Electronic Supplementary Material (ESI) for Organic & Biomolecular Chemistry.

Supporting Information

Calcium Carbide Catalytically Activated with Tetra-*n*-butyl Ammonium Fluoride for Sonogashira Cross Coupling Reactions

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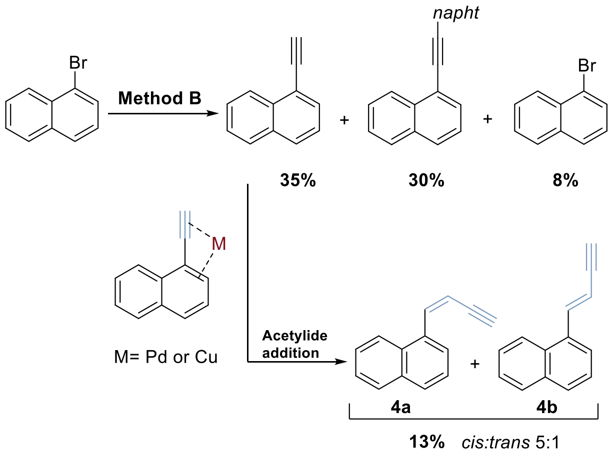
[c]*Institute of Inorganic and Analytical Chemistry, Justus-Liebig University, Heinrich-Buff-Ring 17, 35392 Giessen, Germany.*



Scheme S1. Cross-dimerization of 1-ethynylnaphthalene with CaC_2 derived acetylide reagent.

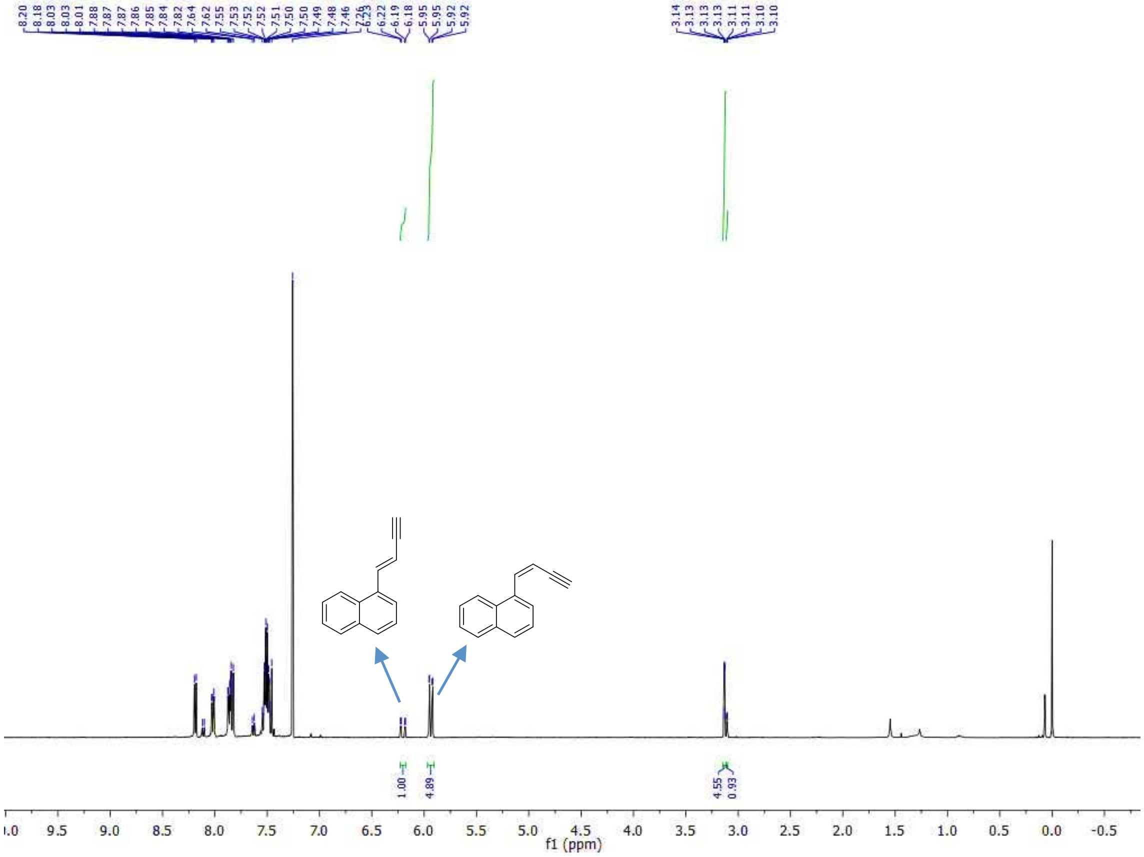


Figure S1 H NMR ($CDCl_3$) mixture of the (E) and (Z) 1-(But-1-en-3-ynyl)naphthalene isomers.

Characterization of copper and palladium nanoparticles.

Nanoparticles obtained using the standard protocol (method A) out of CaC_2 and arylbromide. The samples were analyzed by Scanning electron microscopy (SEM) to verify the shape, and formation of the nanoparticles. SEM studies were performed with a Zeiss MERLIN scanning electron microscope equipped with an energy-dispersive X-ray spectroscope (EDS, Oxford Instruments). To prepare the SEM sample, a few microliters were dropped onto a cleaned silicon wafer and allowed to dry in freeze-dryer. The TEM measurements were conducted using a Philips CM30 STEM (300 kV, LaB6-cathode) equipped with a GATAN digital camera. TEM samples were prepared by placing a 10-µL drop of solution of NPs on a carbon-coated copper grid, and then images were recorded using Digital Micrograph.

Preparation of copper nanoparticles: An oven-dried Schlenk tube equipped with a magnetic stir bar under argon atmosphere was charged with $Cu(acac)_2$ (6.6 mg, 0.025 mmol), PPh_3 (27 mg, 0.1 mmol) and DMSO (3 mL) and the solution was purged with argon (5 min). Then TBAF stock solution (0.5 mmol, 1 mL) was successively added to the solution. The mixture was stirred at 65 °C for 3 h. The reaction was allowed to reach room temperature, and then a few microliter of the solution was placed on a silicon chip followed by freeze-drying to remove the solvent. Analysis by SEM (Figure S2) and TEM (Figure S3) confirmed the formation of copper nanoparticles.

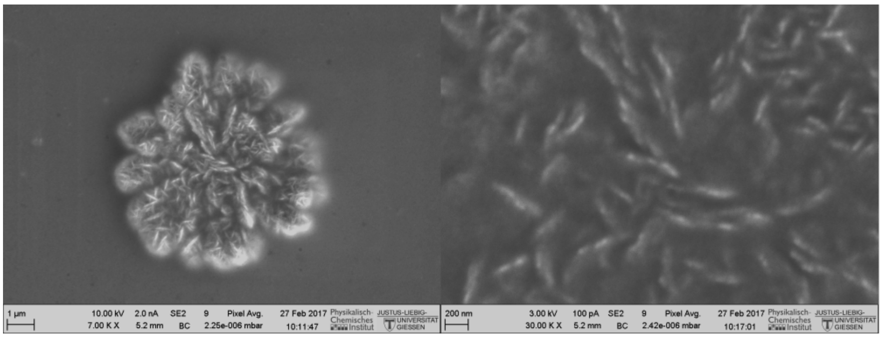


Figure S2 SEM image of copper nanoparticles.

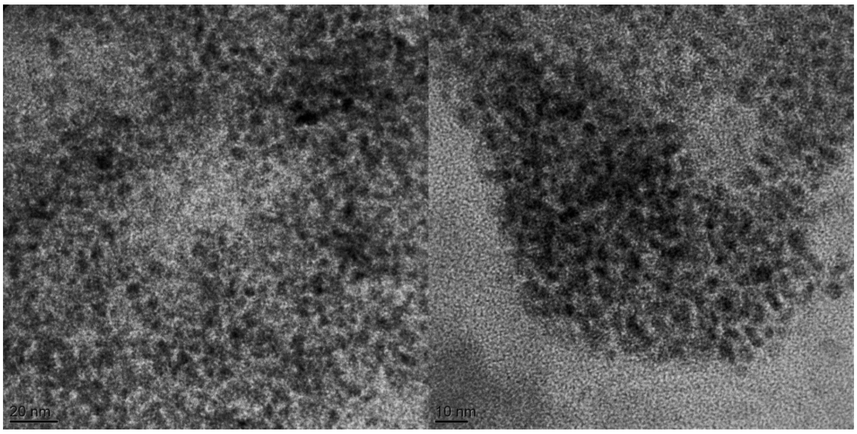


Figure S3 TEM image of copper nanoparticles.

Preparation of palladium nanoparticles: An oven-dried Schlenk tube equipped with a magnetic stir bar under argon atmosphere was charged with $Pd(OAc)_2$ (5.6 mg, 0.025 mmol), PPh_3 (27 mg, 0.1 mmol) and DMSO (3 mL) and the solution was purged with argon (5 min). Then TBAF stock solution (0.5 mmol, 1 mL) was successively added to the solution. The mixture was stirred at 65 °C for 3 h. The reaction was allowed to reach room temperature, and then a few microliter of the solution was placed on a silicon chip followed by freeze-drying to remove the solvent. Analysis by SEM (Figure S4) and TEM (Figure S5) confirm the formation of palladium nanoparticles.

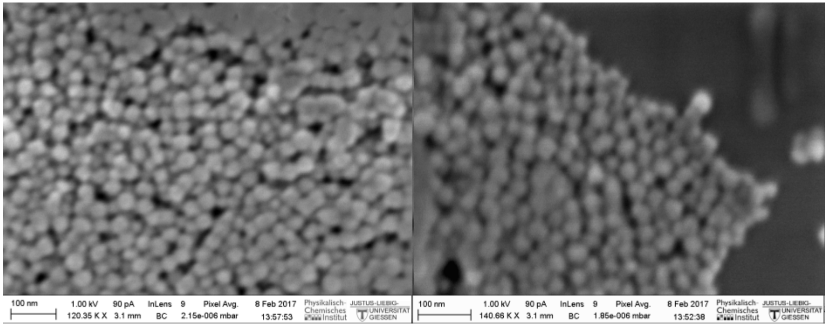


Figure S4 SEM image of palladium nanoparticles.

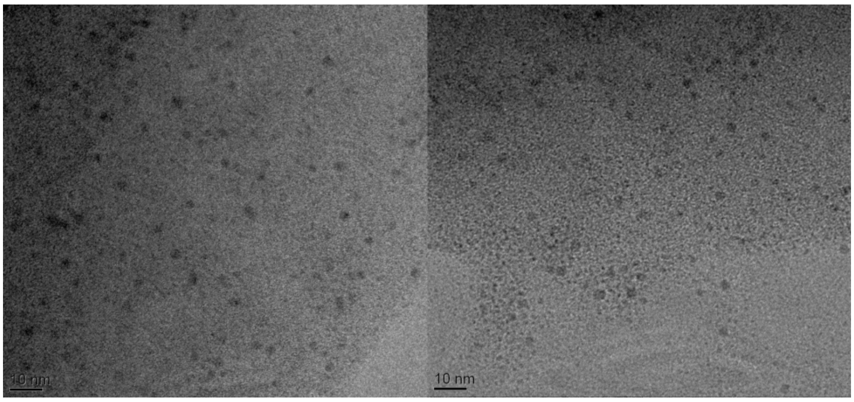
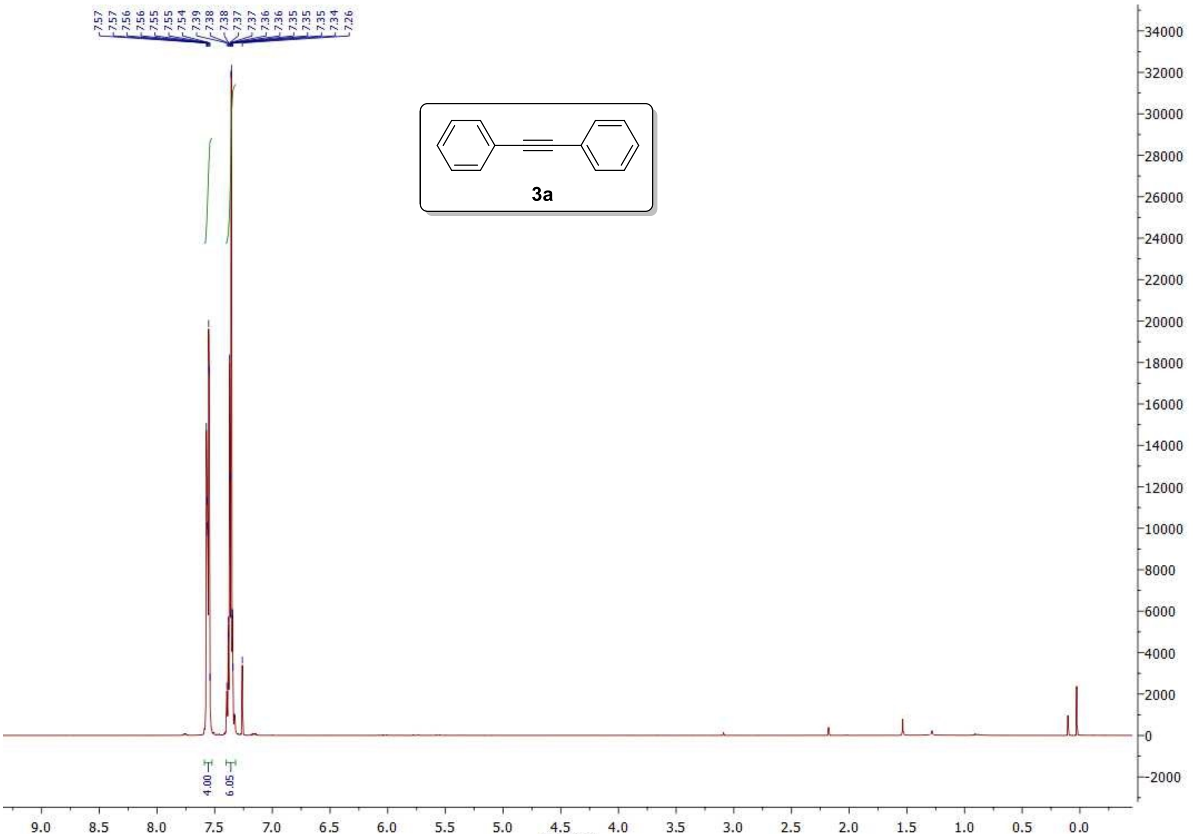


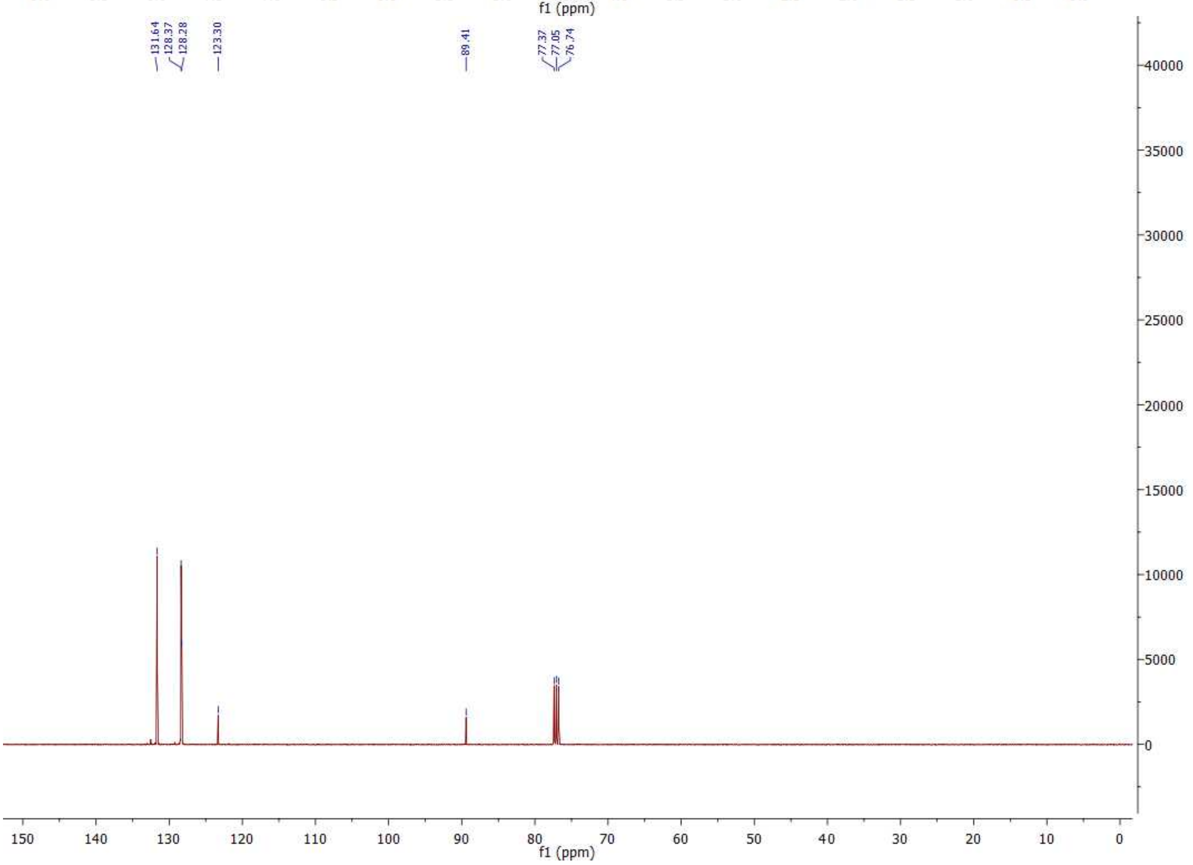
Figure S5 TEM image of palladium nanoparticles.

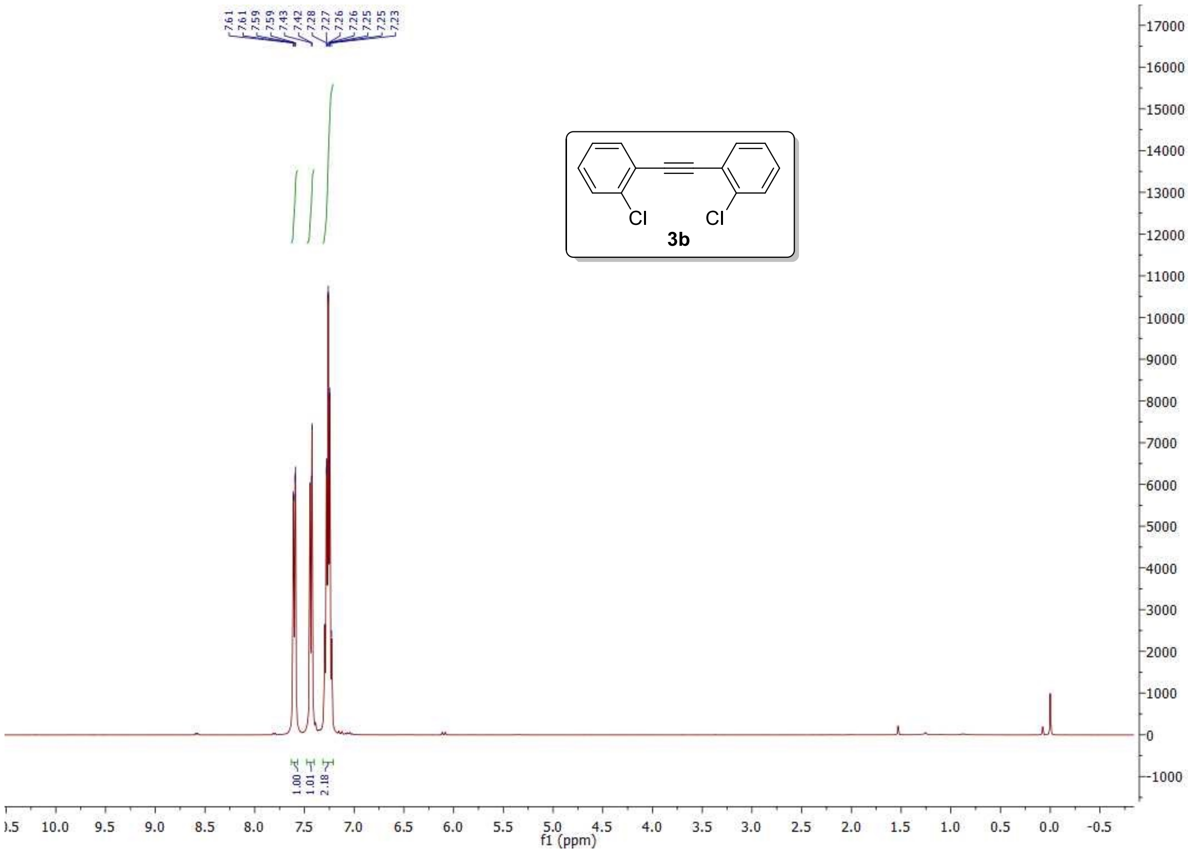
Scale up synthesis of diphenylacetylene (3a) according to method A:

An oven-dried Schlenk tube equipped with a magnetic stir bar under argon atmosphere was charged with $Pd(OAc)_2$ (0.14 g, 0.625 mmol), $Cu(acac)_2$ (0.165 g, 0.625 mmol), PPh_3 (0.675 g, 2.5 mmol) and DMSO (75 mL) and the solution was purged with argon (5 min). Then TBAF stock solution (12.5 mmol, 25 mL), calcium carbide (2.25 g, 34 mmol) and bromobenzene (12.5 mmol) were successively added to the solution. The mixture was stirred at 65 °C for 24 h. The reaction was allowed to reach room temperature and quenched with an aqueous ammonium chloride solution (5%), extracted with diethyl ether and washed with brine. The organic layer was dried over Na_2SO_4, concentrated in vacuo, and the crude product was purified by column chromatography to give diphenylacetylene **3a** (1.09 g, 85%).

^{1}H and ^{13}C Spectra



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7.23
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Cl
3b
1.00
1.01
2.18
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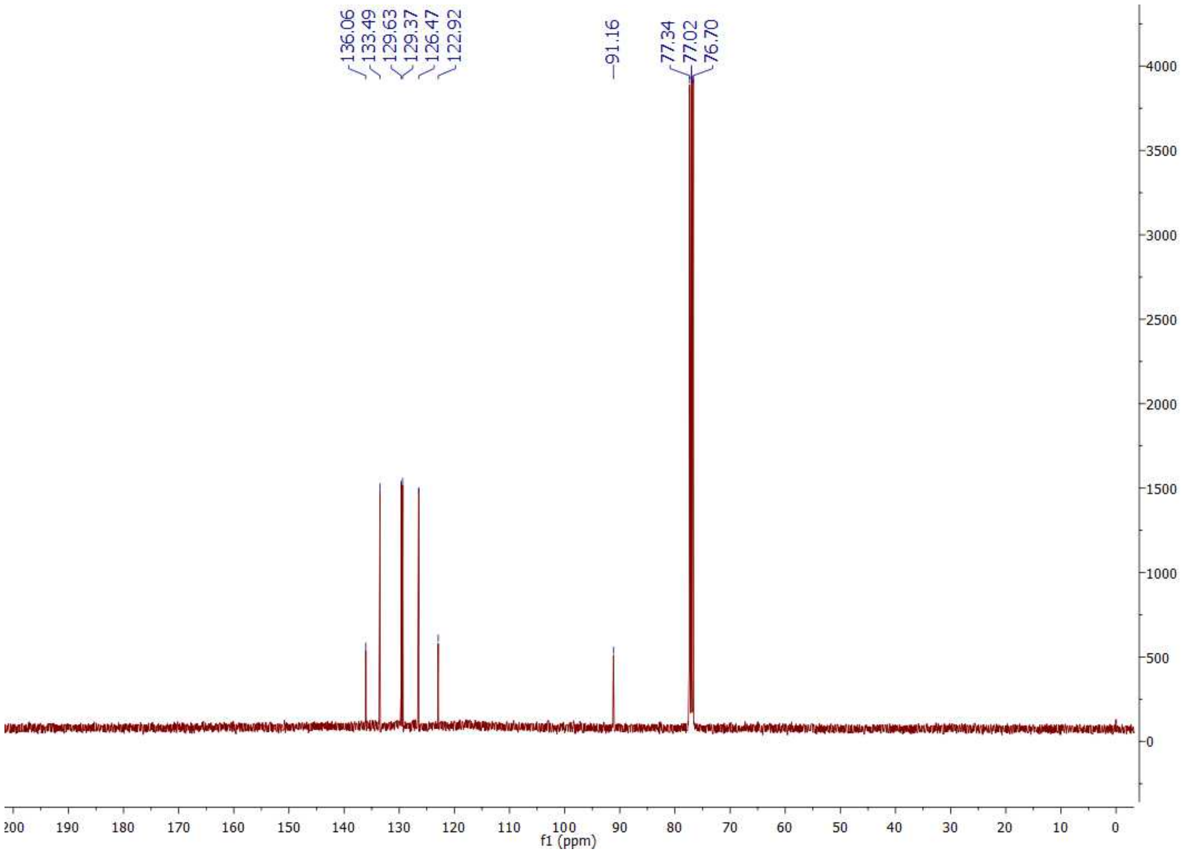
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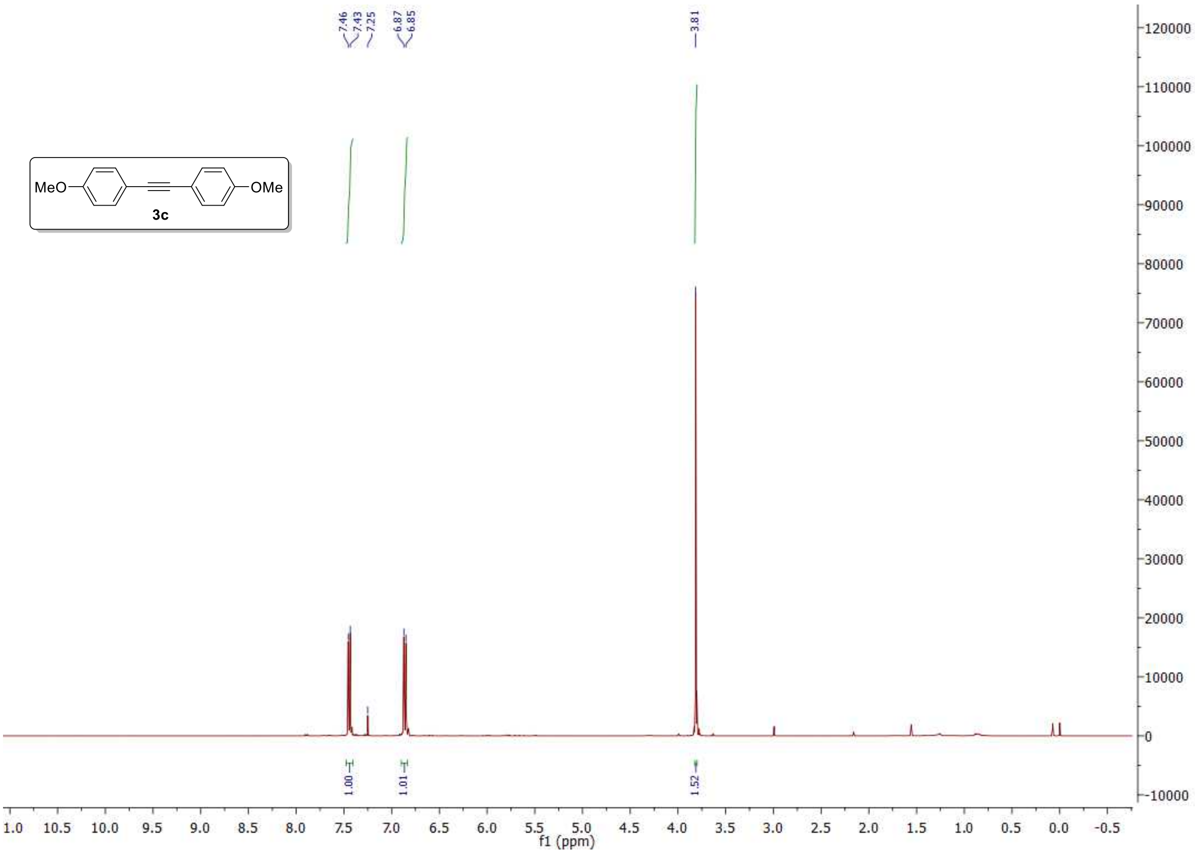
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10.5
10.0
9.5
9.0
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7.5
7.0
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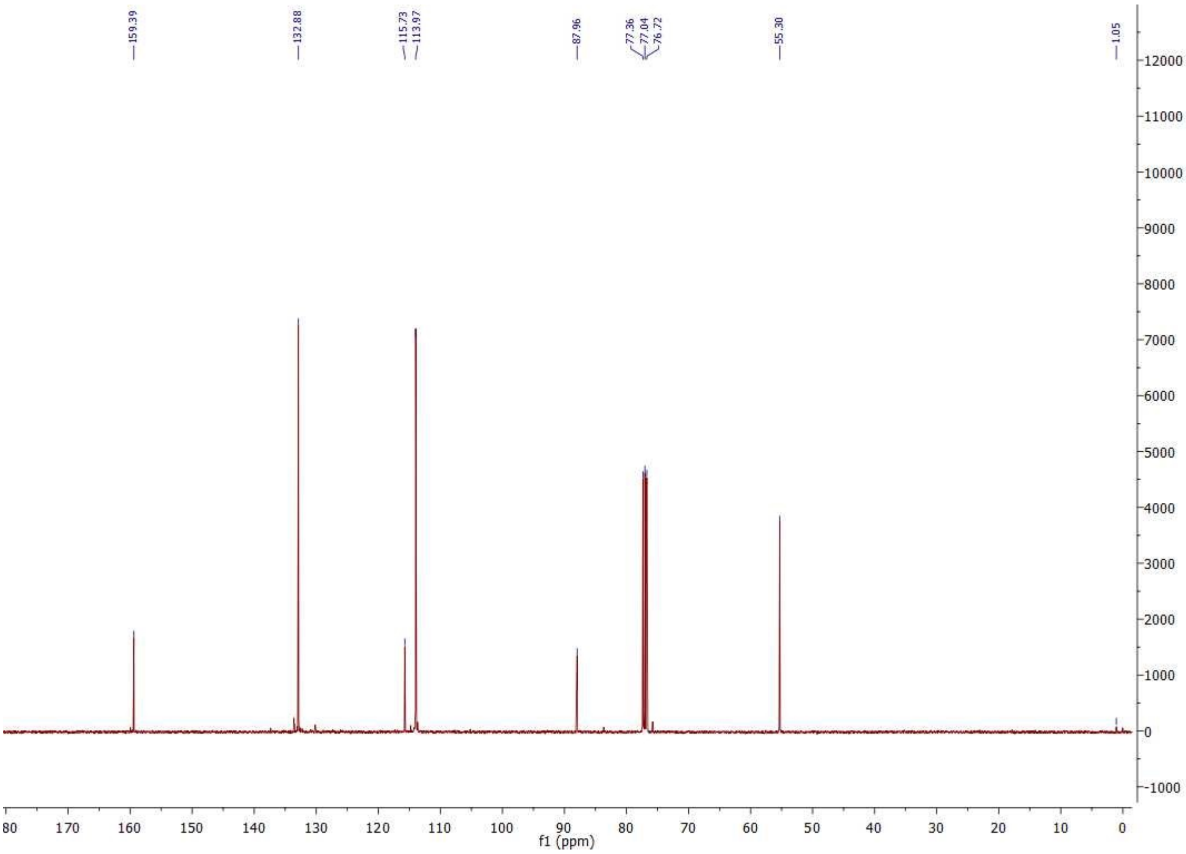
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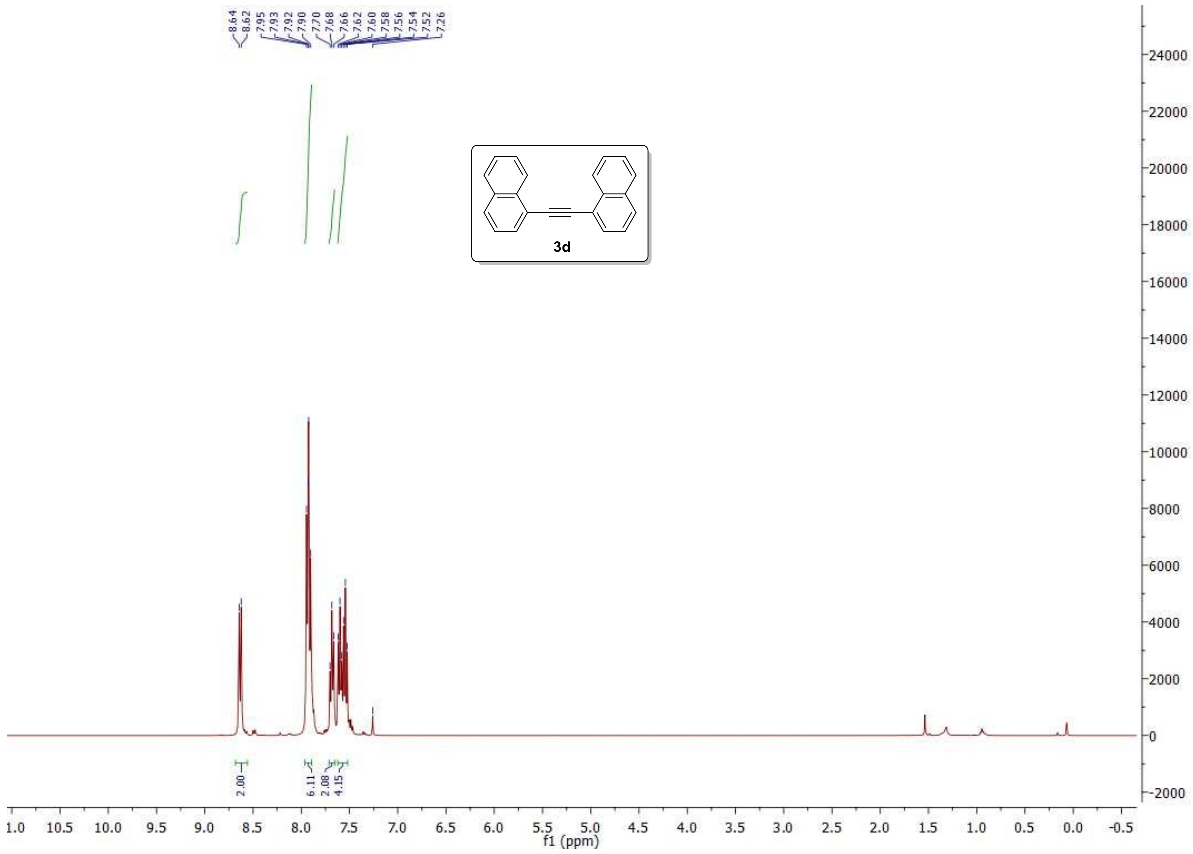
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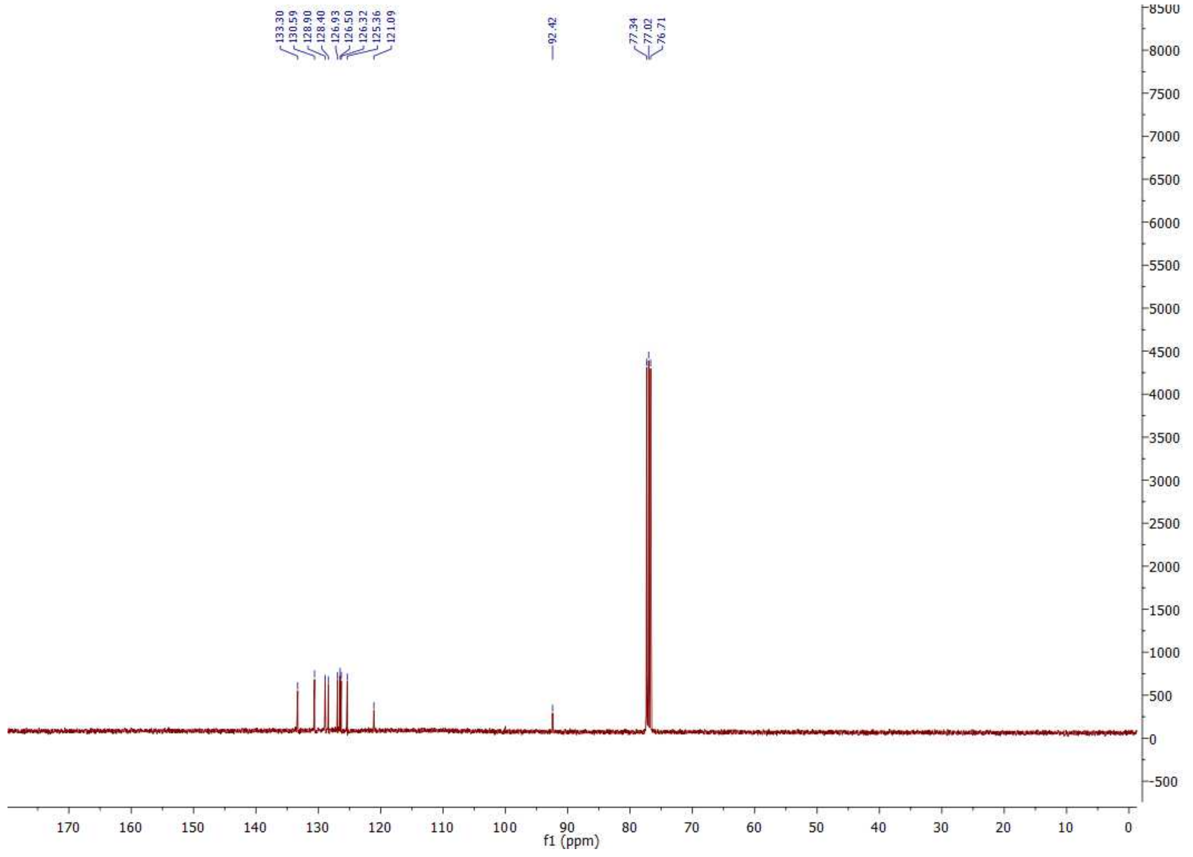
f1 (ppm)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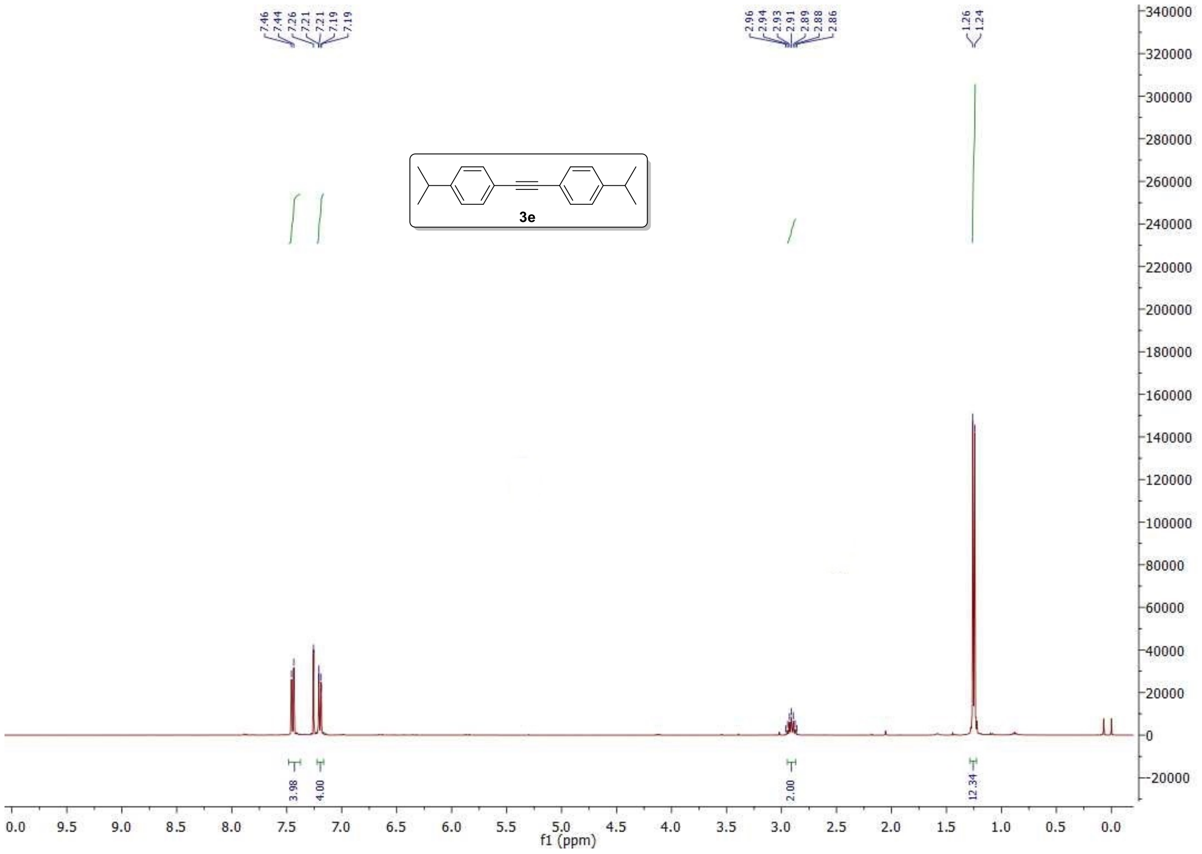
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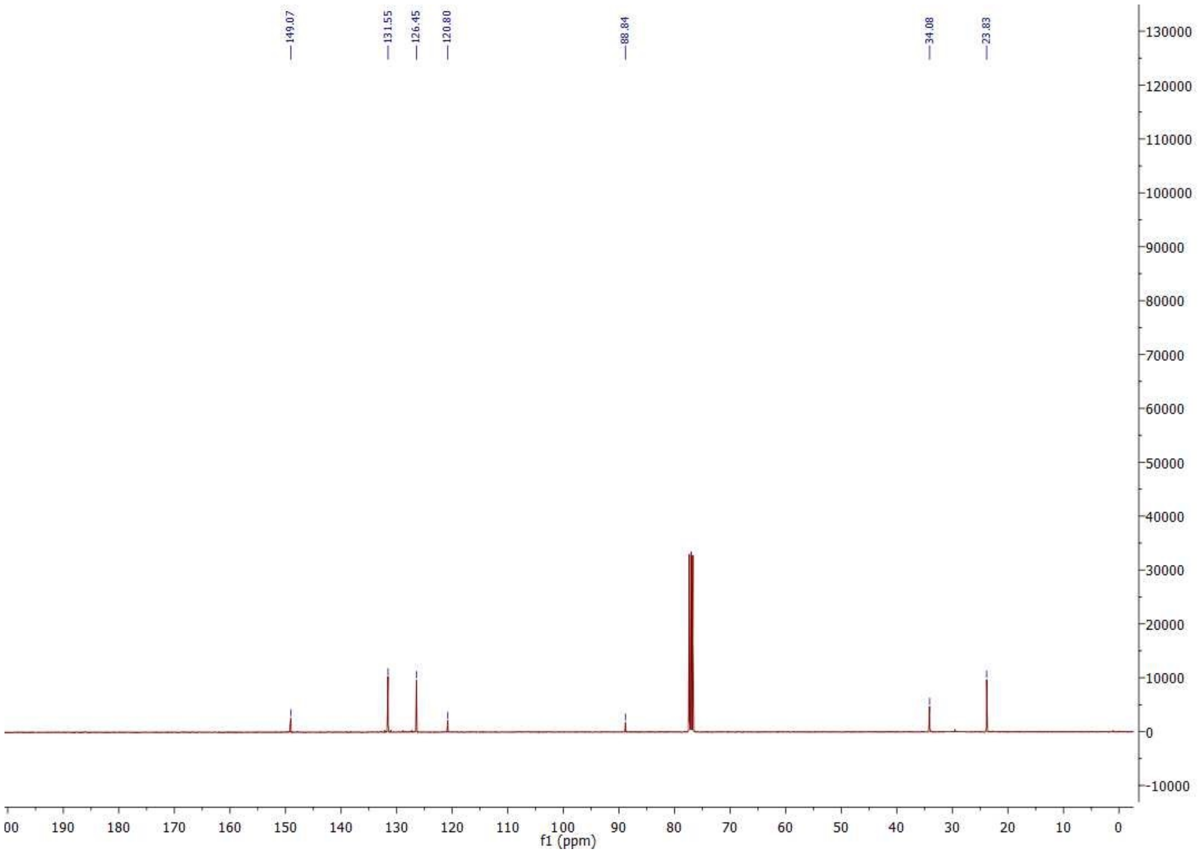
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0
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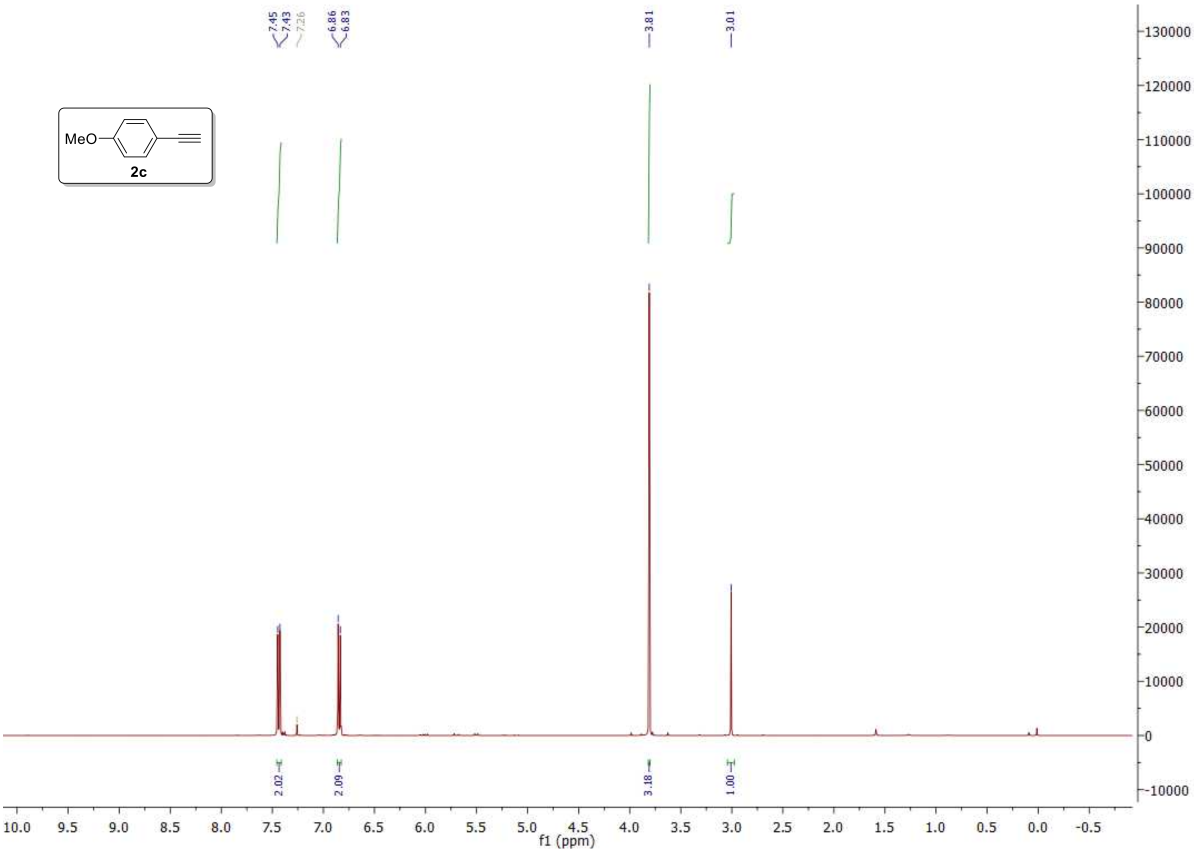
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120000
110000
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90000
80000
70000
60000
50000
40000
30000
20000
10000
0
-10000
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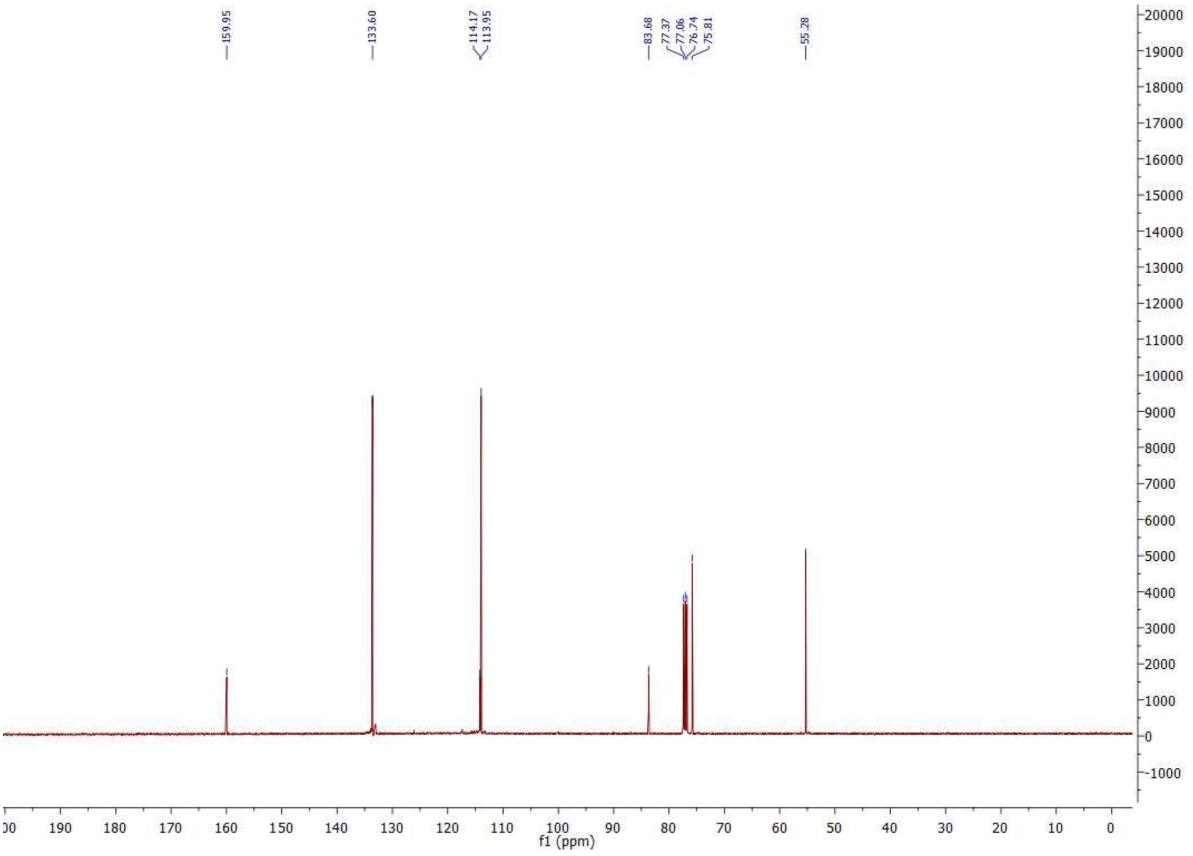
f1 (ppm)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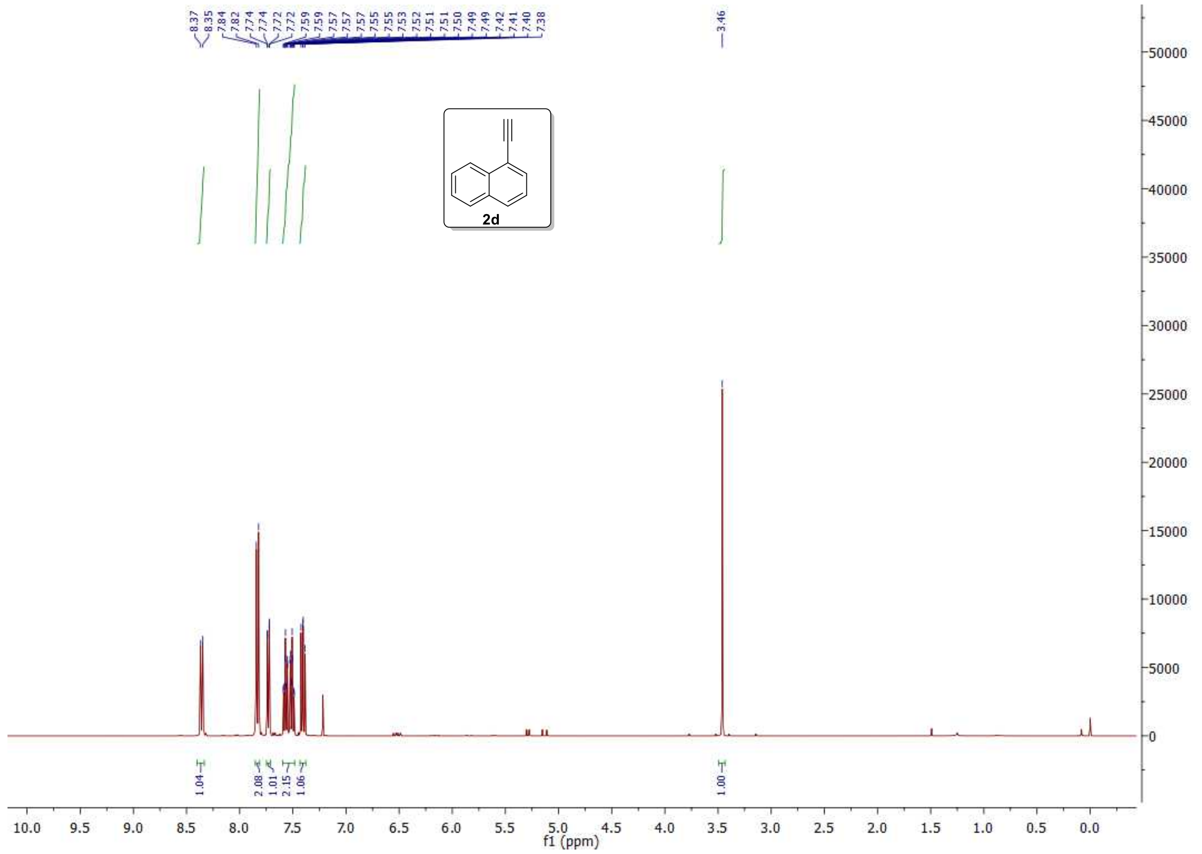
f1 (ppm)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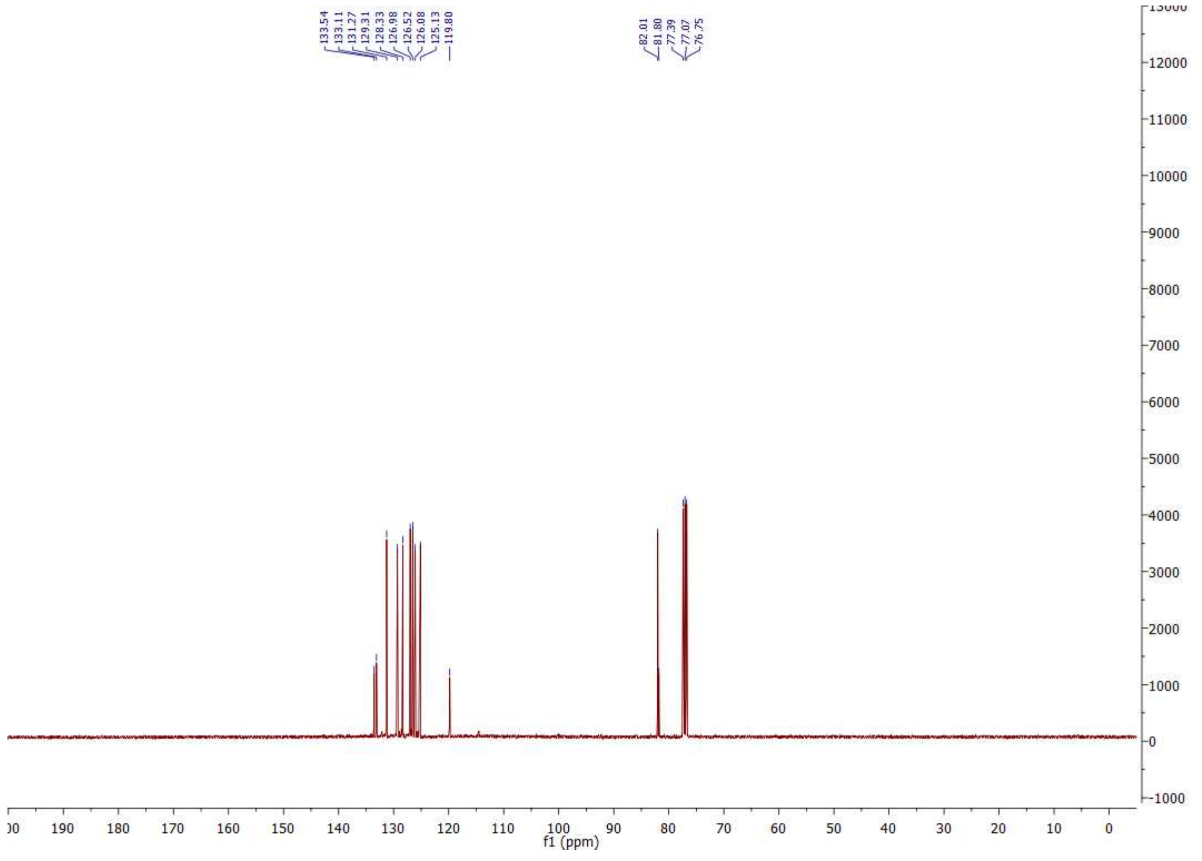
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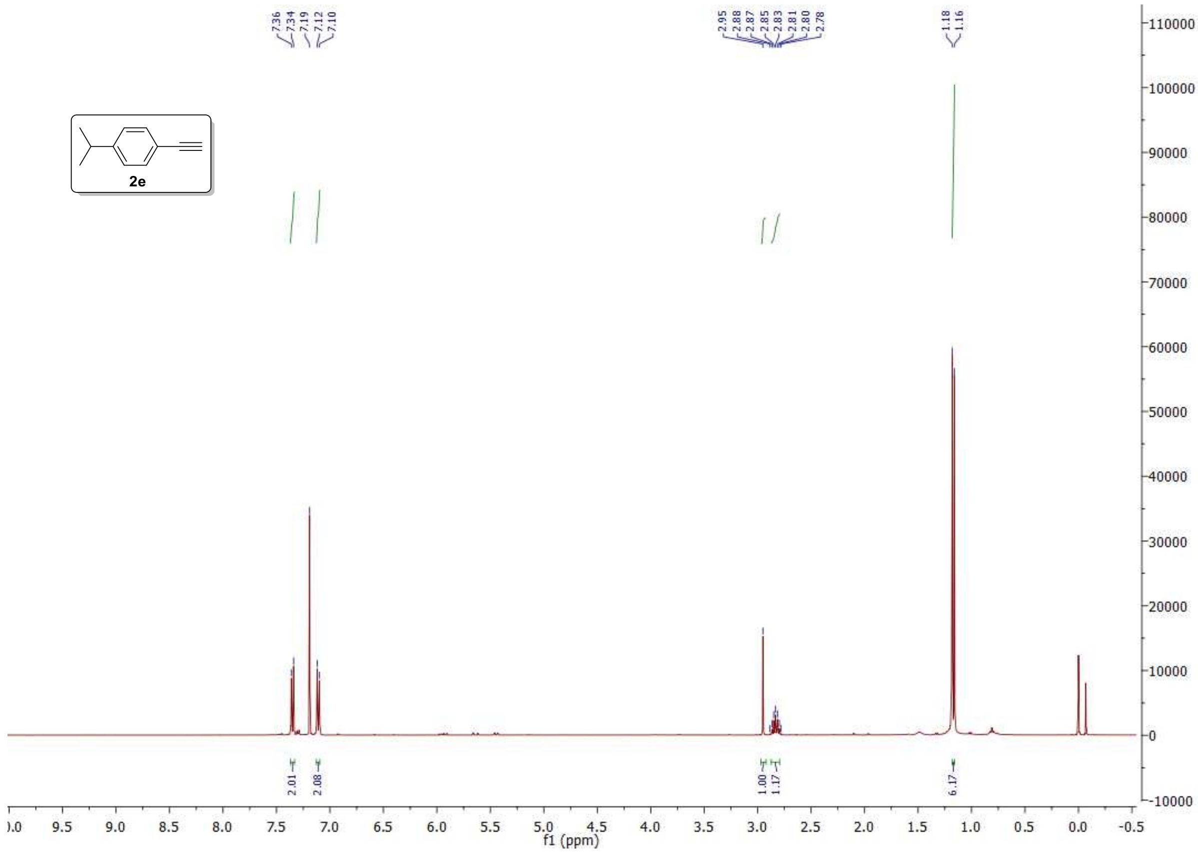
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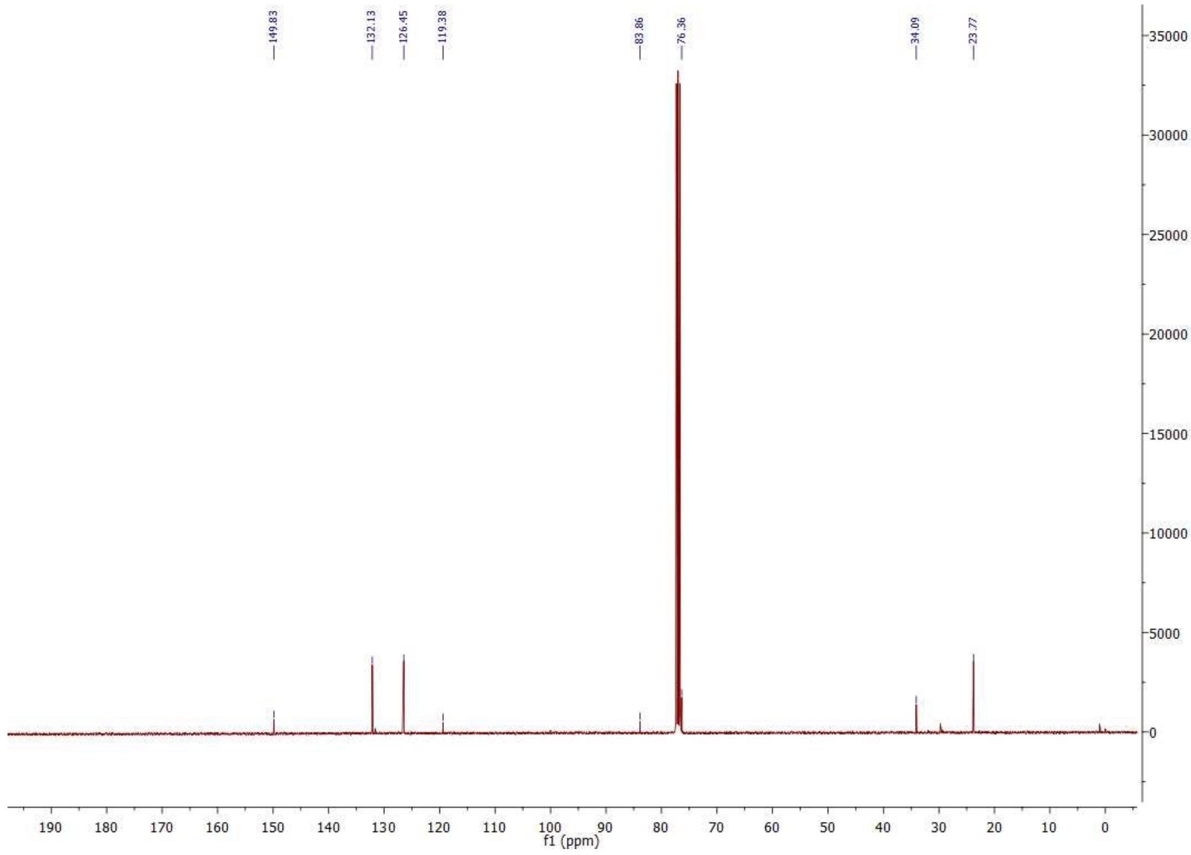
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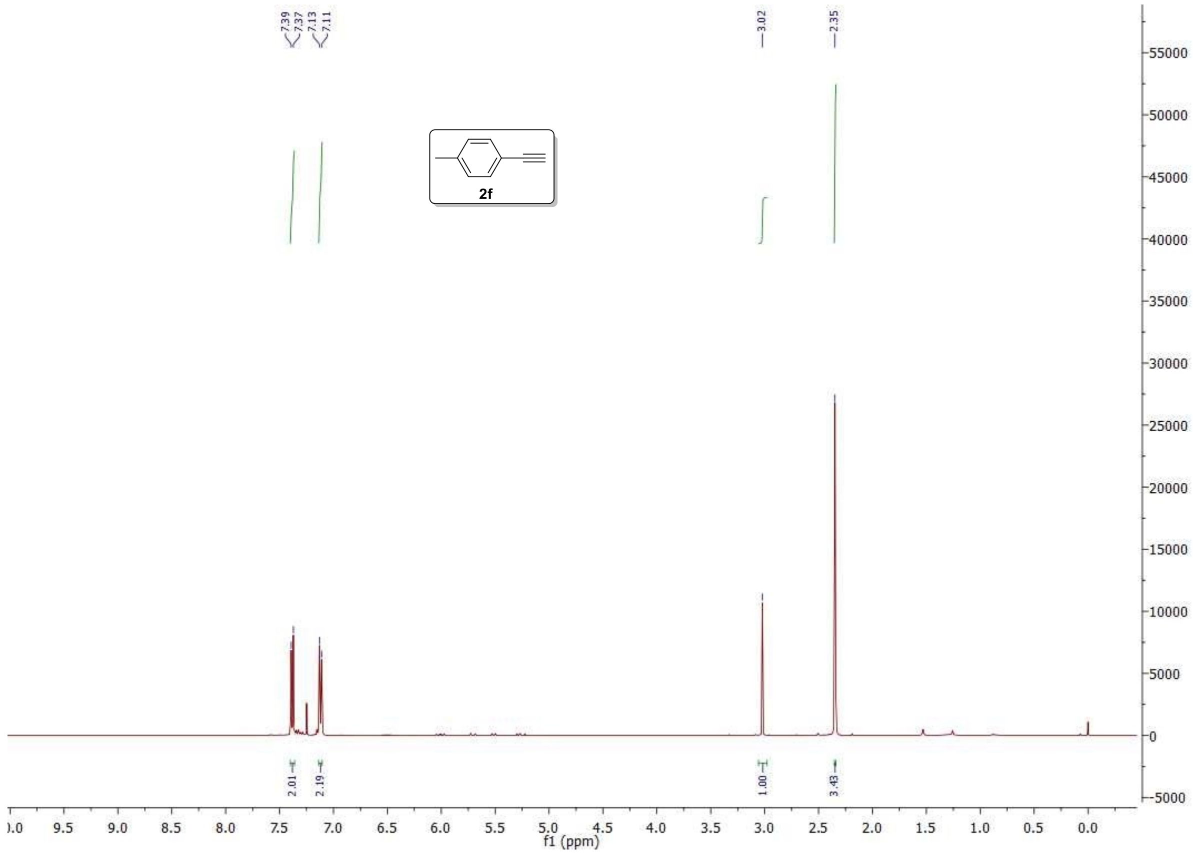

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1.00
3.43
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50000
45000
40000
35000
30000
25000
20000
15000
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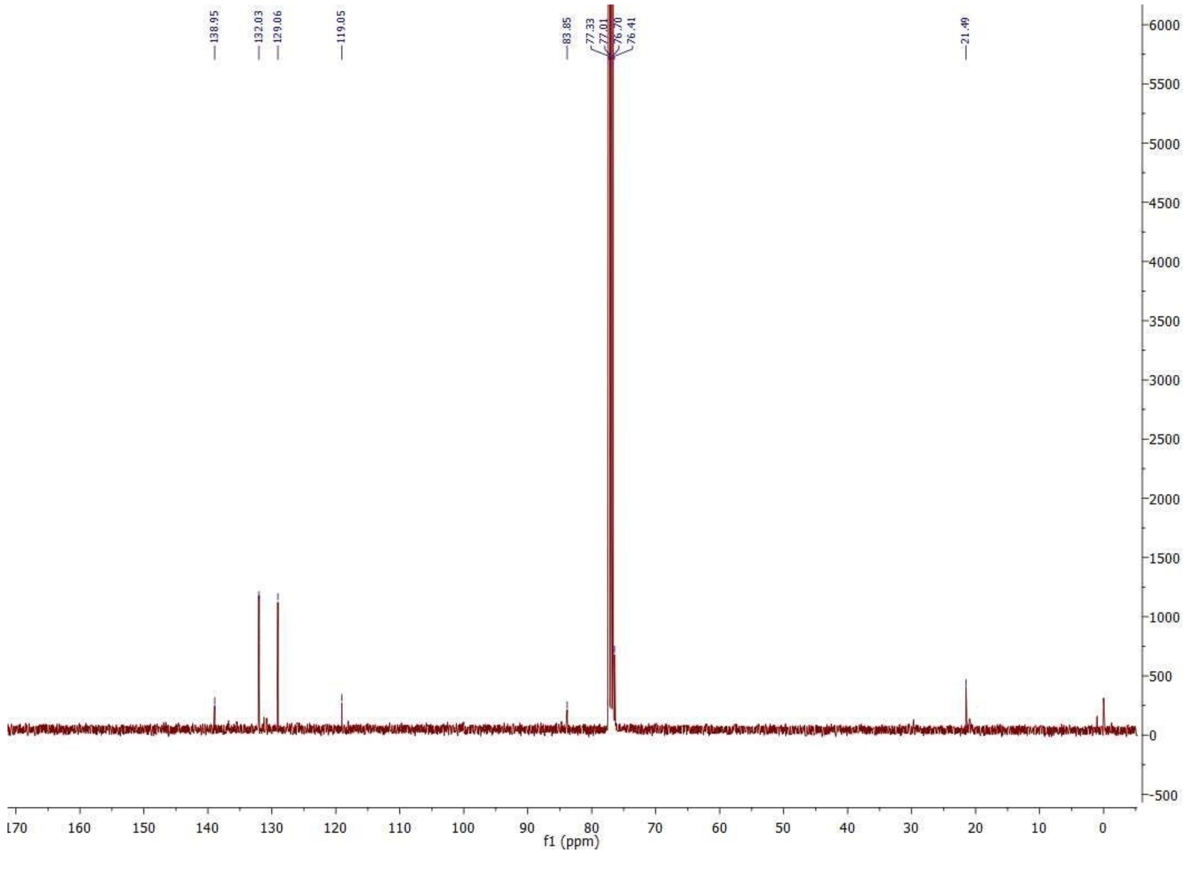

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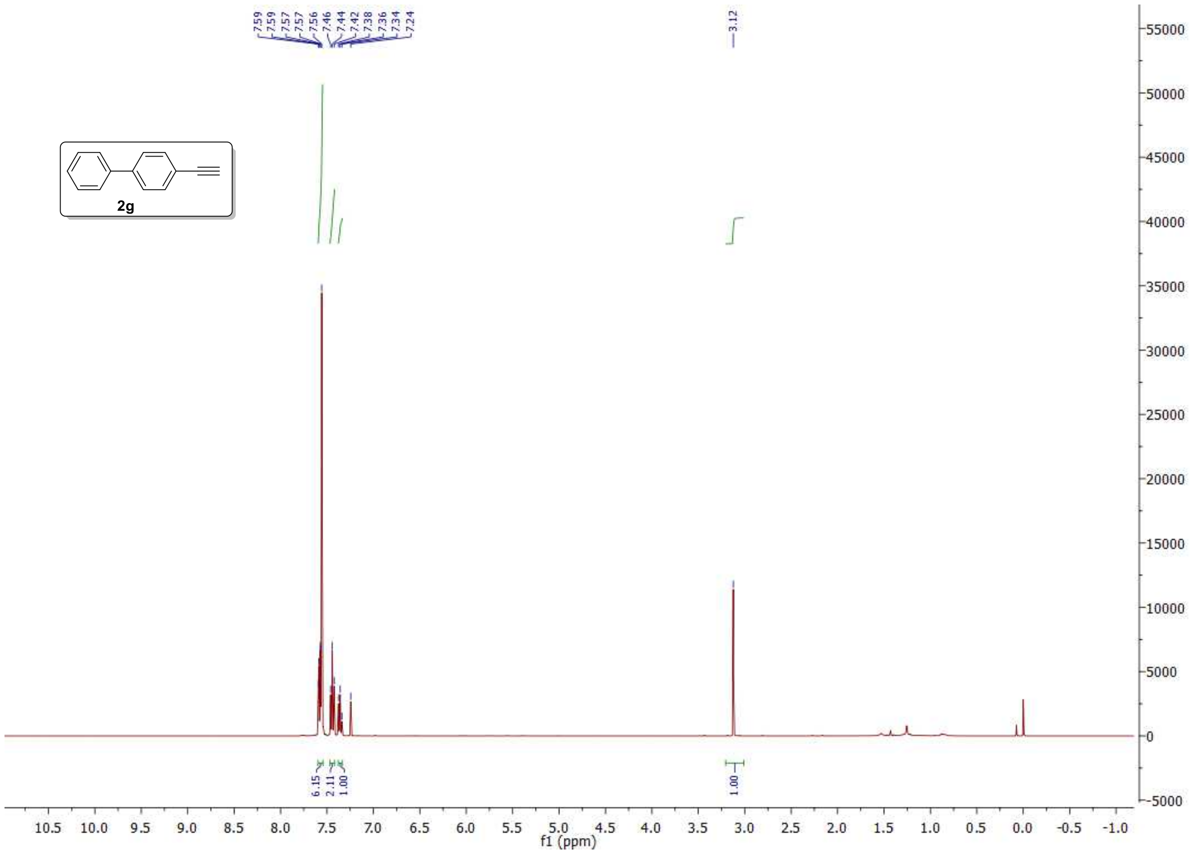
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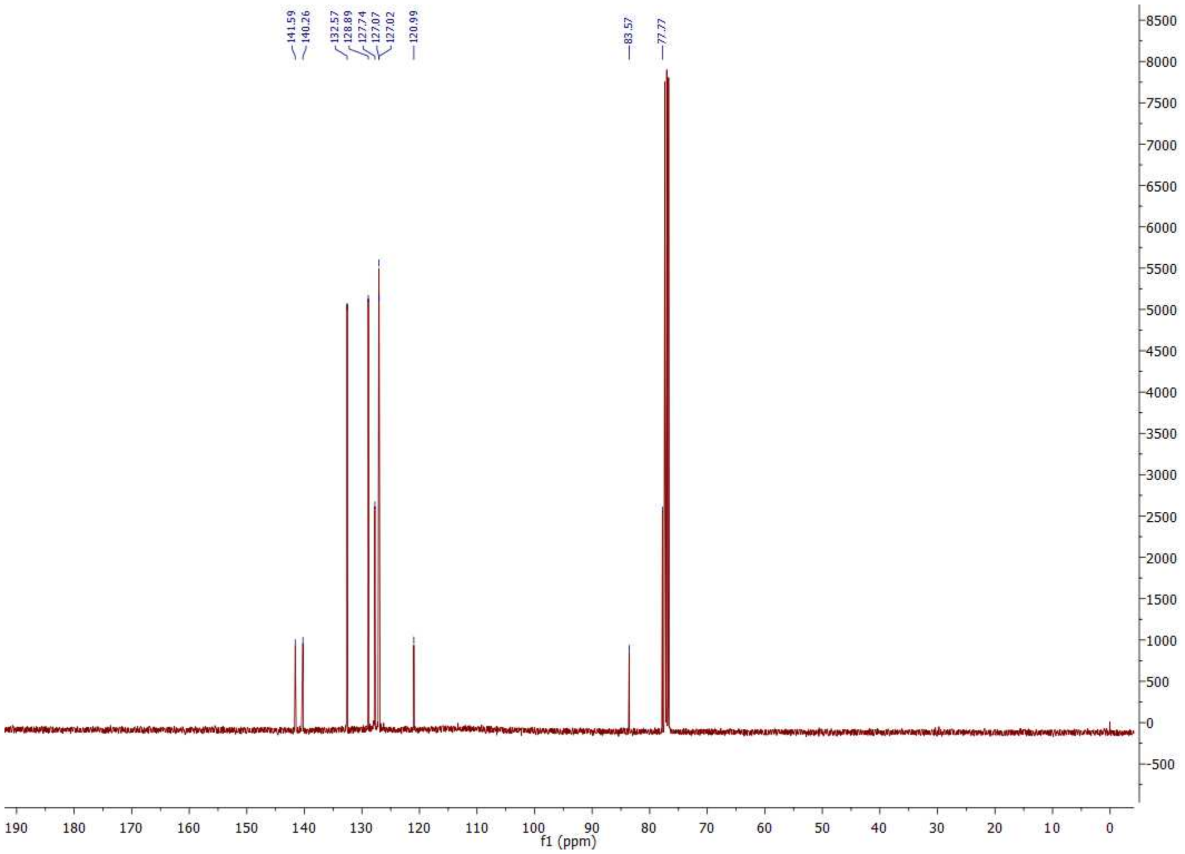
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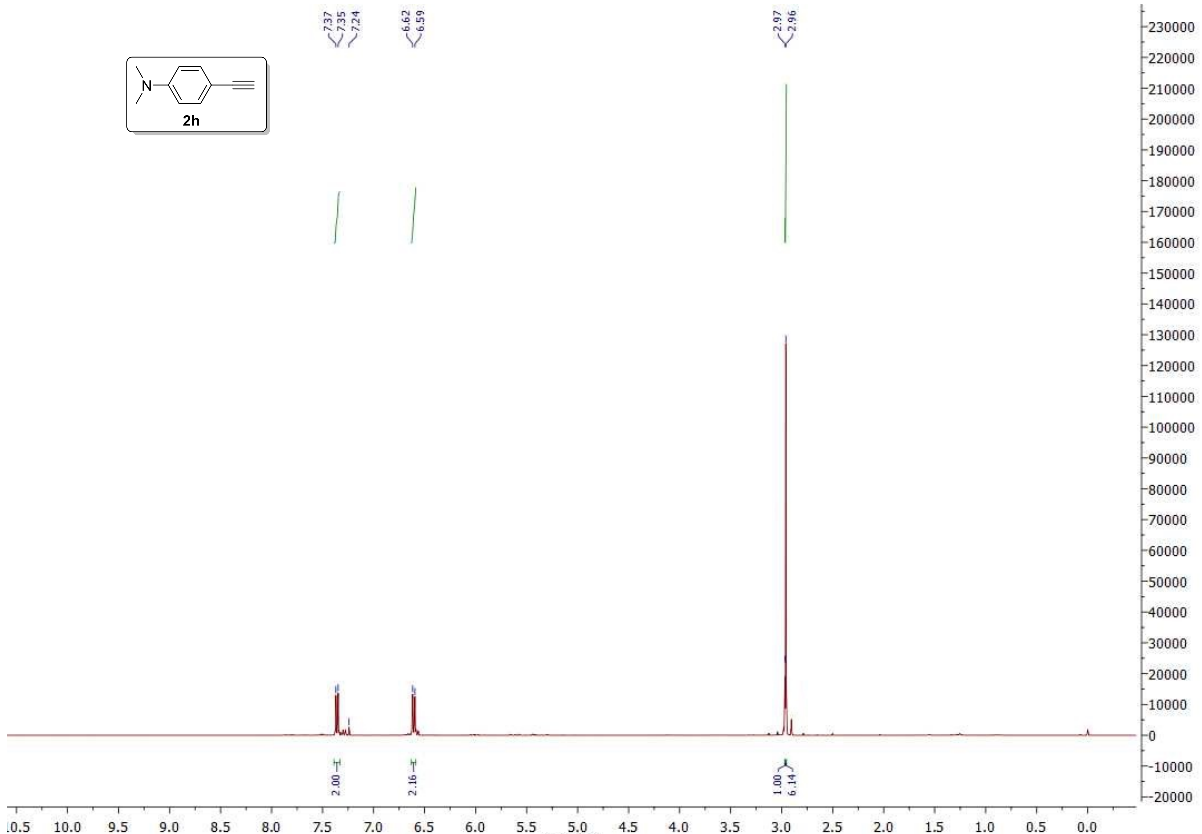
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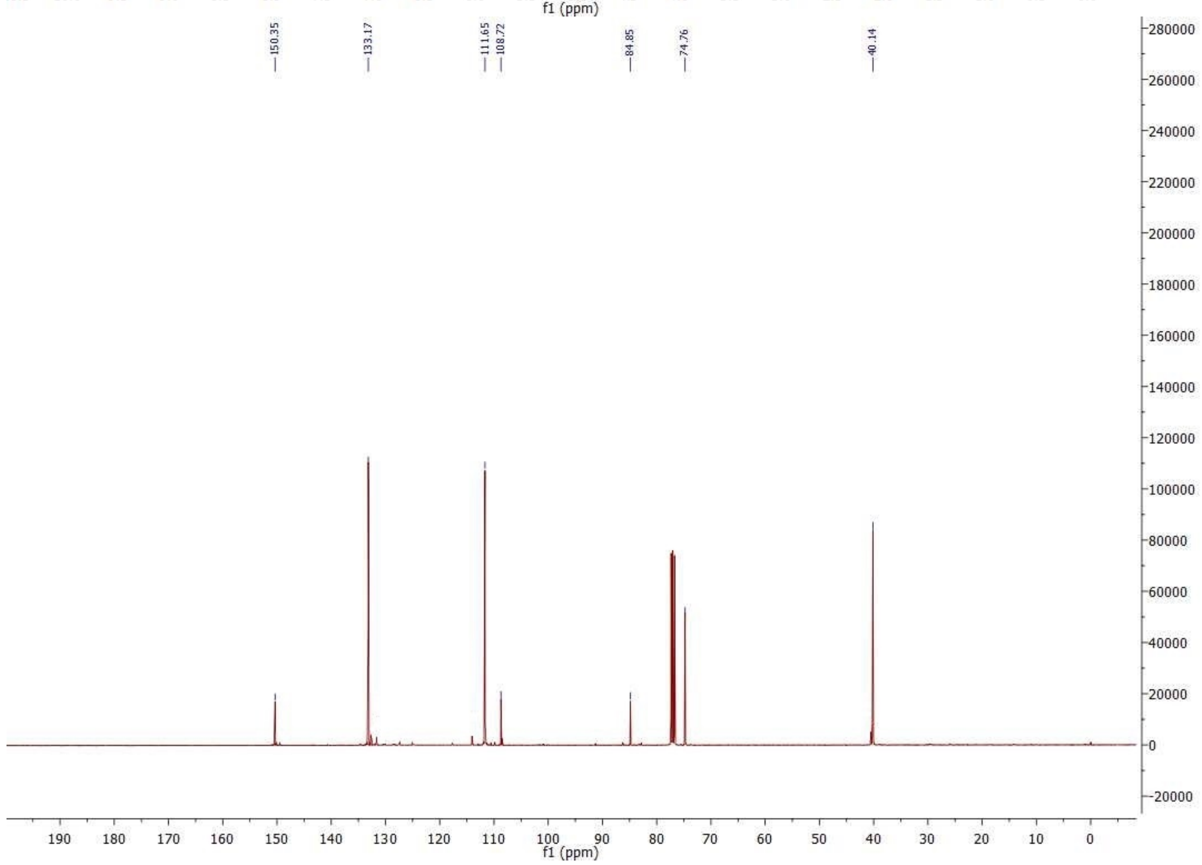
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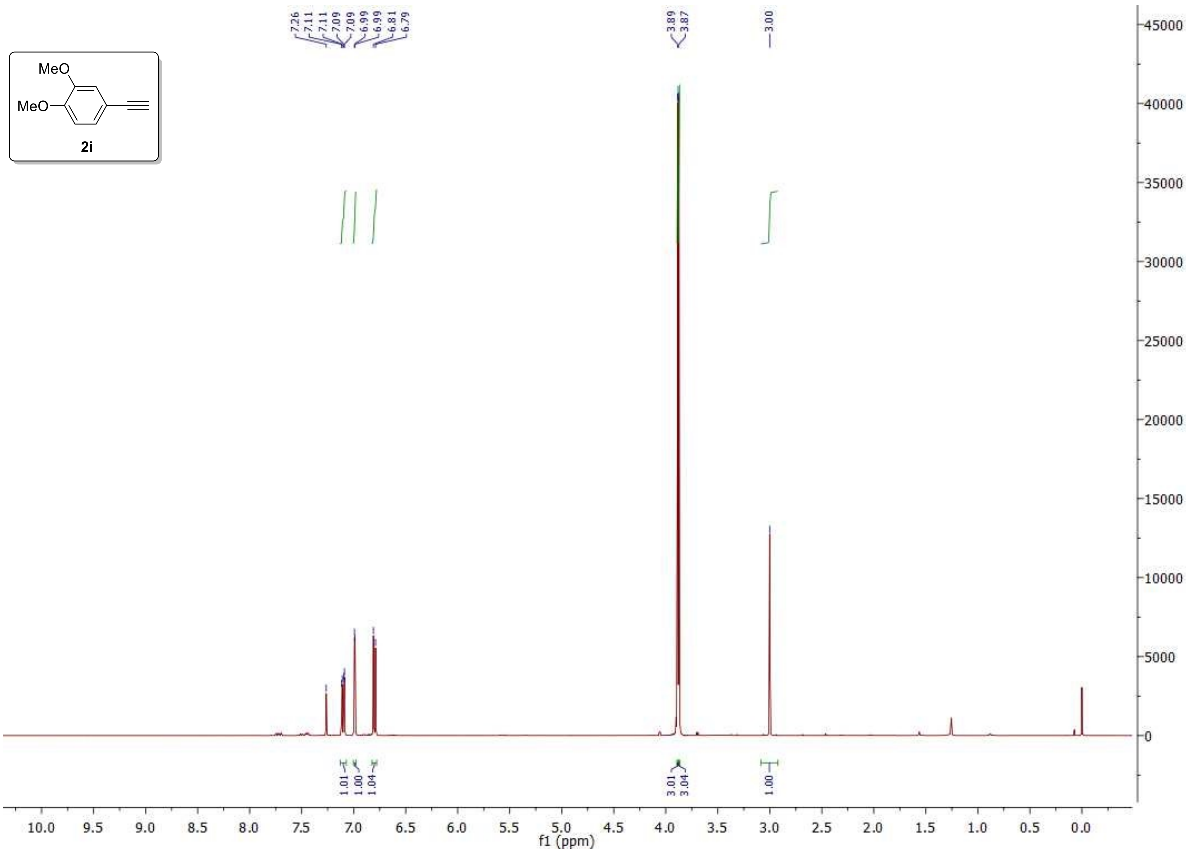
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2.0
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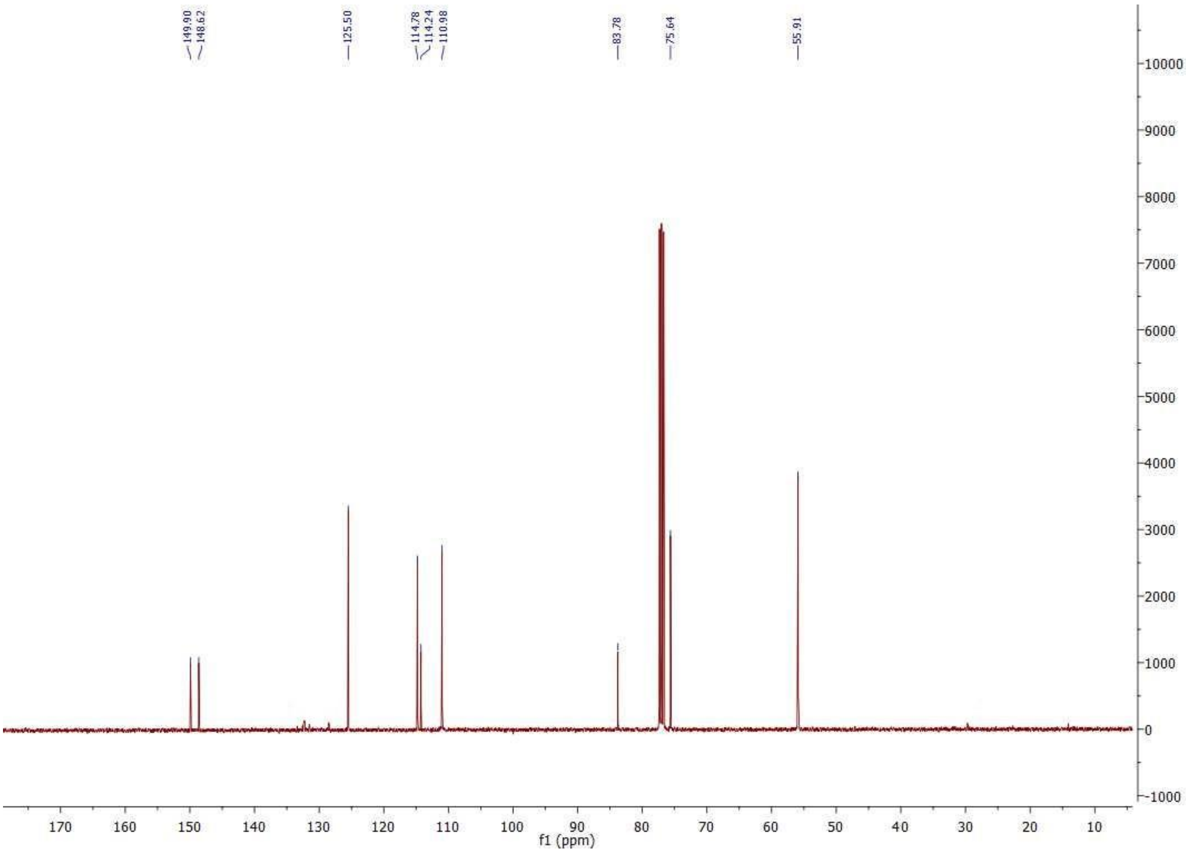
0.5
0.0
f1 (ppm)


149.90
148.62
125.50
114.78
114.24
110.98
83.78
75.64
55.91
10000
9000
8000
7000
6000
5000
4000
3000
2000
1000
0
-1000
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
f1 (ppm)