Copper bronze Catalyzed Heck Reaction in Ionic Liquids

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Supporting information

General Remarks

All the starting materials and ionic liquids were commercially available and were used without further purification. Copper bronze was purchased by BDH. The cross-coupling products were identified by comparison of their physical and spectroscopic data with those reported in the literature.

TEM morphological characterisation

All the samples were observed at 100 kV under a PHILIPS 400T TEM. Evaluation of the copper nanoparticles' core diameter was performed manually over more than 600 particles, selected in different regions of the micrographs.

Typical procedure for the copper bronze catalyzed Heck reaction.

To tetrabutylammonium bromide (3 g, 9.3 mmol) were added tetrabutylammonium acetate (0.452 g 1.5 mmol), iodobenzene (0.204 g, 1 mmol), butyl acrylate (0.154 g, 1.2 mmol) and copper bronze (BDH flakes, 99% or Aldrich copper bronze 99%) (1.91 mg, 0.03 mmol, 3%). The reaction was heated at 130 °C under nitrogen atmosphere with stirring for the proper time. At the end of the reaction and after cooling to r.t., the solid mixture was extracted with cyclohexane (5x20 ml) leaving the catalyst in the ionic liquid that can be recycled. The extracted phases were collected and washed with diluite HCl to remove tributylamine. After the solvent removal, *in vacuo*, the mixture was chromatographed on a silica pad affording cinnamates in high purity as shown by ^{1}H and ^{13}C NMR spectra reported below.

Procedure for the catalyst recycling.

After completion of the reaction and after cooling to r.t., the products and the unreacted reagents were extracted with cyclohexane (5x20 mL). After removal of residual organic solvent under vacuum; the resulting solid mixture, containing both the IL and the catalyst, was charged with fresh reagents and heated at 130 °C under nitrogen atmosphere with stirring for the proper time.

Spectral data of cinnamates:

(E)-3-(4-Methoxy-phenyl)-acrylic acid butyl ester. **^{1}H NMR** ($CDCl_3$, 500 MHz) δ 0.95 (t, *J*= 7.4 Hz, 3H), 1.37-1.48 (m, 2H), 1.63-1.72 (m, 2H), 3.81 (s, 3H), 4.19 (t, *J*= 6.7 Hz, 2H), 6.30 (d, *J*= 16.0, 1H), 6.85-6.92 (m, 2H), 7.43-7.48 (m, 2H), 7.62 (d, *J*= 16.0, 1H); **^{13}C NMR** 13.69, 19.13, 30.73, 55.25, 64.17, 114.20, 115.65, 127.09, 129.60, 144.12, 161.23, 167.35.

(E)-3-Phenyl-acrylic acid butyl ester. **^{1}H NMR** ($CDCl_3$, 500 MHz) δ 0.97 (t, *J*= 7.4 Hz, 3H), 1.38-1.49 (m, 2H), 1.64-1.73 (m, 2H), 4.21 (t, *J*= 6.7 Hz, 2H), 6.45 (d, *J*= 16.0, 1H), 7.34-7.41 (m, 3H), 7.49-7.55 (m, 2H), 7.68 (d, *J*= 16.0, 1H); **^{13}C NMR** 13.70, 19.15, 30.72, 64.37, 118.22, 127.99, 128.81, 130.15, 134.40, 144.49, 167.05.

(E)-3-(4-Bromo-phenyl)-acrylic acid butyl ester. **^{1}H NMR** ($CDCl_3$, 500 MHz) δ 0.96 (t, *J*= 7.4 Hz, 3H), 1.36-1.48 (m, 2H), 1.61-1.73 (m, 2H), 4.20 (t, *J*= 6.7 Hz, 2H), 6.42 (d, *J*= 16.0, 1H), 7.32-7.41 (m, 2H), 7.47-7.54 (m, 2H), 7.60 (d, *J*= 16.0, 1H); **^{13}C NMR** 13.69, 19.12, 30.68, 64.48, 118.92, 124.38, 129.35, 132.04, 133.31, 143.07, 166.74.

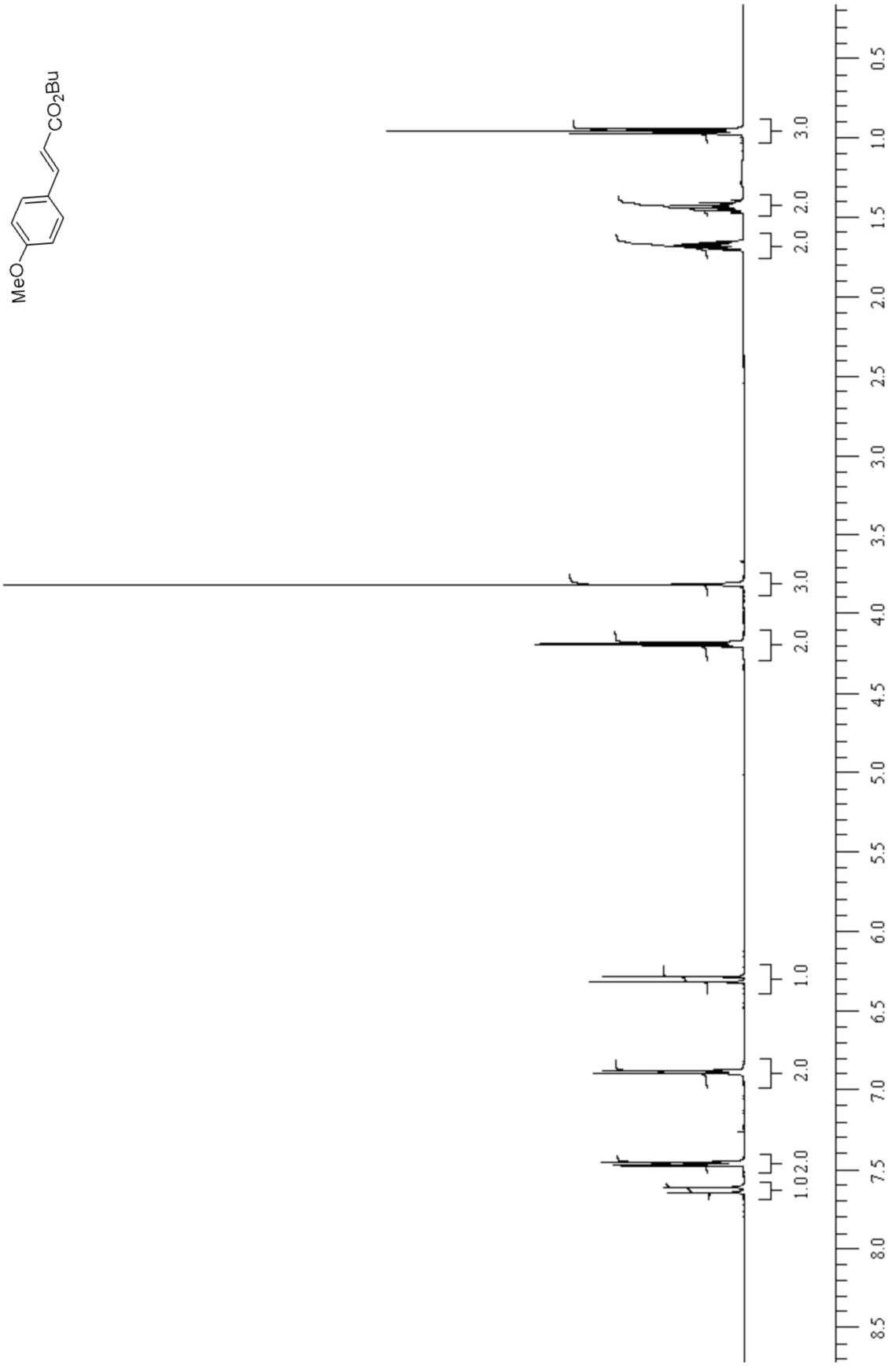
(E)-3-(4-Cyano-phenyl)-acrylic acid butyl ester. **^{1}H NMR** ($CDCl_3$, 500 MHz) δ 0.95 (t, *J*= 7.4 Hz, 3H), 1.35-1.48 (m, 2H), 1.63-1.72 (m, 2H), 4.21 (t, *J*= 6.9 Hz, 2H), 6.51 (d, *J*= 16.0, 1H), 7.57-7.70 (m, 5H); **^{13}C NMR** 13.66, 19.09, 30.61, 64.77, 113.25, 118.30, 121.80, 128.31, 132.57, 138.68, 142.03, 166.17.

(E)-3-p-Tolyl-acrylic acid butyl ester. **^{1}H NMR** ($CDCl_3$, 500 MHz) δ 0.97 (t, *J*= 7.4 Hz, 3H), 1.38-1.50 (m, 2H), 1.61-1.78 (m, 2H), 2.37 (s, 3H), 4.20 (t, *J*= 6.6 Hz, 2H), 6.39 (d, *J*= 16.0 Hz, 1H), 7.12-7.23 (m, 2H), 7.38-7.47 (m, 2H), 7.66 (d, *J*= 16.0 Hz, 1H); **^{13}C NMR** 13.73, 19.19, 21.44, 30.77, 64.32, 117.17, 128.02, 129.57, 131.72, 140.58, 144.52, 167.28.

(E)-3-(4-Acetyl-phenyl)-acrylic acid butyl ester. **^{1}H NMR** ($CDCl_3$, 500 MHz) δ 0.97 (t, *J*= 7.4 Hz, 3H), 1.34-1.52 (m, 2H), 1.62-1.76 (m, 2H), 2.61 (s, 3H), 4.22 (t, *J*= 6.6 Hz, 2H), 6.53 (d, *J*= 16.0 Hz, 1H), 7.54-7.64 (m, 2H), 7.69 (d, *J*= 16.0 Hz, 1H), 7.92-8.01 (m, 2H); **^{13}C NMR** 13.71, 19.15, 26.66, 30.67, 64.66, 120.82, 128.09, 128.82, 137.93, 138.78, 142.94, 166.57, 197.30.

(E)-4-(2-Butoxycarbonyl-vinyl)-benzoic acid butyl ester. Pale yellow oil, **^{1}H NMR** ($CDCl_3$, 500 MHz) δ 0.97 (two triplets partially overlapped, *J*= 7.4 Hz, 6H), 1.36-1.54 (m, 4H), 1.64-1.80 (m, 4H), 4.21 (t, *J*= 6.6 Hz, 2H), 4.32 (t, *J*= 6.6 Hz, 2H), 6.51 (d, *J*= 16.0 Hz, 1H), 7.54-7.62 (m, 2H), 7.68 (d, *J*= 16.0 Hz, 1H), 8.00-8.08 (m, 2H); **^{13}C NMR** 13.72, 19.1, 19.22, 30.69, 64.60, 65.03, 120.55, 127.81, 130.00, 131.67, 138.53, 143.13, 165.99, 166.60; **IR** liquid film ν 2960, 2873, 1717,

1639, 1569, 1456, 1412, 1386, 1277, 1203, 1172, 1105, 1018, 849, 774 cm^{-1}; **MS** (*m/z*) 304 (M^+, 8), 248 (15), 231 (40); 192 (100), 175 (34), 147 (31), 102 (16), 91 (12), 77 (12), 57 (40), 56 (46), 41 (77); **HRMS** calcd. for $C_{18}H_{24}O_4$ 304.1675, found 304.1655.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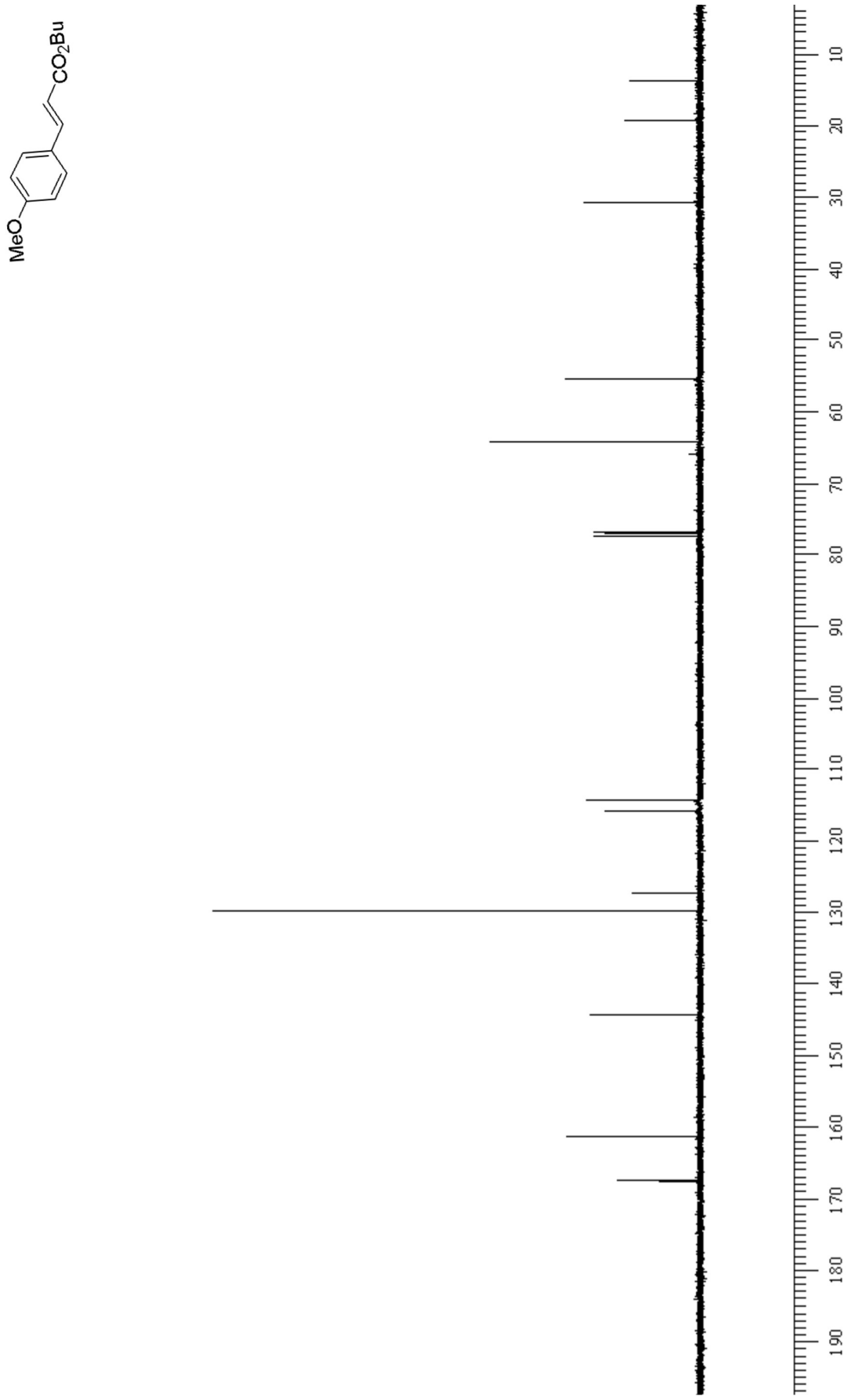
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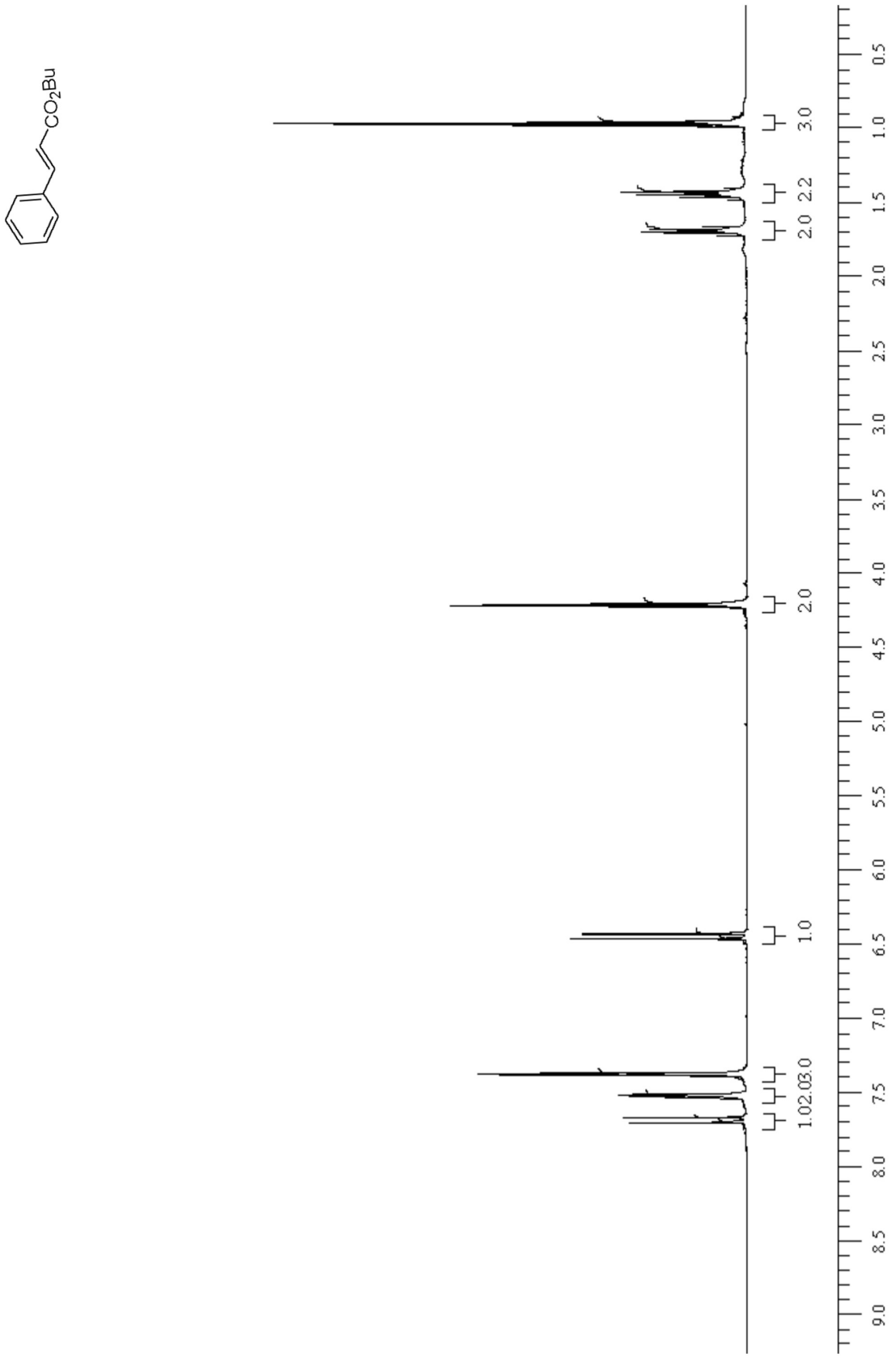
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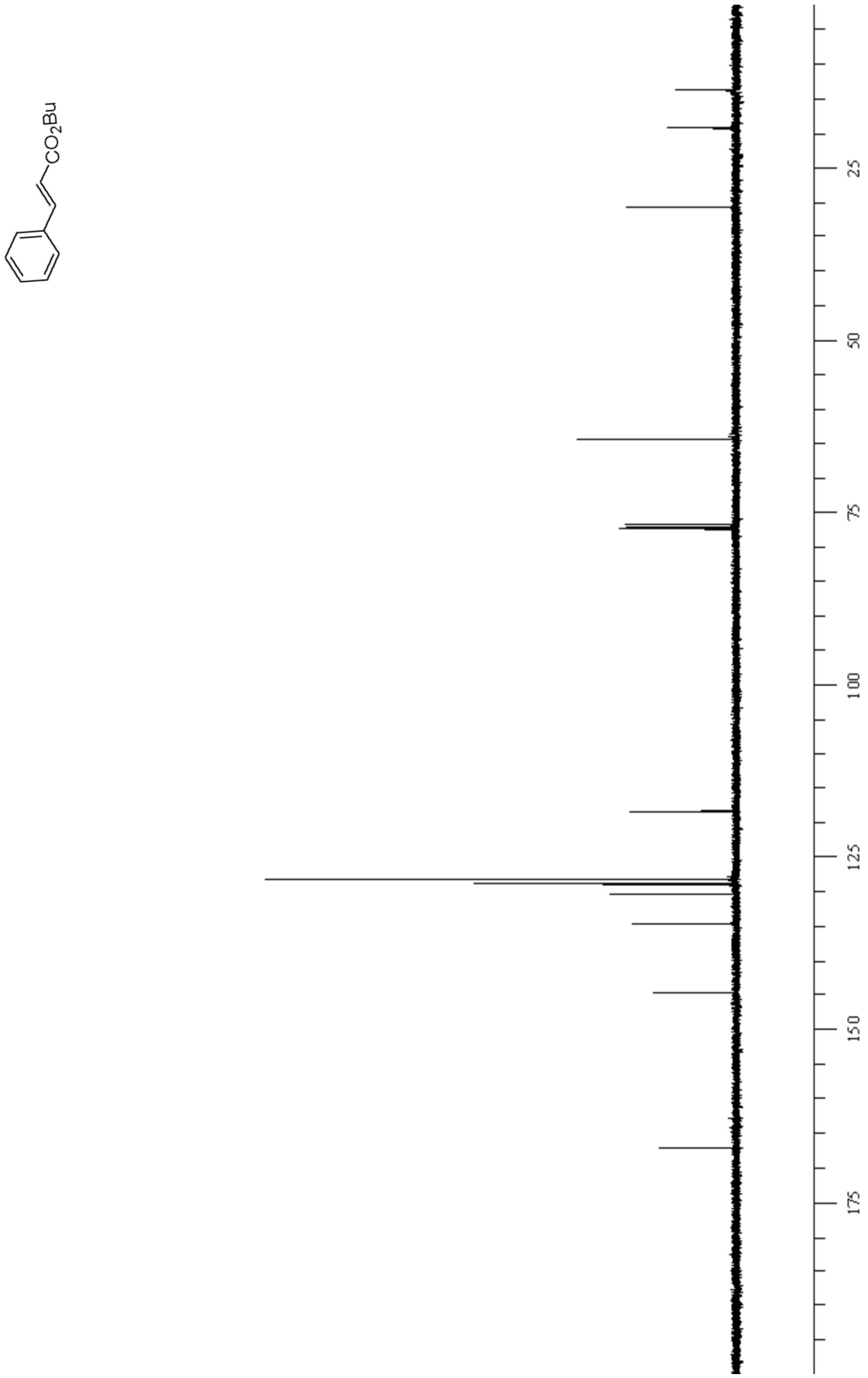
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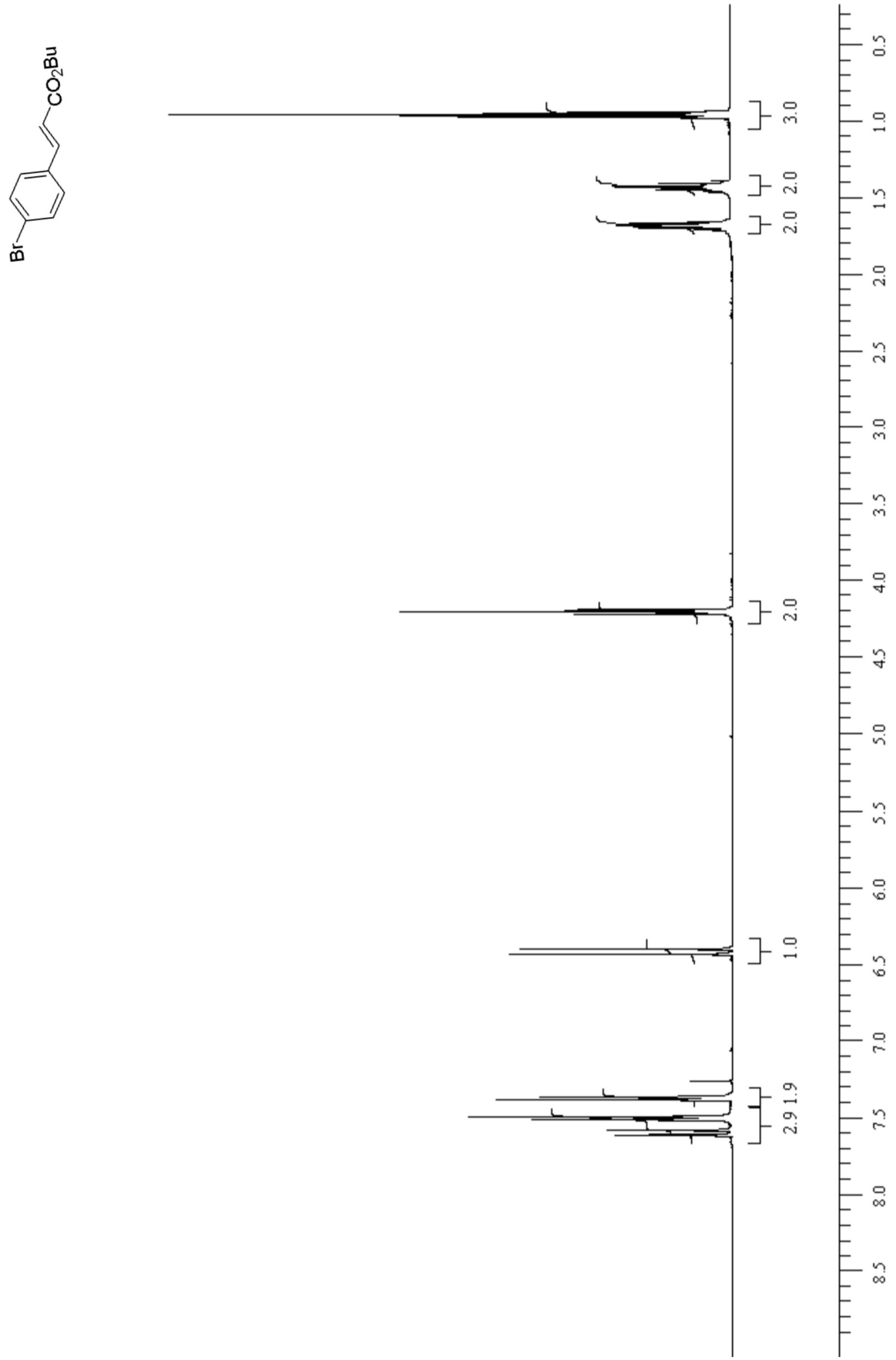
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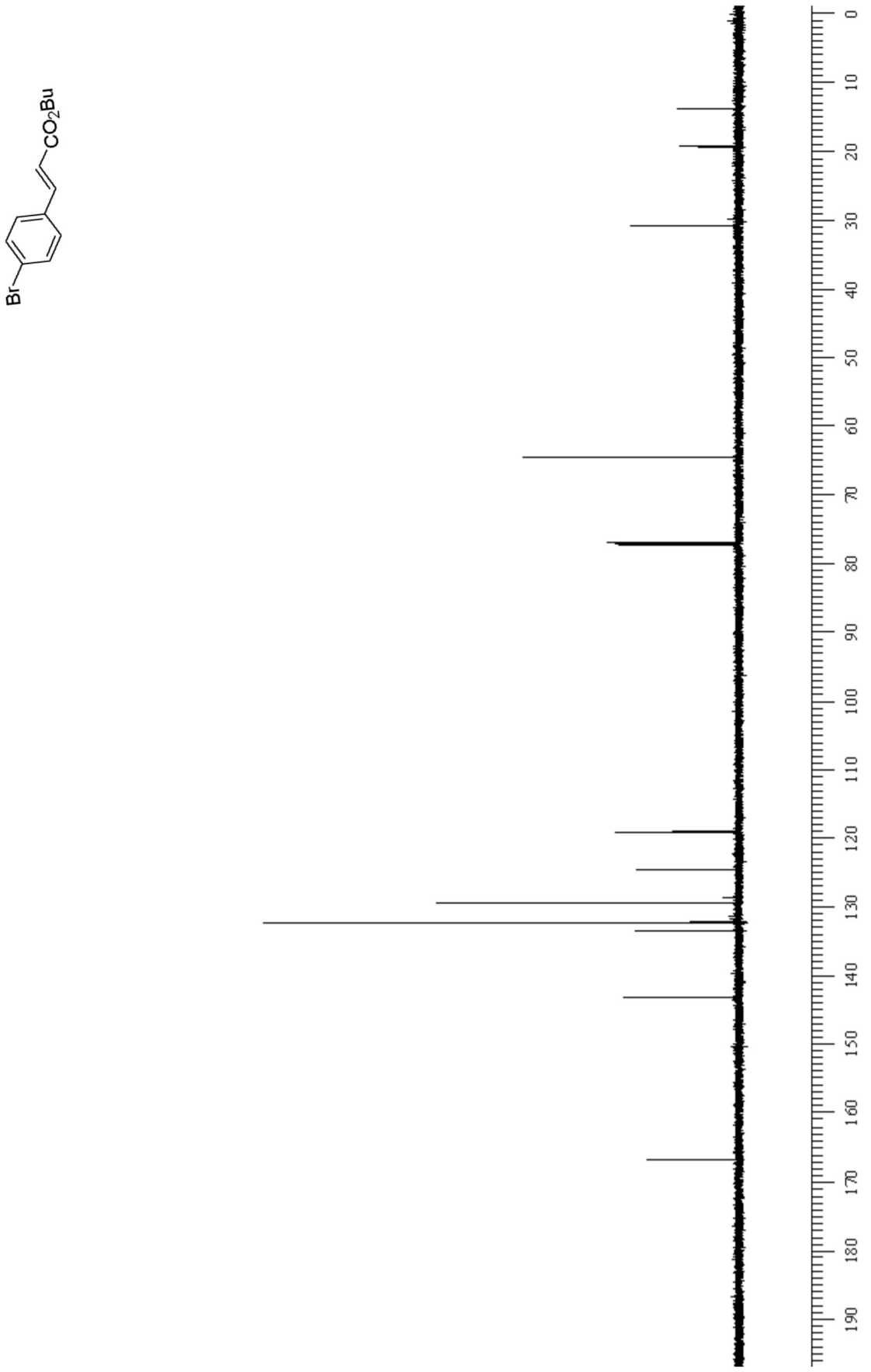
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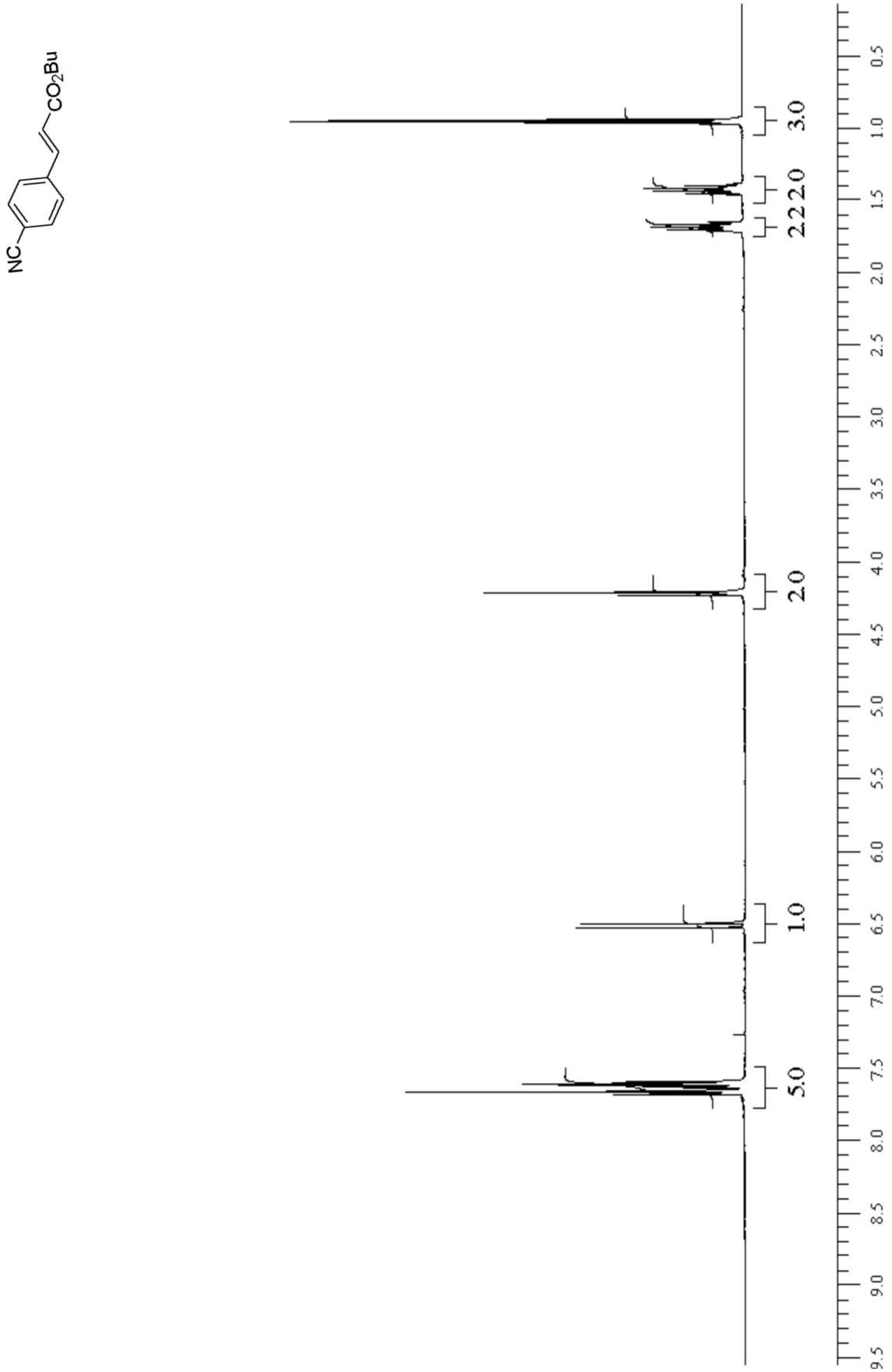
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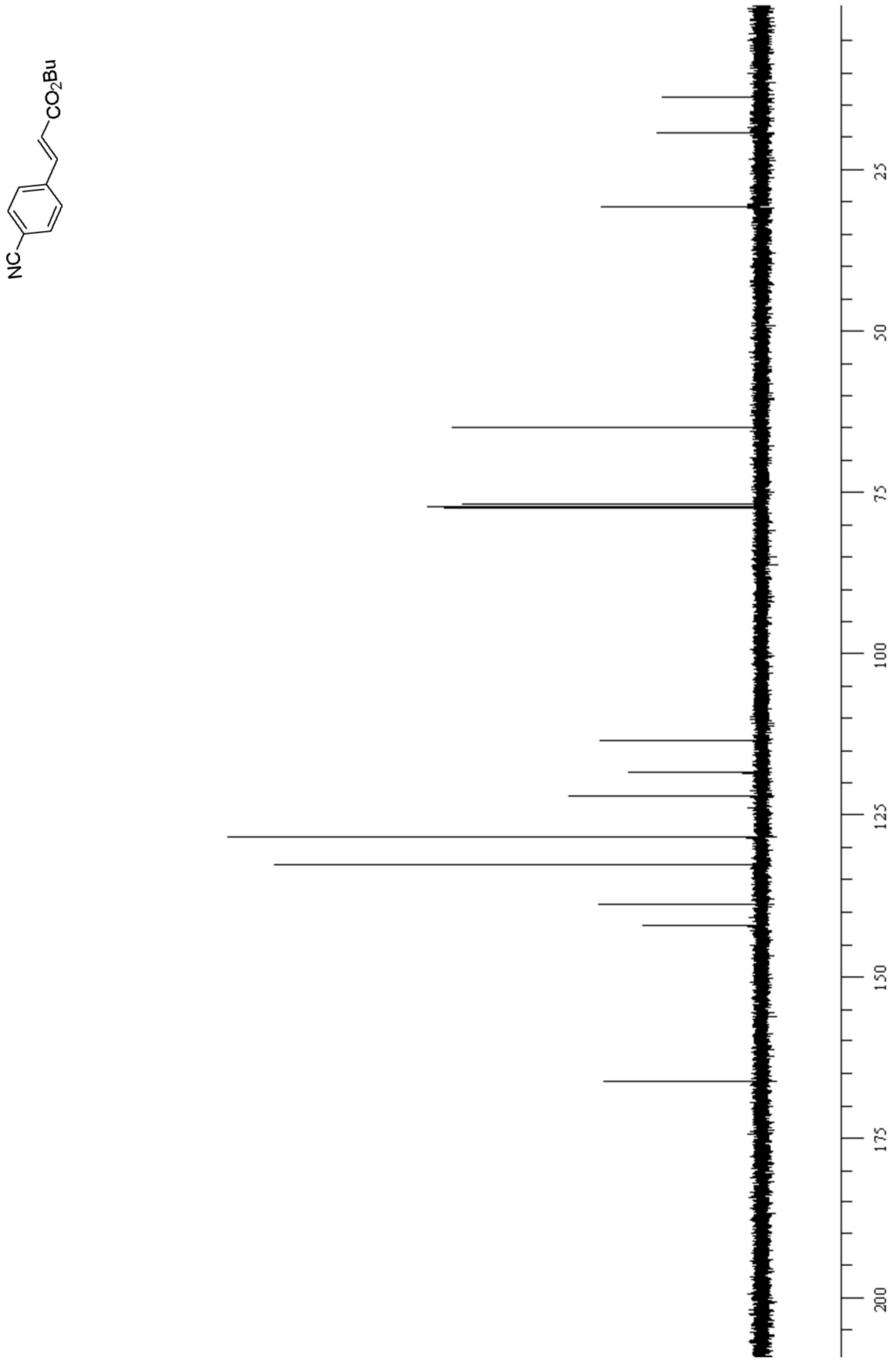
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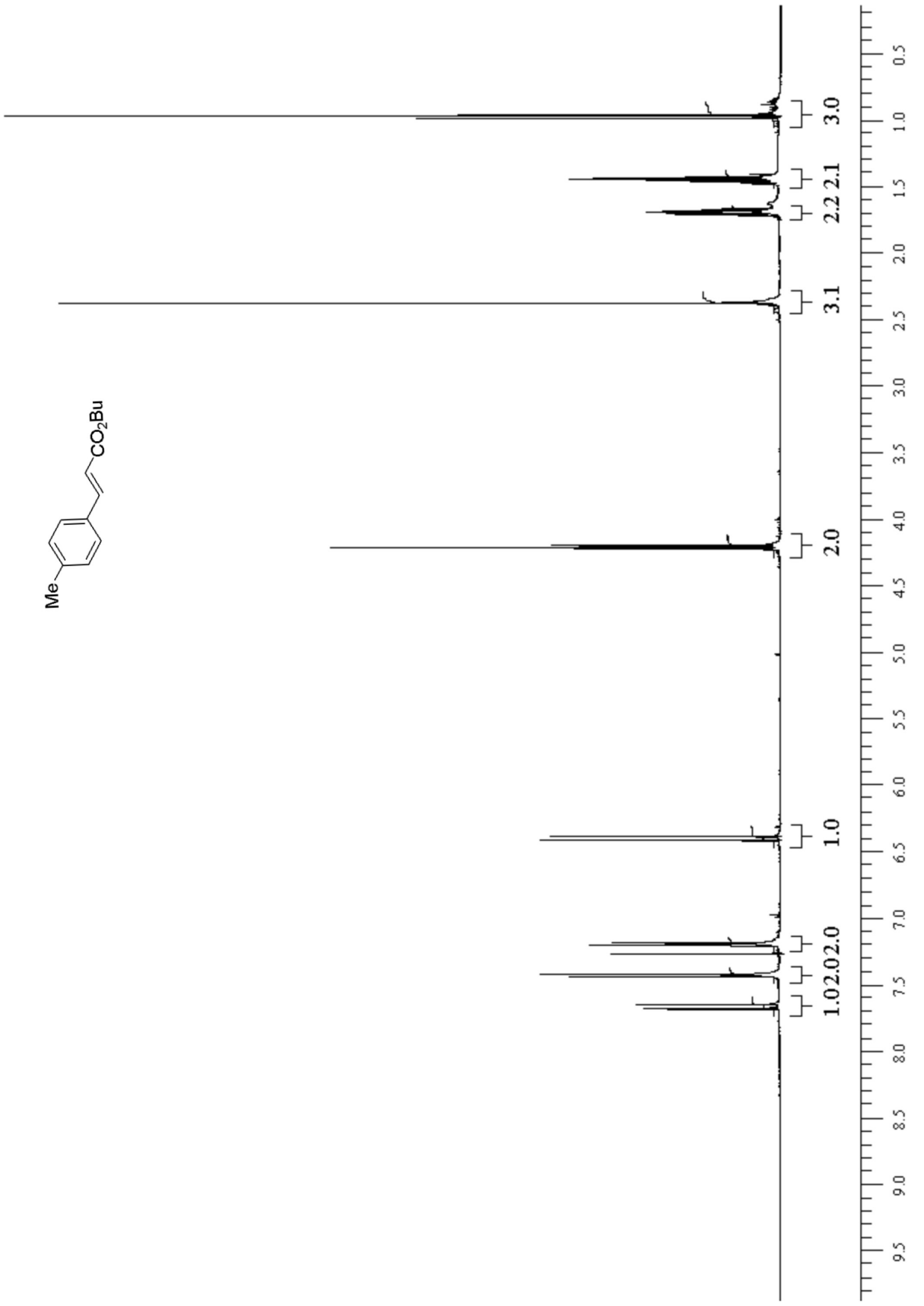
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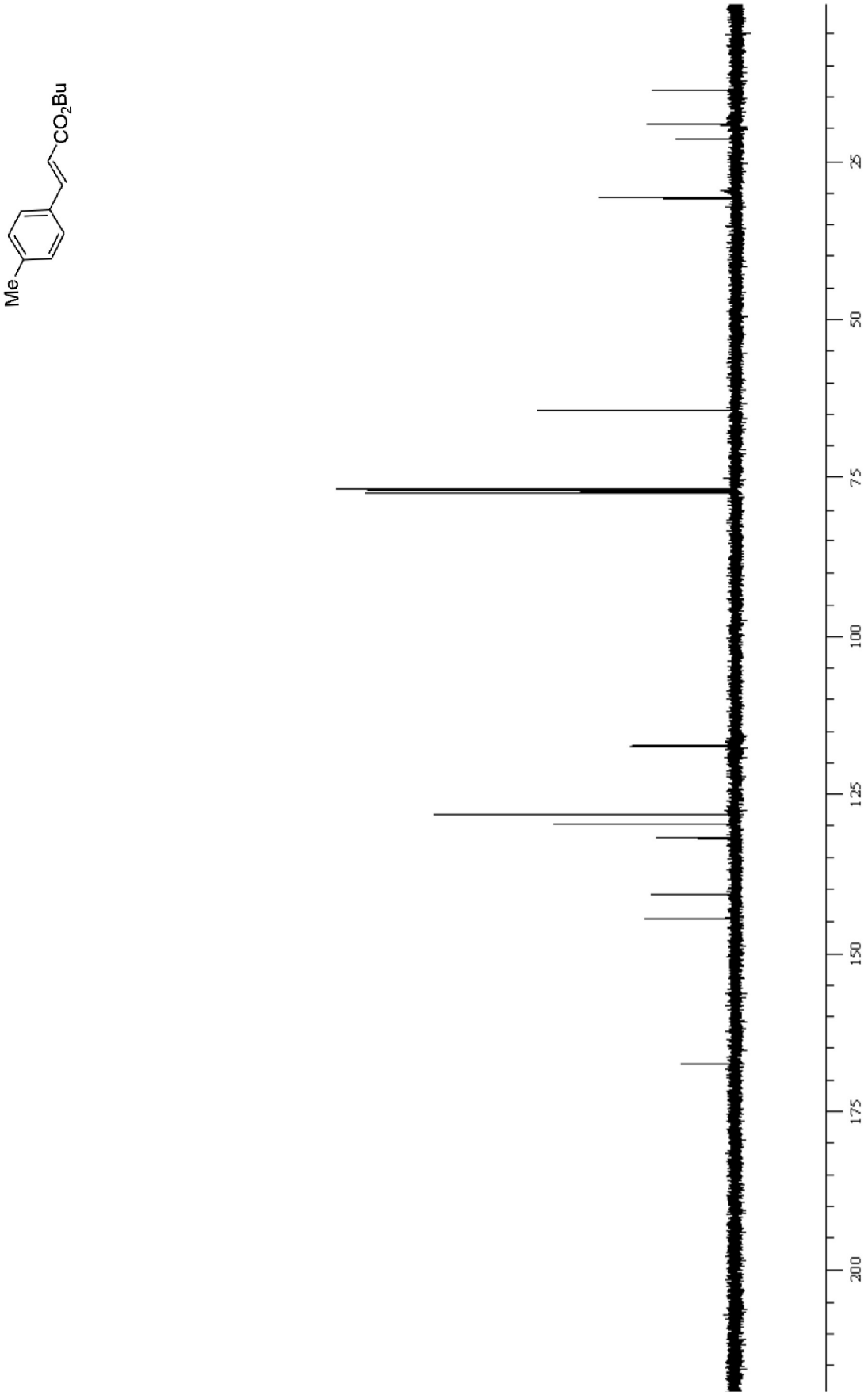
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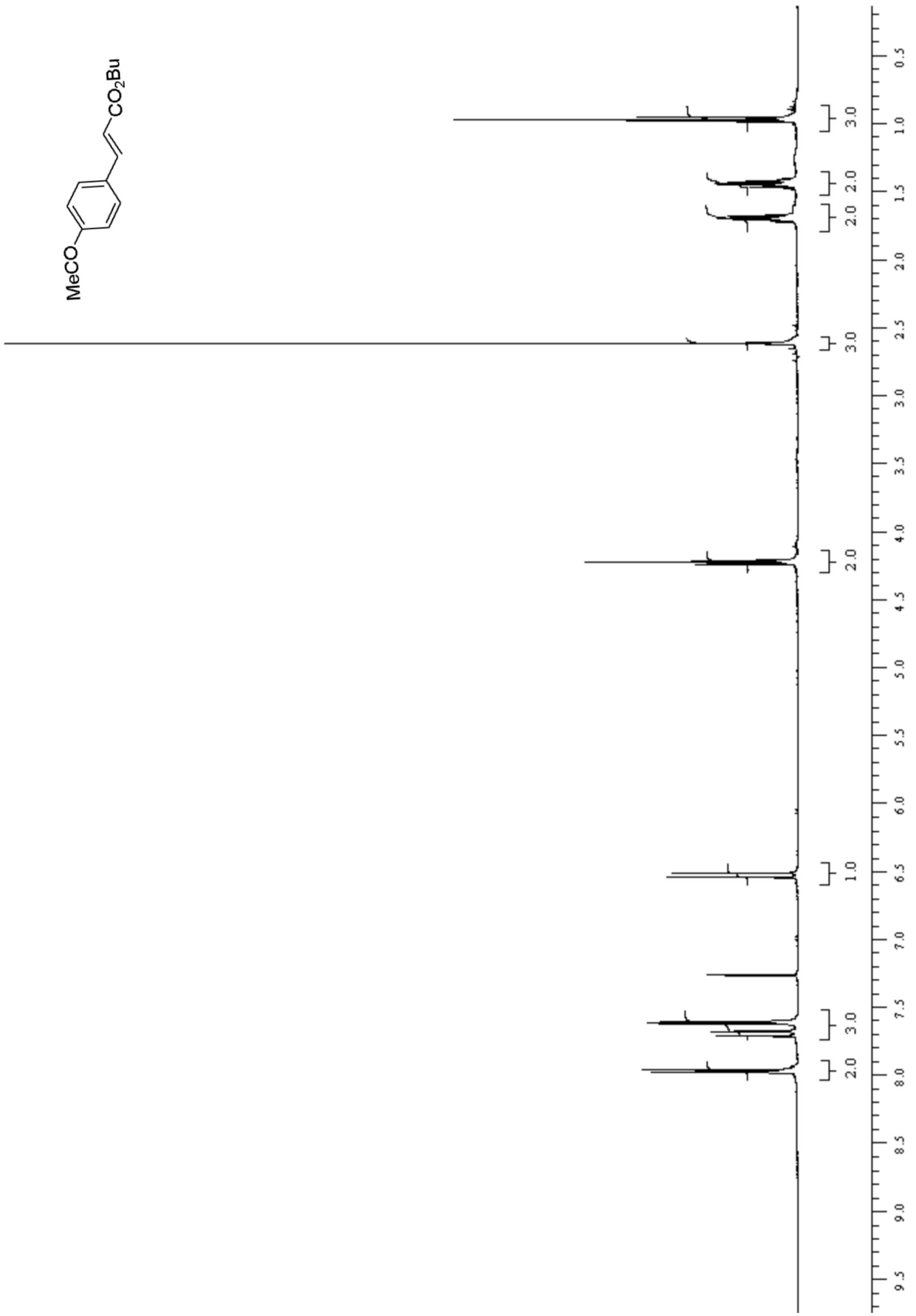
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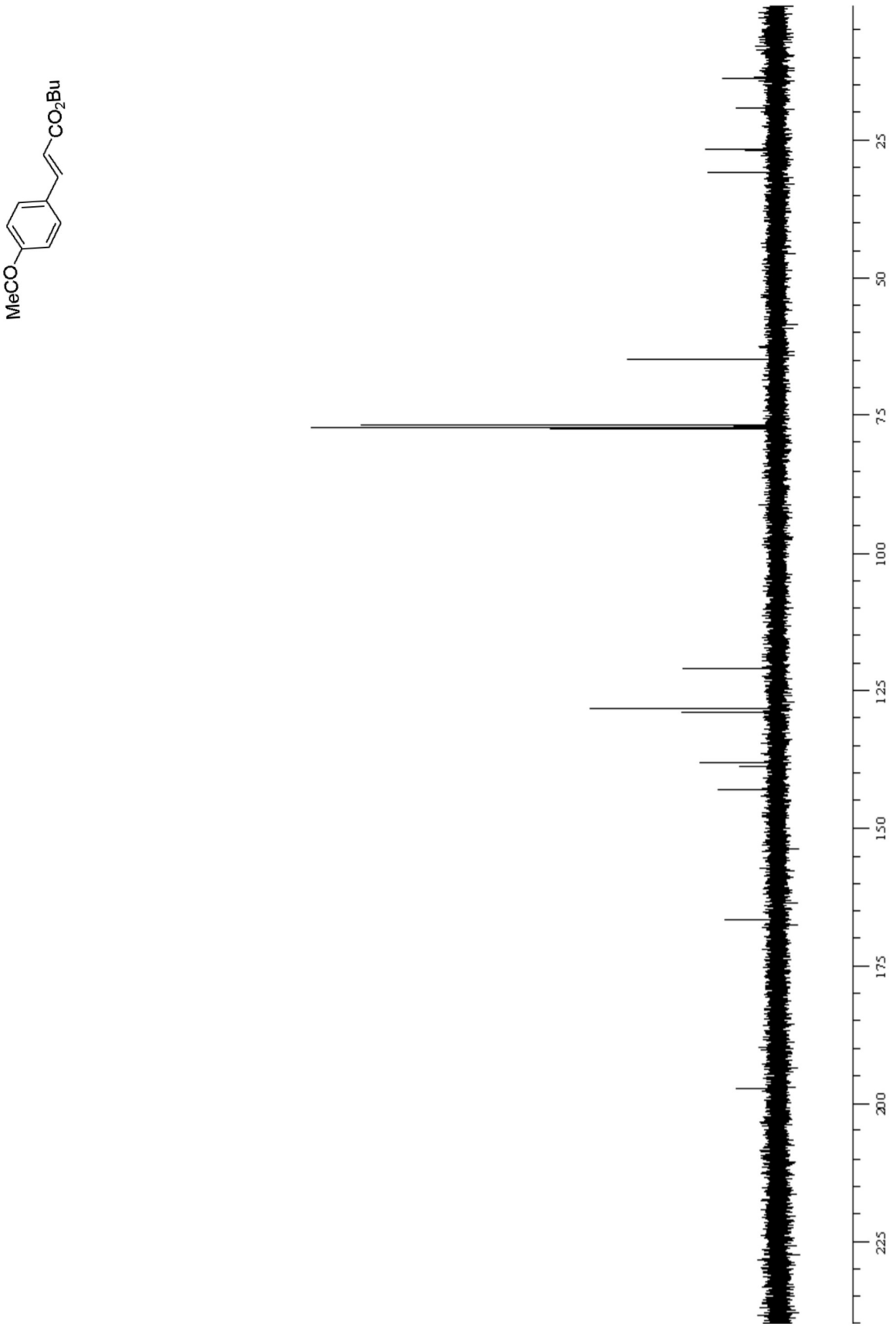
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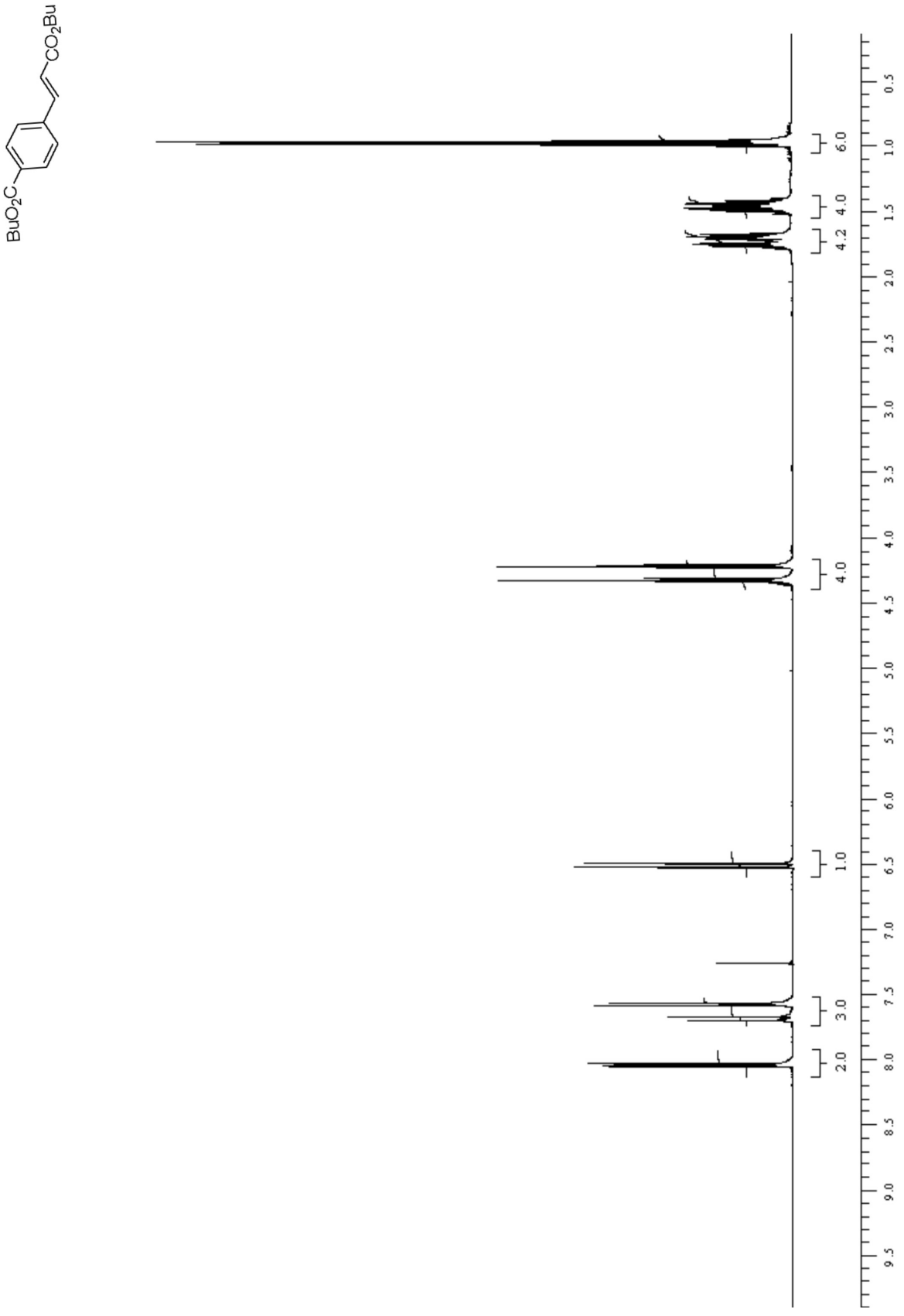
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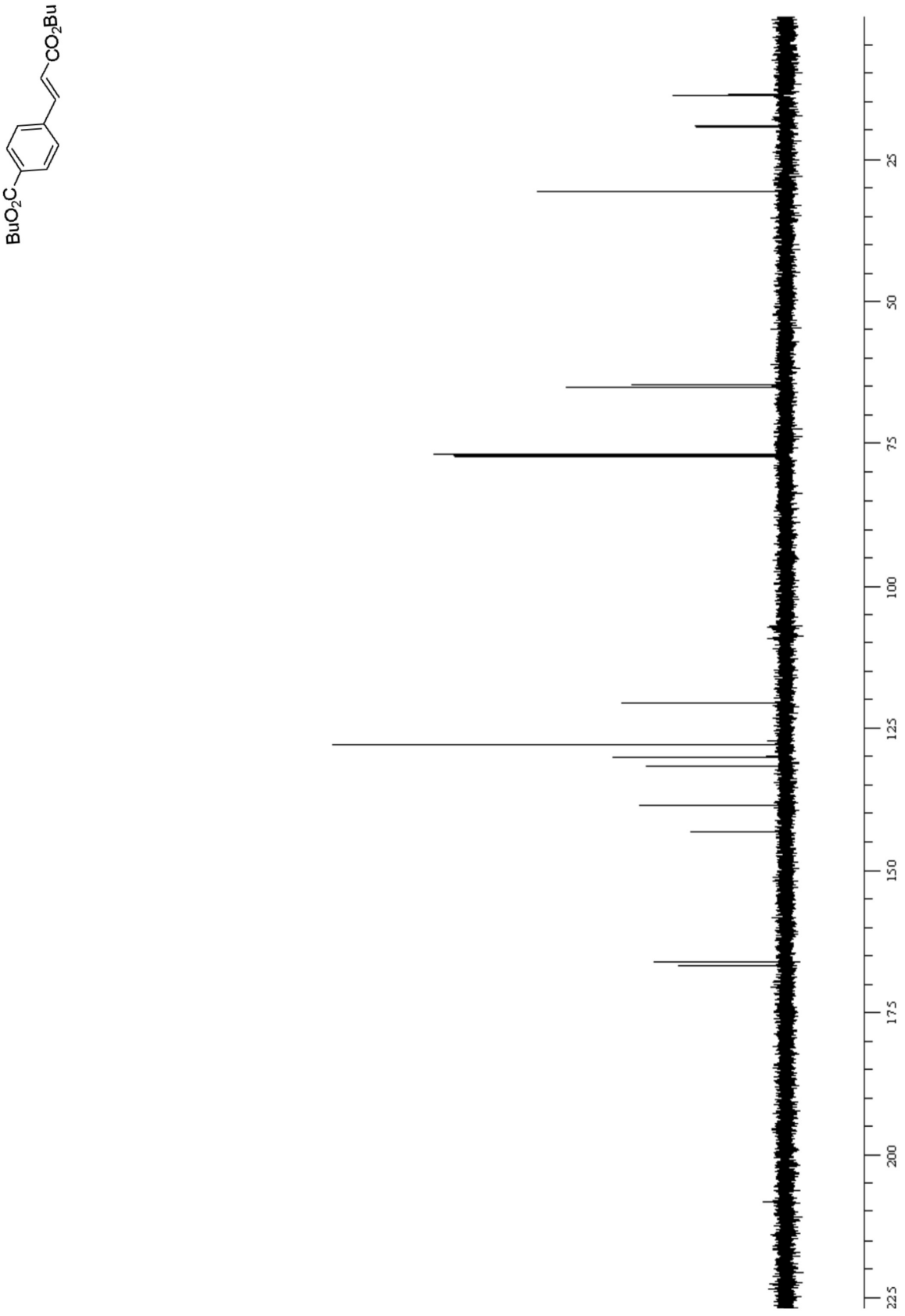
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