Electronic Supporting Information

Efficient and environment-friendly Glaser coupling of terminal alkyne catalyzed by multinuclear copper complexes under base-free condition

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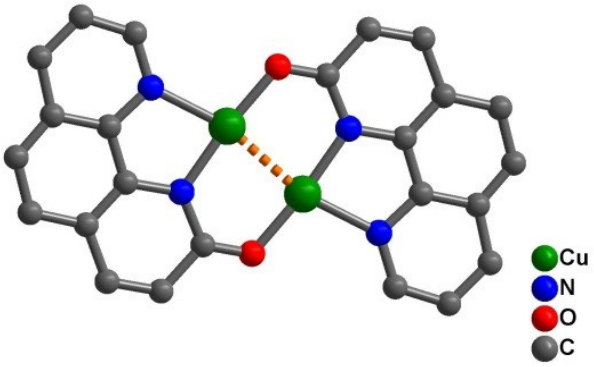
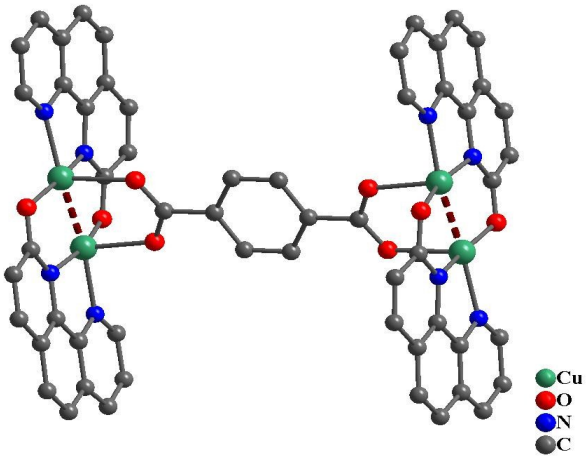
1、General information

All the solvents were obtained from commercial suppliers and used without further purification. Thin layer chromatography (TLC) employed glass 0.25 mm silica gel plates. Flash chromatography columns were packed with 200-300 mesh silica gel in petroleum (bp. 60-90°C). GC-MS spectra were recorded on a Thermo Fisher GC-MS Poparis Q. GC yields were recorded with Agilent 7820A gas chromatography instrument with a FID detector. All new compounds were characterized by ^{1}H NMR, ^{13}C NMR and GC-MS. The known compounds were characterized by ^{1}H NMR. ^{1}H and ^{13}C NMR datas were recorded with ASCend TM 600 MHz with tetramethylsilane as an internal standard. All chemical shifts (δ) were reported in ppm and coupling constants (*J*) in Hz. All chemical shifts were reported relative to tetramethylsilane (0 ppm for 1H), and $CDCl_3$(77.16 ppm for ^{13}C), respectively.

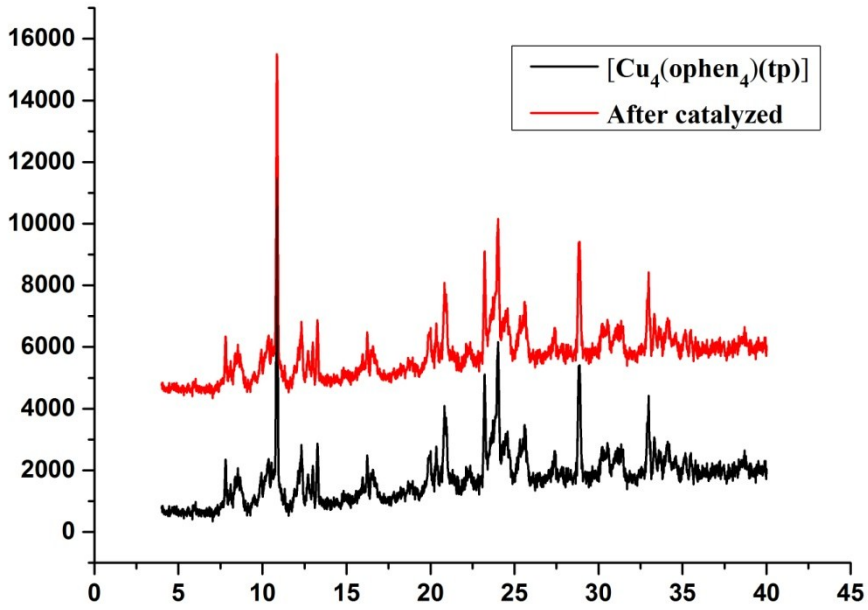
2、View of planar dinuclear structure of compound 1 [$Cu_2(ophen)_2$].



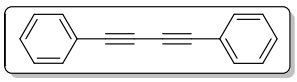
3、View of tetranuclear mixed-valence compound 2 [$Cu_4(ophen)_4(tp)$].



4、 The PXRD patterns of the fresh and after catalyzed compound 2.

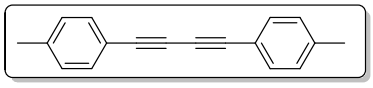


5、NMR analytical data of homocoupling products



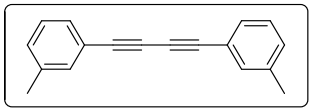
1,4-Diphenyl-1,3-butadiyne (2a)[1]:

White solid; ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.47-7.46 (d, *J* = 6.0 Hz, 4H), 7.31-7.27 (m, *J* = 6.0 Hz, 6H). ^{13}C NMR (150 MHz, $CDCl_3$) δ 131.5, 128.2, 127.4, 120.8, 80.5, 72.9.



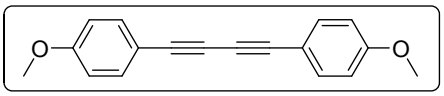
1,4-Bis(*p*-methylphenyl)-1,3-butadiyne (2b)[1]:

White solid; ^{1}H NMR (600 MHz, $CDCl_3$): δ 7.42-7.40 (d, *J* = 6.0 Hz, 4H), 7.14-7.13 (d, *J* = 6.0 Hz, 4H), 2.36 (s, 6H). ^{13}C NMR (150 MHz, $CDCl_3$) δ 138.5, 131.4, 128.2, 117.8, 80.5, 72.4, 20.6.



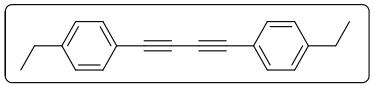
1,4-Bis(*m*-methylphenyl)-1,3-butadiyne (2c)[1]:

White solid; ^{1}H NMR (600 MHz, $CDCl_3$): δ 7.27-7.25 (d, *J* = 6.0 Hz, 4H), 7.16-7.13 (m, *J* = 6.0 Hz, 2H), 7.11-7.10 (d, *J* = 6.0 Hz, 2H), 2.26 (s, *J* = 6.0 Hz , 6H). ^{13}C NMR (150 MHz, $CDCl_3$) δ 137.1, 132.0, 129.1, 128.6, 127.3, 120.6, 80.6, 72.6, 20.2.



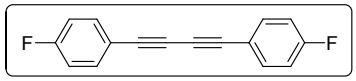
1,4-Bis(*p*-methoxyphenyl)-1,3-butadiyne (2d)[1]:

White solid; ^{1}H NMR (600 MHz, $CDCl_3$): δ 7.40-7.38 (d, *J* = 6.0 Hz, 4H), 6.79-6.78 (d, *J* = 6.0 Hz, 4H), 3.76 (s, 6H). ^{13}C NMR (150 MHz, $CDCl_3$) δ 139.5, 132.4, 129.2, 118.8, 81.5, 73.4, 21.6.



1,4-Bis(*p*-ethylphenyl)buta-1,3-diyne (2e)[2]:

White solid; ^{1}H NMR (600 MHz, $CDCl_3$): δ7.38-7.37 (d, *J* = 6 Hz, 4 H), 7.10-7.09 (d, *J* = 6 Hz, 4 H), 2.61-2.58 (m, *J* = 6 Hz, 4 H), 1.18-1.15 (m, *J* = 6 Hz, 6 H). ^{13}C NMR (150 MHz, $CDCl_3$) δ 144.7, 131.5, 127.0,118.00, 80.5, 72.4, 27.9, 14.2.

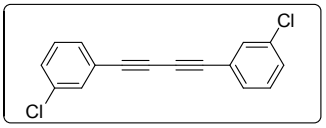


1,4-Bis(*p*-fluorophenyl)buta-1,3-diyne (2f)[2]:

White solid; ^{1}H NMR(600 MHz, $CDCl_3$): δ 7.45-7.43 (m, *J* = 6 Hz, 4 H), 6.98-6.96 (m, *J* = 6 Hz, 4 H). ^{13}C NMR (150 MHz, $CDCl_3$) δ 161.2, 133.5, 116.8, 114.9, 79.4, 72.5.

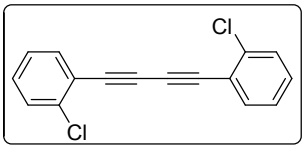
1,4-Bis(*p*-chlorophenyl)buta-1,3-diyne(2g) [7]:

White solid; ^{1}H NMR (600 MHz, $CDCl_3$): δ 7.47-7.46 (m, *J* = 6 Hz, 4H), 7.34-7.33 (m, *J* = 6 Hz, 4H). ^{13}C NMR (150 MHz, $CDCl_3$) δ 133.7, 130.8.8, 128.9.8, 121.8, 76.2, 71.6.



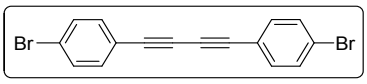
1,4-Bis(*m*-chlorophenyl)-1,3-butadiyne (2h)[1]:

^{1}H NMR (600 MHz, $CDCl_3$):δ7.44 (s, *J* = 6 Hz, 2H), 7.35-7.33 (m, *J* = 6 Hz, 2H), 7.30-7.28 (m, *J* = 6 Hz, 2H), 7.21-7.19(m, *J* = 6 Hz, 2H). ^{13}C NMR (150 MHz, $CDCl_3$) δ 133.3, 131.3, 129.6, 128.7, 122.3, 79.5, 73.7.



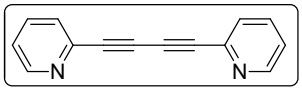
1,4-Bis(*o*-chlorophenyl)-1,3-butadiyne (2i)[4]:

White solid; ^{1}H NMR (600 MHz, $CDCl_3$): δ7.52-7.50 (m, *J* = 6 Hz, 2H), 7.36-7.35 (d, *J* = 6 Hz, 2H), 7.25-7.23 (m, *J* = 6 Hz, 2H), 7.18-7.17 (m, *J* = 6 Hz, 2H). ^{13}C NMR (150 MHz, $CDCl_3$) δ 136.0, 133.4, 129.3, 128.4, 125.5, 120.8, 78.4, 75.8.



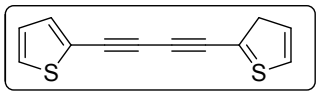
1,4-Bis(*p*-bromophenyl)buta-1,3-diyne (2j)[3]:

Pale yellow solid; ^{1}H NMR (600 MHz, $CDCl_3$): δ 7.42-7.41 (d, *J* = 6 Hz, 4H), 7.32-7.31 (d, *J* = 6 Hz, 4H). ^{13}C NMR (150 MHz, $CDCl_3$) δ 132.8, 131.7, 130.8, 110.6, 76.2, 72.6.



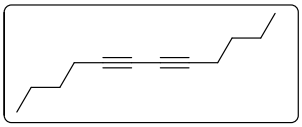
1,4-Bis(2-pyridyl)buta-1,3-diyne (2k)[10]:

White solid; ^{1}H NMR (600 MHz, $CDCl_3$): δ8.56-8.55 (d, *J* = 6 Hz, 2H), 7.62-7.61 (m, *J* = 6 Hz, 2H), 7.49-7.47 (m, *J* = 6 Hz, 2H), 7.24-7.23 (m, *J* = 6 Hz, 2H). ^{13}C NMR (150 MHz, $CDCl_3$) δ 149.4, 140.9, 135.2, 127.4, 122.8, 79.9, 72.2.



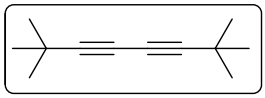
1,4-Bis(4-thienylophenyl)-1,3-butadiyne (2l)[6]:

White solid; ^{1}H NMR (600 MHz, $CDCl_3$): δ7.28-7.27 (d, *J* = 6 Hz, 2H), 7.26-7.25 (d, *J* = 6 Hz, 2H), 6.94-6.92 (m, *J* = 6 Hz, 2H). ^{13}C NMR (150 MHz, $CDCl_3$) δ133.4, 127.9, 126.2, 120.9, 76.7, 75.6.



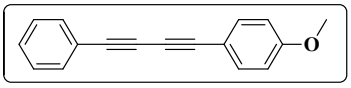
5,7-Dodecadiyne (2m)[5]:

White solid; ^{1}H NMR (600 MHz, $CDCl_3$): δ 2.19-2.17 (m, *J* = 6 Hz, 4H), 1.44-1.42 (m, *J* = 6 Hz, 4H), 1.36-1.34 (m, *J* = 6 Hz, 4H) 0.85-0.82 (m, *J* = 6 Hz, 6H). ^{13}C NMR (150 MHz, $CDCl_3$) δ76.5, 64.2, 29.4, 28.7, 20.9, 17.9, 12.5.



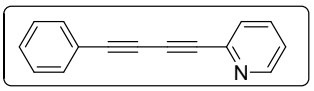
2,2,7,7-Tetramethylocta-3,5-diyne (2n)[8]:

White solid; ^{1}H NMR (600 MHz, $CDCl_3$): δ 1.28 (s, *J* = 6.0 Hz, 18H). ^{13}C NMR (150 MHz, $CDCl_3$) δ 85.3, 62.6, 29.6, 27.0.



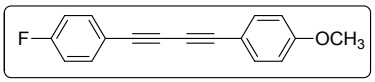
1-methoxy-4-(phenylbuta-1,3-diynyl)benzene (3a)[11]:

White solid; ^{1}H NMR (600 MHz, $CDCl_3$): δ7.54-7.53 (d, *J* = 6 Hz, 2H), 7.50-7.48 (d, *J* = 6 Hz, 2H), 7.39-7.34 (m, *J* = 6 Hz, 3H), 6.88-6.87 (d, *J* = 6 Hz, 2H), 3.84 (s, *J* = 6 Hz, 3H). ^{13}C NMR (150 MHz, $CDCl_3$) δ 150.3, 133.1, 131.4, 128.0, 127.4, 121.0, 113.1, 112.7, 80.8, 79.9, 73.1, 71.7, 54.3.



2-(phenylbuta-1,3-diynyl)pyridine (3b)[12]:

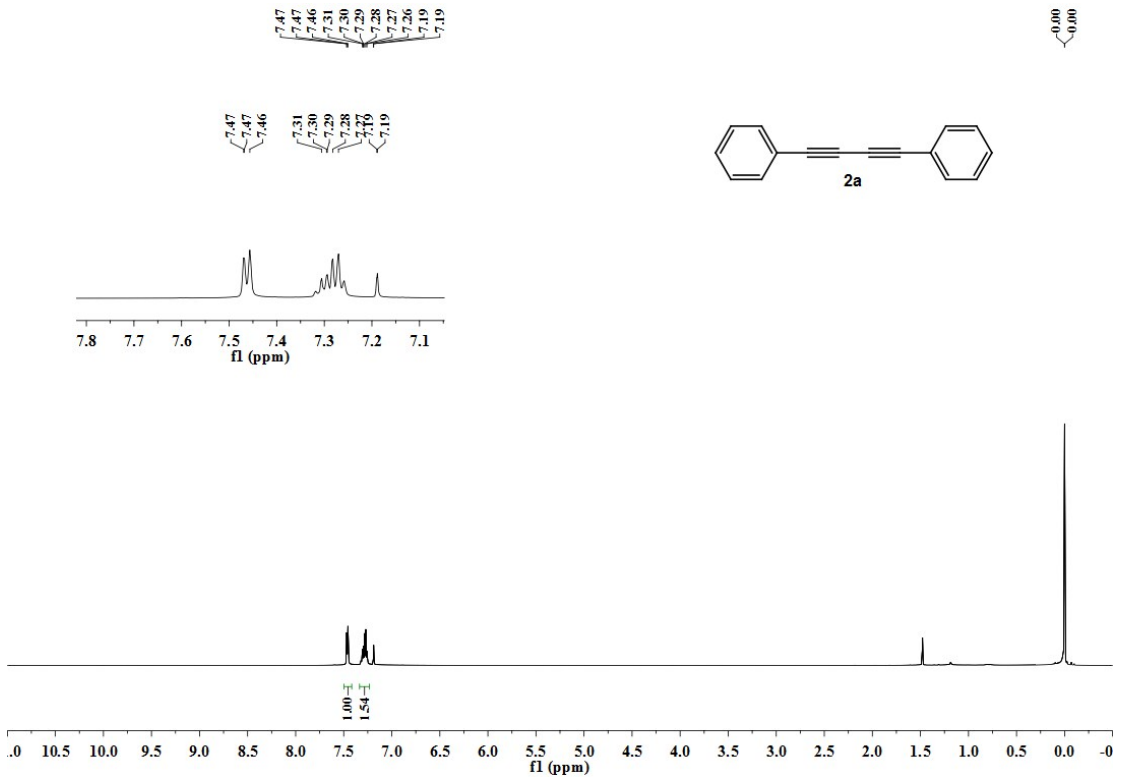
White solid; ^{1}H NMR (600 MHz, $CDCl_3$): δ8.64 (s, *J* = 6 Hz, 1H), 7.70-7.69 (m, *J* = 6 Hz, 1H), 7.58-7.54 (m, *J* = 6 Hz, 3H), 7.43-7.36 (m, *J* = 6 Hz, 3H), 7.31-7.29 (m, *J* = 6 Hz, 1H). ^{13}C NMR (150 MHz, $CDCl_3$) δ 150.4, 142.3, 136.2, 132.7, 129.6, 128.5, 128.1, 123.5, 121.3, 82.5, 80.2, 73.8, 73.6.



4-methoxy-(4-fluorophenyl)buta-1,3-diynyl)benzene (3c):

White solid; ^{1}H NMR (600 MHz, $CDCl_3$): δ7.53-7.48 (m, *J* = 6 Hz, 4H), 7.06-7.03 (m, *J* = 6 Hz, 2H), 6.88-6.87 (m, *J* = 6 Hz, 2H), 3.84 (s, *J* = 6 Hz, 3H). ^{13}C NMR (150 MHz, $CDCl_3$) δ 162.7, 161.1, 159.4, 133.4, 133.1, 117.1, 114.9, 114.7, 113.1, 112.6, 80.8, 78.9, 72.9, 71.5, 54.3.

6. NMR spectra of homocoupling products.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0.00
2a
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7.7
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7.5
7.4
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7.2
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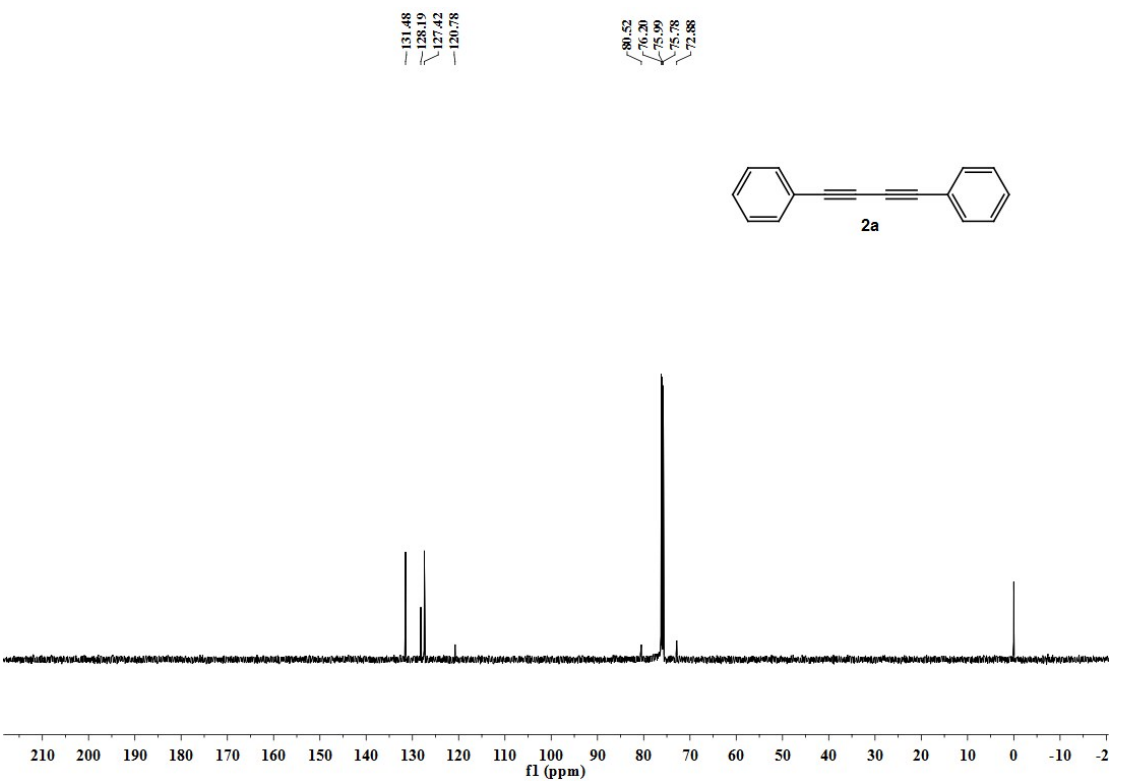
1.54
f1 (ppm)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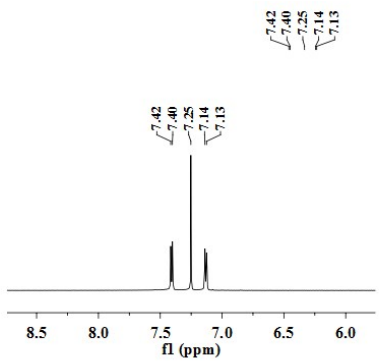
f1 (ppm)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7.0
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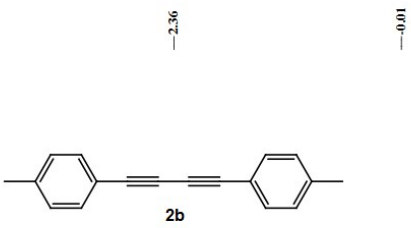
f1 (ppm)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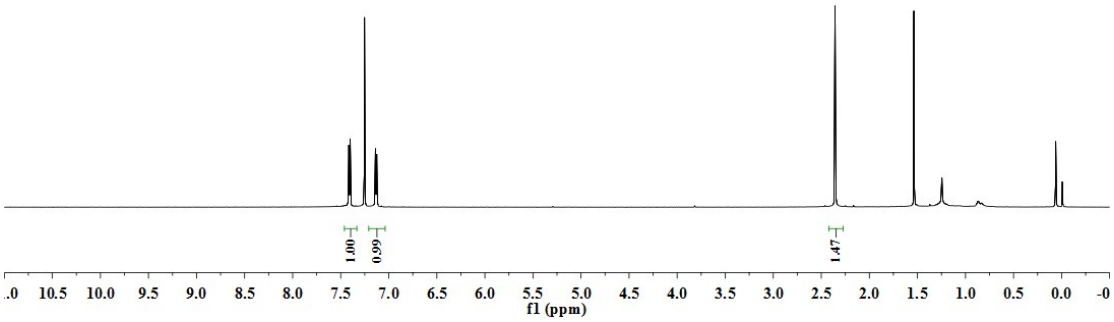
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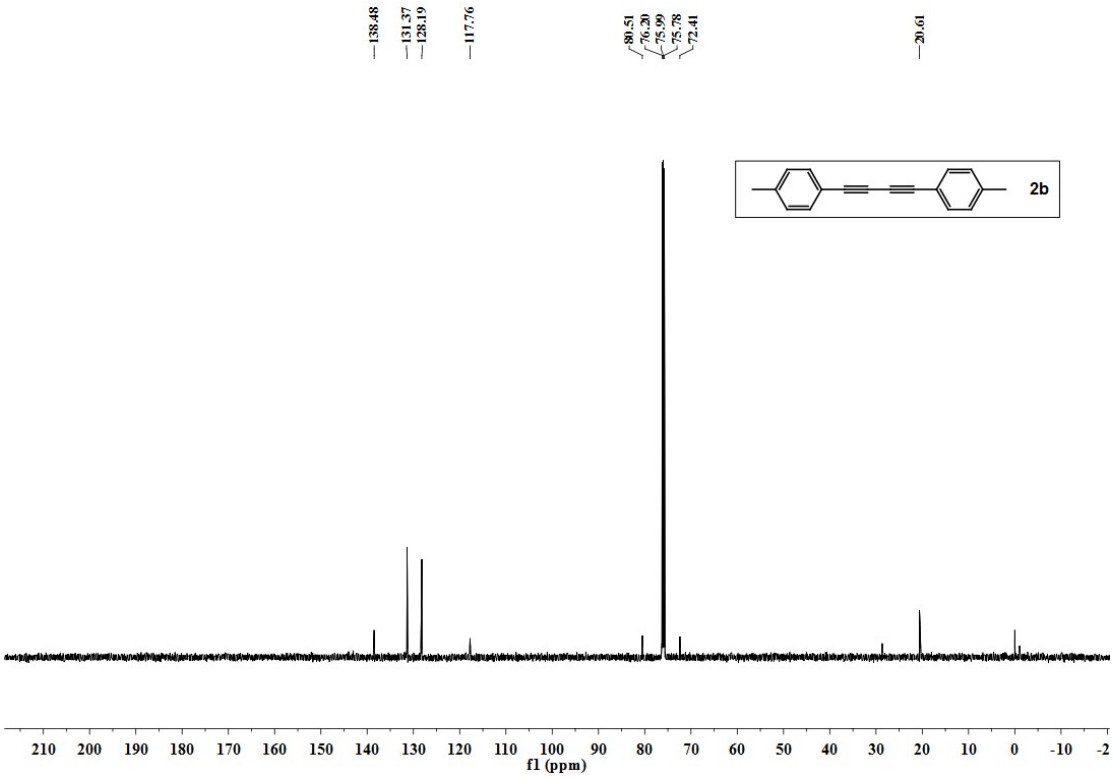
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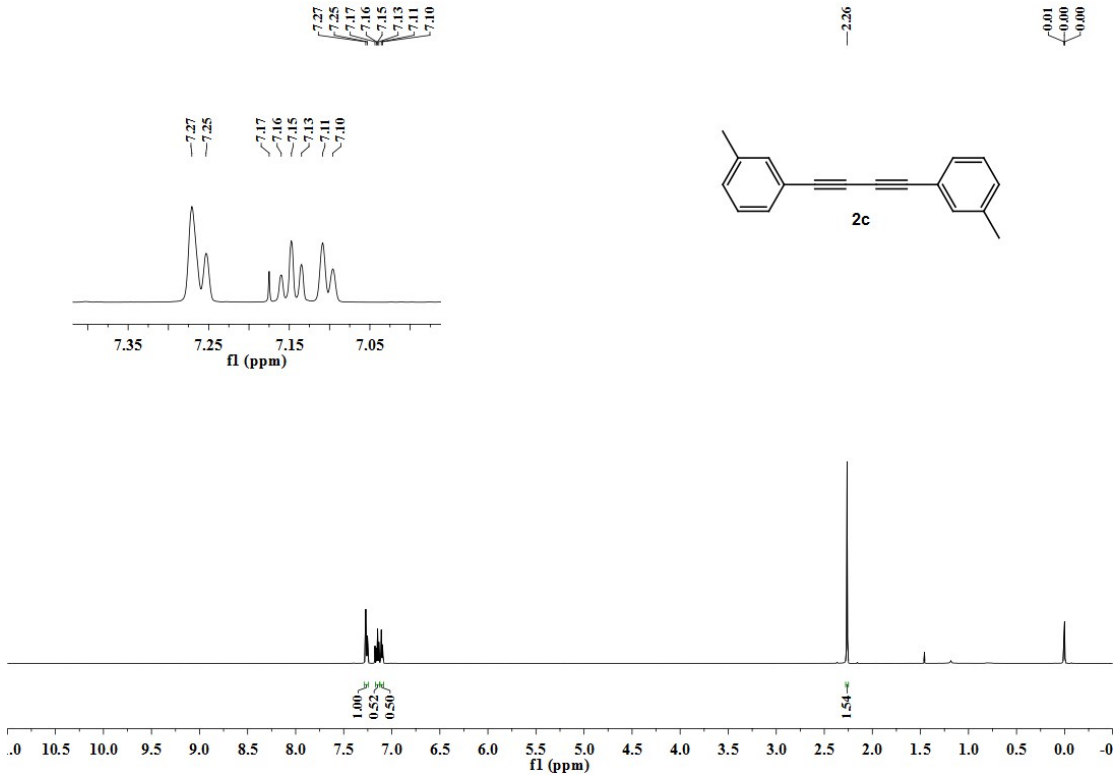
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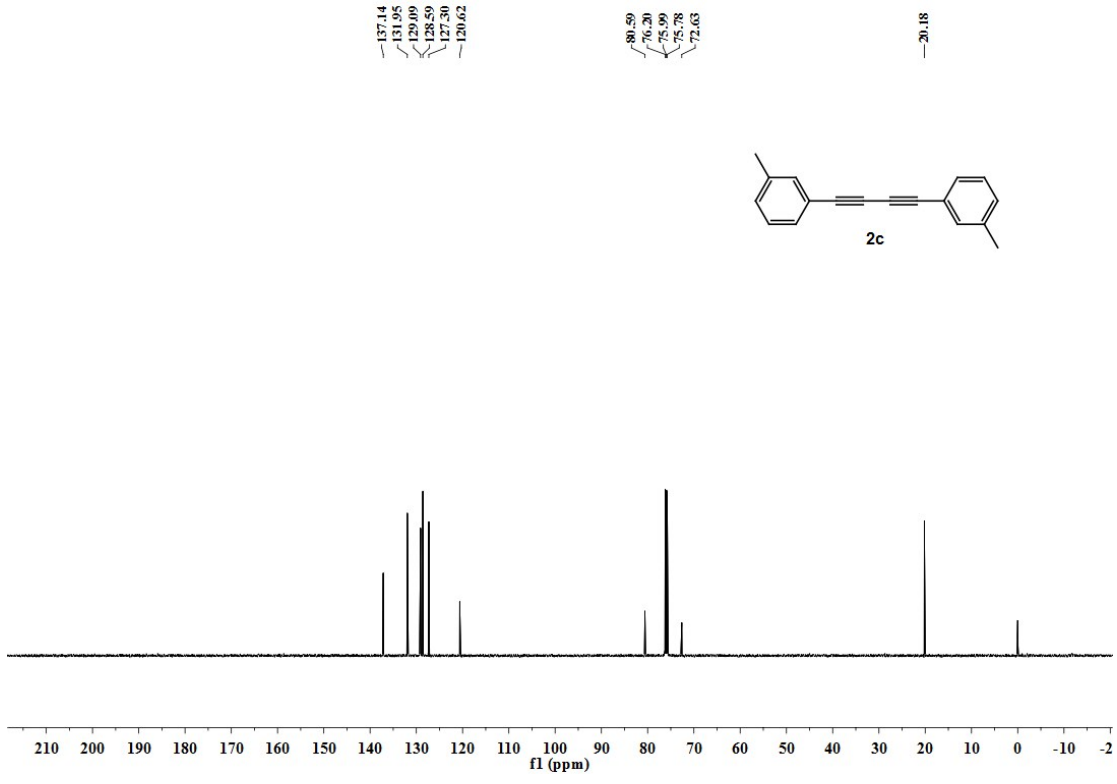
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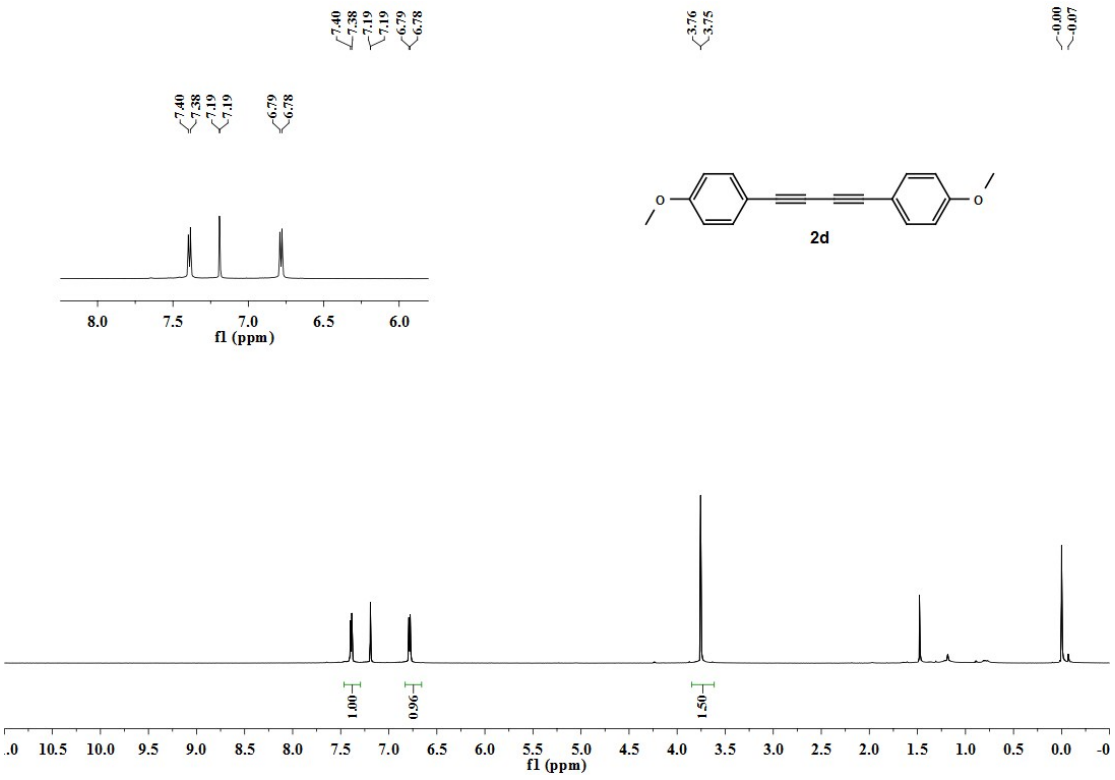
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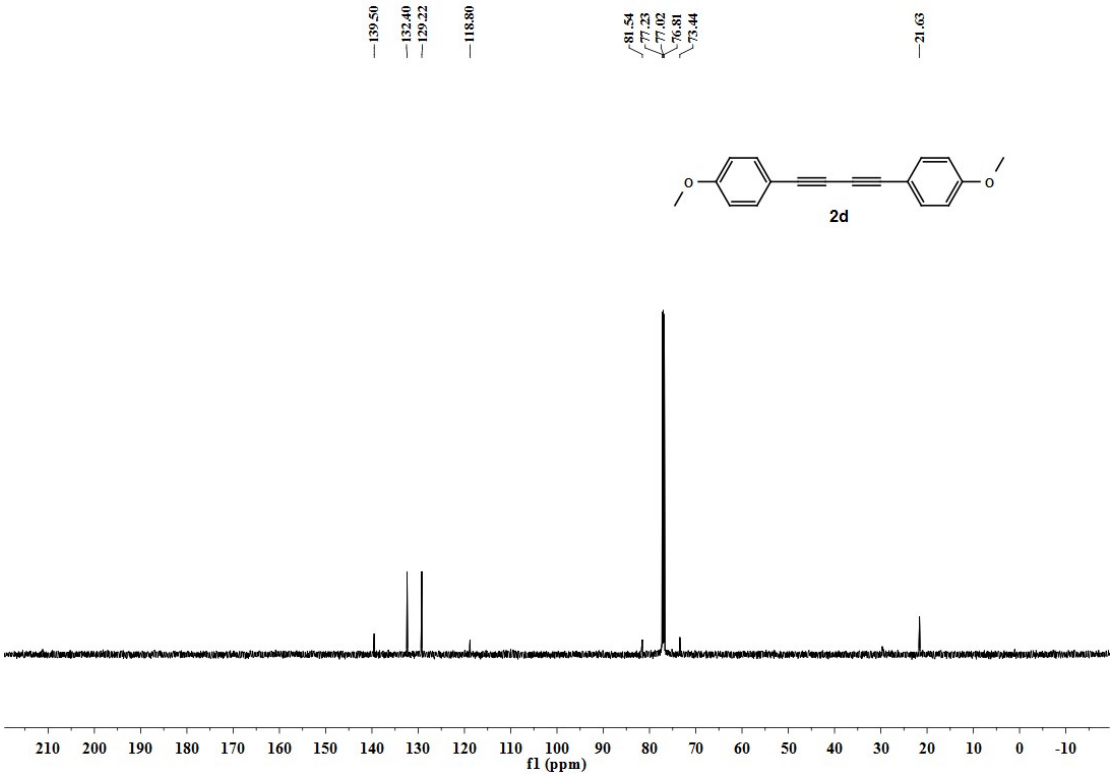
f1 (ppm)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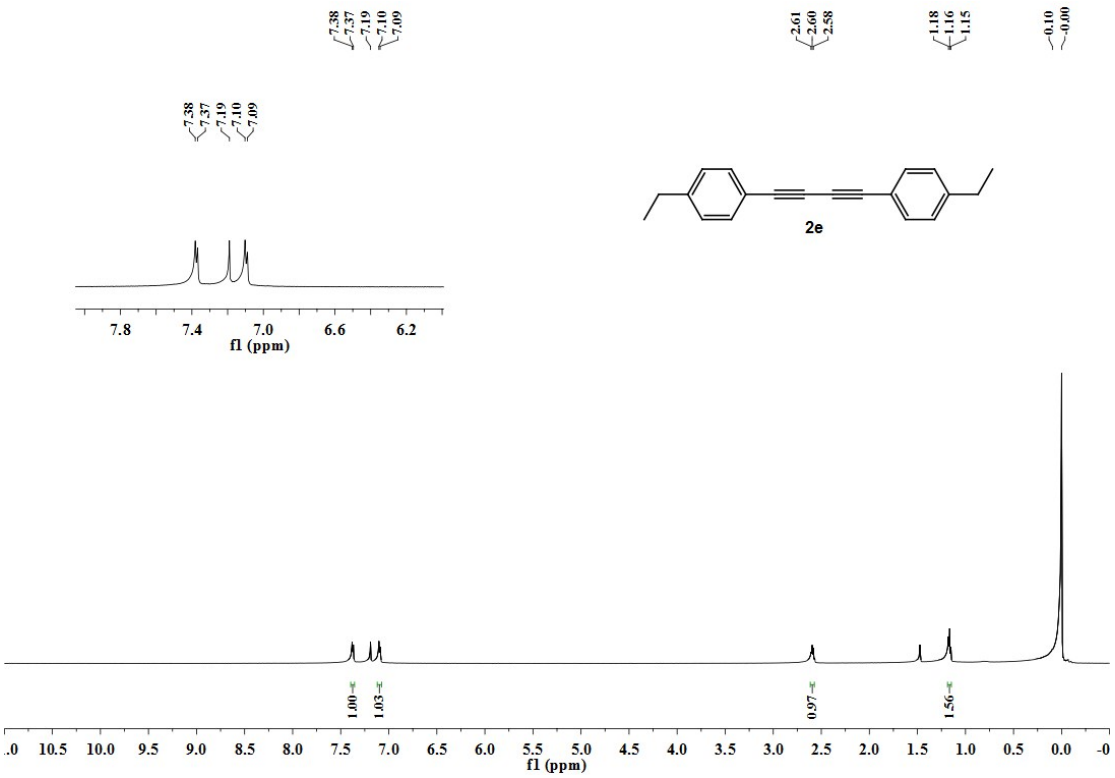
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6.2
f1 (ppm)
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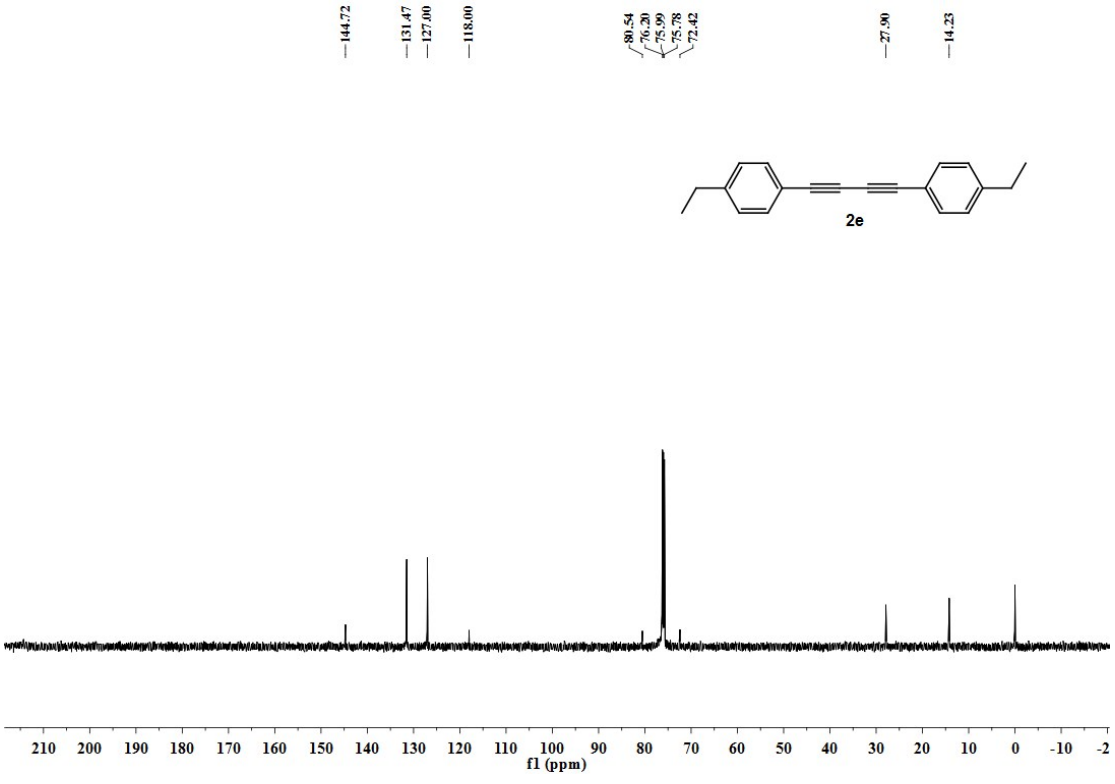
f1 (ppm)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75.78
72.42
27.90
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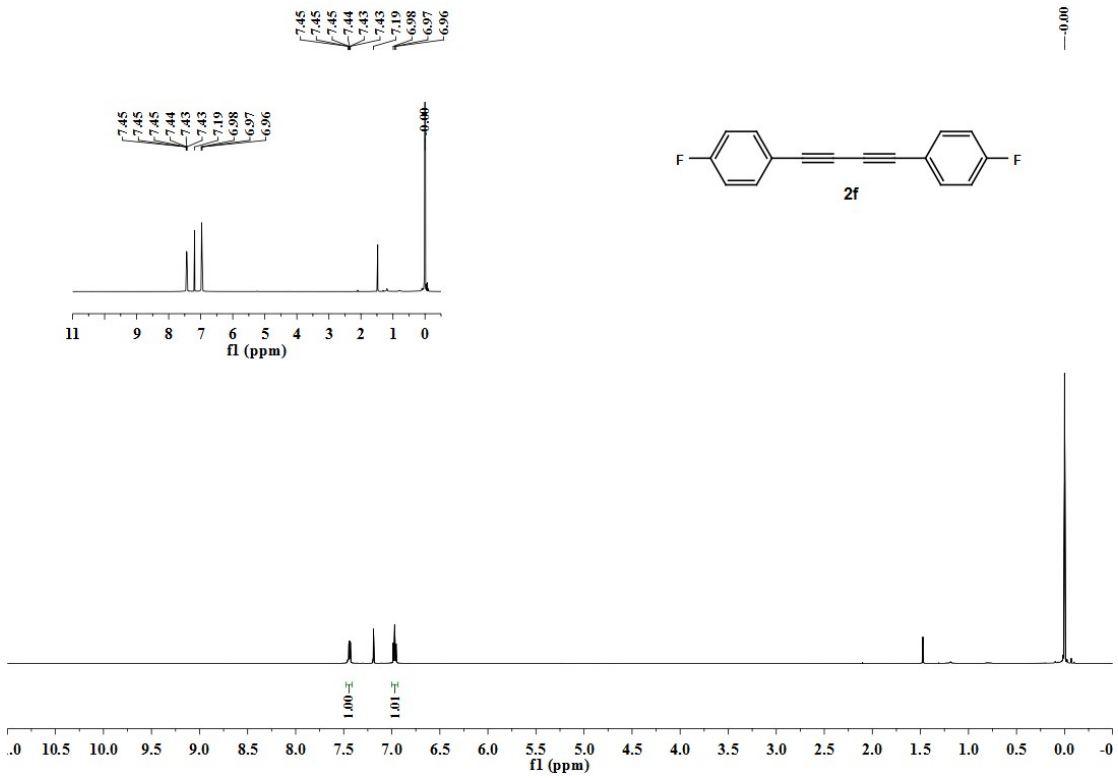
2e
f1 (ppm)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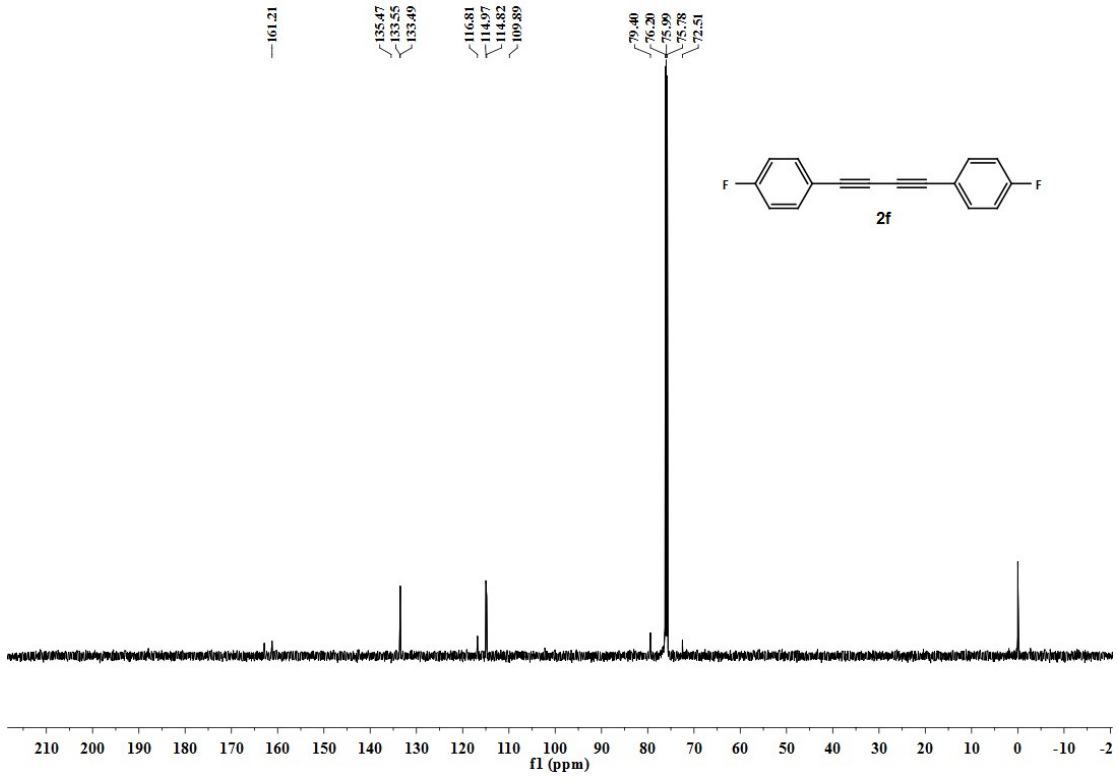
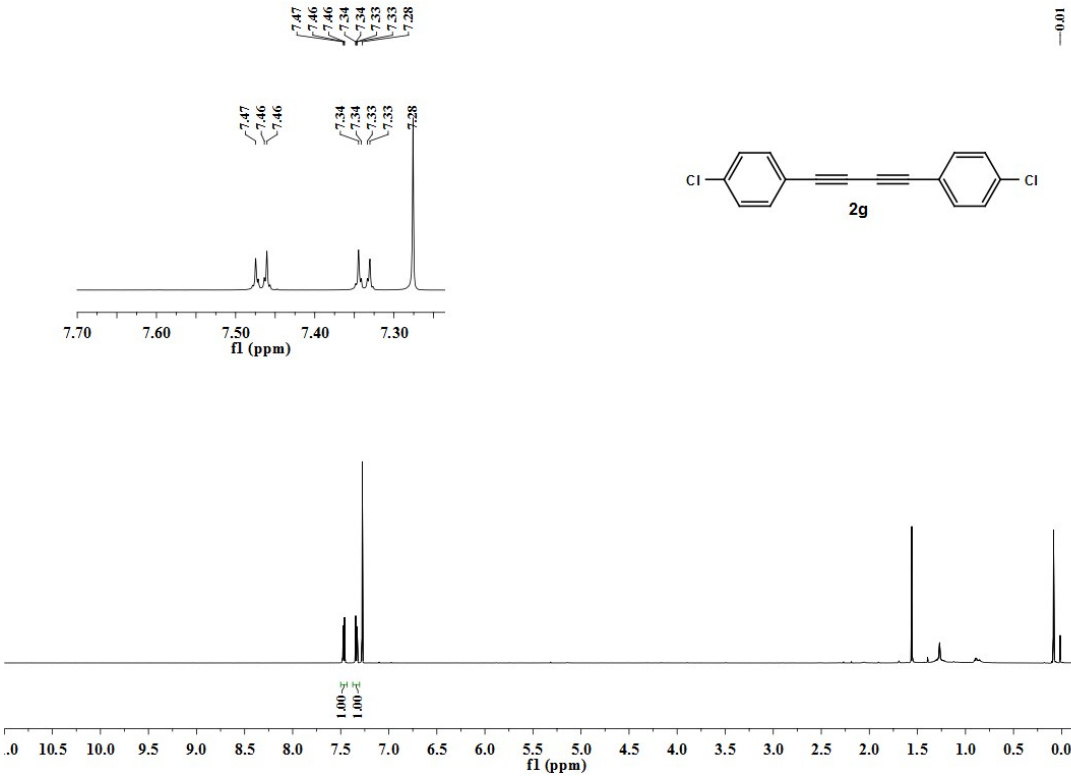
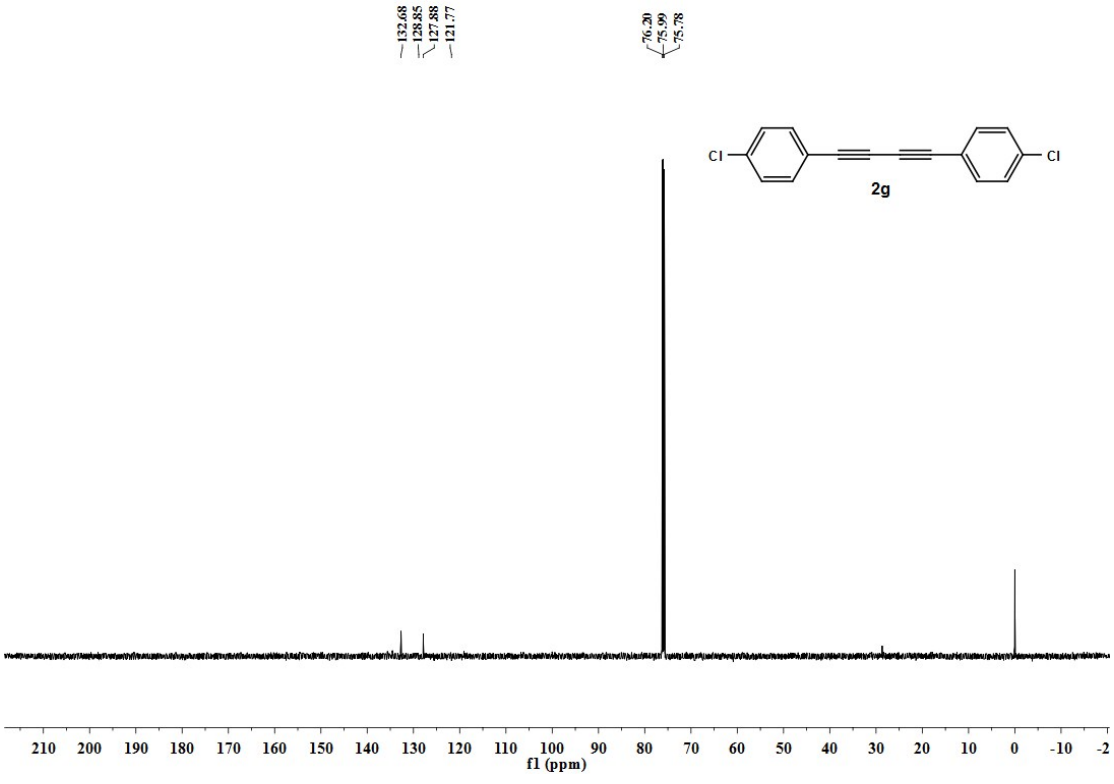
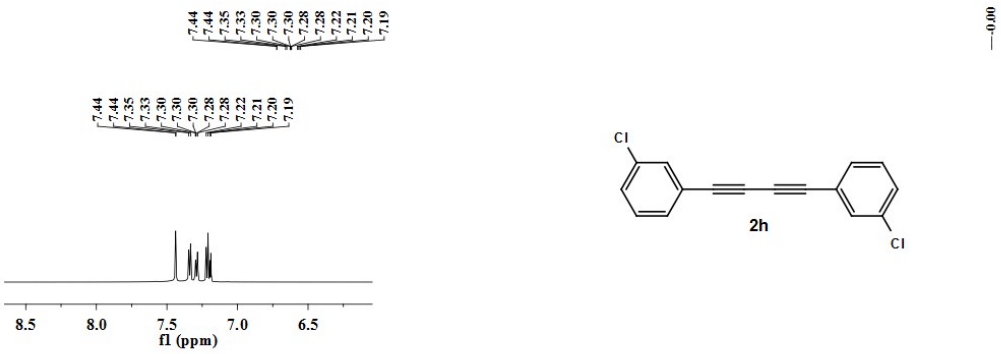
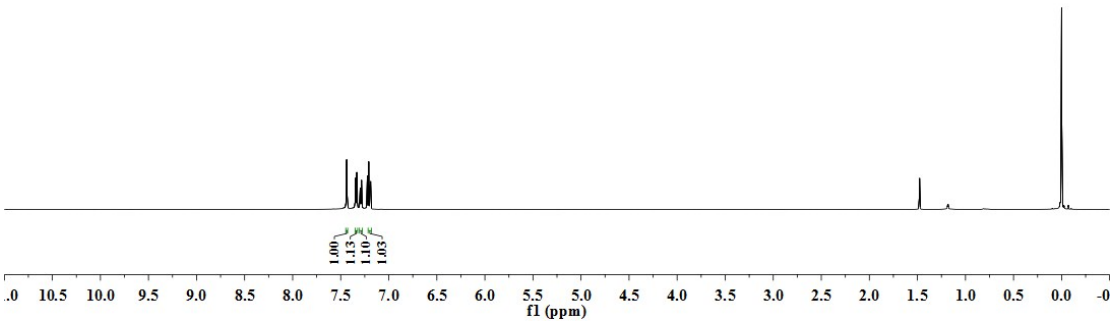
7.45
7.45
7.44
7.43
7.43
7.19
6.98
6.97
6.96
0.00
F
F
2f
1.00
1.01
fl (ppm)

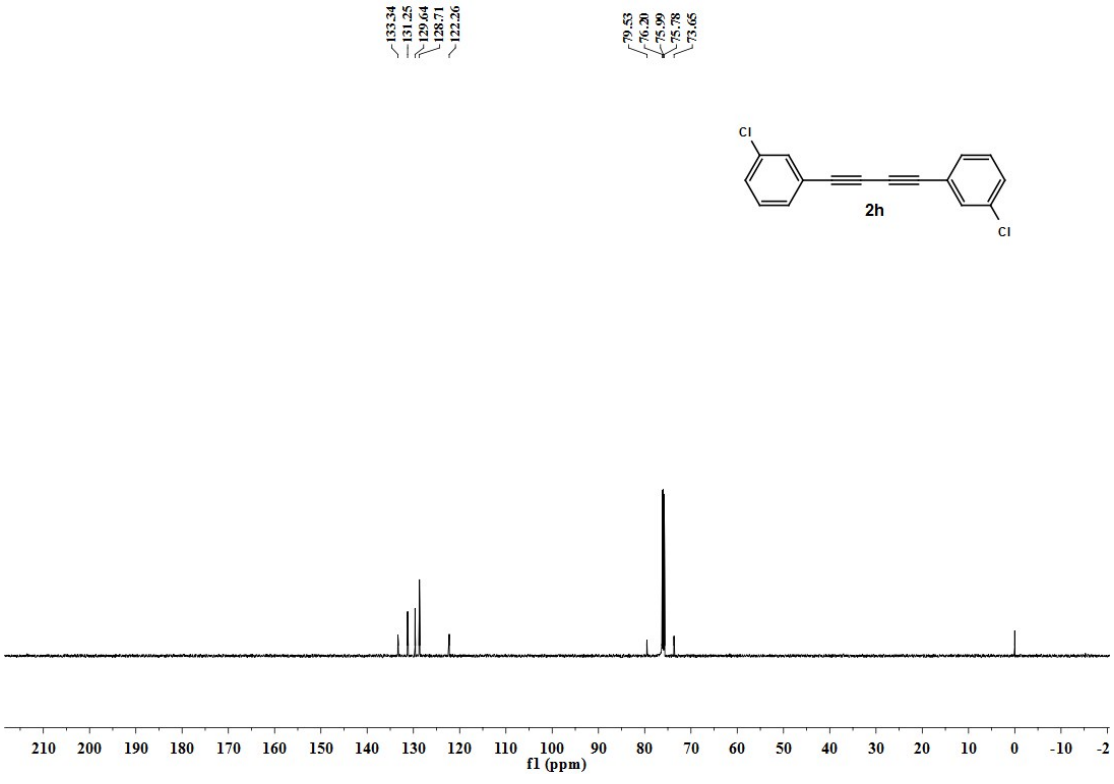

161.21
135.47
133.55
133.49
116.81
114.97
114.82
109.89
79.40
76.20
75.99
75.78
72.51
F
F
2f
fl (ppm)

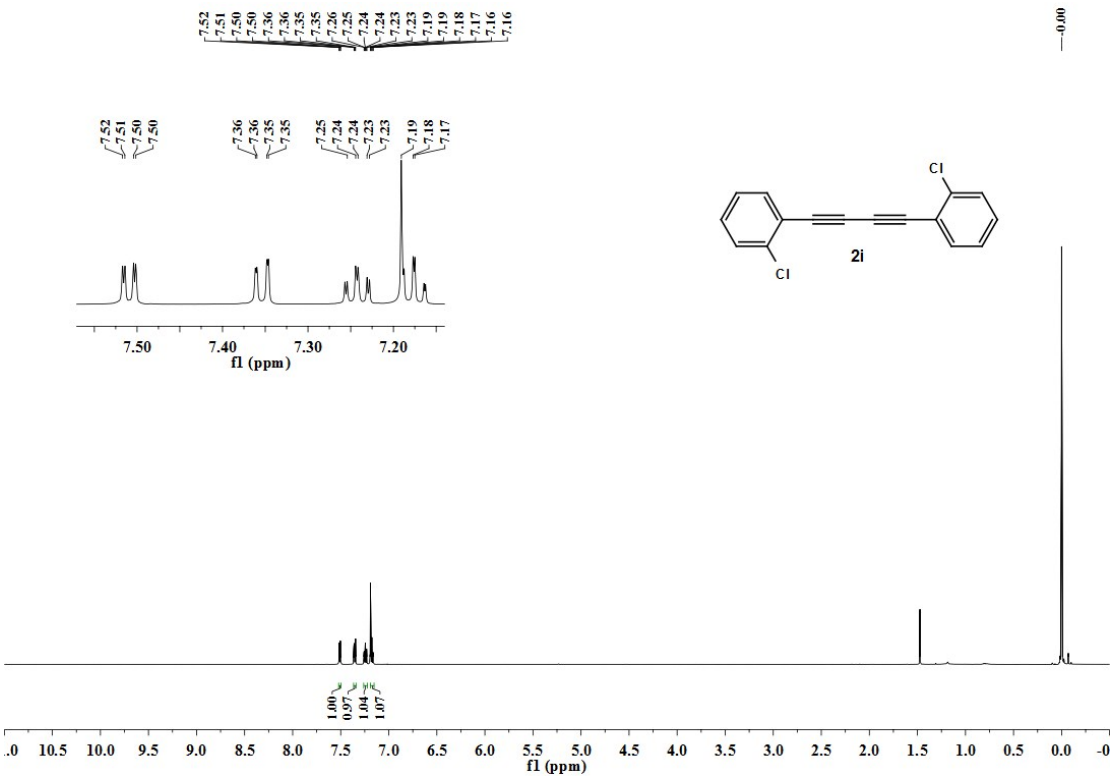

7.47
7.46
7.46
7.34
7.34
7.33
7.33
7.28
0.01
Cl
Cl
2g
7.70
7.60
7.50
7.40
7.30
f1 (ppm)
1.00
1.00
f1 (ppm)

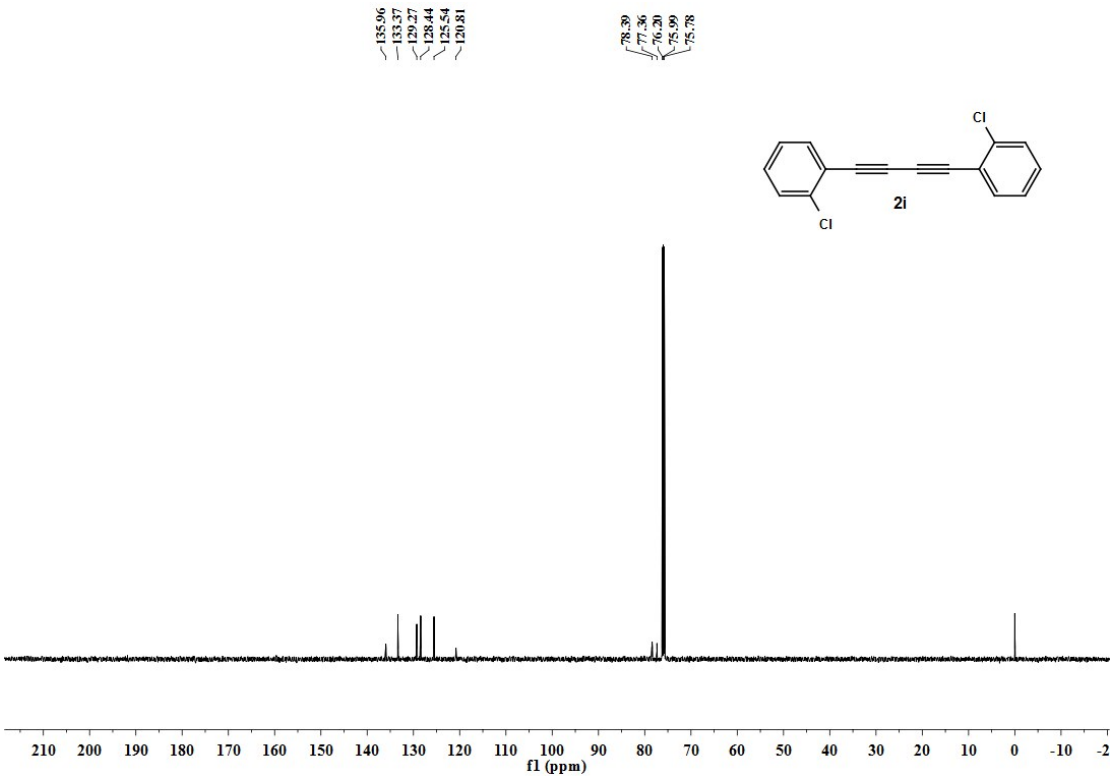

132.68
128.85
127.88
121.77
76.20
75.99
75.78
Cl
Cl
2g
f1 (ppm)

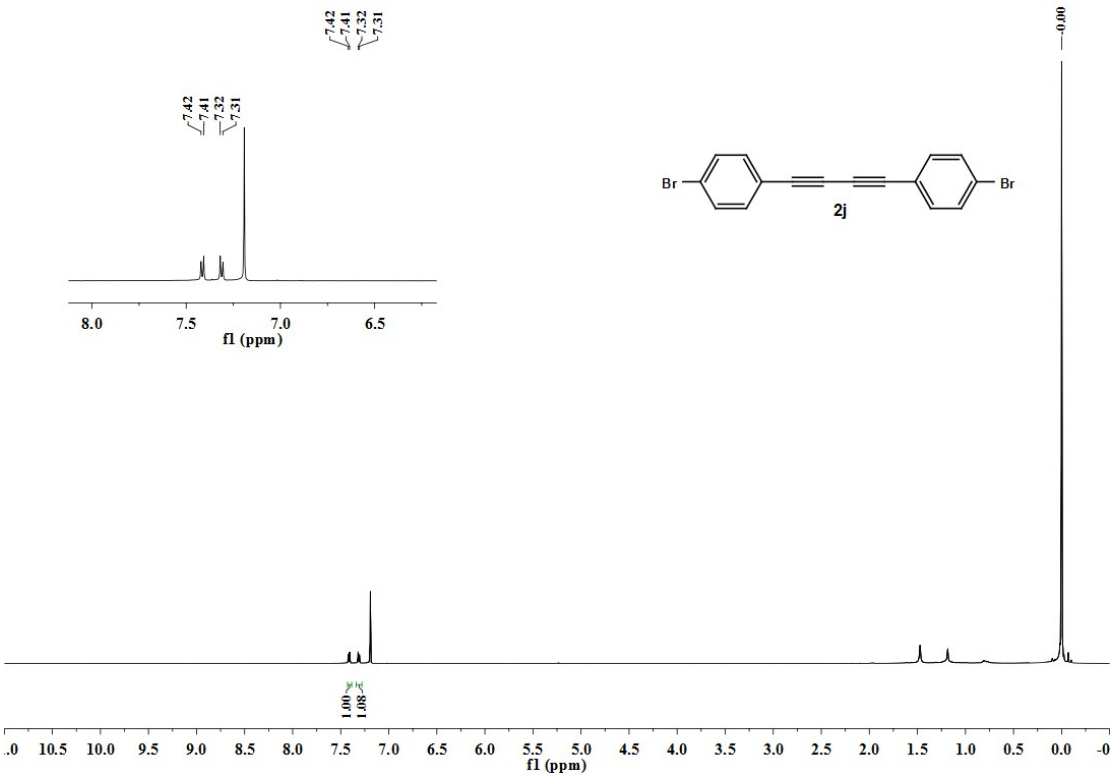

7.44
7.44
7.35
7.33
7.30
7.30
7.30
7.28
7.28
7.22
7.21
7.20
7.19
0.00
Cl
2h
Cl
8.5
8.0
7.5
7.0
6.5
f1 (ppm)

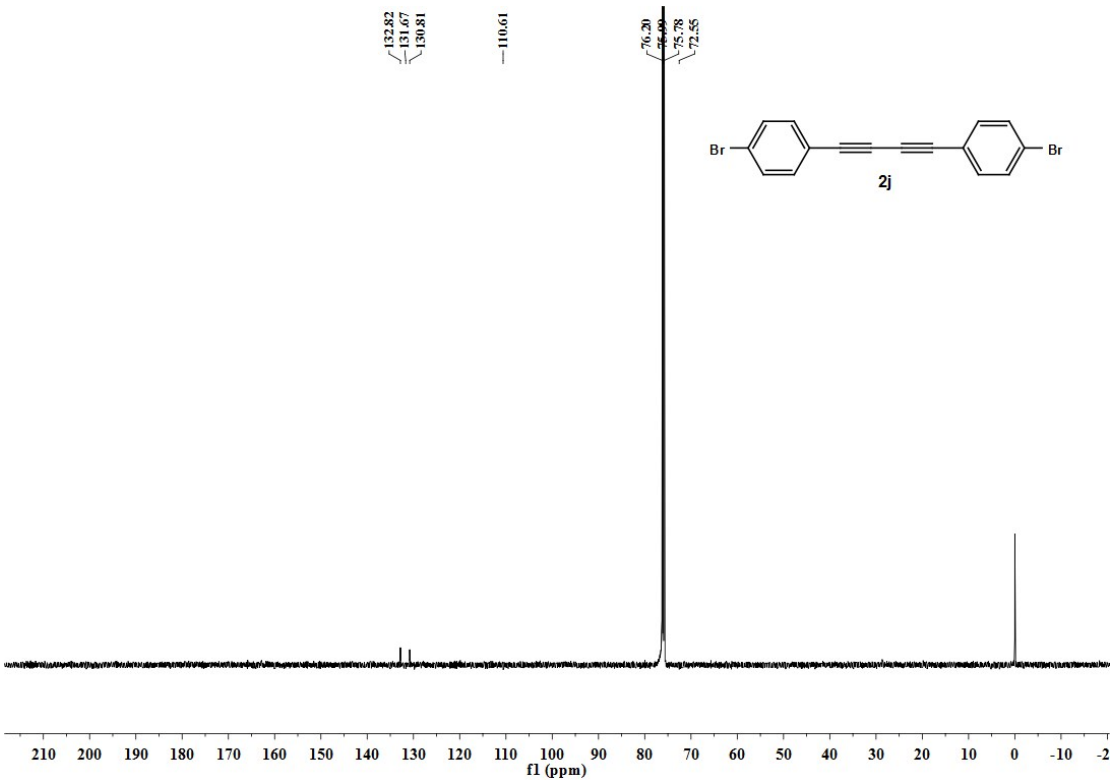

1.00
1.13
1.10
1.03
f1 (ppm)

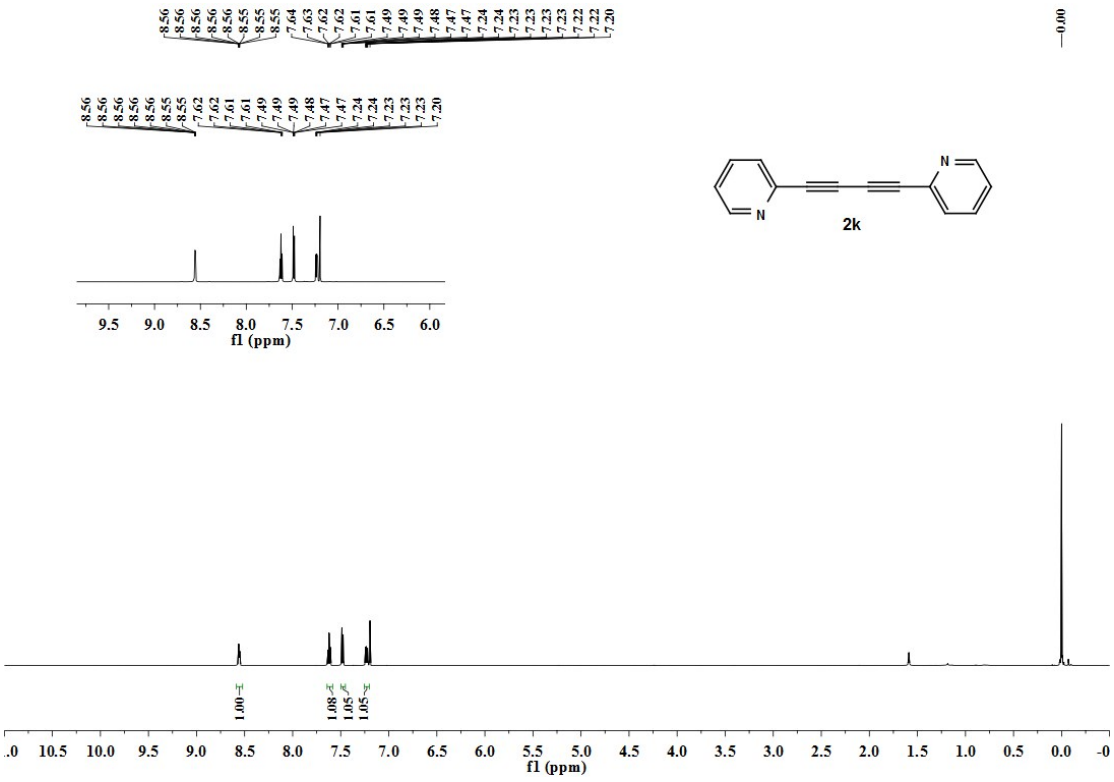

133.34
131.25
129.64
128.71
122.26
79.53
76.20
75.99
75.78
73.65
Cl
2h
Cl
f1 (ppm)

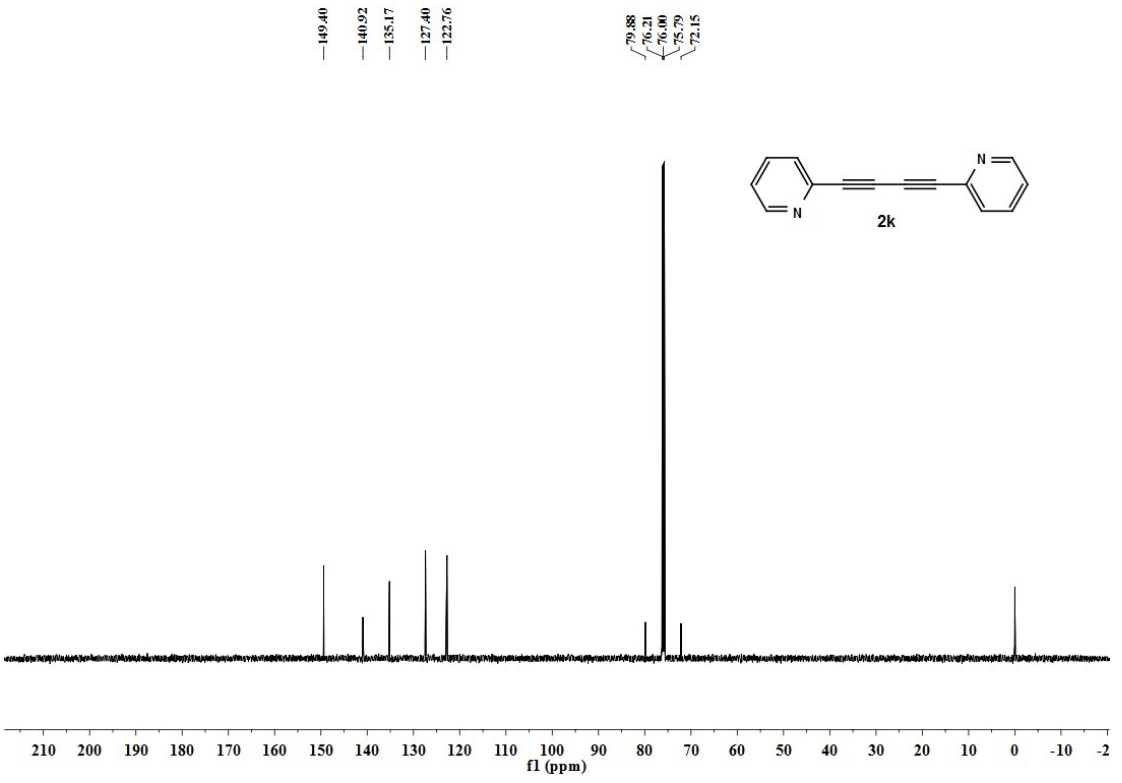

7.52
7.51
7.50
7.50
7.36
7.36
7.35
7.35
7.26
7.25
7.24
7.24
7.23
7.23
7.19
7.19
7.18
7.17
7.16
7.16
0.00
7.52
7.51
7.50
7.50
7.36
7.36
7.35
7.35
7.25
7.24
7.24
7.23
7.23
7.19
7.18
7.17
7.50
7.40
7.30
7.20
f1 (ppm)
Cl
Cl
2i
1.00
0.97
1.04
1.07
10.5
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

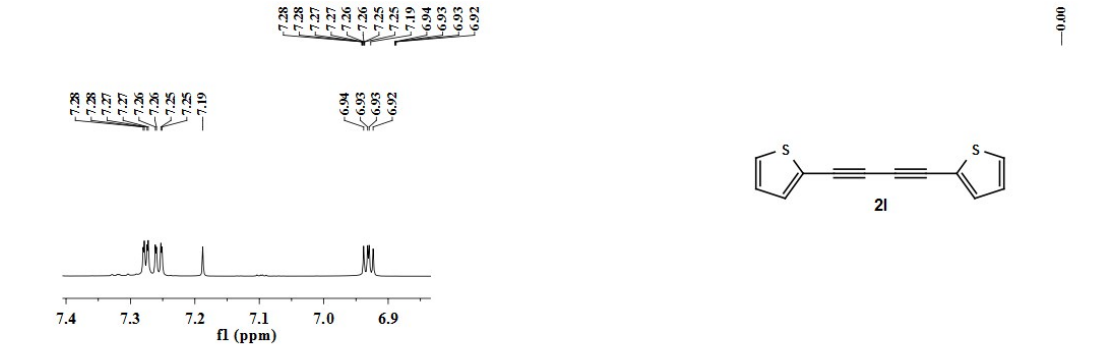

135.96
133.37
129.27
128.44
125.54
120.81
78.39
77.36
76.20
75.99
75.78
Cl
Cl
2i
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
-2
f1 (ppm)

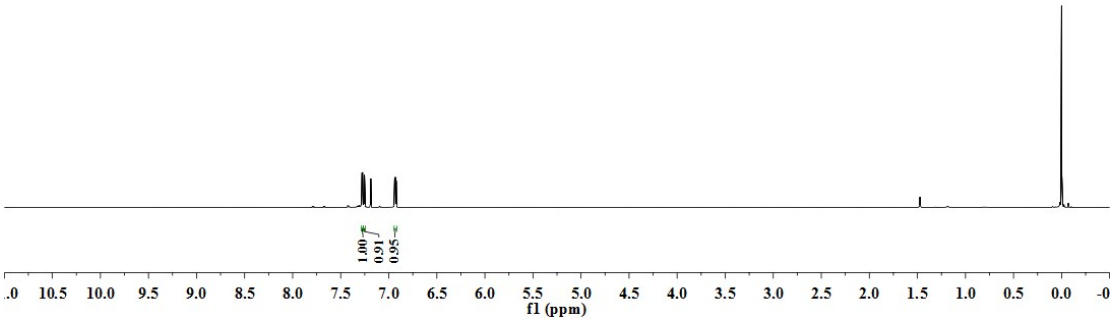

7.42
7.41
7.32
7.31
8.0
7.5
7.0
6.5
f1 (ppm)
Br
Br
2j
0.00
1.00
1.08
f1 (ppm)

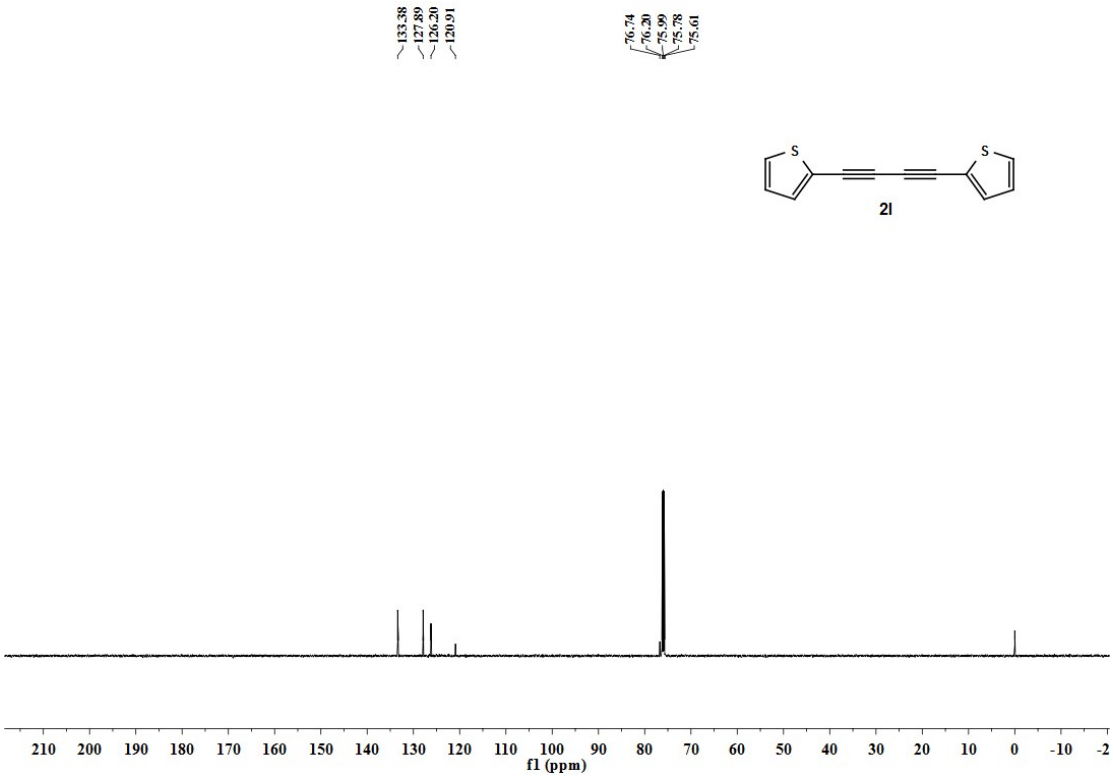

132.82
131.67
130.81
110.61
76.20
75.78
72.55
Br
Br
2j
f1 (ppm)

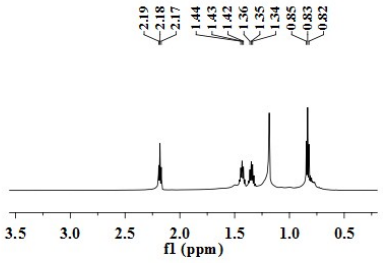

8.56
8.56
8.56
8.56
8.56
8.55
8.55
8.55
7.64
7.63
7.62
7.62
7.61
7.61
7.49
7.49
7.49
7.48
7.47
7.47
7.24
7.24
7.23
7.23
7.23
7.23
7.22
7.22
7.20
0.00
N
N
2k
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0
f1 (ppm)
1.00
1.08
1.05
1.05
.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0
f1 (ppm)

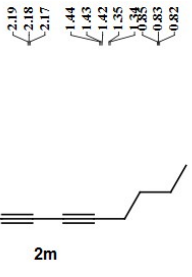

149.40
140.92
135.17
127.40
122.76
79.88
76.21
76.00
75.79
72.15
N
N
2k
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10 -2
f1 (ppm)

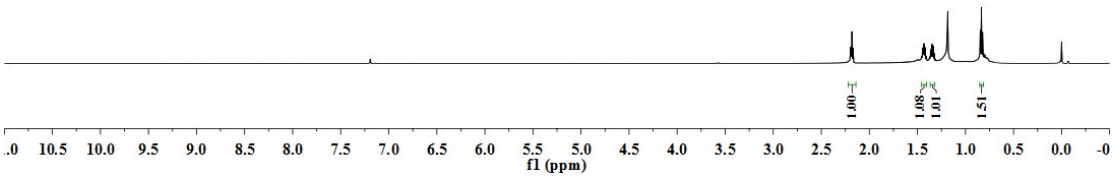

7.28
7.28
7.27
7.27
7.26
7.26
7.25
7.25
7.19
6.94
6.93
6.93
6.92
0.00
S
S
2l
7.4
7.3
7.2
7.1
7.0
6.9
f1 (ppm)

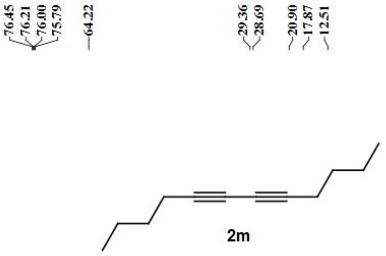

1.00
0.91
0.95
f1 (ppm)

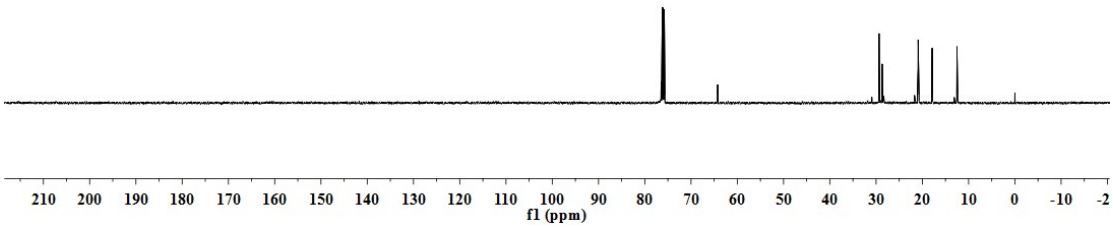

133.38
127.89
126.20
120.91
76.74
76.20
75.99
75.78
75.61
S
S
2l
f1 (ppm)

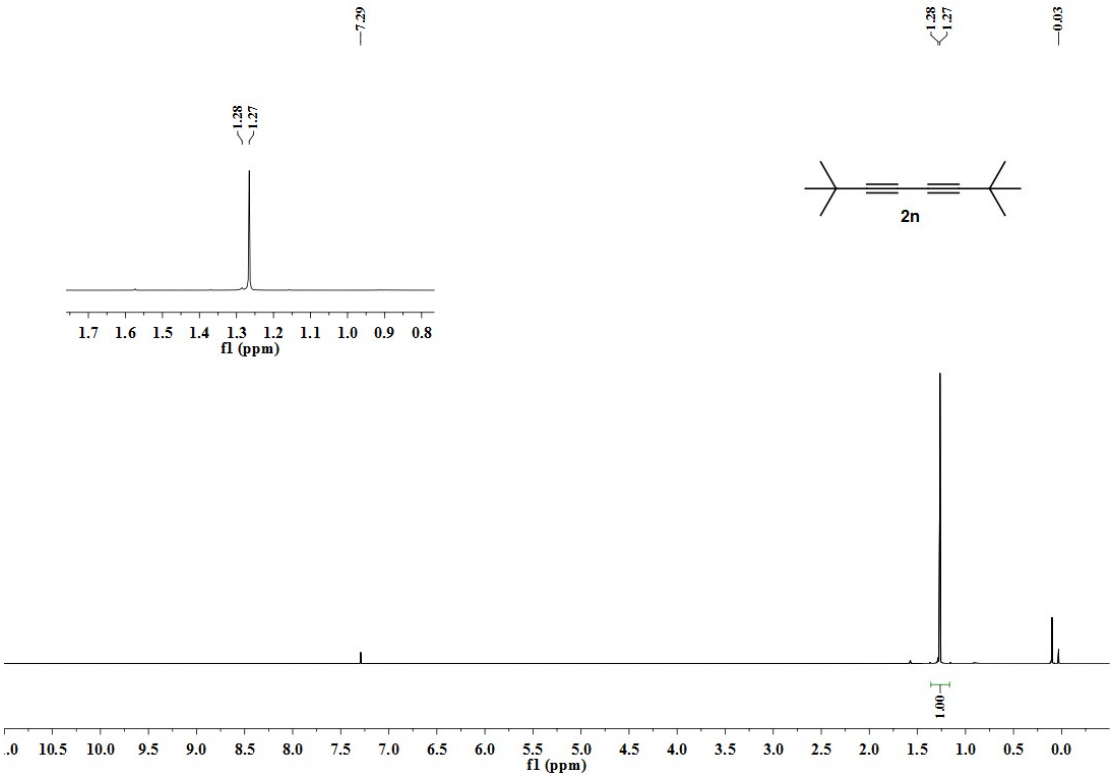

2.19
2.18
2.17
1.44
1.43
1.42
1.36
1.35
1.34
0.85
0.83
0.82
3.5
3.0
2.5
2.0
1.5
1.0
0.5
f1 (ppm)

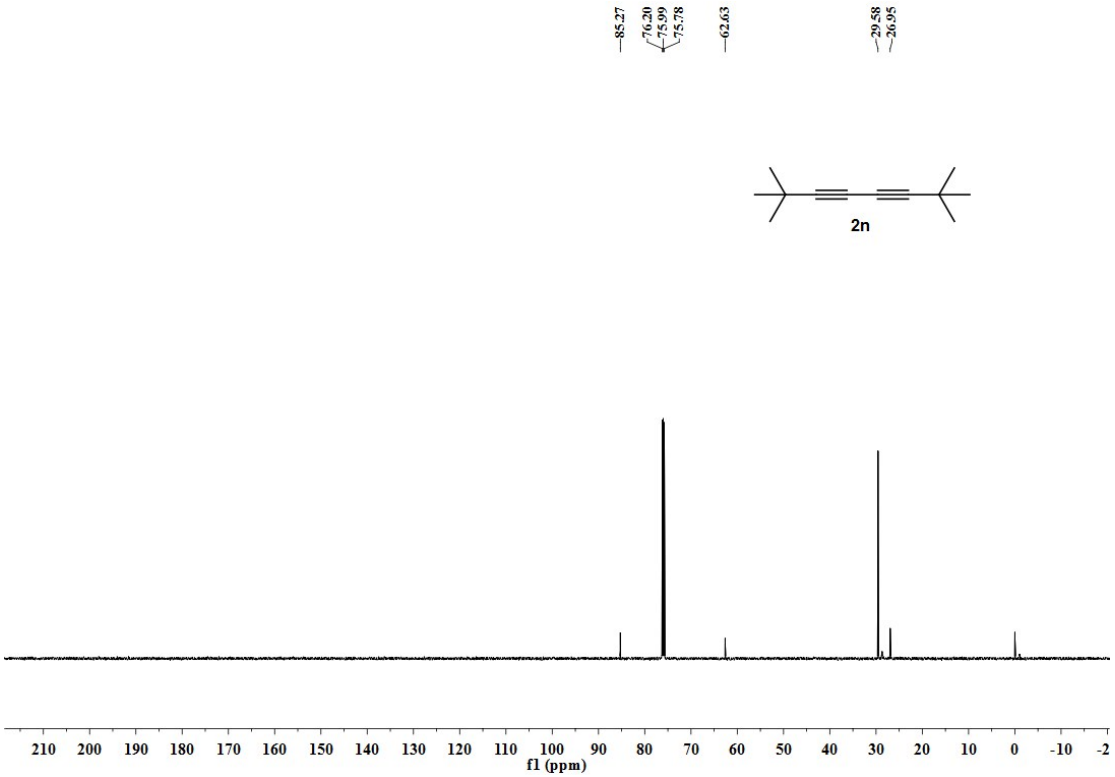

2.19
2.18
2.17
1.44
1.43
1.42
1.35
0.83
0.82
2m

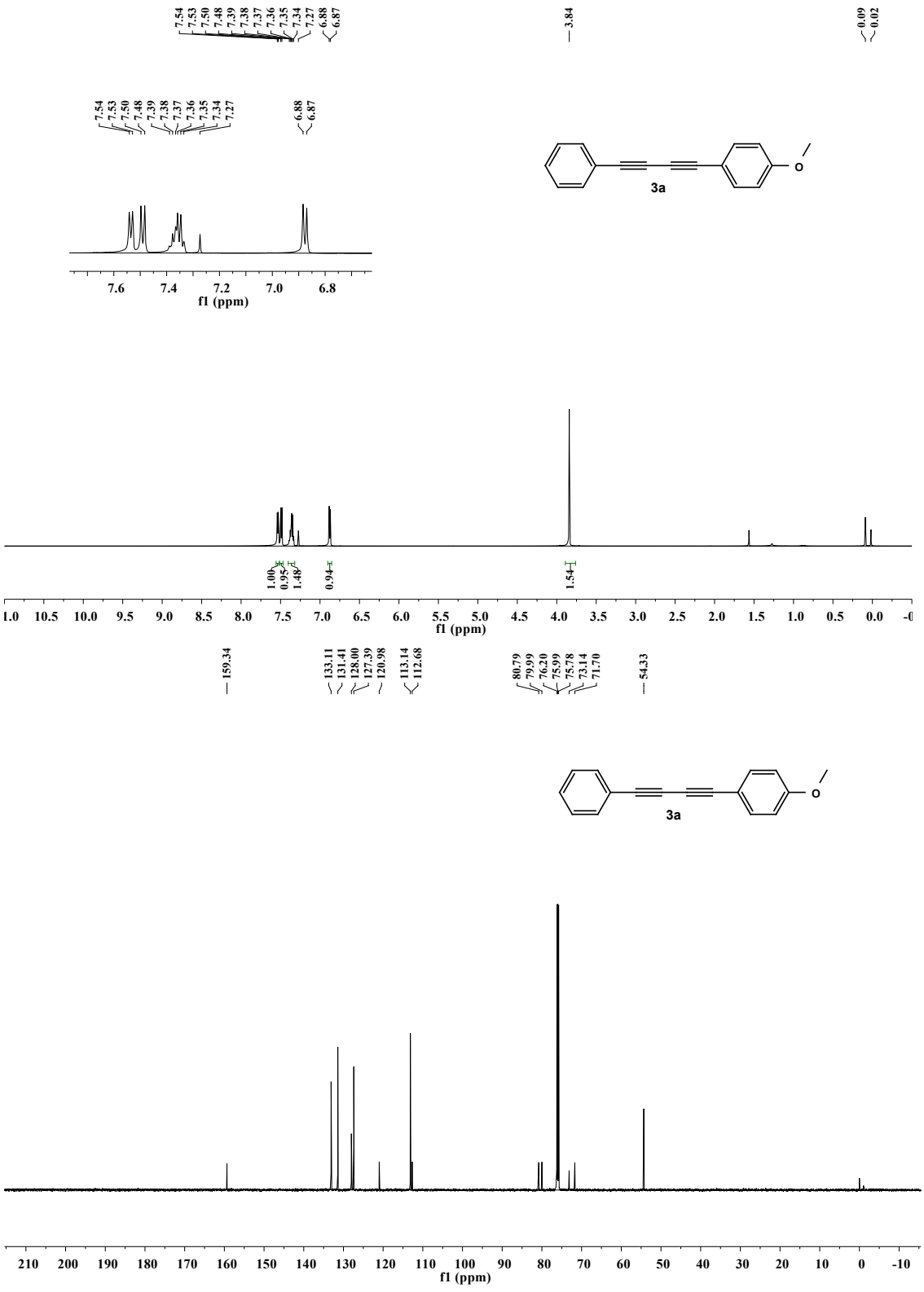

1.00
1.08
1.01
1.51
f1 (ppm)

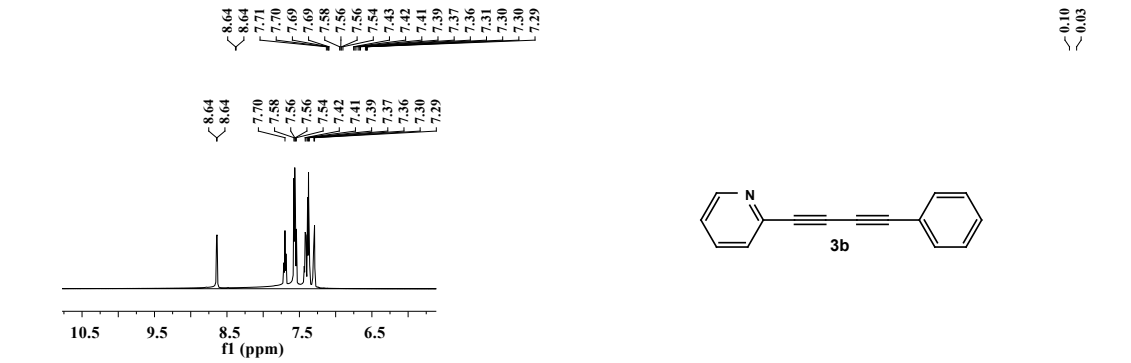

76.45
76.21
76.00
75.79
64.22
29.36
28.69
20.90
17.87
12.51
2m

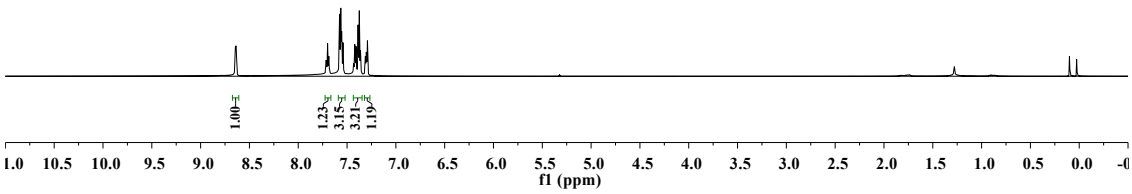

f1 (ppm)

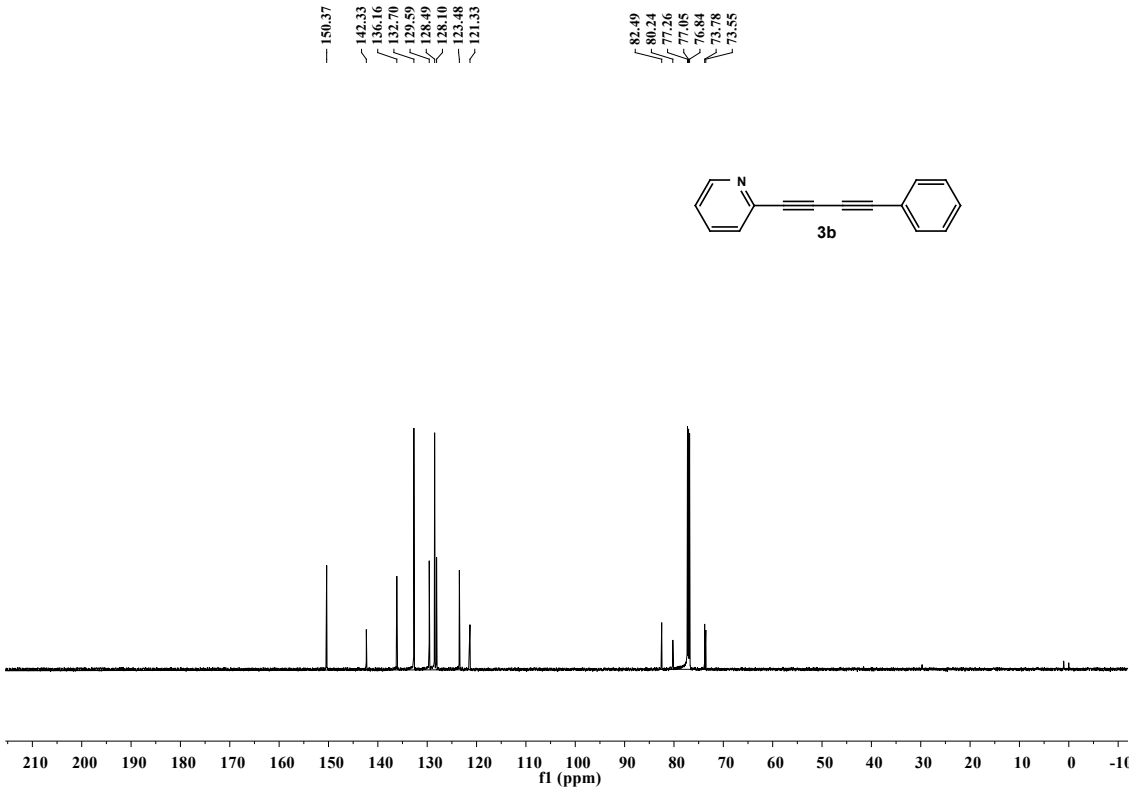

7.29
1.28
1.27
0.03
1.28
1.27
2n
1.7 1.6 1.5 1.4 1.3 1.2 1.1 1.0 0.9 0.8
f1 (ppm)
1.00
.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)

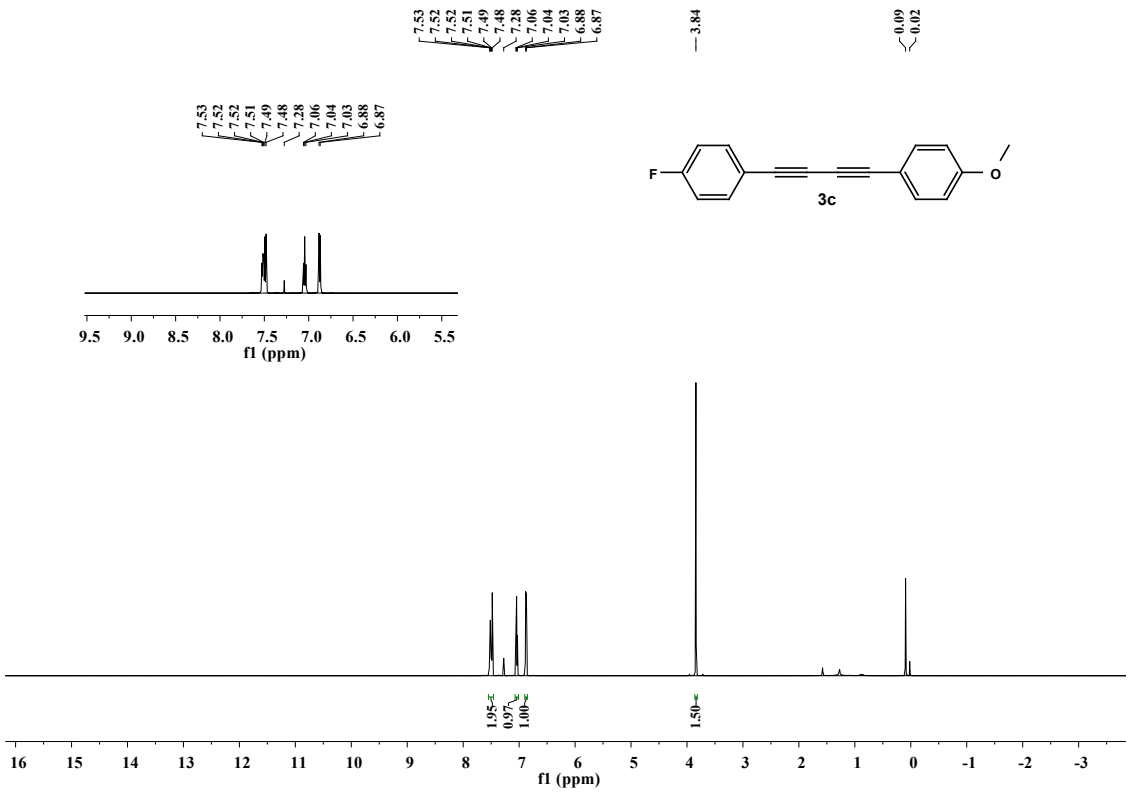

85.27
76.20
75.99
75.78
62.63
29.58
26.95
2n
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10 -2
f1 (ppm)

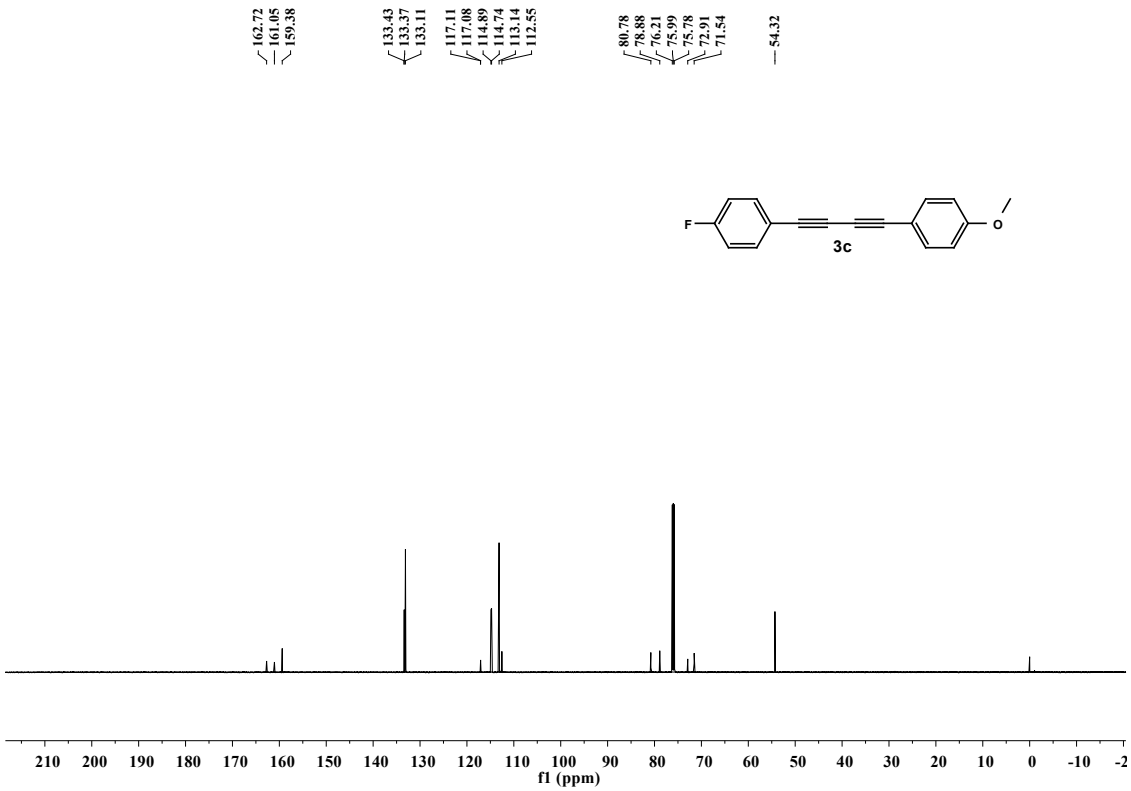

7.54
7.53
7.50
7.48
7.39
7.38
7.37
7.36
7.35
7.34
7.27
6.88
6.87
3.84
0.09
0.02
O
3a
7.6
7.4
7.2
7.0
6.8
f1 (ppm)
1.00
0.95
1.48
0.94
1.54
f1 (ppm)
159.34
133.11
131.41
128.00
127.39
120.98
113.14
112.68
80.79
79.99
76.20
75.99
75.78
73.14
71.70
54.33
O
3a
f1 (ppm)


8.64
8.64
7.71
7.70
7.70
7.69
7.69
7.58
7.56
7.56
7.54
7.43
7.42
7.41
7.39
7.37
7.36
7.31
7.30
7.30
7.29
0.10
0.03
8.64
8.64
7.70
7.58
7.56
7.56
7.54
7.42
7.41
7.39
7.37
7.36
7.30
7.29
10.5
9.5
8.5
7.5
6.5
f1 (ppm)
N
3b

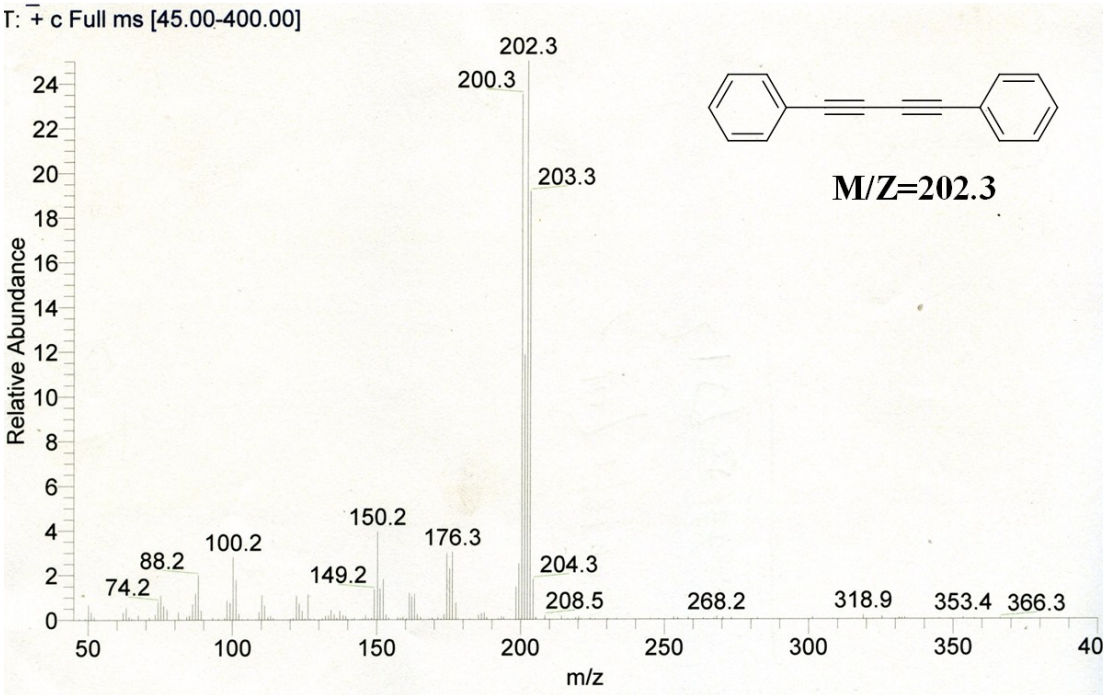

1.00
1.23
3.15
3.21
1.19
1.0
10.5
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

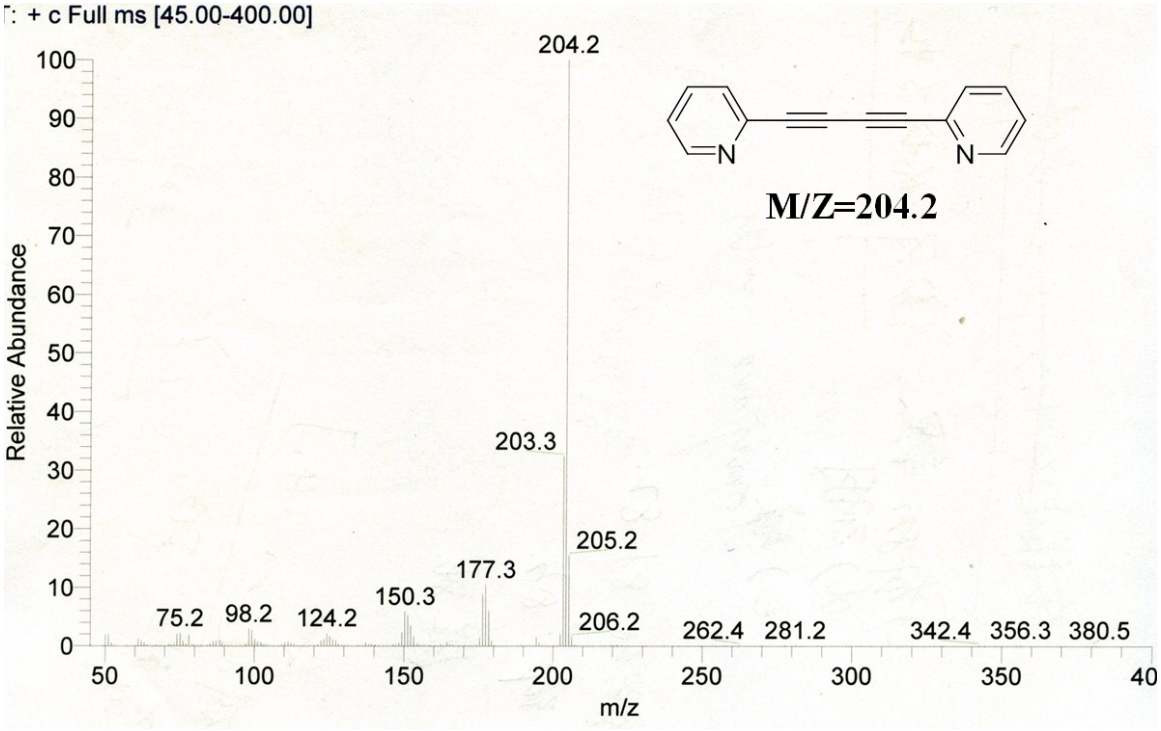

150.37
142.33
136.16
132.70
129.59
128.49
128.10
123.48
121.33
82.49
80.24
77.26
77.05
76.84
73.78
73.55
N
3b
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)


7.53
7.52
7.52
7.51
7.49
7.48
7.28
7.06
7.04
7.03
6.88
6.87
3.84
0.09
0.02
F
O
3c
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5
f1 (ppm)
1.95
0.97
1.00
1.50
16 15 14 13 12 11 10 9 8 7 6 5 4 3 2 1 0 -1 -2 -3
f1 (ppm)


162.72
161.05
159.38
133.43
133.37
133.11
117.11
117.08
114.89
114.74
113.14
112.55
80.78
78.88
76.21
75.99
75.78
72.91
71.54
54.32
F
O
3c
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10 -2
f1 (ppm)

7. MS spectra of 2a, 2k.





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