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Supporting Information

Central Dicyanomethylene -Substituted Unsymmetrical Squaraines and their application in Organic Solar Cells

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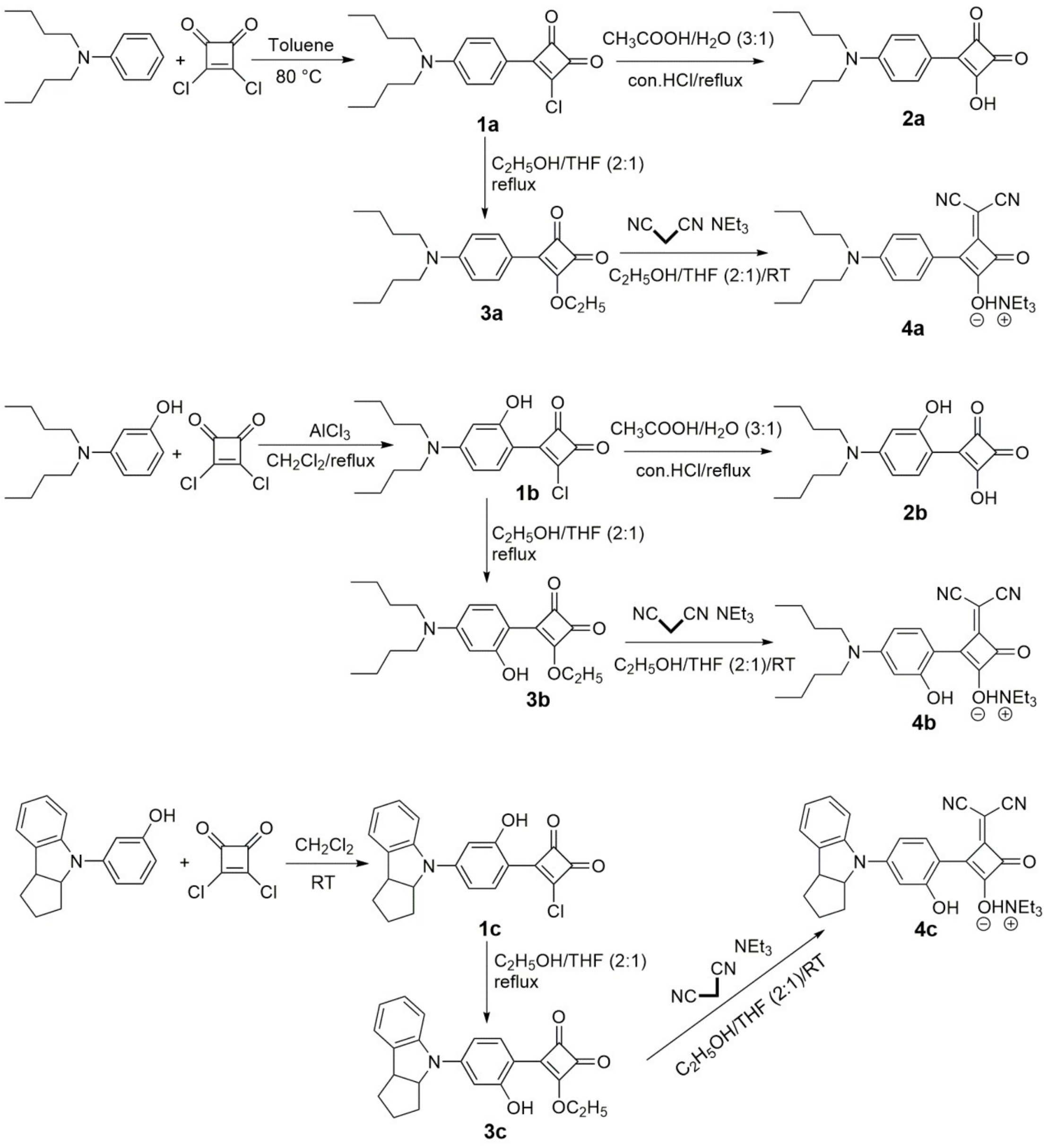
1. Synthesis

Scheme S1 Synthetic Routes to the intermediates.



3-chloro-4-(4-(dibutylamino)phenyl)cyclobutane-1,2-dione [**1a**]. A mixture of squaryl chloride (1.00 g, 6.62 mmol) and *N*,*N*-dibutylaniline (1.37 g, 6.67 mmol) in dried toluene (30 mL) was reacted for 5 h in 80 ºC, then the reaction mixture was cooled and removal of the solvent. The residue was purified by silica gel column chromatography (Petroleum ether/Dichloromethane =3 : 1) to give **1a** (1.26 g, 59.7%) as a yellow solid. ^{1}H NMR (400 MHz, $CDCl_3$, ppm) δ: 8.15 (d, $J = 9.2$ Hz, 2H, ArH), 6.75 (d, $J = 9.2$ Hz, 2H, ArH), 3.44 (t, $J = 7.6$ Hz, 4H, $-CH_2$), 1.69-1.61 (m, 4H, $-CH_2$), 1.46-1.37 (m, 4H, $-CH_2$), 1.03 (t, $J = 7.2$ Hz, 6H, $-CH_3$).

3-(4-(dibutylamino)phenyl)-4-hydroxycyclobutane-1,2-dione [**2a**]. **1a** (1.26 g 3.95 mmol) was dissolved in a mixture solvent of acetic acid (48 mL), concentrated hydrochloric acid (6.5 mL) and water (16 mL). This mixture was refluxed for 4 h under 120 ºC, then cooled to room temperature. Water (200 mL) was added drop wise into the mixture, then the yellow precipitate **2a** (0.8 g, 67.2%) was obtained by filtration, washed with ether and dried. ^{1}H NMR (400 MHz, DMSO-d^6, ppm) δ: 7.86 (s, 2H, ArH), 6.81 (s, 2H, ArH), 3.38 (s, 4H, —CH_2), 1.49 (s, 4H, —CH_2), 1.34-1.23 (m, 4H, —CH_2), 0.92 (t, J = 6.8 Hz, 6H, —CH_3).

3-(4-(dibutylamino)phenyl)-4-ethoxycyclobut-3-ene-1,2-dione [**3a**]. **1a** (3.43 g, 10.76 mmol) was dissolved in 45 mL mixture solvent（Tetrahydrofuran/EtOH = 1 : 2）was refluxed at 80 ºC for 4 h, then cooled and removal of the solvent, and the crude product was purified by column chromatography (DCM) to give **3a** as a yellow solid (1.84g, 51.9%). ^{1}H NMR (400 MHz, $CDCl_3$, ppm) δ: 7.90 (d, J = 9.2 Hz, 2H, ArH), 6.66 (d, J = 9.2 Hz, 2H, ArH), 4.94-4.89 (m, 2H, —CH_2), 3.35 (t, J = 7.6 Hz, 4H, —CH_2), 1.64-1.57 (m, 4H, —CH_2), 1.54 (t, J = 7.2 Hz, 3H, —CH_3), 1.42-1.33 (m, 4H, —CH_2), 0.97 (t, J = 7.6 Hz, 6H, —CH_3).

Triethylammonium2-(2-(4-(dibutylamino)phenyl)-3-hydroxy-4-oxocyclobut-1-en-1-olate [**4a**].

Triethylamine (0.84 mL,) was added dropwise under stirring to a mixture solution of 1.84 g (5.6 mmol) of the **3a** and malononitrile（0.53 g, 8.0 mmol） in 60 mL mixture solvent（THF/EtOH = 1 : 2）was reacted for 10 h at room temperature. Afterwards, the solvent was removed under reduced pressure and the solid residue was purified by column chromatography (silica gel, DCM/MeOH = 95 : 5) to obtain **4a** as a yellow solid (1.54 g, 61.0%). ^{1}H NMR (400 MHz, $CDCl_3$, ppm) δ: 9.30 (s, 1H, —NH), 8.10 (d, J = 8.8 Hz, 2H, ArH), 6.65 (d, J = 9.2 Hz, 2H, ArH), 3.30 (t, J = 7.6 Hz, 4H, —CH_2), 3.26 (t, J = 7.2 Hz, 6H, —NCH_2), 1.61-1.53 (m, 4H, —CH_2), 1.38 (t, J = 6.8Hz, 9H, —NCH_3), 1.32 (t, J = 7.6 Hz, 4H, —CH_2), 0.95 (t, J = 7.6 Hz, 6H, —CH_3).

3-chloro-4-(4-(dibutylamino)-2-hydroxyphenyl)cyclobut-3-ene-1,2-dione [**1b**]. A solution of compound 3-(dibutylamino)phenol (0.34 g, 1.54 mmol) and squaryl chloride in anhydrous CH_2Cl_2 (10 mL) was added drop wise into A solution of compound $AlCl_3$ (5%) solution [Aluminum trichloride] (10 mL), slowly was refluxed at 50 °C for 2.5 h, then the reaction mixture was cooled and decanted into ice water (100 mL). The organic phase was separated and the aqueous phase was extracted with CH_2Cl_2 three times. The combined organic phase was washed with water there time, dried over anhydrous Na_2SO_4, and concentrated in vacuo. The resulting crude product was further purified by silica gel column chromatography (dichloromethane/hexane = 2:1) to give 1b as yellow solid. ^{1}H NMR (400 MHz, $CDCl_3$, ppm) δ: 9.76 (s, 1H, OH), 7.86 (d, J = 9.6 Hz, 1H, ArH), 6.39 (dd, J_1= 9.2 Hz, J_2 = 2.0 Hz, 1H, ArH), 6.14 (d, J = 2.4 Hz, 1H, ArH), 3.36 (t, J = 7.6 Hz, 4H, —CH$_2$), 1.66-1.58 (m, 4H, —CH$_2$), 1.43-1.33 (m, 4H,—CH$_2$), 0.98 (t, J = 6.8 Hz, 6H, —CH$_3$).

3-(4-(dibutylamino)-2-hydroxyphenyl)-4-hydroxycyclobut-3-ene-1, 2-dione [**2b**]. Compound **2b** was prepared as a yellow solid with a yield of 82.5% using a similar procedure as the synthesis of **2a**, but with **1b** rather than **1a** as the reactants.^{1}H NMR (400 MHz, DMSO-d^6, ppm) δ: 10.83 (s, 1H, OH), 7.89 (d, J = 8.0 Hz, 1H, ArH), 6.45 (dd, J_1 = 8.0 Hz, J_2 = 2.0 Hz, 1H, ArH), 6.18 (d, J = 2.4 Hz, 1H, ArH), 3.39 (t, J = 7.6 Hz, 4H, —CH$_2$), 1.58-1.33 (m, 4H, —CH$_2$), 1.33-1.26 (m, 4H, —CH$_2$), 0.88 (t, J = 7.2 Hz, 6H, —CH$_3$).

3-(4-(dibutylamino)-2-hydroxyphenyl)-4-ethoxycyclobut-3-ene-1,2-dione [**3b**]. Compound **3b** was prepared as a yellow solid with a yield of 72.4% using a similar procedure as the synthesis of **3a**, but with **2b** rather than **2a** as the reactants. ^{1}H NMR (400 MHz, $CDCl_3$, ppm) δ: 10.05 (s, H, OH), 7.49 (d, J = 8.8 Hz, 1H, ArH), 6.26 (dd, J_1 = 8.8 Hz, J_2 = 2.0 Hz, 1H, ArH), 6.13 (d, 1H, J = 2.4 Hz, ArH), 4.99-4.93 (m, 2H, —CH$_2$), 3.32 (t, J = 7.6 Hz, 4H, —CH$_2$), 1.63-1.58 (m, 4H, —CH$_2$), 1.58-1.55 (m, 3H, —CH$_3$), 1.41-1.31 (m, 4H, —CH$_2$), 0.97 (t, J = 7.2 Hz, —CH$_3$).

Triethylammonium2-[4-(dibutylamino)-2-hydroxyphenyl)-3-(dicyanomethylidene)-4-oxocyclobut-1-en-1-olate [**4b**]. Compound **4b** was prepared as a yellow solid with a yield of 61.0% using a similar procedure as the synthesis of **4a**, but with **3b** rather than **3a** as the reactants. ^{1}H NMR (400 MHz, DMSO-d^6, ppm) δ: 10.80 (s, 1H, OH), 8.86 (s, 1H, NH$^+$), 7.48 (d, J = 8.8 Hz, 1H, ArH), 6.23 (dd, J = 9.2 Hz,1H, ArH), 6.05(d, J = 2.4 Hz, 1H, ArH), 3.29 (t, J = 8.0 Hz, 4H, —CH$_2$), 3.13-3.07 (m, 6H, —CH$_2$), 2.51-2.49

(m, 4H, —CH_2), 1.54-1.46 (m, 4H, —CH_2), 1.36-1.29 (m, 4H, —CH_2), 1.17(t, *J* = 7.2 Hz, 9H, —CH_3), 0.92 (t, *J* = 7.6 Hz, 6H,—CH_3).

3-ethoxy-4-(2-hydroxy-4-(1,3,3a,8b-tetrahydrocyclopenta[b]indol-4(2H)-yl)phenyl)cyclobut-3-ene-1,2-dione [**3c**]. A solution of compound 3-(2,3,3*a*,8*b*-tetrahydrocyclopenta[*b*]indol-4(1H)-yl)phenol (1.93 g, 7.67 mmol) in anhydrous CH_2Cl_2 (10 mL) was added dropwise into A solution of compound squaryl chloride (1.40 g, 9.27 mmol) solution (20 mL) slowly was stirring at room temperature for 24 h, then the reaction mixture was decanted into ice water (100 mL). The organic phase was separated and the aqueous phase was extracted with CH_2Cl_2 three times. The combined organic phase was washed with water there time, dried over anhydrous Na_2SO_4, and concentrated in vacuo. The resulting crude product was further purified by silica gel column chromatography (dichloromethane) to give **1c** as yellow solid (0.79 g, 28.2%), and then **1c** was dissolved in a mixture of dried tetrahydrofuran (8 mL) and dried ethyl alcohol (24 mL) was refluxed at 80 ºC for 6 h. then the reaction mixture was cooled and removal of the solvent, and the crude product was purified by column chromatography (dichloromethane) to give **3c** as a yellow solid (0.43 g, 53.3%). ^{1}H NMR (400 MHz, $CDCl_3$, ppm) δ: 10.08 (s, 1H, OH), 7.60 (d, *J* = 8.8 Hz, 1H, ArH), 7.29 (d, *J* = 8.0 Hz, ArH), 7.19-7.13 (m, 2H, ArH), 6.95-6.90 (m, 2H, ArH), 6.77 (d, *J* = 2.4 Hz, ArH), 5.03-4.97 (m, 2H, —CH_2), 4.70-4.65 (m, 1H, —CH), 3.91 (s, 1H, —CH), 2.11-2.03 (m, 2H, —CH_2), 2.03-1.90 (m, 2H, —CH_2), 1.72-1.65 (m, 1H, —CH_2), 1.59 (t, *J* = 7.2 Hz, 3H, —CH_3), 1.49-1.37 (m, 1H, —CH_2).

Triethylammonium2-(3-hydroxy-2-(2-hydroxy-4-(1,3,3a,8b-tetrahydrocyclopenta[b]indol-4(2H)-yl)phenyl)-4-oxocyclobut-1-en-1-olate [**4c**]. Compound **4c** was prepared as a yellow solid with a yield of 82.0% using a similar procedure as the synthesis of **4a**, but with **3c** rather than **3a** as the reactants. ^{1}H NMR (400 MHz, $CDCl_3$, ppm) δ: 8.78(s, 1H, NH^+), 7.79 (dd, J_1 = 8.8 Hz, J_2 = 2.4 Hz, 1H, ArH), 7.22 (dd, J_1 = 8.0 Hz, J_2 = 2.4 Hz, 1H, ArH), 7.12-7.06 (m, 2H, ArH), 6.88-6.82 (m, 2H, ArH), 6.74 (s, 1H, ArH), 4.60 (s, 1H, —CH), 3.82 (s, 1H, —CH), 3.30 (m, *J* = 7.2 Hz, 6H, —NCH_2), 2.03-1.94 (m, 2H, —CH_2), 1.92-1.84 (m, 2H, —CH_2), 1.40 (t, *J* = 7.2 Hz, 9H, —CH_3).

Table S1 Summary of crystal data, data collection and refinement parameters for USQ-2 and diCN-USQ-2.

Compound	USQ-2	diCN-USQ-2
Empirical formula	$C_{30}H_{36}N_2O_3S$	$C_{33}H_{36}N_4O_2S$
Formula weight	504.67	552.72
Temperature	143.00(10) K	143.00(10) K
Crystal system	triclinic	monoclinic
Space group	P-1	$P2_1/c$
a/Å	9.3736(9)	8.9009(5)
b/Å	9.8299(12)	29.0765(17)
c/Å	16.506(2)	11.7440(6)
α/°	86.875(10)	90
β/°	85.566(9)	105.910(6)
γ/°	66.162(11)	90
Volume/Å3	1386.6(3)	2923.0(3)
Z	2	4
ρ_{calc}mg/mm^3	1.209	1.256
μ/mm^{-1}	0.149	0.147
F(000)	540.0	1176.0
Crystal size/mm^3	0.4 × 0.4 × 0.4	?
2θ range for data collection	6.628 to 52.74°	5.84 to 52.74°
	$-10 \leq h \leq 11$	$-10 \leq h \leq 11$
Index ranges	$-12 \leq k \leq 11$	$36 \leq k \leq 32$
	$-20 \leq l \leq 20$	$-14 \leq l \leq 14$
Reflections collected	10174	25400
Independent reflections	5642 [Rint = 0.0442]	5961 [Rint = 0.0486]
Data/restraints/parameters	5642/2/334	5961/0/365
Goodness-of-fit on F^2	1.068	1.034
Final R indexes [I>=2σ (I)]	R1 = 0.1294,	R1 = 0.0632,
	$wR_2 = 0.2143$	$wR_2 = 0.1387$
Final R indexes [all data]	R1 = 0.1962,	R1 = 0.0925,
	$wR_2 = 0.2434$	$wR_2 = 0.1552$
Largest diff.peak/hole/e Å^{-3}	0.59/-0.40	0.41/-0.28

2. DFT calculations

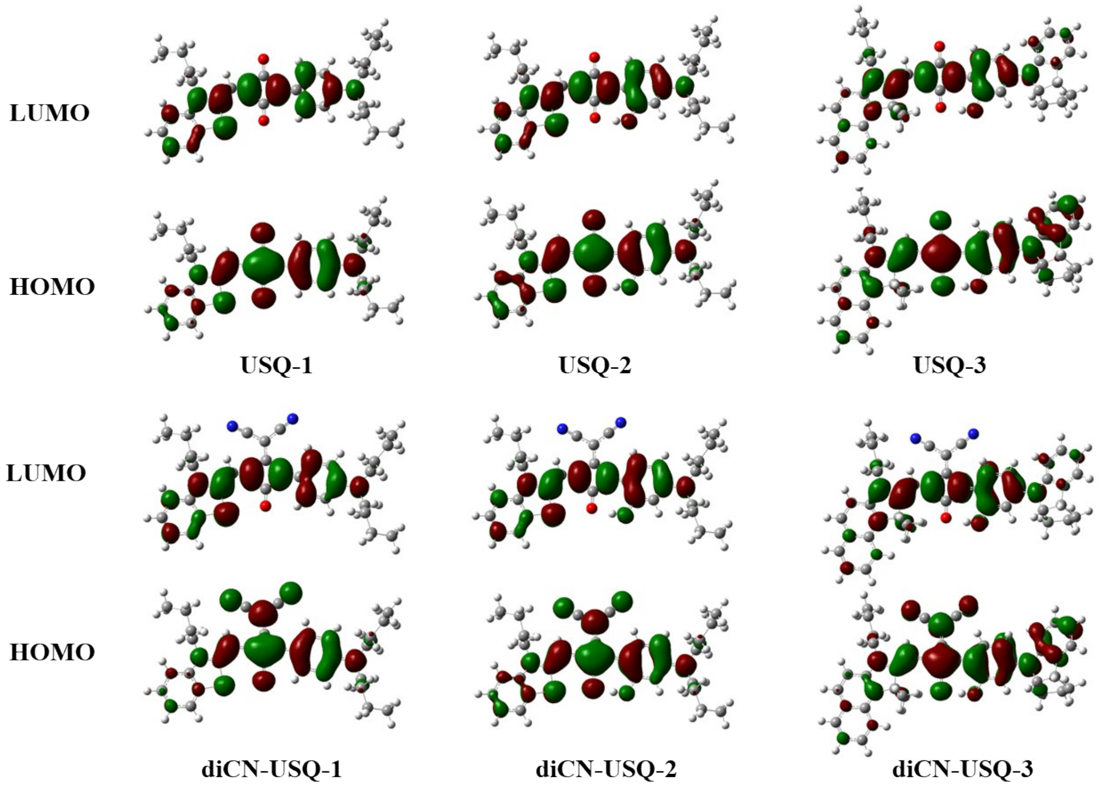


Figure S1 The frontier molecular orbitals of the objective compounds.

Table S2 Summary of integration of blending films absorption and EQE.

Compd.	USQ-1	diCN-USQ-1	USQ-2	diCN-USQ-2	USQ-3	diCN-USQ-3
Integration（ABS）	169.35	199.27	181.43	200.32	219.07	191.35
Integration（EQE）	62.63	120.56	76.20	146.92	143.81	186.52

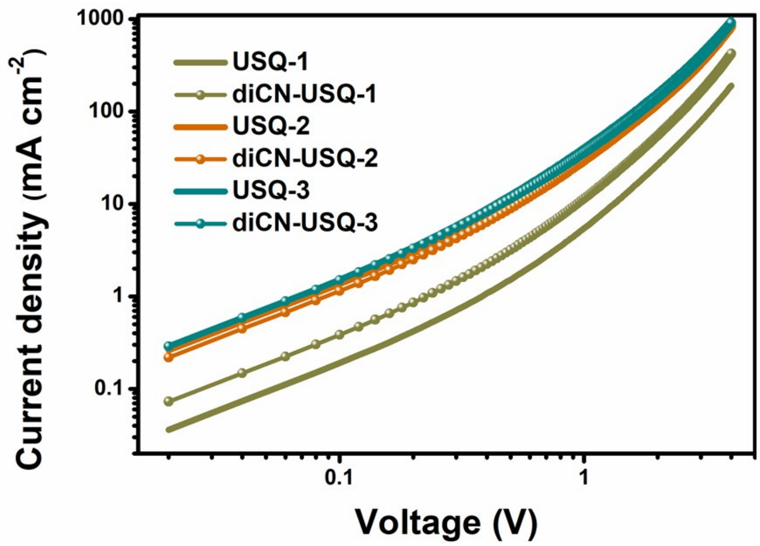
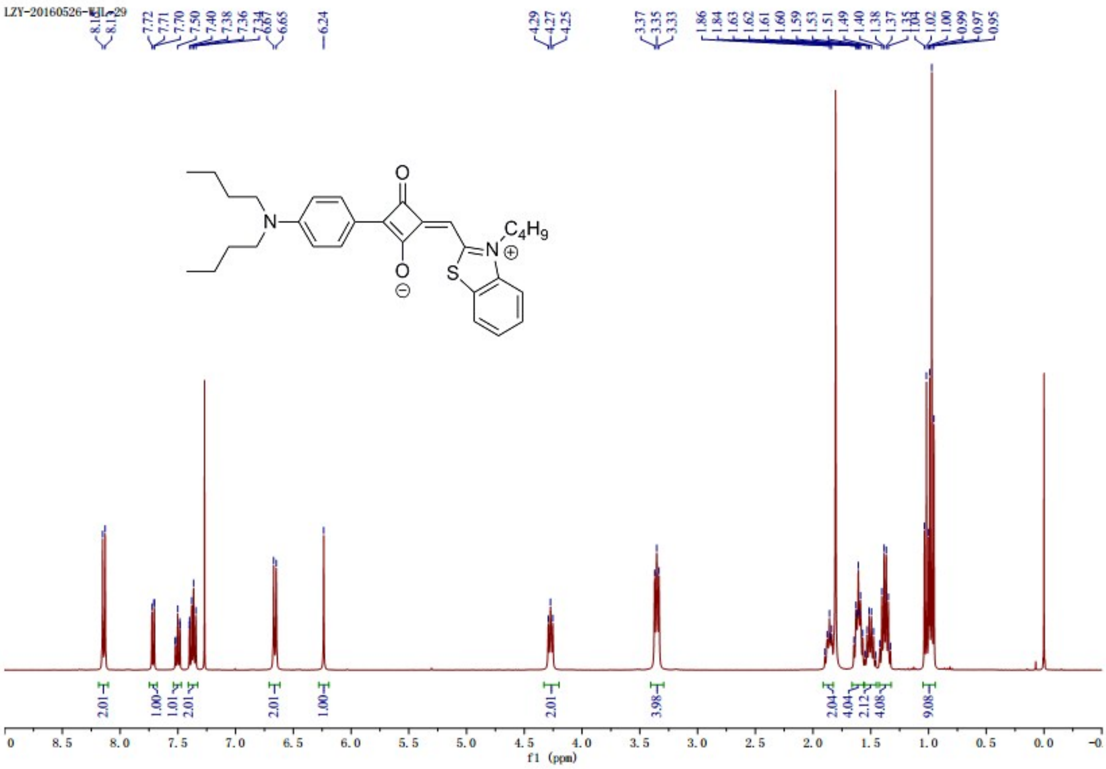
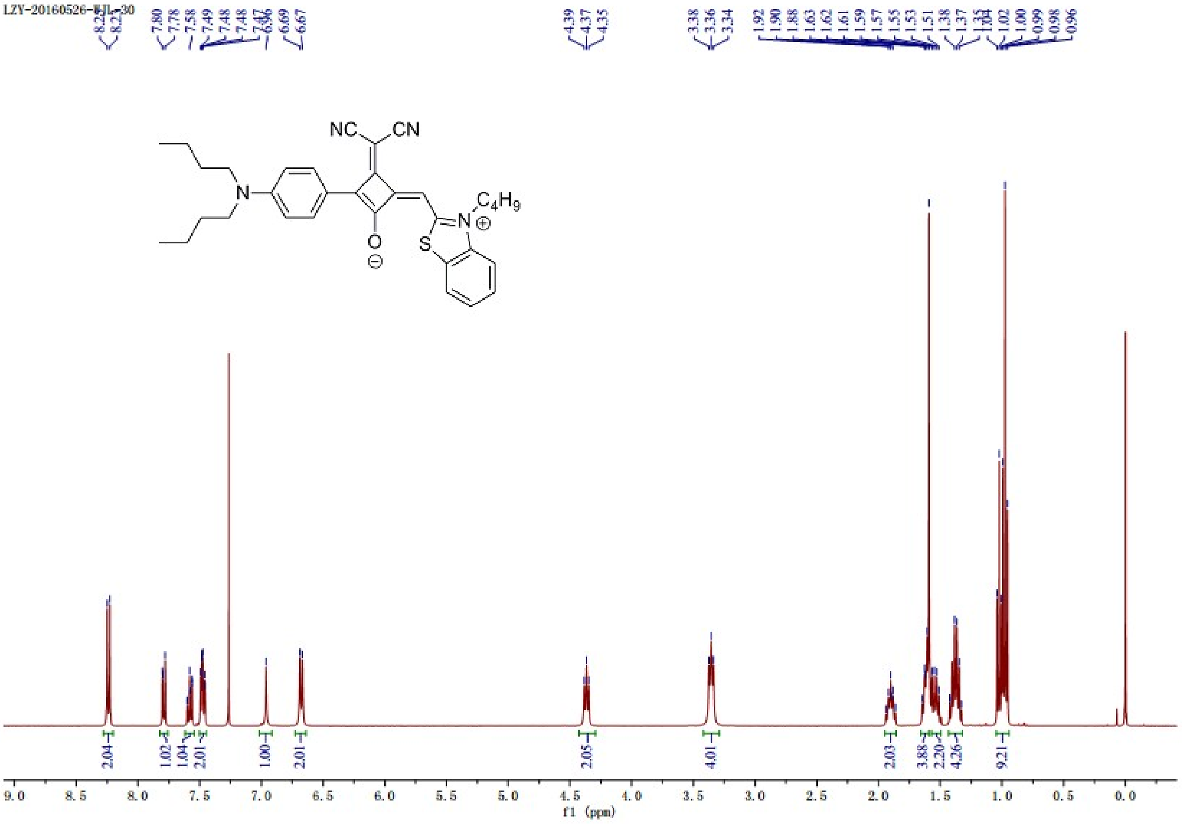


Figure S2 Current density–voltage characteristics of hole-only single carrier devices using USQ:PC$_{71}$BM (1:3) blend films as active layer.

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6.67
4.39
4.37
4.35
3.38
3.36
3.34
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1.90
1.88
1.63
1.62
1.61
1.59
1.57
1.55
1.53
1.51
1.38
1.37
1.35
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1.00
0.99
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0.96
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CN
N
O
C4H9
N
S
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1.02
1.04
2.01
1.00
2.01
2.05
4.01
2.03
3.88
2.20
4.26
9.21
9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
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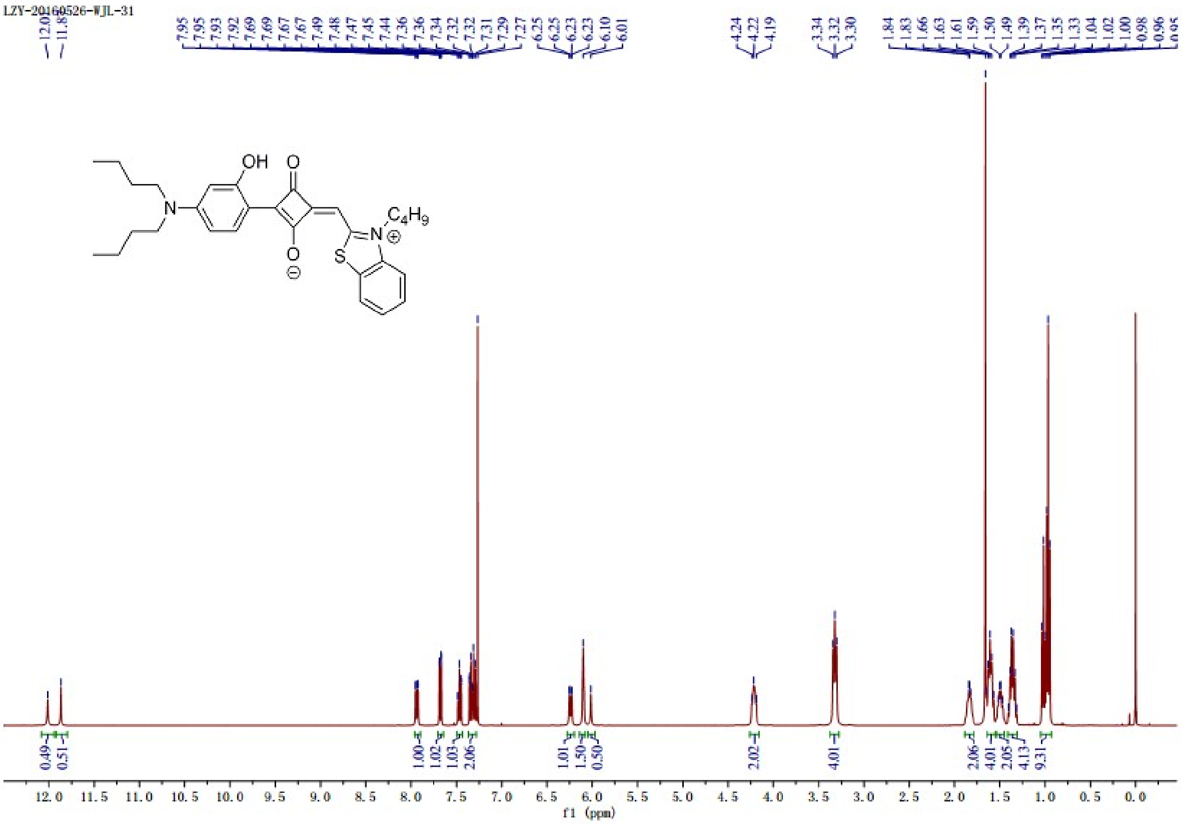
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7.34
7.32
7.32
7.31
7.29
7.27
6.25
6.25
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6.23
6.10
6.01
4.24
4.22
4.19
3.34
3.32
3.30
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1.61
1.59
1.50
1.49
1.39
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1.35
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1.00
1.02
1.03
2.06
1.01
1.50
0.50
2.02
4.01
2.06
4.01
2.05
4.13
9.31
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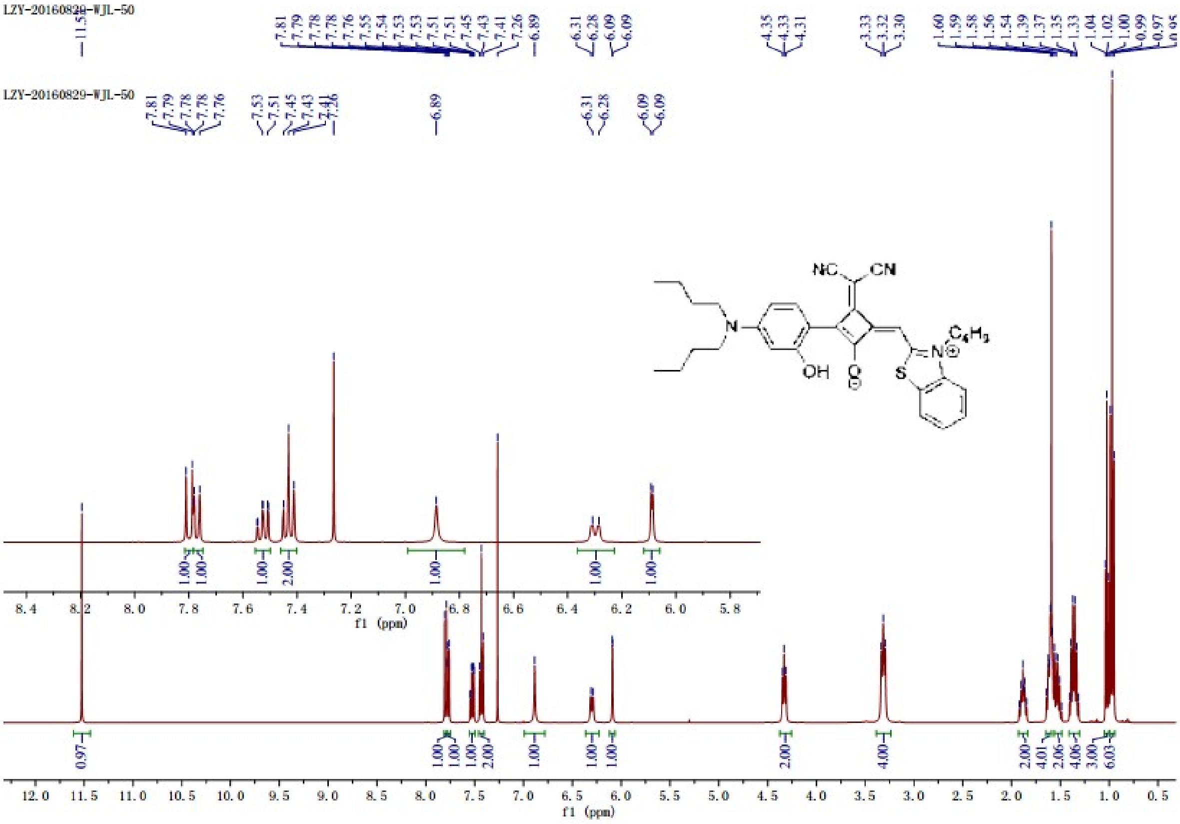
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4.35 4.33 4.31
3.33 3.32 3.30
1.60 1.59 1.58 1.56 1.54 1.39 1.37 1.35 1.33 1.04 1.02 1.00 0.99 0.97 0.95
LZY-20160829-WJL-50
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7.53 7.51 7.45 7.43 7.41 7.26
6.89
6.31 6.28
6.09 6.09
1.00 1.00 1.00 2.00 1.00 1.00 1.00
8.4 8.2 8.0 7.8 7.6 7.4 7.2 7.0 6.8 6.6 6.4 6.2 6.0 5.8
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⊖
S
N
⊕
C4H9
0.97
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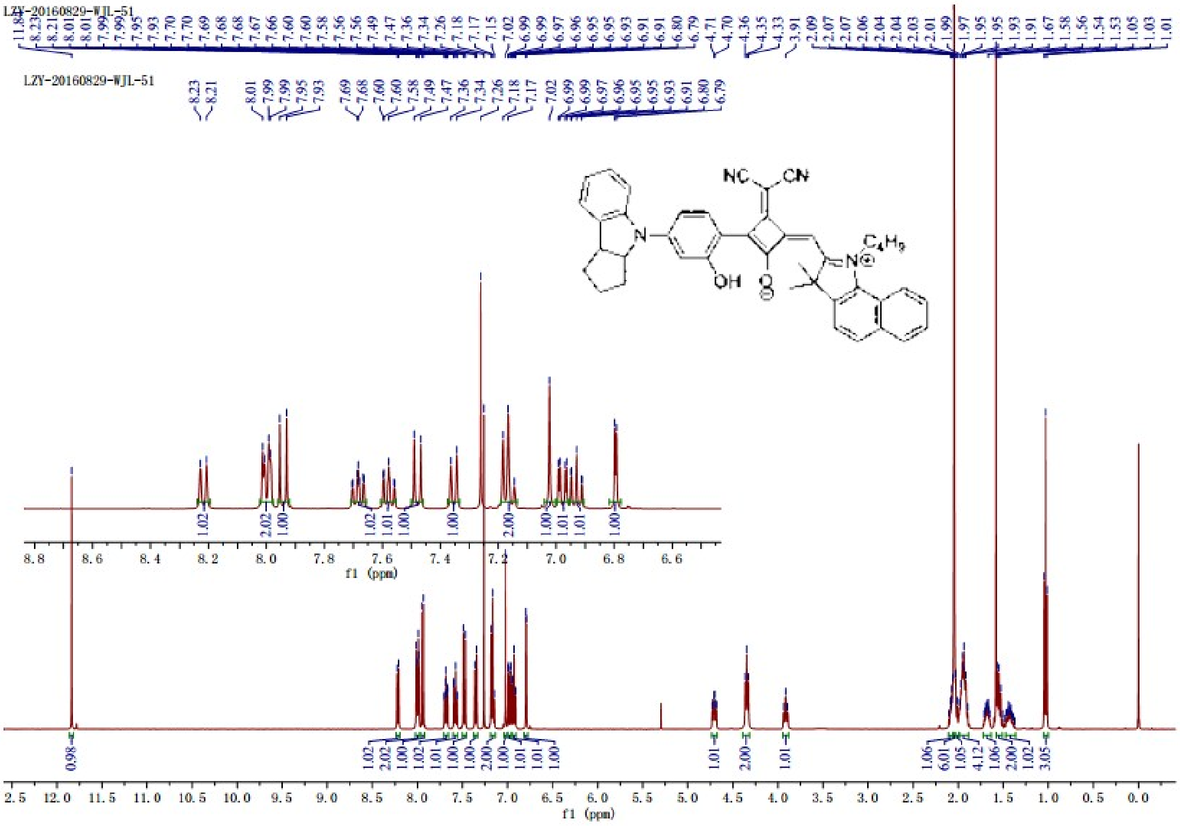
2.00
4.00
2.00 4.01 2.06 4.06 3.00 6.03
12.0 11.5 11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5
f1 (ppm)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⊕
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⊖
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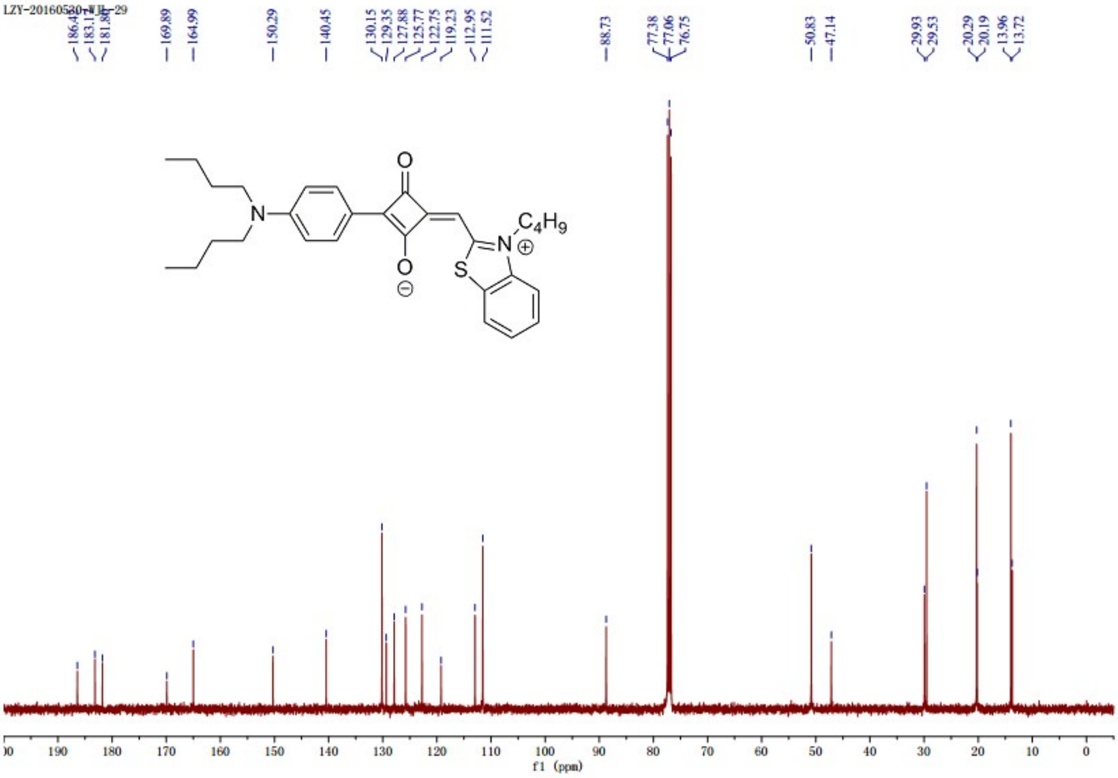
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N
C4H9
⊕
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⊖
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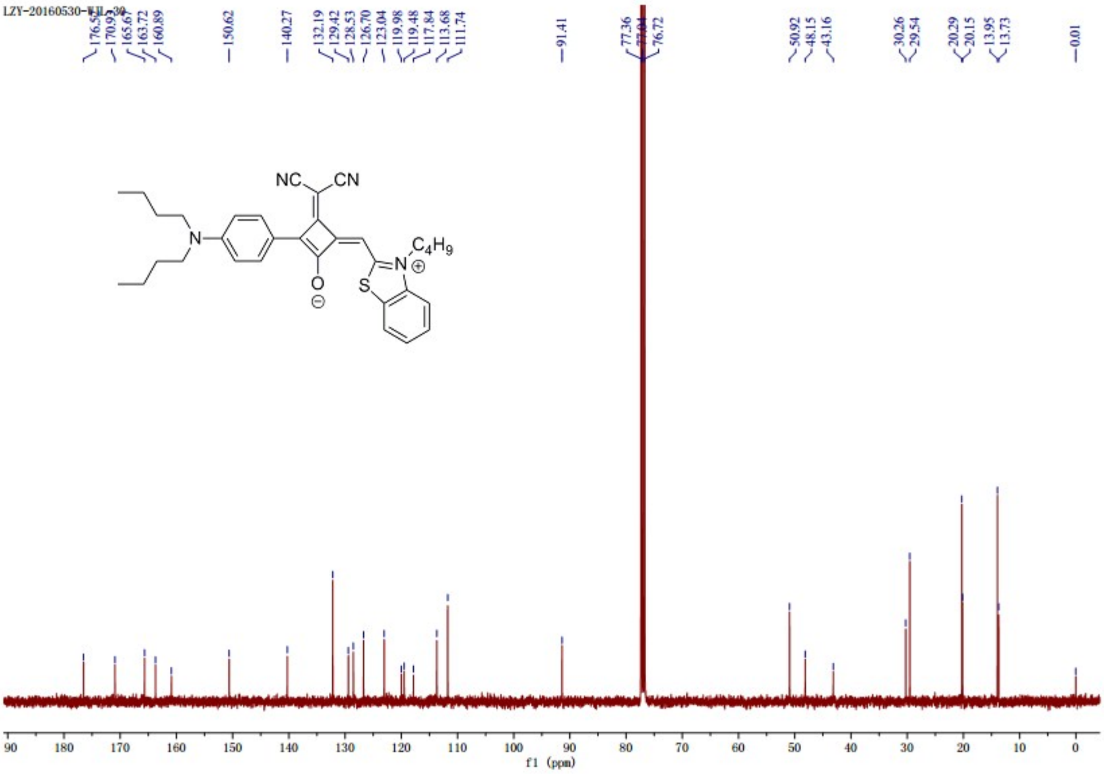
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119.48
117.84
113.68
111.74
91.41
77.36
77.04
76.72
50.92
48.15
43.16
30.26
29.54
20.29
20.15
13.95
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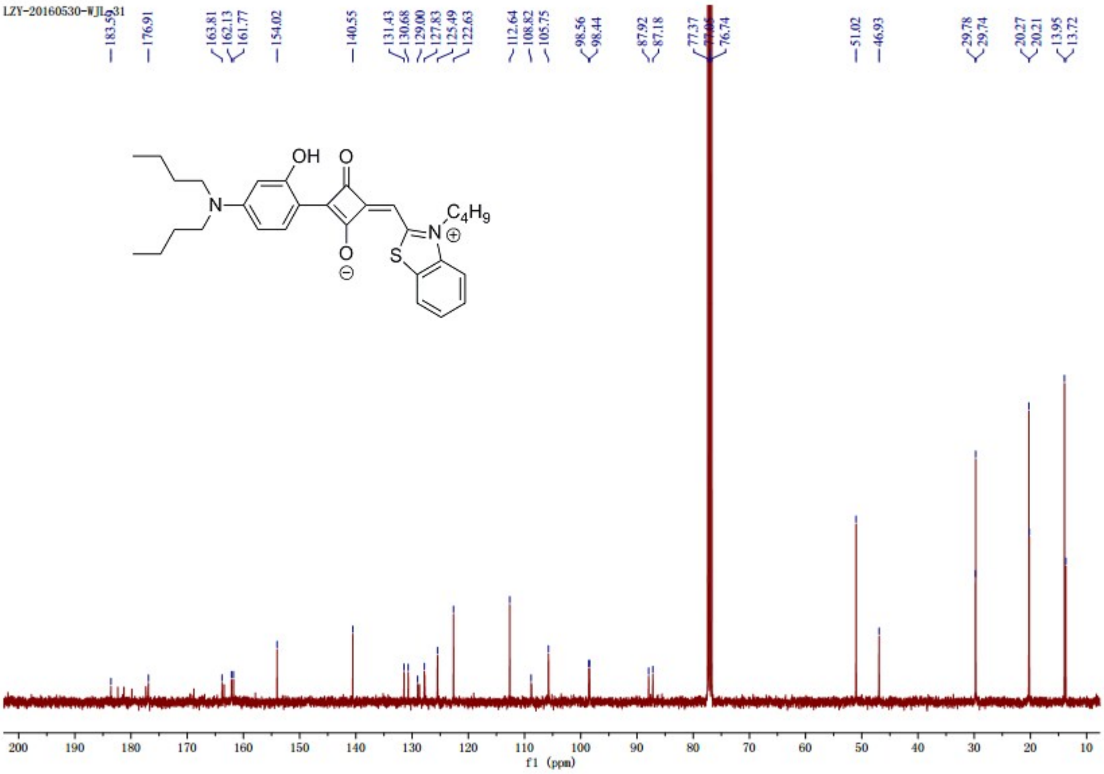
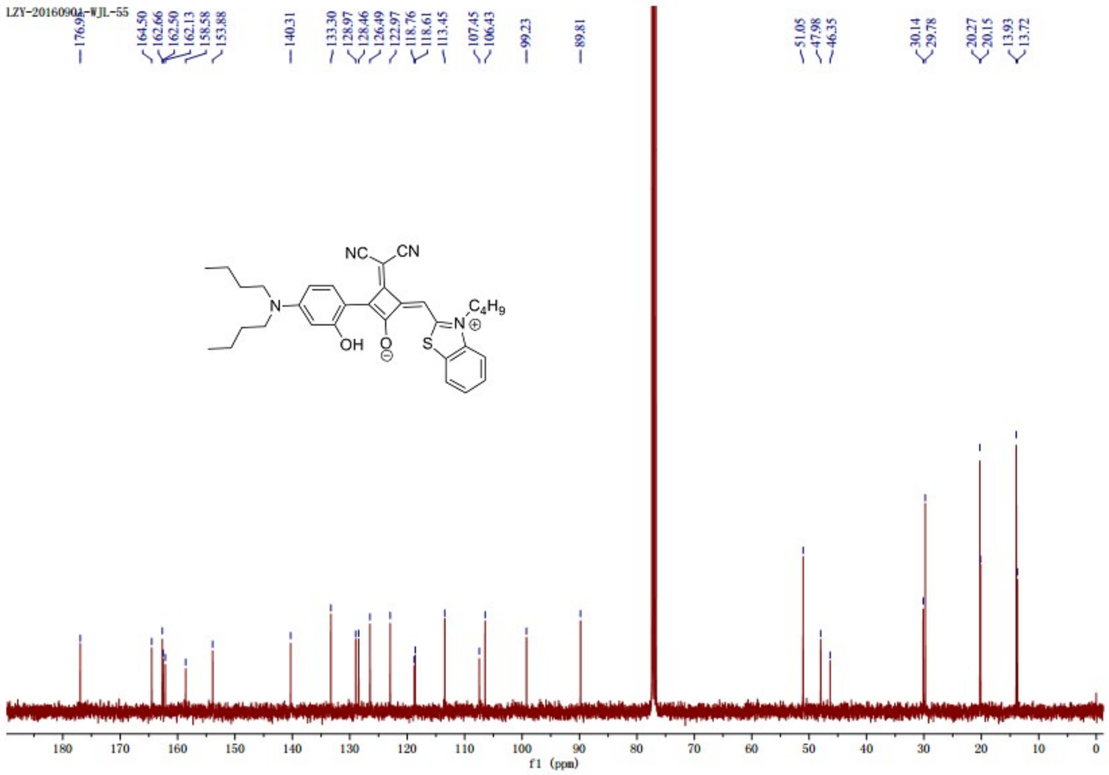
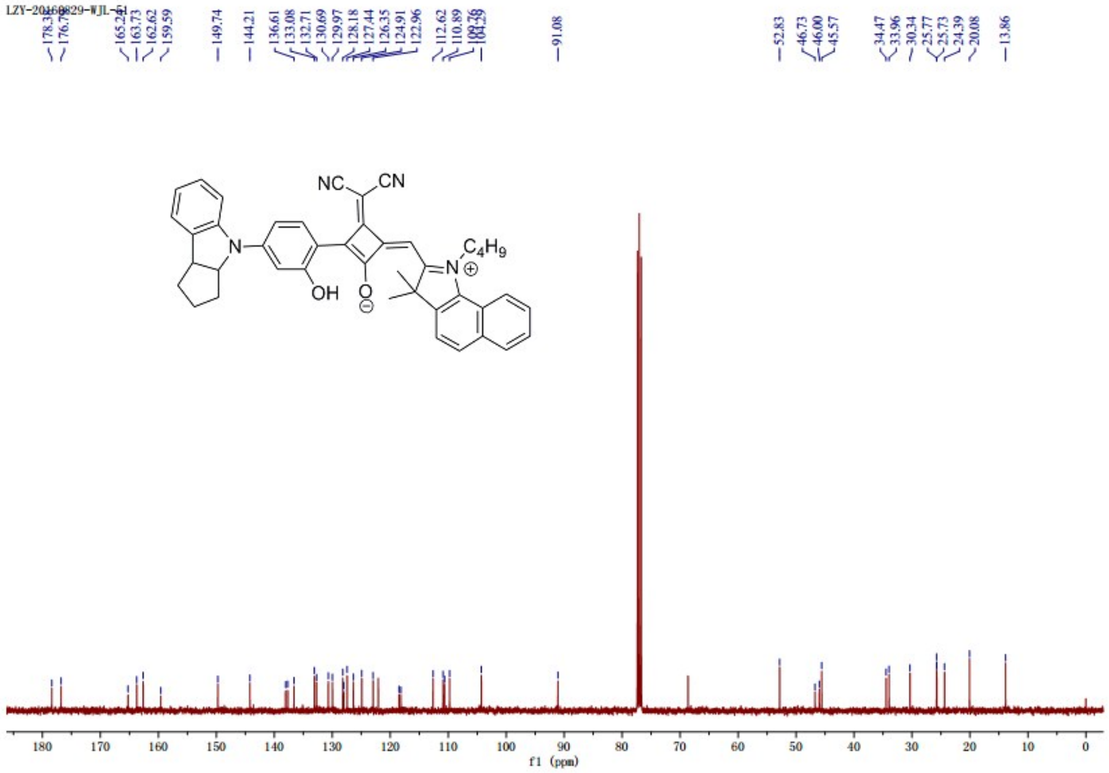
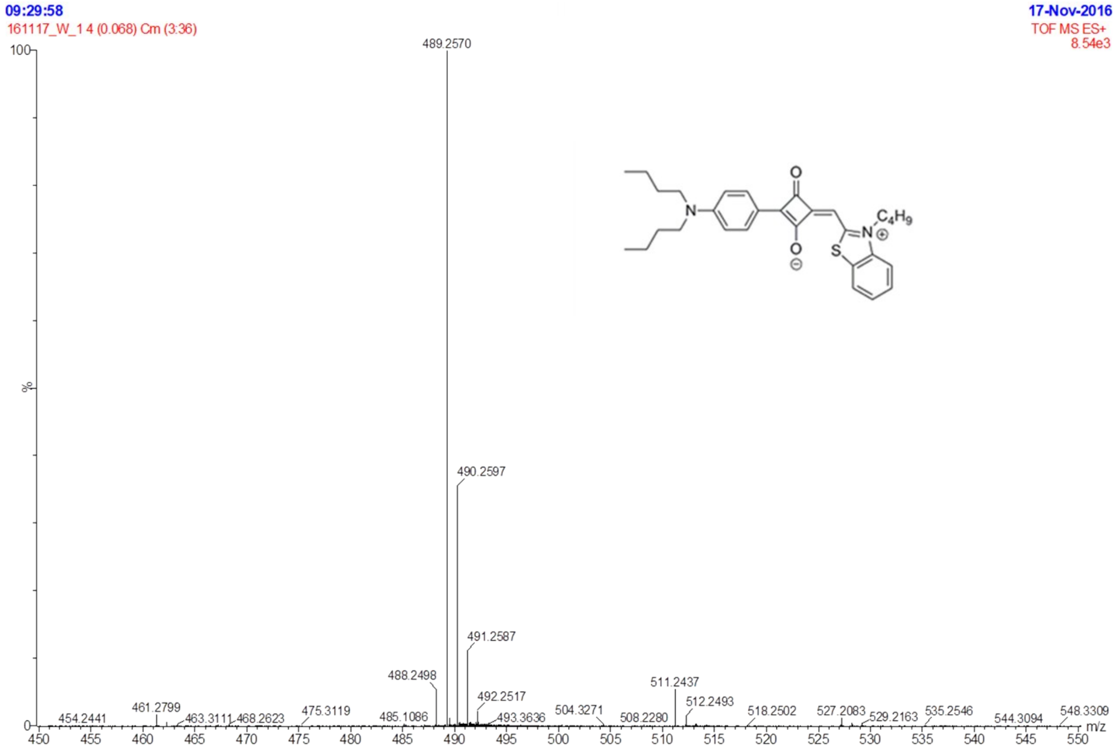
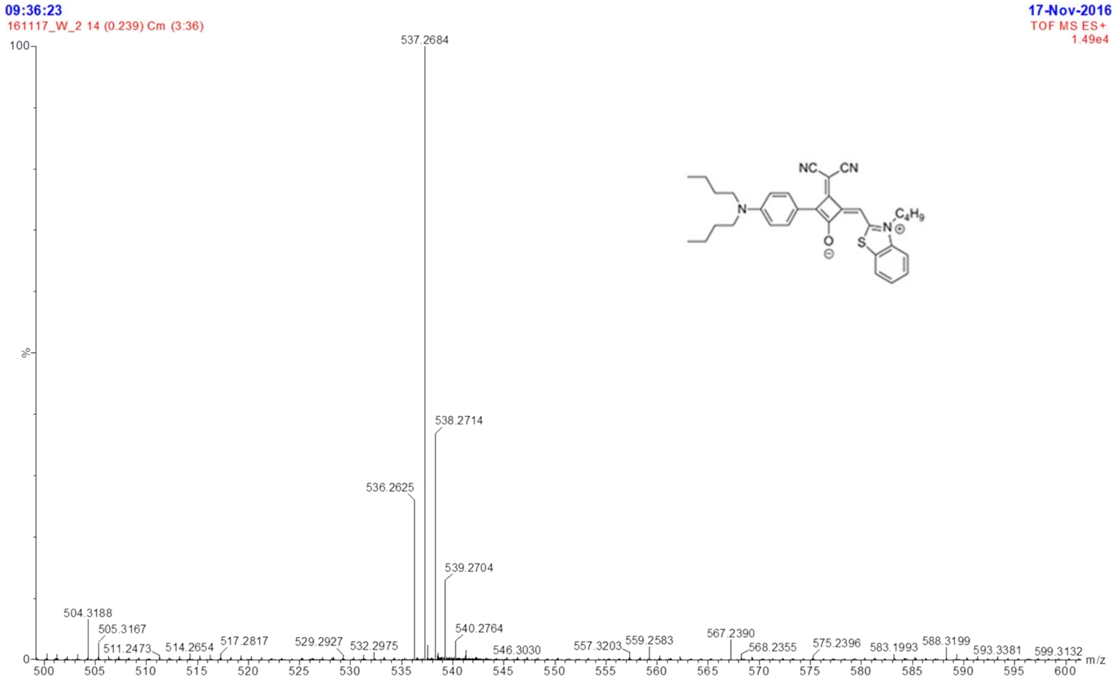
0.01
NC
CN
N
C_4H_9
O
S
90
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

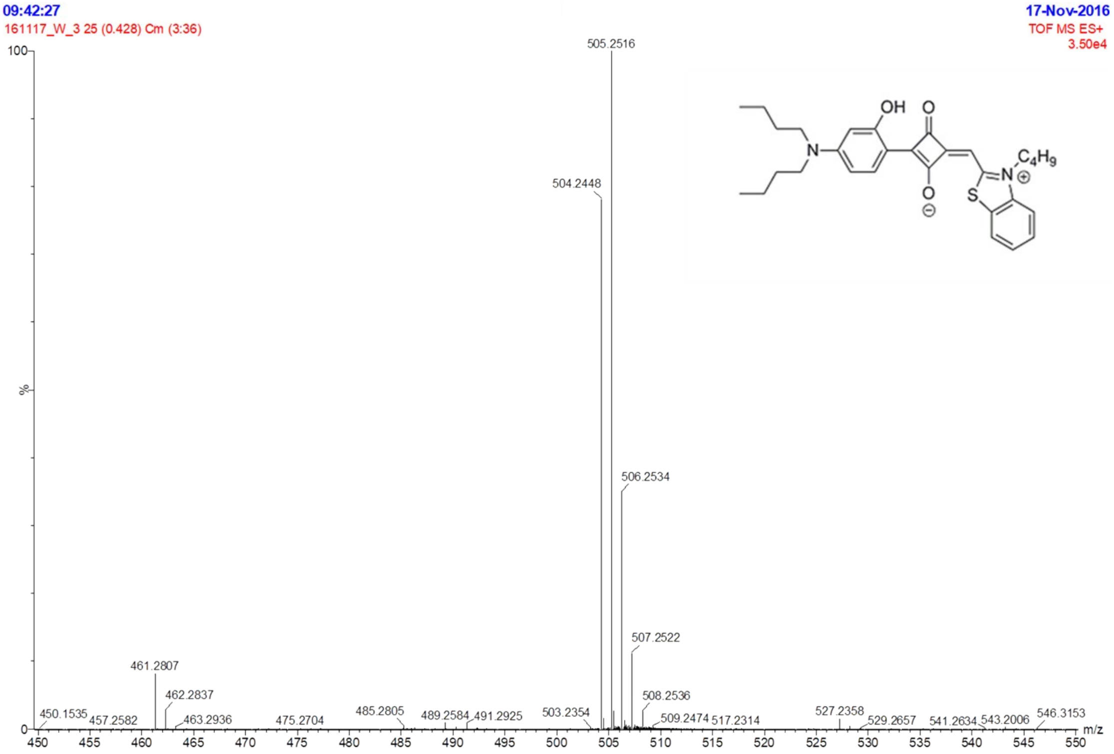

LZY-20160530-WJL-31
183.59
176.91
163.81
162.13
161.77
154.02
140.55
131.43
130.68
129.00
127.83
125.49
122.63
112.64
108.82
105.75
98.56
98.44
87.92
87.18
77.37
77.05
76.74
51.02
46.93
29.78
29.74
20.27
20.21
13.95
13.72
OH
O
N
C_4H_9
O
S
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
f1 (ppm)

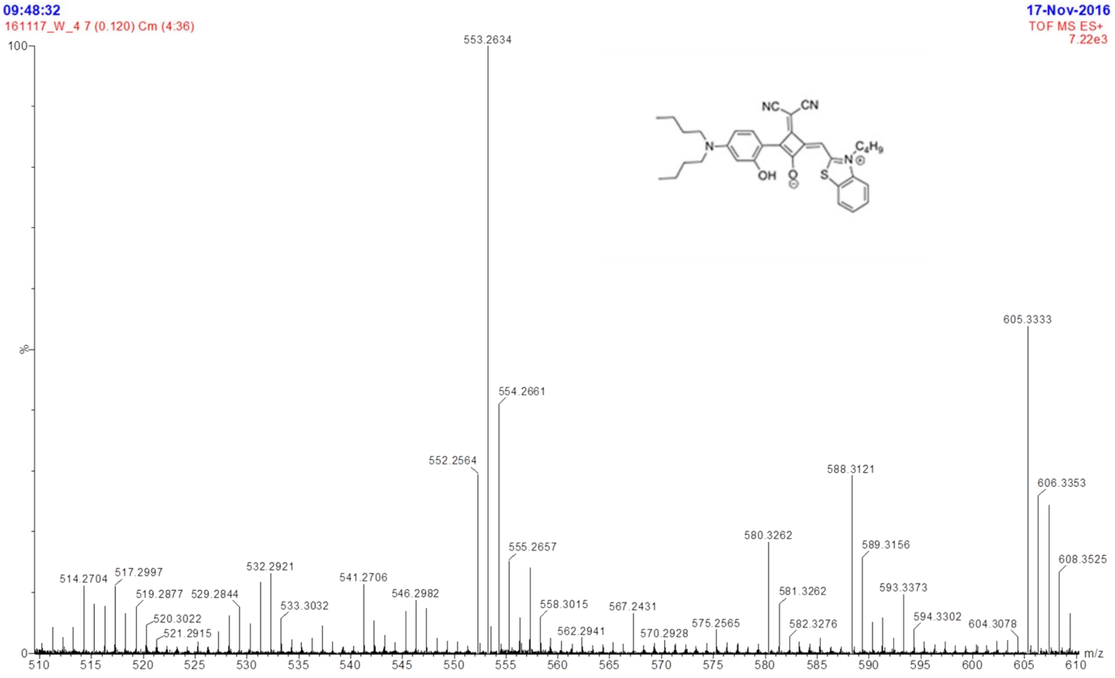

LZY-20160901-WJL-55
176.9
164.50
162.66
162.50
162.13
158.58
153.88
140.31
133.30
128.97
128.46
126.49
122.97
118.76
118.61
113.45
107.45
106.43
99.23
89.81
51.05
47.98
46.35
30.14
29.78
20.27
20.15
13.93
13.72
NC
CN
N
C_4H_9
N⊕
S
OH
O⊖
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)


LZY-20160829-WJL-51
178.3
176.7
165.24
163.73
162.62
159.59
149.74
144.21
136.61
133.08
132.71
130.69
129.97
128.18
127.44
126.35
124.91
122.96
112.62
110.89
109.76
104.29
91.08
52.83
46.73
46.00
45.57
34.47
33.96
30.34
25.77
25.73
24.39
20.08
13.86
NC
CN
N
C_4H_9
N⊕
OH
O⊖
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)


09:29:58
161117_W_1 4 (0.068) Cm (3:36)
17-Nov-2016
TOF MS ES+
8.54e3
100
%
0
489.2570
490.2597
491.2587
488.2498
511.2437
492.2517
512.2493
454.2441
461.2799
463.3111
468.2623
475.3119
485.1086
493.3636
504.3271
508.2280
518.2502
527.2083
529.2163
535.2546
544.3094
548.3309
m/z
450 455 460 465 470 475 480 485 490 495 500 505 510 515 520 525 530 535 540 545 550
O
O
N
C4H9
S
⊕
⊖


09:36:23
161117_W_2 14 (0.239) Cm (3:36)
17-Nov-2016
TOF MS ES+
1.49e4
100
%
0
537.2684
538.2714
536.2625
539.2704
504.3188
505.3167
540.2764
511.2473
514.2654
517.2817
529.2927
532.2975
546.3030
557.3203
559.2583
567.2390
568.2355
575.2396
583.1993
588.3199
593.3381
599.3132
m/z
500 505 510 515 520 525 530 535 540 545 550 555 560 565 570 575 580 585 590 595 600
NC
CN
N
O
C4H9
S
⊕
⊖


09:42:27
161117_W_3 25 (0.428) Cm (3:36)
17-Nov-2016
TOF MS ES+
3.50e4
100
%
0
505.2516
504.2448
506.2534
507.2522
461.2807
462.2837
508.2536
450.1535
457.2582
463.2936
475.2704
485.2805
489.2584
491.2925
503.2354
509.2474
517.2314
527.2358
529.2657
541.2634
543.2006
546.3153
m/z
450
455
460
465
470
475
480
485
490
495
500
505
510
515
520
525
530
535
540
545
550
OH
O
N
O
C4H9
N
S


09:48:32
161117_W_4 7 (0.120) Cm (4:36)
17-Nov-2016
TOF MS ES+
7.22e3
100
%
0
553.2634
605.3333
554.2661
552.2564
588.3121
606.3353
580.3262
589.3156
555.2657
608.3525
514.2704
517.2997
532.2921
541.2706
519.2877
529.2844
546.2982
593.3373
533.3032
581.3262
558.3015
567.2431
520.3022
521.2915
562.2941
570.2928
575.2565
582.3276
594.3302
604.3078
m/z
510
515
520
525
530
535
540
545
550
555
560
565
570
575
580
585
590
595
600
605
610
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CN
N
OH
O
C4H9
N
S

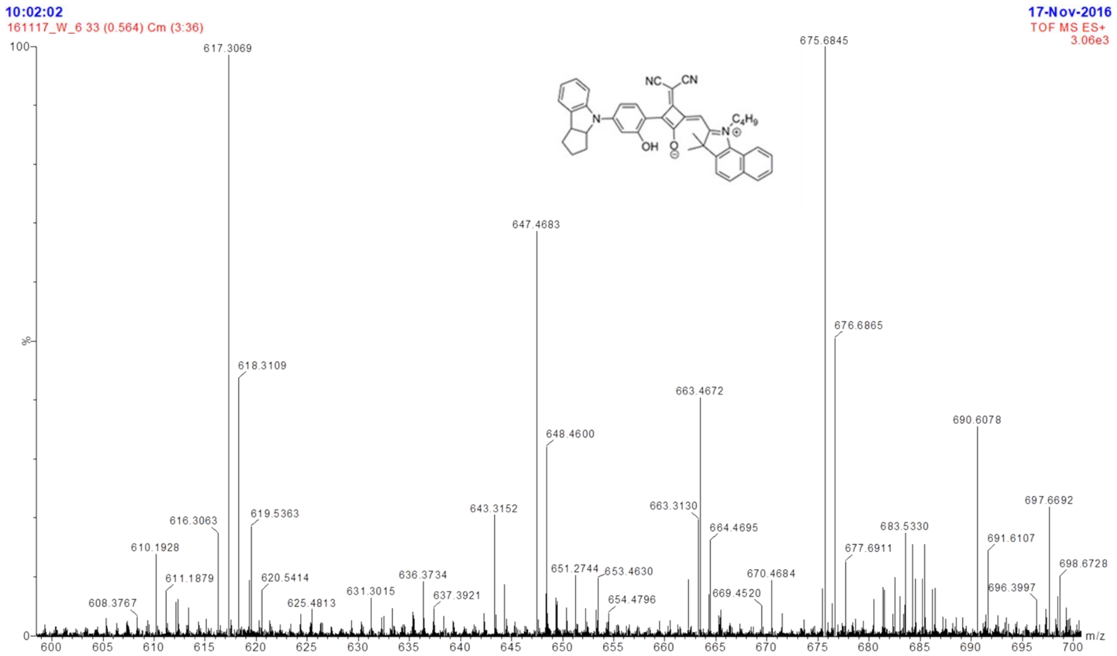

Figure S3 The spectra of ^{1}H NMR, ^{13}C NMR and high resolution mass of the objective compounds.