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N-Heterocyclic Carbene-Catalyzed Cascade Epoxide-opening and Lactonization Reaction to Synthesis of Dihydropyrone Derivatives

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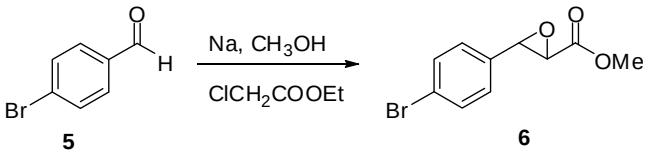
General

The ^{1}H and ^{13}C NMR data were recorded on a Bruker-400 MHz spectrometer. The chemical shifts (δ) are reported in ppm and coupling constants (J) in Hz. IR spectra were recorded on a Nicolet 670 FTIR spectrophotometer and reported in wavenumbers (cm^{-1}). High-resolution mass spectra (HRMS) were obtained on a Bruker Daltonics APEX II 47e FT-ICR mass spectrometer. Column chromatography was generally performed on silica gel (200—300 mesh) and TLC inspections were on silica gel GF254 plates.

Unless stated otherwise, all reactions were carried out in flame-dried glassware under a dry argon atmosphere. All solvents were purified and dried according to standard methods prior to use. Catalysts were synthesized according to the literature procedure.

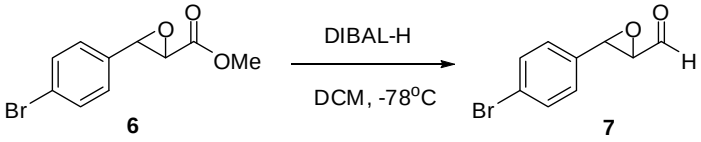
Preparation of pre-substrates:

General Procedure illustrated with 1c: for (**1a - 1j**, **1n** and **1o**)



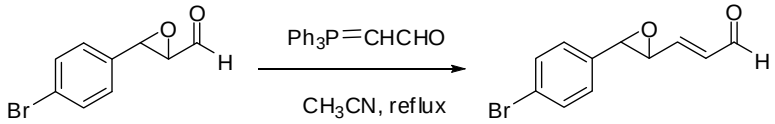
5 **6**

6: Sodium (345 mg, 15 mmol) was added over 10 min to a vigorously stirred absolute methanol (5 mL) at 0°C under argon atmosphere. After sodium was completely disappeared, aldehyde **5** (10 mmol) and ethyl chloroacetate (15 mmol) in methanol (15 mL) was added dropwise and the resulting solution was stirred vigorously for 24 h at room temperature. Then the mixture was poured into ice water and extracted with dichloromethane (3 × 20 mL). The combined organic layers were washed with brine, dried over anhydrous Na_2SO_4 and concentrated in vacuo. The residue was purified by silica gel chromatography （hexane : EtOAc = 30:1） to afford ester **6** as a white solid in 71 % yield.



6 **7**

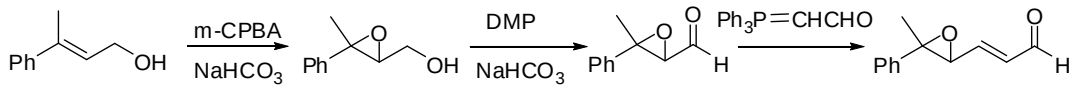
7: A solution of diisobutylaluminum hydride (DIBAL-H) in toluene (1M solution) (4.2 ml, 4.2 mmol) was added over 10 min to a cooled (-78 °C) solution of the ester **6** (889 mg, 3.46 mmol) in DCM (17 mL) under argon atmosphere. After stirring at -78 °C for 1 h, the reaction was quenched by adding MeOH (1.5 mL). The whole mixture was further stirred at -78 °C for 10 min, and then gradually rised to room temperature. Then the reaction was quenched with saturated NH_4Cl solution, filtration, the organic phase was separated and washed with brine, dried over anhydrous Na_2SO_4, filtrated, and purified by silica gel chromatography （hexane: EtOAc = 20:1） to afford **7** as a white solid in 65% yield.



7 **1c**

1c: A solution of **7** (454 mg, 2 mmol) and (triphenylphosphoranylidene) acetaldehyde (669 mg, 2.2 mmol) in CH_3CN (20 mL) was refluxed for 20 min and then concentrated. The residual oil was subjected to column chromatography (hexane: EtOAc = 25:1) to afford **1c** (253 mg, 50%) as a yellow oil.

General Procedure illustrated with 1k: for (**1k, 1l, 1m,** and **1p**)



8 **9** **10** **1k**

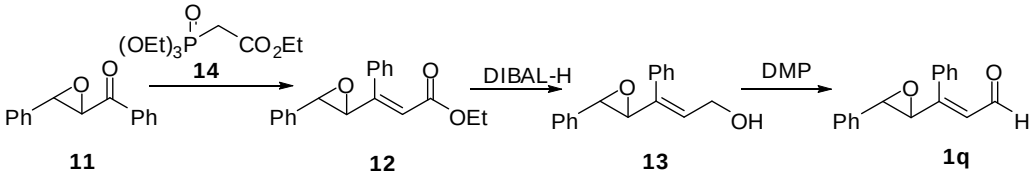
9: To a solution of alcohol **8** (376 mg, 2.5 mmol) in 5 mL DCM, $NaHCO_3$ (420 mg, 5.0 mmol) was added in portions. Then *m*-CPBA (455 mg, 95%) was added. The reaction mixture was stirred at room temperature for 3 h. The reaction was quenched by adding saturated Na_2SO_3 solution. The aqueous phase was extracted with DCM (3 × 20 mL). Then the organic phase was washed by brine, dried over anhydrous Na_2SO_4 and concentrated. Subjecting the residue to column chromatography on silica gel (hexane：EtOAc = 10:1) to afford the desired product **9** (381 mg, 93%) as a colorless oil.

10: To a solution of alcohol **9** (24 6mg, 1.5 mmol) in 5mL DCM, $NaHCO_3$ (252 mg, 3 mmol) was added. Then DMP (763 mg, 1.8 mmol) was added at 0 °C. The resulting mixture was stirred at

room temperature for 2 h. The reaction was quenched by adding saturated aqueous $Na_2S_2O_3$, and extracted by DCM (3 × 20 mL) and then washed with brine. The organic phase was dried over anhydrous Na_2SO_4 and concentrated in vacuo. Purification by chromatography on silica gel (hexane：EtOAc = 5：1) to afford aldehyde **10** (199 mg, 82%) as a colorless oil.

1k was generated in the same way as above from **10** and triphenylphosphoranylidene.

Synthesis of 1q:

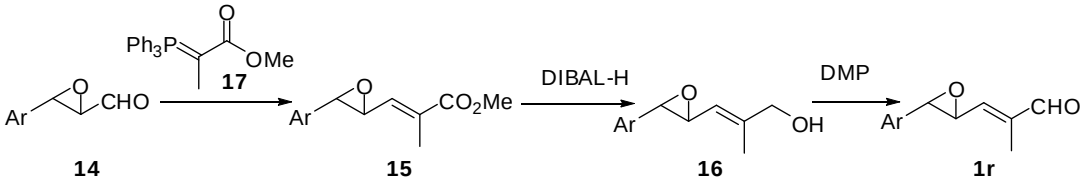


12: To a suspension of NaH (89mg, 60%, 1.0 equiv) in anhydrous THF (20mL) was added compound **14** (497mg, 1.0equiv). Then ketone **11** was added. The reaction mixture was stirred under reflux for 3 h and then cooled to room temperature. Then the reaction was quenched by adding water and extracted by EtOAc (3 x 20 mL), and washed with brine, dried over anhydrous Na_2SO_4. The organic phase was concentrated in vacuo. Purification by chromatography on silica gel (hexane: EtOAc = 20:1) to afford the desired ester **12** (360 mg, 59%) as a colorless oil.

The compound **13** was prepared in the same way above from **12** with 2.2 equiv DIBAL-H and the product was used in the next step without further purification.

1q was generated by Dess-Martin oxidation as described above.

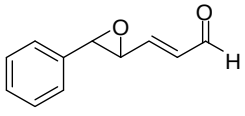
Syhthesis of 1r:



15: To a solution of **14** (456 mg, 2.5 mmol) in 15 mL DCM, the compound **17** was added. The reaction mixture was stirred at room temperature for 1 h and then concentrated. The residual oil was subjected to column chromatography (hexane: EtOAc = 20:1) to afford **15** (512 mg, 80%) as a yellow oil.

1r was generated by two steps as described above from DIBAL-H reduction and Dess-Martin oxidation.

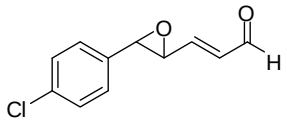
Experimental Data for pre-substrates:



1a

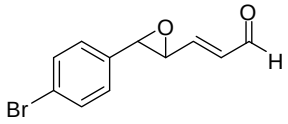
Yellow oil, 79% yield; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 9.63 (d, J = 7.6 Hz,1H), 7.36-7.40 (m, 3H), 7.30-7.32 (m, 2H), 6.69 (dd, J = 15.6, 7.6 Hz, 1H), 6.45 (dd, J = 15.6, 7.6 Hz, 1H), 3.91 (d, J = 1.6 Hz, 1H), 3.60 (dd, J = 6.8, 1.6 Hz, 1H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 192.3, 151.4, 135.6, 133.8, 128.9, 128.7, 125.5, 61.4, 60.4. **IR** (KBr) ν_{max} 2925, 1689, 1457, 1161, 1091, 880, 754,

700, 604 cm^{-1}; **Ms** m/z (%) 174 (M^+, 1), 155 (1), 127 (8), 115 (15), 105 (18), 89 (19), 77 (19), 68 (100), 44 (10).



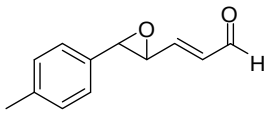
1b

White solid, m.p. 55-56 °C, 60% yield; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 9.62(d, J = 7.6 Hz, 1H), 7.35(d, J = 8.4 Hz, 2H), 7.24(d, J = 8.4 Hz, 2H), 6.67(dd, J = 15.6, 6.8 Hz, 1H), 6.45(dd, J = 15.6, 7.6 Hz, 1H), 3.88(d, J = 1.6 Hz, 1H), 3.55(dd, J = 6.8, 1.6 Hz, 1H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 192.3, 150.9, 134.7, 134.1, 133.9, 128.9, 126.8, 60.7, 60.4 cm^{-1}; **Ms** m/z (%) 208 (M^+, 1), 179 (3), 144 (8), 139 (11), 125 (7), 116 (7), 115 (10), 111 (8), 89 (22), 77 (5), 68 (100), 44(6).



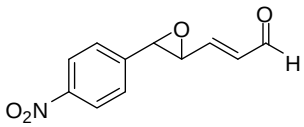
1c

White solid, m.p. 76-78 °C, 50% yield; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 9.61 (d, J = 7.6 Hz, 1H), 7.50 (dd, J = 9.2, 1.6 Hz, 2H), 7.18 (dd, J = 9.2, 1.6 Hz, 2H), 6.66 (dd, J = 15.6, 6.8 Hz, 1H), 6.43 (dd, J = 15.6, 7.6 Hz, 1H), 3.86 (d, J = 1.6 Hz, 1H), 3.55 (dd, J = 6.8, 1.2 Hz, 1H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 192.2, 150.8, 134.7, 133.9, 131.8, 127.1,122.8, 60.8, 60.3; **IR** (KBr) ν_{max} 2824, 1690, 1489, 1087, 973, 812, 604 cm^{-1}; **Ms** m/z (%) 252 (M^+, 1), 250 (1), 223 (2), 221 (2), 185 (8), 183 (9), 155 (6), 153 (6), 144 (10), 116 (12), 89 (20), 77 (6), 68 (100), 40 (26).



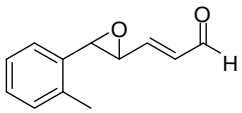
1d

Yellow oil, 67% yield; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 9.61 (d, J = 7.6 Hz, 1H), 7.20(s, 4H), 6.68 (dd, J = 15.6, 6.8 Hz, 1H), 6.43 (dd, J = 15.6, 7.6 Hz, 1H), 3.86(d, J = 2.0 Hz, 1H), 3.58 (dd, J = 6.8, 1.6 Hz, 1H), 2.37 (s, 3H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 192.4, 151.6, 138.7, 133.5, 132.5,129.3, 125.4, 61.4, 60.3, 21.2; **IR** (KBr) ν_{max} 2924, 1690, 1435, 1090, 804, 602 cm^{-1}; **Ms** m/z (%) 188 (M^+, 1), 159 (9), 144 (6), 131 (10), 119 (52), 105 (24), 103 (16), 91 (27), 77 (13), 44 (2).



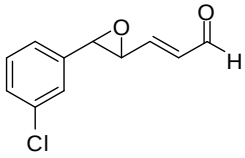
1e

Yellow solid, m.p. 134-136 °C, 70% yield; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 9.64 (d, J = 7.6 Hz, 1H), 8.25 (d, J = 8.8 Hz, 1H), 7.49 (d, J = 8.4 Hz), 6.68 (dd, J = 16.0, 6.4 Hz, 1H), 6.48 (dd, J = 16.0, 7.6 Hz, 1H), 4.02 (s, 1H), 3.60 (d, J = 6.0 Hz, 1H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 192.0, 149.7, 148.2, 142.9, 134.4, 126.4, 124.0, 60.7, 60.2; **IR** (KBr) ν_{max} 2922, 1689, 1520, 1347, 1090, 976, 855, 696 cm^{-1}; **Ms** m/z (%) 219 (M^+, 1), 190 (3), 165 (2), 149 (6), 115 (12), 99 (5), 85 (11), 77 (9), 71 (14), 68 (100), 57 (14), 44 (46).



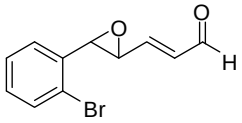
1f

Light yellow oil, 78% yield; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 9.63 (d, J = 8.0 Hz, 1H), 7.22-7.26 (m, 3H), 7.17-7.19 (m, 1H), 6.72 (dd, J = 16.0, 6.8 Hz, 1H), 6.46 (dd, J = 16.0, 7.6 Hz, 1H), 4.03 (d, J = 2.0 Hz, 1H), 3.48 (dd, J = 6.8, 1.2 Hz, 1H), 2.38 (s, 3H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 192.4, 151.6, 135.9, 134.0, 133.8, 128.3, 126.3, 124.0, 59.5, 18.7; **IR** (KBr) ν_{max} 2924, 1690, 1461, 1087, 888, 753 cm^{-1}; **Ms** m/z (%) 188 (M^+, 1), 159 (7), 141 (7), 131 (10), 119 (53), 105 (15), 103 (20), 91 (40), 77 (18), 68 (100), 44 (8).



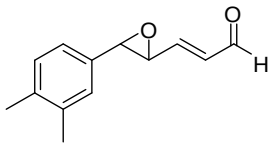
1g

Yellow oil, 78% yield; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 9.61 (d, J = 8.0 Hz, 1H), 7.27-7.32 (m,3H), 7.19-7.21 (m, 1H), 6.66 (dd, J = 15.6, 6.8 Hz, 1H), 6.44 (dd, J = 15.6, 7.6 Hz, 1H), 3.87 (d, J = 1.6 Hz, 1H), 3.56 (dd, J = 6.8, 1.6 Hz, 1H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 192.2, 150.7, 137.7, 134.8, 134.0, 130.0, 128.9 125.5, 123.8, 60.5, 60.4; **IR** (KBr) ν_{max} 2924, 2828, 1690, 1480, 1160, 1087, 974, 870, 786, 692 cm^{-1}; **Ms** m/z (%) 208 (M^+, 1), 179 (2), 144 (5), 139 (10), 127 (3), 125 (5), 115 (16), 111 (8), 89 (17), 77 (6), 68 (100), 44 (8).



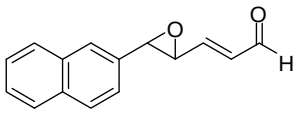
1h

Colorless oil, 51% yield; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 9.64 (d, J = 7.6 Hz, 1H), 7.57 (d, J = 0.8 Hz, 1H), 7.32-7.55 (m, 1H), 7.27-7.29 (m, 1H), 7.19-7.24 (m, 1H), 6.73 (dd, J = 15.6, 6.4 Hz, 1H), 6.47 K (dd, J = 15.6, 7.2 Hz, 1H), 4.17 (d, J = 1.6 Hz, 1H), 3.46 (dd, J = 6.8, 1.2 Hz, 1H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 192.3, 150.8, 135.3, 134.1, 132.4, 129.9, 127.8, 126.1, 122.5, 61.1, 59.7; **IR** (KBr) ν_{max} 2924, 1691, 1473, 1090, 974, 756, 602 cm^{-1}; **Ms** m/z (%) 254 (M^+, 1), 252 (M^+, 1), 185 (8), 183 (11), 157 (4), 155 (3), 144 (8), 116 (9), 89 (19), 68 (100), 44 (21).



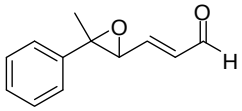
1i

Colorless oil, 54% yield; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 9.62 (d, J = 7.6 Hz, 1H), 7.15 (d, J = 7.6 Hz,1H), 7.04-7.07 (m,2H), 6.68 (dd, J = 15.6, 6.8 Hz, 1H), 6.44 (dd, J = 15.6, 7.6 Hz, 1H), 3.85 (d, J = 1.6 Hz, 1H), 3.59 (dd, J = 6.8, 1.2 Hz, 1H), 2.28 (s, 6H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 192.4, 151.8, 137.5, 137.1, 133.6, 132.9, 129.9, 126.6, 123.1, 61.5, 60.4, 19.7, 19.5; **IR** (KBr) ν_{max} 2923, 1690, 1453, 1126, 974, 810 cm^{-1}; **Ms** m/z (%) 202 (2), 173 (10), 158 (11), 145 (14), 134 (52), 133(100), 119 (30), 105 (30), 91 (21), 77 (14), 68 (37).



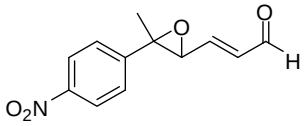
1j

White solid, m.p. 120-122 °C, 83% yield; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 9.65 (d, J = 7.6 Hz, 1H), 7.83-7.89 (m, 4H), 7.50-7.55 (m, 2H), 7.35-7.37 (m, 1H), 6.73 (dd, J = 15.6, 6.8 Hz, 1H), 6.48 (dd, J = 15.6, 7.6 Hz, 1H), 4.07 (d, J = 1.2 Hz, 1H), 3.70 (dd, J = 6.8, 1.2 Hz, 1H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 192.4, 151.4, 133.8, 133.5,133.0,132.9, 128.7, 127.8, 126.6, 126.5, 125.4, 122.4, 61.7, 60.5; **IR** (KBr) ν_{max} 2923, 1689, 1127, 1088, 972, 861, 814, 750 cm^{-1}; **Ms** m/z (%) 254 (M^+, 3), 195 (16), 167 (19), 156 (100), 139 (34), 127 (34), 115 (8), 89 (5), 77 (4), 68 (10).



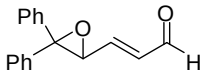
1k

A light yellow oil, 99% yield; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 9.63 (d, J = 8.0 Hz, 1H), 7.28-7.35 (m, 5H), 6.78 (dd, J = 15.6, 6.4 Hz, 1H), 6.41 (dd, J = 15.6, 7.6 Hz, 1H), 3.48 (d, J = 6.4 Hz, 1H), 1.67 (s, 3H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 192.2, 149.3, 139.5, 135.4, 133.8, 128.7, 127.7, 126.5, 63.5, 63.5, 17.5; **IR** (KBr) ν_{max} 2927, 1692, 1450, 1116, 974, 873 cm^{-1}; **Ms** m/z (%) 188 (M^+, 1), 159 (9), 155 (12), 149 (20), 119 (32), 105 (36), 95 (39), 81 (62), 77 (24), 68 (100), 57 (97), 44 (57).



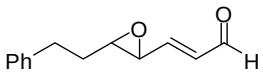
1l

Yellow solid, m.p. 98-100 °C, 79% yield; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 9.65 (d, J = 7.6 Hz, 1H, 8.22 (d, J = 9.2 Hz, 1H), 7.55 (d, J = 8.8 Hz, 1H), 6.79 (dd, J = 15.6, 6.4 Hz, 1H), 6.45 (dd, J = 15.6, 7.6 Hz, 1H), 3.53 (d, J = 6. 4Hz, 1H), 1.75 (s, 3H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 192.0, 148.3, 148.1, 147.5,135.8, 126.1, 123.8, 64.5, 63.3, 17.3; **IR** (KBr) ν_{max} 2926, 1690, 1602, 1520, 1348, 1098, 977, 858, 698 cm^{-1}; **Ms** m/z (%) 233 (M^+, 1), 204 (1), 165 (2), 150 (4), 129 (3), 103 (7), 77 (20), 68 (100), 43 (7).



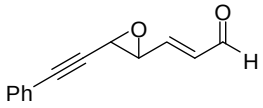
1m

Colorless oil, 95% yield; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 9.39 (d, J = 7.6 Hz, 1H), 7.39-7.43 (m, 5H), 7.34-7.36 (m, 5H), 6.39 (dd, J = 16.0, 7.6 Hz, 1H), 6.26 (dd, J = 16.0, 7.6 Hz, 1H), 4.00 (d, J = 7.6 Hz, 1H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 192.3, 150.6, 139.4, 135.7, 135.4, 128.7, 128.5, 128.5, 128.4, 128.3, 128.2, 128.1, 126.5, 68.9, 64.8; **IR** (KBr) ν_{max} 3060, 2924, 1690, 1449, 1146, 1086, 1145, 1086, 975, 758, 700 cm^{-1}; **Ms** m/z (%) 250 (M^+, 1), 221 (4), 182 (54), 165 (100), 115 (10), 105 (70), 77 (18), 68 (23), 44 (10).



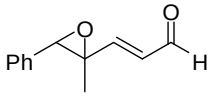
1n

Colorless oil, 83% yield; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 9.53 (d, J = 7.6 Hz, 1H), 7.18-7.32 (m, 5H), 6.46 (dd, J = 15.6, 7.2 Hz, 1H), 6.28 (dd, J = 15.6, 8.0 Hz, 1H), 3.22 (d, J = 2.0 Hz, 1H), 2.97-3.21(m, 1H), 2.72-2.96(m, 2H), 1.88-2.06(m, 2H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 192.4, 152.6, 140.6, 133.6, 128.6, 128.3, 126.3, 61.1, 56.4, 33.6, 32.0; **IR** (KBr) ν_{max} 3432 2924 1689 1495 1452 1105 974 881 750 700 603 cm^{-1}; **Ms** m/z (%) 202 (M^+, 1), 173 (10), 149 (1), 133 (6), 118 (26), 117 (38), 105 (22), 104 (34), 91 (100), 77 (9), 68 (20), 44 (6).



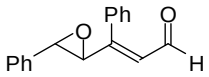
1o

Light yellow oil, 89% yield; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 9.60 (d, J = 7.2 Hz, 1H), 7.46-7.49 (m, 2H), 7.31-7.43 (m, 3H), 6.57 (dd, J = 15.6, 6.4 Hz, 1H), 6.47 (dd, J = 15.6, 7.2 Hz, 1H), 3.86 (dd, J = 6.4, 2.0 Hz, 1H), 3.61 (d, J = 2.0 Hz, 1H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 192.1, 149.9, 134.6, 131.9, 129.2, 128.4, 121.4, 85.2, 83.7, 76.7, 58.2, 48.7; **IR** (KBr) ν_{max} 3059, 2827, 2225, 1691, 1491, 1327, 1092, 974, 871, 759, 692 cm^{-1}; **Ms** m/z (%) 198 (6), 169 (10), 141 (16), 130 (12), 129 (12), 114 (100), 102 (21), 88 (21), 77 (6), 68 (82), 44 (5).



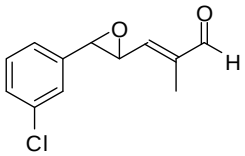
1p

Colorless oil, 76% yield; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 9.63 (d, J = 7.6 Hz, 1H), 7.31-7.41 (m, 5H), 6.75 (d, J = 16.0 Hz, 1H), 6.38 (dd, J = 16.0, 8.0 Hz, 1H), 4.08 (s, 1H), 1.28 (s, 3H);
^{13}C NMR (100 MHz, $CDCl_3$) δ 192.8, 157.4, 134.2, 132.2, 128.3, 128.2, 126.5, 66.1, 61.2, 14.2; **IR** (KBr) ν_{max} 3367 2927 1690 1451 1387 1264 1122 976 848 742 701 cm^{-1}; **Ms** m/z (%) 188 (M^+, 1), 159 (10), 131 (5), 115 (9), 105 (17), 91 (11), 89 (16), 82 (100), 77 (24), 53 (17), 43 (16), 39 (13).



1q

Colorless oil, 74% yield; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 10.5 (d, J = 7.6Hz, 1H), 7.53-7.55 (m, 2H), 7.39-7.46 (m, 8H), 4.12 (d, J = 2.0 Hz, 1H), 3.92 (d, J = 2.0 Hz, 1H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 192.0, 153.8, 136.2, 135.5, 130.3, 129.0, 128.9, 128.9, 128.8, 127.1, 125.6, 61.4, 60.2; **IR** (KBr) ν_{max} 3060, 1666, 1452, 1135, 874, 751, 696 cm^{-1}; **Ms** m/z (%) 250 (M^+, 1), 221 (12), 160 (52), 144 (57), 132 (29), 115 (44), 105 (52), 103 (100), 89 (14), 77 (45), 44 (44).

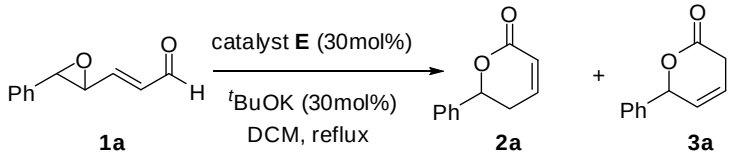


1r

Yellow oil, 67% yield; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 9.46 (s, 1H), 7.32-7.34 (m, 3H), 7.22-7.24 (m, 1H), 6.16 (dd, J = 8.4, 1.2 Hz, 1H), 3.96 (d, J = 1.6 Hz, 1H), 3.73 (dd, J = 8.4, 1.6 Hz, 1H),

1.91 (d, J = 1.2 Hz, 3H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 193.6, 147.0, 143.0, 138.1, 134.9, 130.0, 128.9, 125.5, 123.9, 59.5, 58.9, 9.7; **IR** (KBr) ν_{max} 3065, 1690, 1440, 1315, 1209, 1084, 1009, 878, 787, 689 cm^{-1}; **Ms** m/z (%) 222 (M^+, 1), 193 (4), 165 (2), 139 (10), 111 (9), 89 (10), 82 (100), 81 (36), 77 (6), 54 (15), 44 (17).

General Procedure for the Synthesis of Dihydropyrones illustrated 2a and 3a:

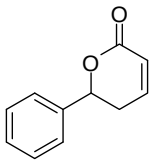


1a **2a** **3a**

A round-bottomed flask was charged with ^{t}BuOK (17 mg, 0.15 mmol) thiazolium salt **E** (57 mg, 0.15 mmol) in 25 mL DCM under argon atmosphere. The resulting mixture was stirred at room temperature for 15 min, and then substrate **1a** (86 mg, 0.5 mmol) was added. The reaction mixture was stirred under reflux for 24 h. The solvent was removed, and then the residue was purified by silica gel chromatography (hexane: EtOAc = 10:1) to afford **2a** and **3a** in overall 89% yield.

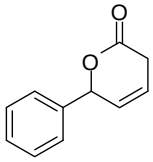
Syntheses of other dihydropyrones were following this general procedure as above.

Experimental Data for products:



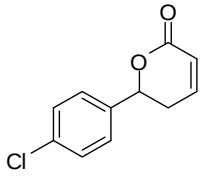
2a

Yellow solid, m.p. 54-56 °C; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.33-7.42 (m, 5H), 6.95-7.00 (m, 1H), 6.14 (d, J = 8.8 Hz, 1H), 5.46 (dd, J = 10.8, 5.2 Hz, 1H), 2.59-2.71 (m, 2H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 164.0, 144.9, 138.4, 128.6, 128.5, 126.0, 121.6, 79.2, 31.6; **IR** (KBr) ν_{max} 3423, 2920, 1721, 1456, 1379, 1244, 1059, 1023, 908, 814, 757, 698 cm^{-1}; **HRMS** (ESIMS) calcd for $C_{11}H_{11}O_2^+$ $[M + H]^+$ 175.0754, Found 175.0759.



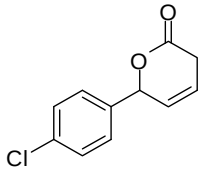
3a

Yellow oil; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.35-7.42 (m, 5H), 6.00-6.06 (m, 3H), 3.81 (s, 2H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 168.3, 138.2, 128.9, 126.9, 126.2, 121.8m 81.3, 29.9; **IR** (KBr) ν max 3371, 2921, 1733, 1456, 1368, 1217, 1064, 748, 696 cm^{-1}; **HRMS** (ESIMS) calcd for $C_{11}H_{11}O_2^+$ $[M + H]^+$ 175.0754, Found 175.0756.



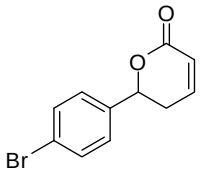
2b

White solid, m.p. 74-75 °C; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.34-7.40 (m, 4H), 6.94-6.99 (m,1 H), 6.14 (dt, J = 10.0, 1.6 Hz, 1H), 5.43 (t, J = 8.0 Hz, 1H), 2.59-2.63 (m, 2H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 163.7, 144.7, 137.0, 134.4, 128.8, 127.4,121.7, 78.4, 31.6; **IR** (KBr) νmax 3429, 2920, 1723, 1493, 1381, 1244, 1063, 1030, 1014, 914, 815 cm^{-1}; **HRMS** (ESIMS) calcd for $C_{11}H_{10}ClO_2^+$ $[M + H]^+$ 209.0364, found 209.0367.



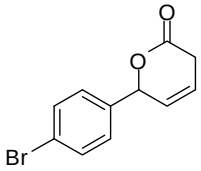
3b

Yellow solid, m.p. 64-66 °C ; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.36 (d, J = 8.0 Hz, 2H), 7.29 (d, J = 8.0 Hz, 2H), 6.00-6.02 (m, 2H), 5.95-5.97 (m, 1H), 3.16-3.17 (m. 1H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 167.9, 136.7, 134.8, 129.0, 128.2, 125.7, 122.3, 80.4, 29.8; **IR** (KBr) ν_{max} 3394, 2922, 1738, 1491, 1220, 1072, 817, 657 cm^{-1}; **HRMS** (ESIMS) calcd for $C_{11}H_{10}ClO_2^+$ $[M + H]^+$ 209.0364, found 209.0369.



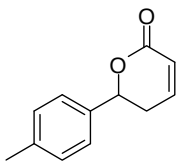
2c

White solid, m.p. 88-90 °C; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.52 (d, J = 8.4 Hz, 2H), 7.29 (d, J = 8.4 Hz, 2H), 6.95-6.99 (m, 1H), 6.14 (dd, J = 9.6, 0.8 Hz, 1H), 5.42 (t, J = 8.0 Hz, 1H), 2.59-2.62 (m, 2H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 163.7, 144.7, 137.5, 131.8, 127.7, 122.6, 121.7, 78.5, 31.6; **IR** (KBr) ν_{max} 3424, 2919, 1726, 1491, 1381, 1245, 1064, 1010, 913, 814 cm^{-1}; **HRMS** (ESIMS) calcd for $C_{11}H_{10}BrO_2^+$ 252.9859, found 252.9854.



3c

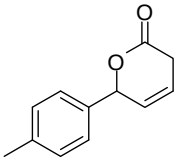
White solid, m.p. 91-92°C; **^{1}H NMR** (400 MHz, CDCl3) δ 7.52 (d, J = 8.4Hz, 2H), 7.22 (d, J = 8.4Hz, 2H), 5.94-6.02 (m, 3H), 3.17-3.18 (t, J = 2.4Hz, 2H); **^{13}C NMR** (100 MHz, CDCl3) δ 167.9, 137.2, 132.0, 131.8, 128.5, 127.7, 125.6, 122.9, 122.3, 80.4, 29.8; **IR** (KBr) ν_{max} 3452, 2921, 1737, 1488, 1364, 1220, 1070, 841, 815 cm^{-1}; **HRMS** (ESIMS) calcd for $C_{11}H_{10}BrO_2^+$ 252.9859, found 252.9863.



2d

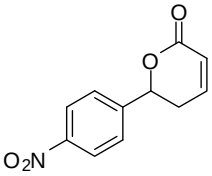
Colorless oil; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.31 (d, J = 8 Hz, 2H), 7.21 (d, J = 8 Hz, 2H),

6.95-6.99 (m, 1H), 6.13-6.16 (m, 1H), 5.43 (dd, *J* = 11.6, 4.8 Hz, 1H), 2.57-2.67 (m, 1H), 2.37 (s, 3H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 164.2, 144.9, 138.4, 135.5, 129.3, 126.0, 121.7, 79.2, 31.6; **IR** (KBr) ν_{max} 3430, 2921, 1724, 1382, 1245, 1063, 1024, 913, 814 cm^{-1}; **HRMS** (ESIMS) calcd for $C_{12}H_{13}O_2^+$ $[M + H]^+$ 189.0910, found 189.0904.



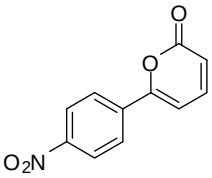
3d

Colorless oil; **^{1}H NMR** (400 MHz, CDCl3) δ 7.26 (s, 1H), 7.18-7.24 (q, *J* = 8.0Hz, 2H), 5.94-6.02 (m, 3H), 3.15-3.16 (m, 2H), 2.38 (s, 3H); **^{13}C NMR** (100 MHz, CDCl3) δ 168.4, 138.8, 135.2, 129.5, 126.9, 126.3, 121.7, 81.2, 29.9, 21.2; **IR** (KBr) ν_{max} 3389, 2921, 1735, 1218, 1066, 811 cm^{-1}; **HRMS** (ESIMS) calcd for $C_{12}H_{13}O_2^+$ $[M + H]^+$ 189.0910, found 189.0906.



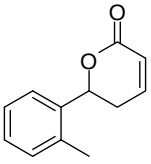
2e

White solid, m.p. 99-101°C; **^{1}H NMR** (400 MHz, CDCl3) δ 8.27 (d, *J* = 8.8Hz, 2H), 7.62 (d, *J* = 8.8Hz, 2H), 6.99-7.03 (m, 1H), 6.18 (d, *J* = 9.6Hz, 1H), 5.58 (dd, *J* = 12.0, 4.8Hz, 1H), 2.58-2.75 (m, 2H); **^{13}C NMR** (100 MHz, CDCl3) δ 163.1, 147.9, 145.4, 144.4,126.7, 124.0, 121.7, 76.7, 31.5; **IR** (KBr) ν_{max} 3431, 3113, 2921, 1726, 1521, 1350, 1244, 1067, 1032, 857, 816 cm^{-1}; **HRMS** (ESIMS) calcd for $C_{11}H_{10}NO_4^+$ $[M + H]^+$ 220.0604, found 220.0610.



4e

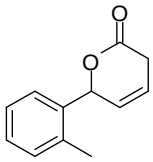
Yellow solid, m.p. 198-199 °C; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.32 (d, *J* = 8.8Hz), 8.00 (d, *J* = 9.2 Hz, 2H), 7.49 (dd, *J* = 9.2, 6.8 Hz, 1H), 6.82 (d, *J* = 6.8 Hz, 1H), 6.42 (d, *J* = 9.2 Hz, 1H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 160.9, 158.2, 148.8, 143.0, 136.8, 126.3, 124.2, 116.2, 103.4; **IR** (KBr) ν_{max} 3431, 2923, 1731, 1516, 1344, 1108, 856 cm^{-1}; **HRMS** (ESIMS) calcd for $C_{11}H_8NO_4^+$ $[M + H]^+$ 218.0448, found 218.0443.



2f

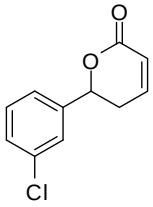
Colorless oil; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.49-7.51 (m, 1H), 7.22-7.49 (m, 2H), 7.17-7.19 (m, 1H), 6.97-7.02 (m, 1H), 6.15 (dd, *J* = 10.4, 2.4 Hz, 1H), 5.65 (dd, *J* = 12.0, 4.4 Hz, 1H), 2.51-2.66 (m, 2H), 2.36 (s, 3H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 164.3, 145.1, 136.3, 134.7, 130.6, 128.4, 126.4, 126.1, 121.5, 76.6, 30.4, 19.0; **IR** (KBr) ν_{max} 3426, 2921, 1720, 1461, 1379, 1243, 1057,

1021, 814, 756 cm^{-1}; **HRMS** (ESIMS) calcd for $C_{12}H_{13}O_2^+$ $[M + H]^+$ 189.0910, found 189.0906



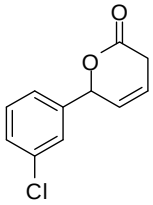
3f

Yellow oil; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.21-7.28 (m, 4H), 6.21-6.23 (m, 1H), 5.99-6.06 (m, 2H), 3.17-3.18 (m, 2H), 2,44 (s, 3H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 168.5, 136.4,135.7, 131.1, 129.0, 126.8, 126.3, 125.8, 122.2, 78.8, 30.0, 19.0; **IR** (KBr) ν_{max} 3449, 2923, 1736, 1462, 1367, 1220, 1068, 752 cm^{-1}; **HRMS** (ESIMS) calcd for $C_{12}H_{13}O_2^+$ $[M + H]^+$ 189.0910, found 189.0908.



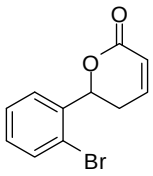
2g

Colorless oil; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.43 (s, 1H), 7.27-7.36 (m, 3H), 6.95-7.00 (ddd, J = 4.4 Hz, 1H), 6.15 (d, J = 10.0 Hz, 1H), 5.43 (t, J = 8.0 Hz, 1H), 2.61-2.65 (m, 2H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 163.6, 144.6, 140.4, 134.6, 130.0, 128.7, 126.2, 124.1, 121.7, 78.3, 31.6;
IR (KBr) ν_{max} 3421, 2921, 1728, 1379, 1241, 1061, 1027, 813, 786, 664 cm^{-1}; **HRMS** (ESIMS) calcd for $C_{11}H_{13}NO_2^+$ $[M + NH_4]^+$ 226.0269, found 226.0267.



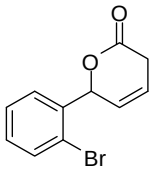
3g

Yellow oil; **^{1}H NMR** (400 MHz, CDCl3) δ 7.33 (d, J = 3.2Hz, 3H), 7.24-7.26 (m, 1H), 5.96-6.05 (m, 3H), 3.18 (s, 2H); **^{13}C NMR** (100 MHz, CDCl3) δ 167.8, 140.2, 134.8, 130.2, 129.0, 127.0, 125.5, 122.4, 80.4, 29.8; **IR** (KBr) ν_{max} 3395, 2920, 1736, 1215, 1068, 781, 726, 666 cm^{-1}; **HRMS** (ESIMS) calcd for $C_{11}H_{13}NO_2^+$ $[M + NH_4]^+$ 226.0269, found 226.0265.



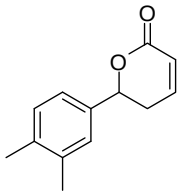
2h

Colorless oil; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.65 (d, J = 8.0 Hz, 1H), 7.56 (d, J = 7.6 Hz, 1H), 7.40 (t, J = 7.6 Hz, 1H), 7.22 (t, J = 8.0 Hz, 1H), 6.97-7.02 (m, 1H), 6.17 (dd, J = 9.6, 2.4 Hz, 1H), 5.79 (dd, J = 12.4, 3.2 Hz, 1H), 2.81-2.99 (m, 1H), 2.40-2.48 (m, 1H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 163.9, 144.9, 137.9, 132.8, 129.9, 128.0, 127.8, 121.5, 121.1, 78.3, 30.4; **IR** (KBr) ν_{max} 3431, 2922, 1728, 1380, 1243, 1062, 1020, 815, 757 cm^{-1}; **HRMS** (ESIMS) calcd for $C_{11}H_{10}BrO_2^+$ $[M + H]^+$ 252.9859, found 252.9856.



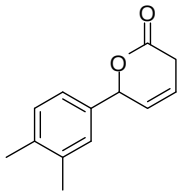
3h

Colorless oil; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.60 (d, J = 8.0 Hz, 1H), 7.36-7.59 (m, 2H), 7.20-7.24 (m, 1H), 6.39-6.41 (m, 1H), 5.97-6.06 (m, 2H), 3.21 (dt, J = 4.8, 1.6 Hz); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 168.1, 137.4, 133.2, 130.1, 128.0, 127.9, 125.2, 122.1, 121.8, 80.3, 29.8; **IR** (KBr) ν_{max} 3448, 2920, 1738, 1470, 1440, 1363, 1220, 1159, 1069, 1024, 910,731, 661 cm^{-1}; **HRMS** (ESIMS) calcd for $C_{11}H_{10}BrO_2^+$ $[M + H]^+$ 252.9859, found 252.9863.



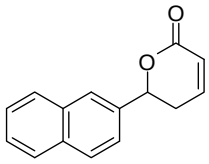
2i

Yellow solid, m.p. 59-61 °C; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.06-7.32 (m, 3H), 6.95-6.99 (m, 1H), 6.14 (dd, J = 9.6, 1.6 Hz, 1H), 5.40 (dd, J = 11.6, 3.6 Hz, 1H), 2.55-2.71 (m, 2H), 2.2 9(s, 3H), 2.28 (s, 3H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 164.3, 145.0, 137.1, 136.9, 135.9, 129.8, 127.3, 123.4, 121.6, 79.2, 31.6, 19.8, 19.5; **IR** (KBr) ν_{max} 3421, 2920, 1725, 1380, 1242, 1064, 1026, 815 cm^{-1}; **HRMS** (ESIMS) calcd for $C_{12}H_{15}O_2^+$ $[M + H]^+$ 203.1067, found 203.1070



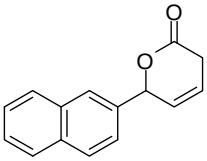
3i

Yellow oil; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.06-7.16 (m, 4H), 5.93-6.04 (m, 3H), 3.16-3.18 (m, 2H), 2.28 (s, 6H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 168.4, 137.5,137.2, 135.6, 130.0, 128.2, 126.3, 124.3, 121.5, 81.3, 29.9, 19.8, 19.5; **IR** (KBr) ν_{max} 3415, 2922, 1737, 1545, 1218, 1068, 667 cm^{-1}; **HRMS** (ESIMS) calcd for $C_{12}H_{15}O_2^+$ $[M + H]^+$ 203.1067, found 203.1064.



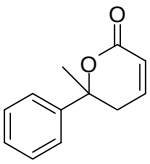
2j

White solid, m.p 121-123 °C; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.85-7.89 (m, 4H), 7.50-7.53 (m, 3H), 6.97-7.01 (m, 1H), 6.17 (d, J = 9.6 Hz, 1H), 5.61(dd, J = 10.8, 5.2 Hz, 1H), 2.69-2.74 (m, 2H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 164.0, 144.9, 135.7, 133.2, 133.0, 128.5, 128.1, 127.7, 126.5, 126.4, 125.1, 123.5, 121.6, 79.2, 31.6; **IR** (KBr) ν_{max} 3410, 2916, 1713, 1383, 1254, 1025, 820, 743, 718 cm^{-1}; **HRMS** (ESIMS) calcd for $C_{15}H_{12}NaO_2^+$ $[M + Na]^+$ 247.0730, found 247.0724.



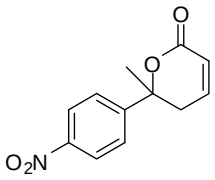
3j

White solid, m.p. 112-113 °C; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.81-7.90 (m, 4H), 7.51-7.54 (m, 2H), 7.44 (dd, J = 8.8, 2.0 Hz, 1H), 6.03-6.16 (m, 3H), 3.22 (dt, J = 4.8, 1.6 Hz, 2H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 168.3, 135.5, 133.3, 133.1, 128.9, 128.1, 127.7, 126.6, 126.5, 126.1, 125.9, 124.3, 122.0, 81.4, 30.0; **IR** (KBr) ν_{max} 3429, 2921, 1728, 1224, 1058, 805, 753 cm^{-1}; **HRMS** (ESIMS) calcd for $C_{15}H_{12}NaO_2^+$ $[M + Na]^+$ 247.0730, found 247.0732.



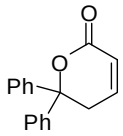
2k

Yellow oil; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.34-7.40 (m, 4H), 7.27-7.30 (m, 5H), 6.73-6.78 (m, 1H), 6.02 (d, J = 9.6 Hz, 1H), 2.78-3.00 (m, 2H), 1.73 (s, 3H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 163.9, 143.9, 143.4, 128.5, 127.6, 124.5, 121.8, 83.1, 35.4, 30.1; **IR** (KBr) ν_{max} 3408, 2921, 1711, 1379, 1260, 1062, 813, 761, 699 cm^{-1}.



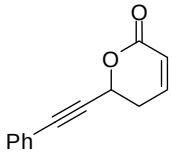
2l

Yellow solid, m.p. 114-115 °C; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.2 (d, J = 8.8 Hz, 2H), 7.58 (d, J = 8.8 Hz, 2H), 6.79-6.83 (m, 1H), 6.04 (d, J = 10.0 Hz, 1H), 2.85-3.00 (m, 2H), 1.75 (s, 3H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 162.9, 151.1, 147.2, 143.2, 125.6, 123.9, 123.8, 121.7, 82.5, 35.1, 29.5; **IR** (KBr) ν_{max} 3410, 2924, 1719, 1620, 1350, 1261, 1067, 855, 814 cm^{-1}; **HRMS** (ESIMS) calcd for $C_{12}H_{12}NO_2^+$ $[M + H]^+$ 234.0761, found 234.0767.



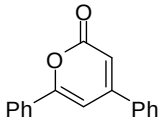
2m

White solid, m.p. 102-104 °C; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.33-7.40 (m, 4H), 7.30-7.32 (m, 4H), 7.24-7.28 (m, 2H), 6.88 (dt, J = 10.0, 4.4 Hz, 1H), 6.01 (dt, J = 9.6, 1.6 Hz, 1H), 3.24 (dd, J = 4.4, 1.6 Hz, 2H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 163.6, 143.7, 143.0, 128.4, 127.7, 125.9, 122.7, 86.2, 34.7; **IR** (KBr) ν_{max} 3424, 3056, 1730, 1265, 739, 703 cm^{-1}; **HRMS** (ESIMS) calcd for $C_{17}H_{15}O_2^+$ $[M + H]^+$ 251.1067, found 251.1064.



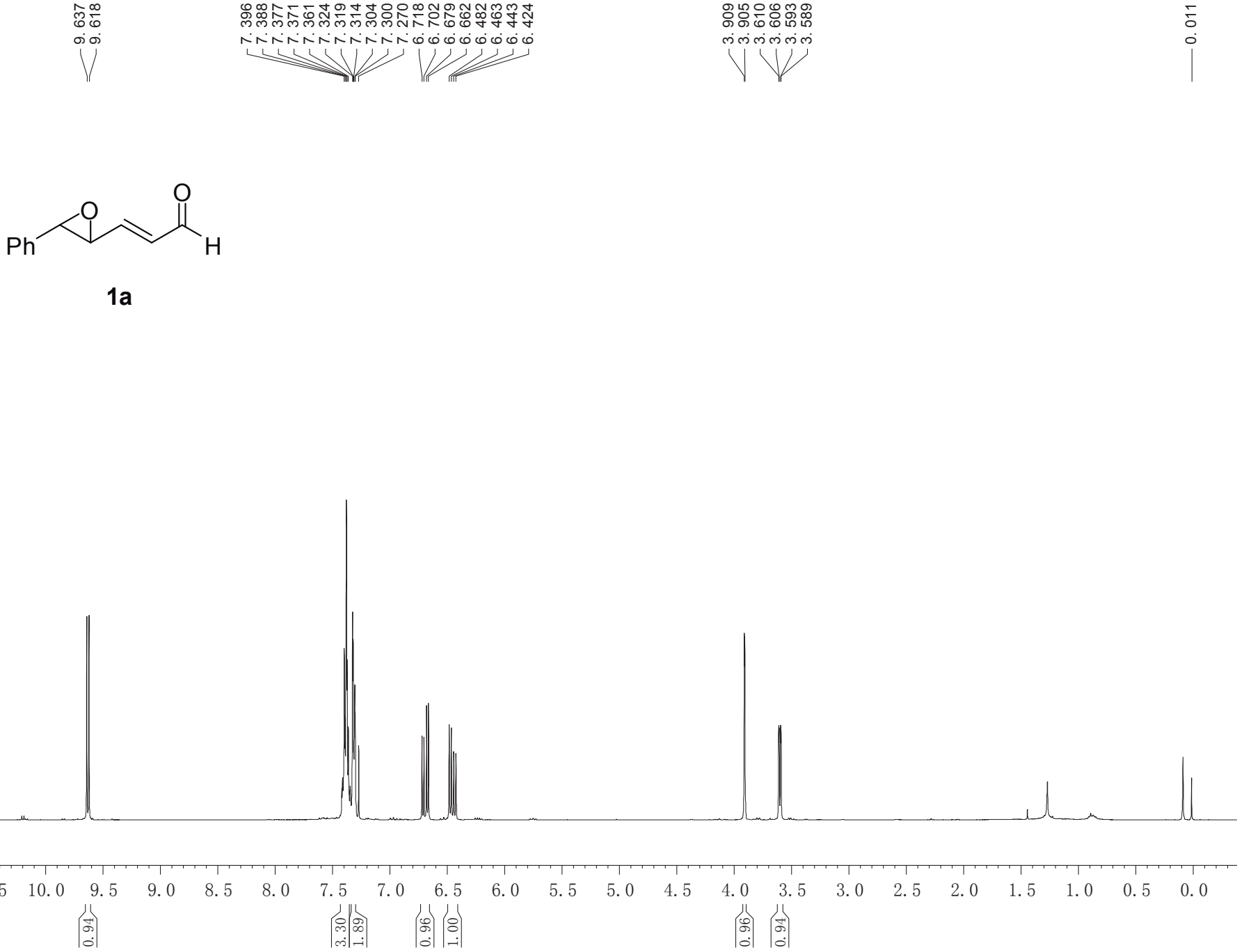
2o

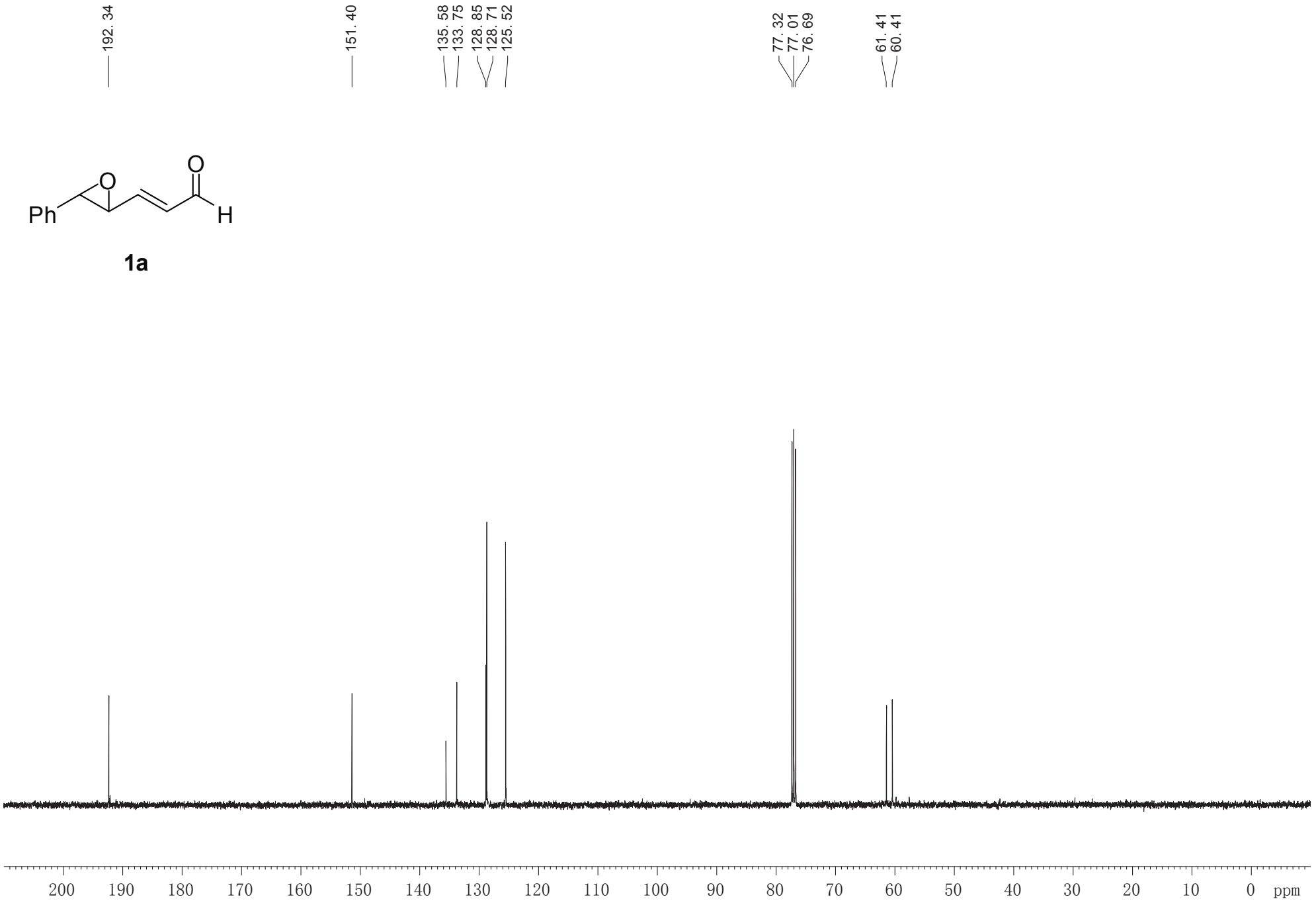
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.43-7.45 (m, 2H), 7.30-7.36 (m, 3H), 6.92 (dt, J = 10.0, 4.0 Hz, 1H), 6.10 (dt, J = 10.0, 1.6 Hz, 1H), 5.42 (dd, J = 6.8, 6.4 Hz, 1H), 2.74-2.78 (m, 2H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 162.6, 144.0, 131.8, 129.0, 128.3, 121.5, 86.5, 84.4, 67.6, 29.6;
IR (KBr) ν_{max} 2926, 2254, 1728, 1380, 1242, 1039, 909, 734 cm^{-1}; **HRMS** (ESIMS) calcd for $C_{13}H_{11}O_2^+$ $[M + H]^+$ 199.0754, found 199.0751.



4q

White solid, m.p. 66-68 ^{o}C; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.89-7.92 (m, 2H), 7.64-7.66 (m, 2H), 7.47-7.52 (m, 6H), 6.96 (d, J = 1.6 Hz, 1H), 6.47 (d, J = 1.2 Hz, 1H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 162.6, 160.4, 155.6, 136.1, 131.6, 130.9, 130.7, 129.2, 129.0, 126.7, 125.8, 109.3, 101.4;
IR (KBr) ν_{max} 3101, 1704, 1537, 1450, 1079, 1013, 846, 764, 689 cm^{-1}; **HRMS** (ESIMS) calcd for $C_{17}H_{12}NaO_2^+$ $[M + Na]^+$ 271.0730, found 271.0732.





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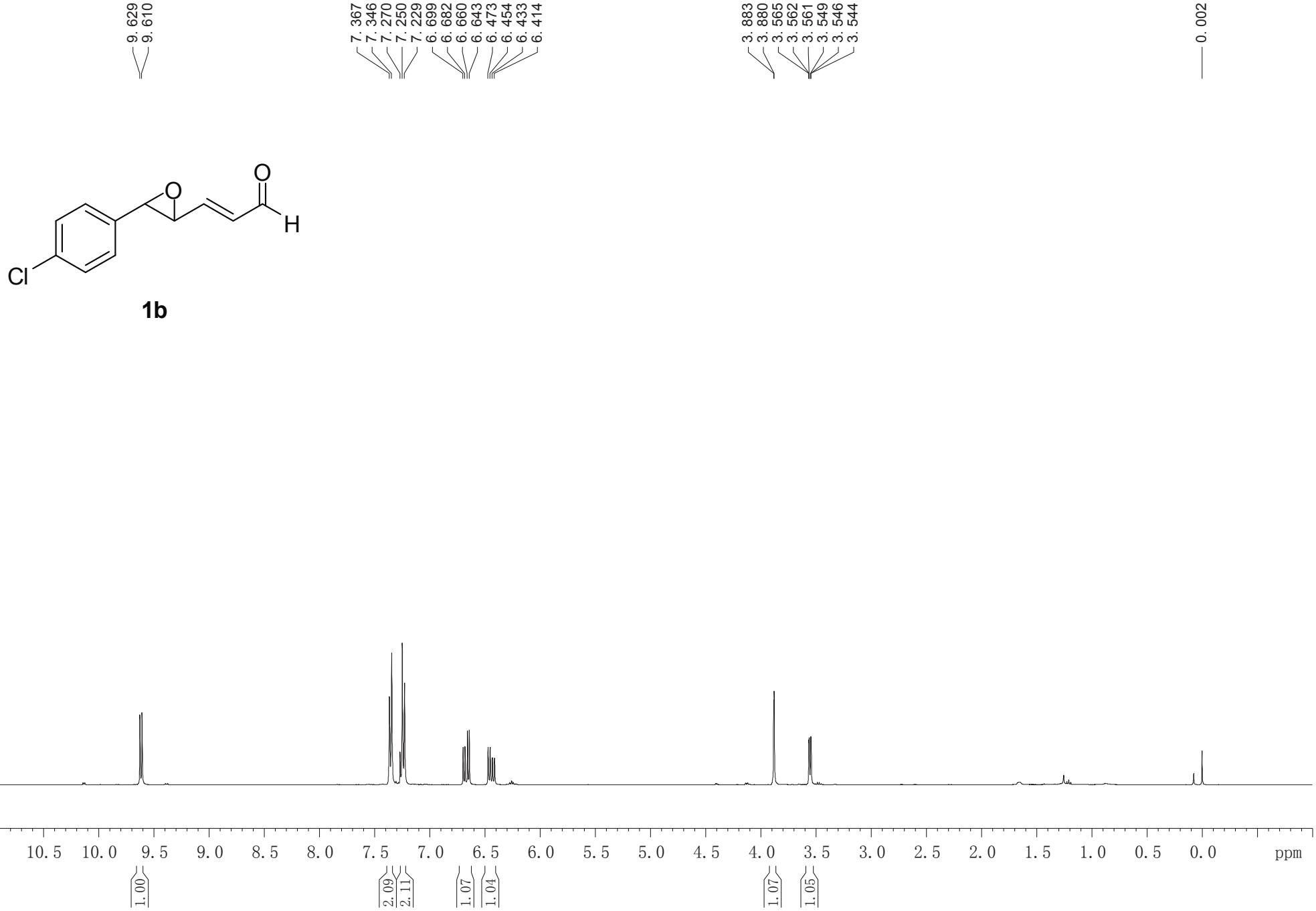

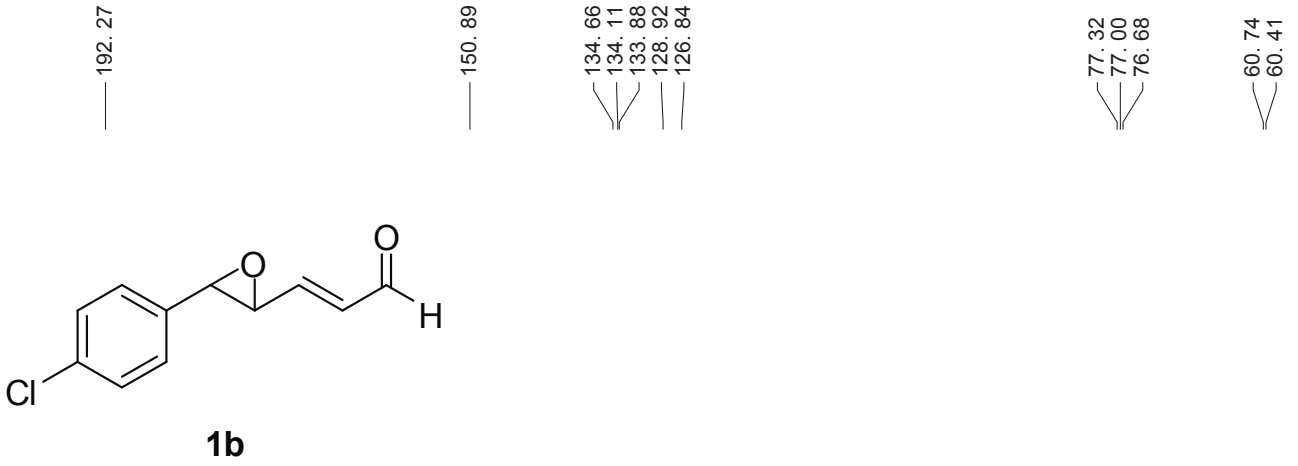

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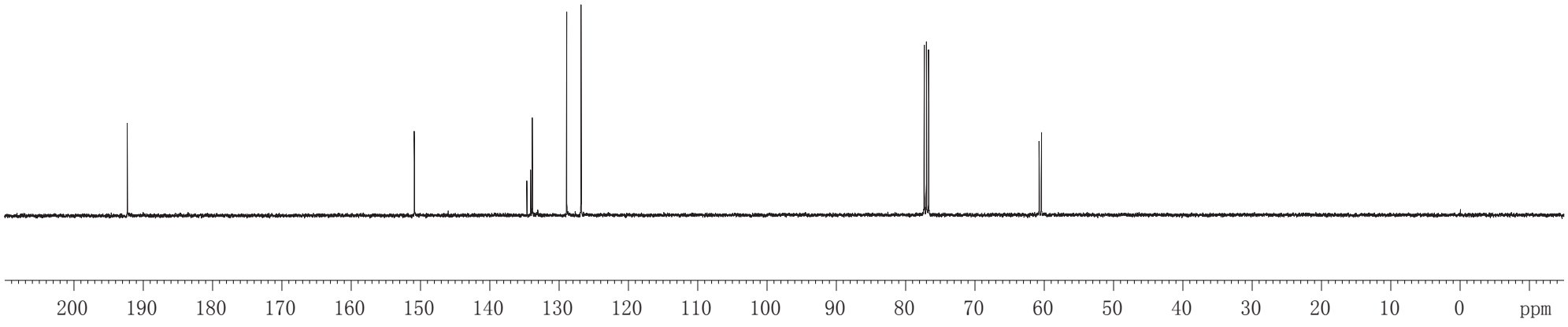

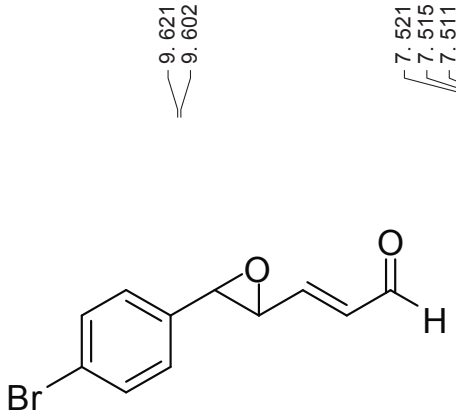

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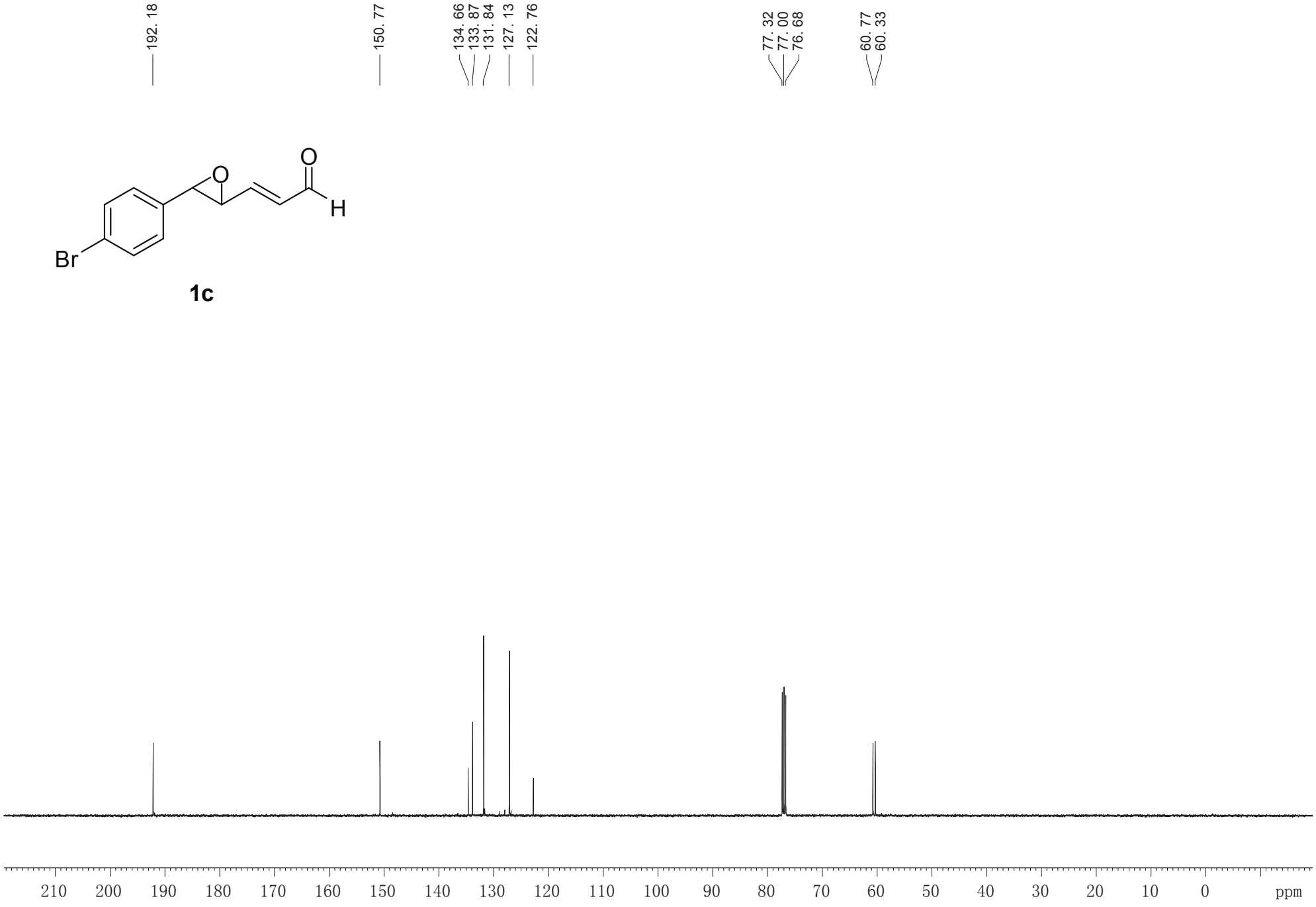

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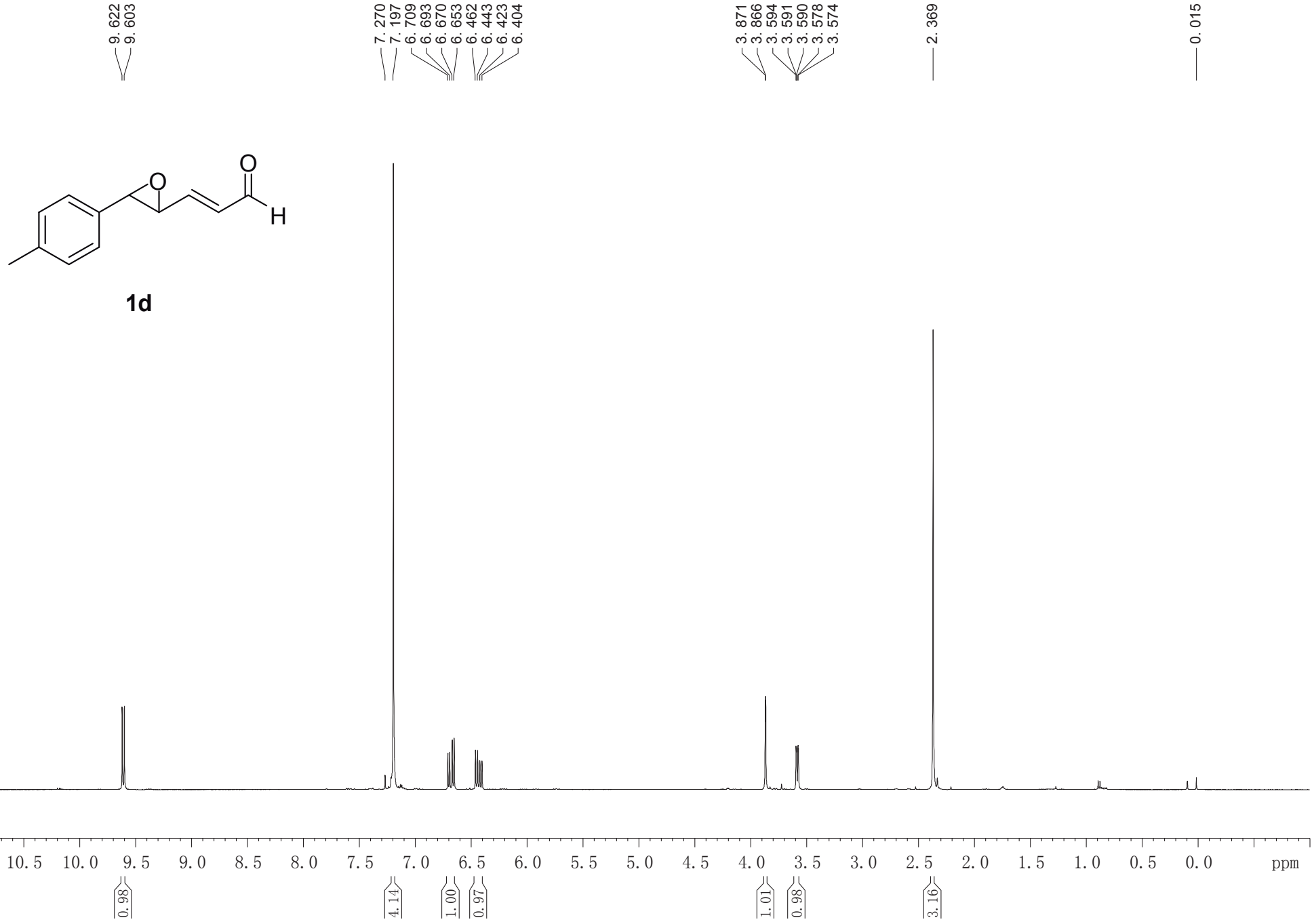

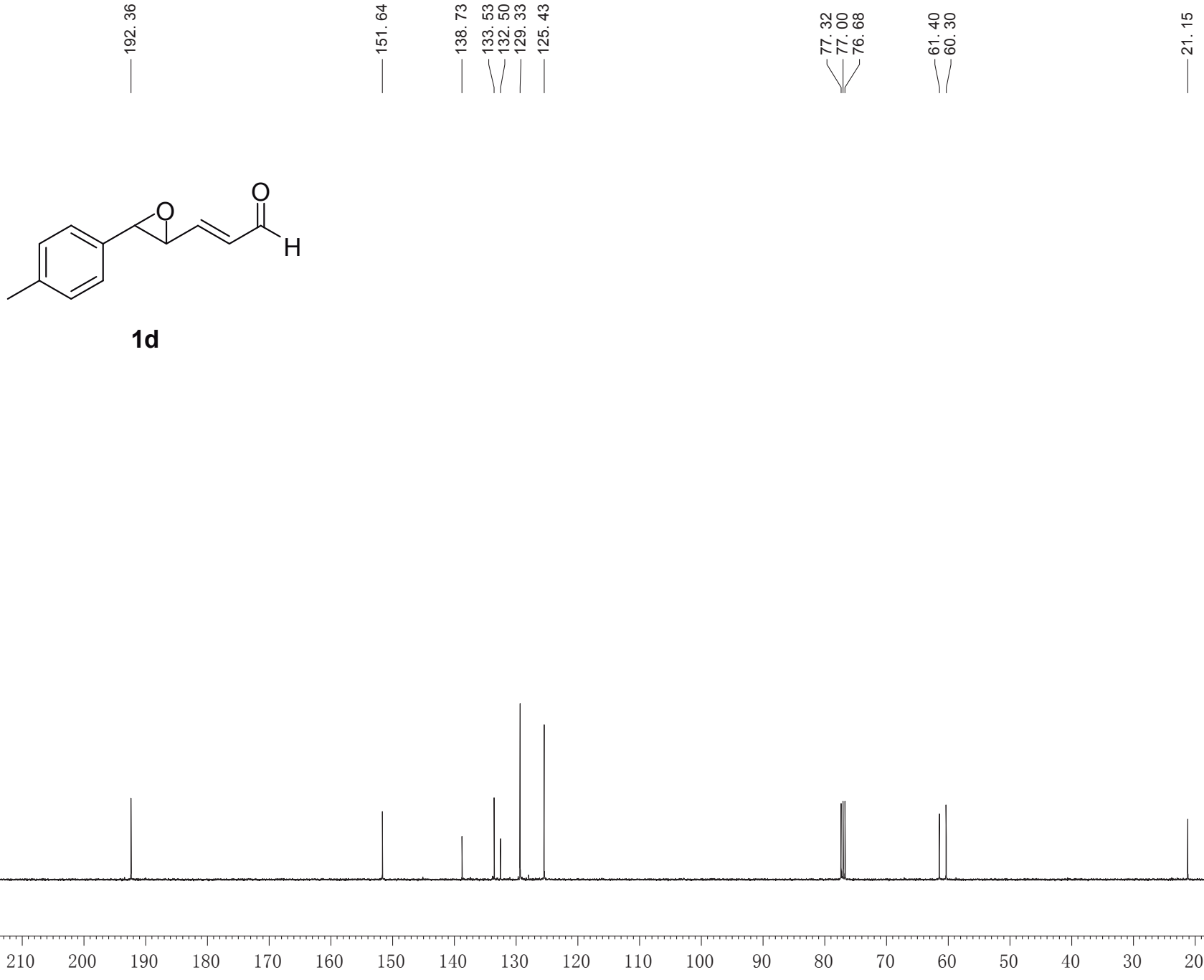

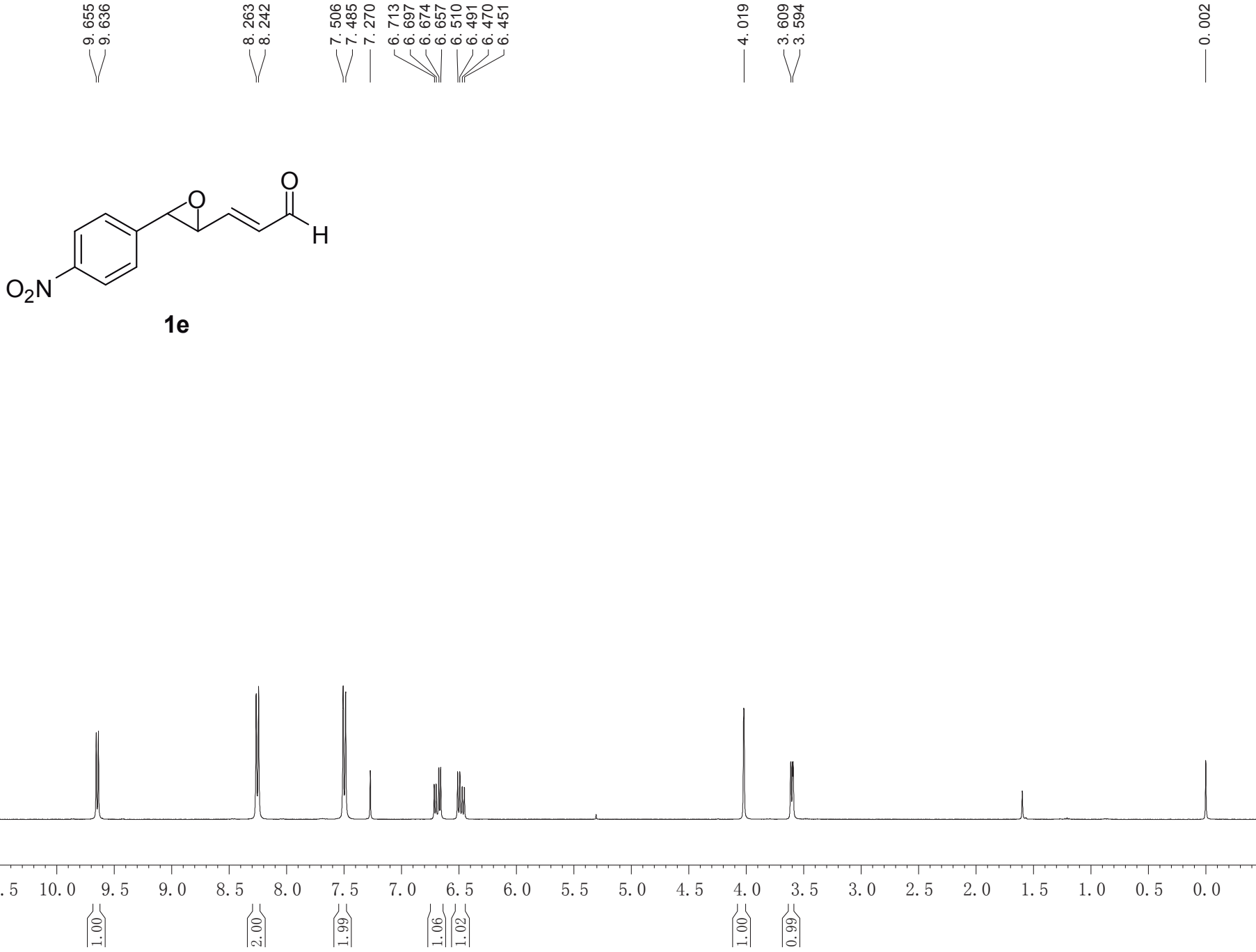

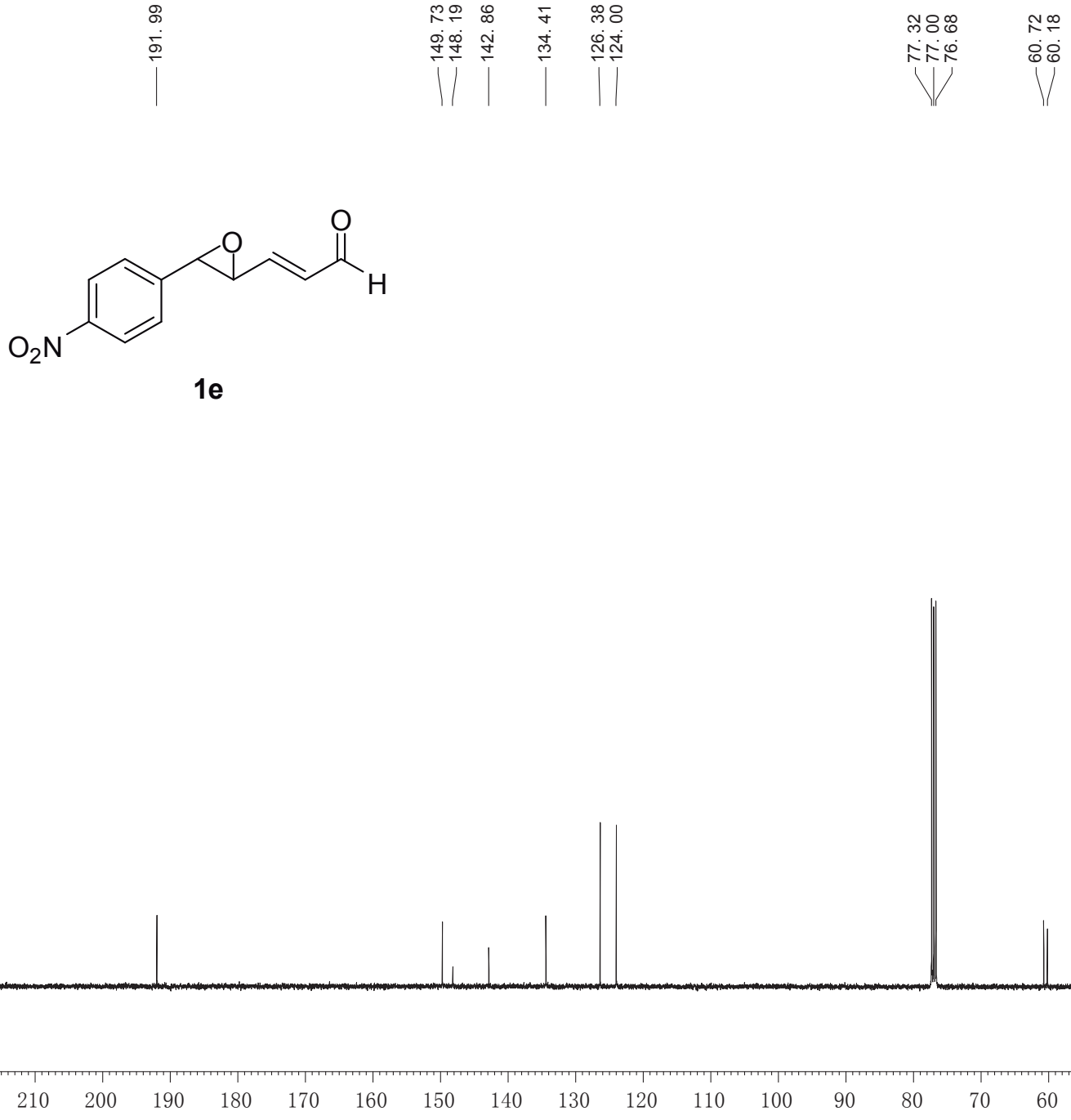

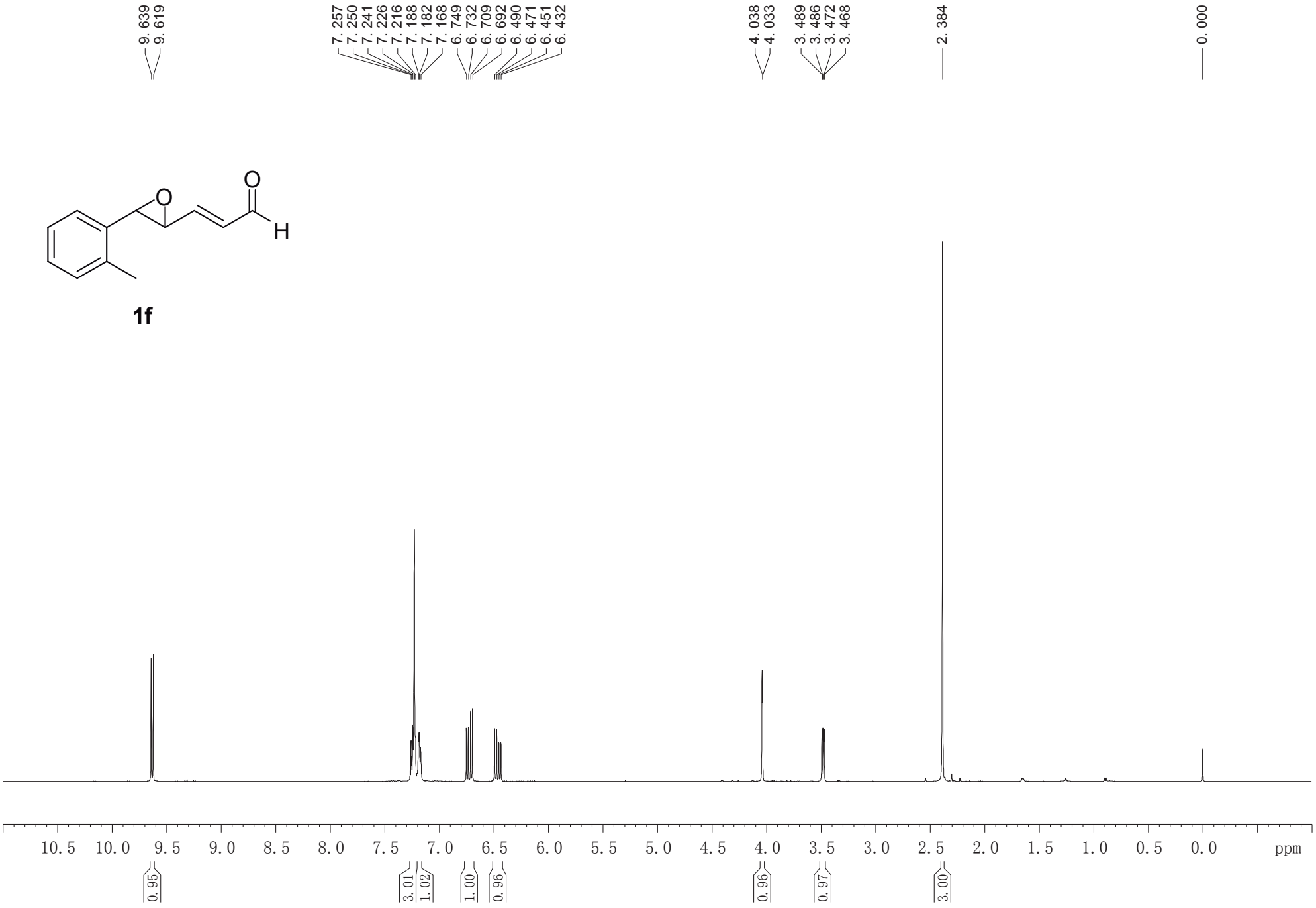

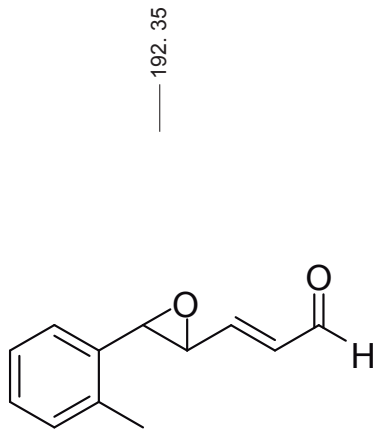

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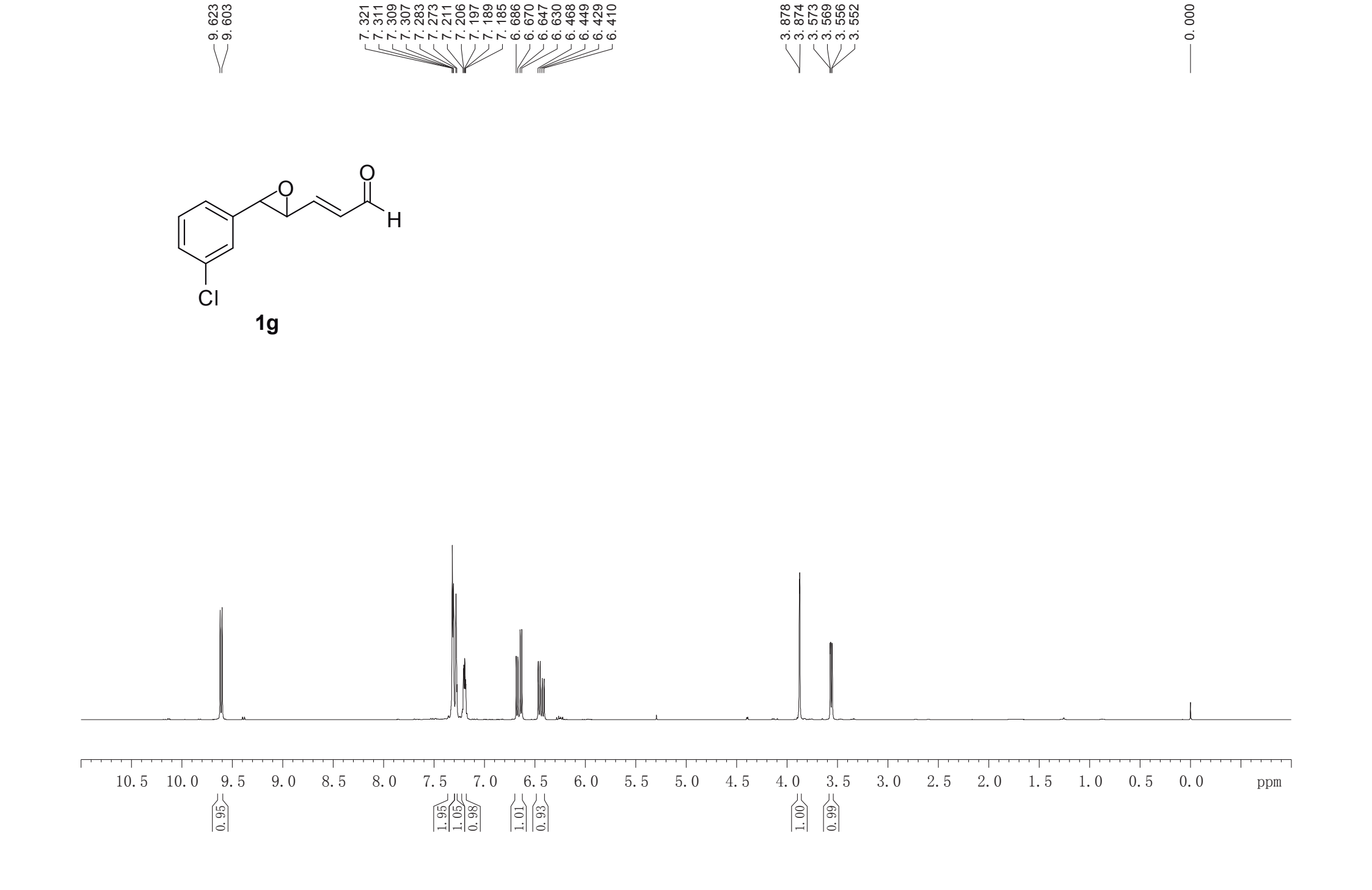

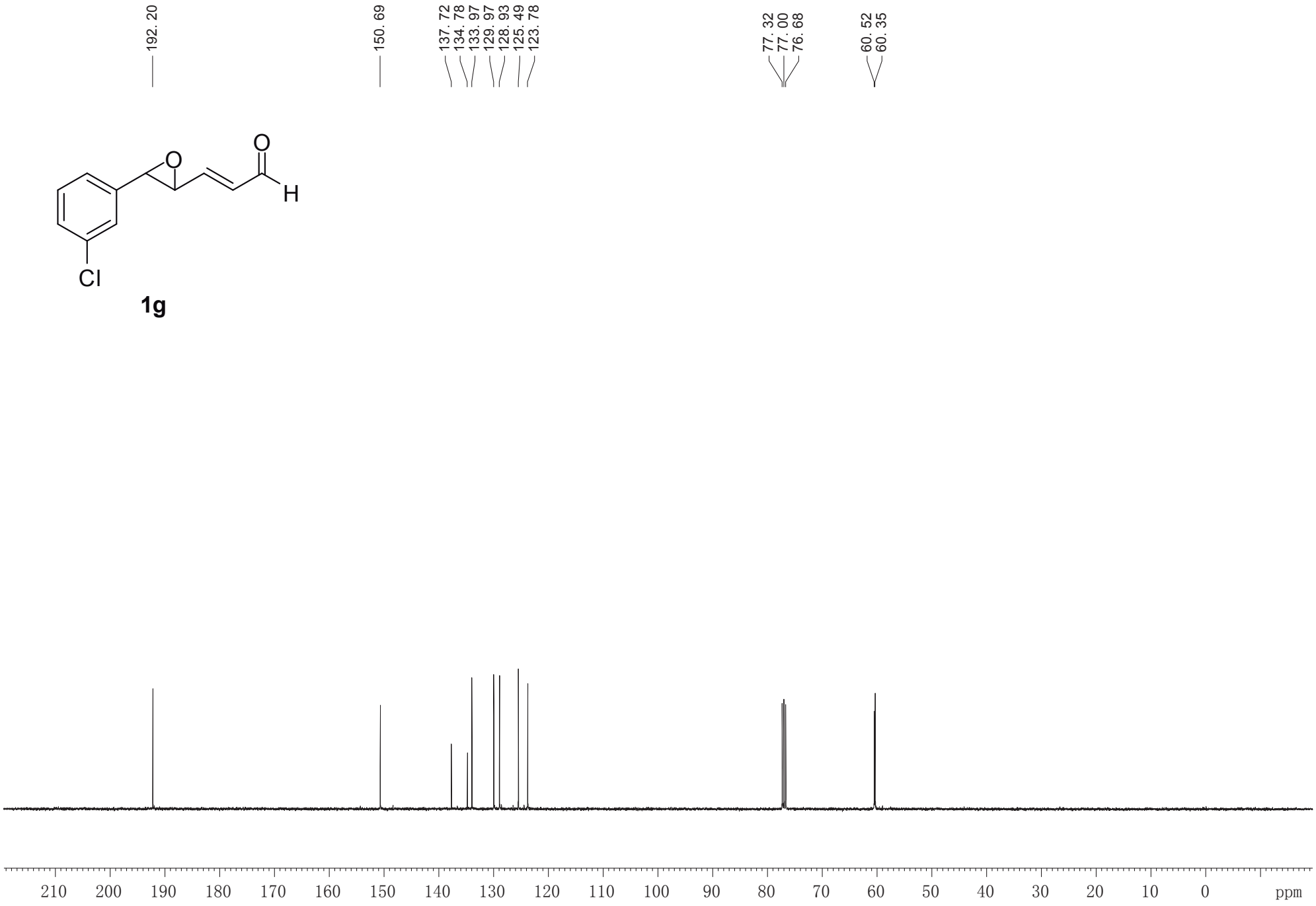

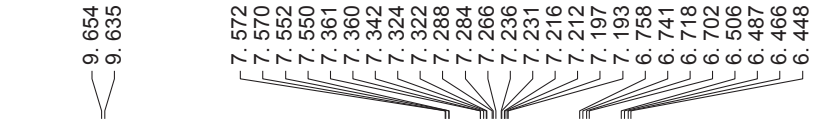

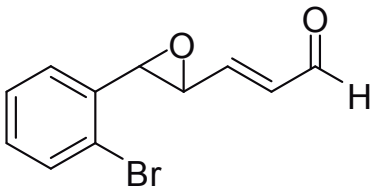

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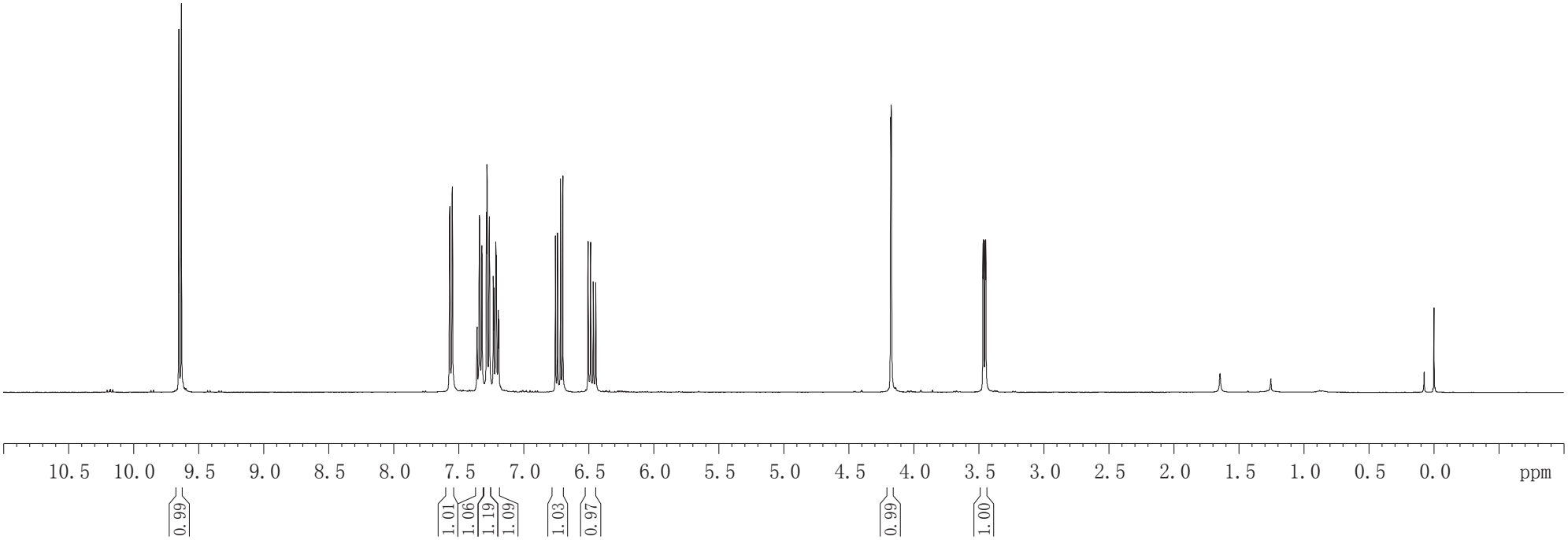

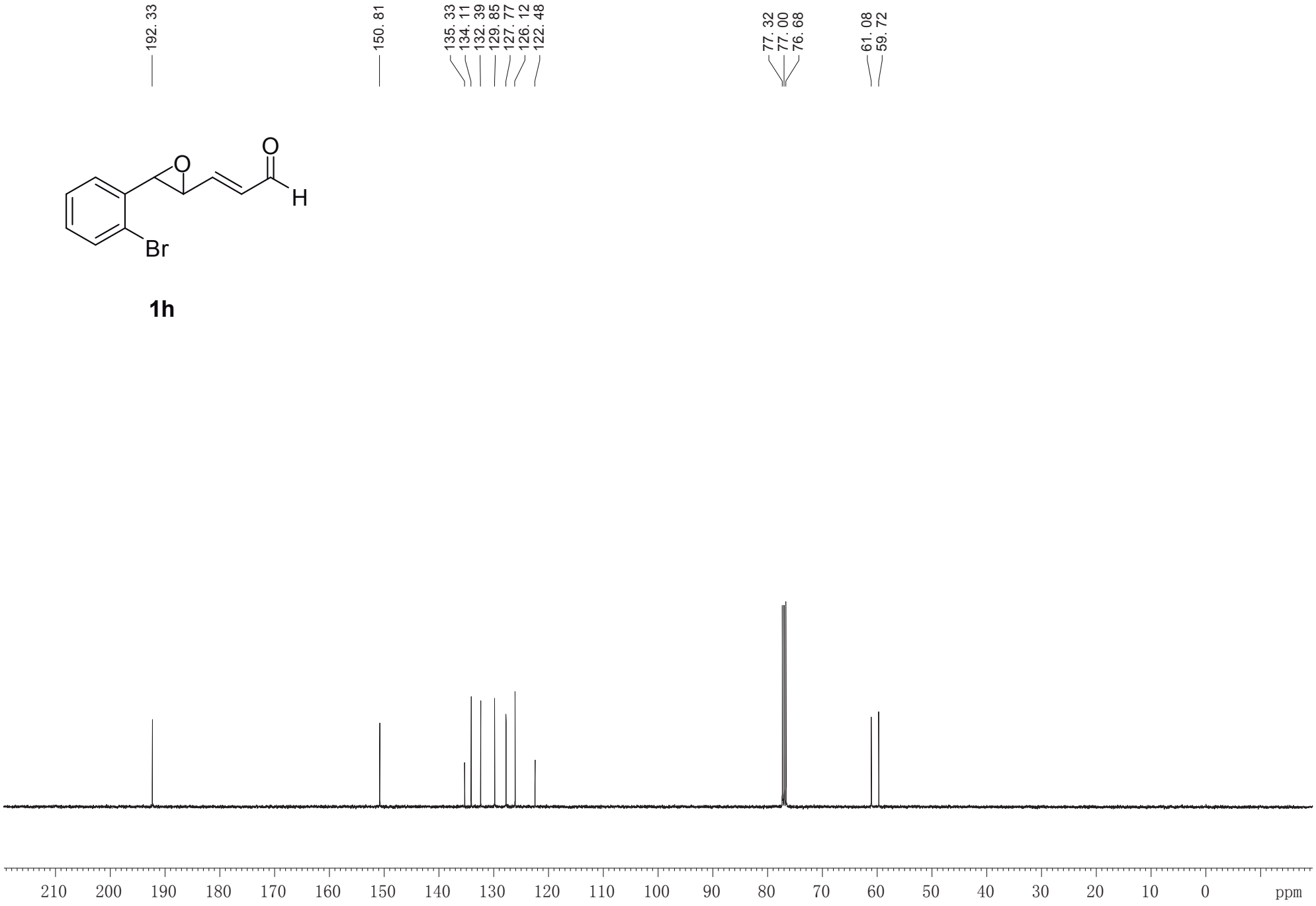

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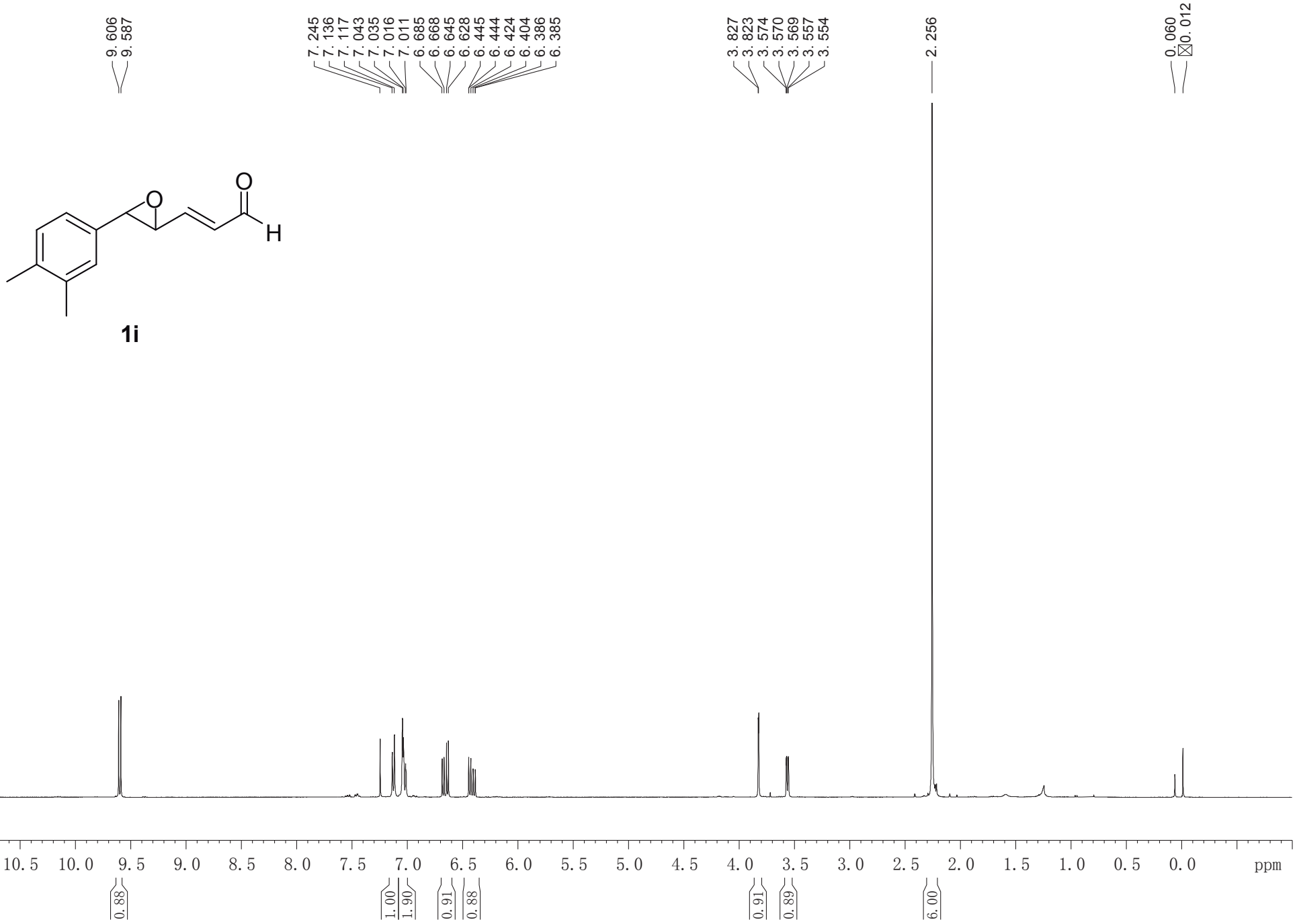

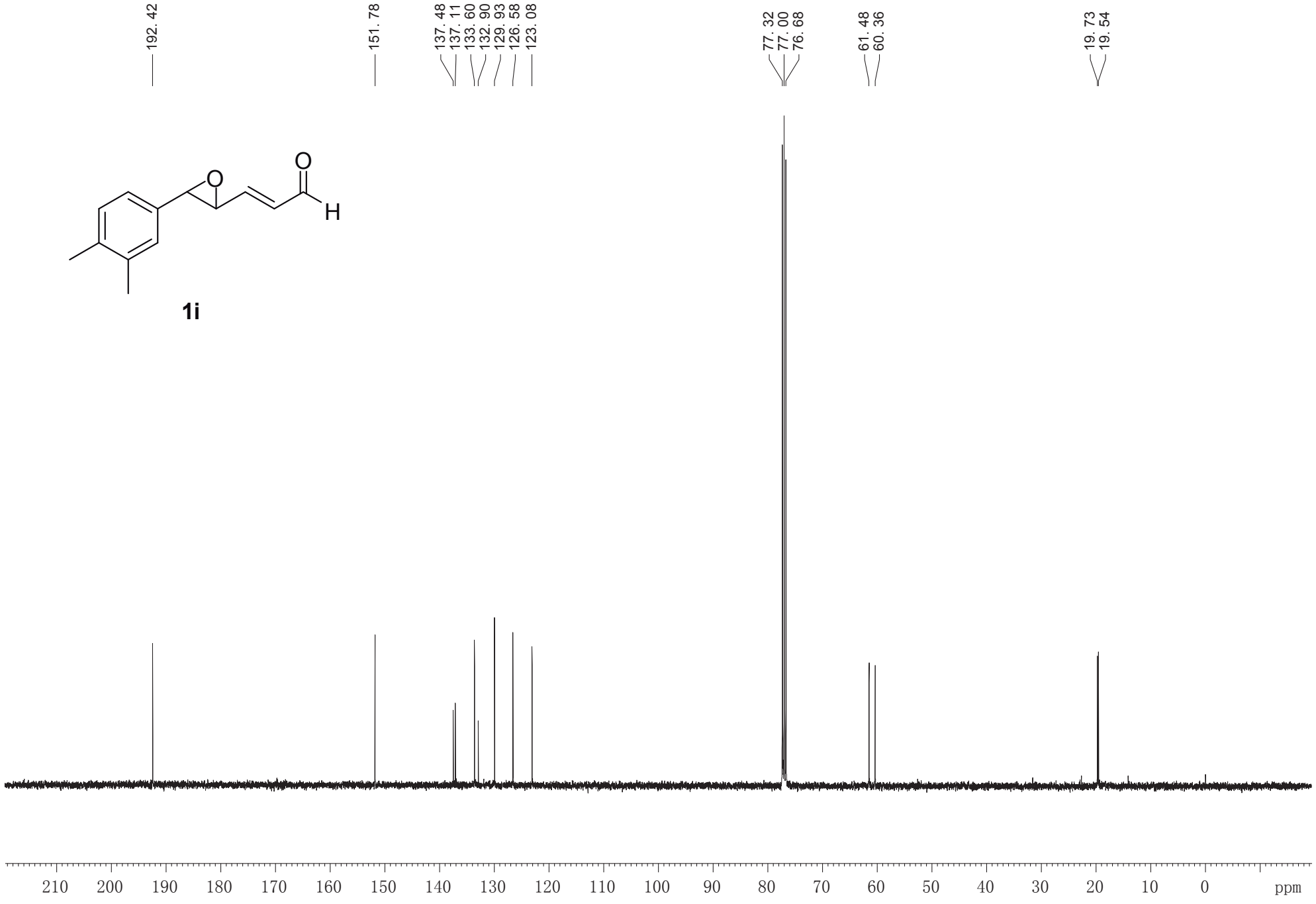

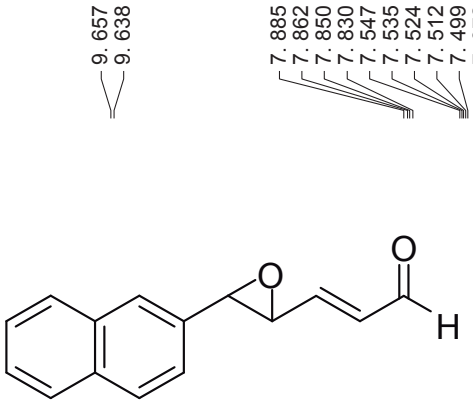

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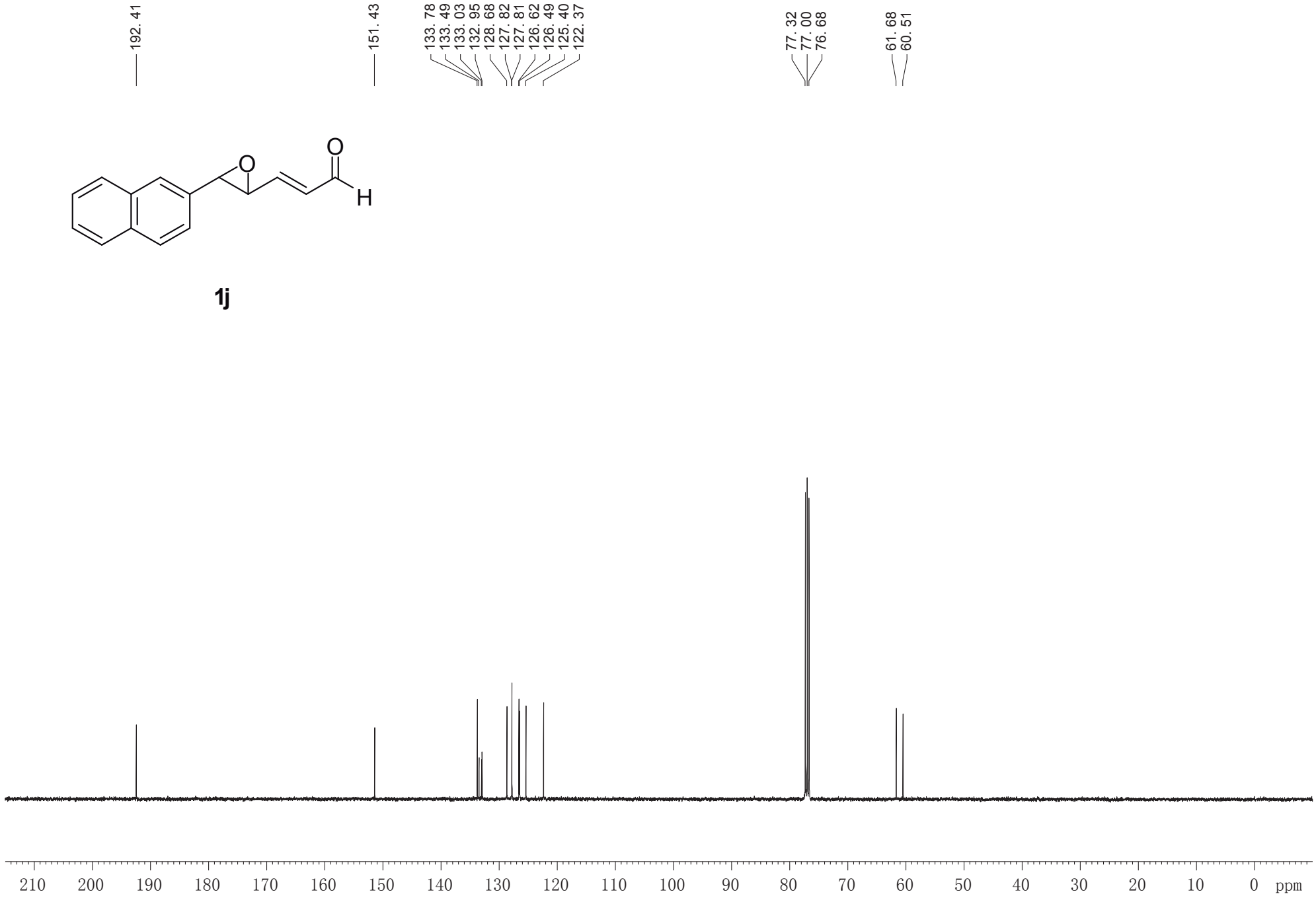

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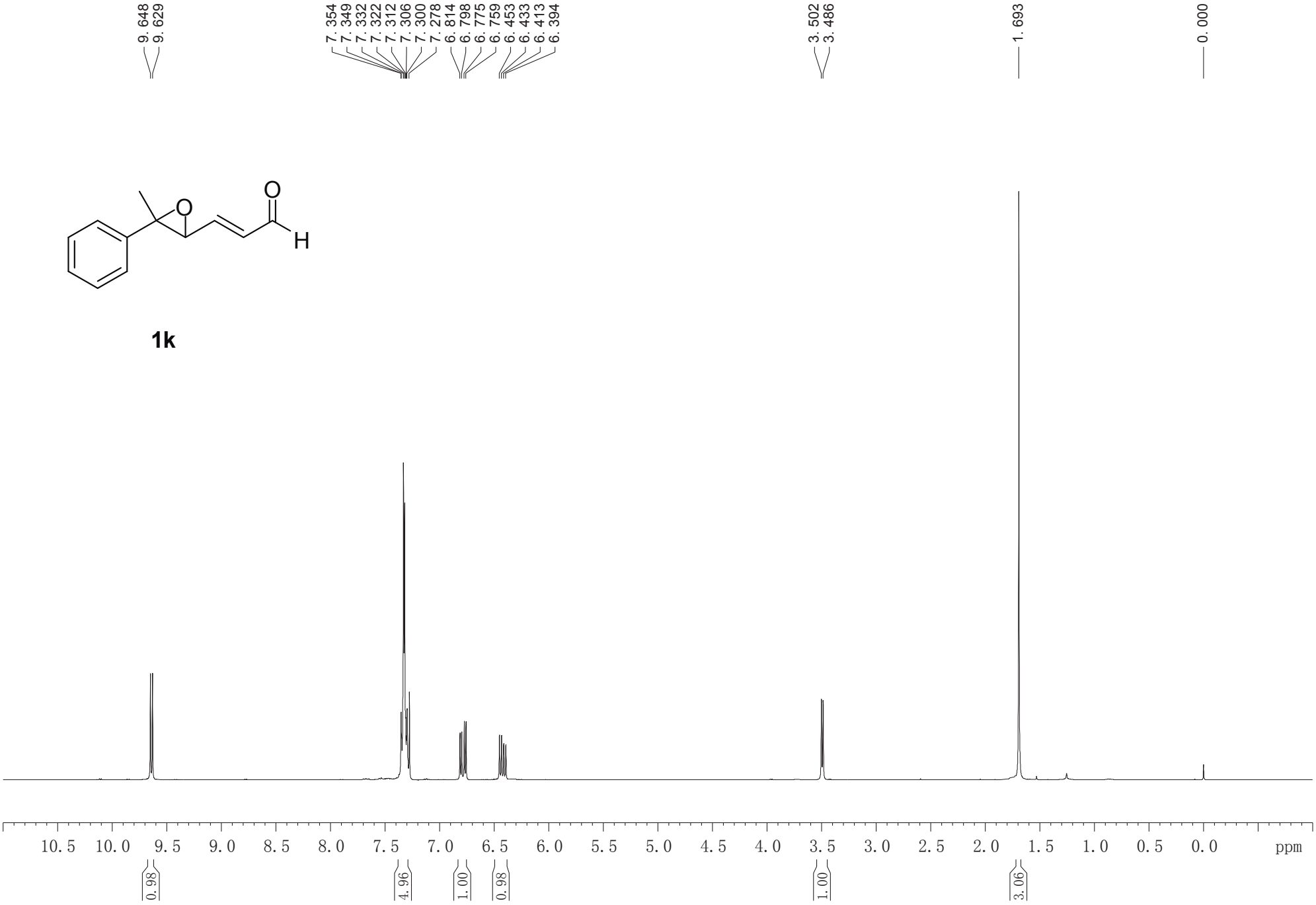

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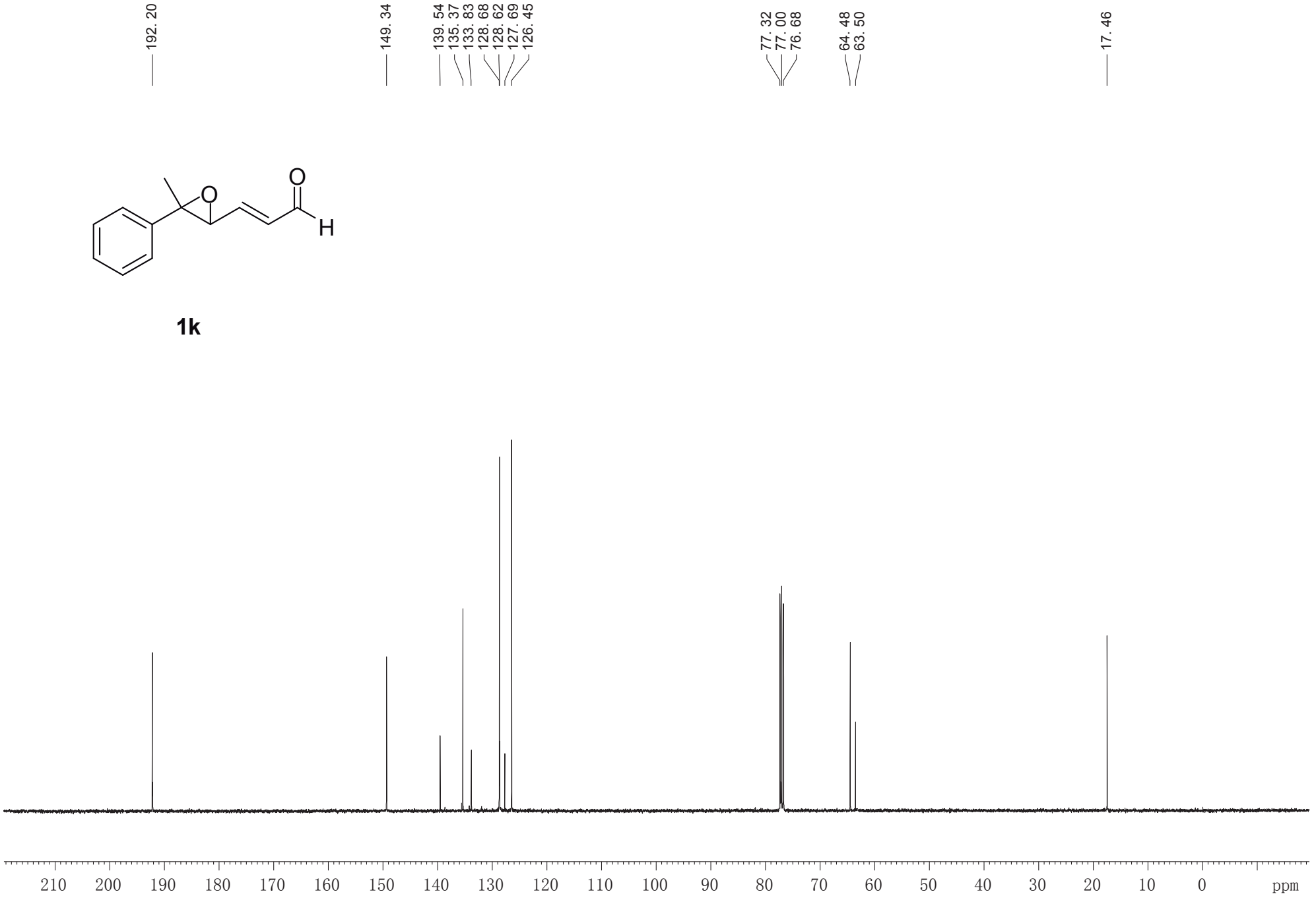

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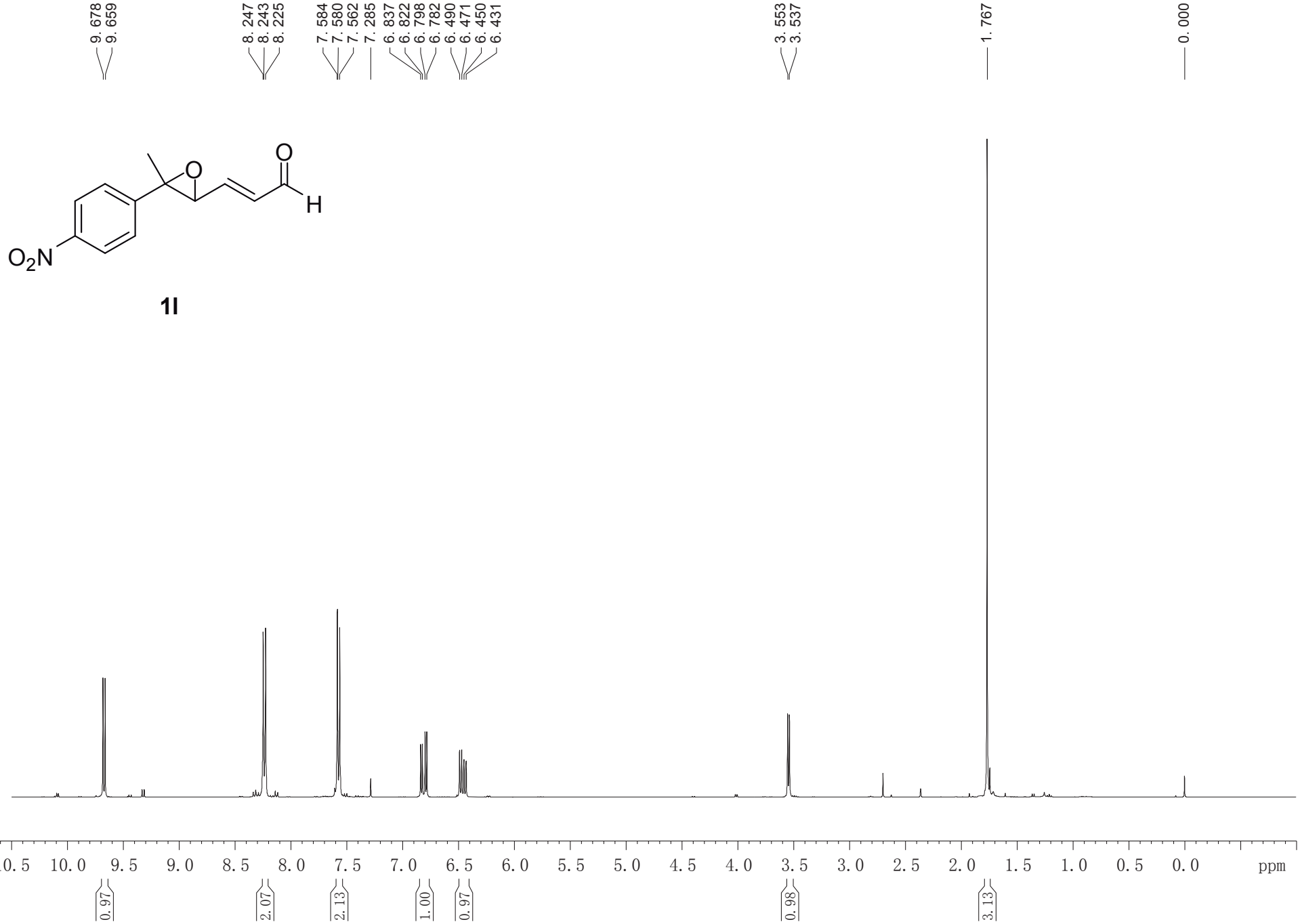

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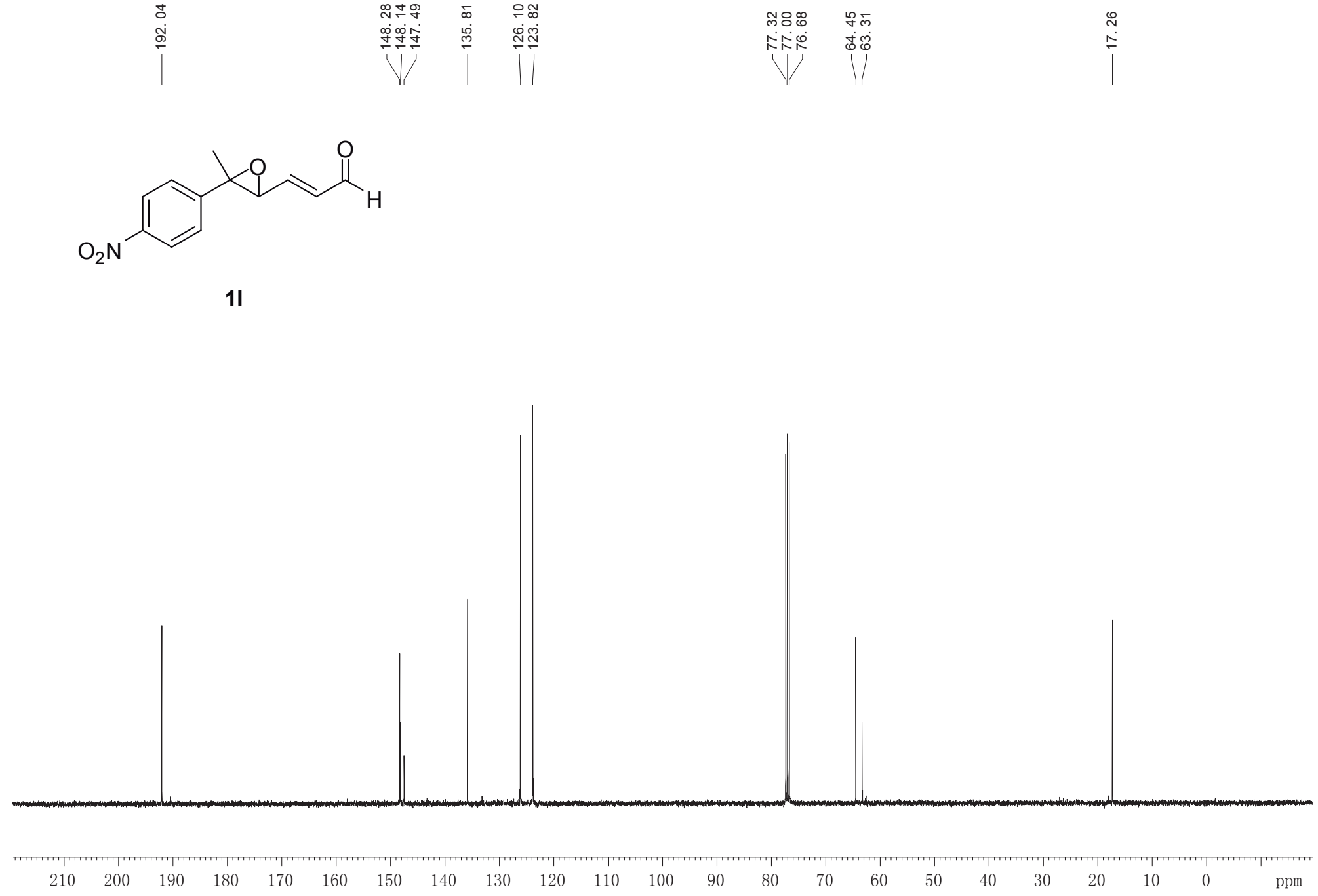

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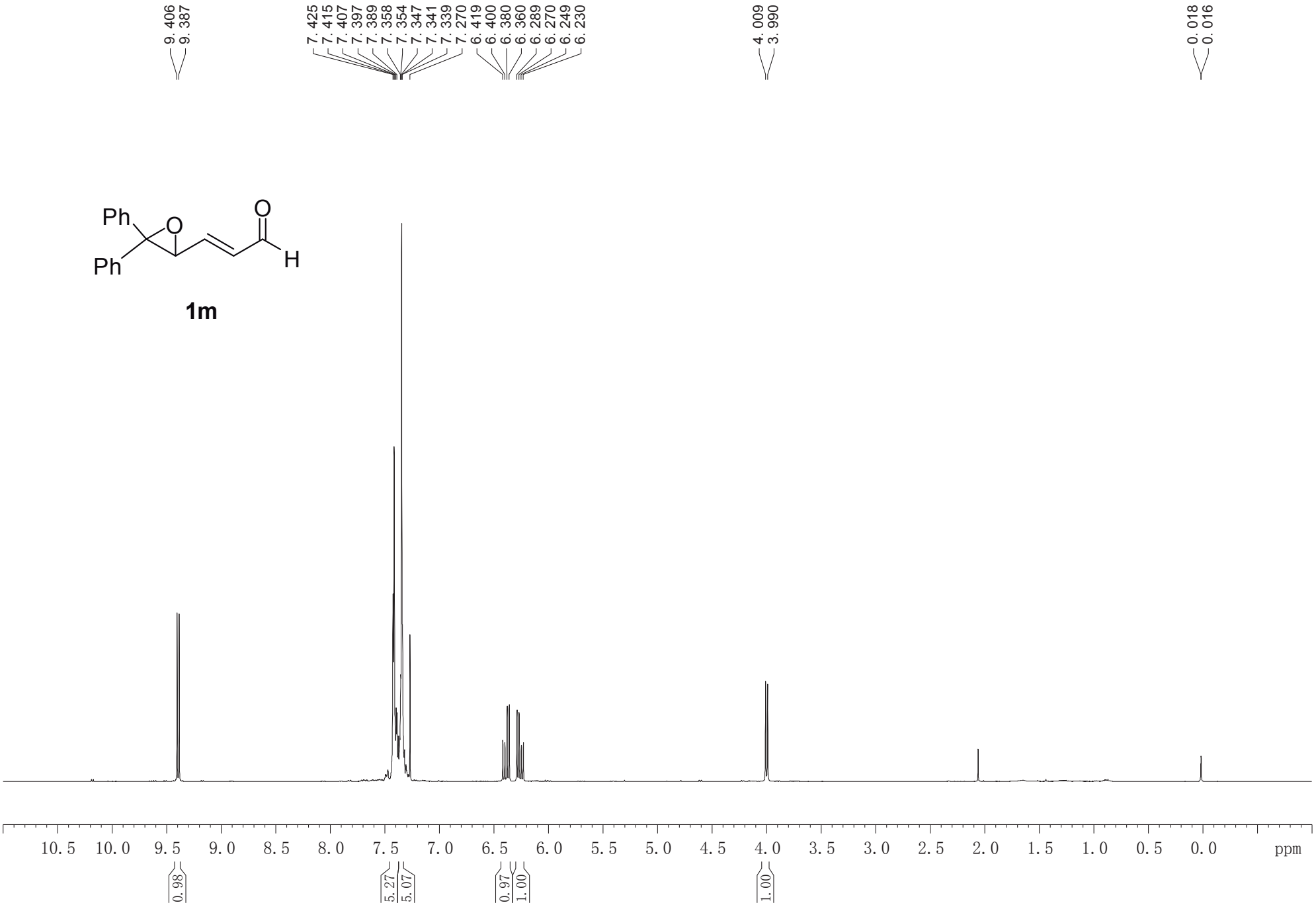

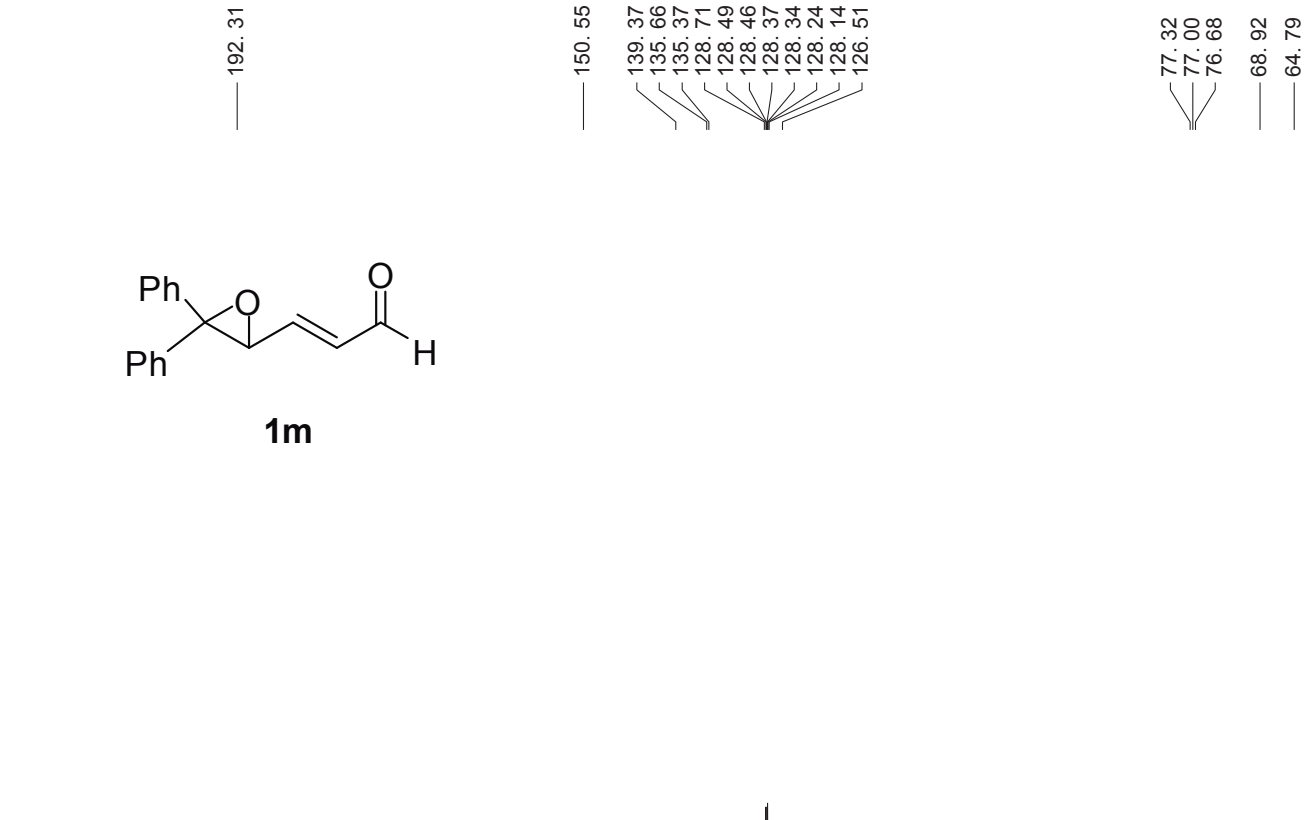

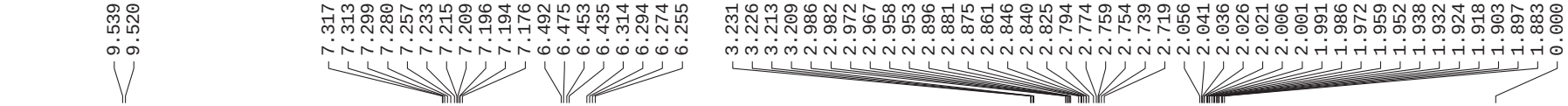

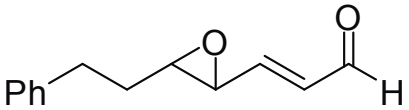

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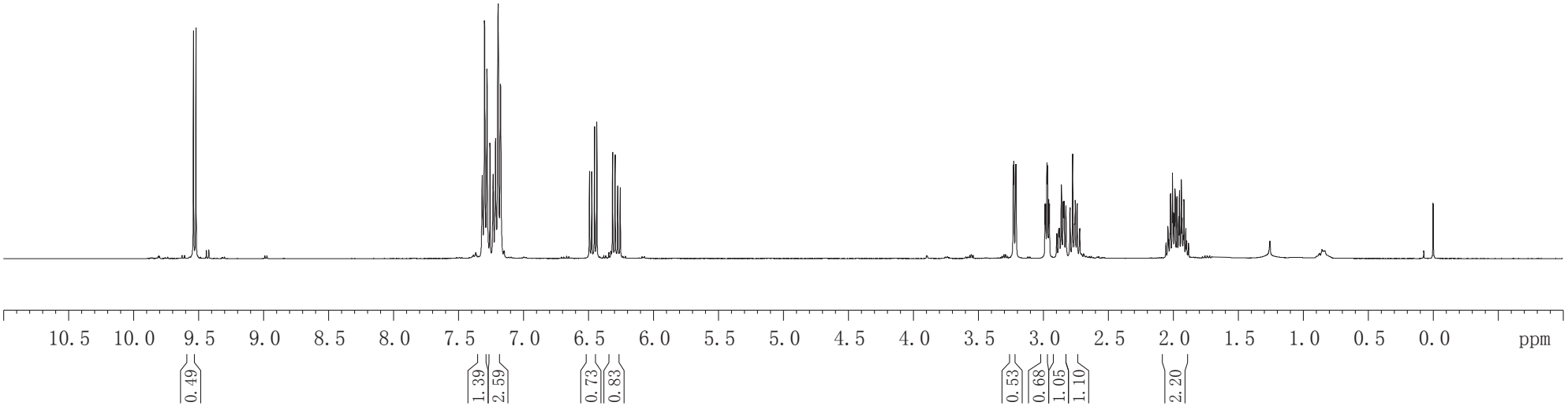

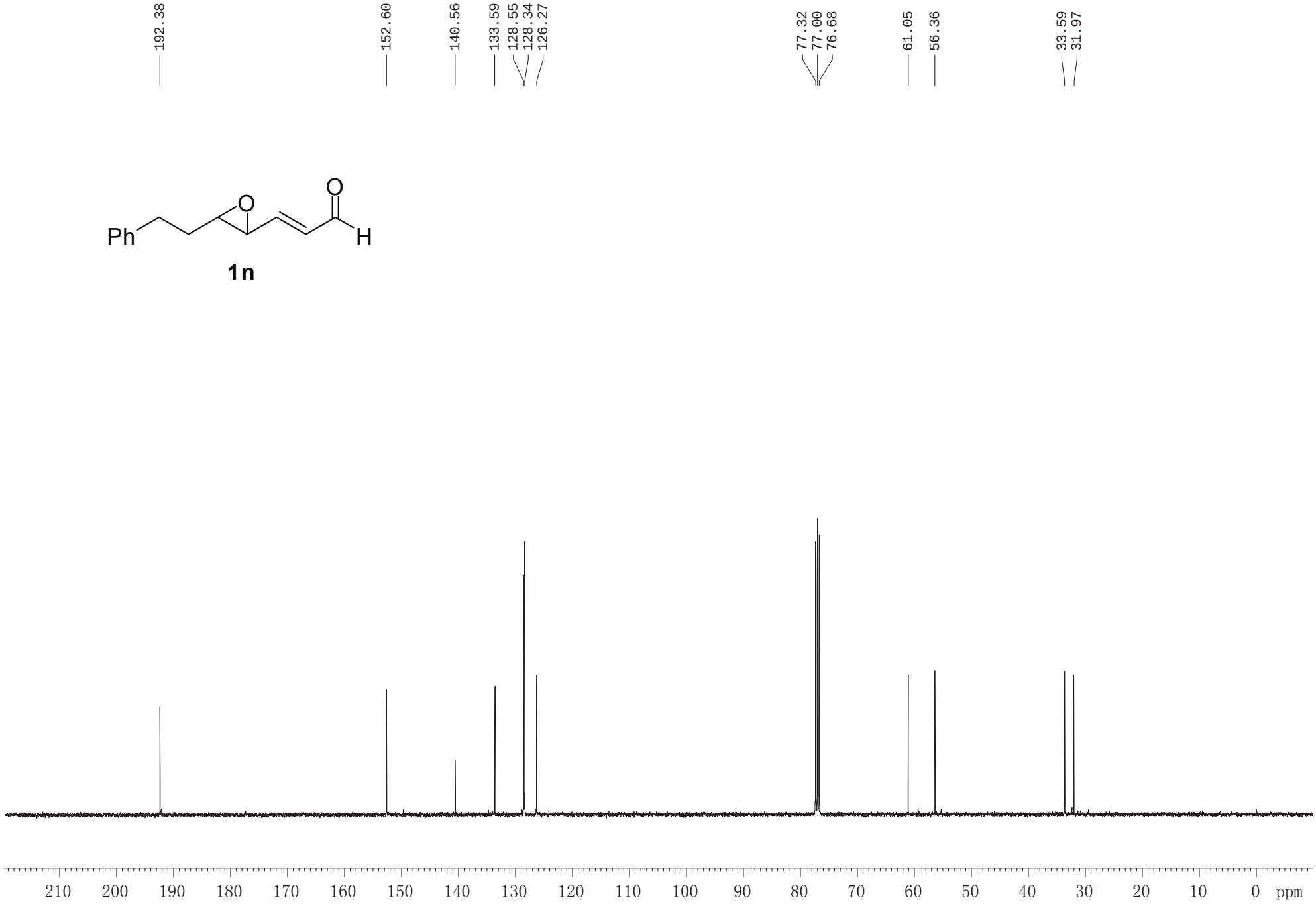

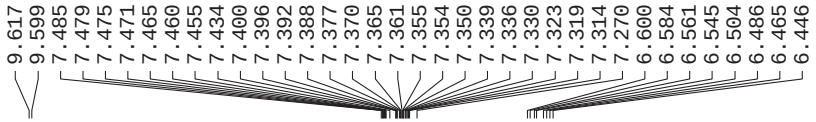

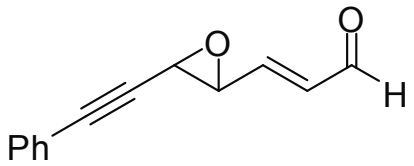

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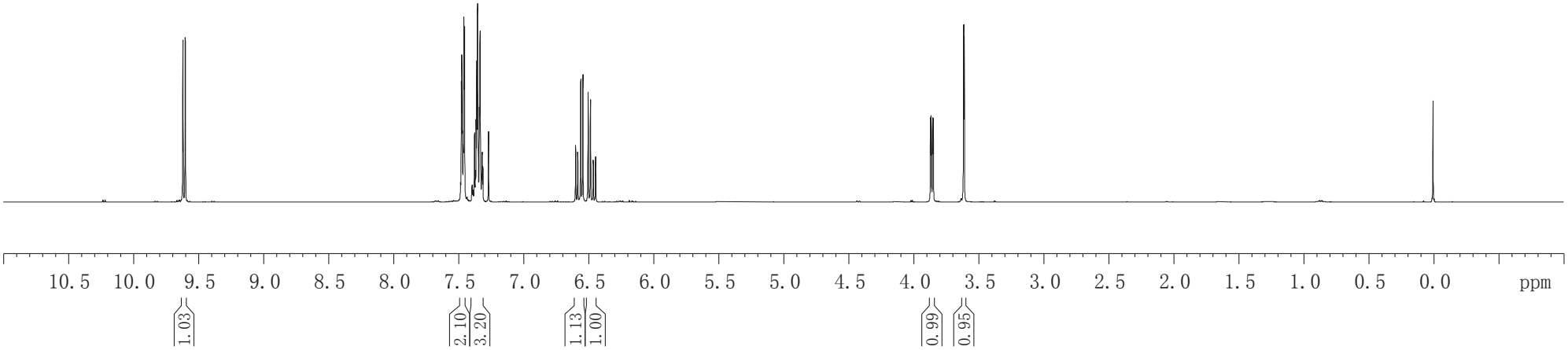

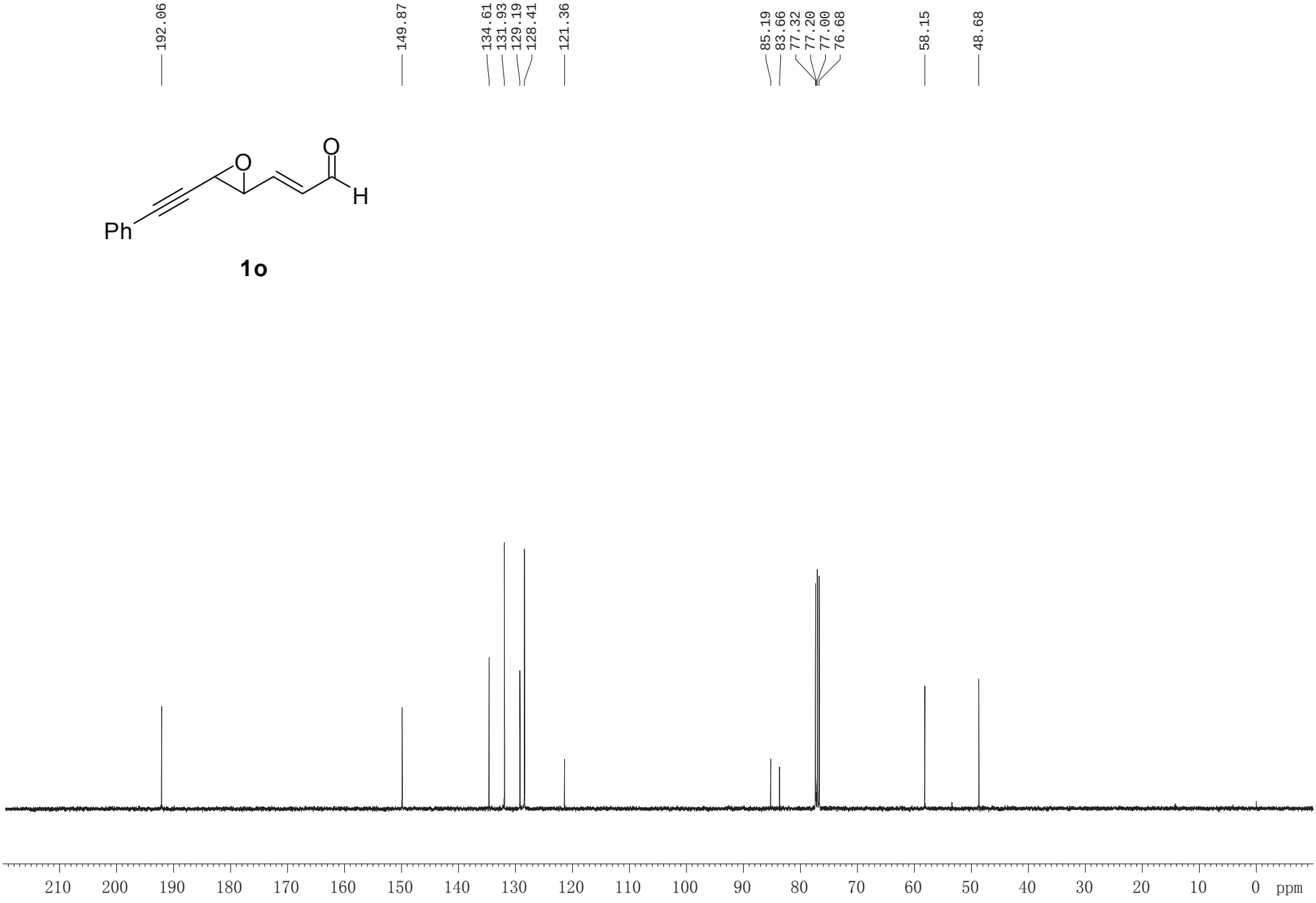

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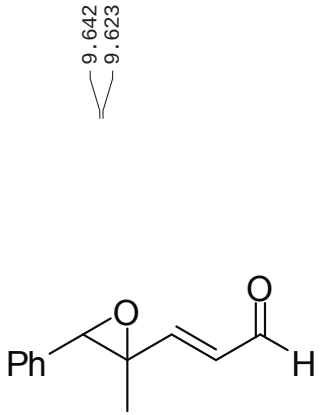

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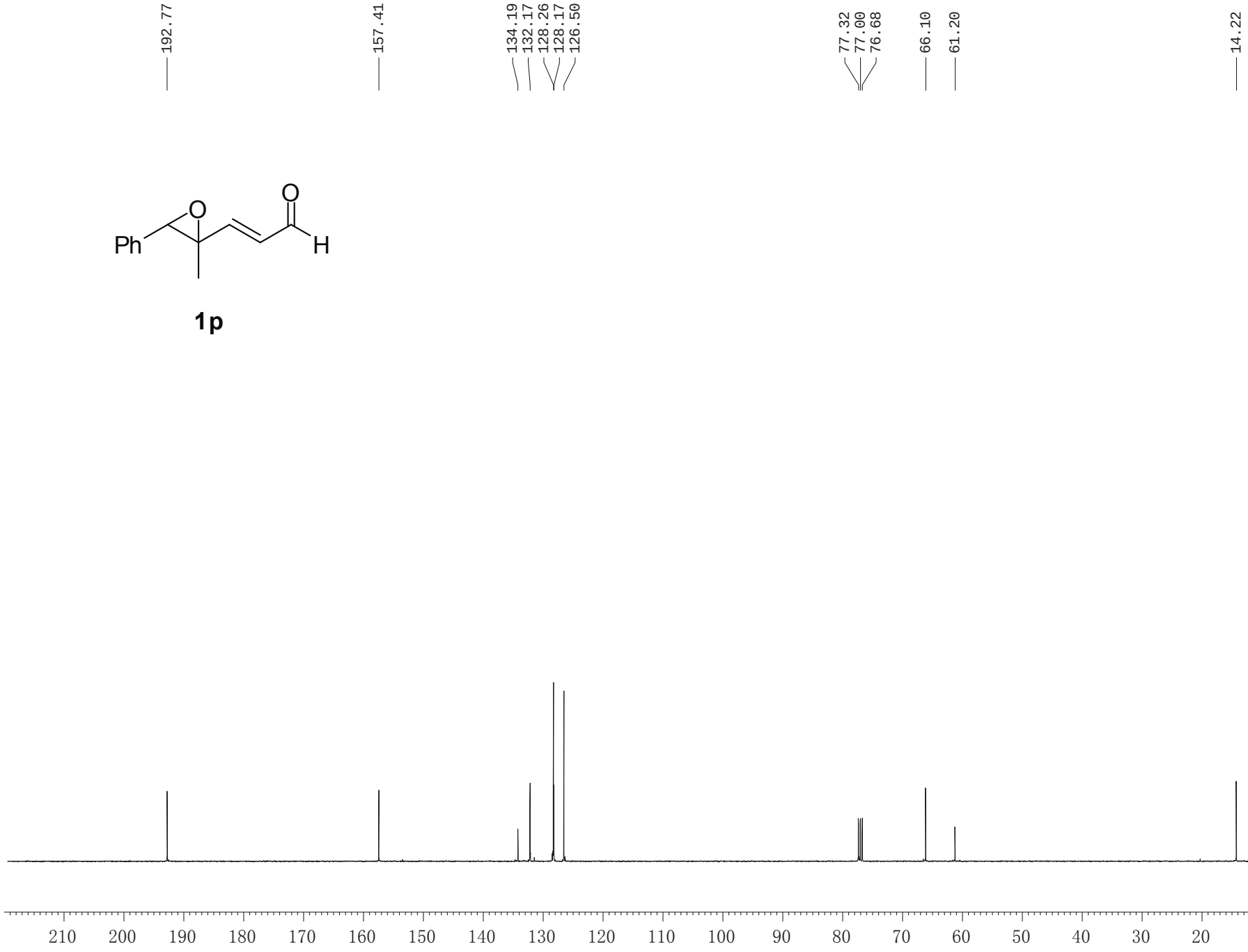

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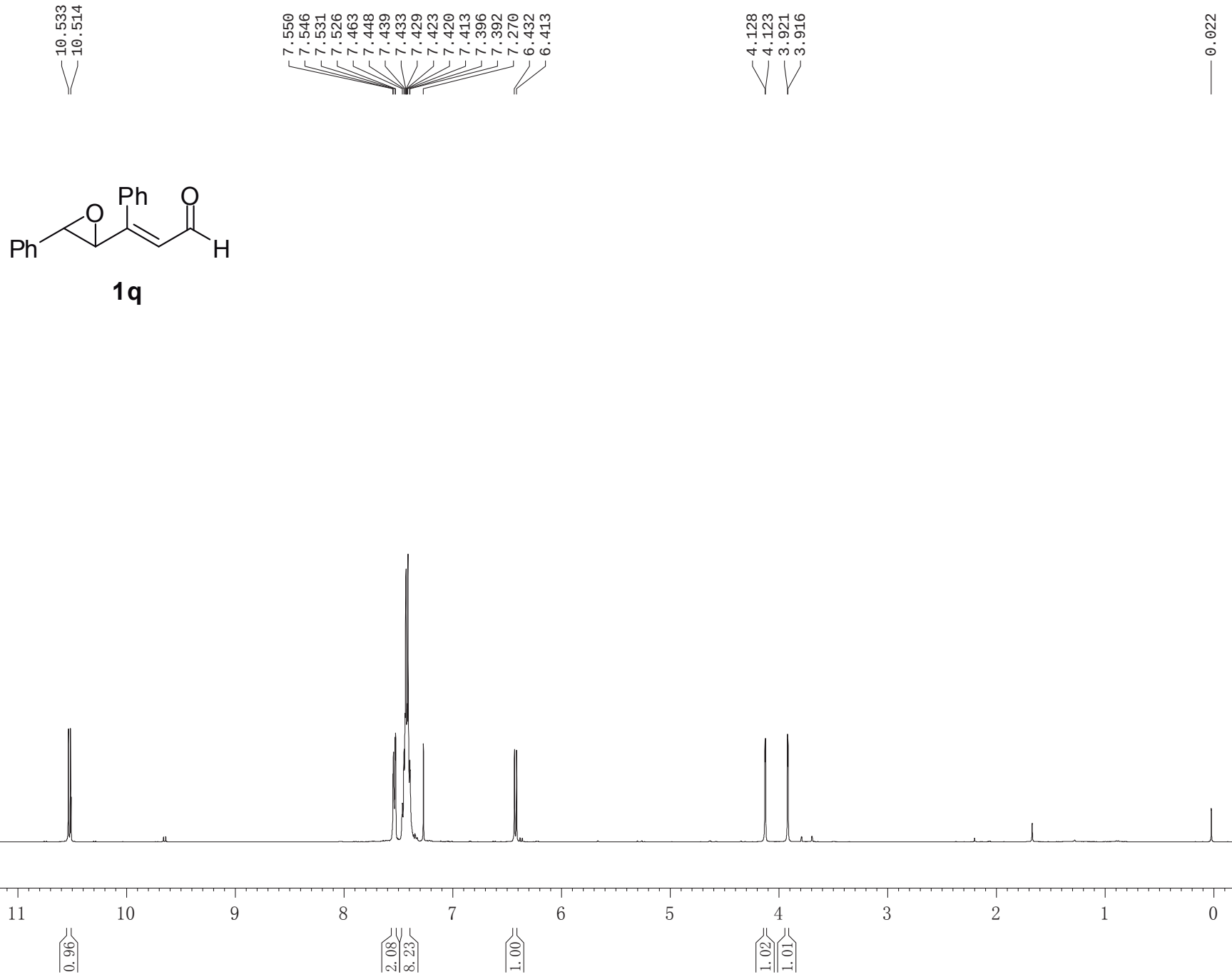

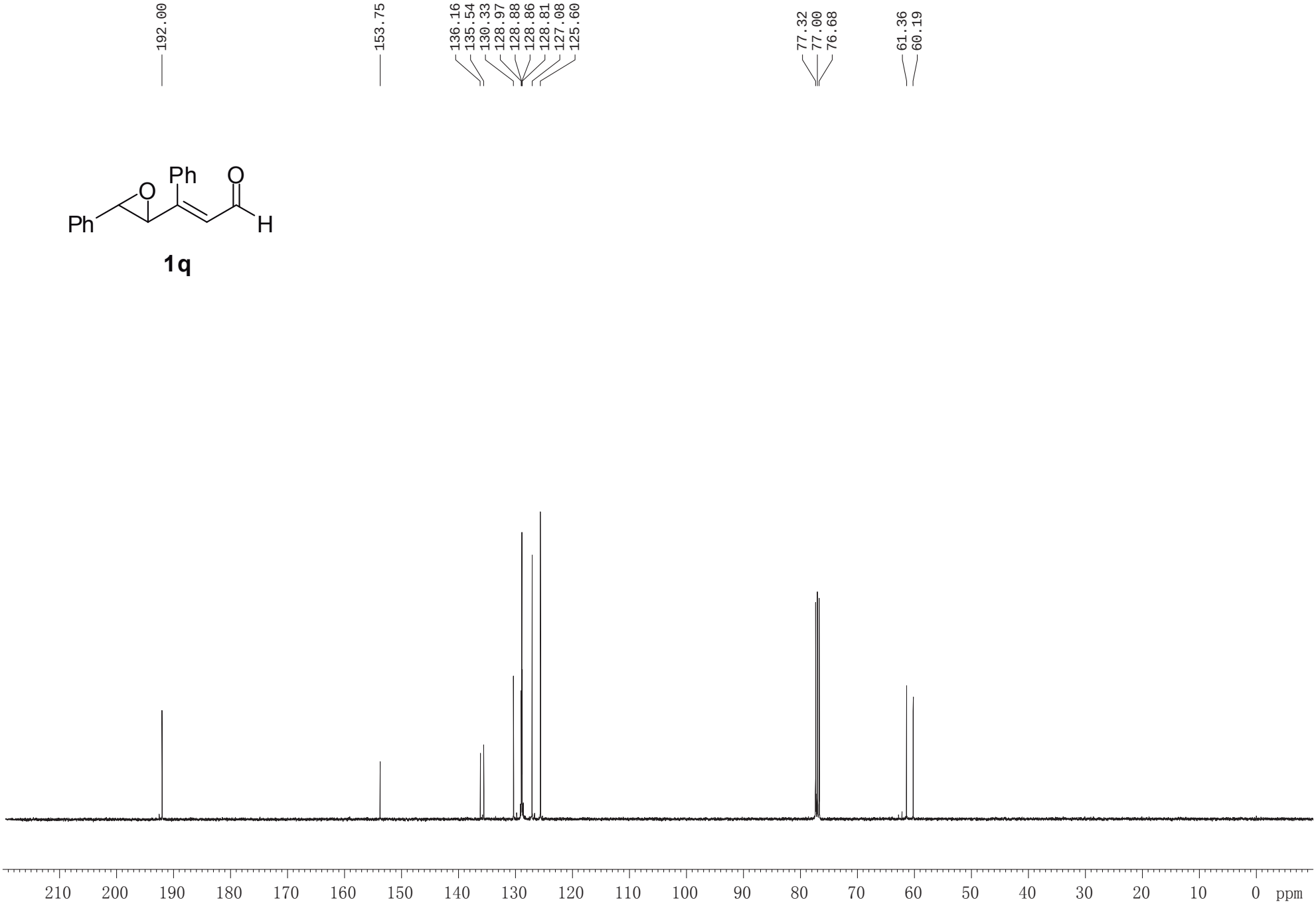

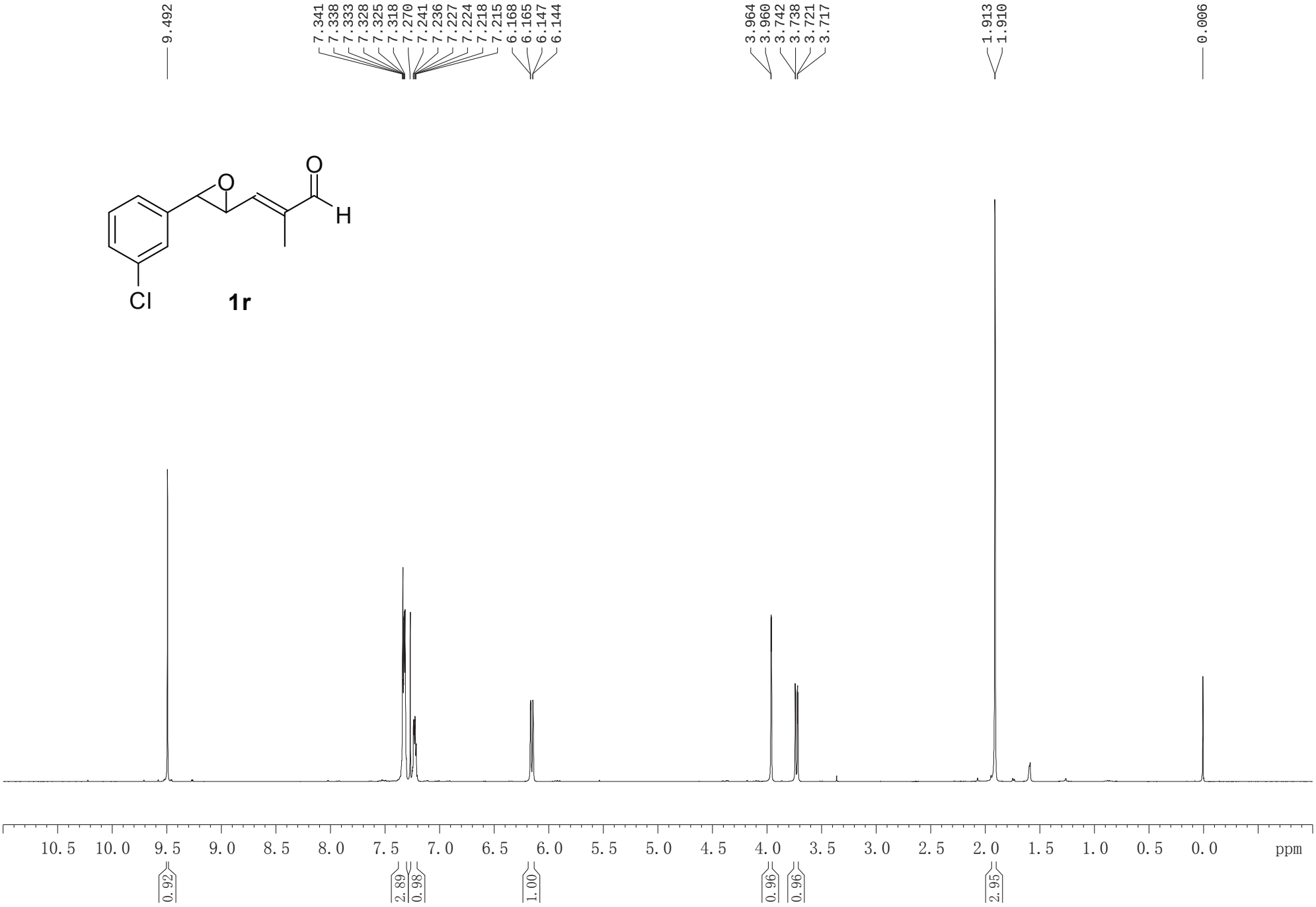

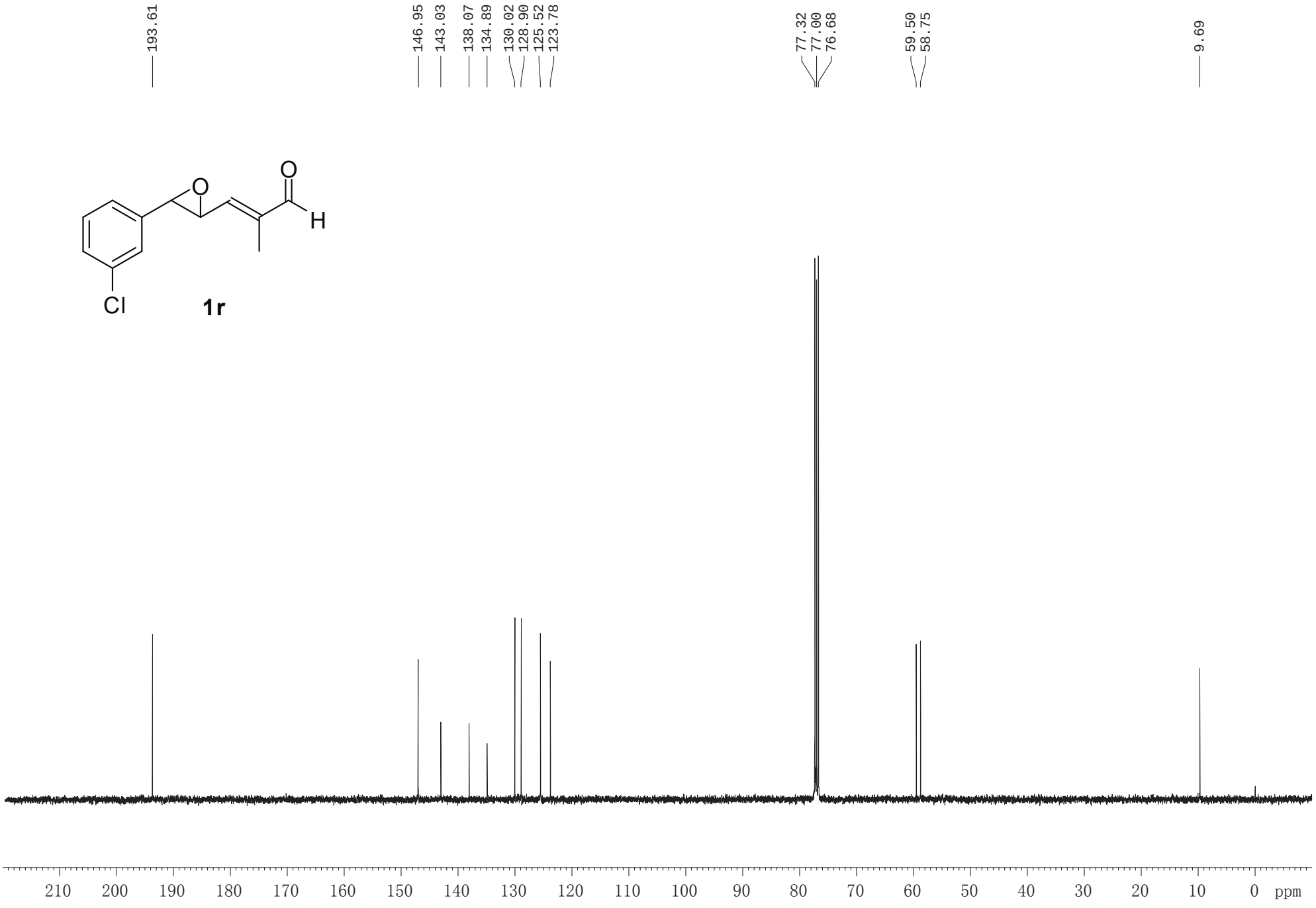

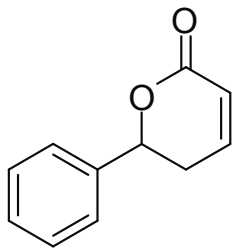

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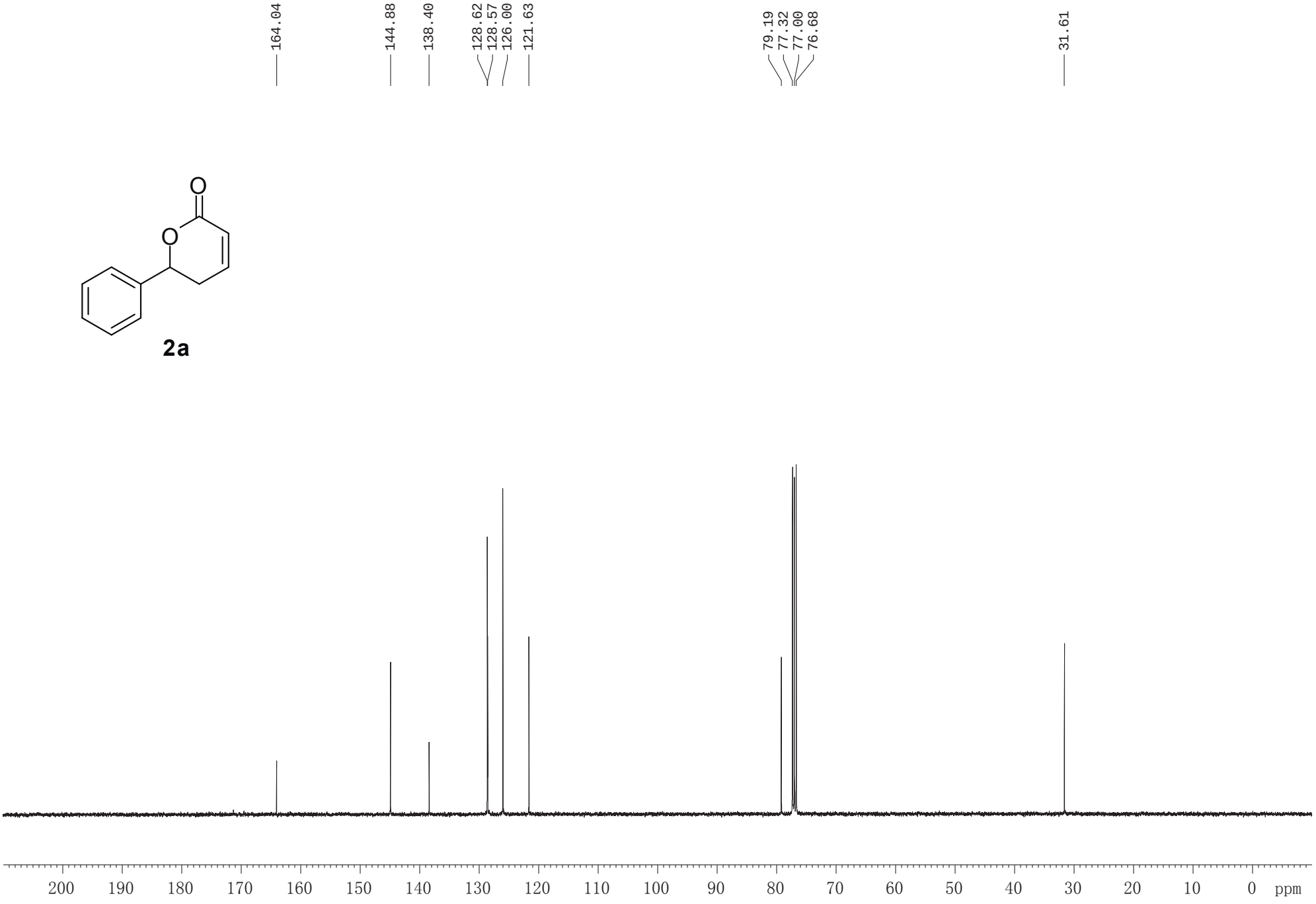

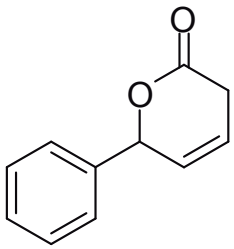

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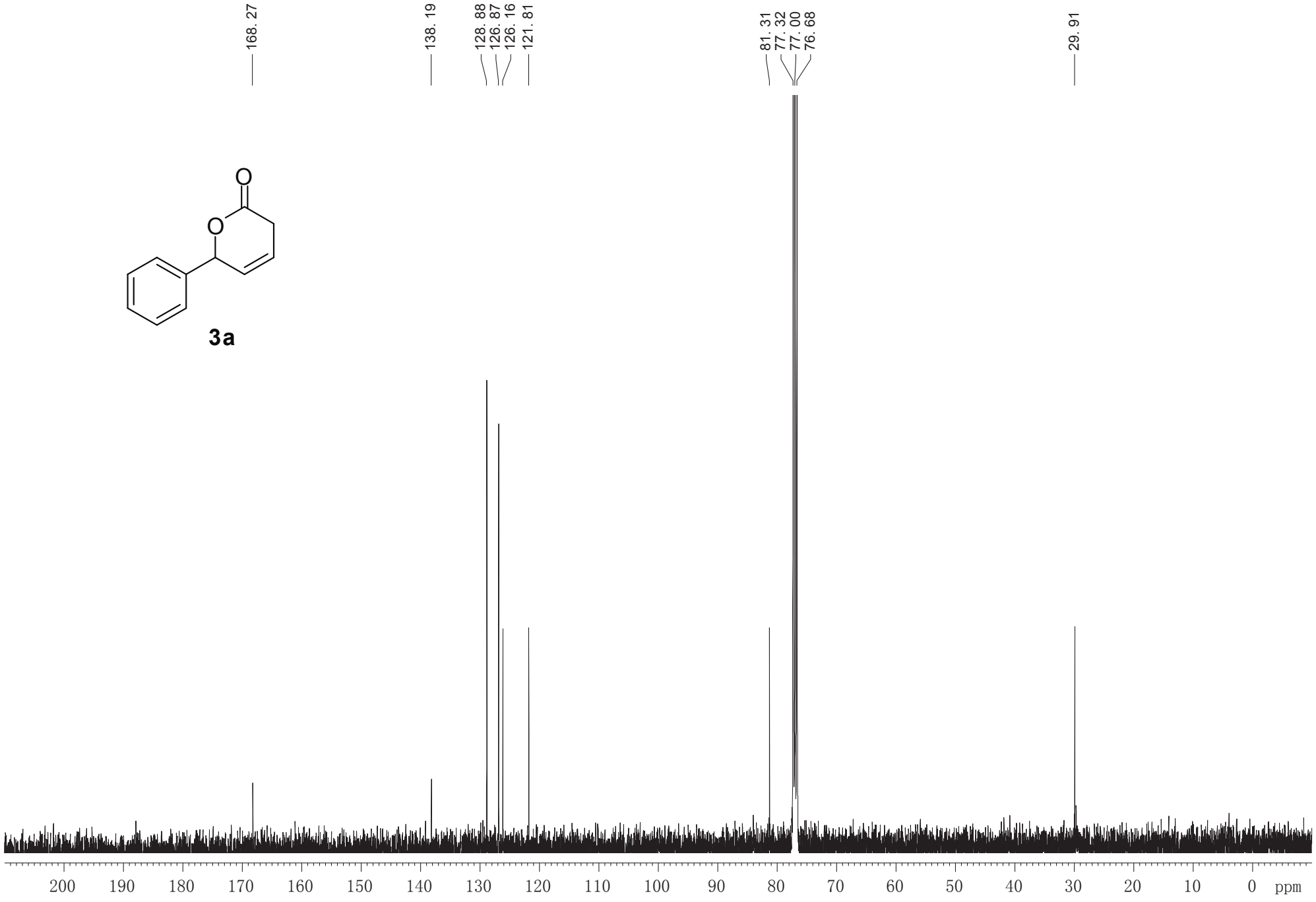

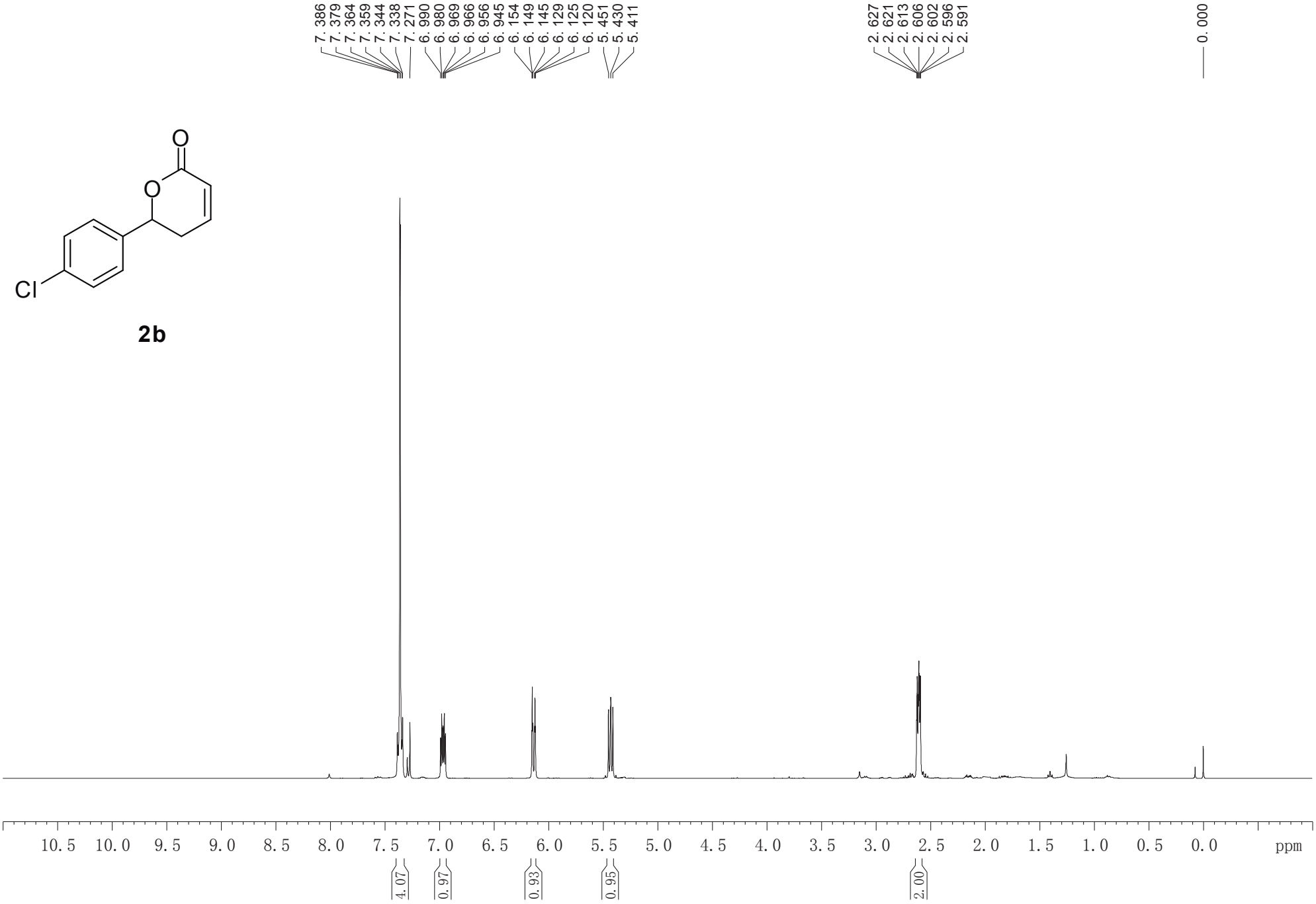

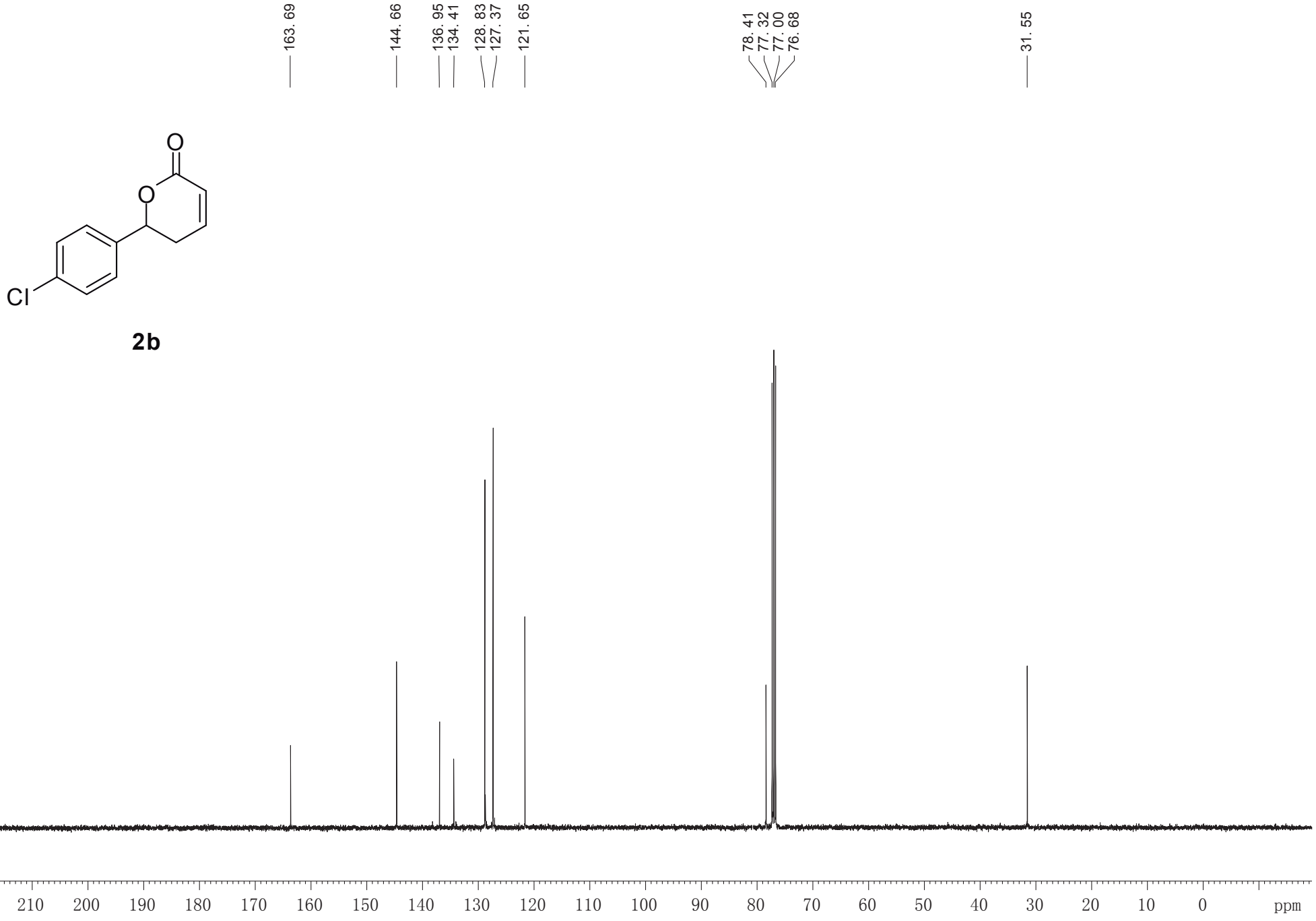

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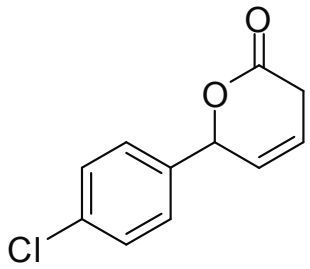

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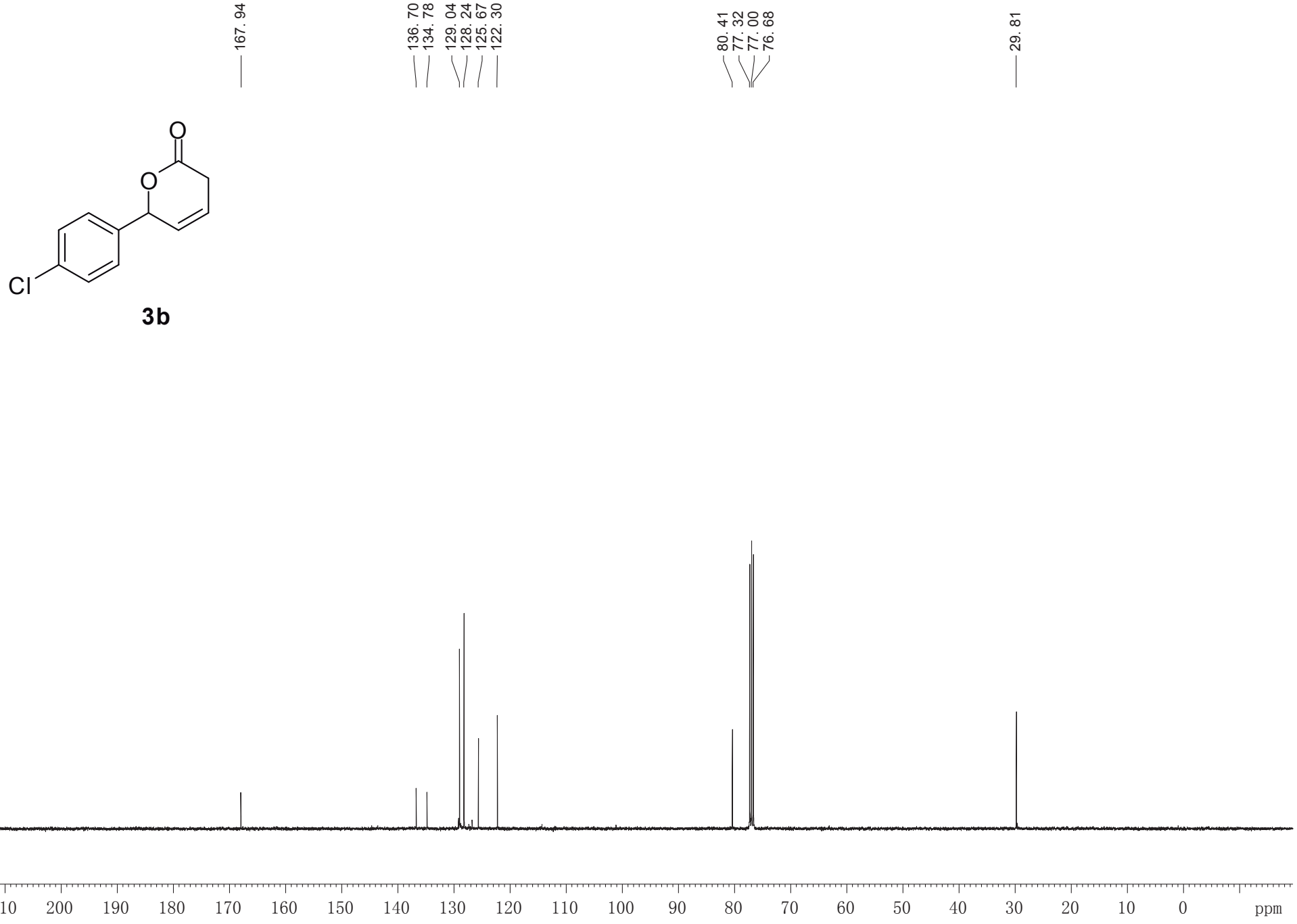

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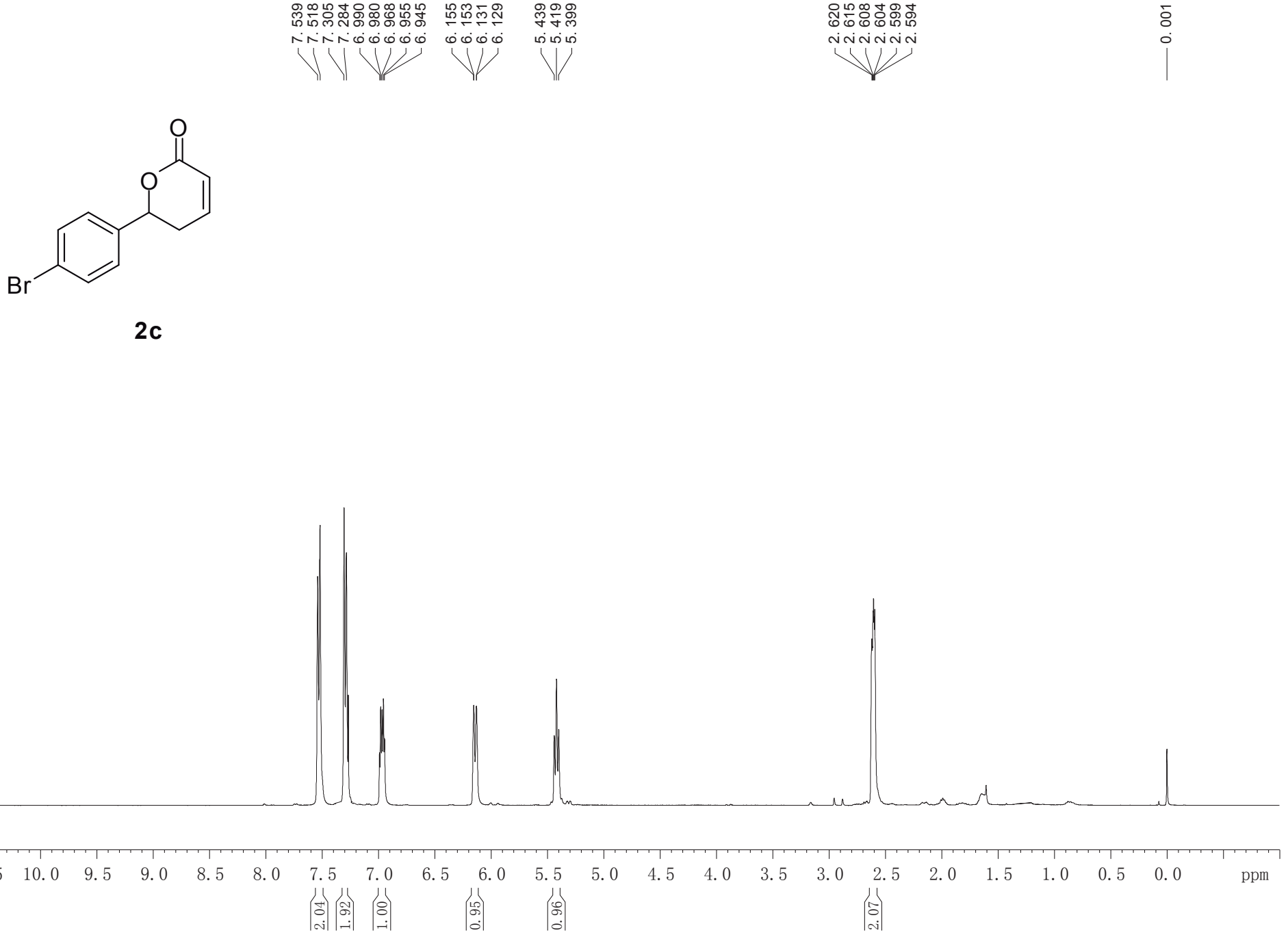

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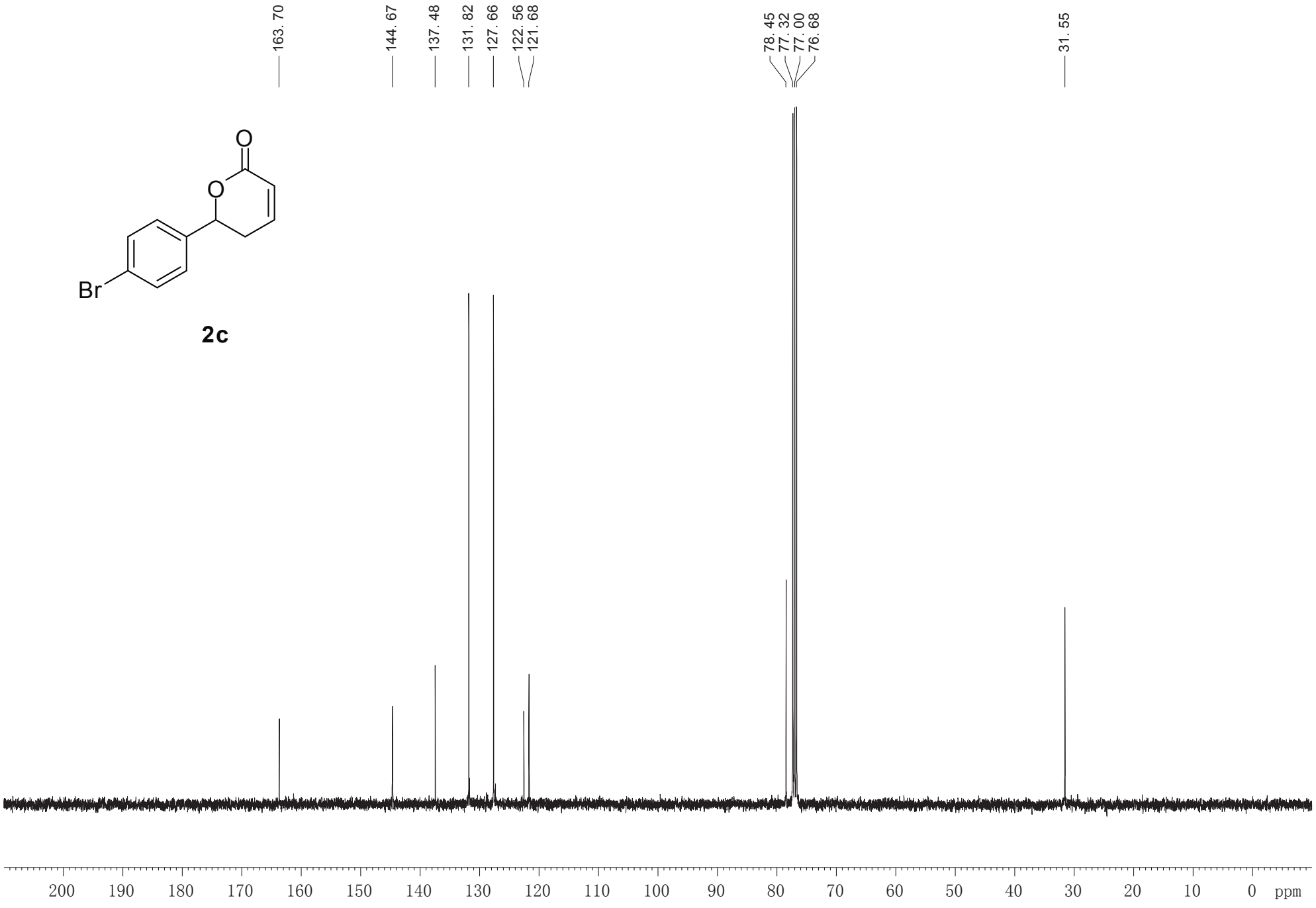

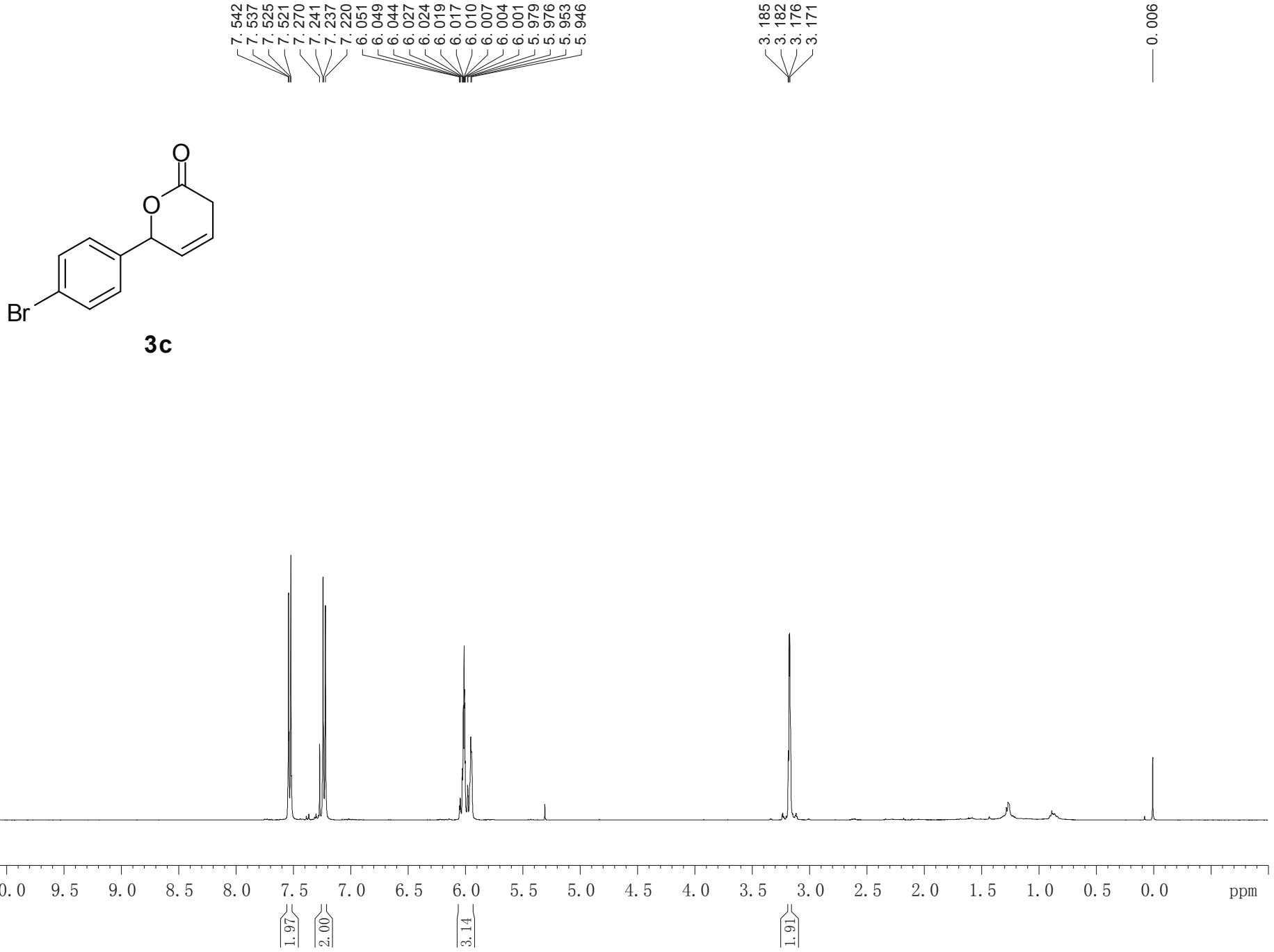

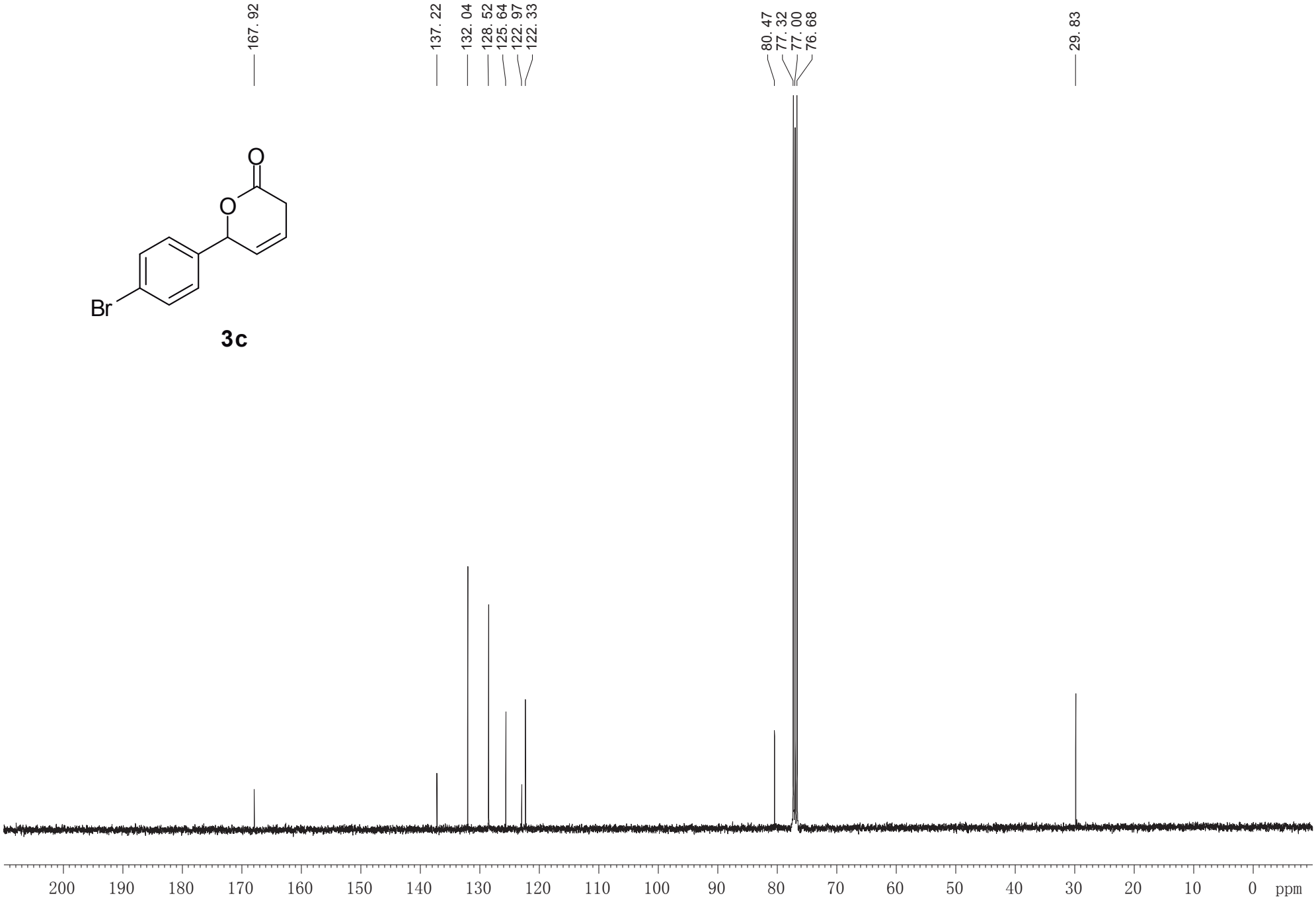

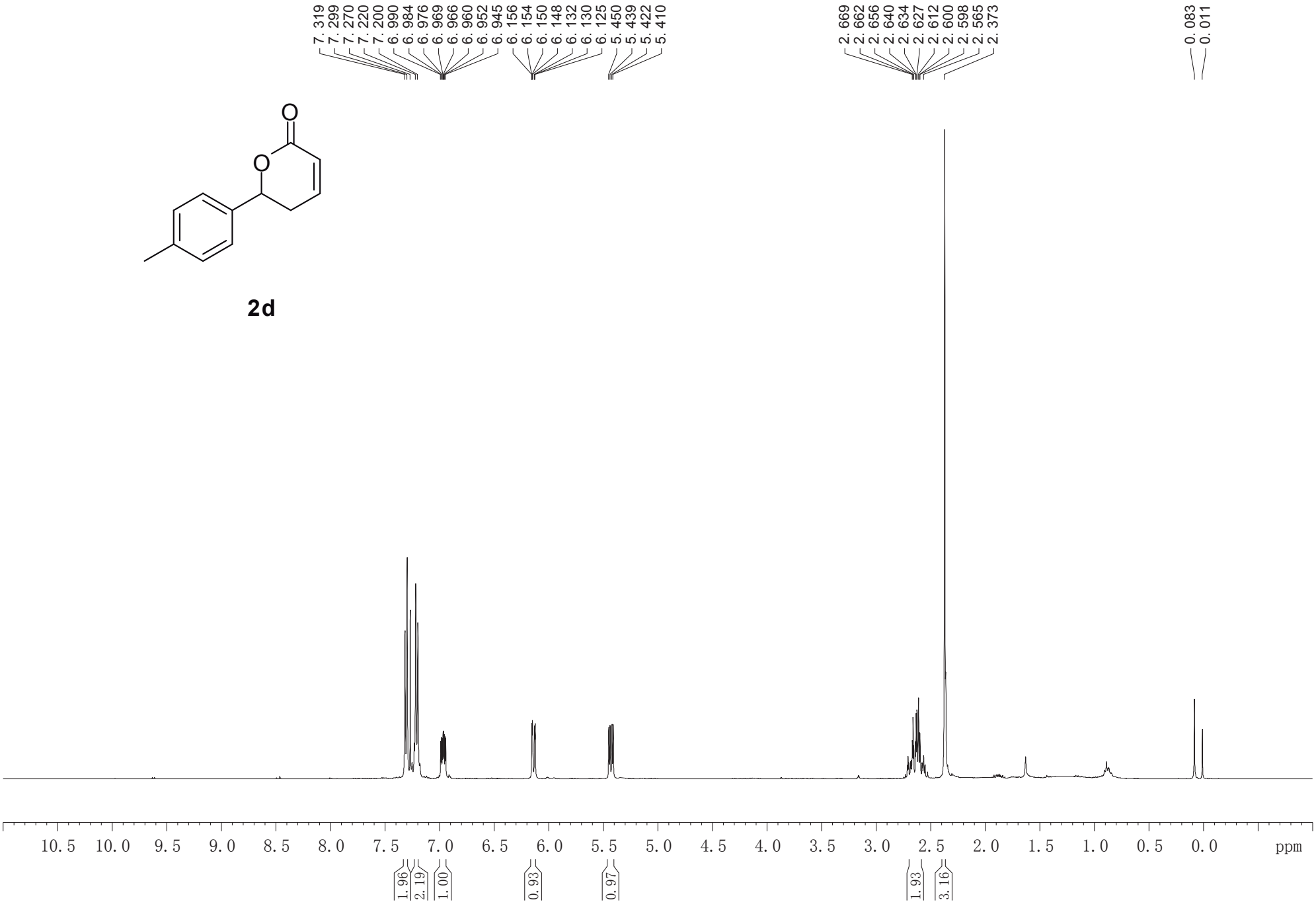

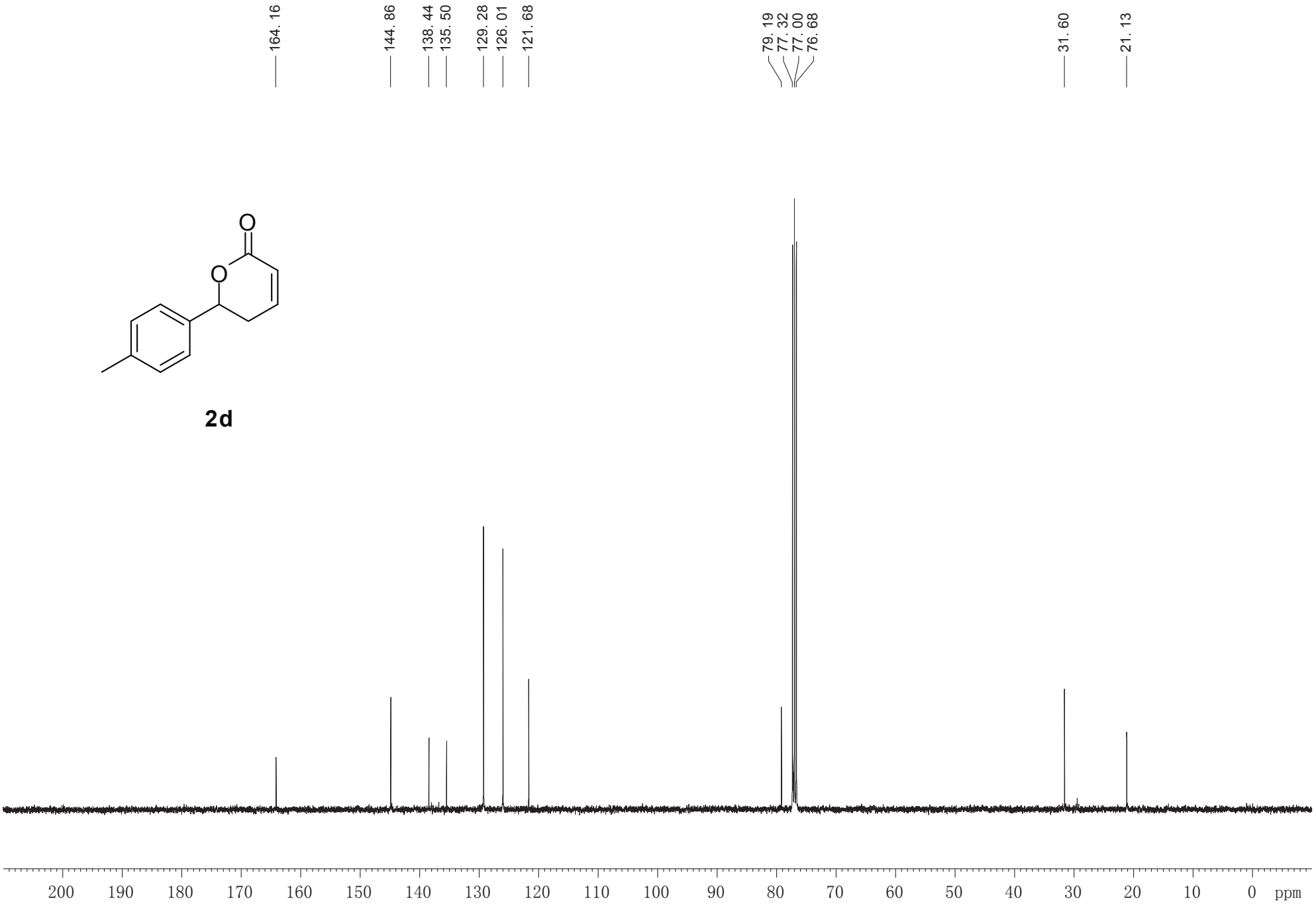

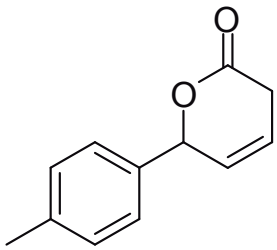

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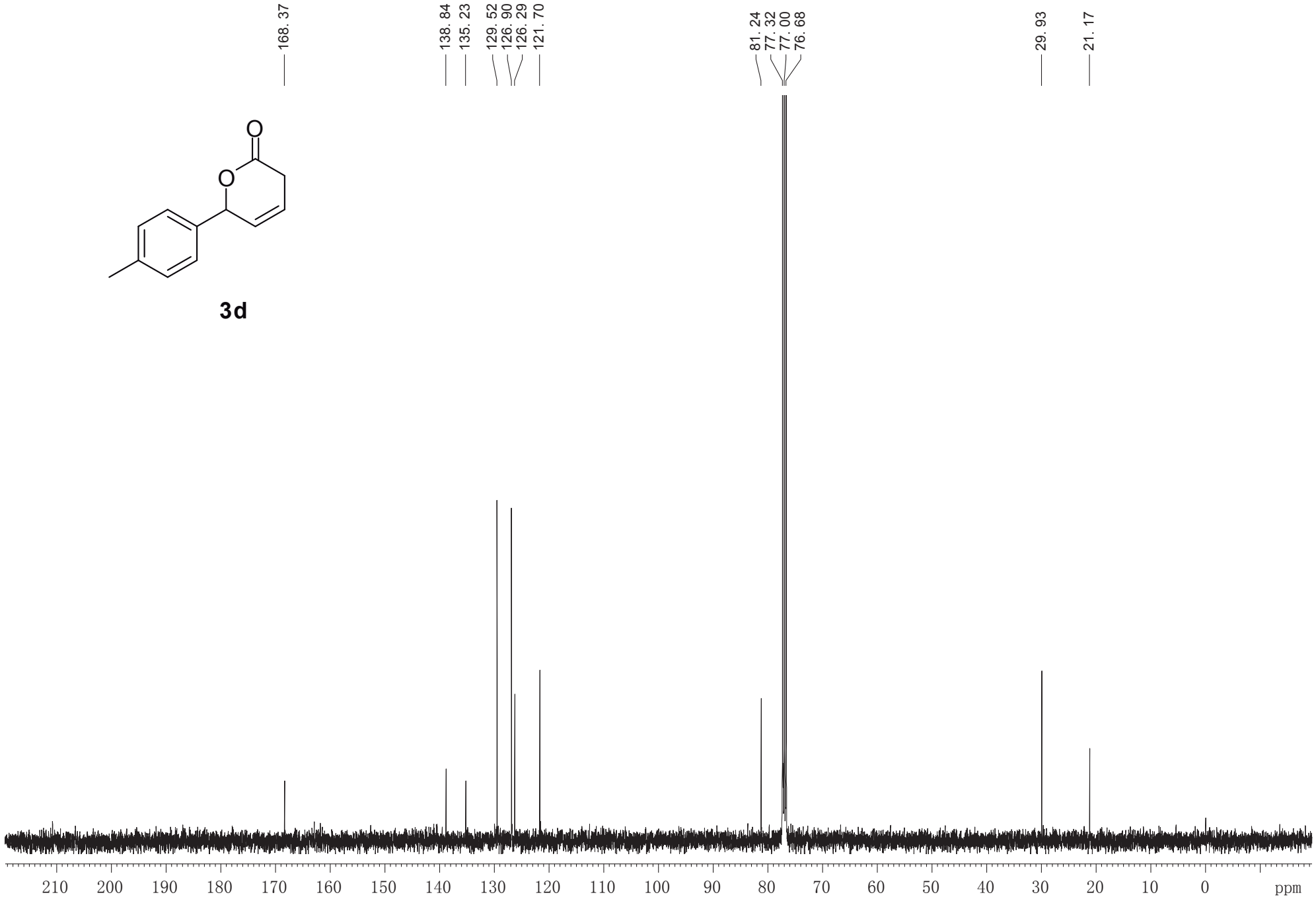

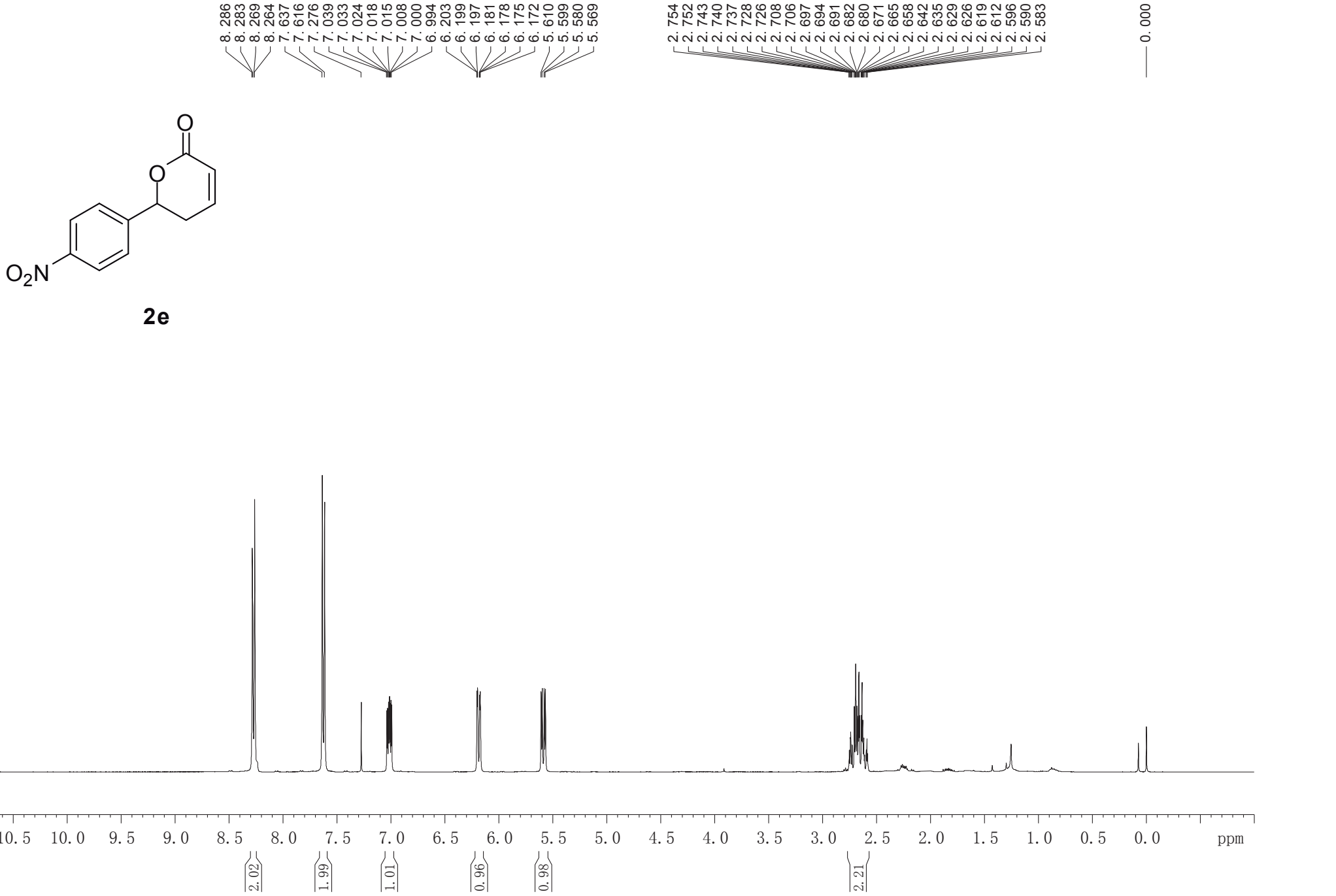

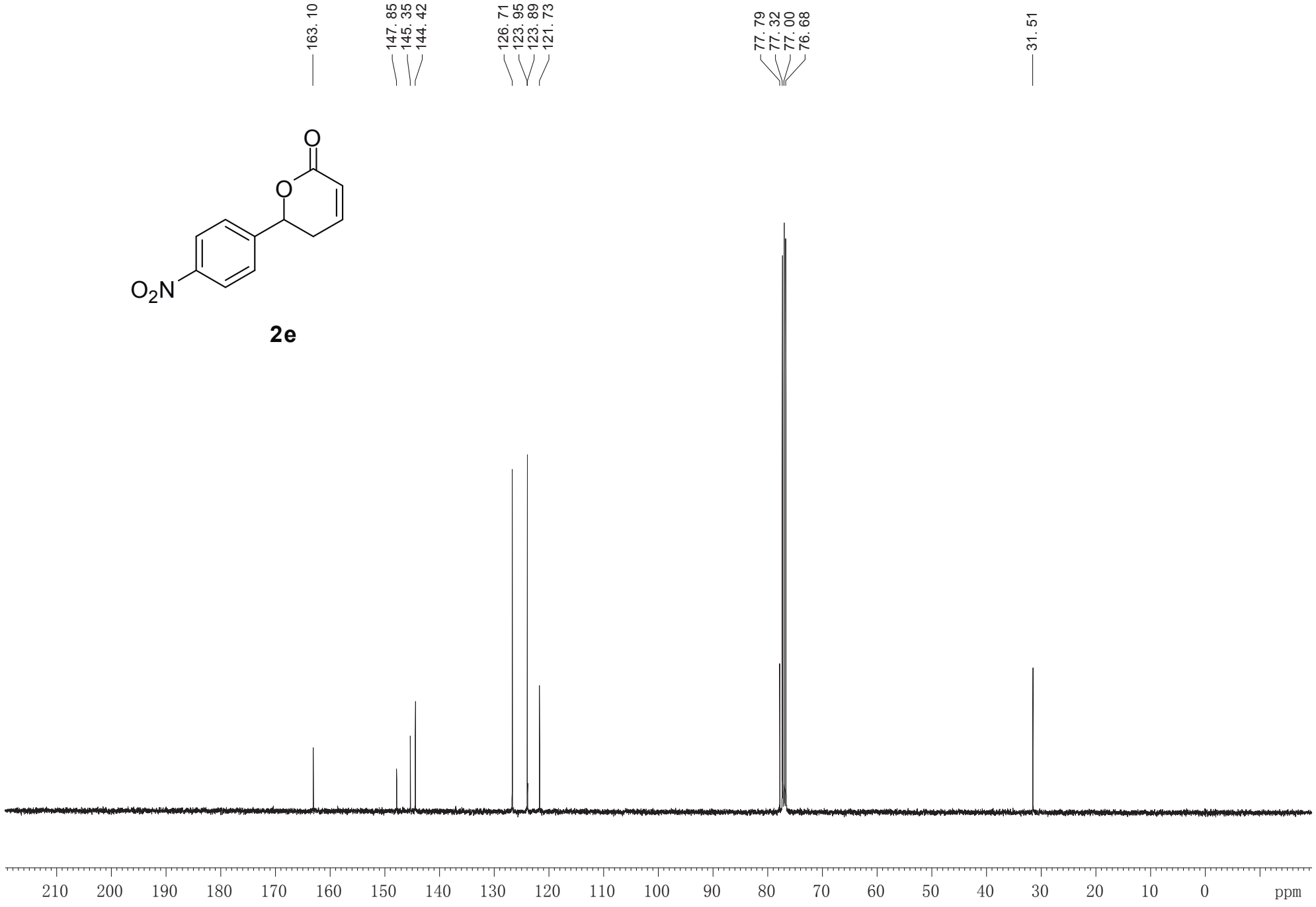

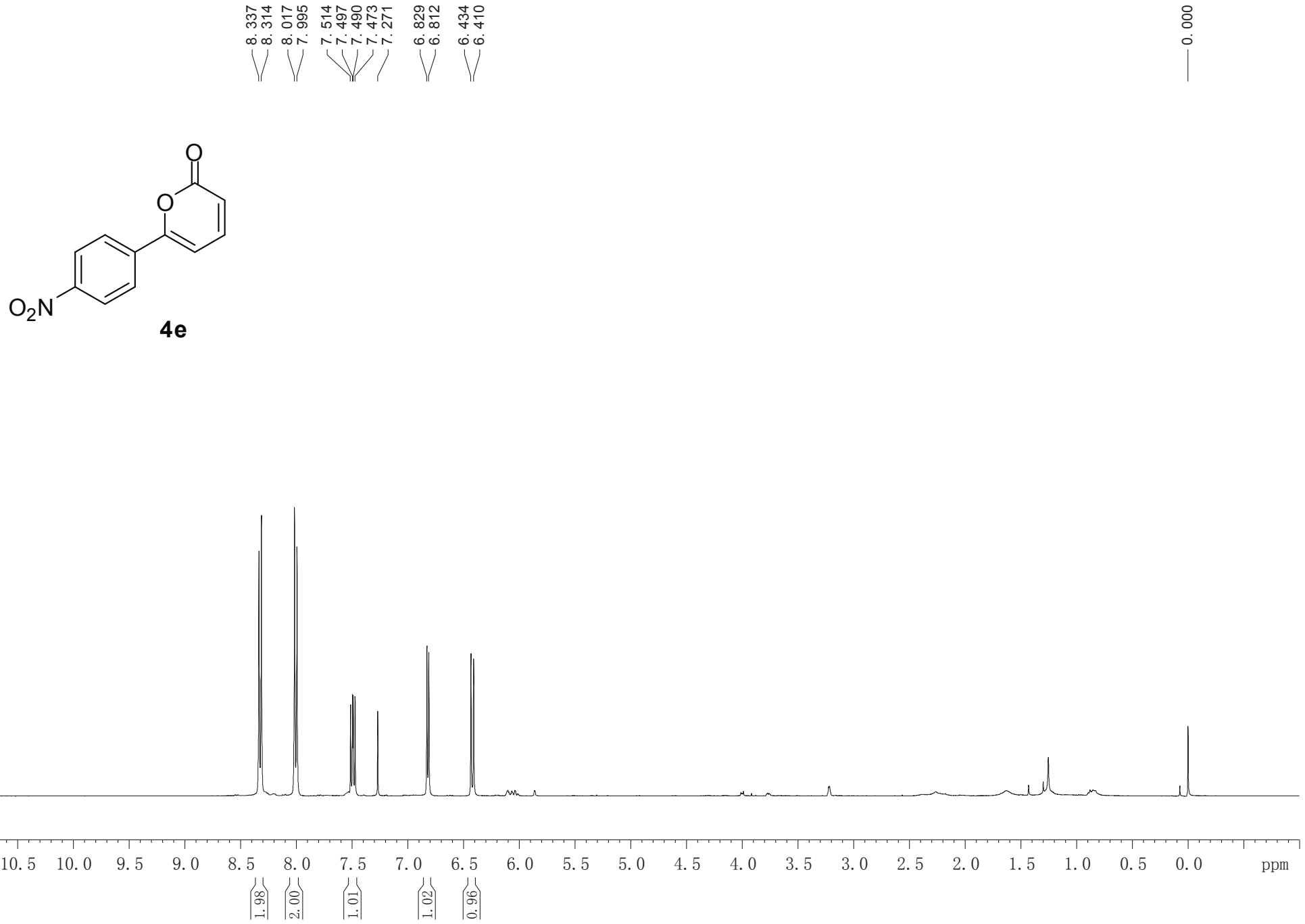

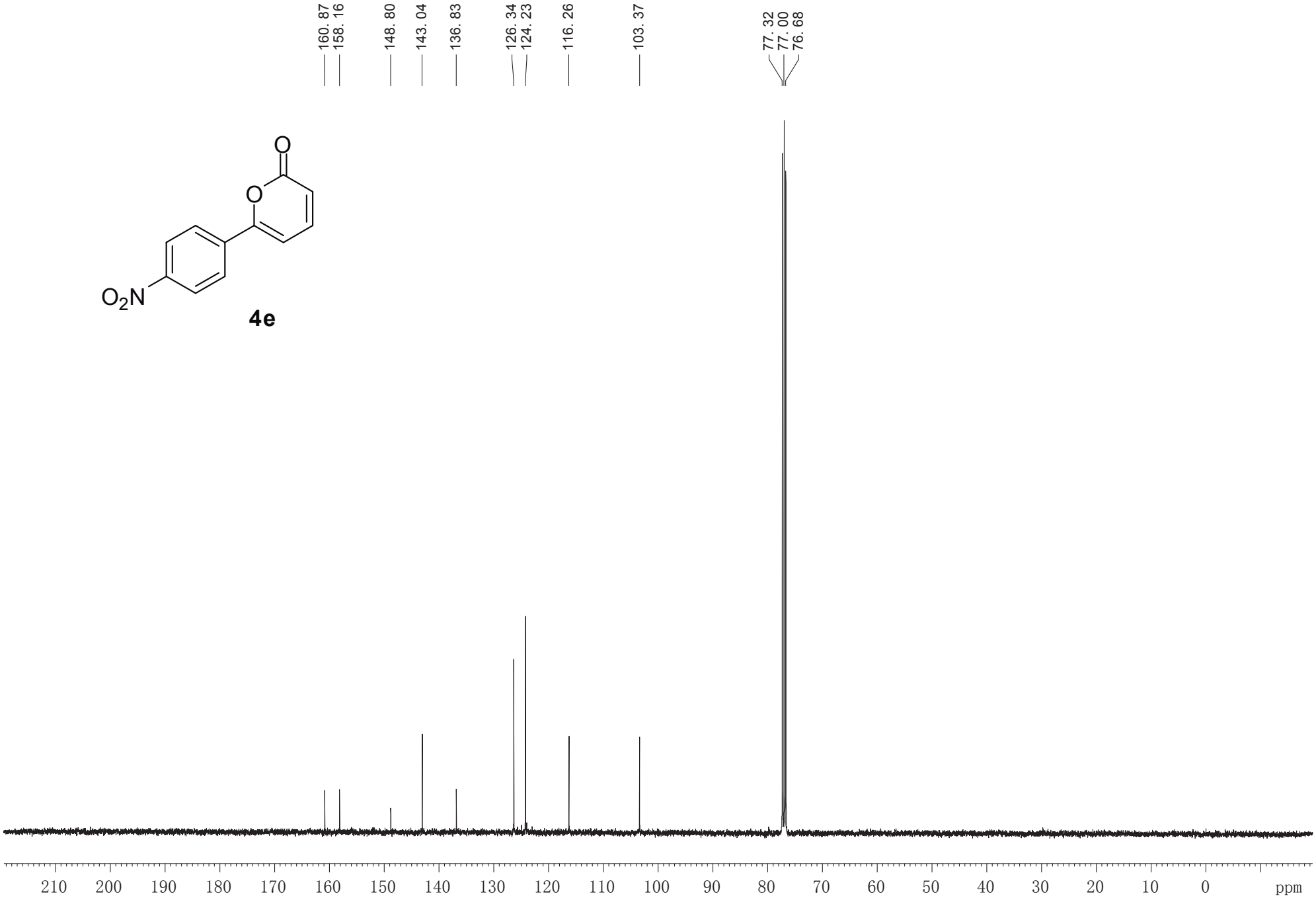

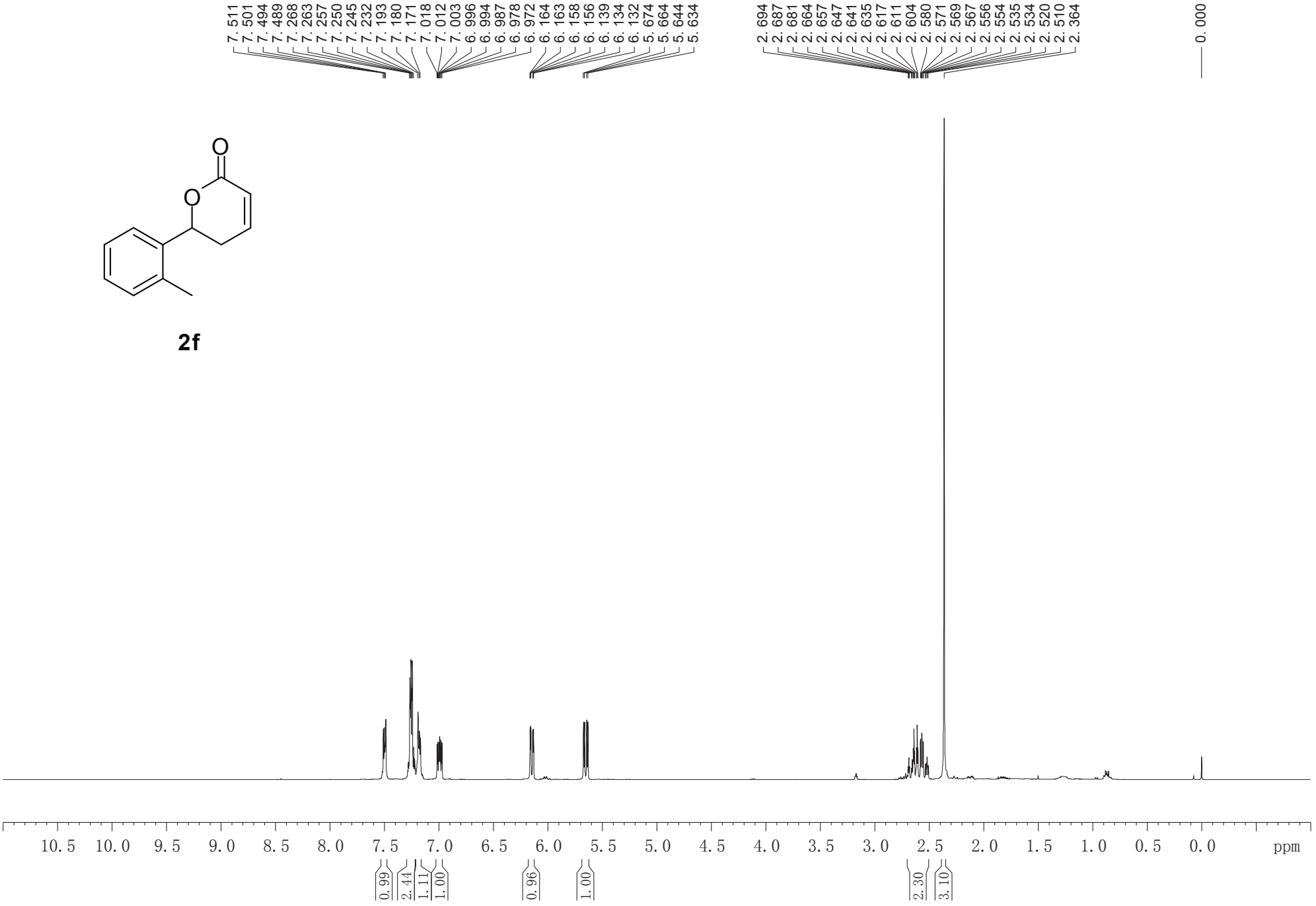

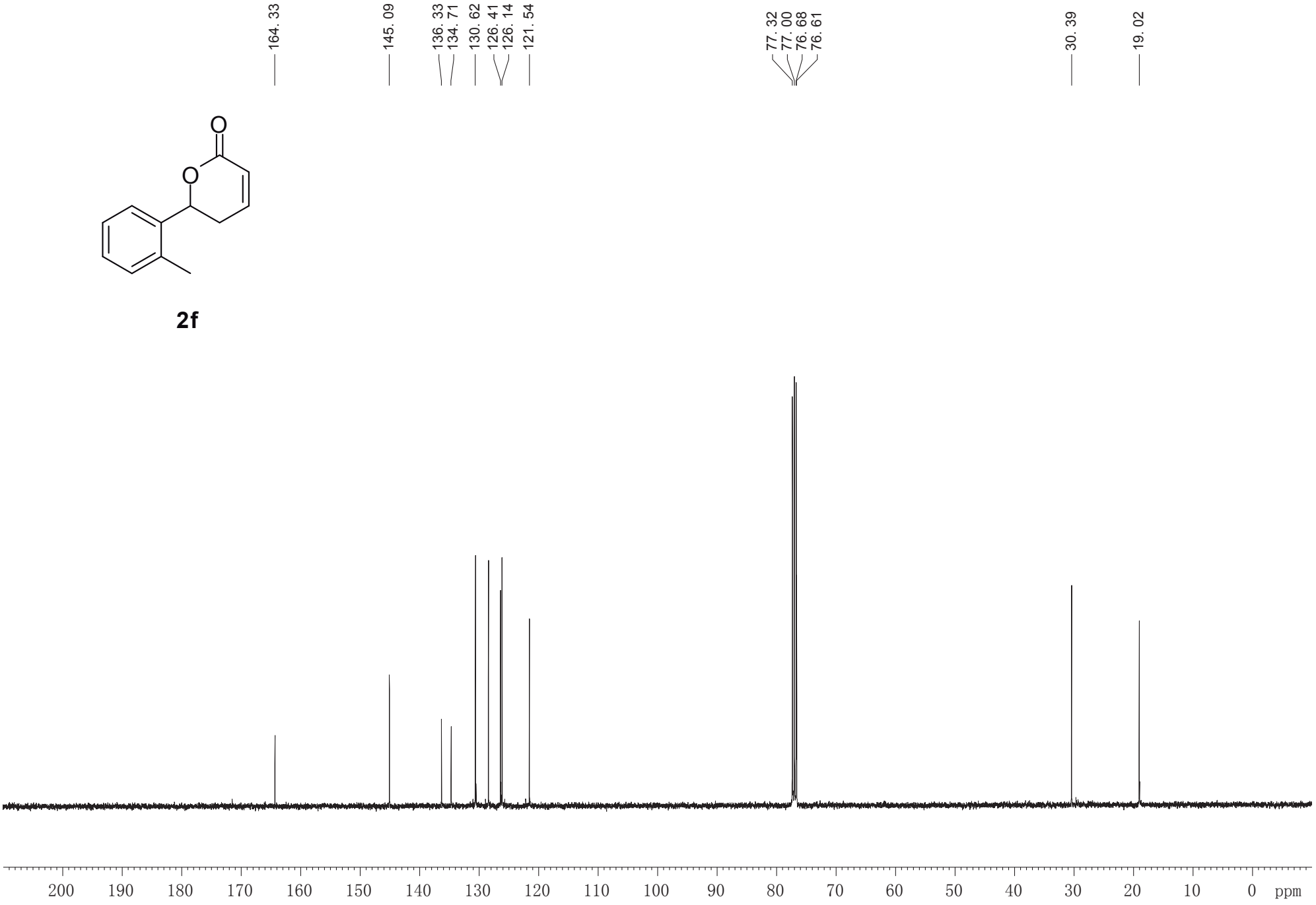

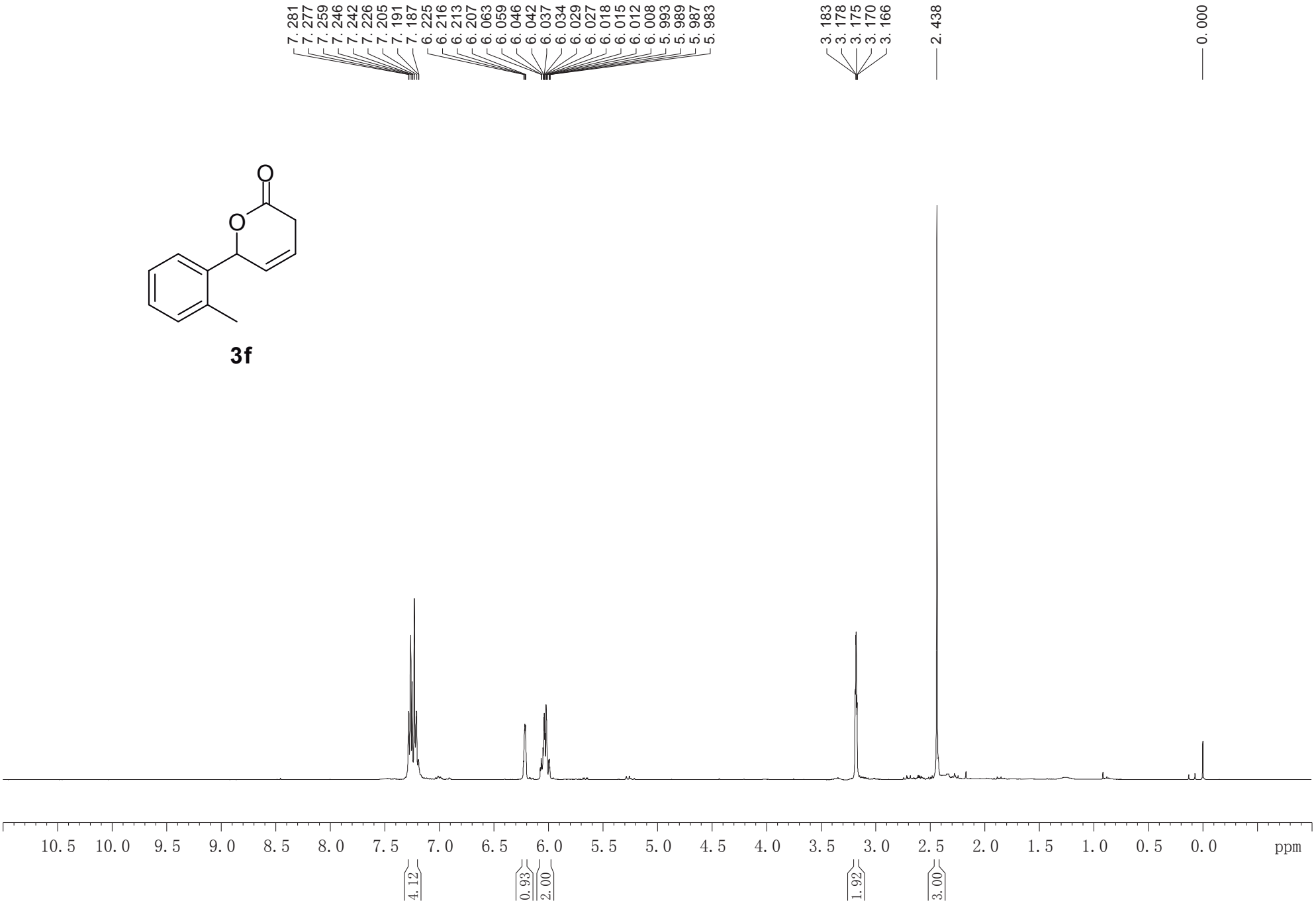

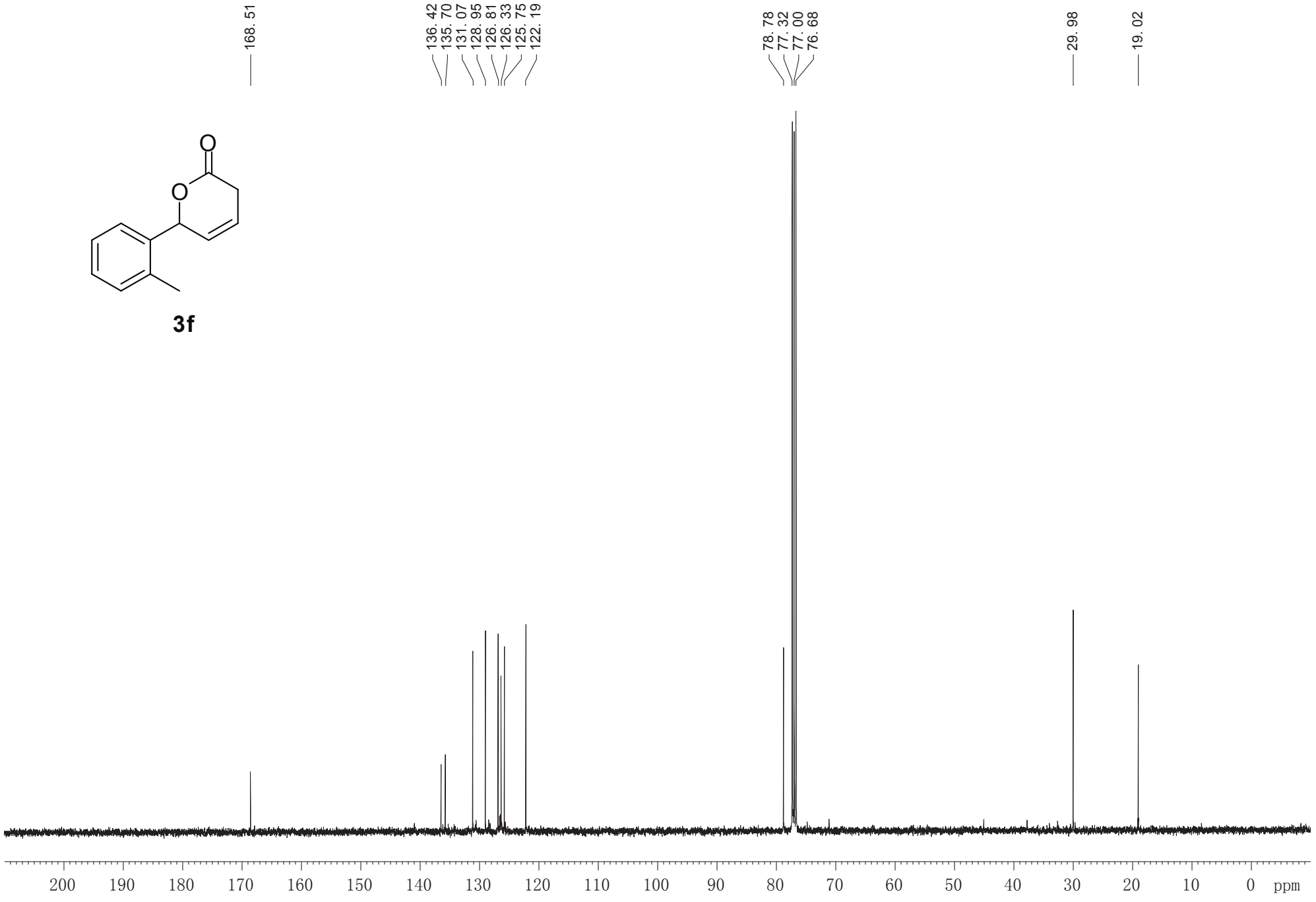

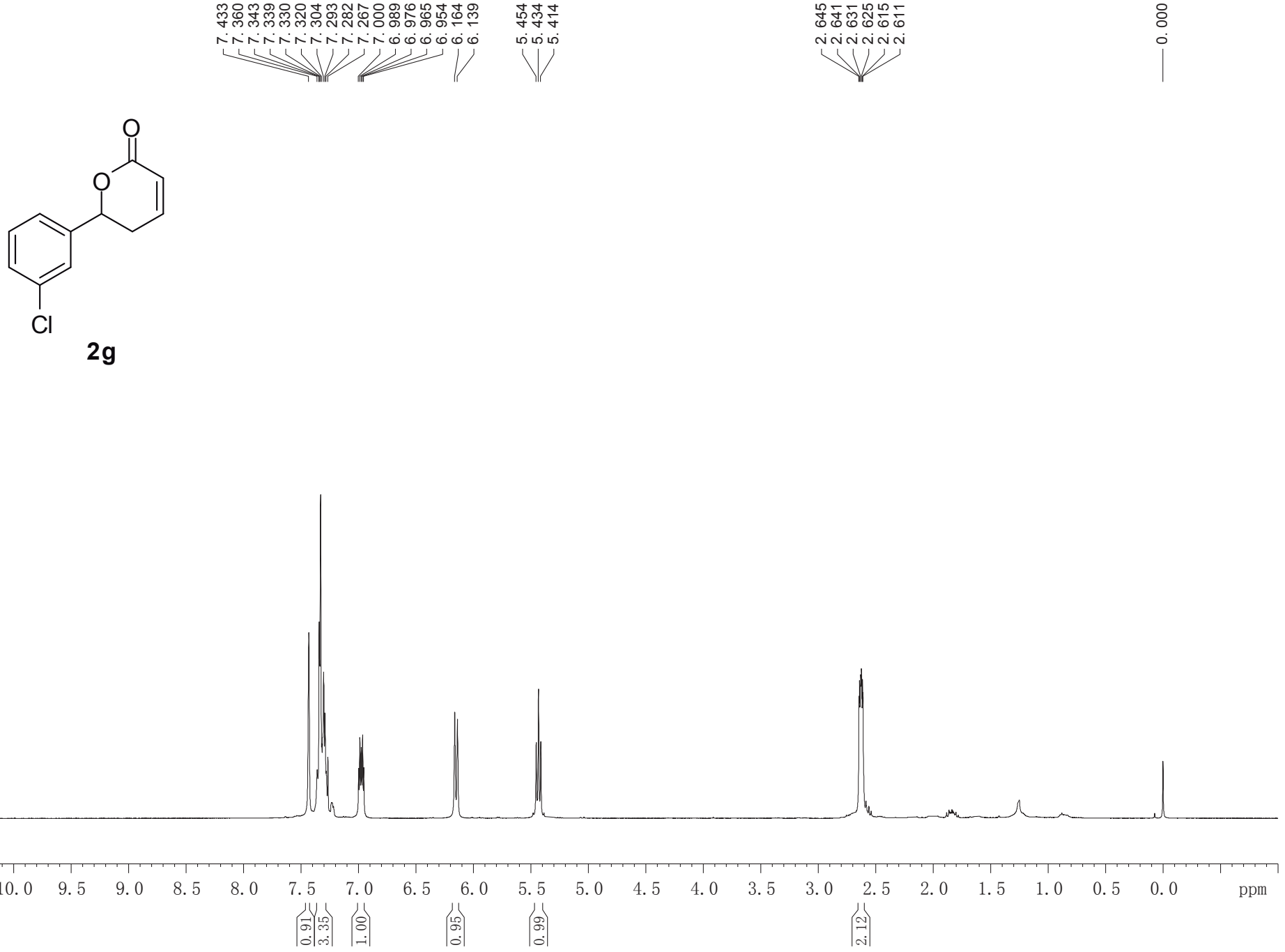

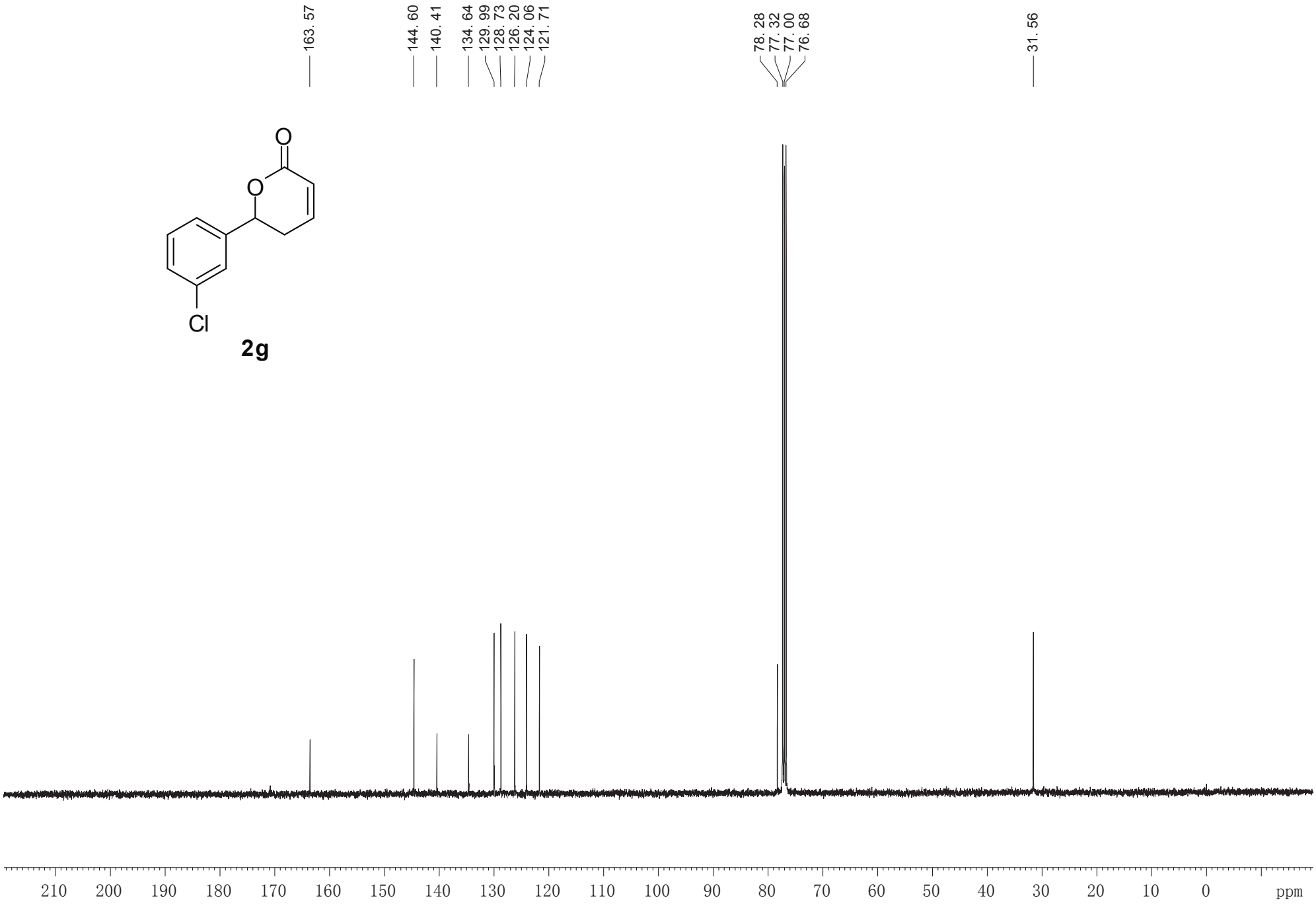

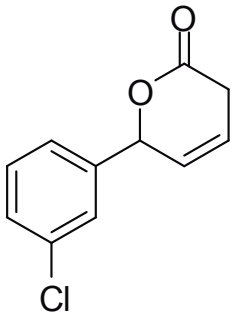

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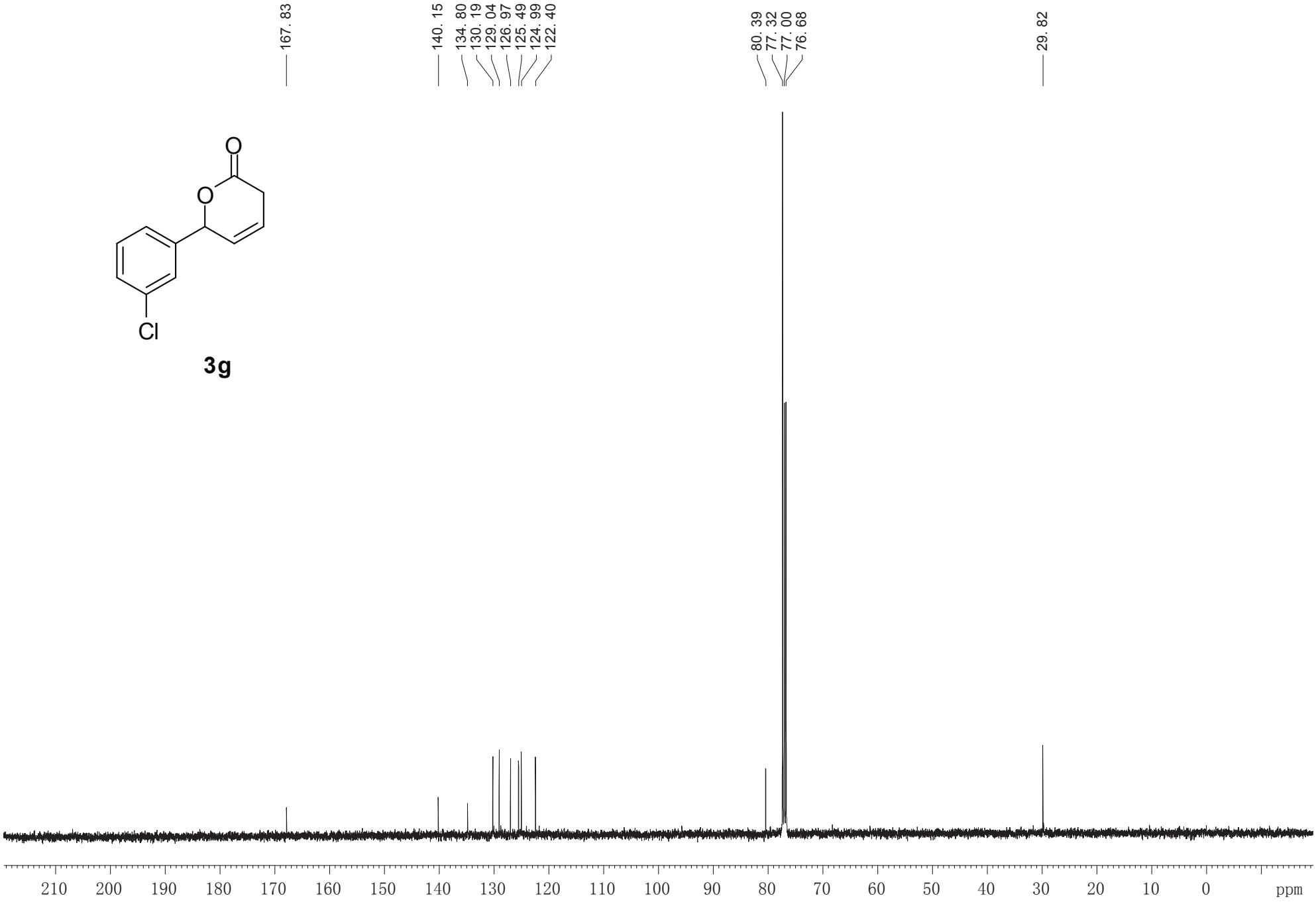

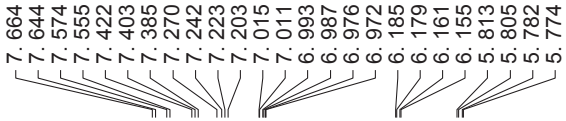

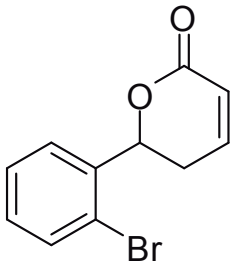

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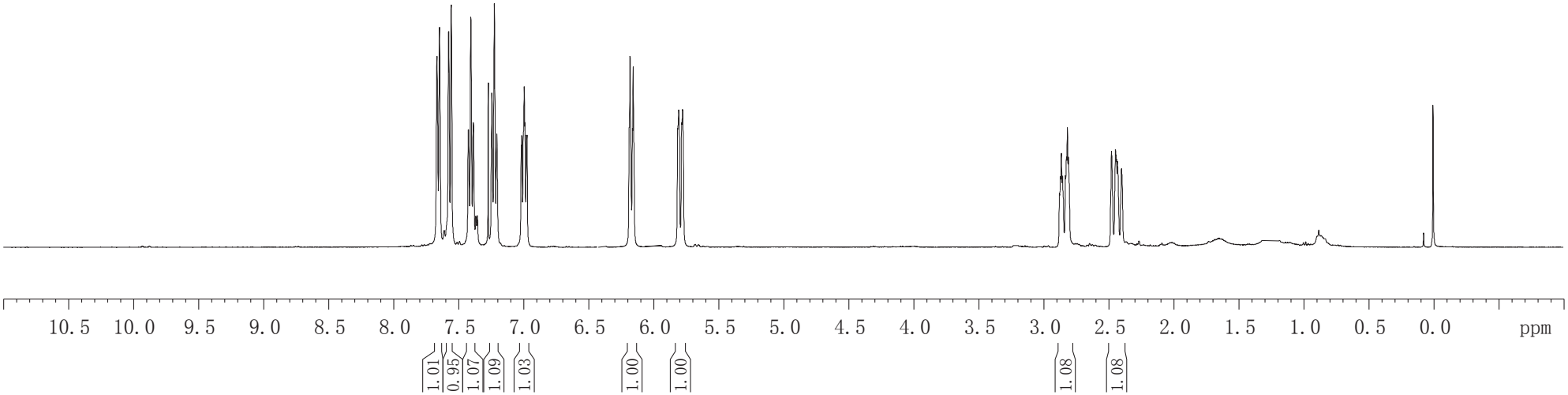

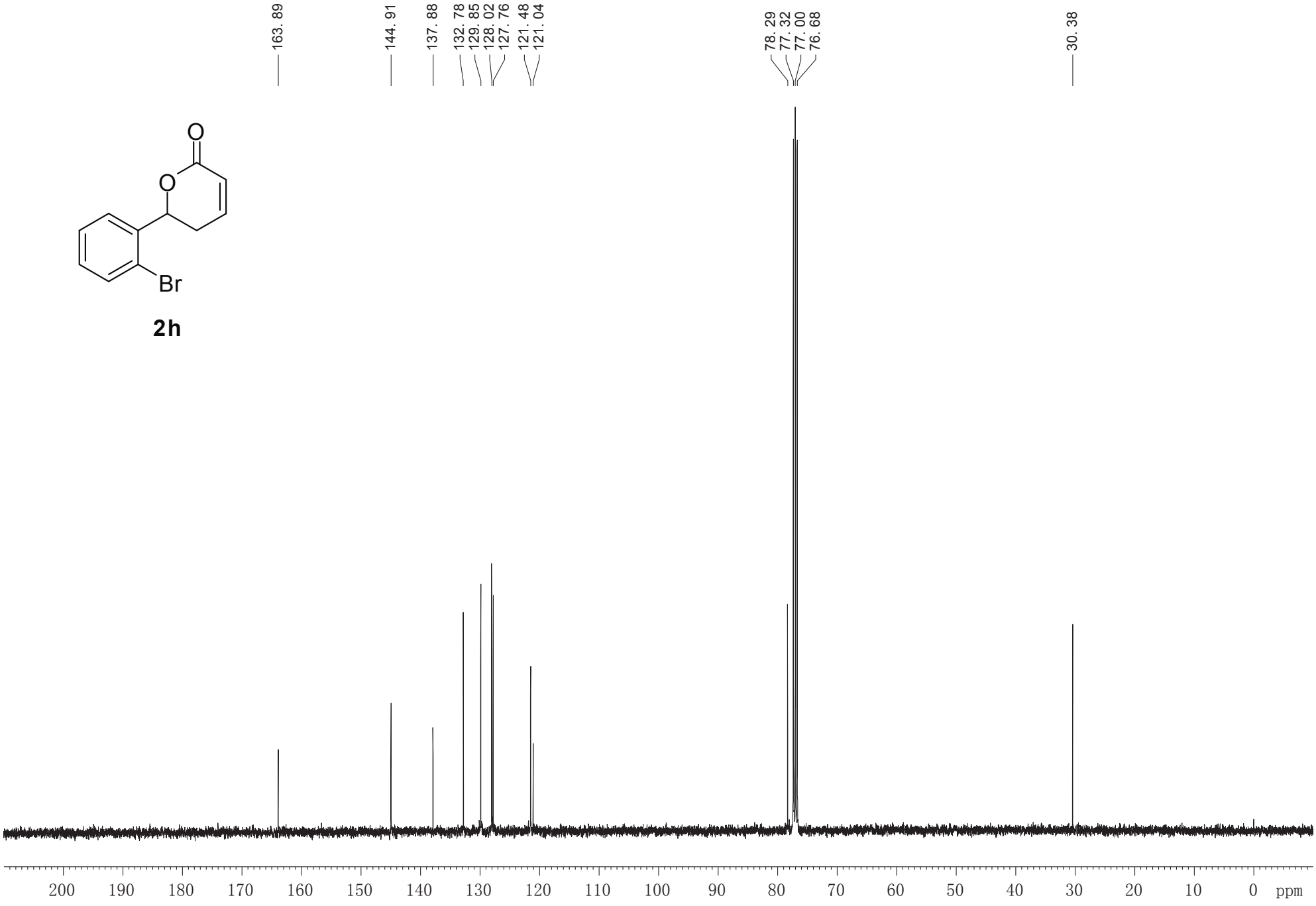

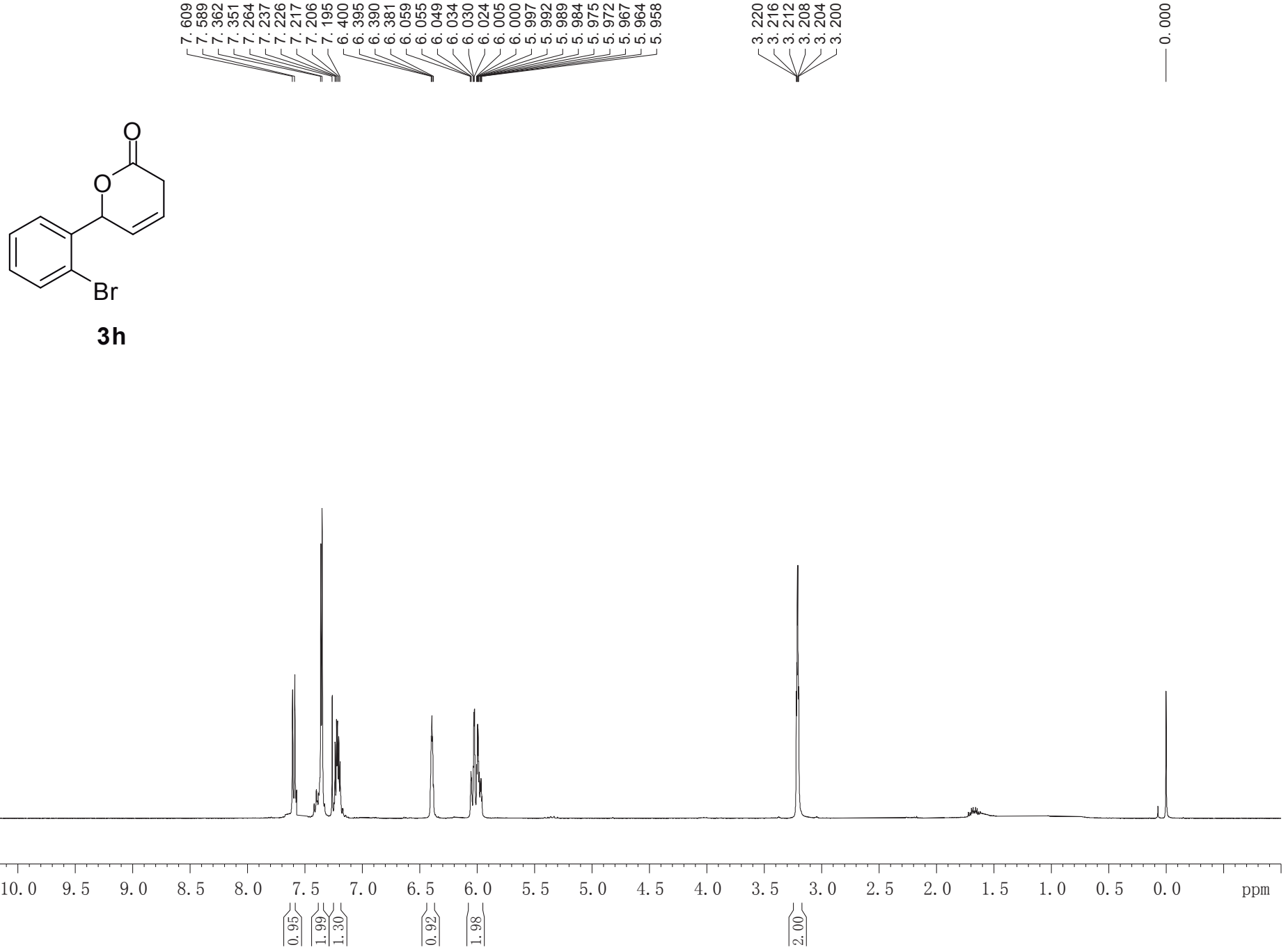

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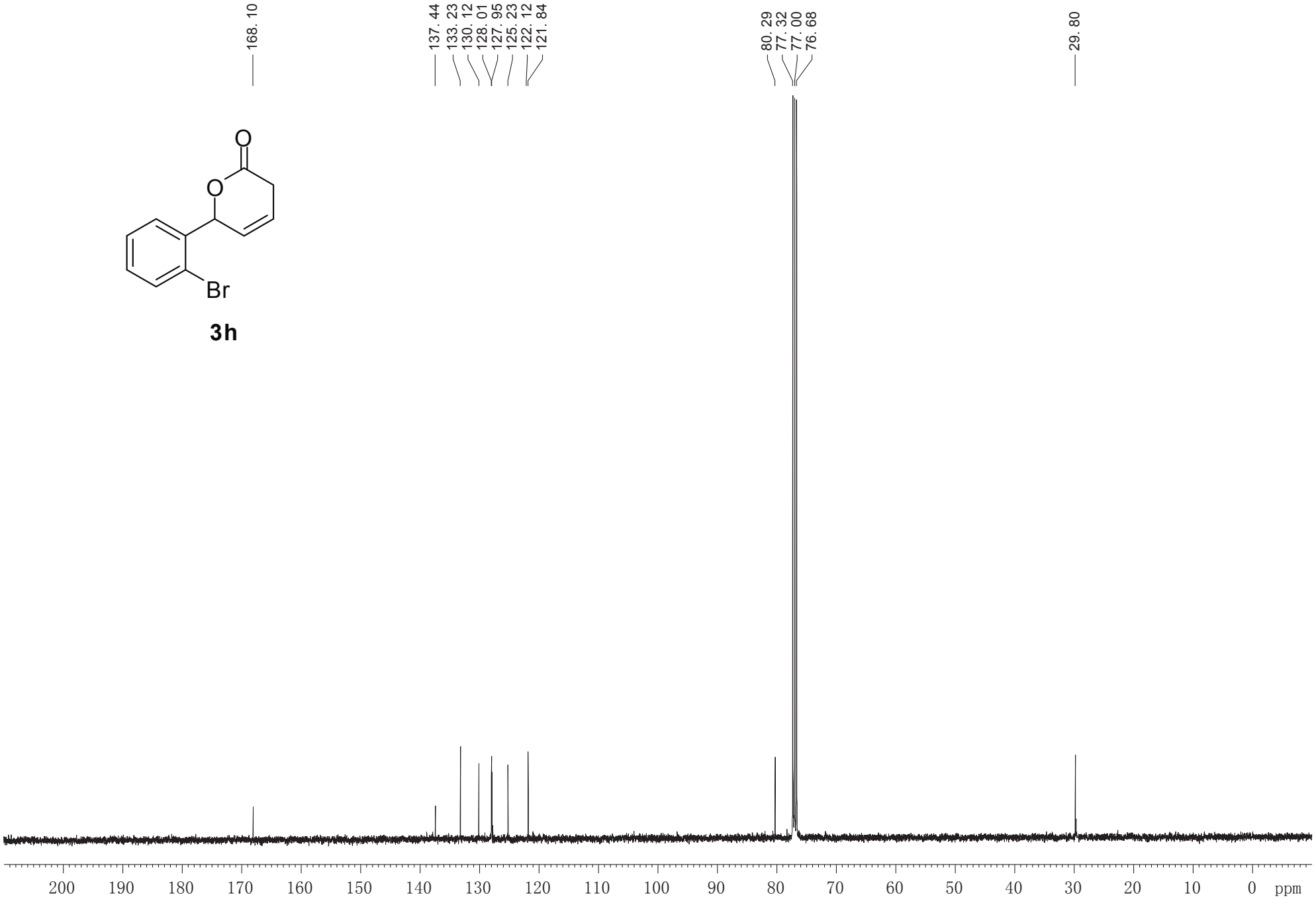

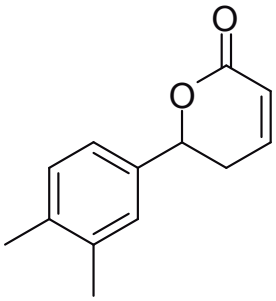

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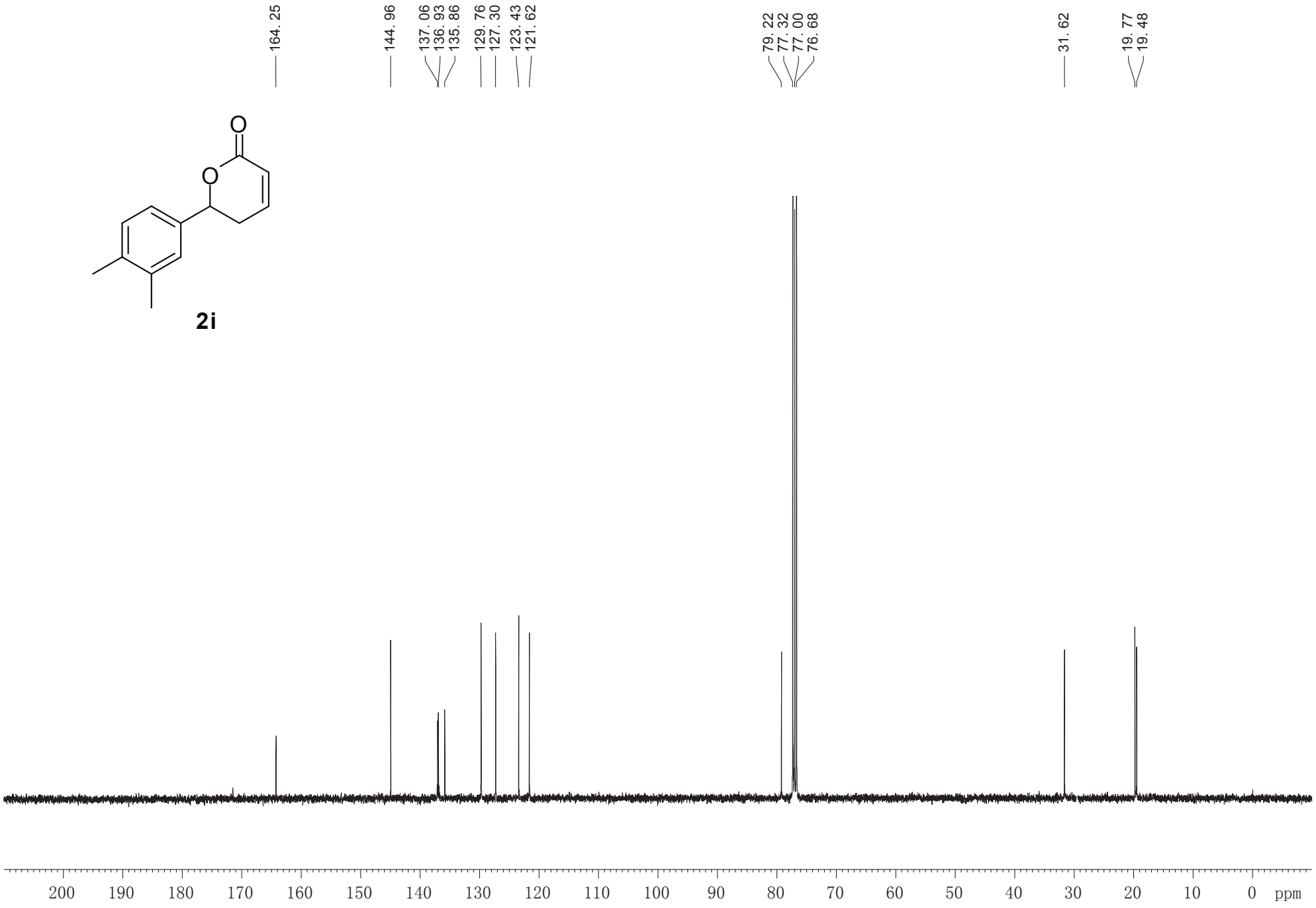

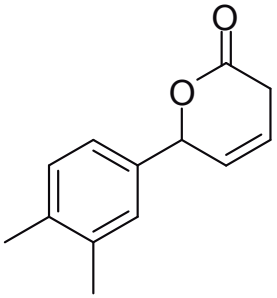

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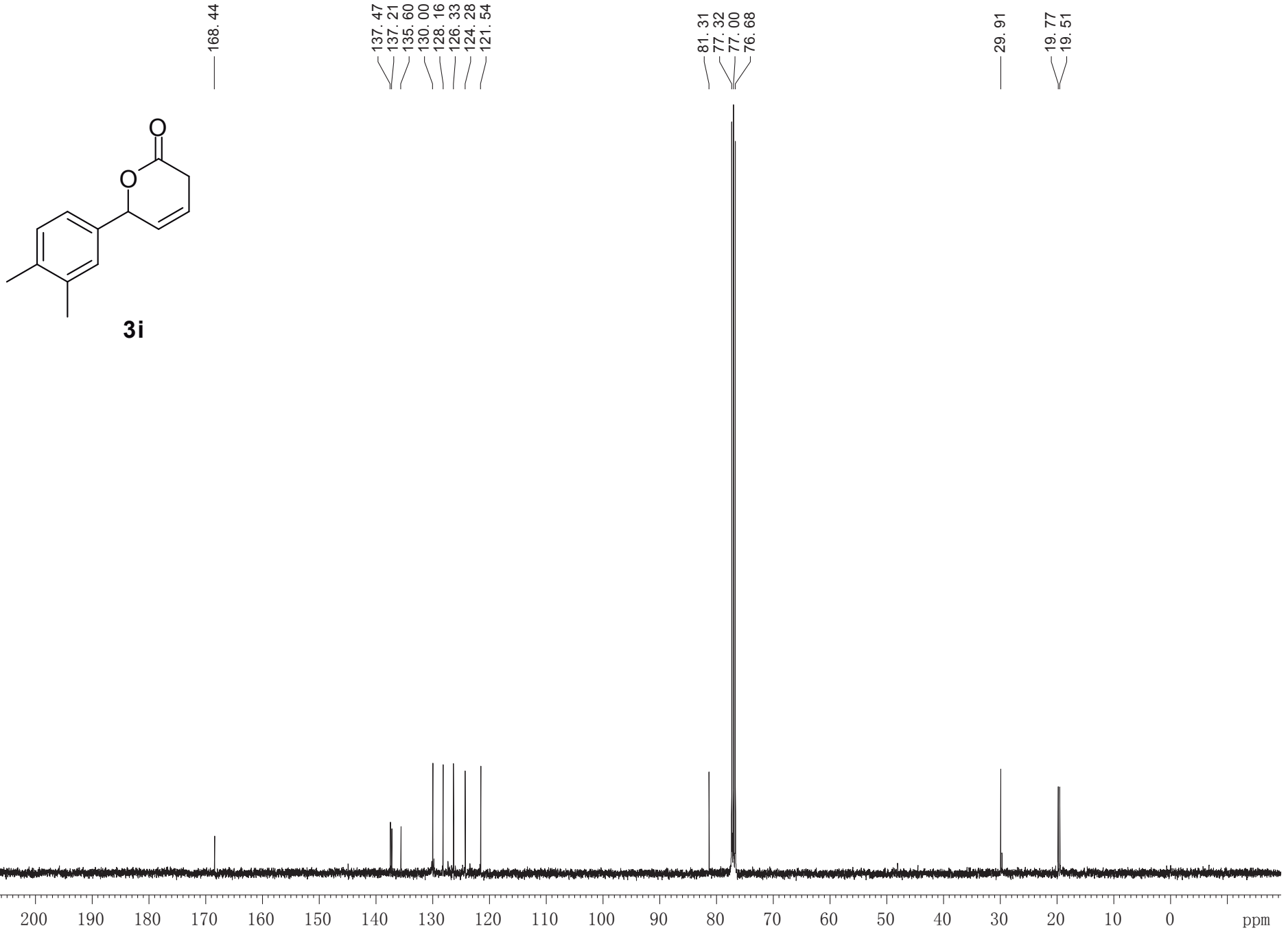

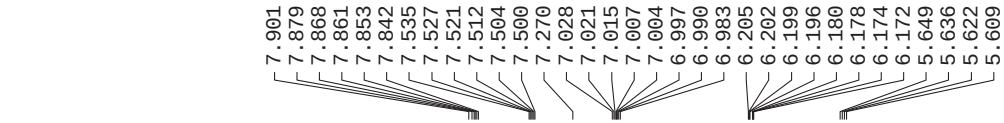

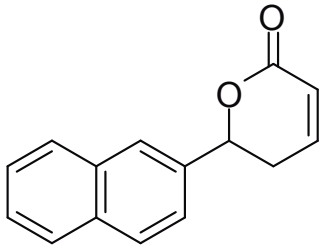

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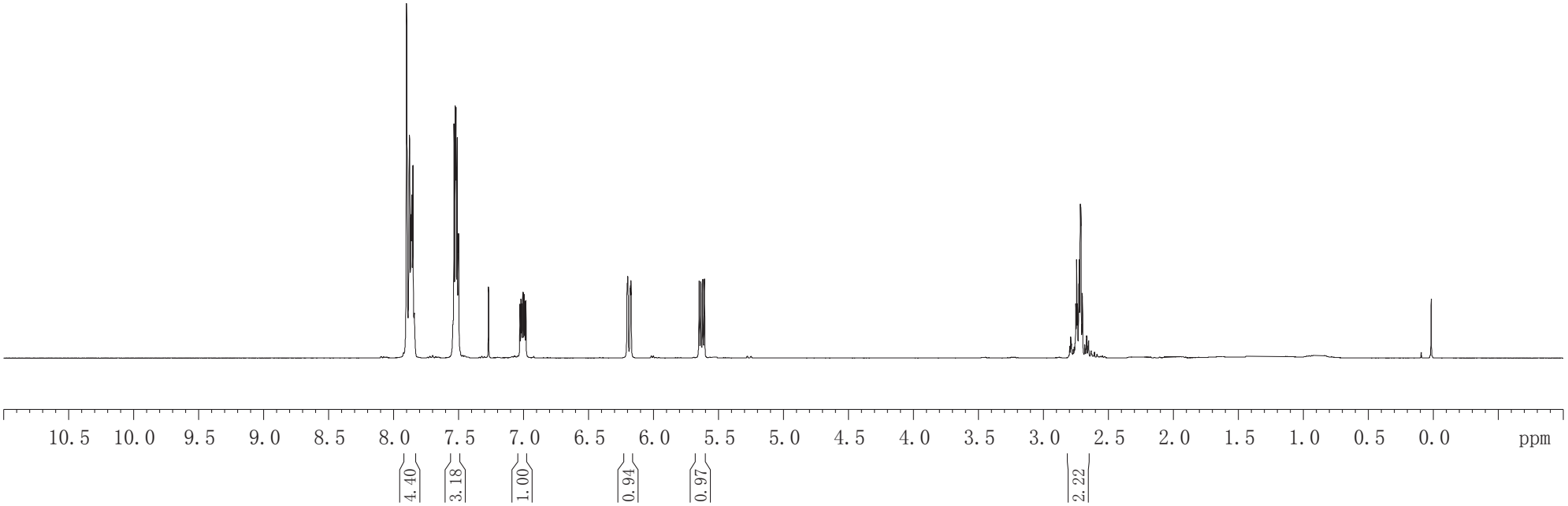

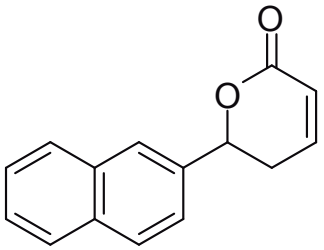

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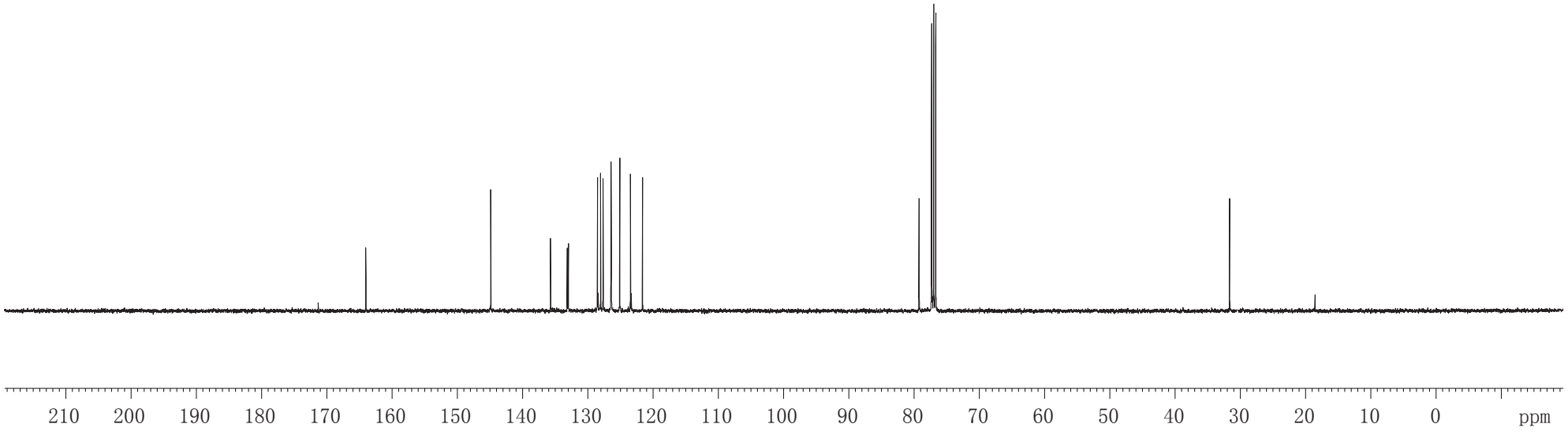

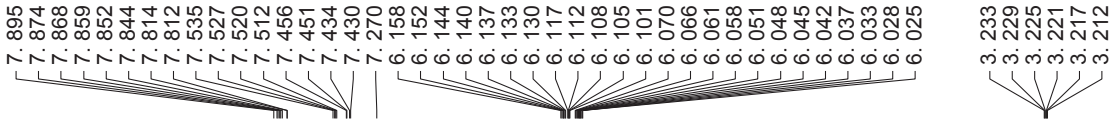

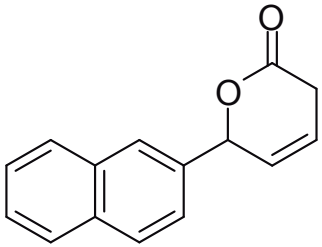

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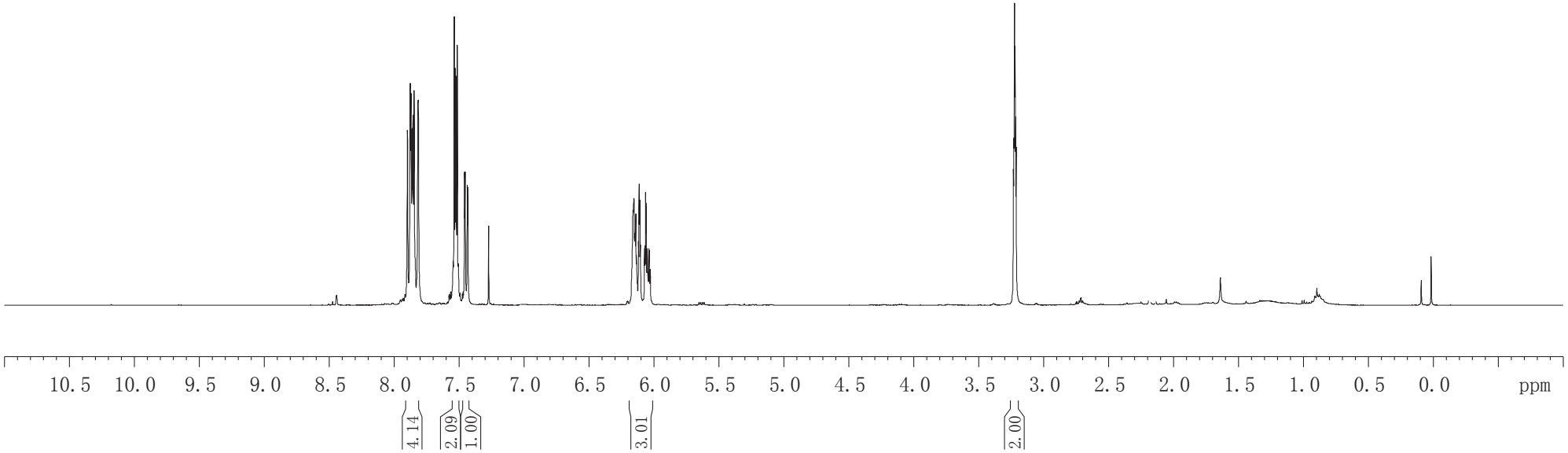

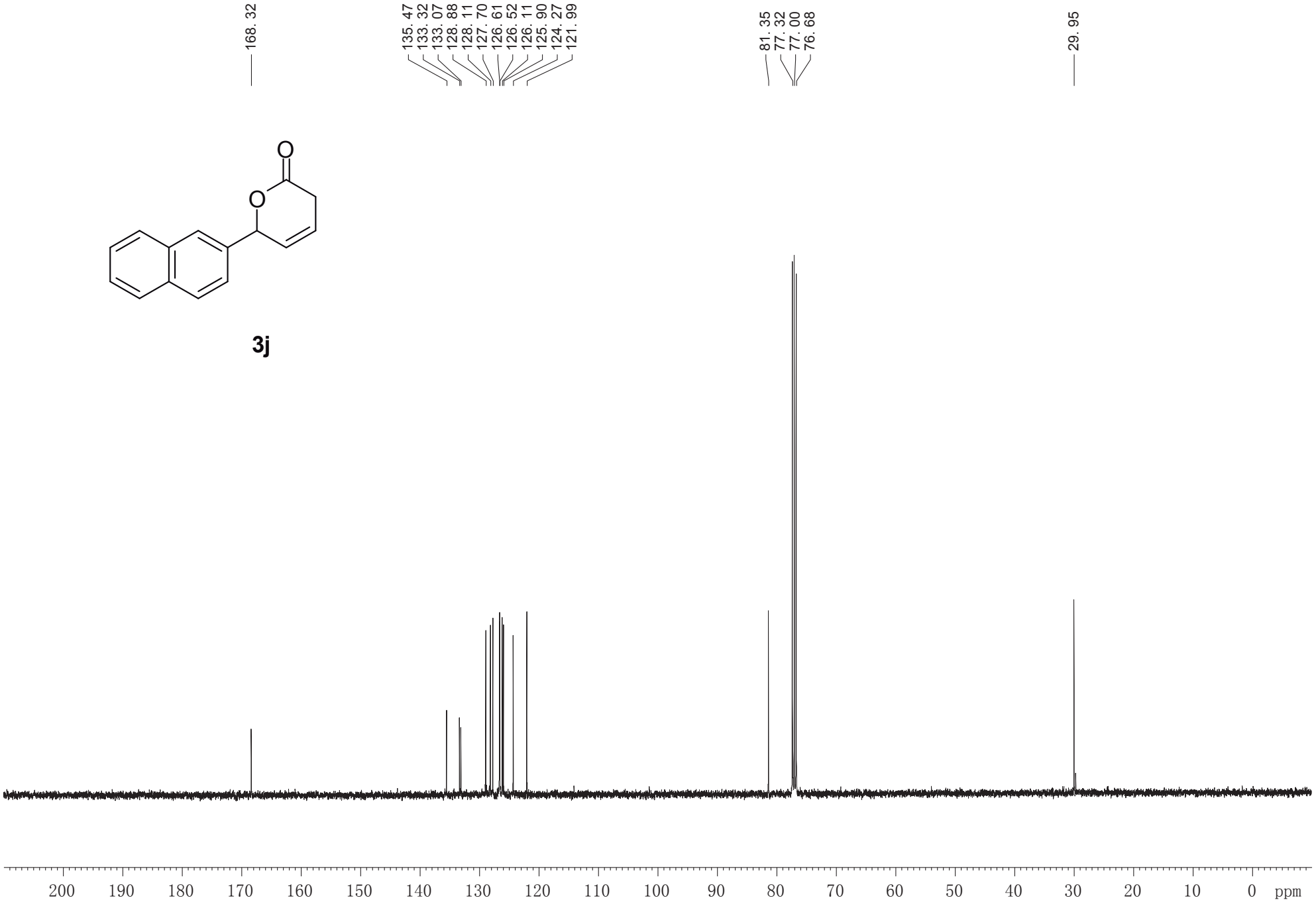

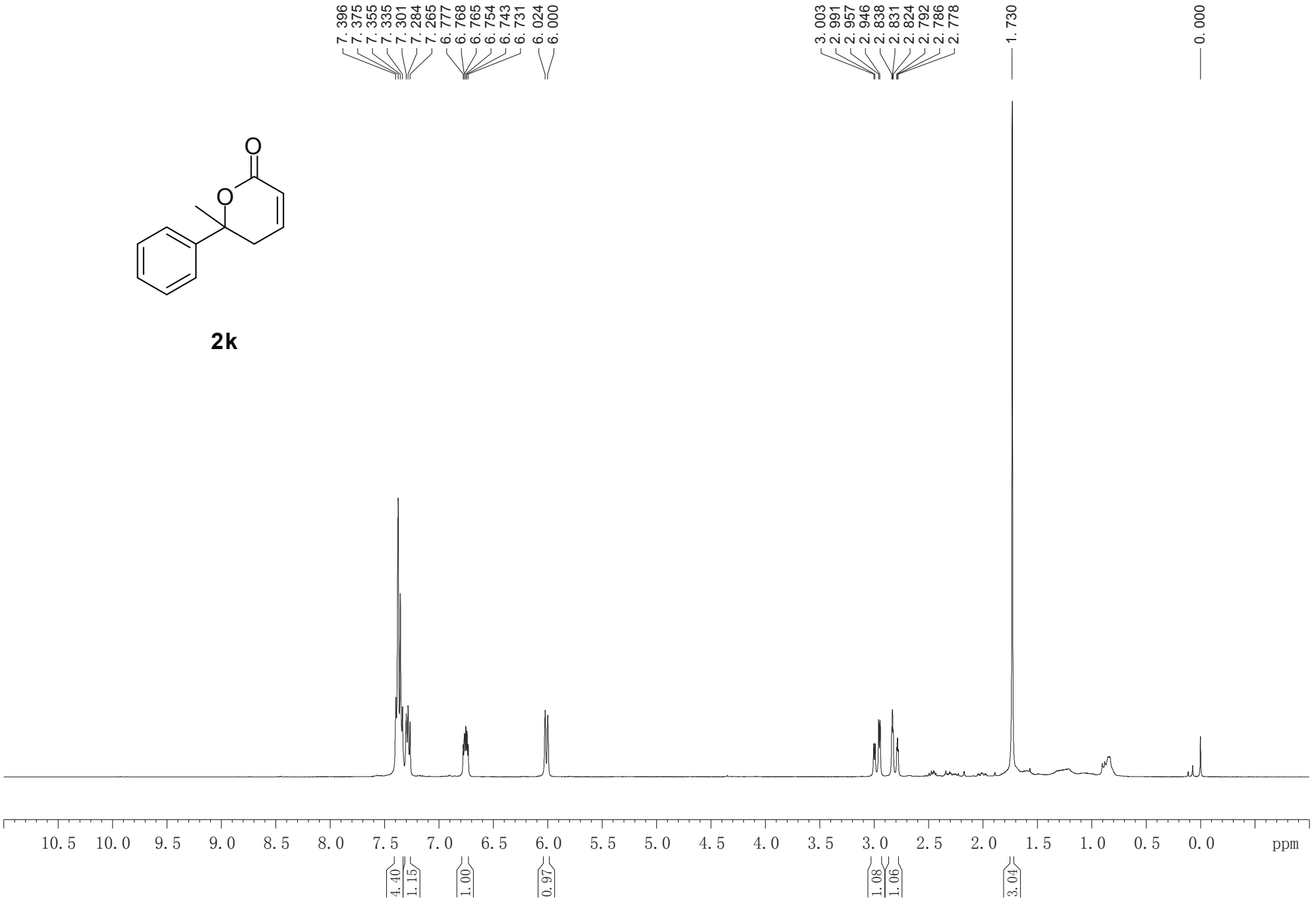

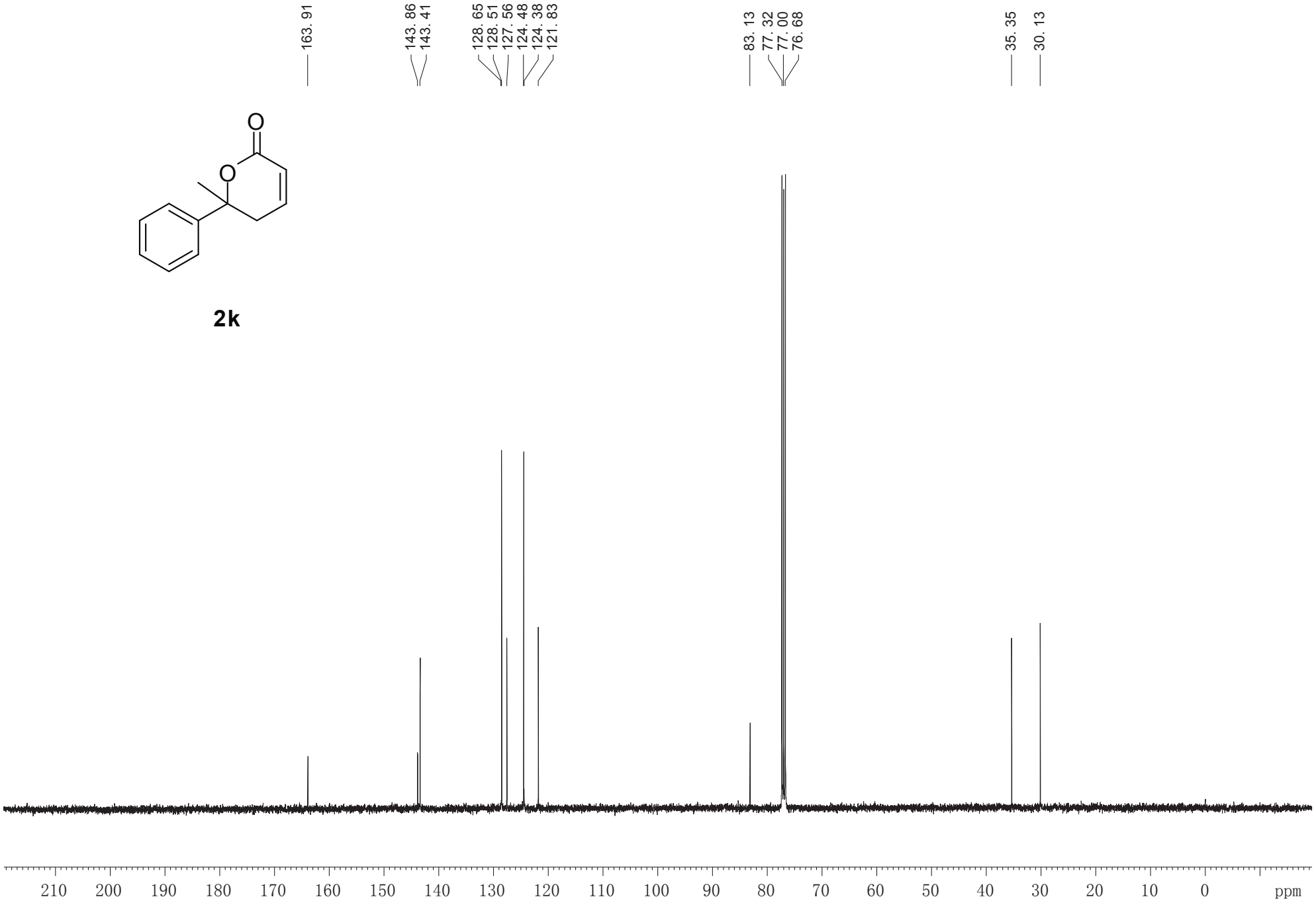

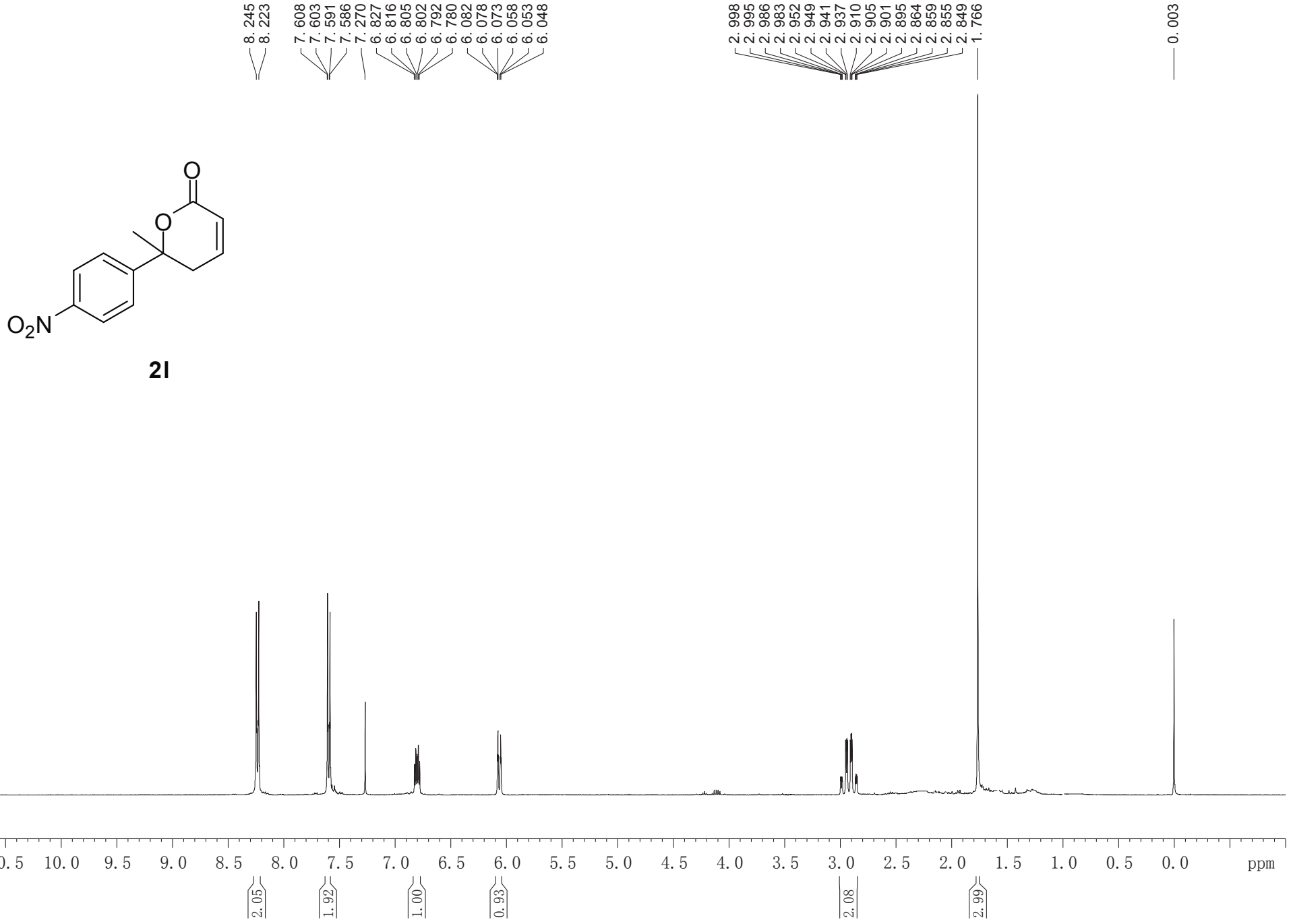

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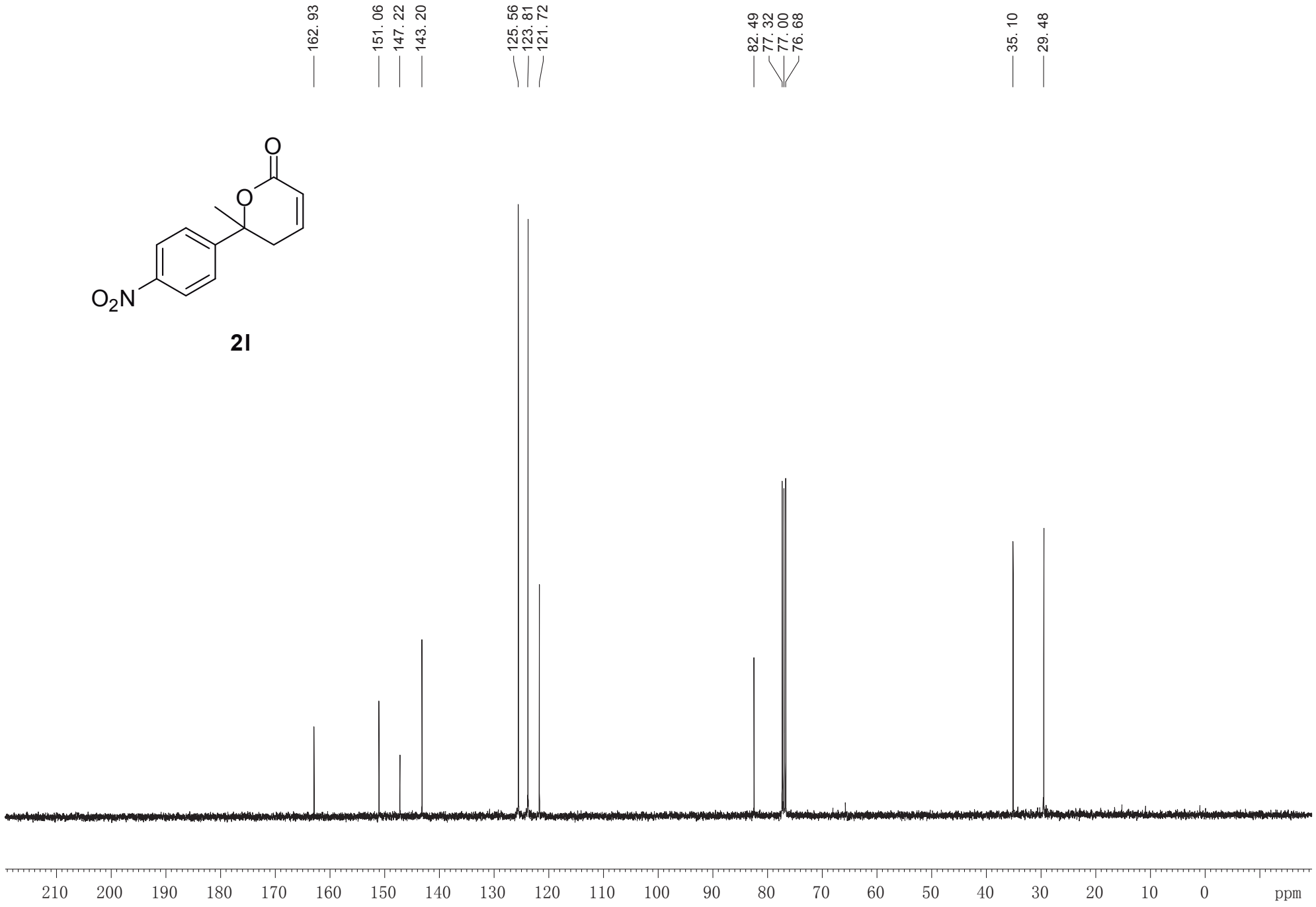

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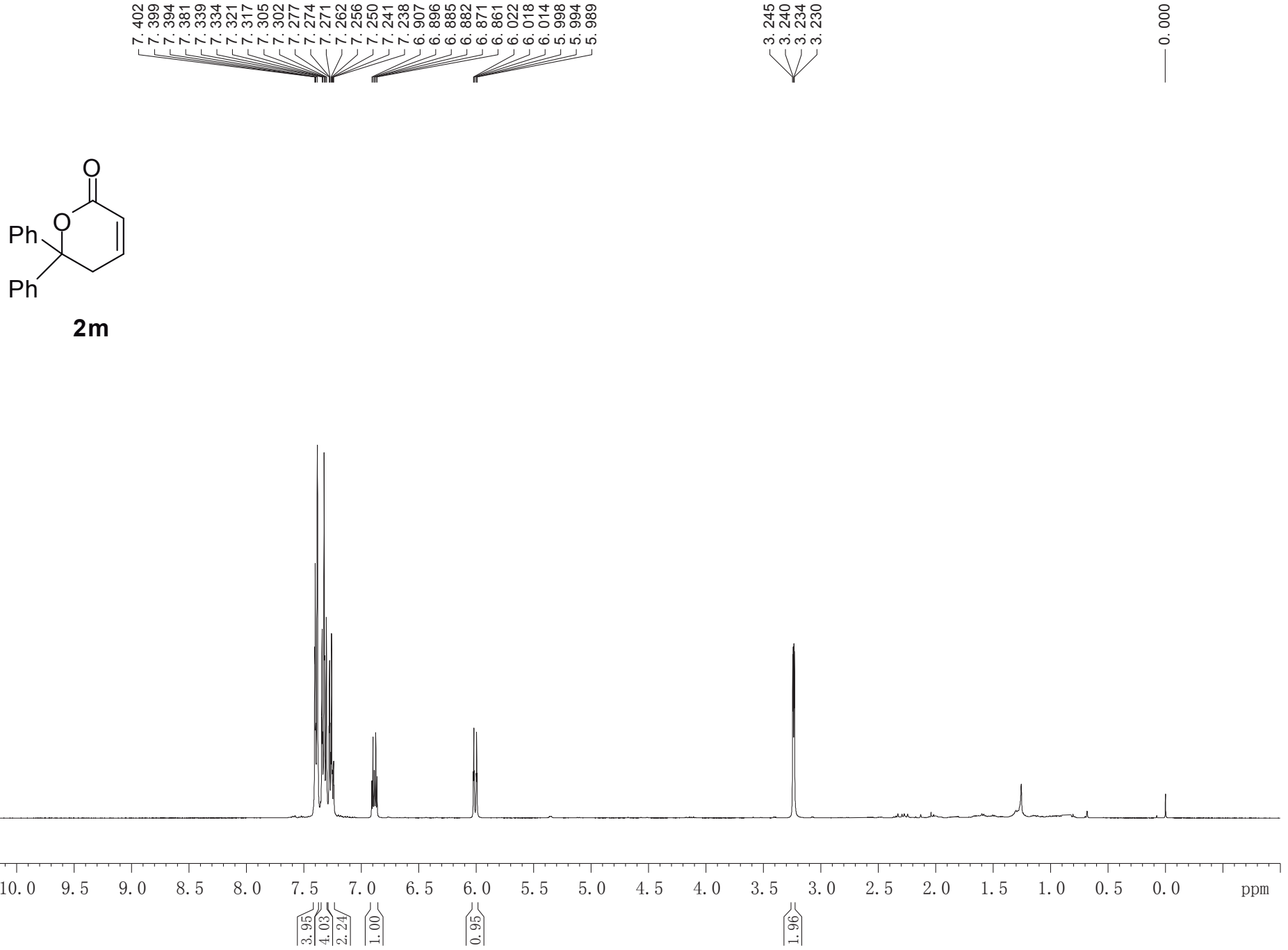

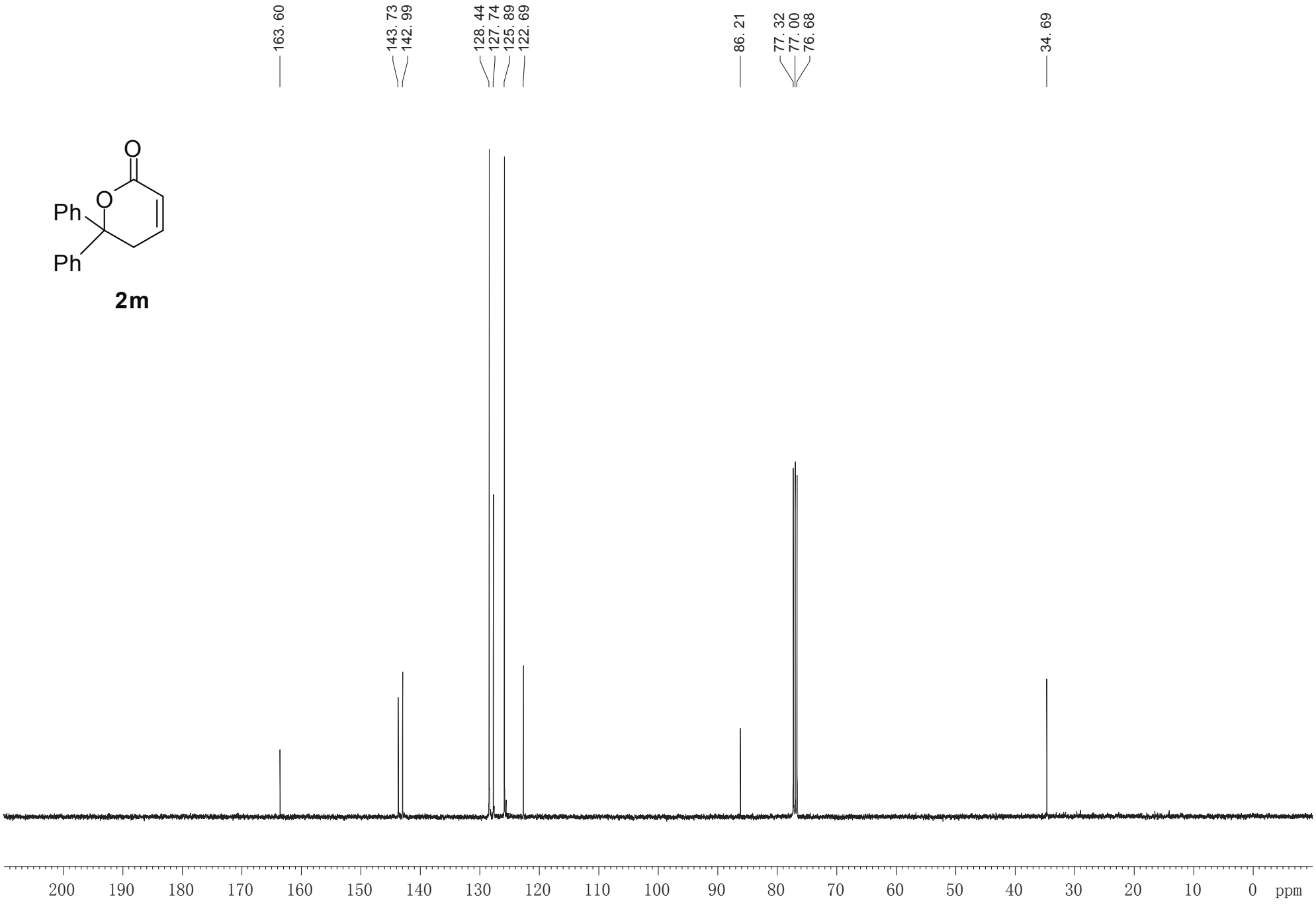

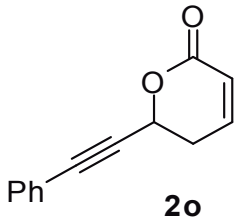

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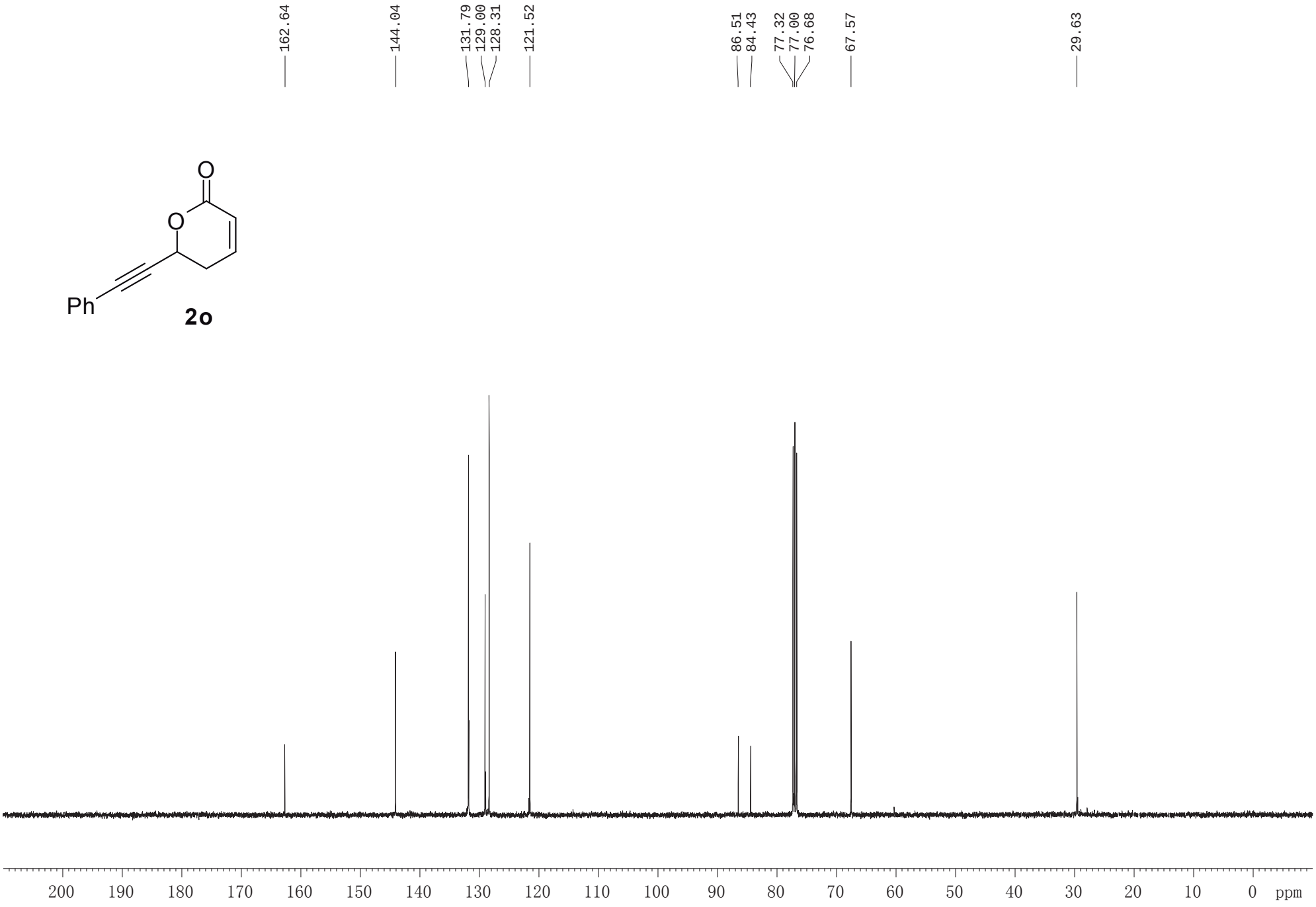

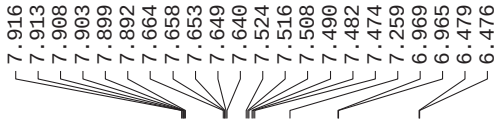

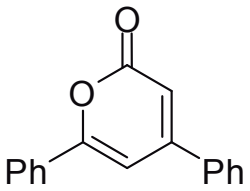

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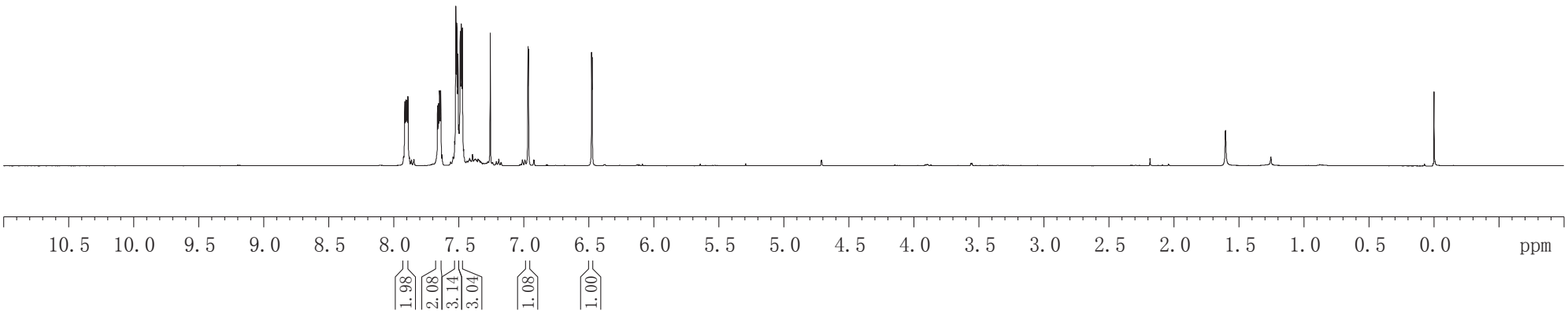

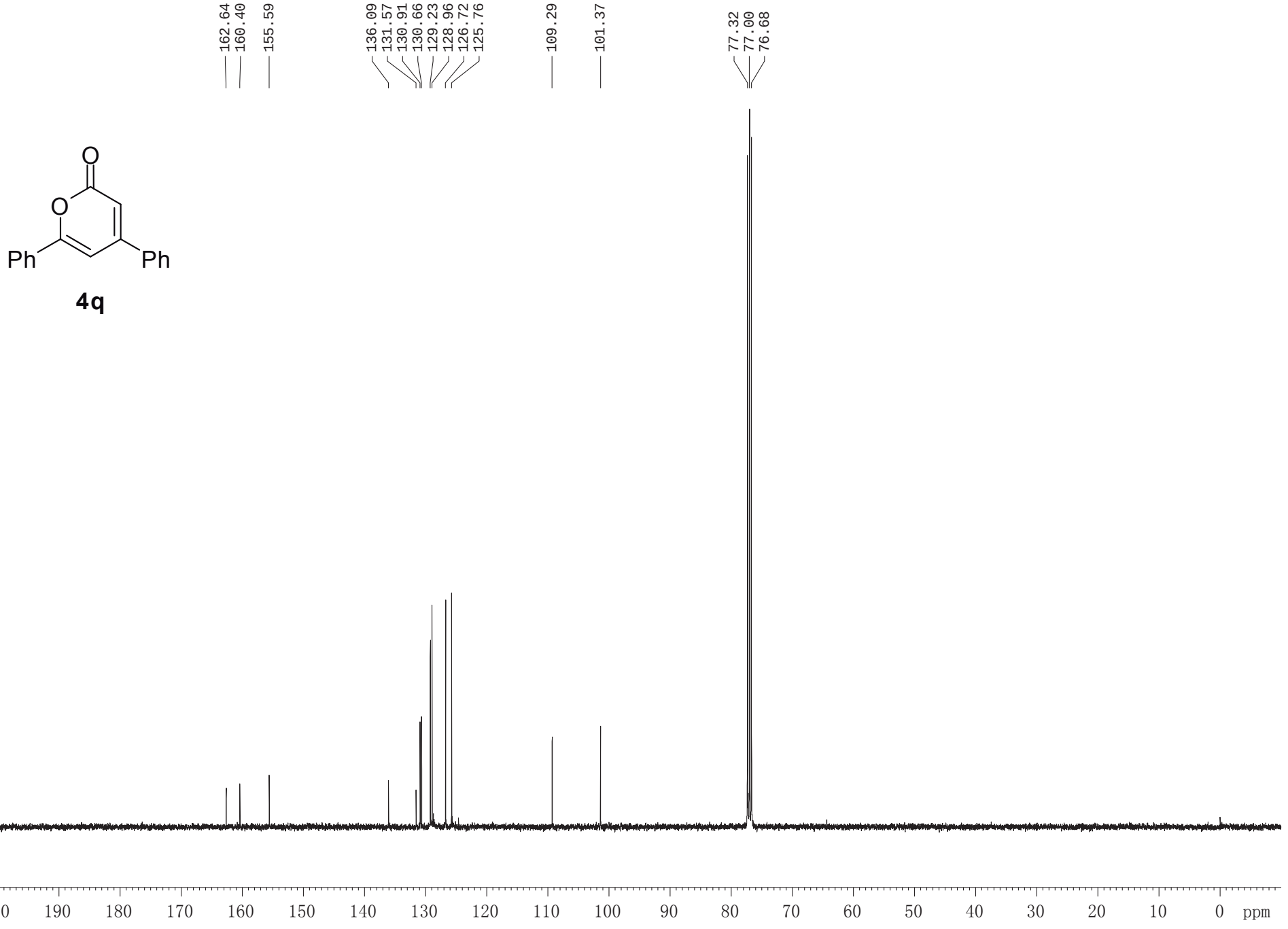

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