Electronic Supplementary Information for

Visible light-driven Giese reaction with alkyl tosylates catalysed by nucleophilic cobalt

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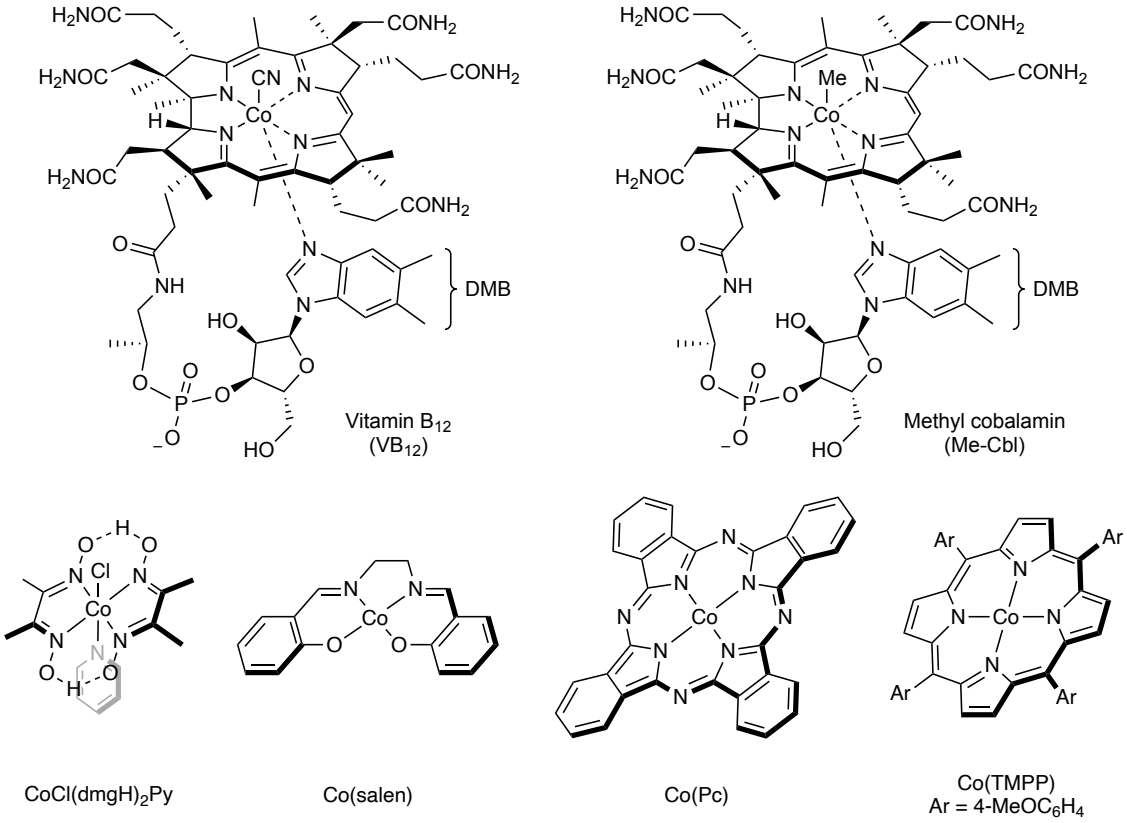
1. General information

All reactions were performed on oven-and flame-dried glassware under argon using standard Schlenk techniques. Flash-column chromatography was performed with silica-gel 60 (KANTO Chemical Co. Inc., 40–50 nm). TLC monitoring was carried out with silica-gel aluminum sheets (Merck, type 60 F_{254}). Gas chromatography (GC) monitoring was carried out on Shimadzu GC-2014. Nuclear magnetic resonance (NMR) spectra were recorded with Varian-400 (^{1}H NMR: 400 MHz; ^{13}C NMR: 101 MHz) spectrometer or Varian-500 (^{1}H NMR: 500 MHz; ^{13}C NMR: 126 MHz) spectrometers calibrated from residual deuterated chloroform as an internal standard at 7.26 ppm for ^{1}H NMR spectra and at 77.0 ppm for ^{13}C NMR spectra, respectively. High-resolution mass spectrum (HRMS) was performed by the Natural Science Centre for Basic Research and Development (N-BARD) of Hiroshima University using LTQ Orbitrap XL from Thermo Fisher Scientific.

2. Materials

Cobalt complexes and manganese power were purchased from Nacalai Tesque, Inc. [for VB_{12} and Mn] and Tokyo Chemical Industry Co., Ltd. [for Co(salen), Co(Pc), Co(TMPP), and methylcobalamin hydrate (Me-Cbl)], respectively and were used without purifications. $CoCl(dmgH)_2Py$ was prepared according to literature.[1] Alkyl tosylates[2,3] and activated olefins[4,5] were prepared on the basis of reported methods. DMF was dried over activated MS 4Å, distilled, and stored with activated MS 4Å under argon. Unless otherwise noted, commercially available reagents were used as received without further purification.



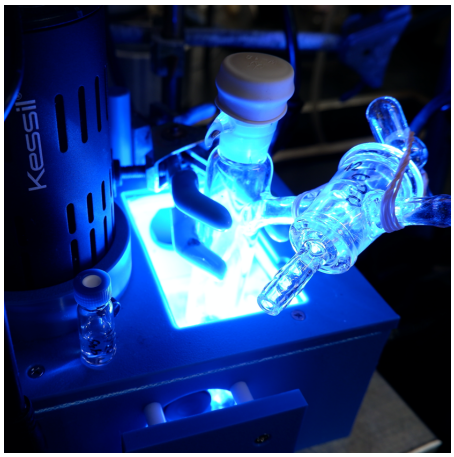


Figure S1. Reaction setup for the nucleophilic cobalt-catalysed Giese reaction under blue-light irradiation.

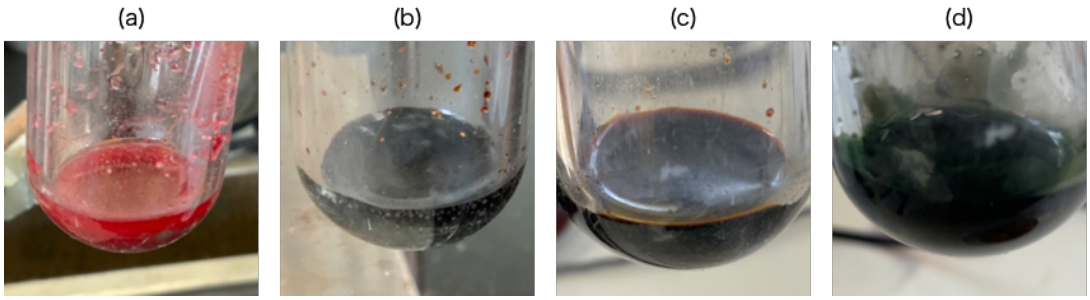


Figure S2. The color changes of the reaction mixture in each step: (a) Mn + Et_3N·HCl + VB_{12} + DMF; (b) Solution a + TMSCl (*ca.* 6 μL); (c) After stirring for 8 h with photo-irradiation; (d) After stirring for 16 h with photo-irradiation.

References

1 A. Panagiotopoulos, K. Ladomenou, D. Sun, V. Artero and A. G. Coutsolelos, *Dalton Trans.*, 2016, **45**, 6732–6738.

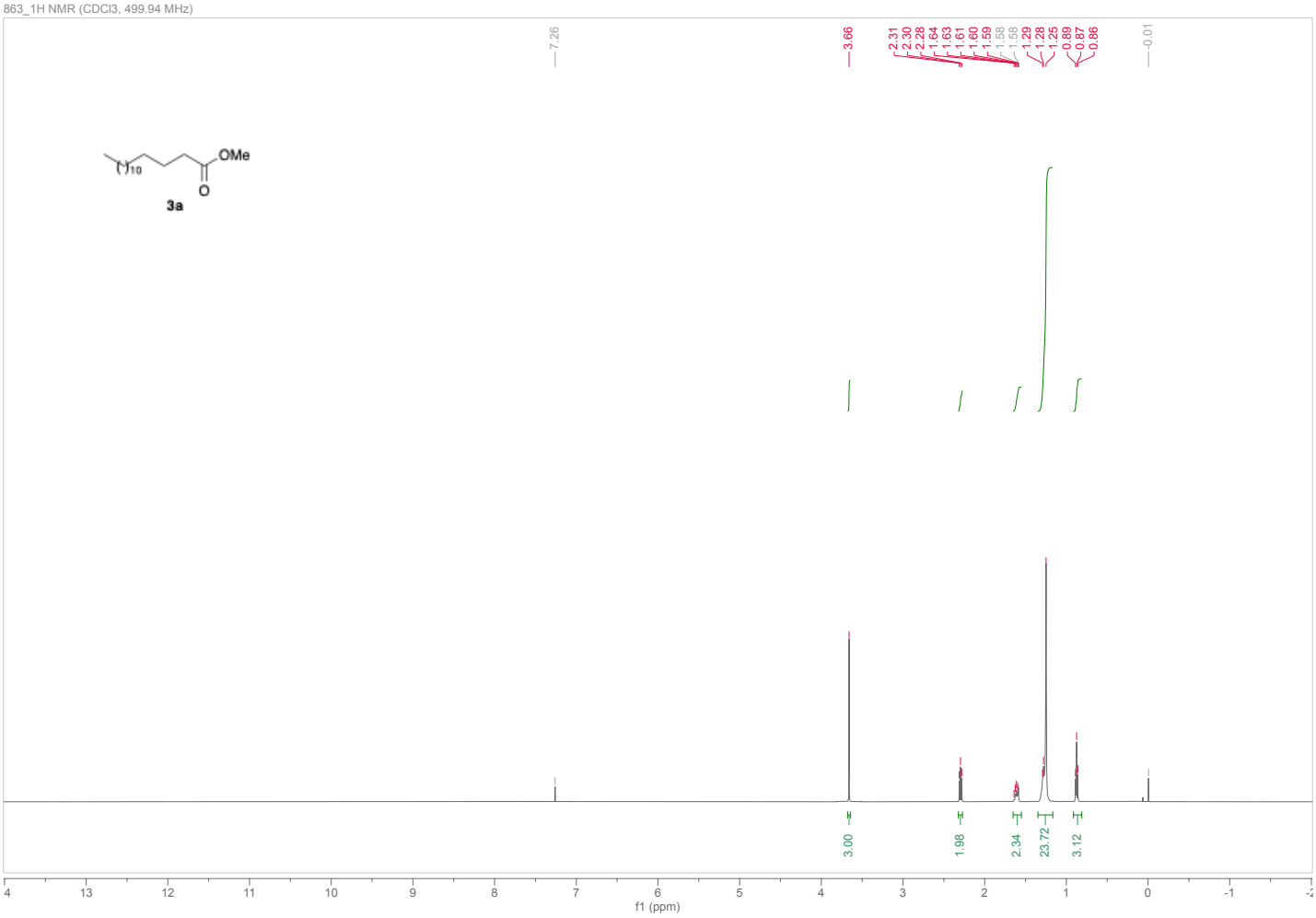
2 T. Michiyuki, I. Osaka and K. Komeyama, *Chem. Commun.*, 2020, **56**, 1247–1250.

3 K. Tani and B. M. Stoltz, *Nature*, 2006, **441**, 731–734.

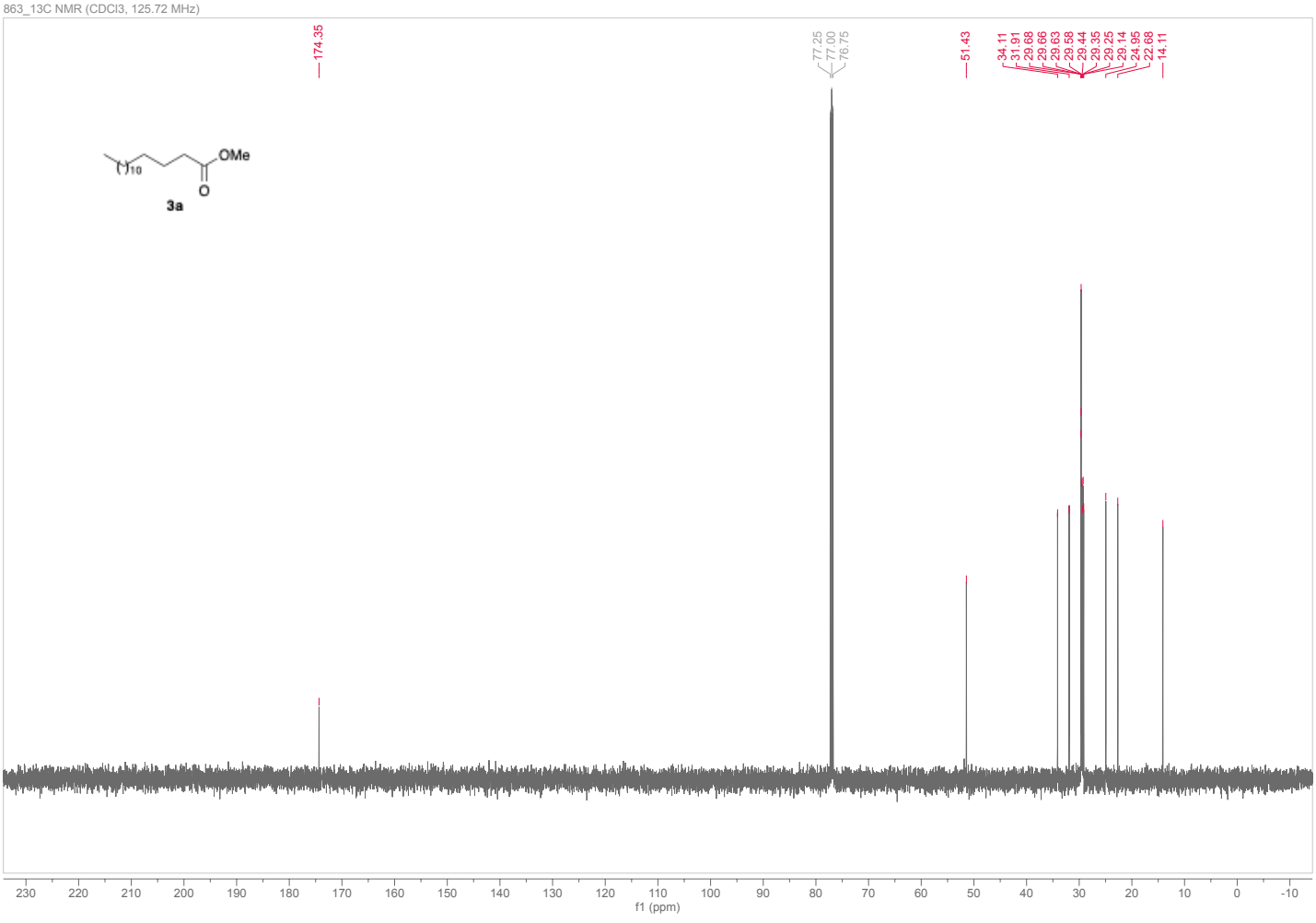
4 S. Eggers, T. Eckert and V. Abetz, *J. Polym. Sci., Part A: Polym. Chem.*, 2018, **56**, 399–411.

5 S. M. Hell, C. F. Meyer, G. Laudadio, A. Misale, M. C. Willis, T. Noël, A. A. Trabanco and V. Gouverneur, *J. Am. Chem. Soc.*, 2020, **142**, 720–725.

863_1H NMR (CDCl3, 499.94 MHz)



863_13C NMR (CDCl3, 125.72 MHz)



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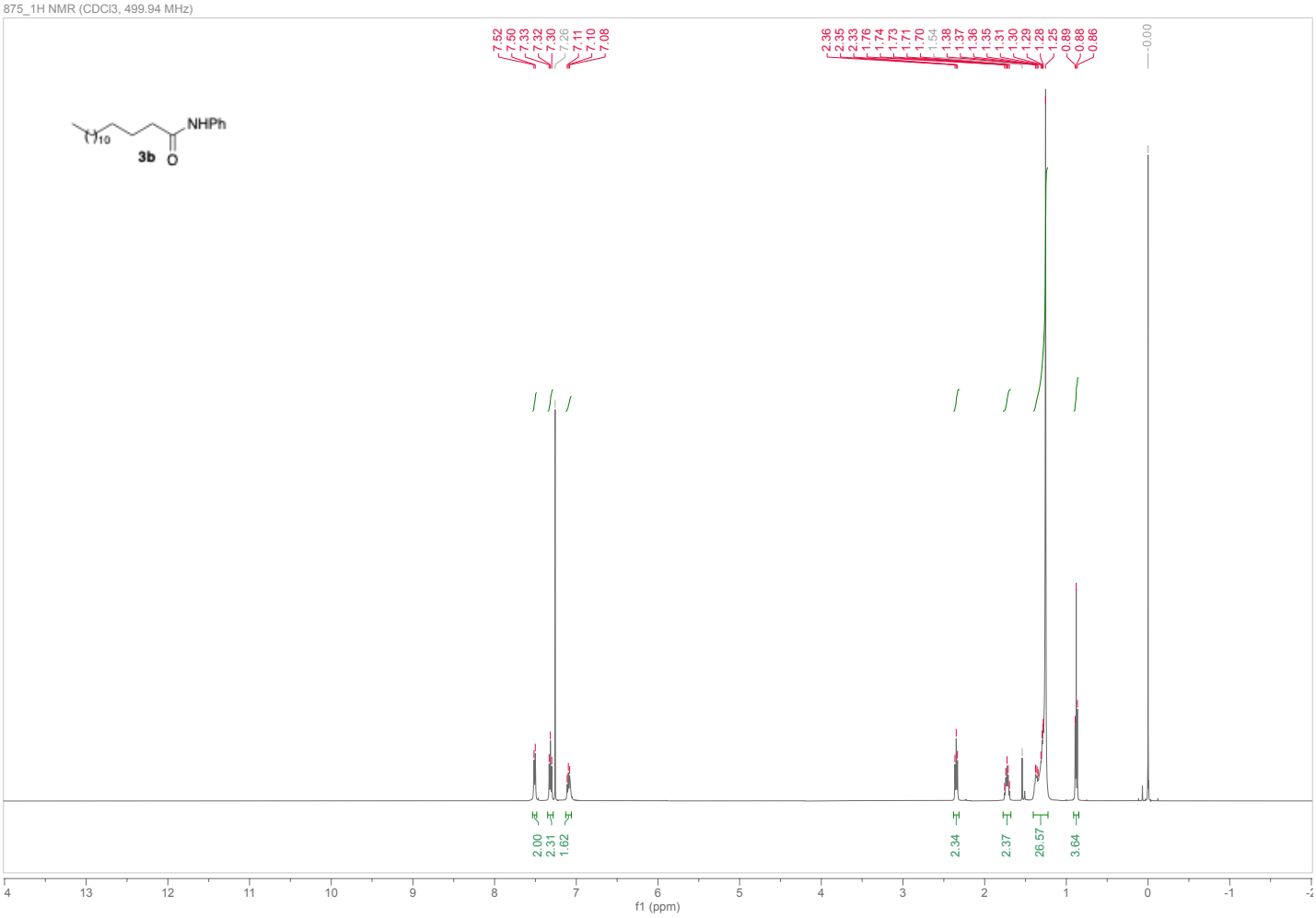

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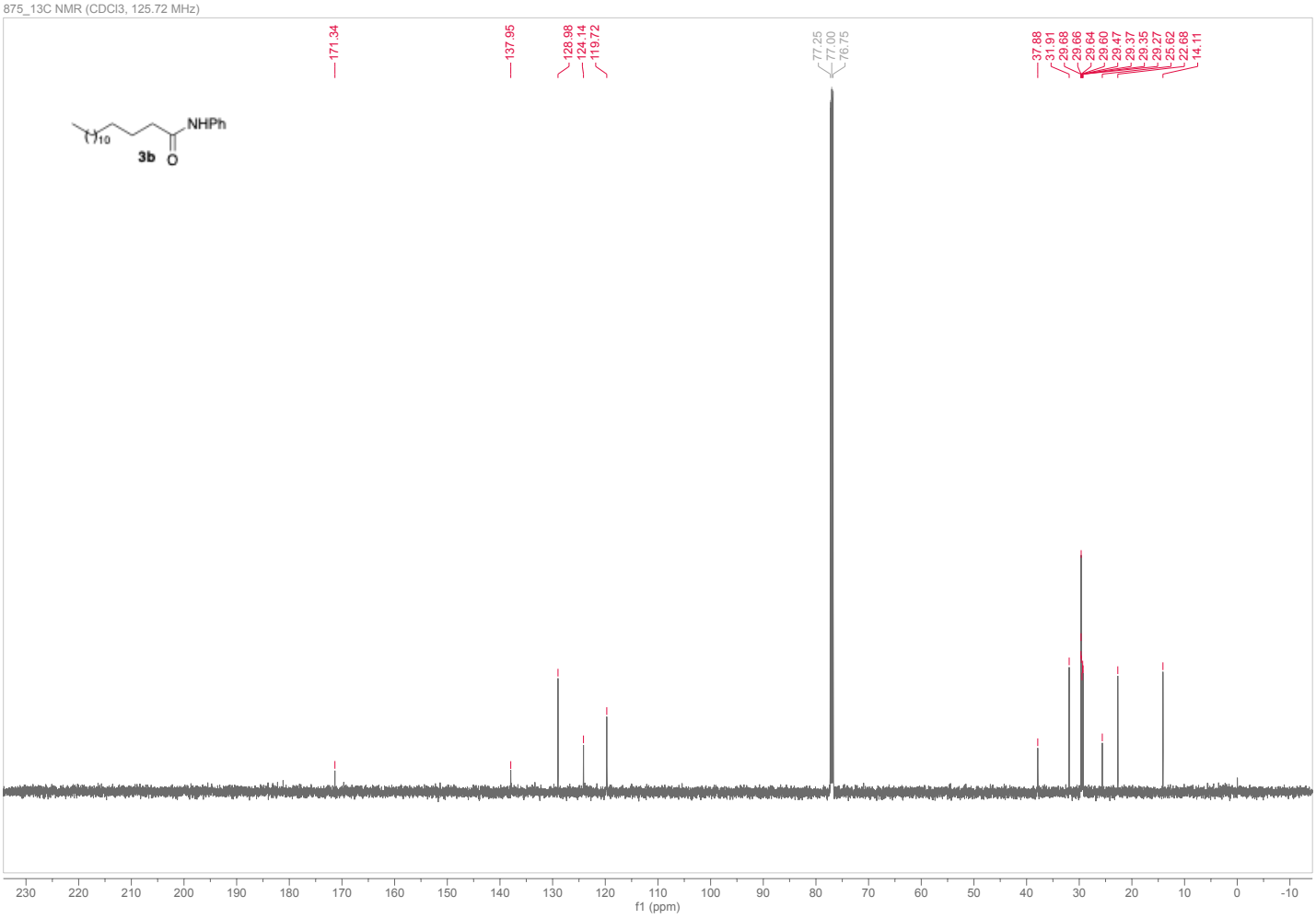

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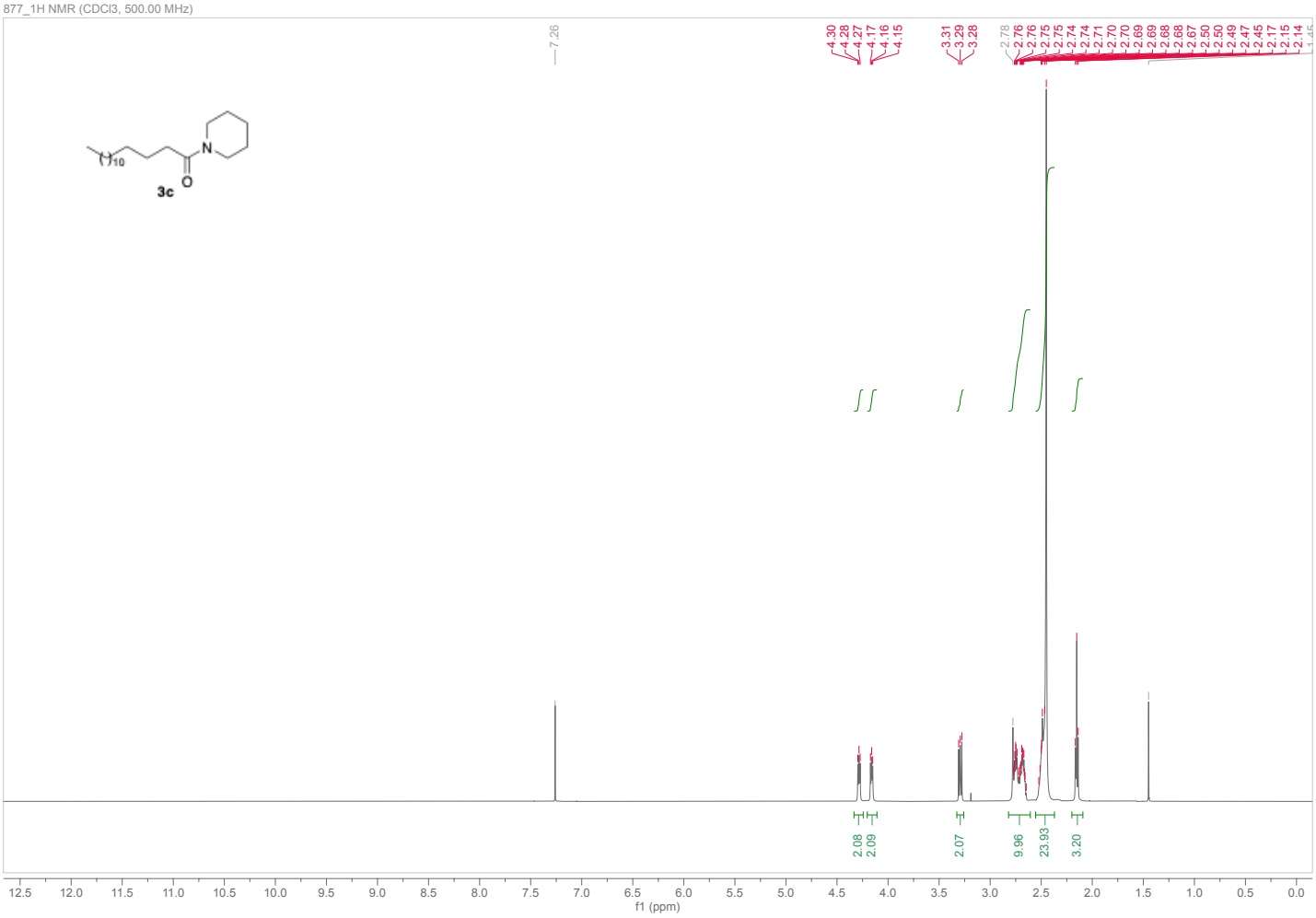

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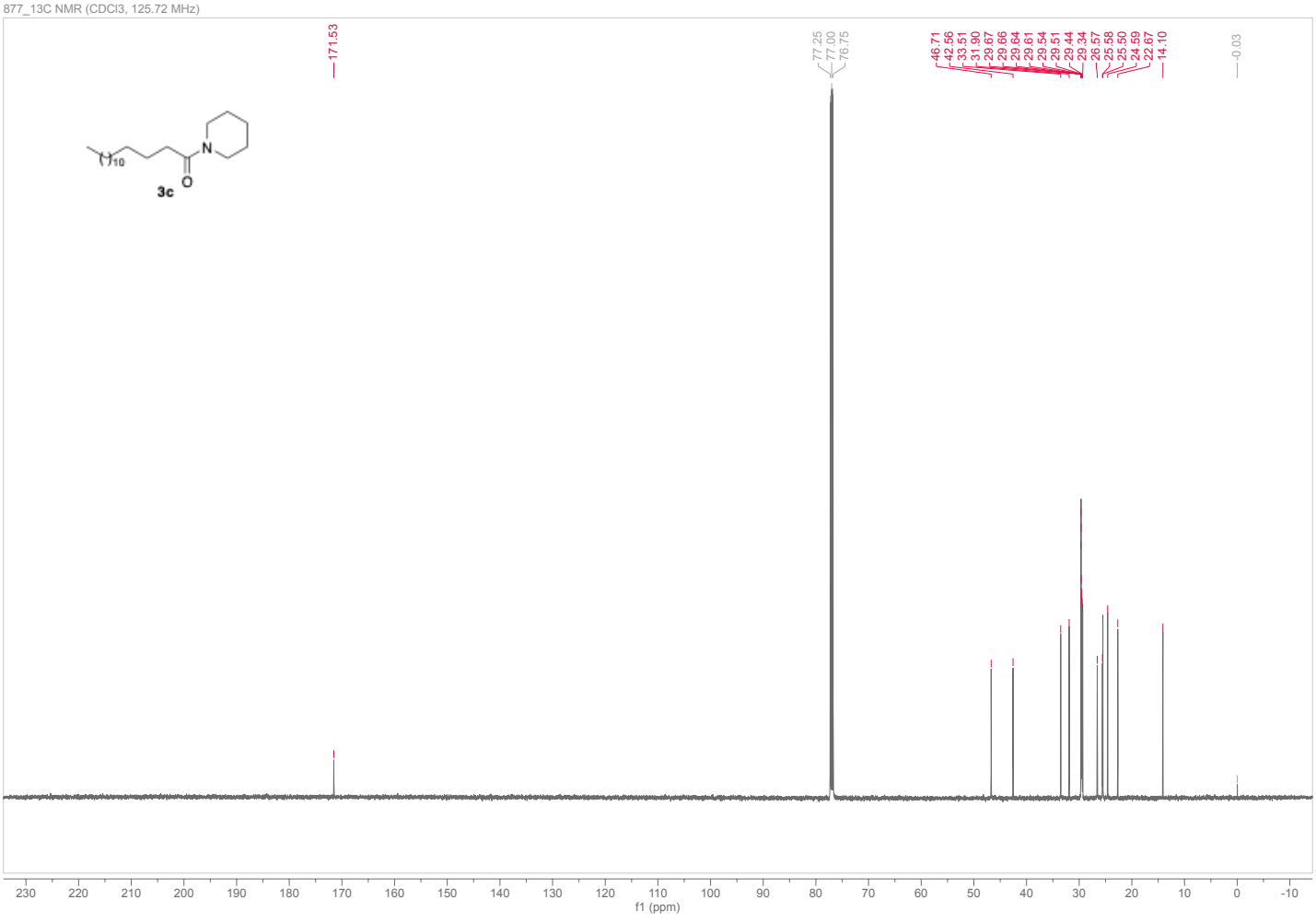

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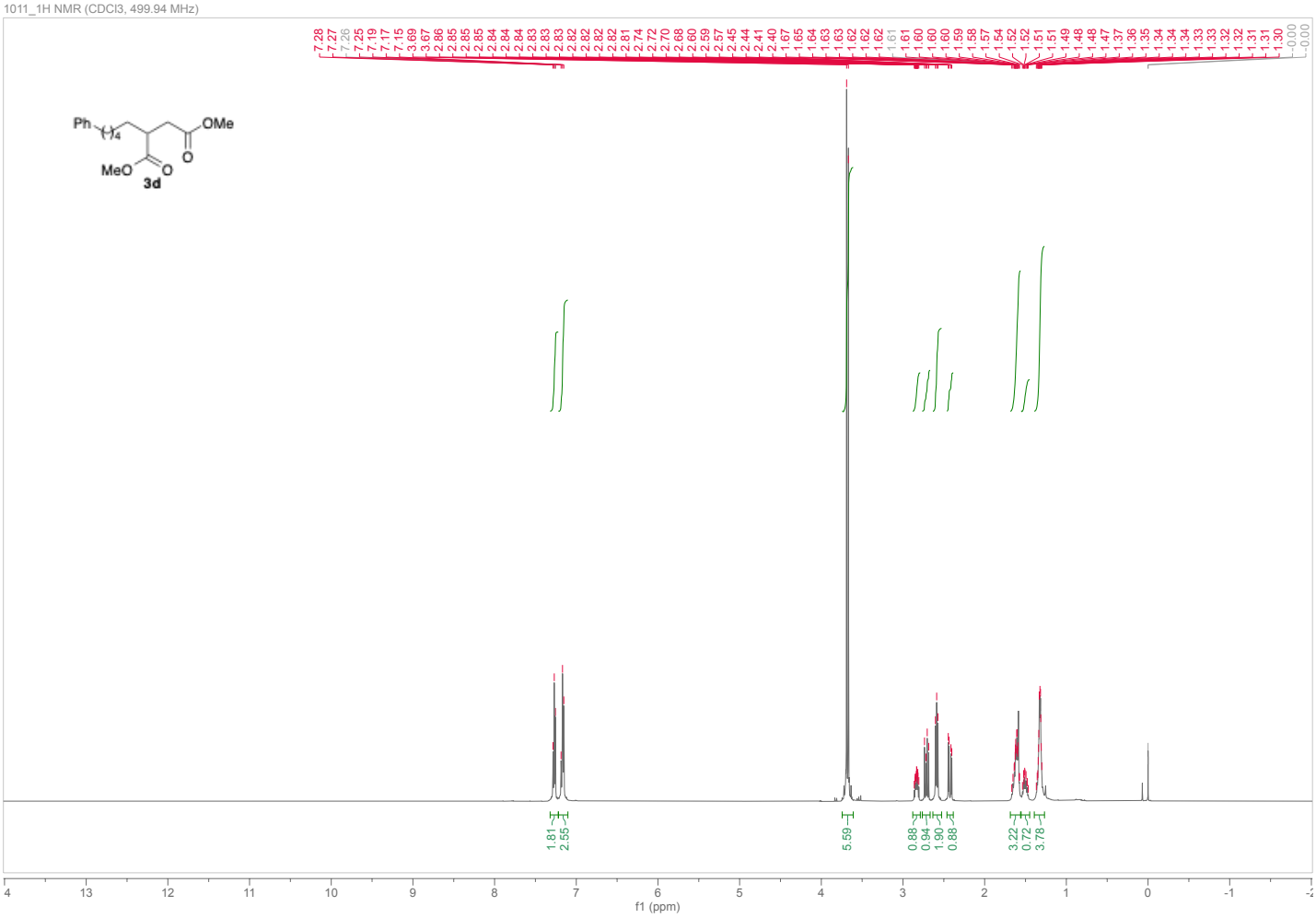

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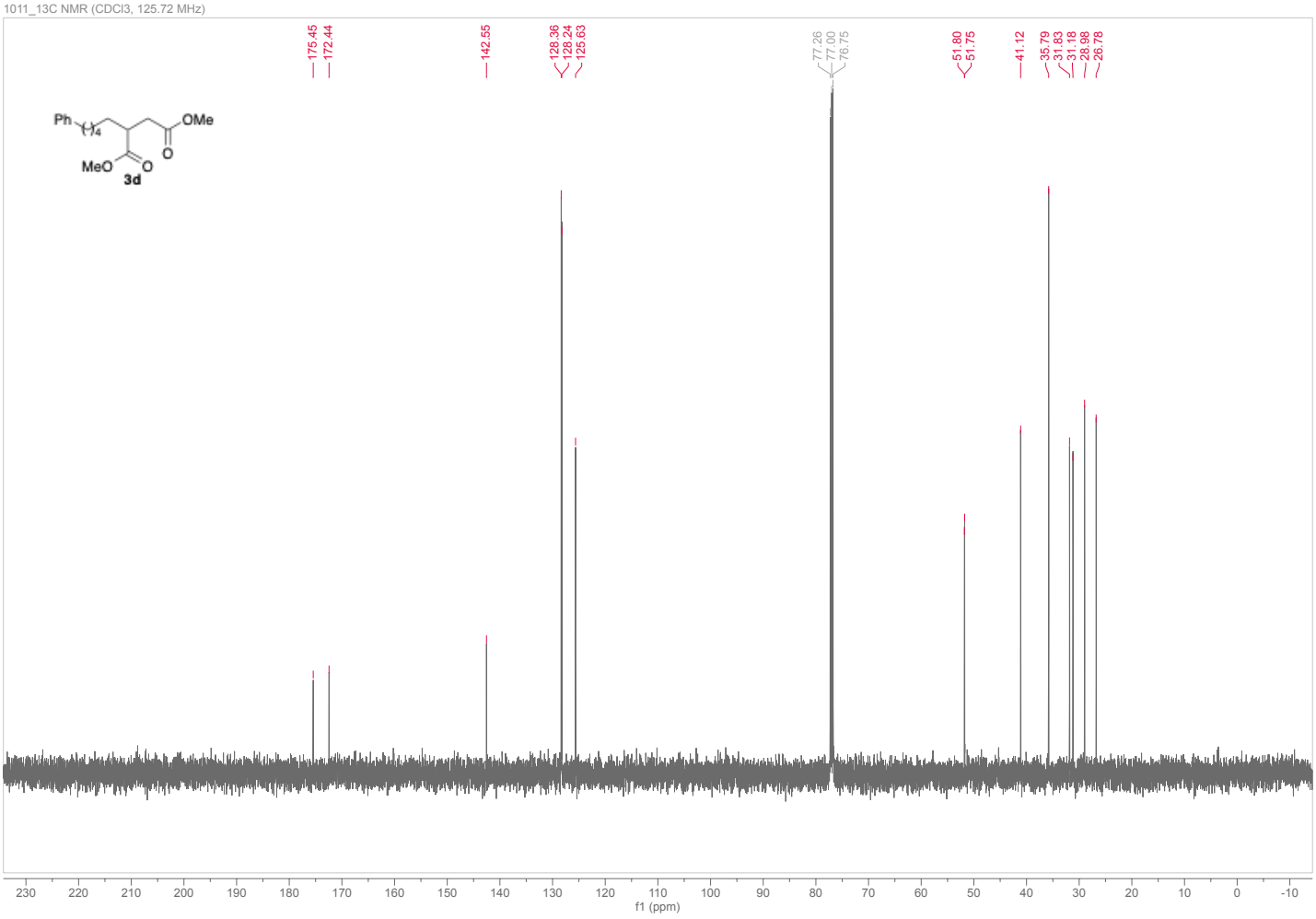

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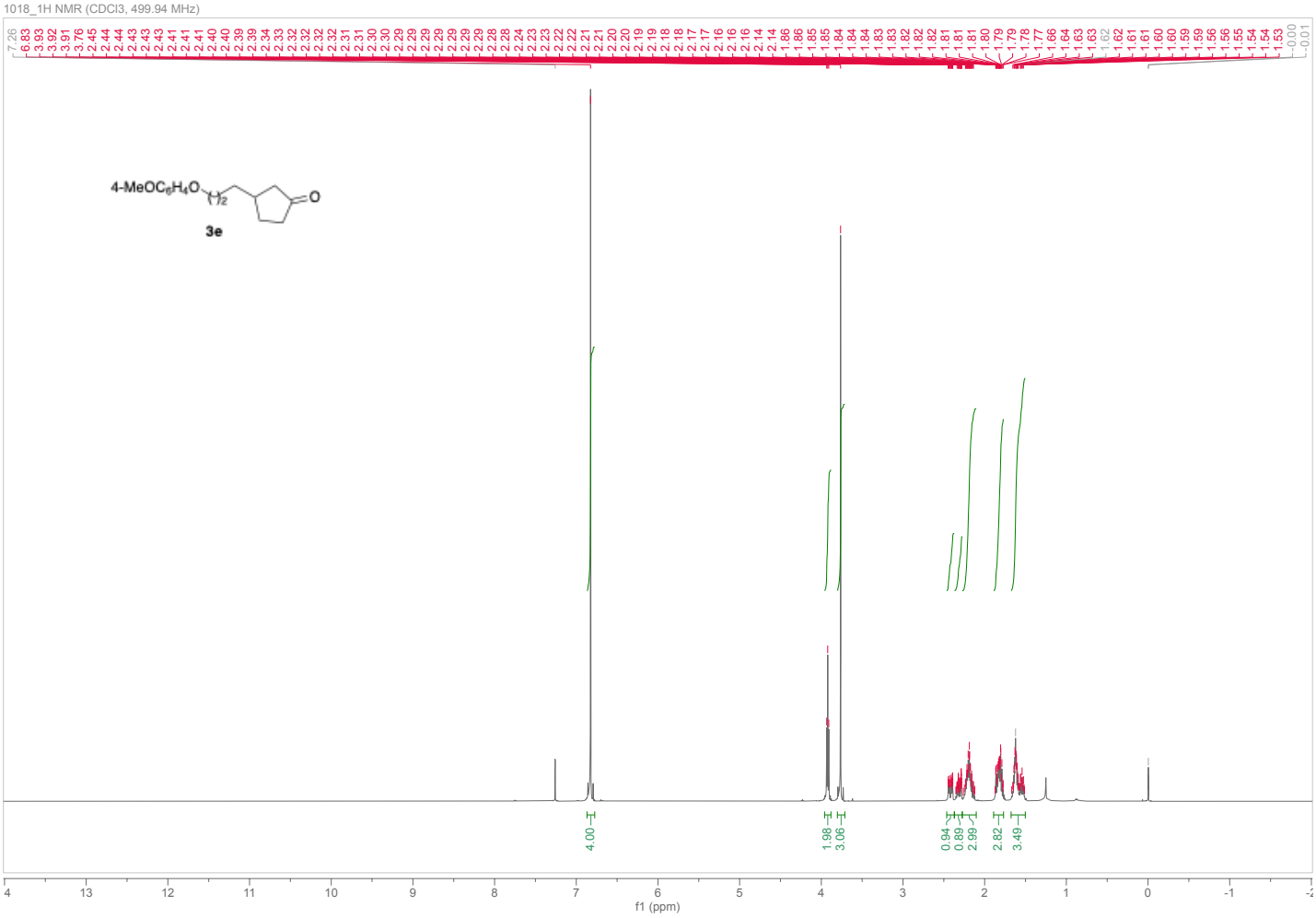

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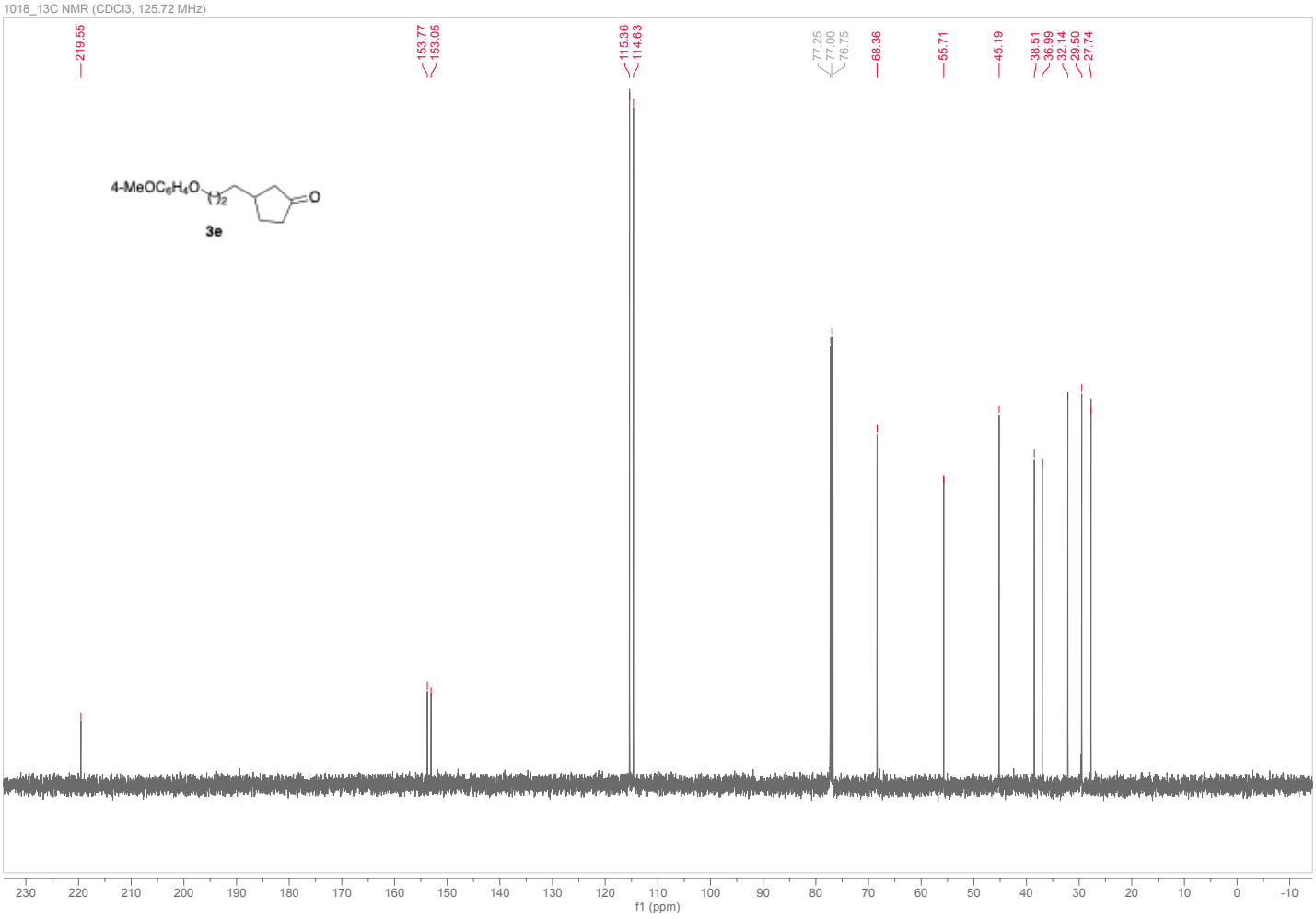

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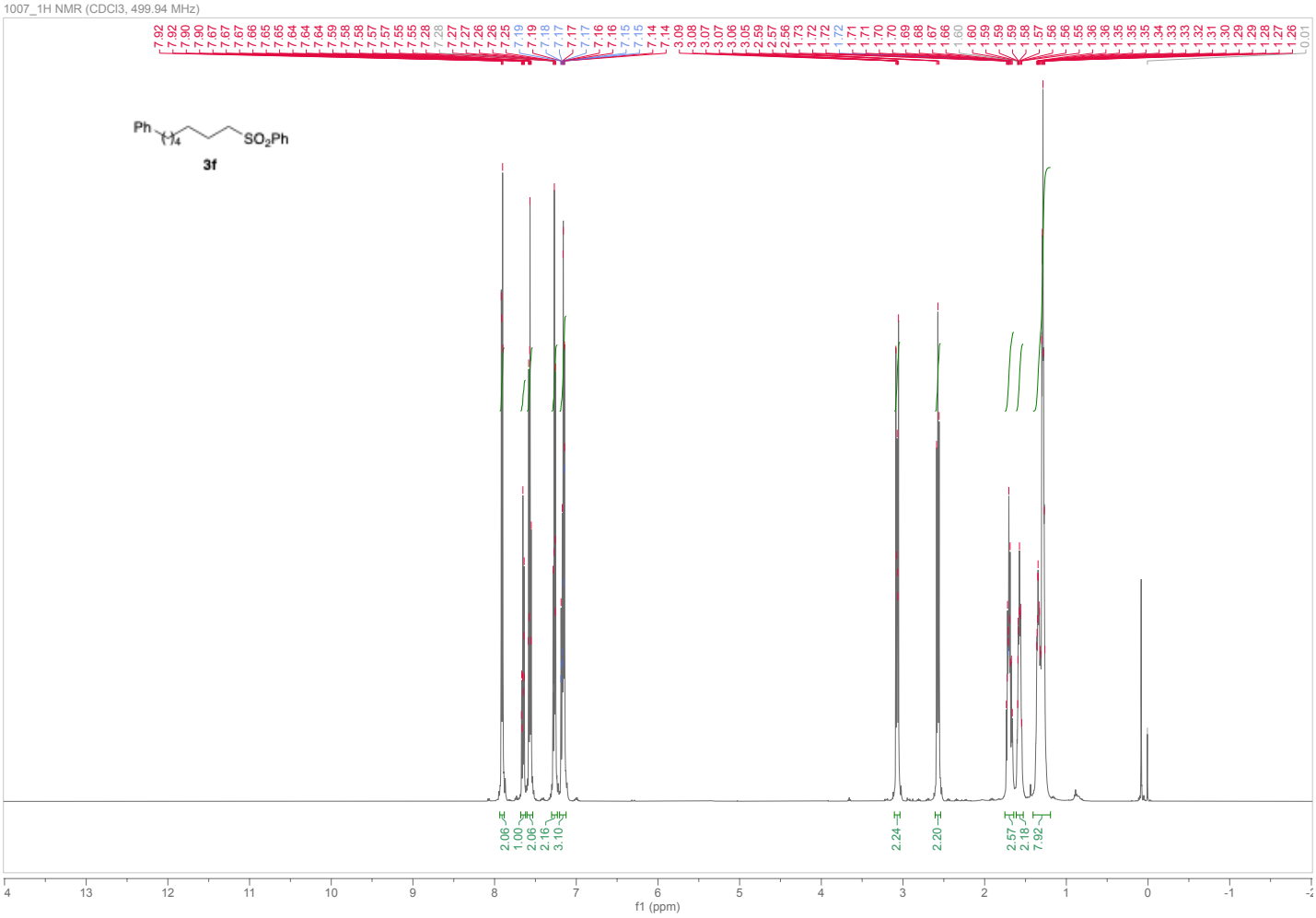

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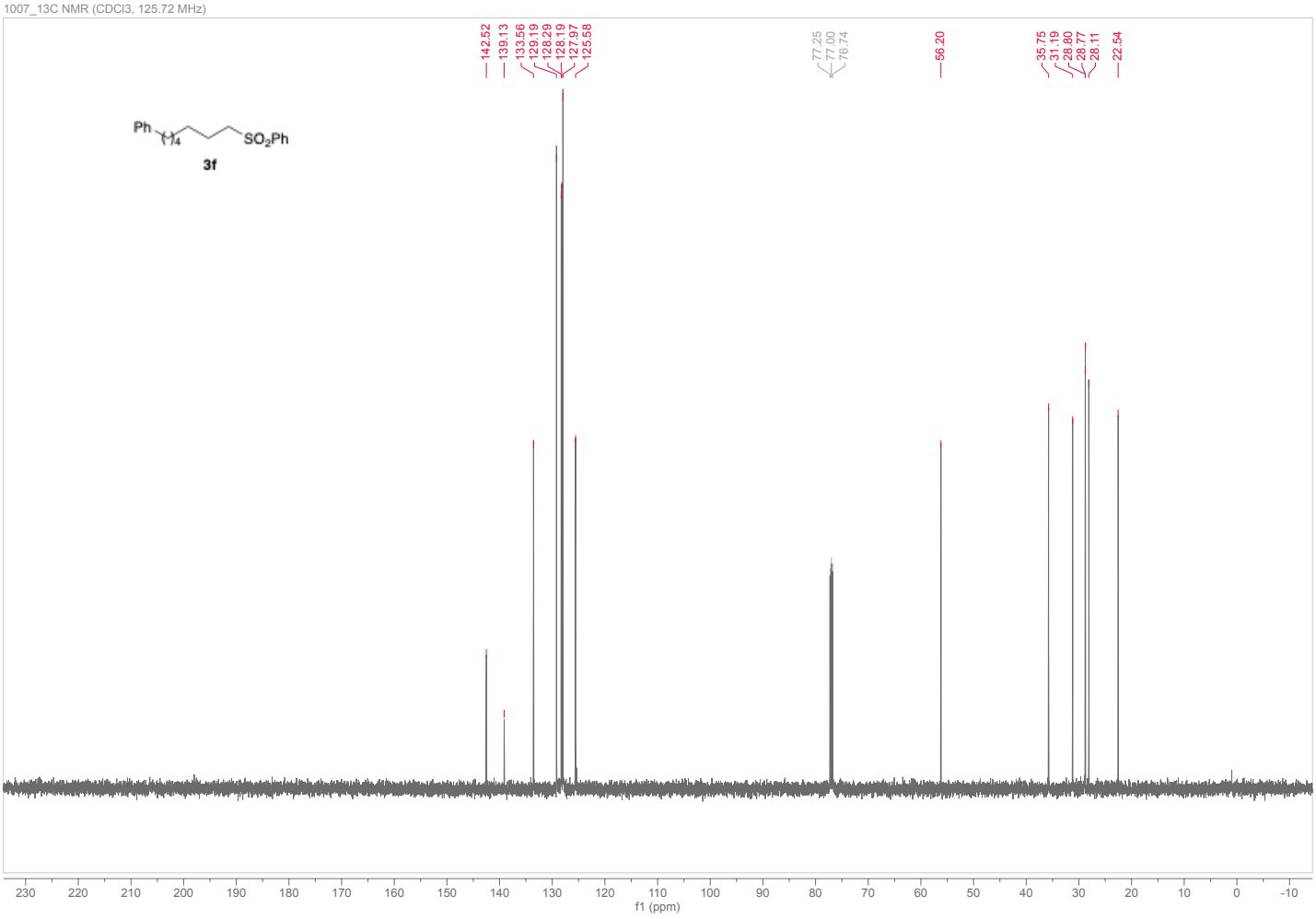

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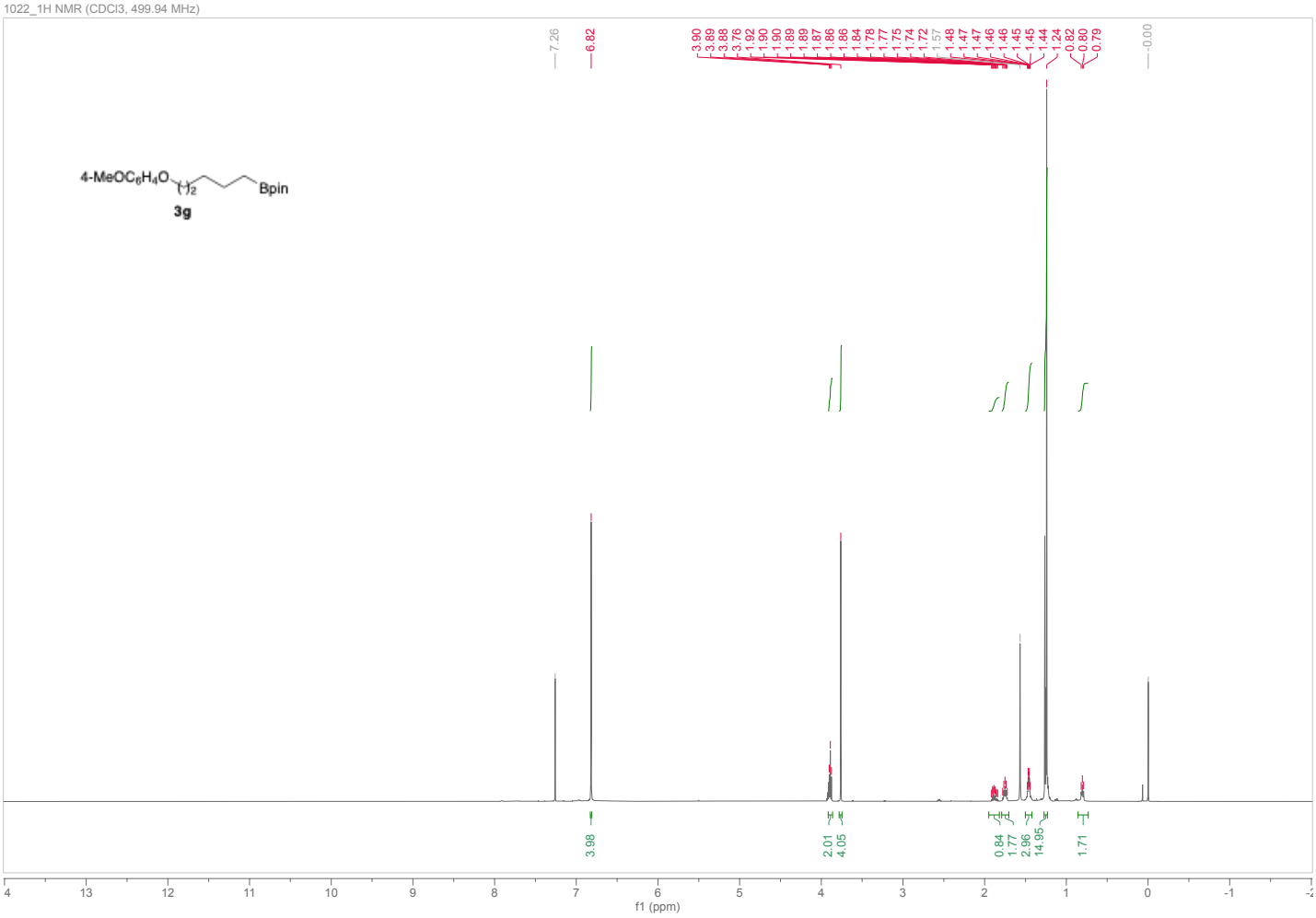

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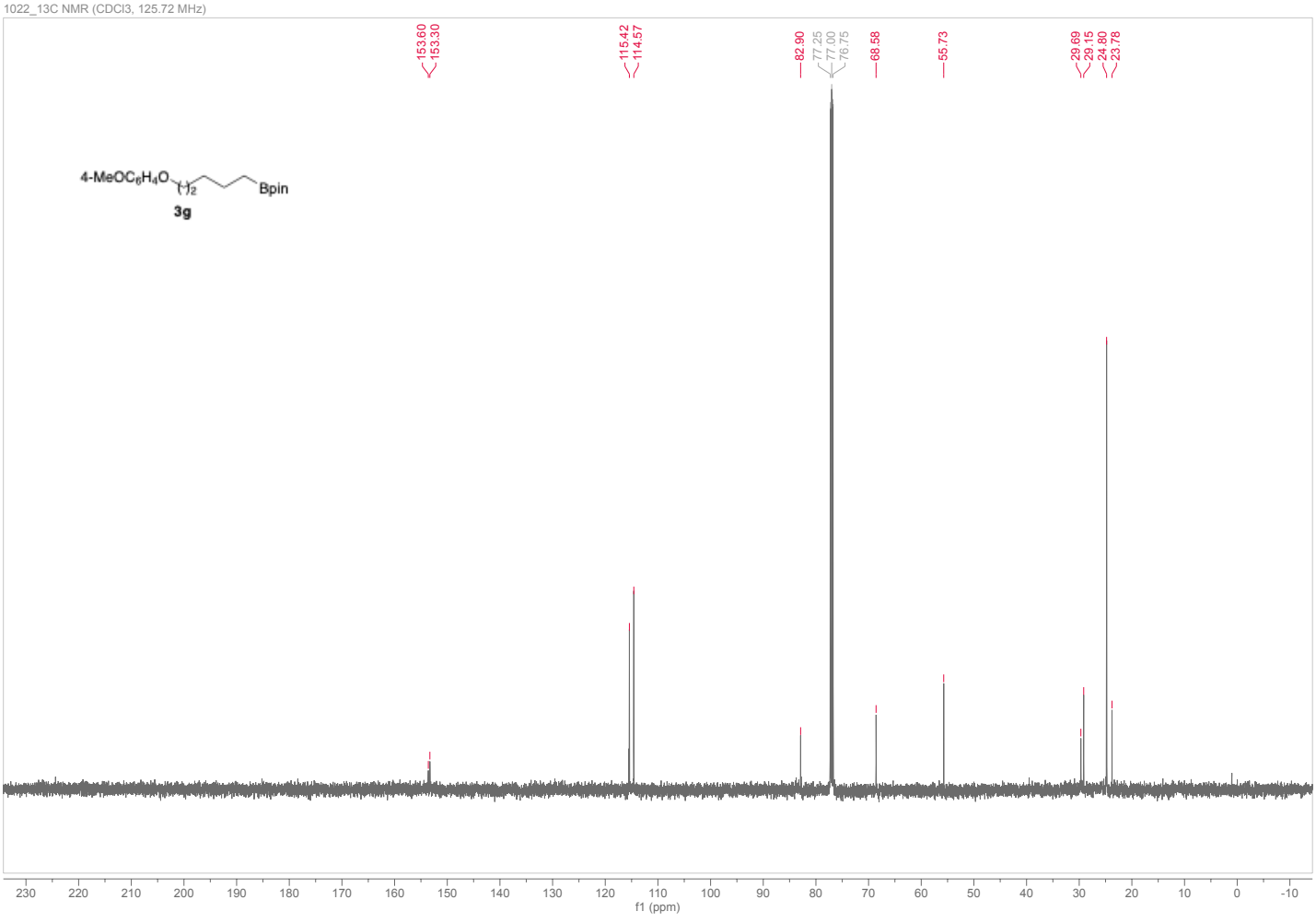

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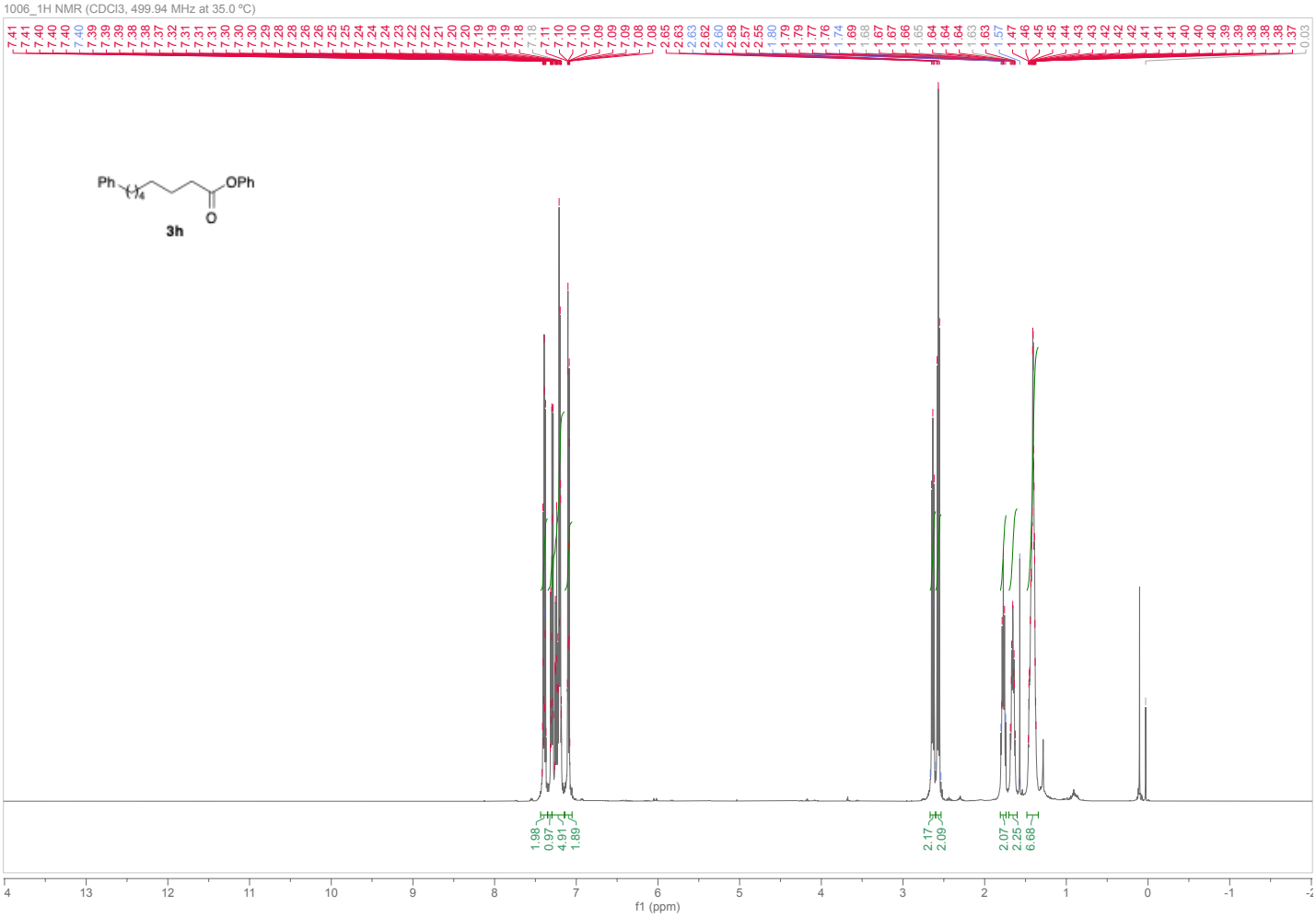

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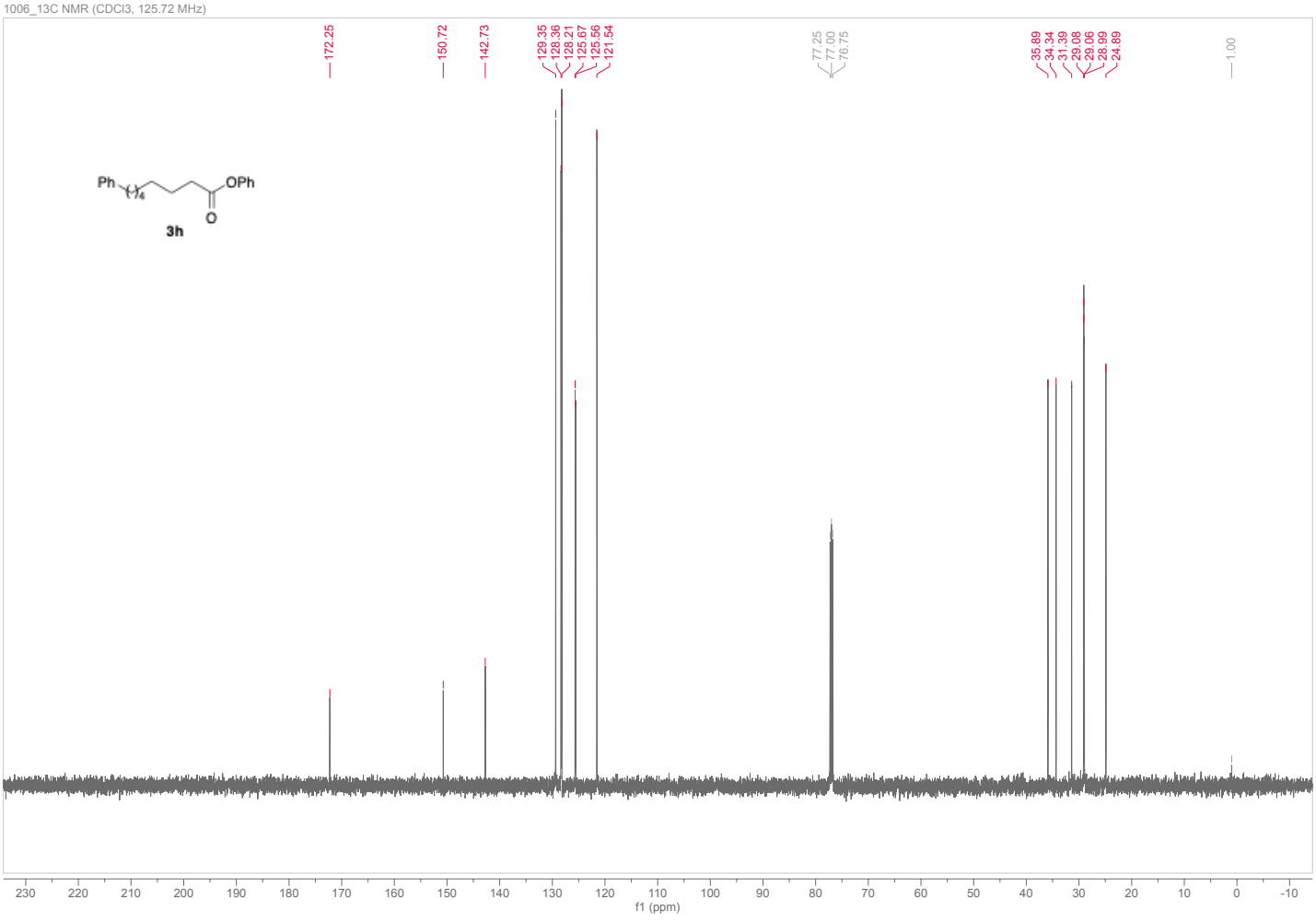

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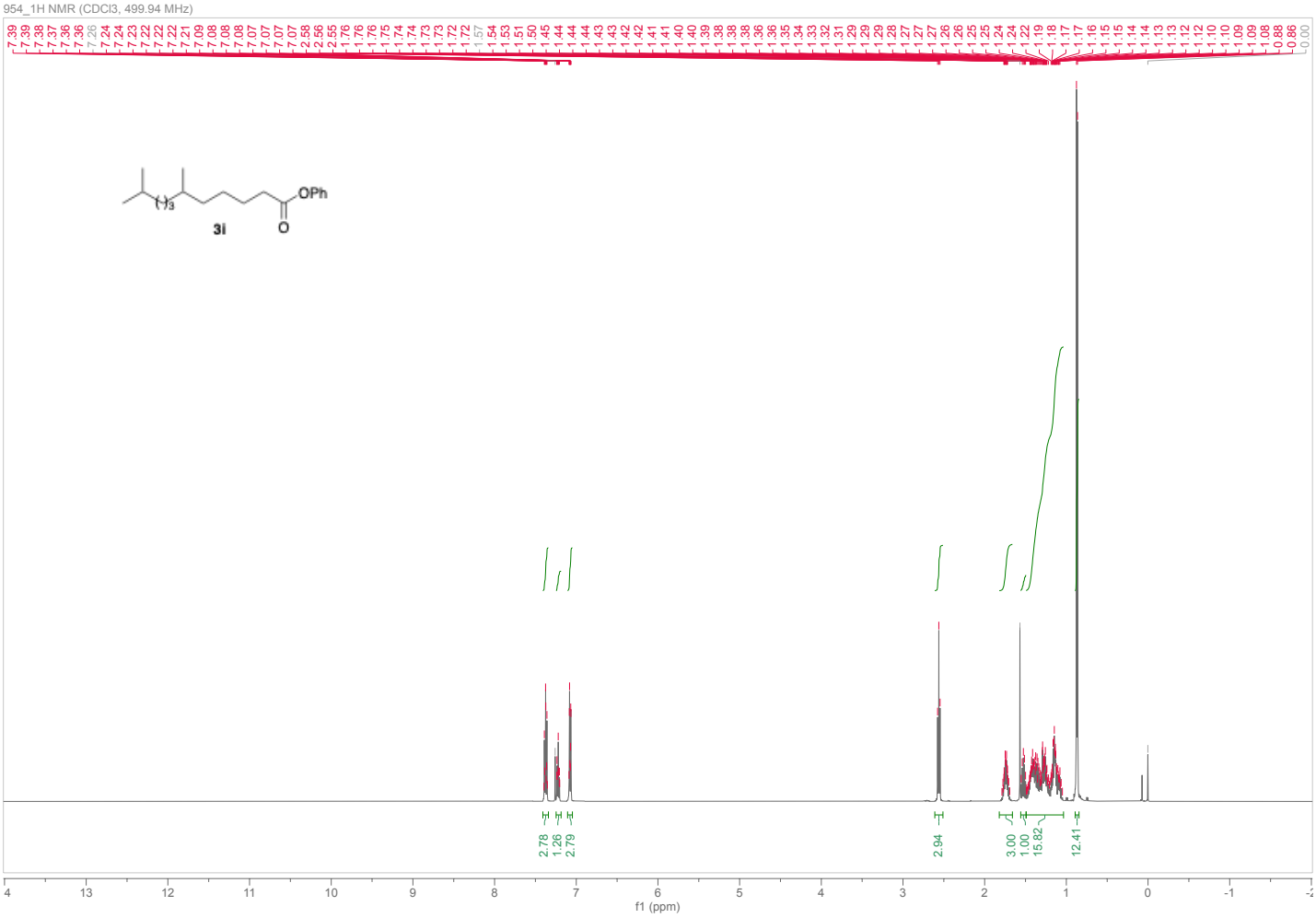

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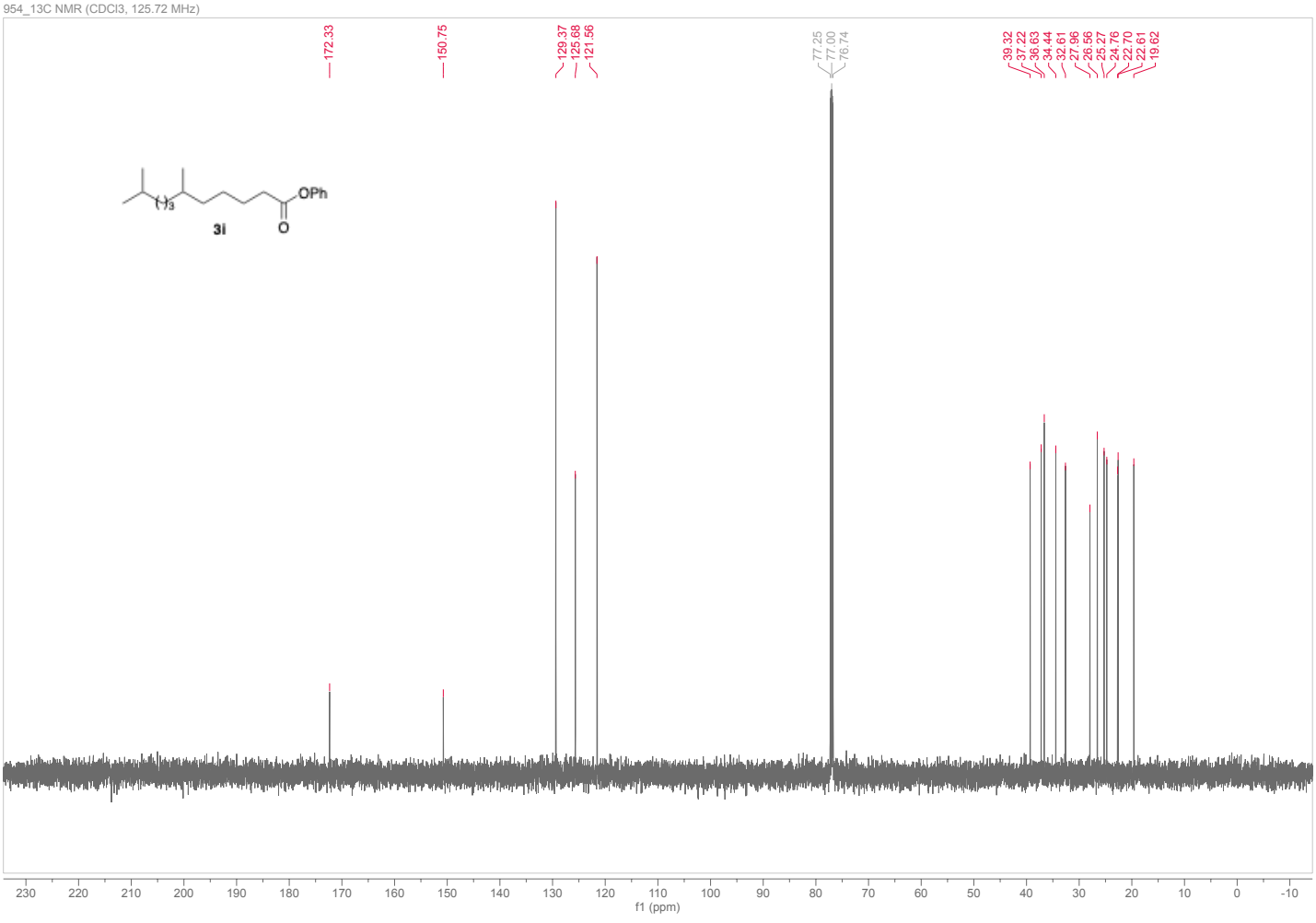

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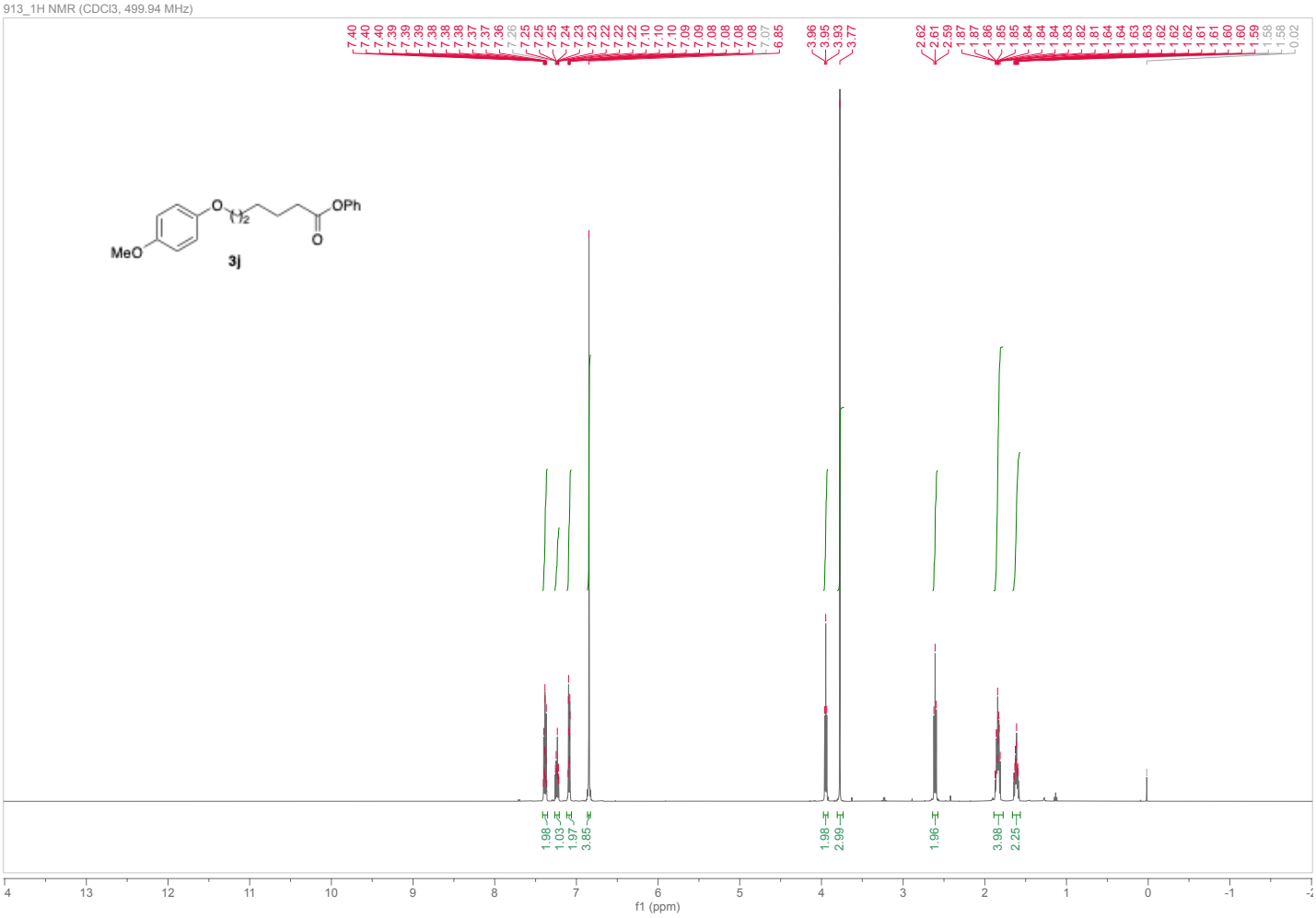

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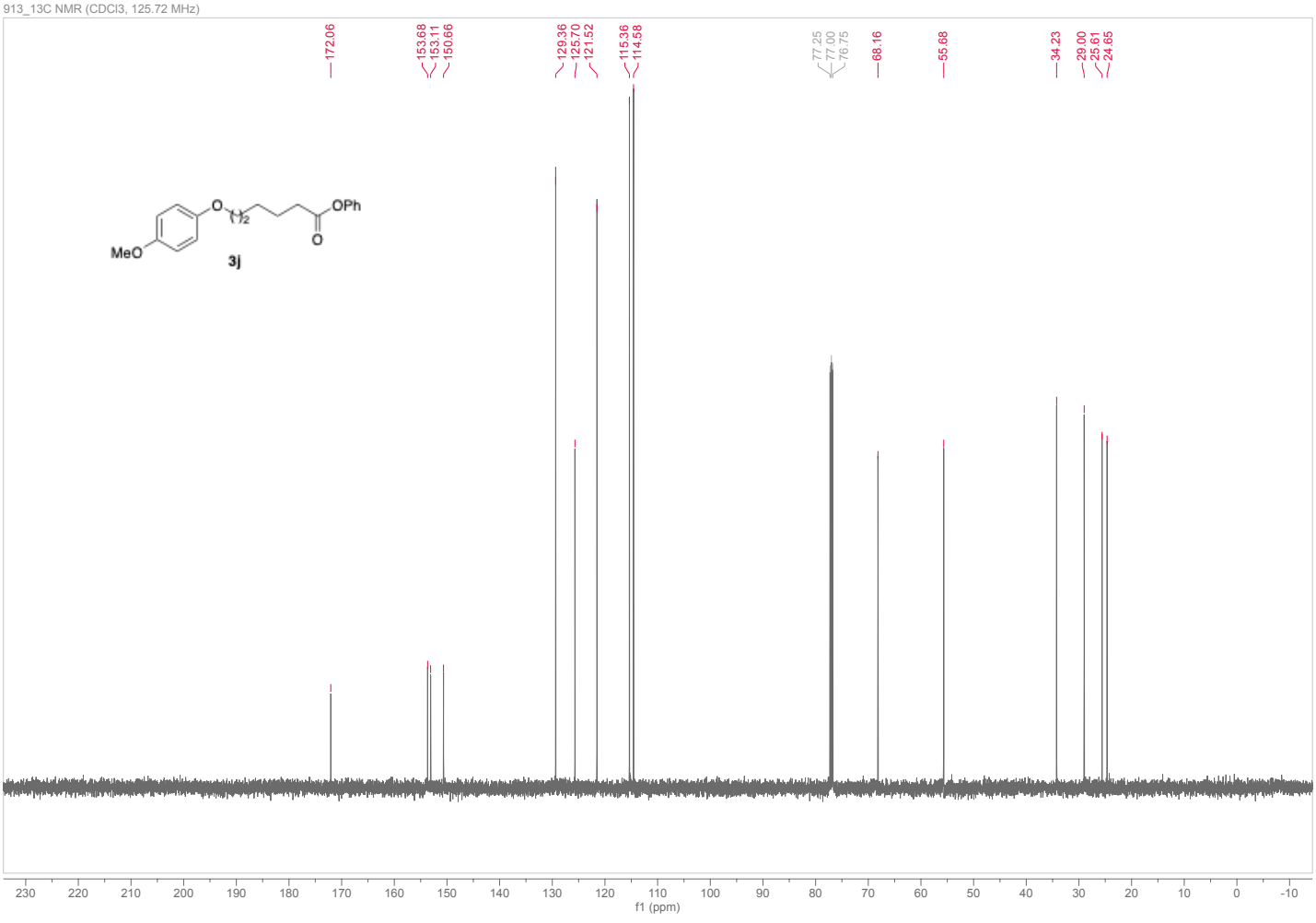

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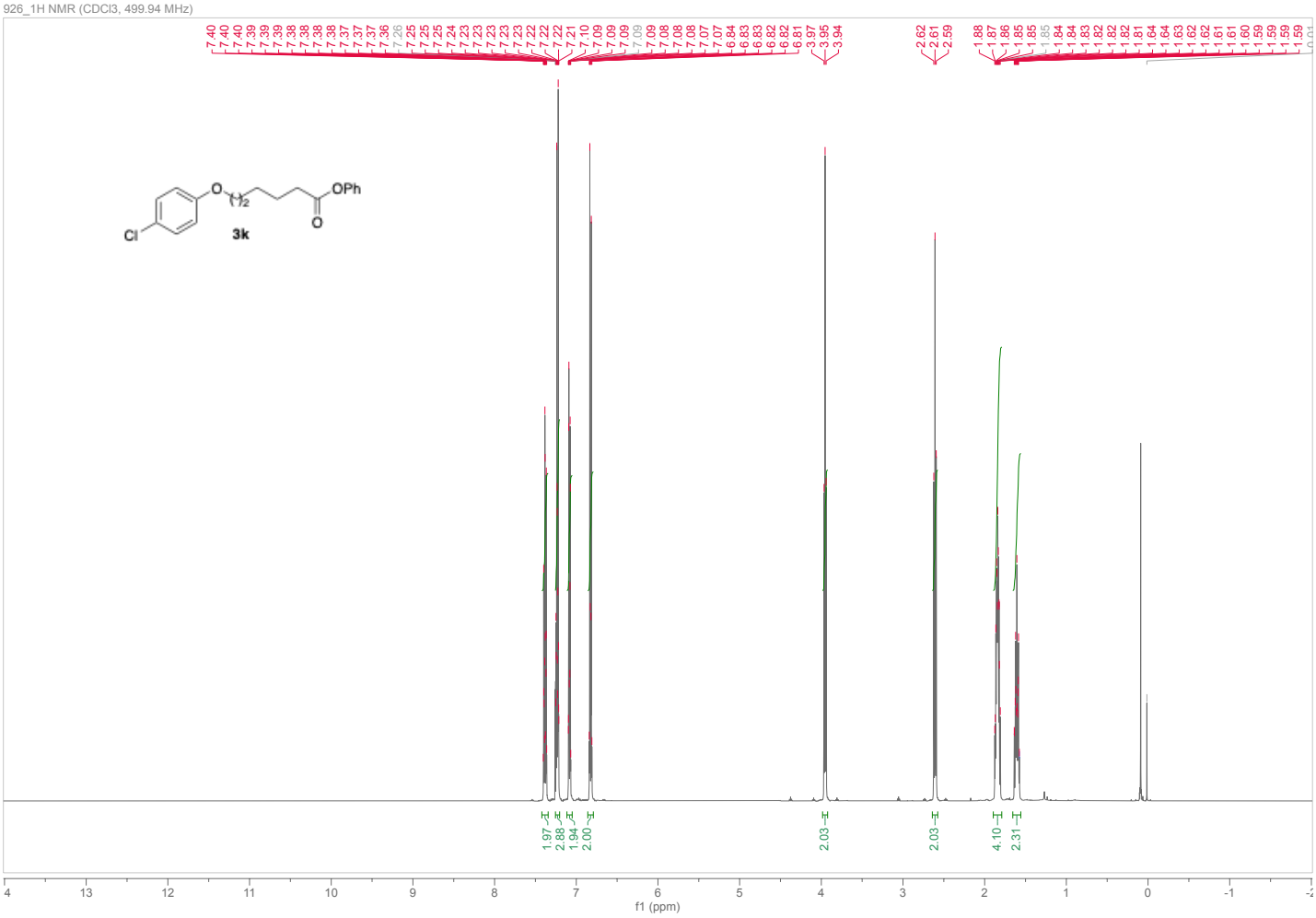

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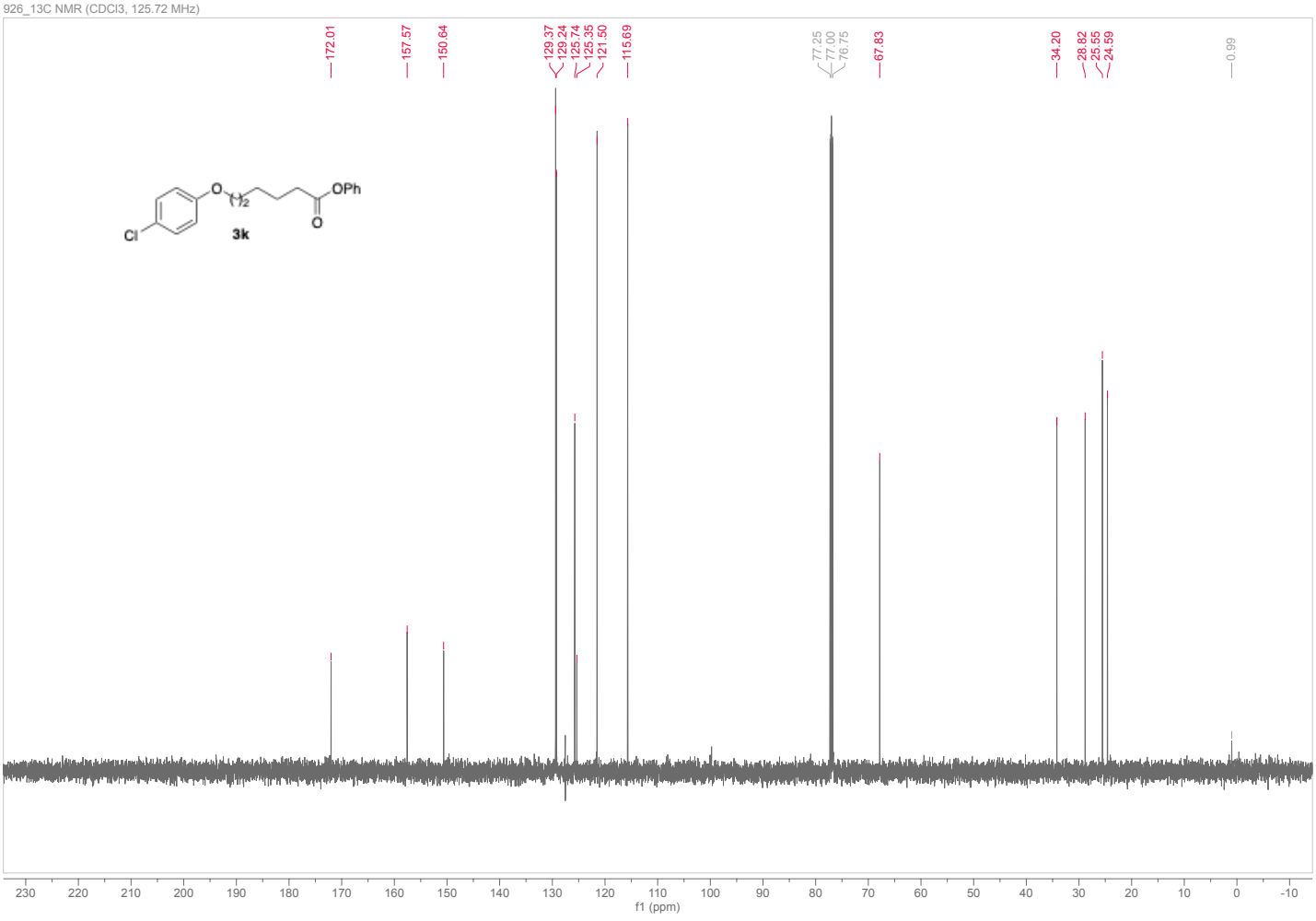

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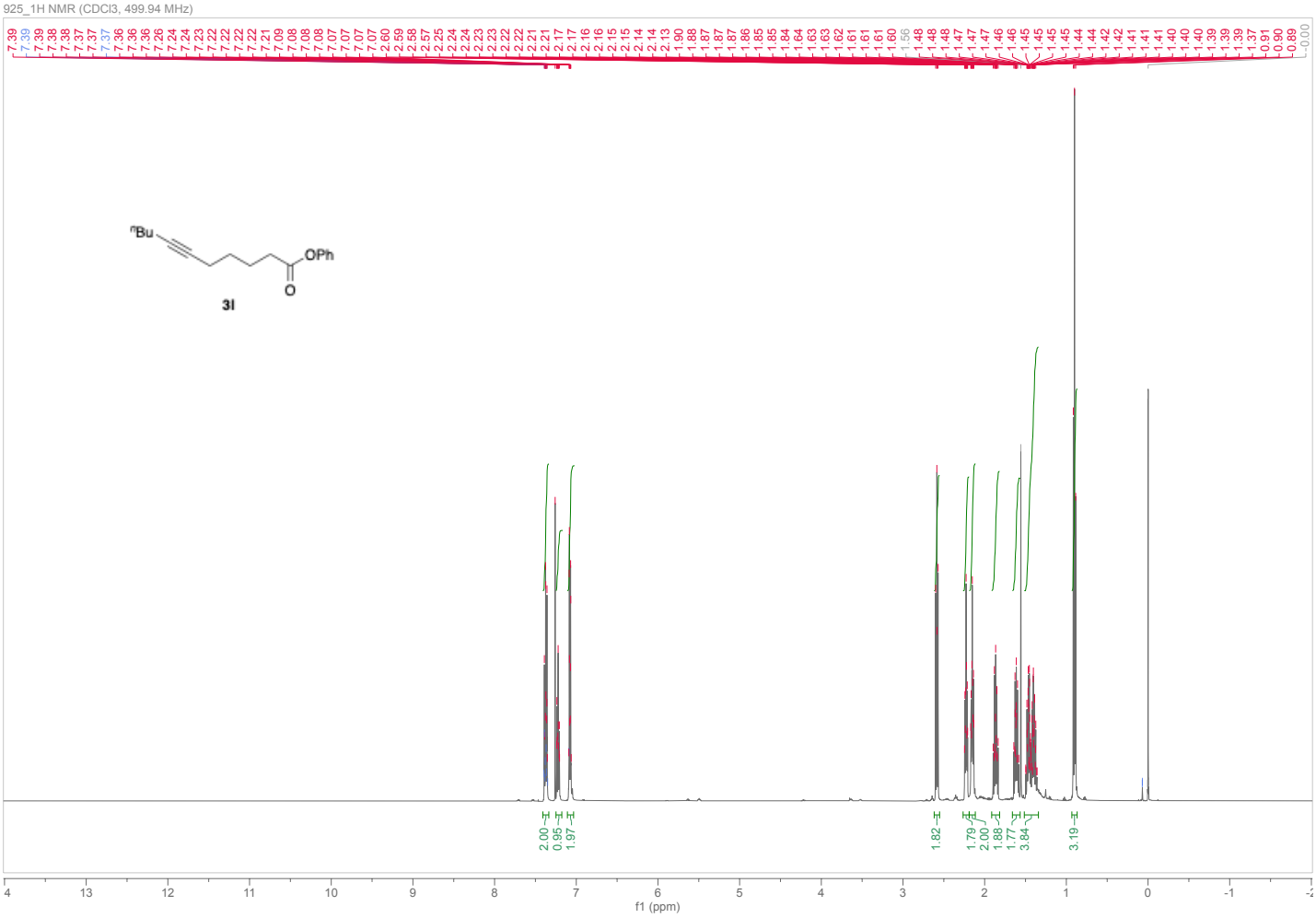

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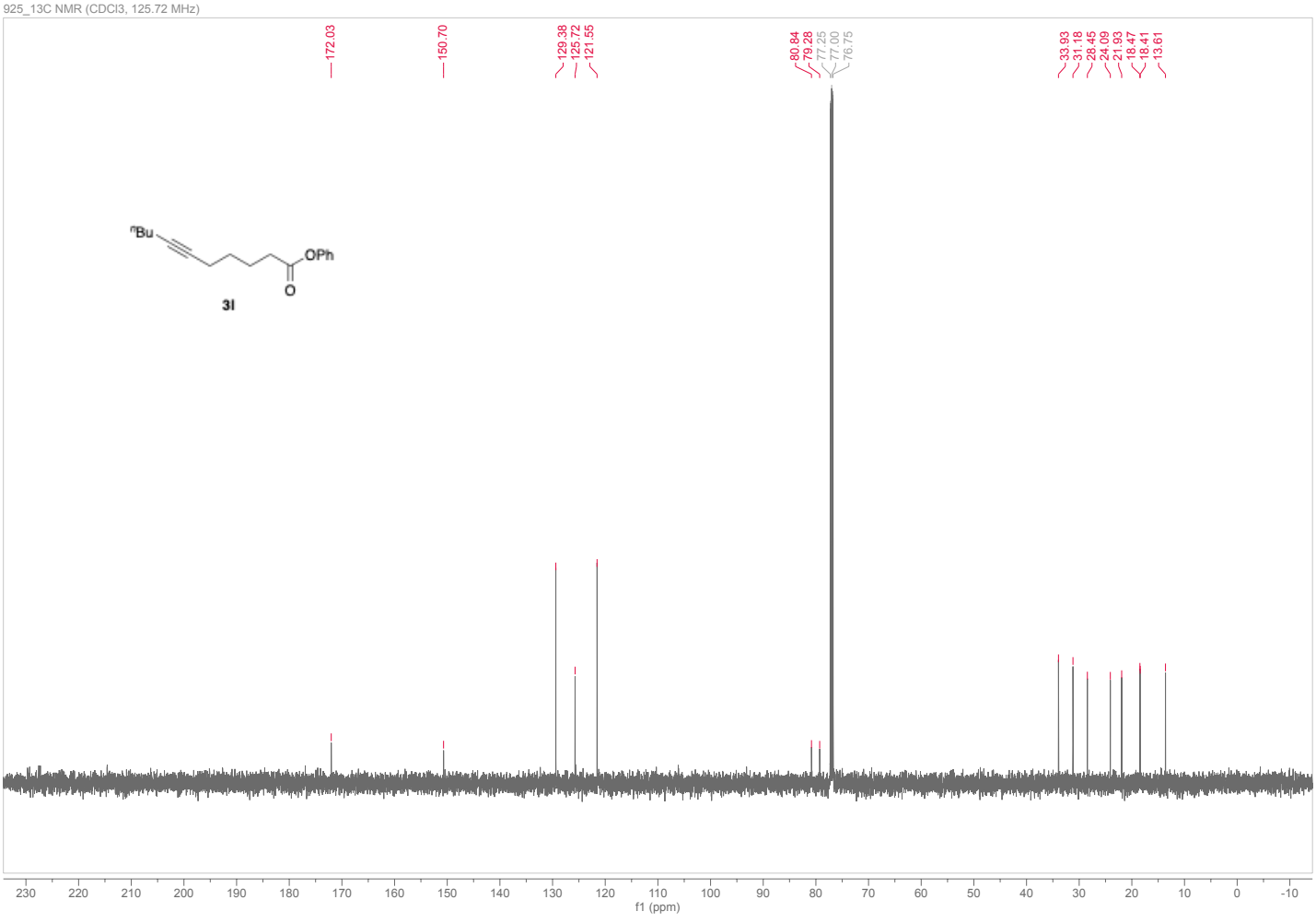

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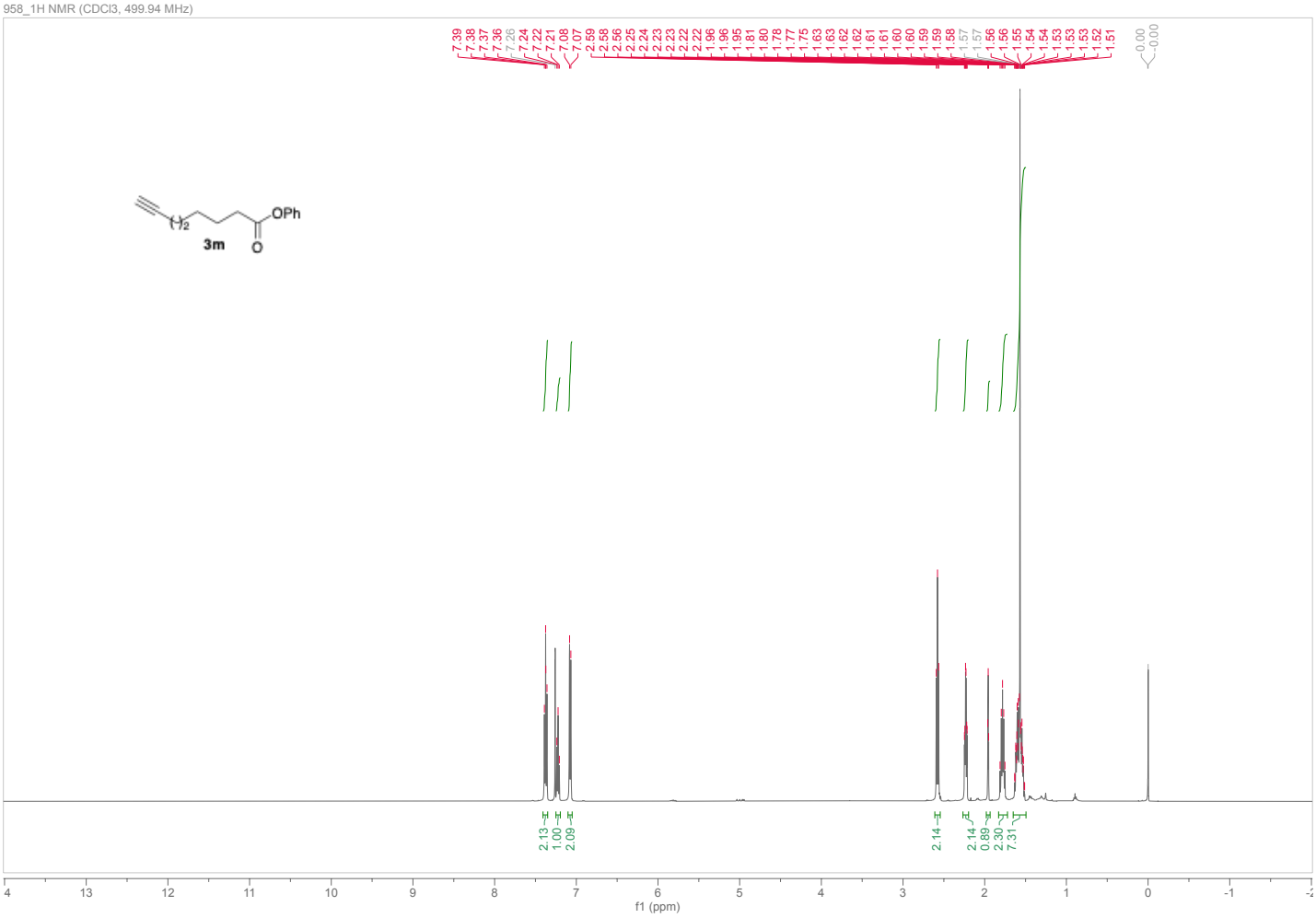

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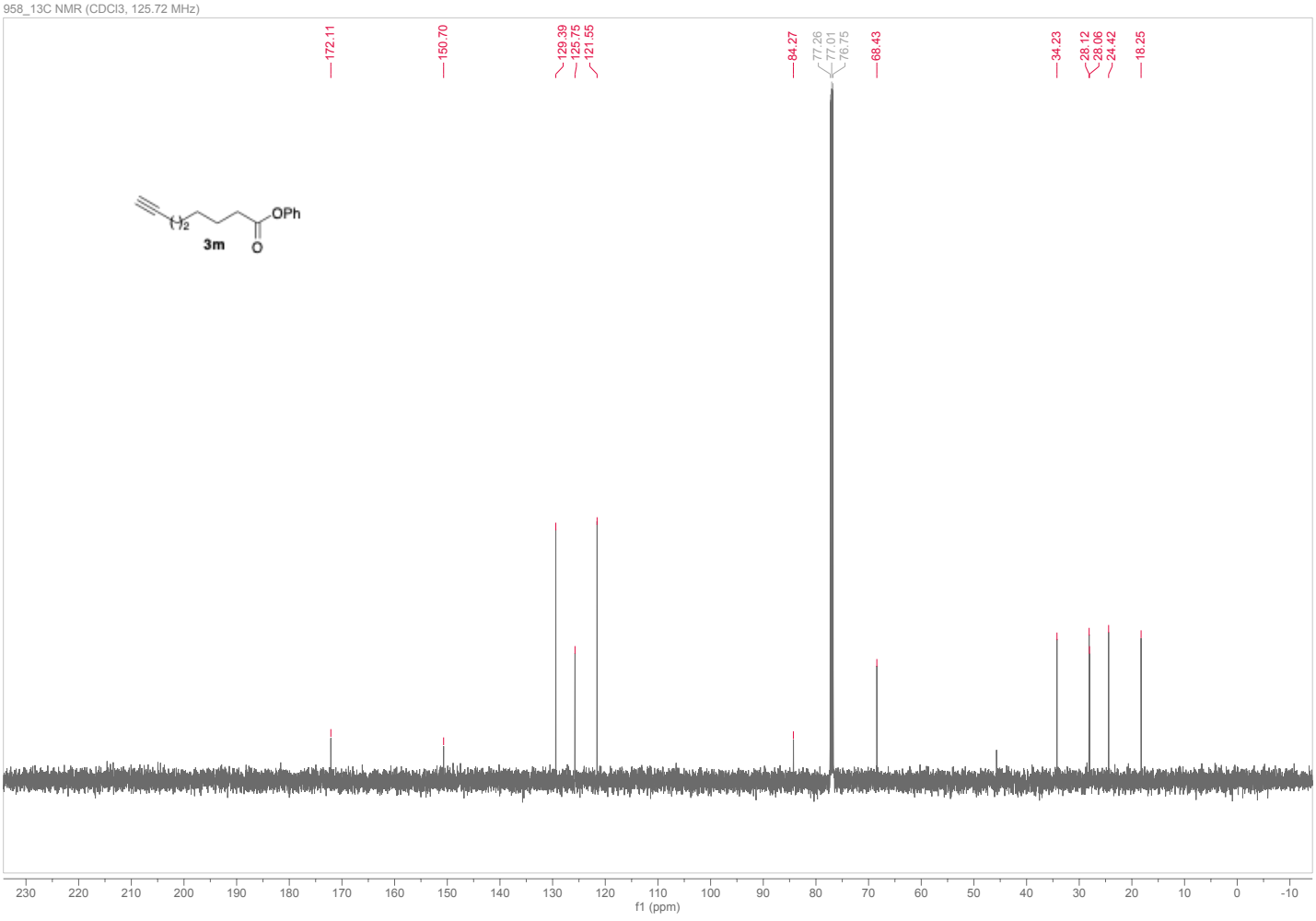

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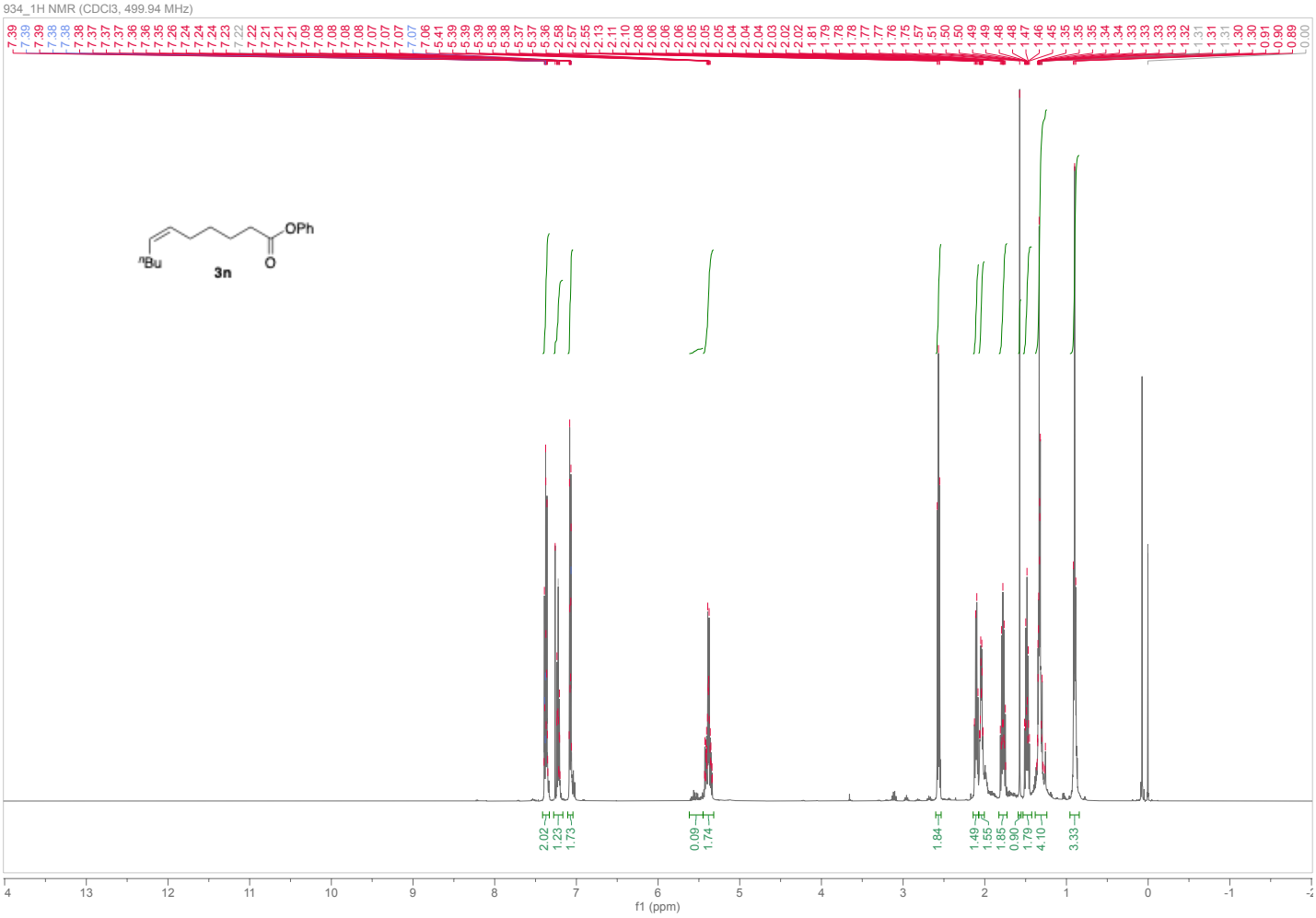

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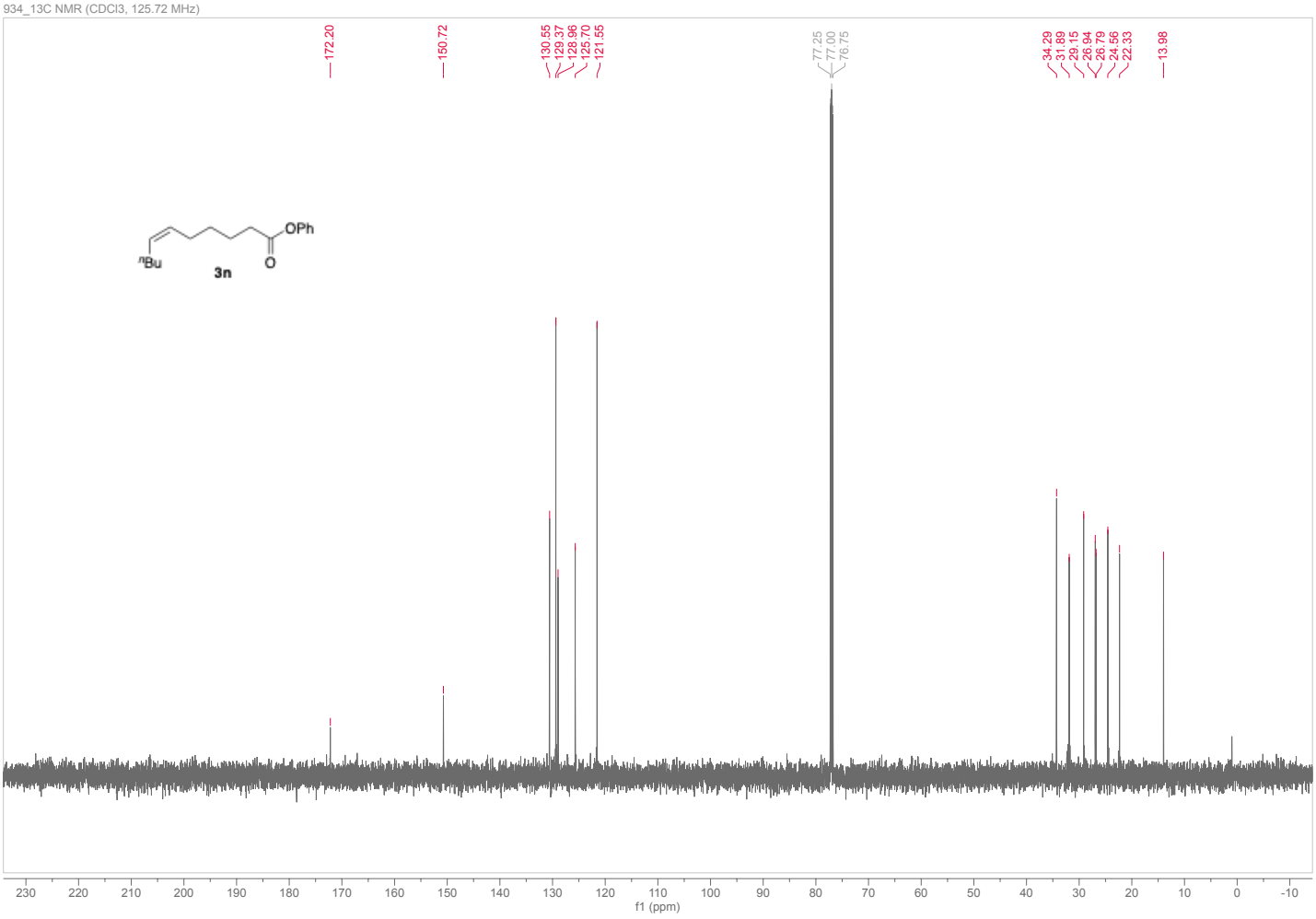

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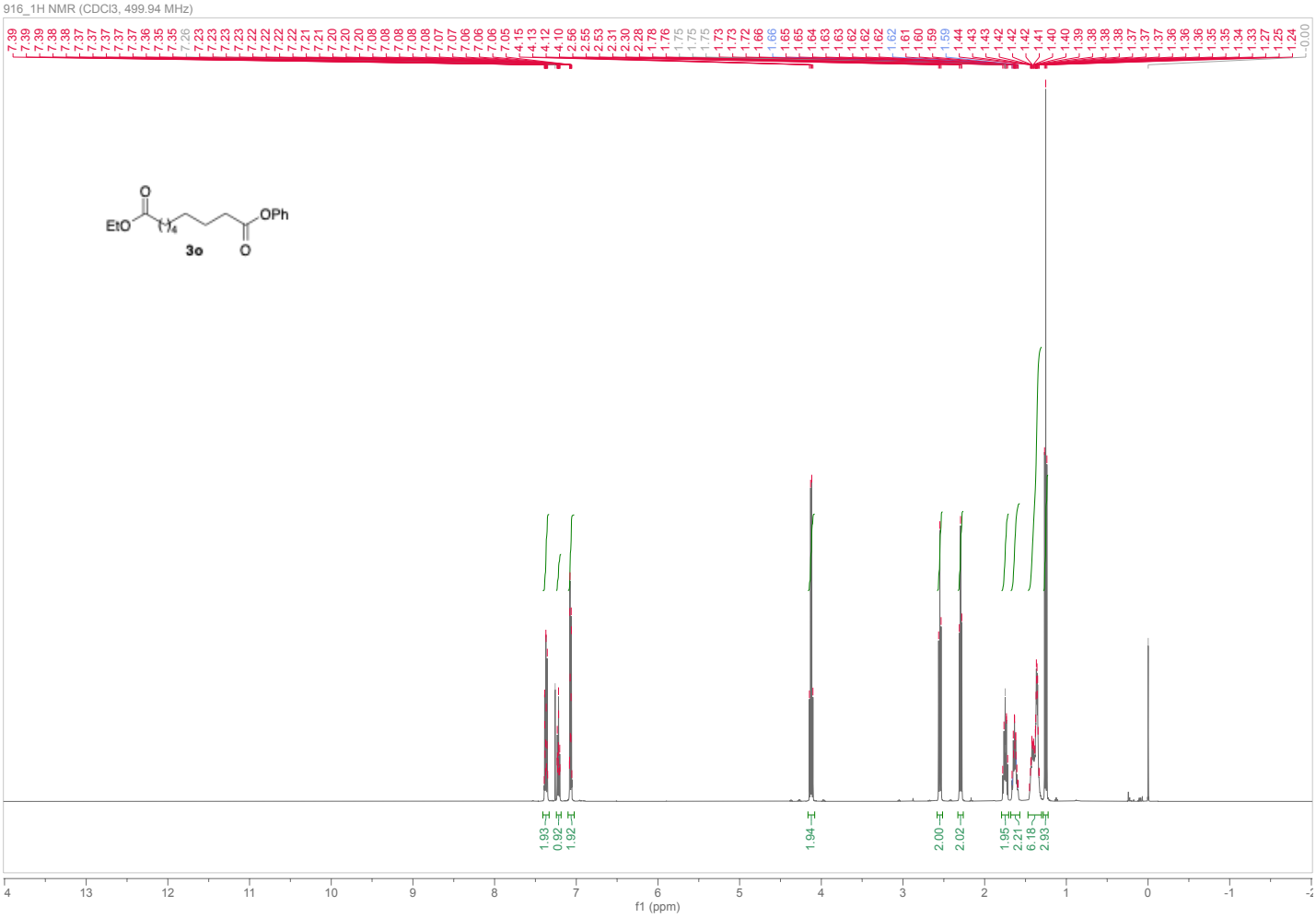

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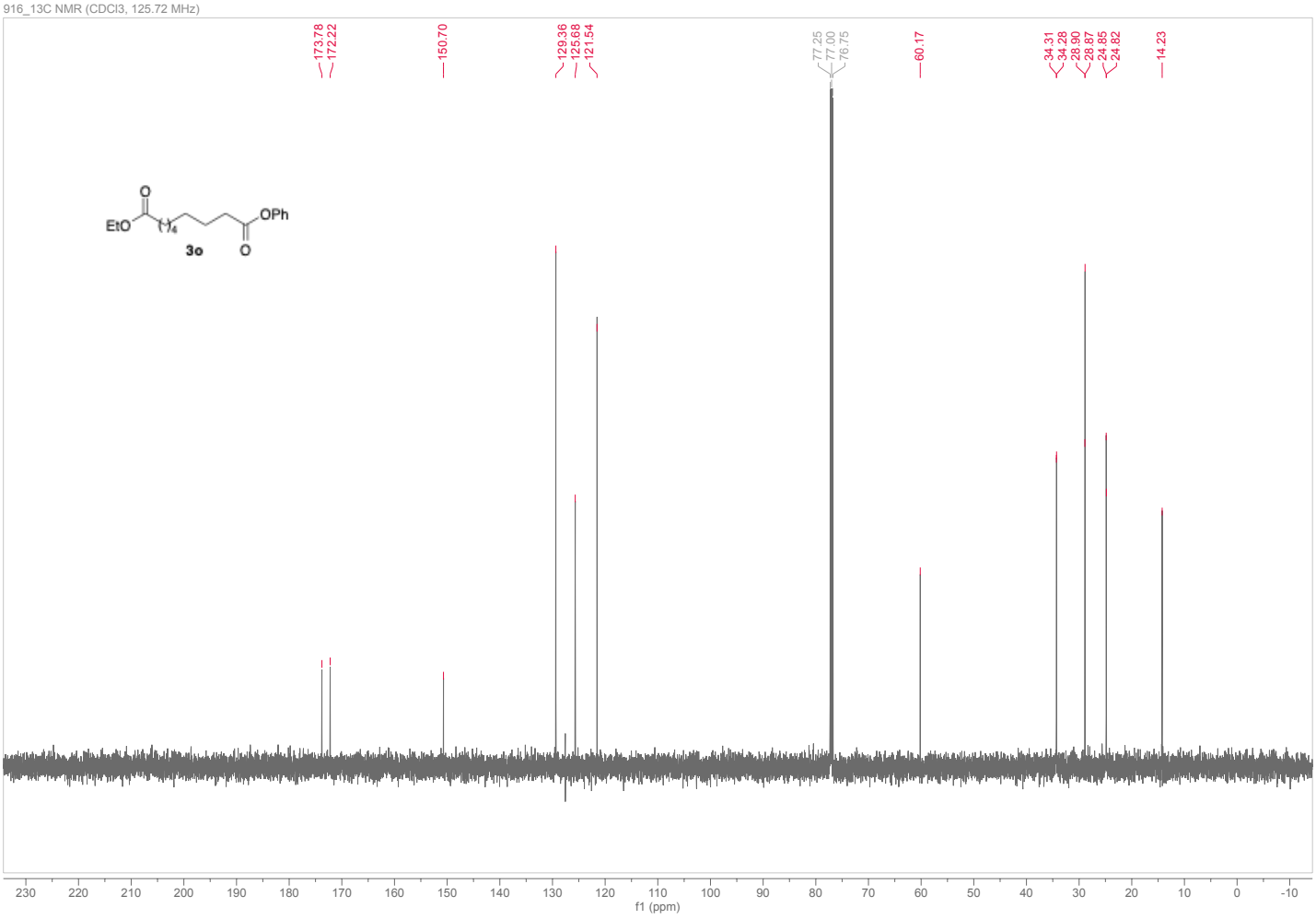

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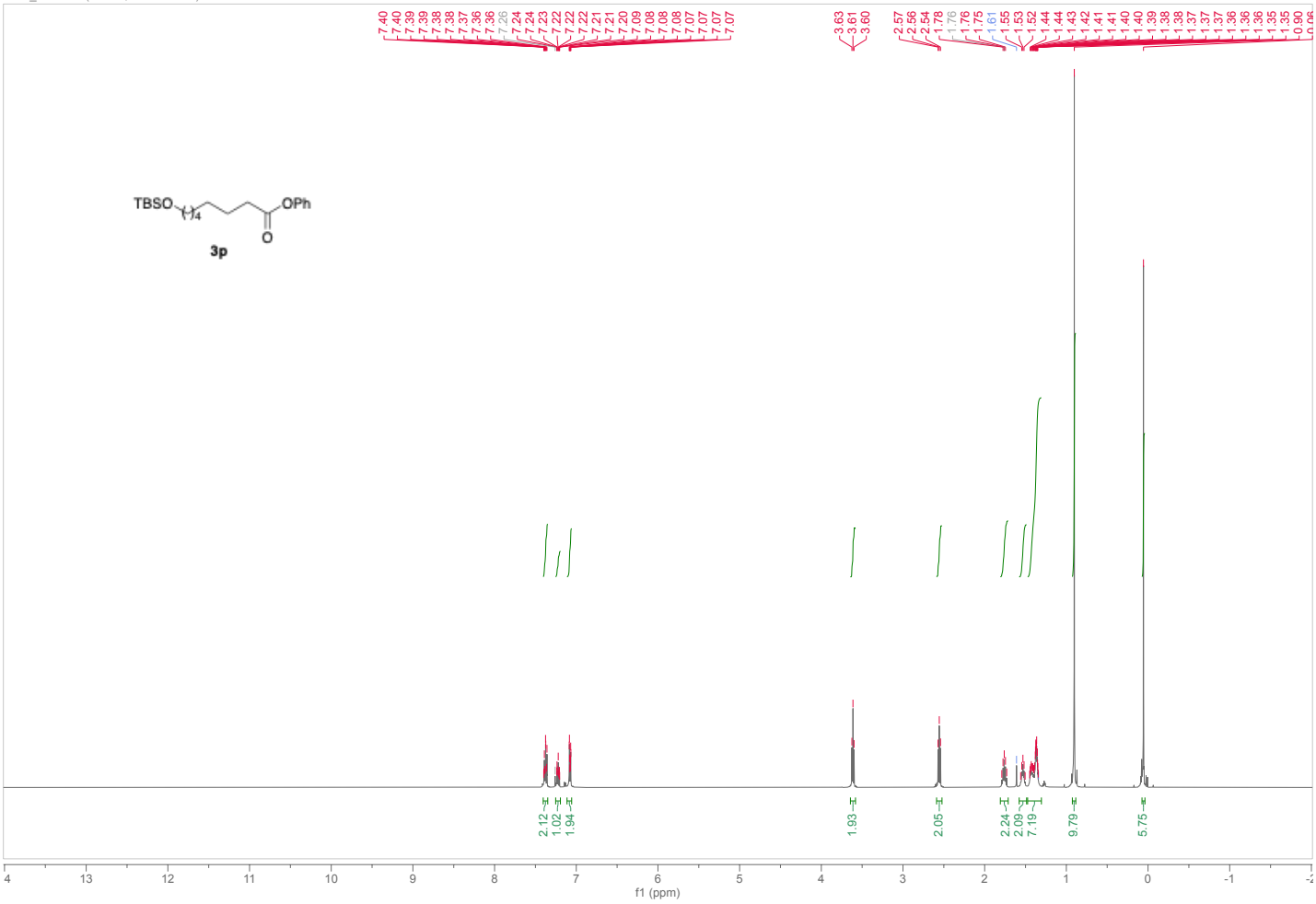

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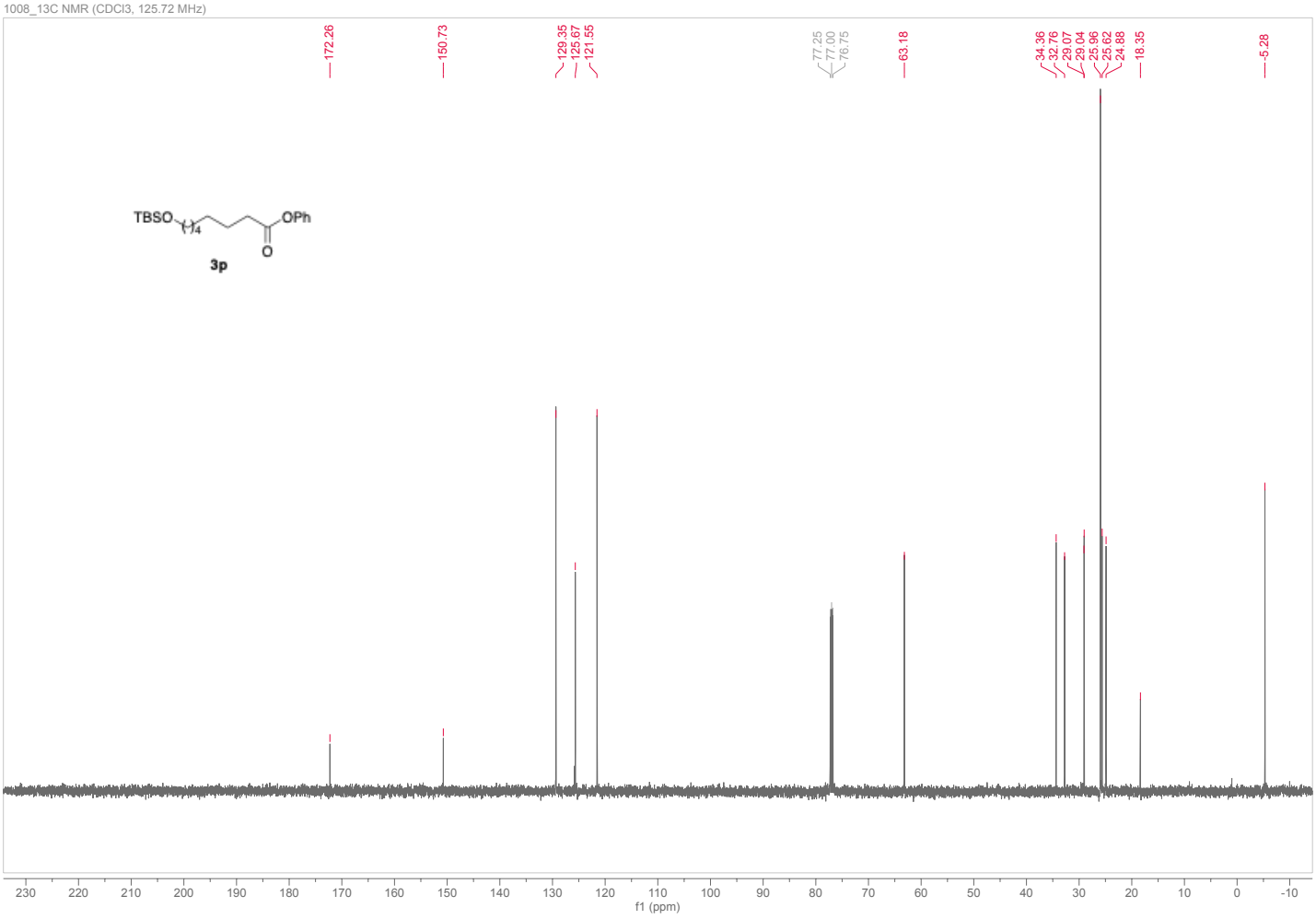

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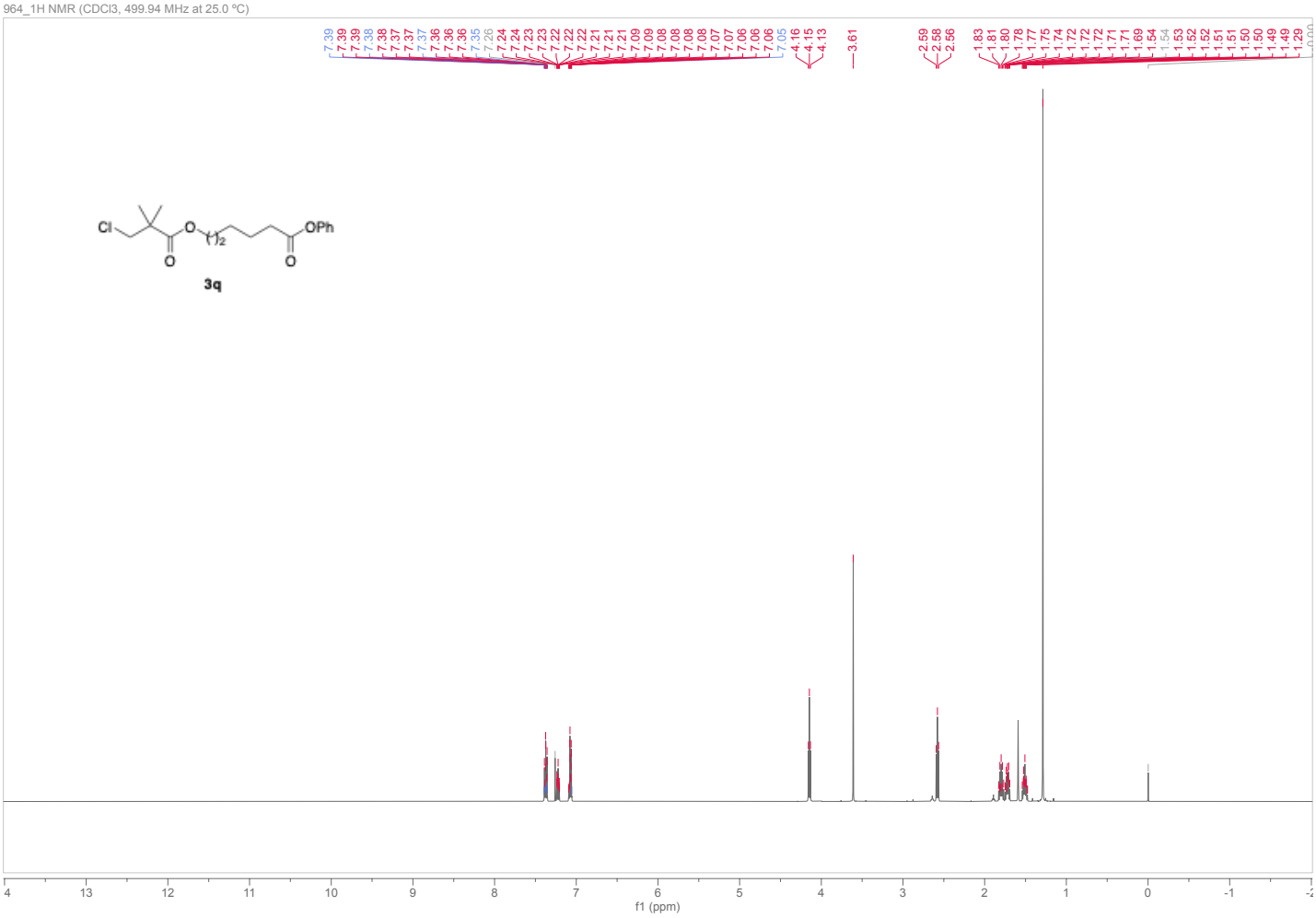

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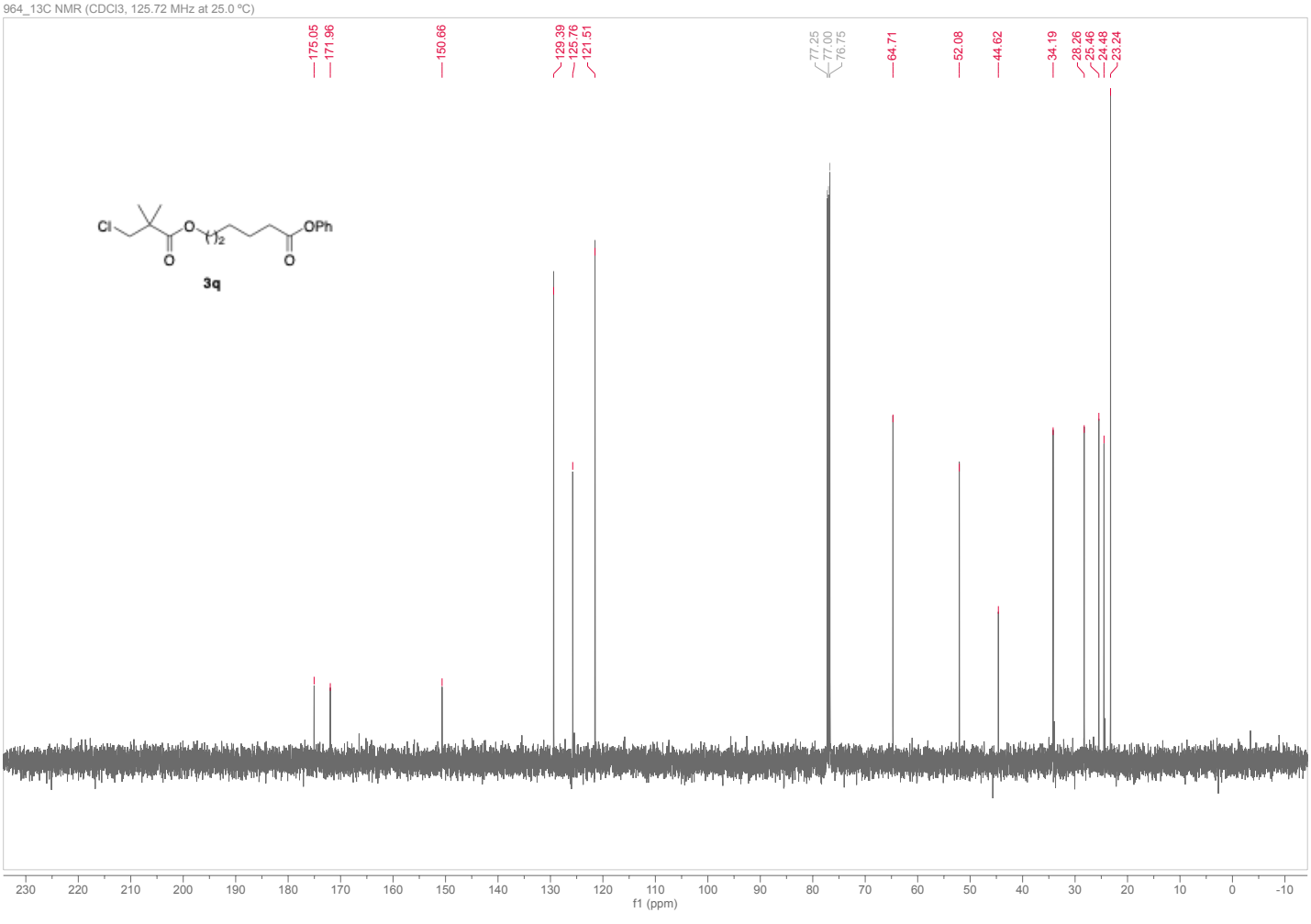

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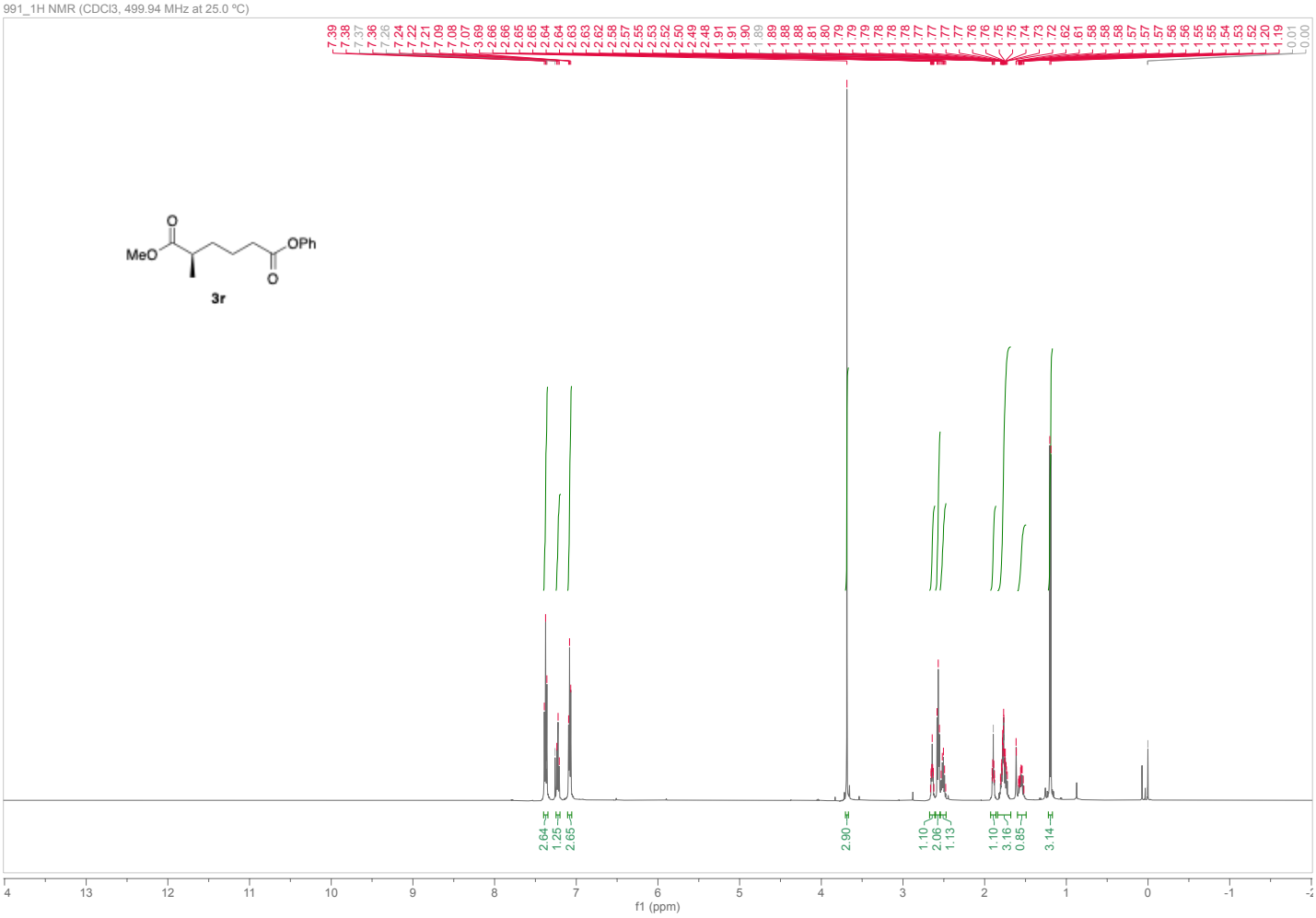

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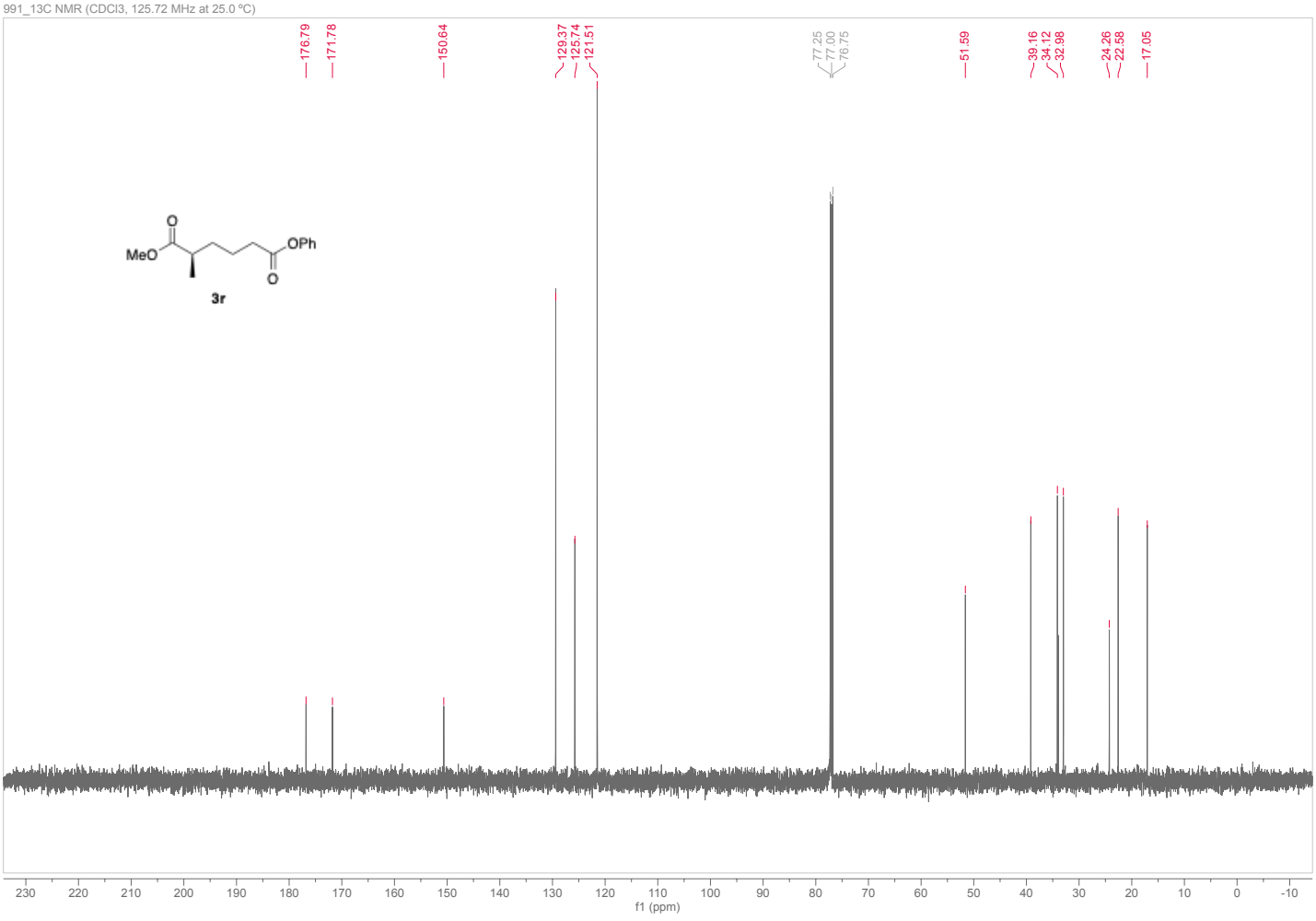

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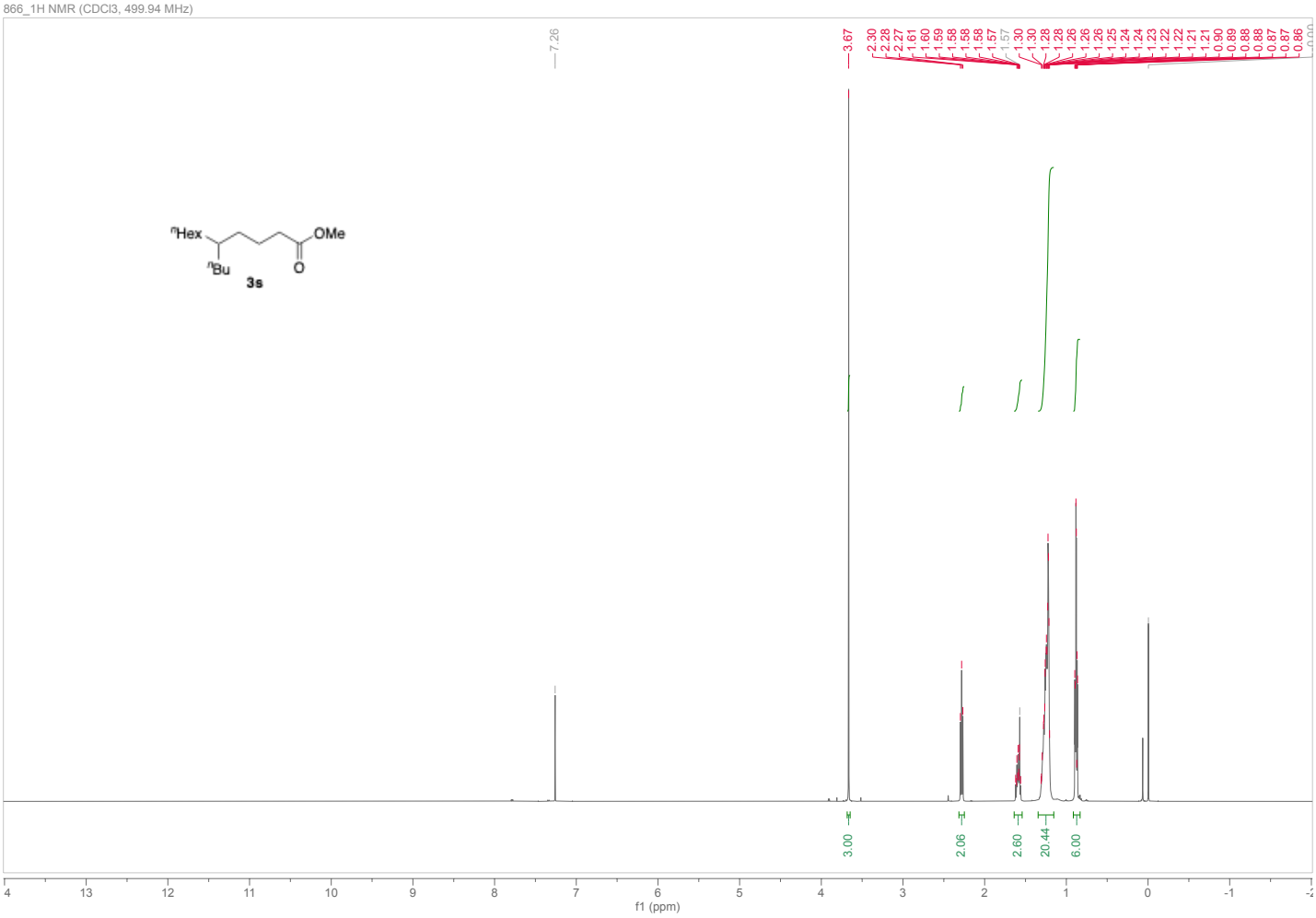

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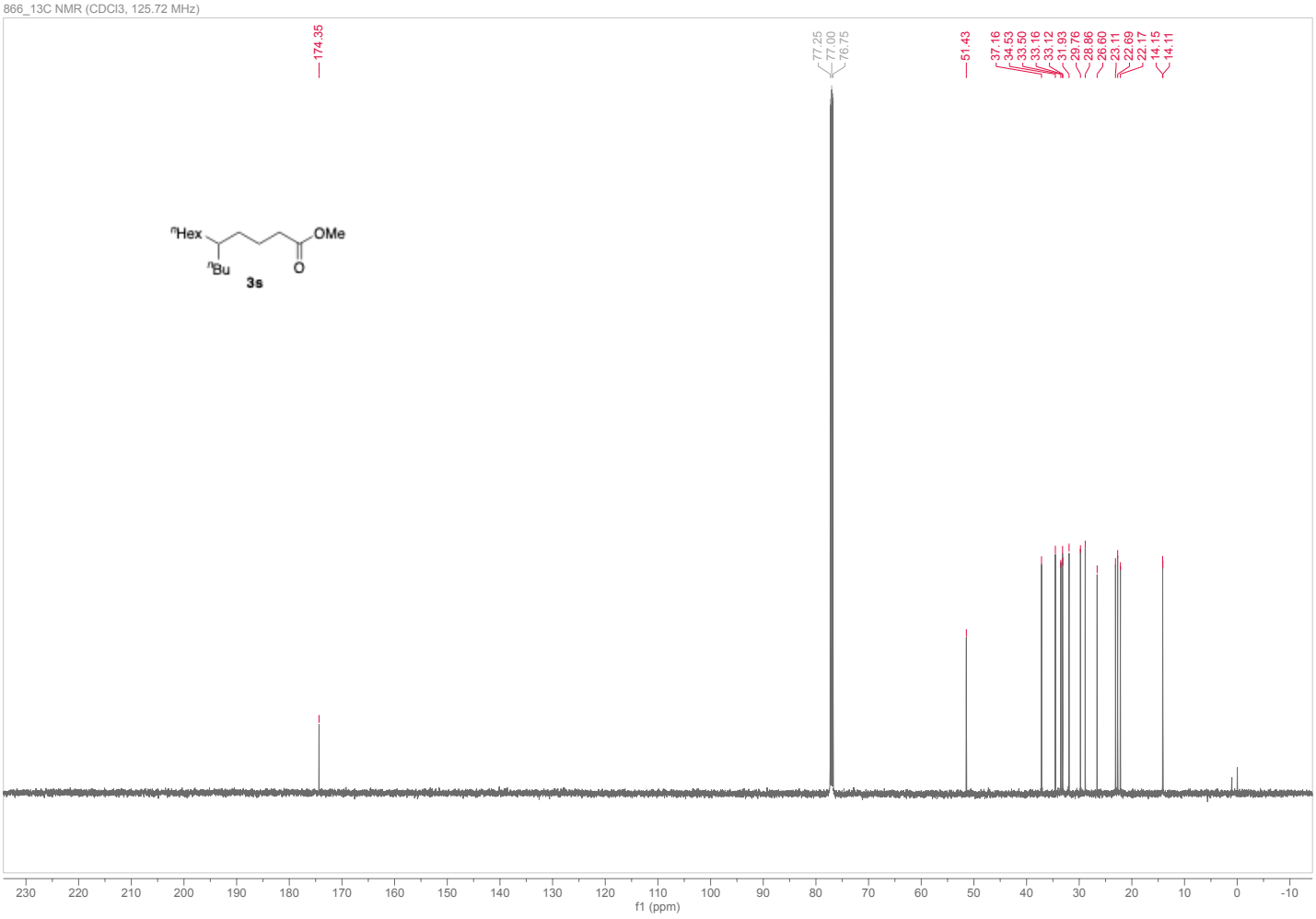

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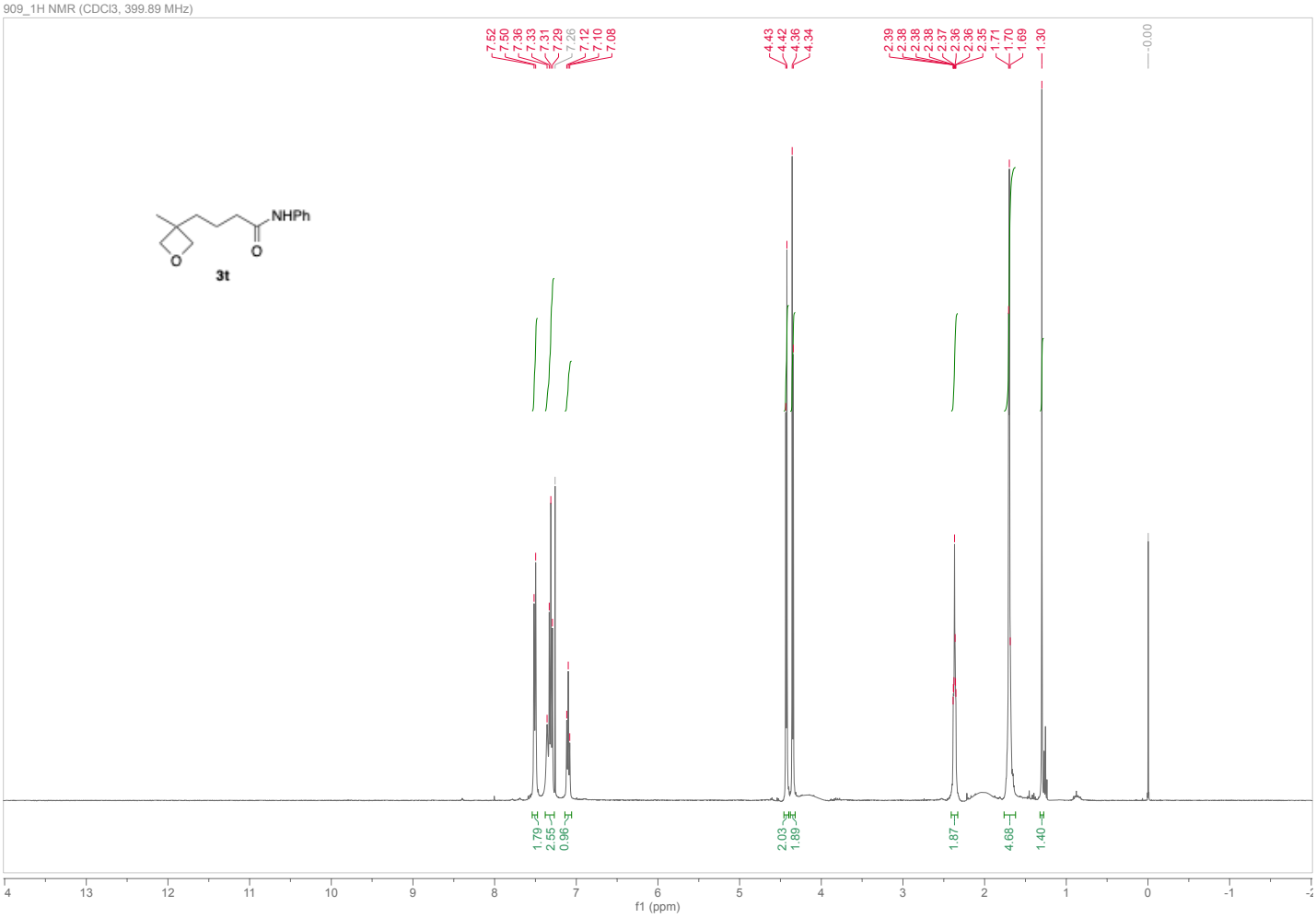

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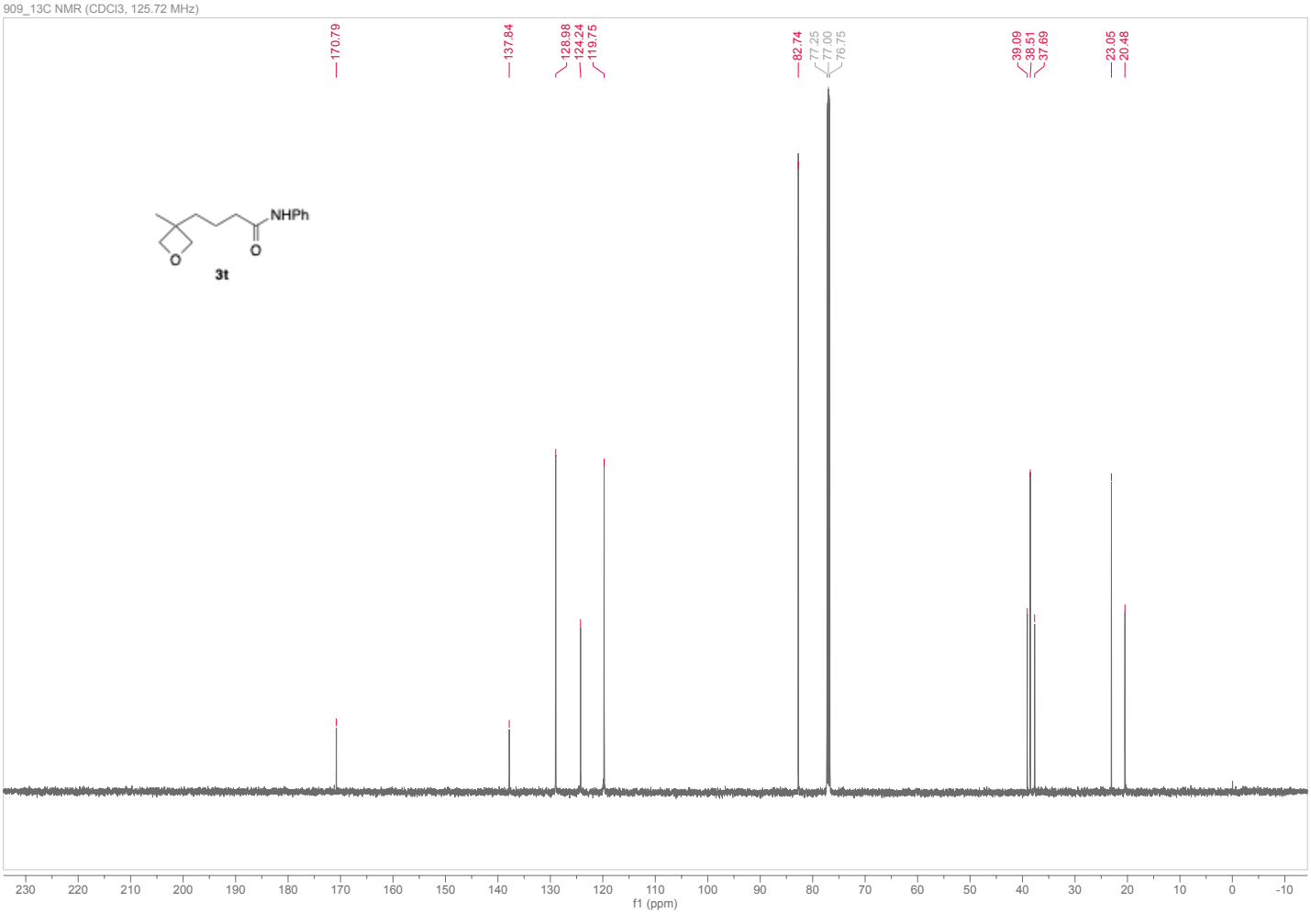

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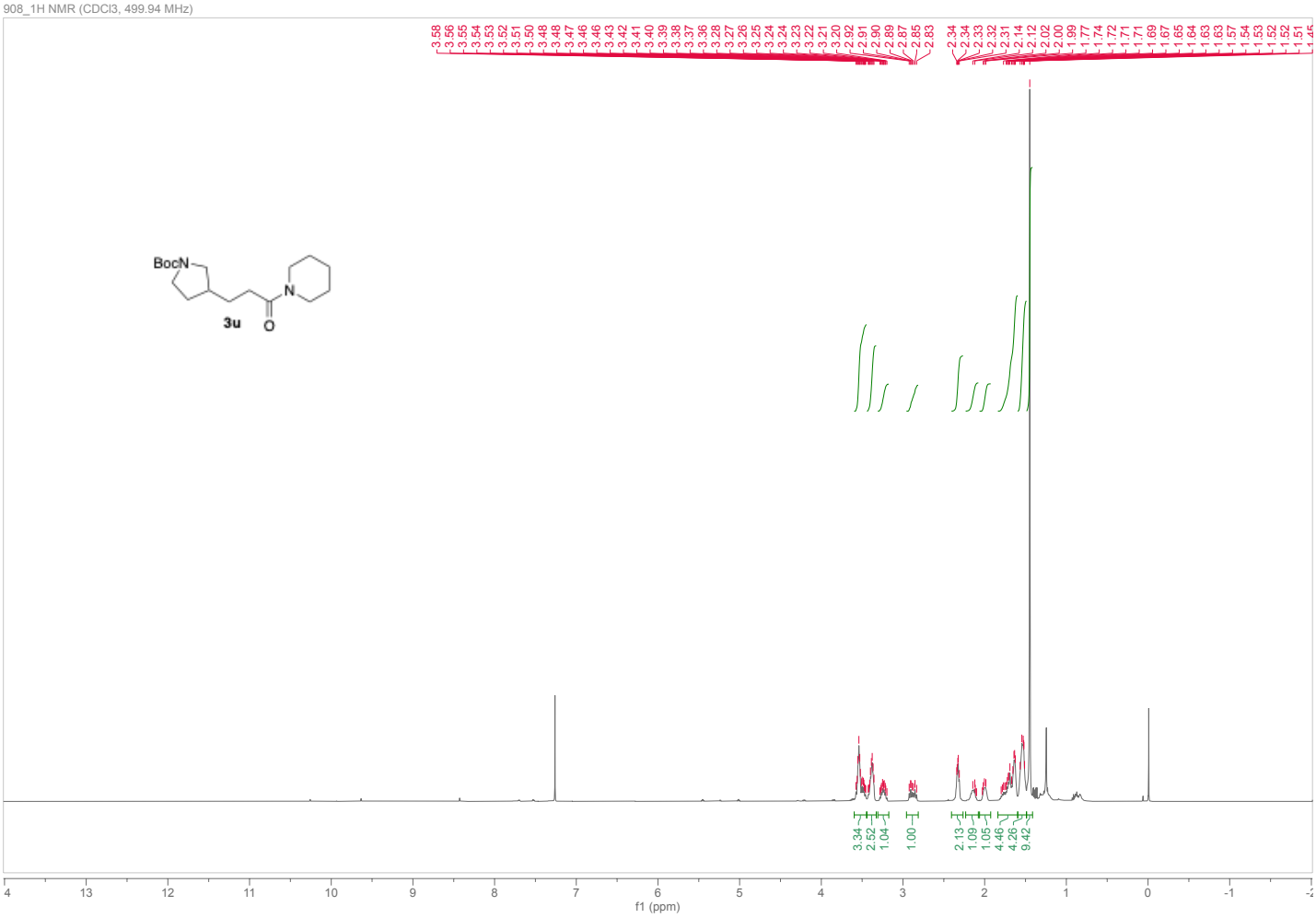

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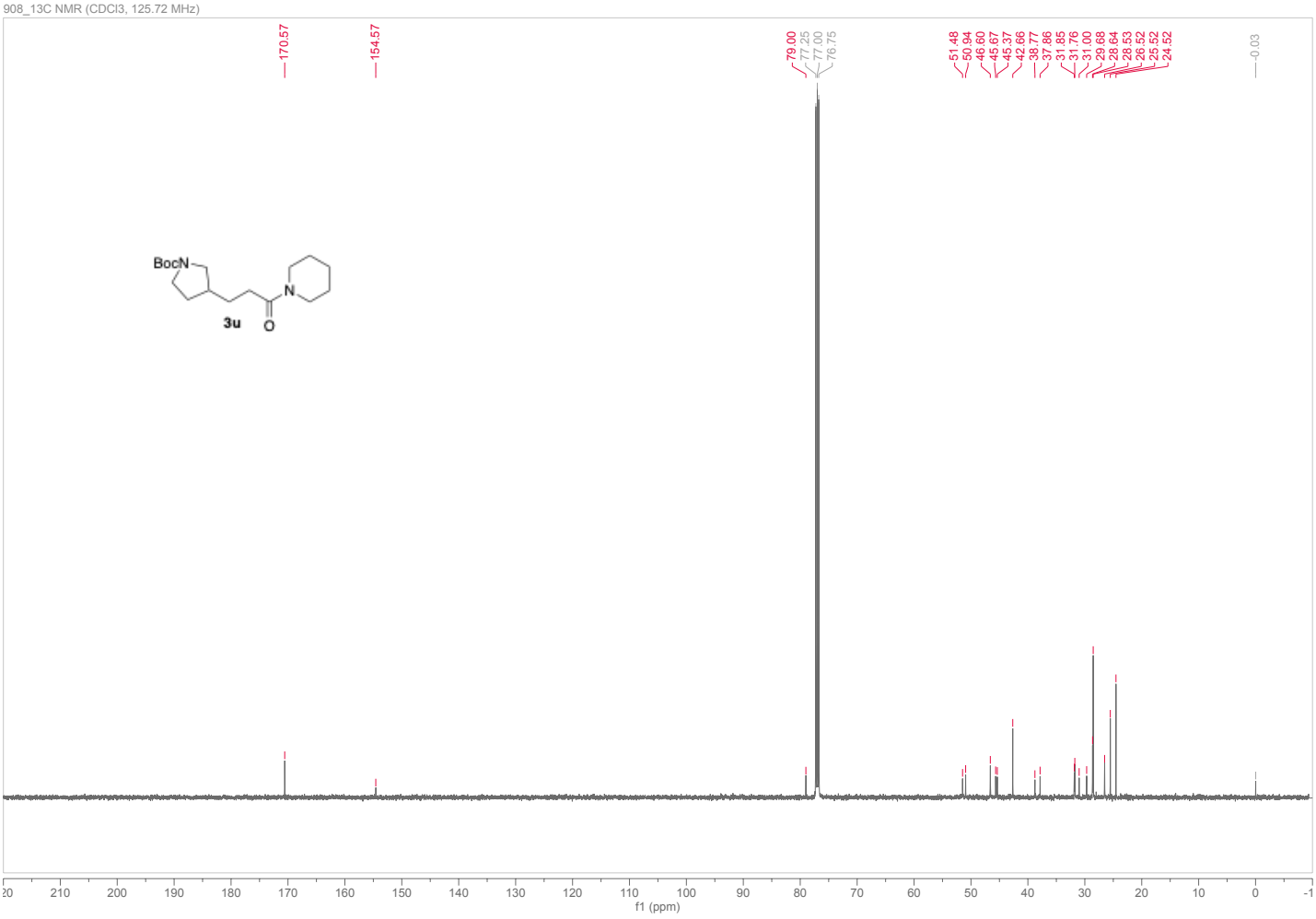

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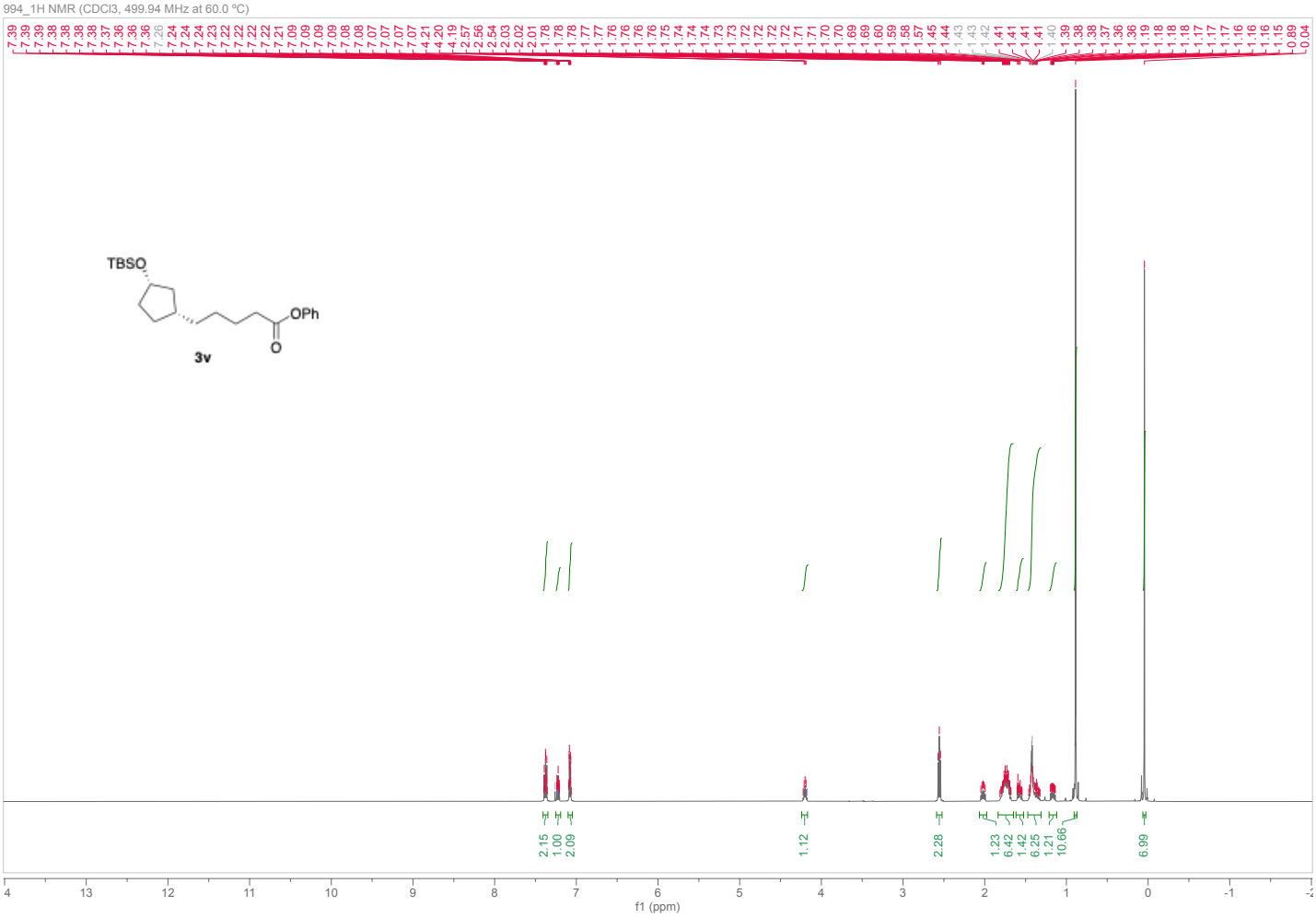

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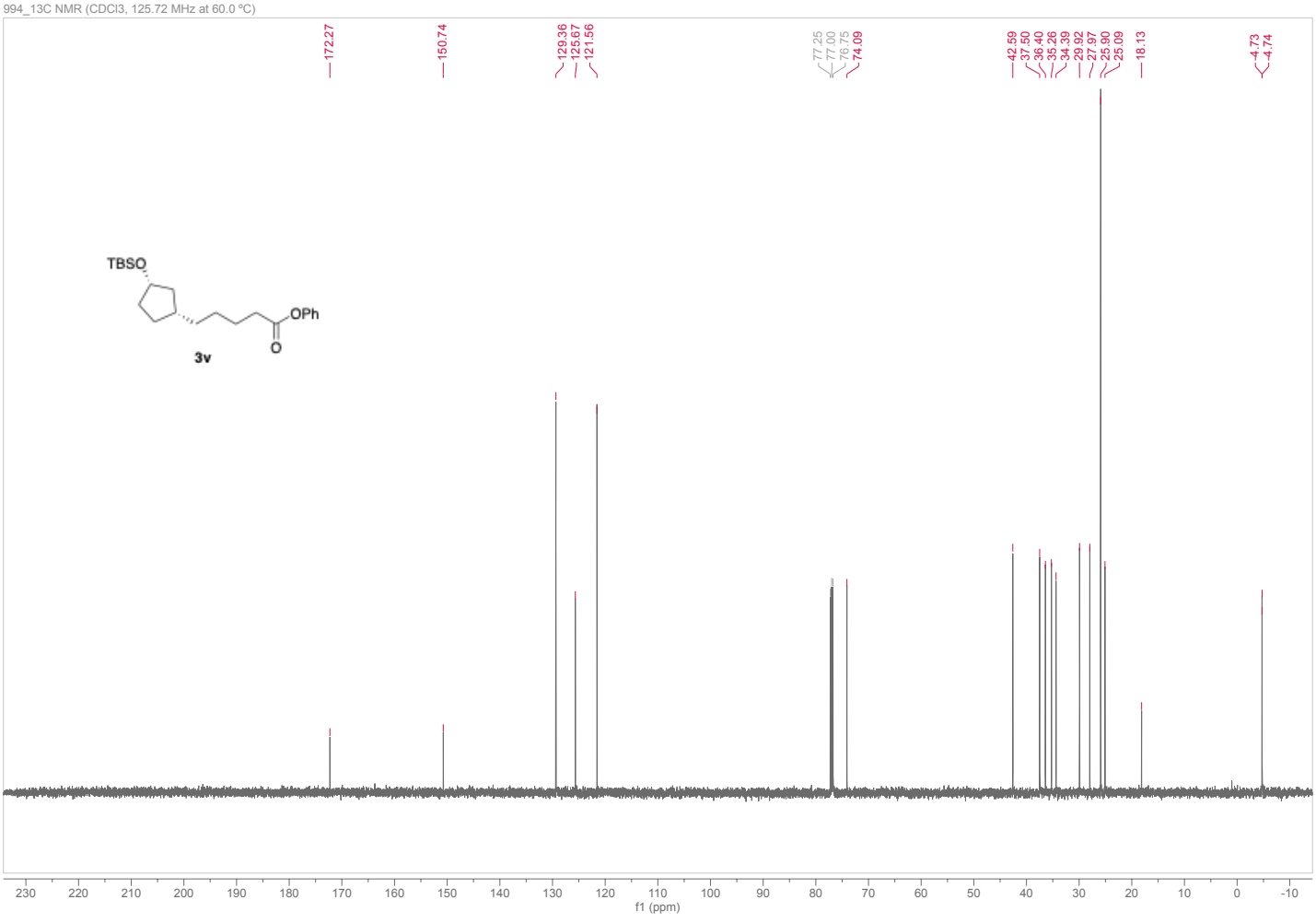

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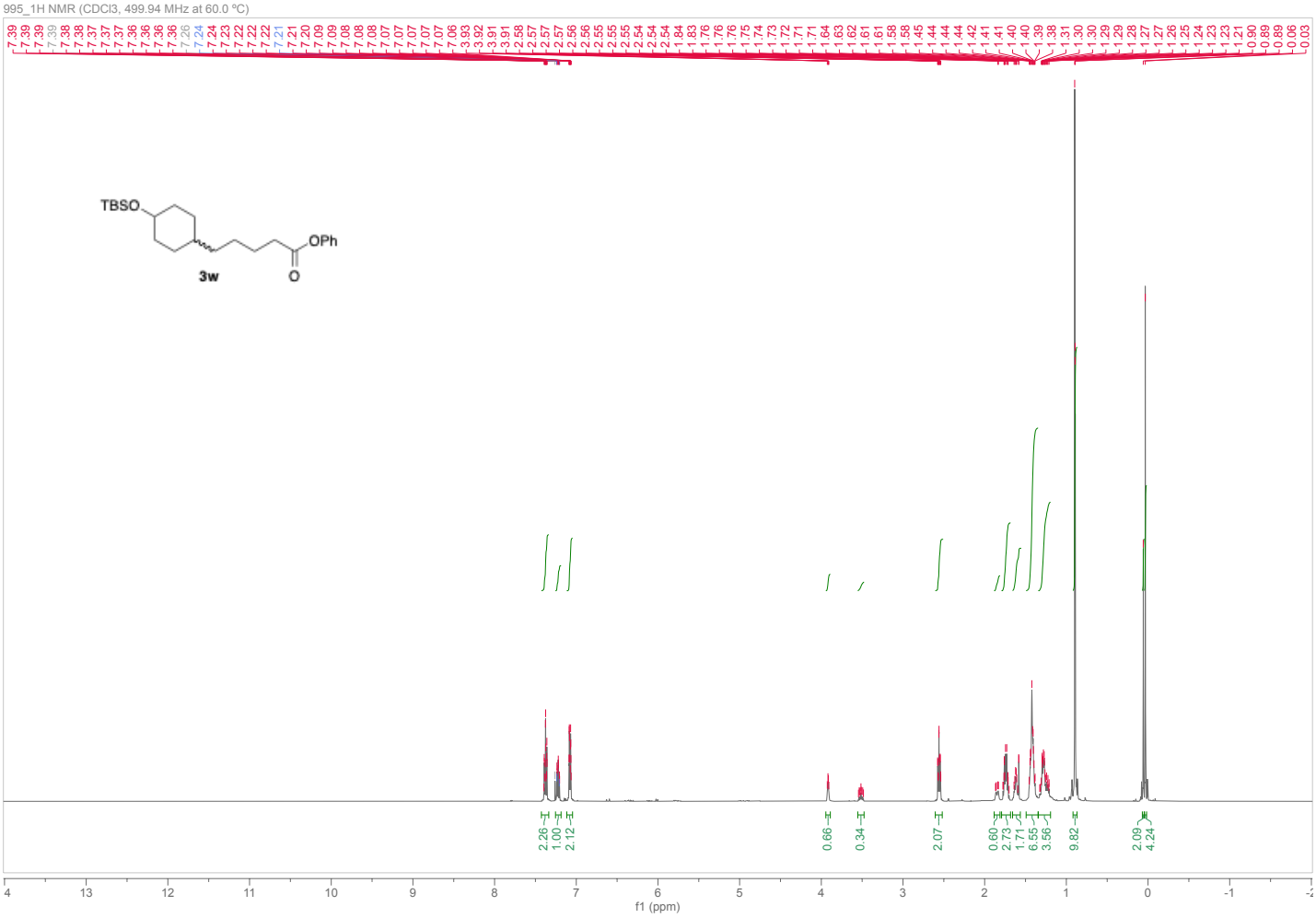
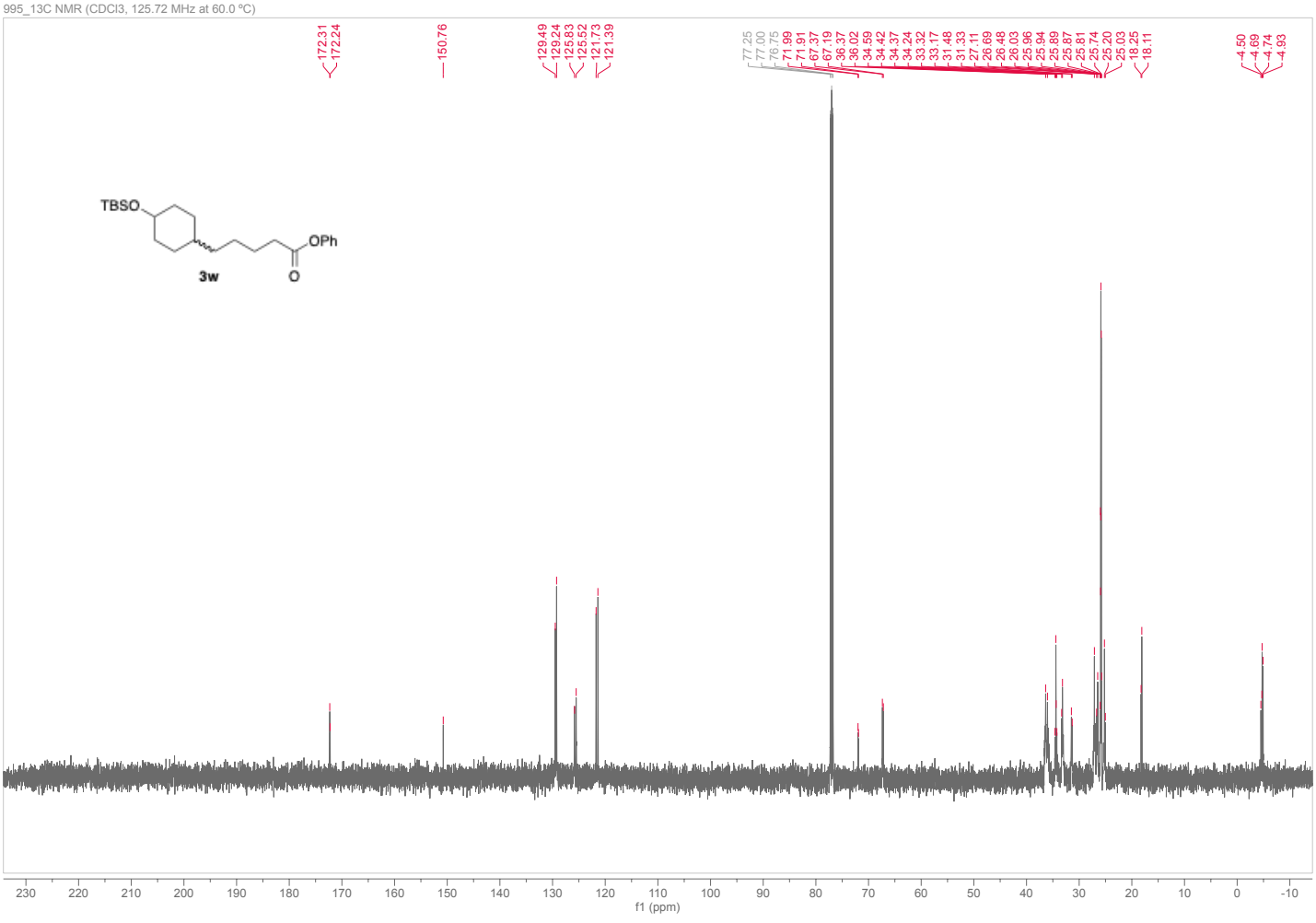
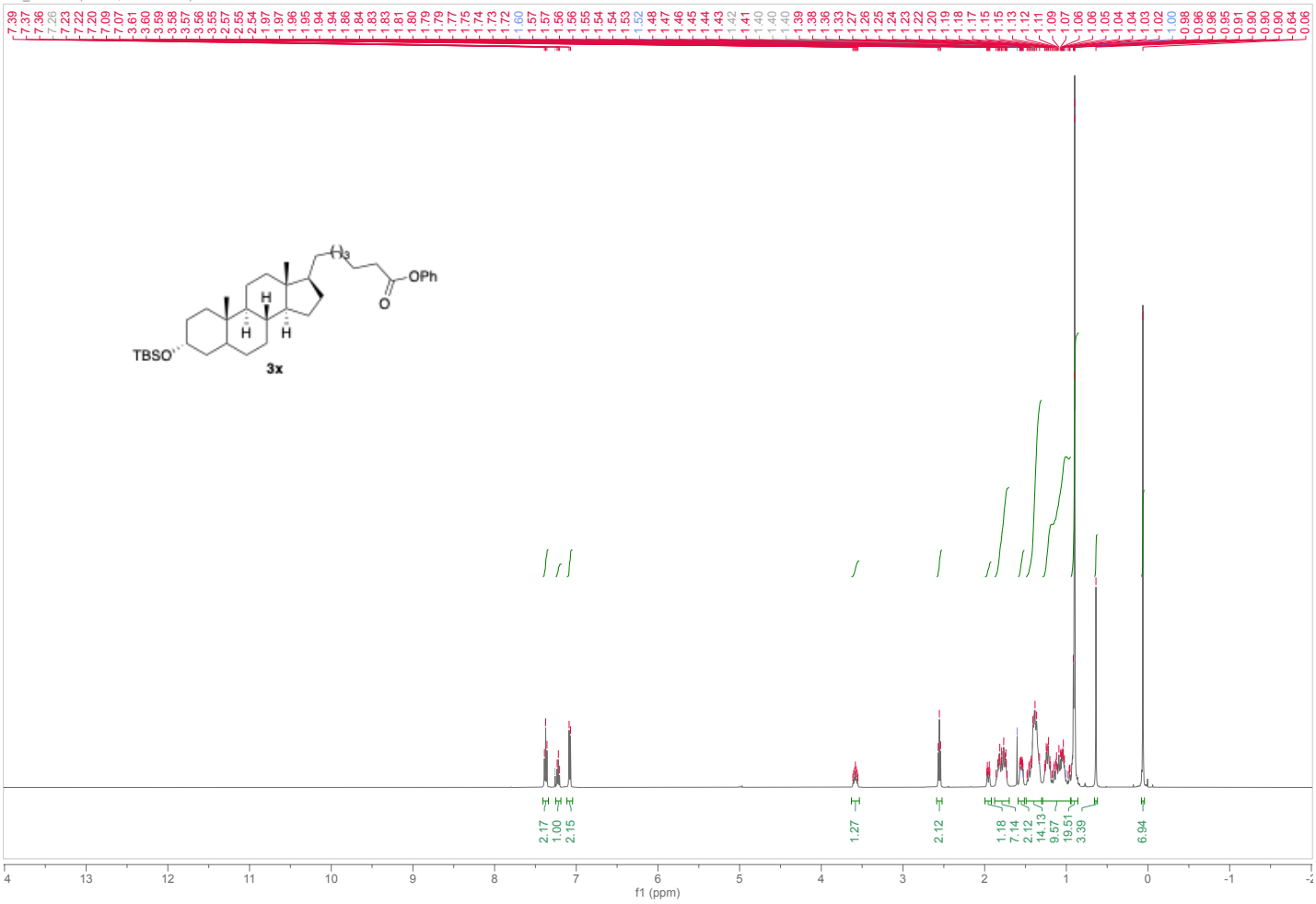


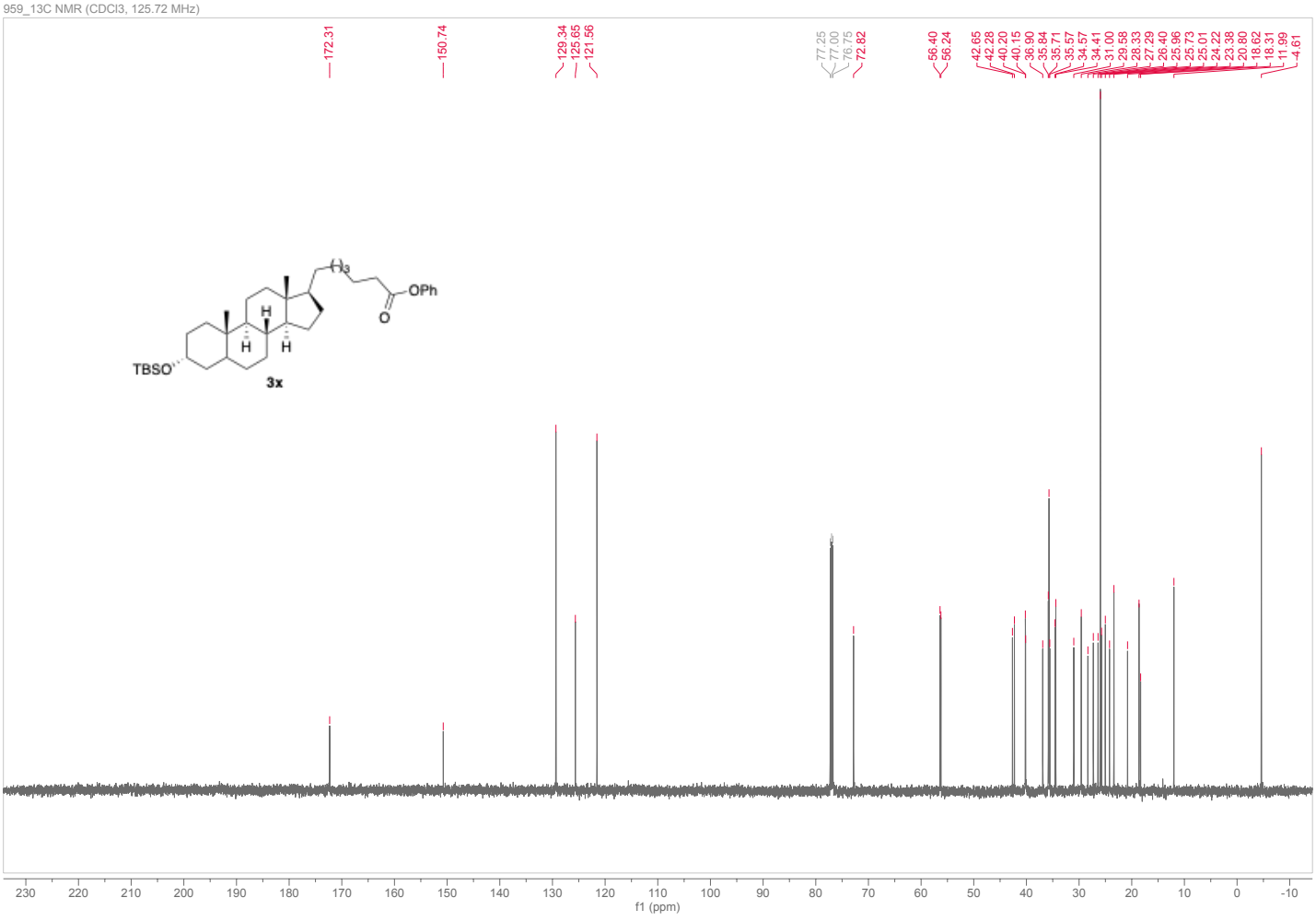
995_13C NMR (CDCl3, 125.72 MHz at 60.0 °C)



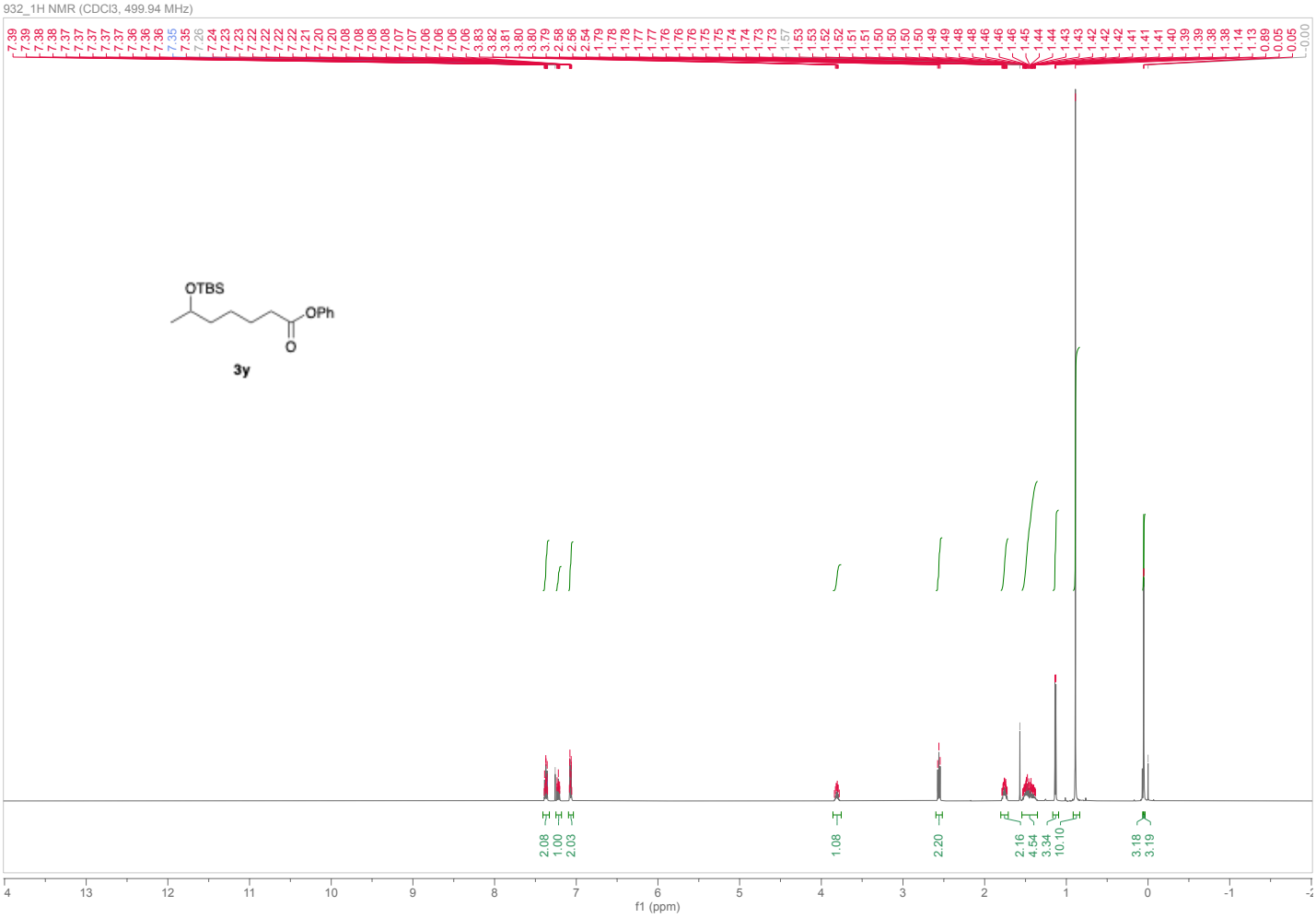
959_1H NMR (CDCl3, 499.94 MHz)



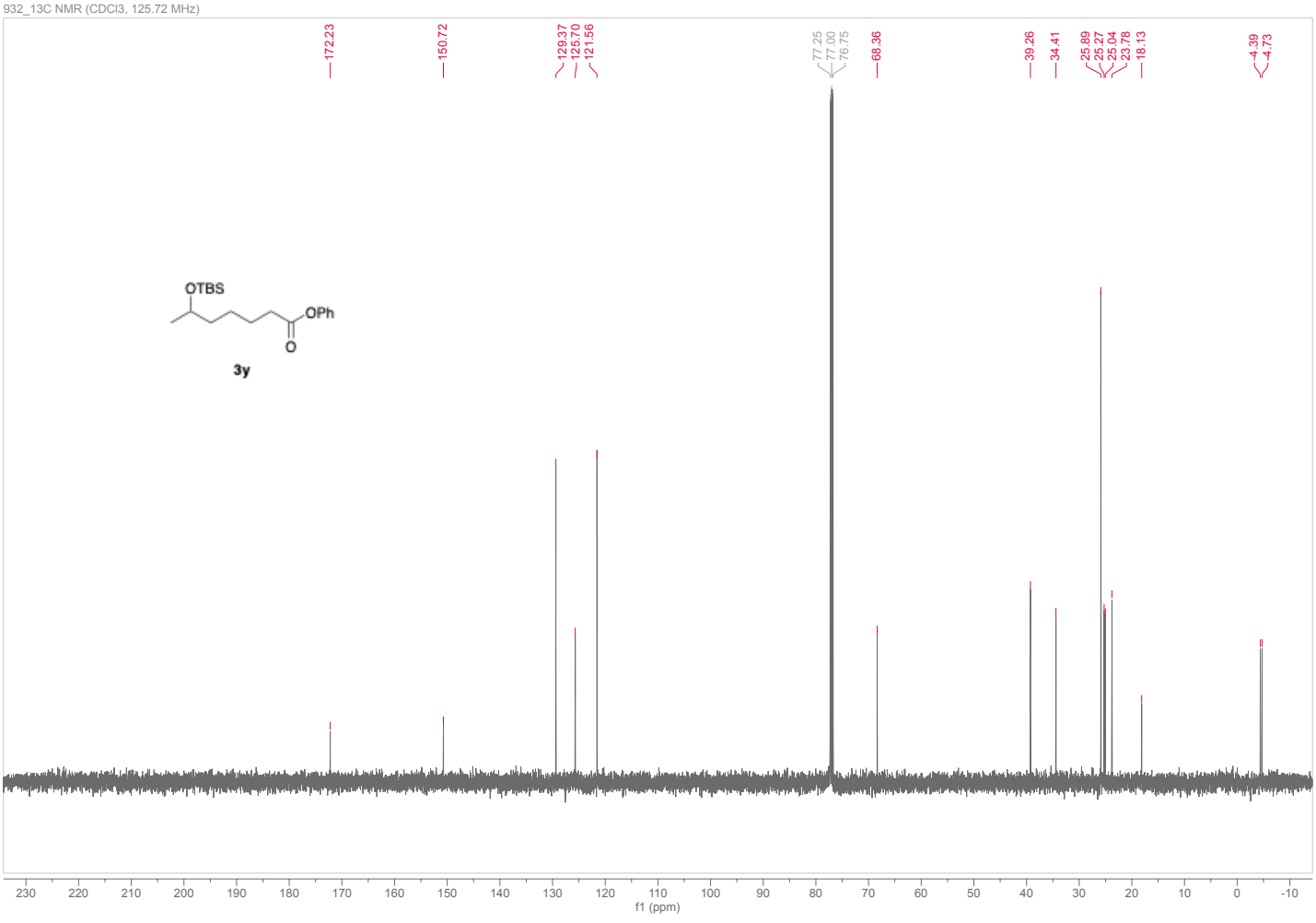
959_13C NMR (CDCl3, 125.72 MHz)



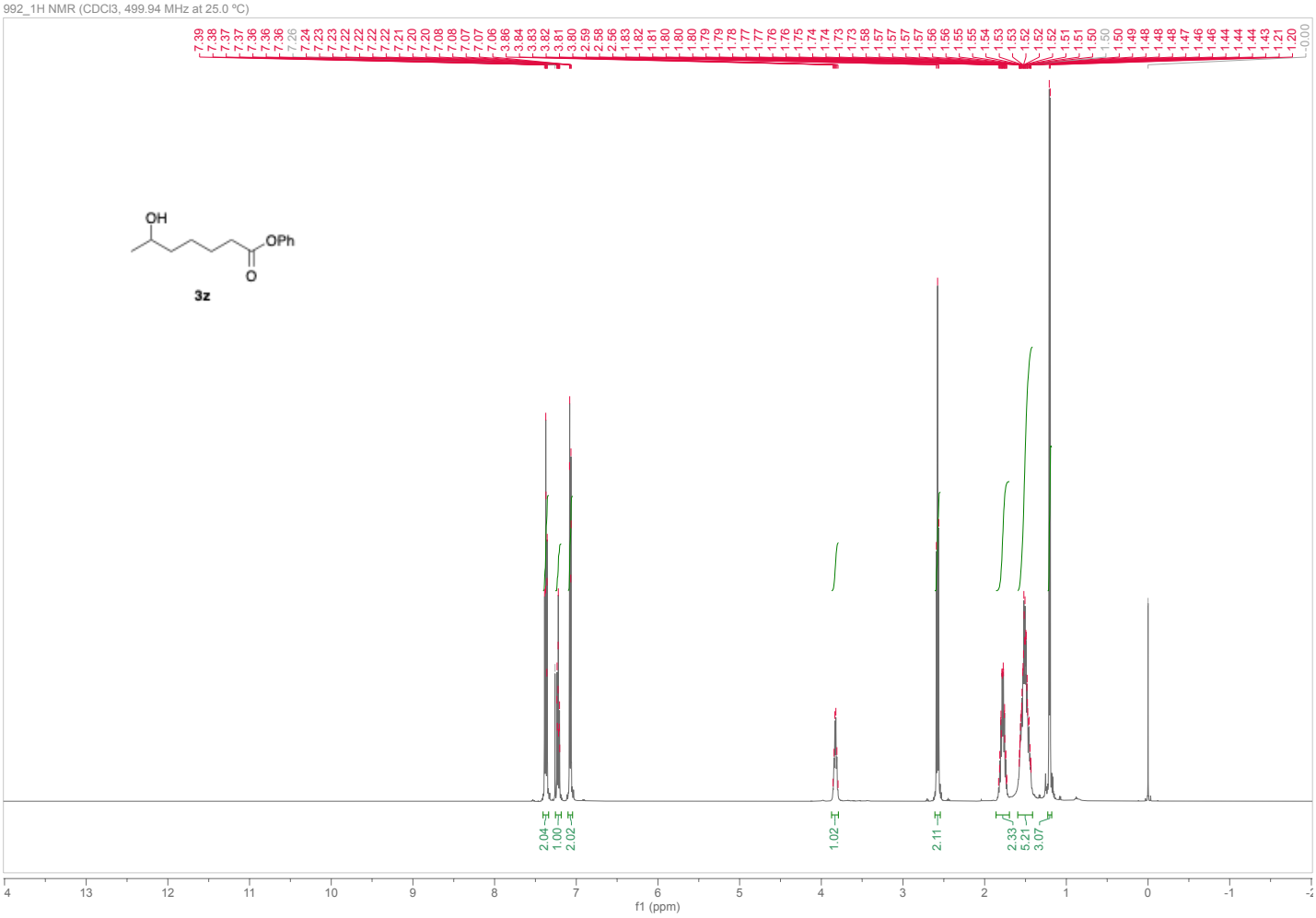
932_1H NMR (CDCl3, 499.94 MHz)



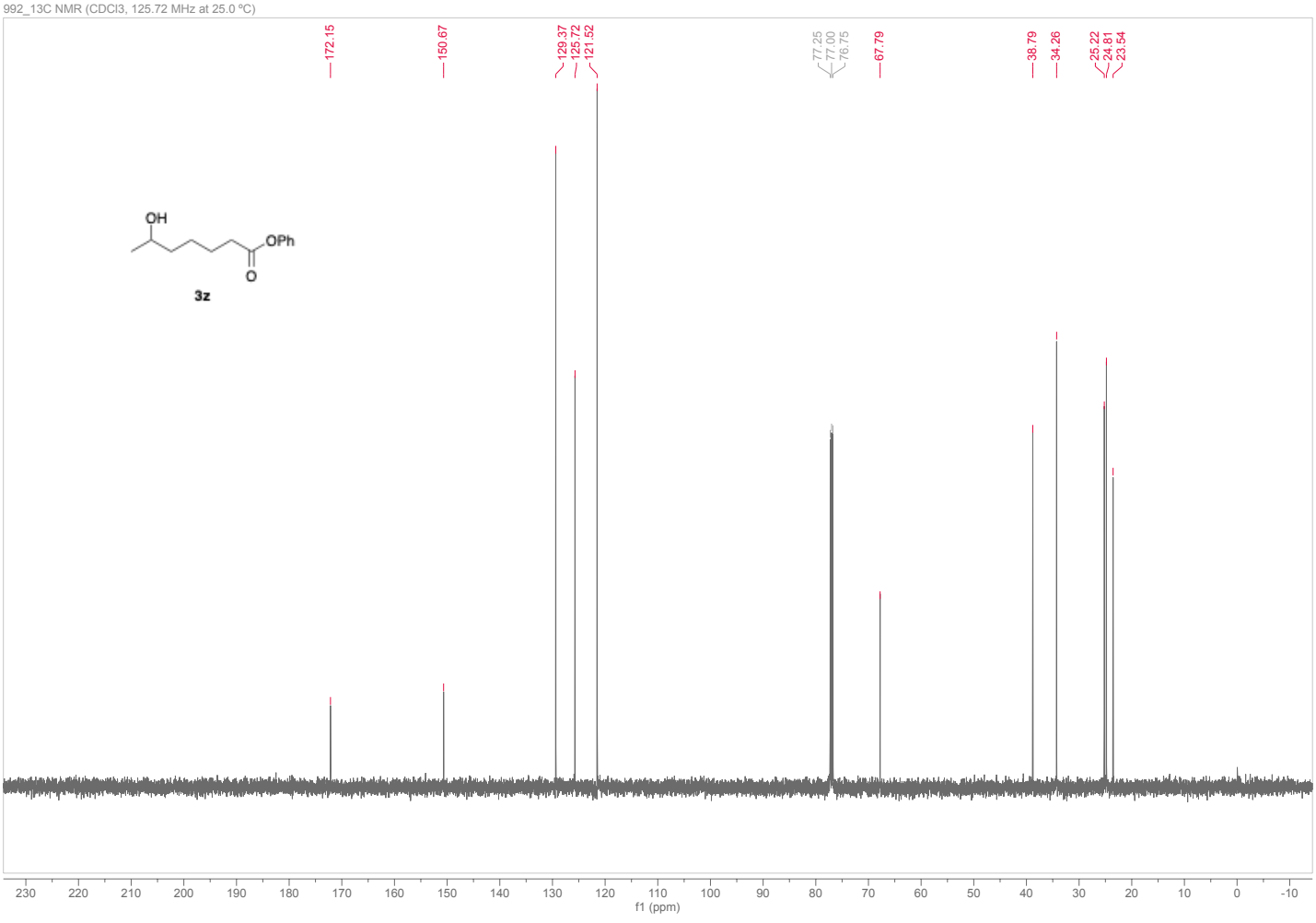
932_13C NMR (CDCl3, 125.72 MHz)



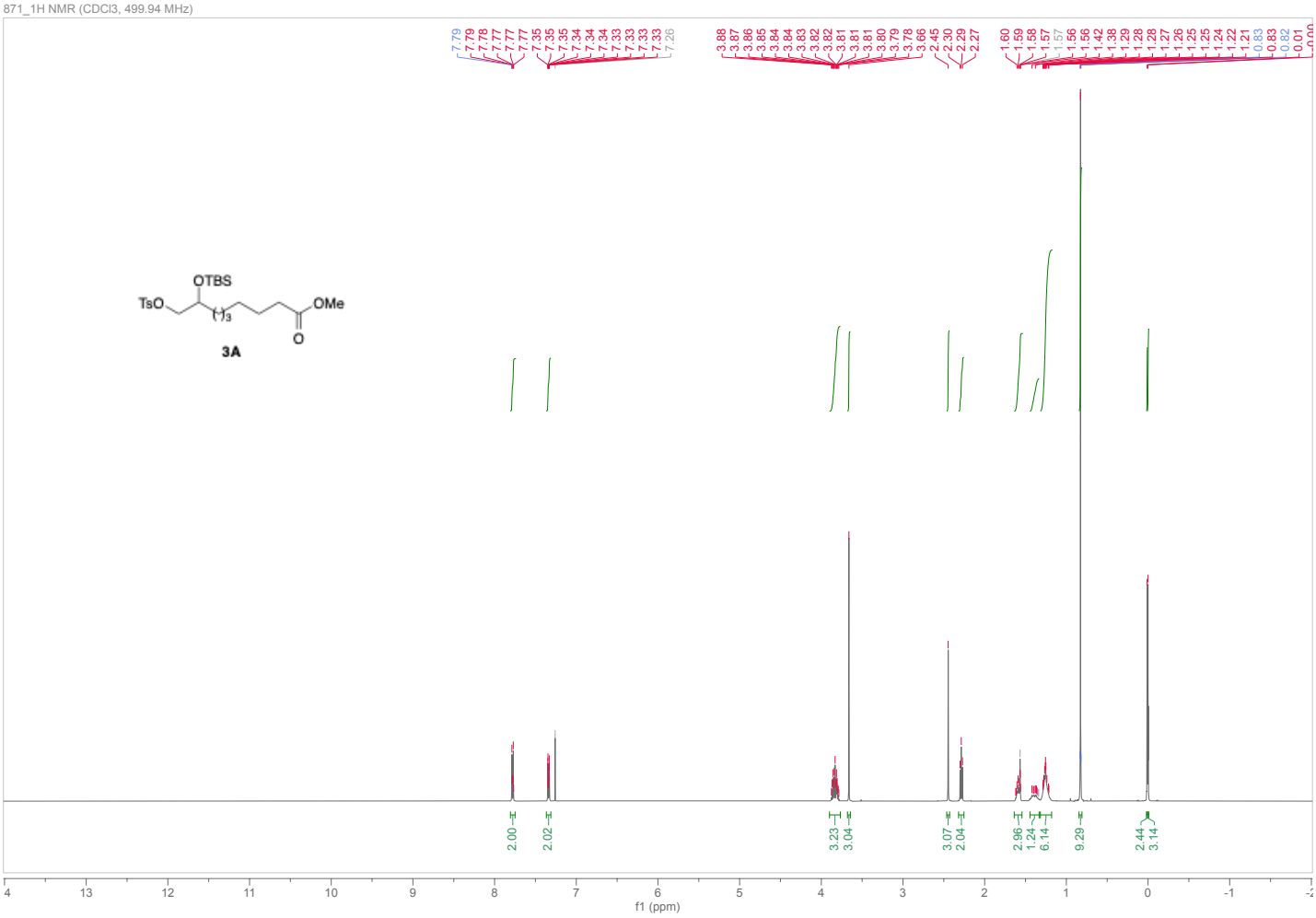
992_1H NMR (CDCl3, 499.94 MHz at 25.0 °C)



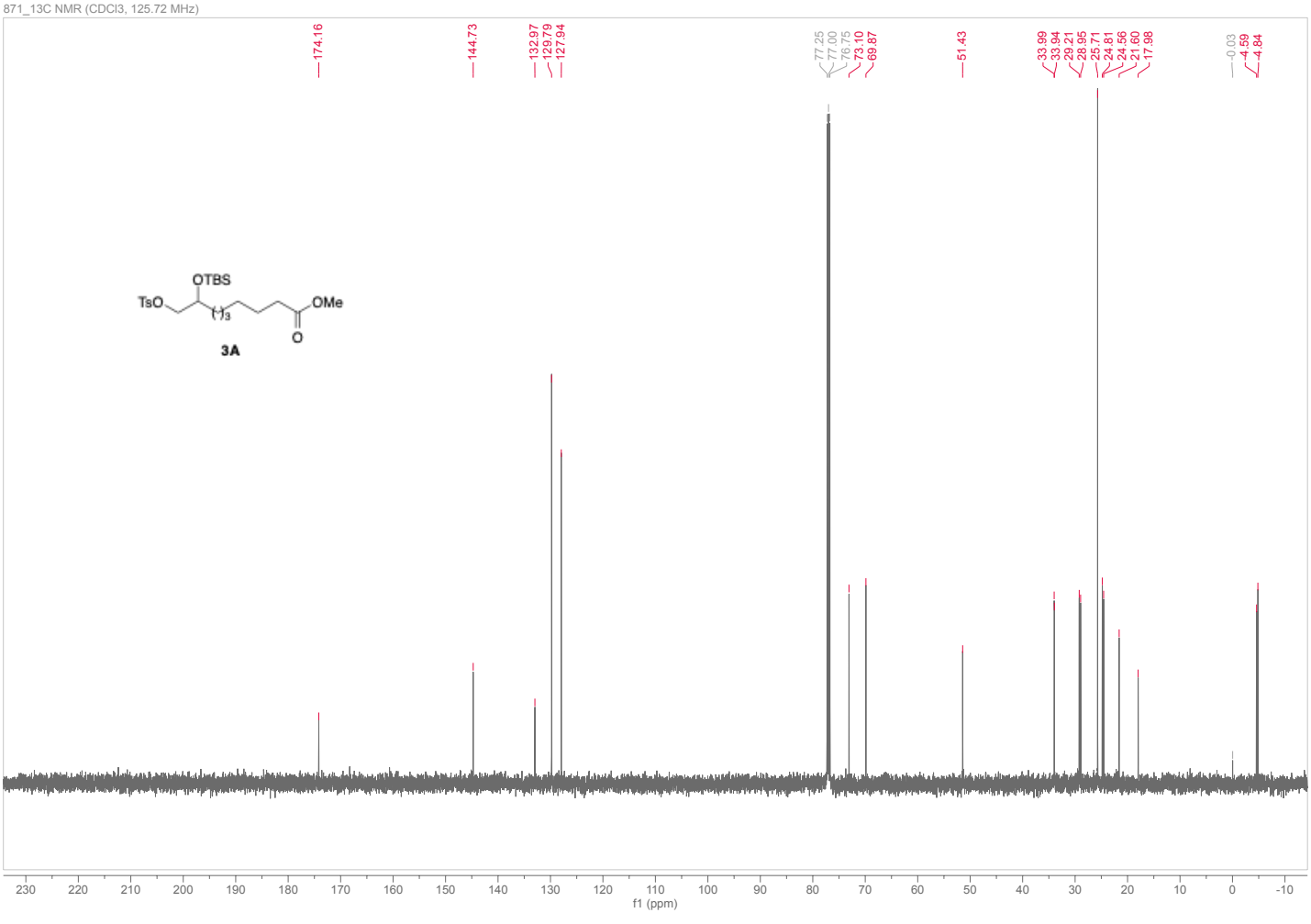
992_13C NMR (CDCl3, 125.72 MHz at 25.0 °C)



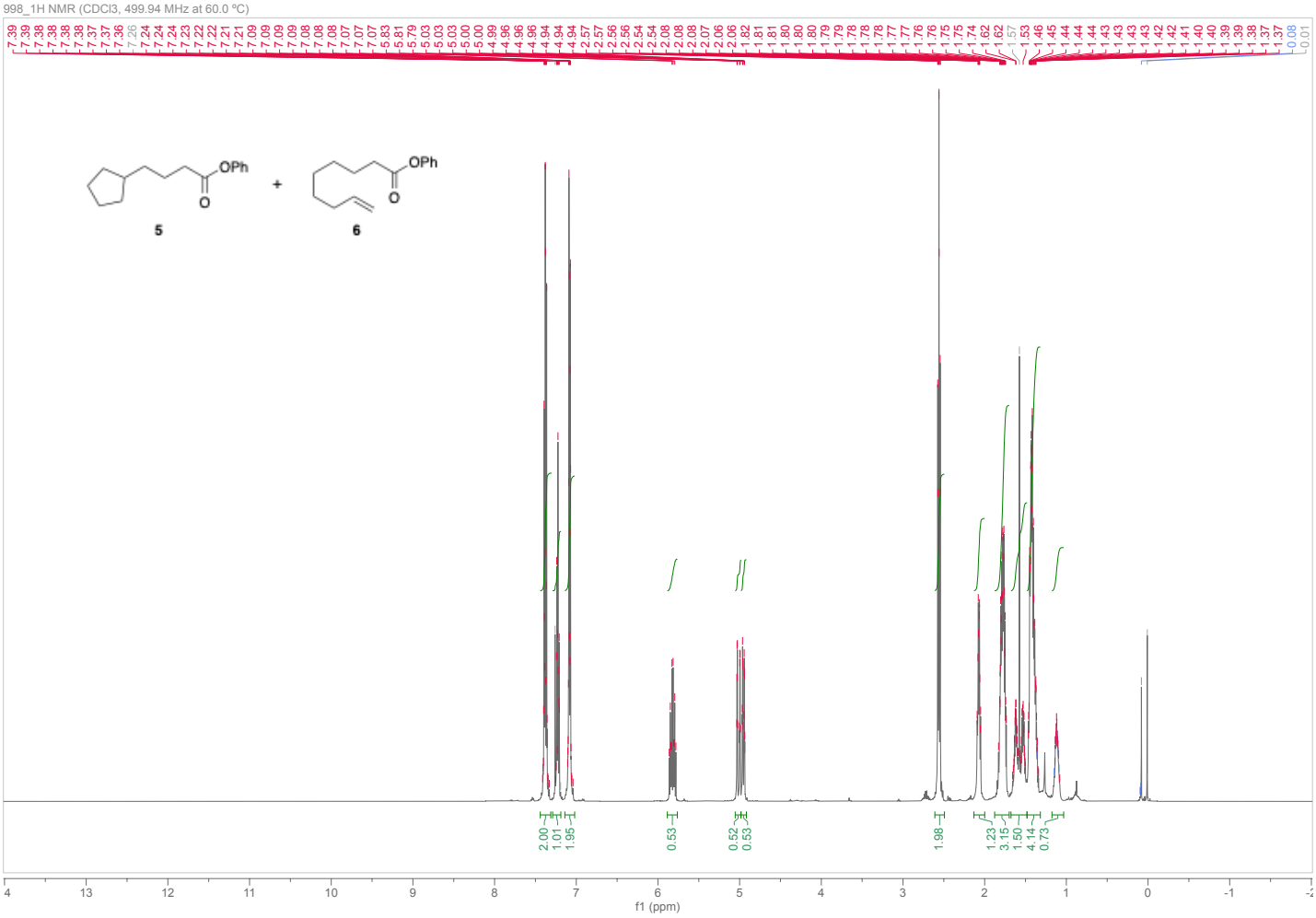
871_1H NMR (CDCl3, 499.94 MHz)



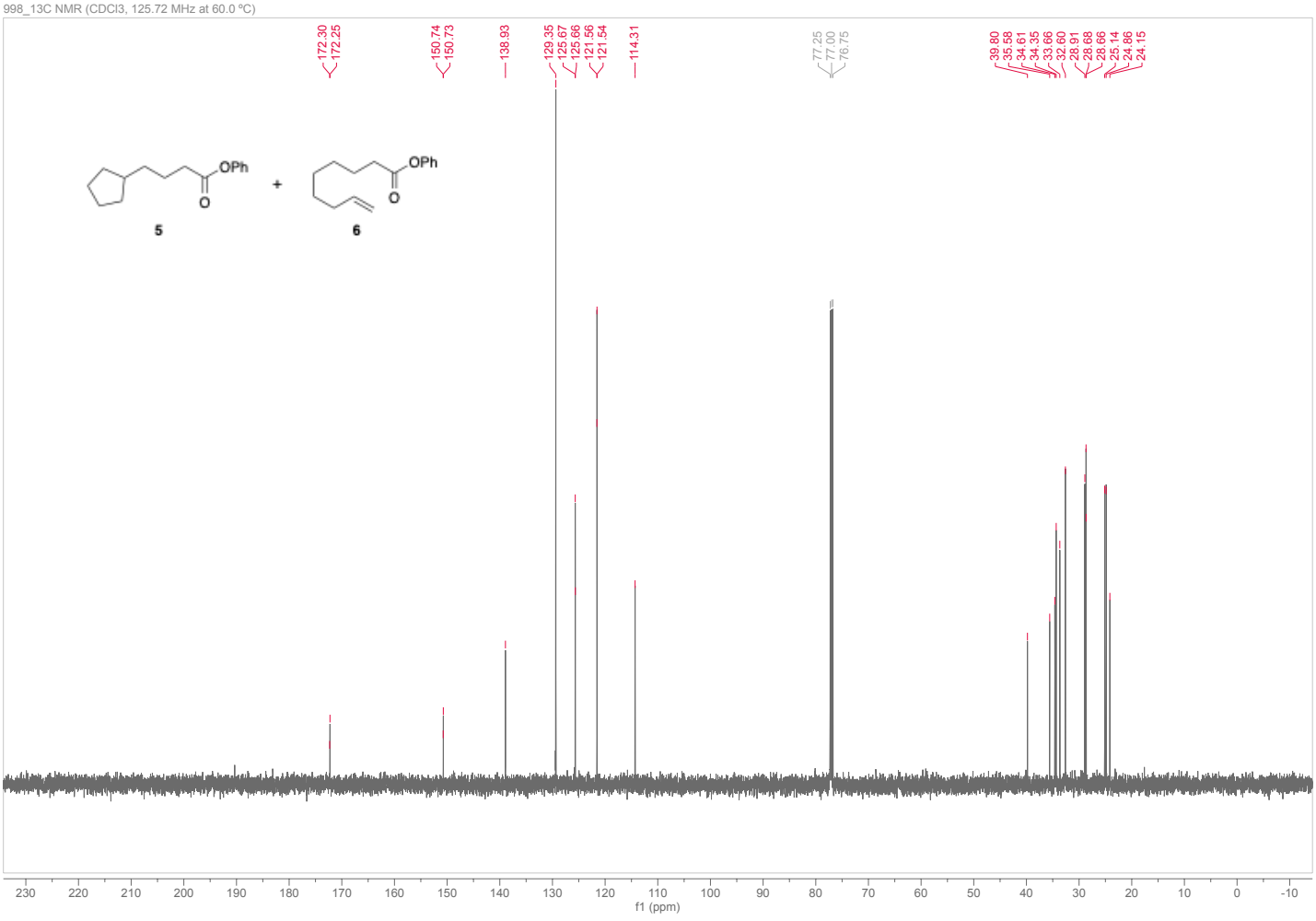
871_13C NMR (CDCl3, 125.72 MHz)



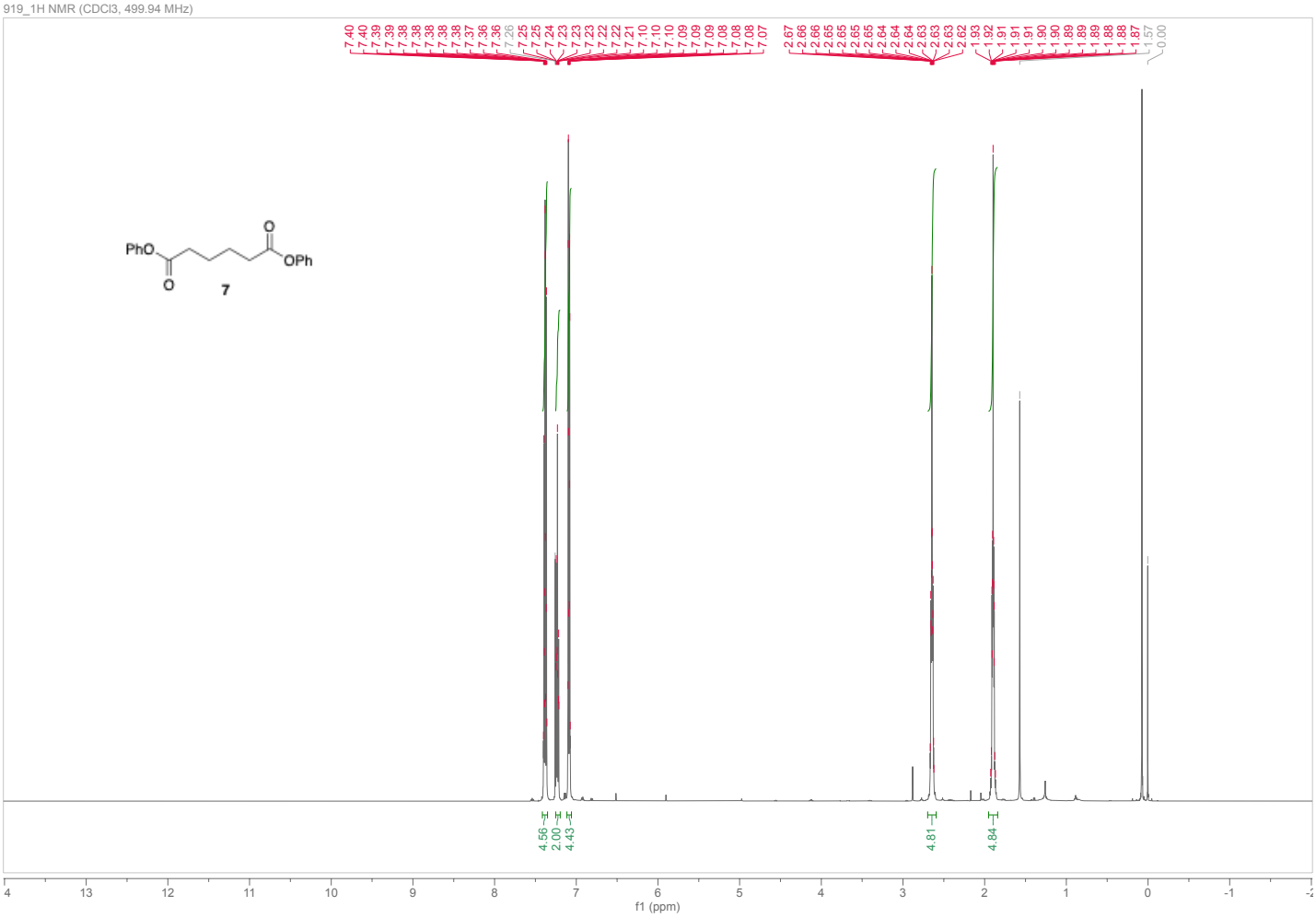
998_1H NMR (CDCl3, 499.94 MHz at 60.0 °C)



998_13C NMR (CDCl3, 125.72 MHz at 60.0 °C)



919_1H NMR (CDCl3, 499.94 MHz)



919_13C NMR (CDCl3, 125.72 MHz)