Supporting Information

Solvent-Free Solid Acid-Catalyzed Nucleophilic Substitution of Propargylic Alcohols: A Green Approach for the Synthesis of 1,4-diynes

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Experimental

General methods and materials. NMR spectra were in $CDCl_3$ (^1H at 400 MHz and ^{13}C at 100 MHz). Column chromatography was performed on silica gel (300-400 mesh). Unless otherwise noted, all reagents were obtained commercially and used without further purification.

Acid-treatment procedure. A mixture of K10 montmorillonite (10 g) and hydrochloric acid (200 ml) was stirred at certain temperature for 6 h. The slurry obtained was filtered and washed with deionized water until no Cl^- could be detected by a silver nitrate test. The clay was then dried at 110 ^oC to afford the H-mont K10 as a whitish-gray powder.

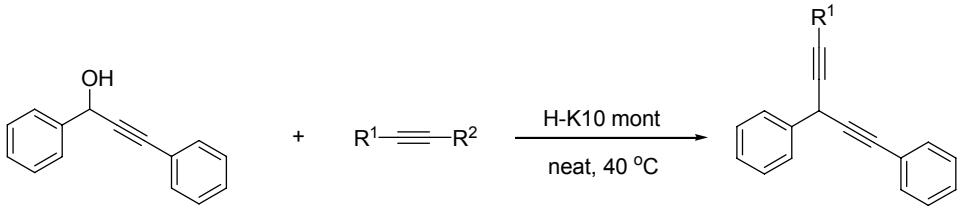
General procedure for alkynylation of propargylic alcohol. A mixture of propargylic alcohol (1 mmol), alkynylsilane (1 mmol) and H-K10 mont (20 wt% of propargylic alcohol) was stirred at 40 ^oC in a round-bottom flask. When the reaction was completed (monitored by TLC), the product was dissolved in ethyl acetate and separated from catalyst by filtration. The solvent was removed under reduced pressure, and then the residue was further purified by silica gel column chromatography (petroleum ether) to afford 1,4-diyne. The recovered catalyst could be reused after drying at 110 ^oC for 1 hour.

NH_3-TPD (Ammonia Temperature-programmed Desorption) Measurement. The sample was first treated for 1 h at 373 K under He flow, and ammonia was adsorbed at the same temperature by 0.5 %NH_3/He gas flow. NH_3-TPD was then carried out under He flow at a reduced pressure (160 Torr) from 373 K to 1073 K at a heating rate of 10 K min^{-1}. The desorbed NH_3 was detected by a mass spectrometer.

Details for 'Sheldon test'. A mixture of propargylic alcohol **1a** (1 mmol), alkynylsilane **2a** (5 mmol) and H-K10 mont (20 wt% of **1a**) was stirred at 40 ^oC in a round-bottom flask. After stirred for 5 min, **1a** had partially transformed to 1,4-diyne **3aa**, the molar ratio of **1a** and **3aa** was 3.7:1 (monitored by ^1H NMR spectroscopy). By then the reaction mixture was filtered at 40 ^oC and the filtrate was further stirred at same temperature. ^1H NMR analysis showed that after 2 h, the molar ratio of **1a** and

3aa in the reaction mixture was still unchanged. This result indicated that **1a** failed to transform any more in the absence of H-K10 mont even with prolonged reaction time. The substitution reaction proved to be a heterogeneous reaction.

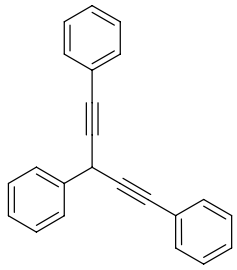
Table S1 Substitution of propargylic alcohol **1a** with other nucleophiles[a]



1a **2** **3**

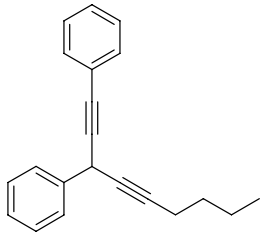
entry	R^1	R^2	time	yield (%)
1	Phenyl	H	20 min	trace [b]
2	p- MeO-phenyl	H	20 min	trace [b]
3	p-Br-phenyl	H	20 min	trace [b]
4[c]	Phenyl	H	3 h	trace [b]
5	H	TMS	24 h	n. r. [d]
6	*n*-Bu	TMS	24 h	n. r. [d]
7	1-cyclohexenyl	TMS	6.5 h	not detected [b]

[a] Reaction conditions: **1a** (1 mmol), **2** (1 mmol), H-K10 mont (20 wt% of **1a**), solvent-free, 40 °C. [b] Obtained as a complex mixture. [c] Performed at room temperature. [d] n. r. = no reaction. Starting materials were recovered.



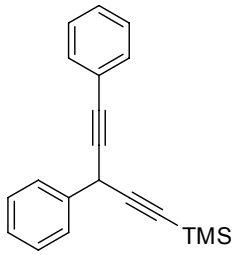
3aa

penta-1,4-diyne-1,3,5-triyltribenzene (**3aa**)[1,2]: A pale yellow oil. δ_H (400 MHz; $CDCl_3$) 5.26 (s, 1H), 7.32-7.36 (m, 7H), 7.43-7.46 (m, 2H), 7.52-7.55 (m, 4H), 7.72-7.74 (m, 2H) ppm; δ_C (100 MHz; $CDCl_3$) 30.2, 83.0, 86.7, 123.1, 127.5, 127.7, 128.3, 128.4, 128.9, 132.0, 138.1 ppm; HRMS (APCI) m/z calc. for $C_{23}H_{17}$ [$M+H^+$]: 293.1325, found: 293.1324.



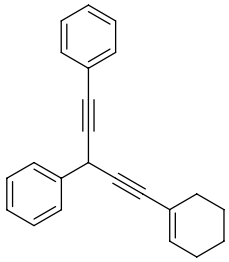
3ba

nona-1, 4-diyne-1,3-diyldibenzene (**3ba**): A colourless oil. δ_H (400 MHz; $CDCl_3$) 0.94 (t, 3H, J = 7.2 Hz), 1.43-1.50 (m, 2H), 1.52-1.58 (m, 2H), 2.28 (dt, 2H, J = 2 and 7.2 Hz), 4.99 (t, 1H, J = 2 Hz), 7.29-7.33 (m, 4H), 7.37-7.42 (m, 2H), 7.45-7.49 (m, 2H), 7.62-7.65 (m, 2H) ppm; δ_C (100 MHz; $CDCl_3$) 13.8, 18.7, 22.1, 29.7, 30.9, 77.3, 82.4, 83.5, 87.7, 123.3, 127.3, 127.4, 128.2, 128.3, 128.7, 131.9, 138.8 ppm; HRMS (APCI) m/z calc. for $C_{21}H_{21}$ [M+H$^+$]: 273.1638, found: 273.1638.



3ca

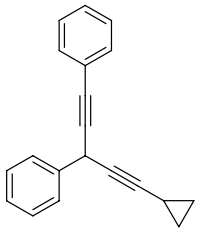
(3,5-diphenylpenta-1,4-diynyl)trimethylsilane (**3ca**): A pale yellow oil. δ_H (400 MHz; $CDCl_3$) 0.24 (s, 9H), 5.05 (s, 1H), 7.30-7.35 (m, 4H), 7.39-7.43 (m, 2H), 7.47-7.51 (m, 2H), 7.63-7.66 (m, 2H) ppm; δ_C (100 MHz; $CDCl_3$) 0.1, 30.6, 82.9, 86.7, 87.6, 102.7, 123.2, 127.4, 127.6, 128.3(2), 128.8, 131.9, 137.9 ppm; HRMS (APCI) m/z calc. for $C_{20}H_{21}Si$ [M+H$^+$]: 289.1407, found: 289.1408.



3da

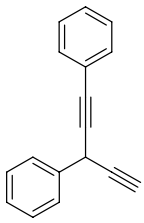
(5-cyclohexenylpenta-1,4-diyne-1,3-diyl)dibenzene (**3da**): A pale yellow oil. δ_H (400 MHz; $CDCl_3$) 1.55-1.66 (m, 4H), 2.07-2.10 (m, 2H), 2.14-2.19 (m, 2H), 5.10 (s, 1H),

6.14-6.17 (m, 1H), 7.27-7.32 (m, 4H), 7.36-7.40 (m, 2H), 7.45-7.48 (m, 2H), 7.60-7.63 (m, 2H) ppm; δ_C (100 MHz; $CDCl_3$) 21.7, 22.4, 25.8, 29.3, 30.1, 82.6, 83.8, 84.8, 87.2, 120.5, 123.3, 127.4, 127.5, 128.3, 128.3, 128.8, 131.9, 135.2, 138.5 ppm; HRMS (APCI) m/z calc. for $C_{23}H_{21}$ [M+H$^+$]: 297.1638, found: 297.1639.



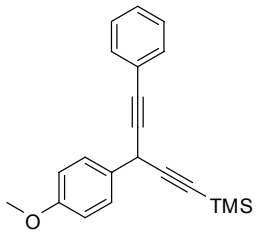
3ea

(5-cyclopropylpenta-1,4-diyne-1,3-diyl)dibenzene (**3ea**): A pale yellow oil. δ_H (400 MHz; $CDCl_3$) 0.71-0.81 (m, 4H), 1.28-1.36 (m, 1H), 4.95 (d, 1H, J = 0.8 Hz), 7.28-7.32 (m, 4H), 7.36-7.41 (m, 2H), 7.46-7.49 (m, 2H), 7.59-7.62 (m, 2H) ppm; δ_C (100 MHz; $CDCl_3$): -0.2, 8.3, 29.6, 72.5, 82.5, 86.3, 87.5, 123.3, 127.3, 127.5, 128.3, 128.3, 128.7, 131.9, 138.7 ppm; HRMS (APCI) m/z calc. for $C_{20}H_{17}$ [M+H$^+$]: 257.1325, found: 257.1321.



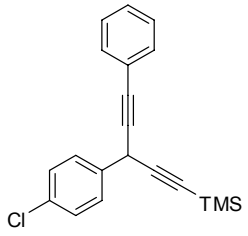
3fa

penta-1,4-diyne-1,3-diyldibenzene (**3fa**)[3]: A pale yellow oil. δ_H (400 MHz; $CDCl_3$) 2.46 (d, 1H, J = 2.4 Hz), 5.03 (d, 1H, J = 2.4 Hz), 7.31-7.37 (m, 4H), 7.41-7.45 (m, 2H), 7.48-7.53 (m, 2H), 7.64-7.67 (m, 2H) ppm; δ_C (100 MHz; $CDCl_3$) 29.4, 71.1, 81.4, 83.1, 86.1, 122.9, 127.3, 127.8, 128.3, 128.5, 128.9, 131.9, 137.4 ppm; HRMS (APCI) m/z calc. for $C_{17}H_{13}$ [M+H$^+$]: 217.1012, found: 217.1014.



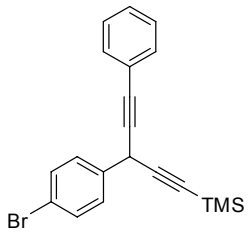
3ga

(3-(4-methoxyphenyl)-5-phenylpenta-1,4-diynyl)trimethylsilane (**3ga**): δ_H (400 MHz; $CDCl_3$) 0.23 (s, 9H), 3.83 (s, 3H), 4.99 (s, 1H), 6.92-6.95 (m, 2H), 7.30-7.33 (m, 3H), 7.47-7.48 (m, 2H), 7.52-7.55 (m, 2H) ppm; δ_C (100 MHz; $CDCl_3$) 0.1, 29.8, 55.4, 82.6, 87.0, 87.2, 103.0, 114.2, 123.2, 128.3(2), 128.4, 129.9, 131.9, 159.1 ppm; HRMS (ESI) m/z calc. for $C_{21}H_{21}OSi$ [M-H$^+$]: 317.1367, found: 317.1366.



3ha

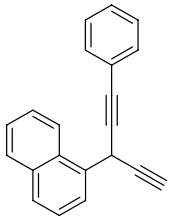
(3-(4-chlorophenyl)-5-phenylpenta-1,4-diynyl)trimethylsilane (**3ha**): A pale yellow oil. δ_H (400 MHz; $CDCl_3$) 0.23 (s, 9H), 5.00 (s, 1H), 7.31-7.33 (m, 3H), 7.35-7.38 (m, 2H), 7.46-7.49 (m, 2H), 7.55-7.58 (m, 2H) ppm; δ_C (100 MHz; $CDCl_3$) 0.0, 30.0, 83.2, 86.1, 88.0, 102.1, 122.9, 128.4, 128.5, 128.8, 128.9, 131.9, 133.5, 136.4 ppm; HRMS (ESI) m/z calc. for $C_{20}H_{18}ClSi$ [M-H$^+$]: 321.0872, found: 321.0870.



3ia

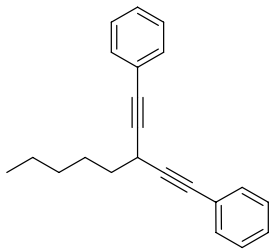
(3-(4-bromophenyl)-5-phenylpenta-1,4-diynyl)trimethylsilane (**3ia**): A pale yellow solid. δ_H (400 MHz; $CDCl_3$): 0.22 (s, 9H), 4.97(s, 1H), 7.30-7.31 (m, 1H), 7.32-7.33 (m, 2H), 7.45-7.47 (m, 1H), 7.47-7.48 (m, 1H), 7.50-7.51 (m, 4H) ppm; δ_C (100 MHz;

$CDCl_3$) 0.0, 30.1, 83.2, 86.0, 88.0, 102.0, 121.6, 122.9, 128.4, 128.5, 129.2, 131.9, 131.9, 137.0 ppm; HRMS (ESI) m/z calc. for $C_{20}H_{18}BrSi$ [M-H^+]: 365.0367, found: 365.0366.



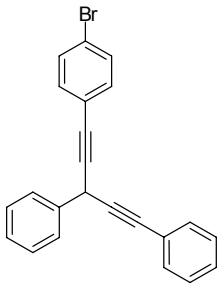
3ka

1-(1-phenylpenta-1,4-diyn-3-yl)naphthalene (**3ka**): A pale yellow oil. δ_H (400 MHz; $CDCl_3$) 2.46 (d, 1H, *J* = 2.4 Hz), 5.56 (d, 1H, *J* = 2.4 Hz), 7.27-7.31 (m, 3H), 7.44-7.46 (m, 2H), 7.49-7.54 (m, 2H), 7.59-7.64 (m, 1H), 7.85 (d, 1H, *J* = 8.4 Hz), 7.90-7.95 (m, 2H), 8.32-8.34 (m, 1H) ppm; δ_C (100 MHz; $CDCl_3$) 27.6, 71.6, 81.3, 83.6, 86.1, 123.0, 123.9, 125.5, 125.7, 126.1, 126.5, 128.3, 128.5, 128.9, 129.0, 130.6, 131.9, 133.0, 134.3 ppm; HRMS (APCI) m/z calc. for $C_{21}H_{15}$ [M+H^+]: 267.1168, found: 267.1165.



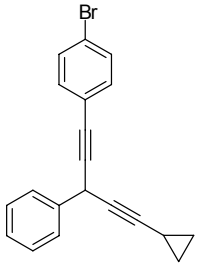
3la

(3-pentylpenta-1,4-diyne-1,5-diyl)dibenzene (**3la**): A pale yellow oil. δ_H (400 MHz; $CDCl_3$) 0.93 (t, 3H, *J* = 7.2 Hz), 1.35-1.40 (m, 4H), 1.63-1.67 (m, 2H), 1.87-1.93 (m, 2H), 3.81 (t, 1H, *J* = 7.2 Hz), 7.27-7.32 (m, 6H), 7.43-7.47 (m, 4H) ppm; δ_C (100 MHz; $CDCl_3$) 14.0, 22.5, 24.6, 26.7, 31.3, 36.0, 81.2, 88.0, 123.3, 128.0, 128.2, 131.8 ppm; HRMS (APCI) m/z calc. for $C_{22}H_{23}$ [M+H^+]: 287.1794, found: 287.1796.



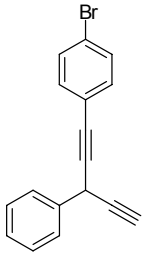
3ab

(5-(4-bromophenyl)penta-1,4-diyne-1,3-diyl)dibenzene (**3ab**): A pale yellow oil. δ_H (400 MHz; $CDCl_3$) 5.20 (s, 1H), 7.30-7.37 (m, 6H), 7.40-7.46 (m, 4H), 7.48-7.51 (m, 2H), 7.65-7.69 (m, 2H) ppm; δ_C (100 MHz; $CDCl_3$) 30.3, 81.9, 83.1, 86.4, 88.0, 122.1, 122.7, 123.0, 127.4, 127.8, 128.4, 128.5, 128.9, 131.6, 132.0, 133.4, 137.9 ppm; HRMS (ESI) m/z calc. for $C_{23}H_{14}Br$ [M-H^+]: 369.0284, found: 369.0285.



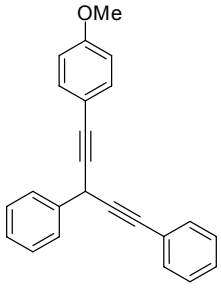
3eb

1-bromo-4-(5-cyclopropyl-3-phenylpenta-1,4-diynyl)benzene (**3eb**): A colourless oil. δ_H (400 MHz; $CDCl_3$) 0.69-0.80 (m, 4H), 1.28-1.32 (m, 1H), 4.91 (d, 1H, J = 1.6 Hz), 7.28-7.32 (m, 3H), 7.35-7.39 (m, 2H), 7.40-7.44 (m, 2H), 7.55-7.58 (m, 2H) ppm; δ_C (100 MHz; $CDCl_3$) -0.2, 8.3, 29.7, 72.2, 81.4, 86.5, 88.8, 122.2, 122.5, 127.3, 127.6, 128.8, 131.6, 133.4, 138.4 ppm; HRMS (ESI) m/z calc. for $C_{20}H_{14}Br$ [M-H^+]: 333.0284, found: 333.0284.



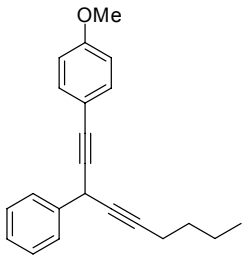
3fb

1-bromo-4-(3-phenylpenta-1,4-diynyl)benzene (**3fb**): A colourless oil. δ_H (400 MHz; $CDCl_3$) 2.43 (d, 1H, *J* = 2.4 Hz), 4.97 (d, 1H, *J* = 2.4 Hz), 7.30-7.36 (m, 3H), 7.38-7.40 (m, 2H), 7.41-7.45 (m, 2H), 7.58-7.61 (m, 2H) ppm; δ_C (100 MHz; $CDCl_3$) 29.5, 71.3, 81.1, 82.0, 87.4, 121.9, 122.8, 127.3, 127.9, 129.0, 131.7, 133.4, 137.2 ppm; HRMS (ESI) m/z calc. for $C_{17}H_{10}Br$ [M-H^+]: 292.9971, found: 292.9970.



3ac

(5-(4-methoxyphenyl)penta-1,4-diyne-1,3-diyl)dibenzene (**3ac**): A pale yellow oil. δ_H (400 MHz; $CDCl_3$) 3.81 (s, 3H), 5.22 (s, 1H), 6.84-6.86 (m, 2H), 7.30-7.34 (m, 4H), 7.40-7.47 (m, 4H), 7.49-7.52 (m, 2H), 7.69-7.72 (m, 2H) ppm; δ_C (100 MHz; $CDCl_3$) 30.2, 55.4, 82.8(2), 85.2, 87.0, 114.0, 115.2, 123.2, 127.5, 127.6, 128.3(2), 128.8, 131.9, 133.4, 138.3, 159.7 ppm; HRMS (ESI) m/z calc. for $C_{24}H_{17}O$ [M-H^+]: 321.1285, found: 321.1283.



3bc

1-methoxy-4-(3-phenylnona-1,4-diynyl)benzene (**3bc**): A pale yellow oil. δ_H (400 MHz; $CDCl_3$) 0.93 (t, 3H, *J* = 7.2 Hz), 1.41-1.49 (m, 2H), 1.51-1.58 (m, 2H), 2.27 (dt, 2H, *J* = 2.4 and 7.2 Hz), 3.80 (s, 3H), 4.96 (t, 1H, *J* = 2.4 Hz), 6.81-6.84 (m, 2H), 7.29-7.32 (m, 1H), 7.36-7.43 (m, 4H), 7.60-7.63 (m, 2H) ppm; δ_C (100 MHz; $CDCl_3$): 13.8, 18.7, 22.1, 29.6, 30.9, 55.4, 77.4, 82.2, 83.4, 86.1, 113.9, 115.4, 127.3(2), 128.7,

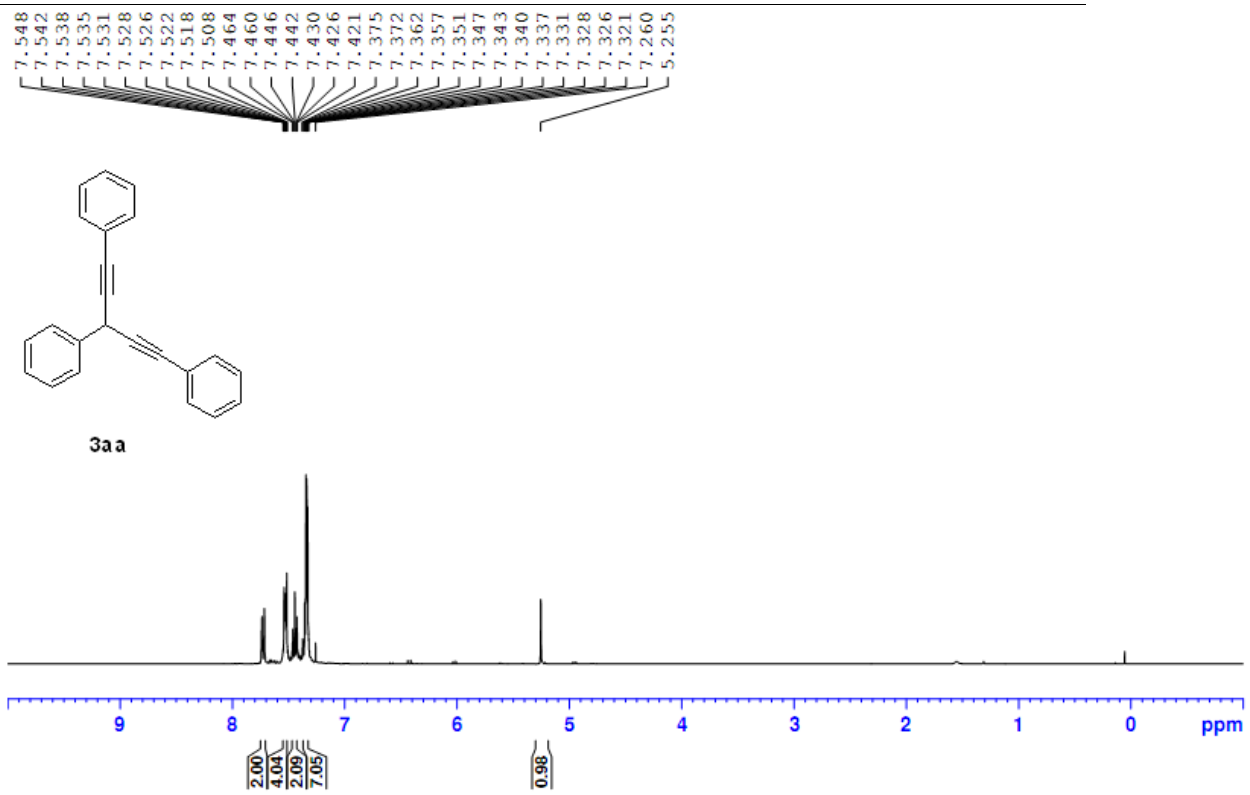
133.3, 139.0, 159.6 ppm; HRMS (ESI) m/z calc. for $C_{22}H_{21}O$ [M-H^+]: 301.1598, found: 301.1597.

Reference:

1 Y. Kuninobu, E. Ishii and K. Takai, *Angew. Chem. Int. Ed.*, 2007, **46,** 3296-3299.

2 J. S. Yadav, B. V. Subba Reddy, N. Thrimurtulu, N. Mallikarjuna Reddy and A. R. Prasad, *Tetrahedron Lett.,* 2008, **49,** 2031-2033.

3 D. Renard, H. Rezaei and S. Z. Zard, *Synlett,* 2002, **8,** 1257-1260.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7.357
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7.347
7.343
7.340
7.337
7.331
7.328
7.326
7.321
7.260
5.255
3aa
9
8
7
6
5
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7.05
0.98

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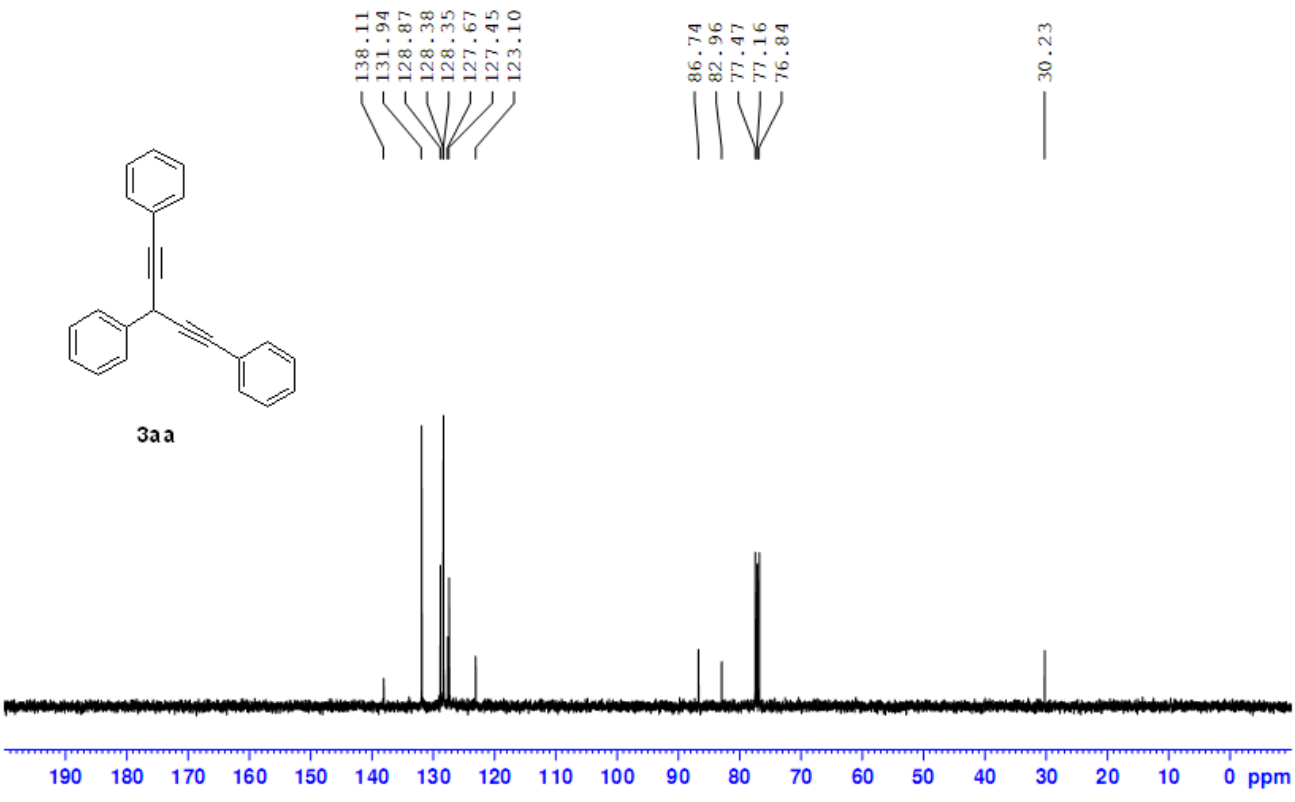
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127.67
127.45
123.10
86.74
82.96
77.47
77.16
76.84
30.23
3aa
190
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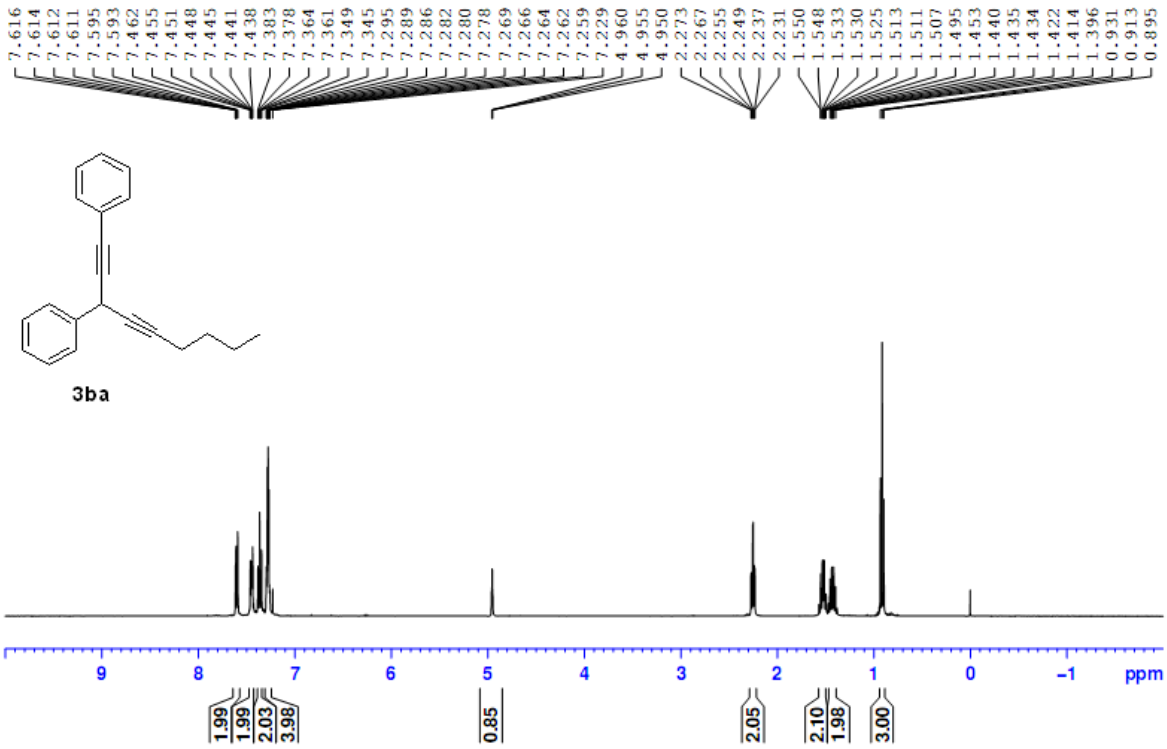

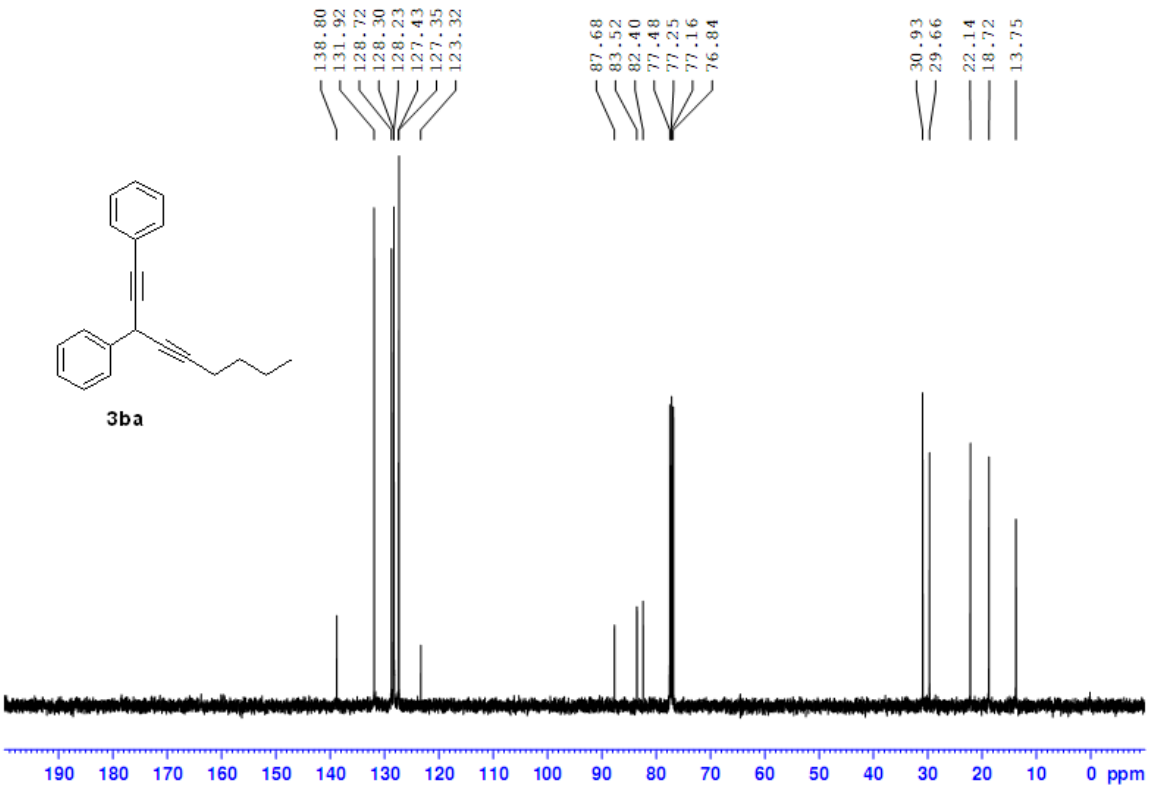

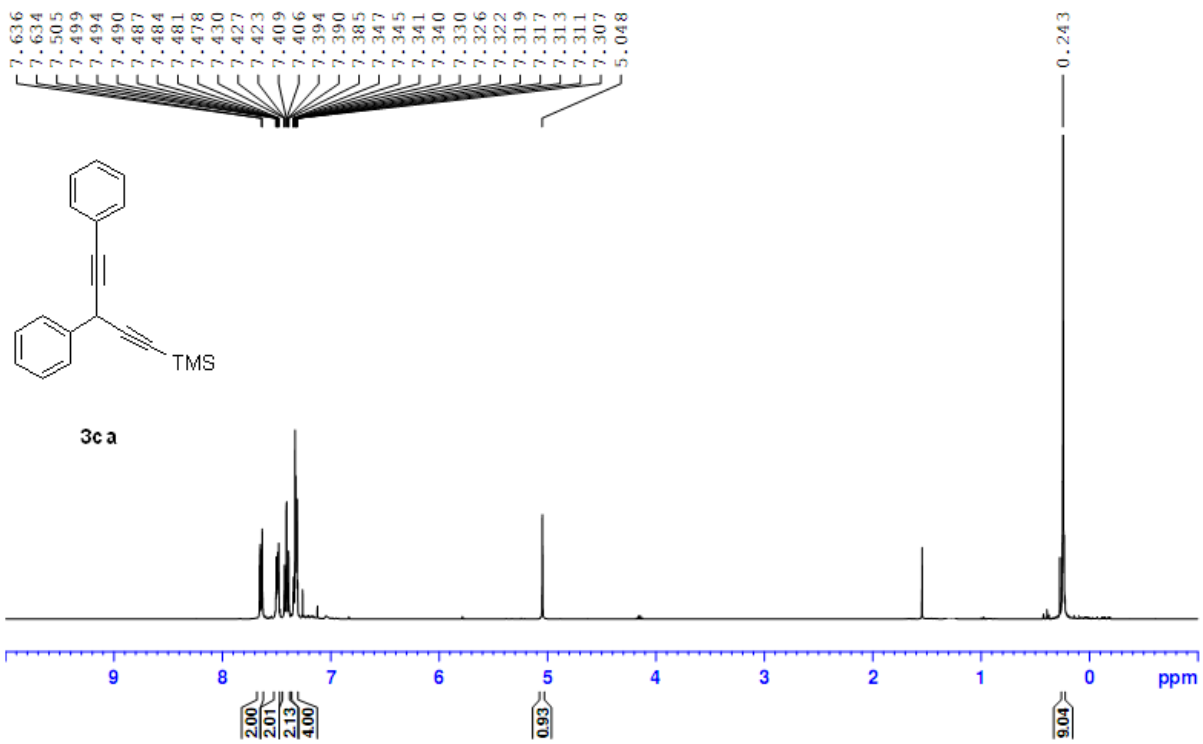
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7.409
7.406
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7.340
7.330
7.326
7.322
7.319
7.317
7.313
7.311
7.307
5.048
0.243
TMS
3ca
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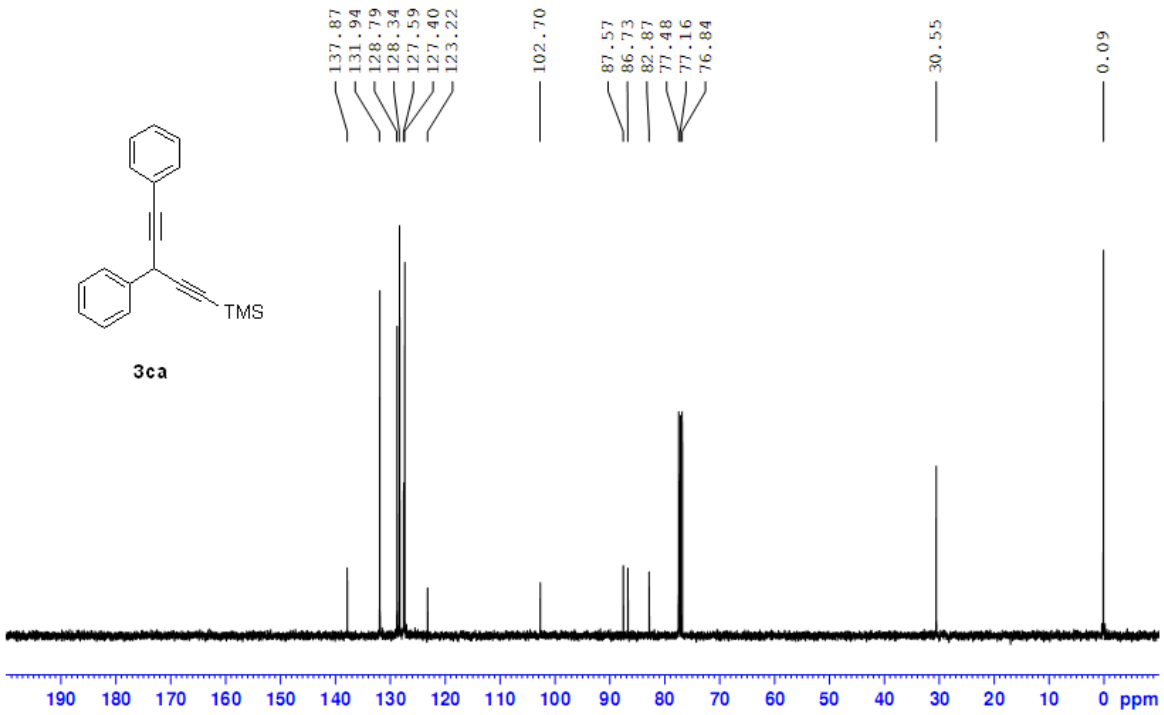
9.04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76.84
30.55
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TMS
3ca
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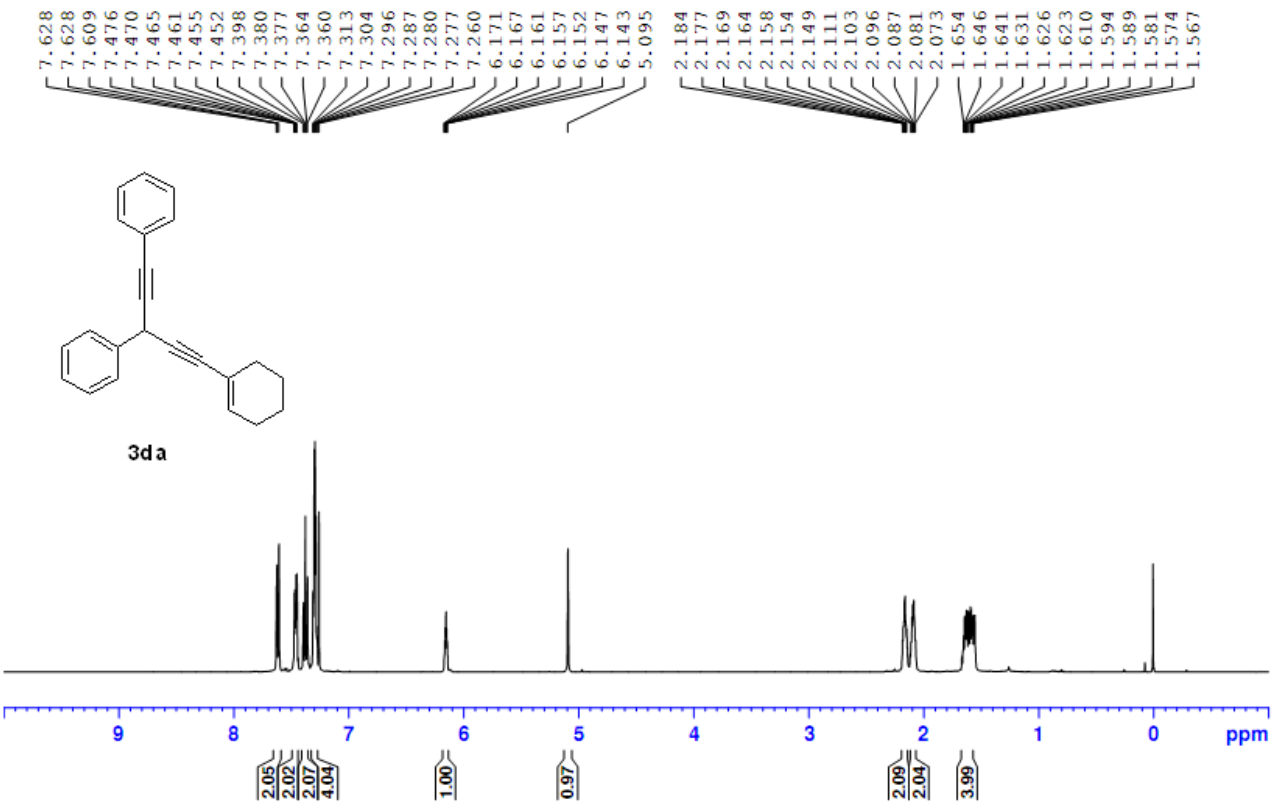
ppm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7.377
7.364
7.360
7.313
7.304
7.296
7.287
7.280
7.277
7.260
6.171
6.167
6.161
6.157
6.152
6.147
6.143
5.095
2.184
2.177
2.169
2.164
2.158
2.154
2.149
2.111
2.103
2.096
2.087
2.081
2.073
1.654
1.646
1.641
1.631
1.626
1.623
1.610
1.594
1.589
1.581
1.574
1.567
3da
9
8
7
6
5
4
3
2
1
0
ppm
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2.04
3.99

1

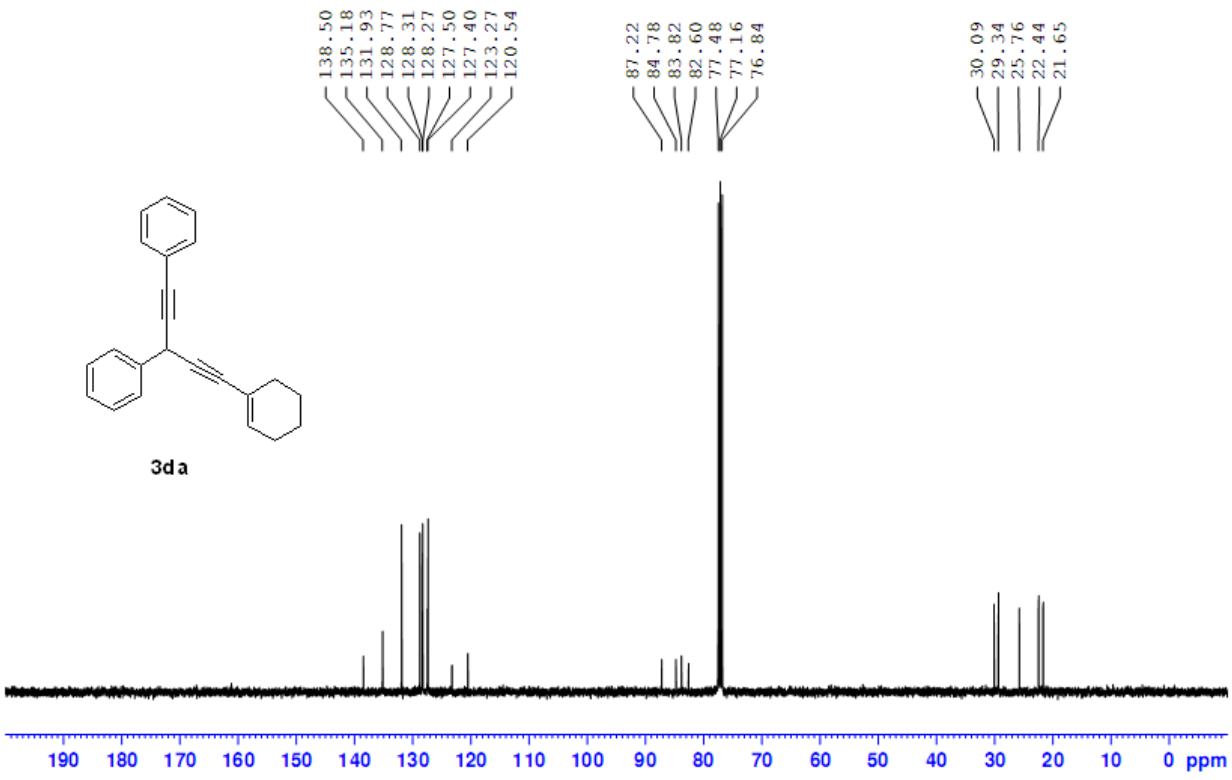
2

3

4

5

6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77.48
77.16
76.84
30.09
29.34
25.76
22.44
21.65
3da
190
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140
130
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20
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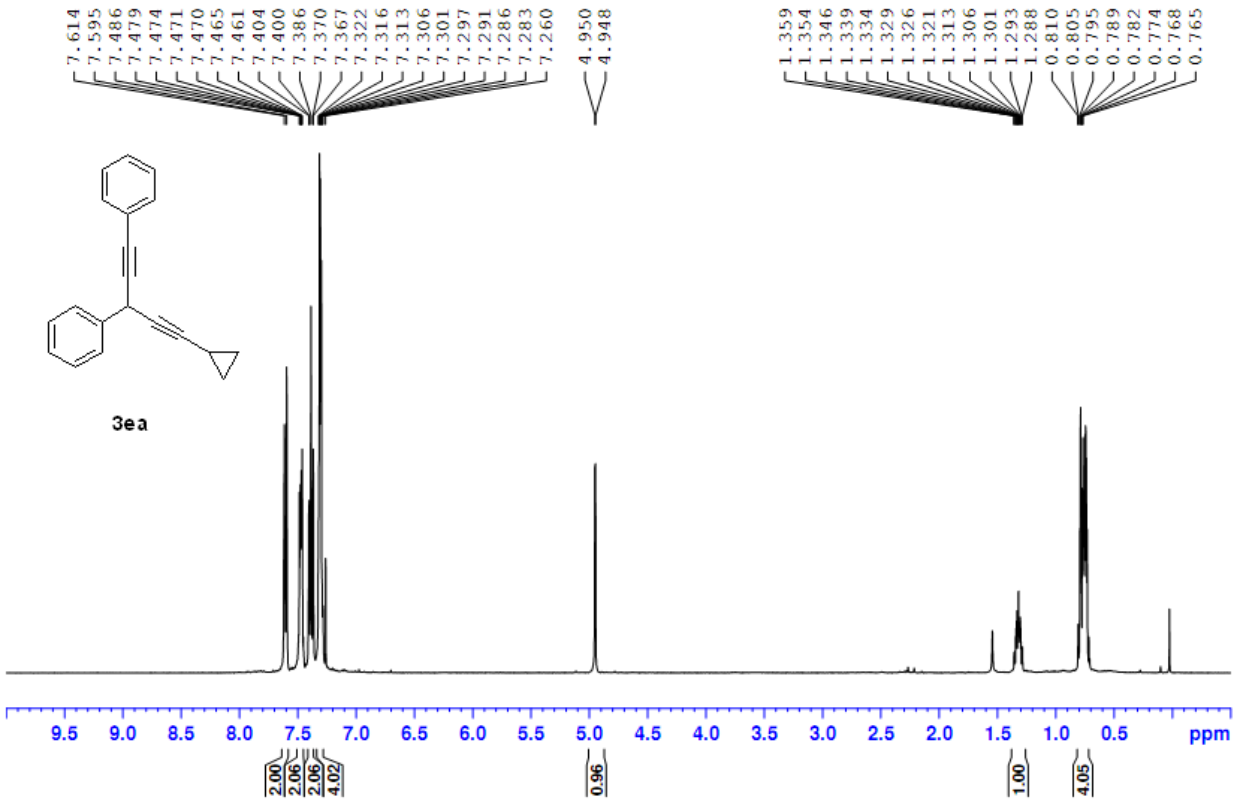
7



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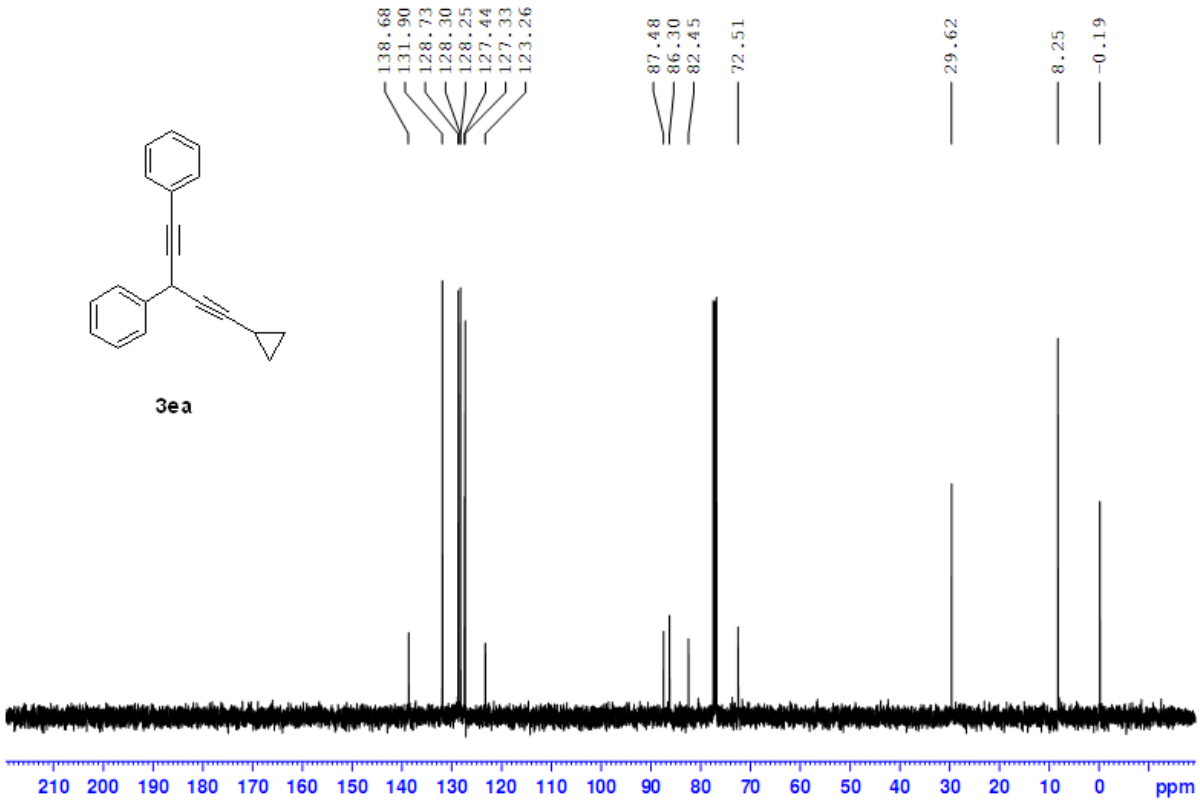

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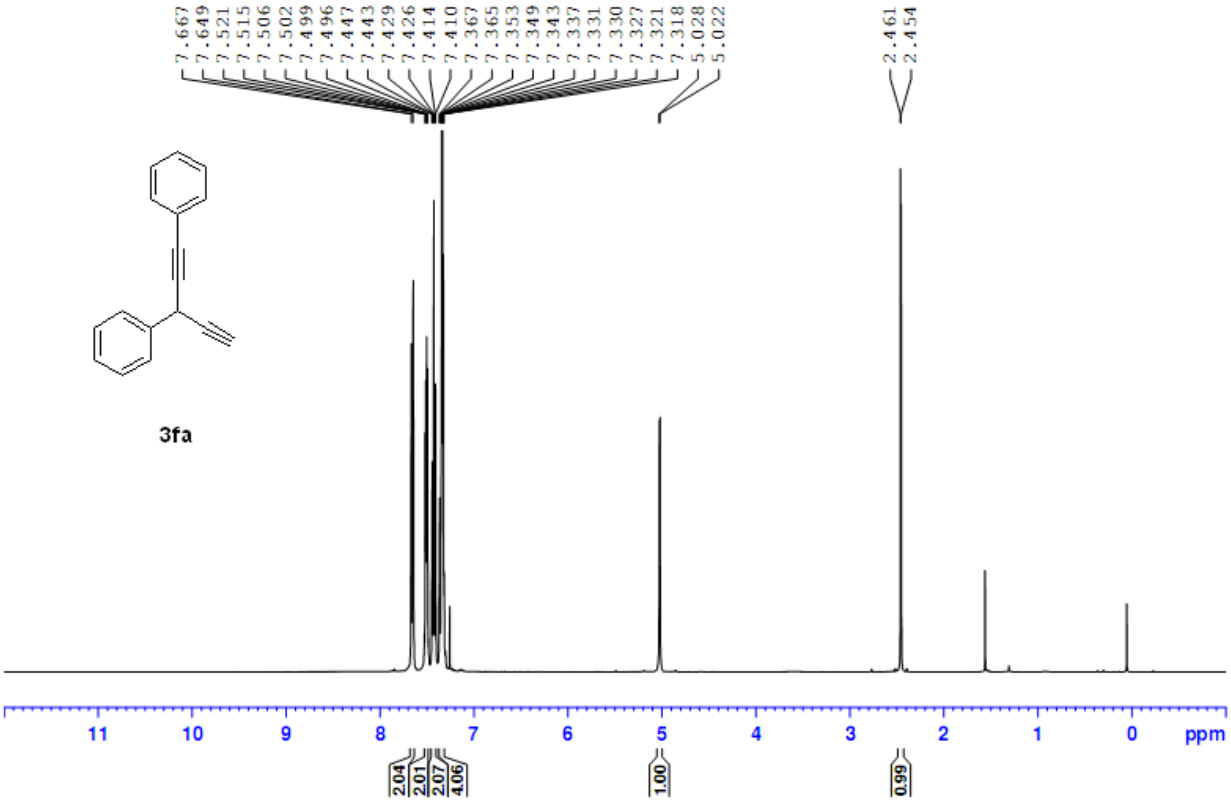

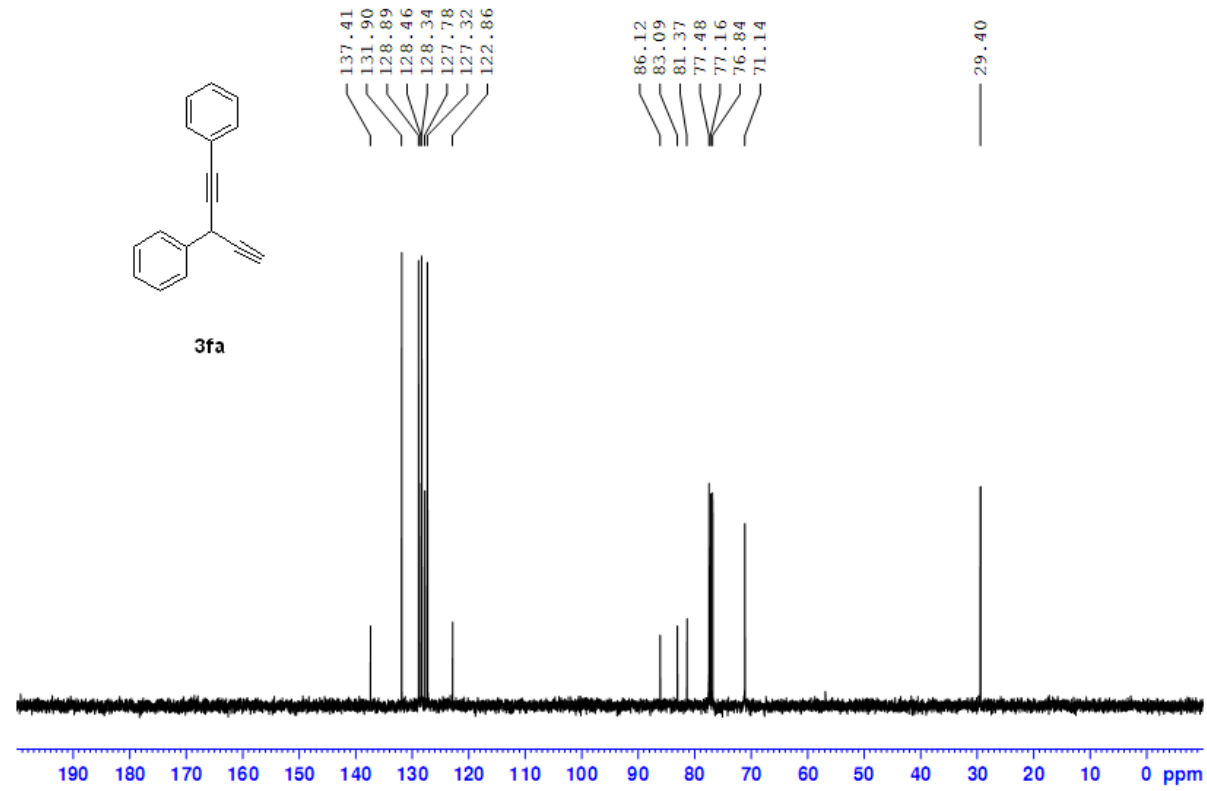

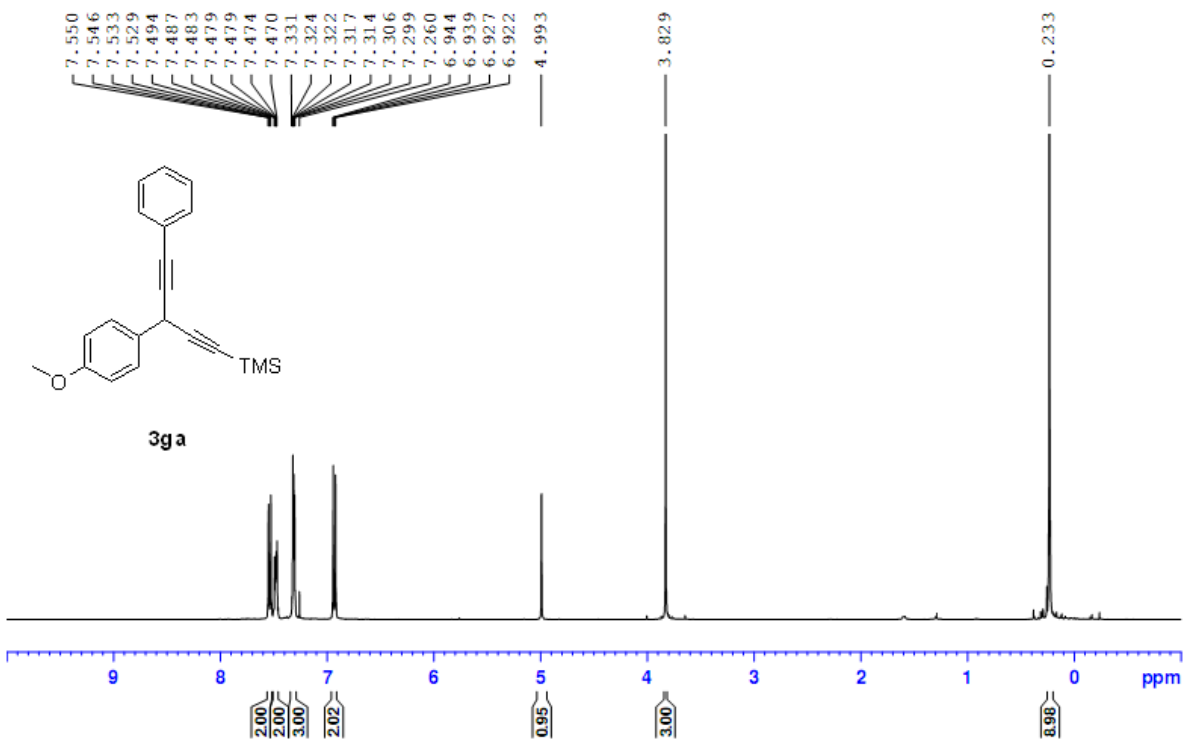
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7.483
7.479
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7.474
7.470
7.331
7.324
7.322
7.317
7.314
7.306
7.299
7.260
6.944
6.939
6.927
6.922
4.993
3.829
0.233
TMS
O
3g a
9
8
7
6
5
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3
2
1
0
ppm
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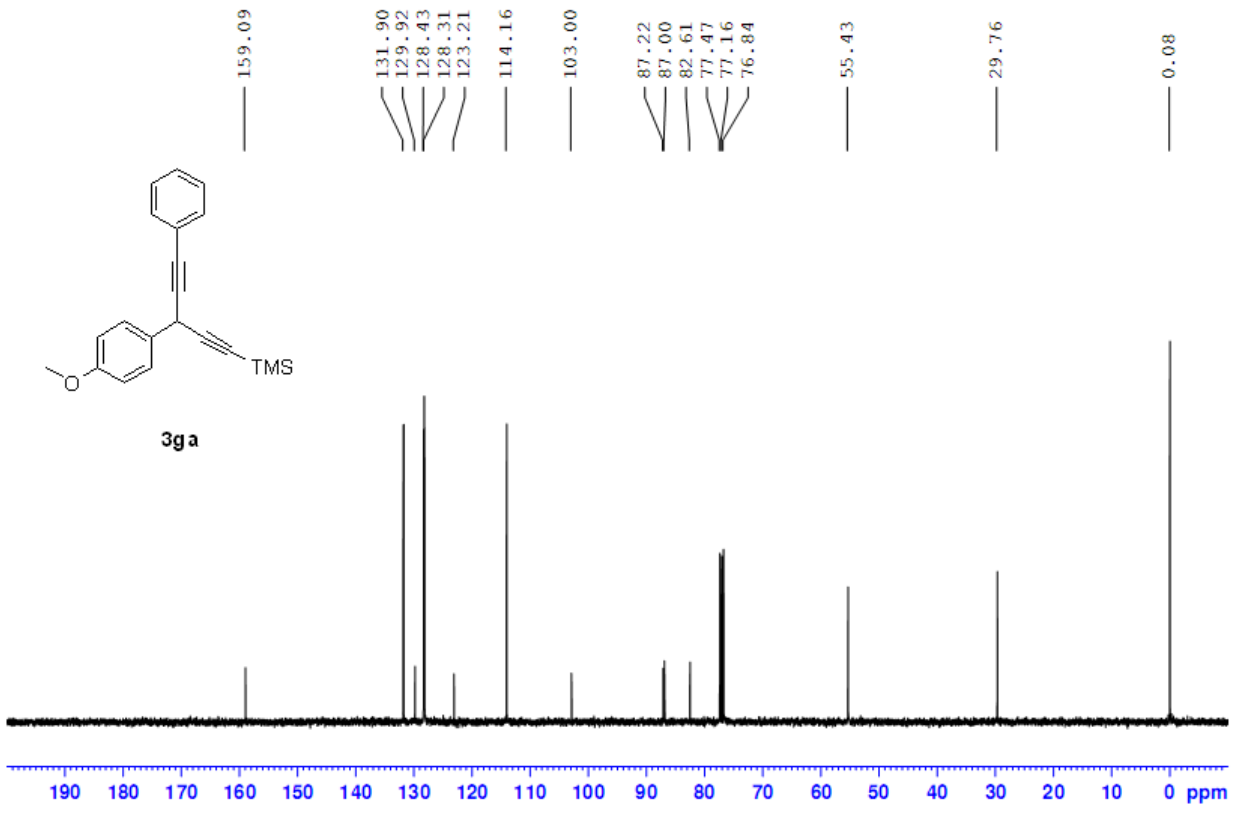
2.00
3.00
2.02
0.95
3.00
8.98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103.00
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87.00
82.61
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77.16
76.84
55.43
29.76
0.08
TMS
O
3g a
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140
130
120
110
100
90
80
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60
50
40
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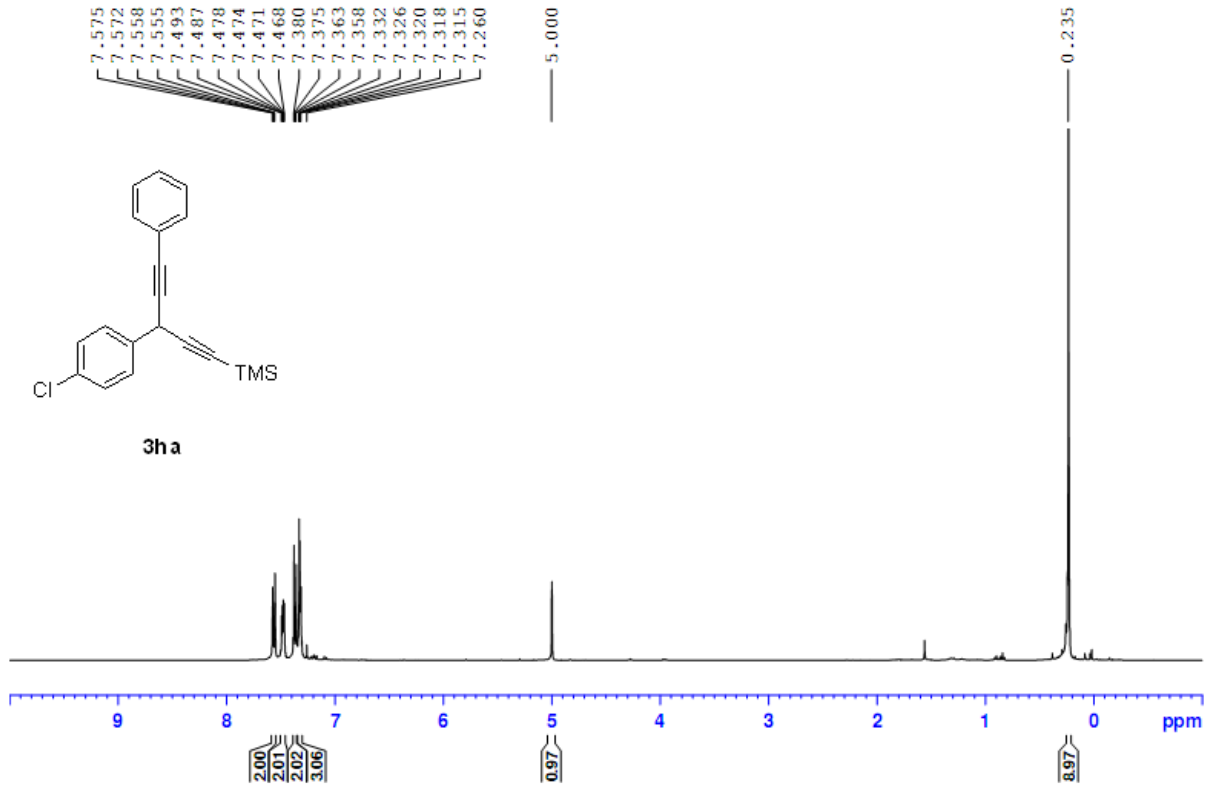
20
10
0
ppm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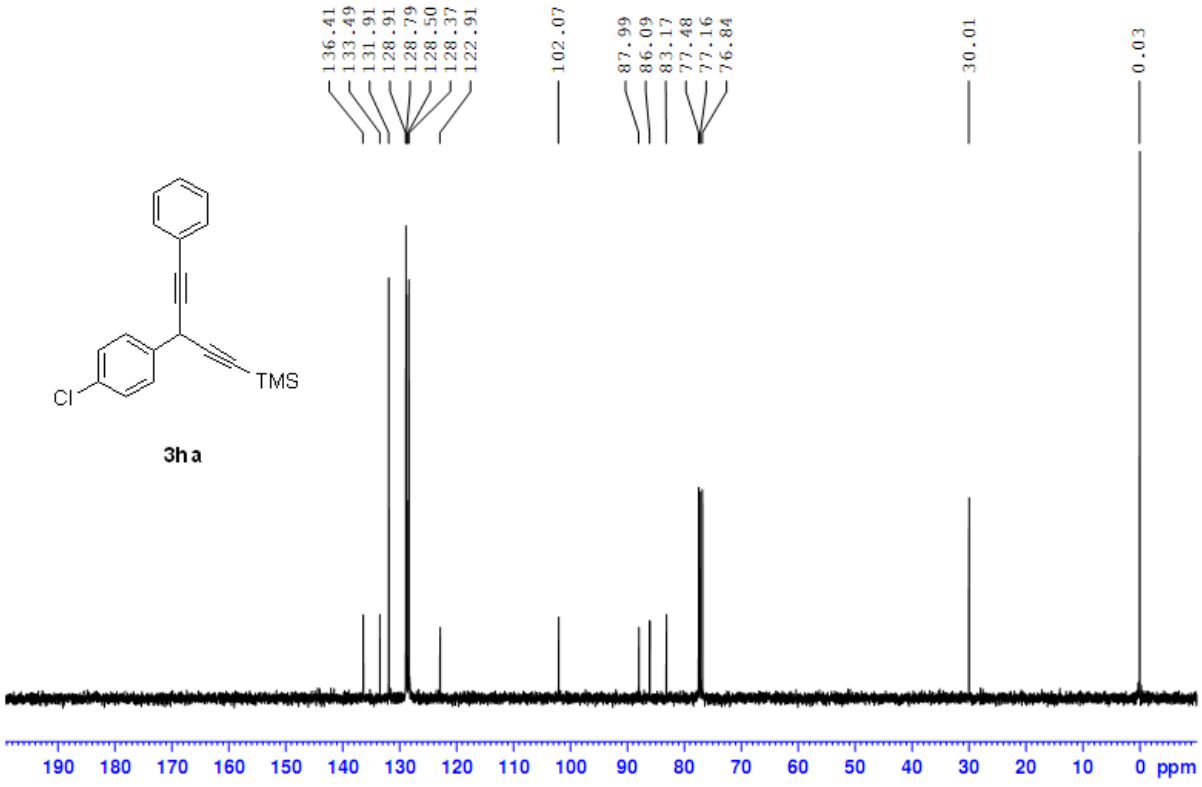
7.487
7.478
7.474
7.471
7.468
7.380
7.375
7.363
7.358
7.332
7.326
7.320
7.318
7.315
7.260
5.000
0.235
Cl
TMS
3ha
9
8
7
6
5
4
3
2
1
0
ppm
2.00
2.01
2.02
3.06
0.97
8.97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77.48
77.16
76.84
30.01
0.03
Cl
TMS
3ha
190
180
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140
130
120
110
100
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60
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20
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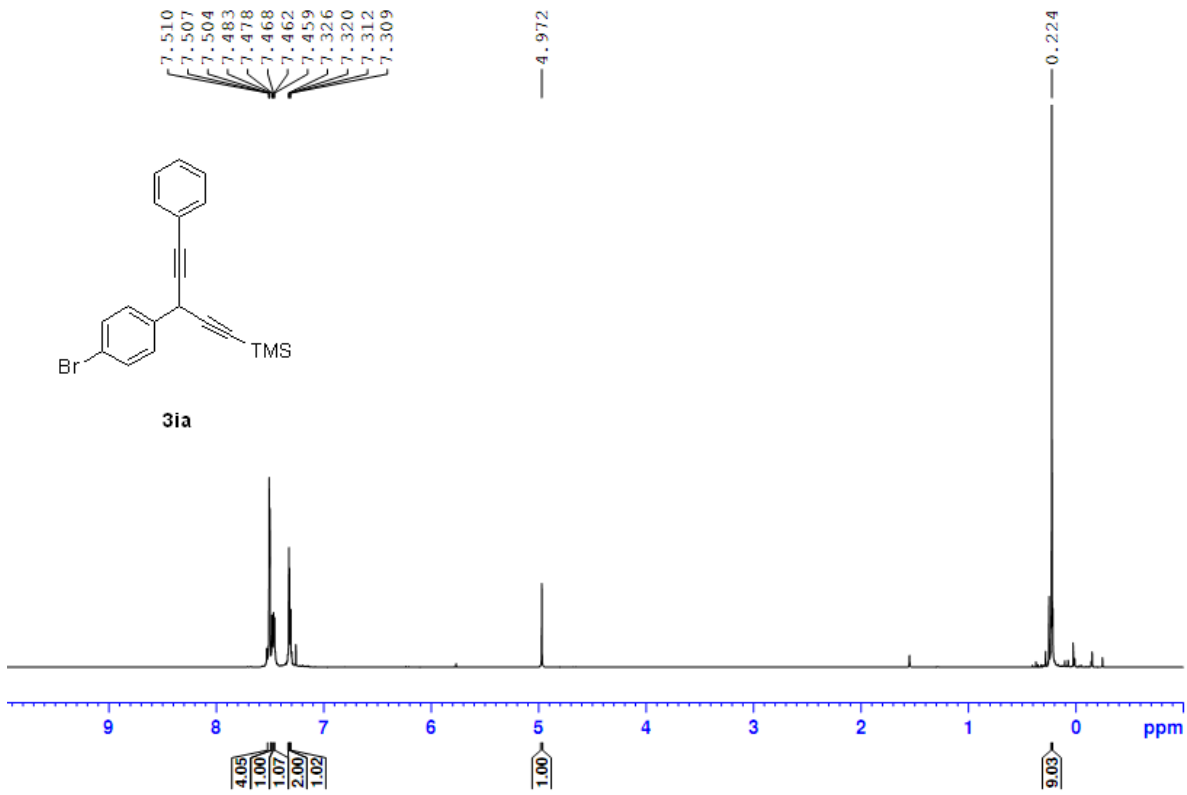
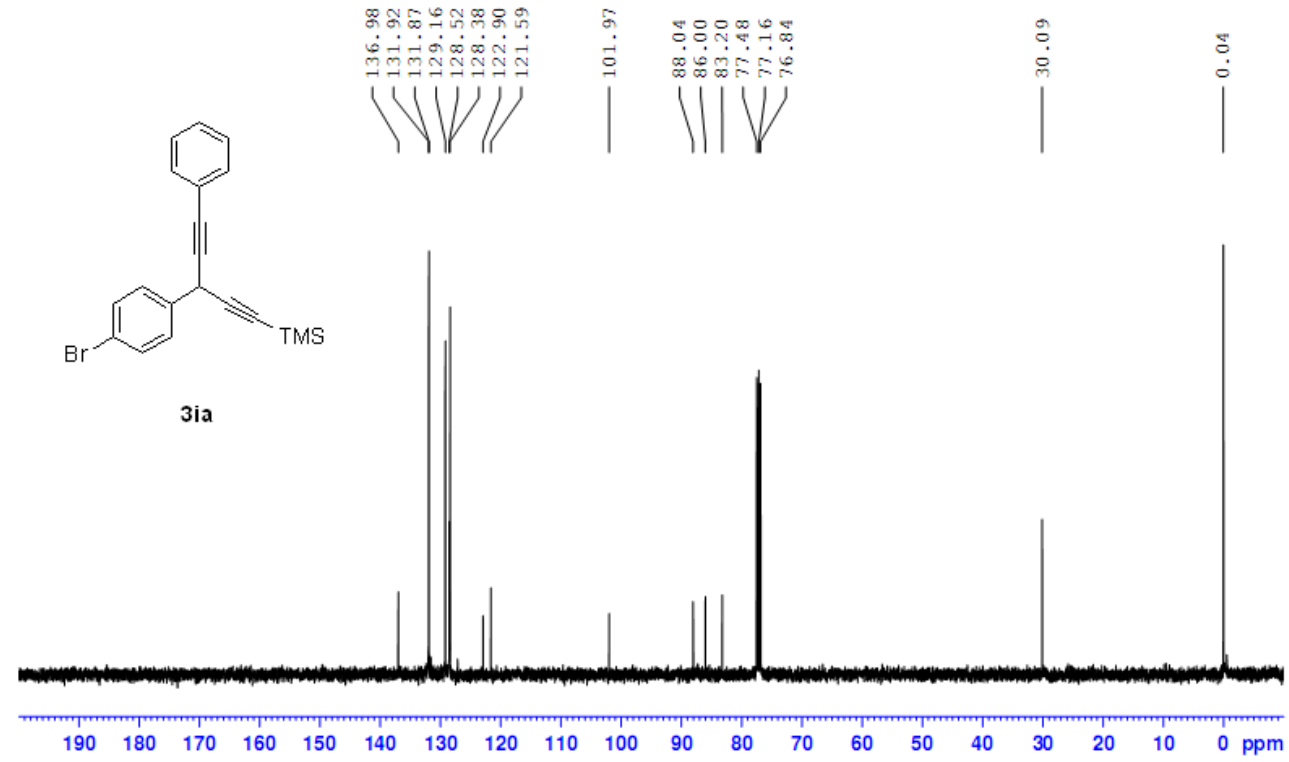
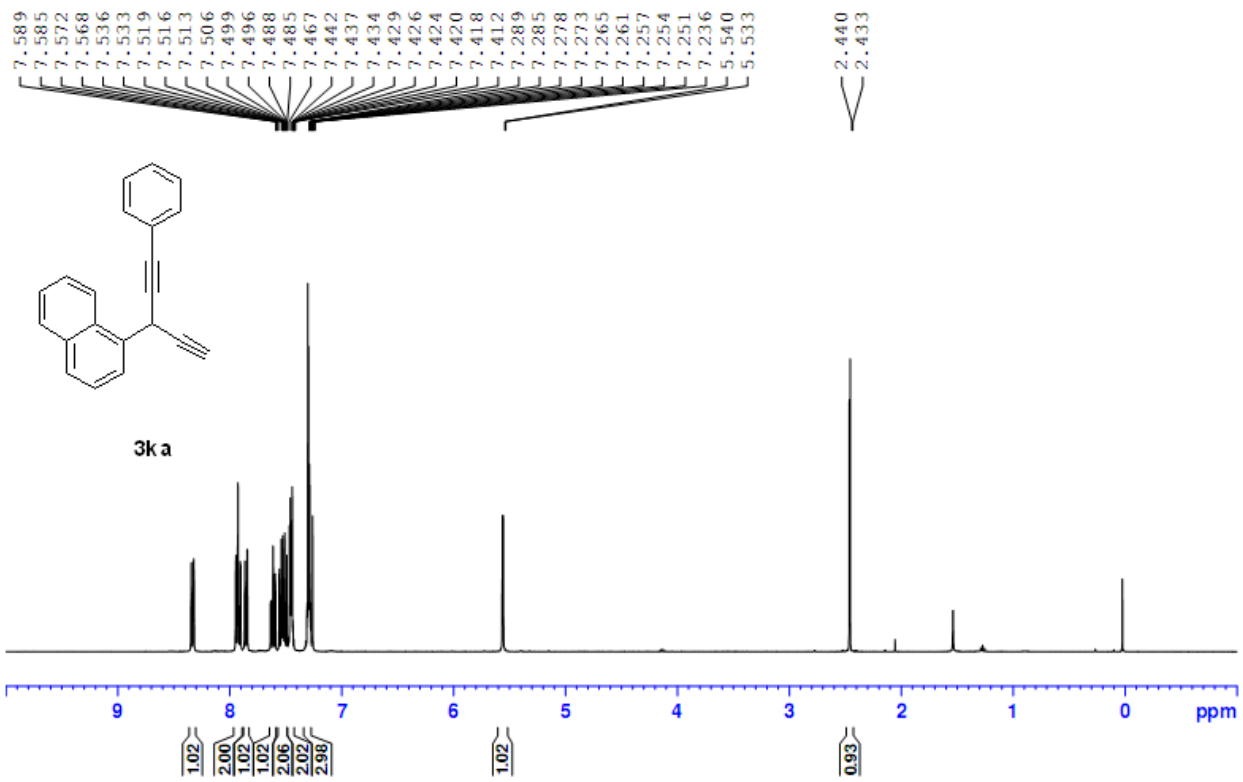
0
ppm



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7.485
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7.442
7.437
7.434
7.429
7.426
7.424
7.420
7.418
7.412
7.289
7.285
7.278
7.273
7.265
7.261
7.257
7.254
7.251
7.236
5.540
5.533
2.440
2.433
3k a
9
8
7
6
5
4
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2
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ppm
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2.06
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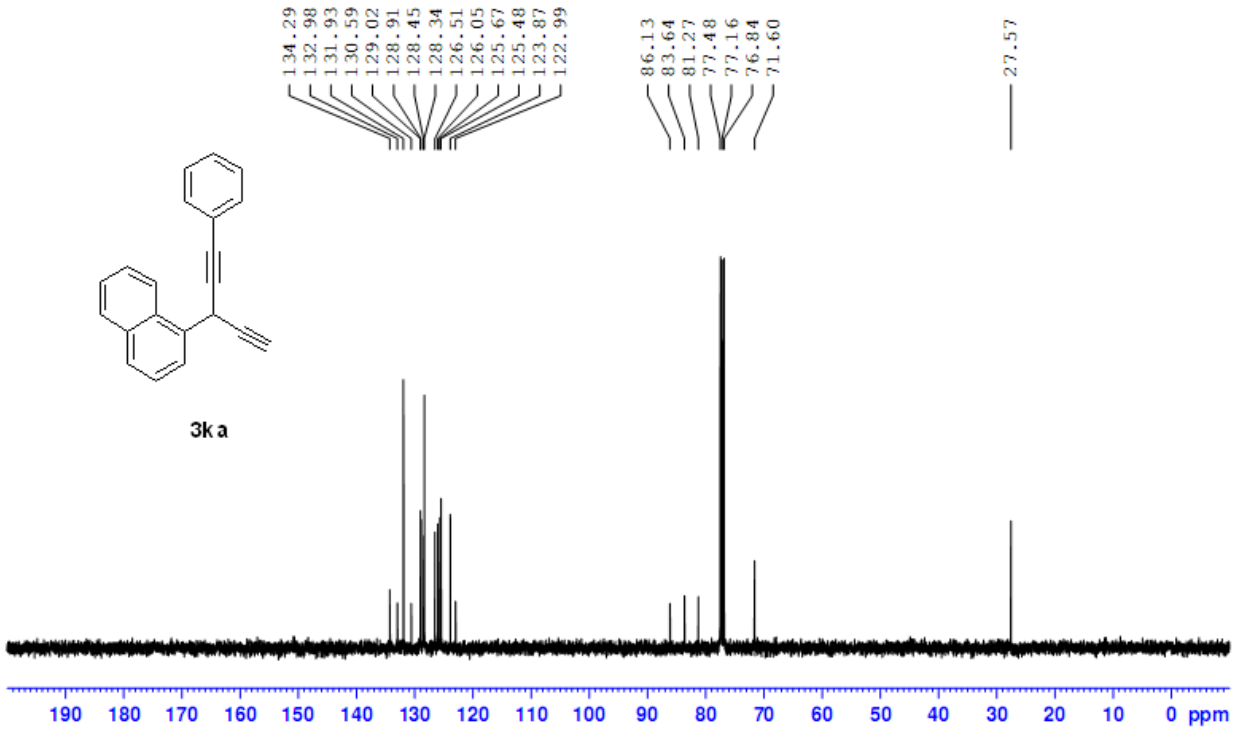
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128.34
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126.05
125.67
125.48
123.87
122.99
86.13
83.64
81.27
77.48
77.16
76.84
71.60
27.57
3k a
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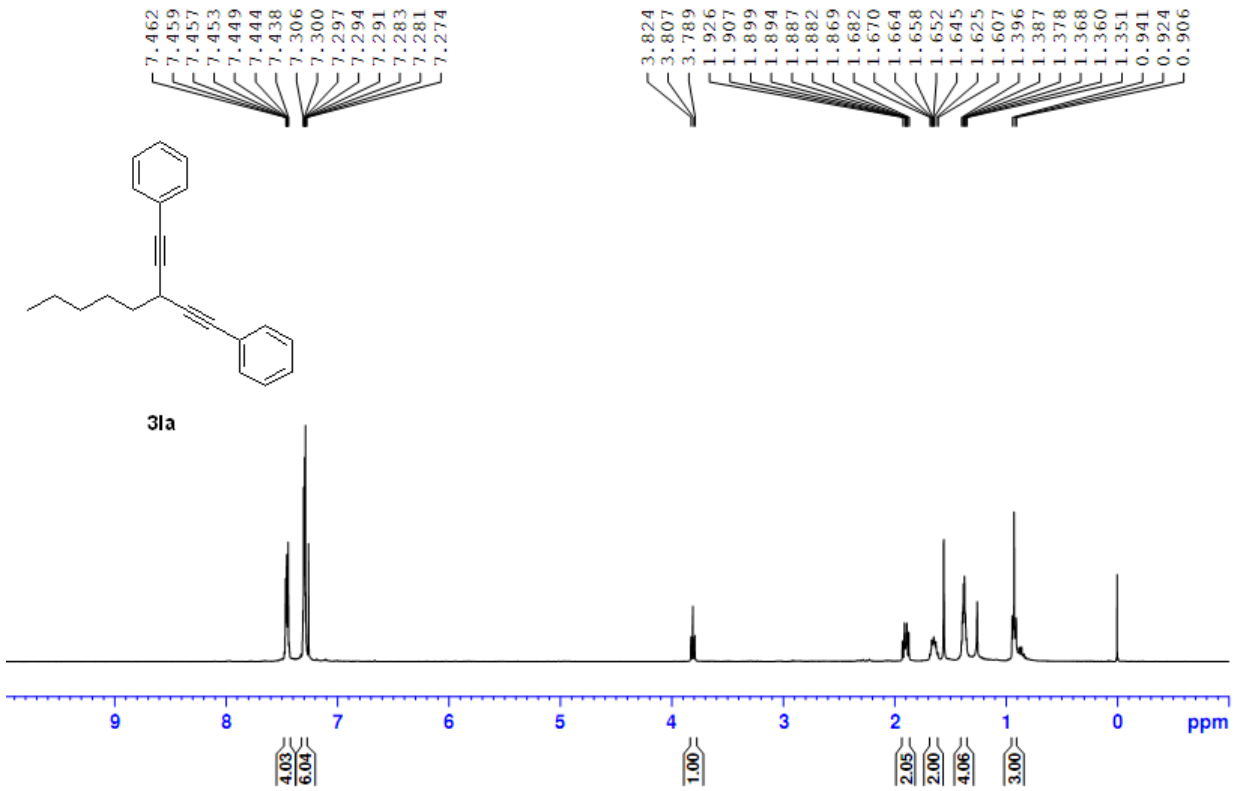
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0 ppm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7.300
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7.283
7.281
7.274
3.824
3.807
3.789
1.926
1.907
1.899
1.894
1.887
1.882
1.869
1.682
1.670
1.664
1.658
1.652
1.645
1.625
1.607
1.396
1.387
1.378
1.368
1.360
1.351
0.941
0.924
0.906
3la
9
8
7
6
5
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ppm
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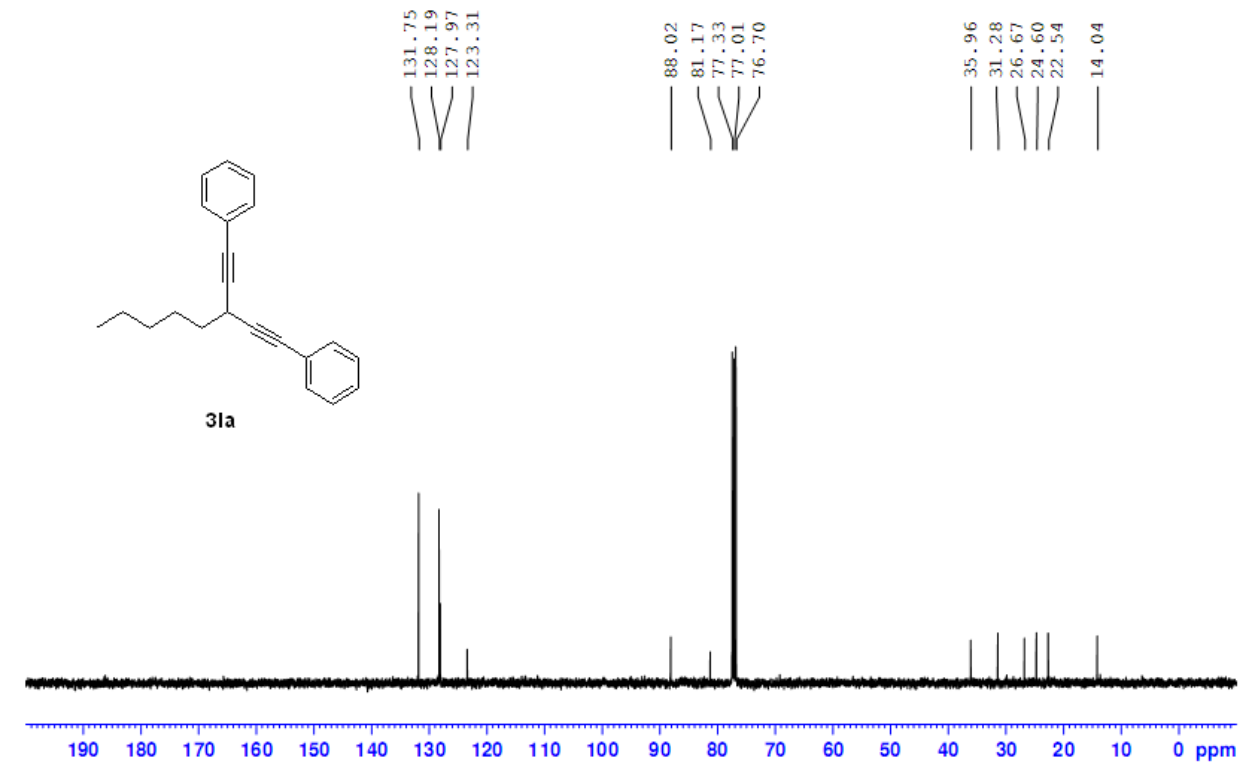
6.04
1.00
2.05
2.00
4.06
3.00

1

2

3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22.54
14.04
3la
190
180
170
160
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100
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30
20
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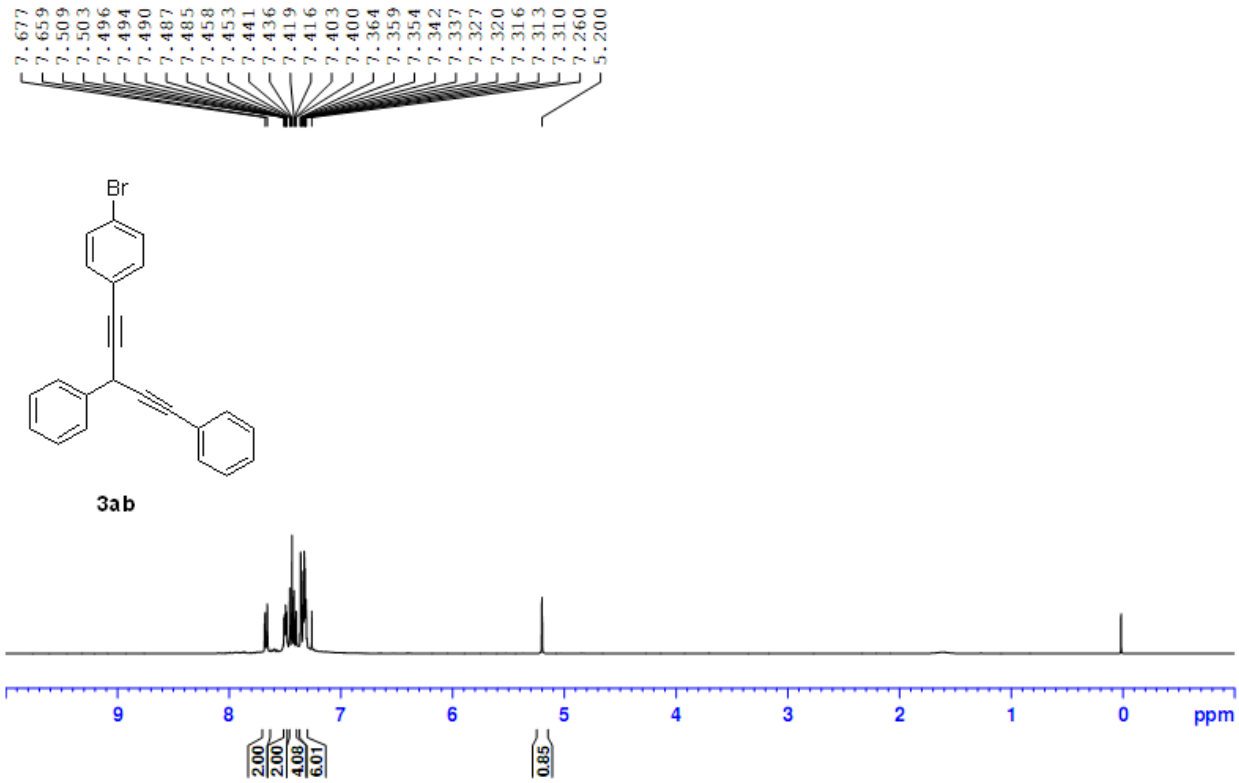
0 ppm

4

5

6

7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7.436
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7.416
7.403
7.400
7.364
7.359
7.354
7.342
7.337
7.327
7.320
7.316
7.313
7.310
7.260
5.200
Br
3ab
9
8
7
6
5
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ppm
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0.85

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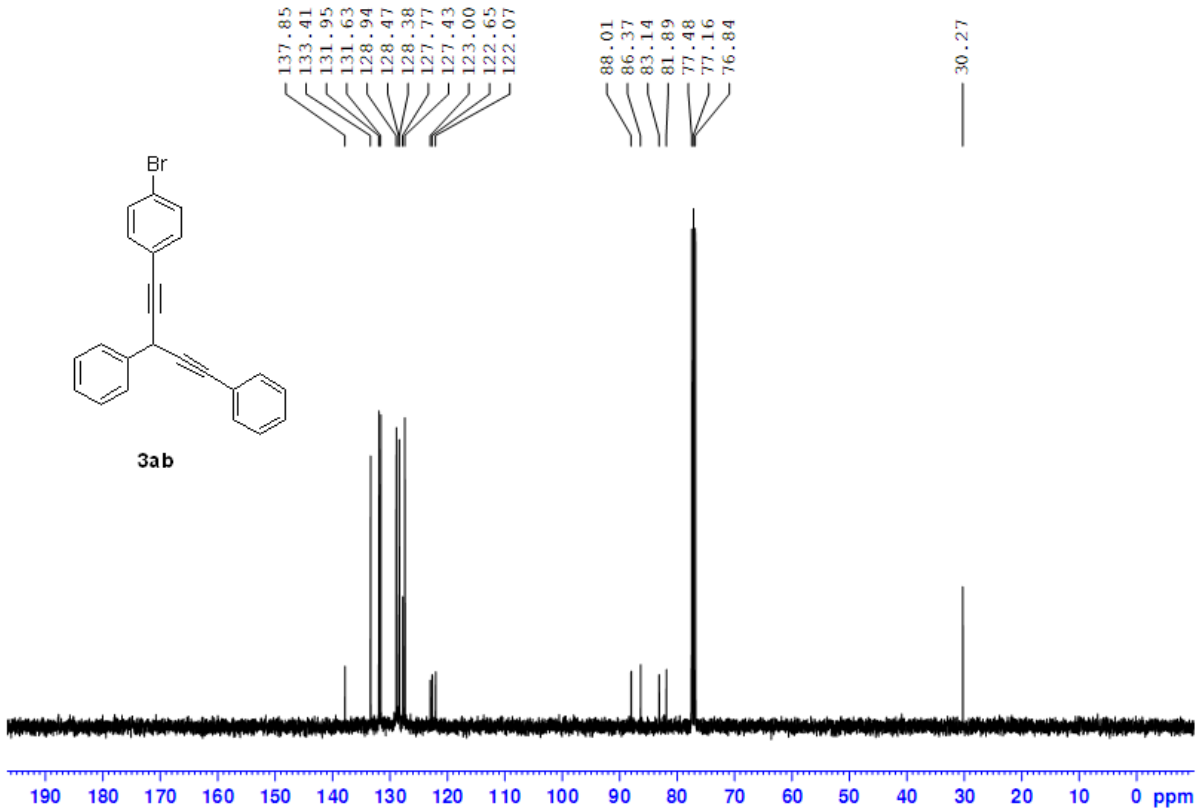
3
4
5
6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122.65
122.07
88.01
86.37
83.14
81.89
77.48
77.16
76.84
30.27
Br
3ab
190
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130
120
110
100
90
80
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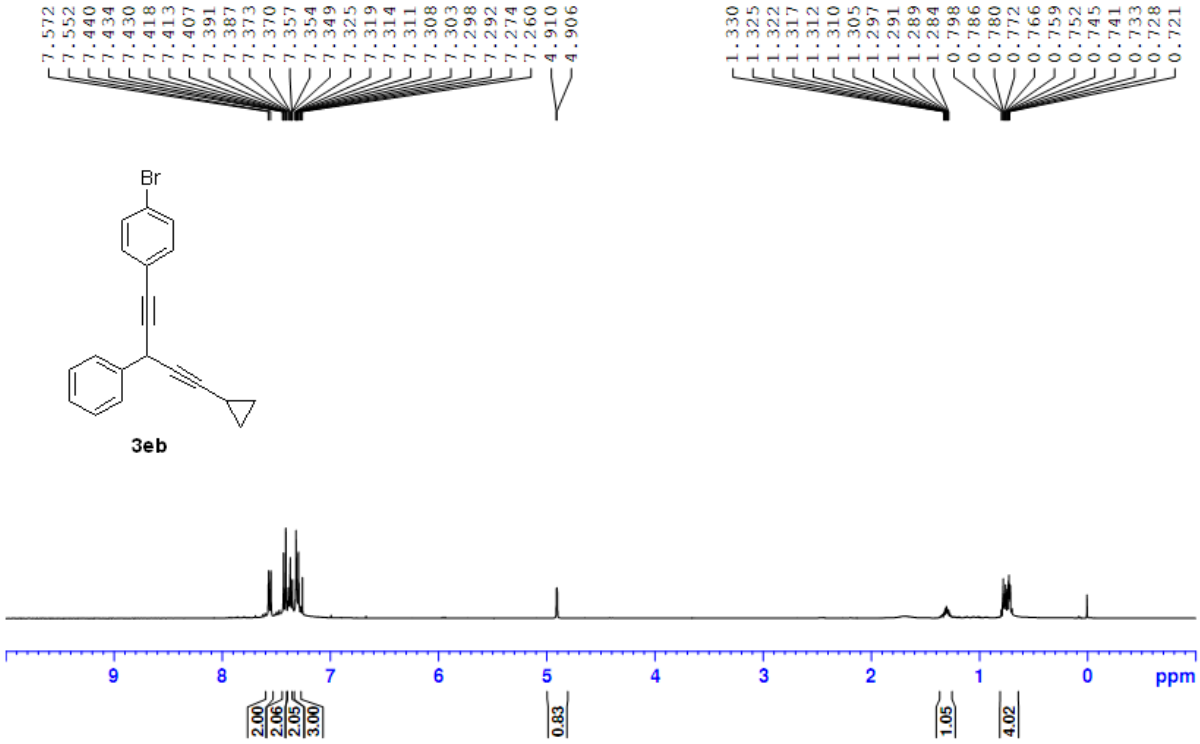
50
40
30
20
10
0
ppm

7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7.357
7.354
7.349
7.325
7.319
7.314
7.311
7.308
7.303
7.298
7.292
7.274
7.260
4.910
4.906
1.330
1.325
1.322
1.317
1.312
1.310
1.305
1.297
1.291
1.289
1.284
0.798
0.786
0.780
0.772
0.766
0.759
0.752
0.745
0.741
0.733
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0.721
Br
3eb
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8
7
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5
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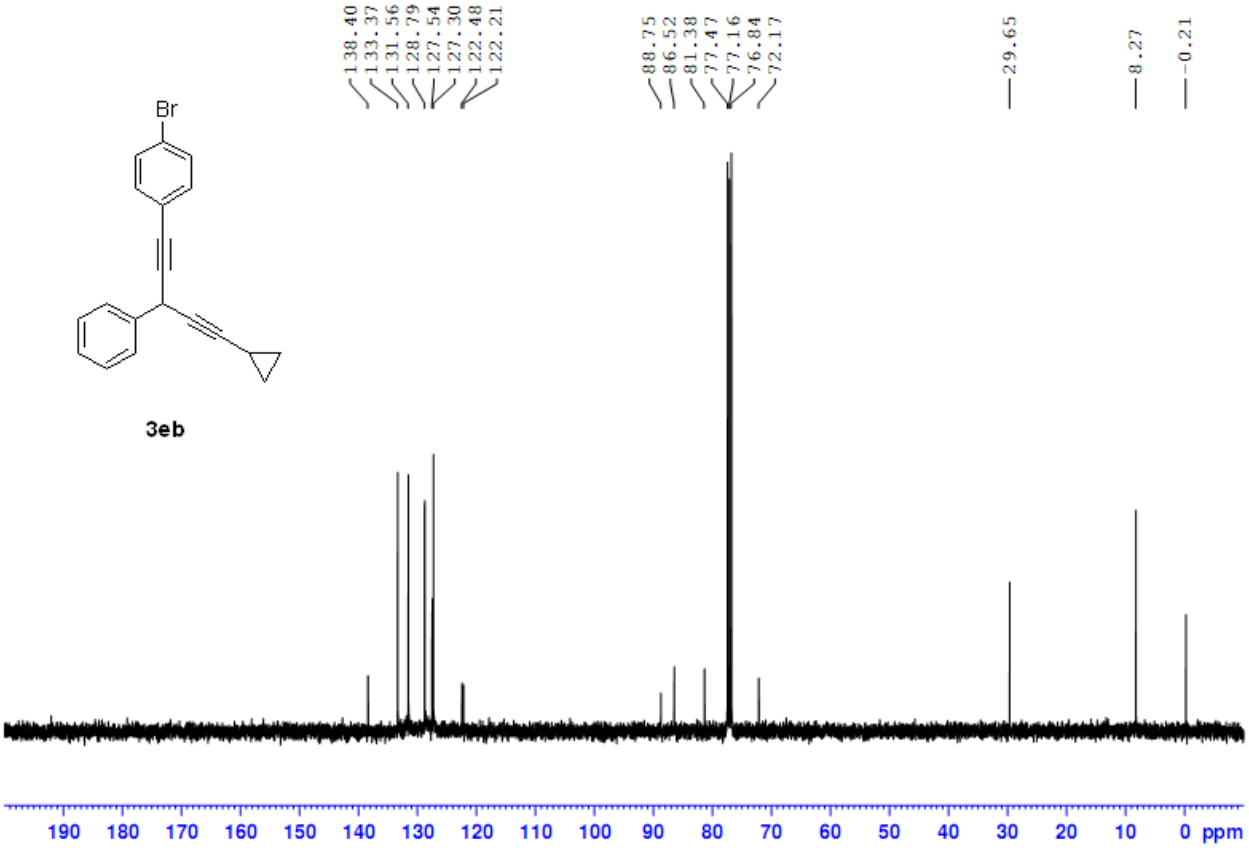
1

2

3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77.16
76.84
72.17
29.65
8.27
-0.21
Br
3eb
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120
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100
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50
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10
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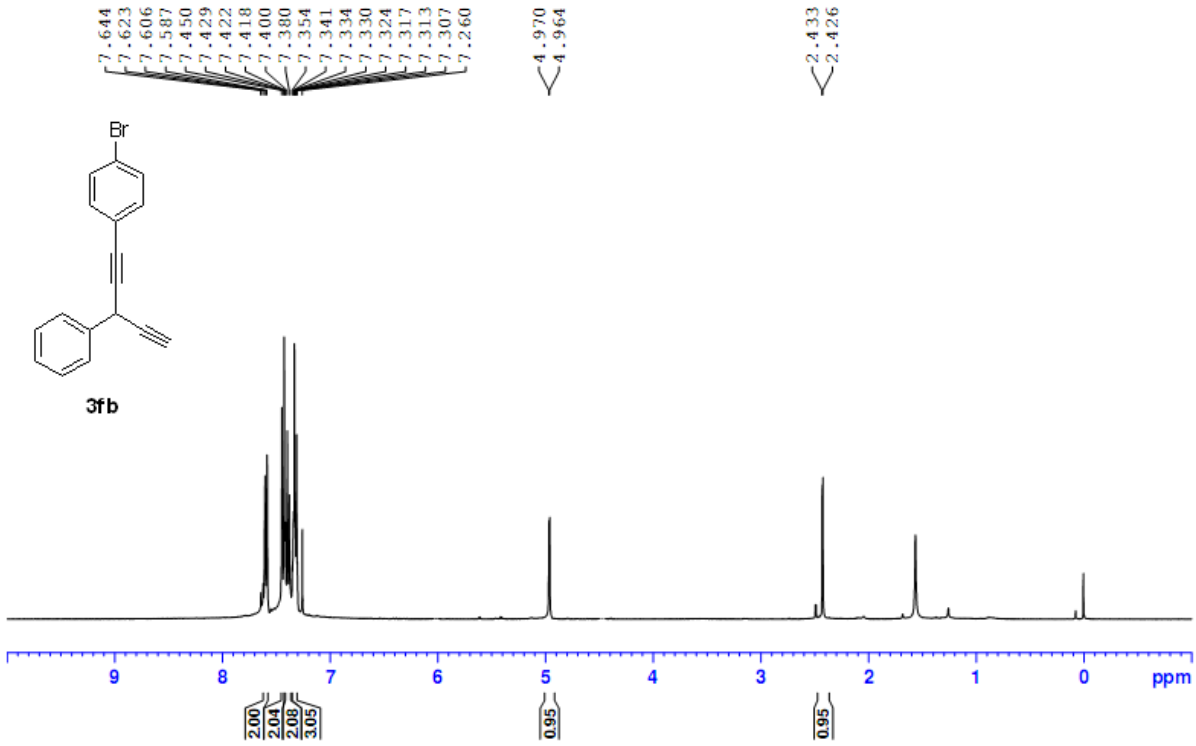
ppm

4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7.334
7.330
7.324
7.317
7.313
7.307
7.260
4.970
4.964
2.433
2.426
Br
3fb
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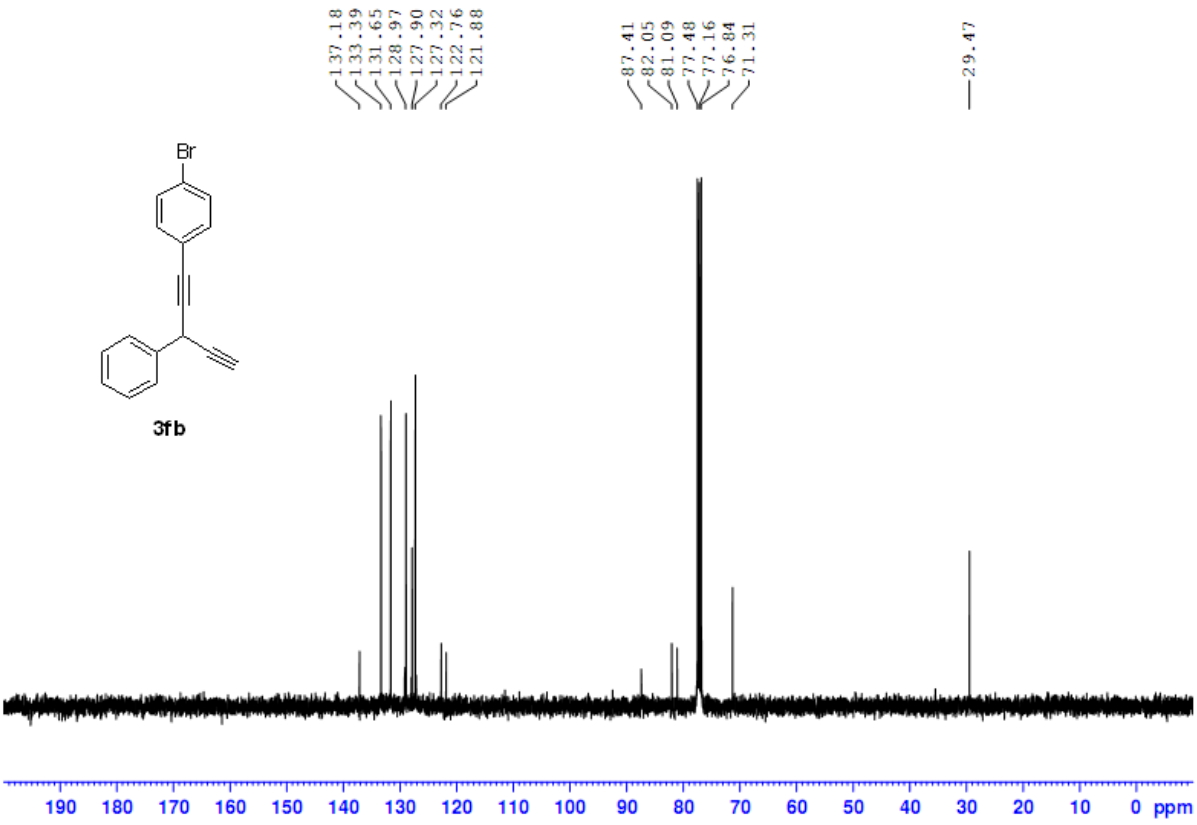
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77.48
77.16
76.84
71.31
29.47
Br
3fb
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100
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20
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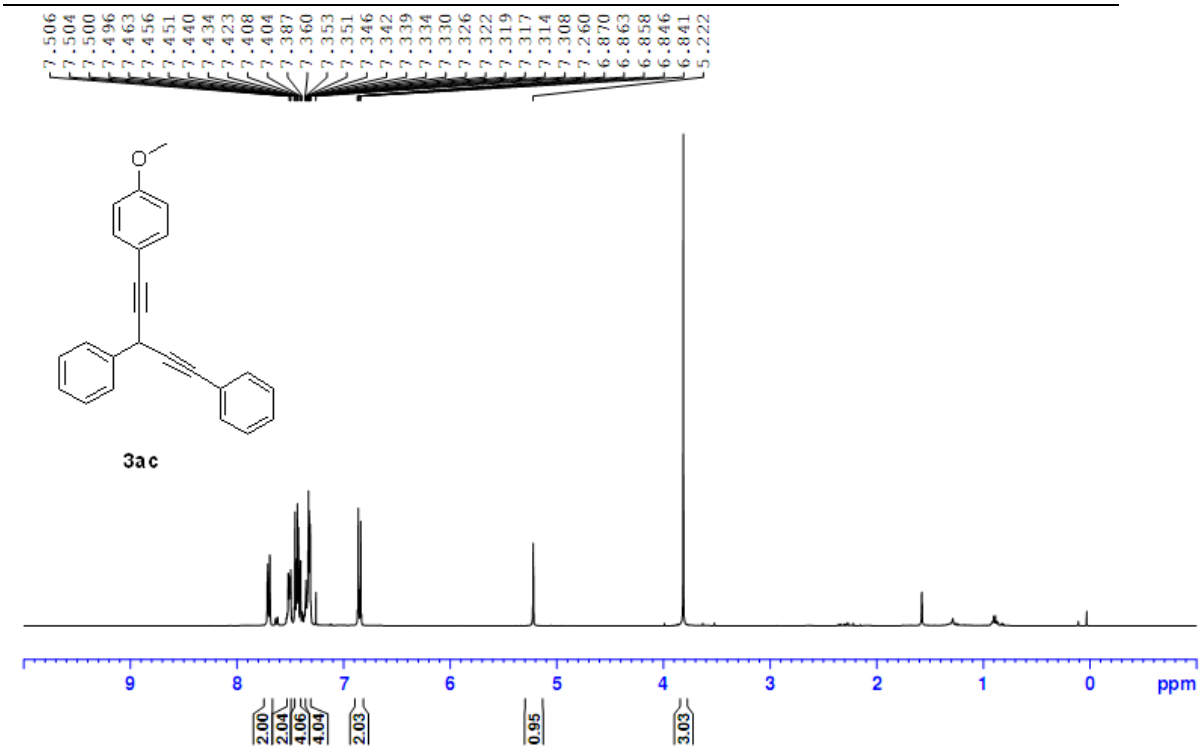
ppm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7.387
7.360
7.353
7.351
7.346
7.342
7.339
7.334
7.330
7.326
7.322
7.319
7.317
7.314
7.308
7.260
6.870
6.863
6.858
6.846
6.841
5.222
3ac
9
8
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5
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ppm
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2.04
4.06
4.04
2.03
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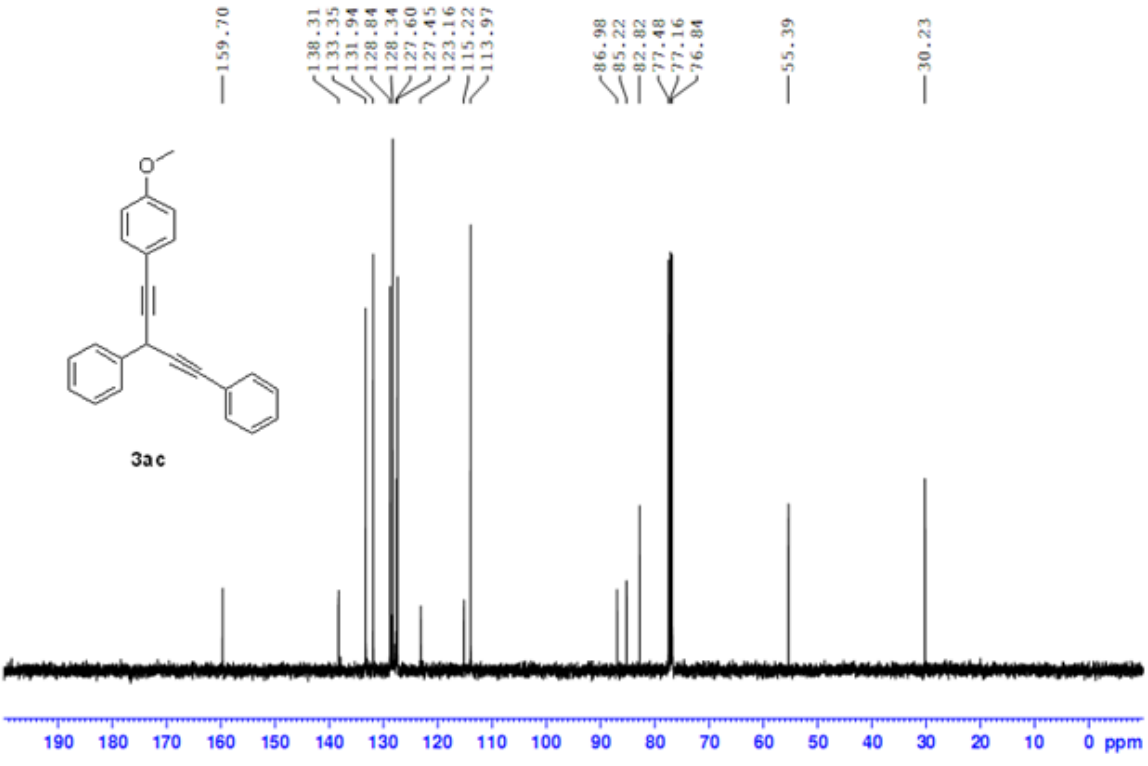
3.03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115.22
113.97
86.98
85.22
82.82
77.48
77.16
76.84
55.39
30.23
3ac
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60
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30
20
10
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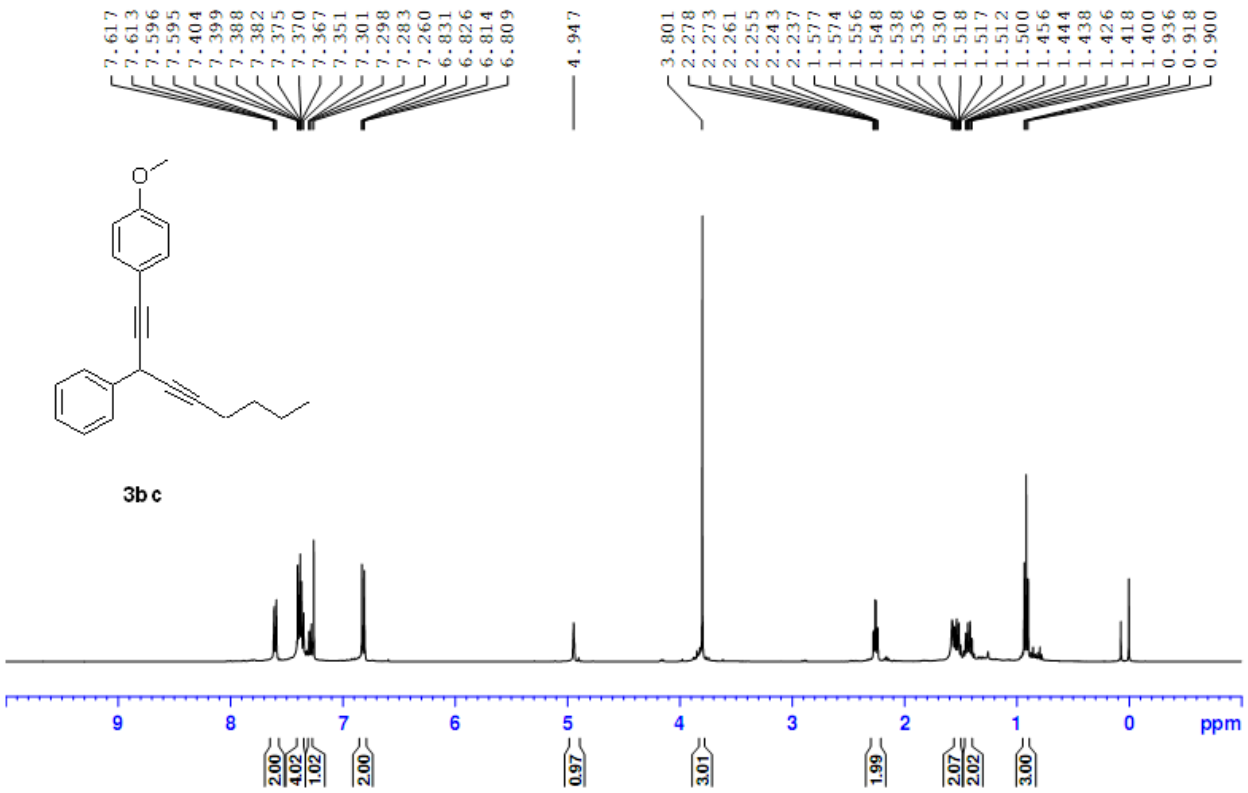
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7.298
7.283
7.260
6.831
6.826
6.814
6.809
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8
7
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5
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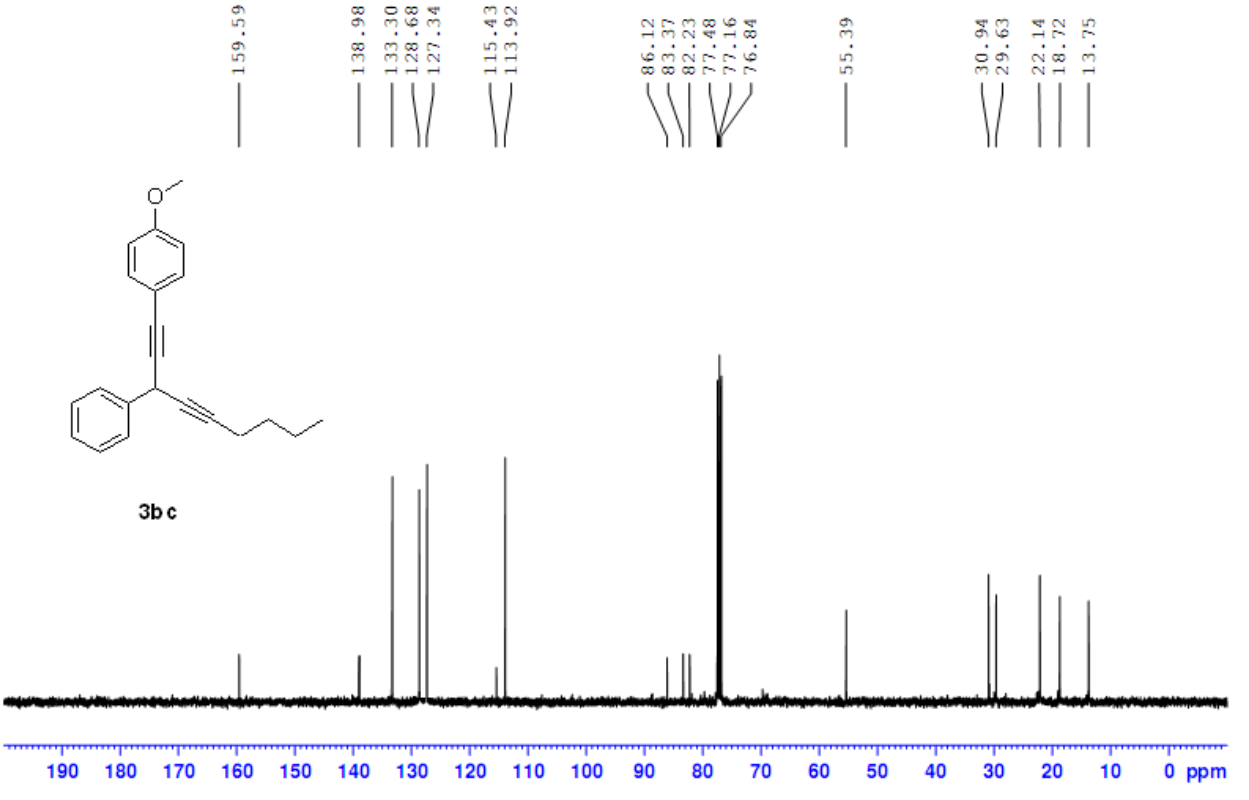
2

3

4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18.72
13.75
3bc
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180
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130
120
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30
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ppm

5