Supporting Information for

Selective C-C coupling of terminal alkynes under air condition without base over Cu-Nx-C catalyst

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[†]The authors contribute equally to the work

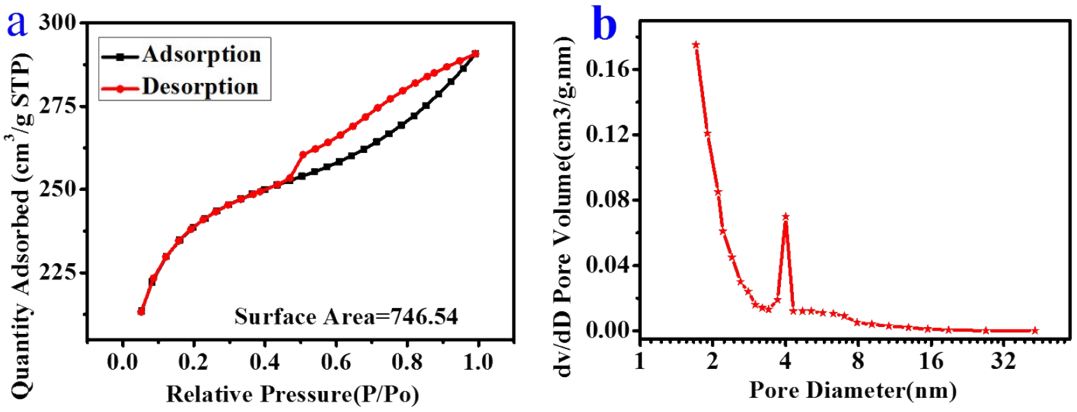


Fig S1. a) Nitrogen adsorption-desorption isotherms and b) the corresponding BJH pore-size distribution curve of Cu–Nx–C.

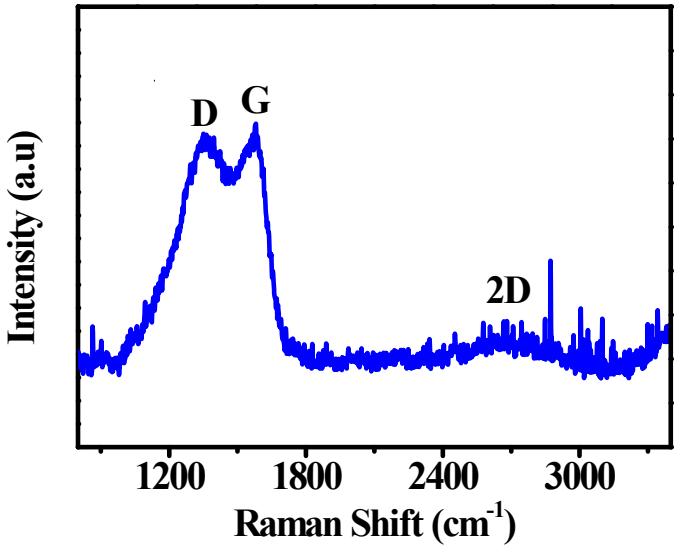


Fig. S2 Raman spectra of Cu–Nx–C.

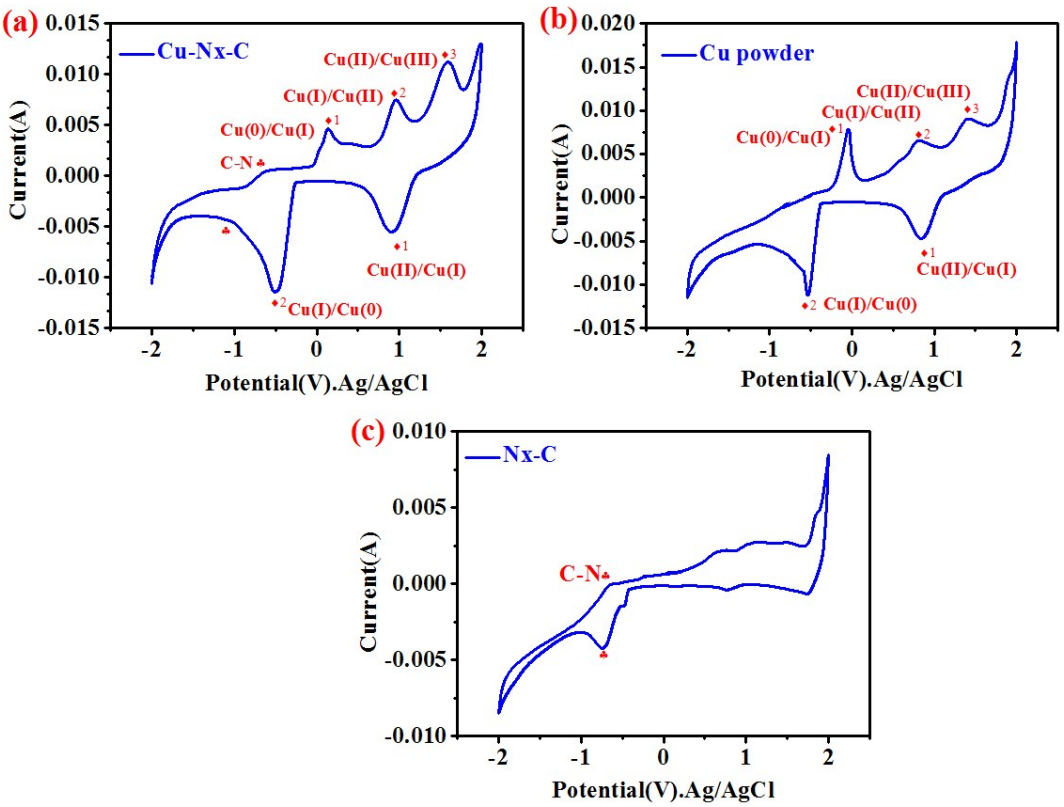


Fig. S3 Cyclic voltammetry of the Cu-Nx-C(a), Cu powder(b), and silk fibroin-driven porous carbon (Nx–C) without copper(c).

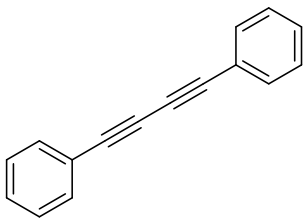
The Cu powder and the Cu-Nx-C displays the reversible formation of the Cu (0)-Cu(I)-Cu(II)-Cu(III)-Cu(0) species. The reversible oxidation of Cu(0)/Cu(I) to Cu(II) and Cu(III) could be observed both from Cu-Nx-C and Cu powder.[1] An additional peak was found in the CV of Cu-Nx-C, attributing to the Nx–C active site, which also appeared in the CV of Nx–C materials.[2] The presence of Nx–C also led to the positive shift of the reversible oxidation potential of Cu–Nx–C, due to the increasement of electron density near the copper sites.

Reference

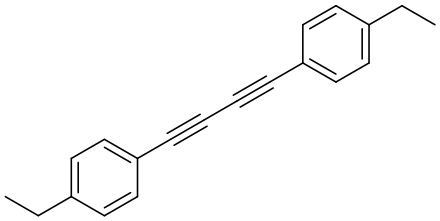
1 H. H. Hassan, I. H. A. Badr, H. T. M. Abdel-Fatah, E. M. S. Elfeky and A. M. Abdel-Aziz, *Arabian Journal of Chemistry*, 2018, 11, 171.

2 S. Haldar, D. Chakraborty, B. Roy, G. Banappanavar, K. Rinku, D. Mullangi, P. Hazra, D. Kabra and R. Vaidhyanathan, *Journal of the American Chemical Society*, 2018, 140, 13367.

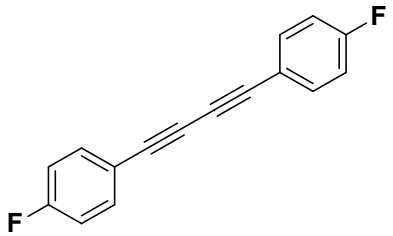
Data of final product



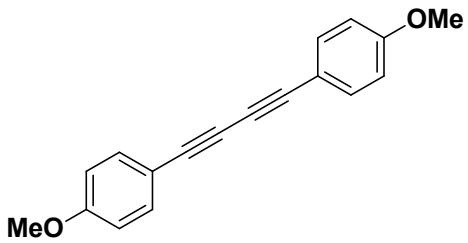
1,4-diphenylbuta-1,3-diyne (2a): Yield: 98%; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.62 – 7.53 (m, 4H), 7.51 – 7.32 (m, 6H). **^{3}C NMR** (100 MHz, $CDCl_3$) δ 132.52, 129.22, 128.46, 121.83, 81.58, 73.95.



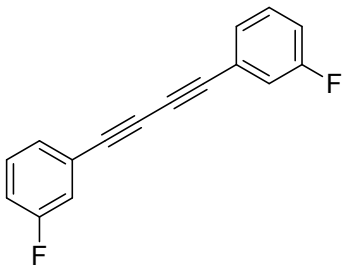
1,4-bis(4-ethylphenyl)buta-1,3-diyne (2b): Yield: 94%; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.52 – 7.44 (m, 4H), 7.24 – 7.15 (m, 4H), 2.69 (q, *J* = 7.6 Hz, 4H), 1.26 (t, *J* = 7.6 Hz, 6H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 145.76, 132.51, 128.03, 119.05, 81.58, 73.47, 28.93, 15.24.



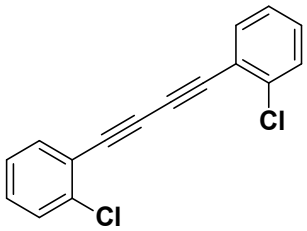
1,4-bis(4-fluorophenyl)buta-1,3-diyne (2c): Yield: 71%; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.58 – 7.45 (m, 4H), 7.11 – 7.01 (m, 4H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 164.32, 161.82, 134.50, 134.58, 117.82, 116.02, 115.80, 80.43, 73.55, 29.71.



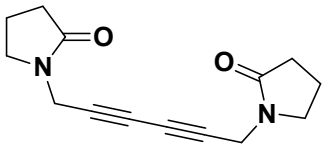
1,4-bis(4-methoxyphenyl)buta-1,3-diyne (2d): Yield: 91%; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.56 – 7.42 (m, 4H), 6.95 – 6.82 (m, 4H), 3.85 (s, 6H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 160.25, 134.04, 113.97, 114.14, 81.23, 72.95, 55.34.



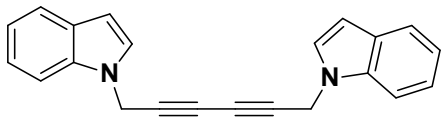
1,4-bis(3-fluorophenyl)buta-1,3-diyne (2e): Yield: 92%; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.55 – 7.28 (m, 4H), 7.24 (dd, *J* = 8.5, 1.9 Hz, 2H), 7.22 – 6.99 (m, 2H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 162.28 (d, *J* = 247.5 Hz), 130.15 (d, *J* = 8.6 Hz), 128.48 (d, *J* = 3.1 Hz), 123.40 (d, *J* = 9.5 Hz), 119.35, 119.12, 117.02, 116.81, 80.64 (d, *J* = 3.6 Hz), 74.43.



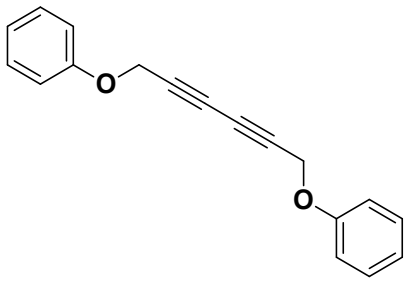
1,4-bis(2-chlorophenyl)buta-1,3-diyne (2f): Yield: 86%; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.60 (dd, *J* = 7.6, 1.6 Hz, 2H), 7.45 (dd, *J* = 8.0, 1.0 Hz, 2H), 7.30 (dtd, *J* = 8.8, 7.5, 1.5 Hz, 4H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 137.00, 134.38, 130.27, 129.46, 126.55, 121.85, 79.42, 78.40.



1,1'-(hexa-2,4-diyne-1,6-diyl)bis(pyrrolidin-2-one) (2g): Yield: 63%; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 4.18 (s, 2H), 3.48 (t, *J* = 7.1 Hz, 2H), 2.40 (t, *J* = 8.1 Hz, 2H), 2.16 – 1.98 (m, 2H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 174.54, 72.70, 68.05, 46.44, 32.54, 30.47, 17.59.

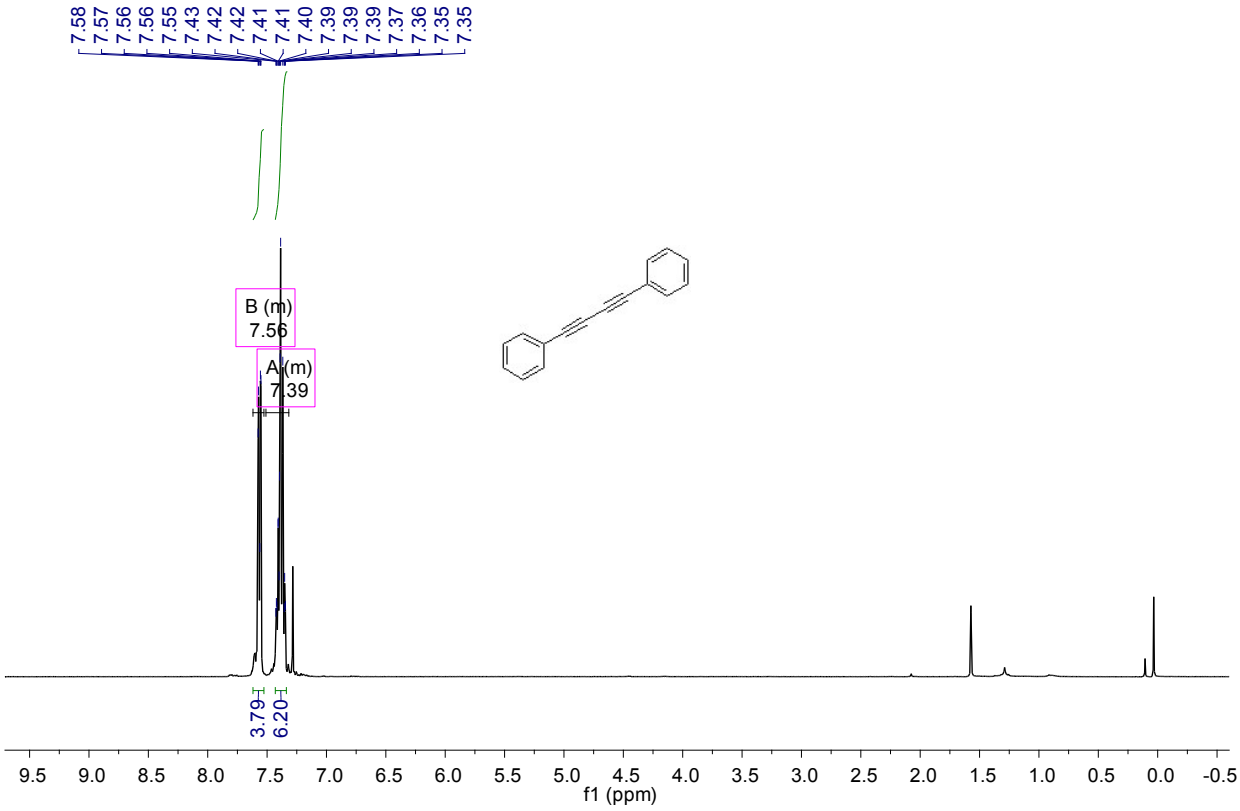


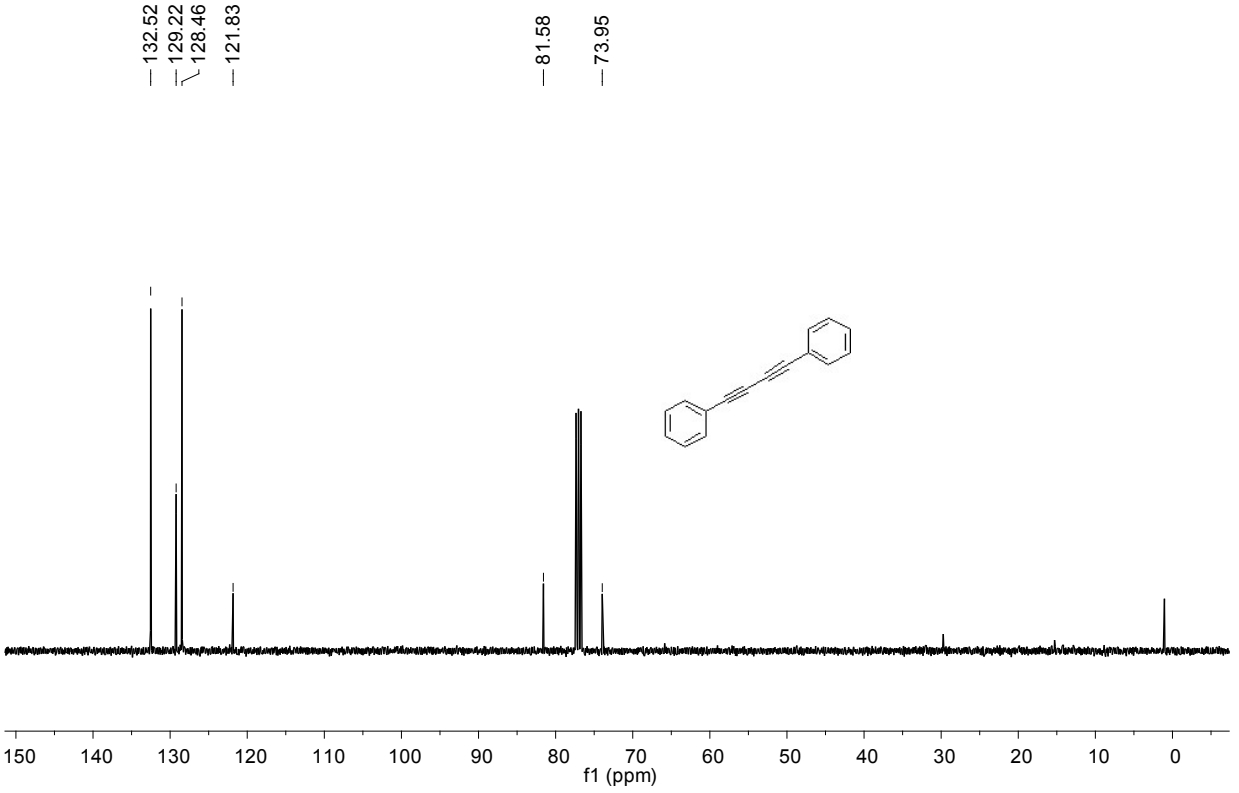
1,6-di(1H-indol-1-yl)hexa-2,4-diyne (2h): Yield: 88%; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.66 (d, *J* = 7.9 Hz, 2H), 7.38 (dd, *J* = 8.2, 0.7 Hz, 2H), 7.30 – 7.25 (m, 2H), 7.20 – 7.12 (m, 4H), 6.56 (dd, *J* = 3.2, 0.7 Hz, 2H), 4.94 (s, 4H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 135.78, 128.88, 127.22, 122.10, 121.17, 120.03, 119.78, 109.22, 102.50, 73.30, 69.09, 36.34.

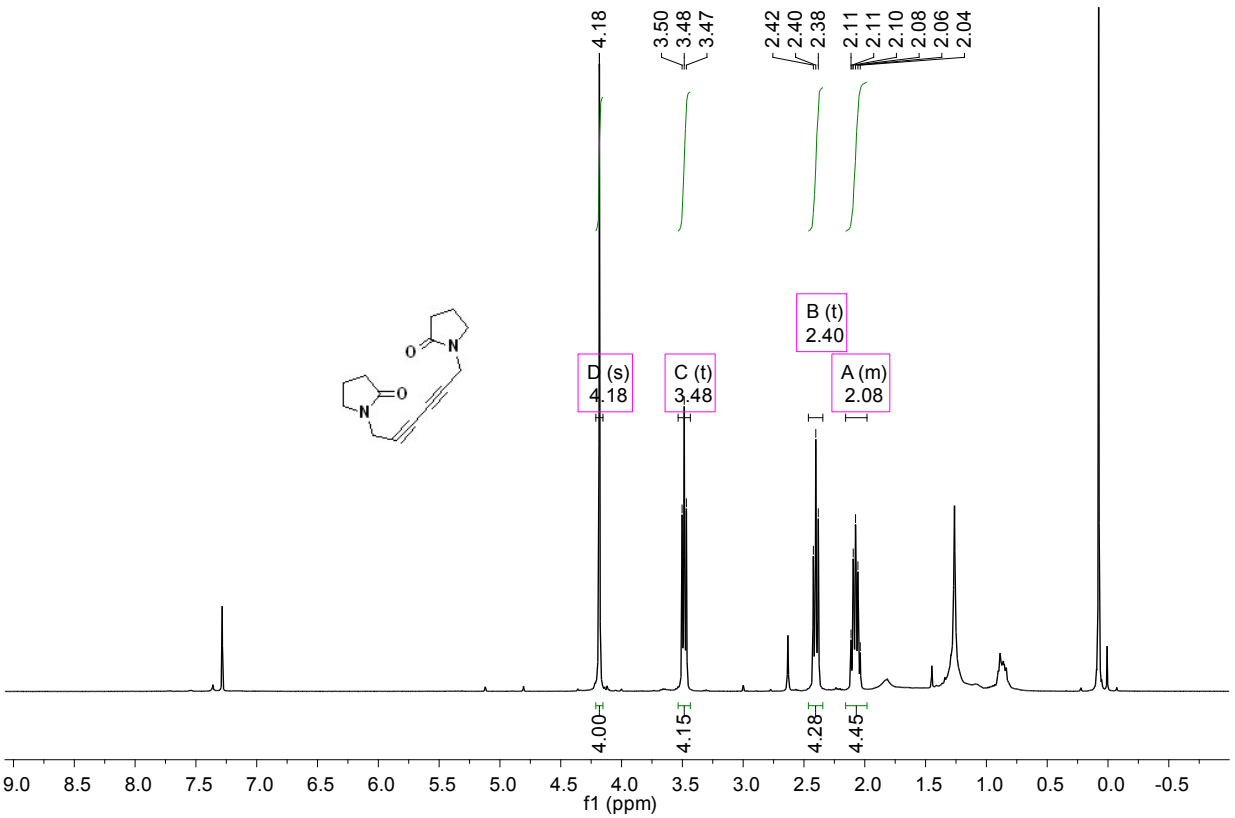


1,6-diphenoxyhexa-2,4-diyne (2i): Yield: 72%; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.44 – 7.27 (m, 4H), 7.08 – 6.92 (m, 6H), 4.78 (s, 4H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 157.43, 129.57, 121.79, 114.90, 74.71, 71.04, 56.19.

Spectra Data



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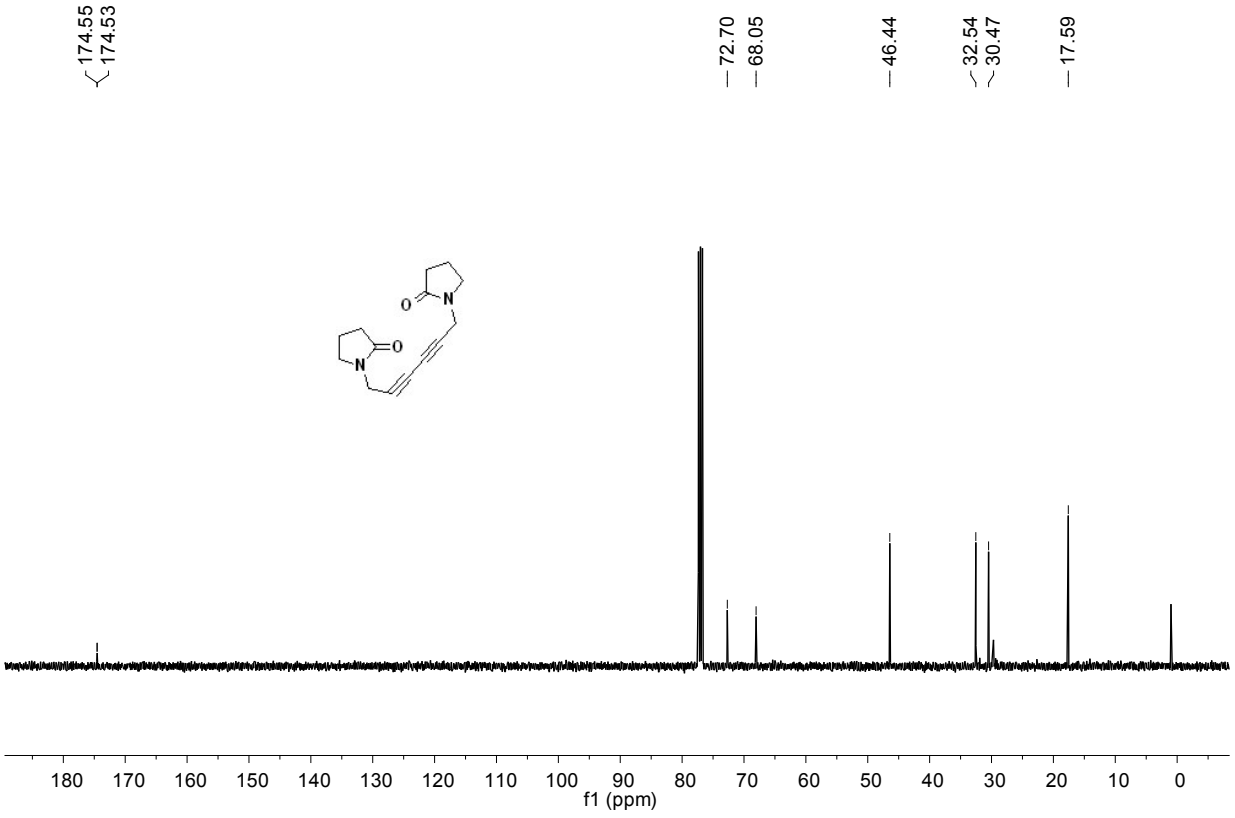
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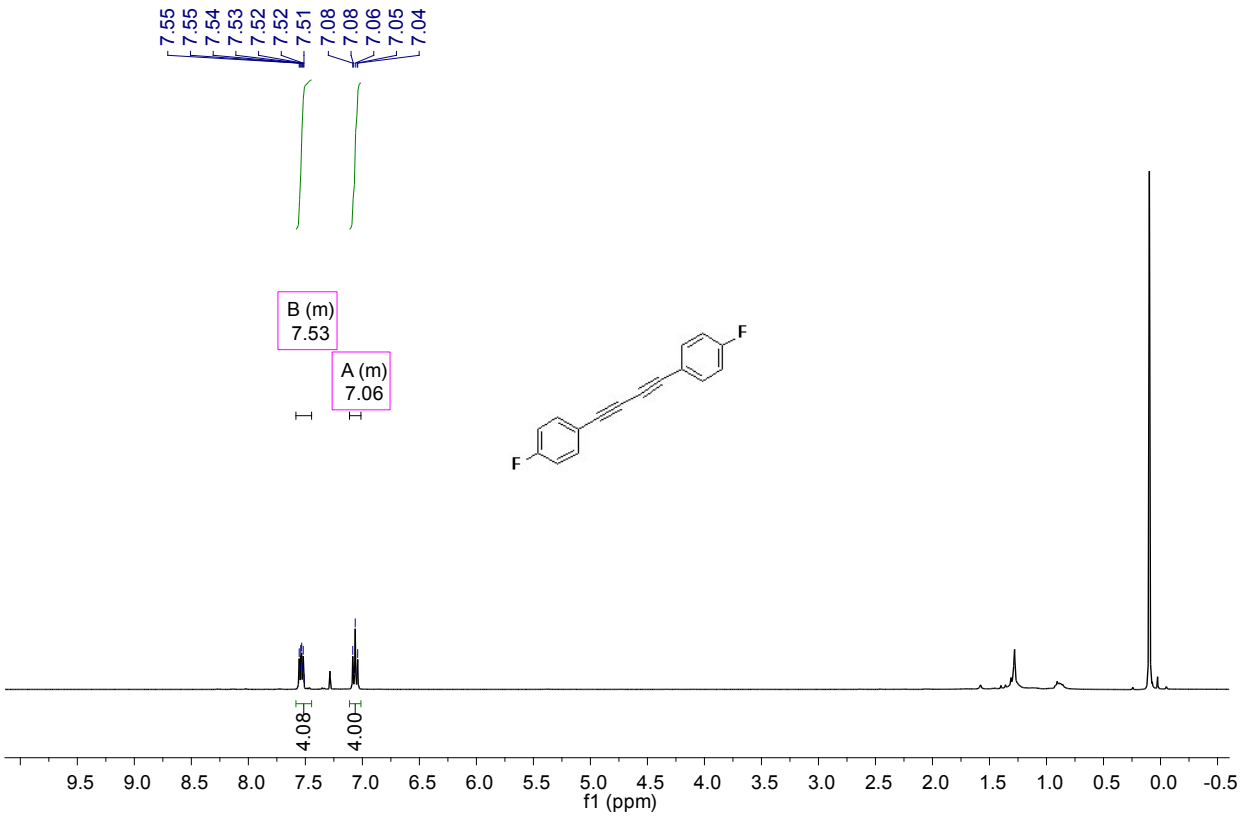
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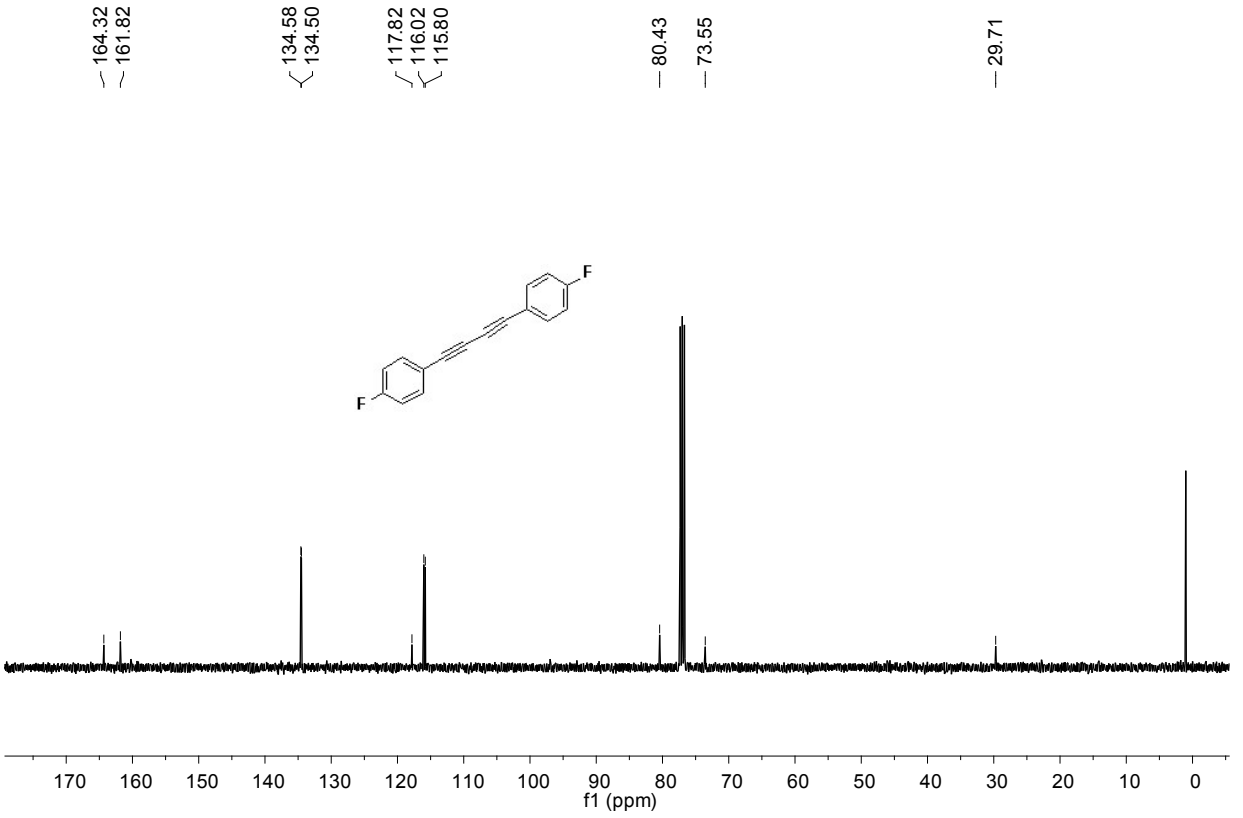
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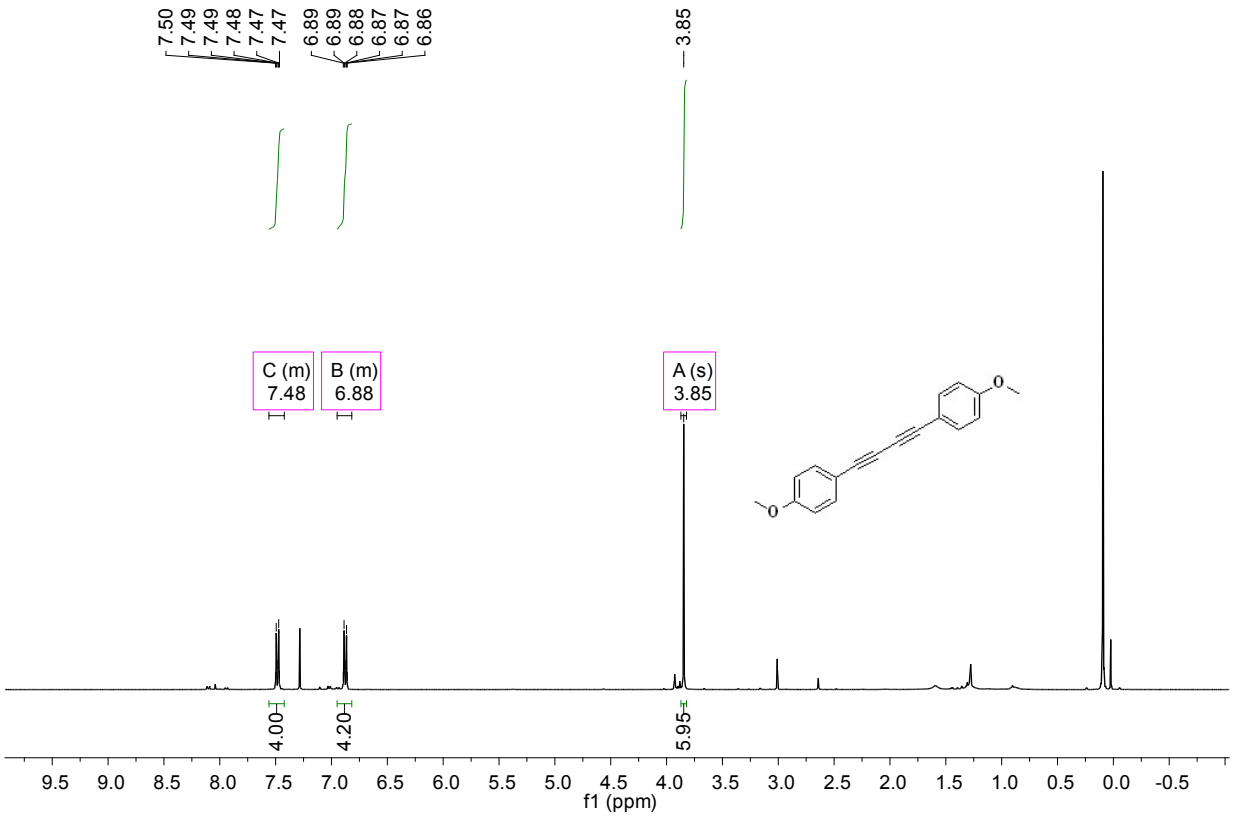
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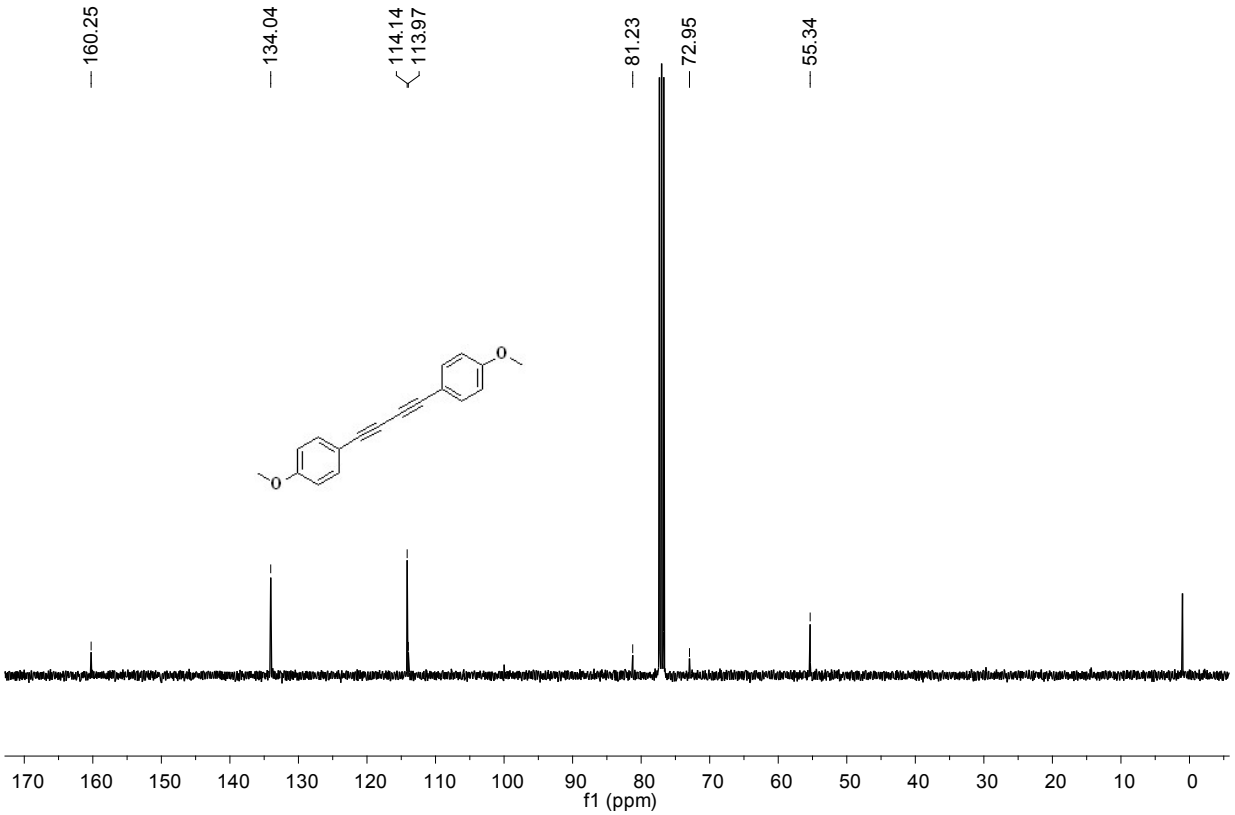
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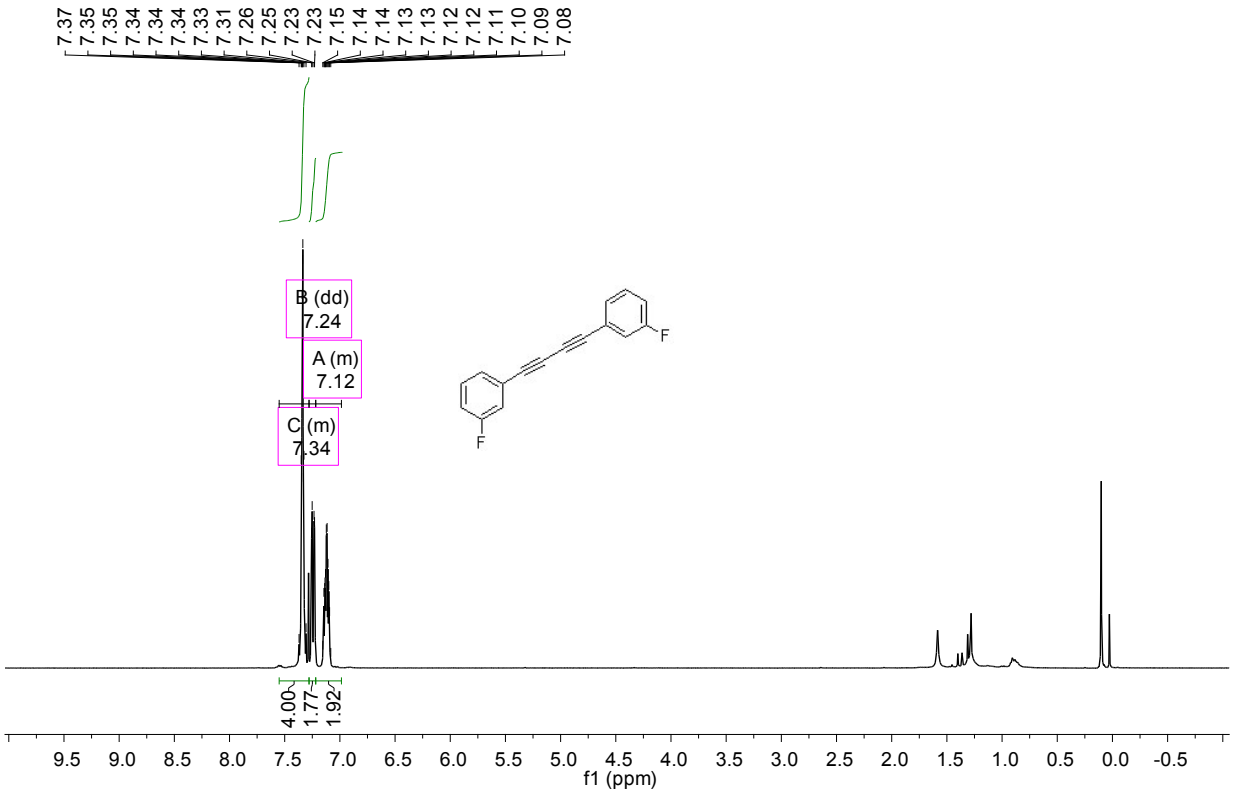
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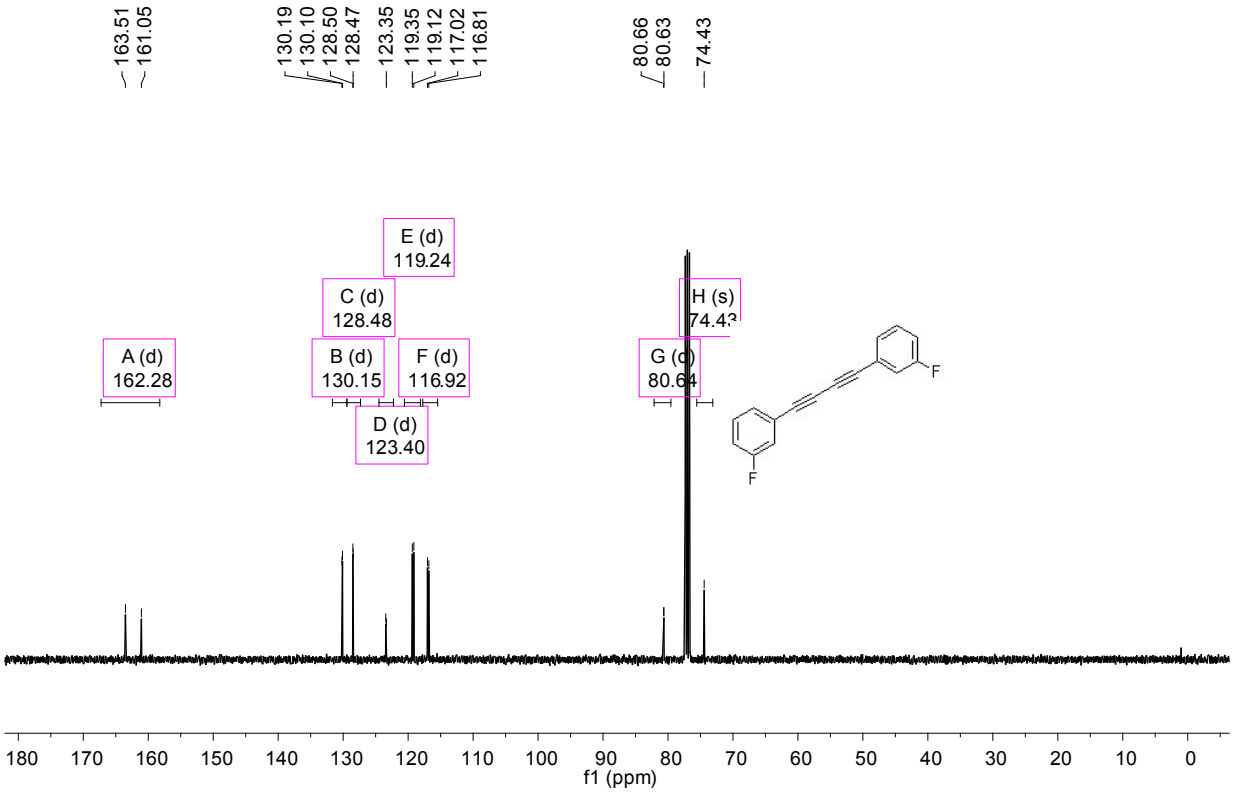
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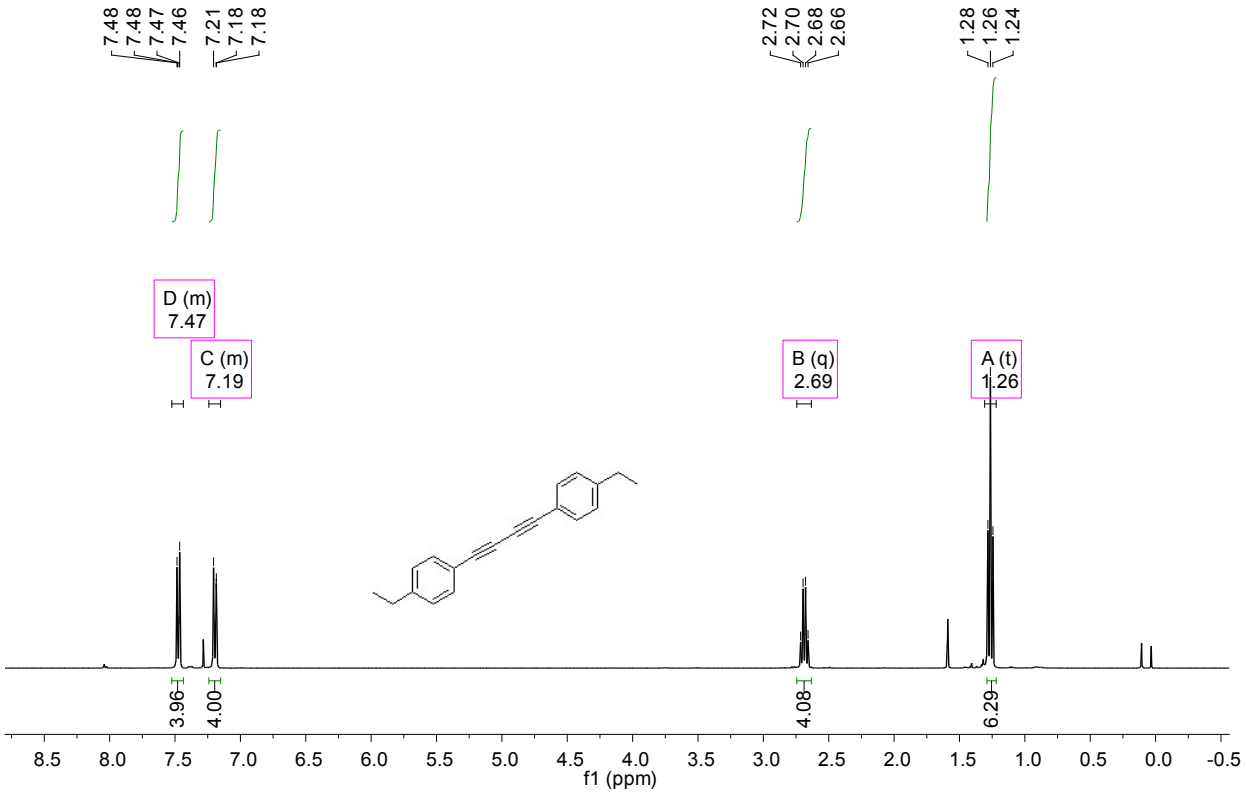
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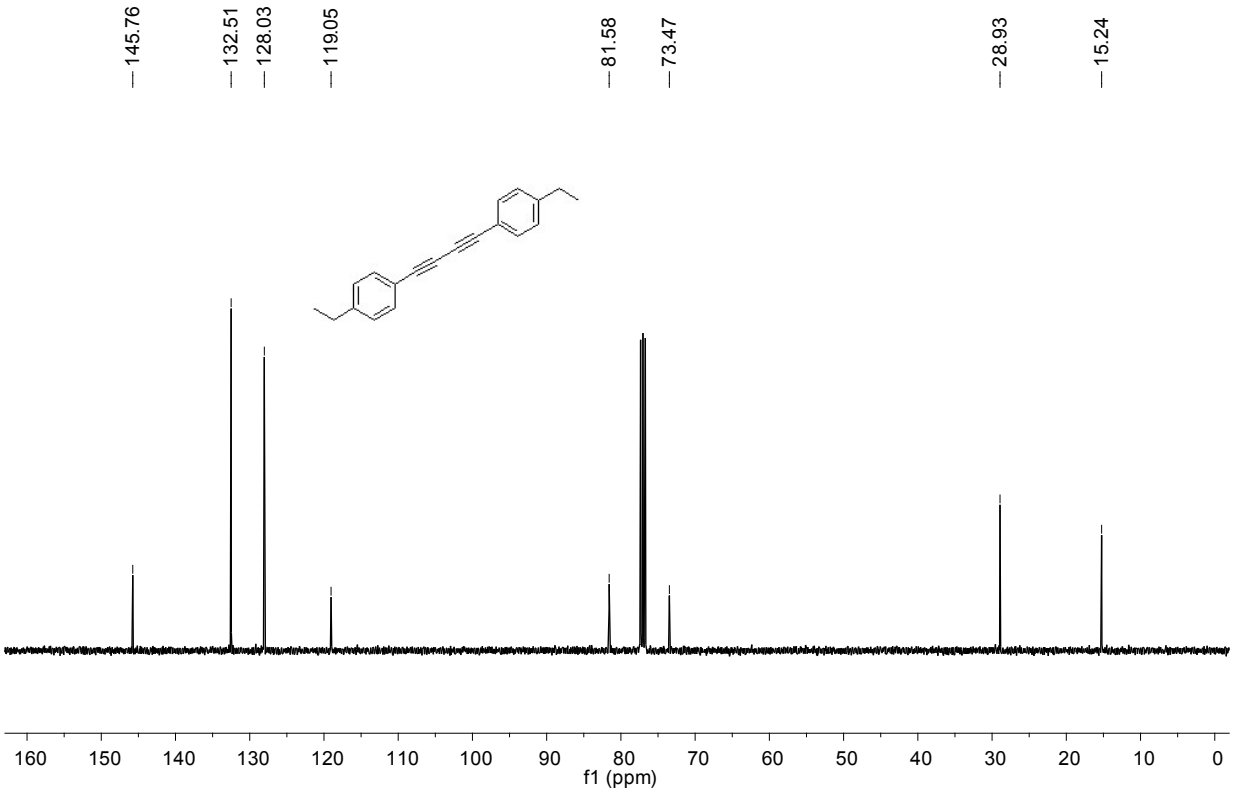
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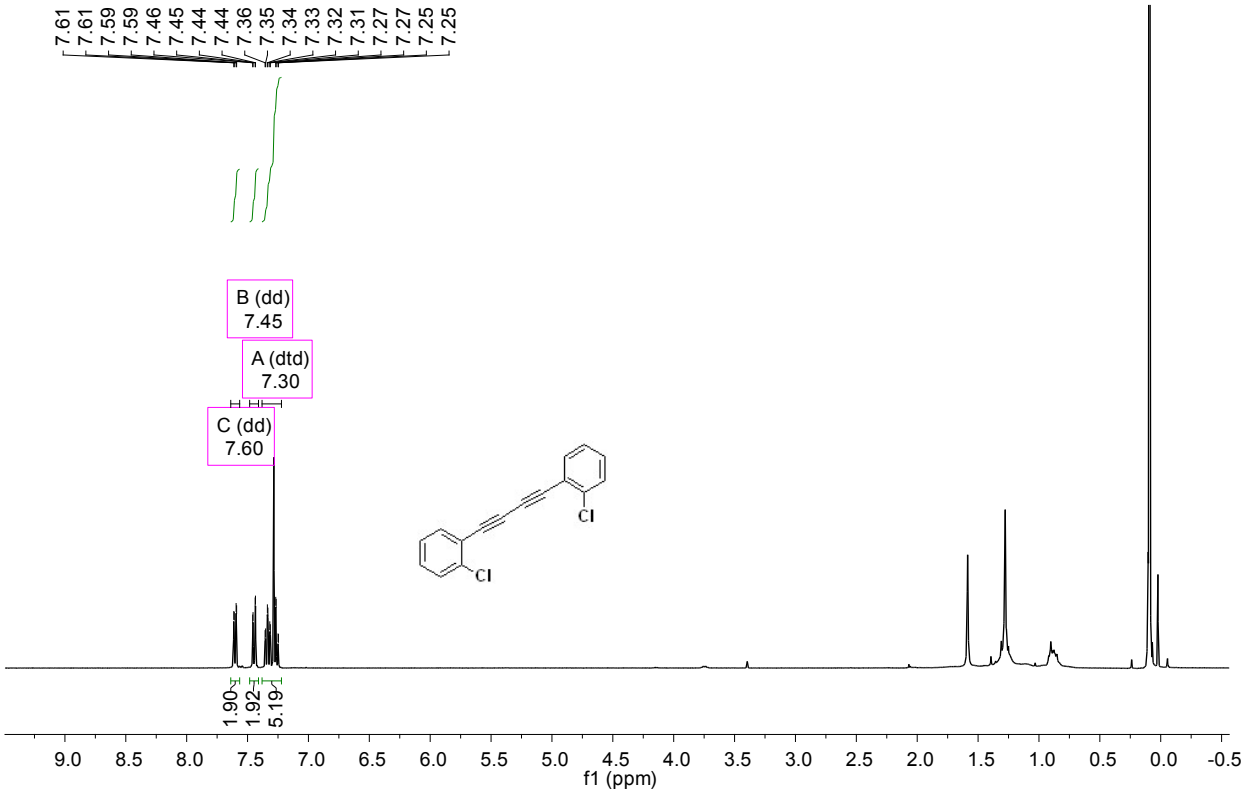
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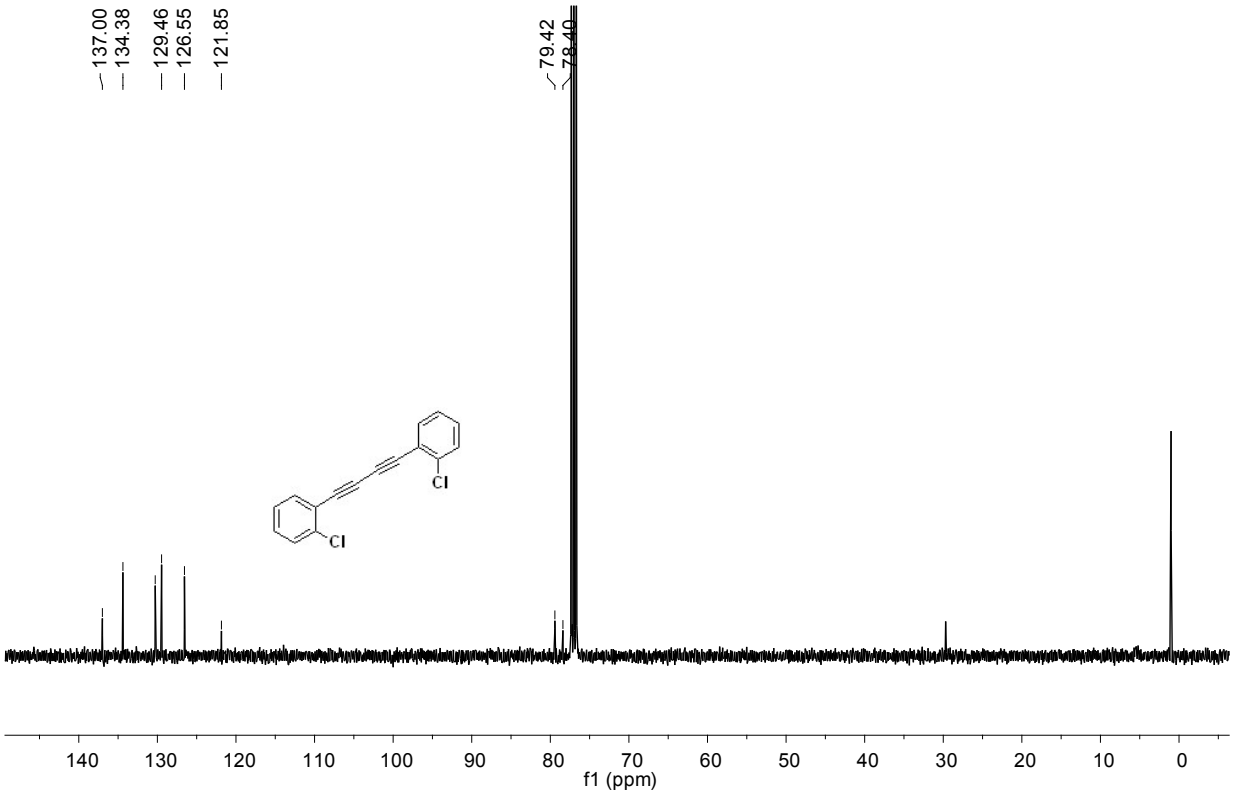
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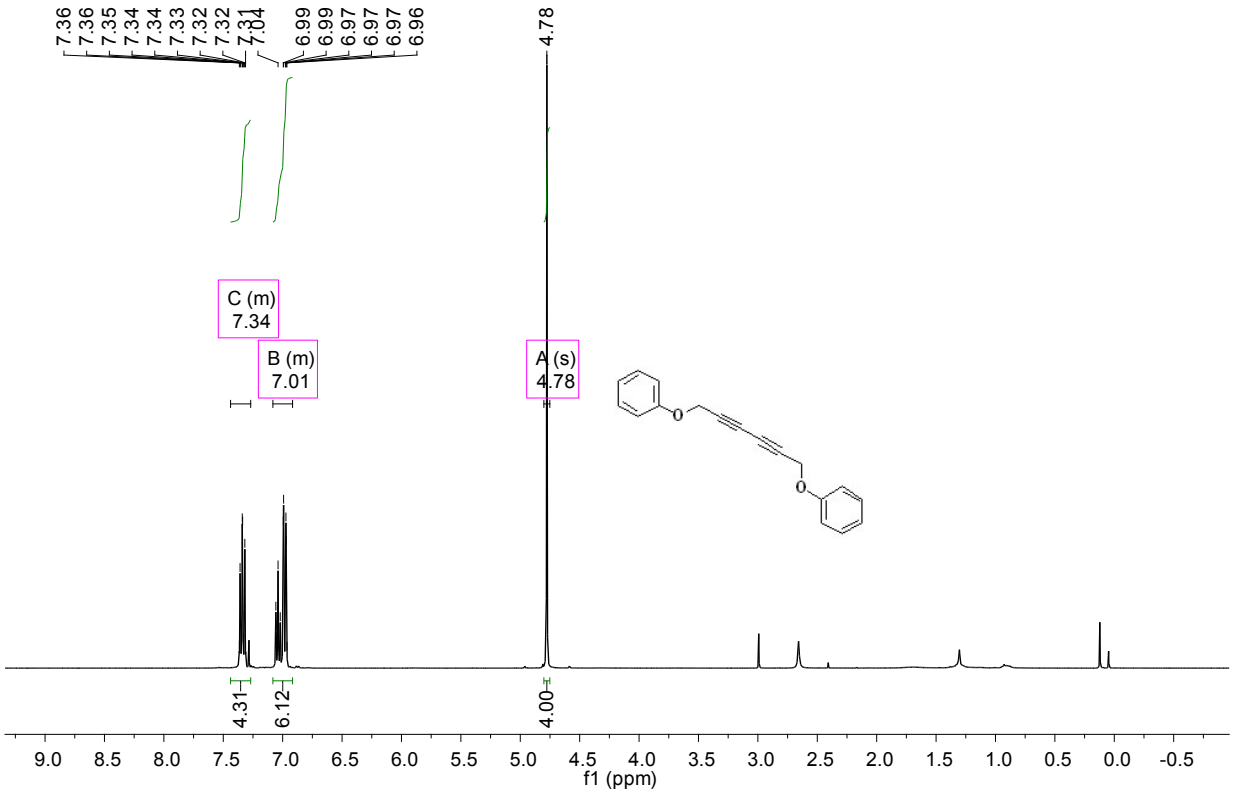
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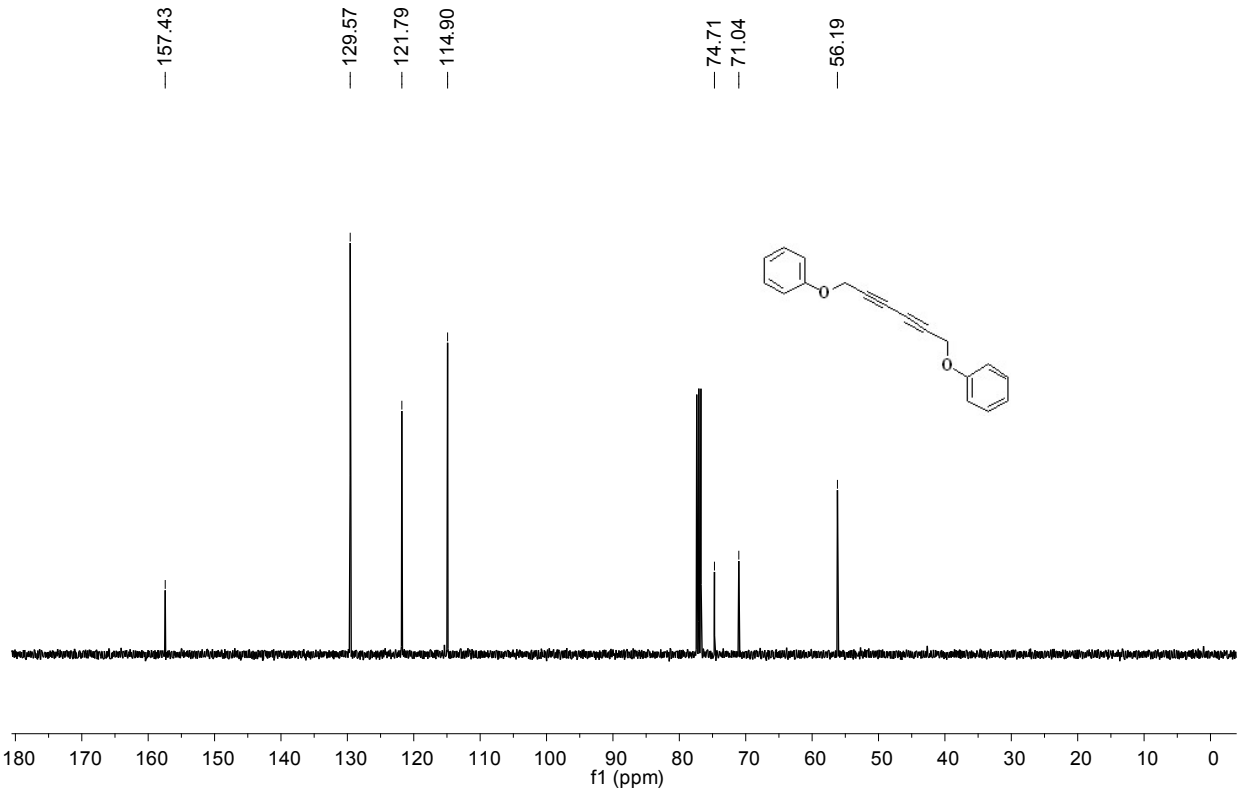
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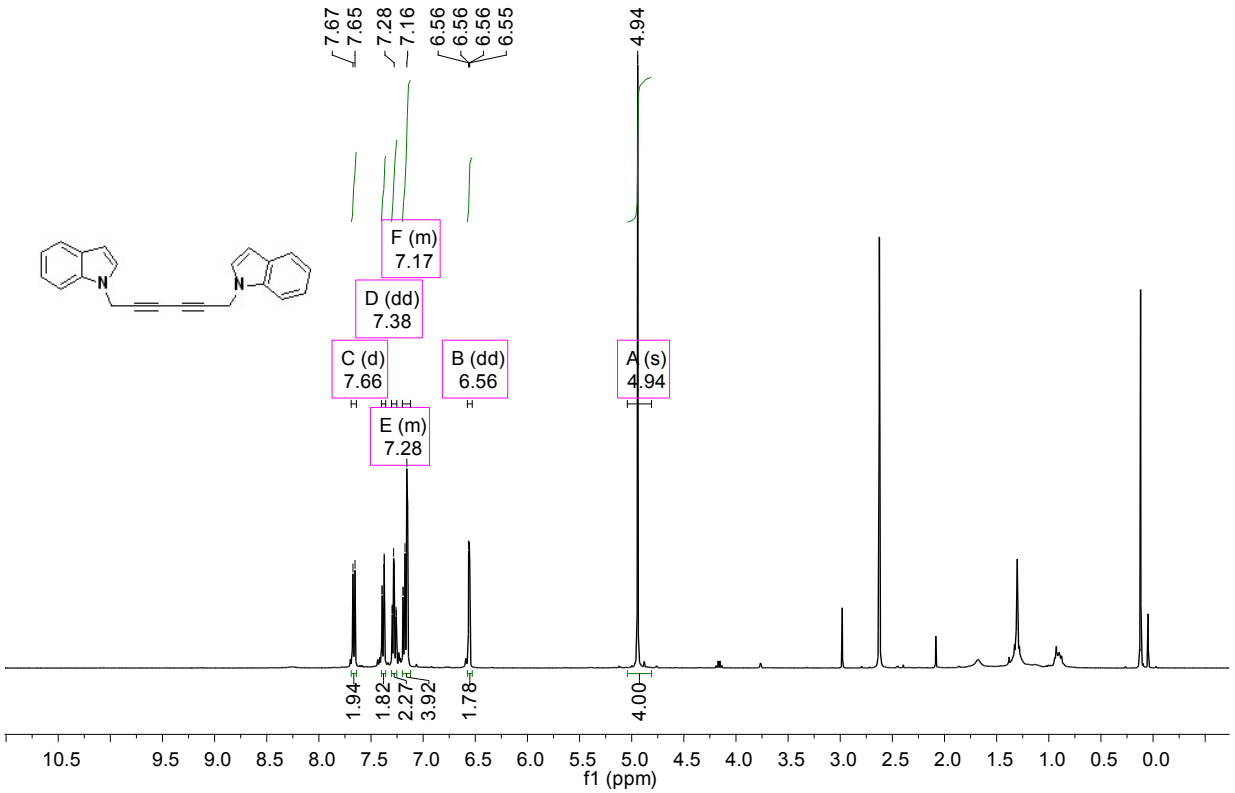
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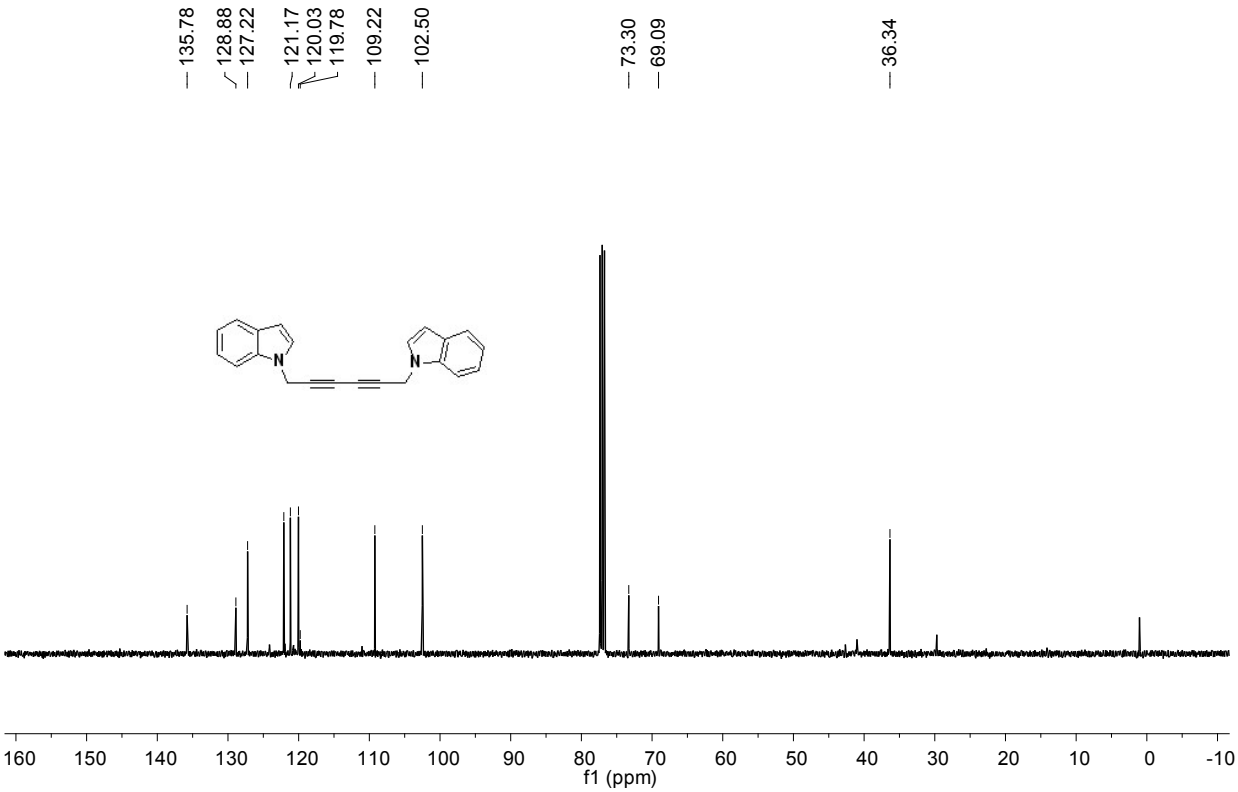
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)


135.78
128.88
127.22
121.17
120.03
119.78
109.22
102.50
73.30
69.09
36.34
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)