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Supporting Information

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Selective One-Pot Carbon-Carbon Bond Formation via Catalytic Carbon-Hydrogen Bond Functionalization Based Boronation of Cycloalkenes

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Contents:

Experimental Procedures and Characterization of the Prepared Compounds

All reactions were conducted under argon atmosphere by employing standard manifold techniques. The ^{1}H-NMR and ^{13}C-NMR spectra were recorded in $CDCl_3$ (internal standard: 7.26 ppm, ^{1}H; 77.36 ppm,^{13}C) solutions at room temperature by a Varian 400 MHz spectrometer. For column chromatography, Merck silica gel 60 (230-400 mesh) was used.

Method A. General procedure for allylation reactions. Catalyst **2** (0.003 mmol, 2 mol%, 2 mg), **3** (0.15 mmol, 38 mg) and DBU (0.075 mmol, 11.4 mg) were dissolved in neat **1a** (1.97 mmol, 0.2 ml). Then this reaction mixture was stirred at 70 ^{o}C for 4 hours. After cooling to room temperature the corresponding aldehyde **4a-d** (0.18 mmol) was added to the mixture and the stirring was continued for the allotted times and temperatures given in Table 1 (RCII). The crude reaction mixture was evaporated and the residue was purified by silica gel column chromatography.

Method B. General procedure for vinyl functionalization. Catalyst **2** (0.003 mmol, 2 mol%, 2 mg) and **3** (0.15 mmol, 38 mg) were dissolved in neat **1a-c** (0.1 ml). The reaction mixture was stirred for the given times and temperatures in Table 1 (RCI). After cooling to room temperature the reaction mixture was diluted with a dioxane/water (4:1) mixture (0.25 ml), whereafter the corresponding aryl iodides **5a-c** (0.15 mmol), $Pd(PPh_3)_4$ (0.0075 mmol, 5 mol%, 8 mg) and Cs_2CO_3 (0.30 mmol, 97 mg) were added. Then stirring was continued for the allotted times and temperatures given in Table 1 (RCII). The crude reaction mixture was evaporated and the residue was purified by silica gel column chromatography.

2-Cyclohexenyl(phenyl)methanol (6a). This compound was prepared from **4a** according to method A. The NMR data obtained for **6a** is identical with the literature values.[1a-b] ^{1}H NMR ($CDCl_3$): 7.35 (d, 4.4 Hz, 4H), 7.28 (m, 1H), 5.82 (dt, 4.9 Hz, 10.2 Hz, 1H), 5.39 (dd, 5.1 Hz, 10.2 Hz, 1H), 4.59 (d, 6.5 Hz, 1H), 2.51 (m, 1H), 1.99 (m, 2H), 1.87 (br, 1H, *OH*), 1.74 (m, 2H), 1.53 (m, 2H). ^{13}C NMR ($CDCl_3$): 143.2,

130.8, 128.6, 128.4, 127.8, 126.9, 77.7, 43.4, 25.6, 24.2, 21.5. HRMS (ESI): calc for $[C_{13}H_{16}O\text{-}OH]^+$: m/z, 171.1168, found: 171.1165.

2-Cyclohexenyl(4-bromo-phenyl)methanol (6b). This compound was prepared from **4b** according to method A except that p-toluenesulfonic acid (0.03 mmol, 20 mol%, 4 mg) was also added in the second step. The diastereoselectivity of **6b** is assigned on the basis of ^{1}H-NMR data given in the literature for analog stereodefined homoallyl alcohols (such as **6a**). ^{1}H NMR ($CDCl_3$): 7.47 (d, 8.5 Hz, 2H), 7.22 (d, 8.5 Hz, 2H), 5.85 (dt, 4.0 Hz, 10.2 Hz, 1H), 5.39 (d, 10.2 Hz, 1H), 4.58 (d, 6.1 Hz, 1H), 2.46 (m, 1H), 1.98 (m, 2H), 1.86 (br, 1H, *OH*), 1.75 (m, 1H), 1.64 (m, 1H), 1.49 (m, 2H). ^{13}C NMR ($CDCl_3$): 142.2, 131.6, 131.3, 128.6, 127.9, 121.5, 76.9, 43.3, 25.5, 23.9, 21.4. HRMS (ESI): calc for $[C_{13}H_{15}BrO\text{-}OH]^+$: m/z, 249.0273, found: 249.0273.

2-Cyclohexenyl(4-nitro-phenyl)methanol (6c). This compound was prepared from **4c** according to method A except that p-toluenesulfonic acid (0.03 mmol, 20 mol%, 4 mg) was also added in the second step. The diastereoselectivity of **6c** is assigned on the basis of ^{1}H-NMR data given in the literature for analog stereodefined homoallyl alcohols (such as **6a**). ^{1}H NMR ($CDCl_3$): 8.20 (d, 8.7 Hz, 2H), 7.52 (d, 8.7 Hz, 2H), 5.93 (dt, 2.7 Hz, 10.1 Hz, 1H), 5.45 (d, 10.1 Hz, 1H), 4.79 (d, 5.4 Hz, 1H), 2.53 (m, 1H), 2.00 (m, 3H), 1.74 (br, 1H, *OH*), 1.50 (m, 3H). ^{13}C NMR ($CDCl_3$): 150.4, 147.5, 132.4, 127.5, 127.4, 123.7, 76.4, 43.4, 25.4, 23.2, 21.3. HRMS (ESI): calc for $[C_{13}H_{15}NO_3\text{-}OH]^+$: m/z, 216.1019, found: 216.1015.

(E)-1-(2-cyclohexeneyl)-3-phenyl-2-propen-1ol (6d). This compound was prepared from **4d** according to method A. The NMR data obtained for **6d** is identical with the

literature values.[1b] ^{1}H NMR ($CDCl_3$): 7.39 (d, 8.1 Hz, 2H), 7.32 (t, 8.1 Hz, 2H), 7.24 (t, 8.1 Hz, 1H), 6.61 (d, 16.0 Hz, 1H), 6.25 (dd, 6.8 Hz, 16.0 Hz, 1H), 5.86 (dt, 3.5 Hz, 10.2 Hz, 1H), 5.65 (dd, 2.1 Hz, 10.2 Hz, 1H), 4.21 (t, 6.8 Hz, 1H), 2.39 (m, 1H), 2.00 (m, 2H), 1.80 (m, 2H), 1.63 (br, 1H, *OH*), 1.52 (m, 2H). ^{13}C NMR ($CDCl_3$): 137.2, 131.8, 130.9, 130.6, 128.9, 128.0, 126.8, 76.4, 42.2, 25.6, 24.5, 21.7. HRMS (ESI): calc for $[C_{15}H_{18}O\text{-}OH]^+$: m/z, 197.1325, found: 197.1326.

1-Phenyl-1-cyclohexene (7a). This compound was prepared according to method B from **1a** and **5a** except that a THF/water (4:1) mixture (0.25 ml) was used as co-solvent in the second step of the coupling reaction. The NMR data obtained for **7a** is identical with the literature values.[2] ^{1}H NMR ($CDCl_3$): 7.39 (d, 7.3 Hz, 2H), 7.31 (t, 7.3 Hz, 1H), 7.21 (t, 7.3 Hz, 1H), 6.12 (dd, 3.4 Hz, 6.2 Hz, 1H), 2.42 (m, 2H), 2.22 (m, 2H), 1.79 (m, 2H), 1.67 (m, 2H). ^{13}C NMR ($CDCl_3$): 143.1, 136.9, 128.5, 126.8, 125.3, 125.1, 27.7, 26.2, 23.4, 22.5. HRMS (APCI): calc for $[C_{12}H_{14}]^+$: m/z, 158.1090, found: 158.1095.

1-Chloro-4-(1-cyclohexenyl)benzene (7b). This compound was prepared according to method B from **1a** and **5b** except that a THF/water (4:1) mixture (0.25 ml) was used as co-solvent and barium hydroxide (0.3 mmol, 95 mg) was employed as base in the second step of the coupling reaction. The NMR data obtained for **7b** is identical with the literature values.[3] ^{1}H NMR ($CDCl_3$): 7.30 (d, 8.7 Hz, 2H), 7.26 (d, 8.7 Hz, 2H), 6.11 (ddd, 1.6 Hz, 3.2 Hz, 4.0 Hz, 1H), 2.37 (m, 2H), 2.20 (m, 2H), 1.78 (m, 2H), 1.66 (m, 2H). ^{13}C NMR ($CDCl_3$): 141.4, 135.9, 132.5, 128.6, 126.5, 125.7, 27.7, 26.2, 23.3, 22.4. HRMS (APCI): calc for $[C_{12}H_{13}Cl]^+$: m/z, 192.0700, found: 192.0703.

1-Chloro-2-(1-cyclohexenyl)benzene (7c). This compound was prepared according to method B from **1a** and **5c** except that barium hydroxide (0.3 mmol, 95 mg) was used as base in the second step of the coupling reaction. ^{1}H NMR ($CDCl_3$): 7.33 (d, 6.5 Hz, 1H), 7.16 (m, 3H), 5.66 (ddd, 1.8 Hz, 3.9 Hz, 5.8 Hz, 1H), 2.29 (m, 2H), 2.18 (m, 2H), 1.76 (m, 2H), 1.69 (m, 2H). ^{13}C NMR ($CDCl_3$): 143.8, 138.0, 132.8, 130.5, 129.8, 128.1, 127.6, 126.9, 29.5, 25.7, 23.2, 22.4. HRMS (APCI): calc for $[C_{12}H_{13}Cl]^+$: m/z, 192.0700, found: 192.0706.

1-Phenyl-1-cycloheptene (7d). This compound was prepared according to method B from **1b** and **5a** except that a THF/water (4:1) mixture (0.25 ml) was used as solvent in the second step of the coupling reaction. The NMR data obtained for **7d** is identical with the literature values.[4] ^{1}H NMR ($CDCl_3$): 7.31 (m, 4H), 7.20 (t, 6.8 Hz, 1H), 6.09 (t, 6.7 Hz, 1H), 2.62 (m, 2H), 2.29 (m, 2H), 1.84 (m, 2H), 1.65 (m, 2H), 1.56 (m, 2H). ^{13}C NMR ($CDCl_3$): 145.3, 145.3, 130.8, 128.4, 126.6, 126.0, 33.1, 33.1, 29.2, 27.3, 27.1. HRMS (APCI): calc for $[C_{13}H_{16}]^+$: m/z, 172.1247, found: 172.1247.

1-Phenyl-1-cyclooctene (7e). This compound was prepared according to method B from **1c** and **5a** except that that barium hydroxide (0.3 mmol, 95 mg) was used as base in the second step of the coupling reaction. The NMR data obtained for **7e** is identical with the literature values.[2] ^{1}H NMR ($CDCl_3$): 7.41 (d, 7.8 Hz, 2H), 7.30 (t, 7.8 Hz, 2H), 7.21 (t, 7.8 Hz, 1H), 6.01 (t, 8.3 Hz, 1H), 2.63 (m, 2H), 2.30 (m, 2H), 1.65 (m, 2H), 1.56 (m, 6H). ^{13}C NMR ($CDCl_3$): 143.5, 140.6, 128.5, 128.3, 126.8, 126.1, 30.3, 29.8, 28.8, 27.8, 27.3, 26.5. HRMS (APCI): calc for $[C_{14}H_{18}]^+$: m/z, 186.1403, found: 186.1401.

References

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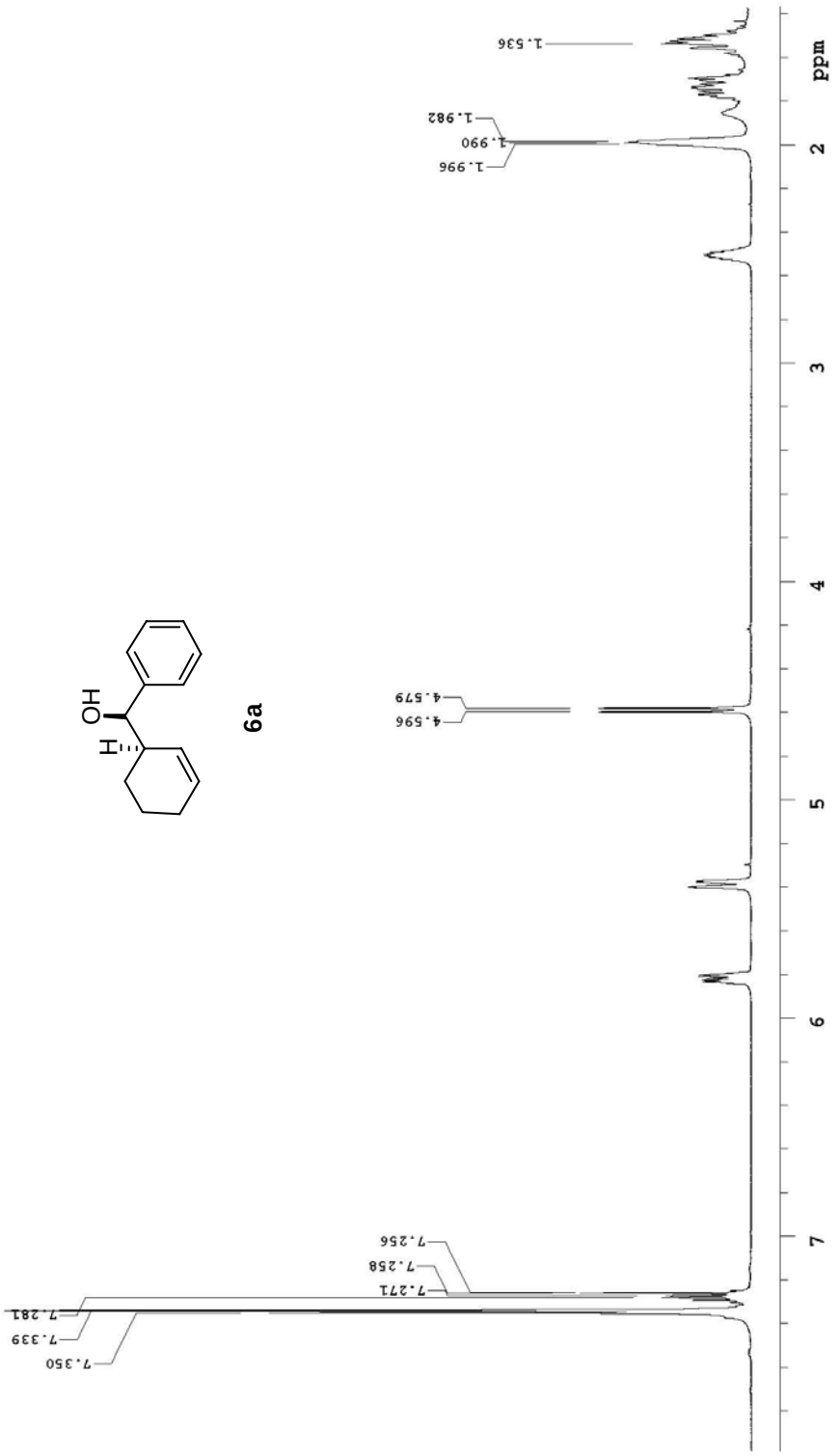
[2] A. Furstner, B. Scheiper, M. Bonnekessel, H. Krause, *J. Org. Chem.* **2004**, *69*, 3943.

[3] Y. Nakamura, S. Takeuchi, Y. Ohgo, M. Yamoaka, A. Yoshida, K. Mikami, *Tetrahedron*. **1999**, *55*, 4595.

[4] B. De Costa, G. Clifford, L. Guiying, H. Xiao-shu, *J. Org. Chem.* **1994**, *59*, 482.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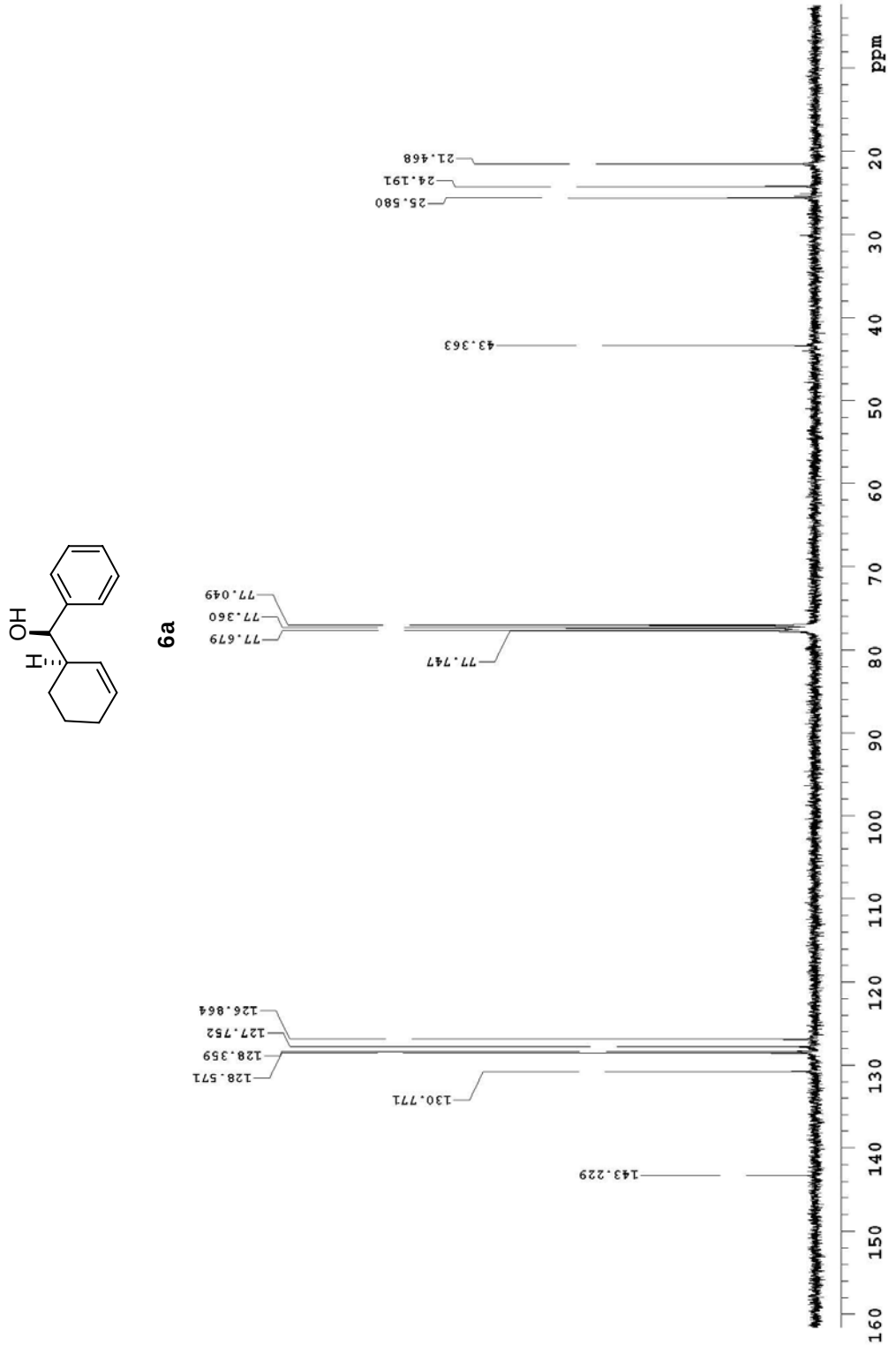
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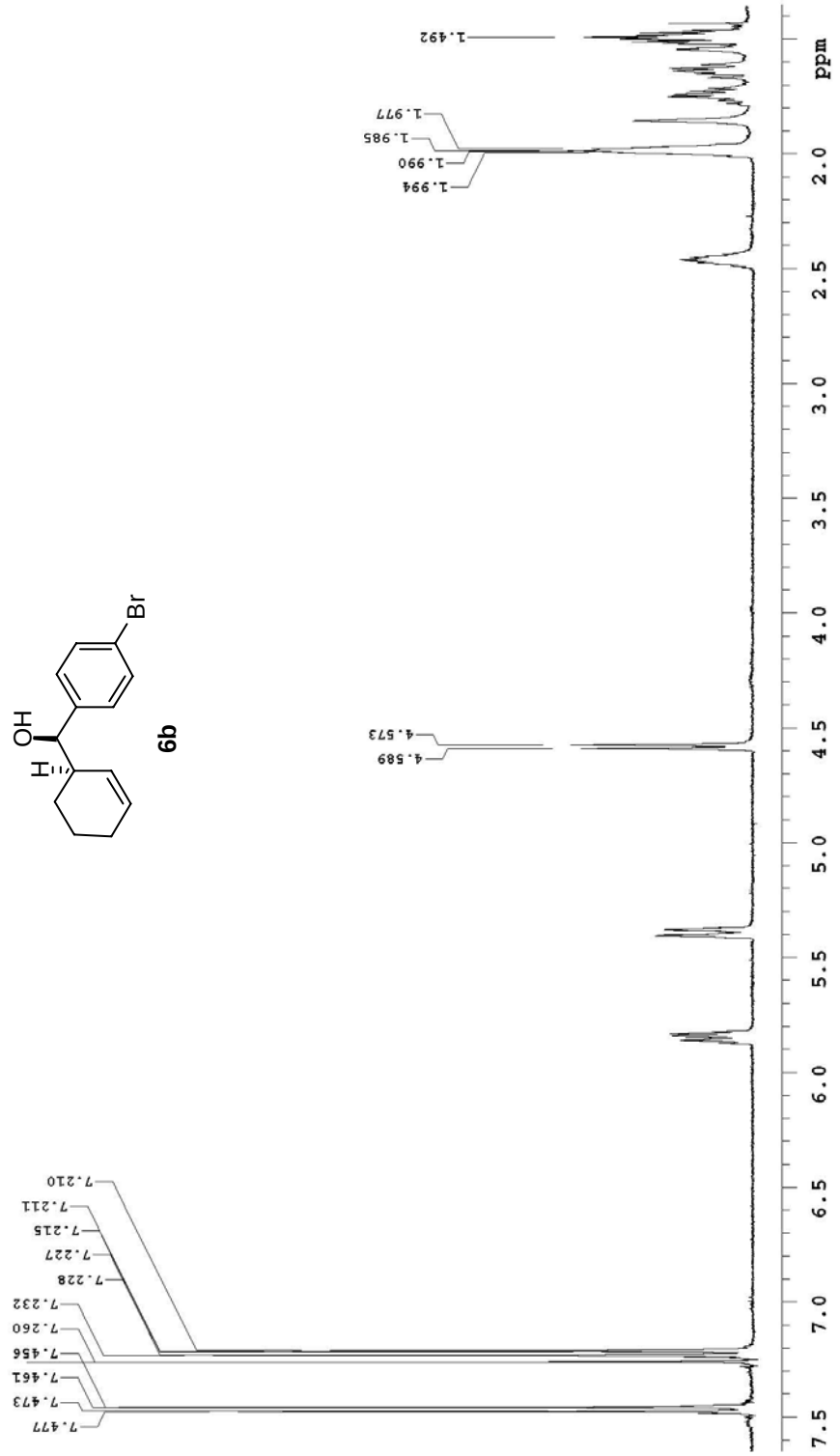
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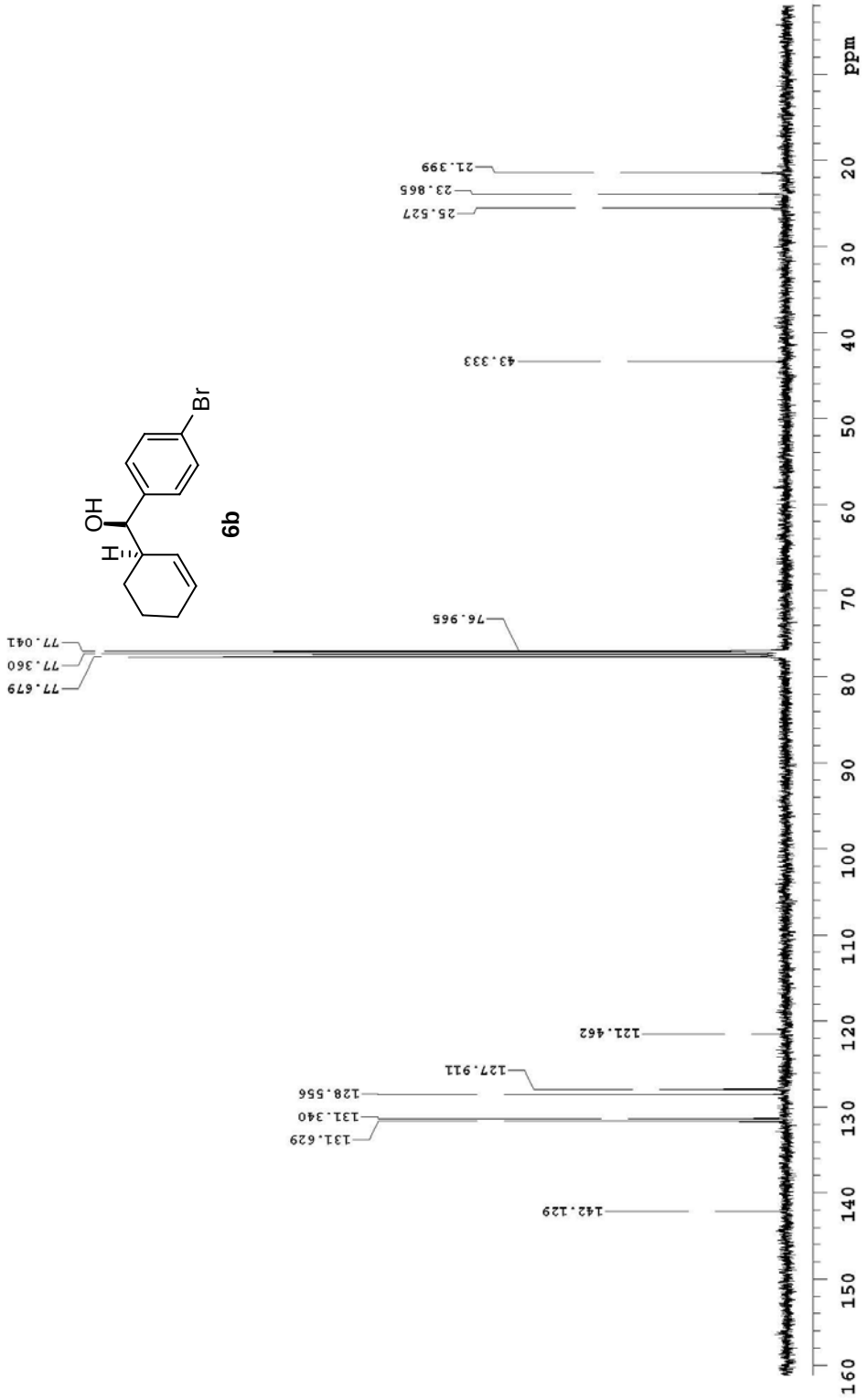
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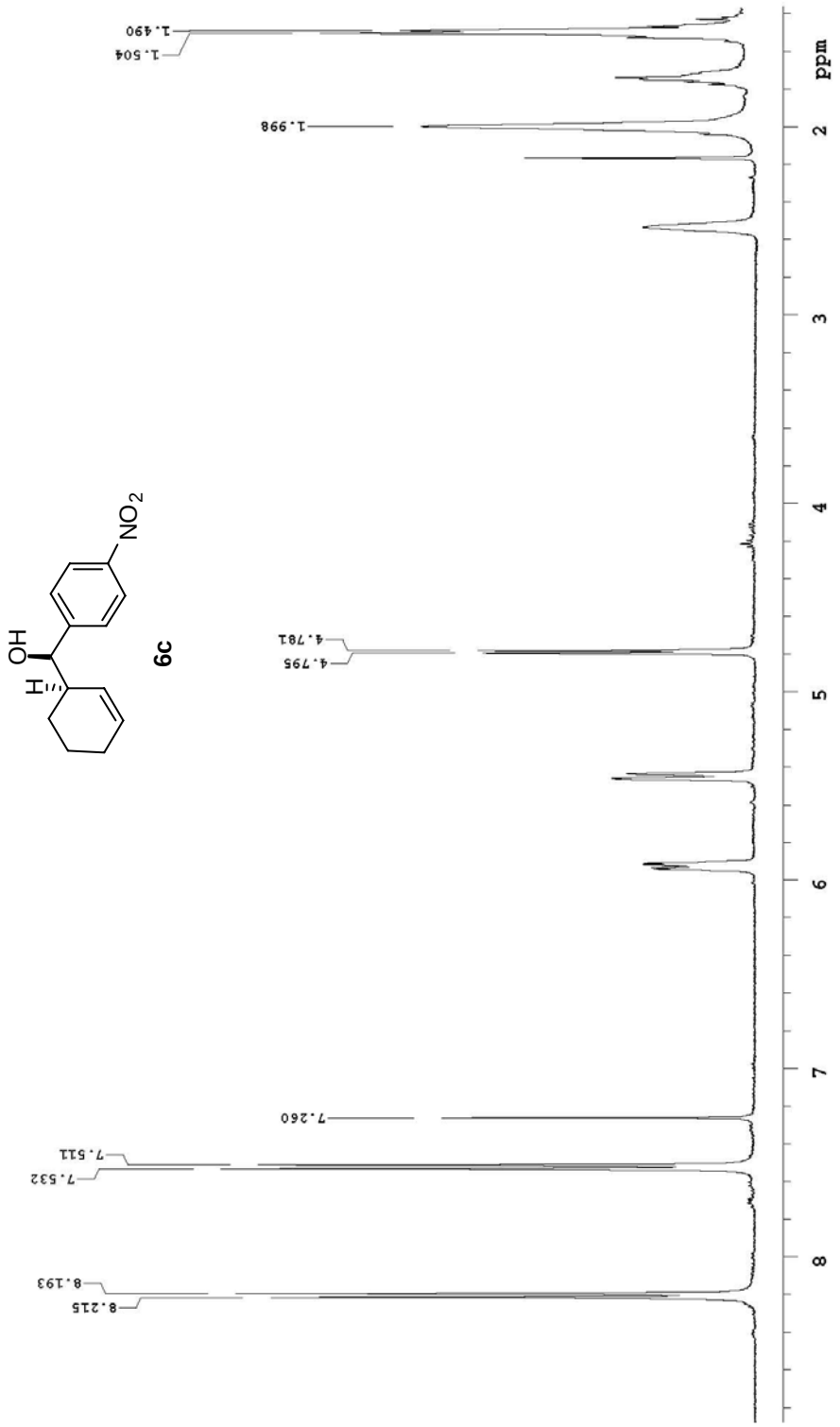
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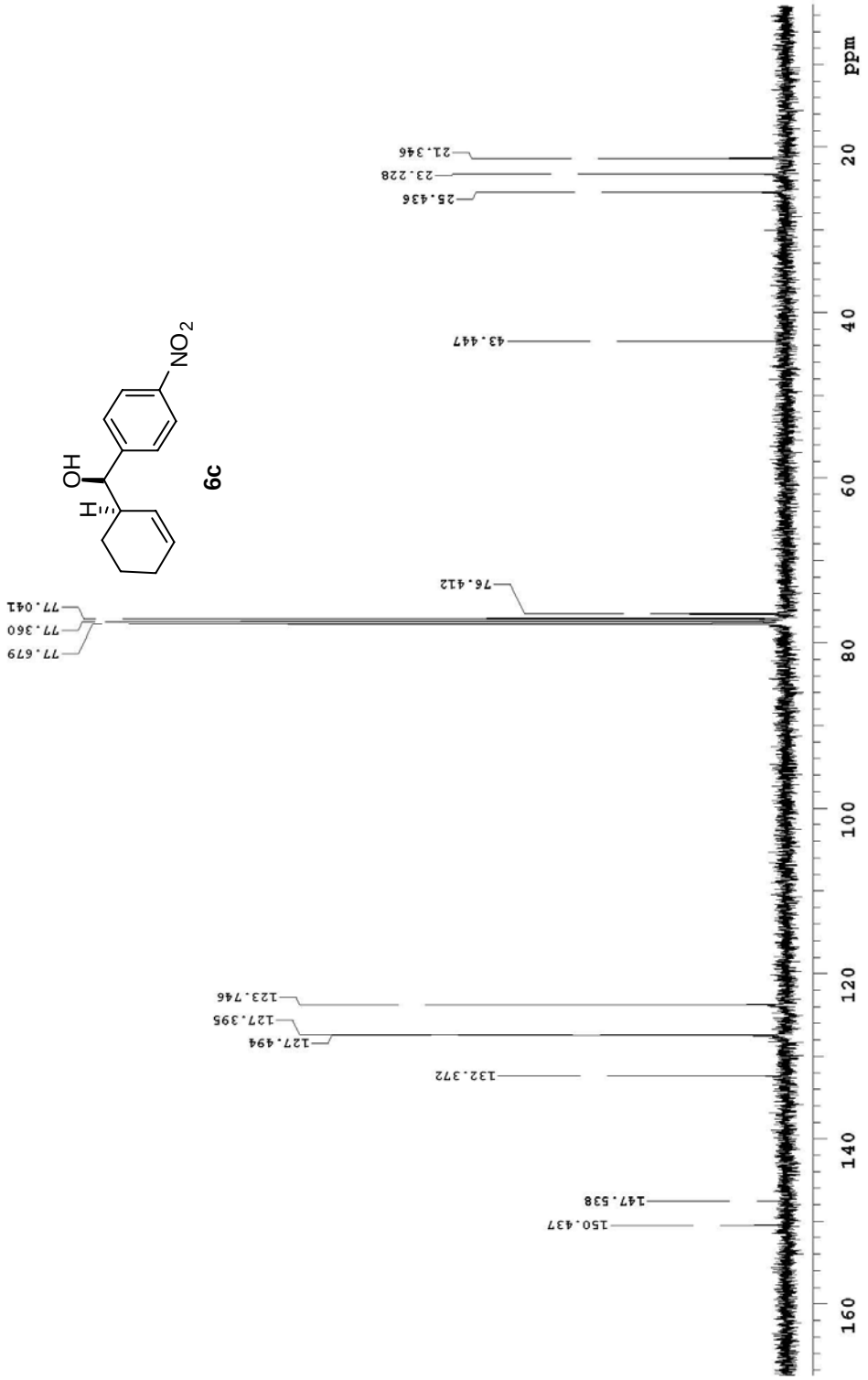
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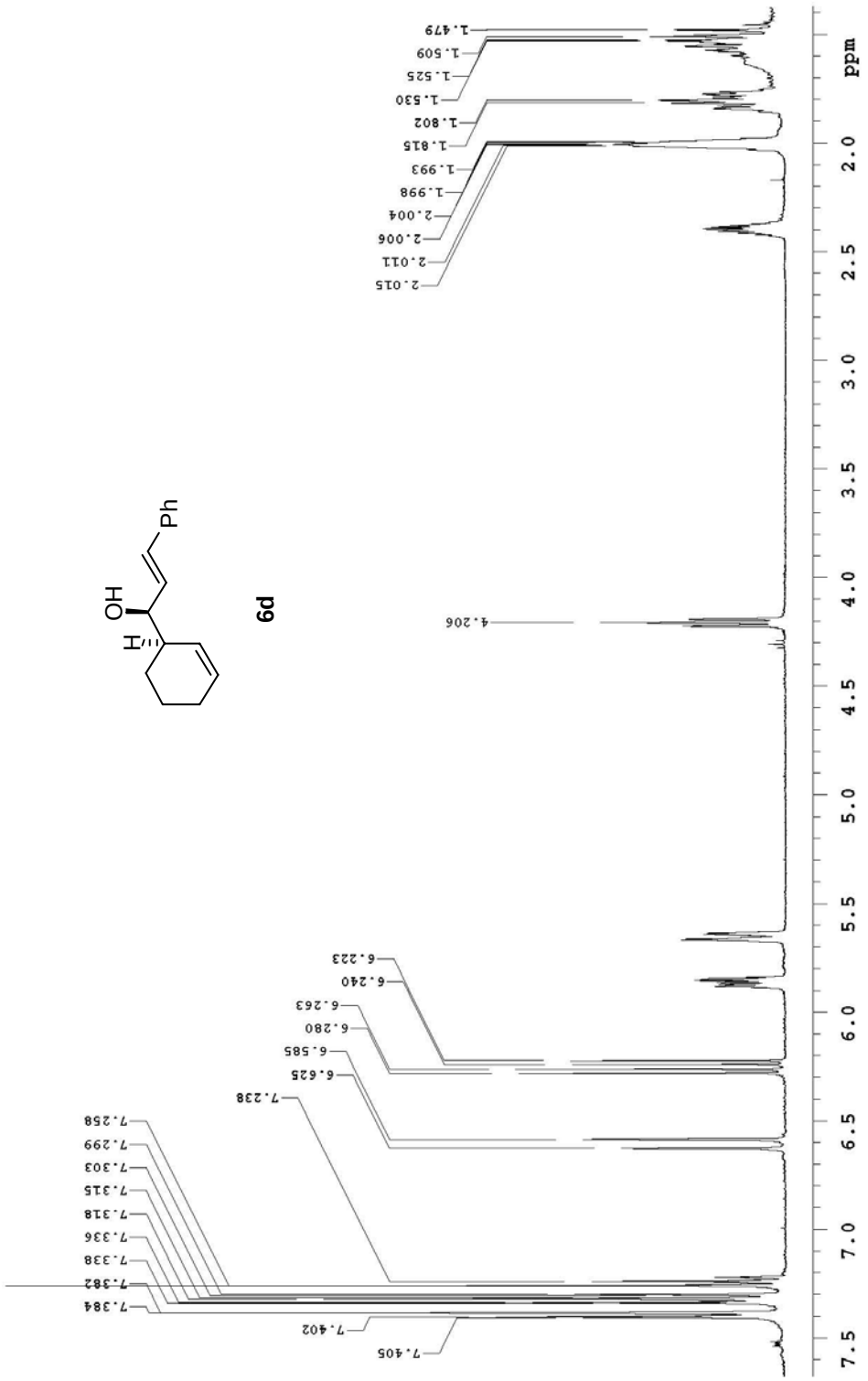
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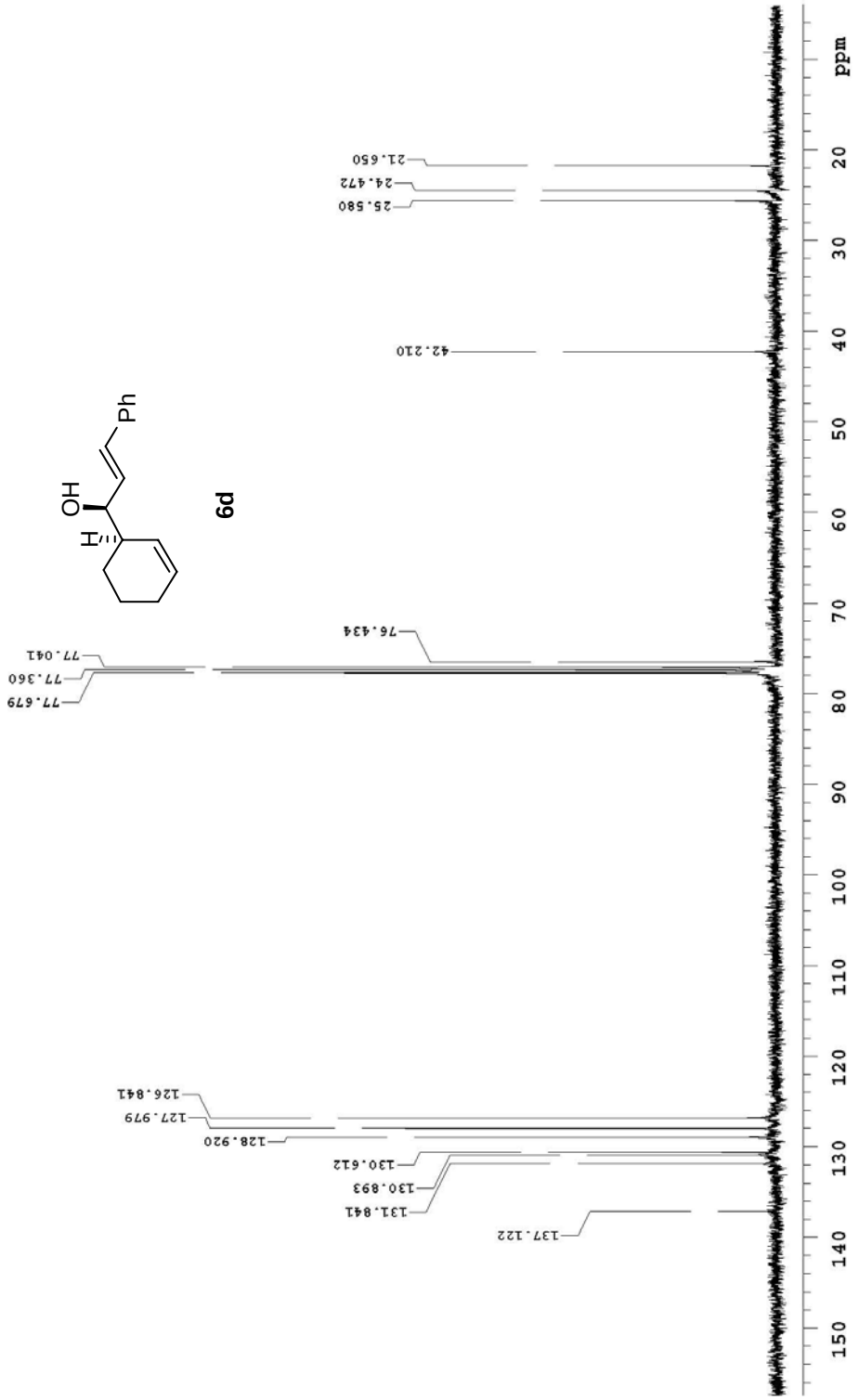
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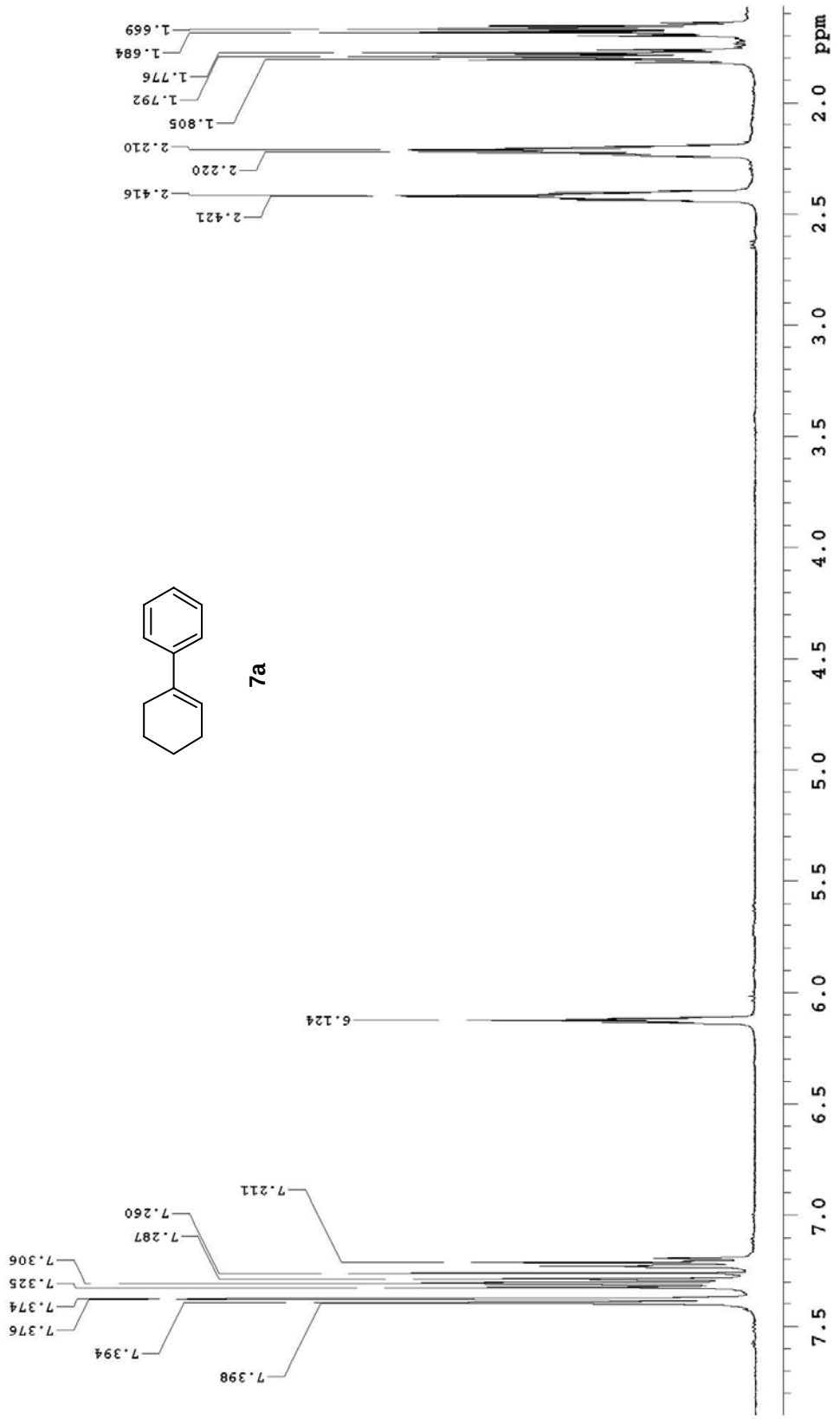
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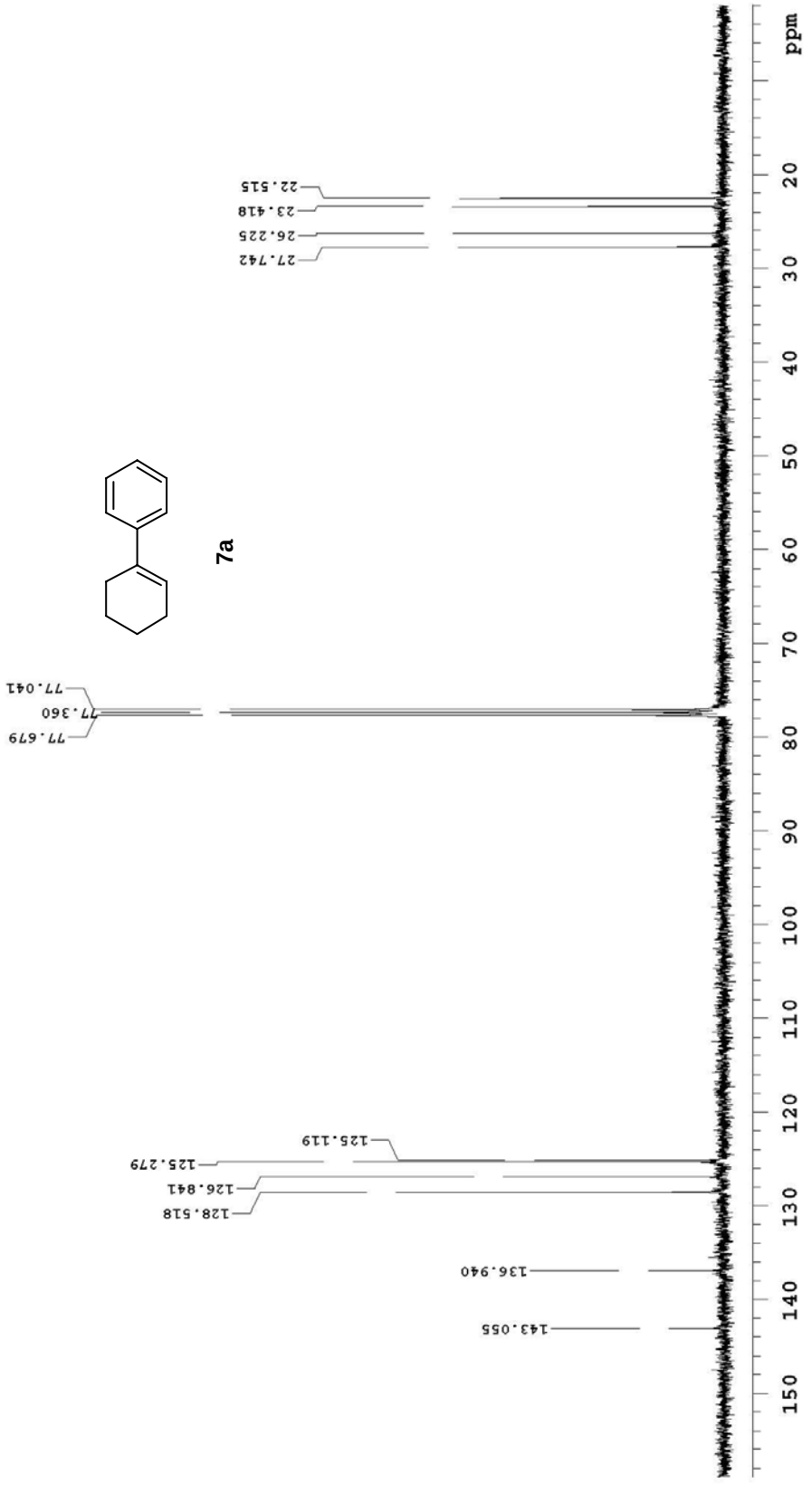
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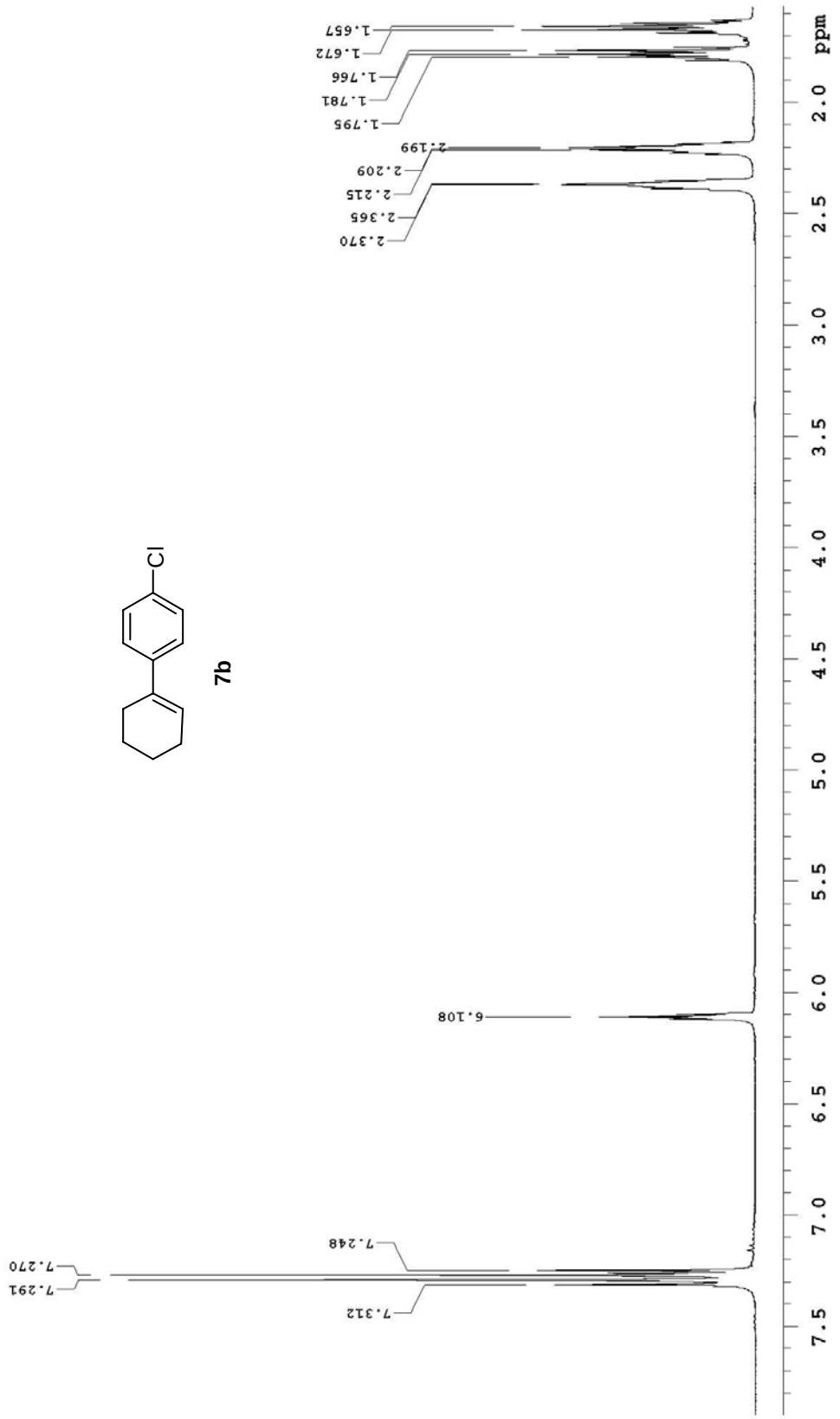
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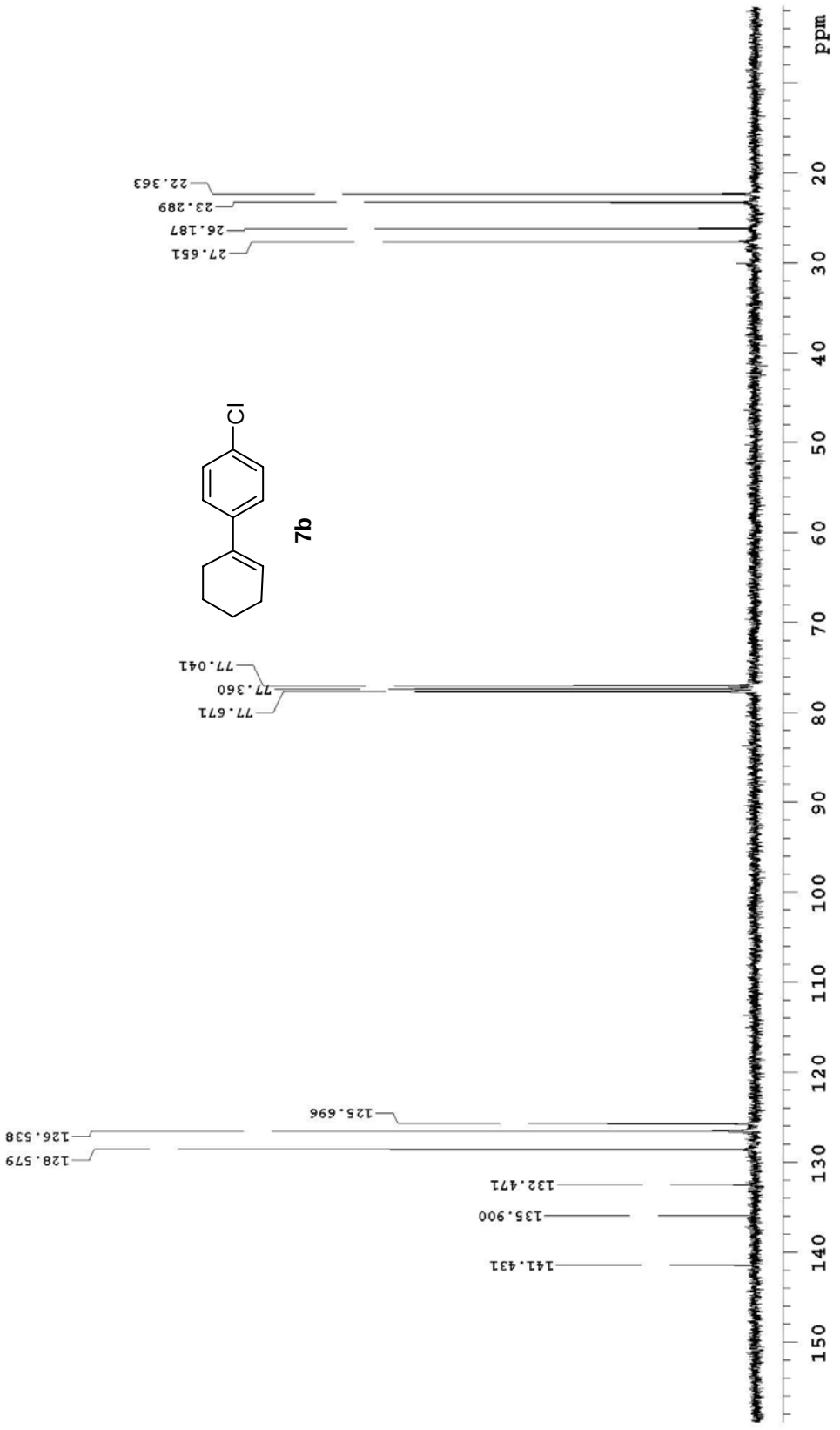
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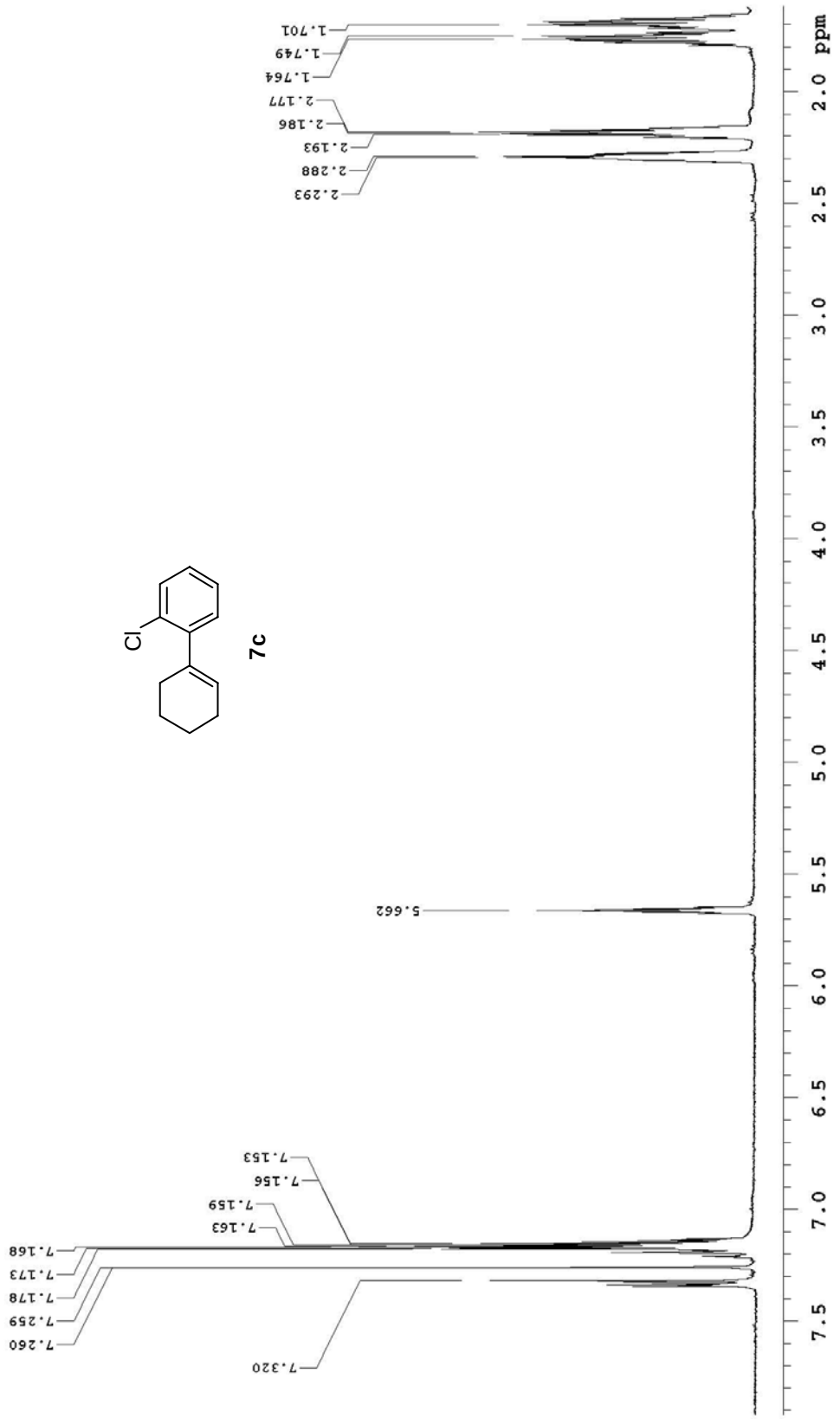
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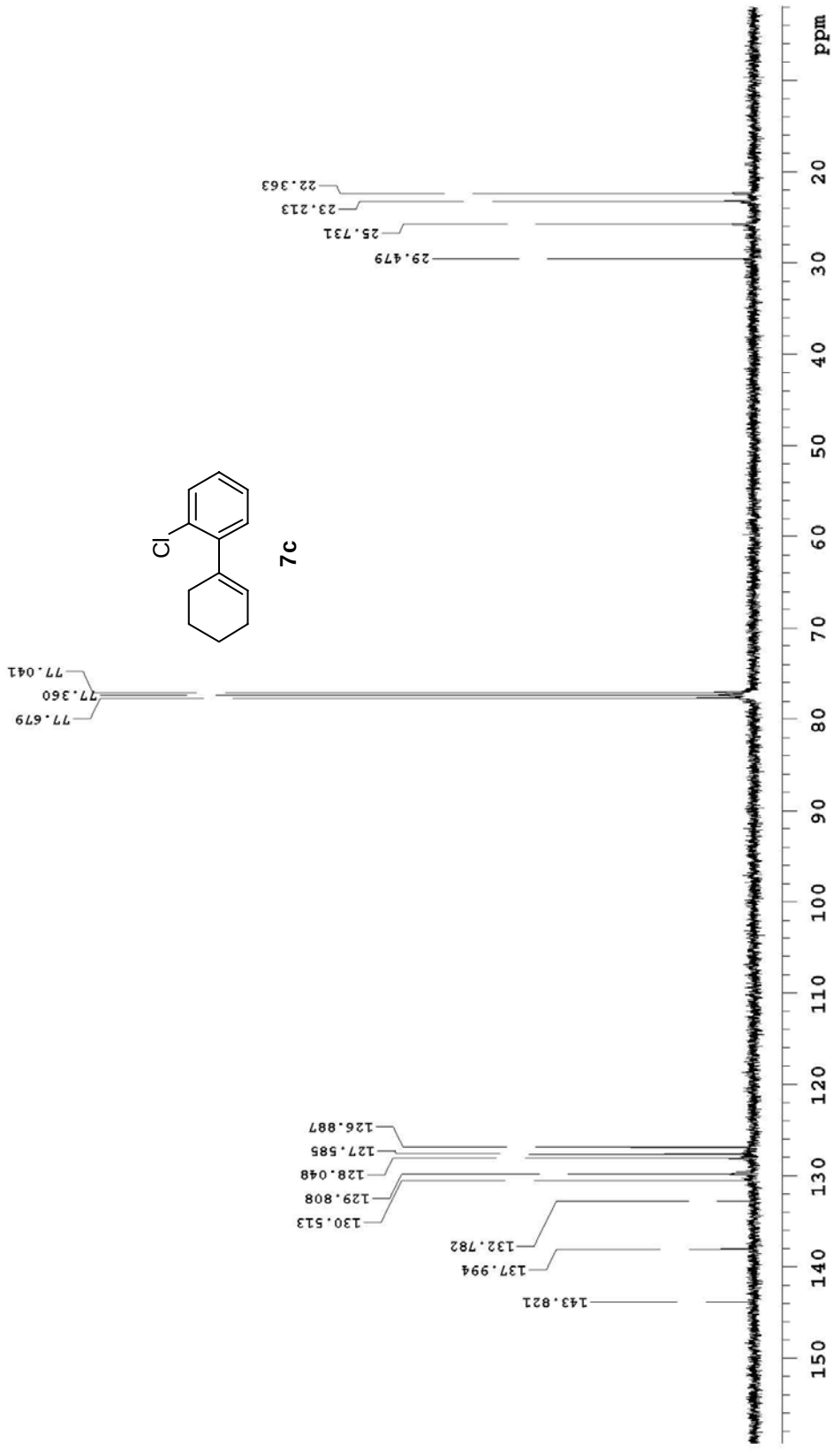
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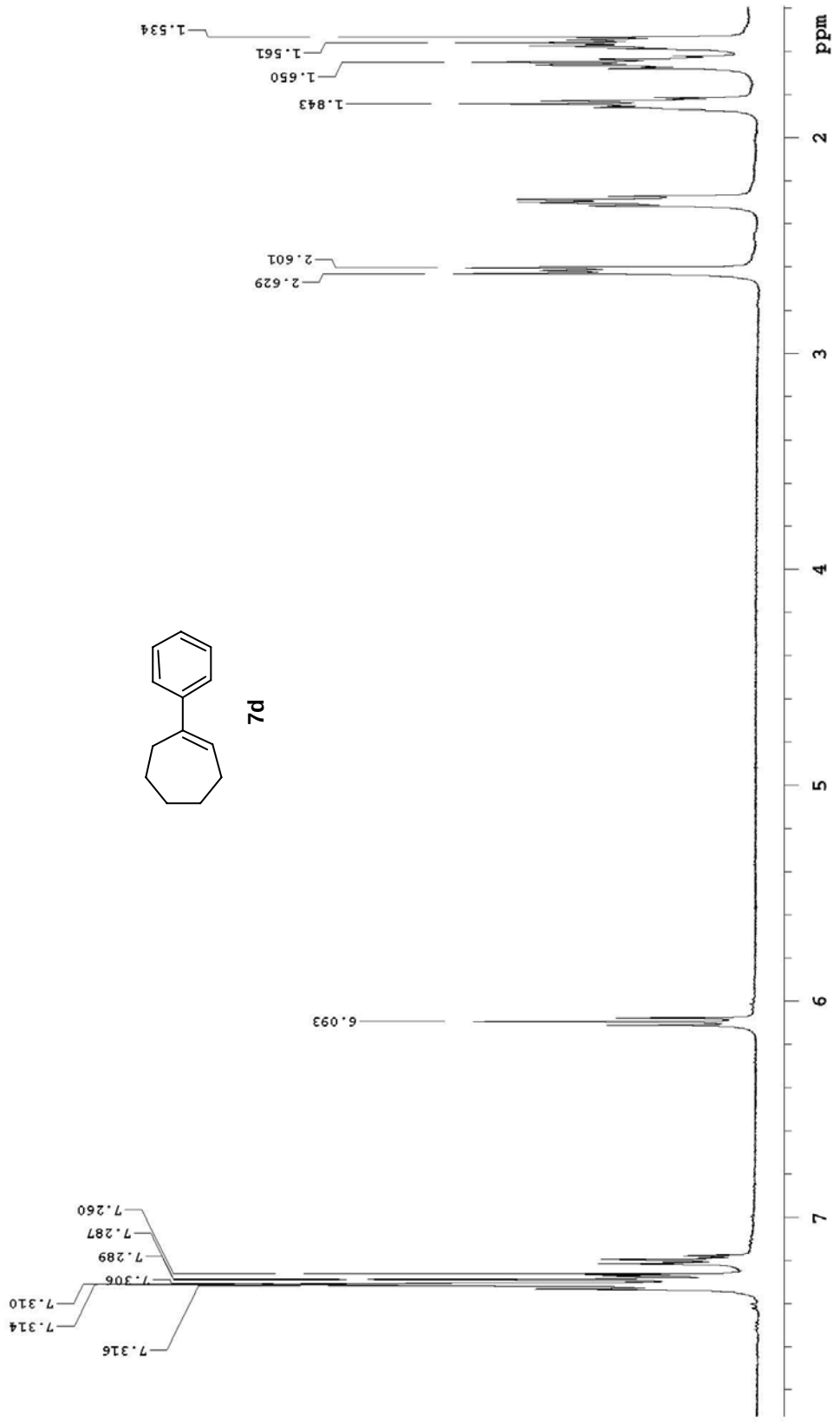
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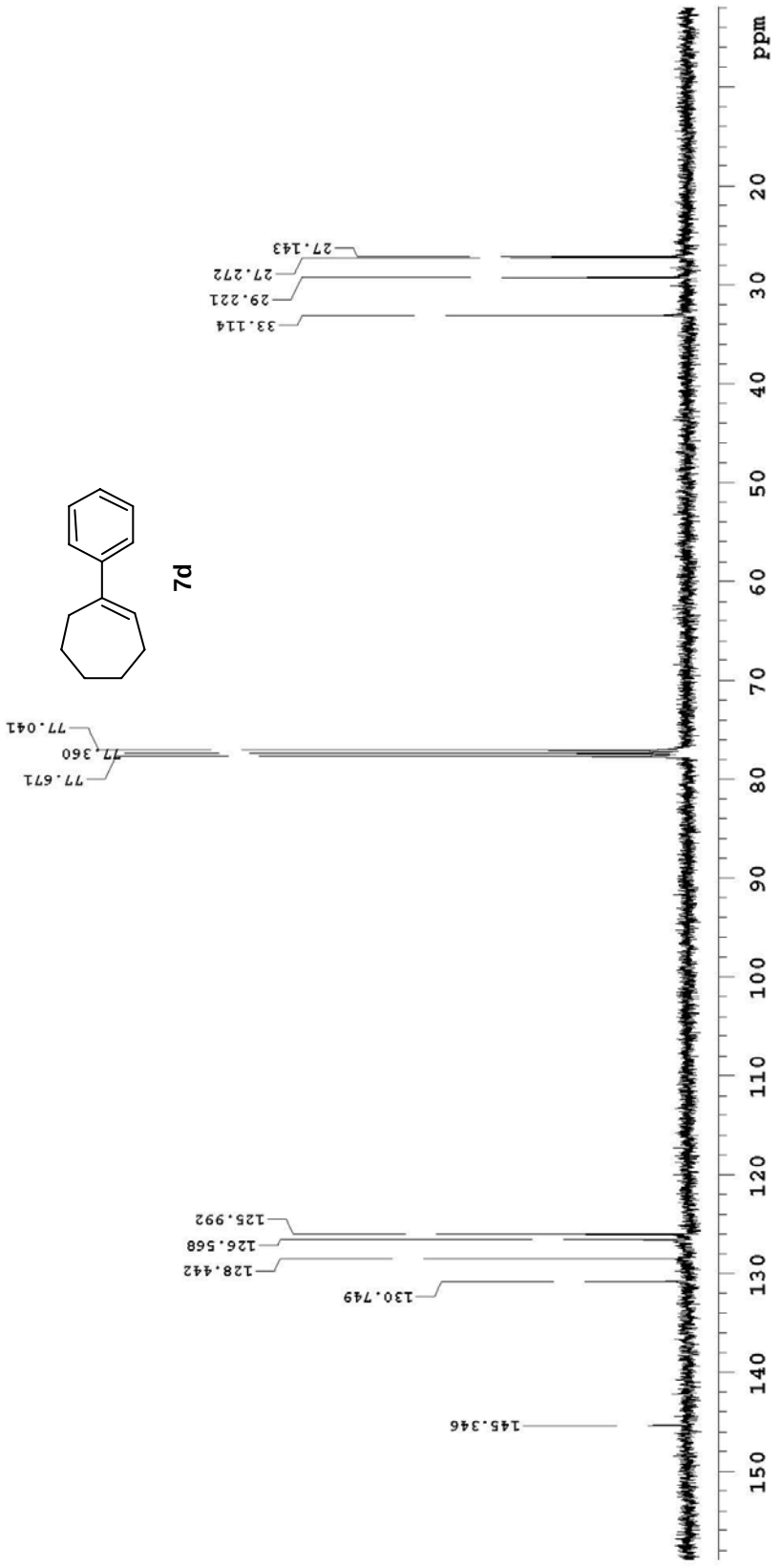
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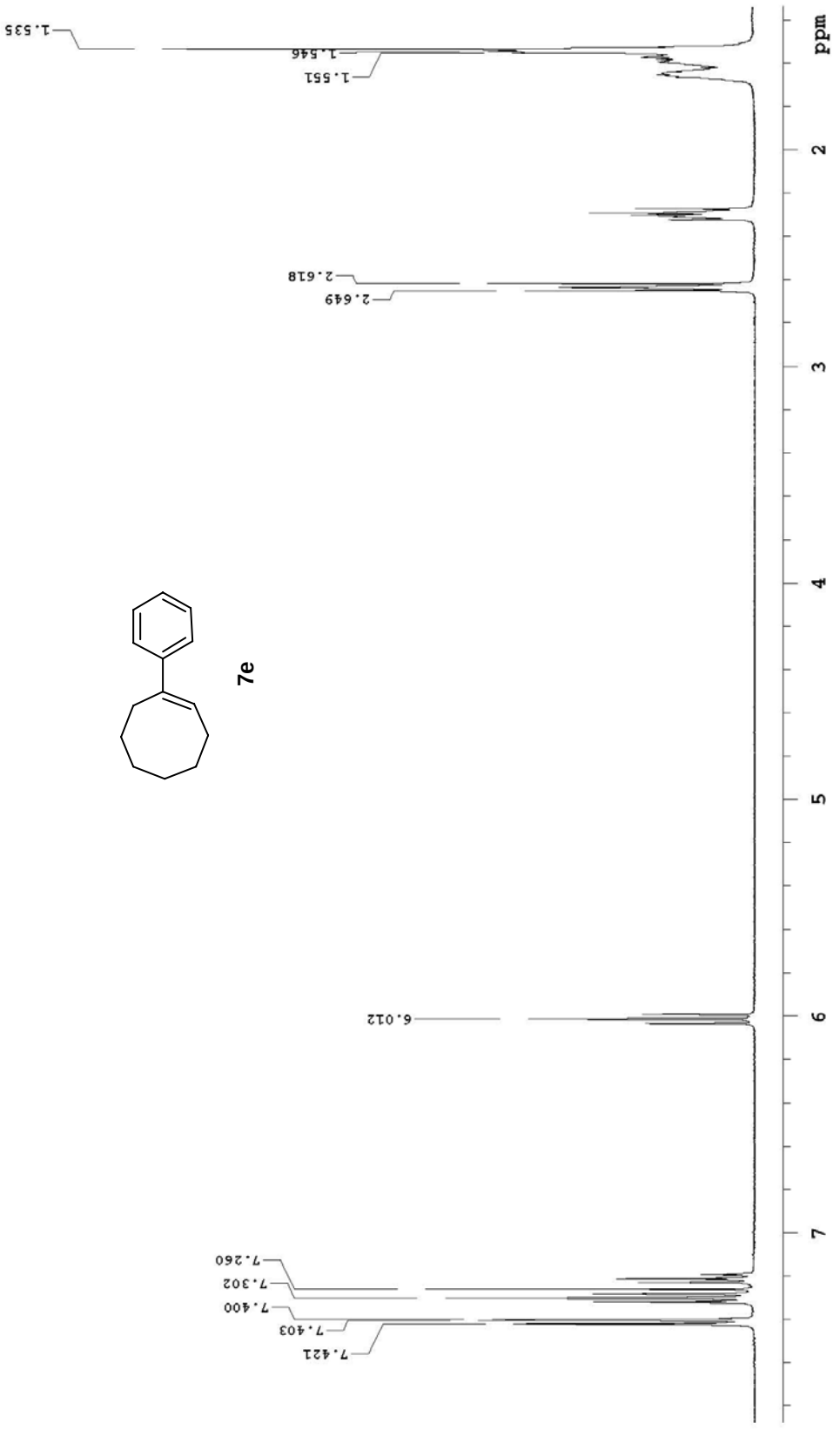
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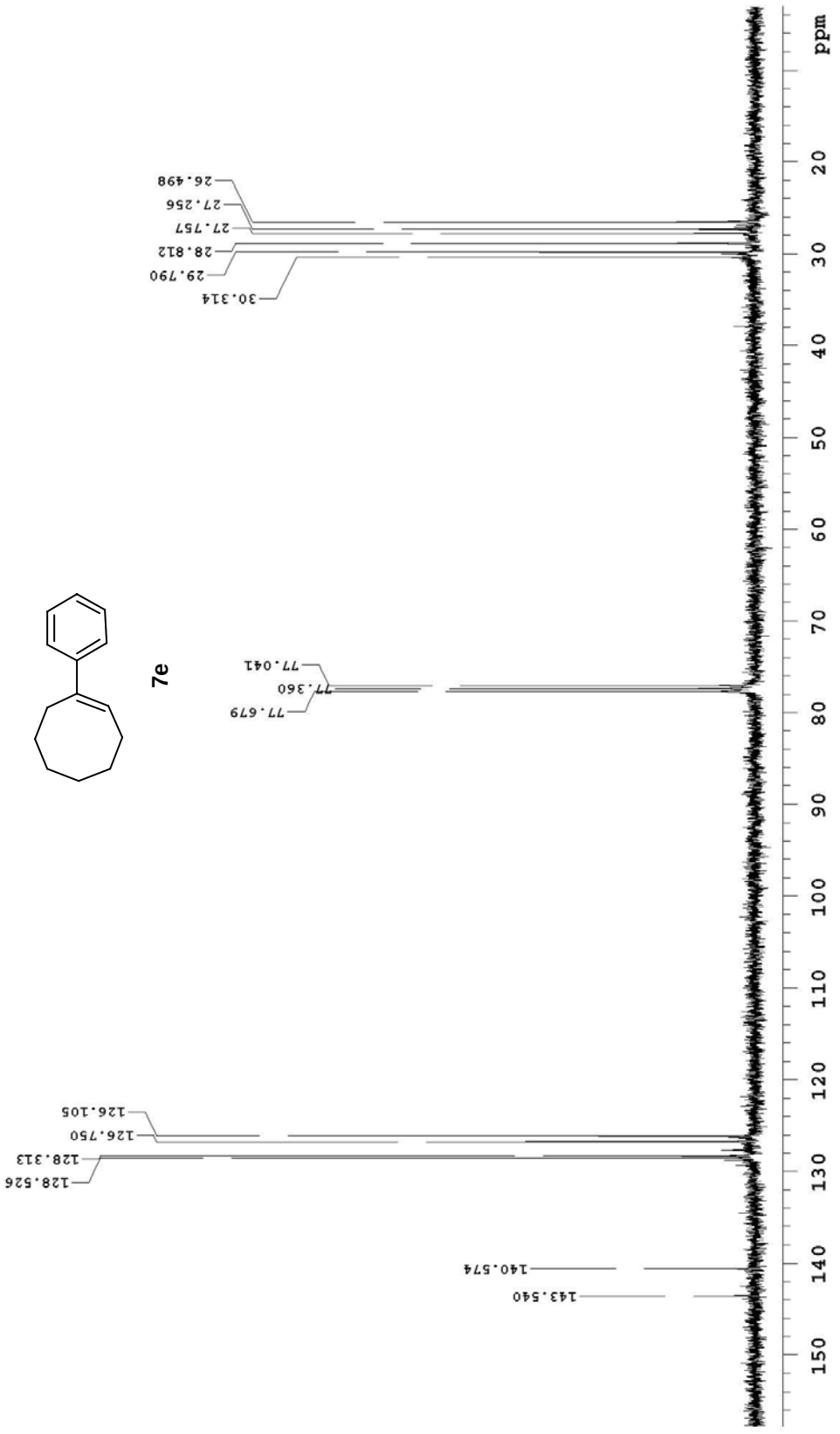
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