Tetracene Derivatives as Potential Red Emitters for Organic LEDs

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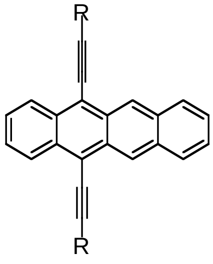
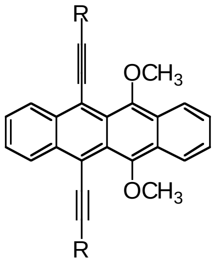
Supplementary Information

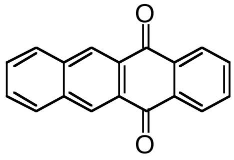
All materials and solvents were obtained from Aldrich Chemical Co. (Milwaukee, WI) or Acros Organics (Pittsburgh, PA) and were used without further purification unless other wise noted. Commercially obtained alkynes were purchased from GFS Chemicals (Powell, OH). Moisture sensitive reactions were carried out in oven-dried glassware cooled under dry nitrogen. For solvents used in moisture sensitive reactions, diethylether was purified by passage through activated alumina, and dry THF was obtained from EM Science (DriSolv). All ^{1}H NMR spectra were obtained at 399.727 MHz, and all ^{13}C NMR spectra were recorded at 100.511 MHz using a Varian Inova 400 MHz NMR. ^{1}H NMR and ^{13}C NMR data are reported in parts per million (δ) downfield from tetramethylsilane. Melting points were recorded using differential scanning calorimetry using a TA Instruments Differential Scanning Calorimeter model number DSC 2920. UV-Vis absorbance spectra were obtained using a Shimadzu UV-Vis recording spectrophotometer model UV-2501PC. Solution photoluminescence spectra and solid-state electroluminescence spectra were recorded using a Jobin Yvon-Spex Fluorolog-3 Fluorimeter model number FL3-11. Fluorescence Quantum Efficiencies were recorded using HPLC grade hexanes as the solvent, and the standard used was rubrene in hexanes, following a literature procedure.[1] Thin layer chromatography was performed on MERCK Silica Gel 60 think layer plates. Silica gel chromatography was performed on Sorbent Technologies brand silica gel (32 – 63 μm, Standard Grade). Elemental analysis was performed by Complete Analysis Laboratories Inc., Parsippany, New Jersey. The evaporation system used to fabricate organic light-emitting diodes (OLEDs) was a modified system purchased from Cressington. Mass spectra for MALDI time-of-flight data were obtained using a Kratos Kompact SEQ spectrometer. Mass spectra for EI were obtained using a Finnigan Polaris Q using an ion trap mass analyzer.

Synthetic Procedures and Characterization

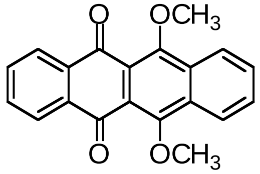




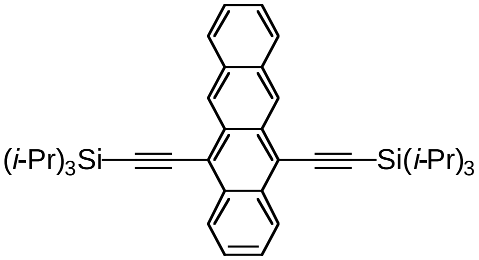
General Procedure for the Synthesis of Tetracene Derivatives: One equivalent of the appropriate alkyne was dissolved in 20 mL of anhydrous diethyl ether in a 250 mL oven-dried round bottom flask under nitrogen atmosphere. 0.9 equivalents of *n*-butyl lithium (2.5 M solution in hexanes) were added by syringe and the solution was stirred at room temperature for 30 minutes. Then 0.33 equivalents of 5,12-tetracene quinone (**1**) or 5,12-dimethoxy-6,13-tetracene quinone (**2**) were added followed by 20 mL of anhydrous diethyl ether, and the reaction was allowed to stir at room temperature overnight. To the solution was then added 100 mL of saturated $SnCl_2$ in 10% aqueous HCl solution and THF was added to increased miscibility of the aqueous and organic layers. Upon addition, the flask was stirred under nitrogen for 30 minutes, and the reaction was monitored by TLC. Upon completion, the mixture was extracted with dichloromethane or hexanes and was washed with water. The solution was dried with $MgSO_4$ and was flushed through a cake of silica gel and was concentrated by rotary evaporation. The product was further purified by flash column chromatography with silica gel using either hexanes, 9:1 hexanes:dichloromethane, or 1:1 hexanes:dichloromethane, yielding a solid.



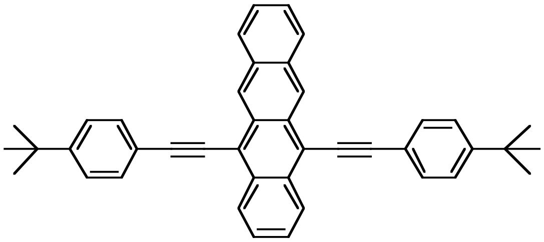
(**1**) 5,12-tetracene quinone**.** To an 500 mL round bottom flask under nitrogen atmosphere was added 1,4-napthoquinone (1 g, 6.2 mmol), tetrabromo-*o*-xylene (10 g, 23.9 mmol), sodium iodide (23g, 163 mmol), calcium carbonate (5 g, 50 mmol), and *N,N*-dimethylformamide (75 mL). The mixture was sparged with nitrogen at room temperature for 30 minutes. The reaction was then brought to 55ºC to stir for two days. The mixture was poured into 200 mL of water, and the yellow solid was filtered and washed with acetone. To remove calcium carbonate from the product, the solid was recrystallized with acetone. The product, a yellow solid, was obtained in 65% yield. The spectra data are consistent of a previous reported synthesis of this compound.[2]



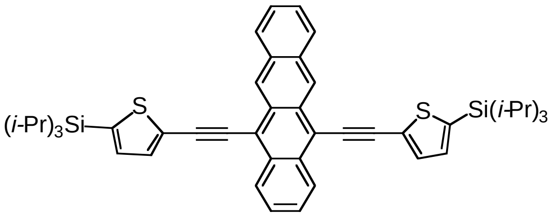
(**2**) 5,12-dimethoxy-6,13-tetracene quinone. 5,12-dihydroxy-6,13-tetracenequinone (1 g, 3.4 mmol), acetone (500 mL), and dioxane (150 mL) were combined in round bottom flask, and dimethyl sulfate (9.4 mL, 57 mmol) and anhydrous potassium carbonate (5 g, 39.4 mmol) were added. The solvents were sparged with nitrogen for 30 minutes and then heated to reflux under nitrogen for two days whereupon a yellow precipitate formed. The reaction mixture was poured into ice water to complete precipitation of the product, which was filtered and recrystallized from acetone. The product, a yellow solid, was isolated in 85% yield and had spectral data consistent with material reported in the literature.[3]



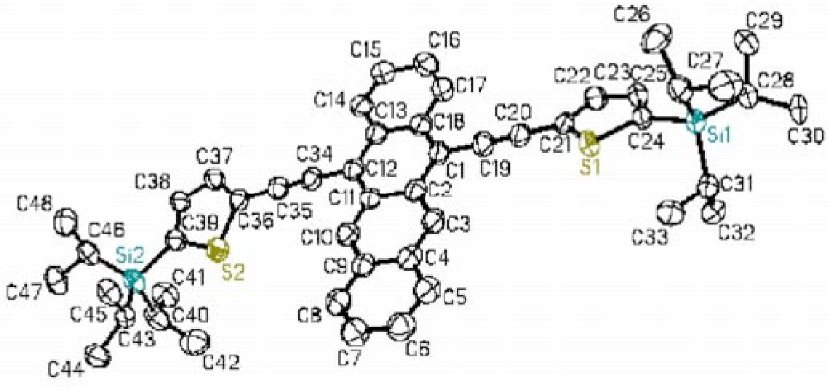
(**3**) 5,12-bis(triisopropylsilylethynyl)tetracene was prepared following the general tetracene procedure using triisopropylsilyl acetylene and **1**. The product was recrystallized from acetone. ^{1}H NMR ($CDCl_3$) d 1.35 (s, 42 H), 7.48 (dd, 2 H, *J* = 2.8, 6.4 Hz), 7.56 (dd, 2 H, *J* = 2.8, 6.8 Hz), 8.04 (dd, 2 H, *J* = 2.8, 6.8 Hz), 8.65 (dd, 2 H, *J* = 2.8, 6.4 Hz), 9.34 (s, 2 H). ^{13}C NMR ($CDCl_3$) d 11.81, 19.17, 104.15, 106.06, 118.81, 126.21, 126.52, 126.89, 127.62, 128.79, 130.56, 132.38, 132.83. MS (m/z, EI) 588 (M+, 100%), 545 (M+ - *i*-Pr). Anal Calcd for $C_{42}H_{36}Si_2$: C, 81.56; H, 8.89. Found C, 81.61; H, 9.15. Melting point: 130 °C. Fluorescence Quantum Efficiency: 0.79. Yield: 98%. UV-Vis (hexanes) l$_{nm}$ (log e): 291 (5.27), 316 (4.18), 332 (4.07), 351 (3.62), 466 (3.76), 498 (4.23), 535 (4.42).

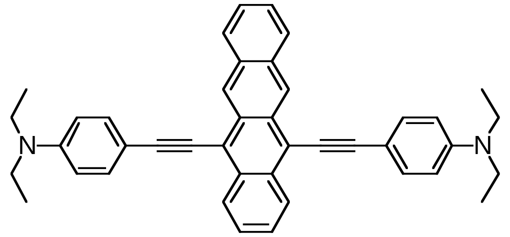


(**4**) 5,12-bis(4-*t*-butylphenylethynyl)tetracene was prepared using the general tetracene procedure using 4-*t*-butylphenylacetylene and **1**. The material was purified by chromatography on silica gel (hexanes eluent). ^{1}H NMR ($CDCl_3$) d 1.42 (s, 18 H), 7.48 (dd, 2 H, *J* = 2.8, 6.4 Hz), 7.54 (d, 4 H, *J* = 6.8 Hz), 7.58 (dd, 2 H, *J* = 3.2, 6.8 Hz), 7.79 (d, 4H, *J* = 6.8 Hz), 8.12 (dd, 2 H, *J* = 3.2, 6.4 Hz), 8.70 (dd, 2 H, *J* = 3.2, 6.8 Hz), 9.32 (s, 2 H). ^{13}C NMR ($CDCl_3$) d 31.46, 35.18, 86.79, 103.64, 118.56, 120.78, 125.85, 126.13, 126.31, 126.71, 127.65, 128.80, 130.17, 131.72, 132.31, 132.45, 152.35. MS (m/z, EI) 540 (M+, 100%), 525 (M+ - CH_3). Anal Calcd for $C_{42}H_{36}$: C, 93.29; H, 6.71. Found C, 93.15; H, 6.62. Melting point: 132 °C. Fluorescence Quantum Efficiency: 0.81. Yield: 98%. UV-Vis (hexanes) l$_{nm}$ (log e): 290 (5.44), 357 (4.42), 485 (3.87), 514 (4.24), 556 (4.38).



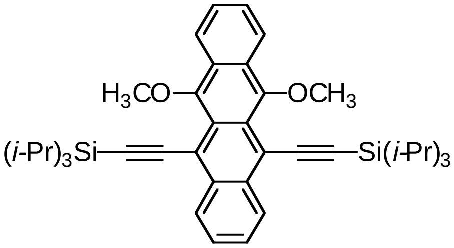
(**5**) 5,12-bis(5-triisopropylsilylthienylethynyl)tetracene was prepared using the general tetracene procedure using 5-triisopropylsilyl-2-ethynyl thiophene and **1**. ^{1}H NMR (CDCl$_3$) d 1.19 (d, 18 H, *J* = 7.2 Hz), 1.44 (septet, 6 H, *J* = 7.2 Hz), 7.31 (d, 2 H, *J* = 3.6 Hz), 7.49 (dd, 2 H, *J* = 2.8, 6.8 Hz), 7.58 (dd, 2 H, *J* = 3.2, 6.8 Hz), 7.66 (d, 2 H, *J* = 3.2 Hz), 8.13 (dd, 2 H, *J* = 3.2, 6.4 Hz), 8.62 (dd, 2 H, *J* = 3.2, 6.8 Hz), 9.22 (s, 2 H). ^{13}C NMR (CDCl$_3$) d 12.06, 18.81, 92.45, 96.84, 118.39, 126.24, 126.93, 127.60, 128.38, 128.83, 129.70, 129.87, 132.29, 132.39, 133.28, 135.96, 139.12. MS (m/z, EI) 752 (M+), 710 (100%, M+ - *i*-Pr). Anal Calcd for $C_{48}H_{56}S_2Si_2O_2$ (endoperoxide formed during shipment): C, 73.41; H, 7.18. Found C, 74.73; H, 7.28. Melting point: 187 °C. Fluorescence Quantum Efficiency: 0.69. Yield: 55%. UV-Vis (hexanes) l $_{nm}$ (log e): 280 (5.33), 376 (4.36), 470 (3.62), 531 (4.28), 570 (4.41). Structure further confirmed by X-ray crystallographic analysis:



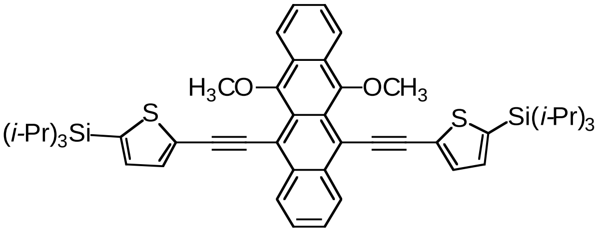


(**6**) 5,12-bis(4-(N,N-diethylamino)phenylethynyl)tetracene was prepared by the general procedure using 4-(diethylamino)phenylacetylene and **1**. The product was purified by recrystallization from 2-butanone. ^{1}H NMR (CDCl$_3$) d 1.26 (t, 12 H, *J* = 6.4 Hz), 3.47 (q, 8 H, *J* = 6.4 Hz), 6.76 (d, 4 H, *J* = 8.4 Hz), 7.46 (dd, 2 H, *J* = 3.2, 6.8 Hz), 7.55 (dd, 2 H, *J* = 3.2, 6.8 Hz), 7.74 (d, 4 H, *J* = 8.4 Hz), 8.11 (dd, 2 H, *J* = 3.2, 6.4 Hz), 8.70 (dd, 2 H, *J* = 3.2, 6.8 Hz), 9.32 (s, 2H). ^{13}C NMR (CDCl$_3$) d 12.81, 44.67, 85.71, 105.20, 109.50, 111.59, 118.50, 125.82, 126.29, 126.40, 127.83, 130.16, 132.13, 133.36, 148.04. MS (m/z, MALDI) = 570 (M+). Anal Calcd for $C_{42}H_{36}N_2$: C. 88.69; H, 6.37; N, 4.92. Found

C, 87.99; H, 6.58; N, 5.15. Melting point: 250 °C (dec.). Fluorescence Quantum Efficiency: 0.10. Yield: 49%. UV-Vis (hexanes) l_{nm} (log e): 277 (5.96), 352 (4.37), 380 (4.42), 556 (4.51), 595 (4.61).



(**7**) 5,12-dimethoxy-6,11-bis(triisopropylsilylethynyl)tetracene was prepared using the general tetracene procedure with triisopropylsilyl acetylene and **2**. The product was purified by recrystallization from acetone, yielding material suitable for X-ray analysis. ^{1}H NMR ($CDCl_3$) d 1.32 (br. s, 42 H), 4.07 (s, 6 H), 7.48 (dd, 2 H, *J* = 3.2, 6.8), 7.55 (dd, 2 H, *J* = 3.2, 6.8 Hz), 8.33 (dd, 2 H, *J* = 3.2, 6.8 Hz), 8.90 (dd, 2 H, *J* = 3.2, 6.8 Hz). ^{13}C NMR ($CDCl_3$) d 12.03, 19.12, 64.05, 106.02, 106.80, 115.81, 123.30, 124.95, 125.61, 126.08, 126.99, 127.92, 134.29, 149.94. MS (m/z, EI) 648 (100%, M+), 633 (80%, M+ - Me). Anal Calcd for $C_{42}H_{56}O_2Si_2$: C, 77.72; H, 8.69. Found C, 77.79; H, 9.01. Melting point: 124 °C. Fluorescence Quantum Efficiency: 0.19. Yield: 88%. UV-Vis (hexanes) l_{nm} (log e): 300 (5.29), 329 (4.12), 347 (3.95), 380 (3.62), 501 (3.81), 538 (4.19), 580 (4.32).



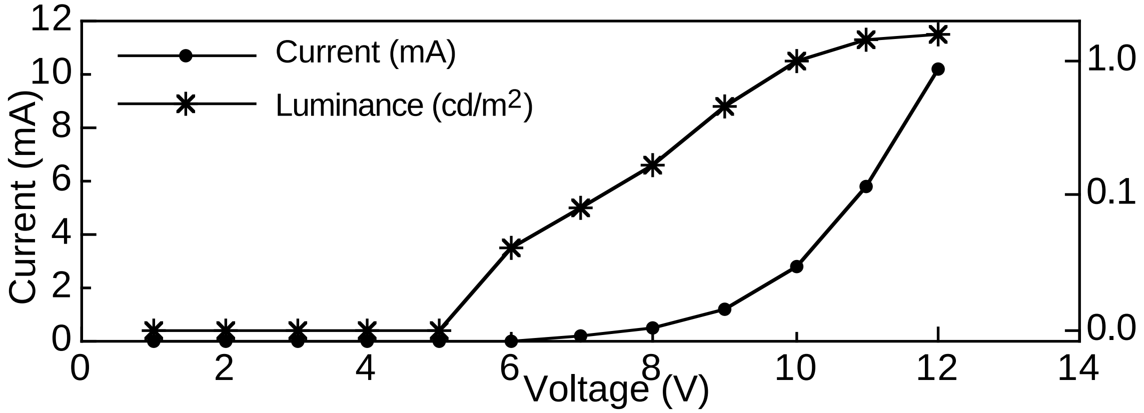
(**8**) 5,12-dimethoxy-6,11-bis(5-triisopropylsilylthienylethynyl)tetracene was prepared using the general tetracene procedure with 5-triisopropylsilyl-2-ethynyl thiophene and **2**. The product was purified by repeated chromatography on silica gel (hexanes:methylene chloride 9:1). ^{1}H NMR ($CDCl_3$) d 1.19 (d, 36 H, *J* = 7.2 Hz), 1.43 (septet, 6 H, *J* = 7.2 Hz), 4.24 (s, 6H), 7.28 (d, 2 H, *J* = 8 Hz), 7.51 (dd, 2 H, *J* = 3.2, 6.8 Hz), 7.62 (d, 2 H *J* = 3.2 Hz), 7.64 (dd, 2 H, *J* = 3.2, 6.8 Hz), 8.40 (dd, 2 H, *J* = 2.8, 6.4 Hz), 8.84 (dd, 2 H, *J*= 3.2, 6.8 Hz). ^{13}C NMR ($CDCl_3$) d 12.06, 18.81, 64.16, 96.44, 96.65, 115.22, 123.29, 124.70, 125.77, 126.27, 127.37, 127.52, 129.42, 132.80, 133.11, 136.01, 138.75, 149.89. MS (m/z, EI) 813 (50%, M+), 786 (50%, M+ - 2 Me). Anal Calcd for $C_{50}H_{60}S_2Si_2O_4$ (endoperoxide formed during shipment): C, 71.04; H, 7.15. Found C, 71.51; H, 7.39. Melting point: 164 °C. Fluorescence Quantum Efficiency: 0.36. Yield: 17%. UV-Vis (hexanes) l $_{nm}$ (log e): 303 (4.65), 389 (4.32), 412 (4.15), 532 (3.25), 571 (3.74), 617 (3.89).

Fabrication of OLEDs

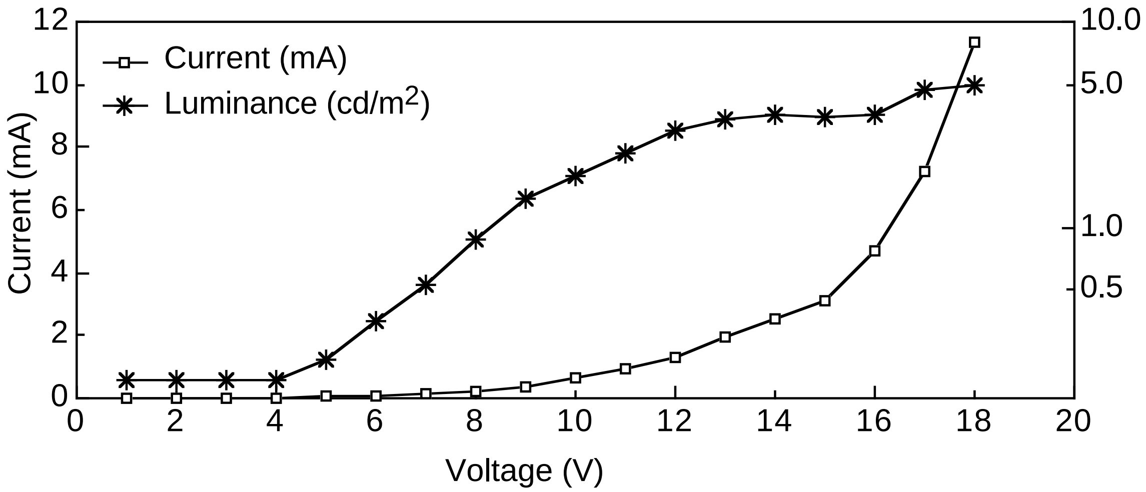
ITO glass was provided by Gentex Corporation. The ITO glass was patterned by using a shadow mask to spray lacquer onto the ITO glass, then removing the exposed ITO using an *aqua regia* bath (10:10:1::H_2O:HCl:HNO_3, 20 min.). The lacquer was removed with acetone. The remaining ITO was treated with sonication in a dilute *aqua regia* bath (2:7:25::HNO_3:HCl:H_2O) until the ITO turned from red-violet to blue-gold (approx. 20 min.). The ITO glass was treated with an RCA bath (1:1:5::H_2O_2:NH_4OH:H_2O, 30 min.). The substrates were washed with sonication in water (5 min.), isopropanol (5 min.), and acetone (5 min.) after which they were dried under nitrogen. The substrates were further dried in an oven (110^{o}C, 15 min.).

Following the substrate preparation, layers of compounds were deposited via evaporation under a vacuum of 10^{-5} mbar. The layers used were the hole-transporting layer (TPD, 40 nm), the light-emitting layer (tetracene derivative, 30 nm), a buffer layer (LiF, 0.8 nm), and the cathode (aluminum, 60 – 100 nm). Current and luminance data were recorded for the OLEDs. Examples of the voltage-current-luminance data are shown below.

Current, Voltage, Luminance Data for OLED with Compound **3:**



Current, Voltage, Luminance Data for OLED with Compound **7**:



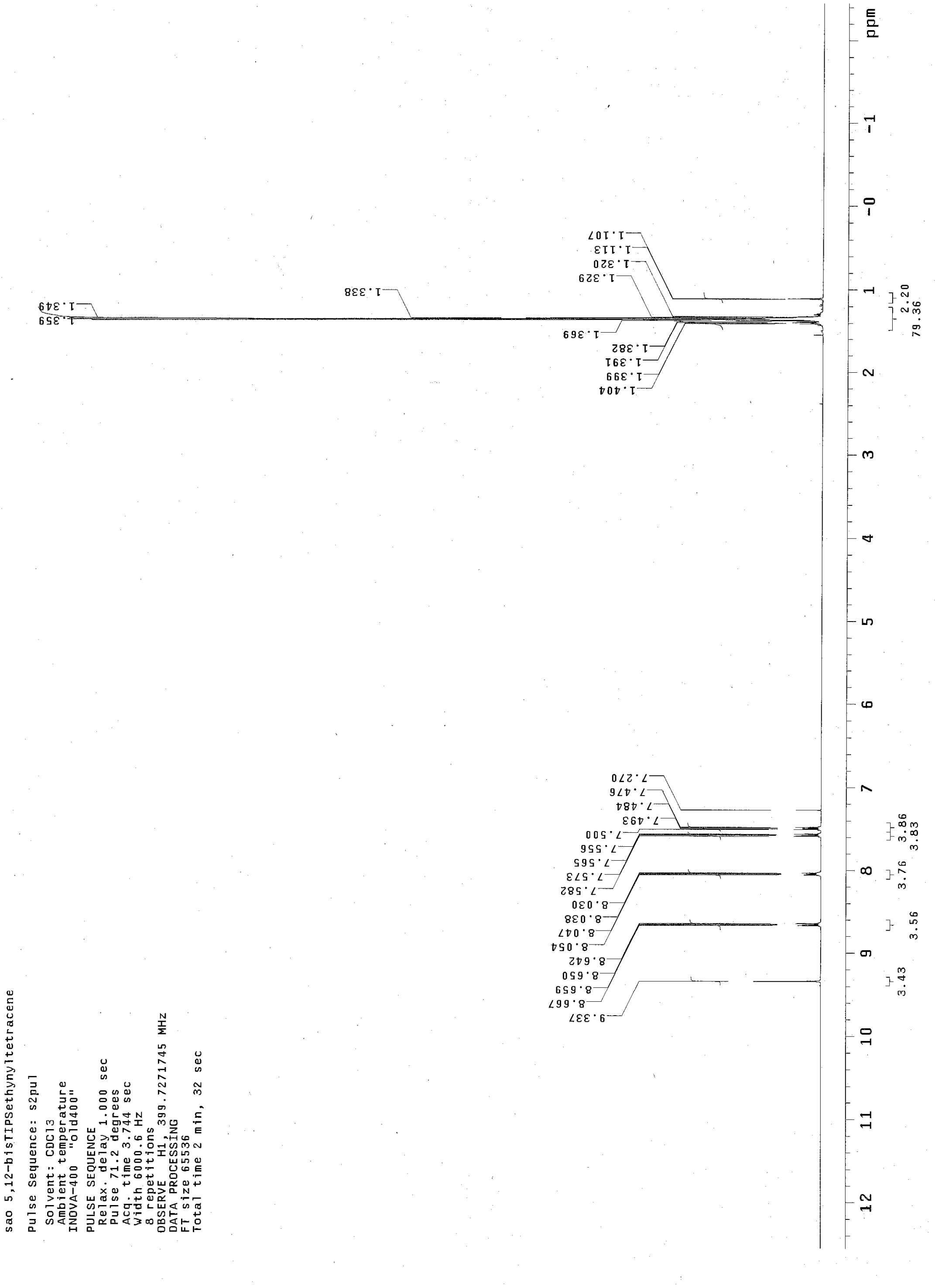
References:

1. Fery-Forgues, S.; Lavabre, D. *J. Chem. Ed.* **199**, *76*, 1260.
2. Hanhela, P. J.; Paul, D. B. *Aust. J. Chem.* **1981**, *34*, 1701.

3. Khanapure, S. P.; Reddy, R. T.; Biehl, E. R. *J. Org. Chem.* **1987**, *52*, 5685.

Compound 3

^{1}H NMR

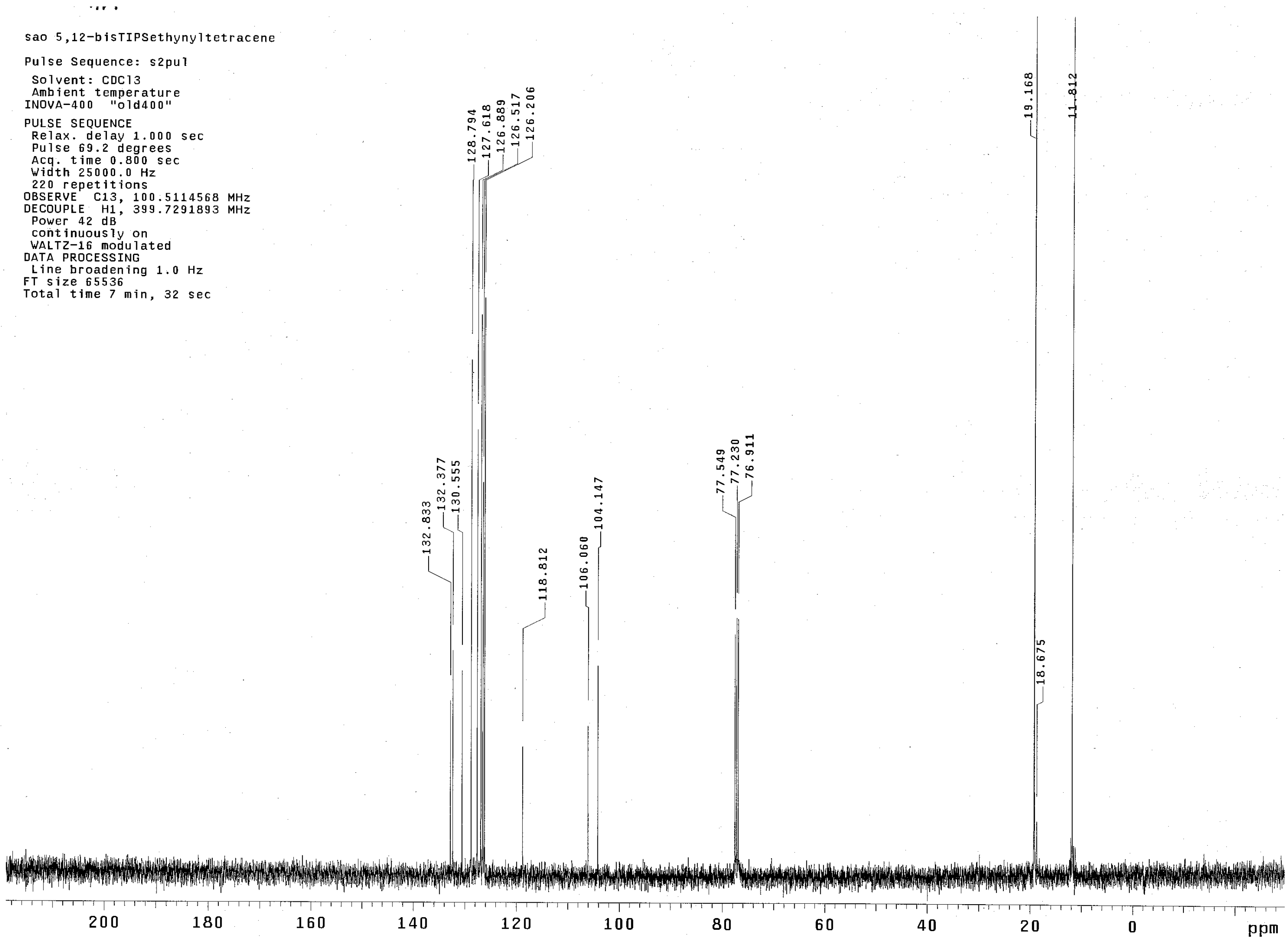


sao 5,12-bisTIPSethynyltetracene

Pulse Sequence: s2pul

Solvent: CDCl3
Ambient temperature
INOVA-400 "old400"
PULSE SEQUENCE
Relax. delay 1.000 sec
Pulse 71.2 degrees
Acq. time 3.744 sec
Width 6000.6 Hz
8 repetitions
OBSERVE H1, 399.7271745 MHz
DATA PROCESSING
FT size 65536
Total time 2 min, 32 sec

Compound 3
^{13}C NMR



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sao 5,12-bisTIPSethynyltetracene

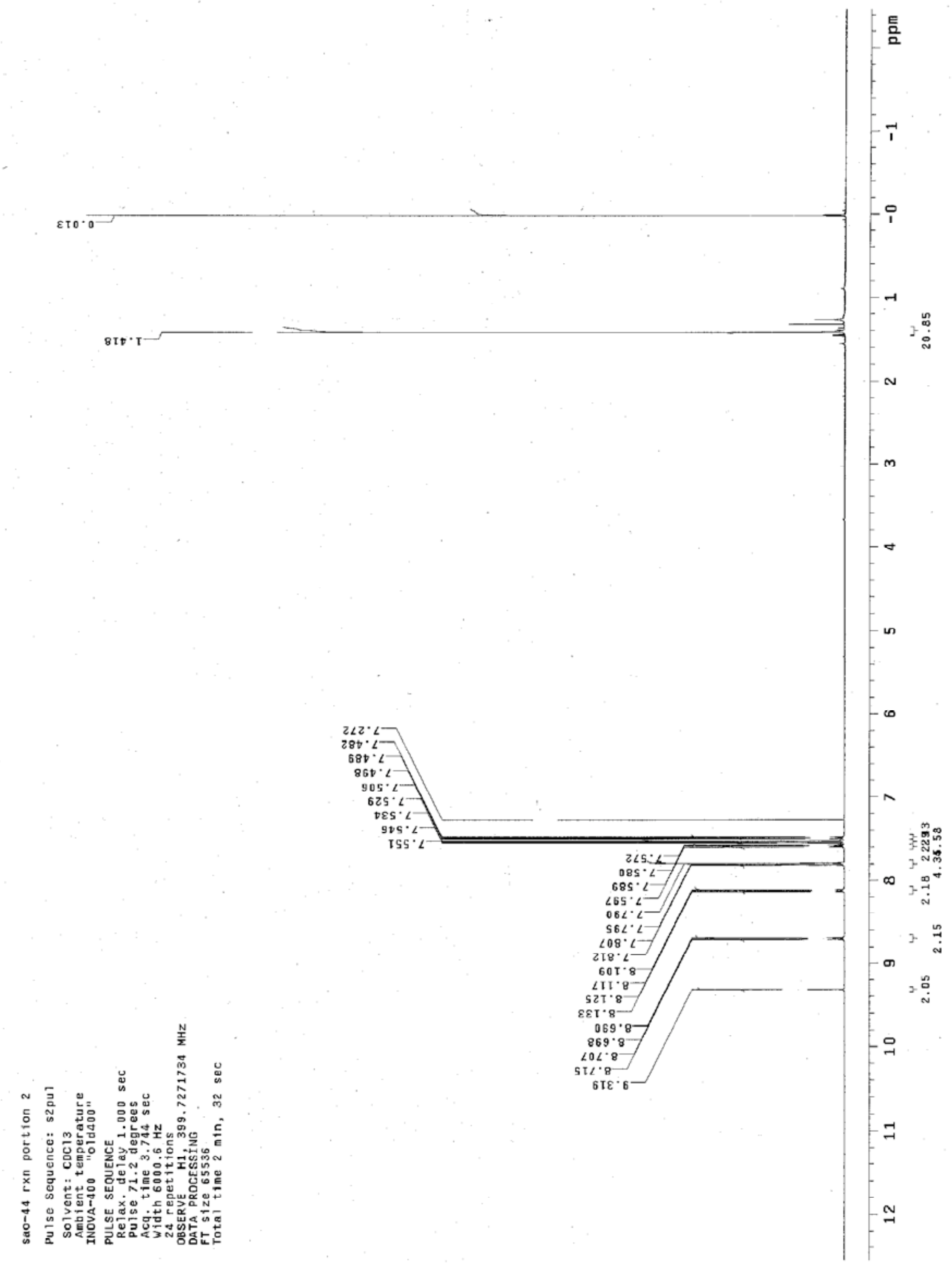
Pulse Sequence: s2pul

 Solvent: CDCl3
 Ambient temperature
INOVA-400  "old400"

PULSE SEQUENCE
 Relax. delay 1.000 sec
 Pulse 69.2 degrees
 Acq. time 0.800 sec
 Width 25000.0 Hz
 220 repetitions
OBSERVE  C13, 100.5114568 MHz
DECOUPLE  H1, 399.7291893 MHz
 Power 42 dB
 continuously on
 WALTZ-16 modulated
DATA PROCESSING
 Line broadening 1.0 Hz
FT size 65536
Total time 7 min, 32 sec
```

Compound 4

^1H NMR



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sao-44 rxn portion 2

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 Ambient temperature
INOVA-400  "old400"

PULSE SEQUENCE
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 Pulse 71.2 degrees
 Acq. time 3.744 sec
 Width 6000.6 Hz
 24 repetitions
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DATA PROCESSING
FT size 65536
Total time 2 min, 32 sec
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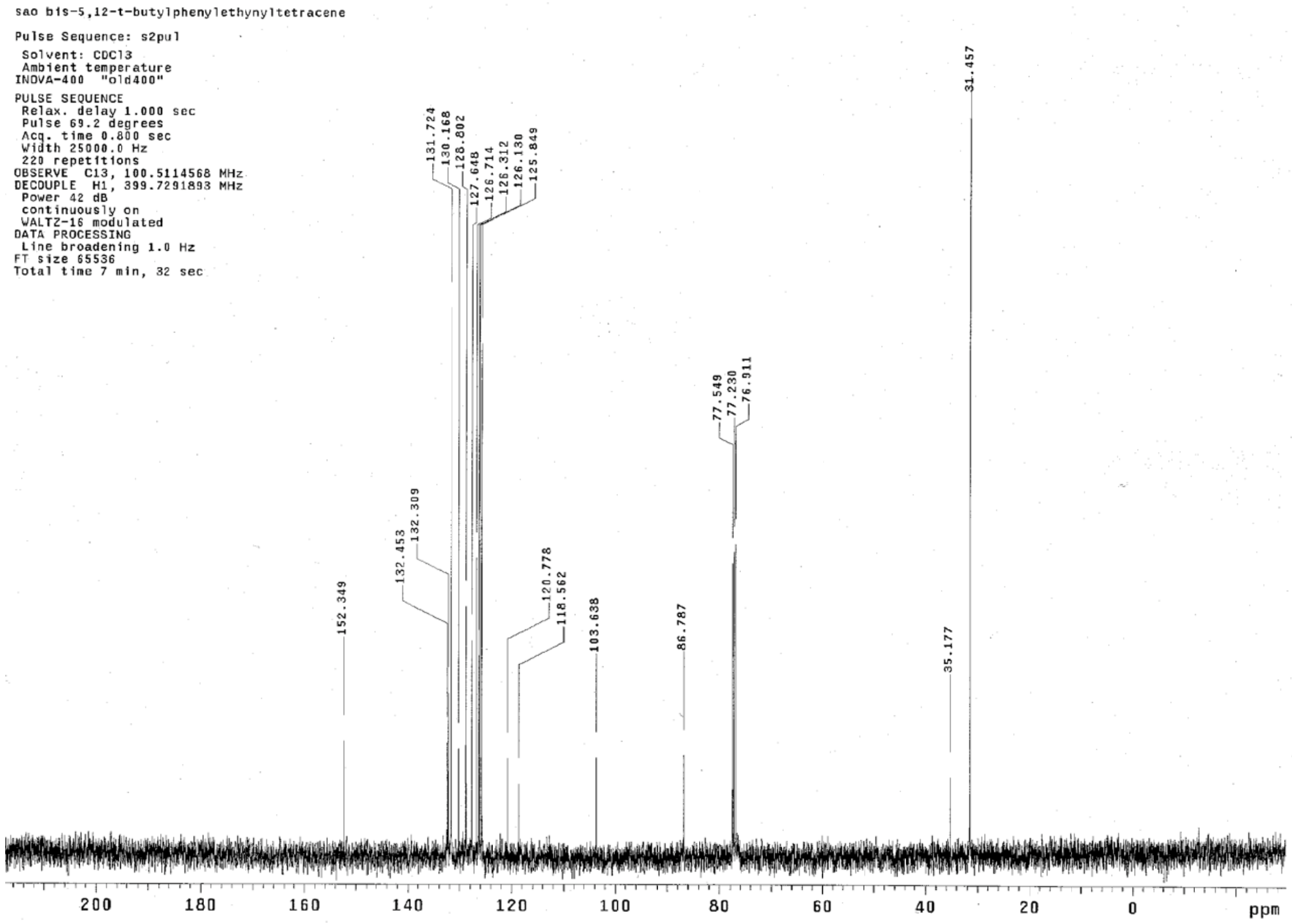
Compound 4
^{13}C NMR



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sao bis-5,12-t-butylphenylethynyltetracene

Pulse Sequence: s2pul
 Solvent: CDCl3
 Ambient temperature
INOVA-400  "old400"
PULSE SEQUENCE
 Relax. delay 1.000 sec
 Pulse 69.2 degrees
 Acq. time 0.800 sec
 Width 25000.0 Hz
 220 repetitions
OBSERVE  C13, 100.5114568 MHz
DECOUPLE  H1, 399.7291893 MHz
 Power 42 dB
 continuously on
 WALTZ-16 modulated
DATA PROCESSING
 Line broadening 1.0 Hz
FT size 65536
Total time 7 min, 32 sec
```

Compound 5

^{1}H NMR

```
sao 5,12-bis-(TIPSthienylethynyl)tetracene

Pulse Sequence: s2pul

 Solvent: CDCl3
 Ambient temperature
INOVA-400  "old400"

PULSE SEQUENCE
 Relax. delay 1.000 sec
 Pulse 71.2 degrees
 Acq. time 3.744 sec
 Width 6000.6 Hz
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OBSERVE   H1, 399.7271741 MHz
DATA PROCESSING
 Line broadening 1.0 Hz
FT size 65536
Total time 2 min, 32 sec
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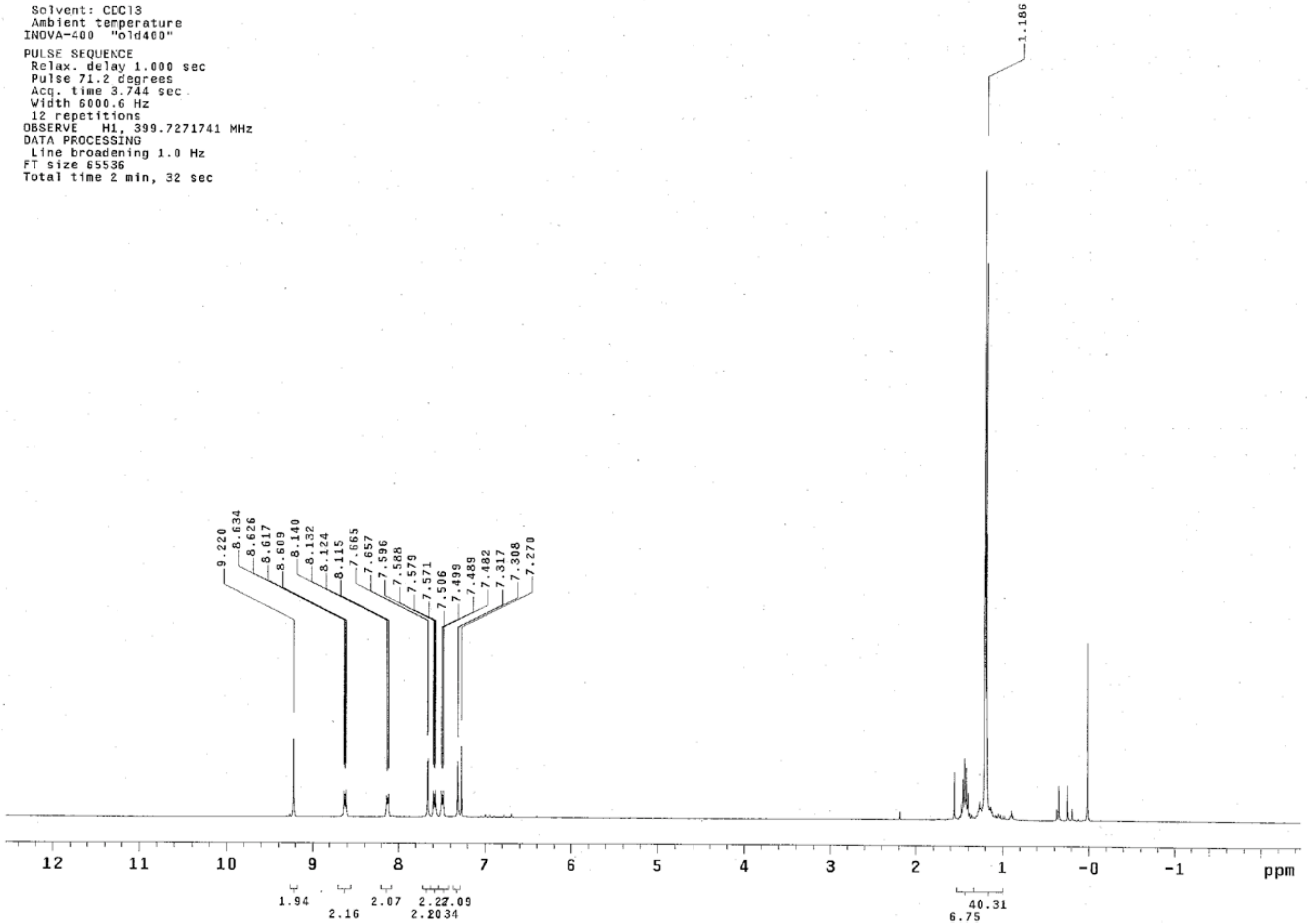
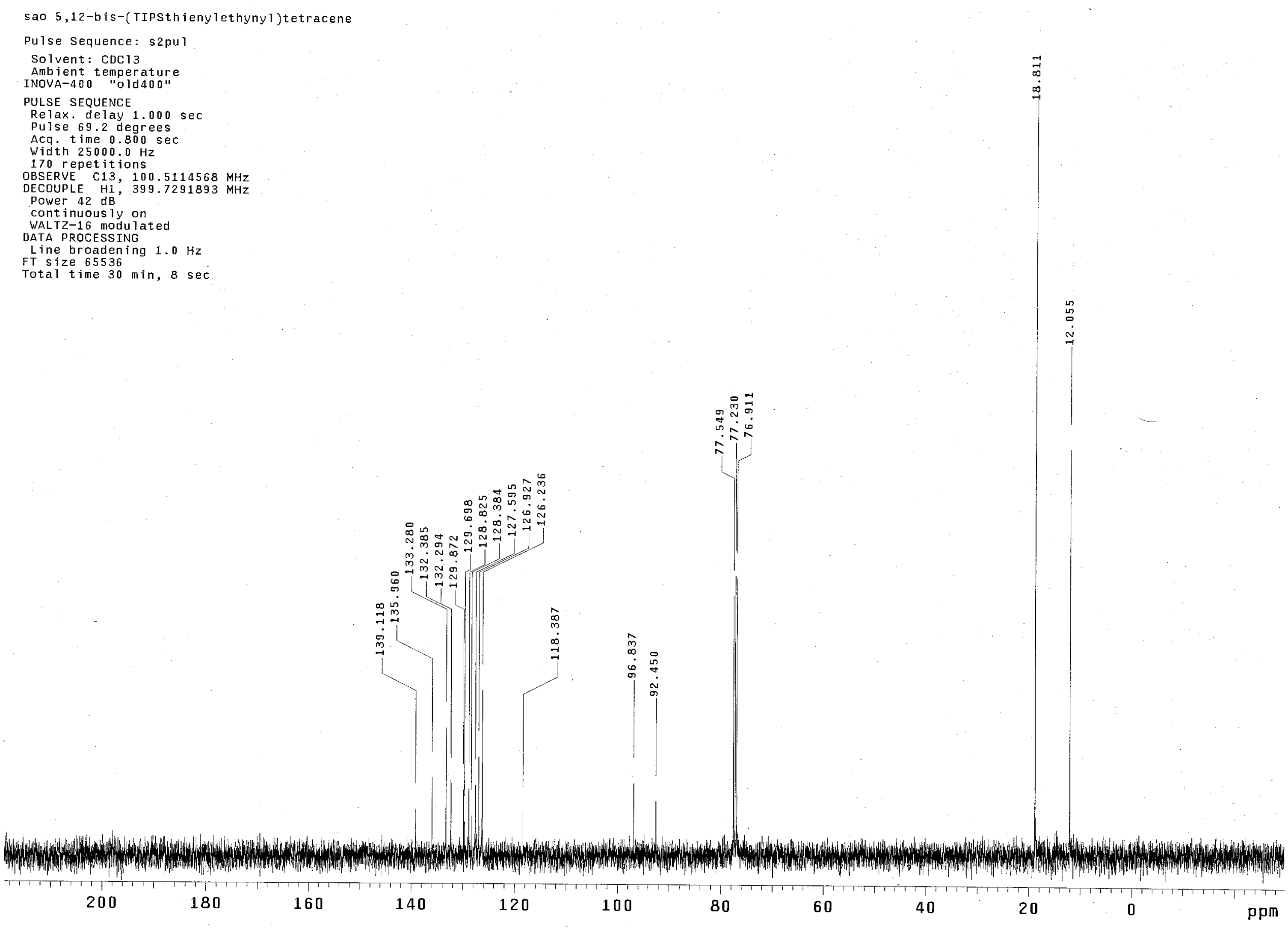


Compound 5
^{13}C NMR



```
sao 5,12-bis-(TIPSthienylethynyl)tetracene

Pulse Sequence: s2pul

 Solvent: CDCl3
 Ambient temperature
INOVA-400  "old400"

PULSE SEQUENCE
 Relax. delay 1.000 sec
 Pulse 69.2 degrees
 Acq. time 0.800 sec
 Width 25000.0 Hz
 170 repetitions
OBSERVE  C13, 100.5114568 MHz
DECOUPLE  H1, 399.7291893 MHz
 Power 42 dB
 continuously on
 WALTZ-16 modulated
DATA PROCESSING
 Line broadening 1.0 Hz
FT size 65536
Total time 30 min, 8 sec
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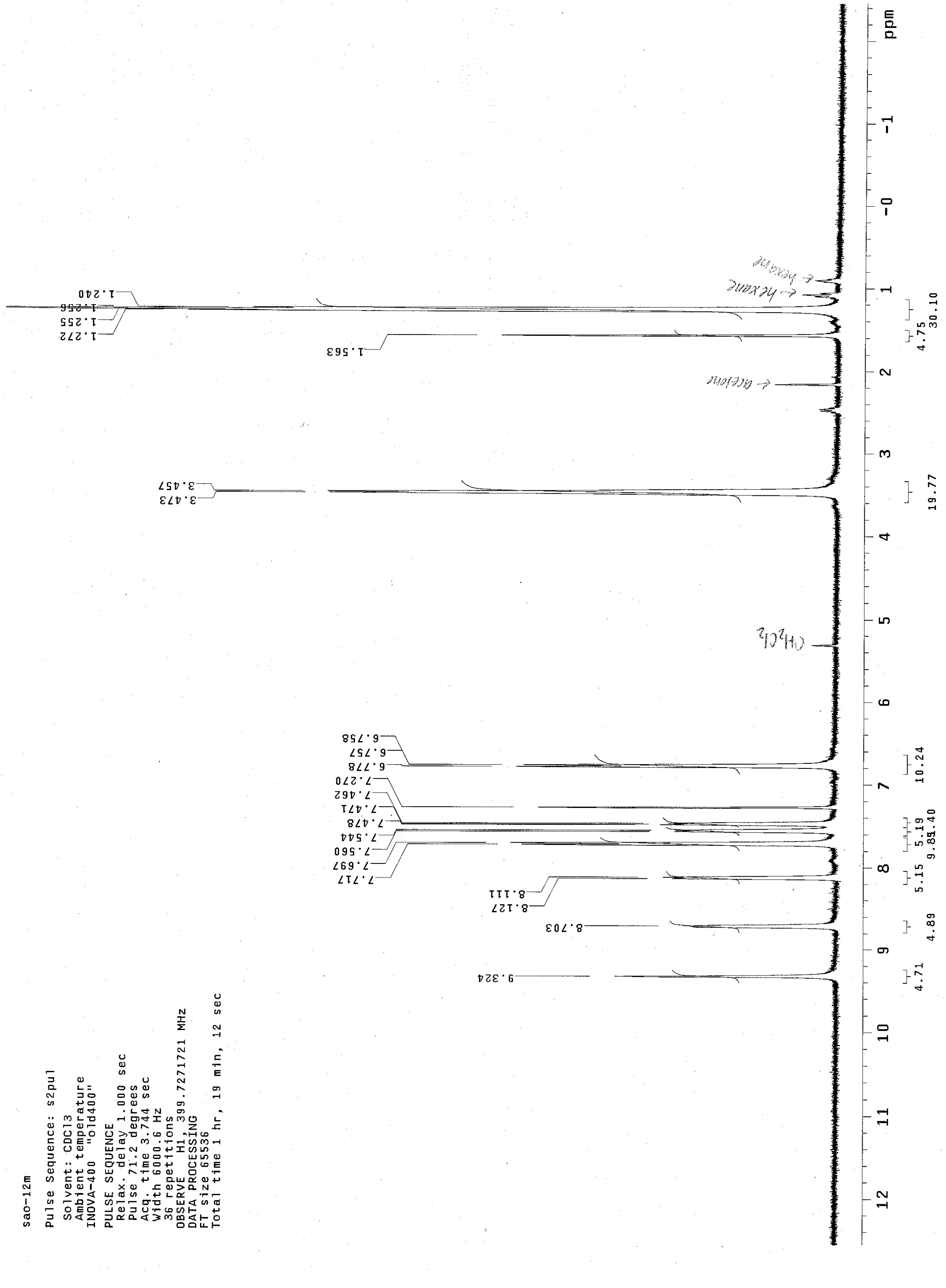
Compound 6

^{1}H NMR



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sao-12m
Pulse Sequence: s2pul
 Solvent: CDCl3
 Ambient temperature
 INOVA-400  "old400"
 PULSE SEQUENCE
 Relax. delay 1.000 sec
 Pulse 71.2 degrees
 Acq. time 3.744 sec
 Width 6000.6 Hz
 36 repetitions
OBSERVE  H1, 399.7271721 MHz
DATA PROCESSING
FT size 65536
Total time 1 hr, 19 min, 12 sec
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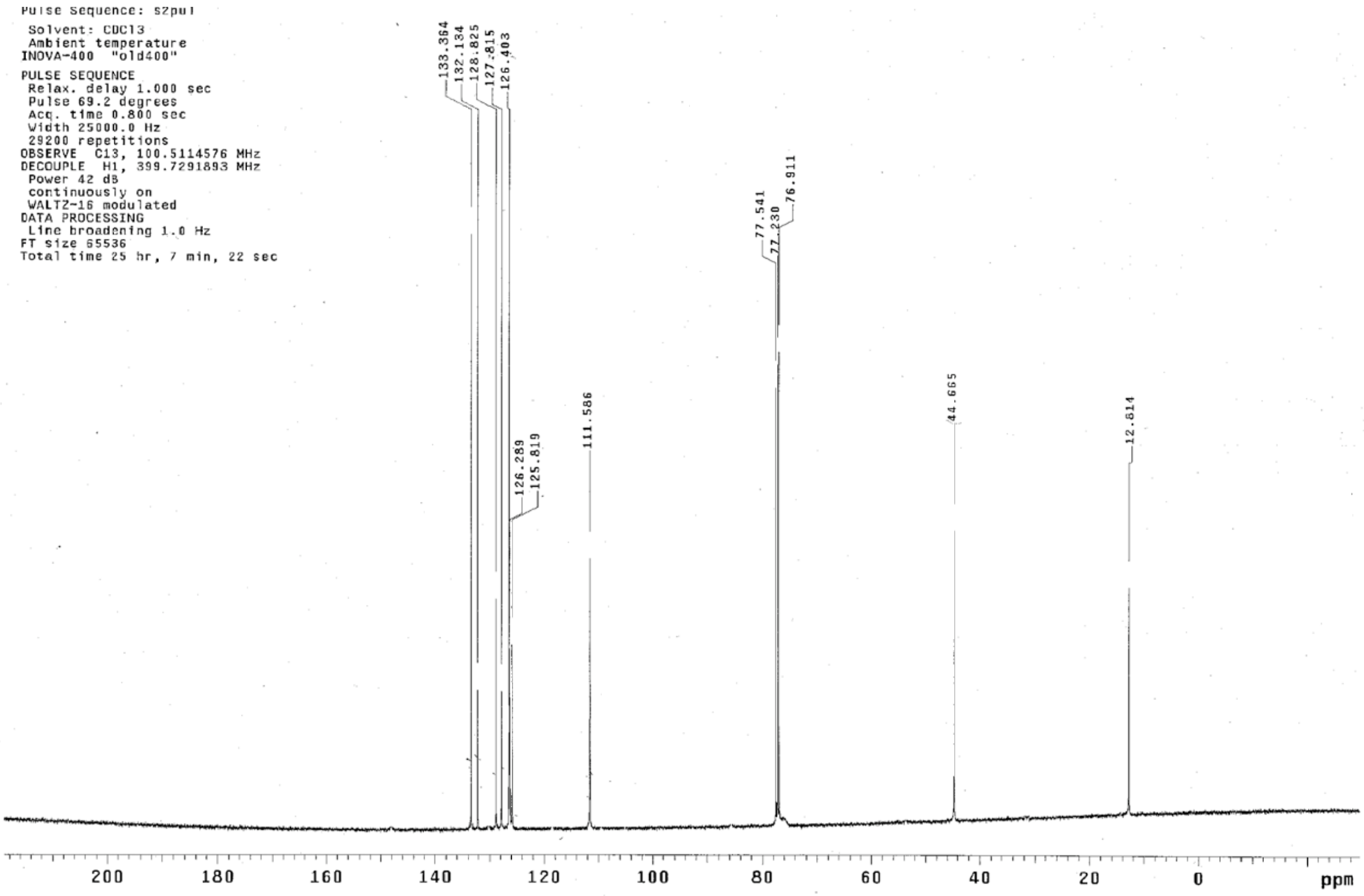
Compound 6
^{13}C NMR



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Pulse Sequence: s2pul
 Solvent: CDCl3
 Ambient temperature
INOVA-400  "old400"
PULSE SEQUENCE
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 Pulse 69.2 degrees
 Acq. time 0.800 sec
 Width 25000.0 Hz
 29200 repetitions
OBSERVE  C13, 100.5114576 MHz
DECOUPLE  H1, 399.7291893 MHz
 Power 42 dB
 continuously on
 WALTZ-16 modulated
DATA PROCESSING
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FT size 65536
Total time 25 hr, 7 min, 22 sec
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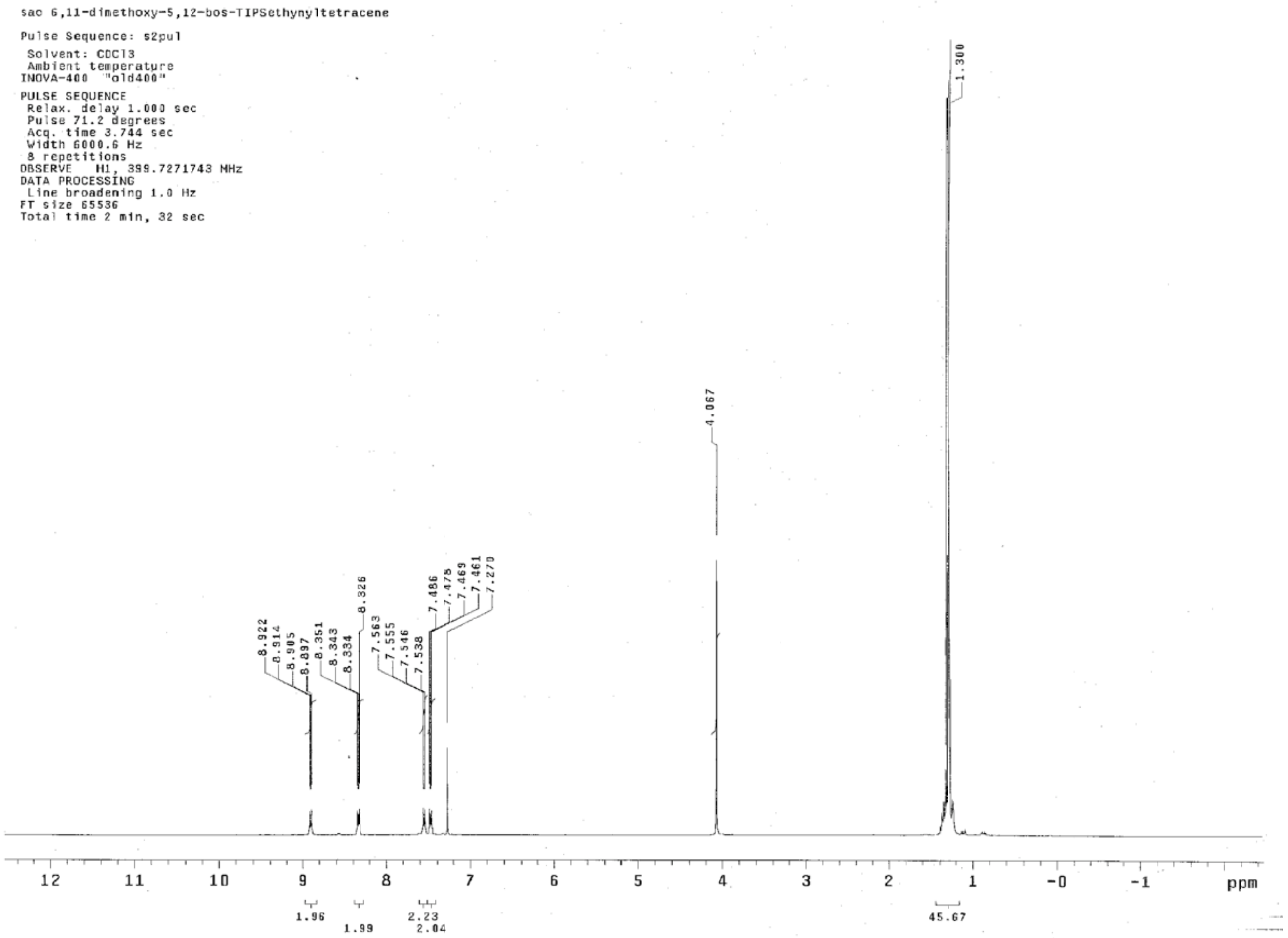
Compound 7
^{1}H NMR



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sao 6,11-dimethoxy-5,12-bos-TIPSethynyltetracene

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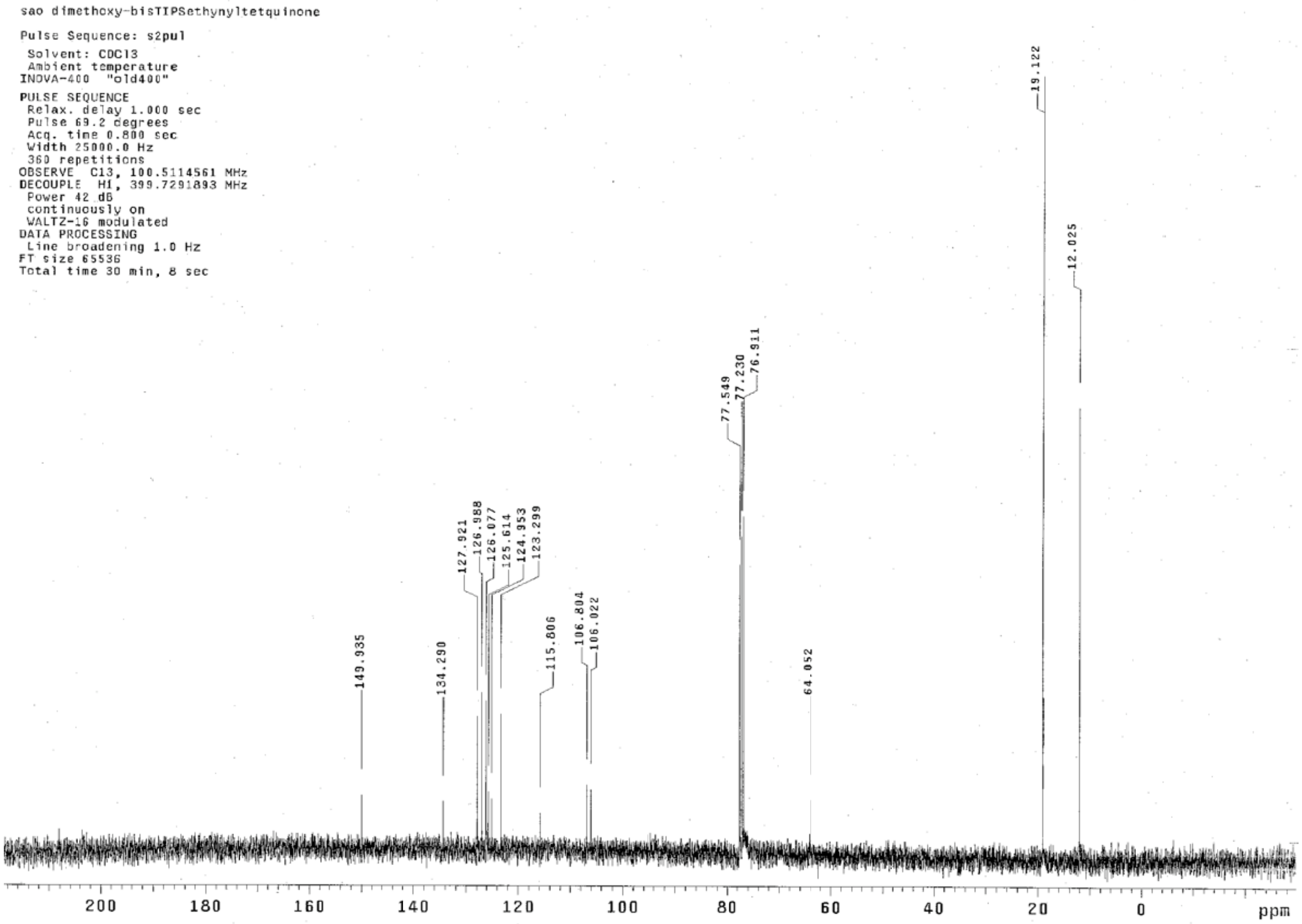
 Solvent: CDCl3
 Ambient temperature
INOVA-400  "old400"
PULSE SEQUENCE
 Relax. delay 1.000 sec
 Pulse 71.2 degrees
 Acq. time 3.744 sec
 Width 6000.6 Hz
 8 repetitions
OBSERVE   H1, 399.7271743 MHz
DATA PROCESSING
 Line broadening 1.0 Hz
FT size 65536
Total time 2 min, 32 sec
```

Compound 7
^{13}C NMR



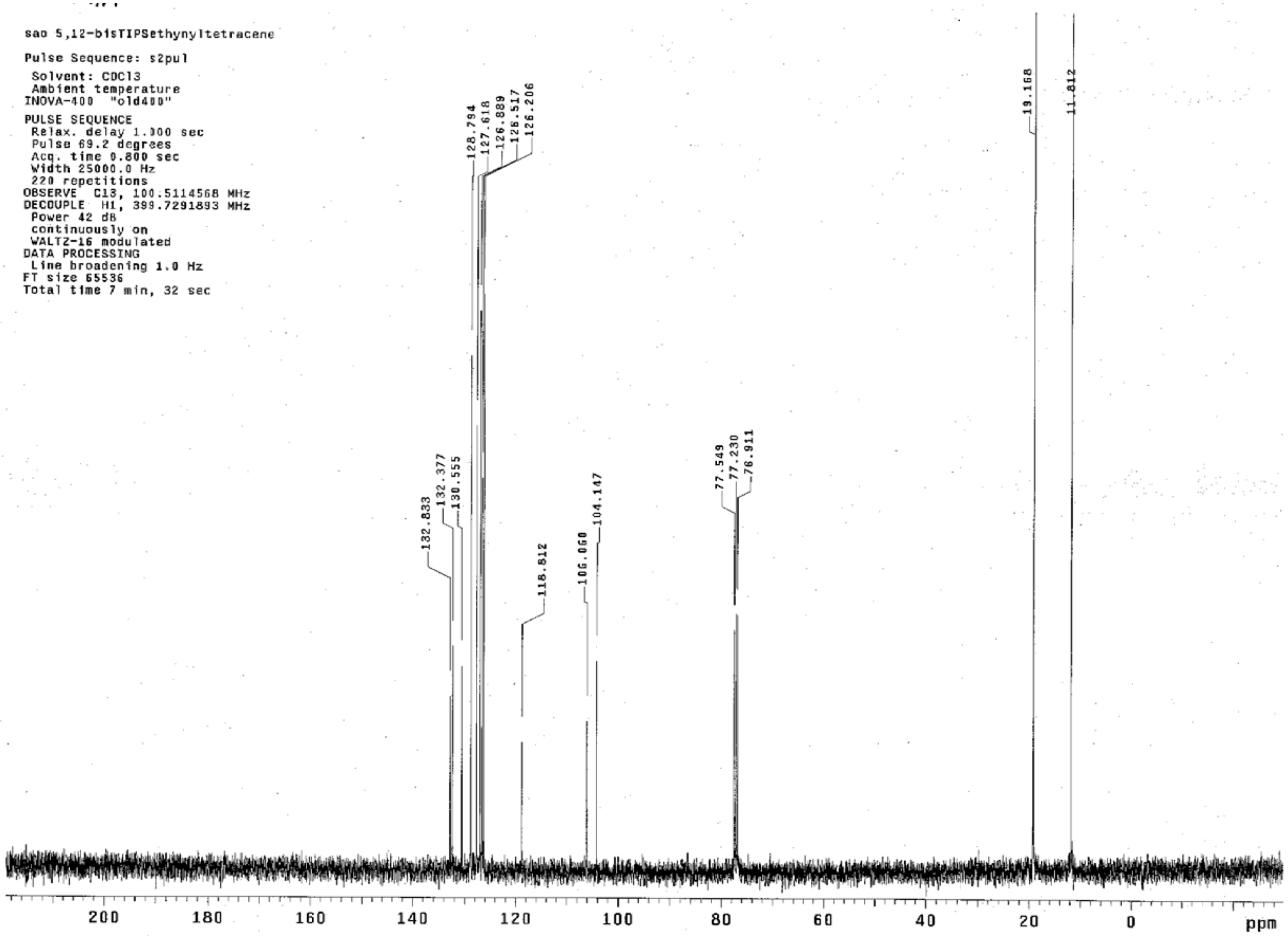
```
sao dimethoxy-bisTIPSethynyltetquinone

Pulse Sequence: s2pul

 Solvent: CDCl3
 Ambient temperature
INOVA-400  "old400"

PULSE SEQUENCE
 Relax. delay 1.000 sec
 Pulse 69.2 degrees
 Acq. time 0.800 sec
 Width 25000.0 Hz
 360 repetitions
OBSERVE  C13, 100.5114561 MHz
DECOUPLE  H1, 399.7291893 MHz
 Power 42 dB
 continuously on
 WALTZ-16 modulated
DATA PROCESSING
 Line broadening 1.0 Hz
FT size 65536
Total time 30 min, 8 sec
```

Compound 8
^{1}H NMR



```
sao 5,12-bisTIPSethynyltetracene

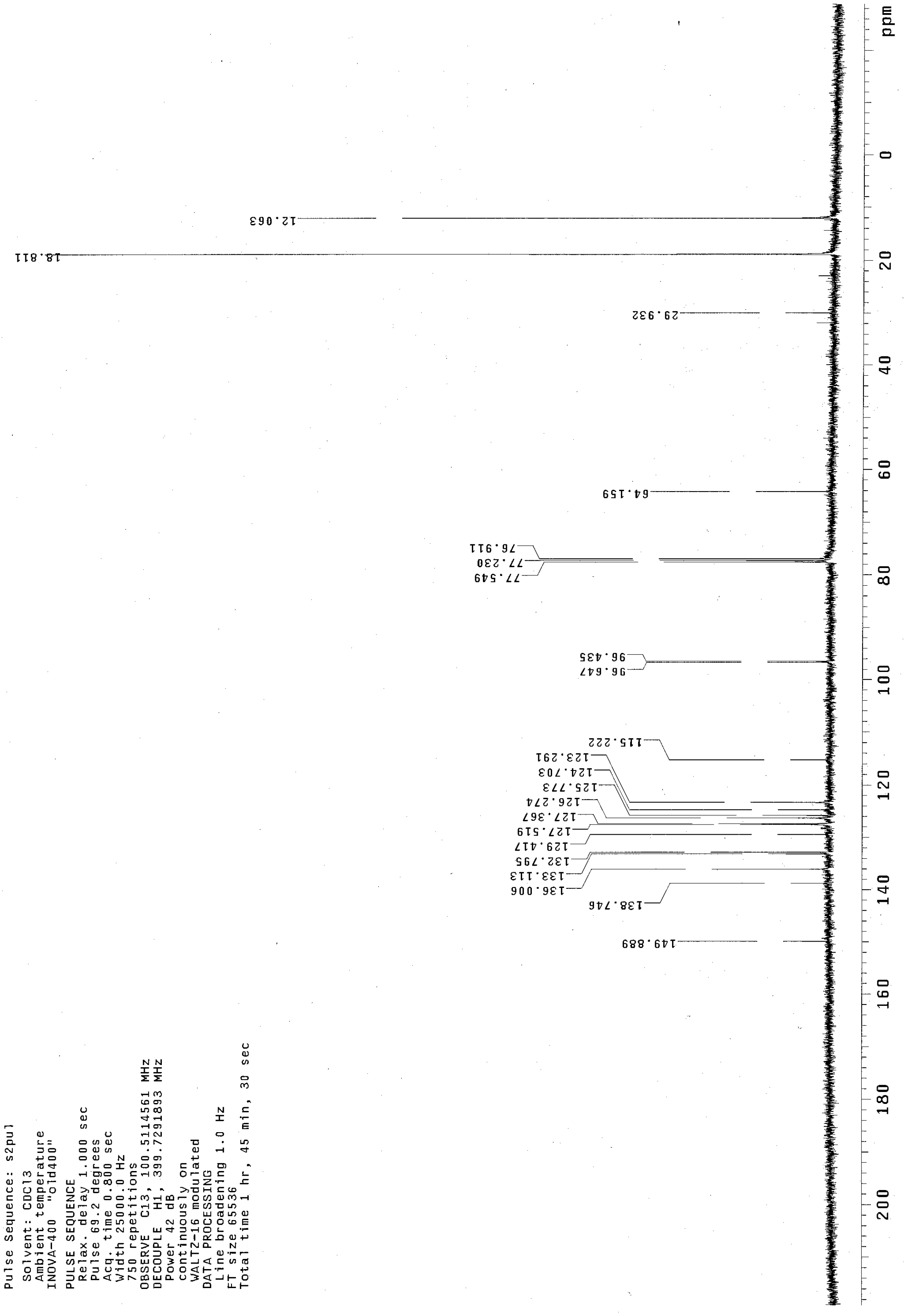
Pulse Sequence: s2pul

 Solvent: CDCl3
 Ambient temperature
INOVA-400  "old400"

PULSE SEQUENCE
 Relax. delay 1.000 sec
 Pulse 69.2 degrees
 Acq. time 0.800 sec
 Width 25000.0 Hz
 220 repetitions
OBSERVE  C13, 100.5114568 MHz
DECOUPLE  H1, 399.7291893 MHz
 Power 42 dB
 continuously on
 WALTZ-16 modulated
DATA PROCESSING
 Line broadening 1.0 Hz
FT size 65536
Total time 7 min, 32 sec
```

Compound 8

^{13}C NMR



```
sao-59m

Pulse Sequence: s2pul
  Solvent: CDCl3
   Ambient temperature
INOVA-400   "old400"

PULSE SEQUENCE
  Relax. delay 1.000 sec
  Pulse 69.2 degrees
  Acq. time 0.800 sec
  Width 25000.0 Hz
   750 repetitions
OBSERVE  C13, 100.5114561 MHz
DECOUPLE  H1, 399.7291893 MHz
  Power 42 dB
  continuously on
  WALTZ-16 modulated
DATA PROCESSING
  Line broadening 1.0 Hz
FT size 65536
Total time 1 hr, 45 min, 30 sec
```