# Supporting Information

## A concise method to prepare novel fused heteroaromatic diones through double Friedel-Crafts acylation

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## Contents:

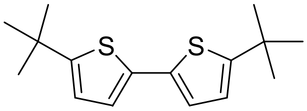
# General information:

All reactions were performed under Argon protection. The solvents were purified and dried according to standard procedures. The aluminum chloride was purchased from Alfa Aesar and the other commercial available products were purchased from Alfa Aesar, Sigma-Aldrich, Acros Ltd and used as received.

NMR spectra were recorded with a Bruker AV 400 Spectrometer at 400 MHz ($^{1}$H NMR) and 101 MHz ($^{13}$C NMR) or a Bruker AV 300 Spectrometer at 300 MHz ($^{1}$H NMR) and 75 MHz ($^{13}$C NMR). High Resolution Mass Spectra (HRMS) were recorded on Waters ACQUITY UPLC® System.

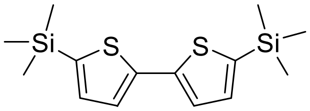
# 1. Preparation of various substrates and the analytical data.

**5,5'-di-*t*-butyl-2,2'-bithiophene(1b)[1][Masui, 2004 #2336]**:



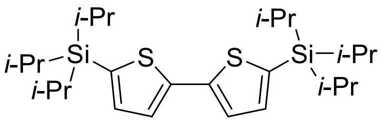
The title compound was prepared based on the literature method. $PdCl_2(PhCN)_2$ (0.132 g, 0.34 mmol), 2-*t*-butylthiophene[2] (0.80 g, 5.71 mmol) and anhydrous DMSO (30.0 mL) were placed in a two-neck 100 mL flask. To this was added silver(I) fluoride (1.53 g, 12.0 mmol), and the resulting mixture was stirred at 60 °C for 6 h under Argon atmosphere. The resulting mixture was cooled to room temperature and passed through a pad of Celite, which was successively washed well with $CH_2Cl_2$. The filtrate was washed with water (60 mL) and the aqueous layer was extracted with $CH_2Cl_2$ (100 mL x 3). The combined organic layer was dried over anhydrous sodium sulfate and then concentrated under reduced pressure to leave a crude product. Purification by column chromatography on silica gel using hexane gave 5,5'-di-*t*-butyl-2,2'-bithiophene (white solid, 450 mg, 56% yield).$^1$H NMR (400 MHz, $CDCl_3$): δ 6.90 (d, $J = 3.6$ Hz, 2H), 6.70 (d, $J = 3.6$ Hz, 2H), 1.39 (s, 18H); $^{13}$C NMR (100 MHz, $CDCl_3$): δ 156.2, 134.8, 122.3, 121.8, 34.6, 32.4; HRMS: calculated for $C_{16}H_{22}S_2 + H^+$, 279.1241; found: 279.1252 (M+).

**5,5'-Bis(trimethylsilyl)-2,2'-bithiophene (1d)[3]**:



$^1$H NMR (300 MHz, $CDCl_3$): δ 7.23 (d, $J = 3.3$ Hz, 2H), 7.13 (d, $J = 3.6$ Hz, 2H), 0.33 (s, 18H).

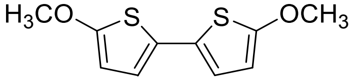
**5,5'-Bis(triisopropylsilyl)-2,2'-bithiophene (1e)[4]**:



The title compound was prepared based on the literature method. *n*-BuLi (2.5M in hexane, 5.0 mL, 12.5 mmol) was added dropwise to a solution of 2,2-bithiophene (1.0 g, 6.0 mmol) in dry THF (22 mL) at −78 °C in Argon atmosphere. The mixture was stirred at −78 °C for 30 min, followed by addition of triisopropylsilyl chloride (2.4 g, 2.75 mL, 12.6 mmol). After stirring for 3 h at room temperature, hexane was added and the organic phase was washed with water, dried over $Na_2SO_4$, filtered, and concentrated *in vacuo*. The residue was subjected to column chromatography (hexane) to give **1e** (white solid, 2.1 g, 73%). $^1$H NMR (300 MHz, $CDCl_3$): δ 7.31 (d, $J = 3.3$ Hz, 2H), 7.16 (d, $J = 3.6$ Hz, 2H), 1.41–1.28 (m, 6H), 1.15–1.13 (d, 36H); $^{13}$C

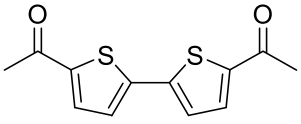
NMR (75 MHz, $CDCl_3$): δ 142.4, 136.4, 133.5, 124.7, 18.6, 11.8; HRMS: calculated for $C_{26}H_{46}S_2Si_2 + H^+$, 479.2658; found: 479.2690 (M+).

### 5,5'-dimethoxyl-2,2'-bithiophene(1f)[5]:



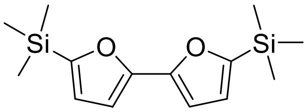
$^1$H NMR (300 MHz, $CDCl_3$): δ 6.61 (d, $J$ = 3.9 Hz, 2H), 6.07 (d, $J$ = 3.9 Hz, 2H), 3.88 (s, 6H)

### 5,5'-diacetyl-2,2'-bithiophene(1g)[6]:



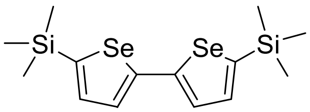
$^1$H NMR (300 MHz, $CDCl_3$): δ 7.61 (d, $J$ = 3.0 Hz, 2H), 7.30 (d, $J$ = 3.0 Hz, 2H), 2.57 (s, 6H)

### 5,5'-Bis(trimethylsilyl)-2,2'-bifuran(3a)[7]:



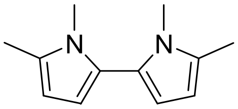
The title compound was prepared based on the literature method. $n$-BuLi (2.5M in hexane, 4.0 mL, 10.0 mmol) was added dropwise to a solution of 2,2'-bifuran (600 mg, 4.48 mmol) in dry THF (40 mL) at −78 °C in Argon atmosphere. The mixture was stirred at −78 °C for 30 min and at room temperature for another 1 h. The solution was cooled again to −78 °C and the chlorotrimethylsilane (1.07 g, 1.28 mL, 9.8 mmol) was added dropwise. After stirring for 3 h at room temperature, the mixture was quenched with water, extracted with hexane, dried over $Na_2SO_4$, filtered, and concentrated *in vacuo*. The residue was subjected to column chromatography (hexane) to give **1j** (white solid, 312 mg, 25%). $^1$H NMR (400 MHz, $CDCl_3$): δ 6.65 (s, 2H), 6.57 (s, 2H), 0.29 (s, 18H); $^{13}$C NMR (100 MHz, $CDCl_3$): δ 159.8, 150.8, 121.1, 105.4, –1.57; HRMS: calculated for $C_{16}H_{22}O_2Si_2 + H^+$, 279.1237; found: 279.1246 (M+).

### 5,5'-Bis(trimethylsilyl)-2,2'-biselenophene(3b)[8]:



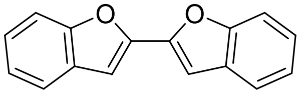
The title compound was prepared based on the literature method. $n$-BuLi (2.5M in hexane, 1.8 mL, 4.5 mmol) was added dropwise to a solution of 2,2'-biselenophene (520 mg, 2.0 mmol) in dry THF (20 mL) at −78 °C in Argon atmosphere. The mixture was stirred at −78 °C for 30 min and at room temperature for another 1 h. The solution was cooled again to −78 °C and the chlorotrimethylsilane (480 mg, 0.56 mL, 4.4 mmol) was added dropwise. After stirring for 6 h at room temperature, hexane was added and the organic phase was washed with water, dried over $Na_2SO_4$, filtered, and concentrated *in vacuo*. The residue was subjected to column chromatography (hexane) to give **1i** (white solid, 210 mg, 26%). $^1$H NMR (400 MHz, $CDCl_3$): δ 7.38 (d, *J* = 3.2 Hz, 2H), 7.31 (d, *J* = 2.8 Hz, 2H), 0.32 (s, 18H); $^{13}$C NMR (100 MHz, $CDCl_3$): δ 149.4, 148.3, 136.9, 128.5, 0.22; HRMS: calculated for $C_{14}H_{22}Se_2Si_2$ + $H^+$, 406.9669; found: 406.9667 (M+).

**1,1-dimethyl-5,5'-dimethyl-2,2'-bipyrrole(3c)[9]:**



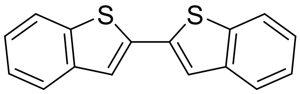
The title compound was prepared based on the literature method. N,N'-dimethyl-2,2'-bipyrrole[10] (1.6 g, 10 mmol) and THF (20 mL) were added to a nitrogen purged three-neck round-bottom flask and cooled to –78 °C. *n*BuLi (2.5M in hexane, 10 mL, 25 mmol) was added dropwise and the solution was stirred overnight, allowing to warm slowly to room temperature. The solution was again cooled to –78 °C and methyl iodide (1.86 mL, 30 mmol) was added in slowly. The reaction was stirred at –78 °C for four hours and was then allowed to warm slowly for 24 hours. The reaction was quenched by adding $H_2O$ (20 mL) and was then extracted with $Et_2O$. The organics were dried with $MgSO_4$, filtered, and concentrated *in vacuo*. The residue was subjected to column chromatography using neutral aluminum oxide (hexane: ethyl acetate=30:1) to give **1k** (white solid, 242 mg, 13%).$^1$H NMR (400 MHz, $CDCl_3$): 6.06 (d, *J* = 3.2 Hz, 2H), 5.95 (d, *J* = 2.8 Hz, 2H), 3.35 (s, 6H), 2.28 (s, 6H); $^{13}$C NMR (100 MHz, $CDCl_3$): δ 129.5, 124.9, 109.4, 105.7, 31.0, 12.7; HRMS: calculated for $C_{12}H_{16}N_2$ + $H^+$, 189.1392; found: 189.1386 (M+).

**2,2'-Bibenzofuran(5a)[11]:**



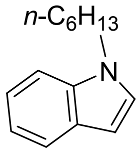
$^1$H NMR (400 MHz, $CDCl_3$): δ 7.63 (d, *J* = 8.0 Hz, 2H), 7.55 (d, *J* = 8.0 Hz, 2H), 7.35–7.26 (m, 4H), 7.17 (s, 2H)

**2,2'-Bibenzothiophene(5b)[12]:**



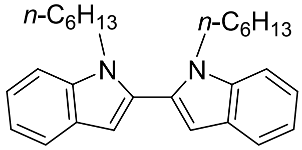
$^1$H NMR (400 MHz, $CDCl_3$): δ 7.83–7.76 (m, 4H), 7.52 (s, 2H), 7.37–7.31 (m, 4H)

**1-*n*-hexylindole[13]:**



$^1$H NMR (400 MHz, $CDCl_3$): δ 7.65 (d, *J* = 8.0 Hz, 1H), 7.36 (d, *J* = 8.4 Hz, 1H), 7.26–7.20 (m, 1H), 7.13–7.10 (m, 1H), 6.50 (d, *J* = 2.4 Hz, 1H), 4.13 (t, *J* = 6.8 Hz, 2H), 1.87–1.81 (m, 2H), 1.32 (s, 6H), 0.89 (t, *J* = 6.4 Hz, 3H)

**1,1'-di-*n*-hexyl-2,2'-Bibenzoindole(5c)**[14]:



The title compound was prepared based on the literature method. *n*-BuLi (1.6M in hexane, 6.3 mL, 10.0 mmol) was added dropwise to a solution of 1-*n*-hexylindole (1.7 g, 8.5 mmol) in dry THF (30 mL) at 0 °C in Argon atmosphere. The mixture was heated at reflux for 4 hours and then cooled down to room temperature. Anhydrous copper (II) chloride (0.94 g, 7 mmol) was then added in one portion and the mixture again heated under reflux for 2 hours. After being allowed to cool to room temperature, the mixture was left to stand for 1 hour before poured into ice/water. The dirty brown-green precipitate was filtered off and washed with methylene chloride, the organic layer was separated, and the aqueous phase was extracted twice with methylene chloride. The combined organic phase was dried over $Na_2SO_4$, filtered, and concentrated *in vacuo*. The residue was subjected to column chromatography (hexane: $CH_2Cl_2$ = 20:1) to give **1n** (sticky liquid, 565 mg, 33%). $^1$H NMR (400 MHz, $CDCl_3$): δ 7.72 (d, *J* = 8.0 Hz, 2H), 7.45 (d, *J* = 8.0 Hz, 2H), 7.31 (t, *J* = 7.6 Hz, 2H), 7.20 (t, *J* = 7.6 Hz, 2H), 6.65 (s, 2H), 4.10 (t, *J* = 7.6 Hz, 4H), 1.73–1.68 (m, 4H), 1.21 (s, 12H), 0.82 (t, *J* = 6.4 Hz, 6H); $^{13}$C NMR (100 MHz, $CDCl_3$): 136.8, 131.1, 127.8, 122.0, 120.9, 119.7, 110.1, 104.6, 44.1, 31.3, 30.0, 26.5, 22.5, 13.9; HRMS: calculated for $C_{28}H_{36}N_2 + H^+$, 401.2957; found: 401.2979 (M+).

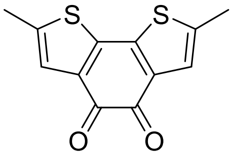
# 2. Typical procedure of the Friedal-Crafts Acylation and the analytical data

Typical procedures of the Friedal-Crafts Acylation with substrate **5,5'-dimethyl-2,2'-bithiophene(1a):**

To a solution of aluminium chloride (600 mg, 4.5 mmol) in 1,2-DCE (15 mL) cooled down to –20 ºC was added dropwise, in succession, a solution of oxalyl chloride (229 mg, 1.8 mmol) in 1,2-DCE (0.5 mL), a solution of dimethyl-2,2'-bithiophene **1a** (292 mg, 1.5 mmol) and pyridine (284 mg, 3.6 mmol) in 1,2-DCE (1.0 mL)(0.5 hour). After keeping the mixture for 20 minutes between –20 ºC and –15 ºC, the temperature was raised to 0 ºC and the mixture was poured over ice and extracted with methylene chloride. The extract was washed to neutral reaction with water and dried over magnesium sulfate. After removing the solvent under reduced pressure, the residue was purified by column chromatography (eluent: $CH_2Cl_2$) to give **2a** as a blue solid (120 mg, 32%).

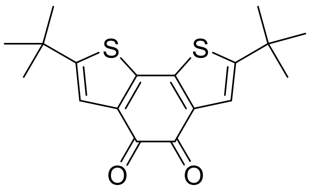
The following compounds were obtained in the similar method described above. For the column chromatography condition, the ratio of $CH_2Cl_2$:Hexane ranges from 1:1 to pure $CH_2Cl_2$. For some substrates, due to their low solubility, they need to be sonicated for 10 min to 30 min to make them easy to inject into the flask.

**2,7-dimethylbenzo[2,1-b:3,4-b']dithiophene-4,5-diones(2a)**:



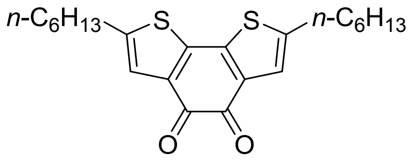
Yield: 32%. Blue solid; $^1$H NMR (300 MHz, $CDCl_3$): δ 7.08 (s, 2H), 2.45 (s, 6H); $^{13}$C NMR (100 MHz, $CDCl_3$): δ 174.4, 142.7, 140.4, 134.8, 125.2, 15.2; HRMS: calculated for $C_{12}H_8O_2S_2 + H^+$, 249.0044; found: 249.0027 (M+).

**2,7-di-*t*-butylbenzo[2,1-b:3,4-b']dithiophene-4,5-diones(2b)**:



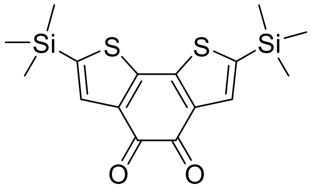
Yield: 48%. Blue solid; $^1$H NMR (300 MHz, $CDCl_3$): δ 7.16 (s, 2H), 1.38 (s, 18H); $^{13}$C NMR (75 MHz, $CDCl_3$): δ 174.8, 158.3, 142.3, 134.4, 121.4, 34.9, 32.0; HRMS: calculated for $C_{18}H_{20}O_2S_2 + H^+$, 333.0983; found: 333.0981 (M+).

**2,7-di-*n*-hexylbenzo[2,1-b:3,4-b']dithiophene-4,5-diones(2c)**:



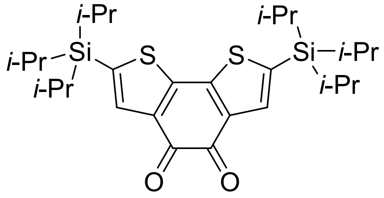
Yield: 37%. Blue solid; $^1$H NMR (300 MHz, CDCl$_3$): δ 7.11 (s, 2H), 2.75 (t, *J* = 7.5 Hz, 4H), 1.74–1.32 (m, 4H), 1.39–1.25 (s, 12H), 0.90 (t, *J* = 6.6 Hz, 6H); $^{13}$C NMR (100 MHz, CDCl$_3$): δ 174.7, 146.5, 142.6, 134.6, 124.0, 31.4, 30.9, 29.8, 28.5, 22.5, 14.0; HRMS: calculated for $C_{22}H_{28}O_2S_2 + H^+$, 389.1609; found: 389.1613 (M+).

2**,7-Bis(trimethylsilyl)benzo[2,1-b:3,4-b']dithiophene-4,5-diones(2d)**[15]:



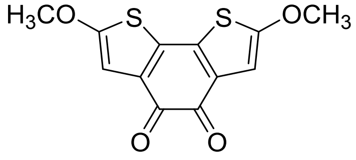
Yield: 28%. $^1$H NMR (400 MHz, CDCl$_3$): δ 7.57 (s, 2H), 0.34 (s, 18H)

**2,7-Bis(triisopropylsilyl)benzo[2,1-b:3,4-b']dithiophene-4,5-diones(2e)**:



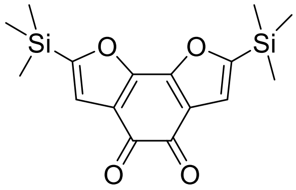
Yield: 45%. Blue solid; $^1$H NMR (300 MHz, CDCl$_3$): δ 7.62 (s, 2H), 1.40–1.30 (m, 6H), 1.13–1.11 (d, 36H); $^{13}$C NMR (100 MHz, CDCl$_3$): 175.3, 148.4, 136.8, 135.9, 135.7, 18.4, 11.6; HRMS: calculated for $C_{28}H_{44}O_2S_2Si_2 + H^+$, 533.2400; found: 533.2394.2690 (M+).

**2,7-dimethoxylbenzo[2,1-b:3,4-b']dithiophene-4,5-diones(2f)**:



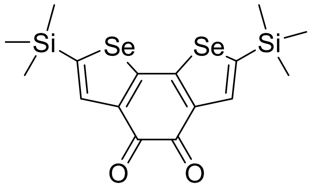
Yield: 25%. Blue solid; $^1$H NMR (300 MHz, CDCl$_3$): δ 6.48 (s, 2H), 3.92 (s, 6H). $^{13}$C NMR (100 MHz, CDCl$_3$): δ 174.0, 165.2, 133.0, 132.6, 102.1, 60.5; HRMS: calculated for $C_{12}H_9O_4S_2 + H^+$, 280.9942; found: 280.9941 (M+).

### 2,7-Bis(trimethylsilyl)benzo[2,1-b:3,4-b’]difuran-4,5-diones(4a):



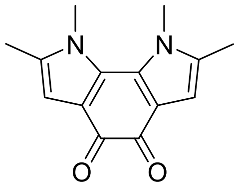
Yield: 16%. Red solid. $^{1}$H NMR (400 MHz, CDCl$_3$): δ 6.96 (s, 2H), 0.35 (s, 18H); $^{13}$C NMR (100 MHz, CDCl$_3$): δ 176.0, 165.7, 155.5, 120.1, 118.5, –1.94; HRMS: calculated for $C_{16}H_{22}S_2$ + $H^+$, 279.1237; found: 279.1246 (M+). HRMS: calculated for $C_{16}H_{20}O_4Si_2$ + $H^+$, 333.0556; found: 333.0569 (M+).

### 2,7-Bis(trimethylsilyl)benzo[2,1-b:3,4-b’]diselenophene-4,5-diones(4b)[15]:



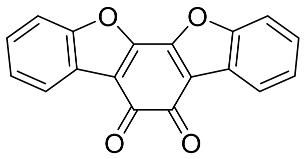
Yield: 37%. $^{1}$H NMR (400 MHz, CDCl$_3$): δ 7.91 (s, 2H), 0.34 (s, 18H)

### 1,1-dimethyl-2,7-dimethylbenzo[2,1-b:3,4-b’]dipyrrole-4,5-diones(4c):



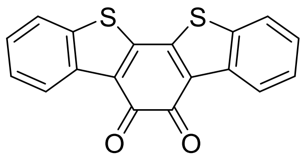
Yield: 32%. Deep-Blue solid. $^{1}$H NMR (400 MHz, CDCl$_3$): δ 6.20 (s, 2H), 3.61 (s, 6H), 2.15 (s, 6H); $^{13}$C NMR (100 MHz, CDCl$_3$): δ 176.9, 134.1, 134.0, 120.0, 109.3, 35.8, 12.6; HRMS: calculated for $C_{14}H_{14}N_2O_2$ + $H^+$, 243.1134; found: 243.1128 (M+).

### Dibenzo[d,d’]benzo[2,1-b:3,4-b’]difuran-6,7-diones(6a):



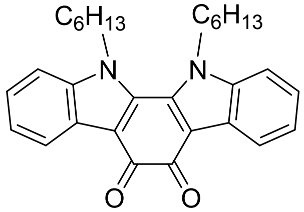
Yield: 35%. Dark-purple solid. $^{1}$H NMR (400 MHz, CDCl$_3$): δ 8.14–8.12 (m, 2H), 7.67–7.65 (m, 2H), 7.48–7.46 (m, 4H); $^{13}$C NMR (100 MHz, CDCl$_3$): δ 175.5, 156.4, 153.1, 127.6, 126.4, 123.5, 122.3, 116.6, 112.4; HRMS: calculated for $C_{18}H_8O_4$ + $H^+$, 289.0501; found: 289.0494 (M+).

**Dibenzo[d,d’]benzo[2,1-b:3,4-b’]dithiophene-6,7-diones(6b):**



Yield: 58 %. Dark-brown solid. $^1$H NMR (400 MHz, CDCl$_3$): δ 8.68 (d, *J* = 8.4 Hz, 2H), 7.85 (d, *J* = 8.0 Hz, 2H), 7.55 (t, *J* = 7.6 Hz, 2H), 7.46 (t, *J* = 7.6 Hz, 2H); $^{13}$C NMR (100 MHz, CDCl$_3$): δ 175.0, 146.6, 137.0, 128.7, 127.7, 127.0, 125.4, 122.6; HRMS: calculated for $C_{18}H_8O_2S_2 + H^+$, 321.0044; found: 321.0036 (M+).

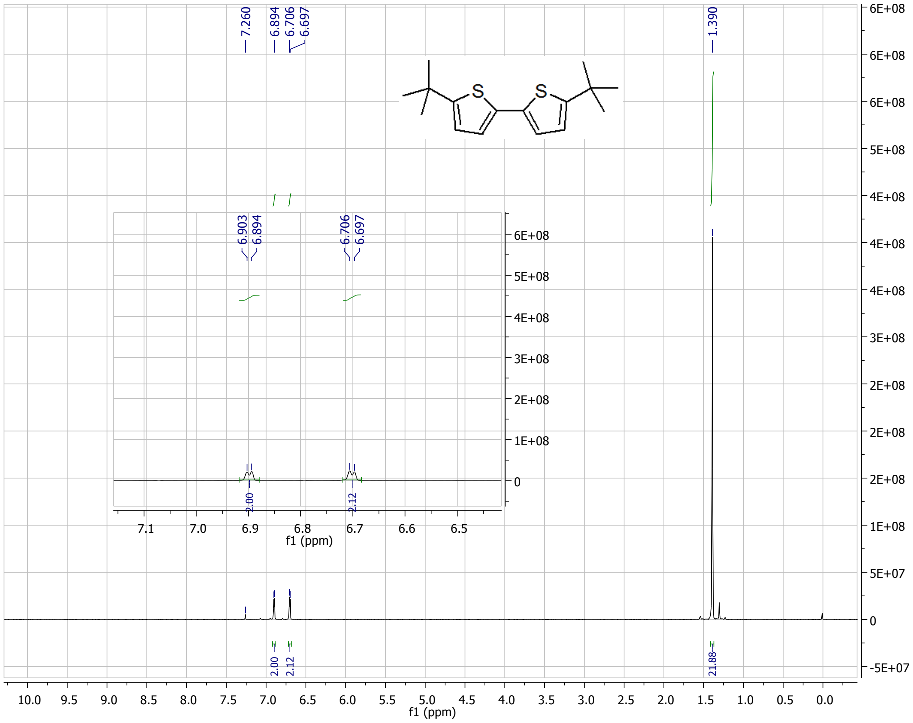
**1,1’-di-*n*-hexylbenzo[2,1-b:3,4-b’]diindole-6,7-diones(6c):**

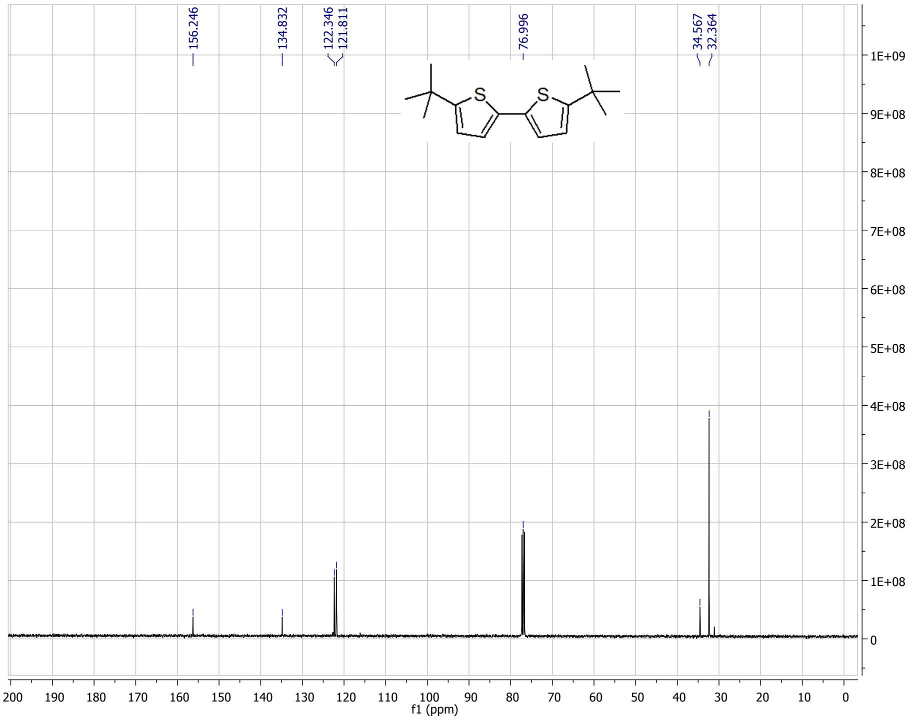


Yield: 85%. Dark-green solid.$^1$H NMR (400 MHz, CDCl$_3$): δ 8.28–8.26 (m, 2H), 7.42–7.40 (m, 2H), 7.31–7.28 (m, 4H), 4.40 (t, *J* = 7.6 Hz, 4H), 1.86–1.81 (m, 4H), 1.17 (s, 12H), 0.75 (t, *J* = 6.0 Hz, 6H); $^{13}$C NMR (100 MHz, CDCl$_3$): 177.1, 139.6, 139.5, 127.4, 124.8, 124.7, 122.2, 115.1, 112.1, 48.3, 31.0, 29.5, 26.2, 22.3, 13.7; HRMS: calculated for $C_{30}H_{34}N_2O_2 + H^+$, 455.2699; found: 455.2677 (M+).

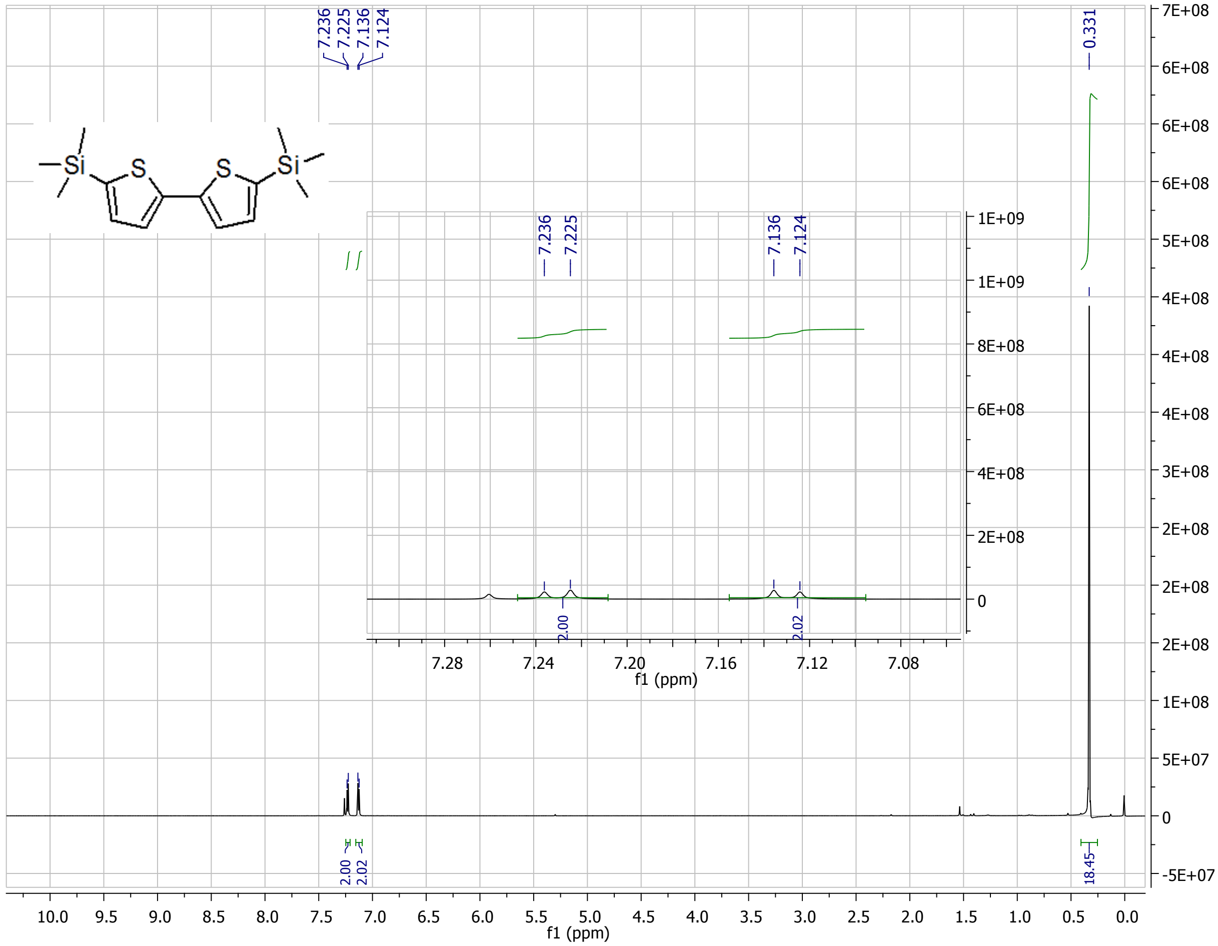
# 3. NMR spectra for the substrates

## 5,5’-di-*t*-butyl-2,2’-bithiophene(1b):

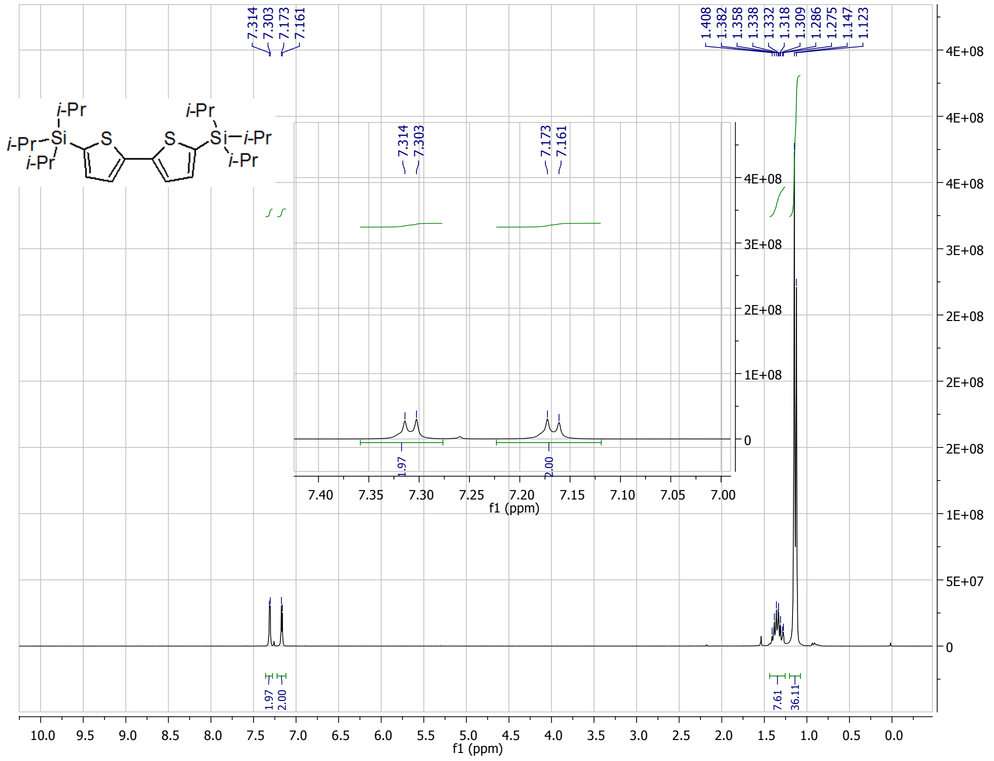


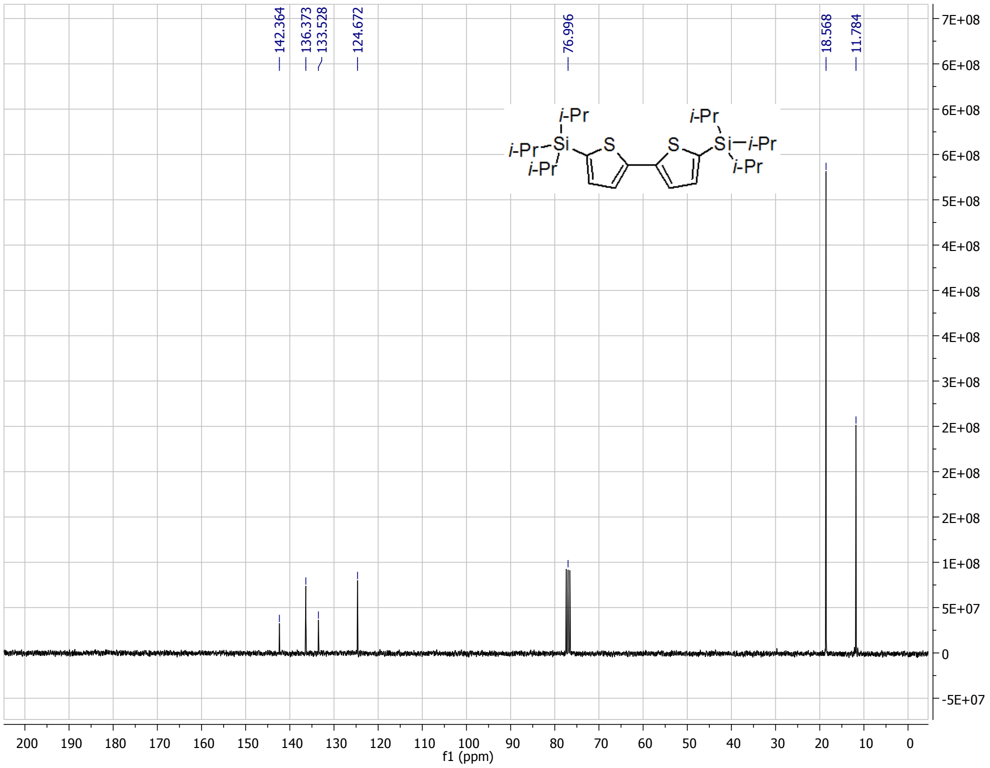


**5,5’-Bis(trimethylsilyl)-2,2’-bithiophene (1d)[3]:**

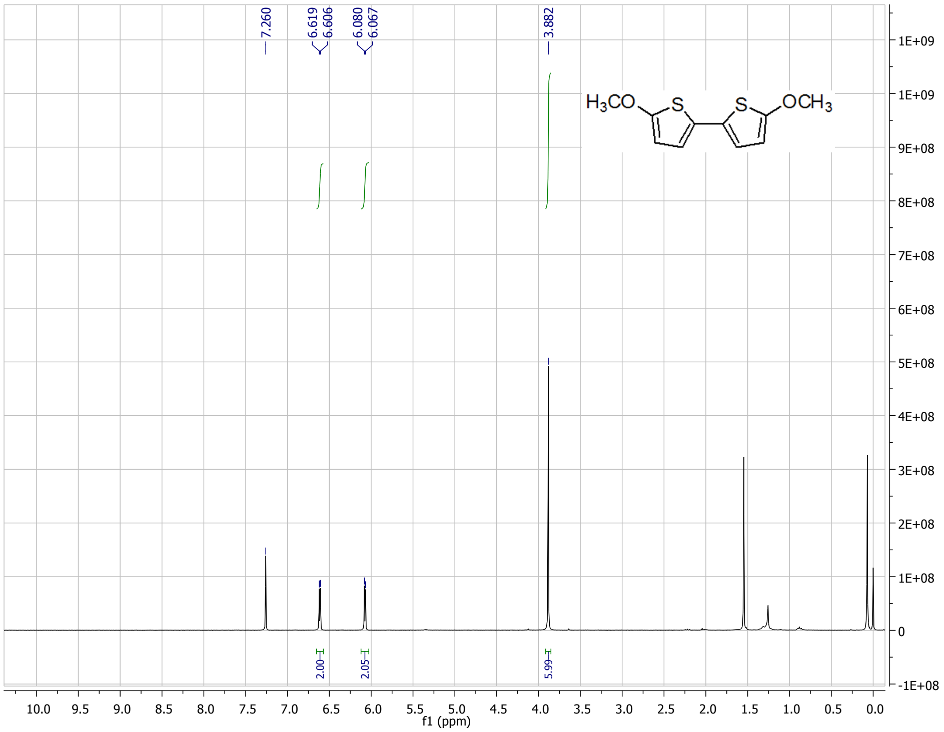


## 5,5’-Bis(triisopropylsilyl)-2,2’-bithiophene (1e):

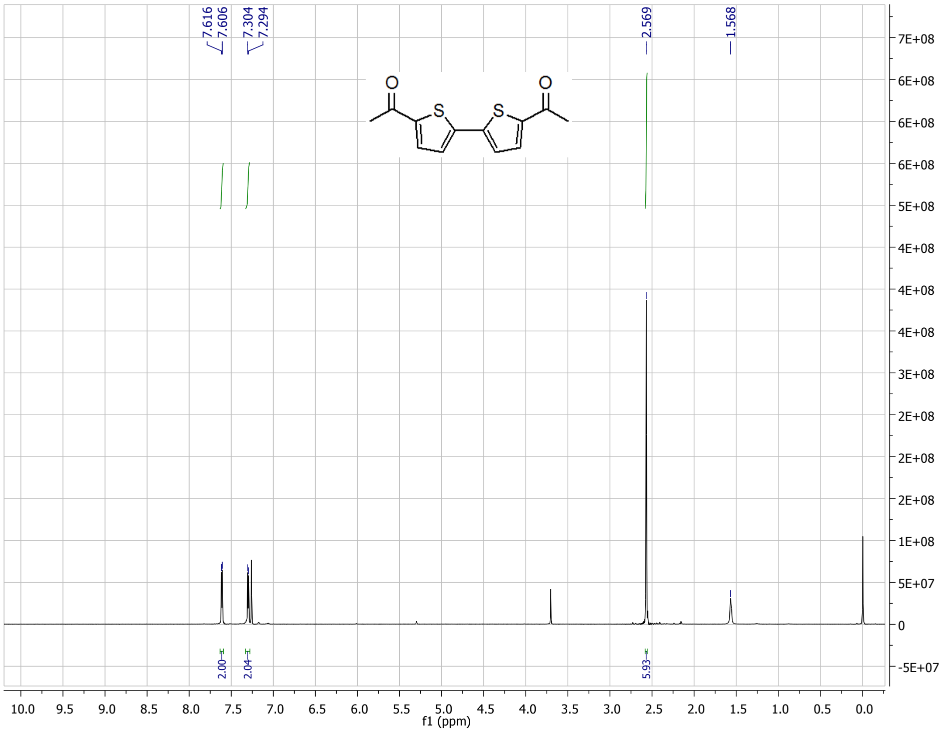




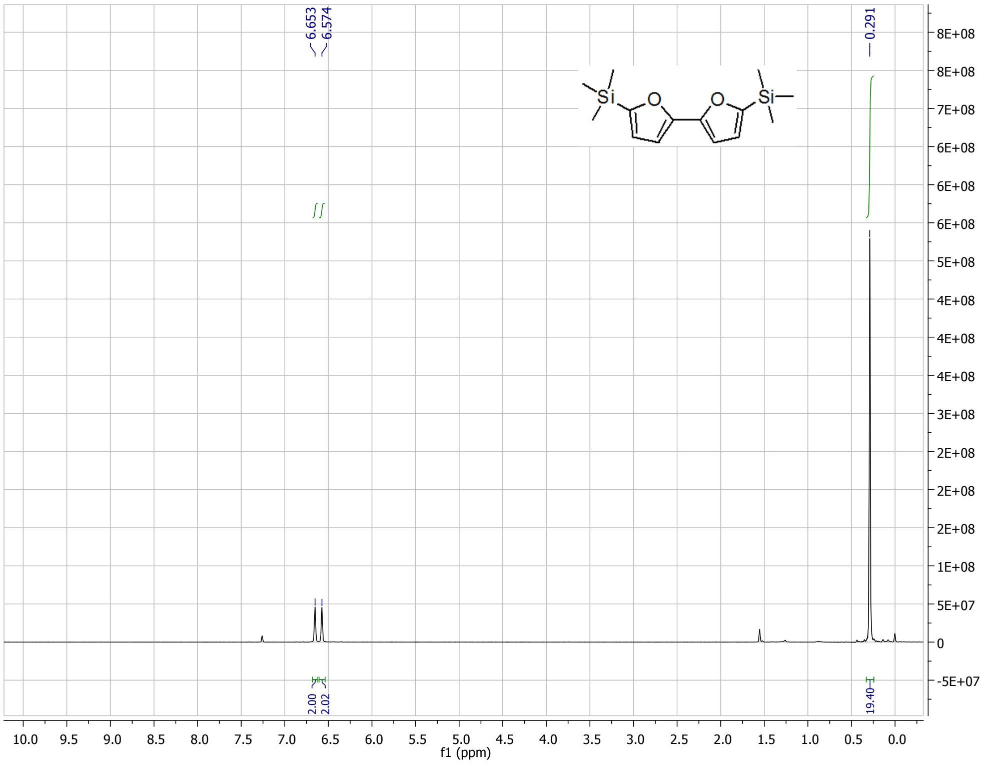
## 5,5’-dimethoxyl-2,2’-bithiophene(1f):

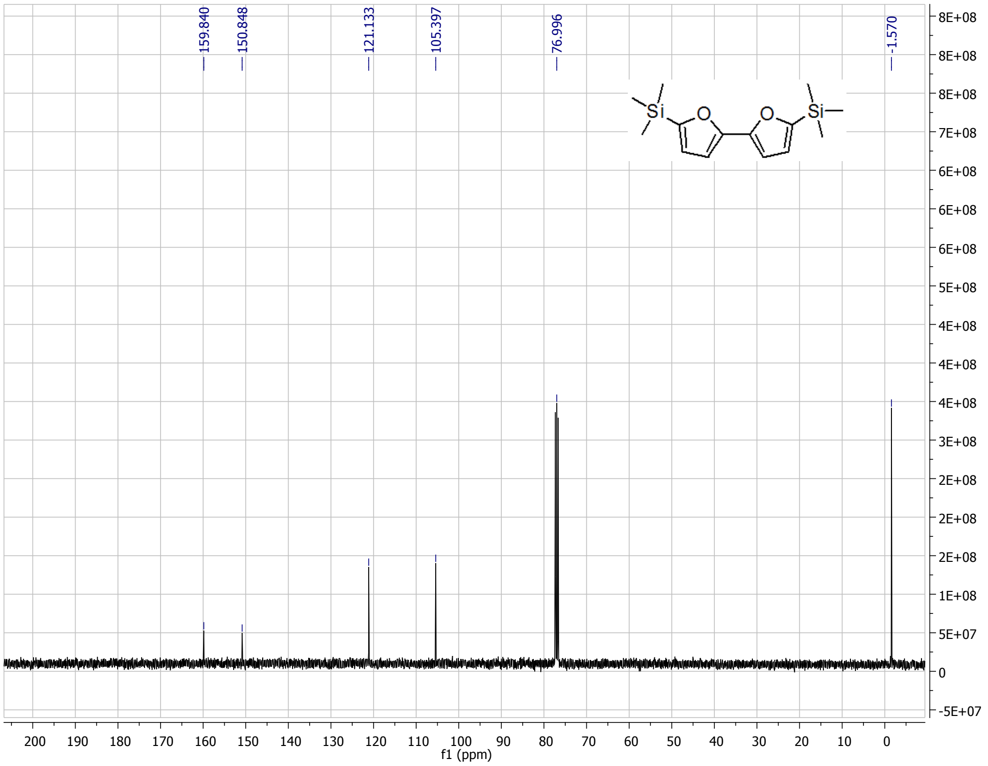


## 5,5’-diacetyl-2,2’-bithiophene(1g):

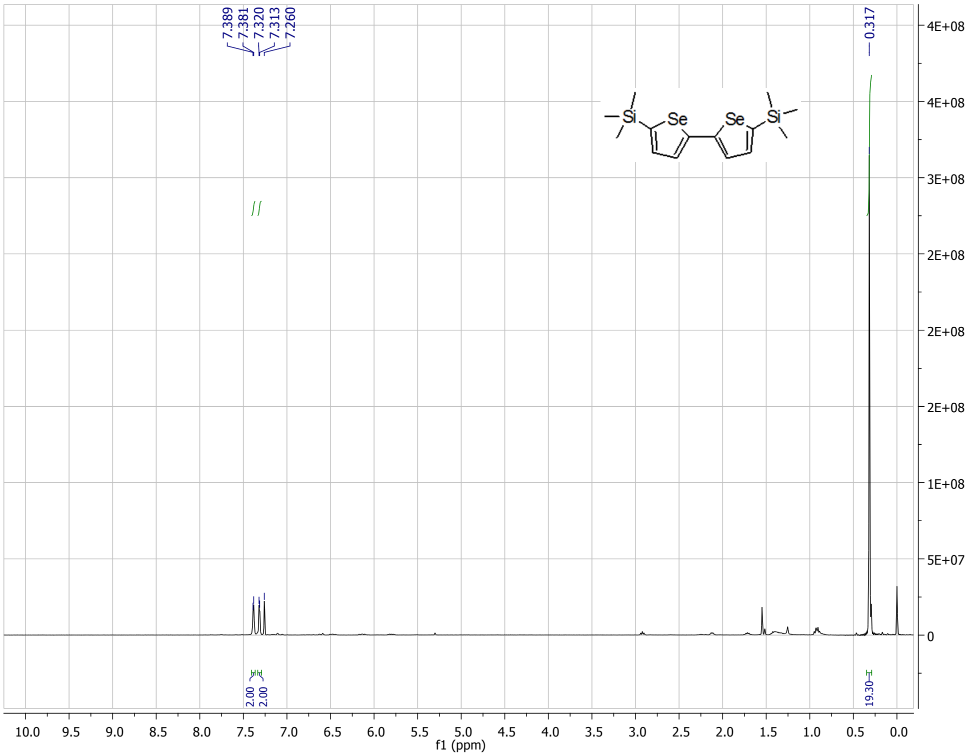


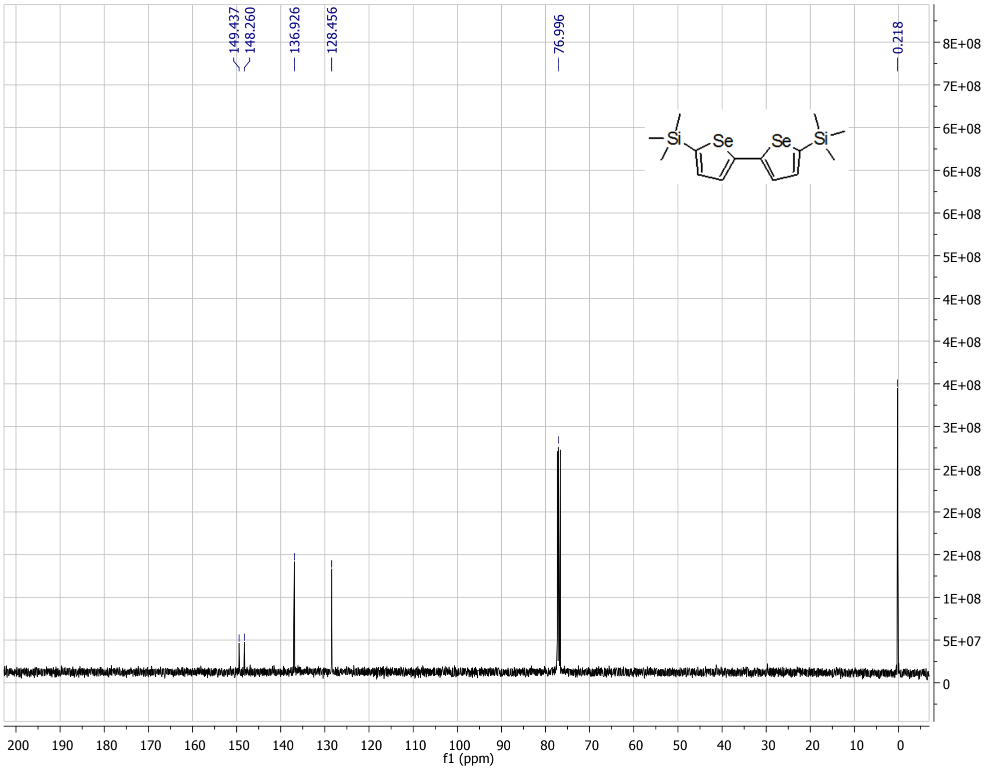
### 5,5’-Bis(trimethylsilyl)-2,2’-bifuran(3a):



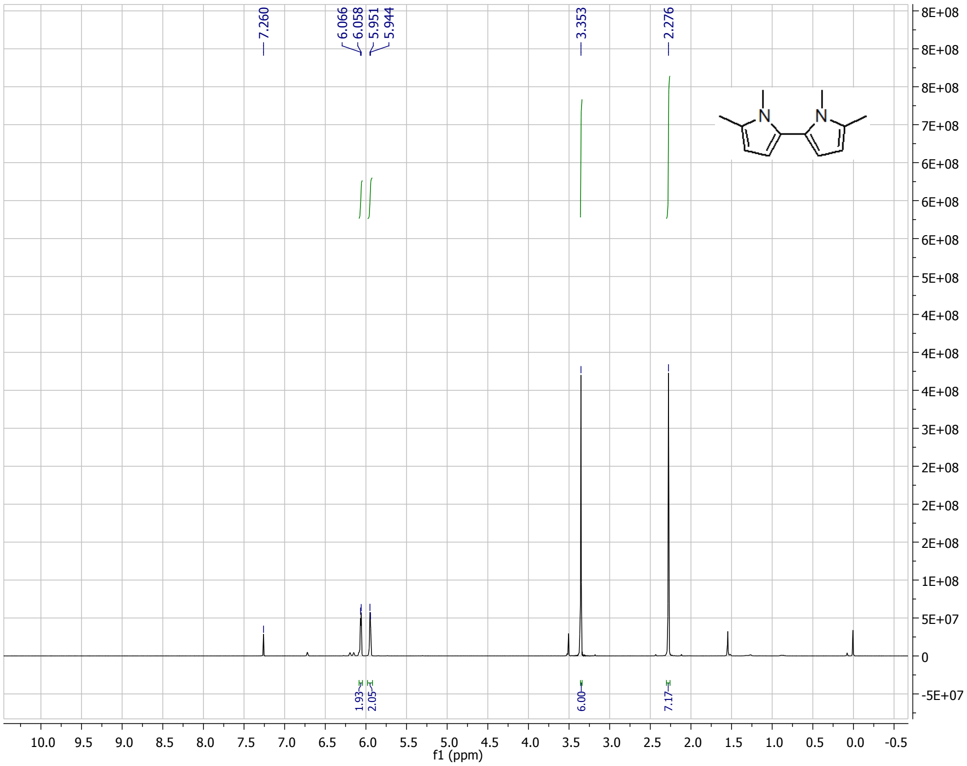


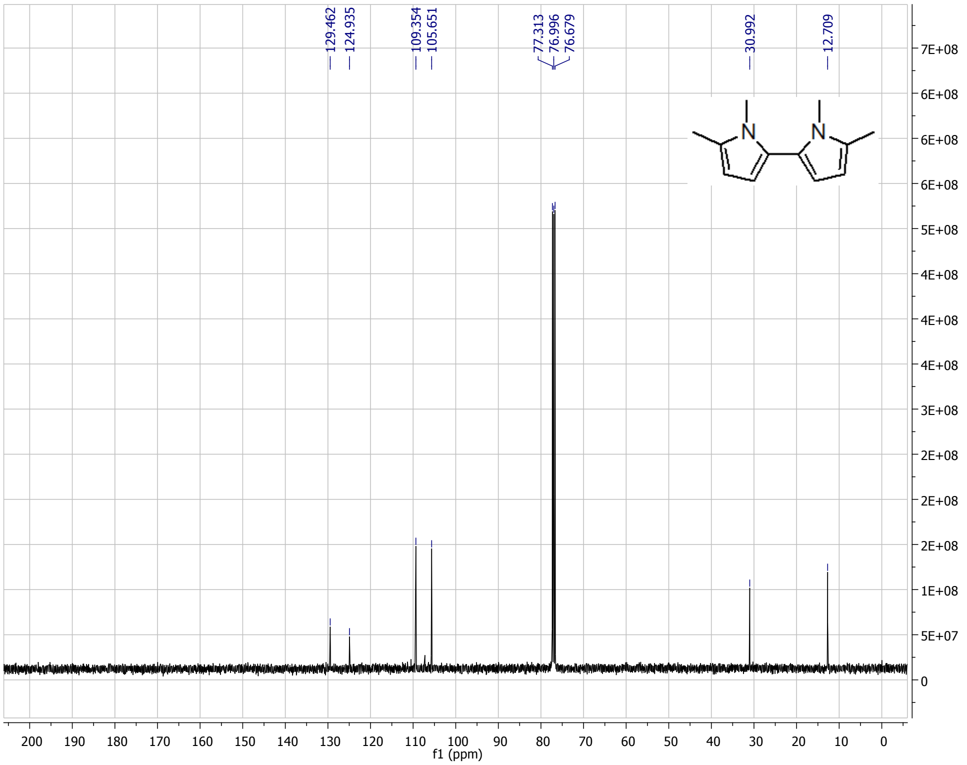
## 5,5’-Bis(trimethylsilyl)-2,2’-biselenophene(3b):



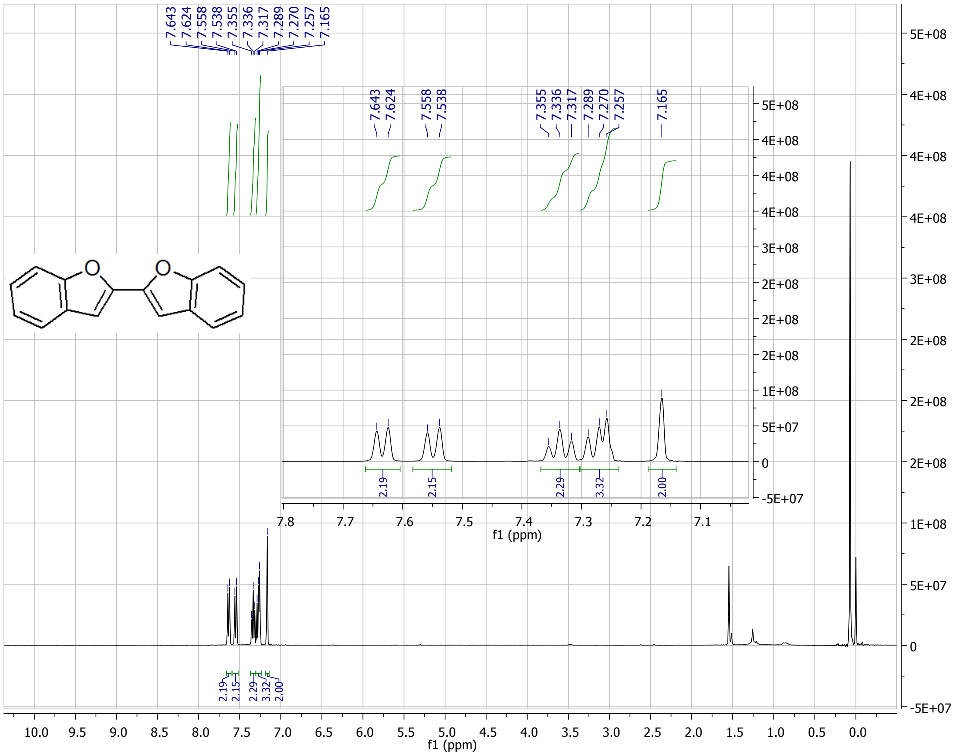


## 1,1-dimethyl-5,5’-dimethyl-2,2’-bipyrrole(3c):

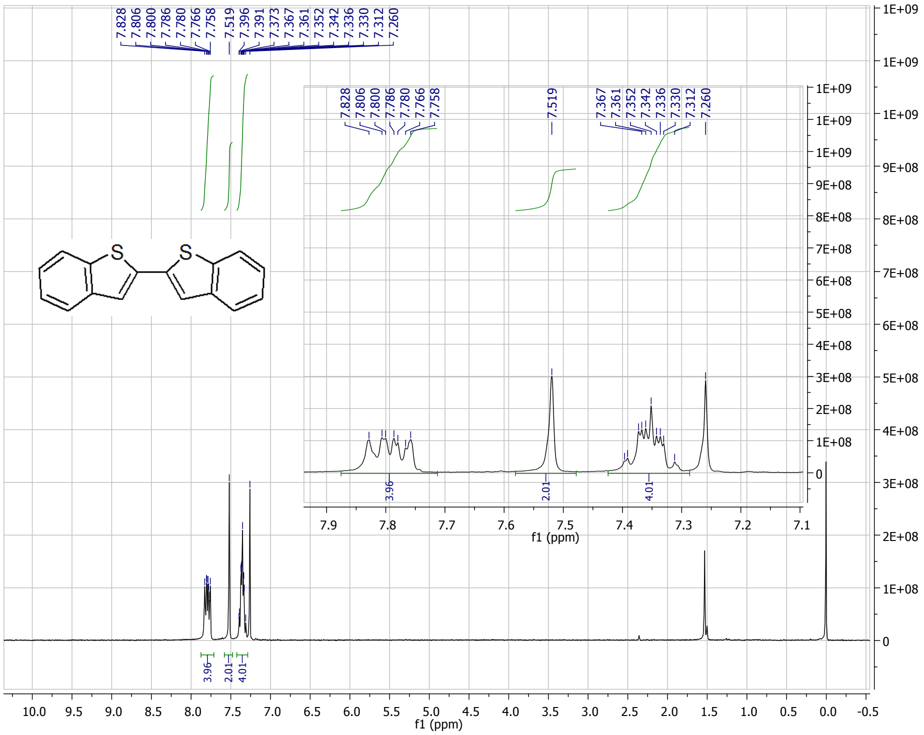




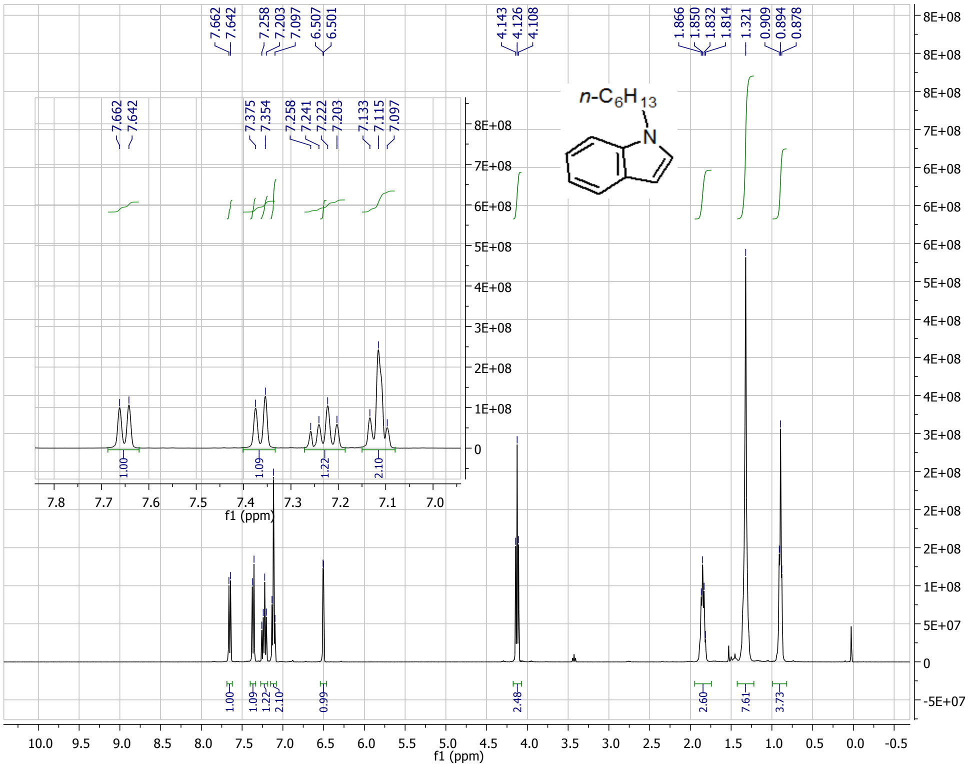
## 2,2’-Bibenzofuran(5a):



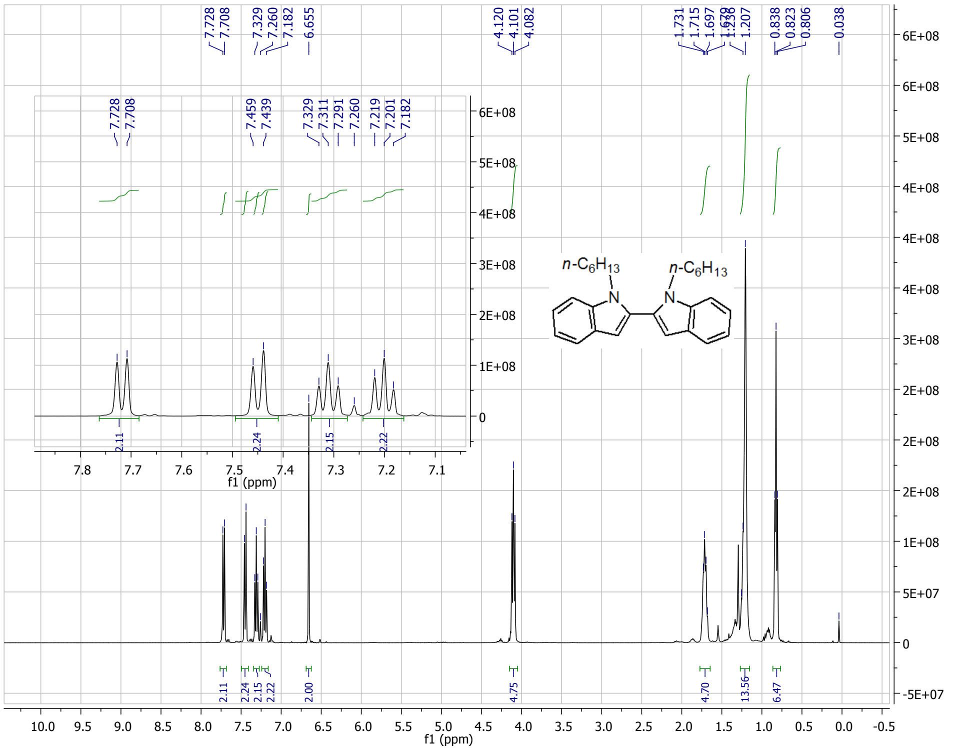
## 2,2’-Bibenzothiophene(5b):

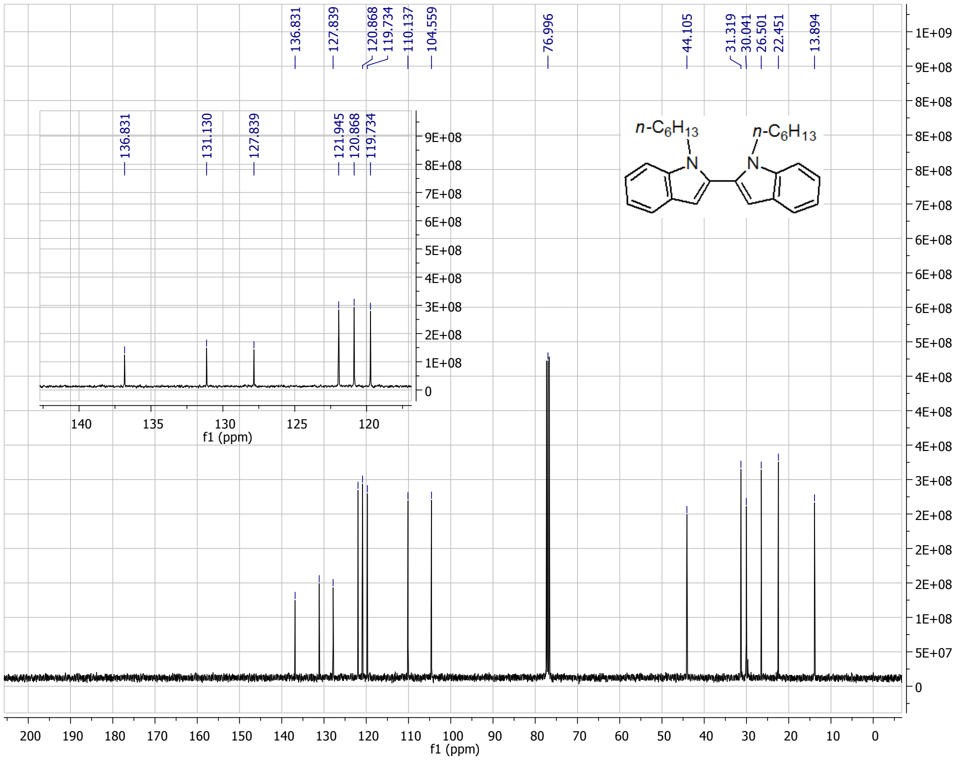


## 1-*n*-hexylindole:



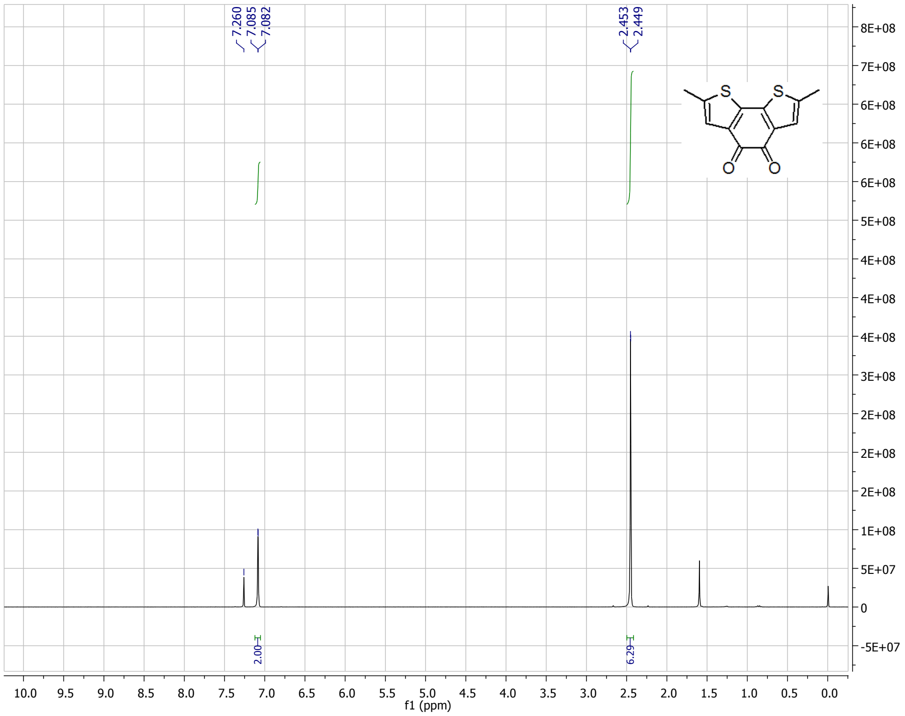
## 1,1’-di-*n*-hexyl-2,2’-bibenzoindole(5c):

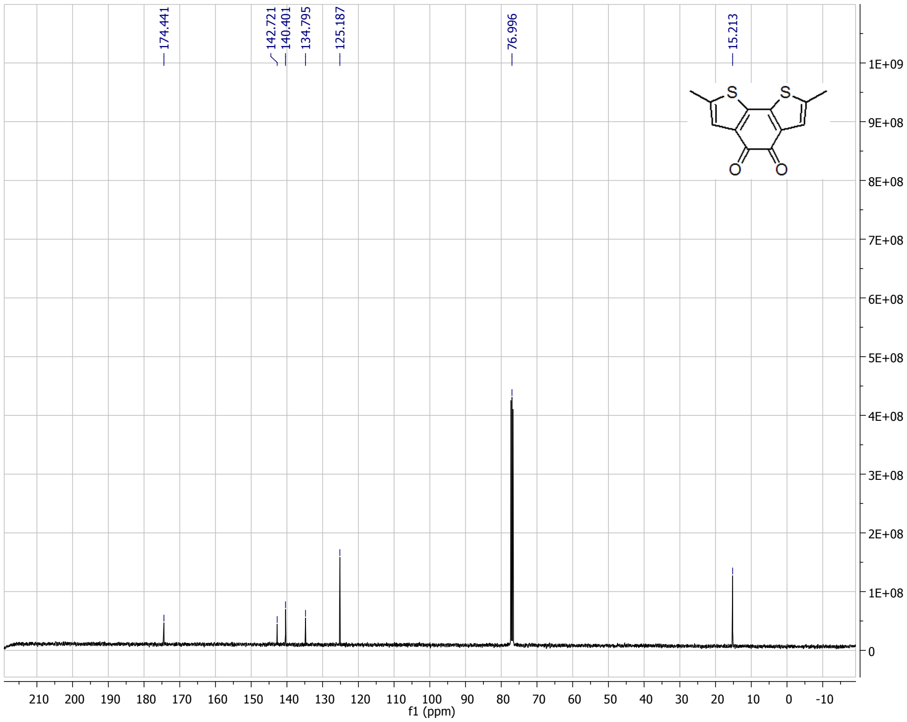




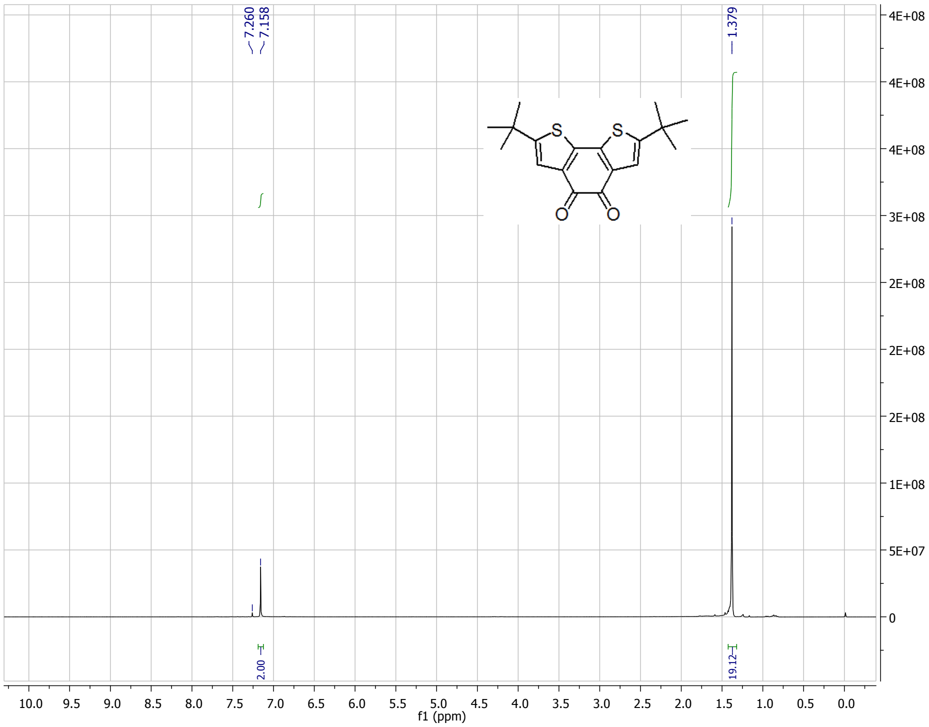
# 4. NMR spectra for diones

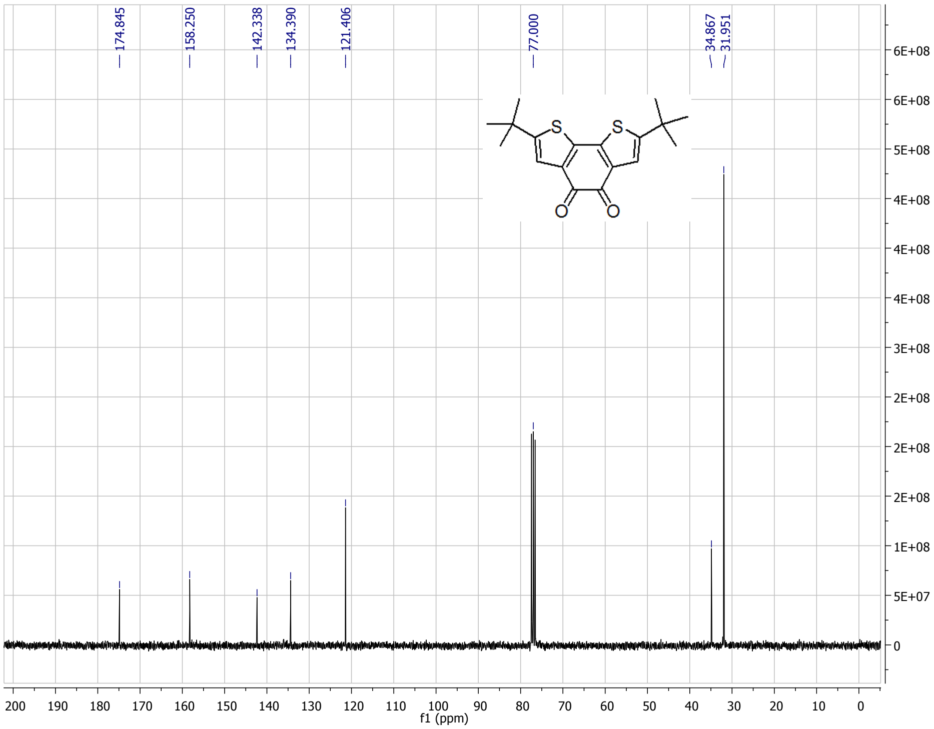
## 2,7-dimetheylbenzo[2,1-b:3,4-b']dithiophene-4,5-diones(2a):



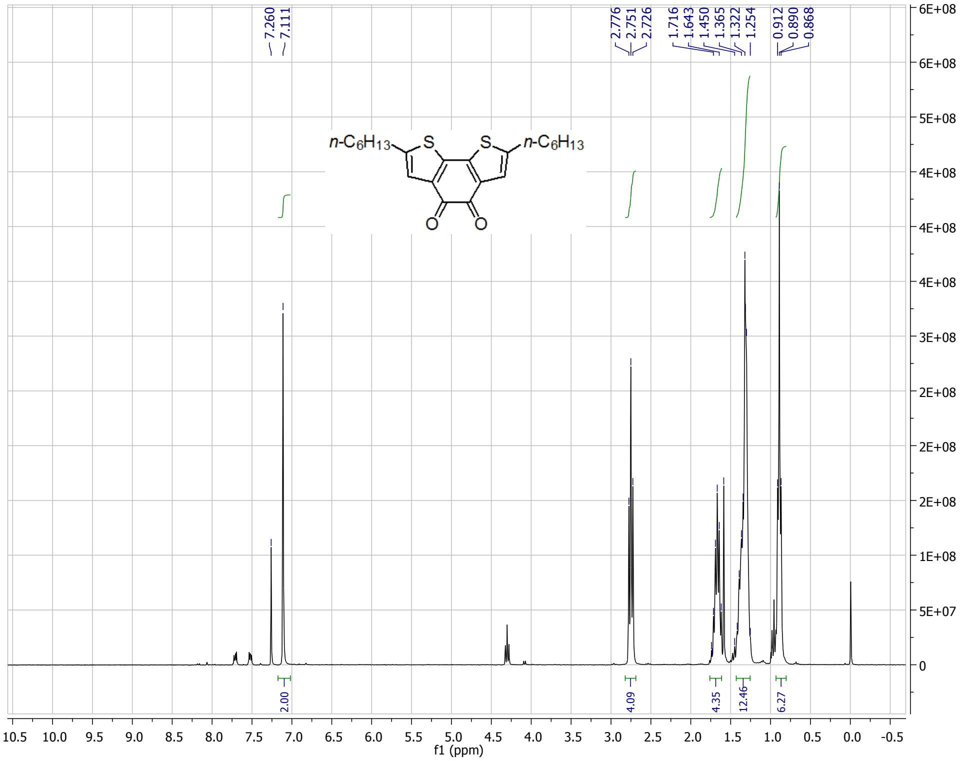


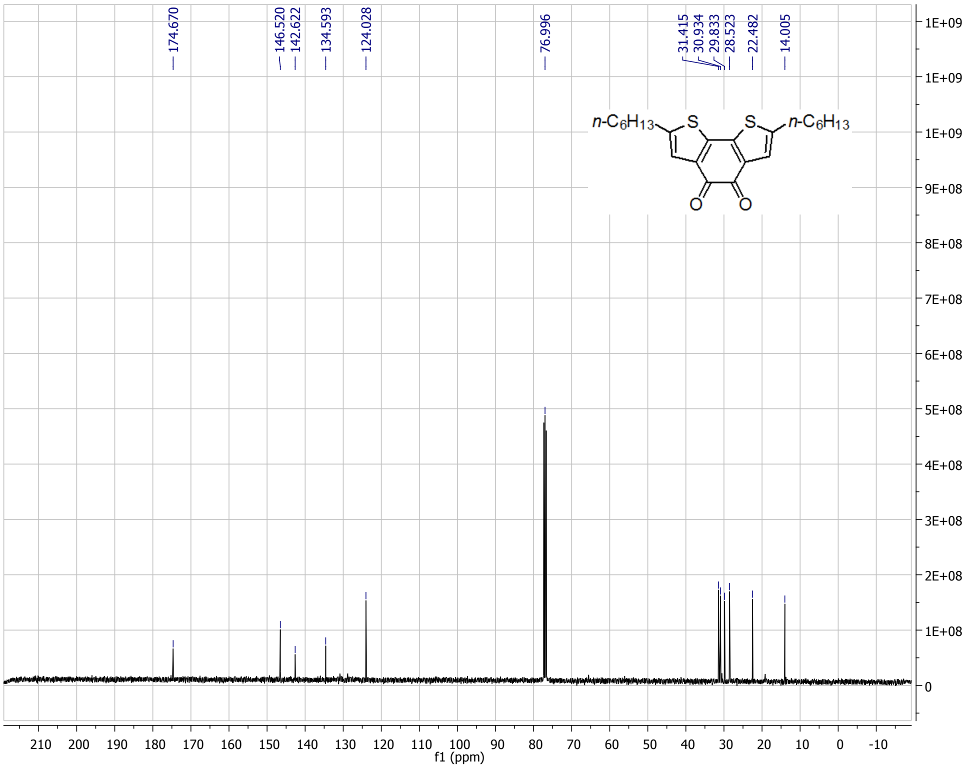
## 2,7-di-*t*-butylbenzo[2,1-b:3,4-b']dithiophene-4,5-diones(2b):



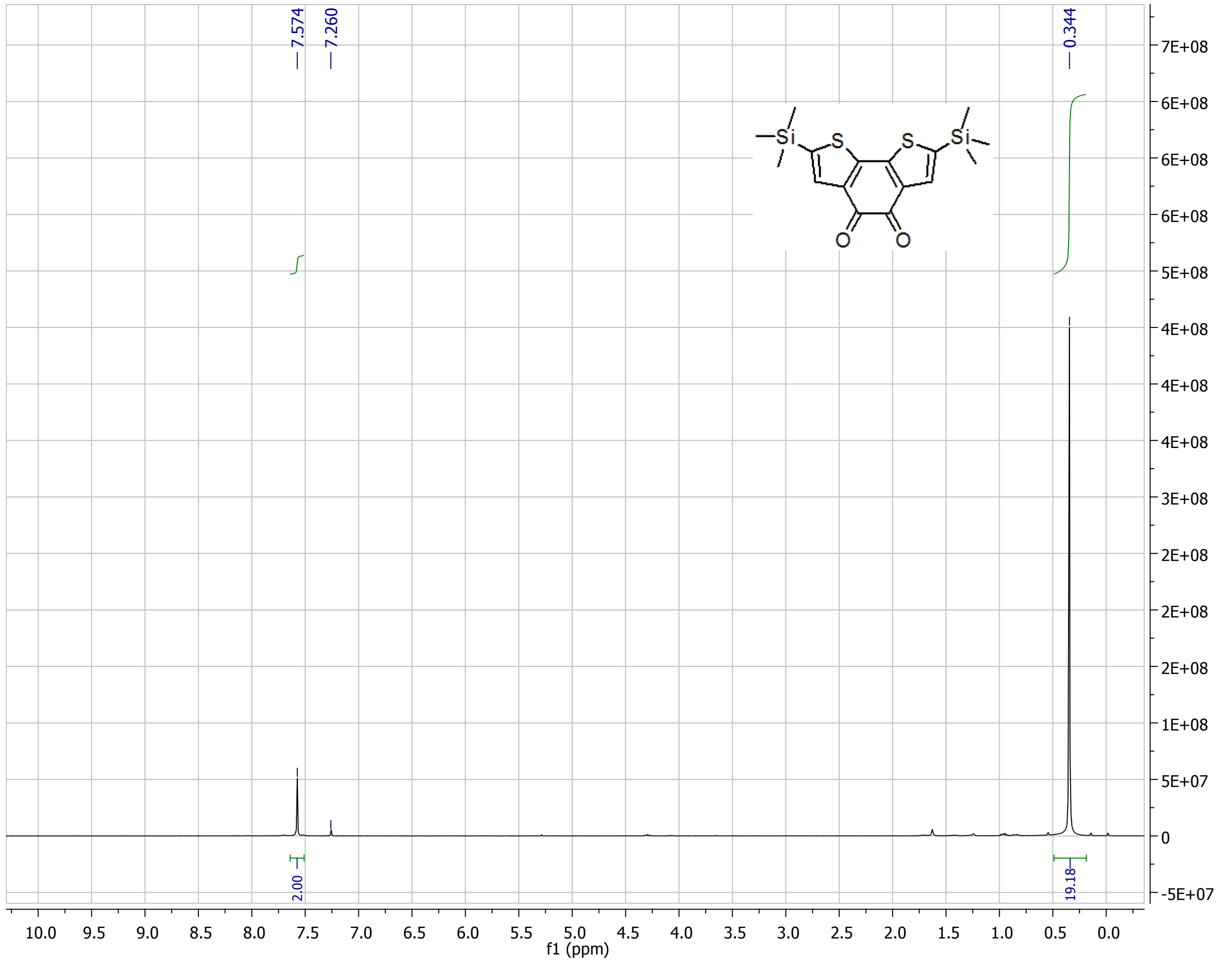


## 2,7-di-*n*-hexylbenzo[2,1-b:3,4-b’]dithiophene-4,5-diones(2c):

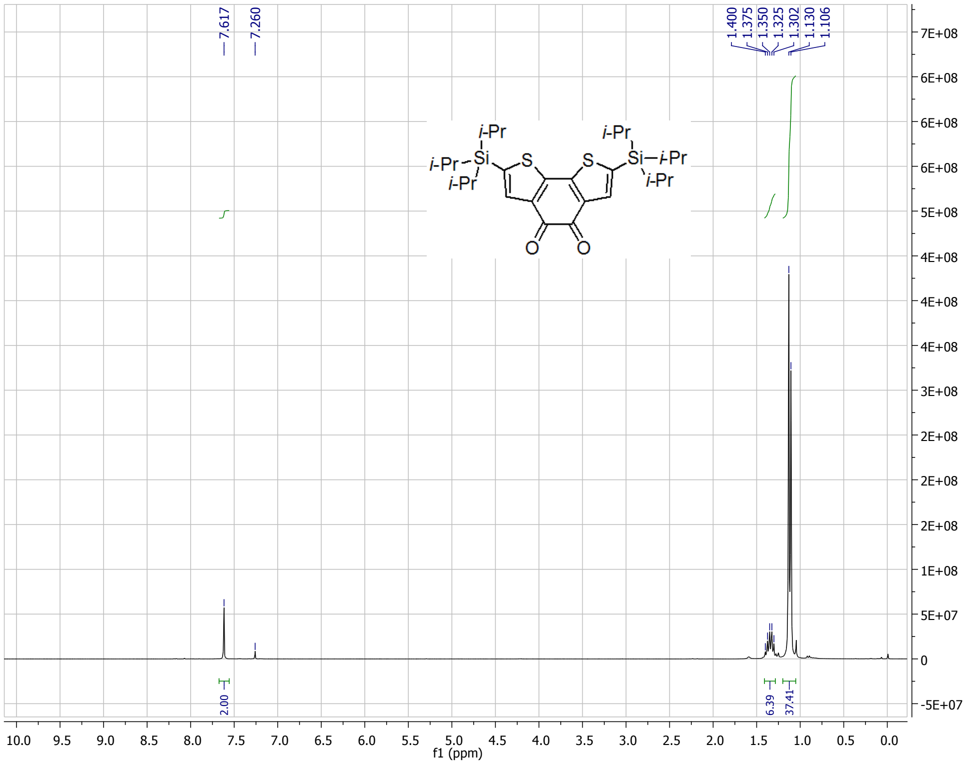


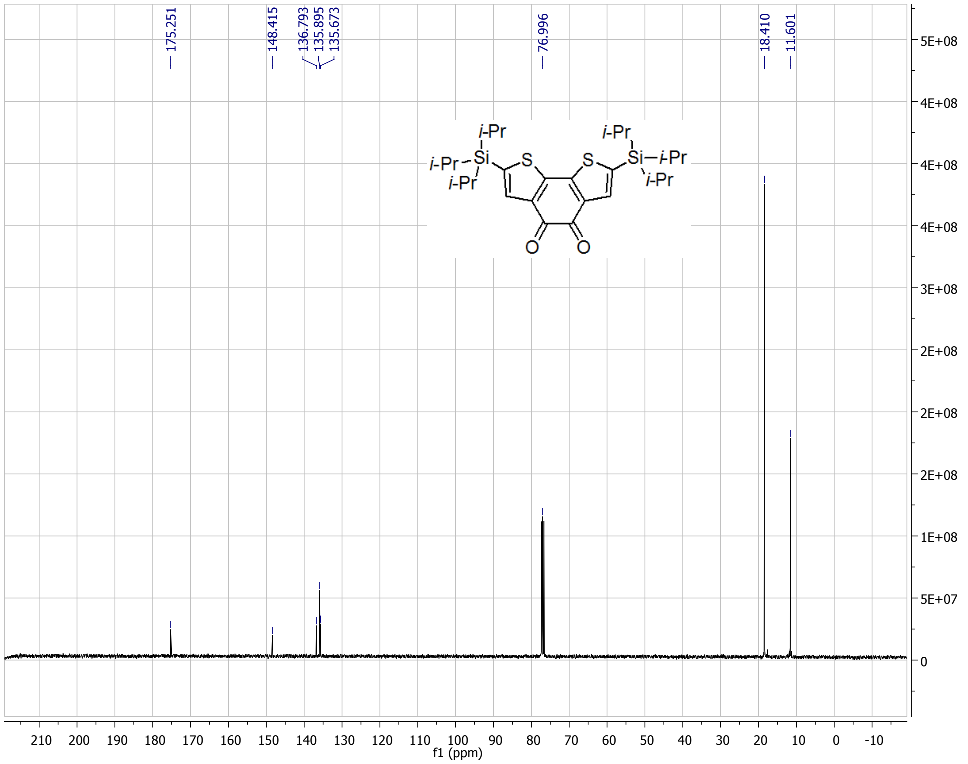


### 2,7-Bis(trimethylsilyl)benzo[2,1-b:3,4-b']dithiophene-4,5-diones(2d)[15]:

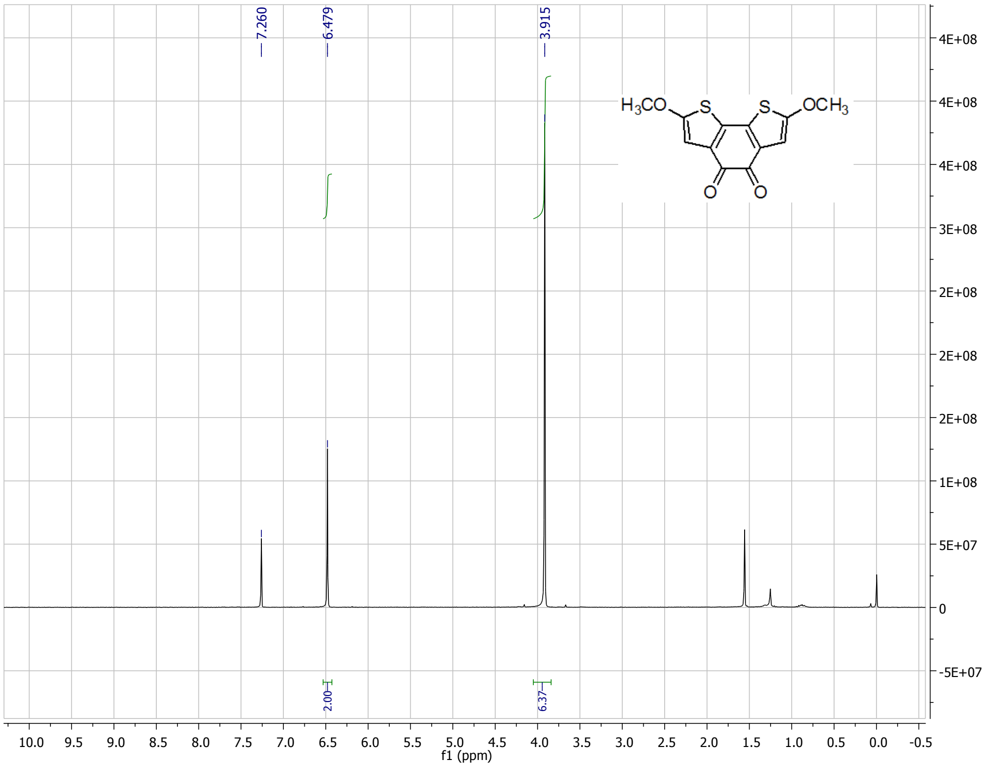


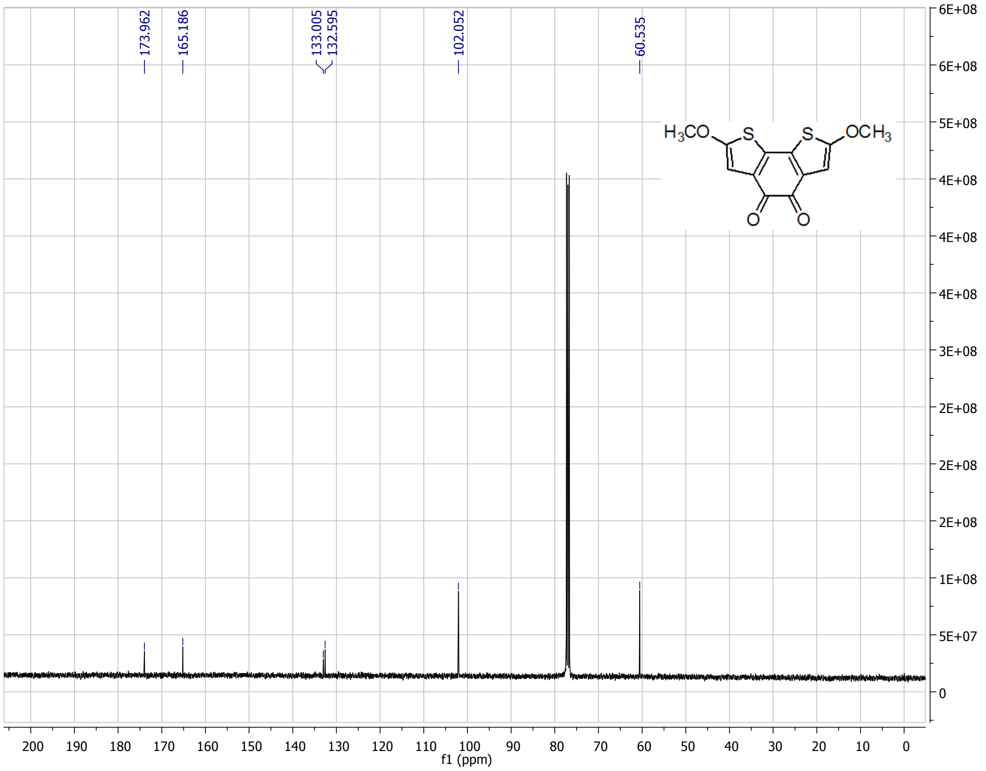
## 2,7-Bis(triisopropylsilyl)benzo[2,1-b:3,4-b’]dithiophene-4,5-diones(2e):



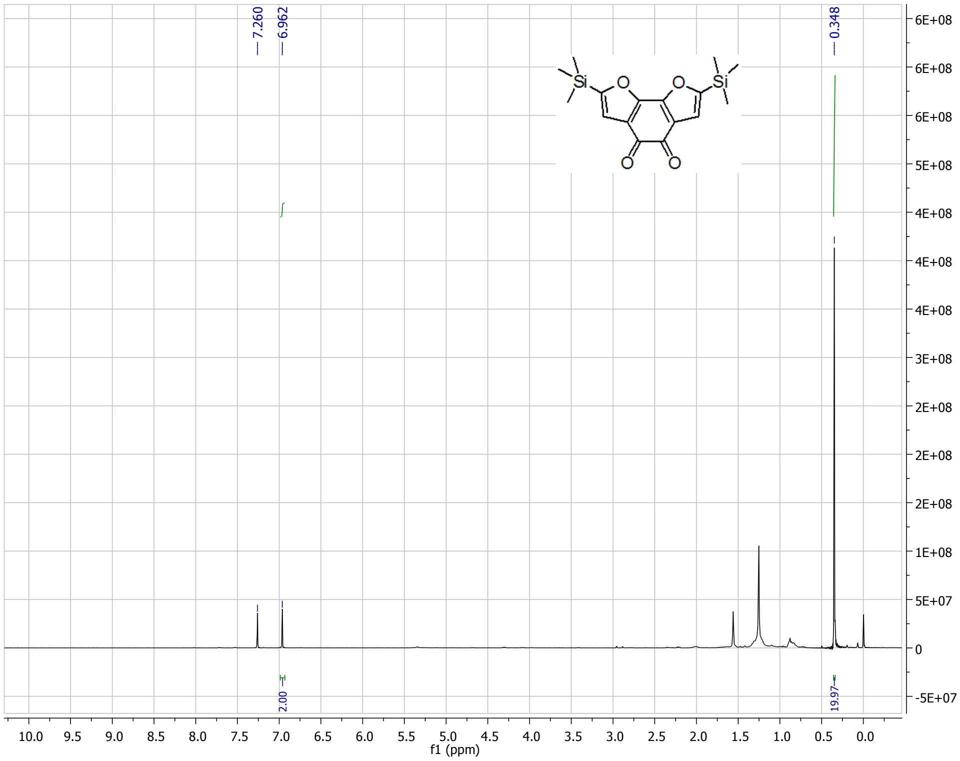


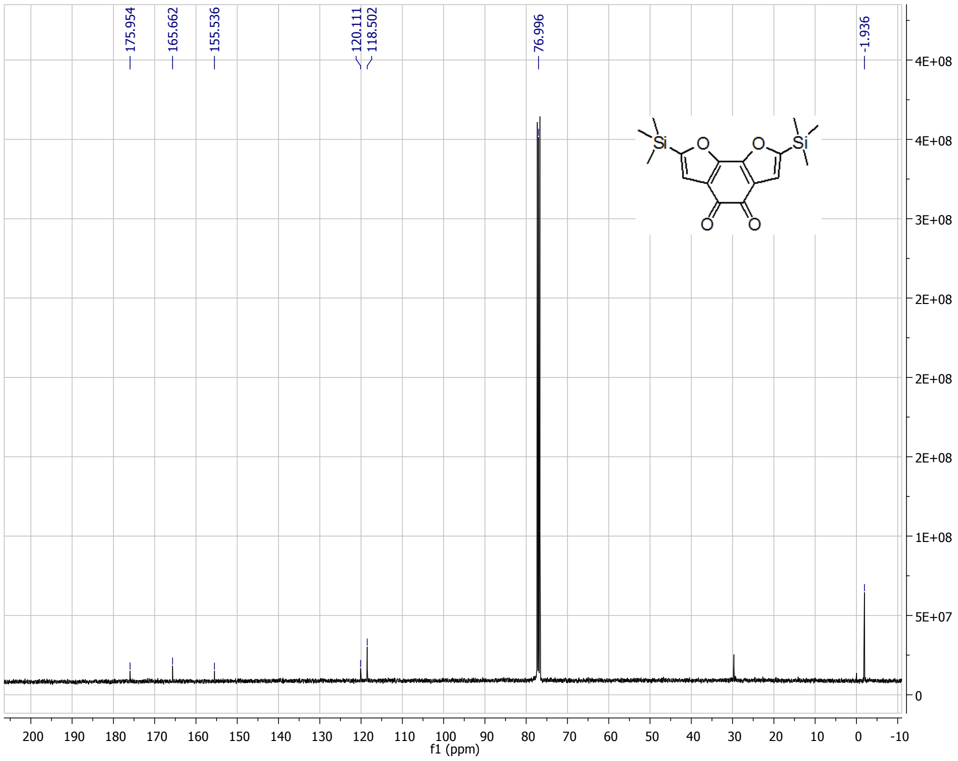
## 2,7-dimethoxylbenzo[2,1-b:3,4-b’]dithiophene-4,5-diones(2f):



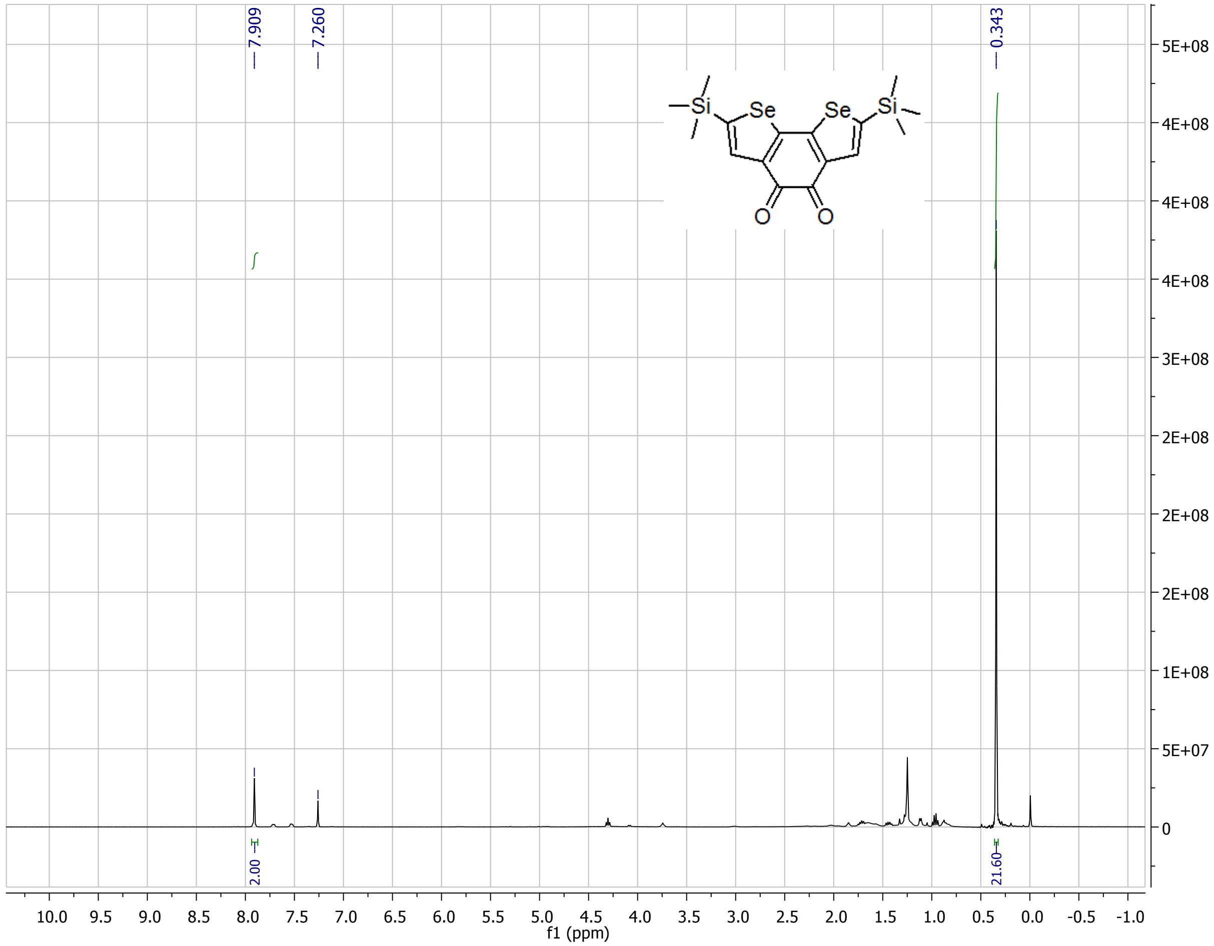


## 2,7-Bis(trimethylsilyl)benzo[2,1-b:3,4-b']difuran-4,5-dione(4a):

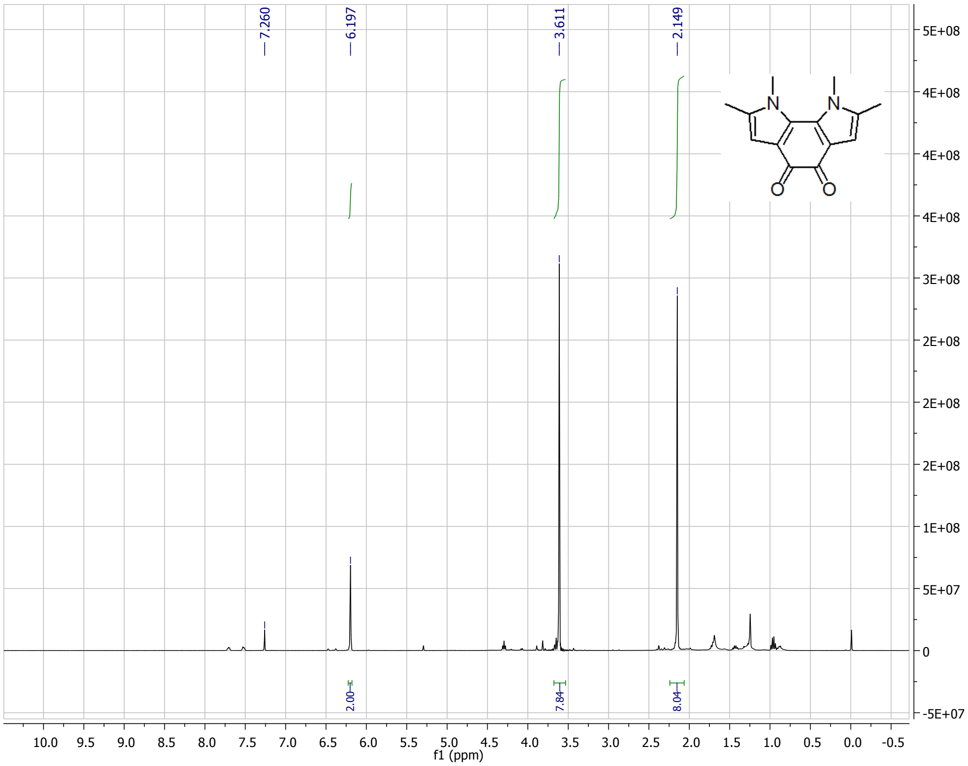


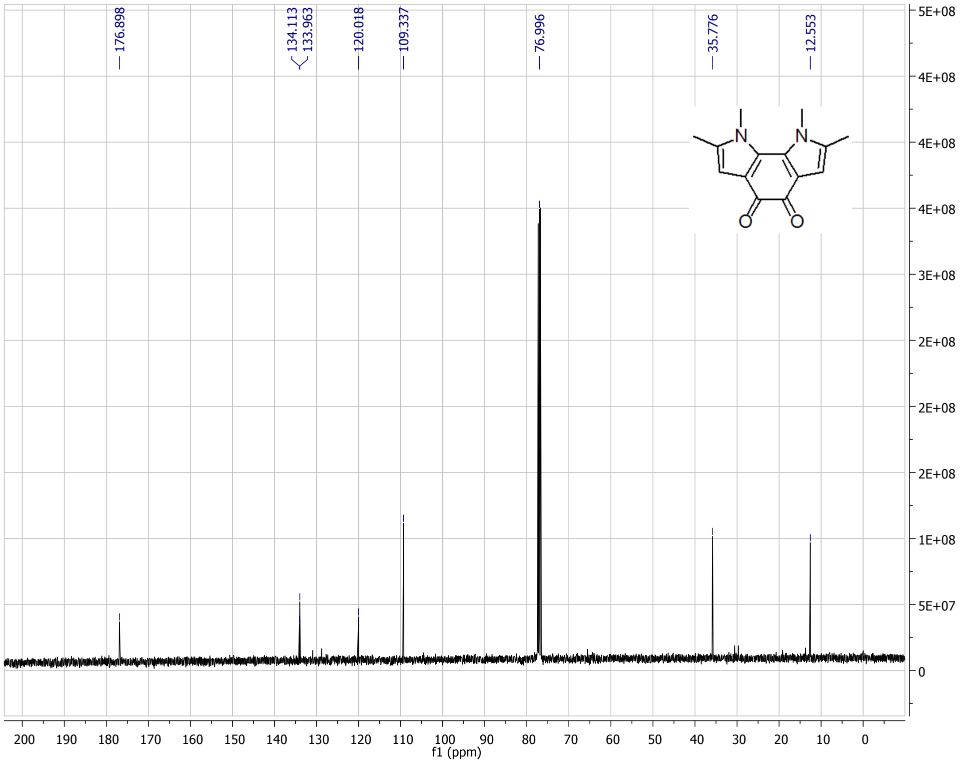


### 2,7-Bis(trimethylsilyl)benzo[2,1-b:3,4-b’]diselenophene-4,5-dione(4b)[15]:

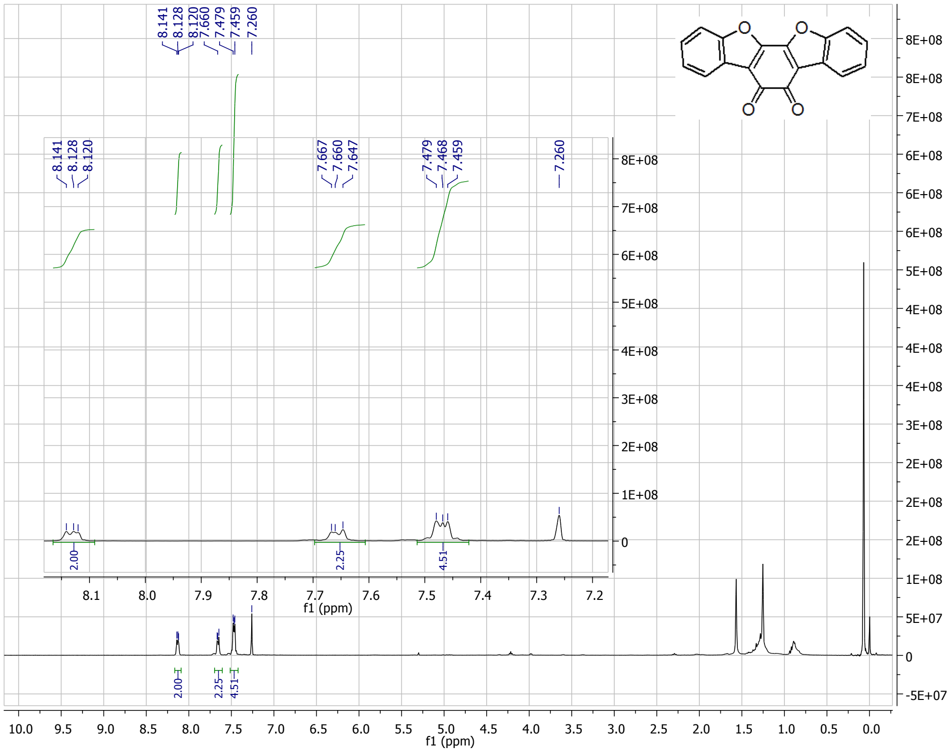


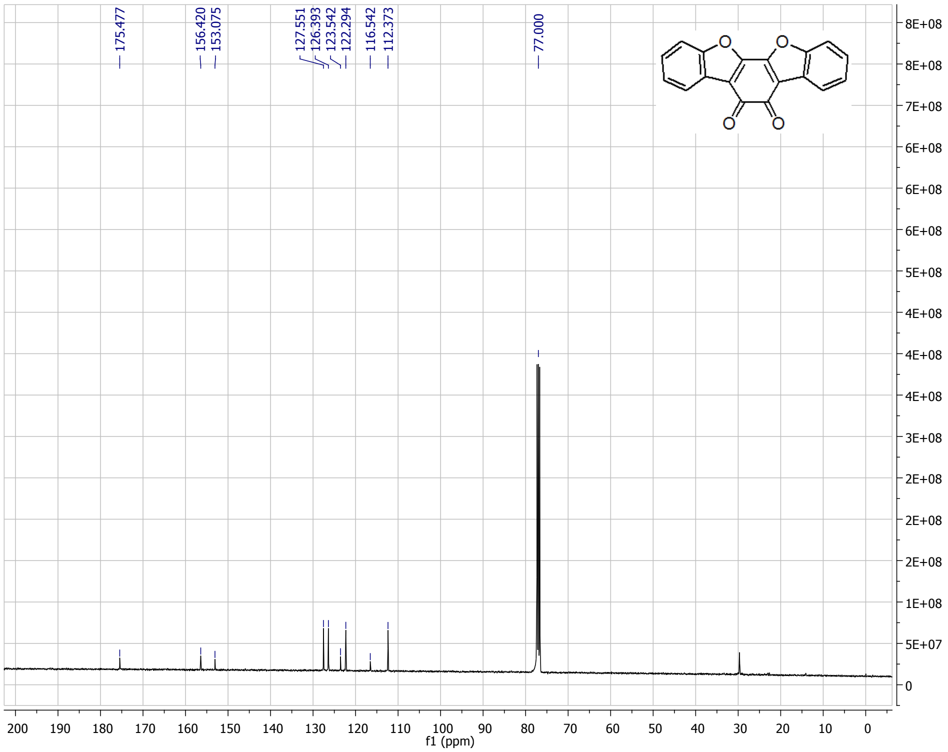
## 1,1-dimethyl-2,7-dimethylbenzo[2,1-b:3,4-b’]dipyrrole-4,5-diones(4c):





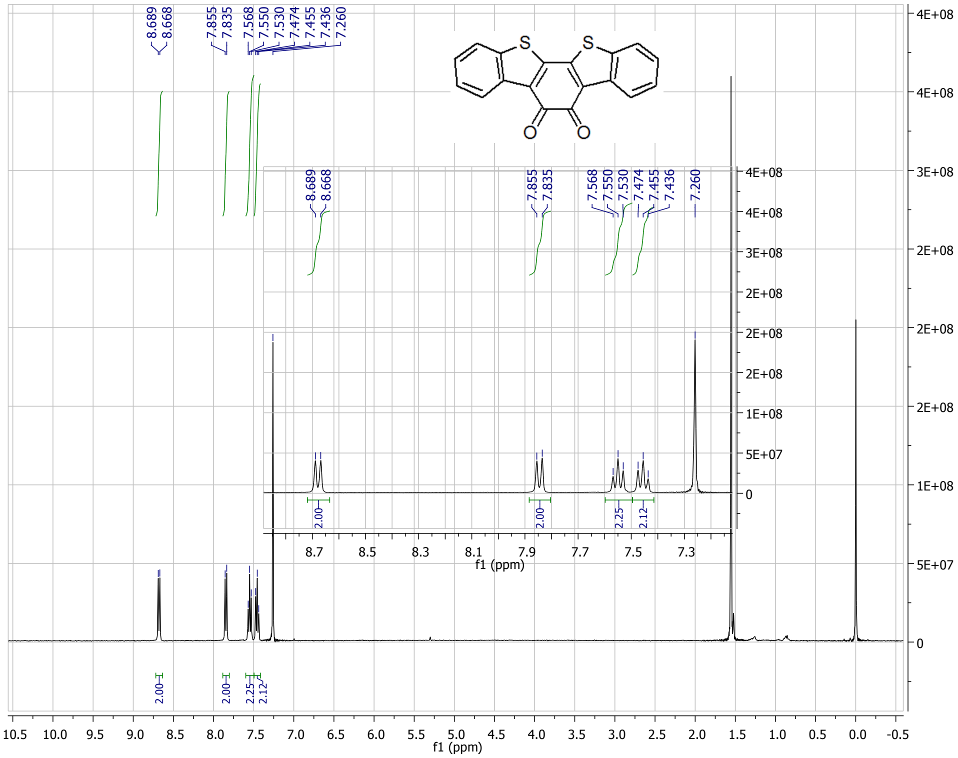
## Dibenzo[d,d’]benzo[2,1-b:3,4-b’]difuran-6,7-diones(5a):

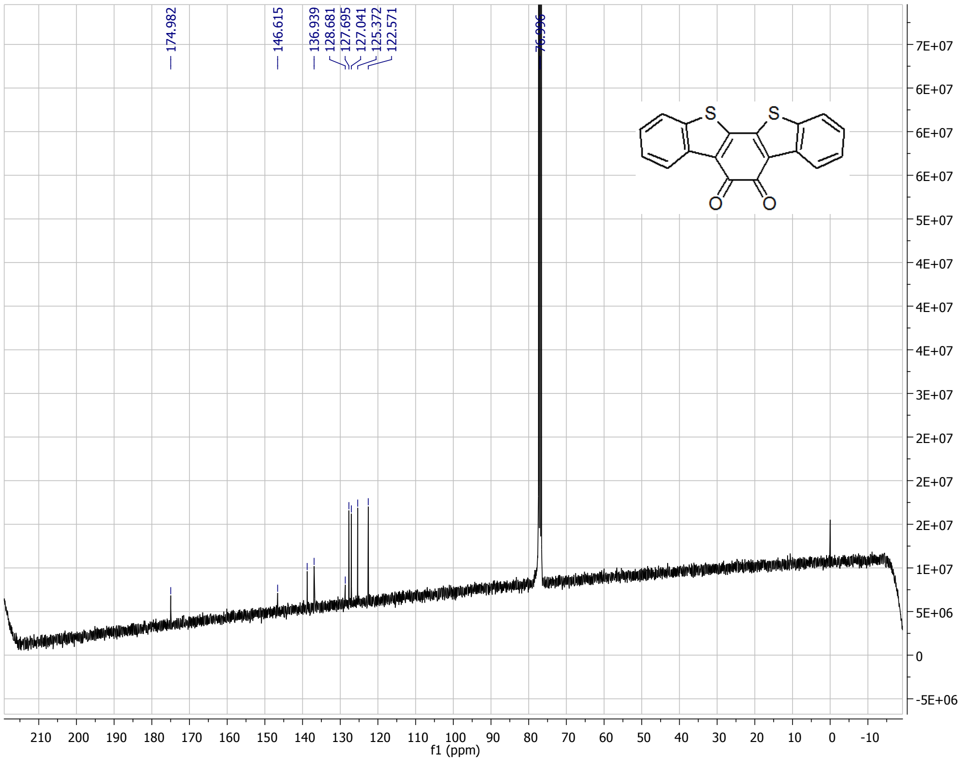




$^{13}$C NMR overnight

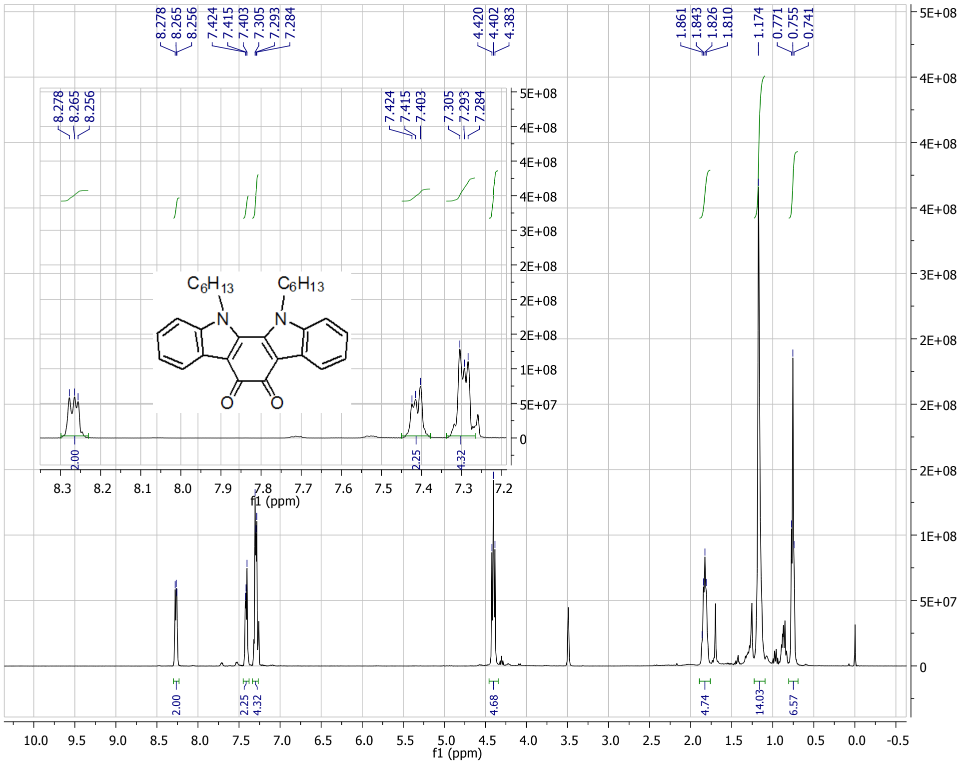
## Dibenzo[d,d’]benzo[2,1-b:3,4-b’]dithiophene-6,7-diones(5b):

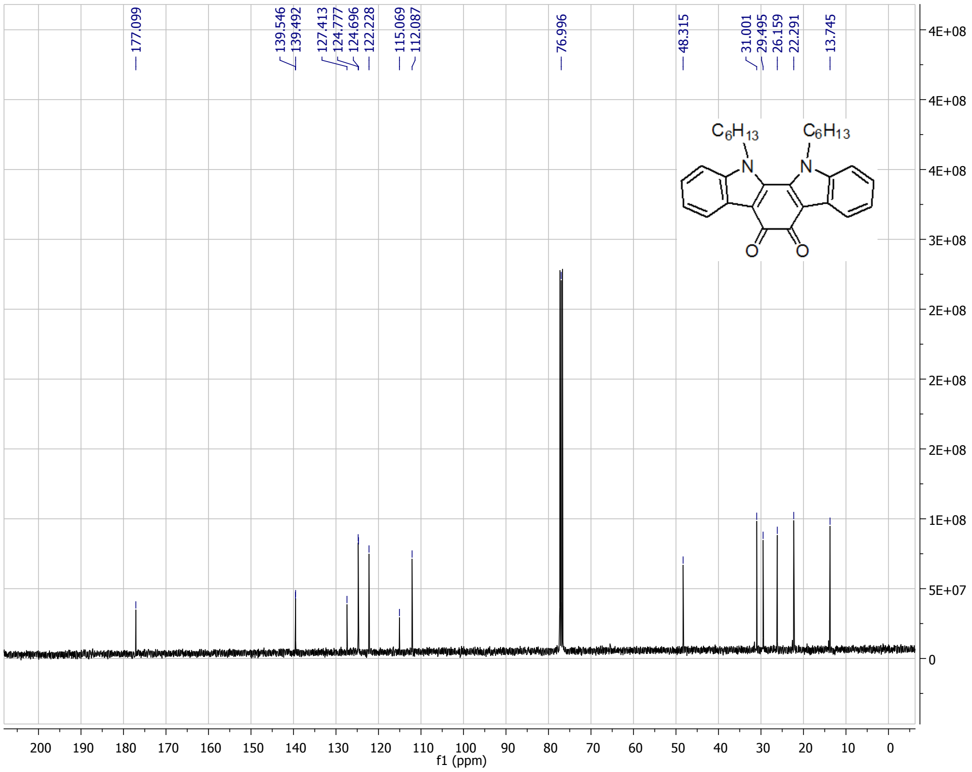




**$^{13}$C NMR overnight**

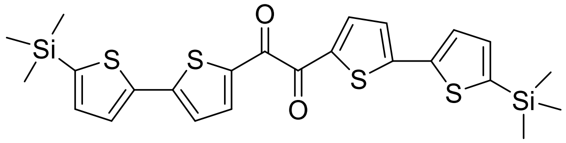
## 1,1’-di-*n*-hexylbenzo[2,1-b:3,4-b’]diindole-6,7-diones(5c):



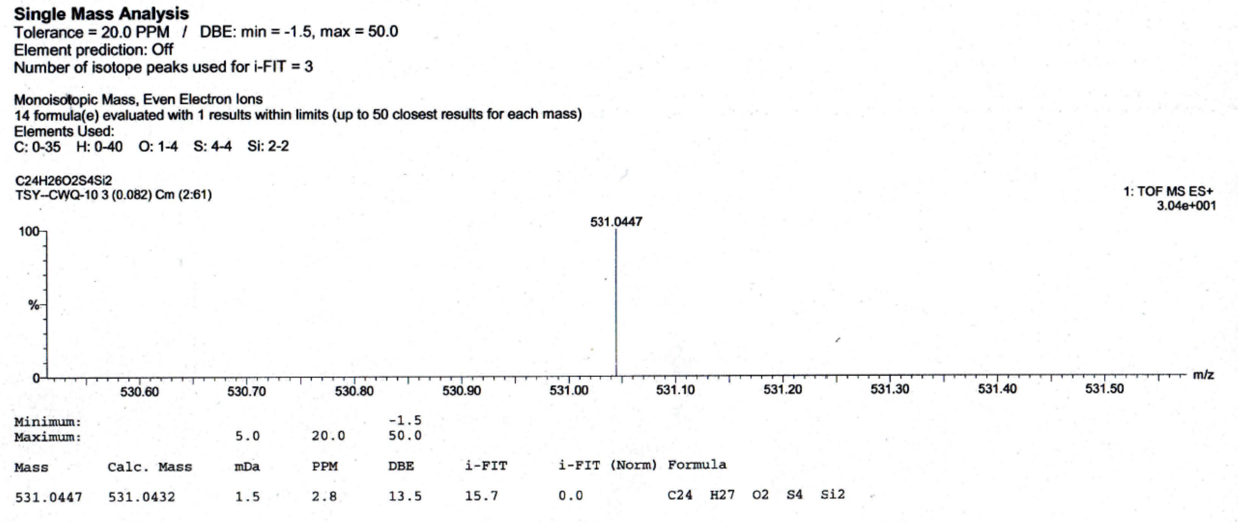


# 5 Analytical data for the byproduct

**1,2-bis(5-(5-(trimethylsilyl)thiophen-2-yl)thiophen-2-yl)ethane-1,2-dione(M1):**



Red solid; $^1$H NMR (400 MHz, CDCl$_3$): δ 8.04 (d, $J$ = 4.0 Hz, 2H), 7.47 (d, $J$ = 3.2 Hz, 2H), 7.27 (d, $J$ = 4.4 Hz, 2H), 7.22 (d, $J$ = 3.2 Hz, 2H), 0.38 (s, 18H); $^{13}$C NMR (100 MHz, CDCl$_3$): 181.4, 149.6, 143.8, 140.8, 138.4, 136.1, 135.1, 127.5, 124.7, –0.23; HRMS: calculated for $C_{24}H_{26}O_2S_4Si_2 + H^+$, 531.0432; found: 531.0447 (M+).



**Single Mass Analysis**

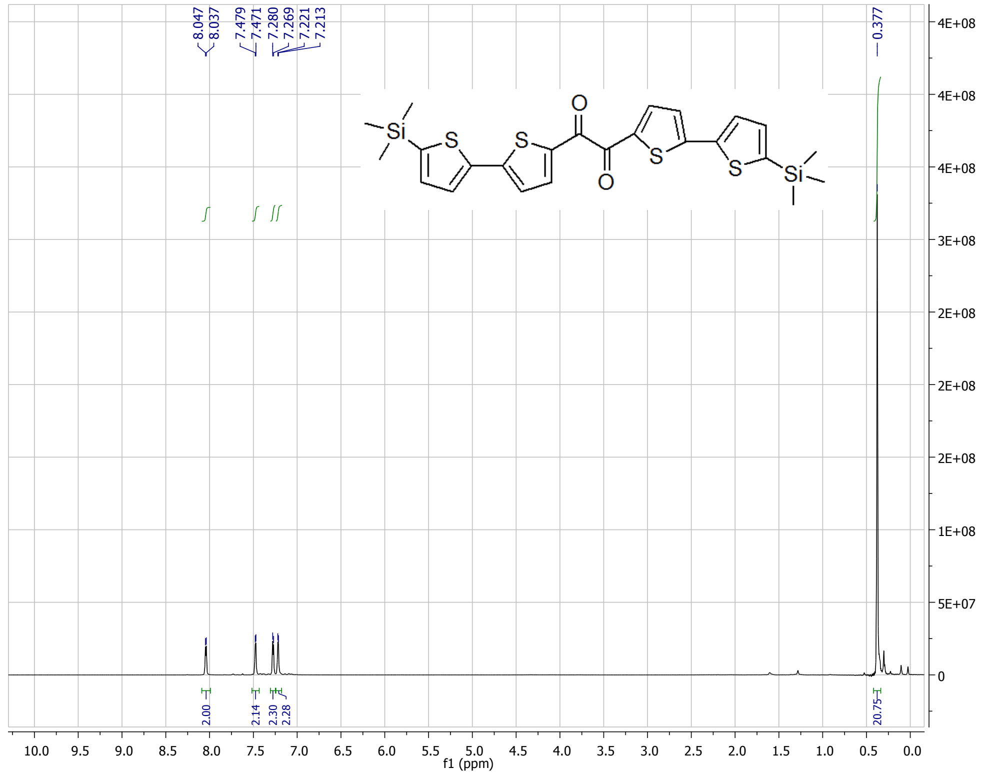
Tolerance = 20.0 PPM / DBE: min = -1.5, max = 50.0
Element prediction: Off
Number of isotope peaks used for i-FIT = 3

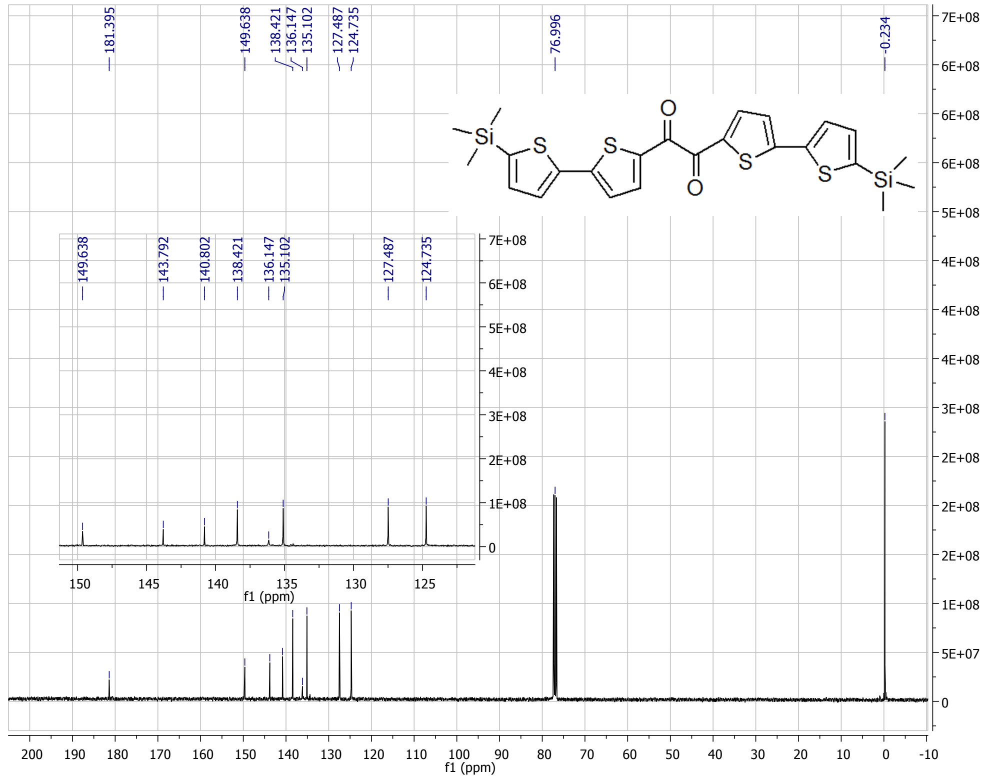
Monoisotopic Mass, Even Electron Ions
14 formula(e) evaluated with 1 results within limits (up to 50 closest results for each mass)
Elements Used:
C: 0-35 H: 0-40 O: 1-4 S: 4-4 Si: 2-2

C24H26O2S4Si2
TSY--CWQ-10 3 (0.082) Cm (2:61)

1: TOF MS ES+
3.04e+001

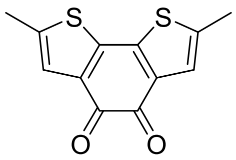
```
Minimum:                                  -1.5
Maximum:                    5.0    20.0   50.0

Mass       Calc. Mass    mDa     PPM    DBE     i-FIT     i-FIT (Norm) Formula

531.0447   531.0432      1.5     2.8    13.5    15.7      0.0          C24  H27  O2  S4  Si2
```

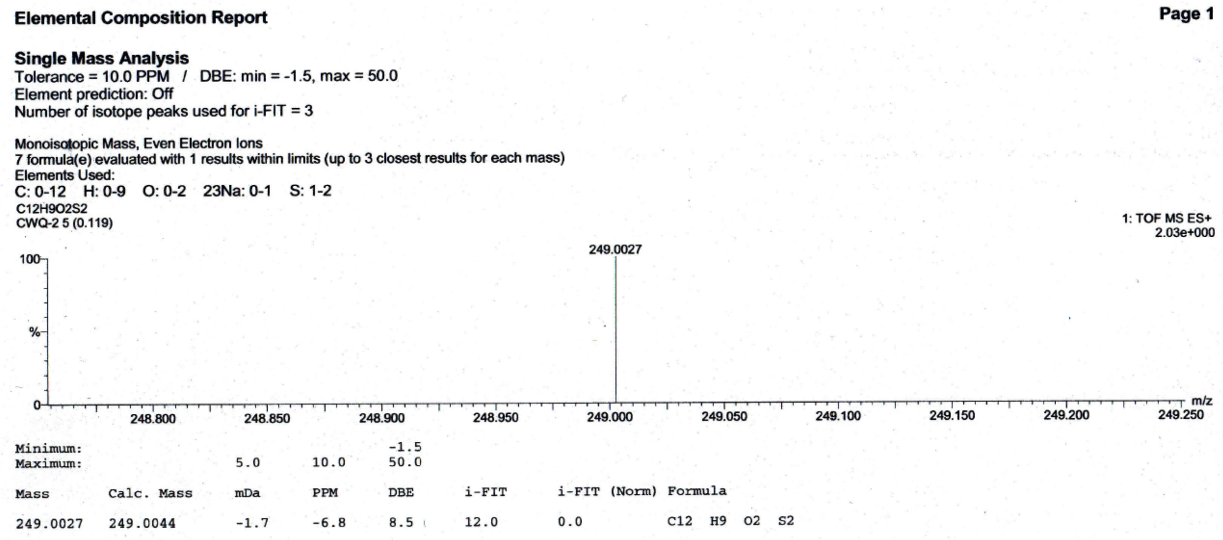

8.047
8.037
7.479
7.471
7.280
7.269
7.221
7.213
0.377
2.00
2.14
2.30
2.28
20.75
Si
S
S
O
O
S
S
Si
4E+08
4E+08
4E+08
3E+08
2E+08
2E+08
2E+08
1E+08
5E+07
0
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)


181.395
149.638
138.421
136.147
135.102
127.487
124.735
76.996
-0.234
Si
S
S
O
O
S
S
Si
149.638
143.792
140.802
138.421
136.147
135.102
127.487
124.735
7E+08
6E+08
5E+08
4E+08
3E+08
2E+08
1E+08
0
150 145 140 135 130 125
f1 (ppm)
7E+08
6E+08
6E+08
6E+08
5E+08
4E+08
4E+08
4E+08
3E+08
2E+08
2E+08
2E+08
1E+08
5E+07
0
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

# 6. HR-MS spectra for the compounds.

**2,7-dimethylbenzo[2,1-b:3,4-b’]dithiophene-4,5-diones(2a):**





**Elemental Composition Report**

**Page 1**

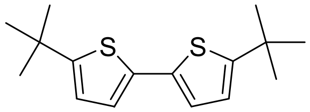
**Single Mass Analysis**
Tolerance = 10.0 PPM / DBE: min = -1.5, max = 50.0
Element prediction: Off
Number of isotope peaks used for i-FIT = 3

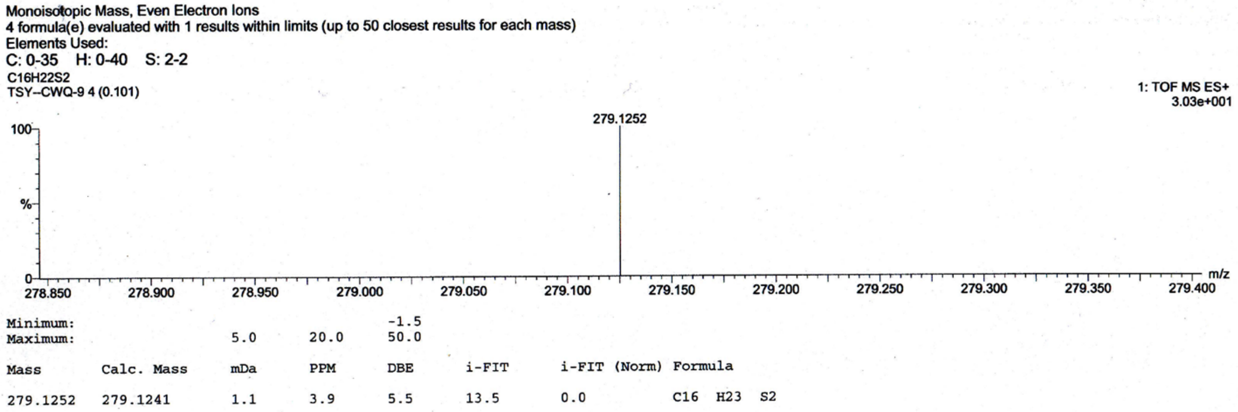
Monoisotopic Mass, Even Electron Ions
7 formula(e) evaluated with 1 results within limits (up to 3 closest results for each mass)
Elements Used:
C: 0-12 H: 0-9 O: 0-2 23Na: 0-1 S: 1-2
C12H9O2S2
CWQ-2 5 (0.119)

1: TOF MS ES+
2.03e+000

```
Minimum:                                    -1.5
Maximum:                 5.0       10.0     50.0

Mass       Calc. Mass    mDa       PPM      DBE      i-FIT     i-FIT (Norm) Formula

249.0027   249.0044      -1.7      -6.8     8.5      12.0      0.0          C12  H9  O2  S2
```

**5,5’-di-*t*-butyl-2,2’-bithiophene (1b):**



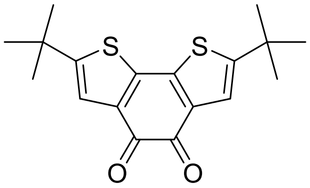


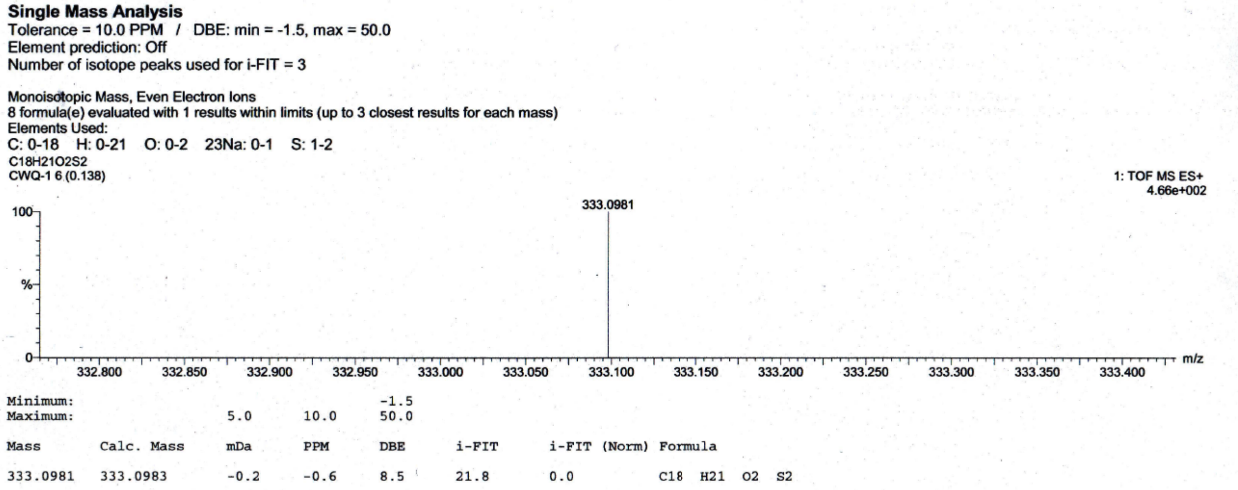
Monoisotopic Mass, Even Electron Ions
4 formula(e) evaluated with 1 results within limits (up to 50 closest results for each mass)
Elements Used:
C: 0-35 H: 0-40 S: 2-2
C16H22S2
TSY--CWQ-9 4 (0.101)

1: TOF MS ES+
3.03e+001

```
Minimum:                                    -1.5
Maximum:                 5.0       20.0     50.0

Mass       Calc. Mass    mDa       PPM      DBE      i-FIT     i-FIT (Norm) Formula

279.1252   279.1241      1.1       3.9      5.5      13.5      0.0          C16  H23  S2
```

## 2,7-di-*t*-butylbenzo[2,1-b:3,4-b’]dithiophene-4,5-diones(2b):





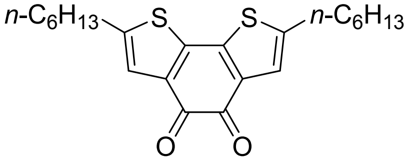
**Single Mass Analysis**
Tolerance = 10.0 PPM / DBE: min = -1.5, max = 50.0
Element prediction: Off
Number of isotope peaks used for i-FIT = 3

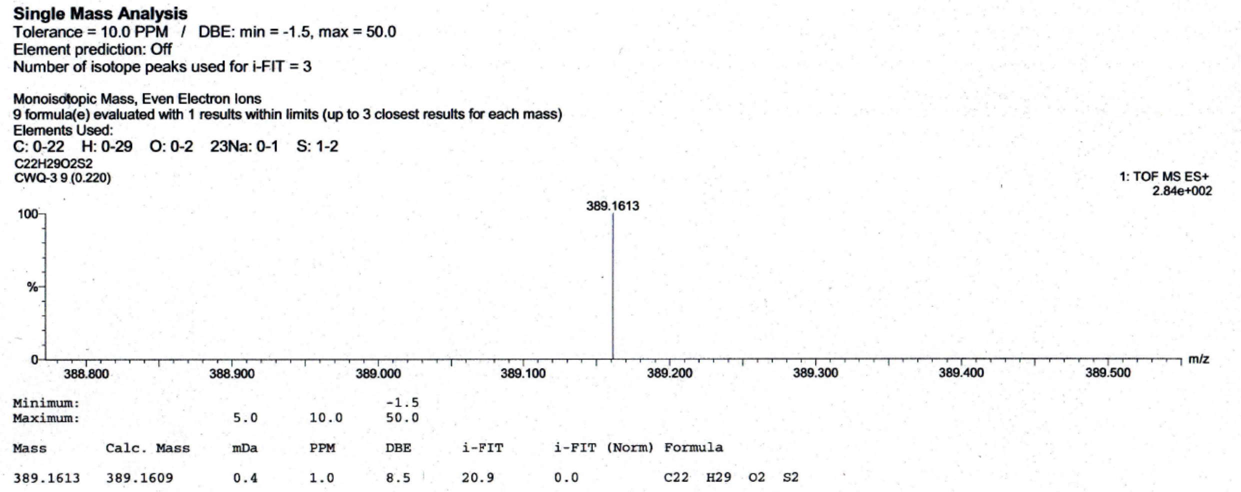
Monoisotopic Mass, Even Electron Ions
8 formula(e) evaluated with 1 results within limits (up to 3 closest results for each mass)
Elements Used:
C: 0-18 H: 0-21 O: 0-2 23Na: 0-1 S: 1-2
C18H21O2S2
CWQ-1 6 (0.138)

1: TOF MS ES+
4.66e+002

```
Minimum:                              -1.5
Maximum:                5.0    10.0   50.0

Mass      Calc. Mass    mDa    PPM    DBE    i-FIT    i-FIT (Norm) Formula

333.0981  333.0983      -0.2   -0.6   8.5    21.8     0.0          C18  H21  O2  S2
```

## 2,7-di-*n*-hexylbenzo[2,1-b:3,4-b’]dithiophene-4,5-diones(2c):





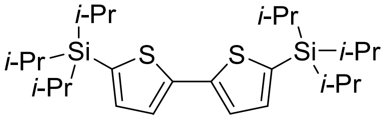
**Single Mass Analysis**
Tolerance = 10.0 PPM / DBE: min = -1.5, max = 50.0
Element prediction: Off
Number of isotope peaks used for i-FIT = 3

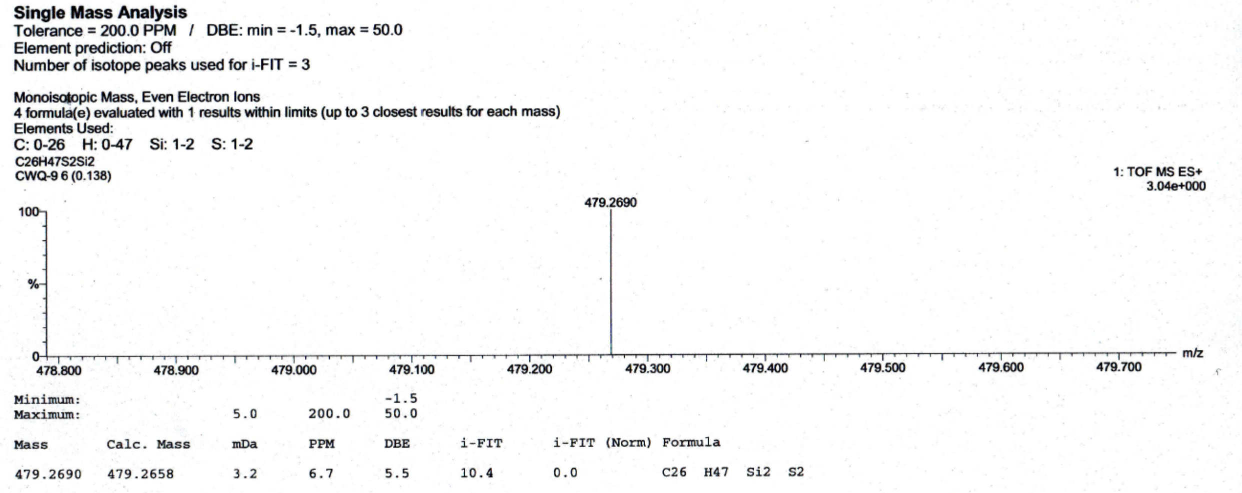
Monoisotopic Mass, Even Electron Ions
9 formula(e) evaluated with 1 results within limits (up to 3 closest results for each mass)
Elements Used:
C: 0-22 H: 0-29 O: 0-2 23Na: 0-1 S: 1-2
C22H29O2S2
CWQ-3 9 (0.220)

1: TOF MS ES+
2.84e+002

```
Minimum:                              -1.5
Maximum:                5.0    10.0   50.0

Mass      Calc. Mass    mDa    PPM    DBE    i-FIT    i-FIT (Norm) Formula

389.1613  389.1609      0.4    1.0    8.5    20.9     0.0          C22  H29  O2  S2
```

**5,5’-Bis(triisopropylsilyl)-2,2’-bithiophene (1e):**



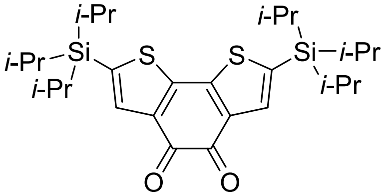


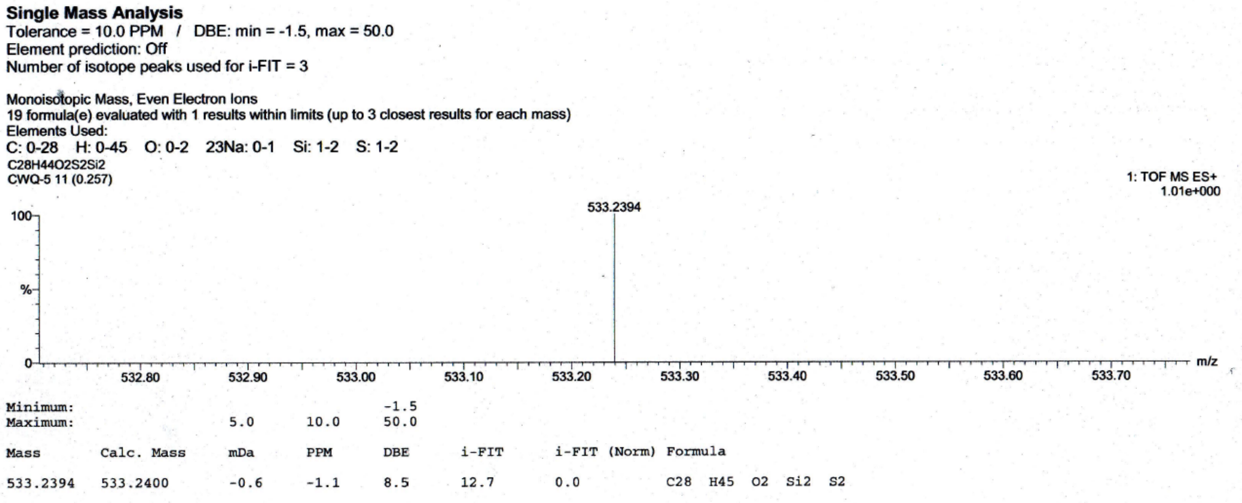
**Single Mass Analysis**
Tolerance = 200.0 PPM / DBE: min = -1.5, max = 50.0
Element prediction: Off
Number of isotope peaks used for i-FIT = 3

Monoisotopic Mass, Even Electron Ions
4 formula(e) evaluated with 1 results within limits (up to 3 closest results for each mass)
Elements Used:
C: 0-26 H: 0-47 Si: 1-2 S: 1-2
C26H47S2Si2
CWQ-9 6 (0.138)

```
Minimum:                              -1.5
Maximum:             5.0     200.0    50.0

Mass      Calc. Mass  mDa    PPM      DBE     i-FIT    i-FIT (Norm) Formula

479.2690  479.2658    3.2    6.7      5.5     10.4     0.0          C26  H47  Si2  S2
```

**2,7-Bis(triisopropylsilyl)benzo[2,1-b:3,4-b’]dithiophene-4,5-diones(2e):**



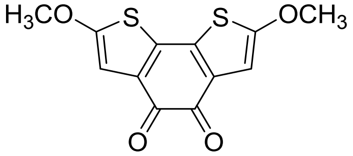


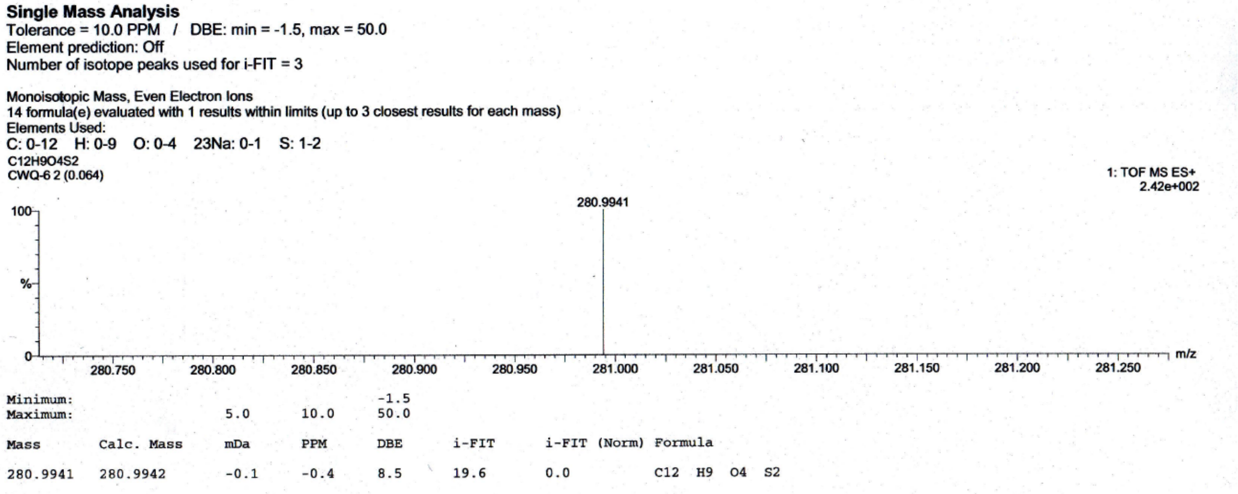
**Single Mass Analysis**
Tolerance = 10.0 PPM / DBE: min = -1.5, max = 50.0
Element prediction: Off
Number of isotope peaks used for i-FIT = 3

Monoisotopic Mass, Even Electron Ions
19 formula(e) evaluated with 1 results within limits (up to 3 closest results for each mass)
Elements Used:
C: 0-28 H: 0-45 O: 0-2 23Na: 0-1 Si: 1-2 S: 1-2
C28H44O2S2Si2
CWQ-5 11 (0.257)

```
Minimum:                              -1.5
Maximum:             5.0     10.0     50.0

Mass      Calc. Mass  mDa    PPM      DBE     i-FIT    i-FIT (Norm) Formula

533.2394  533.2400    -0.6   -1.1     8.5     12.7     0.0          C28  H45  O2  Si2  S2
```

## 2,7-dimethoxylbenzo[2,1-b:3,4-b’]dithiophene-4,5-diones(2f):

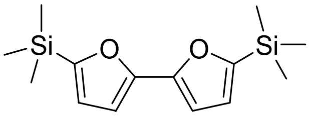


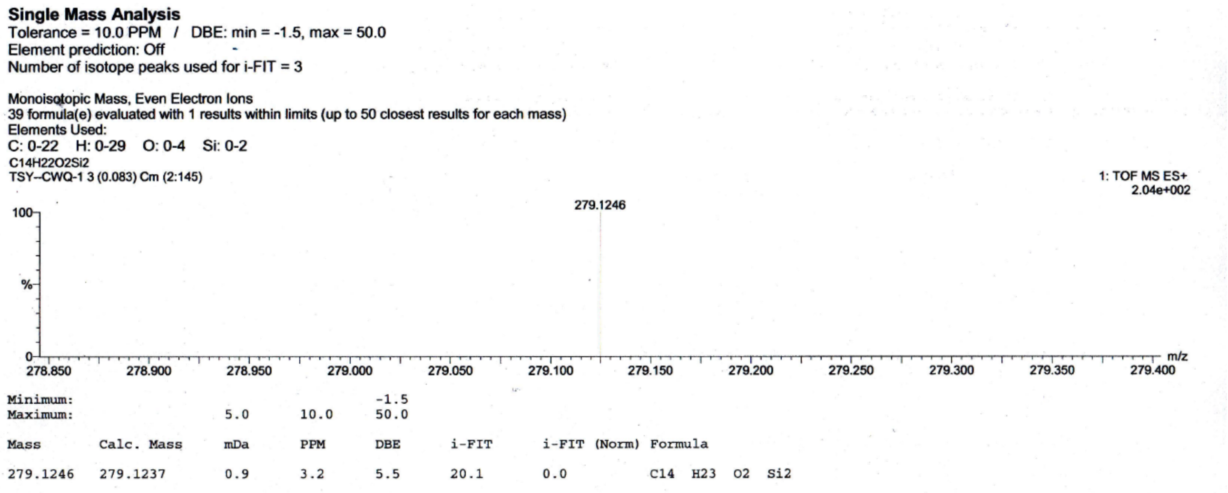

**Single Mass Analysis**
Tolerance = 10.0 PPM / DBE: min = -1.5, max = 50.0
Element prediction: Off
Number of isotope peaks used for i-FIT = 3

Monoisotopic Mass, Even Electron Ions
14 formula(e) evaluated with 1 results within limits (up to 3 closest results for each mass)
Elements Used:
C: 0-12 H: 0-9 O: 0-4 23Na: 0-1 S: 1-2
C12H9O4S2
CWQ-6 2 (0.064)

```
Minimum:                                  -1.5
Maximum:               5.0       10.0     50.0

Mass       Calc. Mass  mDa       PPM      DBE      i-FIT     i-FIT (Norm) Formula

280.9941   280.9942    -0.1      -0.4     8.5      19.6      0.0          C12  H9  O4  S2
```

## 5,5’-Bis(trimethylsilyl)-2,2’-bifuan(3a):

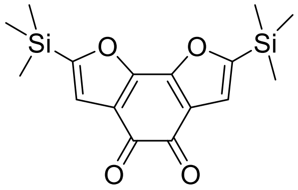


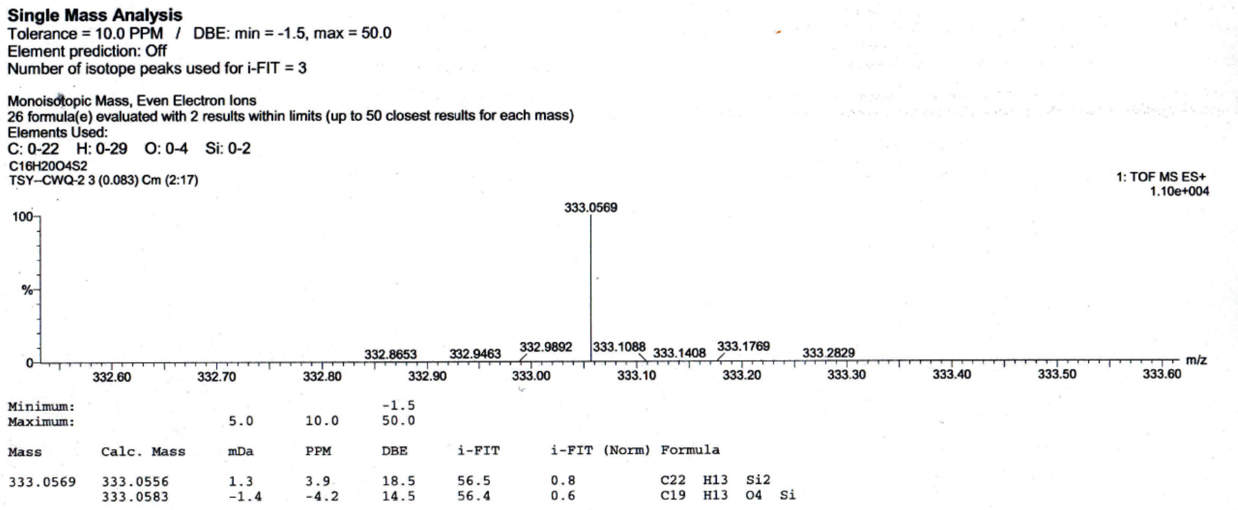

**Single Mass Analysis**
Tolerance = 10.0 PPM / DBE: min = -1.5, max = 50.0
Element prediction: Off
Number of isotope peaks used for i-FIT = 3

Monoisotopic Mass, Even Electron Ions
39 formula(e) evaluated with 1 results within limits (up to 50 closest results for each mass)
Elements Used:
C: 0-22 H: 0-29 O: 0-4 Si: 0-2
C14H22O2Si2
TSY--CWQ-1 3 (0.083) Cm (2:145)

```
Minimum:                                  -1.5
Maximum:               5.0       10.0     50.0

Mass       Calc. Mass  mDa       PPM      DBE      i-FIT     i-FIT (Norm) Formula

279.1246   279.1237    0.9       3.2      5.5      20.1      0.0          C14  H23  O2  Si2
```

**2,7-Bis(trimethylsilyl)benzo[2,1-b:3,4-b']difuran-4,5-diones(4a)**:



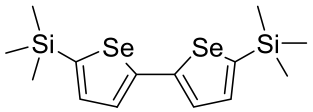


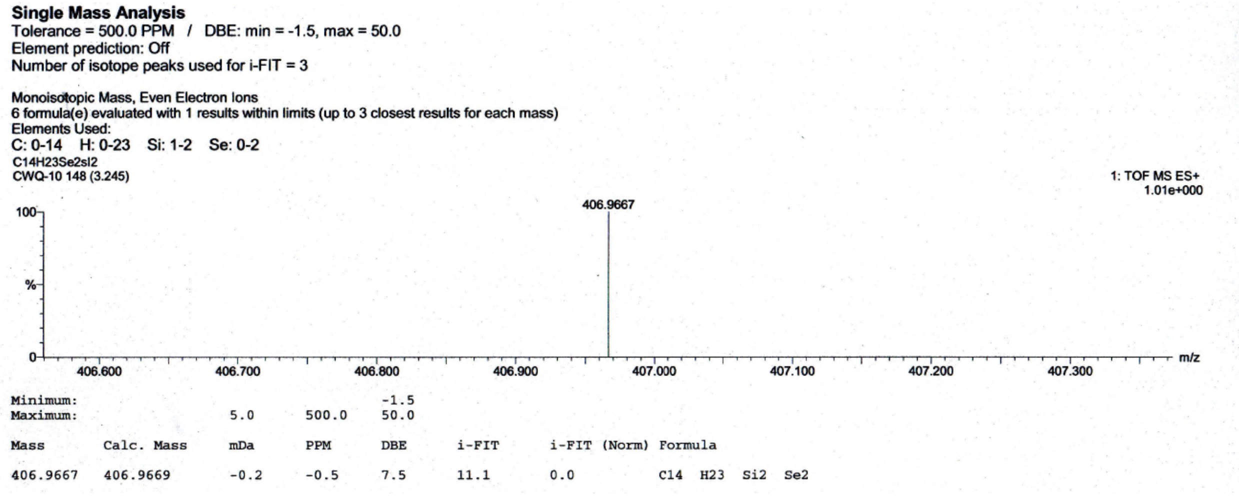
**Single Mass Analysis**
Tolerance = 10.0 PPM / DBE: min = -1.5, max = 50.0
Element prediction: Off
Number of isotope peaks used for i-FIT = 3

Monoisotopic Mass, Even Electron Ions
26 formula(e) evaluated with 2 results within limits (up to 50 closest results for each mass)
Elements Used:
C: 0-22 H: 0-29 O: 0-4 Si: 0-2
C16H20O4S2
TSY--CWQ-2 3 (0.083) Cm (2:17)

```
Minimum:                              -1.5
Maximum:              5.0      10.0   50.0

Mass      Calc. Mass  mDa      PPM    DBE     i-FIT     i-FIT (Norm) Formula

333.0569  333.0556    1.3      3.9    18.5    56.5      0.8          C22  H13  Si2
          333.0583    -1.4     -4.2   14.5    56.4      0.6          C19  H13  O4   Si
```

**5,5'-Bis(trimethylsilyl)-2,2'-biselenophene(3b):**



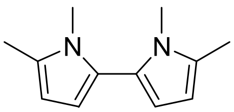


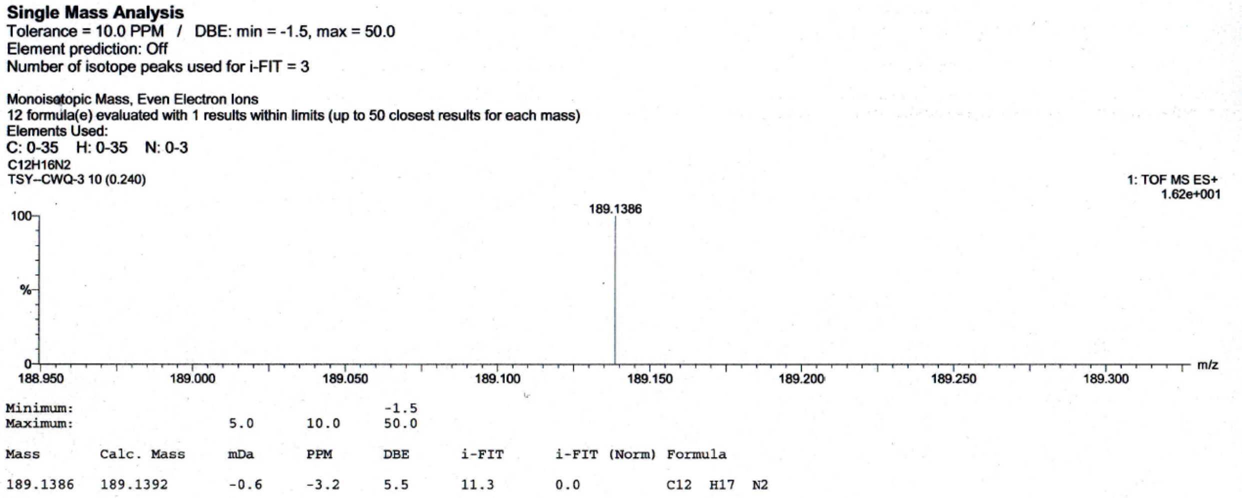
**Single Mass Analysis**
Tolerance = 500.0 PPM / DBE: min = -1.5, max = 50.0
Element prediction: Off
Number of isotope peaks used for i-FIT = 3

Monoisotopic Mass, Even Electron Ions
6 formula(e) evaluated with 1 results within limits (up to 3 closest results for each mass)
Elements Used:
C: 0-14 H: 0-23 Si: 1-2 Se: 0-2
C14H23Se2sI2
CWQ-10 148 (3.245)

```
Minimum:                              -1.5
Maximum:              5.0      500.0  50.0

Mass      Calc. Mass  mDa      PPM    DBE     i-FIT     i-FIT (Norm) Formula

406.9667  406.9669    -0.2     -0.5   7.5     11.1      0.0          C14  H23  Si2  Se2
```

### 1,1-dimethyl-5,5’-dimethyl-2,2’-bipyrrole(3c):



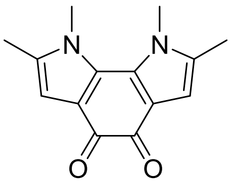


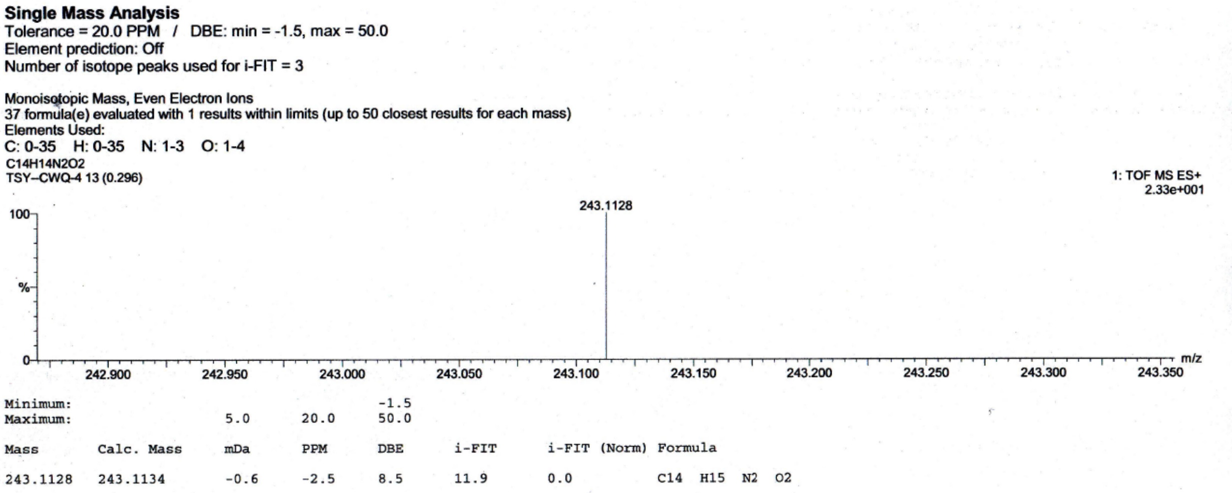
**Single Mass Analysis**
Tolerance = 10.0 PPM / DBE: min = -1.5, max = 50.0
Element prediction: Off
Number of isotope peaks used for i-FIT = 3

Monoisotopic Mass, Even Electron Ions
12 formula(e) evaluated with 1 results within limits (up to 50 closest results for each mass)
Elements Used:
C: 0-35 H: 0-35 N: 0-3
C12H16N2
TSY--CWQ-3 10 (0.240)

```
Minimum:                                 -1.5
Maximum:                5.0      10.0    50.0

Mass       Calc. Mass   mDa      PPM     DBE      i-FIT      i-FIT (Norm) Formula

189.1386   189.1392     -0.6     -3.2    5.5      11.3       0.0          C12  H17  N2
```

### 1,1-dimethyl-2,7-dimethylbenzo[2,1-b:3,4-b’]dipyrrole-4,5-diones(4c):



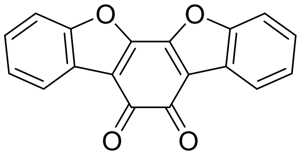


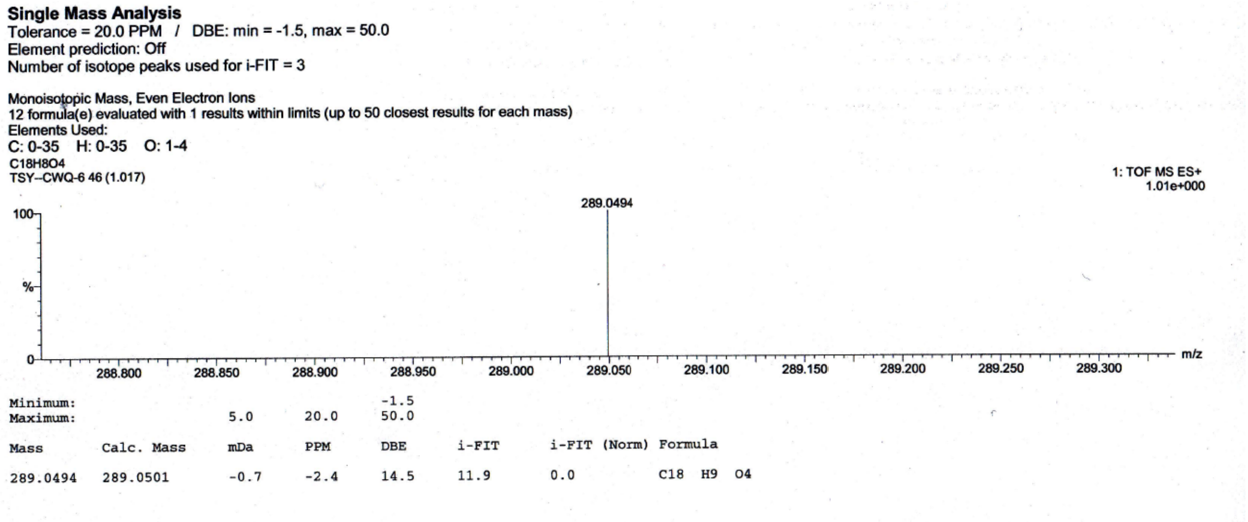
**Single Mass Analysis**
Tolerance = 20.0 PPM / DBE: min = -1.5, max = 50.0
Element prediction: Off
Number of isotope peaks used for i-FIT = 3

Monoisotopic Mass, Even Electron Ions
37 formula(e) evaluated with 1 results within limits (up to 50 closest results for each mass)
Elements Used:
C: 0-35 H: 0-35 N: 1-3 O: 1-4
C14H14N2O2
TSY--CWQ-4 13 (0.296)

```
Minimum:                                 -1.5
Maximum:                5.0      20.0    50.0

Mass       Calc. Mass   mDa      PPM     DBE      i-FIT      i-FIT (Norm) Formula

243.1128   243.1134     -0.6     -2.5    8.5      11.9       0.0          C14  H15  N2  O2
```

## Dibenzo[d,d’]benzo[2,1-b:3,4-b’]difuran-6,7-diones(6a):



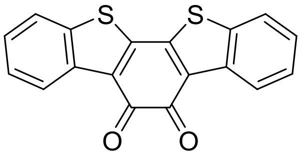


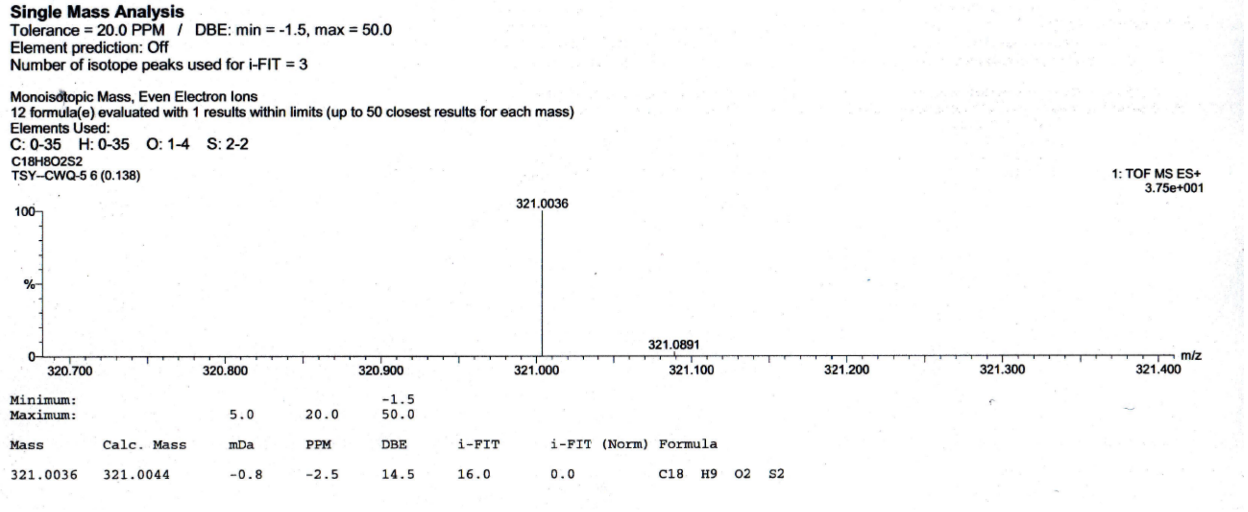
**Single Mass Analysis**
Tolerance = 20.0 PPM / DBE: min = -1.5, max = 50.0
Element prediction: Off
Number of isotope peaks used for i-FIT = 3

Monoisotopic Mass, Even Electron Ions
12 formula(e) evaluated with 1 results within limits (up to 50 closest results for each mass)
Elements Used:
C: 0-35 H: 0-35 O: 1-4
C18H8O4
TSY--CWQ-6 46 (1.017)

```
Minimum:                              -1.5
Maximum:              5.0     20.0    50.0

Mass      Calc. Mass  mDa     PPM     DBE     i-FIT     i-FIT (Norm) Formula

289.0494  289.0501    -0.7    -2.4    14.5    11.9      0.0          C18  H9  O4
```

## Dibenzo[d,d’]benzo[2,1-b:3,4-b’]dithiophene-6,7-diones(6b):



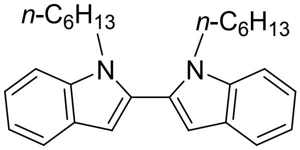


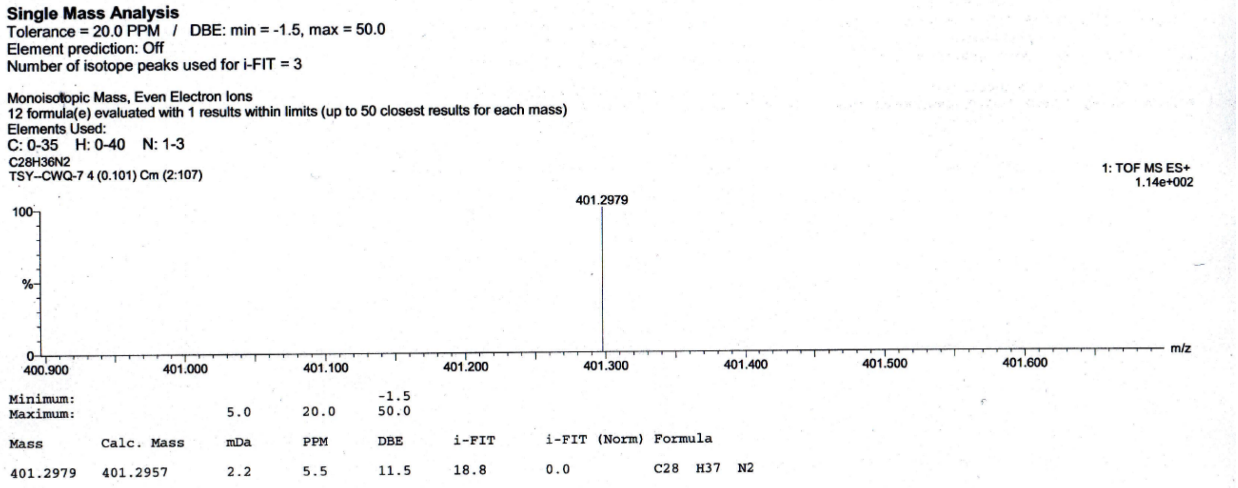
**Single Mass Analysis**
Tolerance = 20.0 PPM / DBE: min = -1.5, max = 50.0
Element prediction: Off
Number of isotope peaks used for i-FIT = 3

Monoisotopic Mass, Even Electron Ions
12 formula(e) evaluated with 1 results within limits (up to 50 closest results for each mass)
Elements Used:
C: 0-35 H: 0-35 O: 1-4 S: 2-2
C18H8O2S2
TSY--CWQ-5 6 (0.138)

```
Minimum:                              -1.5
Maximum:              5.0     20.0    50.0

Mass      Calc. Mass  mDa     PPM     DBE     i-FIT     i-FIT (Norm) Formula

321.0036  321.0044    -0.8    -2.5    14.5    16.0      0.0          C18  H9  O2  S2
```

## **1,1’-di-*n*-hexyl-2,2’-Bibenzoindole(5c)**:



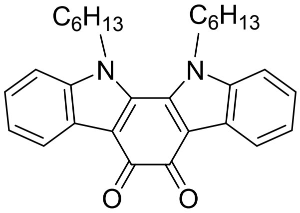


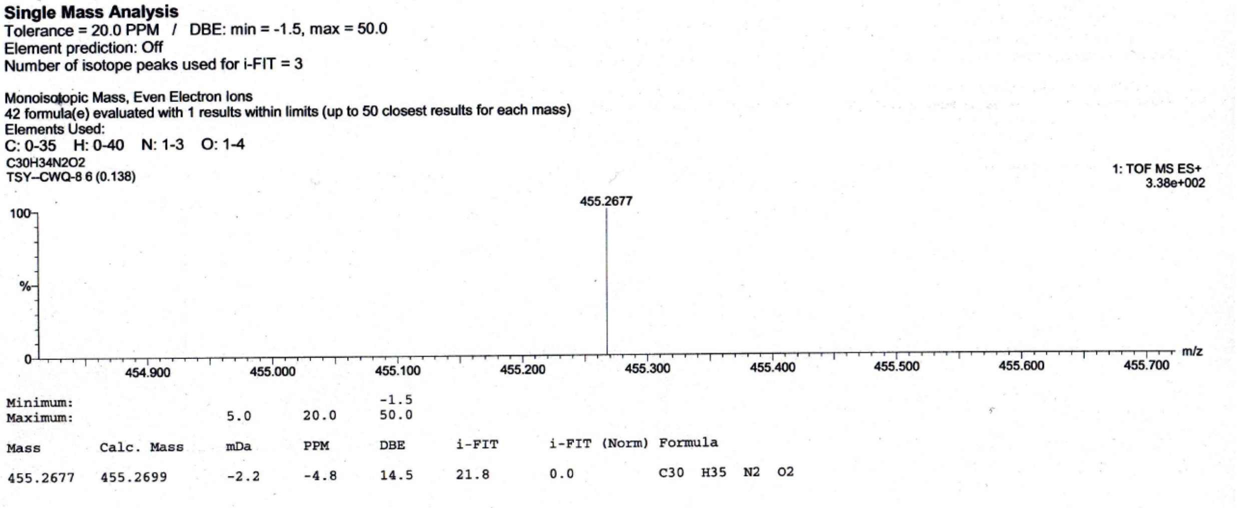
**Single Mass Analysis**
Tolerance = 20.0 PPM / DBE: min = -1.5, max = 50.0
Element prediction: Off
Number of isotope peaks used for i-FIT = 3

Monoisotopic Mass, Even Electron Ions
12 formula(e) evaluated with 1 results within limits (up to 50 closest results for each mass)
Elements Used:
C: 0-35 H: 0-40 N: 1-3
C28H36N2
TSY--CWQ-7 4 (0.101) Cm (2:107)

```
Minimum:                                    -1.5
Maximum:                  5.0      20.0     50.0

Mass       Calc. Mass     mDa      PPM      DBE      i-FIT     i-FIT (Norm) Formula

401.2979   401.2957       2.2      5.5      11.5     18.8      0.0          C28  H37  N2
```

## **1,1’-di-*n*-hexylbenzo[2,1-b:3,4-b’]diindole-6,7-diones(6c):**





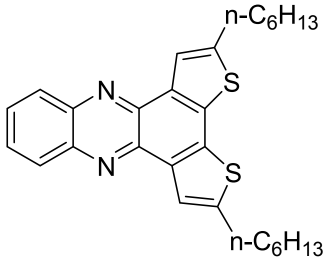
**Single Mass Analysis**
Tolerance = 20.0 PPM / DBE: min = -1.5, max = 50.0
Element prediction: Off
Number of isotope peaks used for i-FIT = 3

Monoisotopic Mass, Even Electron Ions
42 formula(e) evaluated with 1 results within limits (up to 50 closest results for each mass)
Elements Used:
C: 0-35 H: 0-40 N: 1-3 O: 1-4
C30H34N2O2
TSY--CWQ-8 6 (0.138)

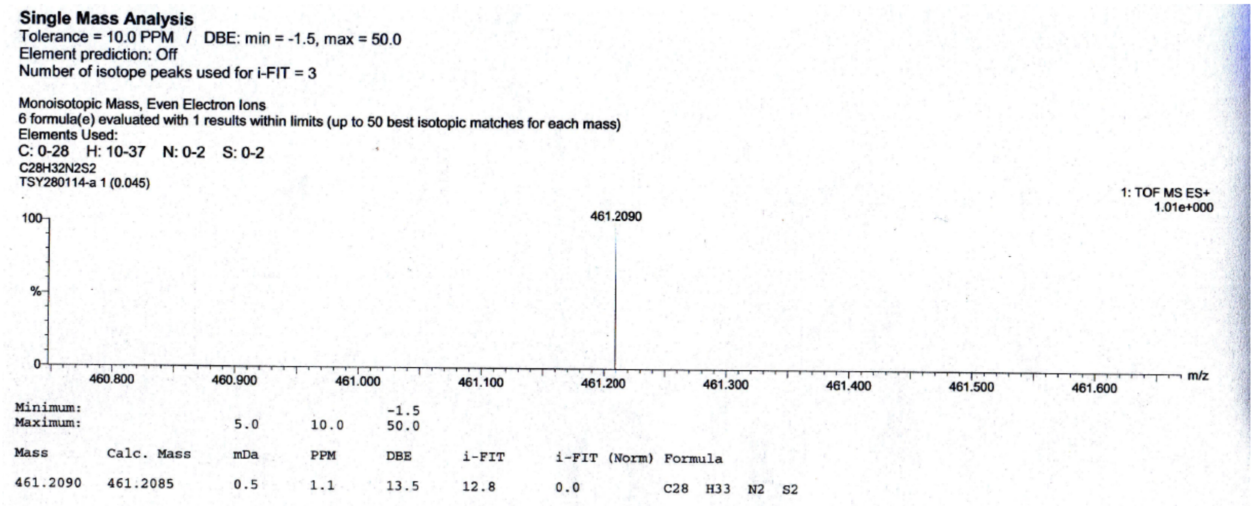
```
Minimum:                                    -1.5
Maximum:                  5.0      20.0     50.0

Mass       Calc. Mass     mDa      PPM      DBE      i-FIT     i-FIT (Norm) Formula

455.2677   455.2699       -2.2     -4.8     14.5     21.8      0.0          C30  H35  N2  O2
```

# 7. Analytical data for the derivative reactions

**7a:**



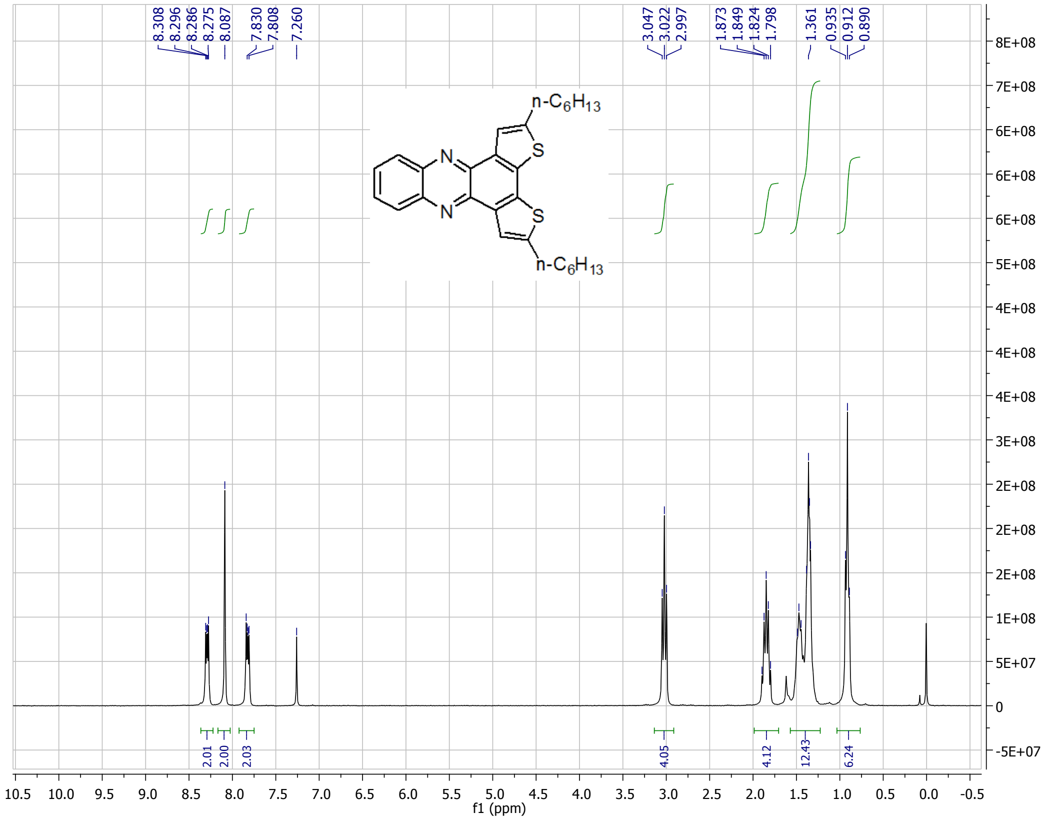
Light yellow solid; $^1$H NMR (400 MHz, CDCl$_3$): δ 8.31–8.28 (m, 2H), 8.09 (s, 2H), 7.84–7.81 (m, 2H), 3.02 (t, *J* = 10.0 Hz, 4H), 1.89–1.80 (m, 4H), 1.49–1.34 (m, 12H), 0.91 (t, *J* = 9.2 Hz, 6H); $^{13}$C NMR (100 MHz, CDCl$_3$):145.2, 141.5, 139.6, 134.8, 134.1, 129.33, 129.28, 121.5, 31.6, 31.5, 30.7, 28.8, 22.6, 14.1; HRMS: calculated for $C_{28}H_{32}N_2S_2 + H^+$, 461.2085; found: 461.2090 (M+).

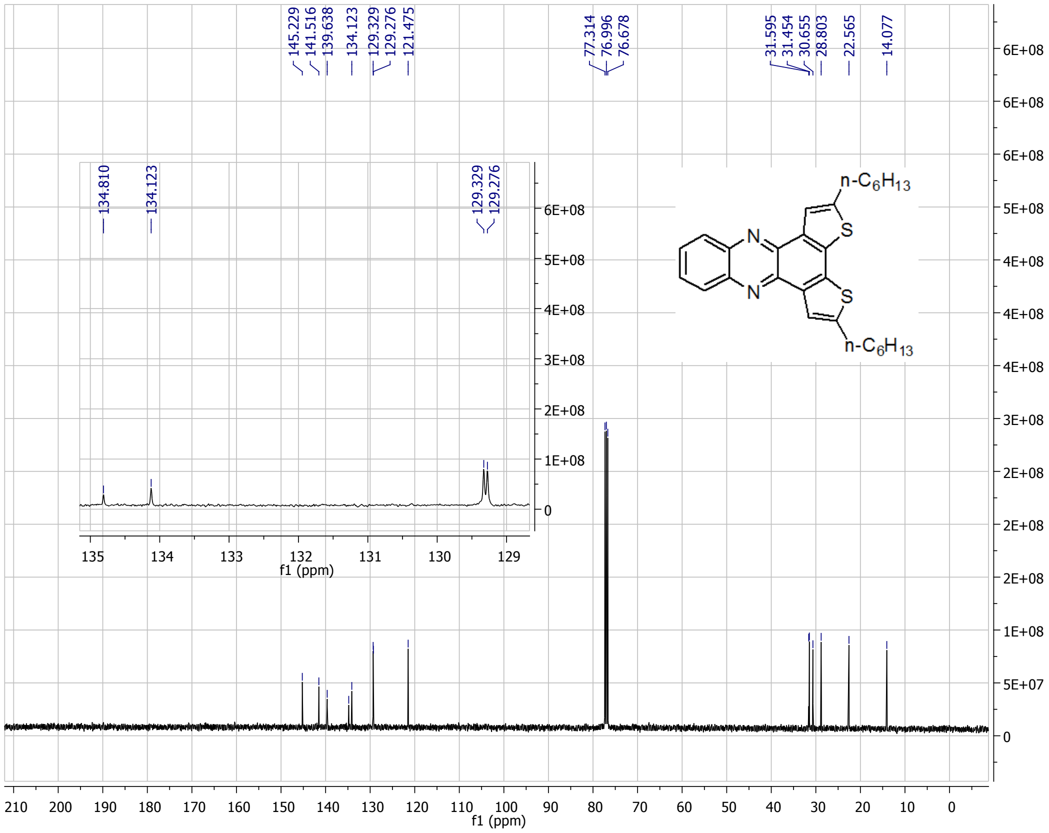


**Single Mass Analysis**
Tolerance = 10.0 PPM / DBE: min = -1.5, max = 50.0
Element prediction: Off
Number of isotope peaks used for i-FIT = 3

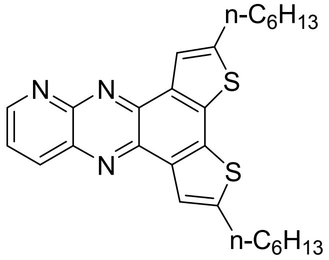
Monoisotopic Mass, Even Electron Ions
6 formula(e) evaluated with 1 results within limits (up to 50 best isotopic matches for each mass)
Elements Used:
C: 0-28 H: 10-37 N: 0-2 S: 0-2
C28H32N2S2
TSY280114-a 1 (0.045)

```
Minimum:                                -1.5
Maximum:                  5.0     10.0   50.0

Mass        Calc. Mass    mDa     PPM    DBE     i-FIT     i-FIT (Norm) Formula

461.2090    461.2085      0.5     1.1    13.5    12.8      0.0          C28  H33  N2  S2
```

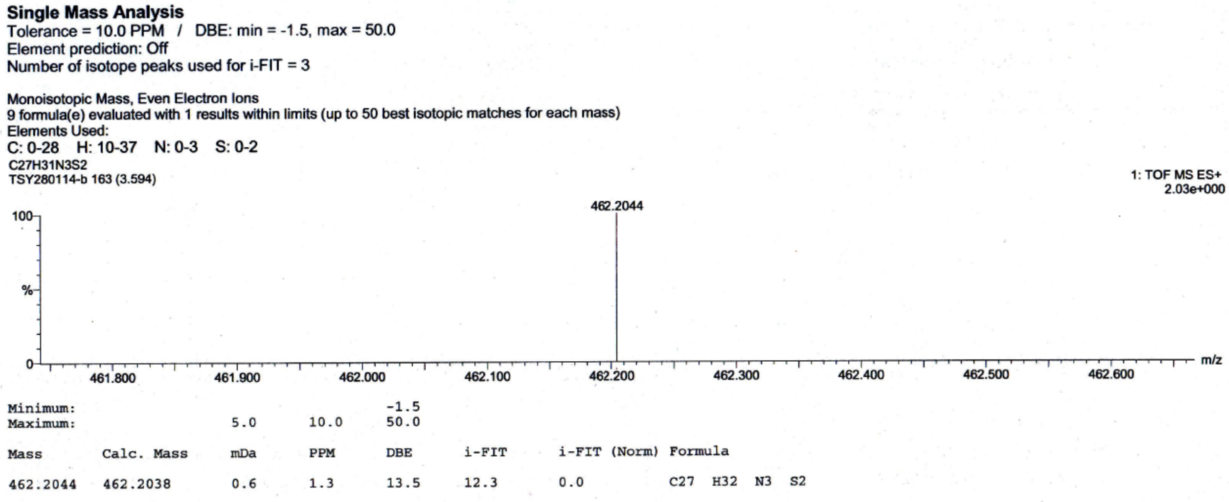

8.308
8.296
8.286
8.275
8.087
7.830
7.808
7.260
3.047
3.022
2.997
1.873
1.849
1.824
1.798
1.361
0.935
0.912
0.890
n-C6H13
N
S
2.01
2.00
2.03
4.05
4.12
12.43
6.24
8E+08
7E+08
6E+08
5E+08
4E+08
3E+08
2E+08
1E+08
5E+07
0
-5E+07
10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5
f1 (ppm)


145.229
141.516
139.638
134.123
129.329
129.276
121.475
77.314
76.996
76.678
31.595
31.454
30.655
28.803
22.565
14.077
134.810
134.123
129.329
129.276
135 134 133 132 131 130 129
f1 (ppm)
n-C6H13
N
S
6E+08
5E+08
4E+08
3E+08
2E+08
1E+08
5E+07
0
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

**7b:**



Yellow solid; $^1$H NMR (400 MHz, CDCl$_3$): δ 9.28 (s, 1H), 8.62 (d, *J* = 10.0 Hz, 1H), 8.23 (s, 1H), 8.02 (s, 1H), 7.78–7.75 (m, 1H), 3.01 (t, *J* = 7.6 Hz, 4H), 1.87–1.80 (m, 4H), 1.47–1.34 (m, 12H), 0.92–0.89 (m, 6H); $^{13}$C NMR (100 MHz, CDCl$_3$): 154.4, 148.7, 145.7, 145.5, 141.3, 140.4, 138.2, 136.7, 136.1, 135.7, 134.0, 133.6, 124.4, 122.2, 121.4, 31.6, 31.4, 31.1, 30.6, 30.5, 28.8, 28.7, 22.5, 14.1; HRMS: calculated for $C_{27}H_{31}N_3S_2 + H^+$, 462.2038; found: 462.2044 (M+).

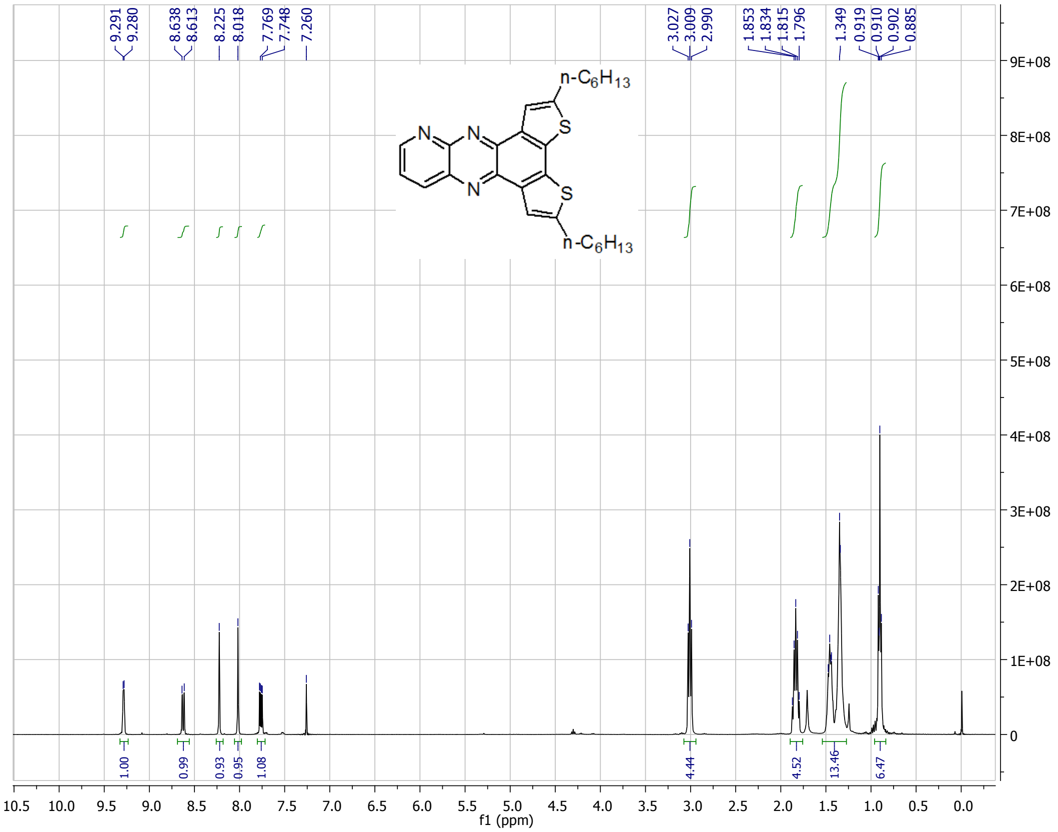


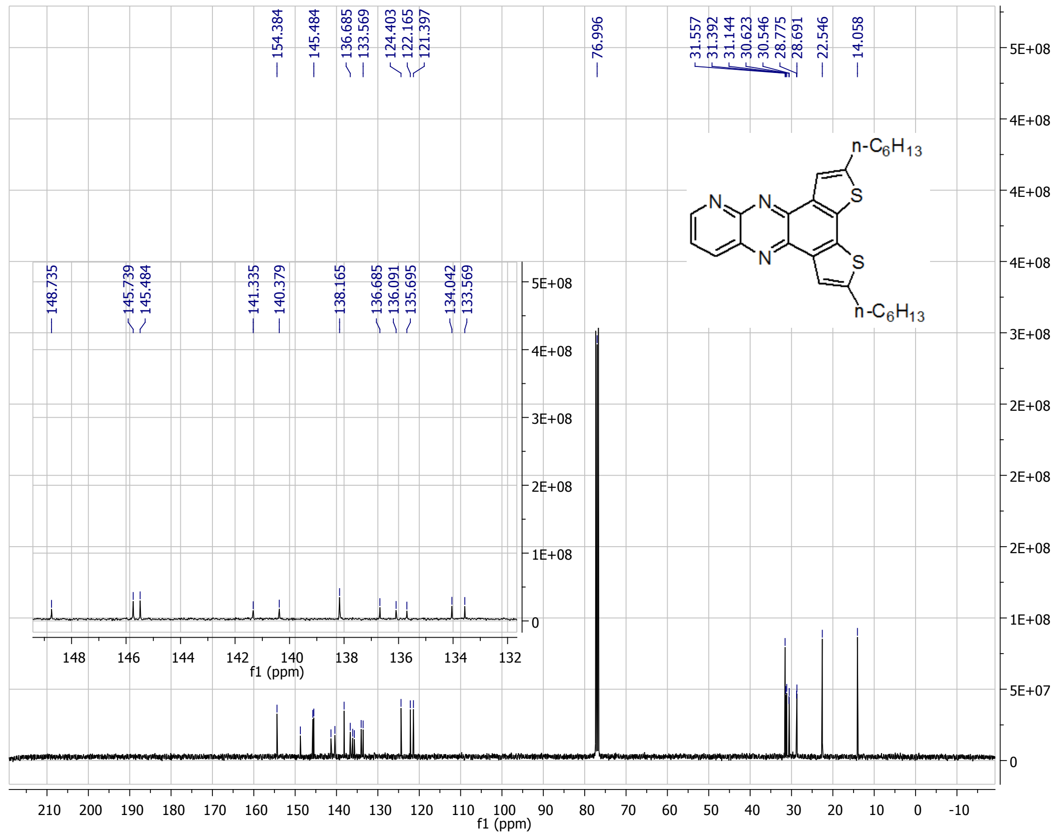
**Single Mass Analysis**
Tolerance = 10.0 PPM / DBE: min = -1.5, max = 50.0
Element prediction: Off
Number of isotope peaks used for i-FIT = 3

Monoisotopic Mass, Even Electron Ions
9 formula(e) evaluated with 1 results within limits (up to 50 best isotopic matches for each mass)
Elements Used:
C: 0-28 H: 10-37 N: 0-3 S: 0-2
C27H31N3S2
TSY280114-b 163 (3.594)

1: TOF MS ES+
2.03e+000

```
Minimum:                              -1.5
Maximum:                5.0    10.0   50.0

Mass      Calc. Mass    mDa    PPM    DBE    i-FIT    i-FIT (Norm) Formula

462.2044  462.2038      0.6    1.3    13.5   12.3     0.0          C27  H32  N3  S2
```


9.291
9.280
8.638
8.613
8.225
8.018
7.769
7.748
7.260
3.027
3.009
2.990
1.853
1.834
1.815
1.796
1.349
0.919
0.910
0.902
0.885
n-C6H13
N
N
N
S
S
n-C6H13
1.00
0.99
0.93
0.95
1.08
4.44
4.52
13.46
6.47
9E+08
8E+08
7E+08
6E+08
5E+08
4E+08
3E+08
2E+08
1E+08
0
10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)


154.384
145.484
136.685
133.569
124.403
122.165
121.397
76.996
31.557
31.392
31.144
30.623
30.546
28.775
28.691
22.546
14.058
n-C6H13
N
N
N
S
S
n-C6H13
148.735
145.739
145.484
141.335
140.379
138.165
136.685
136.091
135.695
134.042
133.569
5E+08
4E+08
3E+08
2E+08
1E+08
0
148 146 144 142 140 138 136 134 132
f1 (ppm)
5E+08
4E+08
4E+08
4E+08
3E+08
2E+08
2E+08
2E+08
1E+08
5E+07
0
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

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