A series of fluorene-based two-photon absorbing molecules: synthesis, linear and nonlinear characterization, and bioimaging

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Supporting information

Content:

1. Description of 2PA cross-section measurements.

The 2PA cross section measurements were performed with a tunable 10 W pumped Ti:sapphire femtosecond laser system (220 fs pulse width, 76 MHz repetition rate) as the excitation source and a spectrofluorimeter with PMT detectors (Figure S-1).

The linear polarization and the power of the laser light were adjusted by the optical attenuator (OA), which consists of two Glan-Thompsom polarizers and a half-waveplate. The laser beam was divided with a beam splitter (BS) from where the transmitted beam was expanded with a bean expander (BE) and passed through the sample (S) after being focused with an objective lens (10X). The reflected beam was sent to the power meter (PM) to monitor the variation of the incident power on the sample (S). The two photon emission (2PE) light was focused by the lens (L) and the upconverted fluorescence was collected by the PMT of the spectrofluorimeter used for fluorescence quantum yield methods at a direction perpendicular to the pump beam. During these measurements this PMT was set to analog mode. A computer was used to record and process all the experimental data. The numerical estimation of the 2PA cross section δ was performed by comparison with a known reference by using equation (i):

$$\delta = \delta_R \frac{\langle I \rangle}{\langle I_R \rangle} \frac{C_R}{C} \frac{n^2}{n_R{}^2} \frac{Q_R}{Q} \frac{P_R{}^2}{P^2} \qquad \text{(i)}$$

where the subscript R refers to the reference, <I> is the integrated intensity from two-photon excitation, C is the concentration, n is the refractive index, Q is the quantum yield and P is the incident power on the sample.

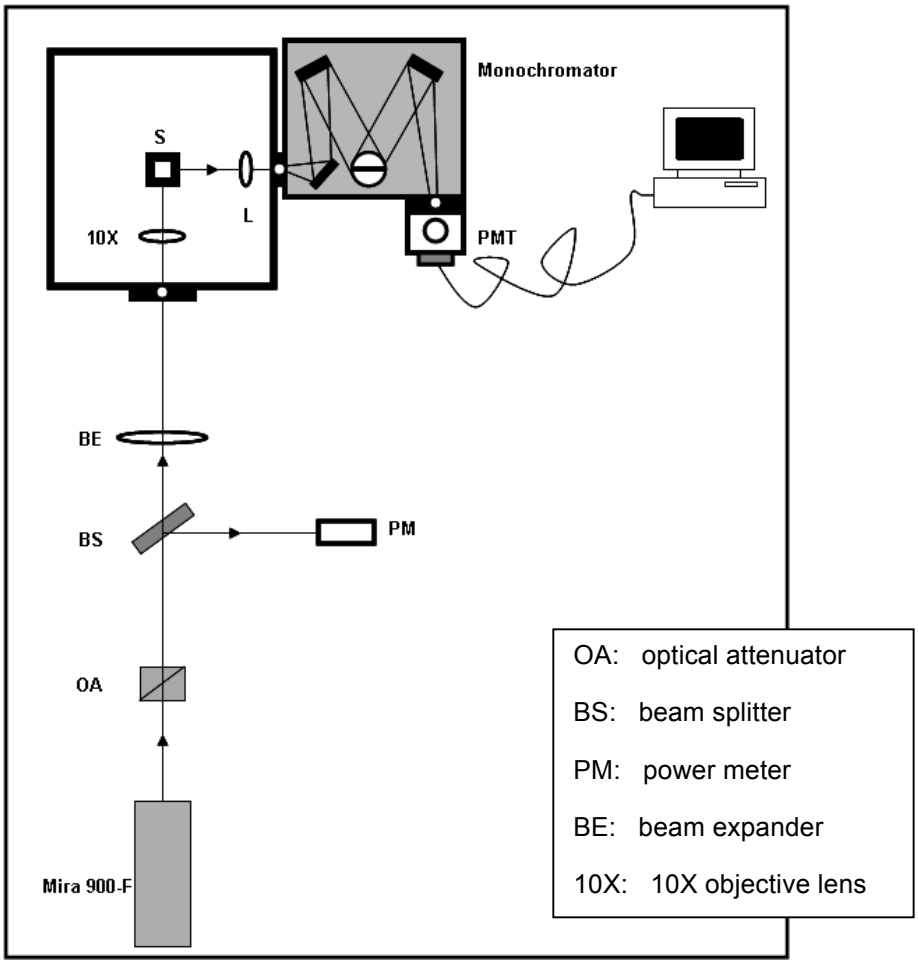
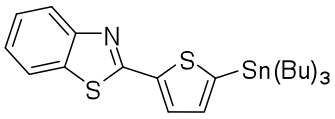
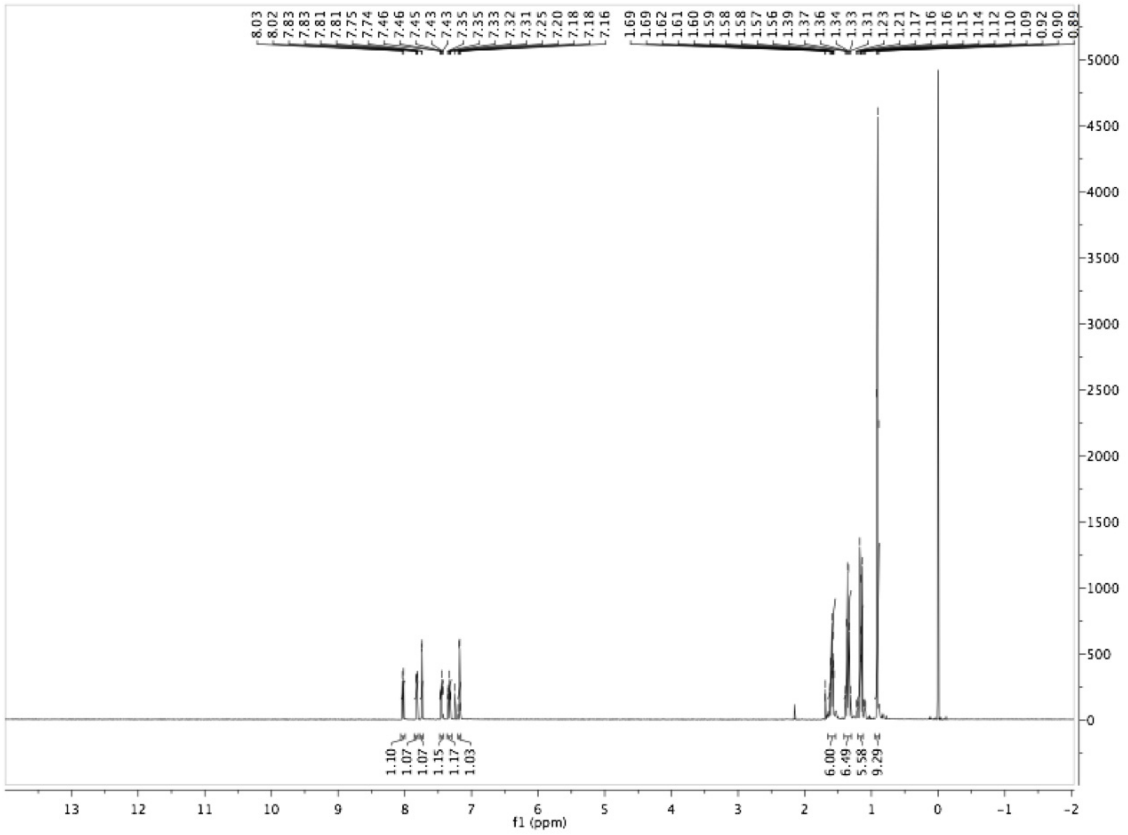


Figure S-1. Experimental setup used to measure the 2PA cross sections of the dyes.

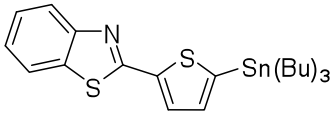
2. NMR data for new compounds. ^{1}H and ^{13}C NMR spectra were recorded in $CDCl_3$ on a NMR spectrometer at 500 and 125 MHz, respectively.

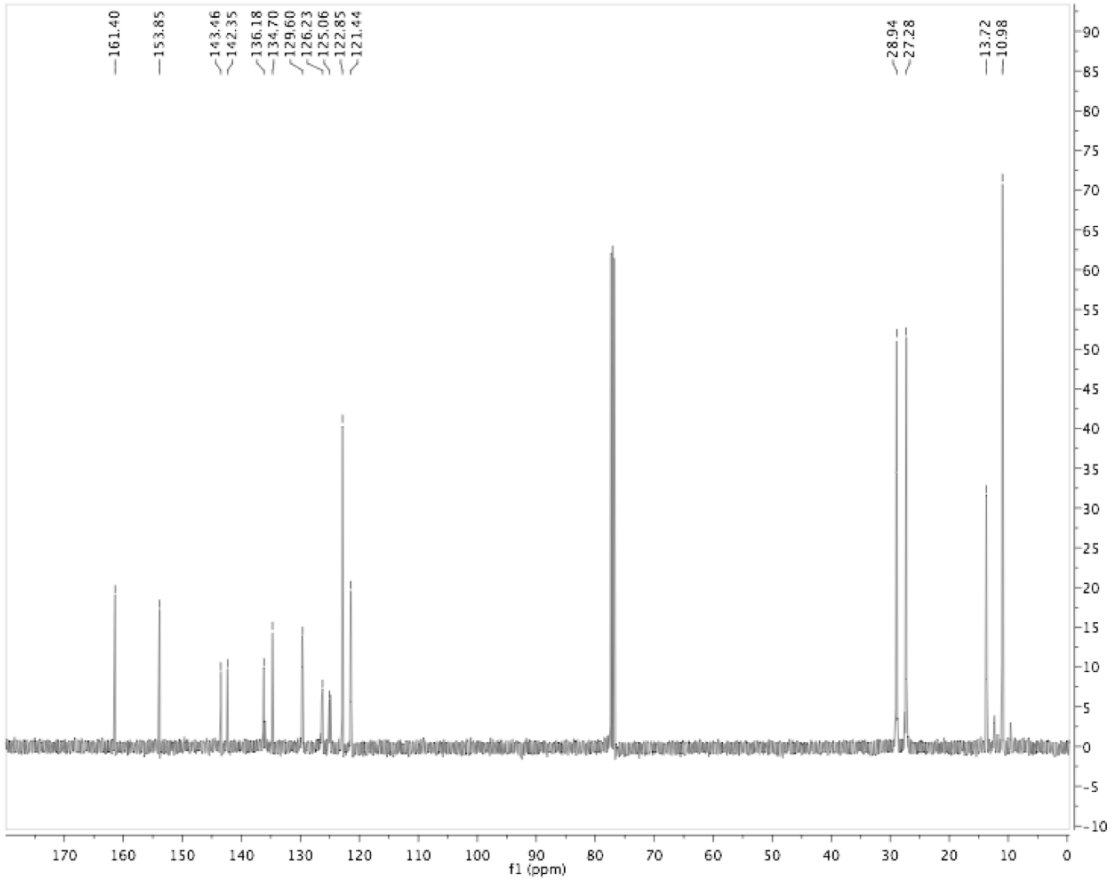
^{1}H NMR for **2**





^{13}C NMR for **2**


N
S
S
Sn(Bu)3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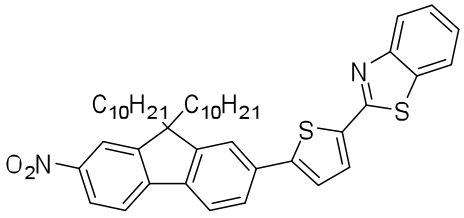
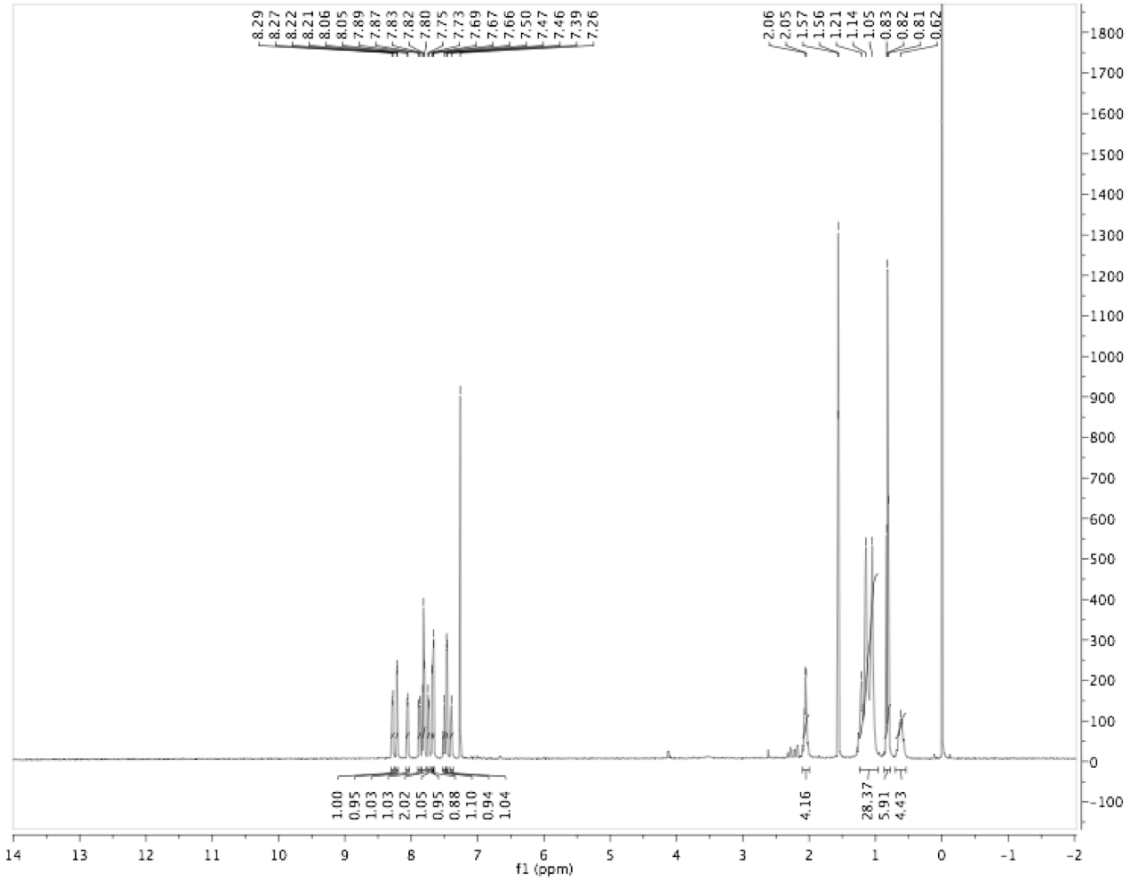
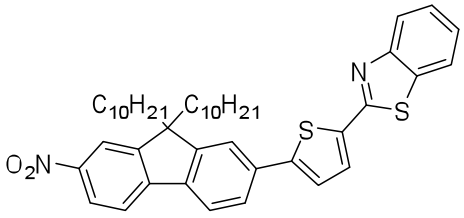
153.85
143.46
142.35
136.18
134.70
129.60
126.23
125.06
122.85
121.44
28.94
27.28
13.72
10.98
f1 (ppm)

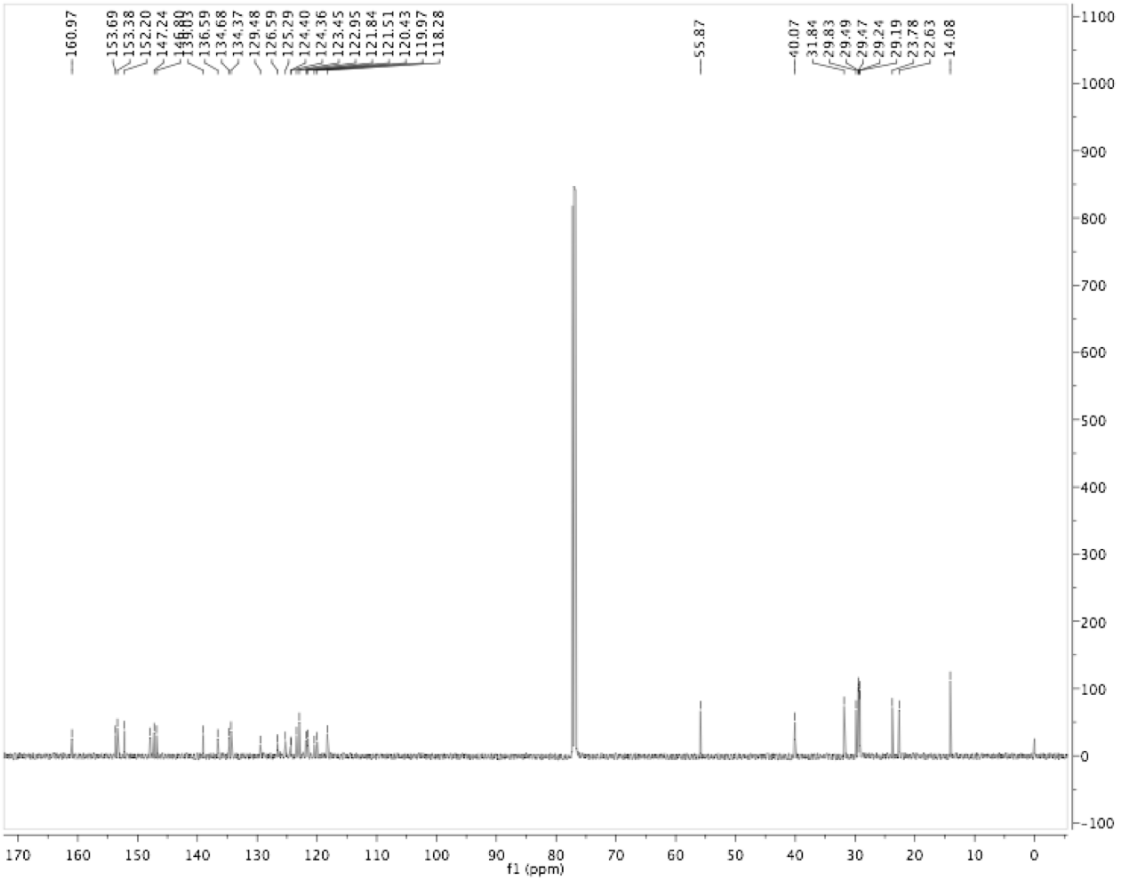
^{1}H NMR for **4**


$C_{10}H_{21}$
$C_{10}H_{21}$
O_2N
S
N
S


8.29
8.27
8.22
8.21
8.06
8.05
7.89
7.87
7.83
7.82
7.80
7.75
7.73
7.69
7.67
7.66
7.50
7.47
7.46
7.39
7.26
2.06
2.05
1.57
1.56
1.21
1.14
1.05
0.83
0.82
0.81
0.62
1.00
0.95
1.03
1.03
2.02
1.05
0.95
0.88
1.10
0.94
1.04
4.16
28.37
5.91
4.43
f1 (ppm)

^{13}C NMR for **4**


C10H21
C10H21
O2N
S
N
S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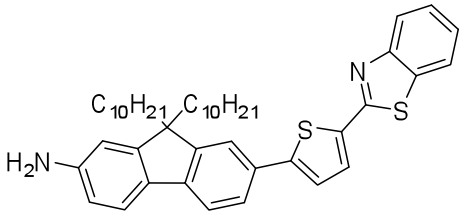
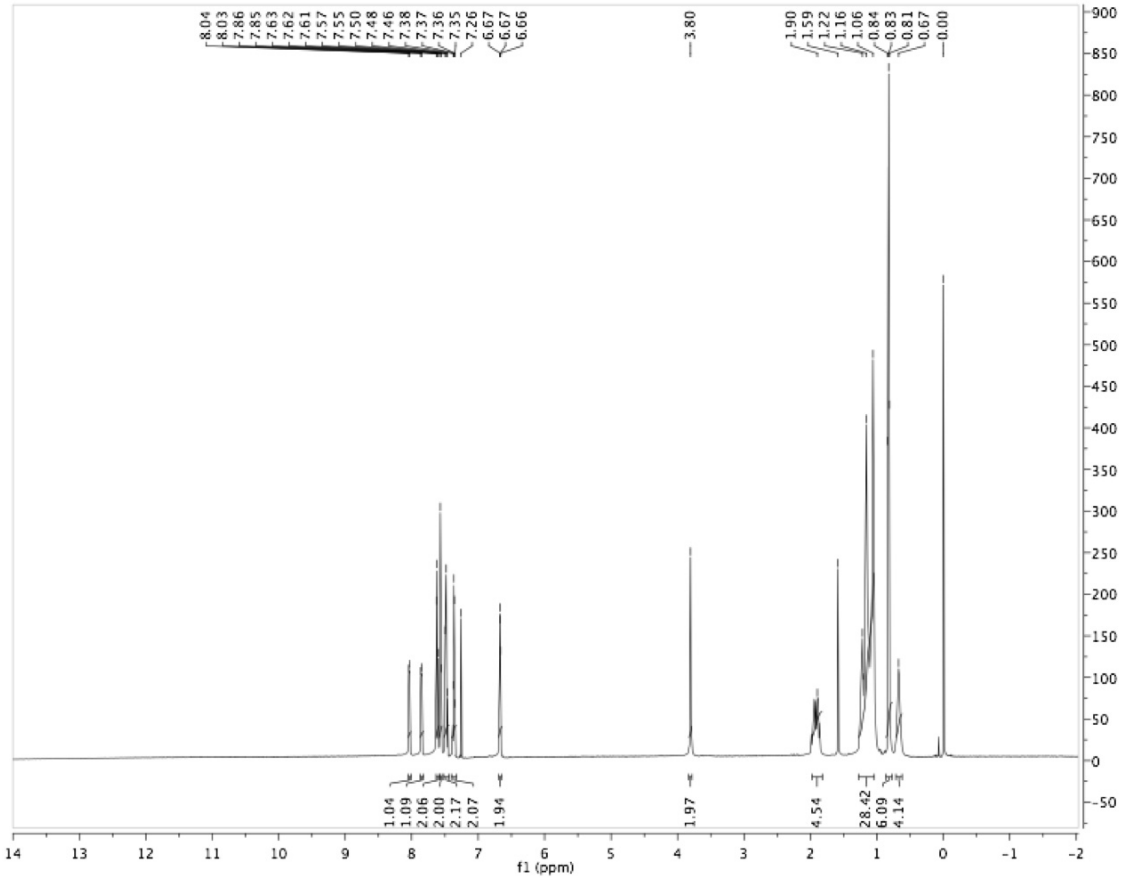
153.69
153.38
152.20
147.24
136.59
134.68
134.37
129.48
126.59
125.29
124.40
124.36
123.45
122.95
121.84
121.51
120.43
119.97
118.28
55.87
60.07
31.84
29.83
29.49
29.47
29.24
29.19
23.78
22.63
14.08
f1 (ppm)

^{1}H NMR for **5**


C10H21
C10H21
H2N
S
N
S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8.03
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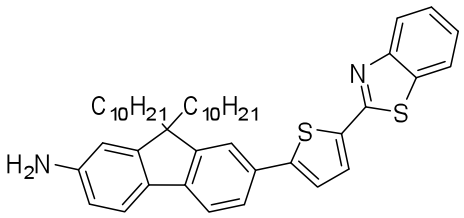
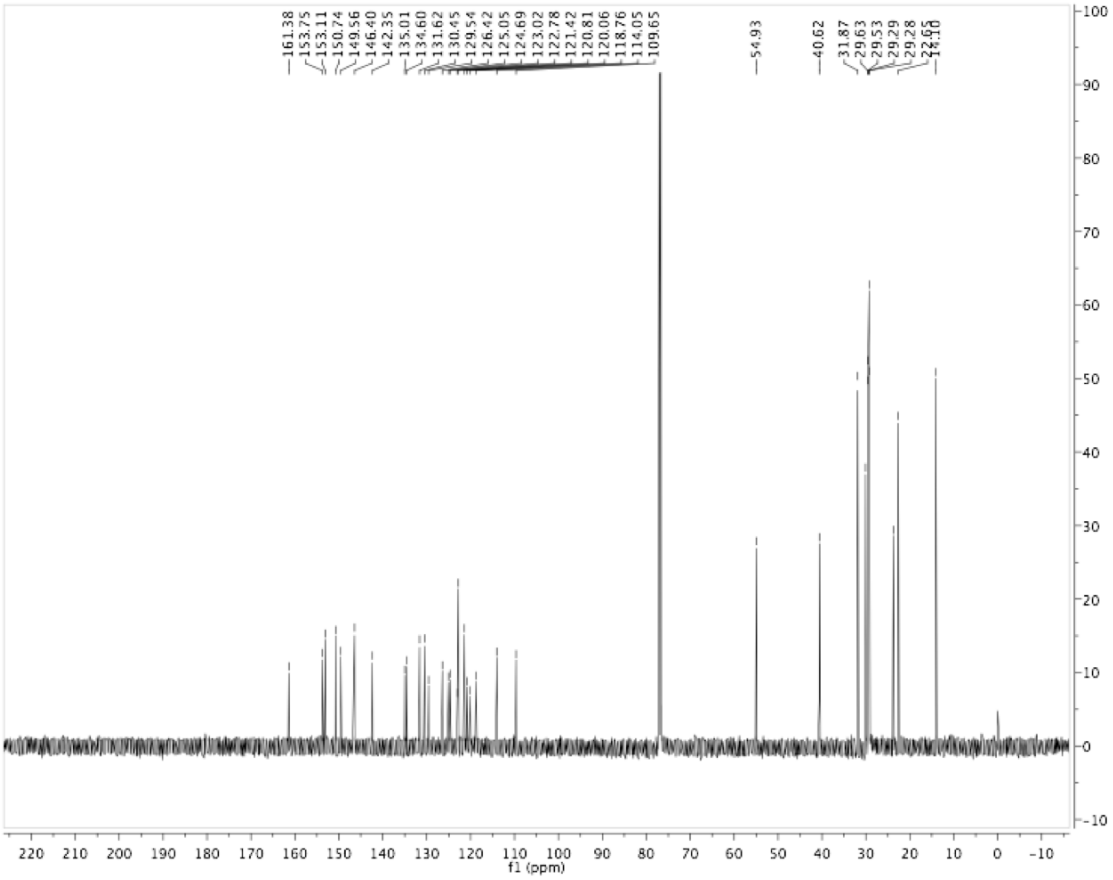
7.85
7.63
7.62
7.61
7.57
7.55
7.50
7.48
7.46
7.38
7.37
7.36
7.35
7.26
6.67
6.67
6.66
3.80
1.90
1.59
1.22
1.16
1.06
0.84
0.83
0.81
0.67
0.00
1.04
1.09
2.06
2.00
2.17
2.07
1.94
1.97
4.54
28.42
6.09
4.14
f1 (ppm)

^{13}C NMR for **5**


C10H21
C10H21
H2N
S
N
S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153.75
153.11
150.74
149.56
146.40
142.35
135.01
134.60
131.62
130.45
129.54
126.42
125.05
124.69
123.02
122.78
121.42
120.81
120.06
118.76
114.05
109.65
54.93
40.62
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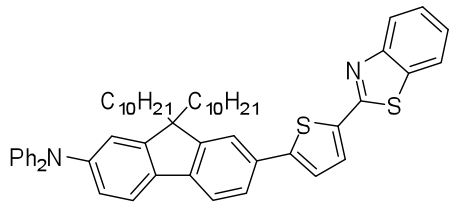
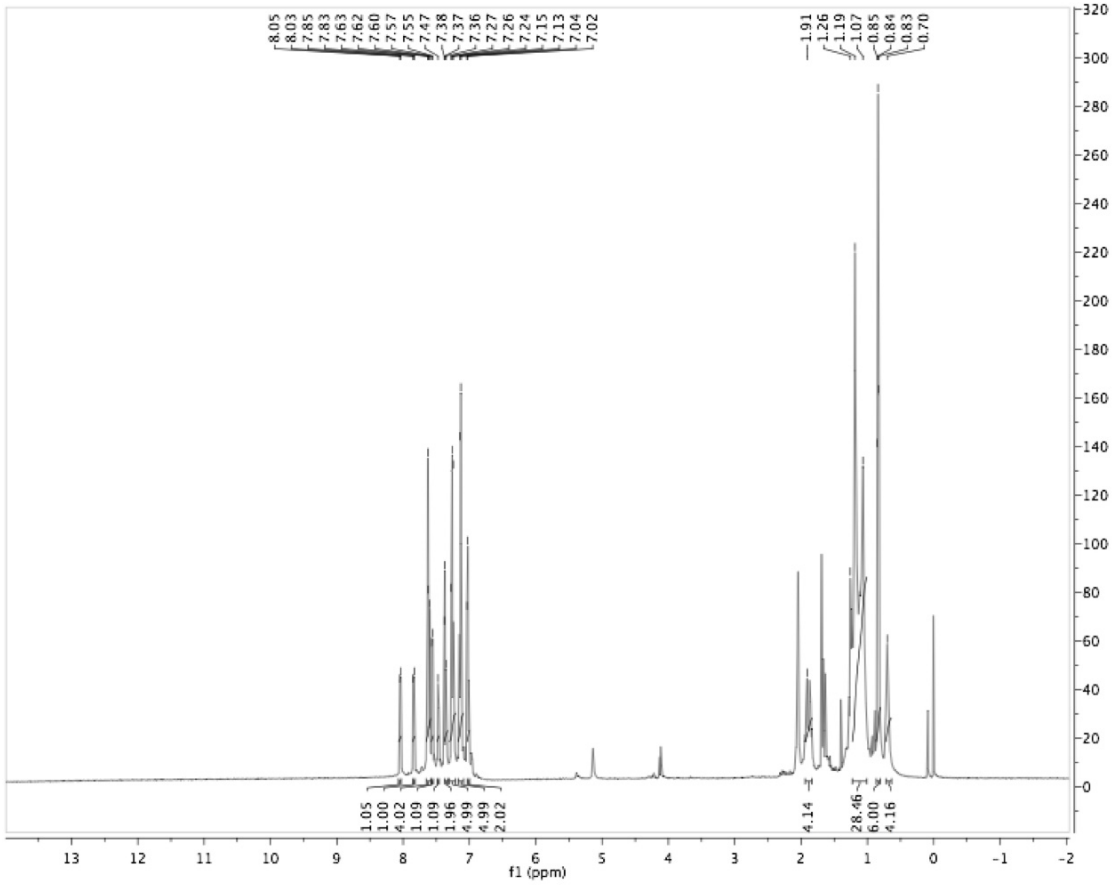
29.63
29.53
29.29
29.28
22.65
14.10
f1 (ppm)

^{1}H NMR for **I**


C10H21
C10H21
Ph2N
S
N
S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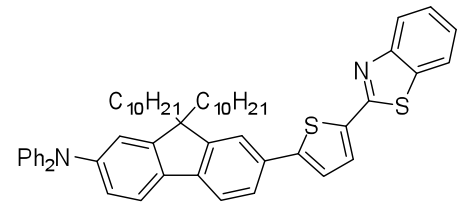
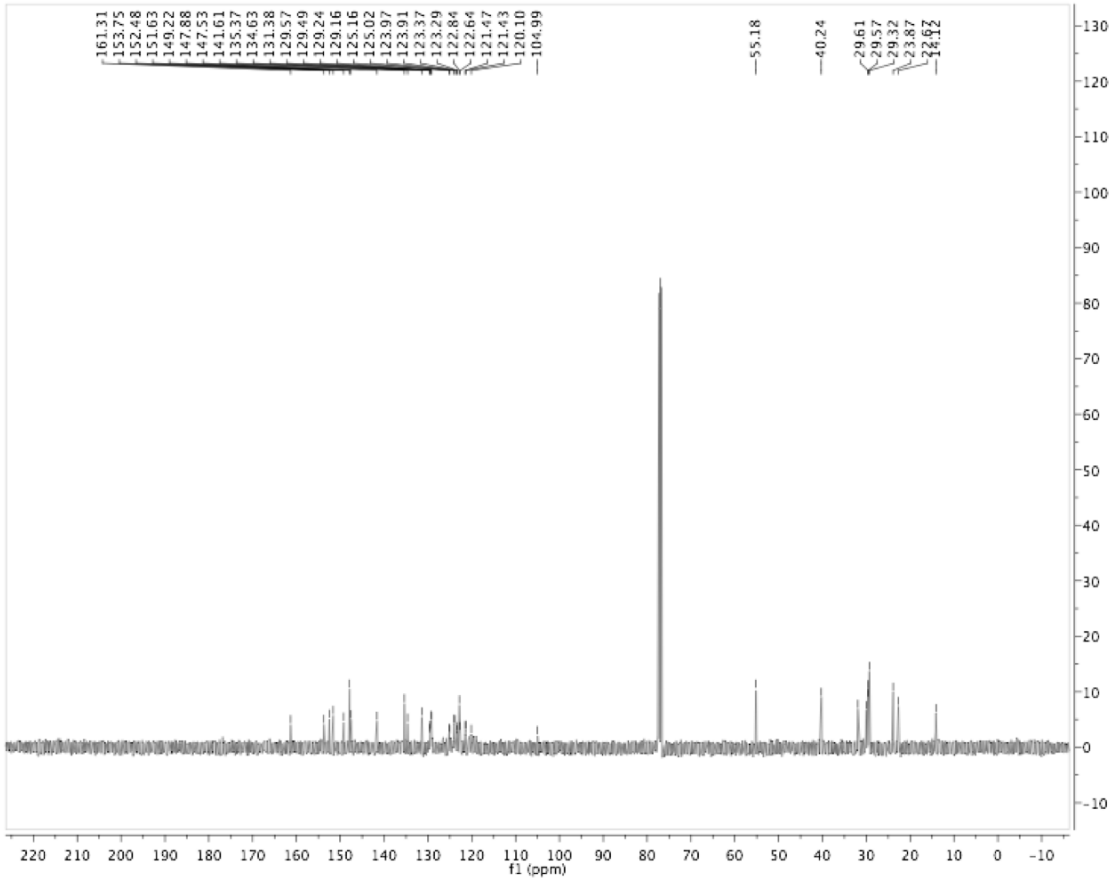
8.03
7.85
7.83
7.63
7.62
7.60
7.57
7.55
7.47
7.38
7.37
7.36
7.27
7.26
7.24
7.15
7.13
7.04
7.02
1.91
1.26
1.19
1.07
0.85
0.84
0.83
0.70
1.05
1.00
4.02
1.09
1.09
1.96
4.99
4.99
2.02
4.14
28.46
6.00
4.16
f1 (ppm)

^{13}C NMR for **I**


C10H21
C10H21
Ph2N
S
N
S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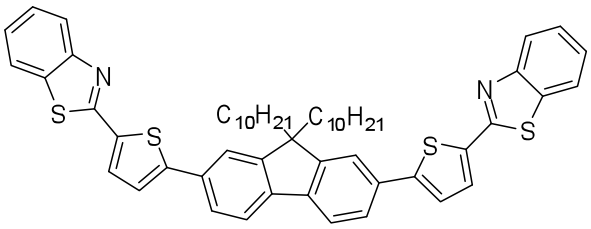
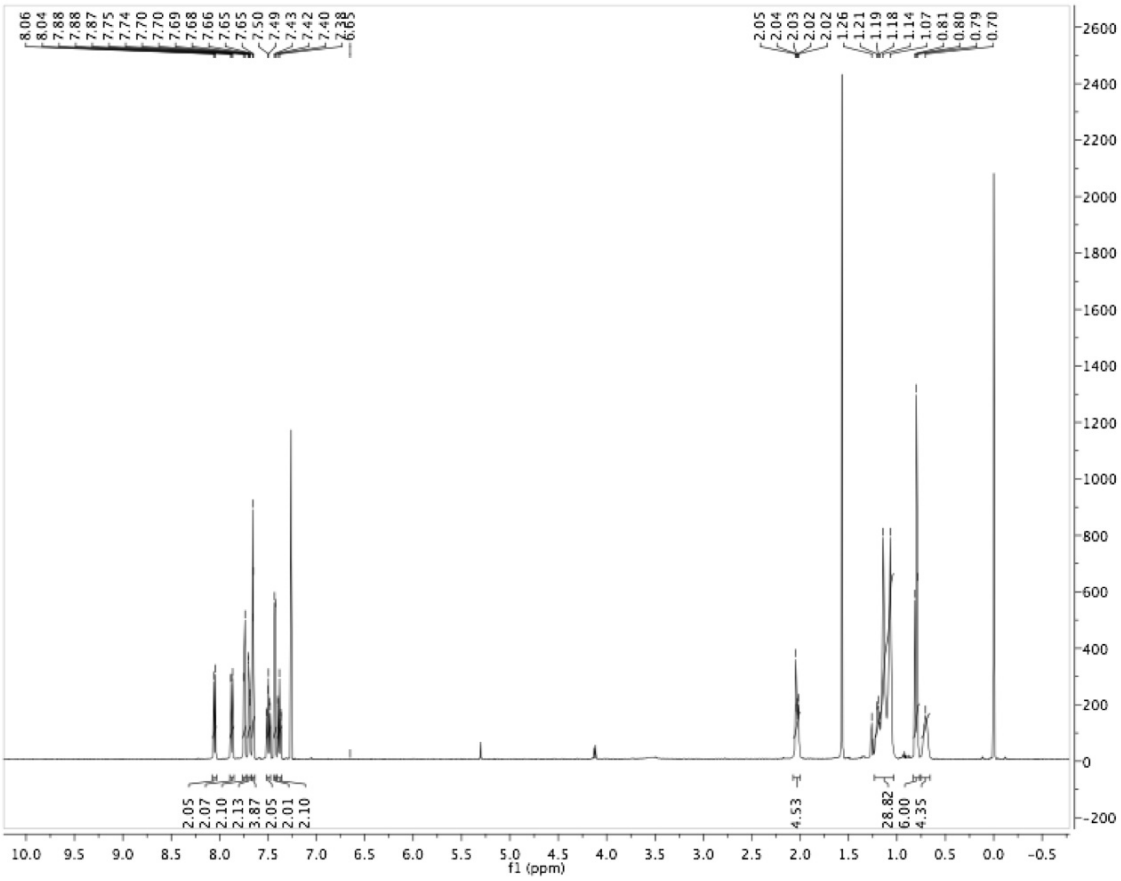
151.63
149.22
147.88
147.53
141.61
135.37
134.63
131.38
129.57
129.49
129.24
129.16
125.16
125.02
123.97
123.91
123.37
123.29
122.84
122.64
121.47
121.43
120.10
104.99
55.18
40.24
29.61
29.57
29.32
23.87
14.12
f1 (ppm)

^{1}H NMR for **II**


N
S
S
C10H21
C10H21
S
N
S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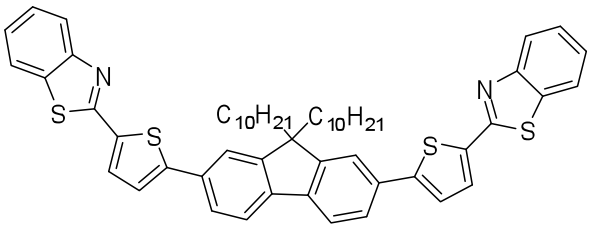
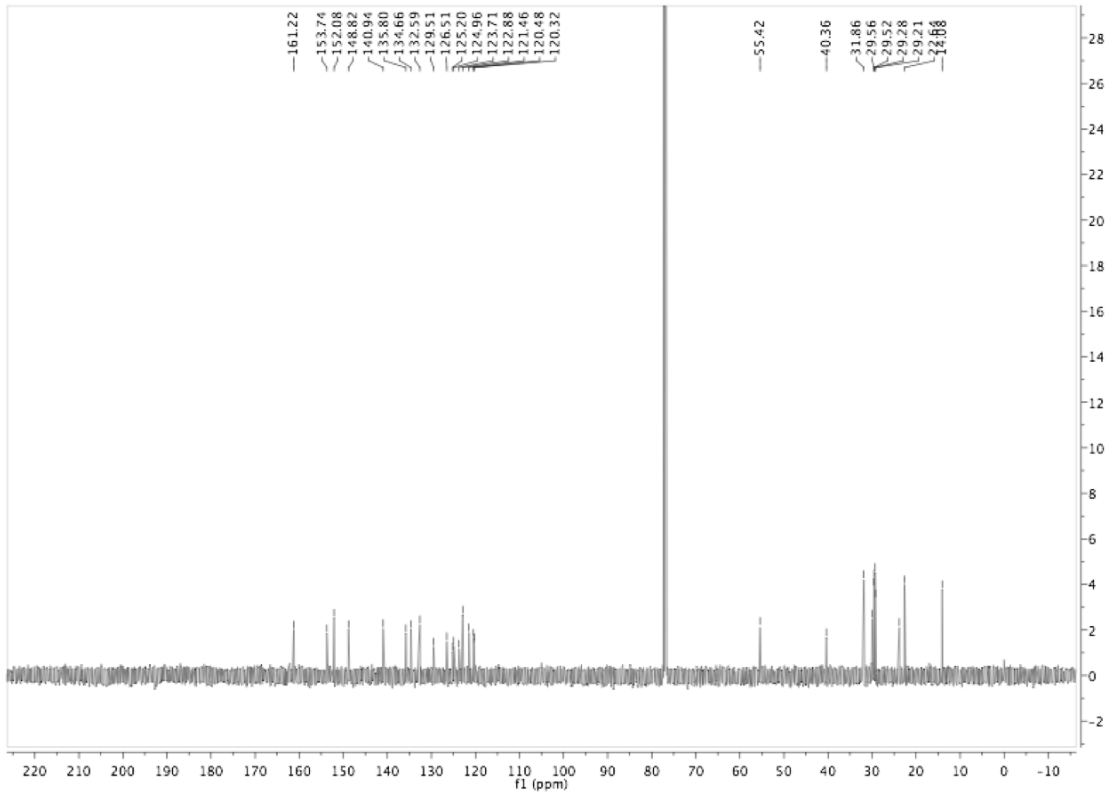
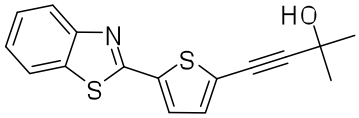
8.04
7.88
7.88
7.87
7.75
7.74
7.70
7.70
7.69
7.68
7.66
7.65
7.65
7.50
7.49
7.43
7.42
7.40
7.38
6.85
2.05
2.04
2.03
2.02
2.02
1.26
1.21
1.19
1.18
1.14
1.07
0.81
0.80
0.79
0.70
2.05
2.07
2.10
2.13
3.87
2.05
2.01
2.10
4.53
28.82
6.00
4.35
f1 (ppm)

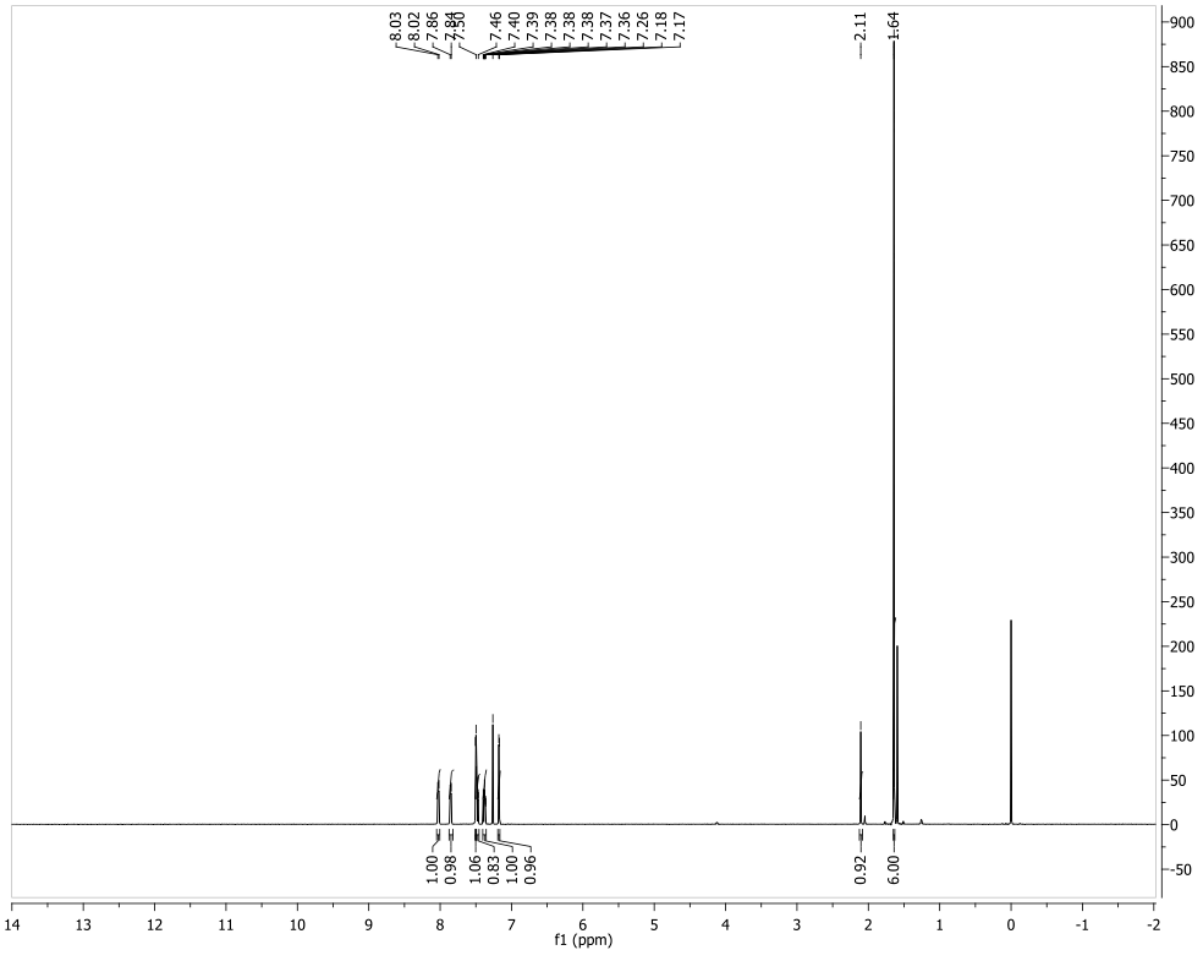
^{13}C NMR for **II**





^{1}H NMR for **7**


HO
N
S
S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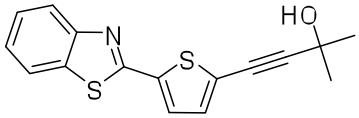
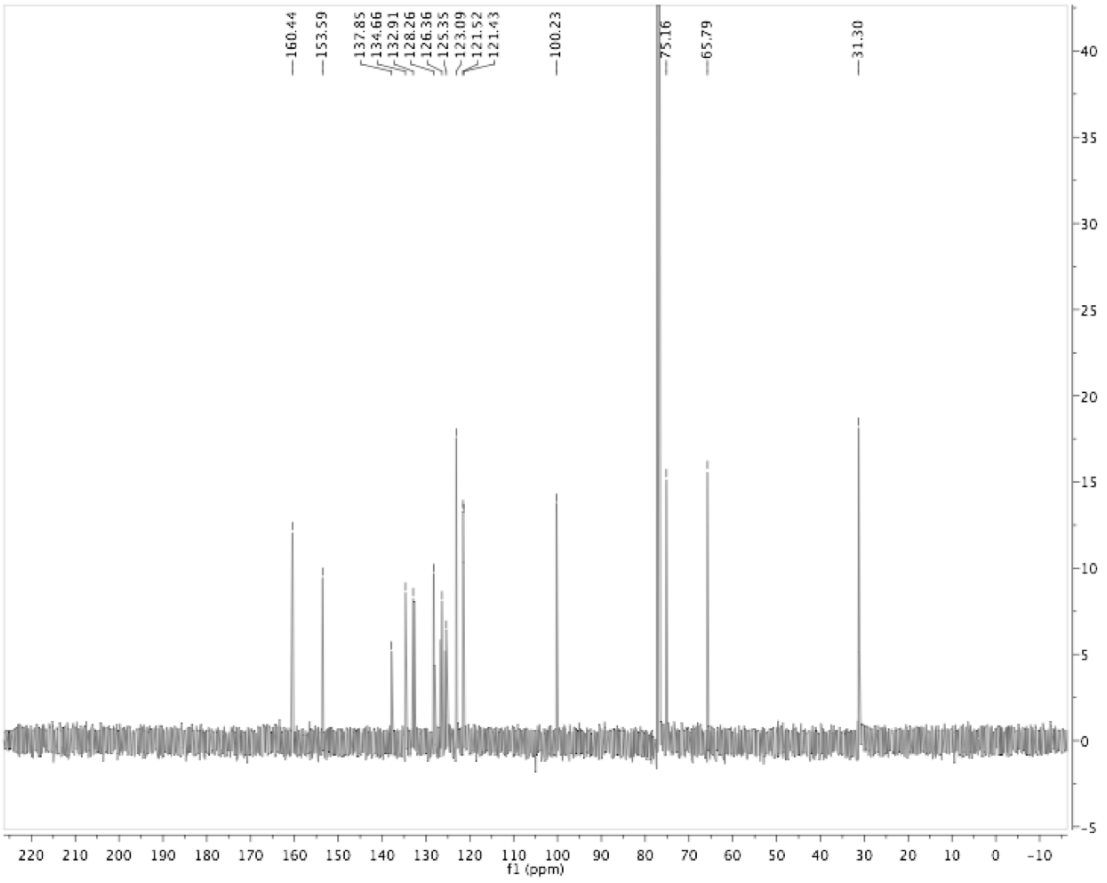
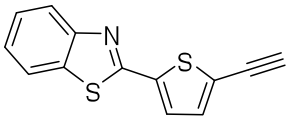
8.02
7.86
7.84
7.50
7.46
7.40
7.39
7.38
7.38
7.38
7.37
7.36
7.26
7.18
7.17
2.11
1.64
1.00
0.98
1.06
0.83
1.00
0.96
0.92
6.00
f1 (ppm)

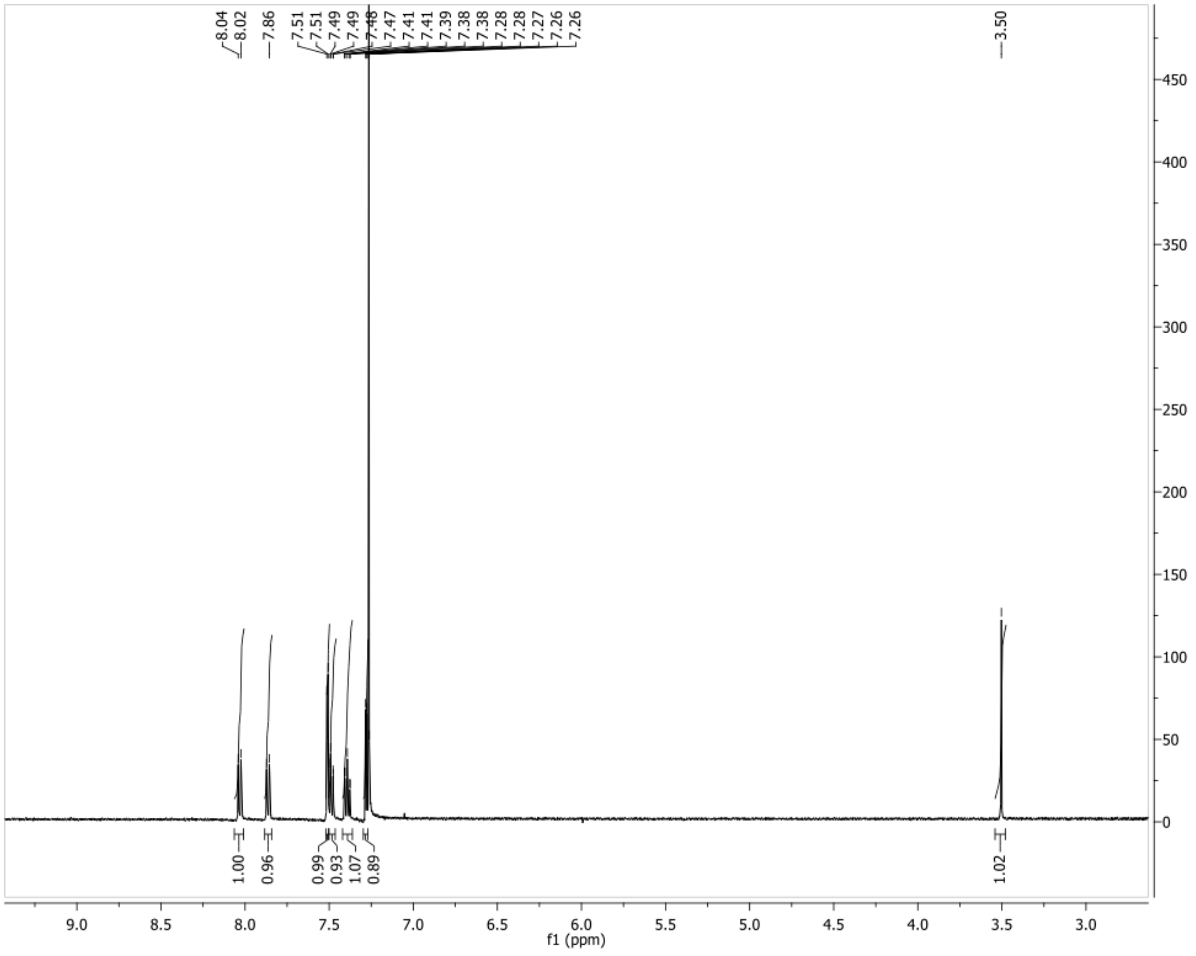
^{13}C NMR for **7**


HO
N
S
S


160.44
153.59
137.85
134.66
132.91
128.26
126.36
125.35
123.09
121.52
121.43
100.23
75.16
65.79
31.30
f1 (ppm)

^{1}H NMR for **8**


N
S
S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8.02
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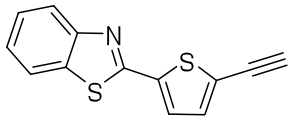
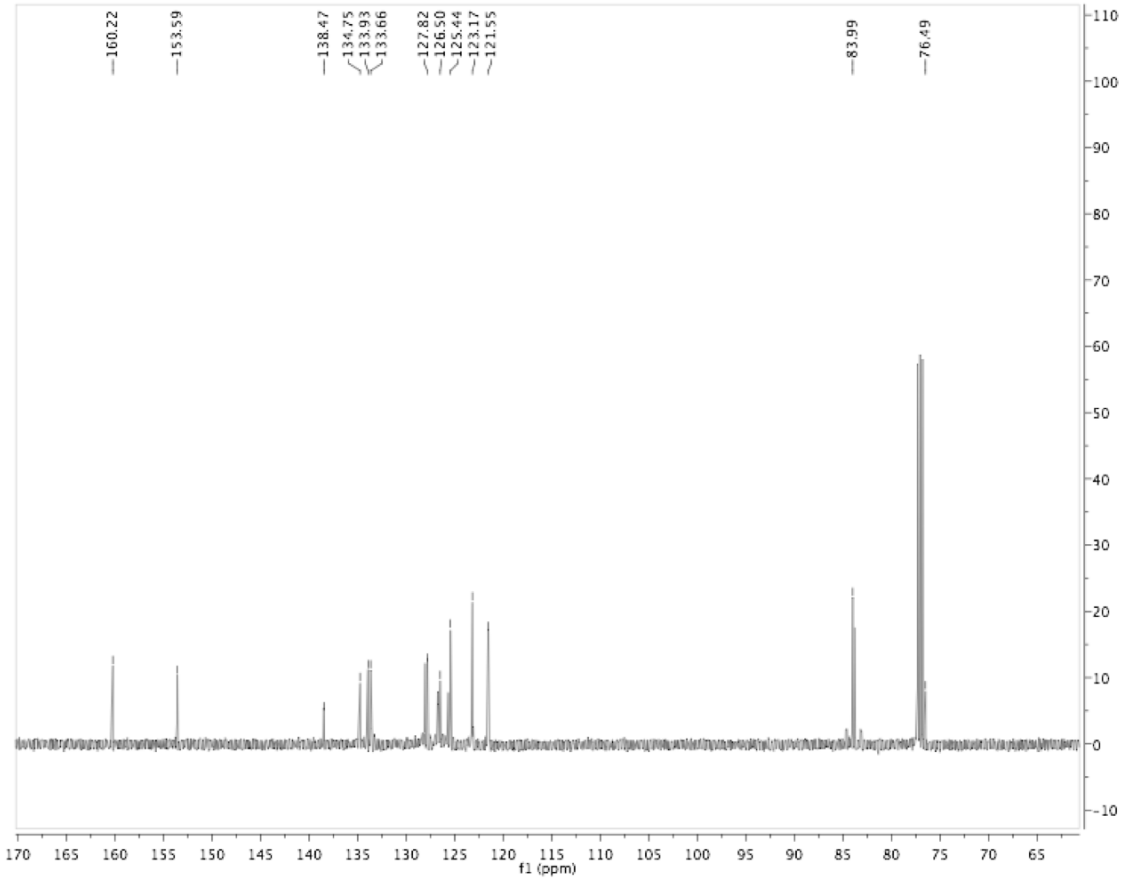
7.51
7.51
7.49
7.49
7.48
7.47
7.41
7.41
7.39
7.38
7.38
7.28
7.28
7.27
7.26
7.26
3.50
1.00
0.96
0.99
0.93
1.07
0.89
1.02
f1 (ppm)

^{13}C NMR for **8**


N
S
S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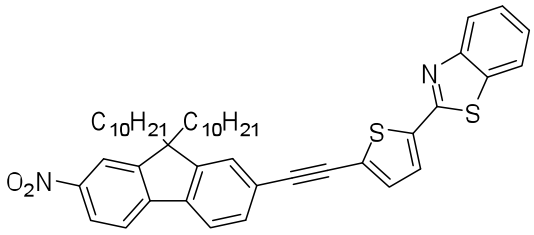
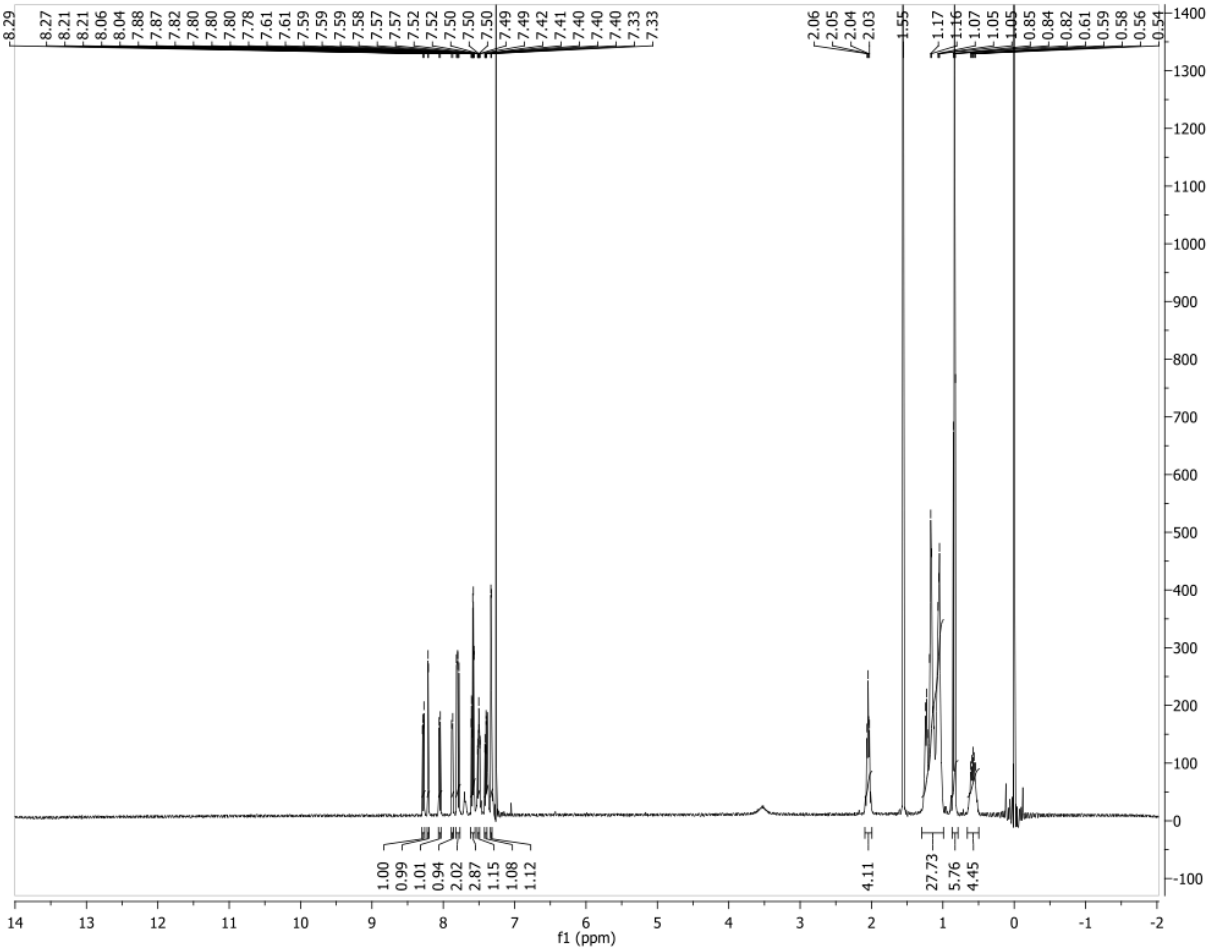
153.59
138.47
134.75
133.93
133.66
127.82
126.50
125.44
123.17
121.55
83.99
76.49
f1 (ppm)

^{1}H NMR for **9**


N
S
S
C10H21
C10H21
O2N


8.29
8.27
8.21
8.21
8.06
8.04
7.88
7.87
7.82
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7.80
7.80
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7.61
7.61
7.59
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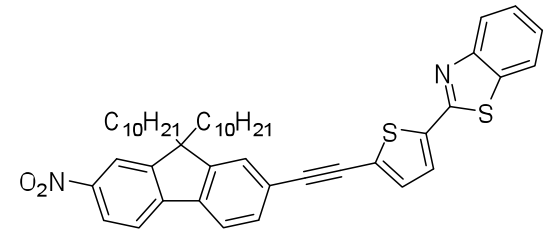
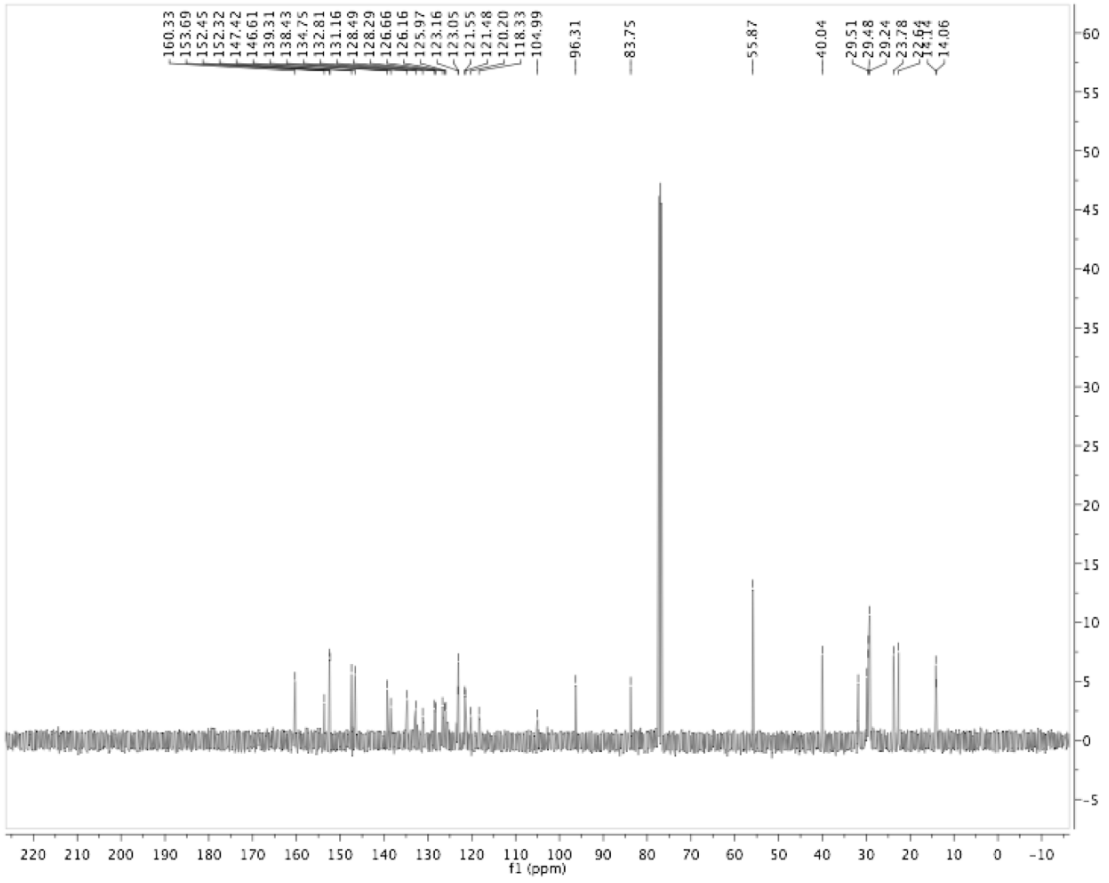
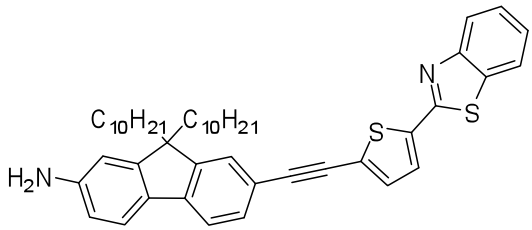
7.49
7.42
7.41
7.40
7.40
7.40
7.33
7.33
2.06
2.05
2.04
2.03
1.55
1.17
1.16
1.07
1.05
1.05
0.85
0.84
0.82
0.61
0.59
0.58
0.56
0.54
1.00
0.99
1.01
0.94
2.02
2.87
1.15
1.08
1.12
4.11
27.73
5.76
4.45
f1 (ppm)

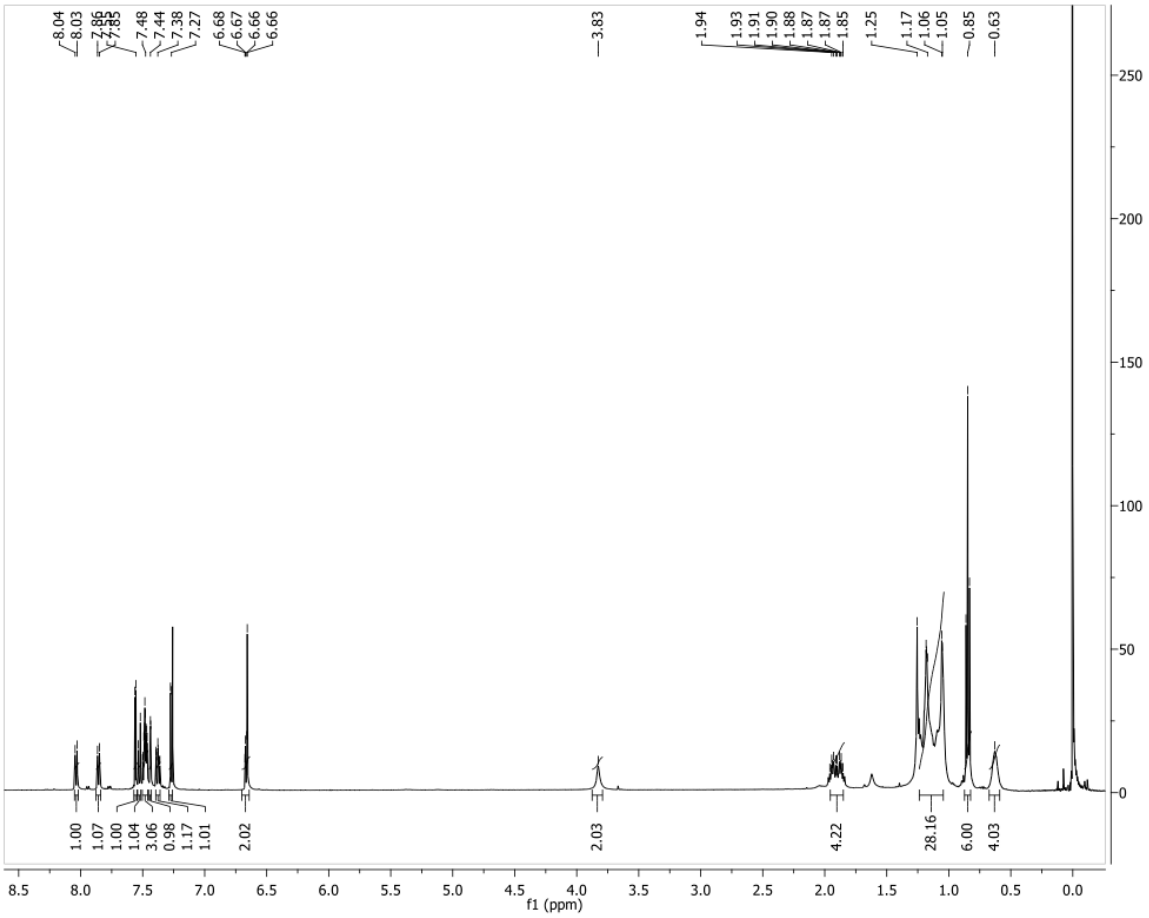
^{13}C NMR for **9**


C10H21
C10H21
O2N
S
N
S

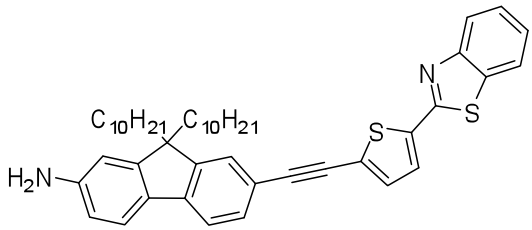

160.33
153.69
152.45
152.32
147.42
146.61
139.31
138.43
134.75
132.81
131.16
128.49
128.29
126.66
126.16
125.97
123.16
123.05
121.55
121.48
120.20
118.33
104.99
96.31
83.75
55.87
40.04
29.51
29.48
29.24
23.78
22.64
14.14
14.06
f1 (ppm)

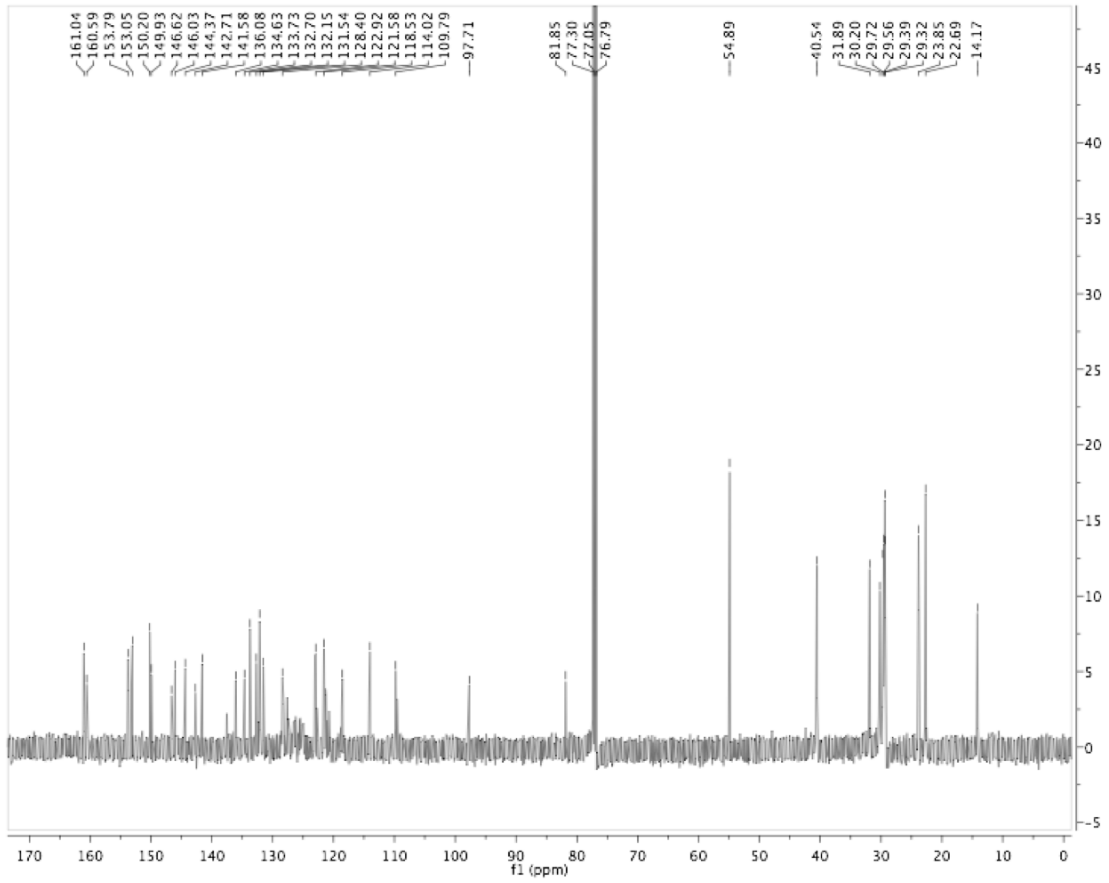
^{1}H NMR for **10**


C10H21
C10H21
H2N
S
N
S

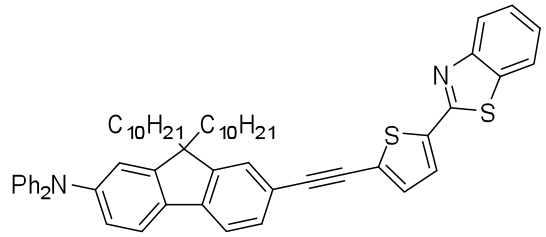

8.04
8.03
7.48
7.44
7.38
7.27
6.68
6.67
6.66
6.66
3.83
1.94
1.93
1.91
1.90
1.88
1.87
1.87
1.85
1.25
1.17
1.06
1.05
0.85
0.63
1.00
1.07
1.00
1.04
3.06
0.98
1.17
1.01
2.02
2.03
4.22
28.16
6.00
4.03
f1 (ppm)

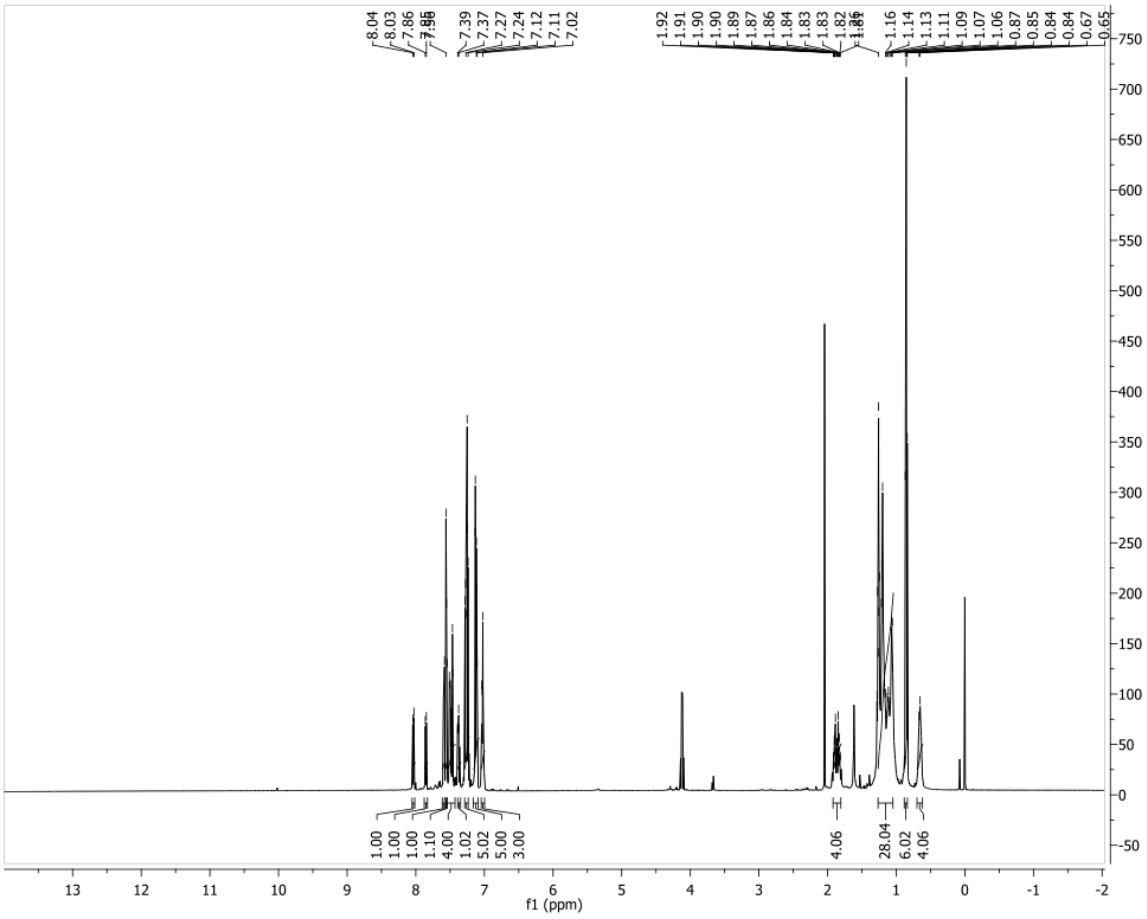
^{13}C NMR for **10**



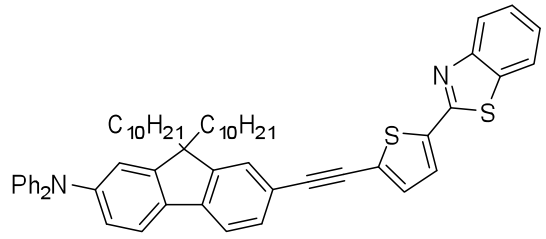


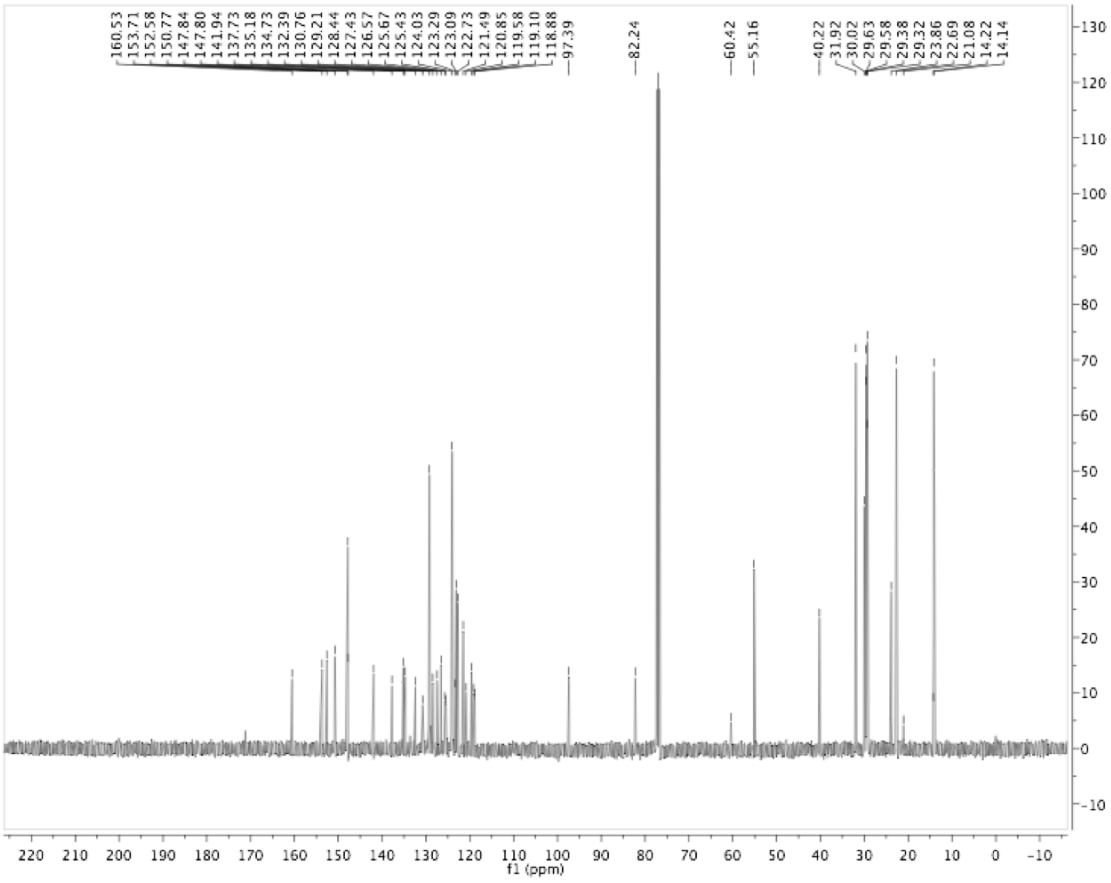
^{1}H NMR for **III**



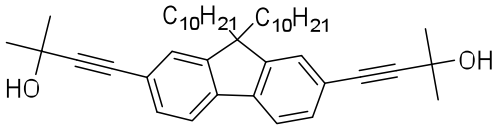


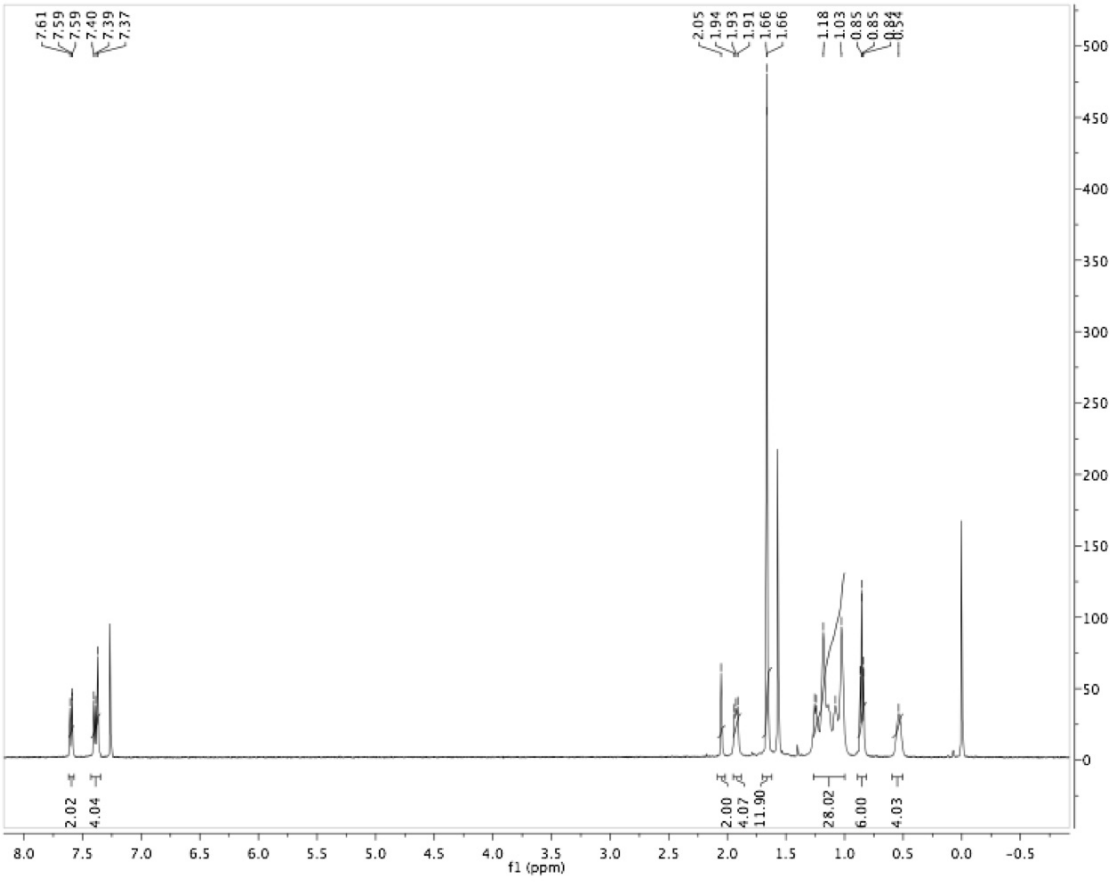
^{13}C NMR for **III**



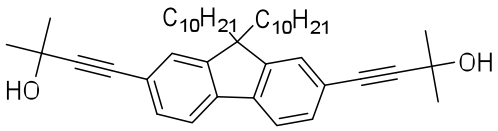


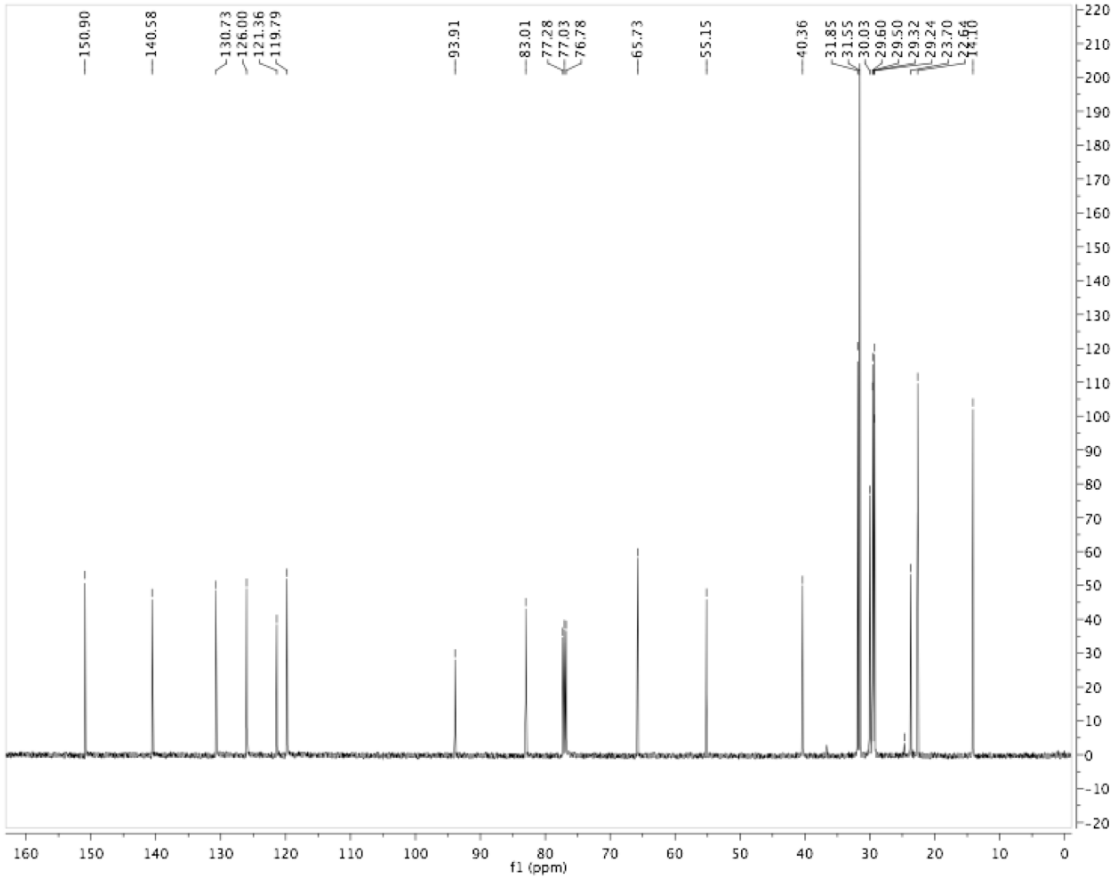
^{1}H NMR for **11**


C10H21
C10H21
HO
OH

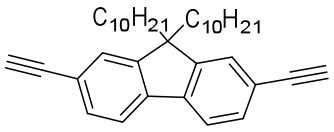

7.61
7.59
7.59
7.40
7.39
7.37
2.05
1.94
1.93
1.91
1.66
1.66
1.18
1.03
0.85
0.85
0.84
0.84
2.02
4.04
2.00
4.07
11.90
28.02
6.00
4.03
f1 (ppm)

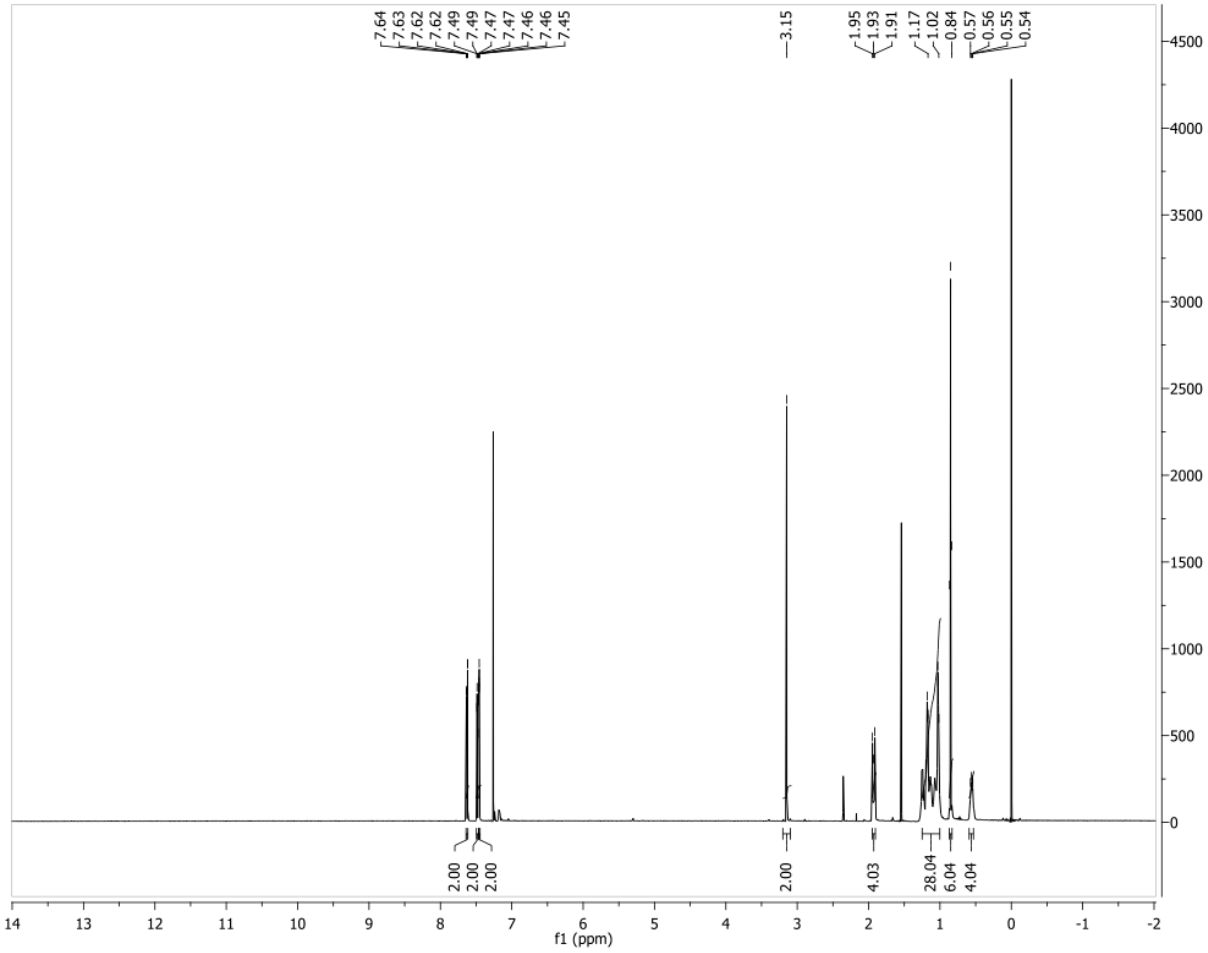
^{13}C NMR for **11**



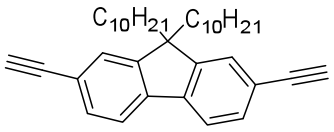


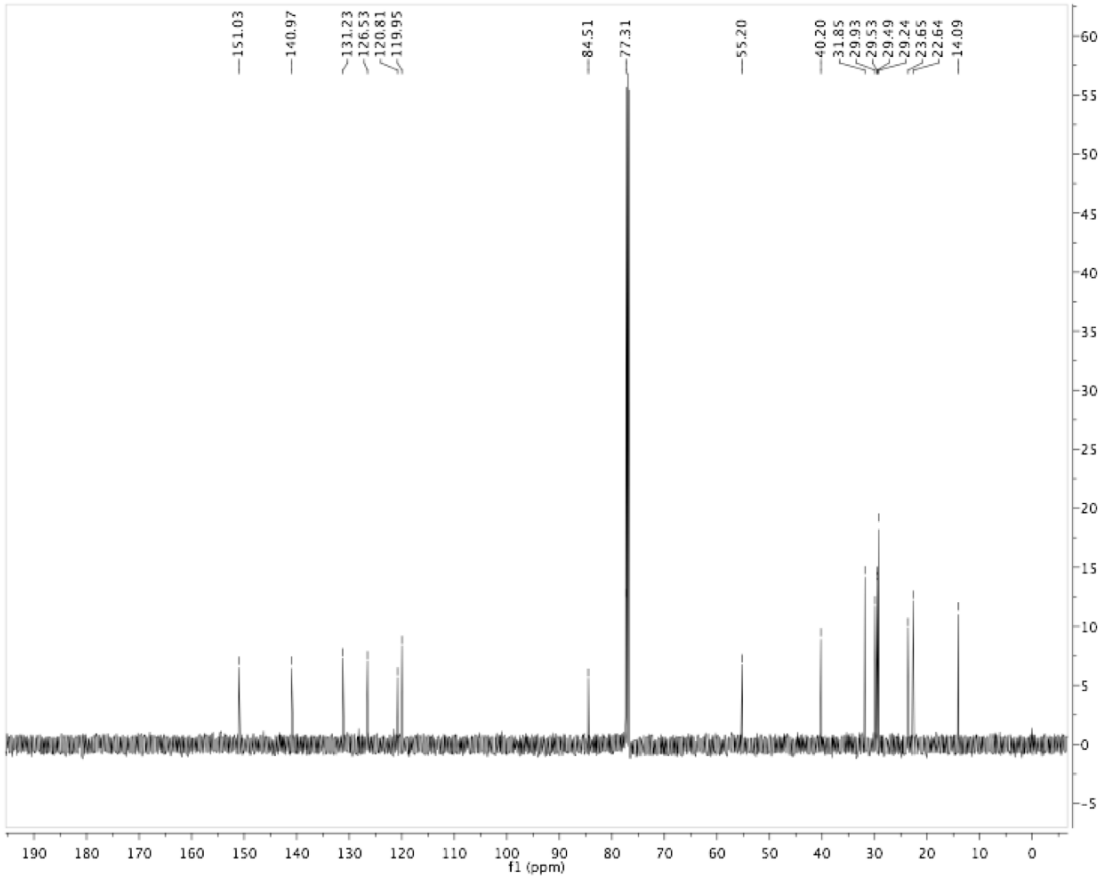
^{1}H NMR for **12**


$C_{10}H_{21}$
$C_{10}H_{21}$

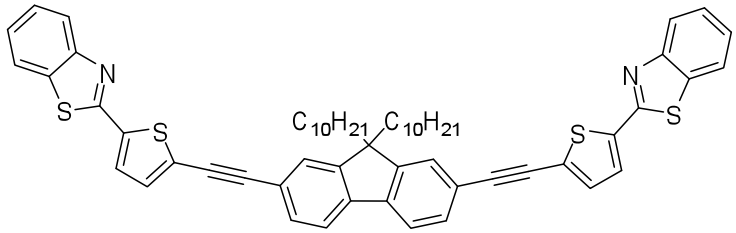

7.64
7.63
7.62
7.62
7.49
7.49
7.47
7.47
7.46
7.46
7.45
3.15
1.95
1.93
1.91
1.17
1.02
0.84
0.57
0.56
0.55
0.54
2.00
2.00
2.00
2.00
4.03
28.04
6.04
4.04
f1 (ppm)

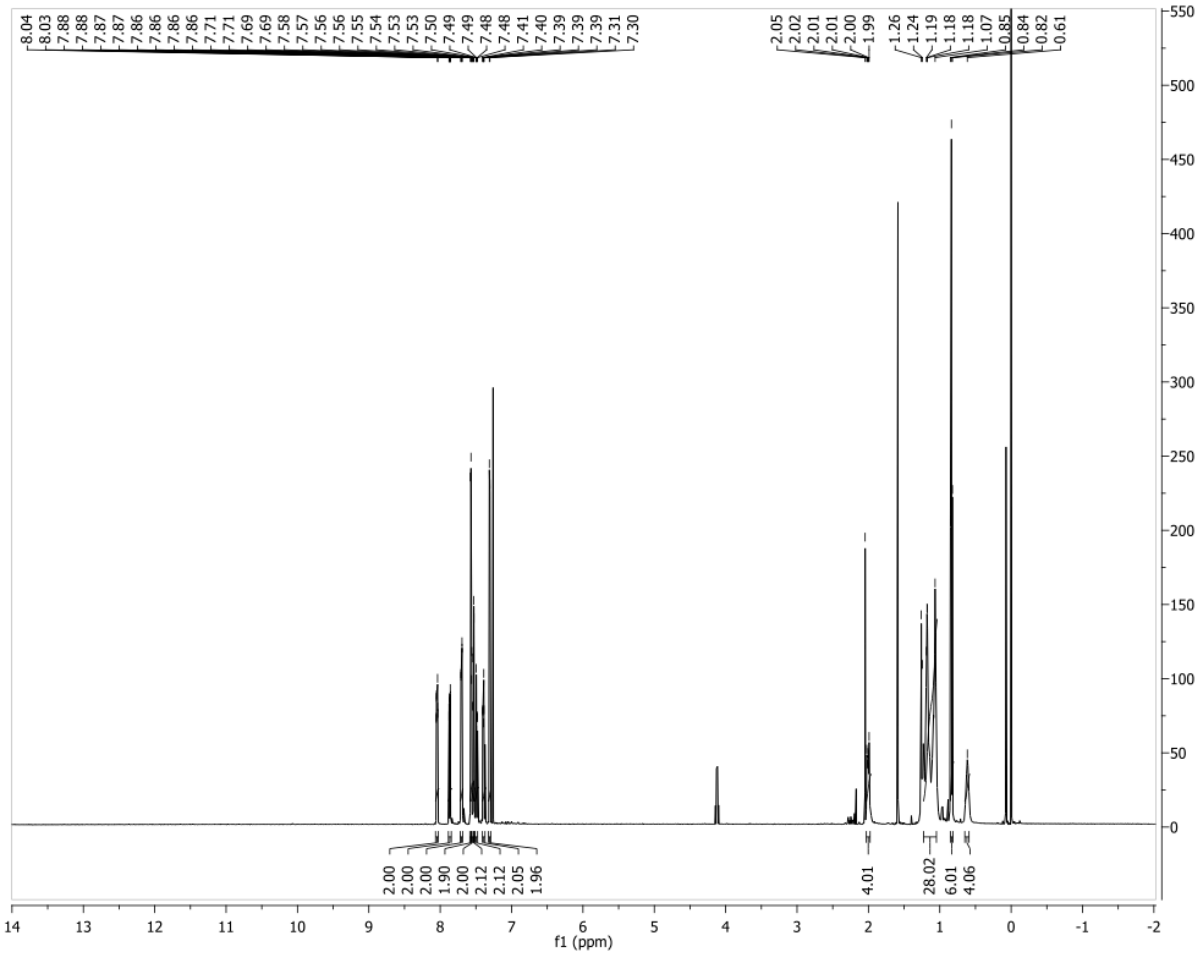
^{13}C NMR for **12**





^{1}H NMR for **IV**


N
S
S
C10H21
C10H21
S
N
S


8.04 8.03 7.88 7.88 7.87 7.87 7.86 7.86 7.86 7.86 7.71 7.71 7.69 7.69 7.58 7.57 7.56 7.56 7.55 7.54 7.53 7.53 7.50 7.49 7.49 7.48 7.48 7.41 7.40 7.39 7.39 7.39 7.31 7.30
2.05 2.02 2.01 2.01 2.00 1.99
1.26 1.24 1.19 1.18 1.18 1.07 0.85 0.84 0.82 0.61
2.00 2.00 2.00 1.90 2.00 2.12 2.12 2.05 1.96
4.01
28.02 6.01 4.06
f1 (ppm)

^{13}C NMR for **IV**