

Supporting information

Cross metathesis of allyl alcohols: how to suppress and how to promote double bond isomerization

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A General Remarks

All experiments were conducted in dry reaction vessels under an atmosphere of dry nitrogen. Solvents were purified by standard procedures. ¹H NMR spectra were obtained at 300 MHz or at 600 MHz in CDCl₃ with CHCl₃ (δ = 7.24 ppm) as an internal standard. Coupling constants (*J*) are given in Hz. ¹³C NMR spectra were recorded at 75 MHz or at 150 MHz in CDCl₃ with CDCl₃ (δ = 77.0 ppm) as an internal standard. The number of coupled protons was analyzed by APT-experiments and is denoted by a number in parentheses following the chemical shift value. IR spectra were recorded neat on NaCl or KBr plates. Wavenumbers (ν) are given in cm⁻¹. The peak intensities are defined as strong (s), medium (m) or weak (w). Mass spectra were obtained at 70 eV. The allyl alcohols **4a**^[1], **4b**^[2], **4c**^[3], **4d**^[4], **4f**^[5], **4g**^[6], **4h**^[7], **4i**^[8], **4j**^[9], **4k**^[10], **4l**^[11], **4m**^[12], **4n**^[13], **4o**^[14], **4p**^[15] were synthesized following literature procedures.

¹ S. V. Ley, A. Armstrong, D. Díez-Martín, M. J. Ford, P. Grice, J. G. Knight, H. C. Kolb, A. Madin, C. A. Marby, S. Mukherjee, A. N. Shaw, A. M. Z. Slawin, S. Vile, A. D. White, D. J. Williams and M. Woods, *J. Chem. Soc., Perkin Trans. 1*, 1991, 667-692.

² S. Jautze and R. Peters, *Angew. Chem., Int. Ed.* 2008, **47**, 9284-9288.

³ J. Stambasky, A. V. Malkov and P. Kocovsky, *J. Org. Chem.* 2008, **73**, 9148-9150.

⁴ D. Wigfield, S. Feiner, G. Malbacho and K. Taymaz, *Tetrahedron* 1974, **30**, 2949-2959.

⁵ H. Azuma, K. Miyasaka, T. Yokotani, T. Tachibana, A. Kojima-Yuasa, I. Matsui-Yuasa, and K. Ogino, *Bioorg. Med. Chem.* 2006, **14**, 1811-1818.

⁶ J. Krauss and D. Unterreitmeier, *Arch. Pharm. Chem. Life Sci.* 2002, **335**, 94-98.

⁷ A. W. J. Logan, M. S. Hallside, J. W. Burton, and J. S. Parker, *Org. Lett.* 2012, **14**, 2940-2943.

⁸ H. Lin, Y. Liu and Z.-L. Wu, *Chem. Comm.* 2011, **47**, 2610-2612.

⁹ B. Trost and R. Kulawiec, *J. Am. Chem. Soc.* 1993, **115**, 2027-2036.

¹⁰ M. E. Maier, H. Kandler, B. U. Haller, J. H. Hofmann and H. Fischer, *H. Liebigs Ann. Chem.* 1990, 323-330.

¹¹ N. Sarkar, A. Nayek, and S. Ghosh, *Org. Lett.* 2004, **6**, 1903-1905.

¹² B. Schmidt, *J. Org. Chem.* 2004, **69**, 7672-7687.

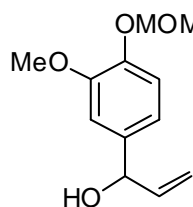
¹³ H. E. Ramsden, J. R. Leebrick, S. D. Rosenberg, E. H. Miller, J. J. Walburn, A. E. Balint and R. Cserr, *J. Org. Chem.* 1957, **22**, 1602-1605.

¹⁴ T. J. Deming, B. M. Novak and J. W. Ziller, *J. Am. Chem. Soc.* 1994, **116**, 2366-2374.

¹⁵ R. G. Woolford, *J. Org. Chem.* 1958, **23**, 2042-2043.

B Experimental procedure, analytical data and copies of NMR spectra of 4e

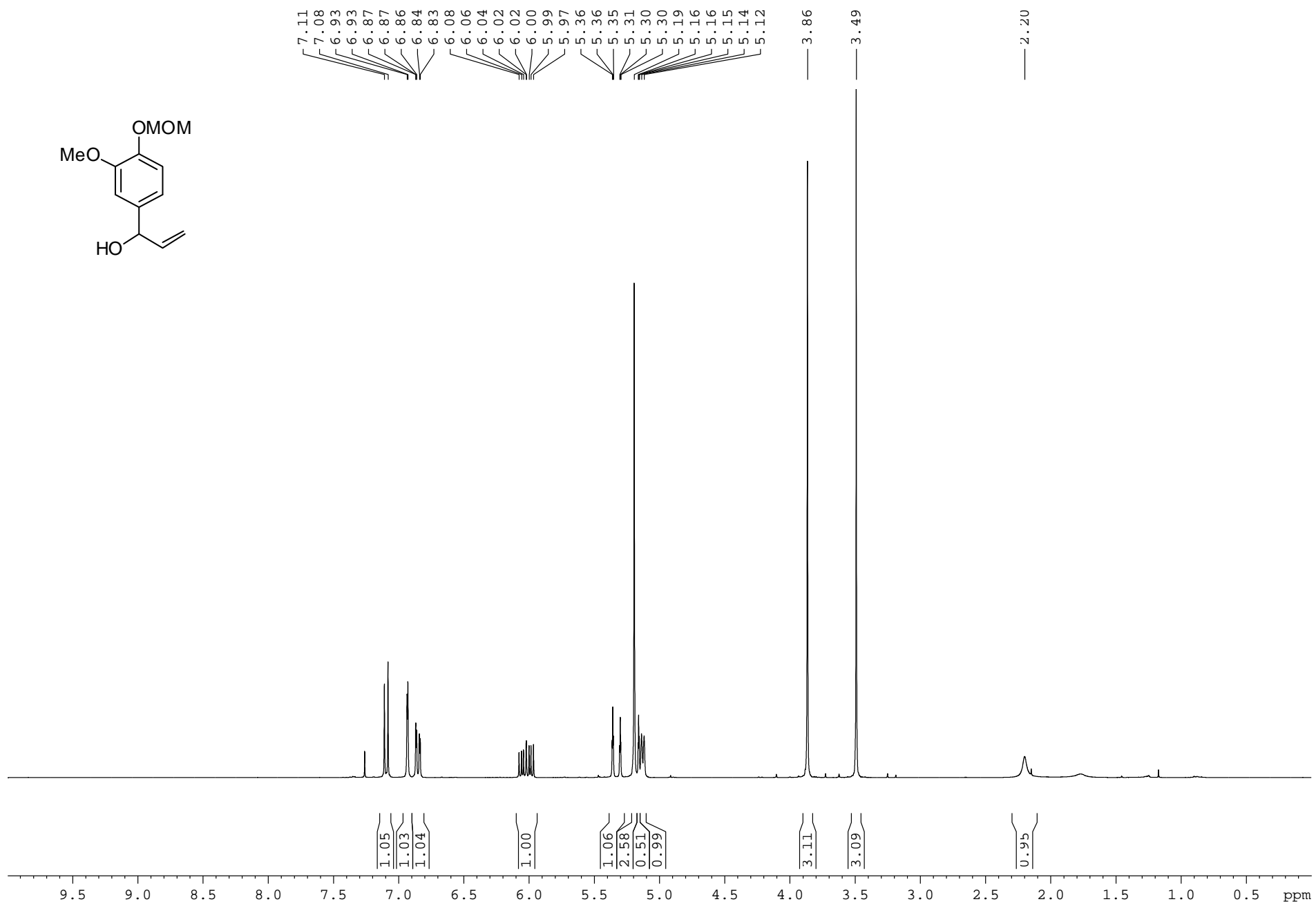
Synthesis of 1-(3-methoxy-4-(methoxymethoxy)-phenyl)-prop-2-en-1-ol (4e)



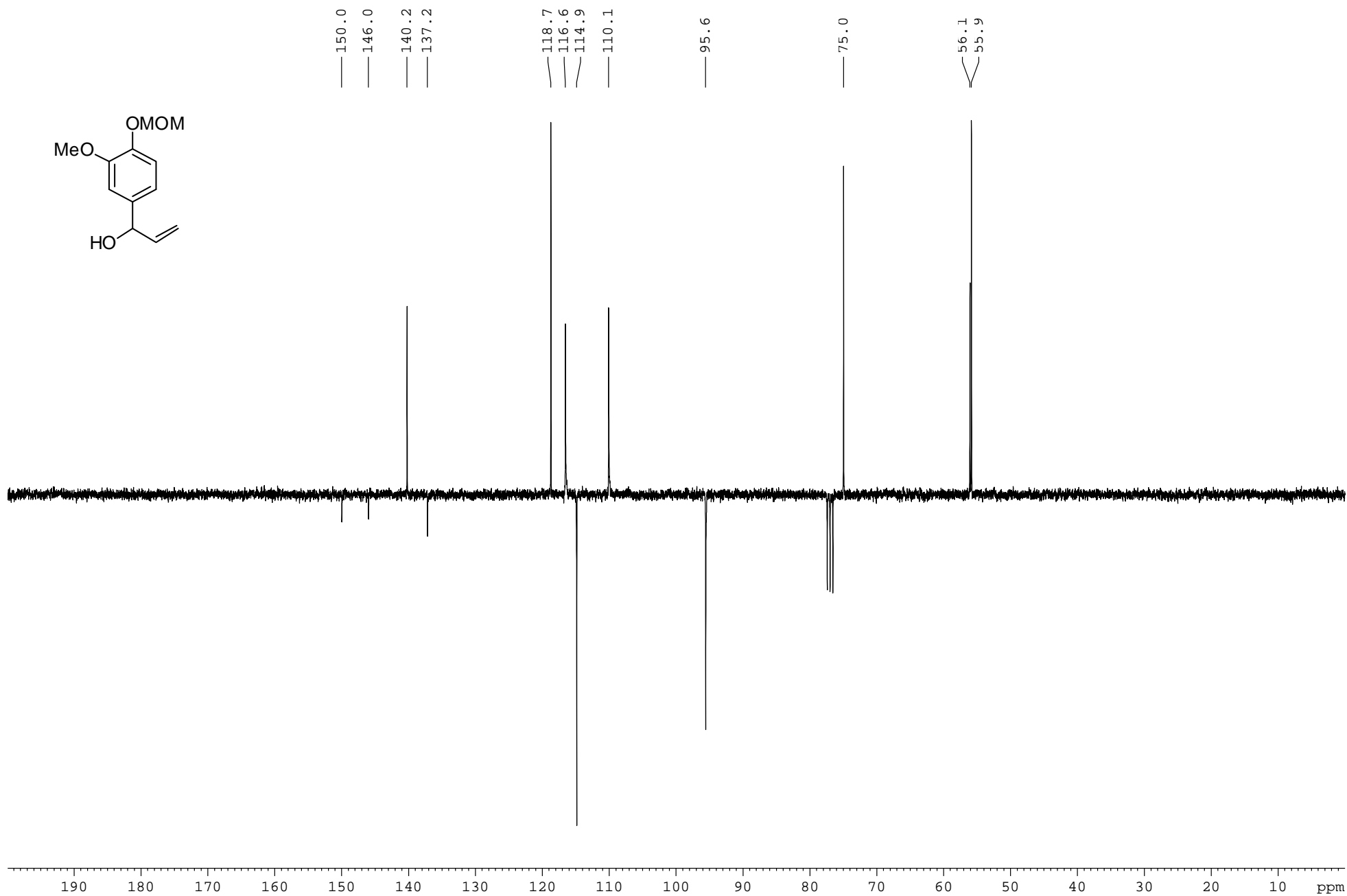
To a solution of MOM-protected vanilline^[16] (577 mg, 2.9 mmol) in CH₂Cl₂ (15 mL) was added a solution of vinyl magnesium chloride in THF (1.7 M, 1.8 mL, 3.1 mmol) at 0°C. The mixture was stirred for 0.5 h and then poured onto an aqueous NH₄Cl solution. The organic layer was separated, and the aqueous layer was extracted twice with MTBE. The combined organic extracts were dried with MgSO₄, filtered, and the solvent was evaporated under reduced pressure. After purification by column chromatography the allyl alcohol **4e** (548 mg, 83%) was obtained as a colourless liquid. ¹H NMR (300 MHz, CDCl₃) δ 7.09 (d, *J* = 8.2, 1H), 6.93 (d, *J* = 1.9, 1H), 6.85 (dd, *J* = 8.2, 1.6, 1H), 6.02 (ddd, *J* = 17.1, 10.3, 5.8, 1H), 5.33 (ddd, *J* = 17.1, 1.4, 1.4, 1H), 5.19 (s, 2H), 5.17 (ddd, *J* = 10.3, 1.4, 1.3, 1H), 5.13 (d, *J* = 5.9, 1H), 3.86 (s, 3H), 3.49 (s, 3H), 2.20 (bs, 3H); ¹³C NMR (75 MHz, CDCl₃) δ 150.0 (0), 146.0 (0), 140.2 (1), 137.2 (0), 118.7 (1), 116.6 (1), 114.9 (2), 110.1 (1), 95.6 (2), 75.0 (1), 56.1 (3), 55.9 (3); IR (neat): ν 3418 (w), 2937 (w), 1509 (s), 1260 (s), 1152 (s), 1131 (s), 985 (s); MS (EI): *m/z* 224 ([M]⁺, 38), 162 (35), 119 (17), 55 (17), 45 (100); HRMS (EI): calcd for C₁₂H₁₆O₄ [M]⁺: 224.1056, found: 224.1049.

¹⁶ Prepared according to: K. Tangdenpaisal, S. Sualek, S. Ruchirawat and P. Ploypradith, *Tetrahedron* 2009, **65**, 4316-4325.

^1H NMR (CDCl_3 , 300 MHz) of **4e**

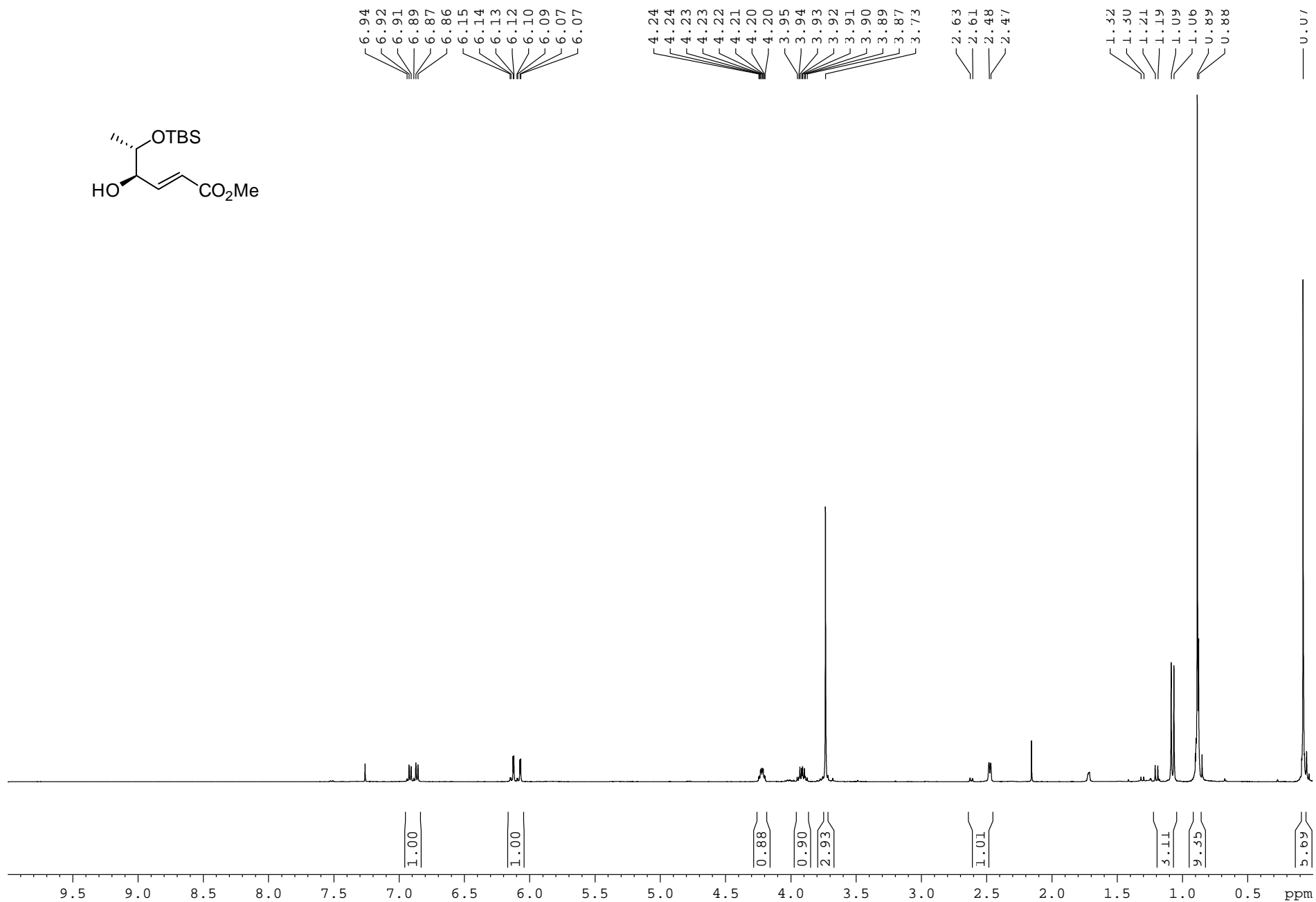
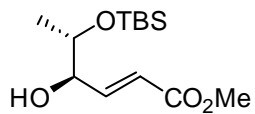


^{13}C NMR-APT (CDCl_3 , 75 MHz) of **4e**

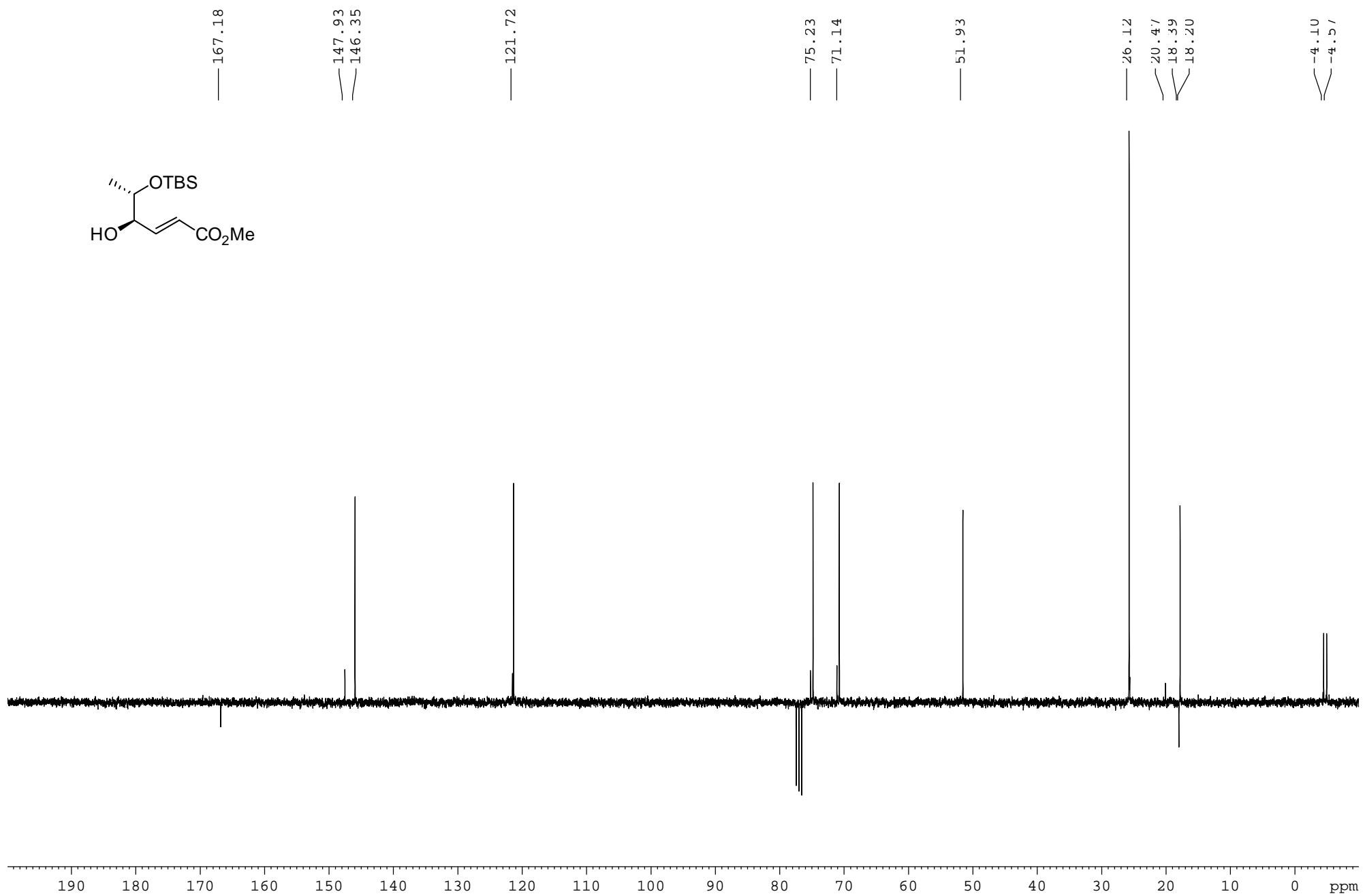


C Copies of NMR spectra of cross metathesis products 5

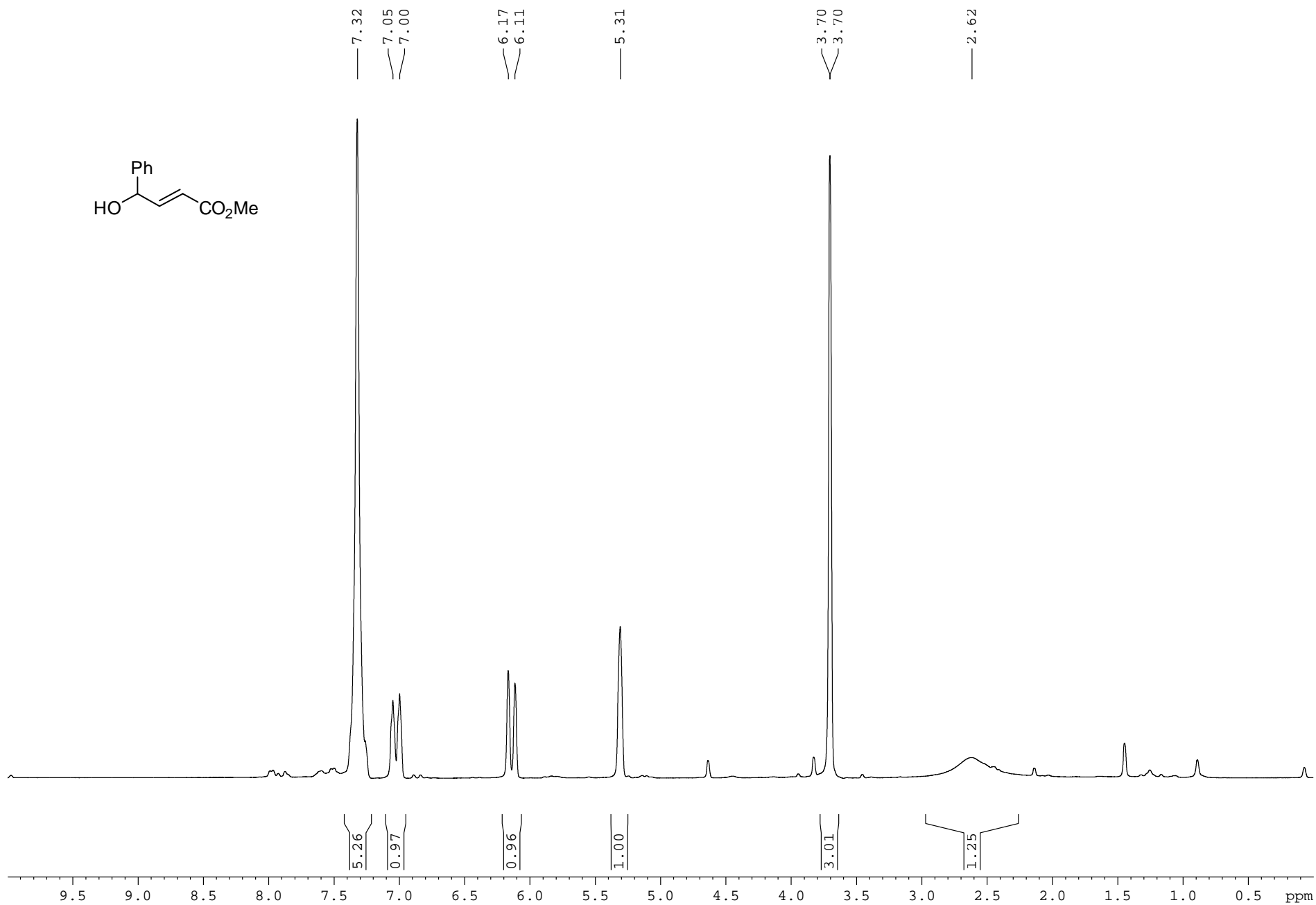
¹H NMR (CDCl₃, 300 MHz) of 5a



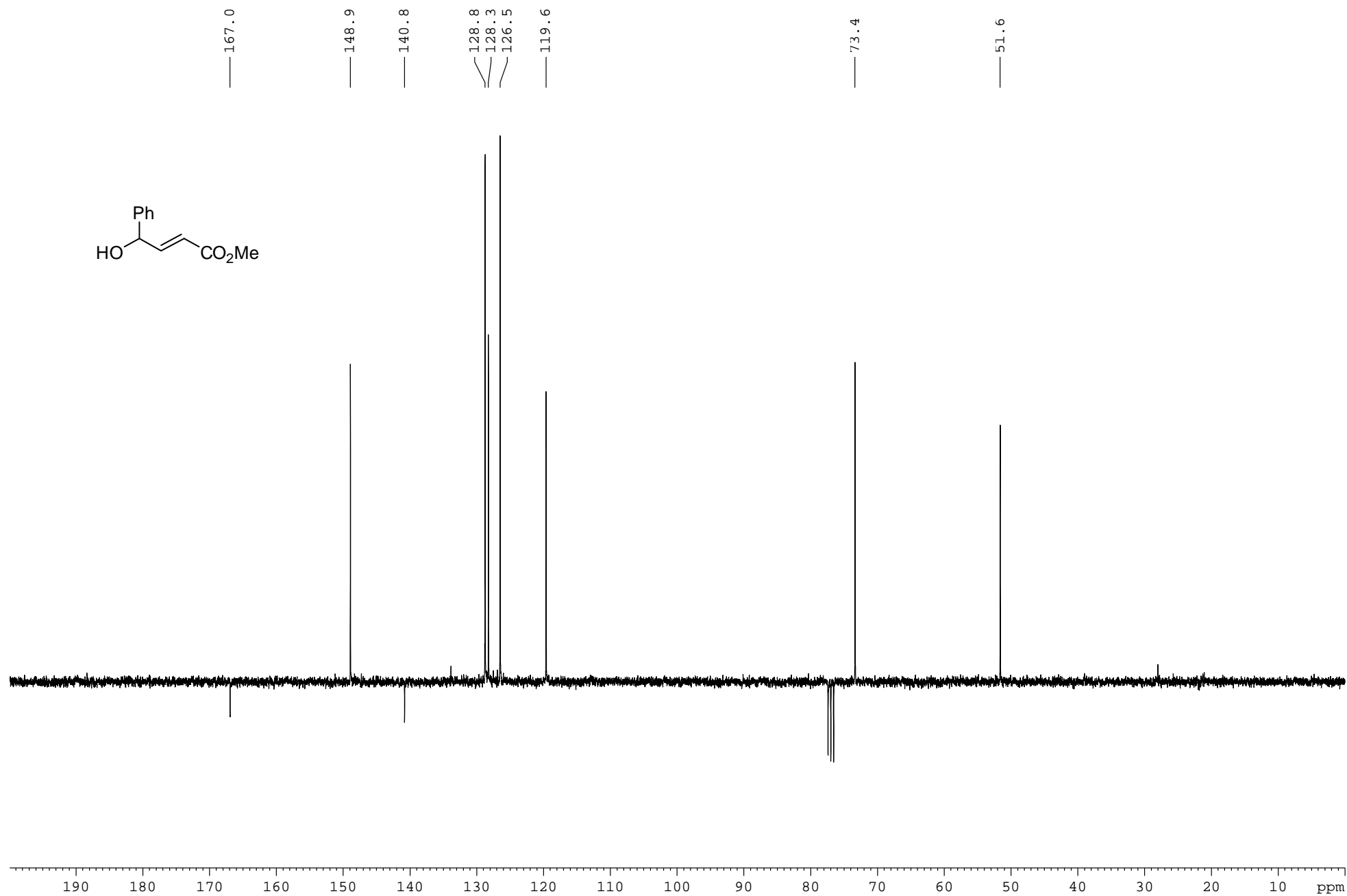
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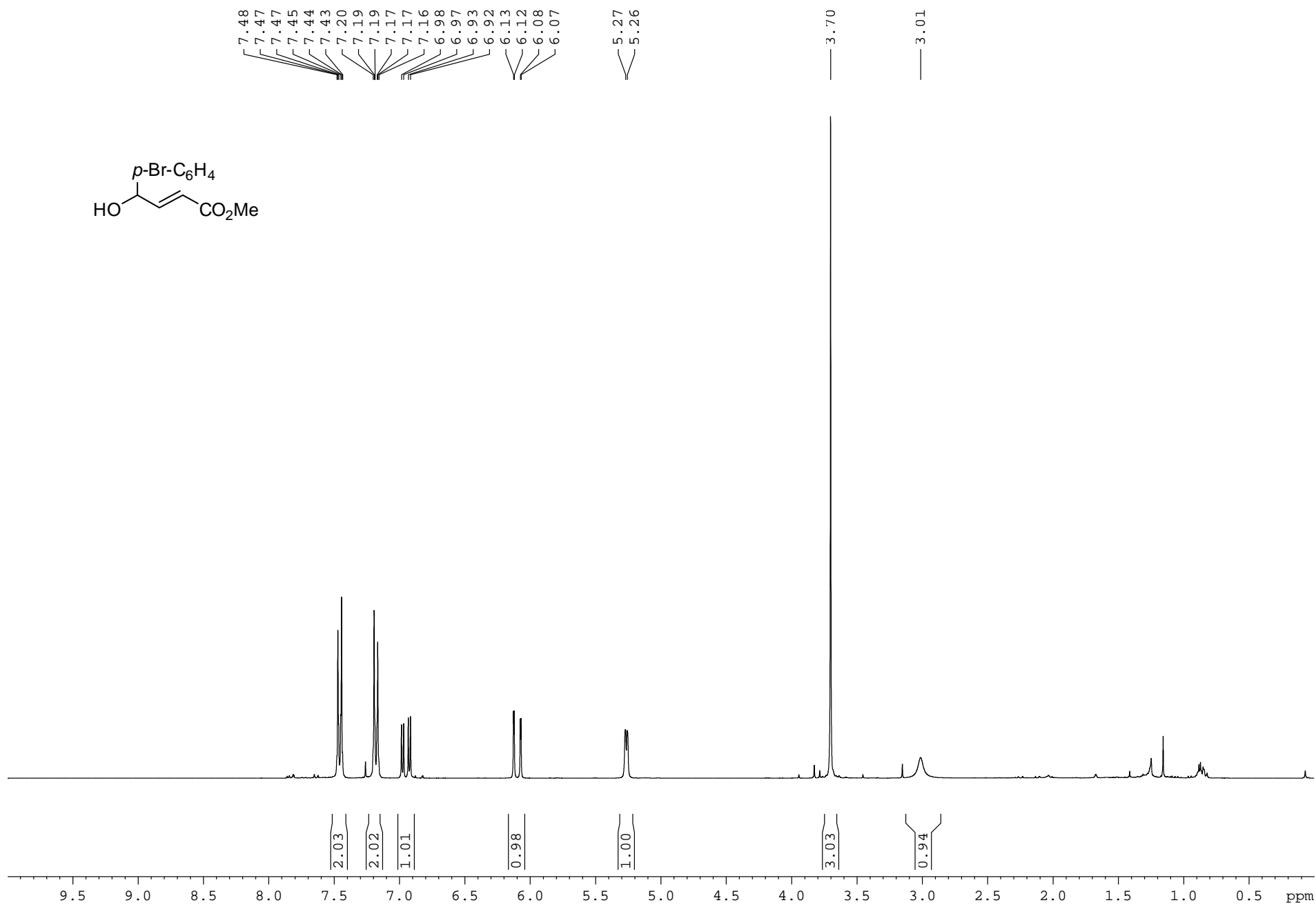
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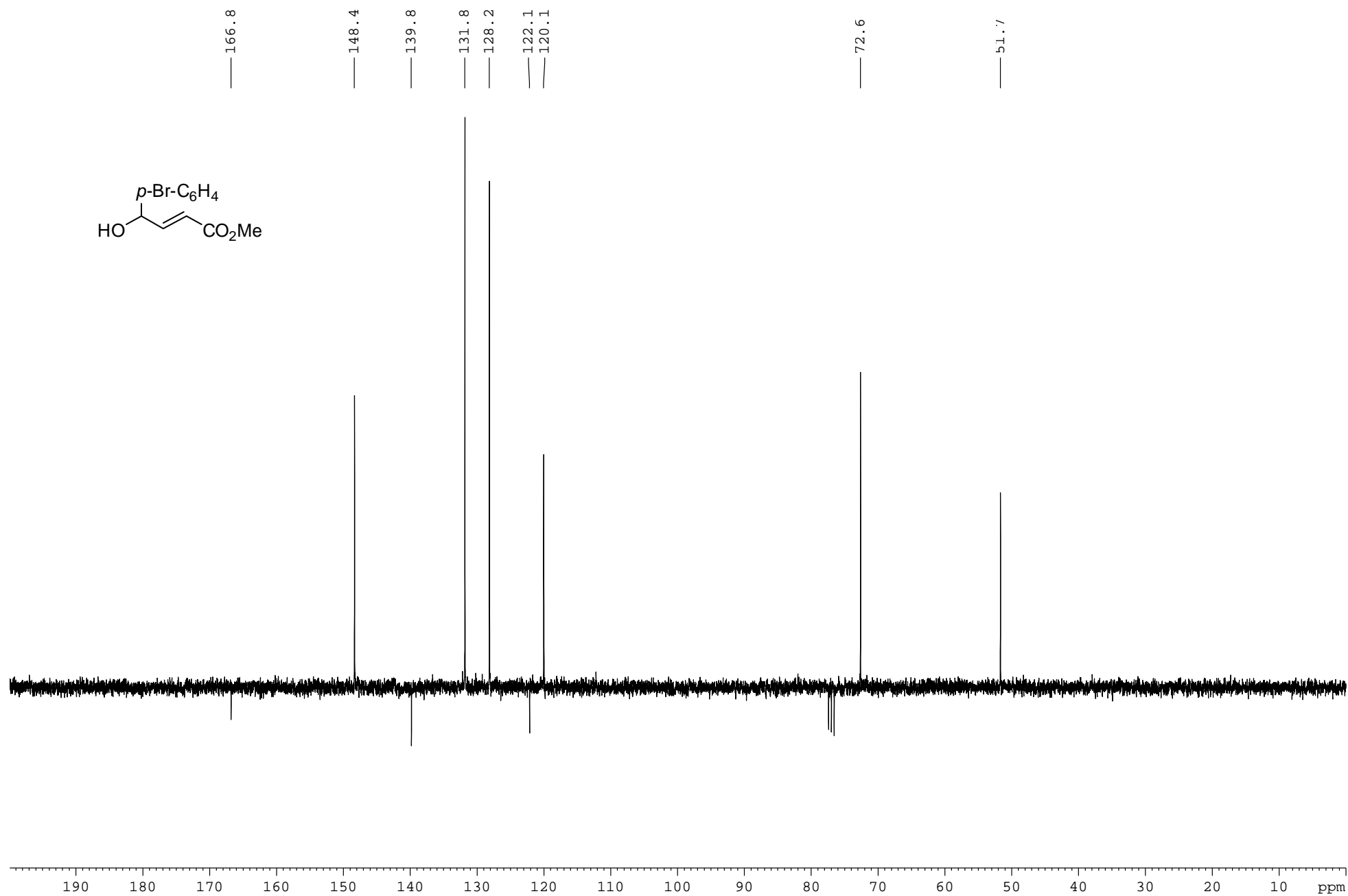
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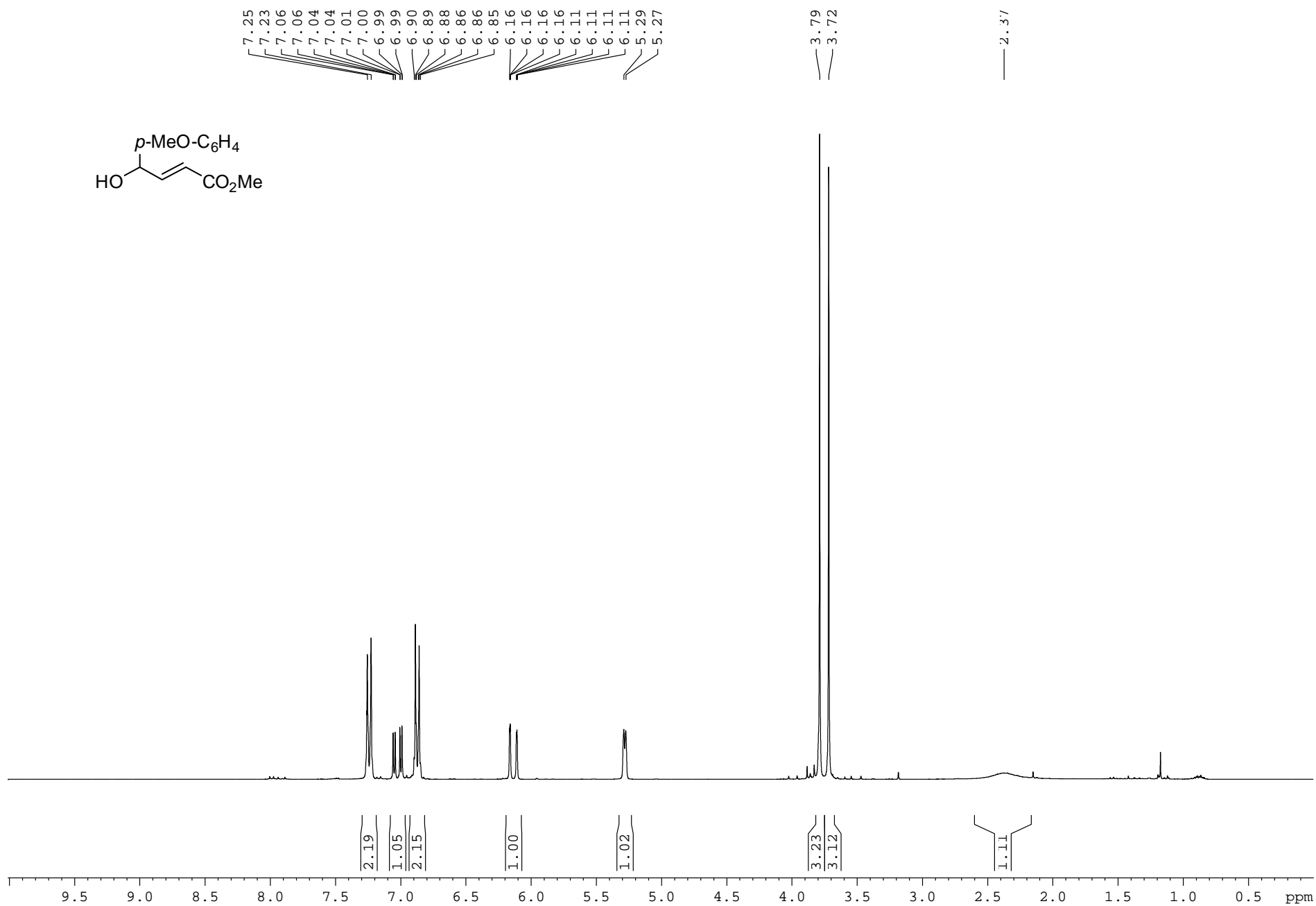
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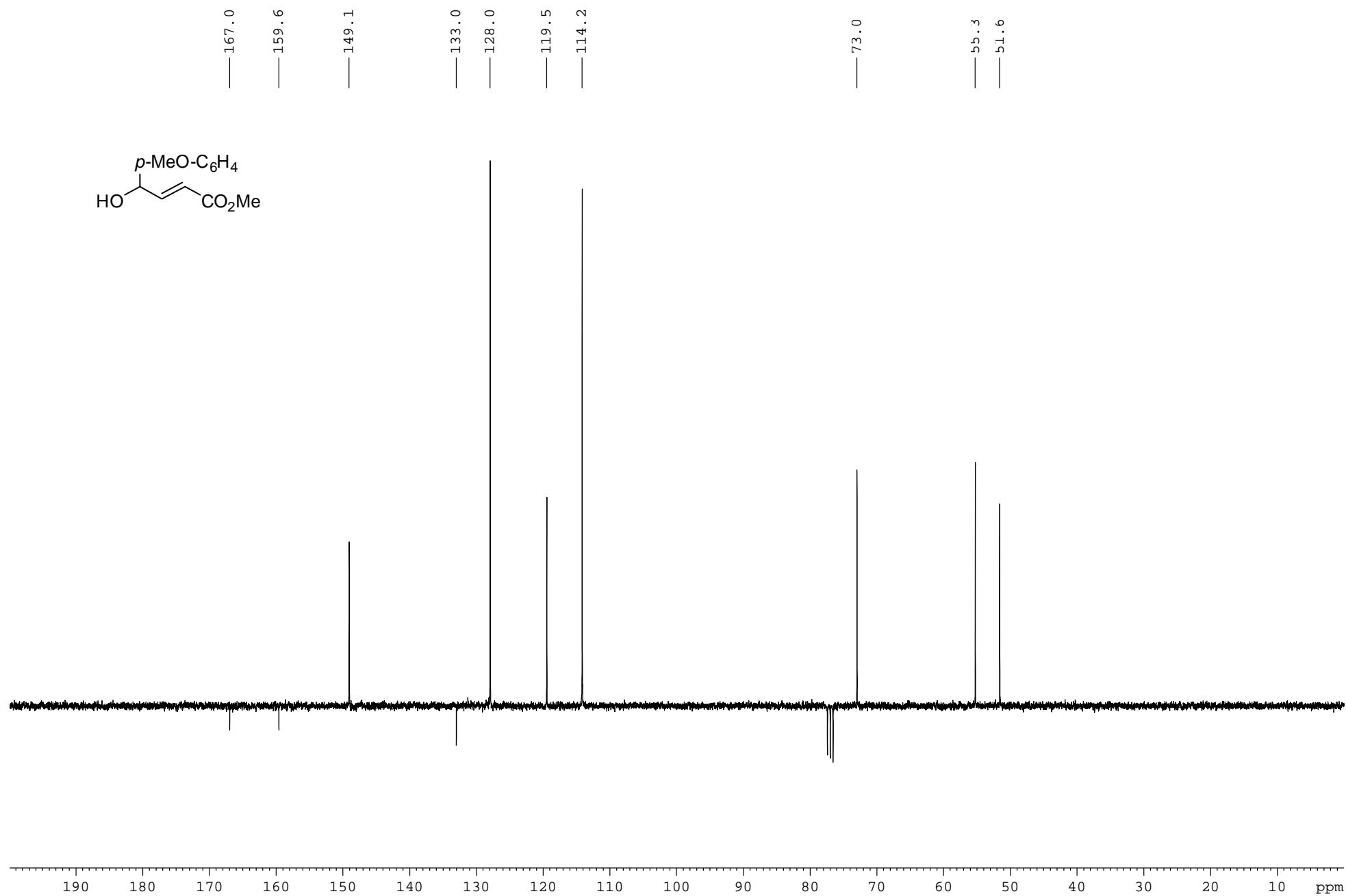
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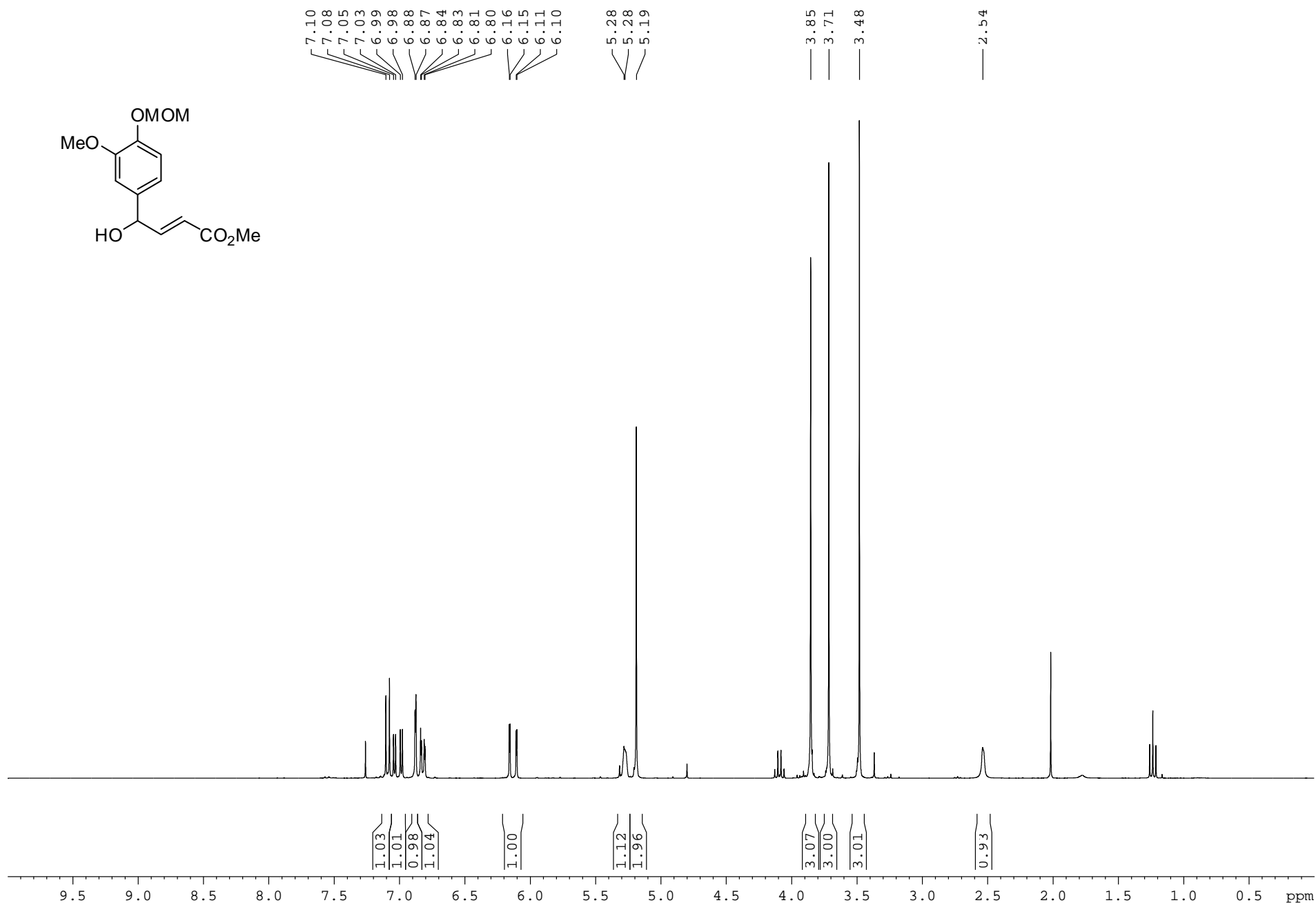
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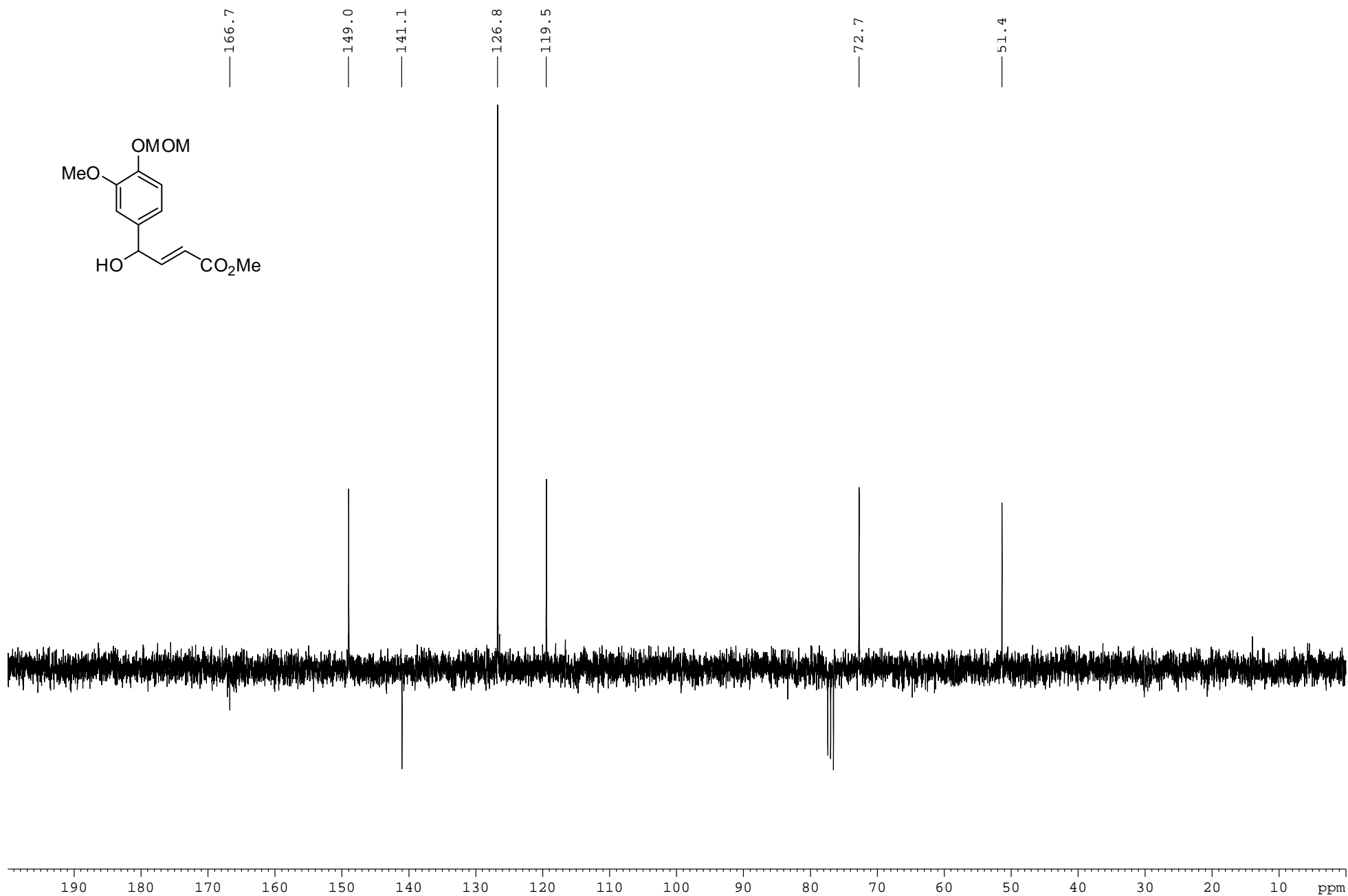
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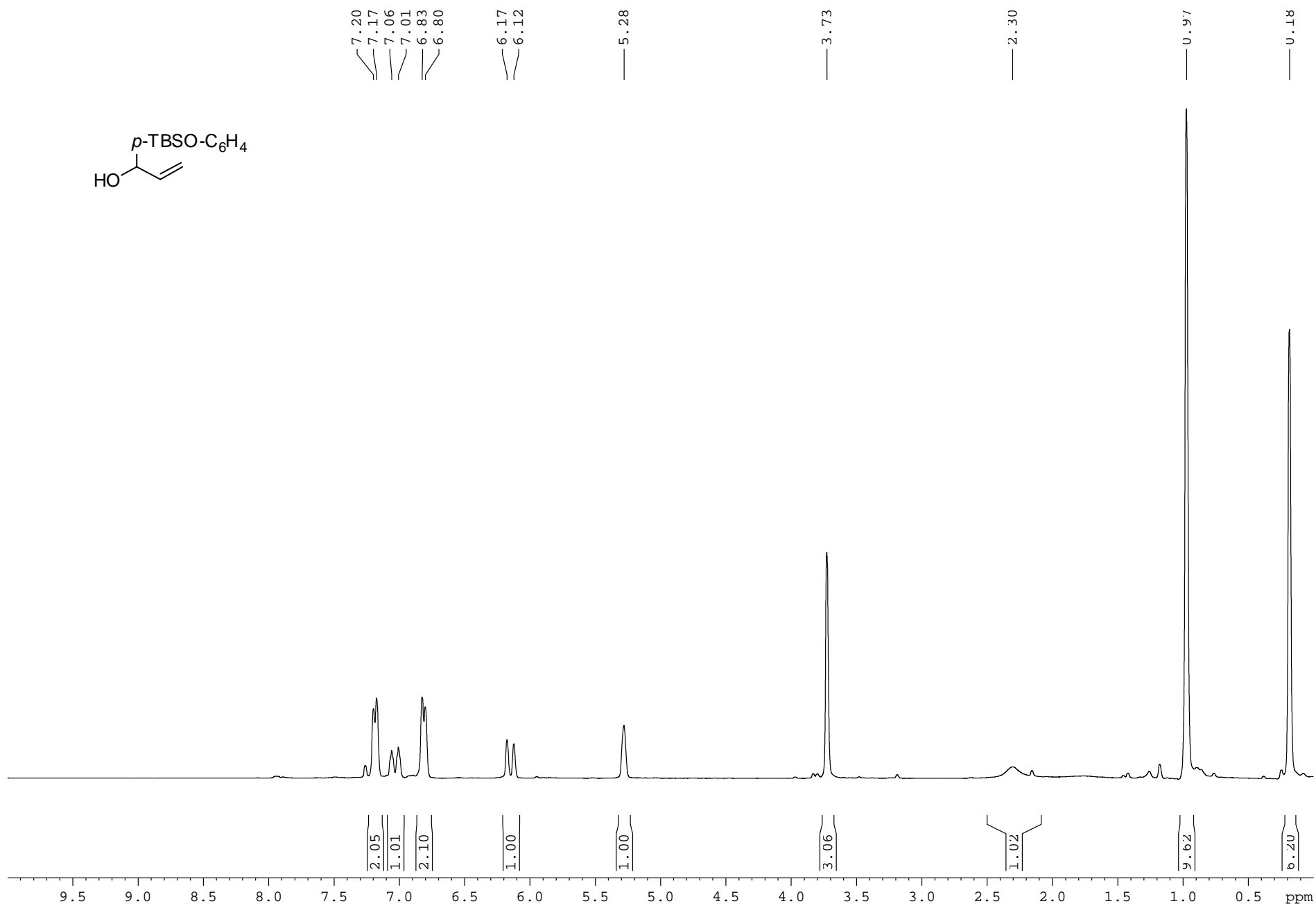
^1H NMR (CDCl_3 + drop of aceton- d_6 , 300 MHz) of **5e**



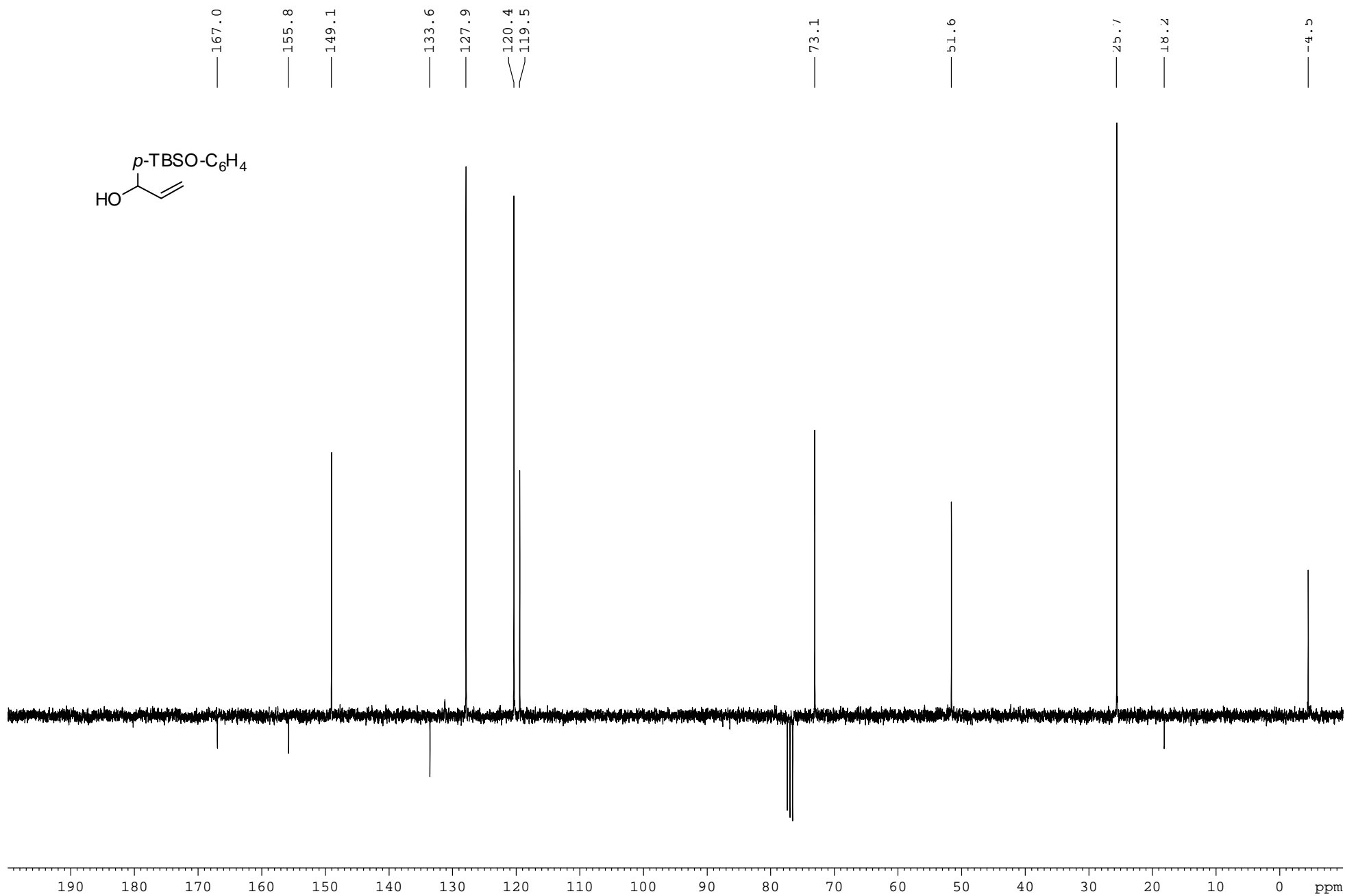
^{13}C NMR-APT (CDCl_3 + drop of aceton- d_6 , 75 MHz) of **5e**



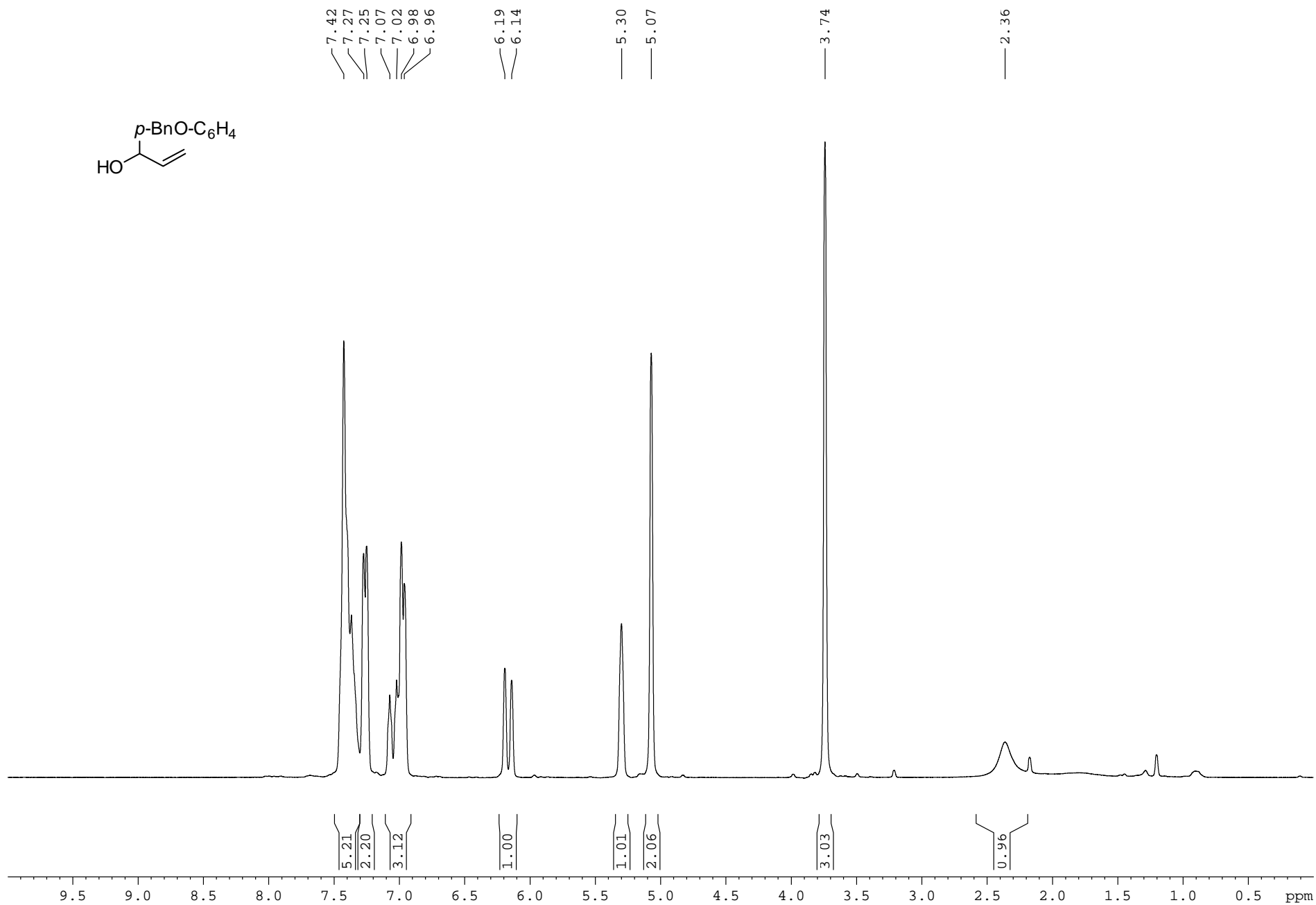
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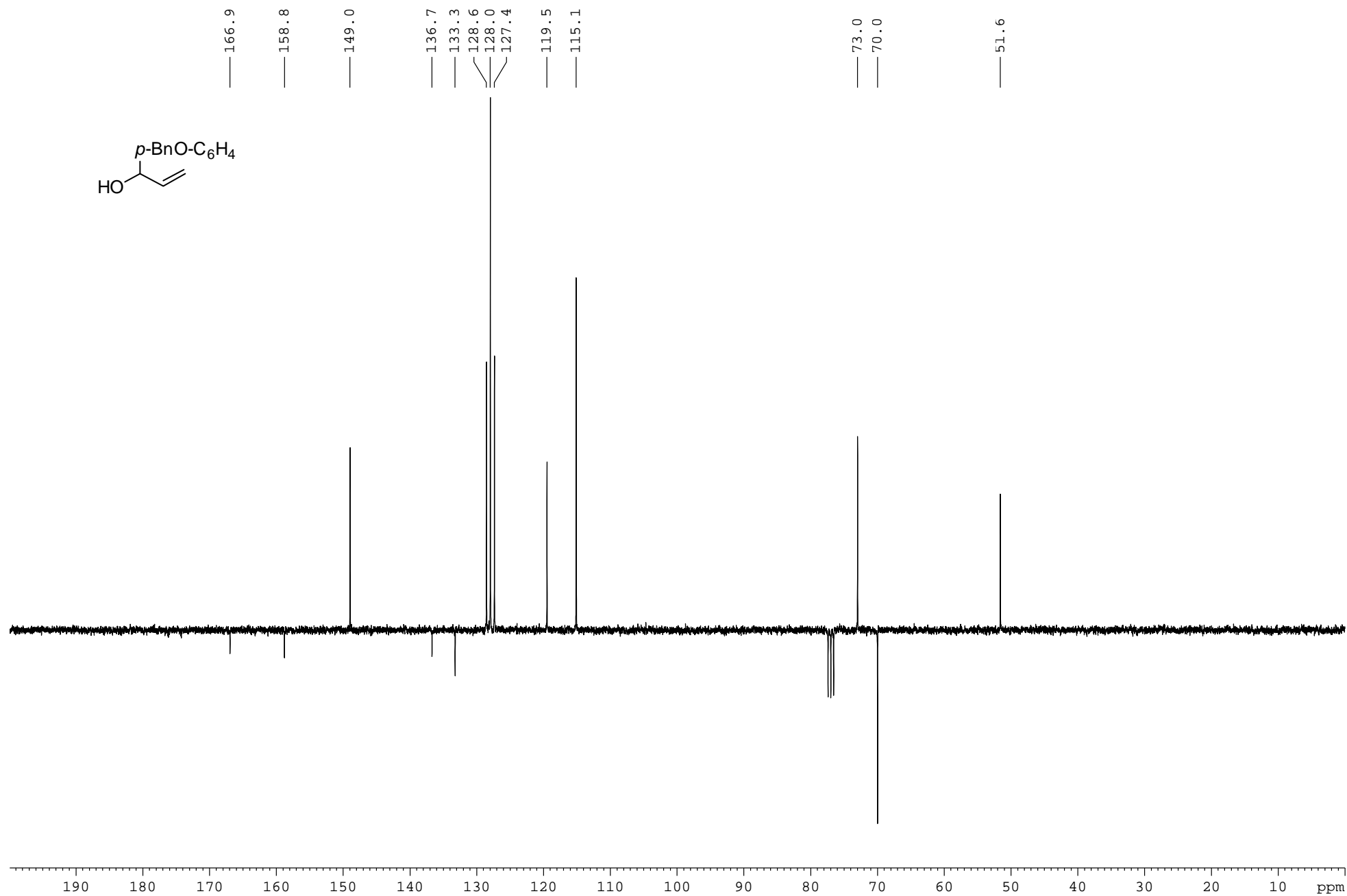
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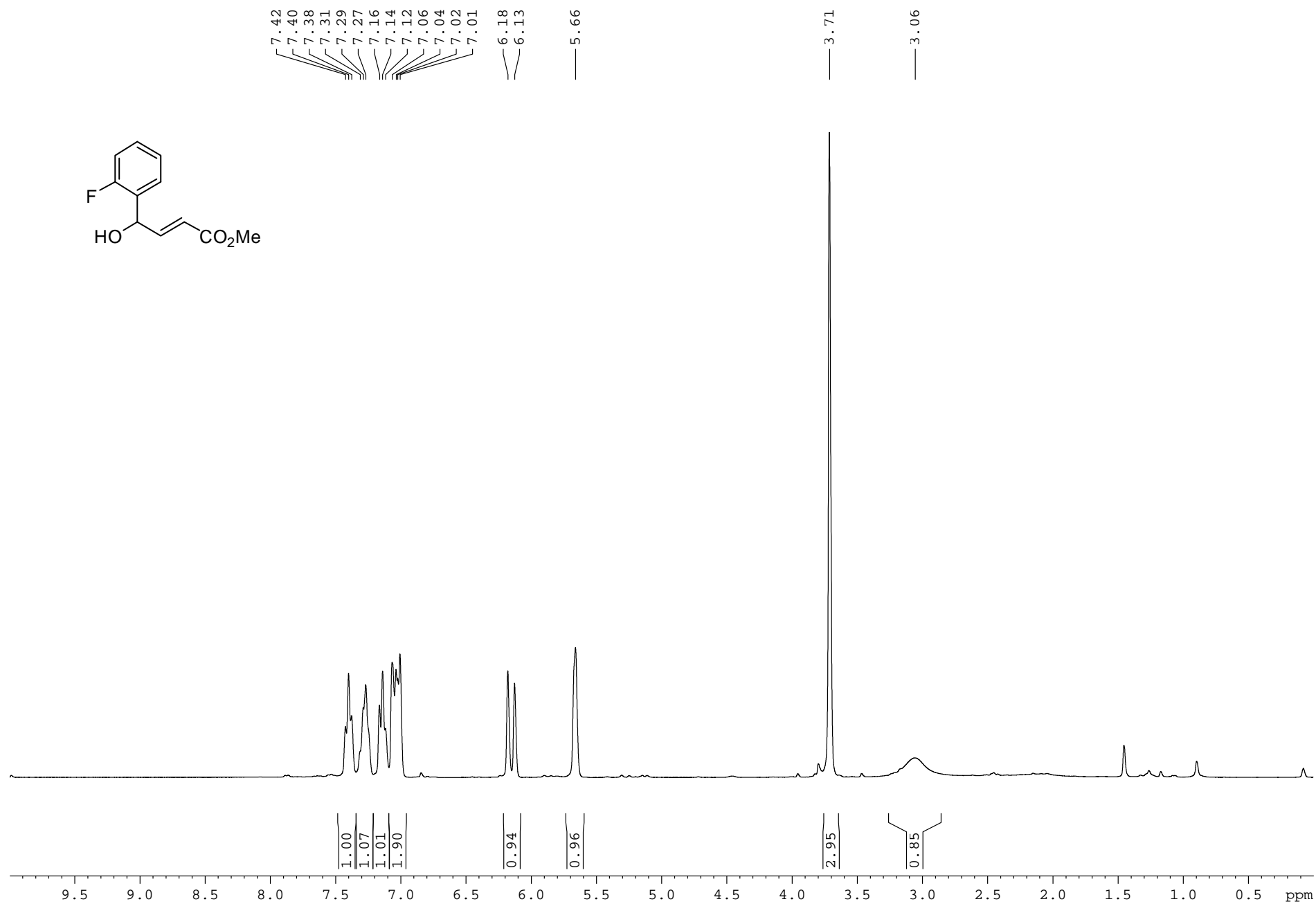
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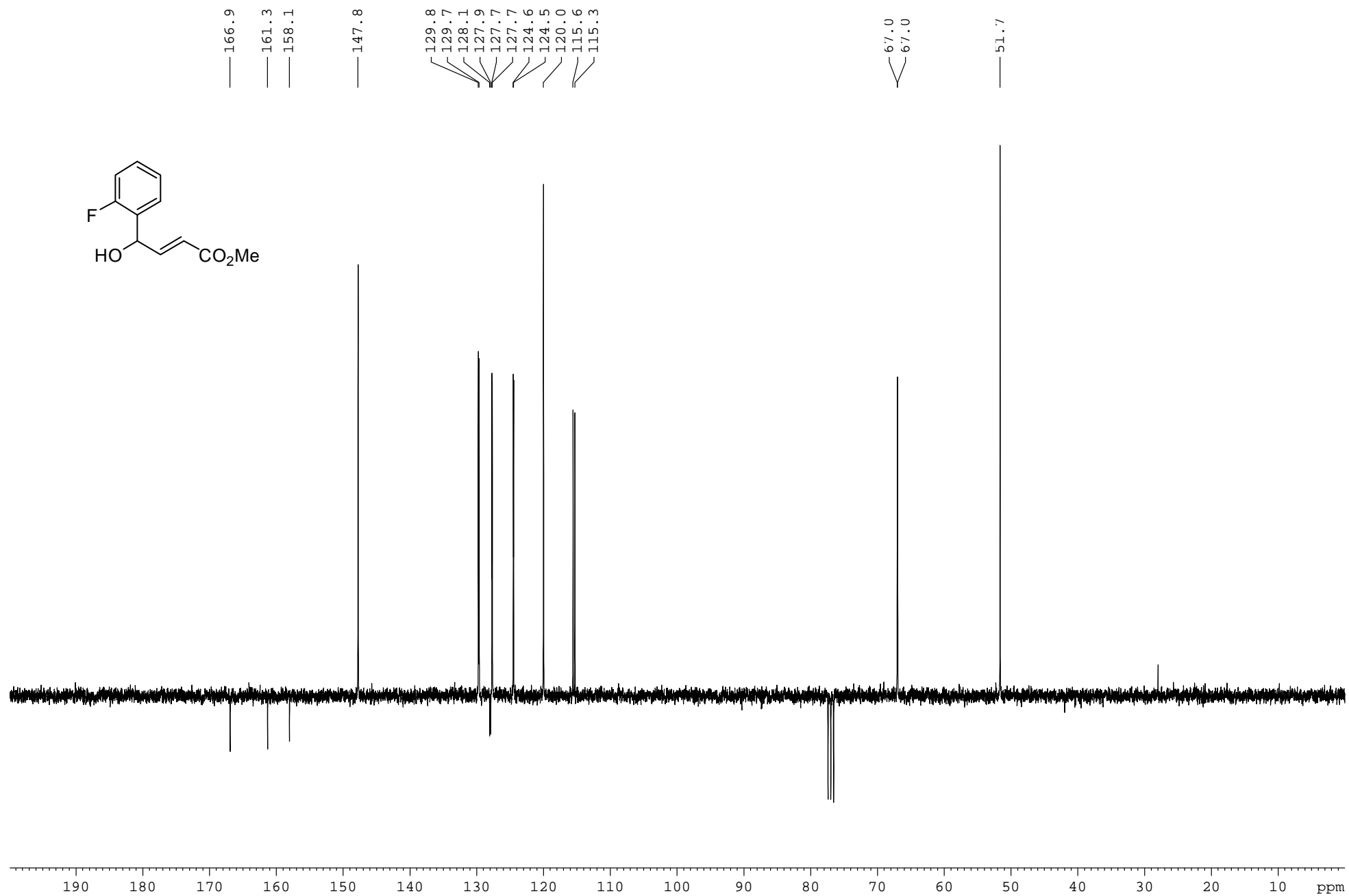
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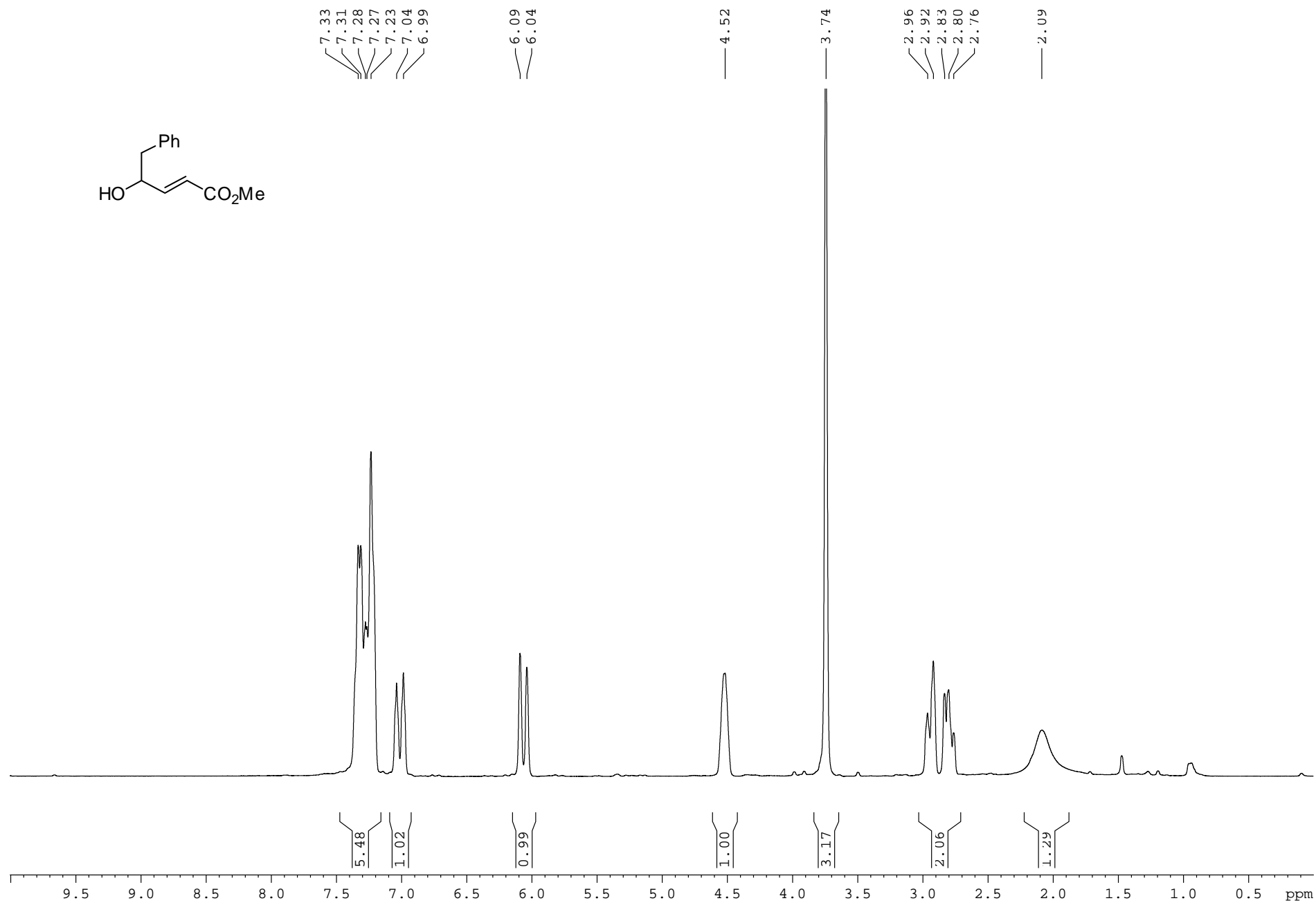
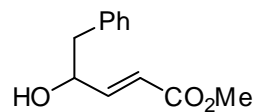
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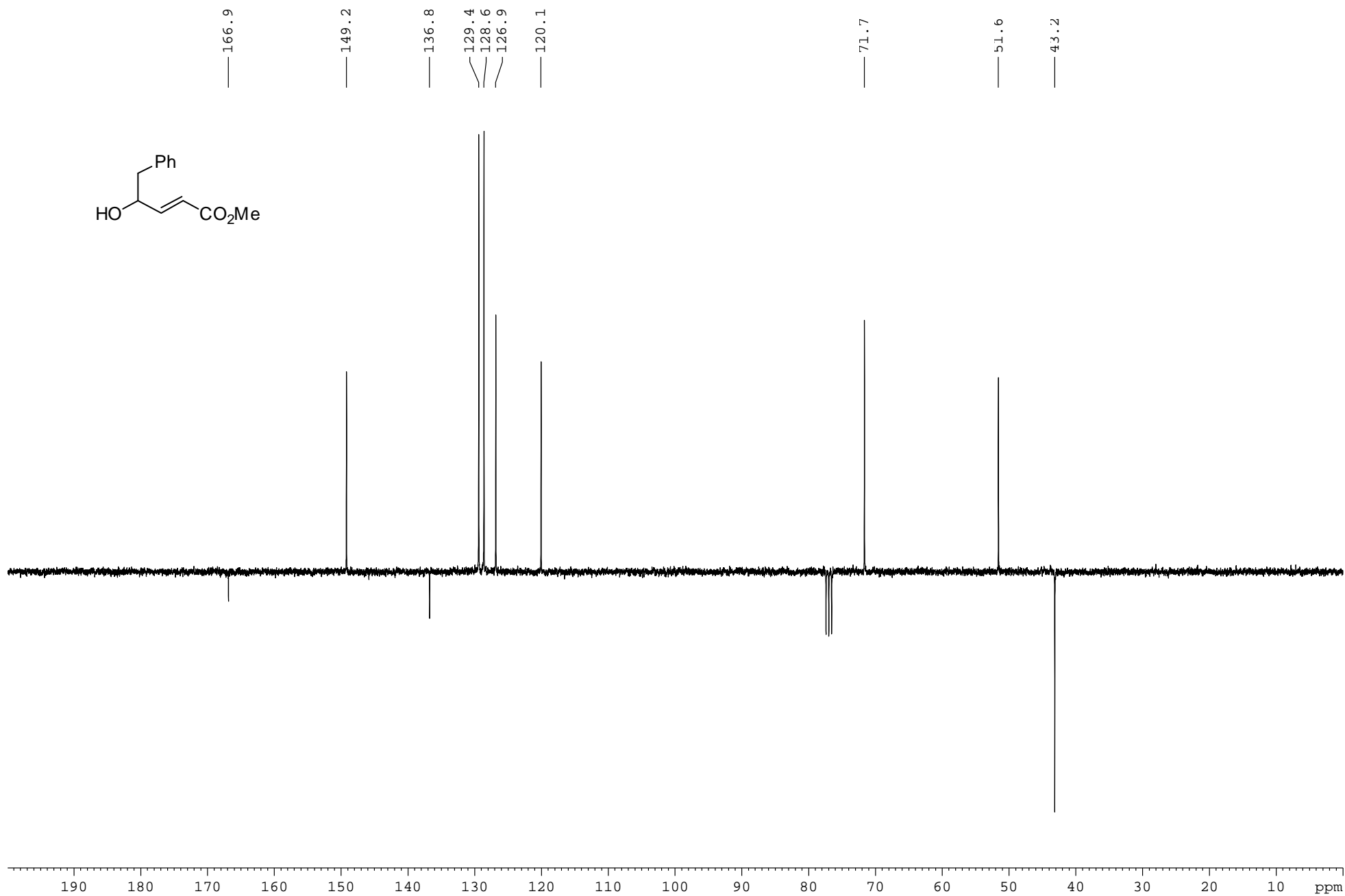
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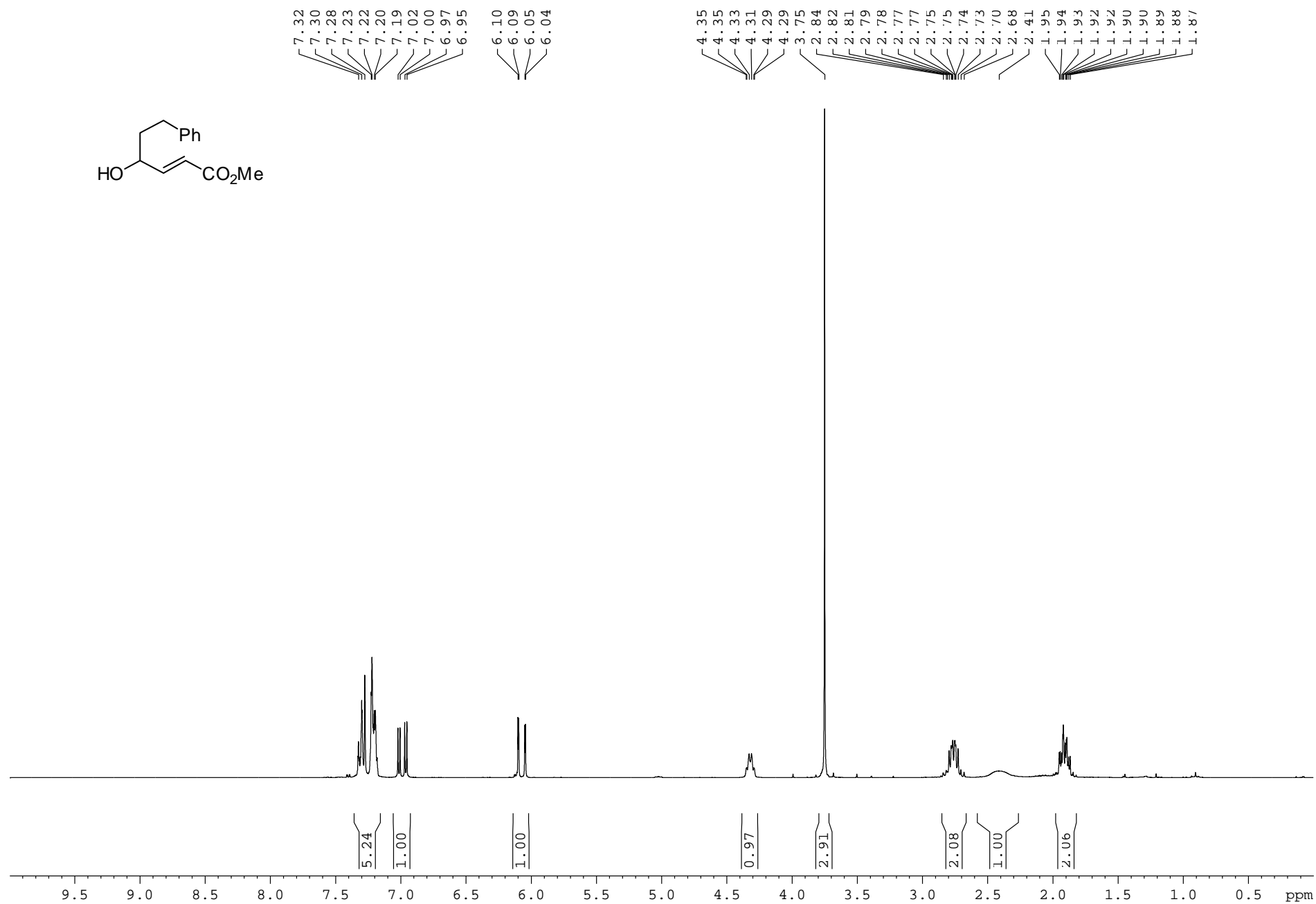
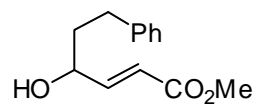
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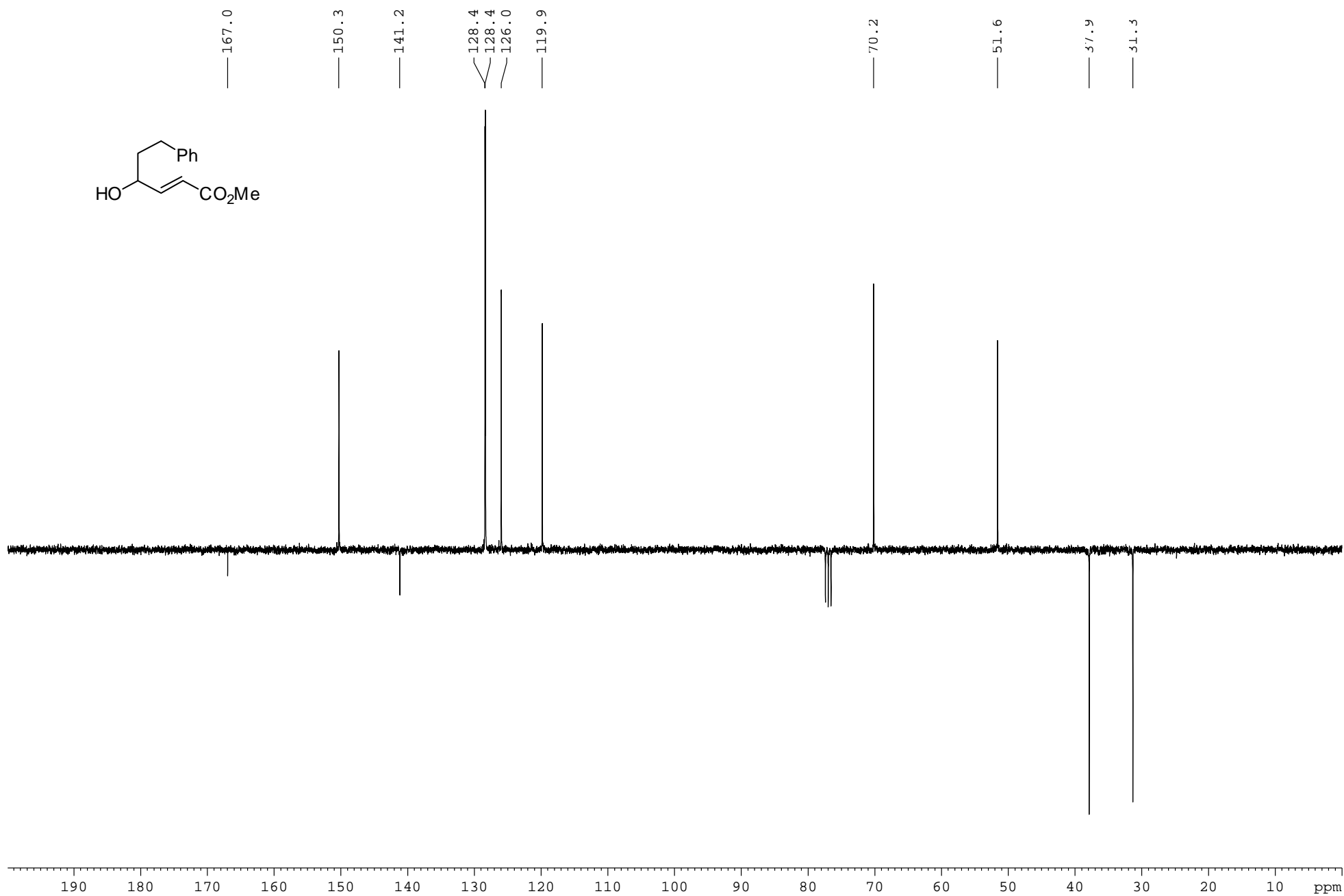
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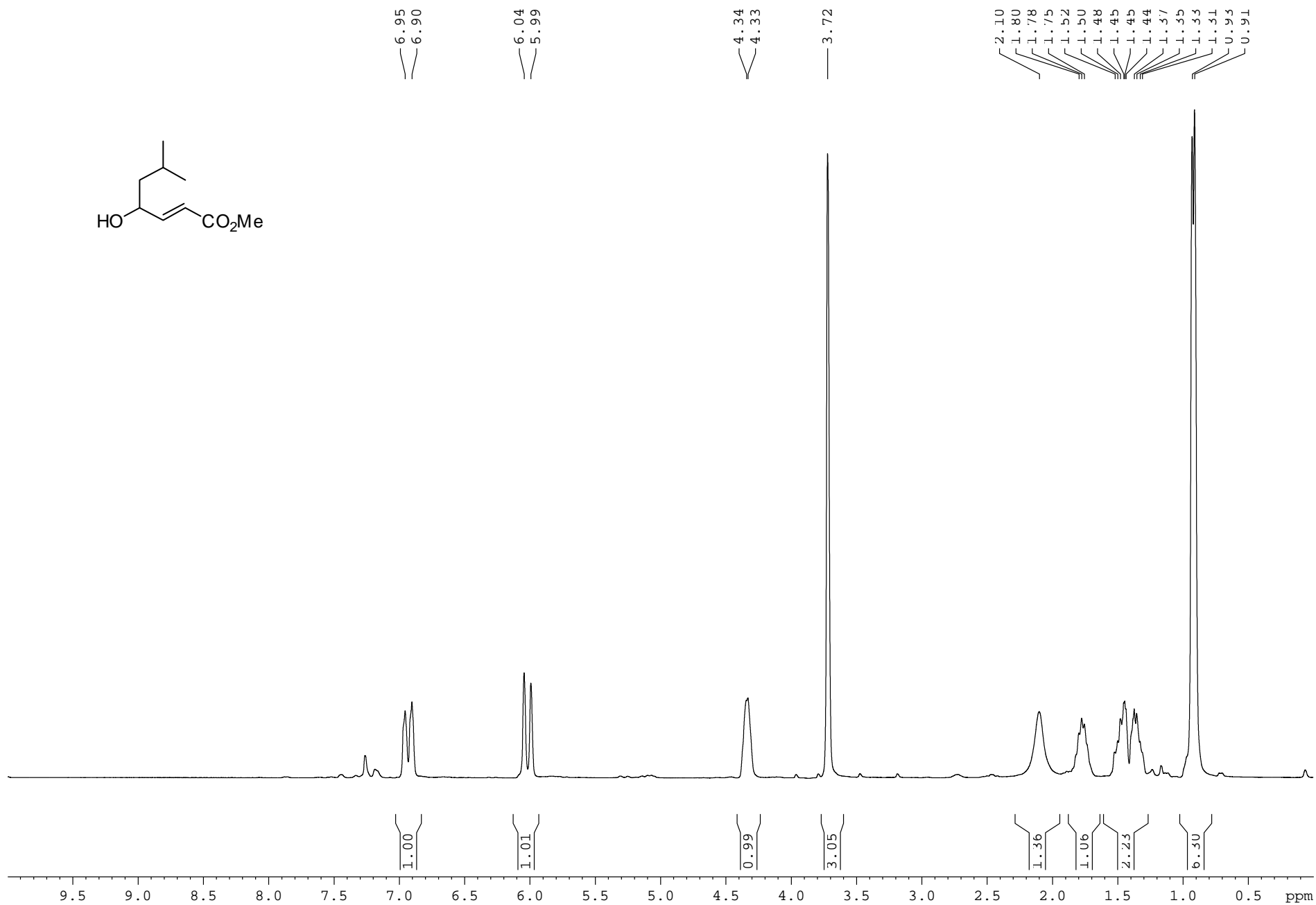
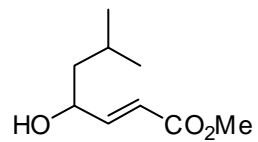
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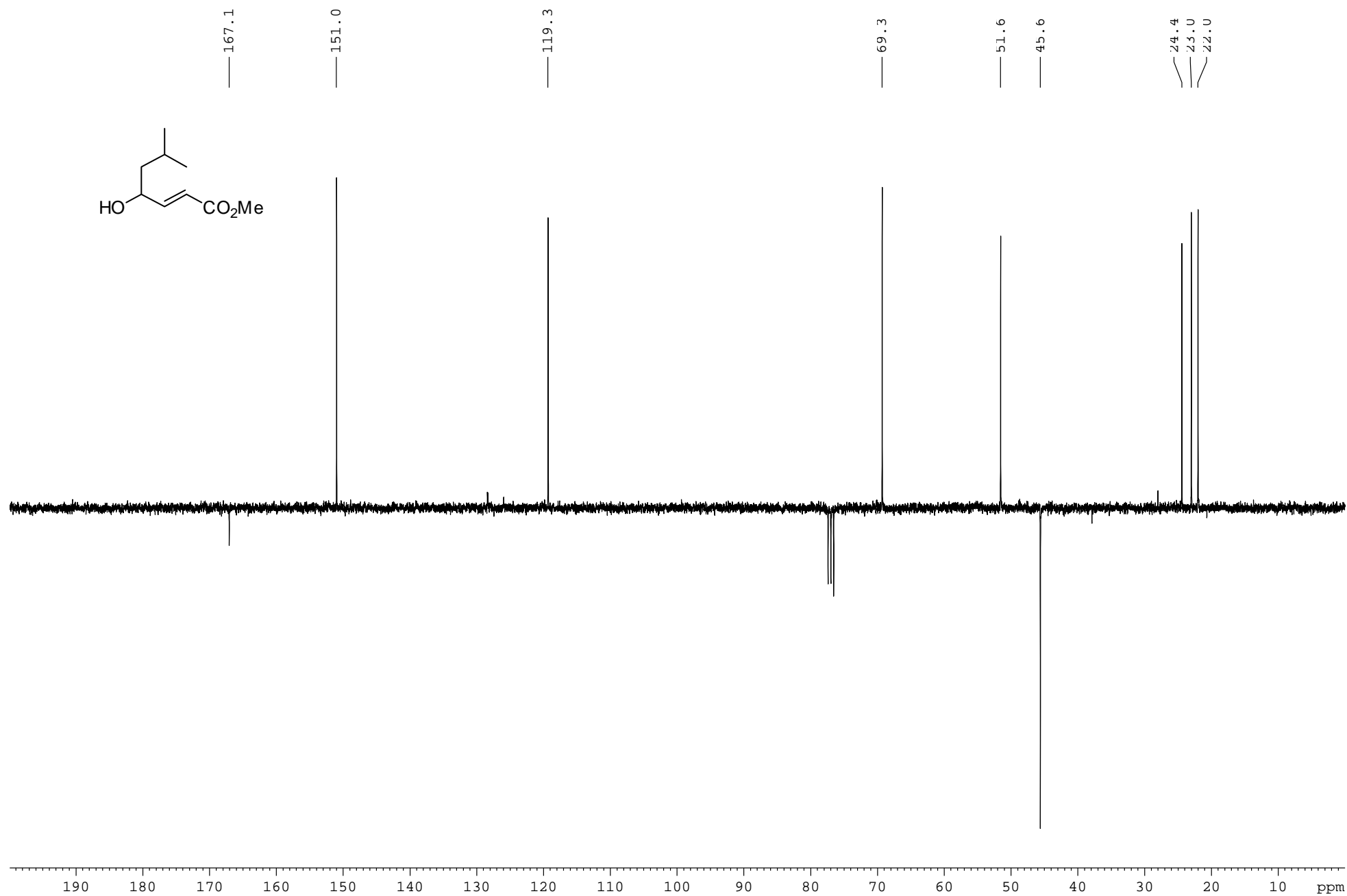
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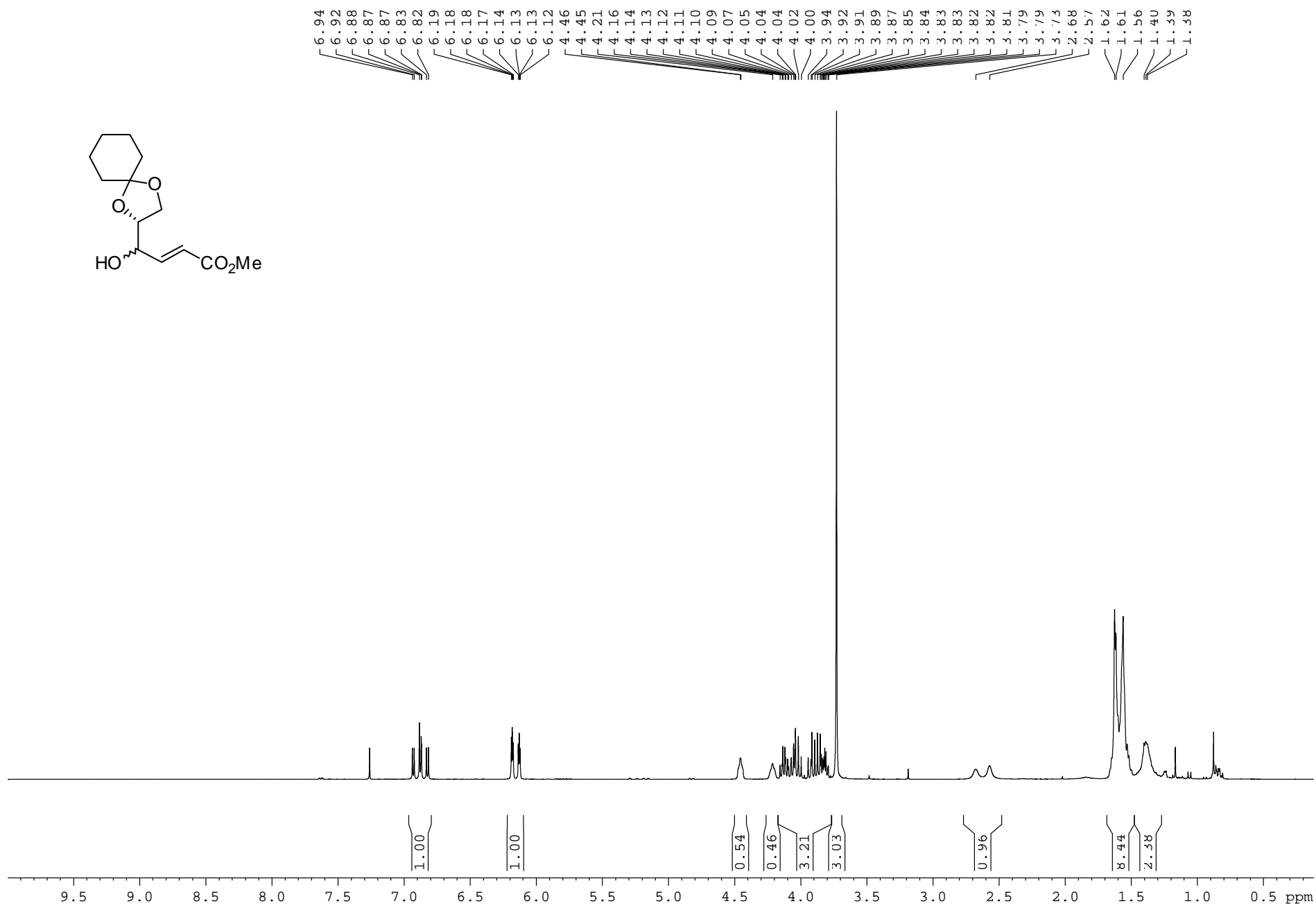
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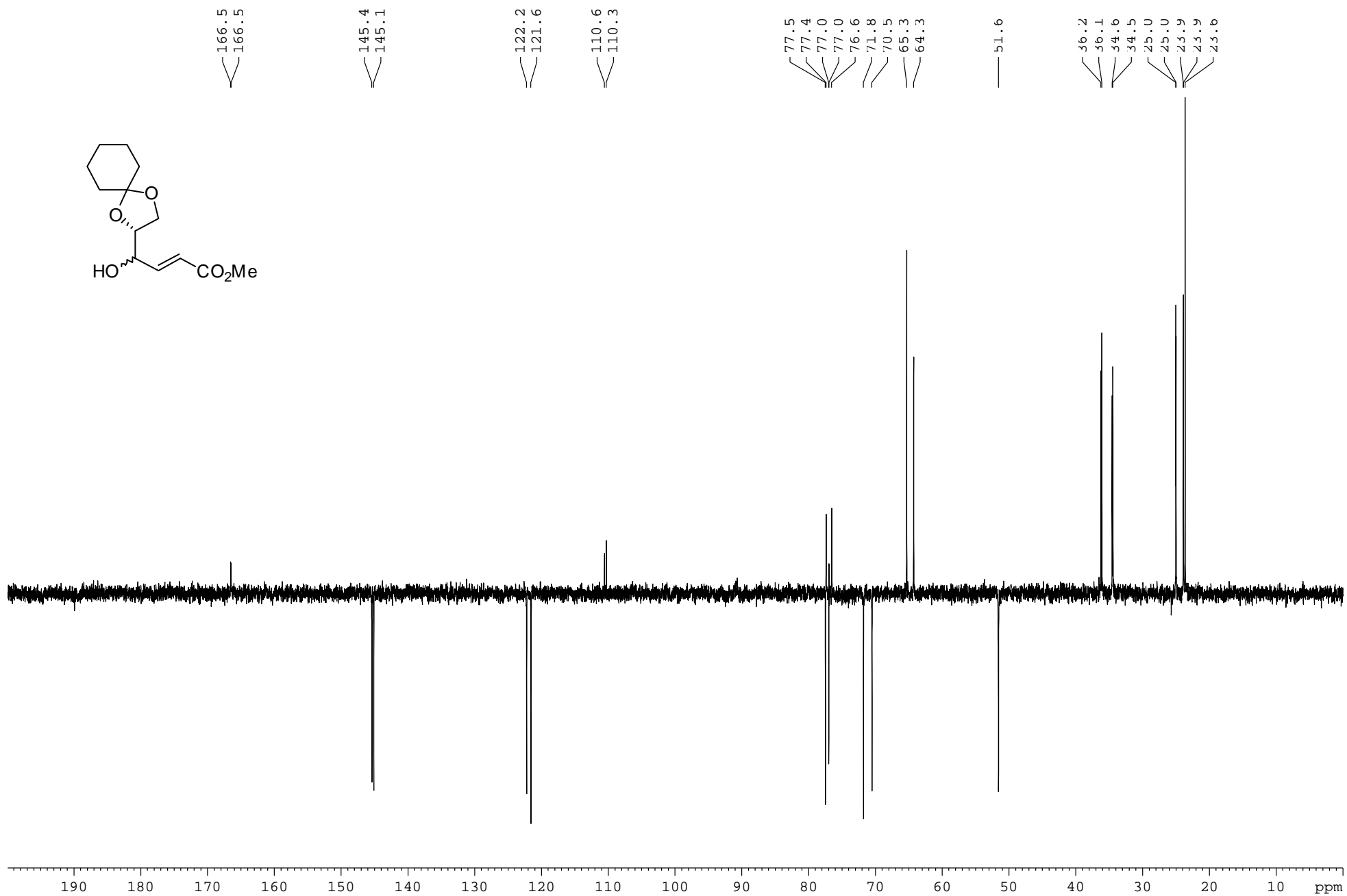
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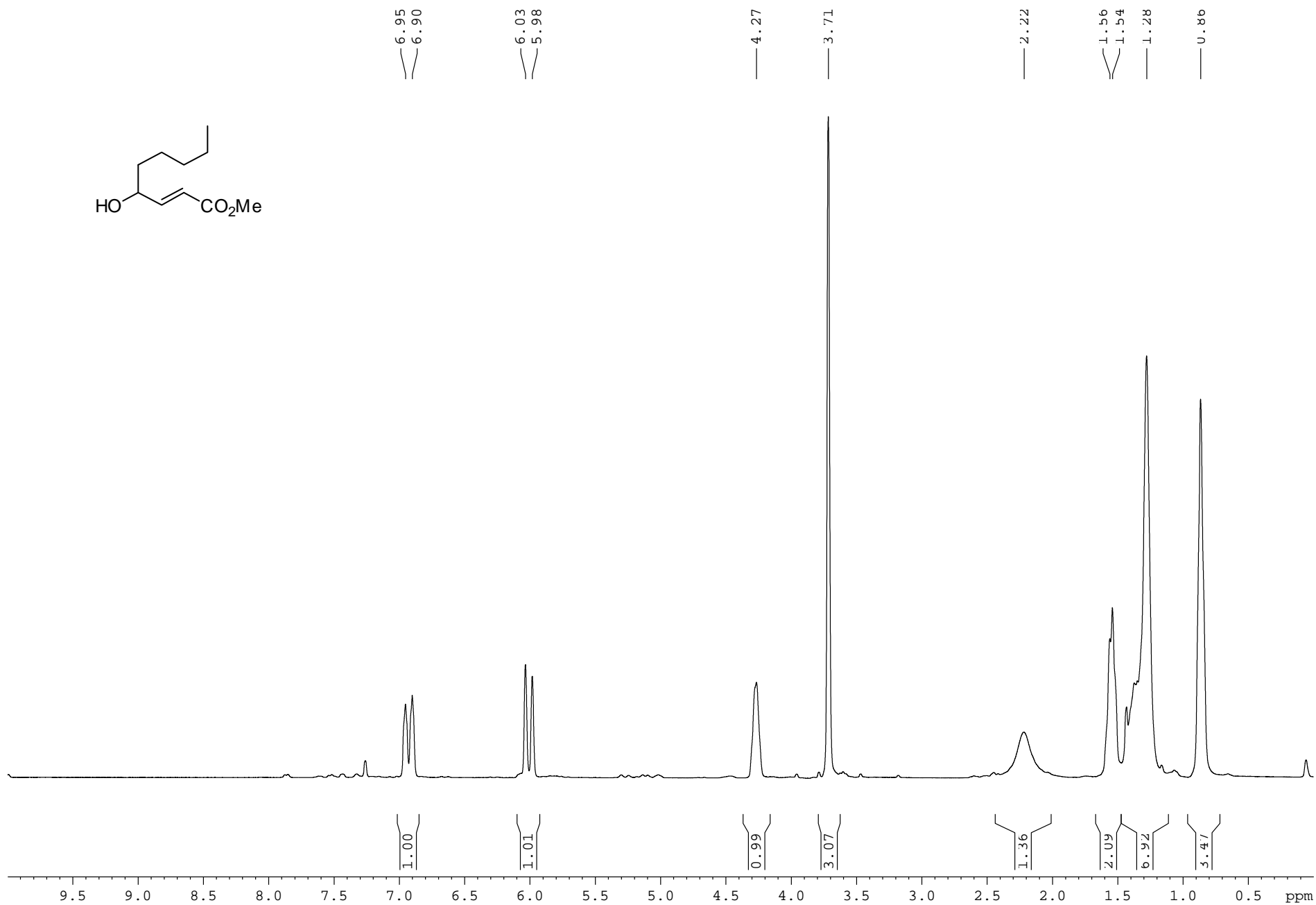
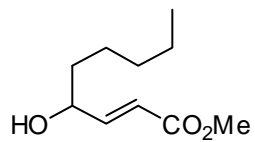
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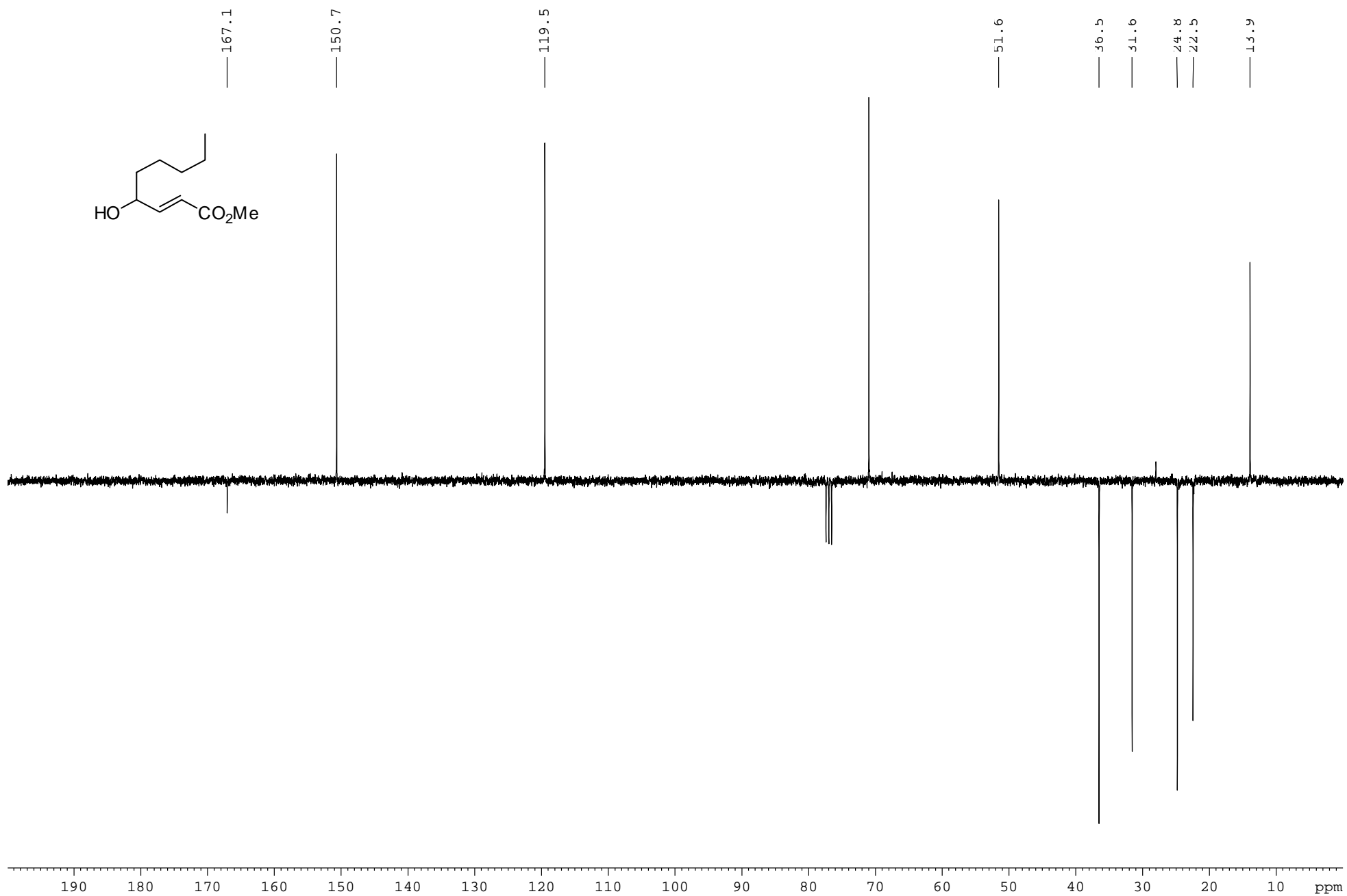
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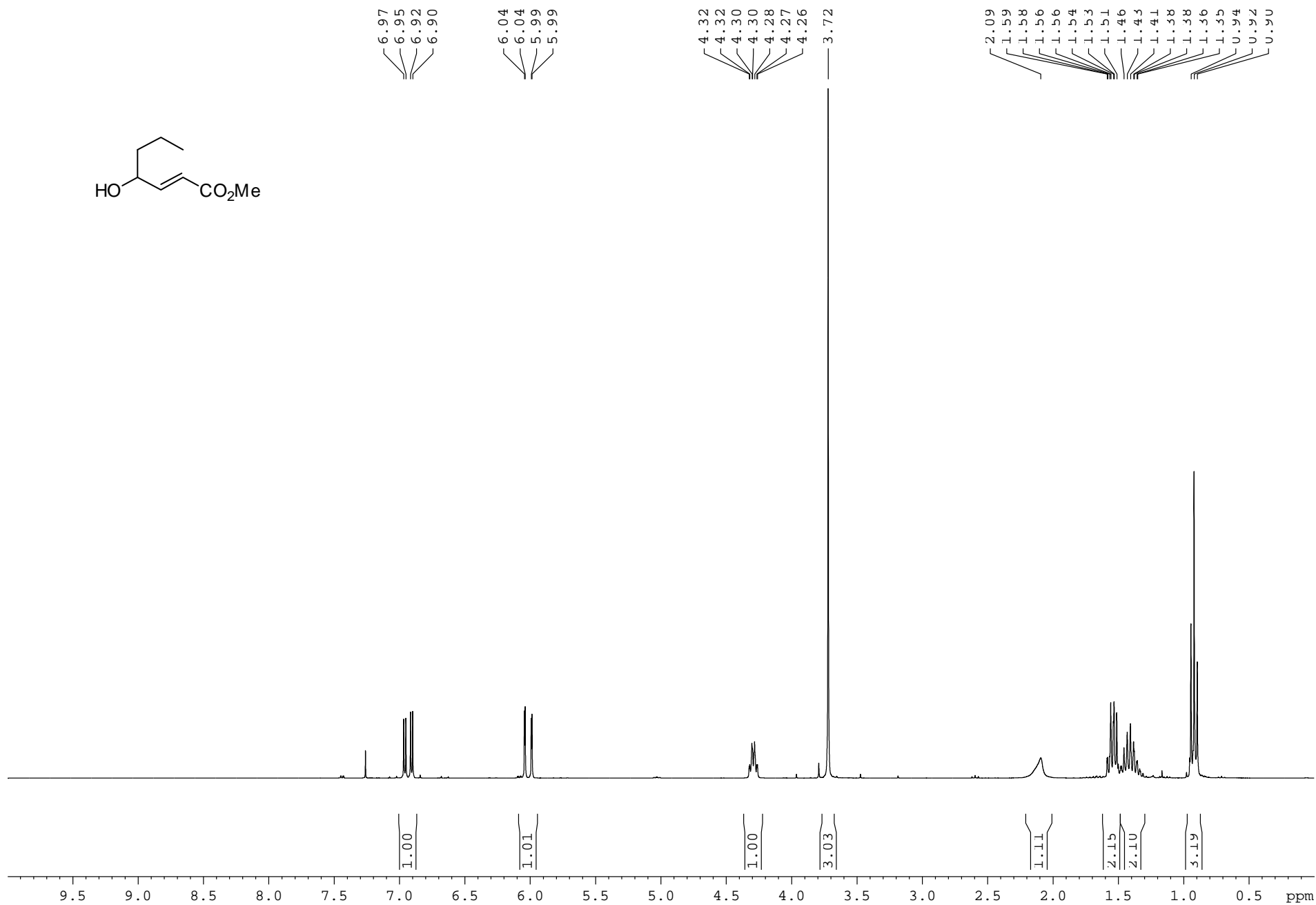
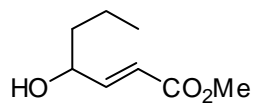
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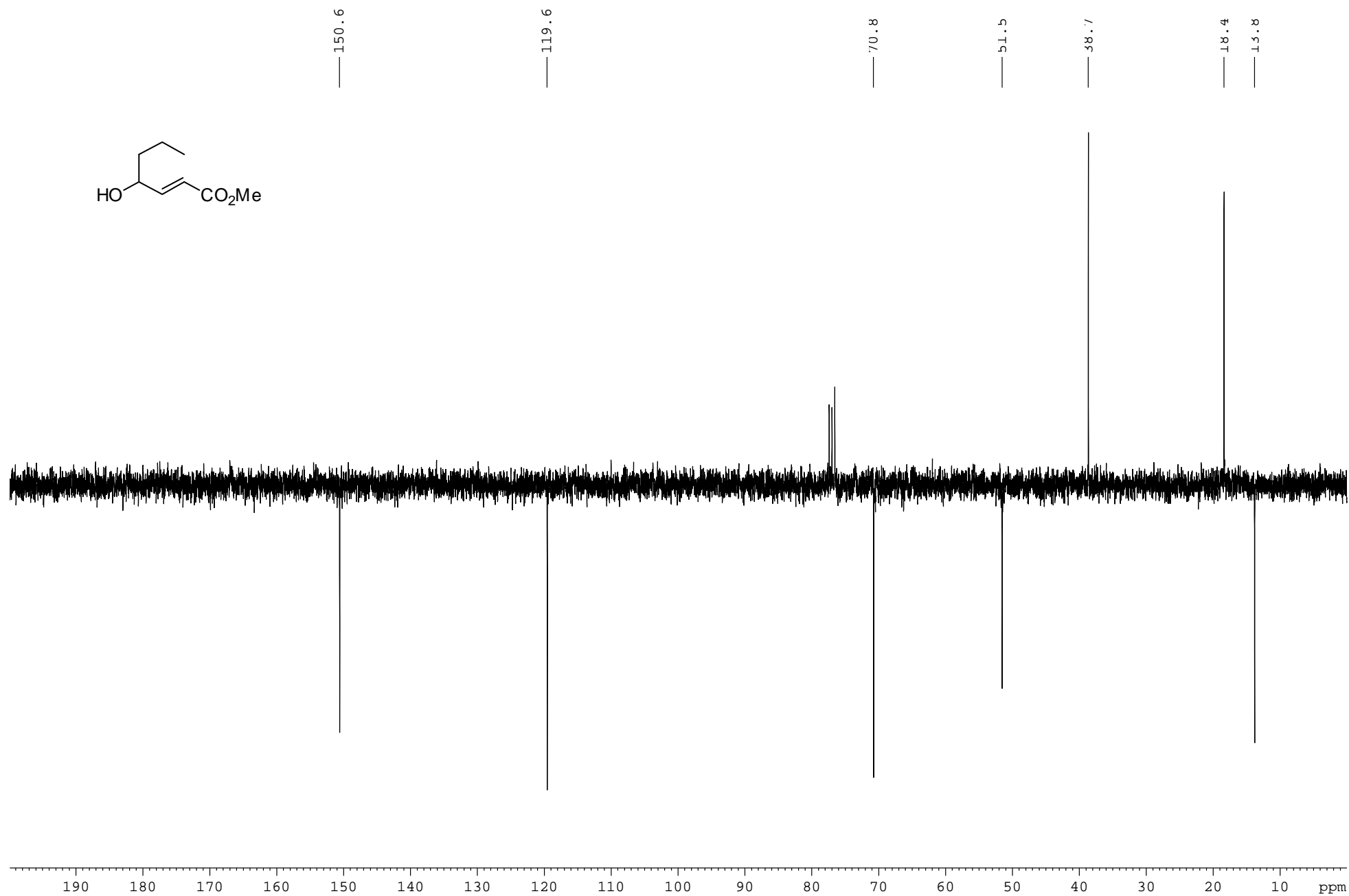
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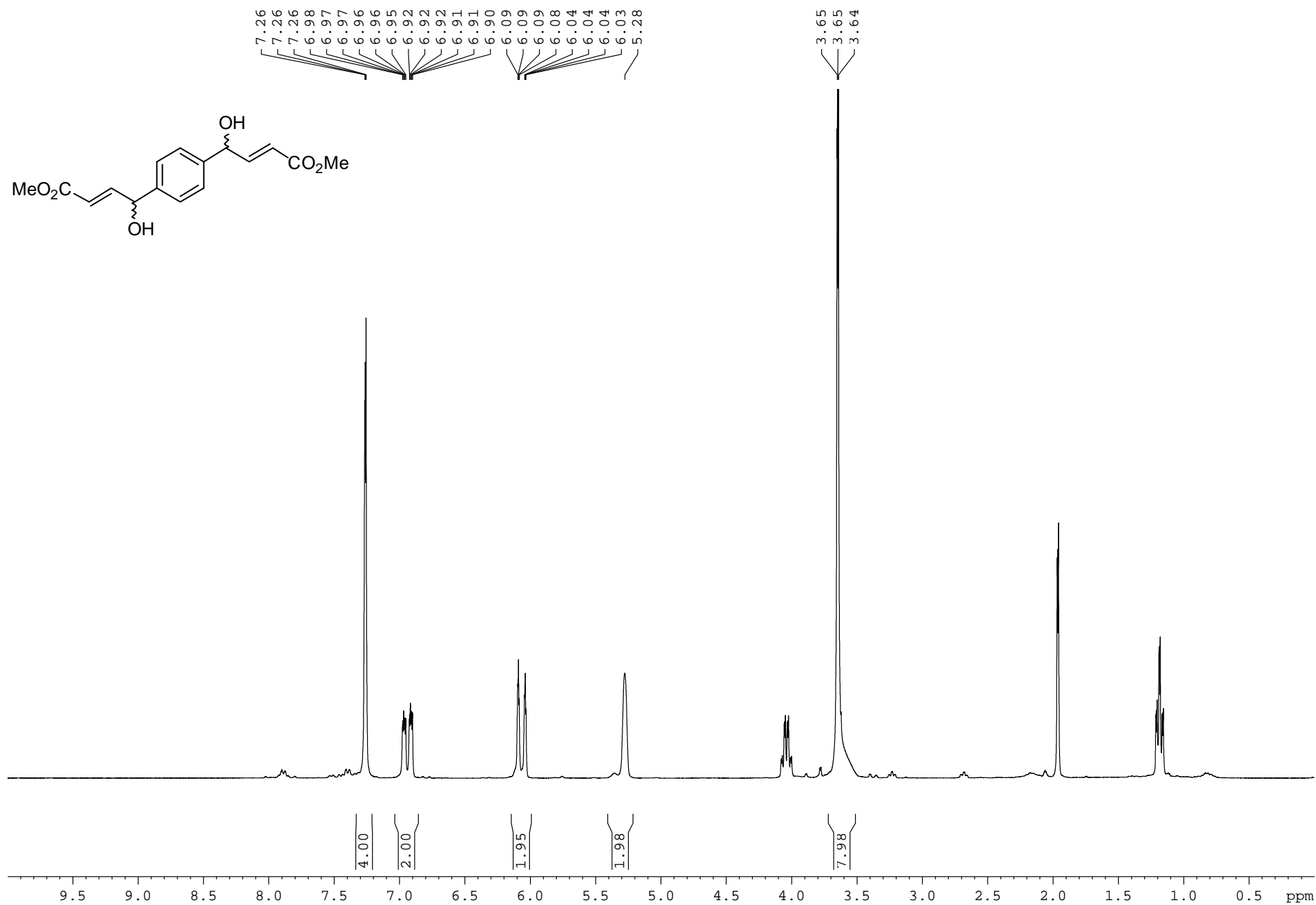
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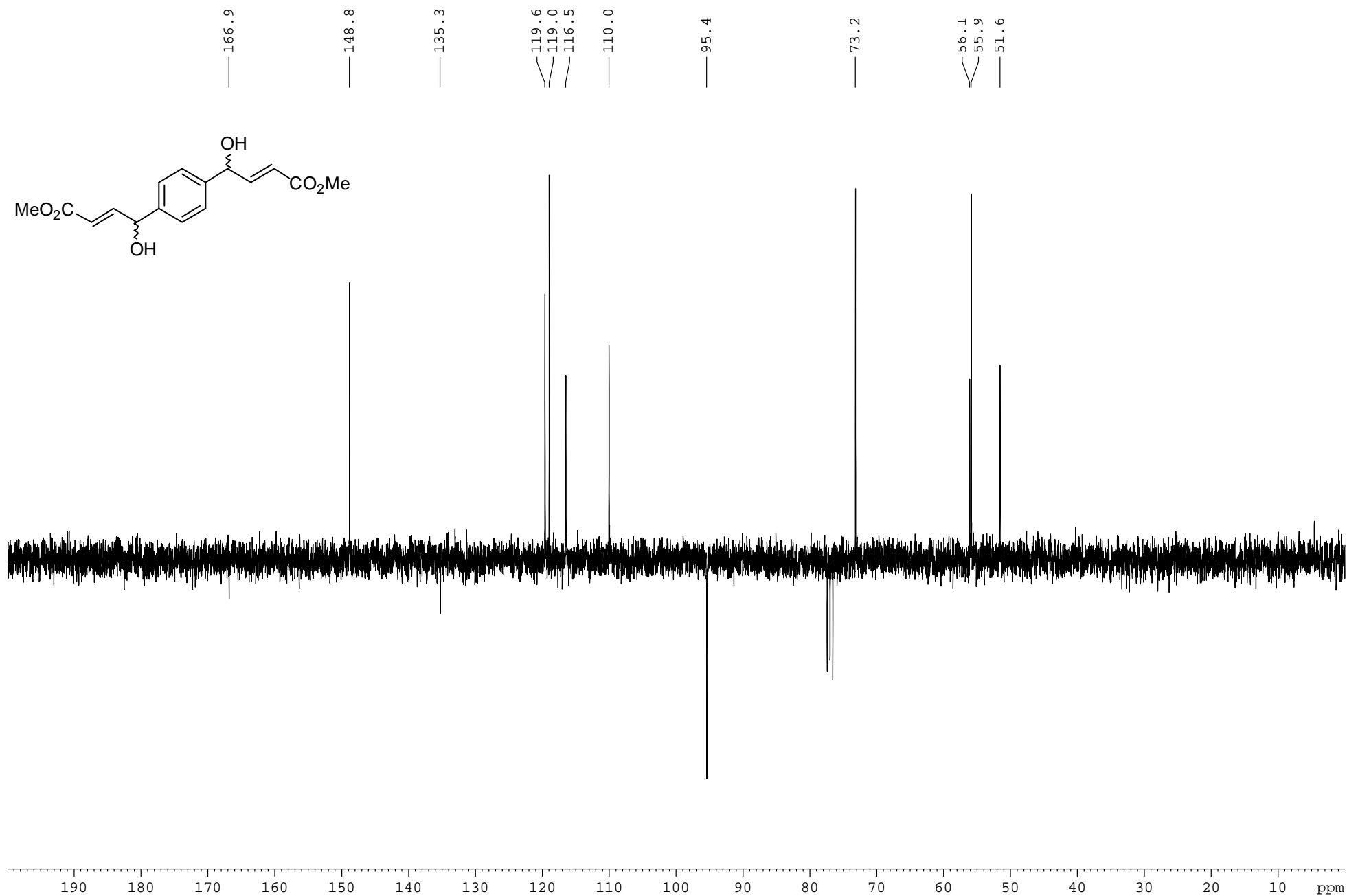
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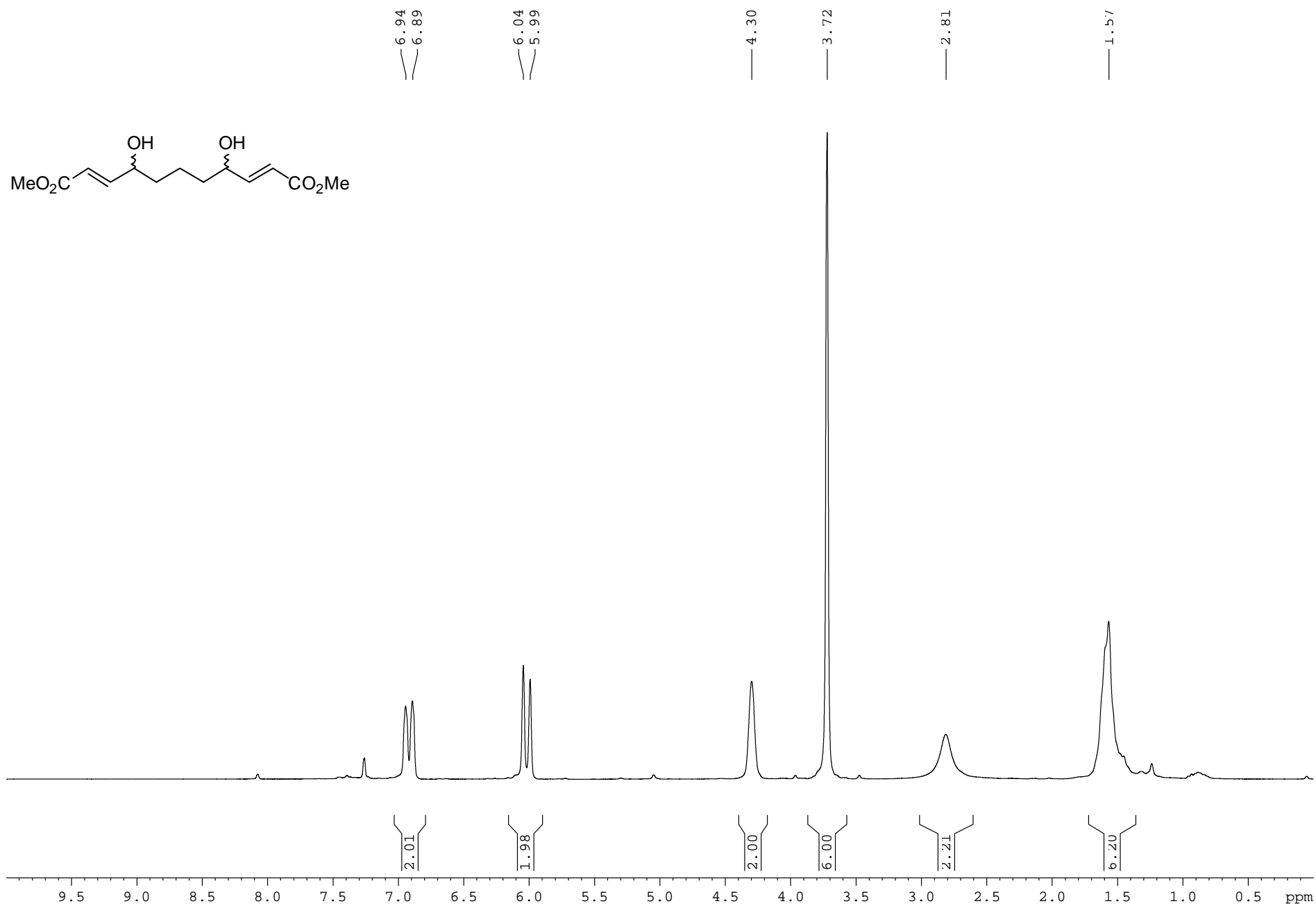
^1H NMR (CDCl_3 + drop of aceton- d_6 , 300 MHz) of **5o**



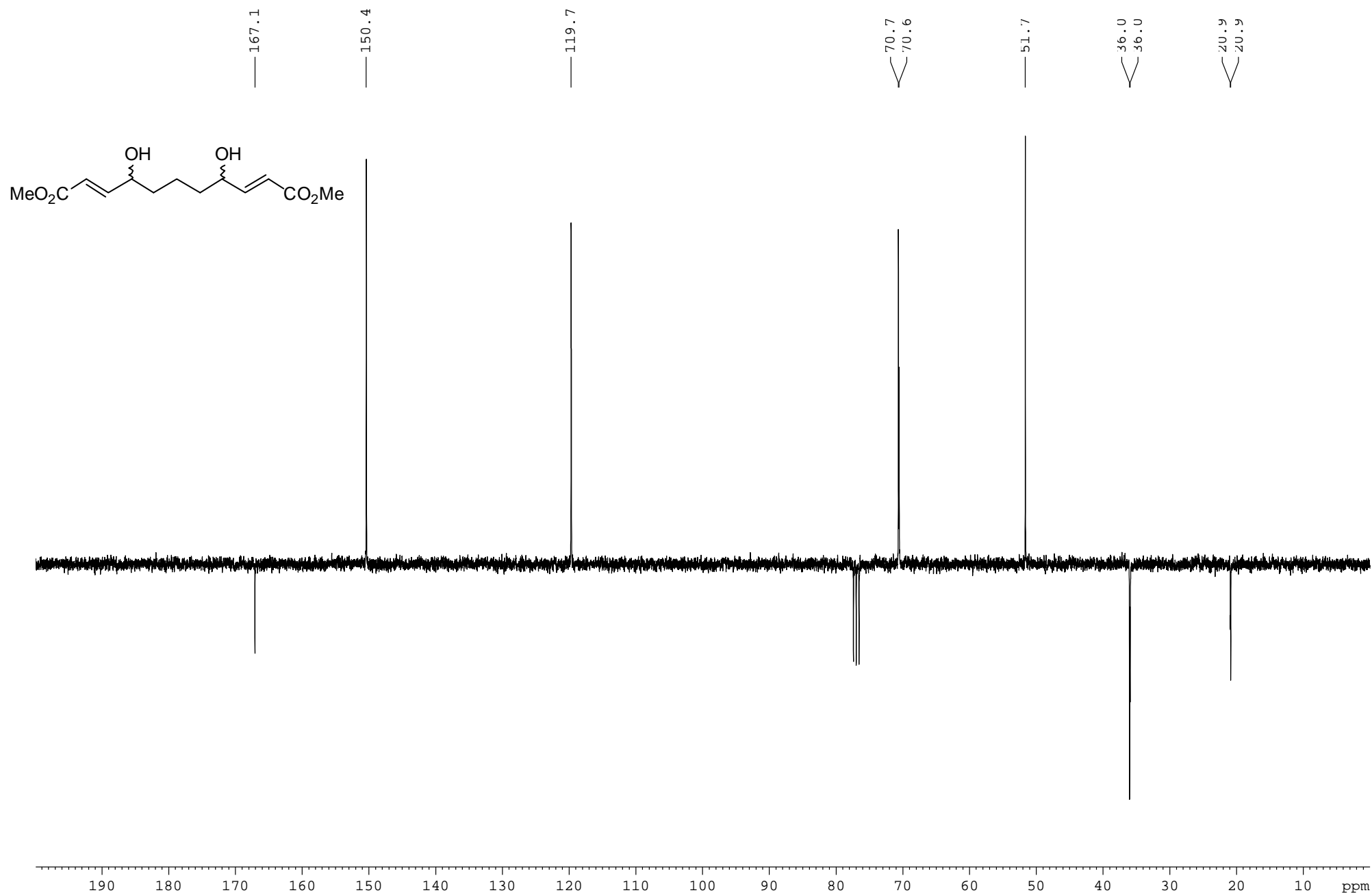
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^1H NMR (CDCl_3 , 300 MHz) of **5p**

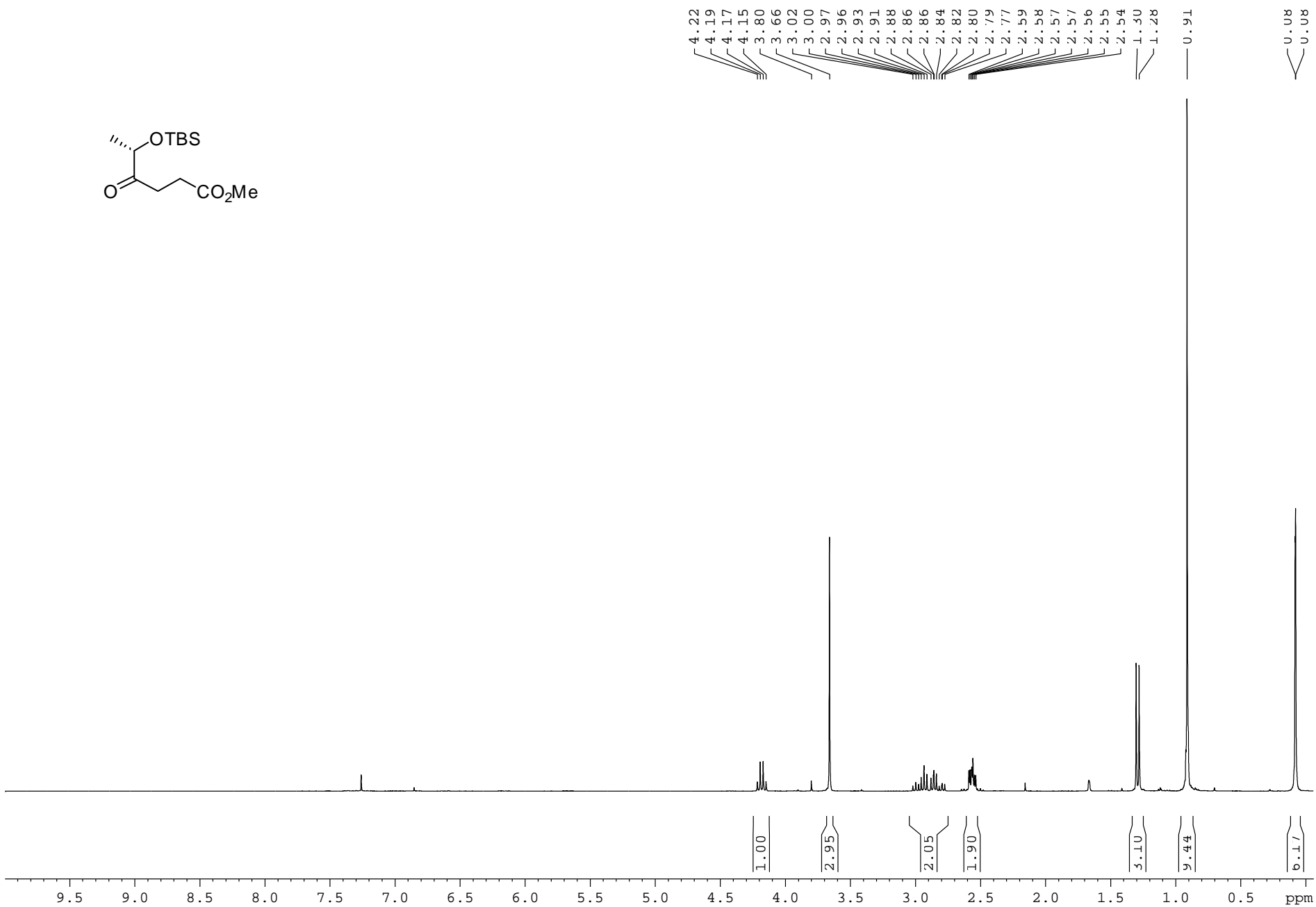
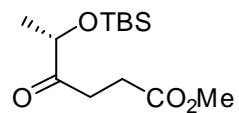


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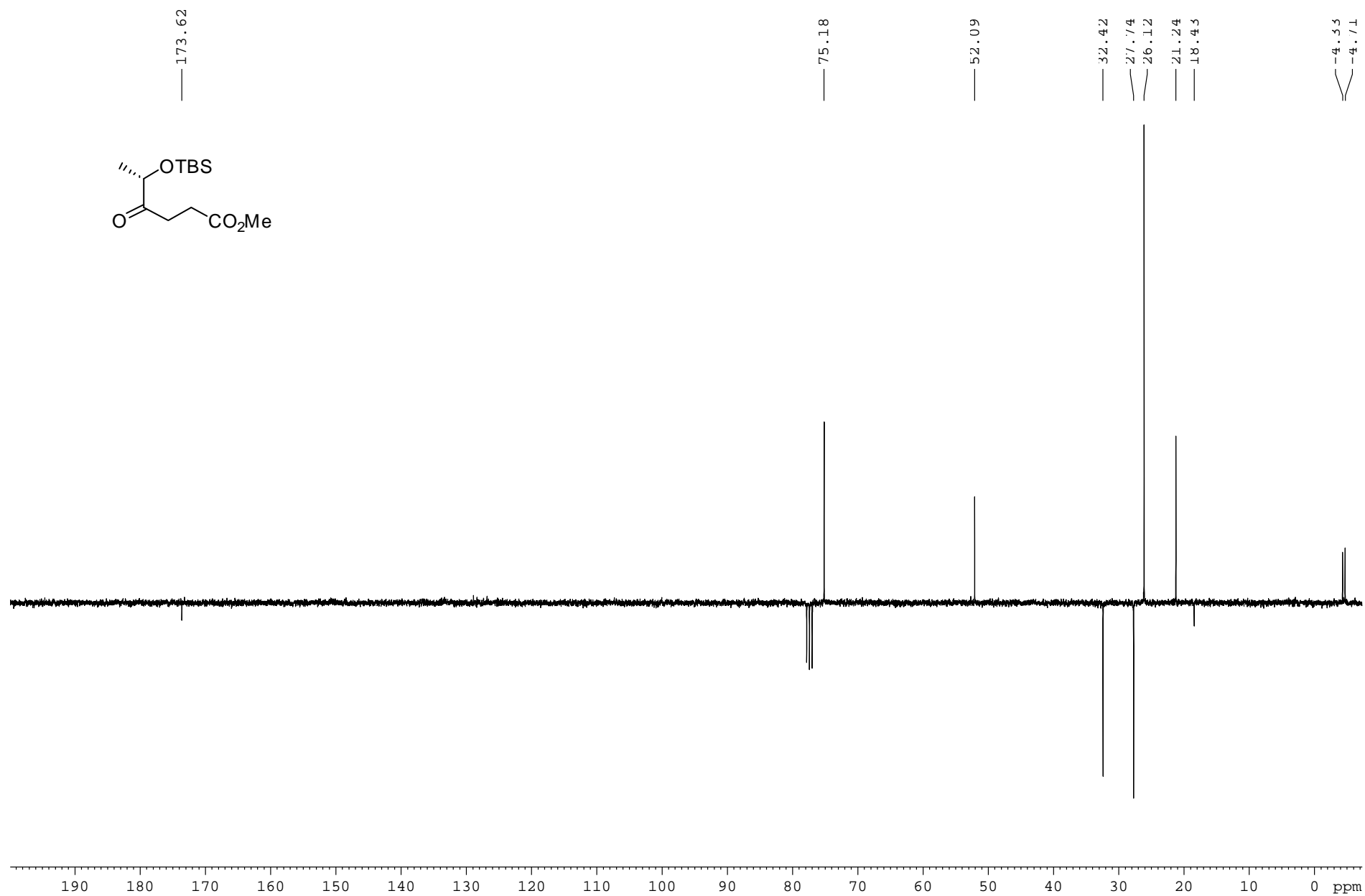


D Copies of NMR spectra of cross metathesis/isomerization products 6

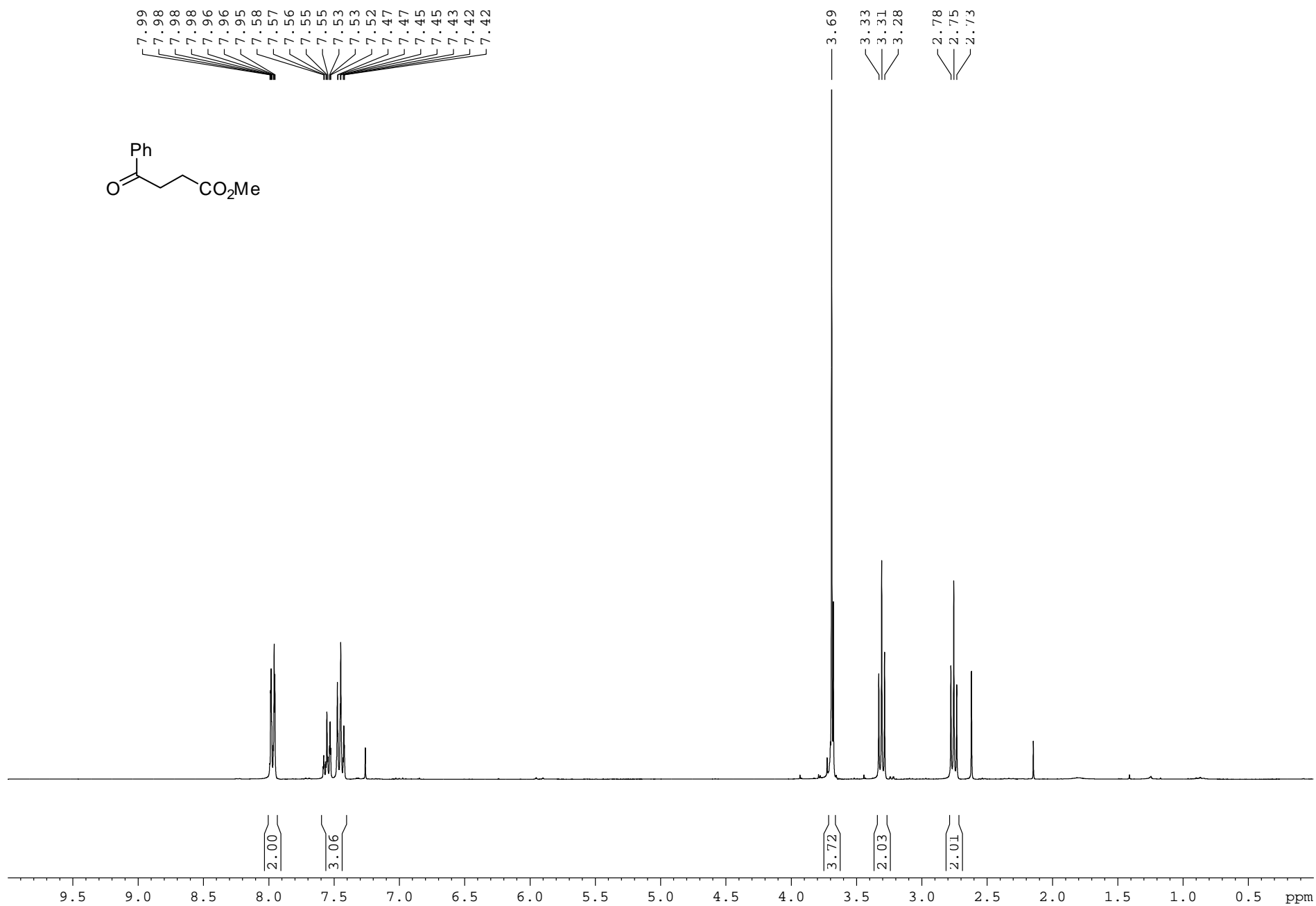
¹H NMR (CDCl₃, 300 MHz) of **6a**



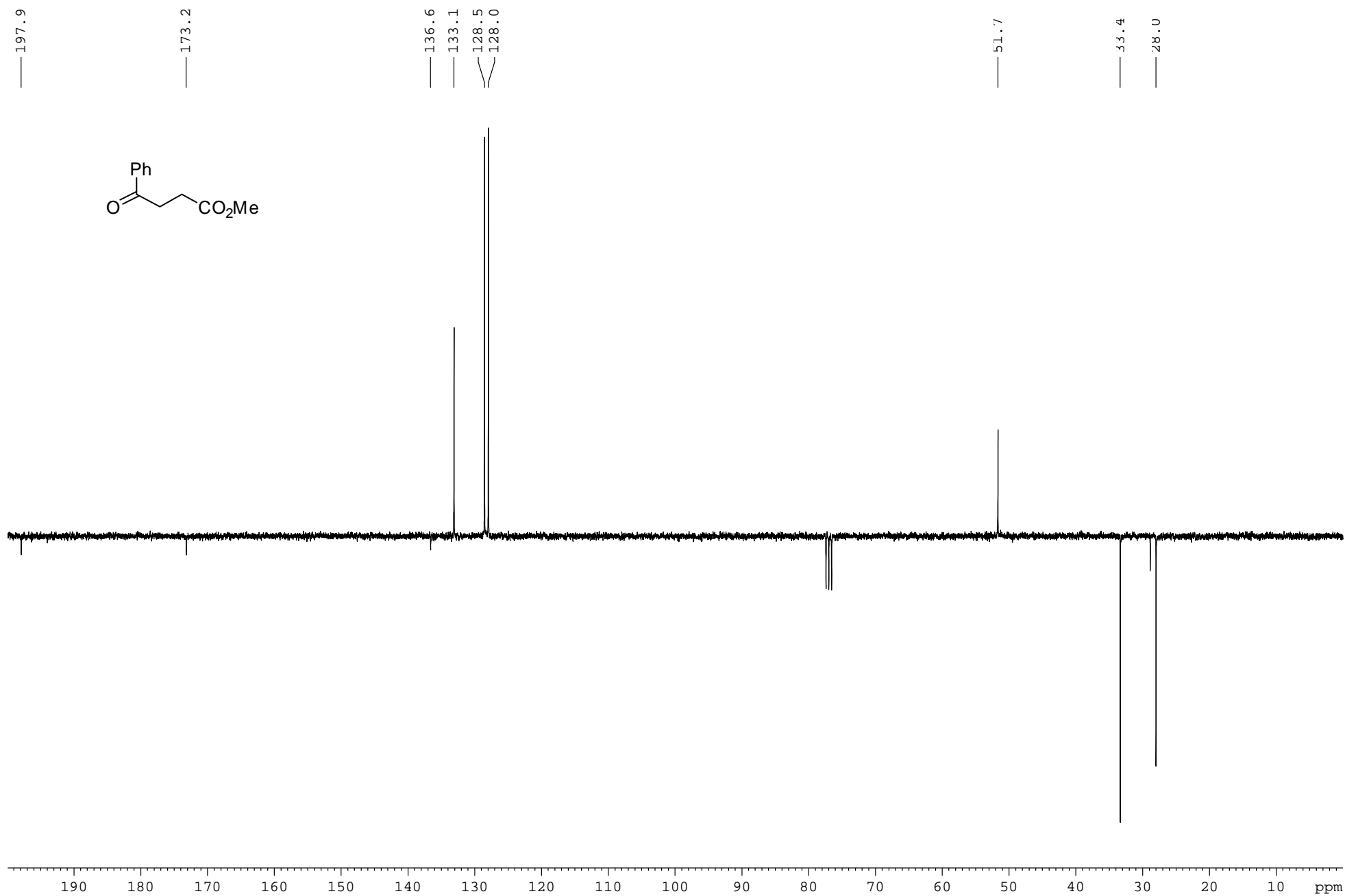
^{13}C NMR-APT (CDCl_3 , 75 MHz) of **6a**



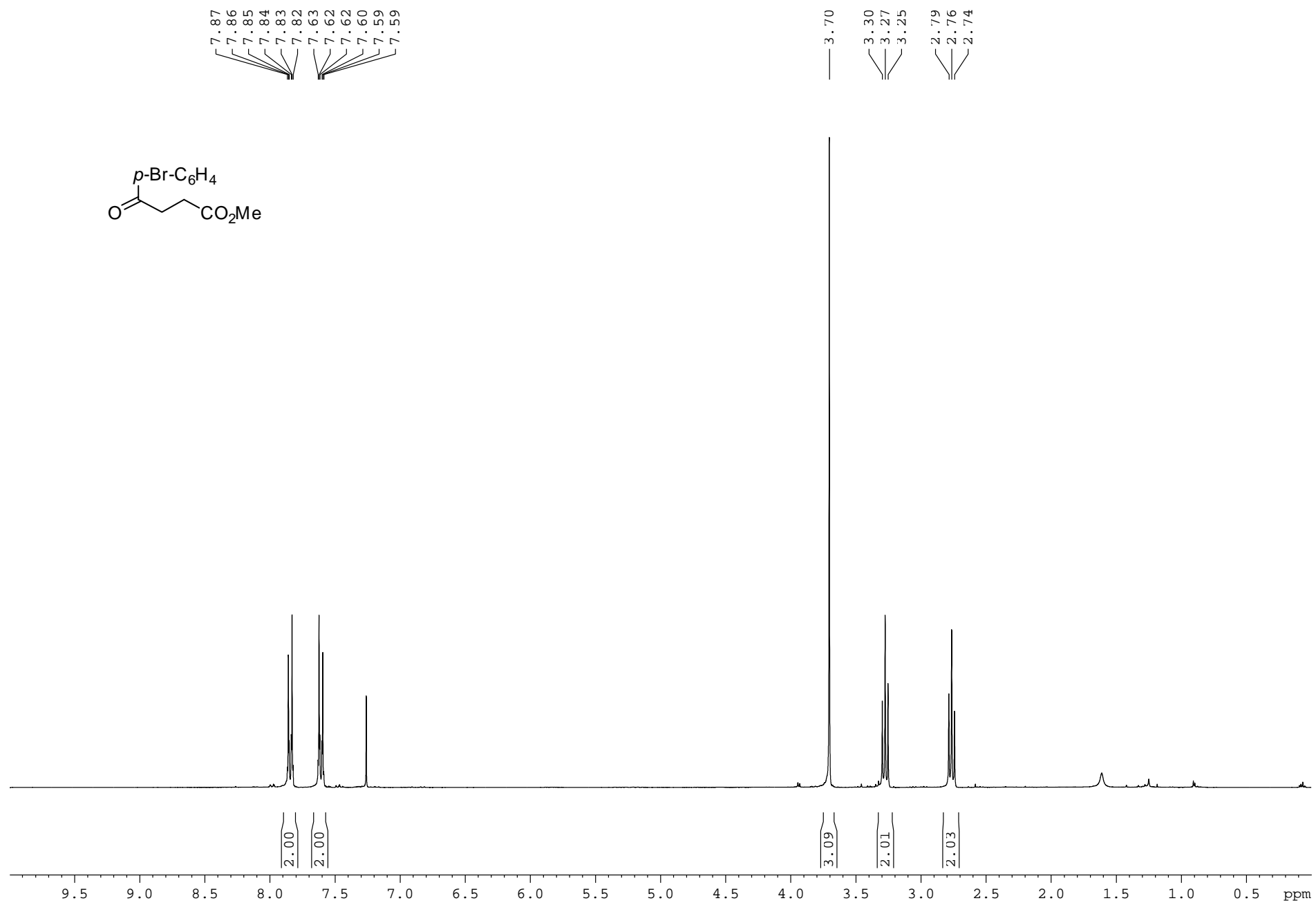
^1H NMR (CDCl_3 , 300 MHz) of **6b**



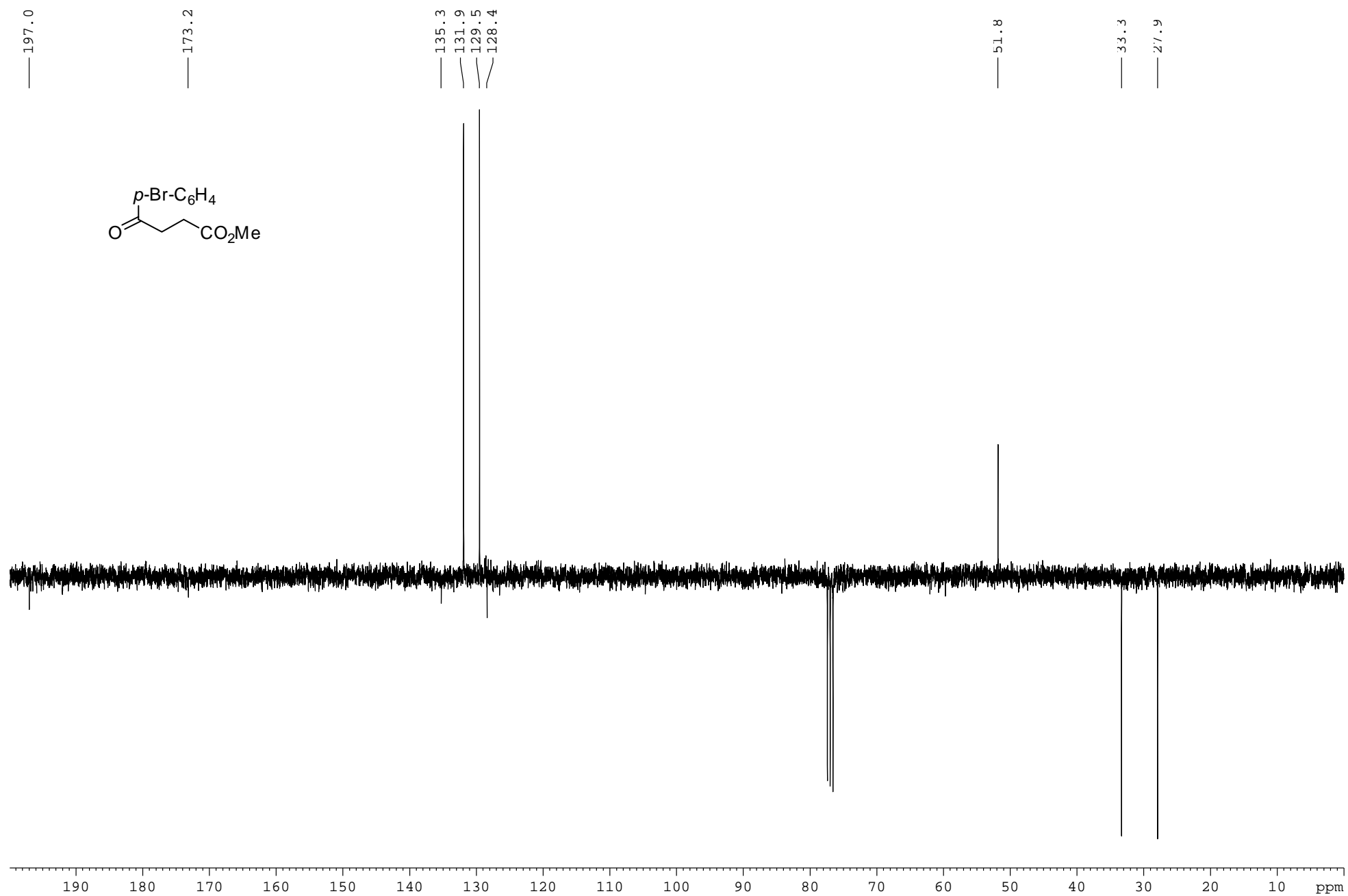
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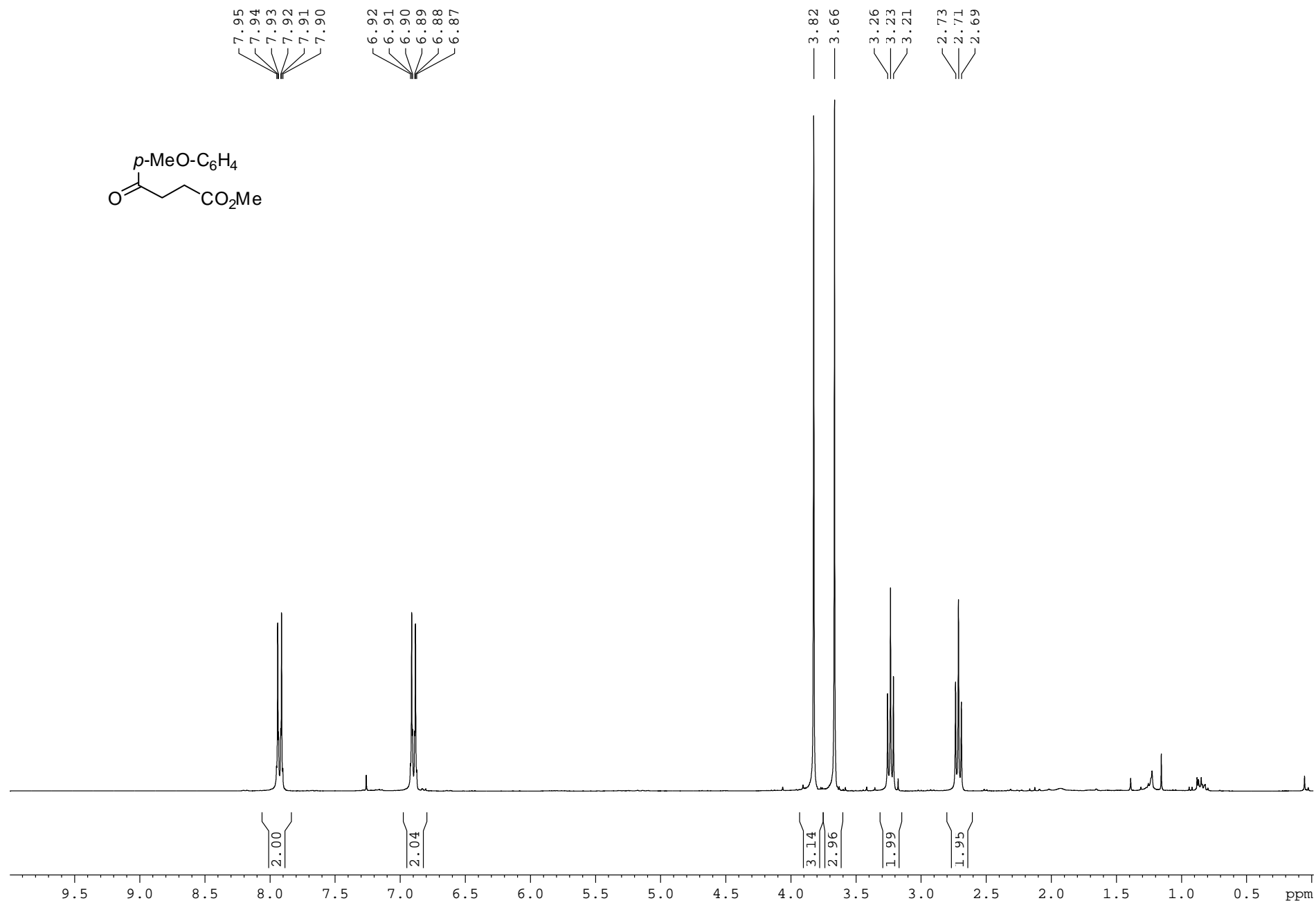
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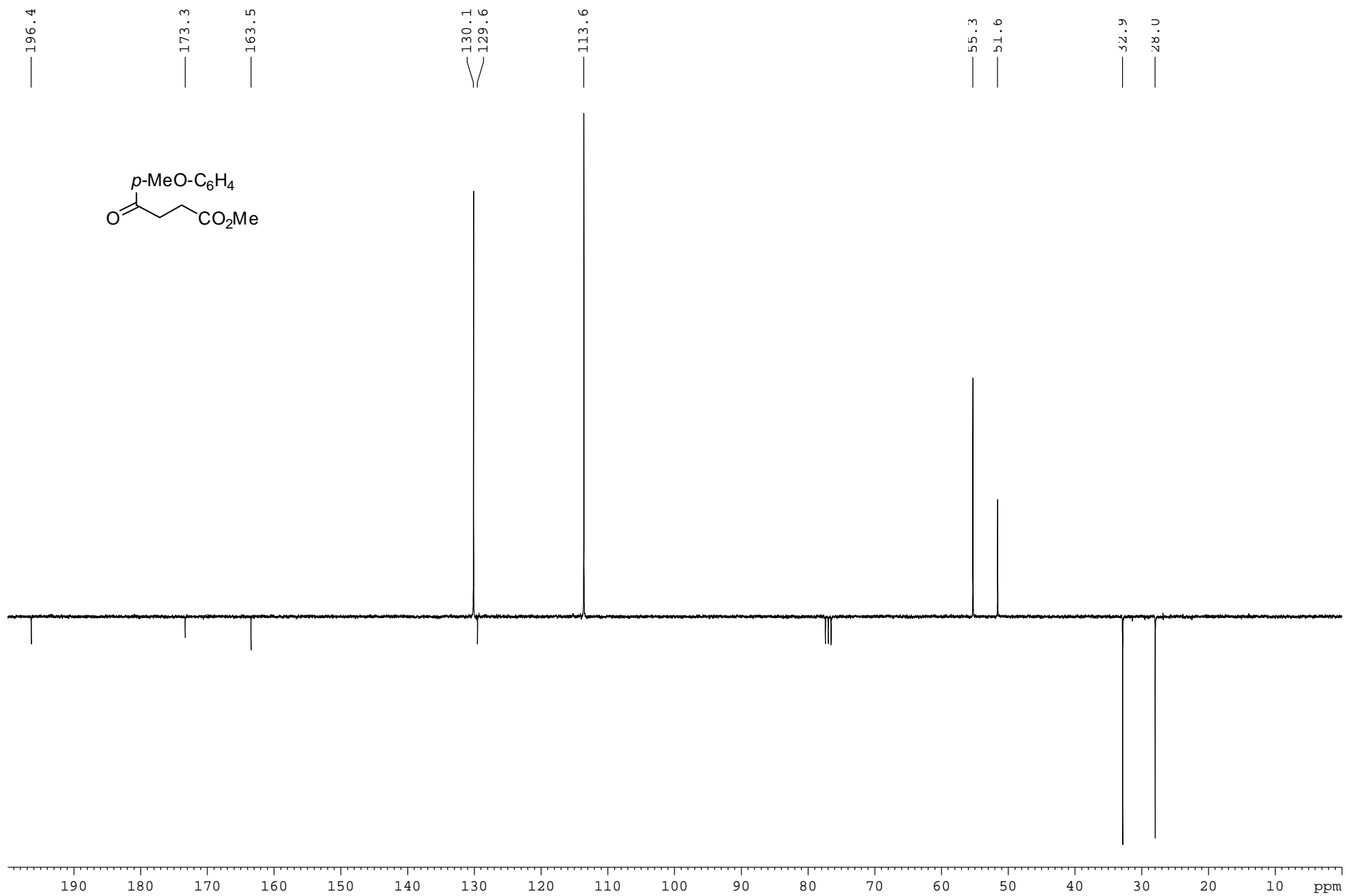
^{13}C NMR-APT (CDCl_3 , 75 MHz) of **6c**



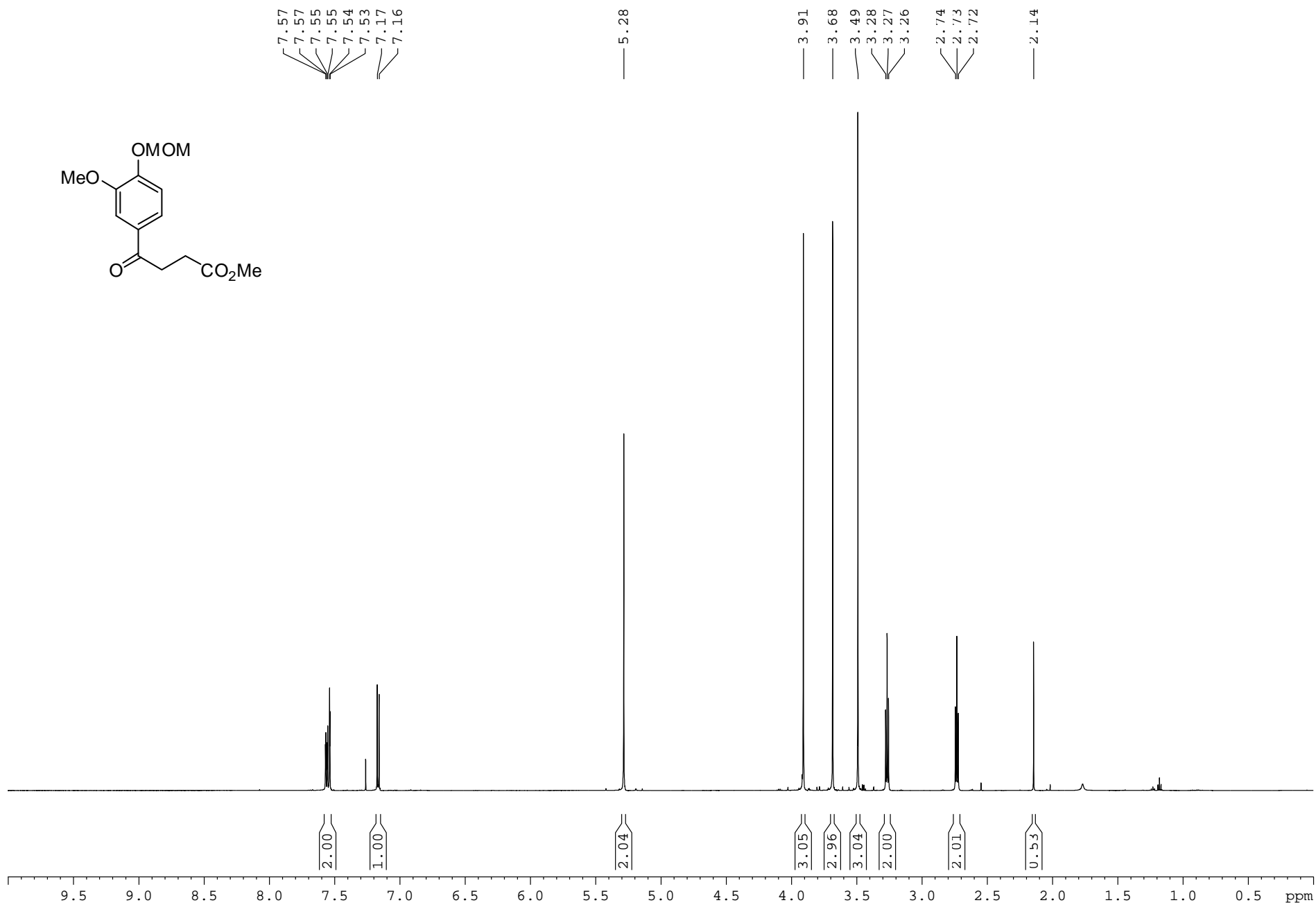
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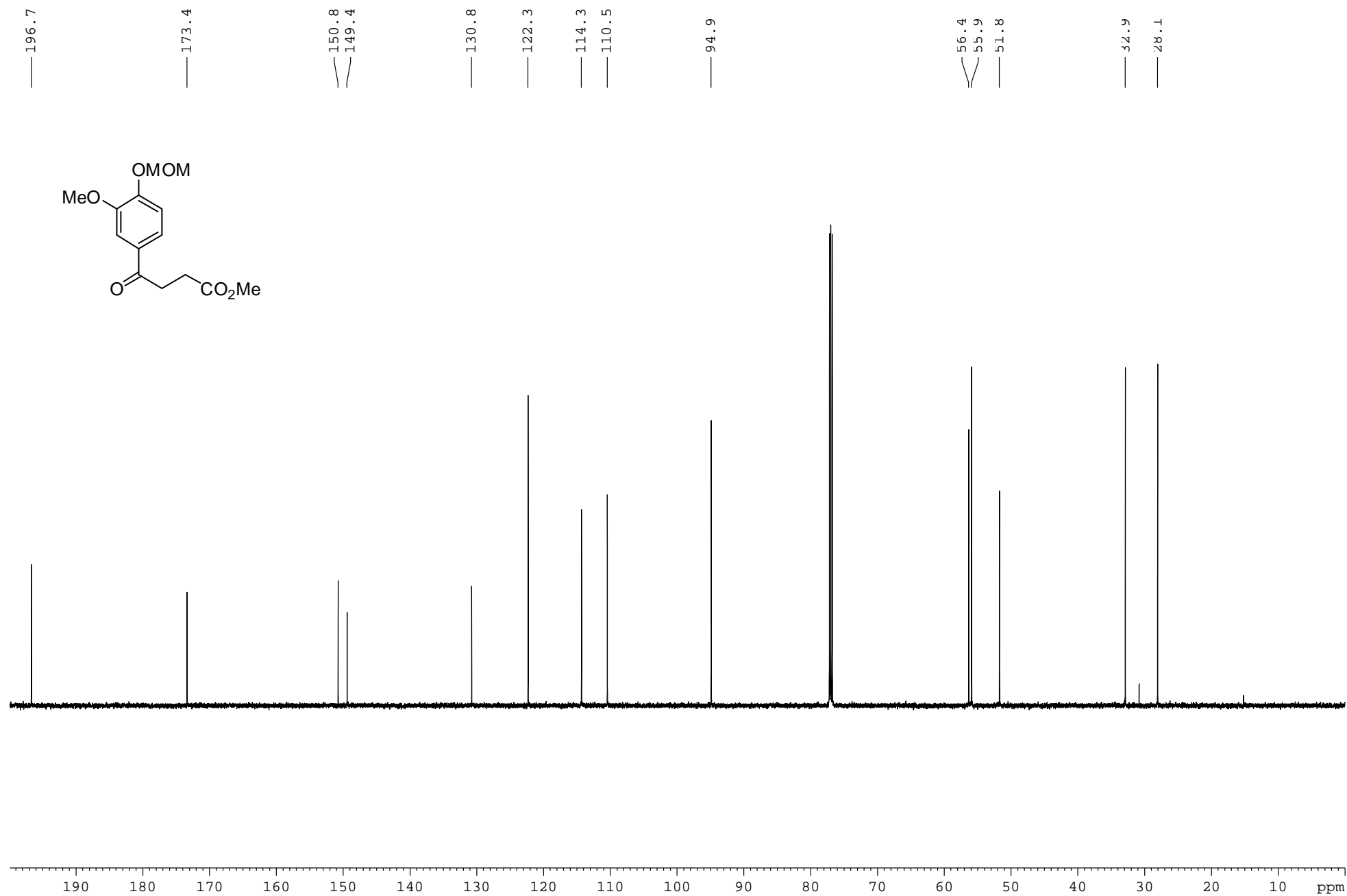
^{13}C NMR-APT (CDCl_3 , 75 MHz) of **6d**



^1H NMR (CDCl_3 , 600 MHz) of **6e**



^{13}C NMR (CDCl_3 , 150 MHz) of **6e**



^1H NMR (CDCl_3 , 300 MHz) of **6f**

7.92
7.91
7.91
7.89
7.88
7.88

6.89
6.88
6.88
6.86
6.85
6.84

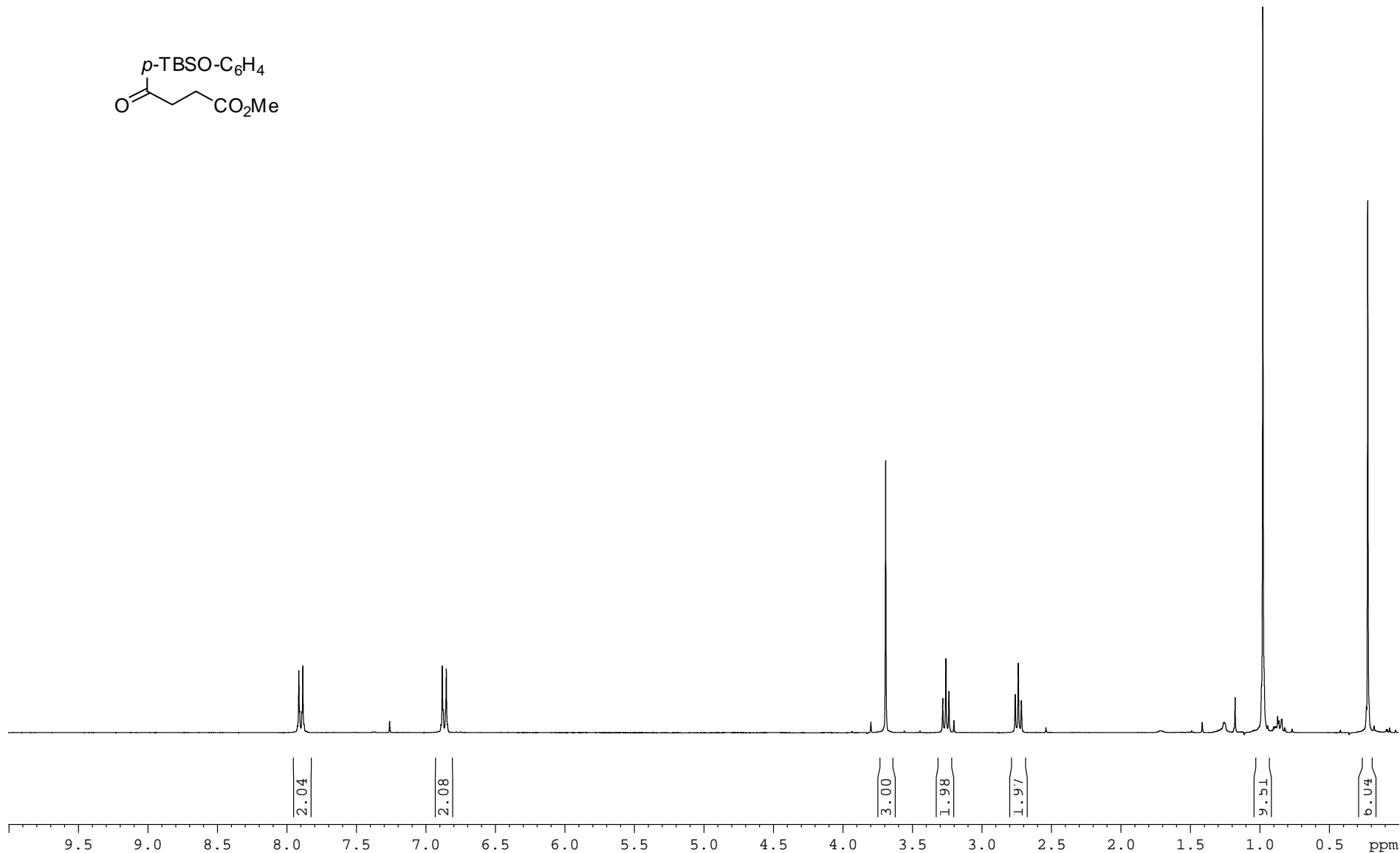
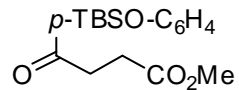
3.69

3.28
3.26
3.24

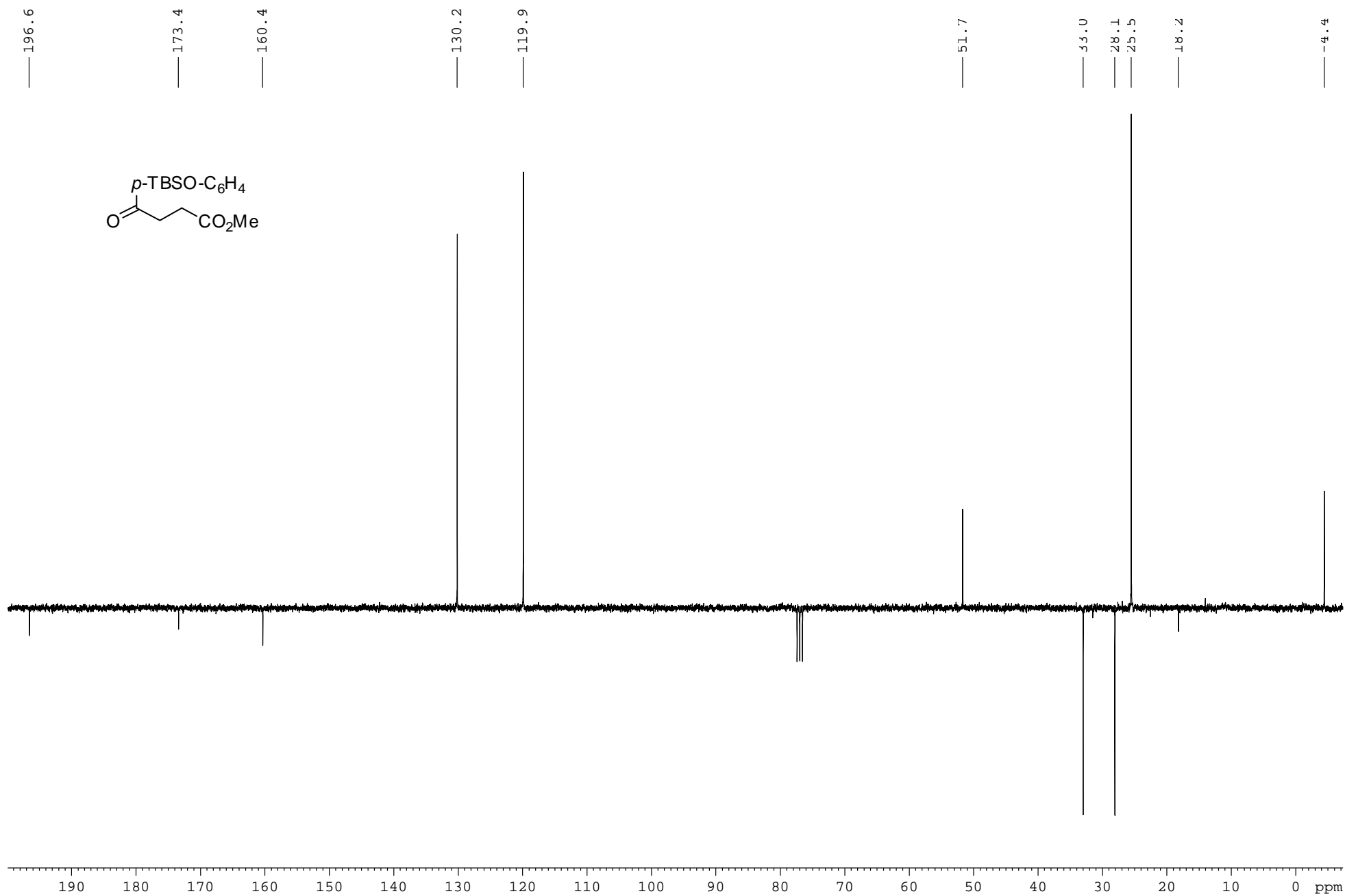
2.76
2.74
2.72

0.98

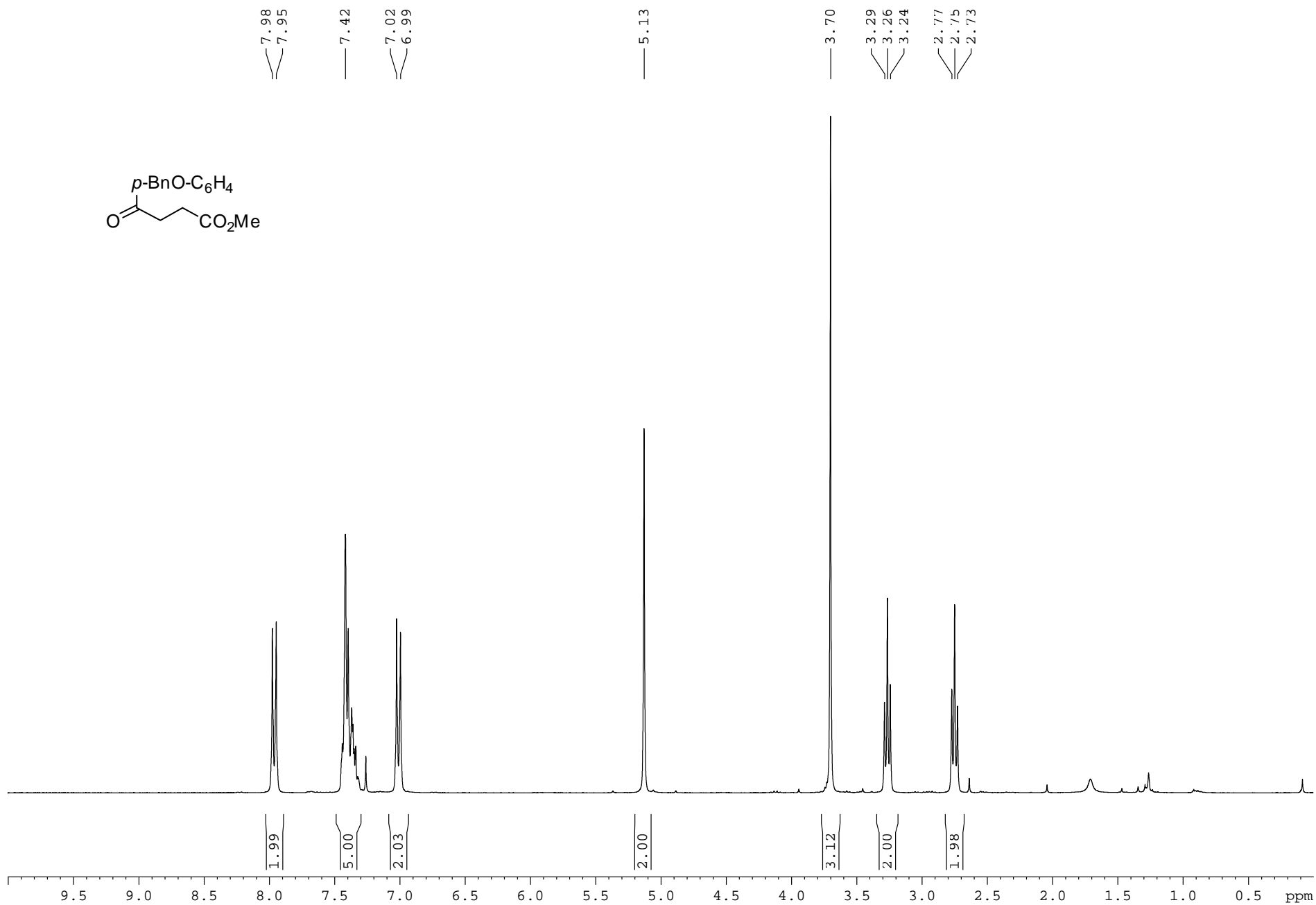
0.22



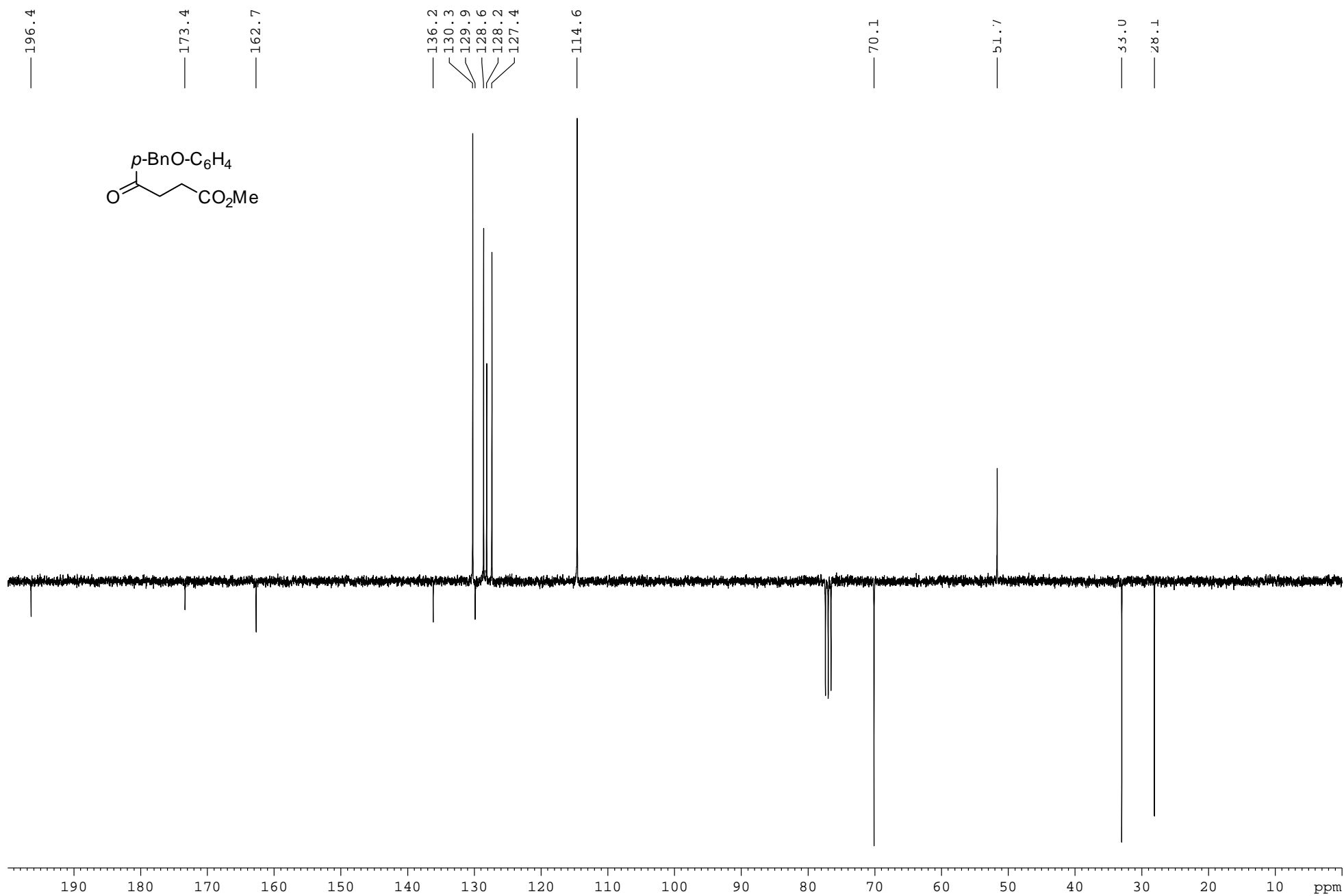
^{13}C NMR-APT (CDCl_3 , 75 MHz) of **6f**



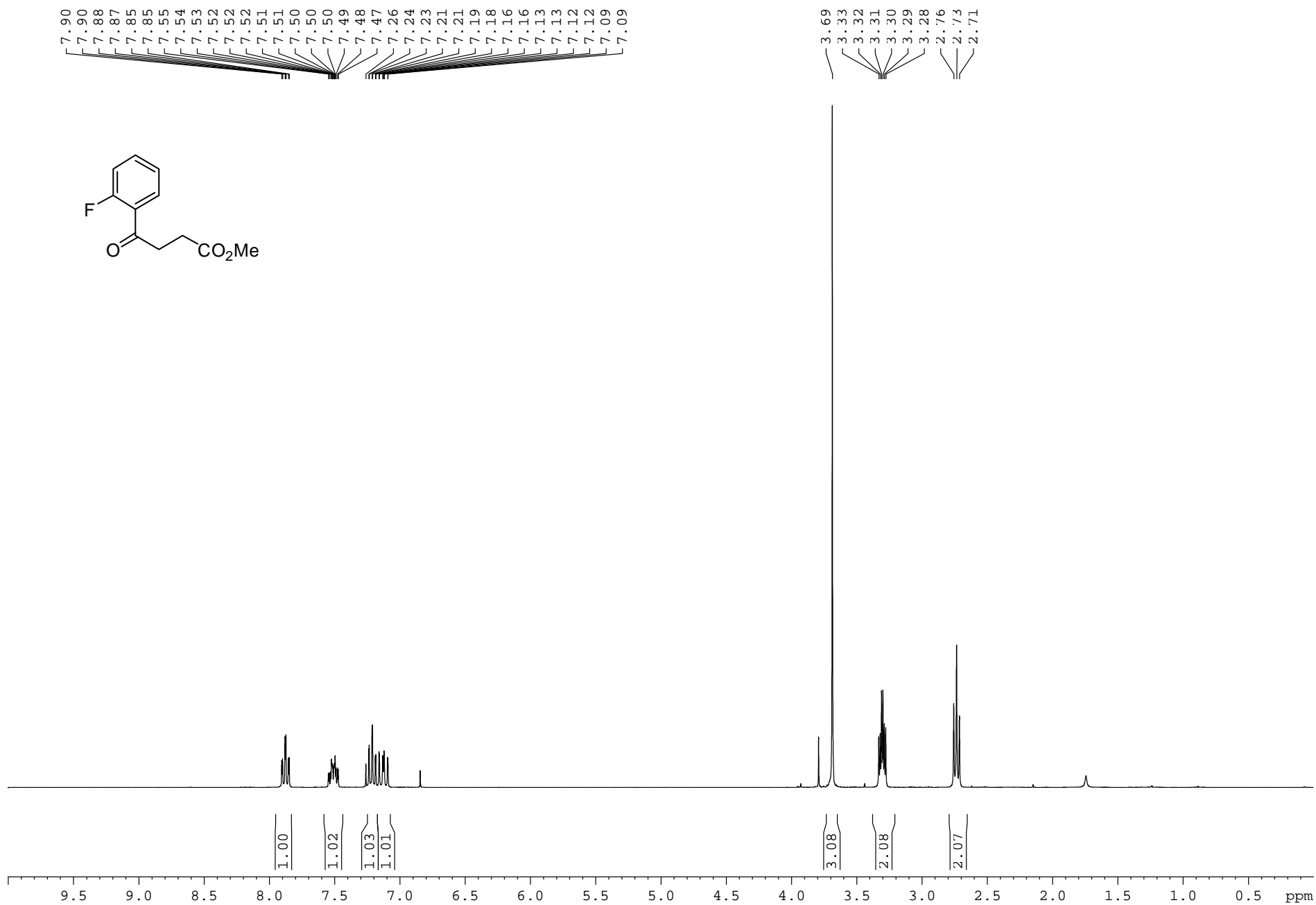
^1H NMR (CDCl_3 , 300 MHz) of **6g**



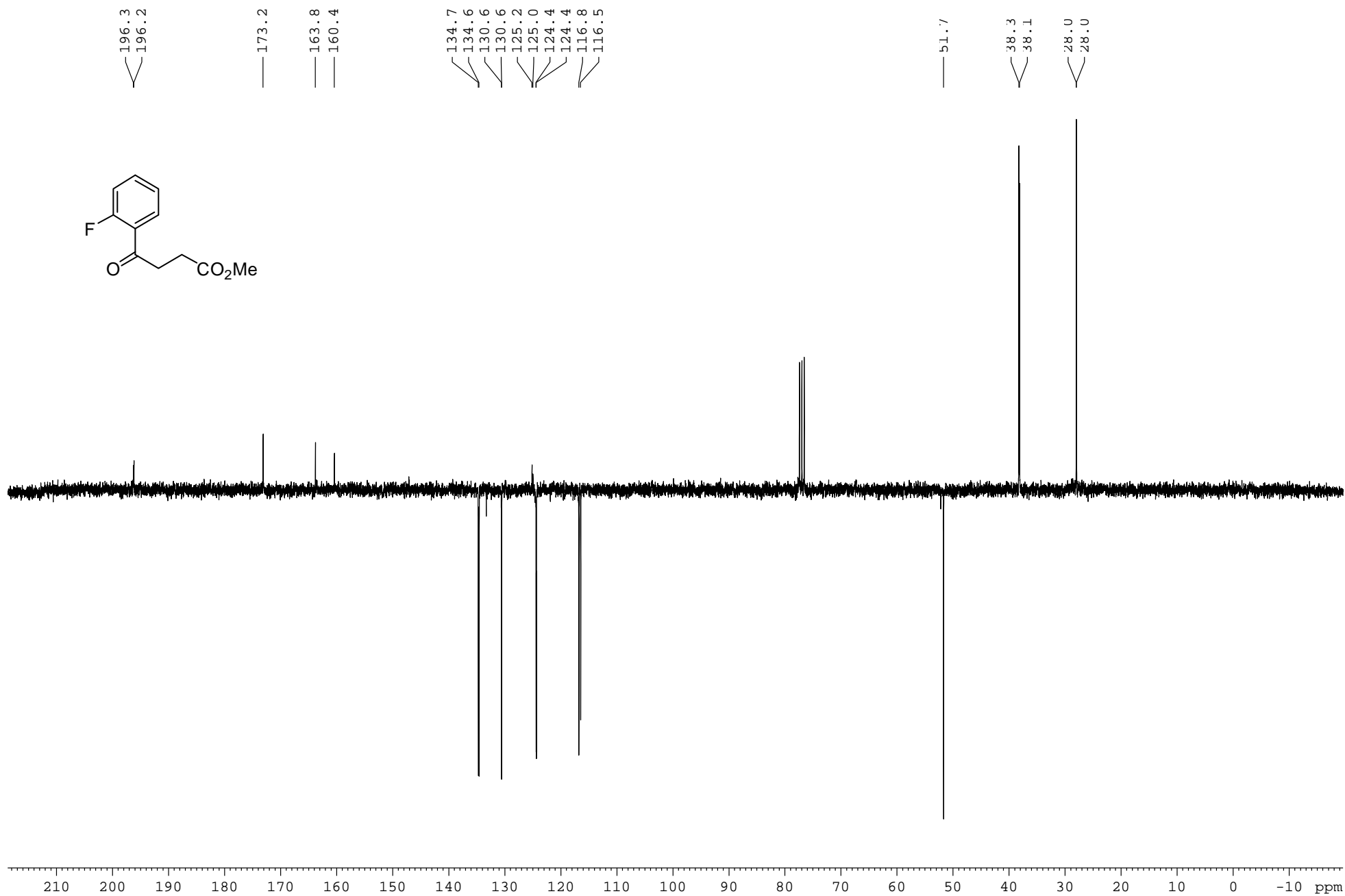
^{13}C NMR-APT (CDCl_3 , 75 MHz) of **6g**



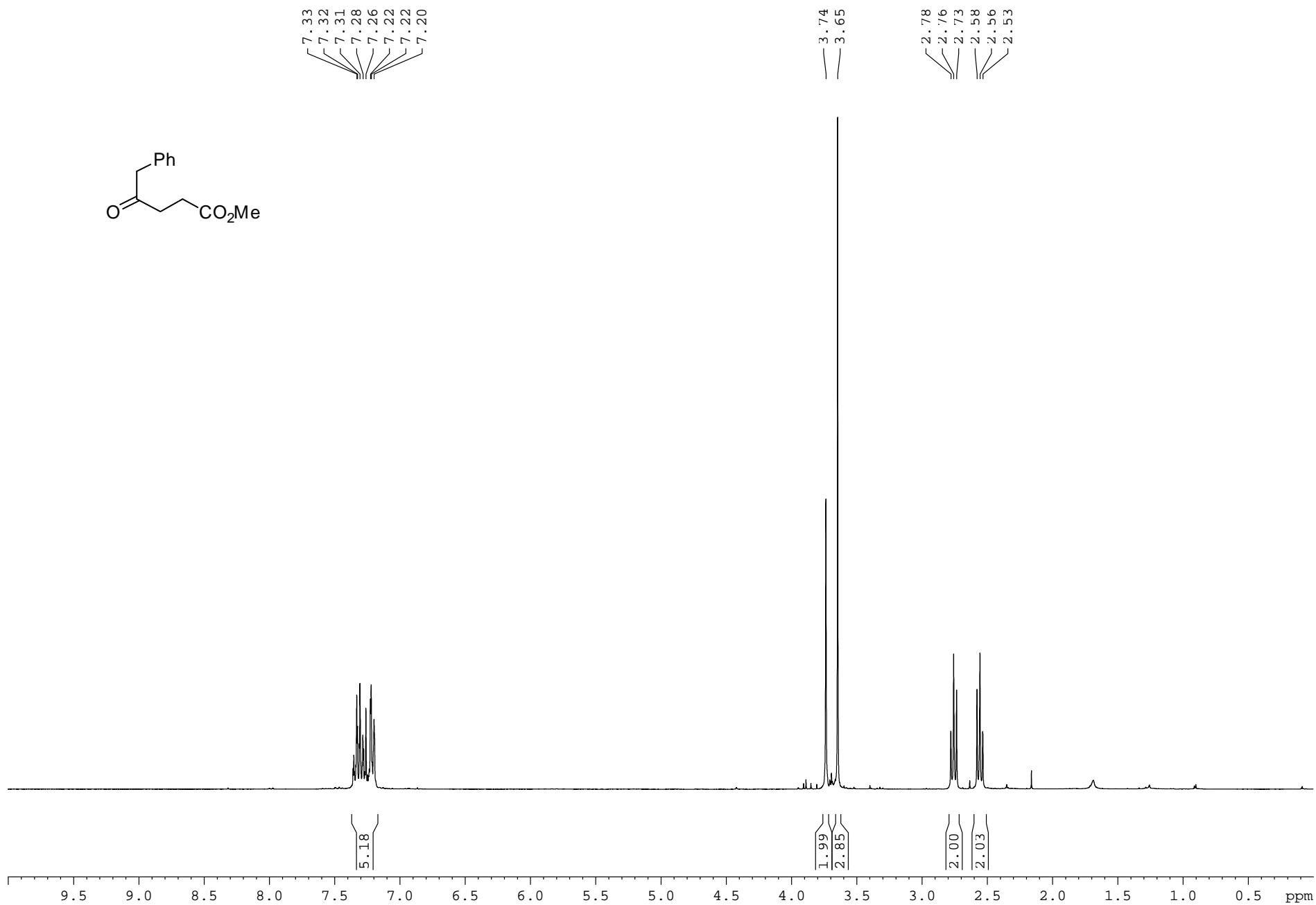
^1H NMR (CDCl_3 , 300 MHz) of **6h**



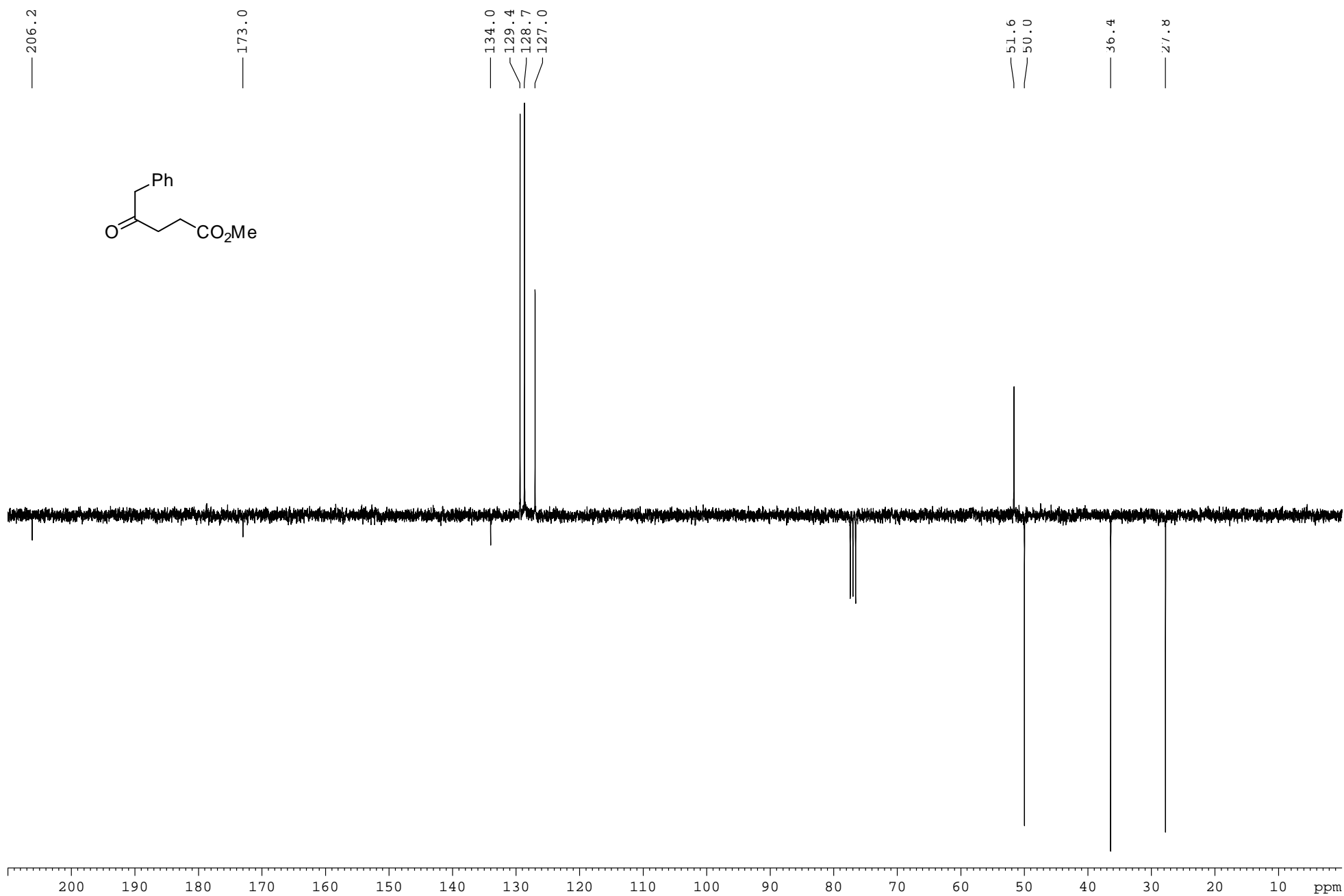
^{13}C NMR-APT (CDCl_3 , 75 MHz) of **6h**



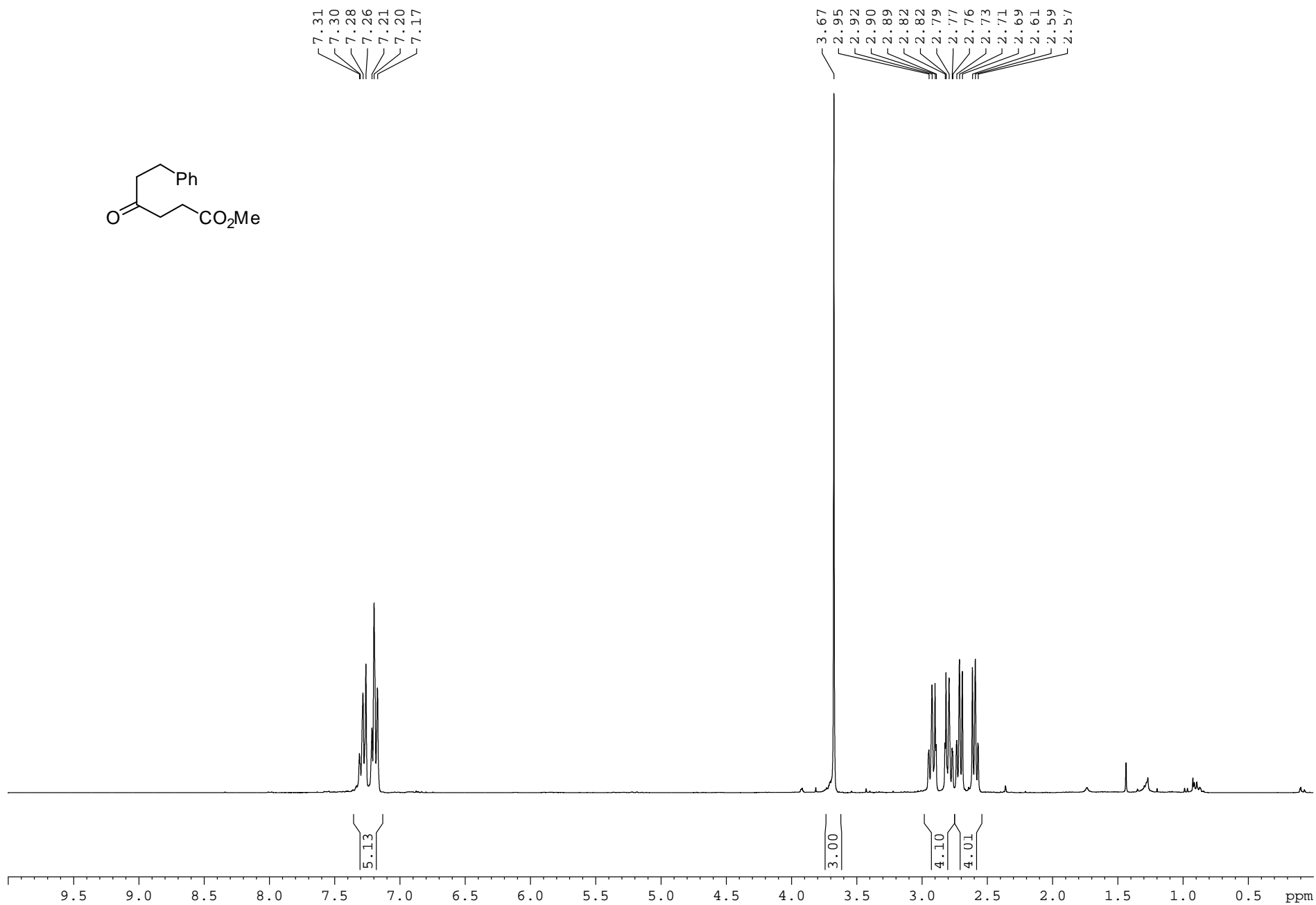
^1H NMR (CDCl_3 , 300 MHz) of **6i**



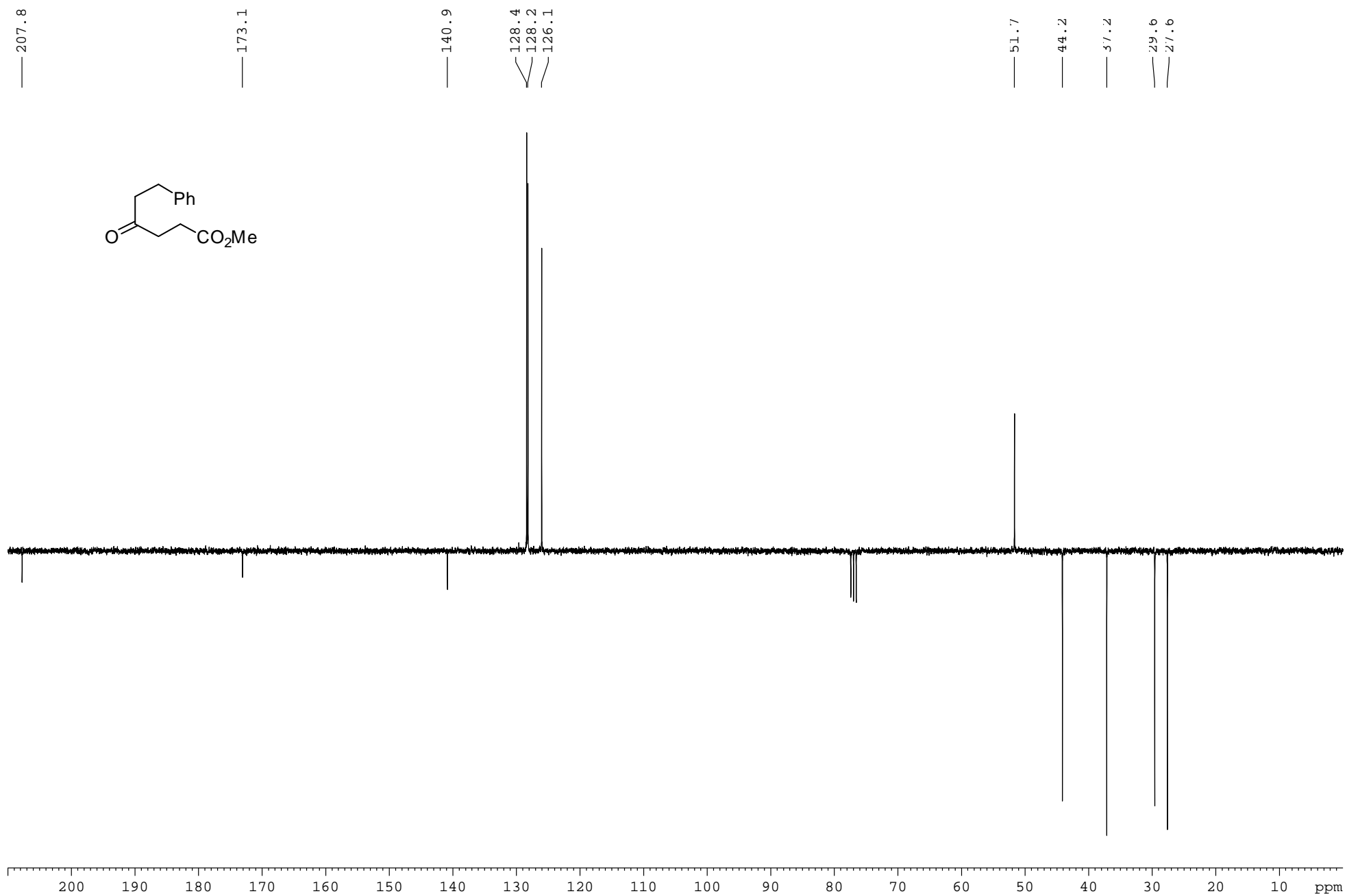
^{13}C NMR-APT (CDCl_3 , 75 MHz) of **6i**



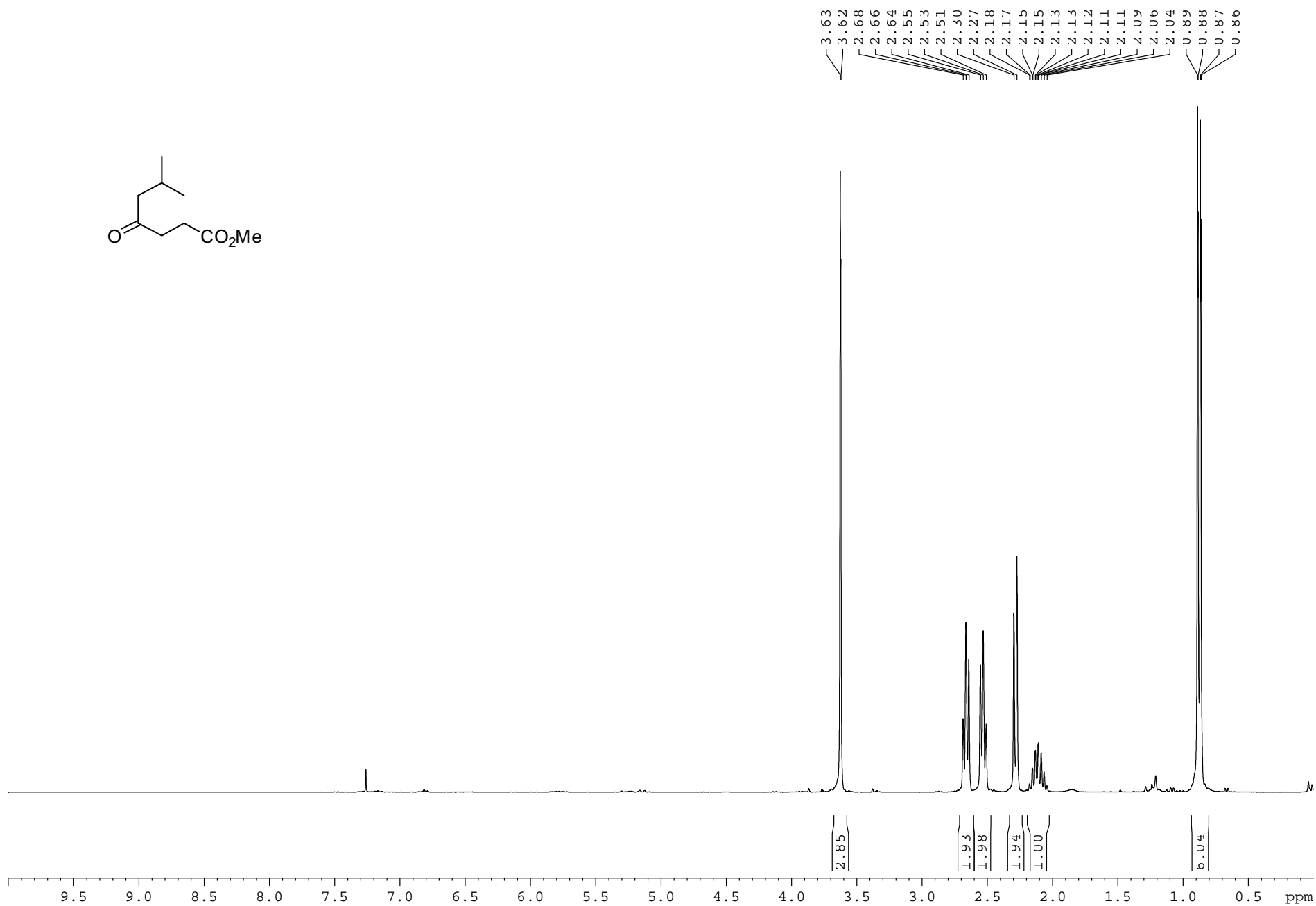
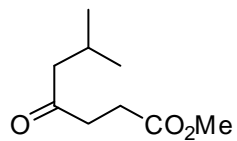
^1H NMR (CDCl_3 , 300 MHz) of **6j**



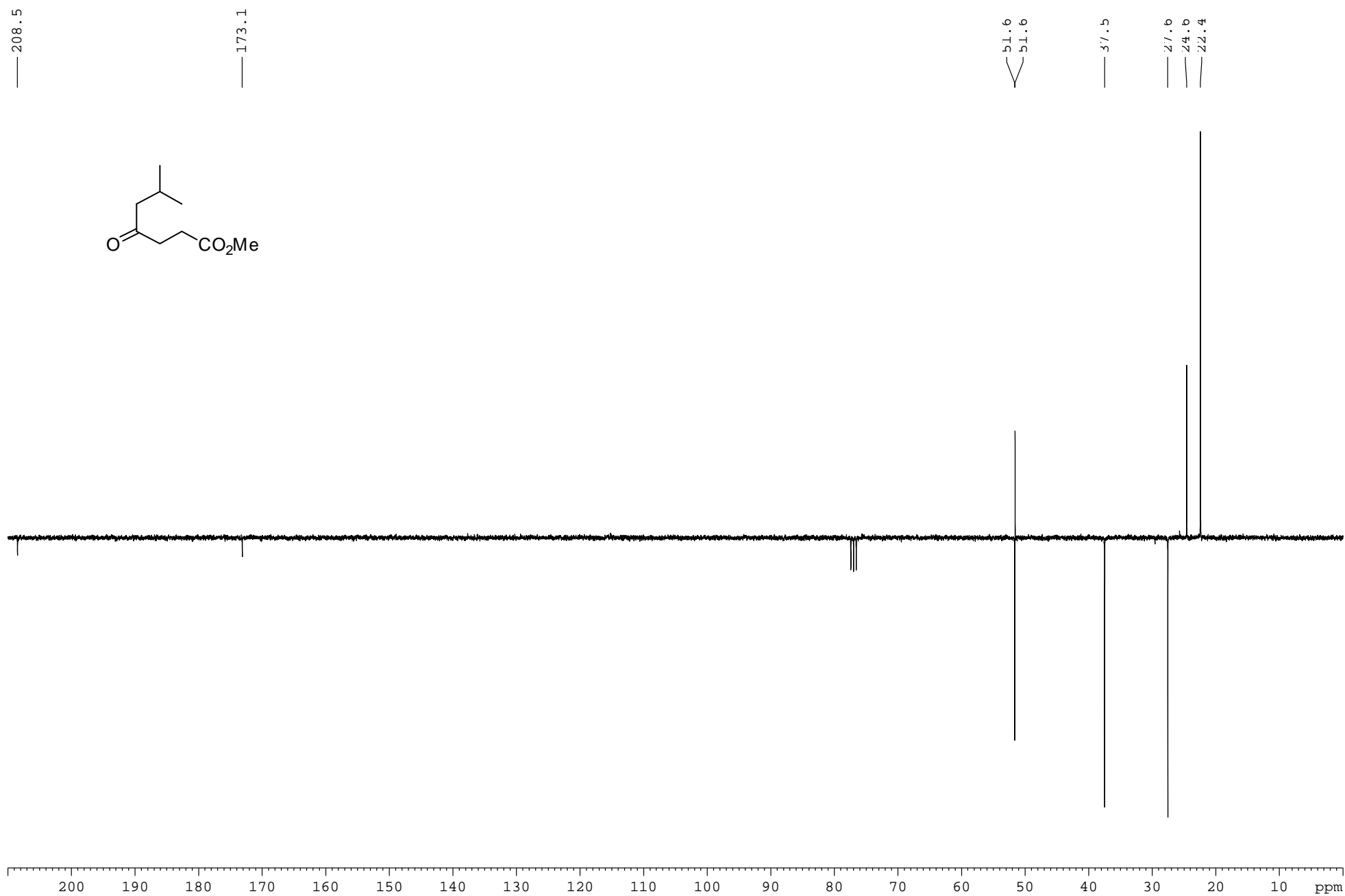
^{13}C NMR-APT (CDCl_3 , 75 MHz) of **6j**



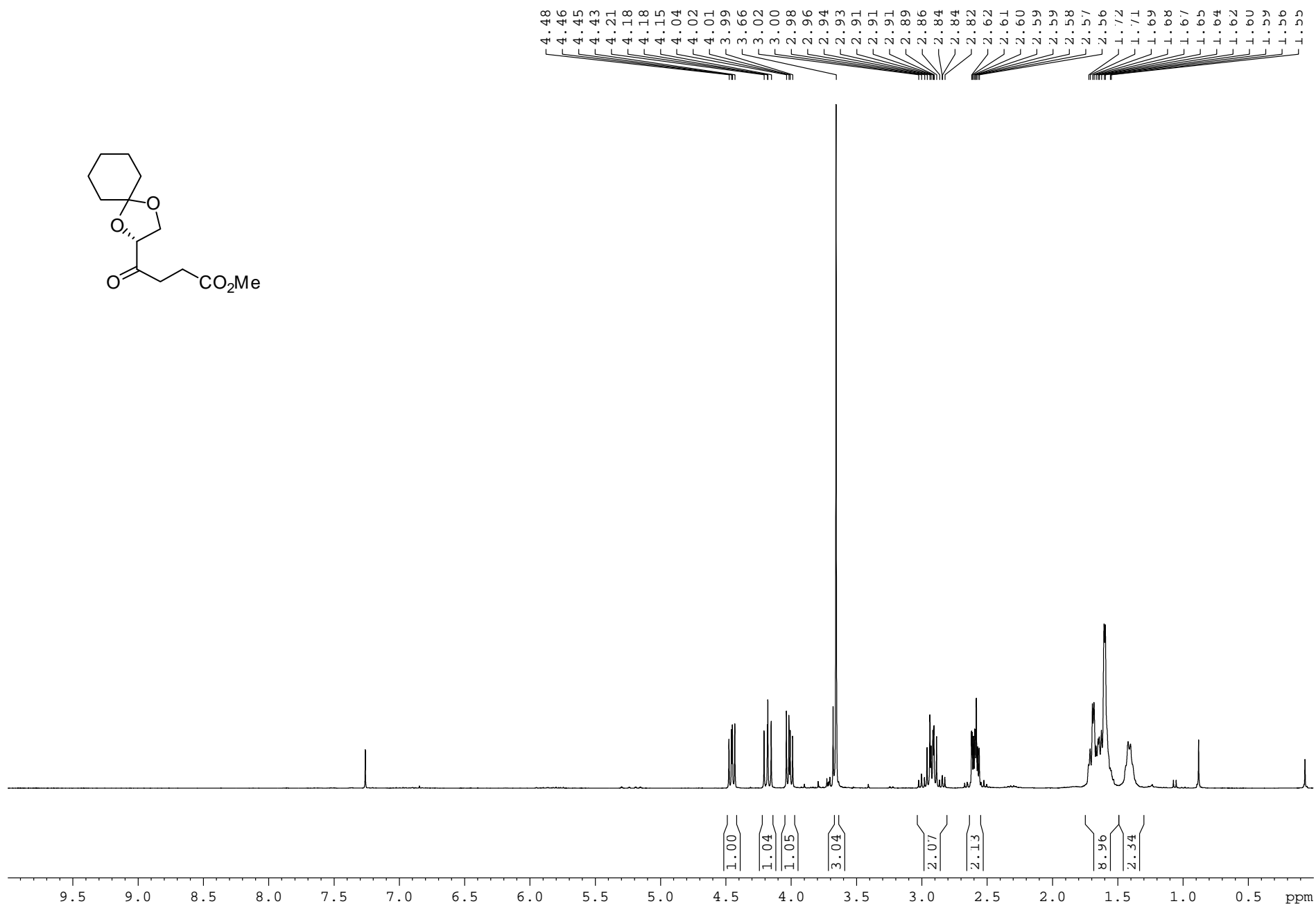
^1H NMR (CDCl_3 , 300 MHz) of **6k**



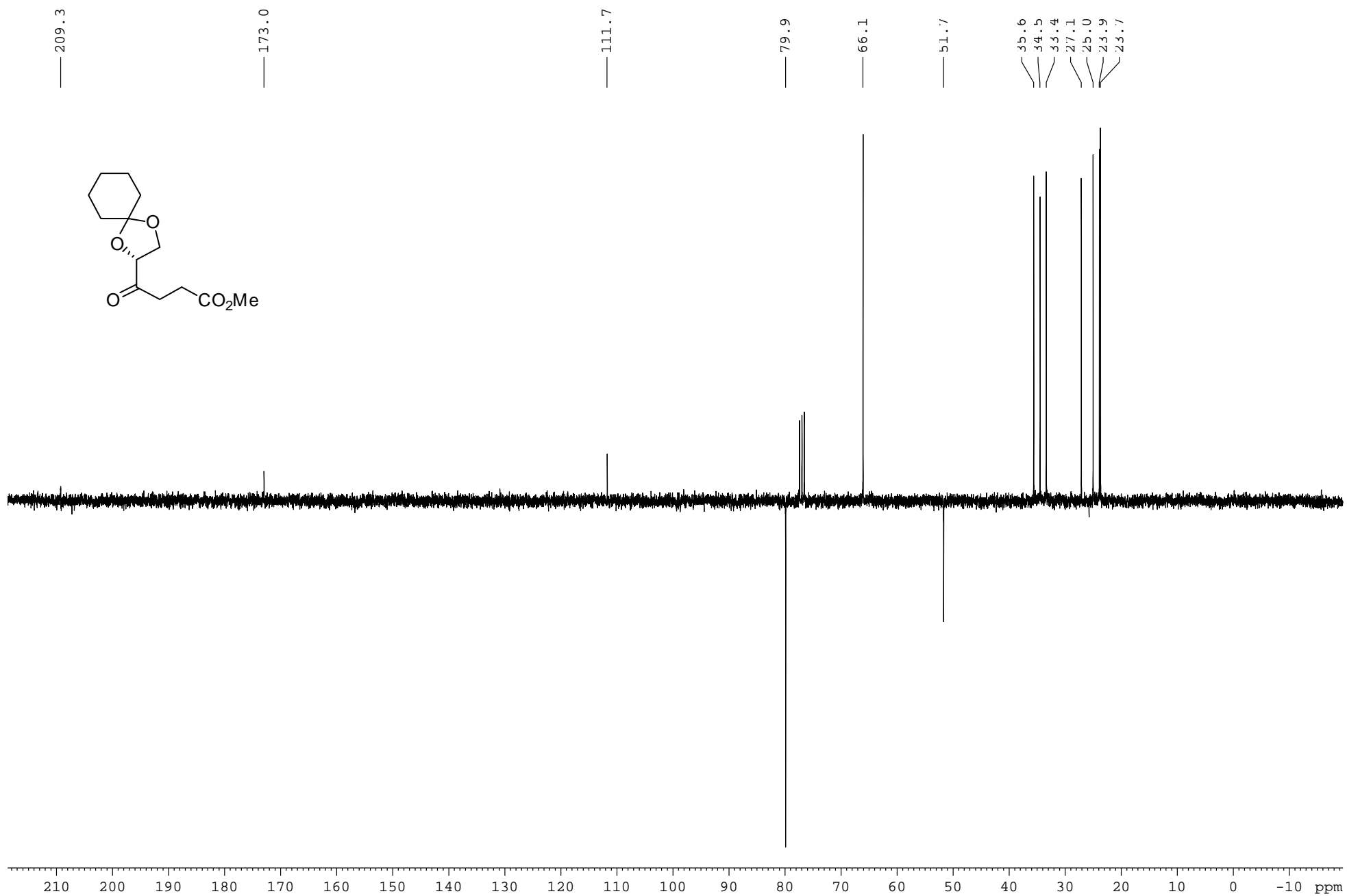
^{13}C NMR-APT (CDCl_3 , 75 MHz) of **6k**



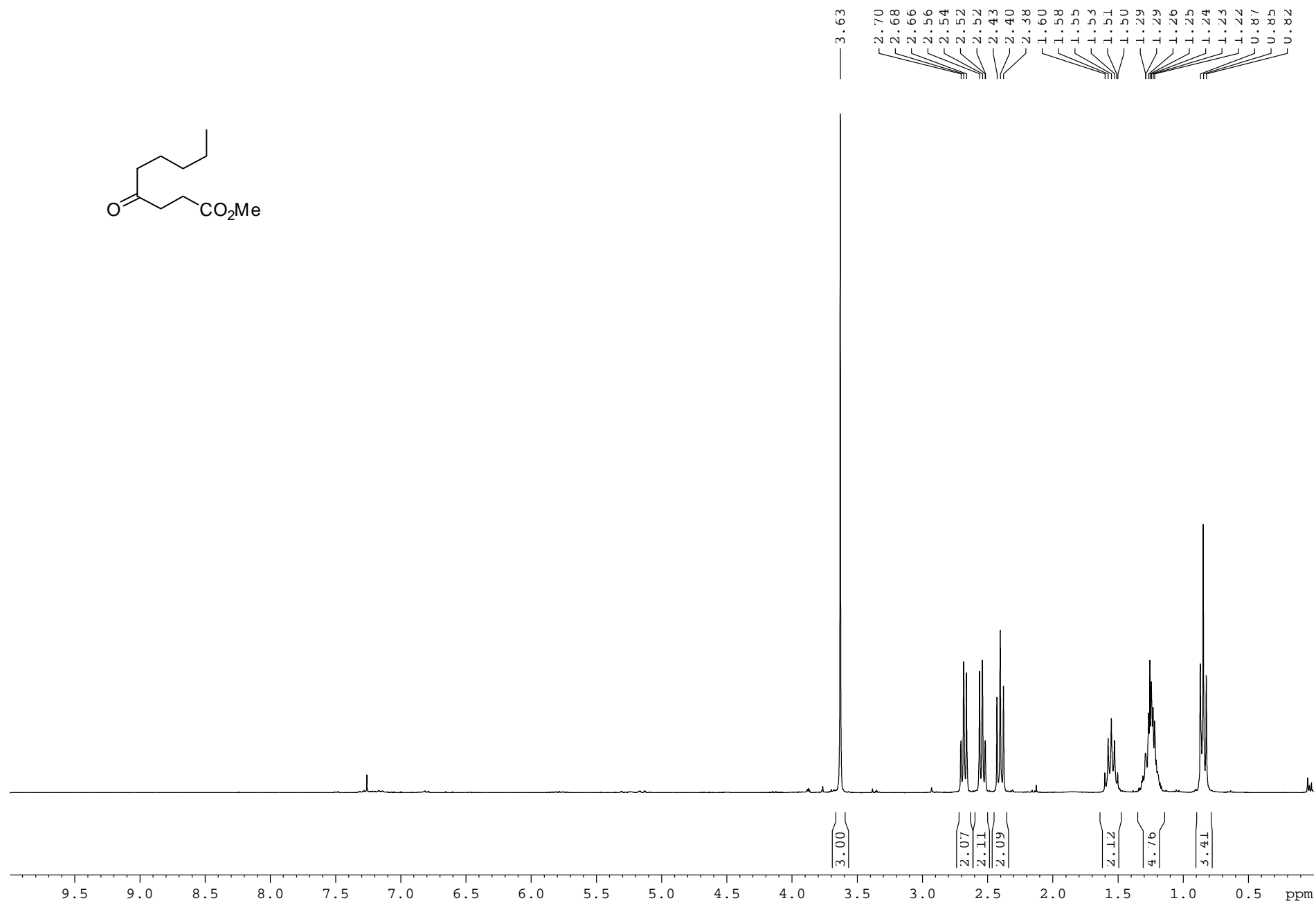
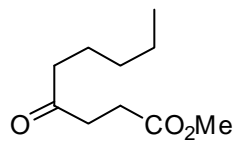
^1H NMR (CDCl_3 , 300 MHz) of **61**



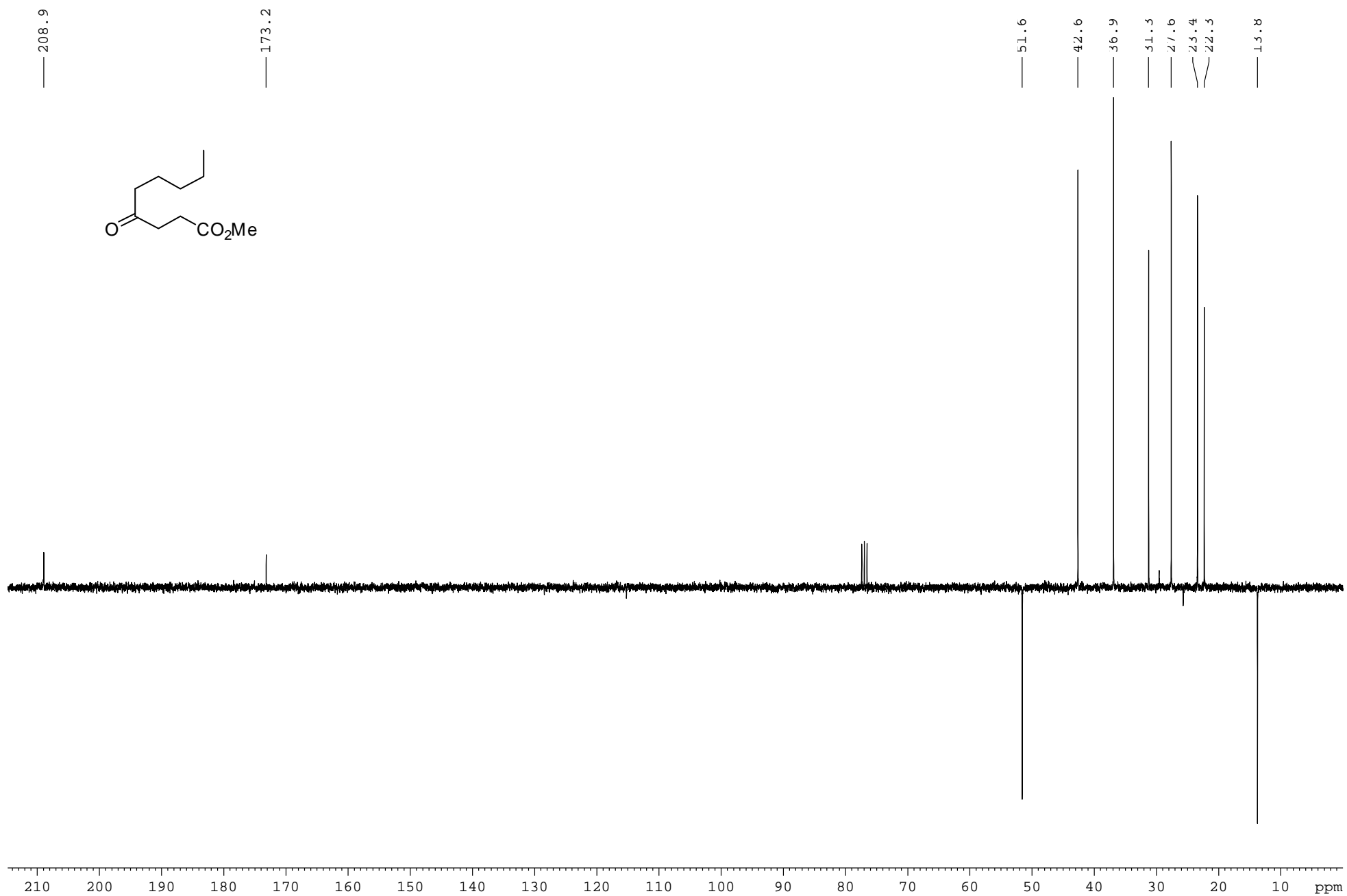
^{13}C NMR-APT (CDCl_3 , 75 MHz) of **61**



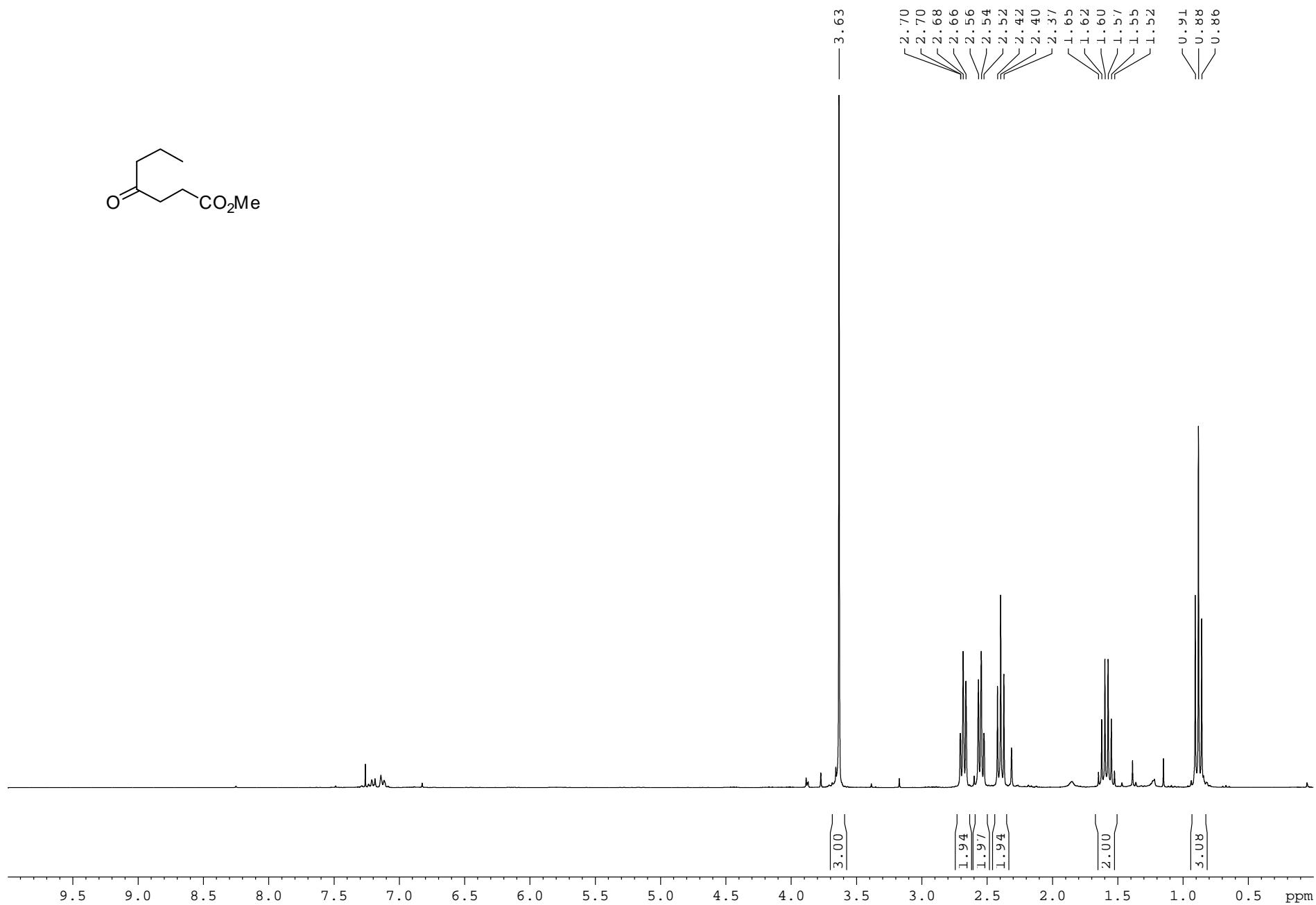
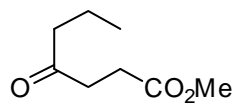
^1H NMR (CDCl_3 , 300 MHz) of **6m**



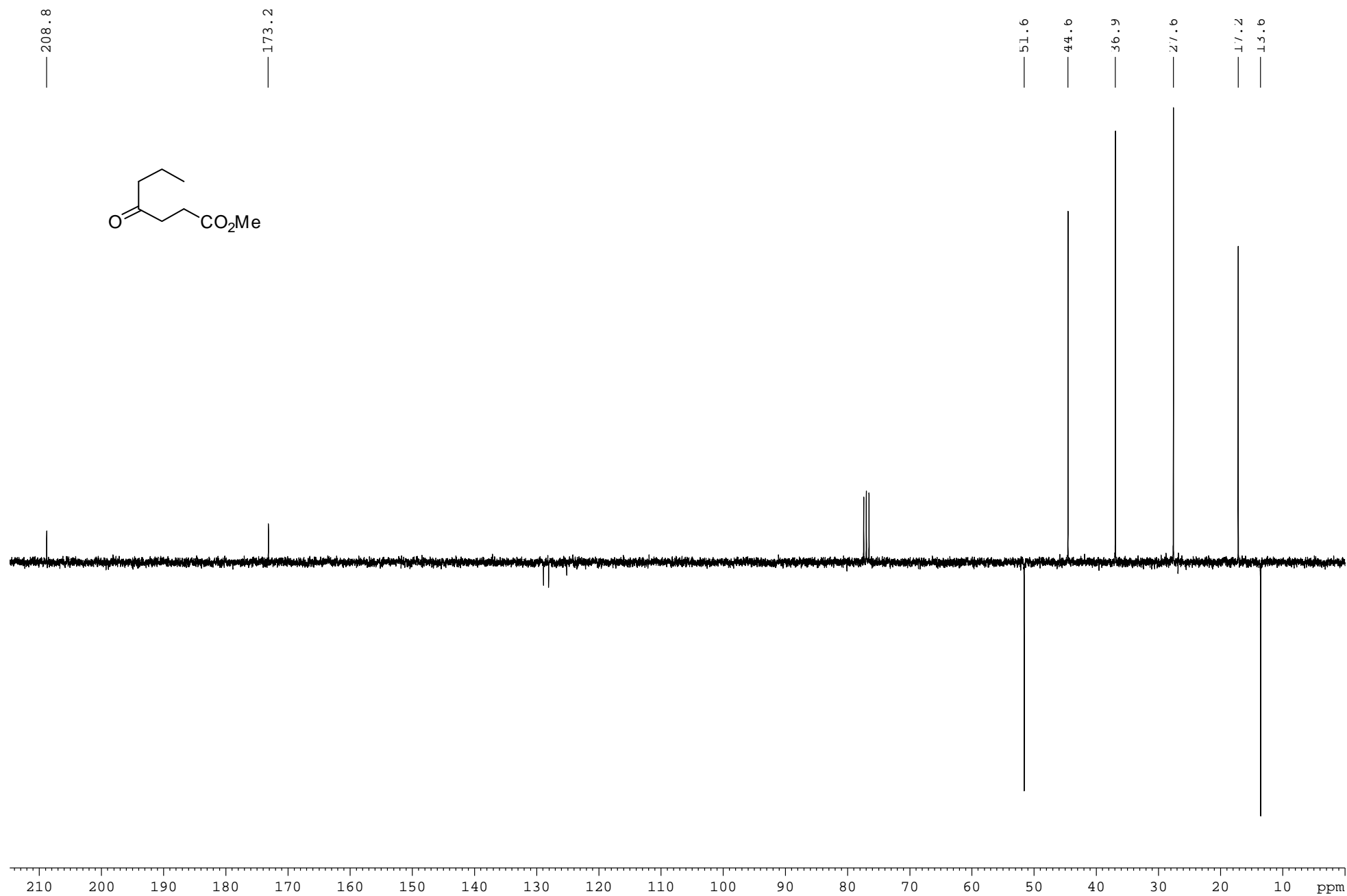
^{13}C NMR-APT (CDCl_3 , 75 MHz) of **6m**



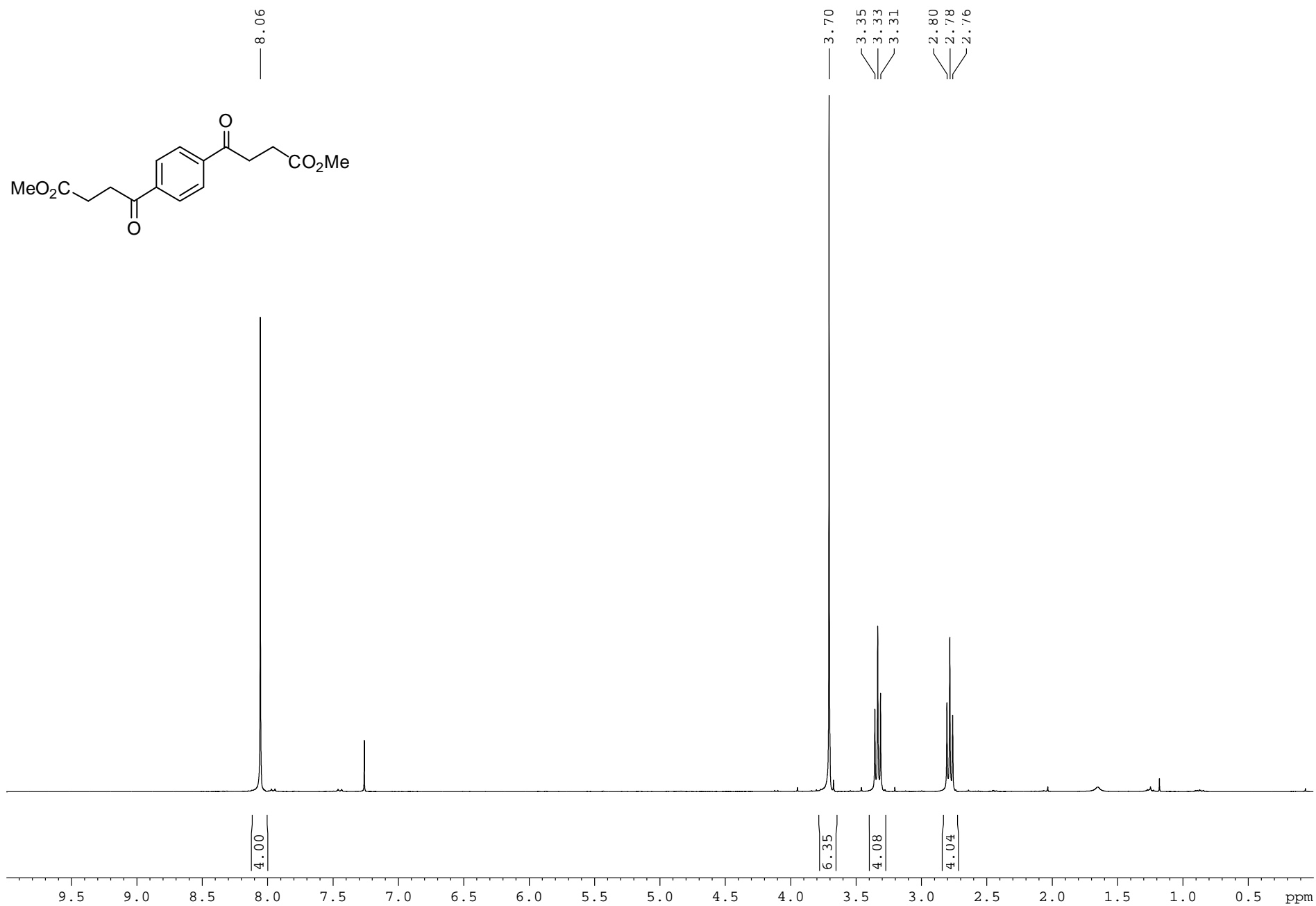
^1H NMR (CDCl_3 , 300 MHz) of **6n**



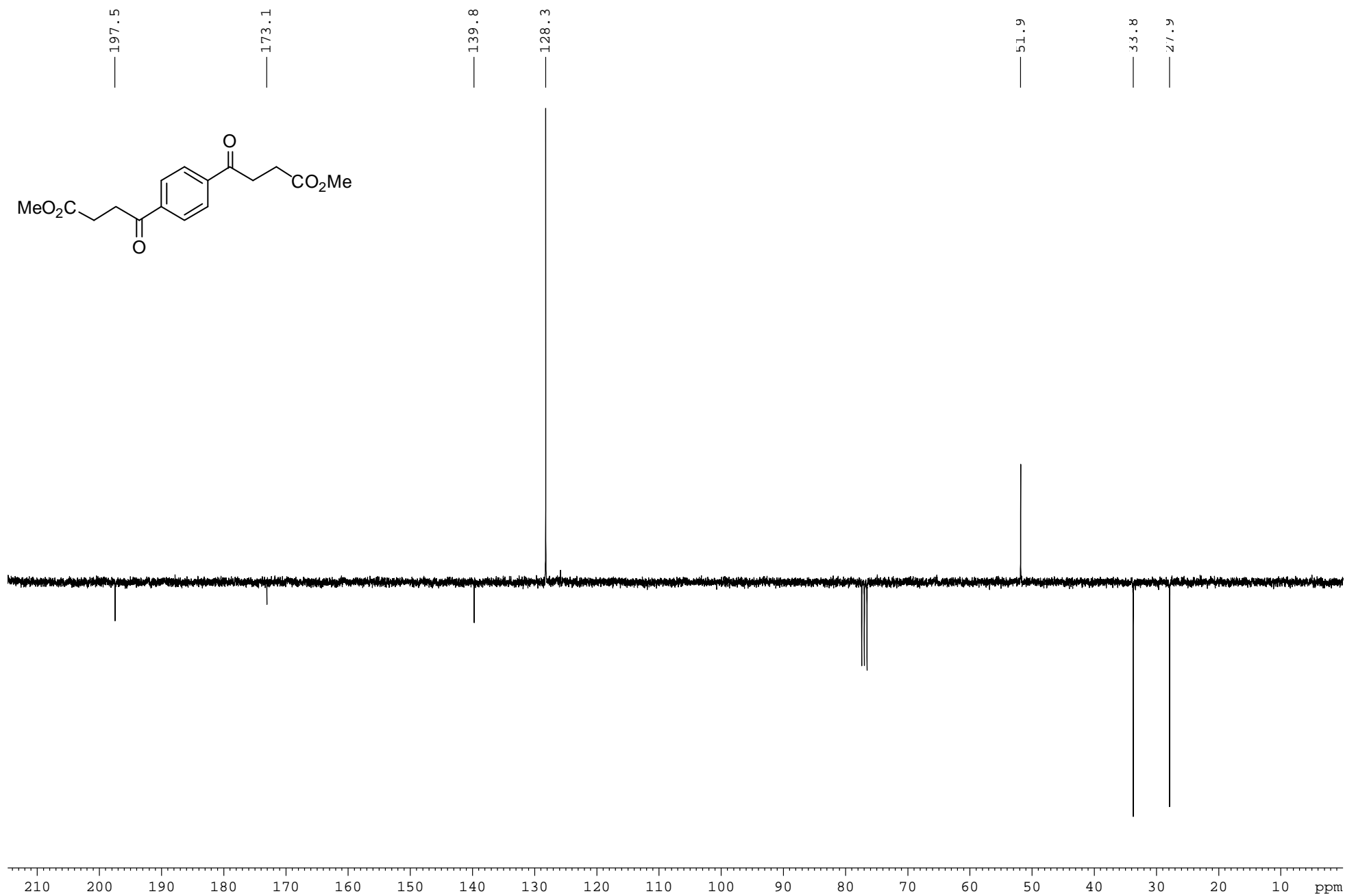
^{13}C NMR-APT (CDCl_3 , 75 MHz) of **6n**



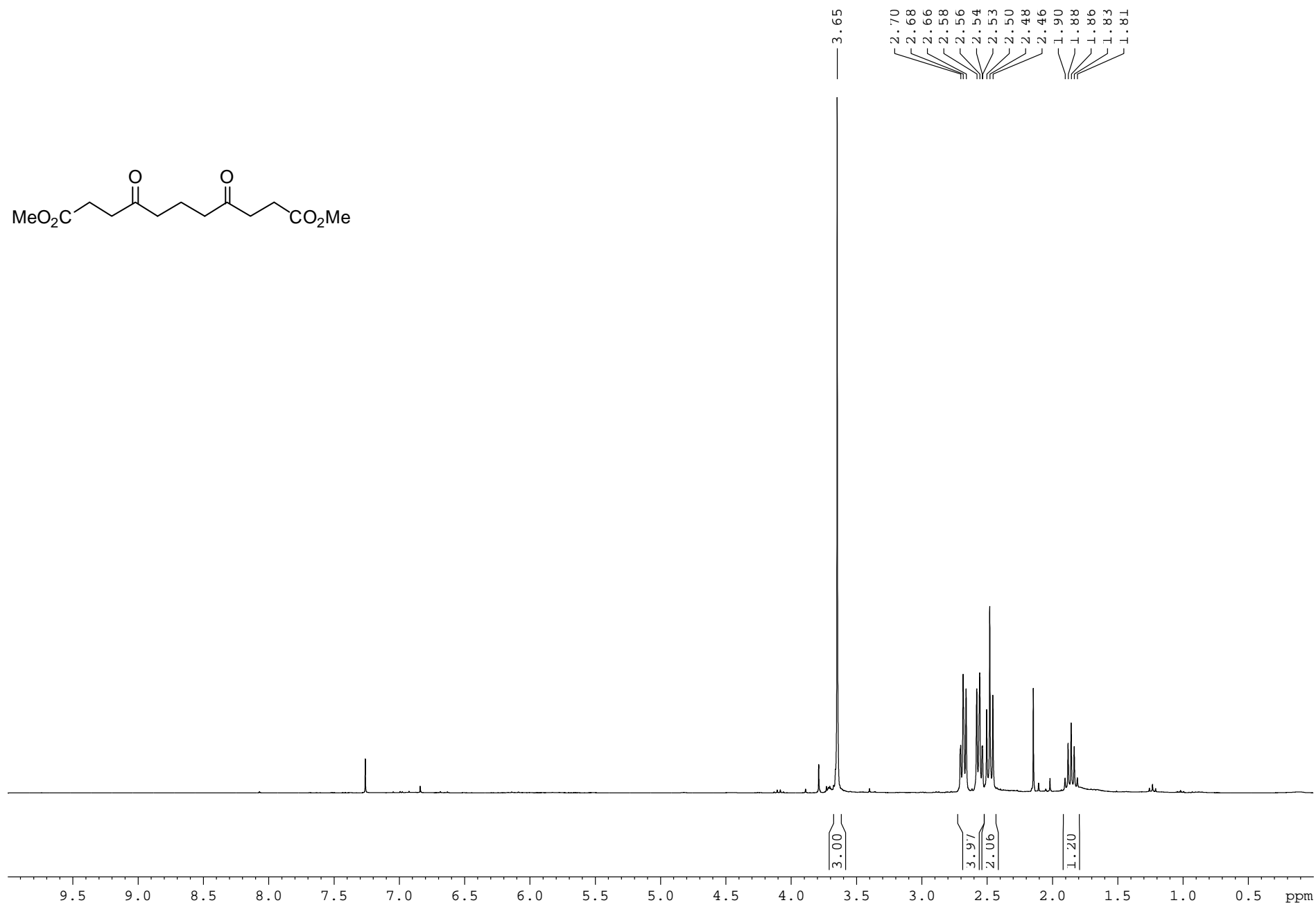
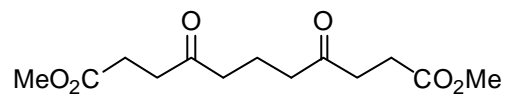
^1H NMR (CDCl_3 , 300 MHz) of **60**



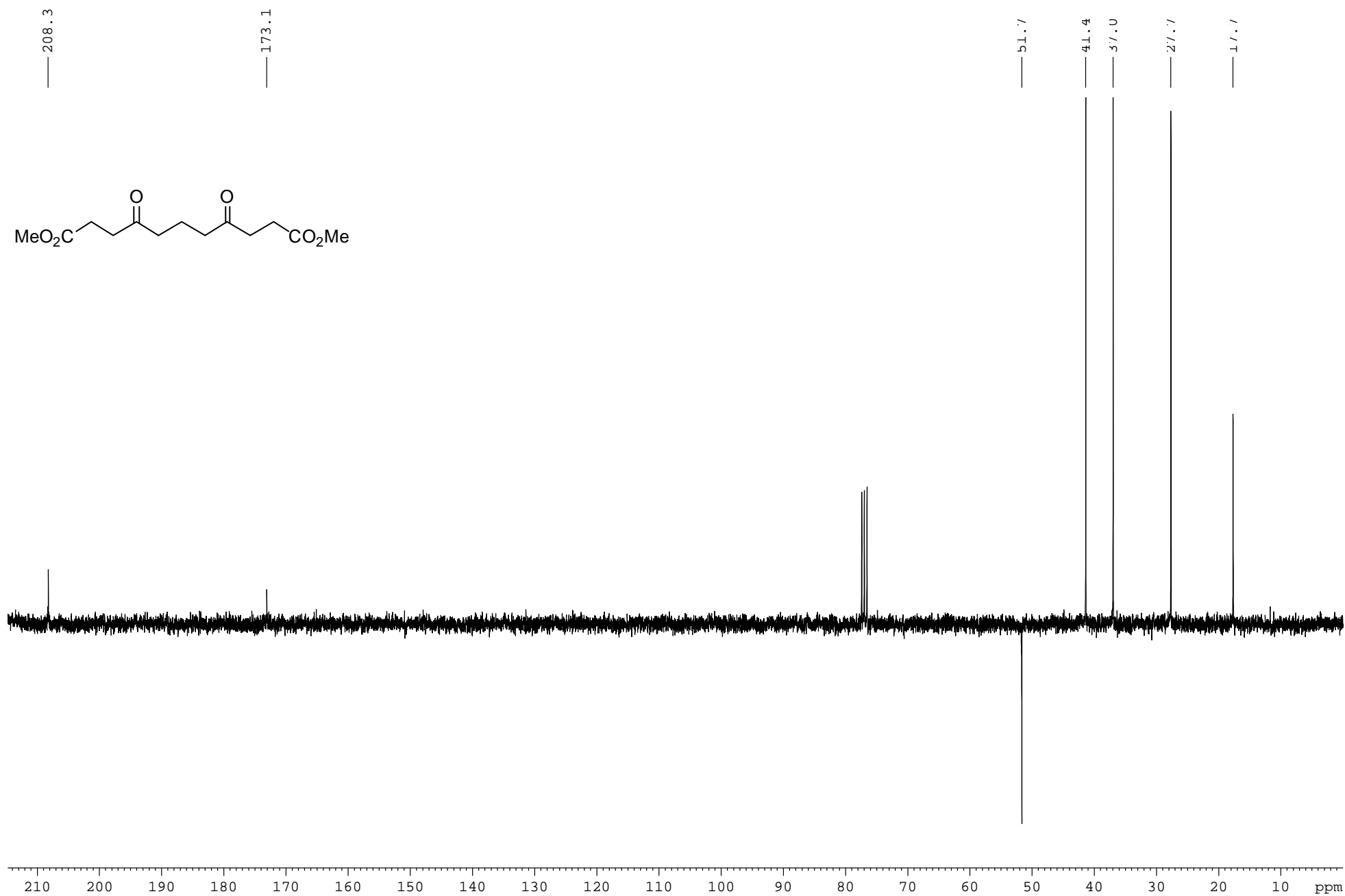
^{13}C NMR-APT (CDCl_3 , 75 MHz) of **60**



^1H NMR (CDCl_3 , 300 MHz) of **6p**

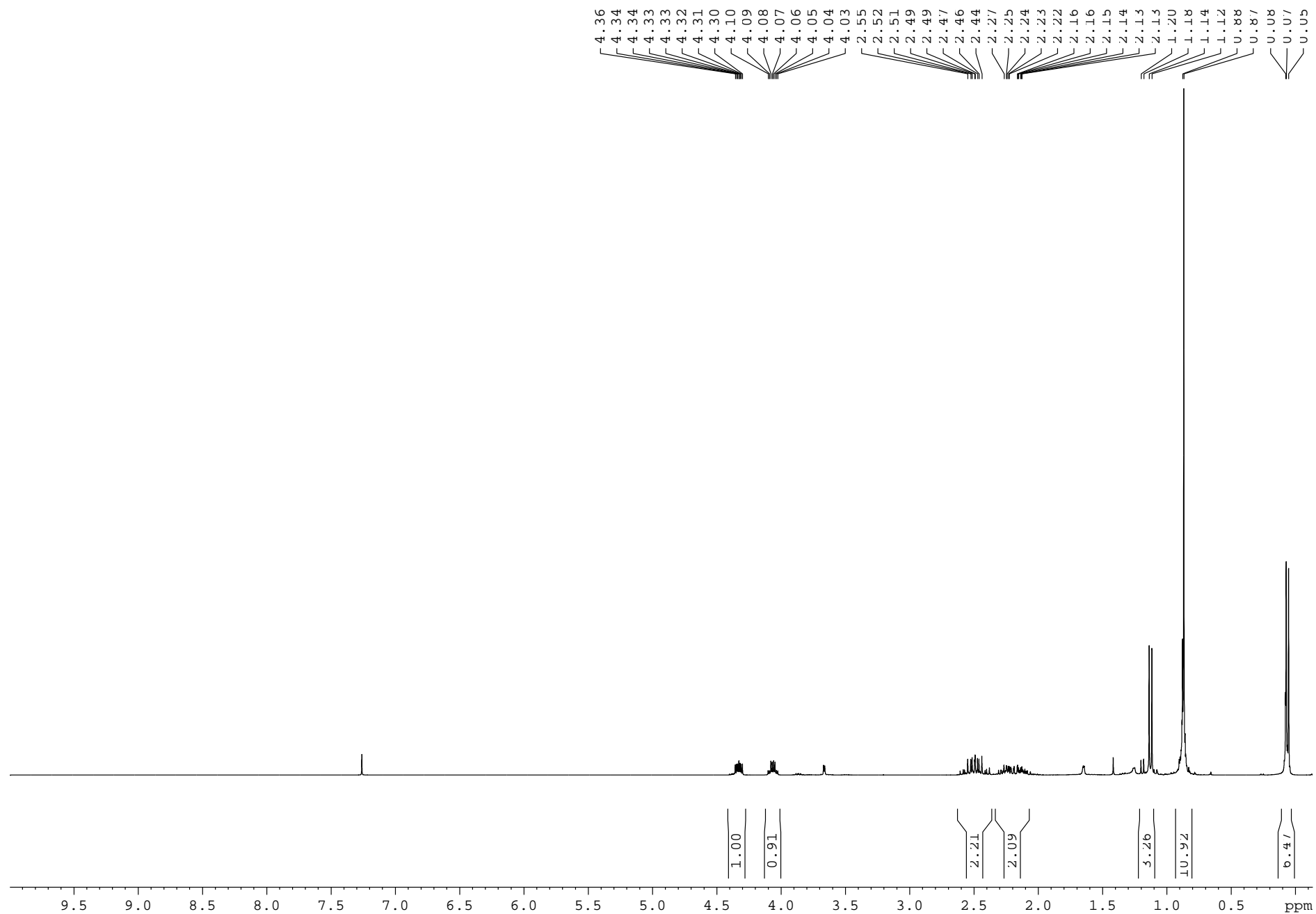


^{13}C NMR-APT (CDCl_3 , 75 MHz) of **6p**

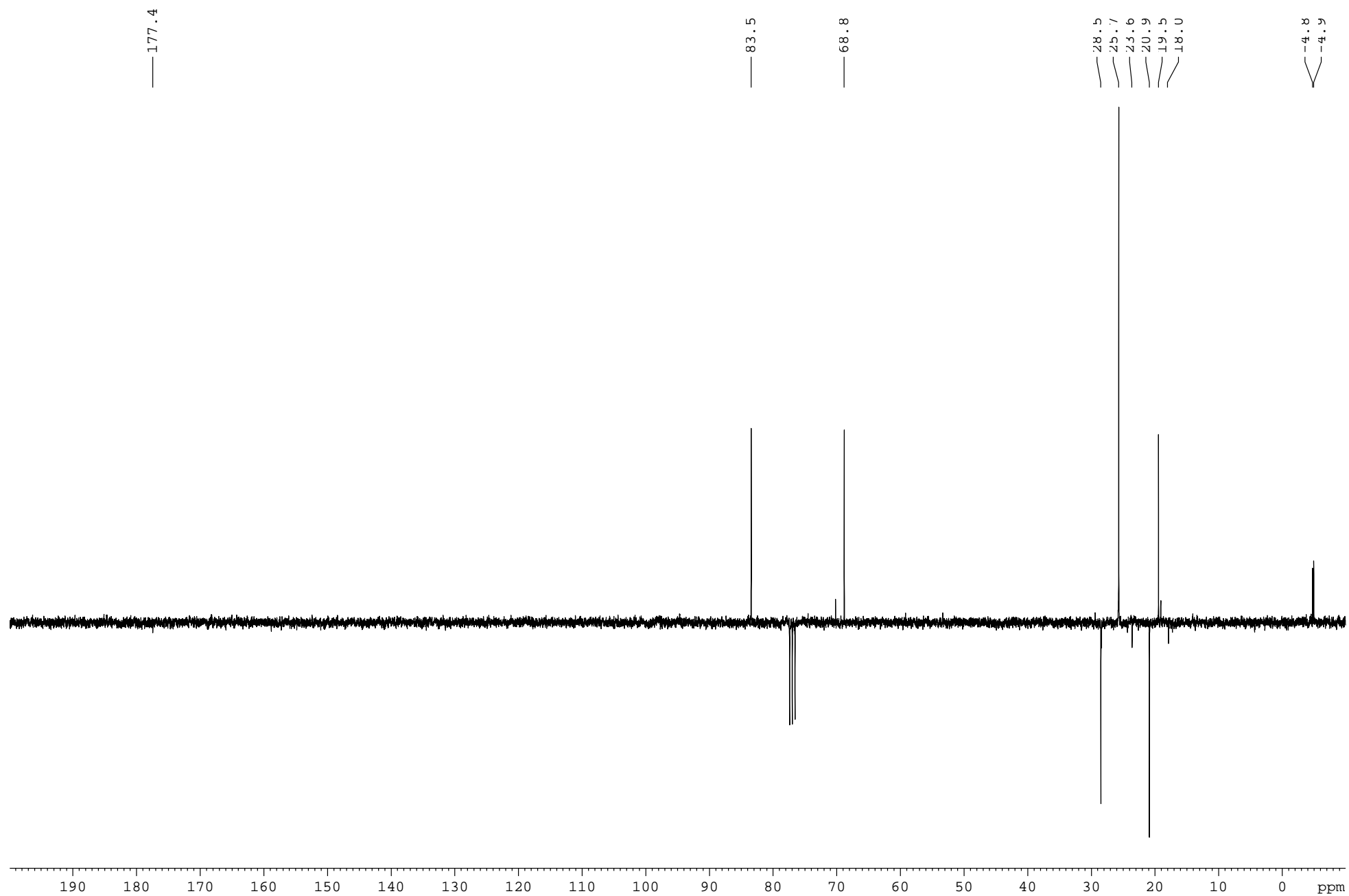


E Copies of NMR spectra of compounds 7, 8a, 8b, 9a, 9b, 10 and 11

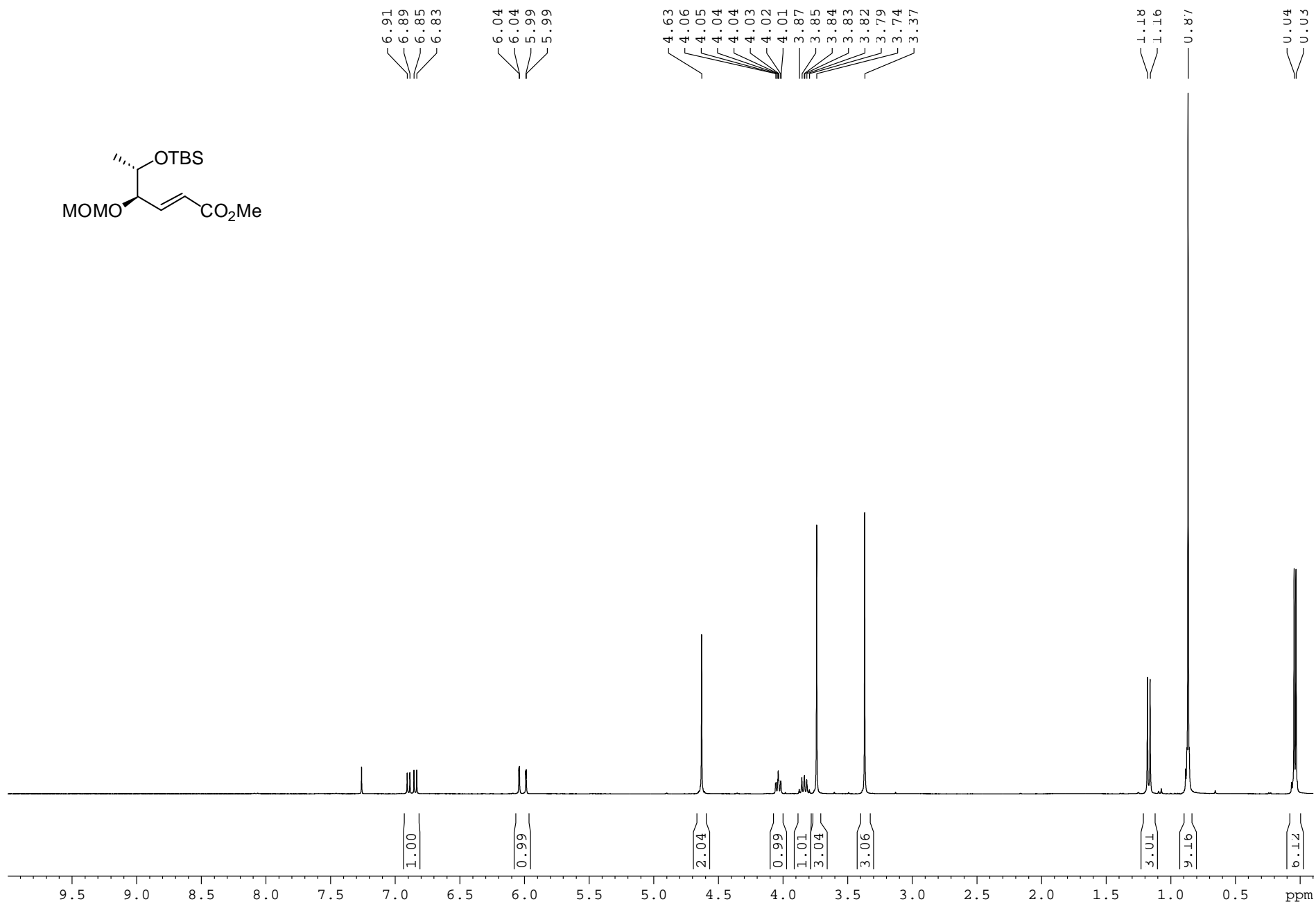
¹H NMR (CDCl₃, 300 MHz) of 7



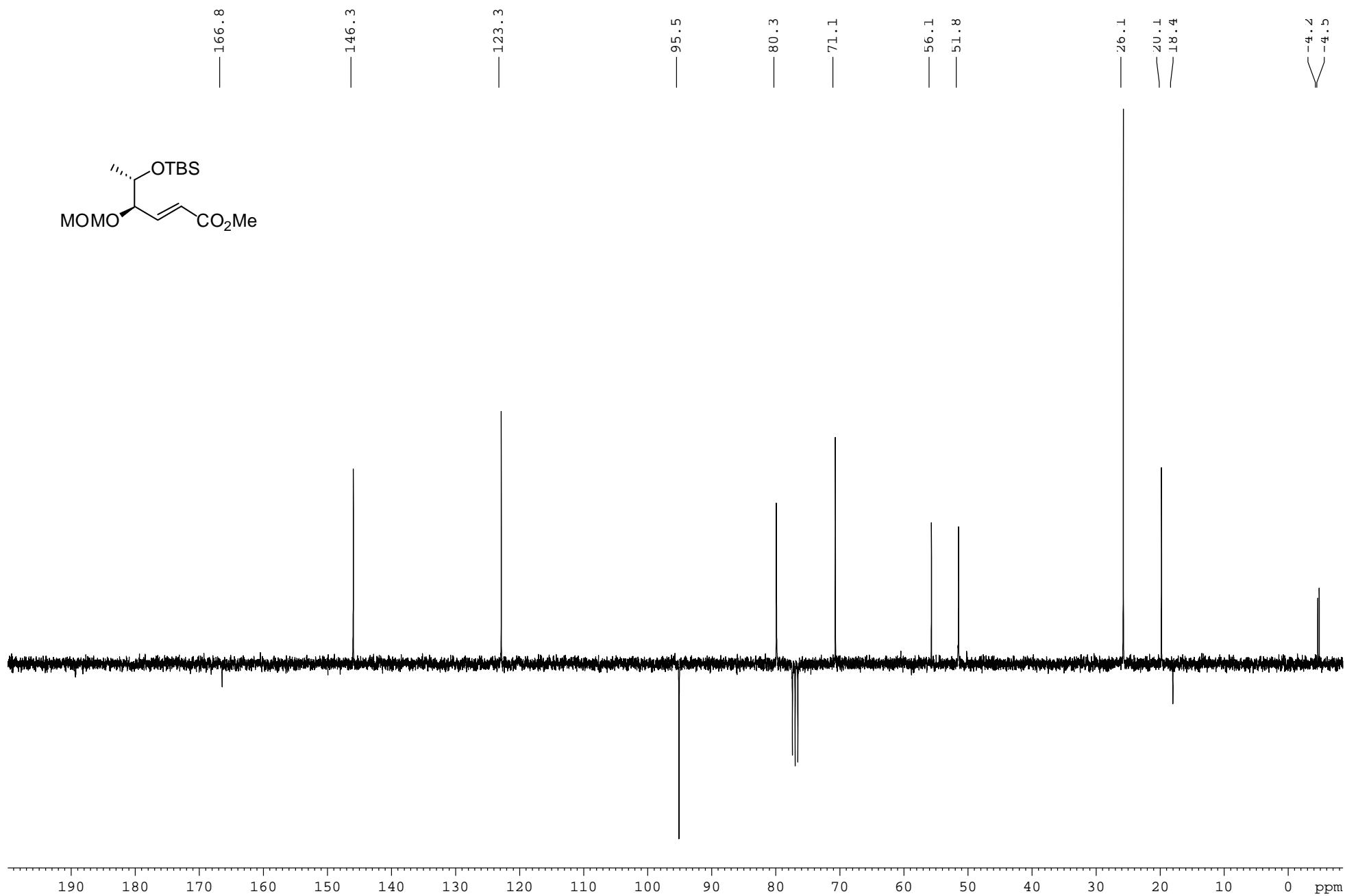
^{13}C NMR-APT (CDCl_3 , 75 MHz) of **7**



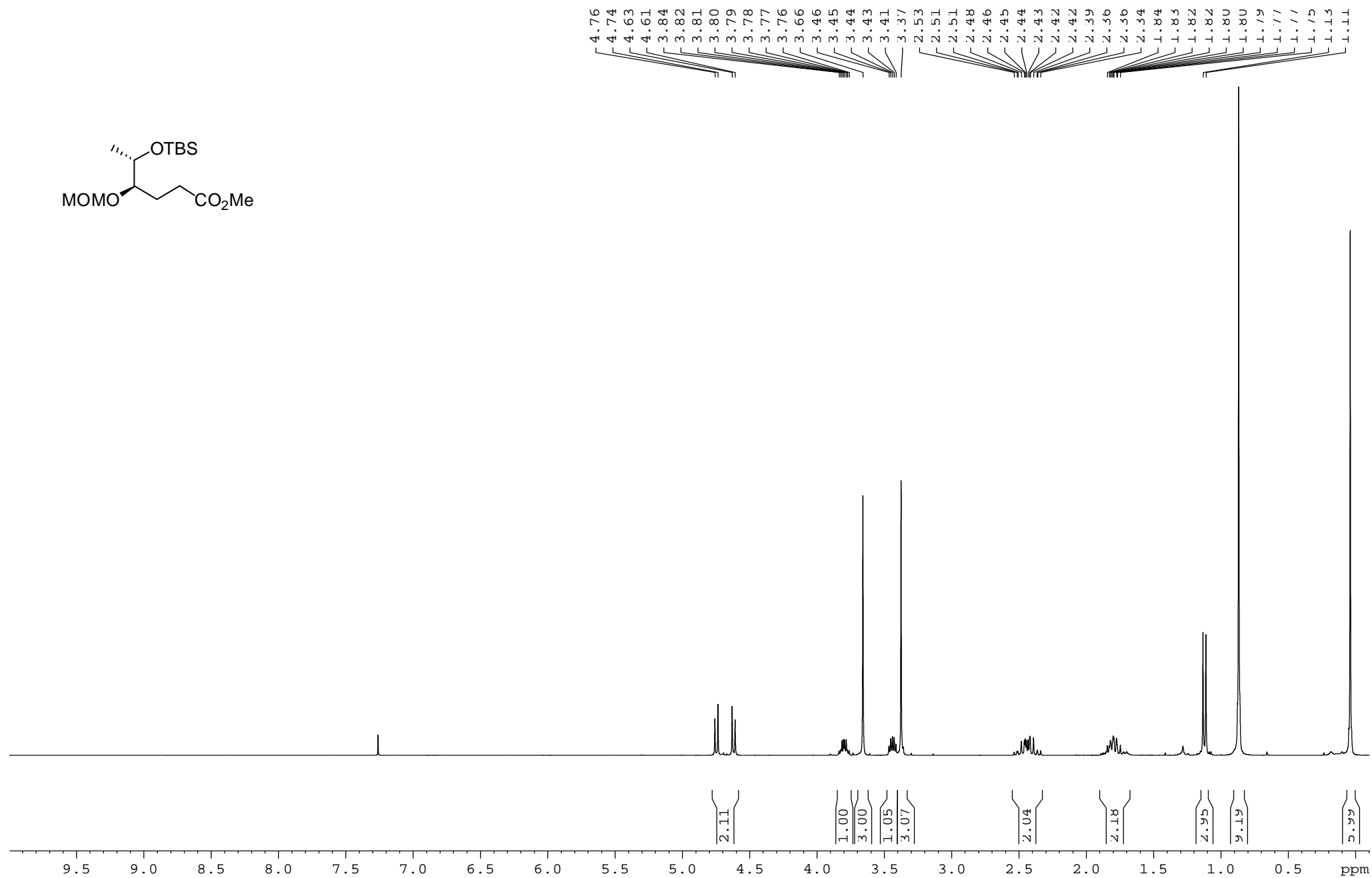
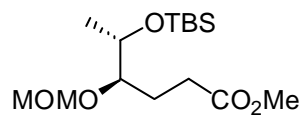
^1H NMR (CDCl_3 , 300 MHz) of **8a**



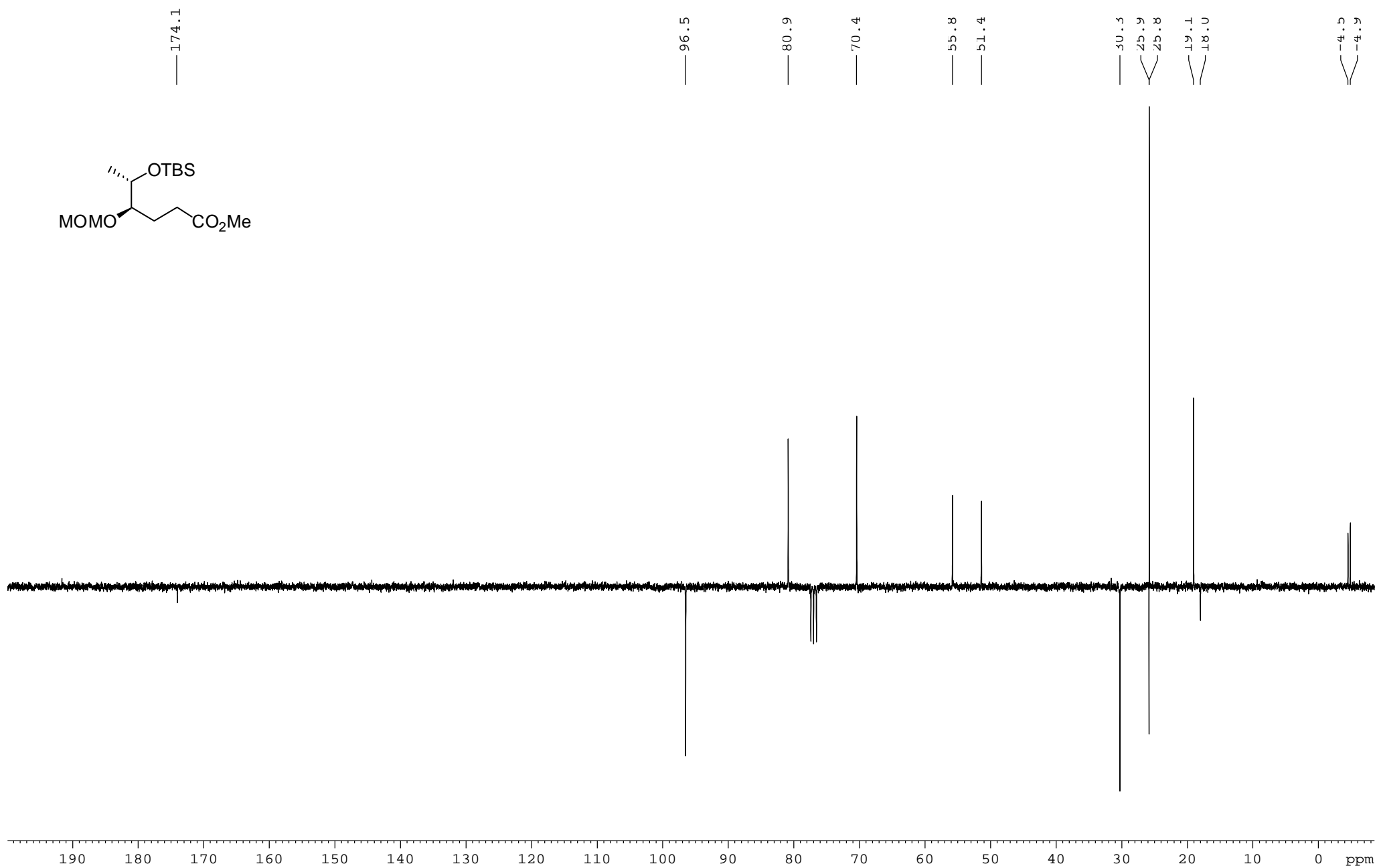
^{13}C NMR-APT (CDCl_3 , 75 MHz) of **8a**



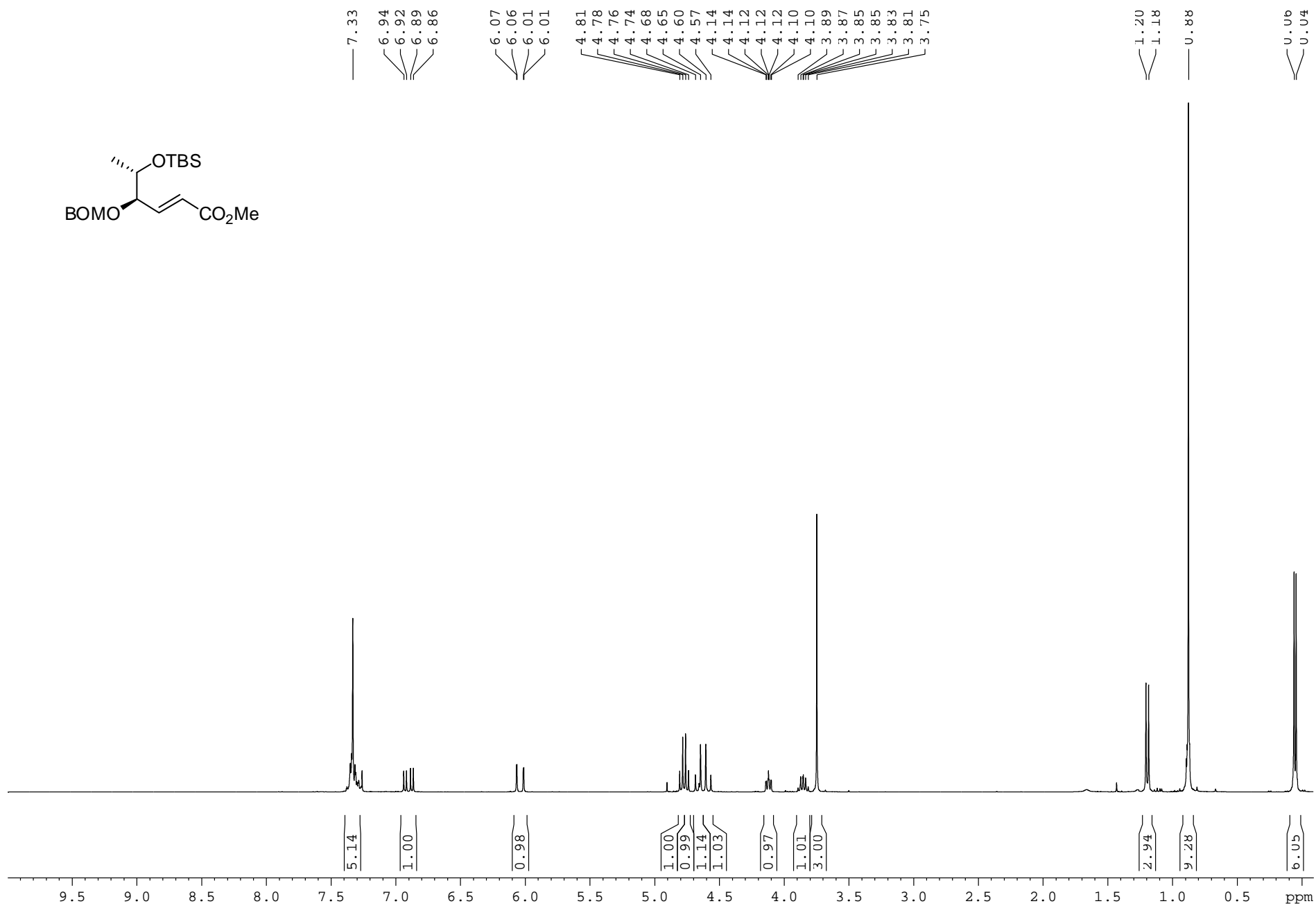
^1H NMR (CDCl_3 , 300 MHz) of **9a**



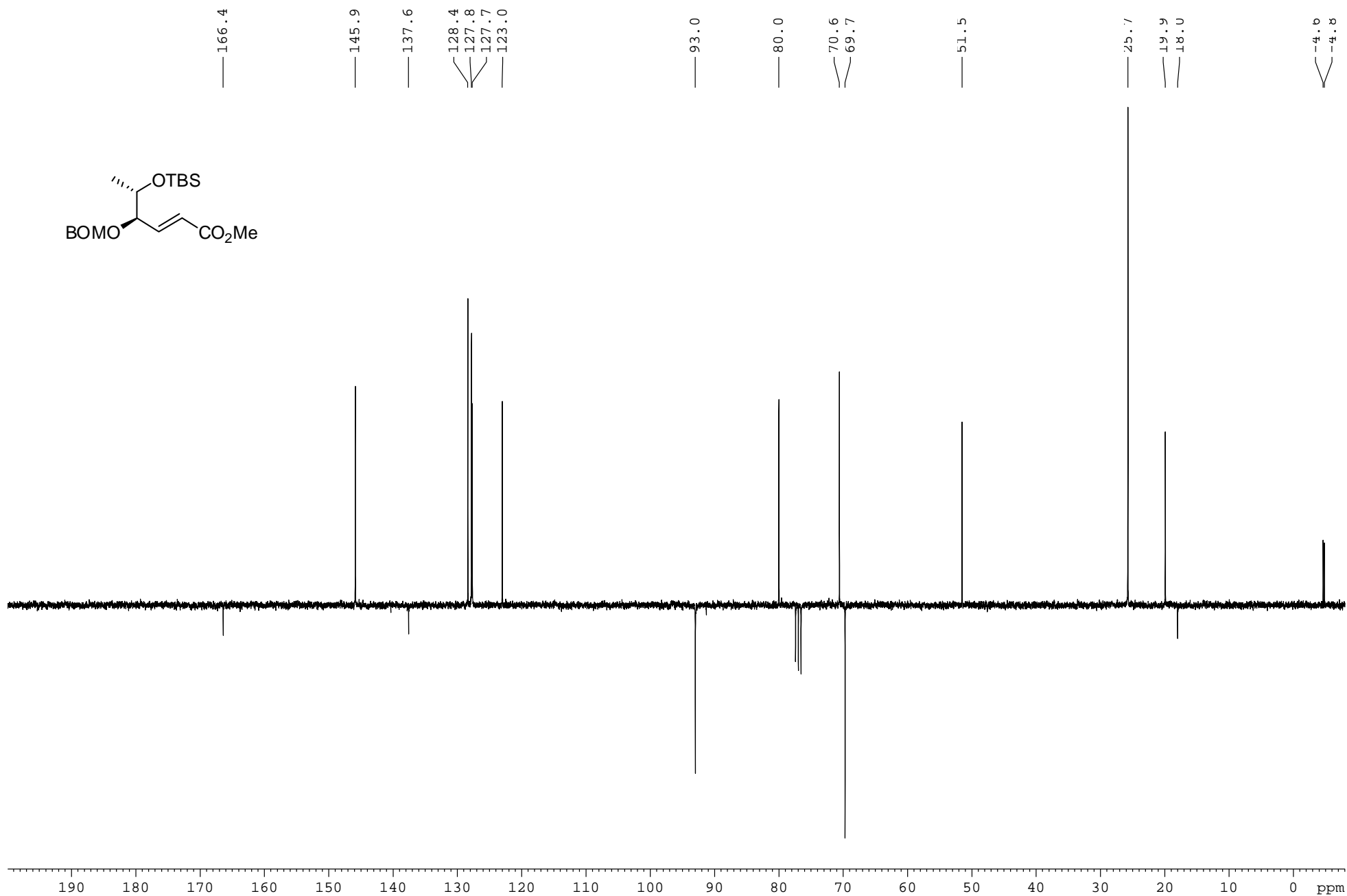
^{13}C NMR-APT (CDCl_3 , 75 MHz) of **9a**



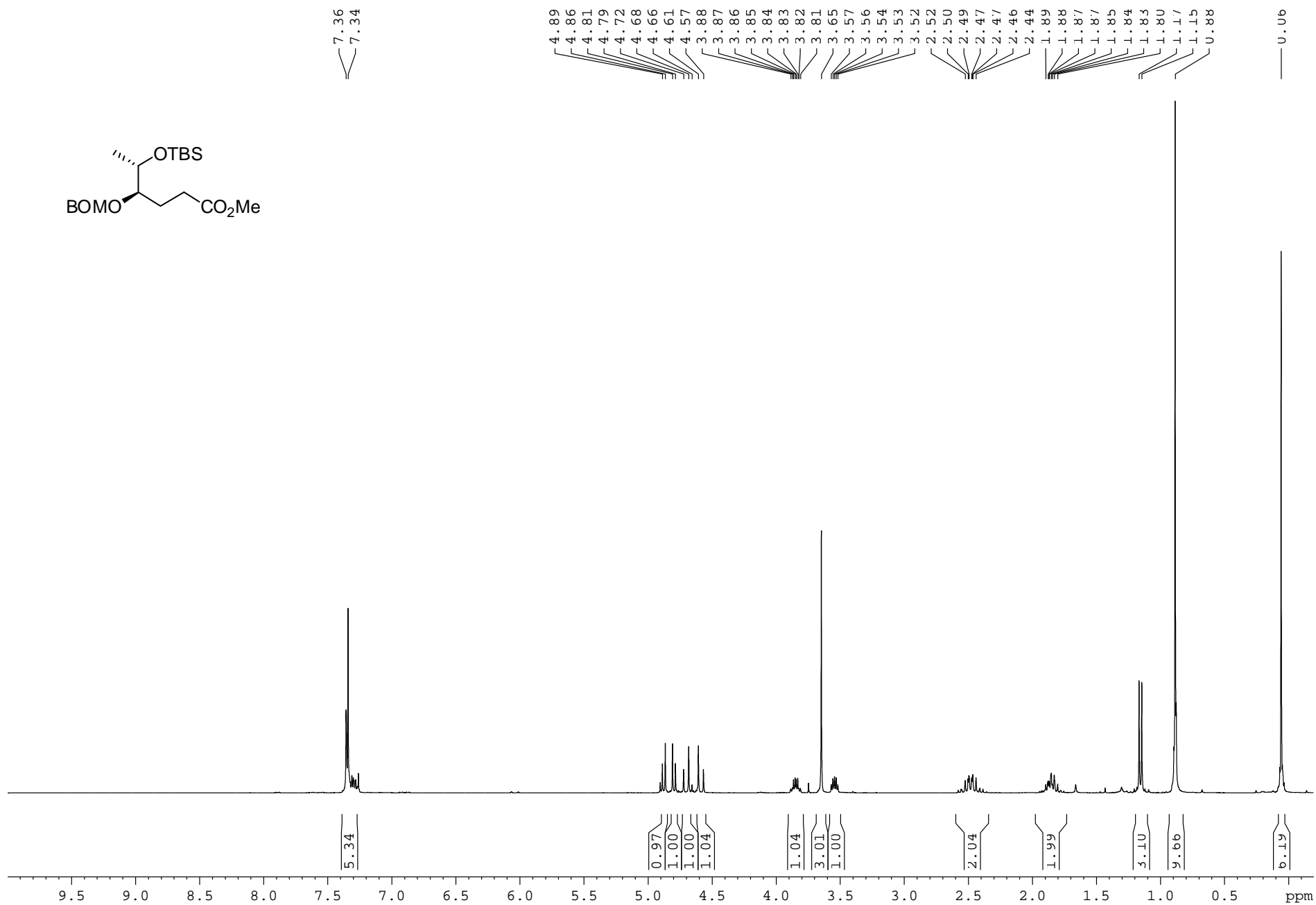
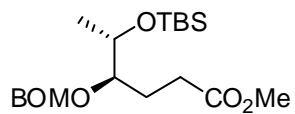
^1H NMR (CDCl_3 , 300 MHz) of **8b**



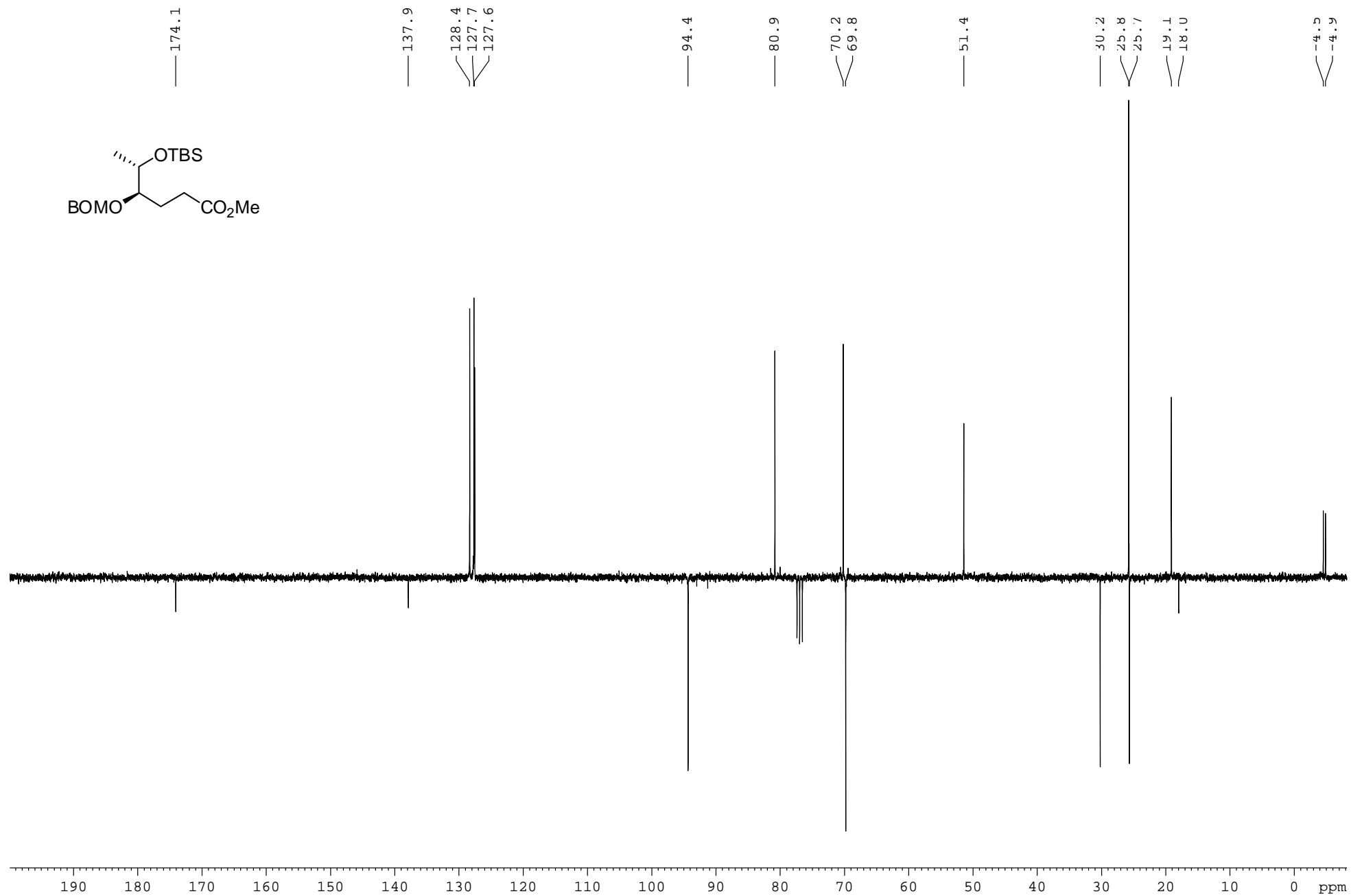
^{13}C NMR-APT (CDCl_3 , 75 MHz) of **8b**



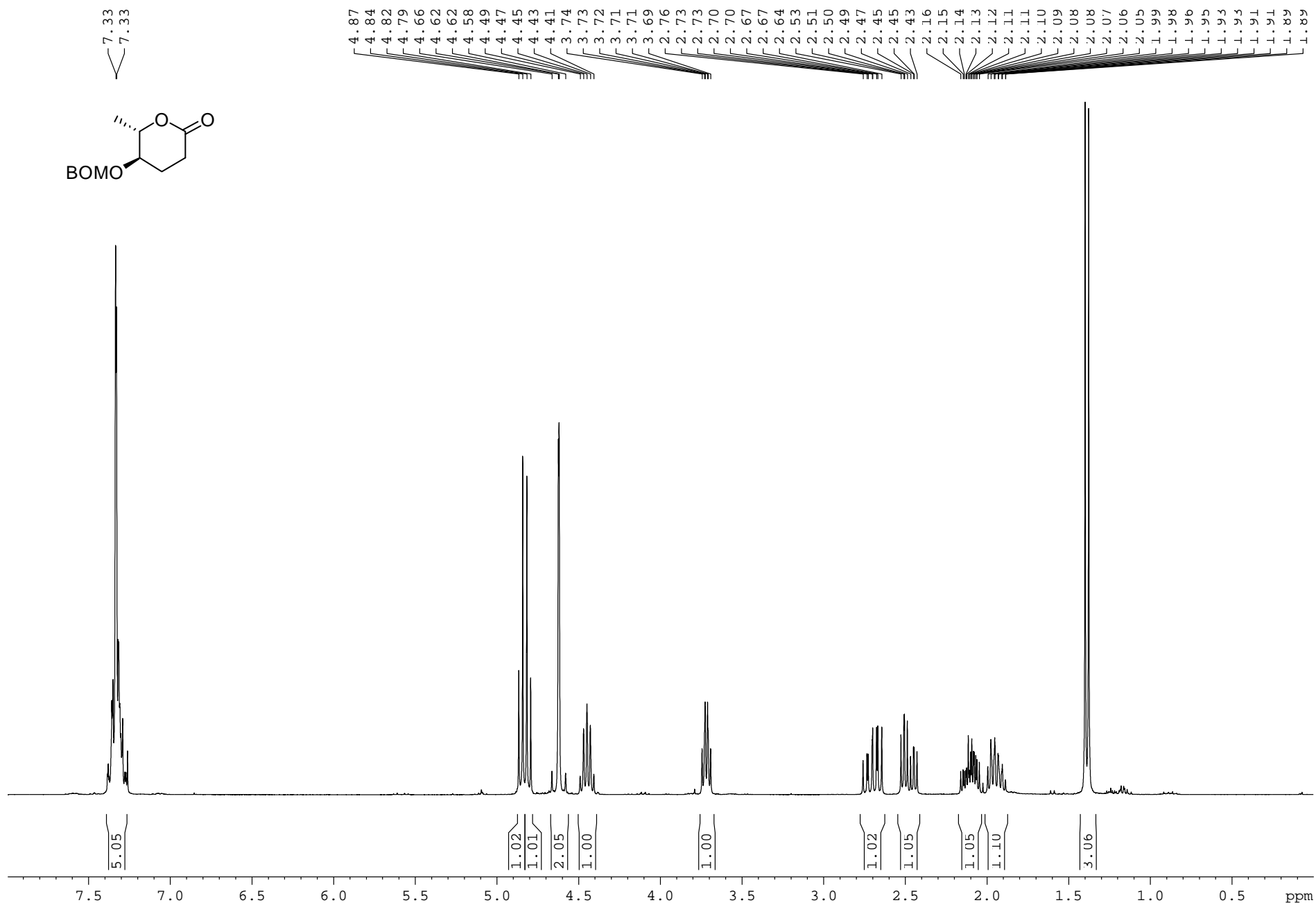
^1H NMR (CDCl_3 , 300 MHz) of **9b**



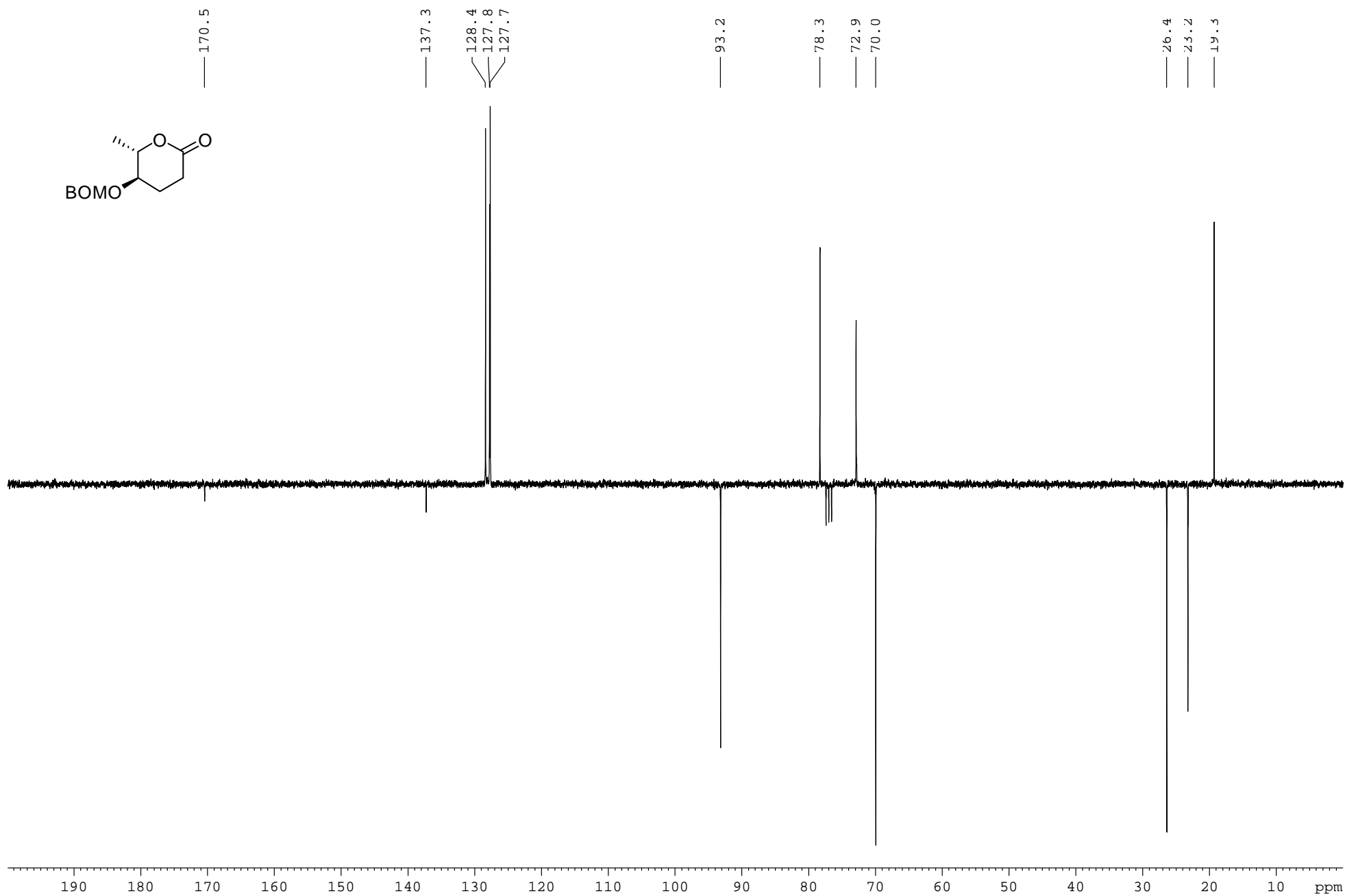
^{13}C NMR-APT (CDCl_3 , 75 MHz) of **9b**



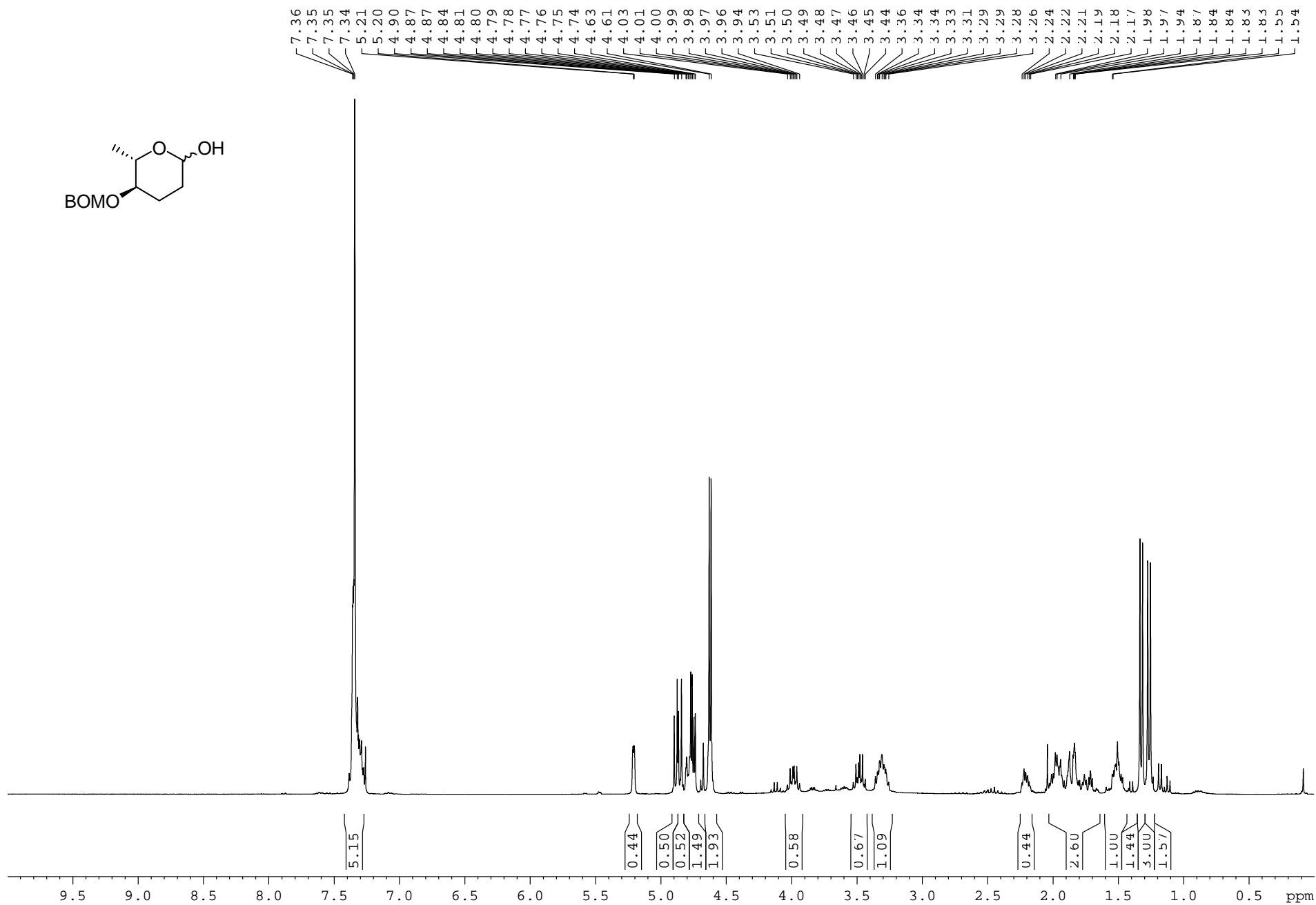
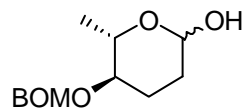
^1H NMR (CDCl_3 , 300 MHz) of **10**



^{13}C NMR-APT (CDCl_3 , 75 MHz) of **10**



^1H NMR (CDCl_3 , 300 MHz) of **11**



^{13}C NMR-APT (CDCl_3 , 75 MHz) of **11**

