Supporting Information for

Synthesis of Ene-yne-enes by Nickel-Catalyzed Double S_N2' substitution of 1,6-Dichlorohexa-2,4-diyne

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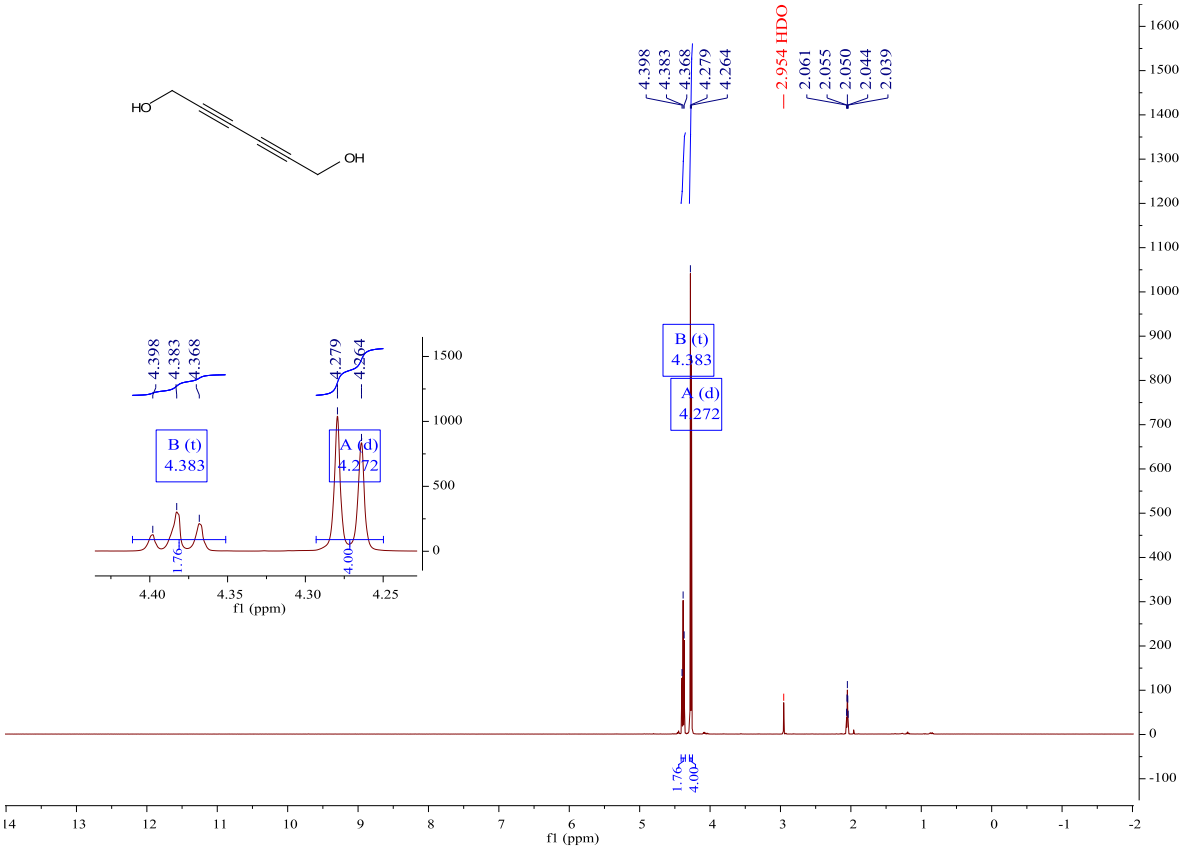
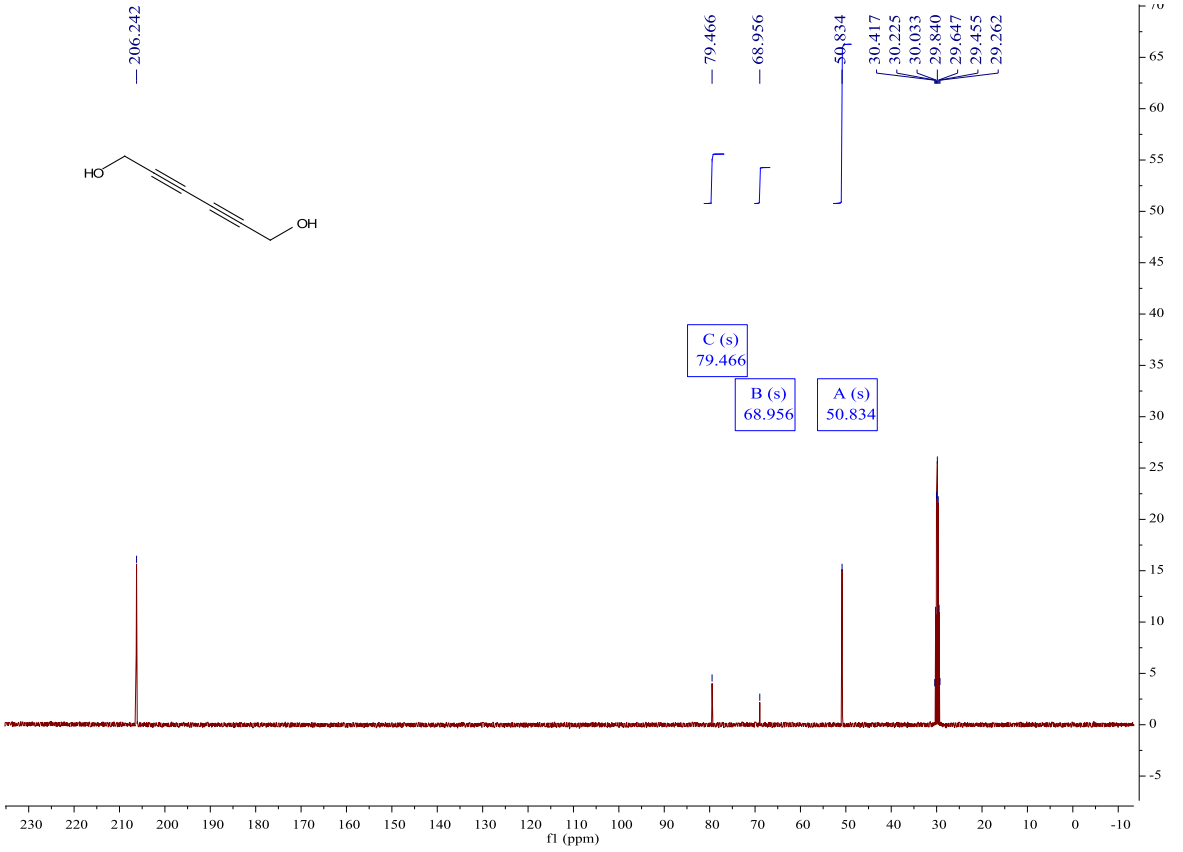
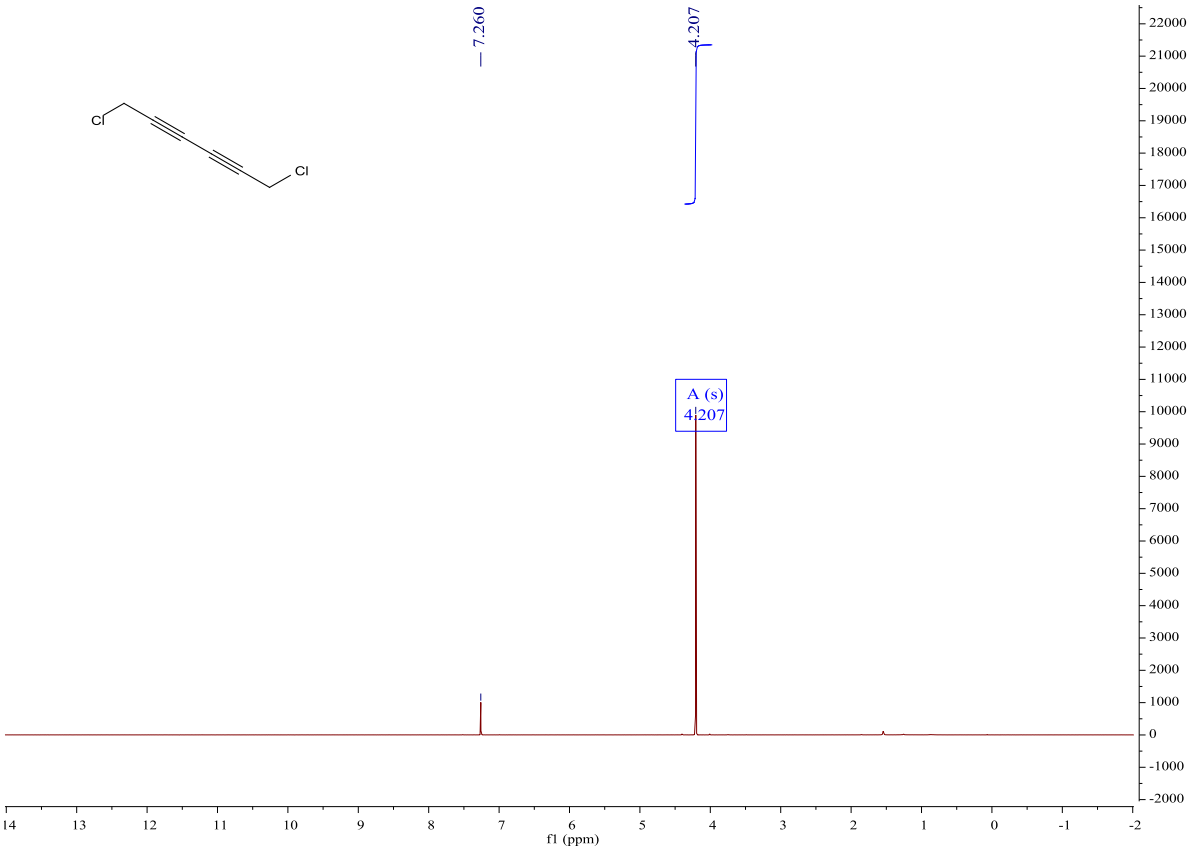
^{1}H , ^{13}C, APT NMR and IR spectra



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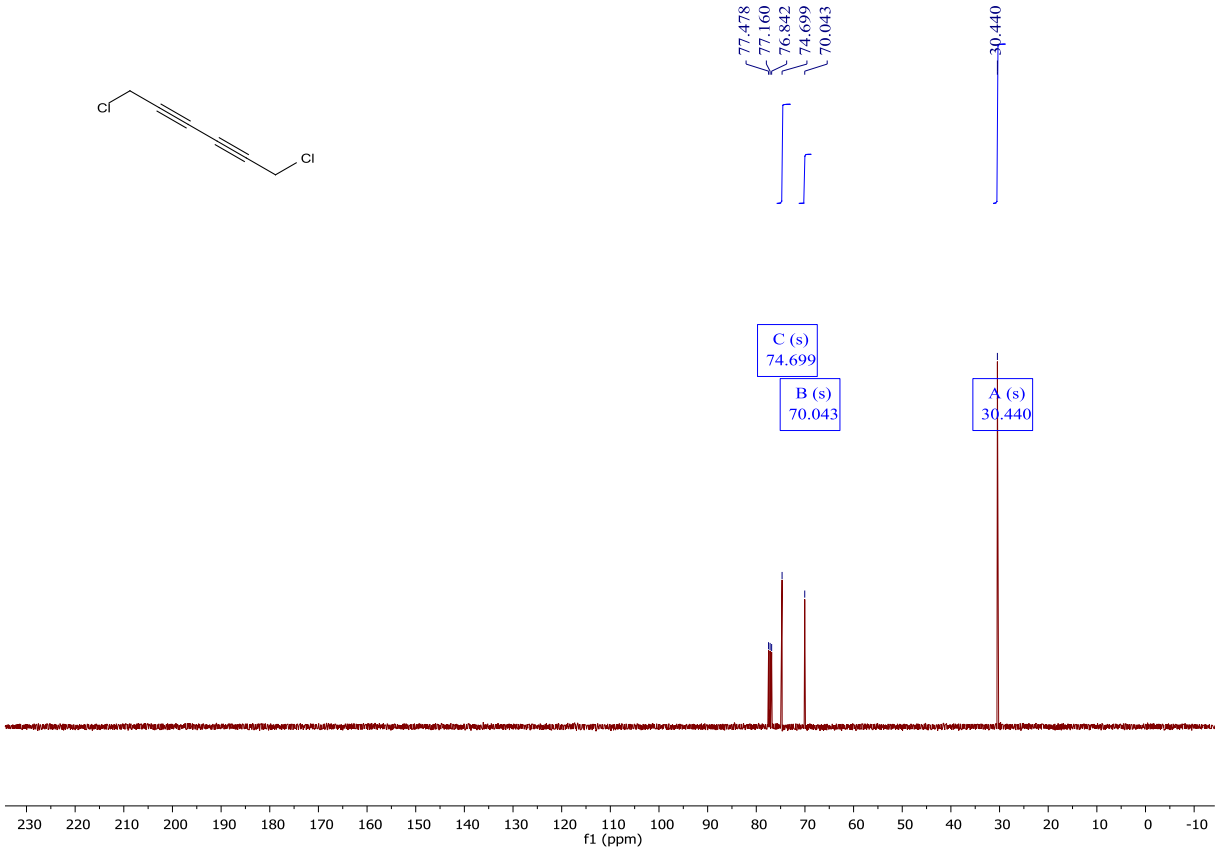
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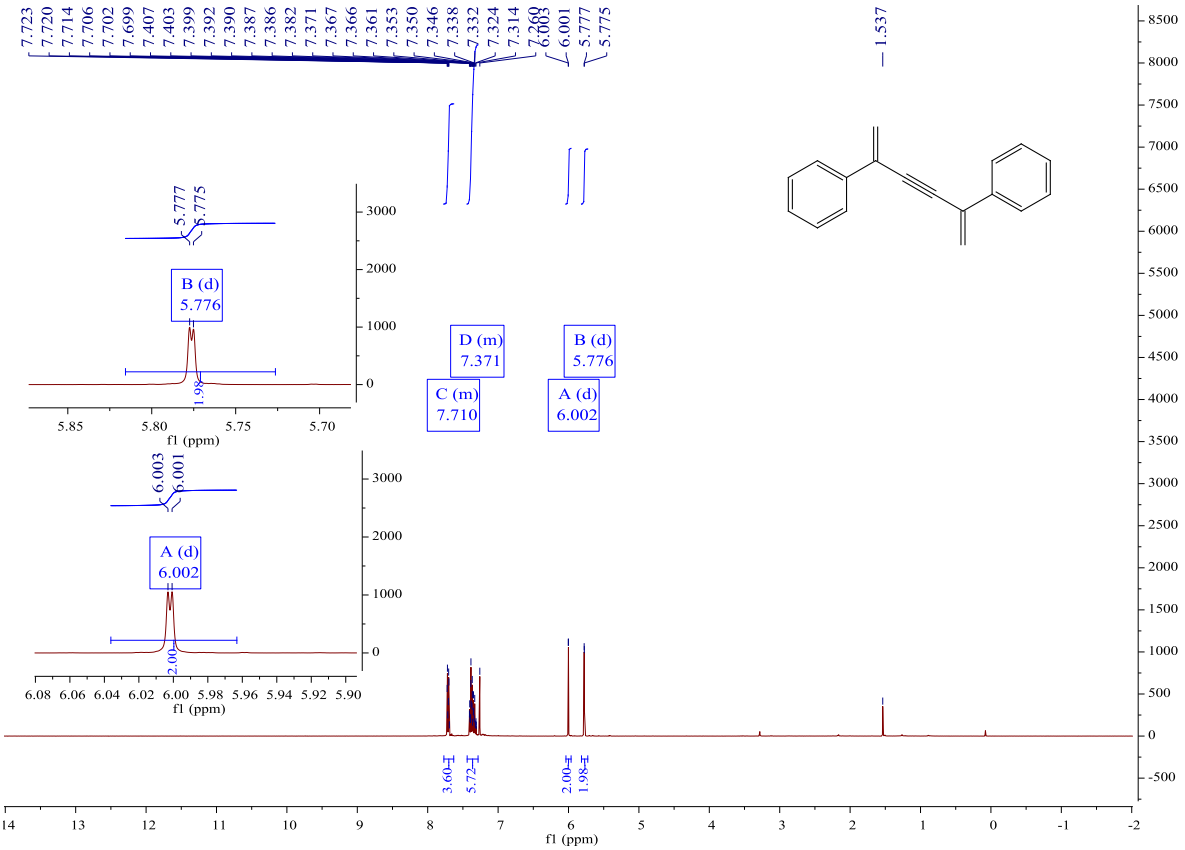
A (s)
30.440
f1 (ppm)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7.314
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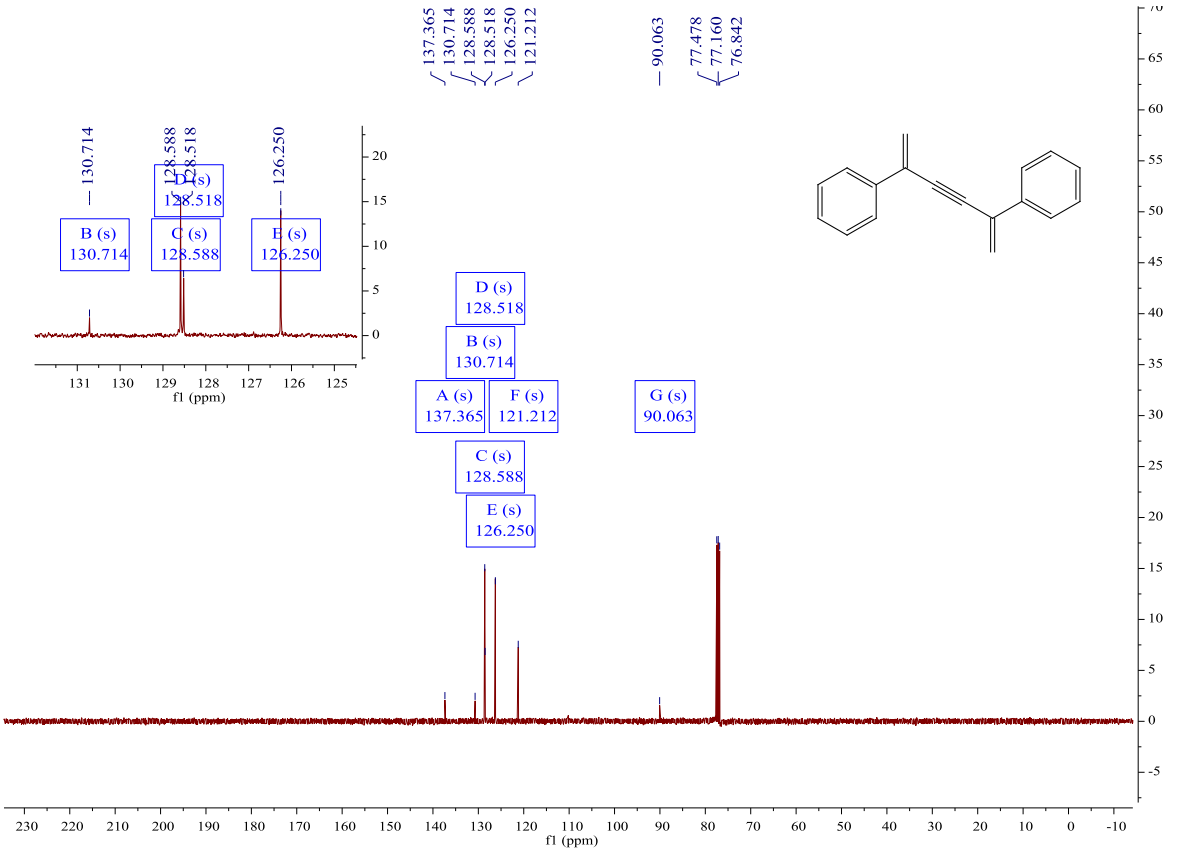
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126.250
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C (s)
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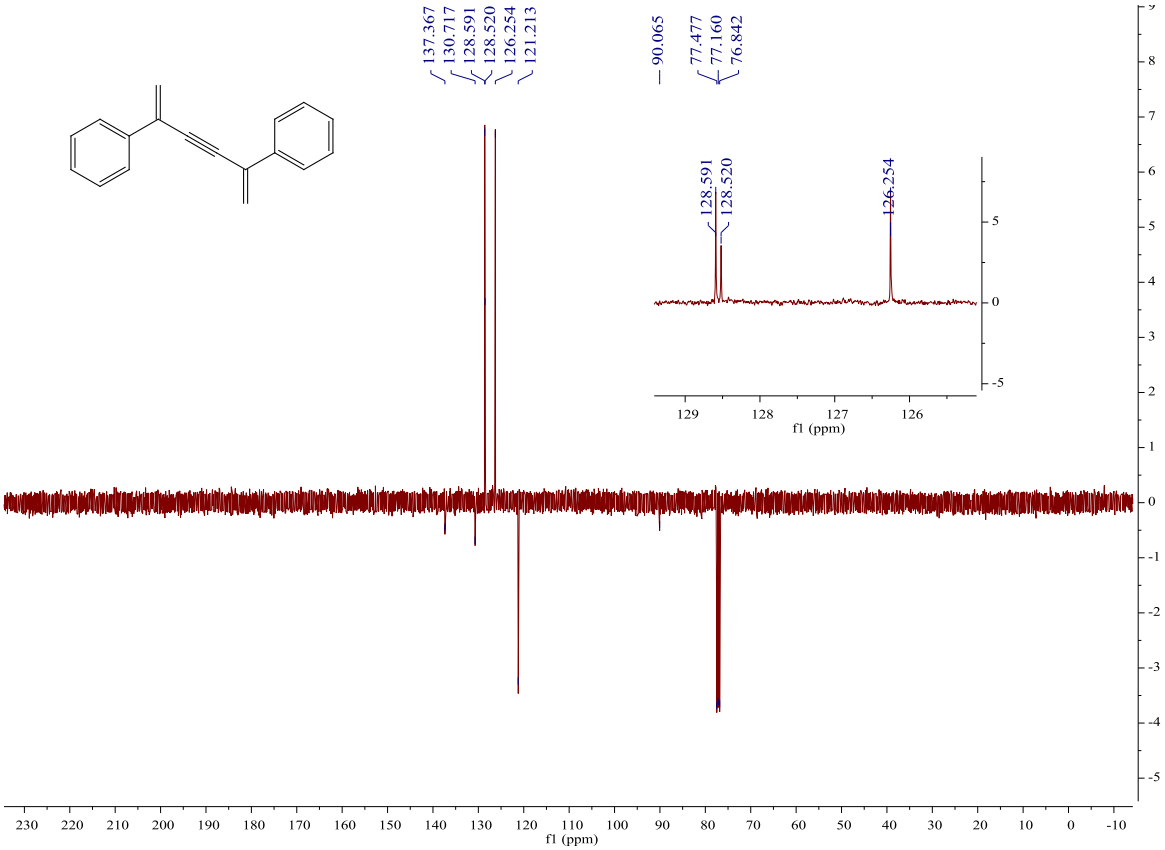
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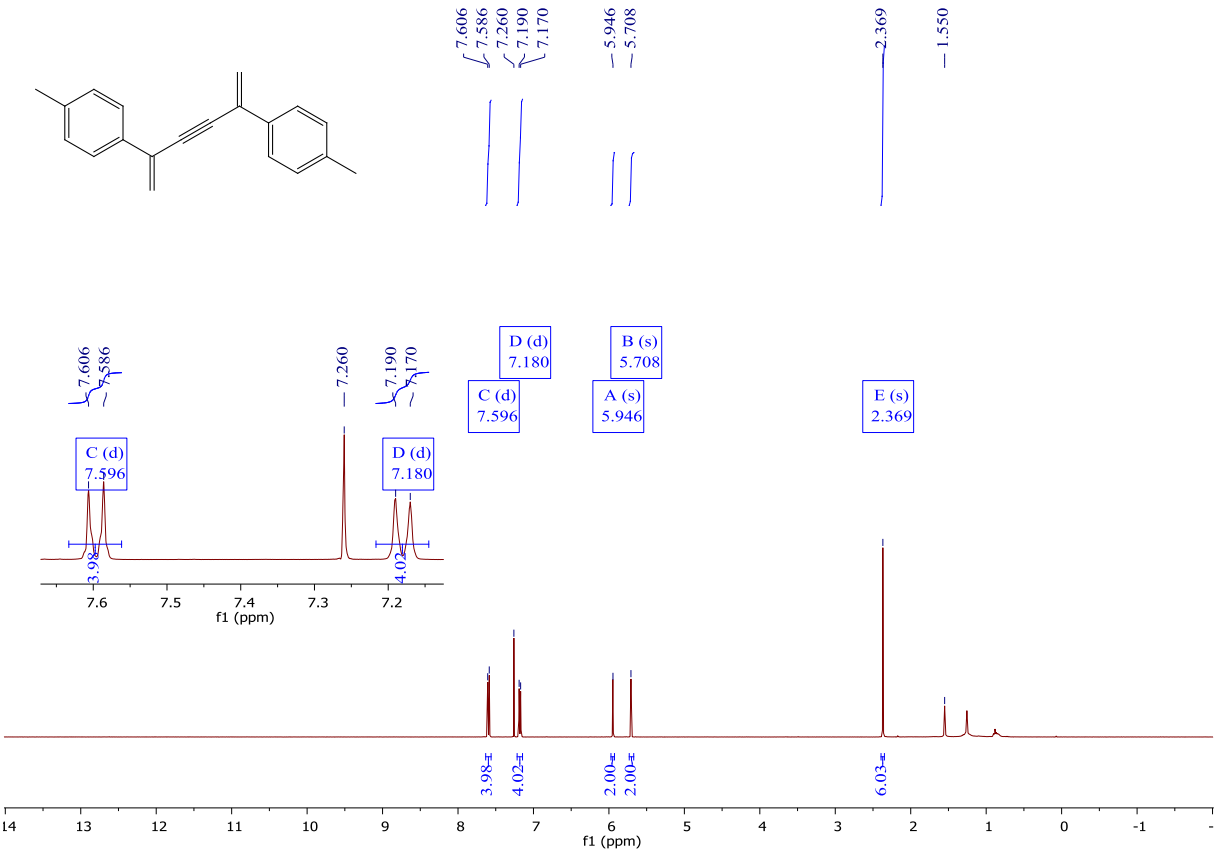
f1 (ppm)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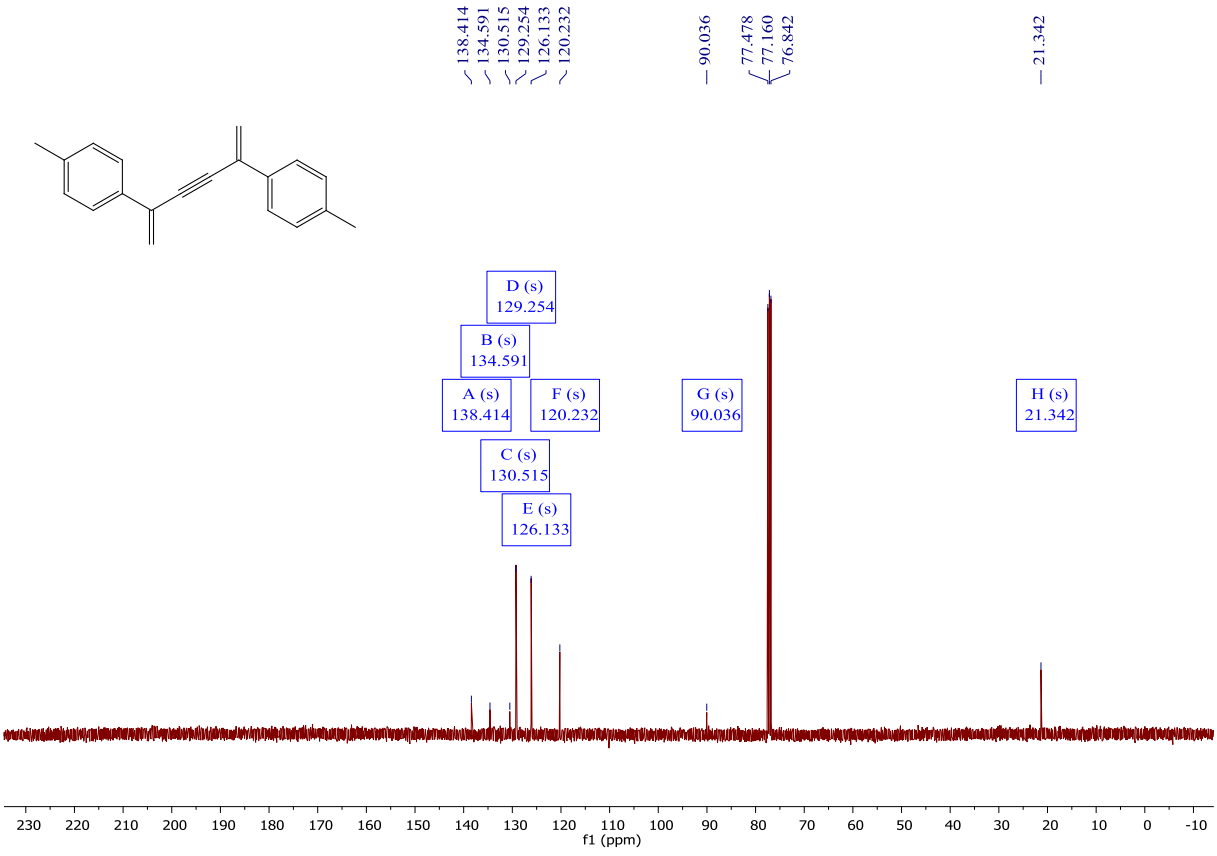
f1 (ppm)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B (s)
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A (s)
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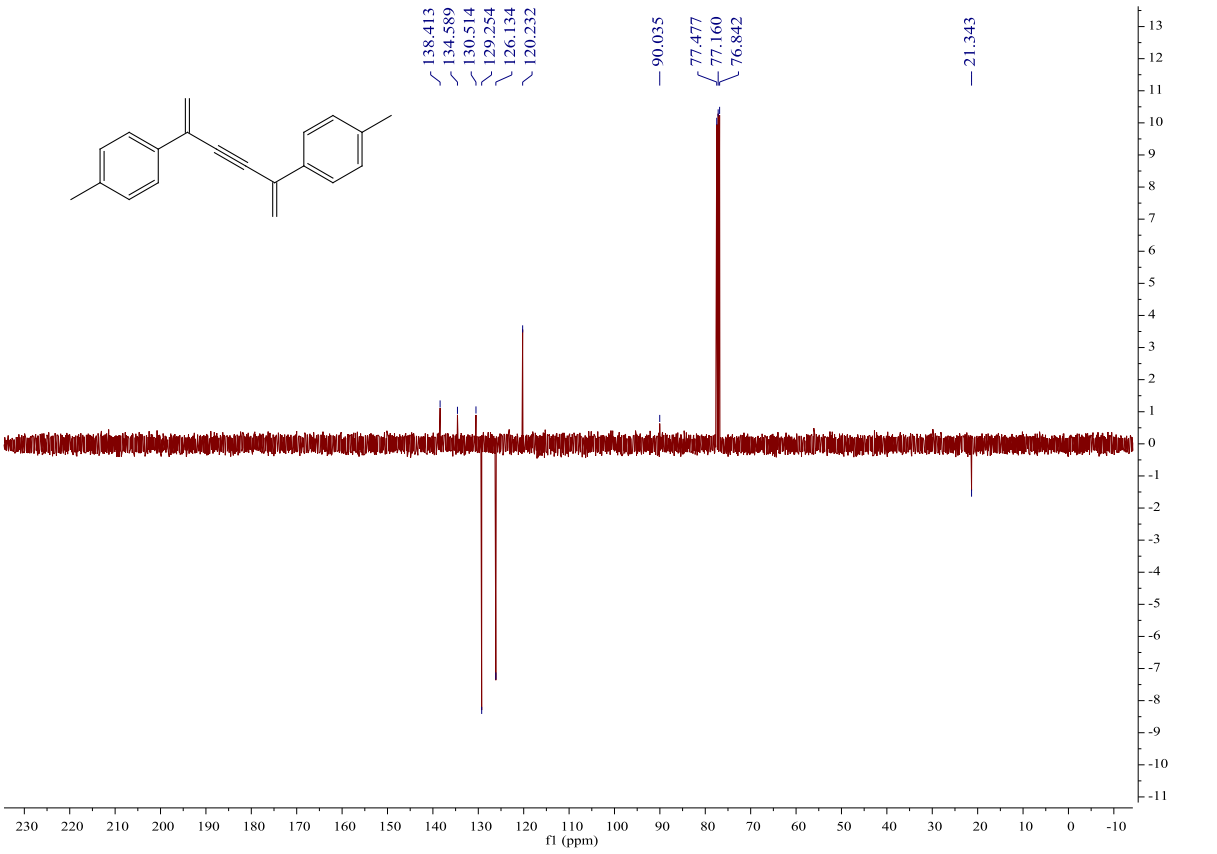
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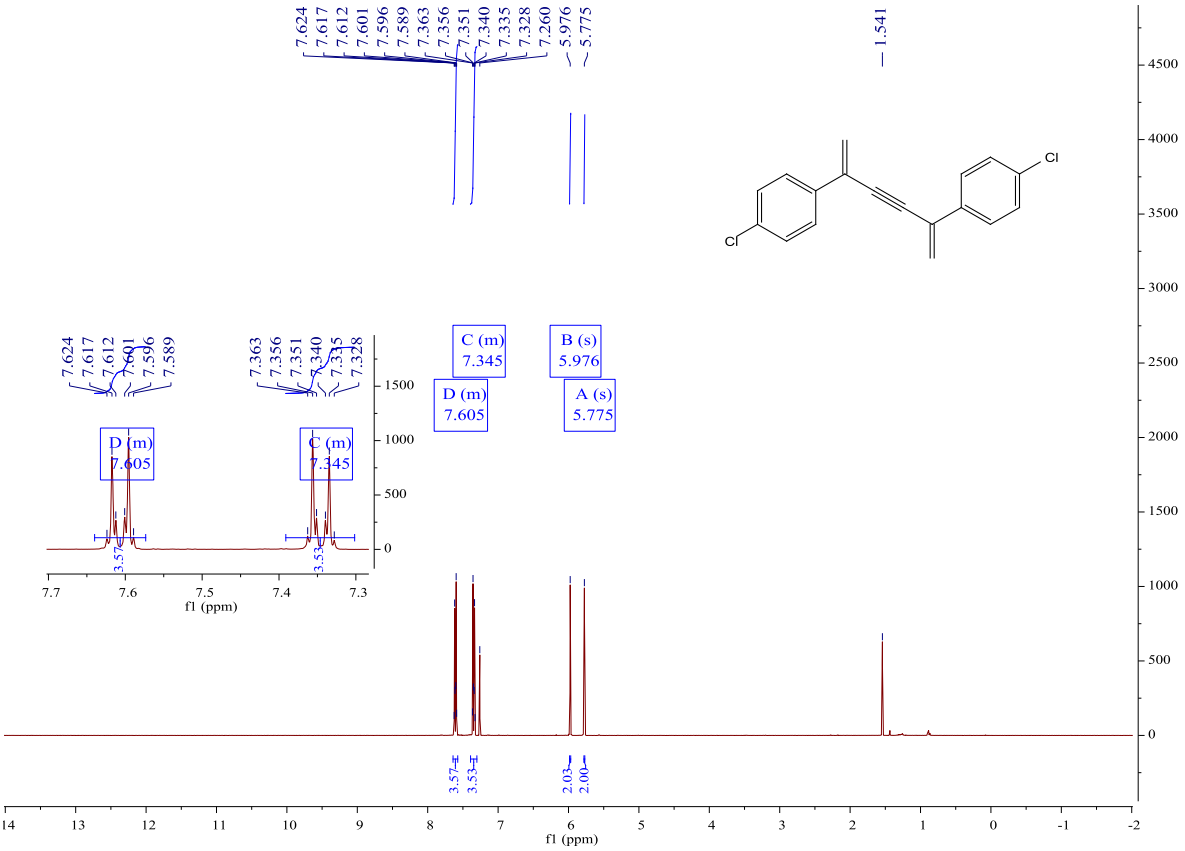
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Cl
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D (m)
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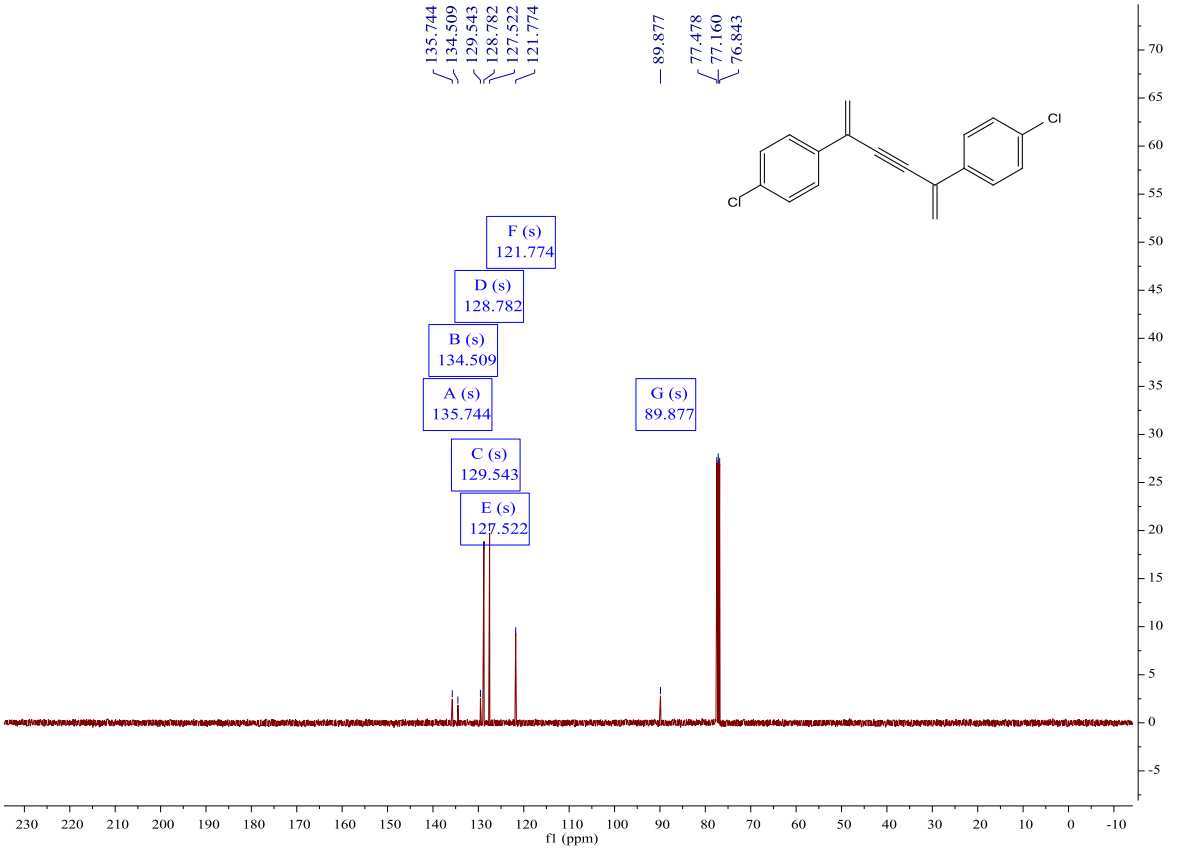
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127.522
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89.877
77.478
77.160
76.843
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Cl
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121.774
D (s)
128.782
B (s)
134.509
A (s)
135.744
G (s)
89.877
C (s)
129.543
E (s)
127.522
f1 (ppm)


135.746
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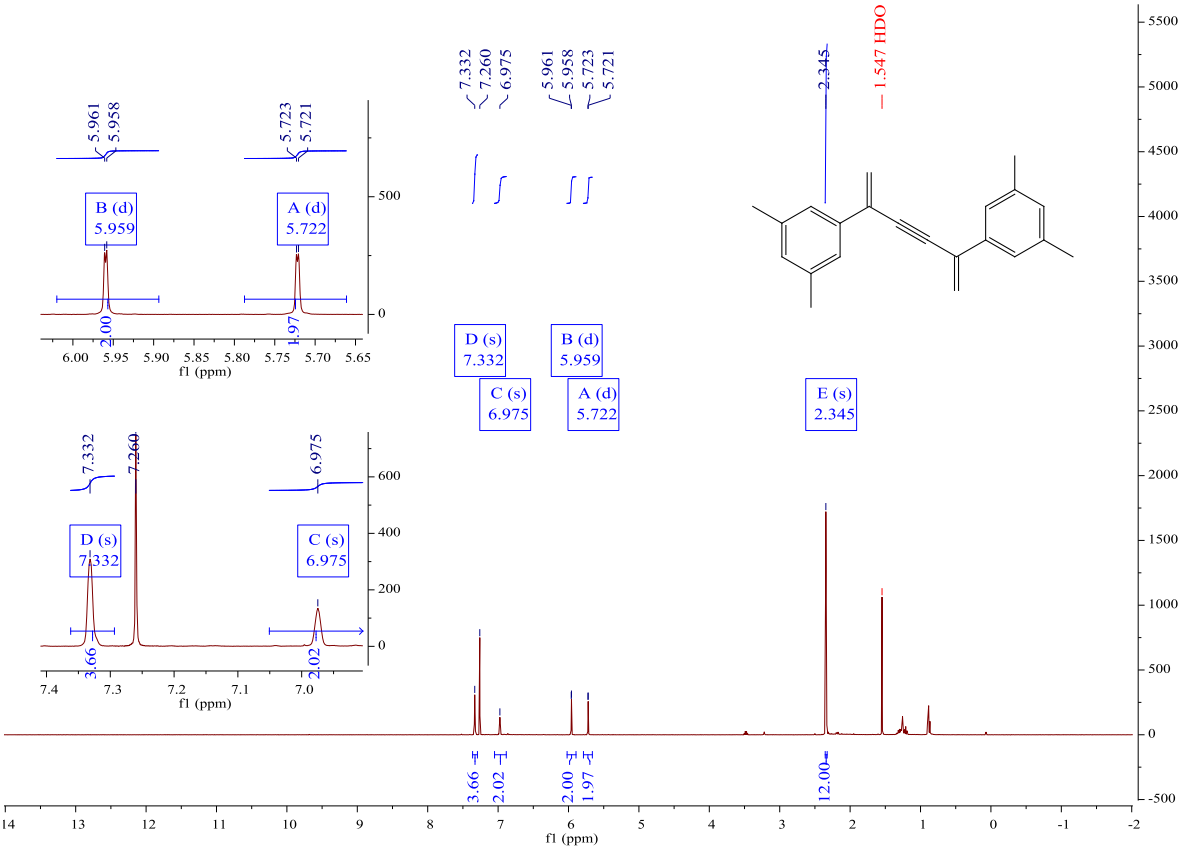
Cl
Cl
f1 (ppm)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6.975
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C (s)
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2.02
f1 (ppm)
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5.958
5.723
5.721
7.332
7.260
6.975
2.345
1.547 HDO
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7.332
B (d)
5.959
C (s)
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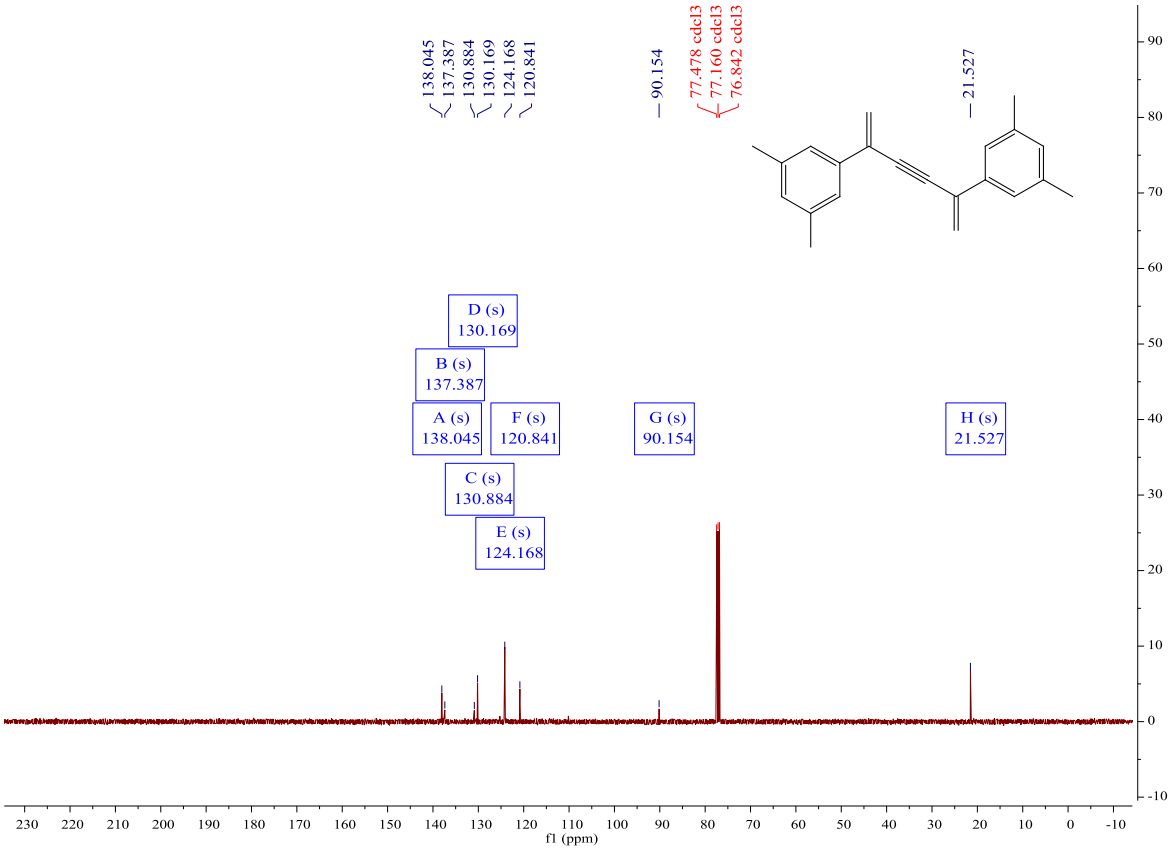
12.00
f1 (ppm)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76.842 cdcl3
21.527
D (s)
130.169
B (s)
137.387
A (s)
138.045
F (s)
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C (s)
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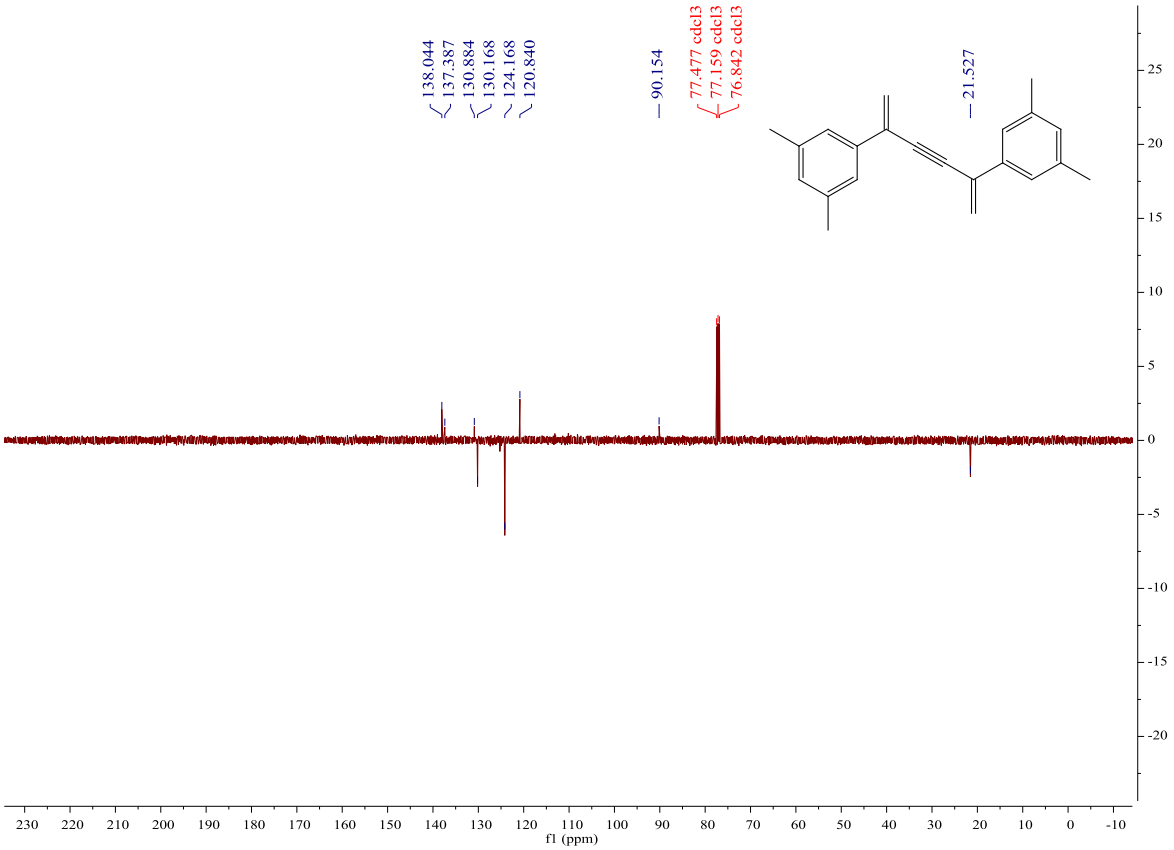
f1 (ppm)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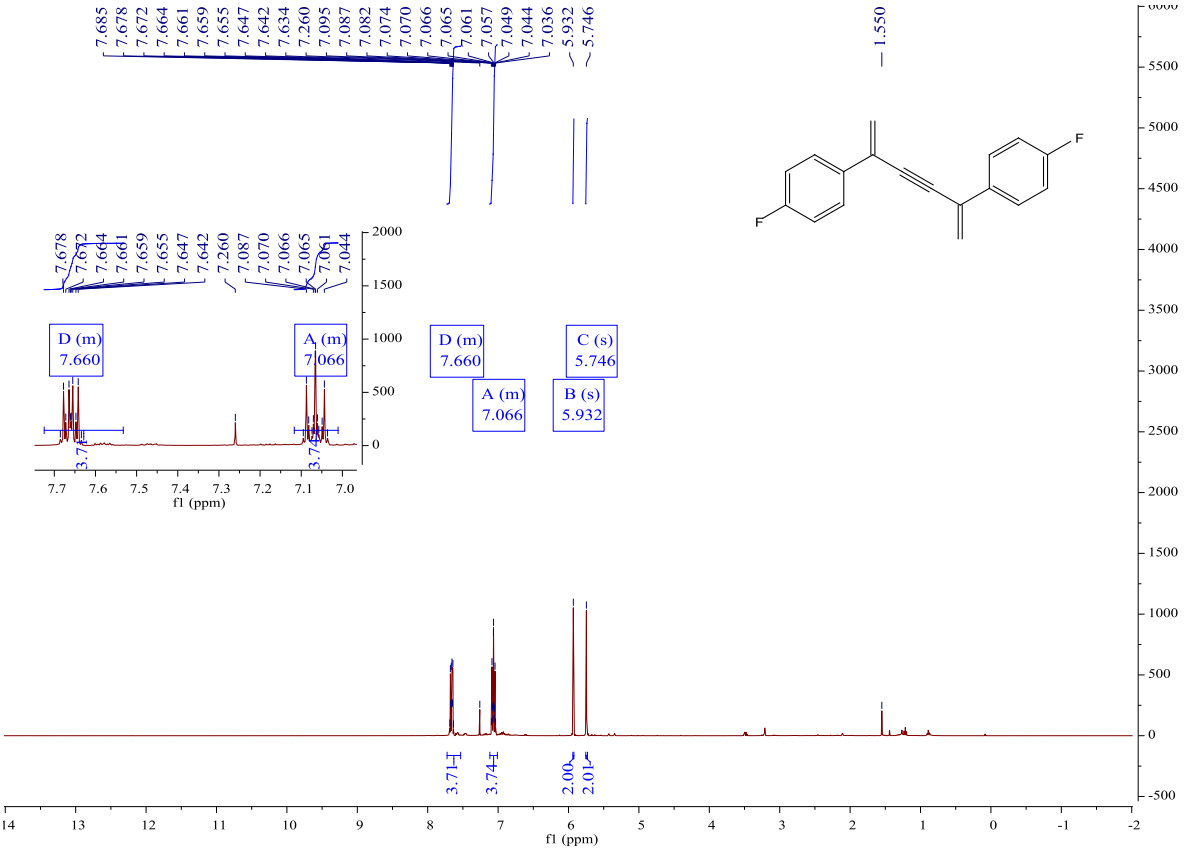
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7.044
7.036
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5.746
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F
F
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A (m)
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D (m)
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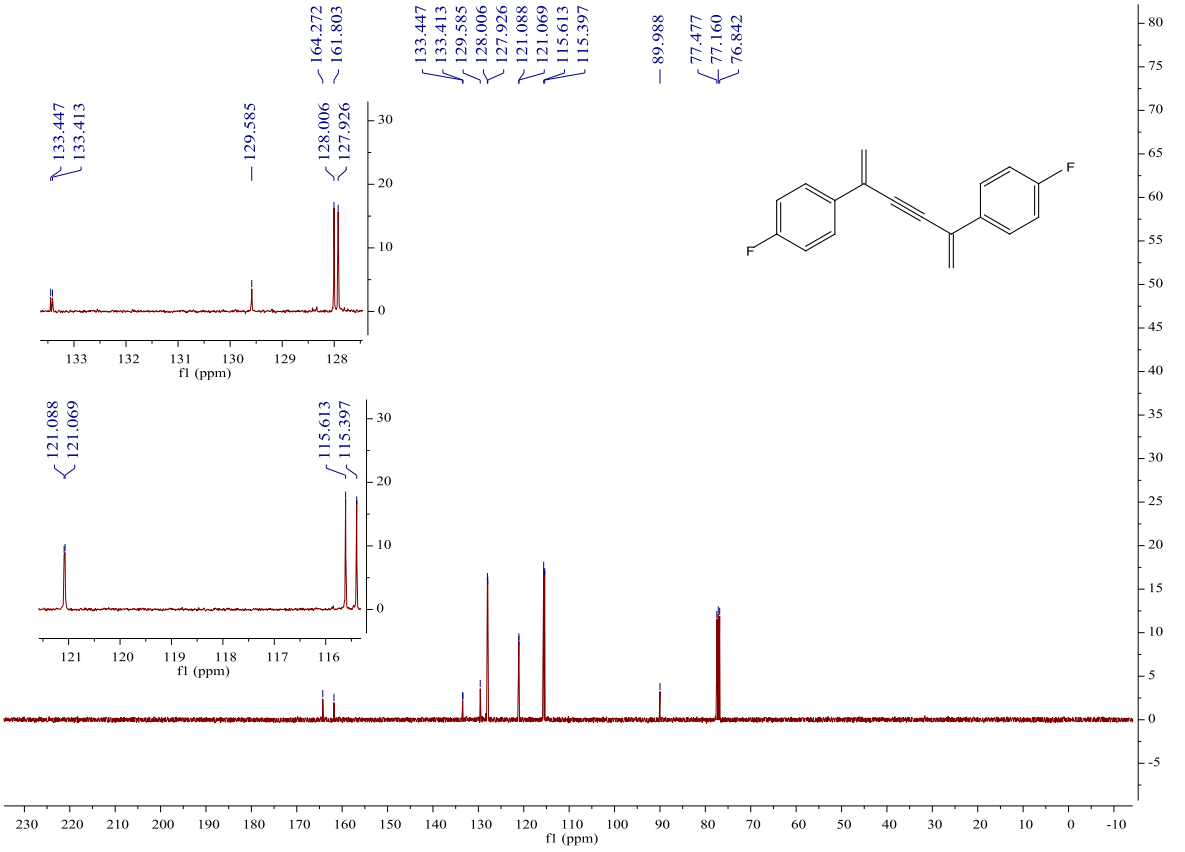
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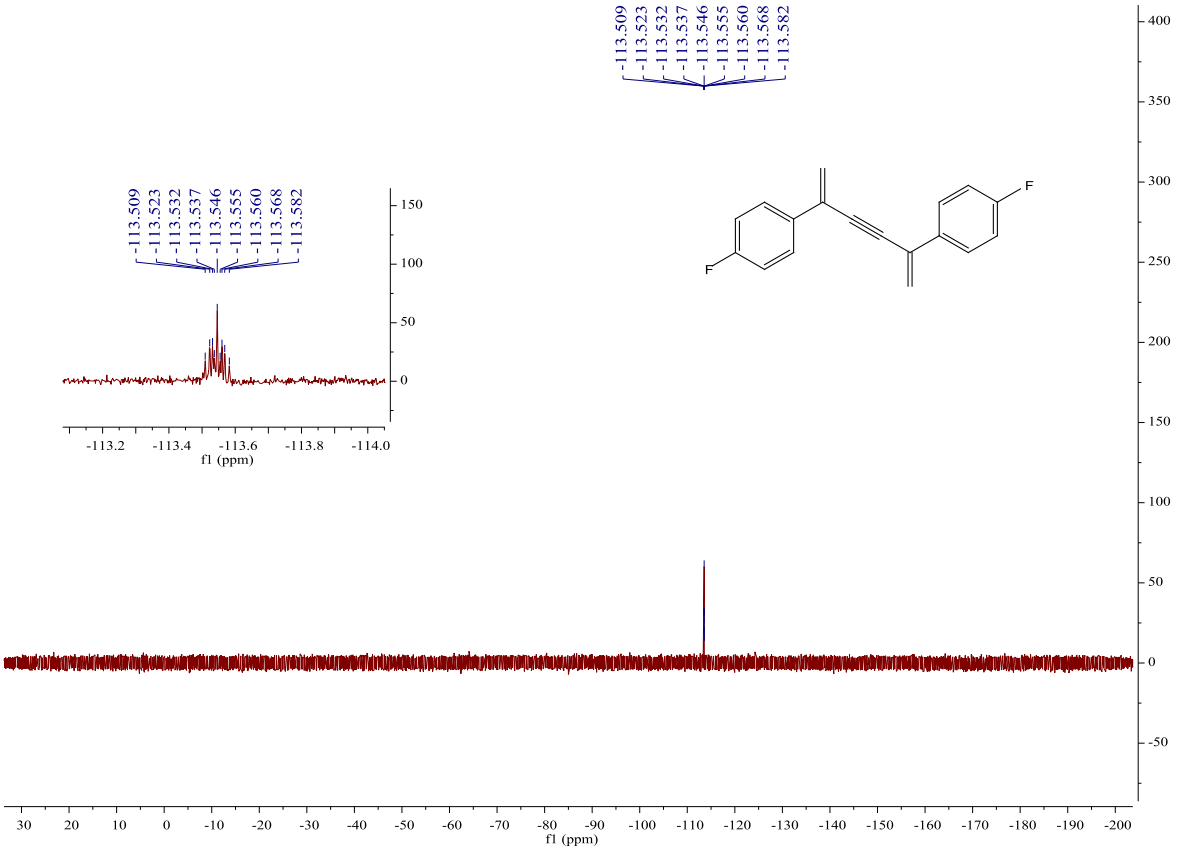
F
F
f1 (ppm)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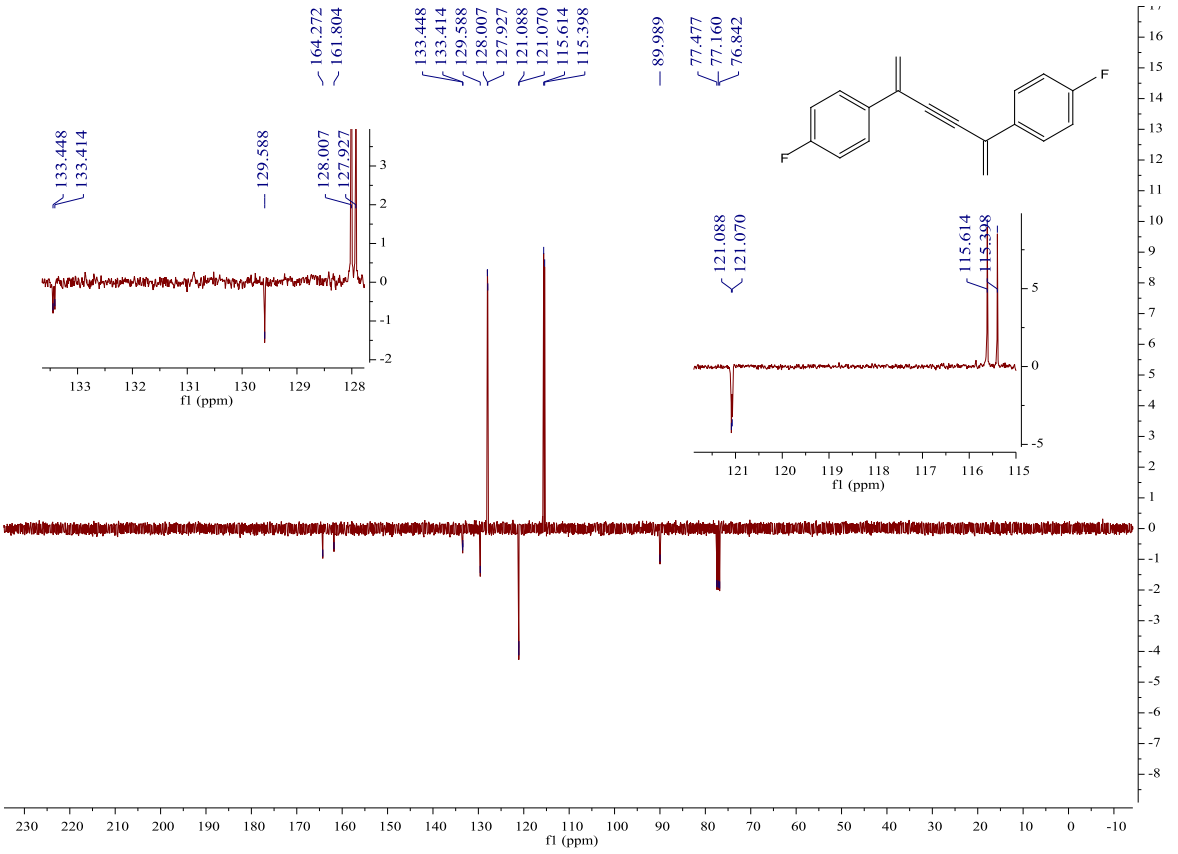
F
f1 (ppm)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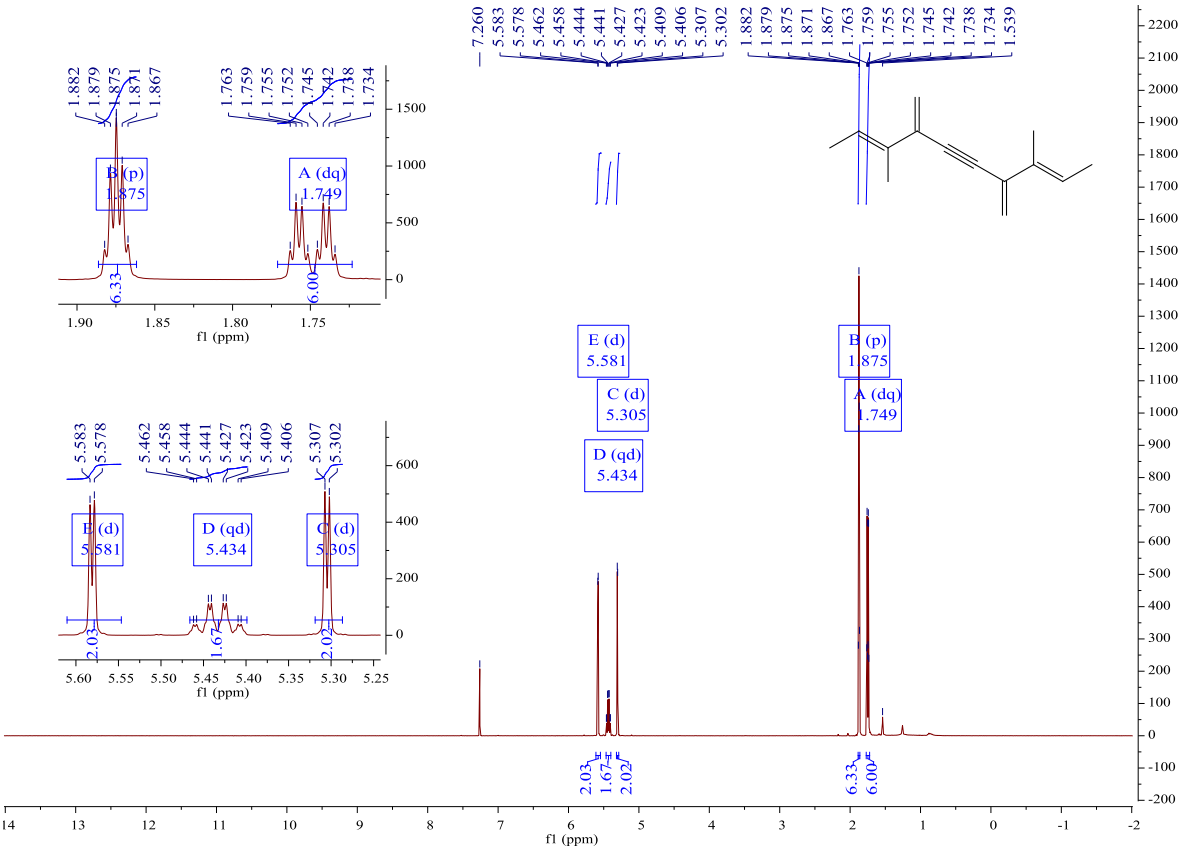
f1 (ppm)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1.871
1.867
1.763
1.759
1.755
1.752
1.745
1.742
1.738
1.734
1.539
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A (dq)
1.749
E (d)
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C (d)
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D (qd)
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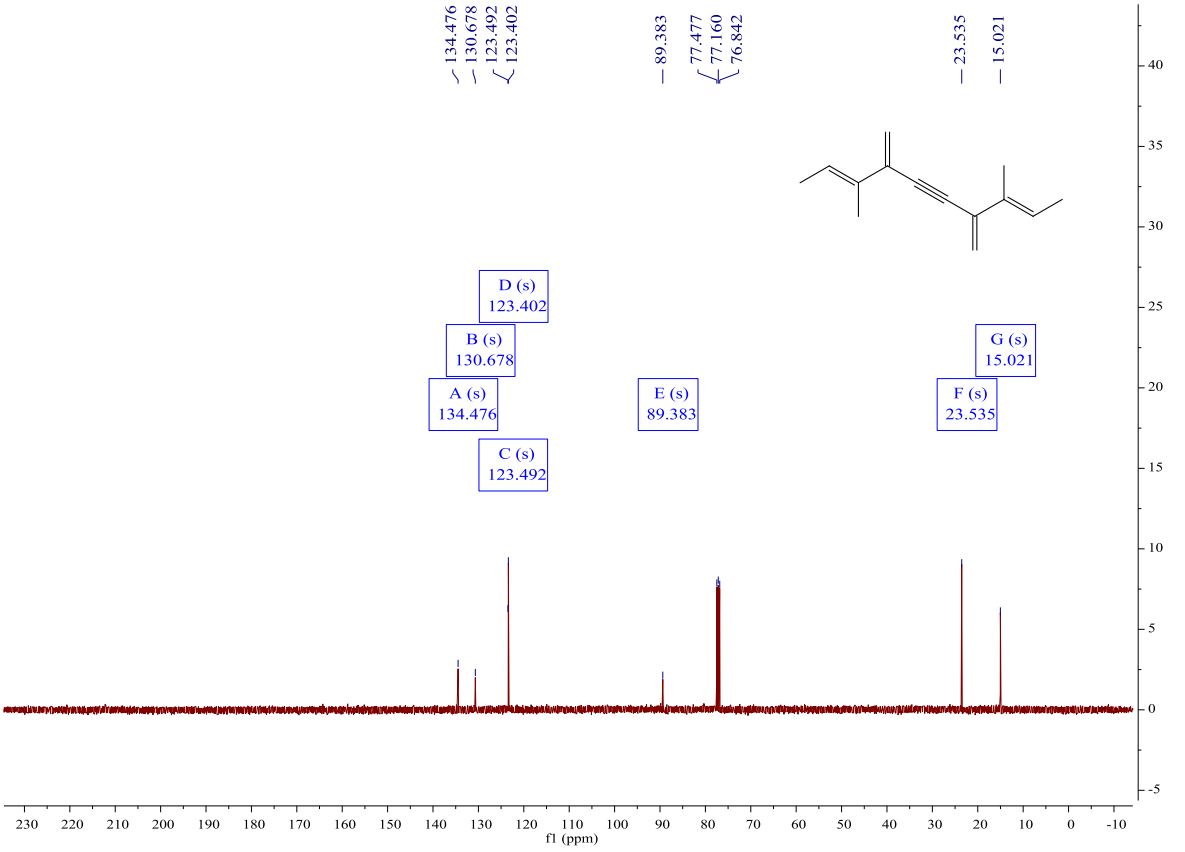
2.02
f1 (ppm)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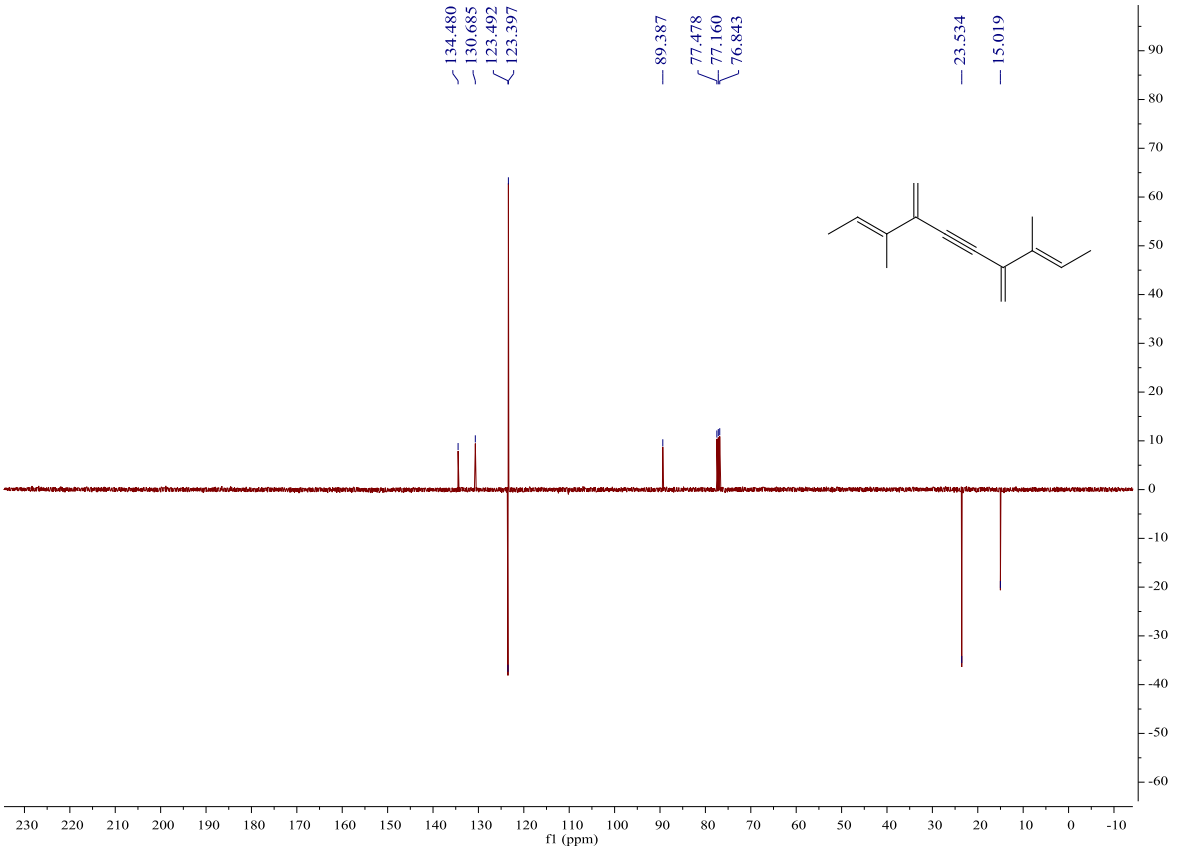
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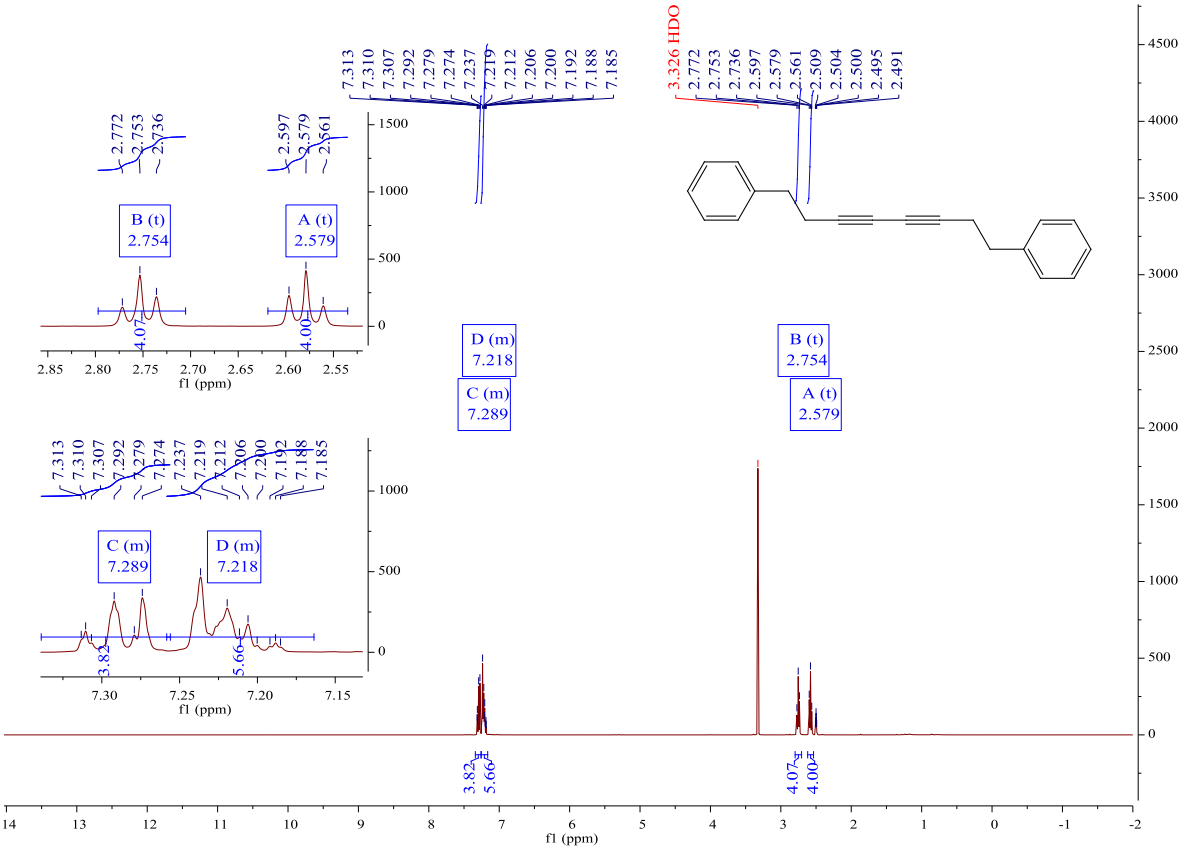
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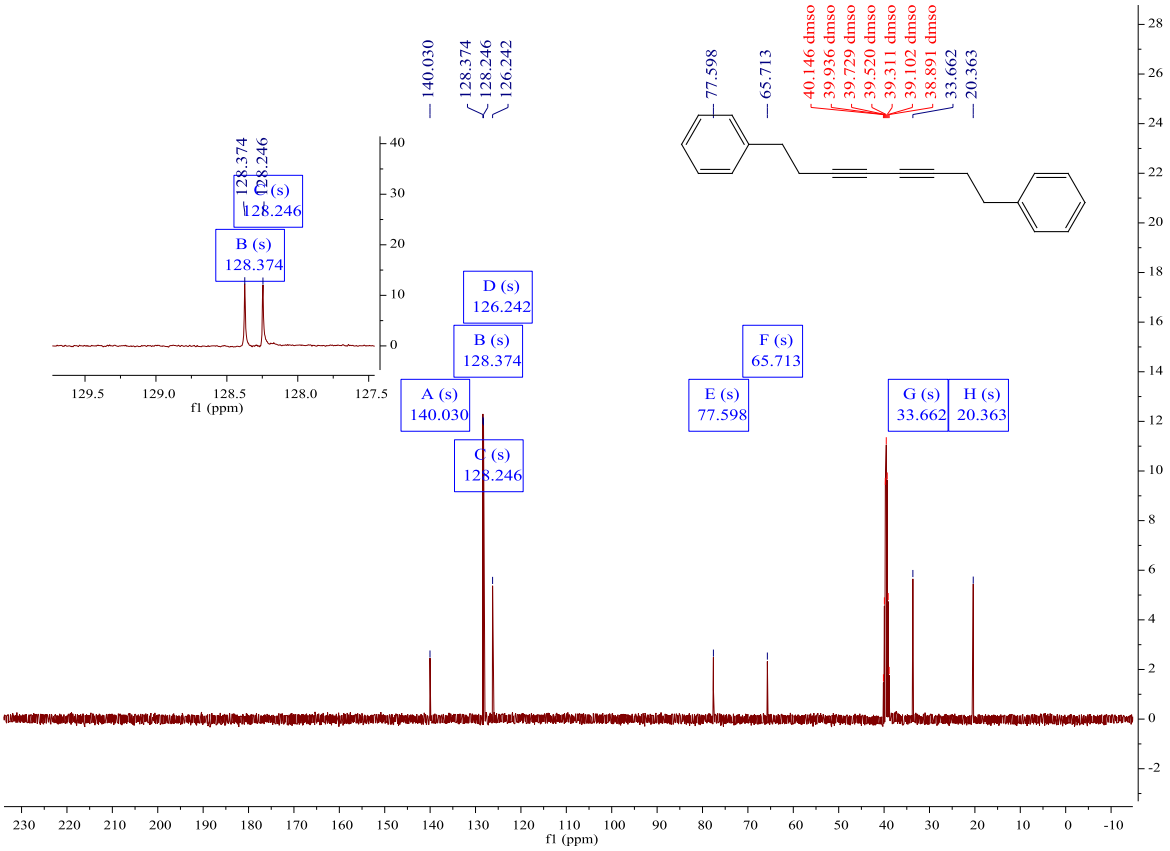
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39.102 dmso
38.891 dmso
33.662
20.363
A (s) 140.030
B (s) 128.374
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G (s) 33.662
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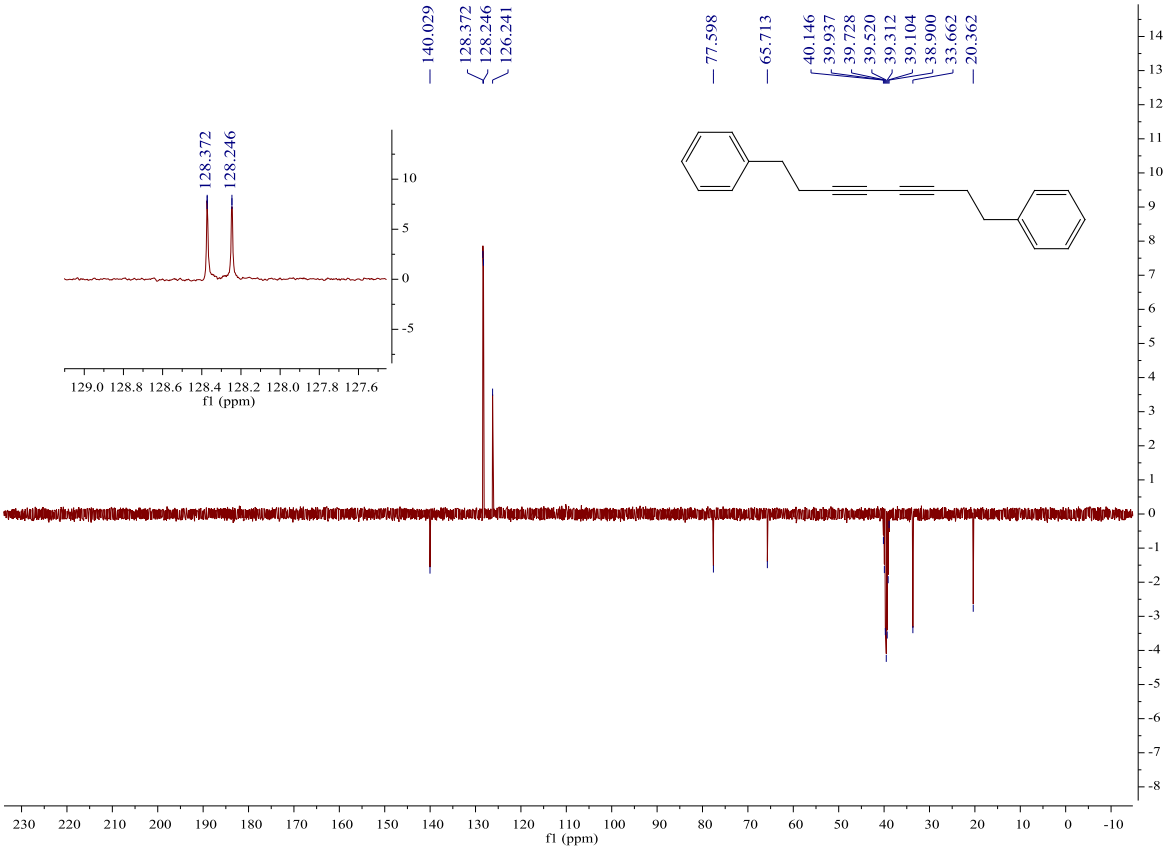
f1 (ppm)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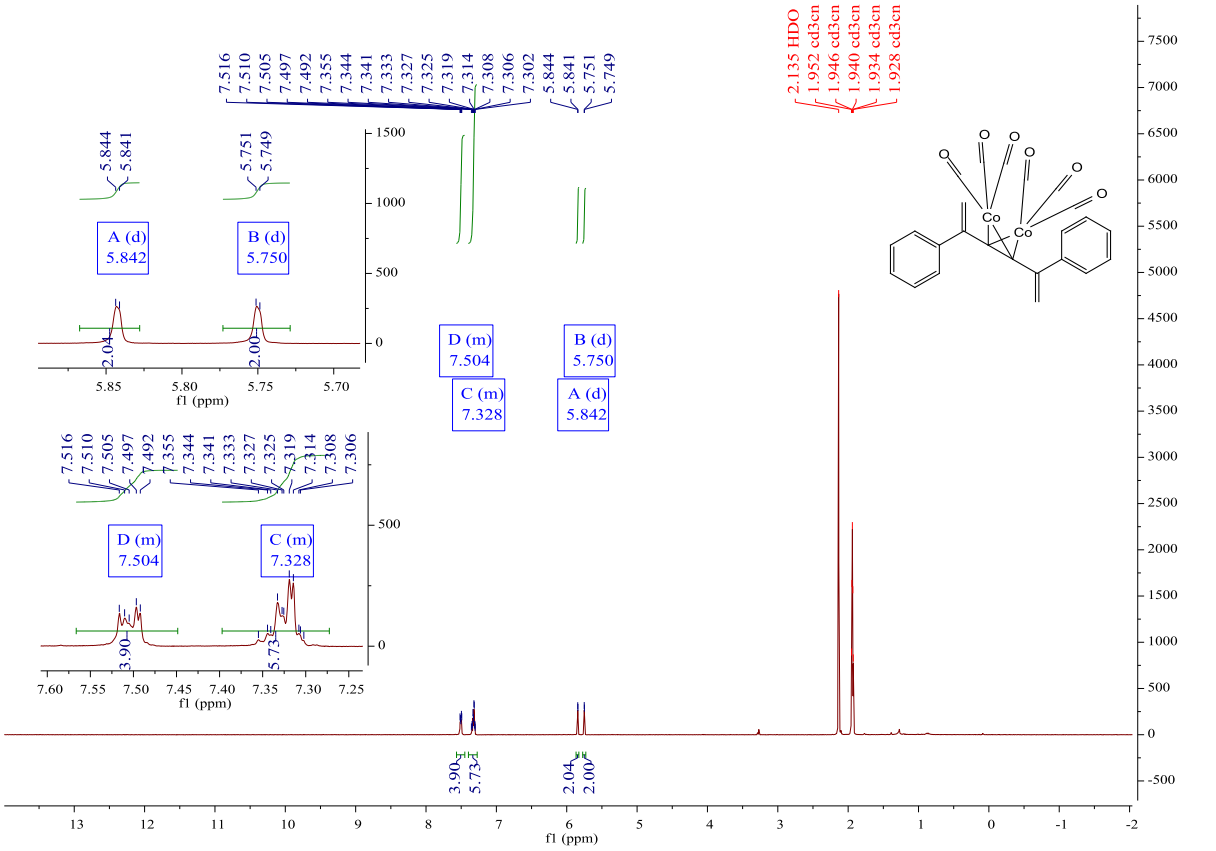
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7.314
7.308
7.306
7.302
5.844
5.841
5.751
5.749
2.135 HDO
1.952 cd3cn
1.946 cd3cn
1.940 cd3cn
1.934 cd3cn
1.928 cd3cn
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B (d)
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D (m)
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C (m)
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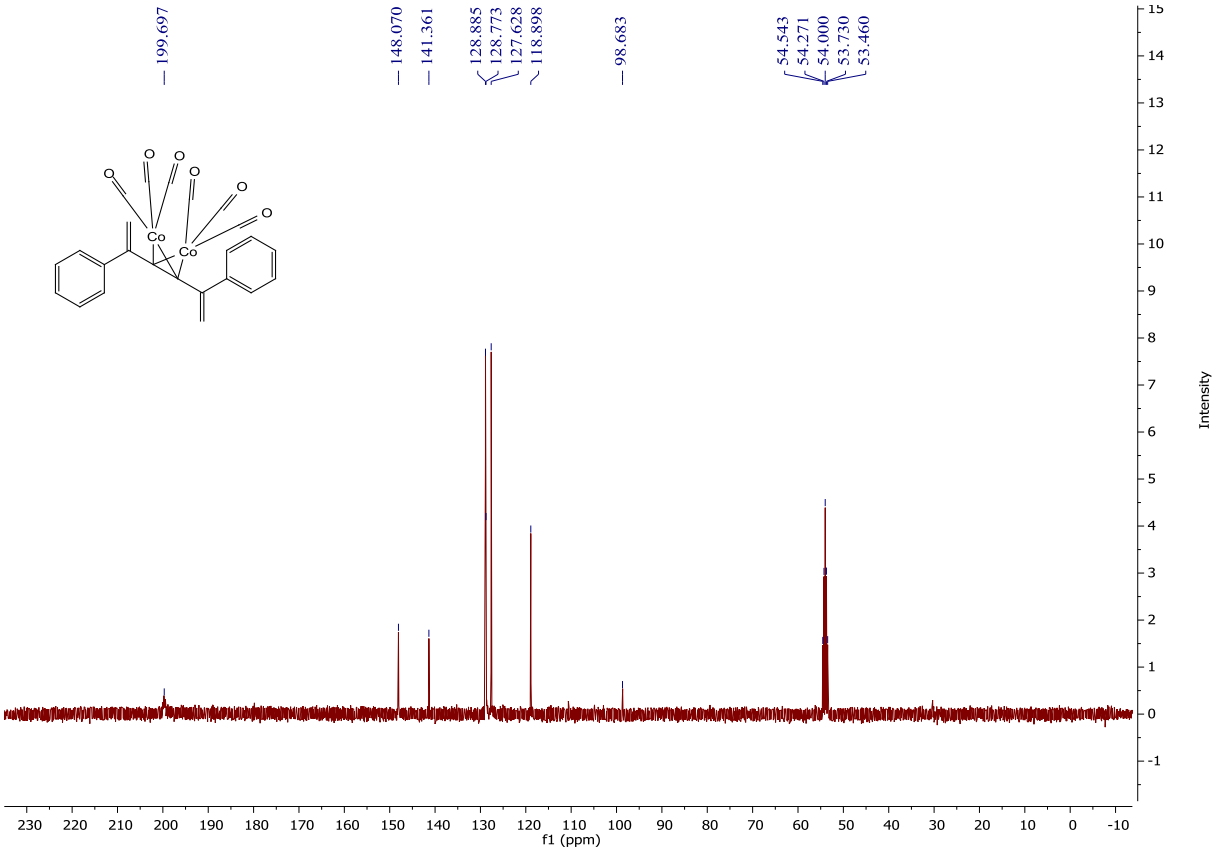
Co
Co
f1 (ppm)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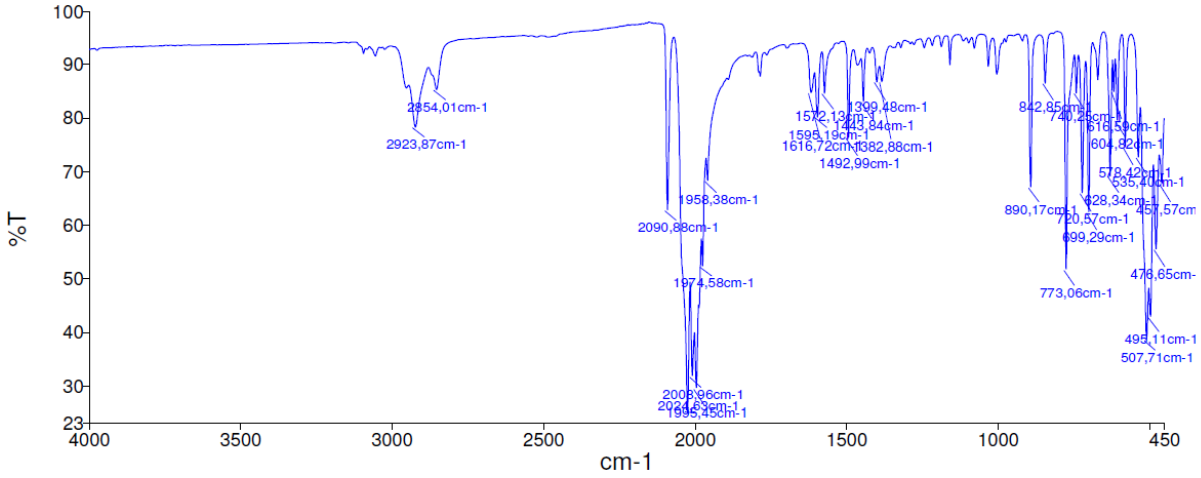
Co
Co
Intensity
f1 (ppm)

IR spectrum of complex 10



X-ray structure determination of dicobalt complex 10

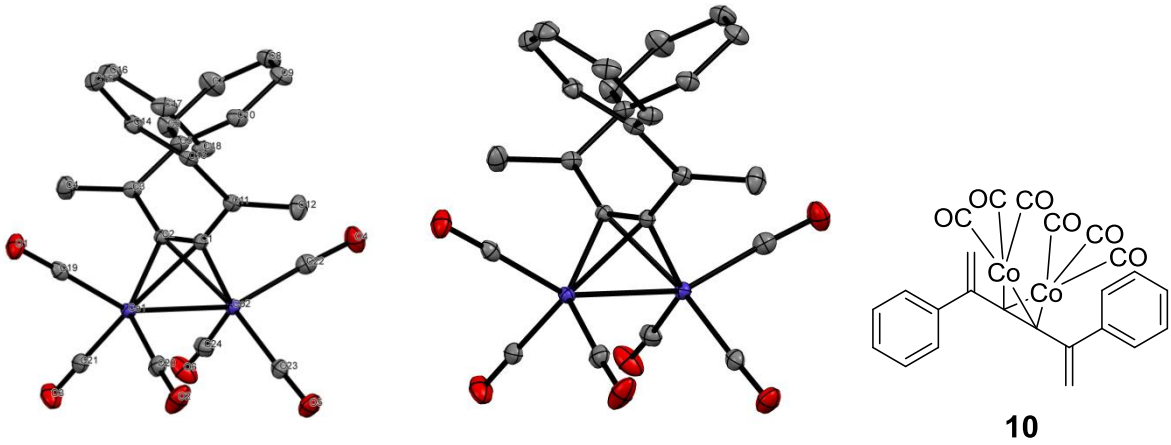


Figure S1 Molecular structure of compound **10**, showing 50% probability ellipsoids. Hydrogen atoms are omitted for clarity.

A single crystal of compound **10** was mounted on top of a cryoloop and transferred into the cold nitrogen stream (100 K) of a Bruker-AXS D8 Venture diffractometer. Data collection and reduction was done using the Bruker software suite APEX3.[1] The final unit cell was obtained from the xyz centroids of 9770 reflections after integration. A multiscan absorption correction was applied, based on the intensities of symmetry-related reflections measured at different angular settings (*SADABS*). The structures were solved by direct methods using *SHELXT*[2] and refinement of the structure was performed using *SHLELXL*.[3] The hydrogen atoms were generated by geometrical considerations, constrained to idealised geometries and allowed to ride on their carrier atoms with an isotropic displacement parameter related to the equivalent displacement parameter of their carrier atoms. Crystal data and details on

data collection and refinement are presented in **Table 1**. The structure was deposited in the CCDC deposition number: 1519007.

Table 1. Crystallographic data for dicobalt complex **10**

chem formula	C24 H14 Co2 O6
M_r	516.21
cryst syst	Triclinic
color, habit	red, block
size (mm)	0.24 x 0.29 x 0.32
space group	P -1
a (Å)	8.4376(11)
b (Å)	10.1022(12)
c (Å)	13.0614(15)
α, deg	98.593(4)
β, deg	92.973(4)
γ, deg	100.142(4)
V ($Å^3$)	1080.1(2)
Z	2
ρ_{calc}, $g.cm^{-3}$	1.587
μ(Mo K$\overline{\alpha}$), cm^{-1}	1.574
F(000)	520
temp (K)	100(2)
θ range (deg)	3.245 – 27.925
data collected (h,k,l)	-11:11, -13:13, -17:17
no. of rflns collected	44480
no. of indpndt reflns	5140
observed reflns	4915 ($F_o \geq 2\ \sigma(F_o)$)
R(F) (%)	1.78
wR(F^2) (%)	4.78
GooF	1.057
Weighting a,b	0.0228, 0.5470
params refined	289
restraints	0
min, max resid dens	-0.294, 0.361

[1] Bruker. *APEX3, SAINT and SADABS. Bruker AXS Inc., Madison, Wisconsin*, *USA*. **2016**.
[2] Sheldrick, G. M. *Acta Cryst.* **2015**, *A71*, 3-8.
[3] Sheldrick, G. M.. *Acta Cryst.* **2008**, ***A64***, 112-122.

GC-MS Spectra

Method

═══ Analytical Line 1 ═══

[GC-2010]

Column Oven Temp.	:50.0 °C
Injection Temp.	:300.00 °C
Injection Mode	:Split
Flow Control Mode	:Linear Velocity
Pressure	:68.1 kPa
Total Flow	:64.1 mL/min
Column Flow	:1.20 mL/min
Linear Velocity	:39.7 cm/sec
Purge Flow	:3.0 mL/min
Split Ratio	:50.0
High Pressure Injection	:OFF
Carrier Gas Saver	:OFF
Splitter Hold	:OFF

Oven Temp. Program

Rate	Temperature(°C)	Hold Time(min)
-	50.0	5.00
10.00	300.0	40.00

< Ready Check Heat Unit >	
Column Oven	: Yes
SPL1	: Yes
MS	: Yes
SPL2	: Yes
MS	: Yes
< Ready Check Detector(FTD) >	
< Ready Check Baseline Drift >	
< Ready Check Injection Flow >	
SPL1 Carrier	: Yes
SPL1 Purge	: Yes
SPL2 Carrier	: Yes
SPL2 Purge	: Yes
< Ready Check APC Flow >	
< Ready Check Detector APC Flow >	
External Wait	:No
Equilibrium Time	:0.0 min

[GC Program]

═══ Analytical Line 2 ═══

[GC-2010]

Injection Temp.	:250.00 °C
Injection Mode	:Split
Flow Control Mode	:Linear Velocity
Pressure	:68.1 kPa
Total Flow	:64.1 mL/min
Column Flow	:1.20 mL/min
Linear Velocity	:39.7 cm/sec
Purge Flow	:3.0 mL/min
Split Ratio	:50.0
High Pressure Injection	:OFF
Carrier Gas Saver	:OFF
Splitter Hold	:OFF

Oven Temp. Program

Rate	Temperature(°C)	Hold Time(min)
-	50.0	5.00
10.00	300.0	40.00

[GCMS-QP2010]

IonSourceTemp	:200.00 °C
Interface Temp.	:225.00 °C
Solvent Cut Time	:3.00 min
Detector Gain Mode	:Relative
Detector Gain	:1.25 kV +0.00 kV
Threshold	:0

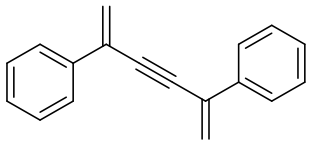
[MS Table]

--Group 1 - Event 1--

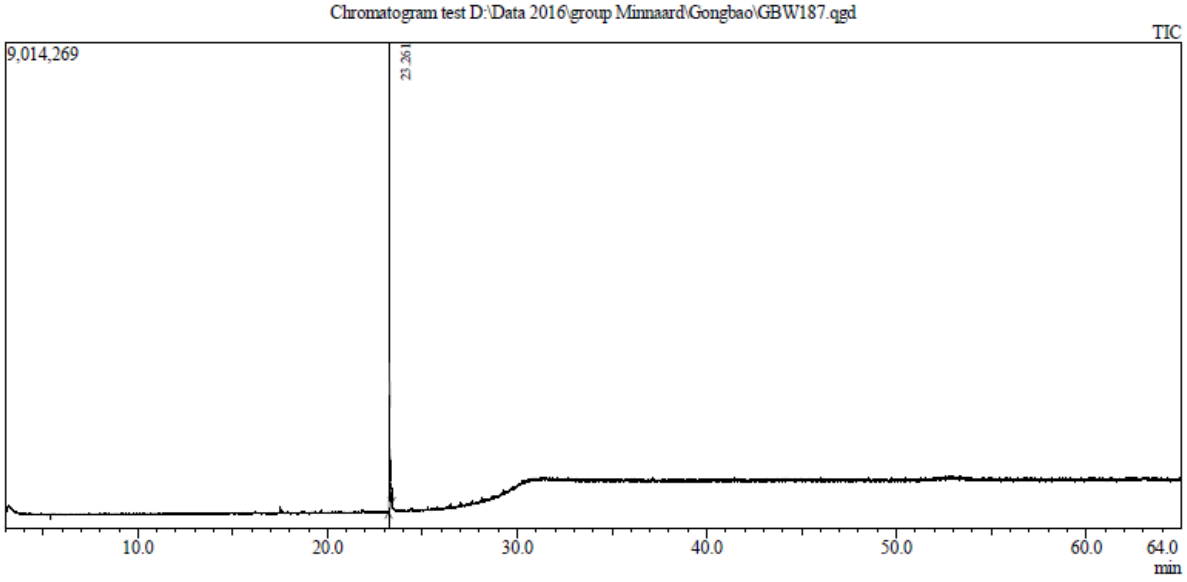
Start Time	:3.00min
End Time	:65.00min
ACQ Mode	:Scan
Event Time	:0.30sec
Scan Speed	:2000
Start m/z	:20.00
End m/z	:550.00
Sample Inlet Unit	:GC
Inlet Line	:Line 2

Sample Information

Analyzed by	: Admin
Analyzed	: 16-3-2016 21:22:49
Sample Type	: Unknown
Sample Name	: test
If(Tray!=)Tray	: Tray1
Sample Amount	: 1
Dilution Factor	: 1
Injection Volume	: 1.00
Modified by	: Admin
Modified	: 4-5-2016 15:02:16



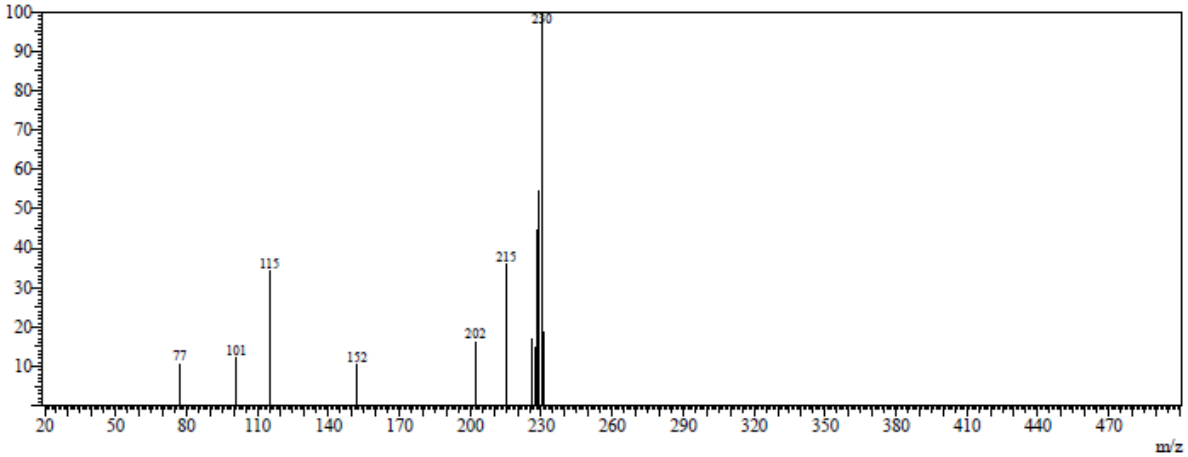
Chromatogram test D:\Data 2016\group Minnaard\Gongbao\GBW187.qgd



Peak Report TIC

Peak#	R.Time	I.Time	F.Time	Area	Area%	Height	Height%	A/H	Mark	Name
1	23.261	23.220	23.390	16471004	100.00	8685542	100.00	1.90		
				16471004	100.00	8685542	100.00			

Spectrum

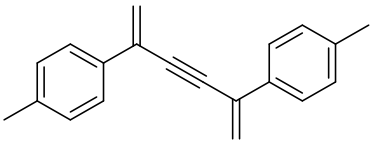


Mass Table

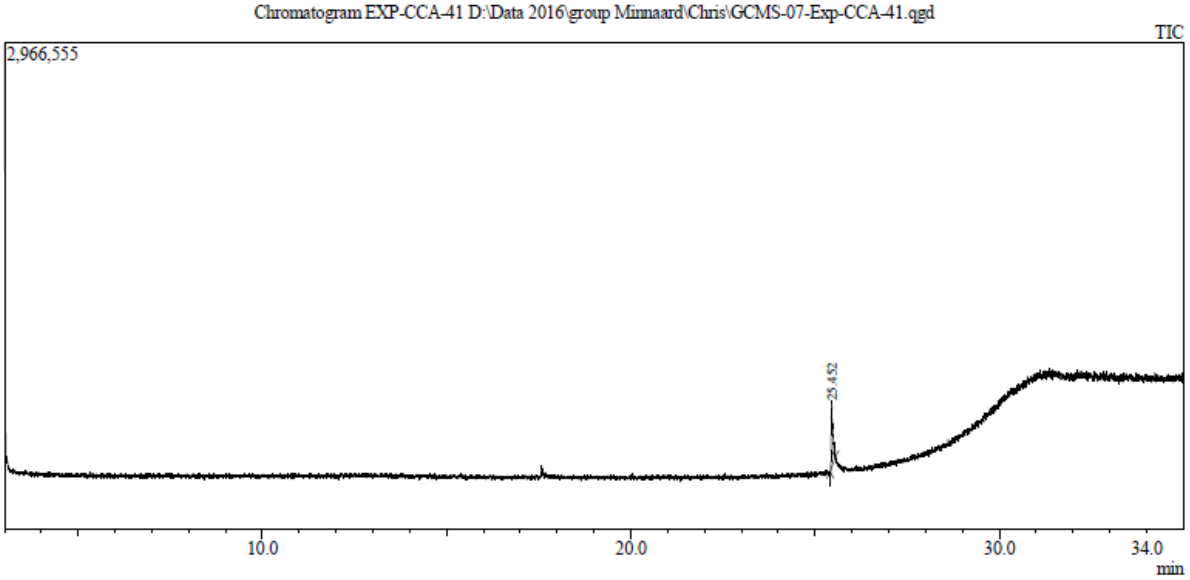
#	m/z	Abs. Int.	Rel. Int.
1	77.10	154992	10.59
2	101.10	175586	12.00
3	115.10	500335	34.20
4	152.15	152138	10.40
5	202.10	235766	16.11
6	215.15	522003	35.68
7	226.15	245221	16.76
8	227.15	215436	14.72
9	228.15	650778	44.48
10	229.15	796592	54.45
11	230.15	1463100	100.00
12	231.15	271316	18.54

Sample Information

Analyzed by	: Admin
Analyzed	: 24-3-2016 18:42:05
Sample Type	: Unknown
Sample Name	: EXP-CCA-41
If(Tray!=)Tray	: Tray1
Sample Amount	: 1
Dilution Factor	: 1
Injection Volume	: 1.00
Modified by	: Admin
Modified	: 24-3-2016 19:17:06



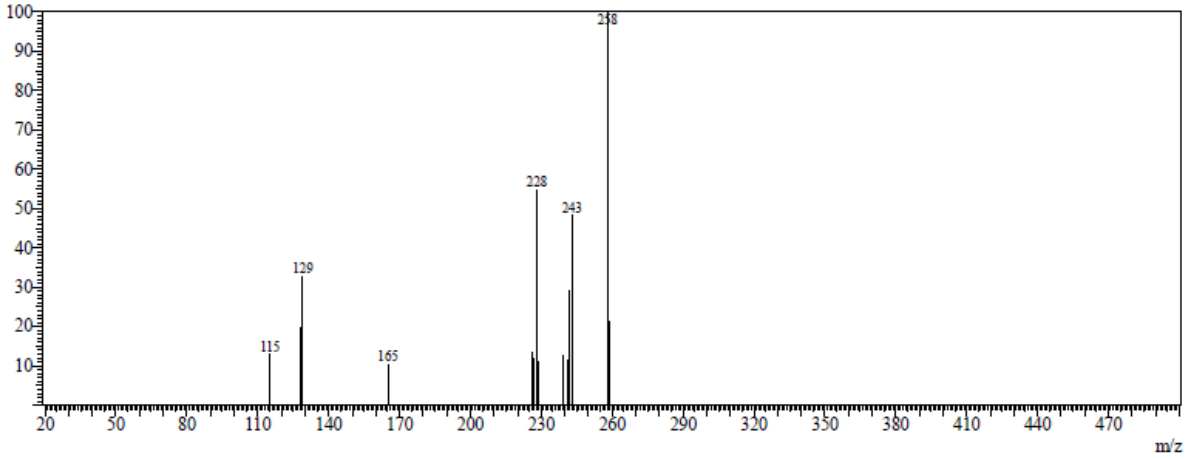
Chromatogram EXP-CCA-41 D:\Data 2016\group Minnaard\Chris\GCMS-07-Exp-CCA-41.qgd



Peak Report TIC

Peak#	R.Time	I.Time	F.Time	Area	Area%	Height	Height%	A/H	Mark	Name
1	25.452	25.415	25.545	1292453	100.00	407181	100.00	3.17		
				1292453	100.00	407181	100.00			

Spectrum

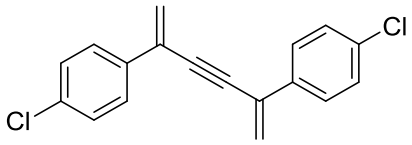


Mass Table

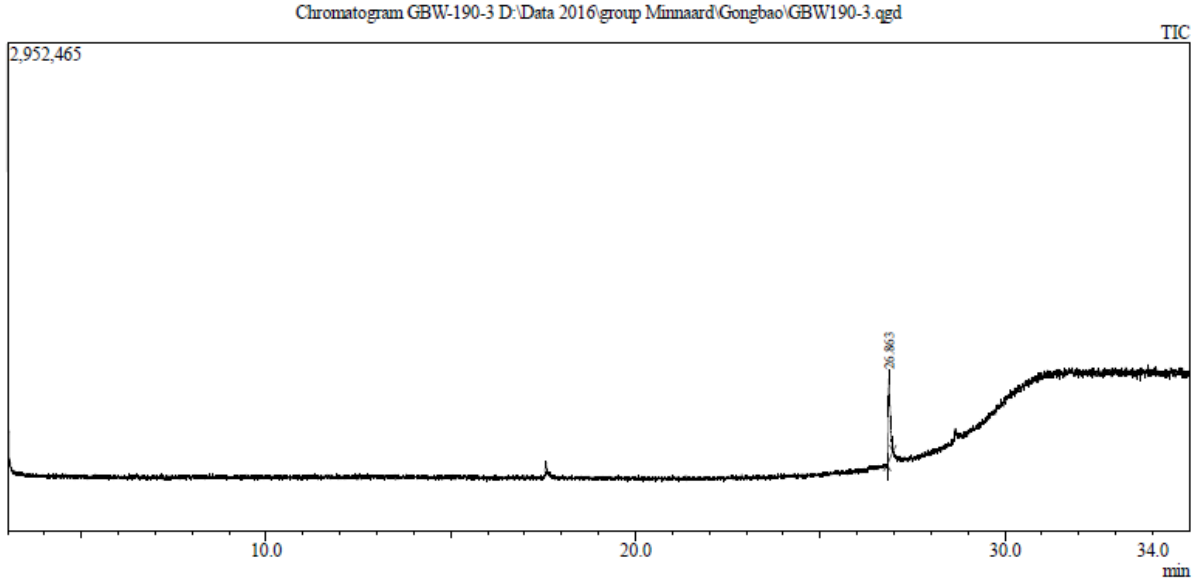
#	m/z	Abs. Int.	Rel. Int.
1	115.10	7883	12.90
2	128.05	11971	19.59
3	129.05	19985	32.71
4	165.05	6284	10.29
5	226.10	8191	13.41
6	226.95	7255	11.87
7	228.05	33419	54.70
8	228.95	6889	11.28
9	239.00	7673	12.56
10	241.00	6981	11.43
11	242.05	17756	29.06
12	243.05	29466	48.23
13	258.05	61095	100.00
14	259.10	13015	21.30

Sample Information

Analyzed by	: Admin
Analyzed	: 24-3-2016 15:56:30
Sample Type	: Unknown
Sample Name	: GBW-190-3
If(Tray!=)Tray	: Tray1
Sample Amount	: 1
Dilution Factor	: 1
Injection Volume	: 1.00
Modified by	: Admin
Modified	: 24-3-2016 16:31:30



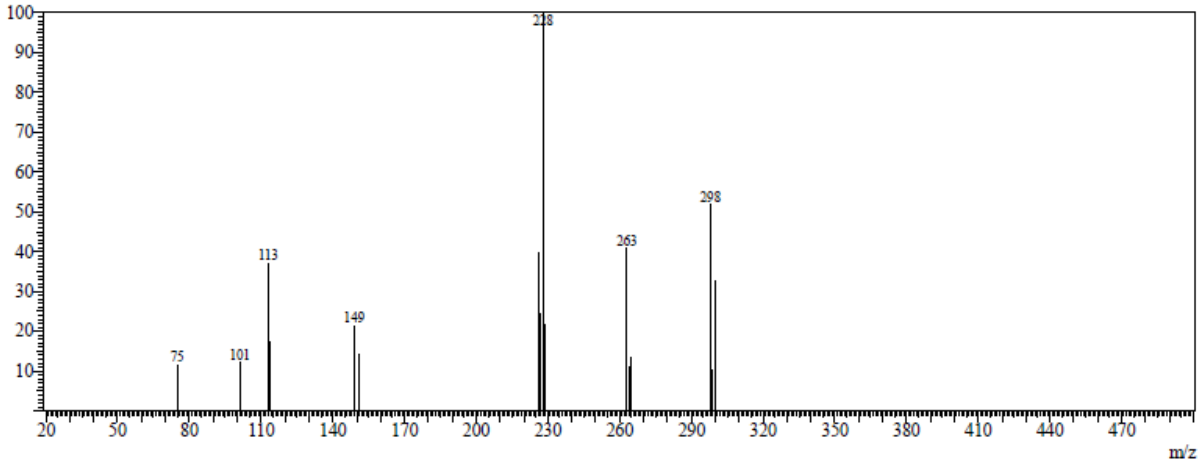
Chromatogram GBW-190-3 D:\Data 2016\group Minnaard\Gongbao\GBW190-3.qgd



Peak Report TIC

Peak#	R.Time	I.Time	F.Time	Area	Area%	Height	Height%	A/H	Mark	Name
1	26.863	26.815	26.970	1854555	100.00	552407	100.00	3.36		
				1854555	100.00	552407	100.00			

Spectrum

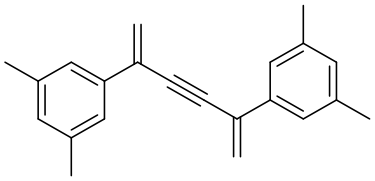


Mass Table

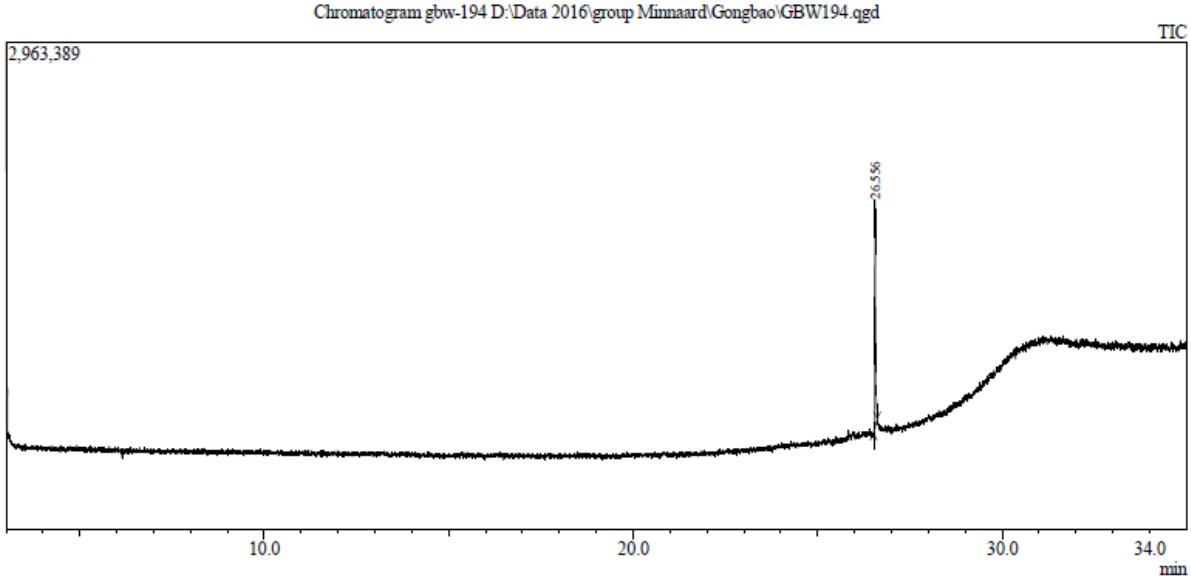
#	m/z	Abs. Int.	Rel. Int.
1	74.95	8926	11.60
2	101.10	9404	12.23
3	113.00	28569	37.14
4	113.95	13391	17.41
5	149.05	16484	21.43
6	151.00	10874	14.14
7	226.00	30662	39.86
8	227.00	18655	24.25
9	228.00	76923	100.00
10	229.00	16657	21.65
11	263.00	31424	40.85
12	264.05	8464	11.00
13	265.00	10340	13.44
14	297.95	39862	51.82
15	298.95	7926	10.30

Sample Information

Analyzed by	: Admin
Analyzed	: 30-3-2016 18:51:25
Sample Type	: Unknown
Sample Name	: gbw-194
If(Tray!=)Tray	: Tray1
Sample Amount	: 1
Dilution Factor	: 1
Injection Volume	: 2.00
Modified by	: Admin
Modified	: 30-3-2016 19:26:25



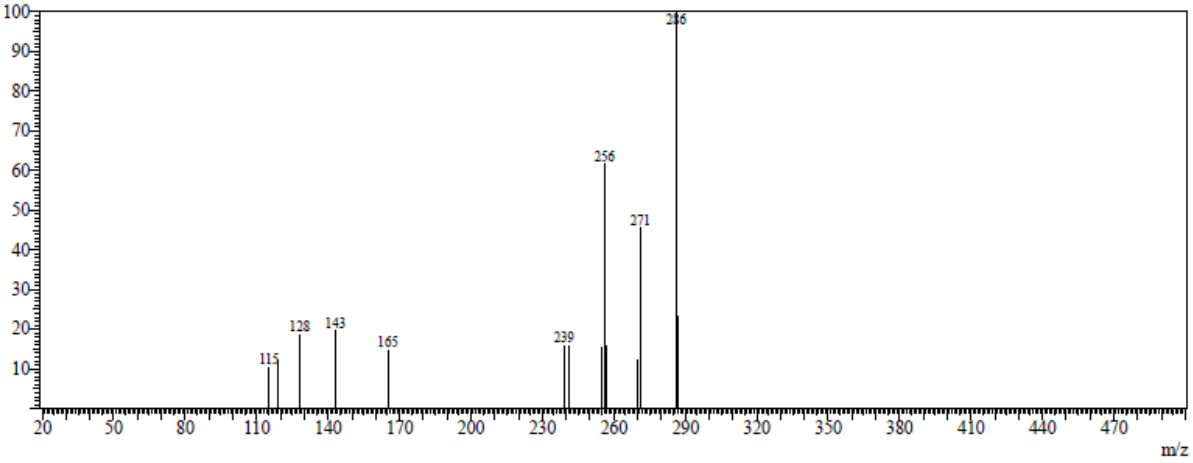
Chromatogram gbw-194 D:\Data 2016\group Minnaard\Gongbao\GBW194.qgd



Peak Report TIC

Peak#	R.Time	I.Time	F.Time	Area	Area%	Height	Height%	A/H	Mark	Name
1	26.556	26.515	26.615	2571569	100.00	1389439	100.00	1.85		
				2571569	100.00	1389439	100.00			

Spectrum

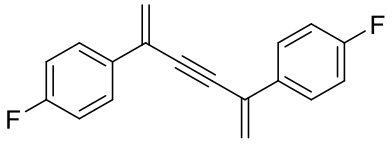


Mass Table

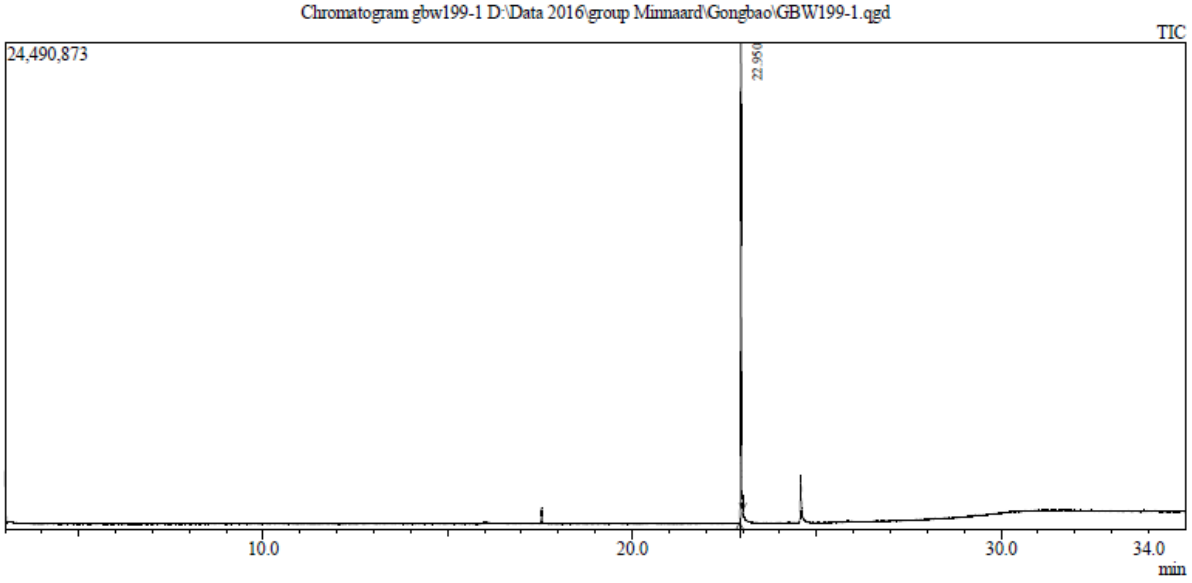
#	m/z	Abs. Int.	Rel. Int.
1	115.10	19791	10.44
2	119.20	23288	12.29
3	128.05	35411	18.68
4	143.10	37179	19.61
5	165.05	27964	14.75
6	239.05	30158	15.91
7	241.05	30129	15.89
8	255.10	28846	15.22
9	256.10	116723	61.58
10	257.10	29807	15.72
11	270.10	23430	12.36
12	271.10	86218	45.48
13	286.15	189558	100.00
14	287.15	43945	23.18

Sample Information

Analyzed by	: Admin
Analyzed	: 5-4-2016 11:16:30
Sample Type	: Unknown
Sample Name	: gbw199-1
If(Tray!=)Tray	: Tray1
Sample Amount	: 1
Dilution Factor	: 1
Injection Volume	: 1.00
Modified by	: Admin
Modified	: 5-4-2016 11:51:30



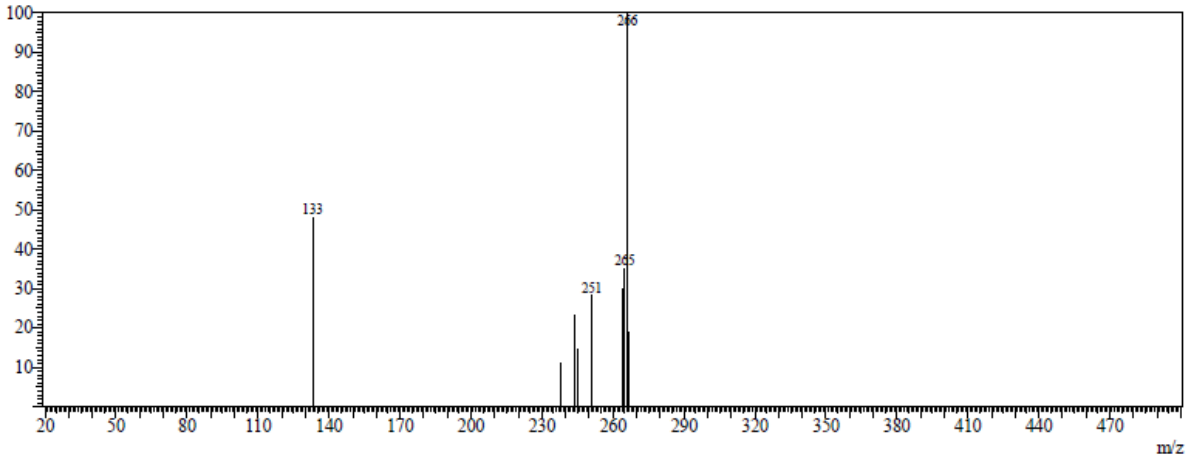
Chromatogram gbw199-1 D:\Data 2016\group Minnaard\Gongbao\GBW199-1.qgd



Peak Report TIC

Peak#	R.Time	I.Time	F.Time	Area	Area%	Height	Height%	A/H	Mark	Name
1	22.950	22.915	23.000	36844705	100.00	23897739	100.00	1.54		
				36844705	100.00	23897739	100.00			

Spectrum

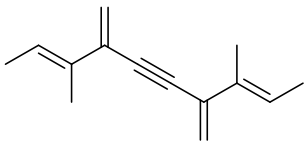


Mass Table

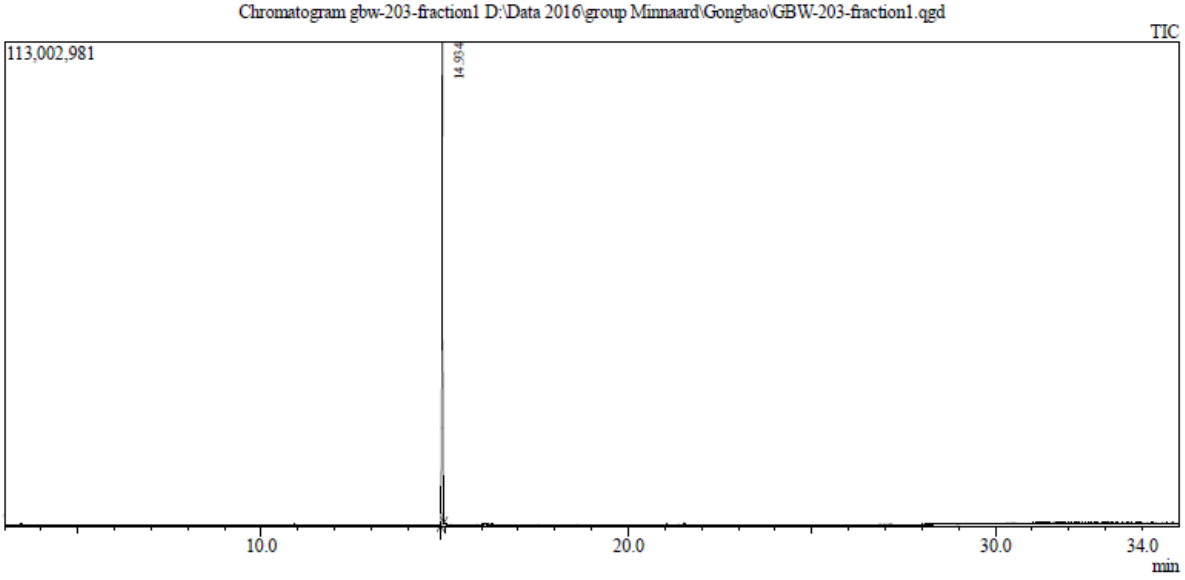
#	m/z	Abs. Int.	Rel. Int.
1	133.05	1886962	48.10
2	238.00	440610	11.23
3	244.05	910797	23.22
4	245.00	566402	14.44
5	251.05	1106053	28.20
6	264.00	1170347	29.84
7	265.00	1376402	35.09
8	266.05	3922608	100.00
9	267.05	738660	18.83

Sample Information

Analyzed by	: Admin
Analyzed	: 13-4-2016 20:23:51
Sample Type	: Unknown
Sample Name	: gbw-203-fraction1
If(Tray!=)Tray	: Tray1
Sample Amount	: 1
Dilution Factor	: 1
Injection Volume	: 1.00
Modified by	: Admin
Modified	: 13-4-2016 20:58:52



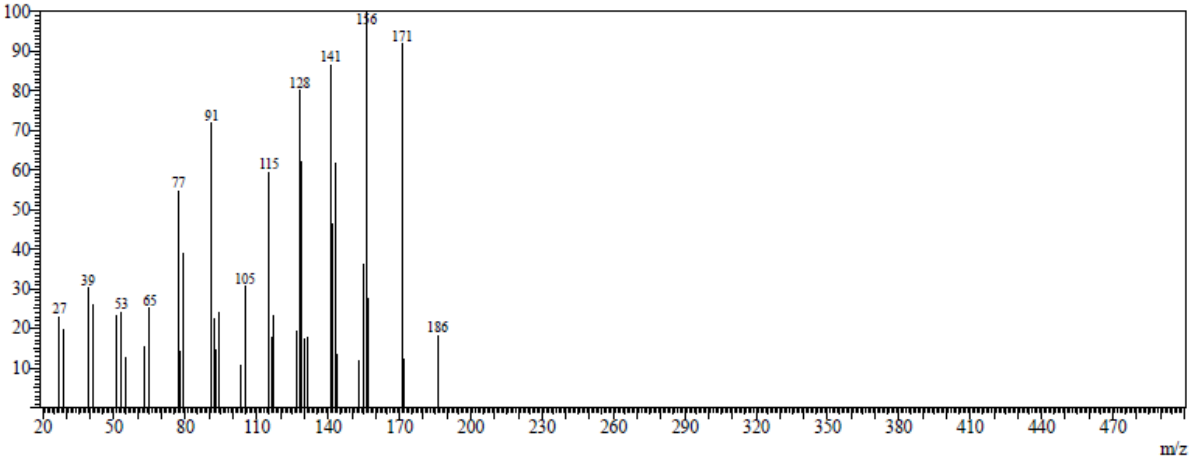
Chromatogram gbw-203-fraction1 D:\Data 2016\group Minnaard\Gongbao\GBW-203-fraction1.qgd



Peak Report TIC

Peak#	R.Time	I.Time	F.Time	Area	Area%	Height	Height%	A/H	Mark	Name
1	14.934	14.885	14.980	176493392	100.00	112478961	100.00	1.57		
				176493392	100.00	112478961	100.00			

Spectrum



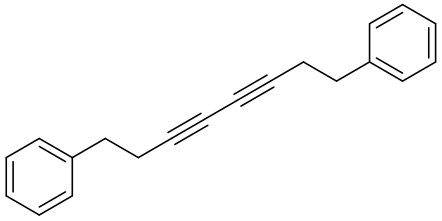
Mass Table

#	m/z	Abs. Int.	Rel. Int.
1	27.05	1582277	22.92
2	29.05	1372585	19.88
3	39.05	2090067	30.28
4	41.05	1798370	26.05
5	51.00	1603031	23.22
6	53.05	1665569	24.13
7	55.05	866829	12.56
8	63.00	1049601	15.21
9	65.00	1736010	25.15
10	77.00	3775611	54.70
11	78.00	984827	14.27
12	79.05	2690214	38.97
13	91.05	4959802	71.85
14	92.05	1558959	22.58
15	93.05	994625	14.41

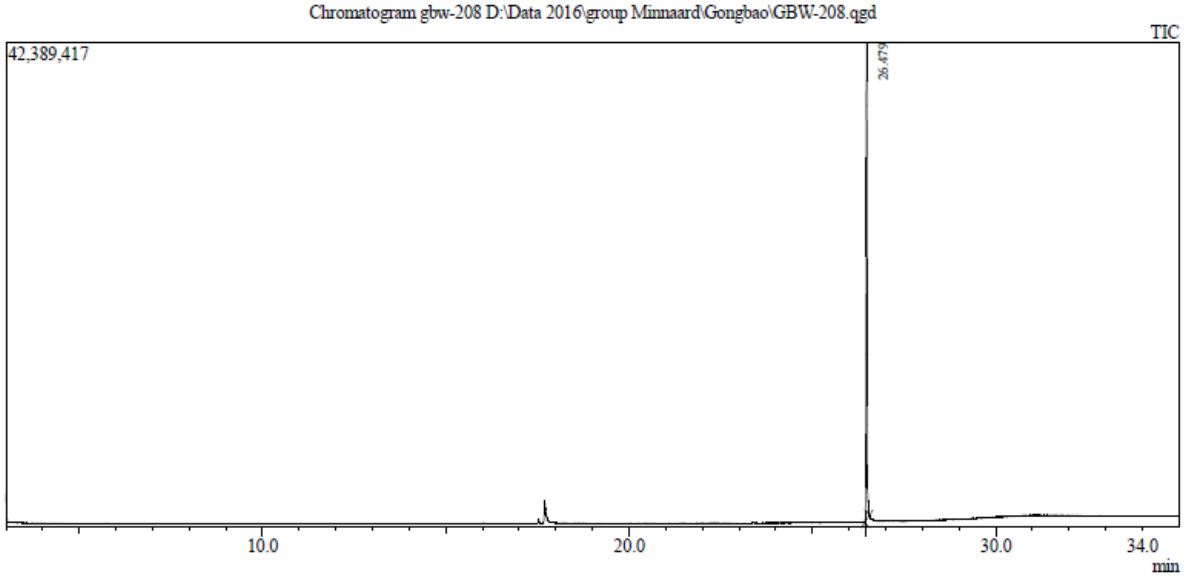
#	m/z	Abs. Int.	Rel. Int.
16	94.05	1644054	23.82
17	103.05	743433	10.77
18	105.05	2115388	30.65
19	115.05	4101506	59.42
20	116.05	1229172	17.81
21	117.05	1602804	23.22
22	127.00	1346991	19.51
23	128.05	5522082	80.00
24	129.05	4286348	62.10
25	130.05	1189401	17.23
26	131.10	1212085	17.56
27	141.05	5968519	86.46
28	142.05	3192094	46.24
29	143.10	4244026	61.48
30	144.10	917719	13.29
31	153.05	828054	12.00
32	155.10	2486721	36.02
33	156.10	6902826	100.00
34	157.10	1904816	27.59
35	171.10	6333245	91.75
36	172.10	856629	12.41
37	186.05	1252671	18.15

Sample Information

Analyzed by	: Admin
Analyzed	: 18-4-2016 19:30:41
Sample Type	: Unknown
Sample Name	: gbw-208
If(Tray!=)Tray	: Tray1
Sample Amount	: 1
Dilution Factor	: 1
Injection Volume	: 1.00
Modified by	: Admin
Modified	: 18-4-2016 20:05:42



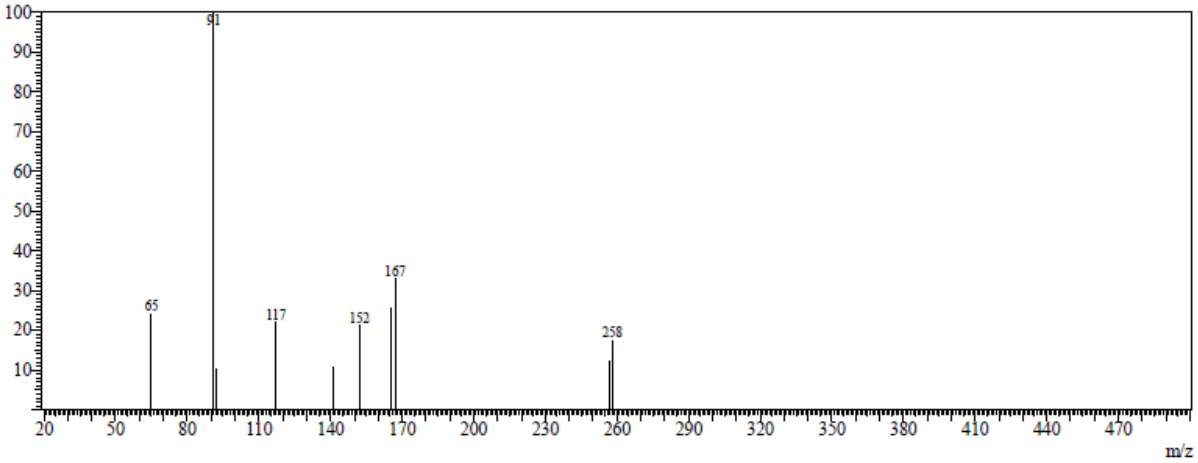
Chromatogram gbw-208 D:\Data 2016\group Minnaard\Gongbao\GBW-208.qgd



Peak Report TIC

Peak#	R.Time	I.Time	F.Time	Area	Area%	Height	Height%	A/H	Mark	Name
1	26.479	26.430	26.555	73296796	100.00	41780630	100.00	1.75		
				73296796	100.00	41780630	100.00			

Spectrum



Mass Table

#	m/z	Abs. Int.	Rel. Int.
1	65.00	2000136	24.12
2	91.05	8293172	100.00
3	92.05	850494	10.26
4	117.10	1826280	22.02
5	141.05	891506	10.75
6	152.10	1757378	21.19
7	165.05	2128326	25.66
8	167.05	2731657	32.94
9	257.05	1024656	12.36
10	258.05	1436980	17.33