Electronic Supplementary Material for

N,N-Dimethylformamide-stabilized copper nanoparticles as a catalyst precursor for Sonogashira–Hagihara cross-coupling reaction

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Experimental

All reagents were commercially available and used without further purification. X-Ray diffraction (XRD) spectra was obtained on a Bruker D2 Phaser X-ray diffractometer. FT-IR spectroscopy was performed using a Shimadzu Ir Affinity-1. Dynamic light Scattering (DLS) were measured with a Malvern Zetasizer ZSP at 25 °C in DMF, which was analyzed using a cumlant method.

Preparation of DMF-stabilized Cu NPs.[1]

The DMF-stabilized Cu NPs was prepared according to the reported method.[1] DMF (50 mL) was added to a 300 mL three necked round bottom flask, and the solution was preheated to 140 °C (± 2 °C) and stirred 1300 to 1500 rpm for 5 min. Then the 0.1 M $CuCl_2$ aq. was added to the hot DMF, which allowed to react for 8 h on stirring (1500 rpm) at 140 °C (± 2 °C).

Compound **3a**[2], **3b**[3] **3c**[3], **3d**[4], **3e**[5], **3f**[6], **3g**[7], **3h**[8], **3i**[9], **3j**[10] is known compound and reported previously.

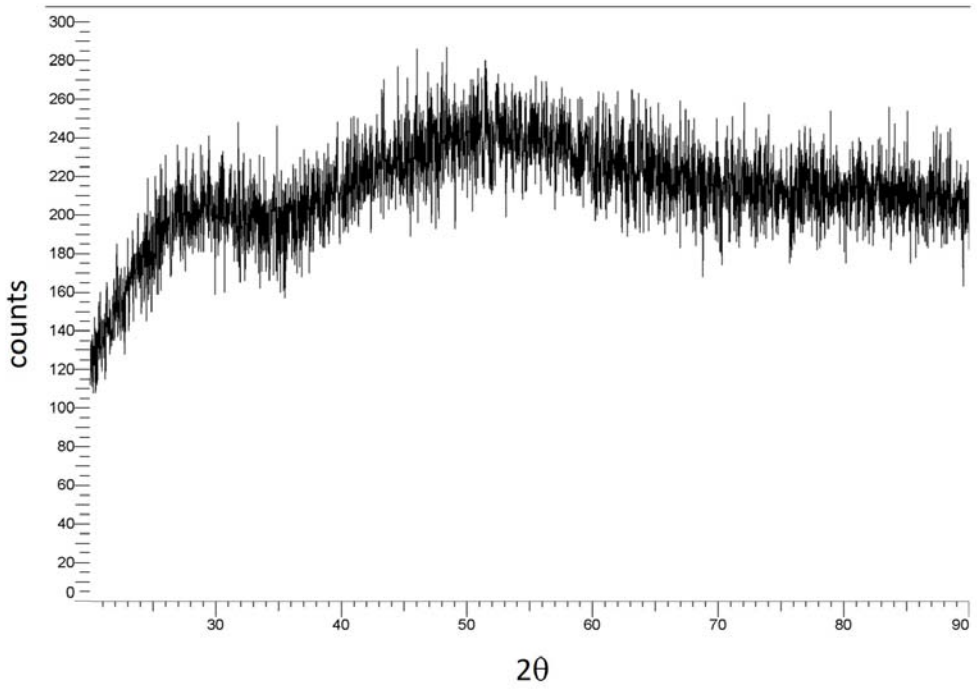

Fig. S1. XRD spectrum of DMF-stabilized Cu NPs.

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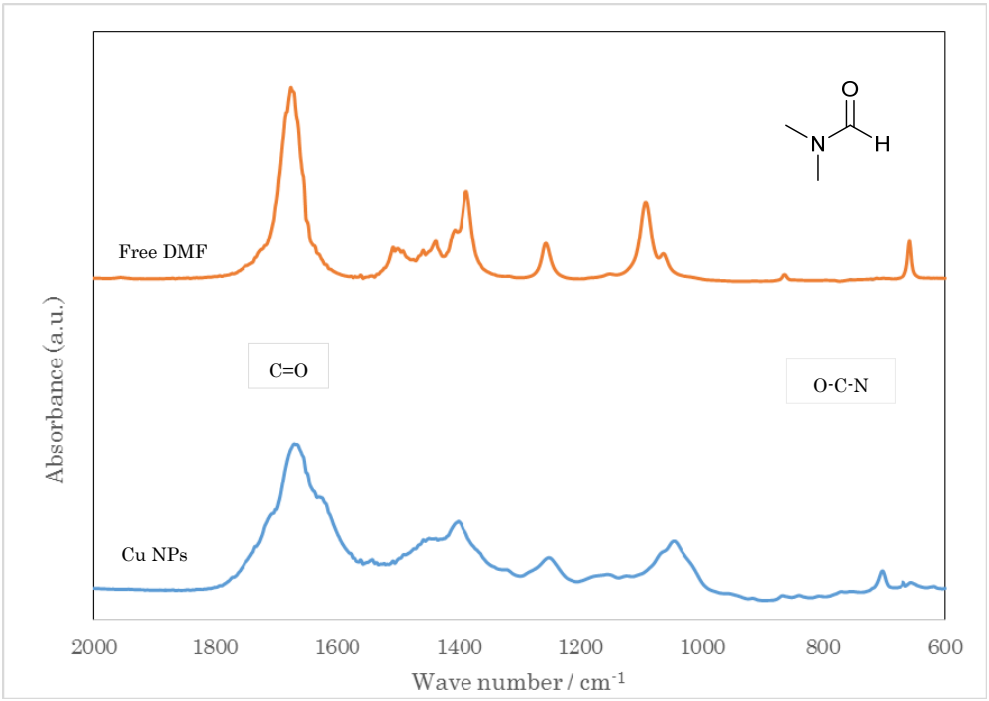

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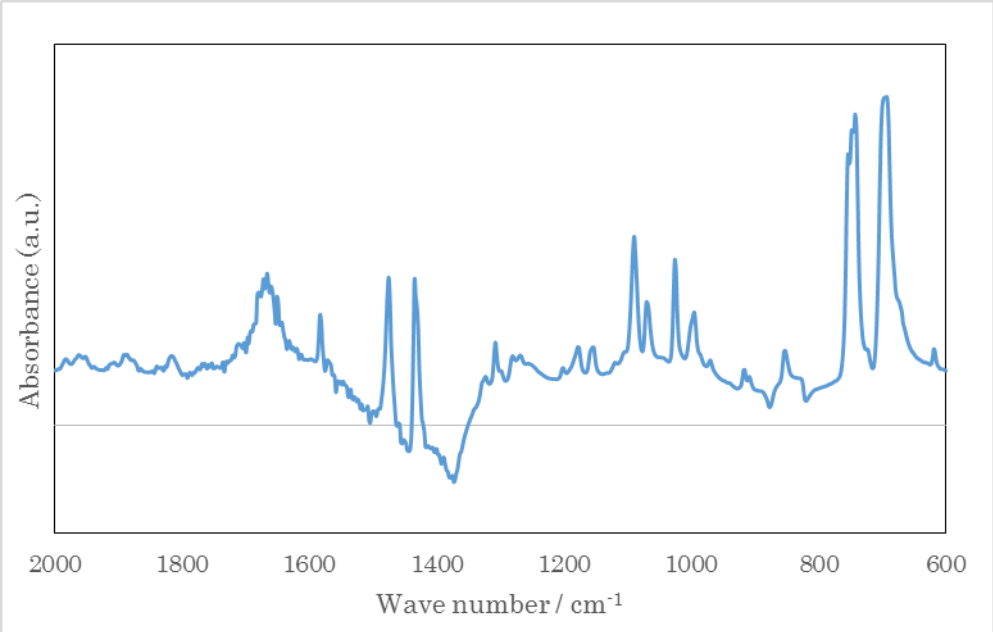
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800
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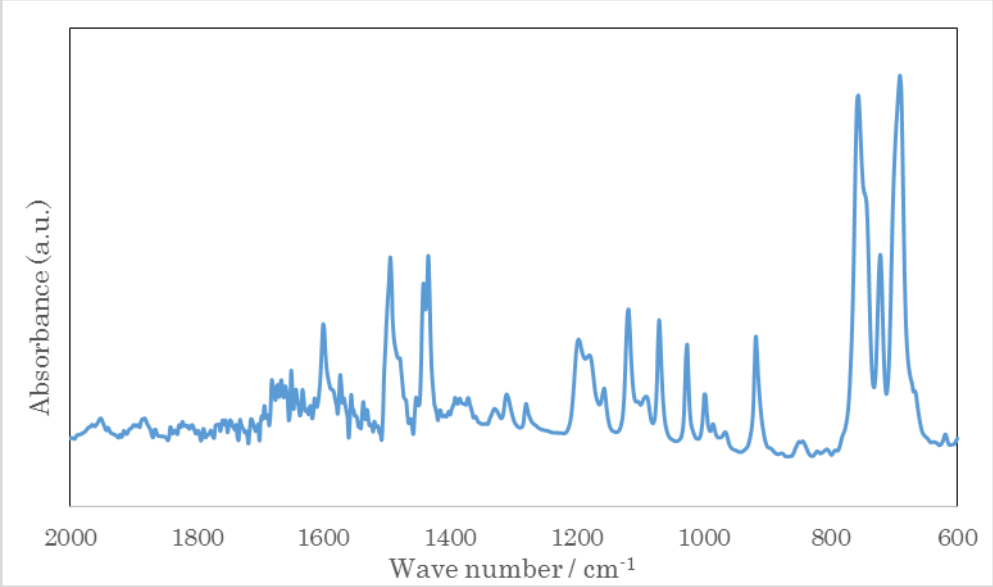
Wave number / cm-1

(c)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Wave number / cm-1

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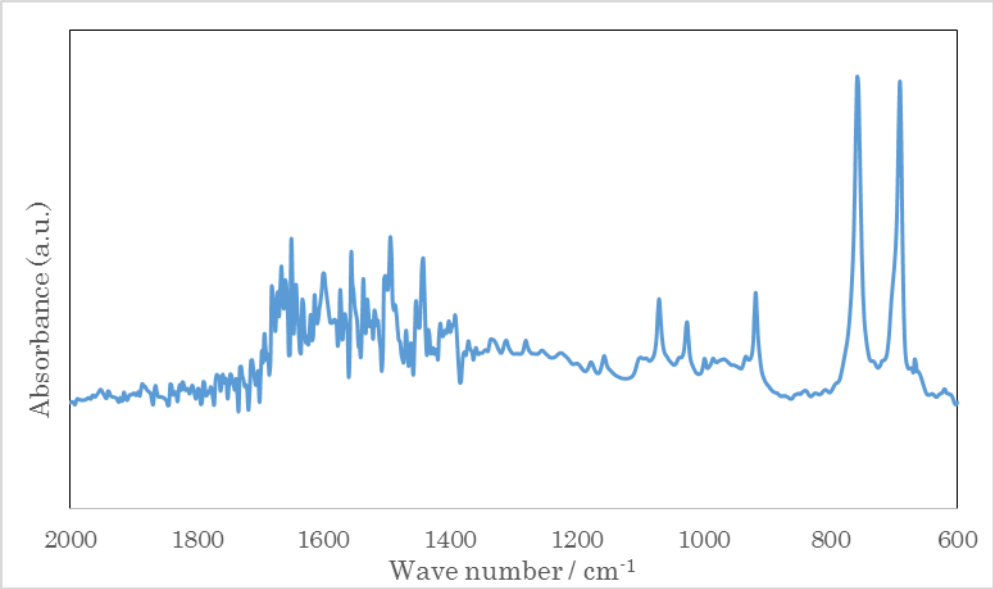

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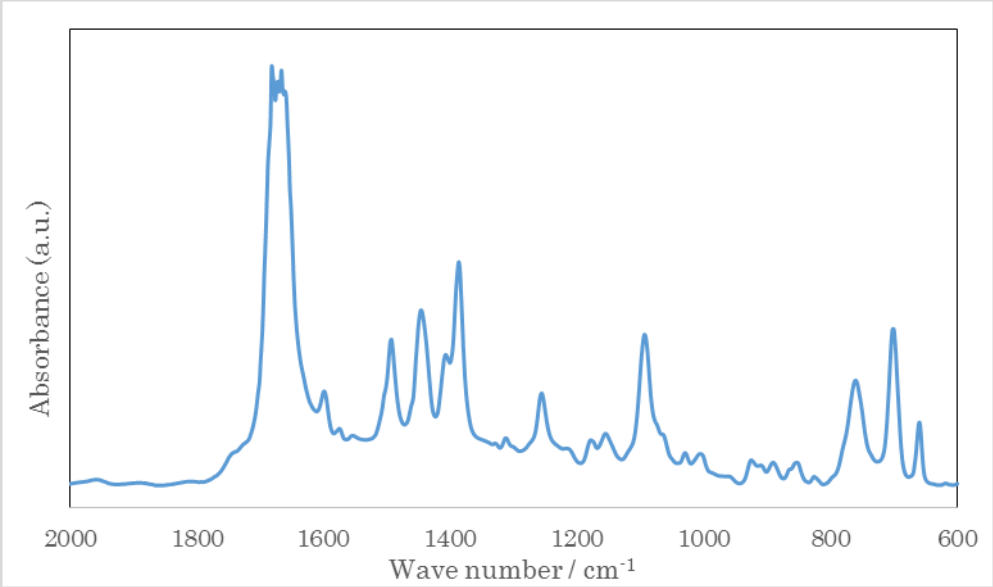


Fig. S2. FT-IR spectra of (a) free DMF (red) and the DMF-stabilized Cu NPs (blue); (b) A mixture of the Cu NPs, PPh_3, **1a**, **2a**, and K_2CO_3 before the reaction began (under the condition of entry 2, Table 1); (c) A mixture of the Cu NPs, PPh_3, **1a**, **2a**, and K_2CO_3 after the reaction finished (under the condition of entry 2, Table 1). (d) A mixture of the Cu NPs, bpy, **1a**, **2a**, and K_2CO_3 after the reaction finished (under the condition of entry 6, Table 1) (e) A mixture of the Cu NPs, PCy_3, **1a**, **2a**, and K_2CO_3 after the reaction finished (under the condition of entry 4, Table 1) .

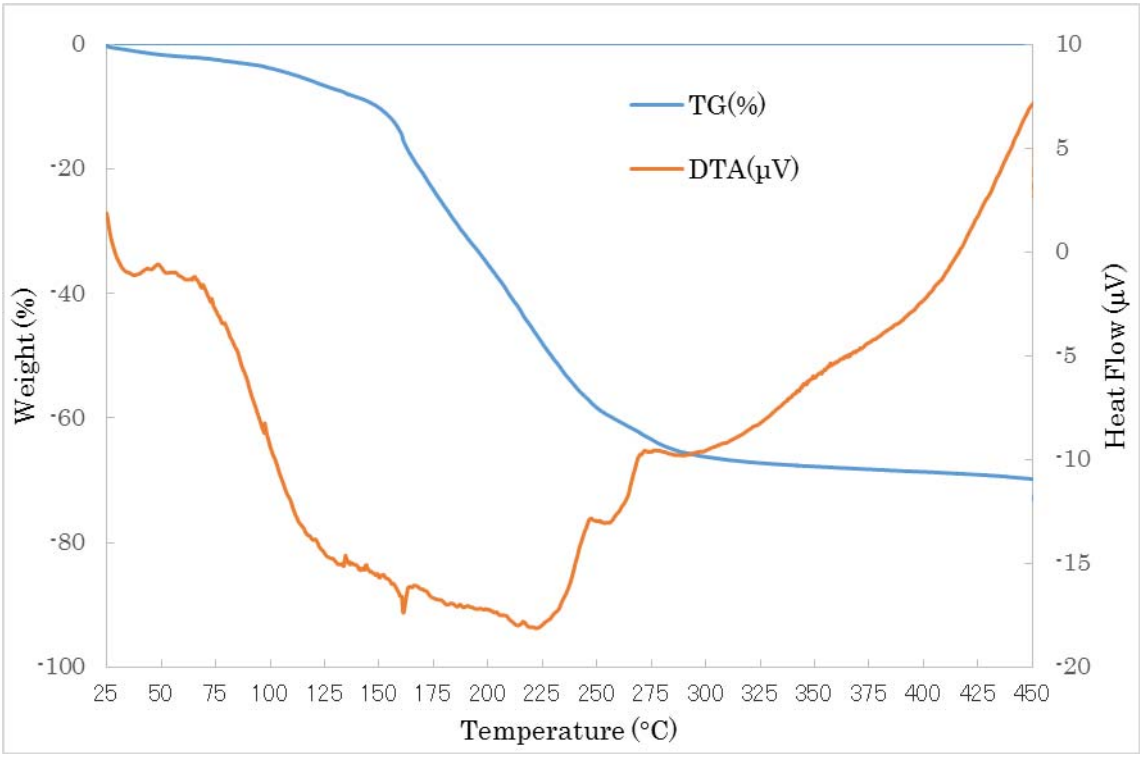
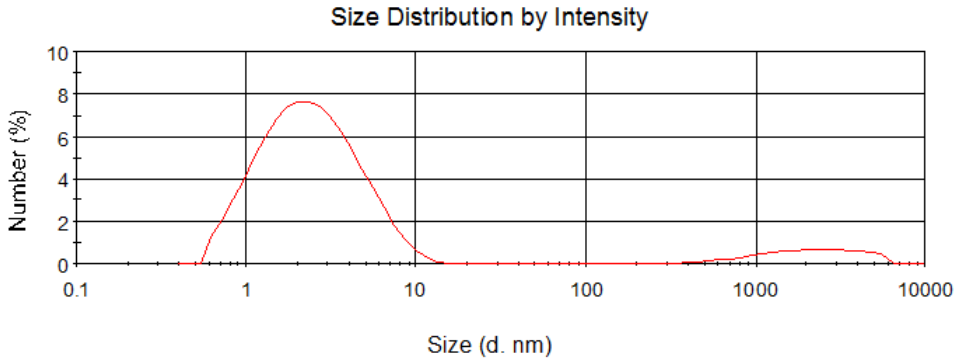
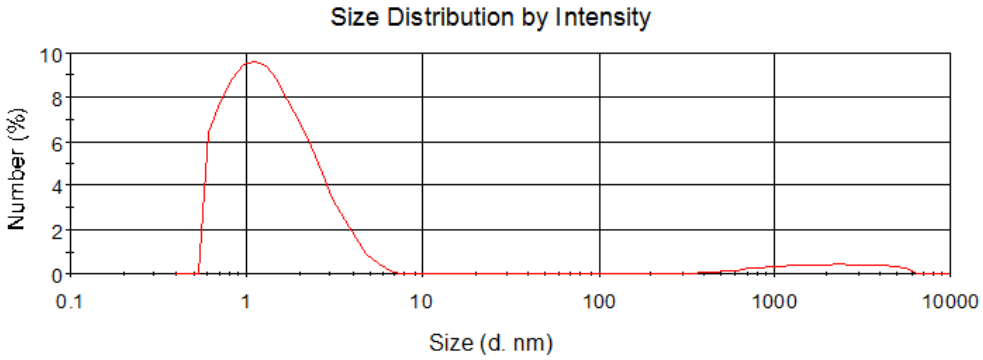


Fig. S3. TG-DTA spectra of the DMF-stabilized Cu NPs

a) DMF-stabilized Cu NPs (100 mM, 25°C)



b) After the reaction under the conditions of entry 2, Table 1 (1 mM, 25°C).



c) After the reaction under the conditions of entry 6, Table 1 (1 mM, 25°C).

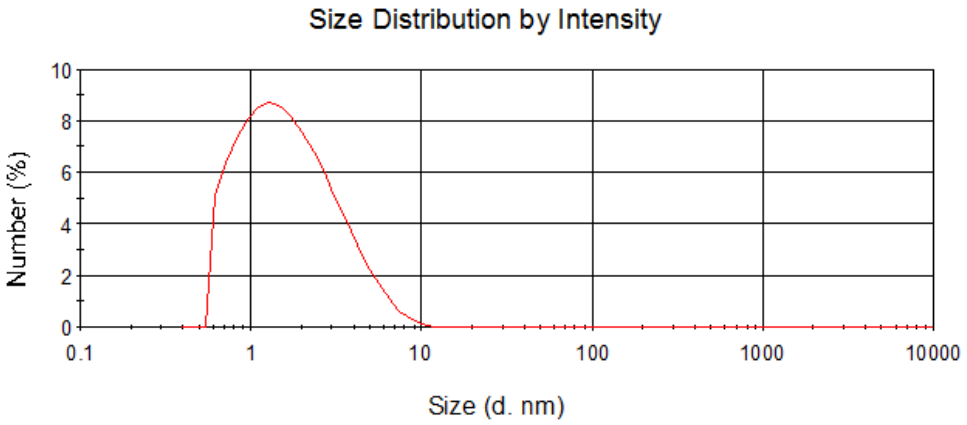


Fig. S4. Particle size distribution by DLS analysis (a) DMF-stabilized Cu NPs and (b) after the reaction using PPh_3 as stabilizer; (c) after the reaction using bpy as stabilizer.

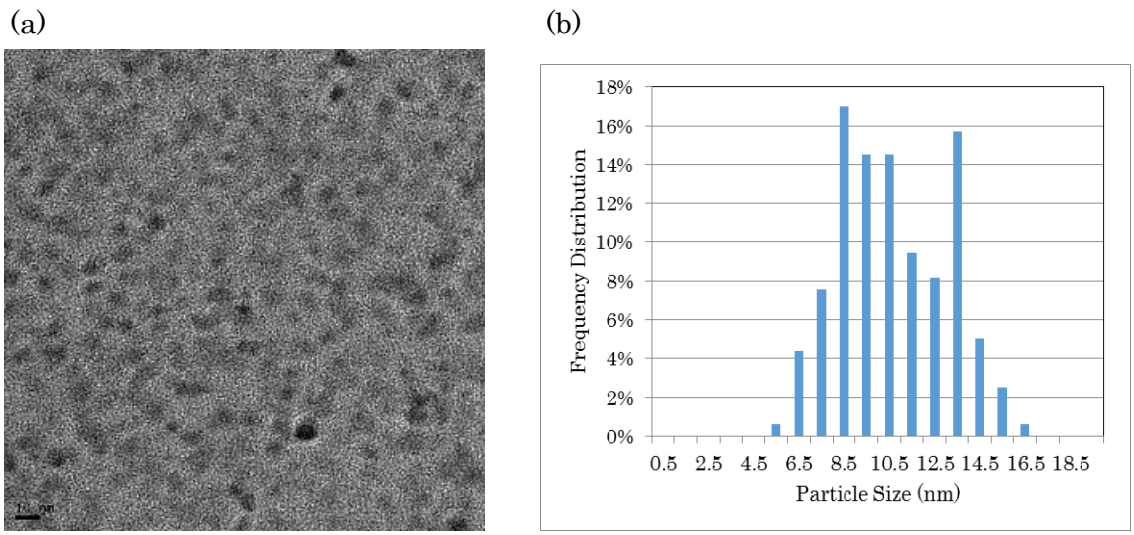


Fig. S5. (a) TEM image (bar scale = 10 nm) and (b) particle size distribution after reaction without PPh_3 (under the conditions of entry 1, Table 1).

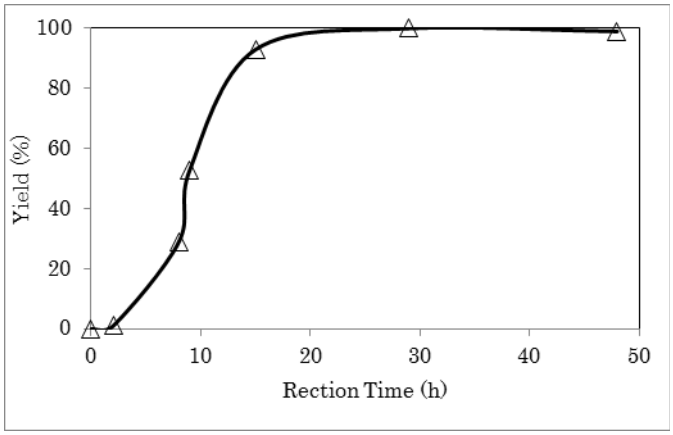


Fig. S6. Time-yield curve for the formation of **3a** under the conditions as entry 2, Table 1.

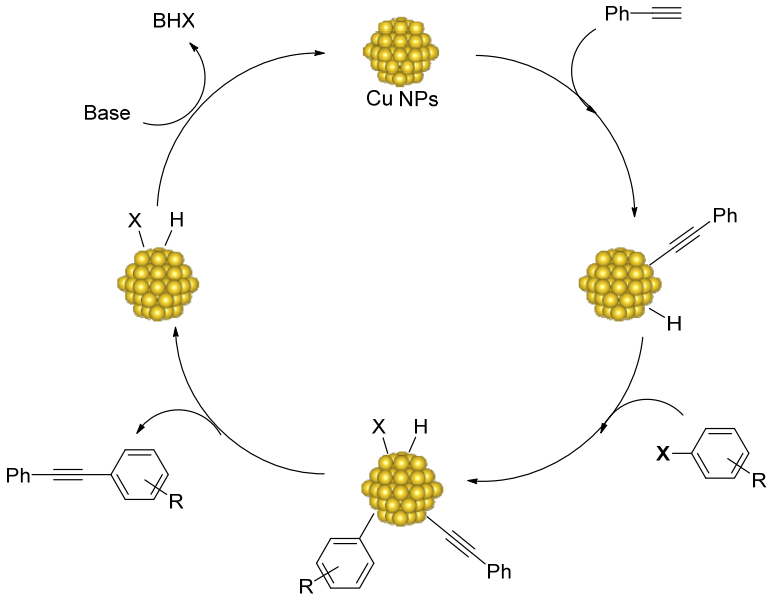


Fig. S7. A plausible reaction mechanism of Cu NPs catalyzed Sonogashira coupling.[11]

Reference

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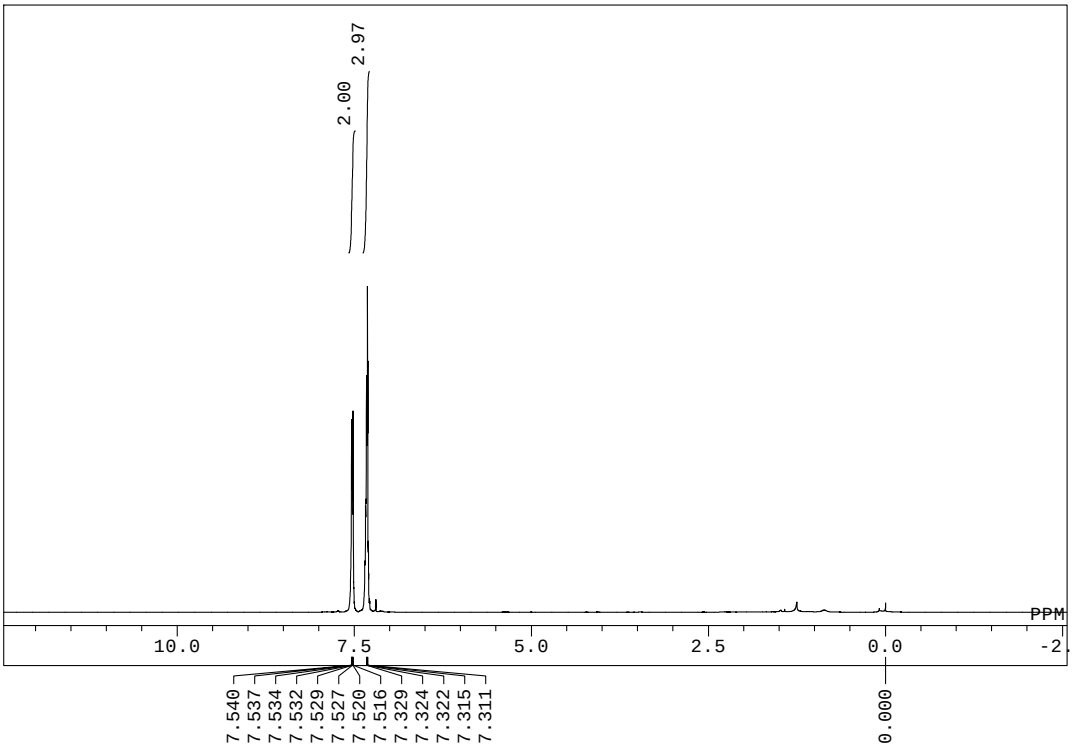
3a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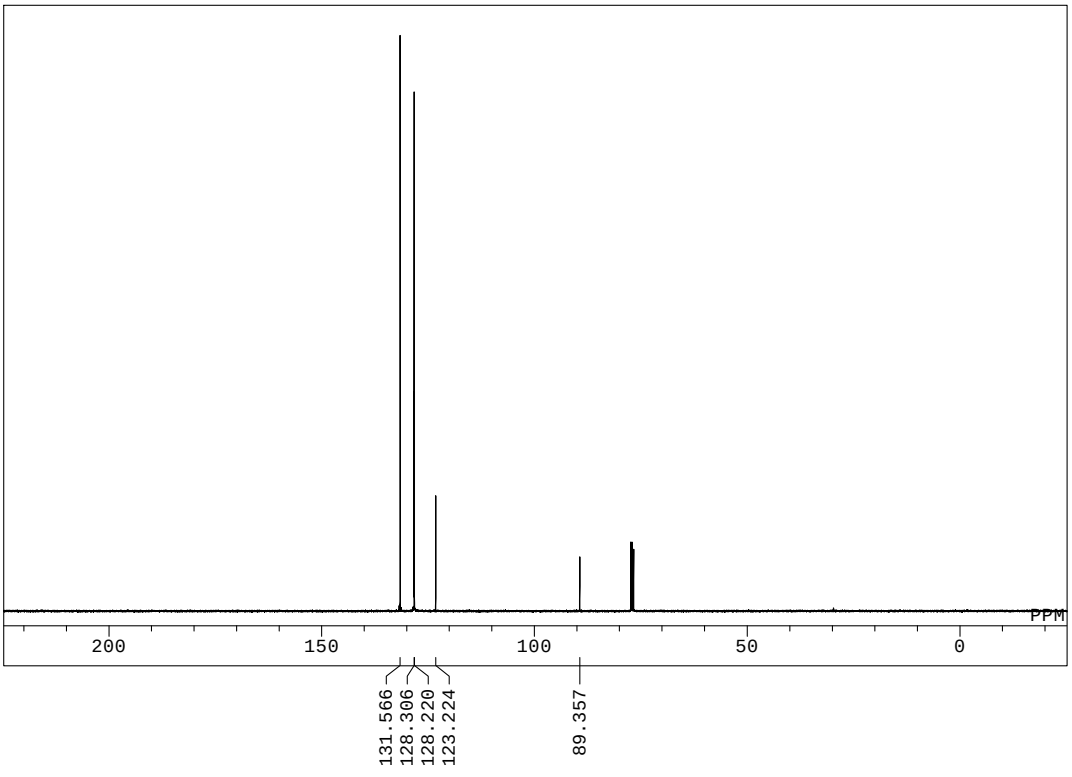
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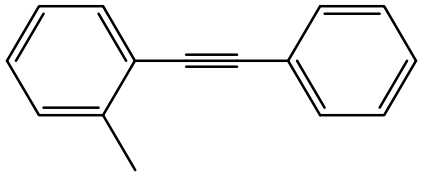

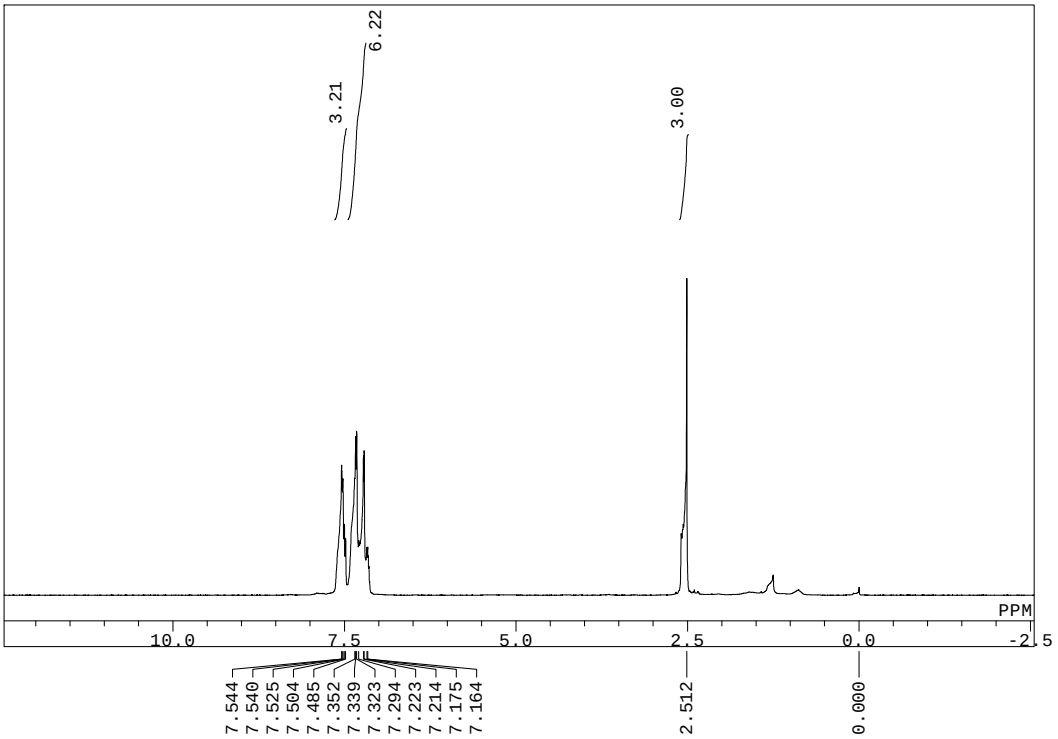
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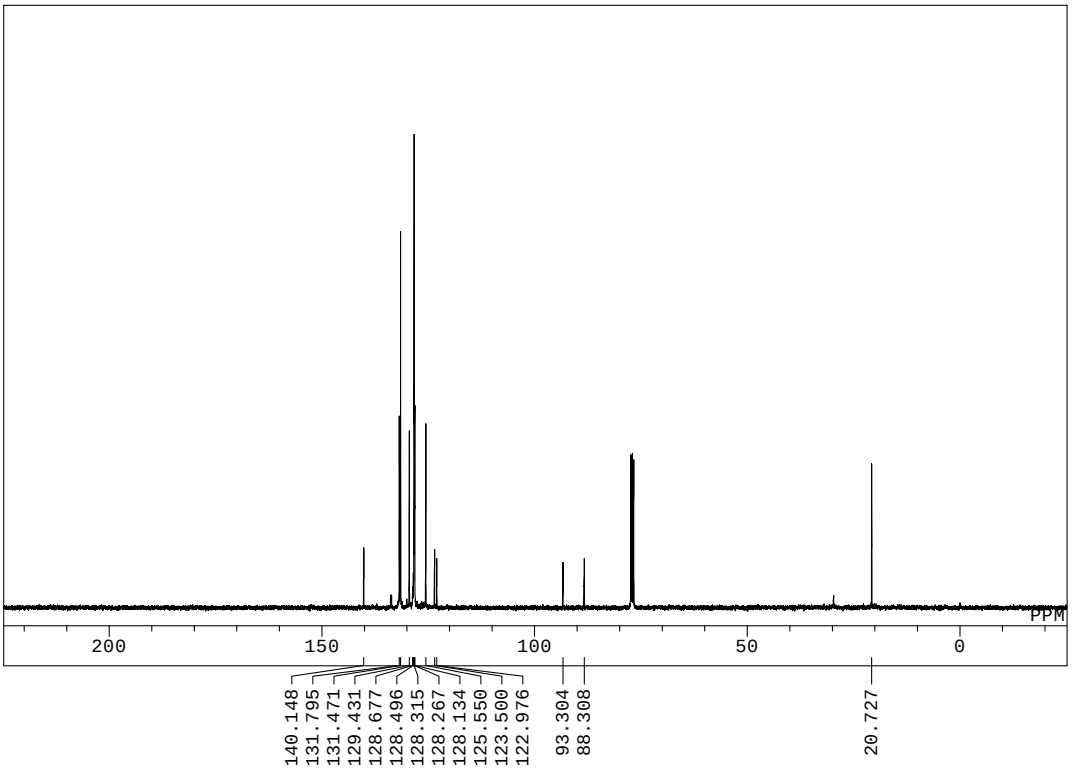
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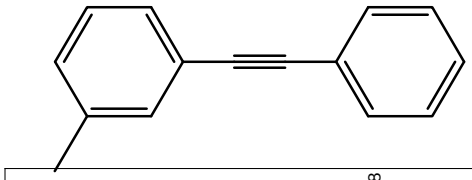

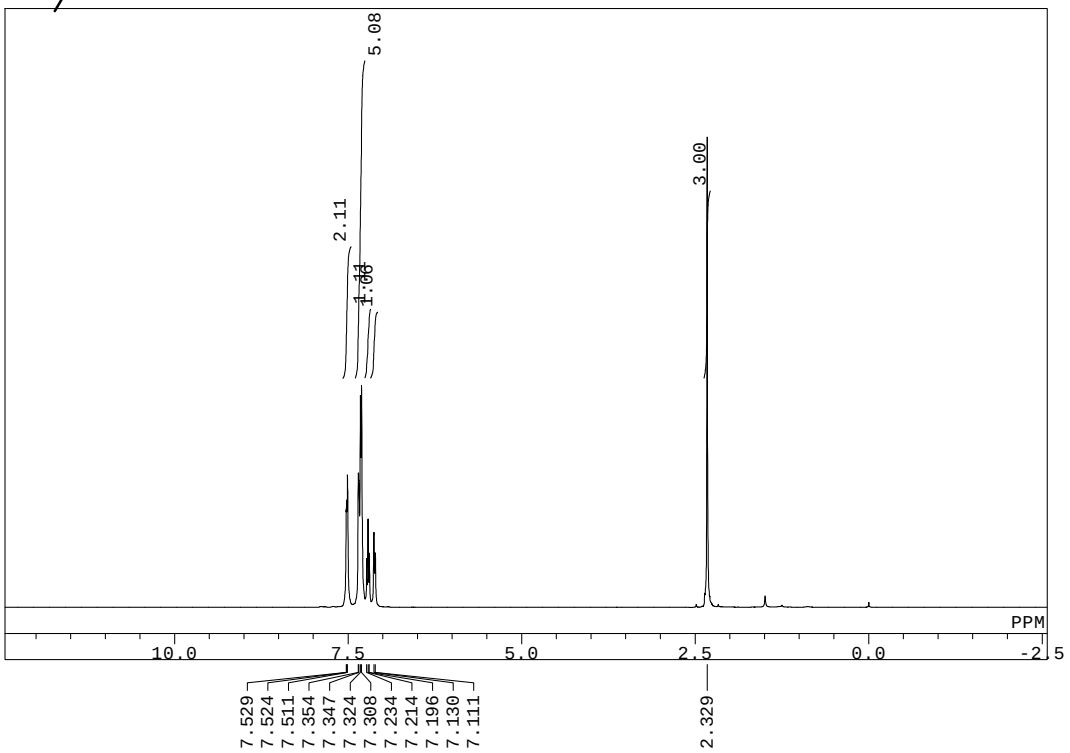
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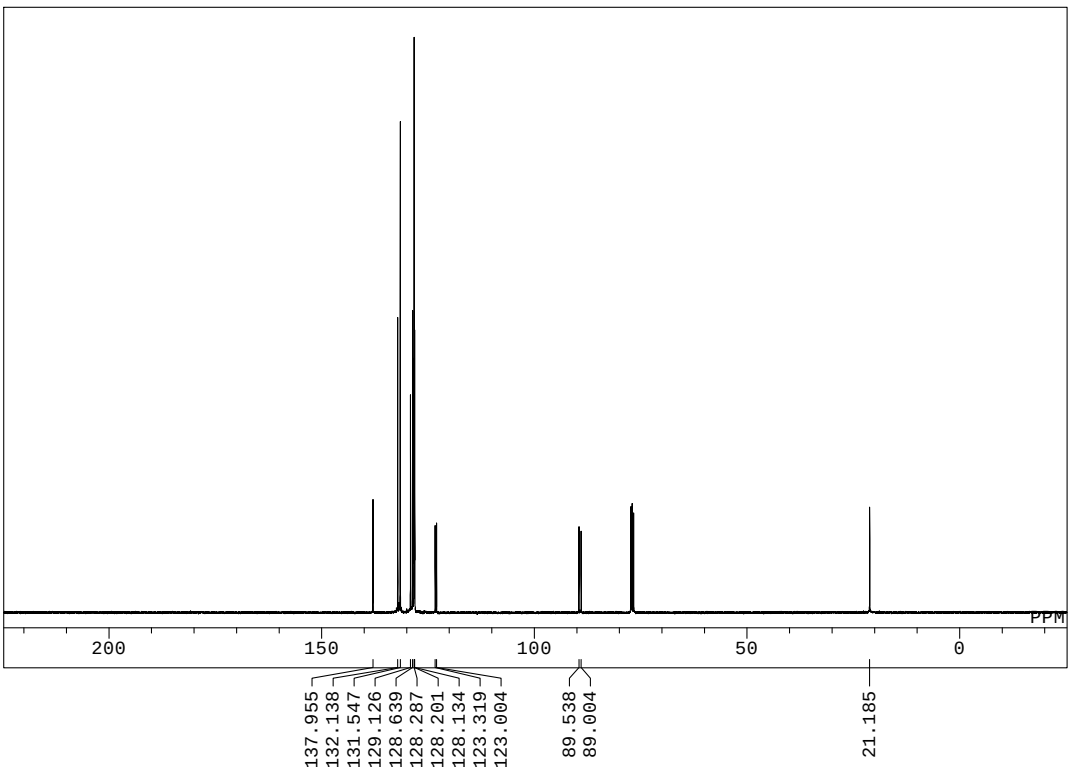
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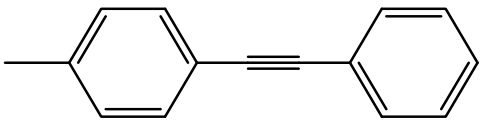

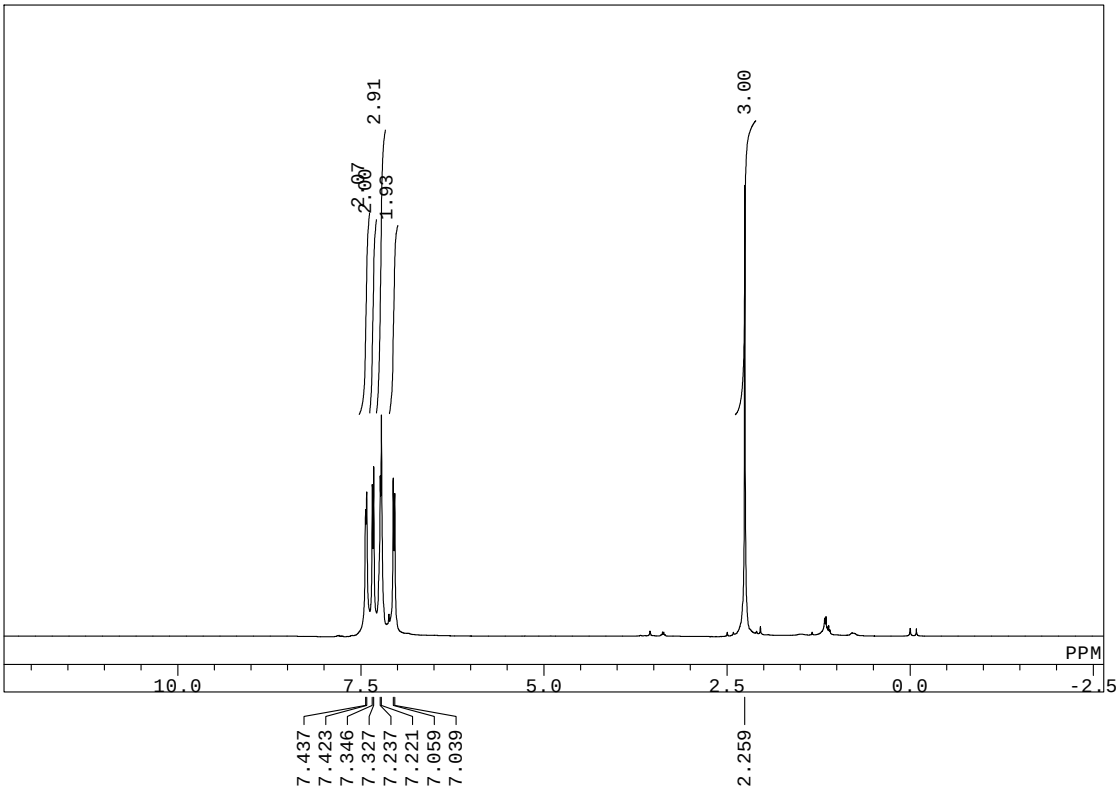
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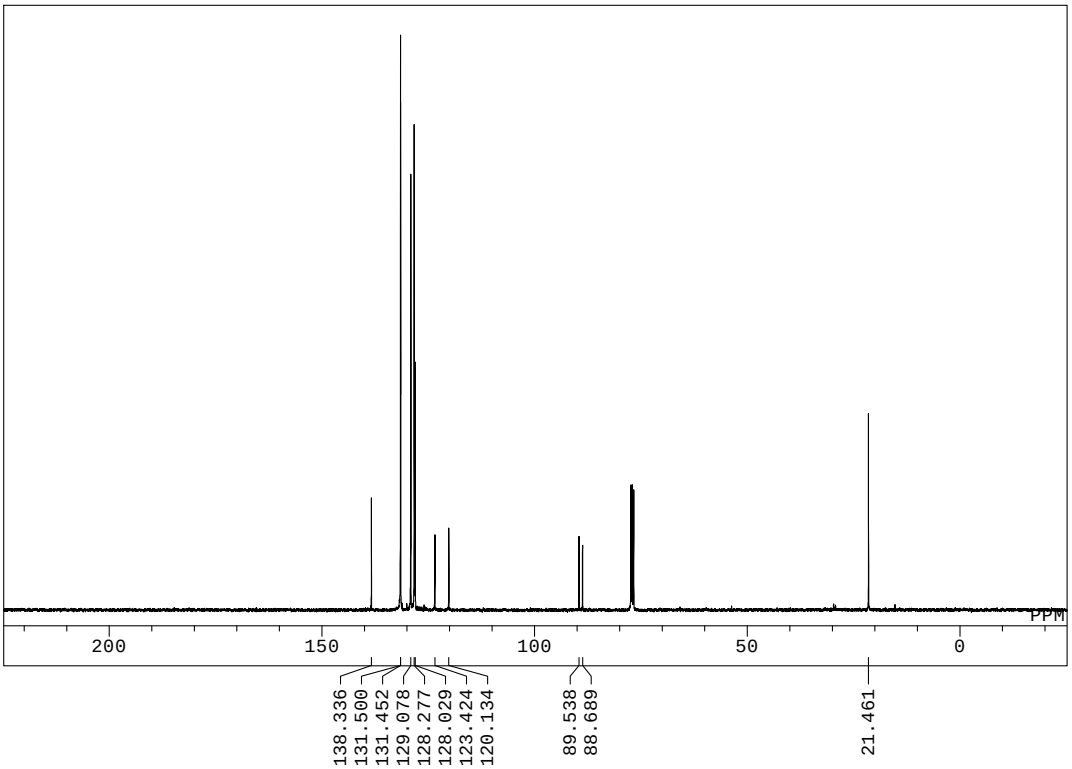
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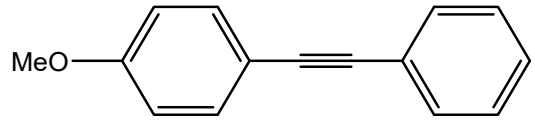
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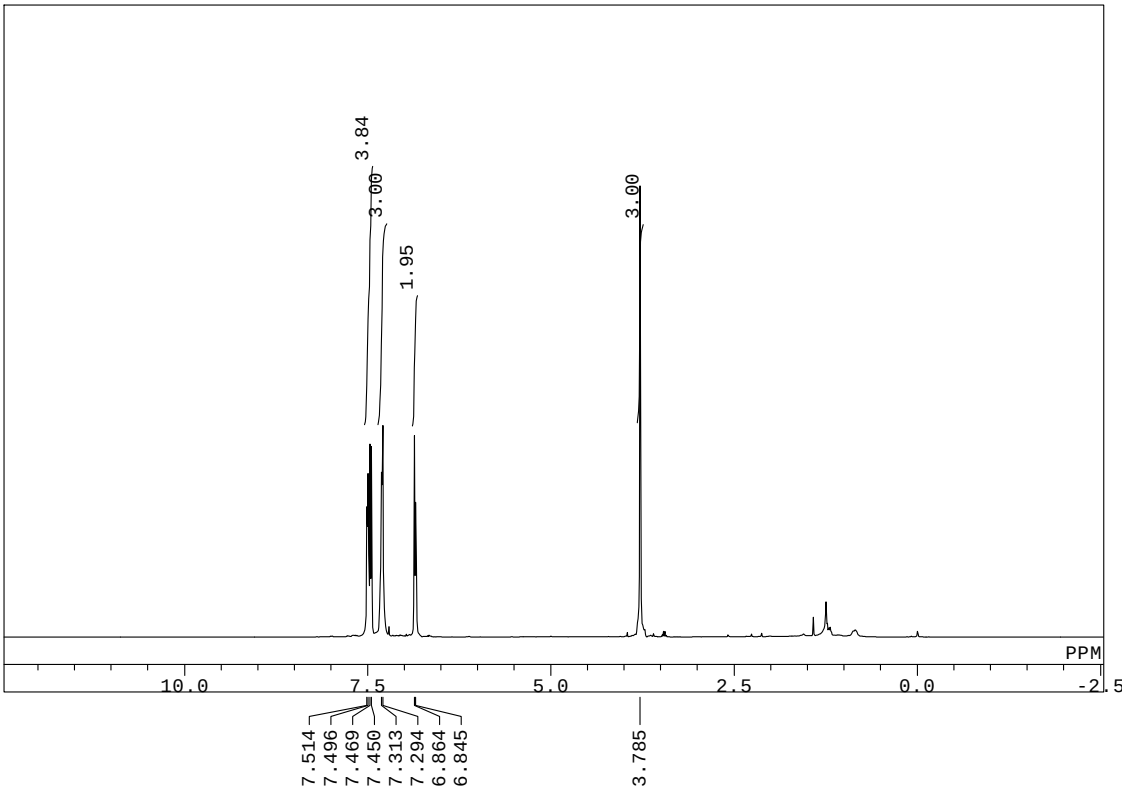
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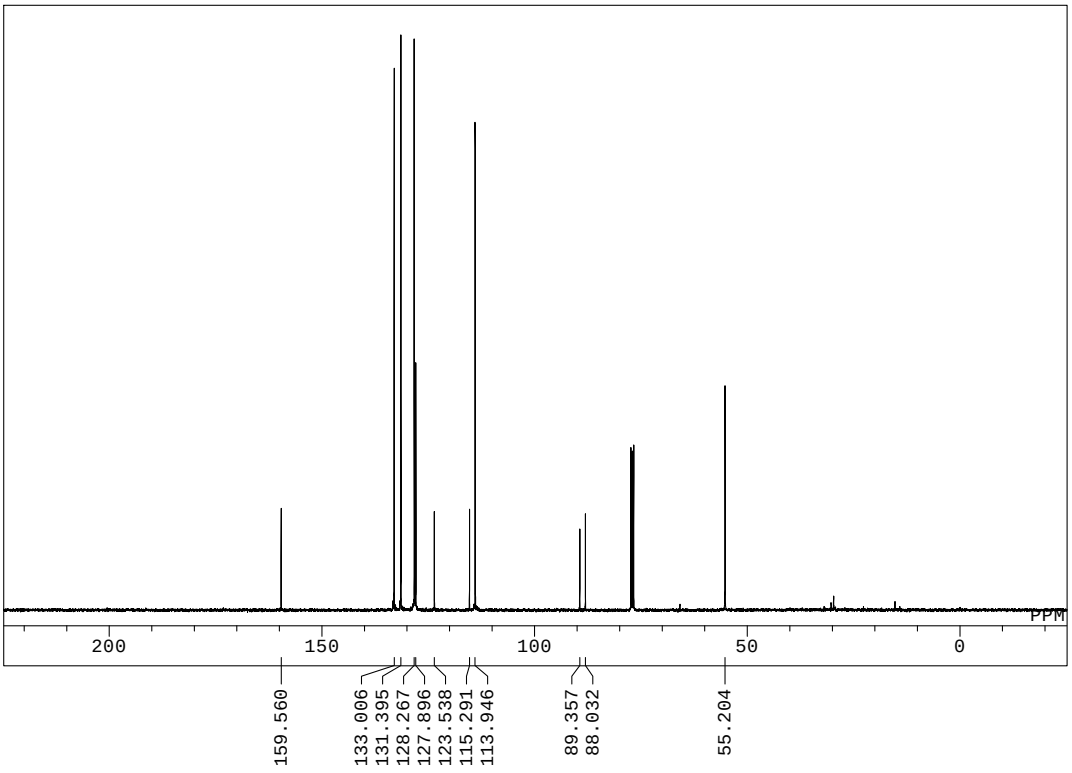
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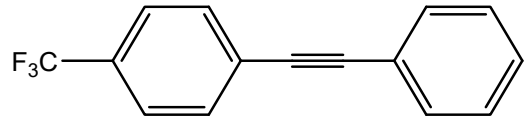
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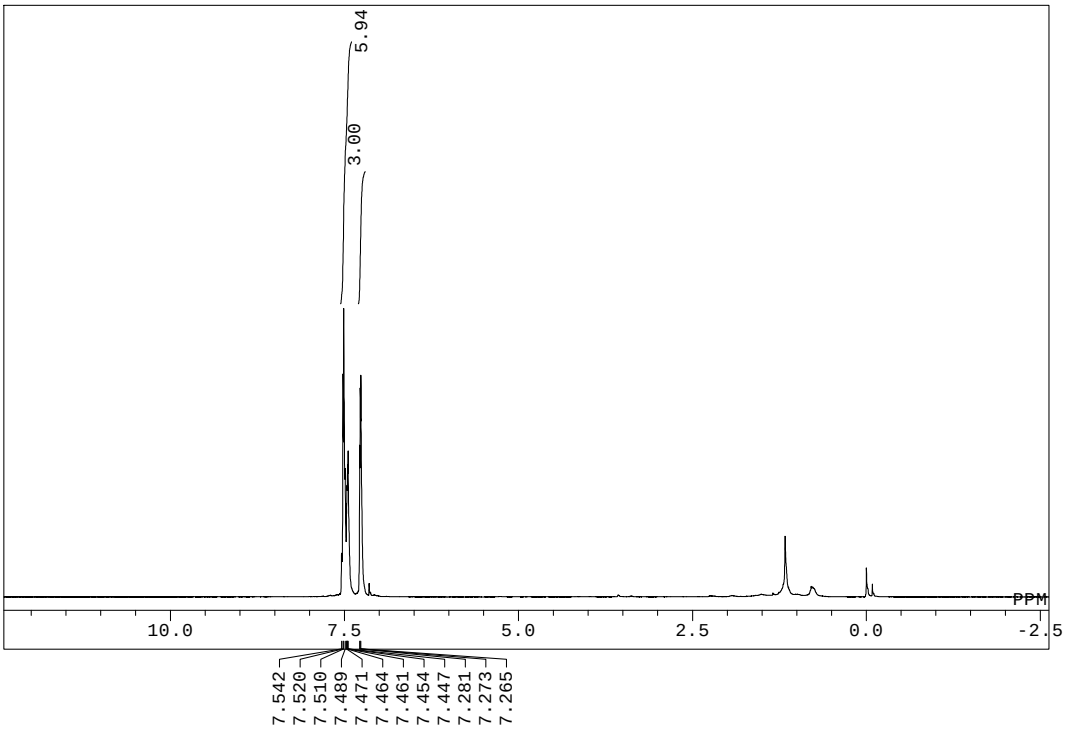
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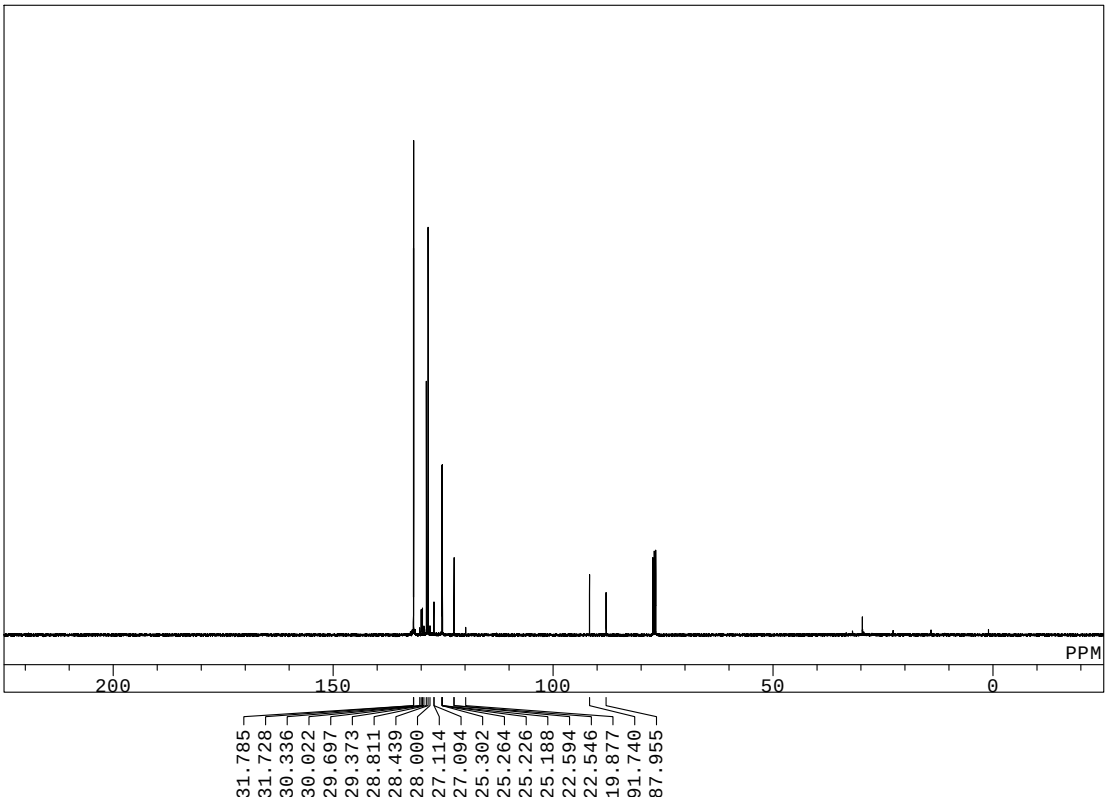
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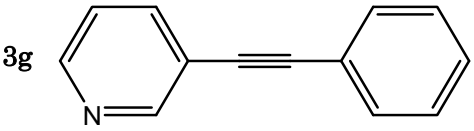
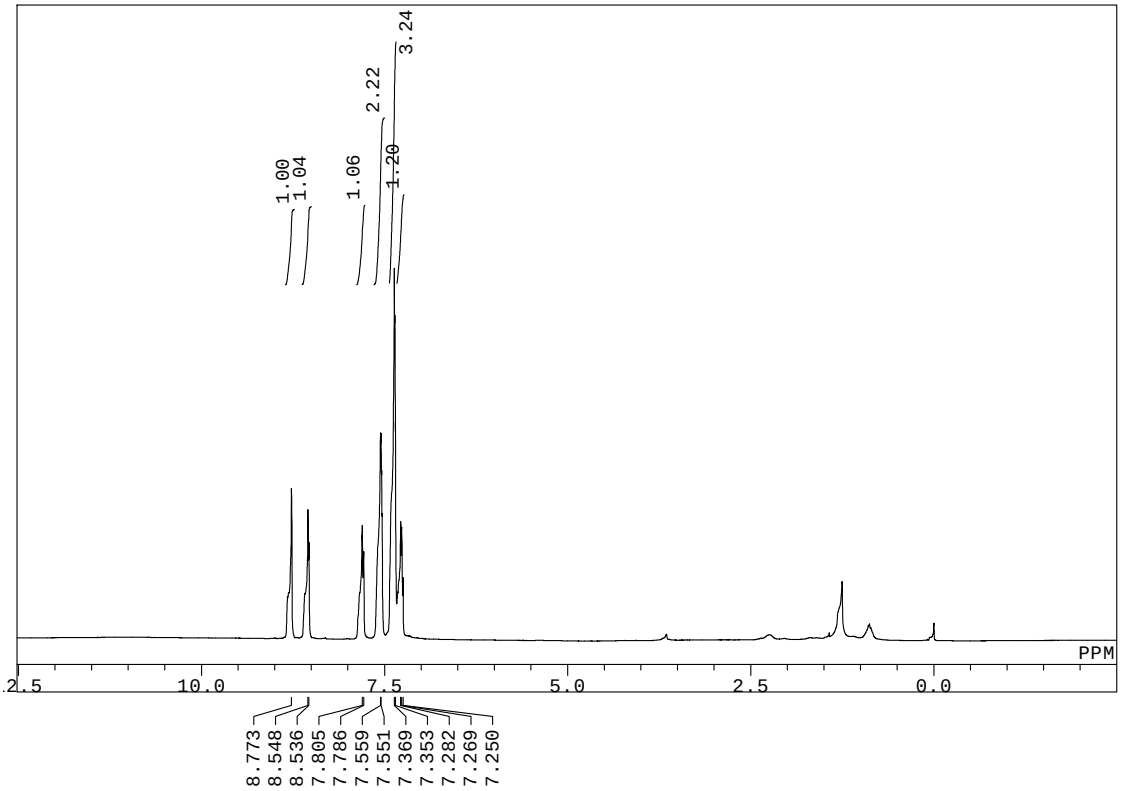
3g

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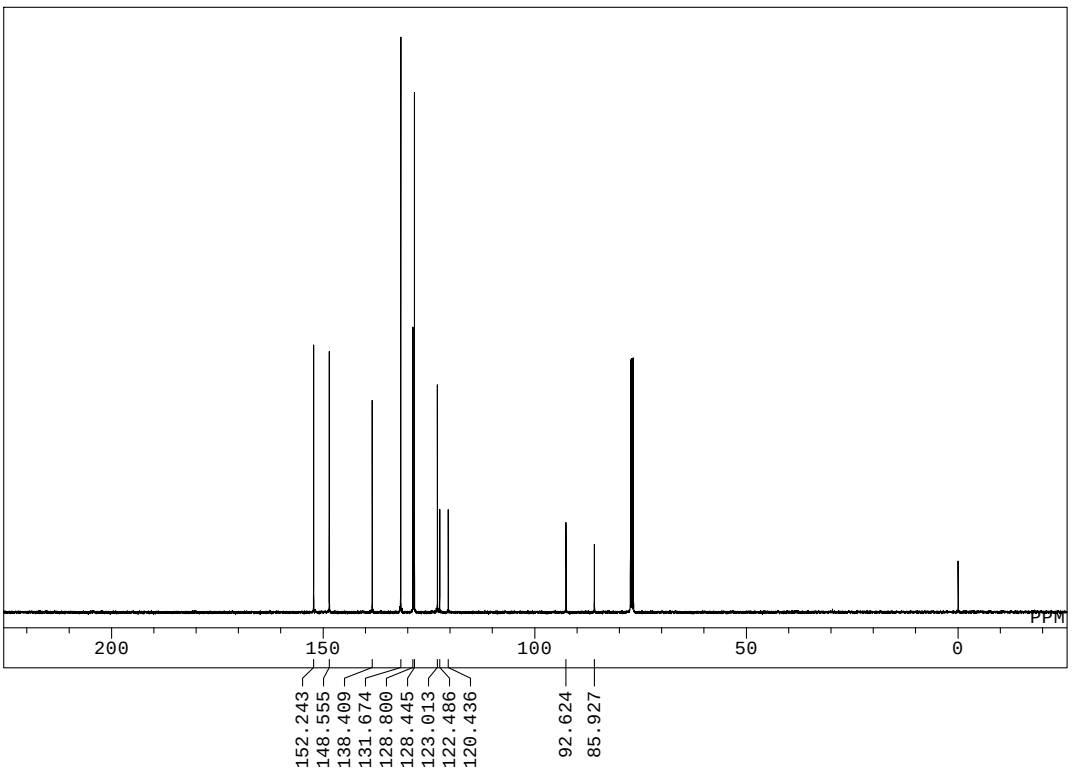
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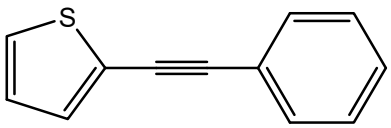
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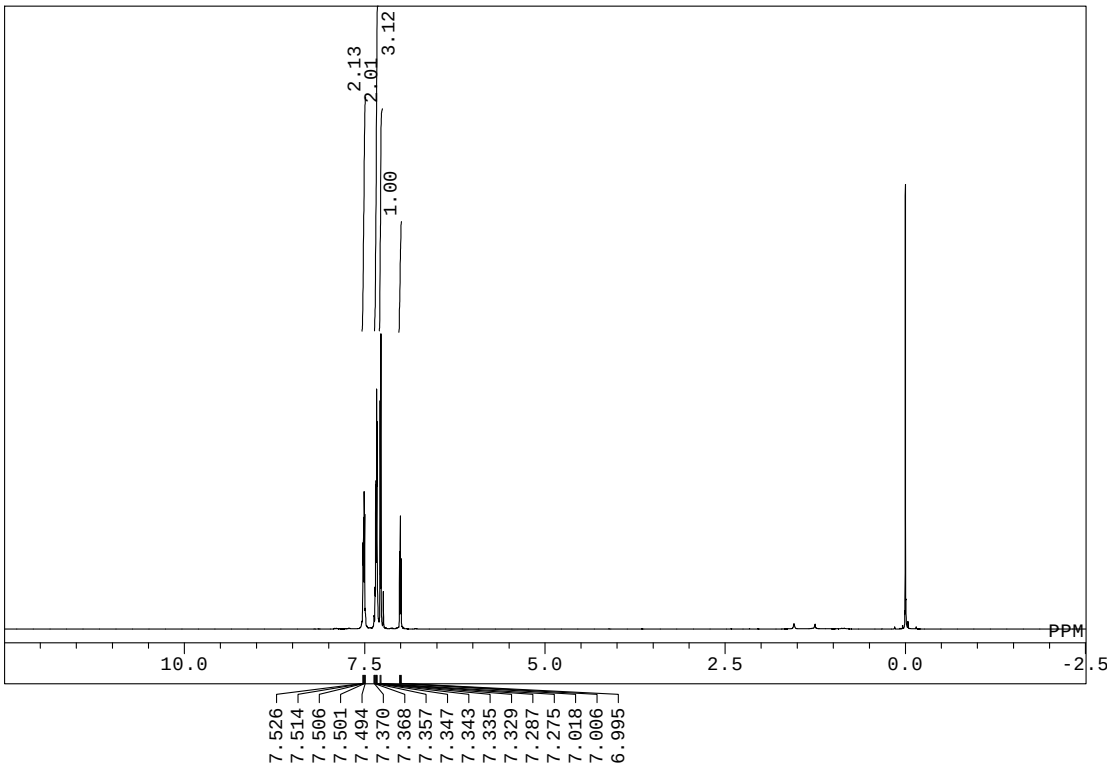
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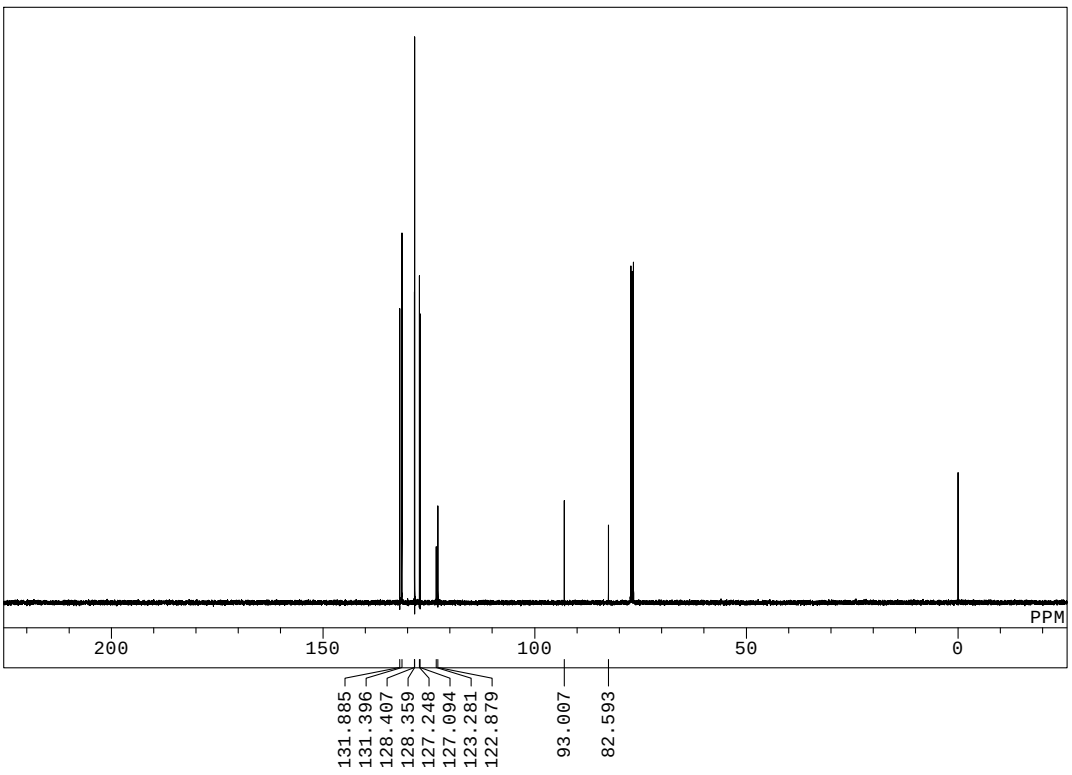
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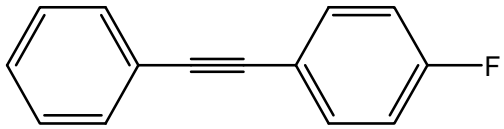
3i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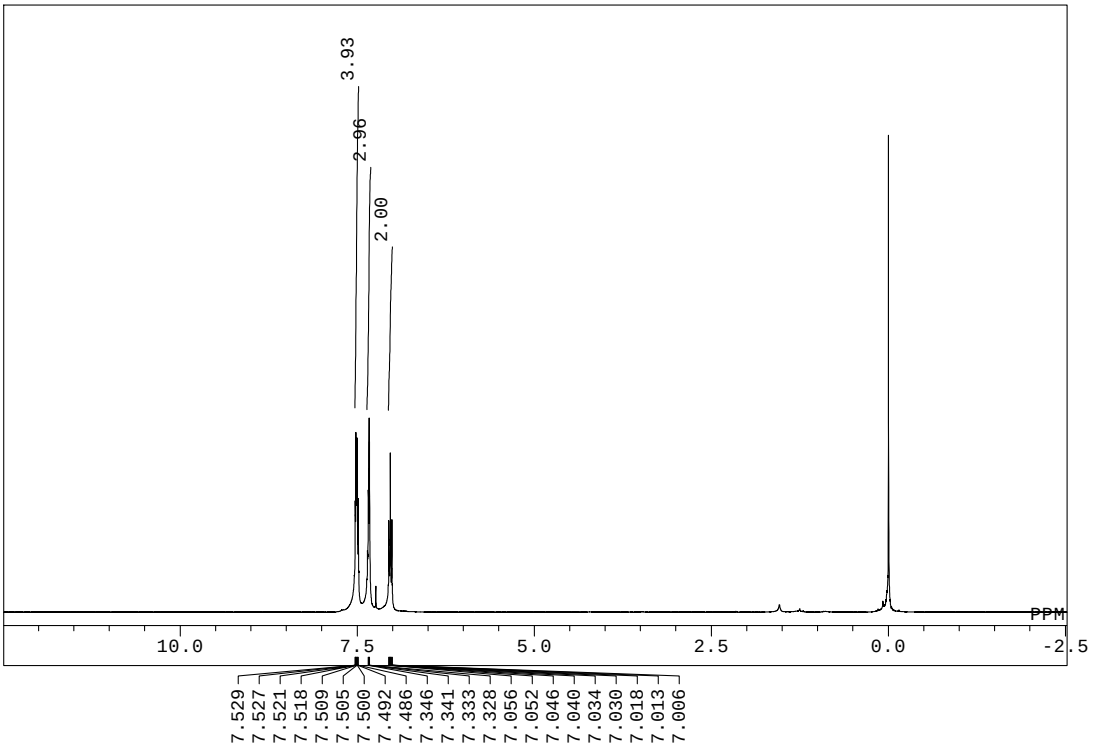
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7.518
7.509
7.505
7.500
7.492
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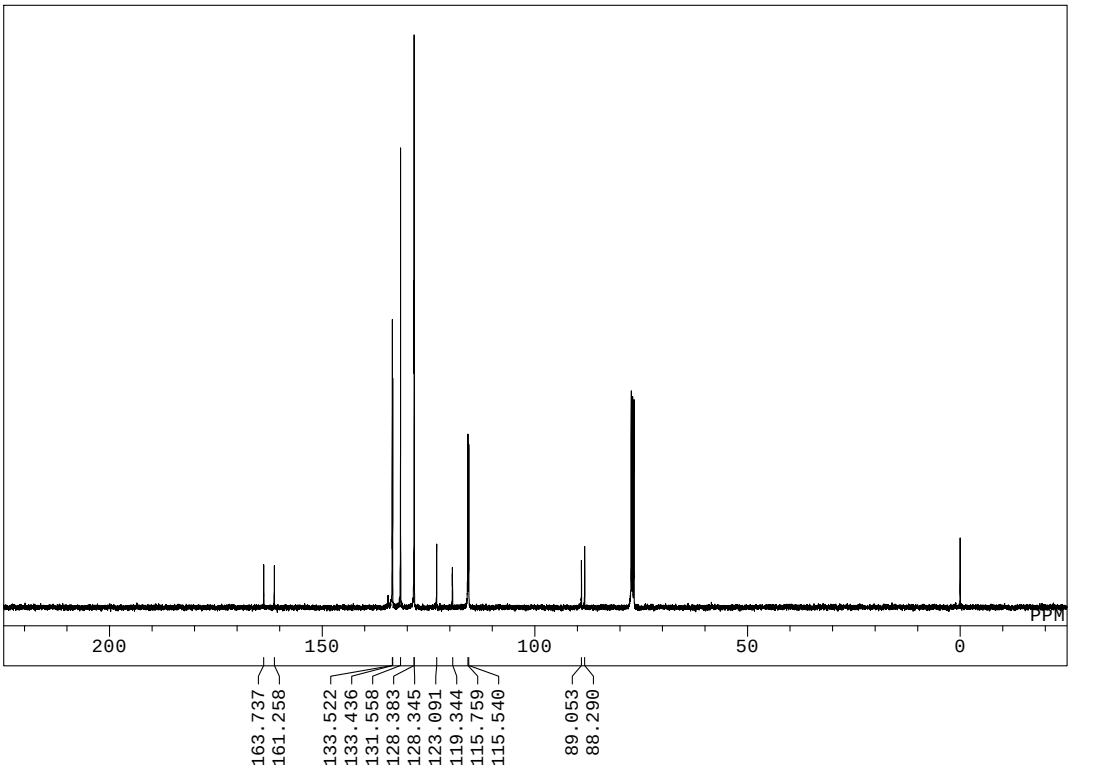
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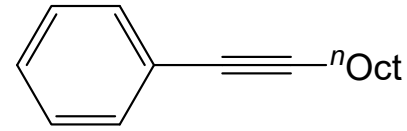
3j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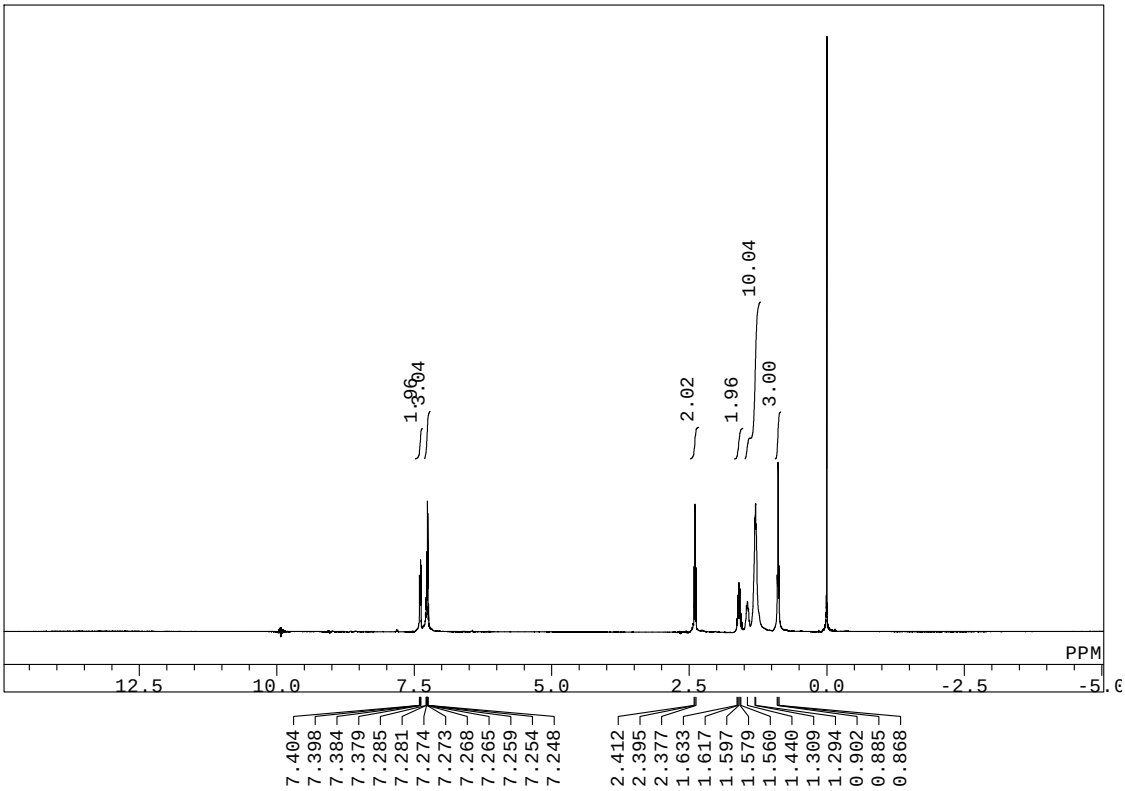
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7.281
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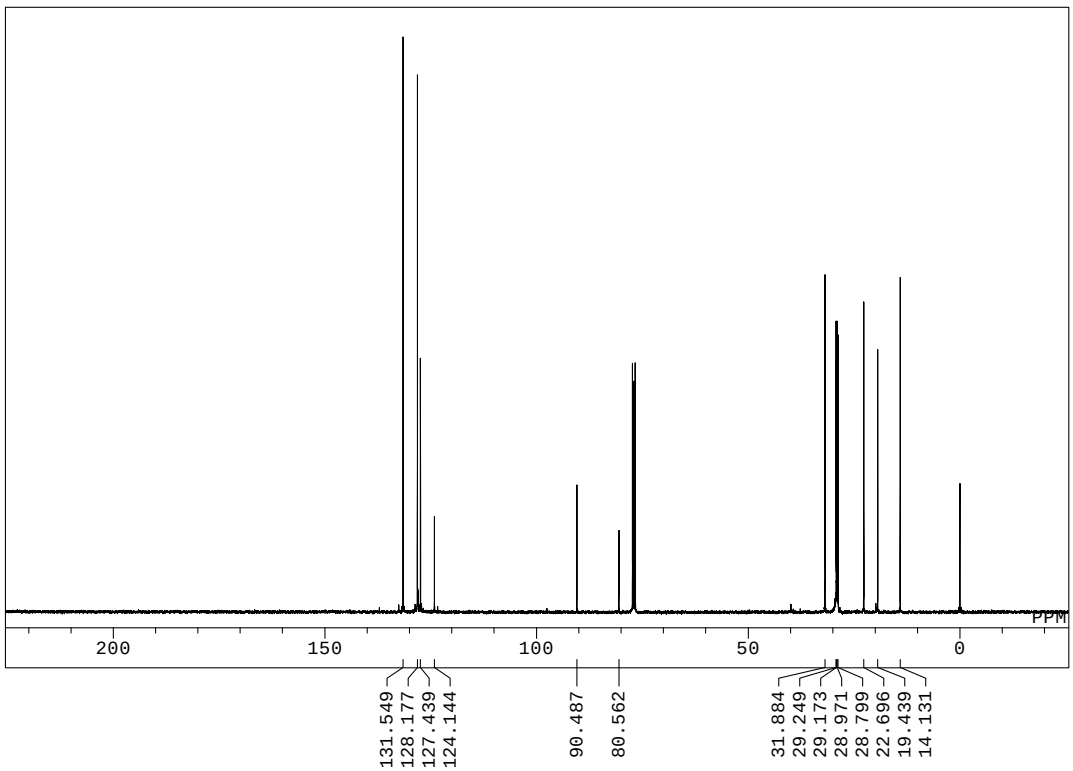
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14.131