

*Electronic Supplementary Information for*

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

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*1-4-1 Kagamiyama, Higashi-Hiroshima City, Hiroshima 739-8527, Japan*

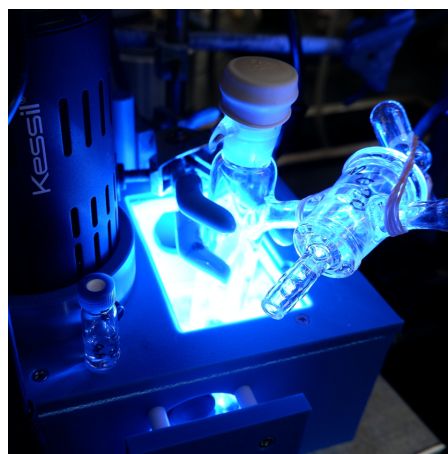
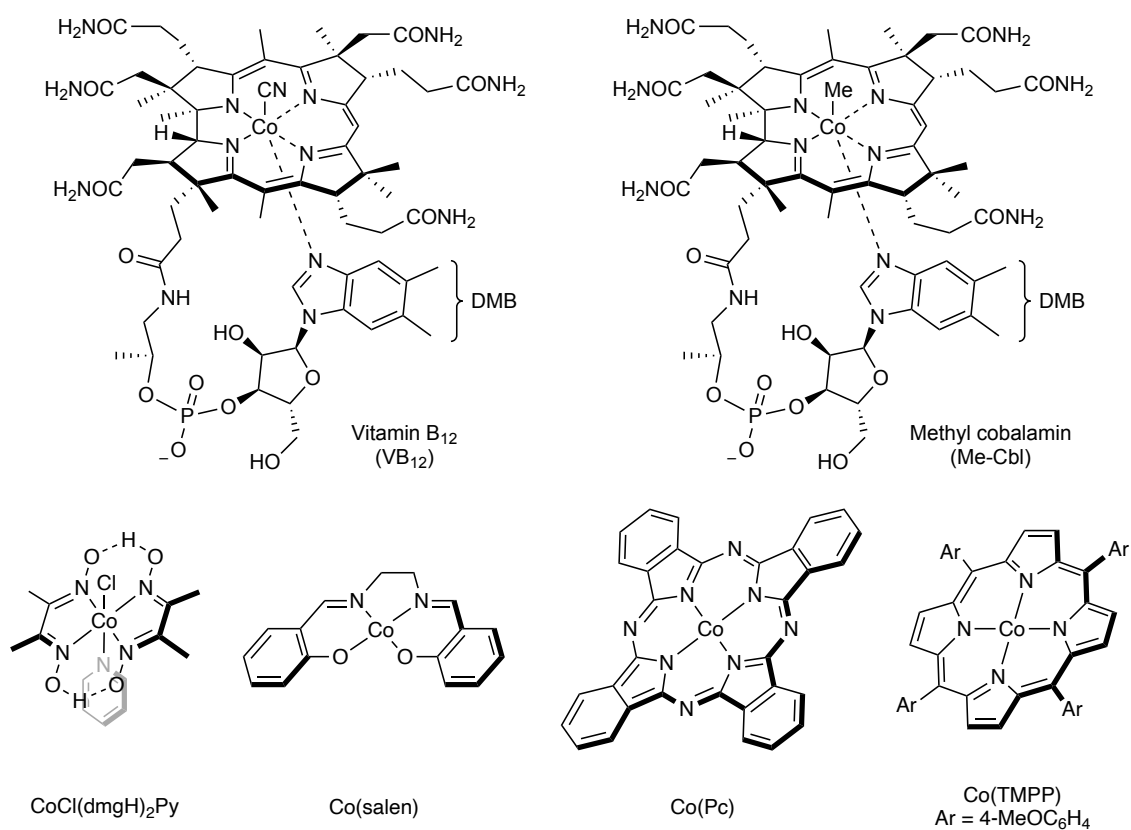
*Email: [kkome@hiroshima-u.ac.jp](mailto:kkome@hiroshima-u.ac.jp)*

**1. General information**

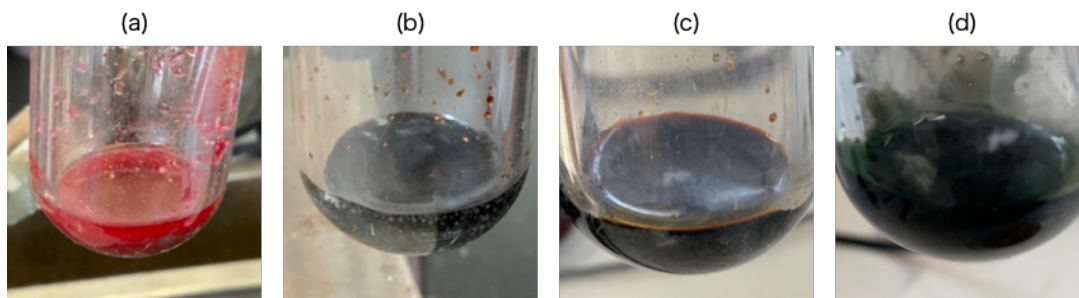
All reactions were performed on oven-and flame-dried glassware under argon using standard Schlenk techniques. Flash-column chromatography was performed with silica-gel 60 (KANTO Chemical Co. Inc., 40–50 nm). TLC monitoring was carried out with silica-gel aluminum sheets (Merck, type 60 F<sub>254</sub>). Gas chromatography (GC) monitoring was carried out on Shimadzu GC-2014. Nuclear magnetic resonance (NMR) spectra were recorded with Varian-400 (<sup>1</sup>H NMR: 400 MHz; <sup>13</sup>C NMR: 101 MHz) spectrometer or Varian-500 (<sup>1</sup>H NMR: 500 MHz; <sup>13</sup>C NMR: 126 MHz) spectrometers calibrated from residual deuterated chloroform as an internal standard at 7.26 ppm for <sup>1</sup>H NMR spectra and at 77.0 ppm for <sup>13</sup>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<sub>12</sub> 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)<sub>2</sub>Py was prepared according to literature.<sup>1</sup> Alkyl tosylates<sup>2,3</sup> and activated olefins<sup>4,5</sup> 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.



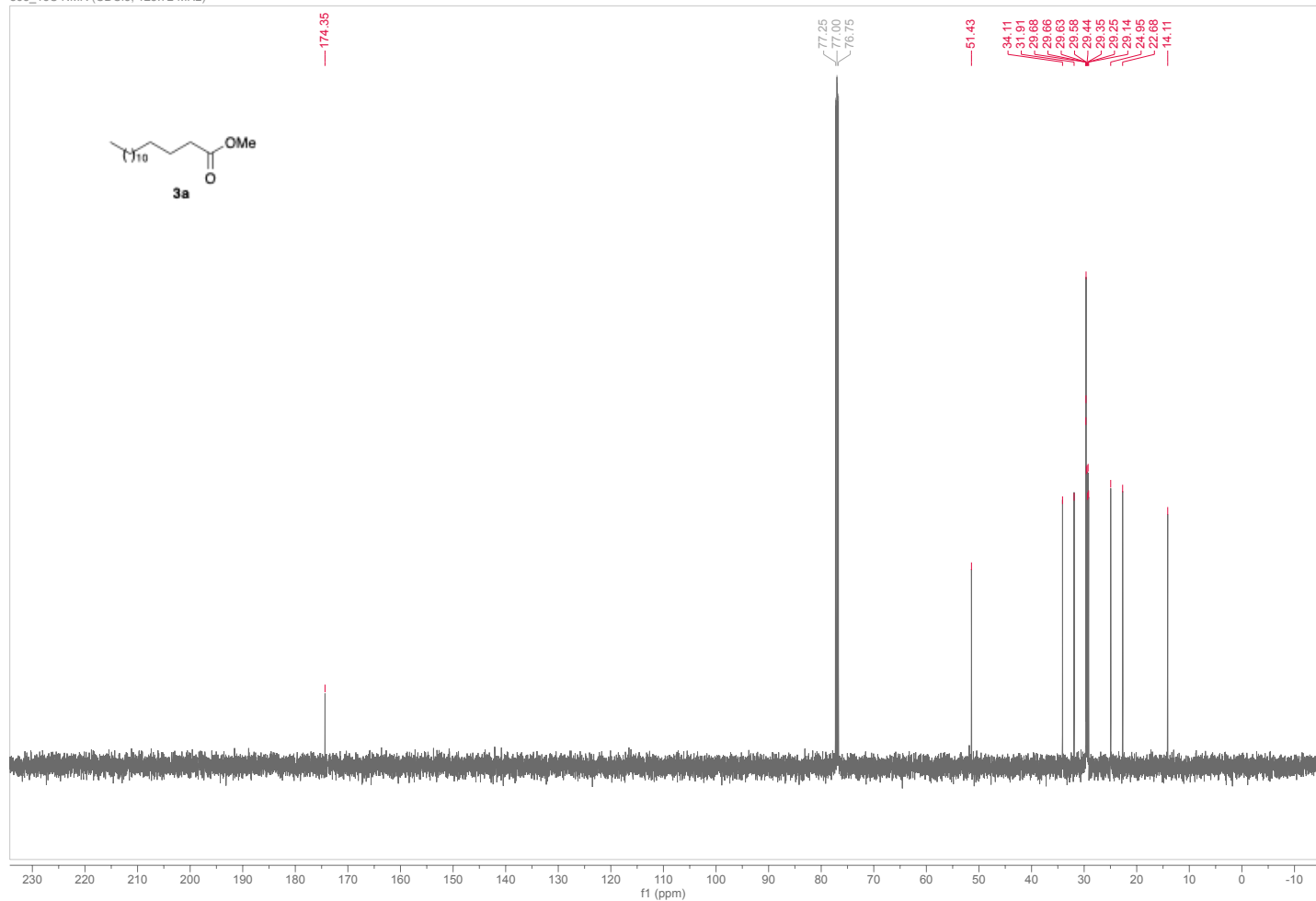
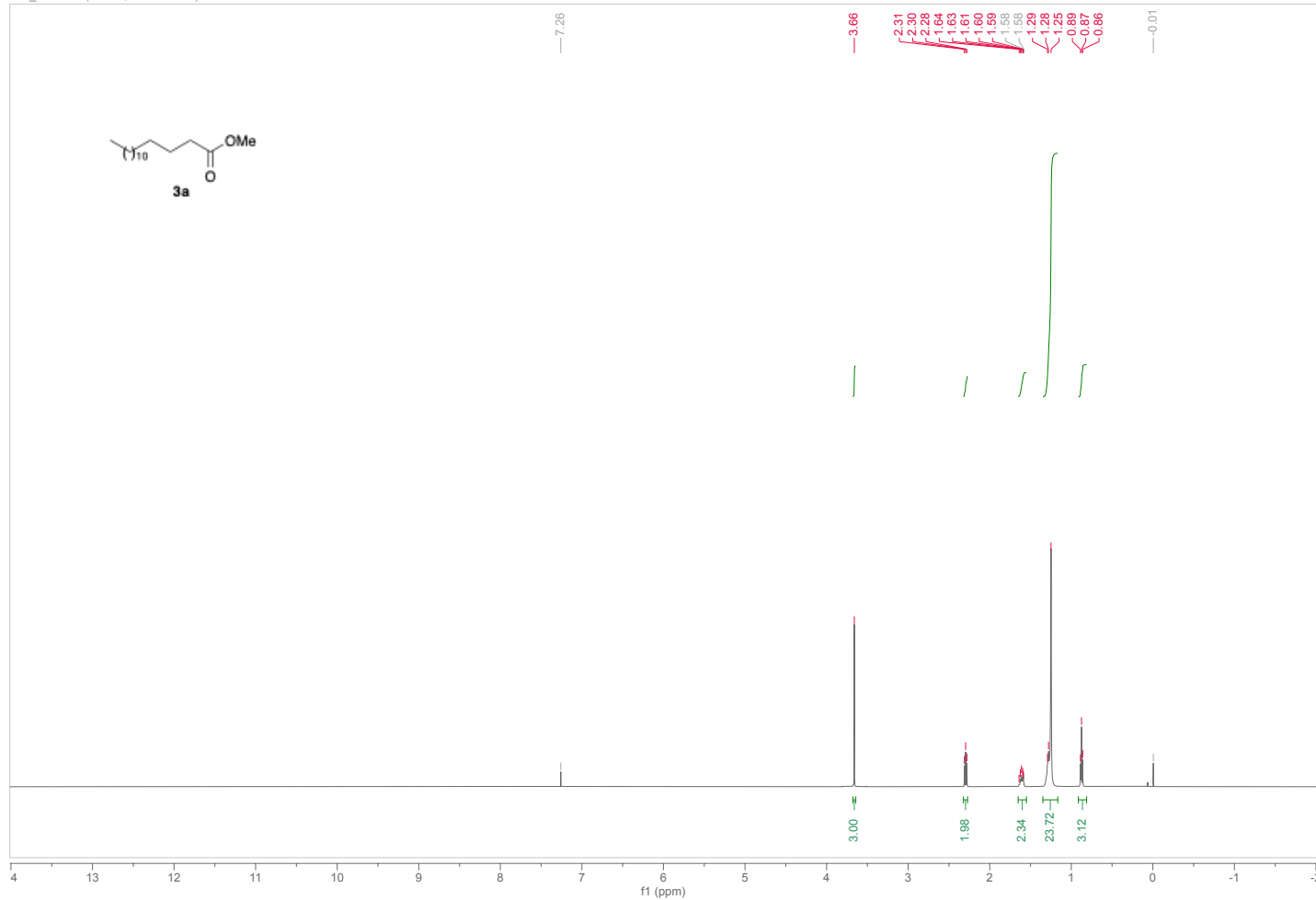
**Figure S1.** Reaction setup for the nucleophilic cobalt-catalysed Giese reaction under blue-light irradiation.



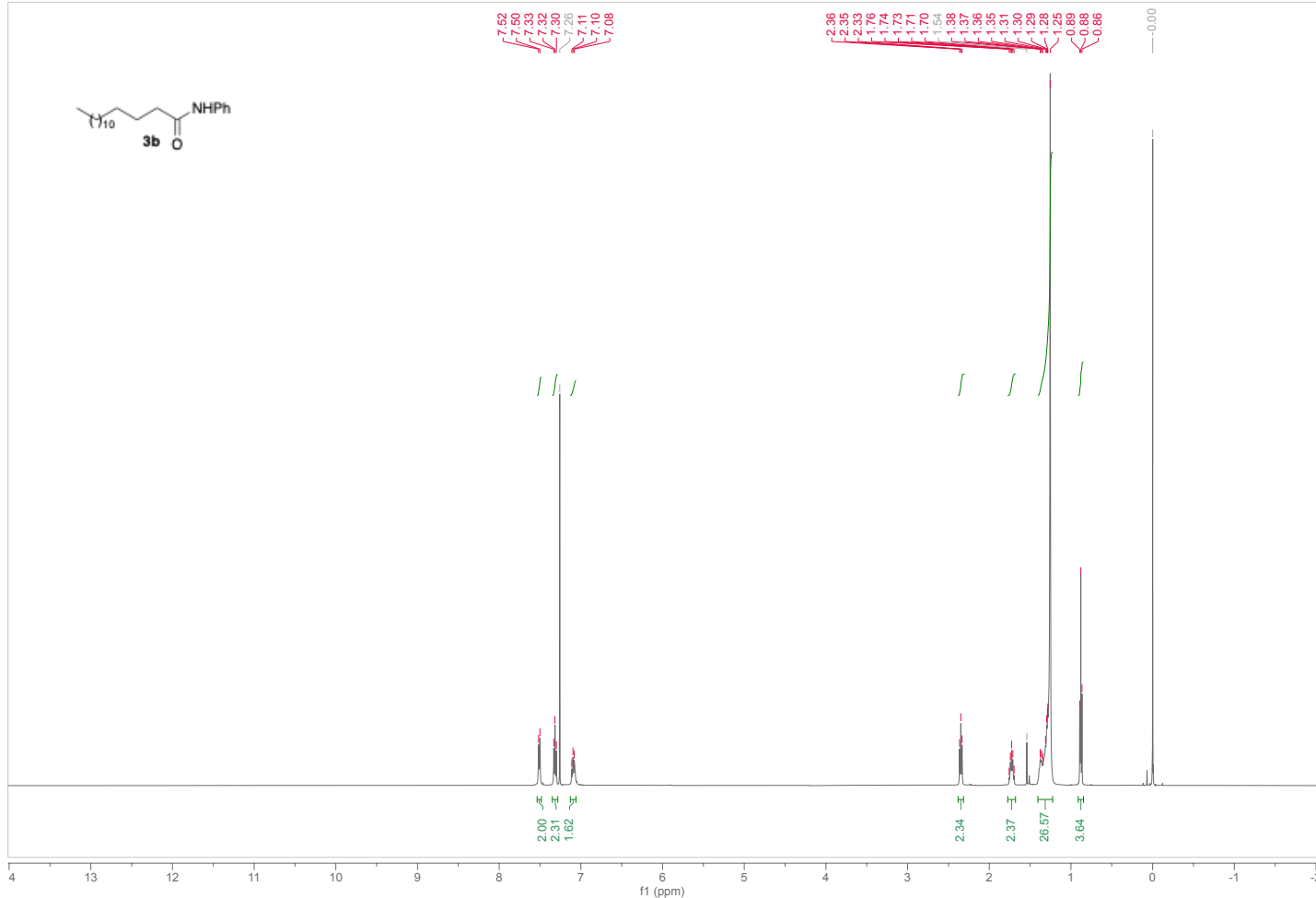
**Figure S2.** The color changes of the reaction mixture in each step: (a) Mn + Et<sub>3</sub>N·HCl + VB<sub>12</sub> + DMF; (b) Solution a + TMSCl (ca. 6 μL); (c) After stirring for 8 h with photo-irradiation; (d) After stirring for 16 h with photo-irradiation.

## References

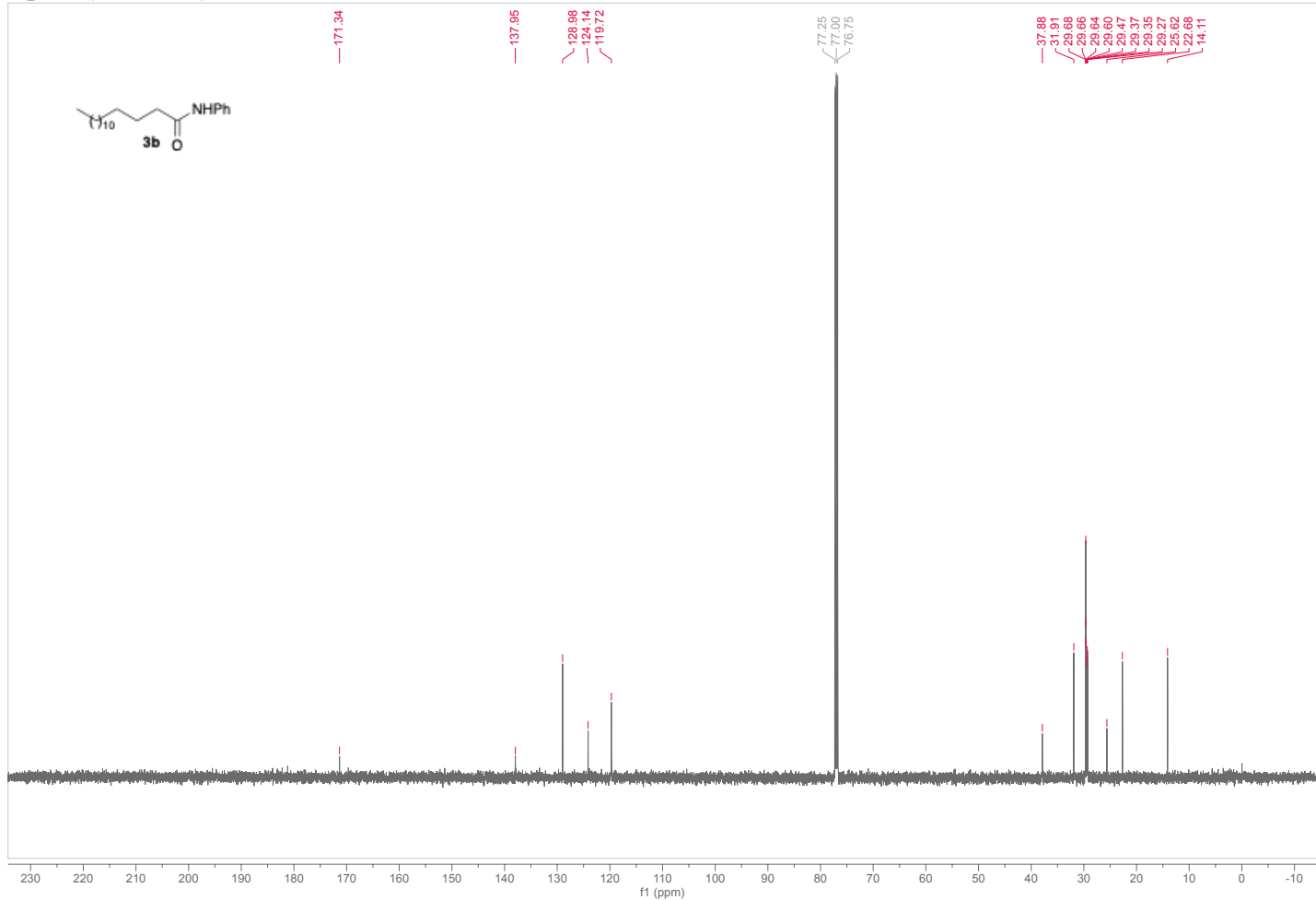
- 1 A. Panagiotopoulos, K. Ladomenou, D. Sun, V. Artero and A. G. Coutsolelos, *Dalton Trans.*, 2016, **45**, 6732–6738.
- 2 T. Michiyuki, I. Osaka and K. Komeyama, *Chem. Commun.*, 2020, **56**, 1247–1250.
- 3 K. Tani and B. M. Stoltz, *Nature*, 2006, **441**, 731–734.
- 4 S. Eggers, T. Eckert and V. 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.



875\_1H NMR (CDCl<sub>3</sub>, 499.94 MHz)



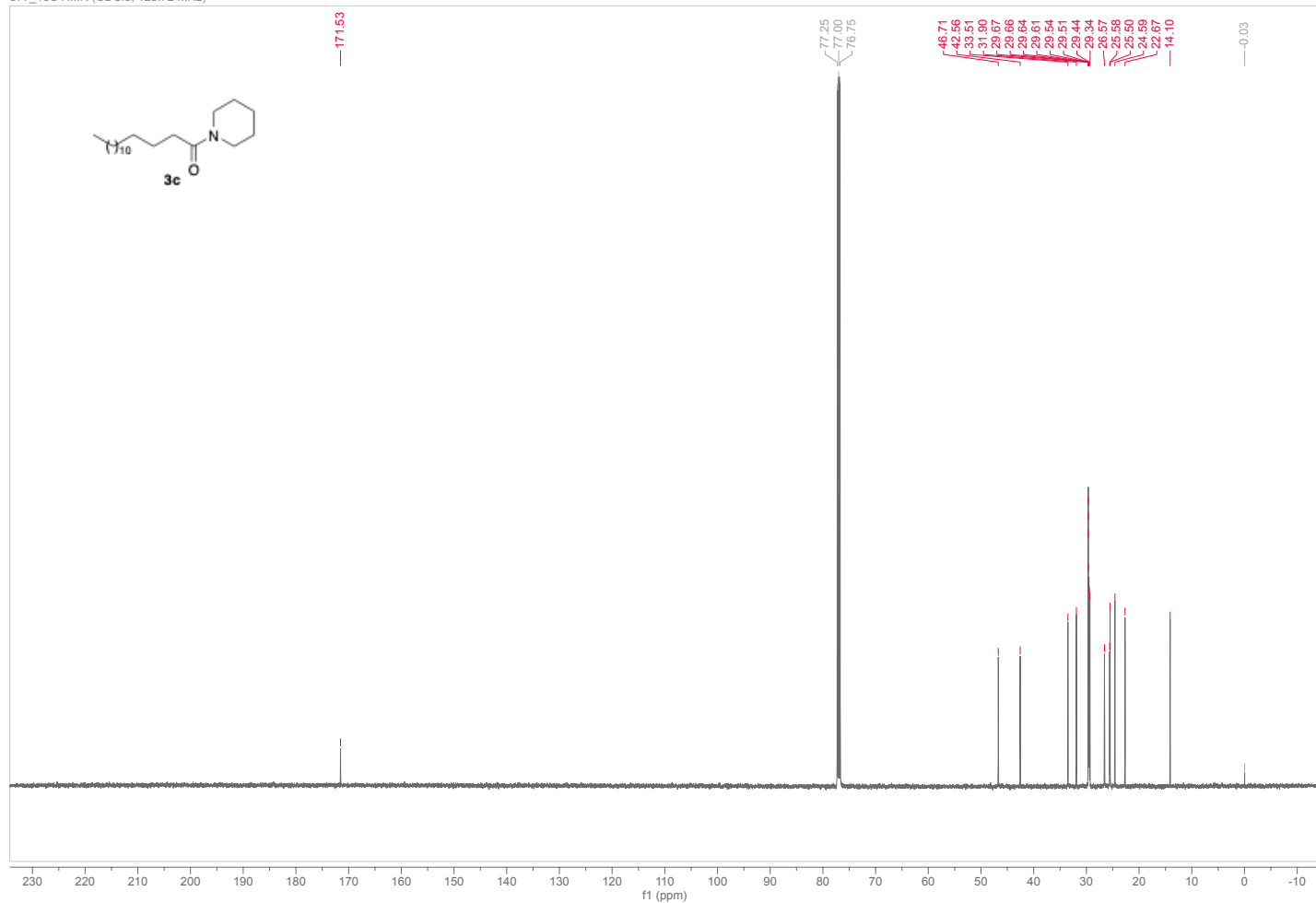
875\_13C NMR (CDCl<sub>3</sub>, 125.72 MHz)



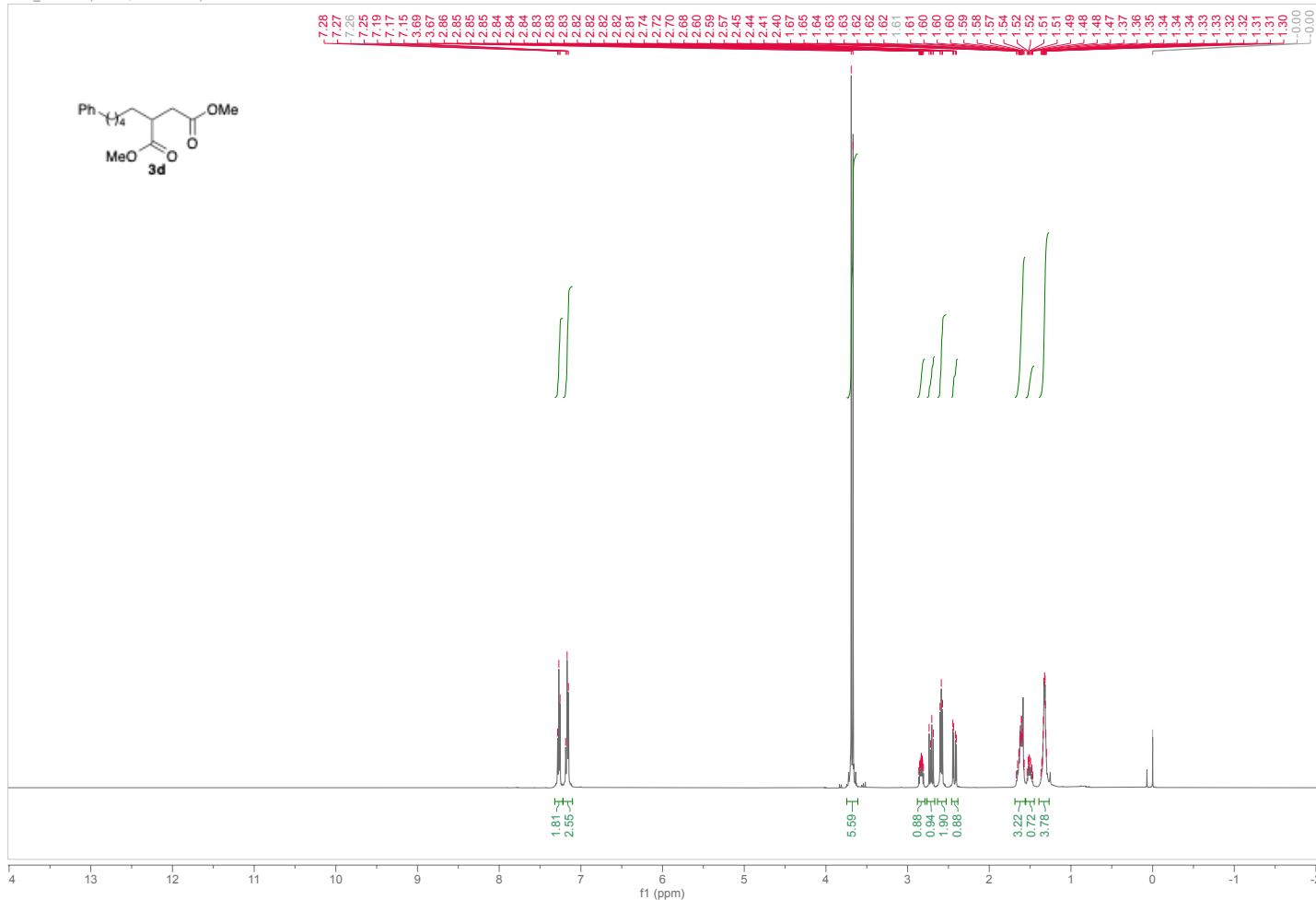
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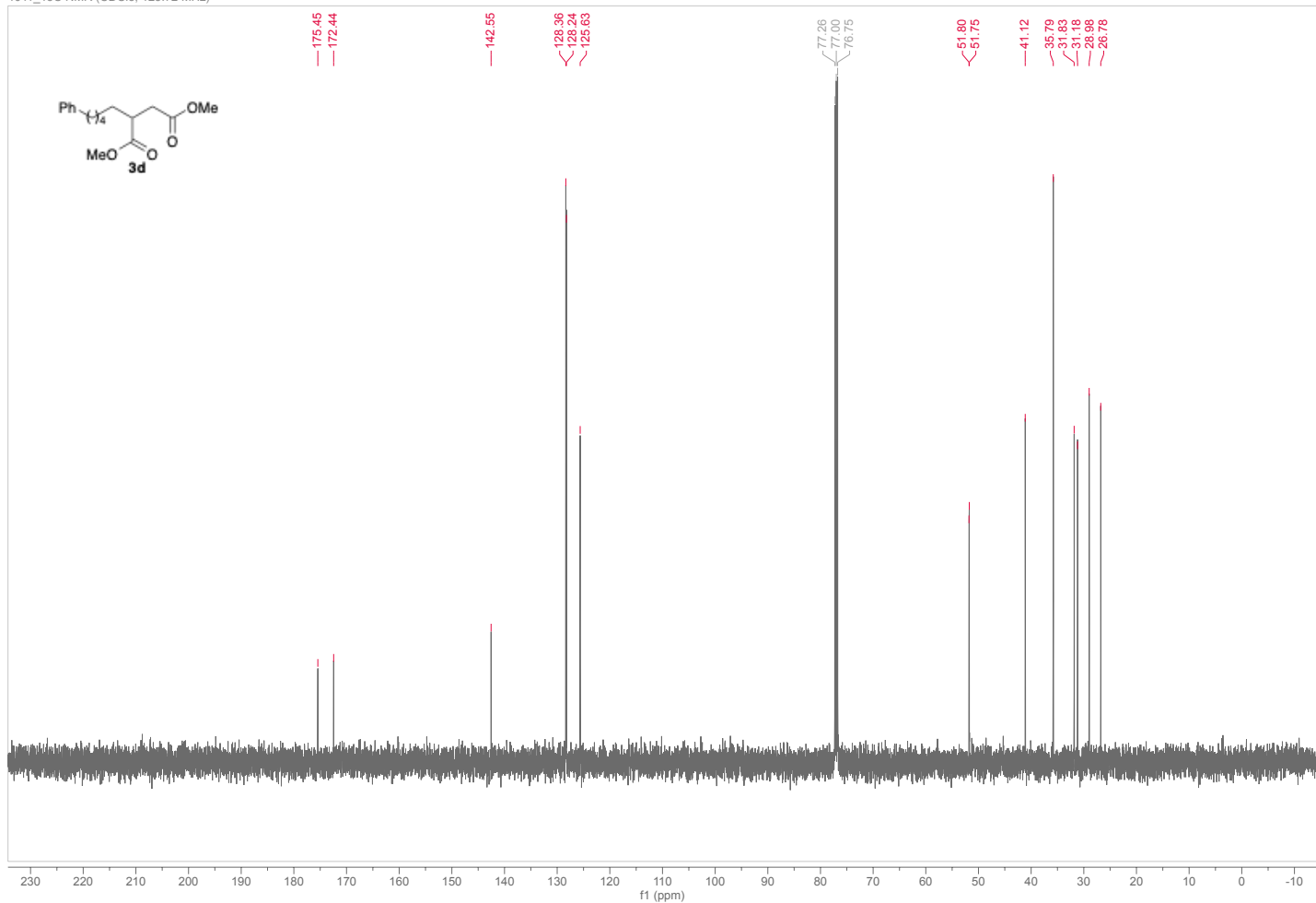
877\_13C NMR (CDCl<sub>3</sub>, 125.72 MHz)



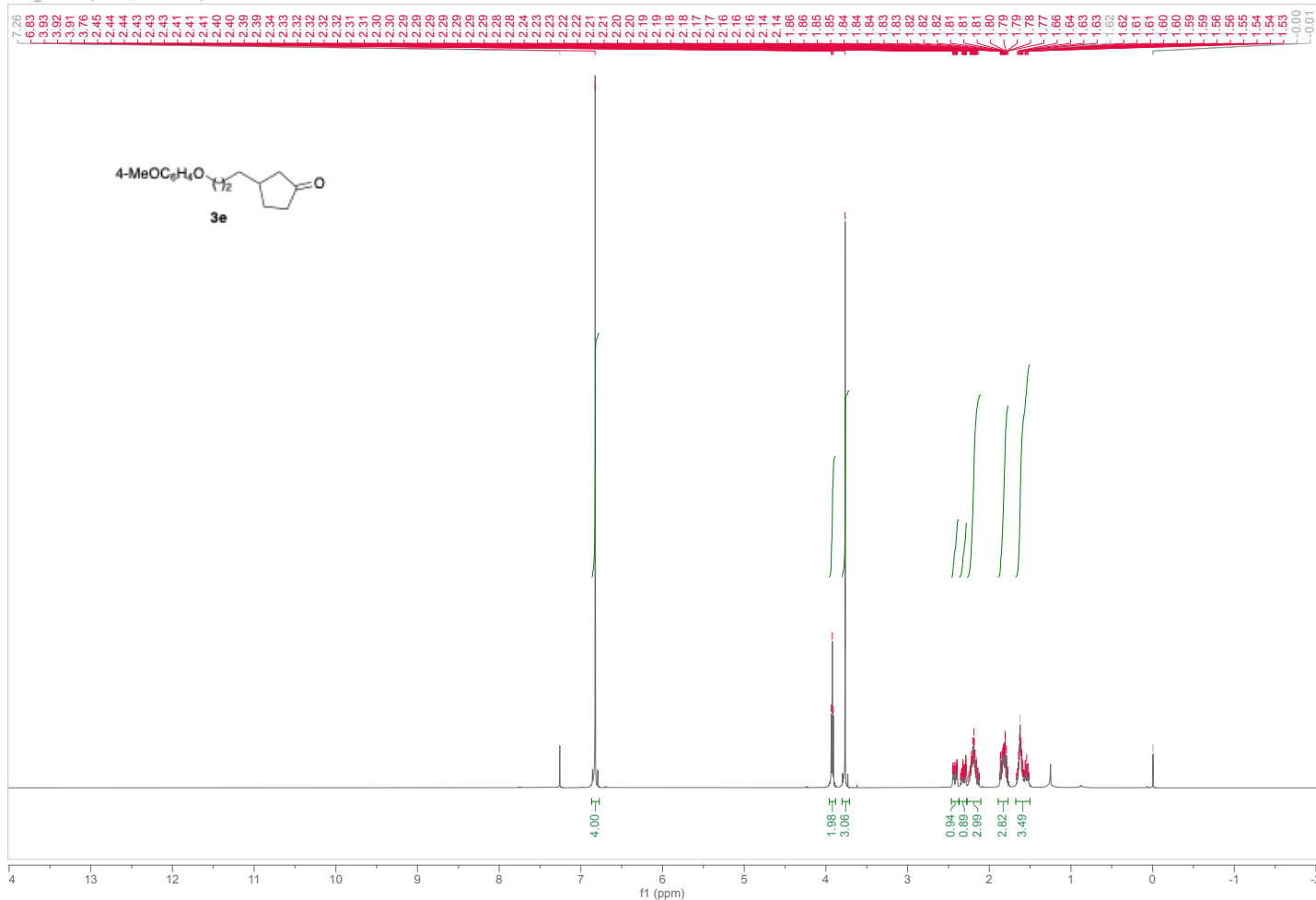
1011\_1H NMR (CDCl<sub>3</sub>, 499.94 MHz)



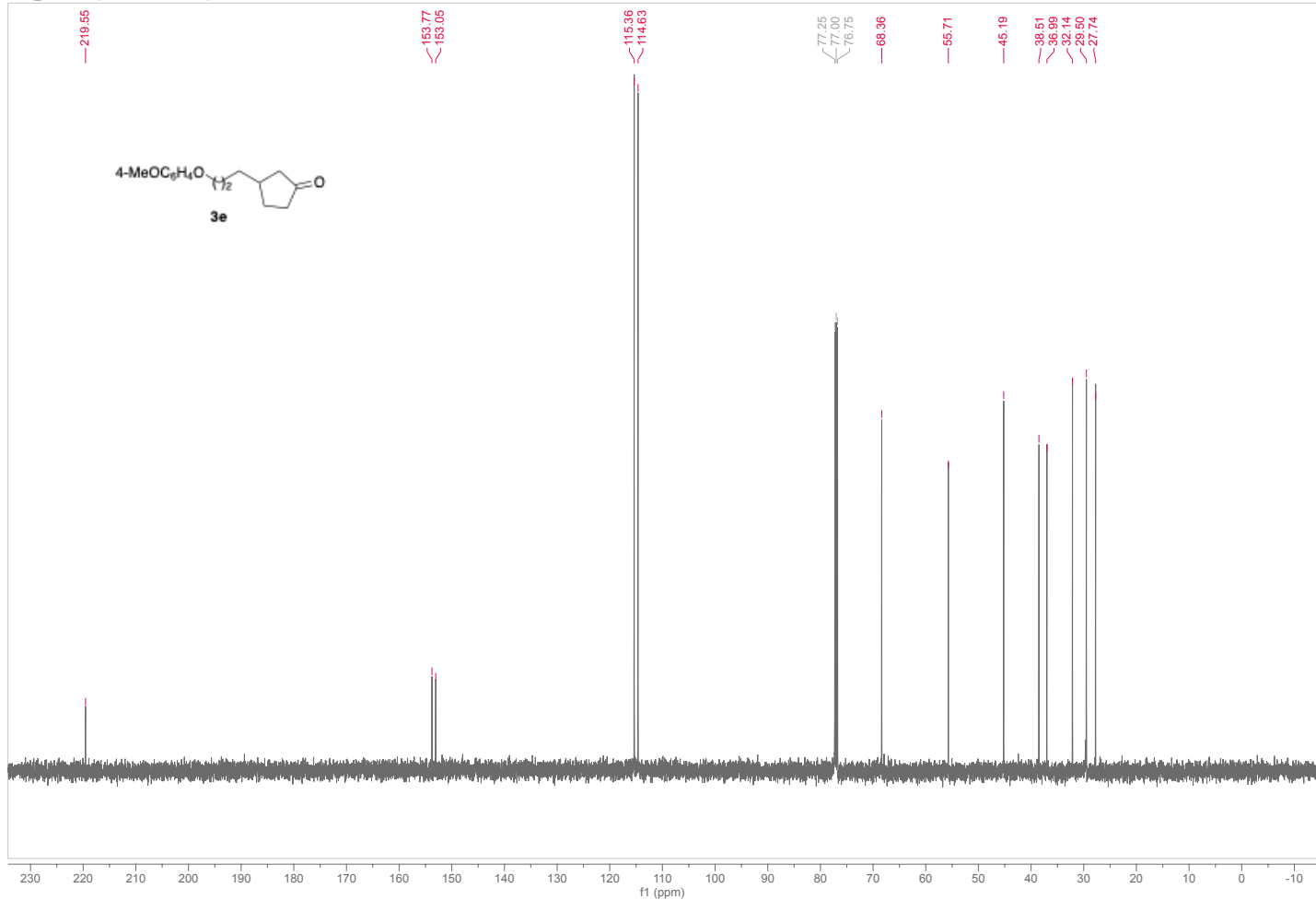
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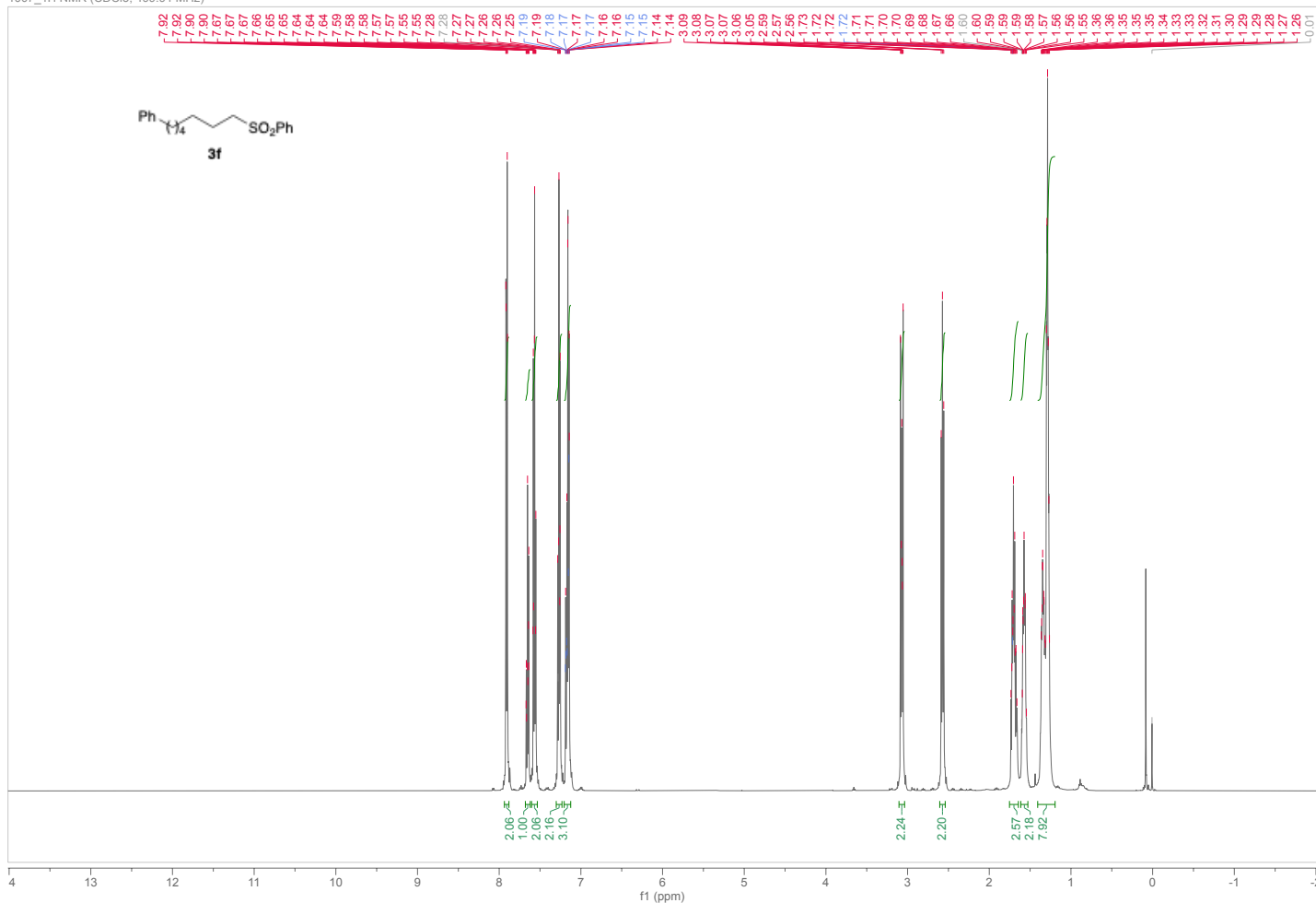
1018\_1H NMR (CDCl<sub>3</sub>, 499.94 MHz)



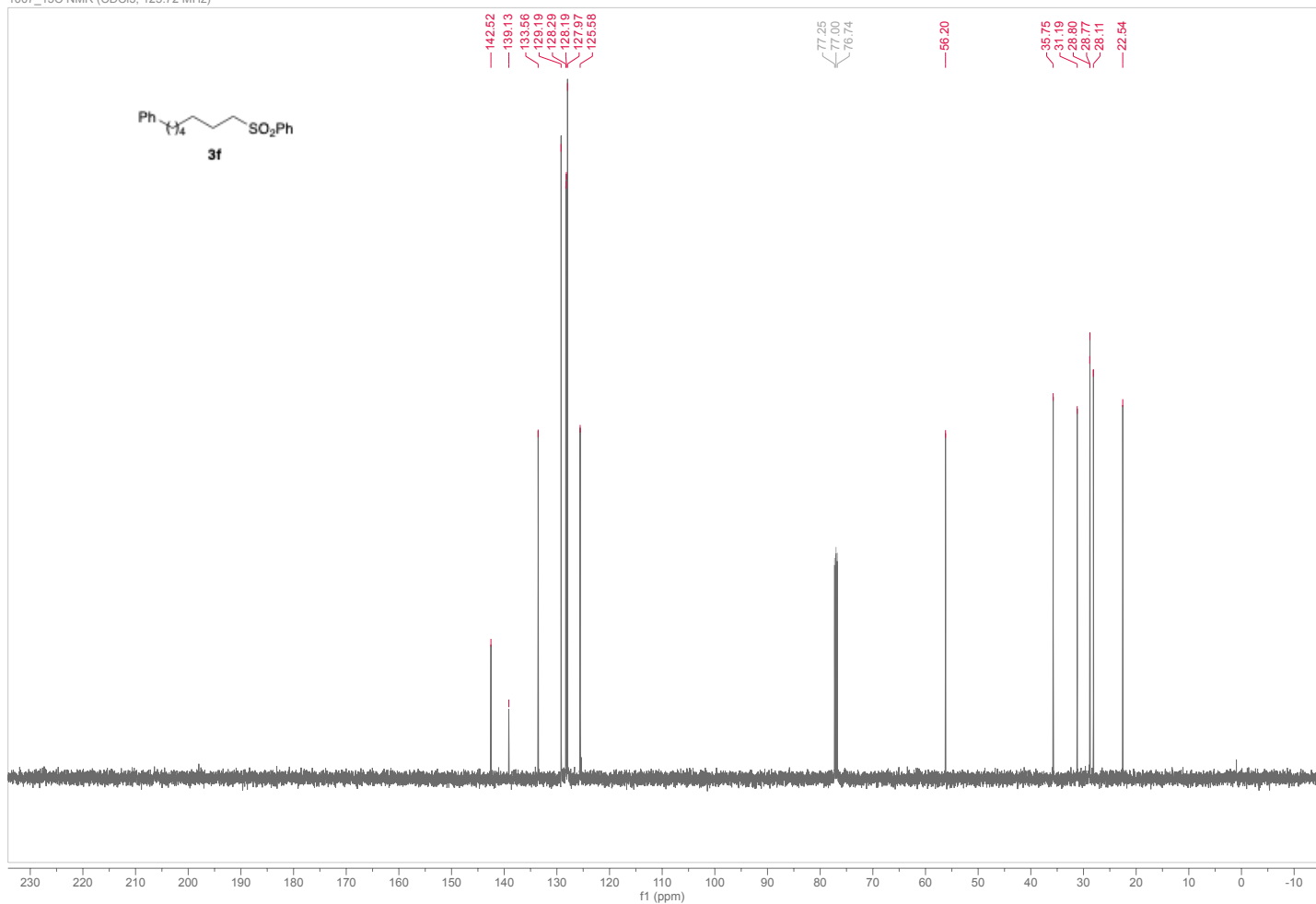
1018\_13C NMR (CDCl<sub>3</sub>, 125.72 MHz)

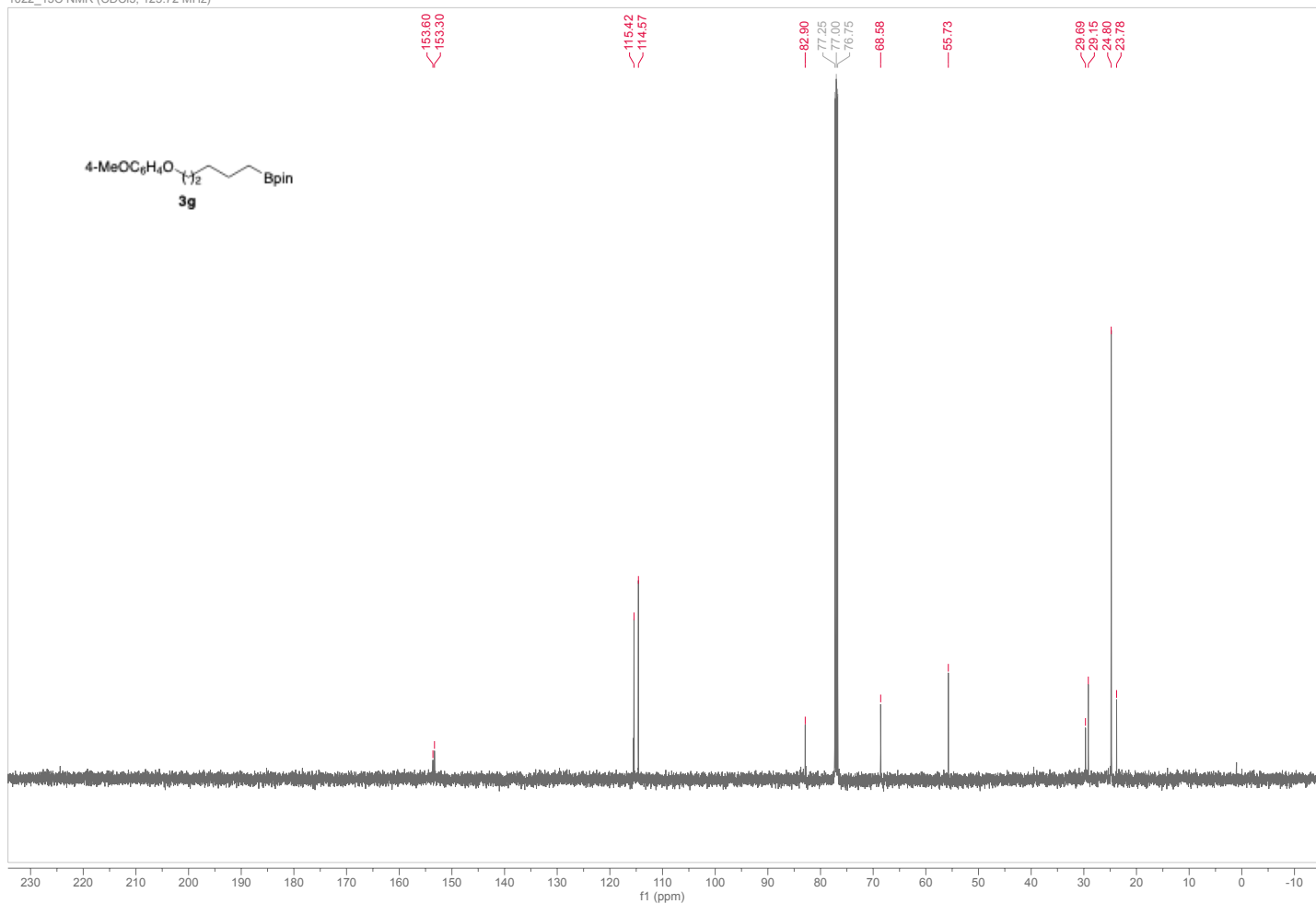
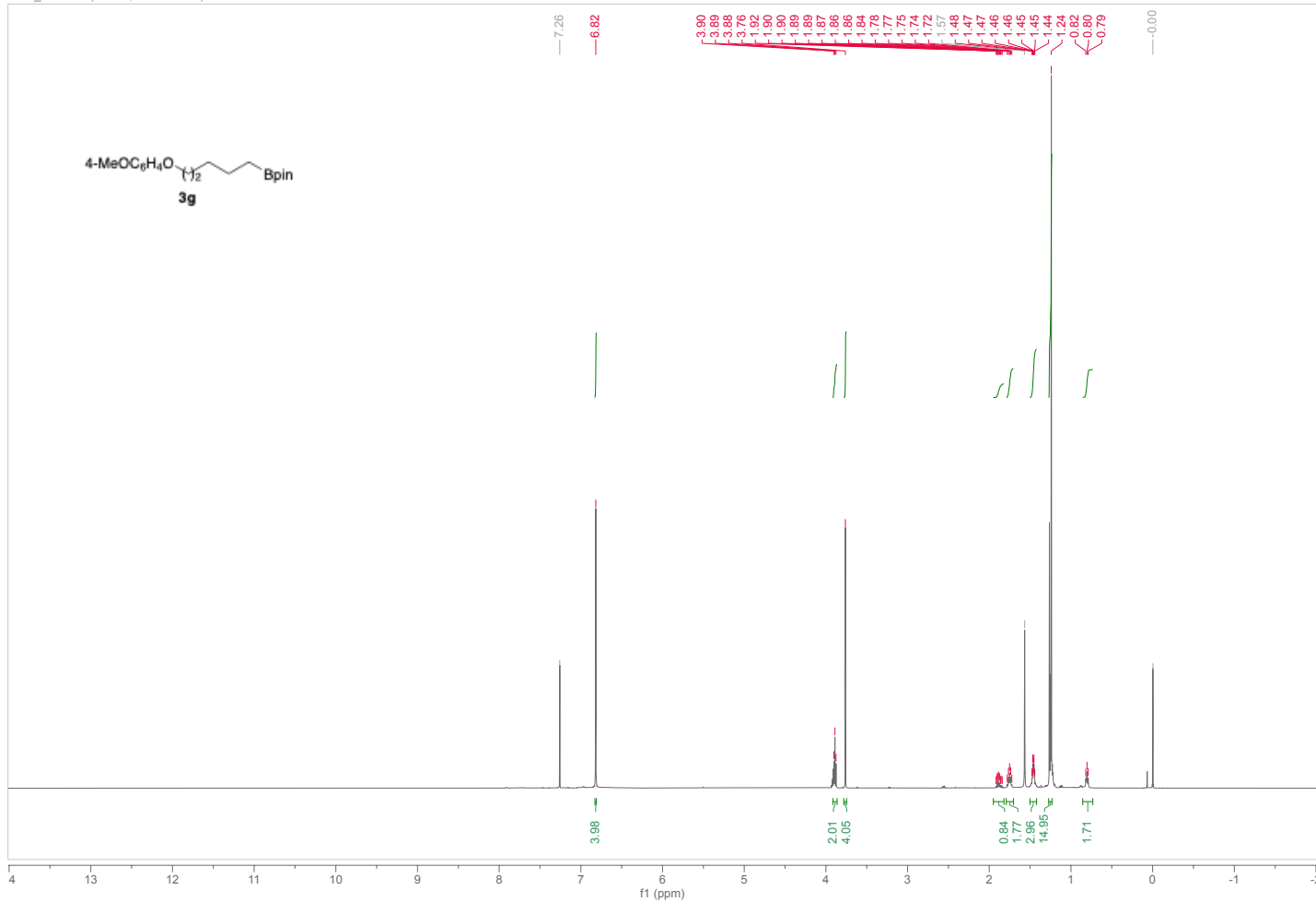


1007\_1H NMR (CDCl<sub>3</sub>, 499.94 MHz)



1007\_13C NMR (CDCl<sub>3</sub>, 125.72 MHz)





Chemical structure of **3h**: CCOC(=O)CCCC1=CC=CC=C1

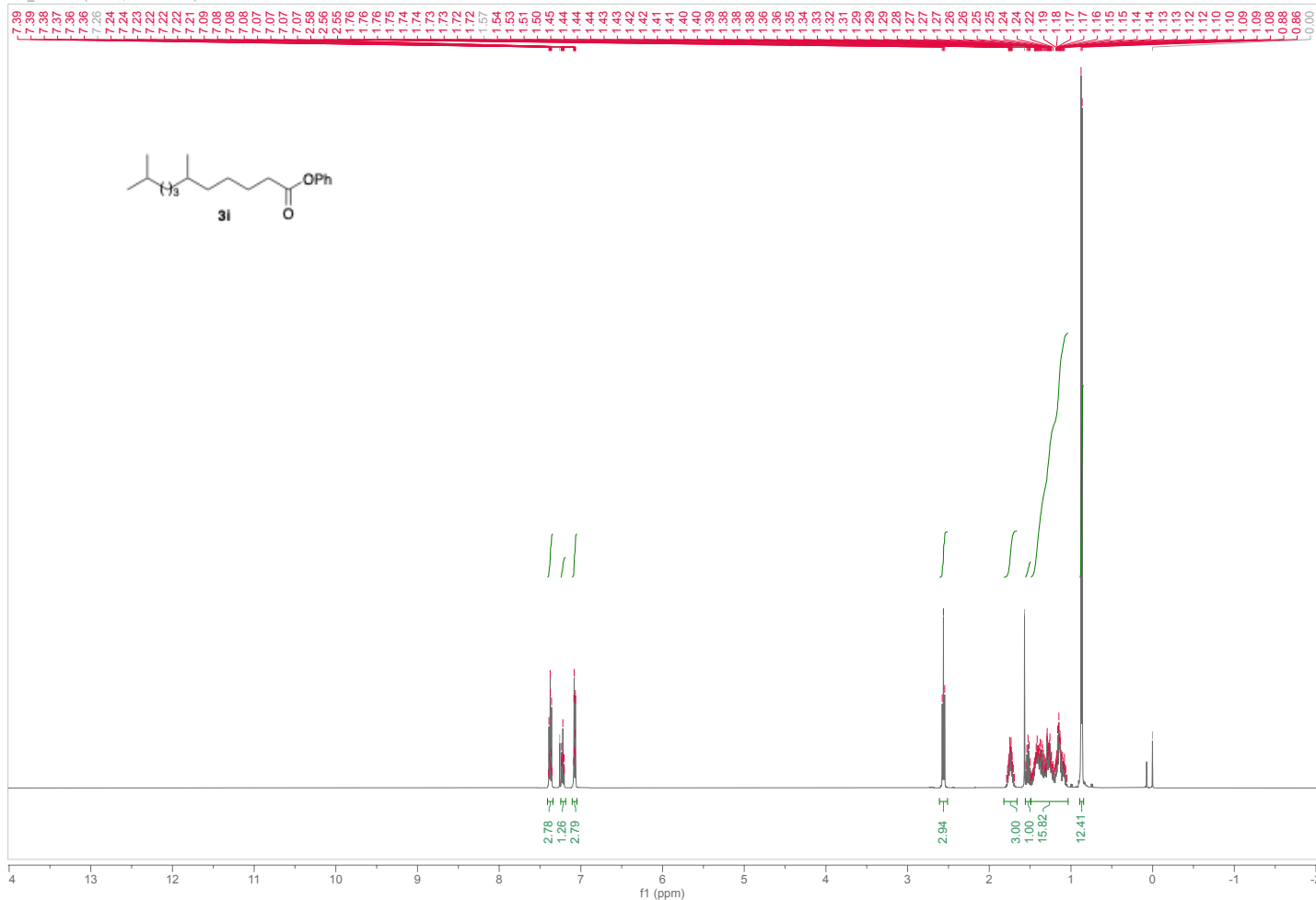
<sup>1</sup>H NMR spectrum (CDCl<sub>3</sub>) of compound **3h**. The x-axis represents the chemical shift in ppm (f1), ranging from 0 to 14. The spectrum shows several multiplets in the aromatic region (7.1–7.4 ppm) and a series of multiplets in the aliphatic region (1.3–2.7 ppm). Integration values are provided below the baseline for several peak groups: 1.96, 0.97, 4.91, 1.89, 2.17, 2.09, 2.07, 2.25, and 6.68. A list of peak chemical shifts (δ) is provided at the top of the spectrum, ranging from 7.45 to 0.03 ppm.

Chemical structure of **3h**: c1ccccc1CCCCC(=O)Oc2ccccc2

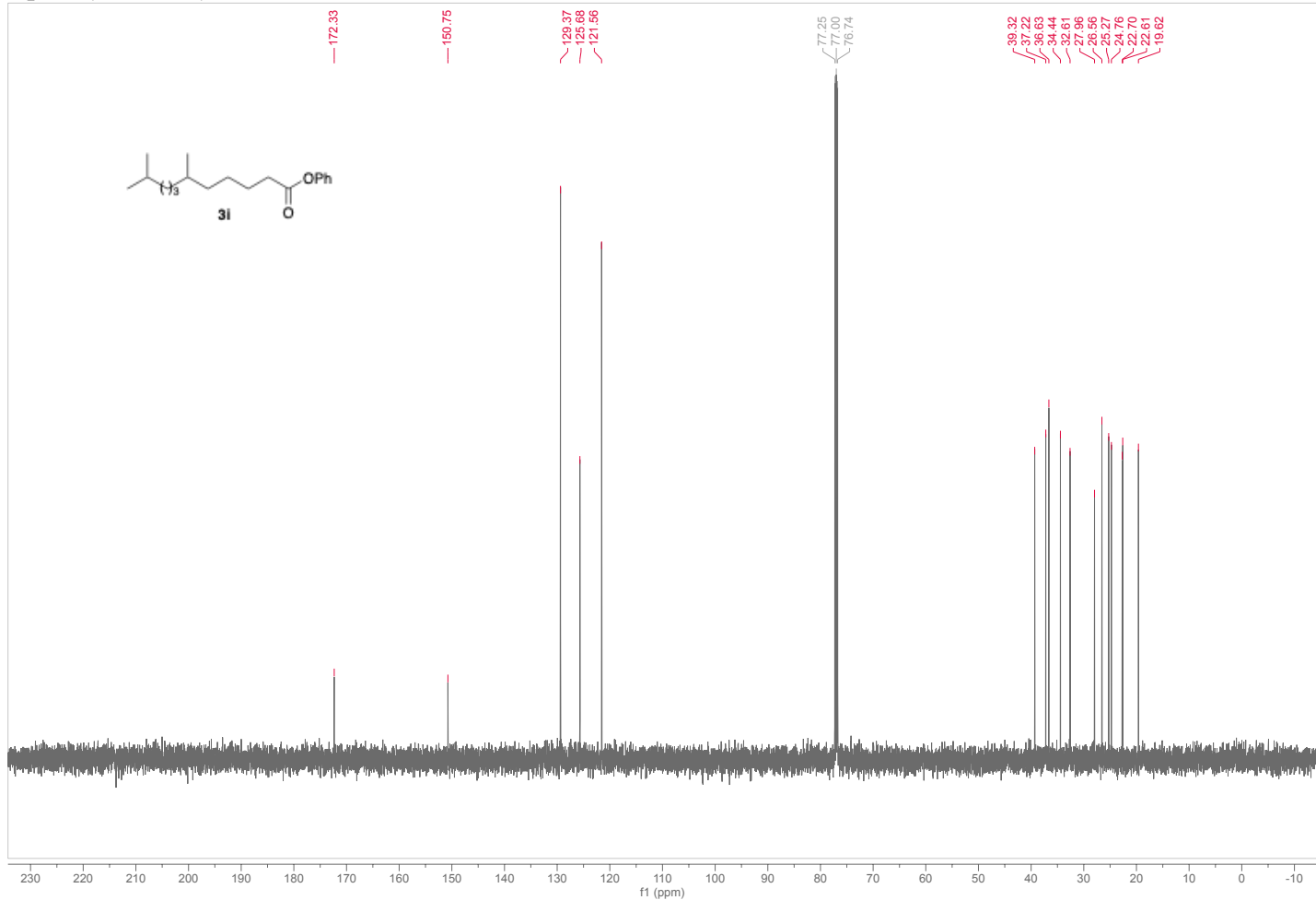
<sup>13</sup>C NMR spectrum (CDCl<sub>3</sub>) of **3h**. The x-axis represents the chemical shift in ppm, ranging from -10 to 230. The spectrum shows several peaks corresponding to the structure, with the following chemical shifts labeled:

- 172.25
- 150.72
- 142.73
- 128.35
- 128.36
- 128.21
- 128.16
- 126.56
- 121.54
- 77.25
- 77.00
- 76.75
- 35.89
- 34.34
- 31.39
- 29.08
- 29.06
- 28.99
- 24.89
- 1.00

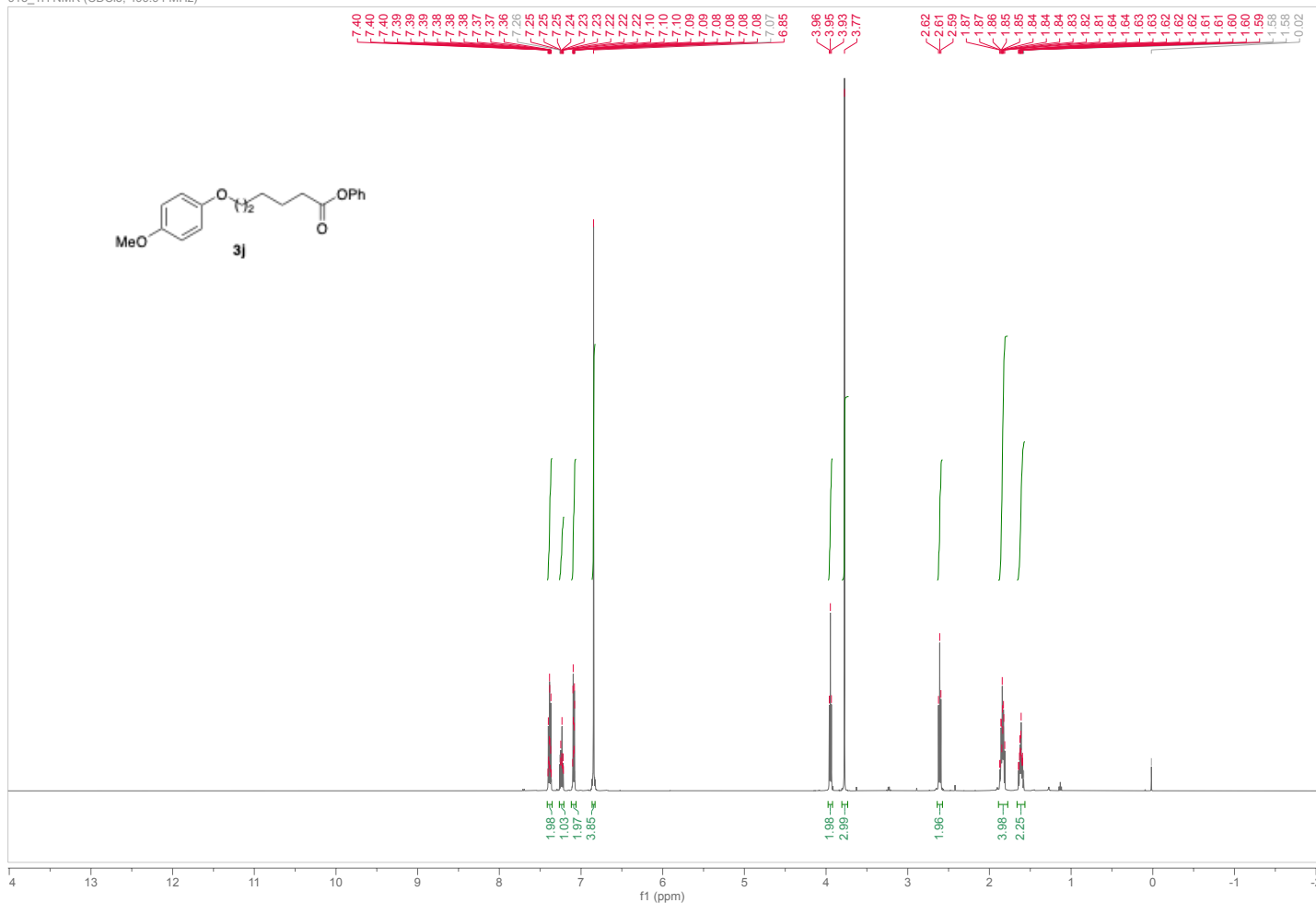
954\_1H NMR (CDCl<sub>3</sub>, 499.94 MHz)



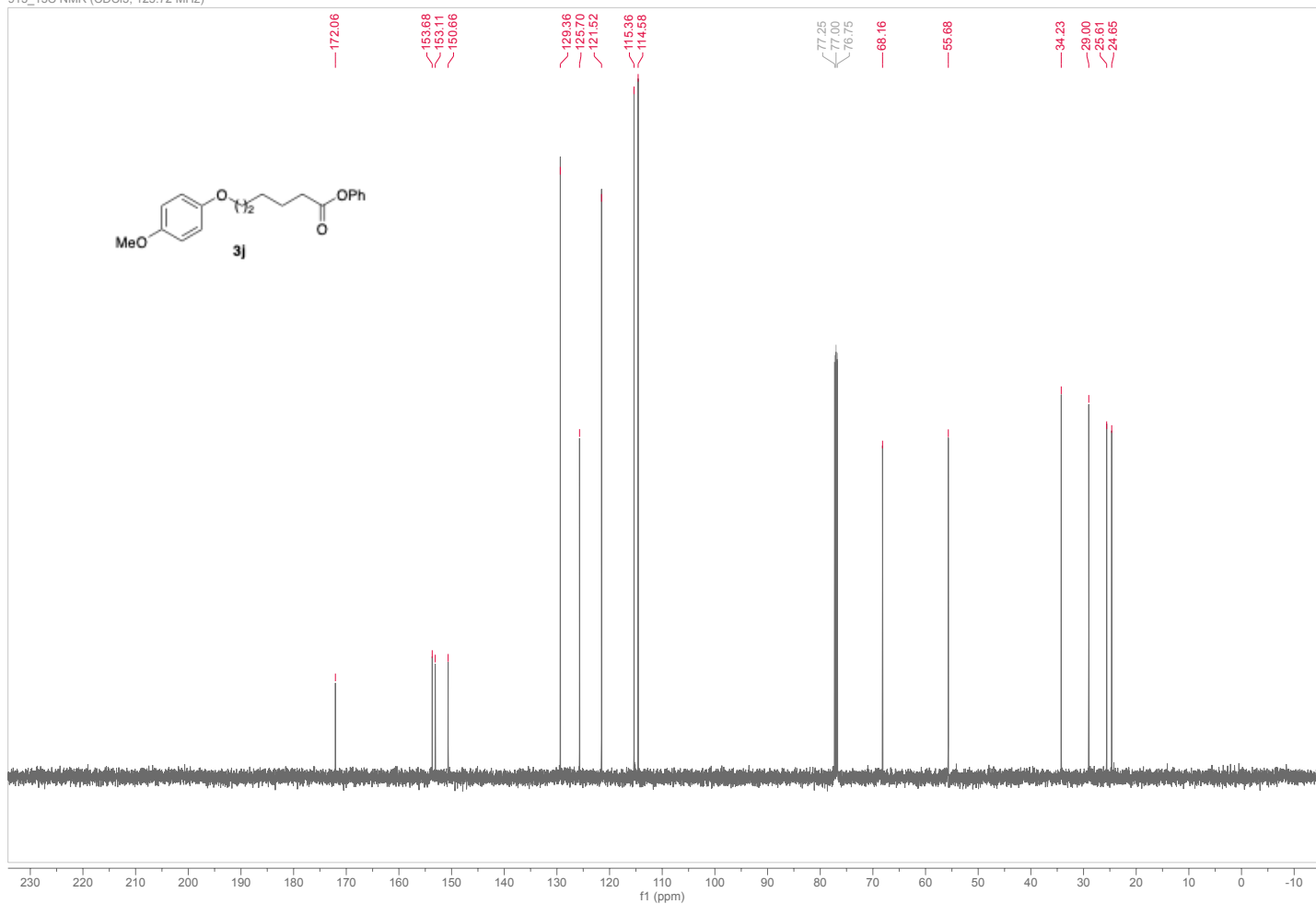
954\_13C NMR (CDCl<sub>3</sub>, 125.72 MHz)



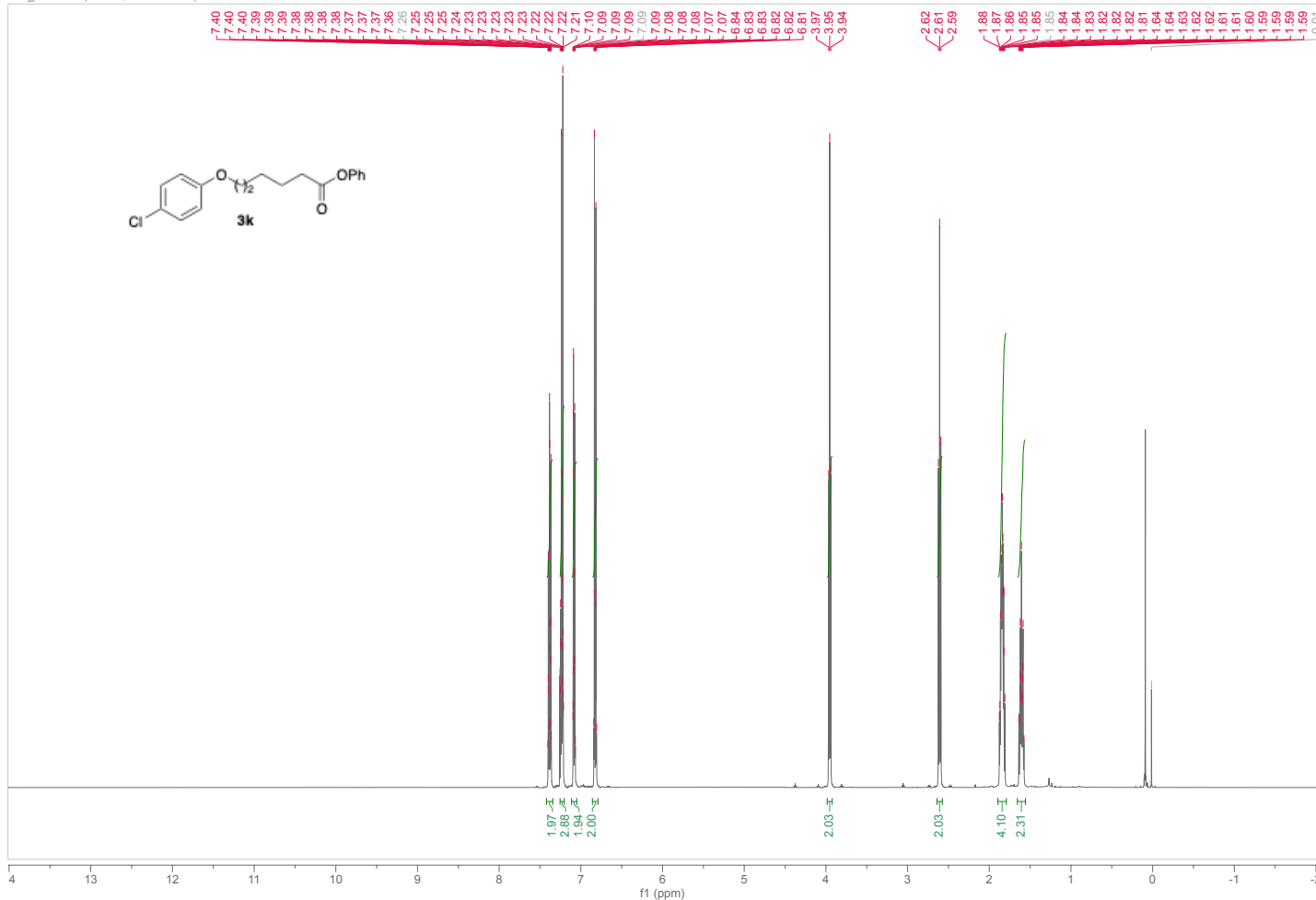
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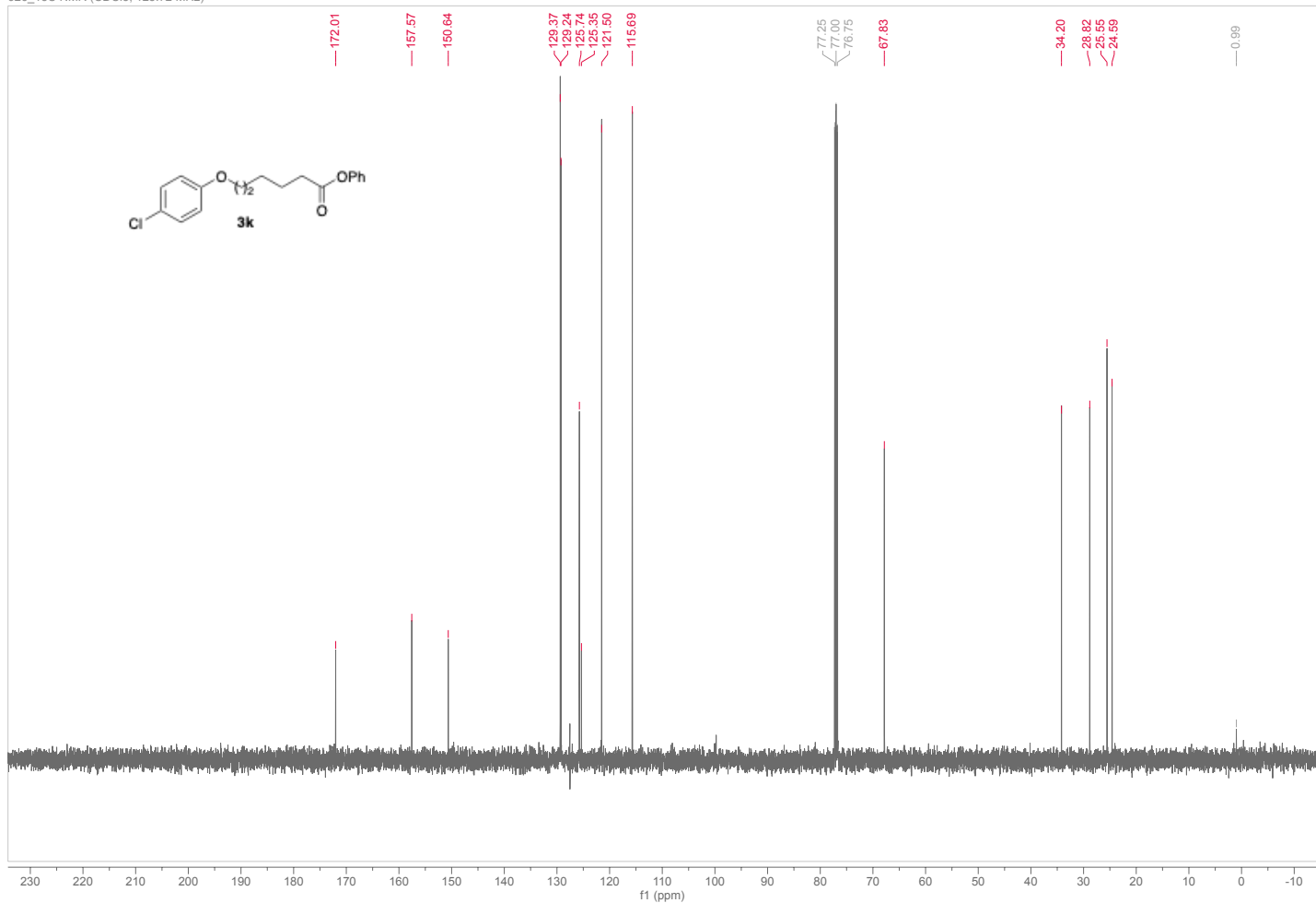
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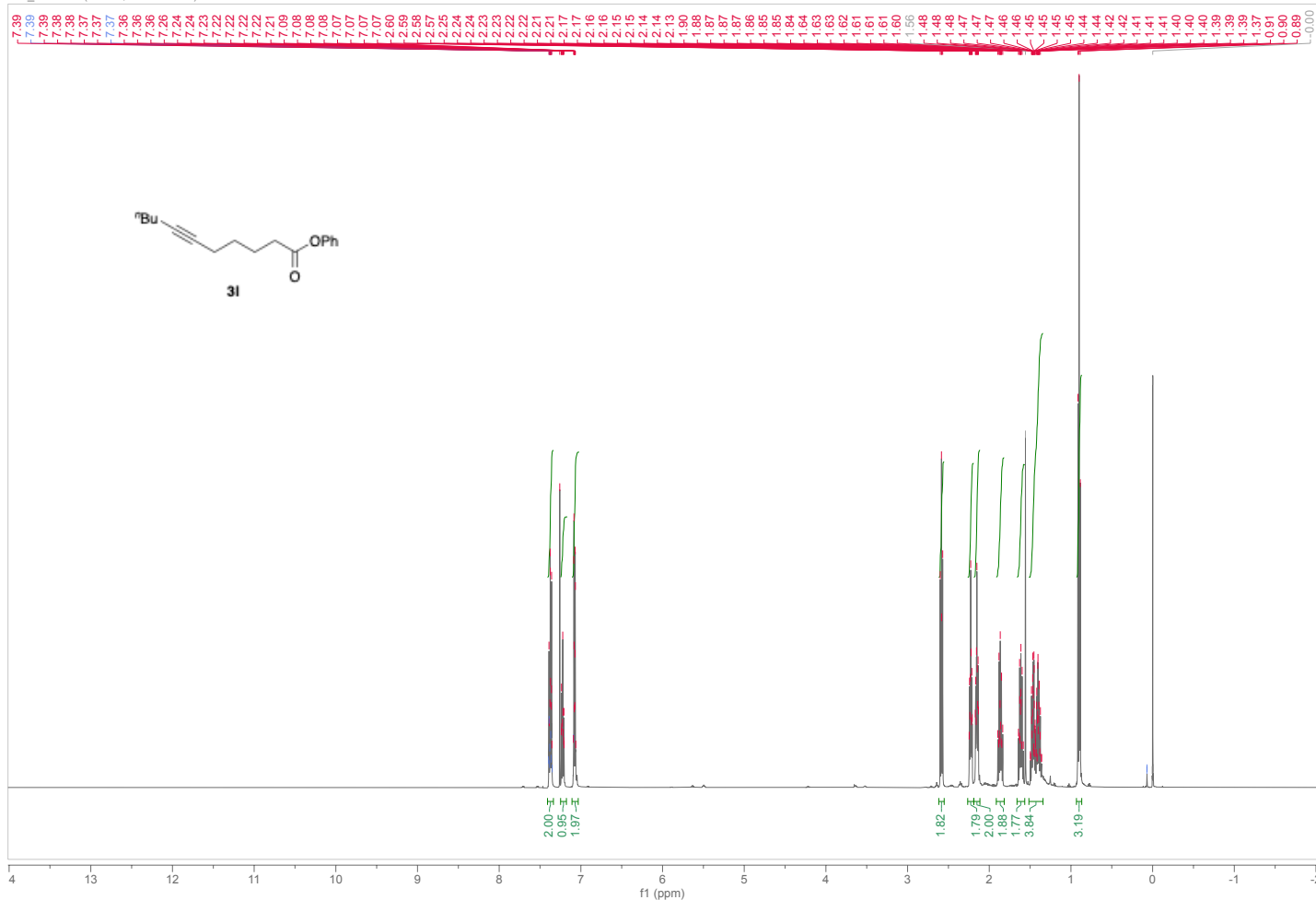
926\_1H NMR (CDCl<sub>3</sub>, 499.94 MHz)



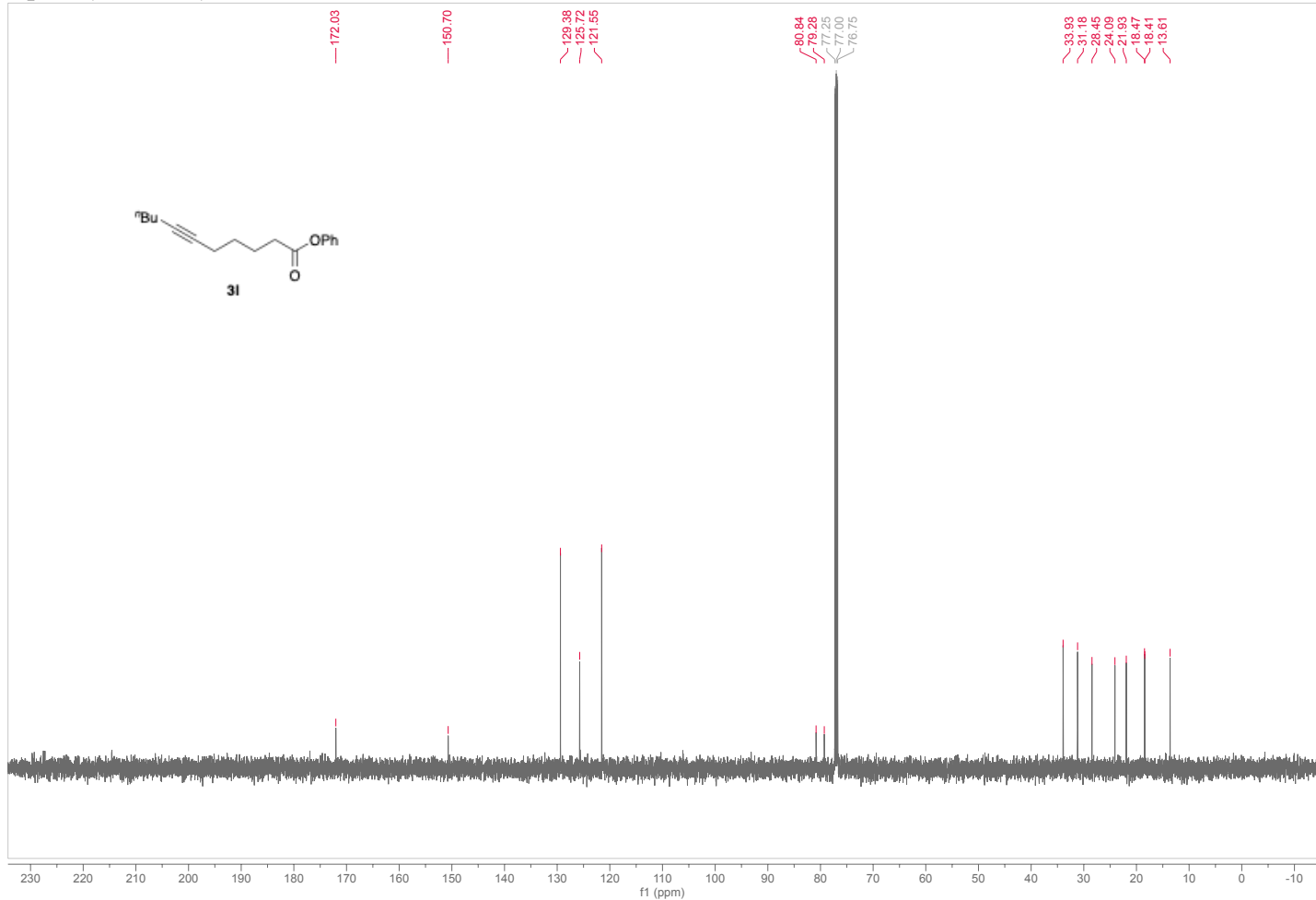
926\_13C NMR (CDCl<sub>3</sub>, 125.72 MHz)

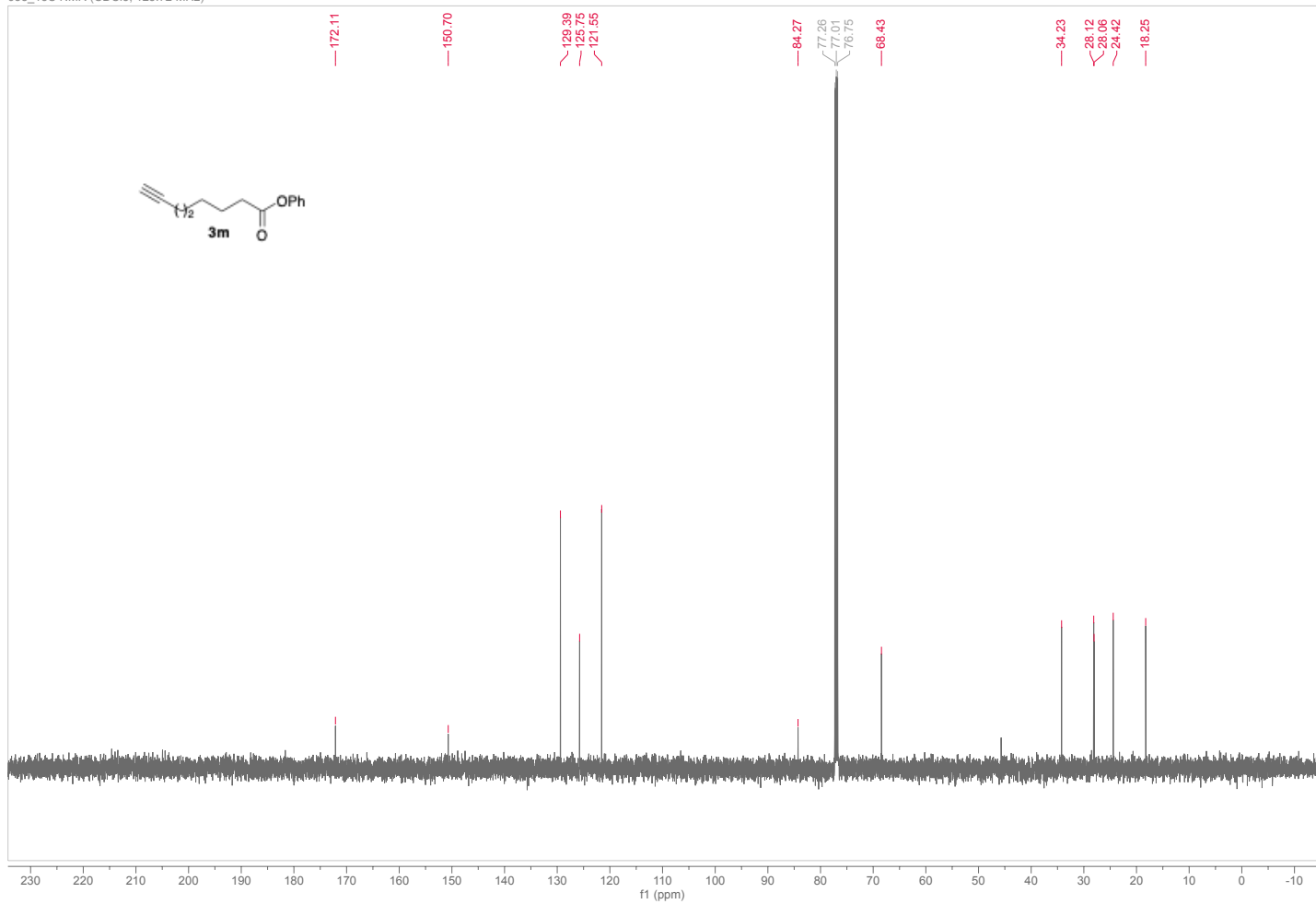
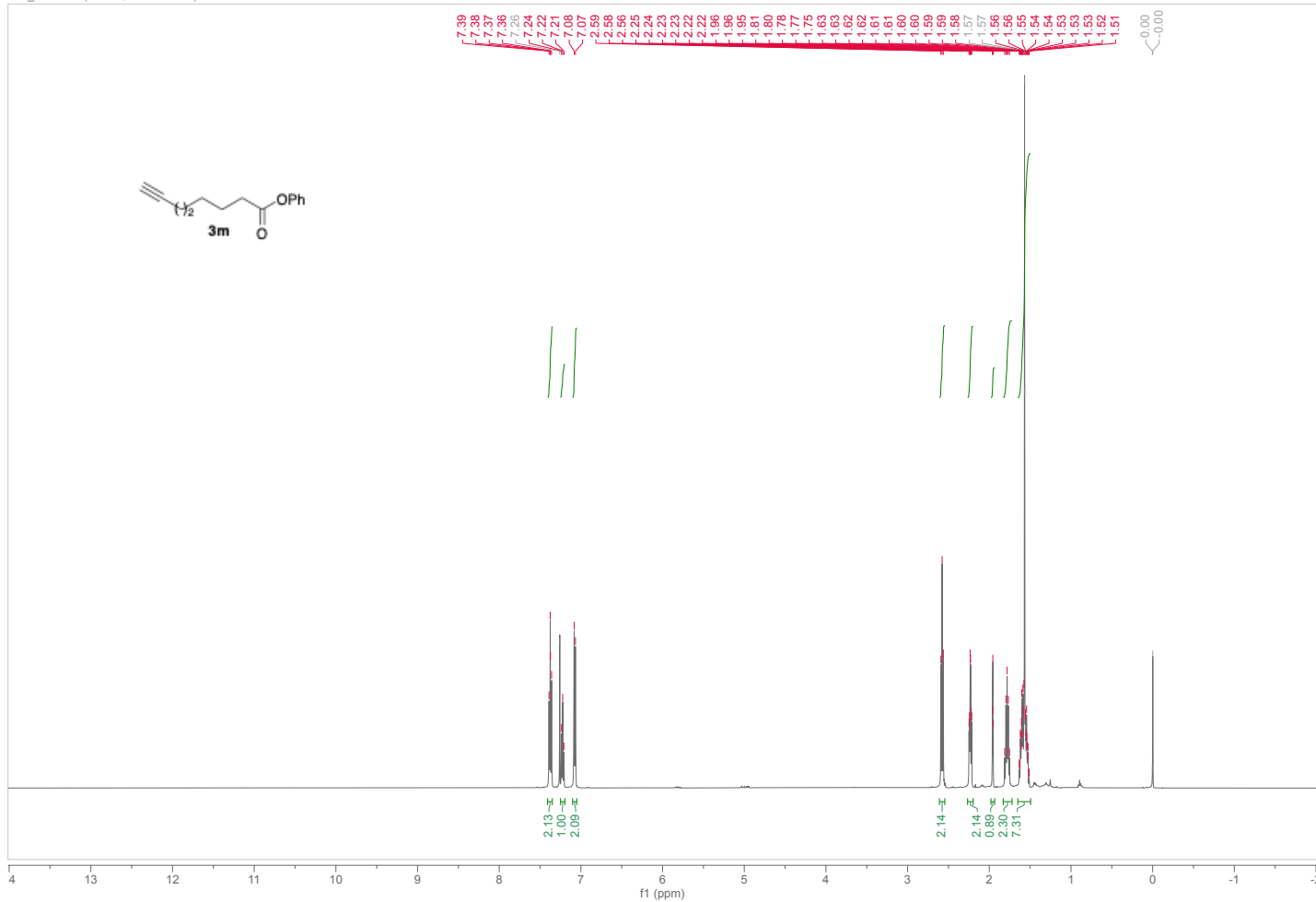


925\_1H NMR (CDCl<sub>3</sub>, 499.94 MHz)

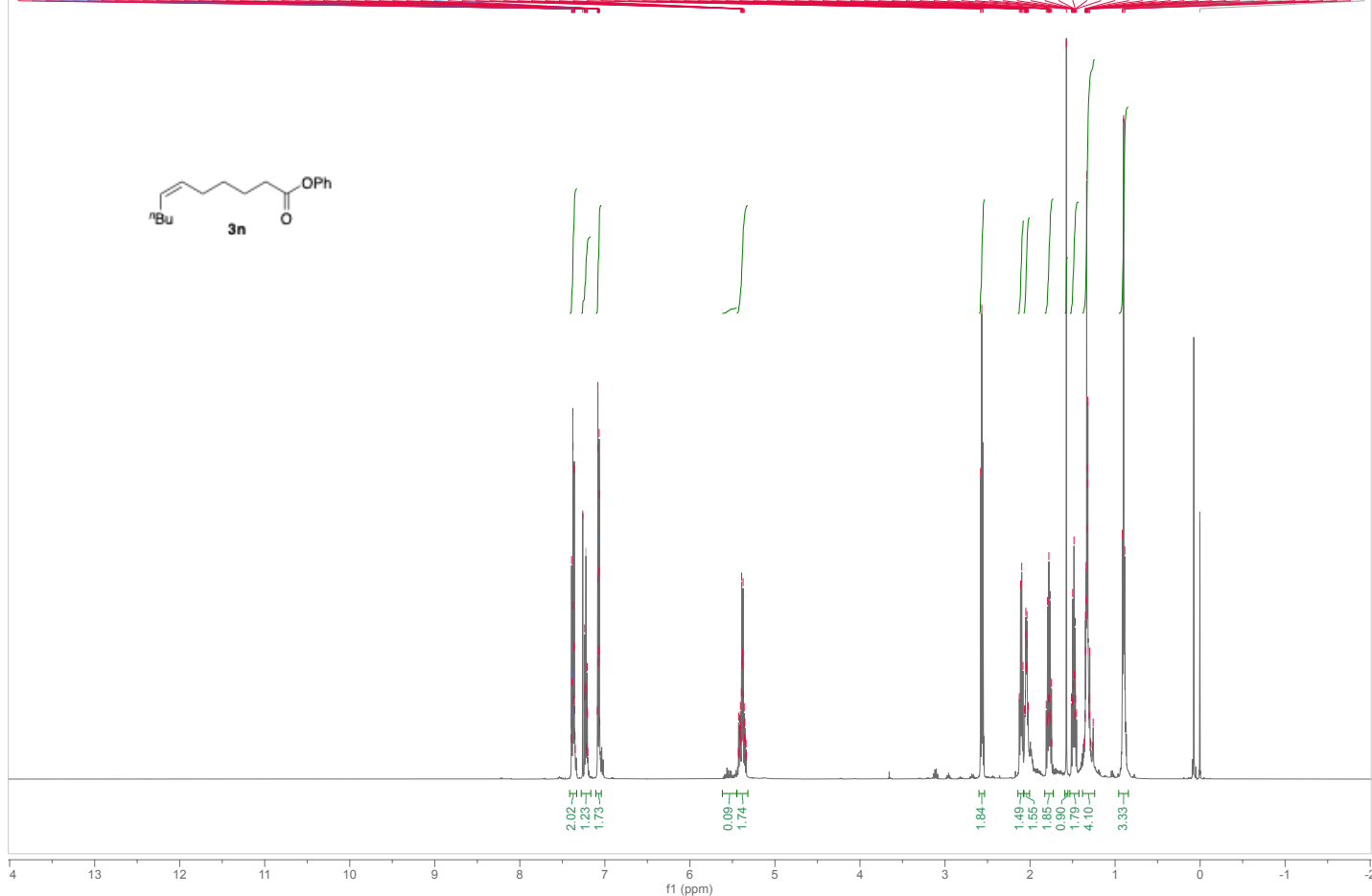


925\_13C NMR (CDCl<sub>3</sub>, 125.72 MHz)

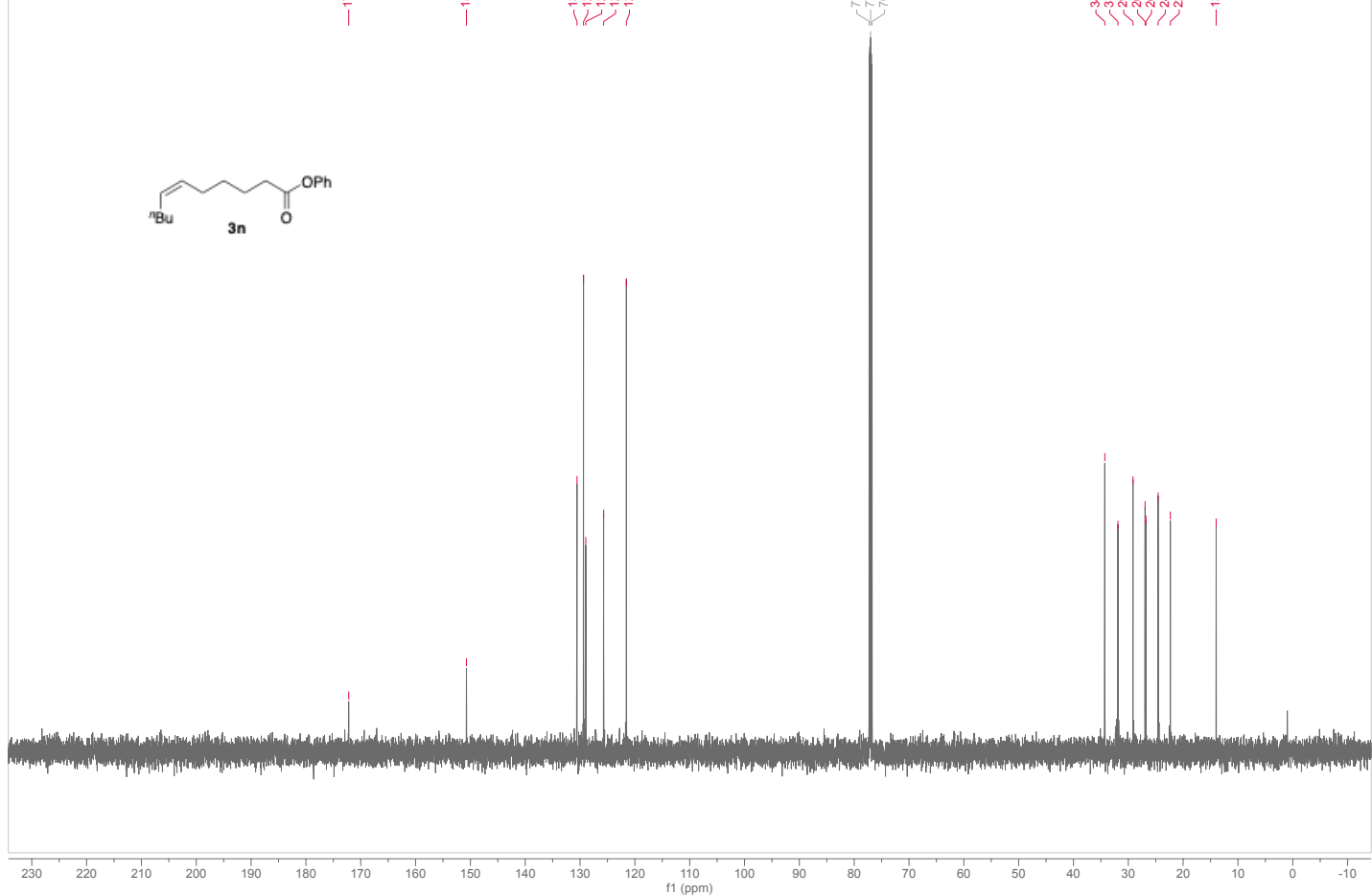




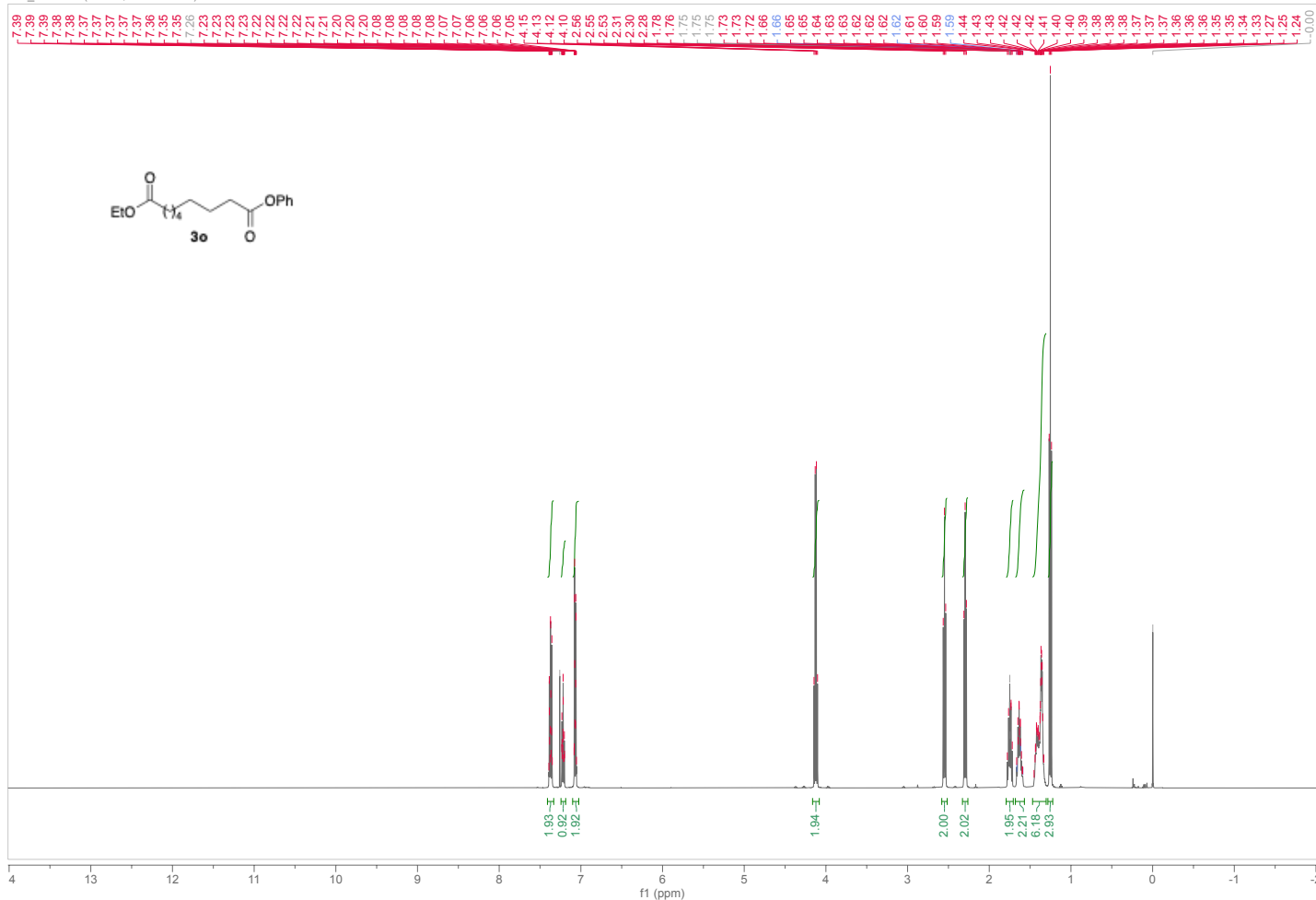
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| 1 | 2 | 3 | 4 | 5 | 6 | 7 | 8 | 9 | 10 | 11 | 12 | 13 | 14 | 15 | 16 | 17 | 18 | 19 | 20 | 21 | 22 | 23 | 24 | 25 | 26 | 27 | 28 | 29 | 30 | 31 | 32 | 33 | 34 | 35 | 36 | 37 | 38 | 39 | 40 | 41 | 42 | 43 | 44 | 45 | 46 | 47 | 48 | 49 | 50 | 51 | 52 | 53 | 54 | 55 | 56 | 57 | 58 | 59 | 60 | 61 | 62 | 63 | 64 | 65 | 66 | 67 | 68 | 69 | 70 | 71 | 72 | 73 | 74 | 75 | 76 | 77 | 78 | 79 | 80 | 81 | 82 | 83 | 84 | 85 | 86 | 87 | 88 | 89 | 90 | 91 | 92 | 93 | 94 | 95 | 96 | 97 | 98 | 99 | 100 |
| 1 | 2 | 3 | 4 | 5 | 6 | 7 | 8 | 9 | 10 | 11 | 12 | 13 | 14 | 15 | 16 | 17 | 18 | 19 | 20 | 21 | 22 | 23 | 24 | 25 | 26 | 27 | 28 | 29 | 30 | 31 | 32 | 33 | 34 | 35 | 36 | 37 | 38 | 39 | 40 | 41 | 42 | 43 | 44 | 45 | 46 | 47 | 48 | 49 | 50 | 51 | 52 | 53 | 54 | 55 | 56 | 57 | 58 | 59 | 60 | 61 | 62 | 63 | 64 | 65 | 66 | 67 | 68 | 69 | 70 | 71 | 72 | 73 | 74 | 75 | 76 | 77 | 78 | 79 | 80 | 81 | 82 | 83 | 84 | 85 | 86 | 87 | 88 | 89 | 90 | 91 | 92 | 93 | 94 | 95 | 96 | 97 | 98 | 99 | 100 |
| 1 | 2 | 3 | 4 | 5 | 6 | 7 | 8 | 9 | 10 | 11 | 12 | 13 | 14 | 15 | 16 | 17 | 18 | 19 | 20 | 21 | 22 | 23 | 24 | 25 | 26 | 27 | 28 | 29 | 30 | 31 | 32 | 33 | 34 | 35 | 36 | 37 | 38 | 39 | 40 | 41 | 42 | 43 | 44 | 45 | 46 | 47 | 48 | 49 | 50 | 51 | 52 | 53 | 54 | 55 | 56 | 57 | 58 | 59 | 60 | 61 | 62 | 63 | 64 | 65 | 66 | 67 | 68 | 69 | 70 | 71 | 72 | 73 | 74 | 75 | 76 | 77 | 78 | 79 | 80 | 81 | 82 | 83 | 84 | 85 | 86 | 87 | 88 | 89 | 90 | 91 | 92 | 93 | 94 | 95 | 96 | 97 | 98 | 99 | 100 |
| 1 | 2 | 3 | 4 | 5 | 6 | 7 | 8 | 9 | 10 | 11 | 12 | 13 | 14 | 15 | 16 | 17 | 18 | 19 | 20 | 21 | 22 | 23 | 24 | 25 | 26 | 27 | 28 | 29 | 30 | 31 | 32 | 33 | 34 | 35 | 36 | 37 | 38 | 39 | 40 | 41 | 42 | 43 | 44 | 45 | 46 | 47 | 48 | 49 | 50 | 51 | 52 | 53 | 54 | 55 | 56 | 57 | 58 | 59 | 60 | 61 | 62 | 63 | 64 | 65 | 66 | 67 | 68 | 69 | 70 | 71 | 72 | 73 | 74 | 75 | 76 | 77 | 78 | 79 | 80 | 81 | 82 | 83 | 84 | 85 | 86 | 87 | 88 | 89 | 90 | 91 | 92 | 93 | 94 | 95 | 96 | 97 | 98 | 99 | 100 |
| 1 | 2 | 3 | 4 | 5 | 6 | 7 | 8 | 9 | 10 | 11 | 12 | 13 | 14 | 15 | 16 | 17 | 18 | 19 | 20 | 21 | 22 | 23 | 24 | 25 | 26 | 27 | 28 | 29 | 30 | 31 | 32 | 33 | 34 | 35 | 36 | 37 | 38 | 39 | 40 | 41 | 42 | 43 | 44 | 45 | 46 | 47 | 48 | 49 | 50 | 51 | 52 | 53 | 54 | 55 | 56 | 57 | 58 | 59 | 60 | 61 | 62 | 63 | 64 | 65 | 66 | 67 | 68 | 69 | 70 | 71 | 72 | 73 | 74 | 75 | 76 | 77 | 78 | 79 | 80 | 81 | 82 | 83 | 84 | 85 | 86 | 87 | 88 | 89 | 90 | 91 | 92 | 93 | 94 | 95 | 96 | 97 | 98 | 99 | 100 |
| 1 | 2 | 3 | 4 | 5 | 6 | 7 | 8 | 9 | 10 | 11 | 12 | 13 | 14 | 15 | 16 | 17 | 18 | 19 | 20 | 21 | 22 | 23 | 24 | 25 | 26 | 27 | 28 | 29 | 30 | 31 | 32 | 33 | 34 | 35 | 36 | 37 | 38 | 39 | 40 | 41 | 42 | 43 | 44 | 45 | 46 | 47 | 48 | 49 | 50 | 51 | 52 | 53 | 54 | 55 | 56 | 57 | 58 | 59 | 60 | 61 | 62 | 63 | 64 | 65 | 66 | 67 | 68 | 69 | 70 | 71 | 72 | 73 | 74 | 75 | 76 | 77 | 78 | 79 | 80 | 81 | 82 | 83 | 84 | 85 | 86 | 87 |    |    |    |    |    |    |    |    |    |    |    |    |     |



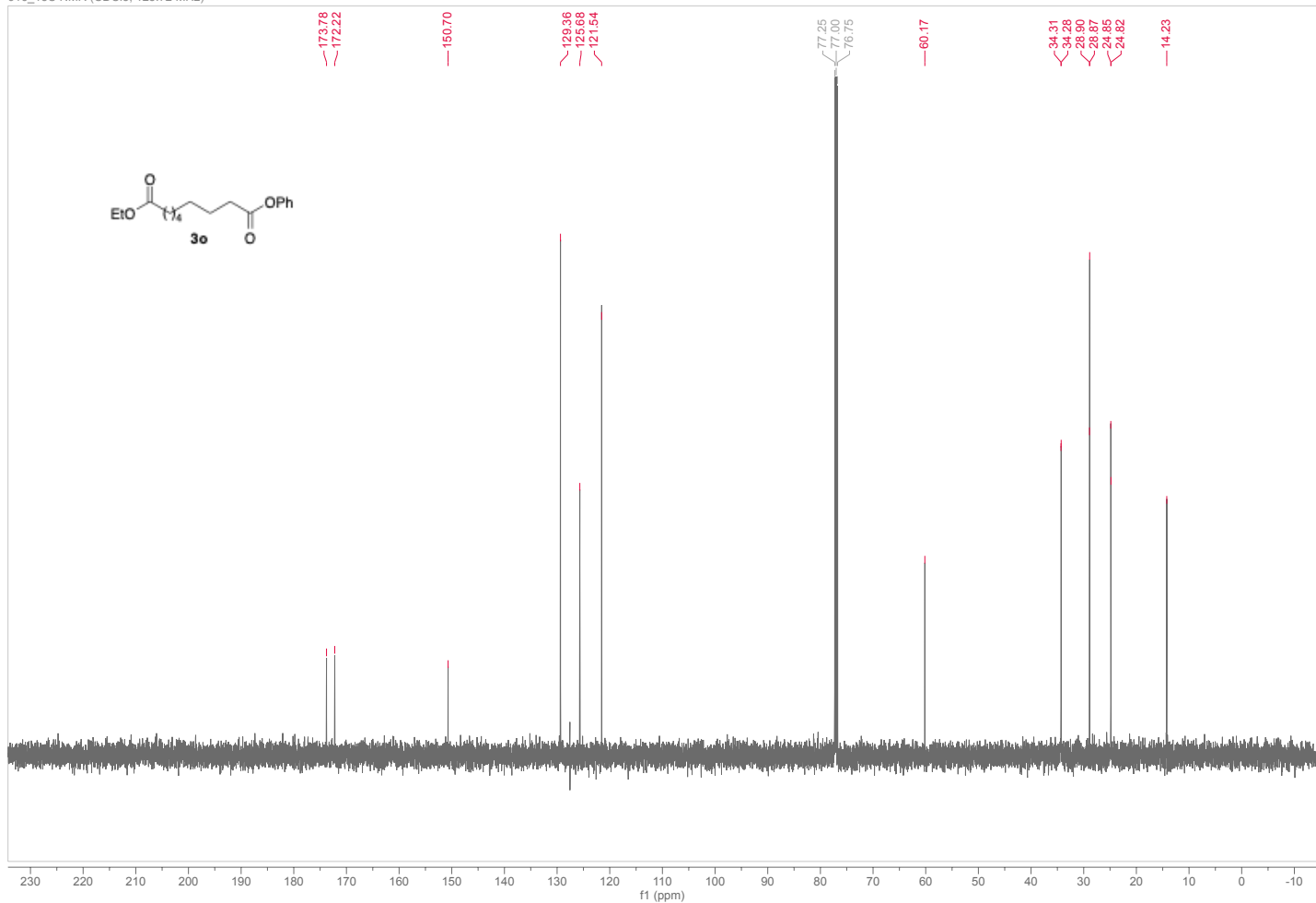
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| 7.90  |        |
| 6.75  | 60.72  |
|       |        |
| 30.55 |        |
| 28.96 |        |
| 28.96 |        |
| 25.70 |        |
| 21.55 |        |
|       |        |
|       |        |
|       |        |
| 4.29  |        |
| 1.89  |        |
| 9.15  |        |
| 6.94  |        |
| 6.79  |        |
| 4.56  |        |
| 2.33  |        |
|       |        |
| 3.98  |        |



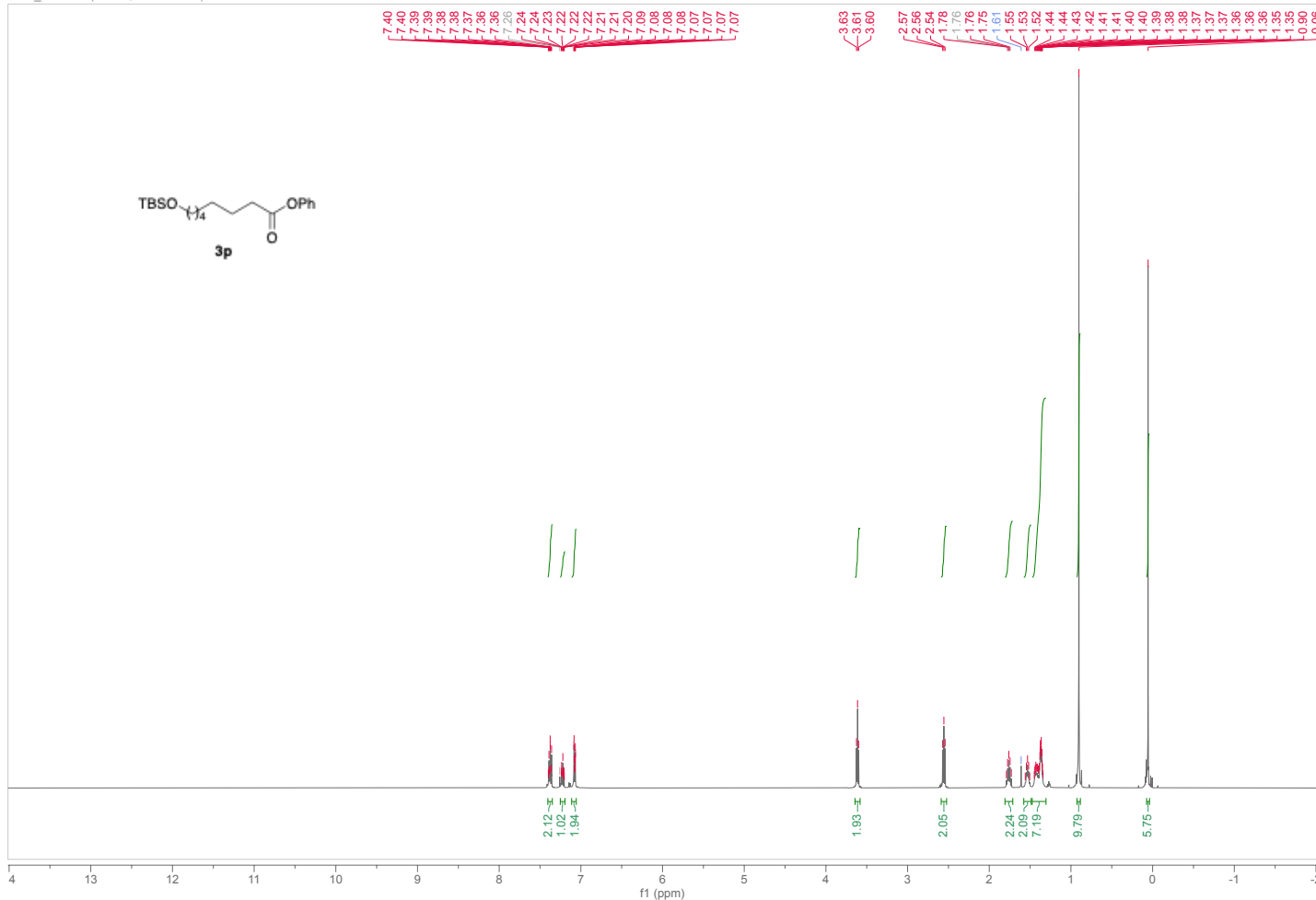
916\_1H NMR (CDCl3, 499.94 MHz)



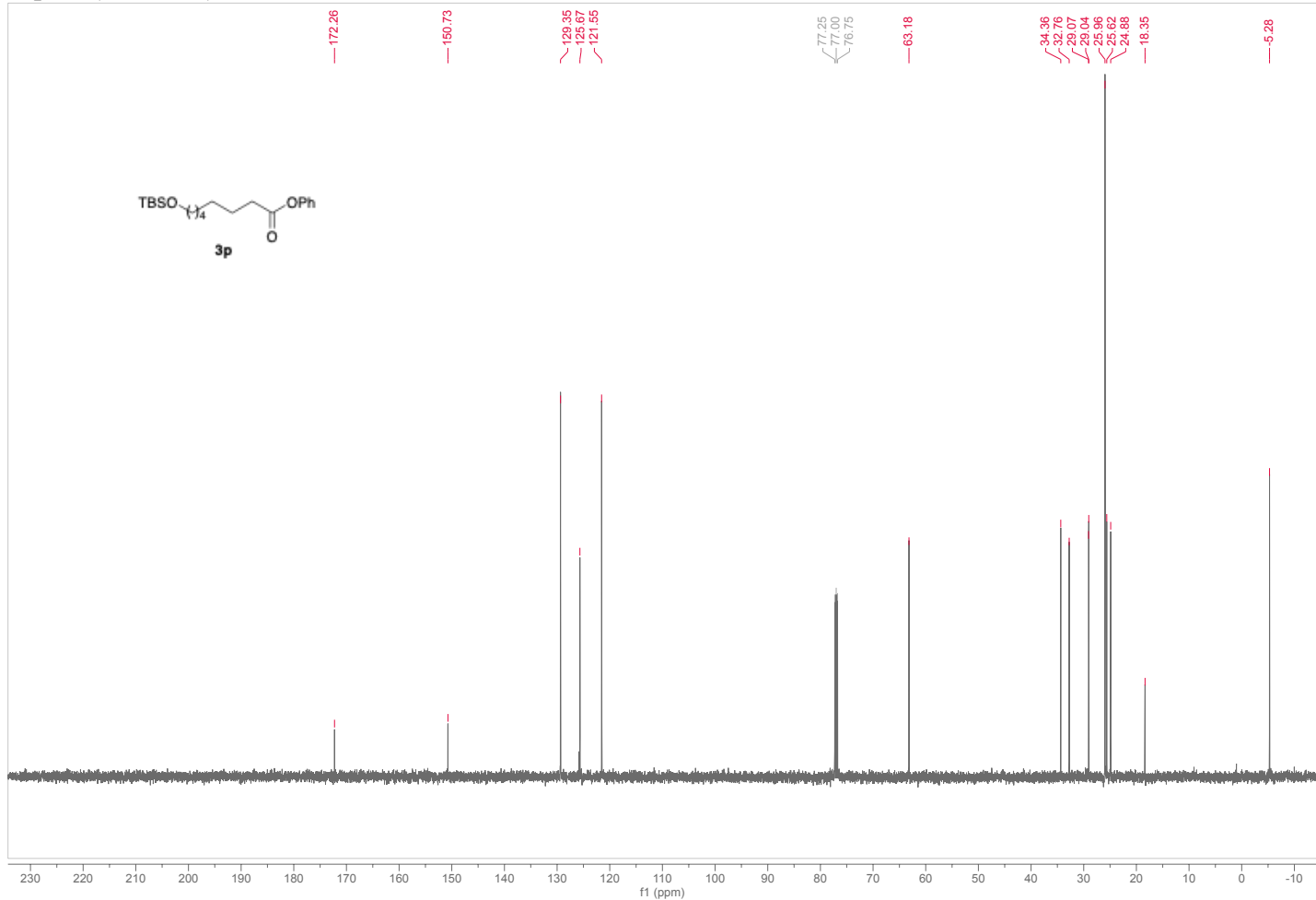
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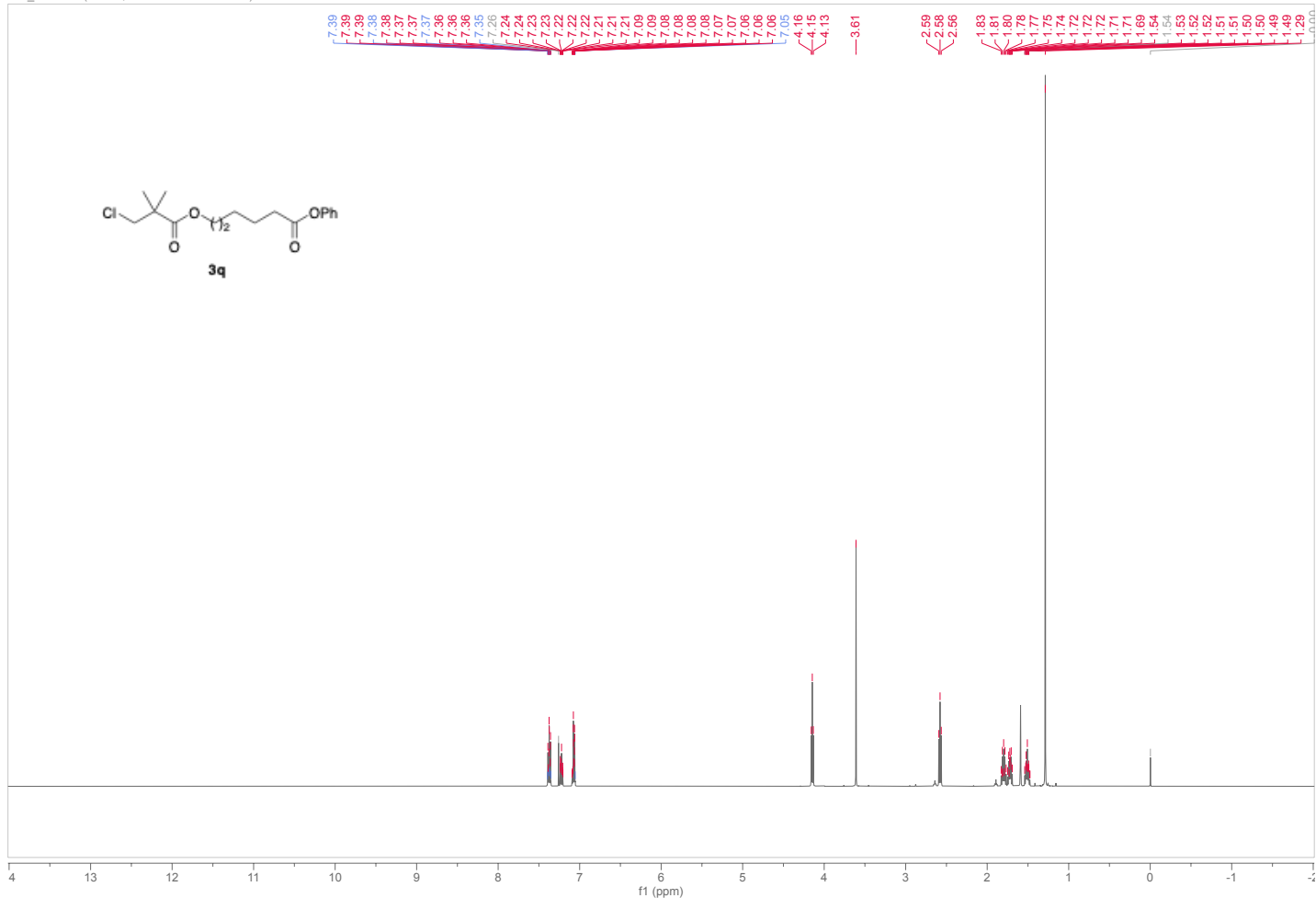
1008\_1H NMR (CDCl<sub>3</sub>, 499.94 MHz)



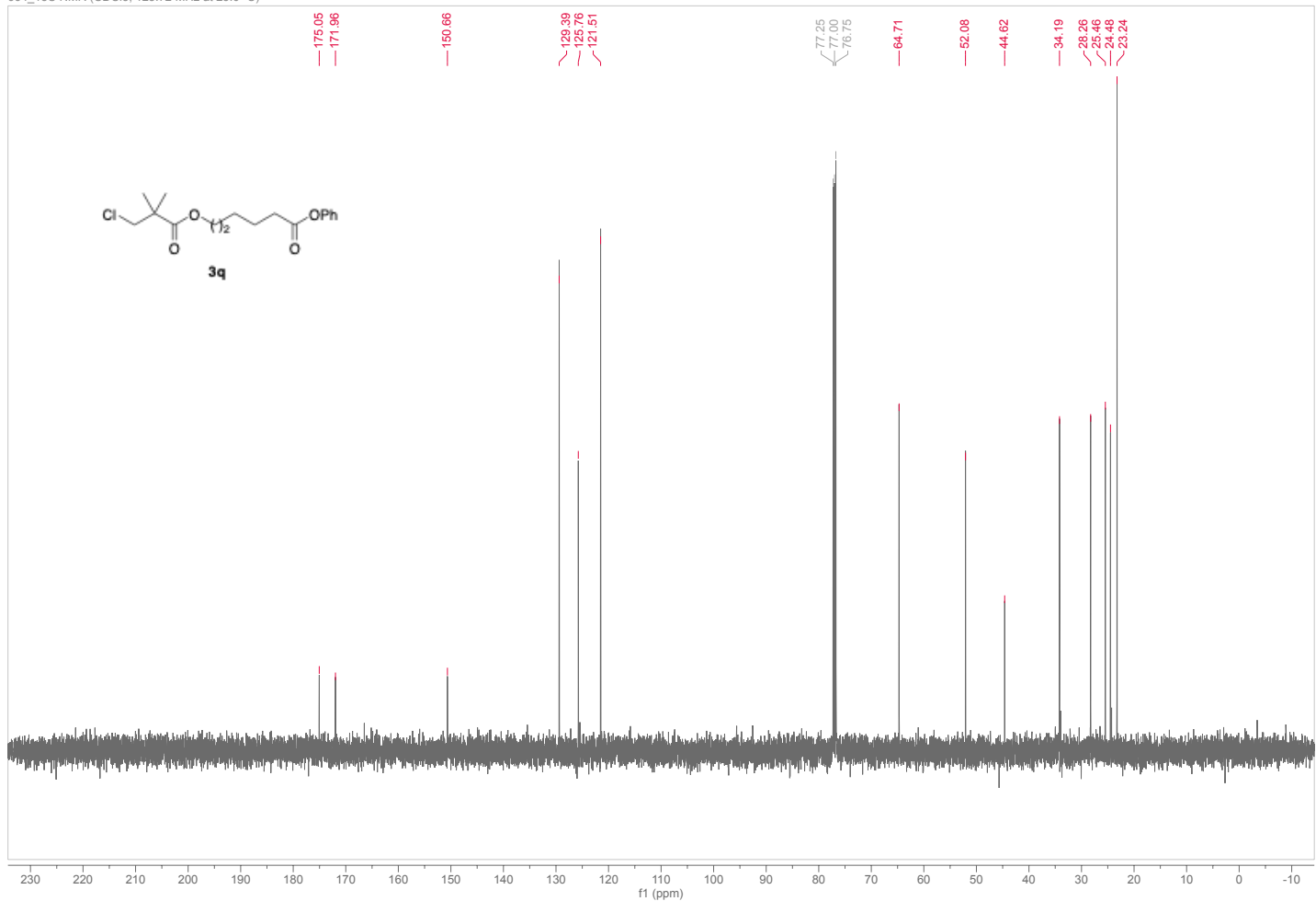
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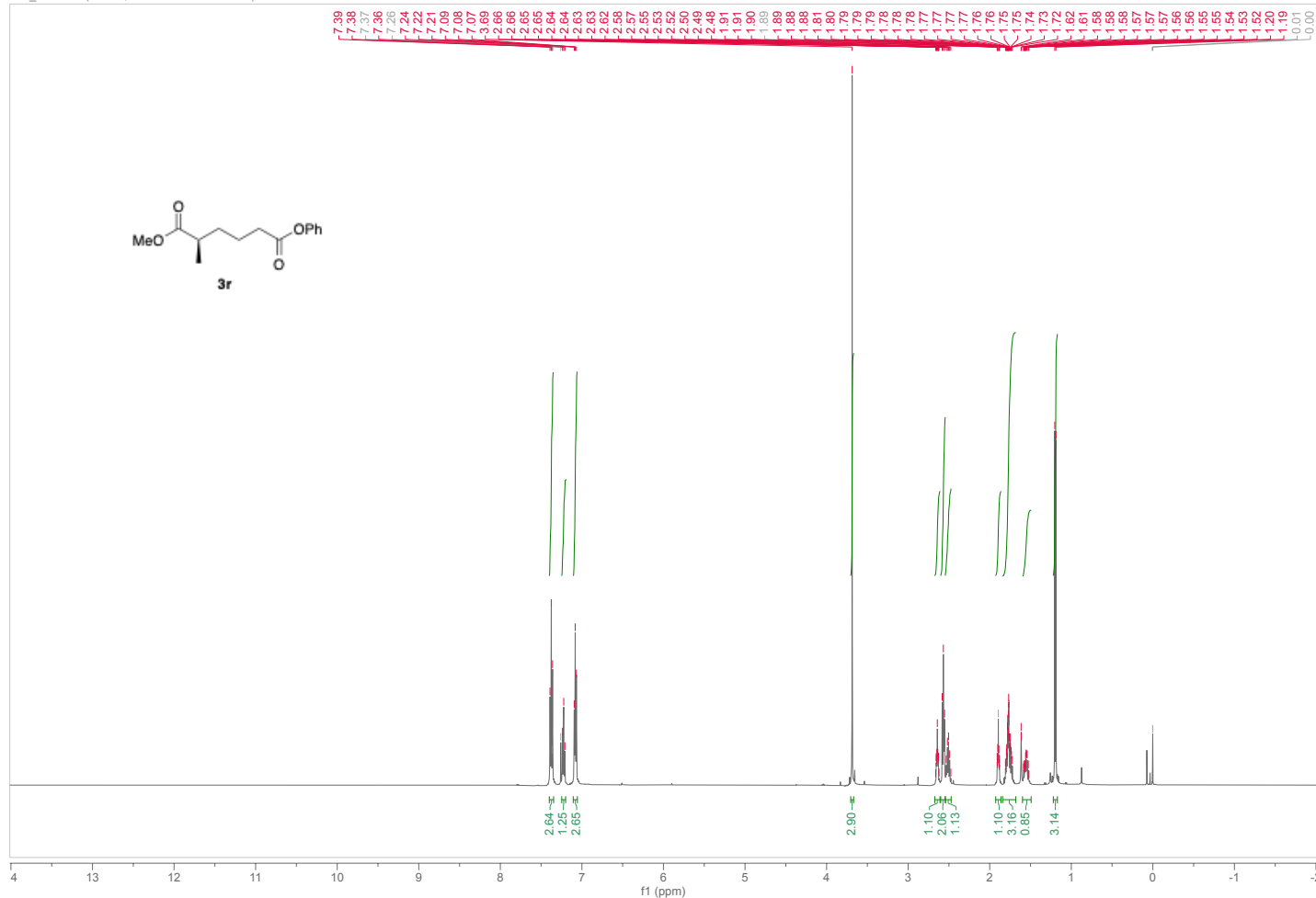
964\_1H NMR (CDCl<sub>3</sub>, 499.94 MHz at 25.0 °C)



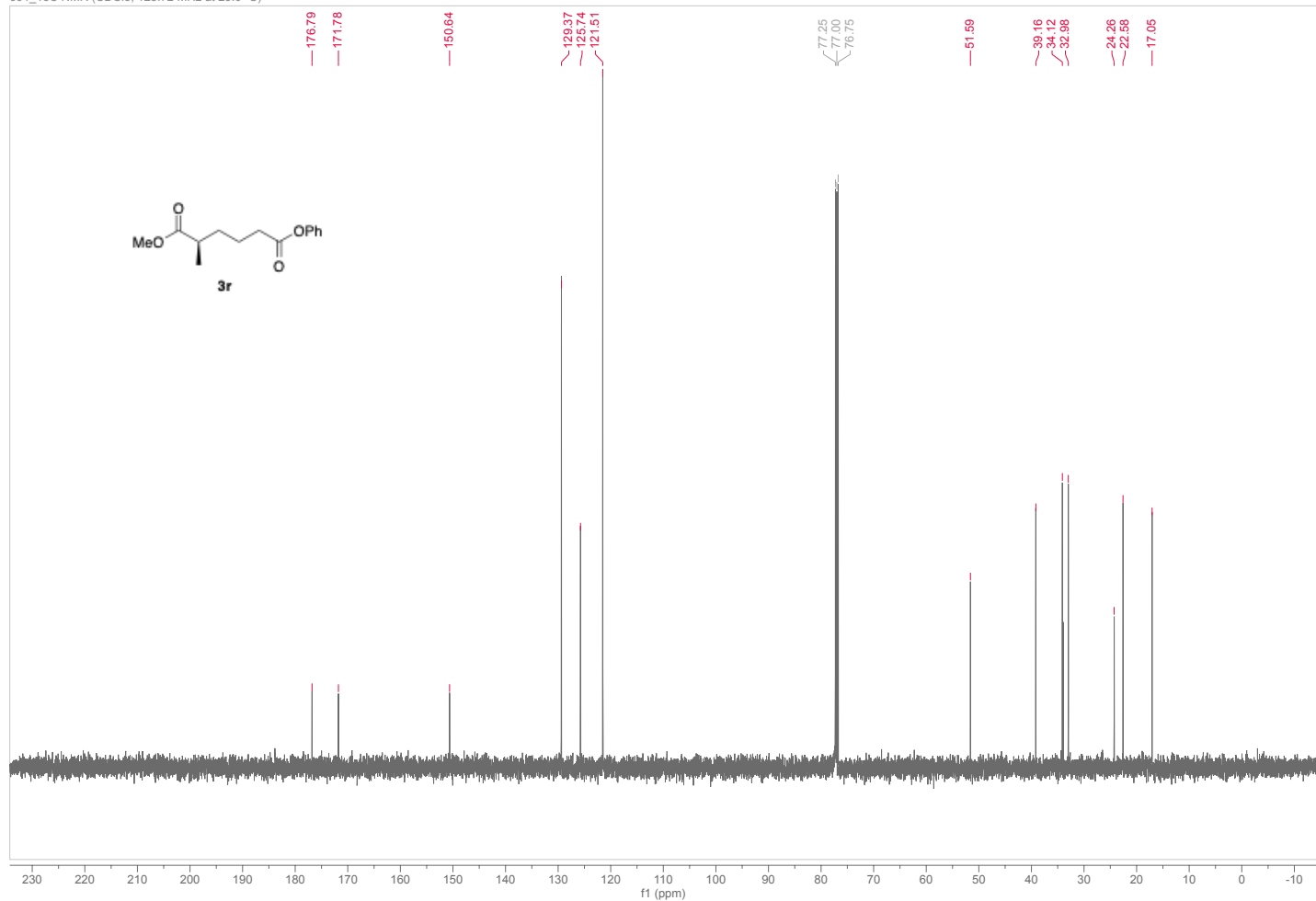
964\_13C NMR (CDCl<sub>3</sub>, 125.72 MHz at 25.0 °C)

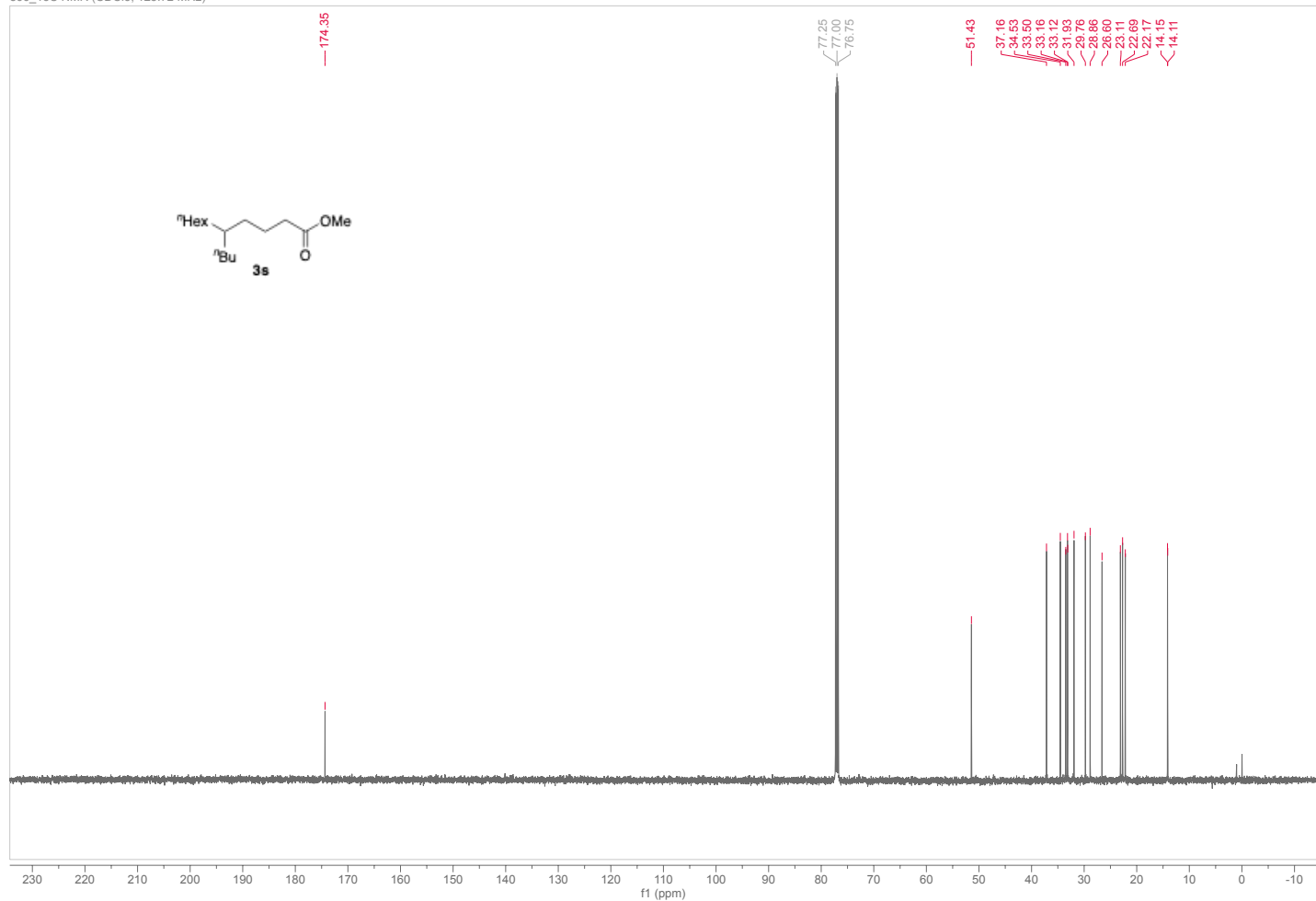
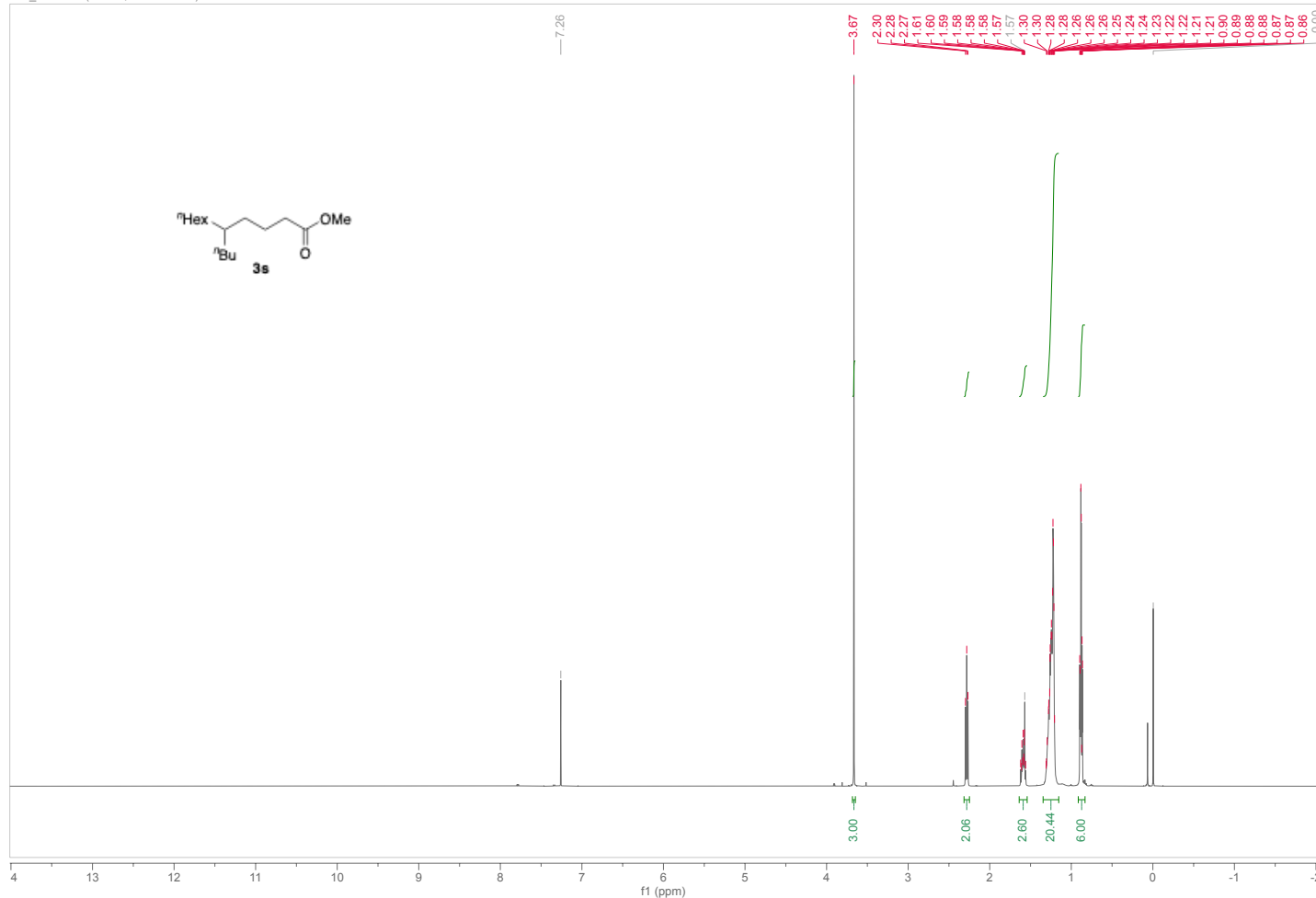


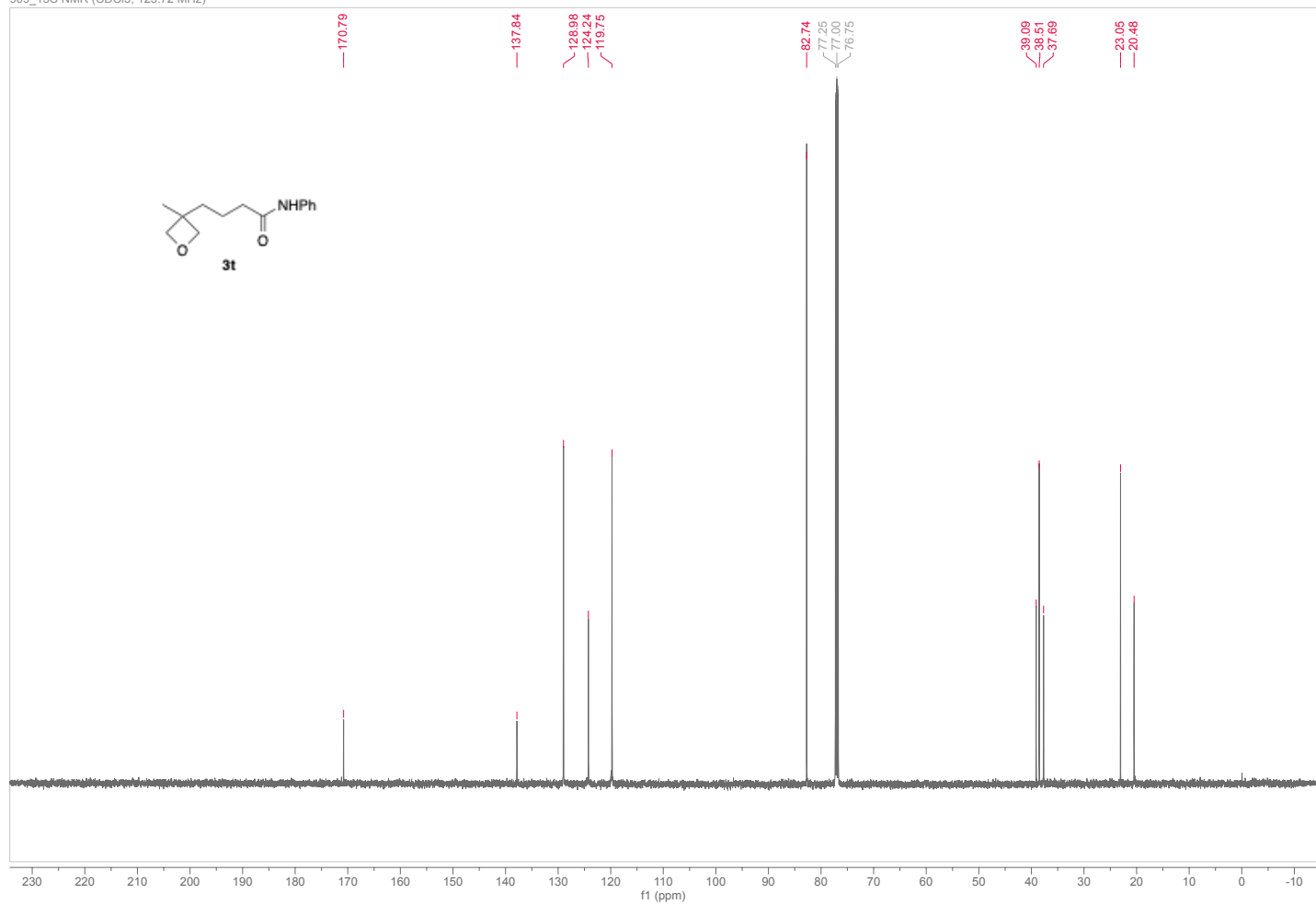
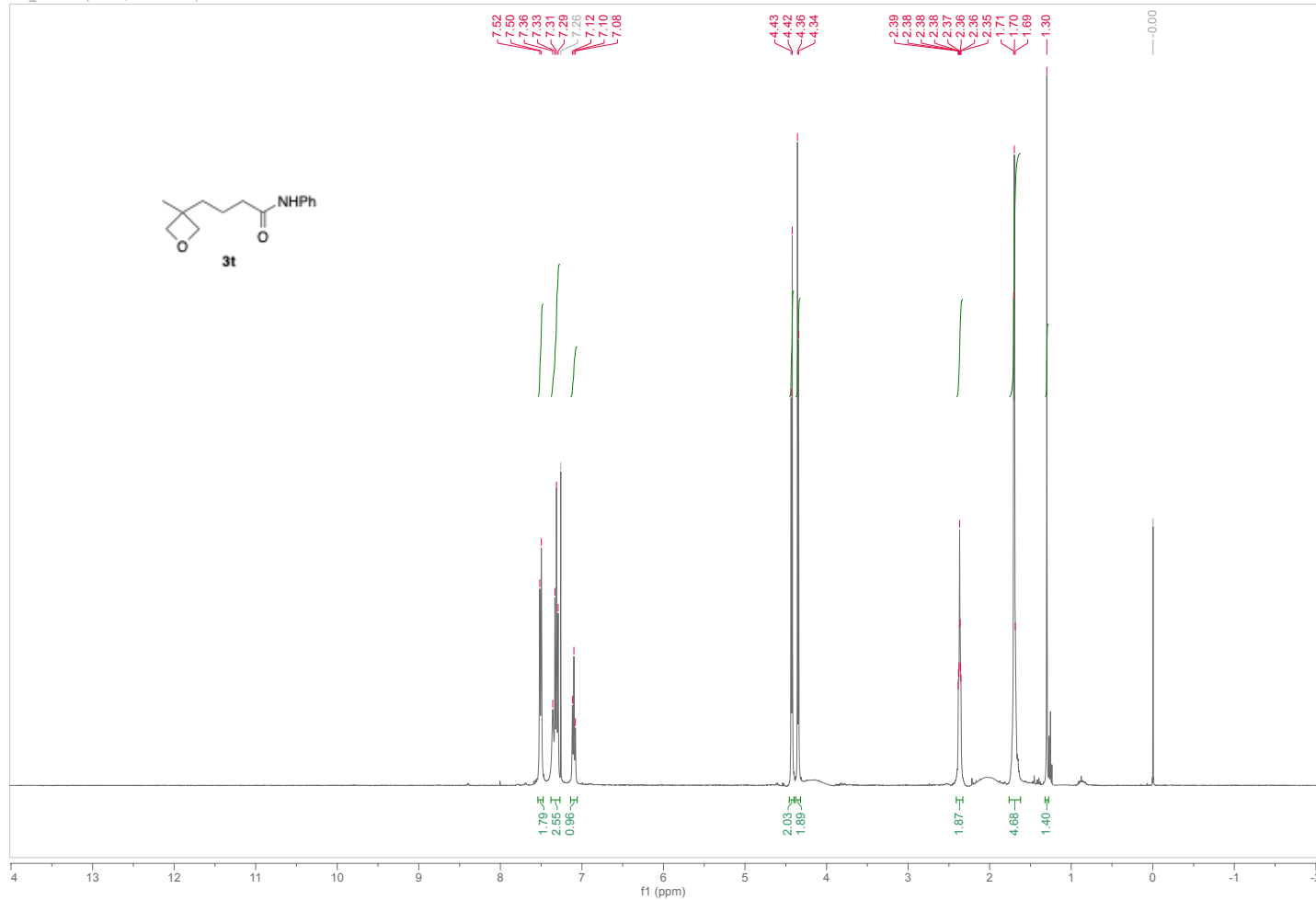
991\_1H NMR (CDCl<sub>3</sub>, 499.94 MHz at 25.0 °C)



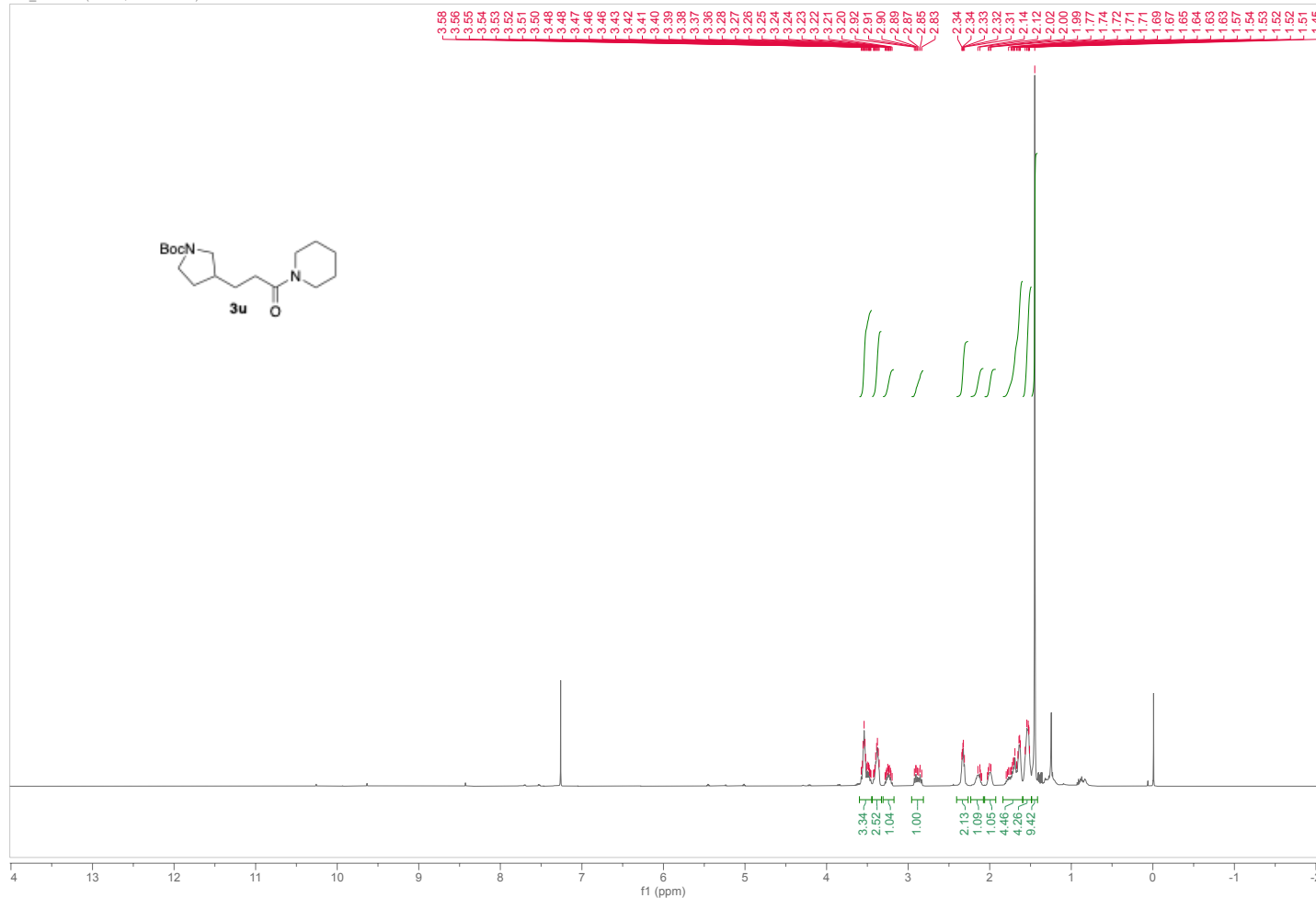
991\_13C NMR (CDCl<sub>3</sub>, 125.72 MHz at 25.0 °C)



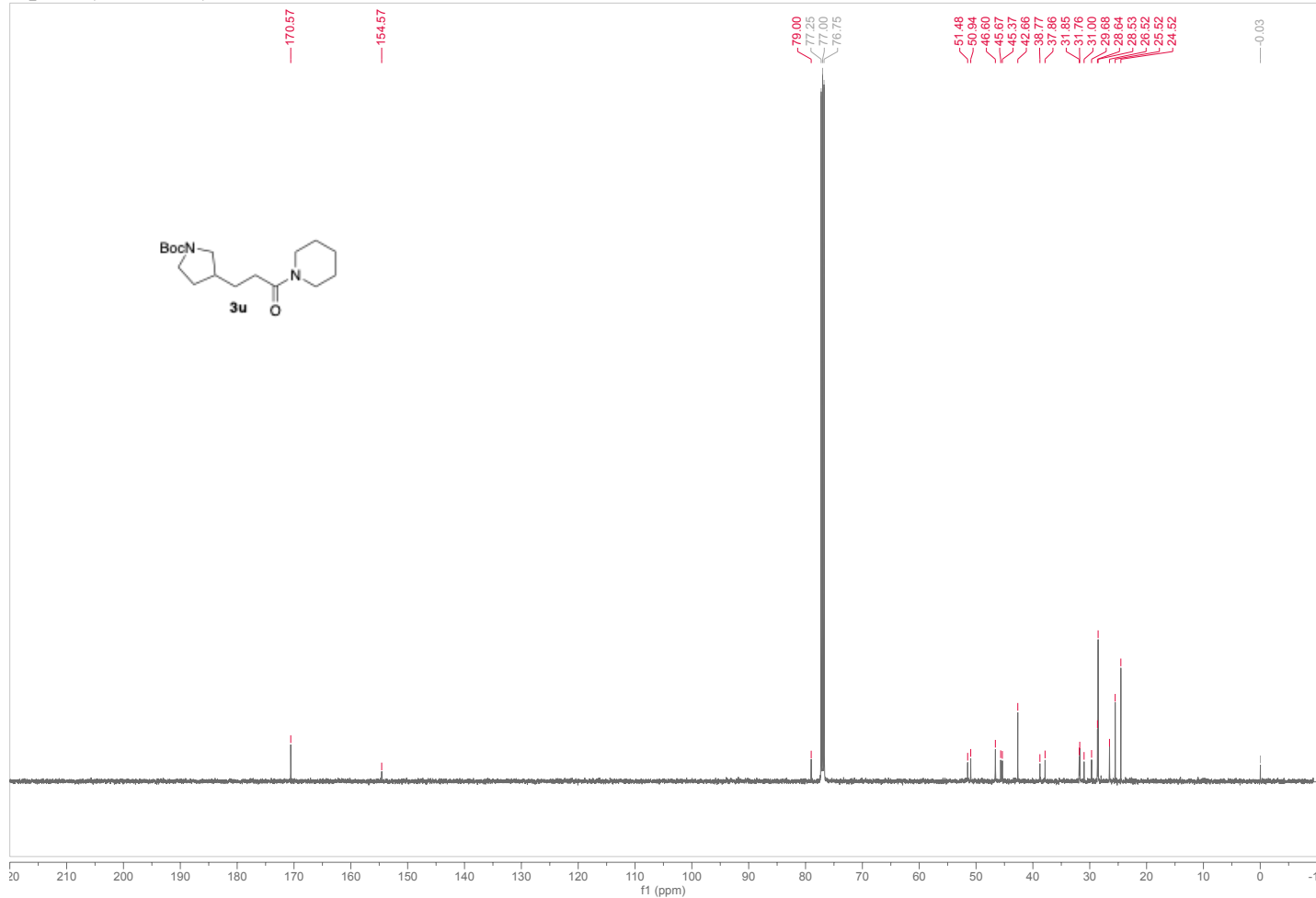




908\_1H NMR (CDCl<sub>3</sub>, 499.94 MHz)



908\_13C NMR (CDCl<sub>3</sub>, 125.72 MHz)



Chemical structure of **3v**: CC(C)(C)Si(C)(C)OC1CCCC[C@H]1CCCC(=O)O

<sup>1</sup>H NMR spectrum (CDCl<sub>3</sub>) of compound **3v**. The x-axis represents the chemical shift in ppm (f1), ranging from 4 to -2. The y-axis represents the intensity. The spectrum shows several peaks, with integration values provided below the baseline.

Integration values (from left to right): 2.15, 2.09, 1.12, 2.28, 1.23, 6.42, 6.42, 1.21, 10.66, 6.99.

Chemical structure of compound **3v** is shown above the spectrum. The structure is a cyclopentane ring substituted with a TBSO group and a (4-oxo-4-phenylbutyl) group. The spectrum displays the <sup>13</sup>C NMR data, with peaks labeled with their corresponding chemical shifts in ppm.

**Chemical structure of 3v:**

CC(C)(C)C(C)(C)C(C)(C)C1CCC(C1)C(=O)C2=CC=CC=C2

**13C NMR peaks (ppm):**

- 172.27
- 150.74
- 129.36
- 125.67
- 121.56
- 77.25
- 77.00
- 76.75
- 74.09
- 42.59
- 37.50
- 36.40
- 35.26
- 34.59
- 30.99
- 27.87
- 25.90
- 25.09
- 18.13
- 4.73
- 4.74

Chemical structure of compound **3w** is shown above the spectrum. The structure is a cyclohexane ring substituted with a TBSO group and a (4-oxo-4-phenylbutyl) group.

<sup>1</sup>H NMR spectrum (CDCl<sub>3</sub>) of compound **3w**. The x-axis represents the chemical shift in ppm (f1), ranging from 0 to 14. The spectrum shows several peaks, with integration values indicated below the baseline.

Integration values (from left to right): 2.26, 1.00, 2.12, 0.66, 0.34, 2.07, 0.60, 4.71, 6.55, 3.56, 9.82, 2.09, 4.24.

Chemical structure of **3x** is shown. The spectrum displays peaks corresponding to the structure, with integration values and chemical shifts (ppm) listed below the baseline and above the spectrum, respectively.

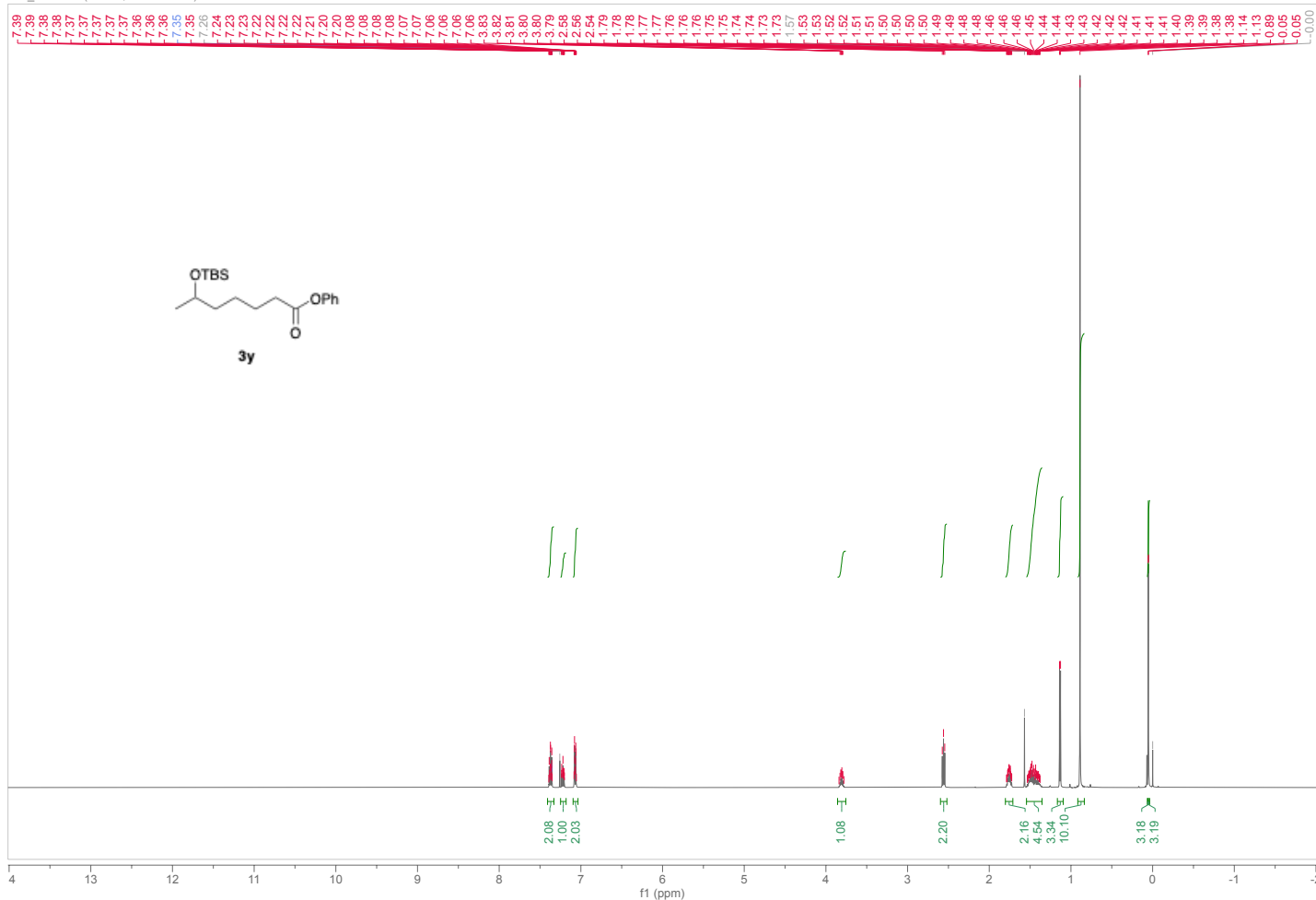
Chemical shifts (ppm) listed above the spectrum (from left to right):

- 7.29, 7.28, 7.27, 7.26, 7.25, 7.22, 7.20, 7.09, 7.07, 3.61, 3.60, 3.59, 3.58, 3.57, 3.56, 2.57, 2.55, 2.54, 1.97, 1.96, 1.95, 1.94, 1.86, 1.84, 1.83, 1.81, 1.80, 1.79, 1.77, 1.75, 1.74, 1.72, 1.60, 1.57, 1.57, 1.56, 1.56, 1.55, 1.54, 1.54, 1.52, 1.48, 1.47, 1.46, 1.45, 1.44, 1.43, 1.42, 1.41, 1.40, 1.40, 1.40, 1.39, 1.38, 1.36, 1.33, 1.27, 1.26, 1.25, 1.24, 1.23, 1.22, 1.20, 1.19, 1.18, 1.17, 1.15, 1.15, 1.13, 1.12, 1.11, 1.09, 1.07, 1.06, 1.05, 1.04, 1.02, 1.02, 1.00, 0.98, 0.96, 0.95, 0.94, 0.90, 0.90, 0.89, 0.86, 0.06.

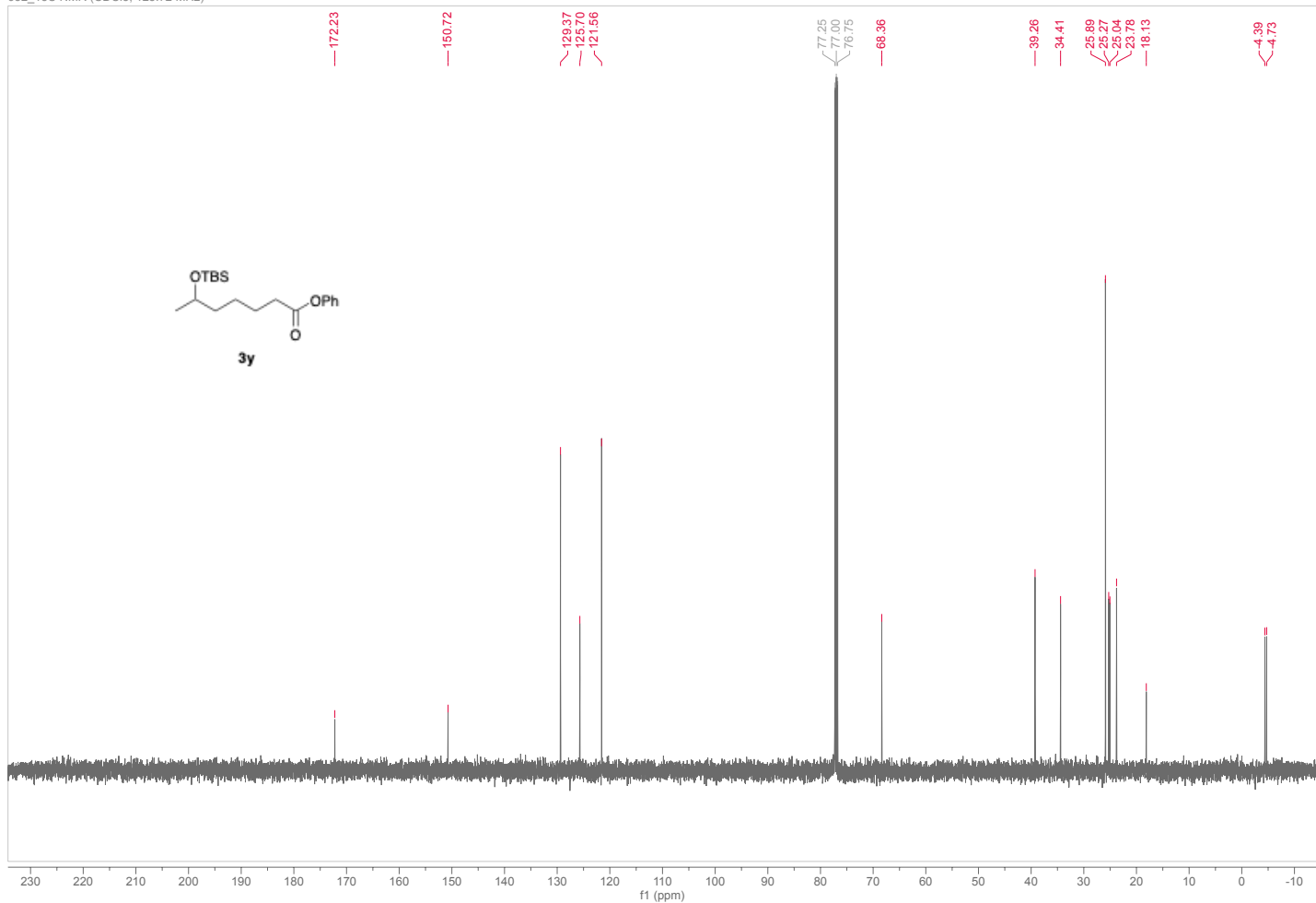
Integration values listed below the baseline (from left to right):

- 2.17, 1.00, 2.15, 1.27, 2.12, 1.18, 7.14, 2.12, 14.13, 19.51, 3.39, 6.94.

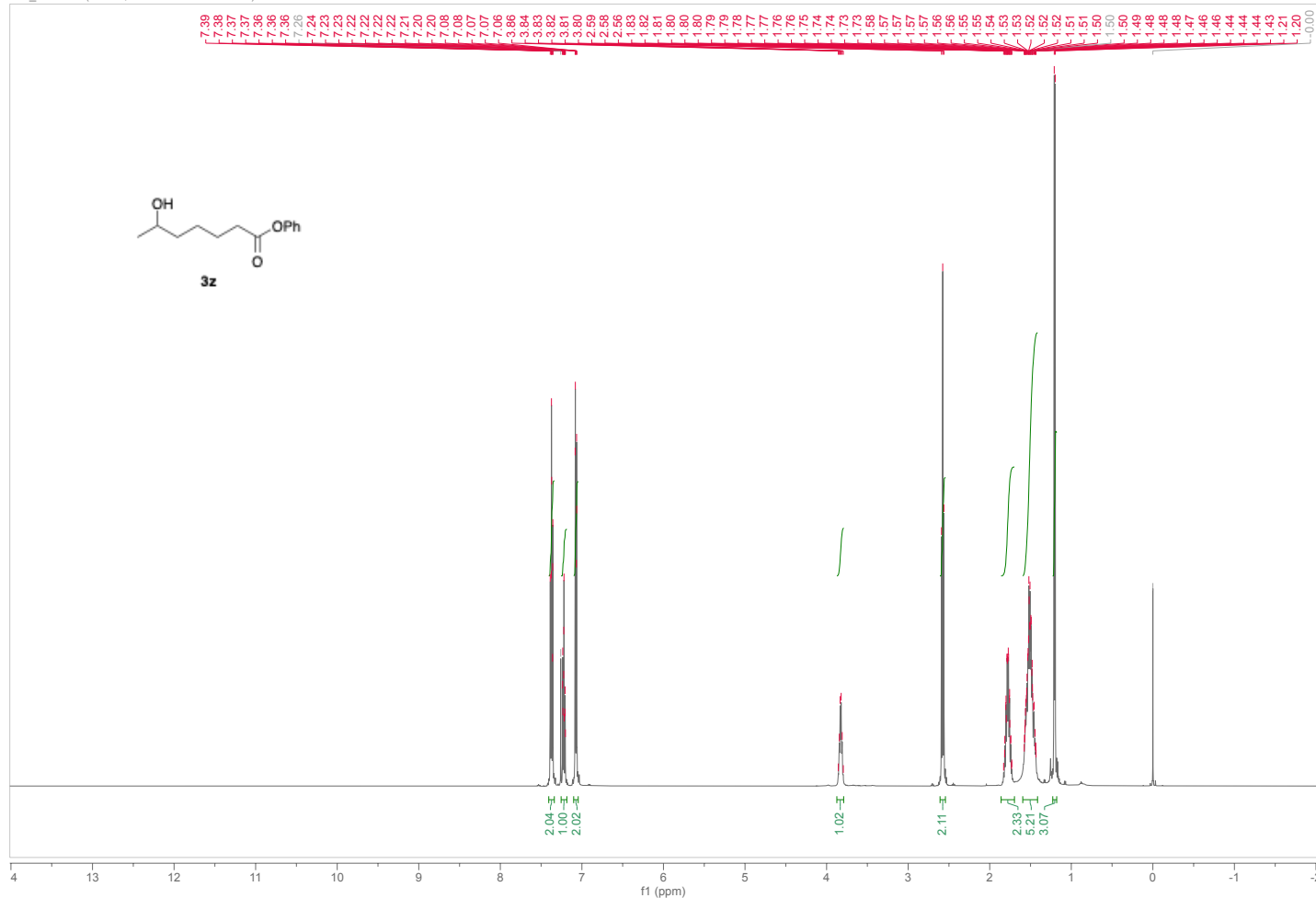
932\_1H NMR (CDCl<sub>3</sub>, 499.94 MHz)



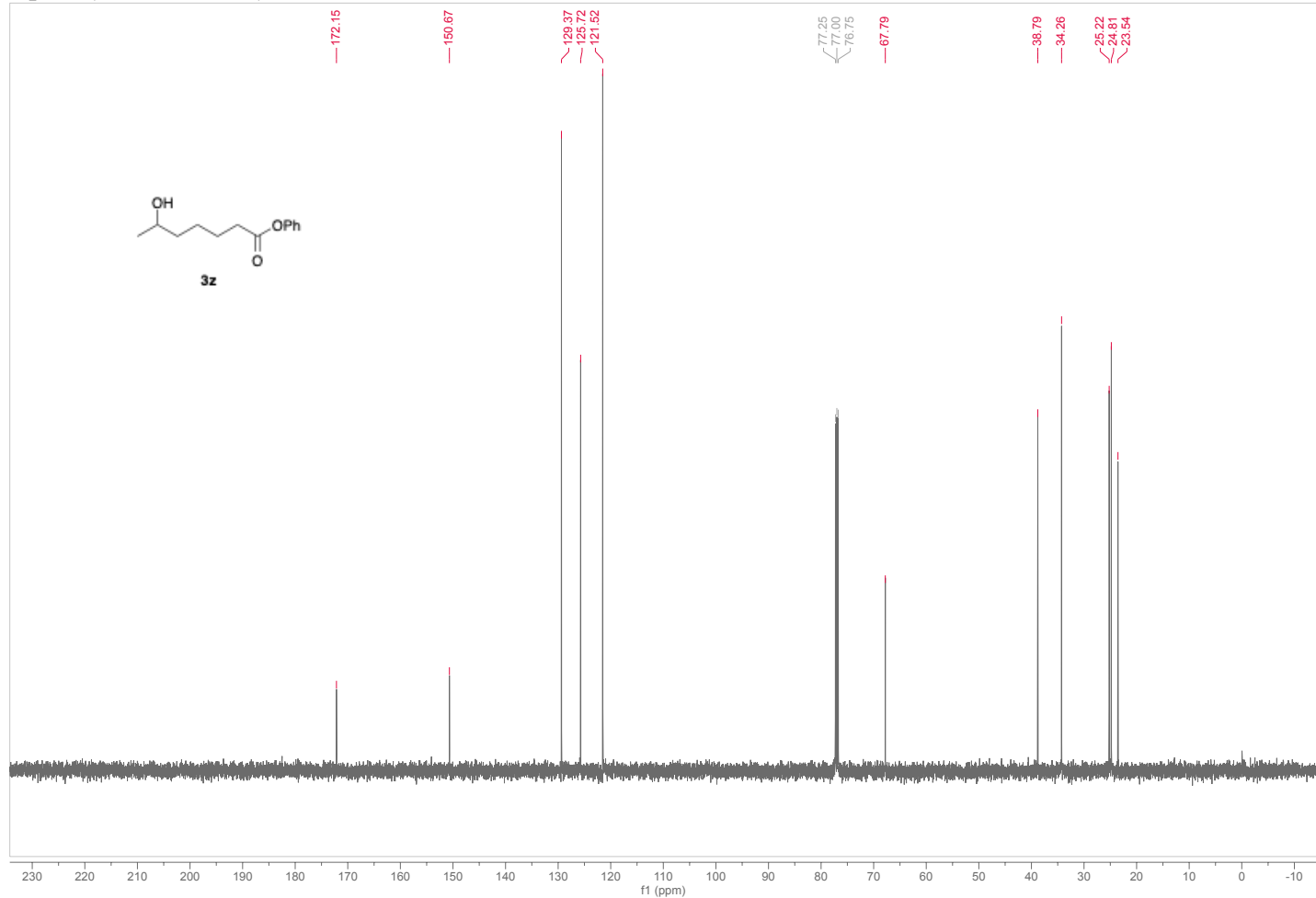
932\_13C NMR (CDCl<sub>3</sub>, 125.72 MHz)



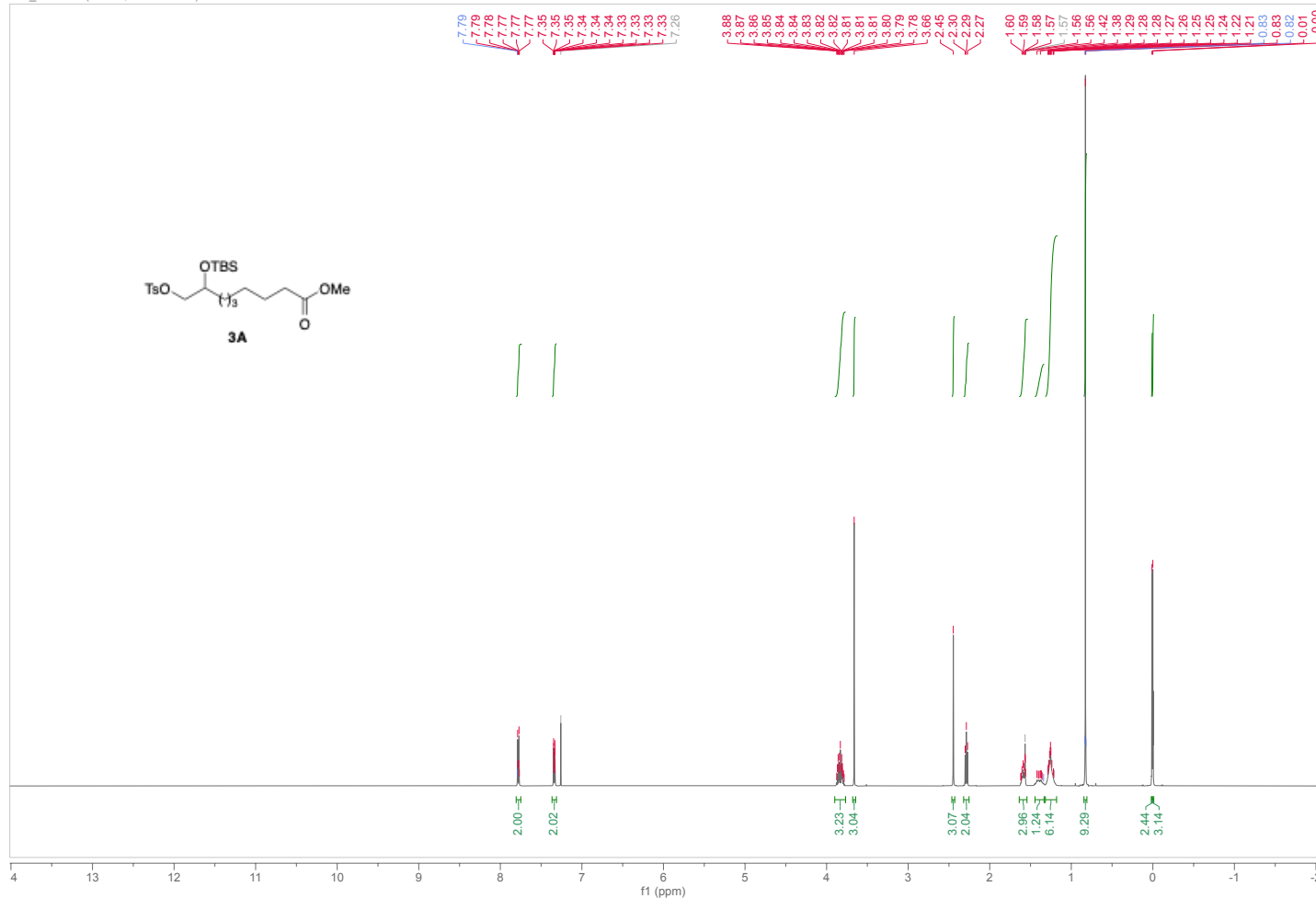
992\_1H NMR (CDCl<sub>3</sub>, 499.94 MHz at 25.0 °C)



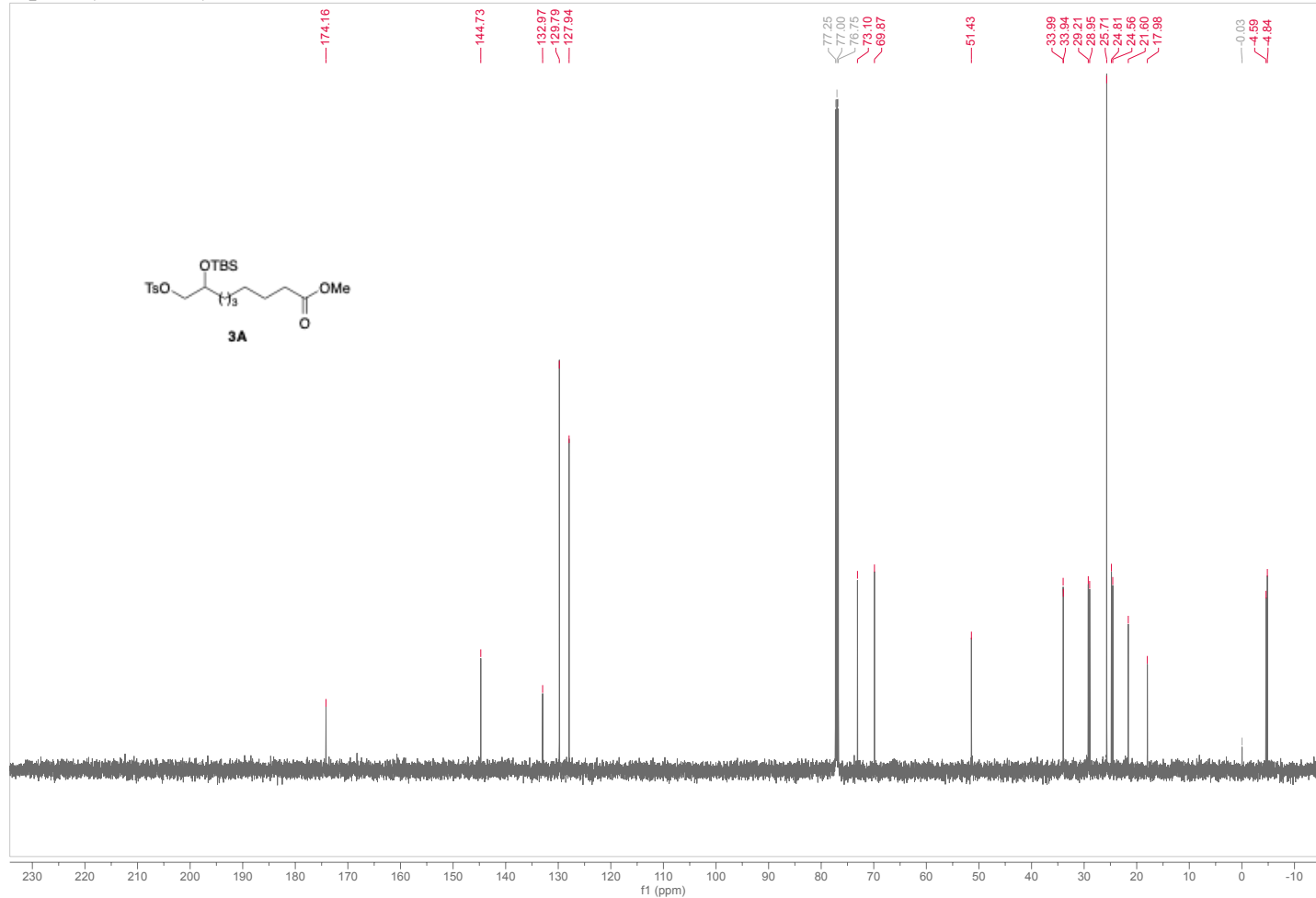
992\_13C NMR (CDCl<sub>3</sub>, 125.72 MHz at 25.0 °C)



871\_1H NMR (CDCl<sub>3</sub>, 499.94 MHz)



871\_13C NMR (CDCl<sub>3</sub>, 125.72 MHz)



Chemical structures of 5 and 6 are shown above the spectrum. The spectrum displays peaks corresponding to the reaction mixture, with integration values provided for several peaks.

Chemical structures of compounds 5 and 6 are shown above the spectrum:

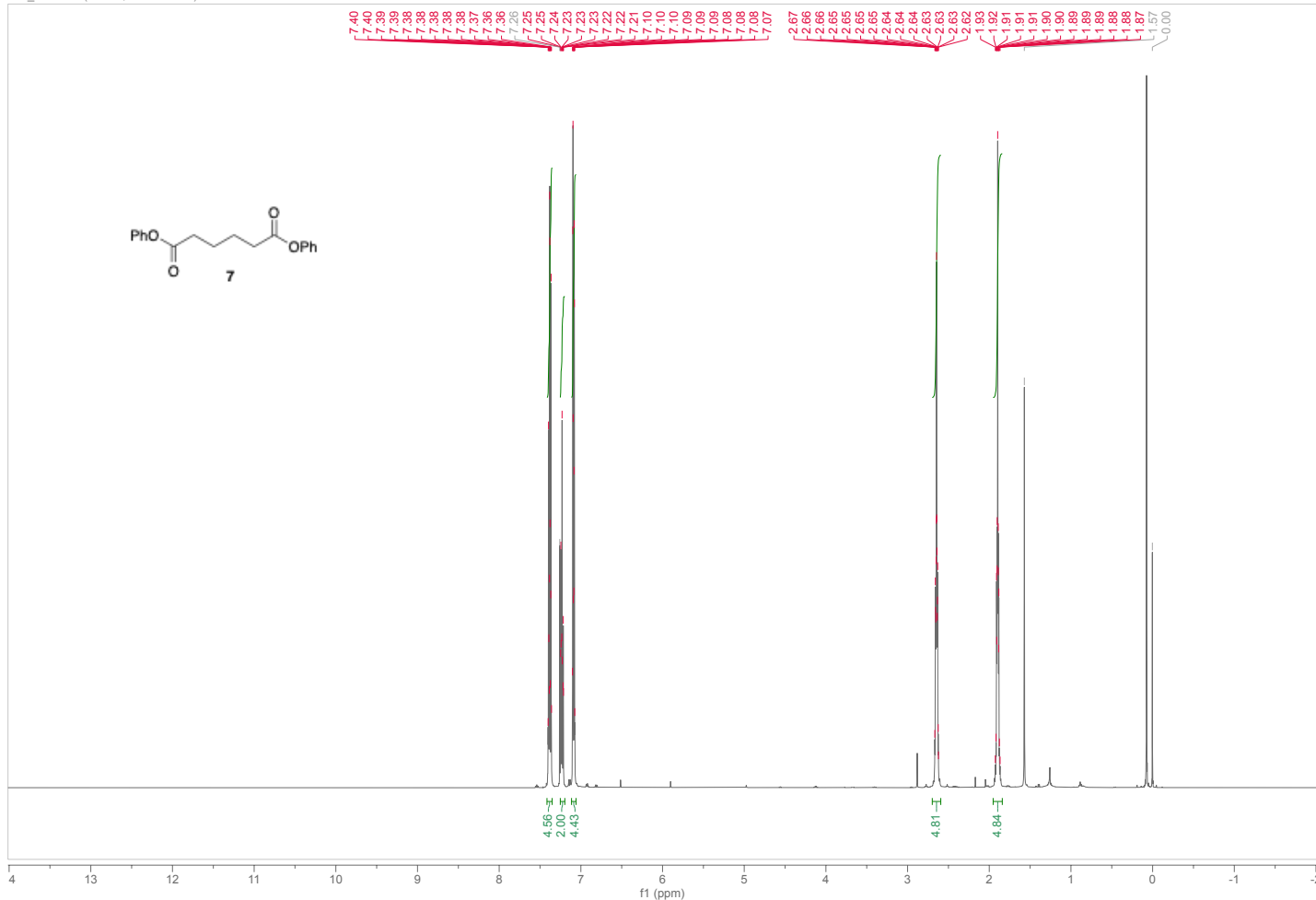
Compound 5: O=C(Oc1ccccc1)CCCC2CCCC2

Compound 6: O=C(Oc1ccccc1)CCCCC=C

The  $^{13}\text{C}$  NMR spectrum (f1 (ppm)) shows the following peak values (ppm):

- 172.30, 172.22
- 150.74, 150.73
- 138.93
- 125.35, 125.67, 125.66, 121.56, 121.54
- 114.31
- 77.25, 77.00, 76.75
- 39.80, 35.86, 34.11, 34.15, 33.25, 33.66, 32.60, 28.91, 28.68, 28.66, 25.14, 24.86, 24.15

919\_1H NMR (CDCl3, 499.94 MHz)



919\_13C NMR (CDCl3, 125.72 MHz)

