

Supporting Information for:

Synthesis and Stability of Soluble Hexacenes

Balaji Purushothaman, Sean R. Parkin, John E. Anthony*

Department of Chemistry, University of Kentucky, Lexington, KY 40506-0055

*anthony@uky.edu

Experimental section:

All solvents were purchased from Pharmco Aaper except anhydrous tetrahydrofuran which was purchased from Aldrich. n-Butyllithium (n-BuLi) was purchased from Aldrich. Trimethylsilyl acetylene was purchased from GFS chemicals. Chromatography was performed on silica gel (60 Å, 40-63 µm) purchased from Sorbent technology. Thin layer chromatography was performed using Silica Gel HL TLC plates (w/UV254) purchased from Sorbent Technologies. UV-Vis absorbance spectra were recorded using Shimadzu UV-Vis Spectrophotometer model UV-2501PC. NMR spectra were recorded on Varian Inova 400MHz instrument. High resolution mass spectra were recorded in EI mode on JOEL JMS-700T MStation. Mass spectra of dimers of TIBS hexacene (**3a**) were recorded in MALDI mode on Bruker Daltonics Autoflex MALDI-TOFMS. Electrochemical analysis was performed using BAS CV-50W voltammetric analyzer performed on 0.1M Bu₄NPF₆ solution in dichloromethane with ferrocene as internal standard. Tricyclopentylsilane¹, tricyclohexylsilyl acetylene², triisobutylsilyl acetylene² and 6,15-Hexacenequinone³ were prepared by previously reported literature methods.

Synthesis of tricyclopentylsilyl acetylene:

To a solution of tricyclopentylsilane¹ (30g, 127 mmol) in 1, 2-dichloroethane (100 ml) was added a solution of bromine (22.3g, 139 mmol) in 1, 2-dichloroethane (100 ml). After the addition was complete, the reaction mixture was heated to reflux for an hour. The reaction was followed by TLC by monitoring the disappearance of silane. The solvent was then removed under reduced pressure to give the bromosilane. In a separate flame dried 250 ml flask cooled under nitrogen was added 100 ml of anhydrous THF. 25 g (254 mmol) of trimethylsilyl acetylene was added and the flask was cooled to 0 °C using an ice water bath. n-BuLi (228 mmol) was added dropwise and the mixture was stirred for couple of hours. The resulting lithium trimethylsilylacetylide was then added to a stirring solution of bromosilane in THF under nitrogen and was allowed to stir overnight. The reaction mixture was quenched with saturated ammonium chloride, extracted into ether, washed with water and dried over anhydrous MgSO₄. The solvent was then removed under reduced pressure to give the crude TMS-protected acetylene (120 mmol) which was dissolved in 1:1 mixture of methanol/THF. 20 g (139 mmol) of K₂CO₃ was added to the reaction mixture and was stirred for an hour. The reaction was followed by GC/MS by monitoring the disappearance of TMS protected acetylene. The undissolved K₂CO₃ was filtered off and washed with ether. The filtrate was then acidified with 10% aqueous HCl and extracted into ether. The combined ether layers were finally washed with water and dried over anhydrous MgSO₄. The solvent was removed under reduced pressure to give the crude

product. The crude acetylene was purified by distillation under reduced pressure. Yield – 29.7 g, 95% (b.p. 90 °C/ 0.2 mm Hg)

¹H NMR (400 MHz, CDCl₃) δ 2.29 (s, 1H), 1.89 – 1.74 (m, 6H), 1.70 – 1.39 (m, 18H), 1.10 – 0.96 (m, 3H). ¹³C NMR (100 MHz, CDCl₃) δ 93.98, 86.98, 29.15, 27.04, 23.66.

MS (EI 70 eV) *m/z* 260 (5%, M⁺), 191 (100%, M⁺ - 69). HRMS (EI) *m/z* (M⁺) 260.4899 (Calcd. for C₁₇H₂₈Si 260.4897)

General procedure for the synthesis of 6,15 – Trialkylsilylethynylated Hexacenes (3a-c):

Synthesis of 6,15-bis((trialkylsilyl)ethynyl)-6,15-dihydrohexacene-6,15-diols: To a flame dried 100 ml flask cooled under nitrogen was added 5.58 mmol of acetylene, followed by 5 ml of hexanes. The reaction mixture was then placed in an ice bath. 2 ml of n-BuLi (4.88 mmol, 2.5 M solution in hexanes) was added dropwise and the reaction mixture stirred at 0 °C for an hour. 13 ml of hexanes was added followed by 2 ml of anhydrous THF. 500 mg (1.4 mmol) of 6,15 – hexacenequinone (**9**) was then added and the reaction mixture allowed to stir overnight. The reaction mixture was quenched with saturated NH₄Cl solution and extracted into ether. The combined ether layers were washed with water and dried over anhydrous MgSO₄. The crude product was then purified by elution through a pad of silica gel initially with hexanes to recover the excess acetylene followed by slowly increasing the ratio of hexanes : DCM to 7:3 to elute the diol. The diols were isolated as a crude mixture of *cis* and *trans* isomers, and were not purified further. Spectral information for the crude diols are provided below:

6,15-bis((triisobutylsilyl)ethynyl)-6,15-dihydrohexacene-6,15-diol (**10a**): 0.847 g, Yield – 75%

¹H NMR (400 MHz, CDCl₃) δ 8.81 (s, 2H), 8.67 (s, 2H), 8.49 (s, 2H), 8.04 (dd, *J* = 6.4, 3.2 Hz, 2H), 7.94 (dd, *J* = 6.1, 3.3 Hz, 2H), 7.56 (dd, *J* = 6.3, 3.2 Hz, 2H), 7.49 (dd, *J* = 6.6, 3.2 Hz, 2H), 3.46 (s, 2H), 1.92 (sept, *J* = 6.8 Hz, 6H), 0.98 (d, *J* = 6.6 Hz, 36H), 0.73 (d, *J* = 7.0 Hz, 12H).

¹³C NMR (100 MHz, CDCl₃) δ 136.14, 135.78, 133.45, 132.49, 131.36, 128.50, 128.30, 127.00, 126.91, 126.45, 126.18, 125.93, 108.74, 92.96, 70.05, 26.50, 25.25, 24.99.

MS (MALDI – DHB matrix) *m/z* 772 (100%, M⁺ - 34), 789 (53%, M⁺ - 17), 805 (9%, M⁺ - 2)

6,15-bis((tricyclopentylsilyl)ethynyl)-6,15-dihydrohexacene-6,15-diol (**10b**): 0.862 g, Yield – 70%

¹H NMR (400 MHz, CDCl₃) δ 8.82 (s, 1H), 8.68 (s, 2H), 8.48 (s, 2H), 8.03 (dd, *J* = 6.4, 3.3 Hz, 2H), 7.92 (dd, *J* = 6.1, 3.3 Hz, 2H), 7.55 (dd, *J* = 6.3, 3.2 Hz, 2H), 7.48 (dd, *J* = 6.6, 3.2 Hz, 2H), 3.49 (s, 2H), 1.89 – 1.75 (m, 12H), 1.66 – 1.35 (m, 36H), 1.17 – 1.01 (m, 6H).

¹³C NMR (100 MHz, CDCl₃) δ 136.6, 136.24, 133.58, 132.56, 131.48, 128.52, 128.35, 127.01, 126.92, 126.44, 126.19, 125.92, 108.82, 90.75, 70.13, 29.24, 27, 23.7.

MS (MALDI – DHB matrix) *m/z* 846(100%, M⁺ - 32), 862 (62%, M⁺ - 16), 878 (46%, M⁺)

6,15-bis((tricyclohexylsilyl)ethynyl)-6,15-dihydrohexacene-6,15-diol (**10c**): 0.944 g, Yield – 70%

¹H NMR (400 MHz, CDCl₃) δ 8.86 (s, 2H), 8.70 (s, 2H), 8.49 (s, 2H), 8.02 (dd, *J* = 6.4, 3.2 Hz, 2H), 7.93 (dd, *J* = 6.1, 3.3 Hz, 2H), 7.55 (dd, *J* = 6.2, 3.2 Hz, 2H), 7.49 (dd, *J* = 6.6, 3.1 Hz, 2H), 3.48 (s, 2H), 1.9 – 1.5 (m, 30H), 1.40 – 1.05 (m, 30H), 1.00 – 0.80 (m, 6H).

¹³C NMR (100 MHz, CDCl₃) δ 136.45, 136.08, 133.45, 132.45, 131.35, 128.45, 128.29, 126.97, 126.90, 126.48, 126.21, 125.87, 109.84, 90.67, 70.14, 28.71, 28.43, 27.07, 23.27.

MS (MALDI – DHB matrix) *m/z* 928 (100%, M⁺ - 34), 945 (19%, M⁺ - 17), 960 (8%, M⁺ - 2)

Deoxygenation of 6,15-bis((trialkylsilyl)ethynyl)-6,15-dihydrohexacene-6,15-diols: Due to the low stability of the hexacenes, material was stored as diols **2**, with the final preparation of hexacenes **3** occurring only as hexacene material was needed. To a flame dried 100 ml flask cooled under nitrogen was added 5.58 mmol of acetylene, followed by 5 ml of hexanes. The reaction mixture was then placed in an ice bath. 2 ml of n-BuLi (4.88 mmol, 2.5 M solution in hexanes) was added dropwise and the reaction mixture stirred at 0 °C for an hour. 13 ml of hexanes was added followed by 2 ml of anhydrous THF. 500 mg (1.4 mmol) of 6,15 – hexacenequinone (**1**) was then added and the reaction mixture allowed to stir overnight. The reaction mixture was quenched with saturated NH₄Cl solution and extracted into ether. The combined ether layers were washed with water and dried over anhydrous MgSO₄. The excess acetylene was recovered from the crude product by elution through a pad of silica gel initially with hexanes. The crude diol was obtained as a mixture of *syn* and *anti* isomers by slowly increasing the ratio of hexanes:DCM to 7:3. To a 50 ml round bottom flask were added 200 mg of crude diol, 20 ml of hexanes and 10 ml of THF. Nitrogen gas was bubbled through the solution for 15 min. A saturated solution of SnCl₂•2H₂O in 10% aqueous HCl was added and the reaction was followed by TLC by monitoring the disappearance of diol. The product mixture was then poured into a thick pad of silica gel and eluted with hexanes to give crude hexacene, which was further purified by chromatography on silica gel using 9:1 hexanes/ DCM. Recrystallization in hexanes/DCM gave crystalline hexacenes. Note that hexacenes **3c**, and **3d** were not sufficiently volatile for HR-EI MS, nor sufficiently stable to obtain combustion analysis.

Note: The conversion of the intermediate diol to final hexacene was performed in the dark. Solvents were degassed by sparging with nitrogen prior to use for recrystallization.

6,15-bis((triisobutylsilyl)ethynyl)hexacene (3a): 19 mg, Yield – 8%

¹H NMR (400 MHz, CDCl₃) δ 9.56 (s, 2H), 9.20 (s, 2H), 8.60 (s, 2H), 7.94 (dd, *J* = 6.6, 3.2 Hz, 2H), 7.91 (dd, *J* = 6.6, 3.2 Hz, 2H), 7.38 (dd, *J* = 6.7, 3.1 Hz, 2H), 7.34 (dd, *J* = 6.8, 3.1 Hz, 2H), 2.24 (sept, *J* = 6.8 Hz, 6H), 1.24 (d, *J* = 6.6 Hz, 36H), 1.01 (d, *J* = 7.0 Hz, 12H).

¹³C NMR (100 MHz, CDCl₃) δ 132.69, 132.5, 131.19, 130.94, 130.42, 128.82, 128.77, 126.97, 126.77, 126.54, 126.32, 125.73, 118.39, 110.68, 105.16, 26.82, 25.7, 25.65

HRMS (EI) *m/z* (M⁺) 772.4859 (Calcd. for C₅₄H₆₈Si₂ 772.4859)

Decomposition temperature – 240 °C

6,15-bis((tricyclopentylsilyl)ethynyl)hexacene (3b): 54 mg, Yield – 20%

¹H NMR (400 MHz, CDCl₃) δ 9.56 (s, 2H), 9.20 (s, 2H), 8.60 (s, 2H), 7.95 (dd, *J* = 6.6, 3.2 Hz, 2H), 7.91 (dd, *J* = 6.5, 3.2 Hz, 2H), 7.38 (dd, *J* = 6.7, 3.1 Hz, 2H), 7.34 (dd, *J* = 6.7, 3.1 Hz, 2H), 2.18 – 2.04 (m, 12H), 1.95 – 1.60 (m, 36H), 1.47 – 1.30 (m, 6H).

^{13}C NMR (100 MHz, CDCl_3) δ 132.71, 132.5, 131.15, 130.96, 130.4, 128.89, 128.78, 127.01, 126.63, 126.3, 126.01, 125.72, 118.4, 108.58, 104.26, 29.67, 27.35, 24.23
HRMS (EI) m/z (M^+) 844.4862 (Calcd. for $\text{C}_{60}\text{H}_{68}\text{Si}_2$ 844.4859)
Decomposition temperature – 218 °C

6,15-bis((tricyclohexylsilyl)ethynyl)hexacene (3c): 98 mg, Yield – 36%

^1H NMR (400 MHz, CDCl_3) δ 9.6 (s, 2H), 9.23 (s, 2H), 8.60 (s, 2H), 7.95 (dd, J = 6.8, 3.2 Hz, 2H), 7.92 (dd, J = 6.8, 3.2 Hz, 2H), 7.39 (dd, J = 6.8, 3.2 Hz, 2H), 7.35 (dd, J = 6.8, 3.2 Hz, 2H), 2.18 – 2.09 (m, 12H), 1.97 – 1.74 (m, 18H), 1.71 – 1.63 (m, 12H), 1.41 – 1.36 (m, 18H), 1.23 (tt, J = 12.8, 2.8 Hz, 6H).

^{13}C NMR (100 MHz, CDCl_3) δ 132.68, 132.49, 131.18, 130.93, 130.44, 128.9, 128.78, 127.04, 126.96, 126.72, 126.33, 125.72, 118.41, 108.58, 105.42, 29.18, 28.69, 27.35, 23.73
MS (EI) m/z 928 (12%, M^+)
Decomposition temperature – 290 °C

Synthesis of 6,15 – bis(tris(trimethylsilyl)silylethynyl)hexacene (3d):

To a flame dried 100 ml flask cooled under nitrogen was added 1.52 g (5.6 mmol) tris(trimethylsilyl)silylacetylene, followed by 3 ml of hexanes. The reaction mixture was then placed in an ice bath. 2 ml of $n\text{-BuLi}$ (4.88 mmol, 2.5 M solution in hexanes) was added dropwise and the reaction mixture stirred at 0 °C for an hour. 3 ml of anhydrous THF followed by 24 ml of hexanes was added. 500 mg (1.4 mmol) of 6, 15 – hexacenequinone (**1**) was then added to the reaction mixture and allowed to stir overnight. The reaction mixture was quenched with saturated NH_4Cl solution and extracted into ether. The combined ether layers were washed with water and dried over anhydrous MgSO_4 . The solvent was removed under reduced pressure to give crude diol (**2d**), which was dissolved in 43 ml of hexanes, 7 ml of THF. A saturated solution of $\text{SnCl}_2 \cdot 2\text{H}_2\text{O}$ in 10% aqueous HCl was added and the reaction was followed by TLC by monitoring the disappearance of diol. The reaction mixture was poured onto a thick pad of silica gel and eluted with hexanes to give crude hexacene, which was further purified by chromatography using 9:1 hexanes/ DCM. Recrystallization in hexanes gave 195 mg (16%) of crystalline TTMS hexacene (**3d**). The very low stability of this material precluded characterization by combustion analysis or HRMS.

Note: The conversion of the intermediate diol to final hexacene was performed in the dark. Solvents were degassed by sparging with nitrogen prior to use for recrystallization.

^1H NMR (400 MHz, CDCl_3) δ 9.54 (s, 2H), 9.19 (s, 1H), 8.57 (s, 2H), 7.93 (dd, J = 6.6, 3.2 Hz, 2H), 7.89 (dd, J = 6.5, 3.2 Hz, 2H), 7.36 (dd, J = 6.7, 3.1 Hz, 2H), 7.32 (dd, J = 6.7, 3.1 Hz, 2H), 0.47 (s, 54H).

^{13}C NMR (100 MHz, CDCl_3) δ 132.53, 132.36, 131.13, 130.88, 130.45, 128.84, 128.77, 126.91, 126.83, 126.65, 126.08, 125.56, 118.60, 107.02, 106.52, 1.00.
MS (EI) m/z 868 (15%, M^+)
Decomposition temperature – 282 °C

Hexacene dimers: These materials were isolated as described in the text. Note that subjecting these materials to M.S. analysis (either EI or LDI / MALDI) caused reversion of the dimers to the monomer units – no parent ion could be detected (See Fig. S6). This is a common problem with use of mass spectrometry to assess the purity of acenes. Combustion analysis would prove useless, as all components of the reaction mixture had the same atomic ratios. The structures of the compounds are proven unambiguously by proton and carbon NMR, as well as single-crystal X-ray structure determination.

Anthracene dimer (4):

Formed by allowing solutions of hexacene **3a** to stand in air exposed to light.

¹H NMR (400 MHz, CDCl₃) δ 8.71 (s, 4H), 7.84 (dd, *J* = 6.5, 3.2 Hz, 4H), 7.56 (s, 4H), 7.45 (dd, *J* = 6.1, 3.3 Hz, 4H), 7.39 (dd, *J* = 6.5, 3.1 Hz, 4H), 7.26 (s, 4H), 7.13 (dd, *J* = 6.2, 3.2 Hz, 4H), 5.94 (s, 4H), 2.22 (sept, *J* = 6.8 Hz, 12H), 1.26 (dd, *J* = 6.6, 2.6 Hz, 18H), 1.06 (d, *J* = 6.9 Hz, 6H).

¹³C NMR (101 MHz, CDCl₃) δ 142.55, 138.96, 132.53, 131.93, 129.95, 128.27, 127.48, 125.78, 125.59, 125.40, 118.91, 105.29, 104.21, 51.60, 27.01, 26.99, 25.72, 25.63.

MS (LDI) *m/z* 772 (100%, M⁺ - 772)

Off-set dimer (5):

Formed by allowing crystals of hexacene **3a** to sit in air exposed to light.

¹H NMR (400 MHz, CDCl₃) δ 9.14 (s, 2H), 8.84 (s, 2H), 8.27 (s, 2H), 8.01 – 7.94 (m, 4H), 7.57 – 7.48 (m, 8H), 7.45 (dd, *J* = 6.7, 3.1 Hz, 2H), 7.23 – 7.16 (m, 4H), 6.75 (dd, *J* = 5.5, 3.2 Hz, 2H), 5.92 (d, *J* = 11.4 Hz, 2H), 5.10 (d, *J* = 11.4 Hz, 2H), 2.41 – 2.20 (m, 12H), 1.37 (d, *J* = 6.6 Hz, 36H), 1.32 (d, *J* = 6.6 Hz, 36H), 1.11 (d, *J* = 8 Hz, 12H), 1.06 (d, *J* = 8 Hz, 12H).

¹³C NMR (100 MHz, CDCl₃) δ 143.71, 143.66, 143.61, 141.53, 141.47, 139.37, 139.31, 132.53, 132.08, 132.03, 130.32, 130.25, 129.82, 129.74, 129.27, 129.22, 128.25, 127.62, 127.55, 127.20, 126.90, 126.87, 126.78, 126.69, 126.45, 126.37, 126.03, 125.96, 125.59, 125.54, 125.26, 125.19, 125.10, 124.86, 123.99, 123.94, 118.79, 118.73, 118.68, 117.78, 117.73, 117.67, 107.73, 104.85, 104.56, 104.15, 77.55, 77.23, 76.91, 54.24, 52.97, 51.61, 28.86, 28.81, 27.66, 27.62, 27.57, 27.52, 26.86, 26.42, 26.38, 26.33, 25.70, 25.20, 25.16, 25.13, 25.09, 25.05, 25.01, 24.55.

MS (LDI) *m/z* 772 (100%, M⁺ - 772)

Decomposition temperature – 270 °C

TIBS Hexacene - Alkyne dimer endoperoxide (6)

Formed during chromatographic workup of hexacene **3a**.

¹H NMR (400 MHz, CDCl₃) δ 9.08 (s, 1H), 9.04 (s, 1H), 8.95 (s, 1H), 8.15 (d, *J* = Hz, 1H), 8.09 (d, *J* = Hz, 1H), 7.98 – 8.00 (m, 2H), 7.89 (d, *J* = Hz, 1H), 7.84 – 7.81 (m, 2H), 7.7 – 7.76 (m, 3H), 7.67 (s, 1H), 7.64 – 7.45 (m, 7H), 7.3 – 7.26 (m, 1H), 7.05 (d, *J* = Hz, 1H), 6.98 (s, 1H), 6.68 (s, 1H), 6.42 (s, 1H), 5.71 (s, 1H), 5.56 (s, 1H), 2.3 (sept, *J* = 6.8 Hz, 3H), 2.15 (sept, *J* = 6.8 Hz, 3H), 1.52 – 1.4 (m, 3H), 1.27 (dd, *J* = 10.4, 6.4 Hz, 21H), 1.18 (dd, *J* = 6.6, 3.2 Hz, 21H), 1.04 (d, *J* = 6.8 Hz, 6H), 0.92 (d, *J* = 6.8 Hz, 6H), 0.82 (dd, *J* = 14.8, 5.2 Hz, 3H), 0.72 (d, *J* = 6.4 Hz, 9H), 0.56 (d, *J* = 6.8 Hz, 9H), 0.49 (d, *J* = 6.4 Hz, 9H), 0.44 (d, *J* = 6.8 Hz, 9H), 0.05 – 0.00 (m, 3H), -0.14 (dd, *J* = 14.8, 7.2 Hz, 3H).

¹³C NMR (100 MHz, CDCl₃) δ 154.67, 148.9, 114.68, 143.10, 141.34, 140.97, 137.74, 135.58, 134.02, 133.98, 133.23, 132.61, 132.39, 132.30, 131.92, 130.57, 130.34, 130, 129.55, 129.42, 129.20, 128.73, 128.39, 128.34, 128.31, 128.23, 128.04, 127.88, 127.61, 126.71, 126.58, 126.49,

126.44, 126.37, 126.26, 126.17, 126.10, 125.84, 124.01, 122.84, 122.52, 116.10, 115.91, 115.47, 105.11, 104.76, 104.62, 103.24, 101.73, 101.51, 78.20, 77.43, 76.72, 57.72, 53.38, 31.17, 27.04, 26.98, 26.92, 26.74, 26.12, 26.03, 25.91, 25.78, 25.75, 25.63, 25.47, 24.87, 24.62, 24.40, 23.48.

Experimental details for UV – visible stability studies:

UV – Visible spectra were recorded using Shimadzu UV-visible Spectrophotometer model UV-2501PC. The spectra were recorded between the wavelength ranges of 350 – 875 nm using quartz cells with 1cm path length. 10^{-4} M solutions of hexacenes (**3a-d**) in degassed toluene (UV Grade, Pharmco Aaper) were made in the dark and an initial spectrum of the hexacene was obtained. The solution was then exposed to a bright full-spectrum light source and the spectra were acquired at regular intervals until the absorption bands at longest wavelength disappeared.

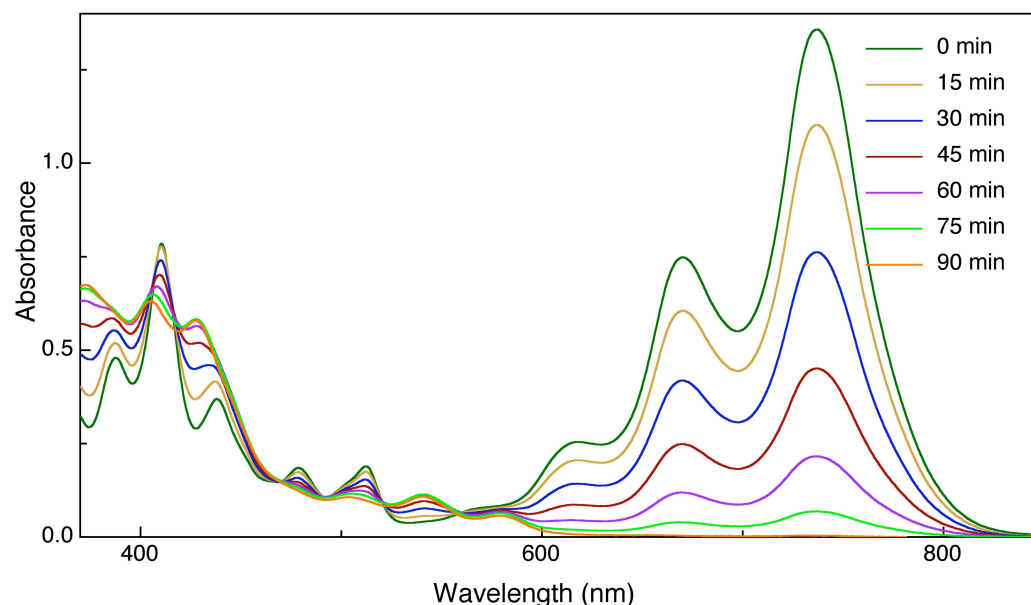


Figure S1: UV-Vis spectra of TCPS Hexacene (**3b**) recorded at regular intervals during exposure to light

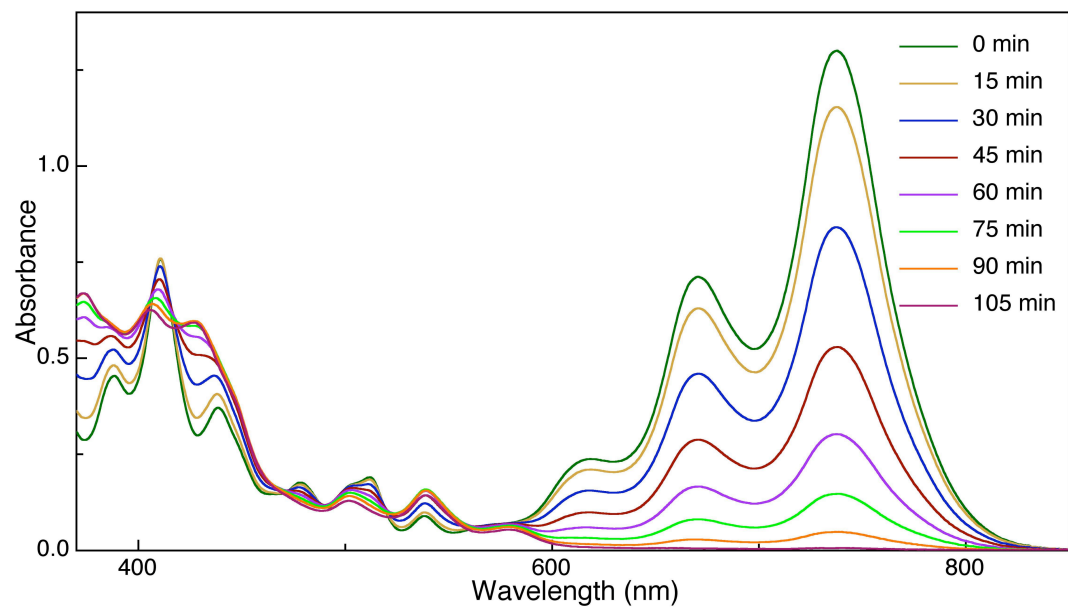


Figure S2: UV-Vis spectra of TCHS Hexacene (**3c**) recorded at regular intervals during exposure to light

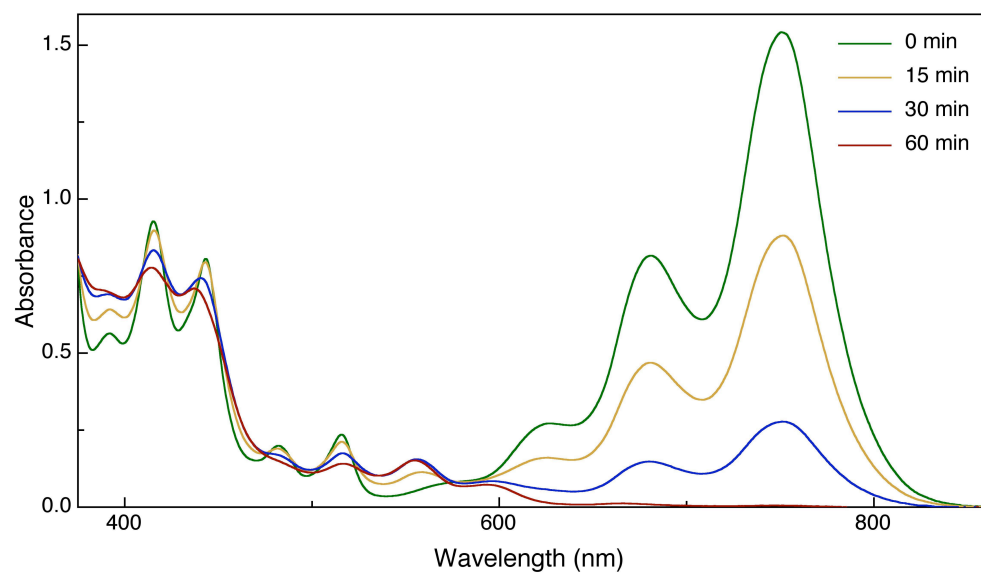


Figure S3: UV-Vis spectra of TTMSS Hexacene (**3d**) recorded at regular intervals during exposure to light

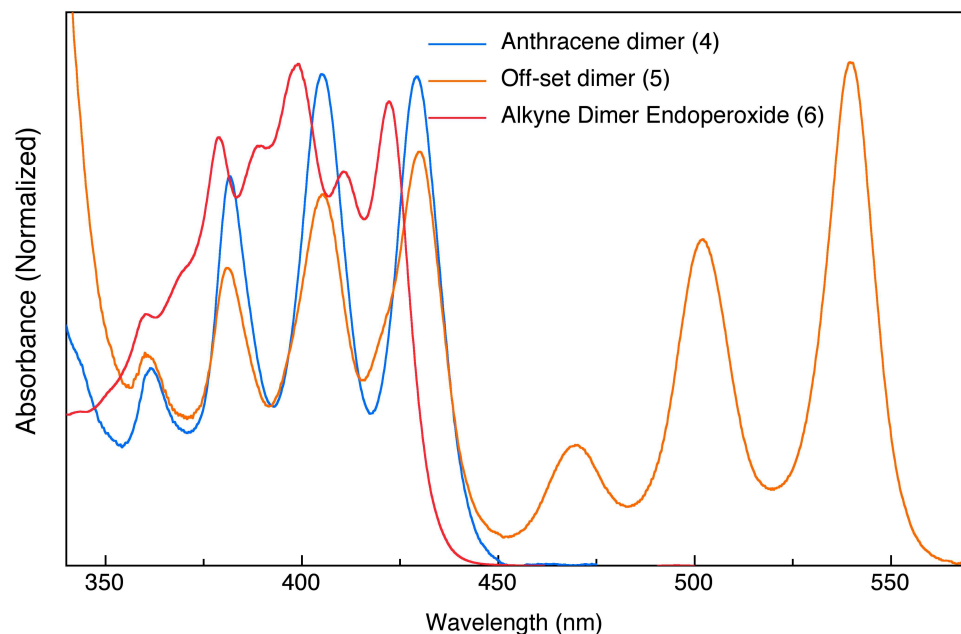


Figure S4: UV – visible spectra for decomposition products of TIBS Hexacene (**3a**)

Experimental details for ^1H NMR stability study:

In order to elucidate the chemical composition of the decomposition products and their relative ratios, a ^1H NMR stability study was performed on TIBS hexacene (**3a**) in deuterated benzene at a concentration of 1wt%. Two different solution stability studies were done, using solutions made from N_2 and O_2 purged benzene- d_6 . The solution of hexacene (**3a**) in benzene- d_6 was made in the dark and an initial ^1H NMR spectrum was recorded. The solution was then exposed to a bright light source and the ^1H NMR spectra was recorded at regular intervals.

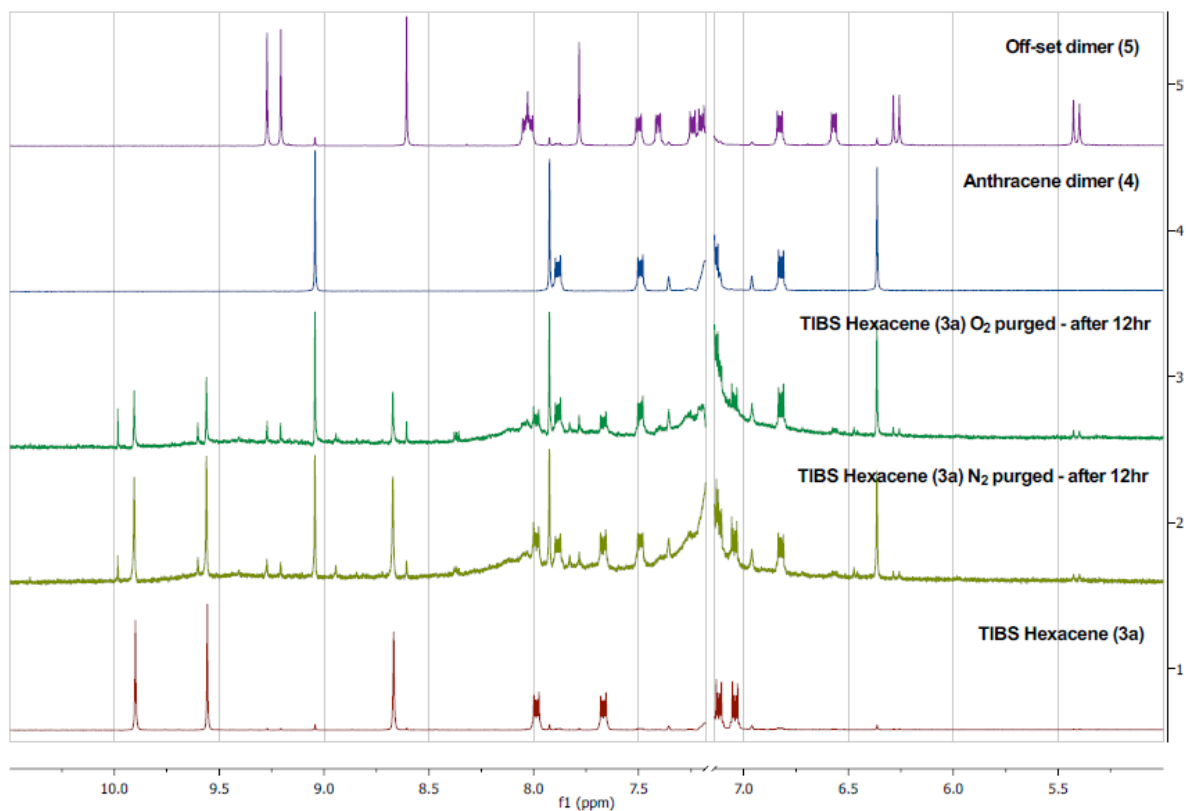


Figure S5: ^1H NMR spectra of **3a** in benzene exposed to a bright light source in comparison with **4** and **5**. N_2 -purged and O_2 -purged samples yielded nearly identical product mixtures.

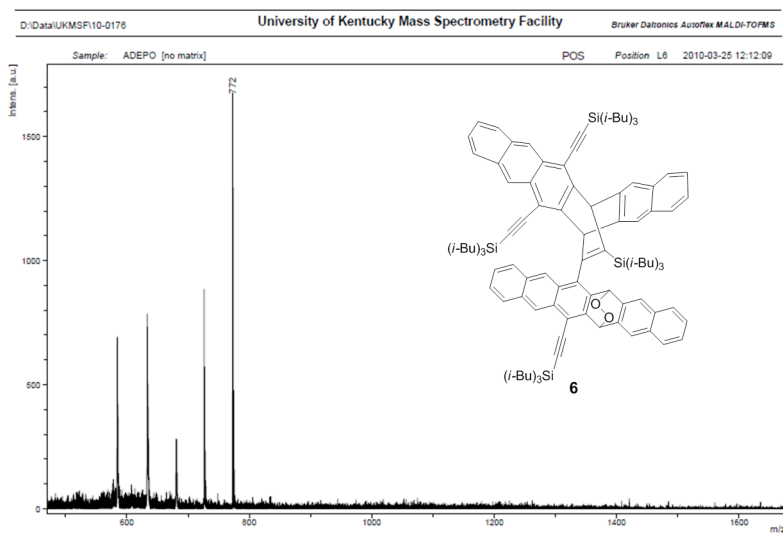


Figure S6: LDI-MS spectrum of endoperoxidized dimer **6**, showing signal only for hexacene **3a**.

Experimental details for Differential Pulse Voltammetry (DPV):

Electrochemical analysis were performed on hexacenes **3a-d** using BAS CV-50W voltammetric analyzer in a three electrode cell configuration consisting of silver wire as a pseudo reference electrode, platinum button as the working electrode and platinum wire as counter electrode. All experiments were done in 0.1M solution of tetrabutylammonium hexafluorophosphate in dichloromethane. Oxidation and reduction potential were calibrated with respect to ferrocene/ferrocenium redox couple. In order to obtain reduction potential, the solution was purged with nitrogen for 10 minutes and the analysis were performed under nitrogen. A scan rate of 20 mV/s was used for DPV measurements. Oxidation and reduction potentials were then converted to vacuum energy levels according to reported literature methods^{5,6}.

References:

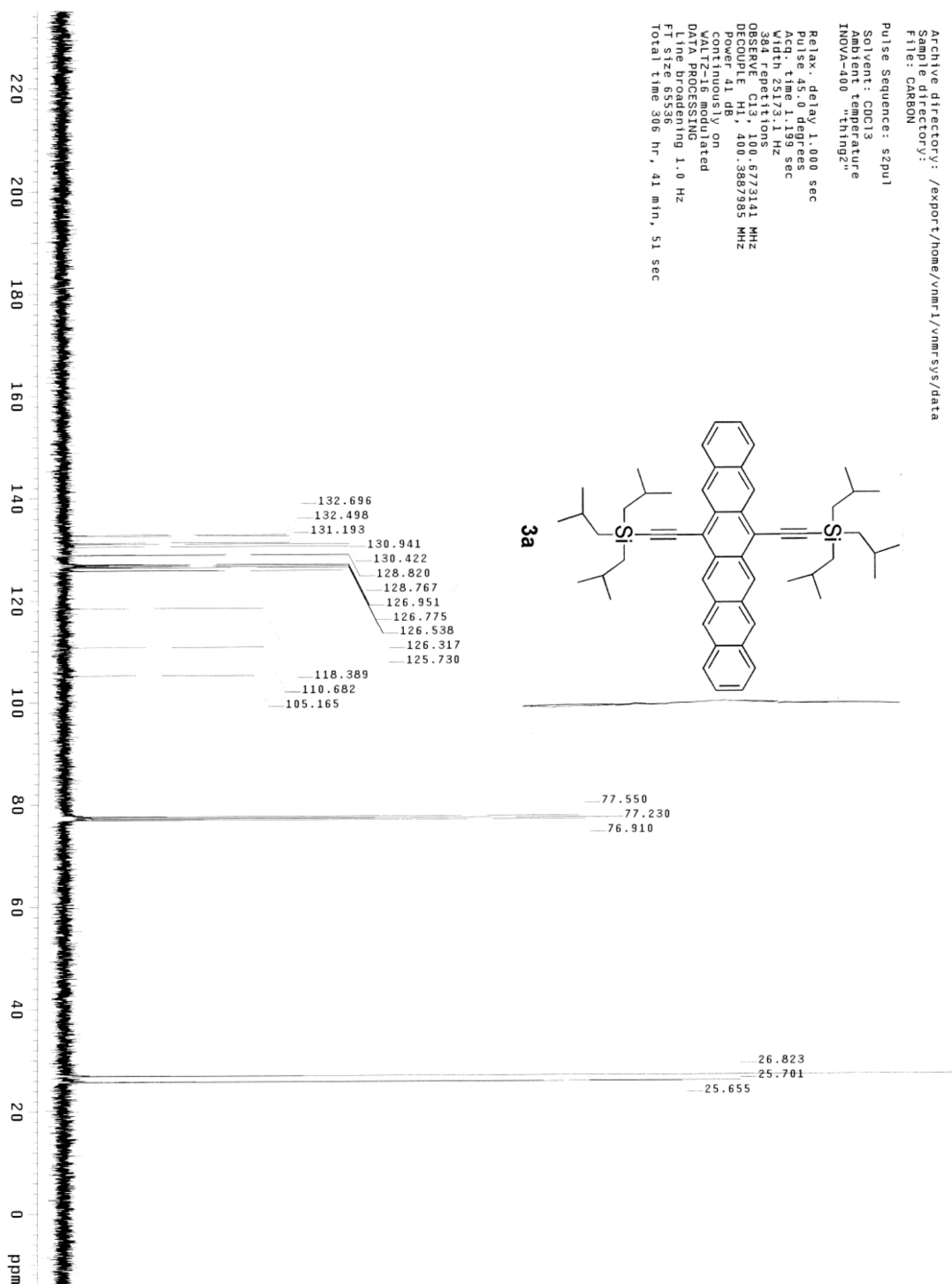
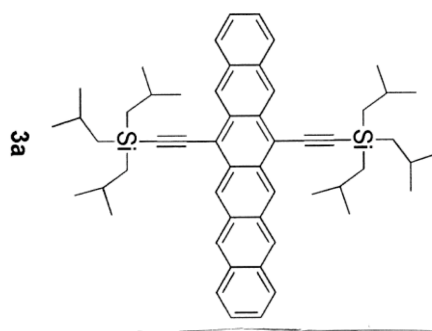
1. Doyle, M. P.; West, C. T. *J. Org. Chem.* **1975**, *40*, 3821.
2. Kamakura, J. M.; Machida, M. O. U.S. Patent 4 714 481, 1987.
3. Payne, M. M.; Parkin, S. R.; Anthony, J. E. *J. Am. Chem. Soc.* **2005**, *127*, 8028.
4. Li, Y.; Cao, Y.; Gao, J.; Wang, D.; Yu, G.; Heeger, A. J. *Synth. Met.* **1999**, *99*, 243.
5. De Leeuw, D. M.; Simenon, M. M. J.; Brown, A. R.; Einerhand, R. E. F. *Synth. Met.* **1997**, *87*, 53.

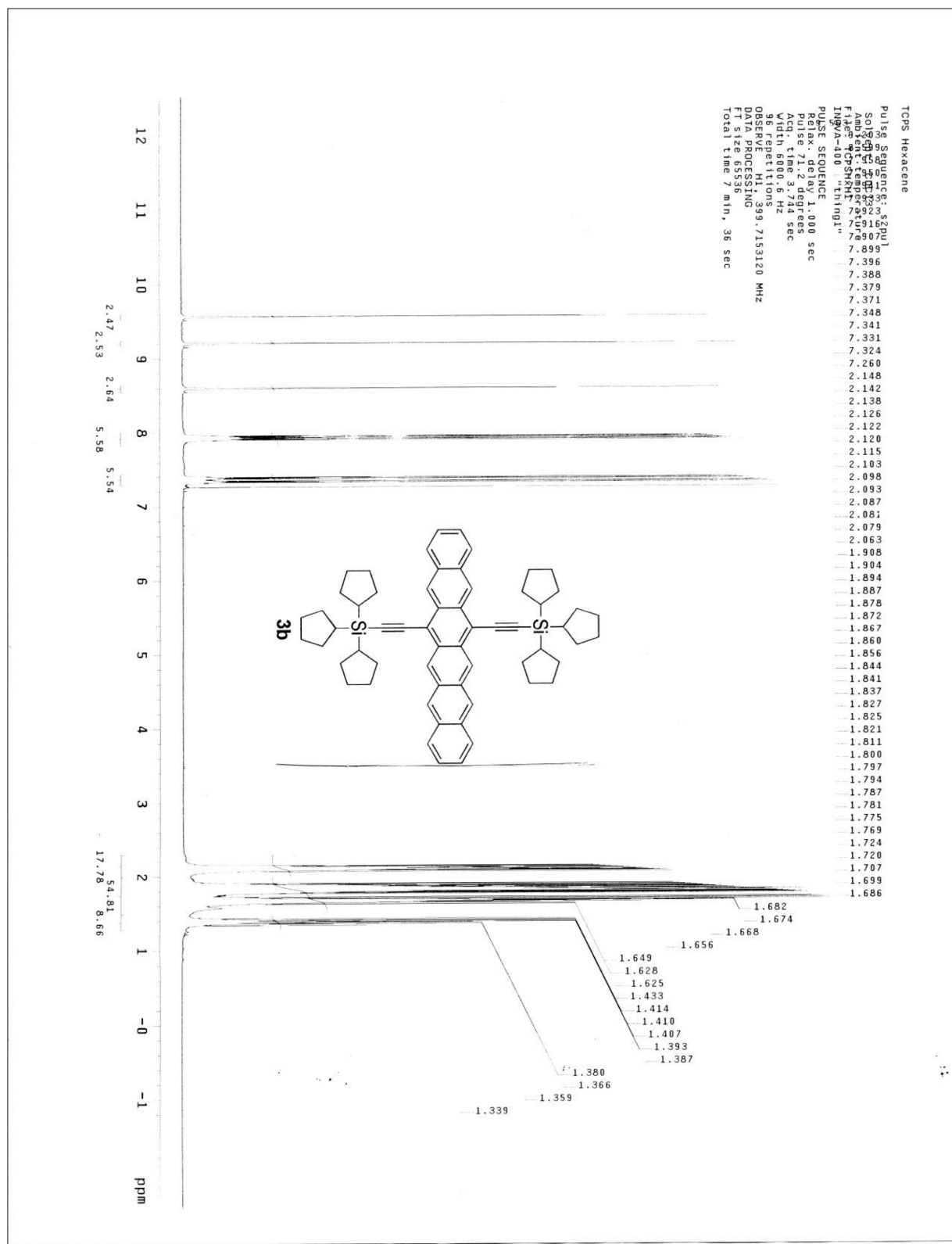
TIBS Hexacene

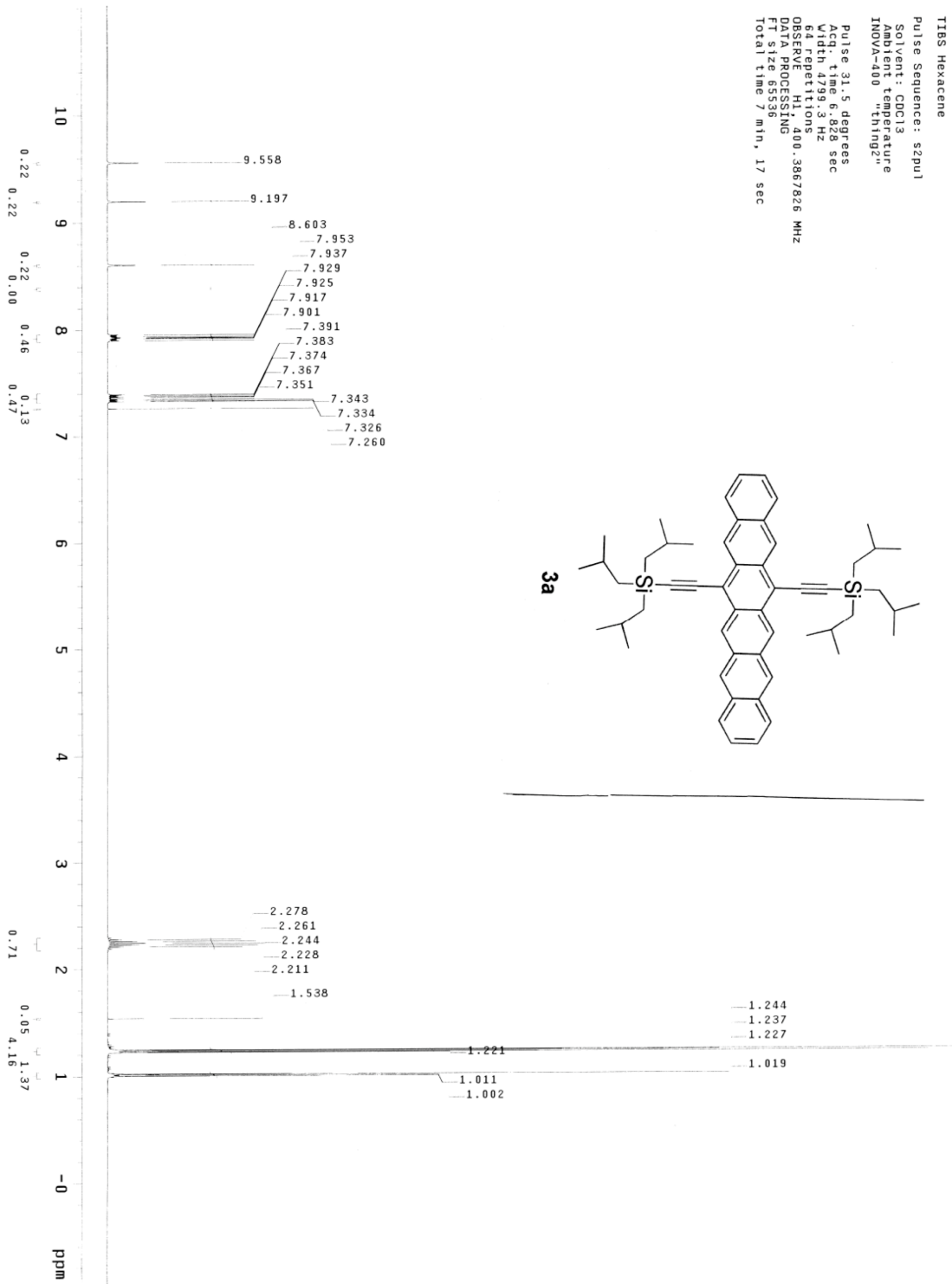
Archive directory: /export/home/vnmr1/vnmrSYS/data
Sample directory:
File: CARBON

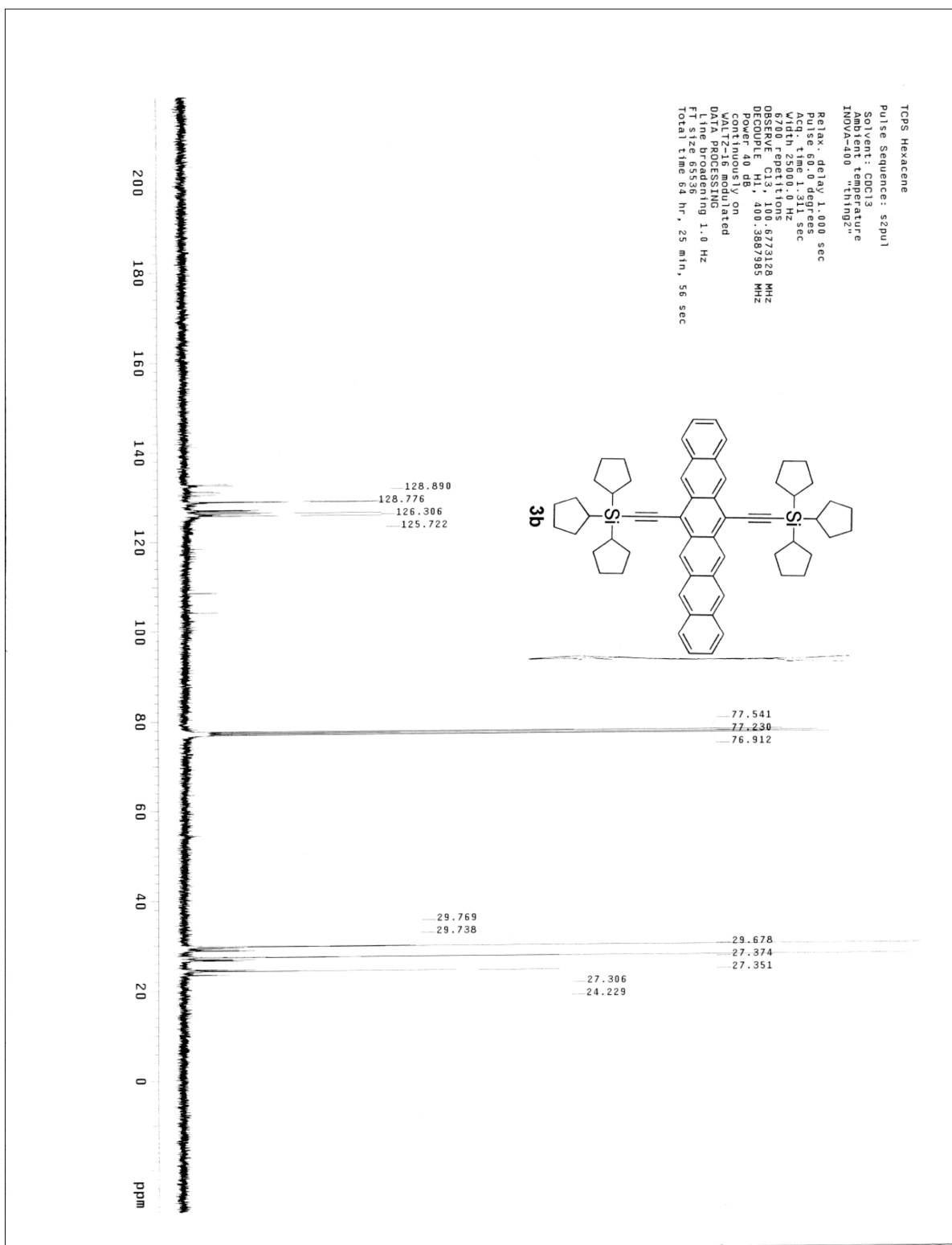
Pulse Sequence: szpul
Solvent: CDCl₃
Ambient temperature
INOVA-400 "thingz"

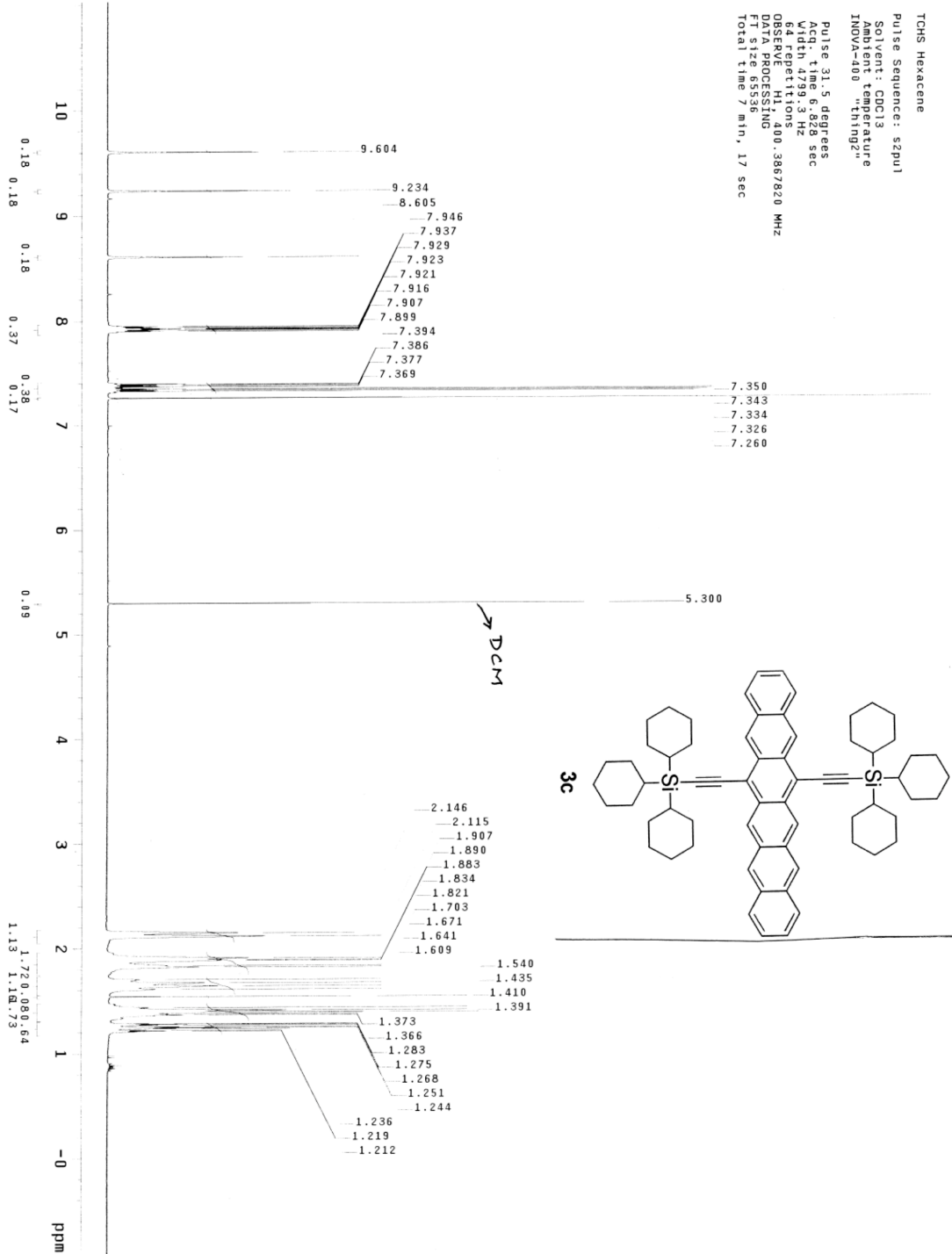
Relax: delay 1.000 sec
Pulse: 4.00 degrees
Acq: time 1.459 sec
Width 25173.1 Hz
384 repetitions
OBSERVE C13, 100.6773141 MHz
DECOUPLE H1, 400.3887985 MHz
Power 41 dB
SFO: 400.3887985 MHz
SFO2: 100.6773141 MHz
DATA PROCESSING
Line broadening 1.0 Hz
FT size 65536
Total time 306 hr, 41 min, 51 sec

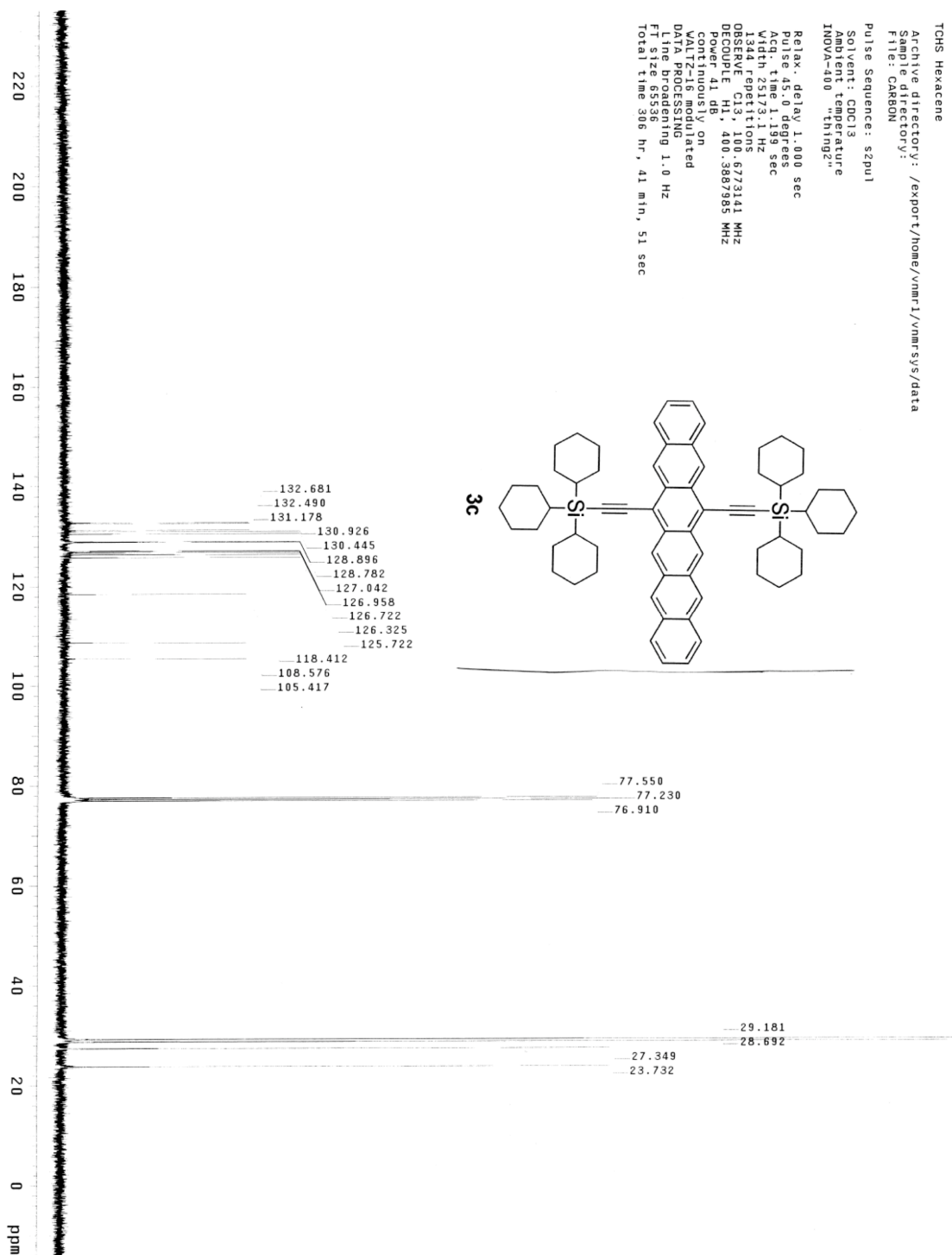




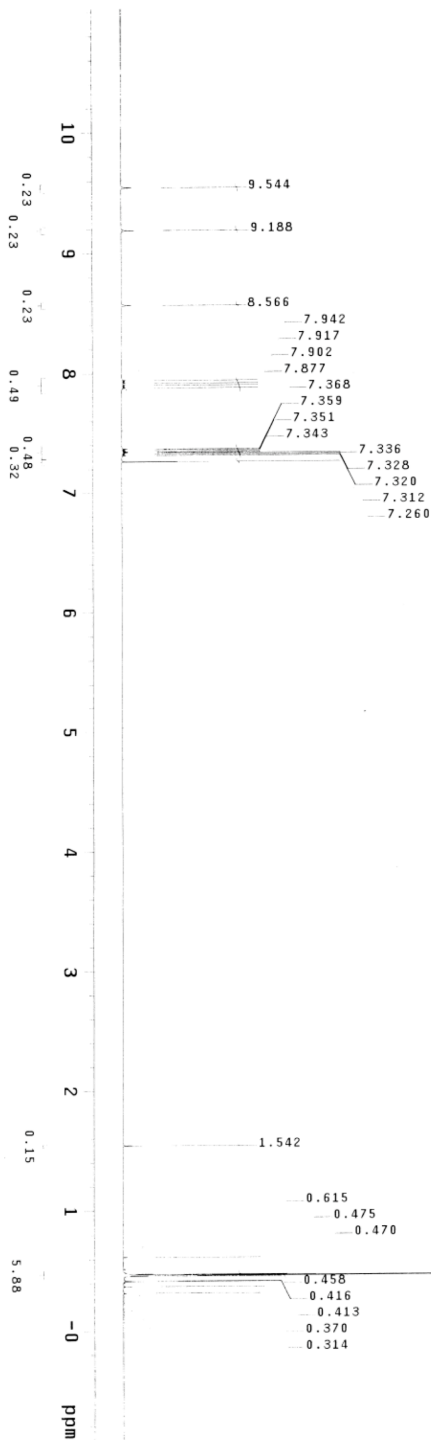
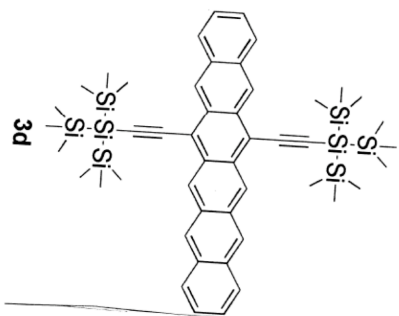


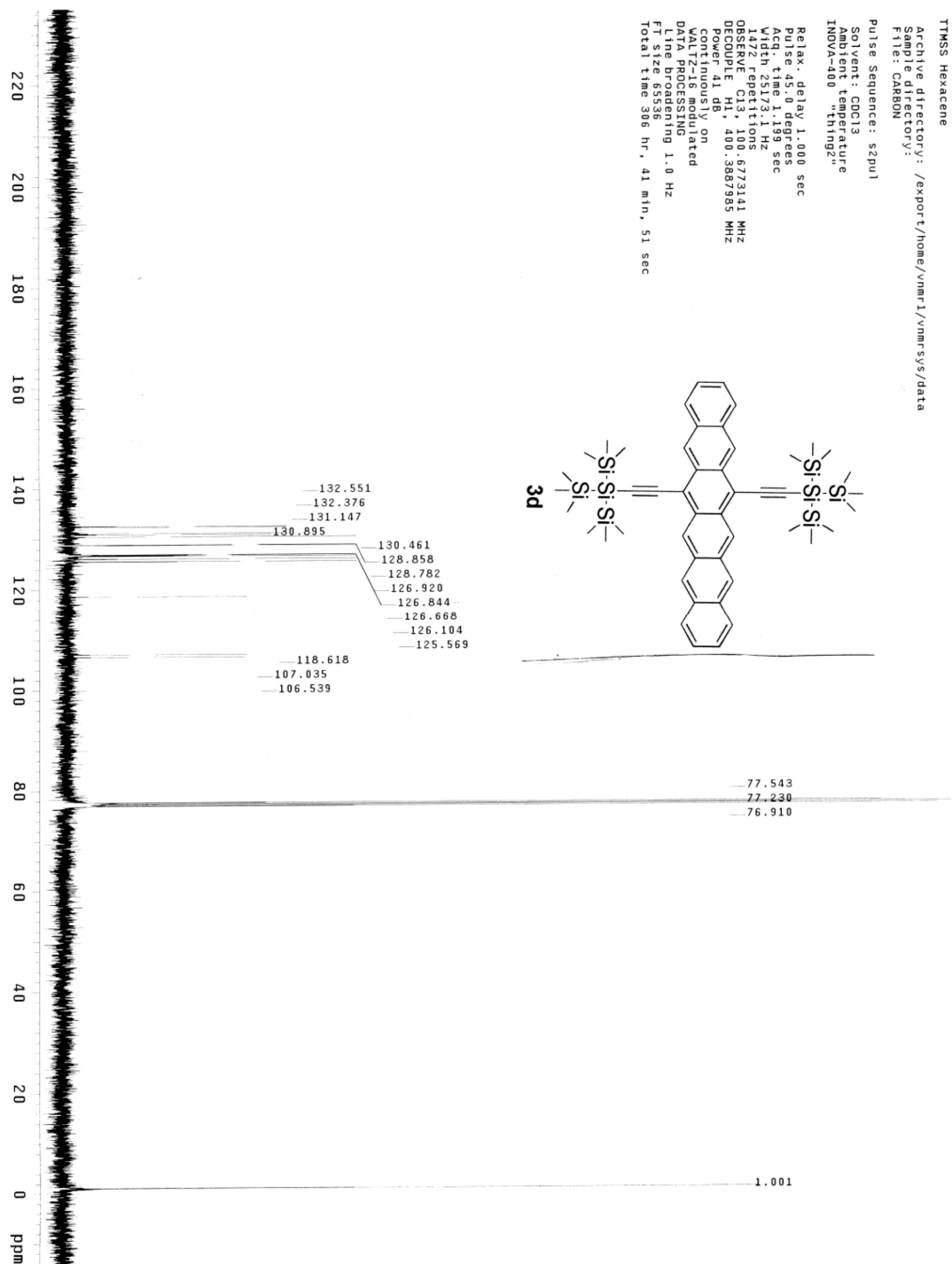


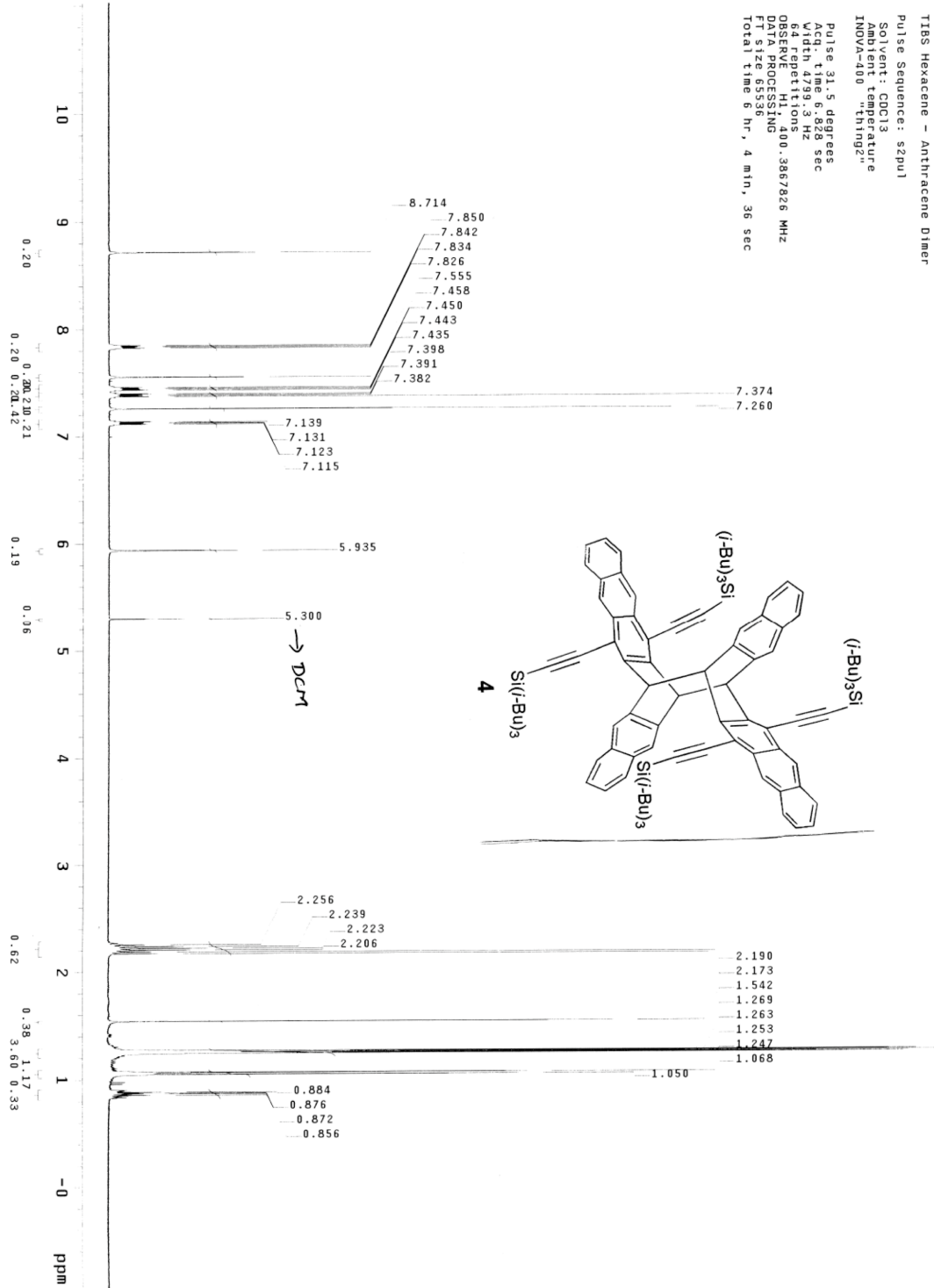




TMS Hexacene
 Pulse Sequence: s2pu1
 Solvent: CDCl3
 Ambient temperature
 INOVA-400 "thing2"
 Pulse 31.5 degrees
 Acq. time 6.022 sec
 Width 773 Hz
 64 repetitions
 OBSERVE H1: 400.3867822 MHz
 DATA PROCESSING
 FT size 65536
 Total time 18 hr, 59 min, 24 sec







TIBS Hexacene - Anthracene Dimer
 Archive directory: /export/home/vnmr1/vnmr/sy/data
 Sample directory:
 File: CARBON
 Pulse Sequence: s2pul
 Solvent: CDCl3
 Ambient temperature
 INOVA-400 "thing2"
 Relax. delay 1.000 sec
 Pulse 45.0 degrees
 Acq. time 1.199 sec
 Width 25173.1 Hz
 Observed F1 100.6273134 MHz
 OBSERVE CH 13C
 DECOUPLE H1. 400.3867985 MHz
 Power 41 dB
 continuously on
 WALTZ-16 modulated
 DATA PROCESSING
 Line broadening 1.0 Hz
 Size 6538
 Total time 386 hr, 41 min, 51 sec

