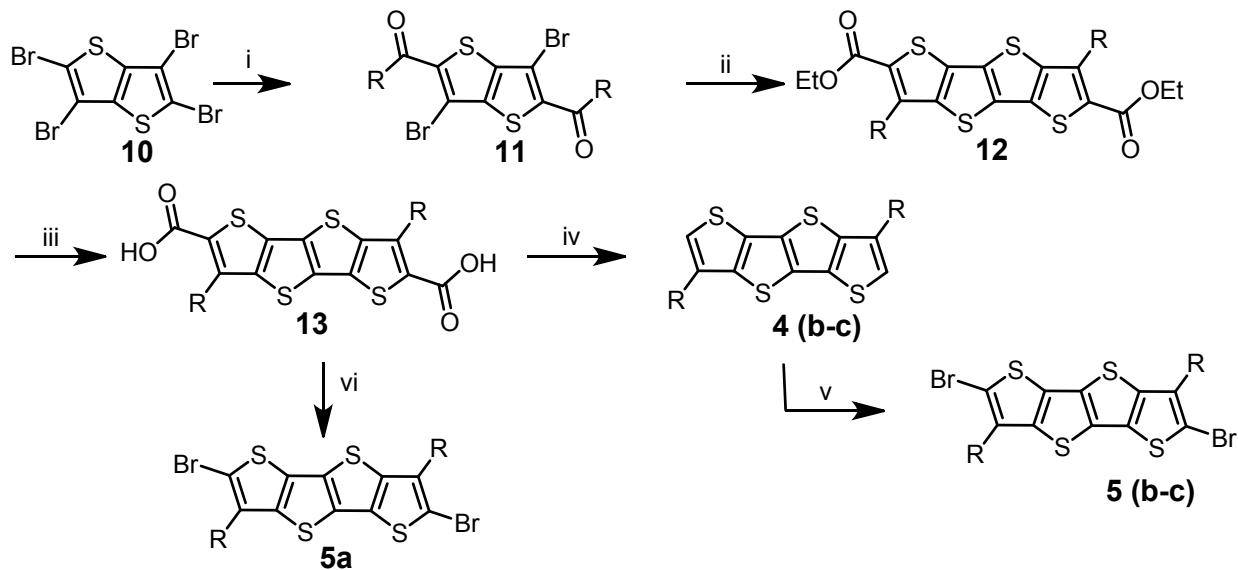


## Supporting Information

### New Branched Alkyl Tetrathienothiophene (TTAR)-Based Organic Sensitizers with Power Conversion Efficiency up to 11%

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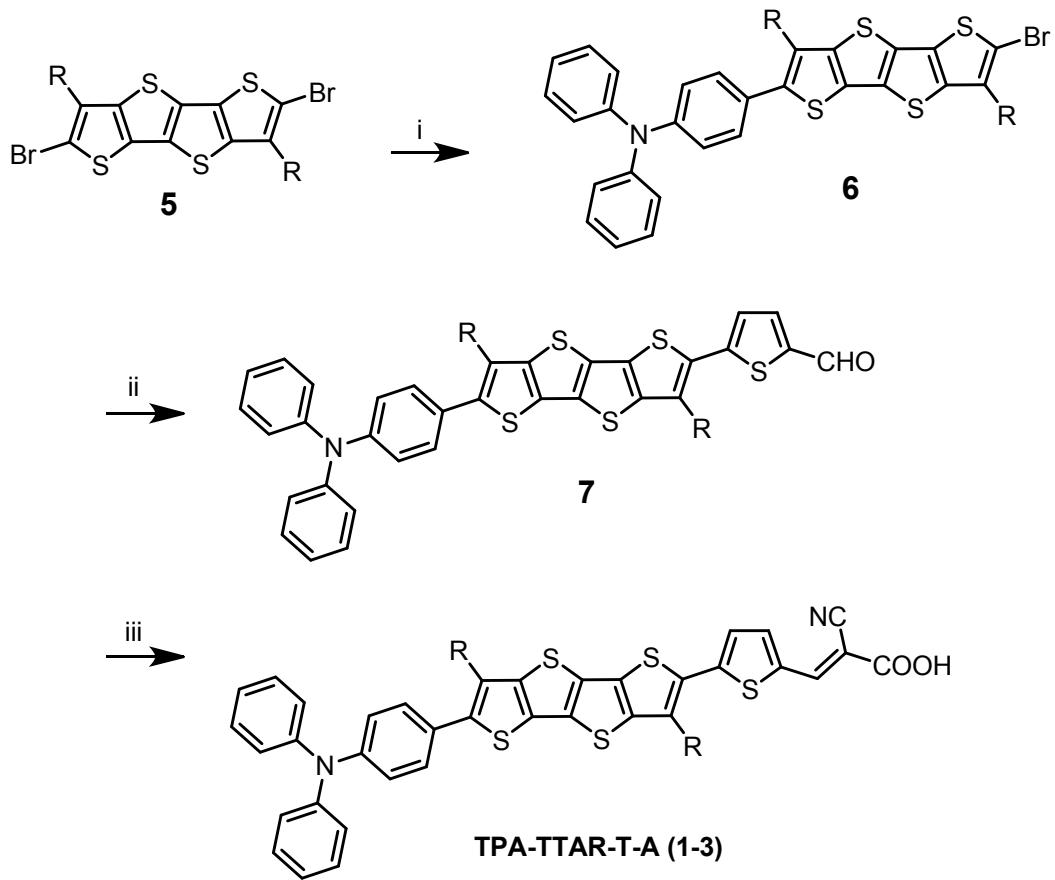
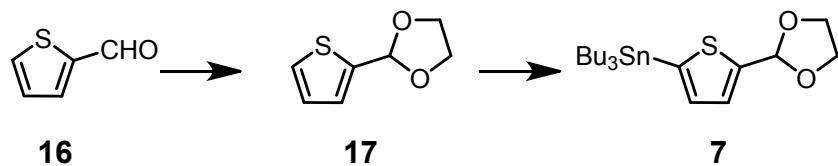
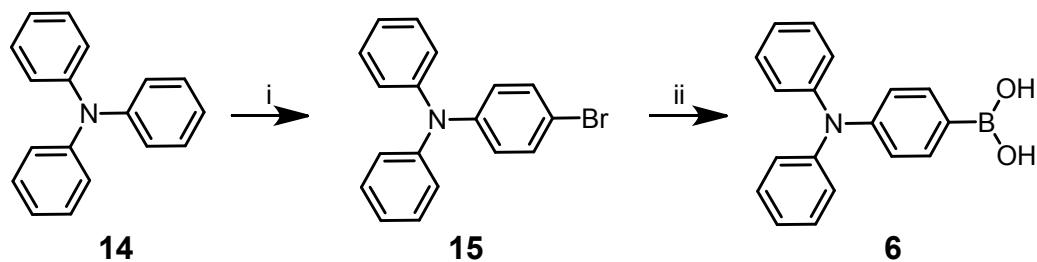
#### 1. Synthetic routes



- a) R= b-C<sub>8</sub>H<sub>17</sub>
- b) R= C<sub>15</sub>H<sub>31</sub>
- c) R= C<sub>9</sub>H<sub>19</sub>

**Scheme S1.** Synthetic route for the dibrominated tetrathienoacene **5 (a-c)**.

Reaction conditions: (i) a) n-BuLi, THF, -78 °C, b) RCOCl; (ii) HS-CH<sub>2</sub>-COOC<sub>2</sub>H<sub>5</sub>, K<sub>2</sub>CO<sub>3</sub>, DMF, 60 °C; (iii) 10% NaOH, THF/MeOH, reflux; (iv) Cu, quinoline, 250 °C; (v) NBS, CH<sub>2</sub>Cl<sub>2</sub>/DMF, rt, under dark; (vi) NBS, NMP.

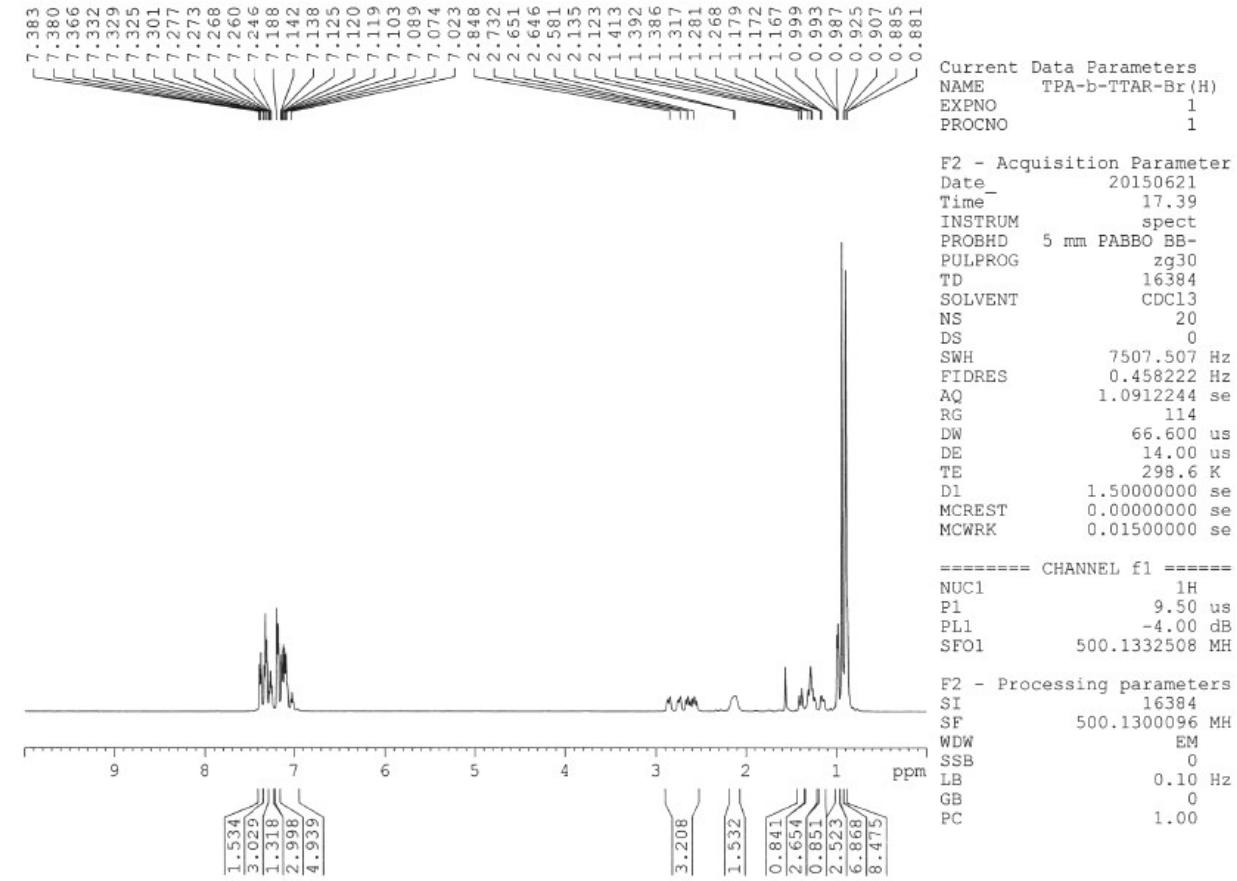


R= a) b-C<sub>8</sub>H<sub>17</sub>  
 b) C<sub>15</sub>H<sub>31</sub>  
 c) C<sub>9</sub>H<sub>19</sub>

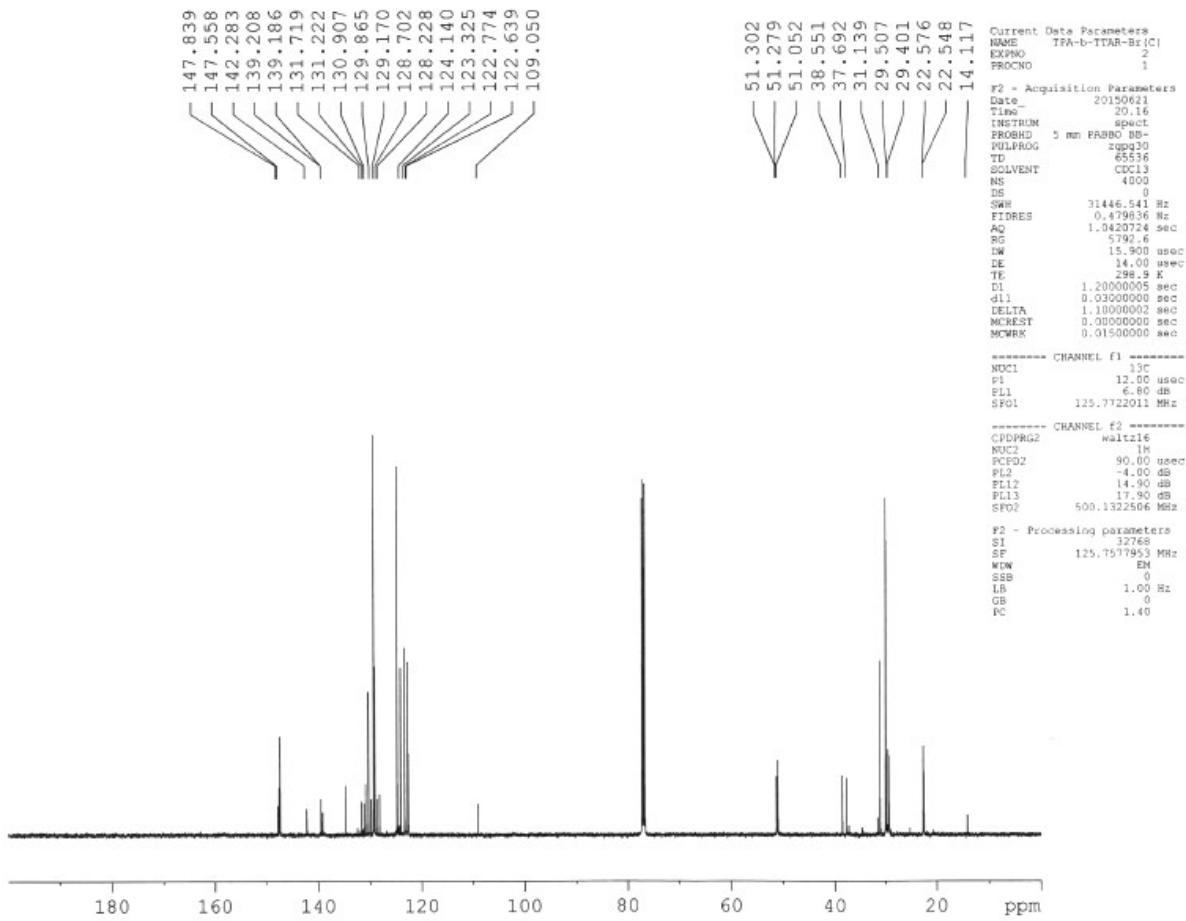
**Scheme S2.** Synthetic route for the sensitizer **TPA-TTAR-T-A (1-3)**.

Reaction conditions: (i) (4-(diphenylamino)phenyl)boronic acid, Pd(PPh<sub>3</sub>)<sub>4</sub>, 2M K<sub>2</sub>CO<sub>3</sub>, toluene, reflux; (ii) a) (5-(1,3-dioxolan-2-yl)thiophen-2-yl)tributylstannane, Pd(PPh<sub>3</sub>)<sub>4</sub>, toluene, reflux, b) dil. HCl; (iii) NC-CH<sub>2</sub>-COOH, piperidine, CHCl<sub>3</sub>, 70 °C.

## 2. <sup>1</sup>H-NMR and <sup>13</sup>C-NMR spectra details



<sup>1</sup>H-NMR of compound 8a



### <sup>13</sup>C-NMR of compound 8a

[ Elemental Composition ]

Data : 1040319-003

Sample: TPA-b-TTAR-Br

Note : HRFAB-797.1853

Inlet : Direct

Date : 19-Mar-2015 10:29

Page: 1

RT : 2.56 min

Ion Mode : FAB+

Scan#: 16

Elements : C 44/0, H 110/0, Br 1/0(79Br 1/0, 81Br 1/0), N 1/0, S 4/0

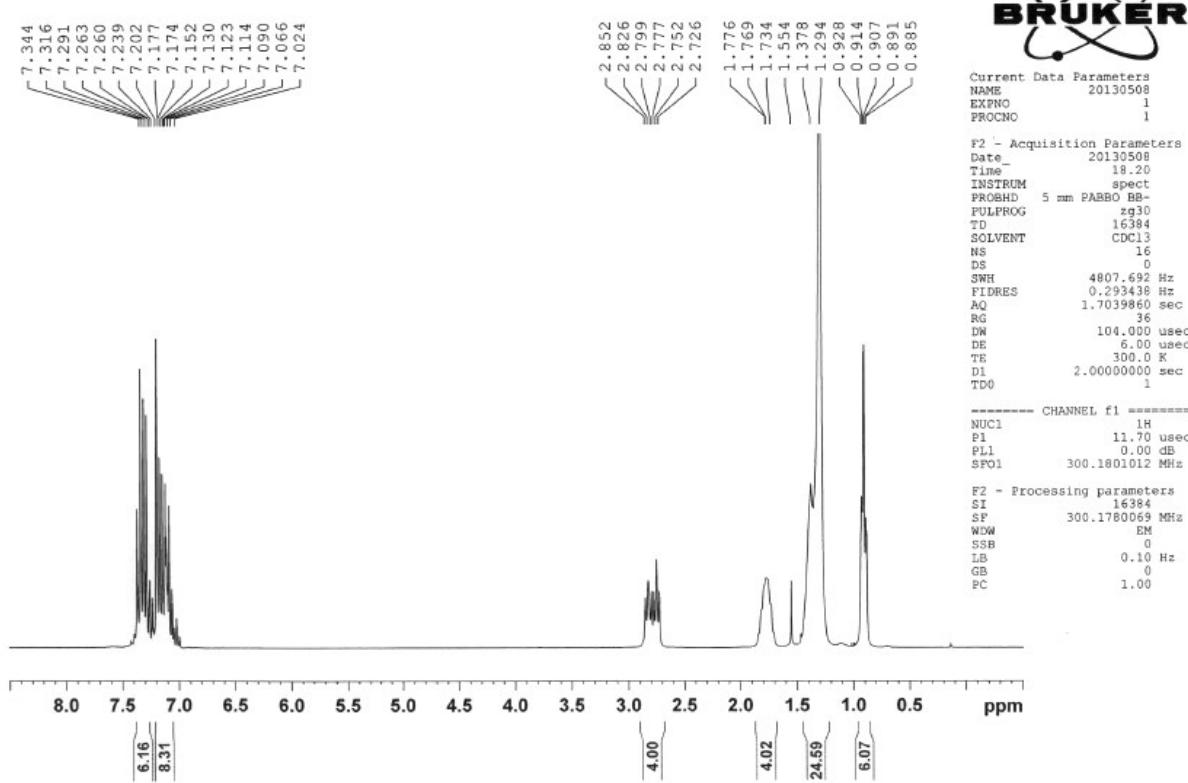
Mass Tolerance : 10ppm, 10mmu if m/z < 1000, 20mmu if m/z > 2000

Unsaturation (U.S.) : -0.5 - 200.0

Observed m/z	Int%	Err [ppm / mmu]	U.S.	Composition
797.1848	80.8	-0.6 / -0.5	25.0	C 44 H 48 79Br N S 4
799.1827	100.0	-0.7 / -0.6	25.0	C 44 H 48 81Br N S 4

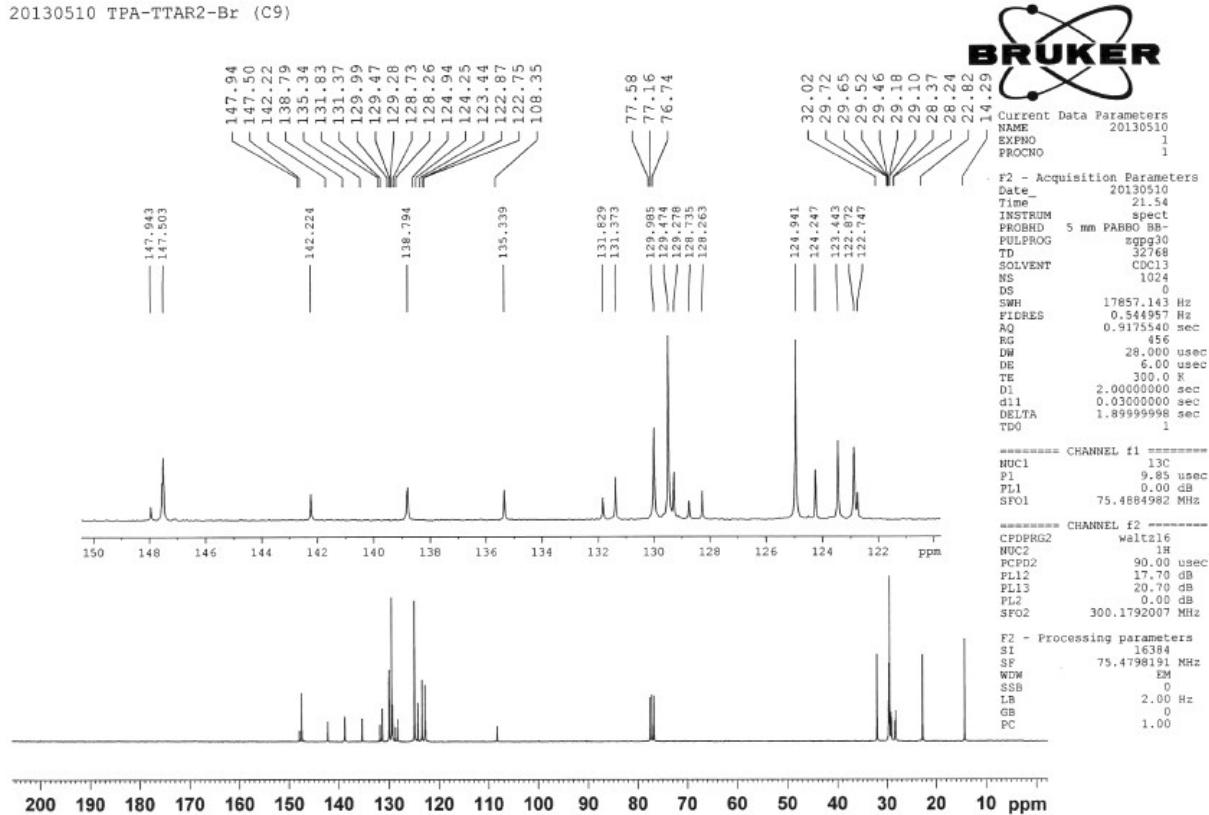
### Mass spectrum of compound 8a

20130508 TPA-TTAR2-Br (C9)



<sup>1</sup>H-NMR of compound 8c

20130510 TPA-TTAR2-Br (C9)



### **<sup>13</sup>C-NMR of compound 8c**

[ Elemental Composition ]

Data : 1030120-003

Sample: TPA-TTAC9-Br

Note : HRFAB-825.2166

Inlet : Direct

Date : 20-Jan-2014 10:36

Page: 1

RT : 3.60 min

Ion Mode : FAB+

Scan# : 19

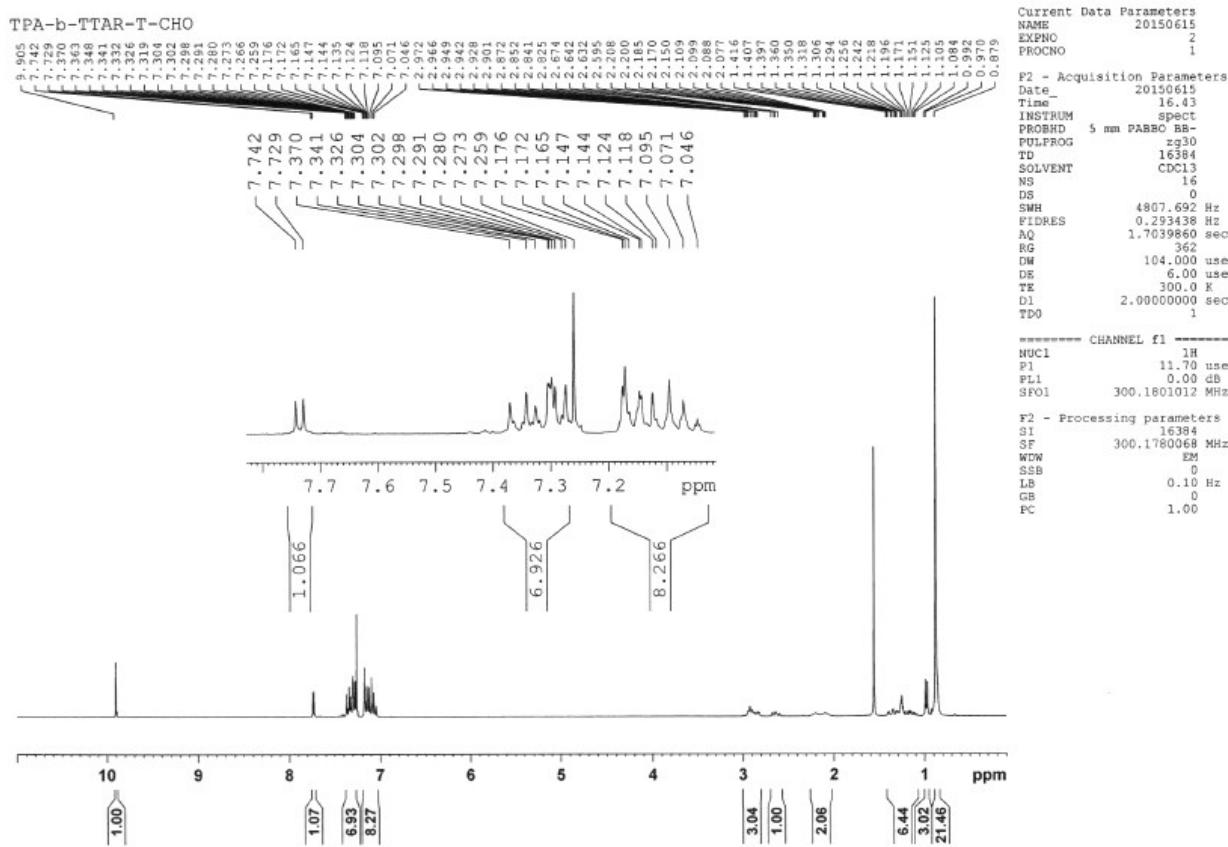
Elements : C 46/0, H 91/0, Br 1/0(79Br 1/0, 81Br 1/0), N 1/0, S 4/0

Mass Tolerance : 10ppm, 10mmu if m/z < 1000, 20mmu if m/z > 2000

Unsaturation (U.S.) : -0.5 - 200.0

Observed m/z	Int%	Err [ppm / mmu]	U.S.	Composition
825.2171	78.0	+0.6 / +0.5	25.0	C 46 H 52 79Br N S 4

### **Mass spectrum of compound 8c**



### <sup>1</sup>H-NMR of compound 9a

[ Elemental Composition ]

Data : 1040319-002

Sample: TPA-b-TTAR-T-CHO

Note : HRFAB-829.2574

Inlet : Direct

Date : 19-Mar-2015 10:20

Page: 1

RT : 2.10 min

Ion Mode : FAB+

Elements : C 49/0, H 110/0, N 1/0, O 1/0, S 5/0

Scan#: 32

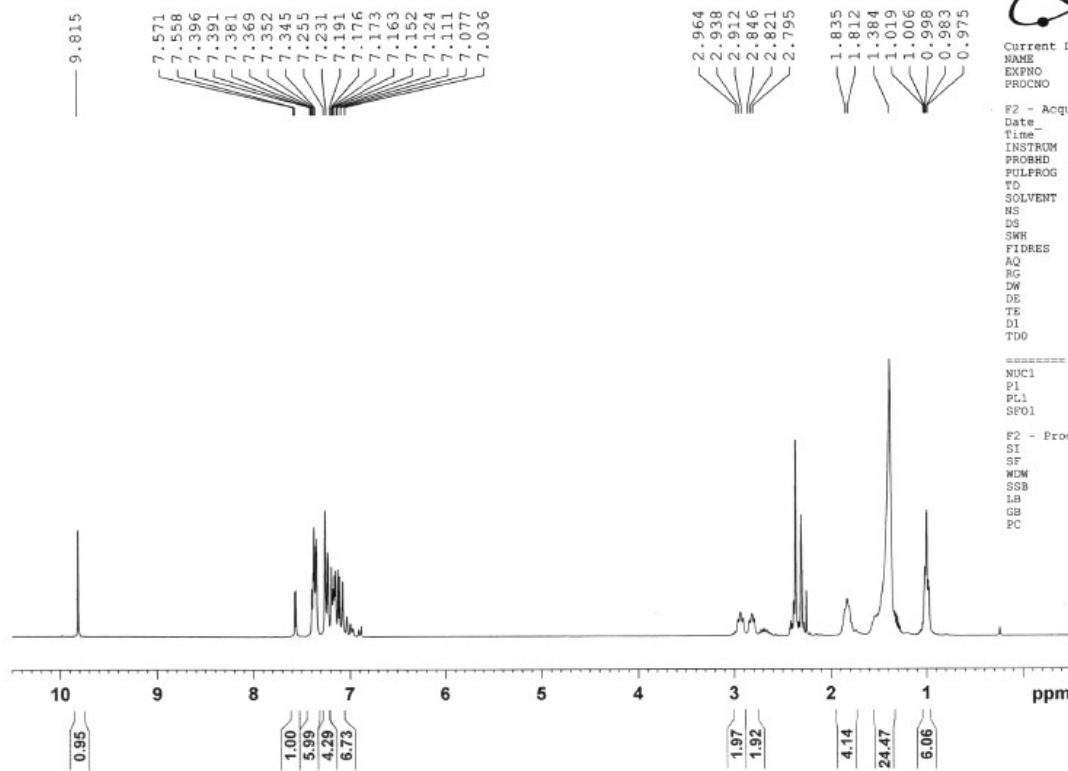
Mass Tolerance : 10ppm, 10mmu if m/z < 1000, 20mmu if m/z > 2000

Unsaturation (U.S.) : -0.5 - 200.0

Observed m/z	Int%	Err [ppm / mmu]	U.S.	Composition
829.2582	23.8	+1.0 / +0.8	30.0	C 49 H 51 N O S 5

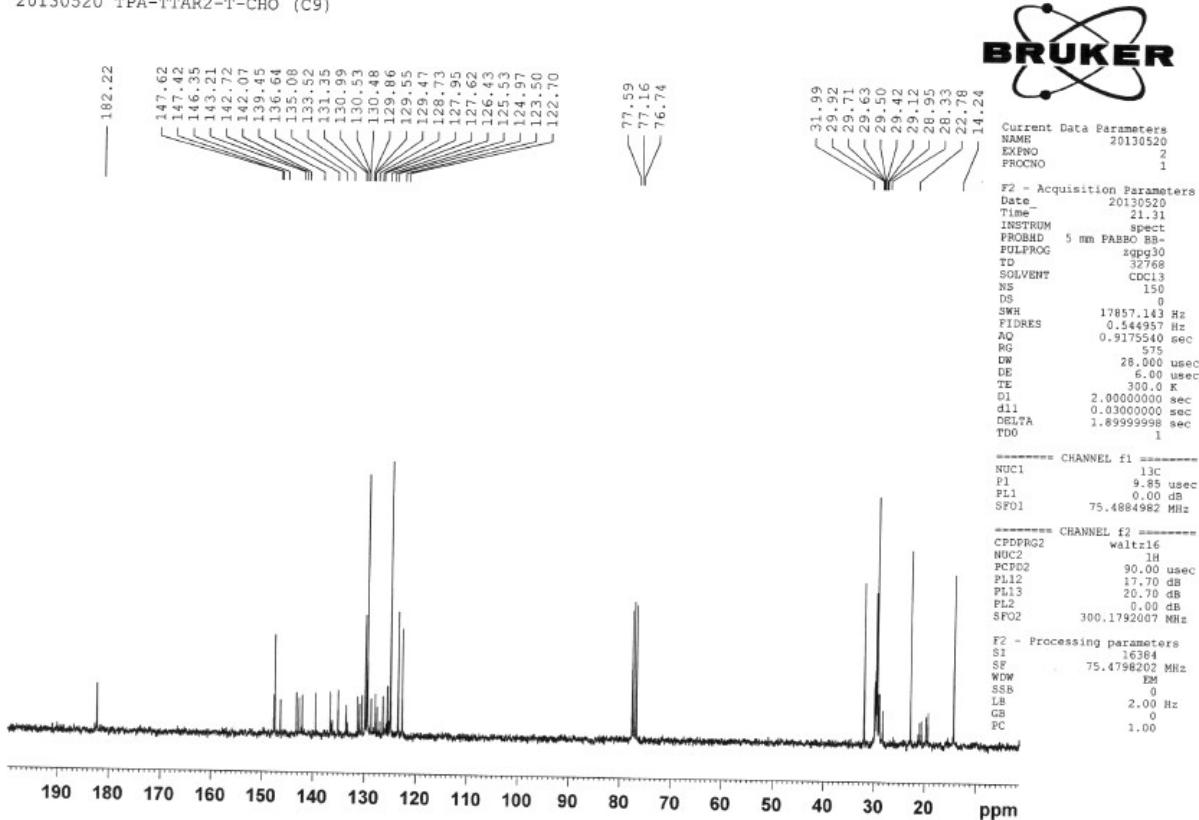
### Mass spectrum of compound 9a

20130521 TPA-TTAR2-T-CHO ( $\text{C}_3$ )



$^1\text{H}$ -NMR of compound 9c

20130520 TPA-TTAR2-T-CHO (C9)



### <sup>13</sup>C-NMR of compound 9c

[ Elemental Composition ]

Data : 1030120-002

Sample: TPA-TTAC9-T-CHO

Note : HRFAB-857.2887

Inlet : Direct

Date : 20-Jan-2014 10:25

Page: 1

RT : 2.49 min

Ion Mode : FAB+

Elements : C 51/0, H 91/0, N 1/0, O 1/0, S 5/0

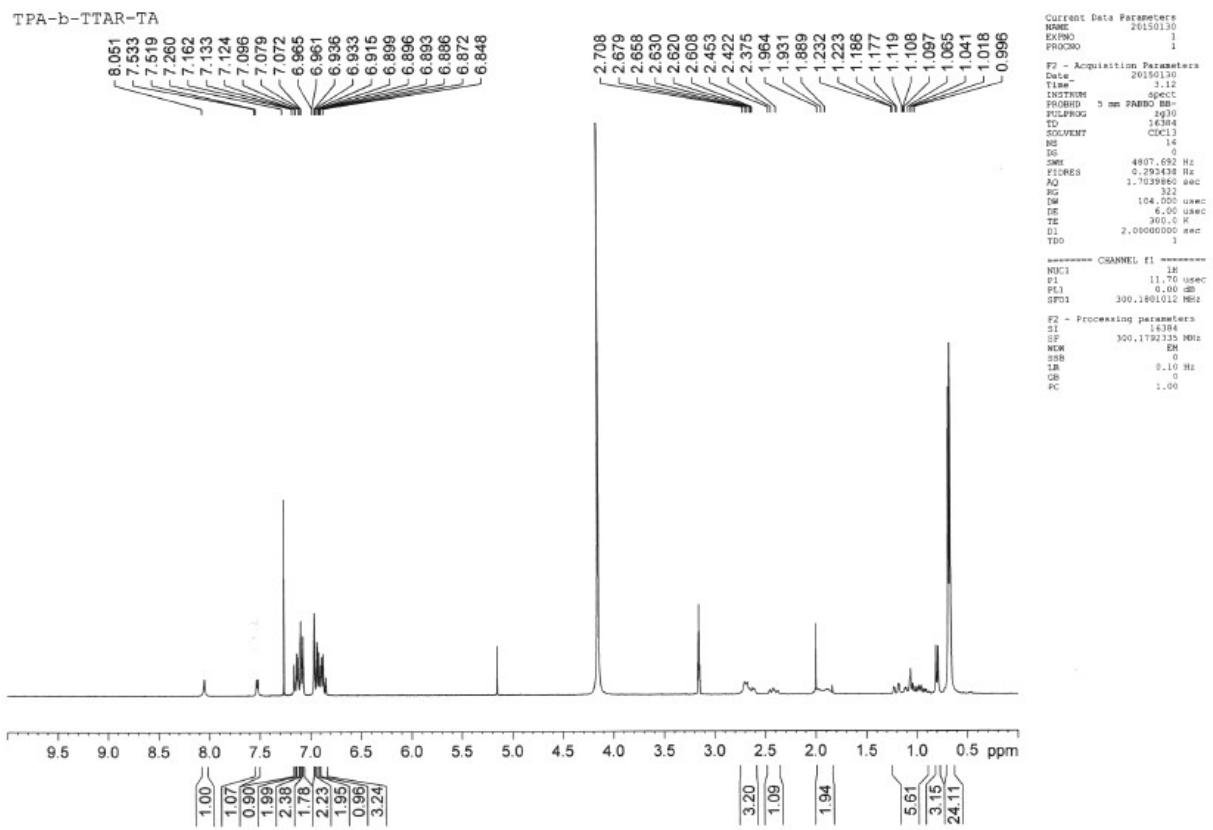
Scan# : 14

Mass Tolerance : 10ppm, 10mmu if m/z < 1000, 20mmu if m/z > 2000

Unsaturation (U.S.) : -0.5 - 200.0

Observed m/z	Int%	Err [ppm / mmu]	U.S.	Composition
857.2889	97.5	+0.3 / +0.2	30.0	C 51 H 55 N O S 5

### Mass spectrum of compound 9c



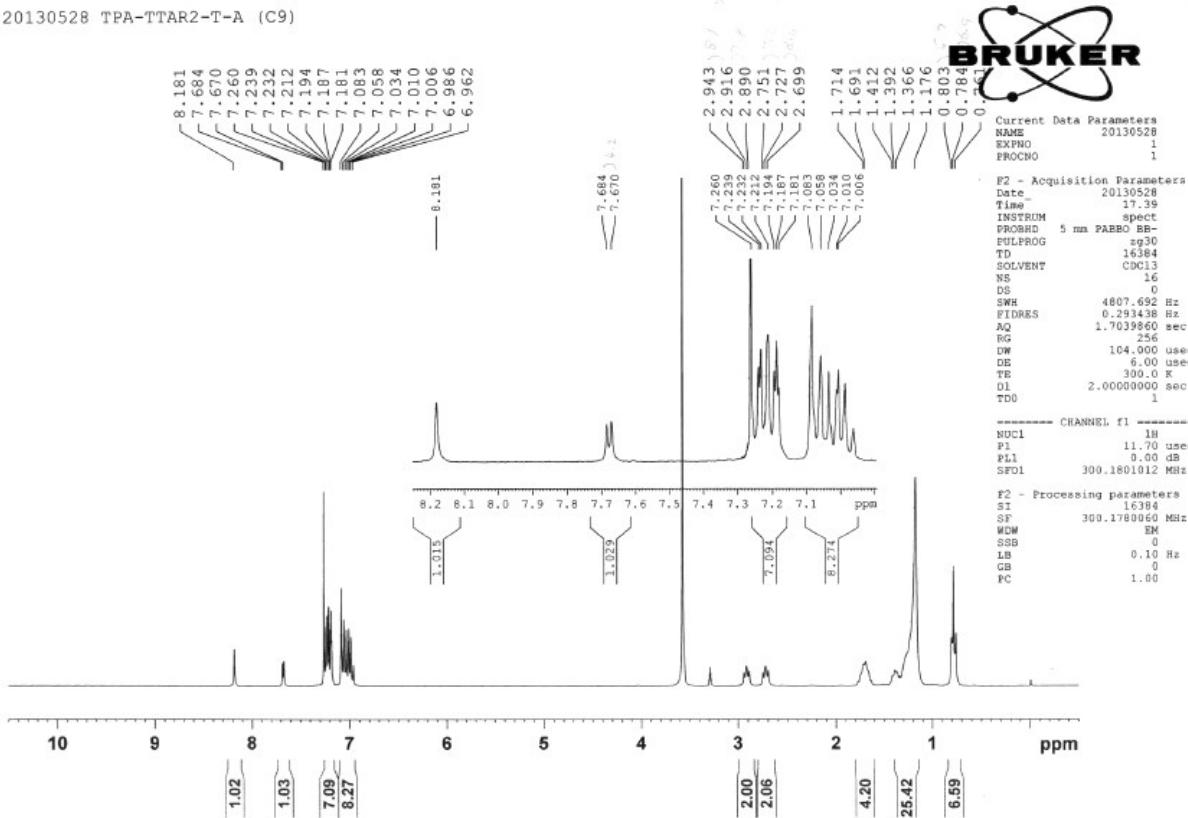
### <sup>1</sup>H-NMR of compound 1

[ Elemental Composition ]  
 Data : 1040319-001 Date : 19-Mar-2015 09:25  
 Sample: TPA-b-TTAR-TA  
 Note : HRFAB-896.263  
 Inlet : Direct Ion Mode : FAB+  
 RT : 2.42 min Scan# : 40  
 Elements : C 52/0, H 110/0, N 2/0, O 2/0, S 5/0  
 Mass Tolerance : 10ppm, 10mmu if m/z < 1000, 20mmu if m/z > 2000  
 Unsaturation (U.S.) : -0.5 - 200.0  
 Observed m/z Int% Err [ppm / mmu] U.S. Composition  
 896.2629 20.7 -0.4 / -0.4 33.0 C 52 H 52 N 2 O 2 S 5

Page: 1

### Mass spectrum of compound 1

20130528 TPA-TTAR2-T-A (C9)



### <sup>1</sup>H-NMR of compound 3

[ Elemental Composition ]

Data : 1030120-001

Date : 20-Jan-2014 10:14

Page: 1

Sample: TPA-TTAC9-TA

Note : HRFAB-924.2945

Ion Mode : FAB+

Inlet : Direct

Scan#: 15

RT : 2.77 min

Elements : C 54/0, H 91/0, N 2/0, O 2/0, S 5/0

Mass Tolerance : 10ppm, 10mmu if m/z < 1000, 20mmu if m/z > 2000

Unsaturation (U.S.) : -0.5 - 200.0

Observed m/z	Int%	Err [ppm / mmu]	U.S.	Composition
924.2948	64.9	+0.3 / +0.3	33.0	C 54 H 56 N 2 O 2 S 5

### Mass spectrum of compound 3