Copper(I)-Catalyzed Homo-Coupling of Terminal Alkynes at Room Temperature under Solvent and Base Free Conditions Using O_2 as an Oxidant

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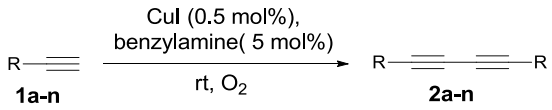
Experimental Section

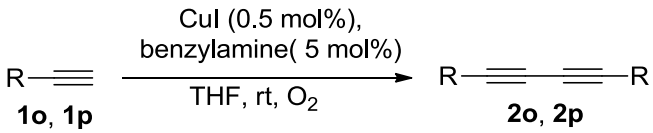
All reagents were used directly without further purification. Silica gel was purchased from Qing Dao Hai Yang Chemical Industry Co. All melting points were determined on a Beijing Science Instrument Dianguang Instrument Factory XT4B melting point apparatus and are uncorrected. ^{1}H and ^{13}C NMR spectra were recorded at 400 and 100 MHz for $CDCl_3$ solutions. HRMS-ESI spectra were obtained on Agilent 6450 spectrometer. IR data were recorded on a Nicolet iS10 spectrometer. The products listed below were determined by ^{1}H, ^{13}C NMR. PE is petroleum ether (60–90 ^{o}C).

General Procedure for the Preparation of symmetric 1,3-diynes 2a–n:



A mixture of CuI (2.9 mg, 0.015 mmol), benzylamine (16 mg, 0.15 mmol) and alkyne **1** (3 mmol) was stirred at room temperature under 1 atm O_2 for 12–48 h. After **1** was exhausted completely (monitored by TLC or by GC for **2l**, **2m**), the crude products was purified by chromatography (silica gel, 1% EtOAc in PE or 20% EtOAc in PE for **2j**) to give **2**.

General Procedure for the Preparation of symmetric 1,3-diynes 2o, 2p:



A mixture of CuI (2.9 mg, 0.015 mmol), benzylamine (16 mg, 0.15 mmol) and alkyne **1** (3 mmol) in THF (3 mL) was stirred at room temperature under 1 atm O_2 for 16–20 h. After **1** was exhausted completely (monitored by TLC), the crude products was purified by chromatography (silica gel, 30% EtOAc in PE) to give **2**.

In 2008, Mizuno et al. reported that monomeric dicopper-substituted silicotungstate was an effective oxidative alkyne homo-coupling catalyst with a TON of 468, which is the highest one among copper-catalyzed oxidative homocoupling catalysts (see the reference 1 of Table S1). Other results reported after 2008 are listed in Table S1.

Table S1. Results of the Homocoupling Reaction of Phenylacetylene

Catalyst (mol%)	Additive (mol%)	Oxidant	Temp. (^oC)	Time (h)	Yield (%)	TON[a]	Ref.
CuI (0.05)	Benzylamine (5)	O_2	r.t.	24	88	1760	This work
		air	r.t.	48	67	1340	
Cu-Silicotungstate (0.2)	–	O_2	100	18	93	468	1
CuI (5)	Na_2CO_3 (200)	I_2	80	24	99	20	2
CuCl (2)	DBU[b] (100) TMEDA[c] (1.5)	O_2	r.t.	18	99	50	3
$Pd(NH_3)_2Cl_2$ (1) CuI (1)	Et_3N (300) TBAB[d] (50)	I_2	r.t.	3	99	99	4
CuI (50)	DIPEA[e] (50)	NBS	r.t.	2	93	2	5
CuNPs (400)	–	–	66	8	90	<1	6
$Cu(OH)_x/TiO_2$ (5)	–	O_2	100	0.5	90	18	7
$NiCl_2$ $6H_2O$ (5) CuI (5)	Et_3N (300) TMEDA (20)	air	r.t.	20	99	20	8
$Cu(OAc)_2$ H_2O (0.2)	Piperidine (100)	air	r.t.	3	60	299	9
Cu-Zeolite (30)	–	air	110	15	97	3	10
$Fe(acac)_3$ (10) $Cu(acac)_2$ (0.1)	K_2CO_3 (200)	air	50	8	94	940	11
$CuCl_2$ (2)	Et_3N (3)	air	60	6	96	48	12
CuCl (2)	Piperidine (10)	air	60	5	96	48	13
$CuNPs/TiO_2$ (1)	Piperidine (30)	air	65	6	96	96	14
$CuCl_2$ (10)	DBU (120)	air	r.t.	24	92	9	15
$Cu(OAc)_2$ H_2O (20)	–	air	90	10	90	5	16
CuCl (10)	TMEDA (10)	air	r.t.	1	93	9	17
$CuCl_2$ H_2O (10)	NaOAc (100)	O_2	120	1.5	99	10	18
$Cu(OH)_x$/OMS-2 (2)	–	O_2	100	0.17	99	50 666[f]	19
$Cu(OAc)_2$ (5)	AFIL 1 (10)[g] NFIS 1 (10)[h]	O_2	60	6	99	20	20
CuI (5)	KF/Al_2O_3 (60 w%)	air	r.t.	0.17	99	19	21
Cu_2SO_4 $5H_2O$ (5)	KOAc (100)	I_2	120	24	99	20	22
CuCl (5)	–	air	90	7	96	19	23
CuI (5)	NaOAc (100)	air	90	30	97	19	24
CuI (5)	Et_3N (300) TMEDA (10)	air	r.t.	20	91	18	25
$Cu(OAc)_2$ H_2O (10)	–	air	160	7	85	9	26
CuI complex (1)	Piperidine (10)	air	r.t.	2	94	94	27
CuCl (10)	TMEDA (30)	air	20	1.5	97	10	28

[a] TON = (phenylacetylene consumed (mol))/(Cu catalyst used (mol)). [b] DBU = 1,8-diazabicyclo[5.4.0]undec-7-ene. [c] TMEDA = *N*,*N*,*N*',*N*'-tetramethylethylenediamine. [d] TBAB = tetrabutyl ammonium bromide. [e] DIPEA = diisopropylethylamine. [f] For 14 repeated runs. [g] Amine-functionalized ionic liquid. [h] 1-Methyl-3-(4-nitrobenzyl)imidazolium hexafluorophosphate.

Reference of Table S1:

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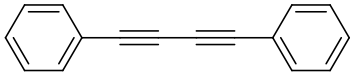
Data of diynes



2a

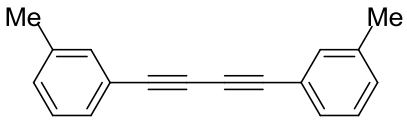
1,4-Diphenyl-1,3-butadiyne (2a)[1]:

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.60-7.46 (m, 4H), 7.45-7.27 (m, 6H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 132.5, 129.2, 128.4, 121.8, 81.6, 73.9.

2b

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

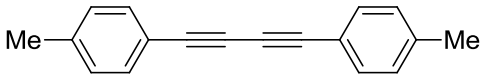
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.49 (d, *J* = 7.6 Hz, 2H), 7.30-7.05 (m, 6H), 2.48 (s, 6H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 141.6, 132.9, 129.5, 129.1, 125.6, 121.7, 81.1, 77.5, 20.7.



2c

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

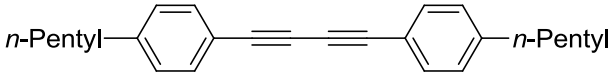
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.36-7.28 (m, 4H), 7.25-7.12 (m, 4H), 2.32 (s, 6H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 138.1, 132.9, 130.1, 129.6, 128.3, 121.6, 81.6, 73.6, 21.2.



2d

1,4-Bis(4-methylphenyl)-1,3-butadiyne (2d)[1]:

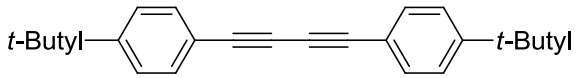
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.41 (d, *J* = 8.0 Hz, 4H), 7.13 (d, *J* = 8.1 Hz, 4H), 2.36 (s, 6H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 139.5, 132.4, 129.2, 118.8, 81.5, 73.4, 21.6.



2e

1,4-Bis(4-*n*-pentylphenyl)-1,3-butadiyne (2e)[2]:

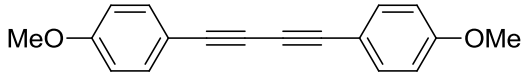
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.42 (d, *J* = 7.7 Hz, 4H), 7.12 (d, *J* = 7.9 Hz, 4H), 2.66-2.52 (m, 4H), 1.65-1.53 (m, 4H), 1.37-1.25 (m, 8H), 0.88 (m, 6H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 144.4, 132.4, 128.5, 119.0, 81.6, 73.5, 35.9, 31.4, 30.8, 22.5, 14.0.



2f

1,4-Bis(4-*t*-butylphenyl)-1,3-butadiyne (2f)[3]:

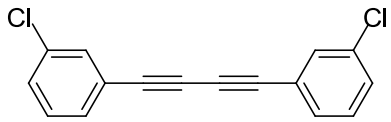
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.50-7.42 (m, 4H), 7.40-7.30 (m, 4H), 1.31 (s, 18H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 152.5, 132., 125.5, 118.8, 81.5, 73.5, 34.9, 31.0.



2g

1,4-Bis(4-methoxyphenyl)-1,3-butadiyne (2g)[1]:

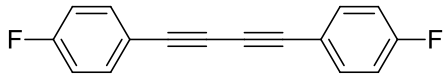
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.45 (d, *J* = 8.6 Hz, 4H), 6.84 (d, *J* = 8.6 Hz, 4H), 3.81 (s, 6H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 160.2, 134.0, 114.1, 113.9, 81.2, 72.9, 55.3.



2h

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

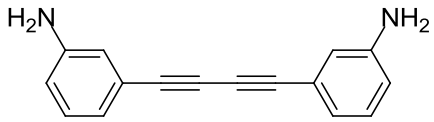
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.49 (s, 2H), 7.43-7.36 (m, 2H), 7.36-7.32 (m, 2H), 7.25 (dd, *J* = 10.0, 5.8 Hz, 2H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 134.3, 132.2, 130.6, 129.7, 123.2, 80.5, 74.7.



2i

1,4-Bis(4-fluorophenyl)-1,3-butadiyne (2i)[1]:

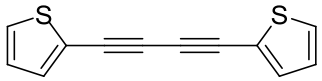
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.56-7.47 (m, 4H), 7.08-6.98 (m, 4H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 163.0 (d, *J* = 251.6 Hz), 134.5 (d, *J* = 8.7 Hz), 117.8 (d, *J* = 3.6 Hz), 115.9 (d, *J* = 22.4 Hz), 80.4, 73.5.



2j

1,4-Bis(3-aminophenyl)-1,3-butadiyne (2j)[4]:

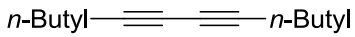
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.10 (t, *J* = 7.8 Hz, 2H), 6.97-6.89 (m, 2H), 6.84-6.77 (m, 2H), 6.68 (ddd, *J* = 8.0, 2.4, 0.9 Hz, 2H), 3.67 (s, 4H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 146.3, 129.3, 122.9, 122.4, 118.4, 116.2, 81.6, 73.4.



2k

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

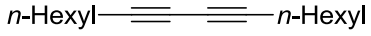
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.33 (d, *J* = 3.6 Hz, 2H), 7.30 (d, *J* = 5.1 Hz, 2H), 7.01-6.96 (m, 2H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 134.4, 128.9, 127.2, 121.8, 77.8, 76.6.



2l

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

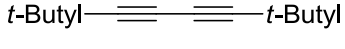
^{1}H NMR (400 MHz, $CDCl_3$) δ 2.18 (t, *J* = 6.9 Hz, 4H), 1.49-1.28 (m, 8H), 0.84 (t, *J* = 7.2 Hz, 6H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 77.3, 65.2, 30.4, 21.9, 18.8, 13.5.



2m

7,9-Hexadecadiyne (2m)[1]:

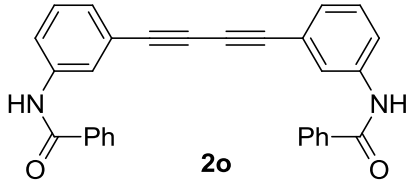
^{1}H NMR (400 MHz, $CDCl_3$) δ 2.28-2.06 (m, 4H), 1.60-1.07 (m, 16H), 0.96-0.74 (m, 6H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 77.3, 65.3, 31.3, 28.5, 28.3, 22.5, 19.1, 13.9.



2n

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

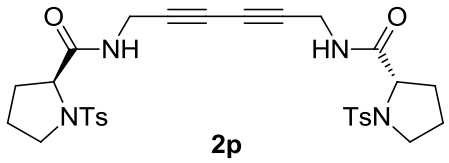
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.73 (s, 18H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 86.2, 63.7, 30.6, 27.9.



2o

***N*,*N*'-(buta-1,3-diyne-1,4-diylbis(3,1-phenylene))dibenzamide (2o):**

gray solid; m.p. 265-266 ℃; IR (KBr): ν 3287, 1645, 1580, 1424, 1307, 1534, 693 cm^{-1}; ^{1}H NMR (400 MHz, DMSO) δ 10.38 (s, 2H), 8.14-7.76 (m, 8H), 7.71-7.19 (m, 10H); ^{13}C NMR (101 MHz, DMSO) δ 166.3, 140.1, 136.0, 132.3, 129.9, 128.9, 128.2, 124.0, 122.5, 121.0, 82.3, 73.7; HRMS m/z (ESI) calcd for $C_{30}H_{21}N_2O_2(M + H)^+$ 441.1603, found 441.1601.



2p

(2*S*,2'*S*)-*N*,*N*'-(hexa-2,4-diyne-1,6-diyl)bis(1-tosylpyrrolidine-2-carboxamide) (2p):

white solid; m.p. 161-162 ℃; $[\alpha]_D^{20}$ = -100° cm^3 g^{-1} dm^{-1} (c = 0.2 g cm^{-3} in $CHCl_3$); IR (KBr): ν 3340, 1661, 1519, 1347, 666 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.73 (d, *J* = 8.2 Hz, 4H), 7.36 (d, *J* = 8.0 Hz, 4H), 7.20 (t, *J* = 5.0 Hz, 2H), 4.27 (dd, *J* = 17.9, 6.2 Hz, 2H), 4.12-4.02 (m, 4H), 3.58 (m, 2H), 3.20 (m, 2H), 2.45 (s, 6H), 2.24-2.11 (m, 2H), 1.77 (m, 2H), 1.66-1.51 (m, 4H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 170.9, 144.5, 132.7, 130.0, 127.8, 73.9, 67.5, 62.4, 49.8, 29.9, 29.8, 24.3, 21.5; HRMS m/z (ESI) calcd for $C_{30}H_{34}N_4O_6S_2Na(M + Na)^+$ 633.1817, found 633.1816.

References

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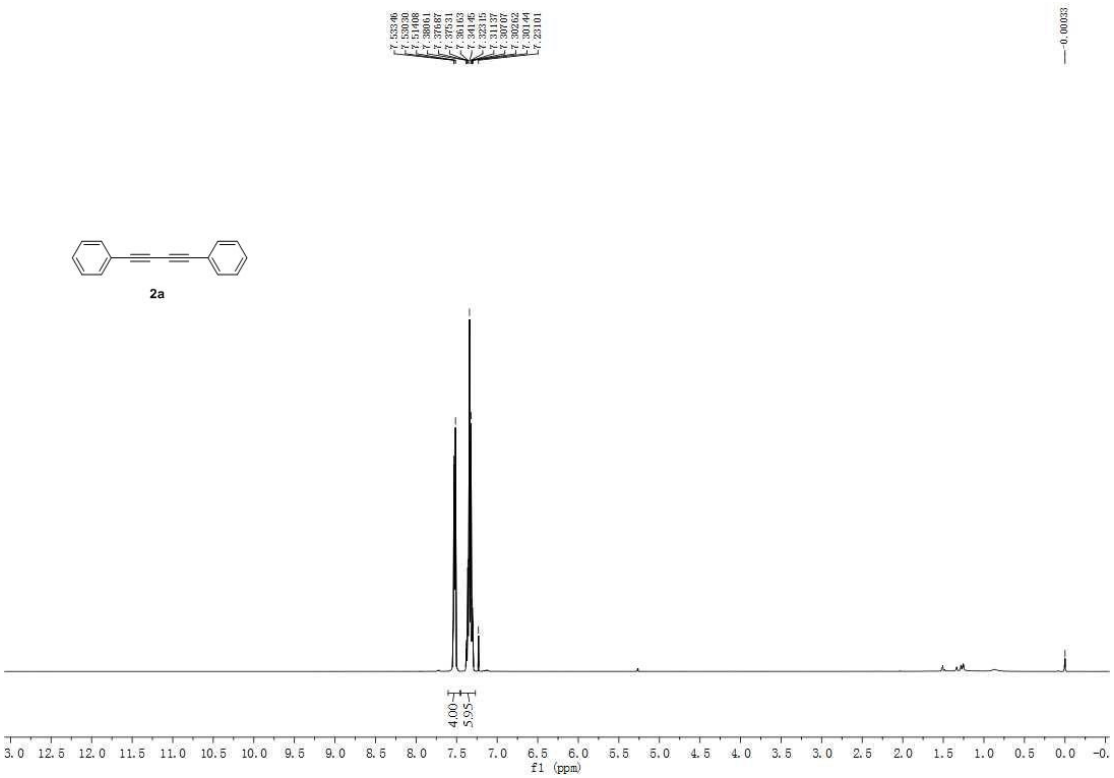
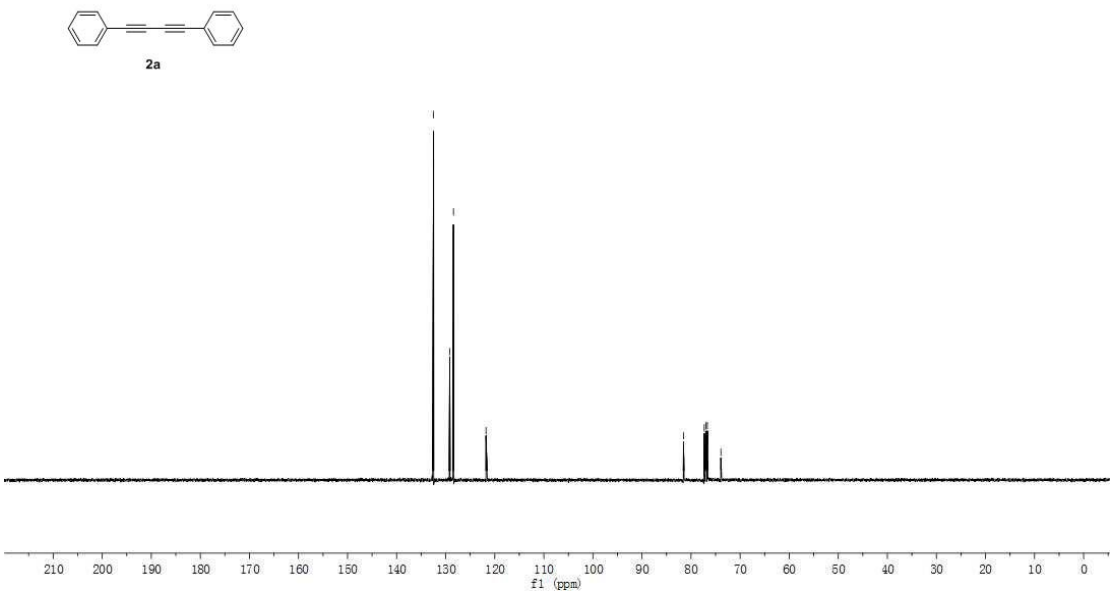
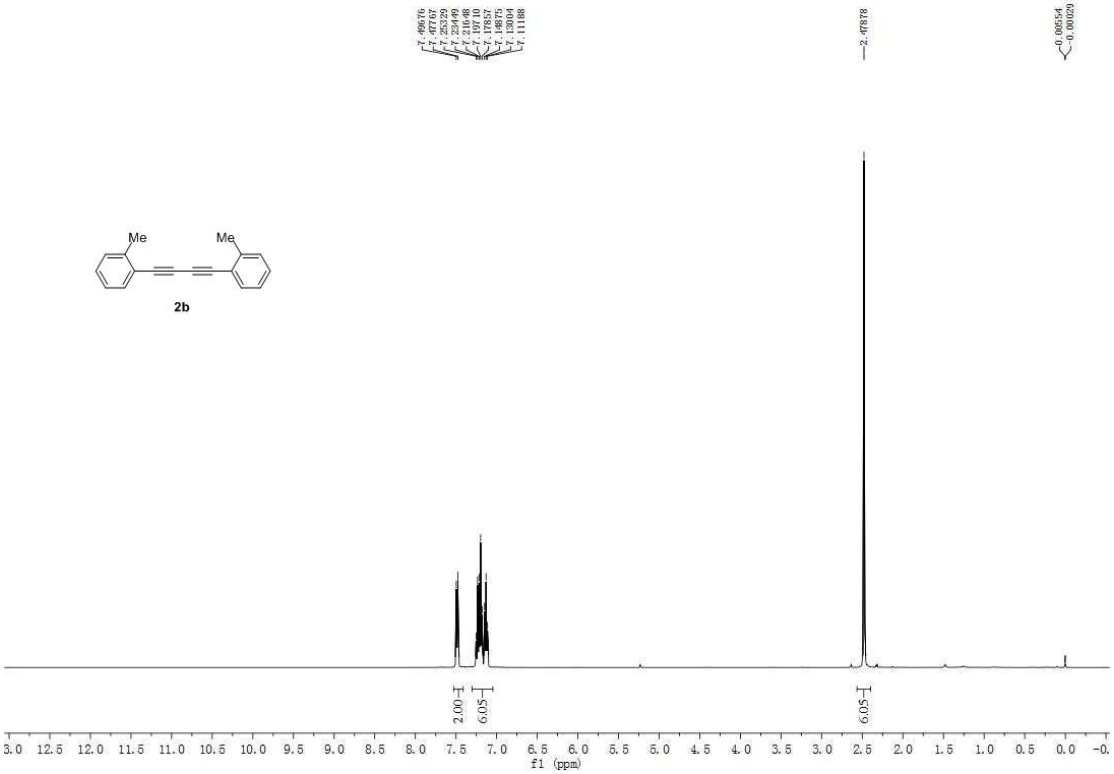
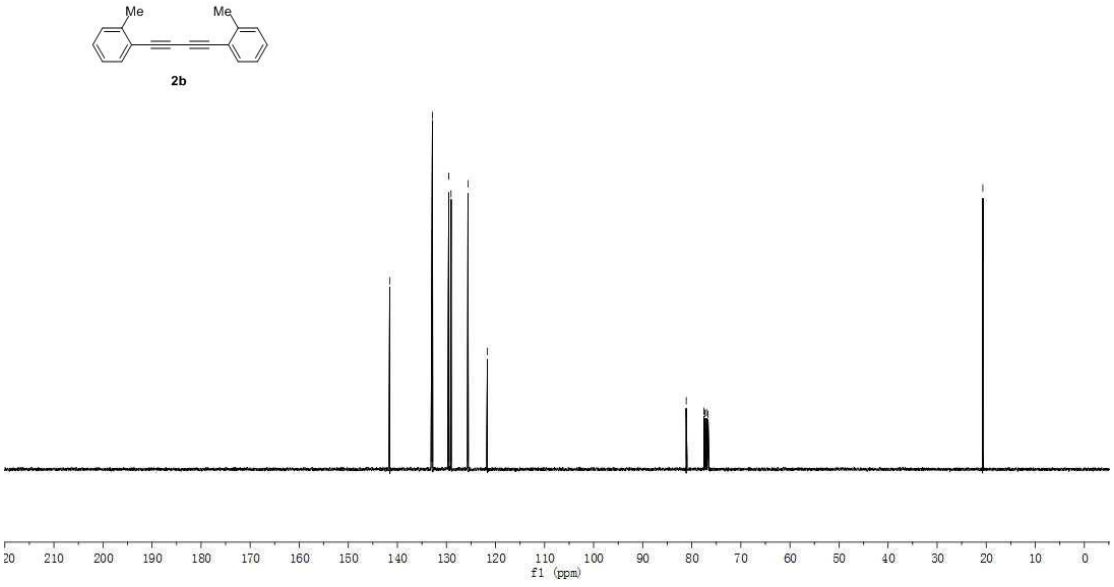
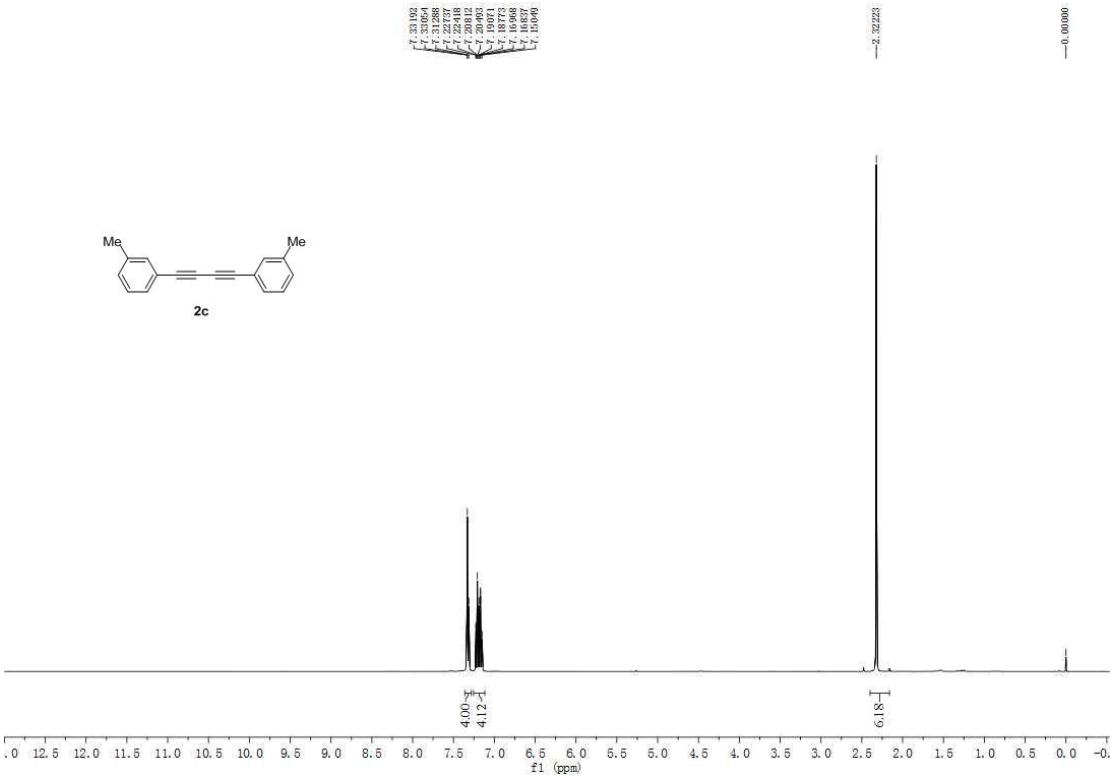

2a
4.00
5.95
f1 (ppm)


2a
f1 (ppm)


Me
Me
2b
2.00
6.05
6.05
f1 (ppm)


Me
Me
2b
f1 (ppm)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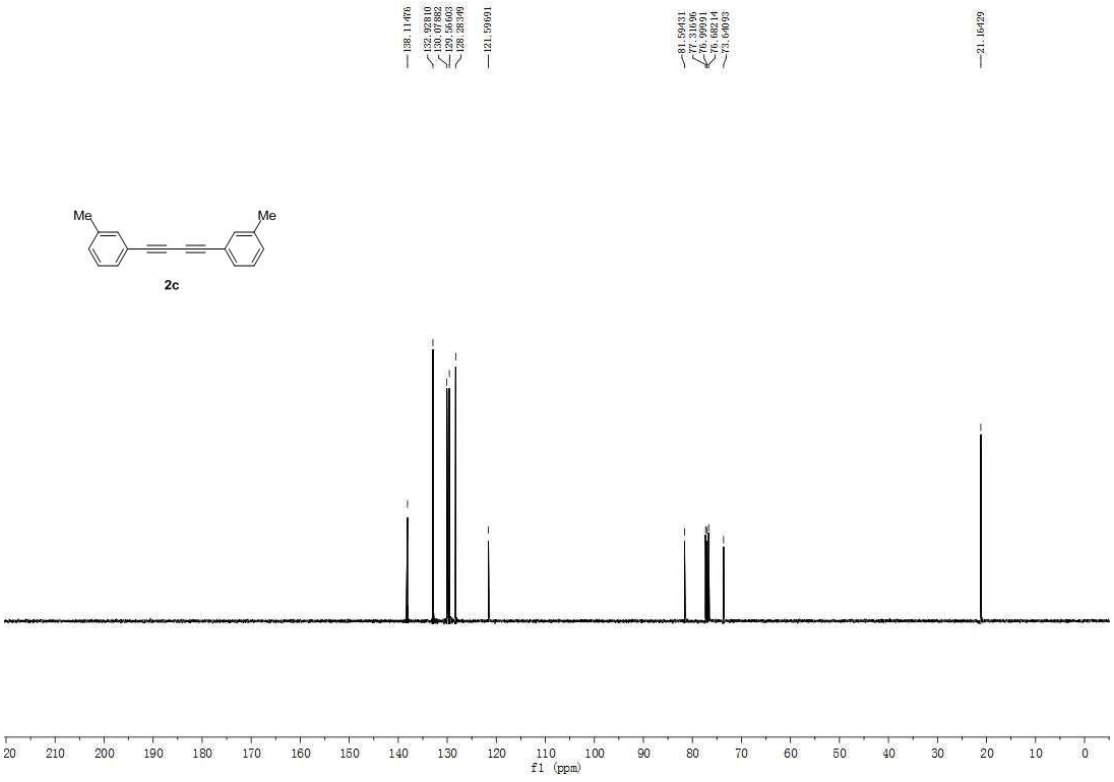
7.33064
7.31398
7.22737
7.22418
7.20812
7.20493
7.19071
7.18773
7.16968
7.16837
7.15049
2.32223
0.00000
Me
Me
2c
4.00
4.12
6.18
f1 (ppm)


138.11476
132.92810
130.07982
129.06466
128.28349
121.59691
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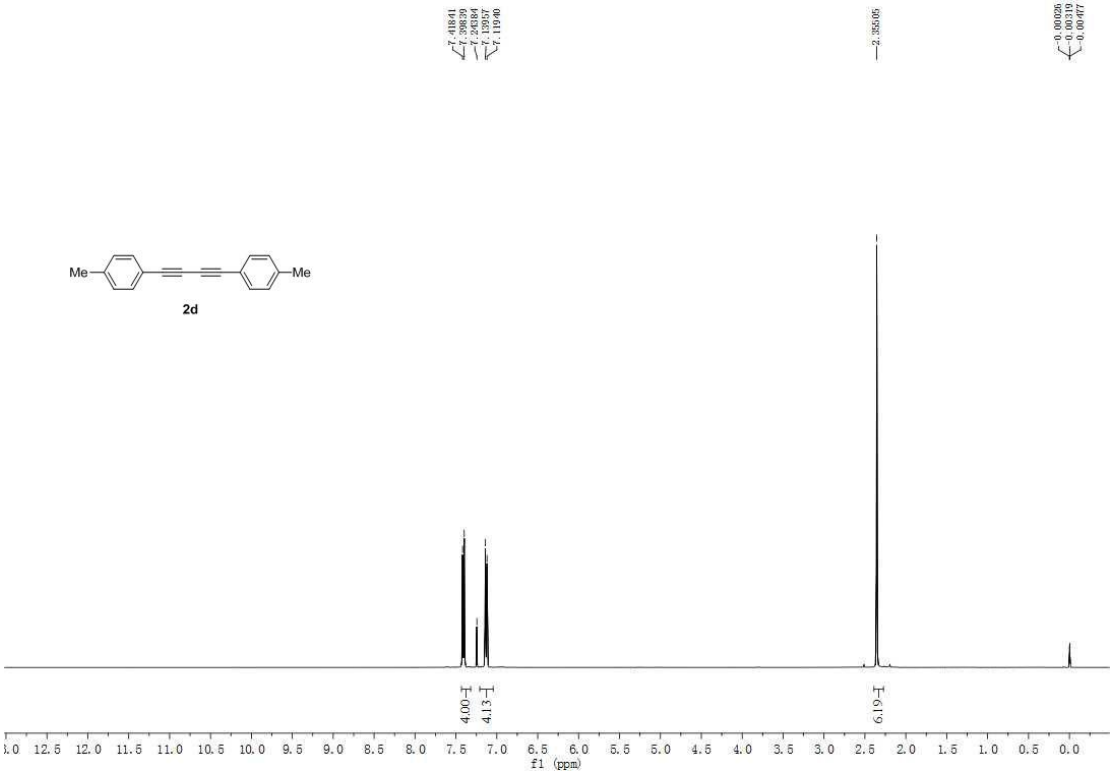
77.31696
76.99991
76.68287
73.04093
21.16429
Me
Me
2c
f1 (ppm)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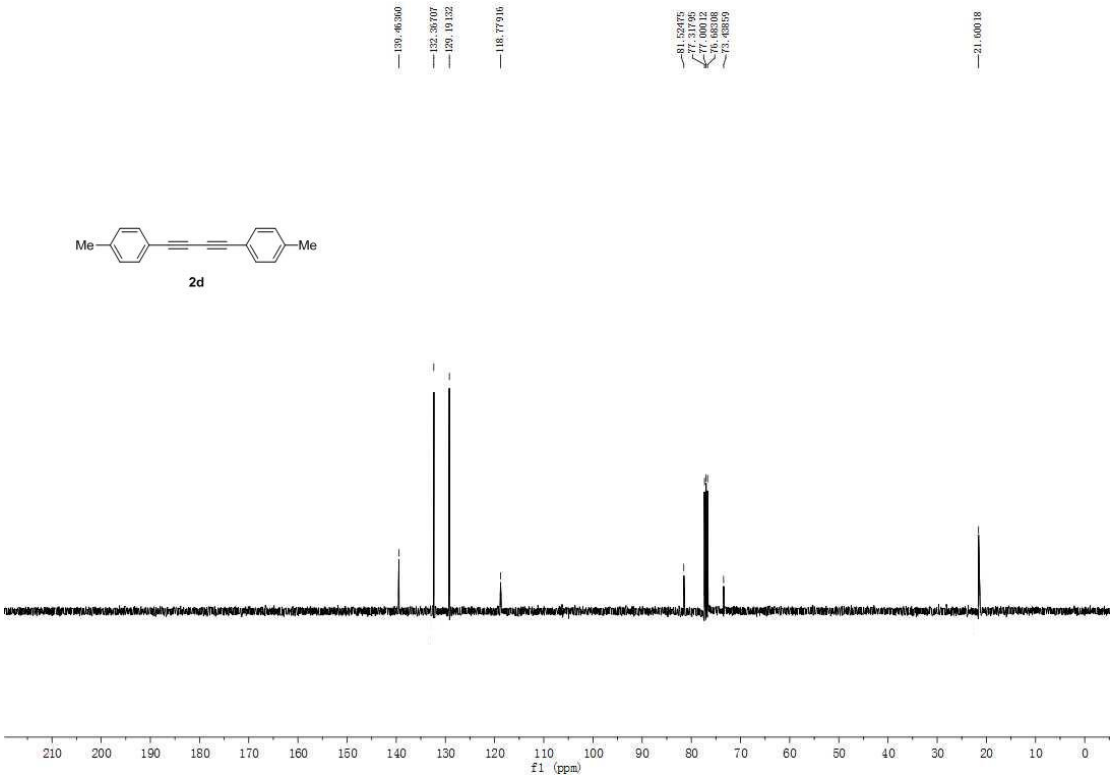
7.40679
7.24384
7.13957
7.11940
2.35505
0.00026
0.00319
0.00477
Me
Me
2d
4.00
4.13
6.19
f1 (ppm)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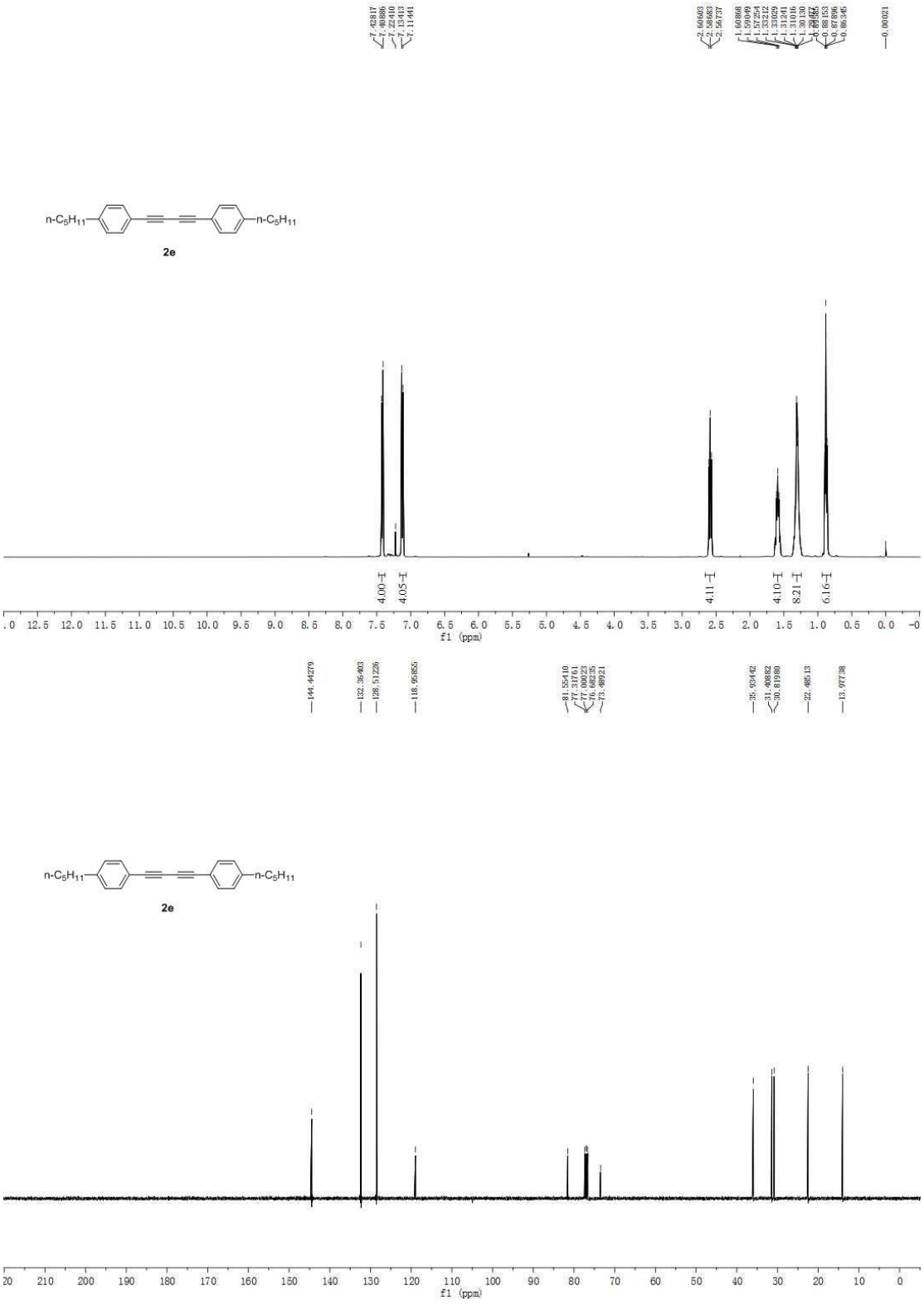
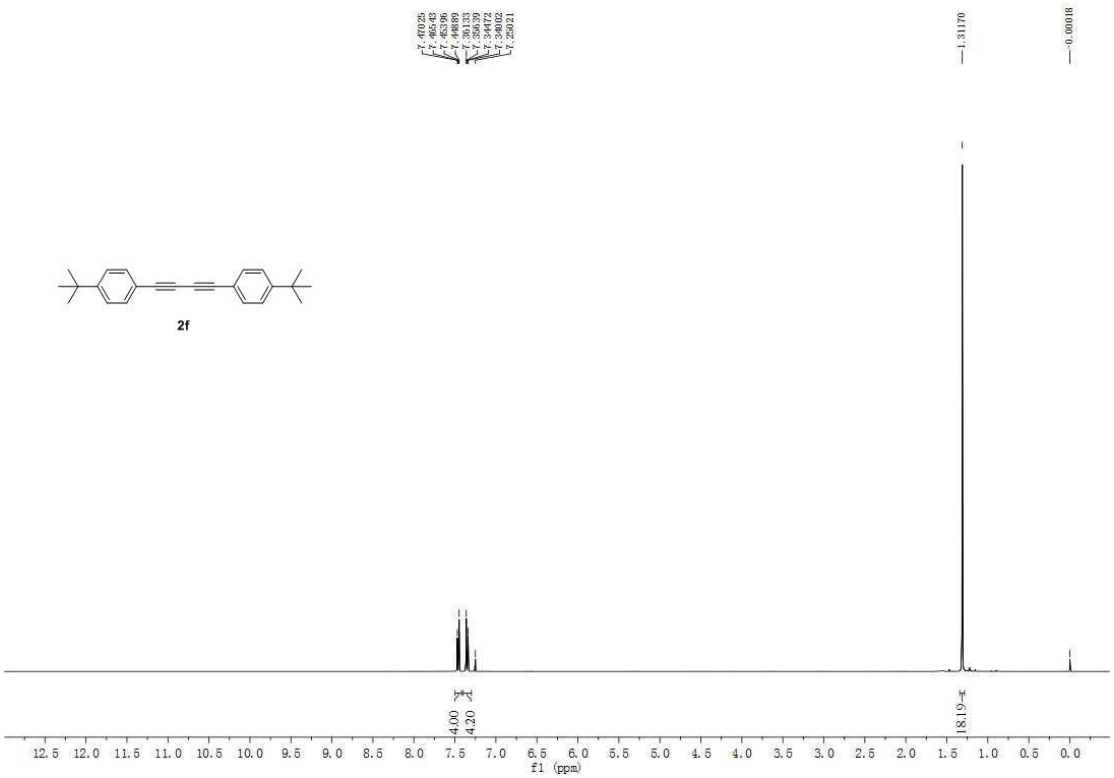
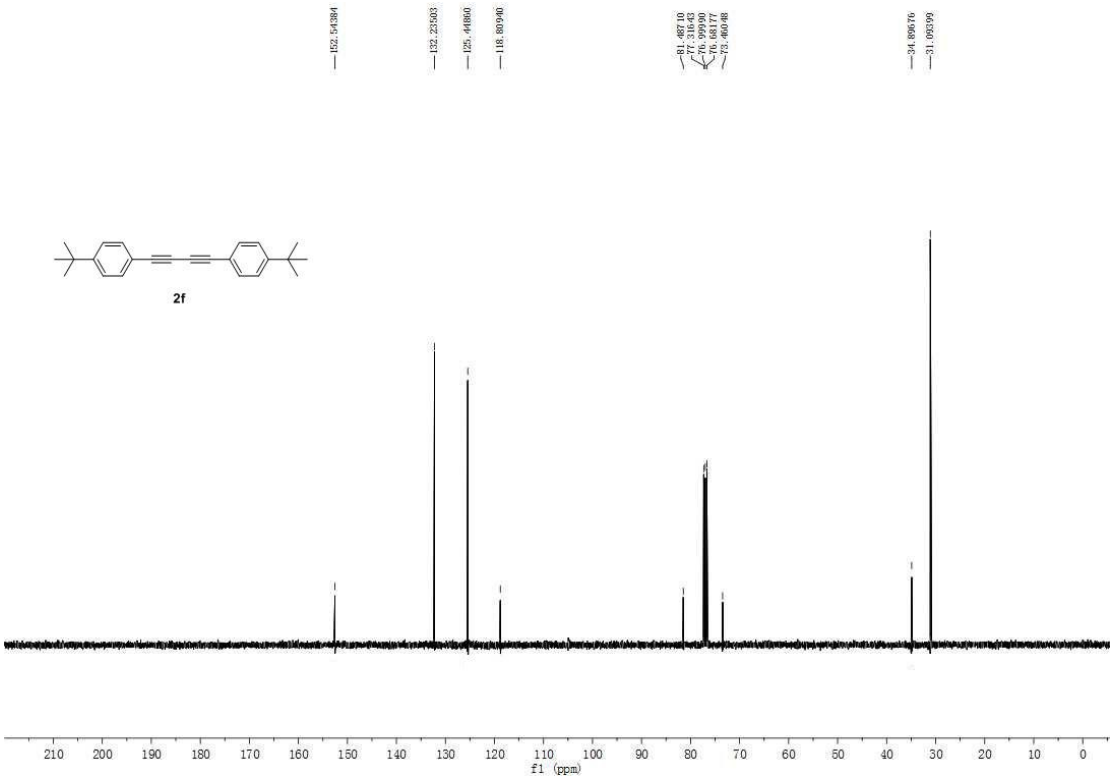
132.36707
129.19132
118.77916
81.52475
77.31795
77.00012
76.68228
73.43859
21.60018
Me
Me
2d
f1 (ppm)


n-C5H11
n-C5H11
2e
4.00
4.05
4.11
4.10
8.21
6.16
f1 (ppm)
n-C5H11
n-C5H11
2e
f1 (ppm)


7.47025
7.46543
7.45396
7.44889
7.36133
7.35639
7.34472
7.34002
7.25021
1.31170
0.00018
2f
4.00
4.20
18.19
f1 (ppm)


152.54384
132.23503
125.44860
118.80940
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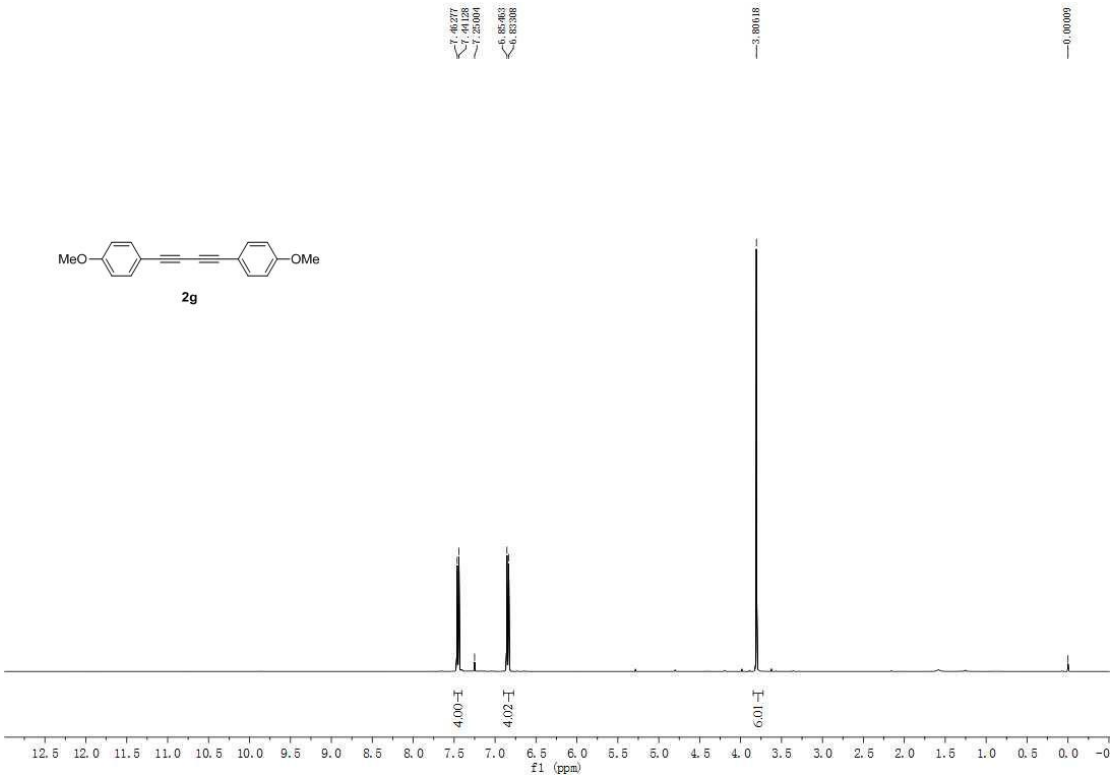
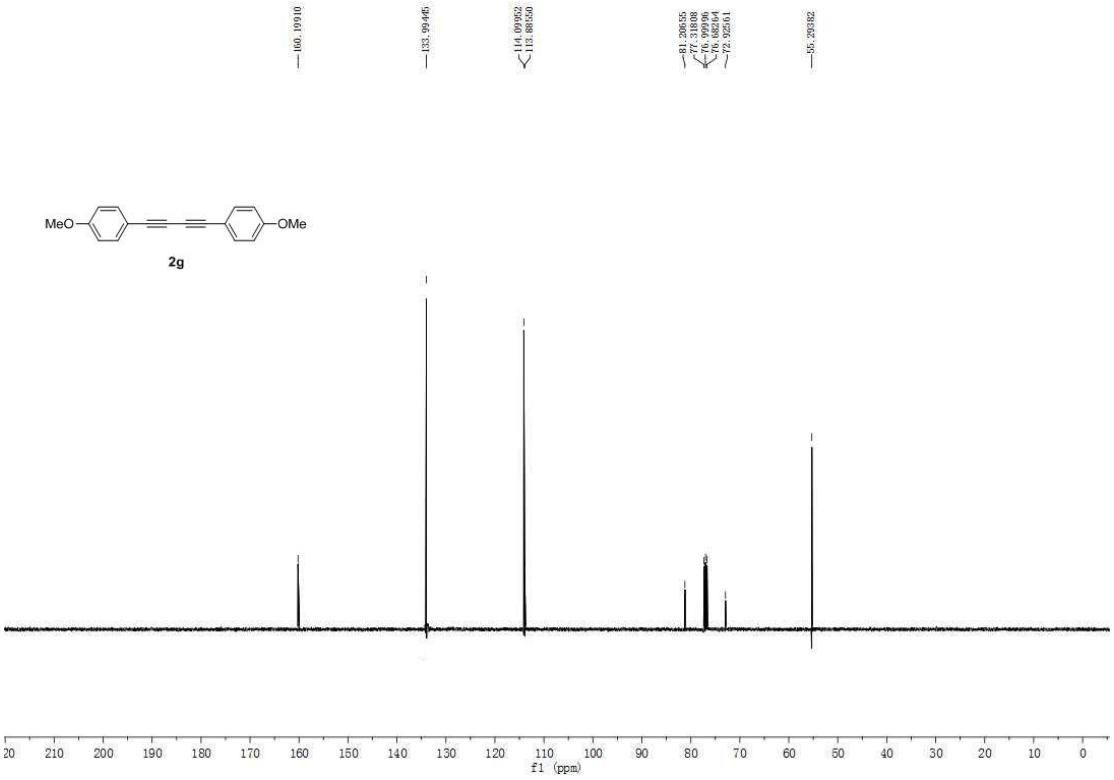
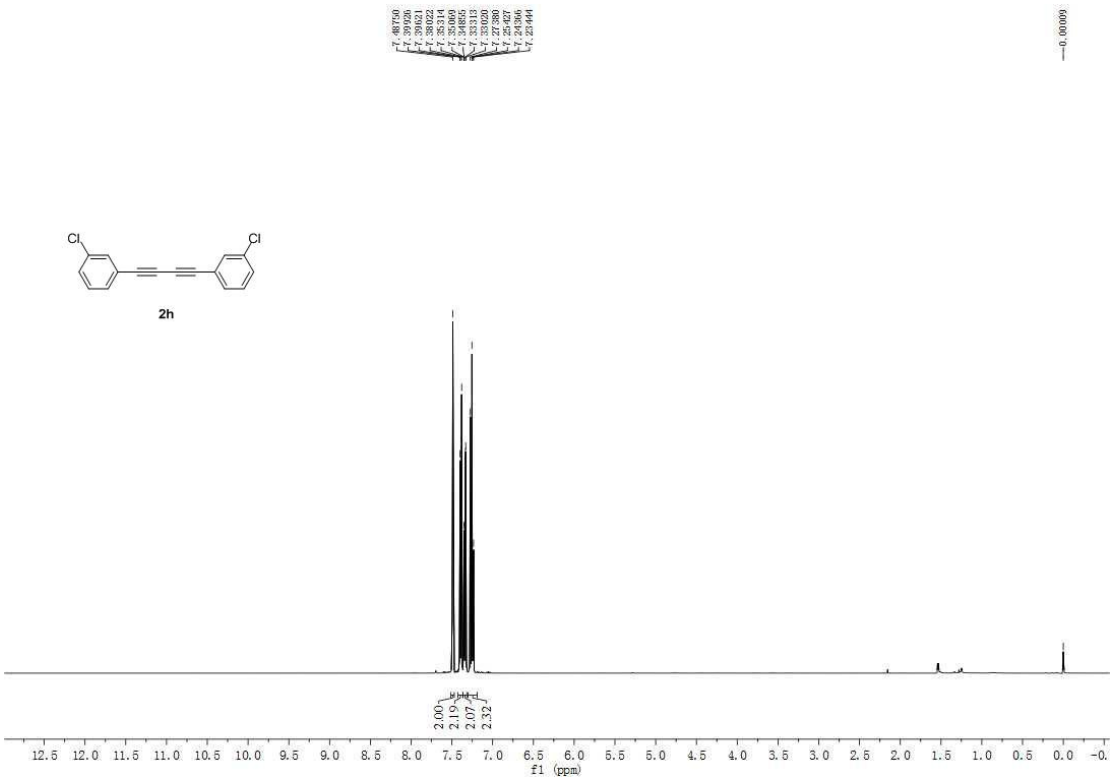
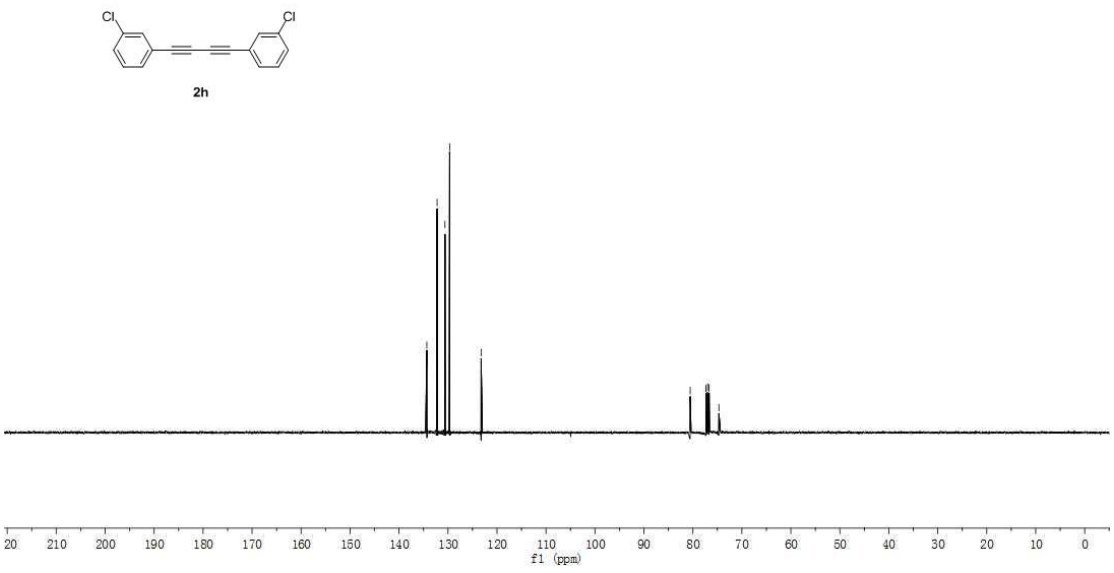
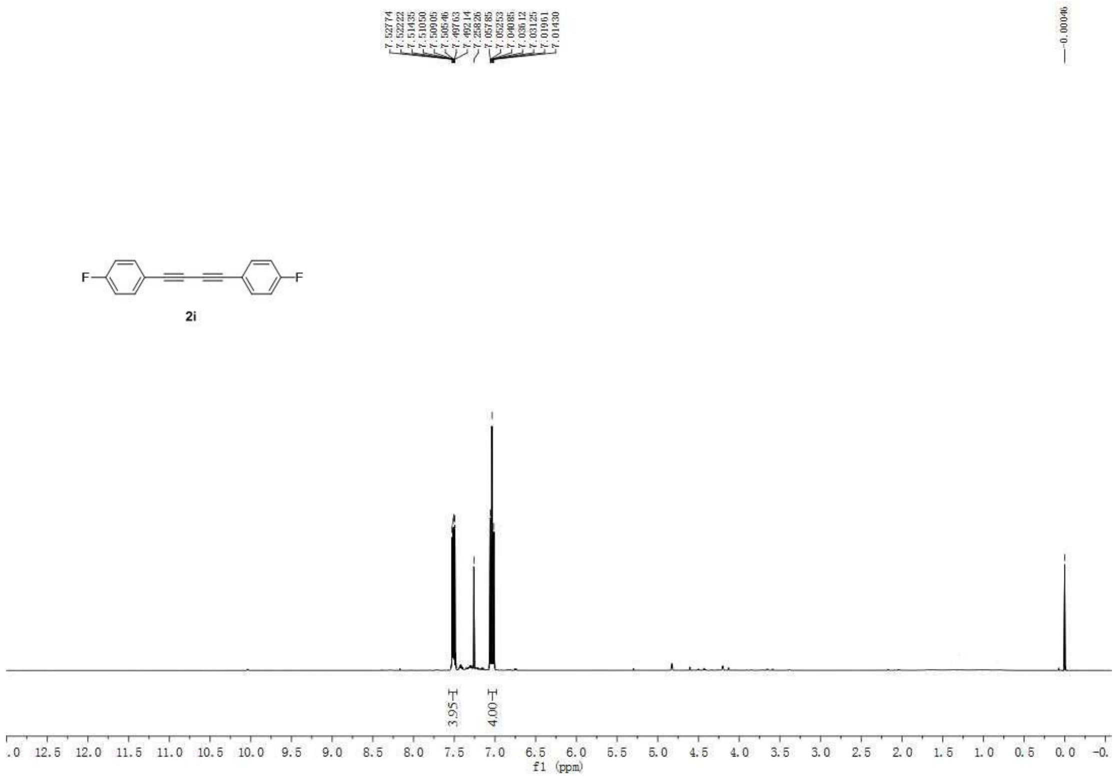
77.31643
76.99990
76.68177
73.46048
34.89676
31.09399
2f
f1 (ppm)

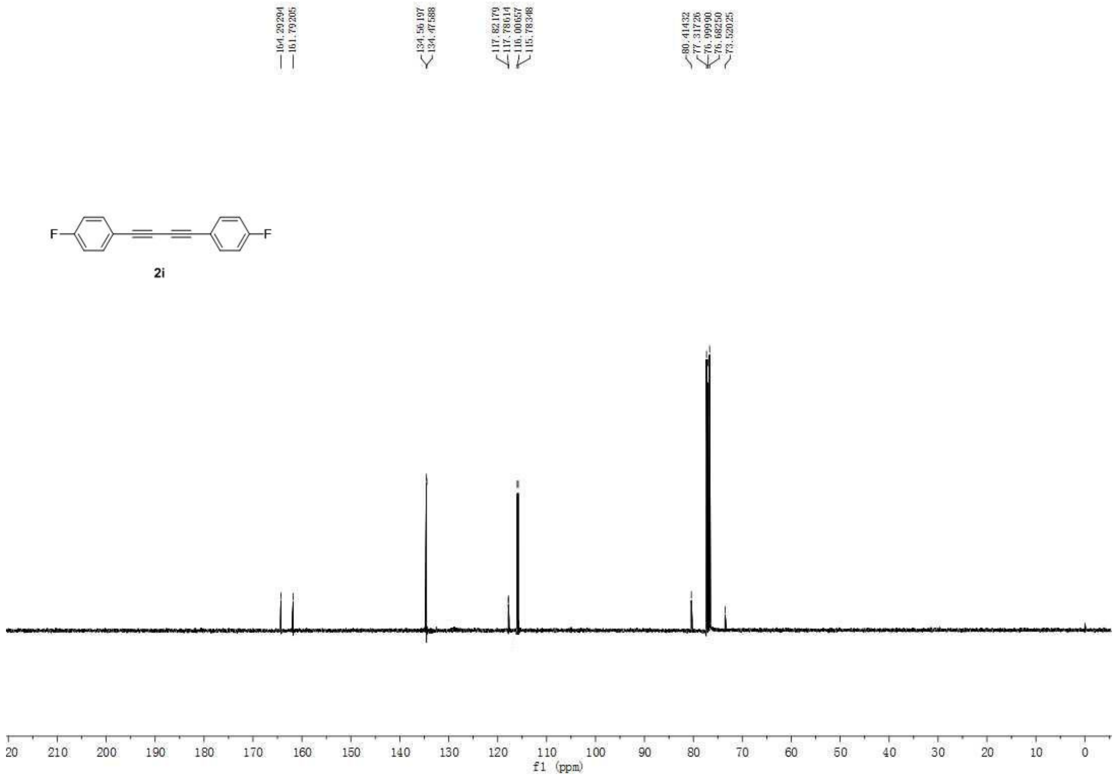

7.46277
7.44128
7.25004
6.85463
6.83308
3.80618
0.00000
MeO
OMe
2g
4.00
4.02
6.01
f1 (ppm)

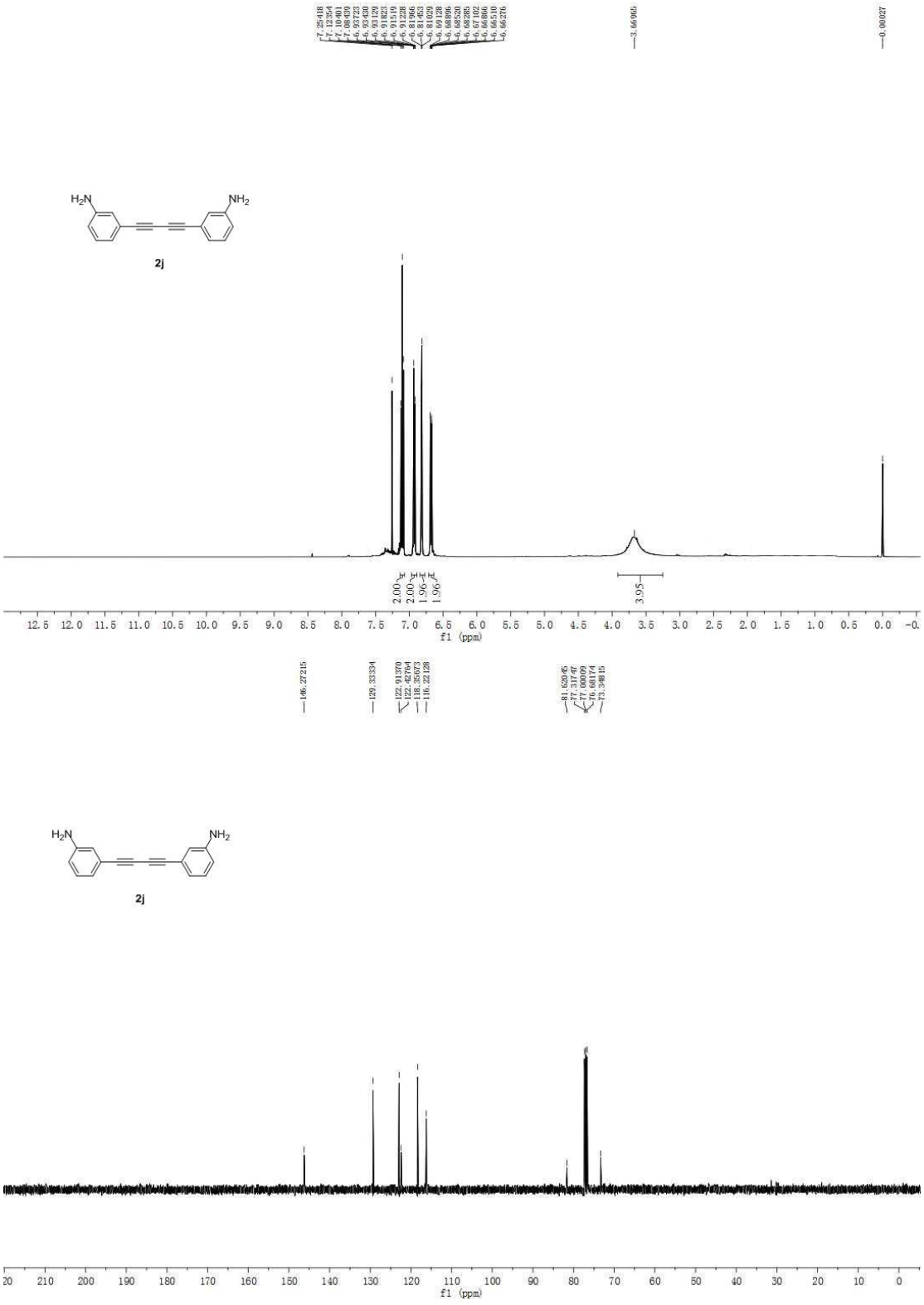

160.19910
133.99445
114.09952
113.88350
81.20655
77.31888
76.99996
76.68104
72.92561
55.29382
MeO
OMe
2g
f1 (ppm)

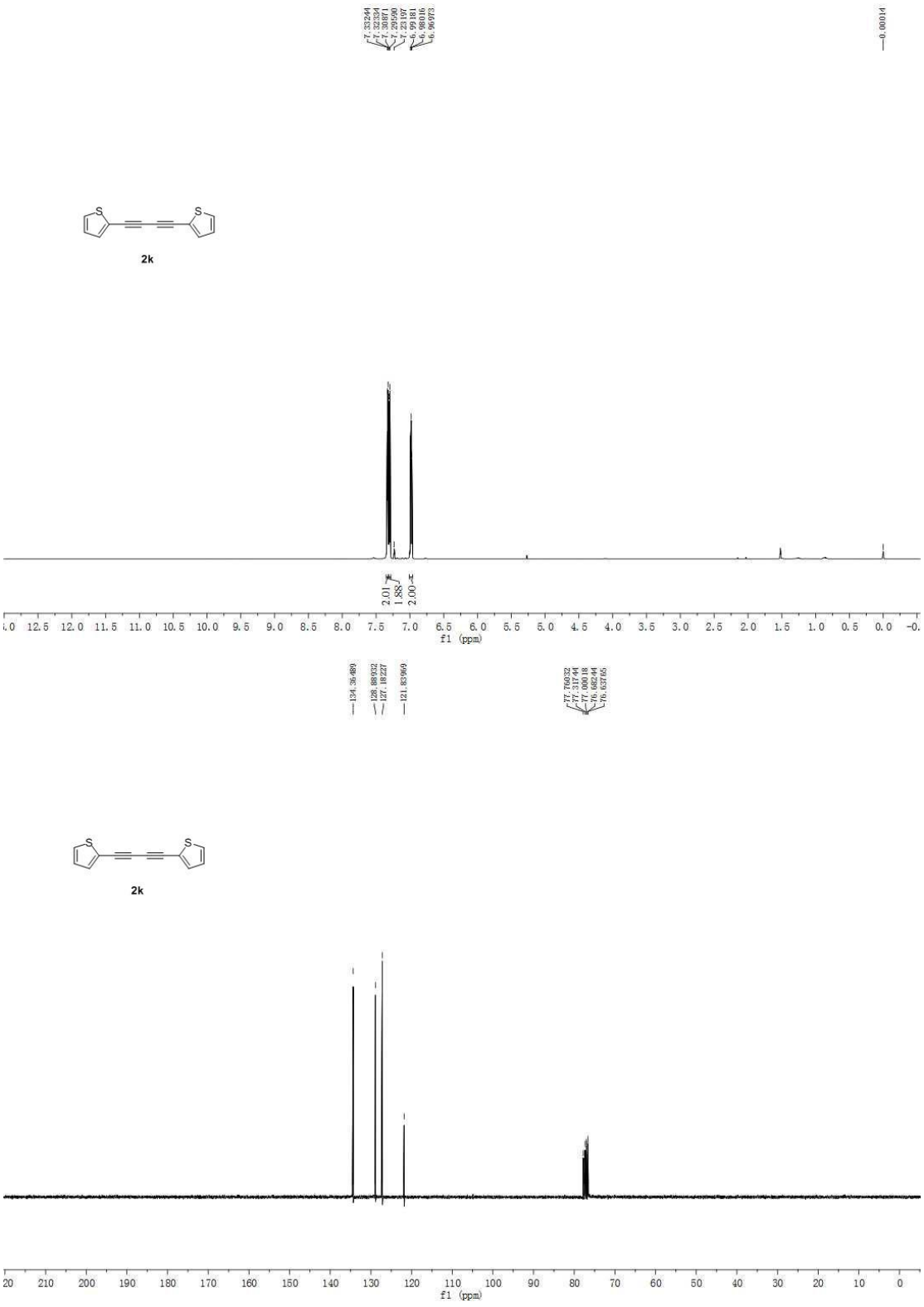

Cl
Cl
2h
2.00
2.19
2.07
2.32
f1 (ppm)


Cl
Cl
2h
f1 (ppm)






H2N
NH2
2j
f1 (ppm)
2j
f1 (ppm)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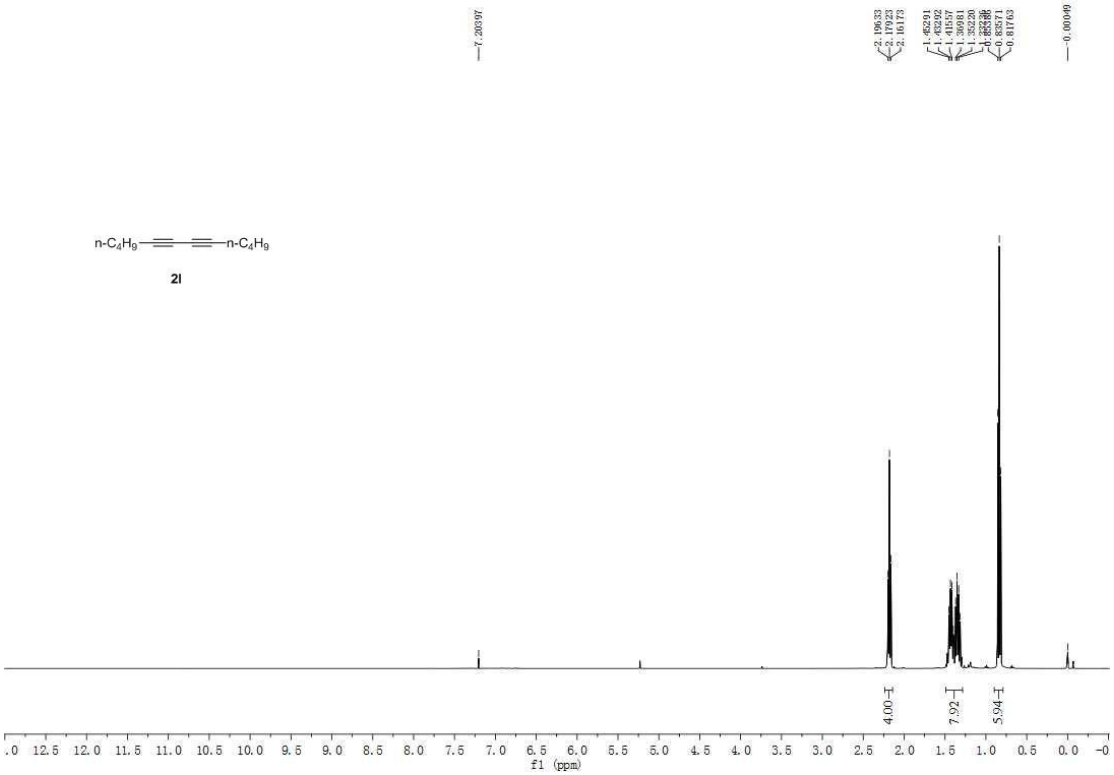
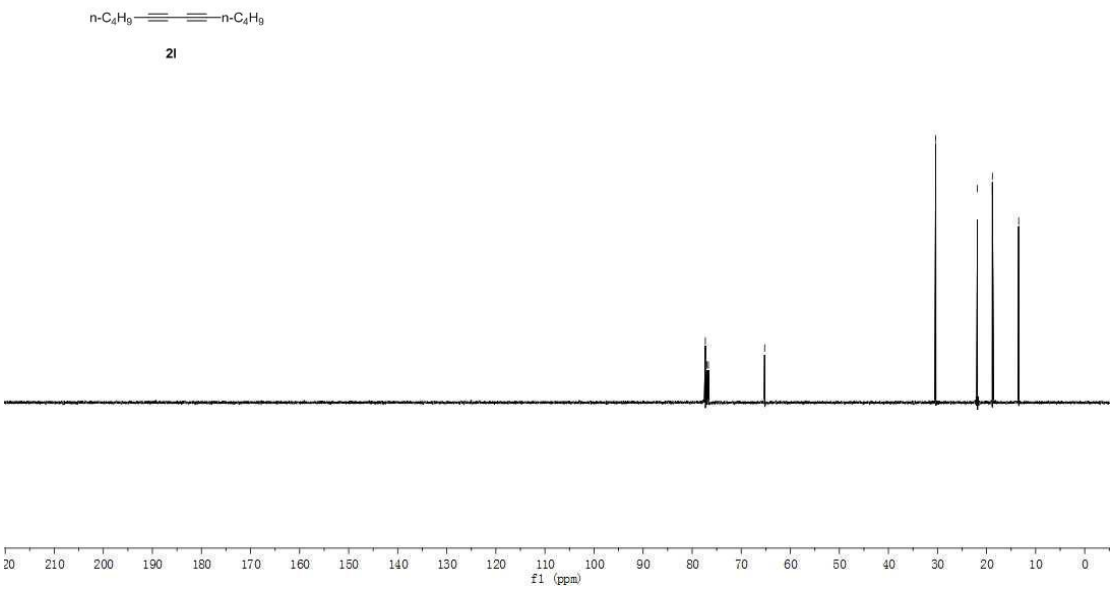
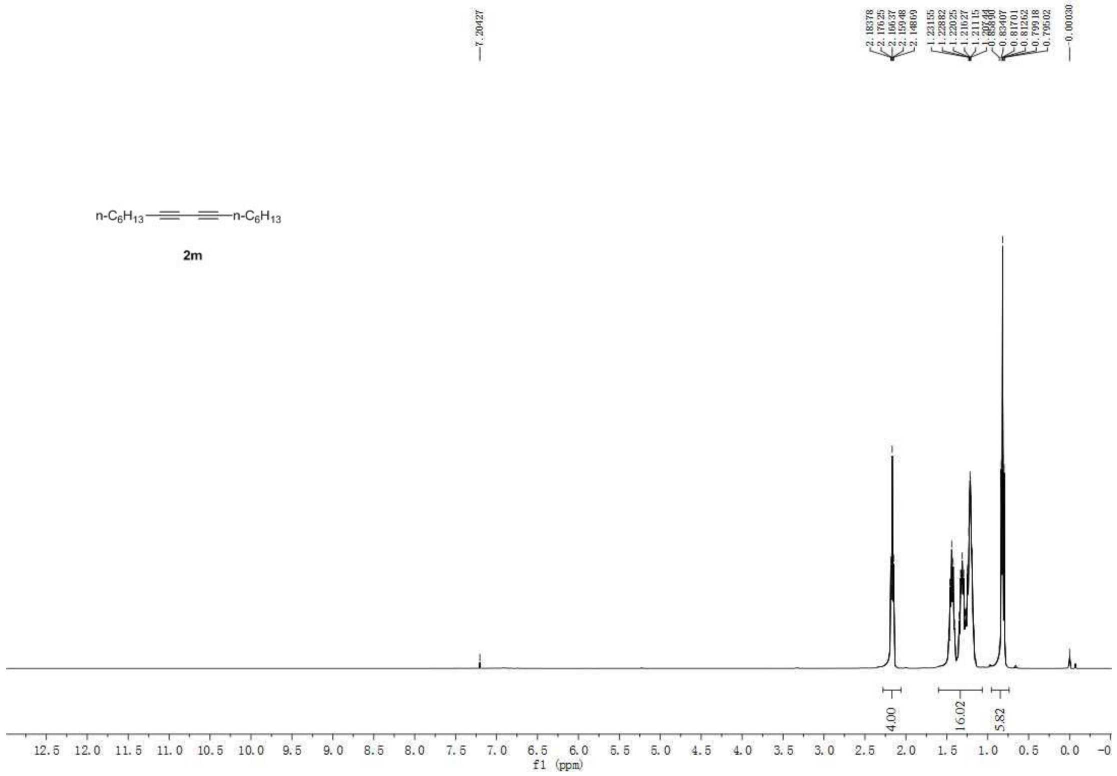
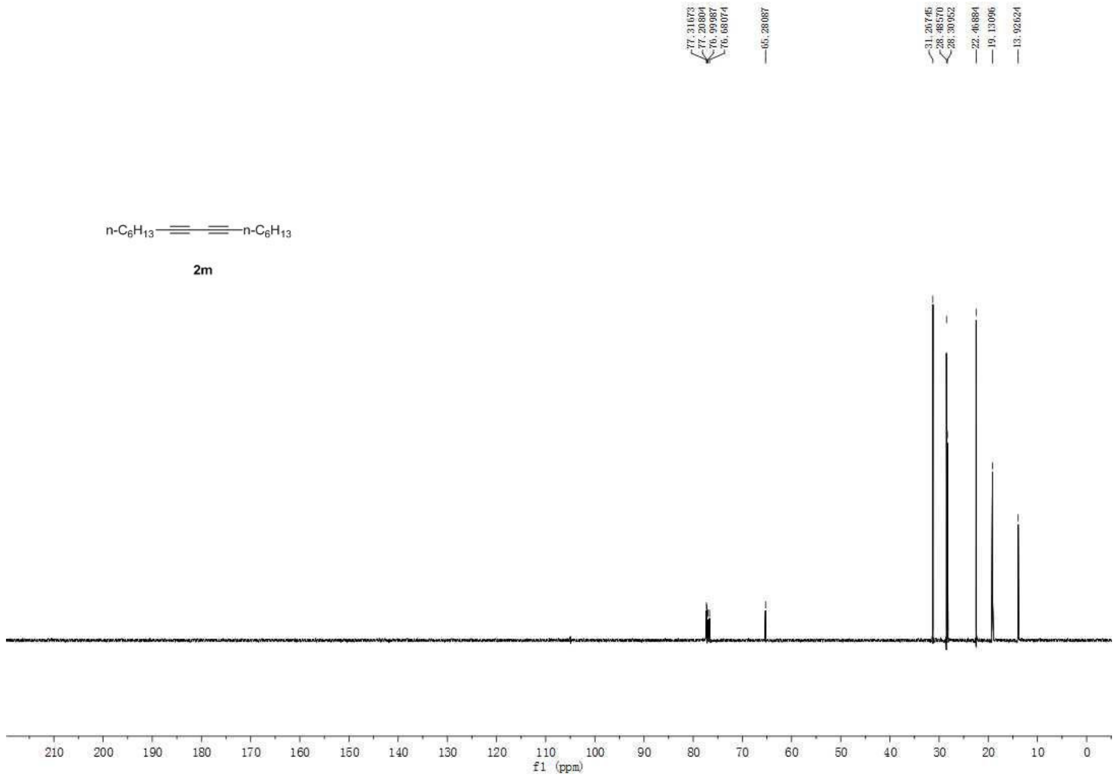
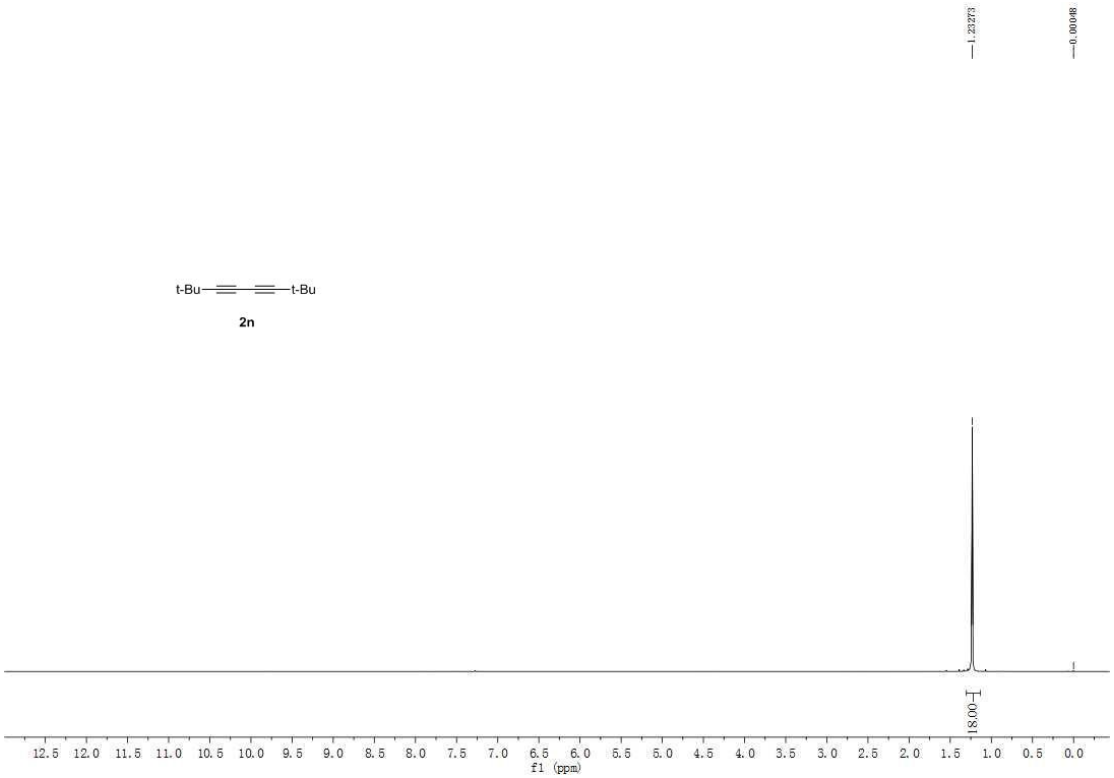
7.32334
7.30967
7.29590
7.23197
6.99181
6.98016
6.96973
0.00014
2k
2.01
1.88
2.00
f1 (ppm)
134.36489
128.88922
127.18127
121.83969
77.76932
77.31744
77.00018
76.68304
76.63705
2k
f1 (ppm)

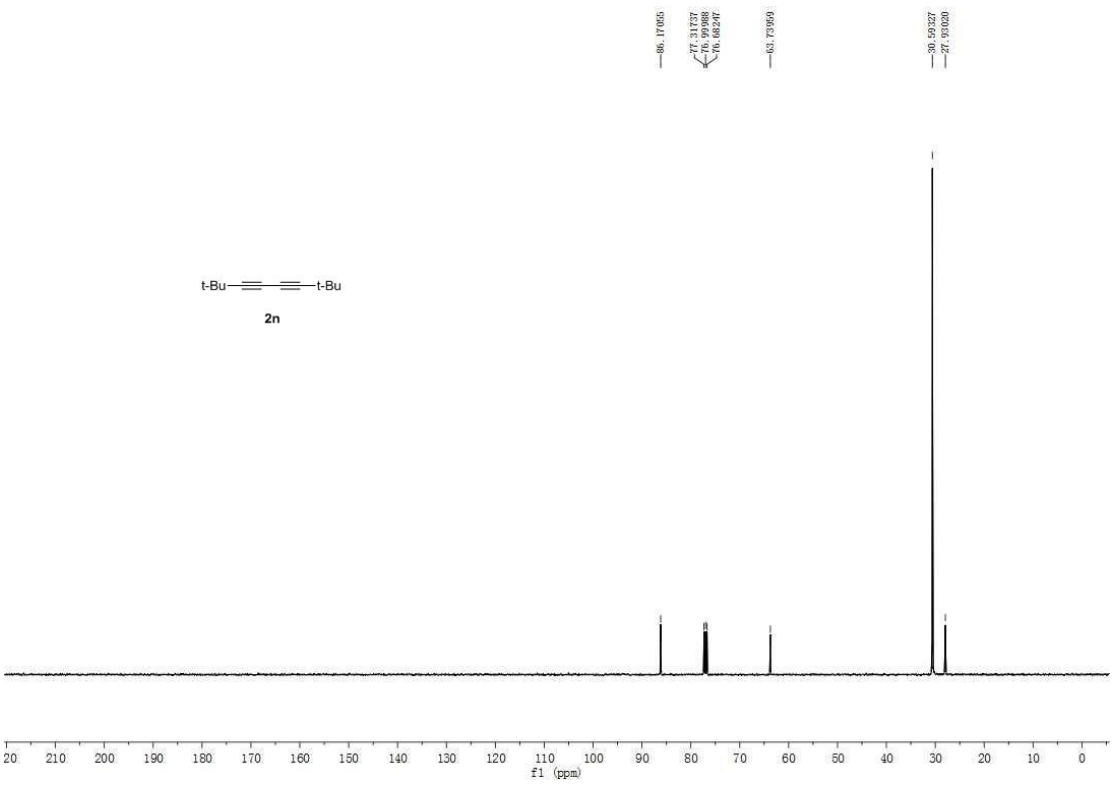

n-C4H9—≡—≡—n-C4H9
2l
7.26097
2.19633
2.17923
2.16173
1.45291
1.43232
1.41557
1.39981
1.35226
0.85571
0.81763
0.00049
4.00
7.92
5.94
f1 (ppm)

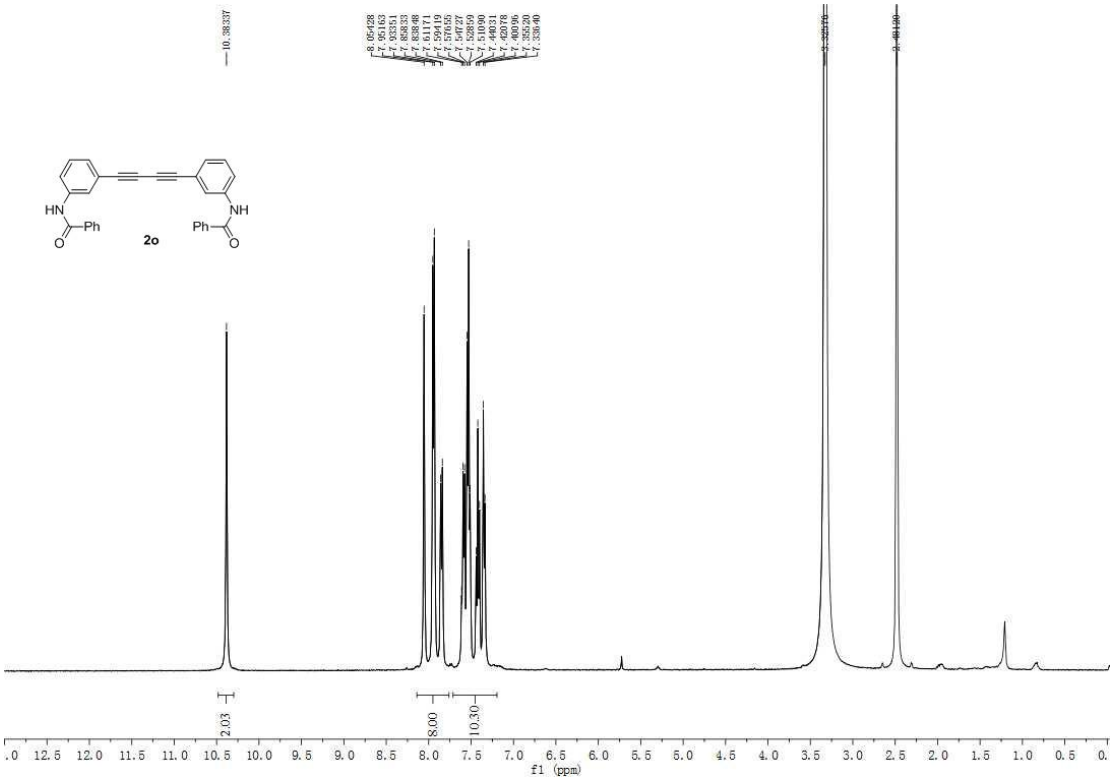

n-C4H9—≡—≡—n-C4H9
2l
77.31486
76.99958
76.68169
65.22544
30.35693
21.86731
18.81575
13.44986
f1 (ppm)

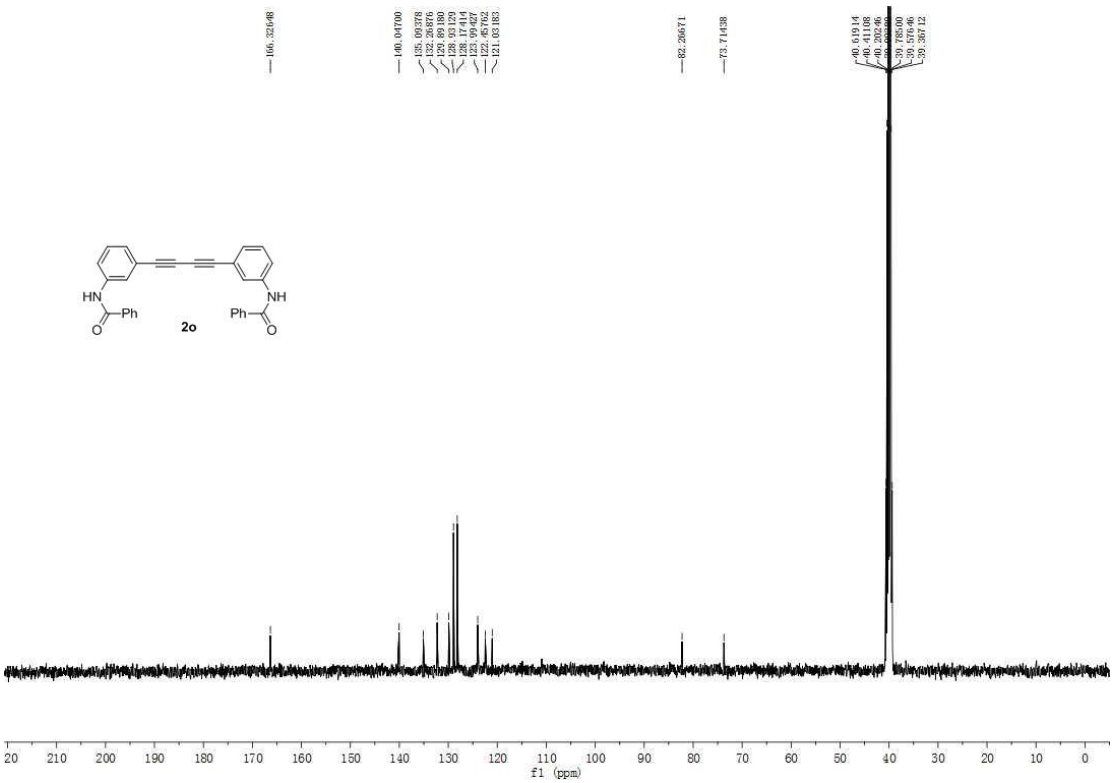


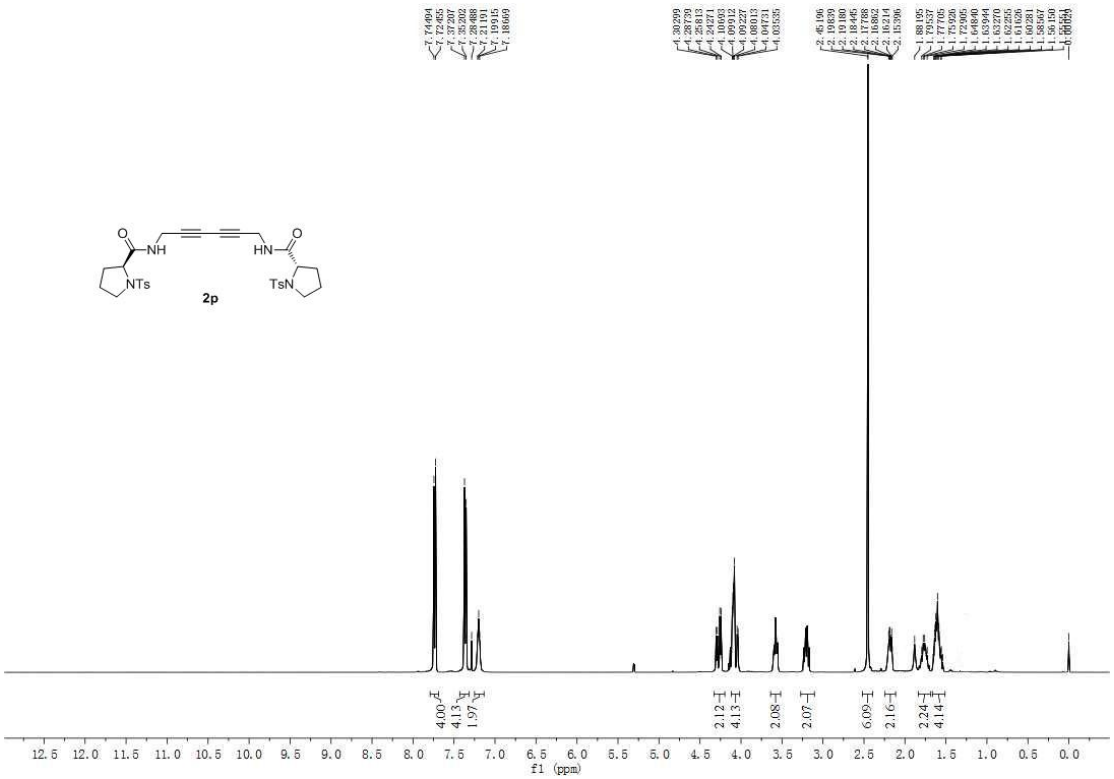


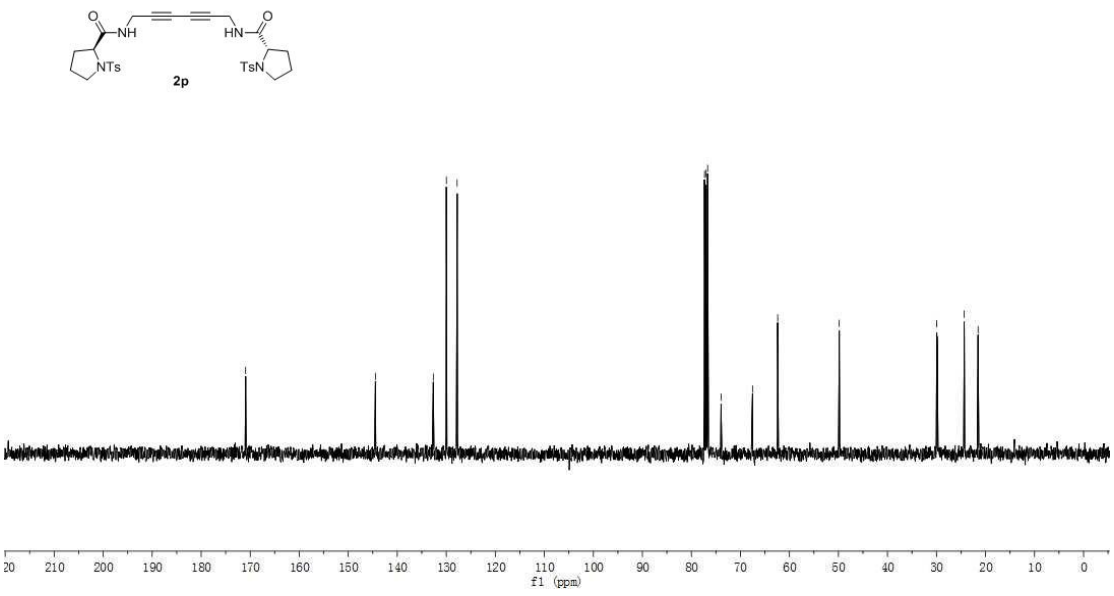

1.23273
0.00048
t-Bu
t-Bu
2n
18.00
f1 (ppm)


86.17055
77.31737
76.99988
76.68259
63.73959
30.59327
27.93020
t-Bu
t-Bu
2n
f1 (ppm)


HN
Ph
O
NH
Ph
O
2o
f1 (ppm)


HN
Ph
O
NH
Ph
O
2o
f1 (ppm)


NH
HN
NTs
TsN
2p
f1 (ppm)


NH
HN
NTs
TsN
2p
f1 (ppm)