Supporting Information for:

Novel Dithienosilole-based Conjugated Copolymers and its Application in Bulk Heterojunction Solar Cells

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1. Quantum Calculation

Quantum calculation results of PBDTDTSi-1

Table S1. Calculated absorption wavelength (nm), oscillator strength (*f*) and transition contributions of **PBDTDTSi-1** in chloroform solvent at TD-B3LYP/6-31G(d,p) level of theory

No.	Energy (cm-1)	Wavelength (nm)	Osc. Strength	Symmetry	Major contribs
1	21001.20928	476.1630565	0.9683	Singlet-A	HOMO→LUMO (95%)
2	22888.55968	436.8994878	0.4269	Singlet-A	H-1→LUMO (91%)
3	23249.092	430.1243249	0.1194	Singlet-A	HOMO→L+1 (84%)
4	24495.2272	408.2427943	0.0516	Singlet-A	HOMO→L+2 (77%)
5	24797.6872	403.263414	0.1735	Singlet-A	H-2→LUMO (44%), H-1→L+1 (43%)
6	25104.98656	398.3272397	0.2421	Singlet-A	H-2→LUMO (46%), H-1→L+1 (37%)
7	25509.07312	392.0173796	0.213	Singlet-A	H-1→L+2 (12%), HOMO→L+3 (71%)
8	26089.79632	383.2916086	0.0179	Singlet-A	H-3→LUMO (56%), HOMO→L+3 (10%)
9	26445.48928	378.1363201	0.0102	Singlet-A	H-3→LUMO (19%), H-1→L+2 (54%), H-1→L+3 (15%)
10	27227.04592	367.2818575	0.0067	Singlet-A	H-1→L+2 (14%), H-1→L+3 (71%)
11	27481.91888	363.8756101	0.0414	Singlet-A	H-2→L+1 (69%)
12	28313.48224	353.1886299	0.2985	Singlet-A	H-4→LUMO (57%)
13	28346.5512	352.7766016	0.0837	Singlet-A	H-5→LUMO (15%), H-3→L+1 (41%), H-3→L+2 (10%)
14	28667.56208	348.8263136	0.2957	Singlet-A	H-4 → LUMO (13%), HOMO → L+4 (43%), HOMO→L+5 (20%)
15	28848.23152	346.6416994	0.0854	Singlet-A	H-1→L+5 (13%), HOMO→L+4 (10%), HOMO→L+5 (34%)
16	28978.08768	345.088334	0.2896	Singlet-A	H-7→LUMO (22%), H-5→LUMO (39%), H-3→L+1 (11%)
17	29121.65536	343.3870732	0.0693	Singlet-A	H-3→L+1 (14%), H-2→L+2 (44%)
18	29533.00096	338.6042622	0.0896	Singlet-A	H-3→L+2 (37%), H-2→L+3 (29%)
19	29632.20784	337.4706351	0.0857	Singlet-A	H-6→LUMO (59%)
20	29816.91008	335.3801575	0.0618	Singlet-A	H-7→LUMO (54%), H-5→LUMO (11%)
21	29911.2776	334.3220619	0.0005	Singlet-A	H-17→L+1 (24%), H-17→L+2 (41%)
22	30087.91424	332.3593626	0.0002	Singlet-A	H-18→L+1 (36%), H-18→L+2 (28%), H-18→L+3 (18%)
23	30181.4752	331.3290664	0.0273	Singlet-A	H-3→L+2 (24%), H-2→L+2 (17%), H-2→L+3 (25%)
24	30314.5576	329.8745155	0.0422	Singlet-A	H-2→L+3 (11%), H-1→L+4 (36%), HOMO→

					L+6 (24%)
25	30687.99488	325.8603255	0.0106	Singlet-A	H-9→LUMO (80%)
26	30778.3296	324.903922	0.1151	Singlet-A	H-4→L+1 (69%), H-4→L+2 (16%)
27	30920.28416	323.412293	0.0848	Singlet-A	H-3→L+3 (67%)
28	31017.87792	322.3947178	0.0238	Singlet-A	H-8→LUMO (59%), H-8→L+1 (10%), H-3→L+3 (12%)
29	31350.9872	318.9692221	0.0937	Singlet-A	H-1→L+4 (36%), HOMO→L+6 (42%)
30	31641.3488	316.042153	0.0789	Singlet-A	H-5→L+1 (28%), H-1→L+5 (39%), HOMO→L+5 (12%)

Quantum calculation results of PBDTDTSi-2

***Table S2*.** Calculated absorption wavelength (nm), oscillator strength (*f*) and transition contributions of **PBDTDTSi-2** in chloroform solvent at TD-B3LYP/6-31G(d,p) level of theory

No.	Energy (cm-1)	Wavelength (nm)	Osc. Strength	Symmetry	Major contribs
1	17879.01552	559.3149124	0.0478	Singlet-A	HOMO→L+1 (89%)
2	18331.49568	545.5092249	0.0592	Singlet-A	HOMO→LUMO (84%)
3	20288.21024	492.8971004	0.0707	Singlet-A	H-1→L+1 (88%)
4	20626.15888	484.8212437	0.9432	Singlet-A	HOMO→L+2 (83%)
5	20765.69376	481.563492	0.1342	Singlet-A	H-1→LUMO (76%), HOMO→L+2 (11%)
6	22676.4344	440.9864366	0.1316	Singlet-A	H-2→L+1 (75%), H-1→L+2 (15%)
7	22856.29728	437.5161855	0.167	Singlet-A	H-3→LUMO (36%), H-2→LUMO (32%), H-1→L+2 (27%)
8	23104.71776	432.8120388	0.0904	Singlet-A	H-3→LUMO (17%), H-2→LUMO (11%), H-2→L+1 (14%), H-1→L+2 (54%)
9	23848.36608	419.3159383	0.1669	Singlet-A	H-3→LUMO (41%), H-2→LUMO (48%)
10	24473.45008	408.6060595	0.0728	Singlet-A	H-3→L+1 (88%)
11	24661.37856	405.4923359	0.6011	Singlet-A	HOMO→L+3 (87%)
12	25220.32464	396.5056018	0.1358	Singlet-A	H-4→L+1 (12%), H-2→L+2 (72%)
13	25596.98816	390.6709624	0.9373	Singlet-A	H-4→L+1 (72%), H-2→L+2 (12%)
14	25923.64496	385.7482239	0.2069	Singlet-A	H-5→LUMO (83%)
15	26165.61296	382.1809952	0.0211	Singlet-A	H-6→L+1 (65%), H-5→L+1 (24%)
16	26483.3976	377.595056	0.0111	Singlet-A	H-3→L+2 (33%), H-1→L+3 (55%)
17	26706.81472	374.4362667	0.0141	Singlet-A	H-3→L+2 (53%), H-1→L+3 (35%)
18	26888.29072	371.9090999	0.0008	Singlet-A	H-6→LUMO (18%), H-4→LUMO (69%)
19	27135.09808	368.5263997	0.0337	Singlet-A	H-6→LUMO (66%), H-4→LUMO (22%)
20	27302.056	366.2727818	0.0009	Singlet-A	H-6→L+1 (27%), H-5→L+1 (67%)
21	27756.14928	360.2805238	0.0025	Singlet-A	H-7→LUMO (12%), H-7→L+1 (82%)

22	28182.01296	354.8362572	0.0114	Singlet-A	H-4→L+2 (29%), HOMO→L+4 (41%)
23	28223.14752	354.3190919	0.0003	Singlet-A	H-7→LUMO (85%), H-7→L+1 (13%)
24	28379.62016	352.3655336	0.0551	Singlet-A	H-9→L+1 (13%), H-8→L+1 (18%), H-4→L+2 (28%)
25	28440.91872	351.606082	0.0488	Singlet-A	H-8→L+1 (14%), H-4→L+2 (17%), HOMO→L+4 (18%)
26	28632.07344	349.2586739	0.0058	Singlet-A	H-9→LUMO (22%), H-8→LUMO (21%), H-8→L+1 (15%), H-5→L+2 (12%)
27	28753.864	347.7793454	0.0246	Singlet-A	H-6→L+2 (12%), H-5→L+2 (34%)
28	28840.16592	346.7386432	0.3801	Singlet-A	H-2→L+3 (18%), HOMO→L+5 (42%)
29	29074.87488	343.9395712	0.0071	Singlet-A	H-9→L+1 (52%), H-8→L+1 (32%)
30	29285.38704	341.4672303	0.031	Singlet-A	H-5→L+2 (10%), H-2→L+3 (32%), HOMO→L+5 (16%)
31	29431.3744	339.773463	0.195	Singlet-A	H-11→L+1 (15%), H-10→L+1 (13%), HOMO→L+6 (23%)
32	29608.01104	337.746429	0.0499	Singlet-A	H-6→L+2 (39%), H-5→L+2 (21%), H-2→L+3 (20%)
33	29709.6376	336.5911135	0.0064	Singlet-A	H-9→LUMO (44%), H-8→LUMO (43%)
34	29746.73936	336.1712986	0.0676	Singlet-A	H-7→L+2 (67%)
35	30020.1632	333.1094483	0.0719	Singlet-A	H-11→L+1 (20%), H-10→L+1 (13%), HOMO→L+6 (21%)
36	30372.62992	329.243797	0.2444	Singlet-A	H-13→L+1 (13%), H-11→L+1 (12%), H-10→LUMO (22%), H-10→L+1 (14%)
37	30394.40704	329.0078989	0.0592	Singlet-A	H-9→L+2 (18%), H-8→L+2 (26%), H-3→L+3 (10%)
38	30442.80064	328.4848894	0.1631	Singlet-A	H-11→L+1 (11%), H-3→L+3 (49%)
39	30567.81744	327.1414461	0.0034	Singlet-A	H-10→LUMO (10%), H-9→L+2 (12%), H-8→L+2 (24%), H-3→L+3 (17%)
40	30843.66096	324.2157282	0.0733	Singlet-A	H-1→L+4 (66%), HOMO→L+6 (15%)
41	31009.00576	322.48696	0.0092	Singlet-A	H-13→LUMO (11%), H-12→L+1 (12%), H-10→LUMO (23%)
42	31084.8224	321.7004064	0.0173	Singlet-A	H-13→LUMO (22%), H-12→L+1 (12%), H-10→LUMO (25%), H-10→L+1 (19%)
43	31137.2488	321.1587531	0.0042	Singlet-A	H-9→L+2 (43%), H-8→L+2 (25%)
44	31758.3	314.8783153	0.0015	Singlet-A	H-13→LUMO (24%), H-11→LUMO (53%)
45	31943.8088	313.0497075	0.0108	Singlet-A	H-4→L+3 (21%), H-1→L+5 (25%), H-1→L+6 (25%)
46	32144.64224	311.0938341	0.0061	Singlet-A	H-14→LUMO (22%), H-12→LUMO (37%), H-11→LUMO (23%)
47	32222.072	310.3462744	0.0065	Singlet-A	H-14→L+1 (19%), H-12→L+1 (23%), H-1→L+5 (11%), HOMO→L+7 (13%)
48	32246.2688	310.1133983	0.005	Singlet-A	H-12→L+1 (10%), H-4→L+3 (24%), H-1→L+5 (30%)
49	32284.17712	309.7492608	0.016	Singlet-A	H-4→L+3 (25%), HOMO→L+7 (32%)

50	32396.28896	308.6773307	0.0124	Singlet-A	H-16→LUMO (51%)

Quantum calculation results of PBDTDTSi-3

Table S3. Calculated absorption wavelength (nm), oscillator strength (*f*) and transition contributions of **PBDTDTSi-3** in chloroform solvent at TD-B3LYP/6-31G(d,p) level of theory

No.	Energy (cm-1)	Wavelength (nm)	Osc. Strength	Symmetry	Major contribs
1	16604.65072	602.2409124	0.0206	Singlet-A	HOMO→L+1 (94%)
2	17039.38656	586.8755876	0.021	Singlet-A	H-1→LUMO (15%), HOMO→LUMO (82%)
3	18271.00368	547.3153076	0.0251	Singlet-A	H-1→L+1 (94%)
4	18743.64784	533.5140782	0.0019	Singlet-A	H-1→LUMO (82%), HOMO→LUMO (15%)
5	21027.82576	475.5603415	0.0238	Singlet-A	H-2→L+1 (92%)
6	21224.6264	471.1508138	0.9334	Singlet-A	H-3→LUMO (12%), H-2→LUMO (12%), HOMO →L+2 (71%)
7	21373.84	467.8616477	0.1341	Singlet-A	H-3→LUMO (24%), H-2→LUMO (49%), HOMO →L+2 (22%)
8	22565.93568	443.1458169	0.0731	Singlet-A	H-3→LUMO (59%), H-2→LUMO (35%)
9	22911.94992	436.4534679	0.0941	Singlet-A	H-3→L+1 (76%), H-1→L+2 (17%)
10	23043.4192	433.9633764	0.3316	Singlet-A	H-3→L+1 (18%), H-1→L+2 (76%)
11	24471.0304	408.6464622	0.6312	Singlet-A	H-4→L+1 (50%), HOMO→L+3 (32%)
12	24670.25072	405.3465088	0.5964	Singlet-A	H-5→LUMO (66%), H-4→L+1 (20%)
13	24797.6872	403.263414	0.1002	Singlet-A	H-5→LUMO (14%), H-4→L+1 (17%), HOMO→ L+3 (58%)
14	25290.49536	395.4054619	0.1573	Singlet-A	H-7→L+1 (45%), H-5→L+1 (19%), H-2→L+2 (27%)
15	25344.53488	394.5623799	0.3491	Singlet-A	H-7→L+1 (21%), H-5→L+1 (10%), H-2→L+2 (50%)
16	25789.756	387.7508574	0.0058	Singlet-A	H-6→L+1 (95%)
17	25830.89056	387.1333811	0	Singlet-A	H-4→LUMO (91%)
18	25876.86448	386.4455838	0.0147	Singlet-A	H-7→LUMO (87%)
19	25959.1336	385.2208689	0.002	Singlet-A	H-7→L+1 (29%), H-5→L+1 (58%)
20	26088.1832	383.3153088	0.057	Singlet-A	H-1→L+3 (82%)
21	26253.528	380.9011878	0.0001	Singlet-A	H-6→LUMO (96%)
22	26890.7104	371.8756348	0.0278	Singlet-A	H-9→L+1 (52%), H-3→L+2 (31%)
23	26980.23856	370.6416449	0.0101	Singlet-A	H-9→L+1 (30%), H-3→L+2 (52%)
24	27185.91136	367.8375857	0.0008	Singlet-A	H-8→L+1 (83%)
25	27218.98032	367.3906914	0.0003	Singlet-A	H-9→LUMO (83%)
26	27830.3528	359.3199149	0.0025	Singlet-A	H-8→LUMO (95%)
27	28349.77744	352.7364552	0.0955	Singlet-A	H-2→L+3 (30%), HOMO→L+4 (41%)

28	28732.89344	348.0331704	0.3833	Singlet-A	H-2→L+3 (23%), HOMO→L+4 (21%), HOMO→L+5 (30%)
29	28970.02208	345.1844107	0.0862	Singlet-A	H-4→L+2 (45%), HOMO→L+5 (16%), HOMO→L+6 (10%)
30	29148.27184	343.0735124	0.114	Singlet-A	H-2→L+3 (16%), H-1→L+5 (14%), HOMO→L+5 (16%), HOMO→L+6 (13%)
31	29206.34416	342.3913635	0.0961	Singlet-A	H-7→L+2 (19%), H-5→L+2 (49%)
32	29279.74112	341.5330743	0.0762	Singlet-A	H-10→L+1 (66%)
33	29541.06656	338.511813	0.179	Singlet-A	H-11→LUMO (11%), H-10→LUMO (45%), H-7→L+2 (10%)
34	29624.14224	337.5625164	0.0295	Singlet-A	H-6→L+2 (53%), H-6→L+3 (10%)
35	29822.556	335.3166643	0.2086	Singlet-A	H-16→LUMO (10%), H-15→LUMO (15%), H-10→LUMO (16%), H-7→L+2 (22%)
36	29837.88064	335.1444468	0.1825	Singlet-A	H-12→L+1 (15%), H-6→L+2 (18%), H-1→L+4 (14%), HOMO→L+6 (14%)
37	30000.80576	333.3243807	0.0035	Singlet-A	H-14→L+1 (24%), H-11→L+1 (37%), H-10→L+1 (11%)
38	30185.508	331.2848006	0.2281	Singlet-A	H-15→LUMO (12%), H-7→L+2 (14%), H-5→L+2 (19%), H-3→L+3 (21%)
39	30423.4432	328.6938935	0.0227	Singlet-A	H-14→L+1 (43%), H-11→L+1 (24%)
40	30530.71568	327.5389973	0.0535	Singlet-A	H-3→L+3 (50%)
41	30570.23712	327.1155523	0.0048	Singlet-A	H-15→LUMO (24%), H-12→LUMO (31%), H-11→LUMO (20%)
42	30611.37168	326.6759851	0.2893	Singlet-A	H-12→L+1 (40%), H-11→L+1 (12%), H-9→L+2 (13%), H-1→L+4 (20%)
43	30629.116	326.4867324	0.0006	Singlet-A	H-15→LUMO (13%), H-14→LUMO (46%), H-11→LUMO (26%)
44	30792.84768	324.7507377	0.0063	Singlet-A	H-16→L+1 (10%), H-15→L+1 (20%), H-12→L+1 (19%)
45	30825.11008	324.4108447	0.0581	Singlet-A	H-9→L+2 (54%), H-1→L+4 (12%)
46	30877.53648	323.8600335	0.0313	Singlet-A	H-16→L+1 (13%), H-15→L+1 (22%), H-1→L+4 (15%), HOMO→L+6 (15%)
47	30970.29088	322.8900897	0.0005	Singlet-A	H-16→LUMO (17%), H-13→L+1 (28%), H-12→LUMO (16%), H-11→LUMO (17%)
48	31014.65168	322.4282543	0.0002	Singlet-A	H-13→L+1 (54%)
49	31113.85856	321.4001883	0.0009	Singlet-A	H-8→L+2 (65%), H-8→L+3 (12%)
50	31342.9216	319.0513038	0.0015	Singlet-A	H-16→LUMO (32%), H-15→LUMO (17%), H-13→LUMO (11%), H-12→LUMO (32%)

2. NMR and HRMS Spectra

NMR, HRMS and IR Spectra of 2

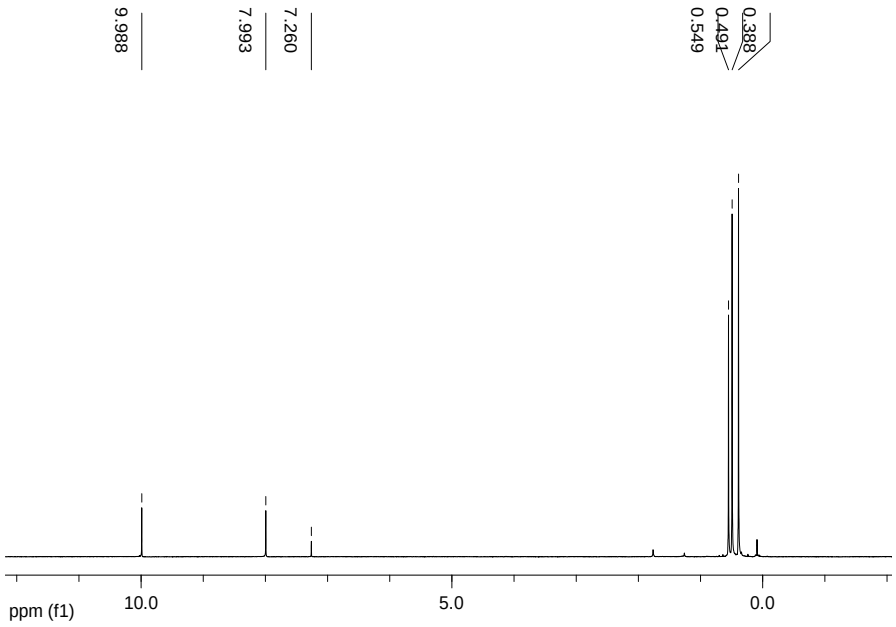


Figure S1. ^{1}H-NMR (400 MHz, $CDCl_3$) spectrum of compound **2**.

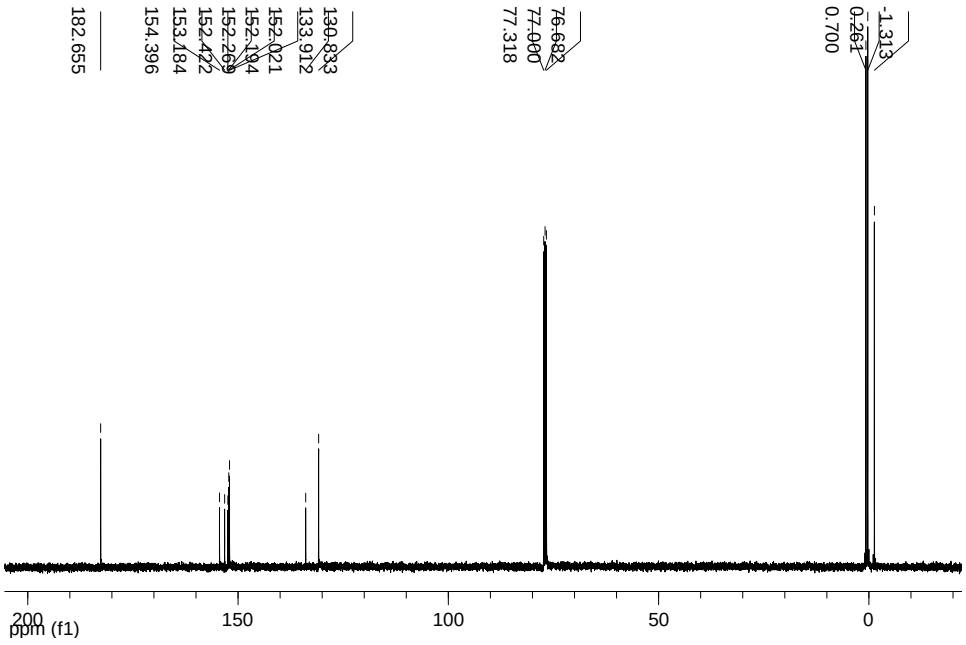
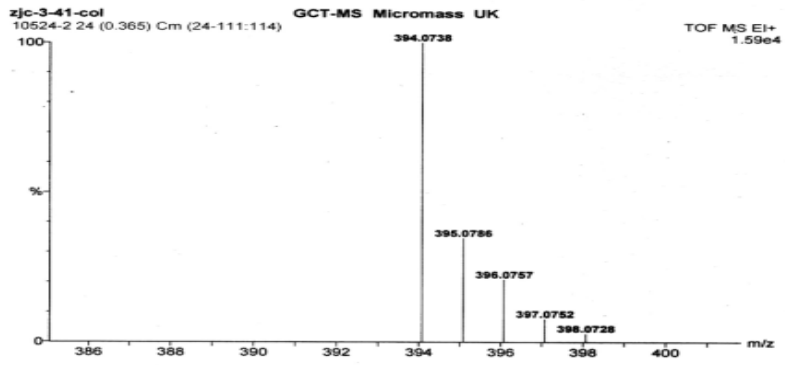


Figure S2. ^{13}C NMR (100 MHz, $CDCl_3$) spectrum of compound **2**



Elemental Composition Report

Tolerance = 10.0 PPM / DBE: min = -1.5, max = 50.0
Isotope cluster parameters: Separation = 1.0 Abundance = 1.0%

Monoisotopic Mass, Odd and Even Electron Ions
25 formula(e) evaluated with 1 results within limits (up to 50 closest results for each mass)

Minimum:	80.00				-1.5		
Maximum:	100.00		200.0	10.0	50.0		
Mass	RA	Calc. Mass	mDa	PPM	DBE	Score	Formula
394.0738	100.00	394.0733	0.5	1.3	8.0	1	C17 H26 O Si3 S2

Figure S3. HRMS data of **2**

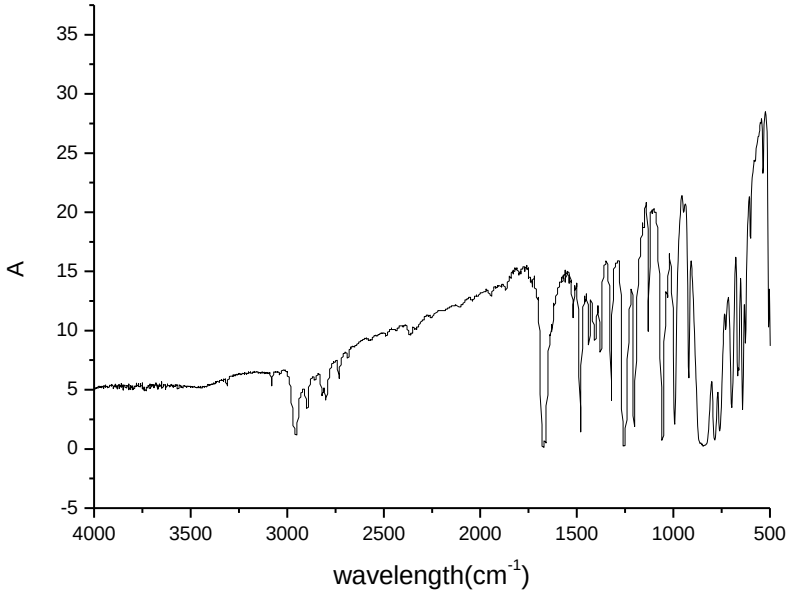


Figure S4. IR spectrum of **2**

NMR, HRMS and IR Spectra of 3

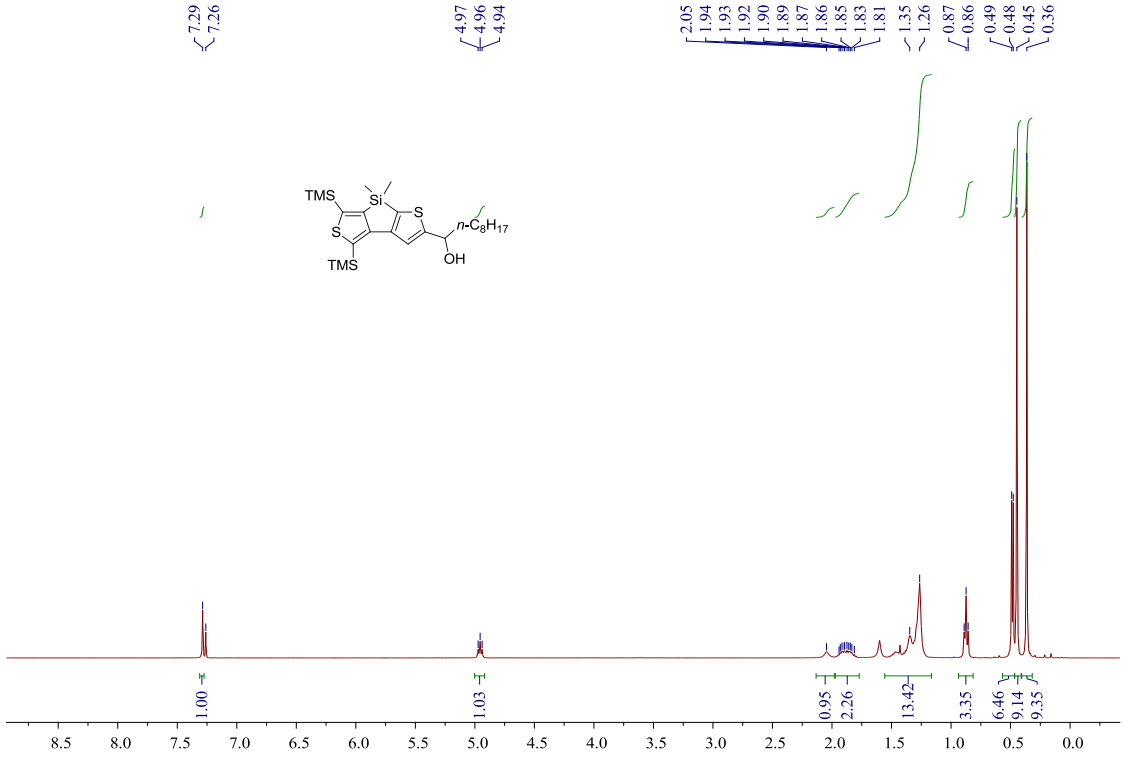
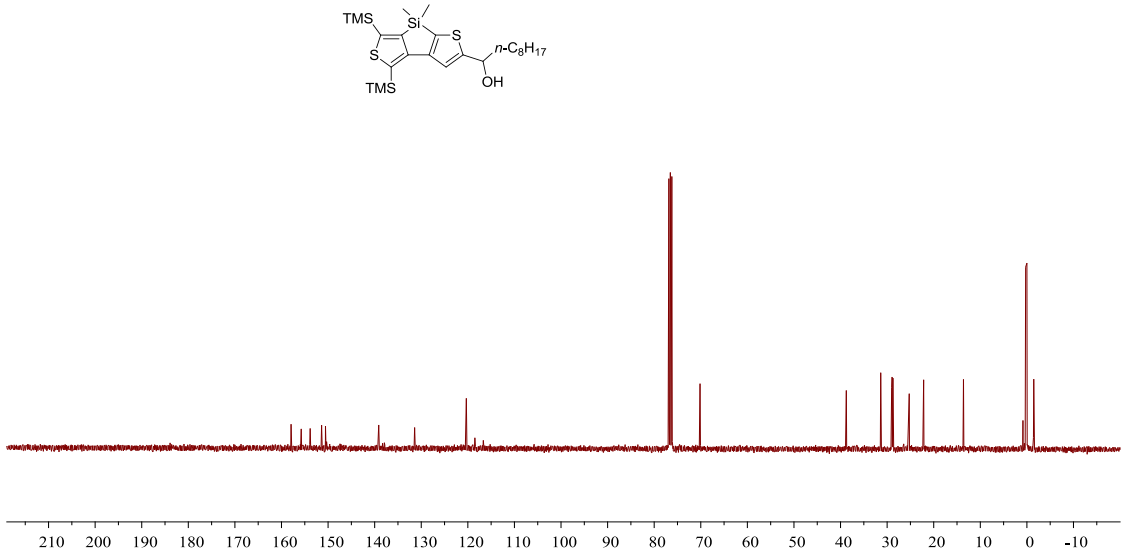


Figure S5. ^{1}H NMR (400 MHz, $CDCl_3$) spectrum of compound **3**



.***Figure S6.*** ^{13}C NMR (100 MHz, $CDCl_3$) spectrum of compound **3**

Shanghai Mass Spectrometry Center
Shanghai Institute of Organic Chemistr
Chinese Academic of Sciences
High Resolution MS DATA REPORT

Instrument: IonSpec 4.7 Tesla FTMS

Card Serial Number : WI14 813

Sample Serial Number: llj-2-50-ptlc2

Operator : HuaQin Date: 2014/05/12

Operation Mode: MALDI/DHB

Elemental Composition Search Report:

Target Mass:
Target m/z = 508.2133 ± 0.002
Charge = +1

Possible Elements:

Element	Exact Mass	Min	Max
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H	1.007825	0	100
O	15.994915	0	3
Si	27.976927	0	3
S	31.972071	0	3

Additional Search Restrictions:
DBE Limit Mode = Both Integer and Half-Integer
Minimum DBE = 0

Search Results:
Number of Hits = 3

m/z	Delta m/z	DBE	Formula
508.21341	-0.00011	8.0	$C_{27}H_{40}O_2S_2^{+1}$
508.21359	-0.00029	4.0	$C_{23}H_{44}OSi_2S_2^{+1}$
508.21382	-0.00052	5.0	$C_{26}H_{44}Si_2S_3^{+1}$

Figure S7. HRMS spectrum of compound **3**

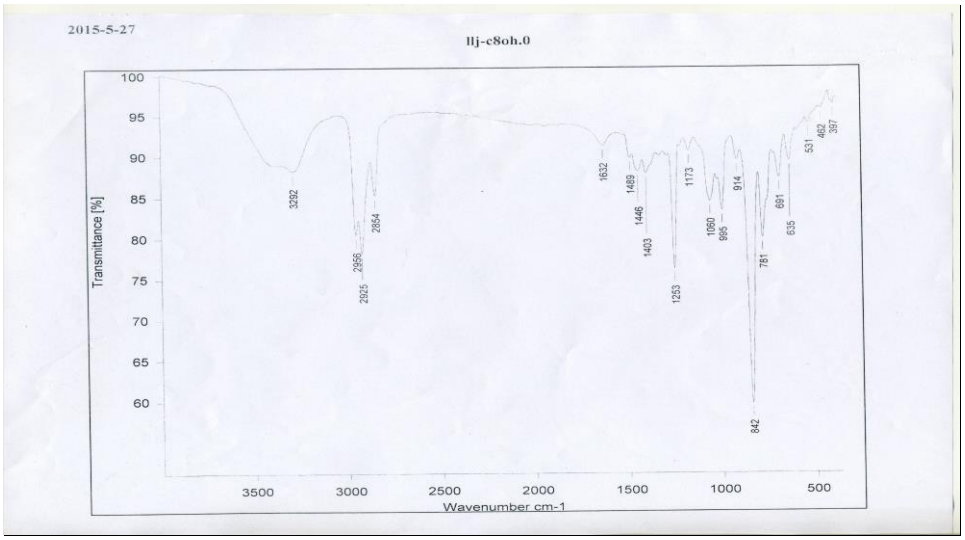


Figure S8 IR spectrum of compound **3**

NMR, HRMS and IR Spectra of 4

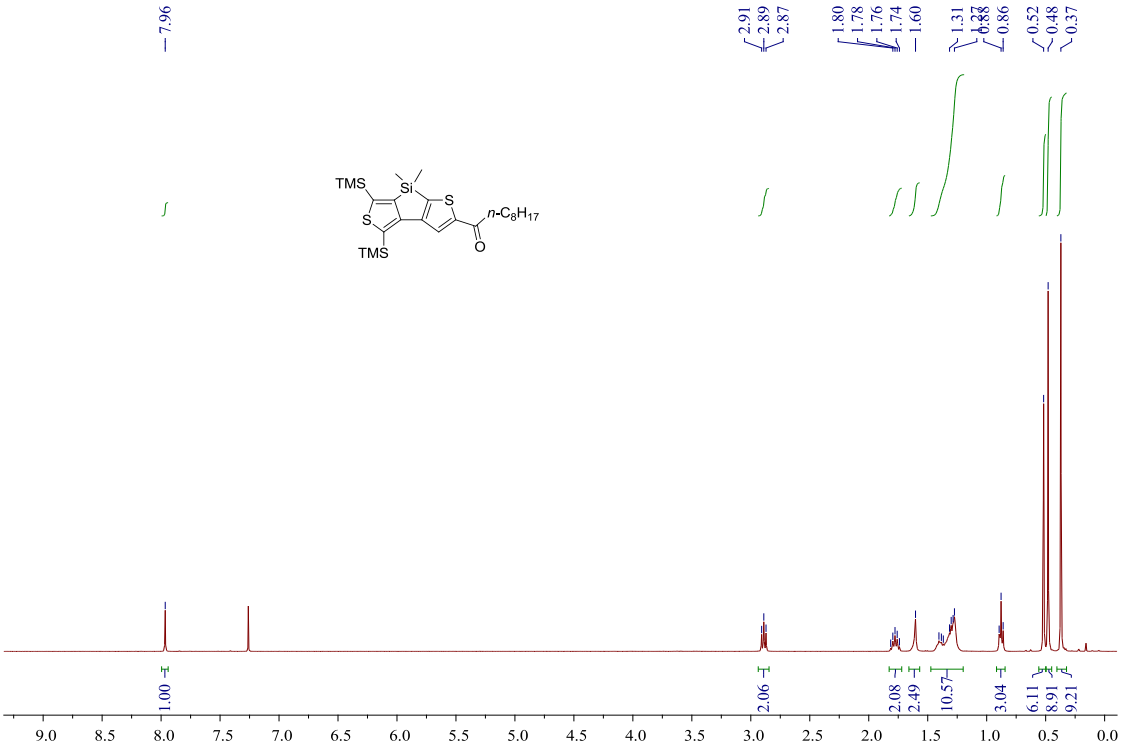


Figure S9 ^{1}H NMR (400 MHz, $CDCl_3$) spectrum of compound **4**

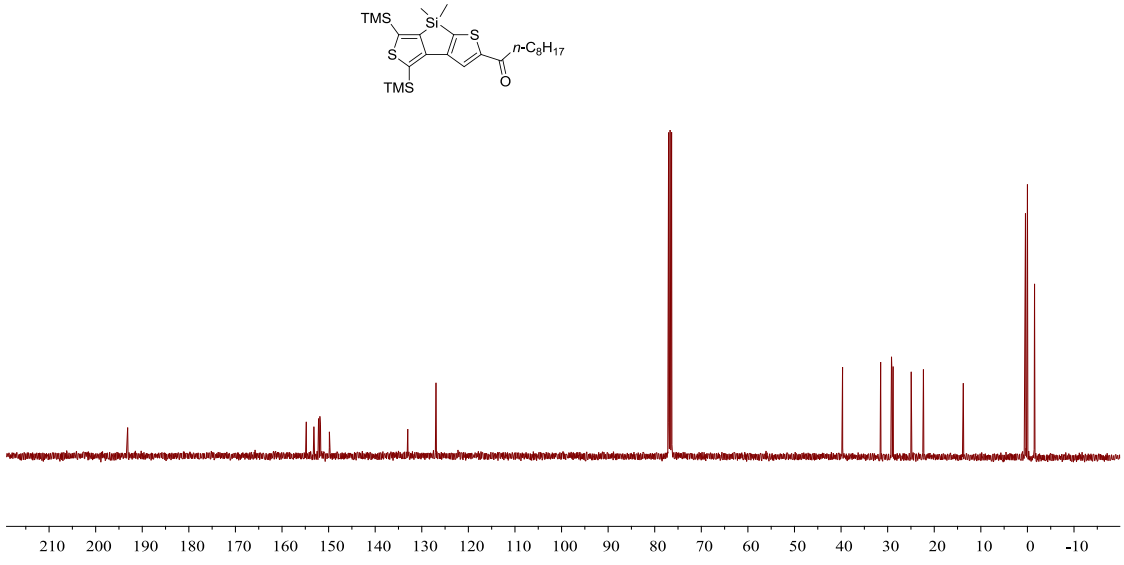


Figure S10 ^{13}C NMR (100 MHz, $CDCl_3$) spectrum of compound **4**

Shanghai Mass Spectrometry Center
Shanghai Institute of Organic Chemistry
Chinese Academic of Sciences
High Resolution MS Data Report

Instrument: Waters Micromass GCT Premier Ionisation Mode: EI+ Electron Energy: 70eV

Card Serial Number: GCT-2-TI4-05-053468

Sample Serial Number: LLJ-2-77-CCL

Operator: Li

Date: 2014/06/06

Elemental Composition Report

Single Mass Analysis
Tolerance = 5.0 PPM / DBE: min = -1.5, max = 50.0
Element prediction: Off

Monoisotopic Mass, Odd and Even Electron Ions
455 formula(e) evaluated with 4 results within limits (all results (up to 1000) for each mass)
Elements Used:
C: 0-60 H: 0-80 O: 0-4 S: 0-3 Si: 0-3

Minimum:				-1.5		
Maximum:		2.0	5.0	50.0		
Mass	Calc. Mass	mDa	PPM	DBE	i-FIT	Formula
506.1983	506.1983	0.0	0.0	9.0	34.9	C27 H38 O3 S3
	506.1981	0.2	0.4	9.0	21.4	C26 H38 O4 S2 Si
	506.1985	-0.2	-0.4	8.0	27.7	C25 H42 O S2 Si3
	506.1987	-0.4	-0.8	8.0	12.6	C26 H42 S2 Si2

Figure S11 HRMS spectrum of compound **4**

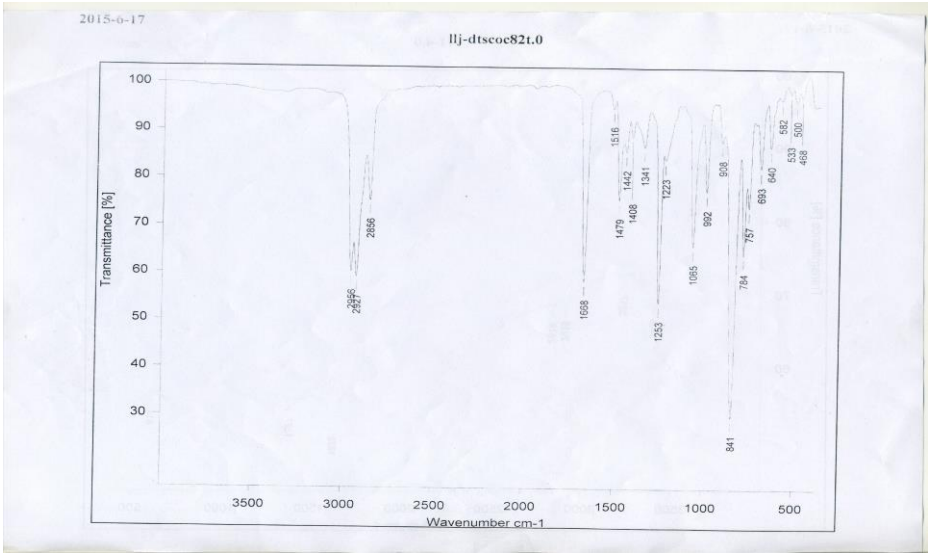


Figure S12 IR spectrum of compound **4**

NMR, HRMS and IR Spectra of 5

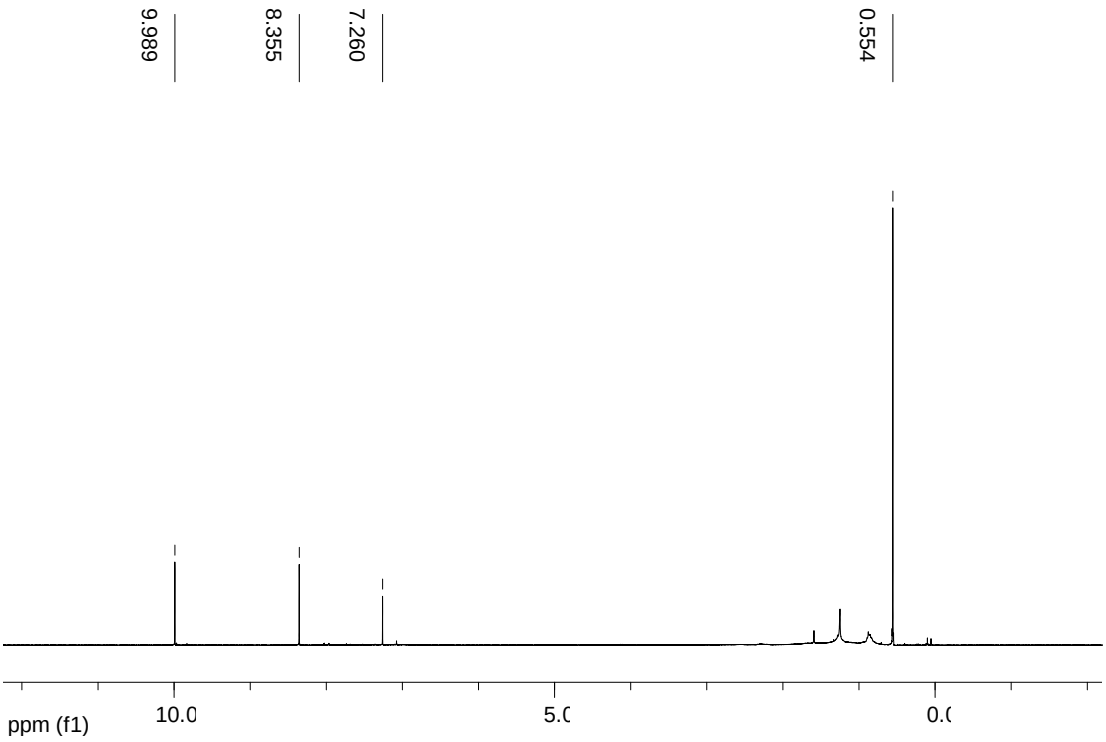


Figure S13. ^{1}H-NMR (400 MHz, $CDCl_3$) spectrum of compound **5.**

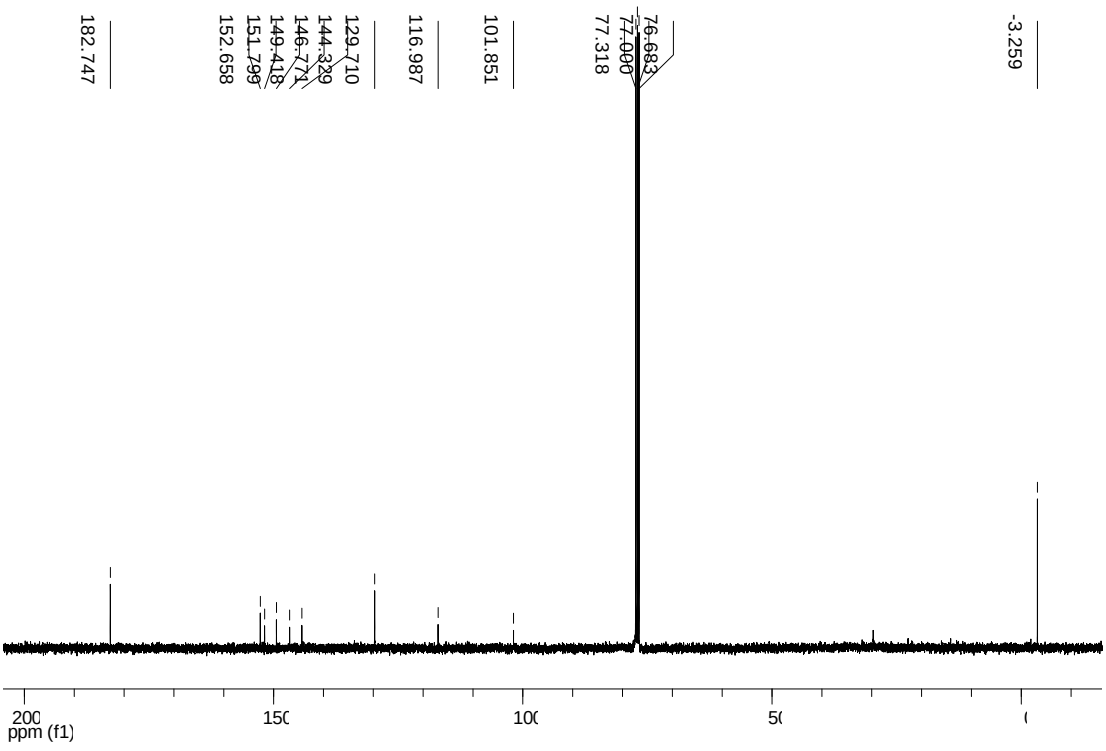


Figure S14. ^{13}C NMR (100 MHz, $CDCl_3$) spectrum of **5**

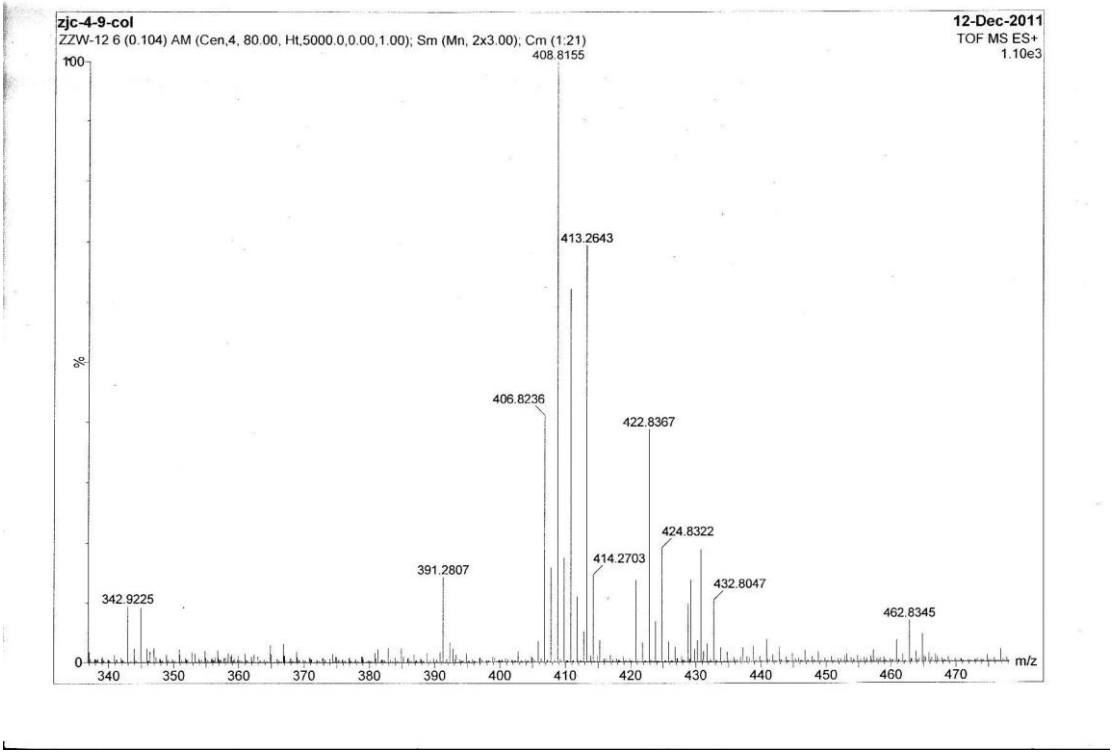


Figure S15. HRMS spectrum of **5**

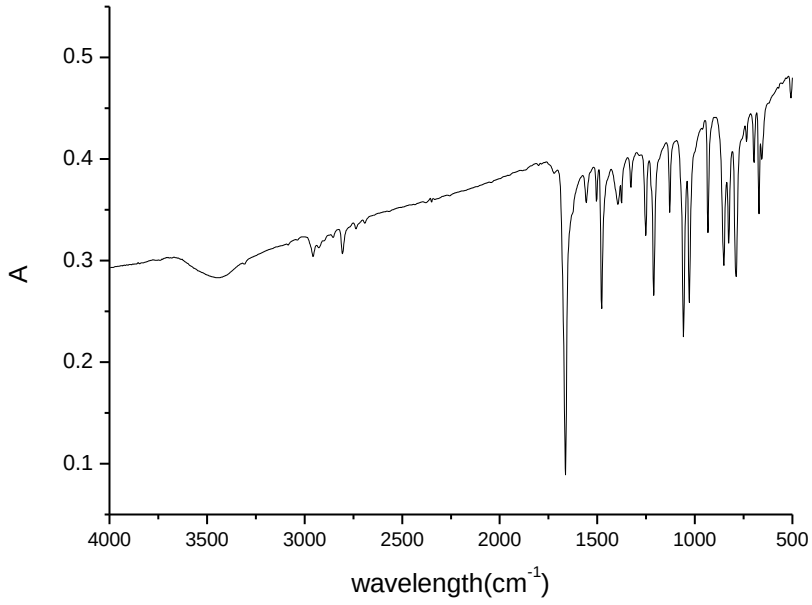


Figure S16. IR spectrum of **5**

NMR, HRMS and IR Spectra of 6

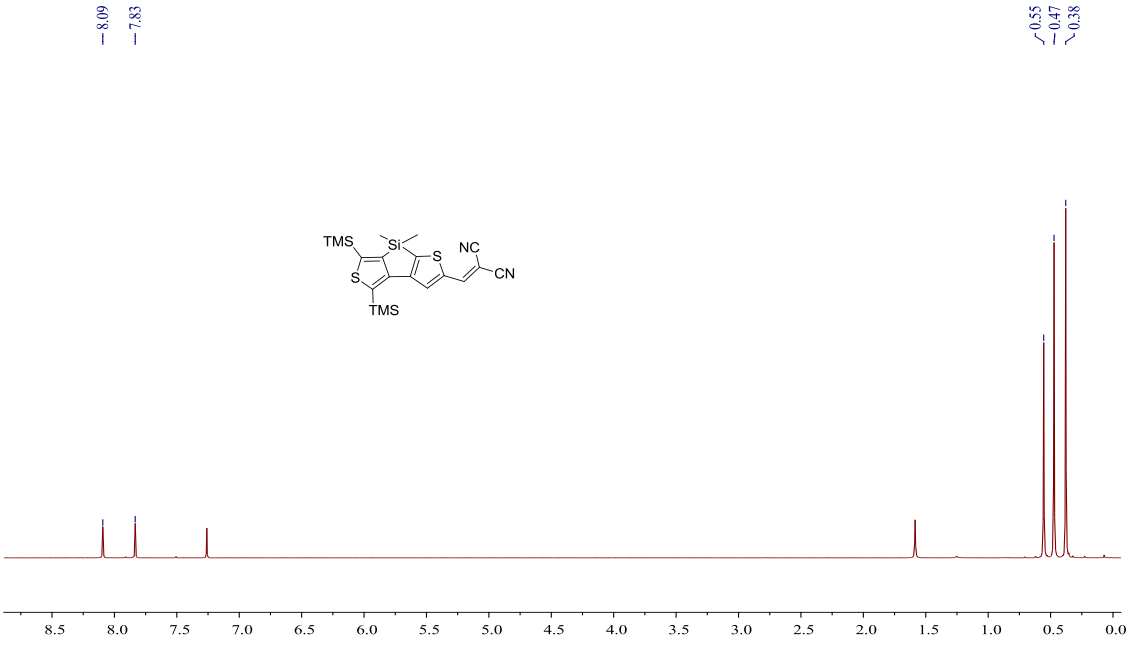


Figure S17 ^{1}H NMR (300 MHz, $CDCl_3$) spectrum of compound **6**

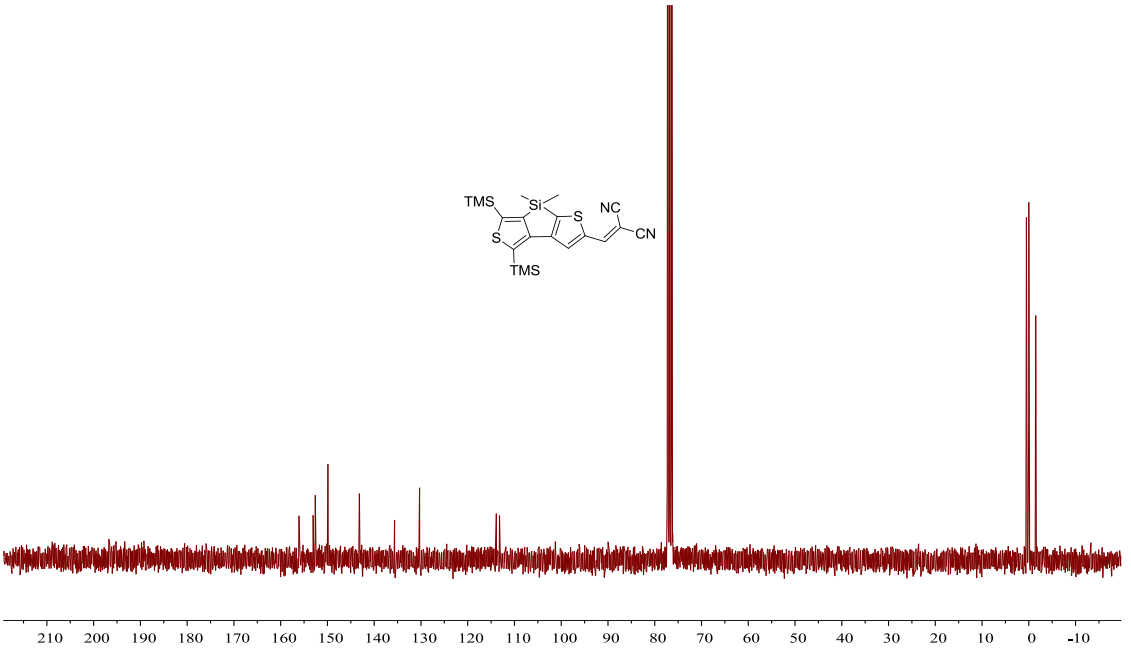


Figure S18 ^{13}C NMR (75 MHz, $CDCl_3$) spectrum of compound **6**

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 FT Ultra

Card Serial Number : M151232

Sample Serial Number: LLJ-3-80-COL

Operator : HUAQIN Date: 2015/04/22

Operation Mode: DART Postive

Elemental composition search on mass 443.09

m/z= 438.09-448.09

m/z	Theo. Mass	Delta (ppm)	RDB equiv.	Composition
443.0913	443.0914	-0.13	12.5	$C_{21}H_{23}O_3N_2S_2Si$
	443.0914	-0.16	22.5	$C_{29}H_{15}O_5$
	443.0912	0.39	12.5	$C_{20}H_{23}O_4N_2SSi_2$
	443.0911	0.42	2.5	$C_{12}H_{31}O_2N_4S_3Si_3$
	443.0916	-0.65	12.5	$C_{22}H_{23}O_2N_2S_3$
	443.0909	0.91	12.5	$C_{18}H_{23}O_5N_2Si_3$
	443.0918	-1.05	11.5	$C_{20}H_{27}N_2S_2Si_3$
	443.0918	-1.08	21.5	$C_{28}H_{19}O_2Si_2$
	443.0907	1.34	3.5	$C_{13}H_{27}O_5N_4S_3Si$
	443.0907	1.43	22.0	$C_{27}H_{17}N_3SSi$

Figure S19 HRMS spectrum of compound **6**

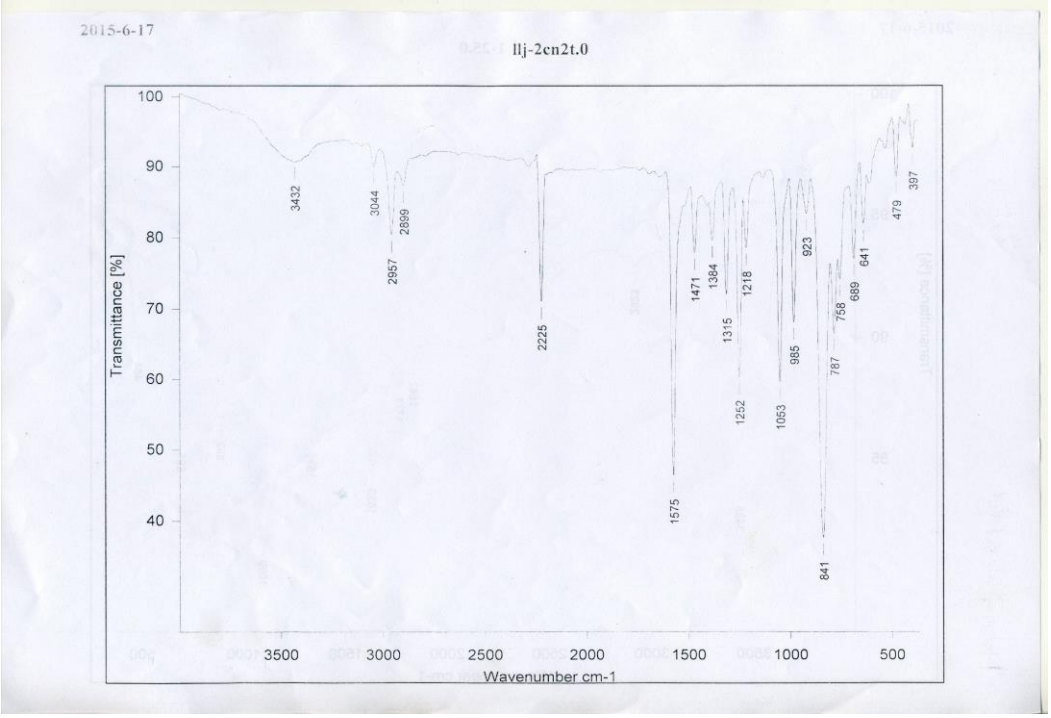


Figure S20 IR spectrum of compound **6**

NMR, HRMS and IR Spectra of M1

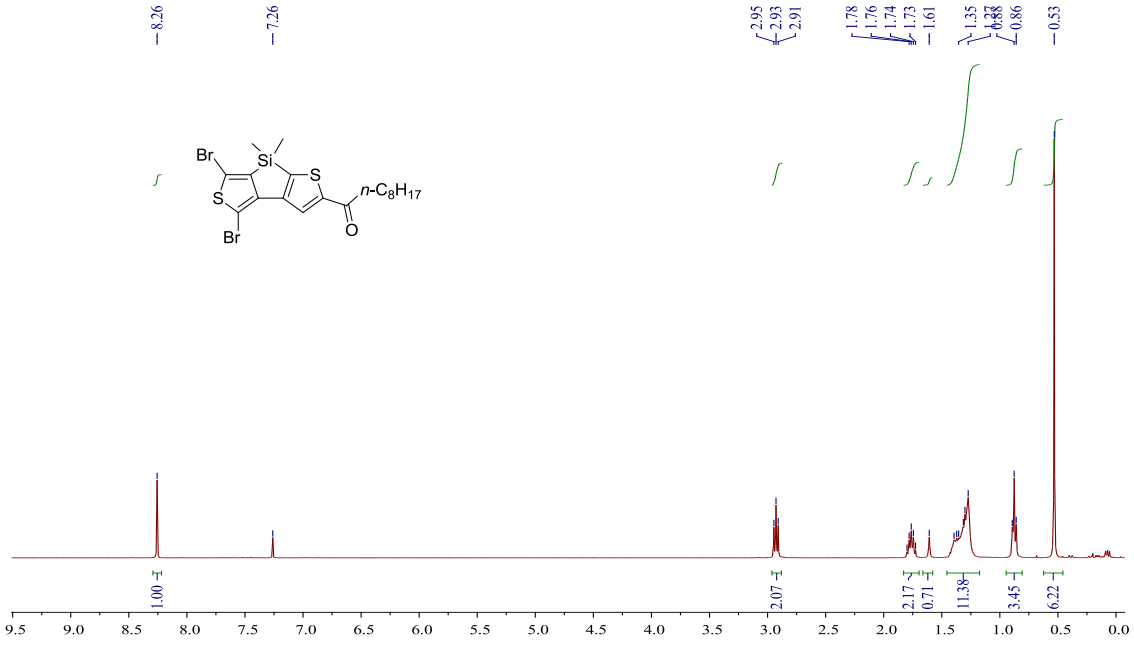


Figure S21 ^{1}H NMR (400 MHz, $CDCl_3$) spectrum of compound **M1**

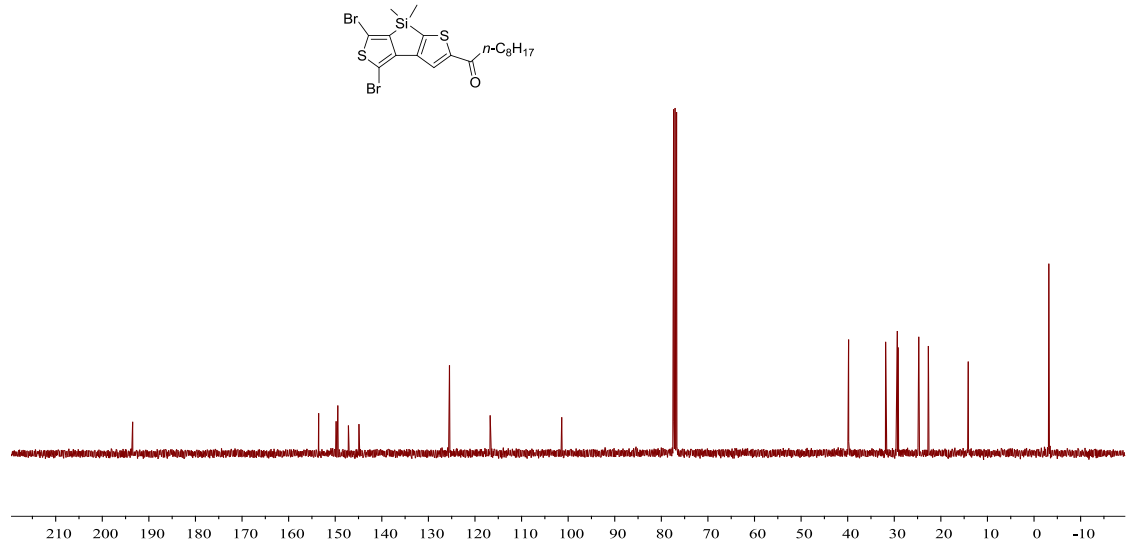


Figure S22 ^{13}C NMR (100 MHz, $CDCl_3$) spectrum of compound **M1**

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

Instrument: IonSpec 4.7 Tesla FTMS

Card Serial Number : WI14 424

Sample Serial Number: LLJ-2-82-COL2

Operator : HuaQin Date: 2014/02/21

Operation Mode: MALDI/DHB

Elemental Composition Search Report:

Target Mass:
Target m/z = 518.9469 ± 0.002
Charge = +1

Possible Elements:

Element	Exact Mass	Min	Max
C	12.000000	0	100
H	1.007825	0	100
O	15.994915	0	1
Si	27.976927	0	1
S	31.972071	0	2
Br	78.918338	0	2

Additional Search Restrictions:
DBE Limit Mode = Both Integer and Half-Integer
Minimum DBE = 0

Search Results:
Number of Hits = 2

m/z	Delta m/z	DBE	Formula
518.94738	-0.00048	29.0	$C_{22}H_{31}OSBr^{+1}$
518.94774	-0.00084	7.5	$C_{19}H_{35}OSiS_2Br_2^{+1}$

Figure S23 HRMS spectrum of compound **M1**

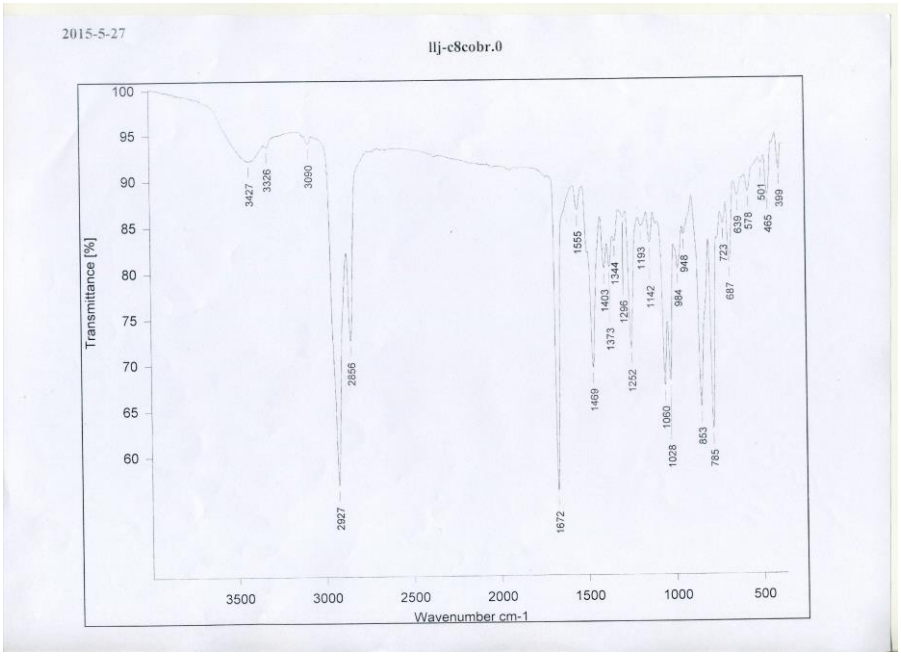


Figure S24 IR spectrum of compound **M1**

NMR, HRMS and IR Spectra of M2

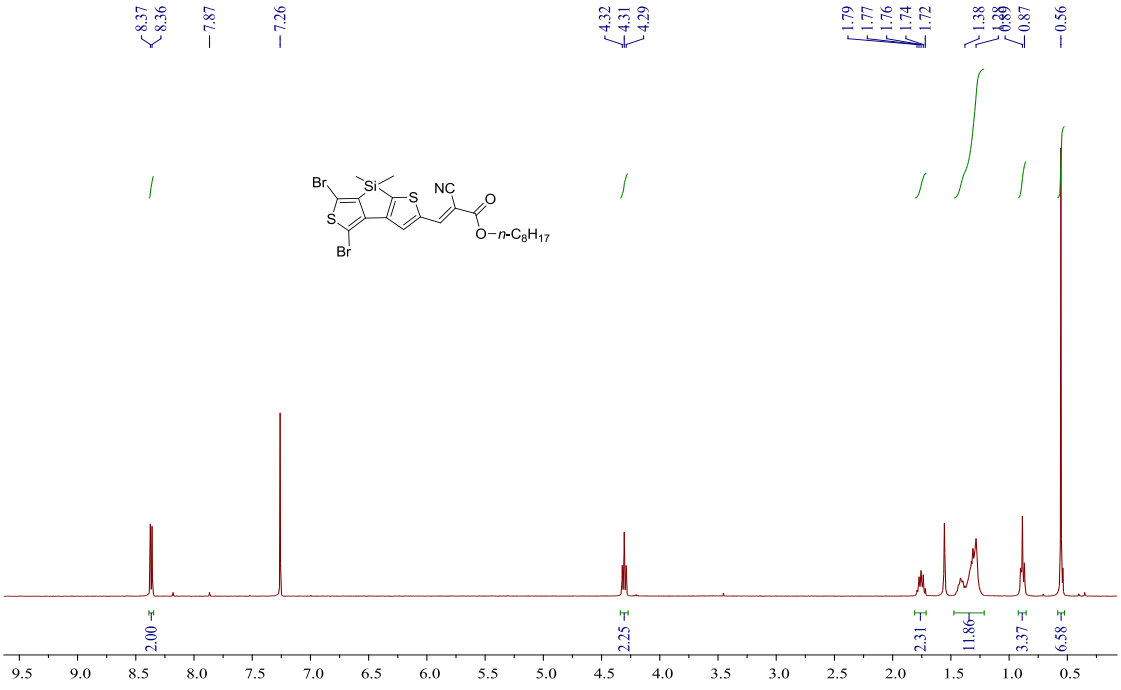


Figure S25 ^{1}H NMR (300 MHz, $CDCl_3$) spectrum of compound **M2**

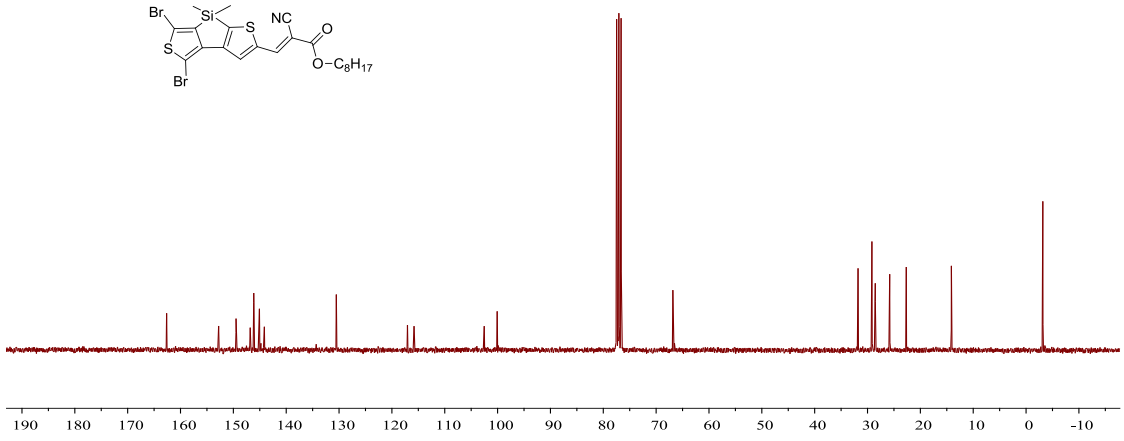


Figure S26 ^{13}C NMR (75 MHz, $CDCl_3$) spectrum of compound **M2**

Shanghai Mass Spectrometry Center
Shanghai Institute of Organic Chemistry
Chinese Academic of Sciences
High Resolution MS Data Report

Instrument: Waters Micromass GCT Ionisation Mode: EI+ Electron Energy: 70eV

Card Serial Number: GCT-*Y14-06*-OS0469

Sample Serial Number: LLJ 2-132-M

Operator: LL

Date: 2014/06/06

Elemental Composition Report

Single Mass Analysis
Tolerance = 2.0 mDa / DBE: min = -1.5, max = 50.0
Isotope cluster parameters: Separation = 1.0 Abundance = 1.0%

Monoisotopic Mass, Odd and even Electron Ions
684 formula(e) evaluated with 4 results within limits (all results (up to 1000) for each mass)

Minimum:				-1.5		
Maximum:		2.0	5.0	50.0		
Mass	Calc. Mass	mDa	PPM	DBE	Score	Formula
584.9467	584.9467	0.0	0.1	42.5	4	C41 H O2 Si S
	584.9469	-0.2	-0.3	42.5	3	C42 H O S2
	584.9463	0.4	0.7	31.0	1	C22 H25 N O2 Si S2 Br2
	584.9459	0.8	1.3	32.0	2	C35 H8 N O2 S Br

Figure S27 HRMS spectrum of compound **M2**

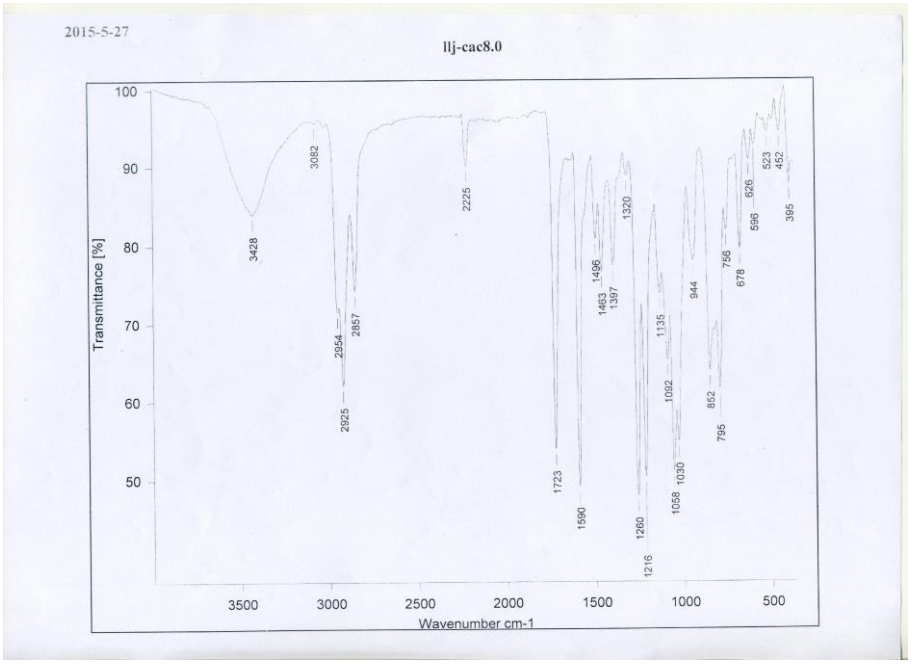


Figure S28 IR of compound **M2**

NMR, HRMS and IR Spectra of M3

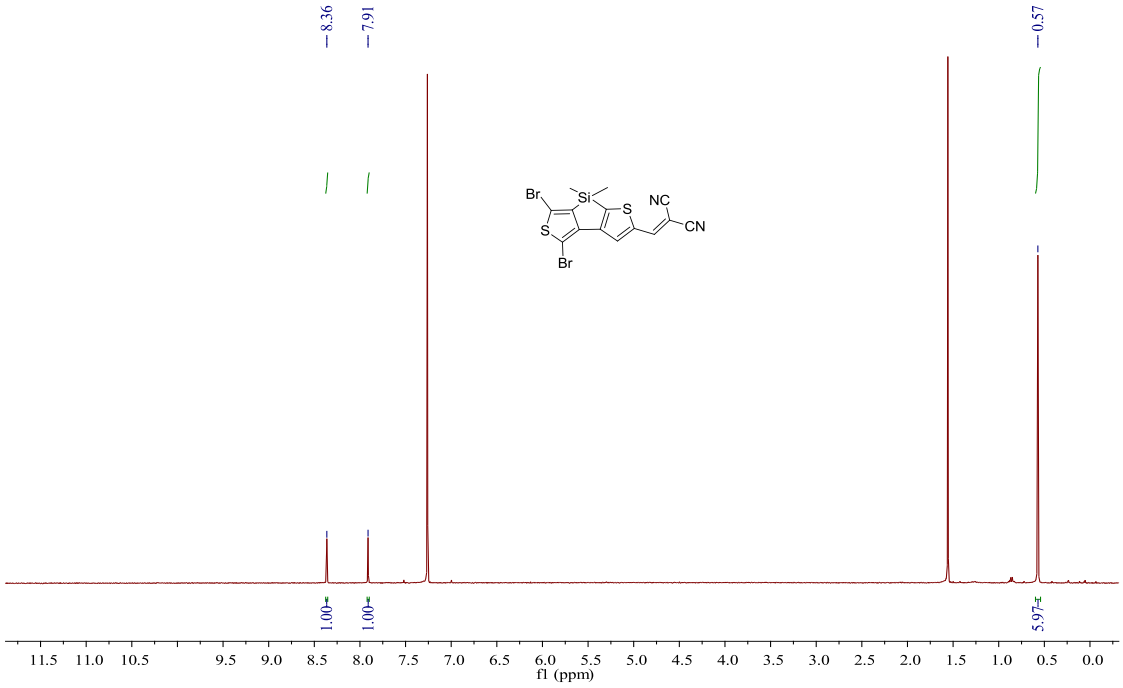


Figure S29 ^{1}H NMR (300 MHz, $CDCl_3$) spectrum of compound **M3**

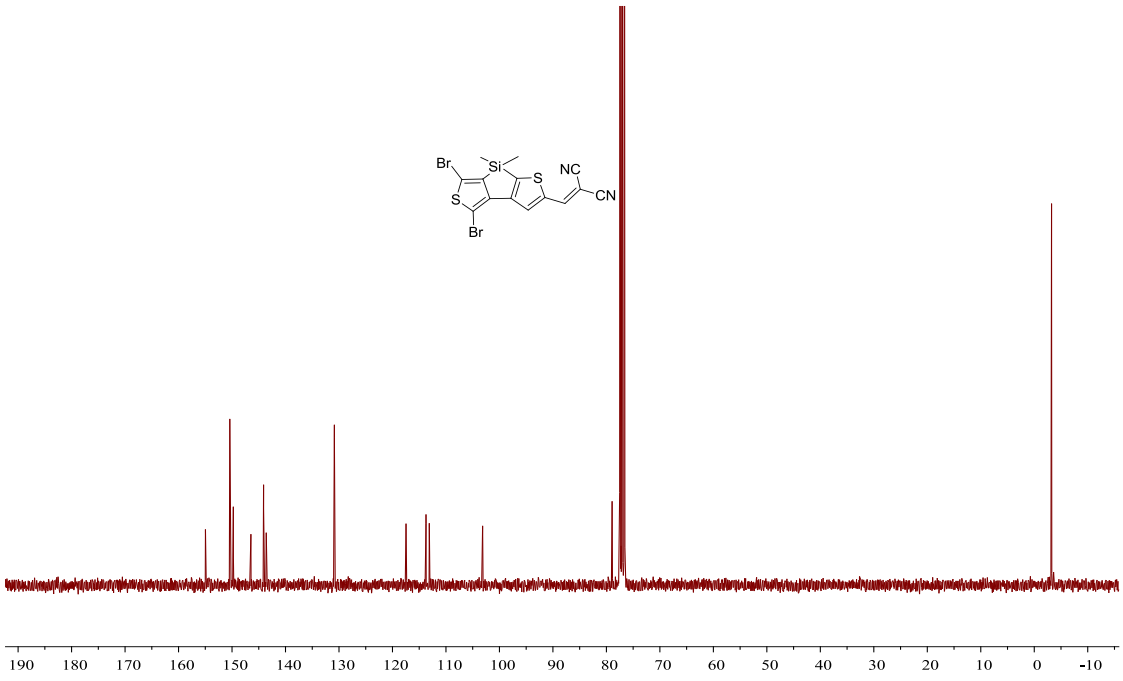


Figure S30 ^{13}C NMR (75 MHz, $CDCl_3$) spectrum of compound **M3**

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 FT Ultra

Card Serial Number : M151231

Sample Serial Number: LLJ-3-83-COL

Operator : HUAQIN Date: 2015/04/22

Operation Mode: DART Postive

Elemental composition search on mass 454.83

m/z= 449.83-459.83

m/z	Theo. Mass	Delta (ppm)	RDB equiv.	Composition
454.8336	454.8335	0.07	11.5	$C_{13}H_9ON_2Br_2SSi_2$
	454.8336	-0.12	13.0	$C_{11}H_6O_3N_3BrS_2Si_3$
	454.8334	0.27	14.0	$C_{13}H_2O_5N_3BrSi_3$
	454.8338	-0.44	11.5	$C_{14}H_9N_2Br_2S_2Si$
	454.8338	-0.46	21.5	$C_{22}HO_2Br_2$
	454.8333	0.57	11.5	$C_{12}H_9O_2N_2Br_2Si_3$
	454.8339	-0.63	13.0	$C_{12}H_6O_2N_3BrS_3Si_2$
	454.8340	-0.94	2.0	$C_6H_{15}O_5NBr_2SSi_3$
	454.8331	0.97	12.5	$C_{14}H_5O_4N_2Br_2S$
	454.8331	1.09	2.5	$C_6H_{13}O_2N_4Br_2S_2Si$

Figure S31 HRMS spectrum of compound **M3**

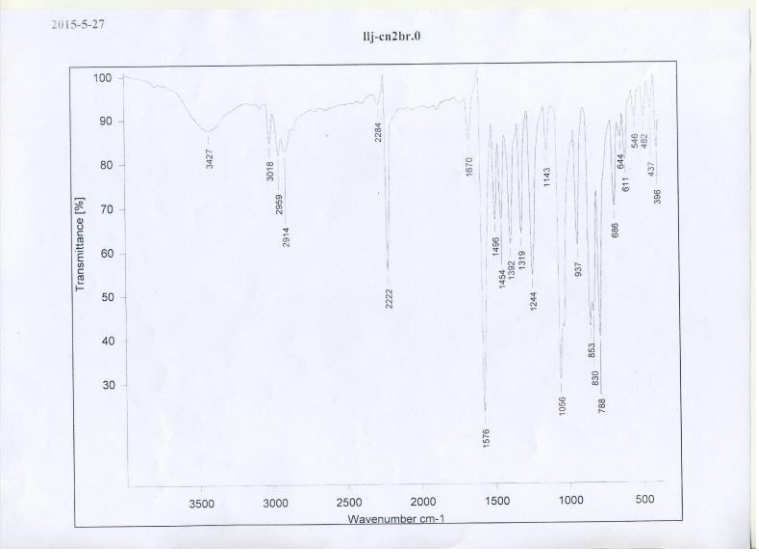


Figure S32 IR spectrum of compound **M3**

^{1}H NMR Spectra of PBDTDTSi-1

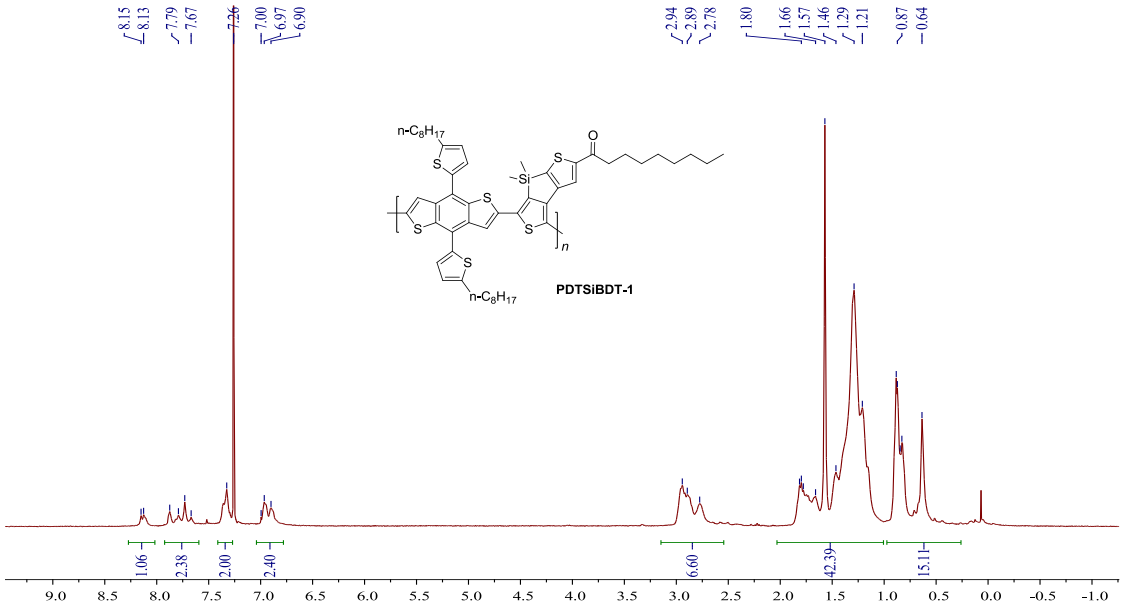


Figure S33 ^{1}H NMR (400 MHz, $CDCl_3$) spectrum of polymer **PBDTDTSi-1**

^{1}H NMR Spectra of PBDTDTSi-2

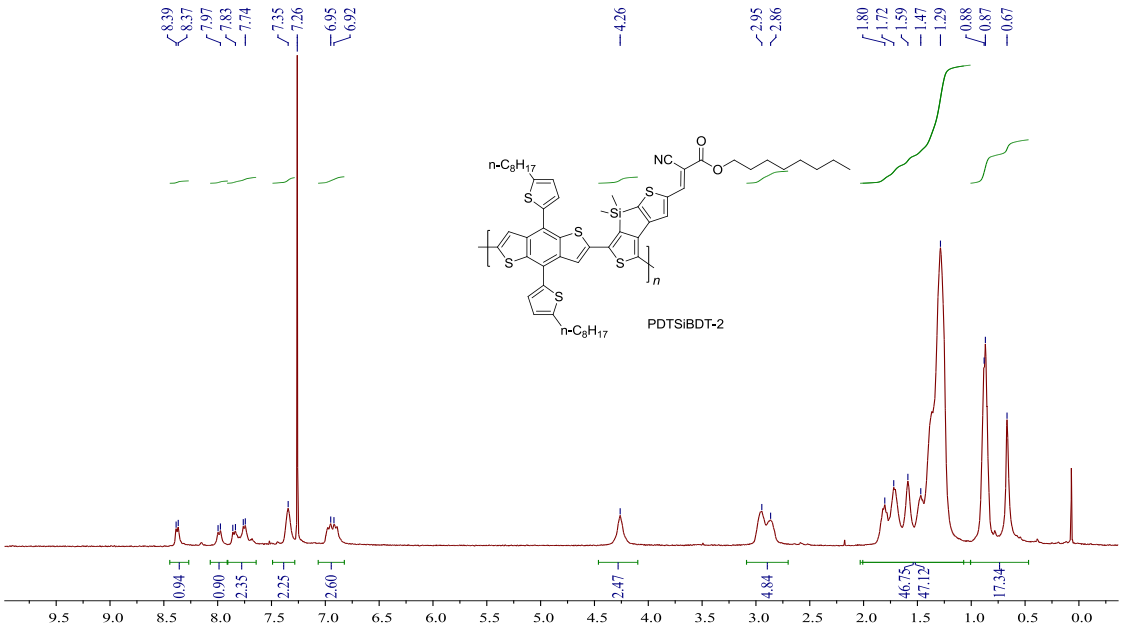


Figure S34 ^{1}H NMR (400 MHz, $CDCl_3$) spectrum of polymer **PBDTDTSi-2**

^{1}H NMR Spectra of PBDTDTSi-3

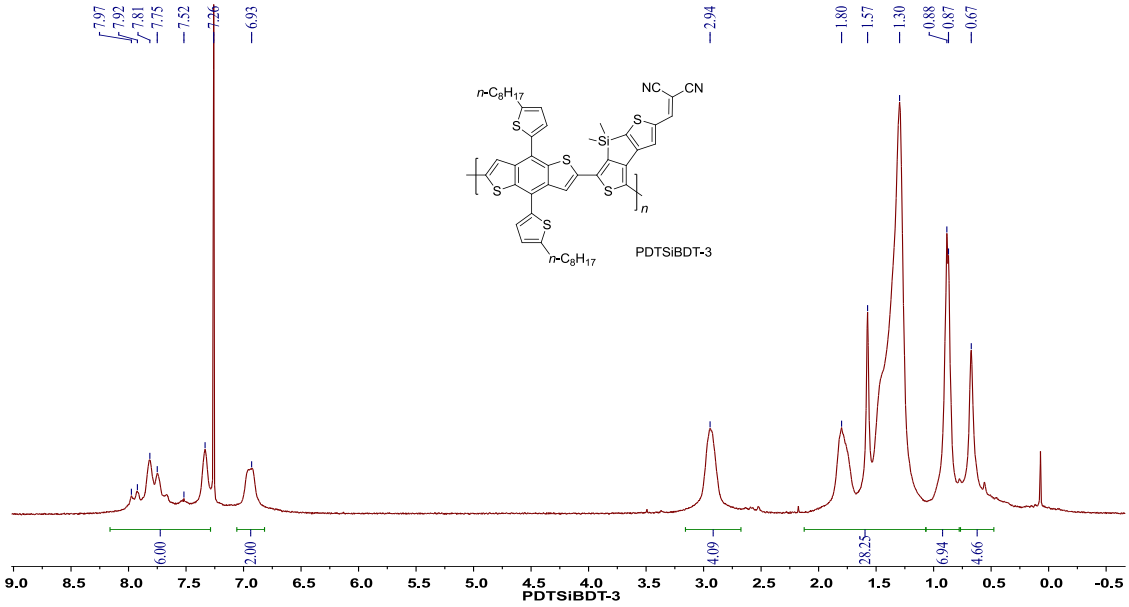
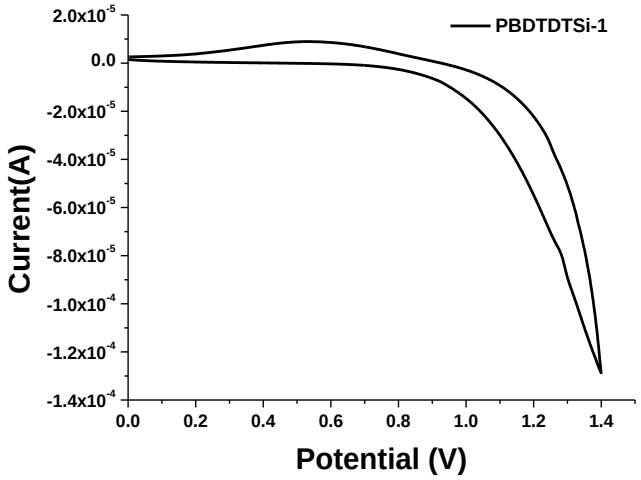


Figure S35 ^{1}H NMR (400 MHz, $CDCl_3$) spectrum of polymer **PBDTDTSi-3**

3. Cyclic voltammetric behaviors of PBDTDTSi polymers



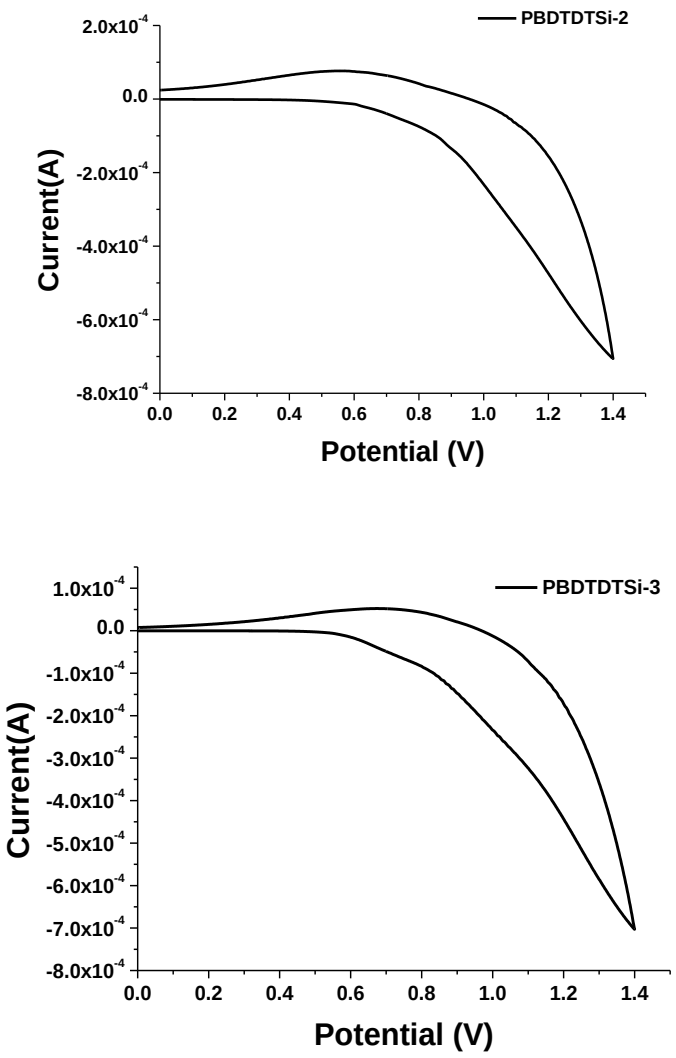


Figure S36. Cyclic voltammograms of polymer films in acetonitrile solution containing 0.1 M Bu_4NPF_6, $Ag/AgNO_3$ as the reference electrode.

4. X-ray crystallographic data

X-ray crystallographic data of 6

Table S4. Crystal data and structure refinement for 6.

Identification code	6
Empirical formula	C22 H25 Br2 N O2 S2 Si
Formula weight	587.46
Temperature	293(2) K

Wavelength	0.71073 A
Crystal system, space group	Triclinic, P-1
Unit cell dimensions	a = 9.117(3) A alpha = 86.3520(10) deg. b = 9.2590(18) A beta = 86.1700(10) deg. c = 16.283(3) A gamma = 69.853(3) deg.
Volume	1286.3(5) A^3
Z, Calculated density	2, 1.517 Mg/m^3
Absorption coefficient	3.378 mm^-1
F(000)	592
Crystal size	0.46 x 0.27 x 0.13 mm
Theta range for data collection	2.35 to 25.00 deg.
Limiting indices	-10<=h<=8, -11<=k<=10, -19<=l<=15
Reflections collected / unique	6569 / 4483 [R(int) = 0.0228]
Completeness to theta = 25.00	99.00%
Absorption correction	Semi-empirical from equivalents
Max. and min. transmission	0.6678 and 0.3056
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	4483 / 13 / 271
Goodness-of-fit on F^2	1.072
Final R indices [I>2sigma(I)]	R1 = 0.0427, wR2 = 0.1221
R indices (all data)	R1 = 0.0586, wR2 = 0.1326
Largest diff. peak and hole	0.837 and -0.623 e.A^-3

Table S5. Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters (A^2 x 10^3) for 6. U(eq) is defined as one third of the trace of the orthogonalized Uij tensor.

	x	y	z	U(eq)
Br(1)	3463(1)	-2848(1)	6804(1)	53(1)
Br(2)	9048(1)	-2286(1)	8406(1)	70(1)
Si(1)	7134(1)	1026(1)	6805(1)	38(1)
S(1)	6379(1)	-3294(1)	7813(1)	49(1)
S(2)	4501(1)	2908(1)	5443(1)	39(1)
O(1)	-796(3)	3618(3)	3761(2)	64(1)
O(2)	-155(3)	5652(3)	3267(2)	50(1)
N(1)	2904(4)	5934(4)	4161(3)	68(1)
C(5)	4673(3)	379(4)	6235(2)	34(1)
C(1)	5081(4)	-2190(4)	7095(2)	40(1)
C(3)	6740(4)	-776(4)	7204(2)	40(1)
C(12)	1414(4)	4013(4)	4263(2)	38(1)
C(11)	1826(4)	2718(4)	4752(2)	39(1)
C(6)	5425(4)	1456(4)	6135(2)	35(1)
C(13)	2255(4)	5062(4)	4207(2)	45(1)

C(7)	3354(4)	730(4)	5757(2)	38(1)
C(14)	38(4)	4376(4)	3743(2)	43(1)
C(15)	-1443(4)	6109(5)	2719(2)	52(1)
C(16)	-1257(5)	7382(6)	2162(3)	77(2)
C(17)	-2527(6)	7974(7)	1546(3)	102(2)
C(18)	-2269(10)	9281(11)	988(6)	185(4)
C(19)	-3190(15)	10545(10)	750(9)	296(8)
C(20)	-2837(14)	11630(10)	148(6)	197(5)
C(21)	-2650(11)	12900(10)	428(5)	170(4)
C(22)	-2407(12)	14042(10)	-193(6)	172(4)
C(2)	5404(4)	-908(4)	6825(2)	37(1)
C(8)	3088(4)	2082(4)	5290(2)	36(1)
C(10)	6842(5)	2381(5)	7645(3)	61(1)
C(4)	7351(4)	-1965(4)	7741(2)	44(1)
C(9)	9086(4)	586(5)	6264(3)	60(1)

Table S6. Bond lengths [A] and angles [deg] for 6.

Br(1)-C(1)	1.877(4)	C(8)-C(11)-H(11A)	114.4
Br(2)-C(4)	1.876(4)	C(5)-C(6)-S(2)	110.8(2)
Si(1)-C(9)	1.857(4)	C(5)-C(6)-Si(1)	113.6(2)
Si(1)-C(10)	1.858(4)	S(2)-C(6)-Si(1)	135.5(2)
Si(1)-C(6)	1.876(3)	N(1)-C(13)-C(12)	178.5(4)
Si(1)-C(3)	1.892(4)	C(8)-C(7)-C(5)	112.5(3)
S(1)-C(1)	1.735(3)	C(8)-C(7)-H(7A)	123.8
S(1)-C(4)	1.741(4)	C(5)-C(7)-H(7A)	123.8
S(2)-C(6)	1.715(3)	O(1)-C(14)-O(2)	124.6(3)
S(2)-C(8)	1.747(3)	O(1)-C(14)-C(12)	123.6(3)
O(1)-C(14)	1.198(5)	O(2)-C(14)-C(12)	111.8(3)
O(2)-C(14)	1.336(4)	O(2)-C(15)-C(16)	106.9(3)
O(2)-C(15)	1.452(4)	O(2)-C(15)-H(15A)	110.3
N(1)-C(13)	1.150(5)	C(16)-C(15)-H(15A)	110.3
C(5)-C(6)	1.388(5)	O(2)-C(15)-H(15B)	110.3
C(5)-C(7)	1.408(5)	C(16)-C(15)-H(15B)	110.3
C(5)-C(2)	1.477(4)	H(15A)-C(15)-H(15B)	108.6
C(1)-C(2)	1.359(5)	C(15)-C(16)-C(17)	112.7(4)
C(3)-C(4)	1.344(5)	C(15)-C(16)-H(16A)	109
C(3)-C(2)	1.446(5)	C(17)-C(16)-H(16A)	109
C(12)-C(11)	1.350(5)	C(15)-C(16)-H(16B)	109
C(12)-C(13)	1.426(5)	C(17)-C(16)-H(16B)	109
C(12)-C(14)	1.489(5)	H(16A)-C(16)-H(16B)	107.8
C(11)-C(8)	1.428(5)	C(16)-C(17)-C(18)	110.3(6)

C(11)-H(11A)	0.93	C(16)-C(17)-H(17A)	109.6
C(7)-C(8)	1.378(5)	C(18)-C(17)-H(17A)	109.6
C(7)-H(7A)	0.93	C(16)-C(17)-H(17B)	109.6
C(15)-C(16)	1.490(6)	C(18)-C(17)-H(17B)	109.6
C(15)-H(15A)	0.97	H(17A)-C(17)-H(17B)	108.1
C(15)-H(15B)	0.97	C(19)-C(18)-C(17)	131.5(9)
C(16)-C(17)	1.515(7)	C(19)-C(18)-H(18A)	104.4
C(16)-H(16A)	0.97	C(17)-C(18)-H(18A)	104.4
C(16)-H(16B)	0.97	C(19)-C(18)-H(18B)	104.4
C(17)-C(18)	1.541(10)	C(17)-C(18)-H(18B)	104.4
C(17)-H(17A)	0.97	H(18A)-C(18)-H(18B)	105.6
C(17)-H(17B)	0.97	C(18)-C(19)-C(20)	126.4(11)
C(18)-C(19)	1.239(11)	C(18)-C(19)-H(19A)	105.7
C(18)-H(18A)	0.97	C(20)-C(19)-H(19A)	105.7
C(18)-H(18B)	0.97	C(18)-C(19)-H(19B)	105.7
C(19)-C(20)	1.459(11)	C(20)-C(19)-H(19B)	105.7
C(19)-H(19A)	0.97	H(19A)-C(19)-H(19B)	106.2
C(19)-H(19B)	0.97	C(21)-C(20)-C(19)	118.1(10)
C(20)-C(21)	1.355(11)	C(21)-C(20)-H(20A)	107.8
C(20)-H(20A)	0.97	C(19)-C(20)-H(20A)	107.8
C(20)-H(20B)	0.97	C(21)-C(20)-H(20B)	107.8
C(21)-C(22)	1.478(10)	C(19)-C(20)-H(20B)	107.8
C(21)-H(21A)	0.97	H(20A)-C(20)-H(20B)	107.1
C(21)-H(21B)	0.97	C(20)-C(21)-C(22)	117.4(9)
C(22)-H(22A)	0.96	C(20)-C(21)-H(21A)	108
C(22)-H(22B)	0.96	C(22)-C(21)-H(21A)	108
C(22)-H(22C)	0.96	C(20)-C(21)-H(21B)	108
C(10)-H(10A)	0.96	C(22)-C(21)-H(21B)	108
C(10)-H(10B)	0.96	H(21A)-C(21)-H(21B)	107.2
C(10)-H(10C)	0.96	C(21)-C(22)-H(22A)	109.5
C(9)-H(9A)	0.96	C(21)-C(22)-H(22B)	109.5
C(9)-H(9B)	0.96	H(22A)-C(22)-H(22B)	109.5
C(9)-H(9C)	0.96	C(21)-C(22)-H(22C)	109.5
C(9)-Si(1)-C(10)	112.3(2)	H(22A)-C(22)-H(22C)	109.5
C(9)-Si(1)-C(6)	116.29(19)	H(22B)-C(22)-H(22C)	109.5
C(10)-Si(1)-C(6)	114.79(17)	C(1)-C(2)-C(3)	112.8(3)
C(9)-Si(1)-C(3)	112.26(17)	C(1)-C(2)-C(5)	133.6(3)
C(10)-Si(1)-C(3)	110.81(18)	C(3)-C(2)-C(5)	113.6(3)
C(6)-Si(1)-C(3)	88.00(15)	C(7)-C(8)-C(11)	124.4(3)
C(1)-S(1)-C(4)	90.05(17)	C(7)-C(8)-S(2)	111.0(2)
C(6)-S(2)-C(8)	92.07(16)	C(11)-C(8)-S(2)	124.7(3)
C(14)-O(2)-C(15)	116.9(3)	Si(1)-C(10)-H(10A)	109.5
C(6)-C(5)-C(7)	113.7(3)	Si(1)-C(10)-H(10B)	109.5
C(6)-C(5)-C(2)	113.9(3)	H(10A)-C(10)-H(10B)	109.5

C(7)-C(5)-C(2)	132.4(3)	Si(1)-C(10)-H(10C)	109.5
C(2)-C(1)-S(1)	112.3(3)	H(10A)-C(10)-H(10C)	109.5
C(2)-C(1)-Br(1)	128.8(3)	H(10B)-C(10)-H(10C)	109.5
S(1)-C(1)-Br(1)	118.91(19)	C(3)-C(4)-S(1)	113.7(3)
C(4)-C(3)-C(2)	111.2(3)	C(3)-C(4)-Br(2)	127.4(3)
C(4)-C(3)-Si(1)	137.8(3)	S(1)-C(4)-Br(2)	119.0(2)
C(2)-C(3)-Si(1)	110.9(2)	Si(1)-C(9)-H(9A)	109.5
C(11)-C(12)-C(13)	122.9(3)	Si(1)-C(9)-H(9B)	109.5
C(11)-C(12)-C(14)	119.6(3)	H(9A)-C(9)-H(9B)	109.5
C(13)-C(12)-C(14)	117.5(3)	Si(1)-C(9)-H(9C)	109.5
C(12)-C(11)-C(8)	131.3(3)	H(9A)-C(9)-H(9C)	109.5
C(12)-C(11)-H(11A)	114.4	H(9B)-C(9)-H(9C)	109.5

Symmetry transformations used to generate equivalent atoms:

Table S7. Anisotropic displacement parameters (A^2 x 10^3) for 6. The anisotropic displacement factor exponent takes the form: -2 pi^2 [h^2 a*^2 U11 + ... + 2 h k a* b* U12]

	U11	U22	U33	U23	U13	U12
Br(1)	53(1)	50(1)	68(1)	8(1)	-10(1)	-33(1)
Br(2)	67(1)	70(1)	75(1)	6(1)	-36(1)	-21(1)
Si(1)	36(1)	39(1)	46(1)	-2(1)	-9(1)	-19(1)
S(1)	54(1)	40(1)	53(1)	9(1)	-11(1)	-18(1)
S(2)	40(1)	38(1)	45(1)	4(1)	-9(1)	-22(1)
O(1)	56(1)	67(2)	83(2)	20(1)	-32(1)	-38(1)
O(2)	48(1)	49(1)	56(2)	9(1)	-20(1)	-19(1)
N(1)	68(2)	59(2)	92(3)	24(2)	-33(2)	-41(2)
C(5)	32(2)	35(2)	39(2)	-5(1)	1(1)	-16(1)
C(1)	39(2)	40(2)	44(2)	3(2)	-6(2)	-18(1)
C(3)	38(2)	37(2)	48(2)	-7(2)	-2(2)	-14(1)
C(12)	34(2)	39(2)	40(2)	-6(2)	-2(2)	-12(1)
C(11)	35(2)	43(2)	45(2)	-8(2)	-2(2)	-18(1)
C(6)	36(2)	35(2)	38(2)	-2(1)	-2(1)	-15(1)
C(13)	45(2)	42(2)	48(2)	6(2)	-17(2)	-15(2)
C(7)	37(2)	39(2)	44(2)	-2(2)	-2(2)	-20(1)
C(14)	39(2)	44(2)	45(2)	-3(2)	-4(2)	-13(2)
C(15)	46(2)	59(2)	51(2)	4(2)	-16(2)	-16(2)
C(16)	63(3)	90(3)	75(3)	30(3)	-18(2)	-25(2)
C(17)	82(3)	126(5)	71(4)	40(3)	-10(3)	-8(3)
C(18)	138(6)	219(7)	150(6)	79(6)	-6(5)	-17(5)
C(19)	326(13)	115(7)	354(16)	52(9)	201(12)	-7(9)
C(20)	326(14)	122(6)	143(8)	10(6)	28(9)	-85(8)

C(21)	183(7)	185(8)	160(8)	77(7)	-74(6)	-89(7)
C(22)	208(9)	143(7)	155(8)	56(6)	-12(7)	-57(6)
C(2)	35(2)	35(2)	41(2)	-1(1)	-1(2)	-15(1)
C(8)	33(2)	40(2)	39(2)	-6(1)	-4(1)	-18(1)
C(10)	78(2)	59(2)	57(3)	-4(2)	-10(2)	-35(2)
C(4)	41(2)	47(2)	48(2)	-1(2)	-10(2)	-17(2)
C(9)	46(2)	50(2)	87(3)	-5(2)	0(2)	-23(2)

Table S8. Hydrogen coordinates (x 10^4) and isotropic displacement parameters (A^2 x 10^3) for **6**.

	x	y	z	U(eq)
H(11A)	1173	2140	4737	47
H(7A)	2731	119	5756	46
H(15A)	-2435	6459	3032	63
H(15B)	-1413	5247	2401	63
H(16A)	-247	7017	1866	93
H(16B)	-1273	8224	2491	93
H(17A)	-3541	8351	1837	122
H(17B)	-2515	7140	1211	122
H(18A)	-1466	9530	1249	222
H(18B)	-1772	8787	485	222
H(19A)	-3591	11117	1244	355
H(19B)	-4064	10333	542	355
H(20A)	-1886	11073	-163	237
H(20B)	-3671	11970	-236	237
H(21A)	-1762	12564	777	204
H(21B)	-3568	13419	773	204
H(22A)	-2422	14939	77	258
H(22B)	-3227	14326	-576	258
H(22C)	-1415	13602	-484	258
H(10A)	7052	3284	7430	92
H(10B)	7541	1890	8074	92
H(10C)	5781	2669	7864	92
H(9A)	9238	1530	6074	89
H(9B)	9146	-29	5802	89
H(9C)	9883	31	6636	89

Table S9. Torsion angles [deg] for 6.

C(4)-S(1)-C(1)-C(2)	0.4(3)
C(4)-S(1)-C(1)-Br(1)	-178.8(2)
C(9)-Si(1)-C(3)-C(4)	62.0(5)
C(10)-Si(1)-C(3)-C(4)	-64.5(5)
C(6)-Si(1)-C(3)-C(4)	179.7(4)
C(9)-Si(1)-C(3)-C(2)	-118.1(3)
C(10)-Si(1)-C(3)-C(2)	115.4(3)
C(6)-Si(1)-C(3)-C(2)	-0.4(3)
C(13)-C(12)-C(11)-C(8)	-0.7(6)
C(14)-C(12)-C(11)-C(8)	178.4(3)
C(7)-C(5)-C(6)-S(2)	-0.3(4)
C(2)-C(5)-C(6)-S(2)	-179.8(2)
C(7)-C(5)-C(6)-Si(1)	177.6(2)
C(2)-C(5)-C(6)-Si(1)	-1.9(4)
C(8)-S(2)-C(6)-C(5)	0.4(3)
C(8)-S(2)-C(6)-Si(1)	-176.8(3)
C(9)-Si(1)-C(6)-C(5)	115.3(3)
C(10)-Si(1)-C(6)-C(5)	-110.7(3)
C(3)-Si(1)-C(6)-C(5)	1.4(3)
C(9)-Si(1)-C(6)-S(2)	-67.5(3)
C(10)-Si(1)-C(6)-S(2)	66.5(3)
C(3)-Si(1)-C(6)-S(2)	178.5(3)
C(11)-C(12)-C(13)-N(1)	-144(16)
C(14)-C(12)-C(13)-N(1)	37(17)
C(6)-C(5)-C(7)-C(8)	-0.1(4)
C(2)-C(5)-C(7)-C(8)	179.4(3)
C(15)-O(2)-C(14)-O(1)	-2.0(5)
C(15)-O(2)-C(14)-C(12)	178.8(3)
C(11)-C(12)-C(14)-O(1)	4.0(6)
C(13)-C(12)-C(14)-O(1)	-176.9(4)
C(11)-C(12)-C(14)-O(2)	-176.8(3)
C(13)-C(12)-C(14)-O(2)	2.4(5)
C(14)-O(2)-C(15)-C(16)	-170.7(3)
O(2)-C(15)-C(16)-C(17)	179.7(4)
C(15)-C(16)-C(17)-C(18)	-179.9(6)
C(16)-C(17)-C(18)-C(19)	-135.8(15)
C(17)-C(18)-C(19)-C(20)	-173.0(11)
C(18)-C(19)-C(20)-C(21)	-104.1(17)
C(19)-C(20)-C(21)-C(22)	-175.7(10)
S(1)-C(1)-C(2)-C(3)	-0.3(4)
Br(1)-C(1)-C(2)-C(3)	178.9(3)
S(1)-C(1)-C(2)-C(5)	-179.7(3)
Br(1)-C(1)-C(2)-C(5)	-0.5(6)

C(4)-C(3)-C(2)-C(1)	-0.1(4)
Si(1)-C(3)-C(2)-C(1)	179.9(3)
C(4)-C(3)-C(2)-C(5)	179.4(3)
Si(1)-C(3)-C(2)-C(5)	-0.5(4)
C(6)-C(5)-C(2)-C(1)	-179.0(4)
C(7)-C(5)-C(2)-C(1)	1.5(7)
C(6)-C(5)-C(2)-C(3)	1.6(4)
C(7)-C(5)-C(2)-C(3)	-177.9(3)
C(5)-C(7)-C(8)-C(11)	-179.6(3)
C(5)-C(7)-C(8)-S(2)	0.4(4)
C(12)-C(11)-C(8)-C(7)	179.9(4)
C(12)-C(11)-C(8)-S(2)	-0.1(6)
C(6)-S(2)-C(8)-C(7)	-0.5(3)
C(6)-S(2)-C(8)-C(11)	179.5(3)
C(2)-C(3)-C(4)-S(1)	0.5(4)
Si(1)-C(3)-C(4)-S(1)	-179.6(3)
C(2)-C(3)-C(4)-Br(2)	-178.1(3)
Si(1)-C(3)-C(4)-Br(2)	1.8(6)
C(1)-S(1)-C(4)-C(3)	-0.5(3)
C(1)-S(1)-C(4)-Br(2)	178.2(2)

Symmetry transformations used to generate equivalent atoms:

X-ray crystallographic data of M2

Table S10. Crystal data and structure refinement for **M2**.

Identification code	**M2**
Empirical formula	C20 H26 N2 S2 Si3
Formula weight	442.82
Temperature	296(2) K
Wavelength	0.71073 A
Crystal system, space group	Monoclinic, P2(1)/c
Unit cell dimensions	a = 12.979(10) A alpha = 90 deg. b = 12.411(9) A beta = 92.684(15) deg. c = 15.532(12) A gamma = 90 deg.
Volume	2499(3) A^3
Z, Calculated density	4, 1.177 Mg/m^3
Absorption coefficient	0.365 mm^-1
F(000)	936
Crystal size	0.30 x 0.25 x 0.23 mm
Theta range for data collection	2.10 to 25.00 deg.
Limiting indices	-15<=h<=12, -14<=k<=14, -18<=l<=18

Reflections collected / unique	12484 / 4405 [R(int) = 0.0527]
Completeness to theta = 25.00	99.70%
Absorption correction	Semi-empirical from equivalents
Max. and min. transmission	0.9208 and 0.8984
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	4405 / 0 / 244
Goodness-of-fit on F^2	1.005
Final R indices [I>2sigma(I)]	R1 = 0.0462, wR2 = 0.1060
R indices (all data)	R1 = 0.0912, wR2 = 0.1276

Table S11. Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters (A^2 x 10^3) for **M2**. U(eq) is defined as one third of the trace of the orthogonalized Uij tensor.

	x	y	z	U(eq)
S(1)	8292(1)	8728(1)	-1681(1)	58(1)
S(2)	6073(1)	11157(1)	1396(1)	58(1)
Si(1)	9468(1)	10830(1)	-2095(1)	59(1)
Si(2)	7139(1)	7078(1)	-606(1)	61(1)
Si(3)	7669(1)	11660(1)	-180(1)	53(1)
N(1)	3096(2)	8831(2)	3520(2)	86(1)
C(7)	7454(2)	8514(2)	-856(2)	47(1)
C(5)	7879(2)	10395(2)	-812(2)	45(1)
C(19)	4398(2)	11052(2)	2796(2)	63(1)
C(4)	8468(2)	10083(2)	-1489(2)	49(1)
C(18)	4312(2)	9946(2)	2603(2)	49(1)
C(16)	8855(2)	12206(3)	355(2)	81(1)
C(3)	9123(3)	12280(2)	-2185(2)	86(1)
C(20)	3622(2)	9337(2)	3111(2)	59(1)
C(13)	6012(2)	9236(2)	780(2)	52(1)
C(12)	6813(2)	10878(2)	543(2)	51(1)
C(6)	7309(2)	9504(2)	-463(2)	44(1)
C(1)	9543(2)	10207(2)	-3177(2)	68(1)
C(15)	6939(2)	12756(2)	-742(2)	77(1)
N(2)	4462(2)	11938(2)	2969(2)	103(1)
C(17)	4846(2)	9443(2)	1992(2)	53(1)
C(2)	10724(3)	10685(3)	-1485(2)	114(2)
C(14)	5585(2)	9859(2)	1417(2)	50(1)
C(11)	6700(2)	9814(2)	281(2)	47(1)
C(10)	5755(2)	6771(2)	-515(2)	77(1)
C(8)	7580(3)	6241(3)	-1512(3)	138(2)

C(9)	7833(3)	6726(3)	420(3)	138(2)

Table S12. Bond lengths [A] and angles [deg] for **M2**.

S(1)-C(4)	1.721(3)	C(4)-C(5)-C(6)	112.4(2)
S(1)-C(7)	1.740(3)	C(4)-C(5)-Si(3)	136.88(19)
S(2)-C(12)	1.708(3)	C(6)-C(5)-Si(3)	110.66(17)
S(2)-C(14)	1.732(3)	N(2)-C(19)-C(18)	178.6(3)
Si(1)-C(2)	1.856(4)	C(5)-C(4)-S(1)	109.38(18)
Si(1)-C(1)	1.858(3)	C(5)-C(4)-Si(1)	131.29(19)
Si(1)-C(3)	1.858(3)	S(1)-C(4)-Si(1)	118.93(14)
Si(1)-C(4)	1.882(3)	C(17)-C(18)-C(19)	124.1(2)
Si(2)-C(9)	1.845(4)	C(17)-C(18)-C(20)	119.7(2)
Si(2)-C(10)	1.849(3)	C(19)-C(18)-C(20)	116.2(2)
Si(2)-C(8)	1.860(4)	Si(3)-C(16)-H(16A)	109.5
Si(2)-C(7)	1.873(3)	Si(3)-C(16)-H(16B)	109.5
Si(3)-C(16)	1.844(3)	H(16A)-C(16)-H(16B)	109.5
Si(3)-C(15)	1.853(3)	Si(3)-C(16)-H(16C)	109.5
Si(3)-C(5)	1.878(3)	H(16A)-C(16)-H(16C)	109.5
Si(3)-C(12)	1.885(3)	H(16B)-C(16)-H(16C)	109.5
N(1)-C(20)	1.143(3)	Si(1)-C(3)-H(3A)	109.5
C(7)-C(6)	1.389(3)	Si(1)-C(3)-H(3B)	109.5
C(5)-C(4)	1.384(3)	H(3A)-C(3)-H(3B)	109.5
C(5)-C(6)	1.450(3)	Si(1)-C(3)-H(3C)	109.5
C(19)-N(2)	1.134(3)	H(3A)-C(3)-H(3C)	109.5
C(19)-C(18)	1.408(4)	H(3B)-C(3)-H(3C)	109.5
C(18)-C(17)	1.354(3)	N(1)-C(20)-C(18)	178.0(3)
C(18)-C(20)	1.435(4)	C(14)-C(13)-C(11)	113.1(2)
C(16)-H(16A)	0.96	C(14)-C(13)-H(13A)	123.4
C(16)-H(16B)	0.96	C(11)-C(13)-H(13A)	123.4
C(16)-H(16C)	0.96	C(11)-C(12)-S(2)	111.40(18)
C(3)-H(3A)	0.96	C(11)-C(12)-Si(3)	111.84(18)
C(3)-H(3B)	0.96	S(2)-C(12)-Si(3)	136.60(15)
C(3)-H(3C)	0.96	C(7)-C(6)-C(5)	115.3(2)
C(13)-C(14)	1.390(3)	C(7)-C(6)-C(11)	131.4(2)
C(13)-C(11)	1.407(3)	C(5)-C(6)-C(11)	113.2(2)
C(13)-H(13A)	0.93	Si(1)-C(1)-H(1A)	109.5
C(12)-C(11)	1.388(3)	Si(1)-C(1)-H(1B)	109.5
C(6)-C(11)	1.480(3)	H(1A)-C(1)-H(1B)	109.5
C(1)-H(1A)	0.96	Si(1)-C(1)-H(1C)	109.5
C(1)-H(1B)	0.96	H(1A)-C(1)-H(1C)	109.5
C(1)-H(1C)	0.96	H(1B)-C(1)-H(1C)	109.5
C(15)-H(15A)	0.96	Si(3)-C(15)-H(15A)	109.5
C(15)-H(15B)	0.96	Si(3)-C(15)-H(15B)	109.5

C(15)-H(15C)	0.96	H(15A)-C(15)-H(15B)	109.5
C(17)-C(14)	1.437(3)	Si(3)-C(15)-H(15C)	109.5
C(17)-H(17A)	0.93	H(15A)-C(15)-H(15C)	109.5
C(2)-H(2A)	0.96	H(15B)-C(15)-H(15C)	109.5
C(2)-H(2B)	0.96	C(18)-C(17)-C(14)	130.5(2)
C(2)-H(2C)	0.96	C(18)-C(17)-H(17A)	114.7
C(10)-H(10A)	0.96	C(14)-C(17)-H(17A)	114.7
C(10)-H(10B)	0.96	Si(1)-C(2)-H(2A)	109.5
C(10)-H(10C)	0.96	Si(1)-C(2)-H(2B)	109.5
C(8)-H(8A)	0.96	H(2A)-C(2)-H(2B)	109.5
C(8)-H(8B)	0.96	Si(1)-C(2)-H(2C)	109.5
C(8)-H(8C)	0.96	H(2A)-C(2)-H(2C)	109.5
C(9)-H(9A)	0.96	H(2B)-C(2)-H(2C)	109.5
C(9)-H(9B)	0.96	C(13)-C(14)-C(17)	122.8(2)
C(9)-H(9C)	0.96	C(13)-C(14)-S(2)	110.24(18)
C(4)-S(1)-C(7)	95.97(12)	C(17)-C(14)-S(2)	126.92(18)
C(12)-S(2)-C(14)	92.60(12)	C(12)-C(11)-C(13)	112.6(2)
C(2)-Si(1)-C(1)	109.80(16)	C(12)-C(11)-C(6)	115.0(2)
C(2)-Si(1)-C(3)	109.60(17)	C(13)-C(11)-C(6)	132.4(2)
C(1)-Si(1)-C(3)	110.95(14)	Si(2)-C(10)-H(10A)	109.5
C(2)-Si(1)-C(4)	107.89(14)	Si(2)-C(10)-H(10B)	109.5
C(1)-Si(1)-C(4)	108.29(13)	H(10A)-C(10)-H(10B)	109.5
C(3)-Si(1)-C(4)	110.24(13)	Si(2)-C(10)-H(10C)	109.5
C(9)-Si(2)-C(10)	108.79(17)	H(10A)-C(10)-H(10C)	109.5
C(9)-Si(2)-C(8)	111.5(2)	H(10B)-C(10)-H(10C)	109.5
C(10)-Si(2)-C(8)	106.11(16)	Si(2)-C(8)-H(8A)	109.5
C(9)-Si(2)-C(7)	107.56(15)	Si(2)-C(8)-H(8B)	109.5
C(10)-Si(2)-C(7)	115.70(12)	H(8A)-C(8)-H(8B)	109.5
C(8)-Si(2)-C(7)	107.27(14)	Si(2)-C(8)-H(8C)	109.5
C(16)-Si(3)-C(15)	109.88(15)	H(8A)-C(8)-H(8C)	109.5
C(16)-Si(3)-C(5)	113.88(13)	H(8B)-C(8)-H(8C)	109.5
C(15)-Si(3)-C(5)	116.78(13)	Si(2)-C(9)-H(9A)	109.5
C(16)-Si(3)-C(12)	115.11(14)	Si(2)-C(9)-H(9B)	109.5
C(15)-Si(3)-C(12)	110.80(14)	H(9A)-C(9)-H(9B)	109.5
C(5)-Si(3)-C(12)	89.16(12)	Si(2)-C(9)-H(9C)	109.5
C(6)-C(7)-S(1)	106.92(17)	H(9A)-C(9)-H(9C)	109.5
C(6)-C(7)-Si(2)	135.65(19)	H(9B)-C(9)-H(9C)	109.5
S(1)-C(7)-Si(2)	116.62(13)		

Symmetry transformations used to generate equivalent atoms:

Table S13. Anisotropic displacement parameters (A^2 x 10^3) for **M2**. The anisotropic displacement factor exponent takes the form: -2 pi^2 [h^2 a*^2 U11 + ...

+ 2 h k a* b* U12]

	U11	U22	U33	U23	U13	U12
S(1)	59(1)	56(1)	62(1)	-3(1)	24(1)	-7(1)
S(2)	70(1)	43(1)	63(1)	-3(1)	24(1)	-7(1)
Si(1)	55(1)	71(1)	52(1)	6(1)	11(1)	-20(1)
Si(2)	54(1)	43(1)	86(1)	10(1)	20(1)	4(1)
Si(3)	60(1)	47(1)	52(1)	0(1)	12(1)	-15(1)
N(1)	76(2)	86(2)	100(2)	27(2)	39(2)	0(1)
C(7)	43(1)	50(2)	50(1)	3(1)	13(1)	-1(1)
C(5)	42(1)	49(2)	43(1)	5(1)	3(1)	-7(1)
C(19)	62(2)	61(2)	67(2)	-11(2)	25(2)	-8(1)
C(4)	46(2)	51(2)	51(2)	3(1)	3(1)	-10(1)
C(18)	49(2)	46(2)	53(2)	3(1)	14(1)	1(1)
C(16)	80(2)	99(2)	64(2)	-20(2)	15(2)	-39(2)
C(3)	125(3)	65(2)	72(2)	-3(2)	35(2)	-33(2)
C(20)	55(2)	57(2)	65(2)	6(1)	19(2)	6(1)
C(13)	62(2)	37(1)	59(2)	3(1)	20(1)	-3(1)
C(12)	54(2)	46(2)	53(2)	-1(1)	12(1)	-6(1)
C(6)	39(1)	46(1)	47(1)	6(1)	3(1)	-4(1)
C(1)	69(2)	69(2)	69(2)	1(2)	28(2)	-4(2)
C(15)	96(2)	53(2)	83(2)	8(2)	17(2)	-2(2)
N(2)	121(2)	68(2)	125(2)	-36(2)	51(2)	-25(2)
C(17)	59(2)	37(1)	65(2)	2(1)	17(2)	-1(1)
C(2)	65(2)	185(4)	91(3)	34(3)	-6(2)	-42(2)
C(14)	58(2)	39(1)	54(2)	3(1)	19(1)	-3(1)
C(11)	48(2)	45(2)	47(1)	5(1)	11(1)	2(1)
C(10)	68(2)	57(2)	109(2)	-6(2)	19(2)	-12(2)
C(8)	165(4)	60(2)	199(4)	-28(2)	112(3)	-4(2)
C(9)	112(3)	112(3)	183(4)	81(3)	-50(3)	-18(3)

Table S14. Hydrogen coordinates (x 10^4) and isotropic displacement parameters (A^2 x 10^3) for **6**.

	x	y	z	U(eq)
H(16A)	9243	12589	-58	121
H(16B)	9264	11626	595	121
H(16C)	8676	12689	807	121
H(3A)	8473	12353	-2501	129
H(3B)	9647	12656	-2482	129
H(3C)	9070	12580	-1619	129
H(13A)	5858	8511	694	63
H(1A)	9732	9462	-3114	102
H(1B)	10052	10576	-3495	102
H(1C)	8884	10260	-3481	102
H(15A)	7388	13142	-1107	116
H(15B)	6673	13240	-325	116
H(15C)	6377	12453	-1086	116
H(17A)	4713	8710	1935	64
H(2A)	10905	9936	-1444	171
H(2B)	10672	10978	-917	171
H(2C)	11247	11066	-1780	171
H(10A)	5490	7175	-47	116
H(10B)	5670	6015	-409	116
H(10C)	5384	6964	-1042	116
H(8A)	7217	6454	-2037	207
H(8B)	7443	5496	-1398	207
H(8C)	8307	6342	-1567	207
H(9A)	7593	7175	872	206
H(9B)	8559	6837	366	206
H(9C)	7707	5984	554	206

Table S15. Torsion angles [deg] for **M2**.

C(4)-S(1)-C(7)-C(6)	1.4(2)
C(4)-S(1)-C(7)-Si(2)	-169.87(15)
C(9)-Si(2)-C(7)-C(6)	-61.7(3)
C(10)-Si(2)-C(7)-C(6)	60.1(3)
C(8)-Si(2)-C(7)-C(6)	178.3(3)
C(9)-Si(2)-C(7)-S(1)	106.4(2)
C(10)-Si(2)-C(7)-S(1)	-131.80(17)
C(8)-Si(2)-C(7)-S(1)	-13.6(2)
C(16)-Si(3)-C(5)-C(4)	-58.2(3)
C(15)-Si(3)-C(5)-C(4)	71.6(3)
C(12)-Si(3)-C(5)-C(4)	-175.5(3)
C(16)-Si(3)-C(5)-C(6)	117.80(19)
C(15)-Si(3)-C(5)-C(6)	-112.4(2)
C(12)-Si(3)-C(5)-C(6)	0.57(19)
C(6)-C(5)-C(4)-S(1)	0.8(3)
Si(3)-C(5)-C(4)-S(1)	176.78(19)
C(6)-C(5)-C(4)-Si(1)	-171.7(2)
Si(3)-C(5)-C(4)-Si(1)	4.3(4)
C(7)-S(1)-C(4)-C(5)	-1.3(2)
C(7)-S(1)-C(4)-Si(1)	172.26(15)
C(2)-Si(1)-C(4)-C(5)	85.2(3)
C(1)-Si(1)-C(4)-C(5)	-156.0(2)
C(3)-Si(1)-C(4)-C(5)	-34.4(3)
C(2)-Si(1)-C(4)-S(1)	-86.7(2)
C(1)-Si(1)-C(4)-S(1)	32.1(2)
C(3)-Si(1)-C(4)-S(1)	153.66(16)
N(2)-C(19)-C(18)-C(17)	-151(13)
N(2)-C(19)-C(18)-C(20)	28(14)
C(17)-C(18)-C(20)-N(1)	49(9)
C(19)-C(18)-C(20)-N(1)	-130(9)
C(14)-S(2)-C(12)-C(11)	-0.6(2)
C(14)-S(2)-C(12)-Si(3)	174.3(2)
C(16)-Si(3)-C(12)-C(11)	-118.3(2)
C(15)-Si(3)-C(12)-C(11)	116.3(2)
C(5)-Si(3)-C(12)-C(11)	-2.2(2)
C(16)-Si(3)-C(12)-S(2)	66.8(3)
C(15)-Si(3)-C(12)-S(2)	-58.6(3)
C(5)-Si(3)-C(12)-S(2)	-177.1(2)
S(1)-C(7)-C(6)-C(5)	-1.2(3)

Si(2)-C(7)-C(6)-C(5)	167.6(2)
S(1)-C(7)-C(6)-C(11)	-178.6(2)
Si(2)-C(7)-C(6)-C(11)	-9.7(5)
C(4)-C(5)-C(6)-C(7)	0.3(3)
Si(3)-C(5)-C(6)-C(7)	-176.76(18)
C(4)-C(5)-C(6)-C(11)	178.1(2)
Si(3)-C(5)-C(6)-C(11)	1.1(3)
C(19)-C(18)-C(17)-C(14)	-0.1(5)
C(20)-C(18)-C(17)-C(14)	-178.9(3)
C(11)-C(13)-C(14)-C(17)	178.7(2)
C(11)-C(13)-C(14)-S(2)	-1.3(3)
C(18)-C(17)-C(14)-C(13)	-175.4(3)
C(18)-C(17)-C(14)-S(2)	4.6(4)
C(12)-S(2)-C(14)-C(13)	1.1(2)
C(12)-S(2)-C(14)-C(17)	-178.9(2)
S(2)-C(12)-C(11)-C(13)	-0.1(3)
Si(3)-C(12)-C(11)-C(13)	-176.29(18)
S(2)-C(12)-C(11)-C(6)	179.51(18)
Si(3)-C(12)-C(11)-C(6)	3.3(3)
C(14)-C(13)-C(11)-C(12)	0.9(3)
C(14)-C(13)-C(11)-C(6)	-178.6(3)
C(7)-C(6)-C(11)-C(12)	174.5(3)
C(5)-C(6)-C(11)-C(12)	-2.9(3)
C(7)-C(6)-C(11)-C(13)	-6.0(5)
C(5)-C(6)-C(11)-C(13)	176.6(3)

Symmetry transformations used to generate equivalent atoms:

5. Photovoltaic Performance Optimization

Table S16. Photovoltaic Performances with different ratios of polymer:$PC_{71}BM$ and different spin speed.

Polymer	**Polymer:$PC_{71}BM$**	***Spin speed (rpm/min)***	**V_{oc} (V)**	**J_{sc} (mA/cm^2)**	***FF***	***PCE* (%)**
PBDTDTSi-1	1:1	2000	1.00	5.09	0.31	1.57
	1:2	2000	1.03	5.93	0.32	1.99
	1:3	2000	1.02	6.23	0.34	2.16
	1:4	2000	1.04	7.13	0.37	2.79
	1:5	2000	1.00	6.71	0.36	2.44
	1:4	1000	1.05	4.84	0.35	1.80
	1:4	1500	1.08	5.60	0.40	2.41
	1:4	2500	1.07	5.52	0.39	2.30
	1:4	3000	1.01	5.43	0.38	2.08

PBDTDTSi-2	1:1	2000	0.95	1.69	0.23	0.36
	1:2	2000	0.87	2.15	0.28	0.53
	1:3	2000	0.87	3.95	0.30	1.04
	1:4	2000	0.80	6.28	0.29	1.46
	1:5	2000	0.85	4.04	0.32	1.10
PBDTDTSi-3	1:1	2000	0.89	1.98	0.27	0.47
	1:2	2000	0.91	2.08	0.27	0.52
	1:3	2000	0.85	3.38	0.29	0.85
	1:4	2000	0.91	3.46	0.29	0.92
	1:5	2000	0.90	3.39	0.29	0.90

Table S17. Photovoltaic Performances with different concentrations of DIO and the interfacial layer.

Polymer	**Polymer:$PC_{71}BM$**	**DIO%**	**TiOx interfacial layer**	V_{oc} **(V)**	J_{sc} **(mA/cm^2)**	***FF***	***PCE* (%)**
PBDTDTSi-1	1:4	0.5	w/o	1.03	7.25	0.37	2.77
PBDTDTSi-1	1:4	1.5	w/o	1.05	7.12	0.40	2.98
PBDTDTSi-1	1:4	2	w/o	1.03	7.49	0.40	3.11
PBDTDTSi-1	1:4	2.5	w/o	1.09	7.31	0.38	3.01
PBDTDTSi-1	1:4	2	with	1.07	7.53	0.41	3.29
PBDTDTSi-2	1:4	2	with	1.01	6.52	0.35	2.30
PBDTDTSi-3	1:4	2	with	1.00	3.88	0.30	1.16

6. Hole Transfer Properties by SCLC method

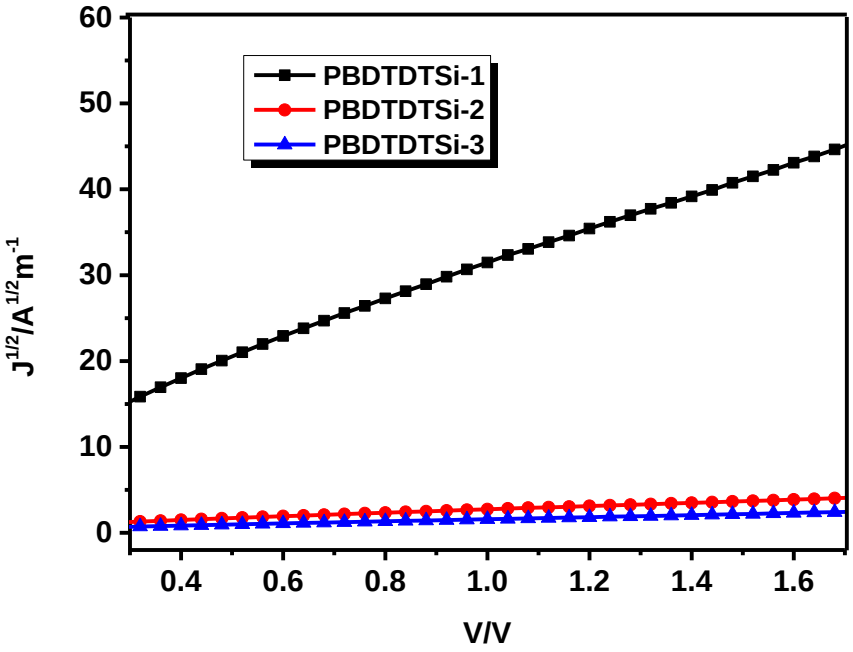


Figure S37. $J^{1/2}$–V curves of hole-only devices.