Electronical Supplementary Information

for

Pentacene based Onsager crosses

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1. Material Synthesis

All reagents and solvents were obtained from ABCR, Sigma-Aldrich, VWR or Grüssing GmbH and were used without further purification. Preparation of air- and moisture-sensitive materials was carried out in flame-dried flasks under an atmosphere of nitrogen by using Schlenk techniques. Thin layer chromatograms were obtained using polygram-TLC-plates (40 × 80 mm, SIL G/UV254, 0.2 mm layer thickness, Macherey-Nagel). For column chromatographical purifications the Isolera Prime flash system with self-packed columns or manual chromatography (SiO_2, grain size 0.04 - 0.063 mm, Macherey-Nagel) was used. Preparative gel permeation chromatography (GPC) was performed on polystyrol (S-X1 Beads, 200-400 Mesh, BioBeads). The syntheses of tetrameric compounds were followed by analytical GPC. Measurements were carried out at rt in stabilizer free THF with PSS-SDV columns (8.0 mm × 30.0 mm, 5 µm particles, 10^2-, 10^3-, 10^5 Å pore size) on a Jasco PU-2050 GPC unit equipped with a Jasco UV-2075 UV- and a Jasco RI-2031 RI-detector. NMR spectra were recorded on Bruker Avance III 600 (^{1}H-NMR: 600 MHz, ^{13}C-NMR: 151 MHz), Avance III 500 (^{1}H-NMR: 500 MHz, ^{13}C-NMR: 125 MHz), and Avance III 300 (^{1}H-NMR: 300 MHz, ^{13}C-NMR: 75 MHz) spectrometers. Carbon signals were assigned using DEPT-experiments. Chemical shifts (δ) are reported in parts per million (ppm) relative to traces of $[H_1]$ solvent in the corresponding deuterated solvent. All NMR spectra were integrated and processed by using ACD/Labs 2012. Melting points for the final products were not determined due to their instability towards oxygen. Mass spectra were recorded on a JEOL JMS-700 magnetic sector, Bruker ApexQe hybrid 9.4 T FT-ICR, Finnigan LCQ quadrupole ion trap, JEOL AccuTOF GCx time-of-flight or Bruker AutoFlex Speed time-of-flight spectrometer. Infrared (IR) spectra were recorded on a Jasco FT/IR-4100 spectrometer and measured in substance.

Chemical formulas were drawn using ChemDraw Ultra 14 and Chem3D Pro 14.0. Iodopentacene **3** and its respective quinone **1** were prepared according to reference [10]. Tetrakis(4-phenylethynyl)silane **7** and Tetrakis(4-bromophenyl)silane **6** were prepared according to reference [11]. Pentacene quinone **2** was prepared according to reference [1].

2-Iodo-6,13-dimethoxy-6,13-bis(triisopropylsilyl)ethynyl-6,13-dihydropentacene (mixture of all stereoisomers) **3d**: Triisopropylsilylacetylene (5.35 mL, 4.35 g, 5.00 equiv.) was dissolved in dry THF (80 mL) under nitrogen atmosphere. The solution was cooled to 0 °C and *n*-butyllithium (11.9 mL 1.60 M in hexane, 19.1 mmol, 4.00 equiv.) was added *via* syringe and the solution stirred for 10 min at this temperature. The acetylide solution was transferred to a flask containing neat 2-iodopentacene-6,13-dione **1** (2.07 g, 4.77 mmol) at 0 °C under constant stirring. The solution was allowed to warm to rt overnight and 2.96 mL methyl iodide (6.76 g, 47.7 mmol, 10.0 equiv.) were added. The resulting solution was stirred at rt overnight, the reaction quenched by addition of DI water (300 mL) and DCM (300 mL). The phases were separated, the aqueous phase extracted with DCM (3 × 200 mL) and the combined organic layers dried over $MgSO_4$. The solvent was removed and the crude product chromatographed over Silica (PE / DCM 2:3), Rf (PE / DCM 1:1) = 0.78 to afford the product as a colorless solid. Yield 1.17 g (1.41 mmol), 30%.

While for **2**, only *trans*-addition of the acetylides was observed and the resulting products are achiral due to their molecular symmetry, in the reaction to **3d** a significant amount of *cis*-addition (ca. 20% according to ^{1}H-NMR spectroscopy) was observed and the additional iodine atom allows for each sp^3-carbon formed to be in *R* or *S* configuration. Both *trans*-enantiomers (*R*,*S*) and (*S*,*R*) each make up ca 40%, while the *cis*-enantiomers (*R*,*R*) and (*S*,*S*) each contribute to ca 10% of the mixture that is summarized as **3d**. As *cis* and *trans*-adducts could not be separated by chromatography, the mixture was employed “as is” for the subsequent Sonogashira coupling with tetrabromide **6** to dearomatized tetramer **X1d**. Characterizations were carried out on the mixture of all stereoisomers. ^{1}H-NMR spectroscopy points to a ratio of *trans*/*cis*-addition of the TIPS-ethynyl-group of roughly 4:1. The signal sets of *trans*- (main product) and *cis*-adduct can be separated in the ^{1}H-spectrum. ^{1}H NMR (600 MHz, $CDCl_3$, 22 °C): δ (ppm) = 8.60-8.57 (m, 3H from *trans*-adduct), 8.53 (s, *cis*-adduct), 8.49 (s, 1H), 8.43 (s, 1H), 8.21-8.19 (m, *cis*-adduct), 8.00-7.93 (m, 2H from *trans*-adduct), 7.91-7.89 (m, *cis*-adduct), 7.83-7.80 (m, 1H), 7.76-7.73 (m, 1H), 7.66-7.63 (*cis*-adduct), 7.56-7.52 (m, 2H from *trans*-adduct), 3.00-2.98 (m, the signal is an overlay of two singuletts from the *trans*-methoxy groups and two *cis*-methoxy-groups), 1.15-1.13 (m, 21H from *trans*-adduct), 1.12-1.10 (m, 21H from *trans*-adduct). ^{13}C {^{1}H} NMR (125.77 MHz, $CDCl_3$, 22 °C): δ (ppm) = 137.90 (CH), 136.67 (C_q), 136.69 (C_q), 136.55 (CH), 136.99 (C_q), 135.92 (C_q), 136.88 (C_q), 136.43 (C_q), 134.99 (C_q), 134.93 (C_q), 134.68 (C_q), 134.42 (C_q), 134.27 (C_q), 132.88 (C_q), 132.67 (C_q), 131.11 (C_q), 131.05 (C_q), 130.97 (C_q), 130.65 (CH), 129.06 (CH), 129.05 (CH), 128.69 (CH), 128.67 (CH), 128.65 (CH), 128.58 (CH), 128.55 (CH); 127.80 (CH), 127.78 (CH), 127.64 (CH), 127.41 (CH), 121.66 (C_q), 109.40 (C_q), 109.36 (C_q), 108.94 (C_q), 93.45 (C_q), 90.10 (C_q), 90.08 (C_q), 89.51 (C_q), 89.43 (C_q), 75.85 (C_q), 75.82 (C_q), 75.47 (C_q), 75.45 (C_q), 52.30 (CH/CH_3), 19.28 (CH/CH_3), 19.25 (CH/CH_3), 12.40 (CH/CH_3), 12.37 (CH/CH_3). The ^{13}C signals are a combination of *cis*- and *trans*-diastereomer pairs. HR-MS (ESI$^+$): *m/z* $[M+Na]^+$ calcd. for $C_{46}H_{59}IO_2Si_2Na$: 849.29960, found: 849.30126, correct isotope distribution.

6,13-Dimethoxy-13-(triisopropylsilyl)ethynyl-6-trimethylsilylethynyl-6,13-dihydropentacene **5**: Pentacene quinone **2** (4.30 g, 13.95 mmol) was suspended in dry THF (75 mL) under nitrogen atmosphere and cooled to 0 °C. In a second flask, triisopropylsilylacetylene (3.75 mL, 3.05 g, 16.73 mmol, 1.20 equiv.) was dissolved in dry THF (35 mL), cooled to -78 °C and *n*BuLi (6.14 mL 2.5M in hexane, 15.34 mmol, 1.10 equiv.) was slowly added (syringe). In a third flask, trimethylsilylacetylene (2.38 mL, 1.64 g, 16.73 mmol, 1.20 equiv. in 25 mL dry THF) was lithiated (6.14 mL, 15.34 mmol, 1.10 equiv.) identically. The acetylide solutions were stirred for 15 min and warmed to 0 °C during this time. The triisopropylsilylacetylide solution was slowly transferred (cannula) into the suspension of pentacene quinone in THF and the resulting mixture stirred at rt for 1.5 h. Stirring was stopped at this point to allow undissolved material to settle to the ground. The overstanding solution was transferred (cannula) into the solution of trimethylsilylacetylide (0 °C); the solid residue was extracted once with additional dry THF (5 mL). The resulting solution was stirred at rt for 2 h. At this point, methyl iodide (8.72 mL, 19.8 g, 139 mmol, 10.0 equiv.) was added and the reaction stirred overnight at rt. The compound was purified as described in the literature.[12] Yield: 4.26 g (6.90 mmol), 50% of a colorless solid. ^{1}H NMR (500 MHz, $CDCl_3$, 25 °C): δ (ppm) = 8.71 (s, 2H), 8.43 (s, 2H), 8.02-7.90 (m, 4H), 7.60-7.53 (m, 4H), 3.04 (s, 3H), 3.03 (s, 3H), 1.27-1.22 (m, 21H), 0.08 (s, 9H). Spectral data in agreement to published literature.[12]

6,13-Dimethoxy-13-(triisopropylsilyl)ethynyl-6-ethynyl-6,13-dihydropentacene **4d**: 2.70 (4.38 mmol) 6,13-dimethoxy-13-(triisopropylsilyl)ethynyl-6-trimethylsilylethynyl-6,13-dihydropentacene **5** were dissolved in 100 mL 1:1 THF/MeOH. K_2CO_3 (1.21 g, 8.75 mmol, 2.00 equiv.) was added and the suspension stirred at rt for 2 h. DCM (500 mL) and DI water (400 mL) were added, the phases separated and the aqueous phase extracted with DCM (3 × 100 mL). The combined organic layers were dried over $MgSO_4$, filtered and the solvent evaporated. The residual material was subjected to automated column chromatography (gradient of PE in DCM). Rf (SiO2, PE/DCM 1:1) = 0.22. Yield: 1.98 g (3.63 mmol), 83% of a colorless solid. ^{1}H NMR (300 MHz, $CDCl_3$, 25 °C): δ (ppm) = 8.72 (s, 2H), 8.45 (s, 2H), 8.03-7.90 (m, 4H), 7.63-7.52 (m, 4H), 3.06 (s, 3H), 3.04 (s, 3H), 2.72 (s, 1H), 1.29-1.23 (m, 21 H). Spectral data in agreement with published literature.[12]

Tetrakis(4-((6,13-dimethoxy-6,13-bis((triisopropylsilyl)ethynyl)-6,13-dihydropentacen-2-yl)ethynyl)phenyl)silane **X1d** *(mixture of all stereoisomers)*: 2-Iodo-6,13-dimethoxy-6,13-bis(triisopropylsilyl)ethynyl-6,13-dihydropentacene (mixture of all stereoisomers) **3d** (200 mg, 242 µmol, 4.20 equiv.) and tetrakis(4-ethynylphenyl)silane **7** (24.9 mg, 57.6 µmol, 1.00 equiv.) were brought under nitrogen atmosphere. To a degassed solution of triethylamine / THF 1:1 (3.5 mL) were added tetrakis(triphenylphosphin)palladium(0) (2.00 mg, 1.73 µmol, 0.03 equiv.) and CuI (658 µg, 3.45 µmol, 0.06 equiv.), the solution stirred for 10 min at rt and the catalyst solution transferred to the educt flask (syringe). The mixture was stirred for 16 h at rt and quenched by addition of 10 mL DCM and 10 mL DI water. The phases were separated, the aqueous phase extracted with DCM (3 x 10 mL), the combined organic layers dried over $MgSO_4$, the solvent removed and the material redissolved in little DCM / PE 1:1. The solution was filtered over a short silica column (Rf = 0.55 in DCM / PE 1:1) and the resulting crude product purified by preparative GPC ($CHCl_3$) to yield the pure stereoisomeric mixture that comprises **X1d** as a film forming solid. Yield: 126 mg (39.1 µmol), 68%. Due to **X1d** being a mixture, for analysis only ^{1}H-NMR spectroscopy and HR-MS were performed. ^{1}H NMR (600 MHz, d_8-THF, 25 °C): δ (ppm) = 8.63-8.57 (m, 16H), 8.23 (s, 4H), 8.02-7.94 (m, 12H), 7.72-7.67 (m, 20H), 7.56-7.52 (m, 8H), 3.01 (s, 12H), 3.00 (s, 12H), 1.16-1.14 (m, 84H), 1.14-1.11 (m, 84H). HRMS (MALDI$^+$): The aromatization within the spectrometer is so fast that only fully aromatized **X1** could be observed.

Tetrakis(4-((6,13-bis((triisopropylsilyl)ethynyl)pentacen-2-yl)ethynyl)phenyl)silane **X1**: *Method A; By cross-coupling of* **3***:* To a degassed solution of 2-iodo-6,13-bis(triisopropylsilyl)ethynyl pentacene **3** (283 mg, 370 µmol, 4.00 equiv.) and tetrakis(4-ethynylphenyl)silane **7**, tetrakis(triphenylphosphine)palladium(0) (10.7 mg, 9.25 µmol, 0.10 equiv.) and CuI (1.76 mg, 9.25 µmol, 0.10 equiv.) in 2:1 THF / NEt_3 were added and the resulting mixture stirred at rt and under light protection overnight. The reaction was quenched by addition of DCM and DI water (10 mL each), phases were separated and the aqueous phase extracted with DCM (3 x 50 mL). The combined organic layers were dried over $MgSO_4$, the solvent evaporated and the residual material redissolved in PE / DCM 1:2 and passed through a short silica column to remove catalyst residue. The dark blue / cyan solution was evaporated and the remaining material dissolved in toluene and purified by preparative GPC (toluene) to yield the product as a blue solution. The toluene was removed by vacuum destillation under nitrogen atmosphere at room temperature to yield **X1** as a black / blue amorphous solid. Yield: 111 mg (37.4 µmol), 40%.

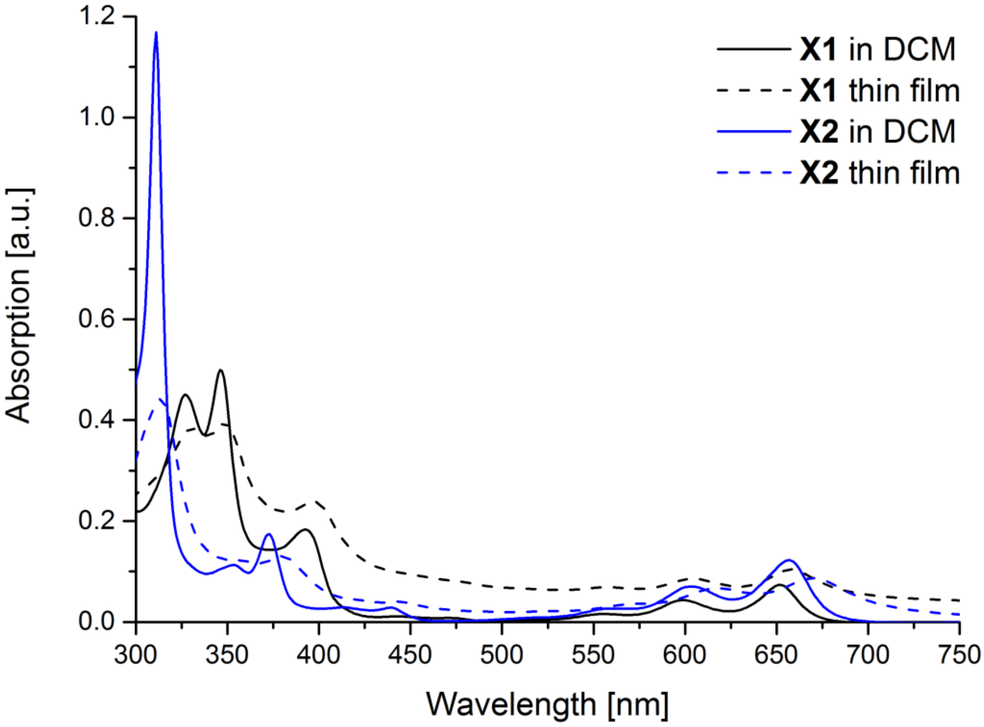
Method B; by reductive aromatization of **X1d***:* **X1d** (70.0 mg, 21.7 µmol) was dissolved in a degassed (N_2) mixture of THF (4.5 mL) and concentrated hydrochloric acid (0.5 mL) containing $SnCl_2$ (41.1 mg, 217 µmol, 10.0 equiv.). The solution quickly changed to a dark blue / cyan color and was stirred for 20 min at rt. The reaction was quenched by addition of chloroform (10 mL) and 10 mL half concentrated $NaHCO_3$-solution. Phases were separated and the aqueous phase extracted with chloroform (3 × 5 mL). The combined organic layers were dried over $MgSO_4$, the solvent removed under high vacuum (cooling trap) and the crude product purified by preparative GPC (toluene). The solvent was removed under high vacuum (cooling trap) to yield **X1** as a dark blue, solid film. 24.0 mg (8.05 µmol), 37%. ^{1}H NMR (600 MHz, $CDCl_3$, 22 °C): δ (ppm) = 9.35-9.26 (m, 16H), 8.25-8.18 (m, 1H), 8.03-7.93 (m, 3H), 7.76-7.66 (m, 3H), 7.66-7.62 (m, 1H), 7.53-7.47 (m, 1H), 7.46-7.41 (m, 2H), 1.42-1.35 (m, 42H). ^{13}C {^{1}H} NMR (150 MHz, $CDCl_3$, 22 °C): δ (ppm) = 136.33 (CH), 136.28 (CH), 133.81 (C_q), 133.53 (C_q), 132.61 (CH), 132.40 (C_q), 132.39 (C_q), 131.95 (C_q), 131.54 (C_q), 131.23 (CH), 131.08 (C_q), 130.94 (C_q), 130.88 (C_q), 130.76 (C_q), 130.72 (C_q), 128.91 (CH), 128.67 (CH), 128.02 (CH), 126.62 (CH), 126.44 (CH), 126.40 (CH), 126.37 (CH), 126.16 (CH), 124.99 (C_q), 124.92 (C_q), 120.41 (C_q), 120.38 (C_q), 118.64 (C_q), 118.54 (C_q), 107.63 (C_q), 107.37 (C_q), 104.45 (C_q), 91.72 (C_q), 91.05 (C_q), 19.03 (CH), 19.00 (CH), 11.66 (CH_3). FT-IR (neat): v (cm^{-1}) = 2942, 2889, 2864, 1465, 1369, 1095, 874, 740. HRMS (MALDI$^+$): *m/z* $[M+H]^+$ calcd. for $C_{208}H_{229}Si_9$: 2980.59098 found: 2980.60523, correct isotope distribution.

Tetrakis(4-((6,13-dimethoxy-13-((triisopropylsilyl)ethynyl)-6,13-dihydropentacen-6-yl)ethynyl)phenyl)silane **X2d**: Compound **4d** (740 mg, 1.36 mmol) and tetrakis(4-bromophenyl)silane **6** (195 mg, 299 µmol, 0.22 equiv.) were dissolved in 30 mL THF / HN*i*Pr_2 2:1 and the mixture degassed. Tris(tertbutyl)phosphonium tetrafluoroborate (78.8 mg, 272 µmol, 0.20 equiv.), bis(dibenzylideneacetone)palladium(0) (156 mg, 272 mg, 0.20 equiv.) and CuI (51.7 mg, 272 µmol, 0.20 equiv.) were added in this sequence and the light brown reaction mixture stirred at rt for 3 days. The reaction was quenched by addition of 100 mL water and DCM (100 mL). Phases were separated; the aqueous layer was extracted (3 × 100 mL DCM) and the combined organic layers dried over anhydrous $MgSO_4$. The solvent was evaporated and the residual material subjected to automated column chromatography (SiO_2). Rf (SiO_2, PE / DCM 1:1) = 0.28. Yield: 694 mg (277 µmol), 93% of a colorless, film-forming compound. ^{1}H NMR (600 MHz, $CDCl_3$, 22 °C): δ (ppm) = 8.71 (s, 8H), 8.44 (s, 8H), 7.98-7.90 (m, 16H), 7.57-7.53 (m, 16H), 7.24-7.12 (m, 16H), 3.08 (s, 12H), 3.03 (s, 12H), 1.27-1.23 (m, 84H). ^{13}C {^{1}H} NMR (150 MHz, $CDCl_3$, 22 °C): δ (ppm) = 136,64 (CH), 133.98 (C_q), 133.48 (C_q), 133.27 (C_q), 133.11 (C_q), 132.74 (C_q), 130.79 (CH), 128.22 (CH), 128.20 (CH), 128.13 (CH), 126.88 (CH), 126.79 (CH), 126.63 (CH), 124.15 (C_q), 105.32 (C_q), 92.82 (C_q), 91.70 (C_q), 85.87 (C_q), 76.02 (C_q), 73.55 (C_q), 52.11 (CH_3), 51.91 (CH_3), 18.78 (CH), 11.38 (CH_3). FT-IR (neat): v (cm^{-1}) = 3057, 2939, 2889, 2862, 2814, 1618, 1335, 1057, 873, 743. HR-MS (MALDI$^+$): *m/z* $[M+H]^+$ calcd. for $C_{172}H_{173}O_8Si_5$: 2507.20104, found: 2507.20513, correct isotope distribution.

Tetrakis(4-((13-((triisopropylsilyl)ethynyl)pentacen-6-yl)ethynyl)phenyl)silane **X2**: Dearomatized pentacene tetramer **X2d** (729 mg, 291 µmol) was added to a degassed solution (10 mL) of $SnCl_2$ (661 mg, 3.49 mmol, 12.0 equiv.) in THF containing some drops of concentrated hydrochloric acid. The solution immediately changed its color to a dark blue. It was stirred overnight at rt under nitrogen atmosphere and light protection. The solution was transferred into a separation funnel containing 10 mL DI water and extracted with DCM until no blue residue remained in the funnel (5 × 5 mL DCM). The combined organic layers were dried over $MgSO_4$, the solvent removed and the remaining amorphous, blueish-black material redissolved in little DCM / PE 2:1 and passed through a short silica column to remove inorganic residues to yield 544 mg raw product. This material was redissolved in chloroform and purified by preparative GPC to yield the product as a blueish/black, amorphous solid. Yield: 429 mg (190 µmol), 65%. ^{1}H NMR (500 MHz, d_8-THF, 22 °C), δ (ppm) = 9.05 (s, 8H), 8.97 (s, 8H), 8.25-8.12 (m, 16H), 7.93-7.80 (m, 16H), 7.46-7.36 (m, 16H), 1.50-1.32 (m, 84H). ^{13}C {^{1}H} NMR (125 MHz, d_8-THF, 22 °C): δ (ppm) = 137.89 (CH), 135.54 (C_q), 133.32 (C_q), 133.24 (C_q), 132.60 (CH), 131.09 (C_q), 130.77 (C_q), 129.60 (CH), 129.45 (CH), 127.11 (CH), 127.03 (CH), 126.96 (C_q), 126.48 (CH), 118.78 (C_q), 118.73 (C_q), 107.44 (C_q), 105.96 (C_q), 105.85 (C_q), 90.94 (C_q), 19.68 (CH/CH_3), 12.85 (CH/CH_3).FT-IR (neat): v (cm^{-1}) = 3052, 2939, 2889, 2862, 1591, 1460, 1060, 874, 740. HR-MS (MALDI$^+$): *m/z* $[M+H]^+$ calcd. for $C_{164}H_{149}Si_5$: 2259.0592, found: 2259.06837, correct isotope distribution.

2. Optical Spectroscopy

Solution and film spectra of crosses **X1** and **X2**. Thin films were spincoated on glass (1500 rpm/s, 1000 rpm/s from 10 mg/mL solutions in toluene) and dried on air.



3. Organic Field Effect Transistors

Prepatterned Si/SiO$_2$ (SiO$_2$ = 230 nm; Frauenhofer IPMS, Dresden) substrates with 30 nm thick Au source and drain contacts on indium tin oxide (ITO) adhesion layer (W = 10000 µm; L = 10 µm or 20 µm) were used to build transistors. First the protection layer from the devices was removed by sonication in acetone for 10 min, rinsing with acetone and drying with an air stream. Further cleaning of the devices and glass substrates was accomplished by sonication in acetone (10 min) and isopropanol (10 min). Between each step all substrates were rinsed with the corresponding solvent and dried with compressed air.

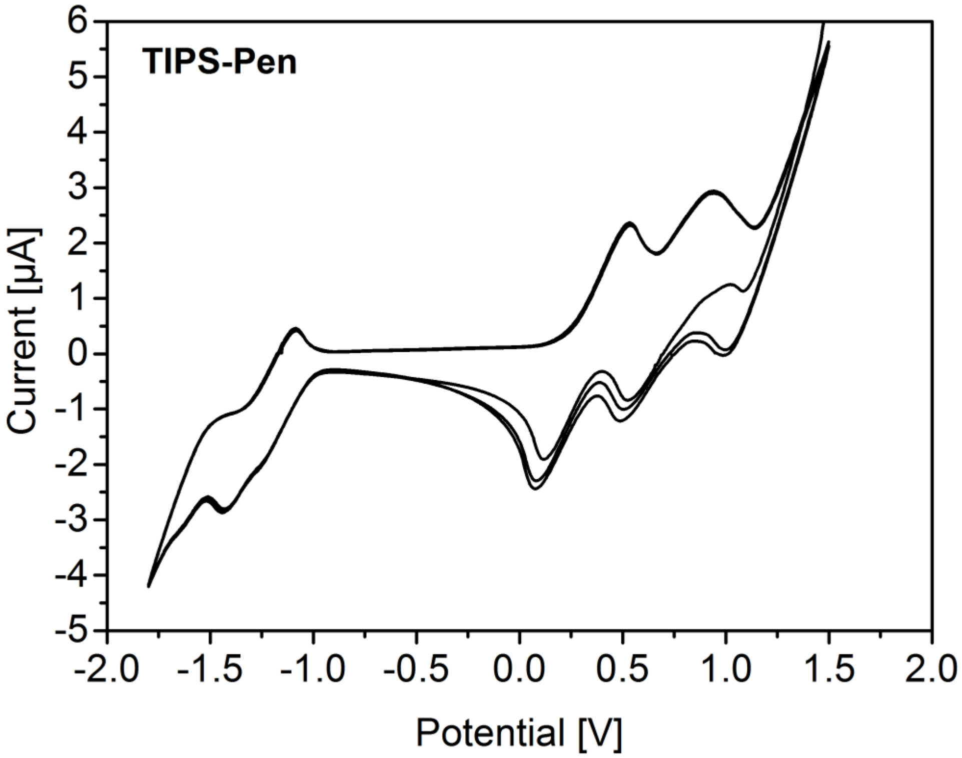
The thin film preparation was performed at room temperature inside a nitrogen-filled glove box. **X1** and **X2** were applied in solution from toluene (10 mg mL^{-1}) by spin coating at 1000 rpm / 20 s and 3000 rpm / 30 s. All electronic measurements were performed with a Keithley 4200-SCS in a nitrogen-filled glove box.

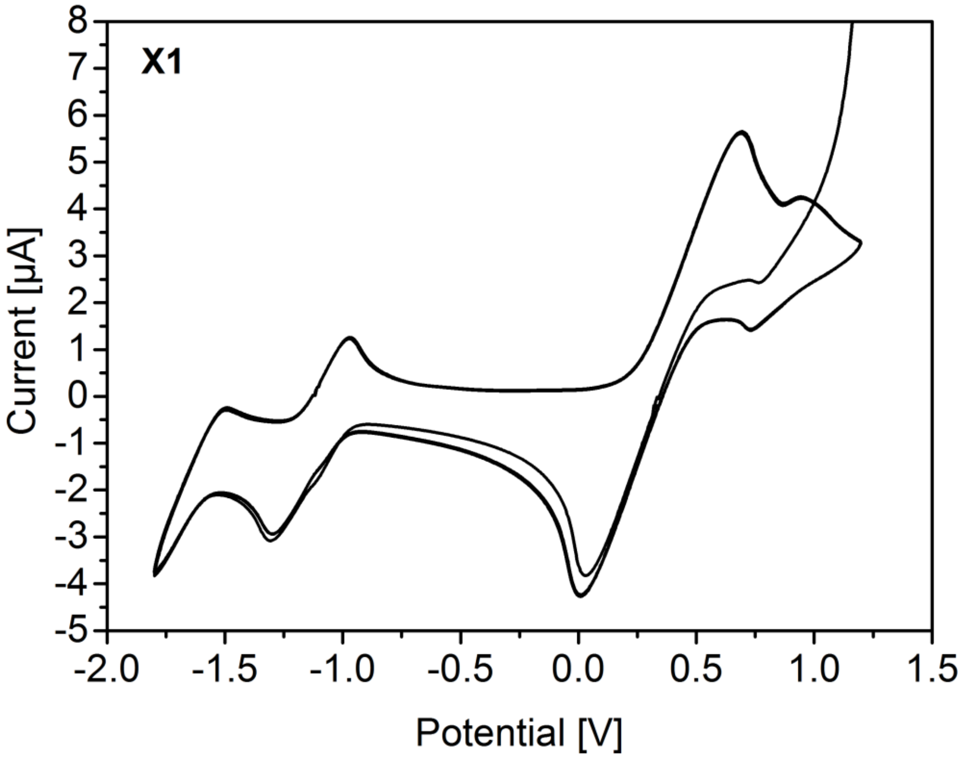
4. Electrochemistry

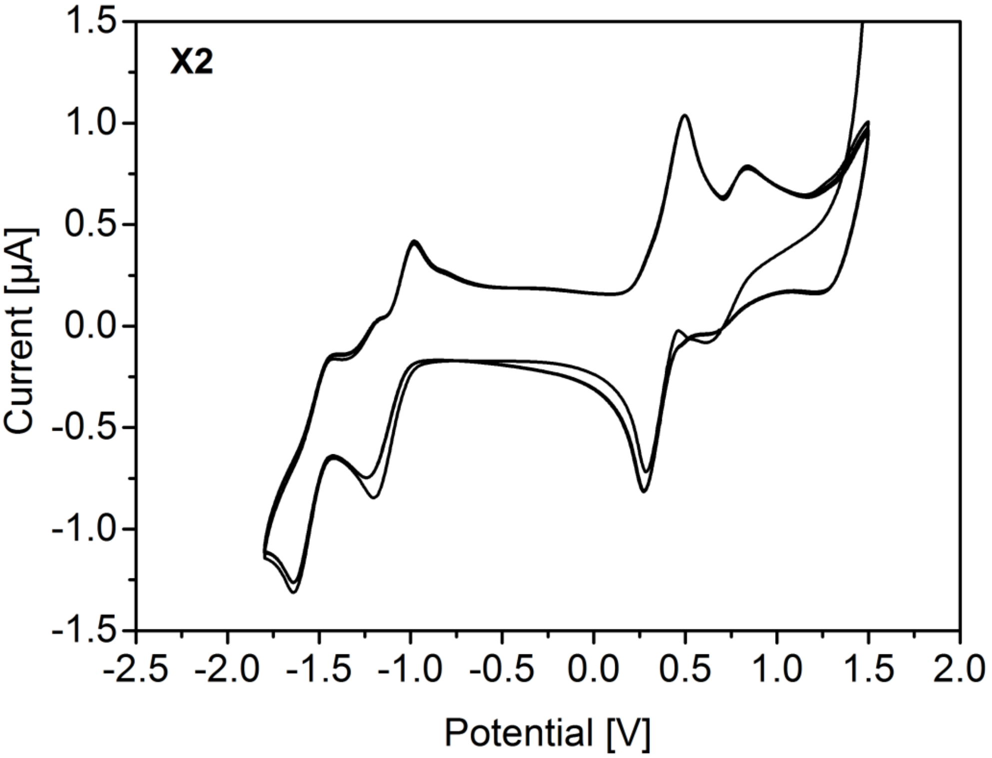
Cyclic voltammetry was performed in DCM solutions of the respective molecule using Bu_4NPF_6 as an electrolyte. For the estimation of the FMO-energies, ferrocene was added as an internal standard. For the HOMO of ferrocene, an energy of -4.8 eV was assumed, allowing to estimate the FMO-energies from the potentials listed in Table S1. The original cyclic voltammograms are listed below.

Table S1

electrochemical potentials	TIPS-Pen	X1	X2
Reduction [V]	-1.57	-1.43	-1.48
Oxidation [V]	0.41	0.46	0.34




X1
Current [µA]
Potential [V]
8
7
6
5
4
3
2
1
0
-1
-2
-3
-4
-5
-2.0
-1.5
-1.0
-0.5
0.0
0.5
1.0
1.5

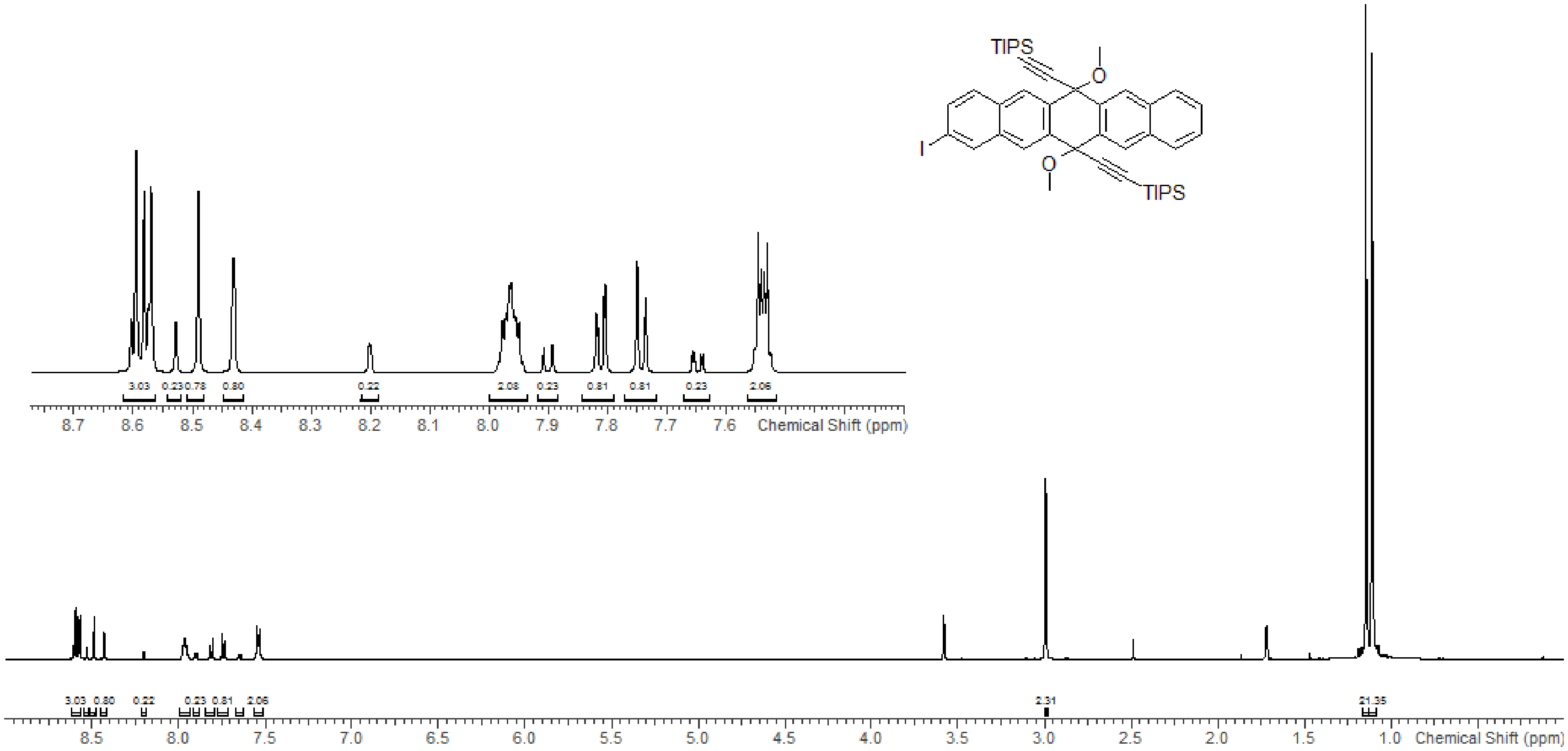

X2
Current [µA]
Potential [V]
1.5
1.0
0.5
0.0
-0.5
-1.0
-1.5
-2.5
-2.0
-1.5
-1.0
-0.5
0.0
0.5
1.0
1.5
2.0

5. NMR-Spectra

2-Iodo-6,13-dimethoxy-6,13-bis(triisopropylsilyl)ethynyl-6,13-dihydropentacene (mixture of all stereoisomers) **1d**

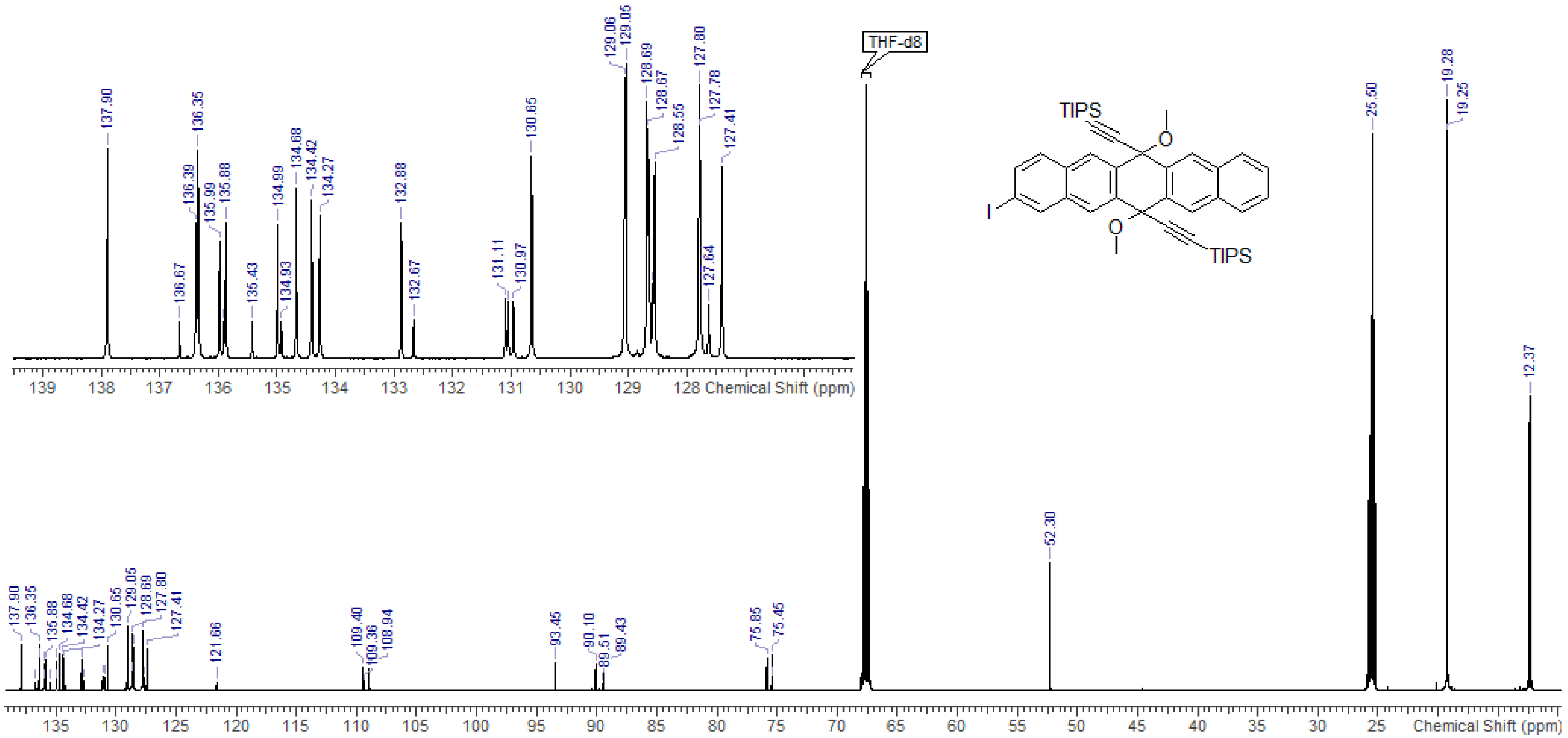
Acquisition Time (sec)	3.6351	*Comment*	kb1027	*D*	0.1	*D1*	0.1
DE	12	*DS*	2				

Frequency (MHz)	600.2438	*GB*	0	*INSTRUM*	<spect>	*LB*	0.3
NS	128	*Nucleus*	1H	*Number of Transients*	128	*Origin*	spect
Original Points Count	65536	*Owner*	ns	*PC*	1	*PROBHD*	<Z132808_0001 (CP QCI 600S3 H/P/C-N-D-05 Z LT)>
PULPROG	<zg30>	*Points Count*	65536	*Pulse Sequence*	zg30	*Receiver Gain*	7.02
SF	600.243829	*SFO1*	600.24683021945			*SI*	65536
SSB	0	*SW(cyclical) (Hz)*	18028.85	*SWH*	18028.8461538462		
Solvent	THF	*Spectrum Offset (Hz)*	2802.8950	*Spectrum Type*	standard	*Sweep Width (Hz)*	18028.57
TD	131072	*TD0*	16	*TE*	295.0005	*Temperature (degree C)*	22.000
UNC1	<1H>	*WDW*	1				



Acquisition Time (sec)	1.0795	***Comment***	kb1027	***D***	0.03	***D1***	2
DE	18	***DS***	4				

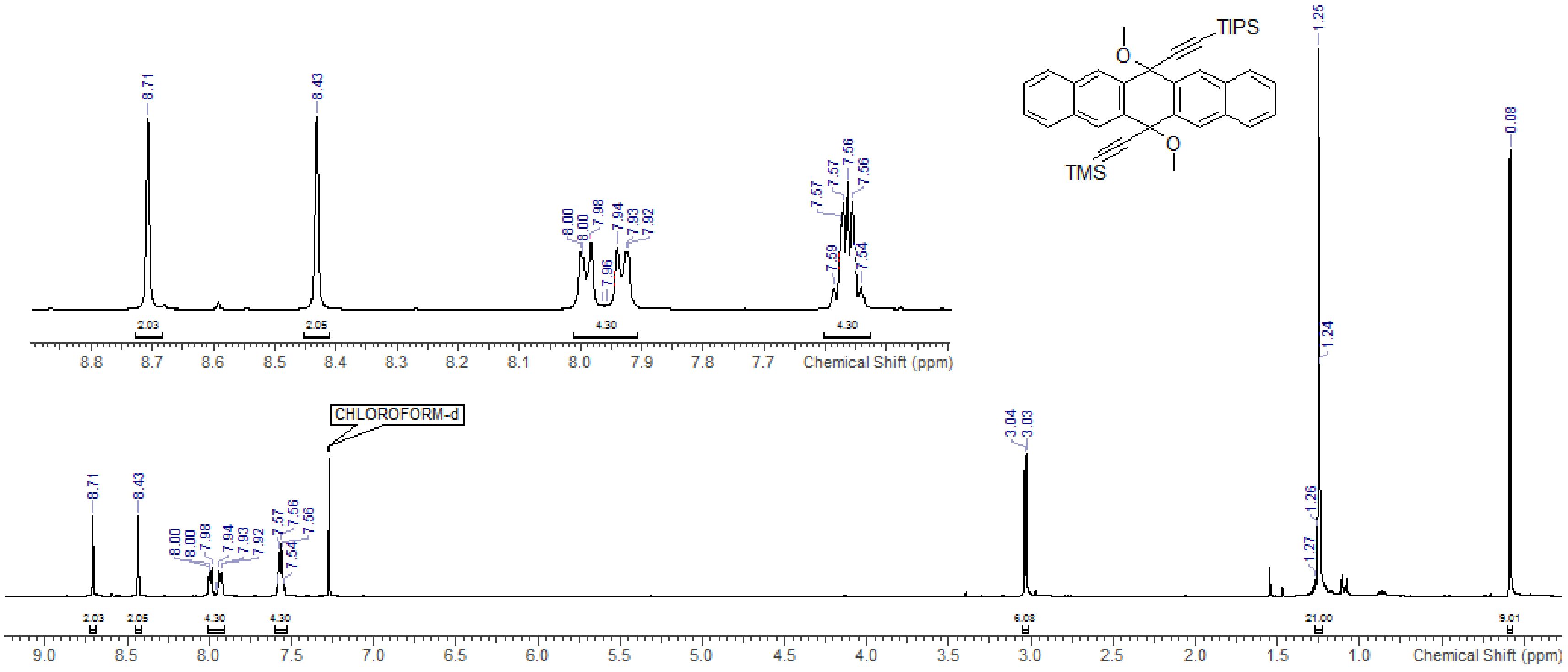
Frequency (MHz)	150.9314	***GB***	0	***INSTRUM***	<spect>	***LB***	1
NS	10240	***Nucleus***	13C	***Number of Transients***	10240	***Origin***	spect
Original Points Count	49066	***Owner***	ns	***PC***	1.4	***PROBHD***	<Z132808_0001 (CP QCI 600S3 H/P/C-N-D-05 Z LT)>
PULPROG	<zgpg30>	***Points Count***	65536	***Pulse Sequence***	zgpg30	***Receiver Gain***	2050.00
SF	150.931431	***SFO1***	150.94803345741			***SI***	65536
SSB	0	***SW(cyclical) (Hz)***	45454.55	***SWH***	45454.5454545455		
Solvent	THF	***Spectrum Offset (Hz)***	16729.5391	***Spectrum Type***	standard	***Sweep Width (Hz)***	45453.85
TD	98132	***TD0***	1280	***TE***	294.9991	***Temperature (degree C)***	21.999
UNC1	<13C>	***WDW***	1				



6,13-Dimethoxy-13-(triisopropylsilyl)ethynyl-6-trimethylsilylethynyl-6,13-dihydropentacen **7**:

Acquisition Time (sec)	3.2768	***Comment***	5 mm PATBO BB-1H/19F/D Z-GRD Z119877/0003			***D***	0.1
D1	0.1	***DE***	6.5	***DS***	2		

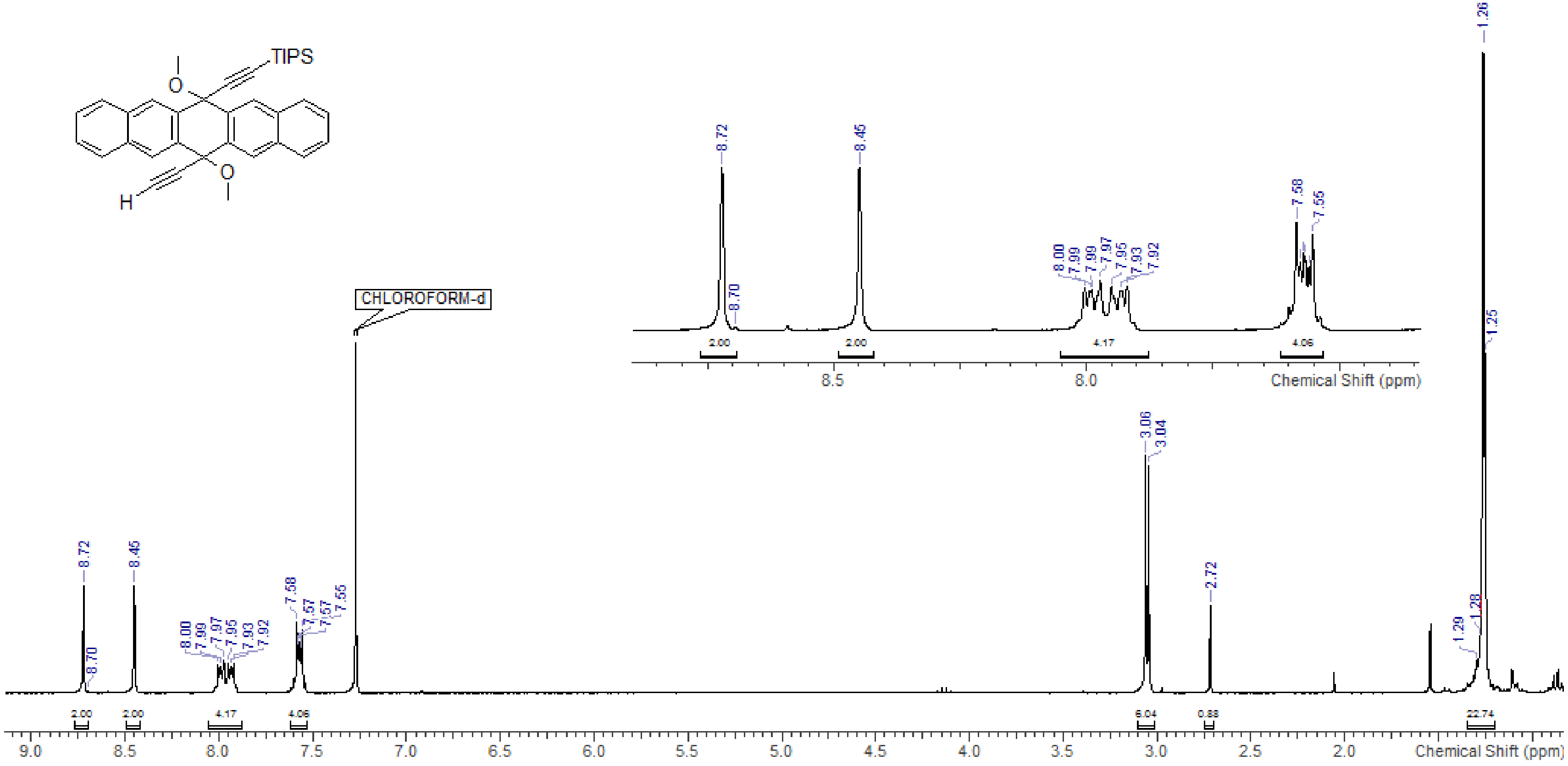
Frequency (MHz)	500.1300	***GB***	0	***INSTRUM***	<spect>	***LB***	0.3
NS	512	***Nucleus***	1H	***Number of Transients***	512	***Origin***	spect
Original Points Count	49152	***Owner***	ns	***PC***	1	***PROBHD***	<5 mm PATBO BB-1H/19F/D Z-GRD Z119877/0003 >
PULPROG	<zg30>	***Points Count***	65536	***Pulse Sequence***	zg30	***Receiver Gain***	362.00
SF	500.130048236742			***SFO1***	500.13250065	***SI***	65536
SSB	0	***SW(cyclical) (Hz)***	15000.00	***SWH***	15000	***Solvent***	CHLOROFORM-d
Spectrum Offset (Hz)	2494.6240	***Spectrum Type***	standard	***Sweep Width (Hz)***	14999.77	***TD***	98304
TD0	2	***TE***	298.1505	***Temperature (degree C)***	25.150	***UNC1***	<1H>
WDW	1						



6,13-Dimethoxy-13-(triisopropylsilyl)ethynyl-6-ethynyl-6,13-dihydropentacen **2d**:

Acquisition Time (sec)	3.6351	*Comment*	5 mm PABBO BB-1H/D Z-GRD Z104275/0201			*D*	0.1
D1	0.1	*DE*	6.5	*DS*	2		

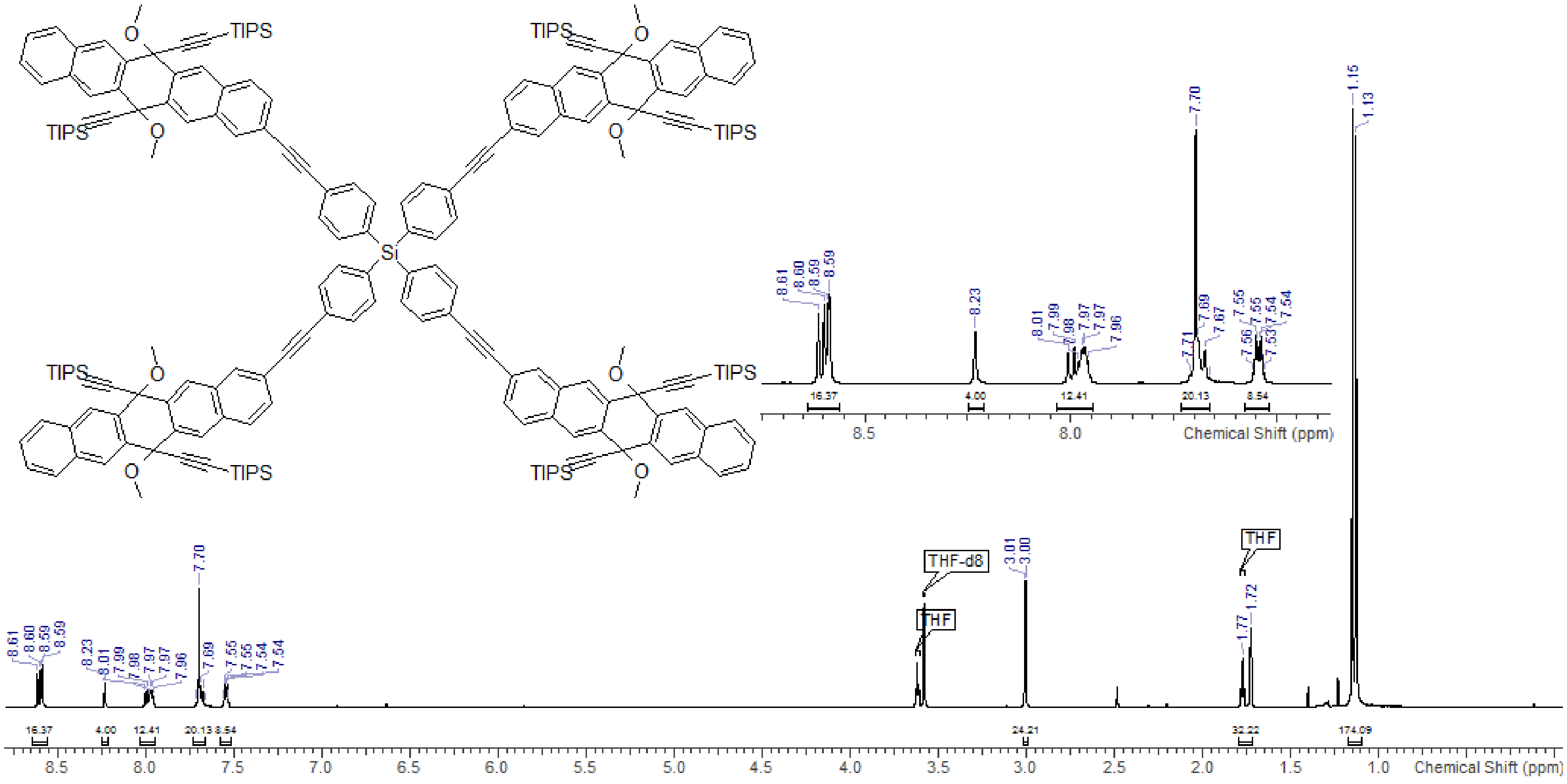
Frequency (MHz)	300.5100	*GB*	0	*INSTRUM*	<spect>	*LB*	0.3
NS	128	*Nucleus*	1H	*Number of Transients*	128	*Origin*	spect
Original Points Count	32768	*Owner*	ns	*PC*	1	*PROBHD*	<5 mm PABBO BB-1H/D Z-GRD Z104275/0201 >
PULPROG	<zg30>	*Points Count*	65536	*Pulse Sequence*	zg30	*Receiver Gain*	724.00
SF	300.510031909609			*SFO1*	300.51150255	*SI*	65536
SSB	0	*SW(cyclical) (Hz)*	9014.42	*SWH*	9014.42307692308		
Solvent	CHLOROFORM-d			*Spectrum Offset (Hz)*	1495.1008	*Spectrum Type*	standard
Sweep Width (Hz)	9014.29	*TD*	65536	*TD0*	16	*TE*	298.9151
Temperature (degree C)	25.915	*UNC1*	<1H>	*WDW*	1		



Tetrakis(4-((6,13-dimethoxy-6,13-bis((triisopropylsilyl)ethynyl)-6,13-dihydropentacen-2-yl)ethynyl)phenyl)silane **X1d** (mixture of all stereoisomers):

Acquisition Time (sec)	3.6351	*Comment*	vb54	*D*	0.1	*D1*	0.1	*DE*	12
DS	2								

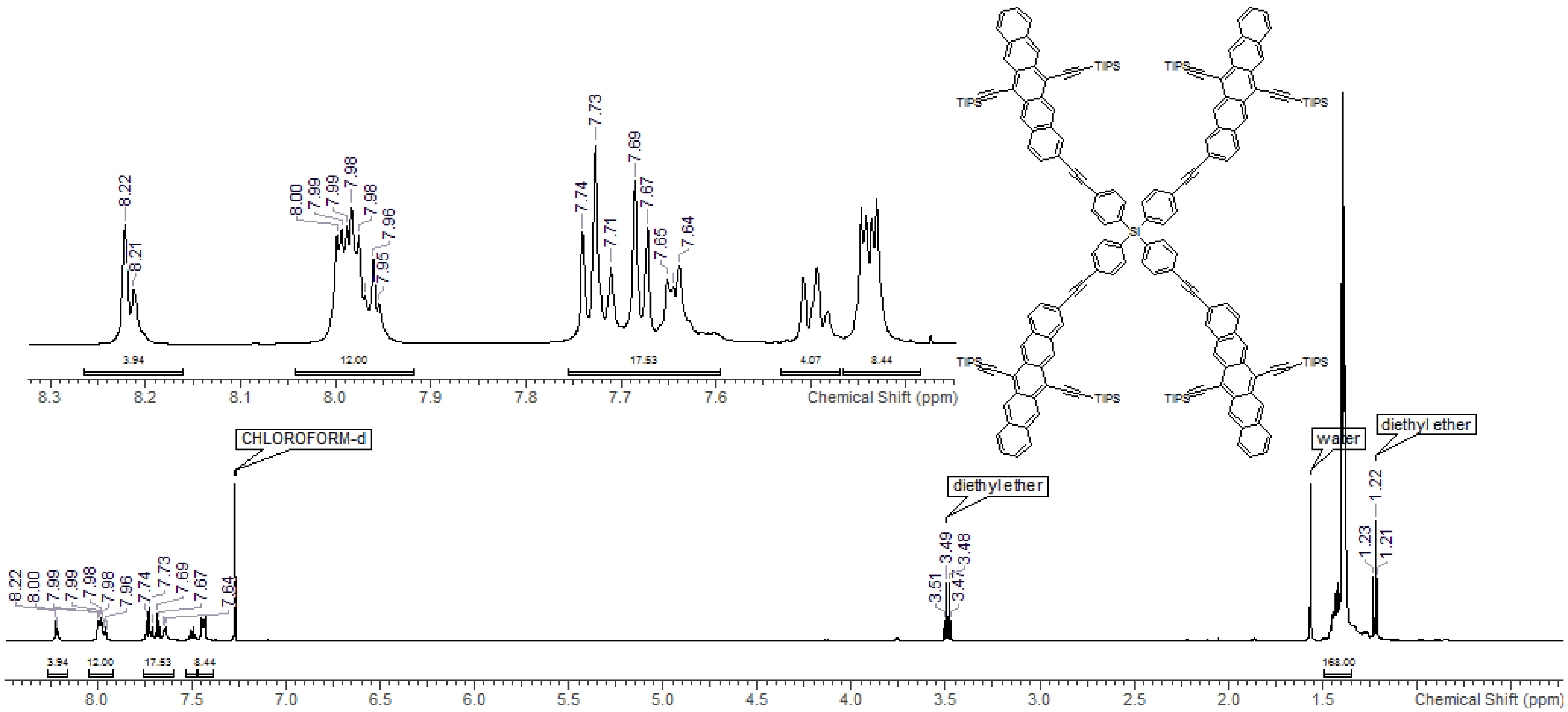
Frequency (MHz)	600.2438	*GB*	0	*INSTRUM*	<spect>	*LB*	0.3	*NS*	128
Nucleus	1H	*Number of Transients*	128	*Origin*	spect	*Original Points Count*	65536	*Owner*	ns
PC	1	*PROBHD*	<Z132808_0001 (CP QCI 600S3 H/P/C-N-D-05 Z LT)>			*PULPROG*	<zg30>	*Points Count*	65536
Pulse Sequence	zg30	*Receiver Gain*	7.02	*SF*	600.243829	*SFO1*	600.246830219145		
SI	65536	*SSB*	0	*SW(cyclical) (Hz)*	18028.85	*SWH*	18028.8461538462		
Solvent	CHLOROFORM-d			*Spectrum Offset (Hz)*	615.9067	*Spectrum Type*	standard	*Sweep Width (Hz)*	18028.57
TD	131072	*TD0*	16	*TE*	294.9998	*Temperature (degree C)*	22.000	*UNC1*	<1H>
WDW	1								



Tetrakis(4-((6,13-bis((triisopropylsilyl)ethynyl)pentacen-2-yl)ethynyl)phenyl)silane **X1**:

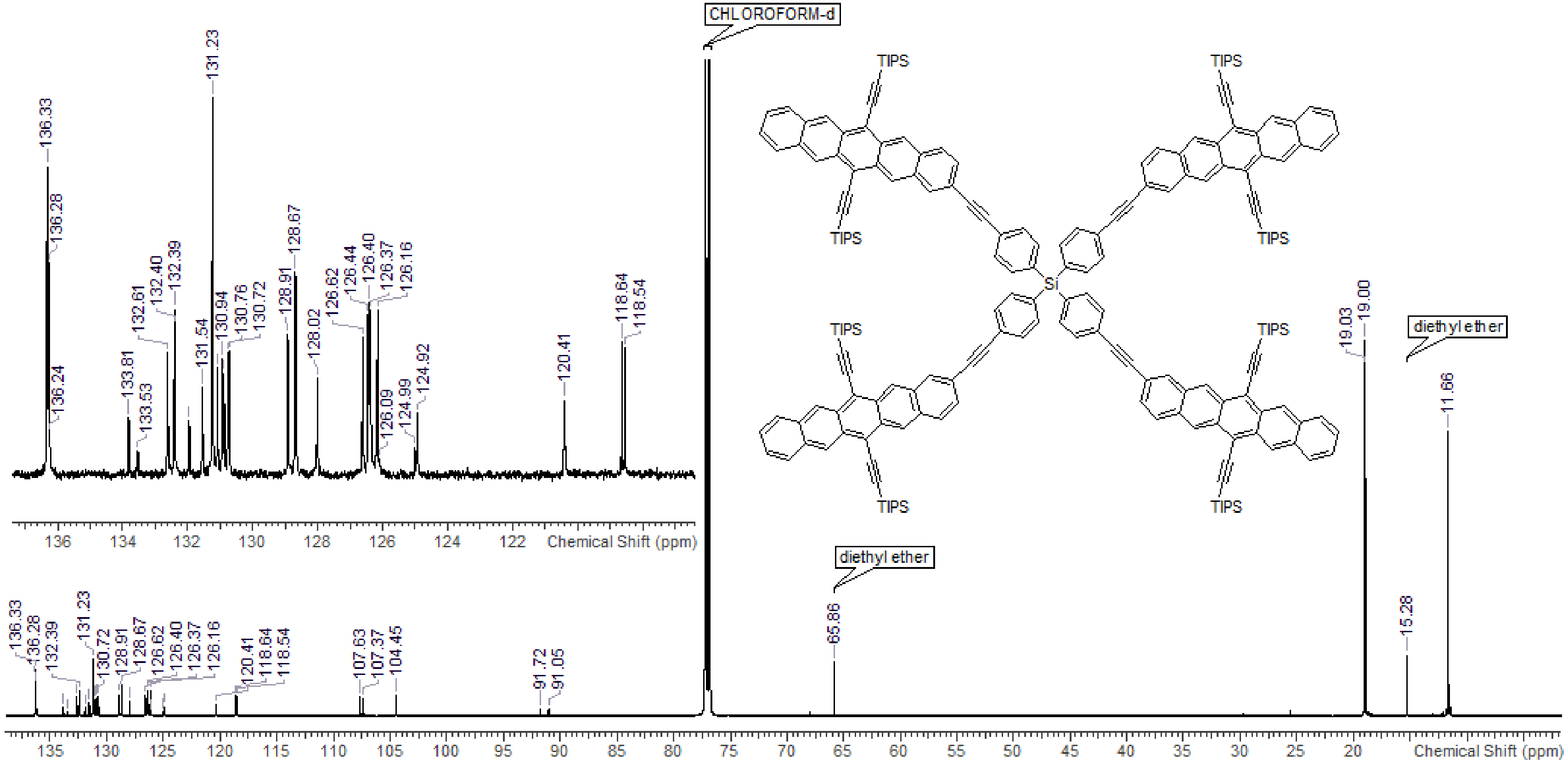
Acquisition Time (sec)	3.6351	*Comment*	FG 213-F1	*D*	0.1	*D1*	0.1
DE	12	*DS*	2	*Date*	03 Sep 2014 04:53:13		
Date Stamp	03 Sep 2014 04:53:13						

Frequency (MHz)	600.2439	*GB*	0	*INSTRUM*	<spect>	*LB*	0.3
NS	128	*Nucleus*	1H	*Number of Transients*	128	*Origin*	spect
Original Points Count	65536	*Owner*	ns	*PC*	1	*PROBHD*	<5 mm CPQCI 1H-31P/13C/15N/D Z-GRD Z132808/0001 >
PULPROG	<zg30>	*Points Count*	65536	*Pulse Sequence*	zg30	*Receiver Gain*	15.35
SF	600.243888581241			*SFO1*	600.246830219145		
SI	65536	*SSB*	0	*SW(cyclical) (Hz)*	18028.85	*SWH*	18028.8461538462
Solvent	CHLOROFORM-d			*Spectrum Offset (Hz)*	2991.6980	*Spectrum Type*	standard
Sweep Width (Hz)	18028.57	*TD*	131072	*TD0*	16	*TE*	295.0023
Temperature (degree C)	22.002	*UNC1*	<1H>	*WDW*	1		

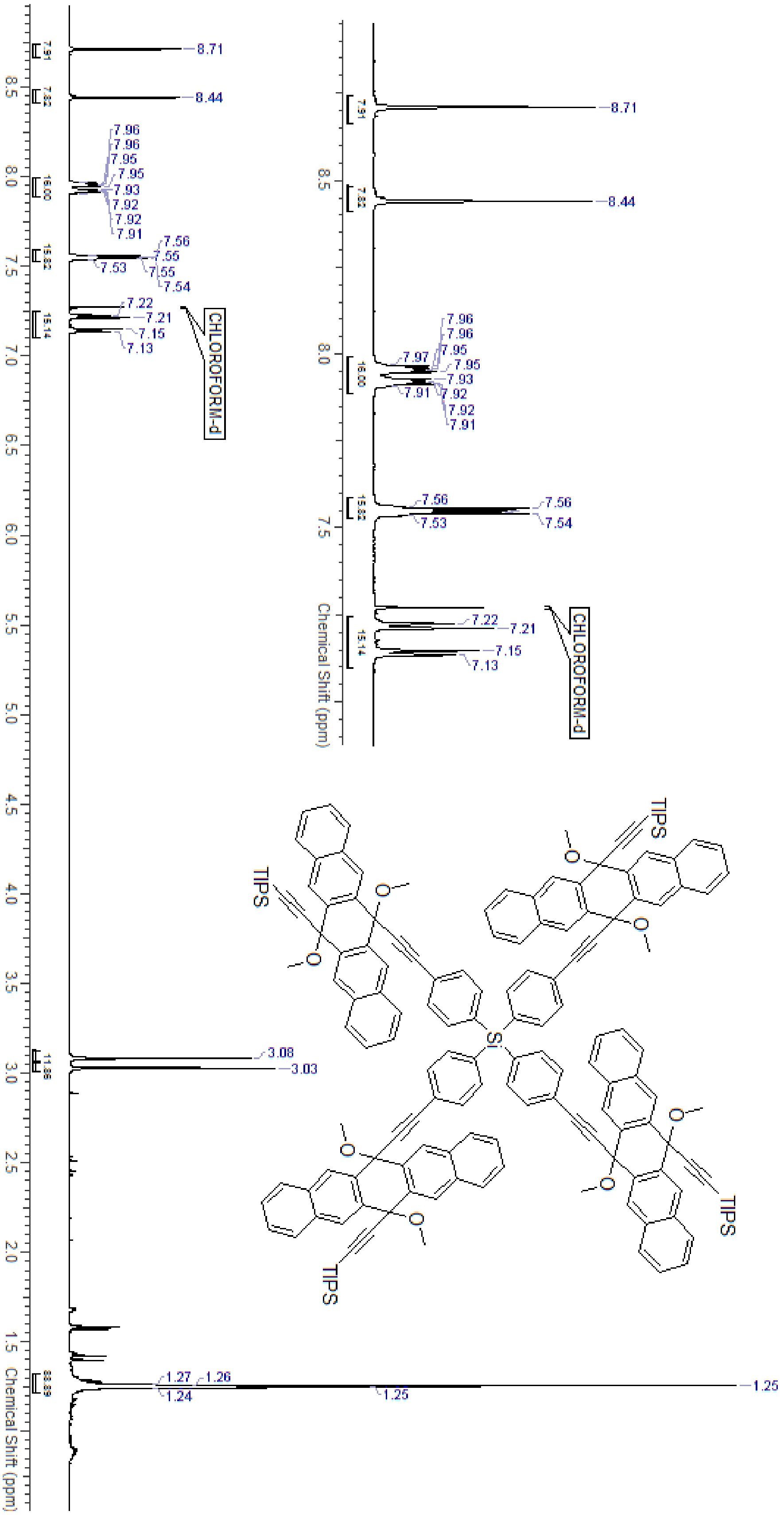


Acquisition Time (sec)	1.0795	***Comment***	FG 213-F1	***D***	0.03	***D1***	2
DE	16	***DS***	4				

Frequency (MHz)	150.9314	***GB***	0	***INSTRUM***	<spect>	***LB***	1
NS	8192	***Nucleus***	13C	***Number of Transients***	8192	***Origin***	spect
Original Points Count	49066	***Owner***	ns	***PC***	1.4		
PROBHD	<5 mm CPQCI 1H-31P/13C/15N/D Z-GRD Z132808/0001 >			***PULPROG***	<zgpg30>	***Points Count***	65536
Pulse Sequence	zgpg30	***Receiver Gain***	2050.00	***SF***	150.931431	***SFO1***	150.94803345741
SI	65536	***SSB***	0	***SW(cyclical) (Hz)***	45454.55	***SWH***	45454.5454545455
Solvent	CHLOROFORM-d			***Spectrum Offset (Hz)***	16599.2109	***Spectrum Type***	standard
Sweep Width (Hz)	45453.85	***TD***	98132	***TD0***	1024	***TE***	294.9992
Temperature (degree C)	21.999	***UNC1***	<13C>	***WDW***	1		



Tetrakis(4-((6,13-dimethoxy-13-((triisopropylsilyl)ethynyl)-6,13-dihydropentacen-6-yl)ethynyl)phenyl)silane **X2d**:

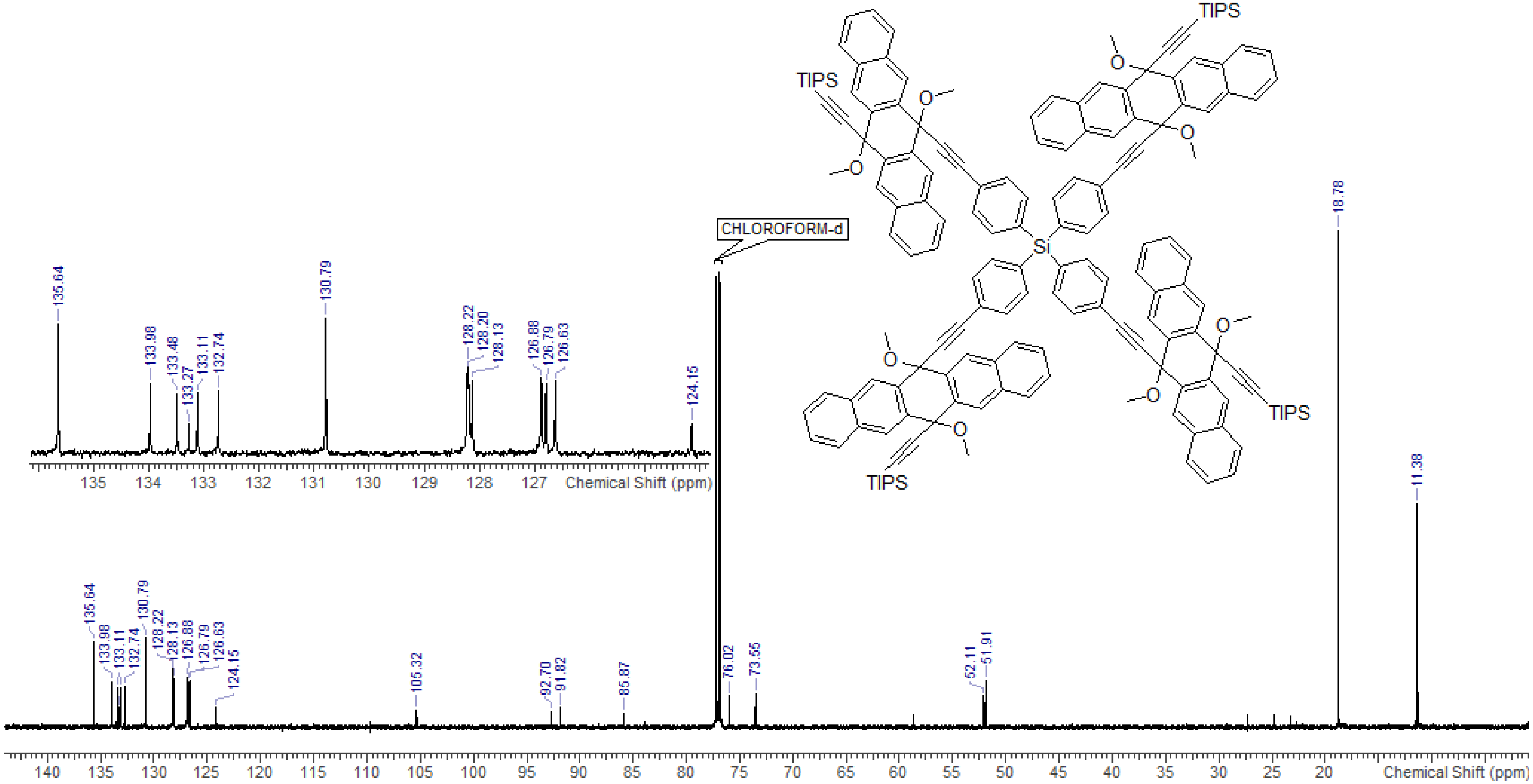


Acquisition Time (sec)	3.6351	Comment	FG 339	D	0.1	D1	0.1	DE	12
DS	2								

Frequency (MHz)	600.2438	GB	0	INSTRUM	<spect>	LB	0.3	NS	128
Nucleus	1H	Number of Transients	128	Origin	spect	Original Points Count	65536	Owner	ns
PC	1	PROBHD	<Z132808_0001 (CP QCI 600S3 H/P/C-N-D-05 Z LT)>			PULPROG	<zg30>	Points Count	65536
Pulse Sequence	zg30	Receiver Gain	10.93	SF	600.243829	SFO1	600.246830219145		
SI	65536	SSB	0	SW(cyclical) (Hz)	18028.85	SWH	18028.8461538462		
Solvent	CHLOROFORM-d			Spectrum Offset (Hz)	2821.1423	Spectrum Type	standard	Sweep Width (Hz)	18028.57
TD	131072	TD0	16	TE	295	Temperature (degree C)	22.000	UNC1	<1H>
WDW	1								

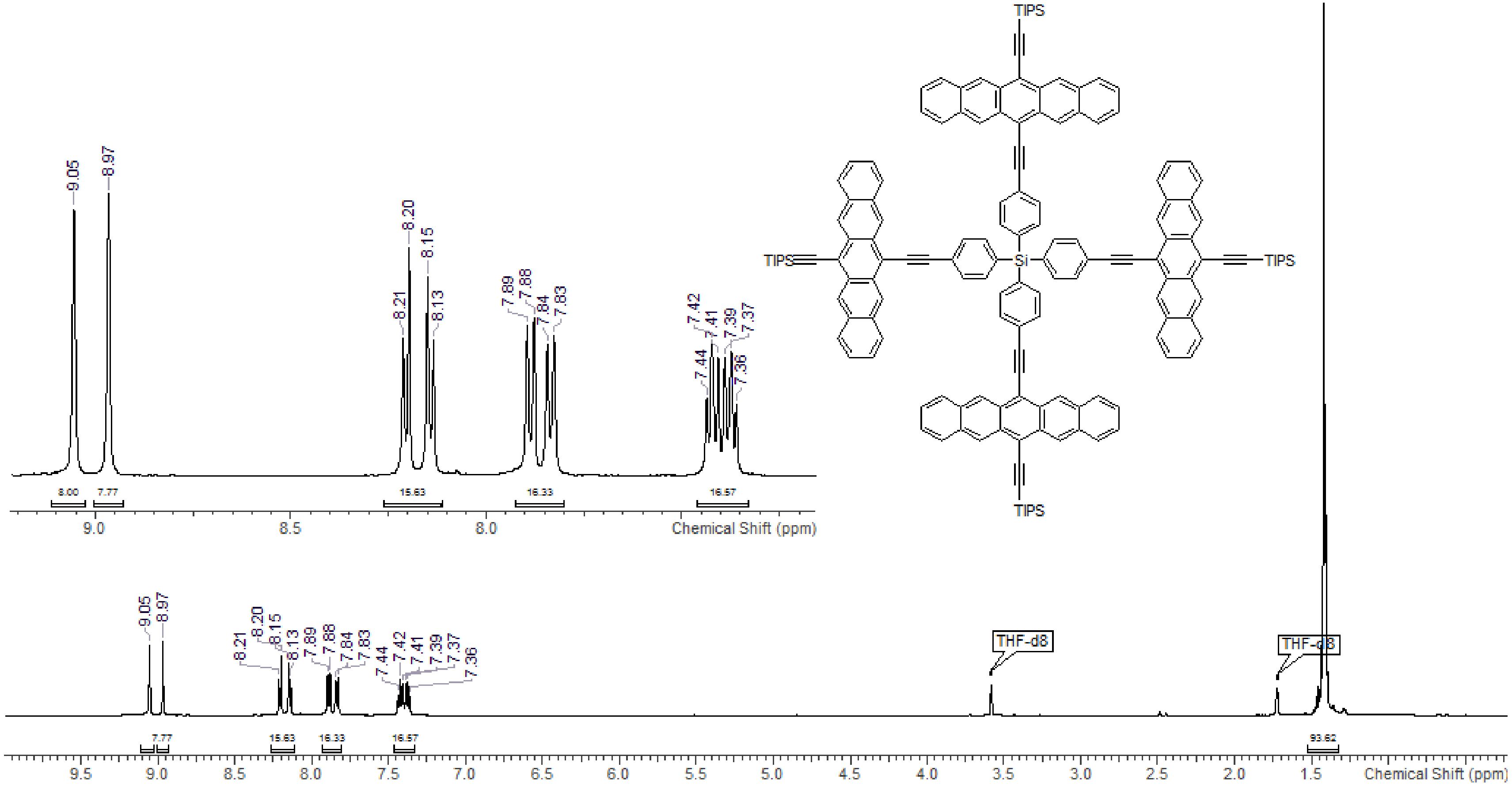
Acquisition Time (sec)	1.0795	*Comment*	FG 339	*D*	0.03	*D1*	2	*DE*	18
DS	4								

Frequency (MHz)	150.9314	*GB*	0	*INSTRUM*	<spect>	*LB*	1	*NS*	4800
Nucleus	13C	*Number of Transients*	4800	*Origin*	spect	*Original Points Count*	49066	*Owner*	ns
PC	1.4	*PROBHD*	<Z132808_0001 (CP QCI 600S3 H/P/C-N-D-05 Z LT)>			*PULPROG*	<zgpg30>	*Points Count*	65536
Pulse Sequence	zgpg30	*Receiver Gain*	1.01	*SF*	150.931431	*SFO1*	150.94803345741		
SI	65536	*SSB*	0	*SW(cyclical) (Hz)*	45454.55	*SWH*	45454.5454545455		
Solvent	CHLOROFORM-d			*Spectrum Offset (Hz)*	16552.7383	*Spectrum Type*	standard	*Sweep Width (Hz)*	45453.85
TD	98132	*TD0*	600	*TE*	294.9983	*Temperature (degree C)*	21.998	*UNC1*	<13C>
WDW	1								

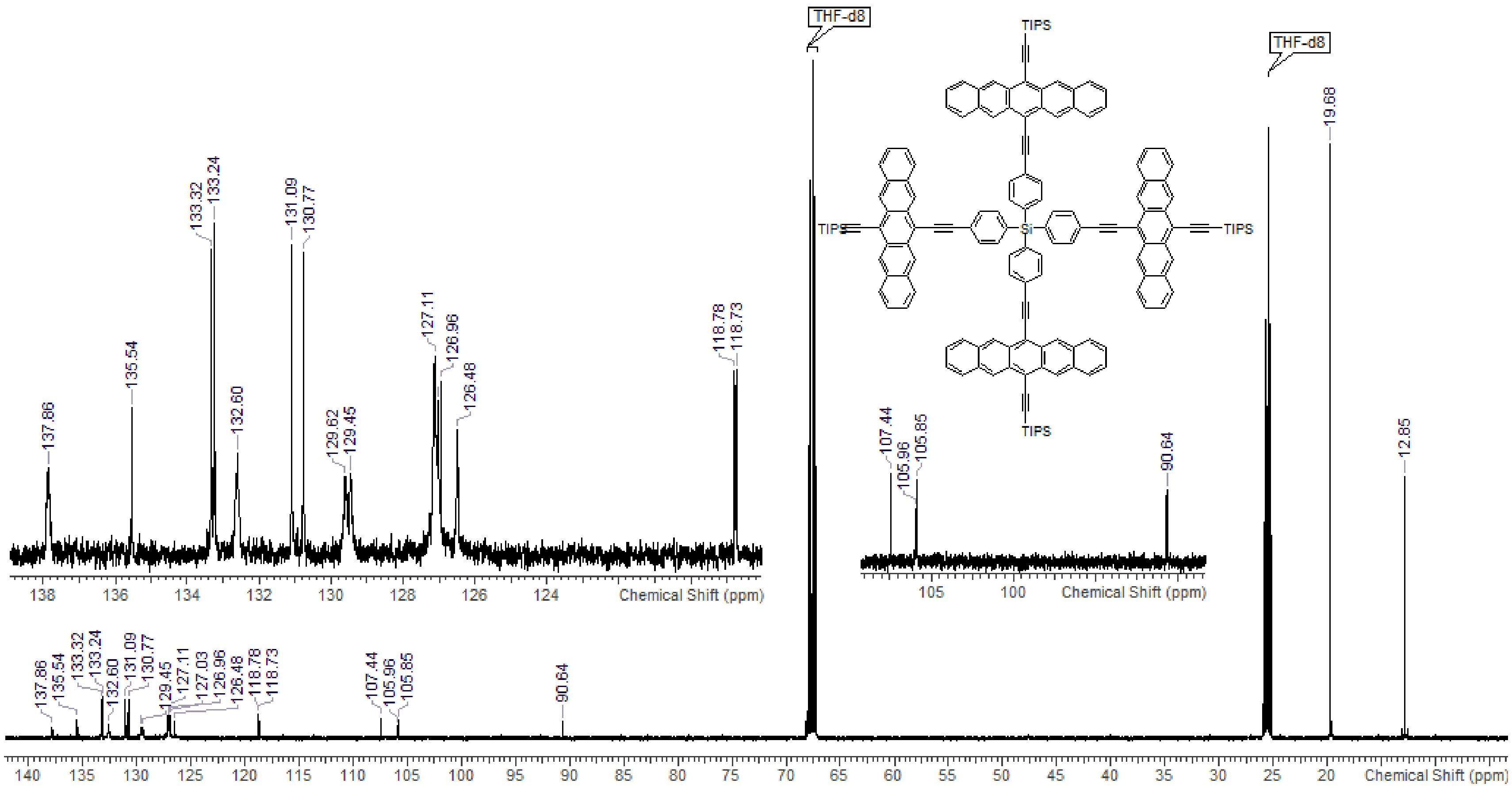


Tetrakis(4-((13-((triisopropylsilyl)ethynyl)pentacen-6-yl)ethynyl)phenyl)silane **X2**:

Acquisition Time (sec)	3.2768	*Comment*	Z119877 0003 (PA TBO 500S2 BB-H/F-D-05 Z)			*D*	0.1	*D1*	0.1
DE	6.5	*DS*	2						
						Frequency (MHz)	500.1300	*GB*	0
INSTRUM	<spect>	*LB*	0.3	*NS*	256	*Nucleus*	1H	*Number of Transients*	256
Origin	spect	*Original Points Count*	49152	*Owner*	ns	*PC*	1		
PROBHD	<Z119877 0003 (PA TBO 500S2 BB-H/F-D-05 Z)>			*PULPROG*	<zg30>	*Points Count*	65536	*Pulse Sequence*	zg30
Receiver Gain	181.00	*SF*	500.13	*SFO1*	500.13250065			*SI*	65536
SSB	0	*SW(cyclical) (Hz)*	15000.00	*SWH*	15000	*Solvent*	CHLOROFORM-d		
Spectrum Offset (Hz)	-275.7724	*Spectrum Type*	standard	*Sweep Width (Hz)*	14999.77	*TD*	98304	*TD0*	2
TE	295.0018	*Temperature (degree C)*	22.002	*UNC1*	<1H>	*WDW*	1		



Acquisition Time (sec)	1.7302	Comment	Z119877_0003 (PA TBO 500S2 BB-H/F-D-05 Z)			D	1.5	D1	1.5
DE	6.5	DS	4						
						Frequency (MHz)	125.7578	GB	0
INSTRUM	<spect>	LB	0.5	NS	2048	Nucleus	13C	Number of Transients	2048
Origin	spect	Original Points Count	65536	Owner	ns	PC	1.4		
PROBHD	<Z119877_0003 (PA TBO 500S2 BB-H/F-D-05 Z)>			PULPROG	<zgpg30>	Points Count	65536	Pulse Sequence	zgpg30
Receiver Gain	1620.00	SF	125.757789	SFO1	125.77162235679			SI	65536
SSB	0	SW(cyclical) (Hz)	37878.79	SWH	37878.7878787879			Solvent	CHLOROFORM-d
Spectrum Offset (Hz)	13285.1846	Spectrum Type	standard	Sweep Width (Hz)	37878.21	TD	131072	TD0	8
TE	295.0007	Temperature (degree C)	22.001	UNC1	<13C>	WDW	1		

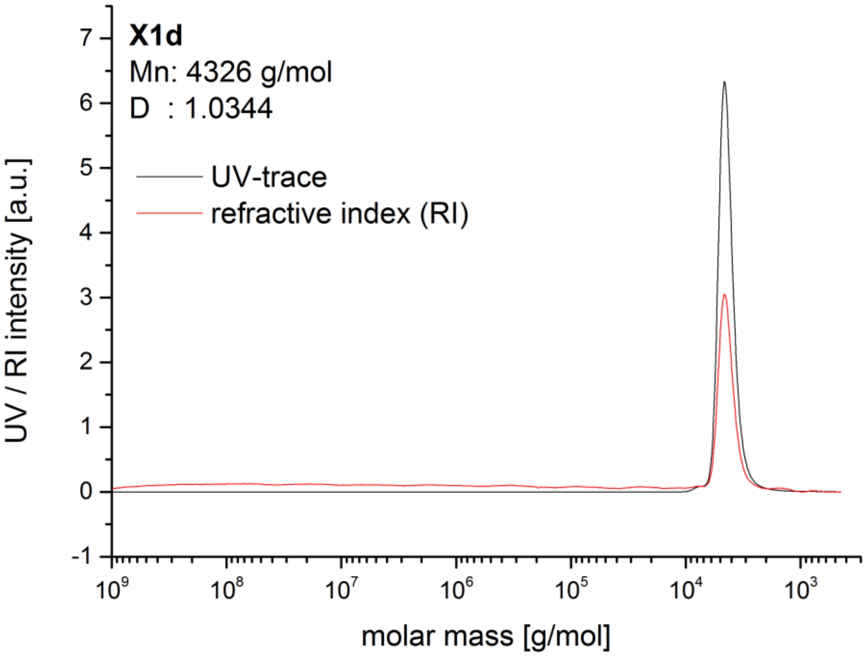


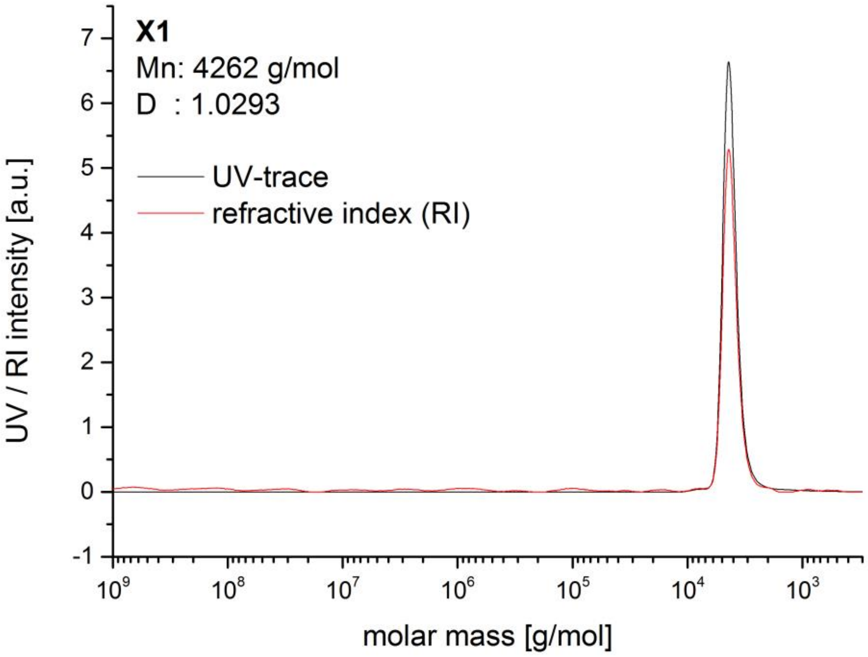
6. Analytical gel permeation chromatography (GPC)

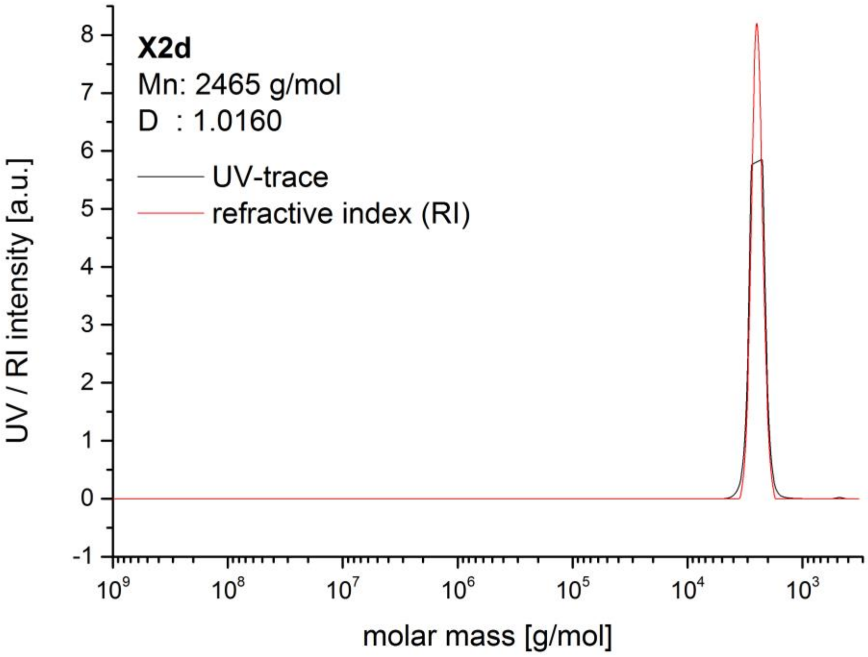
For purity confirmation, each fraction collected in the purification of **X1d**, **X1**, **X2d** and **X2** by preparative GPC was investigated by analytical GPC. All UV-traces were measured at 260 nm. The monodispersity (D = 1) of the product fractions proves their monomolecular structure.

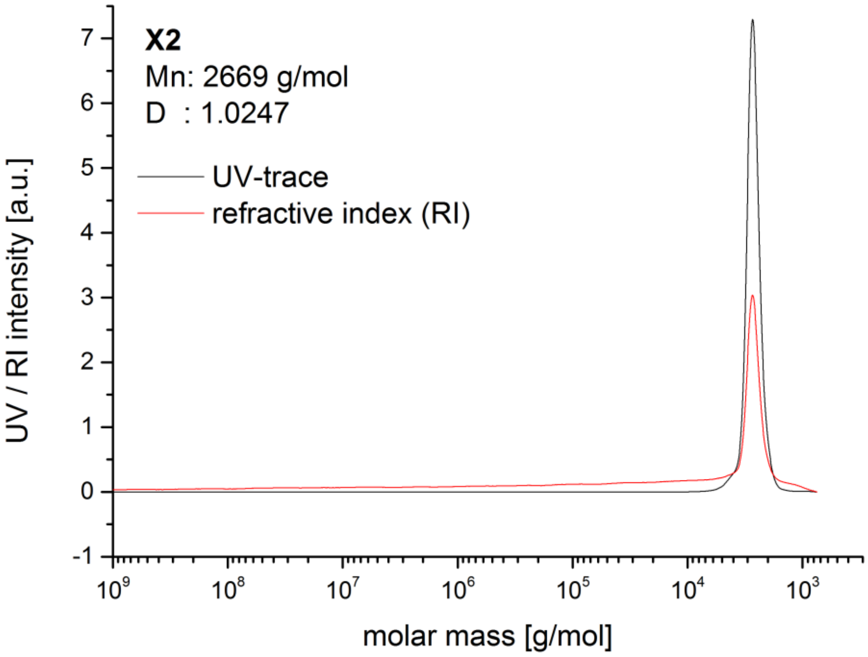
Mn is a function of the hydrodynamic radius of a given macromolecule or large oligomer and was calibrated against a polystyrol-standard. Despite their higher molecular mass, the dearomatized pentacene-oligomers are more compact than their lighter, aromatized counterparts. This can be understood by the formation of four long, rigid linear axes upon the full aromatization from **X1d** and **X2d** to **X1** and **X2**. Due to the large span into all three dimensions, Mn of **X1** and **X1d** are significantly overestimated.

Pure products:

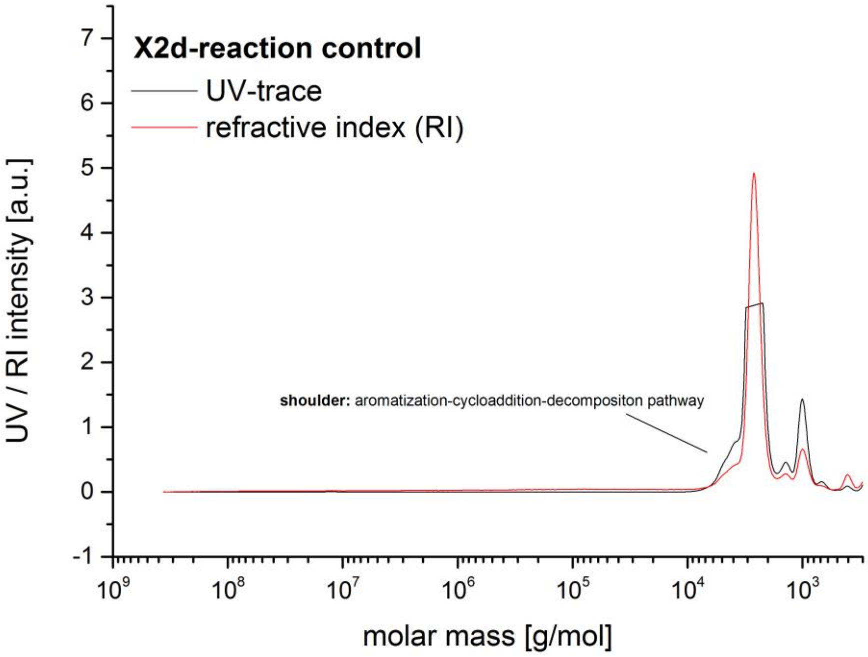



X1
Mn: 4262 g/mol
D : 1.0293
UV-trace
refractive index (RI)
UV / RI intensity [a.u.]
7
6
5
4
3
2
1
0
-1
10^9
10^8
10^7
10^6
10^5
10^4
10^3
molar mass [g/mol]


X2d
Mn: 2465 g/mol
D : 1.0160
UV-trace
refractive index (RI)
UV / RI intensity [a.u.]
8
7
6
5
4
3
2
1
0
-1
10^9
10^8
10^7
10^6
10^5
10^4
10^3
molar mass [g/mol]



Reaction monitoring:



The syntheses of the tetramers are best monitored by analytical GPC. Above is the molecular-weight plot of a reaction control from the synthesis of **X2d**. The main peak is **X2d**, towards the higher molecular weight a small shoulder forms during synthesis. We assume the aromatization of one dearomatized pentacene unit to be a slow side reaction under the coupling conditions; the high molecular weight is explained by a subsequent cyclodimerization of two pentacene units.

A similar decomposition can be observed in the post-aromatization workup: Usually a discrete, small fraction with nearly double the estimated molecular weight can be isolated by preparative GPC. Too long reaction times or faulty workup lead to decomposition into a greenish-blue, high molecular polymer that eventually becomes insoluble and precipitates. Thus, both the coupling and aromatization should be carefully monitored; care has to be taken during the workup and purification of the fully aromatized **X1** and **X2** (see above) as well as for their dearomatized precursors. A molecular-weight plot of an aromatization reaction from **X2d** to **X2** with already a large molecular fraction being formed is depicted below.