SUPPORTING INFORMATION

Iodine-mediated Regio- and Stereoselective Iodothiocyanation of Alkynes in Aqueous Ethanol

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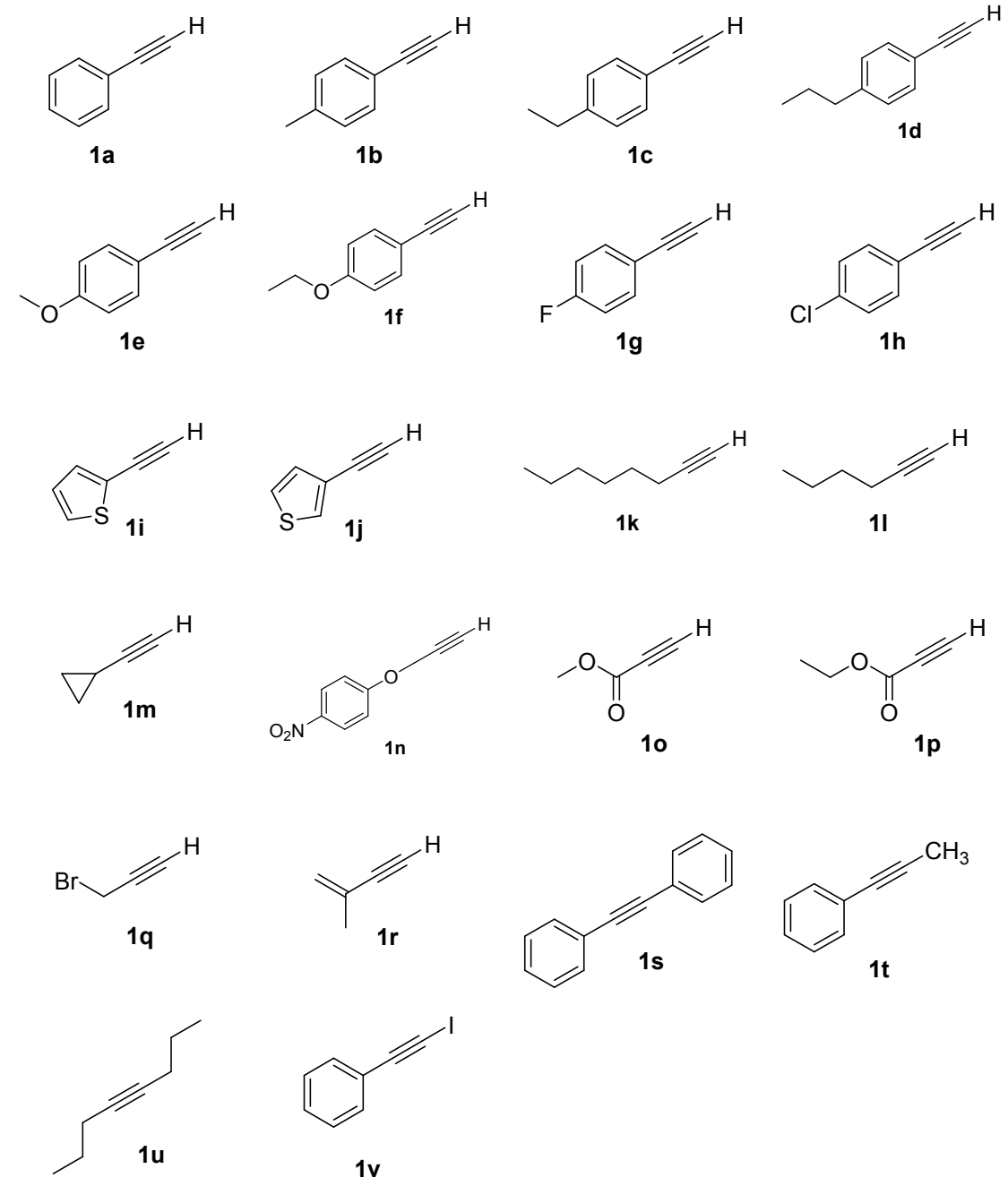
1. General information

^{1}H and ^{13}C NMR spectra were recorded on Varian 400 MHz NMR spectrometer using $CDCl_3$ as solvent and TMS as an internal standard. High-resolution mass spectra (HRMS) were recorded on a Bruker solariX FT-ICR mass spectrometer. Reactions were monitored using thin-layer chromatography (TLC) on commercial silica gel plates (GF254), and was performed under UV light (254 nm). All the new products were further characterized by high resolution mass spectra (HRMS). All commercial reagents and available compounds were obtained from Energy Chemical, Sinopharm Chemical Reagent Co., Ltd and TCI, and used without further purification.

2. General procedure for synthesis of thiocyanates

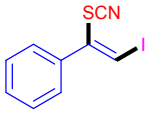
A mixture of alkynes (0.40 mmol), iodine (0.22 mmol), ammonium thiocyanate (0.44 mmol) in ethanol (1.0 ml) and water (0.5 ml) was stired at 80 ^{o}C for 24h under air atmosphere. After completion, the reaction mixture was cooled down to the room temperature. Then the reaction was quenched with saturated solution of sodium thiosulfate (1.0 mL) and extracted with dichloromethane for three times (3 x 3 ml). The organic layers were then combined, washed with brine, dried (anhydrous Na_2SO_4), and concentrated under vacuum. The residue was purified by flash chromatography (Petroleum Ether / EtOAc = 30:1) on silica gel to give the desired product.

3. General procedure for synthesis of thiocyanates

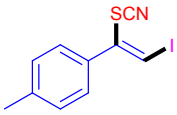


Scheme S1. Substrates employed for the synthesis of thiocyanates

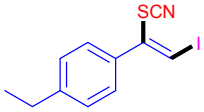
4. NMR spectra of the obtained compounds



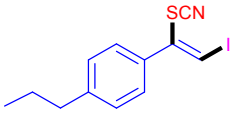
2a[1] Colorless oil (103.3 mg, 90%, Z/E=10:1). ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.32-7.44 (m, 5H), 7.24 (s, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 135.92, 130.84, 130.23, 129.05, 128.96, 109.24, 81.27. HRMS *m/z* (ESI): Calcd for C_9H_6INSNa ($[M+Na]^+$): 309.9158, Found 309.9155.



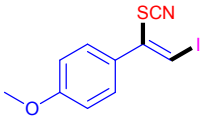
2b Colorless oil (109.5 mg, 91%, Z/E=15:1). ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.32-7.34 (m, 2H), 7.24-7.26 (m, 2H), 7.18 (s, 1H), 2.39 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 140.54, 132.87, 130.97, 129.63, 128.98, 109.44, 80.38, 21.51. HRMS *m/z* (ESI): Calcd for $C_{10}H_8INSNa$ ($[M+Na]^+$): 323.9314, Found 323.9316.



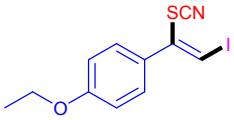
2c Colorless oil (113.4 mg, 90%, Z/E=15:1). ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.35-7.37 (m, 2H), 7.26-7.29 (m, 2H), 7.20 (s, 1H), 2.70 (q, *J*=7.6 Hz, 2H), 1.27 (t, *J*=7.6 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 146.67, 133.03, 130.93, 129.07, 128.40, 109.46, 80.27, 28.75, 15.06. HRMS *m/z* (ESI): Calcd for $C_{11}H_{10}INSNa$ ($[M+Na]^+$): 337.9471, Found 337.9475.



2d Colorless oil (121.1 mg, 92%, Z/E=15:1). ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.15-7.36 (m, 5H), 2.58-2.64 (m, 2H), 1.63-1.70 (m, 2H), 0.94-0.98 (m, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 145.21, 133.02, 130.89, 129.02, 129.01, 128.53, 128.43, 109.52, 80.42, 37.93, 24.24, 13.95. HRMS *m/z* (ESI): Calcd for $C_{12}H_{12}INSNa$ ($[M+Na]^+$): 351.9627, Found 351.9623.

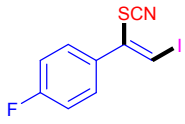


2e Colorless oil (112.9 mg, 89%, Z/E=25:1). ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.38-7.41 (m, 2H), 7.14 (s, 1H), 6.94-6.96 (m, 2H), 3.83 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 160.79, 130.79, 127.71, 114.23, 109.67, 79.97, 55.39. HRMS *m/z* (ESI): Calcd for $C_{10}H_8INSONa$ ($[M+Na]^+$): 339.9263, Found 339.9260.

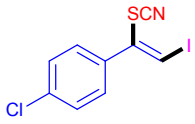


2f Colorless oil (123.2 mg, 93%, Z/E=15:1). ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.36-7.39 (m, 2H), 7.12 (s, 1H), 6.91-6.94 (m, 2H), 4.02-4.06 (m, 2H), 1.39-1.43 (m, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 160.25, 130.75, 130.23, 127.50, 114.66, 114.06, 109.64, 79.97, 63.63, 14.79. HRMS

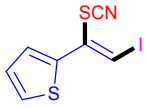
m/z (ESI): Calcd for $C_{11}H_{10}INSONa$ ([M+Na]$^+$): 353.9420, Found 353.9416.



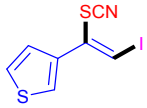
2g Colorless oil (108.7 mg, 89%, Z/E=10:1). ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.41-7.44 (m, 2H), 7.25 (s, 1H), 7.12-7.16 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 164.61, 162.11, 131.38, 131.30, 130.08, 116.38, 116.16, 109.17, 82.60. HRMS *m/z* (ESI): Calcd for $C_9H_5IFNSNa$ ([M+Na]$^+$): 327.9064, Found 327.9060.



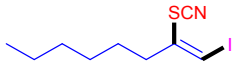
2h Colorless oil (118.5 mg, 92%, Z/E=10:1). ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.36-7.43 (m, 4H), 7.28 (s, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 136.29, 134.36, 130.54, 129.98, 129.36, 128.72, 109.07, 83.23. HRMS *m/z* (ESI): Calcd for $C_9H_5ICINSNa$ ([M+Na]$^+$): 343.8768, Found 343.8772.



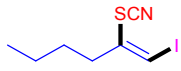
2i Colorless oil (97.3 mg, 83%, Z/E=10:1). ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.58-7.59 (m, 1H), 7.50-7.52 (m, 1H), 7.37 (s, 1H), 7.10-7.12 (m, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 136.95, 131.74, 129.45, 127.42, 124.48, 109.55, 83.01. HRMS *m/z* (ESI): Calcd for $C_7H_4INS_2Na$ ([M+Na]$^+$): 315.8722, Found 315.8718.



2j Colorless oil (103.2 mg, 94%, Z/E=10:1). ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.70-7.71 (m, 1H), 7.41-7.42 (m, 1H), 7.35-7.37 (m, 1H), 7.24 (s, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 135.71, 128.29, 127.48, 126.63, 126.01, 109.40, 81.04. HRMS *m/z* (ESI): Calcd for $C_7H_4INS_2Na$ ([M+Na]$^+$): 315.8722, Found 315.8720.



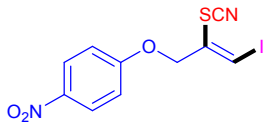
2k Colorless oil (106.4 mg, 90%, Z/E=10:1). ^{1}H NMR (400 MHz, $CDCl_3$) δ: 6.86 (s, 1H), 2.54-2.58 (m, 2H), 1.58-1.60 (m, 2H), 1.29 -1.34 (m, 6H), 0.86-0.89 (m, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 132.24, 109.49, 81.23, 37.35, 31.43, 22.52, 14.08. HRMS *m/z* (ESI): Calcd for $C_9H_{14}INSNa$ ([M+Na]$^+$): 317.9784, Found 317.9780.



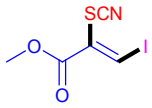
2l Colorless oil (98.3 mg, 92%, Z/E=10:1). ^{1}H NMR (400 MHz, $CDCl_3$) δ: 6.87 (s, 1H), 2.55-2.59 (m, 2H), 1.56-1.59 (m, 2H), 1.36-1.41 (m, 2H), 0.93-0.96 (m, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 132.20, 109.44, 82.47, 37.12, 29.03, 21.92, 13.84. HRMS *m/z* (ESI): Calcd for $C_7H_{10}INSNa$

([M+Na]$^+$): 289.9471, Found 289.9468.

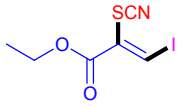
2m Colorless oil (85.4 mg, 85%, Z/E=3:1). ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.07 (s, 1H), 0.99-1.02 (m, 2H), 0.86-0.87 (m, 2H), 0.76 -0.80 (m, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 132.17, 109.94, 85.86, 18.97, 9.48, 7.82. HRMS *m/z* (ESI): Calcd for C_6H_6INSNa ([M+Na]$^+$): 273.9158, Found 273.9156.



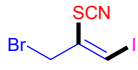
2n White solid (131.7 mg, 91%, Z/E=10:1). ^{1}H NMR (400 MHz, $CDCl_3$) δ: 8.20-8.23 (m, 2H), 7.28 (s, 1H), 6.98-6.99 (m, 2H), 4.79 (s, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 162.19, 125.95, 115.35, 114.36, 96.55, 83,46, 75.10. HRMS *m/z* (ESI): Calcd for $C_{10}H_7IN_2SO_3Na$ ([M+Na]$^+$): 384.9114, Found 384.9118.



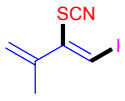
2o White solid (96.9 mg, 90%, Z/E=15:1). ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.61 (s, 1H), 3.86 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 164.38, 141.43, 111.58, 78.18, 54.38. HRMS *m/z* (ESI): Calcd for $C_5H_4INSO_2Na$ ([M+Na]$^+$): 291.8900, Found 291.8902.



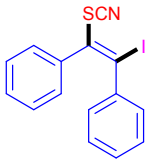
2p White solid (102.1 mg, 90%, Z/E=25:1). ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.59 (s, 1H), 4.29 (q, *J*=7.2 Hz, 2H), 1.36 (t, *J*=7.2 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 163.87, 140.92, 111.71, 79.16, 63.99, 13.96. HRMS *m/z* (ESI): Calcd for $C_6H_6INSO_2Na$ ([M+Na]$^+$): 305.9056, Found 305.9053.



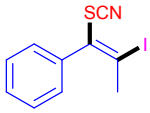
2q Colorless oil (99.7 mg, 82%, Z/E=5:1). ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.28 (s, 1H), 4.07 (s, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 128.90, 110.06, 87.61, 47.98. HRMS *m/z* (ESI): Calcd for $C_4H_3IBrNSNa$ ([M+Na]$^+$): 325.8106, Found 325.8109.



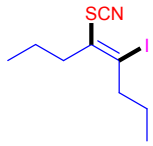
2r Colorless oil (95.4 mg, 96%, Z/E=25:1). ^{1}H NMR (400 MHz, $CDCl_3$) δ: 6.98 (s, 1H), 5.40 (s, 1H), 4.21 (s, 1H), 1.99 (s, 3H),; ^{13}C NMR (100 MHz, $CDCl_3$) δ: 140.21, 133.00, 121.69, 109.16, 80.92, 20.38. HRMS *m/z* (ESI): Calcd for C_6H_6INSNa ([M+Na]$^+$): 273.9158, Found 273.9155.



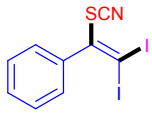
2s White solid (135.0 mg, 93%, Z/E=25:1). ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.33-7.55 (m, 10H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 142.03, 140.31, 131.63, 128.99, 128.97, 128.39, 128.31, 128.14, 123.25, 109.27, 101.01, 89.44. HRMS *m/z* (ESI): Calcd for $C_{15}H_{10}INSNa$ ([M+Na]$^+$): 385.9471, Found 385.9467.



2t Colorless oil (90.2 mg, 75%, Z/E=10:1). ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.40-7.44 (m, 3H), 7.30-7.33 (m, 2H), 2.90 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 141.37, 132.87, 130.97, 129.63, 128.98, 109.44, 80.38, 21.51. HRMS *m/z* (ESI): Calcd for $C_{10}H_8INSNa$ ([M+Na]$^+$): 323.9314, Found 323.9311.



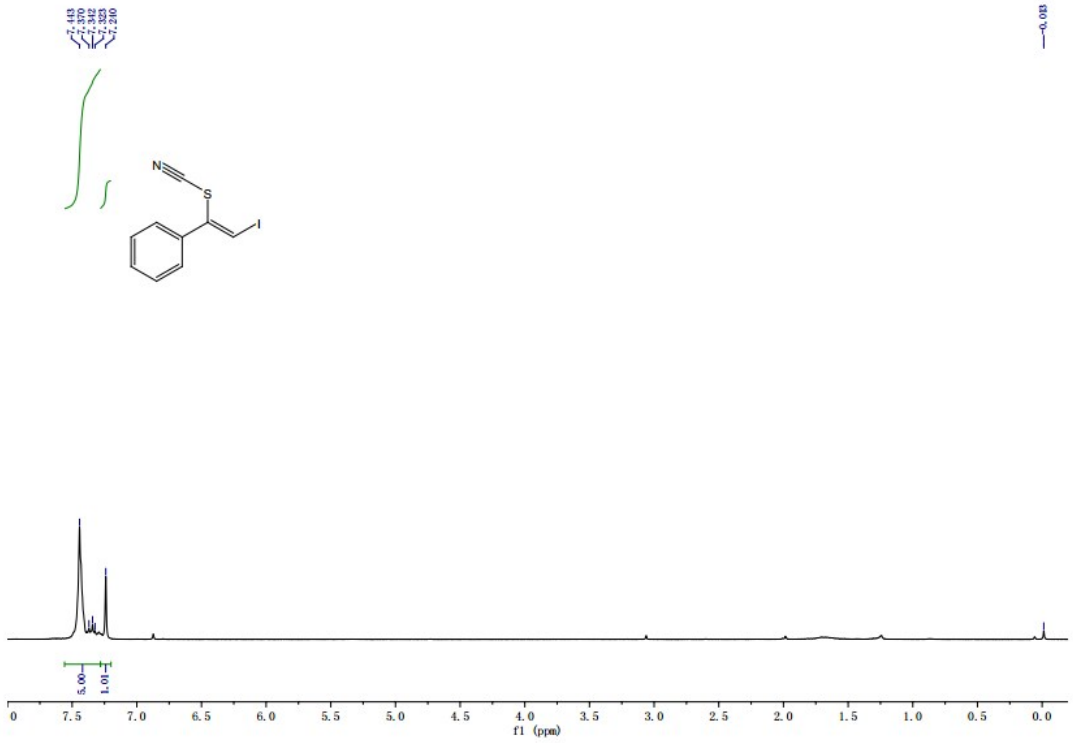
2u Colorless oil (108.5 mg, 95%, Z/E=25:1). ^{1}H NMR (400 MHz, $CDCl_3$) δ: 2.69-2.75 (m, 4H), 1.54-1.67 (m, 4H), 0.87-0.99 (m, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 125.05, 112.63, 109.76, 45.64, 44,44, 22.34, 20.78, 13.30, 12.74. HRMS *m/z* (ESI): Calcd for $C_9H_{14}INSNa$ ([M+Na]$^+$): 317.9784, Found 317.9788.



2v' White solid (143.8 mg, 87%). ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.45-7.47 (m, 3H), 7.30-7.32 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 139.59, 139.48, 130.17, 129.10, 128.49, 109.28, 15.24. HRMS *m/z* (ESI): Calcd for $C_6H_6INSO_2Na$ ([M+Na]$^+$): 435.8124, Found 435.8126.

[1] G. Jiang, C. Zhu, J. Li, W. Wu, and H. F. Jiang, *Adv. Synth. Catal.*, 2017, **359**, 1208–1212.

2a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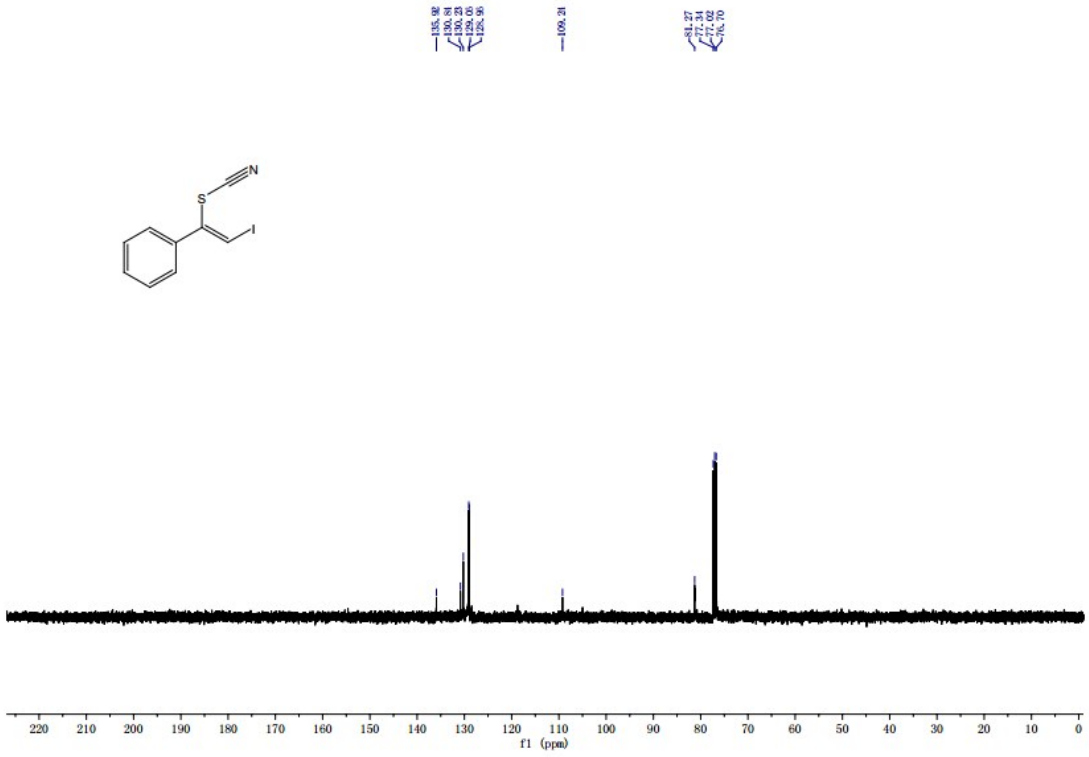
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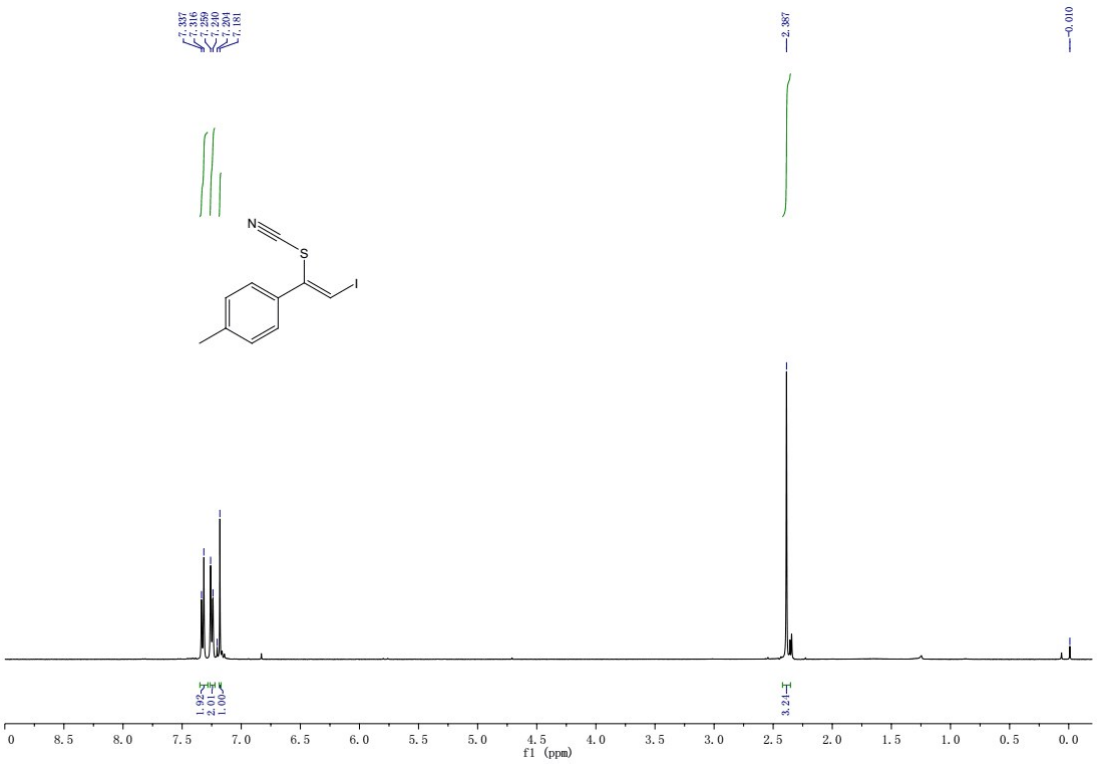
2b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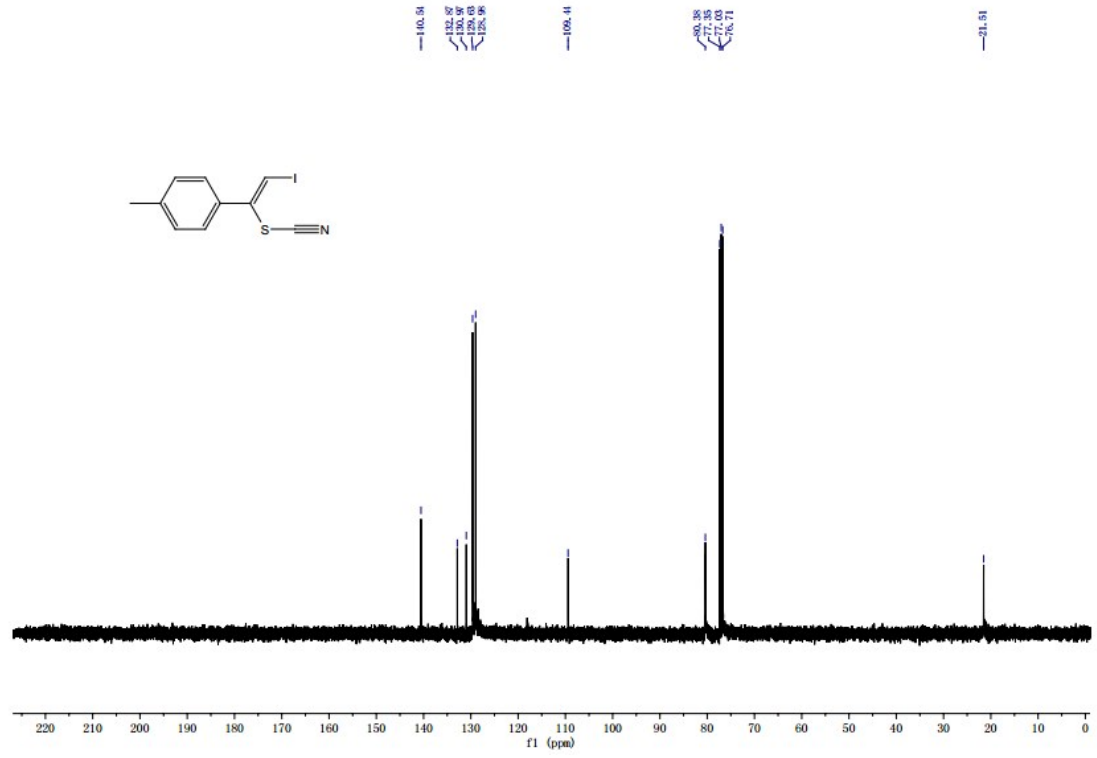
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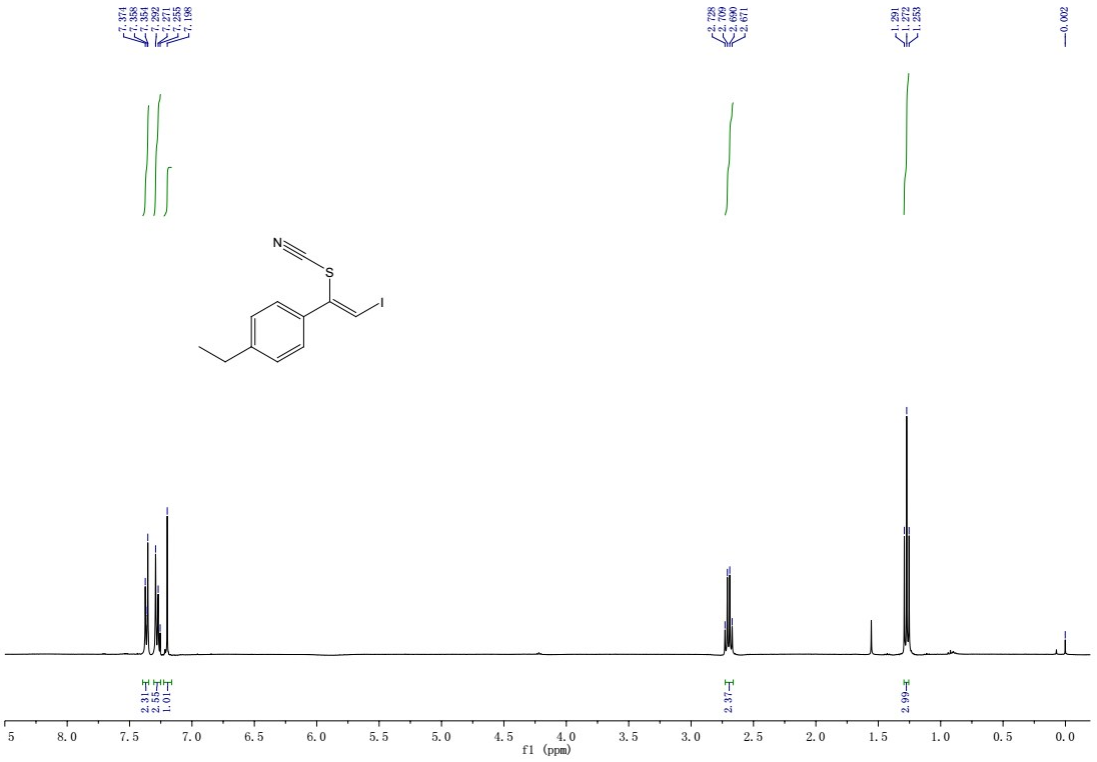
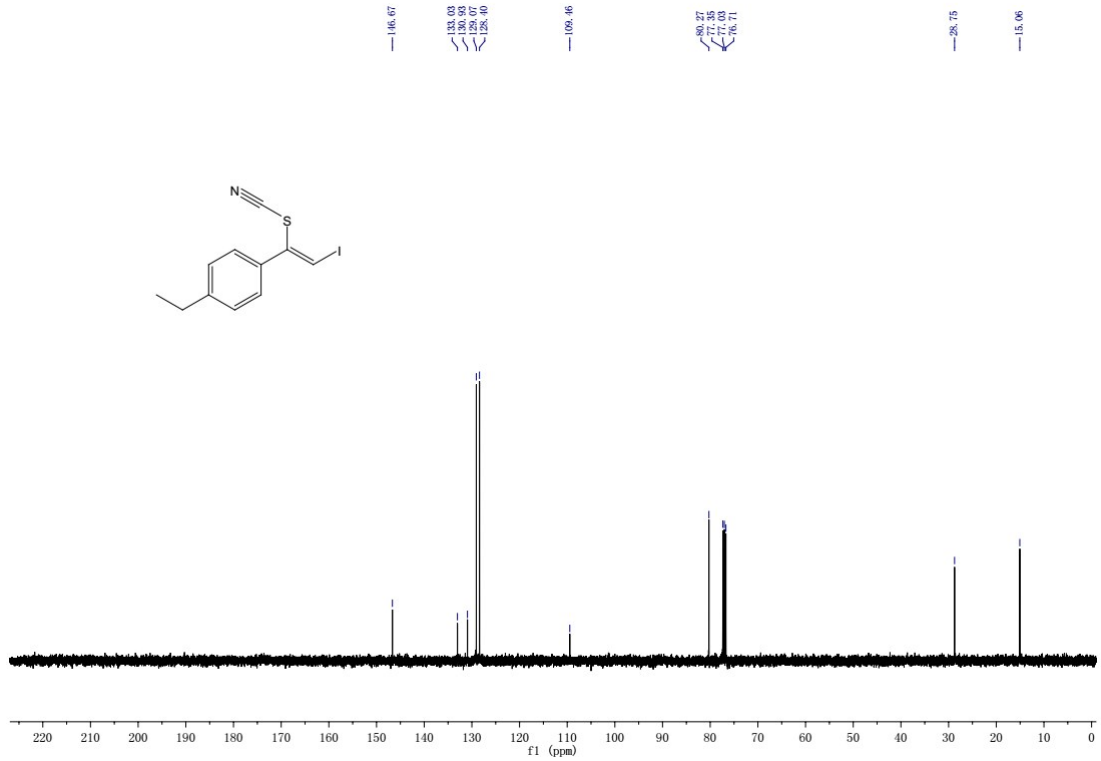
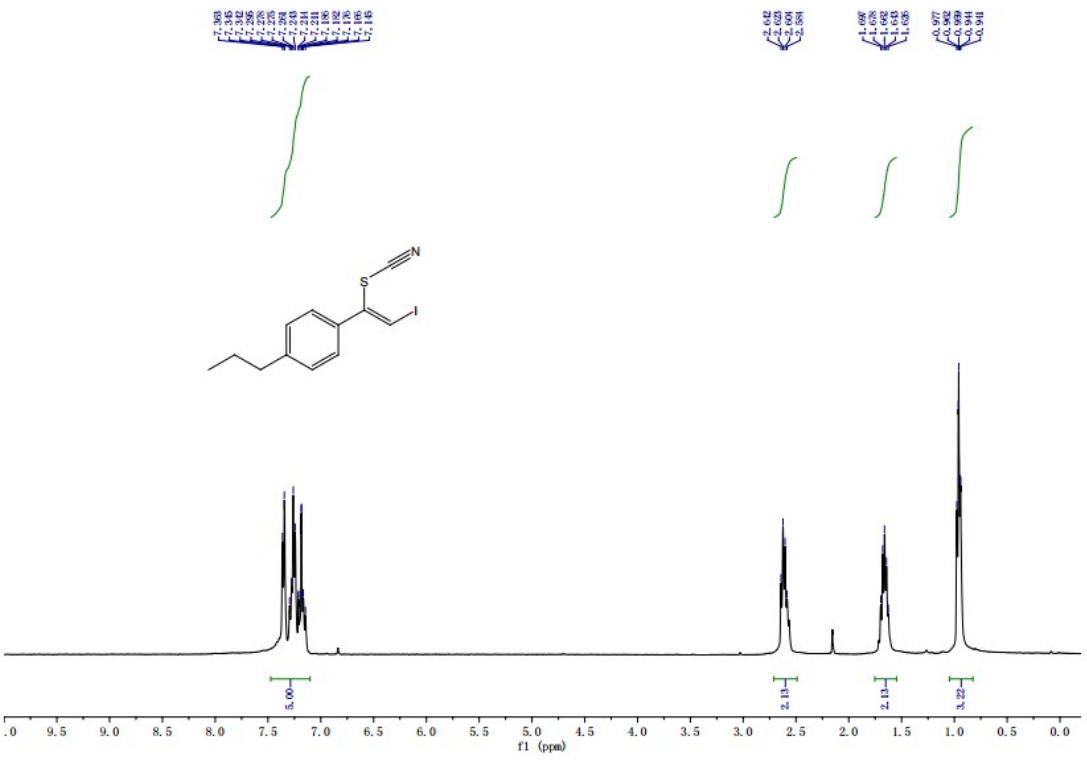
50
40
30
20
10
0
f1 (ppm)

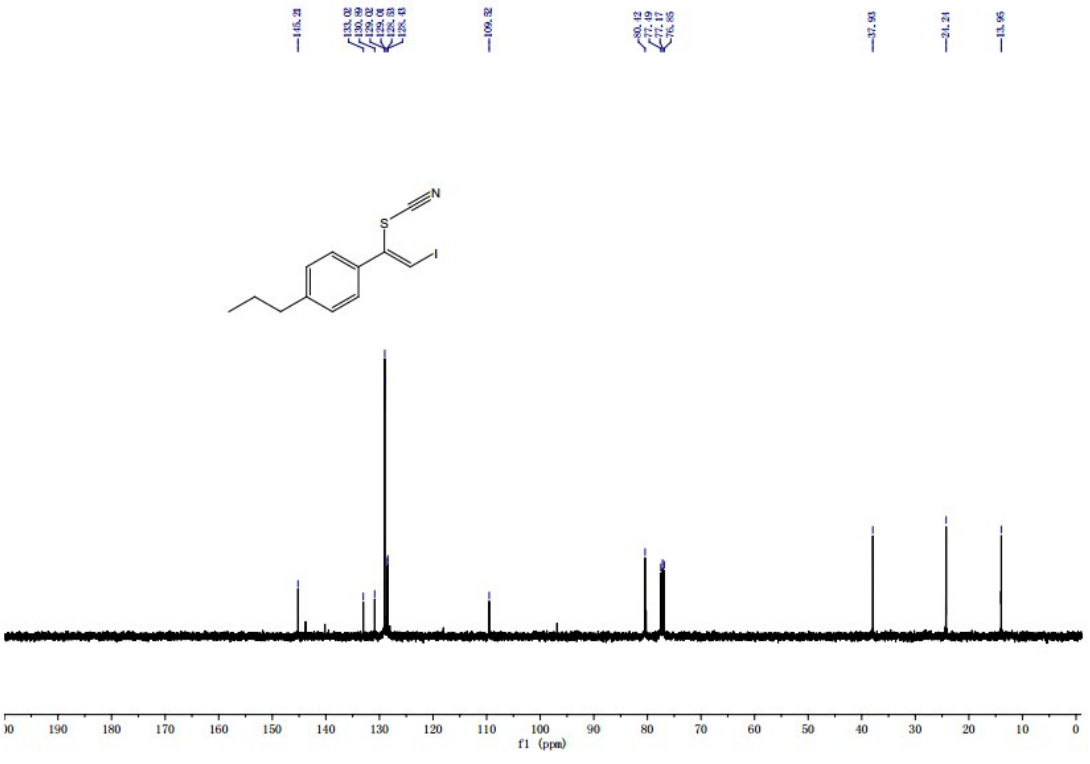
2c


7.374
7.358
7.354
7.292
7.271
7.255
7.198
2.729
2.709
2.690
2.671
1.291
1.272
1.253
0.002
N
S
I
2.31
2.55
1.01
2.37
2.99
f1 (ppm)

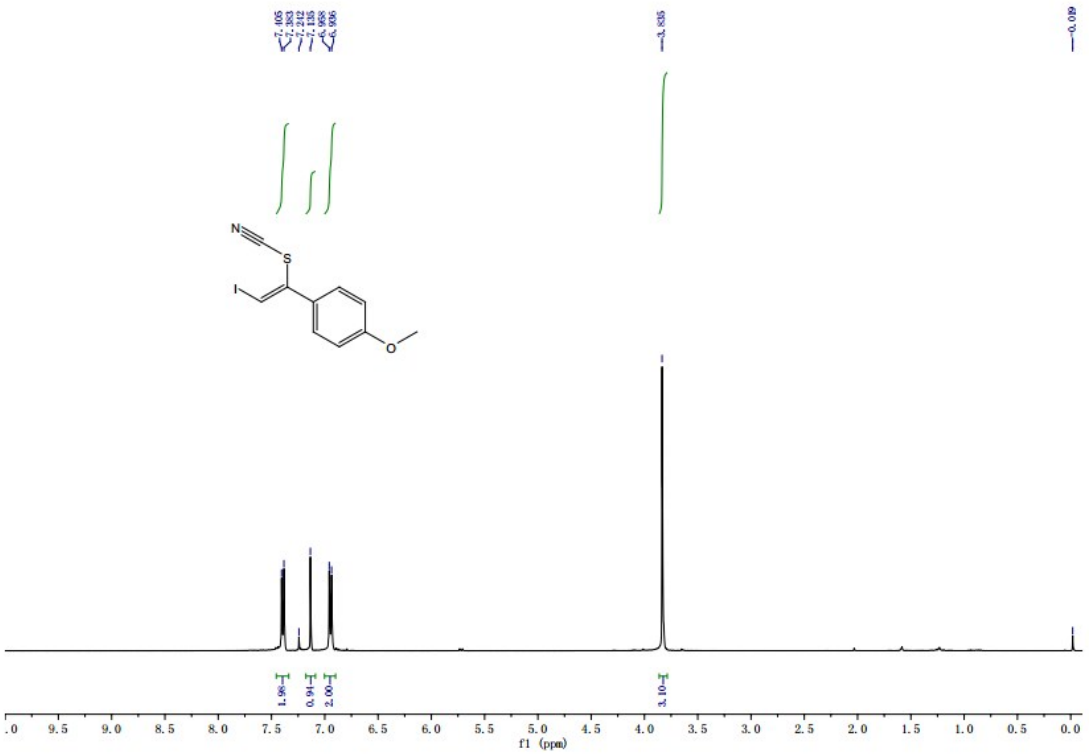

146.67
133.03
130.93
129.07
128.40
109.46
80.27
77.35
77.03
76.71
28.75
15.06
N
S
I
f1 (ppm)

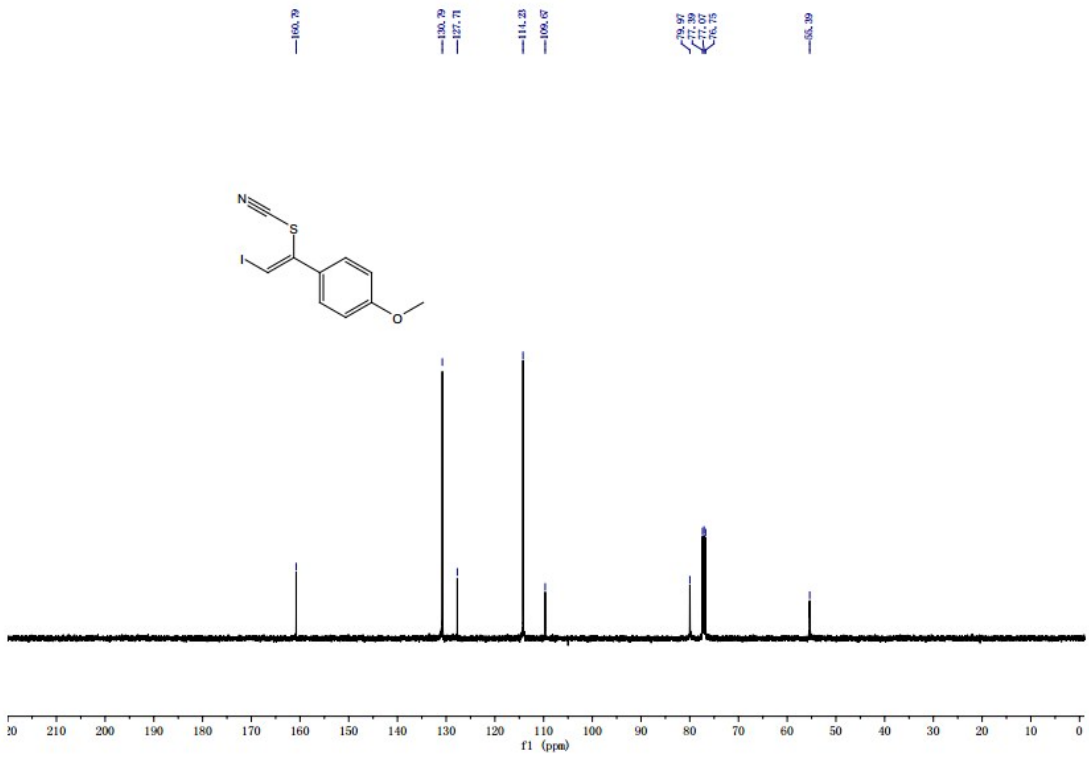
2d


7.363
7.345
7.342
7.306
7.226
7.225
7.204
7.203
7.211
7.186
7.182
7.176
7.166
7.145
2.642
2.625
2.604
2.584
1.697
1.678
1.662
1.645
1.626
0.977
0.962
0.959
0.944
0.941
N
S
I
5.00
2.13
2.13
3.22
f1 (ppm)

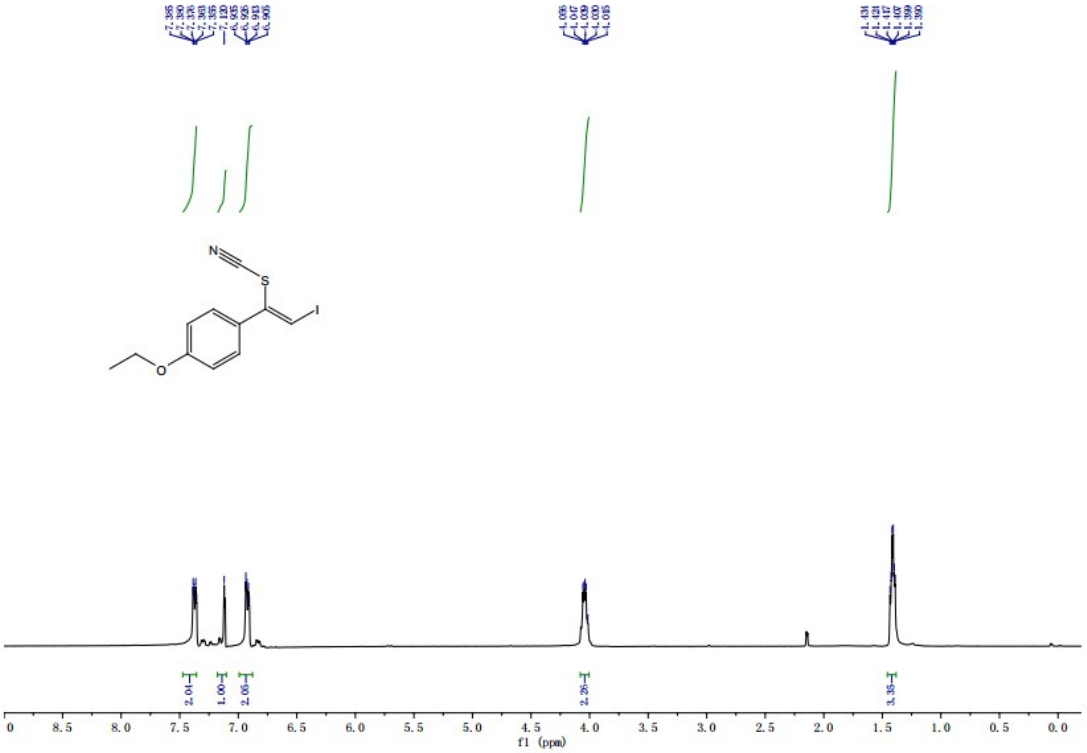

145.21
133.02
130.69
129.02
128.84
128.53
128.43
109.32
80.42
77.49
77.17
76.85
37.93
21.24
13.95
N
S
I
f1 (ppm)

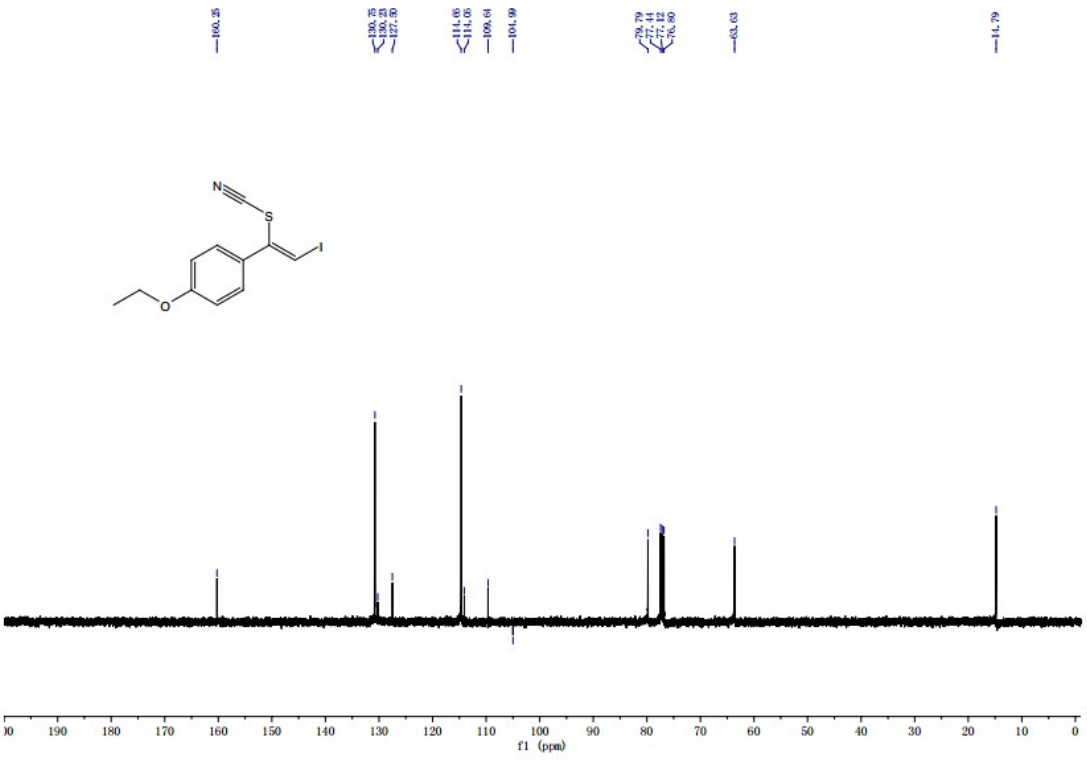
2e


7.405
7.383
7.212
7.191
6.988
6.906
3.835
0.019
N
S
I
O
1.98
0.94
2.00
3.10
f1 (ppm)

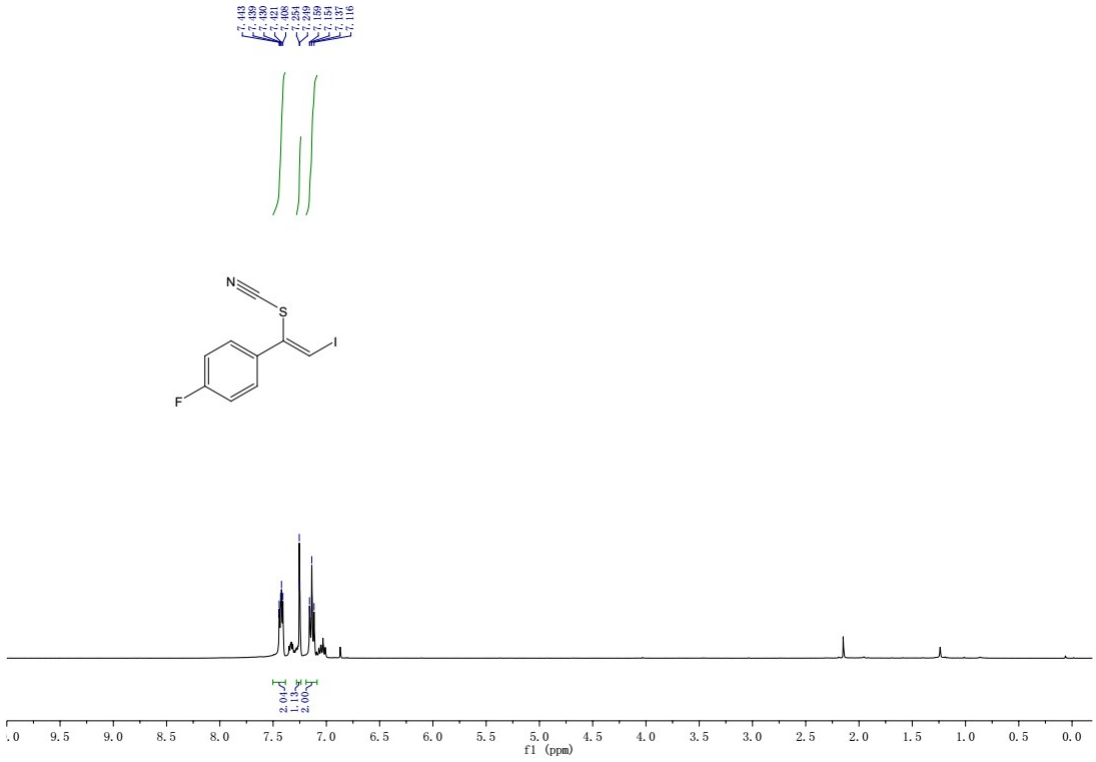

160.79
130.79
127.71
114.23
109.67
79.97
77.39
77.07
76.75
55.39
N
S
I
O
f1 (ppm)

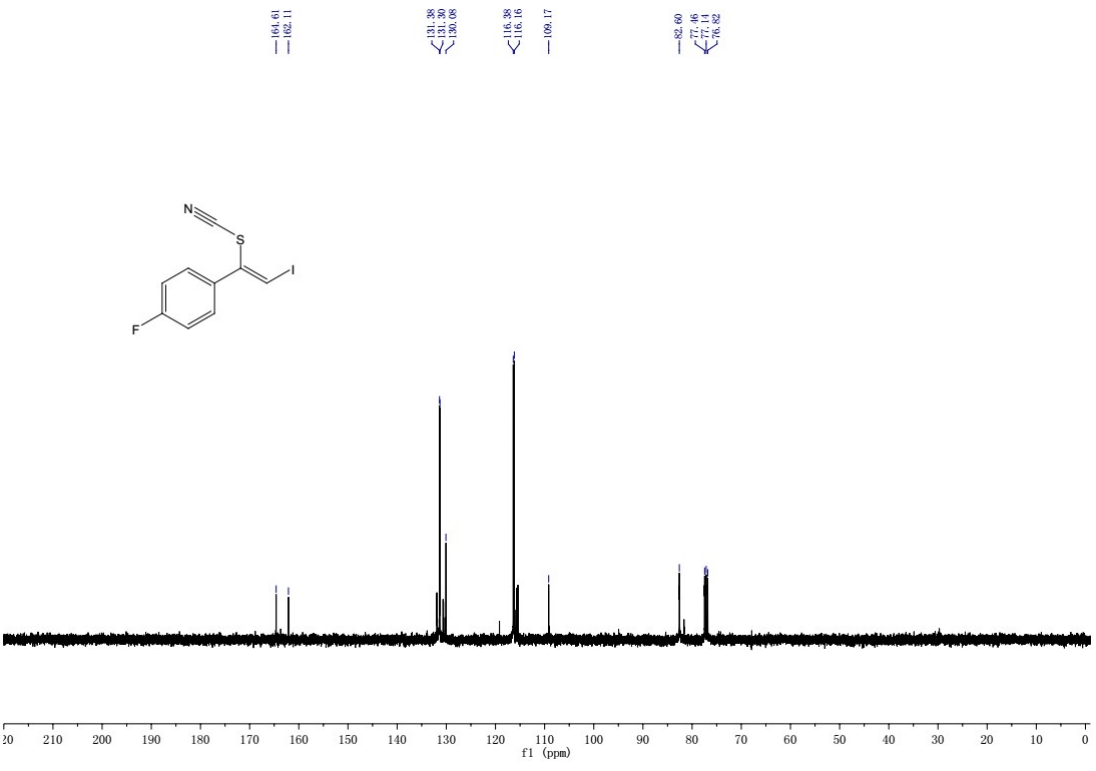
2f



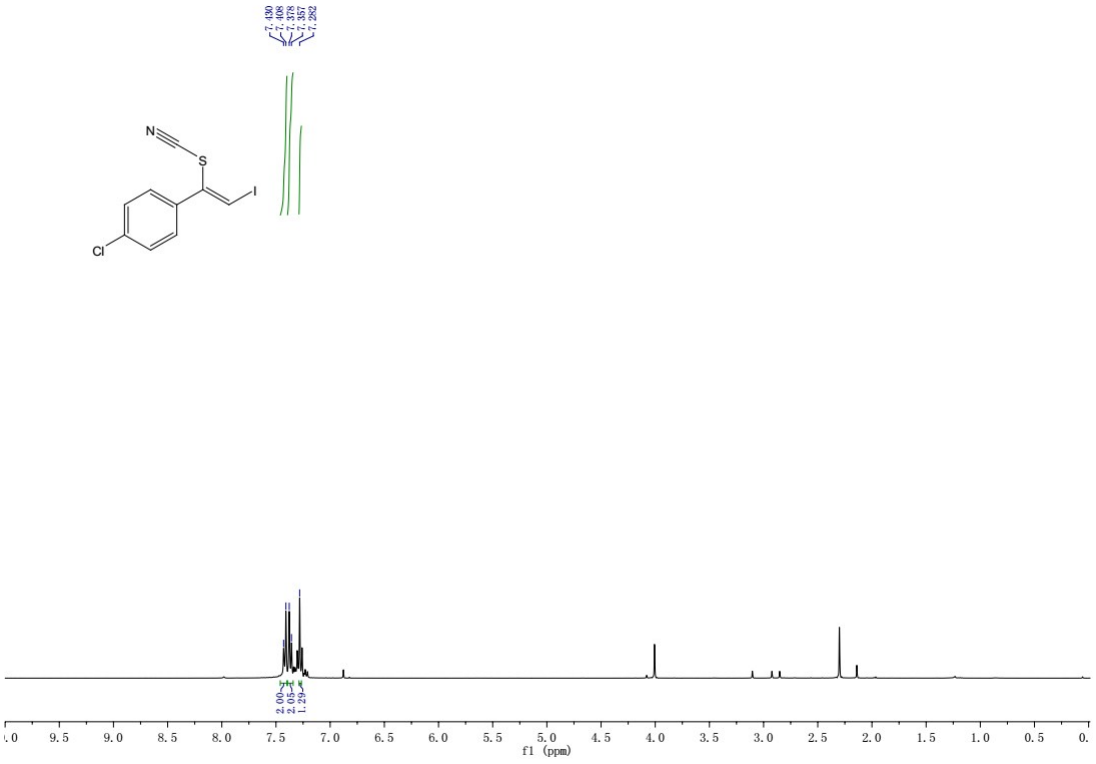


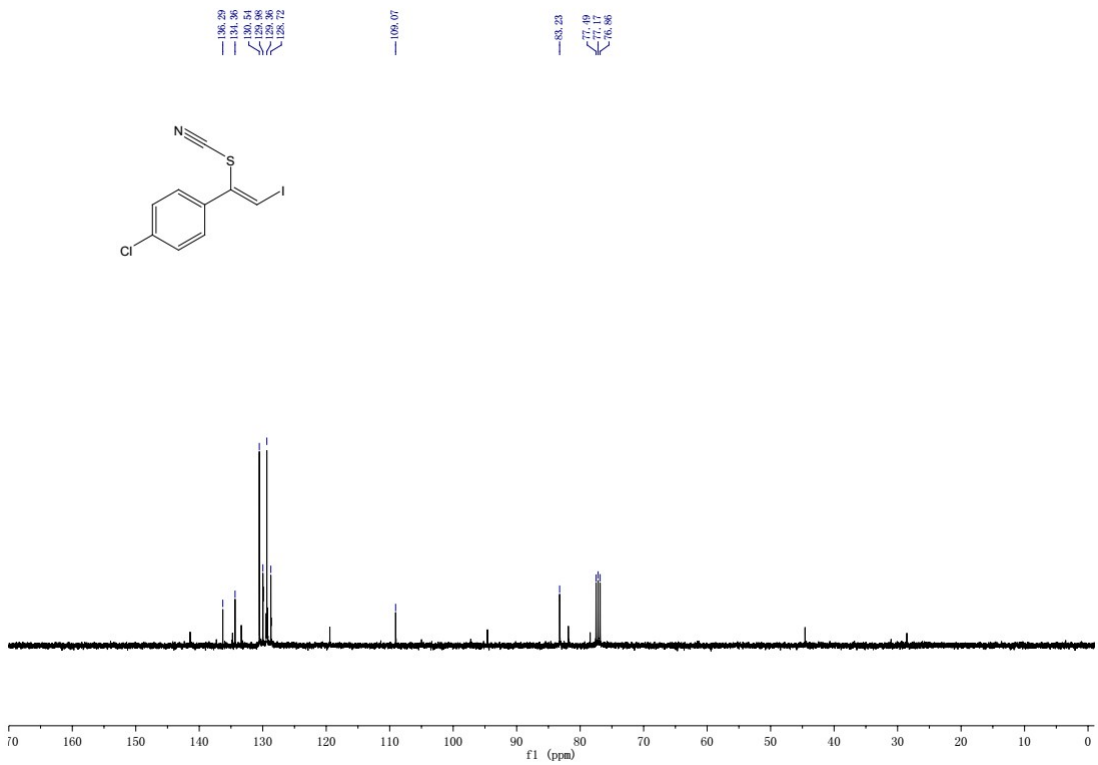
2g


7.443
7.439
7.430
7.427
7.411
7.408
7.254
7.249
7.169
7.154
7.137
7.116
N
S
I
F
2.01
1.13
2.00
f1 (ppm)

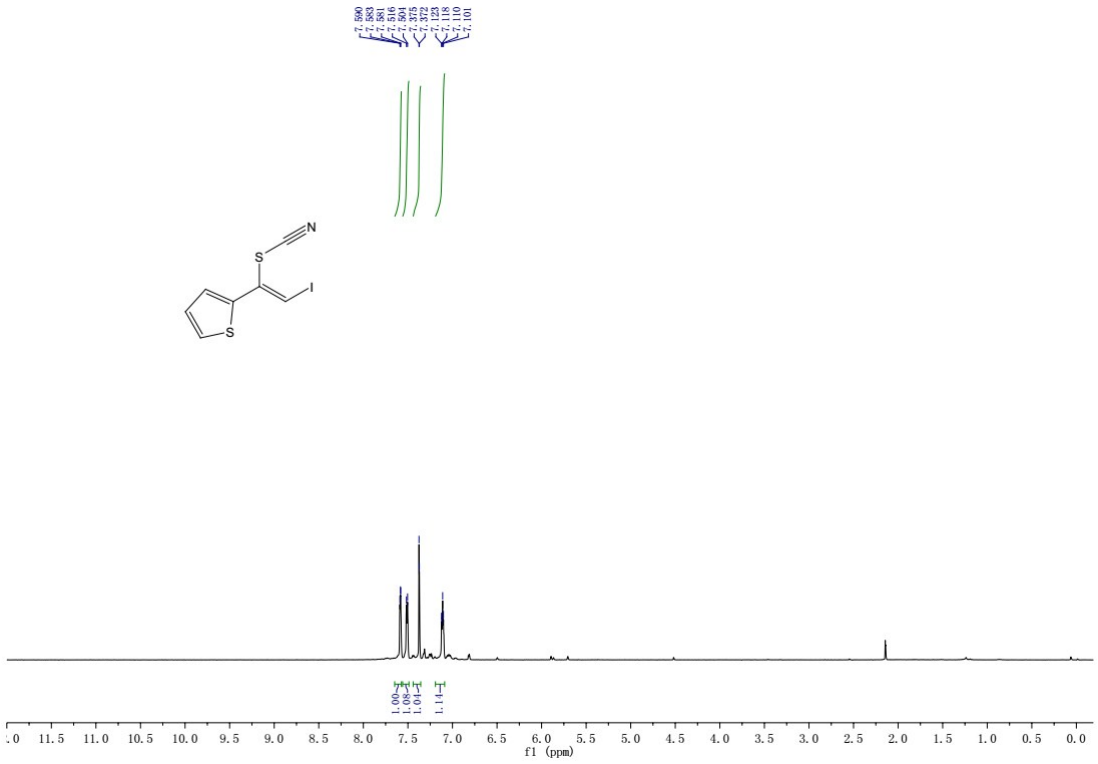

164.61
162.11
131.38
131.30
130.08
116.38
116.16
109.17
82.69
77.46
77.11
76.82
N
S
I
F
f1 (ppm)

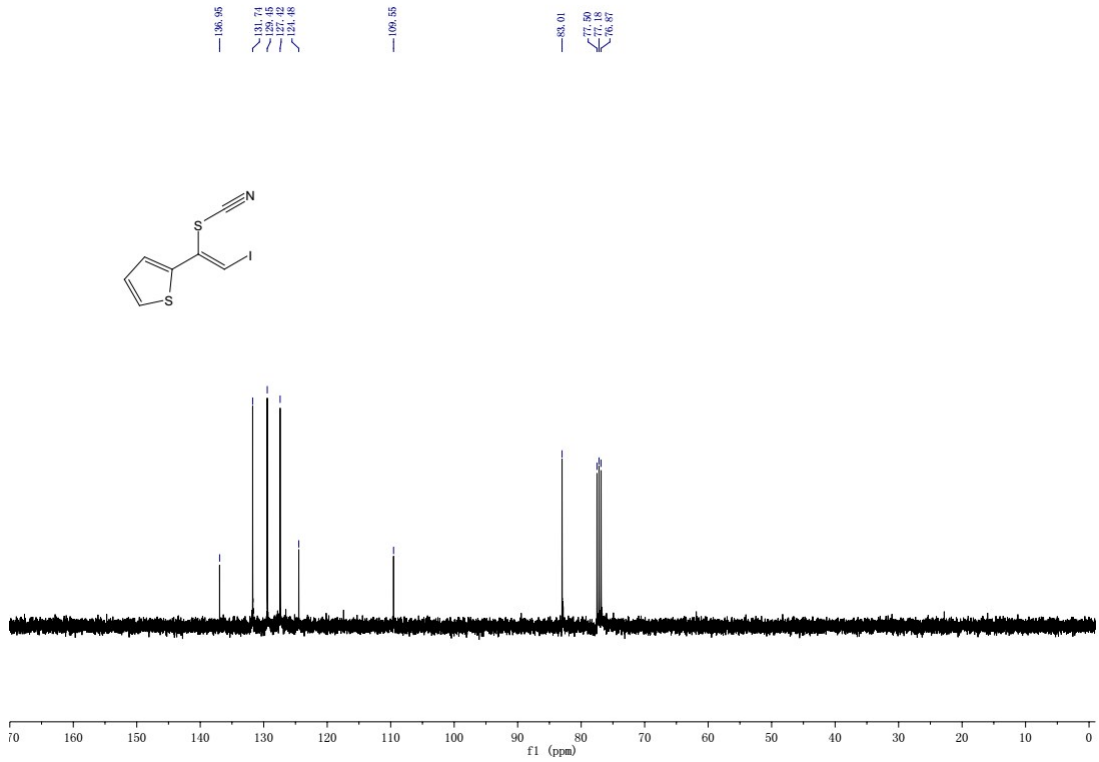
2h


7.430
7.408
7.378
7.357
7.282
N
S
I
Cl
2.00
2.03
1.29
f1 (ppm)

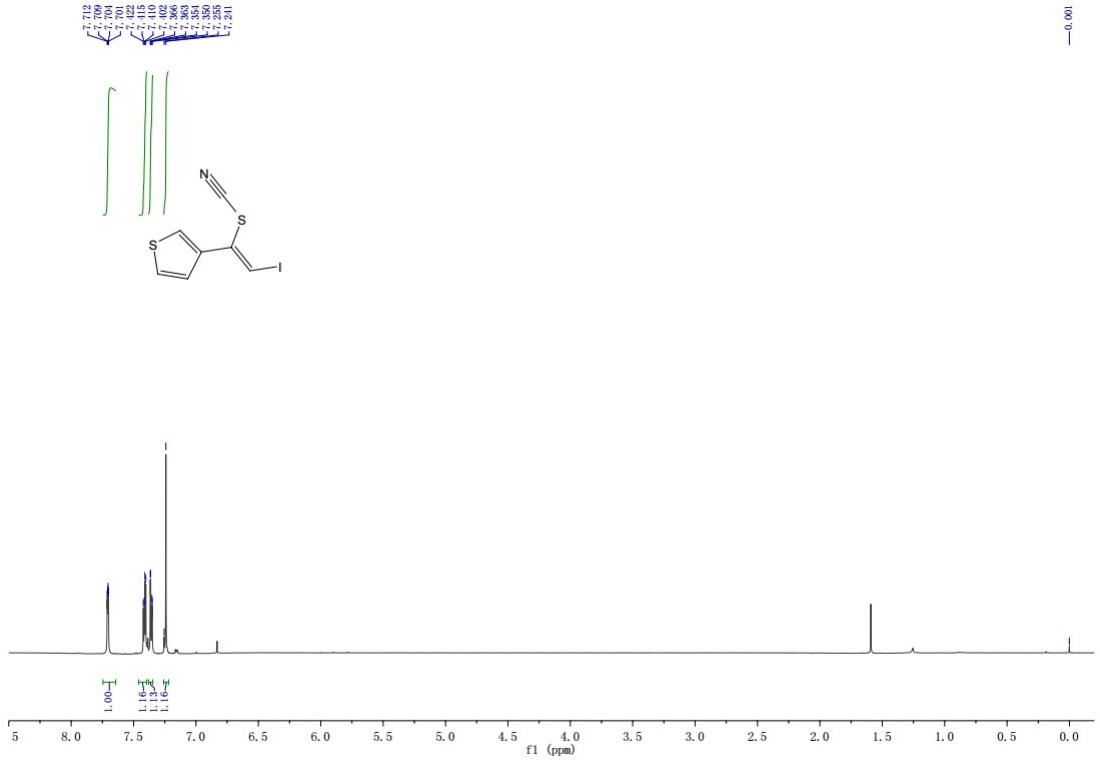

136.29
134.36
130.54
129.98
129.36
128.72
109.07
83.23
77.49
77.17
76.86
N
S
I
Cl
f1 (ppm)

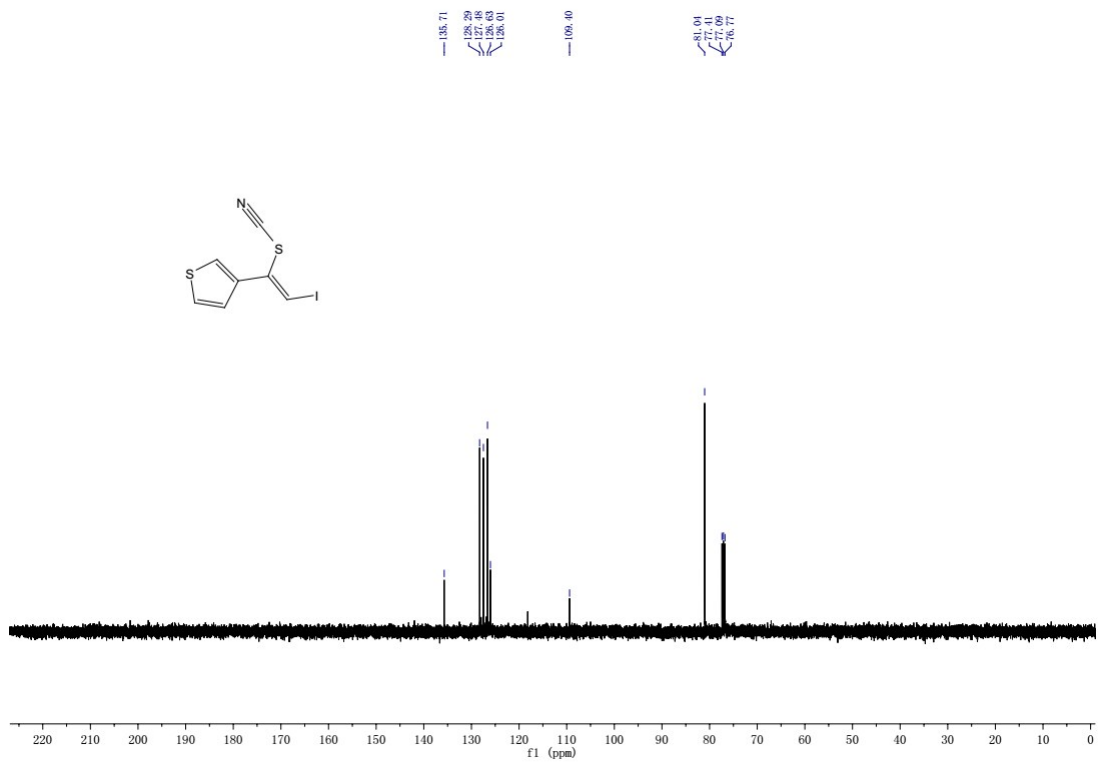
2i


7.590
7.583
7.581
7.516
7.504
7.375
7.372
7.123
7.118
7.110
7.101
N
S
I
S
1.00
1.08
1.04
1.14
f1 (ppm)

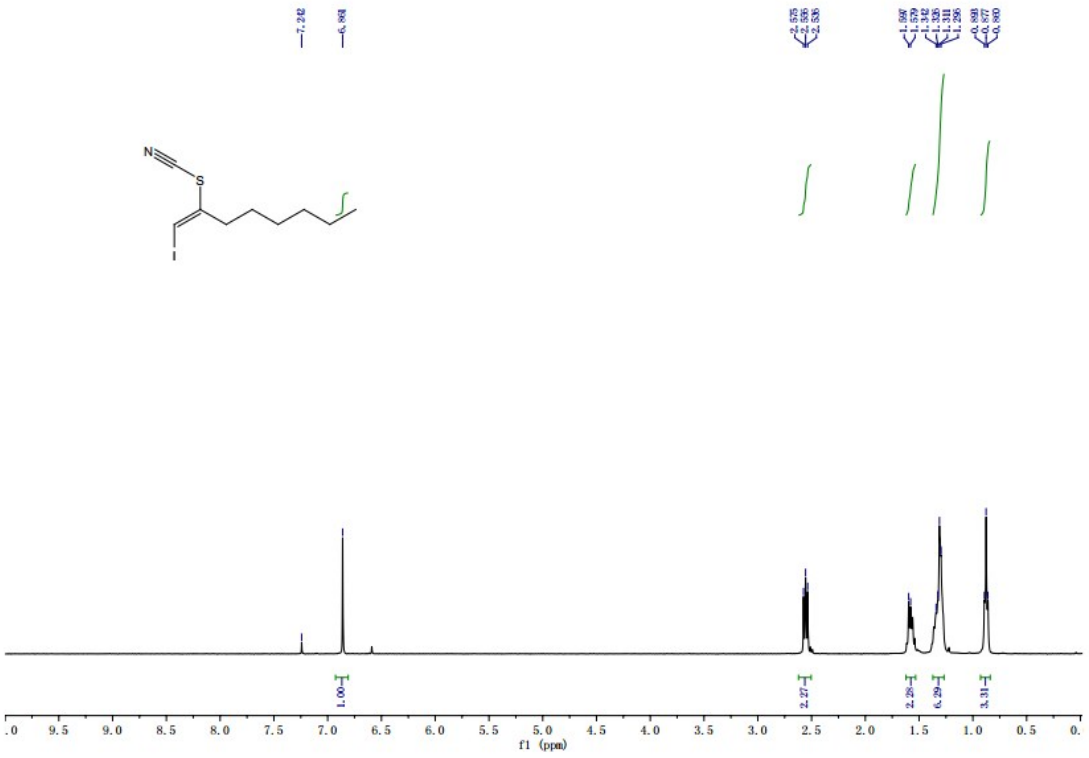

136.95
131.74
129.45
127.42
124.46
109.55
83.01
77.89
77.18
76.87
N
S
I
S
f1 (ppm)

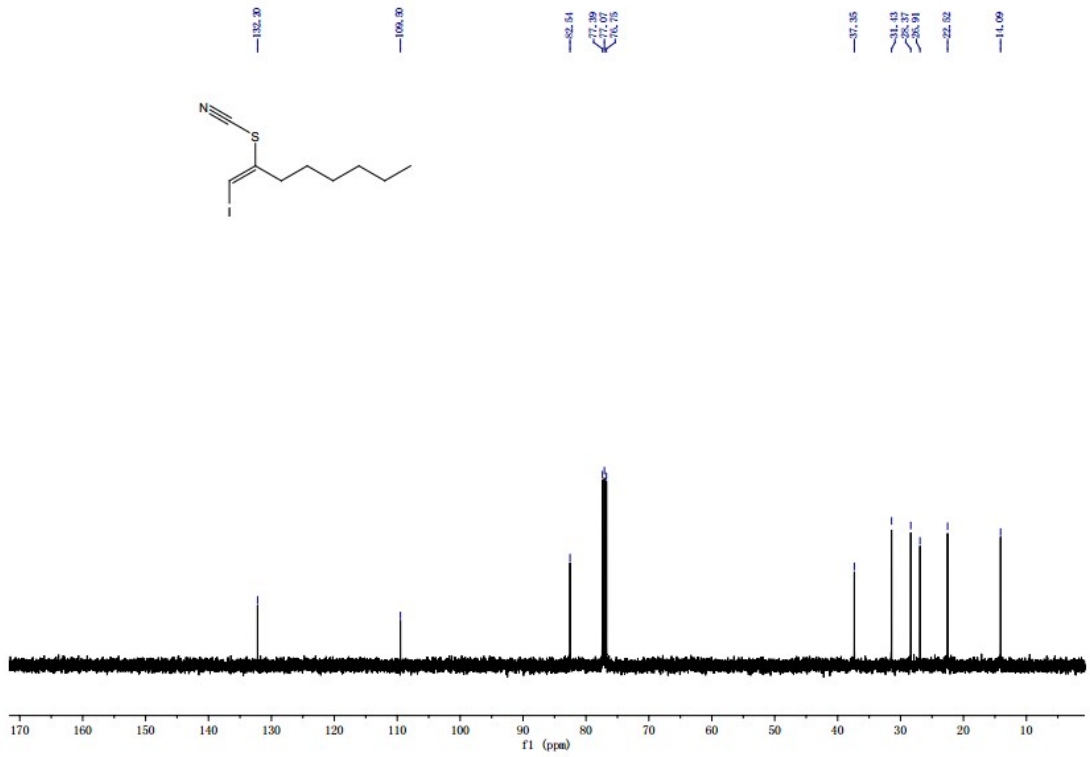
2j


7.712
7.709
7.704
7.701
7.422
7.415
7.410
7.402
7.366
7.363
7.354
7.350
7.255
7.241
0.001
N
S
S
I
1.00
1.16
1.14
1.16
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
f1 (ppm)

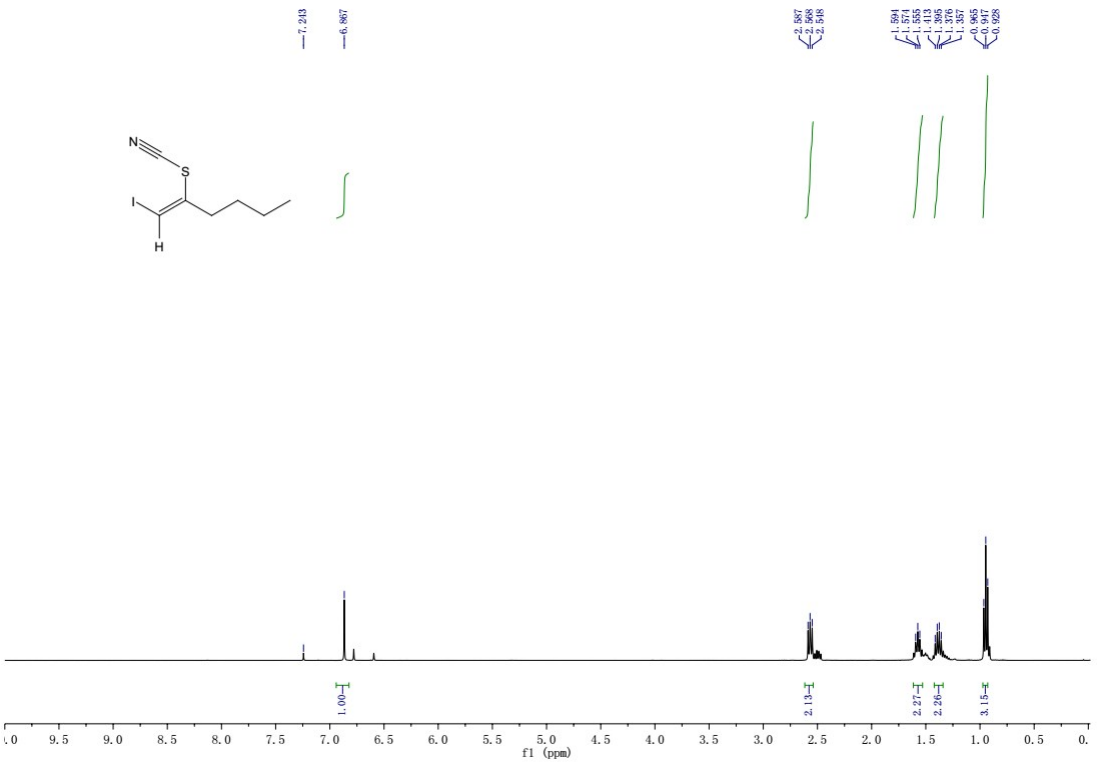

135.71
128.29
127.48
126.63
126.01
109.40
81.04
77.41
77.09
76.77
N
S
S
I
220
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

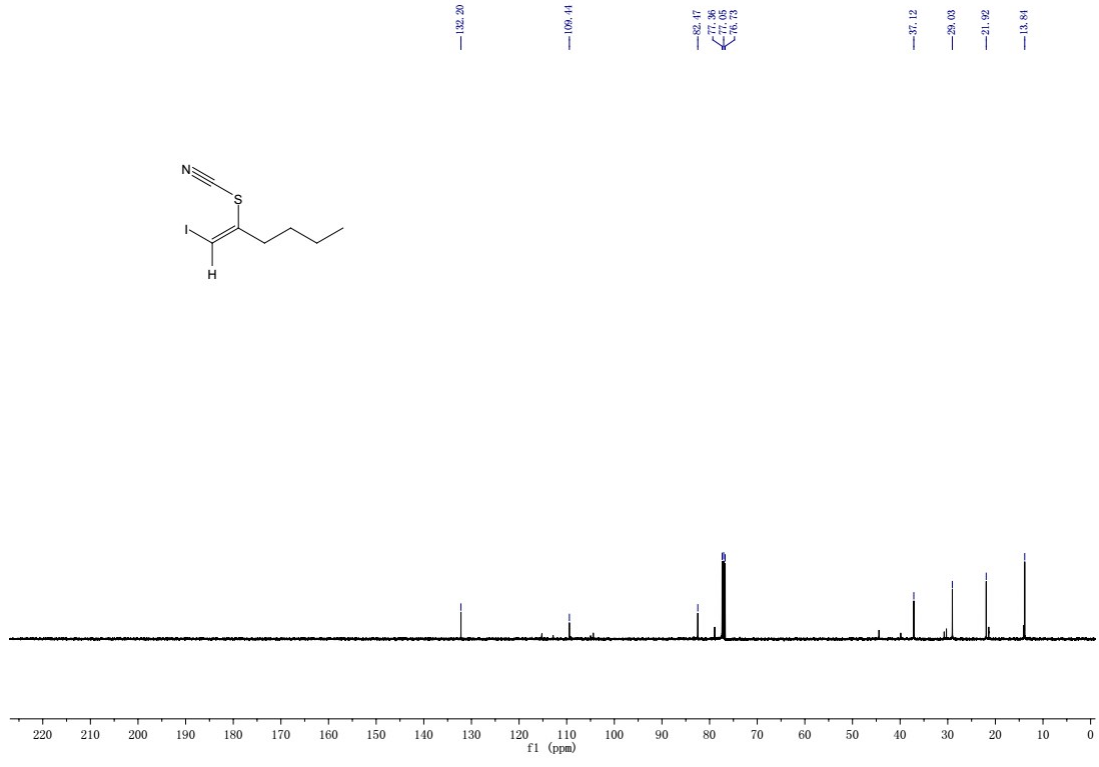
2k


7.242
6.884
2.575
2.555
2.535
1.599
1.579
1.342
1.335
1.311
1.296
0.898
0.877
0.860
N
S
I
1.00
2.27
2.28
6.29
3.31
f1 (ppm)

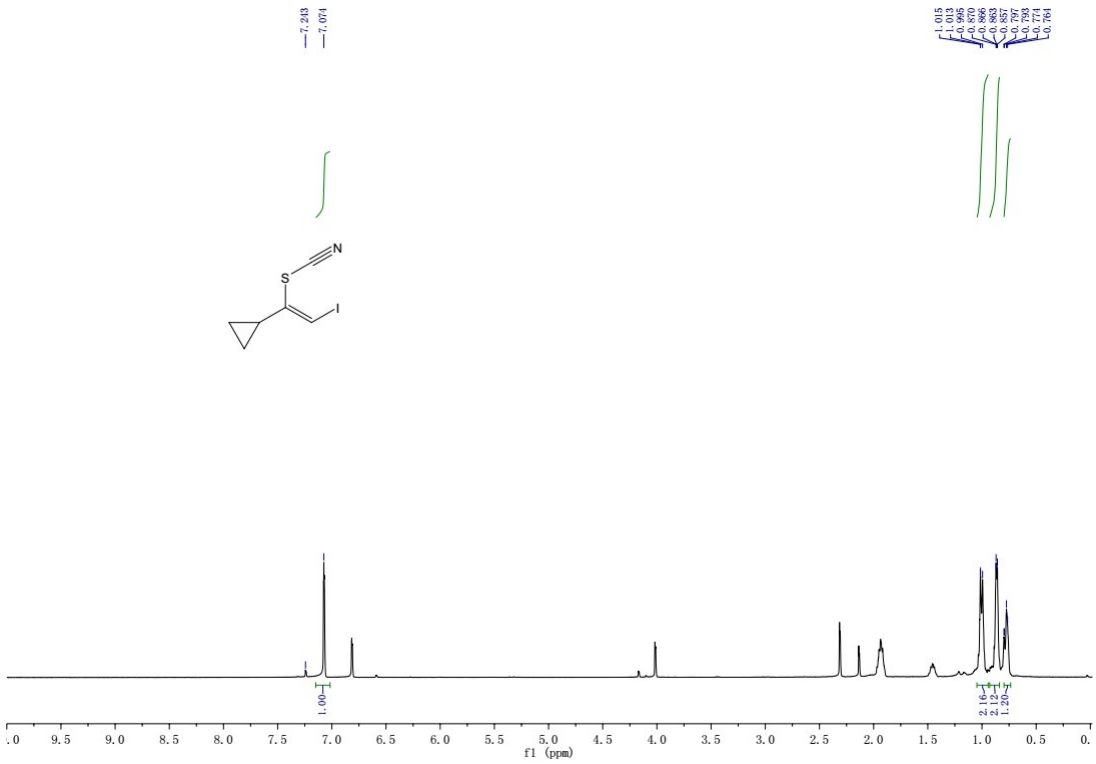

132.30
109.80
82.54
77.39
77.07
76.75
37.35
31.43
28.37
28.91
22.52
14.09
N
S
I
f1 (ppm)

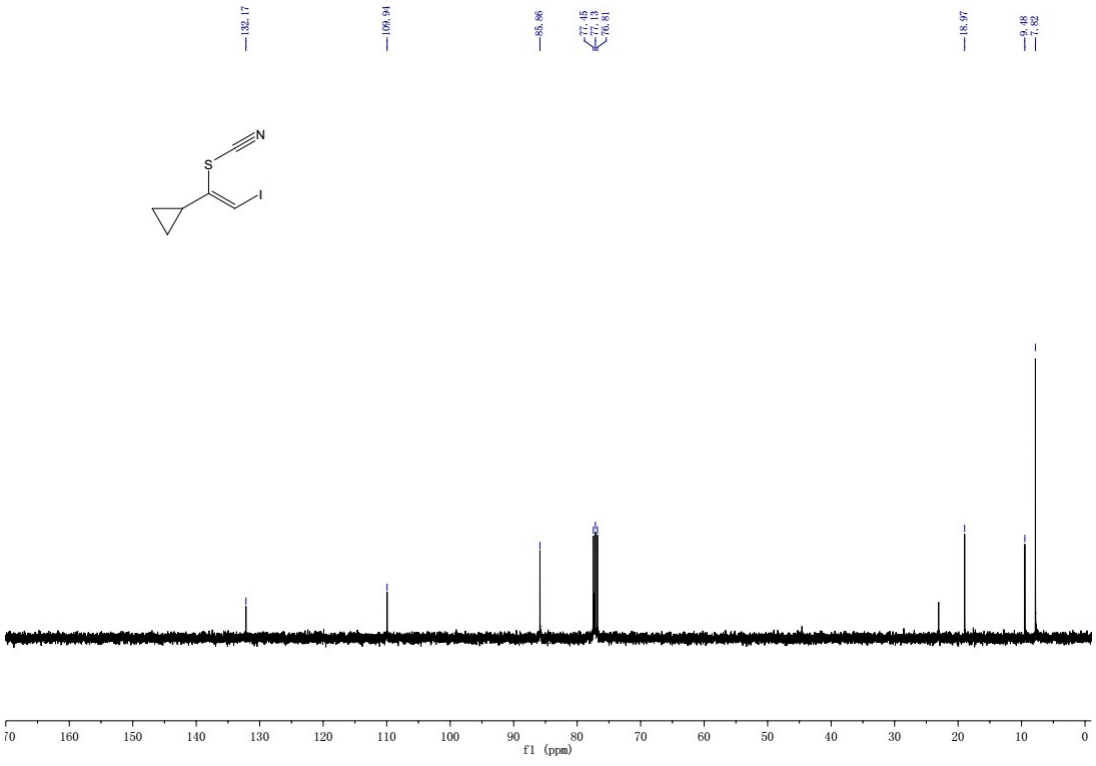
2l


7.243
6.867
2.567
2.558
2.548
1.594
1.571
1.555
1.413
1.395
1.376
1.357
0.965
0.947
0.928
1.00
2.13
2.27
2.26
3.15
f1 (ppm)

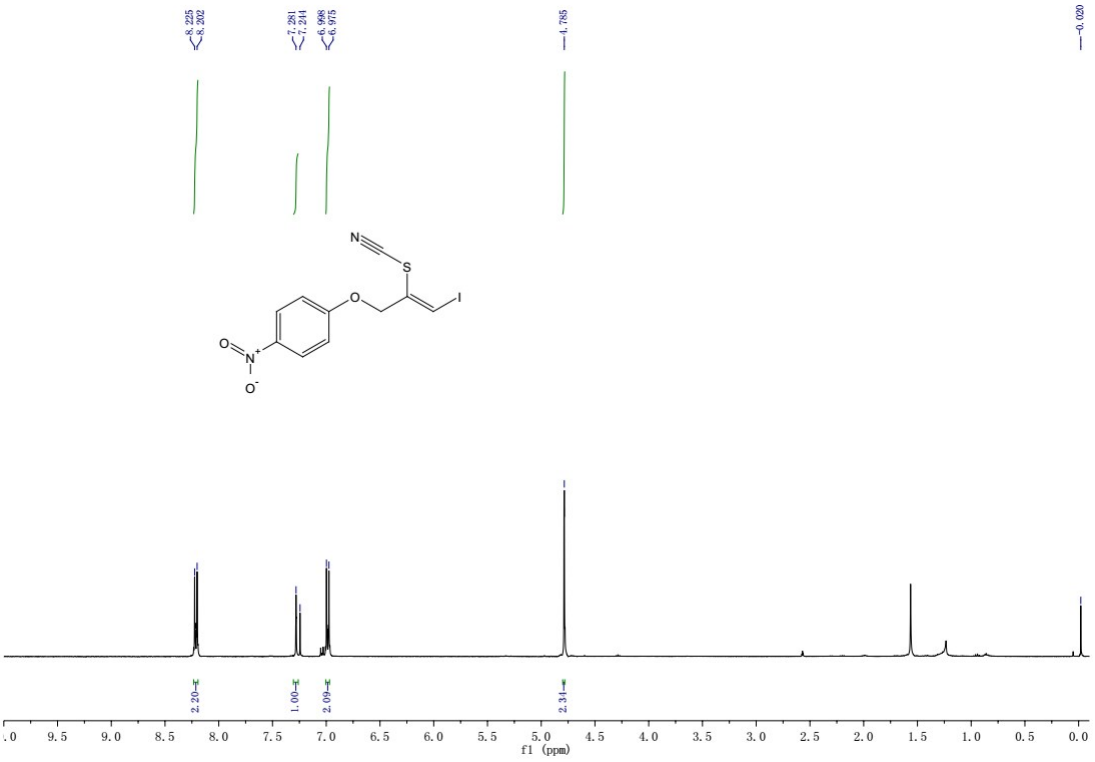

132.20
109.44
82.47
77.36
77.05
76.73
37.12
29.03
21.92
13.84
f1 (ppm)

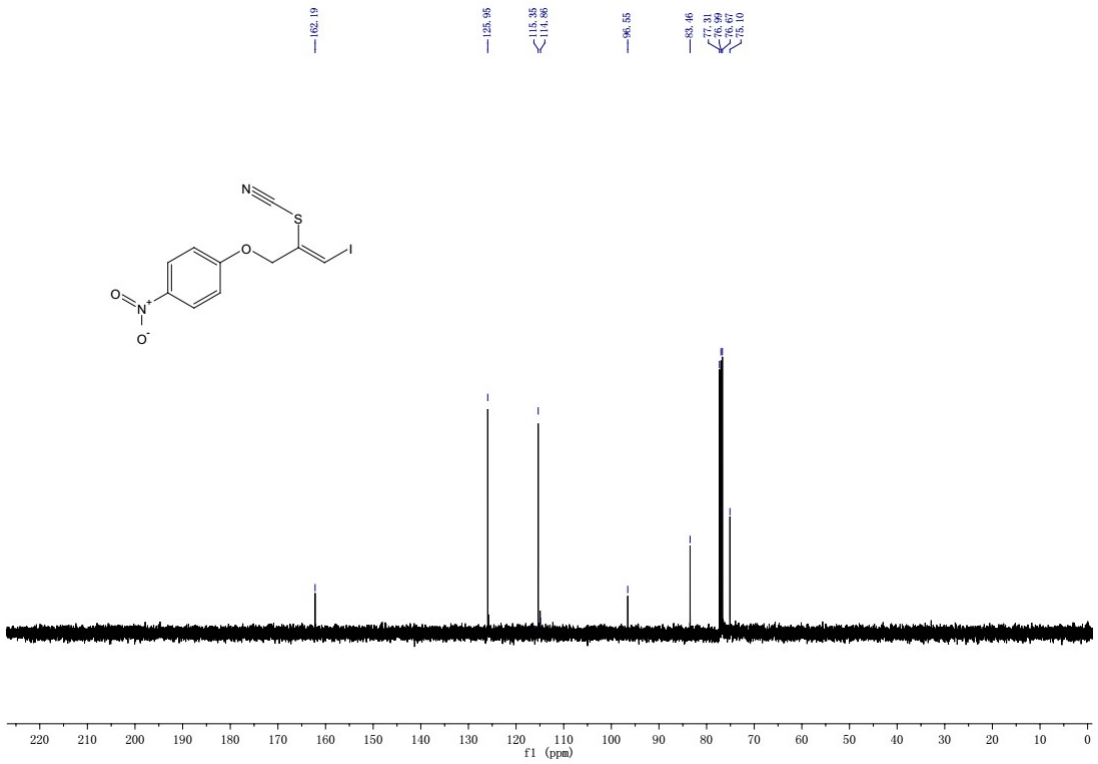
2m


7.213
7.074
1.015
1.013
0.895
0.870
0.866
0.863
0.857
0.797
0.793
0.774
0.761
N
S
I
1.00
2.16
2.12
1.20
f1 (ppm)

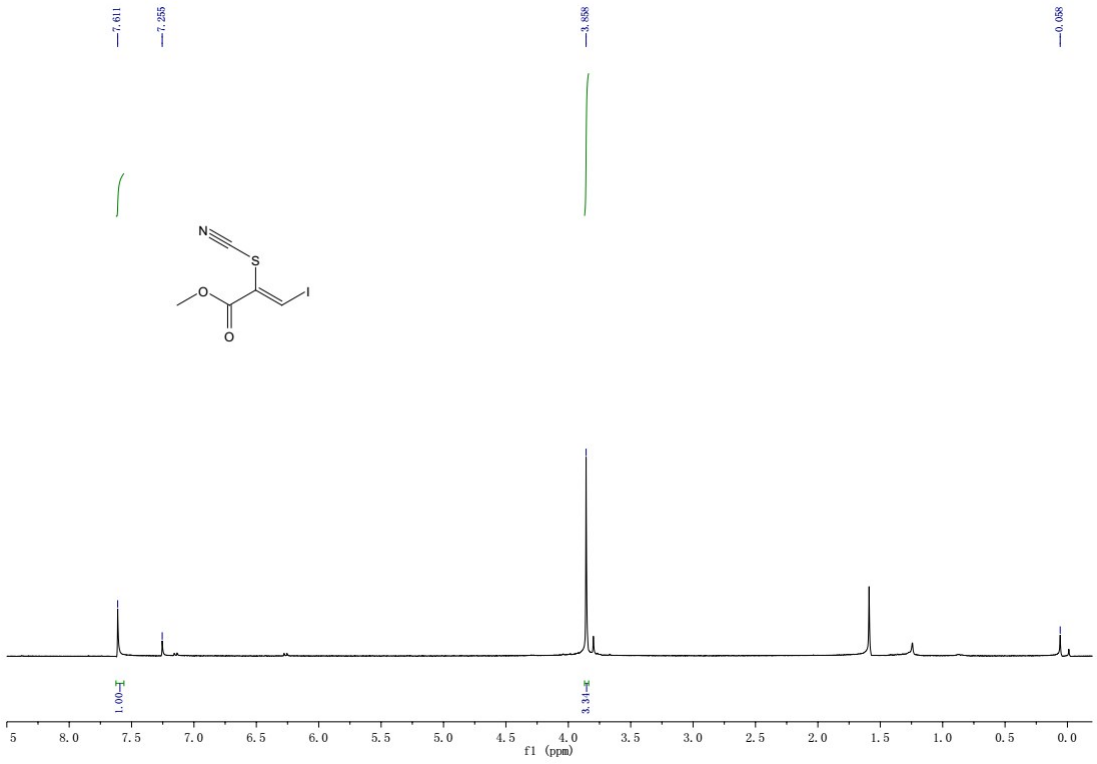

132.17
109.94
85.86
77.45
77.13
76.81
18.97
9.48
7.82
N
S
I
f1 (ppm)

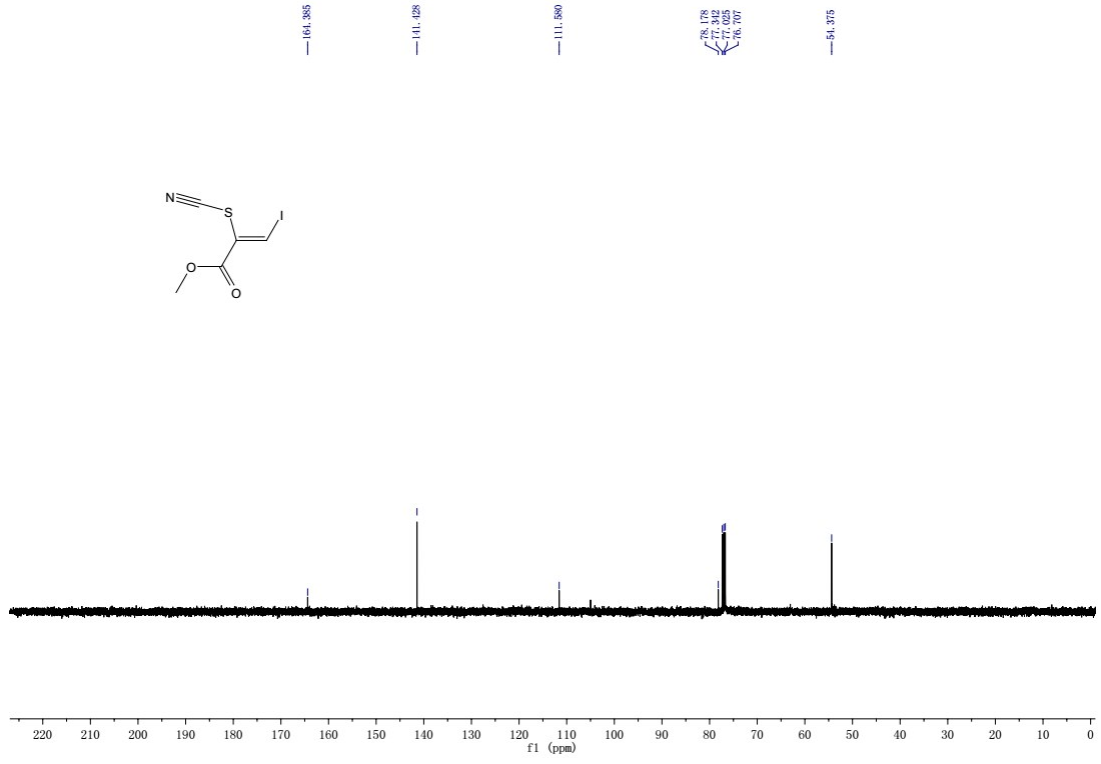
2n


8.225
8.202
7.281
7.244
6.998
6.975
4.785
-0.020
2.20
1.00
2.09
2.34
f1 (ppm)

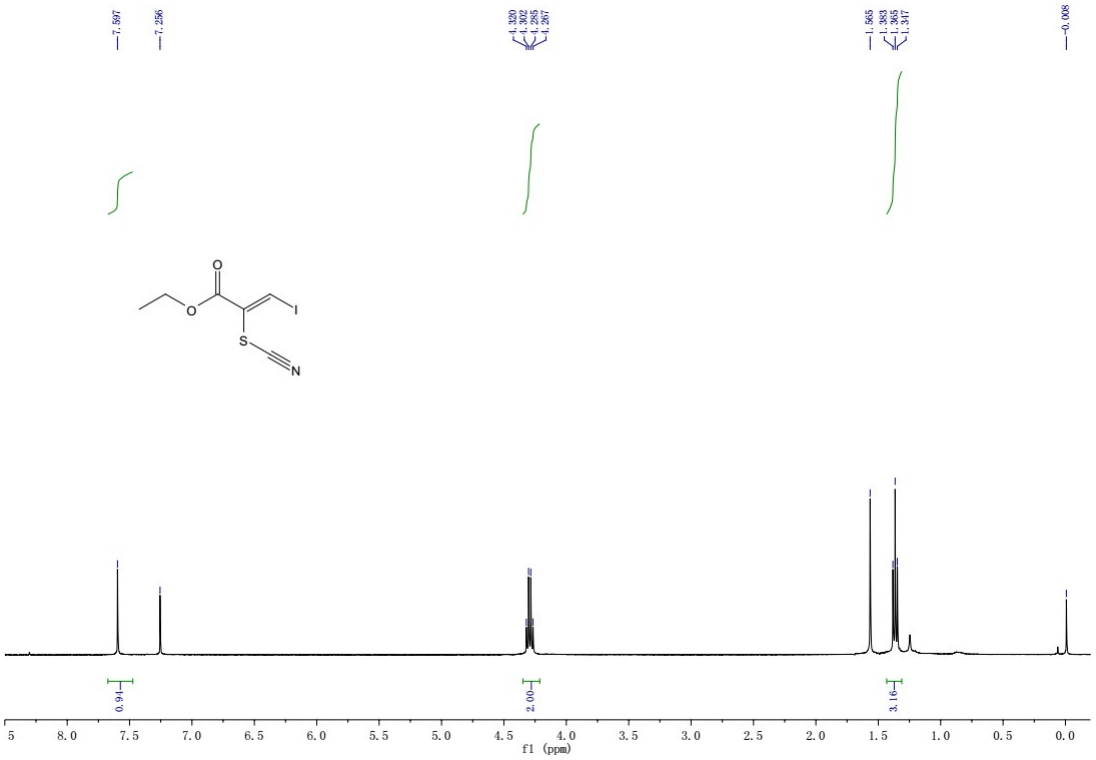

162.19
129.95
118.35
114.86
96.55
83.46
77.31
76.99
76.67
75.10
f1 (ppm)

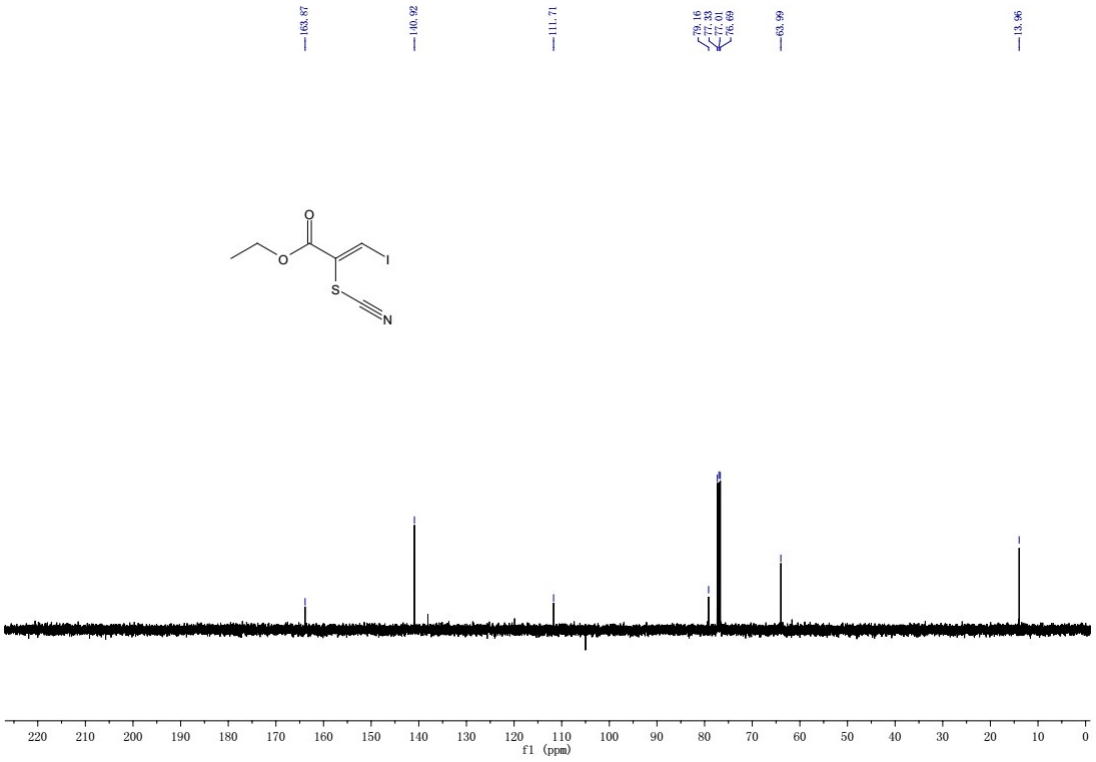
2o


7.611
7.255
3.858
0.058
N
S
O
I
O
1.00
3.34
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
f1 (ppm)

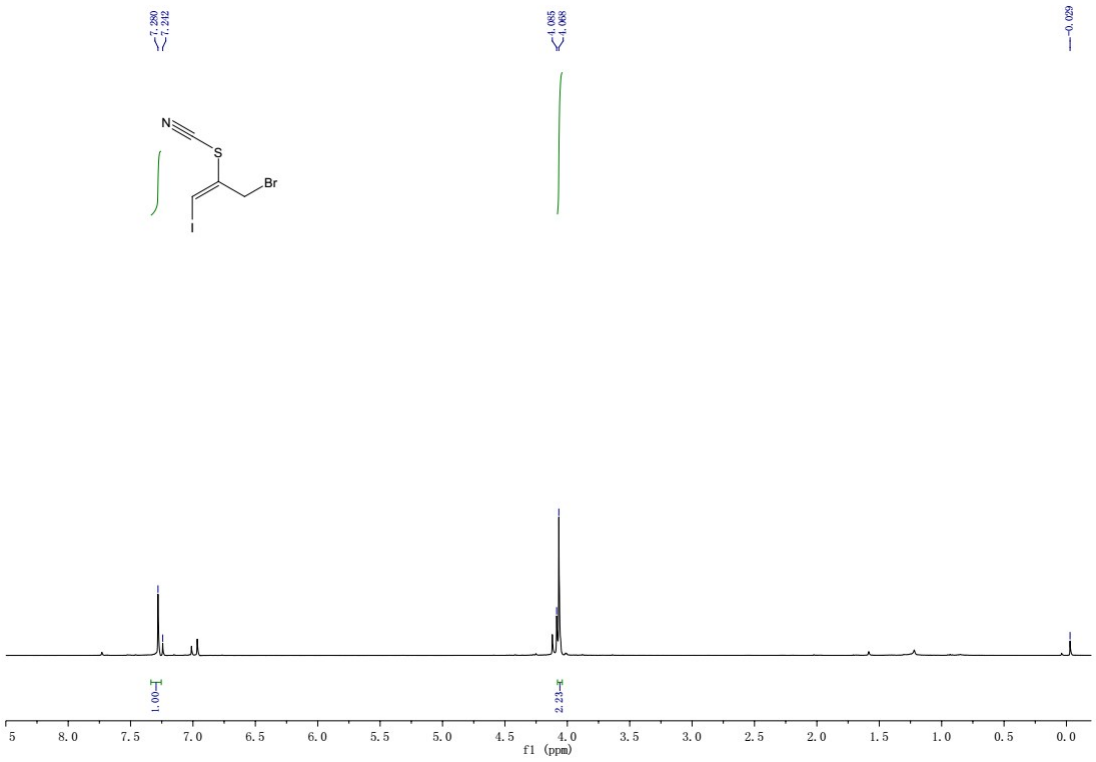

164.385
141.428
111.580
78.178
77.312
77.095
76.707
54.375
N
S
I
O
O
220
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

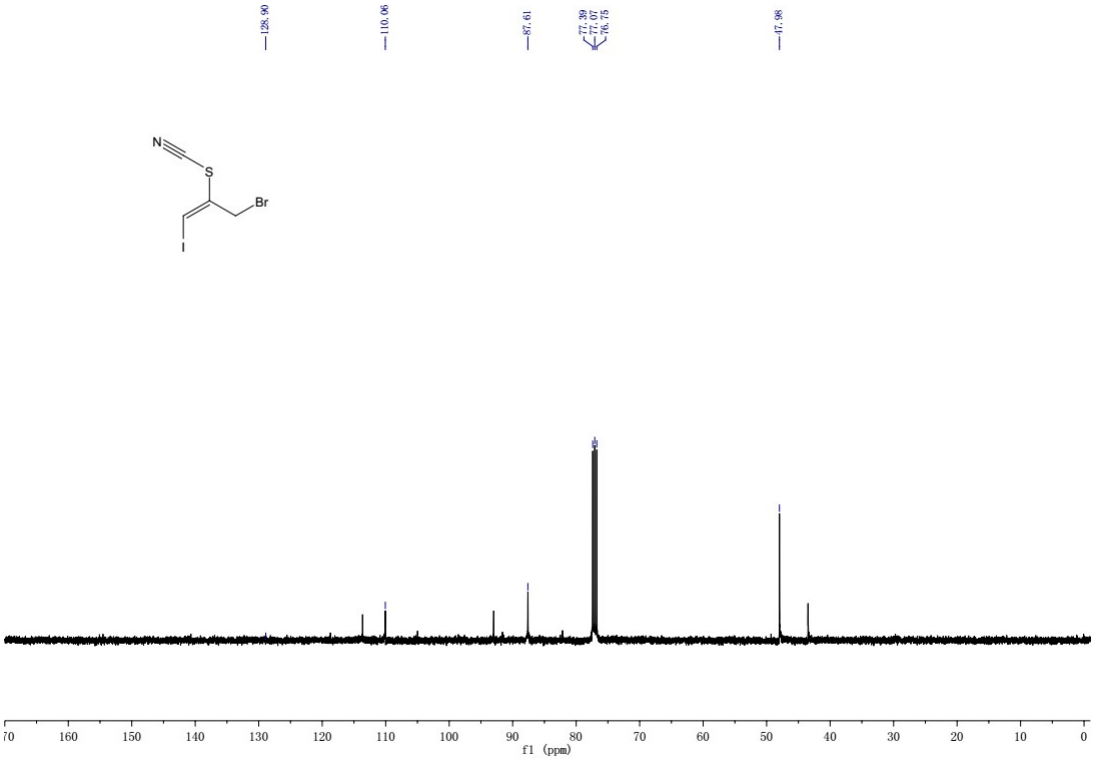
2p


7.597
7.256
4.330
4.302
4.285
4.267
1.565
1.383
1.365
1.347
0.008
O
O
I
S
N
0.94
2.00
3.16
f1 (ppm)

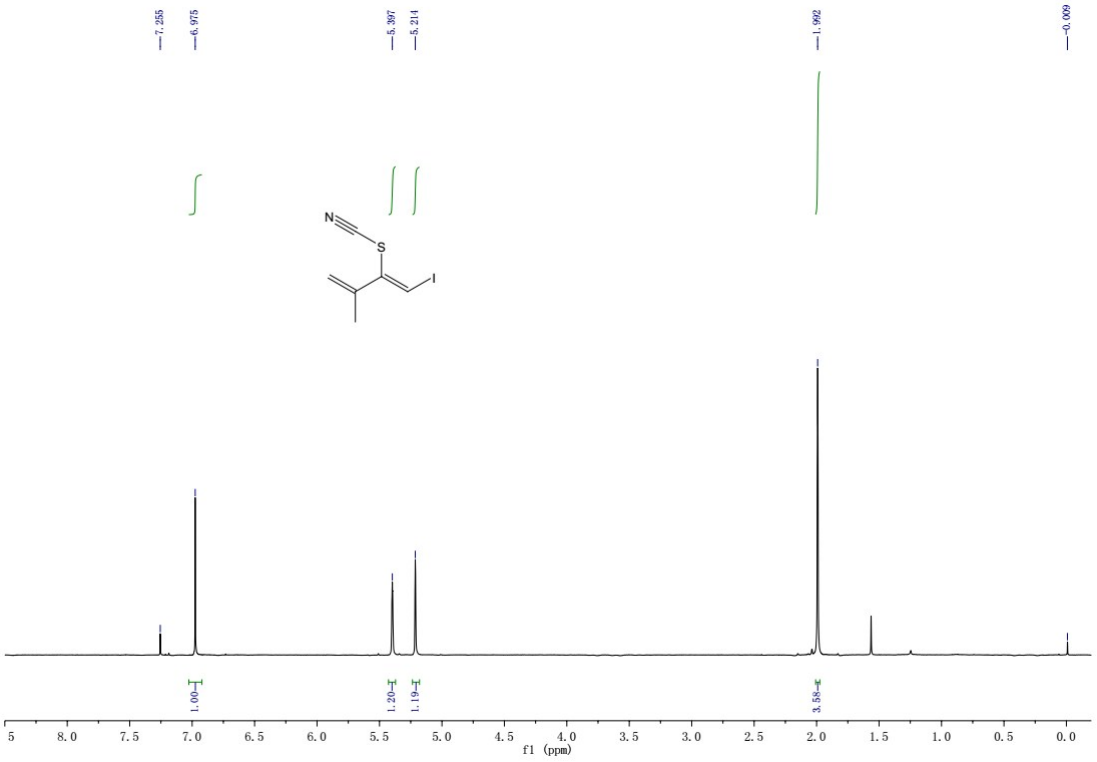

163.87
140.92
111.71
79.16
77.33
77.01
76.69
63.99
13.96
O
O
I
S
N
f1 (ppm)

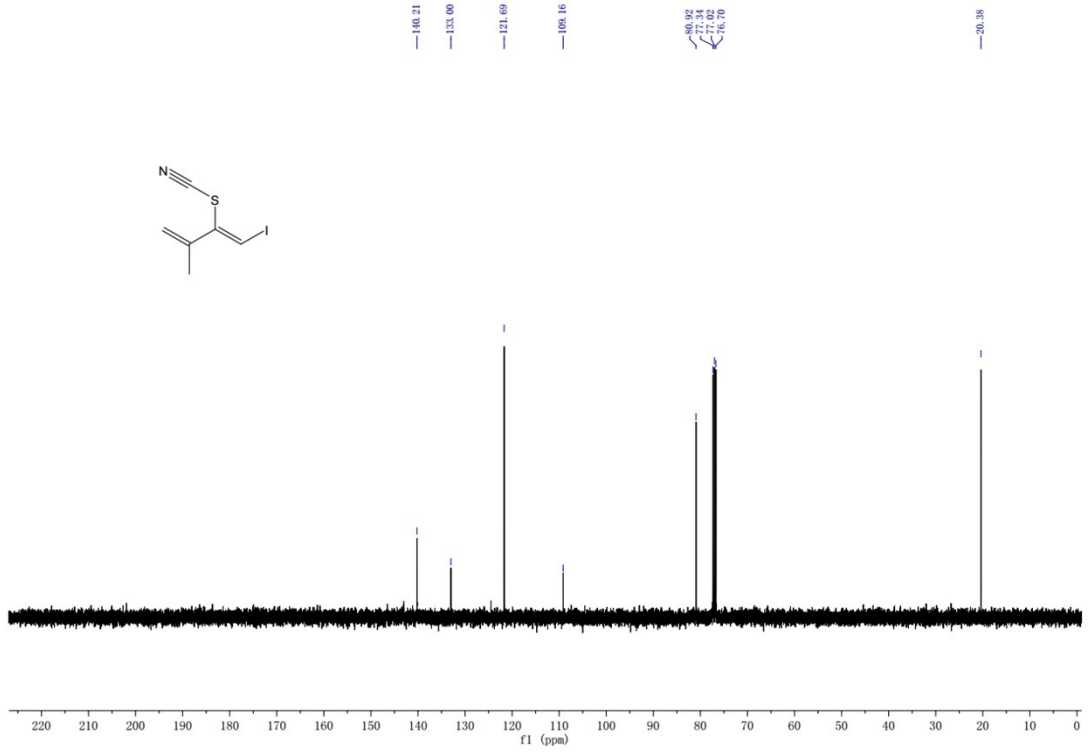
2q


7.280
7.242
4.085
4.068
0.029
N
S
Br
I
1.00
2.23
f1 (ppm)

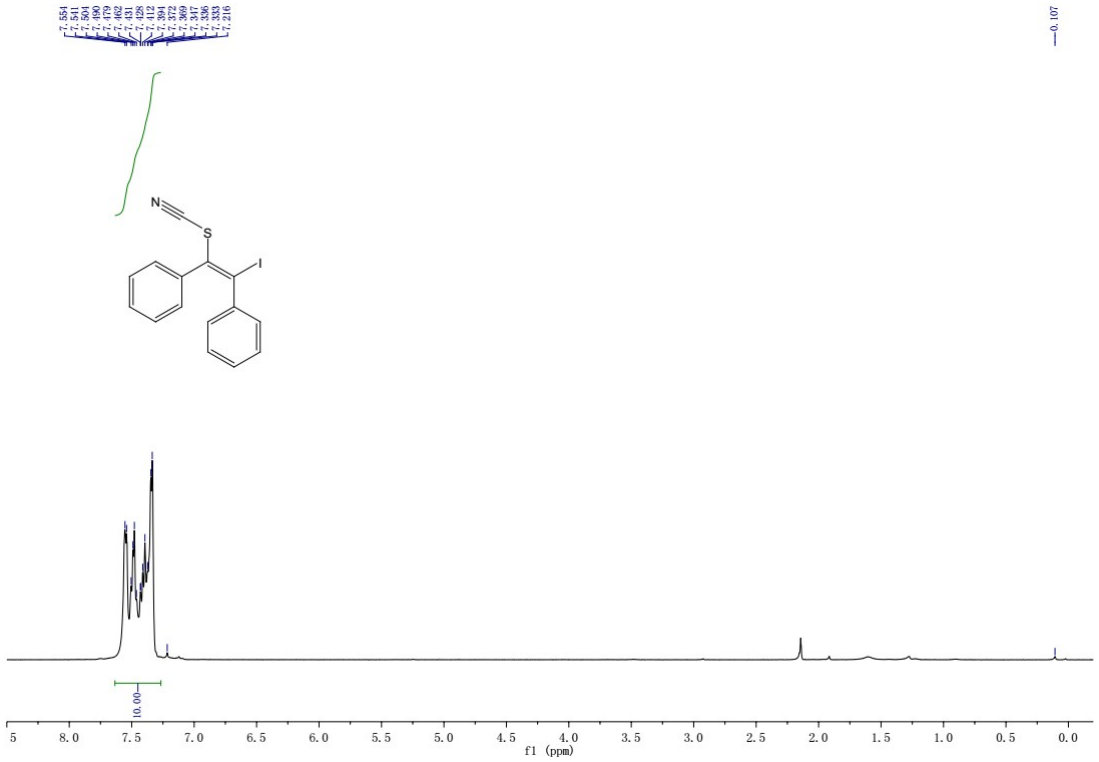

128.90
110.06
87.61
77.39
77.07
76.75
47.98
N
S
Br
I
f1 (ppm)

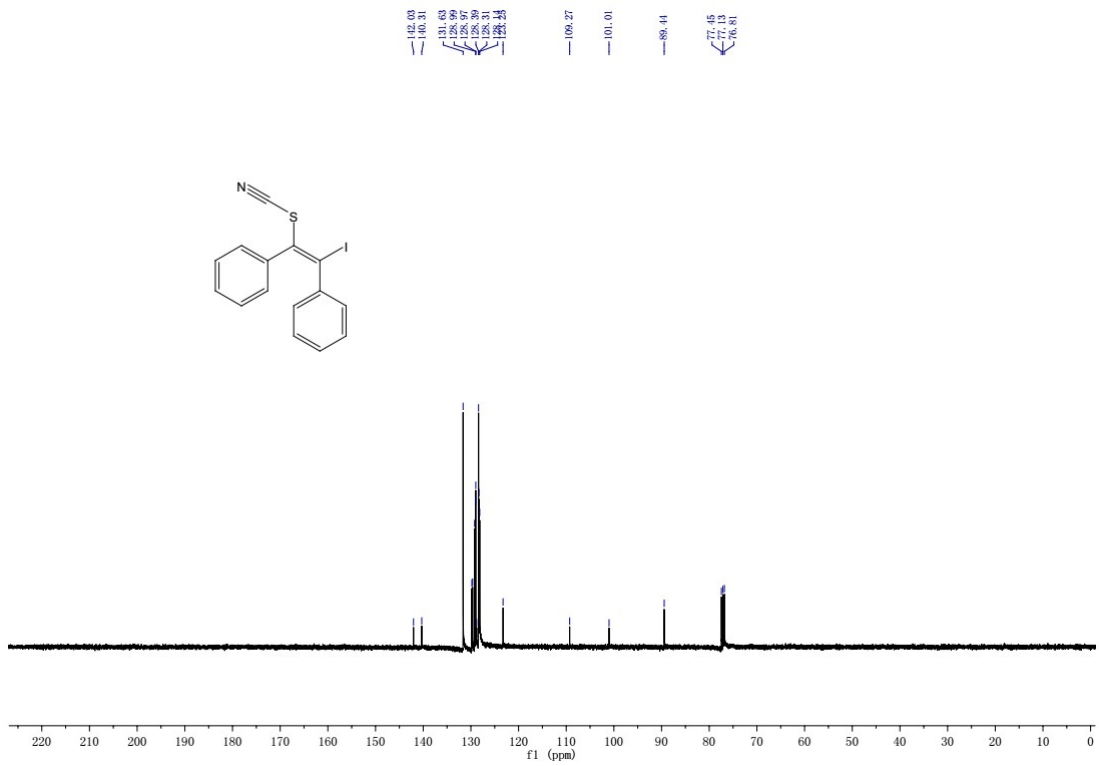
2r


7.255
6.975
5.397
5.214
1.992
0.009
1.00
1.20
1.19
3.58
f1 (ppm)

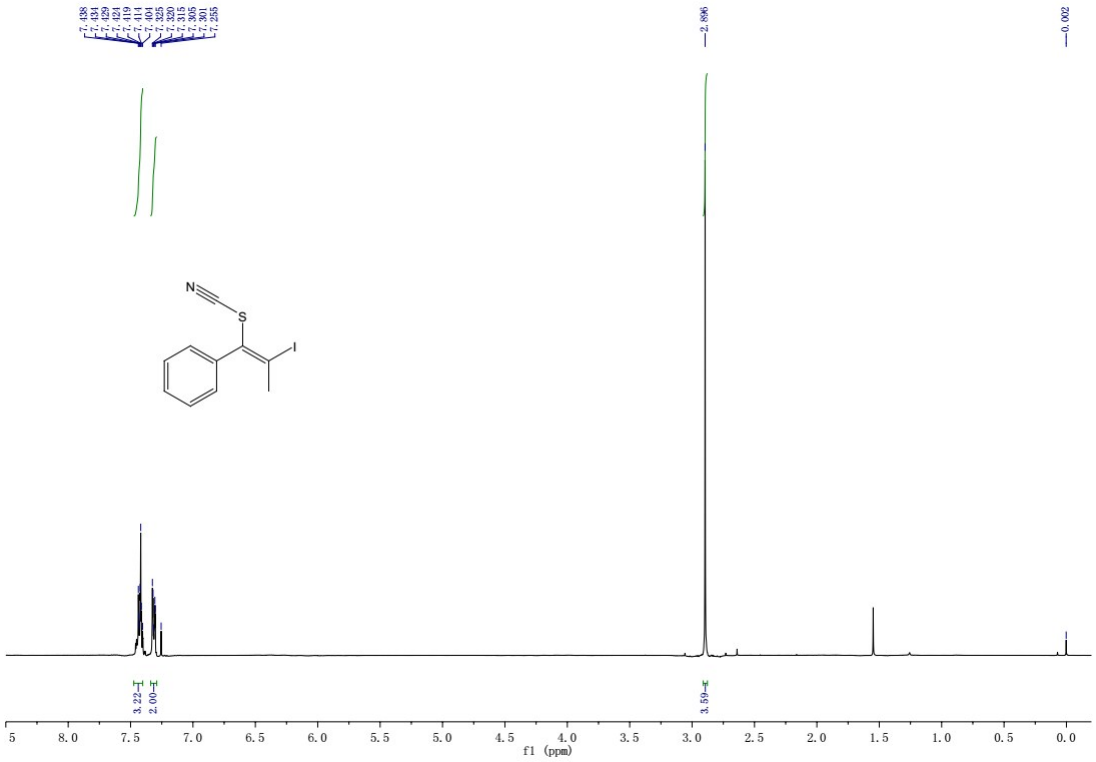

140.21
133.00
121.69
109.16
80.92
77.34
77.02
76.70
20.38
f1 (ppm)

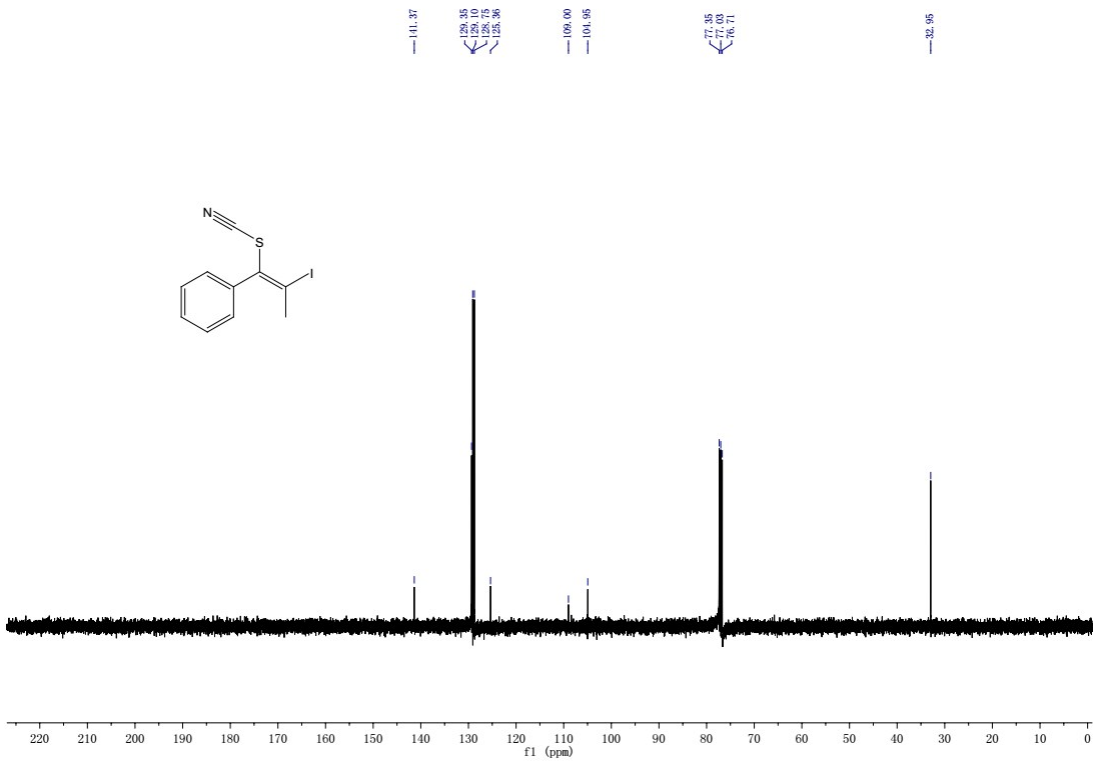
2s


7.554
7.541
7.504
7.490
7.479
7.462
7.431
7.428
7.412
7.394
7.372
7.369
7.347
7.336
7.333
7.216
0.107
N
S
I
10.00
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
f1 (ppm)

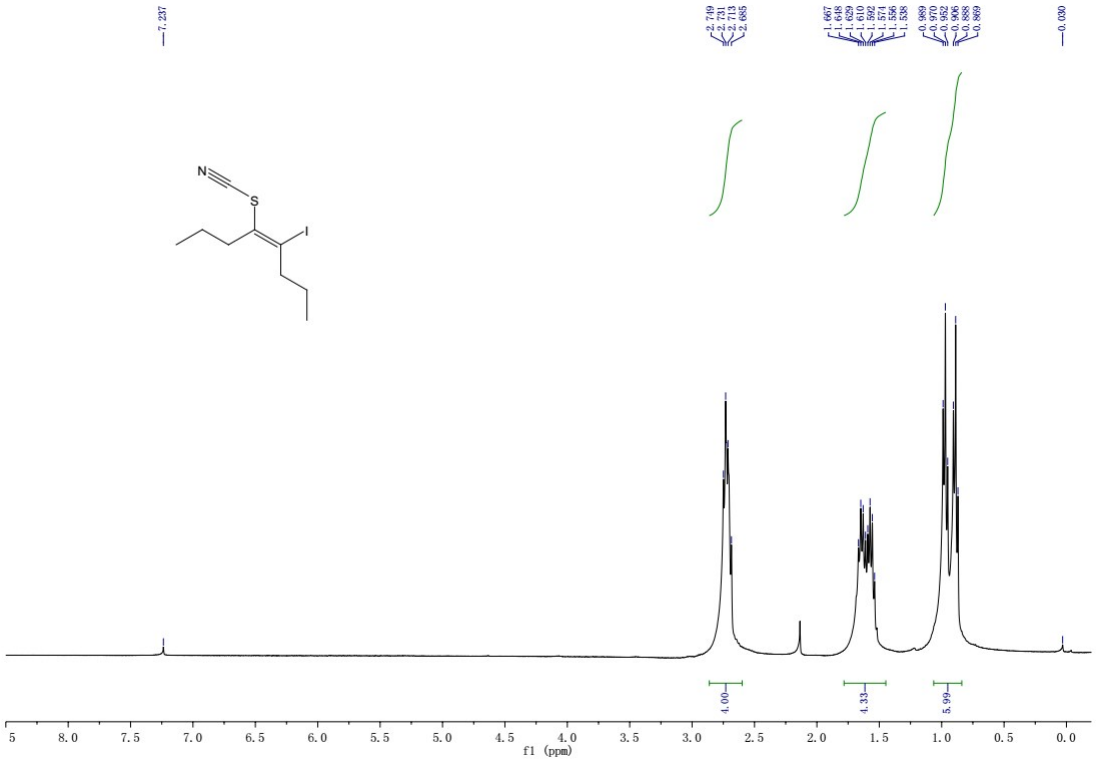

142.03
140.31
131.63
128.99
128.97
128.39
128.31
109.27
101.01
89.44
77.15
77.13
76.81
N
S
I
220
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

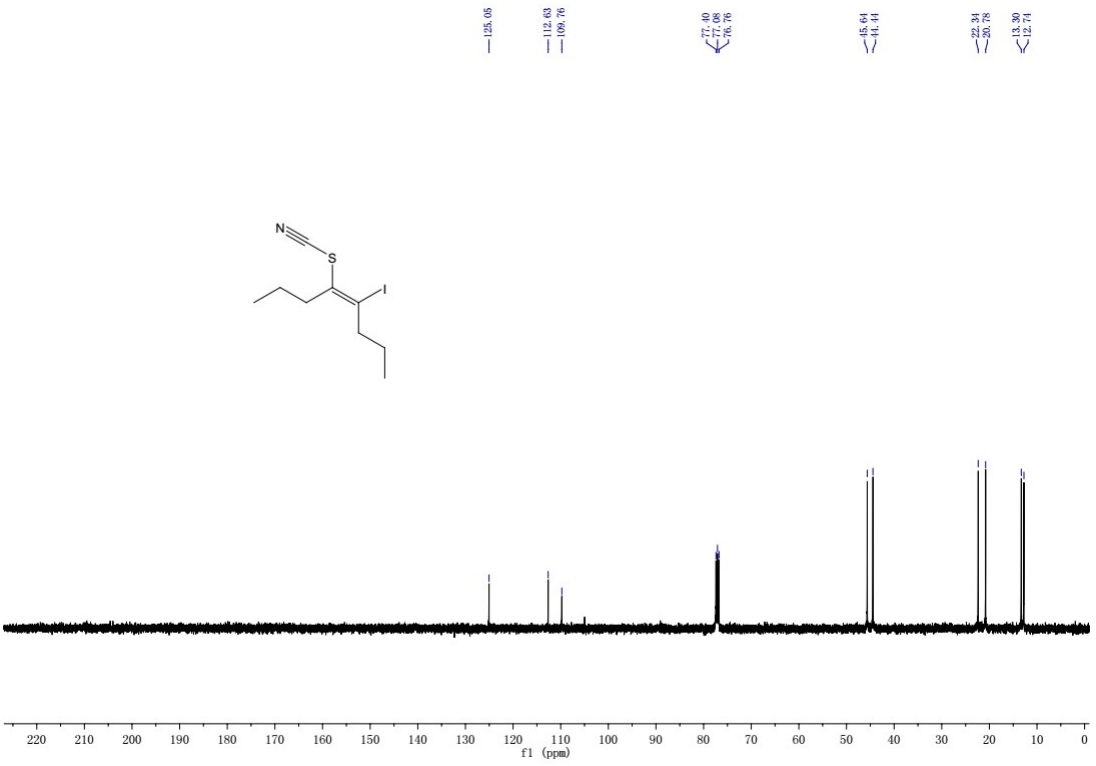
2t


7.138
7.134
7.129
7.123
7.119
7.114
7.104
7.095
7.320
7.315
7.305
7.300
7.255
2.896
0.002
3.22
2.00
3.59
f1 (ppm)

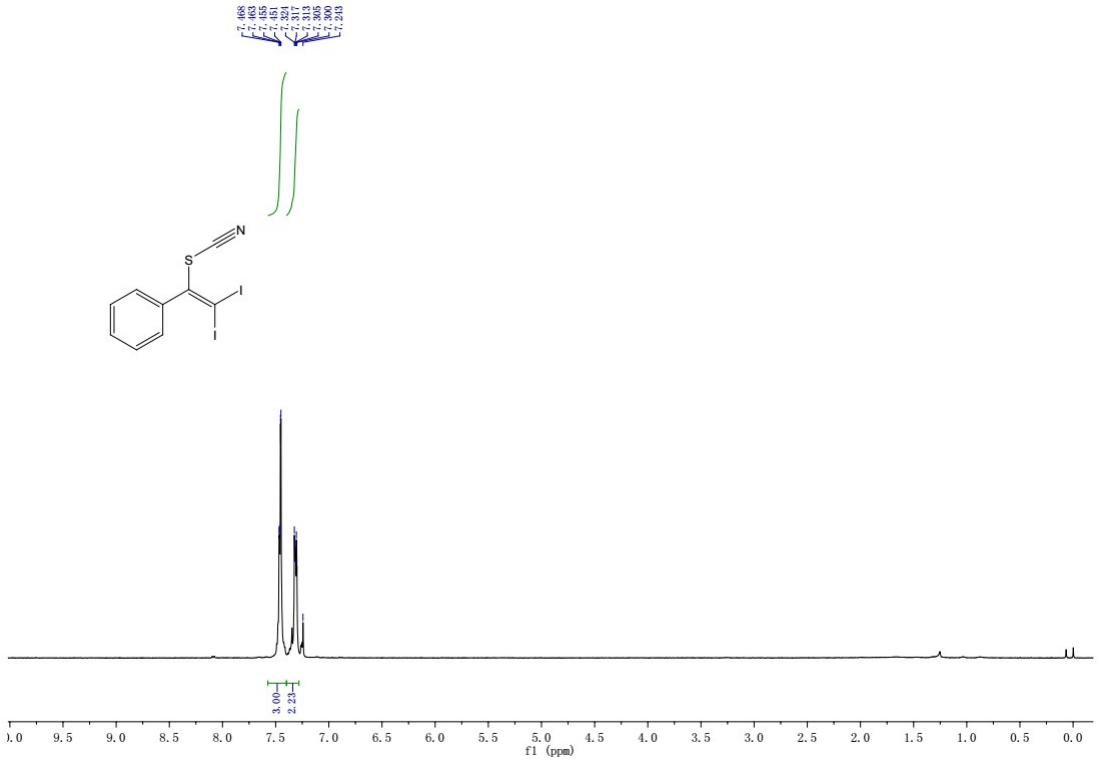

141.37
129.35
129.10
128.75
128.36
109.00
104.95
77.35
77.03
76.71
32.95
f1 (ppm)

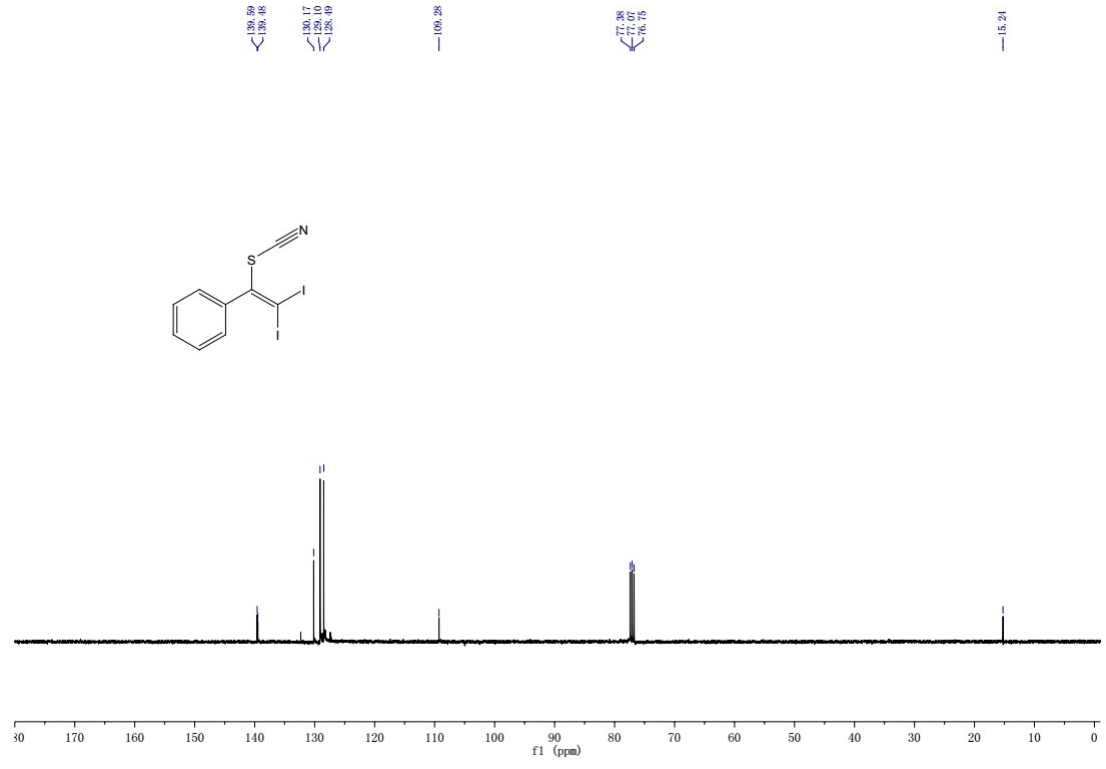
2u


7.257
2.749
2.731
2.713
2.685
1.667
1.648
1.629
1.610
1.592
1.574
1.556
1.538
0.989
0.970
0.952
0.933
0.906
0.888
0.869
0.030
N
S
I
4.00
4.33
5.99
f1 (ppm)

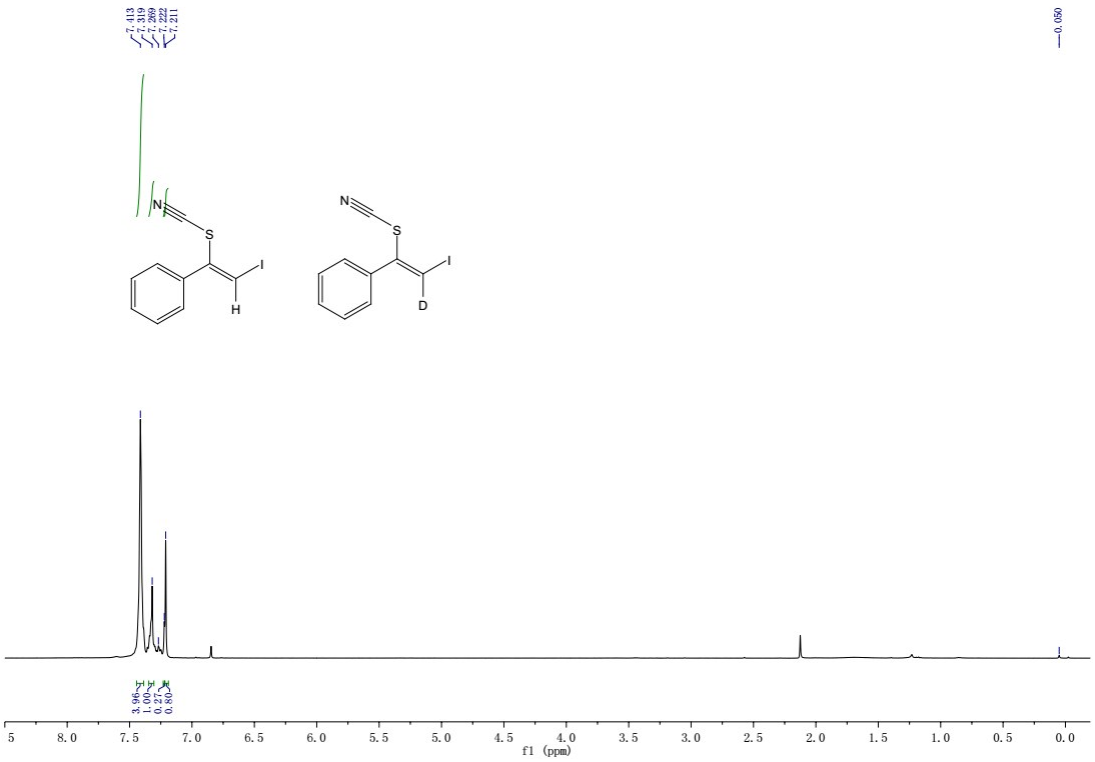

125.05
112.63
109.76
77.40
77.08
76.76
45.64
44.44
22.34
20.78
13.30
12.74
N
S
I
f1 (ppm)

2v


7.468
7.463
7.455
7.451
7.324
7.317
7.313
7.305
7.300
7.243
N
S
I
I
3.00
2.23
f1 (ppm)


139.59
139.48
130.17
129.10
128.49
109.28
77.38
77.07
76.75
15.24
N
S
I
I
f1 (ppm)

2a-H and 2a-D


7.413
7.319
7.269
7.222
7.211
0.000
N
S
I
H
N
S
I
D
3.96
1.00
0.87
0.80
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
f1 (ppm)