs]hexaphene (5a)



Reaction was stopped after 2h. Compound **5a** (5 mg, 0.008 mmol) was afforded in 50 % yield as insoluble red powder.

HRMS (MALDI, matrix: DCTB): m/z for $[C_{52}H_{30}]^+$: 654.2342 - calculated: 654.2348.

9,9',10,10'-tetramethoxy-4,4'-bipyrenyl



Ni(COD)2 (96 mg, 0.35 mmol), 1,5-cyclooctadiene (0.043 mL, 0.35 mmol), and 2,2´-bipyridyl (55 mg, 0.35 mmol) were dissolved in dry toluene (1 mL) and dry N,N-dimethylformamide (2 mL) in a Schlenk flask within a glovebox. The reaction mixture was heated at 60 °C with stirring under argon for 20 min to generate the catalyst, and then a solution of 9-bromo-4,5-dimethoxypyrene (100 mg, 0.29 mmol) in dry toluene (4 mL) was slowly added. The reaction was heated at 80 °C for 24 h and quenched by adding HCl_{aq} (2 M). The resulting product was participated by adding MeOH and column chromatography (SiO2, petroleum ether/CH_2Cl_2 1:1) gave compound 9,9',10,10'-tetramethoxy-4,4'-bipyrenyl (112 mg, 0.21 mmol) as a yellow powder in 74 % yield.

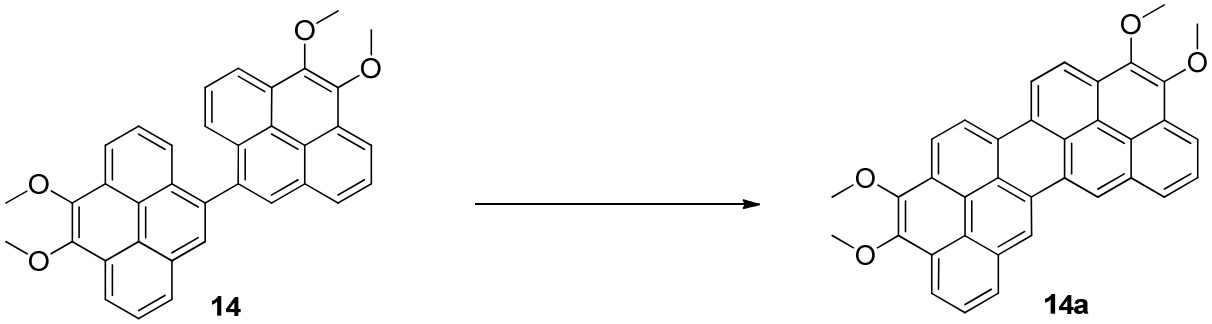
^{1}H NMR (700 MHz, CD_2Cl_2) δ/ppm 8.59 (d, *J* = 8,0 Hz, 2H), 8.51 (d, *J* = 7,6 Hz, 2H), 8.29 (s, 2H), 8.24 (d, *J* = 8,0 Hz, 2H), 8.13 (t, *J* = 7,9 Hz, 2H), 7.79 (t, *J* = 7,7 Hz, 2H), 7.75 (d, *J* = 7,7 Hz, 2H), 4.28 (s, 6H), 4.25 (s, 6H).

^{13}C NMR (176 MHz, CD_2Cl_2) δ/ppm 145.45, 145.33, 138.36, 132.00, 131.41, 129.47, 129.27, 128.94, 126.95, 126.53, 125.29, 124.42, 123.52, 123.20, 120.15, 120.09, 61.70, 61.67.

MS (FD, 8 kV) m/z = 523.4 g/mol – calculated: 522.6 g/mol for $C_{36}H_{26}O_4$.

MALDI (matrix: TCNQ): 522.13 g/mol – calculated: 522.58 g/mol for $C_{36}H_{26}O_4$.

4,5,10,11-tetramethoxydinaphtho[2,1,8,7-defg:2',1',8',7'-ijkl]pentaphene



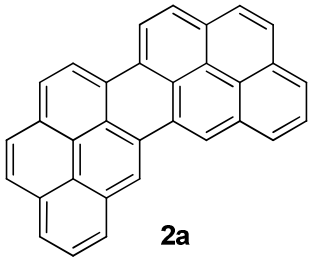
10 mg of precursor **14** (0,019 mmol) was dissolved in 10 mL freshly destilled dichloromethane and purged by a continuous and gentle argon flow for 15 minutes. Then it was cooled to -78 °C and a solution of 8.54 mg $FeCl_3$ (0.053 mmol, 2.75 eqiv) in nitromethane (300 mg $FeCl_3$ / mL) was added dropwise. After a reaction time of 5 minutes the reaction was stopped by adding 50 mL of methanol, which led to the precipitation of the product and **14a** (7.8 mg, 0.015 mmol) was afforded in 78 % yield as red powder.

^{1}H NMR (700 MHz, CD_2Cl_2) δ/ppm 8.96 (s, 2H), 8.83 (d, *J* = 8.4 Hz, 2H), 8.51 (d, *J* = 8.4, 2H), 8.36 (d, *J* = 7.1 Hz, 2H), 8.13 (d, *J* = 7.1 Hz, 2H), 7.97 (t, *J* = 7.1 Hz, 2H), 4.24 (s, 6H), 4.23 (s, 6H).

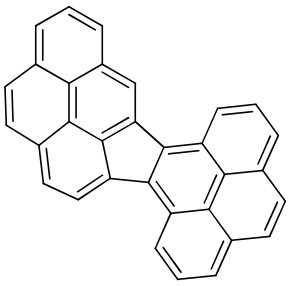
MS (FD, 8 kV) m/z = 520.0 g/mol – calculated: 520.2 g/mol for $C_{36}H_{24}O_4$.

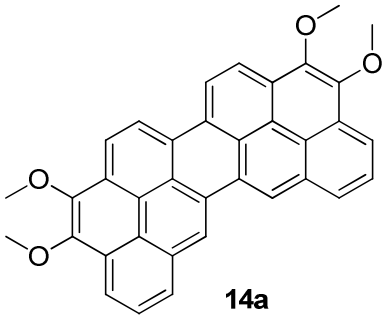
MALDI (matrix: TCNQ): 520.19 g/mol – calculated: 520.17 g/mol for $C_{36}H_{24}O_4$.

S3. Formation of 6 vs. 5 ring during cyclodehydrogenation

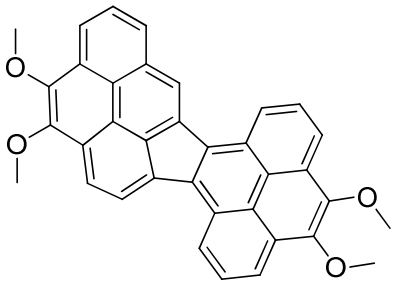


2a





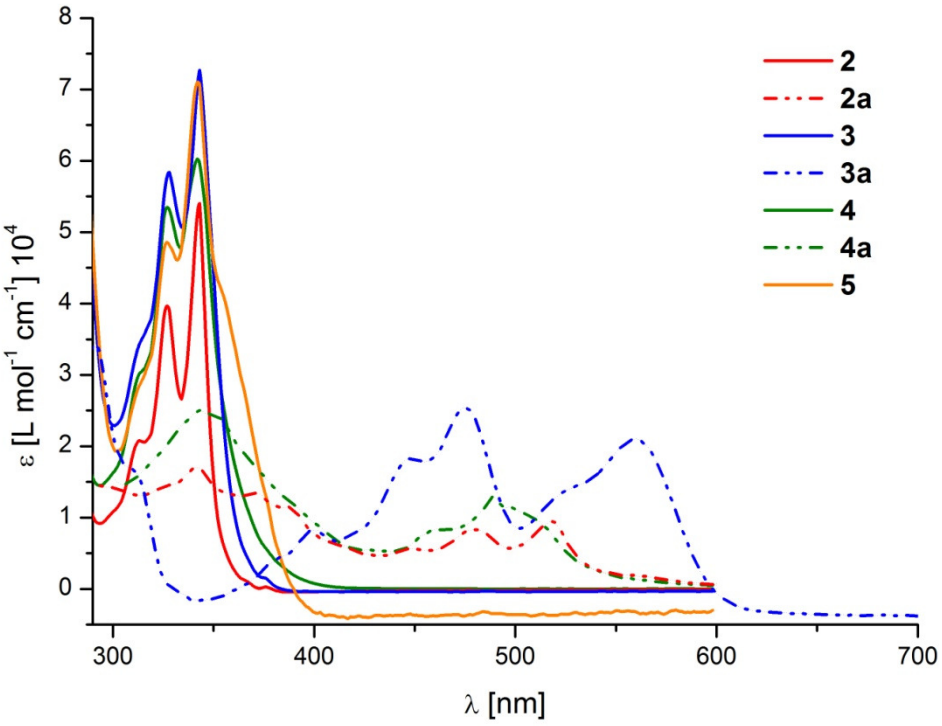
14a



During the cyclodehydrogenation reaction the formation of a five-memebered ring is theoretical conceivable. As discribed in following we excluded the formation of a fiv-membered ring.

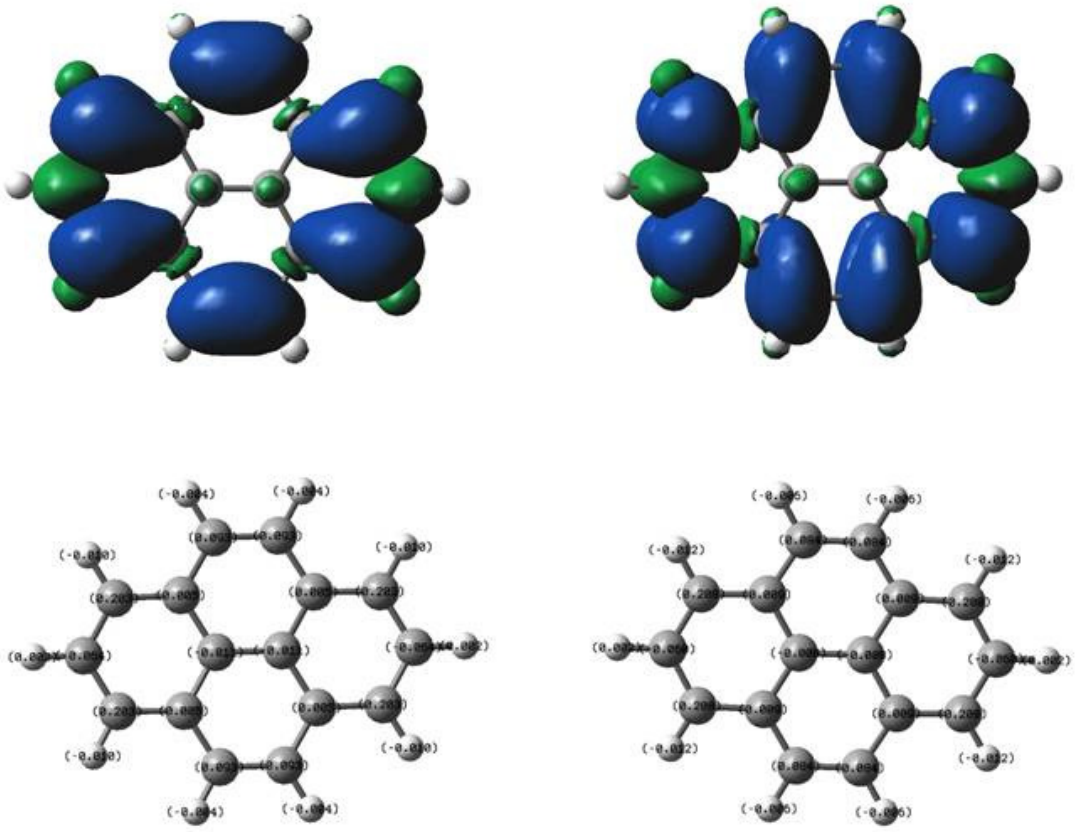
For the ^{1}H NMR spectrum of **2a** 8 different signal groups are expected. Two AB systems, one ABC system and one singlet. This corresponds to 6 doublets, one triplet and one singlet for the symmetric compound **2a**. In the ^{1}H NMR spectrum recorded at 120°C in 1,1,2,2-tetrachloroethane two AB systems and one ABC system were observed, which was proven by H,H-COSY measurements (as well at 120°C in 1,1,2,2-tetrachloroethane). This leads to the fact that the number of signals is not fitting with the formation of a five-membered ring (see above depiction). A five-membered ring would lead to a non symmetric structure with at least 3 triplets, 12 doublets and 1 singlet. A detached signal for the singlet could not be allocated. This singlet is expected as a broad signal detected at the same chemical shift as the doublet at 9.06 ppm. It is consistent with the interpretation of the integrals of the doublet at 9.06 ppm, which shows considerable more than the expected two protons. To clarify this interpretation we synthesized a 4,5,10,11-tetramethoxydinaphtho[2,1,8,7-defg:2',1',8',7'-ijkl]pentaphene (**14a**) using four methoxy groups for solubilising reasons. With this structure we were able to proof the formation of a six-membered, but none five-membered ring. The detected signals of **14a** are consistent with a symmetric compound showing the same symmetry as **2a**. We found the expected AB-system, the ABC-system and one singlet. The singlet of **14a** was detected at 8.96 ppm as a broad signal.

S4. UV/Vis spectra of compounds 2-5 and 2a-4a



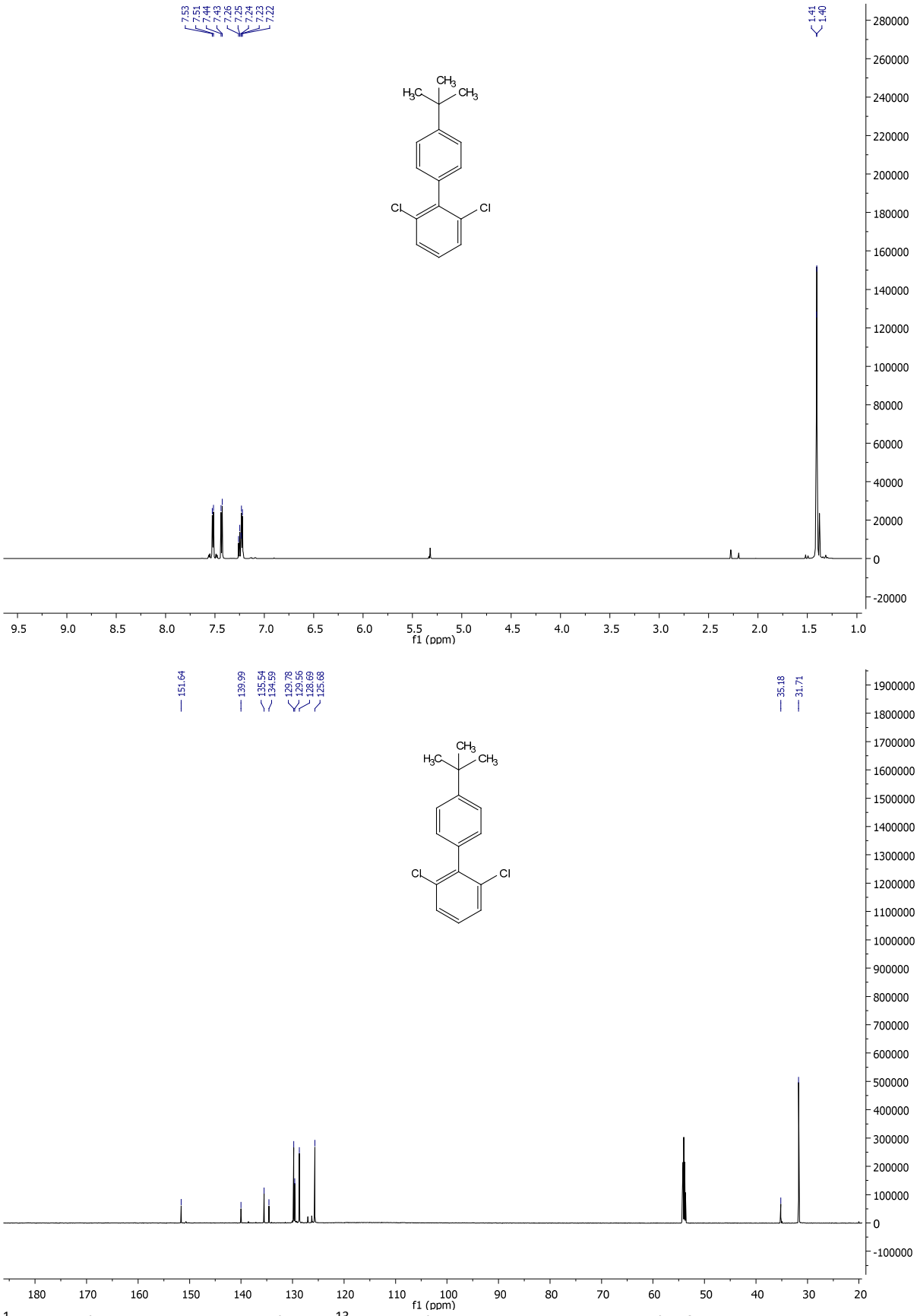
UV-Vis absorption spectra for **2**, **3,4** and **5** (open form = solid line) in THF, for **2a**, **4a** (closed form = dashed line) in toluene and **3a** in 1,3,5-trichlorobenzene at 180 °C.

S5. Computational results

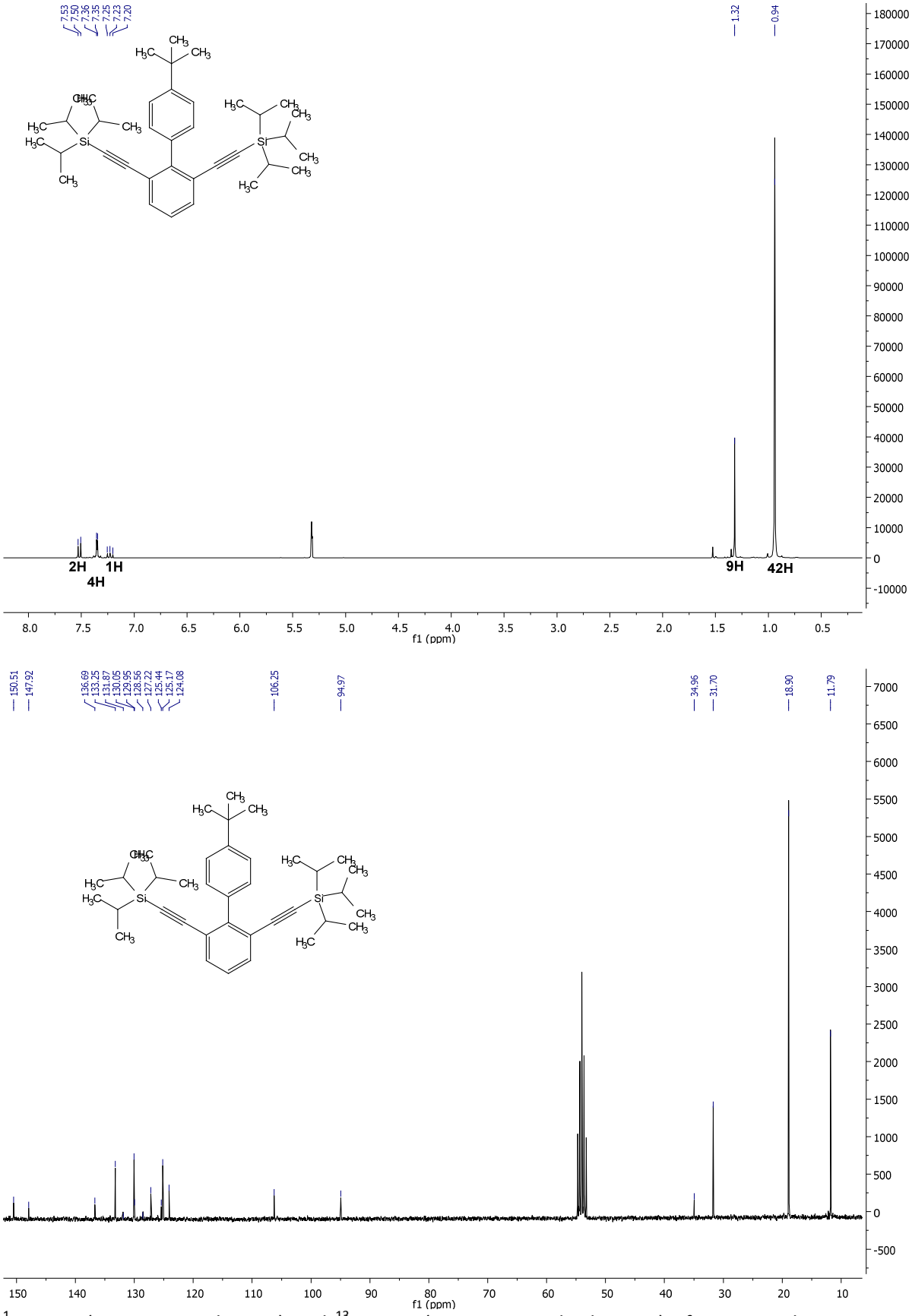


The calculation was performed with Gaussian 03 using density functional theory (DFT) with the B3LYP functional and 6311 G(d) basis set. Spin density of the radical cation (on left side) and the radical anion (on the right side).

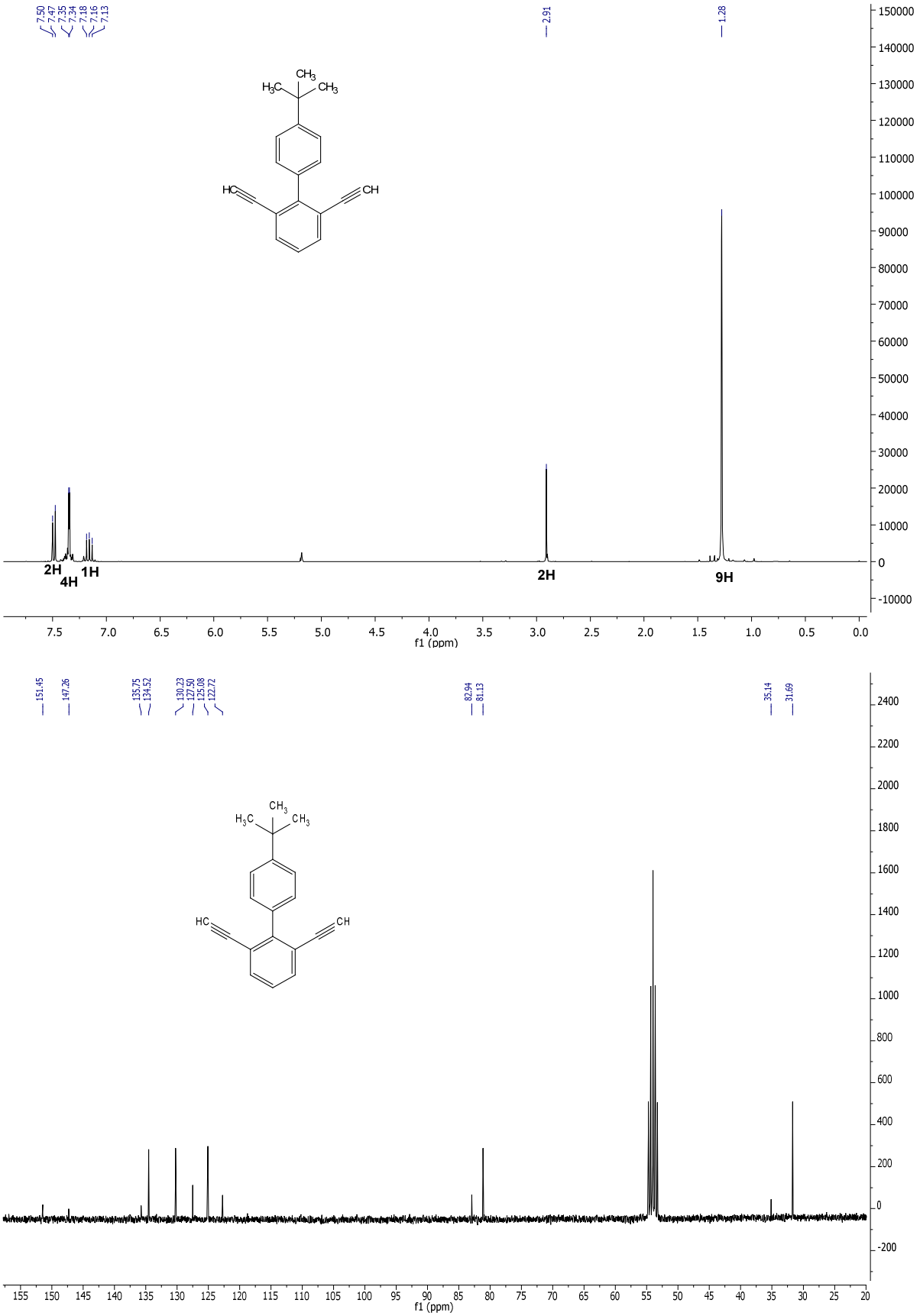
S6. NMR spectra of compounds 2 – 5, 7 – 11



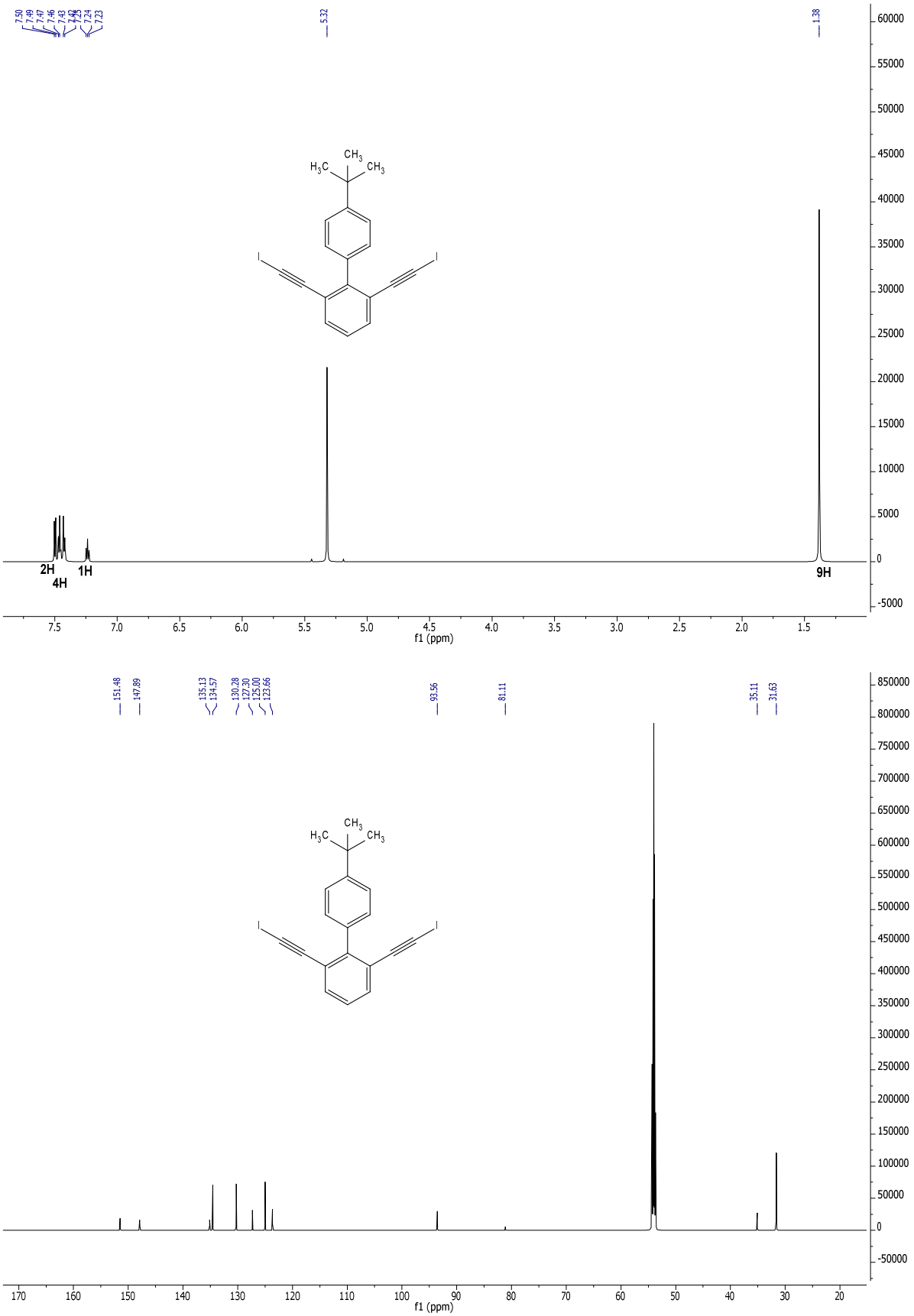
^{1}H NMR (700 MHz at the top) and ^{13}C NMR (176 MHz, at the bottom) of compound **7** at 298K in CD_2Cl_2.



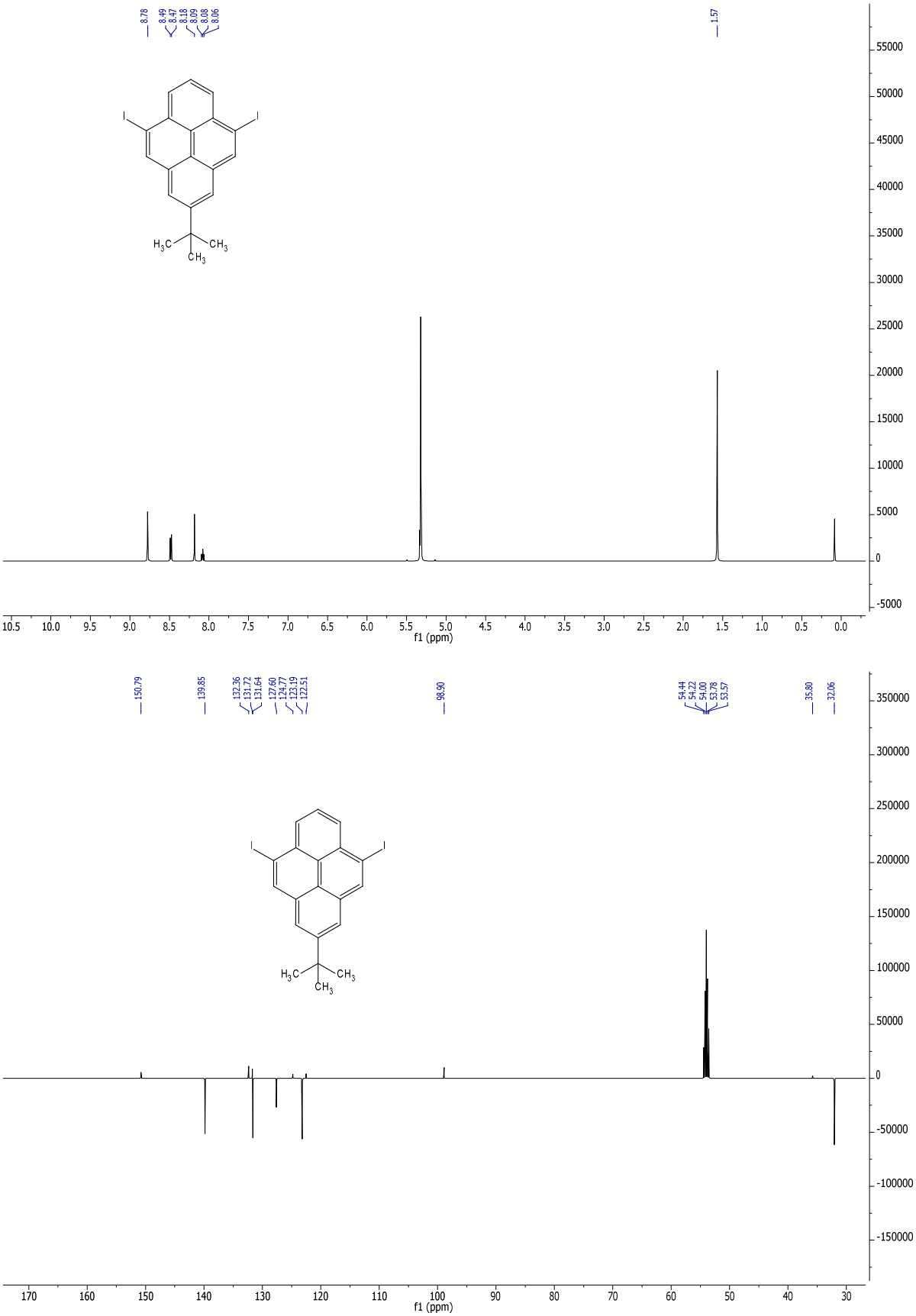
^{1}H NMR (700 MHz at the top) and ^{13}C NMR (176 MHz, at the bottom) of compound **8** at 298K in CD_2Cl_2.



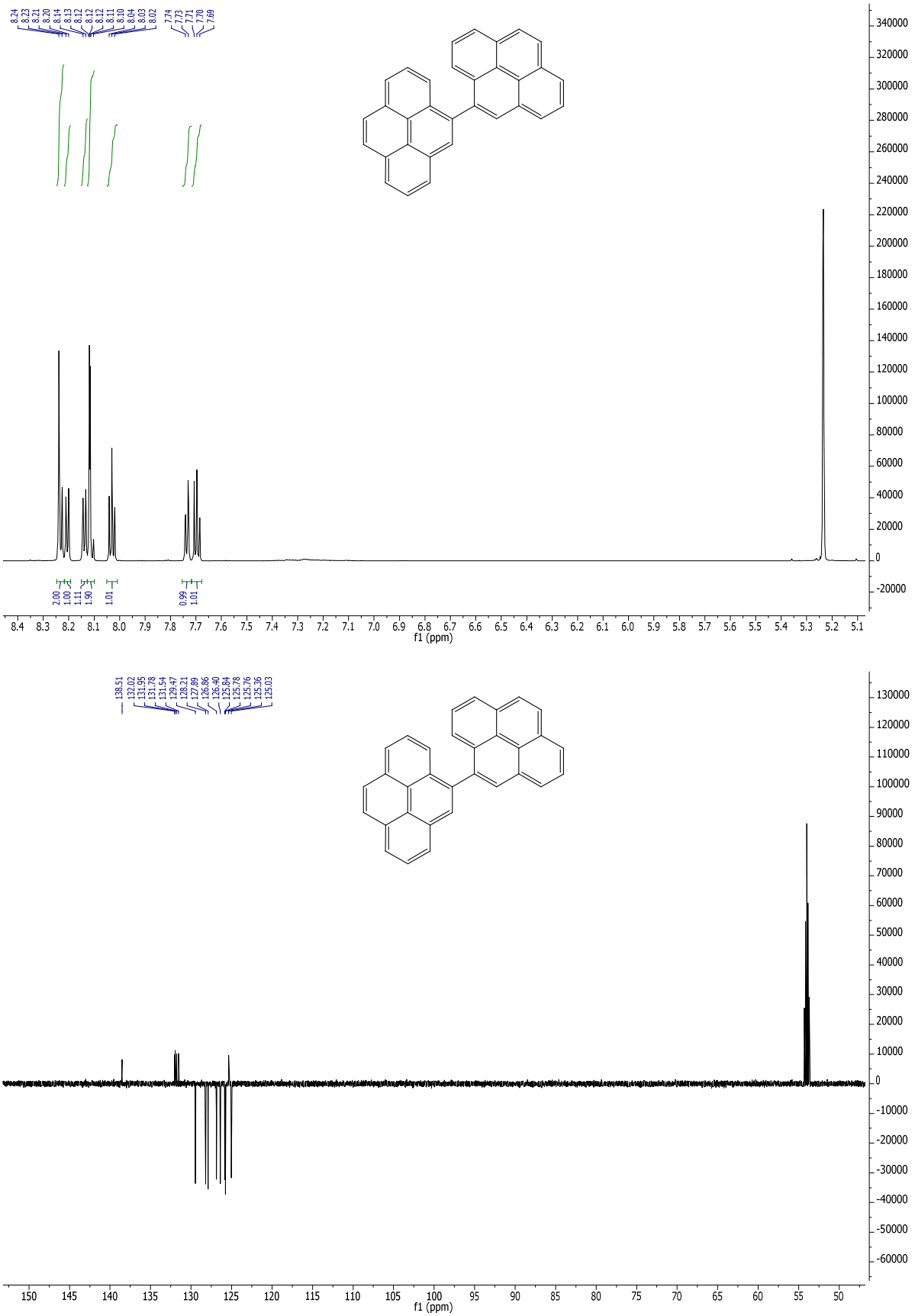
^{1}H NMR (700 MHz at the top) and ^{13}C NMR (176 MHz, at the bottom) of compound **9** at 298K in CD_2Cl_2.



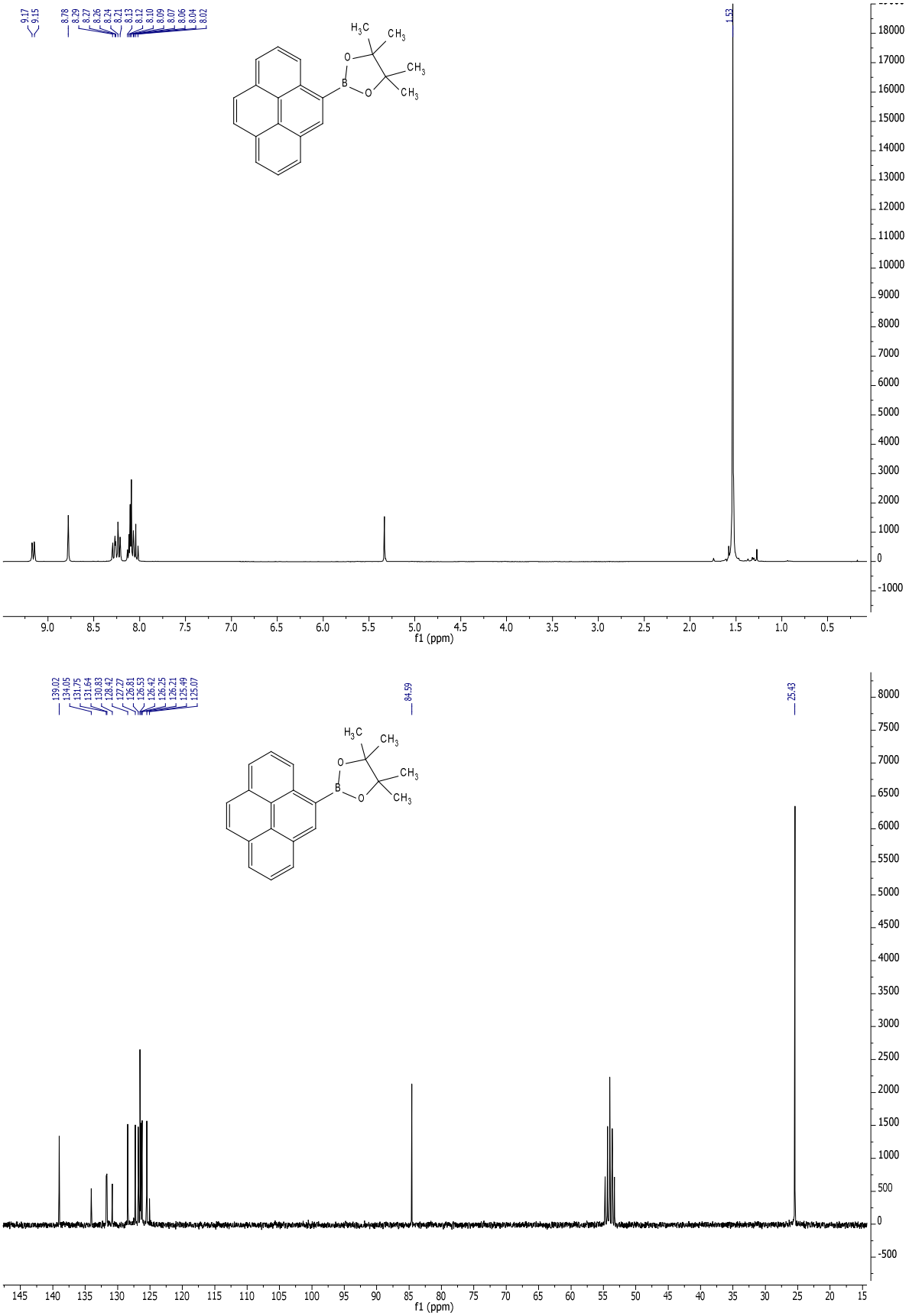
^{1}H NMR (700 MHz at the top) and ^{13}C NMR (176 MHz, at the bottom) of compound **10** at 298K in CD_2Cl_2.



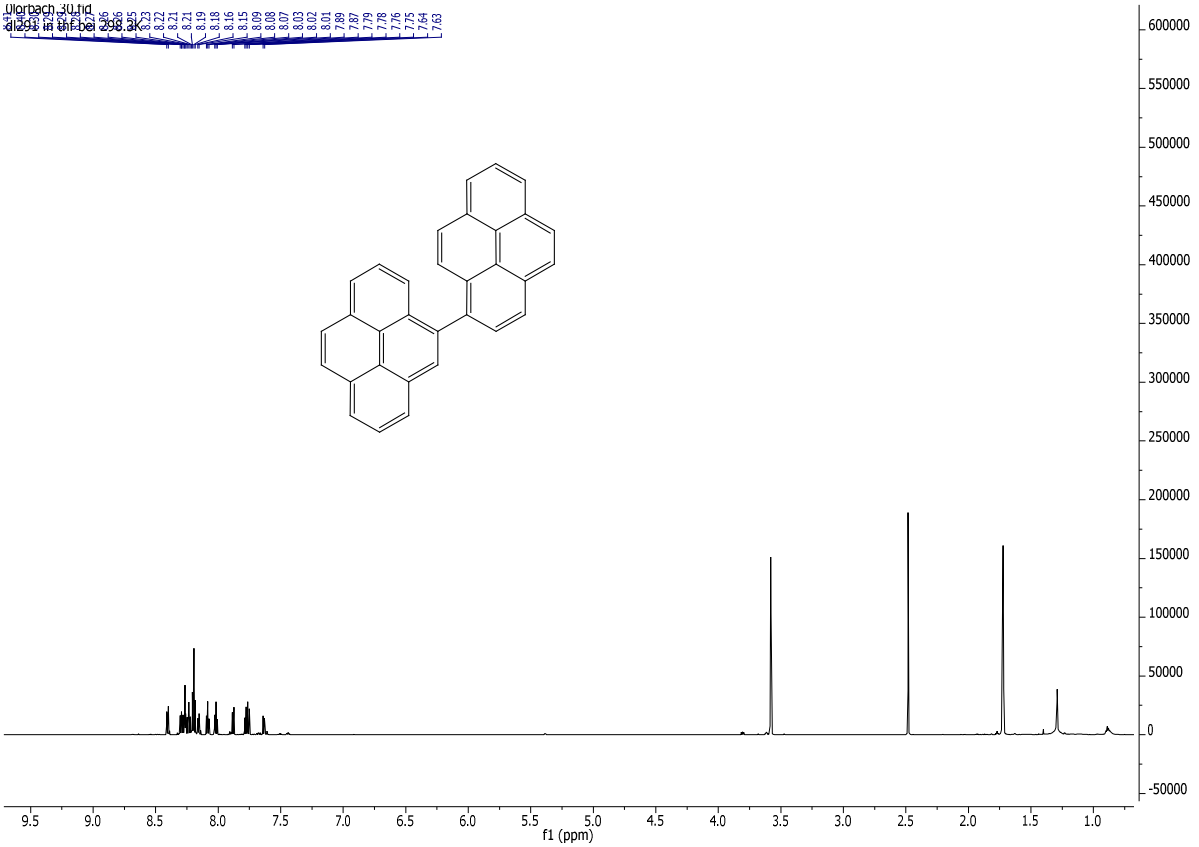
^{1}H NMR (700 MHz at the top) and ^{13}C NMR (176 MHz, at the bottom) of compound **11** at 298K in CD_2Cl_2. The carbon spectrum was measured under the condition to define and differentiate between even and odd number of attached protons on carbons named spin echo or apt for attached proton test (up CH_2 and C; down CH_3 and CH).

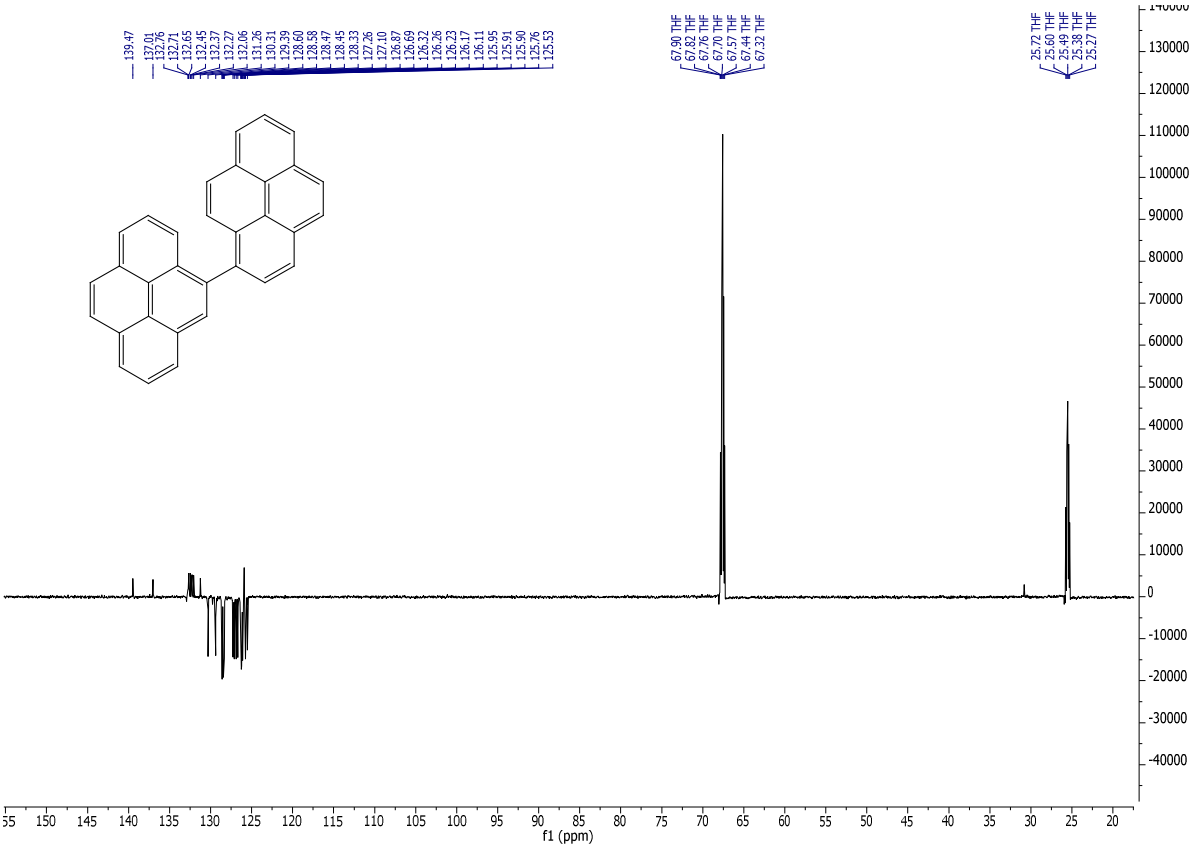


^{1}H NMR (700 MHz at the top) and ^{13}C NMR (176 MHz, at the bottom as an apt) of compound **2** at 298K in CD_2Cl_2.

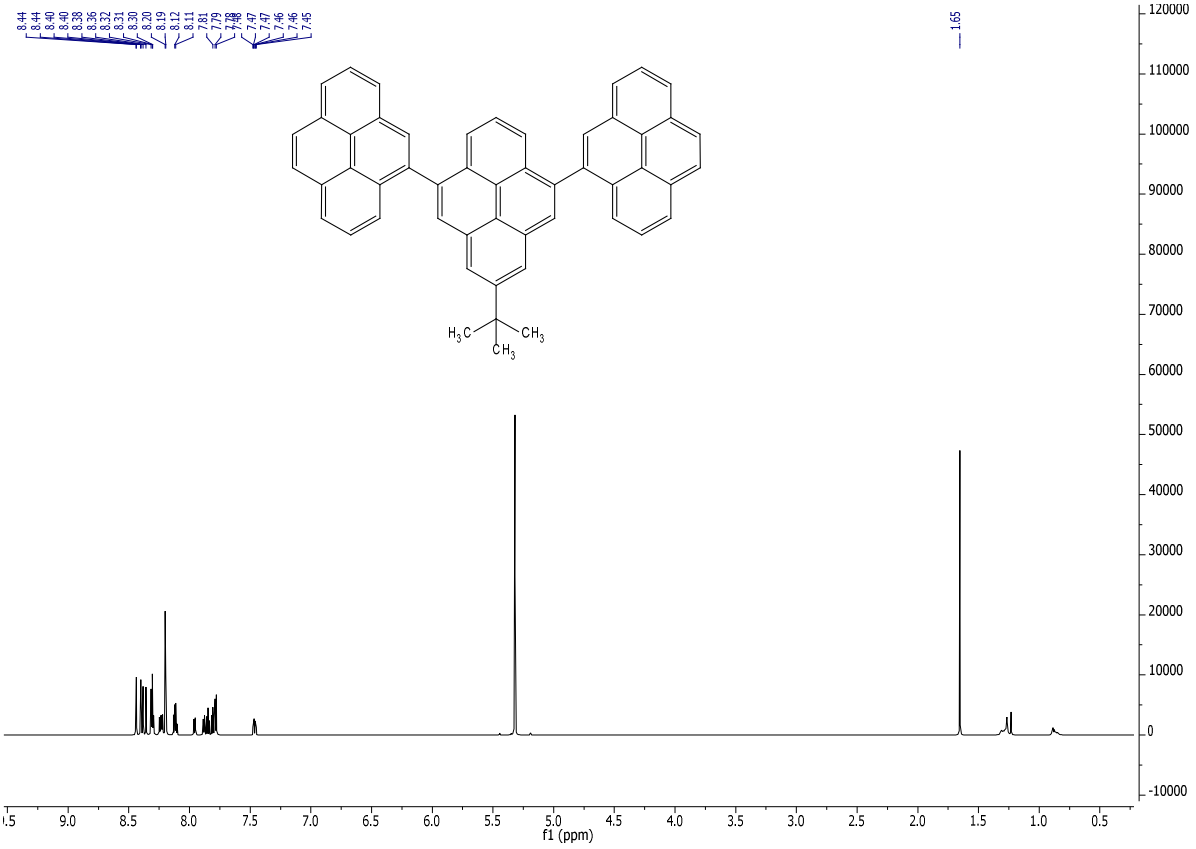


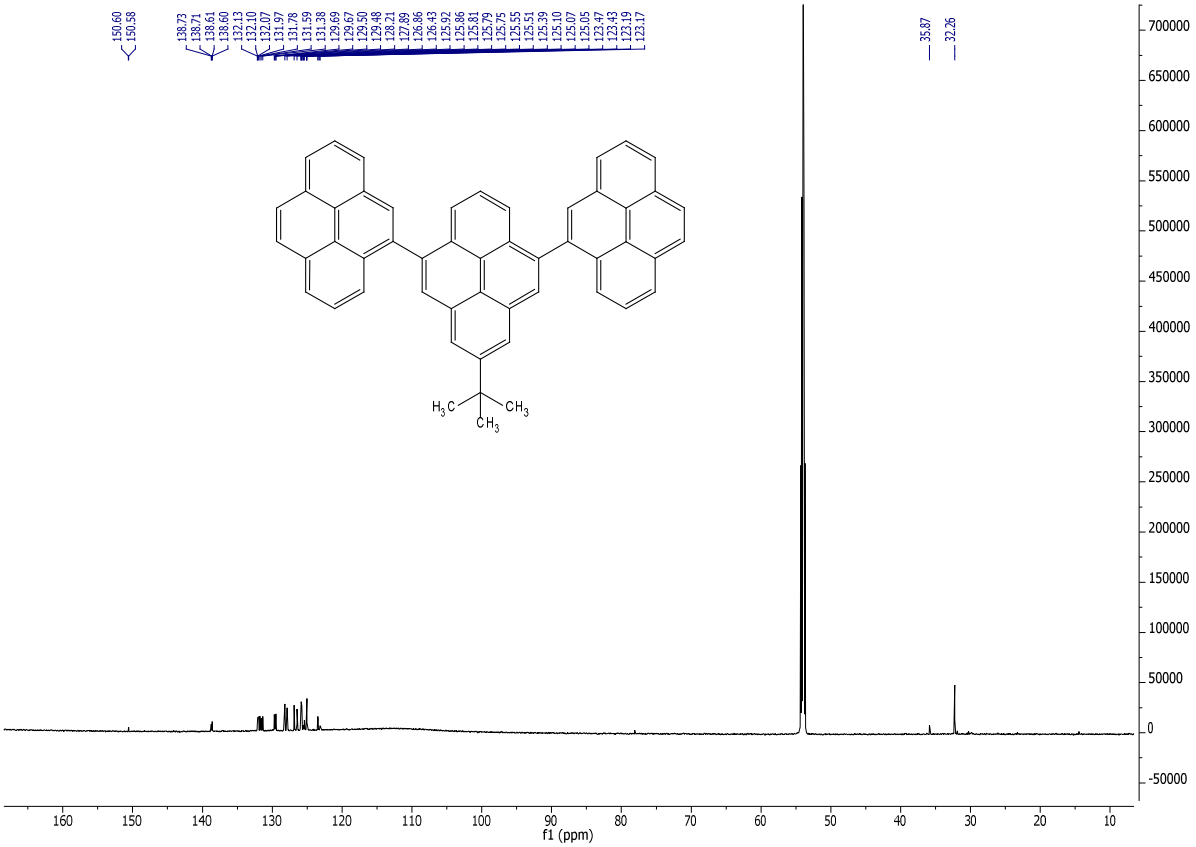
^{1}H NMR (700 MHz at the top) and ^{13}C NMR (176 MHz, at the bottom) of compound **13** at 298K in CD_2Cl_2.



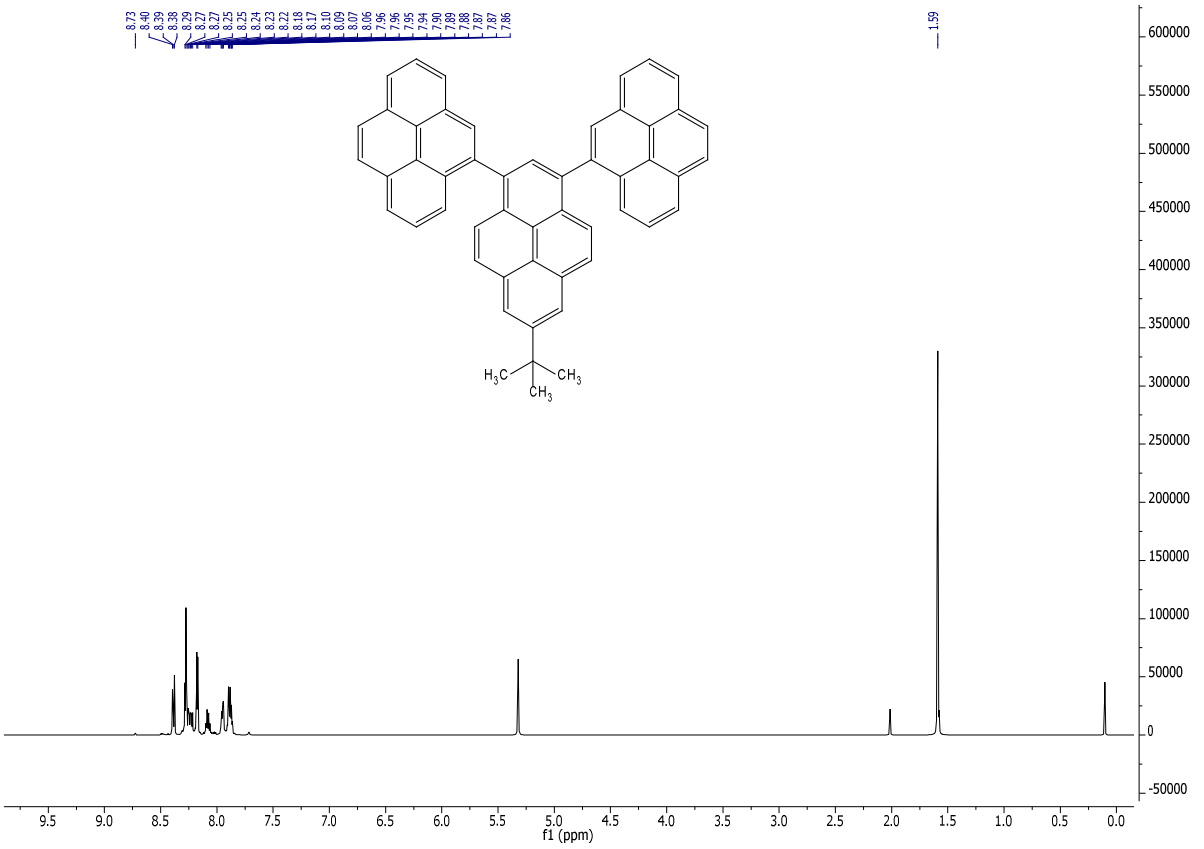


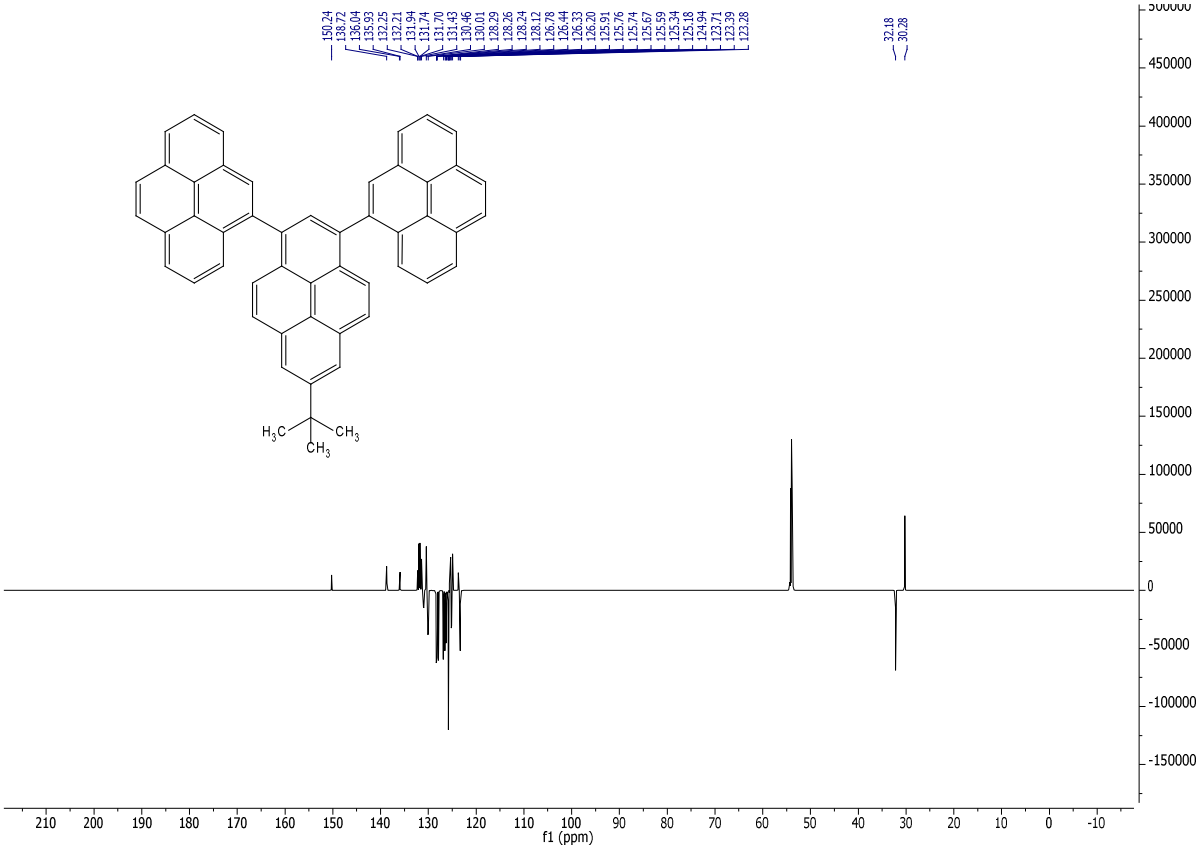
^{1}H NMR (700 MHz at the top) and ^{13}C NMR (176 MHz, at the bottom as an apt) of compound **4** at 298K in THF-d_8.



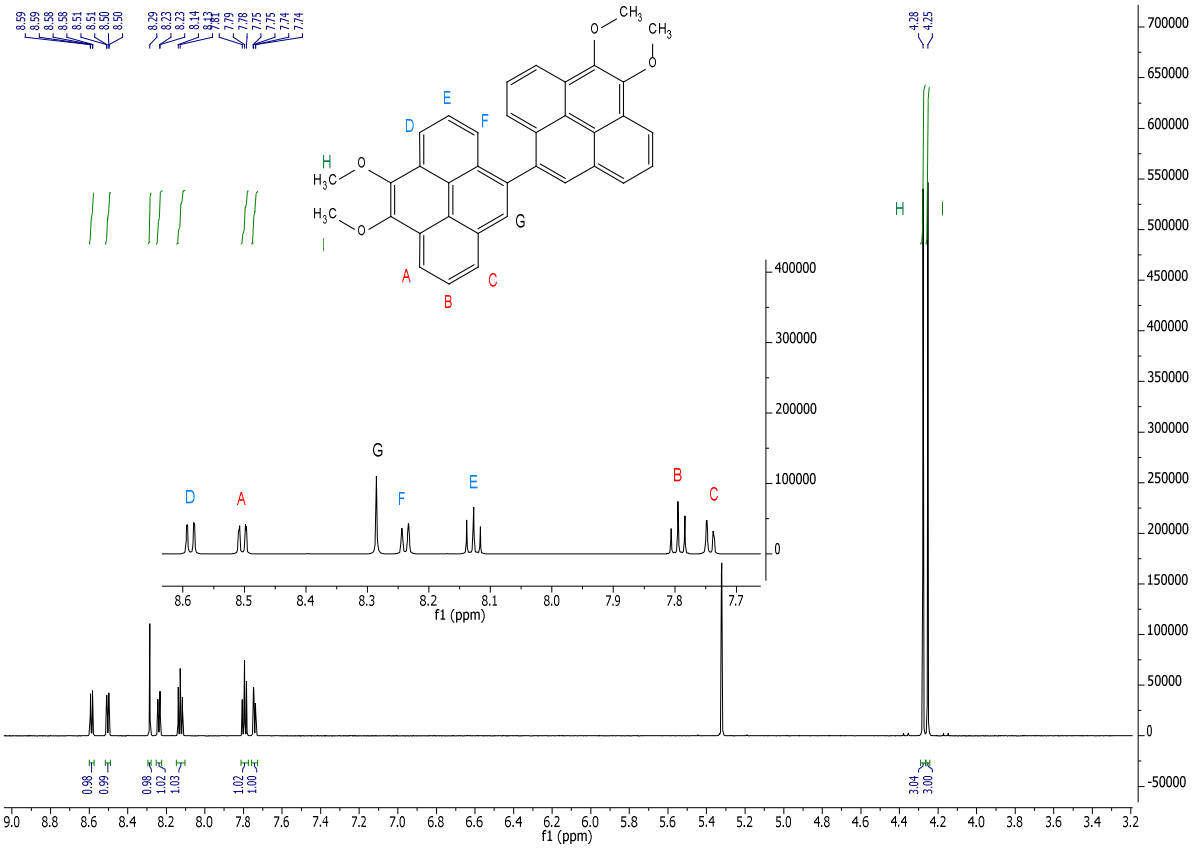


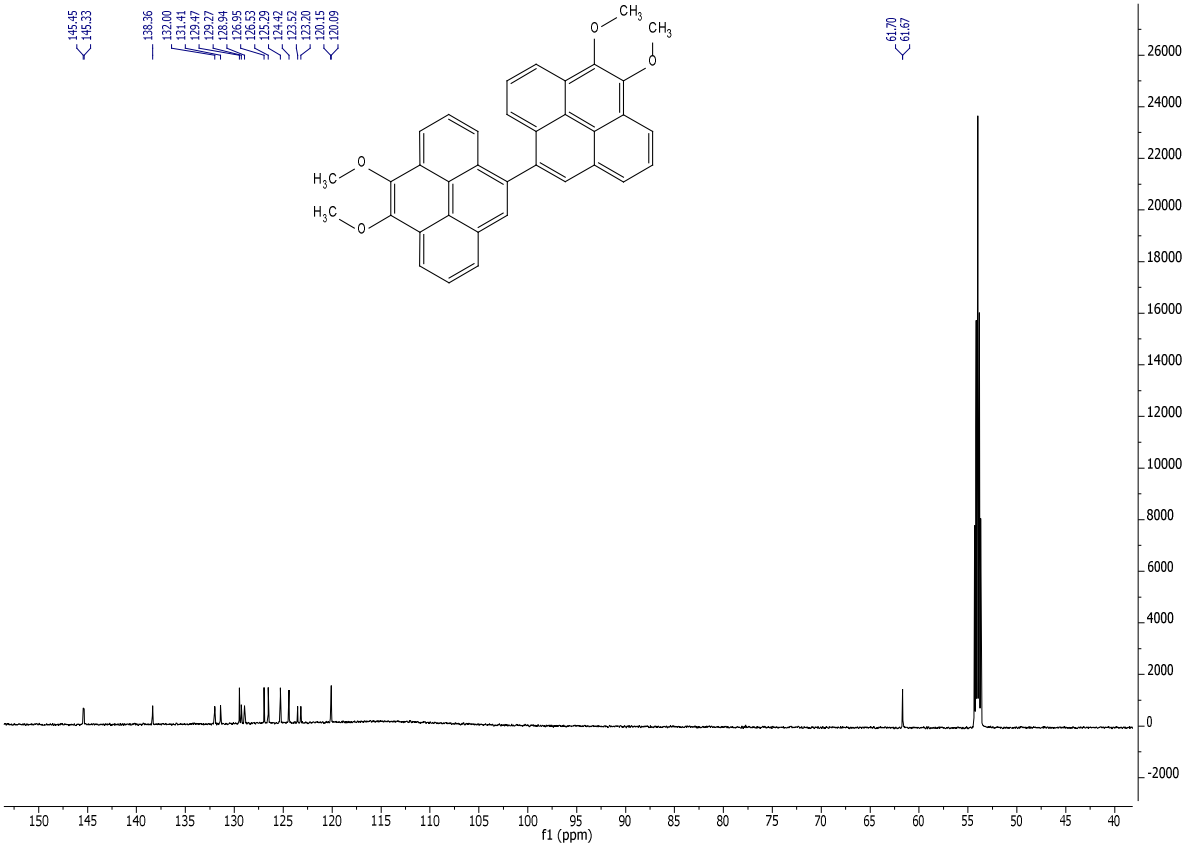
^{1}H NMR (700 MHz at the top) and ^{13}C NMR (176 MHz, at the bottom) of compound **3** at 298K in CD_2Cl_2.



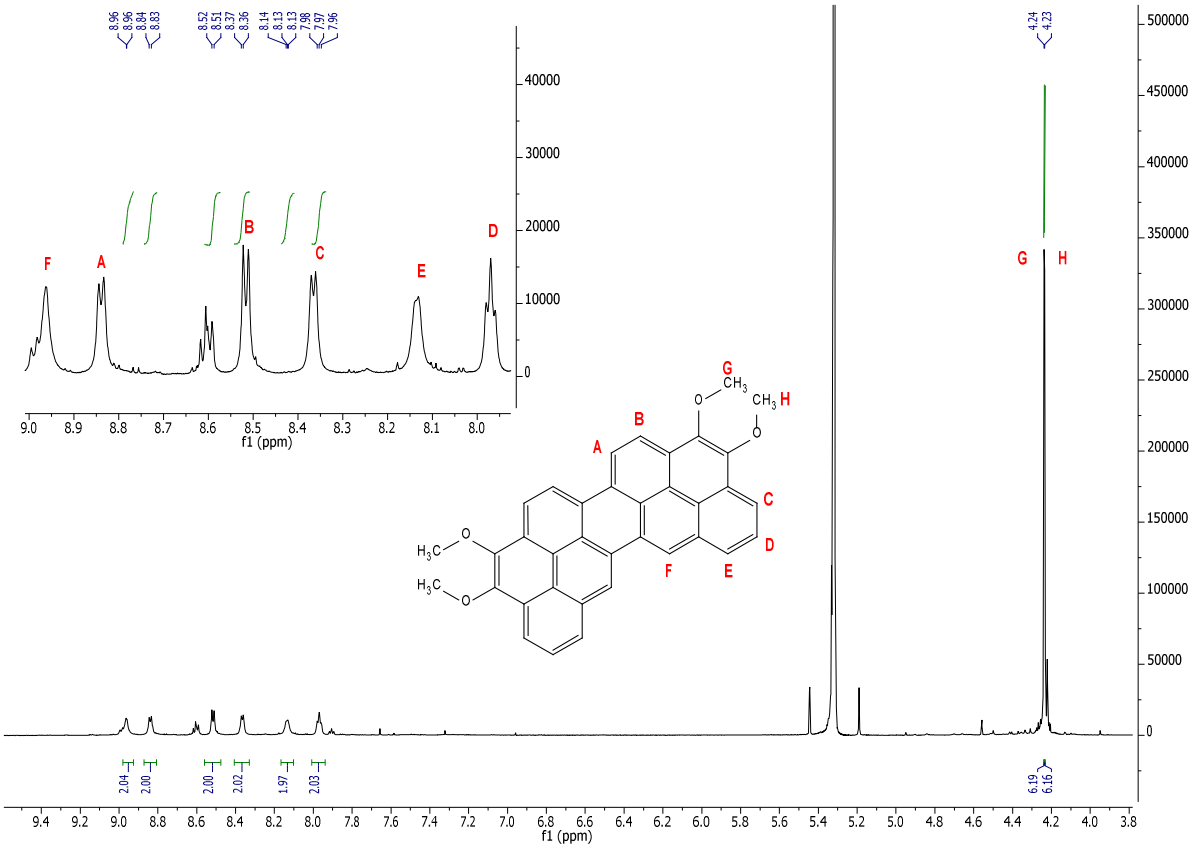


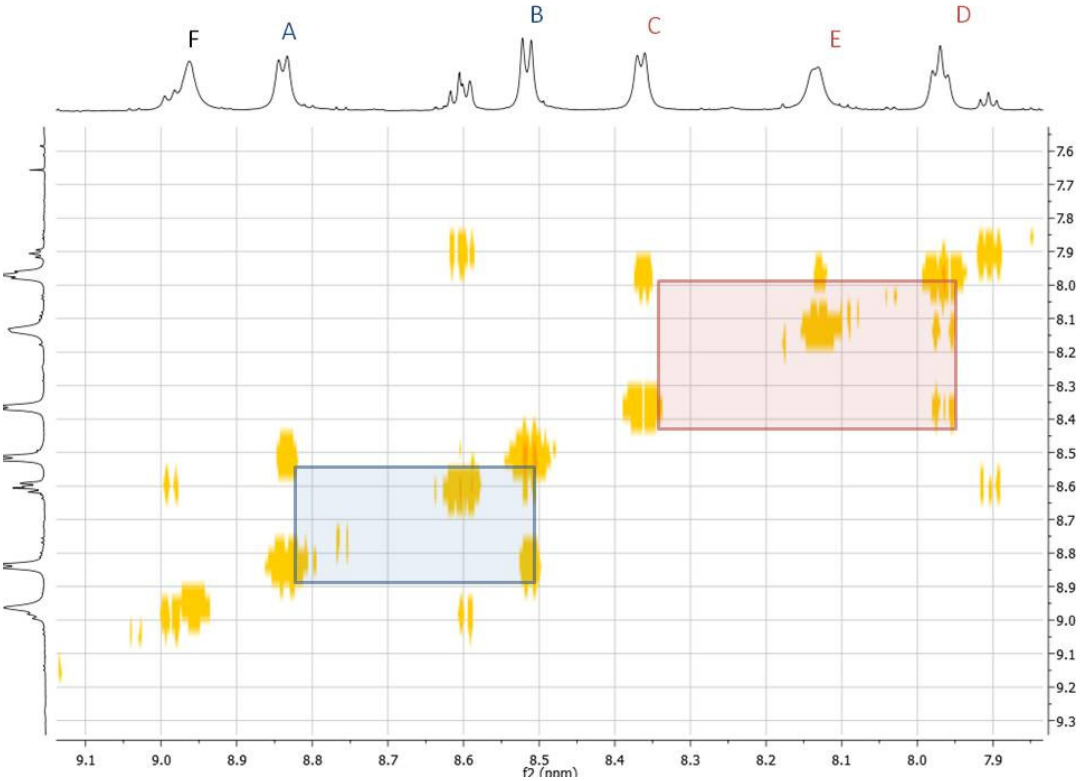
^{1}H NMR (700 MHz at the top) and ^{13}C NMR (176 MHz, at the bottom as an apt) of compound **5** at 298K in CD_2Cl_2.



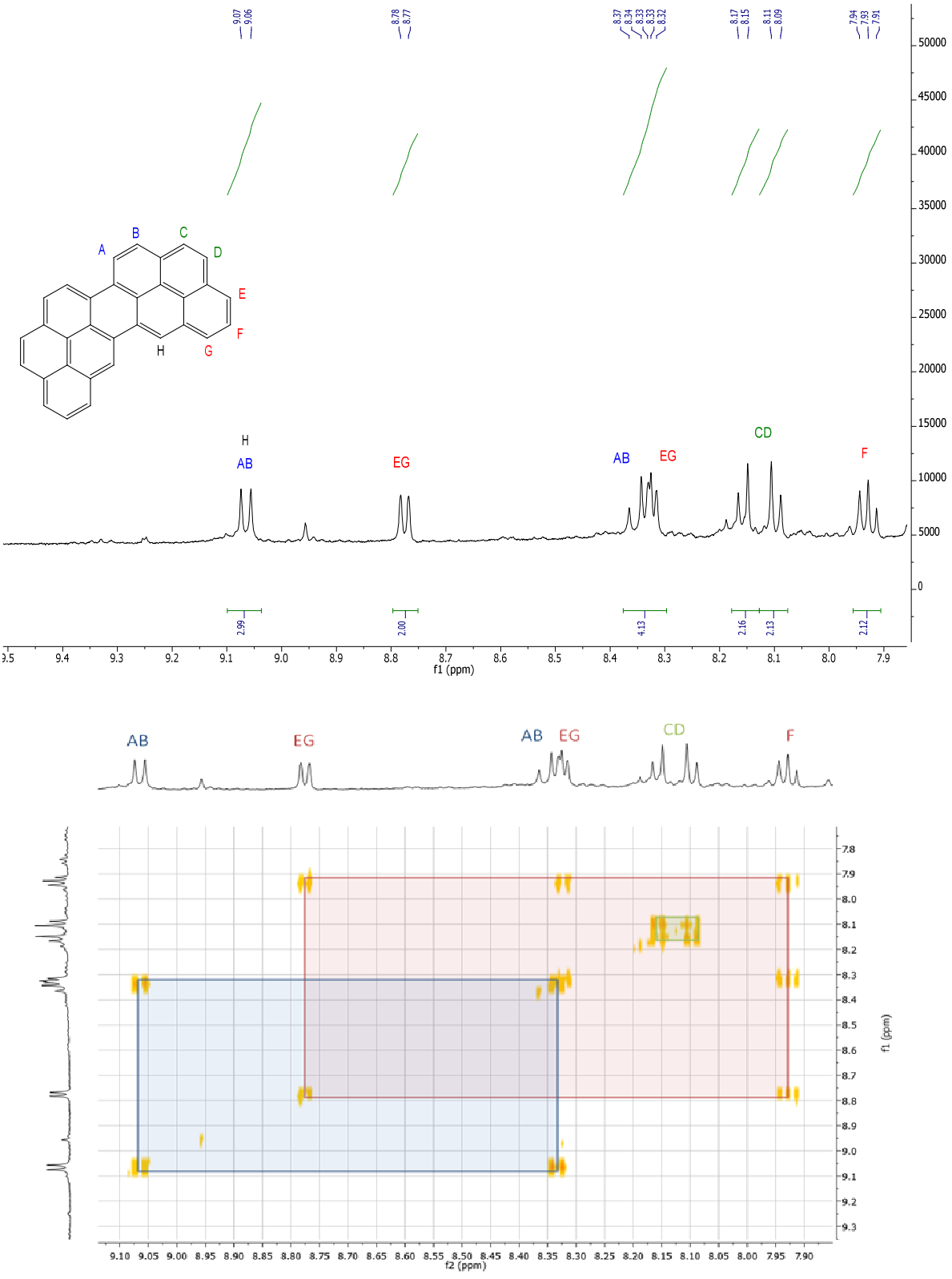


^{1}H NMR (700 MHz at the top) and ^{13}C NMR (176 MHz, at the bottom) of compound **14** at 298K in CD_2Cl_2.



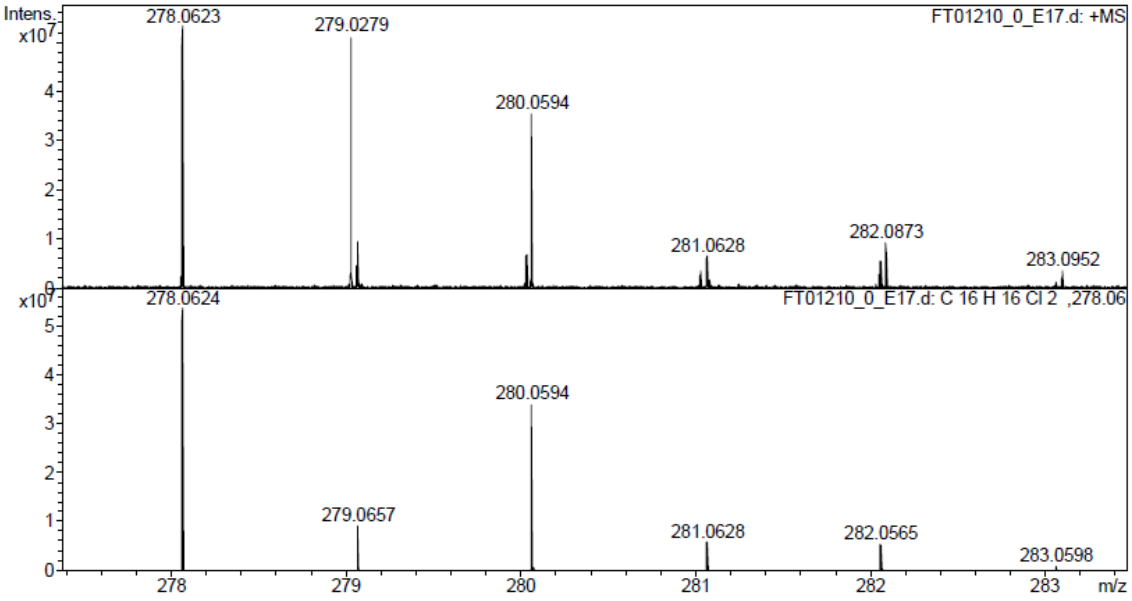


^{1}H NMR (700 MHz at the top) and H,H-COSY NMR (176 MHz, at the bottom) of compound **14a** at 298K in CD_2Cl_2.

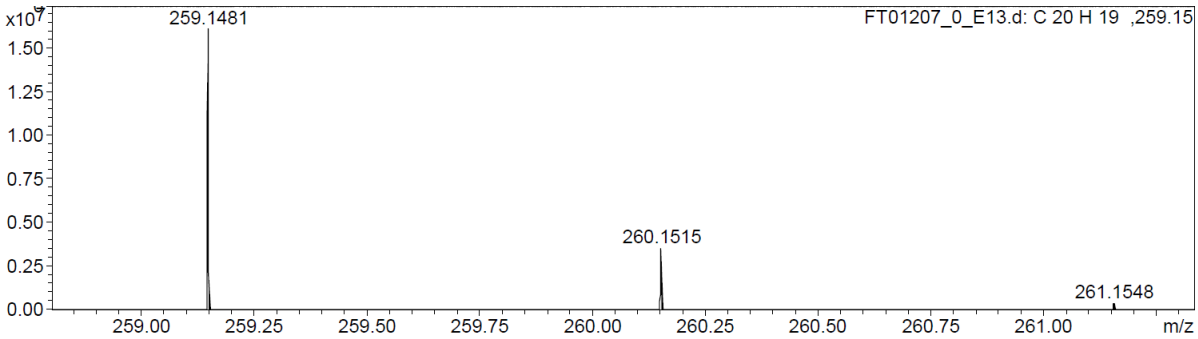


^{1}H NMR (500 MHz at the top) and H,H-COSY NMR (125 MHz, at the bottom) of compound **2a** at 393K in $C_2D_2Cl_4$.

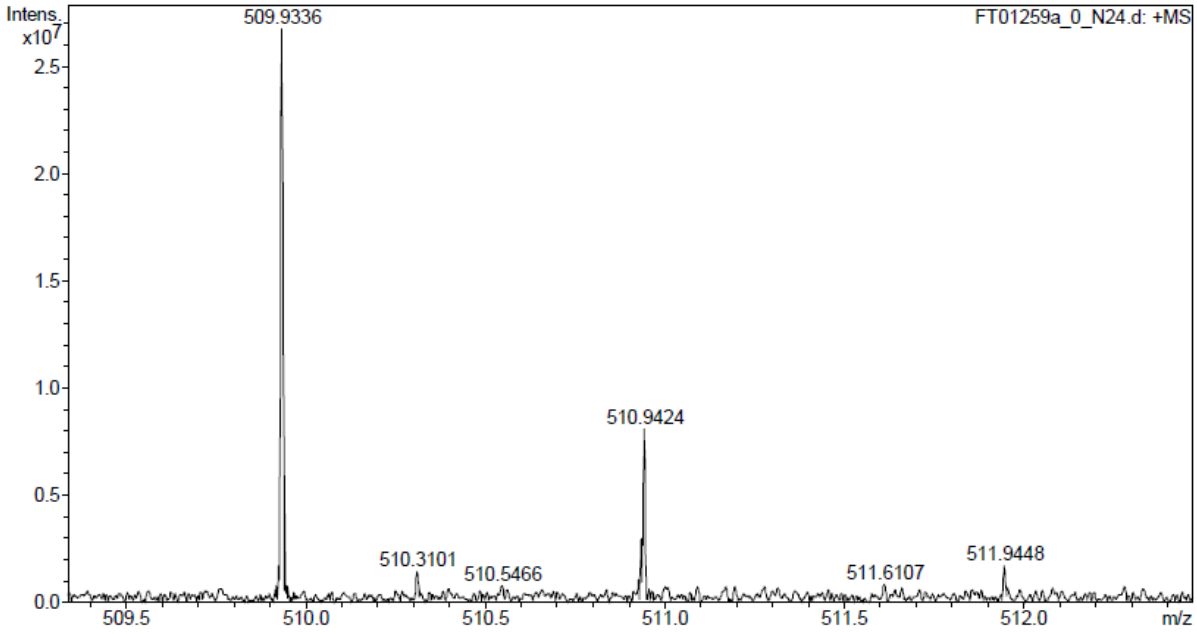
S7. High resolution MALDI



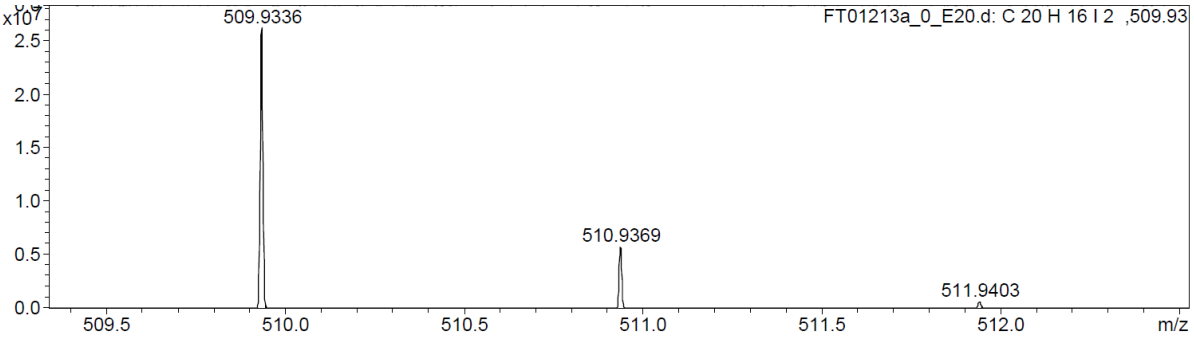
High resolution MALDI spectrum for compound **7** using 3-HPA as matrix (top: measured spectrum; bottom: calculated spectrum).



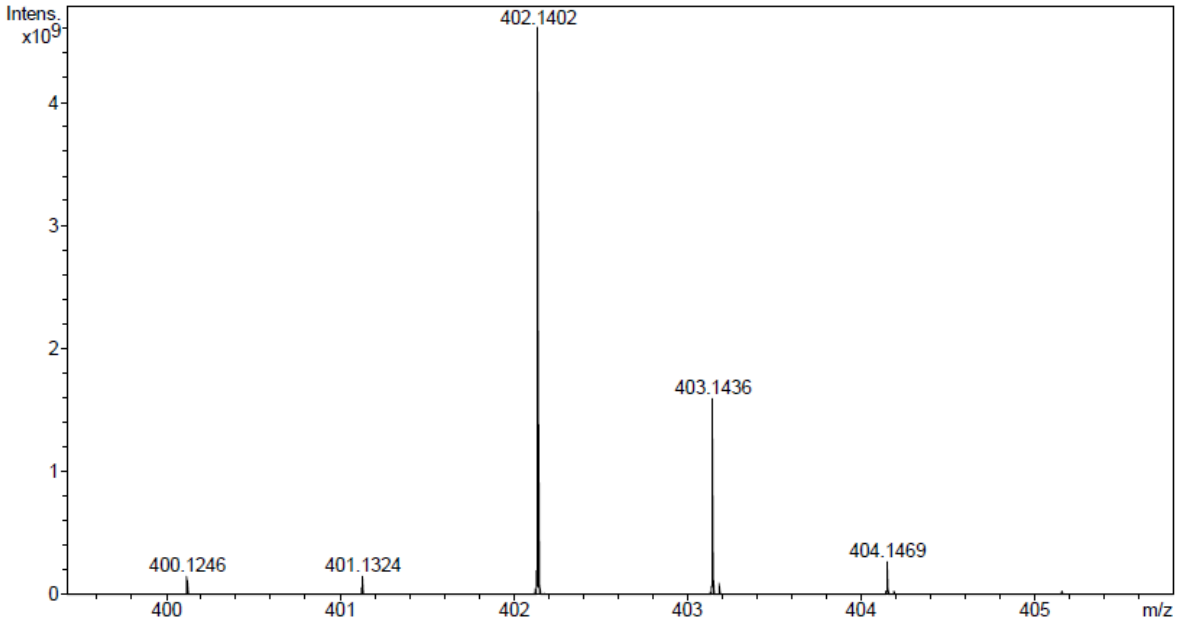
High resolution MALDI spectrum for compound **9** using 3-HPA as matrix.



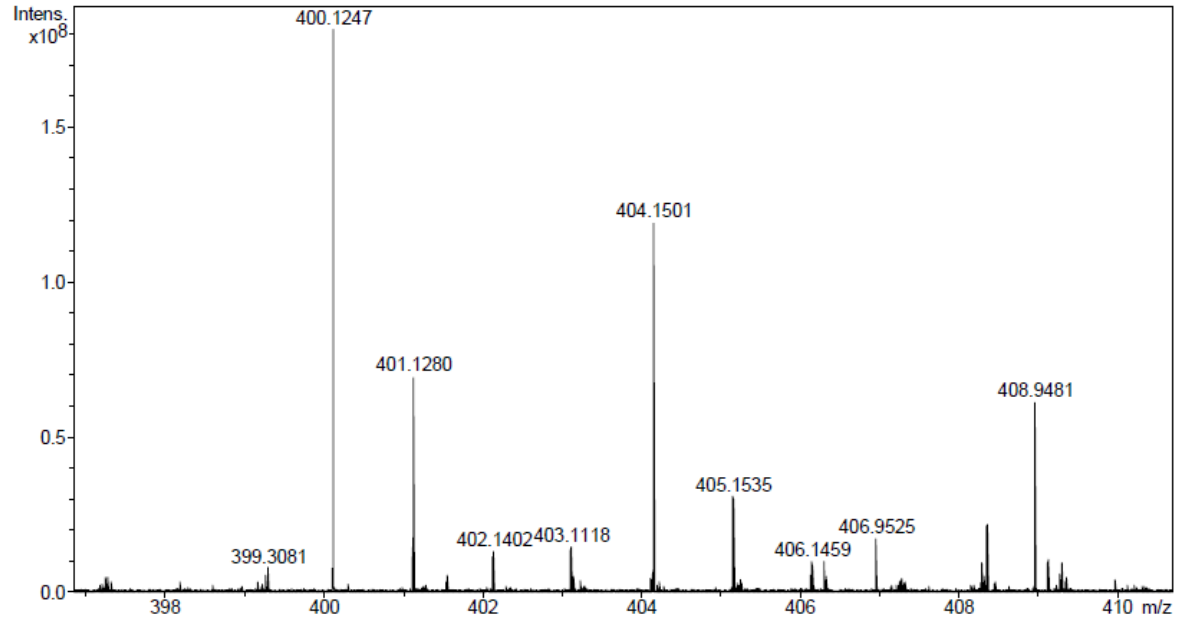
High resolution MALDI spectrum for compound **10** using 3-HPA as matrix.



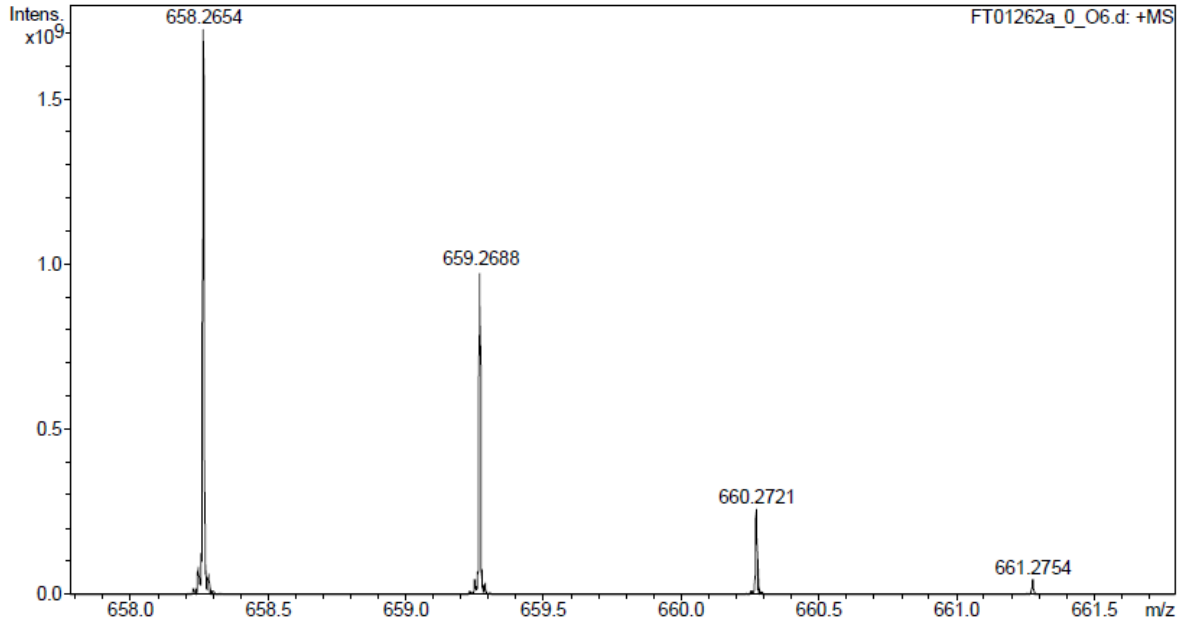
High resolution MALDI spectrum for compound **11** using 3-HPA as matrix.



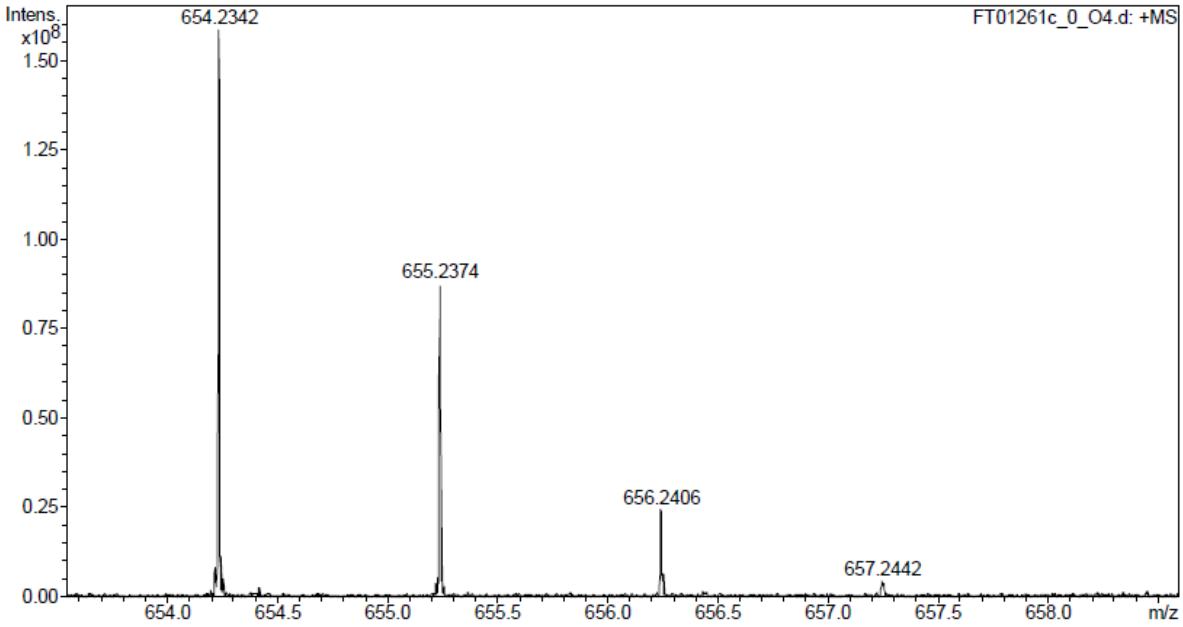
High resolution MALDI spectrum for compound **2** using DCTB as matrix.



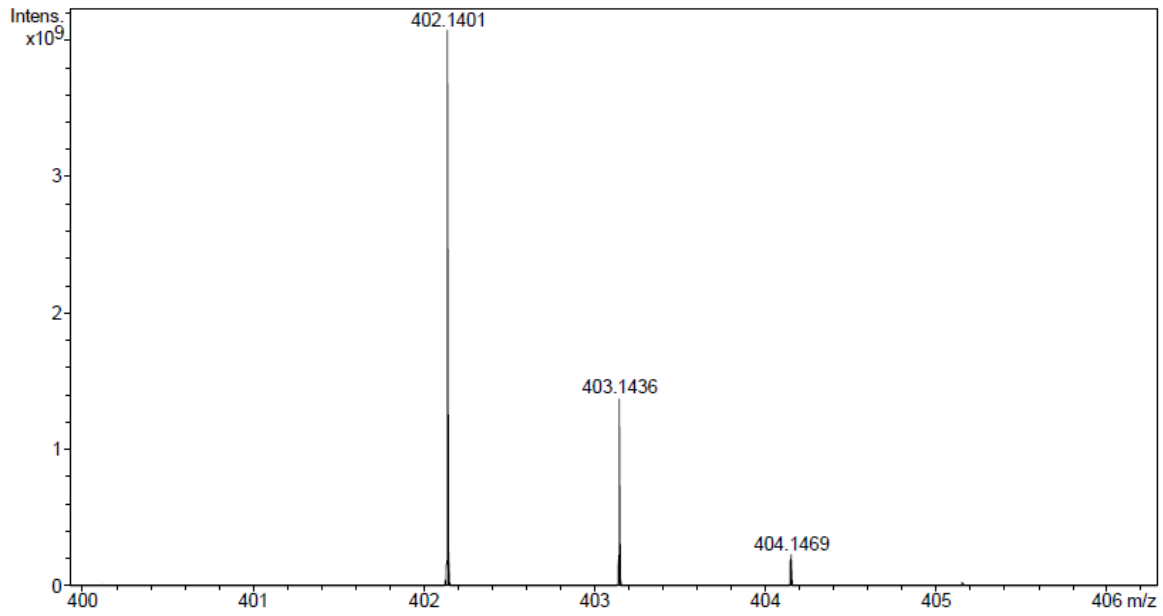
High resolution MALDI spectrum for compound **2a** using DCTB as matrix.



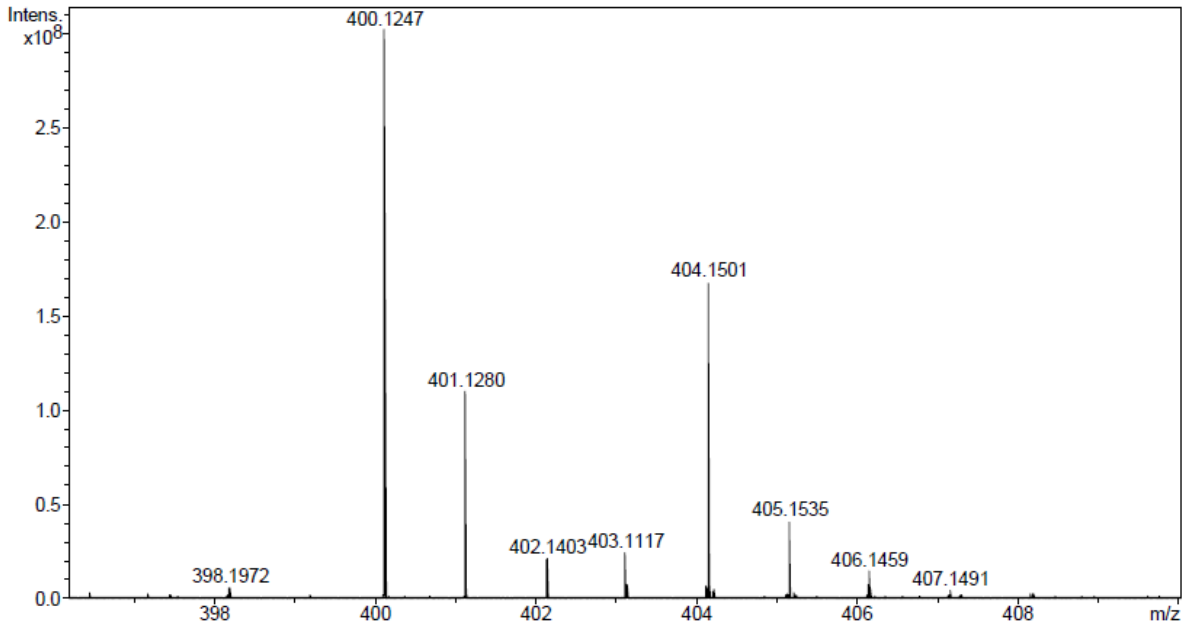
High resolution MALDI spectrum for compound **3** using DCTB as matrix.



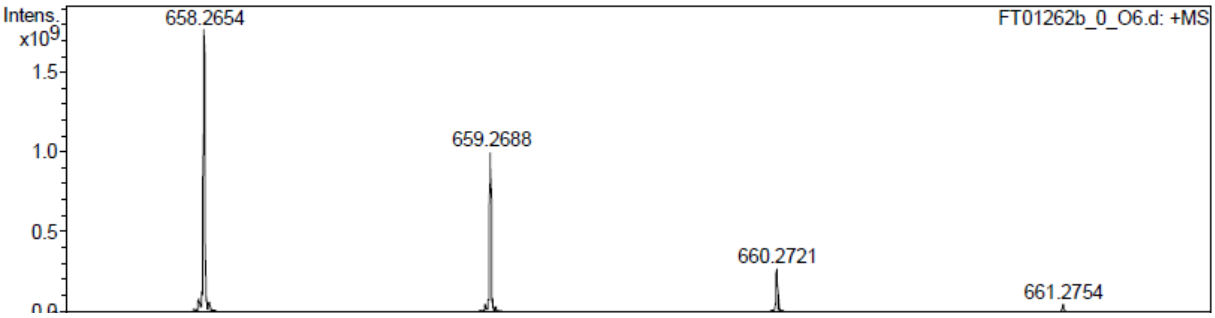
High resolution MALDI spectrum for compound **3a** using DCTB as matrix.



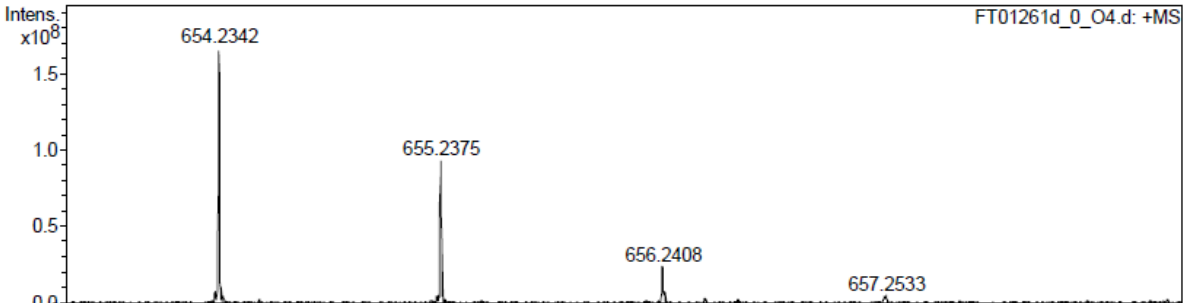
High resolution MALDI spectrum for compound **4** using DCTB as matrix.



High resolution MALDI spectrum for compound **4a** using DCTB as matrix.



High resolution MALDI spectrum for compound **5** using DCTB as matrix.



High resolution MALDI spectrum for compound **5a** using DCTB as matrix.

[1] T. M. Figueira-Duarte, S. C. Simon, M. Wagner, S. I. Drtezhinin, K. A. Zachariasse, K. Müllen, *Angew. Chem. Int. Ed.* **2008**, *47*, 10175.