

Supporting Information

Design and synthesis of a new functionalized-clay composite for stabilization of palladium nanoparticles. Application as a recoverable catalyst for C-C bond formation reactions

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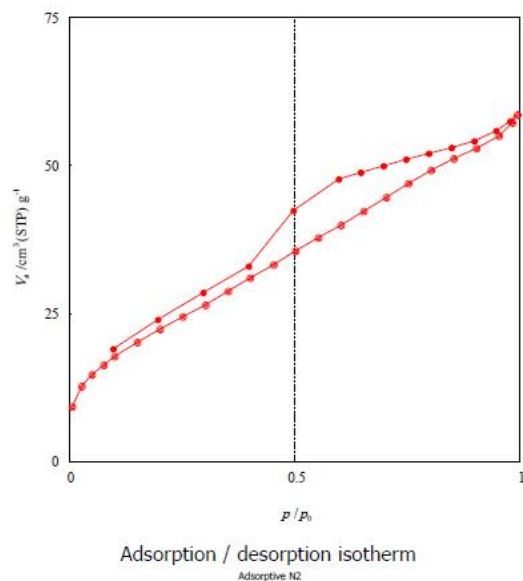


Fig. S1. The adsorption/desorption isotherm for palladium nanoparticles supported on CCPIL

Experimental Section

General

Solvents, reagents and chemicals were purchased from Merck, Fluka, Acros and Sigma Aldrich Chemical Companies. Liquid NMR was obtained on a DMX-250 and DMX-400 MHz Bruker Avance instrument using CDCl_3 as solvent and TMS as internal standard. X-ray diffraction (XRD, D8, Advance, Bruker, axs) spectrum was used to characterize the catalyst. Transmission electron microscope (TEM) analyses were performed on a Philips model CM 10 instrument. The amount of palladium on CCPIL was determined by ICP analyzer (Varian, Vista-pro). Thermogravimetric analysis was conducted from room temperature to 800°C in an oxygen flow using a NETZSCH STA 409 PC/PG instrument. The surface area of the prepared materials was determined by the nitrogen sorption analysis (Belsorp, BELMAX, Japan). FT-IR spectra were recorded using a Bruker Vektor 22 instrument after mixing of samples with KBr.

Gram-scale preparation of phosphinite-functionalized IL supported on the sheets of clay (CCPIL):

The epoxy-functionalized clay was prepared by the method reported in the literature.^{S1} Typically, the glycidylpropyltrimethoxy silane (11.1 mmol) was added to a stirred solution of MgCl₂·6H₂O (8.3 mmol, 1.68 g) in ethanol (50 mL). Sodium hydroxide solution (200 mL, 0.05 M) was added quickly and the white suspension stirred for 24 h at room temperature. The precipitated white solid was isolated by centrifugation, washed with water (3 × 50 mL) and ethanol (1 × 50 mL) and dried at 65 °C in air atmosphere. In order to build up the ionic moiety on the surface of the clay, the epoxy-functionalized clay (1 g) was dispersed in CH₂Cl₂ (10 mL) by sonication (5 min). 1-Methyl imidazole (5 mmol) was added to the reaction vessel followed by diphenyl phosphine chloride (5 mmol) and allowed the reaction to stir at 60 °C for 24 h under argon atmosphere. The resulted material was separated by simple filtration. Subsequently, washing with CH₂Cl₂ in a Soxhlet apparatus for 24 h and drying by evacuation gave the desired organic-inorganic hybrid material.

Gram-scale preparation of palladium nanoparticles deposited on supported IL on the sheets of clay:

Powdered CCPIL (1g) was dispersed in an aqueous solution of PdCl₂ (100 mL, 1 mM) and stirred at room temperature for 24 h. The clay material was separated by simple filtration. Washing the composite with water in a Soxhlet apparatus for 24 h and drying under vacuum at 50°C for 24 h gave the target material **3**.

General procedure for Suzuki-Miyaura reaction:

Aryl halide (1 mmol) and phenyl boronic acid (1.2 mmol, 0.147g) were added to a flask containing the catalyst (0.01 g of the catalyst, 7.2×10^{-4} mmol of palladium) and NaOH (1.5 mmol, 0.06 g) on water (3 mL). The mixture was stirred at 80 °C in air. After completion of the reaction (monitored by TLC or GC), ethyl acetate (15 mL) was added to the reaction vessel. The catalyst was separated by simple filtration. Column chromatography on silica gel eluted with the appropriate solvent gave the desired product in excellent yields (Table 1).

Recycling of the catalyst in Suzuki-Miyaura reaction:

After completion of the reaction in the first run, the aqueous solution was removed by a syringe. Ethyl acetate (5 mL) was added to the reaction mixture to extract the organic compounds. The ethyl acetate solution was removed by a syringe and the remained catalyst was dried under nitrogen flow. After complete drying, the catalyst was charged again into the vessel containing the reacting substrates and the reaction was performed under similar conditions as mentioned above. This recycling was repeated for five consecutive runs.

General procedure for Sonogashira-Hagihara reaction:

Aryl halide (1 mmol) and phenylacetylene (1.5 mmol, 0.18 mL) were added to a flask containing Pd-nanoparticles-clay catalyst (0.01 g, 7.2×10^{-4} mmol of palladium) and KOAc (1.5 mmol, 0.147 g) in polyethylene glycol 400 (PEG400, 2 mL). The mixture was stirred at 80 °C in air. After completion of the reaction (monitored by TLC or GC) water (10 mL) and ethyl acetate (10 mL) were added to the reaction mixture and decanted. The organic phase was dried over anhydrous Na₂SO₄ and filtered. The organic solvent was removed under vacuum and the resulting residue was purified by column chromatography on silica gel using the appropriate solvent to yield the desired pure product (Table 4).

Typical procedure for Mizoroki-Heck reaction:

Bromobenzene (1 mmol, 0.1 mL) and *n*-butyl acrylate (1.5 mmol, 0.21 mL) were added to a flask containing the catalyst (0.05 g, contains 0.0045 mmol of palladium) and ⁿPr₃N (1.5 mmol, 0.29 mL). The mixture was stirred at 130 °C in the air. After completion of the reaction (monitored by TLC), ethyl acetate (15 mL) was added to the reaction vessel. The catalyst was separated by simple filtration. Water (3 × 15 mL) was added to the ethyl acetate phase and decanted. Then, the organic phase was dried over anhydrous Na₂SO₄ and filtered. Evaporation of the solvent gave a residue which was purified by column chromatography on silica gel eluted with the appropriate solvent to give the desired product in a high yield (Scheme 3).

Reference:

S1. N. T. Whilton, S. L. Burkr, S. Mann, *J. Mater. Chem.* 1998, **8**, 1927.

NMR data:

(6a): ^1H NMR (CDCl_3 , 400 MHz): δ (ppm): 7.55-7.36 (m 4H), 7.6-7.56 (m, 4H), 7.50-7.46 (m 2H); ^{13}C NMR (101 MHz, CDCl_3) δ (ppm): 141.3, 128.9, 127.4, 127.3

(6b): ^1H NMR (CDCl_3 , 250 MHz): δ (ppm): 3.72 (s, 2 H), 6.78 (d, 2 H, $J=7.5$ Hz), 7.25-7.72 (m, 7 H); ^{13}C NMR (62.9 MHz, CDCl_3) δ (ppm): 115.39, 126.25, 126.40, 128.00, 128.65.

(6c): ^1H NMR (250 MHz, CDCl_3) δ (ppm): 2.43 (s, 3 H), 7.59-7.39 (m, 7 H), 7.71-7.74 (m, 2 H); ^{13}C NMR (62.9 MHz, CDCl_3) δ (ppm): 142, 141.3, 135, 130.4, 129.9, 129.3, 128.9, 128.2, 127.6, 126.4, 125.9, 20.6.

(6d): ^1H NMR (250 MHz, CDCl_3) δ (ppm): 2.32 (s, 3 H), 7.15-7.52 (m, 9 H); ^{13}C NMR (62.9 MHz, CDCl_3) δ (ppm): 21.11, 126.98, 127.60, 128.72, 129.49, 130.4, 141.3, 142.3.

(6e): ^1H NMR (250 MHz, CDCl_3) δ (ppm): 7.61-7.57 (m 4H), 7.48-7.29 (m, 3H), 7.04-7.01 (d, $J=8.8$, 2H), 3.89 (s, 3H); ^{13}C NMR (101 MHz, CDCl_3) δ (ppm): 159.1, 140.8, 133.8, 128.7, 128.2, 126.8, 126.7, 114.2, 55.3

(6f): ^1H NMR (250 MHz, CDCl_3) δ (ppm): 8.19 (d, 2 H, $J=9.0$ Hz), 7.63 (d, 2H, $J=9.0$ Hz), 7.53 (dd, 2 H, $J=7.5$ Hz, $J'=1.5$ Hz), 7.43-7.36 (m, 3 H); ^{13}C NMR (62.9 MHz, CDCl_3) δ (ppm): 147.6, 147.0, 138.7, 129.1, 128.9, 127.7, 127.3, 124.1.

(6g): ^1H NMR (400 MHz, CDCl_3) δ (ppm): 9.24 (s, 1H), 8.99 (s, 2H), 7.63-7.50 (m, 5H); ^{13}C NMR (101 MHz, CDCl_3) δ (ppm): 157.3, 154.9, 134.4, 134.2, 129.4, 129.1, 127.0.

(6h): ^1H NMR (250 MHz, CDCl_3) δ (ppm): 7.50-7.17 (m, 8 H).

(6i): ^1H NMR (400 MHz, CDCl_3) δ (ppm): 8.8 (s, 1H), 8.60-8.58 (d, $J= 4.4$, 1H), 7.87-7.84 (d, $J= 8$, 1H), 7.58-7.55 (m, 2H), 7.49-7.33 (m, 4H); ^{13}C NMR (101 MHz, CDCl_3) δ (ppm): 148.44, 148.26, 137.77, 136.64, 134.41, 129.11, 128.14, 127.14, 123.62.

(8a): ^1H NMR (CDCl_3 , 250 MHz): δ (ppm): 7.34-7.37 (m, 6 H), 7.53-7.57 (m, 4 H); ^{13}C NMR (CDCl_3 , 62.9 MHz): δ (ppm): 89.38, 123.27, 128.35, 129.21, 131.61.

(8b): ^1H NMR (CDCl_3 , 250 MHz): δ (ppm): 2.44 (s, 3 H), 7.14-7.46 (m, 9 H); ^{13}C NMR (CDCl_3 , 62.9 MHz): δ (ppm): 20.75, 86.01, 94.25, 123.01, 125.58, 128.17, 128.30, 128.35, 129.46, 131.51, 131.83, 140.19.

(8c): ^1H NMR (CDCl_3 , 250 MHz): δ (ppm): 2.28 (s, 3 H), 7.05-7.44 (m, 9 H); ^{13}C NMR (CDCl_3 , 62.9 MHz): δ (ppm): 21.52, 88.74, 89.58, 123.49, 128.08, 128.33, 128.46, 129.13, 131.51, 131.56, 132.51, 138.39.

(8d): ^1H NMR (CDCl_3 , 250 MHz): δ (ppm): 7.61 (s, 3 H), 7.26-7.63 (m, 7 H), 7.94 (d, 2 H, $J= 8.5$ Hz); ^{13}C NMR (CDCl_3 , 62.9 MHz): δ (ppm): 26.63, 88.61, 92.71, 122.63, 128.19, 128.28, 128.45, 128.82, 131.69, 131.74, 136.16, 197.34.

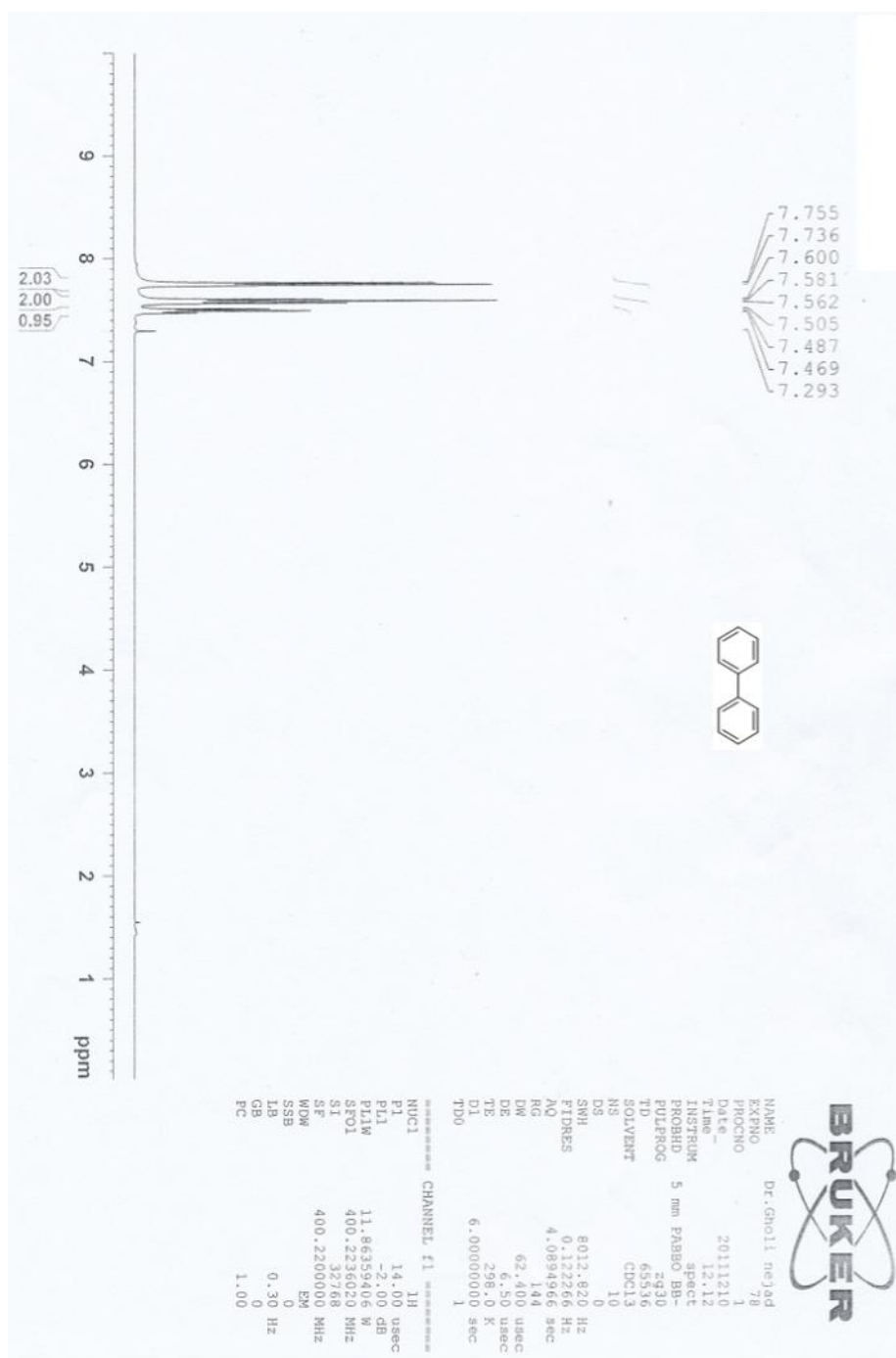
(8e): ^1H NMR (CDCl_3 , 250 MHz): δ (ppm): 7.31-7.59 (m, 7 H), 8.12 (d, 2 H, $J= 7.5$ Hz); ^{13}C NMR (CDCl_3 , 62.9 MHz): δ (ppm): 87.55, 94.71, 122.09, 123.63, 124.83, 128.54, 129.28, 130.25, 131.84, 132.26, 138.64, 146.95.

(8f): ^1H NMR (CDCl_3 , 250 MHz): δ (ppm): 7.29-7.32 (m, 3 H), 7.45-7.48 (m, 2 H), 8.77 (s, 2 H), 9.06 (s, 1 H); ^{13}C NMR (CDCl_3 , 62.9 MHz): δ (ppm): 82.32, 96.30, 119.91, 121.75, 129.12, 131.76, 139.38, 156.66, 158.59.

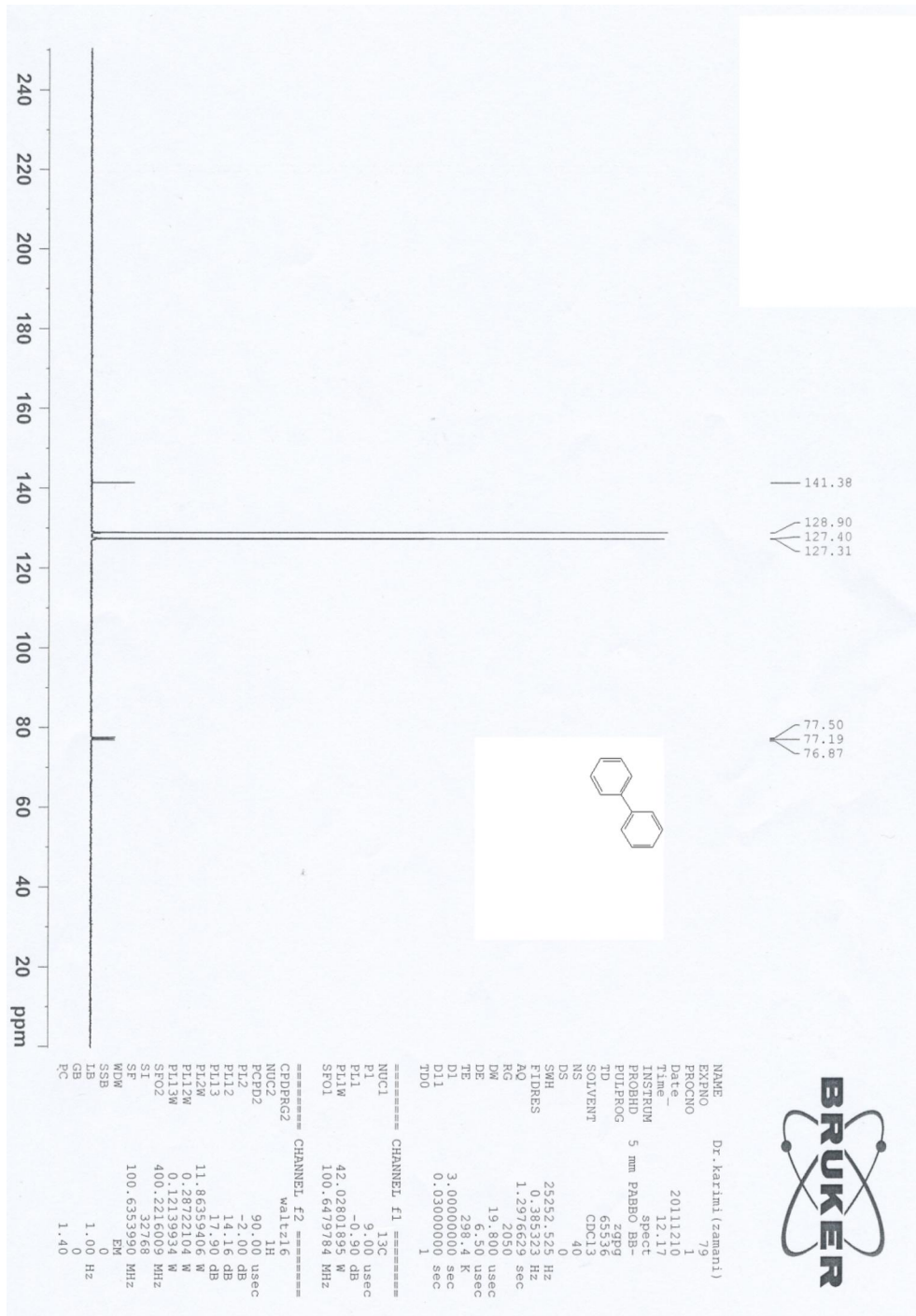
(8g): ^1H NMR (CDCl_3 , 250 MHz): δ (ppm): 7.01-7.68 (m, 8 H); ^{13}C NMR (CDCl_3 , 62.9 MHz): δ (ppm): 87.30, 94.51, 128.33, 128.43, 129.20, 131.51, 132.50.

(10): ^1H NMR (CDCl_3 , 250 MHz): δ (ppm): 0.87-0.98 (m, 3 H), 1.30-1.45 (m, 2 H), 1.58-1.699 (m, 2 H), 4.17 (t, 2 H, $J= 6.8$ Hz), 6.53 (d, 1 H, $J= 16.0$ Hz), 7.51-7.75 (m, 4 H), 8.18 (d, 2 H, $J= 8.8$ Hz); ^{13}C NMR (CDCl_3 , 62.9 MHz): δ (ppm): 13.69, 19.14, 30.66, 64.88, 122.59, 124.14, 128.59, 140.58, 141.55, 166.09.

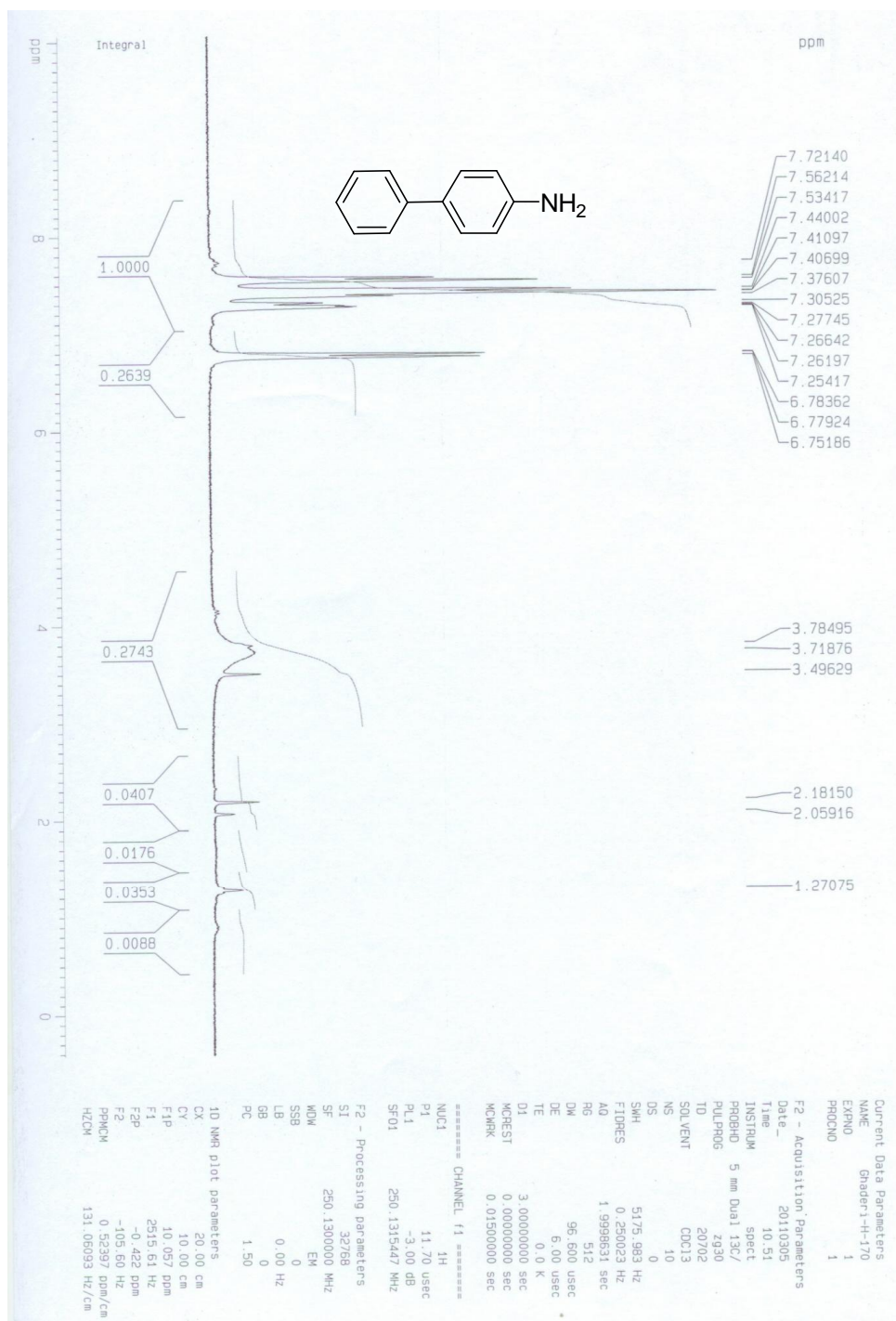
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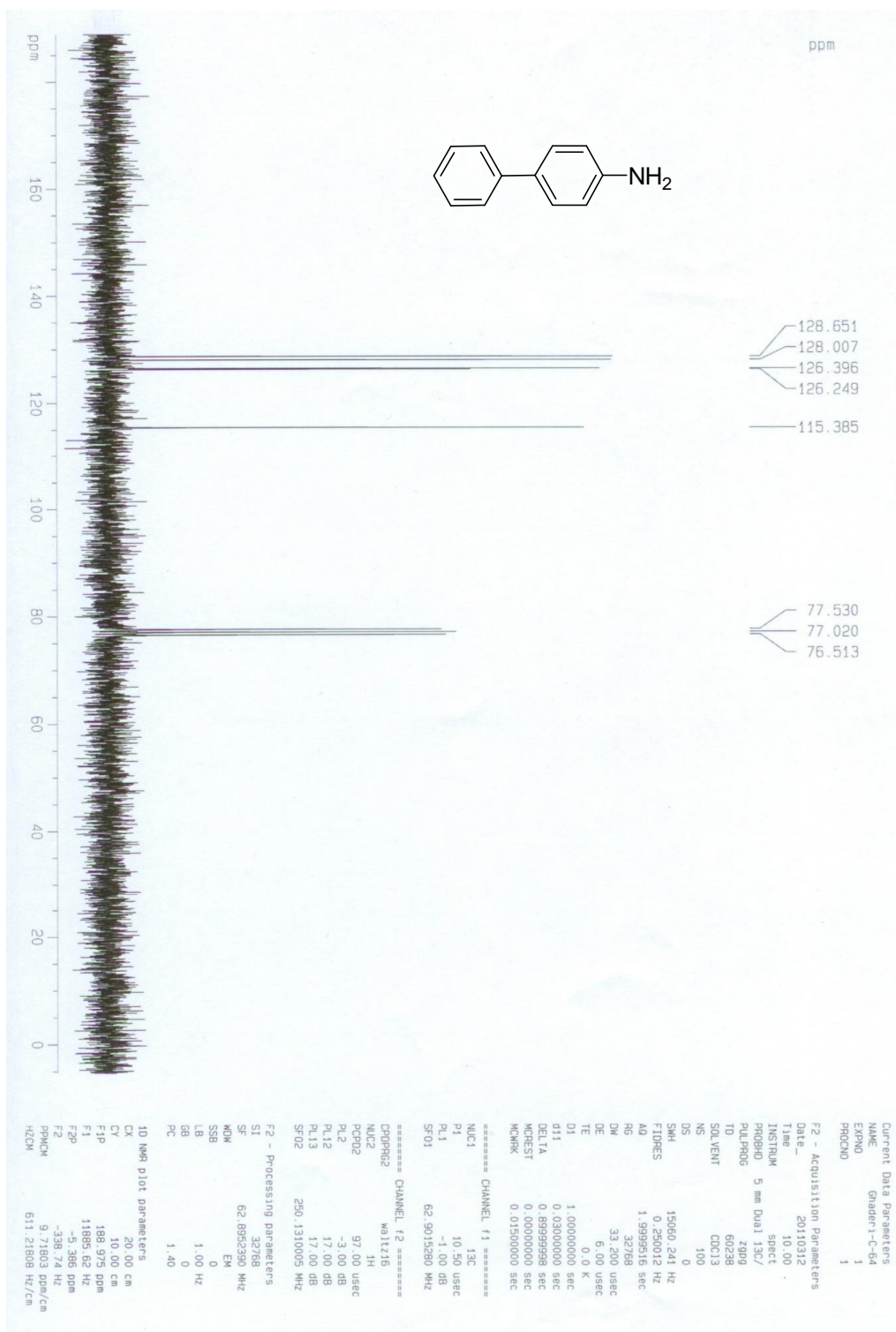
^1H NMR of compound **6a**



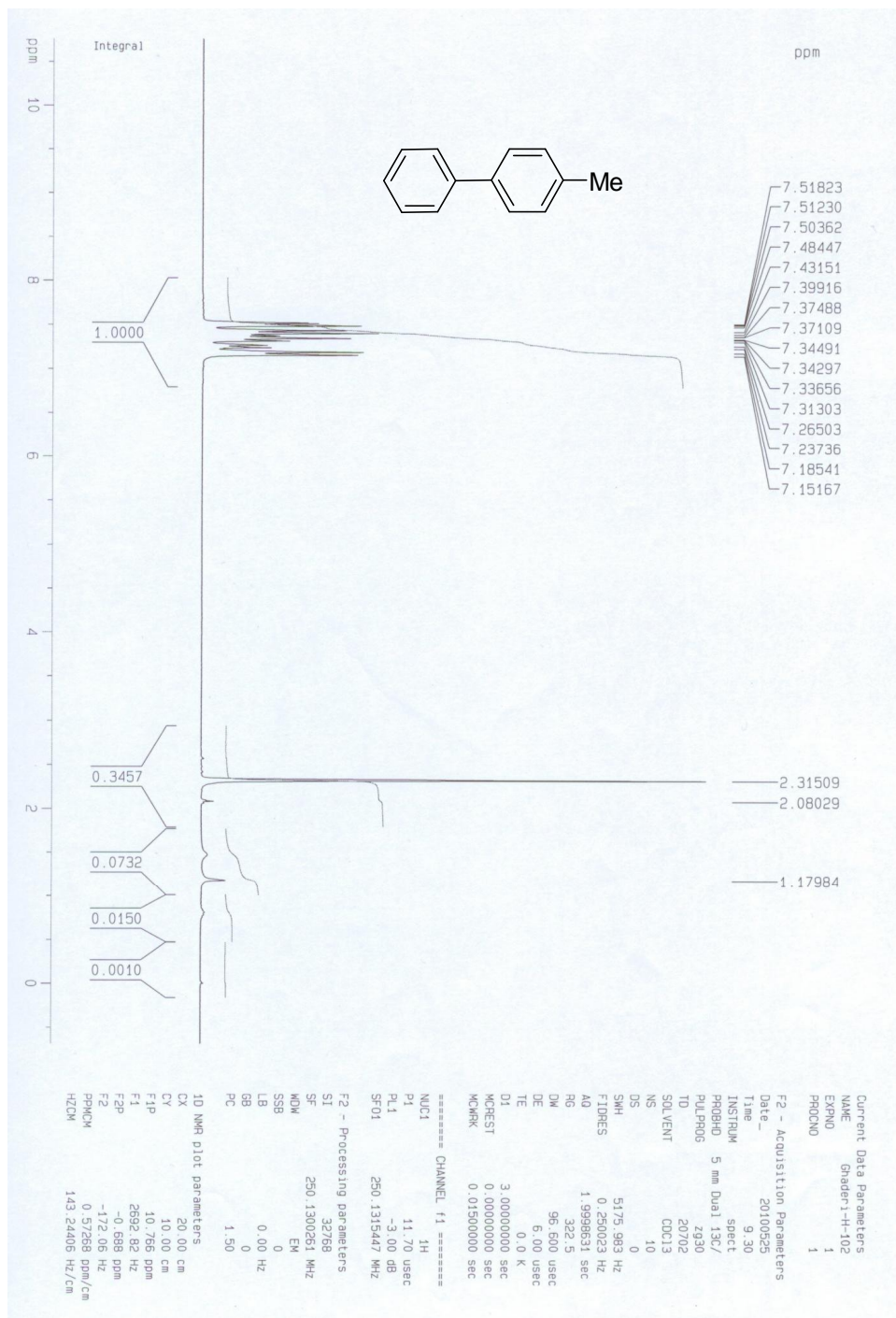
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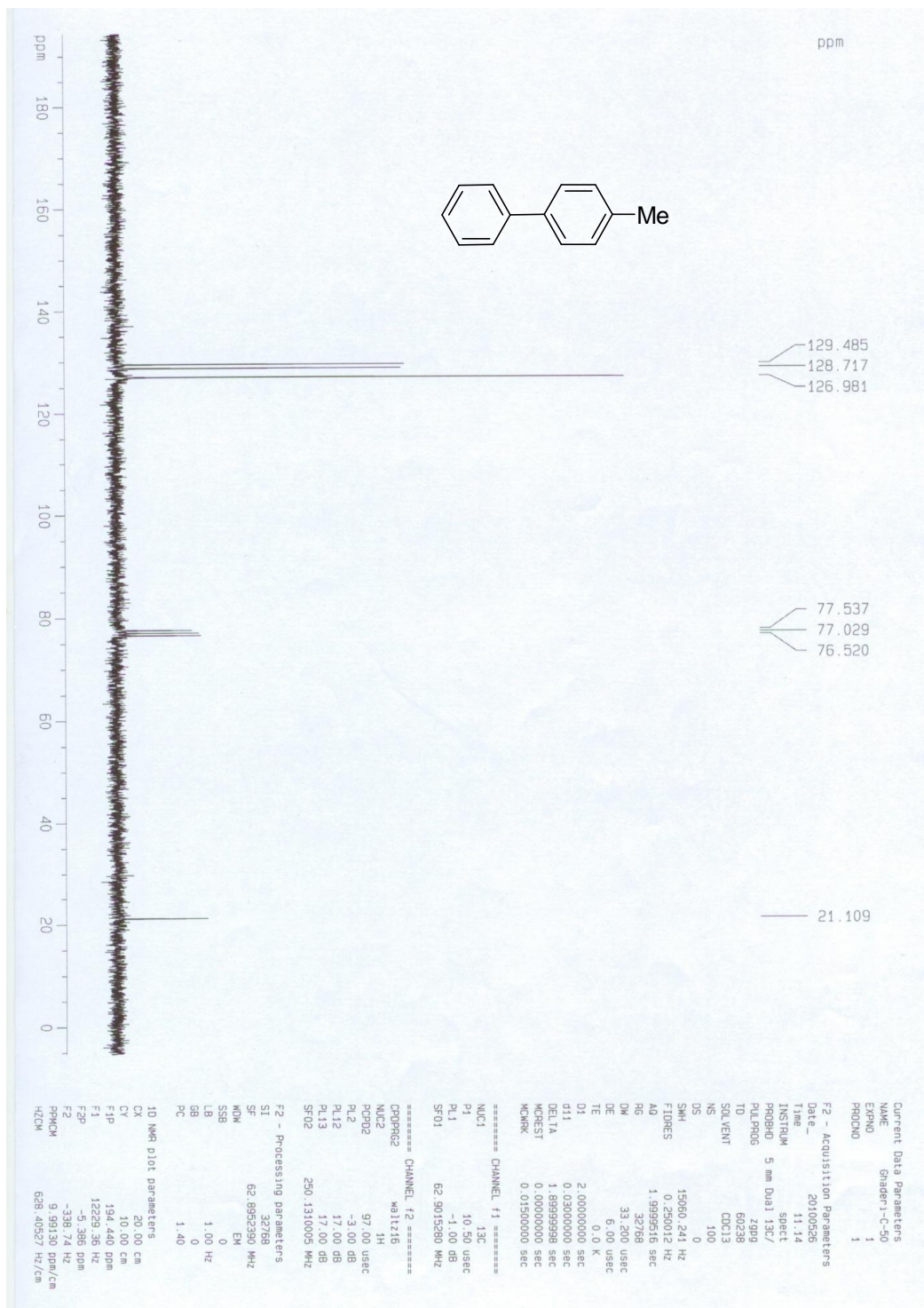
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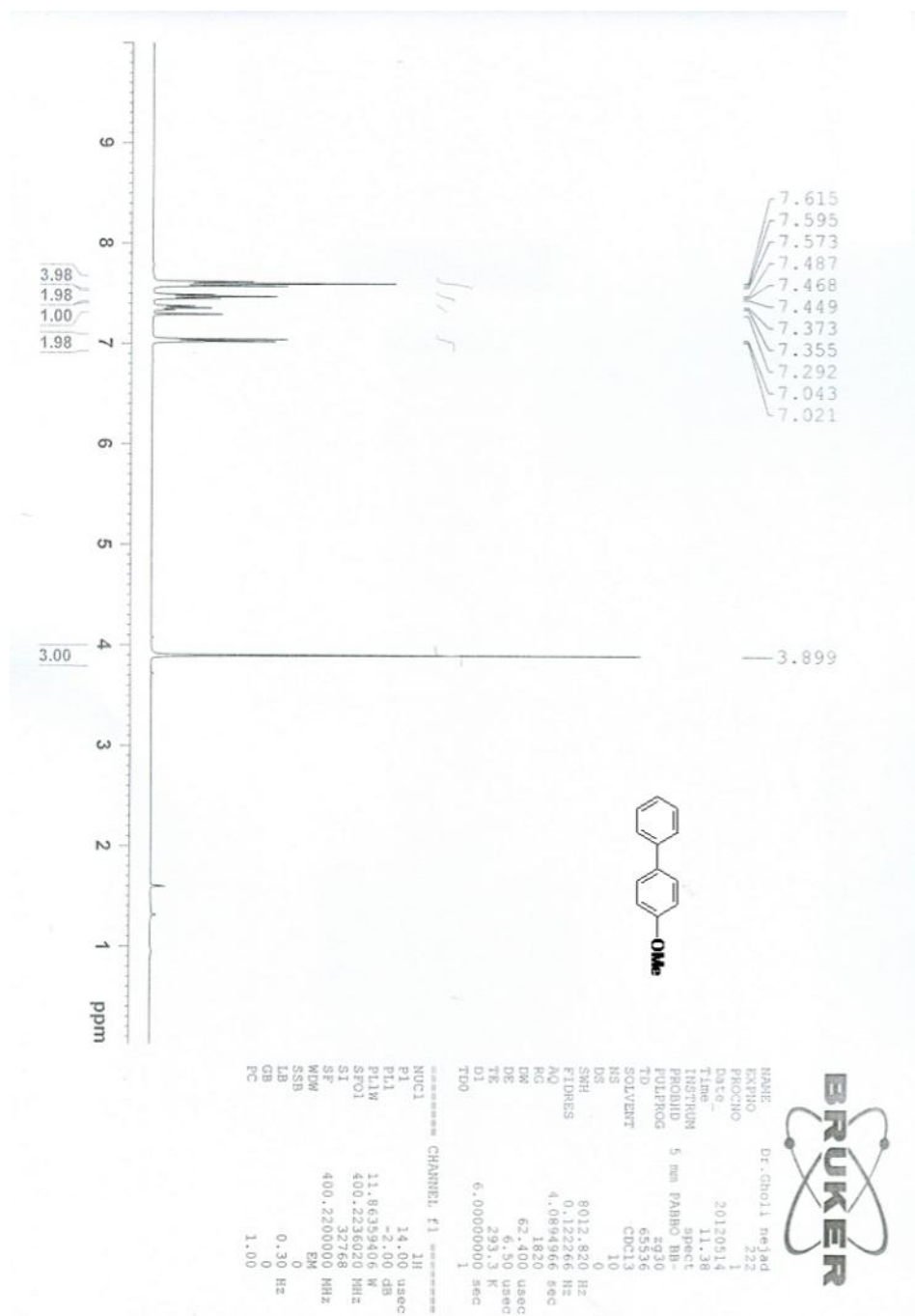
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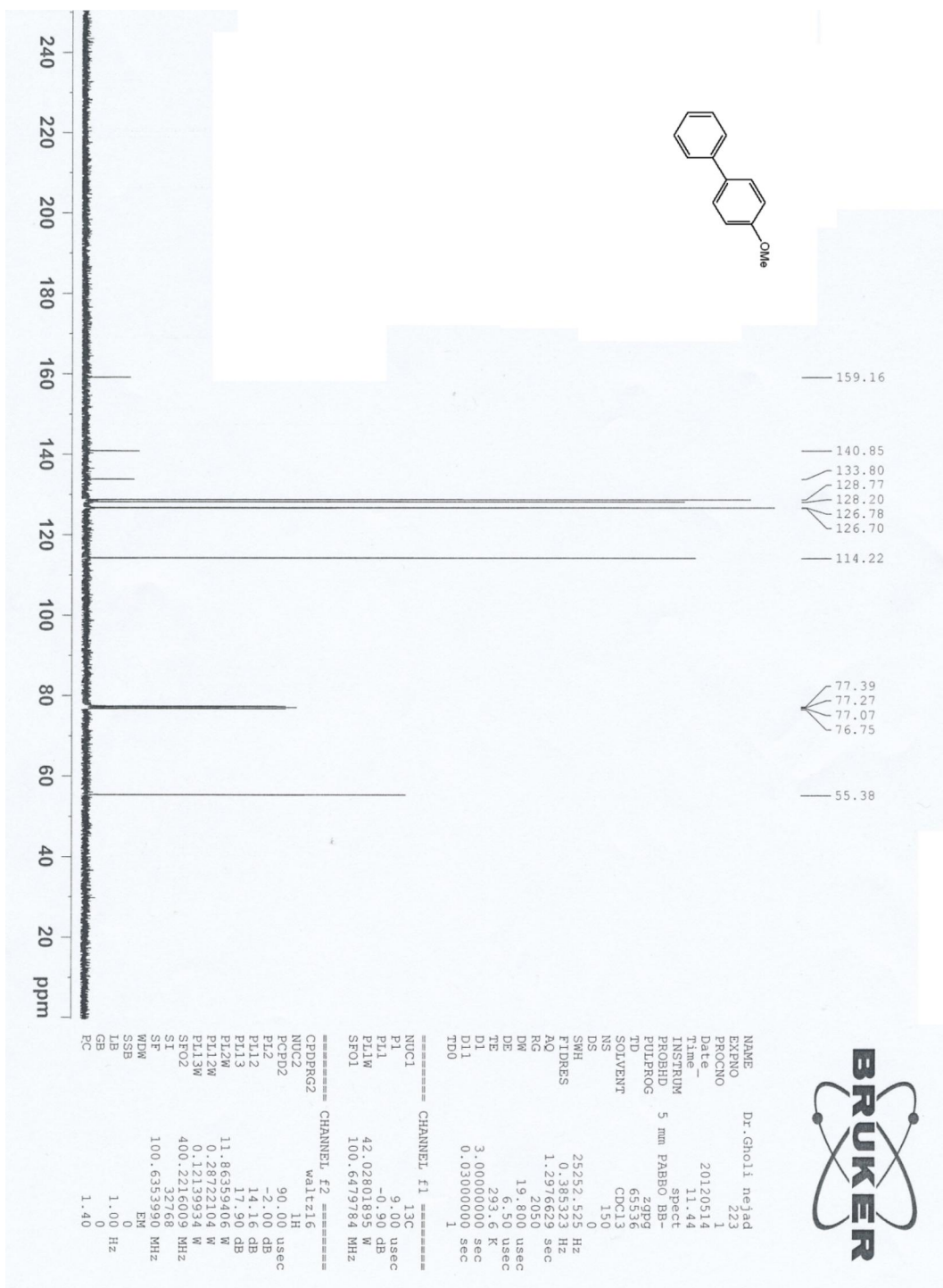
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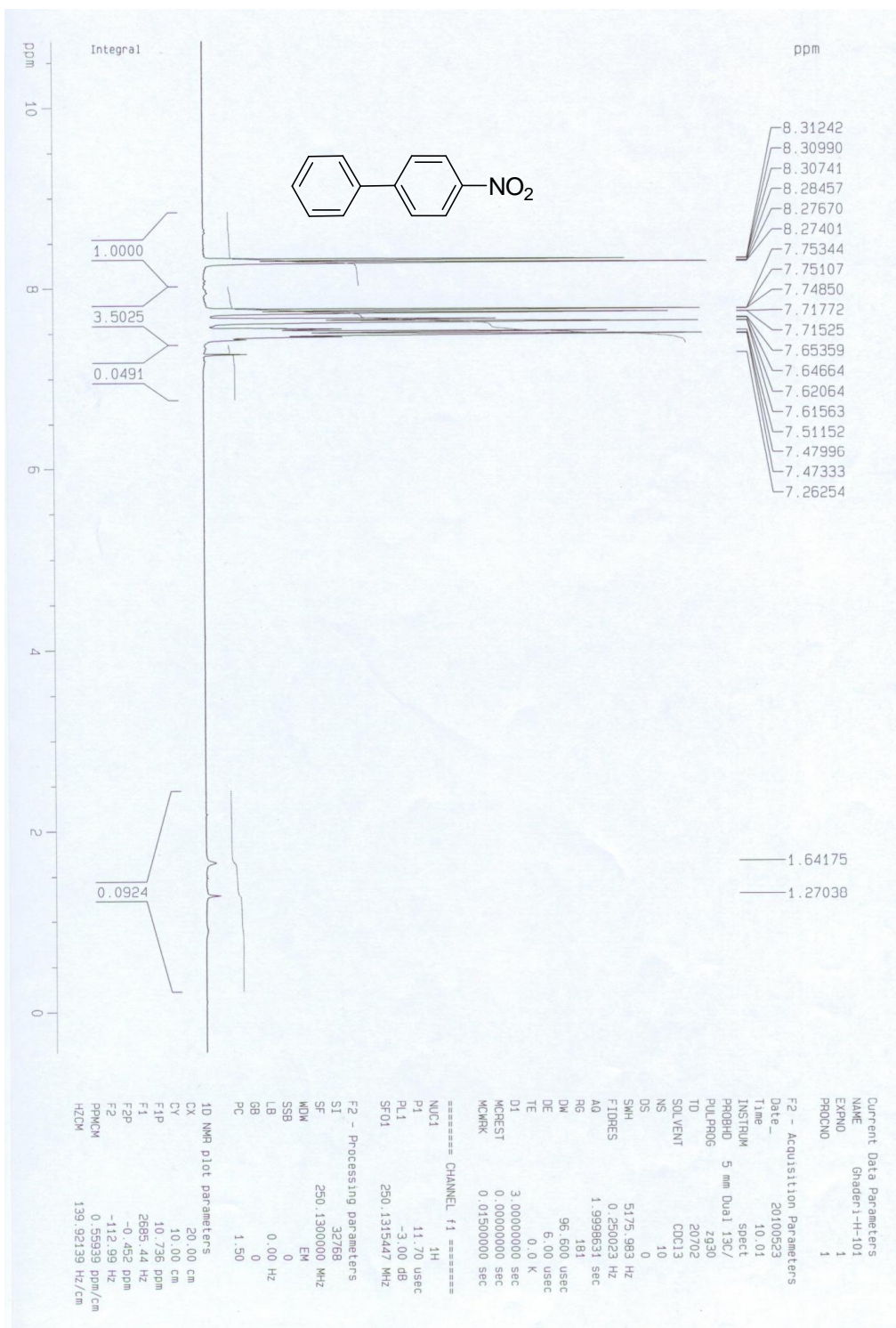
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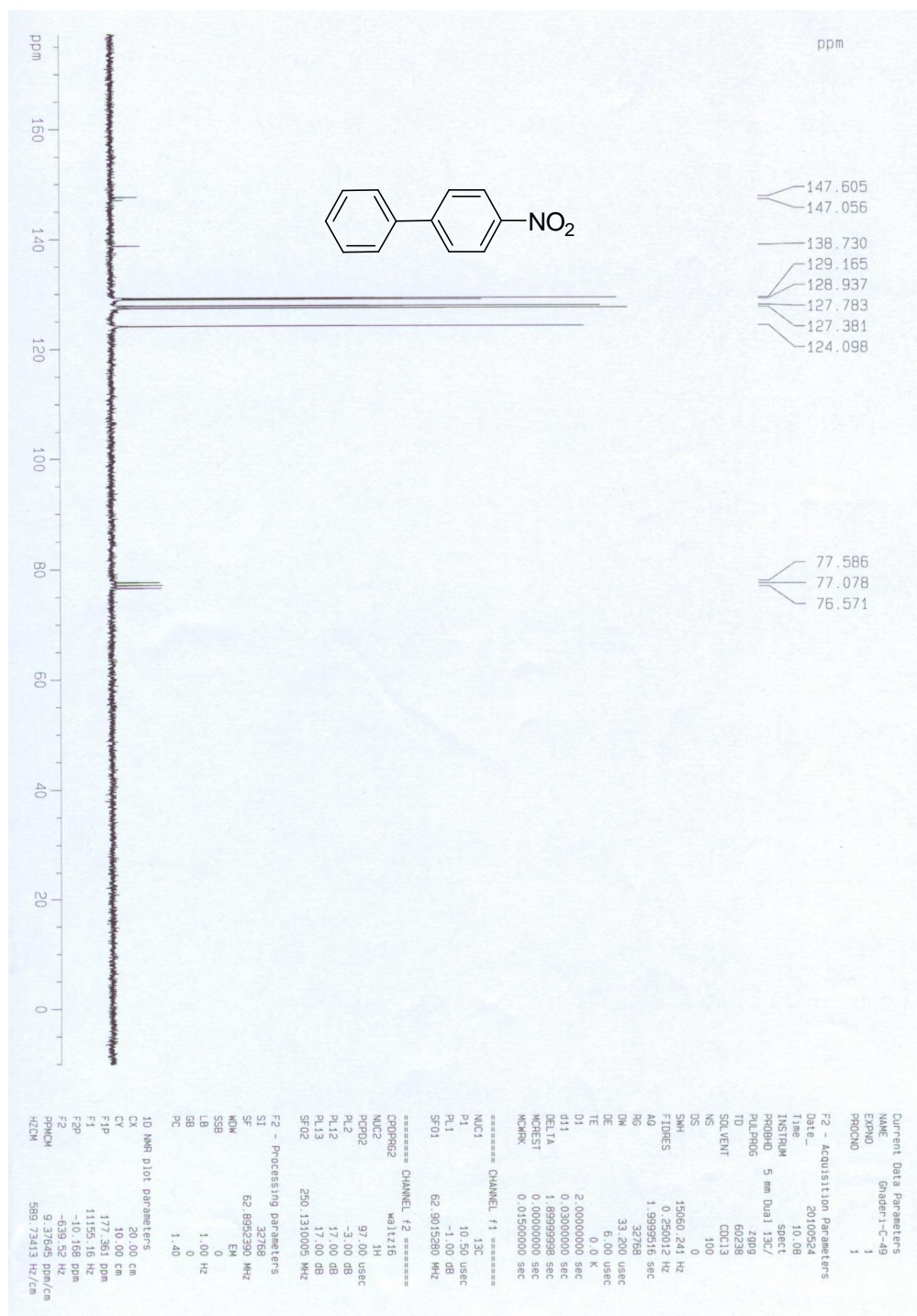
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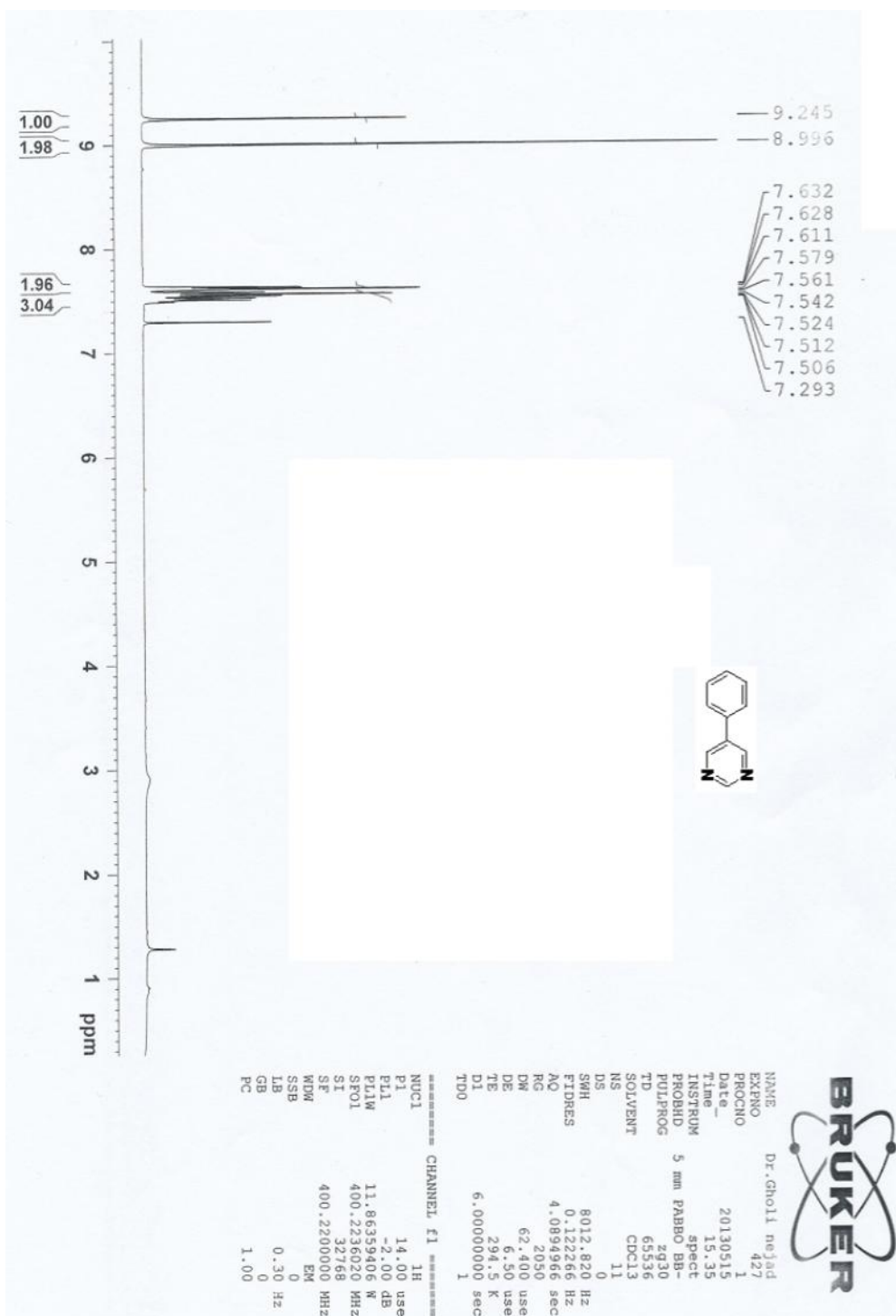
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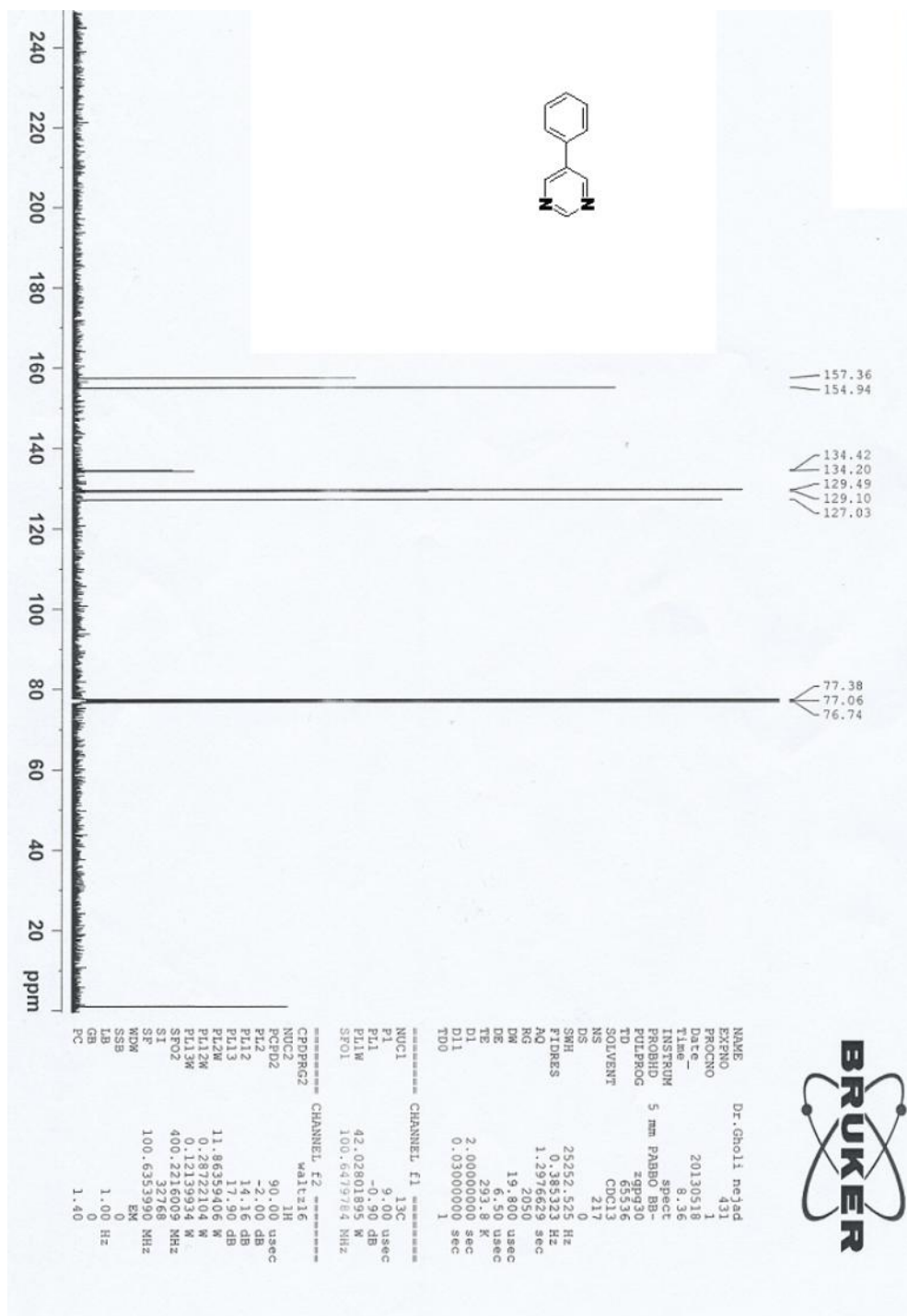
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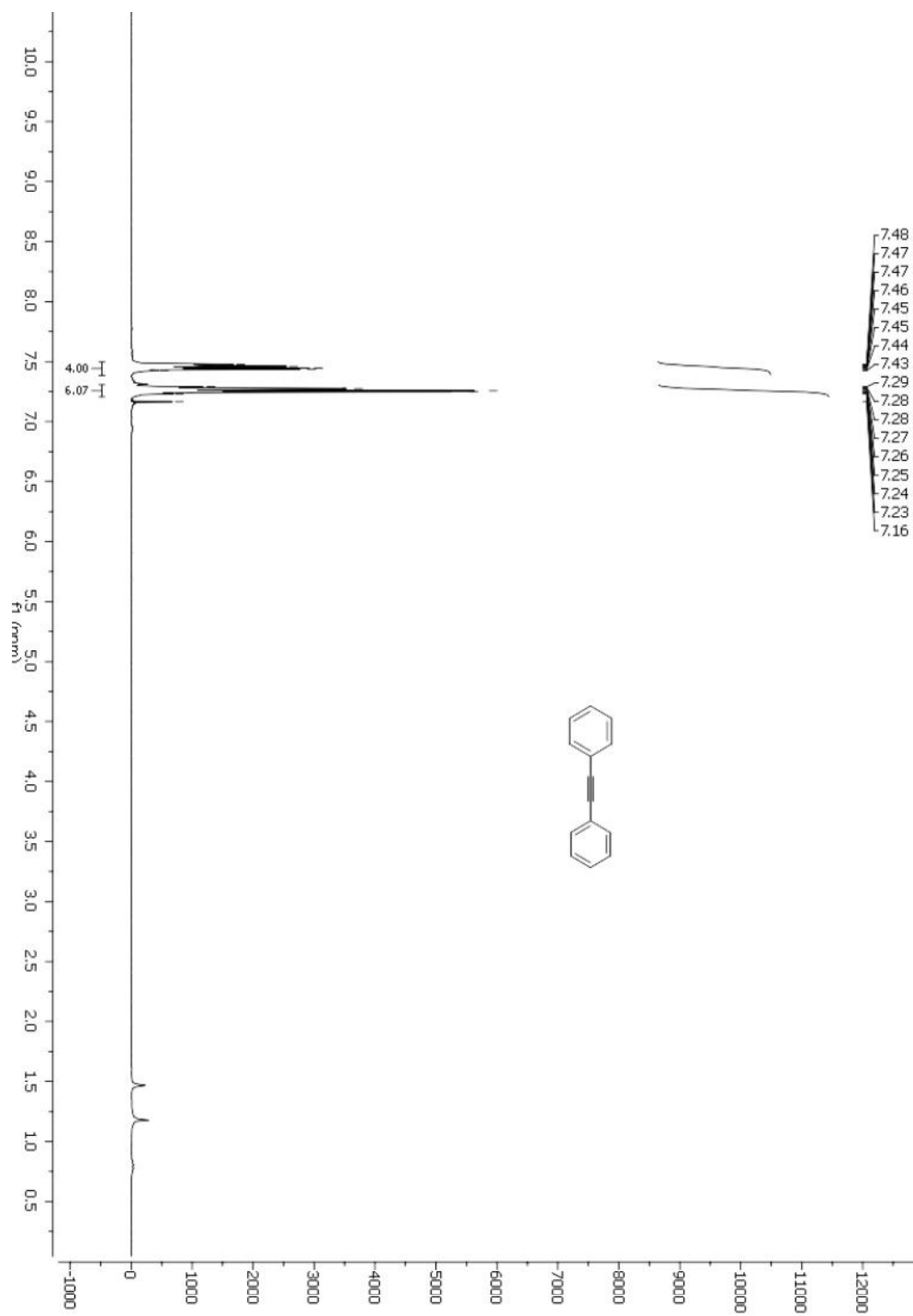
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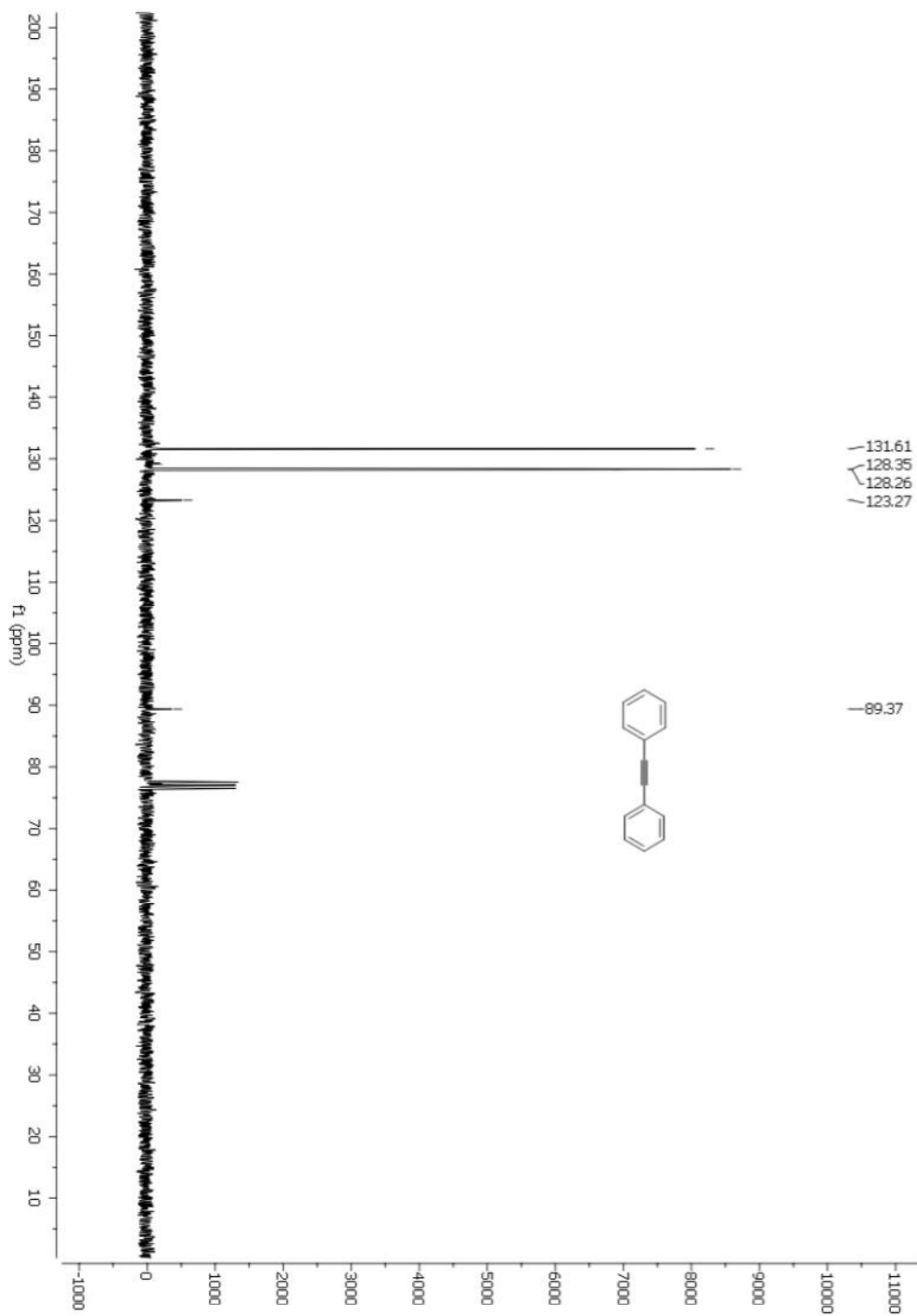
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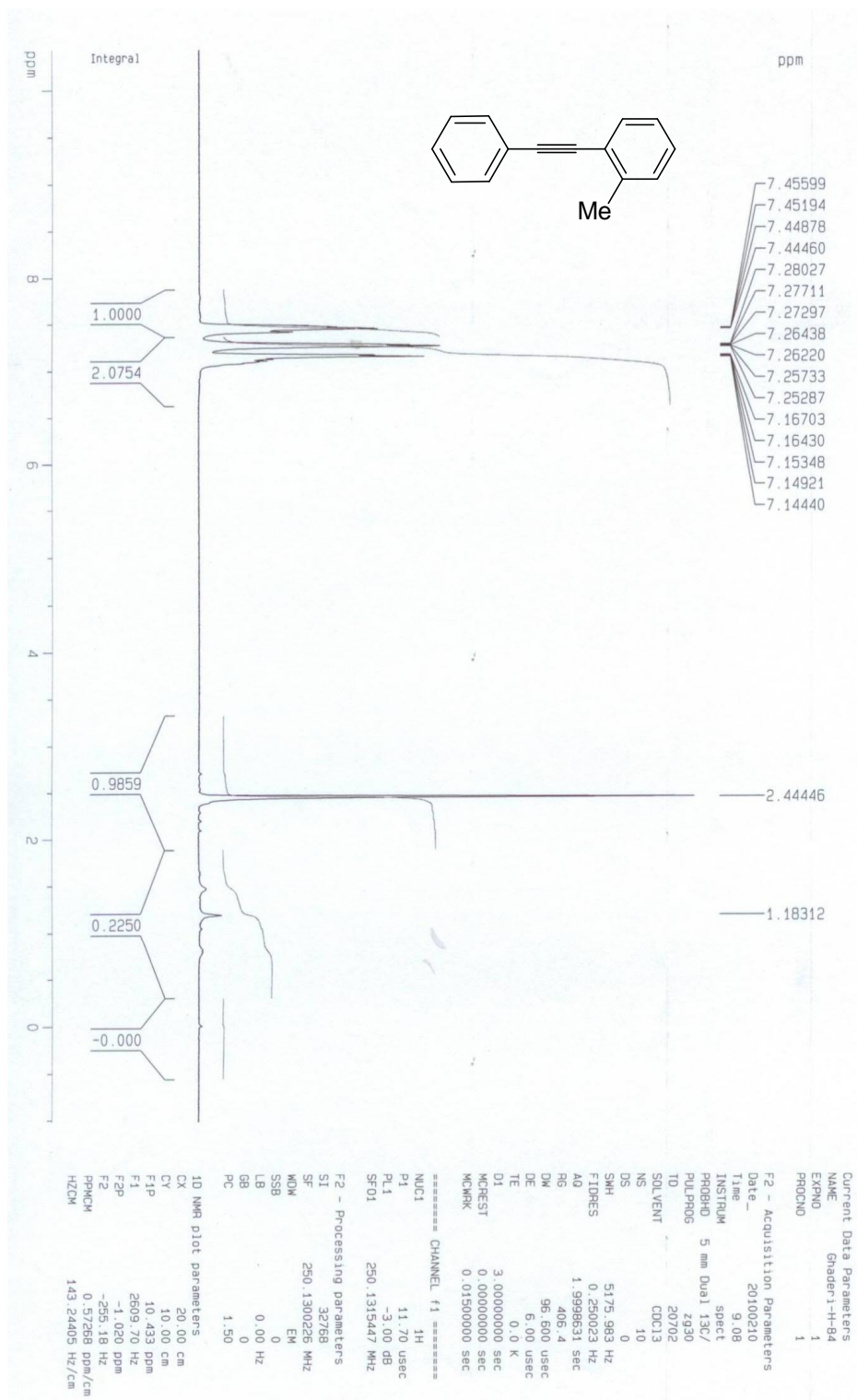
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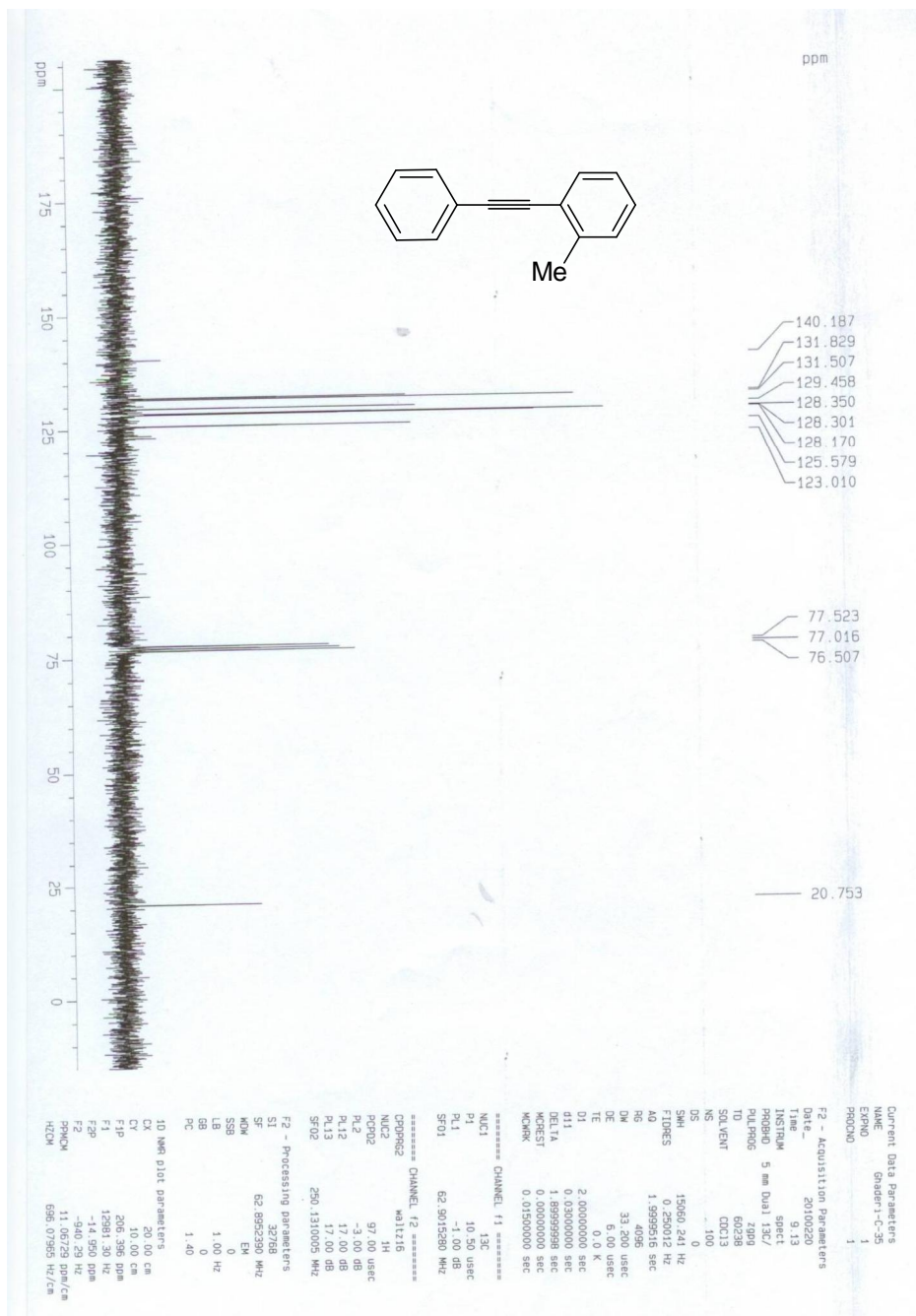
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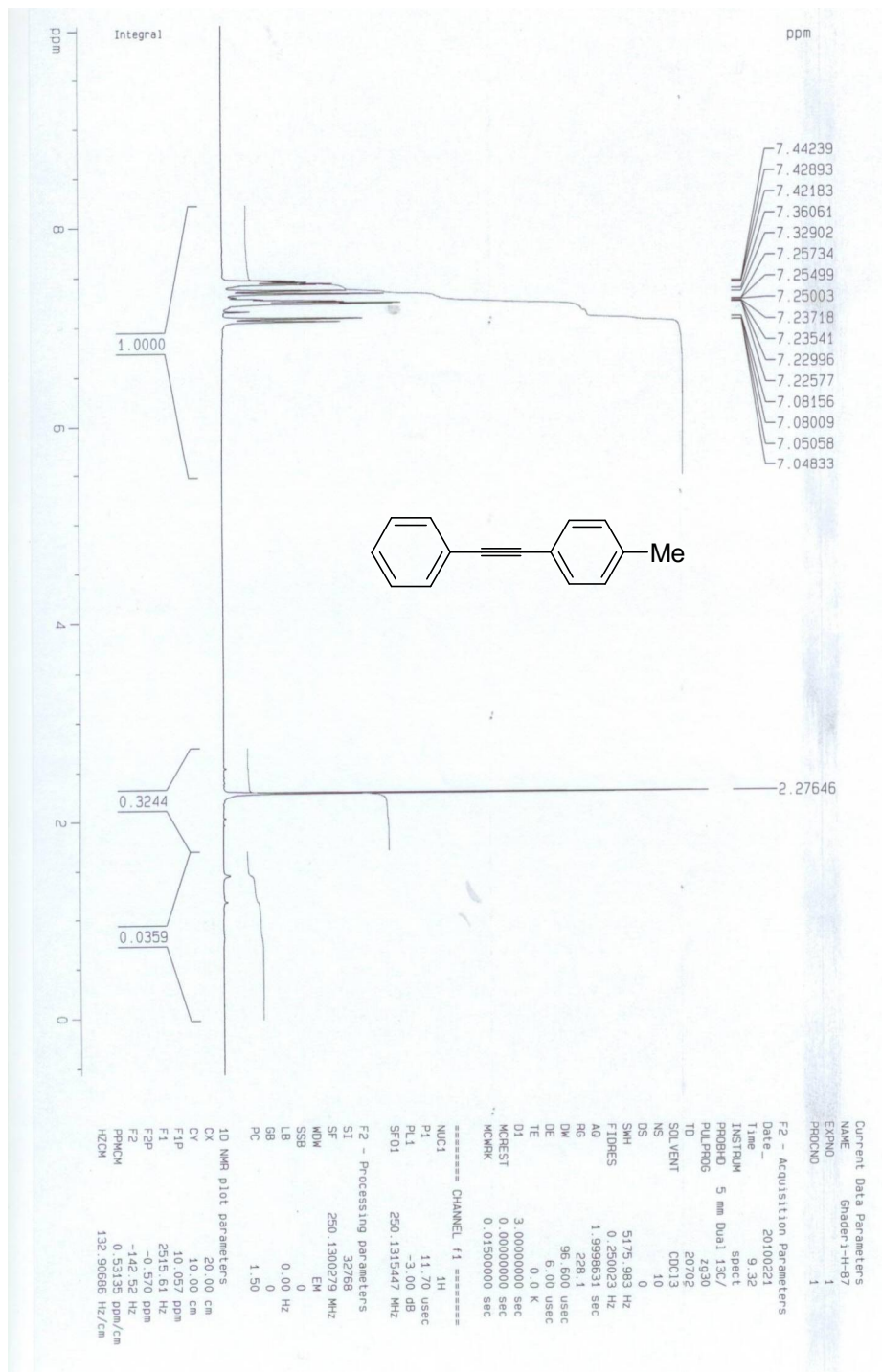
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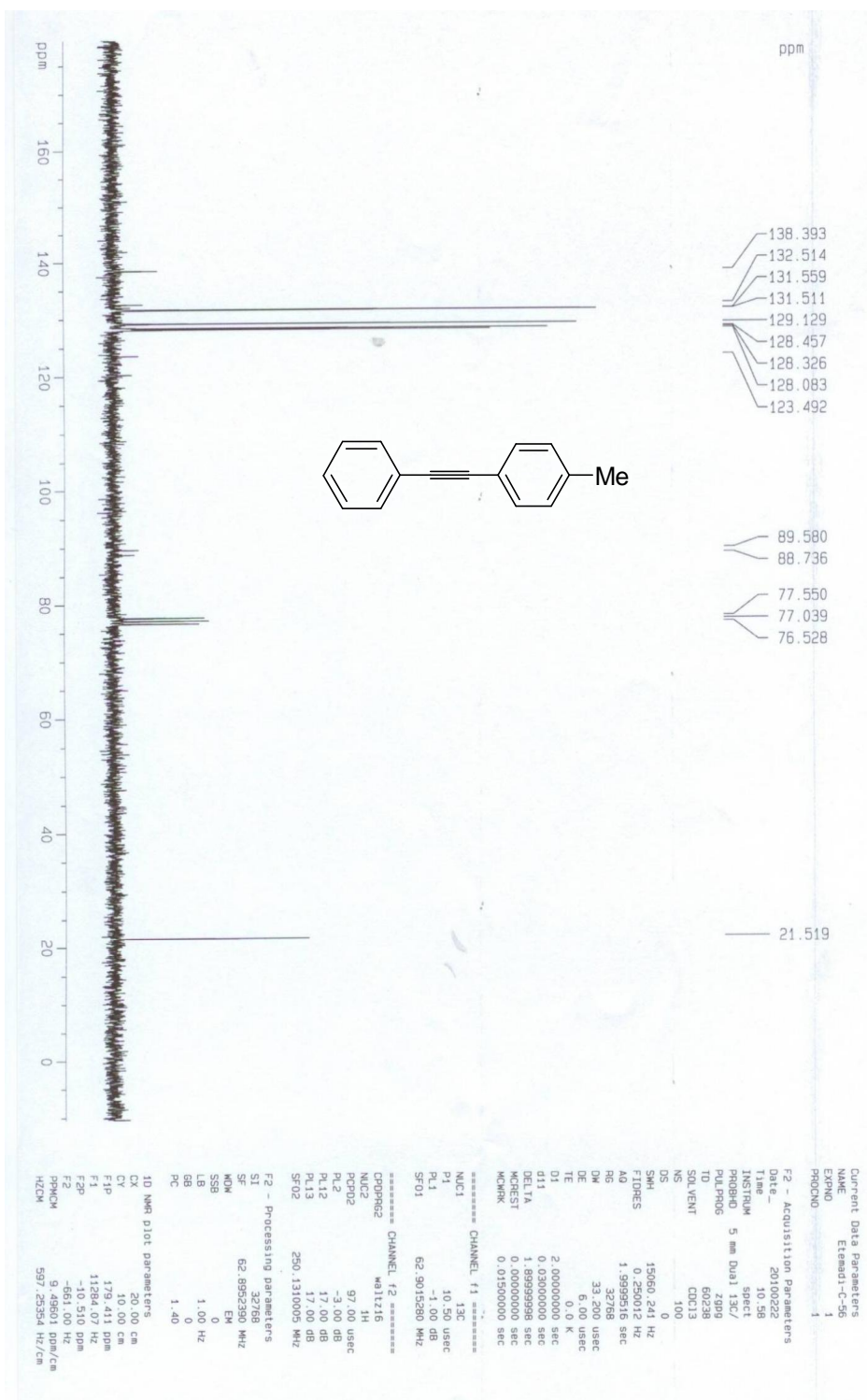
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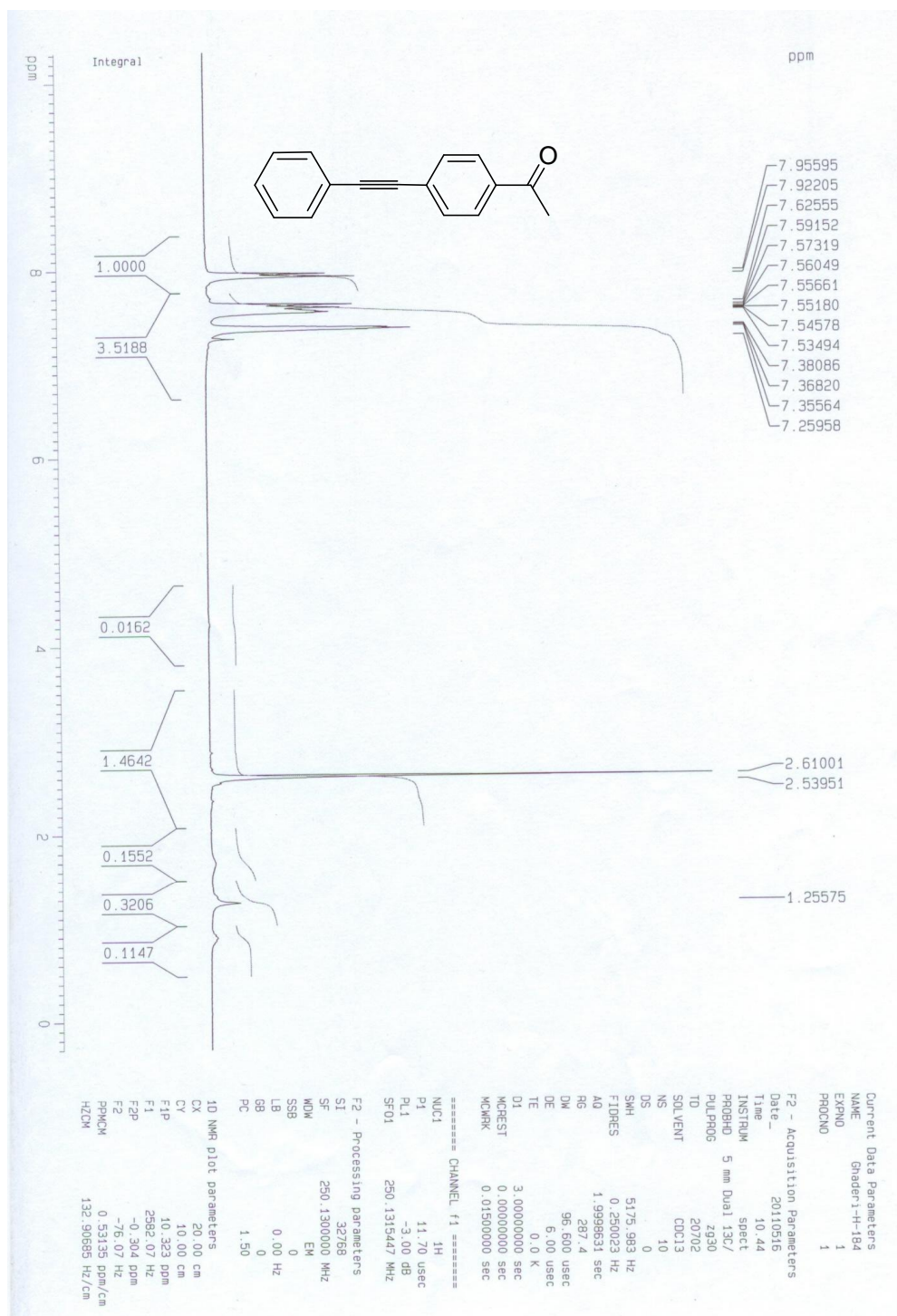
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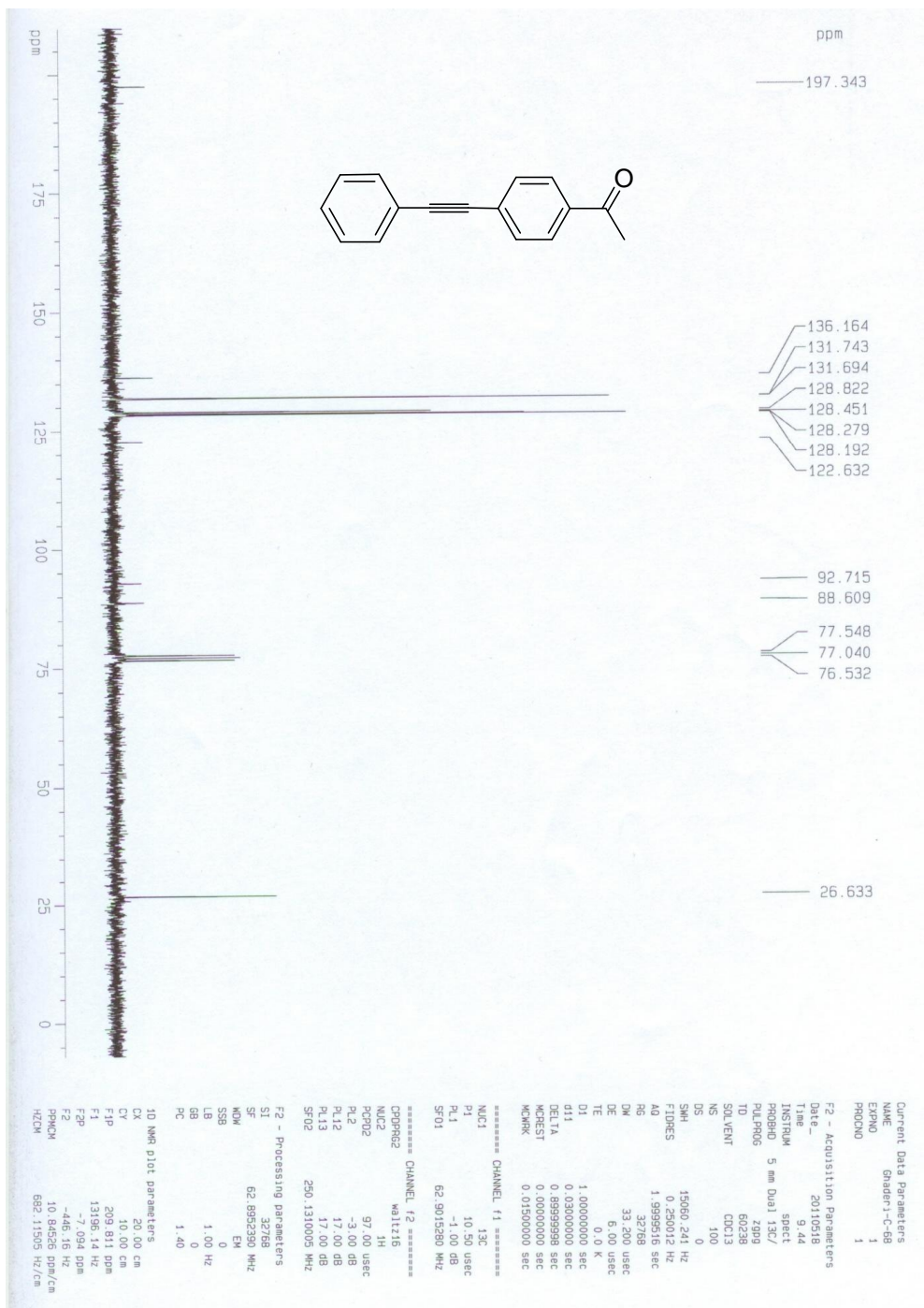
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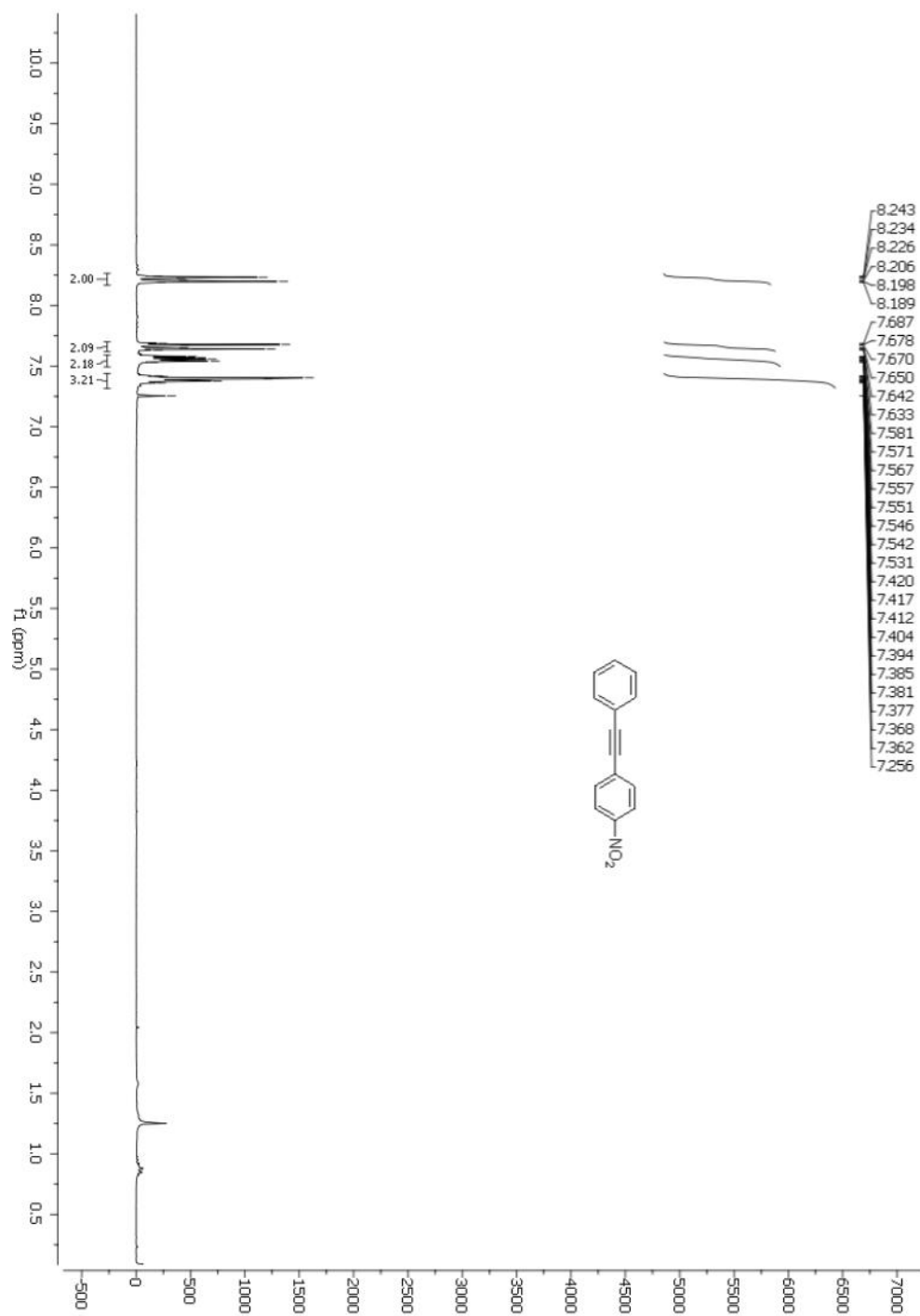
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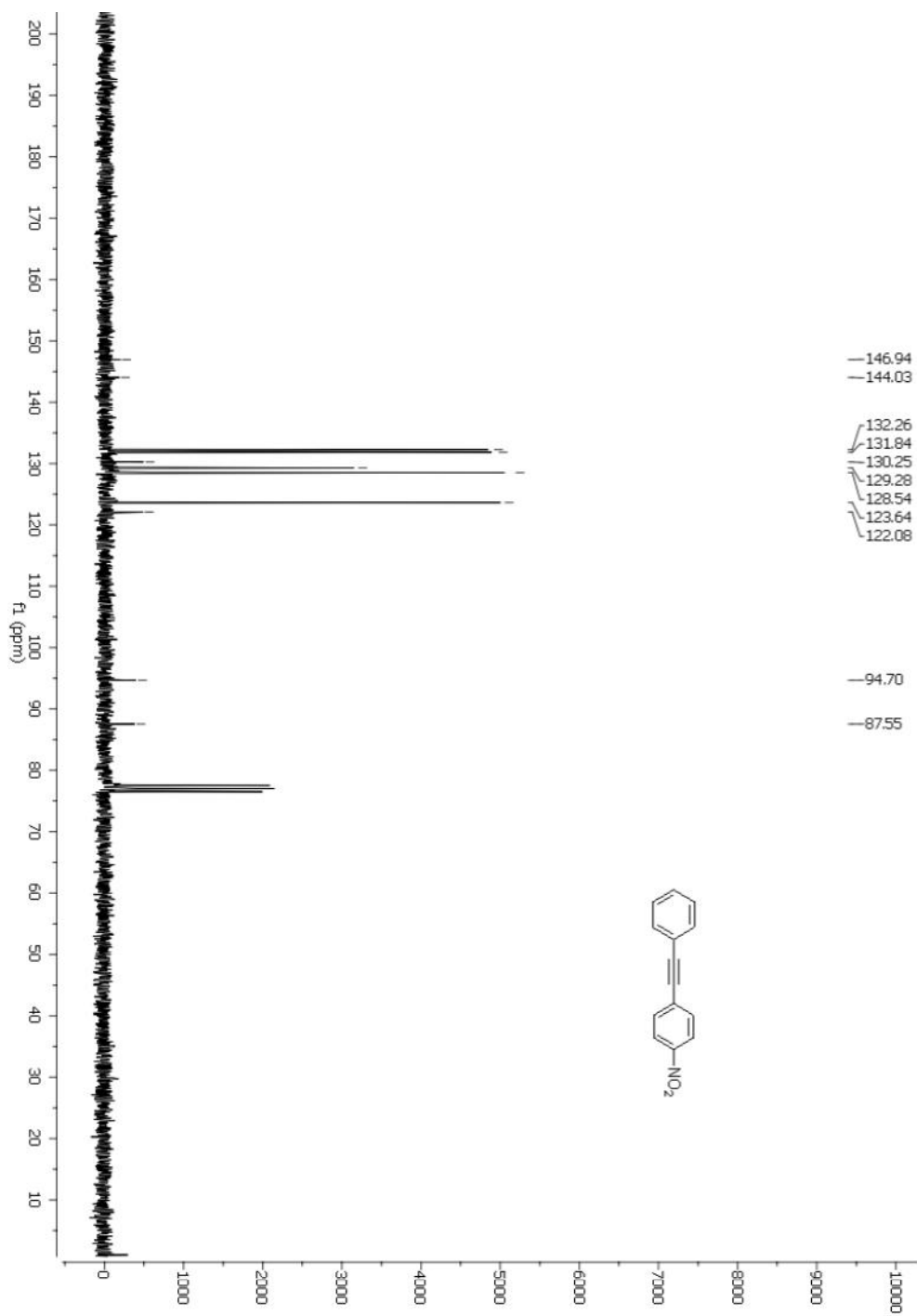
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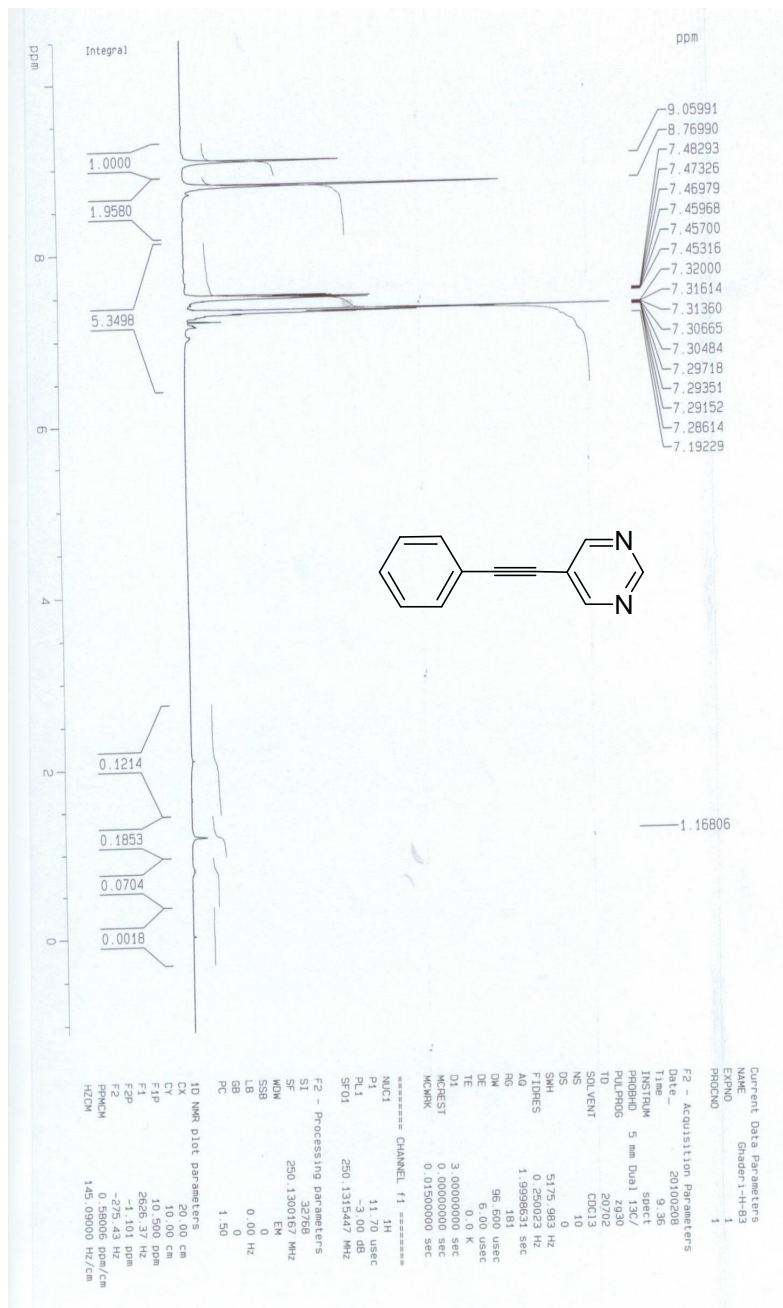
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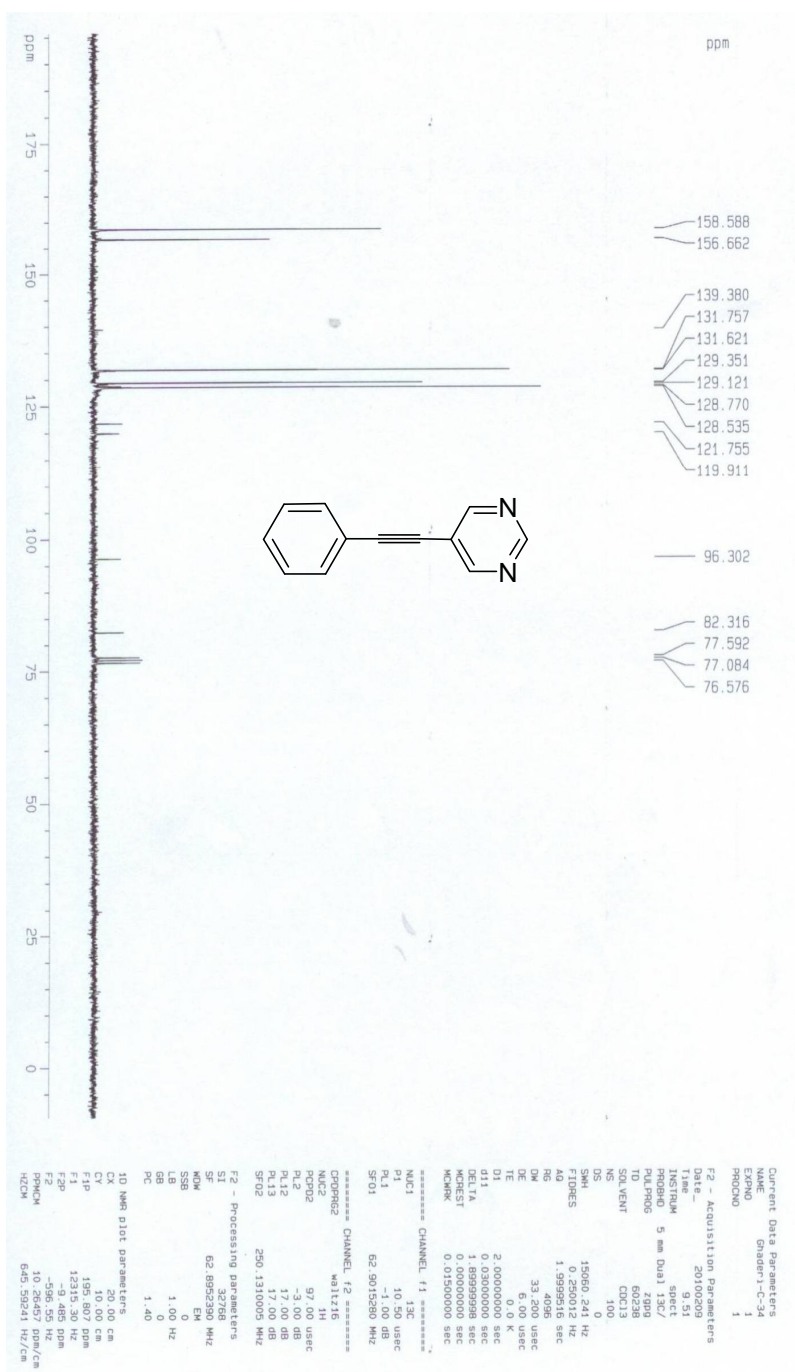
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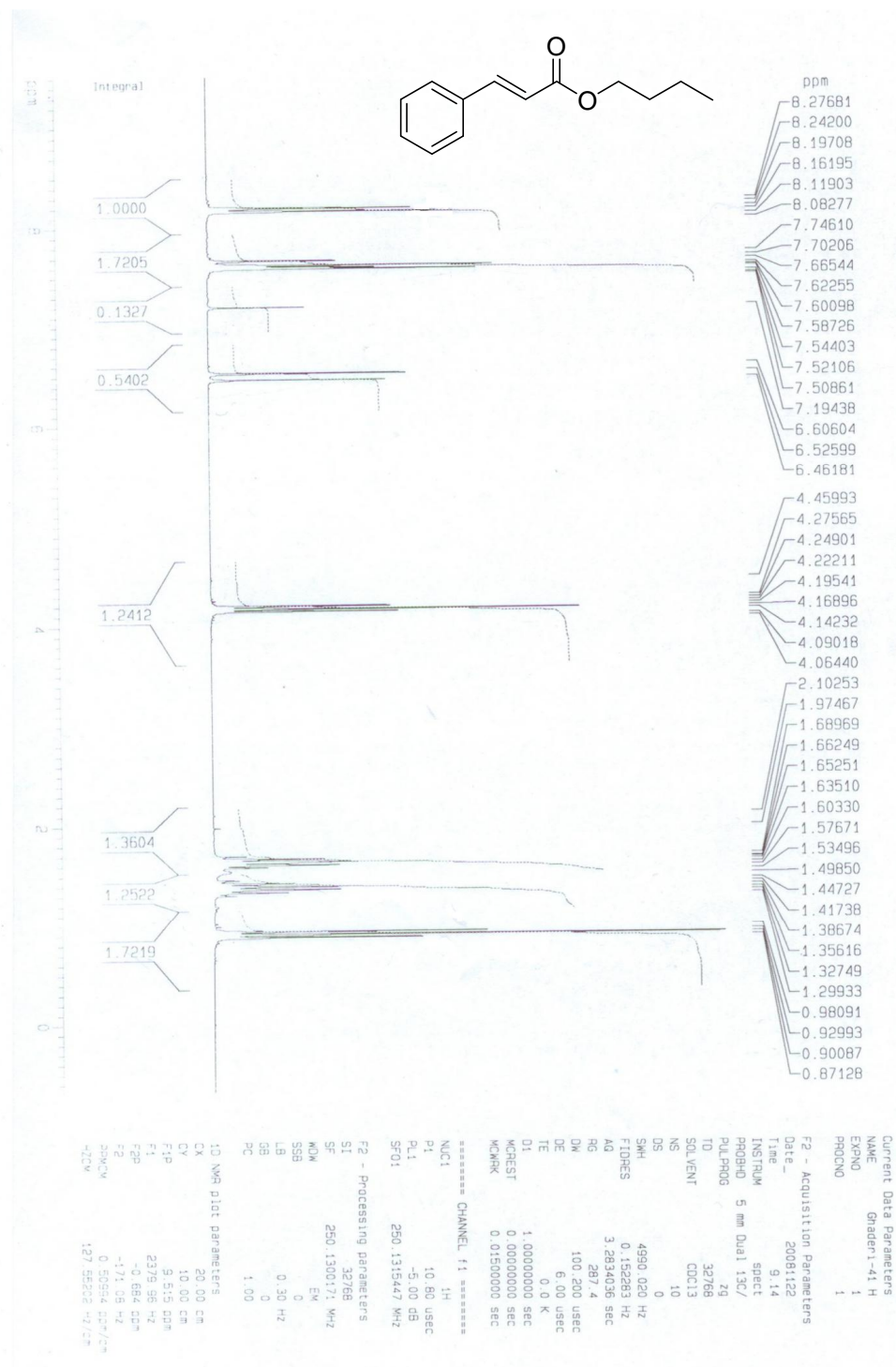
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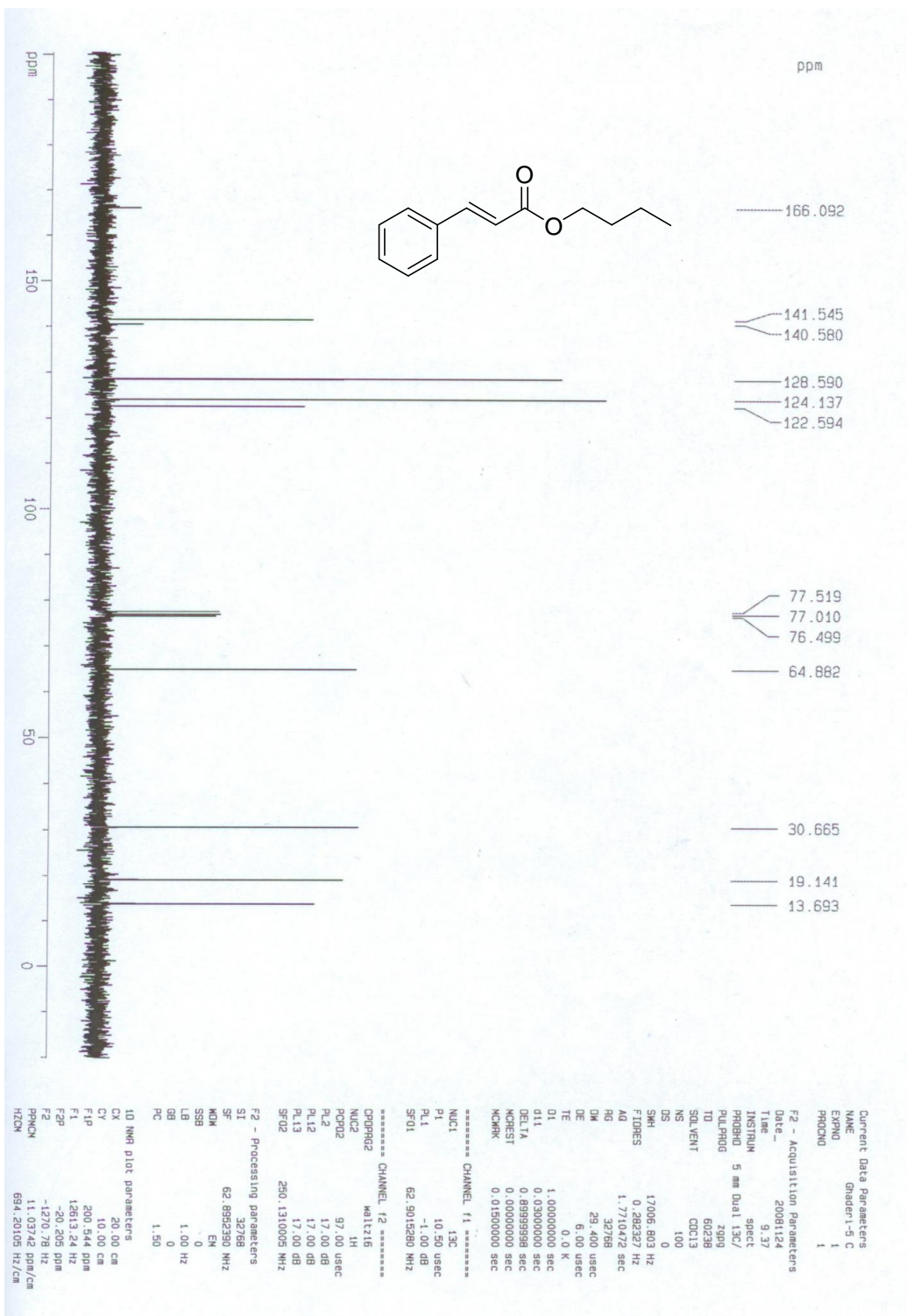
¹H NMR of compound **8f**



¹³C NMR of compound **8f**



¹H NMR of compound 10



^{13}C NMR of compound 10