Supporting information for

Synthesis and Crystal Structures of Unsymmetrical Wave-shaped Heptathienoacenes

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^{1}H NMR, ^{13}C NMR and HRMS Spectra/ Data of new compounds

1. NMR and HRMS Spectra/ Data of **2**

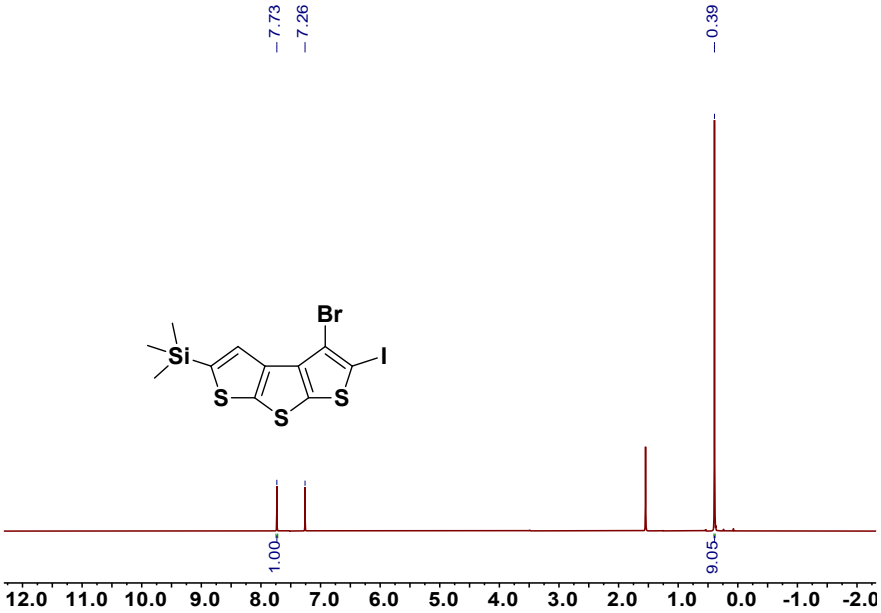

Figure S1. ^{1}H NMR (400 MHz, $CDCl_3$) spectrum of **2**

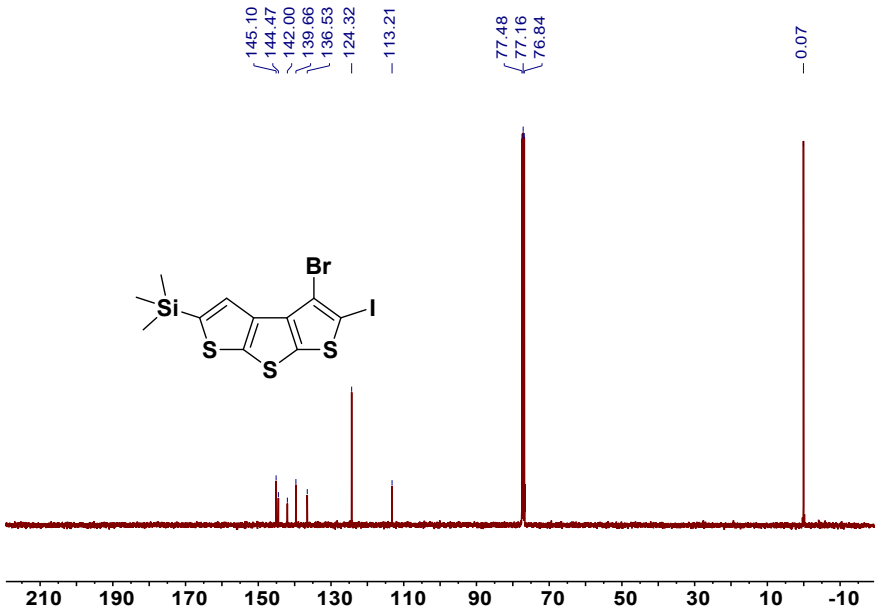

Figure S2. ^{13}C NMR (100 MHz, $CDCl_3$) spectrum of **2**

National Center for Organic Mass Spectrometry in Shanghai
Shanghai Institute of Organic Chemistry
Chinese Academic of Sciences
High Resolution MS DATA REPORT

Instrument: Agilent 7200 GC QTOF MS

Sample Serial Number: Zwj-1-132-w-s

Operator: Zhang, Fang

Date: 2016/05/31

Operation Mode: EI-Positive

Single Mass Analysis

Tolerance = 5.0 ppm / DBE: min = 0, max = 50.0

C: 0-50; H: 0-120; S: 0-10; Si: 0-3; [79Br]: 0-3; I: 0-3

Formula (M)	m/z	m/z (Calc)	Diff (ppm)	DBE
C11 H10 Br I S3 Si	471.7952	471.7936	3.29	7
C13 H8 S7 Si3	471.7952	471.7973	4.51	13
C14 H11 Br3 Si2	471.7952	471.7944	-1.71	10
C15 H7 Br2 I	471.7952	471.7954	0.36	11
C16 H4 S6 Si3	471.7952	471.794	-2.64	18
C20 H Br S3 Si2	471.7952	471.7957	1.02	22
C7 H18 Br2 S4 Si3	471.7952	471.796	1.78	1
C8 H14 Br I S4 Si	471.7952	471.797	3.85	2

Figure S3. HRMS(EI) data of **2**

2. NMR and HRMS Spectra/ Data of **4**

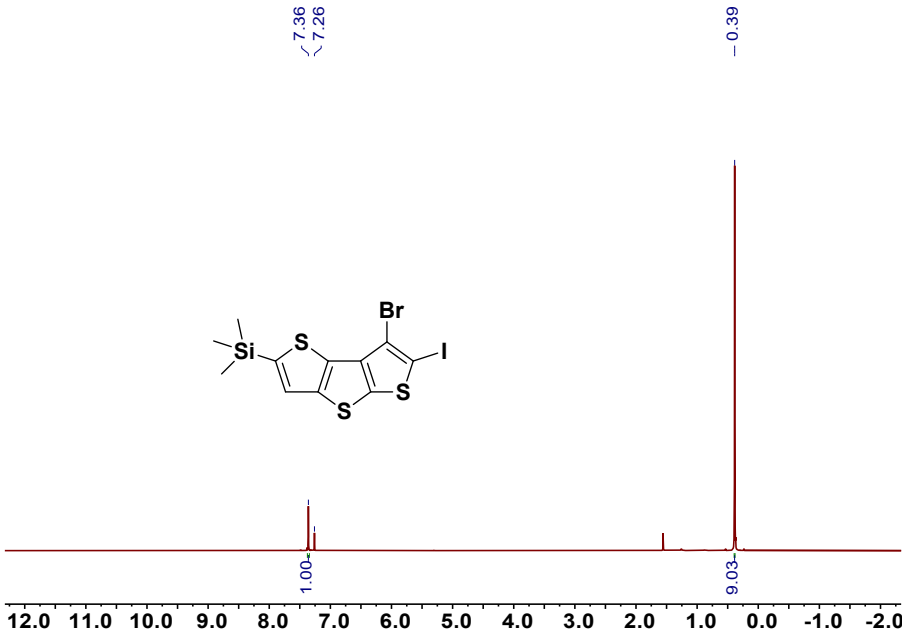

Figure S4. ^{1}H NMR (400 MHz, $CDCl_3$) spectrum of **4**

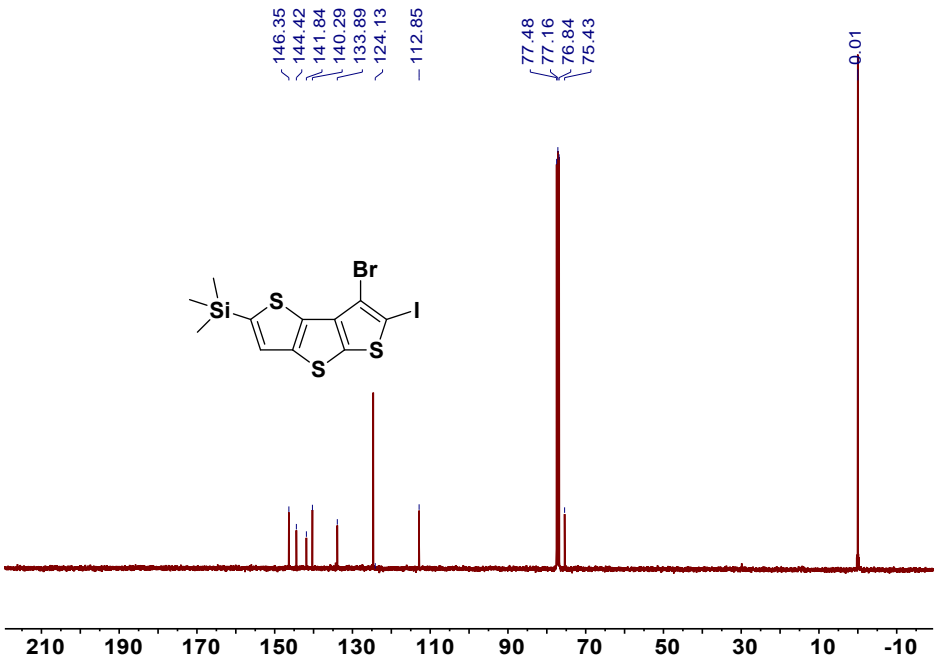

Figure S5. ^{13}C NMR (100 MHz, $CDCl_3$) spectrum of **4**

National Center for Organic Mass Spectrometry in Shanghai
Shanghai Institute of Organic Chemistry
Chinese Academic of Sciences
High Resolution MS DATA REPORT

Instrument: Waters Micromass GCT Premier

Sample Serial Number: Zwj-1-178

Operator: Li, Guangping

Date: 2016/12/29

Operation Mode: EI-Positive

Single Mass Analysis

Tolerance = 2.0 mDa / DBE: min = -1.5, max = 50.0

C: 0-60; H: 0-80; Br: 0-2; I: 0-2; S: 0-3; Si: 0-3

Mass	Calc. Mass	Diff (ppm)	DBE	Formula
471.7944	471.7942	0.4	7.0	C11H10Si3S3BrI
471.7944	471.7932	2.5	6.0	C10H14Si3S3Br2
471.7944	471.7959	-3.2	11.0	C15H7Br2I
471.7944	471.7962	-3.8	22.0	C20HSi2S3Br

Figure S6. HRMS(EI) data of **4**

3. NMR and HRMS Spectra/ Data of **7**

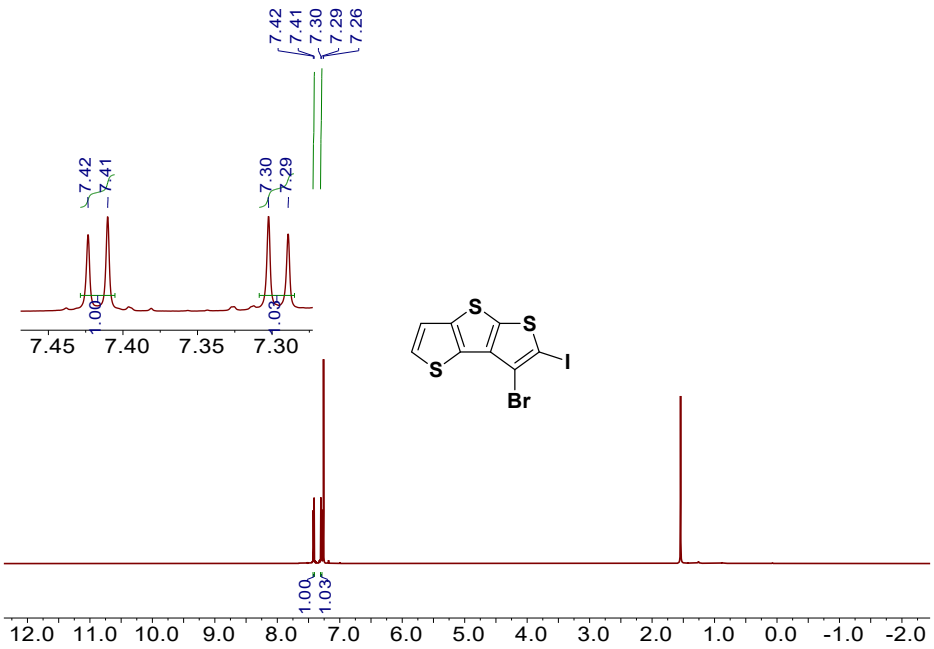

Figure S7. ^{1}H NMR (400 MHz, $CDCl_3$) spectrum of **7**

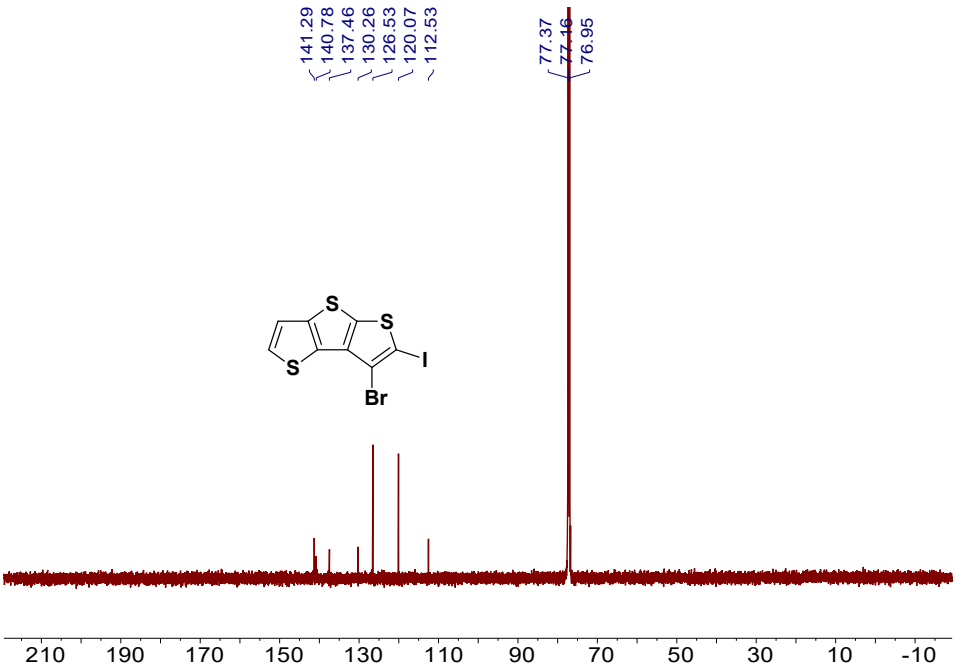

Figure S8. ^{13}C NMR (150 MHz, $CDCl_3$) spectrum of **7**

National Center for Organic Mass Spectrometry in Shanghai
Shanghai Institute of Organic Chemistry
Chinese Academic of Sciences
High Resolution MS DATA REPORT

Instrument: Thermo Fisher Scientific LTQ FTICR-MS

Card Serial Number: W181553

Sample Serial Number: WZP-3-16-col

Operator: Songw Date: 2018/11/01

Operation Mode: DART Positive Ion Mode

Elemental composition search on mass 399.75

m/z= 394.75-404.75

m/z	Theo. Mass	Delta (ppm)	RDB equiv.	Composition
399.7541	399.7541	0.05	7.0	$C_8H_2BrIS_3$
	399.7553	-2.85	3.5	$C_2O_4N_3BrIS_2$

Figure S9. HRMS(DART) data of **7**

4. NMR and HRMS Spectra/ Data of **8**

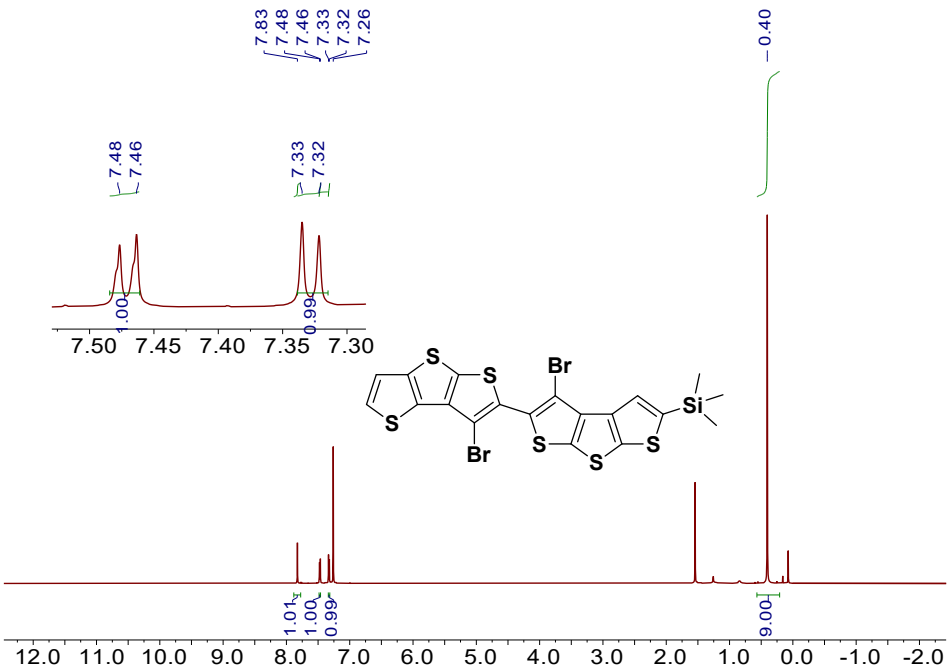

Figure S10. ^{1}H NMR (400 MHz, $CDCl_3$) spectrum of **8**

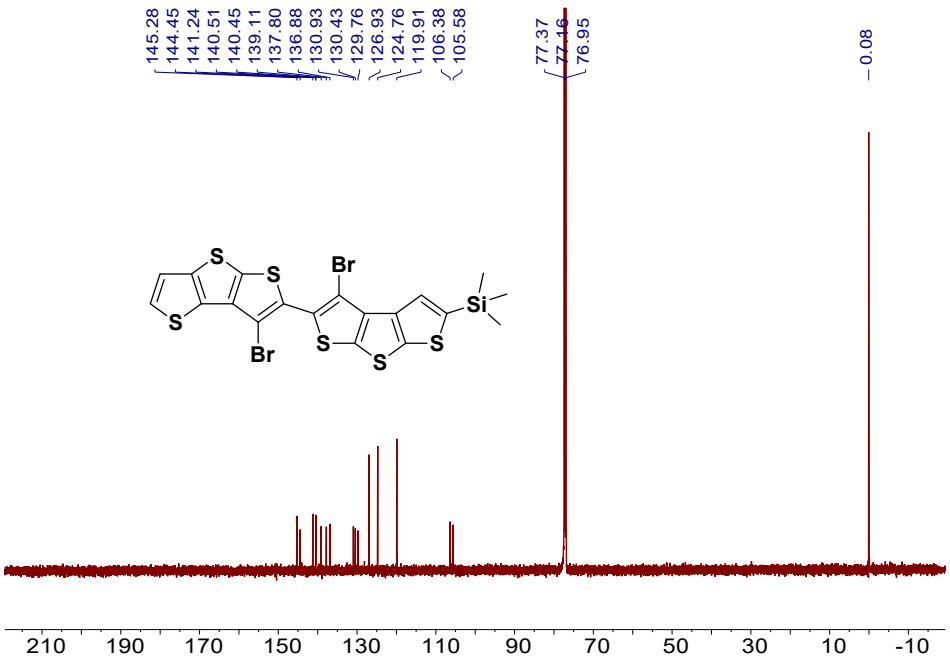

Figure S11. ^{13}C NMR (150 MHz, $CDCl_3$) spectrum of **8**

National Center for Organic Mass Spectrometry in Shanghai
Shanghai Institute of Organic Chemistry
Chinese Academic of Sciences
High Resolution MS DATA REPORT

Instrument: Thermo Fisher Scientific LTQ FTICR-MS

Card Serial Number: W181554

Sample Serial Number: WZP-3-19-col

Operator: Songw Date: 2018/11/01

Operation Mode: DART Positive Ion Mode

Elemental composition search on mass 617.74

m/z= 612.74-622.74

m/z	Theo. Mass	Delta (ppm)	RDB equiv.	Composition
617.7393	617.7394	-0.17	14.0	$C_{19}H_{12}Br_2S_6Si$
	617.7399	-1.02	7.5	$C_{15}H_{16}O_2NBr_4SSi$
	617.7384	1.39	3.5	$C_{12}H_{19}ONBr_3S_5Si$
	617.7381	1.91	2.0	$C_{13}H_{22}Br_4S_3Si$
	617.7365	4.43	12.5	$C_{18}H_{12}O_2NBr_4Si$

Figure S12. HRMS(DART) data of **8**

5. NMR and HRMS Spectra of **10**

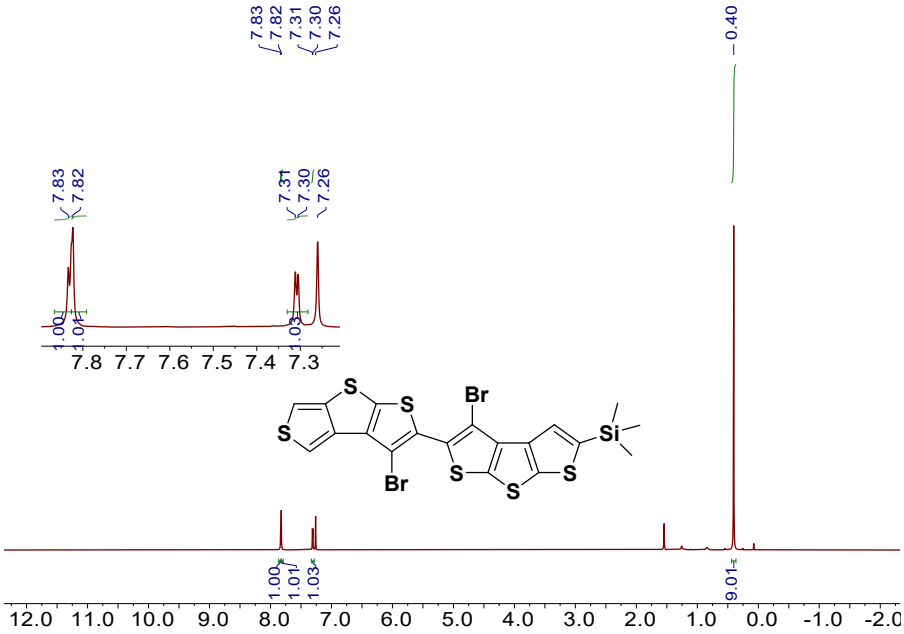

Figure S13. ^{1}H NMR (400 MHz, $CDCl_3$) spectrum of **10**

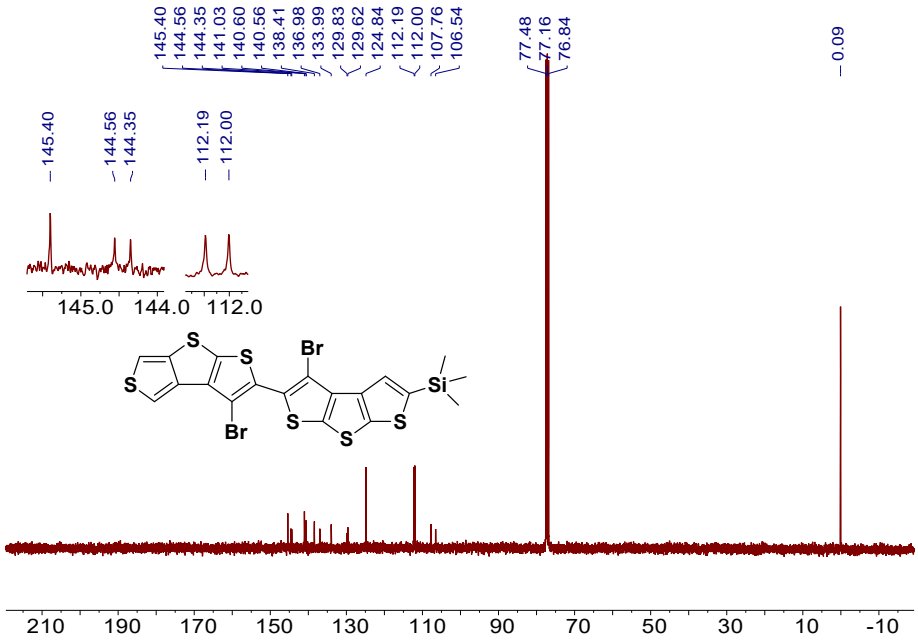

Figure S14. ^{13}C NMR (100 MHz, 323K, $CDCl_3$) spectrum of **10**

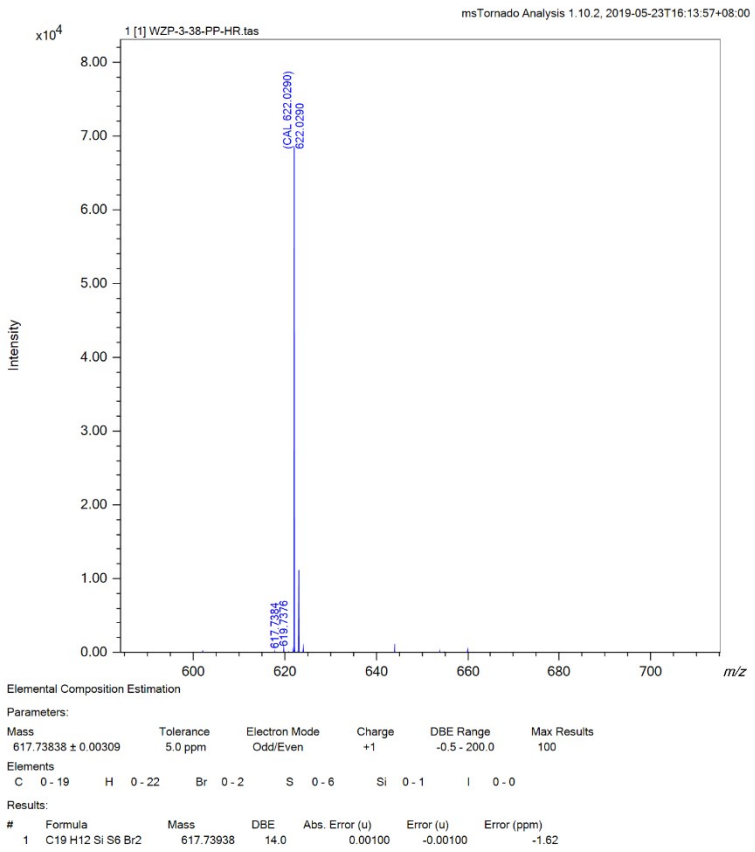

Figure S15. HRMS(MALDI) spectrum of **10**

6. NMR and HRMS Spectra/ Data of **11**

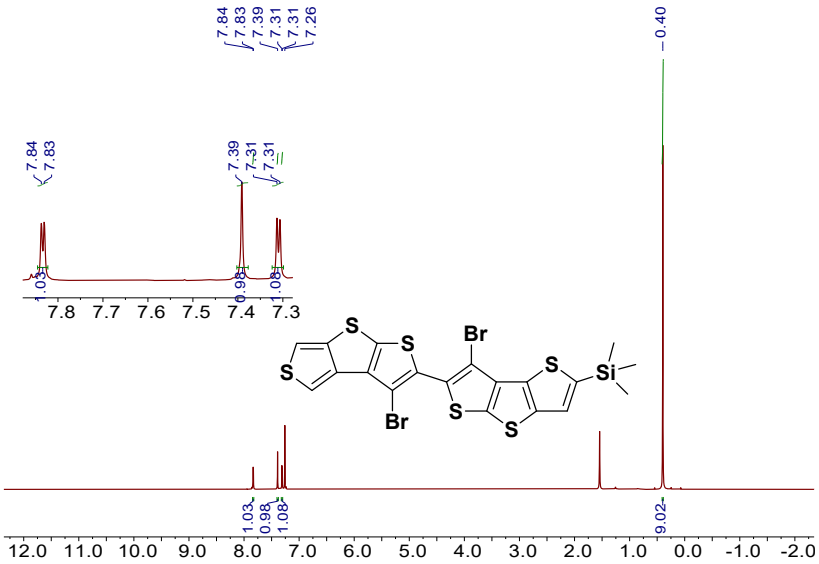

Figure S16. ^{1}H NMR (400 MHz, $CDCl_3$) spectrum of **11**

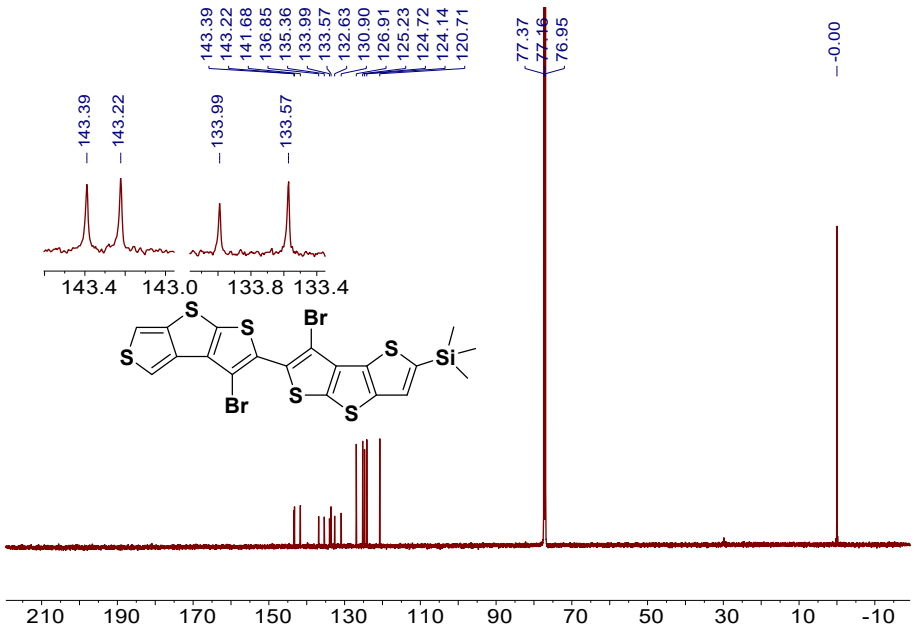

Figure S17. ^{13}C NMR (150 MHz, $CDCl_3$) spectrum of **11**

National Center for Organic Mass Spectrometry in Shanghai
Shanghai Institute of Organic Chemistry
Chinese Academic of Sciences
High Resolution MS DATA REPORT

Instrument: Thermo Fisher Scientific LTQ FTICR-MS

Card Serial Number: W18019

Sample Serial Number: WZP-3-49-PTLC-2-2

Operator: Songw Date: 2018/12/26

Operation Mode: DART Positive Ion Mode

Elemental composition search on mass 618.75

m/z= 613.75-623.75

m/z	Theo. Mass	Delta (ppm)	RDB equiv.	Composition
618.7469	618.7472	-0.42	13.5	$C_{19}H_{13}Br_2S_6Si$
	618.7463	0.98	14.5	$C_{18}H_9O_5Br_2S_4Si$
	618.7484	-2.30	10.0	$C_{13}H_{11}O_4N_3Br_2S_5Si$
	618.7450	3.15	15.0	$C_{16}H_7O_4N_3Br_2S_4Si$
	618.7497	-4.47	9.5	$C_{15}H_{13}O_5Br_2S_5Si$

Figure S18. HRMS(DART) data of **11**

7. NMR and HRMS Spectra of **UHT-1**

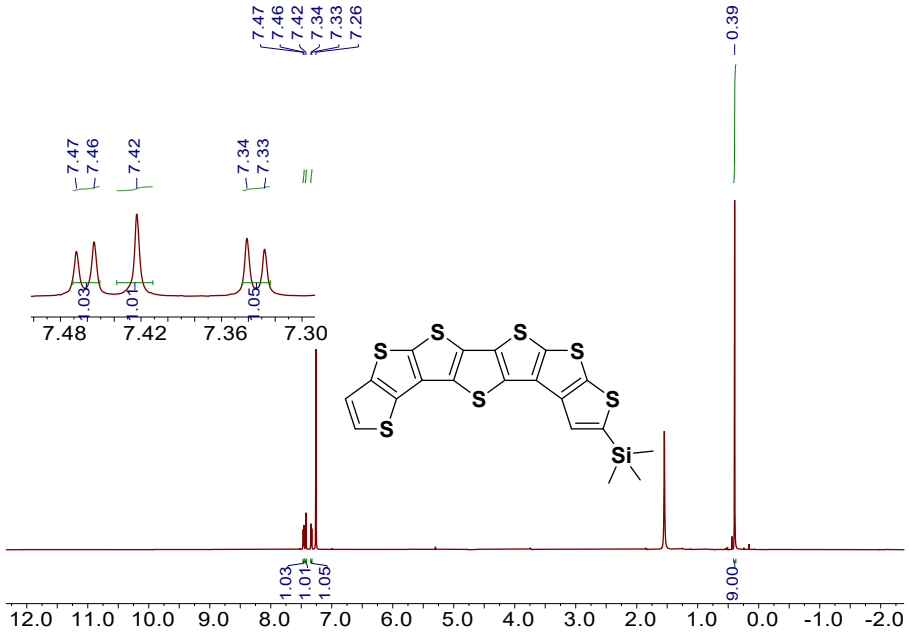

Figure S19. ^{1}H NMR (400 MHz, $CDCl_3$) spectrum of **UHT-1**

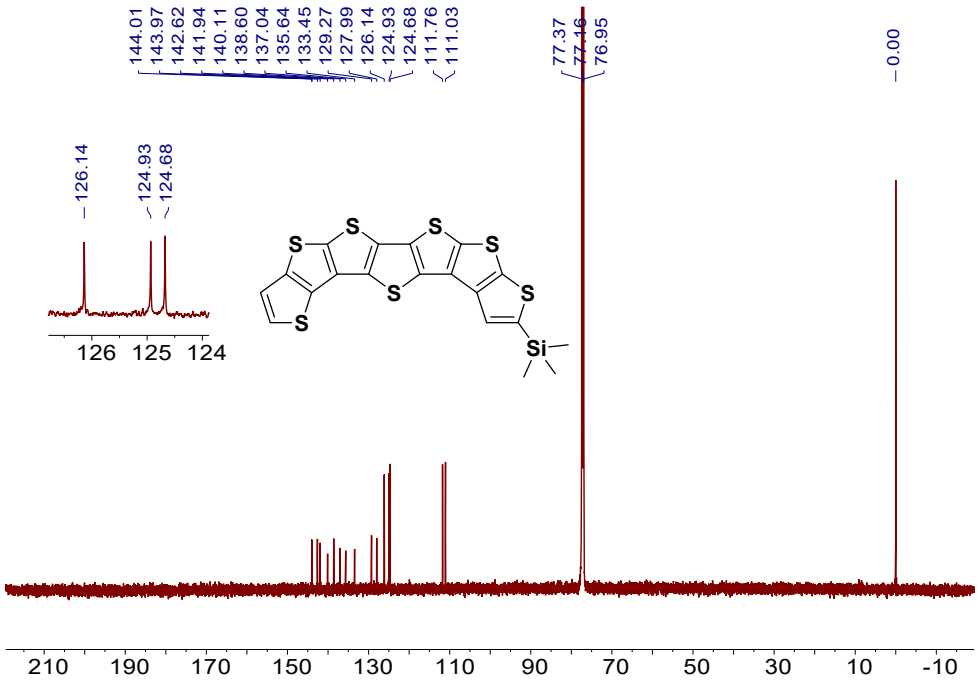

Figure S20. ^{13}C NMR (150 MHz, $CDCl_3$) spectrum of **UHT-1**

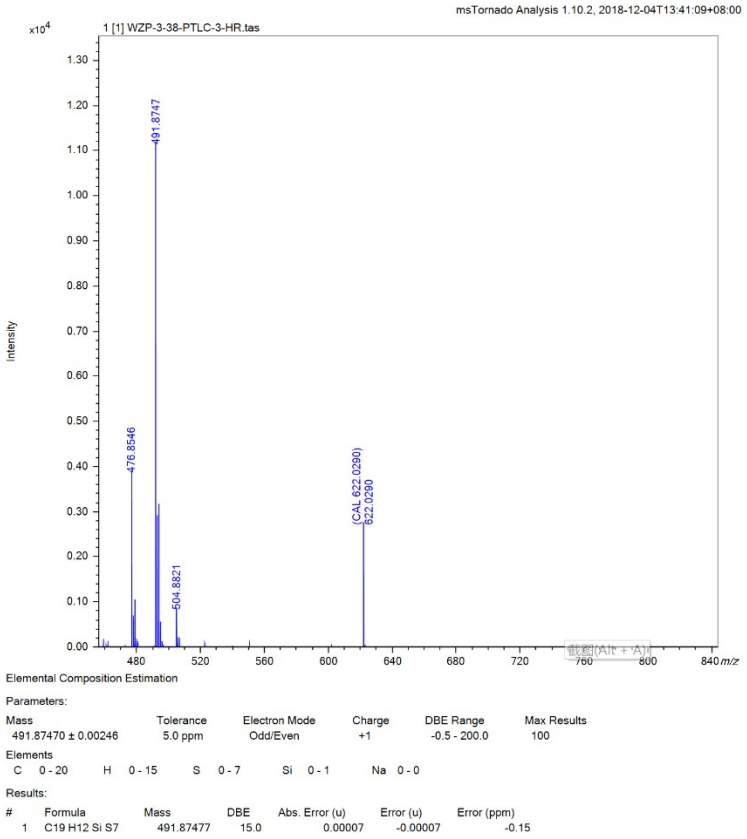

Figure S21. HRMS(MALDI) spectrum of **UHT-1**

8. NMR and HRMS Spectra of **UHT-2**

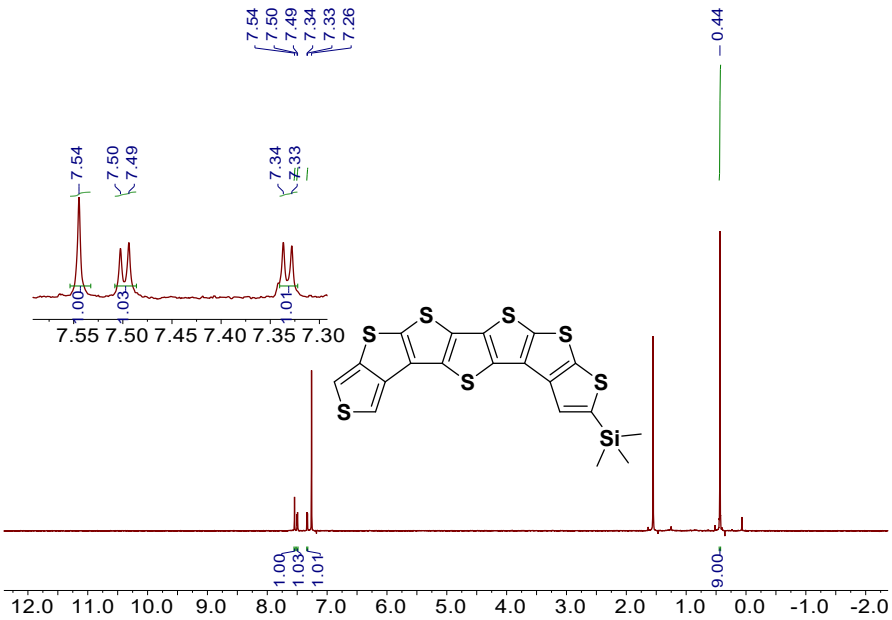

Figure S22. ^{1}H NMR (300 MHz, $CDCl_3$) spectrum of **UHT-2**

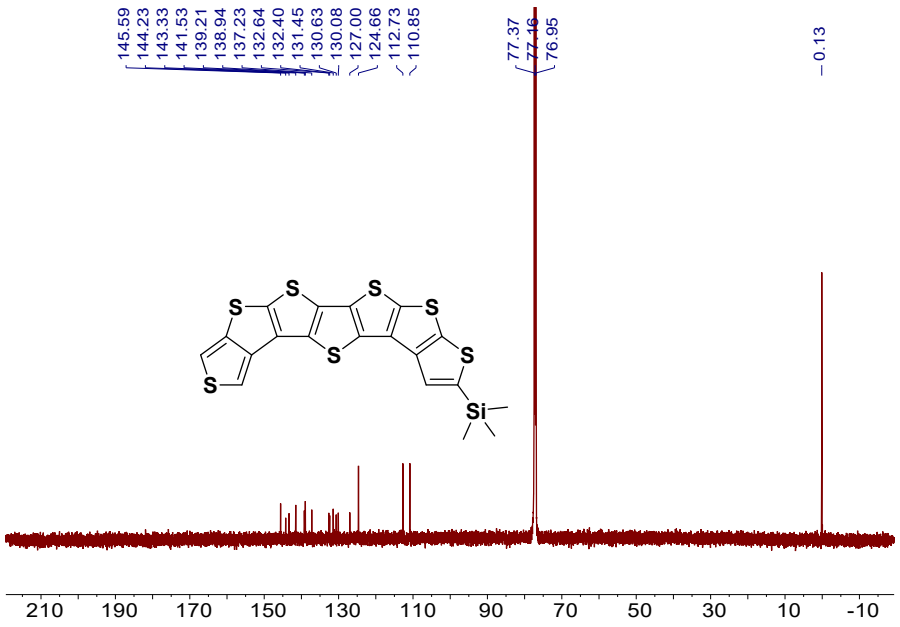

Figure S23. ^{13}C NMR (150 MHz, $CDCl_3$) spectrum of **UHT-2**

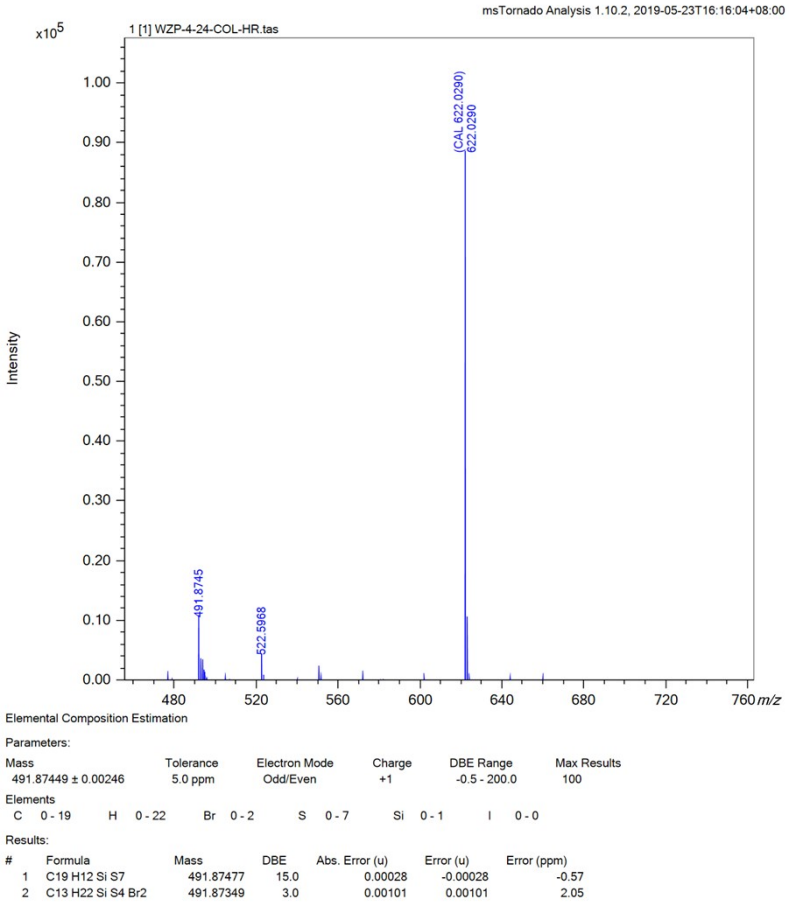

Figure S24. HRMS(MALDI) spectrum of **UHT-2**

9. NMR and HRMS Spectra of **UHT-3**

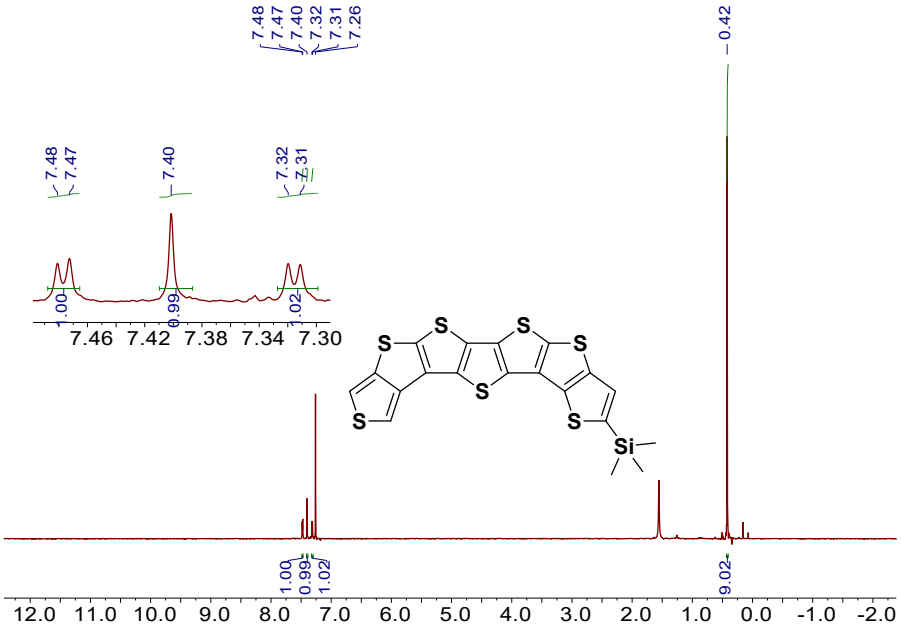

Figure S25. ^{1}H NMR (300 MHz, $CDCl_3$) spectrum of **UHT-3**

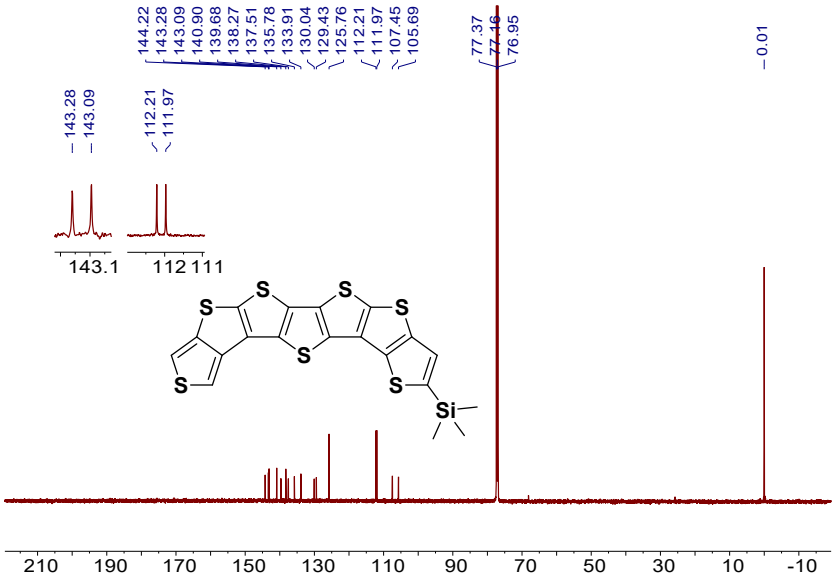

Figure S26. ^{13}C NMR (150 MHz, $CDCl_3$) spectrum of **UHT-3**

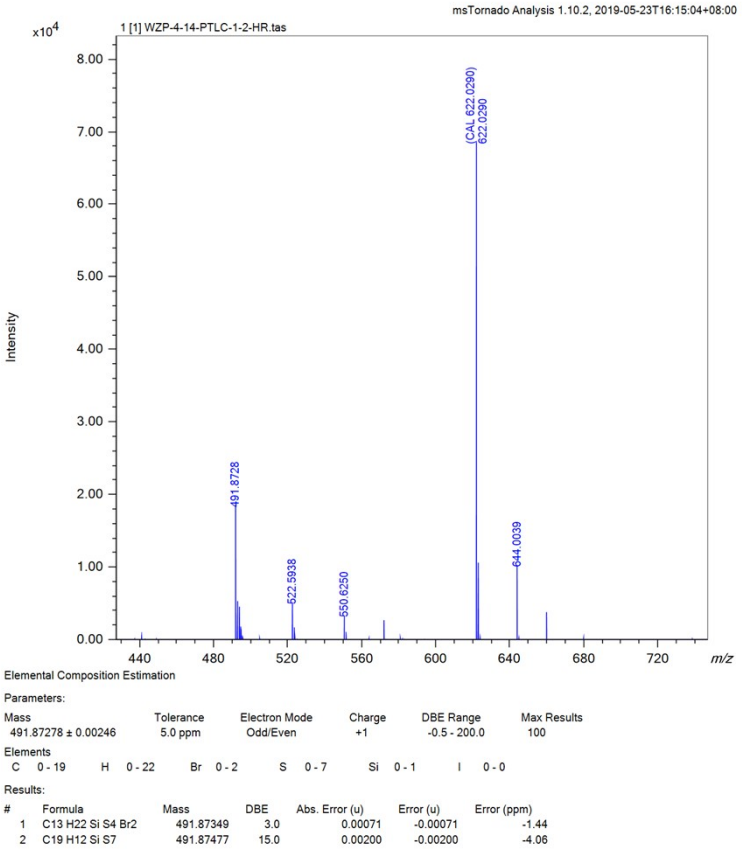

Figure S27. HRMS(MALDI) spectrum of **UHT-3**

X-ray crystallographic data of UHT-1, UHT-2 and UHT-3

Table S1. Crystal data and structure refinement for **UHT-1**, **UHT-2** and **UHT-3**

Identification code	**UHT-1**	**UHT-2**	**UHT-3**
Empirical formula	$C_{19}H_{12}S_7Si$	$C_{19}H_{12}S_7Si$	$C_{19}H_{12}S_7Si$
CCDC	2158361	2158362	2158363
Formula weight	492.80	492.80	492.80
Temperature	150.01 K	150.0 K	149.99 K
Wavelength	0.71073 Å	0.71073 Å	0.71073 Å
Crystal system	Monoclinic	Monoclinic	orthorhombic
Space group	$P_1 2_1/c_1$	$P_1 2_1/c_1$	Ima2
Unit cell dimensions	a = 15.2026 (7) Å	a = 20.2064 (6) Å	a = 7.0326 (3) Å
	b = 10.9247 (5) Å	b = 9.8434 (2) Å	b = 30.5918 (13) Å
	c = 12.3831 (7) Å	c = 10.4751 (3) Å	c = 10.3680 (4) Å
Volume	2042.20 (18) $Å^3$	2034.36 (9) $Å^3$	2030.57 (16) $Å^3$
Z	4	4	4
Density (calculated)	1.603 Mg/m^3	1.609 Mg/m^3	1.467 Mg/m^3
Absorption coefficient	0.834 mm^{-1}	0.838 mm^{-1}	0.764 mm^{-1}
F(000)	1008	1008	1008
Crystal size	0.24 x 0.2 x 0.04 mm^3	0.36 x 0.28 x 0.06 mm^3	0.19 x 0.12 x 0.09 mm^3
Theta range for data collection	2.301 to 28.306°.	2.312 to 28.289°.	5.326 to 52.676°.
Index ranges	-20<=h<=20, -14<=k<=14,	-26<=h<=22, -13<=k<=12,	$-8 \le h \le 4$, $-31 \le k \le 38$,
	-16<=l<=16	-13<=l<=13	$-12 \le l \le 12$
Reflections collected	26055	19939	5150
Independent reflections	5058 [R(int) = 0.0326]	5026 [R(int) = 0.0479]	2278 [Rint = 0.0319]
Max. and min. transmission	0.7457 and 0.6899	0.7457 and 0.6011	0.746 and 0.508
Data / restraints / parameters	5058 / 0 / 247	5026 / 0 / 247	2278/ 7 /162
Goodness-of-fit on F^2	1.068	1.035	1.016
Final R indices [I>2sigma(I)]	R1 = 0.0322, wR2 = 0.0821	R1 = 0.0370, wR2 = 0.0880	$R_1 = 0.0235$, $wR_2 = 0.0618$
R indices (all data)	R1 = 0.0395, wR2 = 0.0876	R1 = 0.0491, wR2 = 0.0960	$R_1 = 0.0237$, $wR_2 = 0.0620$
Largest diff. peak and hole	0.469 and -0.272 e.$Å^{-3}$	0.588 and -0.360 e.$Å^{-3}$	0.40 and -0.29 e.$Å^{-3}$

Optimized structures information for UHT-1, UHT-2 and UHT-3

Table S2. Cartesian Coordinates (Å) and Thermal Eneries of Optimized Structure of **UHT-1** in the Ground State (S_0) Calculated at the B3LYP /6-31G(d,p) Level of Theory.

Atomic Type	Coordinates (Angstroms)		
	x	y	z
S	5.239346	-0.905621	0.001710
S	3.105375	-3.285014	0.004551
S	-0.077896	-3.534558	0.000641
S	-0.851401	0.635891	-0.005659
S	-3.815603	-2.399815	0.000039
S	-6.323025	-0.427459	0.003274
S	-4.118044	3.164134	-0.000801
Si	5.629411	2.266337	0.001297
C	4.541997	0.722888	-0.004176
C	3.168816	0.656703	-0.006428
H	2.543738	1.542984	-0.011997
C	3.664557	-1.624061	0.002714
C	2.648349	-0.675514	-0.002172
C	1.456138	-2.689311	-0.000069
C	1.351518	-1.303186	-0.003083
C	-0.906265	-1.985026	-0.002787
C	-0.021649	-0.910945	-0.004496
C	-2.264878	-1.571763	-0.002479
C	-2.401669	-0.187500	-0.003526
C	-3.762026	0.246949	-0.001797
C	-4.625315	-0.847886	0.000133
C	-4.507078	1.467190	-0.000550
C	-5.883457	1.278835	0.002265
C	-6.638067	2.487054	0.004238
H	-7.719350	2.546672	0.006582
C	-5.817750	3.580500	0.002908
H	-6.104024	4.622843	0.003870
C	4.486491	3.763615	-0.145191
H	3.902164	3.737670	-1.070652
H	3.787168	3.824058	0.695178
H	5.073630	4.688578	-0.150914
C	6.609750	2.344409	1.615639
H	7.259478	1.470662	1.733604
H	7.245634	3.236509	1.644146
H	5.942396	2.379650	2.482837
C	6.818865	2.197833	-1.466147
H	6.274637	2.156304	-2.415189
H	7.464810	3.082835	-1.487409

B3LYP/6-31G(d,p)

E =-3808.09551268 hartree

# of imaginary frequencies = 0

<Thermal Energies>

Zero-point correction=	0.251276 (Hartree/Particle)
Thermal correction to Energy=	0.278129
Thermal correction to Enthalpy=	0.279073
Thermal correction to Gibbs Free Energy=	0.192175
Sum of electronic and zero-point Energies=	-3807.844236
Sum of electronic and thermal Energies=	-3807.817383
Sum of electronic and thermal Enthalpies=	-3807.816439
Sum of electronic and thermal Free Energies=	-3807.903338

Table S3. Cartesian Coordinates (Å) and Thermal Eneries of Optimized Structure of **UHT-2** in the Ground State (S_0) Calculated at the B3LYP /6-31G(d,p) Level of Theory.

Atomic Type	Coordinates (Angstroms)		
	x	y	z
S	0.816888	0.604914	-0.005649
S	-0.027445	-3.552124	0.000657
S	6.287032	-0.567364	0.002889
S	-5.300022	-0.834715	0.001913
S	3.733384	-2.469350	-0.000024
S	-3.206382	-3.249563	0.004790
S	5.623065	3.700148	0.001957
Si	-5.636329	2.343468	0.001129
C	-1.419296	-1.297420	-0.003043
C	0.826950	-2.016848	-0.002793
C	2.192236	-1.625984	-0.002454
C	-2.705474	-0.648164	-0.002039
C	2.353428	-0.243587	-0.003494
C	-3.203574	0.692504	-0.006439
H	-2.563711	1.568214	-0.012179
C	3.718473	0.169043	-0.001951
C	-0.039826	-0.928346	-0.004500
C	-4.575499	0.781828	-0.004214
C	5.886442	1.164311	0.002064
C	4.172401	2.750714	-0.001033
H	3.208037	3.237839	-0.002748
C	4.462290	1.409008	-0.000696
C	-1.547308	-2.681608	-0.000012
C	4.561022	-0.930402	-0.000106
C	6.648276	2.296928	0.003744
H	7.722752	2.404945	0.005975

C	-3.737495	-1.579519	0.002966
C	-4.467318	3.821116	-0.140670
H	-3.770104	3.869307	0.702261
H	-3.880345	3.785516	-1.064155
H	-5.038602	4.755927	-0.148149
C	-6.618703	2.436774	1.613412
H	-7.238161	3.340358	1.641854
H	-7.284702	1.574974	1.728410
H	-5.952894	2.458378	2.482242
C	-6.823415	2.298401	-1.469112
H	-6.277890	2.248745	-2.417014
H	-7.488129	1.428962	-1.424213
H	-7.453638	3.194663	-1.490396

B3LYP/6-31G(d,p)

E =-3808.09201832 hartree

# of imaginary frequencies = 0

<Thermal Energies>

Zero-point correction=	0.251087 (Hartree/Particle)
Thermal correction to Energy=	0.277908
Thermal correction to Enthalpy=	0.278852
Thermal correction to Gibbs Free Energy=	0.191808
Sum of electronic and zero-point Energies=	-3807.840932
Sum of electronic and thermal Energies=	-3807.814111
Sum of electronic and thermal Enthalpies=	-3807.813166
Sum of electronic and thermal Free Energies=	-3807.900211

Table S4. Cartesian Coordinates (Å) and Thermal Eneries of Optimized Structure of **UHT-3** in the Ground State (S_0) Calculated at the B3LYP /6-31G(d,p) Level of Theory.

Atomic Type	Coordinates (Angstroms)		
	x	y	z
C	6.193997	2.899319	-1.542585
H	5.246285	3.447176	-1.577437
H	6.263289	2.300052	-2.456174
H	7.003870	3.637363	-1.562021
C	6.199681	2.892507	1.547861
H	5.251725	3.439486	1.589058
H	6.273172	2.289230	2.458484
H	7.009135	3.631013	1.567223
H	8.782463	1.522188	-0.004416
H	8.019625	0.197339	0.879305
H	8.016906	0.201972	-0.892829
C	-6.771602	2.260662	-0.000085
H	-7.847753	2.350570	-0.000134

C	-5.990760	1.141088	-0.000052
C	-4.570975	1.409777	0.000014
C	-4.303597	2.756122	0.000028
H	-3.347538	3.259427	0.000064
C	-4.630204	-0.931064	0.000014
C	-3.806440	0.182478	0.000052
C	-2.434561	-0.206943	0.000091
C	-2.250263	-1.586692	0.000080
C	-0.878687	-1.953446	0.000064
C	-0.032148	-0.849640	0.000064
C	1.352780	-1.197492	0.000050
C	1.509140	-2.583254	0.000021
C	2.628230	-0.551972	0.000019
C	3.698833	-1.437332	-0.000068
C	4.972726	-0.806450	-0.000214
H	5.915647	-1.340634	-0.000374
C	4.890659	0.569261	-0.000252
C	7.927923	0.836507	-0.004962
S	-5.770053	3.680926	-0.000052
S	-6.362023	-0.597202	-0.000063
S	-3.776926	-2.456054	0.000044
S	-0.913862	0.668526	0.000128
S	0.002498	-3.474742	0.000102
S	3.173247	-3.121462	-0.000141
S	3.199691	1.088895	-0.000145
Si	6.310260	1.813000	0.000032

B3LYP/6-31G(d,p)

E =-3808.09542180 hartree

# of imaginary frequencies = 0

<Thermal Energies>

Zero-point correction=	0.251118 (Hartree/Particle)
Thermal correction to Energy=	0.277910
Thermal correction to Enthalpy=	0.278854
Thermal correction to Gibbs Free Energy=	0.191987
Sum of electronic and zero-point Energies=	-3807.844303
Sum of electronic and thermal Energies=	-3807.817512
Sum of electronic and thermal Enthalpies=	-3807.816568
Sum of electronic and thermal Free Energies=	-3807.903435