Supporting Information for:

Enhancing sensing of nitroaromatic vapours by thiophene-based polymer films

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Contents

1. General Experimental Methods

All chemicals were purchased from commercial sources (Acros, Aldrich, Alfa Aesar, TCI, and Strem) and used without further purification, unless otherwise noted. THF was distilled from sodium-benzophenone ketyl. Common solvents were purchased from EMD (through VWR). Routine monitoring of reactions was carried out on glass-supported EMD silica gel 60 F_{254} TLC plates. Flash chromatography was performed using silica gel from Sorbent Technologies (Standard Grade, 60 Å, 32-63 μm). All ^{1}H and ^{13}C {^{1}H} NMR spectra were recorded on a Bruker Avance 400 spectrometer, unless otherwise noted. Chemical shifts and coupling constants (*J*) are reported in parts per million (δ) and Hertz, respectively. Deuterated solvents were obtained from Cambridge Isotope Laboratories, Inc. Chloroform-D ($CDCl_3$) contained 0.05% v/v tetramethylsilane (TMS) and Chloroform-D peak was set to 7.26 ppm on all proton spectra. Mass spectroscopic methods were performed by the Mass Spectrometry Center at the University of Illinois, Urbana-Champaign.

Gel permeation chromatography (GPC) was done in the NSF-sponsored Materials Research Science and Engineering Center on Polymers (MRSEC) at the University of Massachusetts Amherst. GPC analyses were performed on a Polymer Laboratories GPC50 integrated system with Chloroform using RI detection. Molecular weights were obtained based on PS standards, with toluene as the flow rate marker, and may be overestimated by a factor of 1.5-2.0.

2. Experimental Procedures

2.1 Monomer Syntheses

The synthesis of compounds (1-4 & 6) was reported in our previous paper *Macromolecules*, 2010, **43**, 8045–8050.

4-(2-Bromo-thiophen-3-yl)-1-(1-hexyl-heptyl)-1H-[1,2,3]triazole (5)

To an oven dried round bottom flask, was added $CuSO_4.5H_2O$(462.15 mg, 1.85 mmol) and sodium ascorbate (1.83 g, 9.25 mmol) followed by the addition of tetra-*n*-butyl ammonium fluoride (TBAF) (37 mL) and tetrahydrofuran (THF) (150 mL). To this stirred solution, water (50 mL) was added followed by the addition of 7-Azido-tridecane (4.7 g, 37.03 mmol) and ((2-bromothiophen-3-yl)ethynyl)trimethylsilane (**3**) (4.8 g,18.51 mmol). The reaction was stirred for 16 h. The reaction was quenched with water and extracted with ethyl acetate (2x50 mL). The combined organics were washed with water (2x50 mL), saturated NaCl solution (1x50 mL), dried over Na_2SO_4, filtered, and concentrated under reduced pressure. Purification of the residue by silica gel chromatography (20:80 EtOAc: hexanes) afforded **5** as colorless oil (4.07 g, 70%). ^1H NMR (400 MHz; $CDCl_3$; Me_4Si) δ 8.12 (1H, s, triazole-H), 7.65-7.66 (1H, d, *J*=5.6, thiophene-H), 7.31-7.32(1H ,d, *J* =5.6, thiophene-H),4.48-4.55 (1H, m, CH), 1.83-1.98 (4H, m, CH_2), 1.21-1.27 (16H, m, CH_2), 0.82-0.86(6H, t, *J*=7.0, CH_3). ^{13}C NMR (400 MHz; $CDCl_3$) – 141.72, 131.98, 127.96, 126.29, 118.99, 108.06, 62.48, 35.75, 31.55, 28.81, 25.90, 22.51, 14.01. HRMS(ESI+) Calc for C19H31N3SBr $(M+H)^+$ 412.1422; Found 412.1424.

(2-Bromo-5-iodo-thiophen-3-yl)-1-(1-hexyl-heptyl)-1H-[1,2,3] triazole (7)

Compound **5** (1.2 g, 3.00 mmol) was dissolved in dichloromethane in a Schlenk flask. To this solution, trifluoromethanesulfonic acid (1.33 mL, 15.02 mmol) was added and the solution is cooled to 0°C using an ice bath. N-iodo succinimide (0.676 g, 3.00 mmol) was added in small portions and the reaction mixture was stirred for 2 h at room temperature. The reaction mixture was quenched with ice-water and extracted with CH_2Cl_2 (3x25 mL)**.** The combined organic extracts were washed with aqueous 10 % sodium bisulfate solution and water (2x25 mL), saturated NaCl solution (1x25 mL) and dried over magnesium sulfate and evaporated under reduced pressure. The residue was purified by silica gel chromatography (15:85 EtOAc: hexanes) to provide **7** (0.94 g, 60%) as a yellow liquid. ^1H NMR (400 MHz; $CDCl_3$; Me_4Si) δ 8.07 (1H, s, triazole-H), 7.84 (1H, s, thiophene-H), 4.47-4.54 (1H, m, CH), 1.81-1.96 (4H, m, CH_2), 1.21-1.27 (16H, m, CH_2), 0.82-0.86(6H, t, *J*=7.0, CH_3). ^{13C}H NMR (400 MHz; $CDCl_3$) δ 140.5, 137.5, 133.9, 118.93, 110.59, 72.49, 62.58, 35.72, 31.54, 28.79, 25.89, 22.51,14.03. HRMS(ESI+) Calc for C19H30N3SBrI $(M+H)^+$ 538.0389; Found 538.0388.

4-(2-Bromo-5-tributylstannanyl-thiophen-3-yl)-1-hexyl-1H-[1,2,3]triazole (8)

4-(2-bromo-5-iodothiophen-3-yl)-1-hexyl-1H-1,2,3-triazole (**6**) (0.9 g, 2.044 mmol) was dissolved in THF in a Schlenk flask under argon atmosphere and kept in ice bath. To this solution, t-Butylmagnesium chloride (1.32 mL, 2.249 mmol) was added and the solution is stirred for 2 h maintaining the temperature at 0 °C using an ice bath. After 2 h, tributyltin chloride (2.20 mL, 8.176 mmol) was added and reaction mixture was stirred for further 2 h maintaining the temperature of the ice bath and monitored by TLC. The reaction mixture was quenched with ice-water and extracted with $CHCl_3$ (3x25 mL)**.** The combined organic extracts were washed with aqueous 10 % sodium bisulfate solution and water (2x25 mL), saturated NaCl solution (1x25 mL) and dried over magnesium sulfate and evaporated under reduced pressure. The residue was purified by silica gel chromatography (10:90 EtOAc: hexanes) to provide **8** as a yellow liquid. ^{1}H NMR (400 MHz; $CDCl_{3;}$ Me_4Si) δ 8.19 (1H, s, triazole-H), 7.68 (1H, s, thiophene-H), 4.39-4.42 (2H, m, CH_2), 1.91-1.98 (2H, m, CH_2), 1.55-1.70 (6H, m, CH_2), 1.25-1.40 (12H, m, CH_2), 1.05-1.15 (6H, m, CH_2), 0.87-0.91(12H, m, CH_3). ^{13}C NMR (400 MHz; $CDCl_3$) δ 150.34, 142.01, 130.79, 123.39, 120.74, 107.07, 70.00, 62.43, 50.59, 36.30, 31.14, 30.26, 28.73,26.14, 22.43, 13.97. HRMS(ESI+) Calc for C24H43N3SBrSn $(M+H)^+$ 604.1383; Found 604.1392.

4-(2-Bromo-5-tributylstannanyl-thiophen-3-yl)-1-(1-hexyl-heptyl)-1H-[1,2,3]triazole (9)

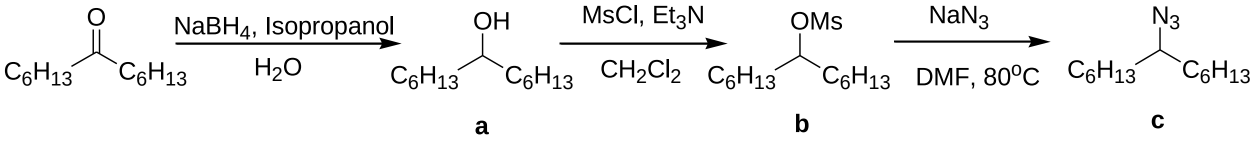
Compound **7** (0.4 g, 0.74 mmol) was dissolved in THF in a Schlenk flask under argon atmosphere and kept in ice bath. To this solution, t-Butylmagnesium chloride (0.48 mL, 0.81 mmol) was added and the solution stirred for 2 h maintaining the temperature at 0 °C using an ice bath. After 2 h, tributyltin chloride (0.80 mL, 2.96 mmol) was added and the reaction mixture was stirred for further 2 h maintaining the temperature of the ice bath and monitored by TLC. The reaction mixture was quenched with ice-water and extracted with $CHCl_3$ (3x25 mL)**.** The combined organic extracts were washed with aqueous 10 % sodium bisulfate solution and water (2x25 mL), saturated NaCl solution (1x25 mL) and dried over magnesium sulfate and evaporated under reduced pressure. The residue was purified by silica gel chromatography (10:90 EtOAc: hexanes) to provide **9** as a yellow liquid. ^{1}H NMR (400 MHz; $CDCl_{3;}$ Me_4Si) δ 8.14 (1H, s, triazole-H), 7.71 (1H, s, thiophene-H), 4.49-4.56 (1H, m, CH), 1.87-1.95 (4H, m, CH_2), 1.57-1.61 (6H, m, CH_2), 1.24-1.37 (28H, m, CH_2), 0.88-0.92 (15H, m, CH_3). ^{13}C NMR (400 MHz; $CDCl_3$) – 141.99, 139.02, 135.78, 132.81, 118.84, 112.49, 62.40, 35.77, 31.56, 28.82, 27.25, 25.89, 22.52, 17.53, 14.02,13.65,10.92. HRMS(ESI+) Calc for C31H57N3SBrSn $(M+H)^+$ 702.2479; Found 702.2473.

Azide Syntheses

1-Azido hexane

In a round bottom flask charged with stirrer, DMSO (60 mL), 1-bromohexane (5 g, 3.62 mmol) and sodium azide (3.52g, 5.43 mmol) were added and stirred overnight. Water was added to quench the reaction and extracted with ethyl acetate (2x50mL). The layers were separated and the aqueous layer was extracted again with ethyl acetate (1x25mL). The combined organics were washed with water (2x50mL), saturated NaCl solution (1x50 mL) and dried over Na_2SO_4, filtered, and concentrated under reduced pressure to afford the colorless oily liquid as product in (3.15 g, 82%) isolated yield. δ_H (400 MHz; $CDCl_3$; Me_4Si) δ 3.23 (2H, t, CH_2), 1.60-1.53 (2H, m, CH_2), 1.36-1.29 (6H,m, CH_2), 0.89 (3H,t, CH_3)

7-Azido-tridecane syntheses.



Tridecan-7-ol (a)

Tridecan-7-one (4.0g, 20.17mmol) was added to an isopropanol/water mixture. Sodium borohydride was added slowly and the reaction was stirred for 12h. After 12 h, ice water (50mL) was added to the reaction mixture and stirred for another 30 min. The layers were separated and the aqueous layer was extracted with hexane (2x25mL). The combined organics were washed with water (2x50mL), saturated NaCl solution (1x50 mL) and dried over Na_2SO_4, filtered, and concentrated under reduced pressure to afford the product (**a**) as white solid (3.5g, 88%) in isolated yield. ^{1}H NMR (400 MHz; $CDCl_3$; Me_4Si) δ 3.58 (1H, m, CH), 1.42-1.28 (20H, m, CH_2), 0.90-0.87 (6H, t, CH_3)

Methanesulfonic acid 1-hexyl-heptyl ester (b)

Tridecan-7-ol (3.0g, 14.97mmol) was dissolved in THF (100mL) and triethylamine (2.29mL, 16.46 mmol) was added to it. To this solution, methanesulfonyl chloride (3.31mL, 42.82mmol) was added dropwise and stirred for 30 min at room temprature. After 30 min, the resulting suspension was filtered and the filtrate was washed with water (1x100mL) and saturated NaCl (1x100mL). The organic layer was dried over Na_2SO_4, filtered, and concentrated under reduced pressure to afford the product (**b)** as yellow oil (3.3g, 80%). It was used in the next step without further purification.

7-Azido-tridecane. (c)

Methanesulfonic acid 1-hexyl-heptyl ester (9.0g, 32.32mmol) was dissolved in DMF (225mL) in a round bottom flask. Sodium azide (10.29g, 158.37mmol) was added slowly to it and the reaction mixture was stirred for 14h in a preheated oil bath at 80 °C. Water was added to quench the reaction and extracted with ethyl acetate (2x50mL). The layers were separated and the aqueous layer was extracted again with ethyl acetate (1x25mL). The combined organics were washed with water (2x50mL), saturated NaCl solution (1x50 mL) and dried over Na_2SO_4, filtered, and concentrated under reduced pressure to afford the product (**c**) as yellow oily liquid ((6.54 g, 90%) isolated yield. ^{1}H NMR (400 MHz; $CDCl_3$; Me_4Si) δ 3.25-3.19 (1H, m, CH), 1.51-1.47 (6H, m, CH_2), 1.30-1.26 (14H, m, CH_2), 0.90-0.87 (6H, t, CH_3)

2.2 Polymer Syntheses

Polymerization Procedure: (P3TzdHT2)

Monomer **7** (175 mg, 0.325 mmol) was dissolved in dry THF in a Schlenk flask (Schlenk-1) covered with aluminum foil under argon atmosphere. The Schlenk was cooled to 0 °C using an ice bath. The reagent *t*-butylmagnesium chloride (0.21 mL, 0.357 mmol) (1.7 M in THF) was added to the solution with a syringe and the mixture was allowed to stir for 2 h. In an another Schlenk flask (Schlenk-2), Ni(dppp)Cl_2 (0.8 mg, 0.0014 mmol) was added in a glove box. The schlenk was taken out of the glove box and 1mL of dry THF was added under argon atmosphere, the solution was stirred for 5 min. The resulting solution was transferred to Schlenk-1. The reaction mixture was taken out from the ice bath and allowed to run for 40 h at 50^{o}C and then quenched using allyl magnesium chloride (0.6 mL, 1.02 mmol). The reaction mixture was precipitated in methanol/water mixture. The polymer was transferred to an extraction thimble and fractionated via Soxhlet extraction with MeOH, $CHCl_3$. The $CHCl_3$ fraction, after concentration under reduced pressure, afforded 80 mg of the polymer. The polymer was washed thrice with hexanes. The polymer isolated was analyzed by GPC. ^{1}H NMR (400 MHz; $CDCl_3$, Me_4Si) δ: 7.68 (1H, s, triazole-H), 7.56 (1H, s, thiophene-H), 4.46(1H, m, CH), 1.83-1.85 (4H, m, CH_2), 1.15 (16H, m, CH_2), 0.75-.0.79 (6H, t, CH_3). M_n= 38.5k, PDI= 1.33

Polymerization Procedure: (P3TzHT)

Monomer **8** (100 mg, 0.165 mmol) and $Pd(PPh_3)_4$ (50 mg, 0.0432 mmol) catalyst were taken in a Schlenk flask inside the glove box. In another Schlenk flask, DMF (2 mL) was degassed for 2 h followed by freeze pump thaw. It was then added to the Schlenk flask containing the monomer and the catalyst. The reaction mixture was degassed again for 3 times by applying vacuum and argon alternately and then transferred to a preheated oil bath (95 ^{o}C). The reaction was carried out for 6 days and the polymer was precipitated into methanol/water mixture. The polymer was transferred to an extraction thimble and fractionated via Soxhlet extraction with MeOH, $CHCl_3$. The $CHCl_3$ fraction, after concentration under reduced pressure, afforded 25 mg of the **P3TzHT** polymer. The polymer was washed thrice with hexanes. The polymer isolated was analyzed by GPC. ^{1}H NMR (400 MHz; $CDCl_{3;}$ Me_4Si) δ: 7.65 (1H, s, triazole-H), 7.64 (1H, s, thiophene-H), 4.36-4.40 (2H, t, CH_2), 1.89-1.95 (2H, m, CH_2), 1.22-1.34 (6H, m, CH_2), 0.80-0.83 (3H, m, CH_3). M_n= 6.3k, PDI= 1.39

Polymerization Procedure: (P3TzdHT)

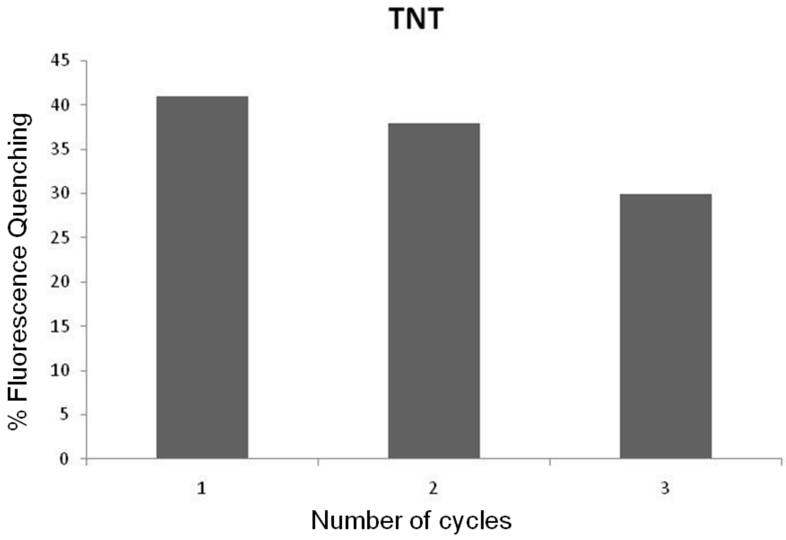
Monomer **9** (153 mg, 0.218 mmol) and $Pd(PPh_3)_4$ (63 mg, 0.0545 mmol) catalyst were taken in a Schlenk flask inside the glove box. In another Schlenk flask, Toluene (2 mL) was degassed for 2 h followed by freeze pump thaw. It was then added to the Schlenk flask containing the monomer and the catalyst. The reaction mixture was degassed again for 3 times by applying vacuum and argon alternately and then transferred to a preheated oil bath (90 ^oC). The reaction was carried out for 4 days and the polymer was precipitated into methanol/water mixture. The polymer was transferred to an extraction thimble and fractionated via Soxhlet extraction with MeOH, $CHCl_3$. The $CHCl_3$ fraction, after concentration under reduced pressure, afforded 30 mg of the **P3TzdHT** polymer. The polymer was washed thrice with hexanes. The polymer isolated was analyzed by GPC. ^1H NMR (400 MHz; $CDCl_{3;}$ Me_4Si) δ: 7.67 (1H, s, triazole-H), 7.56(1H, s, thiophene-H), 4.46 (1H, m, CH), 1.84-1.86 (4H, m, CH_2), 1.15 (16H, m, CH_2), 0.75-0.79 (6H, t, CH_3). M_n= 10.6k, PDI= 1.69

Polymerization Procedure: (P3BSiT)

(4-(2,5-dibromothiophen-3-yl)but-1-yn-1-yl)triisopropylsilane **(12)** (1.722 g, 3.82 mmol) was dissolved in dry THF in a Schlenk flask covered with aluminum foil under argon atmosphere. The reagent *t*-butylmagnesium chloride (2.4 mL, 4.08 mmol) (1.7 M in THF) was added to the solution with a syringe and the mixture was allowed to stir for 18 h. After 18 h, Ni(dppp)Cl_2 (24.4 mg, 0.0045 mmol) was added under argon atmosphere and the reaction mixture was stirred for further 2 h. After 2 h, the reaction mixture was quenched using allyl magnesium bromide (0.6 mL, 1.02 mmol). The reaction mixture was precipitated in ice-cold methanol. The polymer was transferred to an extraction thimble and fractionated via Soxhlet extraction with MeOH, $CHCl_3$. The $CHCl_3$ fraction, after concentration under reduced pressure, afforded 233 mg of the **P3SiBT** polymer. The polymer isolated from the $CHCl_3$ fraction was analyzed by GPC. ^1H NMR (400 MHz; $CDCl_{3;}$ Me_4Si) δ: 7.25 (1H, s, thiophene-H), 3.05-3.08 (2H, t, CH_2), 2.63-2.66 (2H, t, CH_2), 1.04-1.06 (21H, m, TIPS), M_n= 10.7 k, PDI= 1.12.

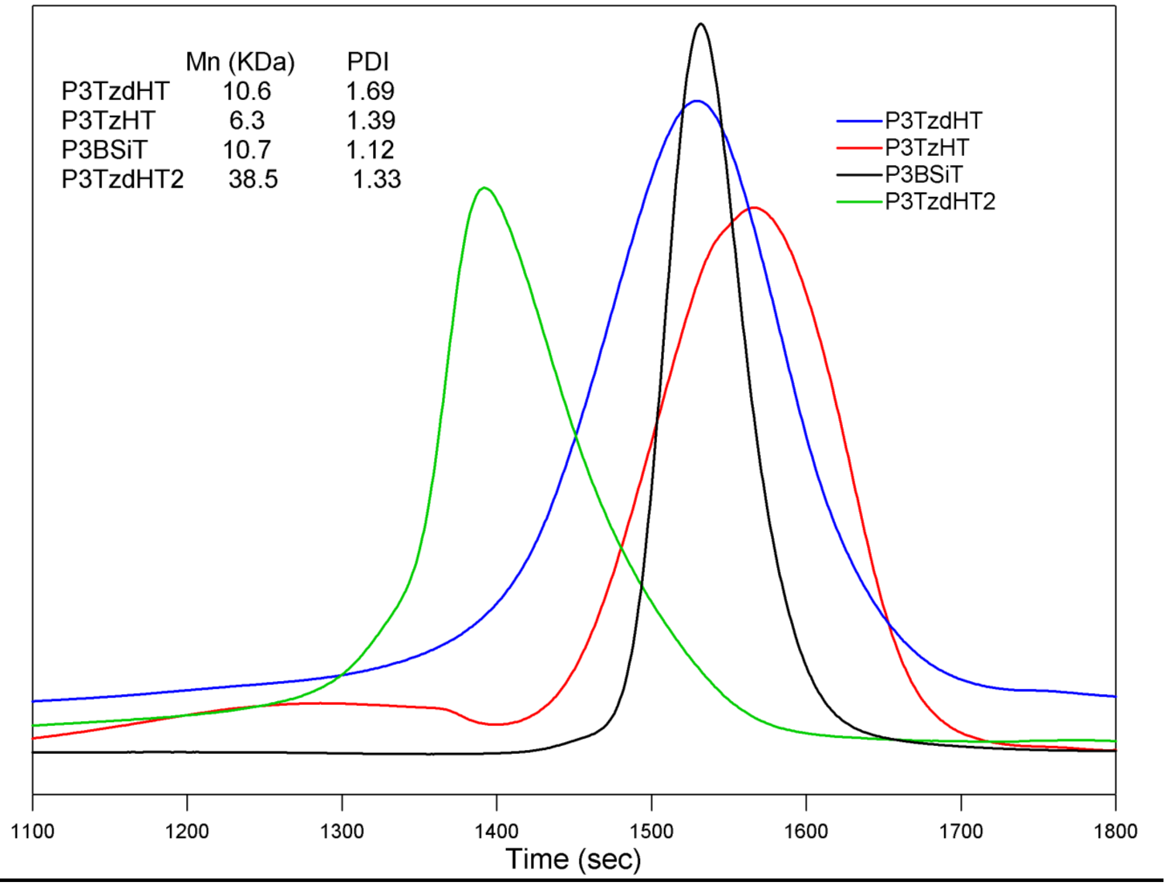
3. Recycled sensitivity of P3TzdHT2 towards TNT

Figure S1. Recycled sensitivity of P3TzdHT2 towards TNT



4. GPC Data

Figure S2. GPC of Polymers



5. Table for C-H----O-N Distance

TableS1. C-H---O-N Distance

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LOLHEA	2.471
LOLHEA	2.438
LOLJAY	2.329
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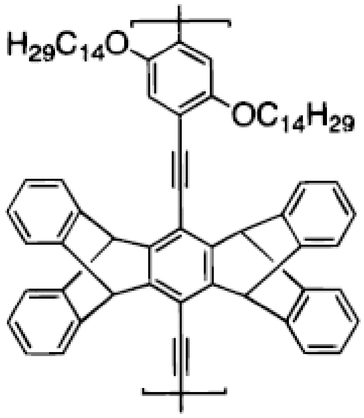
6. Pentiptycene derived polymer structure

Figure S3. Chemical Structure of Polymer 1



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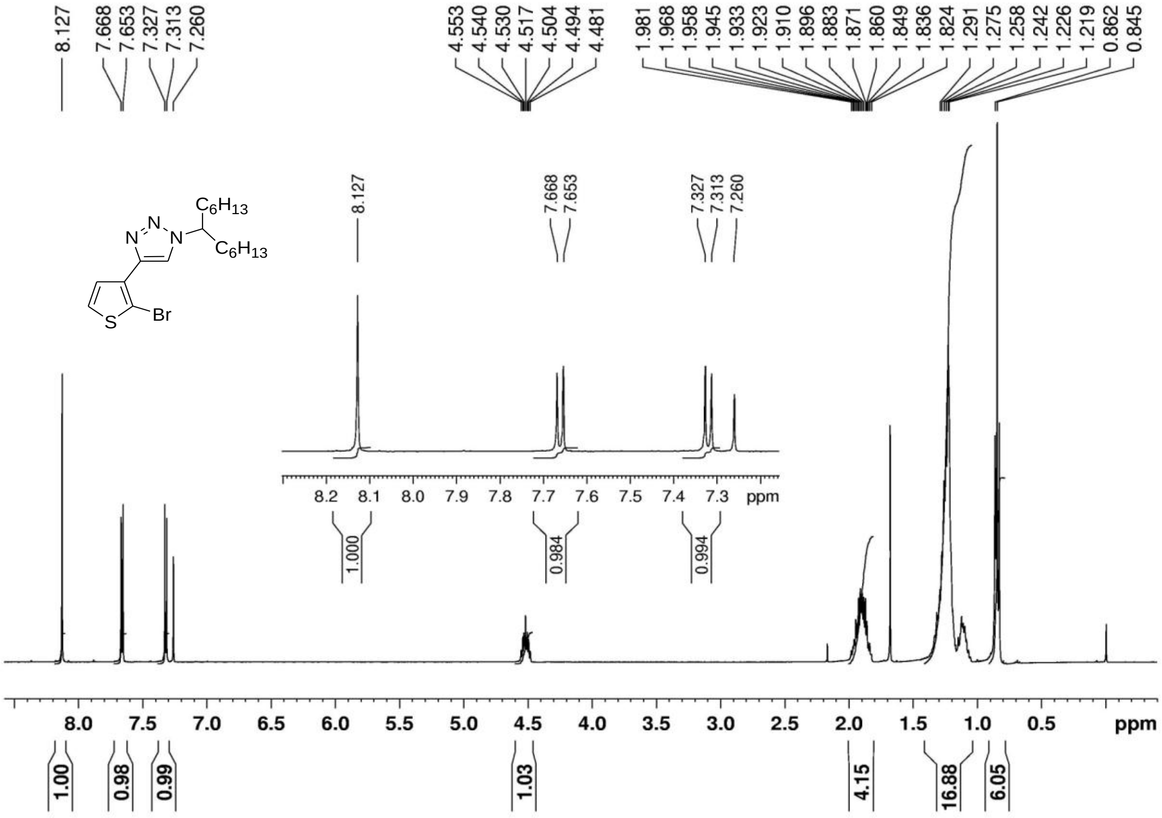
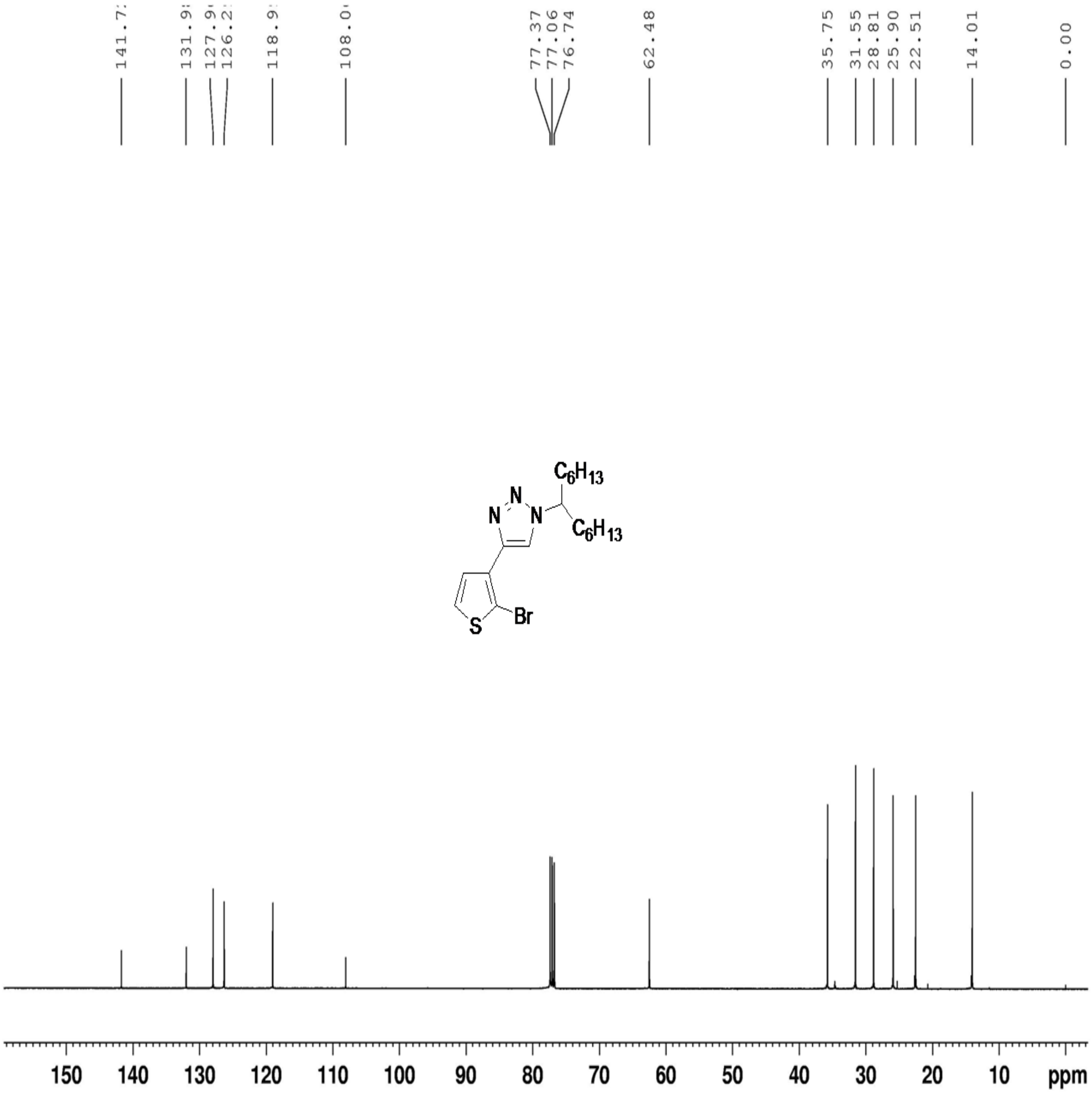
7. NMR Spectra (in $CDCl_3$ unless otherwise indicated)

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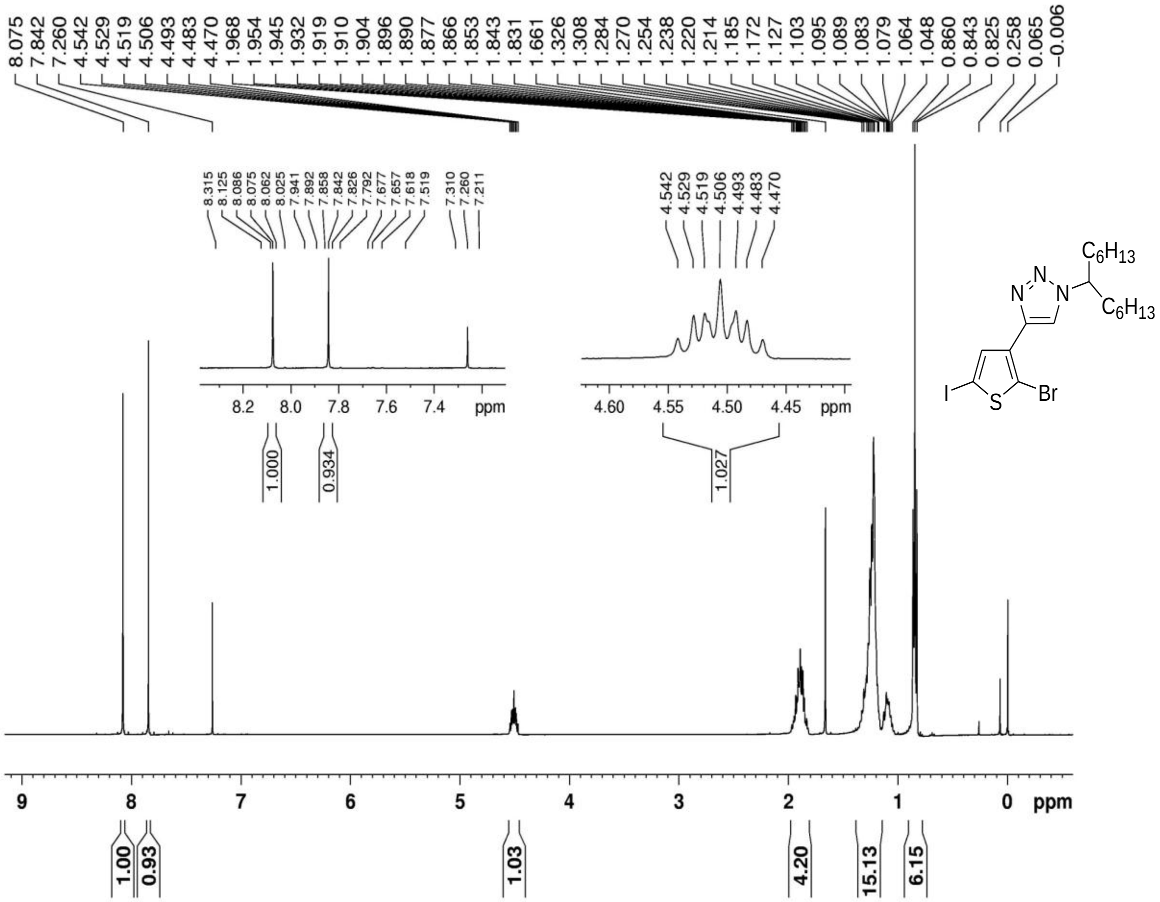
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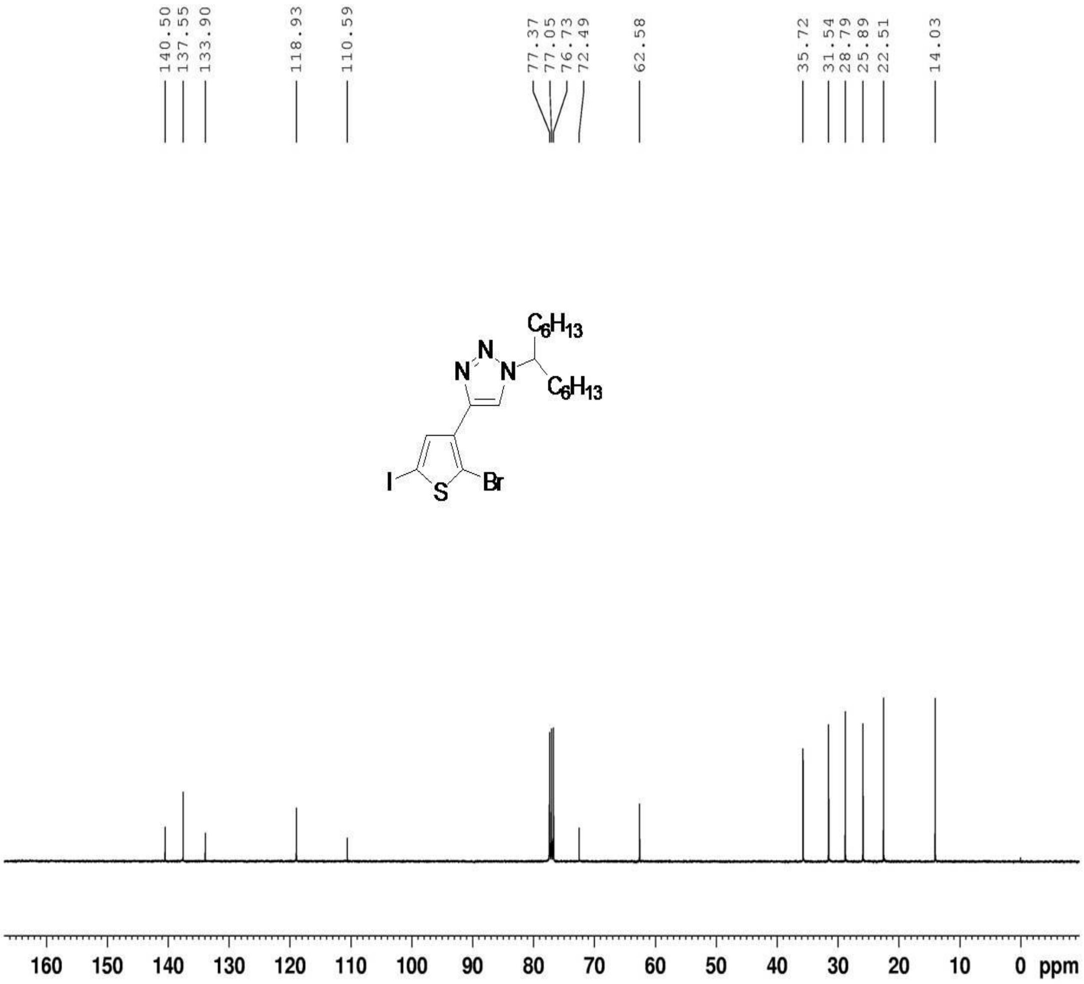
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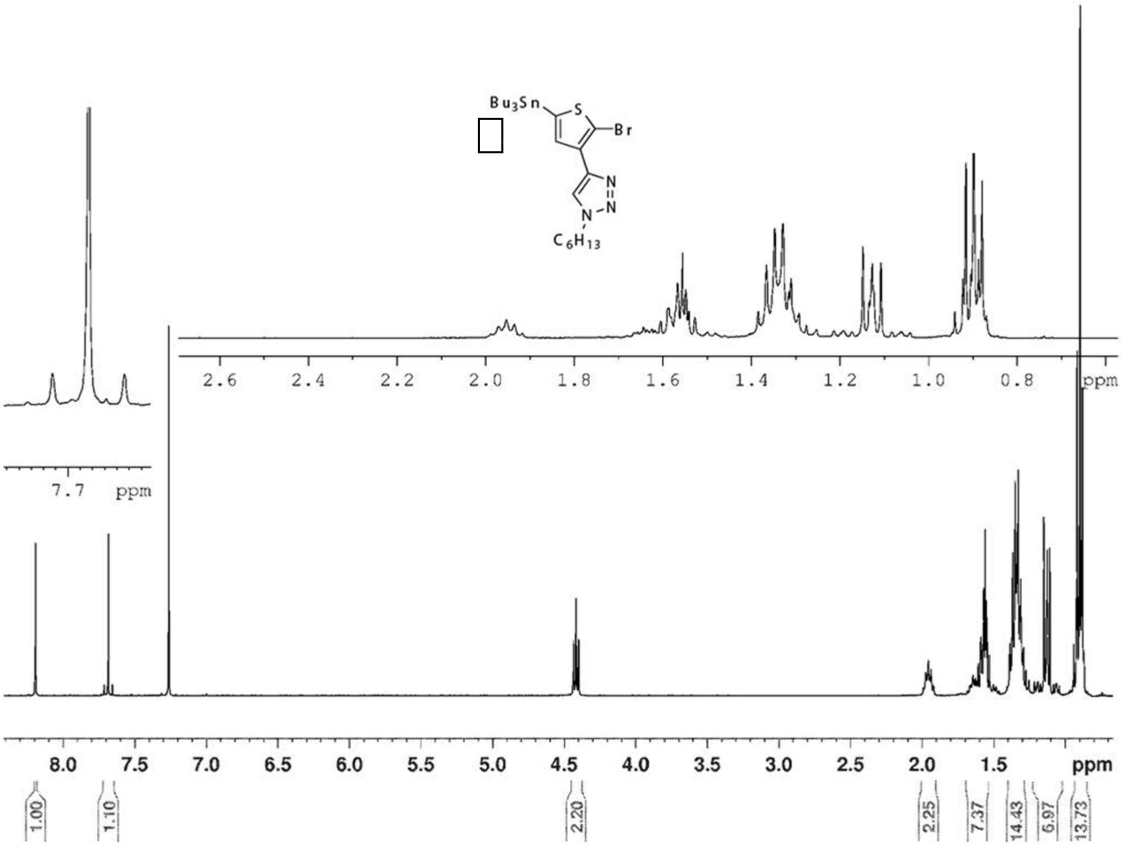
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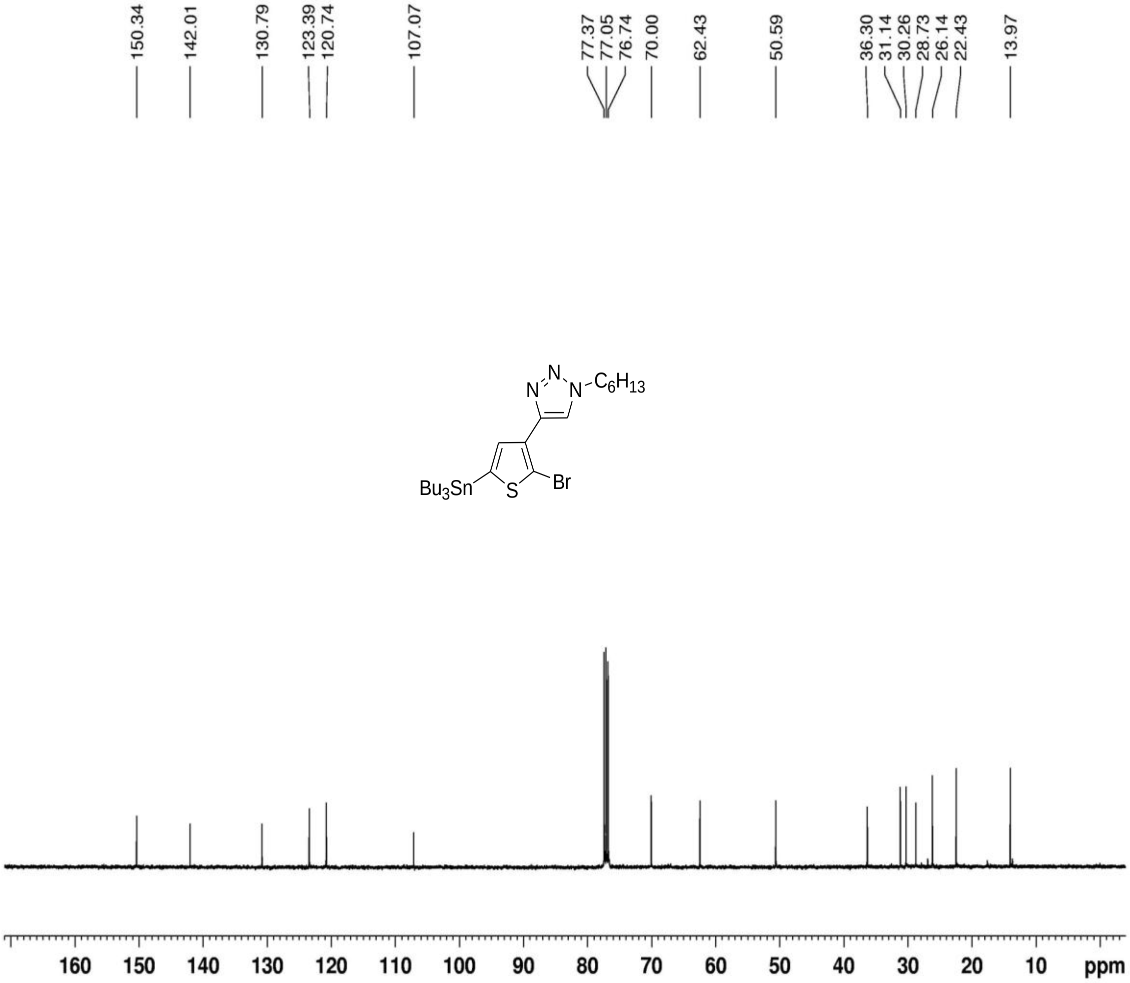
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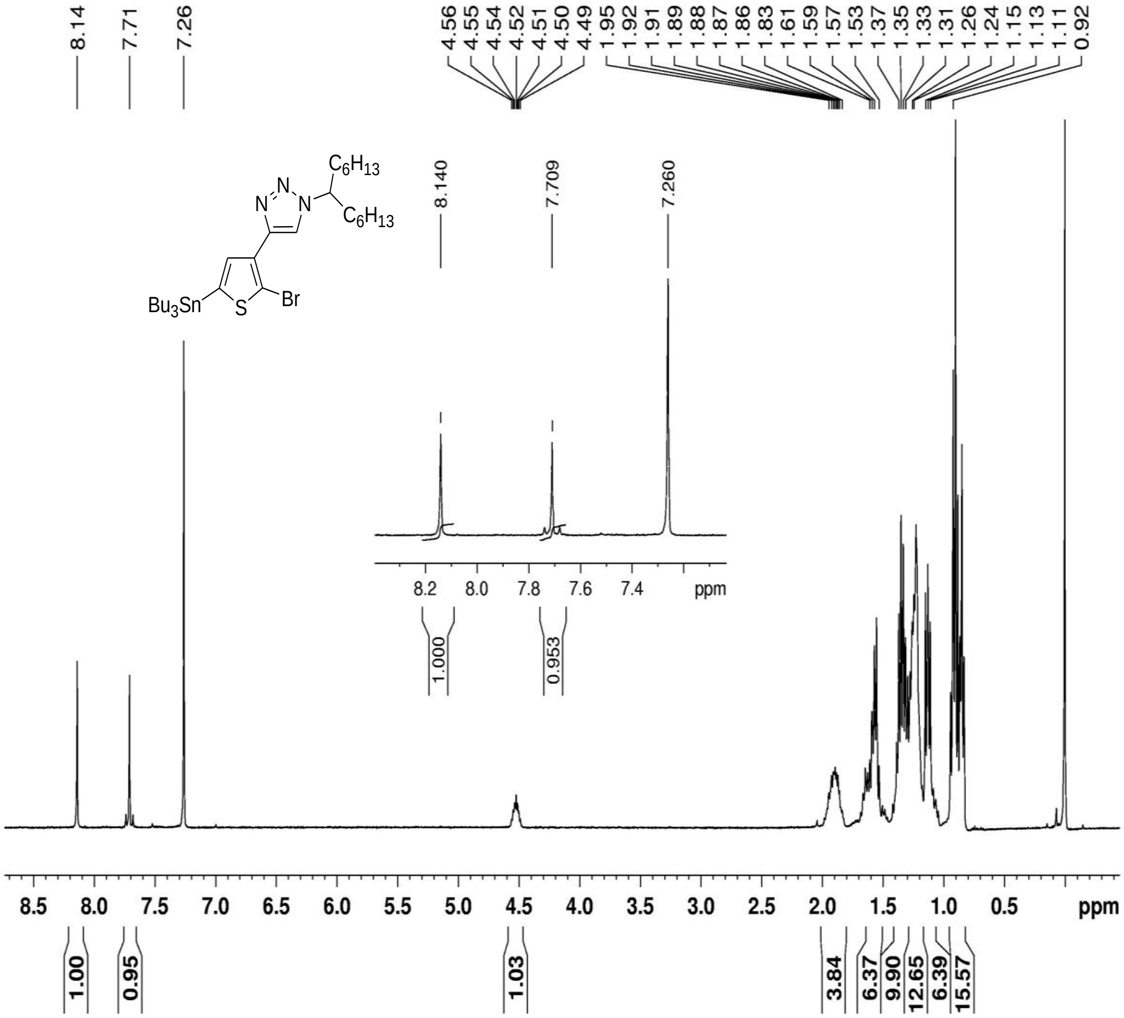
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1.57
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1.31
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C6H13
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6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
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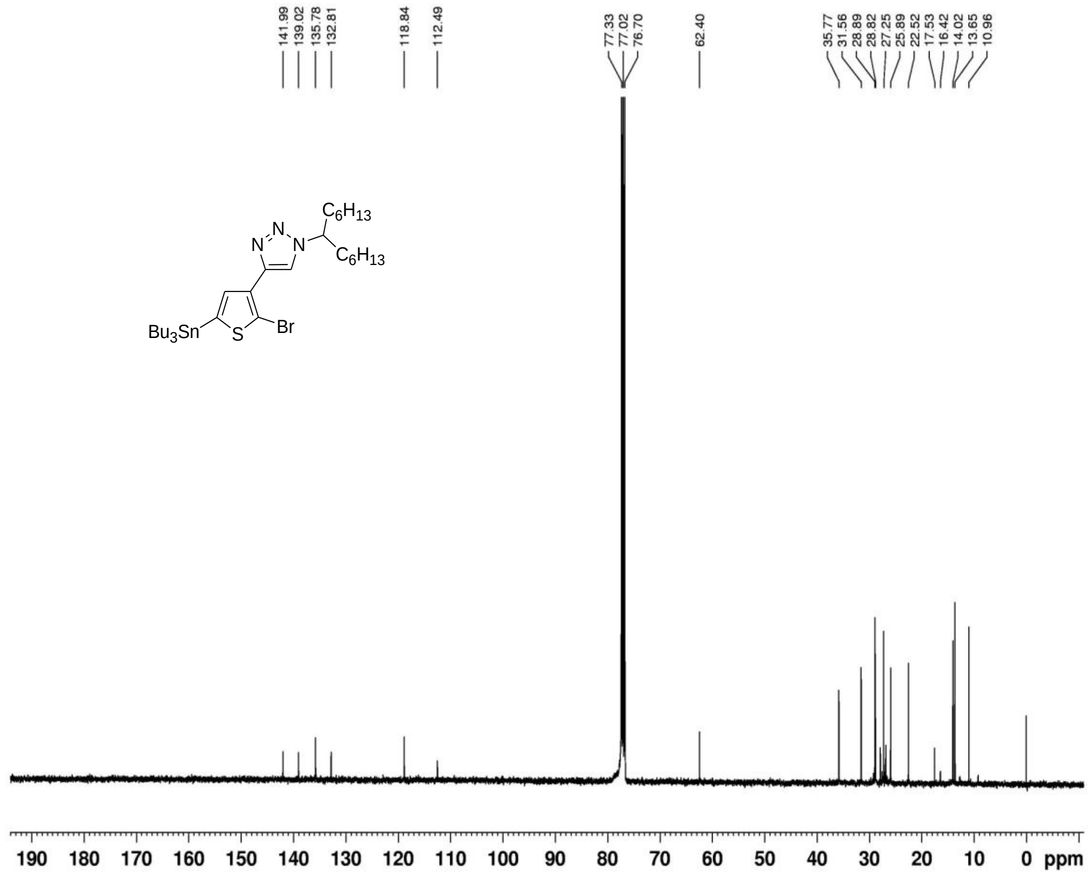
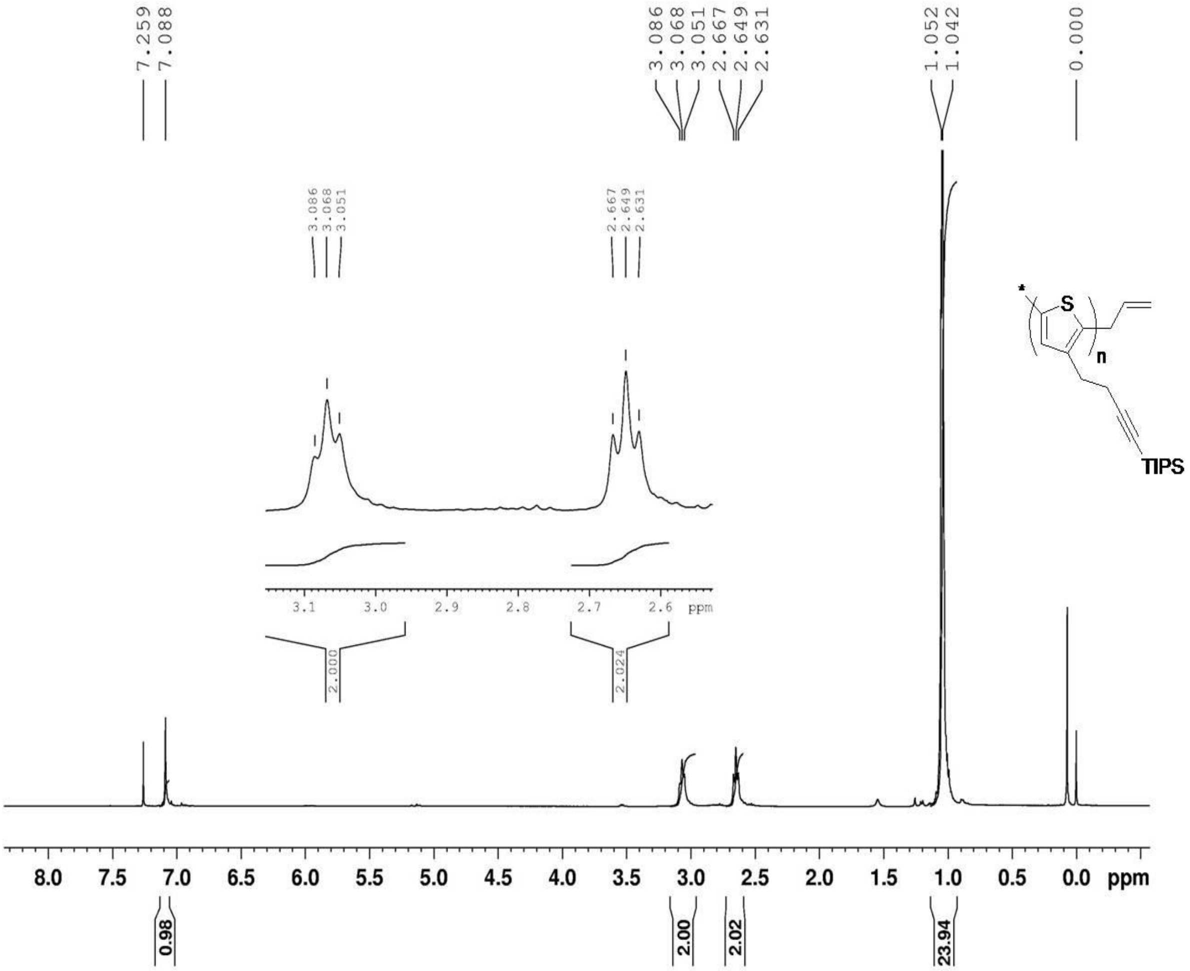
ppm
1.00
0.95
1.03
3.84
6.37
9.90
12.65
6.39
15.57


141.99
139.02
135.78
132.81
118.84
112.49
77.33
77.02
76.70
62.40
35.77
31.56
28.89
28.82
27.25
25.89
22.52
17.53
16.42
14.02
13.65
10.96
C6H13
N
N
N
C6H13
Bu3Sn
S
Br
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
ppm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7.088
3.086
3.068
3.051
2.667
2.649
2.631
1.052
1.042
0.000
3.1
3.0
2.9
2.8
2.7
2.6
ppm
2.000
2.024
S
n
TIPS
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
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2.0
1.5
1.0
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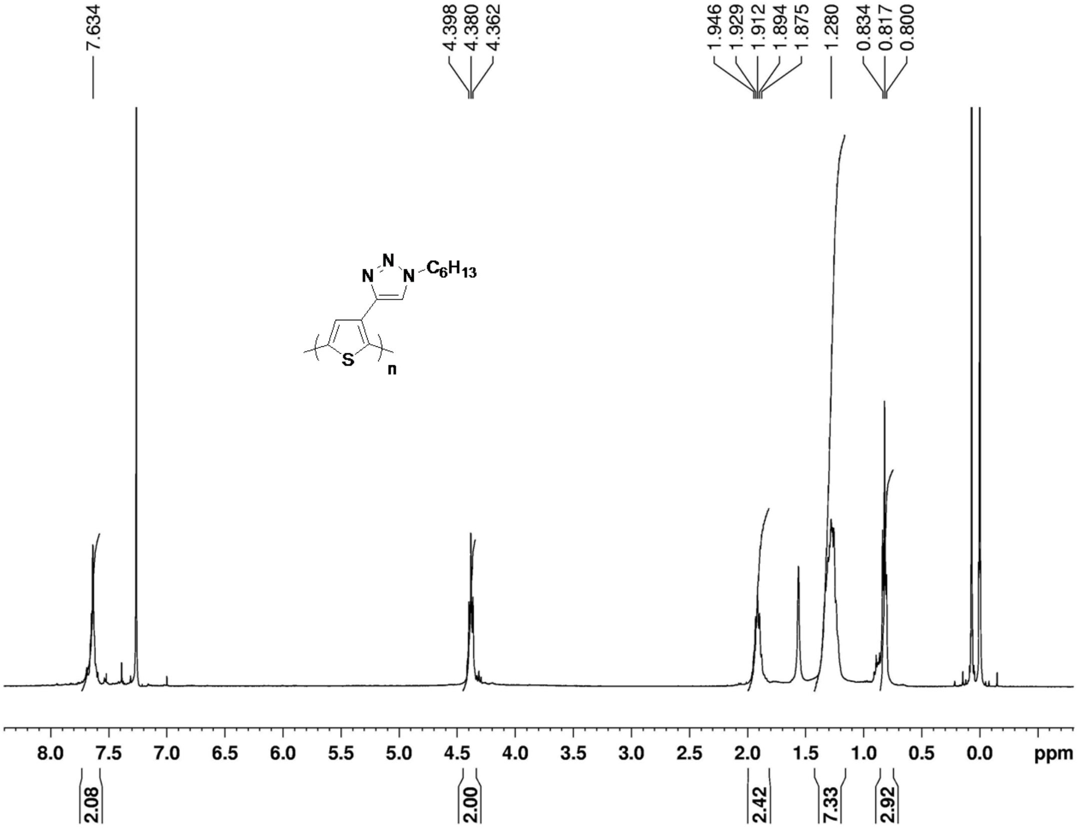
0.0
ppm
0.98
2.00
2.02
23.94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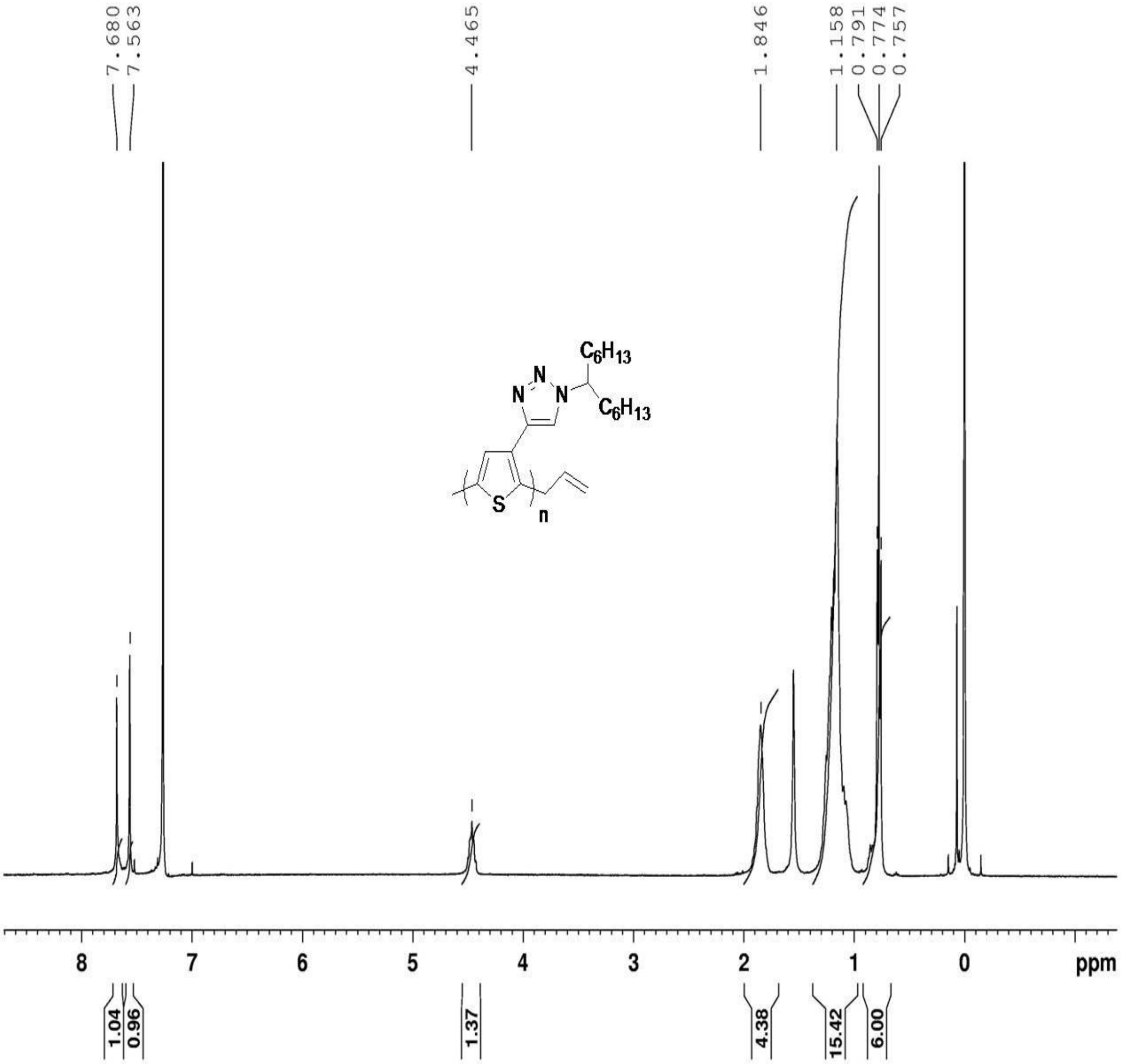
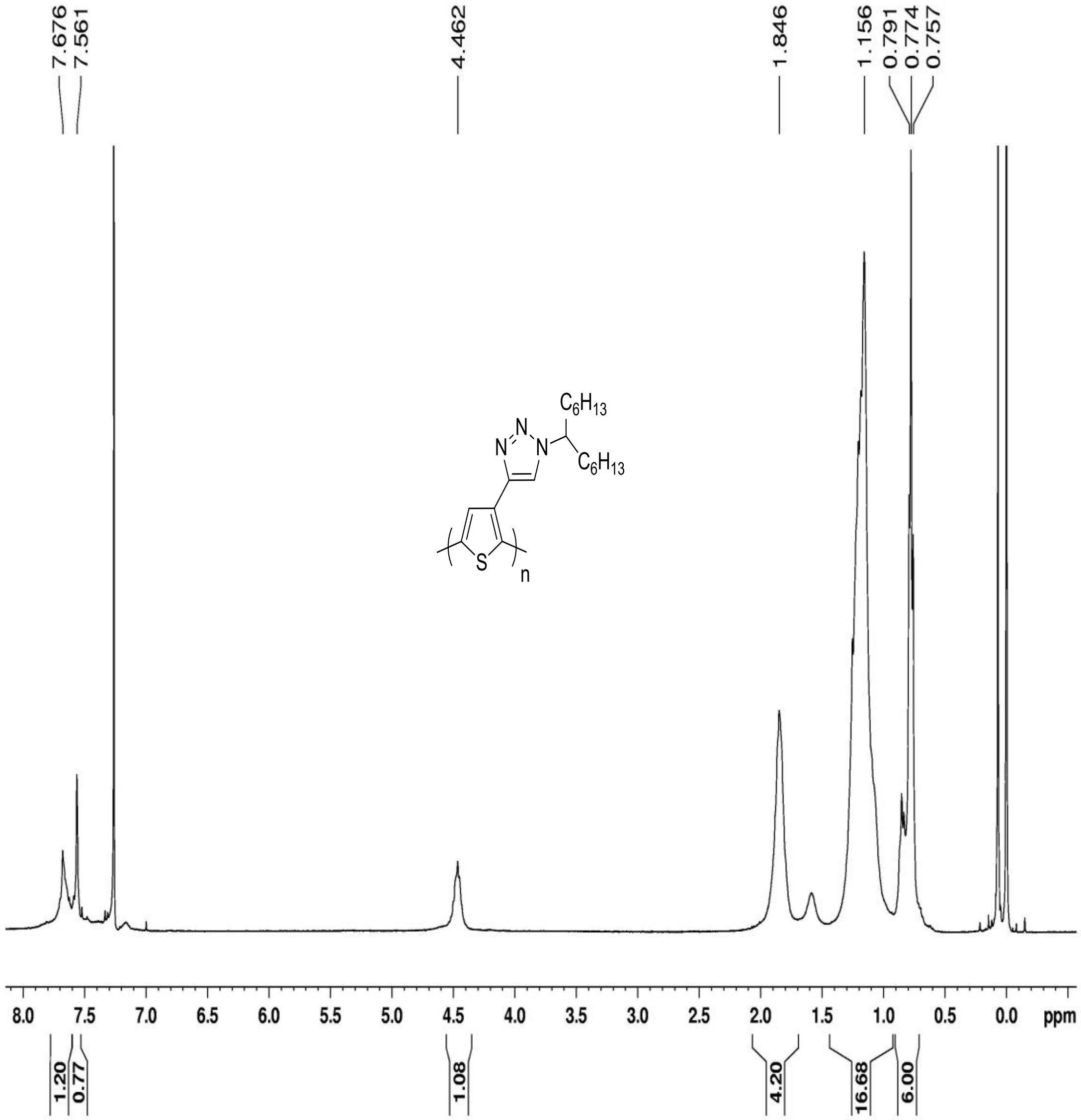
4.398
4.380
4.362
1.946
1.929
1.912
1.894
1.875
1.280
0.834
0.817
0.800
N
N
N
C6H13
S
n
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
ppm
2.08
2.00
2.42
7.33
2.92


7.680
7.563
4.465
1.846
1.158
0.791
0.774
0.757
C6H13
C6H13
N
N
N
S
n
8
7
6
5
4
3
2
1
0
ppm
1.04
0.96
1.37
4.38
15.42
6.00


7.676
7.561
4.462
1.846
1.156
0.791
0.774
0.757
C6H13
N
N
N
C6H13
S
n
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
ppm
1.20
0.77
1.08
4.20
16.68
6.00