Efficient Copper-Free $PdCl_2(PCy_3)_2$-Catalyzed Sonogashira Coupling of Aryl Chlorides with Terminal Alkynes

Chenyi Yi, Ruimao Hua*

Department of Chemistry, Tsinghua University, Innovative Catalysis Program, Key Laboratory of Organic Optoelectronics & Molecular Engineering of Ministry of Education, Beijing 100084, China

Fax: +86-10-62792596; E-mail: ruimao@mail.tsinghua.edu.cn

Supporting Information:

1. General method and characterization of products

(1). General method

All organic starting materials are analytically pure and used without further purification. $PdCl_2(PCy_3)_2$ was prepared by literature method (Alcock, N. W.; Kemp, T. J.; Wimmer, F. L. *J. Chem. Soc. Dalton Trans*. **1981**, 635-638). ^{1}H NMR (300 MHz) chemical shifts (δ) were referenced to TMS, and ^{13}C NMR (75 MHz) chemical shifts (δ) were referenced to internal solvent resonance.

(3) characterization of products

2g and **2i** are new compounds, which were characterized by ^{1}H, ^{13}C-NMR, mass spectra and HRMS. Other cross-coupling products are known compounds and were characterized by ^{1}H, ^{13}C-NMR and mass spectra.

Diphenyl acetylene **2a:** ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.56-7.28 (m, 10H); ^{13}C NMR (75.4 MHz, $CDCl_3$) δ 131.7, 128.4, 128.3, 123.3, 89.4; GCMS *m*/*z* (% rel. inten.) 178(M^+, 100), 152(21), 126(8), 113(2), 98(6), 77(3).

Phenyl-*p*-tolyl acetylene **2b**[1]**:** ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.55-7.12 (m, 9H), 2.37(s, 3H); ^{13}C NMR (75.4MHz, $CDCl_3$) δ 138.4, 131.6, 131.5, 129.1, 128.4, 128.1, 88.5, 81.7, 21.5; GCMS *m*/*z* (% rel. inten.) 192(M^+, 100), 165(27), 139(7), 115(9), 89(5), 63(7).

3,3-Dimethyl-1-butynyl-benzene **2c**[2]**:** ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.40-7.25 (m, 5H), 1.34(s, 9H); ^{13}C NMR (75.4MHz, $CDCl_3$) δ 131.6, 128.6, 127.4, 124.2, 98.6, 79.1, 31.1; GCMS *m*/*z* (% rel. inten.) 158(M^+, 26), 143(100), 128(61), 115(27), 103(8), 77(10).

1-Phenyl-1-octyne **2d**[3]**:** ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.38 -7.25(m, 5H), 2.40 (t, 2H, J = 7.2Hz), 1.70-1.25 (m, 8H), 0.90 (d, 3H, J = 7.0Hz); ^{13}C NMR (75.4MHz, $CDCl_3$) δ 131.6, 128.2, 127.5, 123.7, 90.5, 80.3, 31.4, 28.8, 28.7, 22.6, 19.4, 14.1; GCMS *m*/*z* (% rel. inten.) 186(M^+, 11), 157(9), 143(33), 129(47), 115(100), 91(20), 77(8).

1-Phenyl-1-heptyne **2e**[4]**:** ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.45 -7.15(m, 5H), 2.40 (t, 2H, *J* = 7.2Hz), 1.70-1.15 (m, 6H), 0.92 (d, 3H, *J* = 7.0Hz); ^{13}C NMR (75.4MHz, $CDCl_3$) δ 131.6, 128.2, 127.5, 123.6, 90.2, 80.2, 31.2, 28.5, 22.3, 19.4, 14.0; GCMS *m*/*z* (% rel. inten.) 172(M^+, 13), 157(5), 129(47), 115(100), 89(20), 77(9).

1-(4-methylphenyl)-1-heptyne **2f**[4]**:** ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.30-7.06 (m, 4H), 2.87 (t, 2H, *J* = 7.2Hz), 2.32 (s, 3H), 1.65-1.25 (m, 6H), 0.92 (t, 3H, *J* = 7.2Hz); ^{13}C NMR (75.4MHz, $CDCl_3$) δ 137.4, 131.4, 129.0, 120.7, 89.7, 80.1, 31.2, 28.6, 22.3, 21.4, 19.4, 14.0; GCMS *m*/*z* (% rel. inten.) 186(M^+, 31), 171(10), 157(38), 129(100), 115(32), 91(10), 77(10).

4-(1-heptynyl)-benzyl alcohol **2g:** ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.39-7.25 (m, 4H), 4.66 (s, 2H), 2.39 (t, 2H, *J* = 7.2Hz), 2.0 (s_{br}, 1H), 1.65-1.20 (m, 6H), 0.92 (t, 3H, *J* = 7.0 Hz); ^{13}C NMR (75.4MHz, $CDCl_3$) δ 140.2, 131.8, 126.8, 123.4, 90.7, 80.4, 65.1, 31.2, 28.5, 22.3, 19.4, 14.1; GCMS *m*/*z* (% rel. inten.) 202(M^+, 14), 171(22), 143(46), 129(77), 115(100), 91(15), 77(11); HRMS calcd for $C_{14}H_{18}O$: 202.1357; found: 202.1353.

Methyl 3-(1-heptynyl)-benzoate **2h**[5]**:** ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.06-7.31 (m, 4H), 3.92 (s, 3H), 2.40 (t, 2H, *J* = 6.9 Hz), 1.61-1.35 (m, 6H), 0.92 (t, 3H, *J* = 7.2 Hz); ^{13}C NMR (75.4MHz, $CDCl_3$) δ 166.6, 135.8, 132.8, 130.3, 128.5, 128.3, 124.6, 91.7, 79.7, 52.2, 31.2, 28.4, 22.3, 19.4, 14.0; GCMS *m*/*z* (% rel. inten.) 230(M^+, 30), 201(52), 173(40), 129(100), 115(63), 91(22), 77(10).

4-(1-heptynyl)-benzophenone **2i:** ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.80-7.40 (m, 9H), 2.44 (t, 2H, *J* = 7.2 Hz), 1.65-1.30 (m, 6H), 0.91 (t, 3H, *J* = 6.5 Hz); ^{13}C NMR (75.4MHz, $CDCl_3$) δ 196.1, 136.2, 132.5, 131.4, 130.1, 130.0, 128.4, 94.3, 80.2, 31.2, 28.4, 22.3, 19.6, 14.1; GCMS *m*/*z* (% rel. inten.) 276(M^+, 14), 247(11), 219(5), 191(18), 129(12), 105(100), 77(44); HRMS calcd for $C_{20}H_{20}O$: 276.1514; found: 276.1516.

1-(4-chlorophenyl)-1-heptyne **2j**[6]**:** ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.35-7.20 (m, 4H), 2.38 (t, 2H, *J* = 6.9 Hz), 1.70-1.25 (m, 6H), 0.92 (t, 3H, *J* = 7.2 Hz); ^{13}C NMR (75.4MHz, $CDCl_3$) δ 133.4, 132.8, 128.5, 122.7, 91.6, 79.5, 31.2, 28.4, 22.3, 19.4, 14.0; GCMS *m*/*z* (% rel. inten.) 206(M^+, 26), 177(37), 149(100), 129 (80), 115(79), 101(14) .

1,4-bis(1-heptynyl)benzene **2k**[7]**:** ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.28 (d, 2H x 2, *J* = 9.6 Hz), 2.39 (t, 4H, *J* = 6.9 Hz), 1.70-1.20 (m, 12H), 0.92 (t, 6H, *J* = 7.2 Hz); ^{13}C NMR (75.4MHz, $CDCl_3$) δ 131.4, 123.2, 92.0, 80.4, 31.2, 28.5, 22.3, 19.5, 14.0; GCMS *m*/*z* (% rel. inten.) 266(M^+, 34), 237(17), 209(30), 165(91), 152(100), 141(68), 129(47), 115(33), 77(11).

1-(1-heptynyl)-naphthalene **2l**[4]**:** ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.39-7.41(m, 7H), 2.58 (t, 2H, *J* = 7.2Hz), 1.75-1.35 (m, 6H), 0.97 (t, 3H, *J* = 7.2 Hz); ^{13}C NMR (75.4MHz, $CDCl_3$) δ 133.6, 133.3, 130.0, 128.2, 127.9, 126.5, 126.4, 126.2, 125.3, 121.9, 95.6, 78.6, 31.3, 28.7, 22.3, 19.8, 14.1; GCMS *m*/*z* (% rel. inten.) 222(M^+, 82), 207(19), 193(50), 165(100), 152(46), 128(7), 115(12), 91(2), 77(3)

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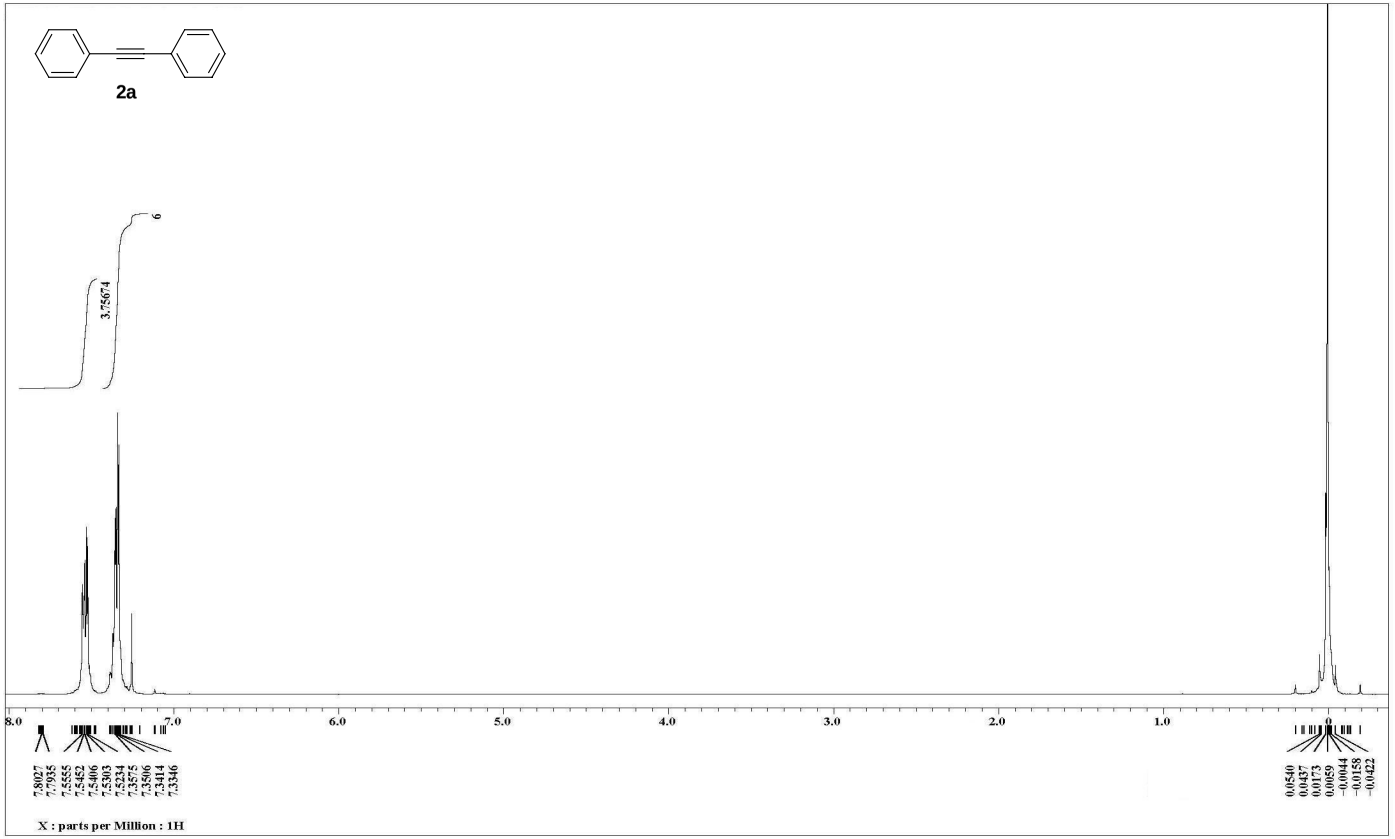
[7] Kamikawa, T.; Hayashi, T. *J. Org. Chem.* **1998**, *63*, 8922-8925.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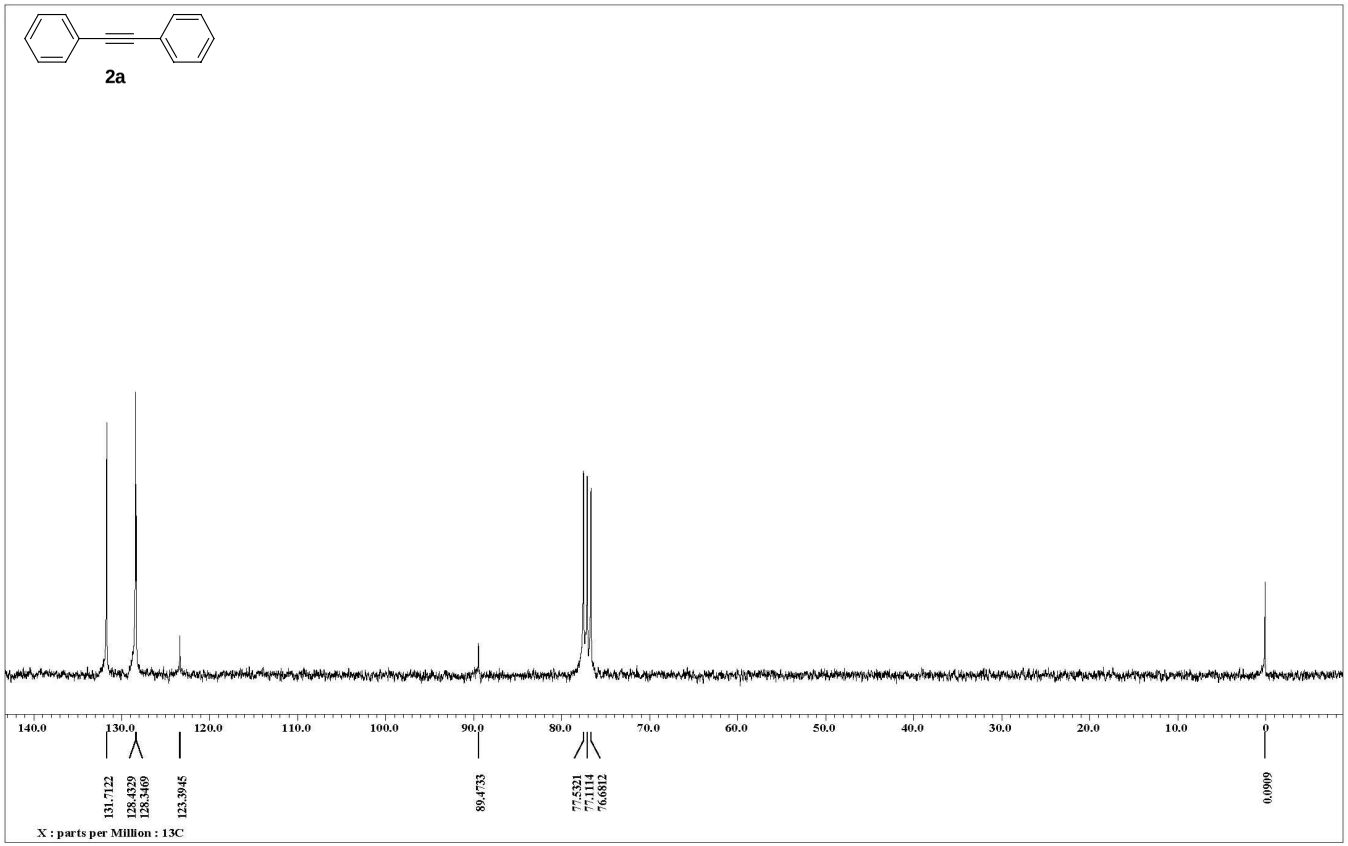
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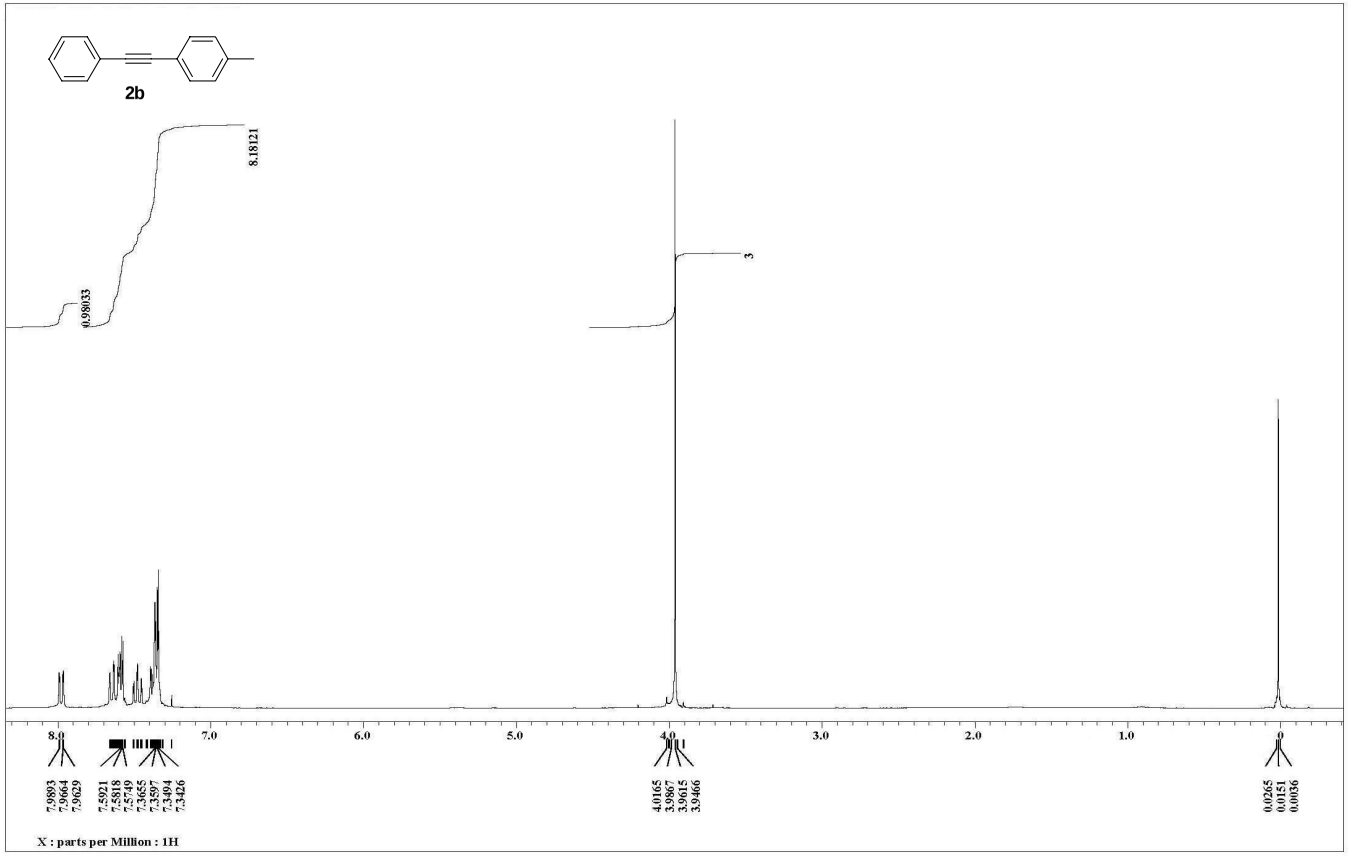
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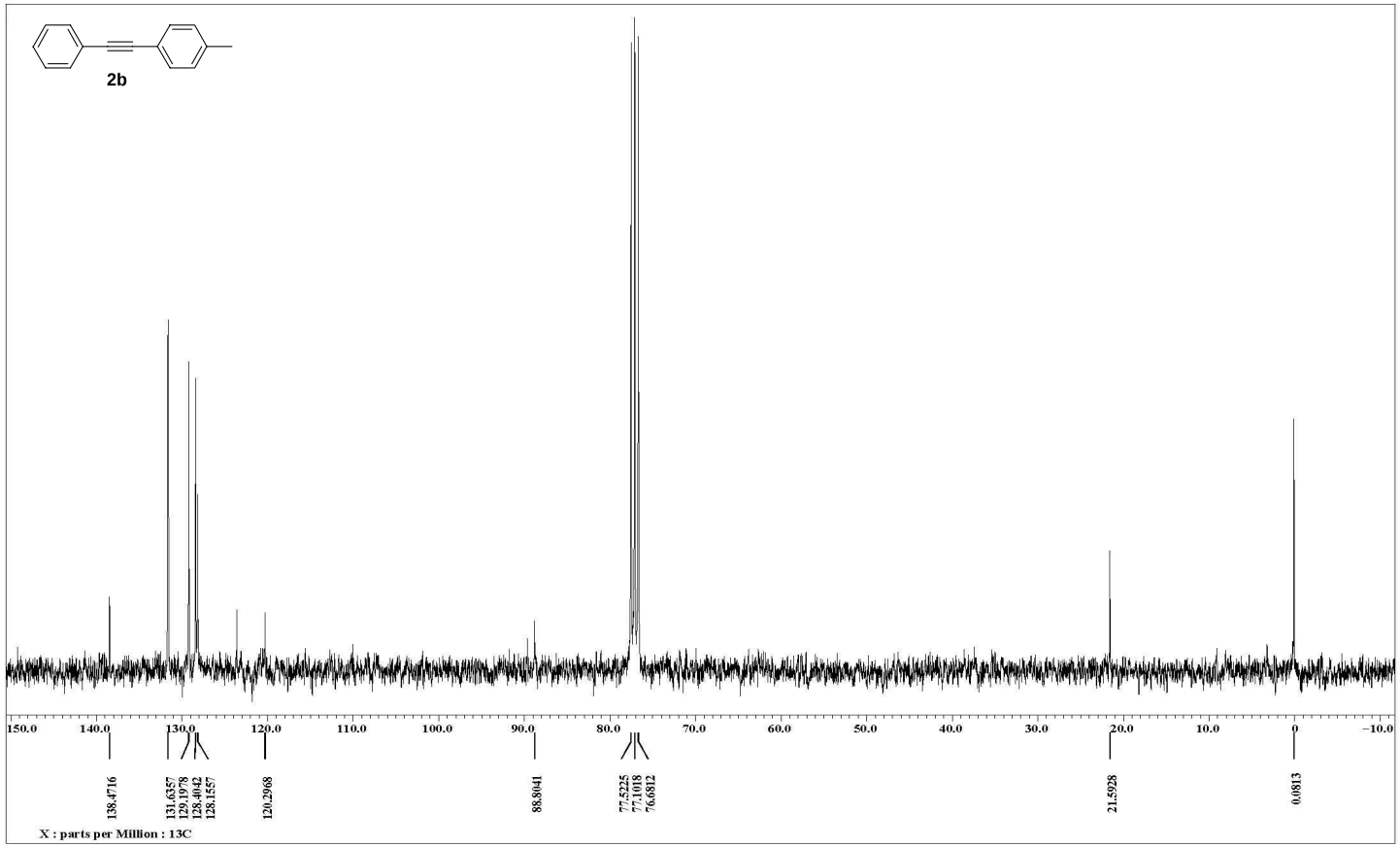
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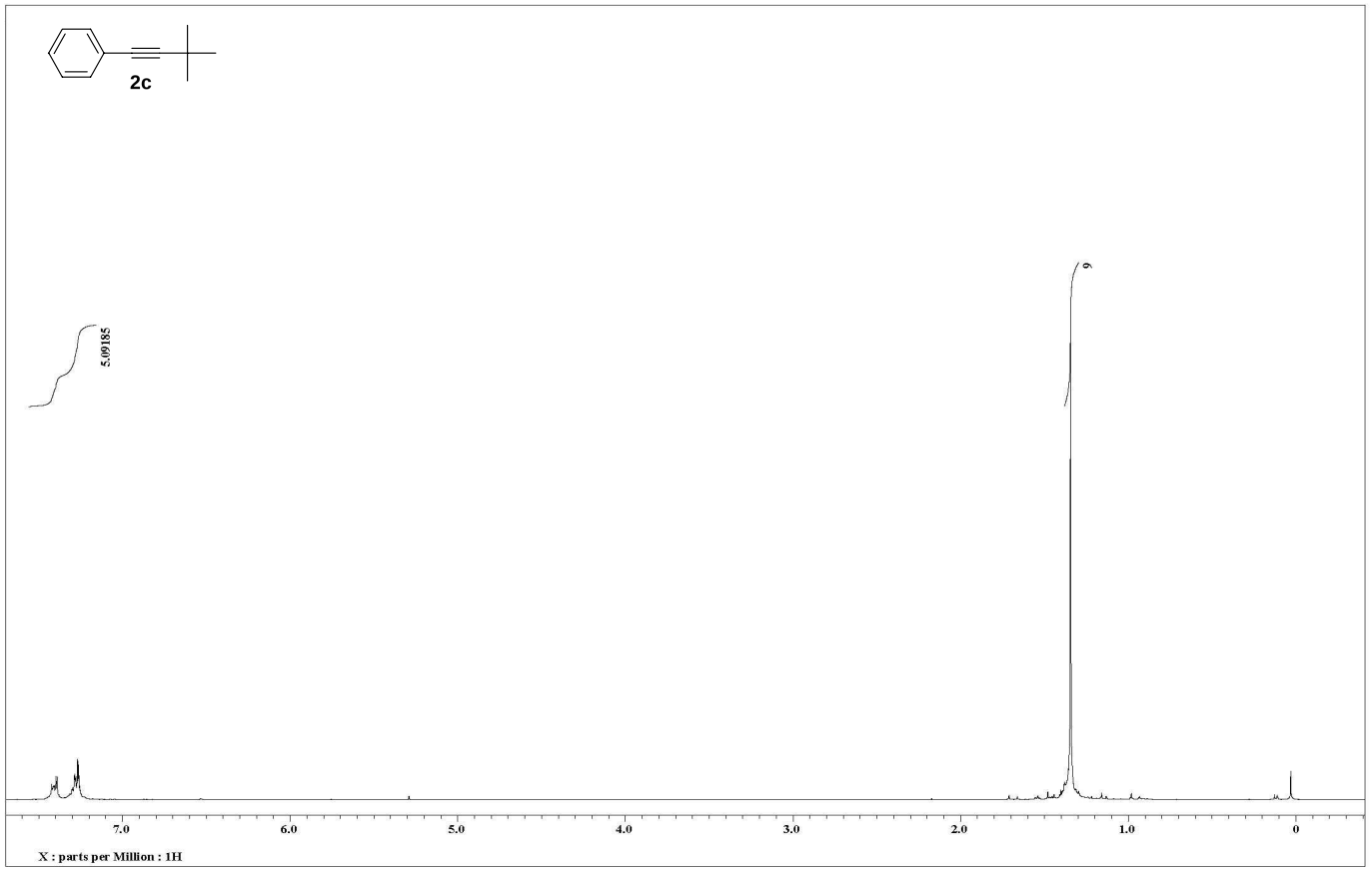
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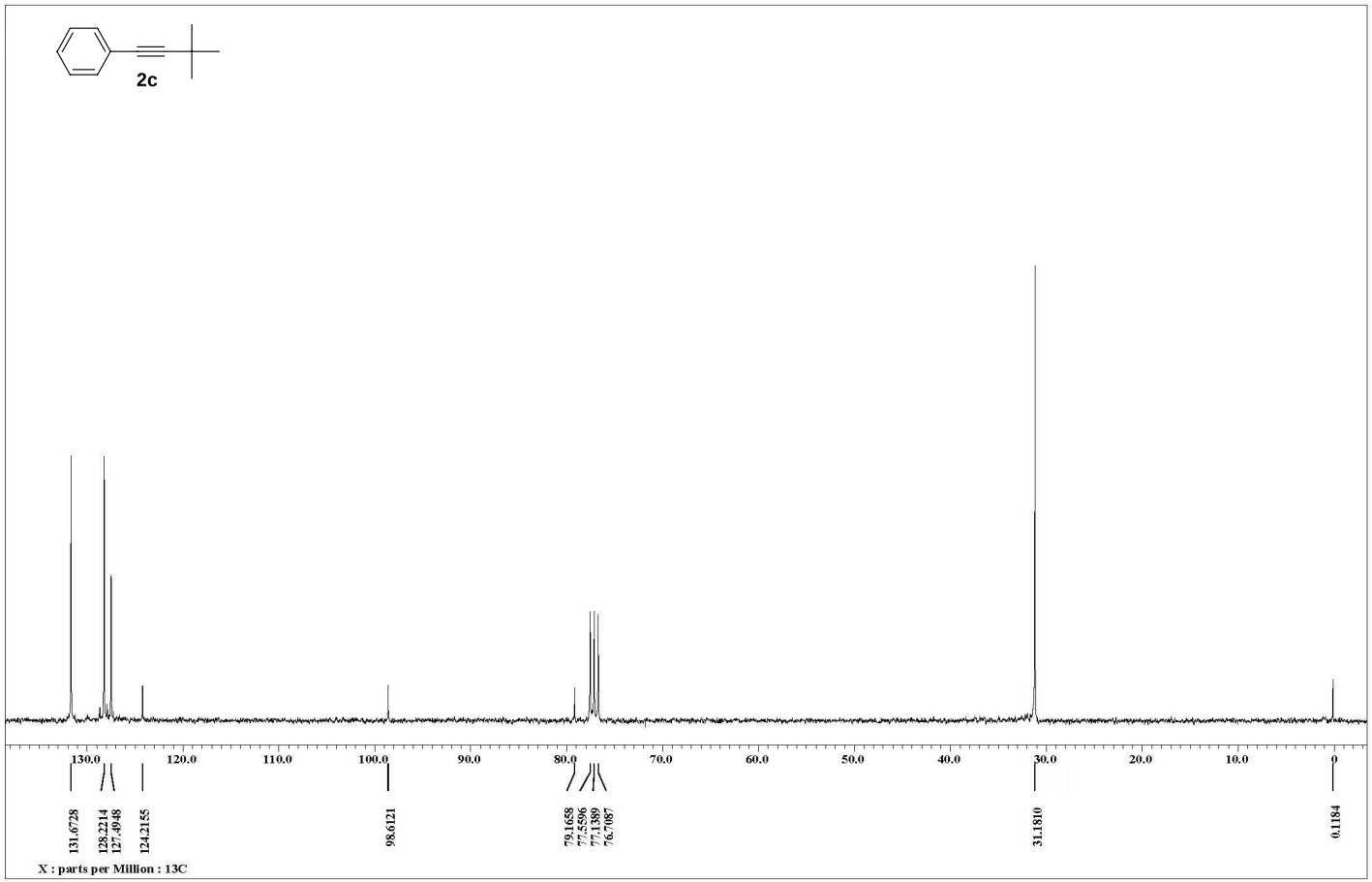
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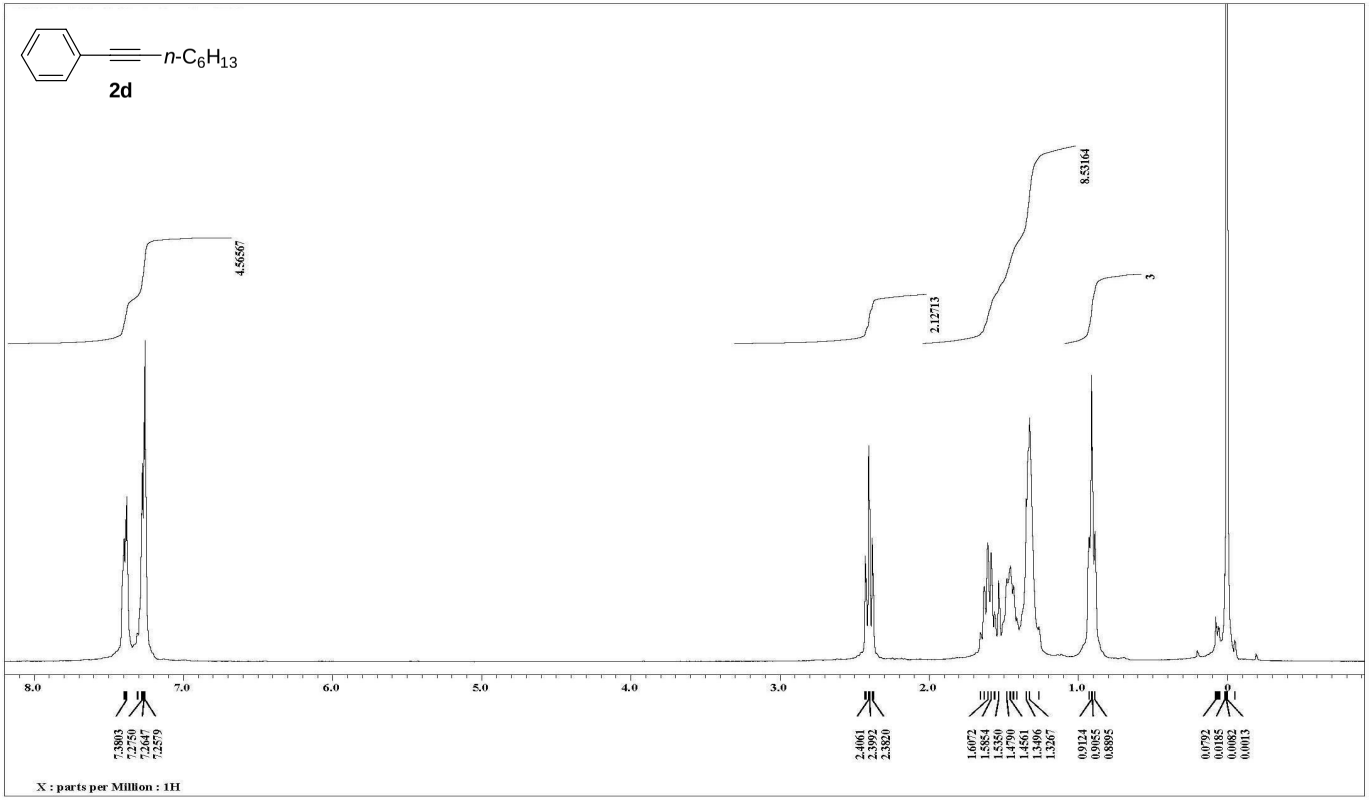
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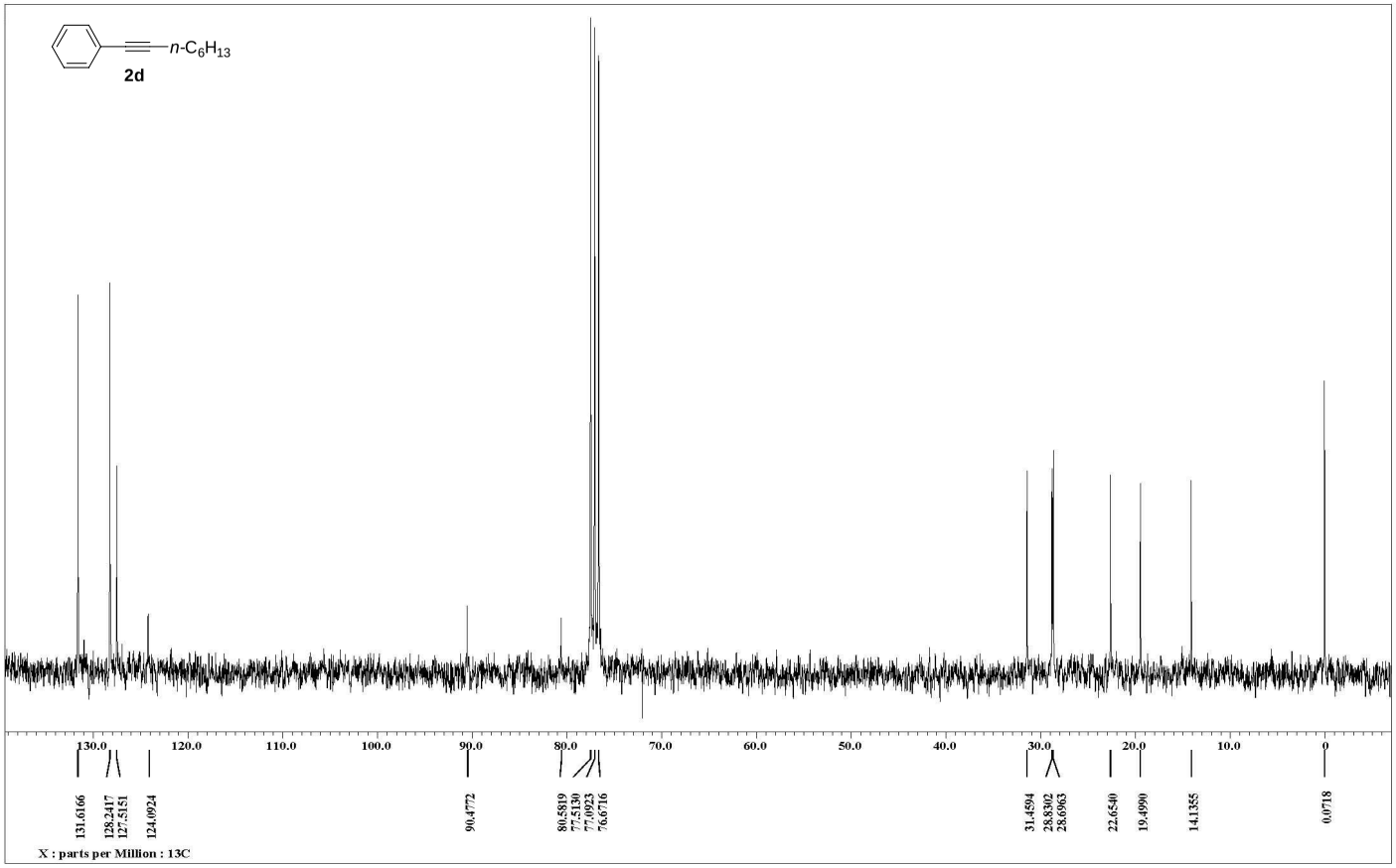
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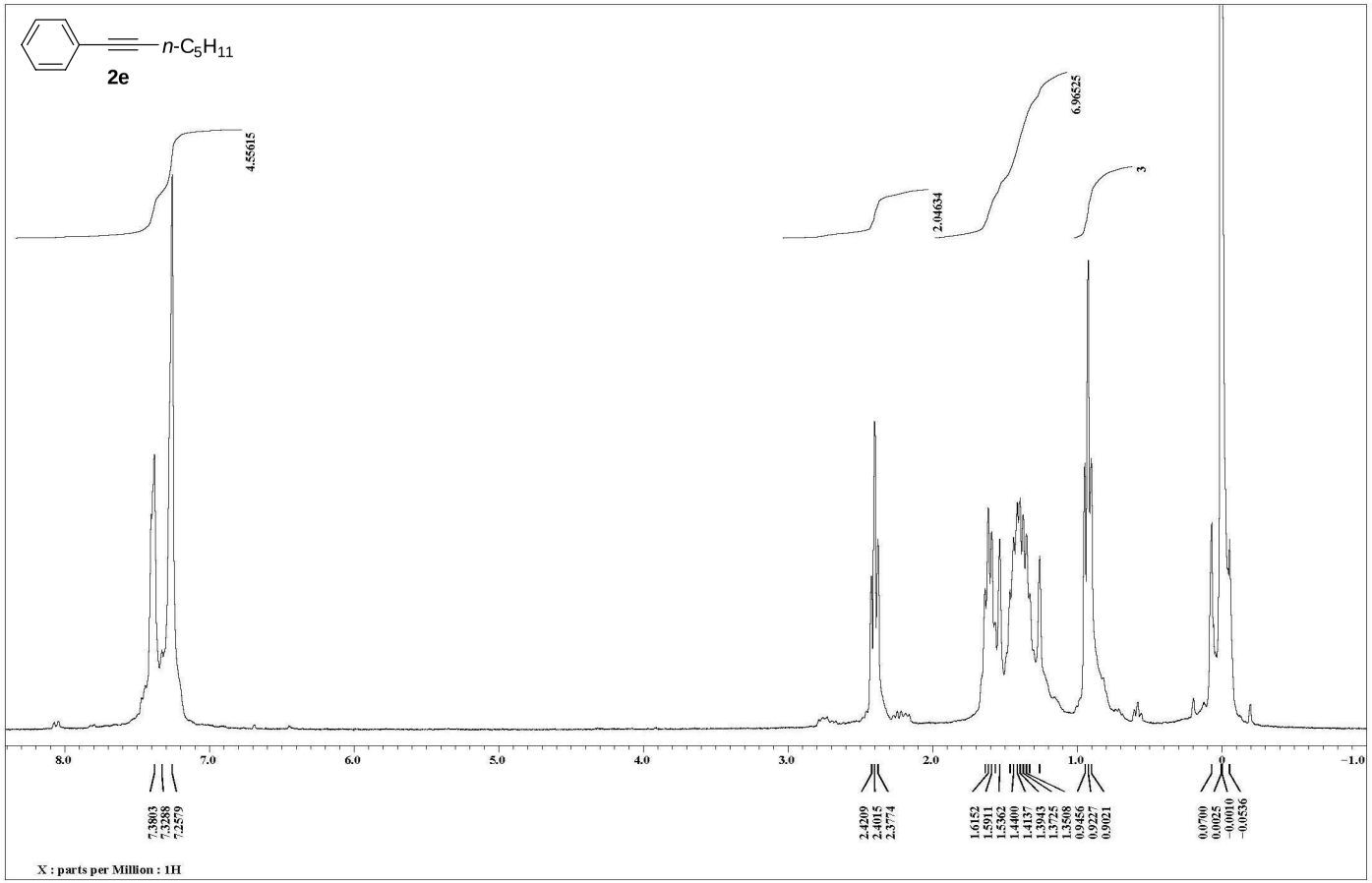
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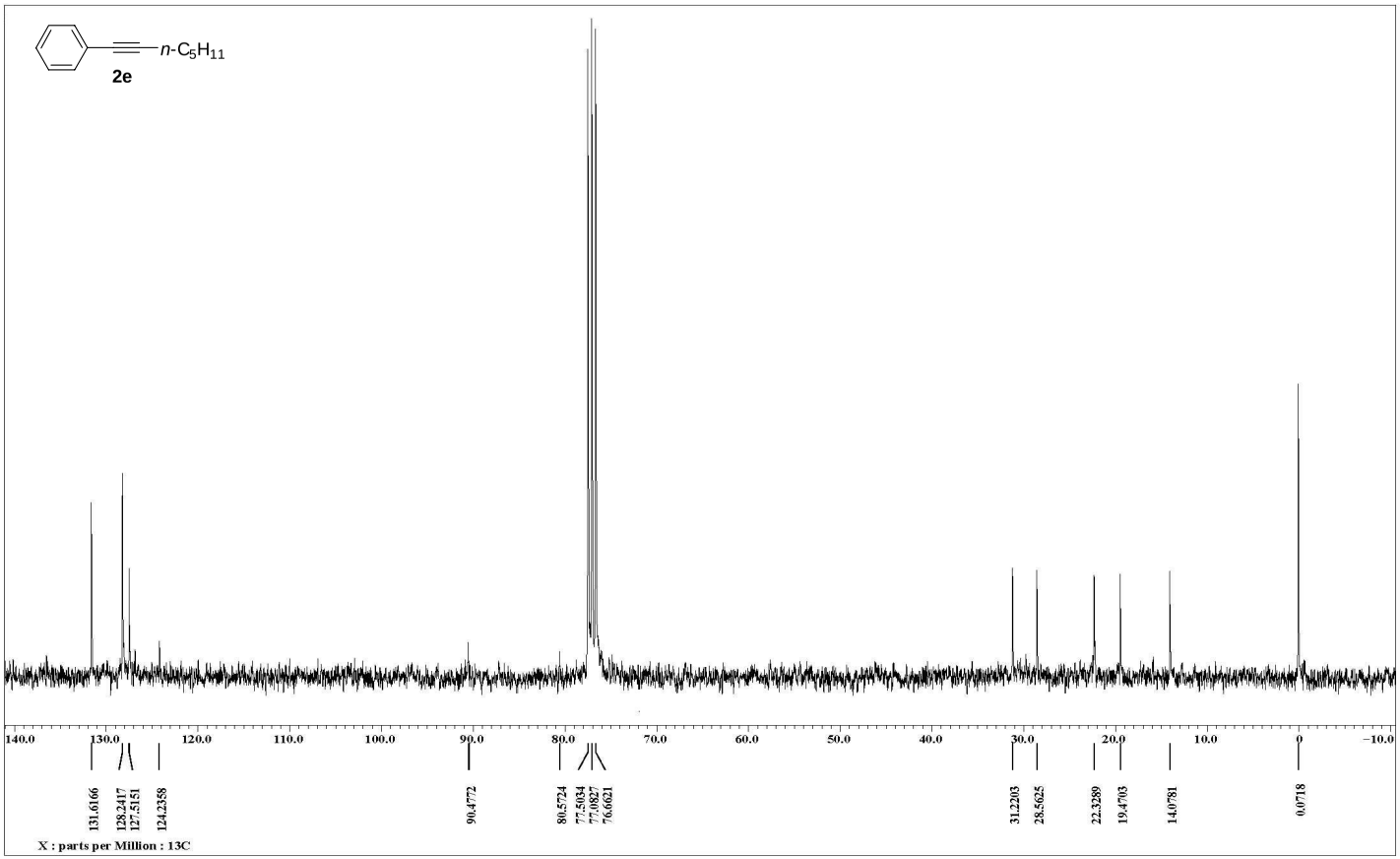
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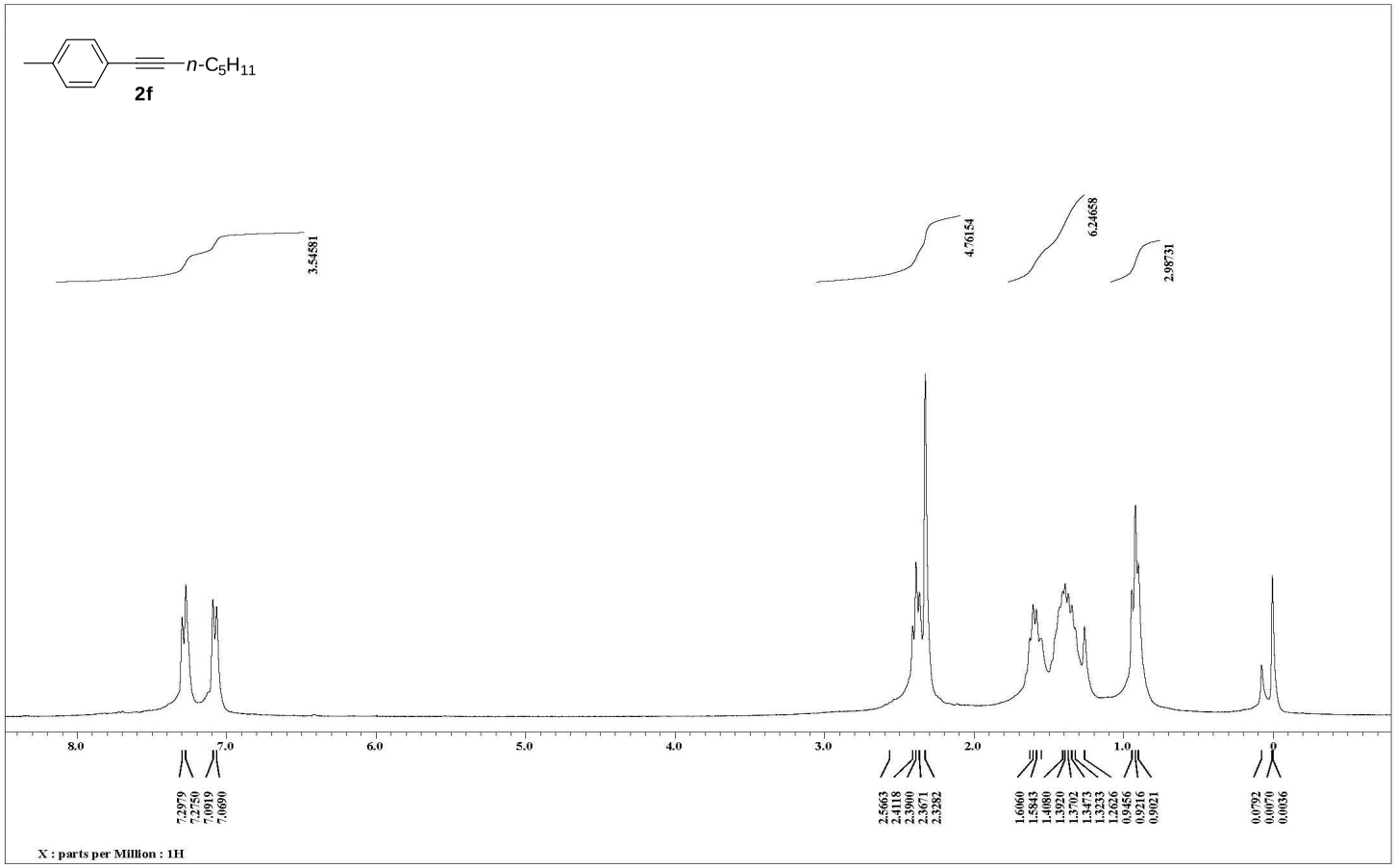
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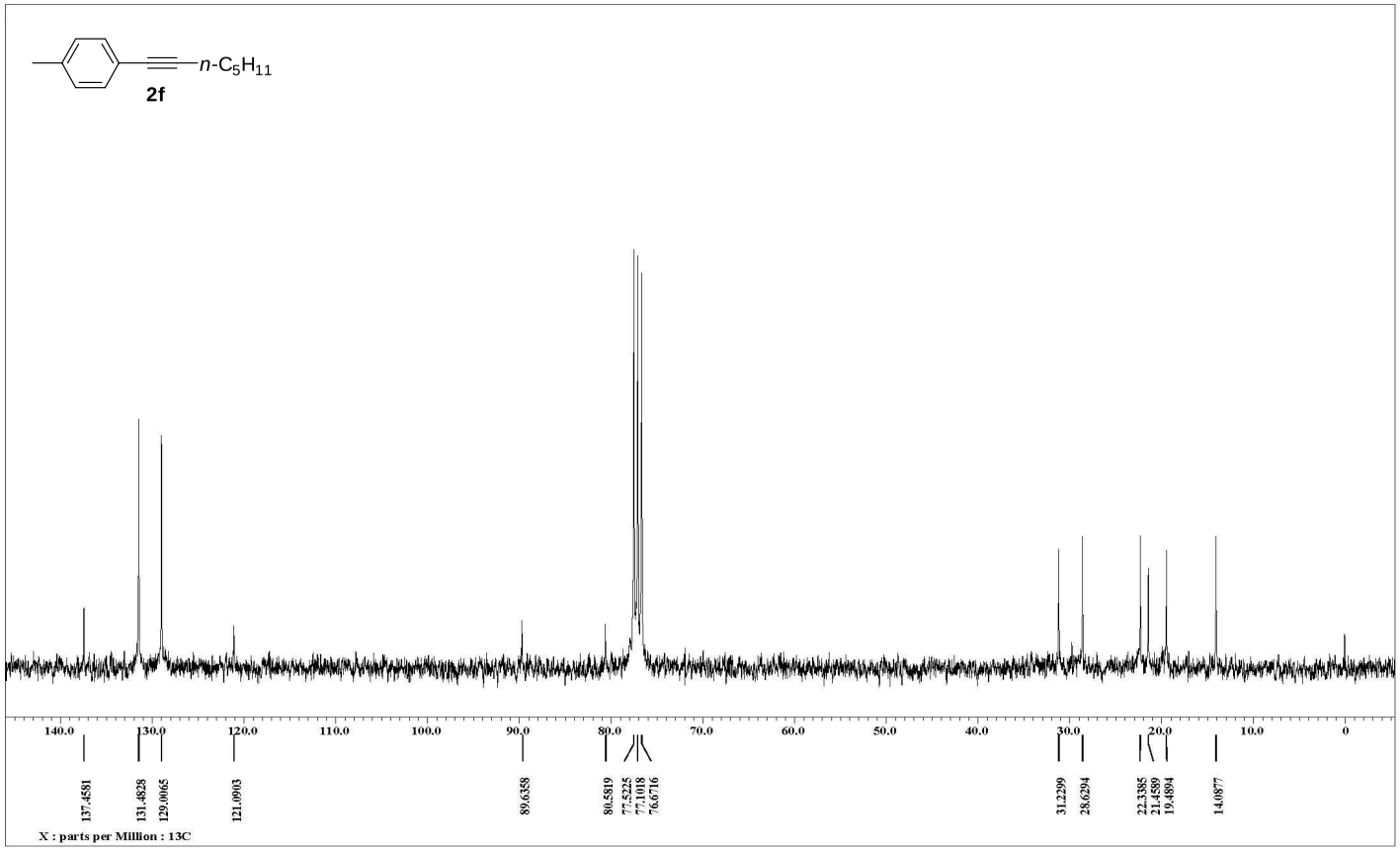
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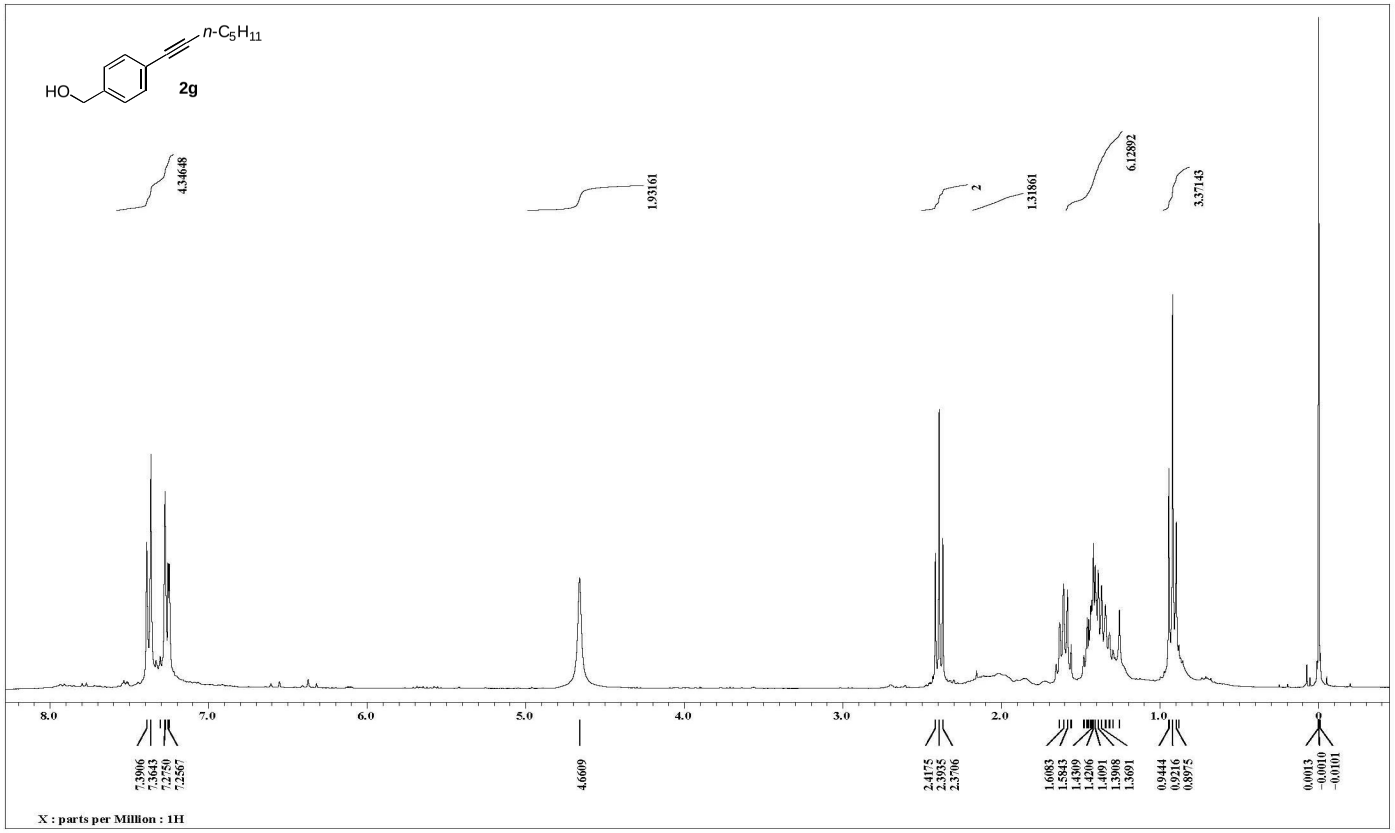
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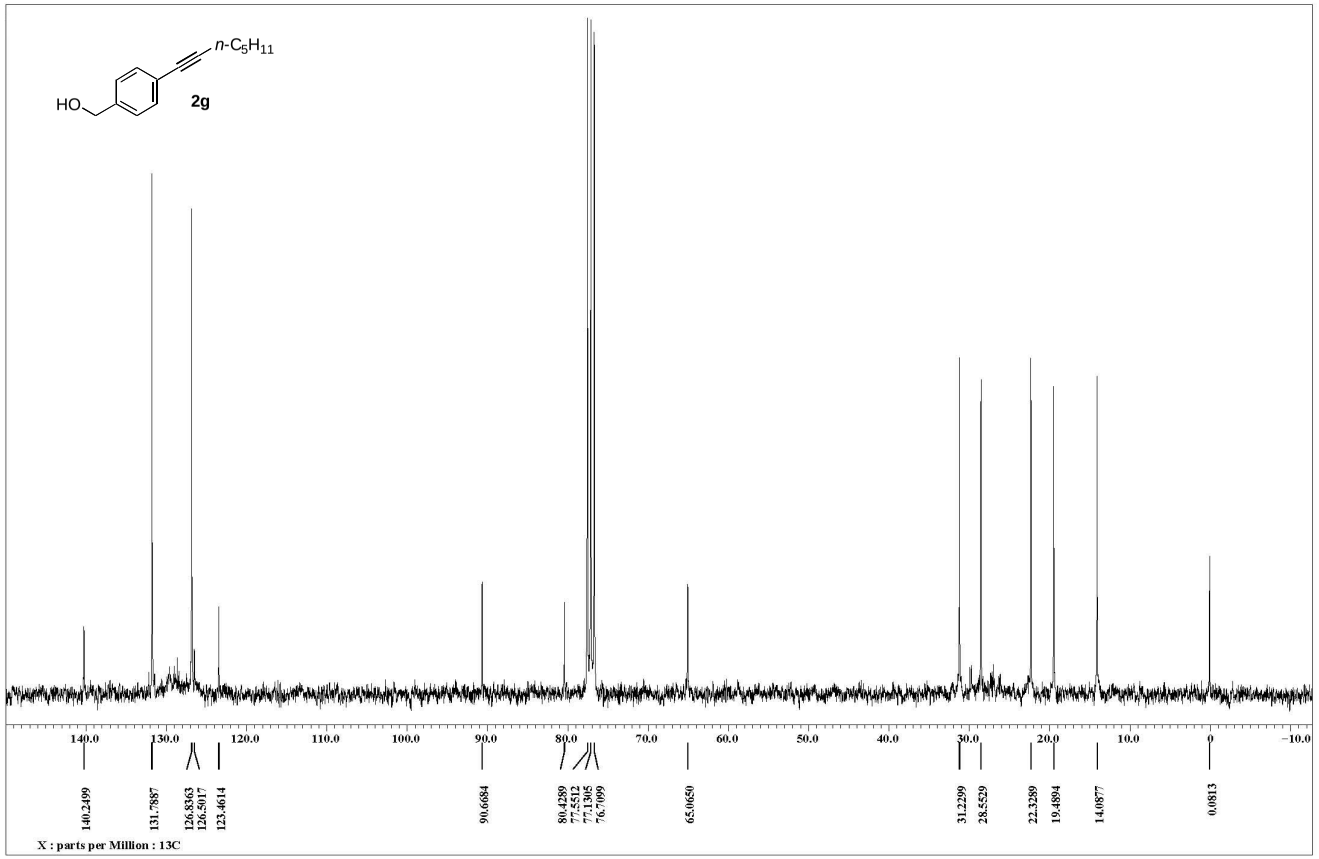
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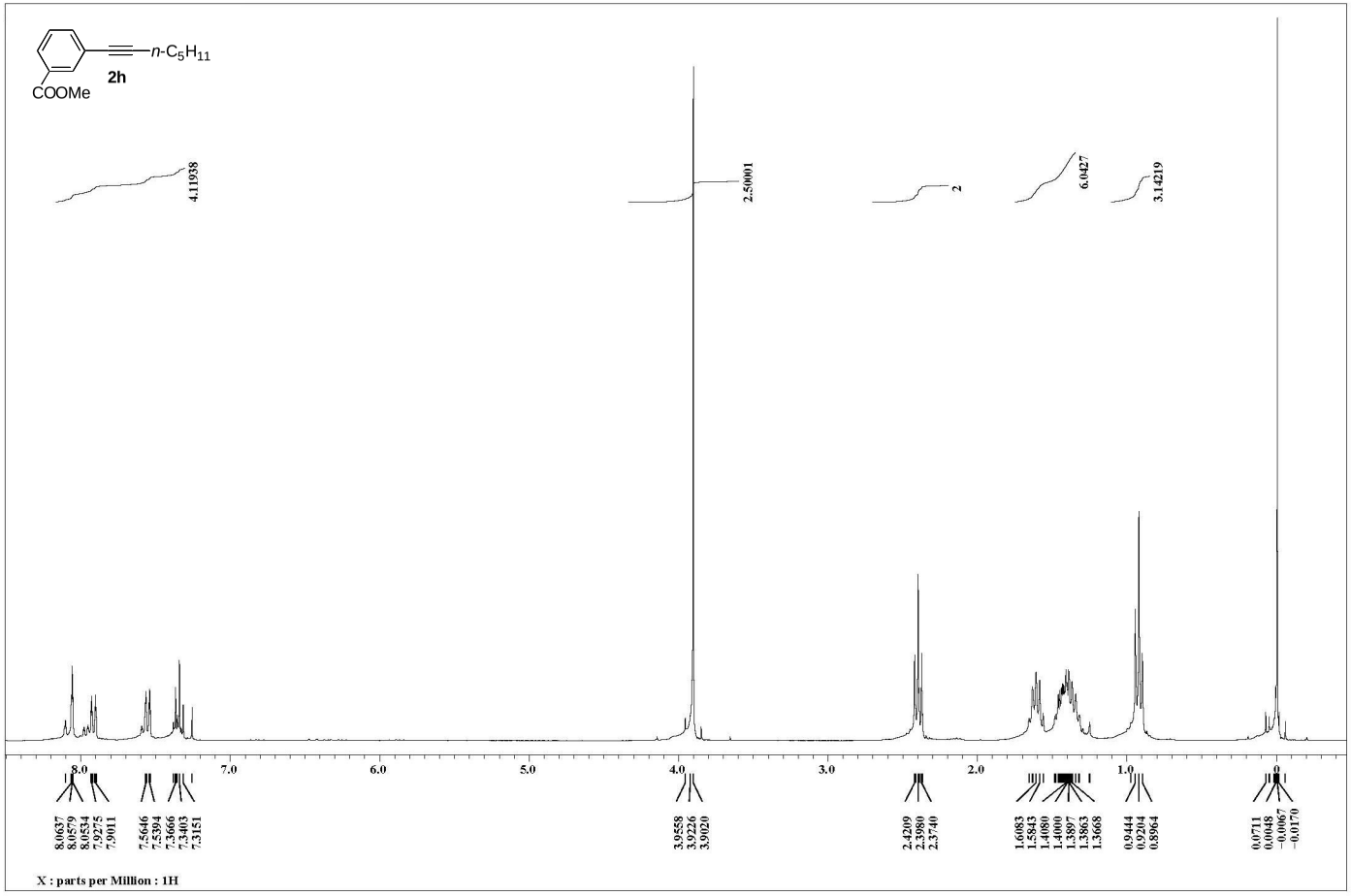
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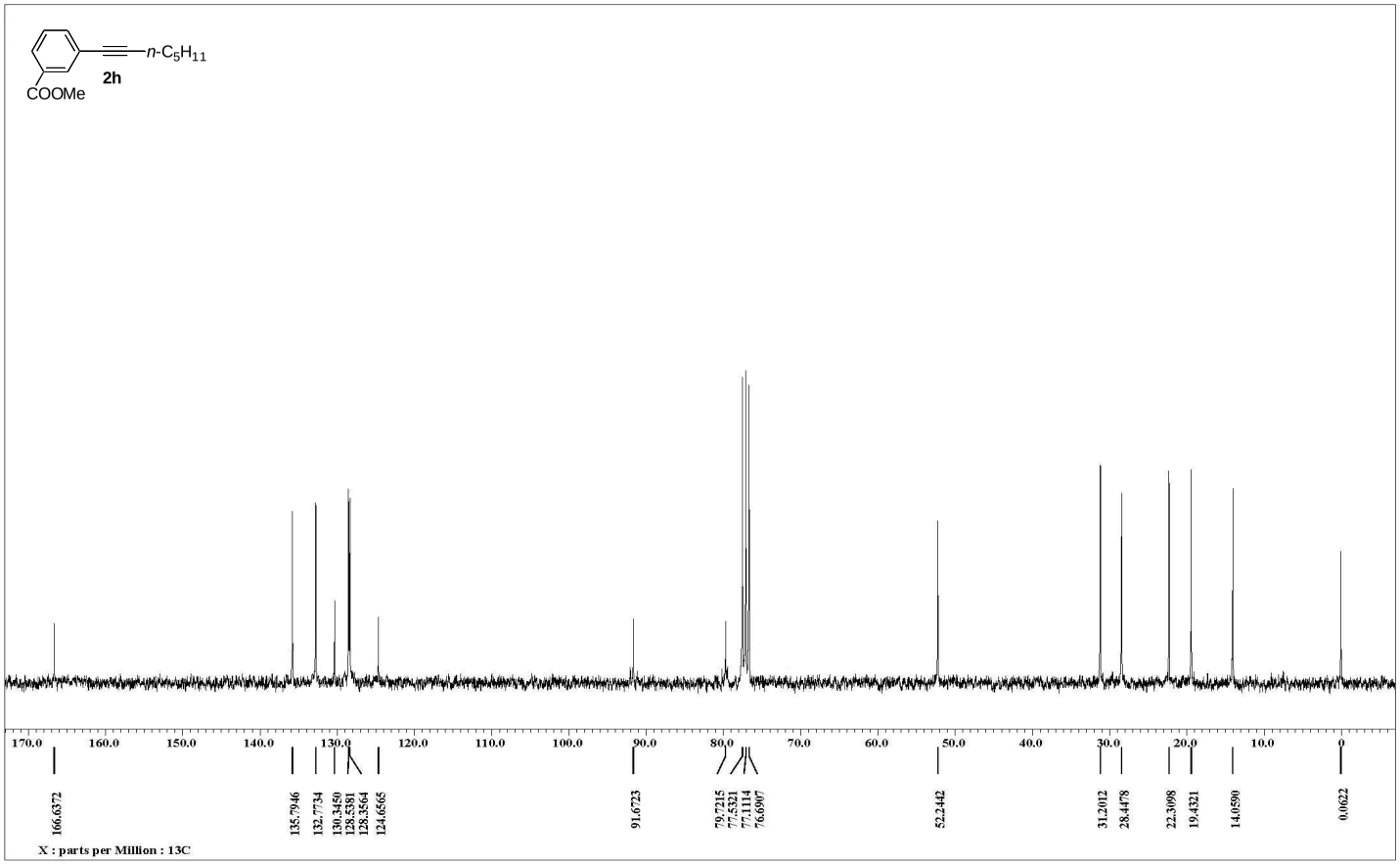
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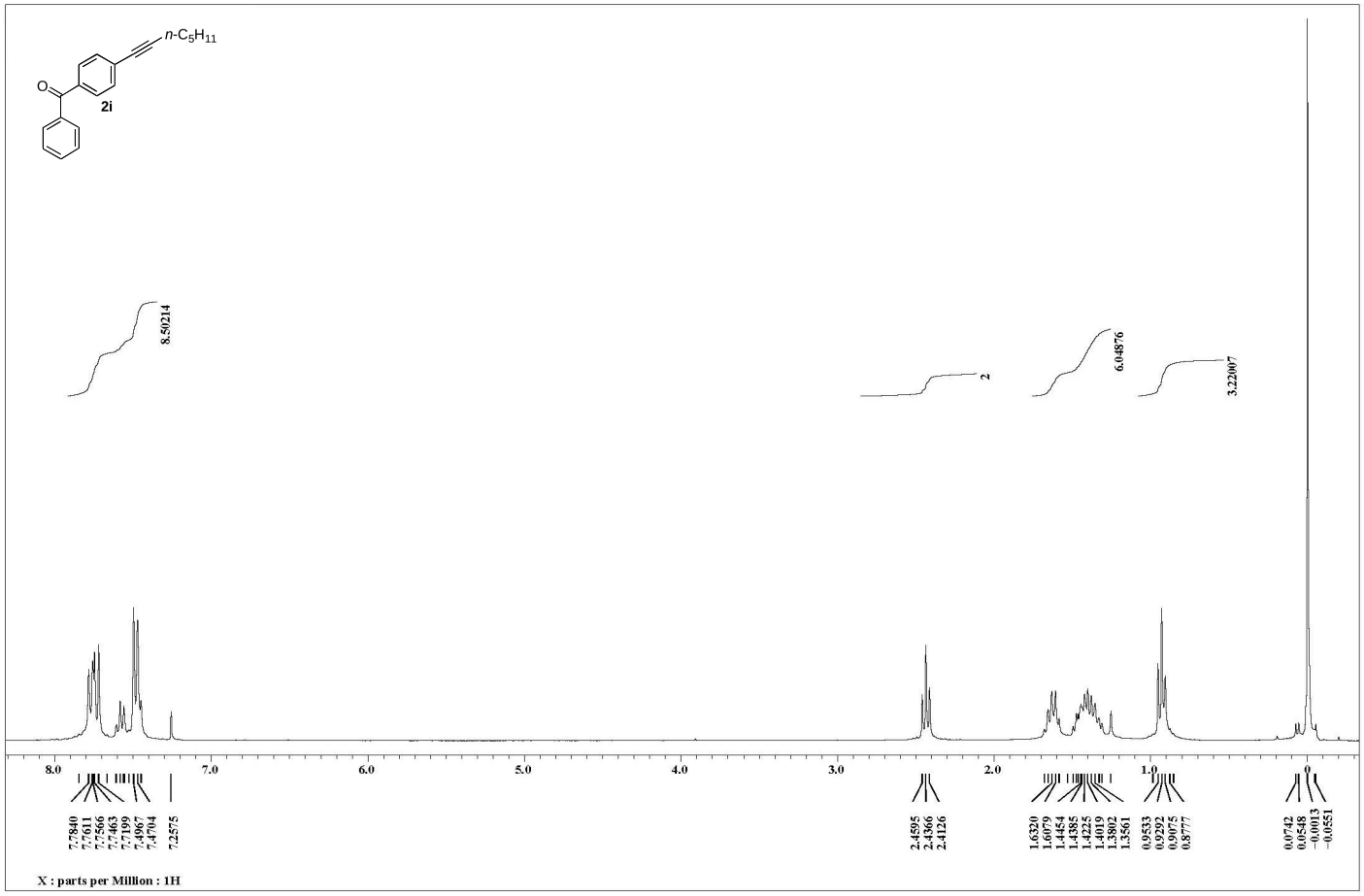
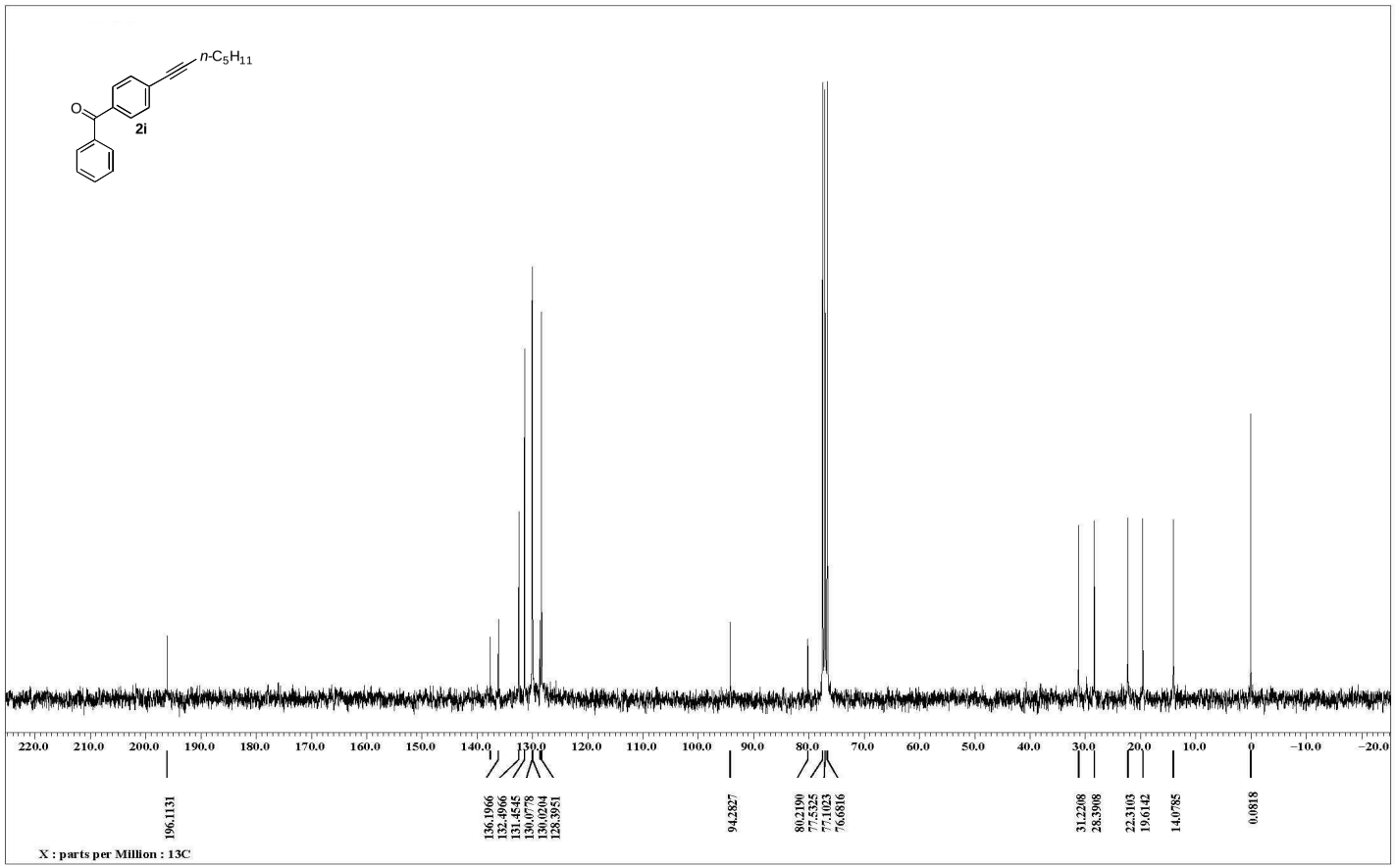
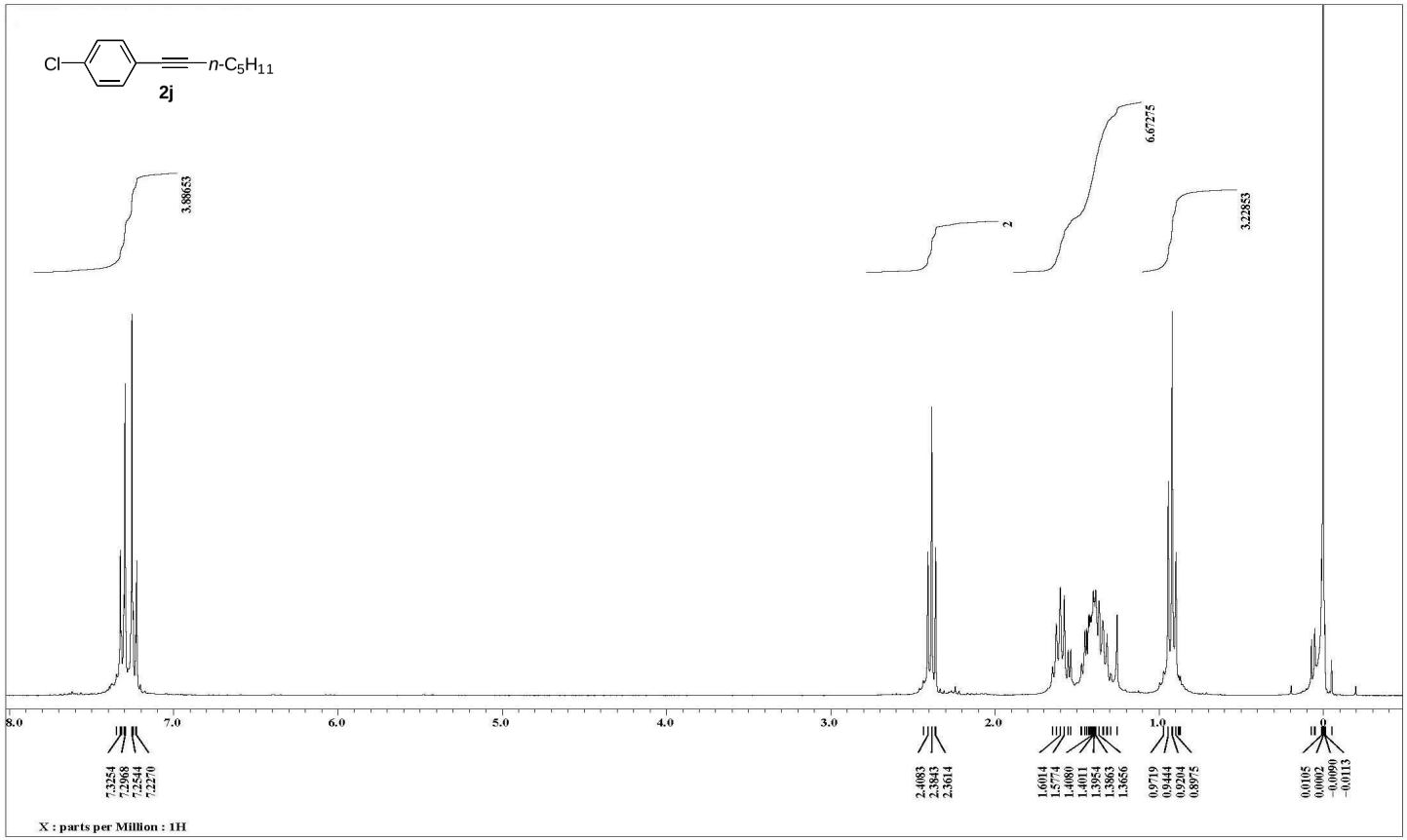
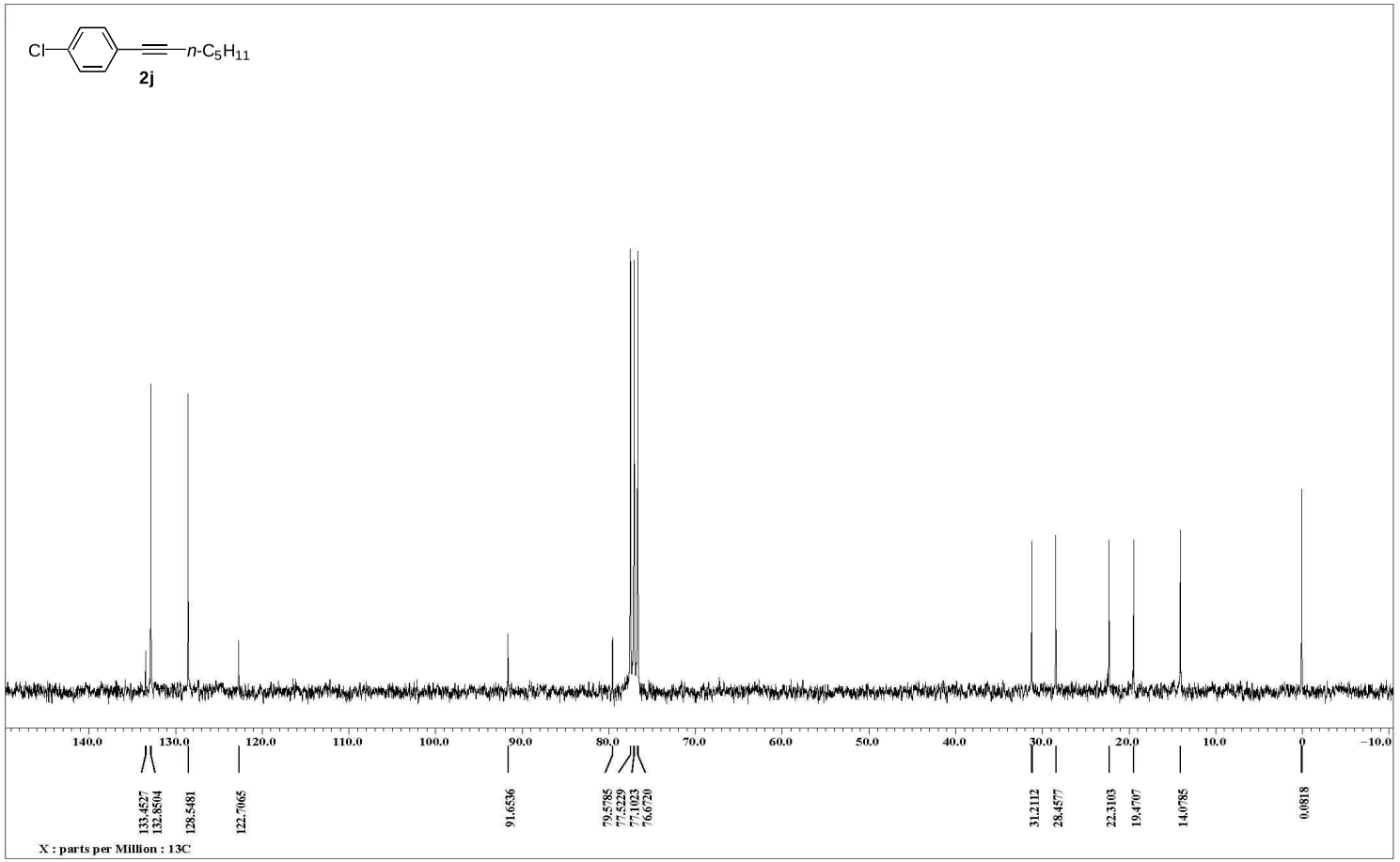
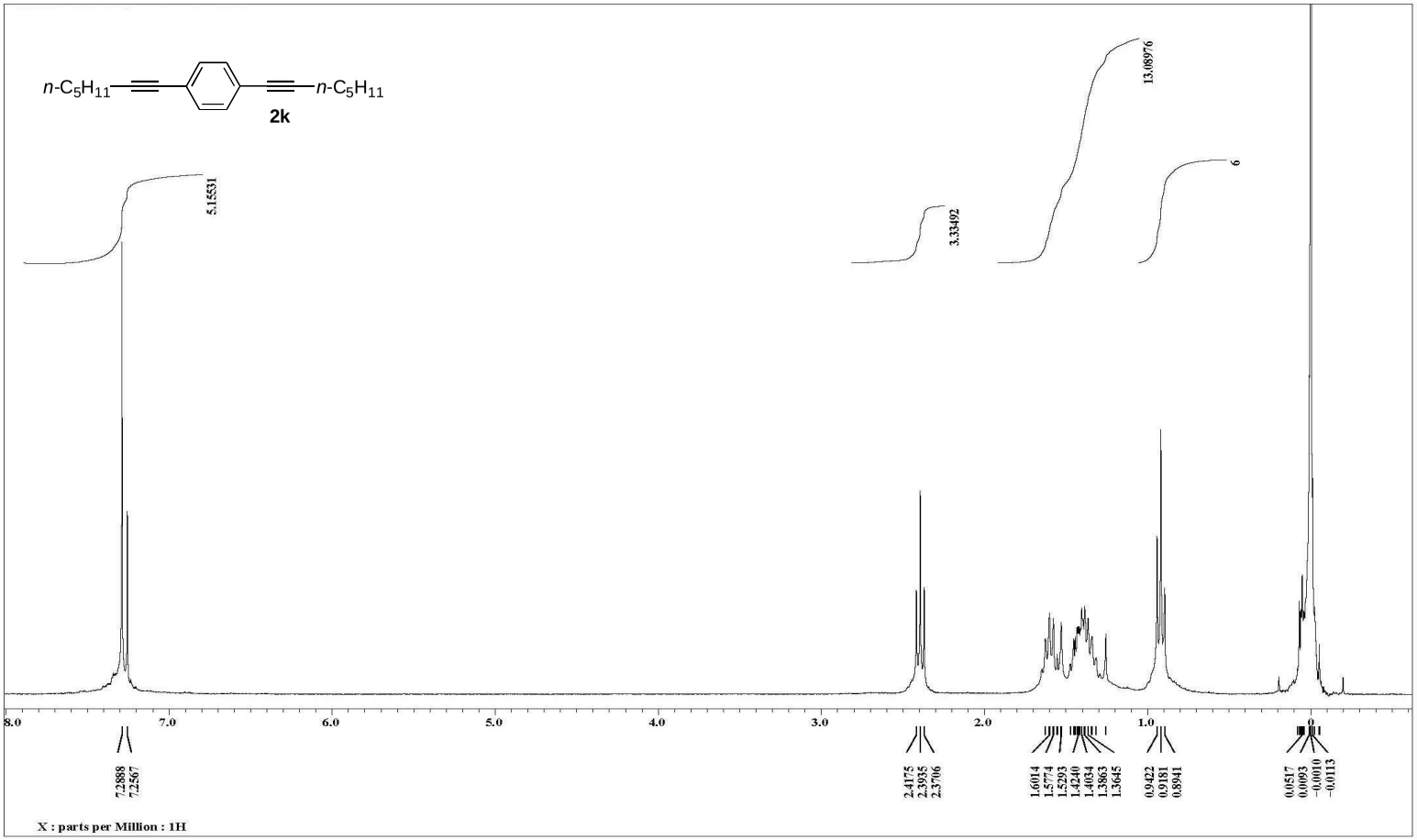
0.0622
X : parts per Million : 13C

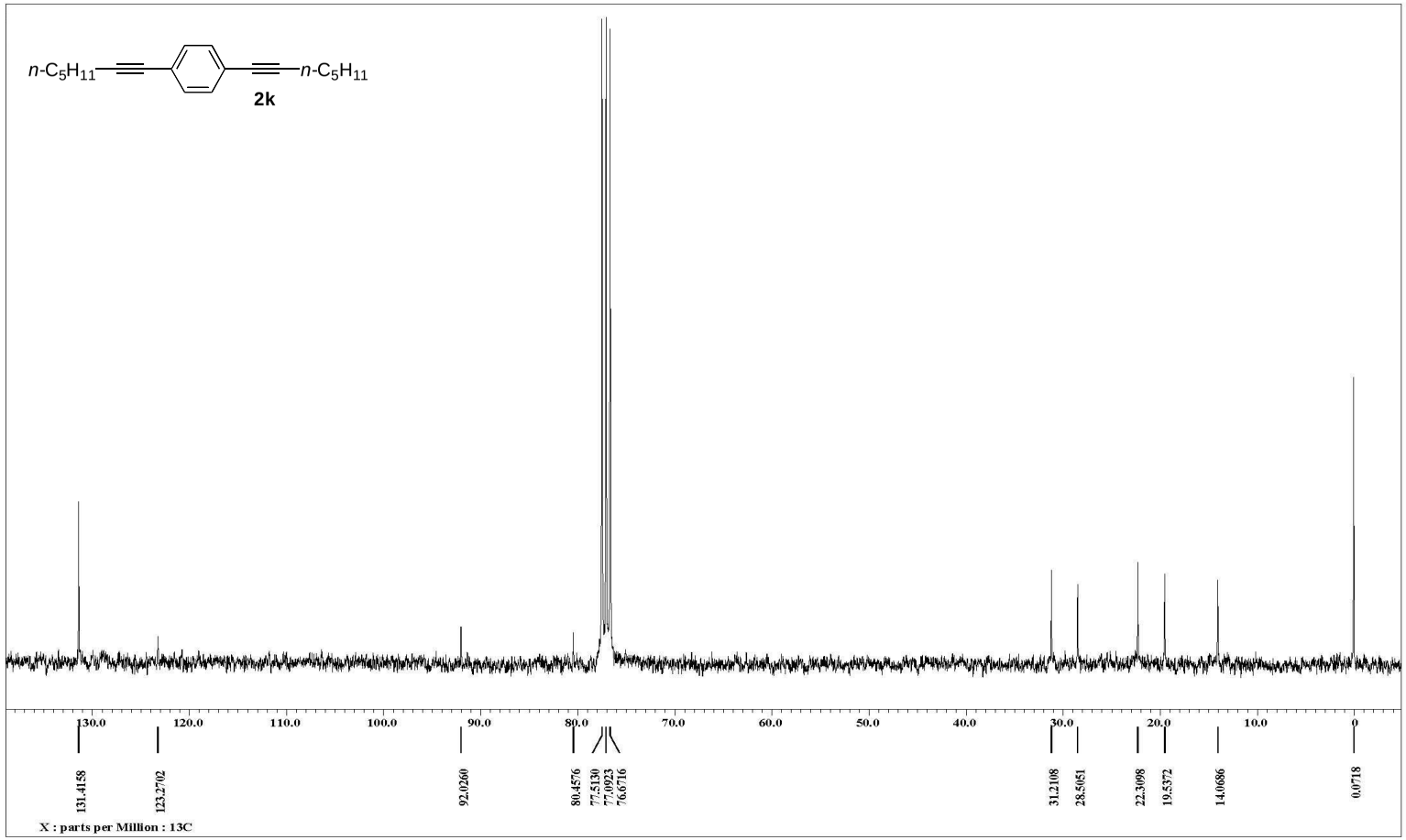

n-C5H11
O
2i
8.50214
2
6.04876
3.22007
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0
7.7840
7.7611
7.7566
7.7463
7.7199
7.4967
7.4704
7.2575
2.4595
2.4366
2.4126
1.6320
1.6079
1.4454
1.4385
1.4225
1.4019
1.3802
1.3561
0.9533
0.9292
0.9075
0.8777
0.0742
0.0548
−0.0013
−0.0551
X : parts per Million : 1H

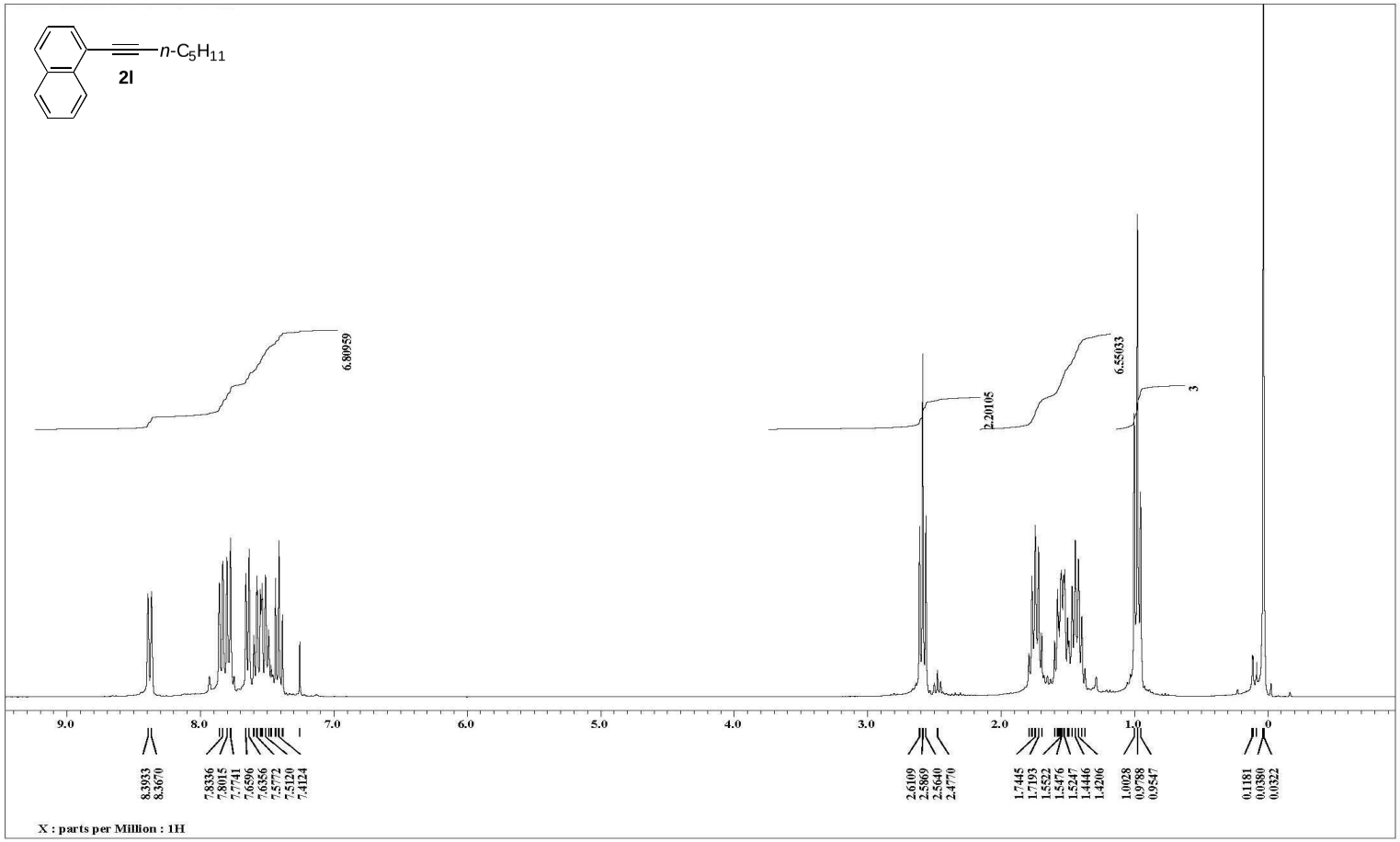

n-C5H11
O
2i
220.0 210.0 200.0 190.0 180.0 170.0 160.0 150.0 140.0 130.0 120.0 110.0 100.0 90.0 80.0 70.0 60.0 50.0 40.0 30.0 20.0 10.0 0 −10.0 −20.0
196.1131
136.1966
132.4966
131.4545
130.0779
130.0204
128.3951
94.2827
80.2190
77.5325
77.1023
76.6816
31.2208
28.3908
22.3103
19.6142
14.0785
0.0818
X : parts per Million : 13C

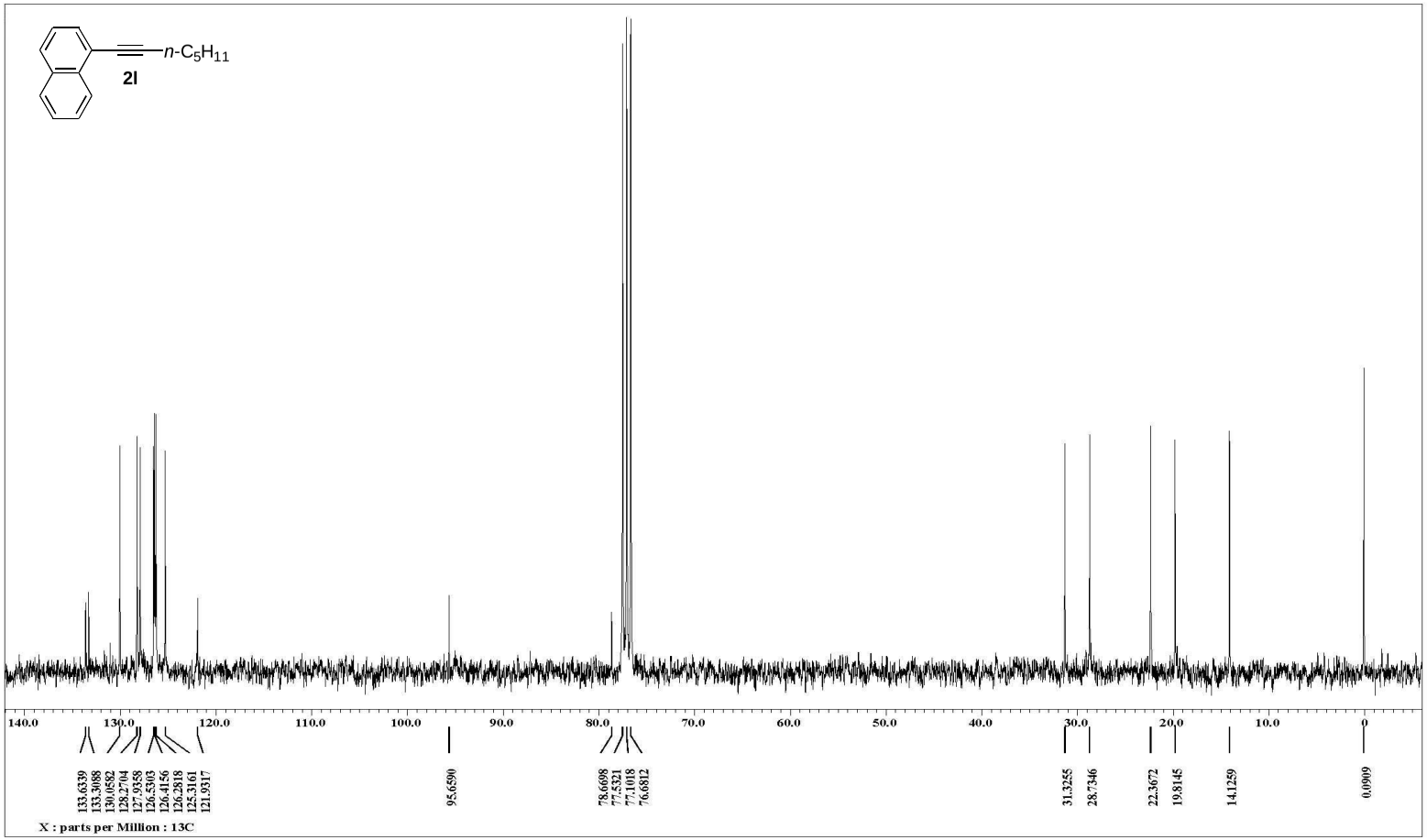

Cl
n-C5H11
2j
3.88653
2
6.67275
3.22853
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
7.3254
7.2968
7.2544
7.2270
2.4083
2.3843
2.3614
1.6014
1.5774
1.4090
1.4011
1.3954
1.3863
1.3656
0.9719
0.9444
0.9204
0.8975
0.0105
0.0002
−0.0090
−0.0113
X : parts per Million : 1H


Cl
n-C5H11
2j
140.0
130.0
120.0
110.0
100.0
90.0
80.0
70.0
60.0
50.0
40.0
30.0
20.0
10.0
0
−10.0
133.4527
132.8504
128.5481
122.7065
91.6536
79.5788
77.5229
77.1023
76.6720
31.2112
28.4577
22.3103
19.4707
14.0785
0.0818
X : parts per Million : 13C


n-C5H11
n-C5H11
2k
5.15531
3.33492
13.08976
6
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0
7.2888
7.2567
2.4175
2.3935
2.3706
1.6014
1.5774
1.5293
1.4240
1.4034
1.3863
1.3645
0.9422
0.9181
0.8941
0.0517
0.0093
−0.0010
−0.0113
X : parts per Million : 1H


n-C5H11
n-C5H11
2k
130.0
120.0
110.0
100.0
90.0
80.0
70.0
60.0
50.0
40.0
30.0
20.0
10.0
0
131.4158
123.2702
92.0260
80.4576
77.5130
77.0923
76.6716
31.2108
28.5051
22.3098
19.5372
14.0686
0.0718
X : parts per Million : 13C


n-C5H11
2l
6.80959
2.20105
6.55033
3
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0
8.3933
8.3670
7.8336
7.8015
7.7741
7.6596
7.6356
7.5772
7.5120
7.4124
2.6109
2.5869
2.5640
2.4770
1.7445
1.7193
1.5522
1.5476
1.5247
1.4446
1.4206
1.0028
0.9788
0.9547
0.1181
0.0380
0.0322
X : parts per Million : 1H


n-C5H11
2l
140.0
130.0
120.0
110.0
100.0
90.0
80.0
70.0
60.0
50.0
40.0
30.0
20.0
10.0
0
133.6339
133.3088
130.0582
128.2704
127.9358
126.5303
126.4156
126.2818
125.3161
121.9317
95.6590
78.6698
77.5321
77.1018
76.6812
31.3255
28.7346
22.3672
19.8145
14.1259
0.0909
X : parts per Million : 13C