

Catalytic decarboxylative alkylation of β -keto acids with sulfonamides via the cleavage of carbon–nitrogen and carbon–carbon bonds

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Supporting information

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General information

^1H and ^{13}C NMR spectra were recorded on a Bruker AC-300 FT (300 MHz and 75 MHz, respectively) using tetramethylsilane as an internal reference, and chemical shifts (δ) and coupling constants (J) were expressed in ppm and Hz, respectively. IR spectra were recorded on a Perkin-Elmer 2000 FTIR spectrometer. High resolution mass spectra (HRMS) were recorded on a LC-TOF spectrometer (Micromass). Electron spray ionization (ESI) high-resolution mass spectrometry data were acquired using a Thermo LTQ Orbitrap XL Instrument equipped with an ESI source and controlled by Xcalibur software. Melting points were uncorrected.

Benzhydrylamine derivatives and sulfonamides were prepared according to known procedures.¹ The preparation of β -keto acids was described below. The rest of chemicals were purchased from the Sinopharm Chemical Reagent Co., Meryer, Acros, and Alfa Aesar, and used as received. The solvents were dried over anhydrous magnesium sulfate prior to use.

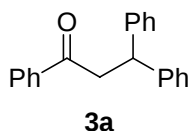
Preparation of β -keto acids²

To a β -keto ester (20 mmol) at room temperature was added aqueous sodium hydroxide (2 N, 20 mL). The mixture was stirred vigorously at room temperature for 12 h, and extracted with ether (2 x 20 mL). The aqueous layer was cooled with ice-water and acidified with aqueous HCl (1 N) until pH $\approx$ 2, and extracted with ether (2 x 60 mL). The combined organic layers were dried over anhydrous sodium sulfate, and evaporated under reduced pressure at a temperature below 30 °C. The residue was pumped at 0.5 mmHg to remove extraneous water. The β -keto acids were stored in a freezer at -20 °C.

General procedure for the decarboxylative alkylation of β -keto acids with sulfonamides (Tables 2 and 3)

To a solution of sulfonamide **2** (0.20 mmol) in 1,2-dichloroethane (1.0 mL) at room temperature were added β -keto acid **1** (0.24 mmol) and FeCl_3 (3.2 mg, 10 mol%). The resulting mixture was stirred at 60 °C until no further transformation was detected by thin layer chromatography (TLC) analysis. The mixture was purified by column chromatography on silica gel, eluting with petroleum ether/ethyl acetate (20:1), to give product **3**.

Analytical data for the products shown in Tables 2 and 3

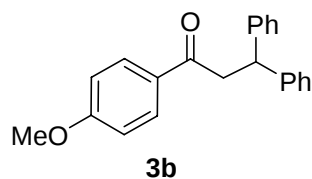


3a,³ white solid, m.p. 91–92 °C; ^1H NMR (300 MHz, CDCl_3): δ 7.91 (d, J = 7.8 Hz, 2H), 7.54–7.39 (m, 3H), 7.39–7.13 (m, 10H), 4.82 (t, J = 7.5 Hz, 1H), 3.72 (d, J = 7.5 Hz, 2H); ^{13}C NMR (75 MHz, CDCl_3): δ 198.1, 144.3, 137.3, 133.1, 128.6, 128.1, 127.9, 126.4, 46.1, 44.8.

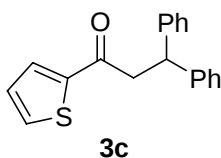
¹ (a) B.-L. Yang and S.-K. Tian, *Chem. Commun.*, 2010, **46**, 6180; (b) C.-R. Liu, F.-L. Yang, Y.-Z. Jin, X.-T. Ma, D.-J. Cheng, N. Li and S.-K. Tian, *Org. Lett.*, 2010, **12**, 3832.

² (a) D. H. Grayson and M. R. J. Tuite, *J. Chem. Soc. Perkin. Trans 1*, 1986, 2137; (b) D. A. Evans, S. Mito and D. Seidel, *J. Am. Chem. Soc.*, 2007, **129**, 11583.

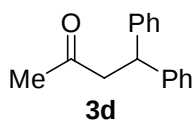
³ P. He, Y. Lu, C.-G. Dong and Q.-S. Hu, *Org. Lett.*, 2007, **9**, 343.



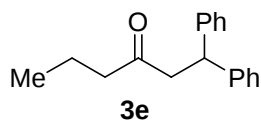
3b,⁴ white solid, m.p. 92–93 °C; ¹H NMR (300 MHz, CDCl₃): δ 7.91 (d, *J* = 8.7 Hz, 2H), 7.26–7.11 (m, 10H), 6.89 (d, *J* = 8.7 Hz, 2H), 4.81 (t, *J* = 7.2 Hz, 1H), 3.82 (s, 3H), 3.67 (d, *J* = 7.2 Hz, 2H); ¹³C NMR (75 MHz, CDCl₃): δ 196.6, 163.5, 144.4, 130.4, 130.3, 128.6, 127.9, 126.4, 113.8, 55.5, 46.1, 44.4.



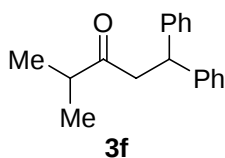
3c,⁵ colorless oil; ¹H NMR (300 MHz, CDCl₃): δ 7.69 (d, *J* = 3.3 Hz, 1H), 7.57 (d, *J* = 4.8 Hz, 1H), 7.27–7.05 (m, 11H), 4.81 (t, *J* = 7.5 Hz, 1H), 3.65 (d, *J* = 7.5 Hz, 2H); ¹³C NMR (75 MHz, CDCl₃): δ 190.9, 144.4, 143.9, 133.7, 131.9, 128.6, 128.1, 127.9, 126.5, 46.2, 45.5.



3d,³ white solid, m.p. 52–53 °C; ¹H NMR (300 MHz, CDCl₃): δ 7.30–7.13 (m, 10H), 4.58 (t, *J* = 7.5 Hz, 1H), 3.16 (d, *J* = 7.5 Hz, 2H), 2.05 (s, 3H); ¹³C NMR (75 MHz, CDCl₃): δ 206.8, 143.9, 128.6, 127.8, 126.5, 49.7, 46.1, 30.7.



3e,⁶ colorless oil; ¹H NMR (300 MHz, CDCl₃): δ 7.29–7.11 (m, 10H), 4.60 (t, *J* = 7.5 Hz, 1H), 3.13 (d, *J* = 7.5 Hz, 2H), 2.27 (t, *J* = 7.2 Hz, 2H), 1.57–1.42 (m, 2H), 0.78 (t, *J* = 7.5 Hz, 3H); ¹³C NMR (75 MHz, CDCl₃): δ 209.1, 144.1, 128.6, 127.8, 126.5, 48.9, 46.1, 45.6, 17.1, 13.7.

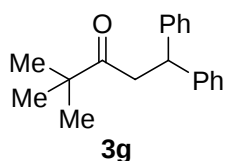


⁴ R. Jana and J. A. Tunge, *Org. Lett.*, 2009, **11**, 971.

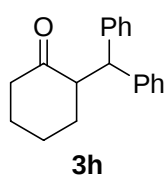
⁵ Y. D. Churkin and N. I. Putokhin, *J. Org. Chem. USSR (Engl. Transl.)*, 1965, **1**, 599.

⁶ E. M. Schultz, W. A. Bolhofer, A. Augenblick, J. B. Bicking, C. N. Habecker, J. K. Horner, S. F. Kwong and A. M. Pietruszkiewicz, *J. Med. Chem.*, 1967, **10**, 717.

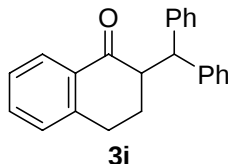
3f,⁷ white solid, m.p. 65–66 °C; ¹H NMR (300 MHz, CDCl₃): δ 7.29–7.11 (m, 10H), 4.62 (t, *J* = 7.5 Hz, 1H), 3.19 (d, *J* = 7.5 Hz, 2H), 2.54–2.40 (m, 1H), 0.96 (d, *J* = 6.9 Hz, 6H); ¹³C NMR (75 MHz, CDCl₃): δ 212.5, 144.2, 128.6, 127.9, 126.4, 46.7, 45.9, 41.4, 17.9.



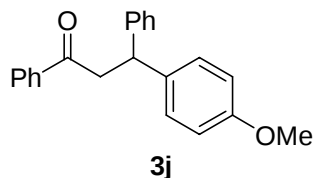
3g,⁸ white solid, m.p. 70–71 °C; ¹H NMR (300 MHz, CDCl₃): δ 7.29–7.10 (m, 10H), 4.66 (t, *J* = 7.2 Hz, 1H), 3.23 (d, *J* = 7.2 Hz, 2H), 1.02 (s, 9H); ¹³C NMR (75 MHz, CDCl₃): δ 213.3, 144.4, 128.5, 127.9, 126.4, 45.7, 44.3, 43.1, 26.2.



3h,⁹ white solid, m.p. 102–103 °C; ¹H NMR (300 MHz, CDCl₃): δ 7.29–7.07 (m, 10H), 4.31 (d, *J* = 10.8 Hz, 1H), 3.41–3.29 (m, 1H), 2.40–2.27 (m, 2H), 2.08–1.96 (m, 1H), 1.84–1.57 (m, 4H), 1.44–1.31 (m, 1H); ¹³C NMR (75 MHz, CDCl₃): δ 212.3, 143.9, 143.1, 128.6, 128.4, 127.6, 126.4, 126.2, 54.9, 51.0, 42.6, 33.5, 29.2, 24.6.



3i,¹⁰ colorless oil; ¹H NMR (300 MHz, CDCl₃): δ 7.91 (d, *J* = 6.6 Hz, 1H), 7.45–7.41 (m, 1H), 7.29–7.14 (m, 12H), 4.67 (d, *J* = 8.4 Hz, 1H), 3.51–3.43 (m, 1H), 3.09–2.87 (m, 2H), 2.17–2.06 (m, 1H), 1.92–1.75 (m, 1H); ¹³C NMR (75 MHz, CDCl₃): δ 199.0, 143.5, 143.3, 142.6, 133.2, 133.0, 128.9, 128.7, 128.5, 128.4, 128.0, 127.7, 126.7, 126.5, 126.3, 51.4, 50.0, 27.9, 26.9.



3j,³ white solid, m.p. 94–95 °C; ¹H NMR (300 MHz, CDCl₃): δ 7.90 (d, *J* = 7.2 Hz, 2H), 7.53–7.46 (m, 1H), 7.43–7.34 (m, 2H), 7.37–7.09 (m, 7H), 6.78 (d, *J* = 8.7 Hz, 2H), 4.77 (t, *J* = 7.5 Hz, 1H), 3.70 (s, 3H), 3.68 (d, *J* = 7.5 Hz, 2H); ¹³C NMR (75 MHz, CDCl₃): δ 198.2, 158.2, 144.7,

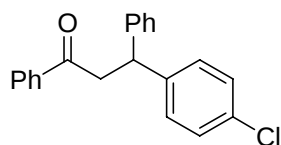
⁷ E. P. Kohler, *Am. Chem. J.*, 1907, **38**, 511.

⁸ P. Yates and M. J. Betts, *J. Am. Chem. Soc.*, 1972, **94**, 1965.

⁹ S. Ozaki, H. Yoshinaga, E. Matsui and M. Adachi, *J. Org. Chem.*, 2001, **66**, 2503.

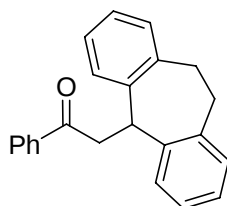
¹⁰ D. Lednicer, *J. Org. Chem.*, 1964, **29**, 2480.

137.2, 136.4, 133.1, 128.8, 128.7, 128.6, 128.1, 127.9, 126.4, 114.0, 55.3, 45.3, 45.0.



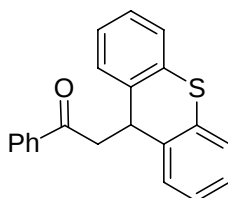
3k

3k,¹¹ white solid, m.p. 117–118 °C; ¹H NMR (300 MHz, CDCl₃): δ 7.91 (d, *J* = 7.2 Hz, 2H), 7.56–7.49 (m, 1H), 7.46–7.37 (m, 2H), 7.30–7.13 (m, 9H), 4.79 (t, *J* = 7.2 Hz, 1H), 3.70 (d, *J* = 7.2 Hz, 2H); ¹³C NMR (75 MHz, CDCl₃): δ 197.7, 143.8, 142.7, 137.0, 133.3, 132.2, 129.3, 128.7, 128.1, 127.8, 126.7, 45.3, 44.6.



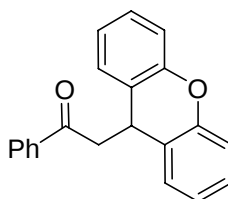
3l

3l, colorless oil; ¹H NMR (300 MHz, CDCl₃): δ 7.87 (d, *J* = 6.9 Hz, 2H), 7.54–7.36 (m, 3H), 7.27–7.21 (m, 2H), 7.12–7.08 (m, 6H), 5.02 (t, *J* = 6.6 Hz, 1H), 3.76 (d, *J* = 6.6 Hz, 2H), 3.43–3.31 (m, 2H), 3.20–3.05 (m, 2H); ¹³C NMR (75 MHz, CDCl₃): δ 198.0, 141.3, 139.3, 137.2, 133.0, 130.4, 129.5, 128.6, 128.1, 126.8, 126.3, 46.6, 33.3; IR (film): ν 3061, 3020, 2933, 1686, 1597, 1580, 1493 cm⁻¹; HRMS (EI): Calcd for C₂₃H₂₀O (M): 312.1514. Found: 312.1491.



3m

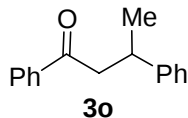
3m, pale yellow solid, m.p. 114–115 °C; ¹H NMR (300 MHz, CDCl₃): δ 7.78–7.73 (m, 2H), 7.43–7.28 (m, 7H), 7.21–7.10 (m, 4H), 4.89 (t, *J* = 7.2 Hz, 1H), 3.42 (d, *J* = 7.2 Hz, 2H); ¹³C NMR (75 MHz, CDCl₃): δ 198.4, 137.7, 137.1, 133.0, 132.7, 129.3, 128.5, 128.1, 127.1, 126.8, 44.6, 40.6; IR (film): ν 3066, 3019, 2927, 1685, 1597, 1582, 1467, 1445 cm⁻¹; HRMS (EI): Calcd for C₂₁H₁₆OS (M): 316.0922. Found: 316.0901.



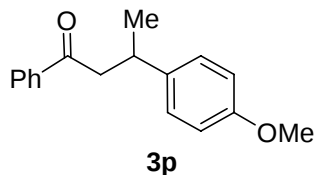
3n

¹¹ L. Dong, Y.-J. Xu, L.-Z. Gong, A.-Q. Mi and Y.-Z. Jiang, *Synthesis*, 2004, 1057.

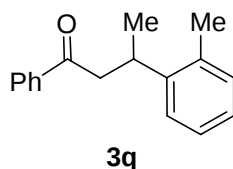
3n,¹² white solid, m.p. 100–101 °C; ¹H NMR (300 MHz, CDCl₃): δ 7.80 (d, *J* = 7.5 Hz, 2H), 7.55–7.44 (m, 1H), 7.39–7.30 (m, 4H), 7.25–6.98 (m, 6H), 4.85 (t, *J* = 6.6 Hz, 1H), 3.34 (d, *J* = 6.6 Hz, 2H); ¹³C NMR (75 MHz, CDCl₃): δ 199.4, 153.8, 138.5, 138.4, 134.6, 134.6, 130.3, 130.0, 129.6, 129.4, 127.0, 125.0, 118.1, 51.2, 36.1.



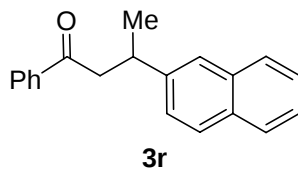
3o,¹³ white solid, m.p. 60–61 °C; ¹H NMR (300 MHz, CDCl₃): δ 7.93 (d, *J* = 7.2 Hz, 2H), 7.59–7.51 (m, 1H), 7.48–7.40 (m, 2H), 7.35–7.18 (m, 5H), 3.58–3.43 (m, 1H), 3.30 (dd, *J* = 16.5, 5.4 Hz, 1H), 3.18 (dd, *J* = 16.5, 8.4 Hz, 1H), 1.34 (d, *J* = 6.9 Hz, 3 H); ¹³C NMR (75 MHz, CDCl₃): δ 199.1, 146.6, 137.3, 133.0, 128.6, 128.1, 126.9, 126.3, 47.0, 35.6, 21.9.



3p,¹³ colorless oil; ¹H NMR (300 MHz, CDCl₃): δ 7.92 (d, *J* = 7.2 Hz, 2H), 7.58–7.40 (m, 3H), 7.18 (d, *J* = 8.7 Hz, 2H), 6.84 (d, *J* = 8.7 Hz, 2H), 3.77 (s, 3H), 3.48–3.39 (m, 1H), 3.26 (dd, *J* = 16.5, 6.0 Hz, 1H), 3.14 (dd, *J* = 16.5, 8.1 Hz, 1H), 1.31 (d, *J* = 6.9 Hz, 3H); ¹³C NMR (75 MHz, CDCl₃): δ 199.3, 158.0, 138.7, 137.3, 133.0, 131.0, 128.6, 128.1, 127.8, 113.9, 55.3, 47.3, 34.9, 22.1.



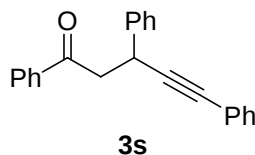
3q, colorless oil; ¹H NMR (300 MHz, CDCl₃): δ 7.93 (d, *J* = 7.5 Hz, 2H), 7.56–7.38 (m, 3H), 7.25–7.05 (m, 4H), 3.82–3.68 (m, 1H), 3.27 (dd, *J* = 16.8, 5.7 Hz, 1H), 3.18 (dd, *J* = 16.8, 8.1 Hz, 1H), 2.38 (s, 3H), 1.29 (d, *J* = 6.9 Hz, 3H); ¹³C NMR (75 MHz, CDCl₃): δ 199.2, 144.9, 137.3, 135.4, 133.1, 130.6, 128.7, 128.1, 126.4, 126.1, 125.3, 46.4, 30.6, 21.5, 19.6; IR (film): ν 3063, 3022, 2967, 2928, 1686, 1598, 1580, 1491, 1449 cm⁻¹; HRMS (EI): Calcd for C₁₇H₁₈O (M): 238.1358. Found: 238.1350.



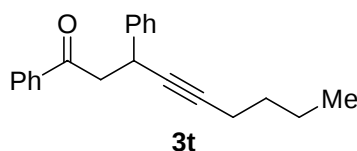
¹² Á. Pintér, A. Sud, D. Sureshkumar and M. Klussmann, *Angew. Chem., Int. Ed.*, 2010, **49**, 5004.

¹³ S. E. Denmark and N. Amishiro, *J. Org. Chem.*, 2003, **68**, 6997.

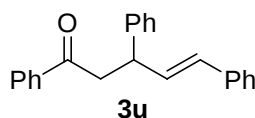
3r,¹⁴ colorless oil; ¹H NMR (300 MHz, CDCl₃): δ 7.93 (d, *J* = 7.2 Hz, 2H), 7.81-7.76 (m, 3H), 7.69 (s, 1H), 7.55-7.48 (m, 1H), 7.47-7.35 (m, 5H), 3.74-3.60 (m, 1H), 3.39 (dd, *J* = 16.5, 5.7 Hz, 1H), 3.26 (dd, *J* = 16.5, 8.1 Hz, 1H), 1.41 (d, *J* = 6.9 Hz, 3H); ¹³C NMR (75 MHz, CDCl₃): δ 199.0, 144.1, 137.3, 133.6, 133.0, 132.3, 128.6, 128.2, 128.1, 127.7, 127.6, 126.0, 125.8, 125.4, 125.0, 45.0, 35.7, 21.9.



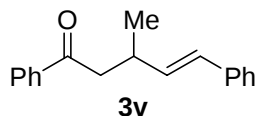
3s,¹⁵ white solid, m.p. 92–93 °C; ¹H NMR (300 MHz, CDCl₃): δ 7.96 (d, *J* = 7.5 Hz, 2H), 7.58-7.24 (m, 13H), 4.68-4.61 (m, 1H), 3.67 (dd, *J* = 16.8, 8.1 Hz, 1H), 3.40 (dd, *J* = 16.8, 6.0 Hz, 1H); ¹³C NMR (75 MHz, CDCl₃): δ 197.2, 141.3, 133.3, 131.7, 128.7, 128.7, 128.3, 128.2, 127.9, 127.6, 127.1, 90.8, 83.3, 47.3, 33.8.



3t,¹⁵ colorless oil; ¹H NMR (300 MHz, CDCl₃): δ 7.93 (d, *J* = 7.2 Hz, 2H), 7.58-7.17 (m, 8H), 4.43-4.35 (m, 1H), 3.52 (dd, *J* = 16.5, 8.1 Hz, 1H), 3.25 (dd, *J* = 16.5, 6.0 Hz, 1H), 2.19-2.11 (m, 2H), 1.46-1.23 (m, 4H), 0.85 (t, *J* = 7.2 Hz, 3H); ¹³C NMR (75 MHz, CDCl₃): δ 197.6, 142.0, 137.1, 133.1, 128.6, 128.2, 127.5, 126.9, 83.6, 81.0, 47.7, 33.4, 31.0, 21.9, 18.5, 13.6.



3u,¹⁶ colorless oil; ¹H NMR (300 MHz, CDCl₃): δ 7.94 (d, *J* = 7.5 Hz, 2H), 7.58-7.14 (m, 13H), 6.42-6.38 (m, 2H), 4.34-4.26 (m, 1H), 3.58-3.42 (m, 2H); ¹³C NMR (75 MHz, CDCl₃): δ 198.2, 143.3, 137.2, 133.1, 132.6, 130.1, 128.7, 128.7, 128.5, 128.1, 127.8, 127.3, 126.7, 126.3, 44.5, 43.9.



3v,¹⁷ colorless oil; ¹H NMR (300 MHz, CDCl₃): δ 7.95 (d, *J* = 7.2 Hz, 2H), 7.58-7.14 (m, 8H), 6.32 (d, *J* = 15.9 Hz, 1H), 6.22 (dd, *J* = 15.9, 6.9 Hz, 1H), 3.16-2.93 (m, 3H), 1.19 (d, *J* = 6.3 Hz, 3H); ¹³C NMR (75 MHz, CDCl₃): δ 199.2, 137.5, 137.4, 135.0, 133.0, 128.6, 128.5, 128.2, 127.1,

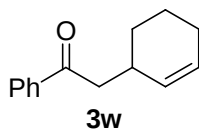
¹⁴ T. Matsuda, M. Makino and M. Murakami, *Org. Lett.*, 2004, **6**, 1257.

¹⁵ Z.-P. Zhan, X.-B. Cai, S.-P. Wang, J.-L. Yu, H.-J. Liu and Y.-Y. Cui, *J. Org. Chem.*, 2007, **72**, 9838.

¹⁶ S. Oi, Y. Honma and Y. Inoue, *Org. Lett.*, 2002, **4**, 667.

¹⁷ S. Ogoshi, T. Haba and M. Ohashi, *J. Am. Chem. Soc.*, 2009, **131**, 10350.

126.1, 45.6, 33.2, 20.3.



3w,¹⁸ colorless oil; ¹H NMR (300 MHz, CDCl₃): δ 7.96 (d, *J* = 7.2 Hz, 2H), 7.59-7.42 (m, 3H), 5.75-5.70 (m, 1H), 5.62-5.57 (m, 1H), 2.97-2.74 (m, 3H), 2.04-1.50 (m, 5H), 1.37-1.24 (m, 1H); ¹³C NMR (75 MHz, CDCl₃): δ 191.3, 137.2, 133.0, 130.8, 128.6, 128.1, 128.0, 44.8, 31.6, 29.1, 25.1, 21.1.

Reaction of sulfonamide (*R*)-2h with β-keto acid 1a

This reaction was performed according to the general procedure for the decarboxylative alkylation of β-keto acids with sulfonamides. The ee of product **3p** was determined to be 1% by chiral stationary phase HPLC analysis [Chiralpak AD column, isopropanol/*n*-hexane (2:98), flow rate = 0.50 mL/min, *t*(major) = 20.3 min, *t*(minor) = 27.3 min].

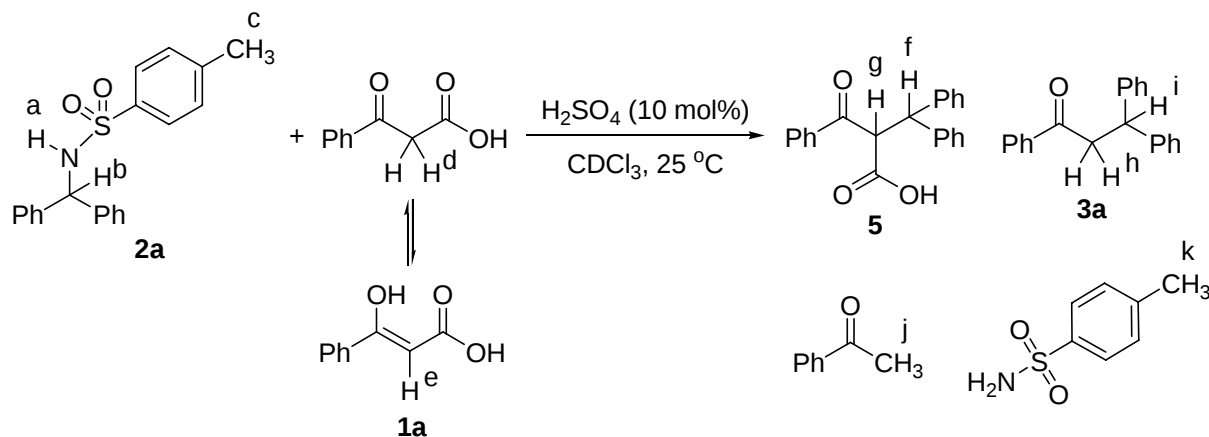
¹H NMR spectroscopic analysis of the reaction mixture

Spectrum A: To a solution of sulfonamide **2a** (6.7 mg, 0.020 mmol) in deuterated chloroform (0.50 mL) at room temperature was added β-keto acid **1a** (3.9 mg, 0.024 mmol). The mixture was stirred vigorously at room temperature for 5 min, and injected into an NMR tube and subjected to ¹H NMR (400 MHz) spectroscopic analysis.

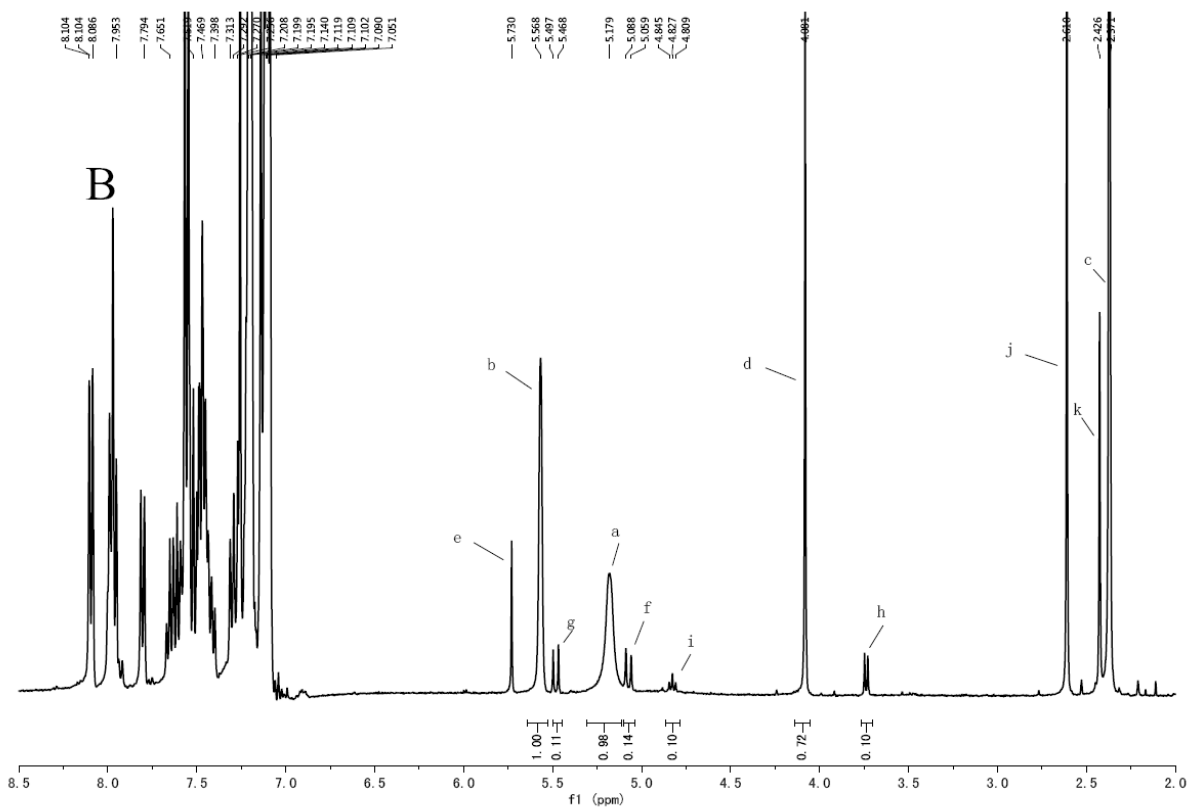
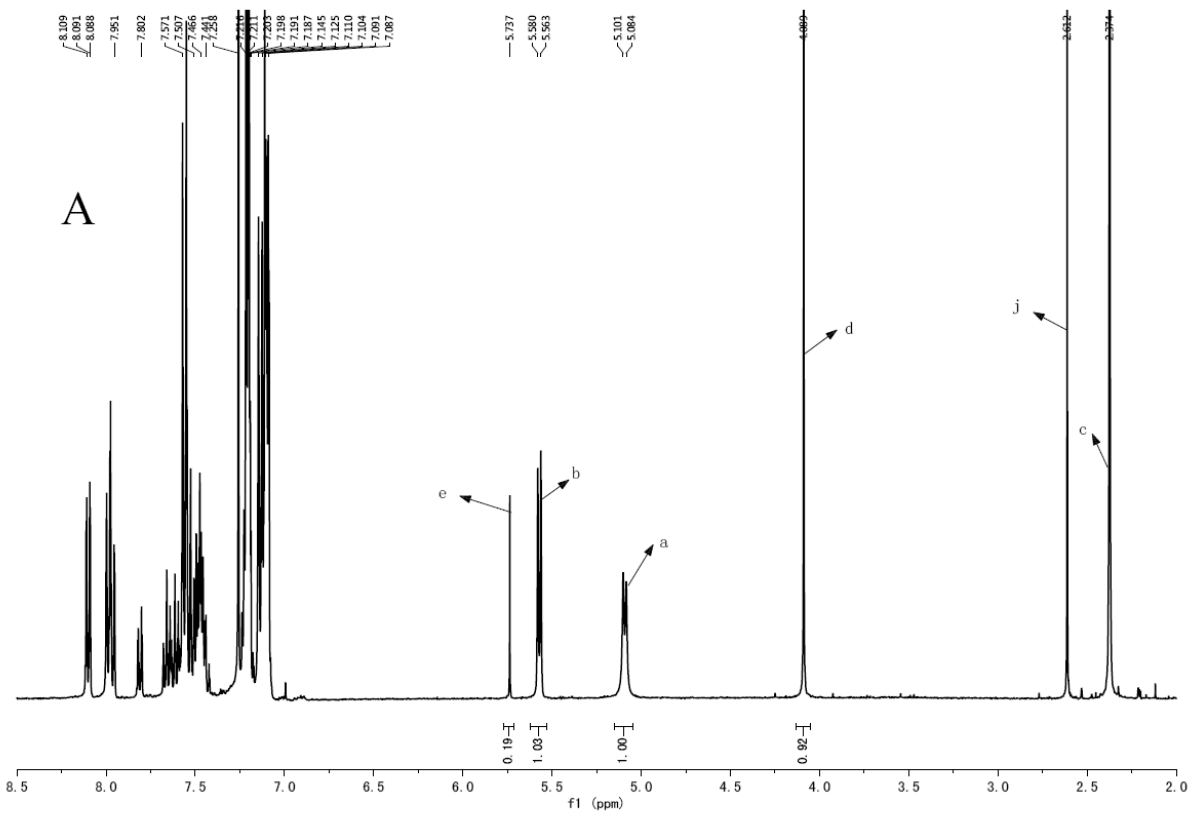
Spectrum B: To a solution of sulfonamide **2a** (67.4 mg, 0.20 mmol) in deuterated chloroform (5.0 mL) at room temperature were added sulfuric acid (2.0 mg, 0.020 mmol) and β-keto acid **1a** (39.4 mg, 0.24 mmol). The mixture was stirred vigorously at room temperature for 2 h, and 0.50 mL of the mixture was injected into an NMR tube and subjected to ¹H NMR (400 MHz) spectroscopic analysis.

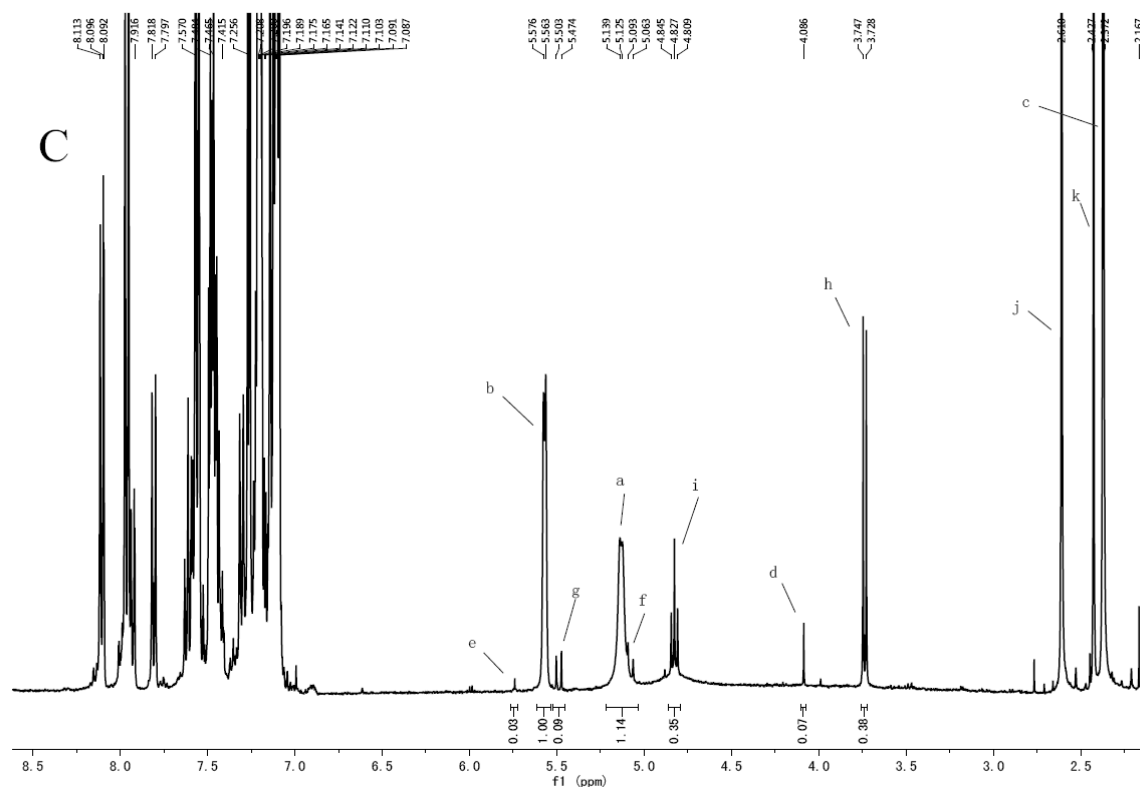
Spectrum C: The above mixture was stirred for 4 h, and 0.50 mL of the mixture was injected into an NMR tube and subjected to ¹H NMR (400 MHz) spectroscopic analysis.

Partial ¹H NMR (400 MHz, CDCl₃) for β-keto acid **5**: δ 5.48 (d, *J* = 11.6 Hz, 1H), 5.07 (d, *J* = 11.6 Hz, 1H).



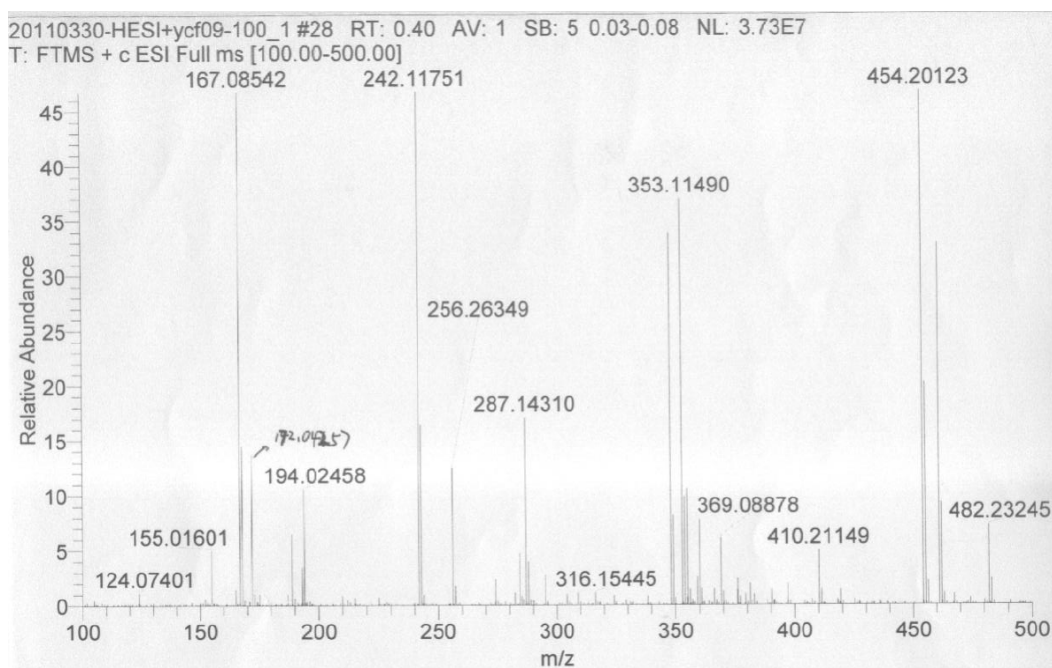
¹⁸ E. C. Burger and J. A. Tunge, *Org. Lett.*, 2004, **6**, 4113.

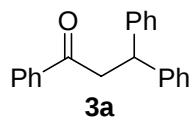




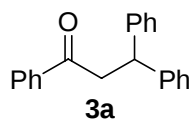
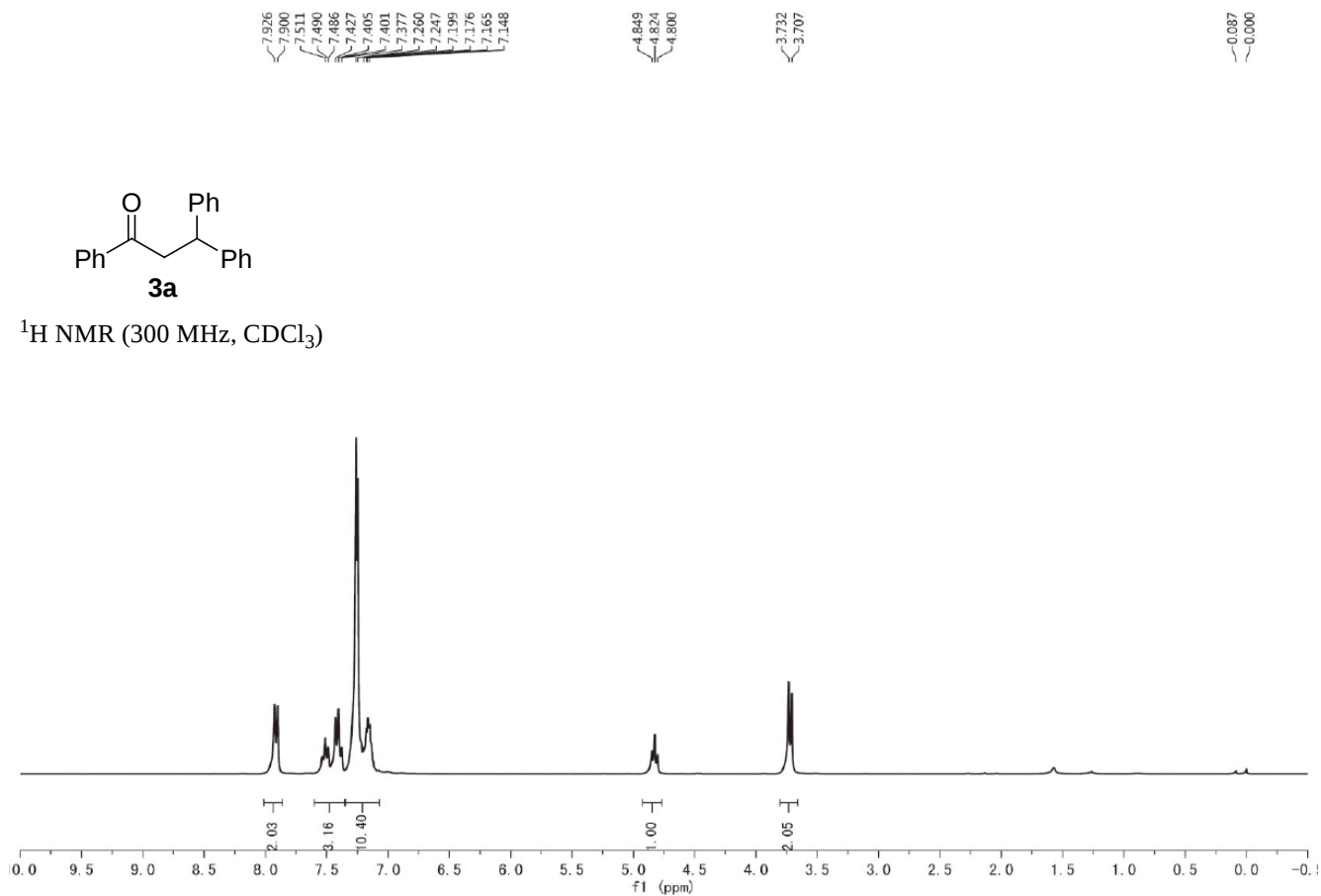
ESI-HRMS spectroscopic analysis of the reaction mixture

To a solution of sulfonamide **2a** (67.4 mg, 0.20 mmol) in deuterated chloroform (5.0 mL) at room temperature were added sulfuric acid (2.0 mg, 0.020 mmol) and β -keto acid **1a** (39.4 mg, 0.24 mmol). The mixture was stirred vigorously at room temperature for 1 h, and subjected to ESI-HRMS (positive model) spectroscopic analysis. Copied below is the ESI-HRMS spectrum we obtained. HRMS (ESI) for β -keto acid **5**: Calcd for $C_{22}H_{18}O_3Na$ ($M + Na$)⁺ 353.1148, found 353.1149.

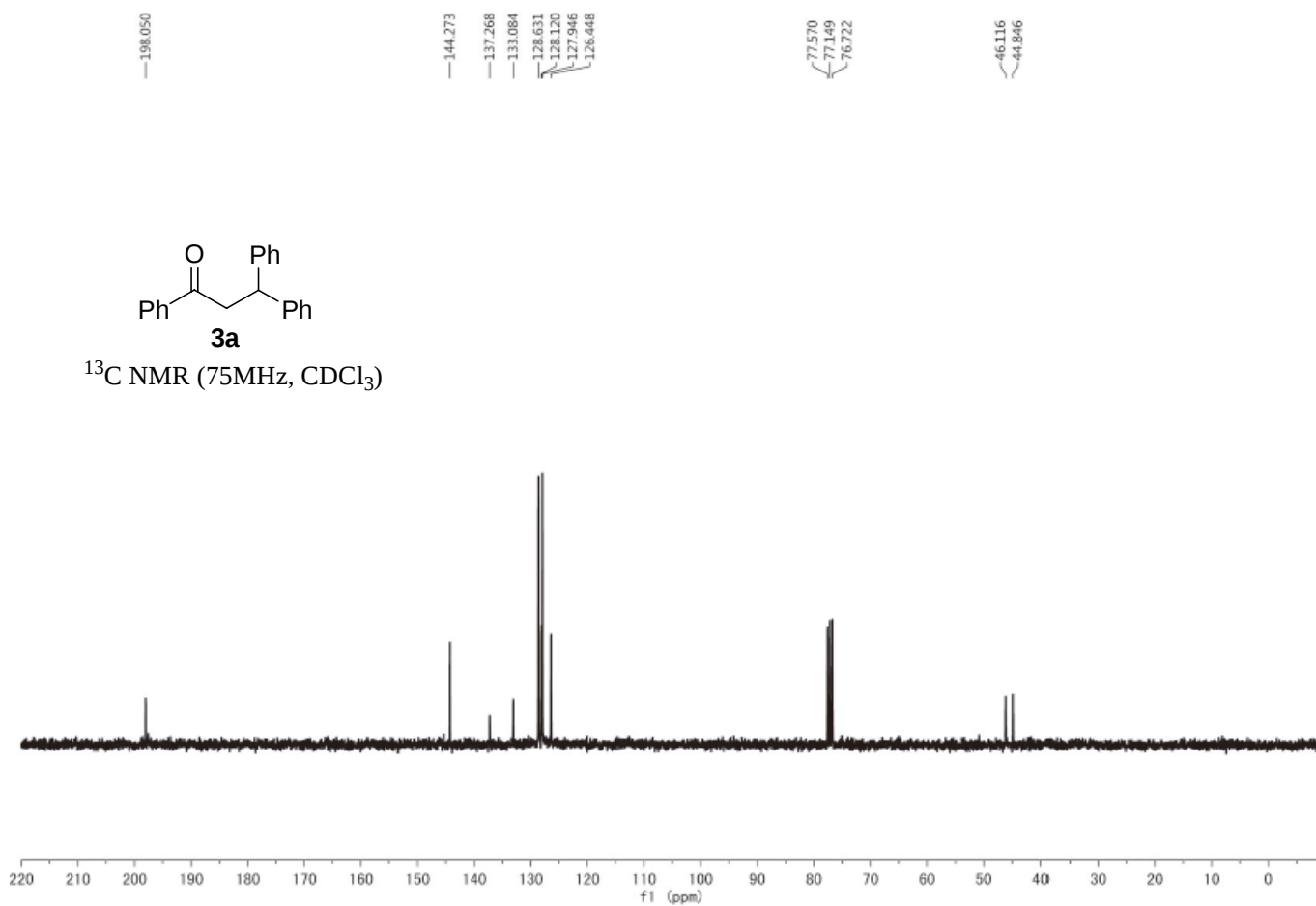


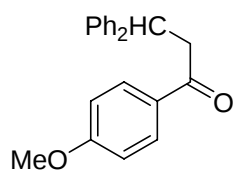


^1H NMR (300 MHz, CDCl_3)



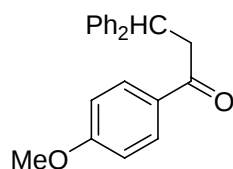
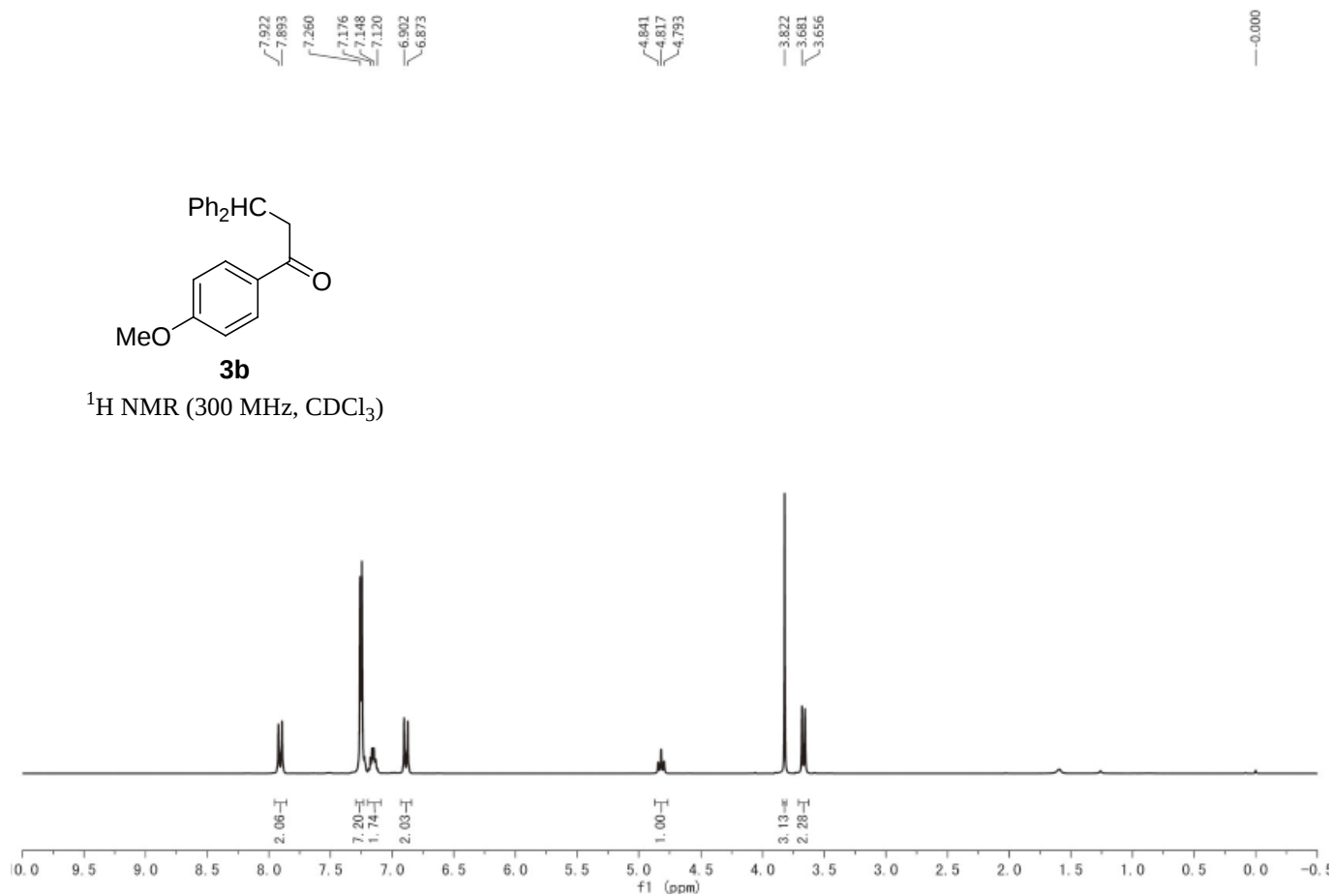
^{13}C NMR (75MHz, CDCl_3)





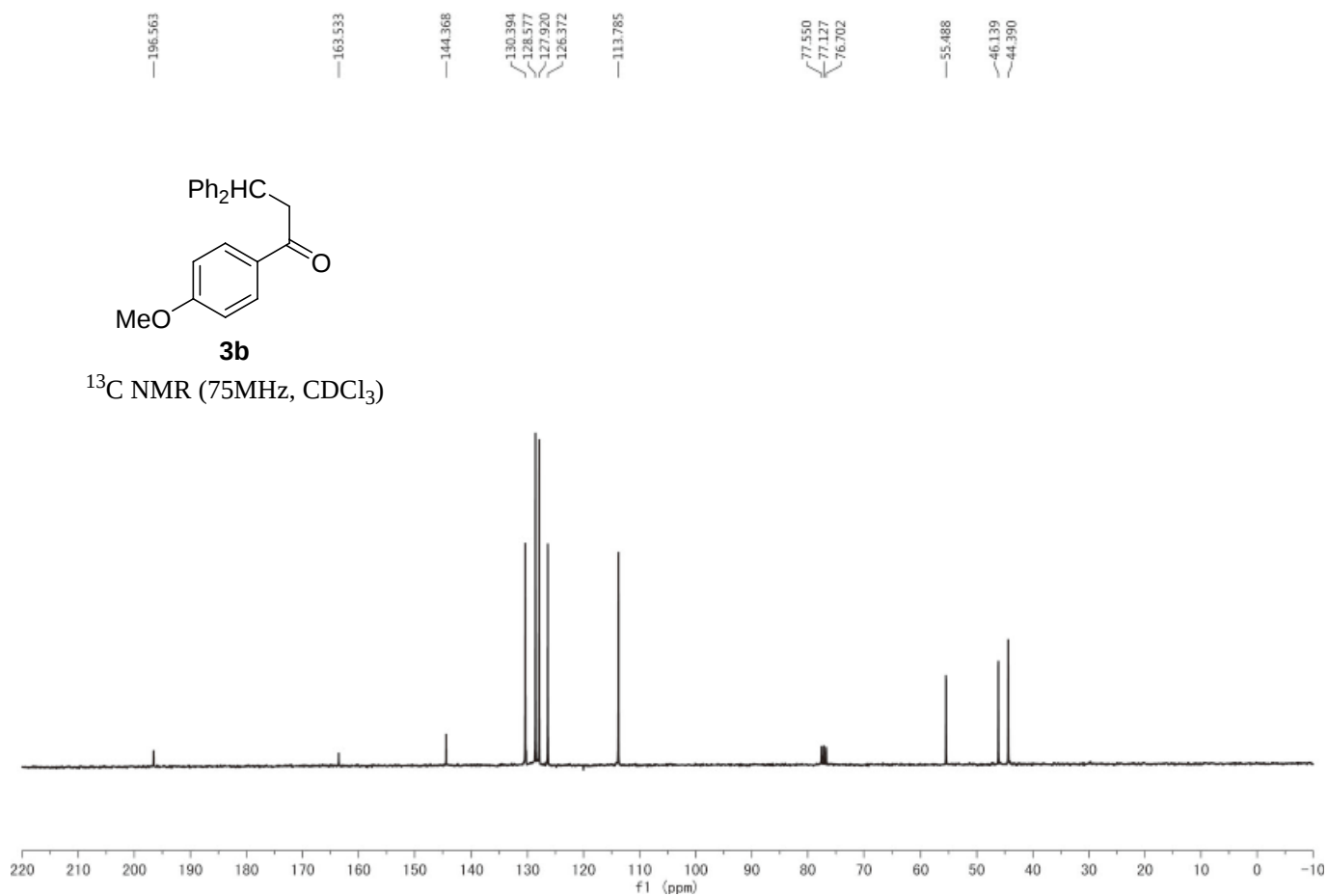
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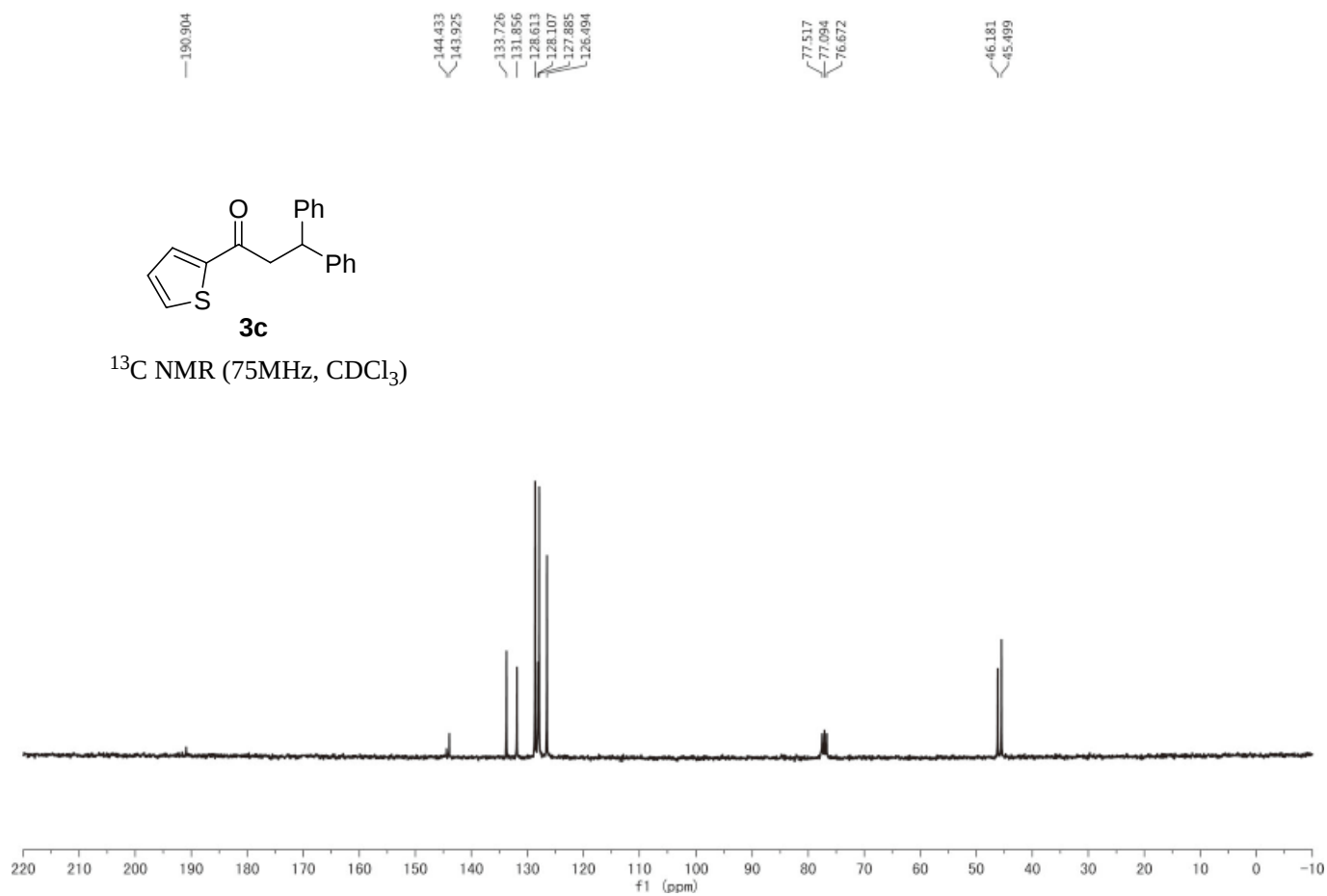
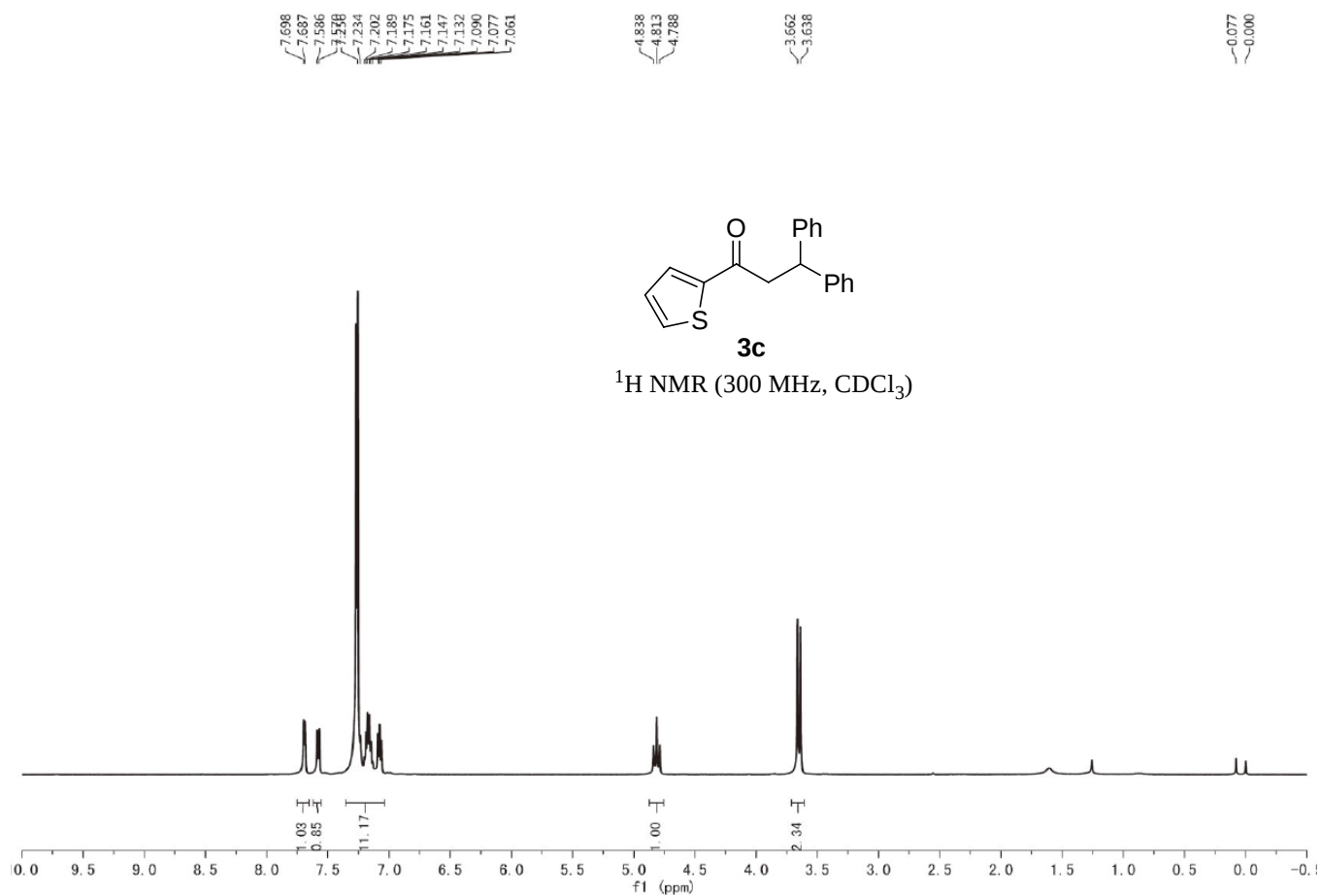
^1H NMR (300 MHz, CDCl_3)

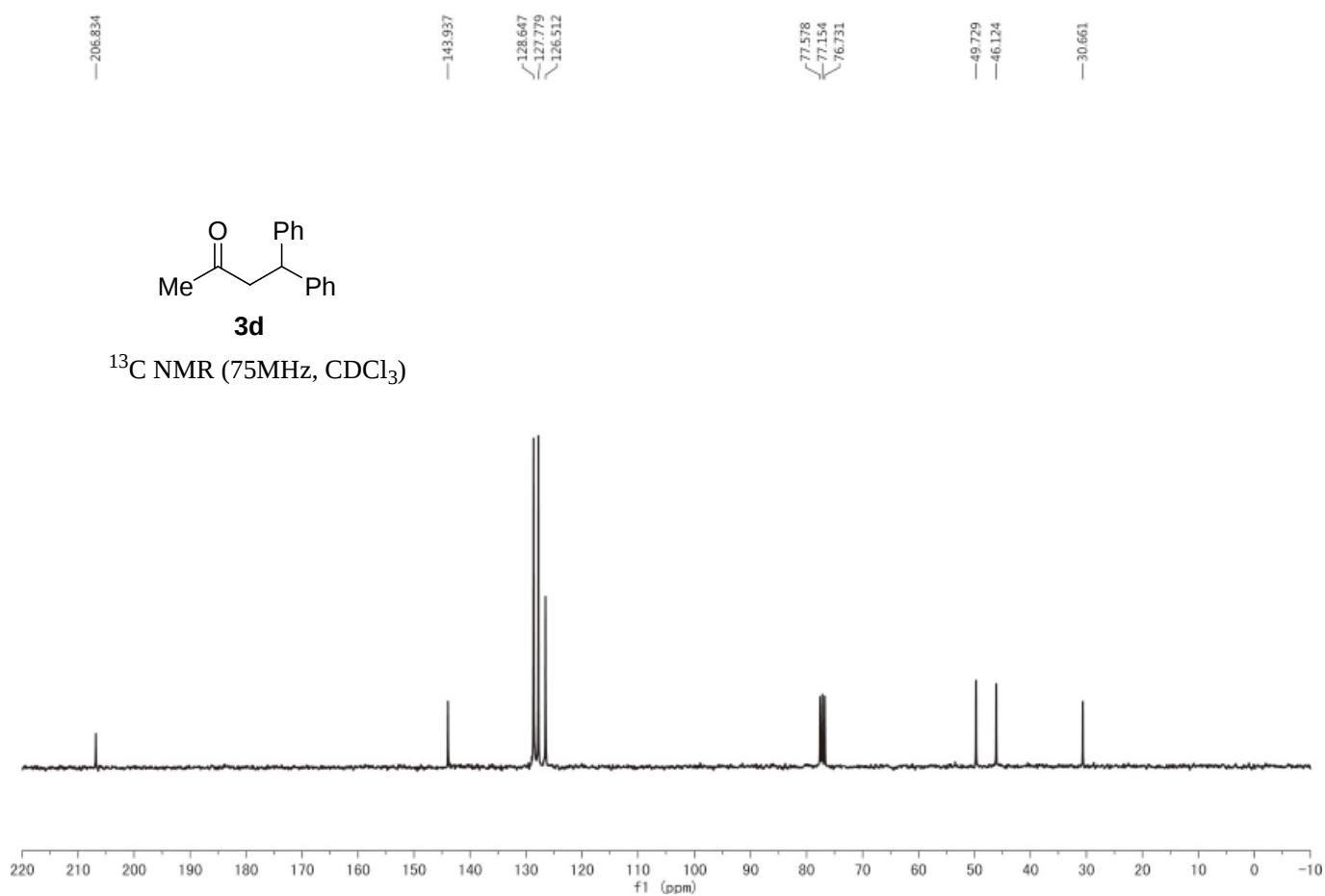
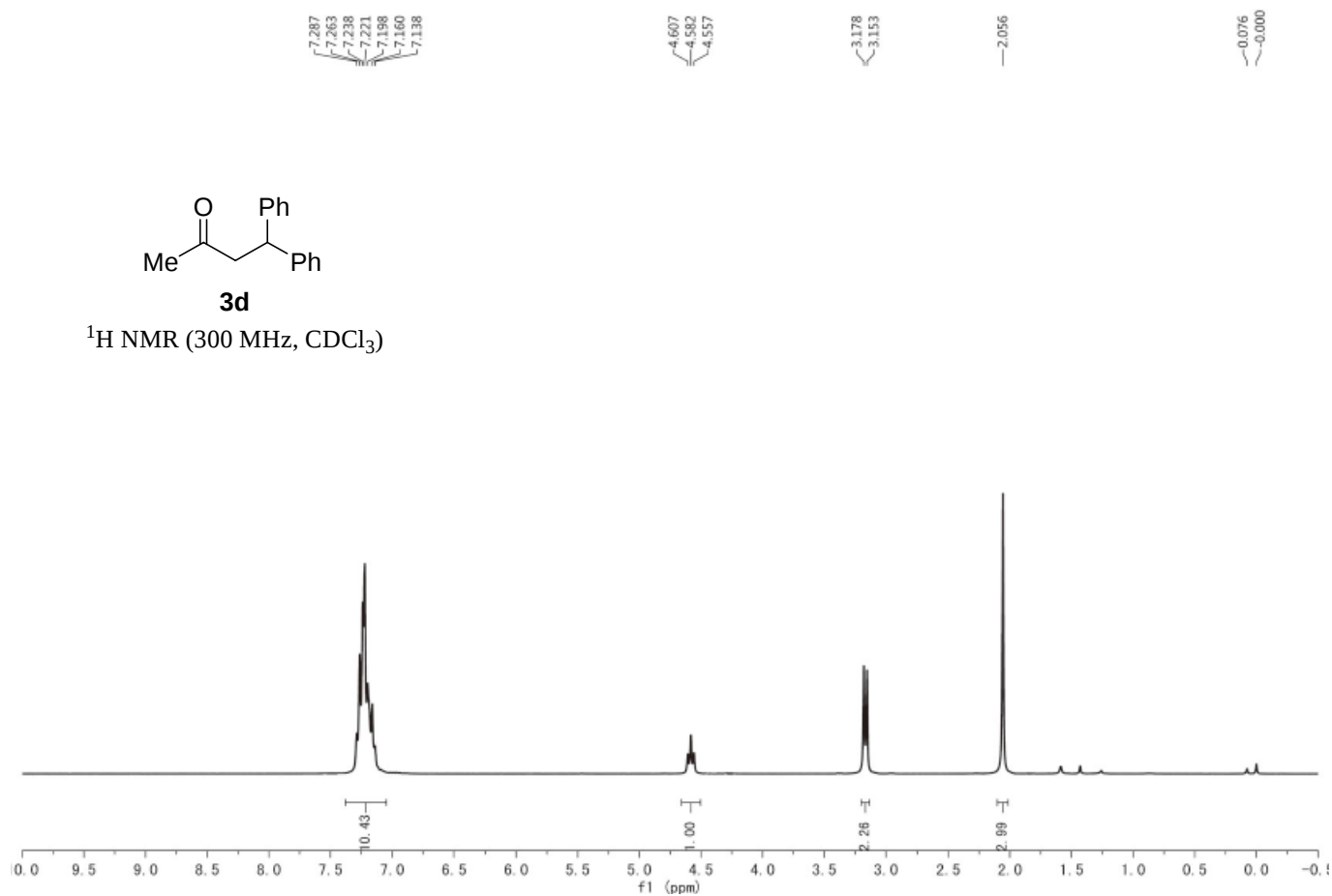


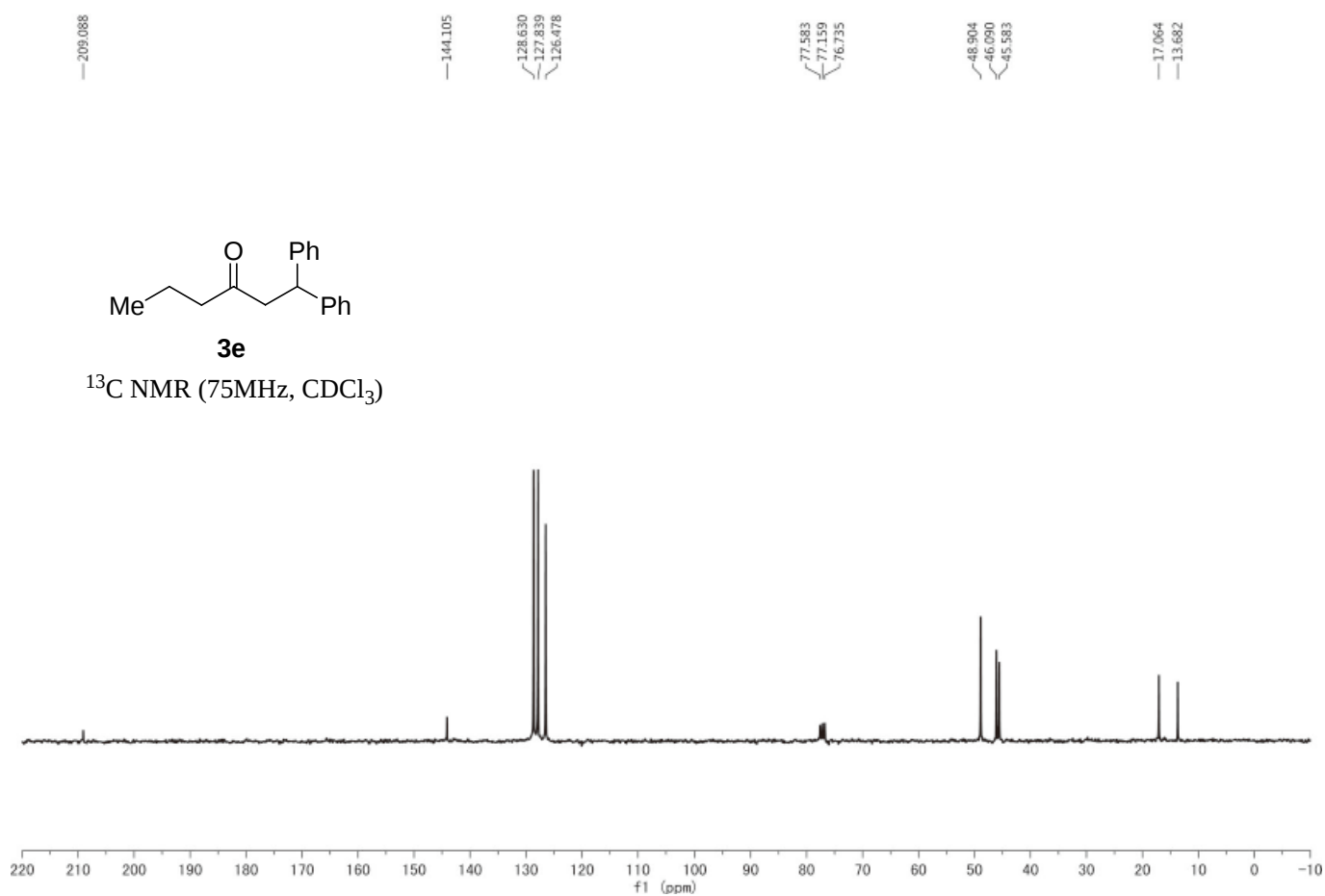
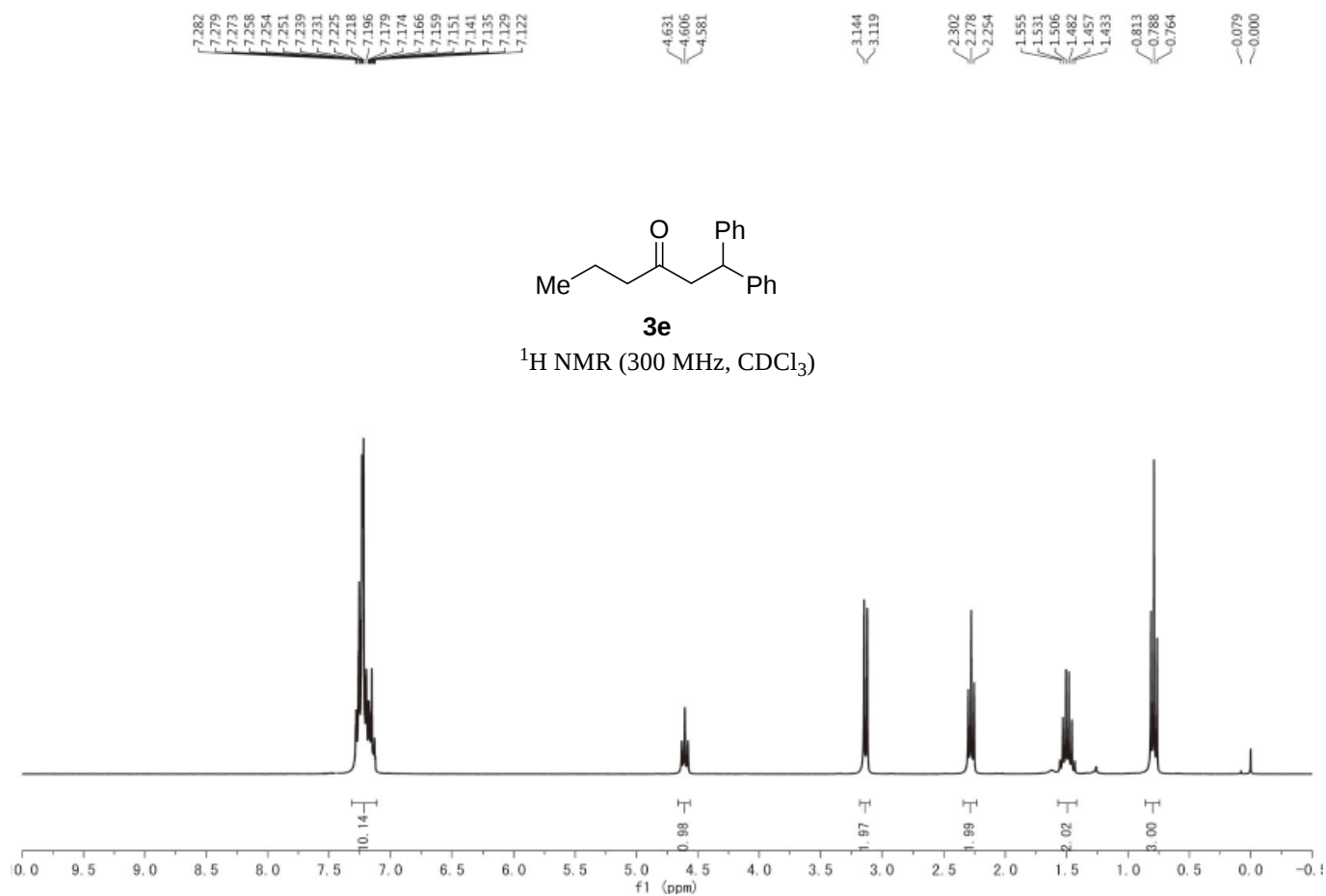
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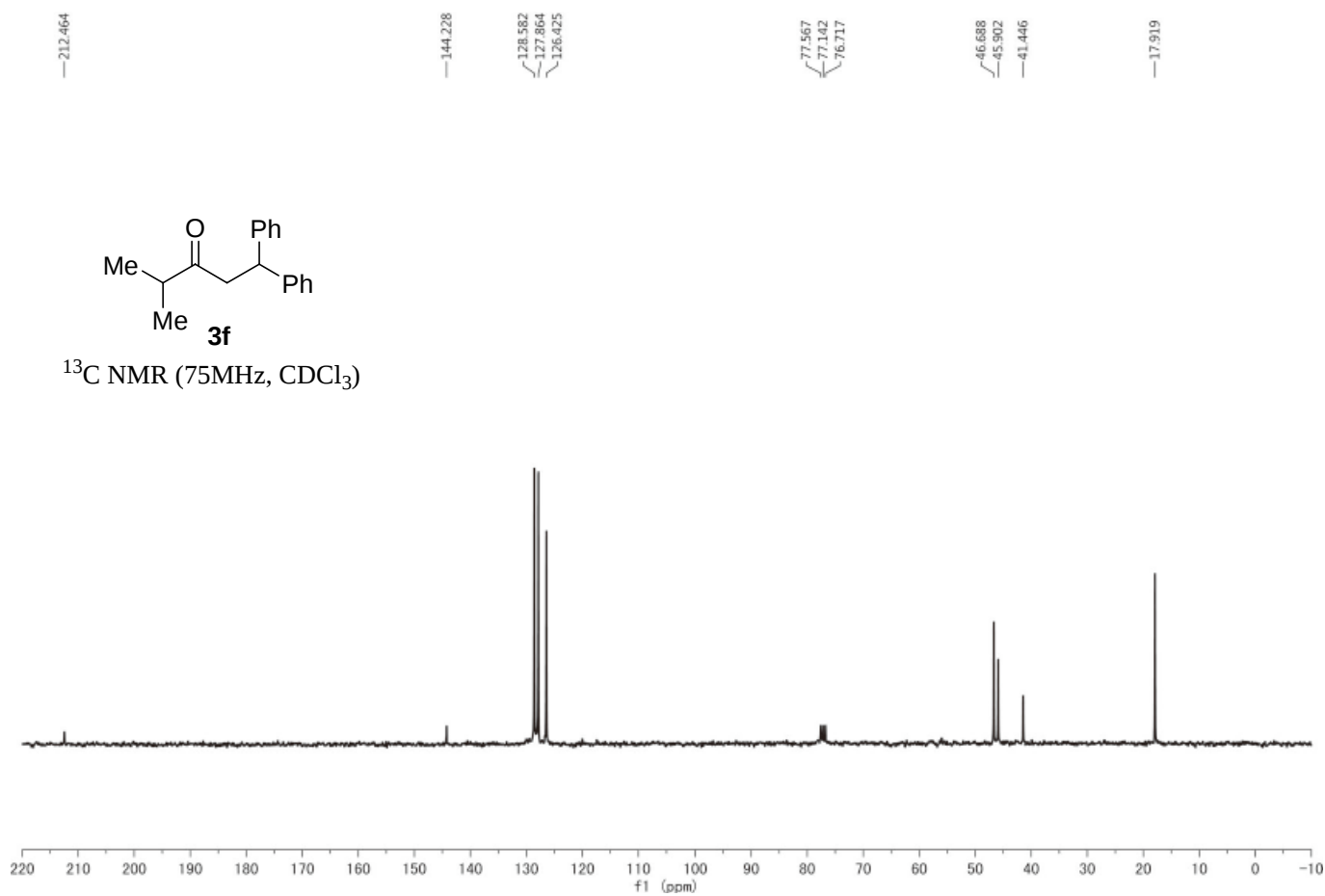
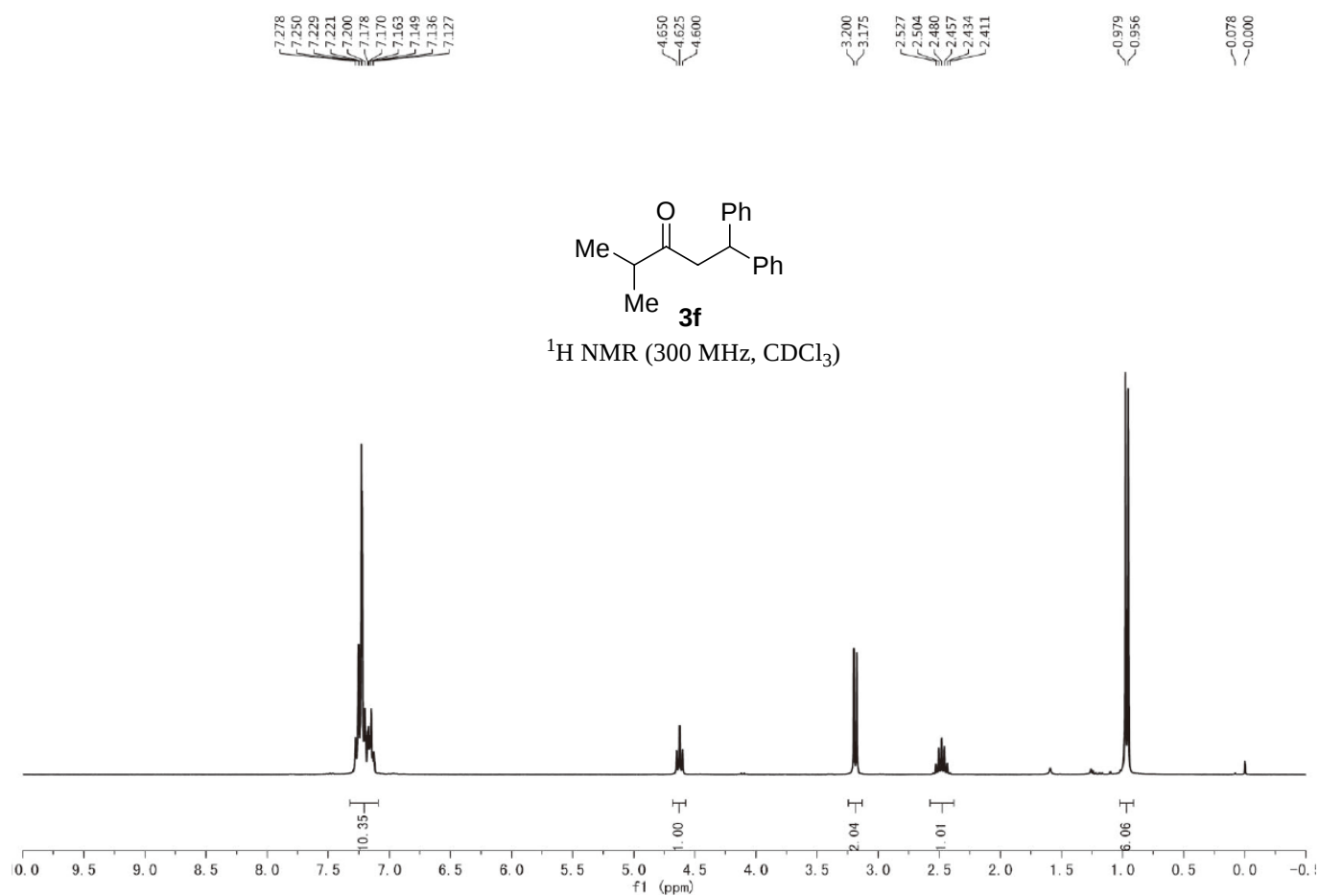
^{13}C NMR (75MHz, CDCl_3)

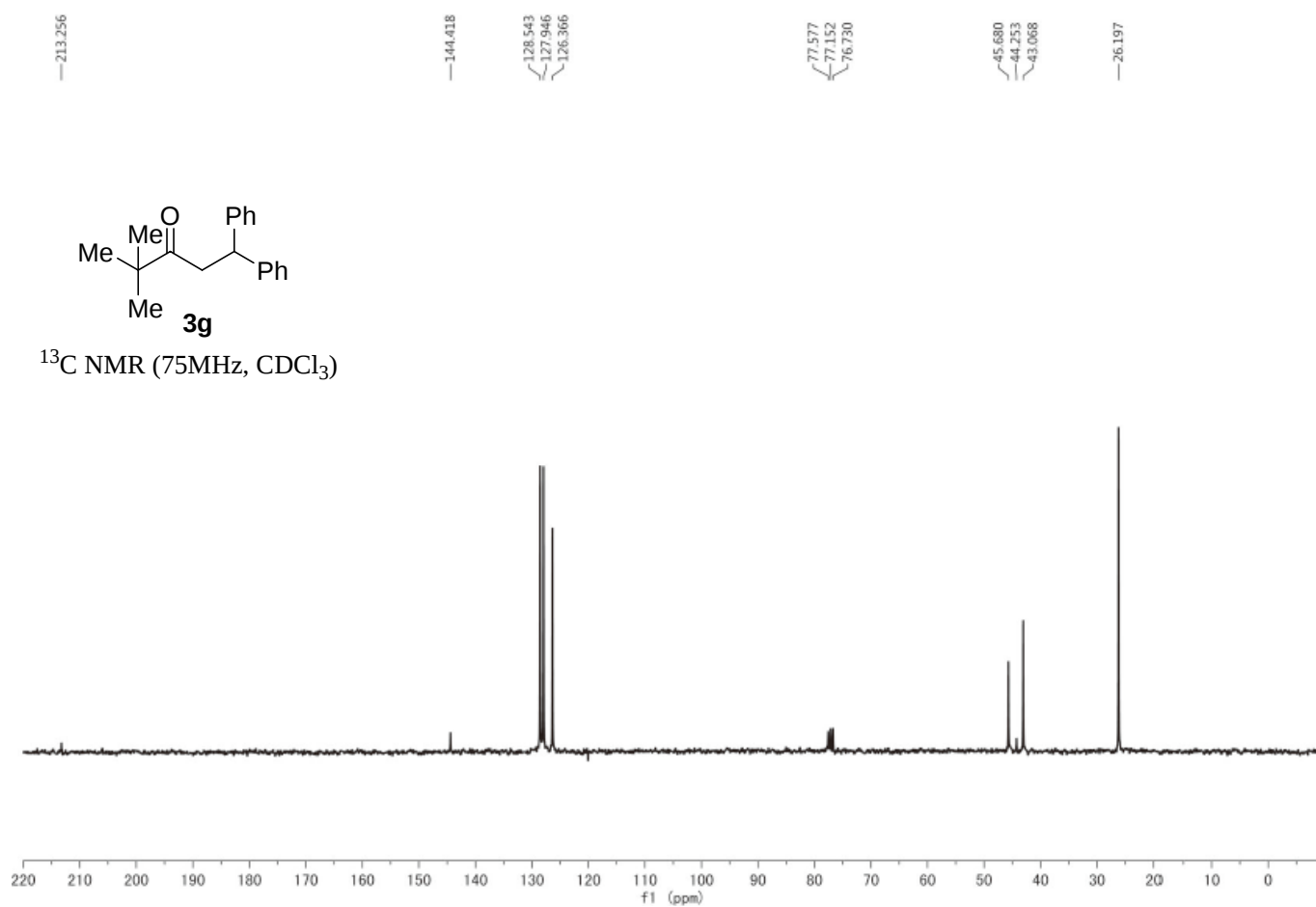
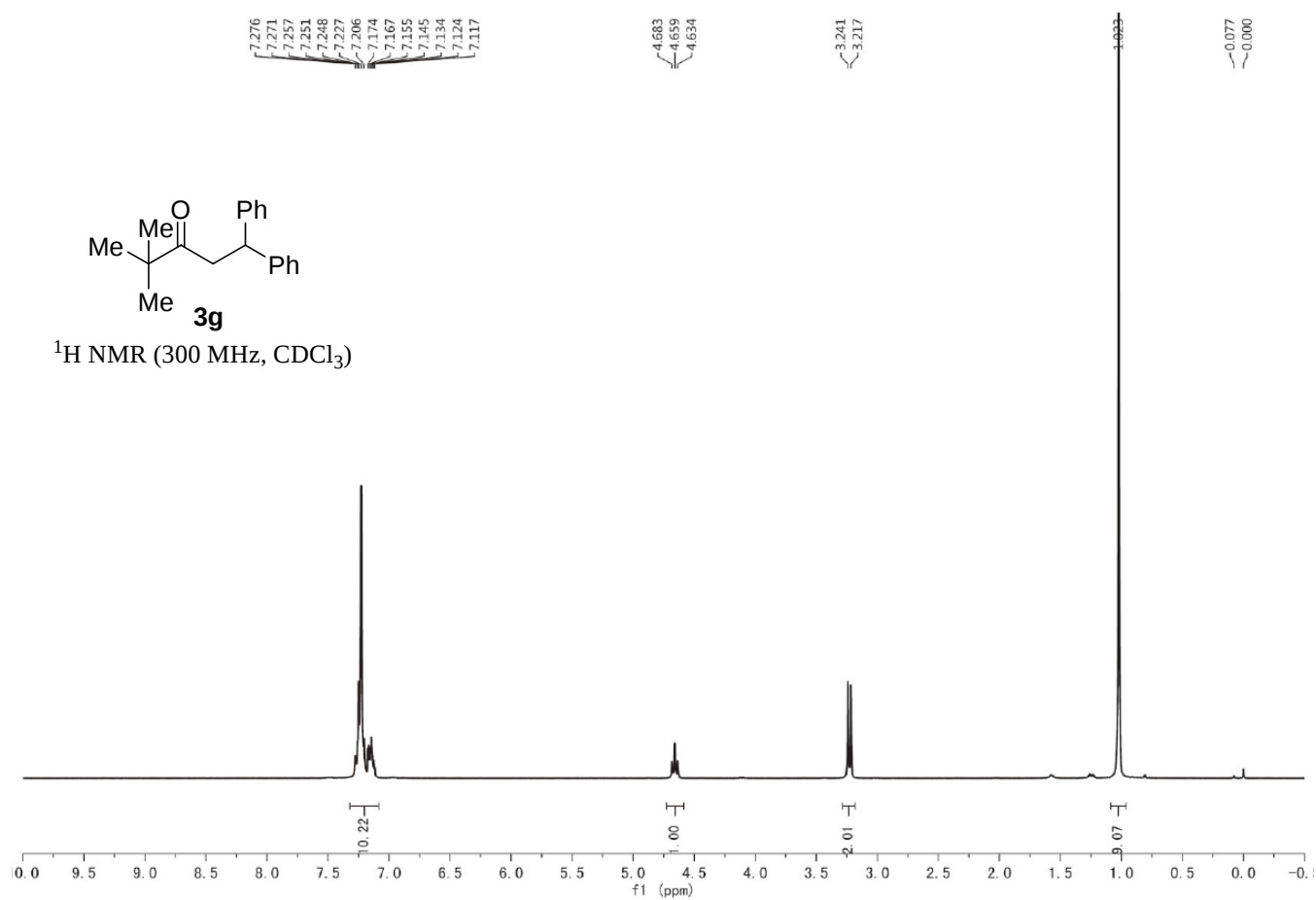


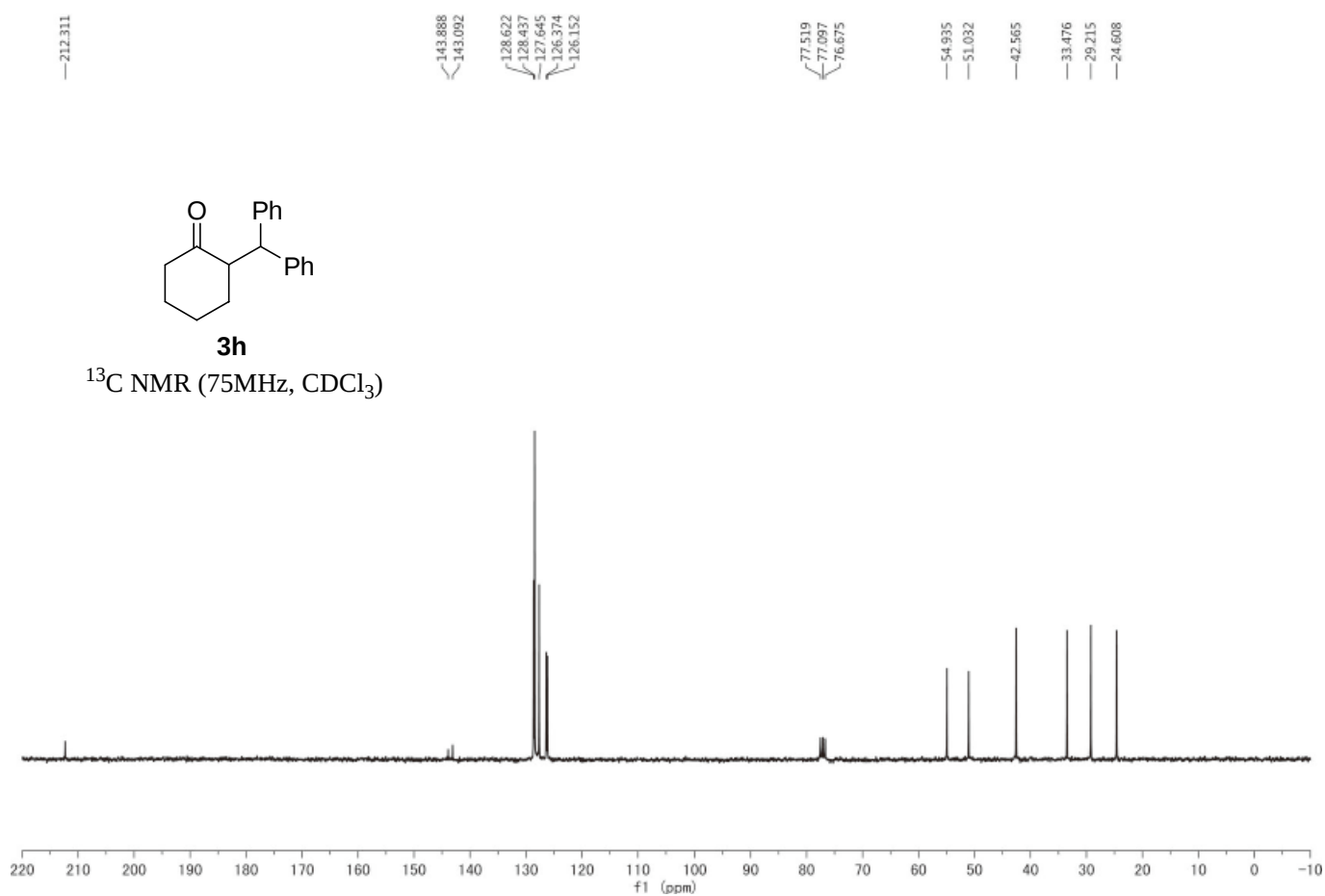
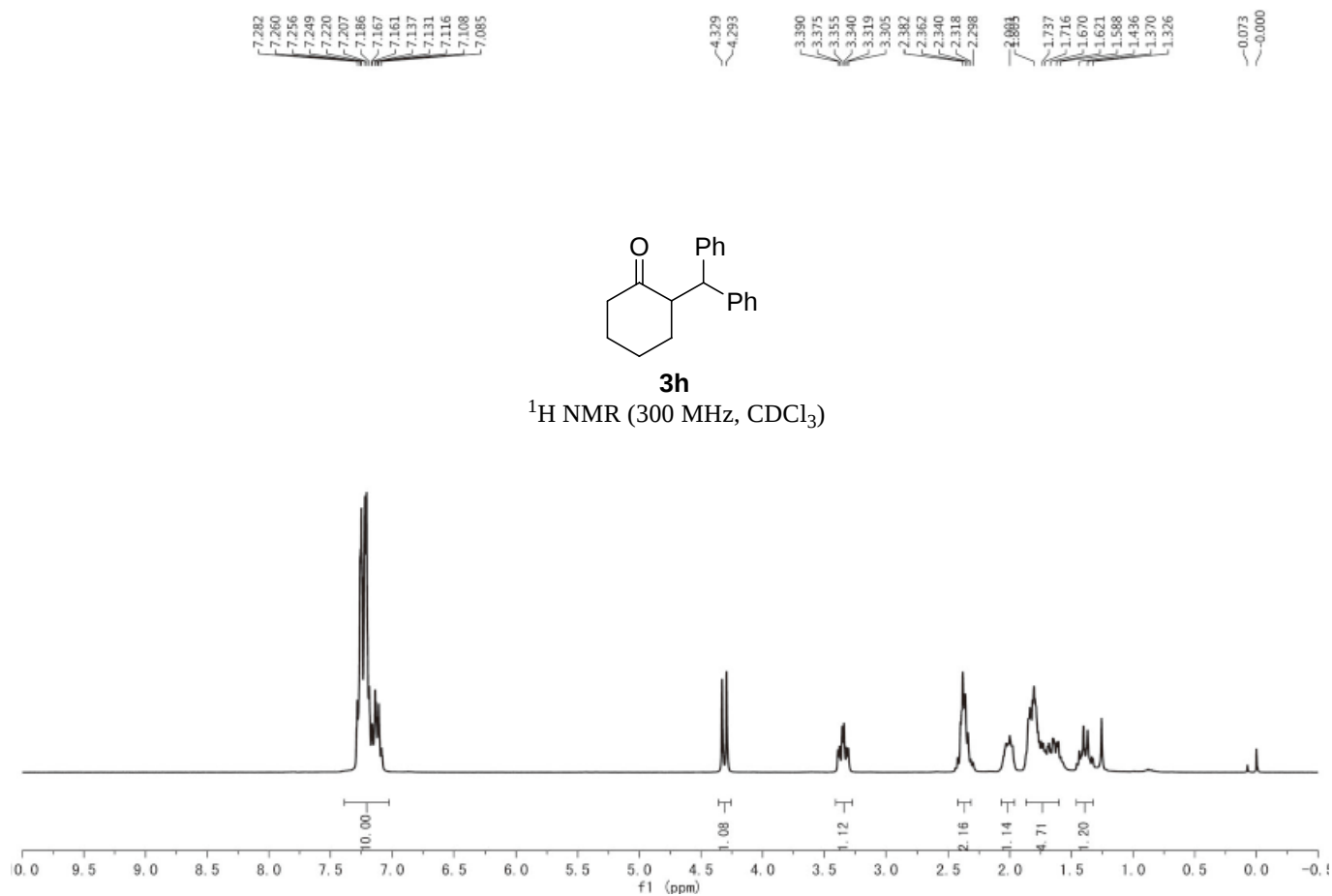


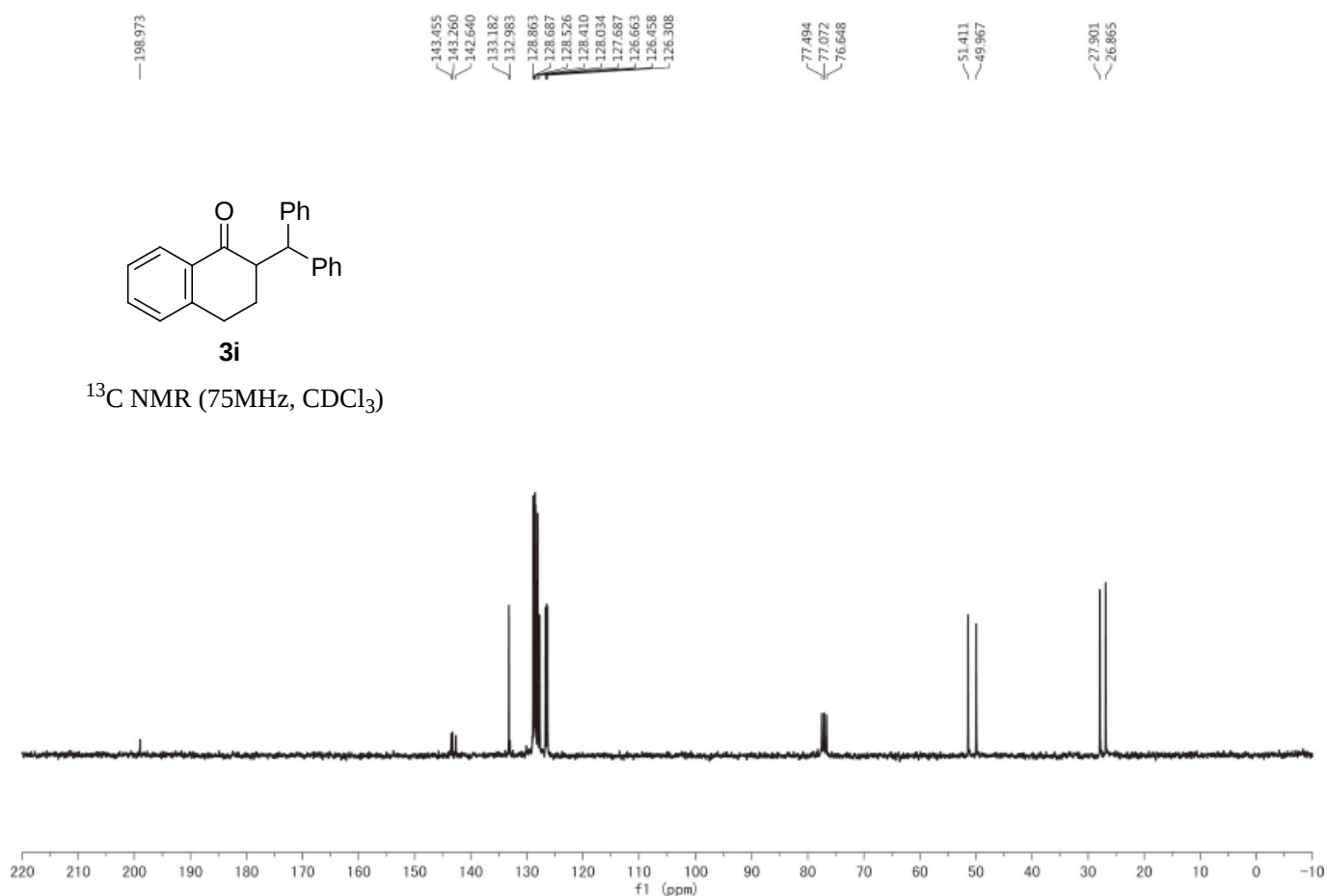
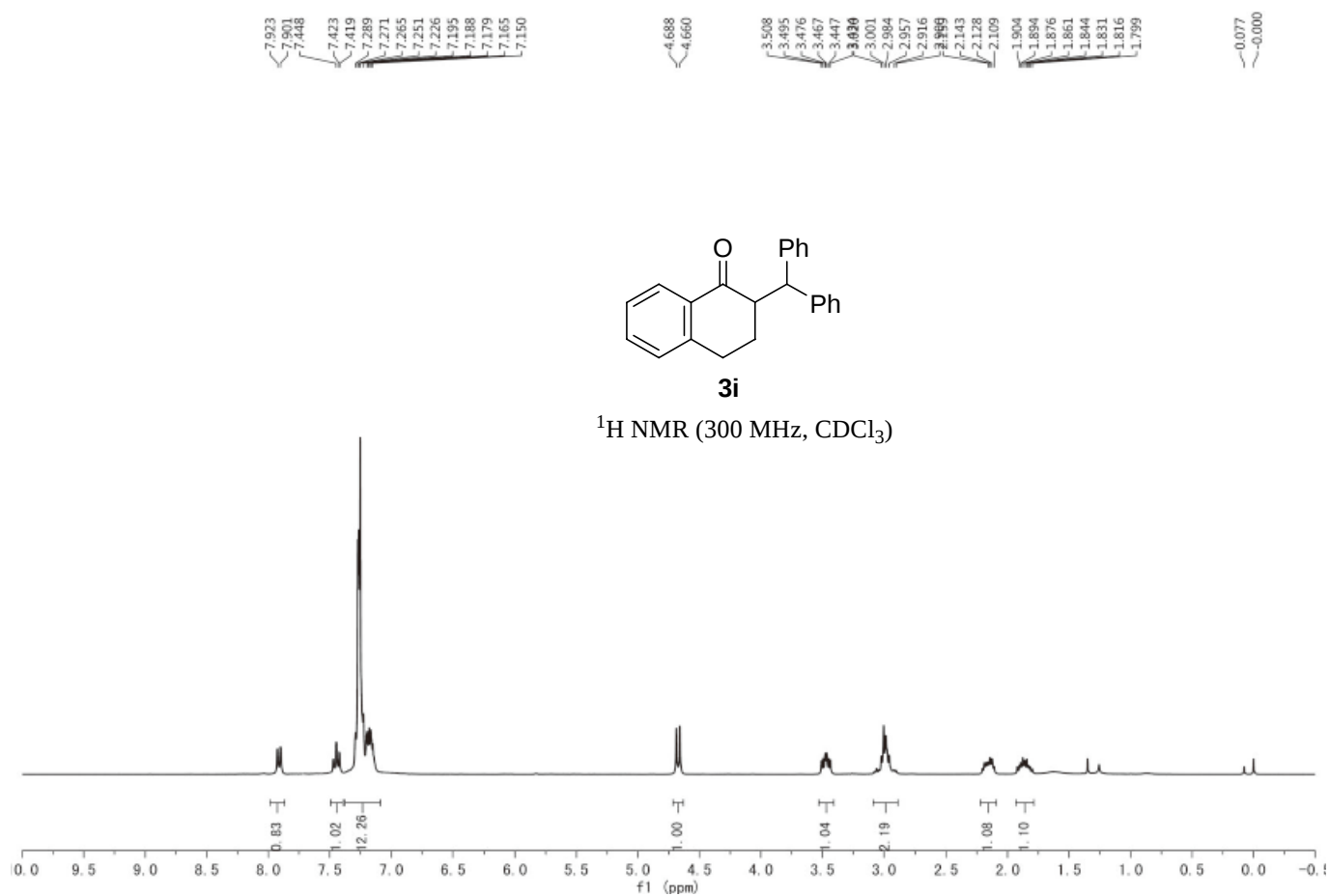


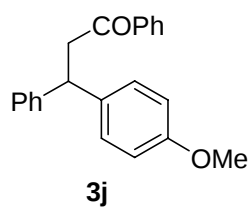




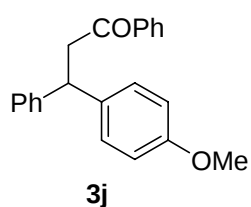
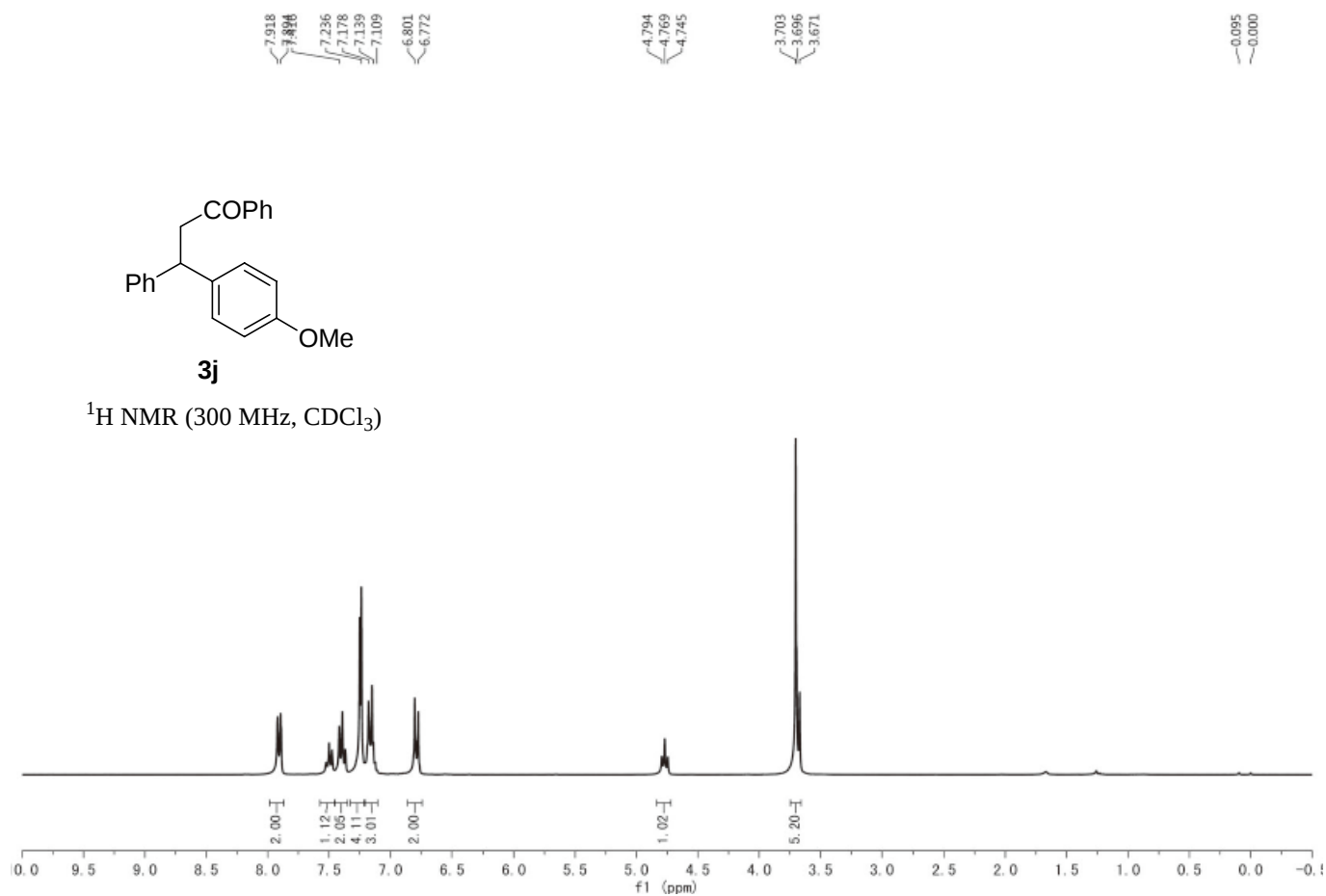




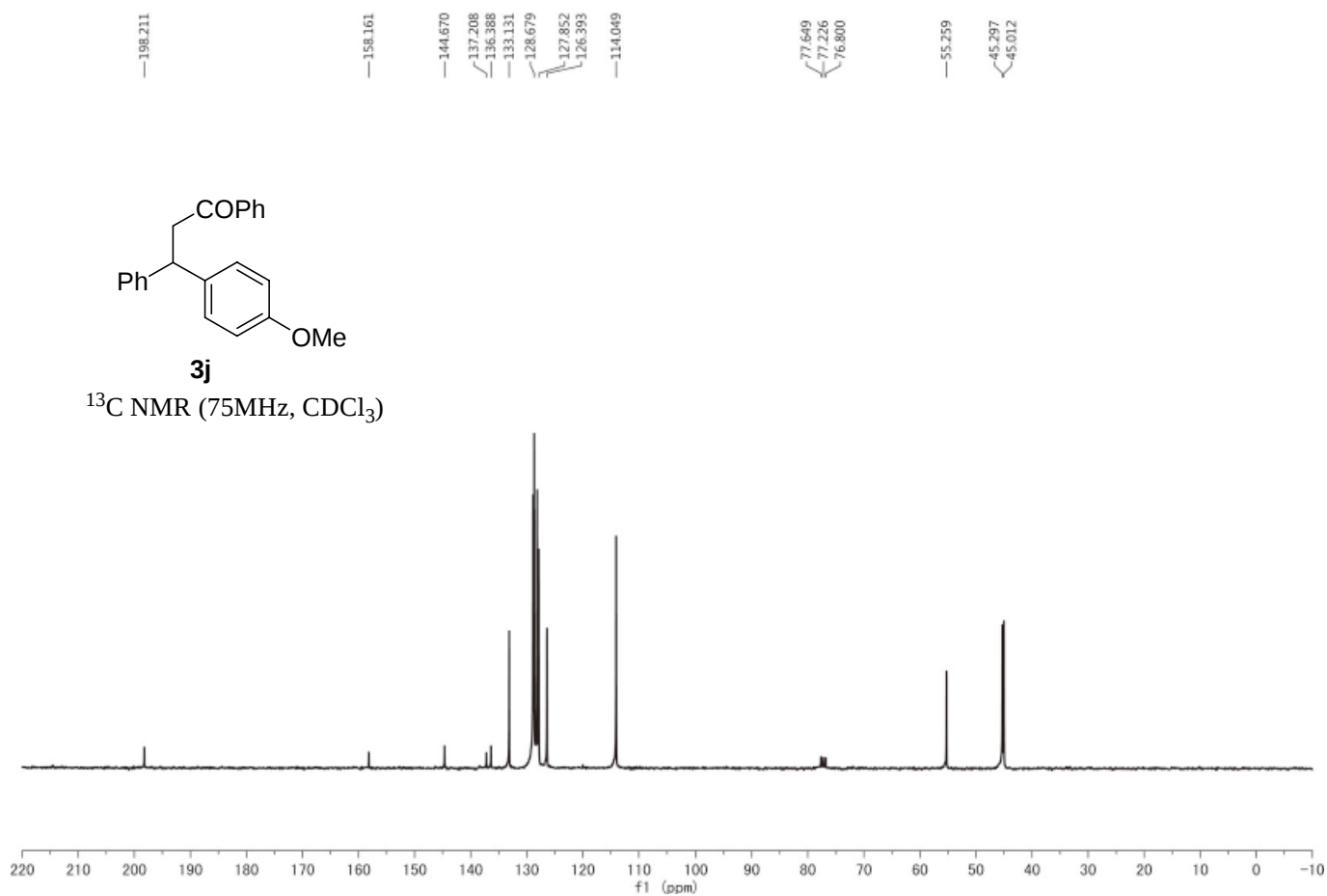


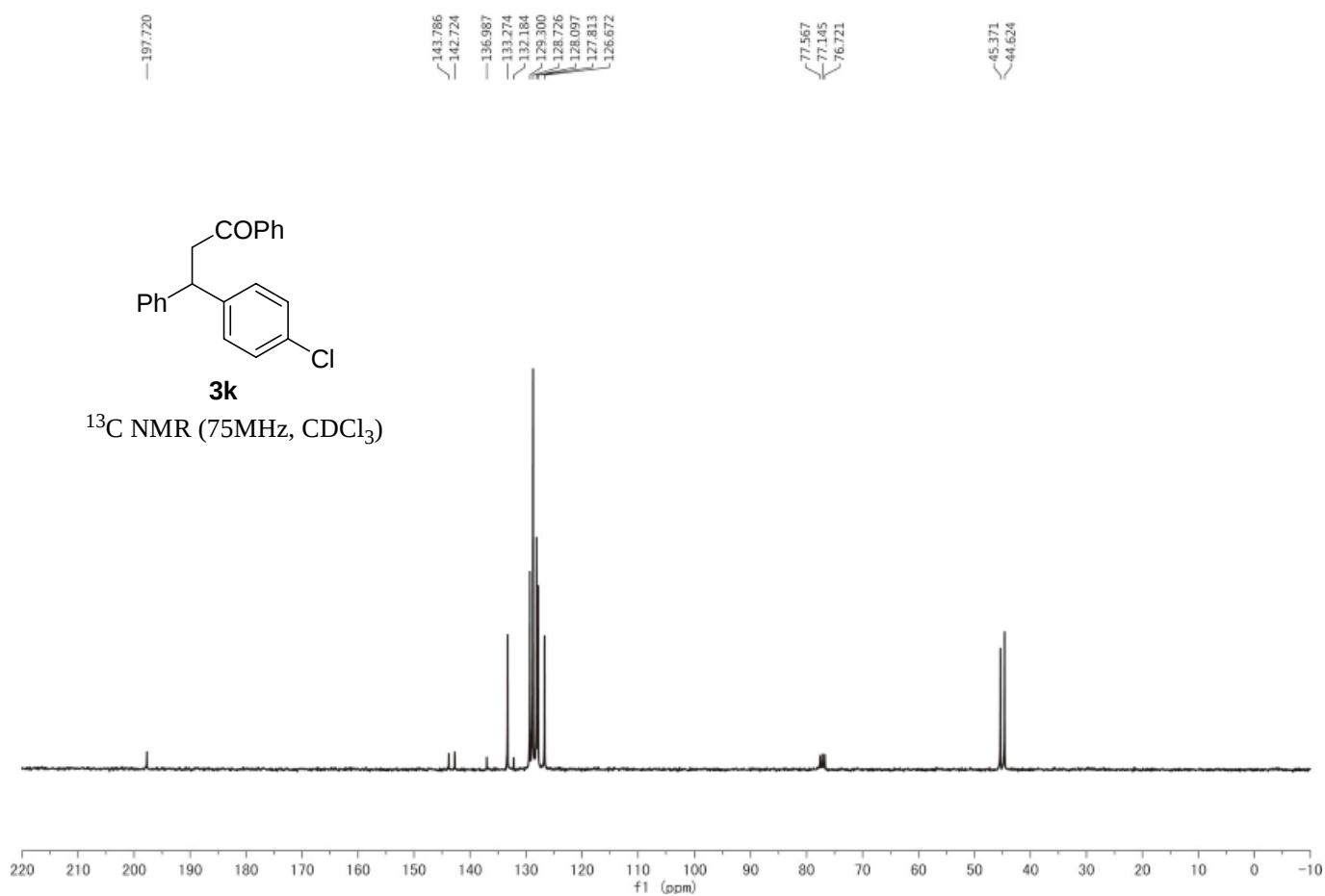
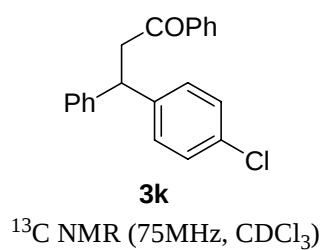
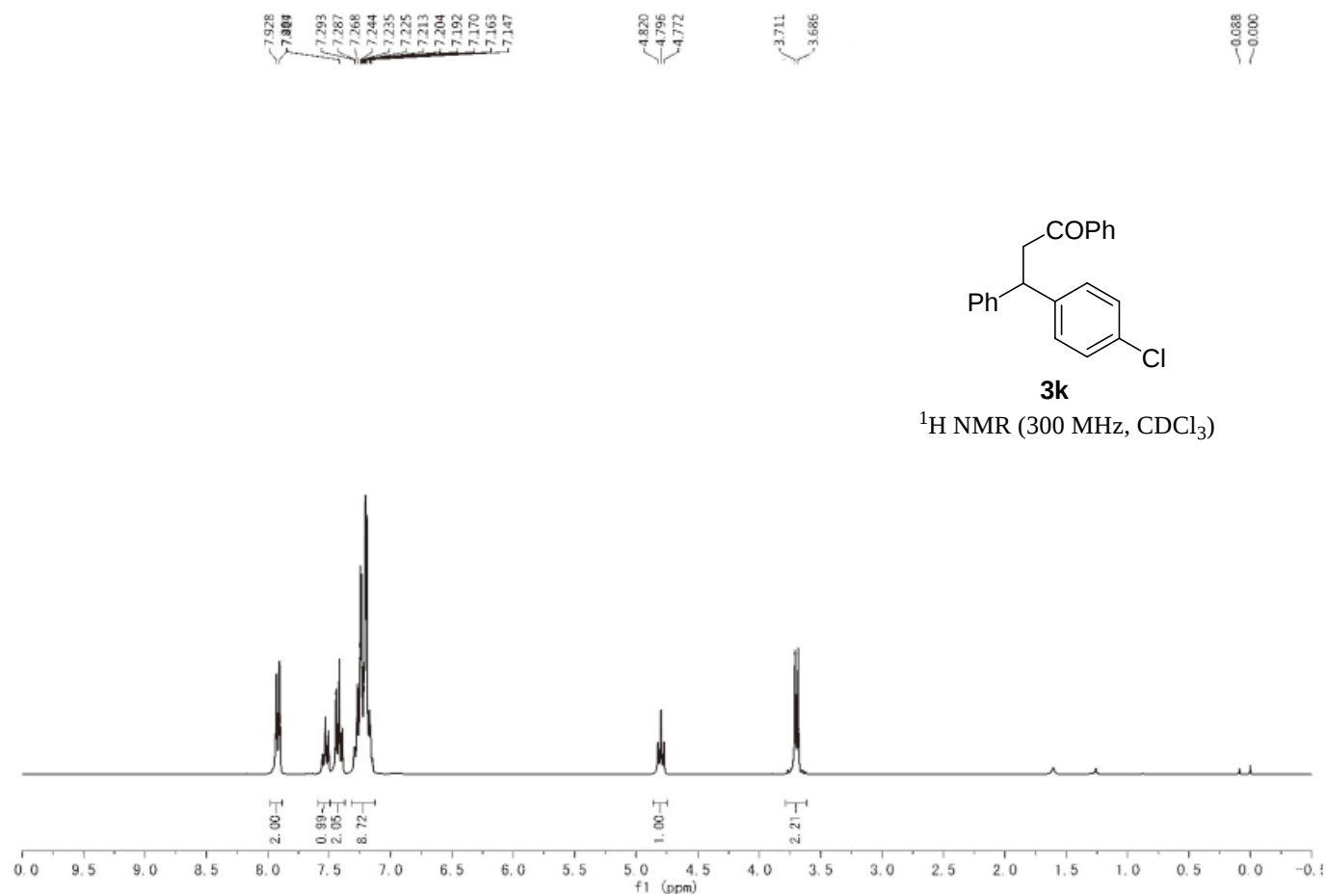
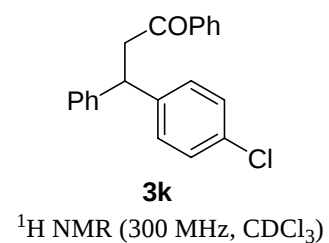


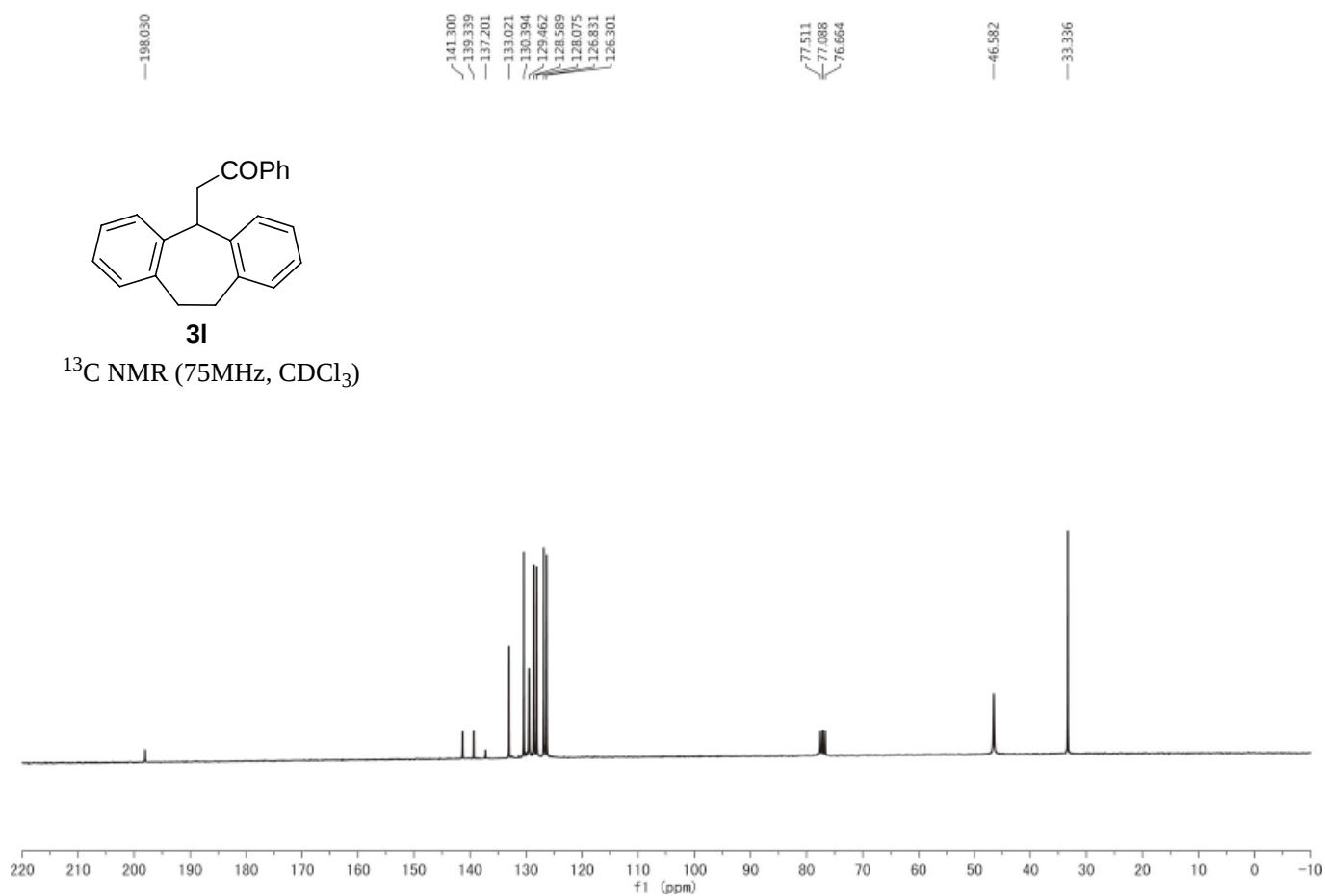
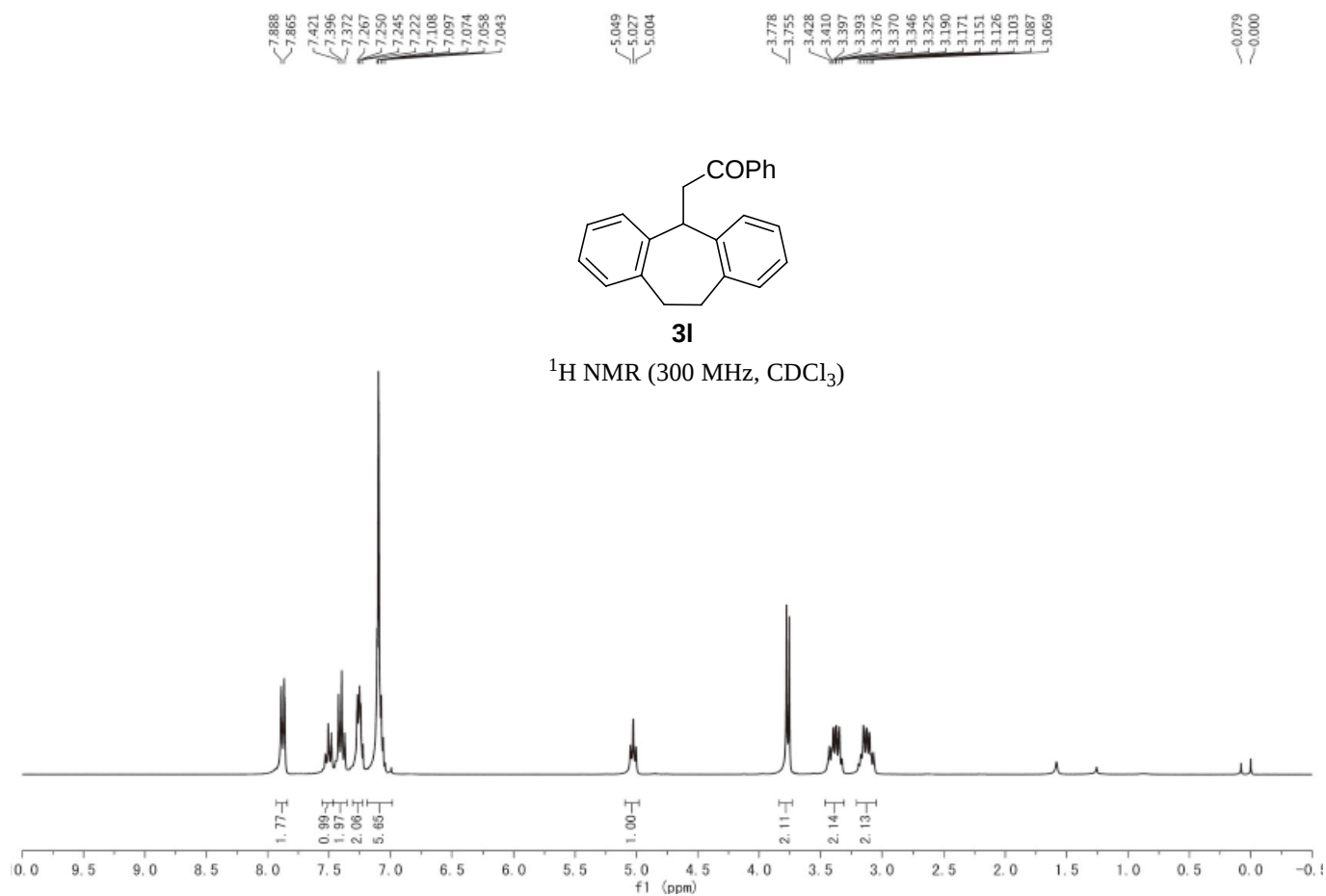
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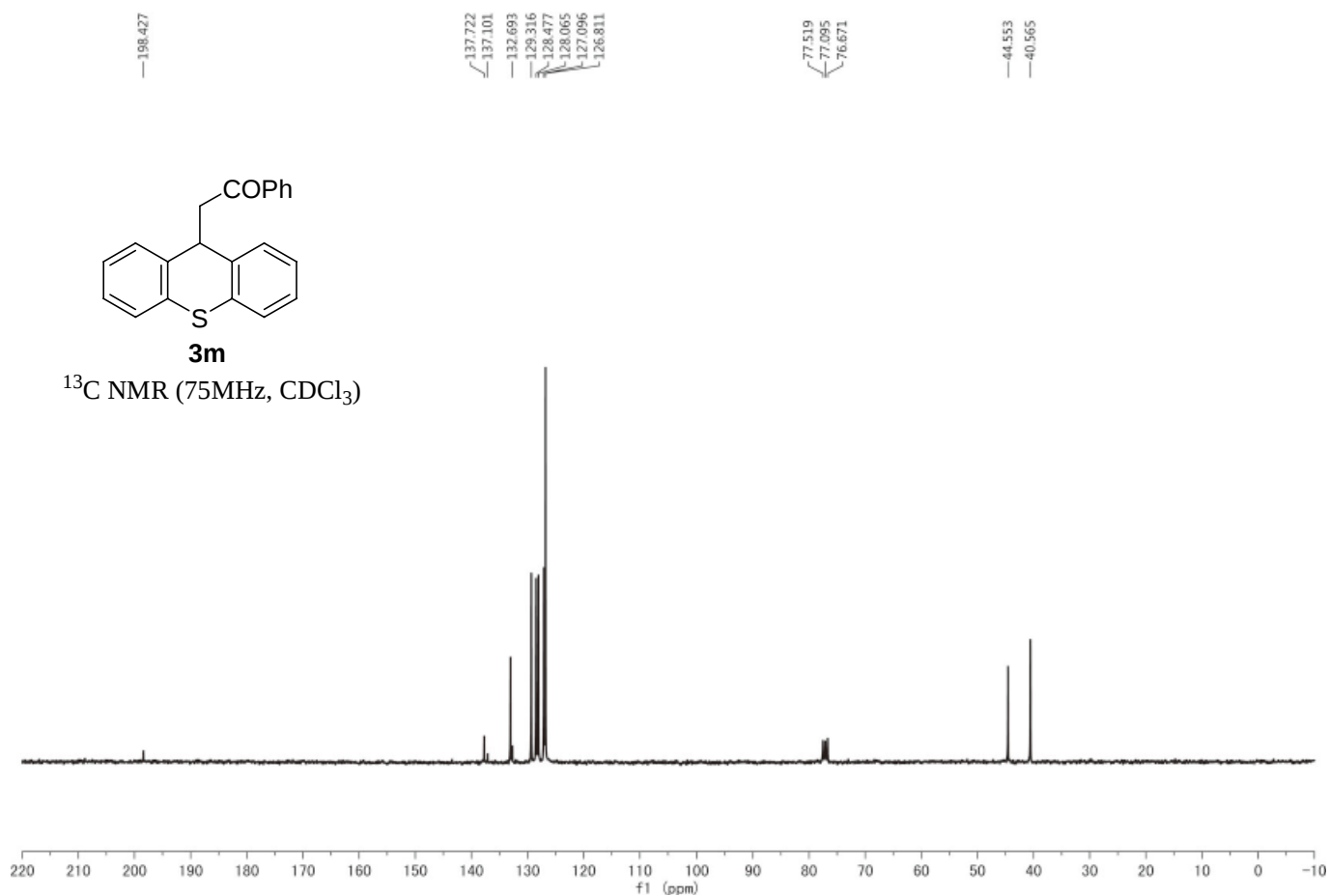
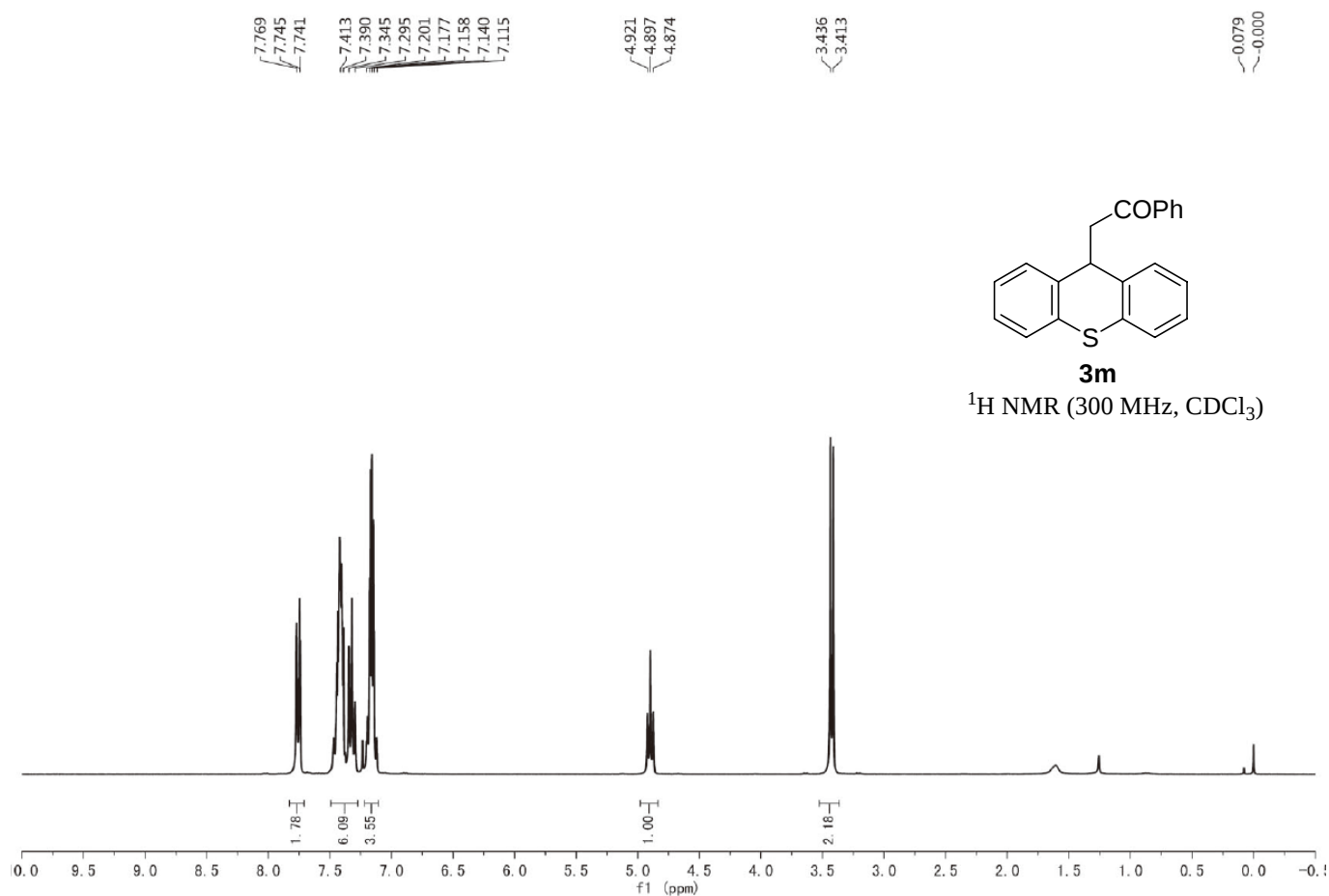


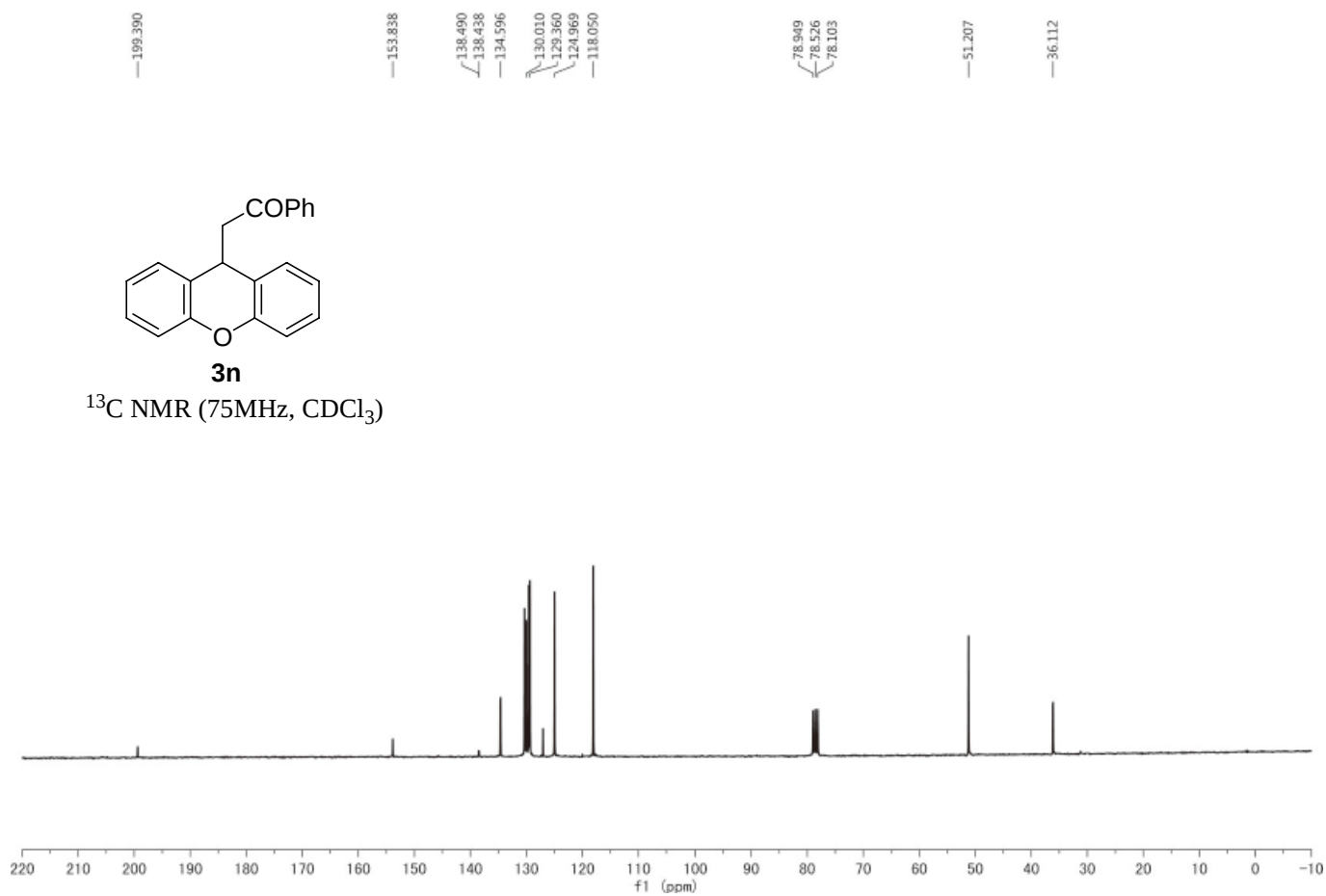
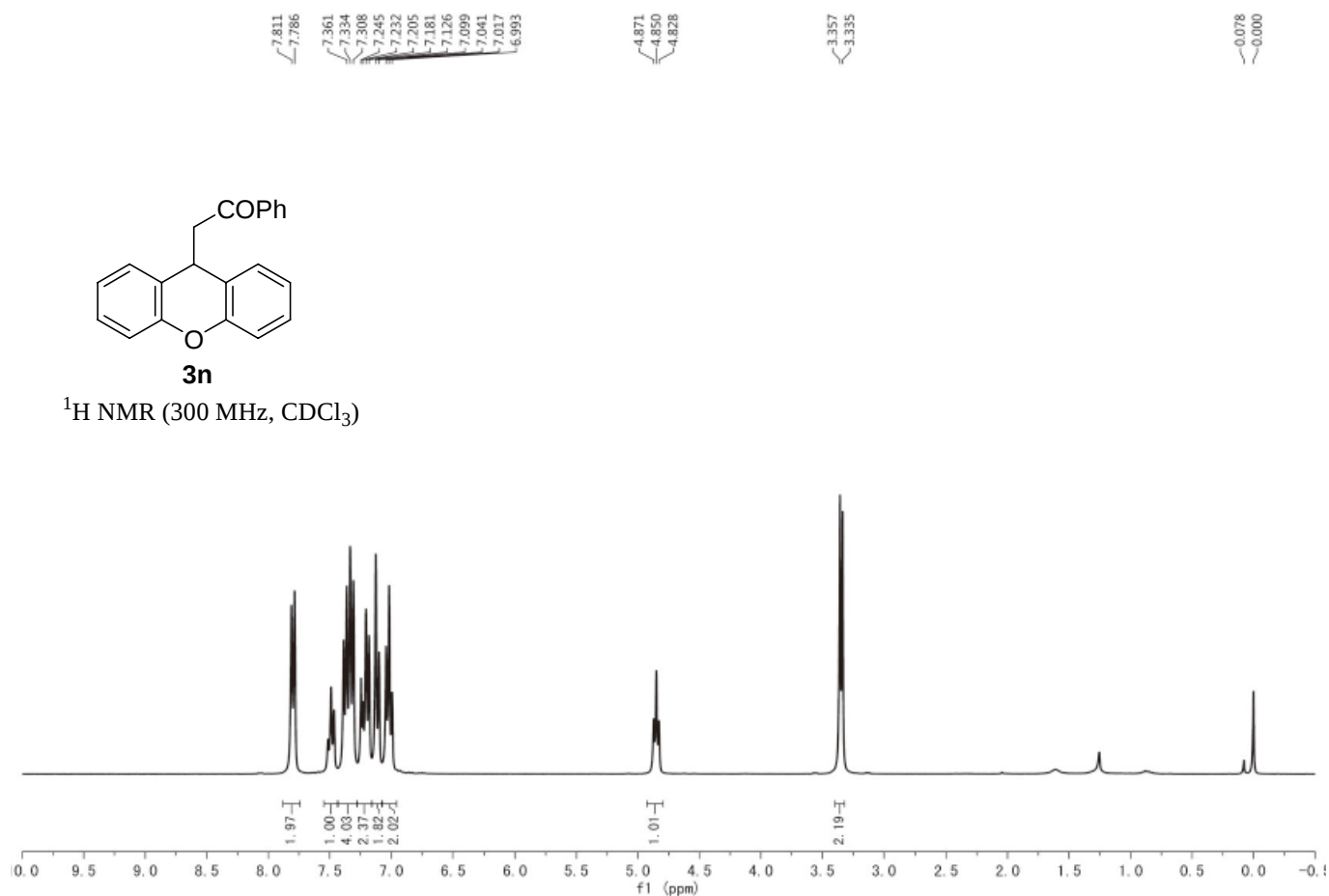
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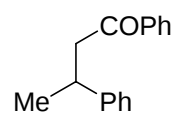






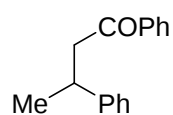
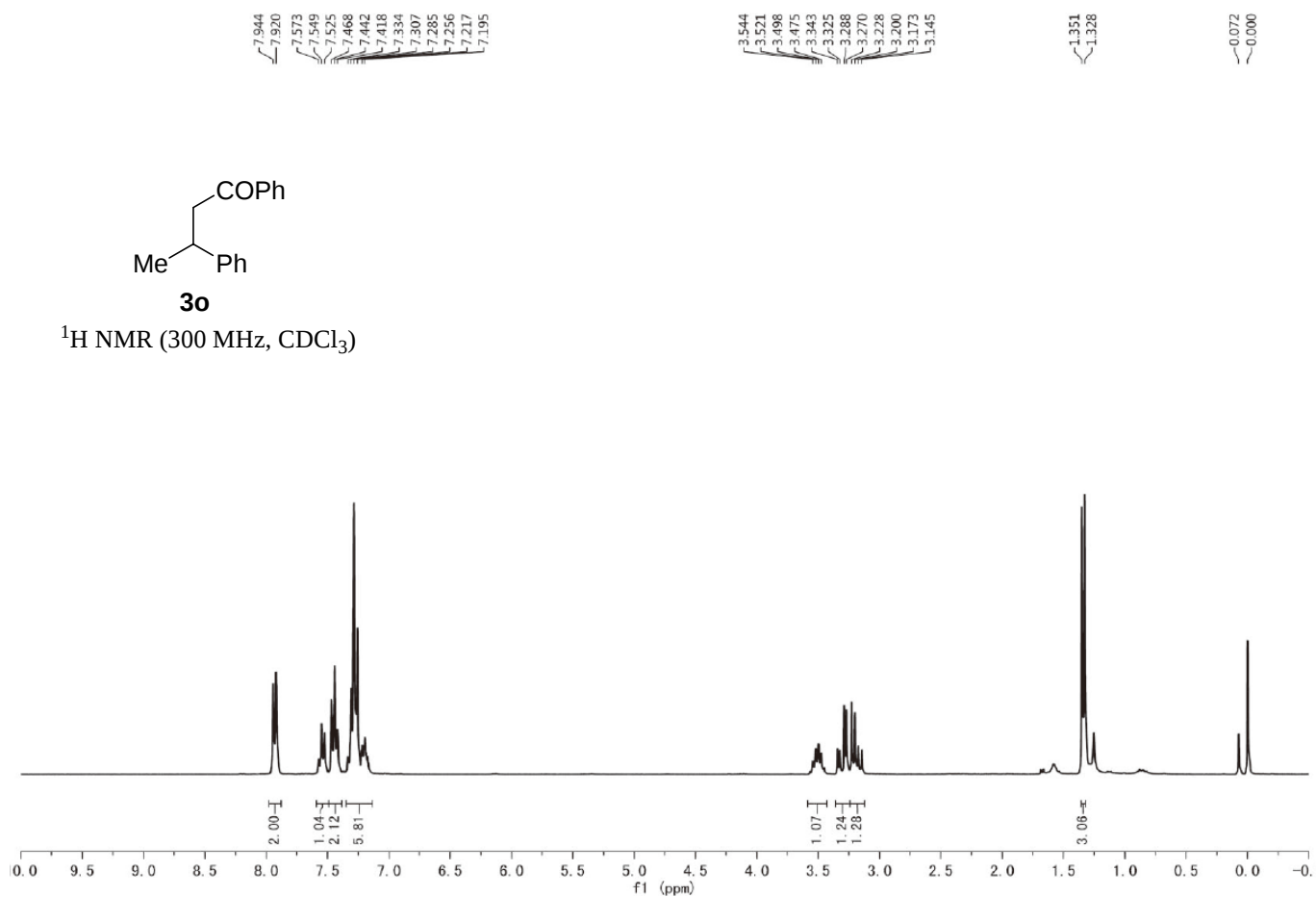






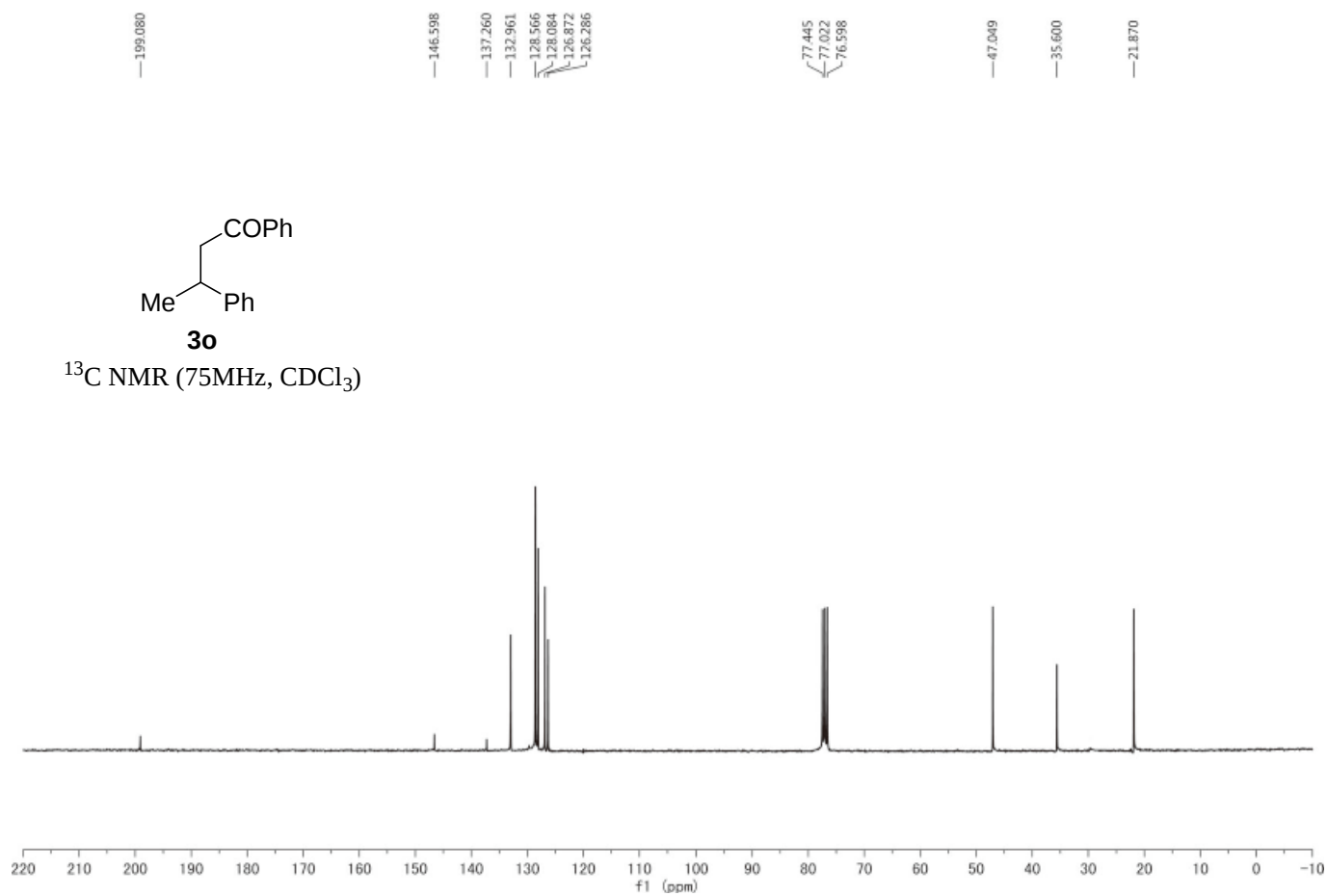
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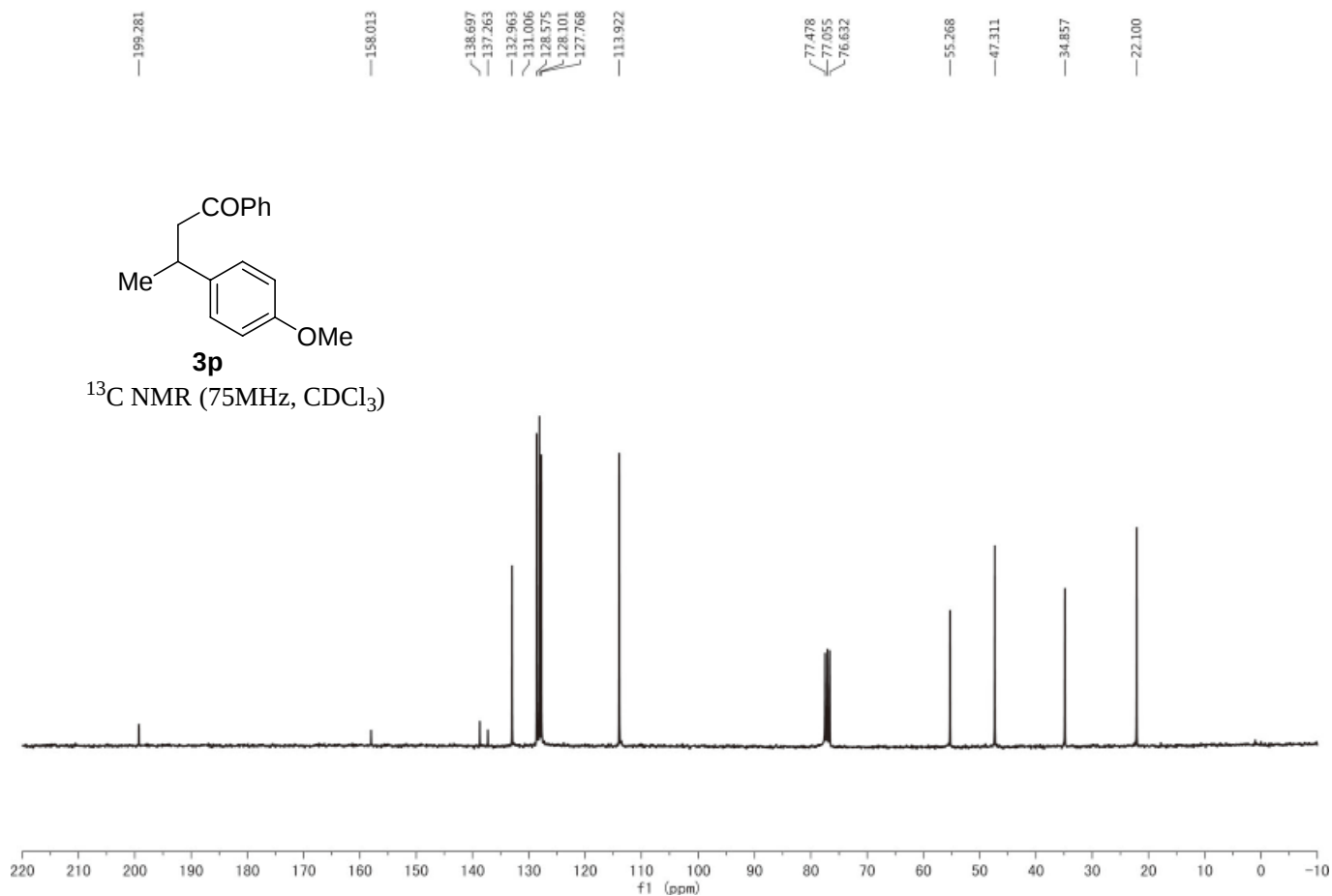
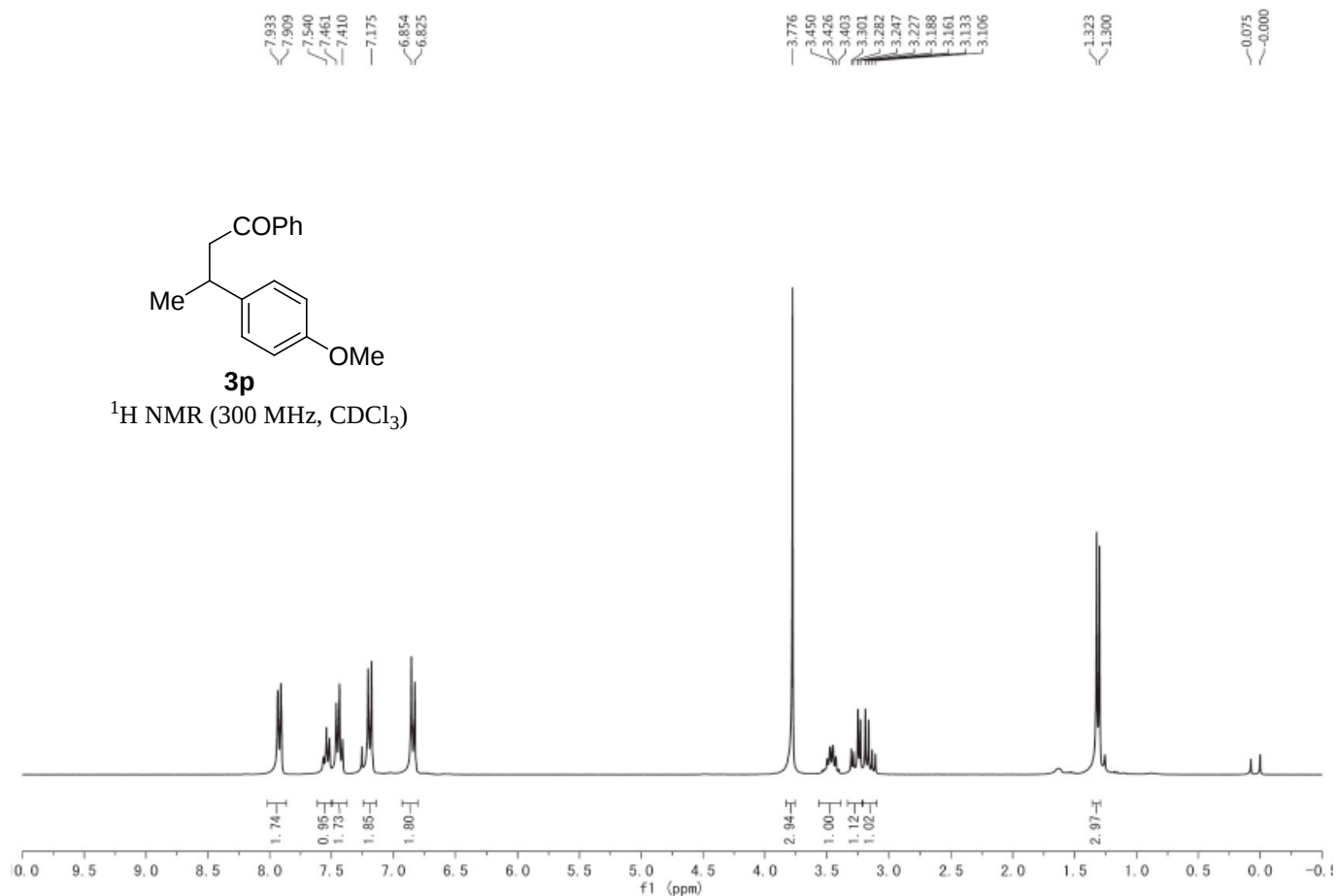
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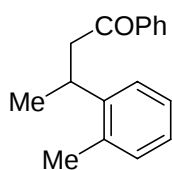


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^{13}C NMR (75MHz, CDCl_3)

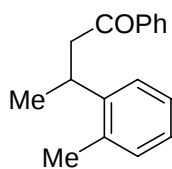
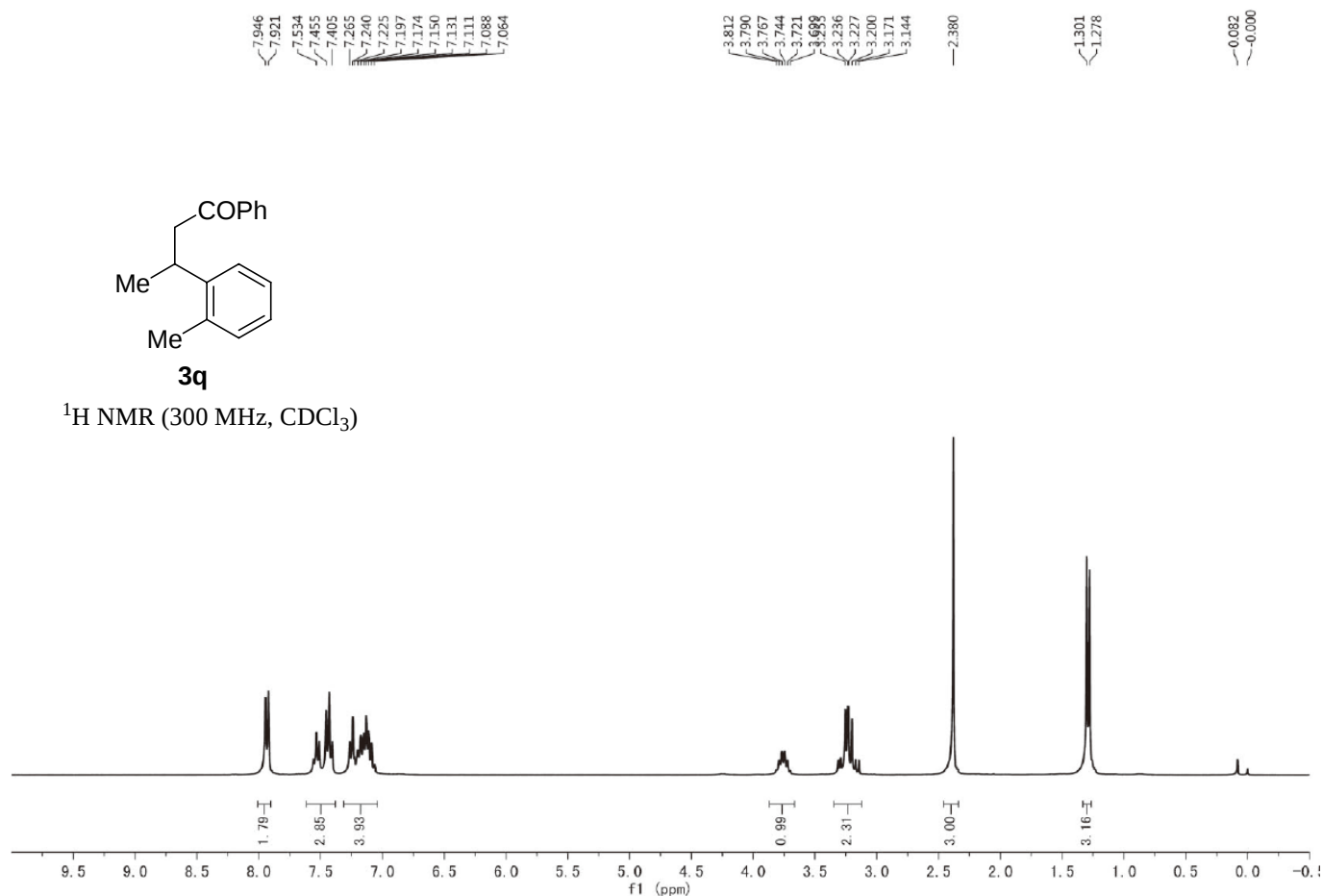






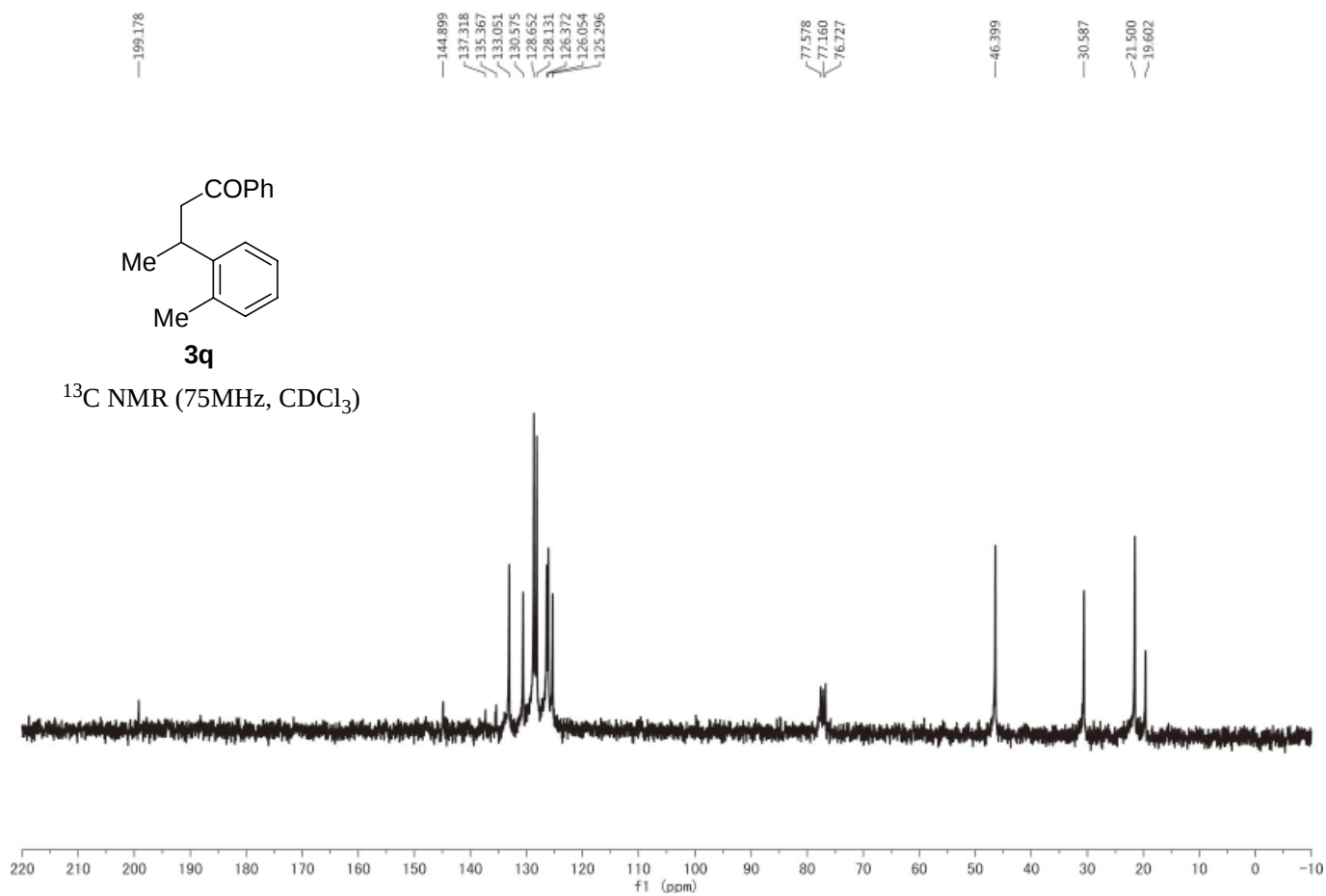
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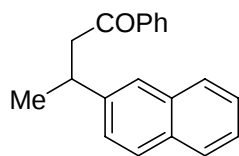
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3q

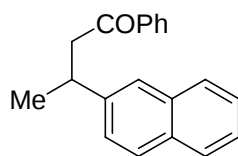
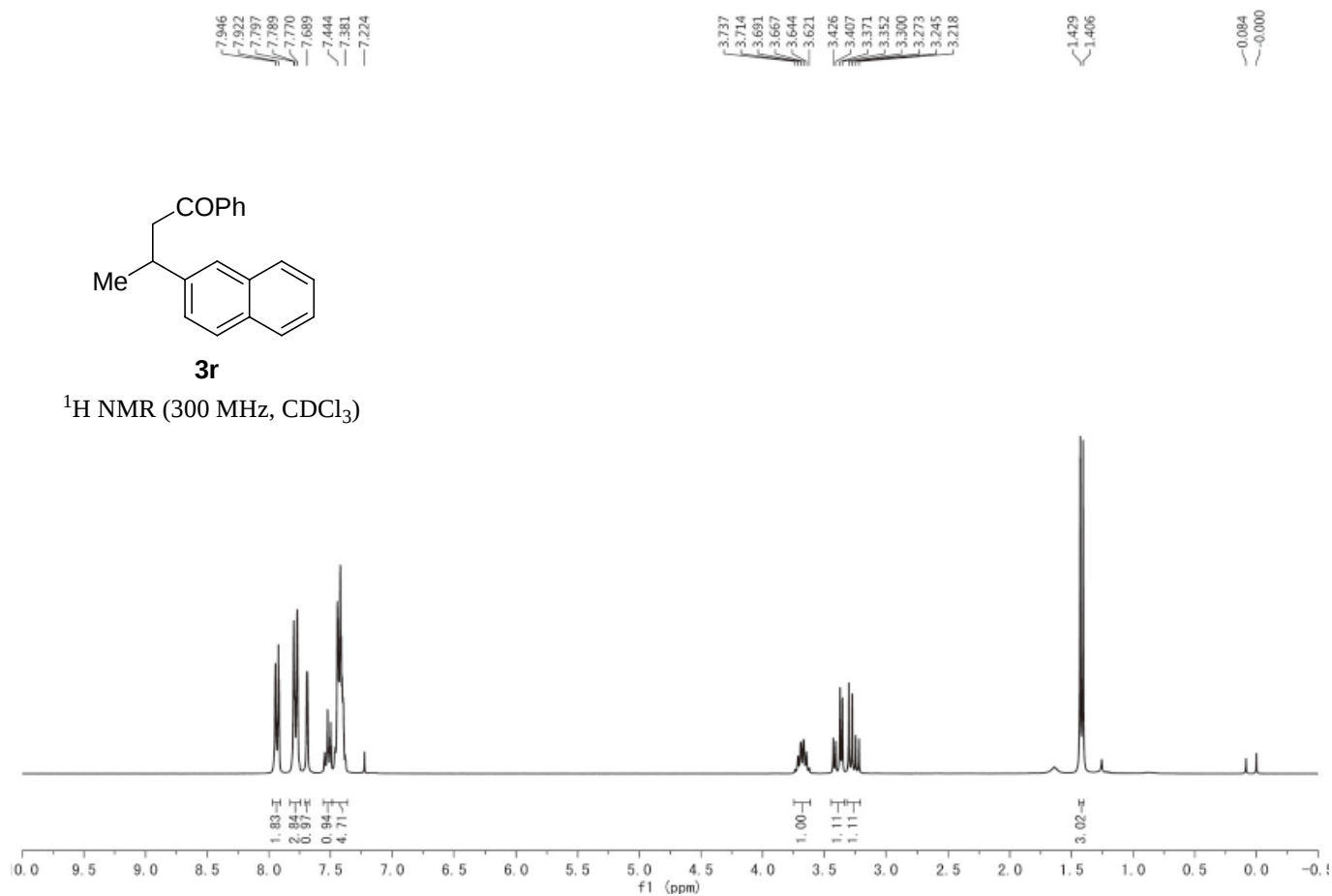
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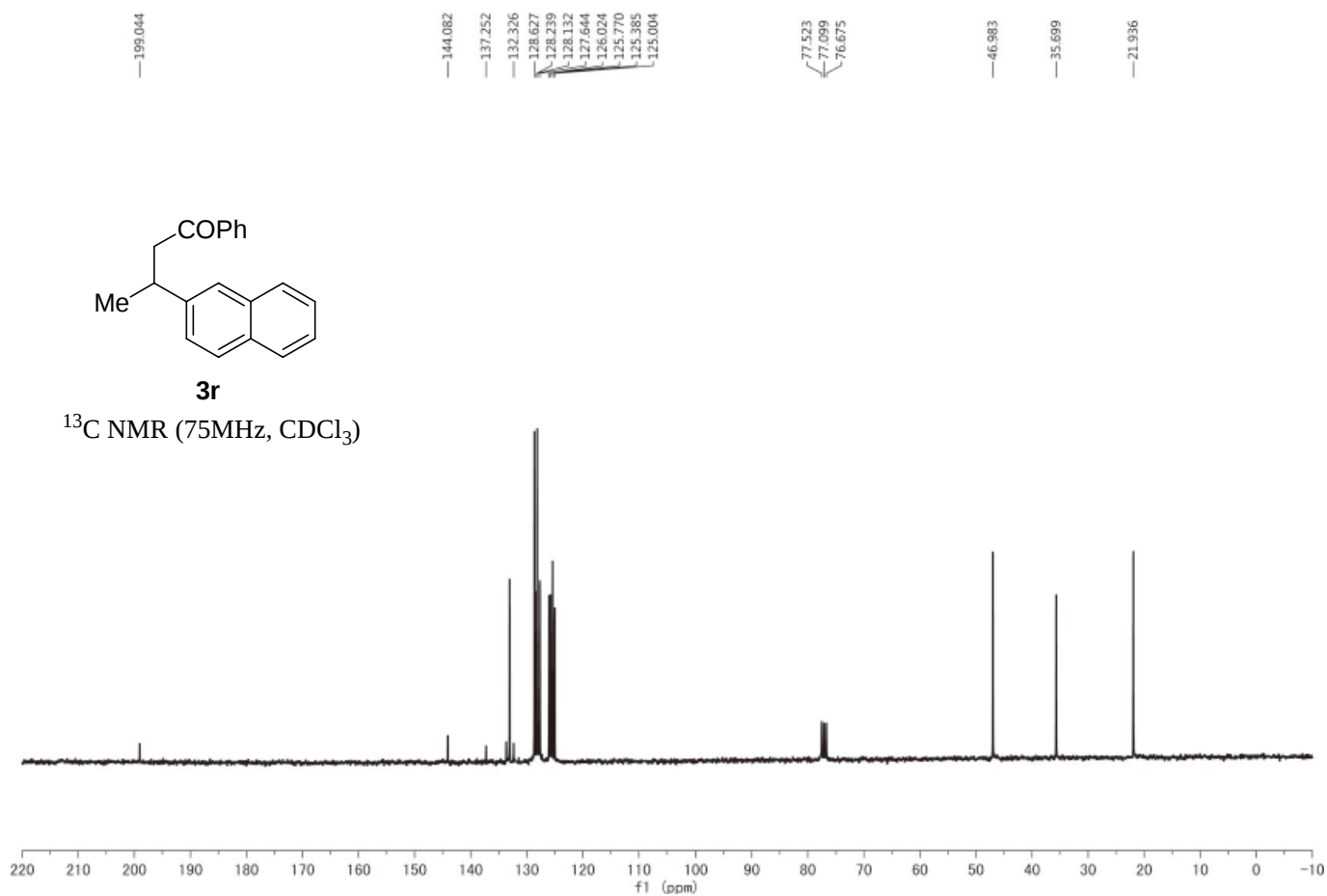
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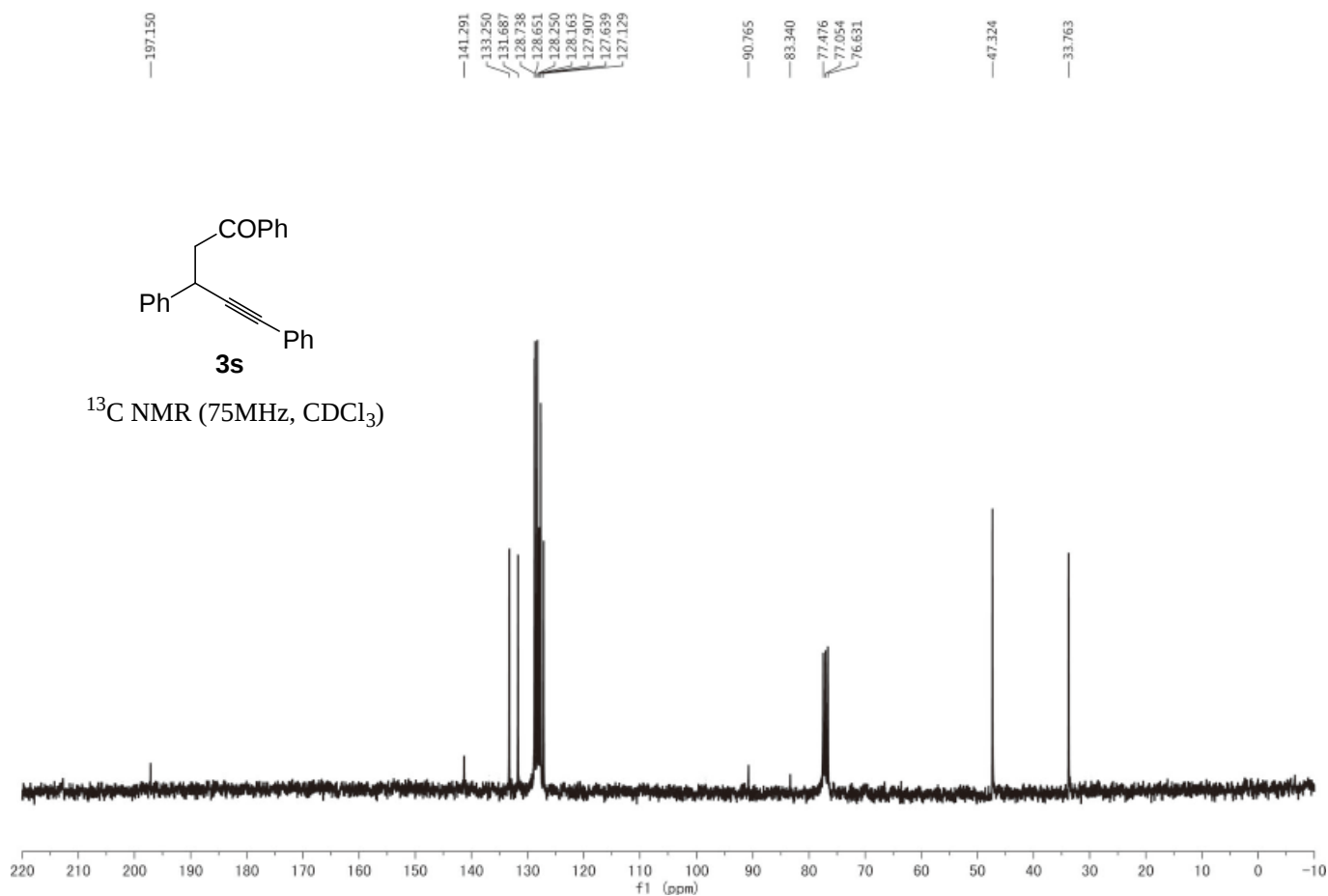
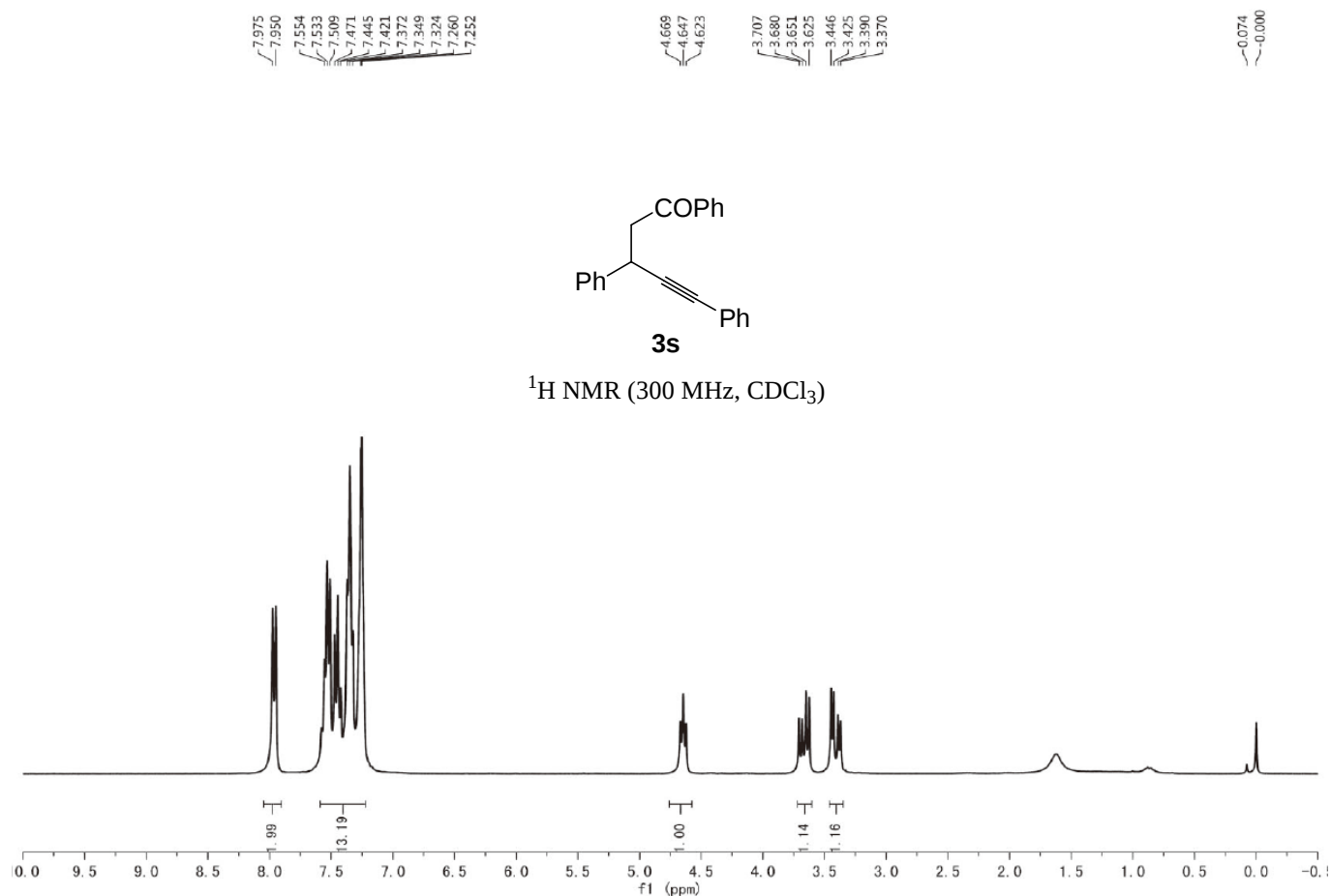
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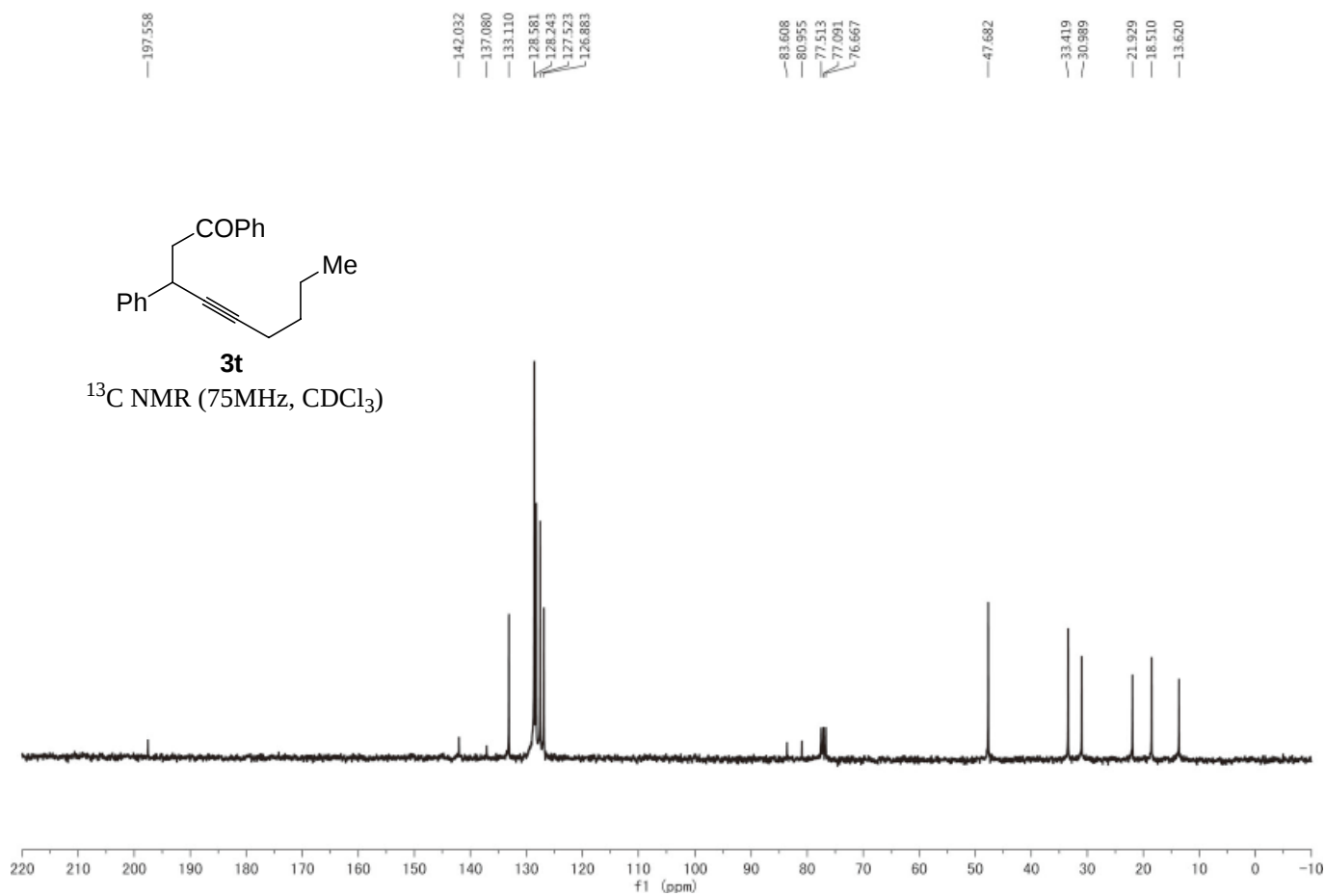
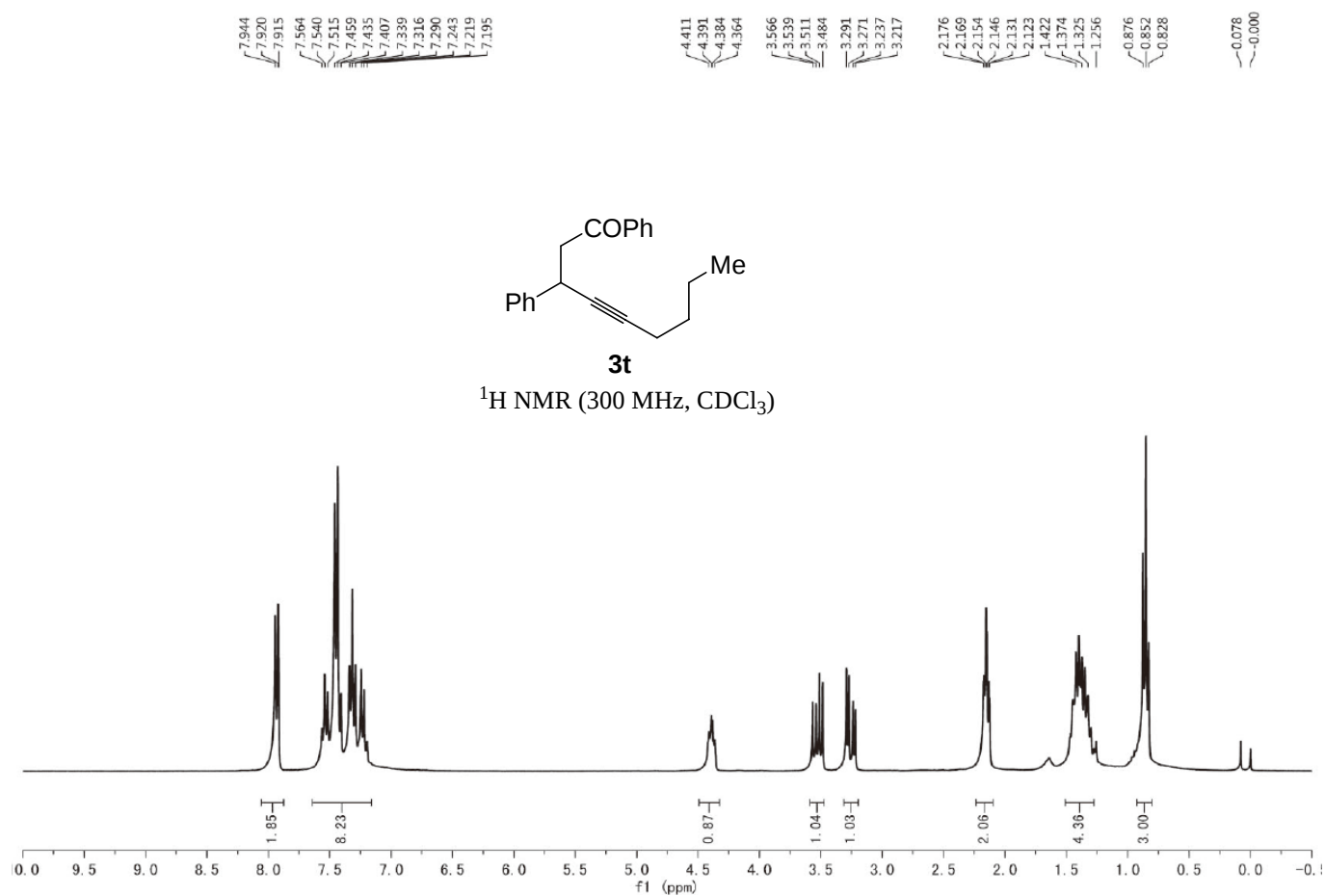


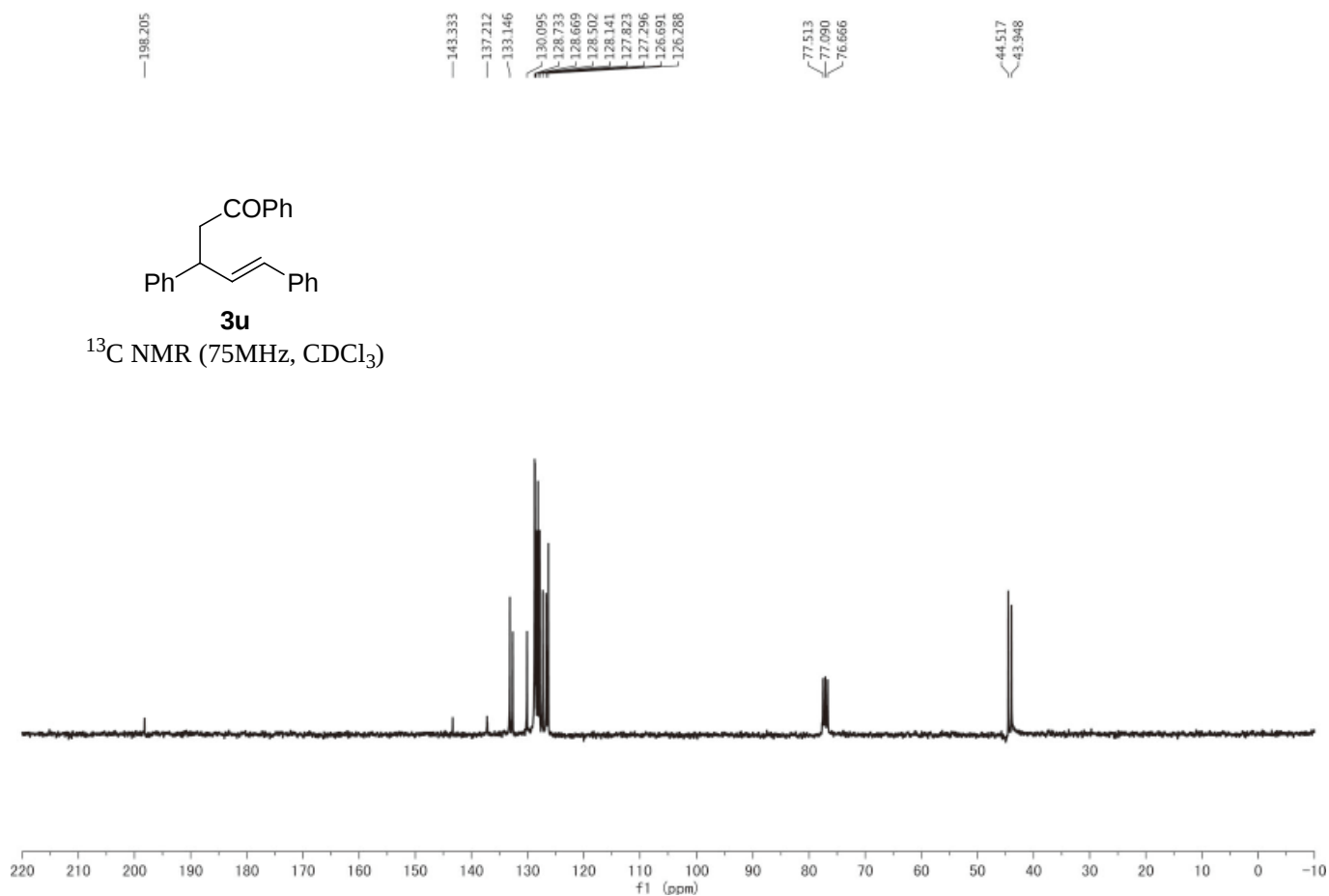
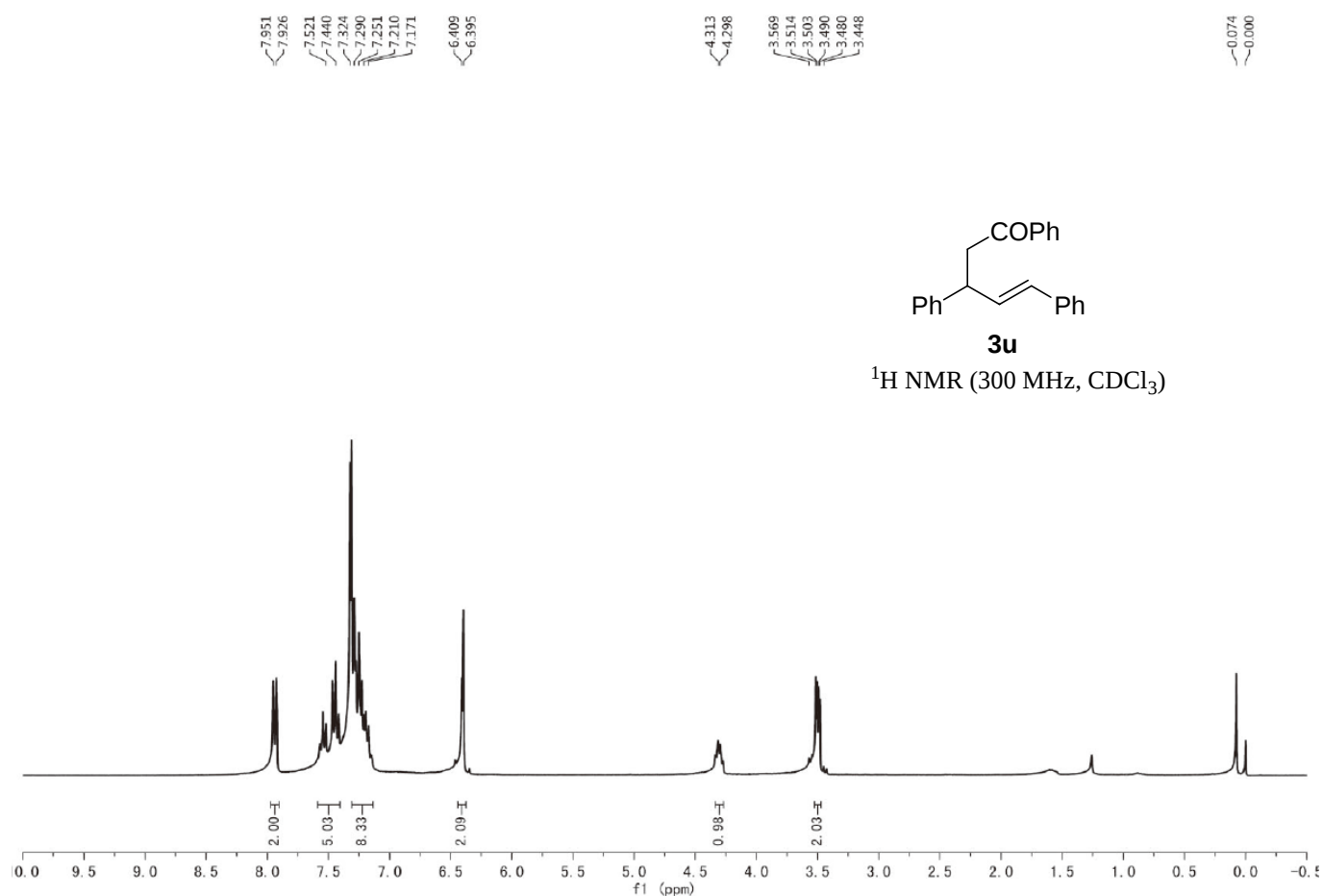
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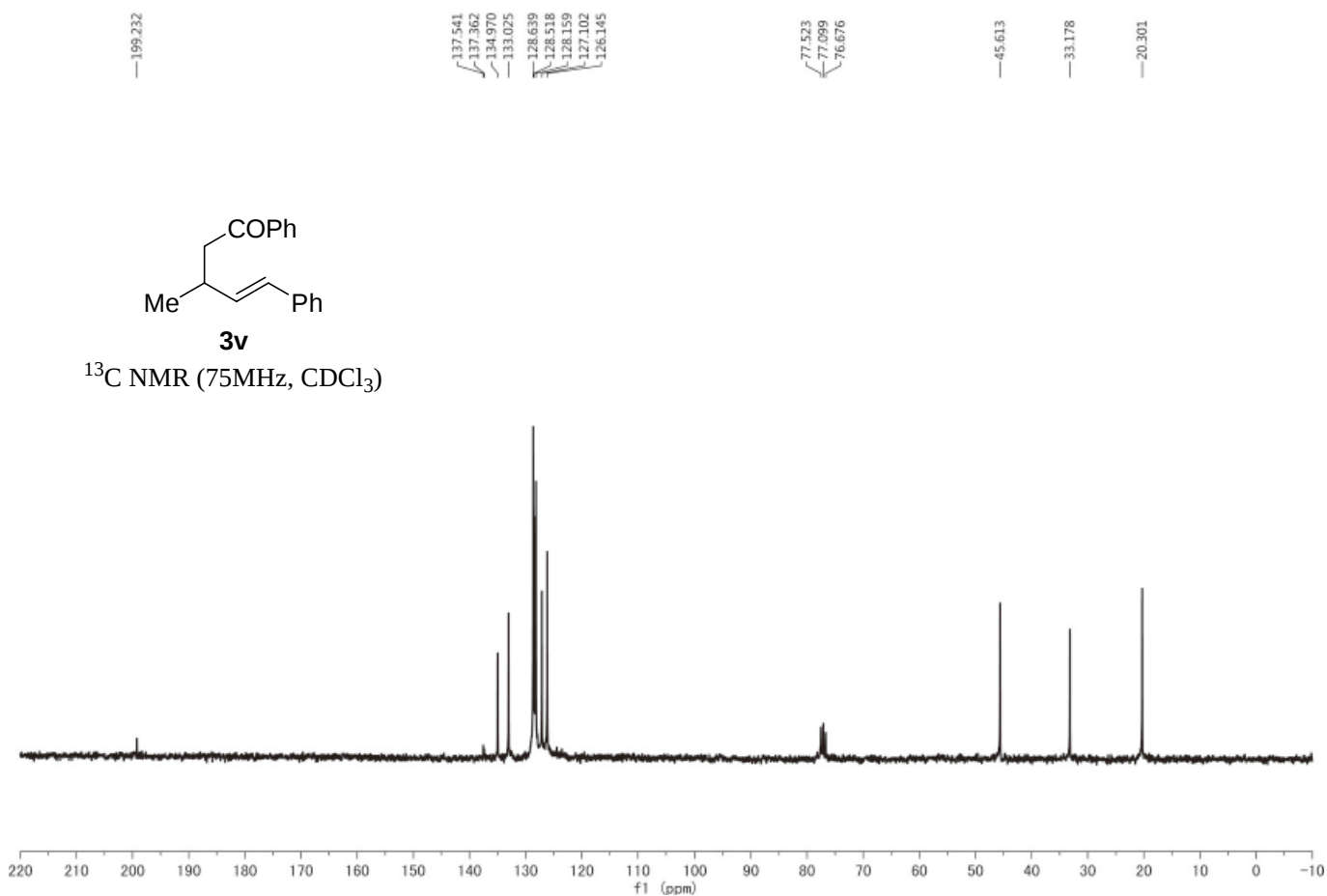
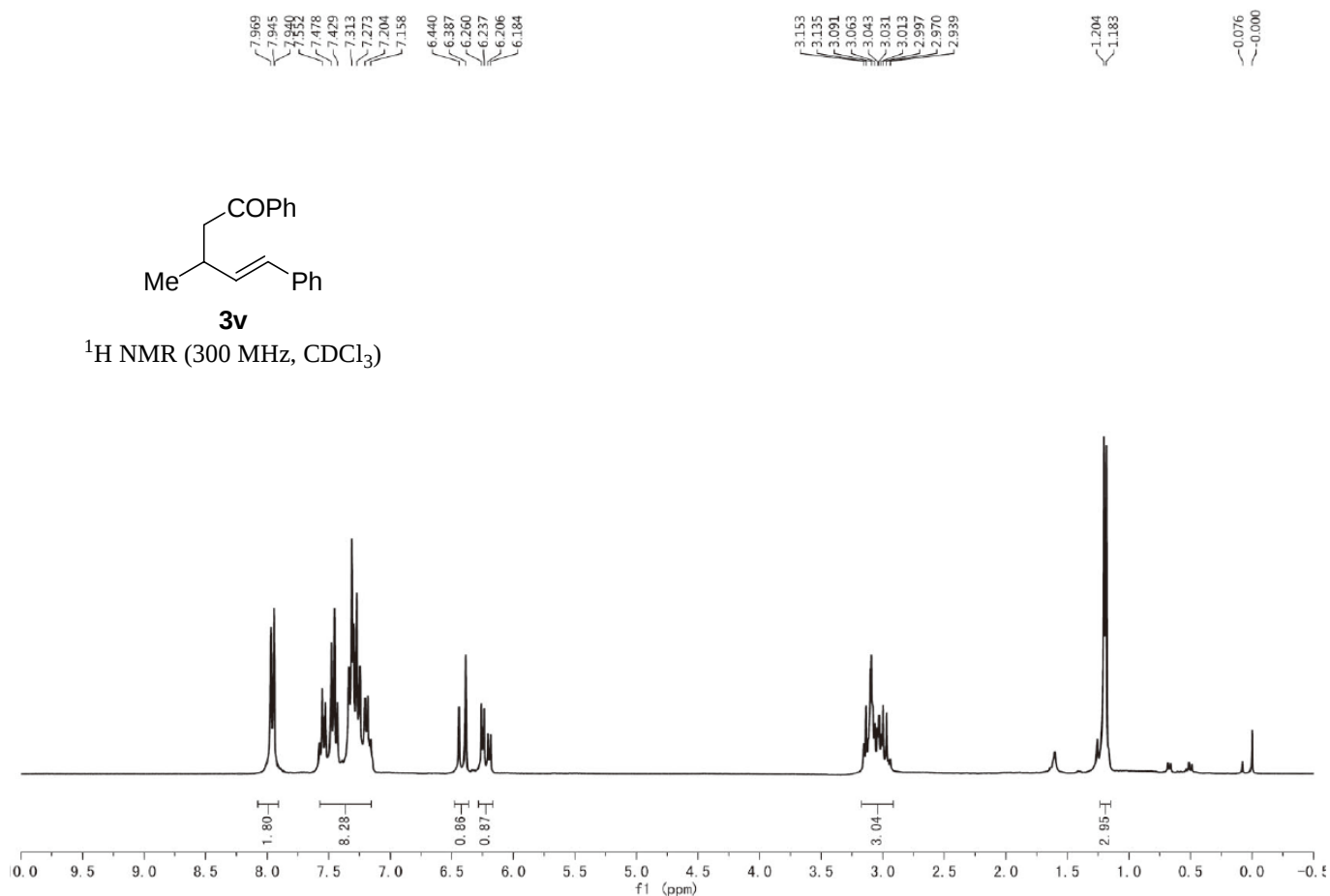
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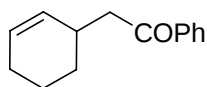






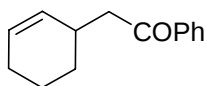
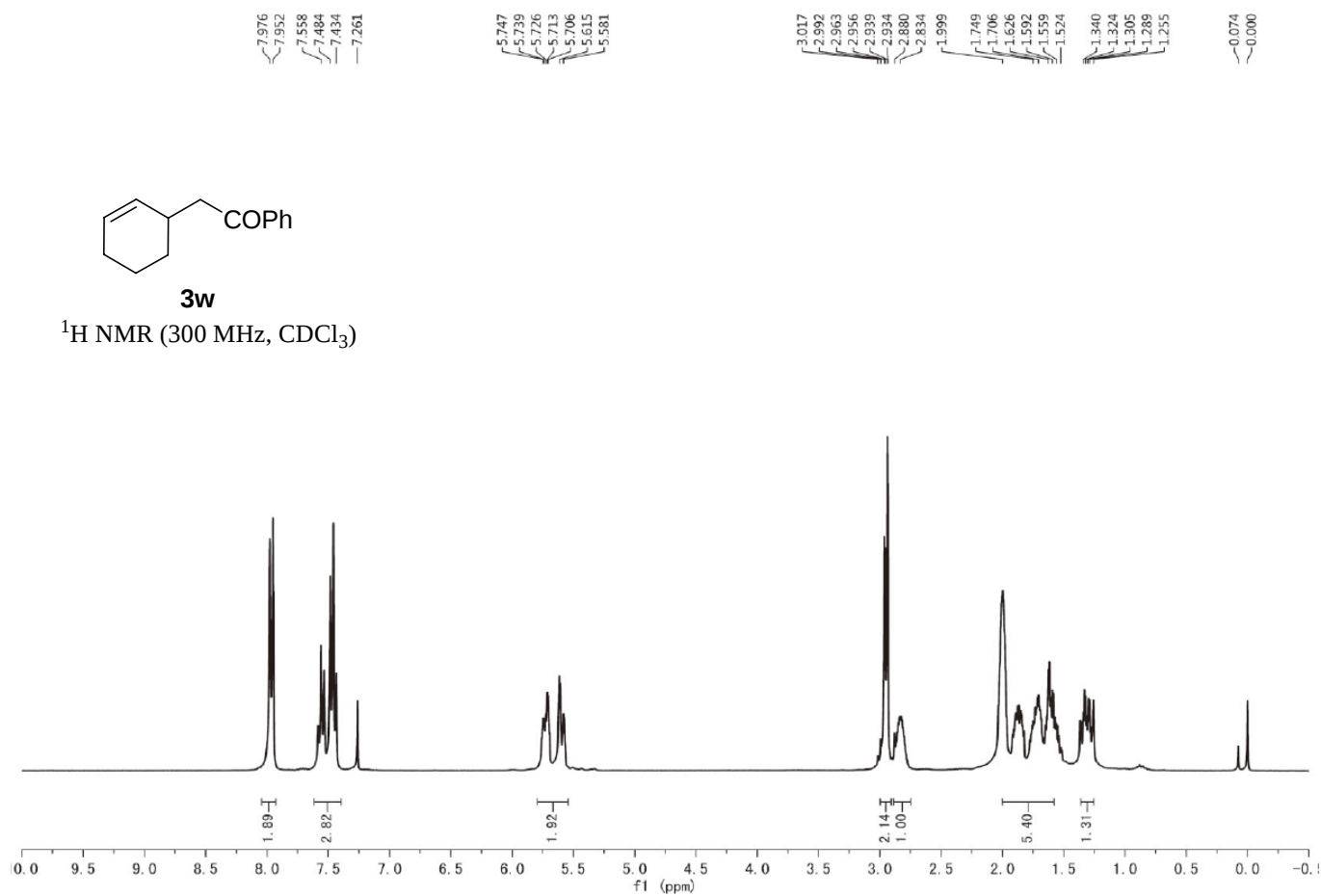






3w

^1H NMR (300 MHz, CDCl_3)



3w

^{13}C NMR (75MHz, CDCl_3)

