Supporting Information for

Highly Enantioselective Transfer Hydrogenation of β,γ-Alkynyl α-Imino Esters by a Brønsted Acid

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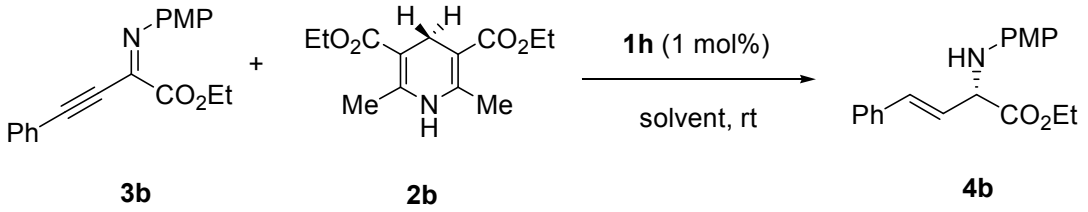
General Methods. Unless stated otherwise, all reactions were carried out in flame-dried glassware under a dry argon atmosphere. All solvents were purified and dried according to standard methods prior to use.

^{1}H and ^{13}C NMR spectra were recorded on a Varian instrument (300 MHz and 75 MHz, respectively) and internally referenced to tetramethylsilane signal or residual protio solvent signals. Data for ^{1}H NMR are recorded as follows: chemical shift (δ, ppm), multiplicity (s = singlet, d = doublet, t = triplet, m = multiplet or unresolved, br = broad singlet, coupling constant(s) in Hz, integration). Data for ^{13}C NMR are reported in terms of chemical shift (δ, ppm).

Table I. Screening of solvents[a]

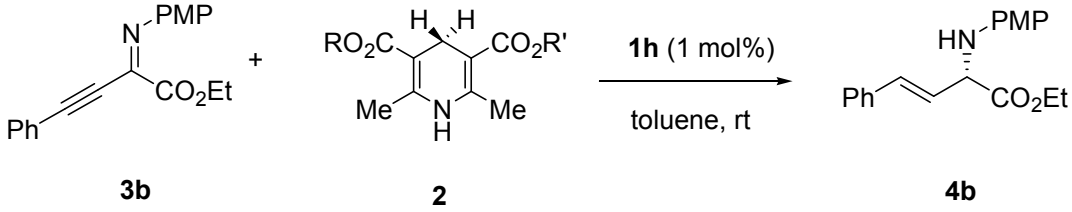


3b **2b** **4b**

entry	solvent	time (h)	ee%[b]
1	Et_2O	24	90
2	Toluene	24	92
3	DCM	24	85
4	THF	24	87
5	^{t}BuOMe	24	85

[a] Reaction conditions: 1 mol% of **1h**, 2.2 equiv of **2b**, 0.05 mol/L of **3b** at room temperature. [b] Determined by chiral HPLC analysis (Chiralcel AD-H). PMP = *para*-methoxyphenyl.

Table II. Investigation of Hantzsch esters[a]



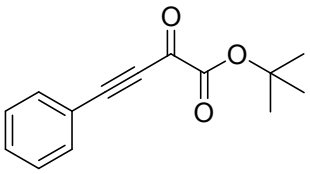
3b **2** **4b**

entry	**2**	time (h)	ee%[b]
1	**2a**: R = Me, R' = Me	24	85
2	**2b**: R = Et, R' = Et	24	92
3	**2c**: R = Me, R' = ^{t}Bu	24	93
4	**2d**: R = ^{t}Bu, R' = ^{t}Bu	24	86

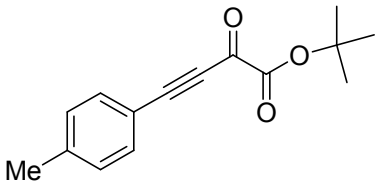
[a] Reaction conditions: 1 mol% of **1h**, 2.2 equiv of **2**, 0.05 mol/L of **3b** at room temperature. [b] Determined by chiral HPLC analysis (Chiralcel AD-H).

Experimental Sections

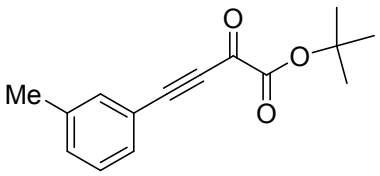
β,γ-alkynyl keto esters **10** were prepared according to the literature method.[1]



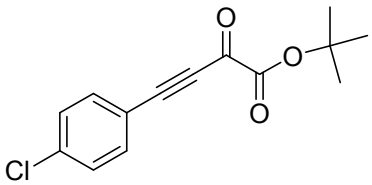
(**10d**). Yellow oil. ^{1}H NMR (300 MHz, $CDCl_3$) δ 1.61 (s, 9H), 7.40-7.45 (m, 2H), 7.50-7.55 (m, 1H), 7.65-7.68 (m, 2H).



(**10e**). Yellow oil. ^{1}H NMR (300 MHz, $CDCl_3$) δ 1.50 (s, 9H), 2.27 (s, 3H), 7.10 (d, J = 8.4 Hz, 2H), 7.42 (d, J = 8.4 Hz, 2H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 21.4, 27.3, 84.3, 87.0, 97.7, 115.7, 129.3, 133.4, 142.4, 157.9, 170.3; IR (film) 2984, 2194, 1747, 1676, 1605, 1509, 1458, 1371, 1305, 1257, 1162, 1077, 1037, 841, 818, 758, 540 cm^{-1}; MS (ESI): 267.1 [M+Na]; HRMS (ESI): Calcd for $C_{15}H_{16}NaO_3$ [M+Na]: 267.0991. Found: 267.1002.

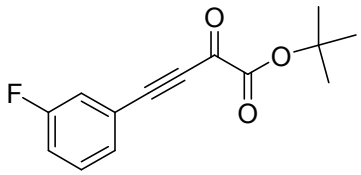


(**10f**). Yellow oil. ^{1}H NMR (300 MHz, $CDCl_3$) δ 1.61 (s, 9H), 2.36 (s, 3H), 7.29-7.32 (m, 2H), 7.44-7.45 (m, 2H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 20.8, 27.4, 84.5, 86.8, 97.4, 118.8, 128.4, 130.6, 132.5, 133.8, 138.4, 158.0, 170.5; IR (film) 2983, 2191, 1750, 1734, 1675, 1371, 1259, 1179, 1098, 1080, 848, 788, 688 cm^{-1}; MS (ESI): 267.2 [M+Na]; HRMS (ESI): Calcd for $C_{15}H_{16}NaO_3$ [M+Na]: 267.0991. Found: 267.1003.

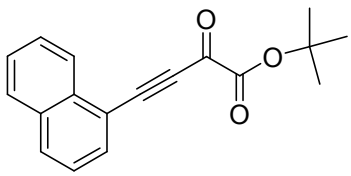


(**10g**). Yellow oil. ^{1}H NMR (300 MHz, $CDCl_3$) δ 1.52 (s, 9H), 7.32 (d, J = 8.1 Hz, 2H), 7.50 (d, J = 8.4 Hz, 2H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 27.6, 84.9, 87.7, 95.5, 117.6, 129.1, 134.7, 138.0, 157.9, 170.5; IR

(film) 2984, 2205, 1734, 1677, 1591, 1490, 1397, 1371, 1256, 1161, 1075, 837, 790, 537 cm^{-1}; MS (ESI): 319.1 [M+MeOH+Na]; HRMS (ESI): Calcd for $C_{14}H_{13}NaClO_3$ [M+Na]: 287.0445. Found: 287.0437.

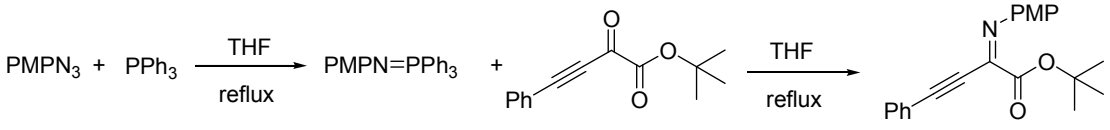


(**10h**). Yellow oil. ^{1}H NMR (300 MHz, $CDCl_3$) δ 1.49 (s, 9H), 7.07-7.15 (m, 1H), 7.17-7.21 (m, 1H), 7.31-7.33 (m, 2H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 27.3, 84.7, 86.9, 94.5, 118.8 (d, J = 21.2 Hz), 119.7 (d, J = 22.9 Hz), 120.7 (d, J = 9.2 Hz), 129.2 (d, J = 2.9 Hz), 130.4 (d, J = 8.6 Hz), 157.6, 161.9 (d, J = 247.3 Hz), 170.3; IR (film) 2985, 2200, 1752, 1683, 1581, 1487, 1431, 1372, 1260, 1183, 1153, 1088, 943, 853, 790, 680, 520 cm^{-1}; MS (ESI): 303.1 [M+MeOH+Na]; HRMS (ESI): Calcd for $C_{14}H_{13}NaFO_3$ [M+Na]: 271.0740. Found: 271.0751.



(**10i**). Yellow solid. ^{1}H NMR (300 MHz, $CDCl_3$) δ 1.66 (s, 9H), 7.48-7.69 (m, 3H), 7.89-7.95 (m, 2H), 8.00-8.03 (m, 1H), 8.45-8.47 (m, 1H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 27.6, 84.9, 92.1, 95.7, 116.6, 125.1, 125.6, 127.0, 127.8, 128.5, 132.6, 132.8, 133.9, 134.3, 157.9, 170.5; IR (film) 2976, 2195, 1749, 1673, 1547, 1366, 1302, 1272, 1118, 828, 775, 753 cm^{-1}; MS (ESI): 303.2 [M+Na]; HRMS (ESI): Calcd for $C_{18}H_{16}NaO_3$ [M+Na]: 303.0991. Found: 303.1013.

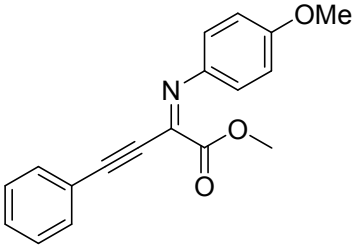
Procedure A: General procedure for preparation of β,γ-alkynyl α-imino esters 3:[2]



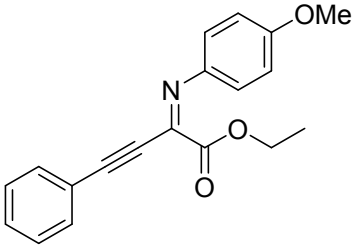
3d

A solution of triphenylphosphine (10mmol) in THF (30 mL) was added dropwise to a solution of the 1-azido-4-methoxybenzene[3] (10 mmol) in THF (20 mL) under

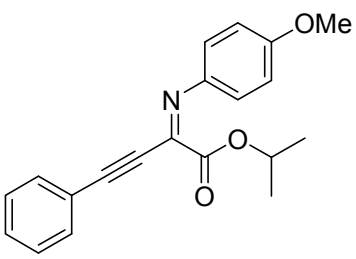
argon over 30 minutes. The reaction mixture was stirred at room temperature for 2 hours and then heated under reflux for 30 minutes then the reaction mixture was allowed to cool to room temperature, whereupon tert-butyl 2-oxo-4-phenylbut-3-ynoate[1] (6 mmol) was added. The mixture was heated under reflux for 4 hours and cooled to room temperature. The solvent was removed *in vacuo*. The crude product was purified by silica gel column chromatography (petroleum ester: ethyl acetate = 20 : 1) to afford **3d** as a jacinth oil.



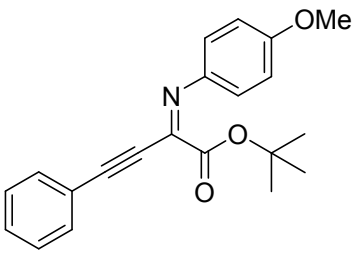
(**3a**). Yellow solid, 88% yield. ^{1}H NMR (300 MHz, $CDCl_3$) δ 3.86 (s, 3H), 4.00 (s, 3H), 6.97 (d, *J* = 9.0 Hz, 2H), 7.36-7.42 (m, 3H), 7.48-7.51 (m, 2H), 7.58 (d, *J* = 8.7 Hz, 2H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 53.5, 55.4, 83.2, 98.3, 113.7, 120.8, 124.9, 128.5, 130.1, 132.4, 138.4, 141.3, 159.5, 163.3; IR (film) 2958, 2204, 1751, 1740, 1604, 1559, 1502, 1293, 1249, 1161, 1099, 1026, 833, 755, 689 cm^{-1}; HRMS (EI) exact mass calculated for ($C_{18}H_{15}NO_3$) requires *m/z* 293.1052. Found *m/z* 293.1051.



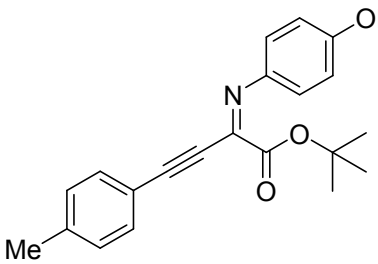
(**3b**). Yellow solid, 86% yield. ^{1}H NMR (300 MHz, $CDCl_3$) δ 1.46 (t, *J* = 7.2 Hz, 3H), 3.87 (s, 3H), 4.47 (q, *J* = 6.9 Hz, 2H), 6.96 (d, *J* = 9.0 Hz, 2H), 7.33-7.42 (m, 3H), 7.46-7.50 (m, 2H), 7.56 (d, *J* = 9.0 Hz, 2H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 14.1, 55.3, 62.6, 83.2, 98.2, 113.6, 120.9, 124.7, 128.4, 130.1, 132.4, 138.9, 141.4, 159.3, 162.7; IR (film) 3014, 2840, 2203, 1739, 1604, 1501, 1289, 1248, 1163, 1096, 1030, 760, 692 cm^{-1}; HRMS (EI) exact mass calculated for ($C_{19}H_{17}NO_3$) requires *m/z* 307.1208. Found *m/z* 307.1218.



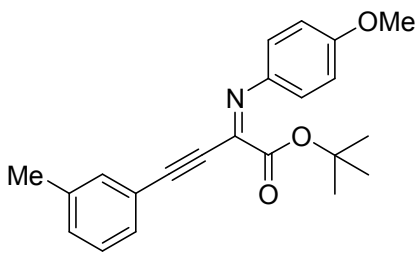
(**3c**). Yellow oil, 86% yield. ^{1}H NMR (300 MHz, $CDCl_3$) δ 1.44 (d, *J* = 6.3 Hz, 6H), 3.86 (s, 3H), 5.24-5.33 (m, 1H), 6.95-6.98 (m, 2H), 7.34-7.48 (m, 2H), 7.53-7.56 (m, 5H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 21.7, 55.4, 70.5, 83.3, 98.1, 113.6, 121.0, 124.7, 128.5, 130.0, 132.4, 139.4, 141.6, 159.2, 162.2; IR (film) 2982, 2200, 1741, 1722, 1606, 1503, 1295, 1249, 1091, 838, 758, 690, 531 cm^{-1}; HRMS (EI) exact mass calculated for ($C_{20}H_{19}NO_3$) requires *m/z* 321.1363 Found *m/z* 321.1365.



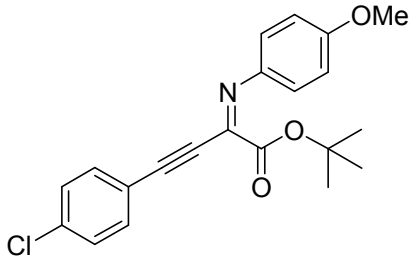
(**3d**). Yellow oil, 90% yield. ^{1}H NMR (300 MHz, $CDCl_3$) δ 1.64 (s, 9H), 3.85 (s, 3H), 6.95 (d, *J* = 9.0 Hz, 2H), 7.31-7.46 (m, 5H), 7.54 (d, *J* = 8.7 Hz, 2H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 27.6, 55.1, 82.9, 83.4, 97.7, 113.4, 120.9, 124.4, 128.3, 129.8, 132.1, 140.0, 141.5, 159.0, 161.2; IR (film) 2980, 2201, 1735, 1721, 1606, 1504, 1370, 1297, 1251, 1160, 1095, 1033, 842, 759, 690, 531 cm^{-1}; HRMS (EI) exact mass calculated for ($C_{21}H_{21}NO_3$) requires *m/z* 335.1521. Found *m/z* 335.1532.



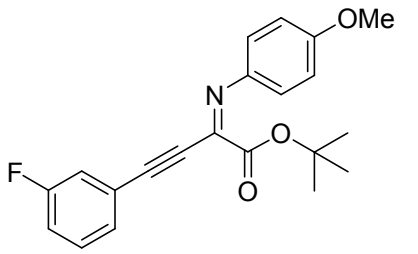
(**3e**). Yellow oil, 95% yield. ^{1}H NMR (300 MHz, $CDCl_3$) δ 1.64 (s, 9H), 2.32 (s, 3H), 3.80 (s, 3H), 6.94 (d, *J* = 8.4 Hz, 2H), 7.13 (d, *J* = 8.1 Hz, 2H), 7.34 (d, *J* = 8.1 Hz, 2H), 7.55 (d, *J* = 8.7 Hz, 2H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 21.3, 27.6, 55.0, 82.7, 83.1, 98.2, 113.3, 117.8, 124.4, 129.0, 132.0, 140.1, 140.3, 141.5, 158.8, 161.2; IR (film) 2980, 2198, 1740, 1604, 1561, 1502, 1369, 1295, 1251, 1160, 1093, 1034, 842, 817, 531 cm^{-1}; MS (ESI): 350.2 [M+H]; HRMS (ESI): Calcd for $C_{22}H_{24}NO_3$ [M+H]: 350.1750. Found: 350.17.



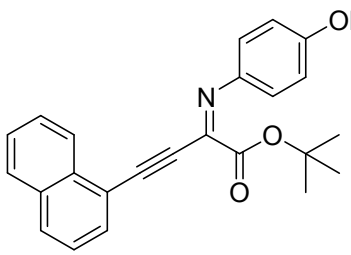
(**3f**). Yellow oil, 86% yield. ^{1}H NMR (300 MHz, $CDCl_3$) δ 1.64 (s, 9H), 2.30 (s, 3H), 3.79 (s, 3H), 6.94 (d, J = 8.7 Hz, 2H), 7.18-7.27 (m, 4H), 7.55 (d, J = 9.3 Hz, 2H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 20.7, 27.5, 54.9, 82.7, 83.0, 98.0, 113.3, 120.6, 124.3, 128.1, 129.2, 130.7, 132.4, 137.9, 139.9, 141.4, 158.9, 161.1; IR (film) 2980, 2191, 1740, 1605, 1502, 1369, 1272, 1251, 1157, 1100, 1034, 839, 786, 689 cm^{-1}; HRMS (ESI): Calcd for $C_{22}H_{24}NO_3$ [M+H]: 350.1750. Found: 350.1758.



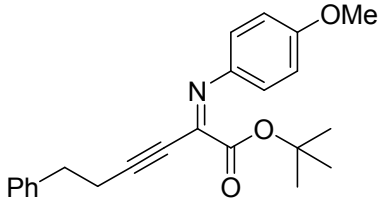
(**3g**). Yellow oil, 87% yield. ^{1}H NMR (300 MHz, $CDCl_3$) δ 1.64 (s, 9H), 3.82 (s, 3H), 6.95 (d, J = 8.4 Hz, 2H), 7.29-7.38 (m, 4H), 7.52 (d, J = 9.3 Hz, 2H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 27.6, 55.1, 83.0, 84.2, 96.2, 113.4, 119.4, 124.3, 128.7, 133.3, 136.0, 139.7, 141.4, 159.0, 161.1; IR (film) 2980, 2202, 1741, 1606, 1560, 1503, 1369, 1295, 1251, 1158, 1034, 830, 528 cm^{-1}; MS (ESI): 370.1 [M+H]; HRMS (ESI): Calcd for $C_{21}H_{21}ClNO_3$ [M+H]: 370.1204. Found: 370.1225.



(**3h**). Yellow oil, 92% yield. ^{1}H NMR (300 MHz, $CDCl_3$) δ 1.65 (s, 9H), 3.82 (s, 3H), 6.95 (d, J = 8.7 Hz, 2H), 7.09-7.16 (m, 2H), 7.22-7.32 (m, 2H), 7.53 (d, J = 9.0 Hz, 2H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 27.6, 55.1, 83.0, 83.8, 95.7, 95.8, 113.4, 117.2 (d, J = 21.2 Hz), 118.6 (d, J = 22.9 Hz), 122.6 (d, J = 9.2 Hz), 124.4, 128.0 (d, J = 3.5 Hz), 130.0 (d, J = 8.0 Hz), 139.5, 141.3, 159.1, 161.0, 161.9 (d, J = 246.2 Hz); IR (film) 2981, 2198, 1739, 1607, 1579, 1503, 1370, 1252, 1151, 1095, 1034, 840, 786, 680, 520 cm^{-1}; HRMS (ESI): Calcd for $C_{21}H_{21}FNO_3$ [M+H]: 354.1500. Found: 354.1517.



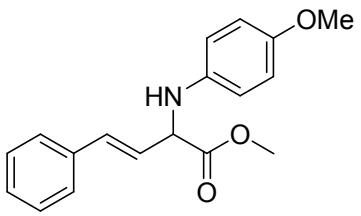
(**3i**). Yellow oil, 97% yield. ^{1}H NMR (300 MHz, $CDCl_3$) δ 1.70 (s, 9H), 3.75 (s, 3H), 6.95 (d, *J* = 9.0 Hz, 2H), 7.32 (t, *J* = 7.5 Hz, 1H), 7.41-7.45 (m, 2H), 7.55 (d, *J* = 9.0 Hz, 2H), 7.60-7.62 (m, 1H), 7.71-7.77 (m, 2H), 8.10-8.13 (m, 1H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 27.5, 54.8, 82.8, 87.8, 95.9, 113.4, 118.2, 123.7, 124.7, 125.4, 126.3, 126.7, 127.9, 130.3, 131.8, 132.4, 133.0, 140.4, 141.8, 158.7, 160.8; IR (film) 2980, 2189, 1739, 1604, 1502, 1248, 1156, 1122, 1030, 837, 773 cm^{-1}; HRMS (ESI): Calcd for $C_{25}H_{24}NO_3$ [M+H]: 386.1750. Found: 386.1769.



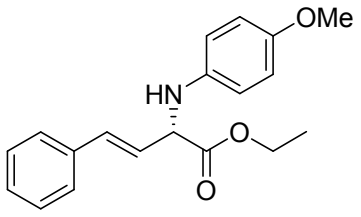
(**3j**). Yellow oil, 88% yield. ^{1}H NMR (300 MHz, $CDCl_3$) δ 1.59 (s, 9H), 2.68 (t, *J* = 7.2 Hz, 2H), 2.84 (t, *J* = 7.2 Hz, 2H), 3.79 (s, 3H), 6.83 (d, *J* = 8.7 Hz, 2H), 7.14-7.27 (m, 5H), 7.34 (d, *J* = 9.0 Hz, 2H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 21.5, 27.7, 33.8, 55.2, 75.7, 82.9, 99.9, 113.4, 124.0, 126.3, 128.2, 128.3, 139.7, 140.8, 141.6, 158.7, 161.8; IR (film) 2981, 2216, 1720, 1606, 1502, 1250, 1146, 1033, 838, 700 cm^{-1}; LRMS-ESI (*m/z*): 364 ($M+H^+$).

Procedure B: General procedure for the asymmetric transfer hydrogenation of β,γ-alkynyl α-imino esters 3:

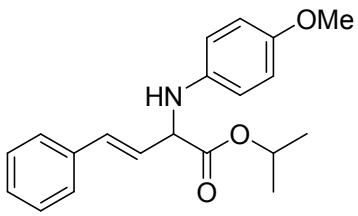
In a dry Schlenk tube containing Et_2O (4 mL), β,γ-alkynyl α-imino ester **3** (0.2 mmol), chiral phosphoric acid **1h** (0.002 mmol) and Hantzsch ester **2** (0.44 mmol) were added under argon. After the reaction was complete (monitored by TLC), the solvent was removed under reduced pressure. The crude product was purified by silica gel column chromatography (ethyl acetate/petroleum ether = 1/20 ~ 1/40) to afford the product.



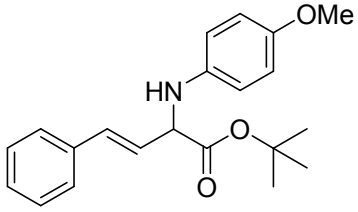
(**4a**). Prepared according to the general procedure to provide the title compound as a pale yellow oil (15% yield, 89% ee) following silica gel chromatography (ethyl acetate/petroleum ether = 1/30, v/v). $[\alpha]_D^{20}$ = +97.0 (c = 0.5, $CHCl_3$). ^1H NMR (300 MHz, $CDCl_3$) δ 3.74 (s, 3H), 3.79 (s, 3H), 4.37 (br, 1H), 4.67 (d, J = 6.0 Hz, 1H), 6.28 (dd, J_1 = 5.7 Hz, J_2 = 15.9 Hz, 1H), 6.63-6.66 (m, 2H), 6.75-6.80 (m, 3H), 7.22-7.39 (m, 5H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 52.7, 55.7, 59.8, 114.8, 115.1, 125.1, 126.6, 128.0, 128.6, 132.9, 136.1, 140.4, 152.7, 172.4; IR (film) 3380, 2973, 1735, 1515, 1380, 1307, 1163, 1130, 952, 817 cm^{-1}; HRMS (ESI): Calcd for $C_{18}H_{20}NO_3$ [M+H]: 298.1437. Found: 298.1449; The enantiomeric ratio was determined by Daicel Chiralcel AD-H (0.46 cm*25 cm), Hexanes / IPA = 90 / 10, 1.0 mL/min^{-1}, λ = 254 nm, t (minor) = 17.71 min, t (major) = 20.83 min.



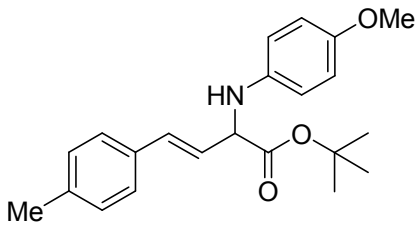
(**4b**). Prepared according to the general procedure to provide the title compound as a pale yellow oil (34% yield, 93% ee) following silica gel chromatography (ethyl acetate/petroleum ether = 1/30, v/v). $[\alpha]_D^{20}$ = +109.5 (c = 0.5, $CHCl_3$). ^1H NMR (300 MHz, $CDCl_3$) δ 1.29 (t, J = 7.2 Hz, 3H), 3.73 (s, 3H), 4.19-4.30 (m, 2H), 4.39 (br, 1H), 4.65 (d, J = 6.3 Hz, 1H), 6.29 (dd, J_1 = 5.7 Hz, J_2 = 15.9 Hz, 1H), 6.64 (d, J = 9.3 Hz, 2H), 6.75-6.81 (m, 3H), 7.24-7.40 (m, 5H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 14.2, 55.7, 59.8, 61.7, 114.8, 115.0, 125.3, 126.6, 127.9, 128.6, 132.7, 136.2, 140.5, 152.6, 171.9; IR (film) 1713, 1513, 1242, 1031, 821 cm^{-1}; HRMS (EI) exact mass calculated for ($C_{19}H_{21}NO_3$) requires *m/z* 311.1521. Found *m/z* 311.1526. The enantiomeric ratio was determined by Daicel Chiralcel AD-H (0.46 cm*25 cm), Hexanes / IPA = 90 / 10, 1.0 mL/min^{-1}, λ = 254 nm, t (minor) = 16.51 min, t (major) = 18.14 min.



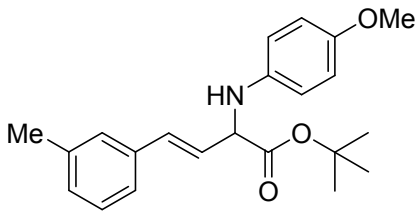
(**4c**). Prepared according to the general procedure to provide the title compound as a colorless solid (51% yield, 95% ee) following silica gel chromatography (ethyl acetate/petroleum ether = 1/30, v/v). $[\alpha]_D^{20}$ = +97.0 (c = 1.1, $CHCl_3$). ^1H NMR (300 MHz, $CDCl_3$) δ 1.23 (d, *J* = 6.0 Hz, 3H), 1.28 (d, *J* = 6.0 Hz, 3H), 3.72 (s, 3H), 4.39 (br, 1H), 4.62 (d, *J* = 5.7 Hz, 1H), 5.05-5.13 (m, 1H), 6.28 (dd, J_1 = 5.4 Hz, J_2 = 15.9 Hz, 1H), 6.63 (d, *J* = 8.7 Hz, 2H), 6.77 (d, *J* = 8.7 Hz, 2H), 6.78 (d, *J* = 14.1 Hz, 1H), 7.21-7.38 (m, 5H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 21.6, 21.8, 55.6, 59.9, 69.4, 114.8, 115.0, 125.3, 126.6, 127.9, 128.5, 132.6, 136.3, 140.5, 152.5, 171.4; IR (film) 3362, 2981, 1728, 1716, 1516, 1247, 1233, 1195, 1182, 1099, 1030, 824, 692 cm^{-1}; HRMS (EI) exact mass calculated for ($C_{20}H_{23}NO_3$) requires *m/z* 325.1683. Found *m/z* 325.1678. The enantiomeric ratio was determined by Daicel Chiralcel AD-H (0.46 cm*25 cm), Hexanes / IPA = 90 / 10, 1.0 mL/min^{-1}, λ = 254 nm, t (major) = 16.65 min, t (minor) = 13.71 min.



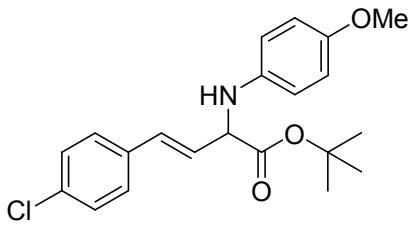
(**4d**). Prepared according to the general procedure to provide the title compound as white solid (58% yield, 94% ee) following silica gel chromatography (ethyl acetate/petroleum ether = 1/20, v/v). $[\alpha]_D^{20}$ = +81.6 (c = 0.8, $CHCl_3$). ^1H NMR (300 MHz, $CDCl_3$) δ 1.47 (s, 9H), 3.74 (s, 3H), 4.38 (br, 1H), 4.54 (d, *J* = 5.1 Hz, 1H), 6.28 (dd, J_1 = 5.4 Hz, J_2 = 15.6 Hz, 1H), 6.63 (d, *J* = 8.7 Hz, 2H), 6.74-6.80 (m, 3H), 7.22-7.40 (m, 5H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 28.0, 55.7, 60.3, 82.4, 114.8, 114.9, 125.8, 126.6, 127.8, 128.5, 132.3, 136.4, 140.7, 152.4, 171.0; IR (film) 3347, 2962, 2835, 1709, 1514, 1368, 1259, 1239, 1097, 1037, 968, 822, 692 cm^{-1}; HRMS (ESI): Calcd for $C_{21}H_{26}NO_3$ [M+H]: 340.1907. Found: 340.1914; The enantiomeric ratio was determined by Daicel Chiralcel AD-H (0.46 cm*25 cm), Hexanes / IPA = 70 / 30, 1.0 mL/min^{-1}, λ = 254 nm, t (minor) = 10.74 min, t (major) = 11.52 min.



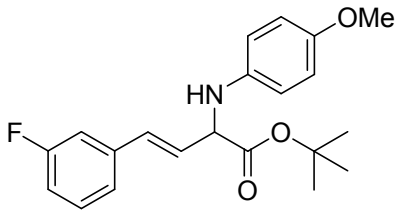
(**4e**). Prepared according to the general procedure to provide the title compound as white solid (42% yield, 95% ee) following silica gel chromatography (ethyl acetate/petroleum ether = 1/40, v/v). $[\alpha]_D^{20}$ = +90.2 (c = 1.0, $CHCl_3$). ^1H NMR (300 MHz, $CDCl_3$) δ 1.46 (s, 9H), 2.33 (s, 3H), 3.73 (s, 3H), 4.35 (br, 1H), 4.53 (d, J = 5.4 Hz, 1H), 6.22 (dd, J_1 = 6.0 Hz, J_2 = 15.9 Hz, 1H), 6.62 (d, J = 9.0 Hz, 2H), 6.73 (d, J = 15.9 Hz, 1H), 6.77 (d, J = 9.0 Hz, 2H), 7.12 (d, J = 8.1 Hz, 2H), 7.27 (d, J = 8.1 Hz, 2H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 21.2, 28.0, 55.7, 60.3, 82.2, 114.7, 114.9, 124.7, 126.5, 129.2, 132.2, 133.6, 137.7, 140.7, 152.4, 171.1; IR (film) 3360, 2981, 1718, 1512, 1367, 1243, 1146, 1034, 822 cm^{-1}; HRMS (ESI): Calcd for $C_{22}H_{28}NO_3$ [M+H]: 354.2063. Found: 354.2074; The enantiomeric ratio was determined by Daicel Chiralcel AD-H (0.46 cm*25 cm), Hexanes / IPA = 80 / 20, 1.0 mL/min^{-1}, λ = 254 nm, t (minor) = 27.35 min, t (major) = 13.81 min.



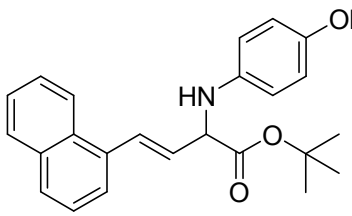
(**4f**). Prepared according to the general procedure to provide the title compound as pale yellow solid (64% yield, 95% ee) following silica gel chromatography (ethyl acetate/petroleum ether = 1/40, v/v). $[\alpha]_D^{20}$ = +71.5 (c = 0.9, $CHCl_3$). ^1H NMR (300 MHz, $CDCl_3$) δ 1.47 (s, 9H), 2.34 (s, 3H), 3.73 (s, 3H), 4.37 (br, 1H), 4.53 (d, J = 5.7 Hz, 1H), 6.26 (dd, J_1 = 5.7 Hz, J_2 = 16.2 Hz, 1H), 6.62 (d, J = 9.0 Hz, 2H), 6.74 (d, J = 16.2 Hz, 1H), 6.77 (d, J = 8.7 Hz, 2H), 7.05-7.07 (m, 1H), 7.19-7.26 (m, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 21.3, 28.0, 55.7, 60.3, 82.3, 114.8, 114.9, 123.7, 125.6, 127.3, 128.4, 132.5, 136.4, 138.1, 140.7, 152.4, 171.0; IR (film) 3384, 2979, 1729, 1514, 1369, 1240, 1151, 1039, 821 cm^{-1}; HRMS (ESI): Calcd for $C_{22}H_{28}NO_3$ [M+H]: 354.2063. Found: 354.2076; The enantiomeric ratio was determined by Daicel Chiralcel AD-H (0.46 cm*25 cm), Hexanes / IPA = 80 / 20, 1.0 mL/min^{-1}, λ = 254 nm, t (minor) = 10.58 min, t (major) = 9.66 min.



(**4g**). Prepared according to the general procedure to provide the title compound as pale yellow solid (47% yield, 96% ee) following silica gel chromatography (ethyl acetate/petroleum ether = 1/40, v/v). $[\alpha]_D^{20}$ = +86.5 (c = 0.88, $CHCl_3$). ^{1}H NMR (300 MHz, $CDCl_3$) δ 1.47 (s, 9H), 3.73 (s, 3H), 4.39 (br, 1H), 4.53 (d, J = 4.2 Hz, 1H), 6.25 (dd, J_1 = 5.4 Hz, J_2 = 16.2 Hz, 1H), 6.62 (d, J = 9.1 Hz, 2H), 6.72 (d, J = 15.6 Hz, 1H), 6.78 (d, J = 8.7 Hz, 2H), 7.23-7.31 (m, 4H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 28.0, 55.7, 60.2, 82.5, 114.8, 114.9, 126.5, 127.8, 128.7, 131.0, 133.4, 134.9, 140.6, 152.5, 170.7; IR (film) 3346, 2982, 1719, 1512, 1244, 1144, 821 cm^{-1}; HRMS (ESI): Calcd for $C_{21}H_{25}ClNO_3$ [M+H]: 374.1517. Found: 374.1532; The enantiomeric ratio was determined by Daicel Chiralcel AD-H (0.46 cm*25 cm), Hexanes / IPA = 80 / 20, 1.0 mL/min^{-1}, λ = 254 nm, t (minor) = 21.60 min, t (major) = 15.65 min.

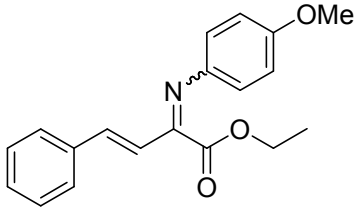


(**4h**). Prepared according to the general procedure to provide the title compound as pale yellow solid (60% yield, 93% ee) following silica gel chromatography (ethyl acetate/petroleum ether = 1/40, v/v). $[\alpha]_D^{20}$ = +70.6 (c = 1.0, $CHCl_3$). ^{1}H NMR (300 MHz, $CDCl_3$) δ 1.48 (s, 9H), 3.73 (s, 3H), 4.40 (br, 1H), 4.54 (d, J = 4.8 Hz, 1H), 6.30 (dd, J_1 = 5.7 Hz, J_2 = 15.9 Hz, 1H), 6.61 (d, J = 9.0 Hz, 2H), 6.73 (d, J = 15.3 Hz, 1H), 6.77 (d, J = 8.4 Hz, 2H), 6.93-6.97 (m, 1H), 7.06-7.13 (m, 2H), 7.23-7.30 (m, 1H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 28.0, 55.7, 60.2, 82.6, 113.0 (d, J = 21.8 Hz), 114.6 (d, J = 21.2 Hz), 114.9 (d, J = 8.0 Hz), 122.5, 122.6, 127.3, 130.0 (d, J = 8.0 Hz), 131.1 (d, J = 2.3 Hz), 140.6, 152.5, 163.0 (d, J = 244.3 Hz), 170.7; IR (film) 3385, 2981, 1733, 1515, 1241, 1151, 1039, 821 cm^{-1}; HRMS (ESI): Calcd for $C_{21}H_{25}FNO_3$ [M+H]: 358.1813. Found: 358.1817; The enantiomeric ratio was determined by Daicel Chiralcel OD-H (0.46 cm*25 cm), Hexanes / IPA = 90 / 10, 1.0 mL/min^{-1}, λ = 254 nm, t (minor) = 6.21 min, t (major) = 7.05 min.



(**4i**). Prepared according to the general procedure to provide the title compound as pale yellow oil (27% yield, 83% ee) following silica gel chromatography (ethyl acetate/petroleum ether = 1/40, v/v). $[\alpha]_D^{20}$ = +46.3 (c = 0.8, $CHCl_3$). ^1H NMR (300 MHz, $CDCl_3$) δ 1.51 (s, 9H), 3.75 (s, 3H), 4.67 (dd, J_1 = 1.5 Hz, J_2 = 5.7 Hz, 1H), 6.29 (dd, J_1 = 5.7 Hz, J_2 = 15.6 Hz, 1H), 6.70 (d, J = 9.0 Hz, 2H), 6.81 (d, J = 9.3 Hz, 2H), 7.41-7.56 (m, 5H), 7.67-7.85 (m, 2H), 7.97-8.01 (m, 1H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 28.0, 55.7, 60.6, 82.4, 114.8, 115.1, 123.9, 124.0, 125.5, 125.8, 126.1, 128.1, 128.4, 129.1, 130.0, 131.1, 133.5, 134.5, 140.7, 152.5, 170.9; IR (film) 3375, 2980, 1739, 1514, 1370, 1244, 1154, 1037, 823, 775 cm^{-1}; HRMS (MALDI/DHB): Calcd for $C_{25}H_{27}NO_3Na$ [M+Na]: 412.1884. Found: 412.1883; The enantiomeric ratio was determined by Daicel Chiralcel AD-H (0.46 cm*25 cm), Hexanes / IPA = 90 / 10, 1.0 mL/min^{-1}, λ = 254 nm, t (minor) = 14.25 min, t (major) = 16.75 min.

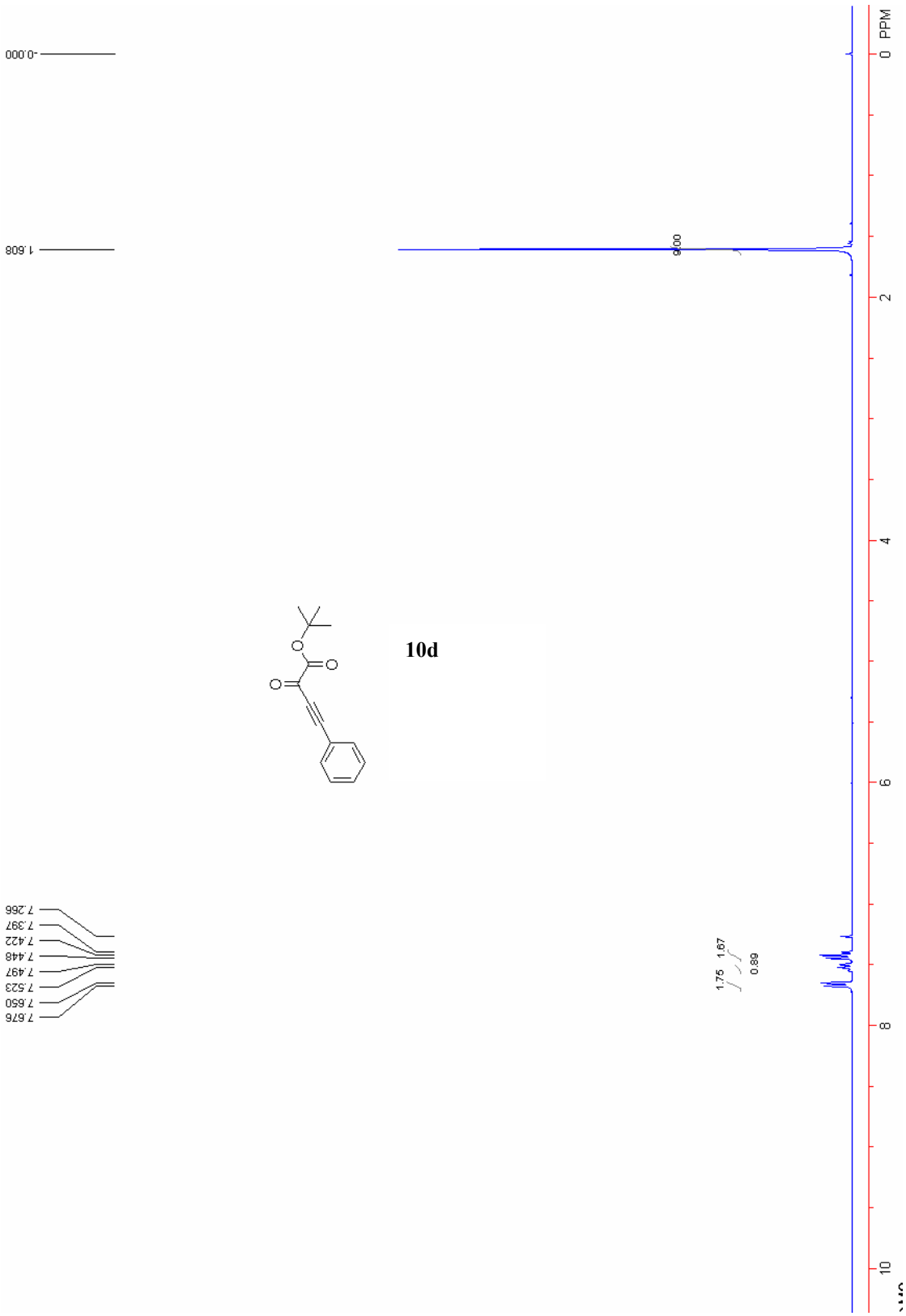
Data for the study of proposed mechanism:



(**7**). Yellow oil. Isomer mixtures (major isomer: minor isomer = 10:9). ^1H NMR (300 MHz, $CDCl_3$) δ 1.06 (t, J = 7.2 Hz, 3H, major), 1.44 (t, J = 7.2 Hz, 3H, minor), 3.77 (s, 3H, major), 3.80 (s, 3H, minor), 4.17 (q, J = 7.5 Hz, 2H, major), 4.47 (q, J = 7.5 Hz, 2H, minor), 6.77-6.96 (m, 9H, major + minor), 6.99-7.14 (m, 2H, major + minor), 7.29-7.53 (m, 11H, major + minor); ^{13}C NMR (75 MHz, $CDCl_3$) δ (major + minor) 13.7, 14.0, 55.2, 61.3, 61.9, 113.9, 114.0, 117.3, 121.2, 122.2, 125.9, 127.4, 127.5, 128.7, 128.7, 129.5, 129.7, 135.1, 135.2, 140.5, 141.5, 141.5, 143.0, 157.2, 157.3, 158.2, 159.9, 164.9, 165.0; IR (film) 3314, 1729, 1674, 1644, 1515, 1247, 1173, 1081, 1031, 832, 814, 744, 695, 515 cm^{-1}; HRMS (EI): Calcd for $C_{19}H_{19}NO_3$: 309.1365. Found: 309.1368.

References:

1. Guo, M.; Li, D.; Zhang, Z. *J. Org. Chem.* **2003**, *68*, 10172-10174
2. Hemming, K.; Bevan, M. J.; Loukou, C.; Patel, S. D.; Renaudeau, D. *Synlett* **2000**, 1565-1568
3. Pagliai, F.; Pirali, T.; Grosso, E. D.; Brisco, R. D.; Tron, G. C.; Sorba, G.; Genazzani, A. A. *J. Med. Chem.* **2006,** *49,* 467-470.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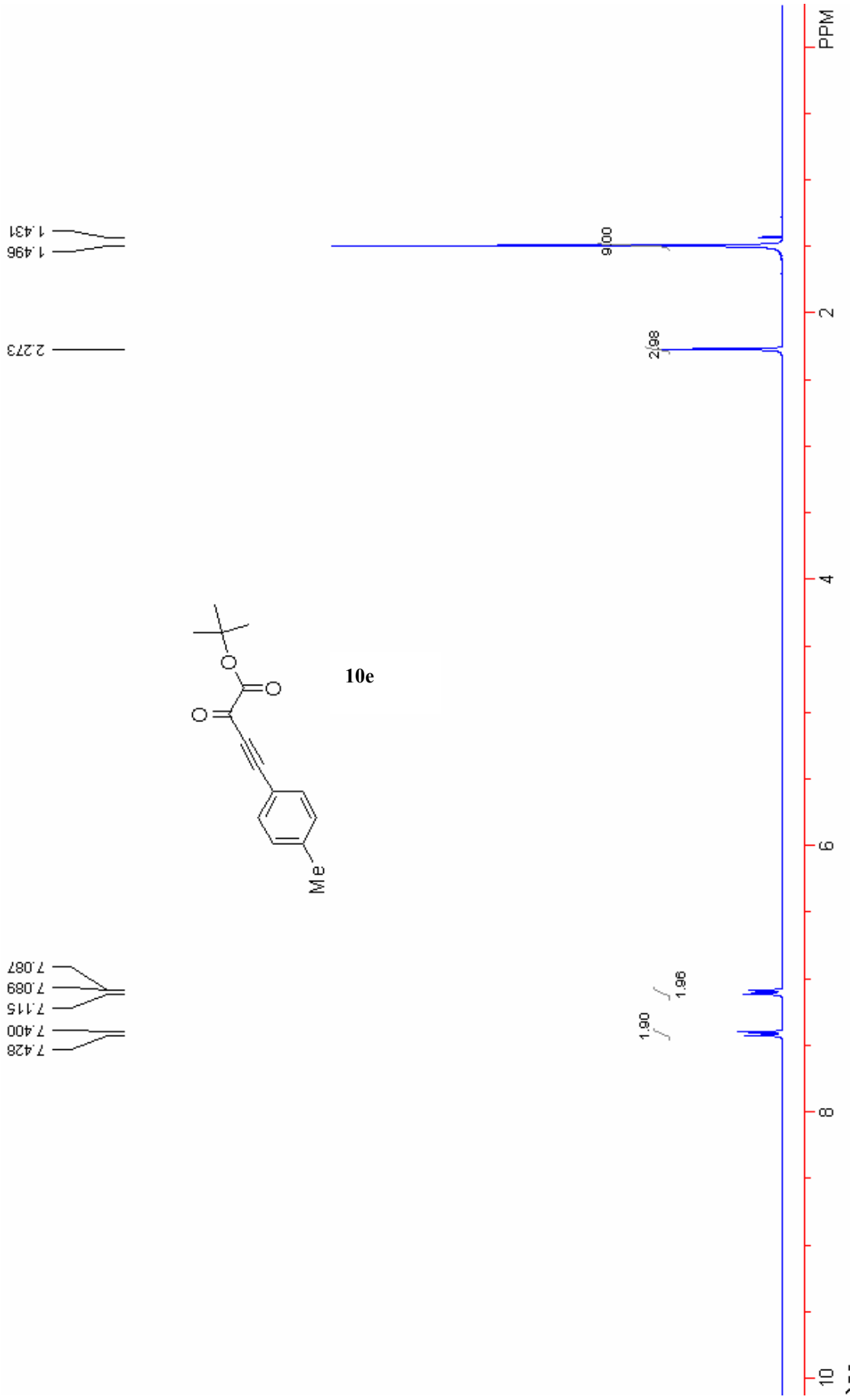
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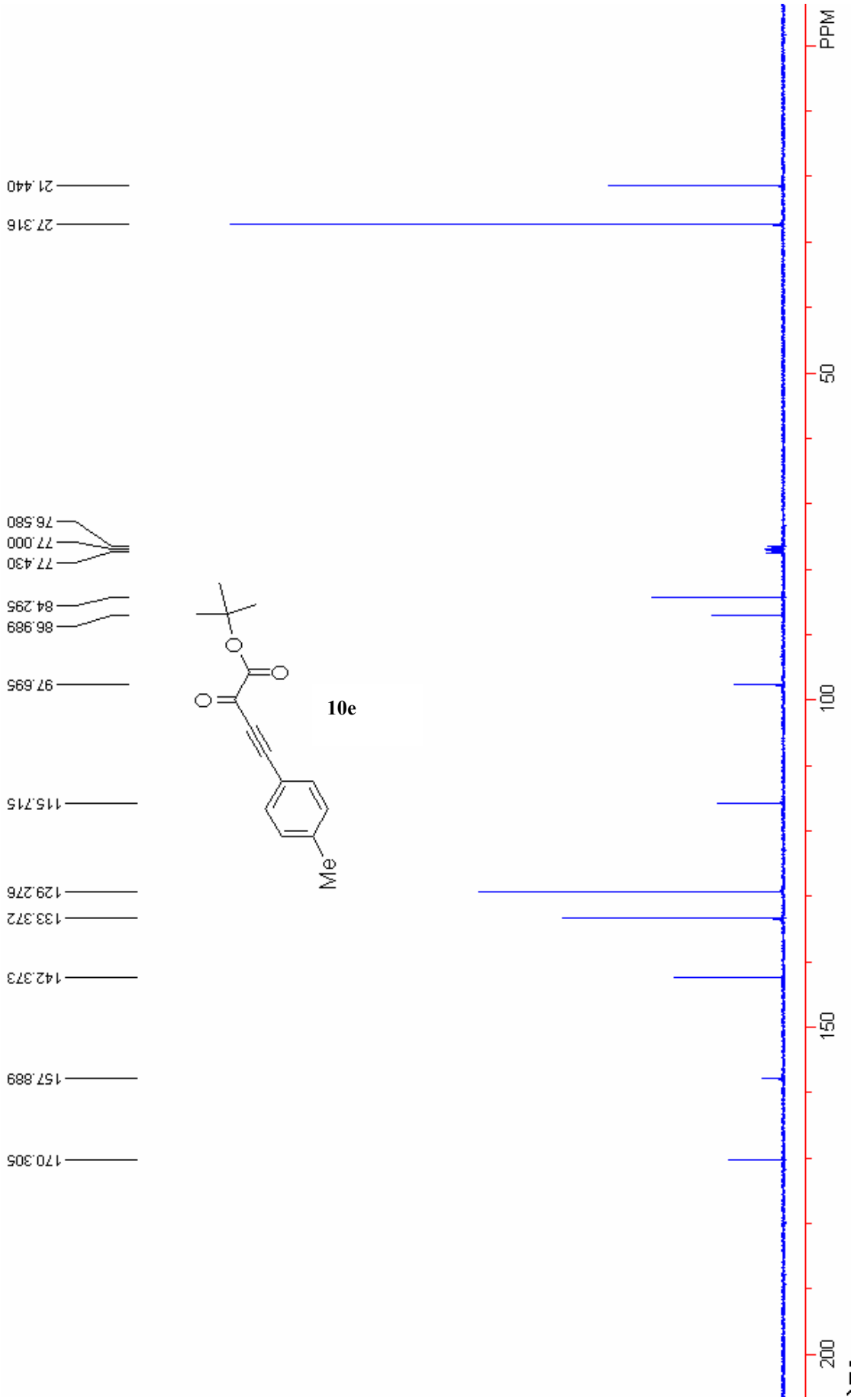
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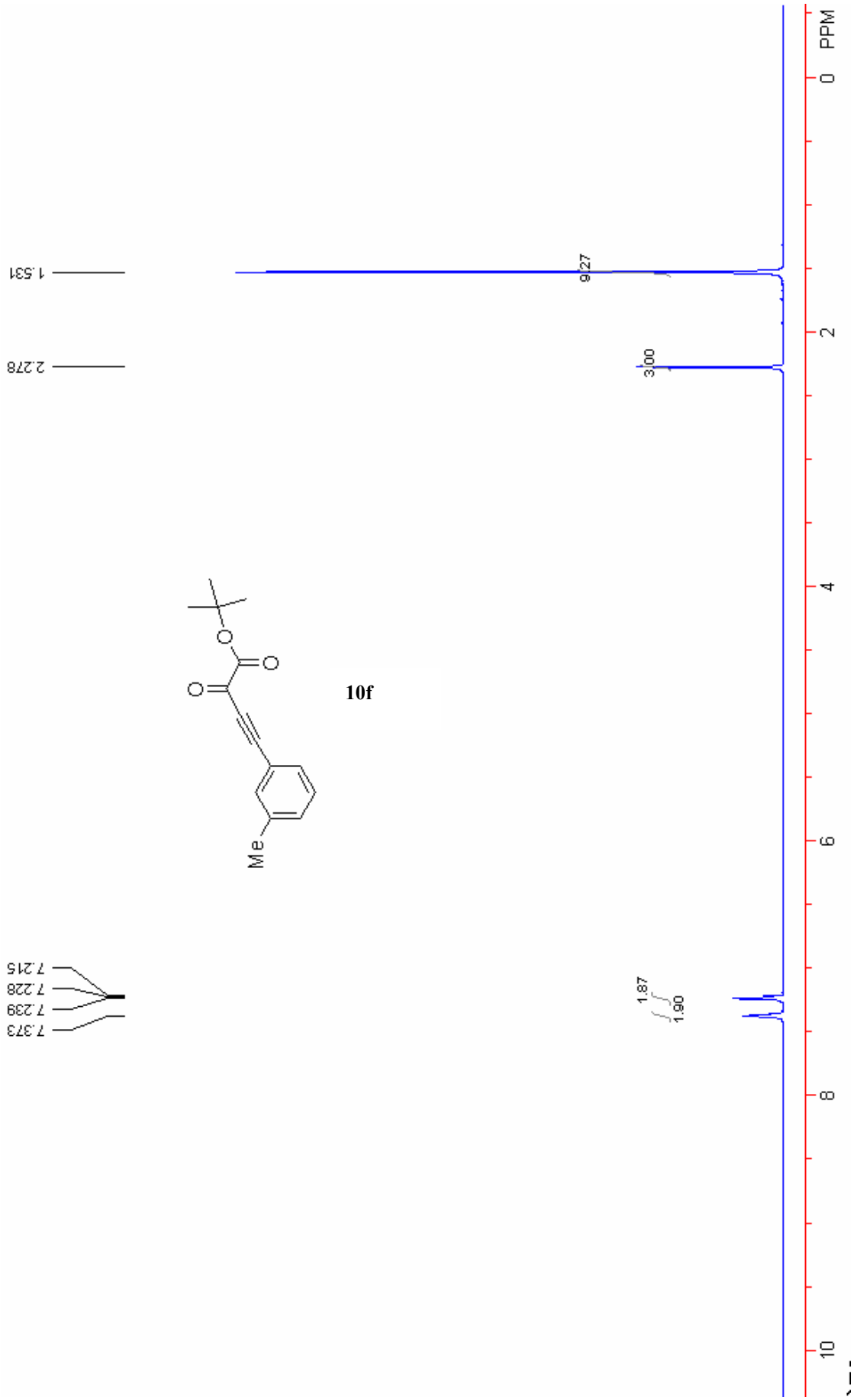
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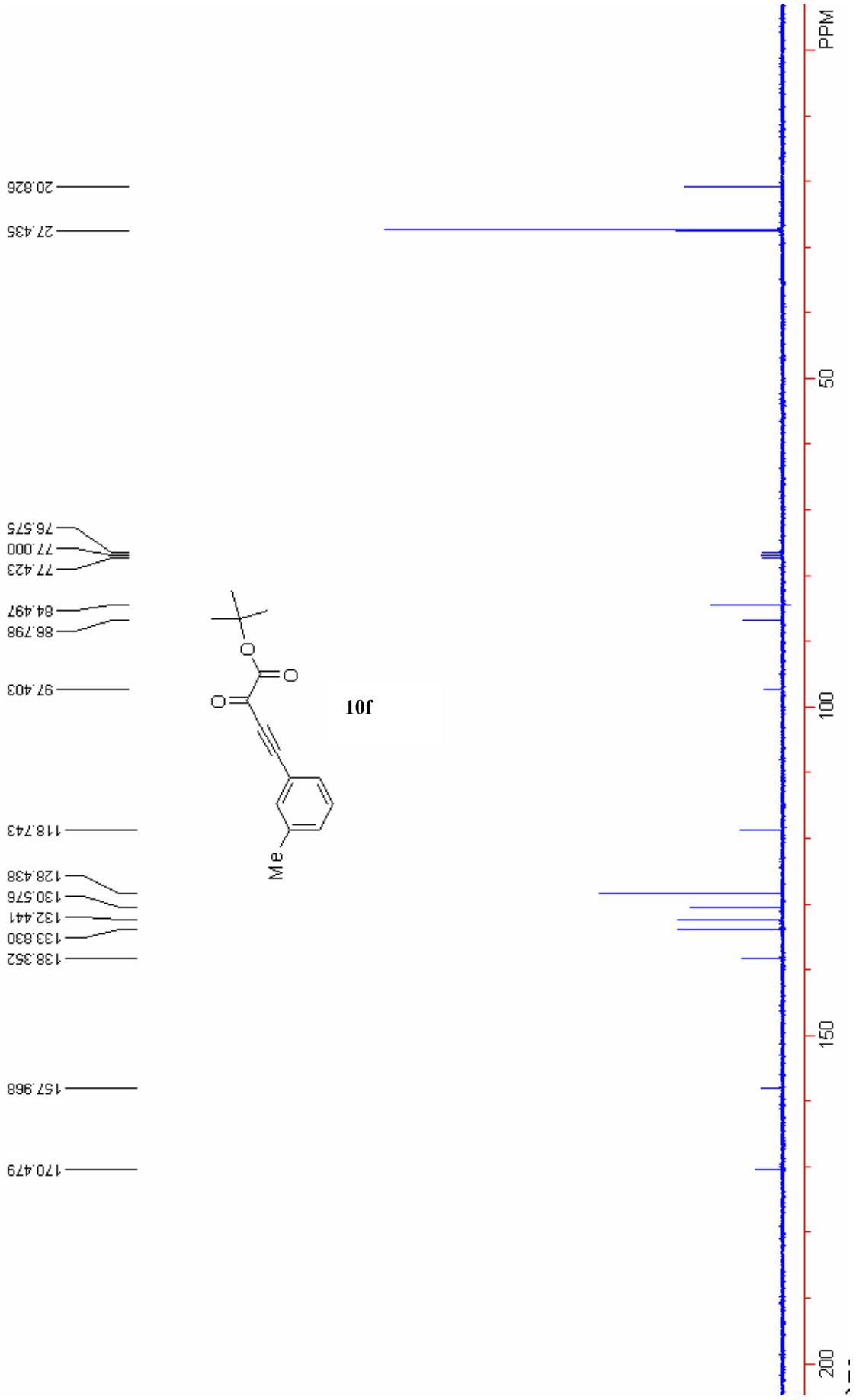
10f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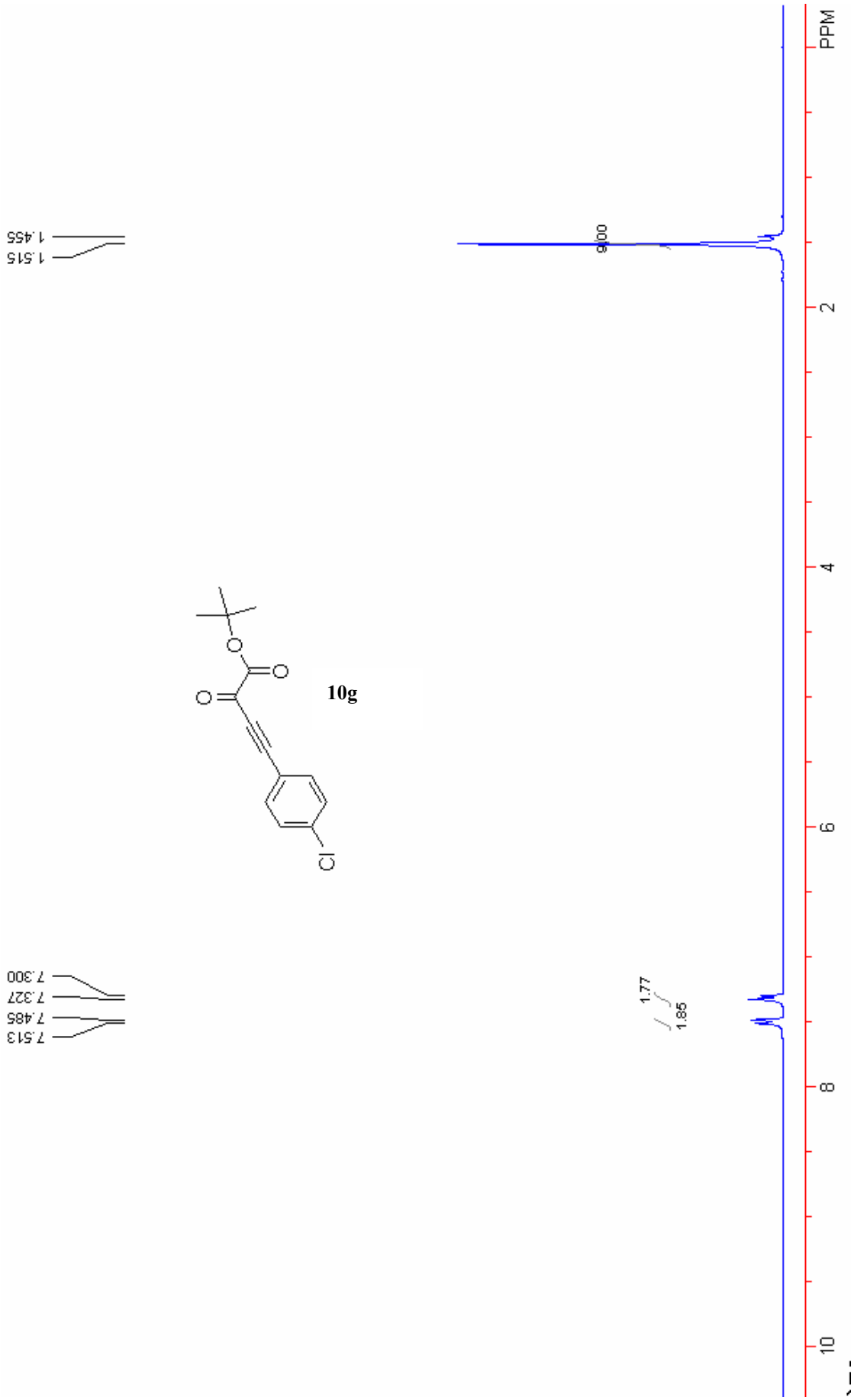
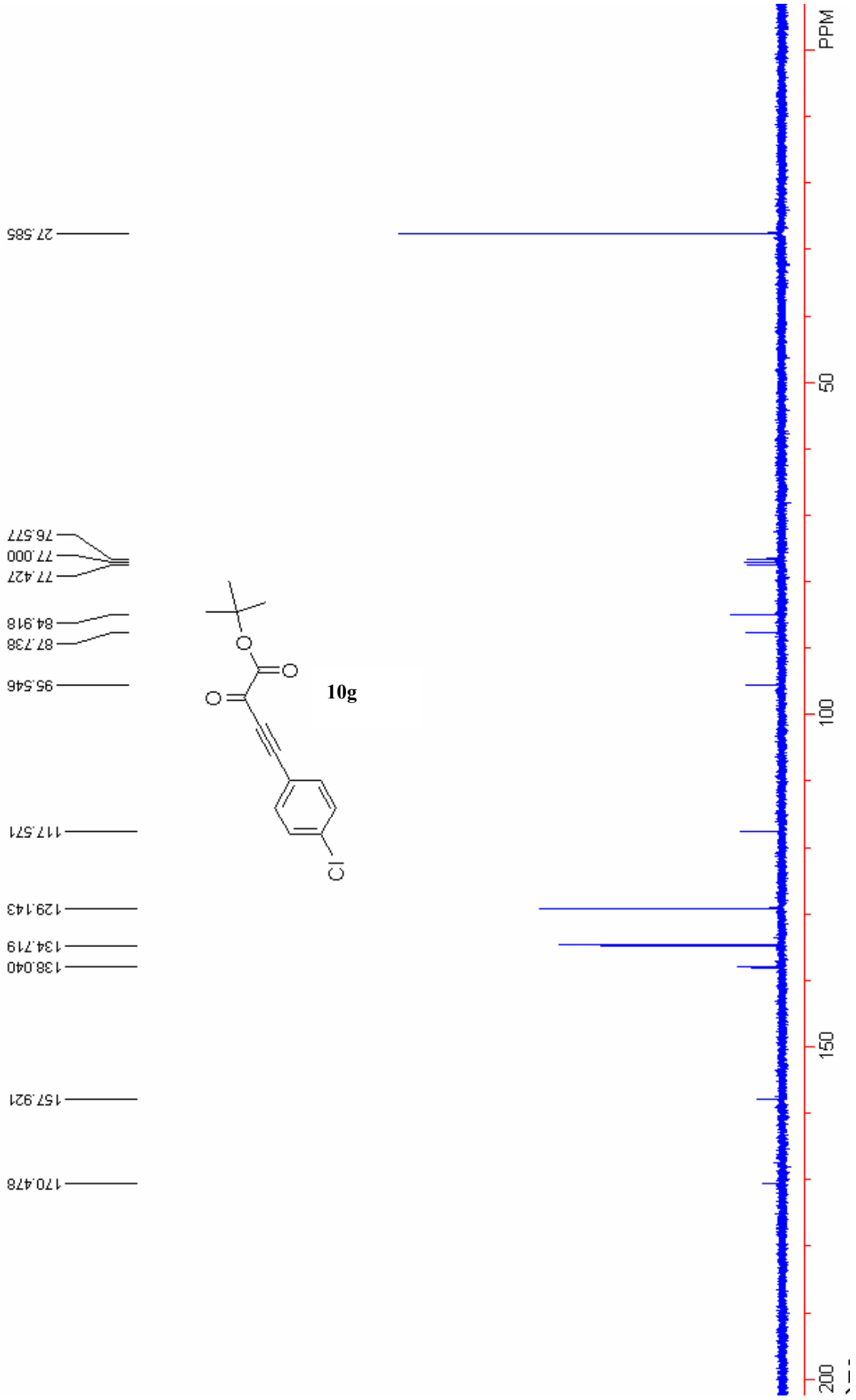
150
200

10f



10g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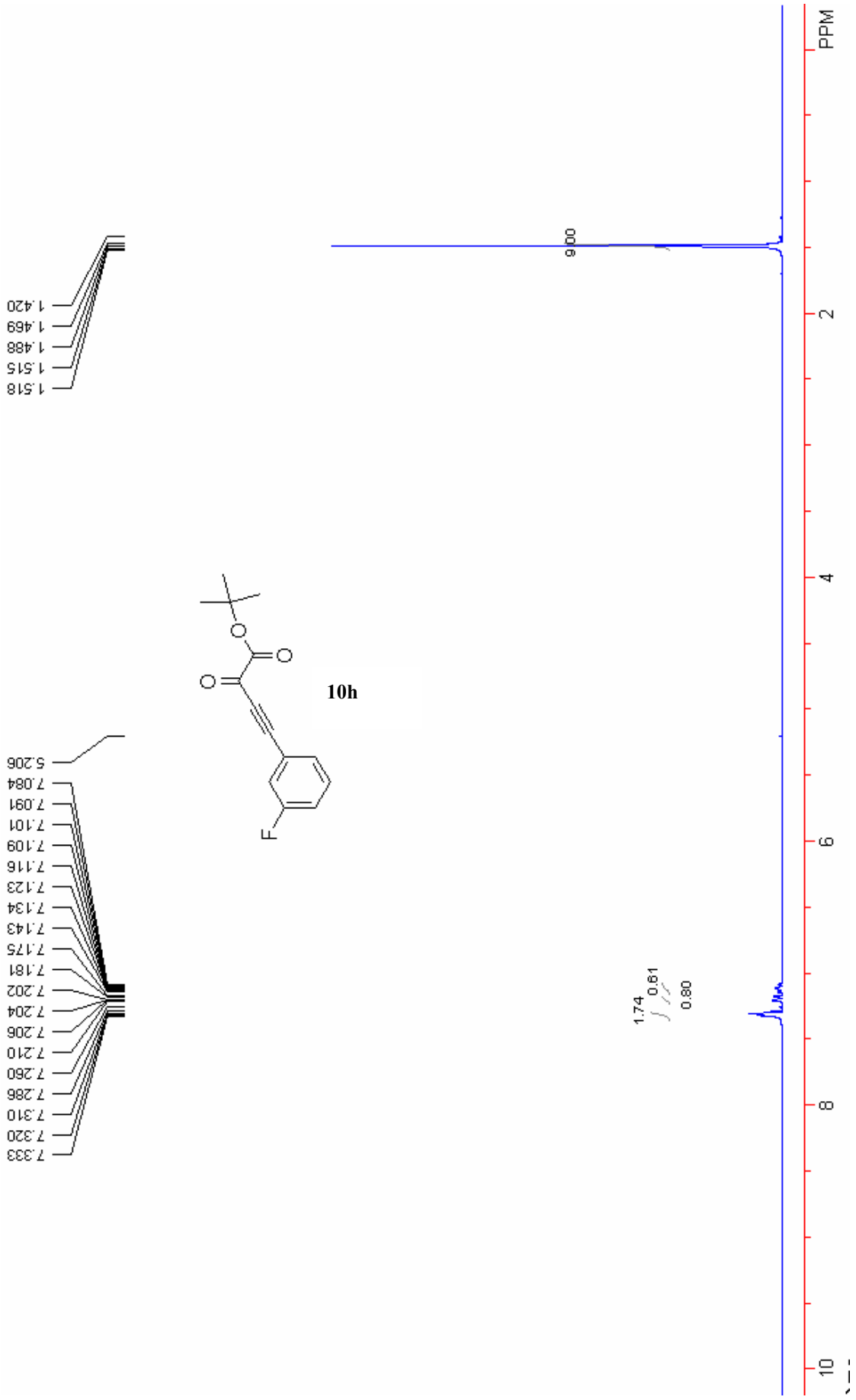
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7.202
7.204
7.206
7.210
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7.320
7.333
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6
4
2
10h


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94.454
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129.265
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157.617
160.219
163.514
170.270
F
10h
200
150
100
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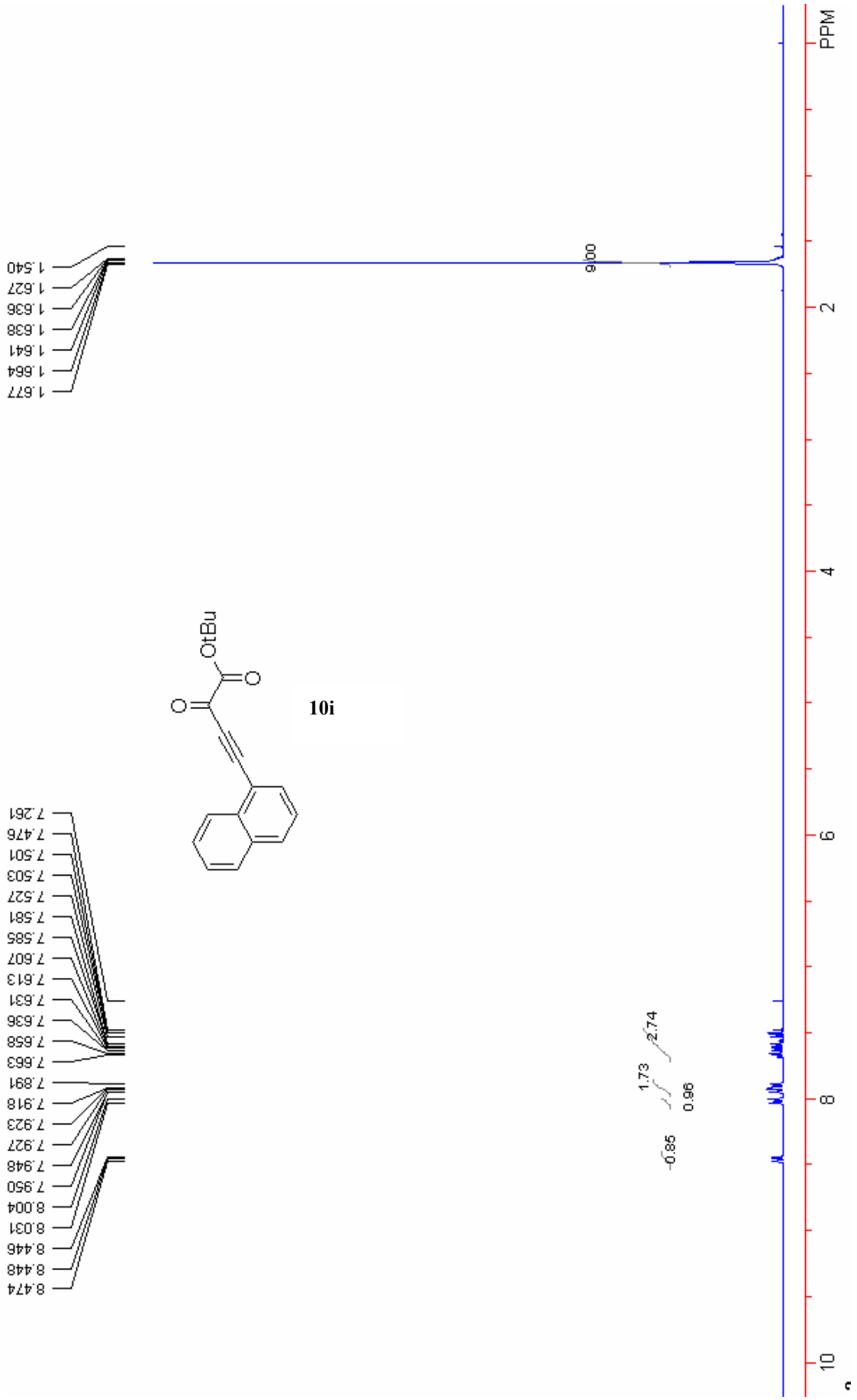
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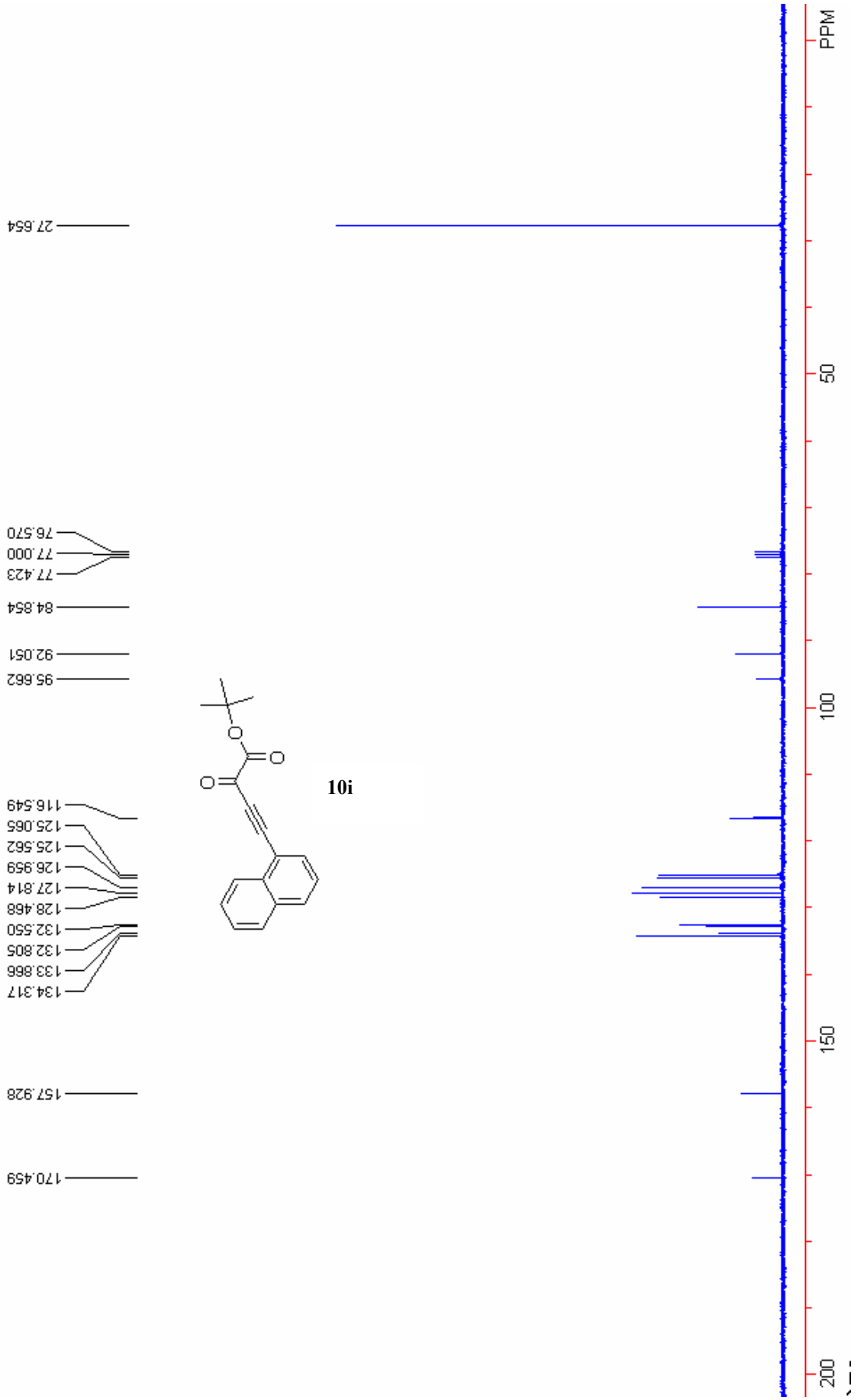
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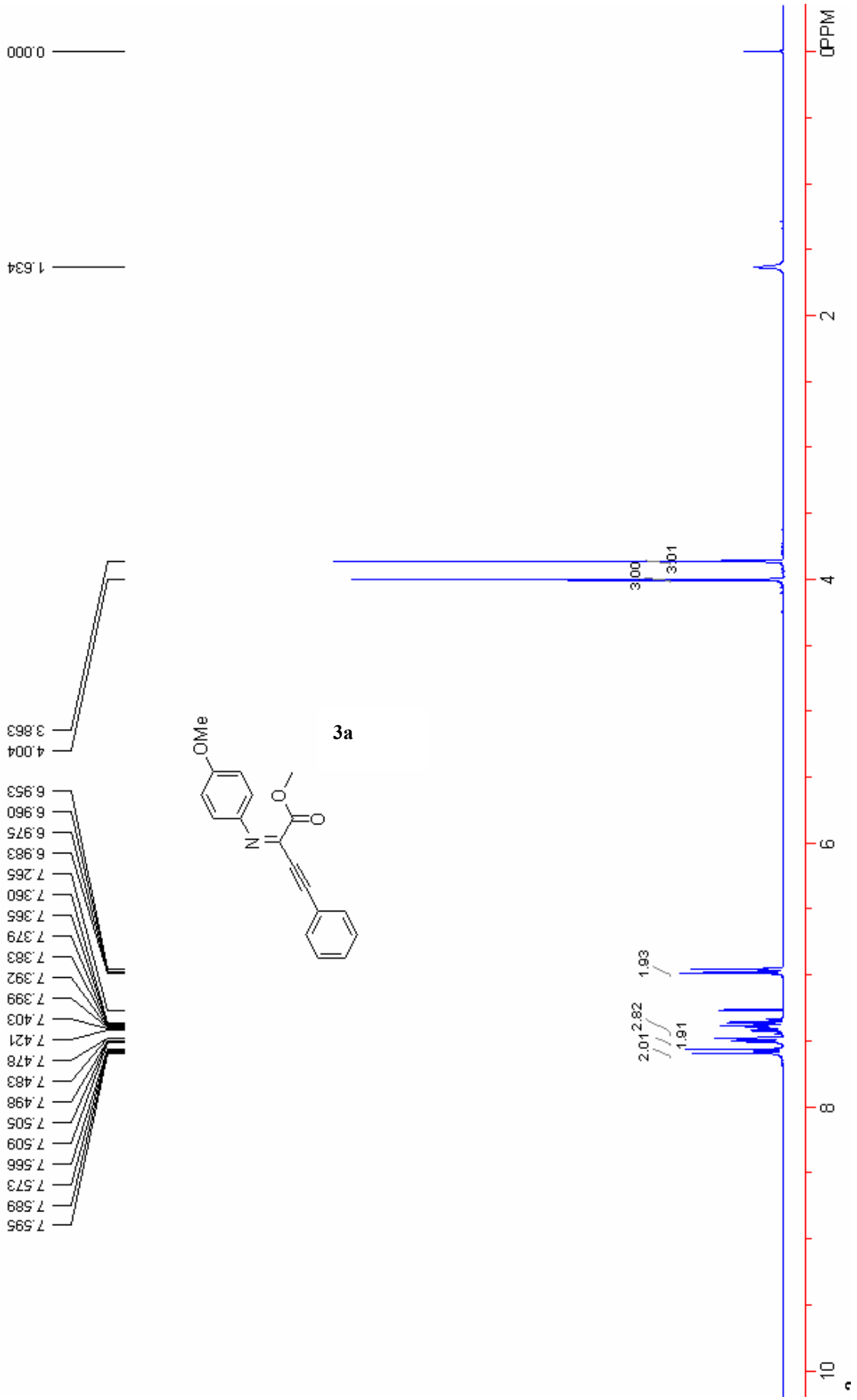
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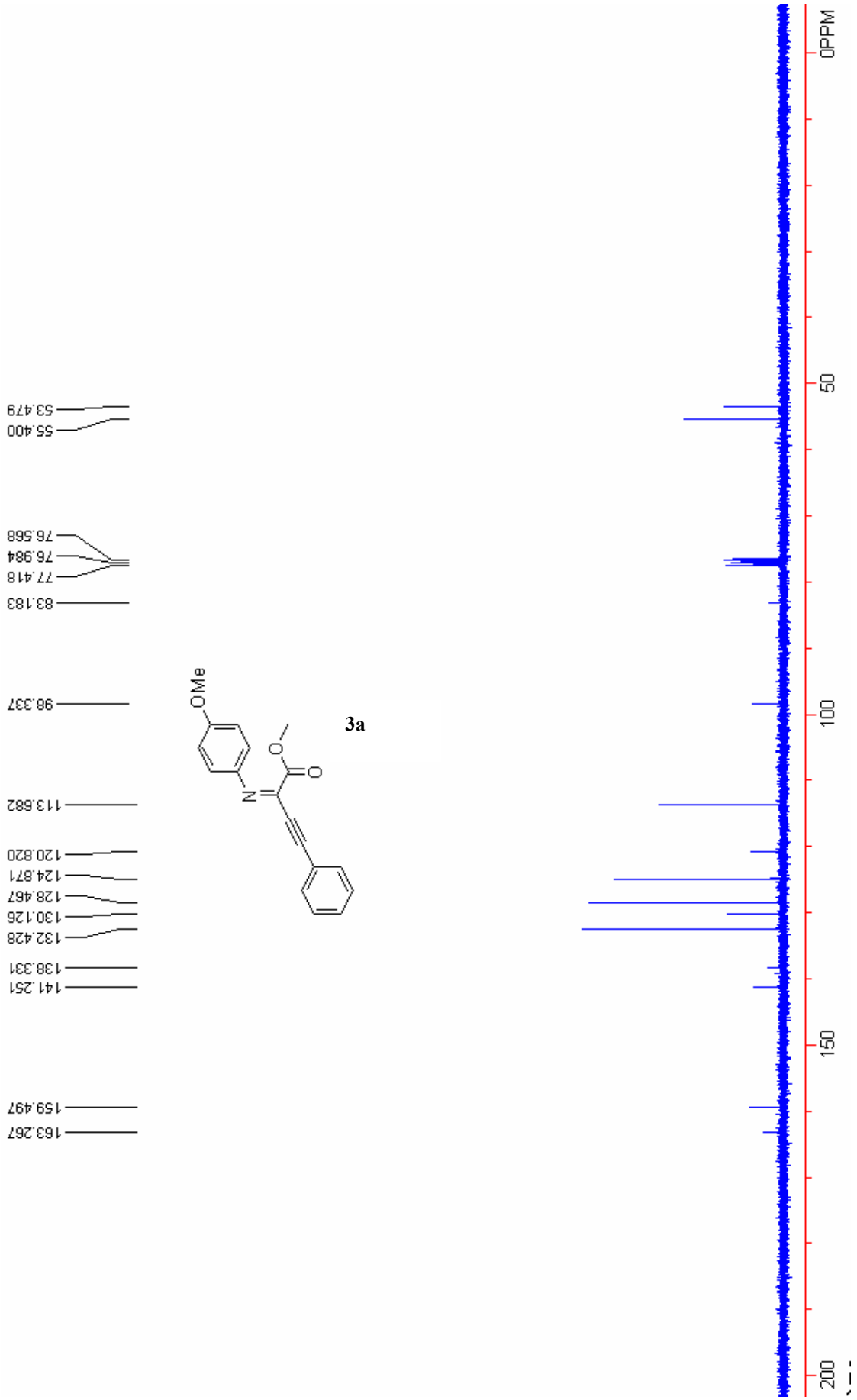
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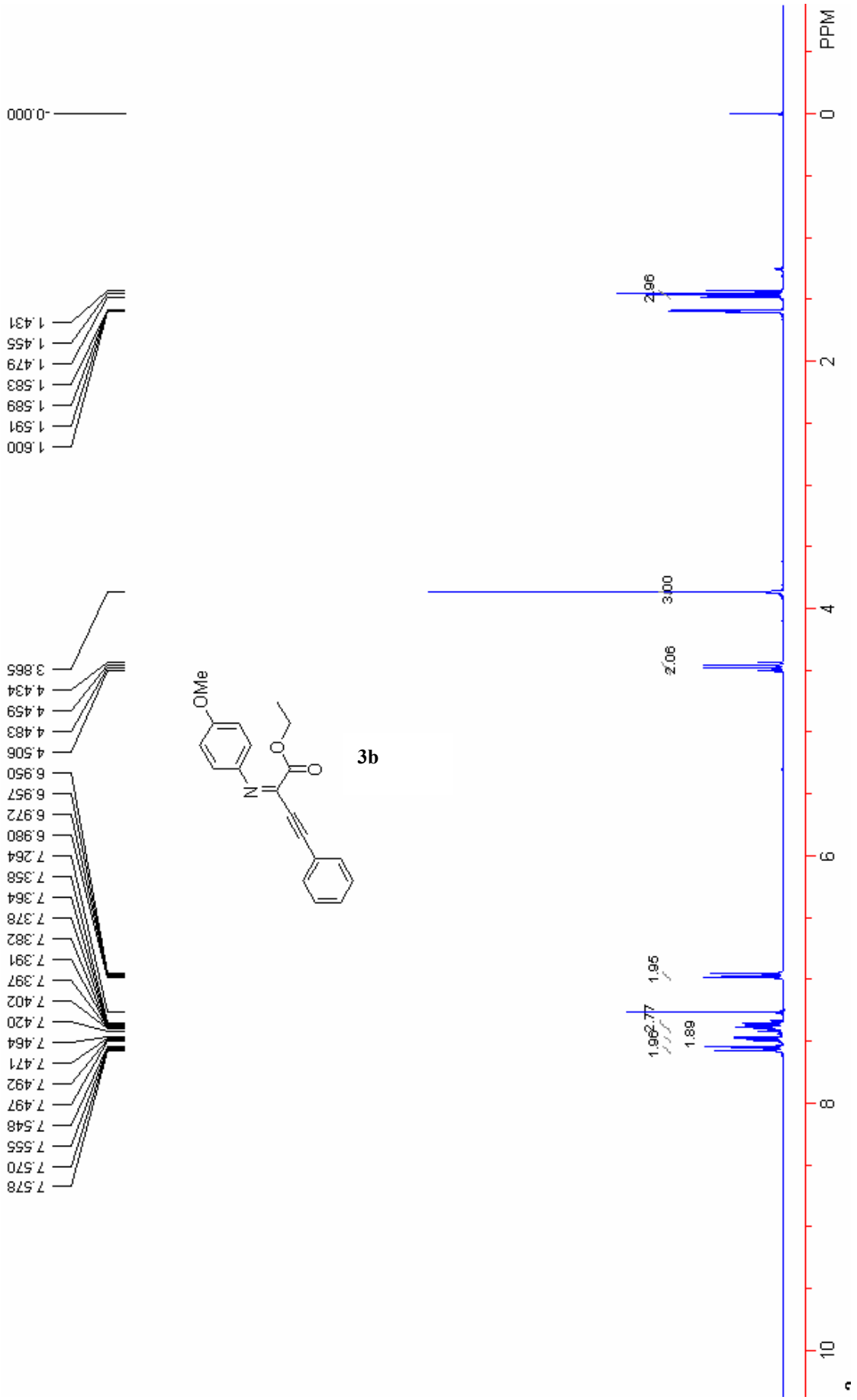
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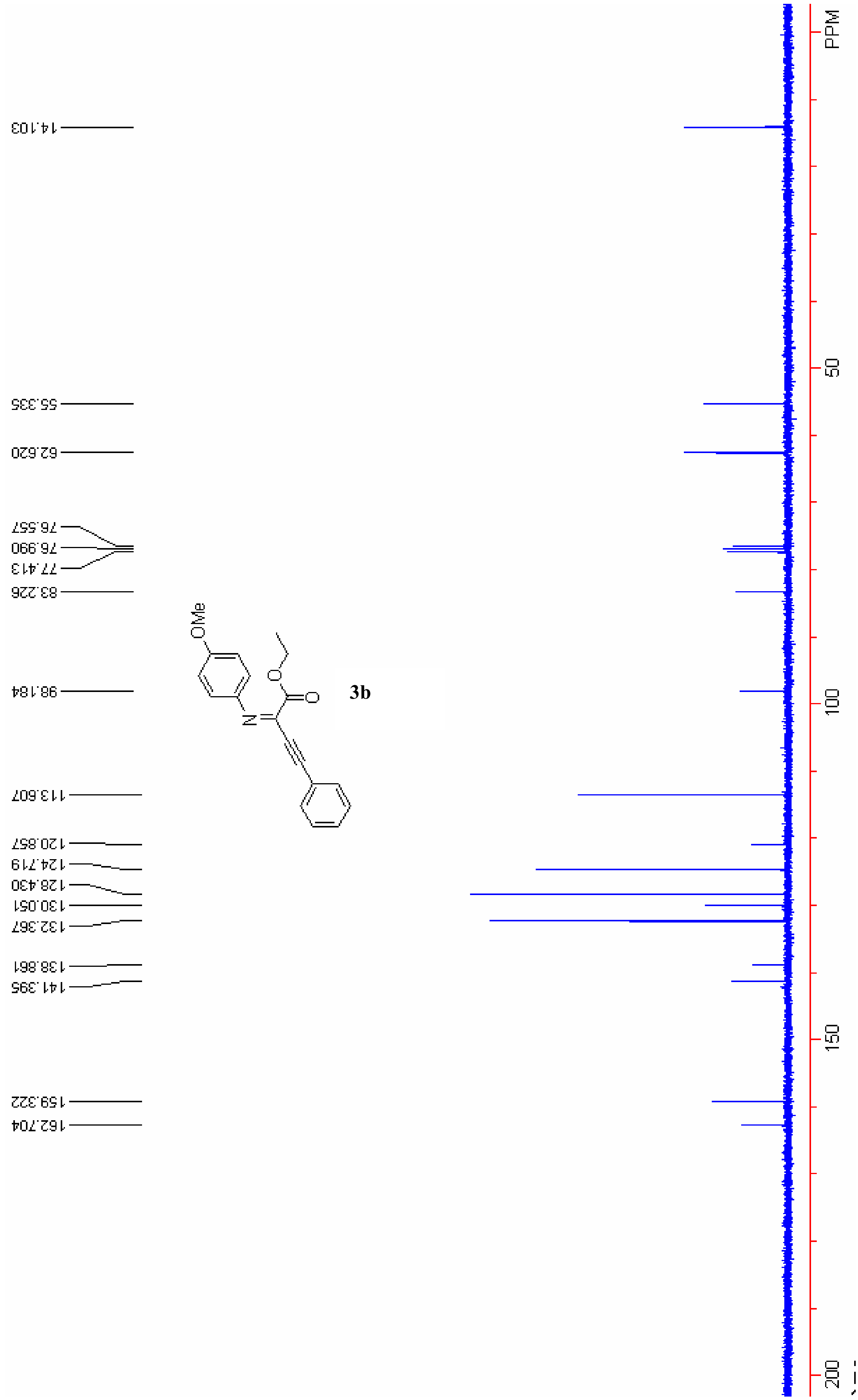

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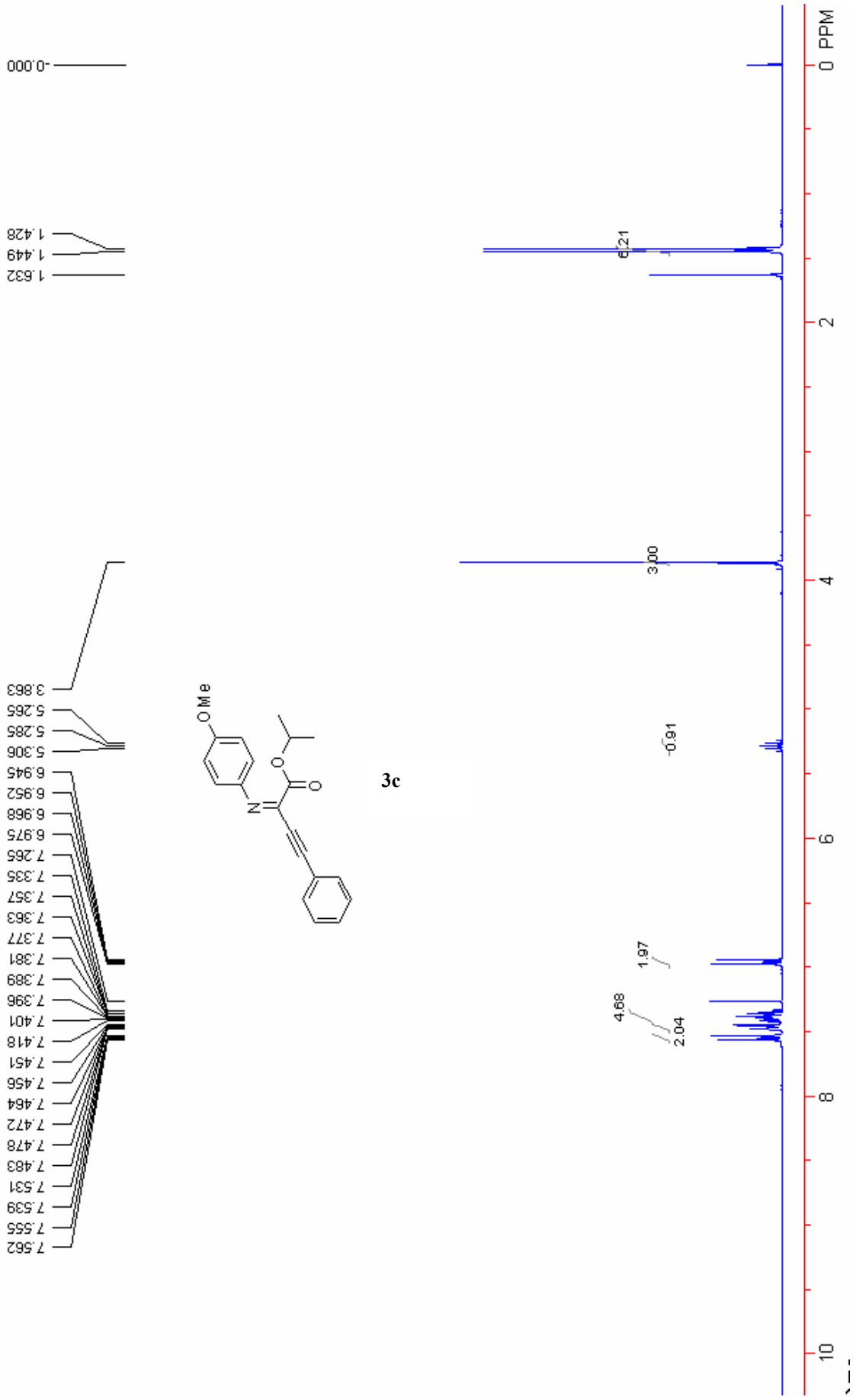
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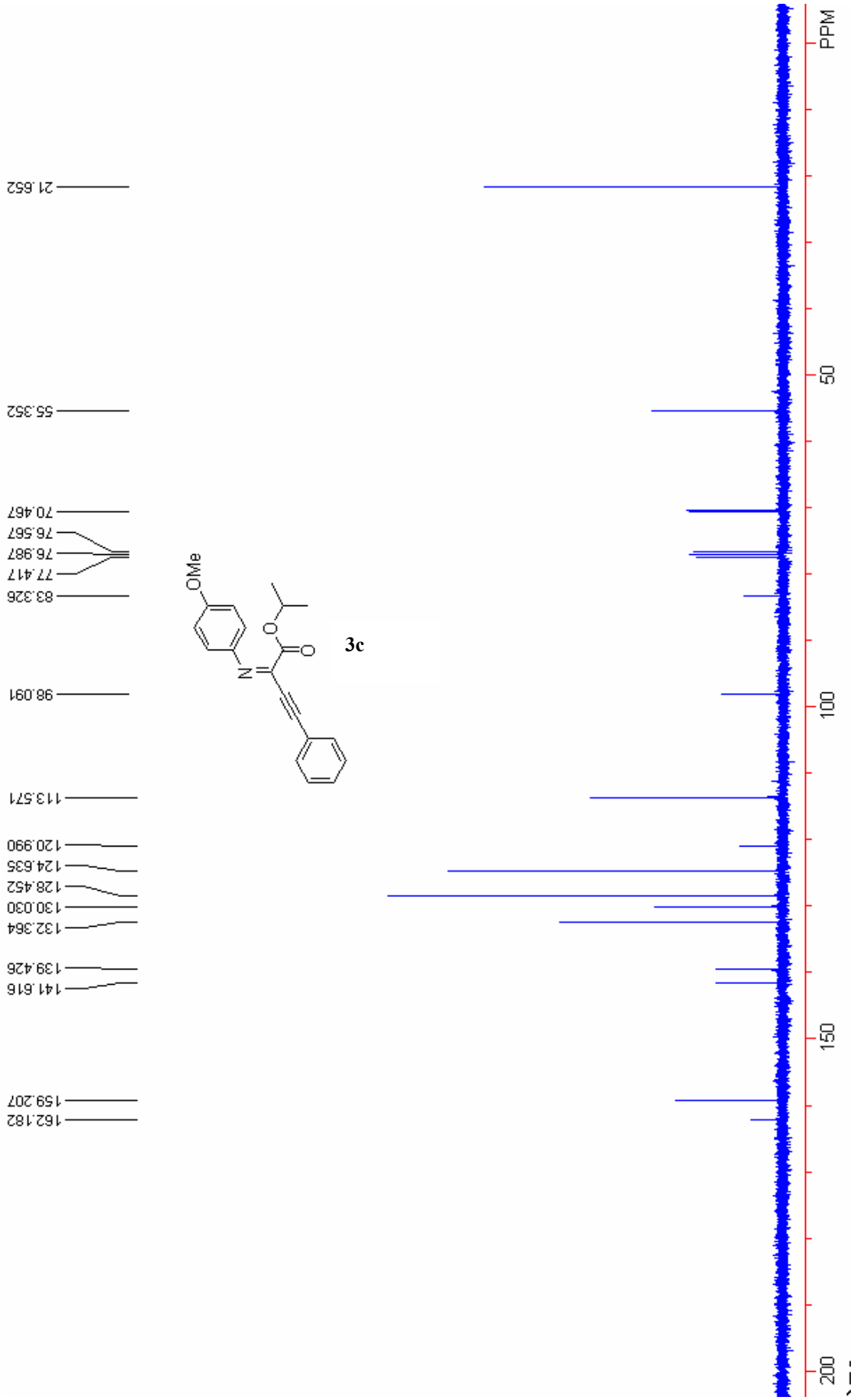
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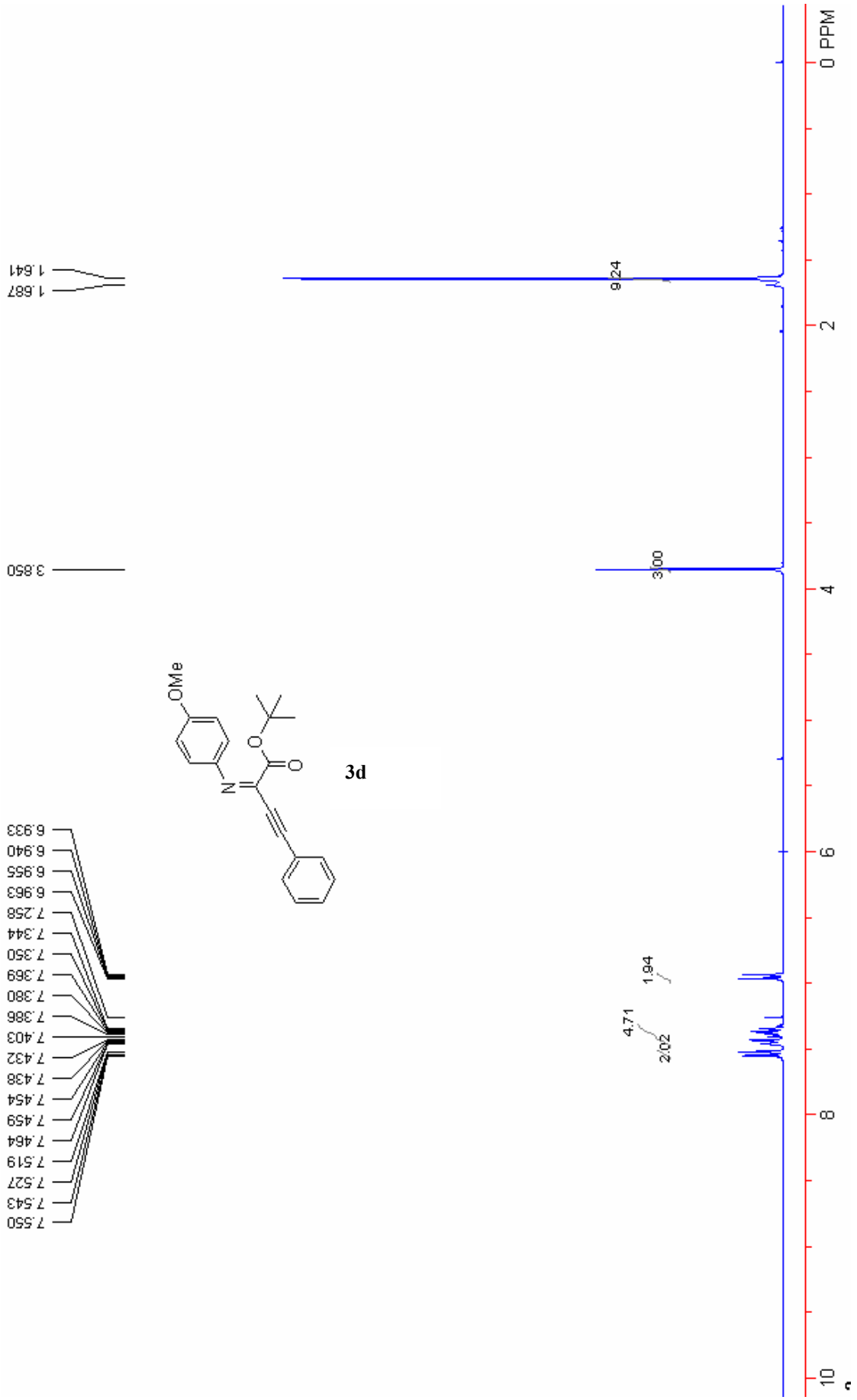
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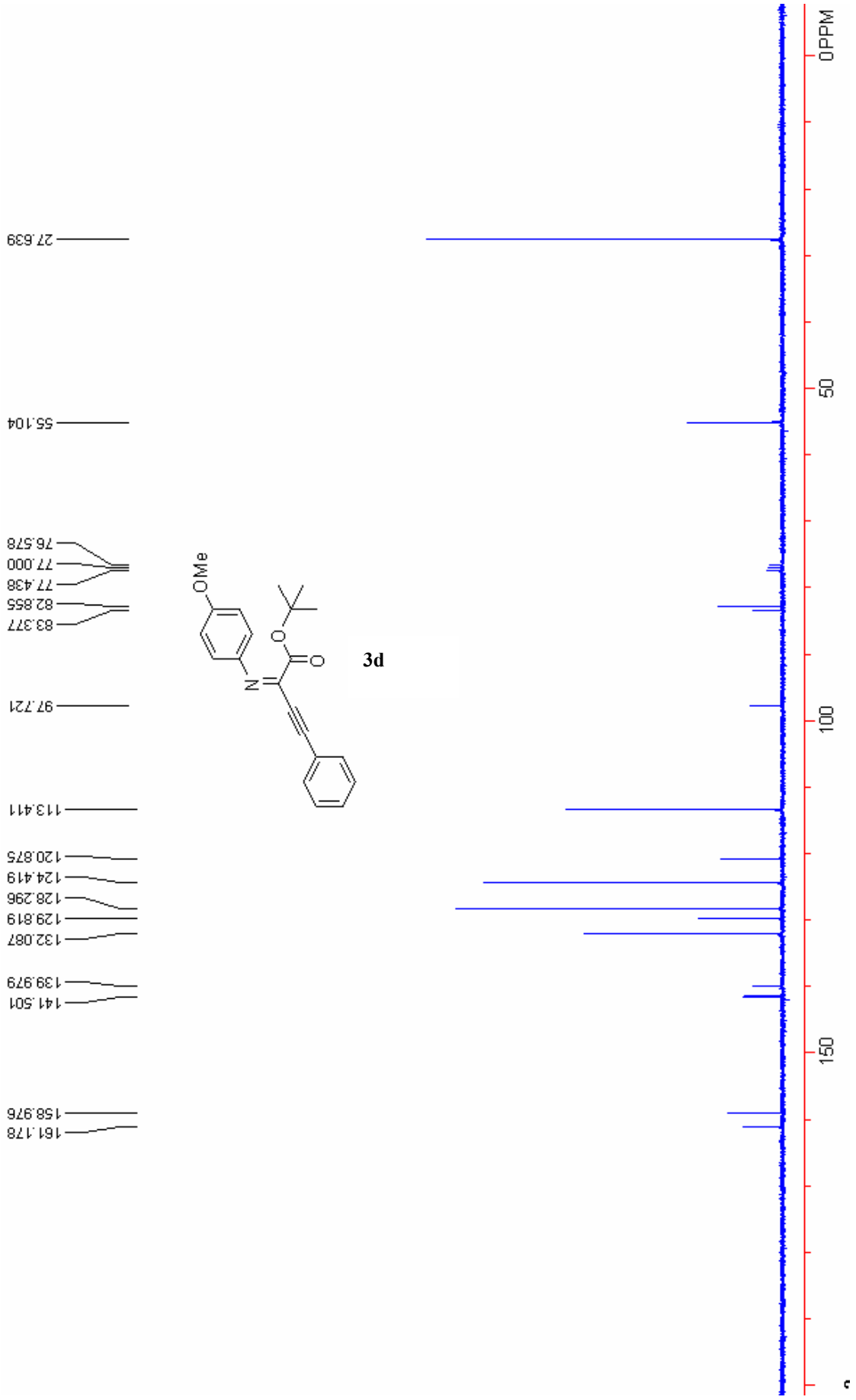
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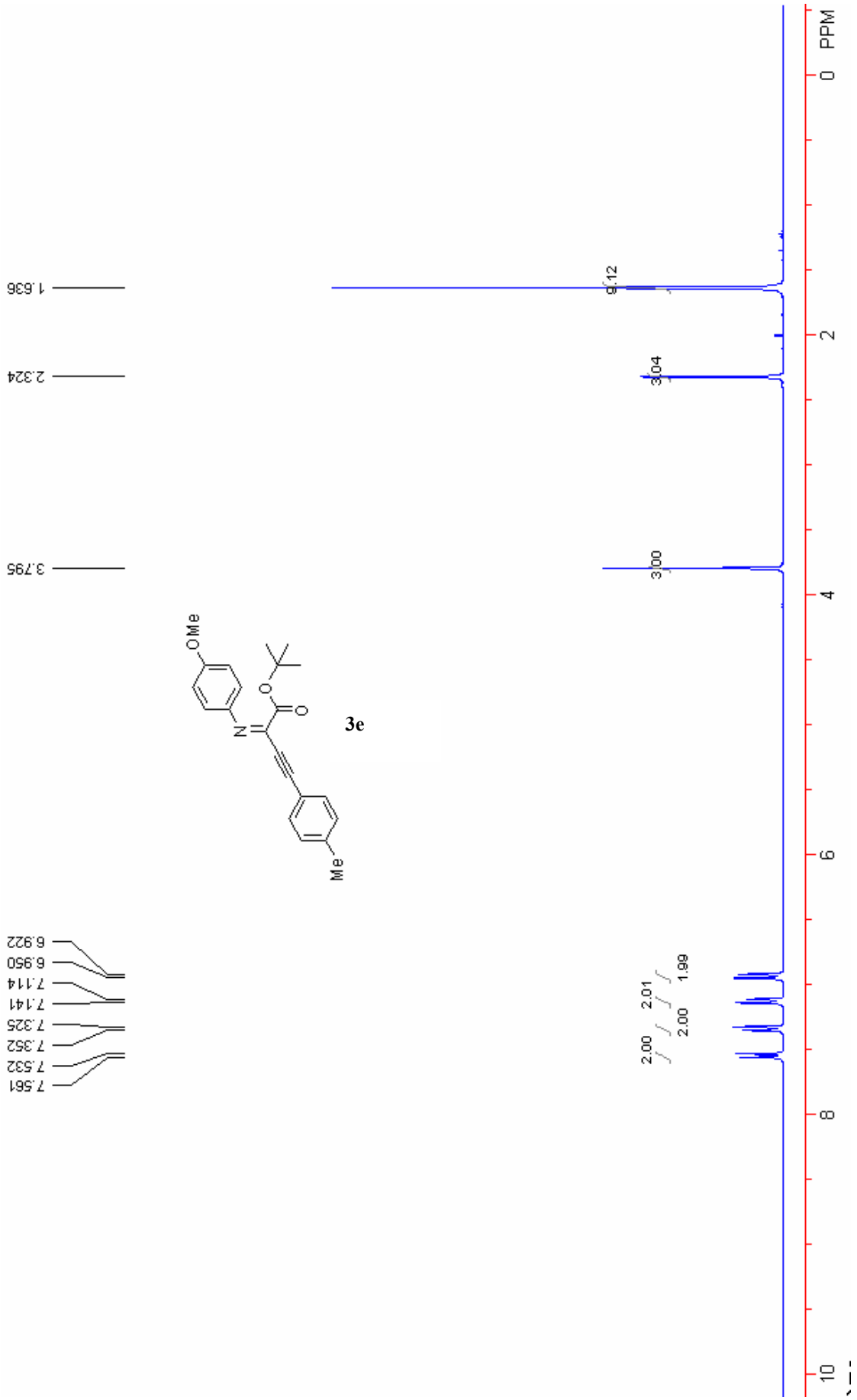
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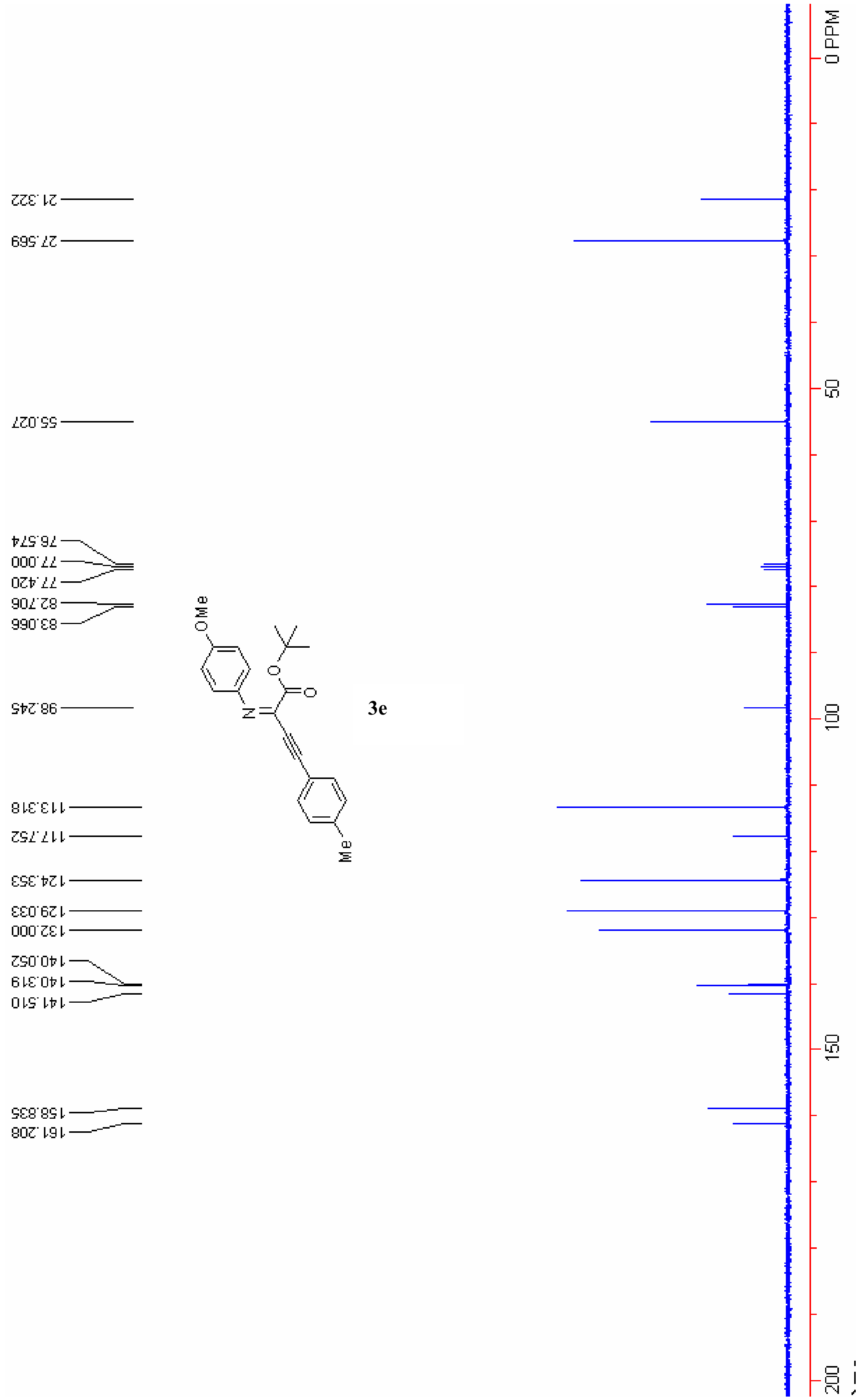
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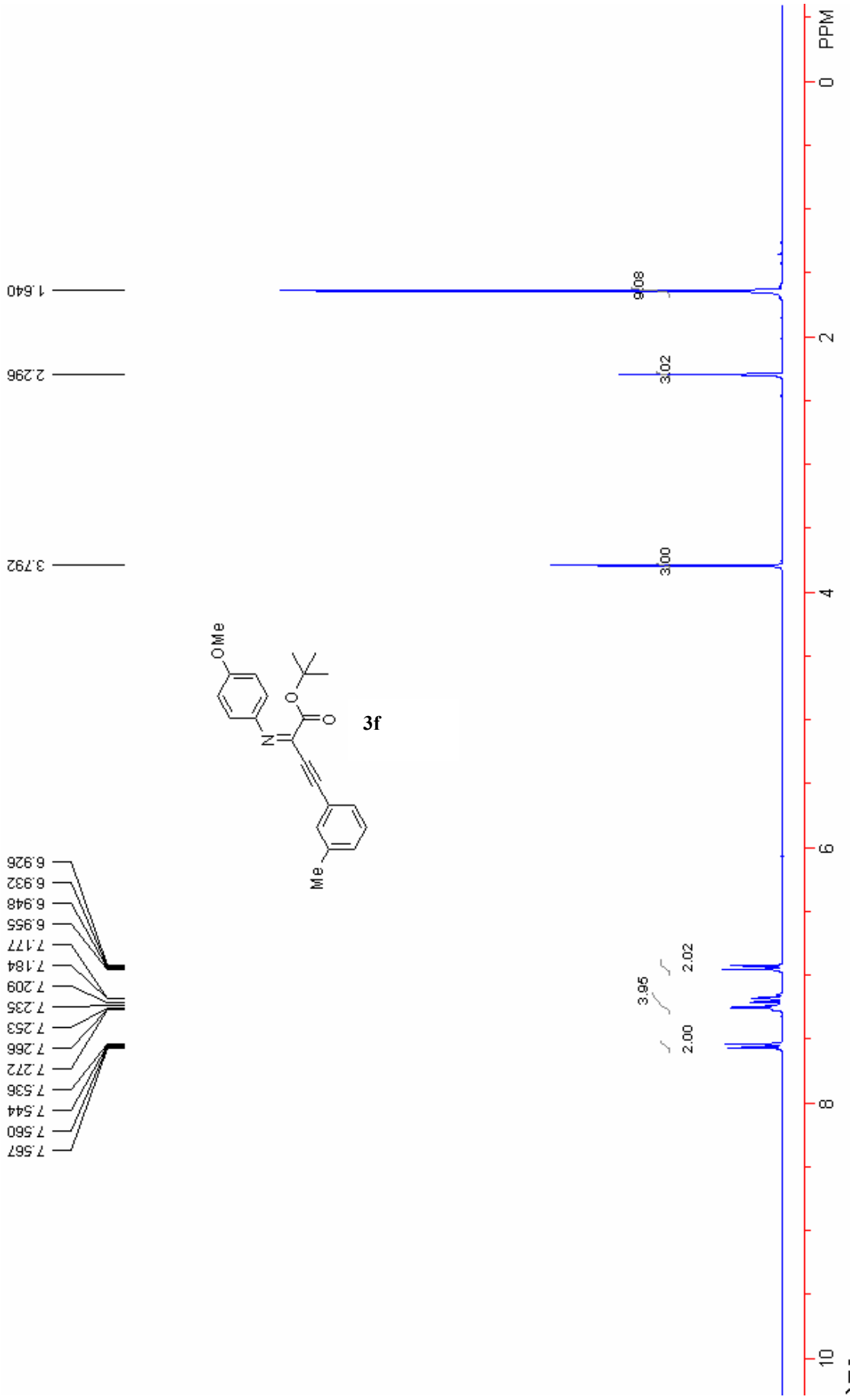
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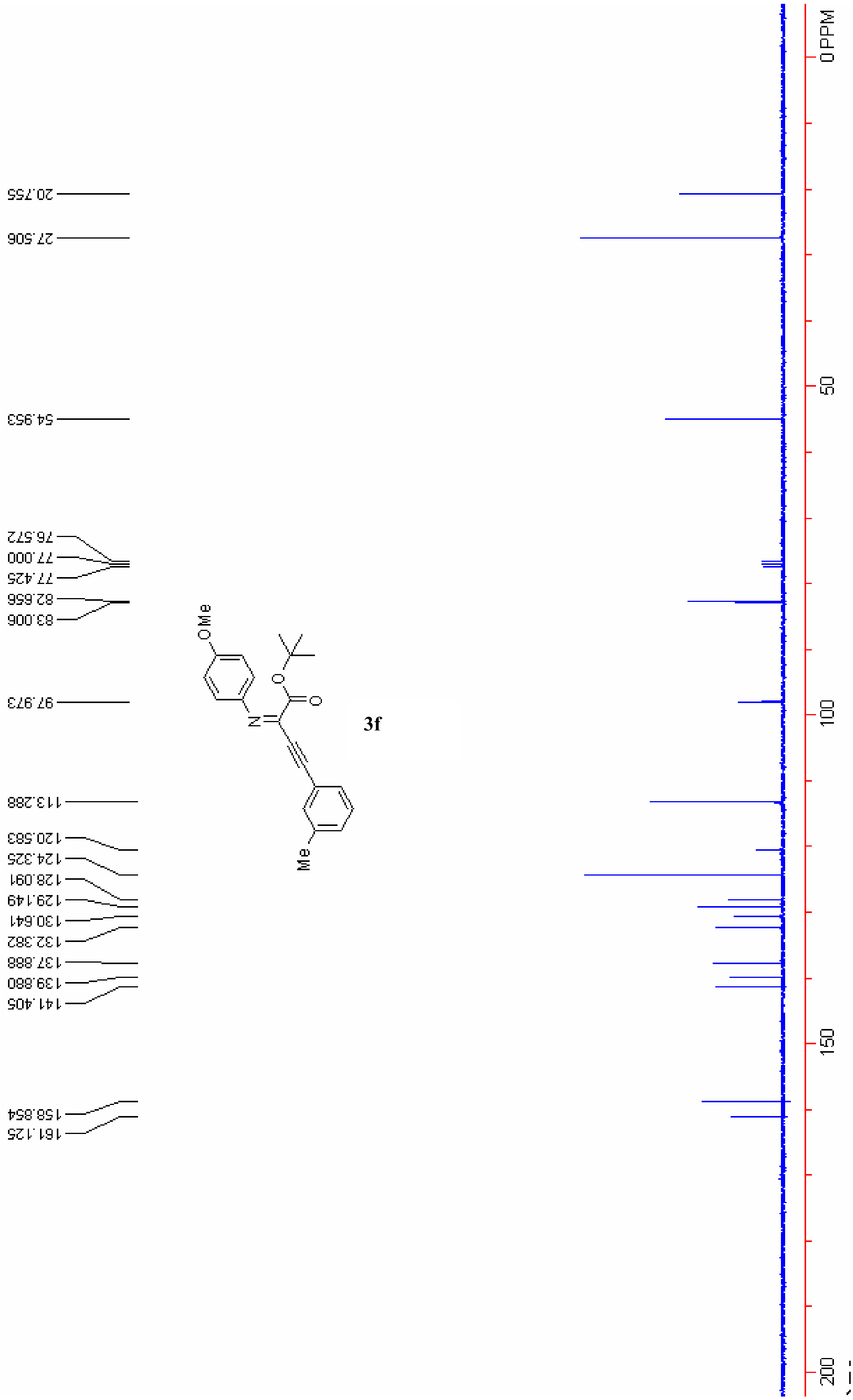
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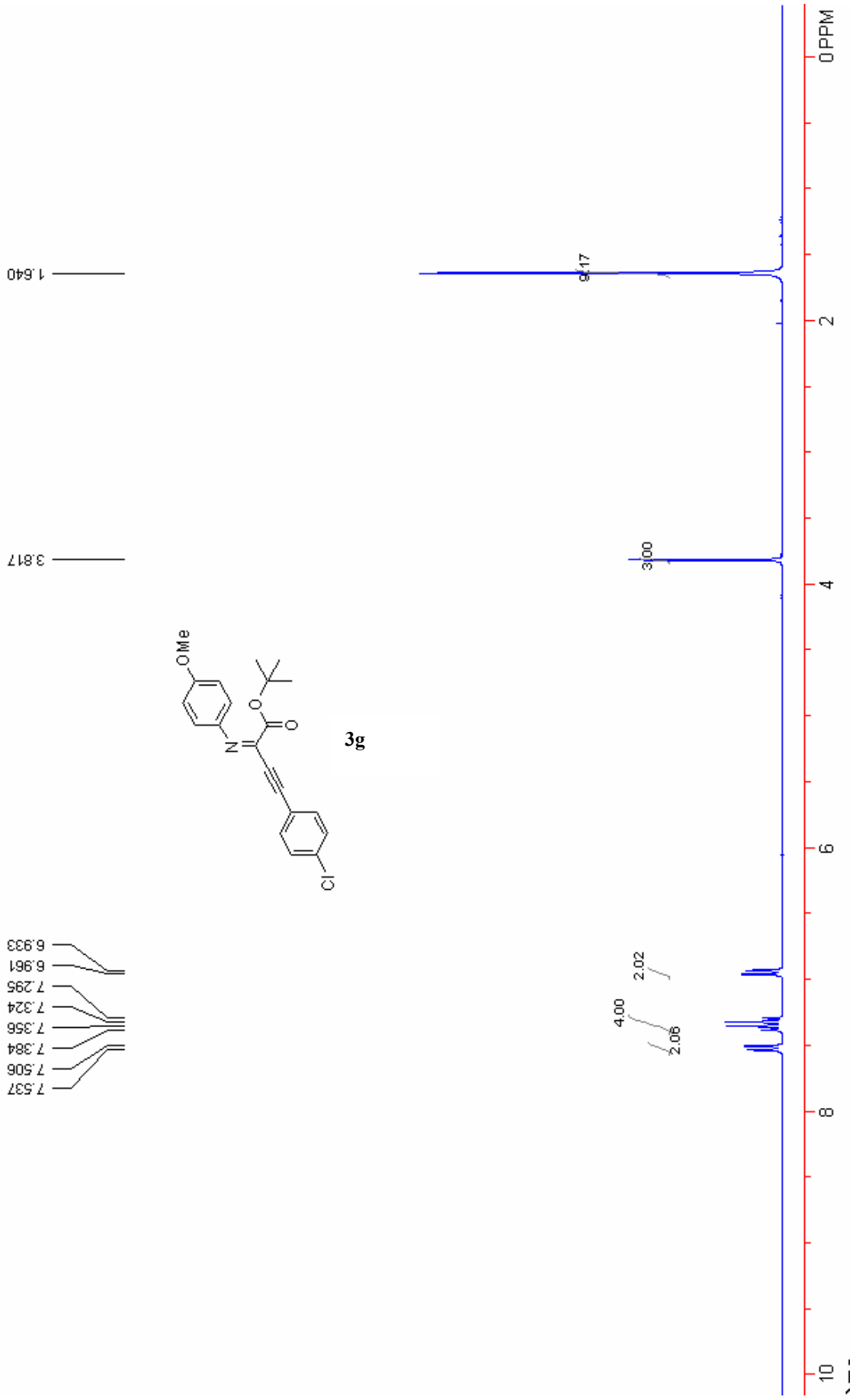
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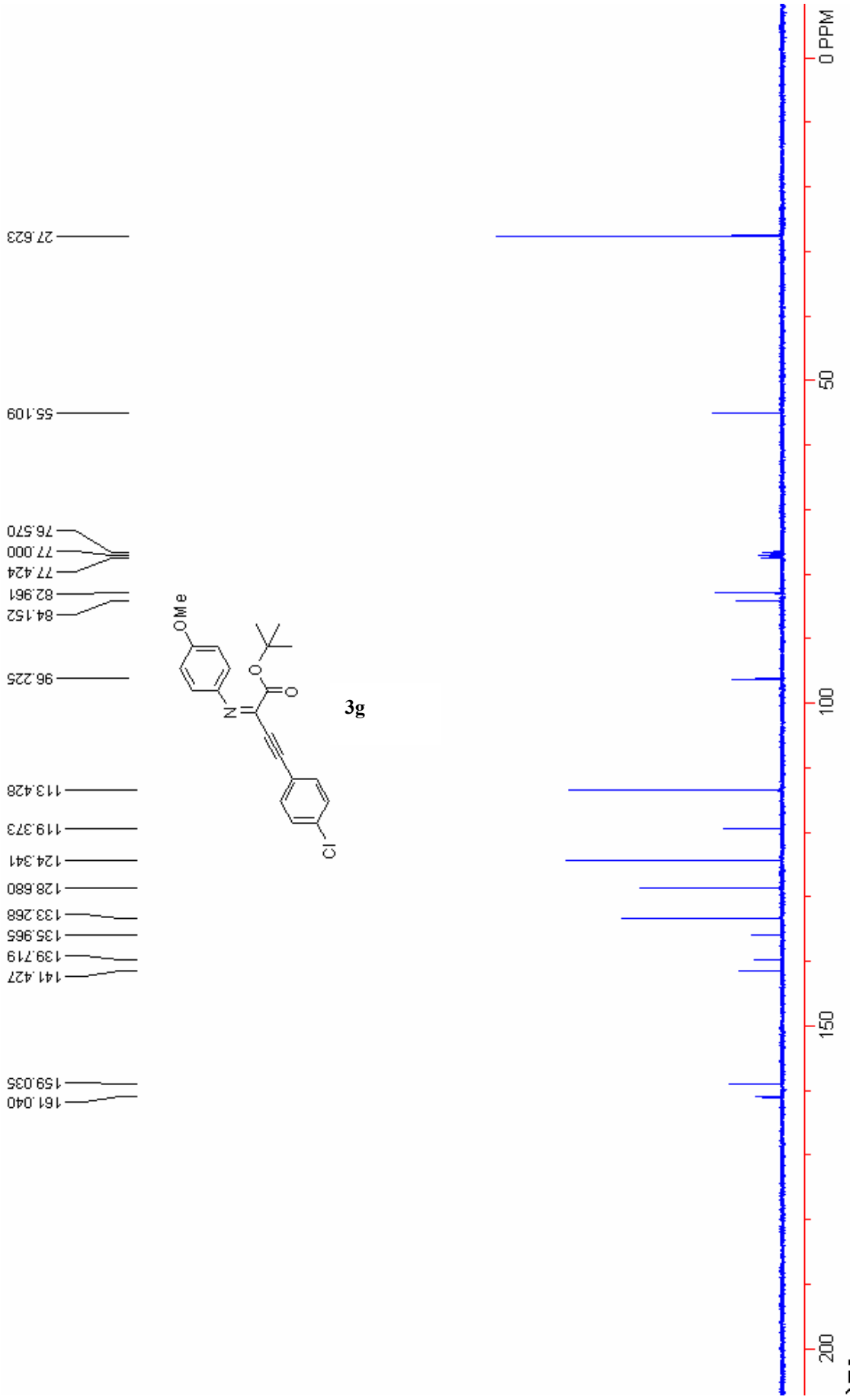
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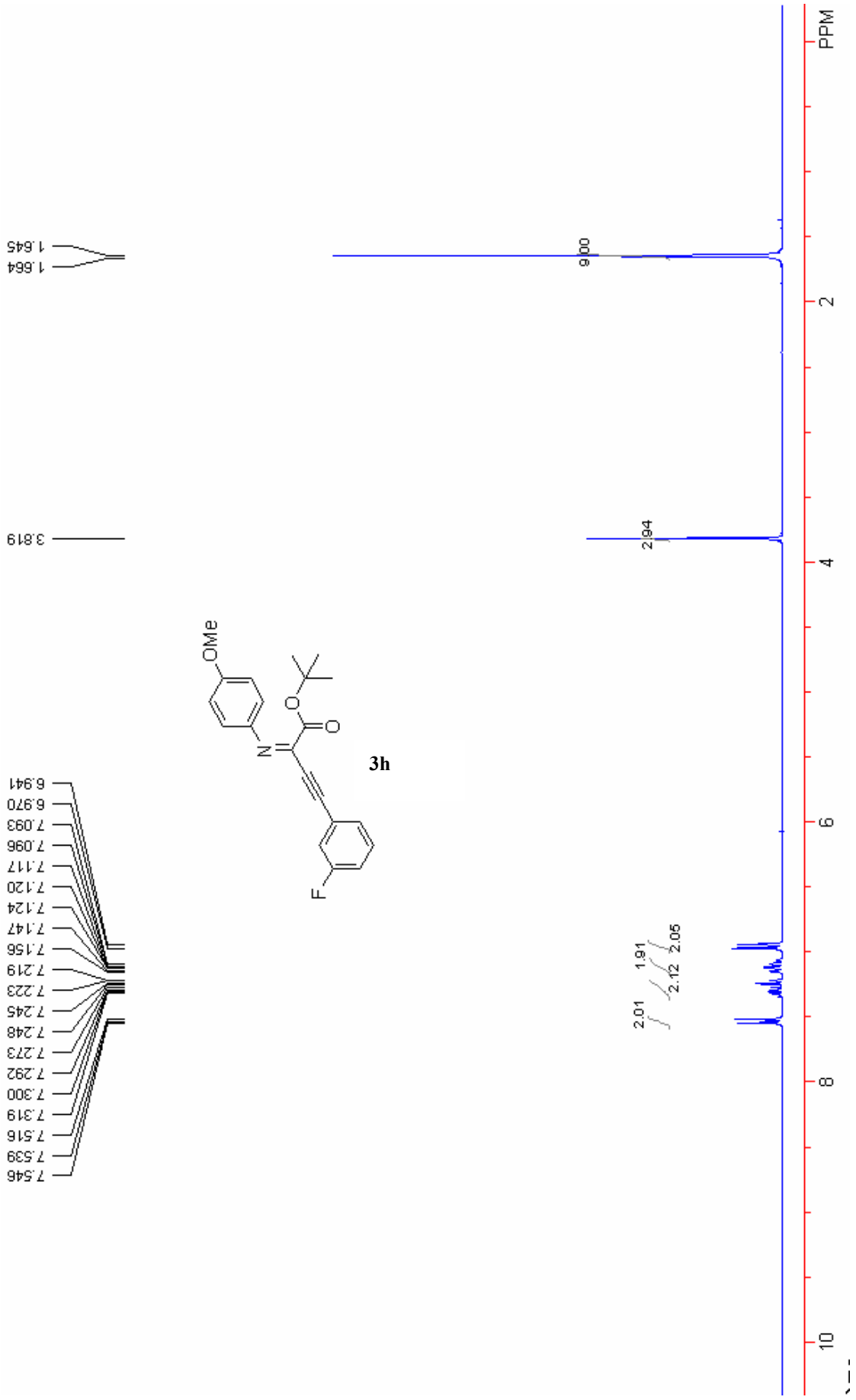
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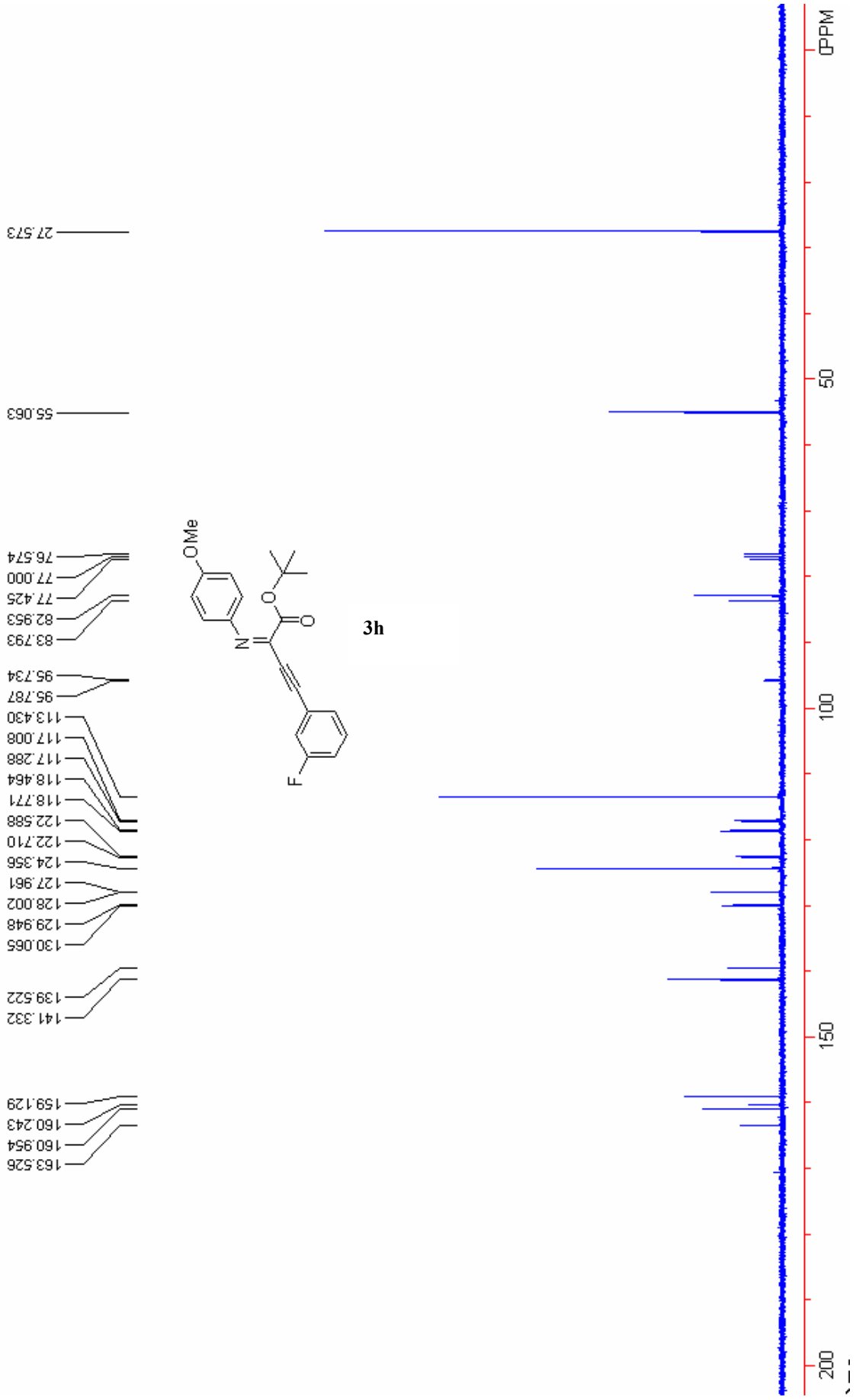
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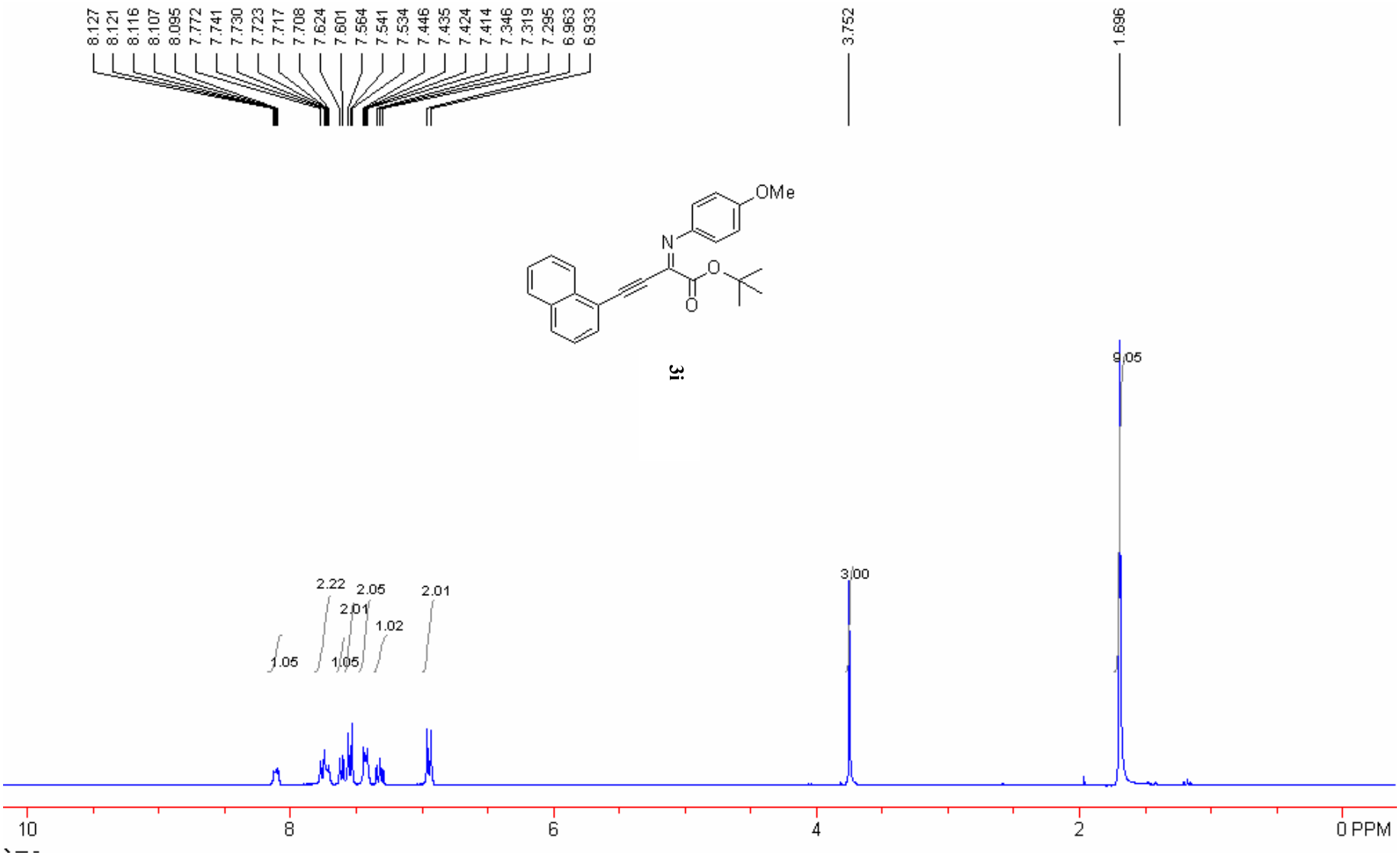
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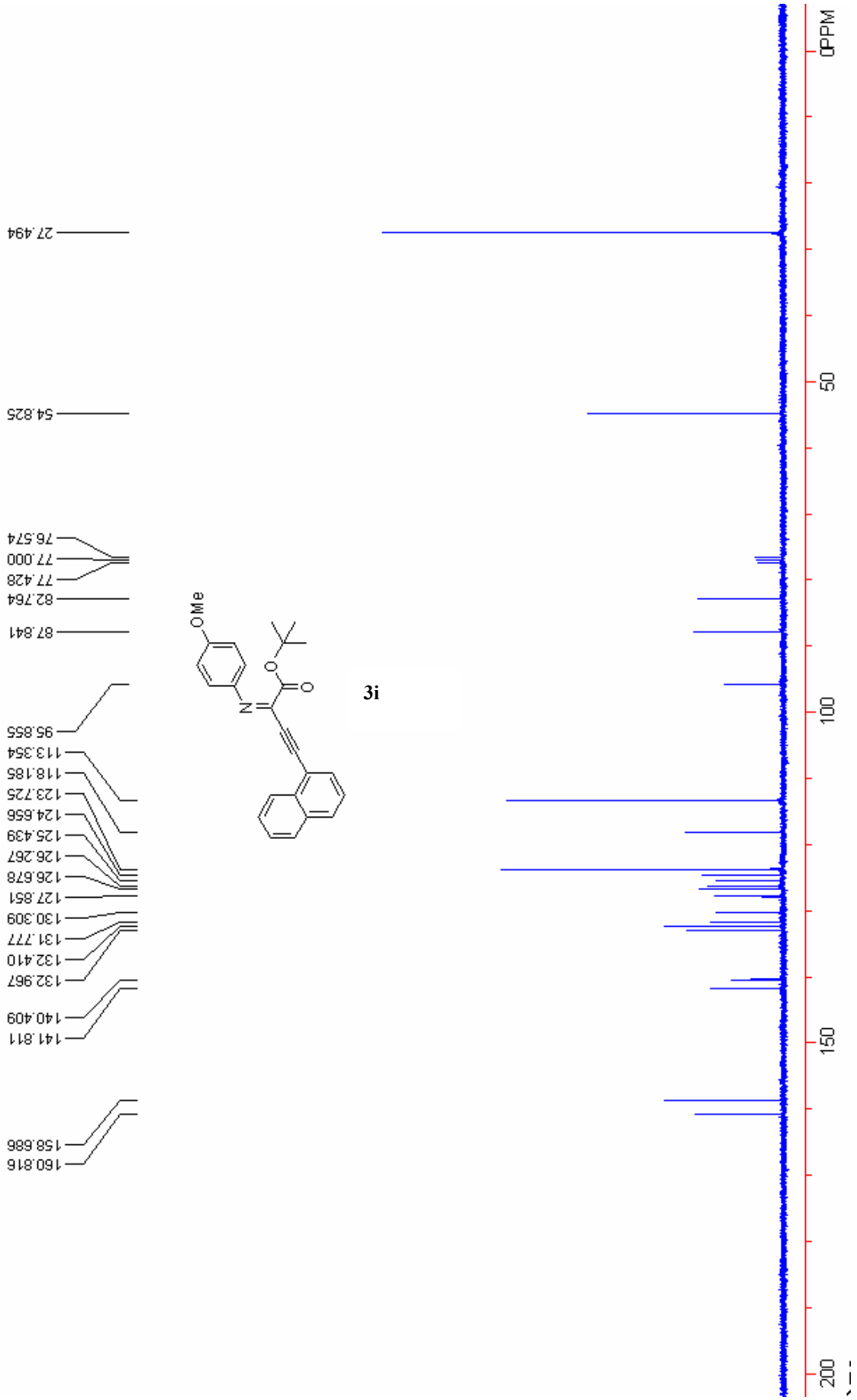
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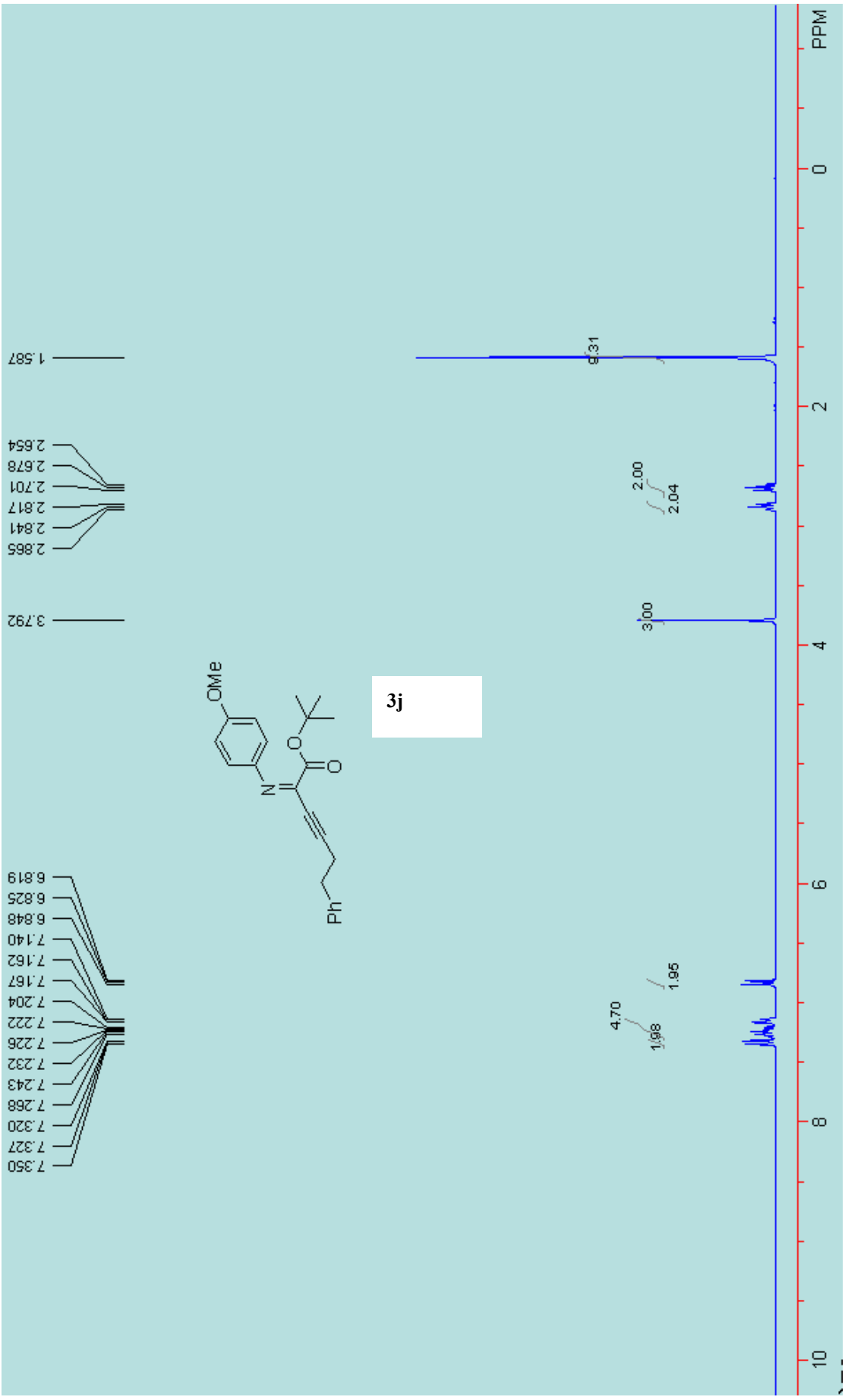
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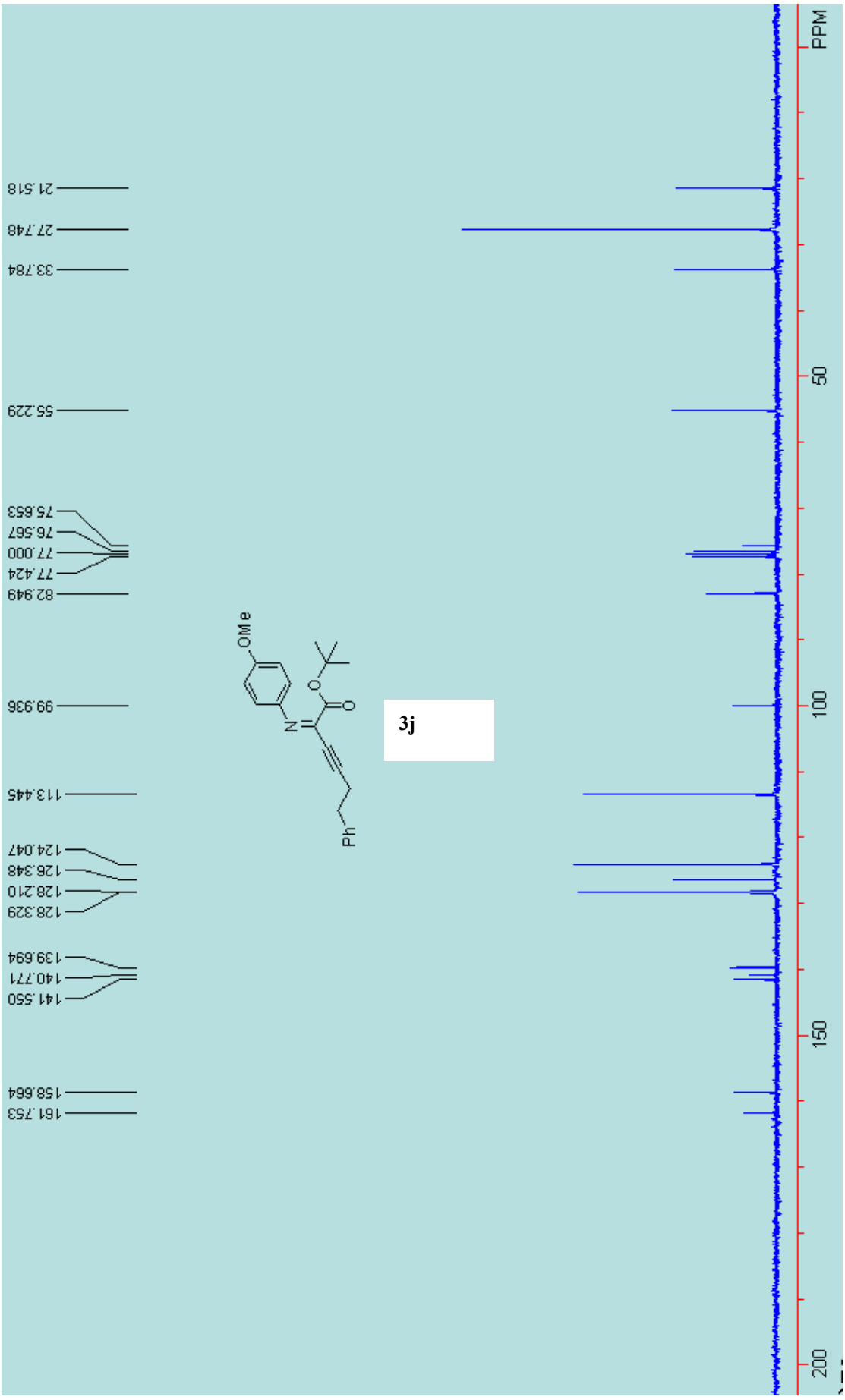
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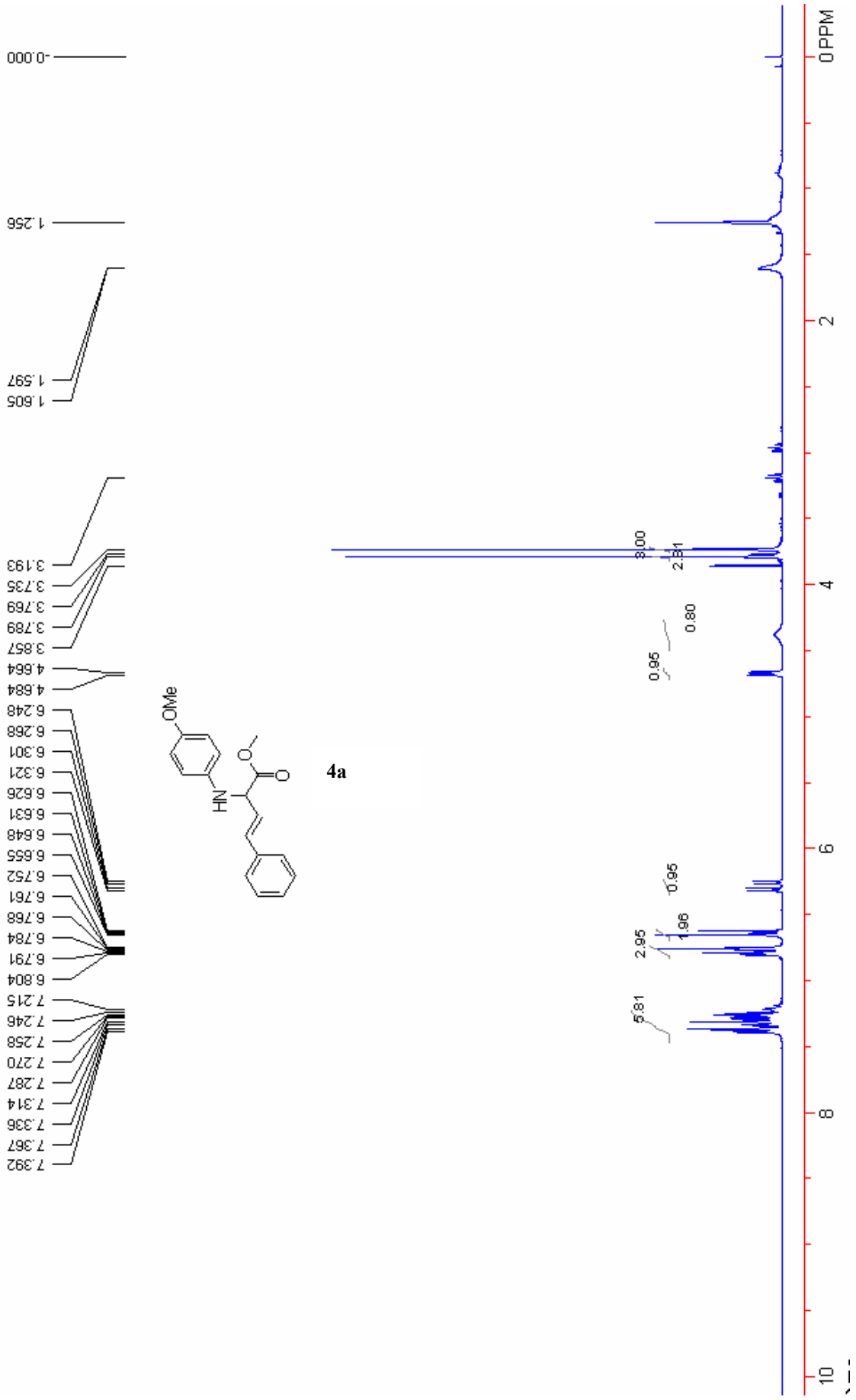
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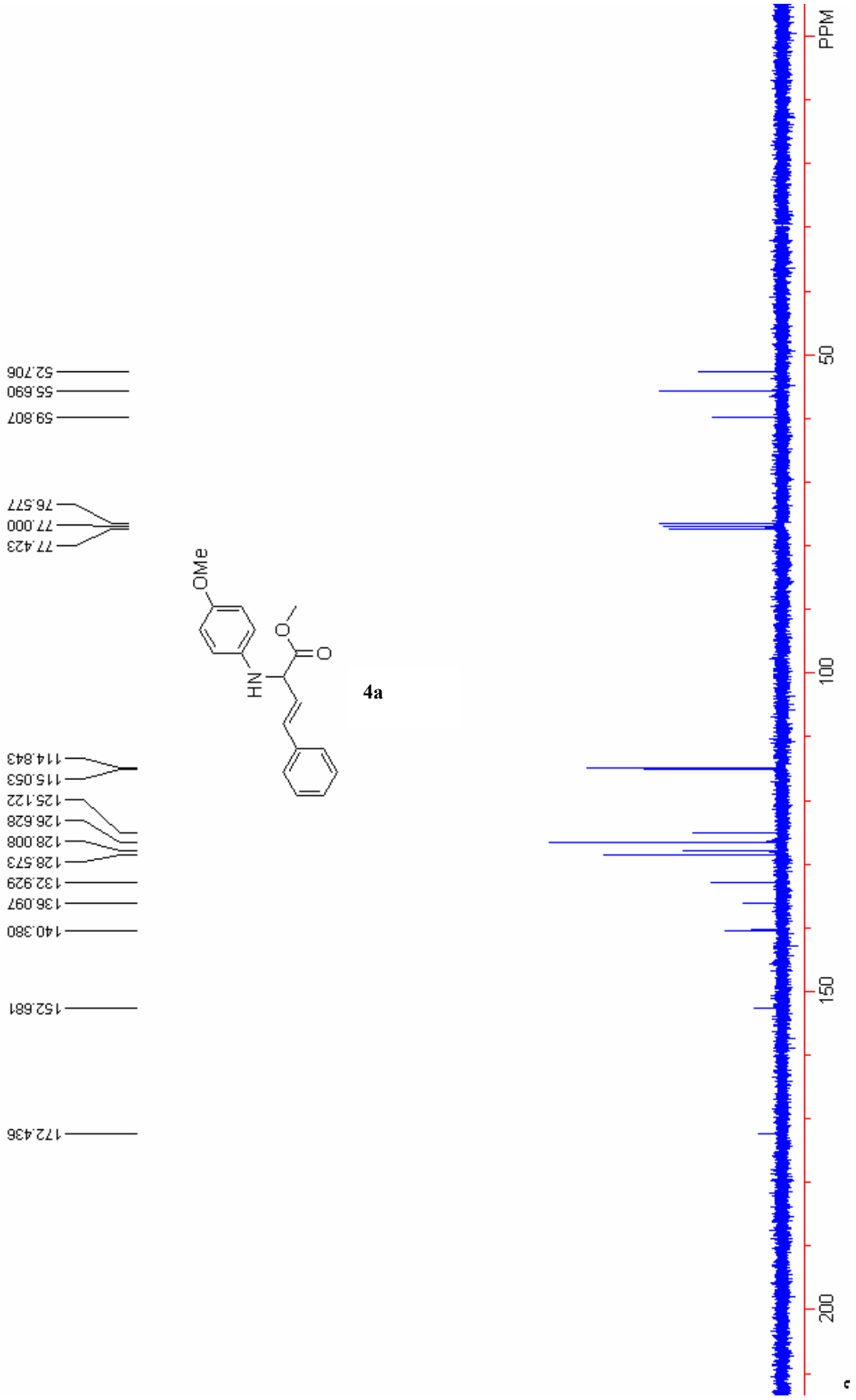
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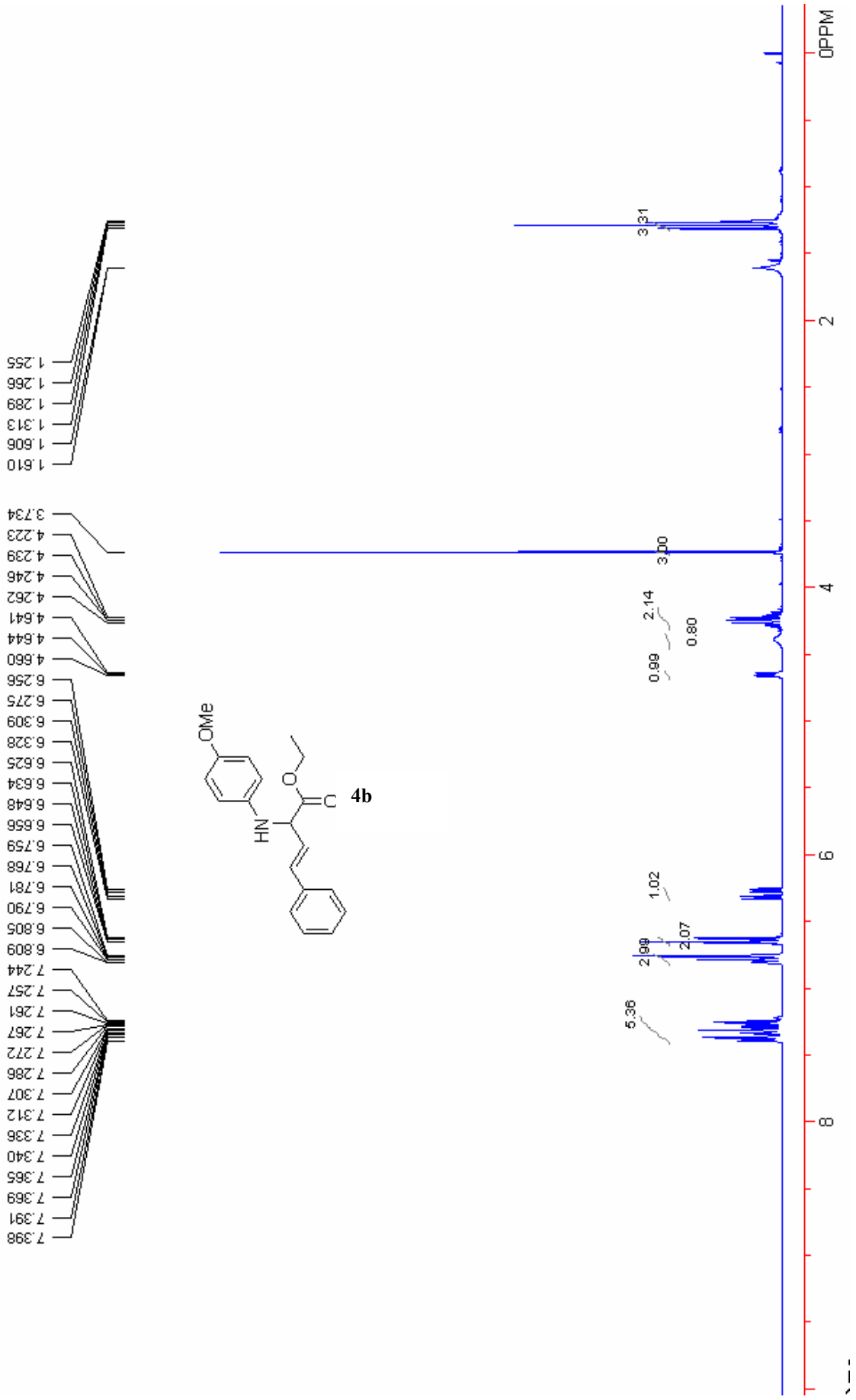
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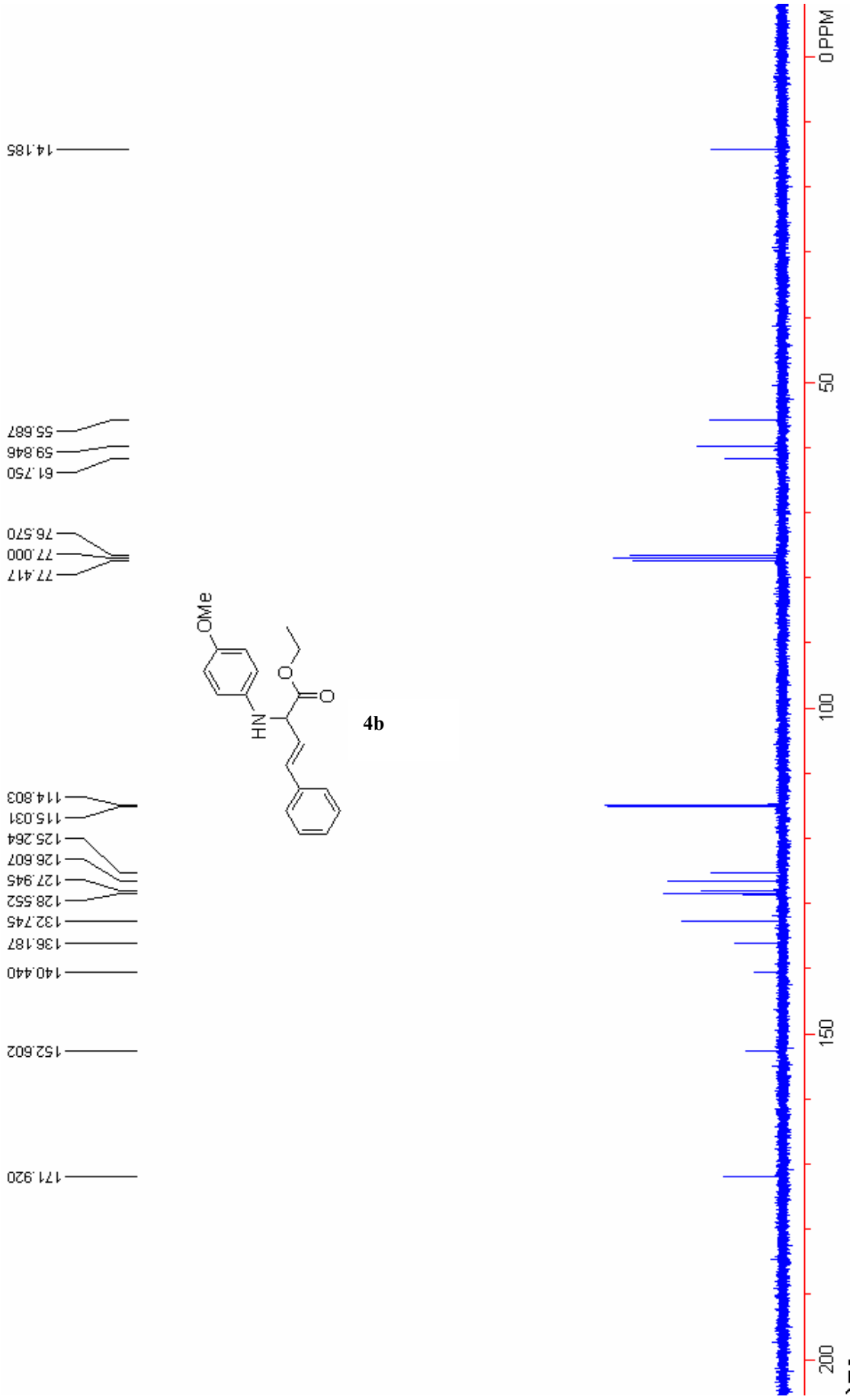
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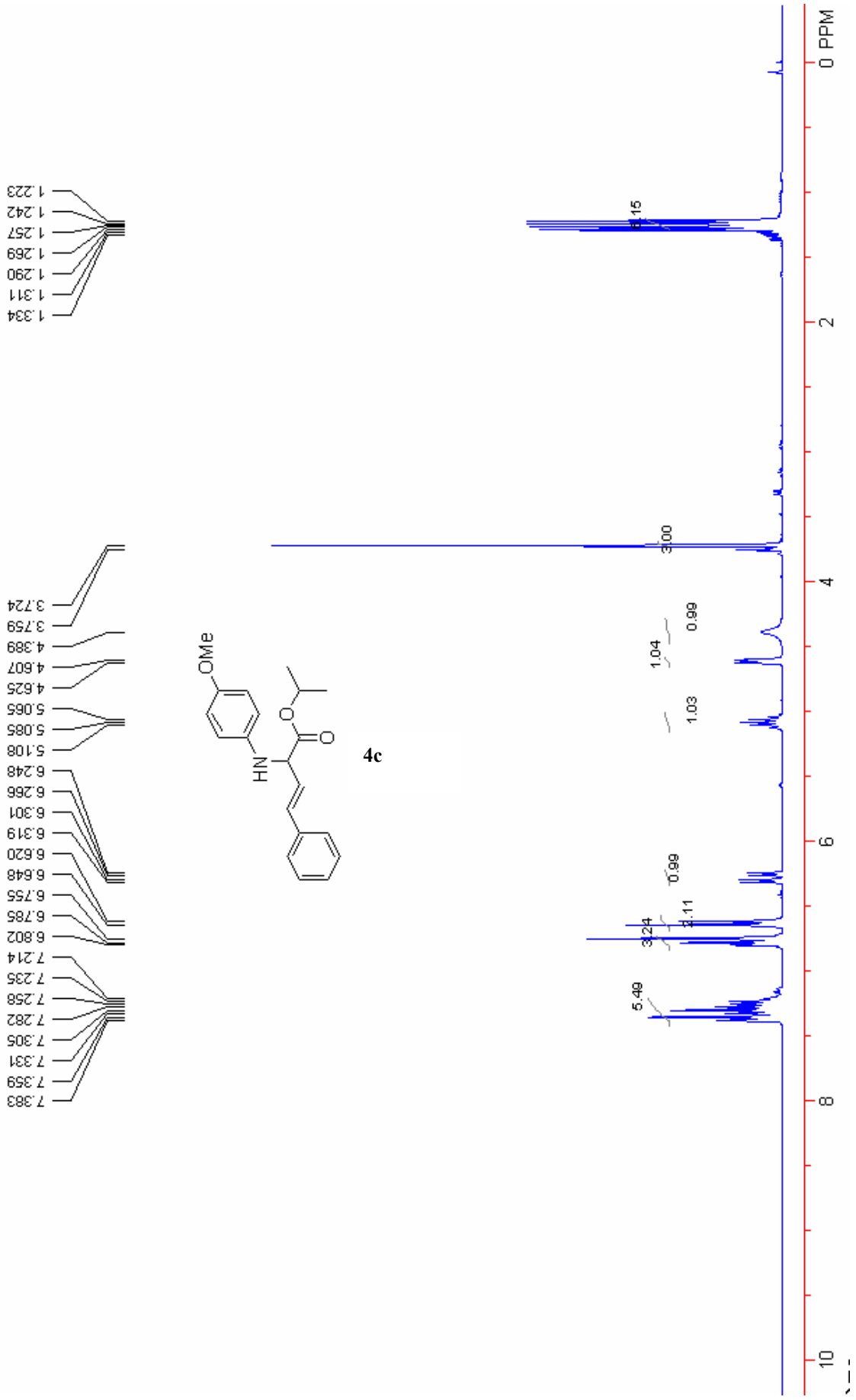
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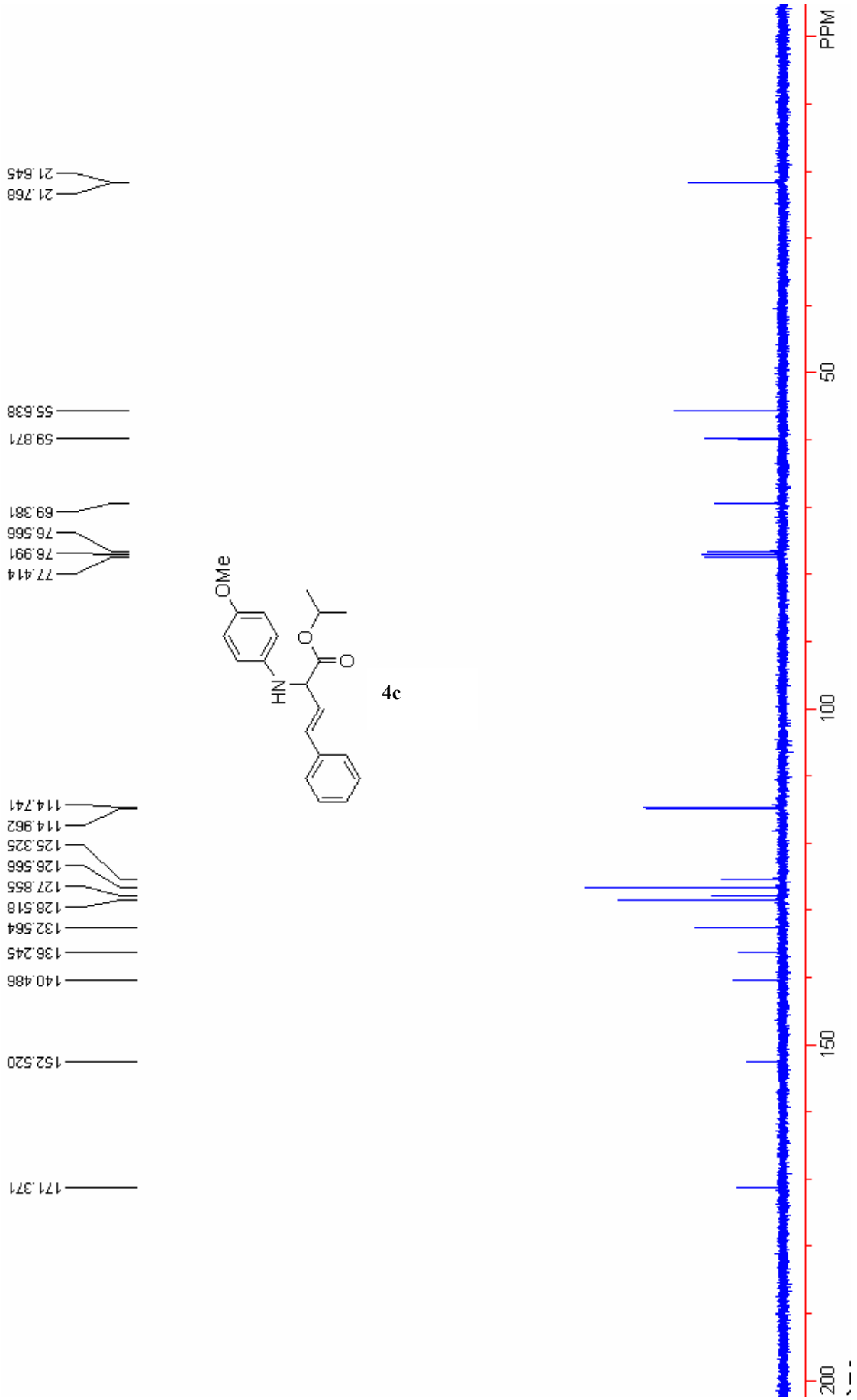
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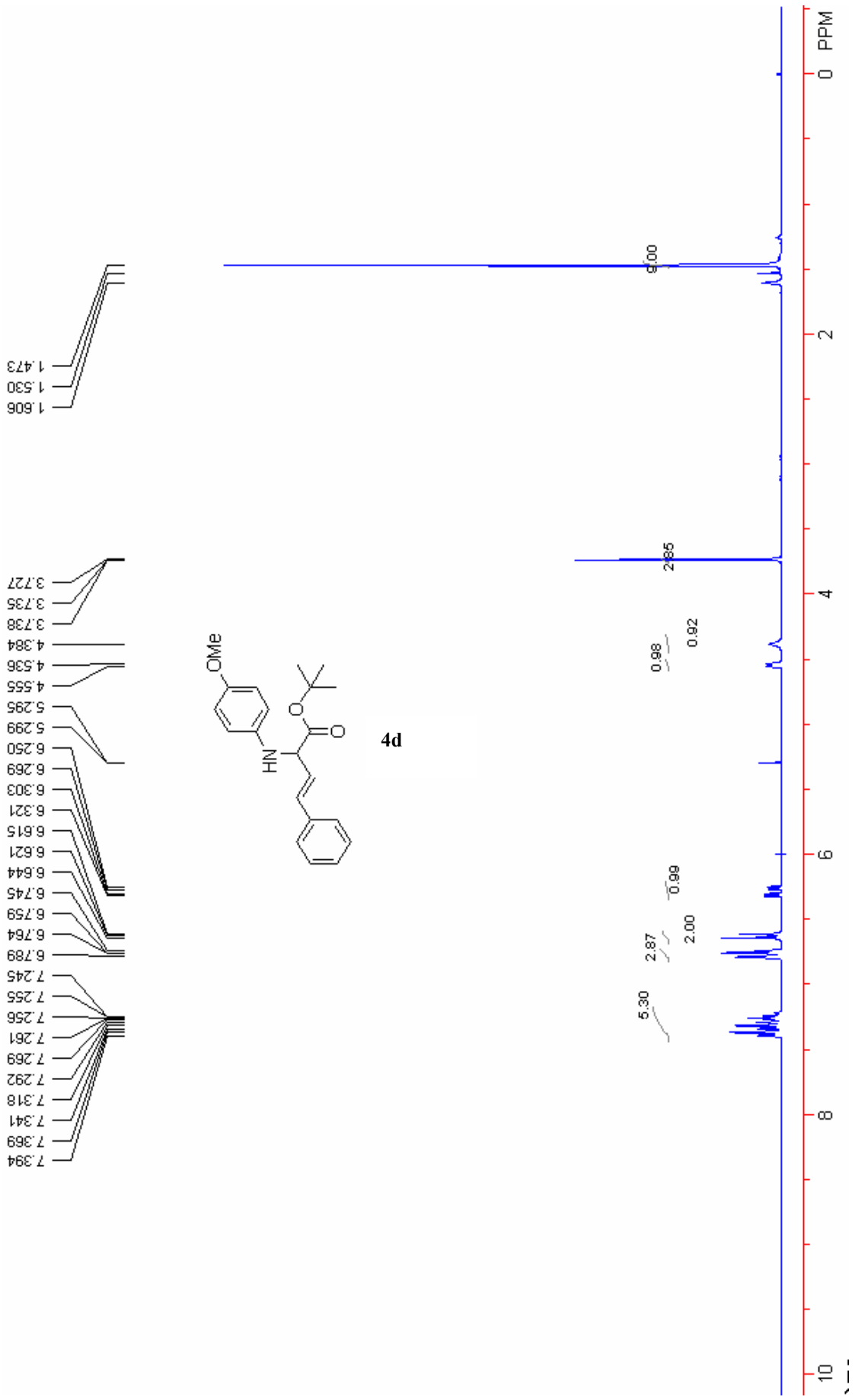
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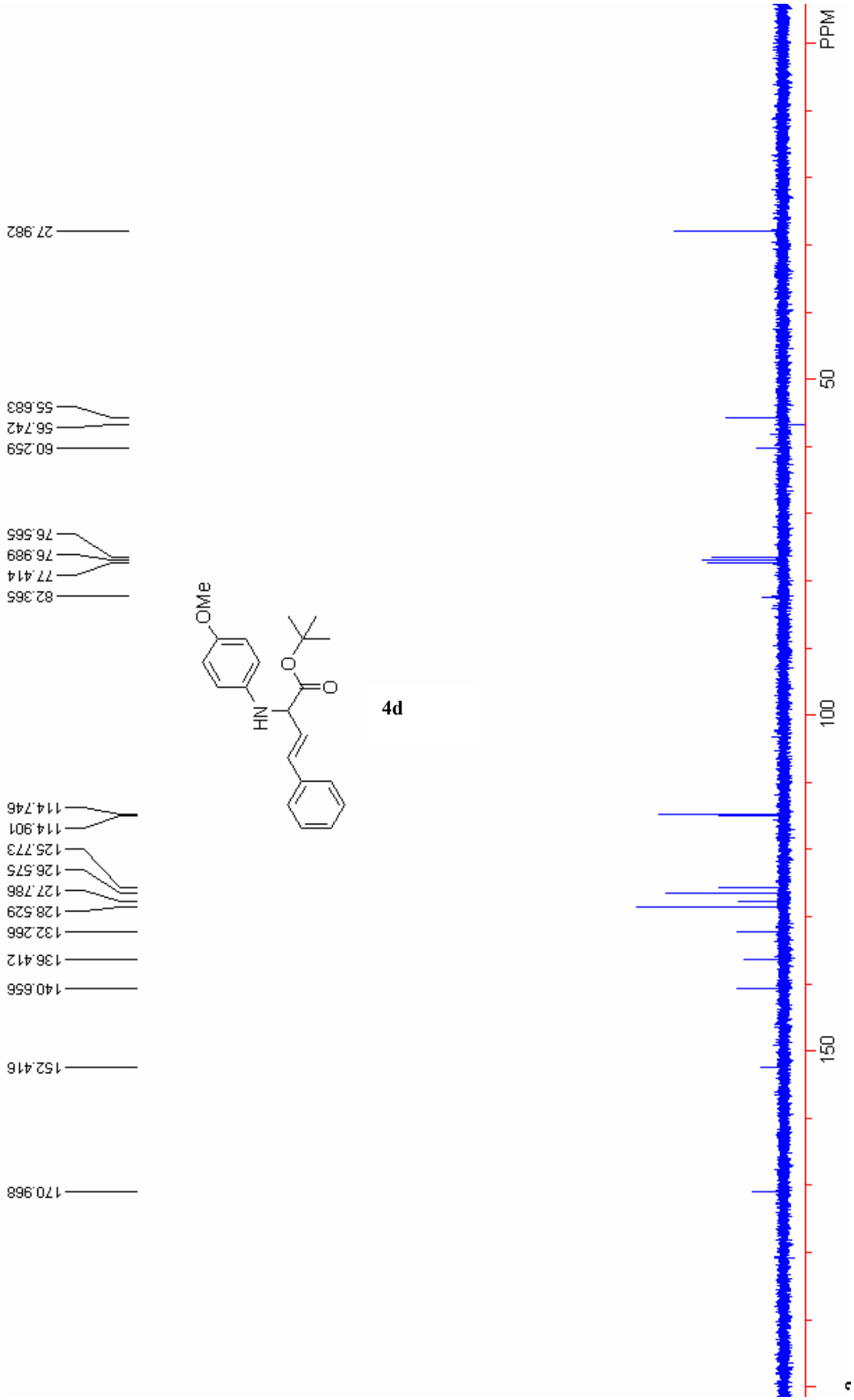
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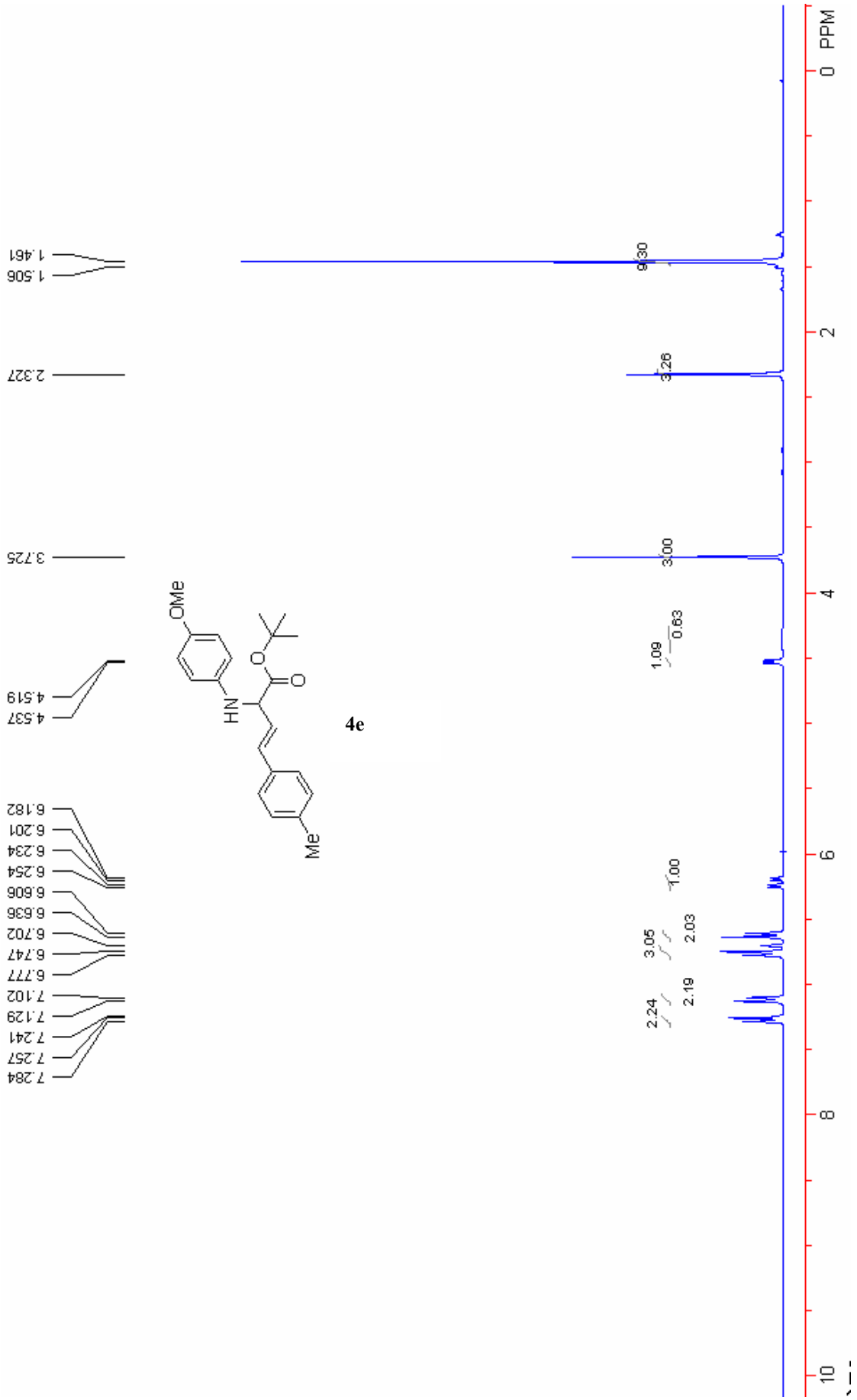
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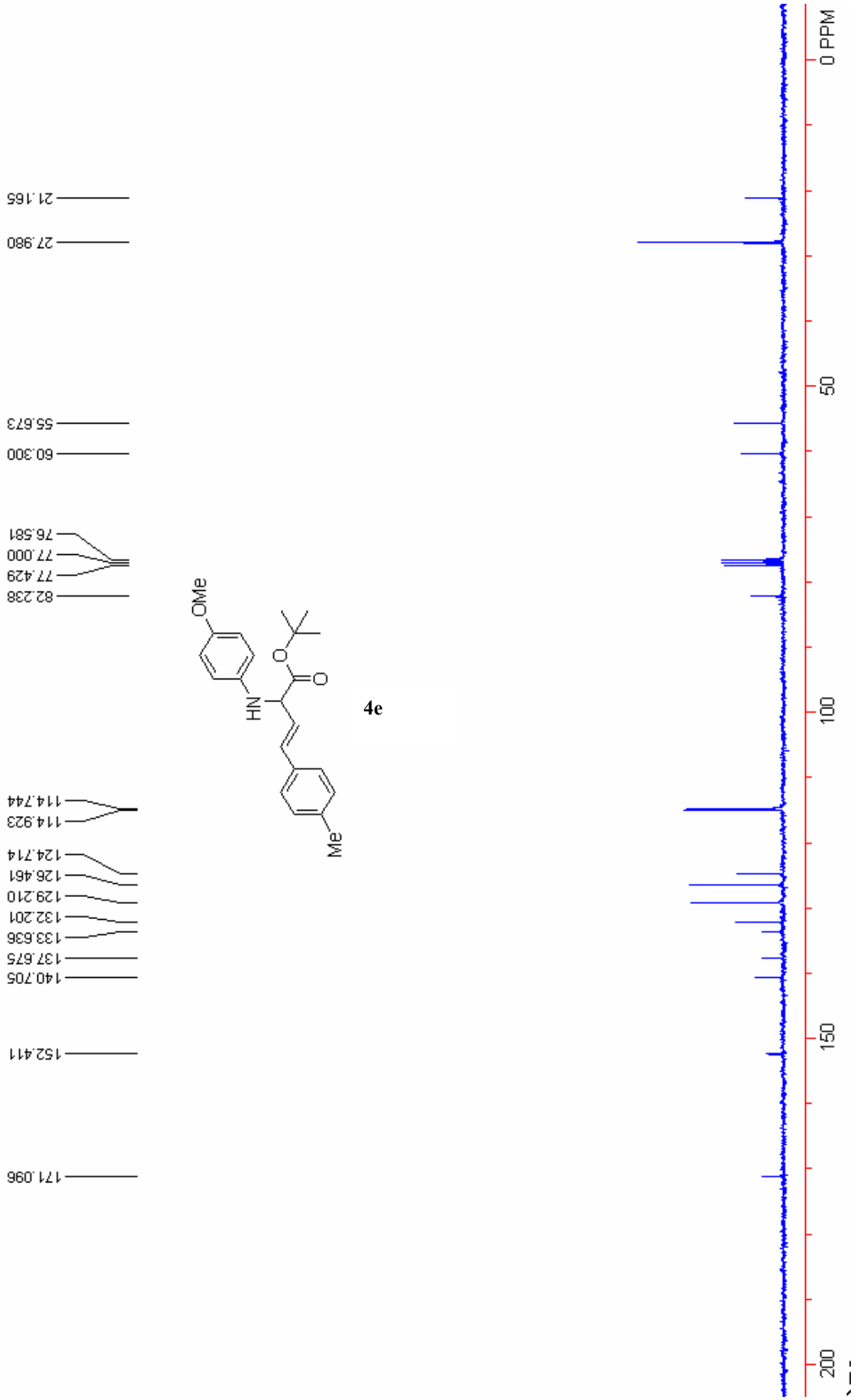
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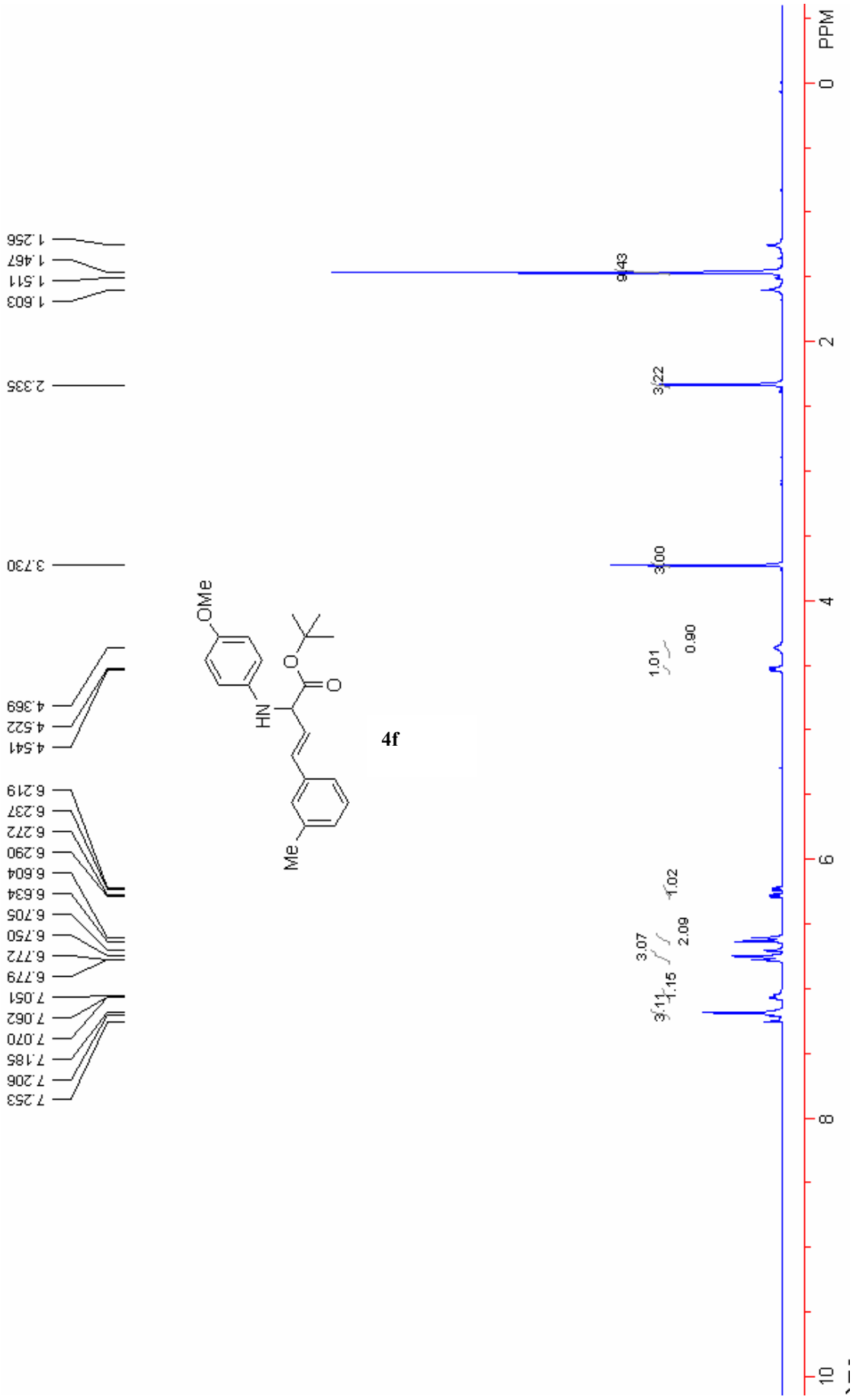
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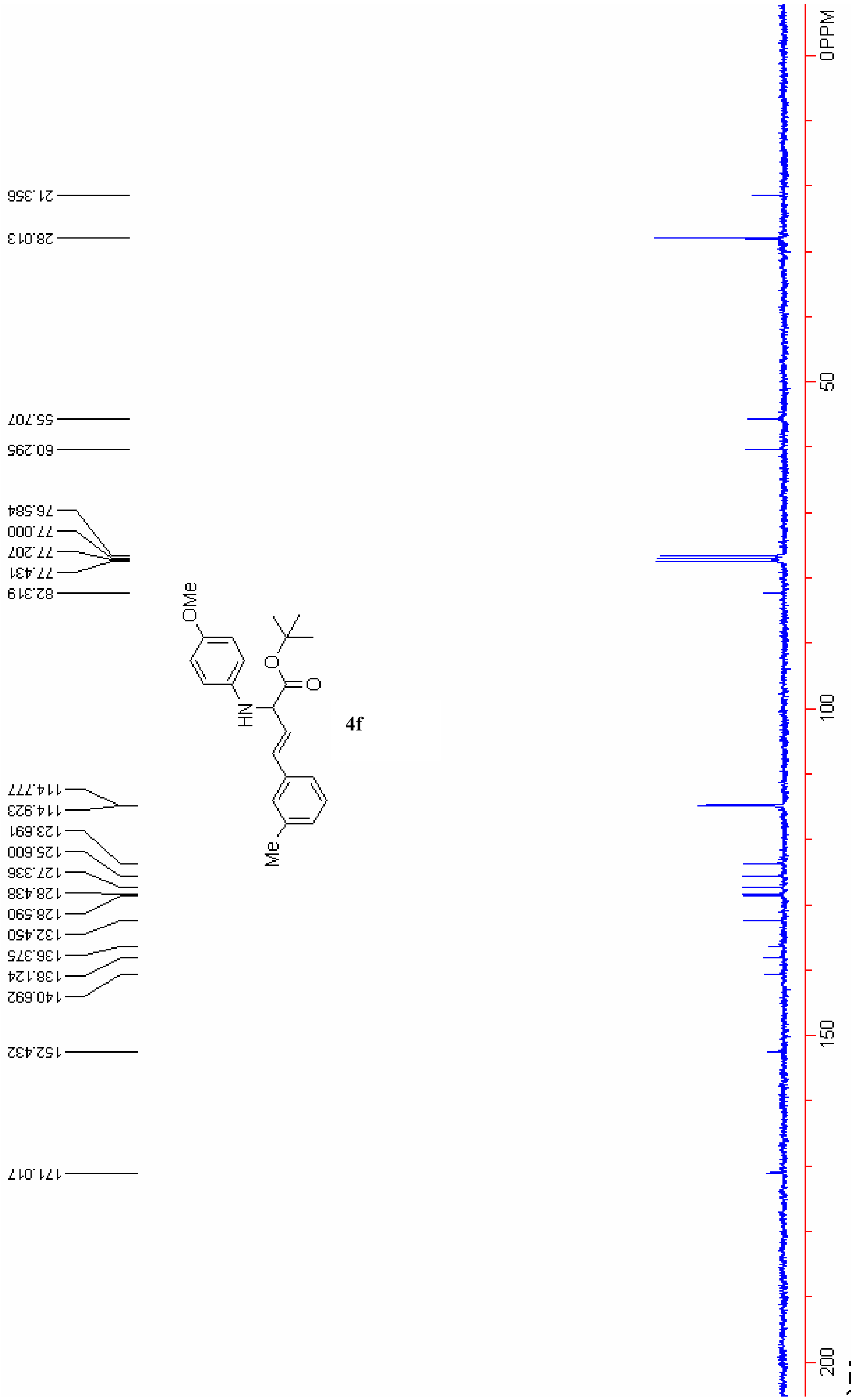

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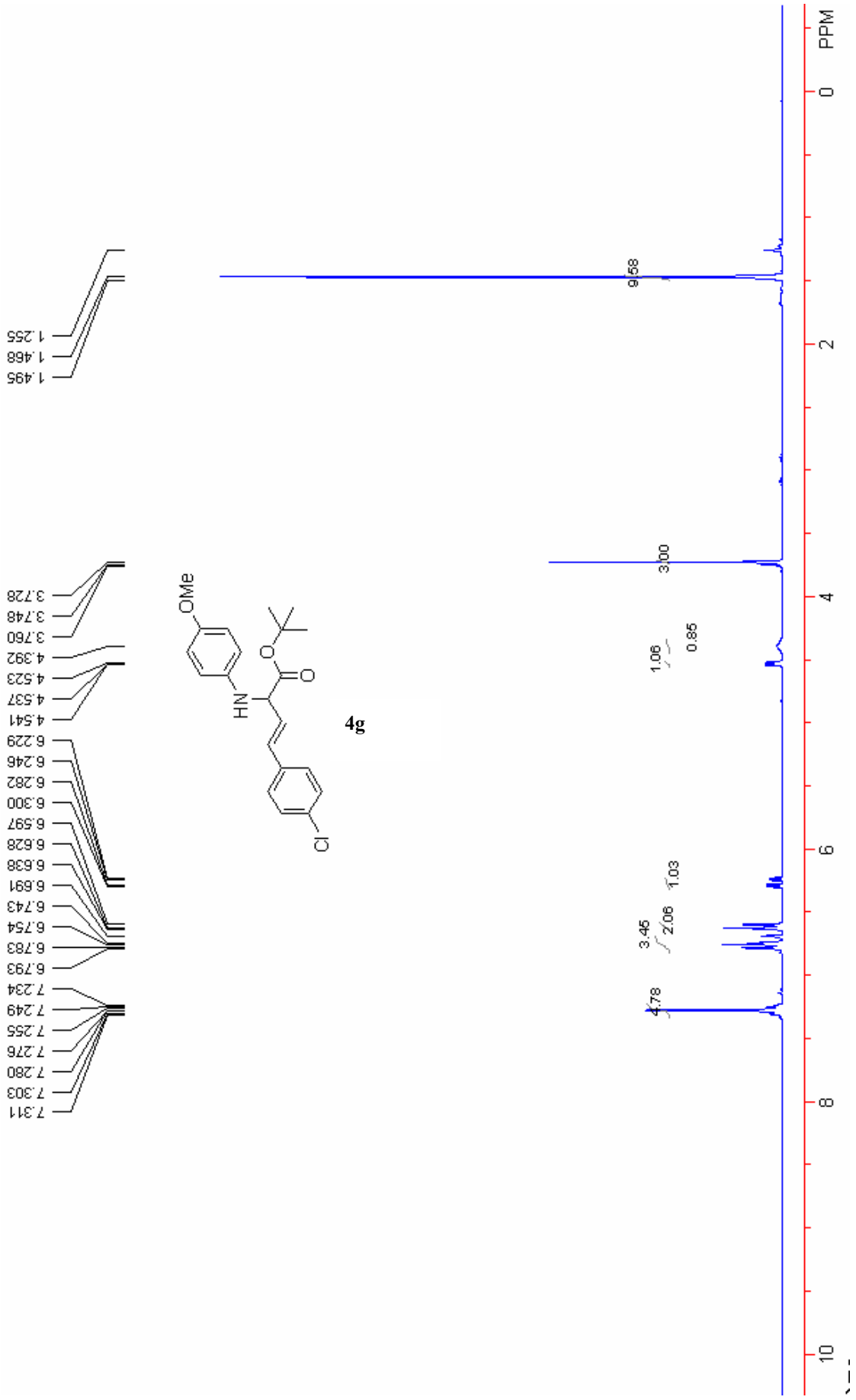
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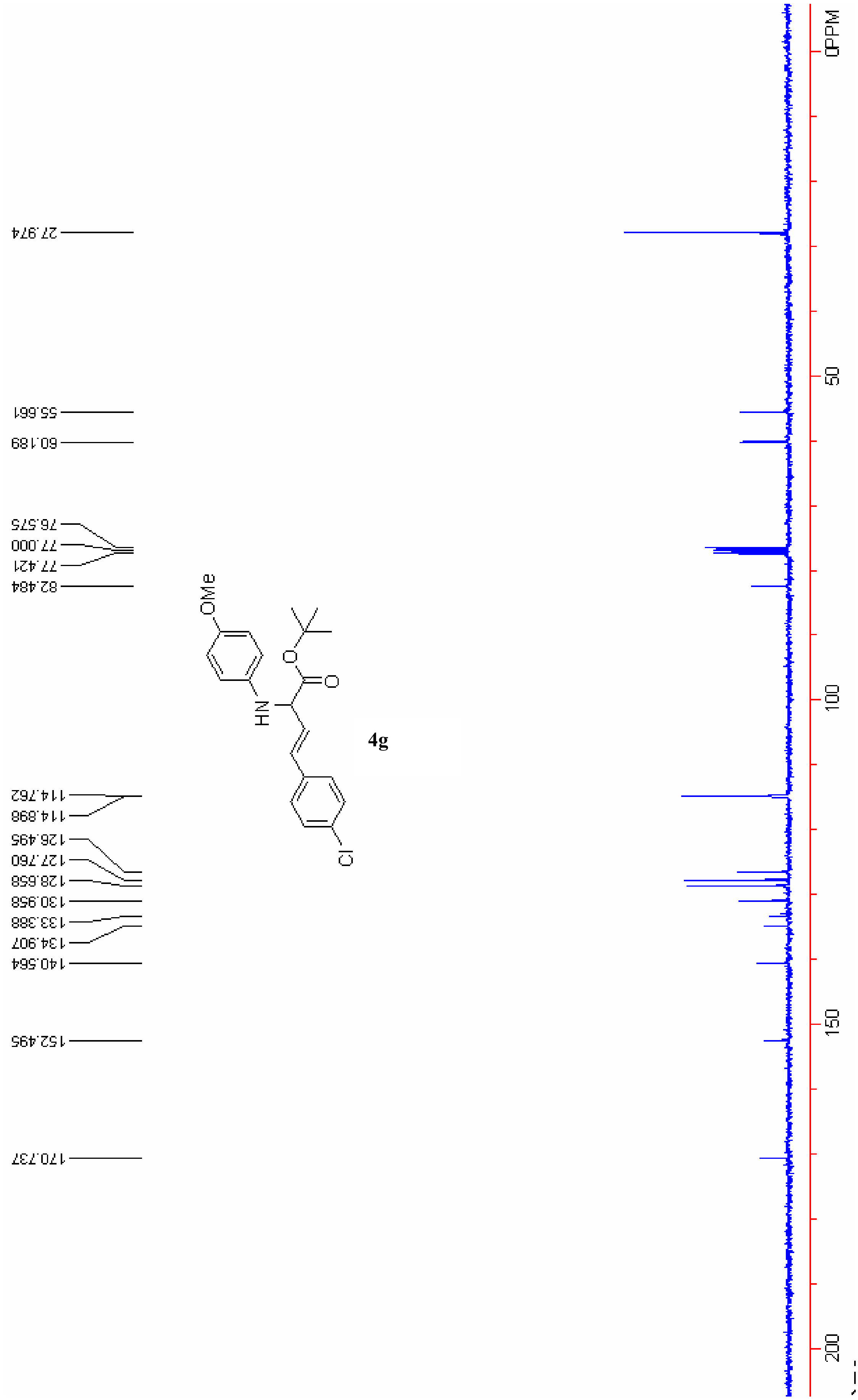
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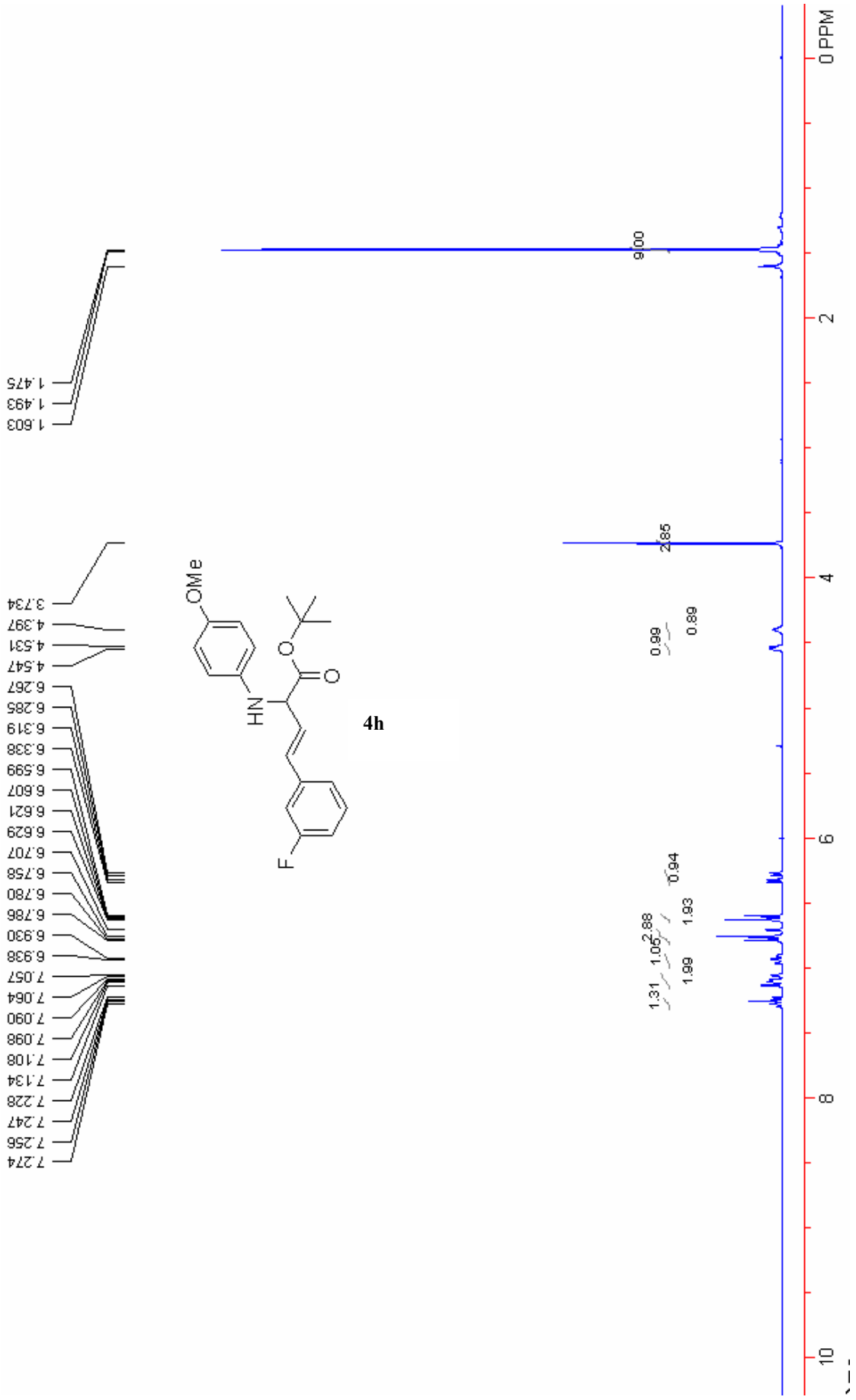
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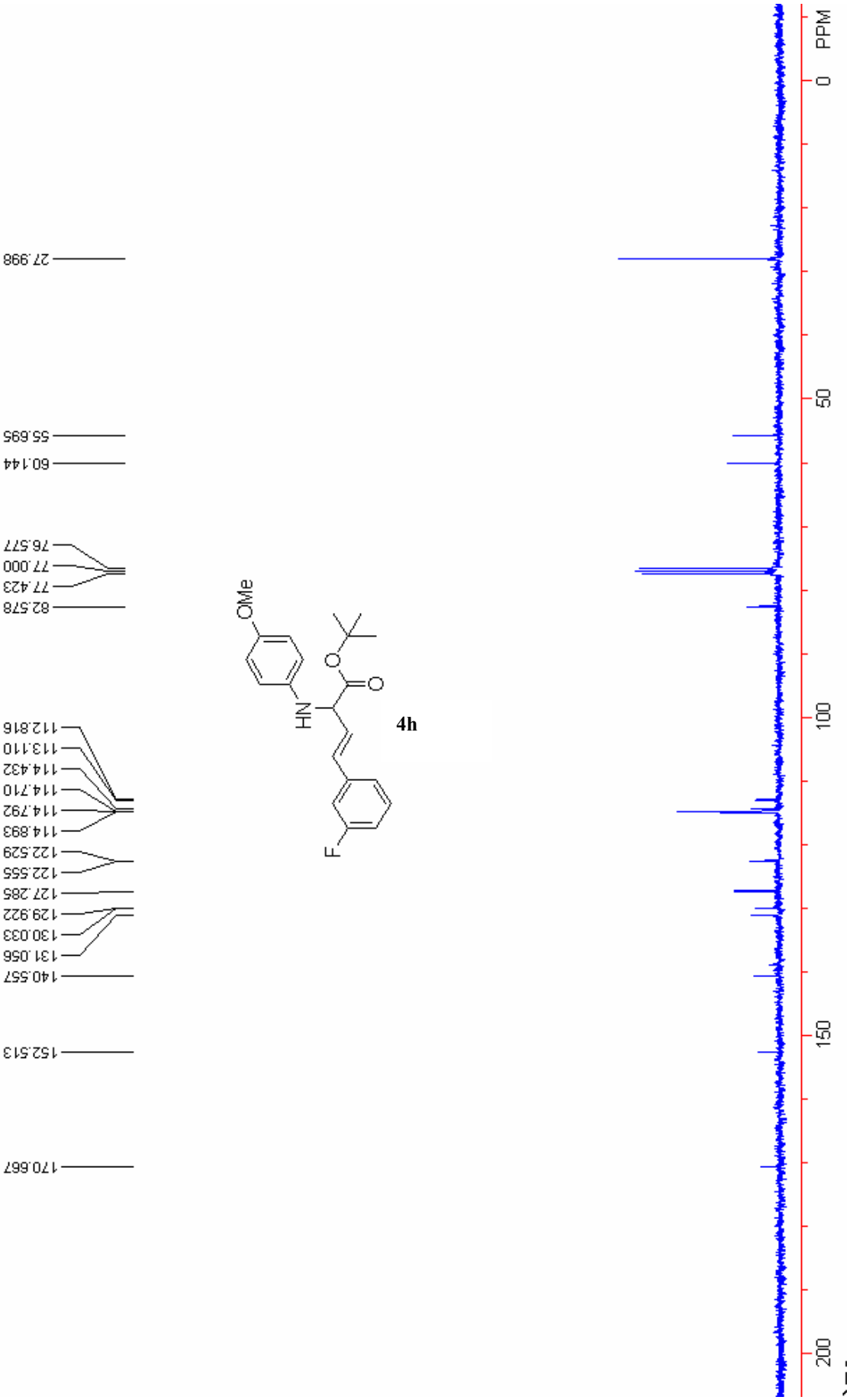
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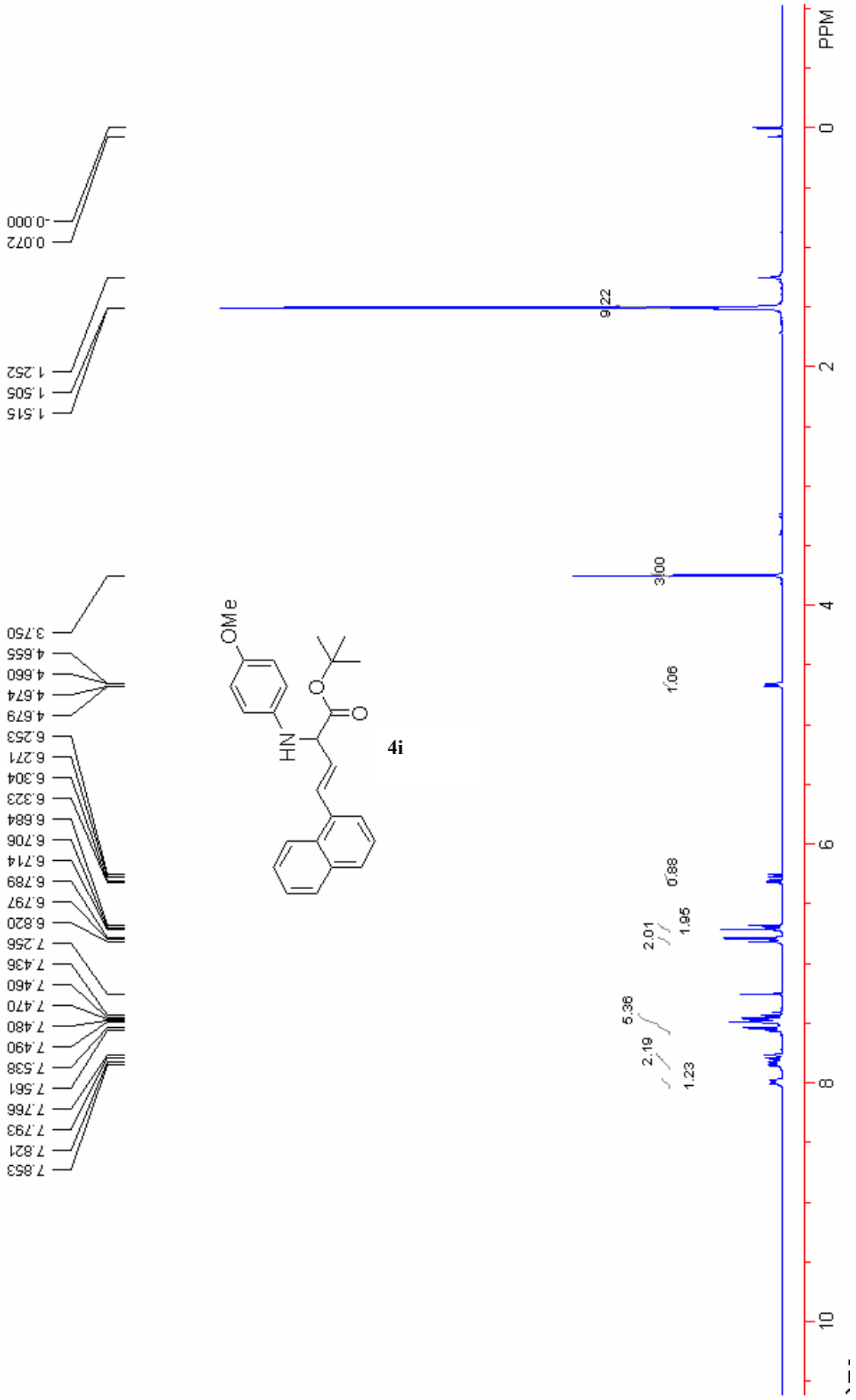
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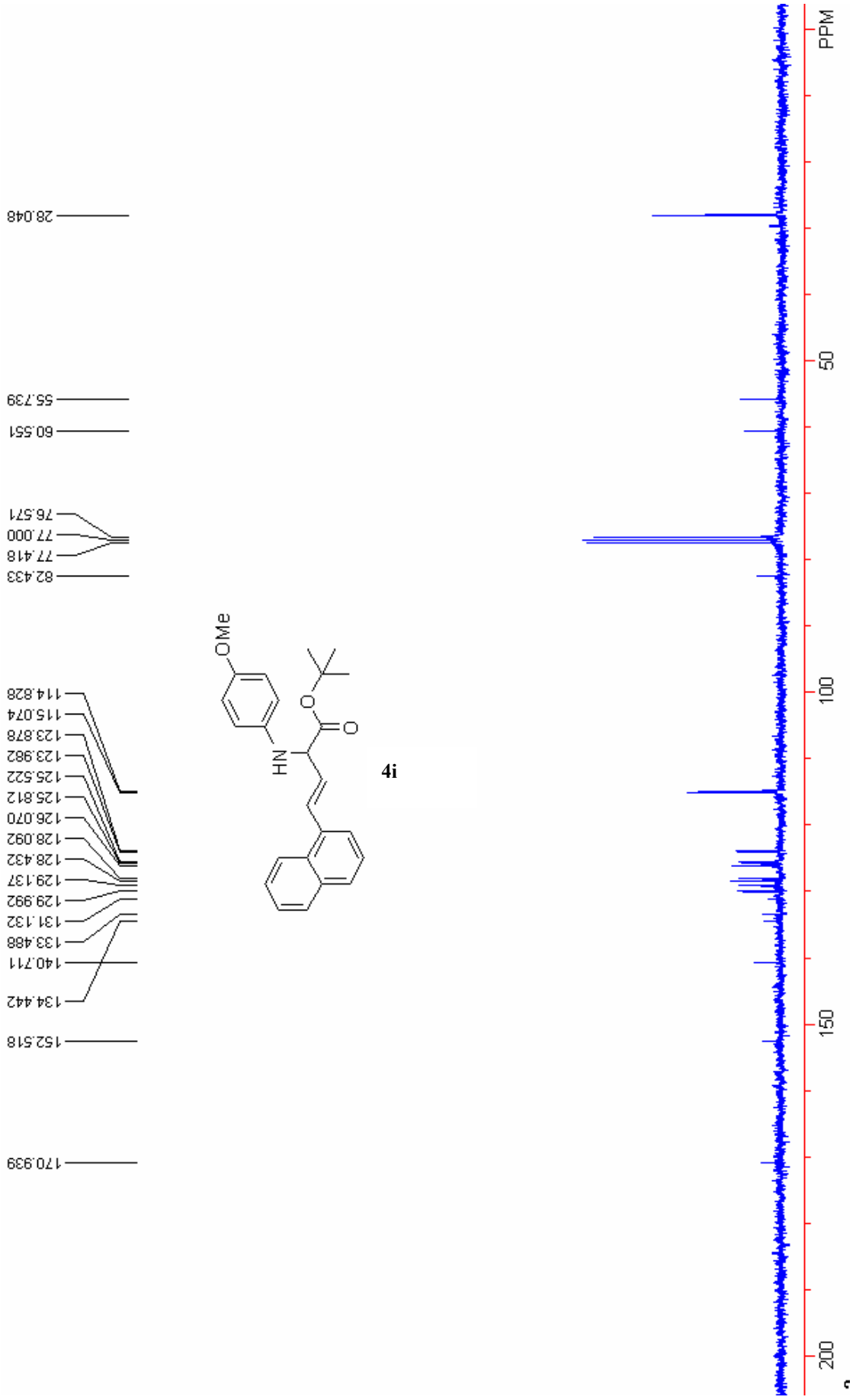
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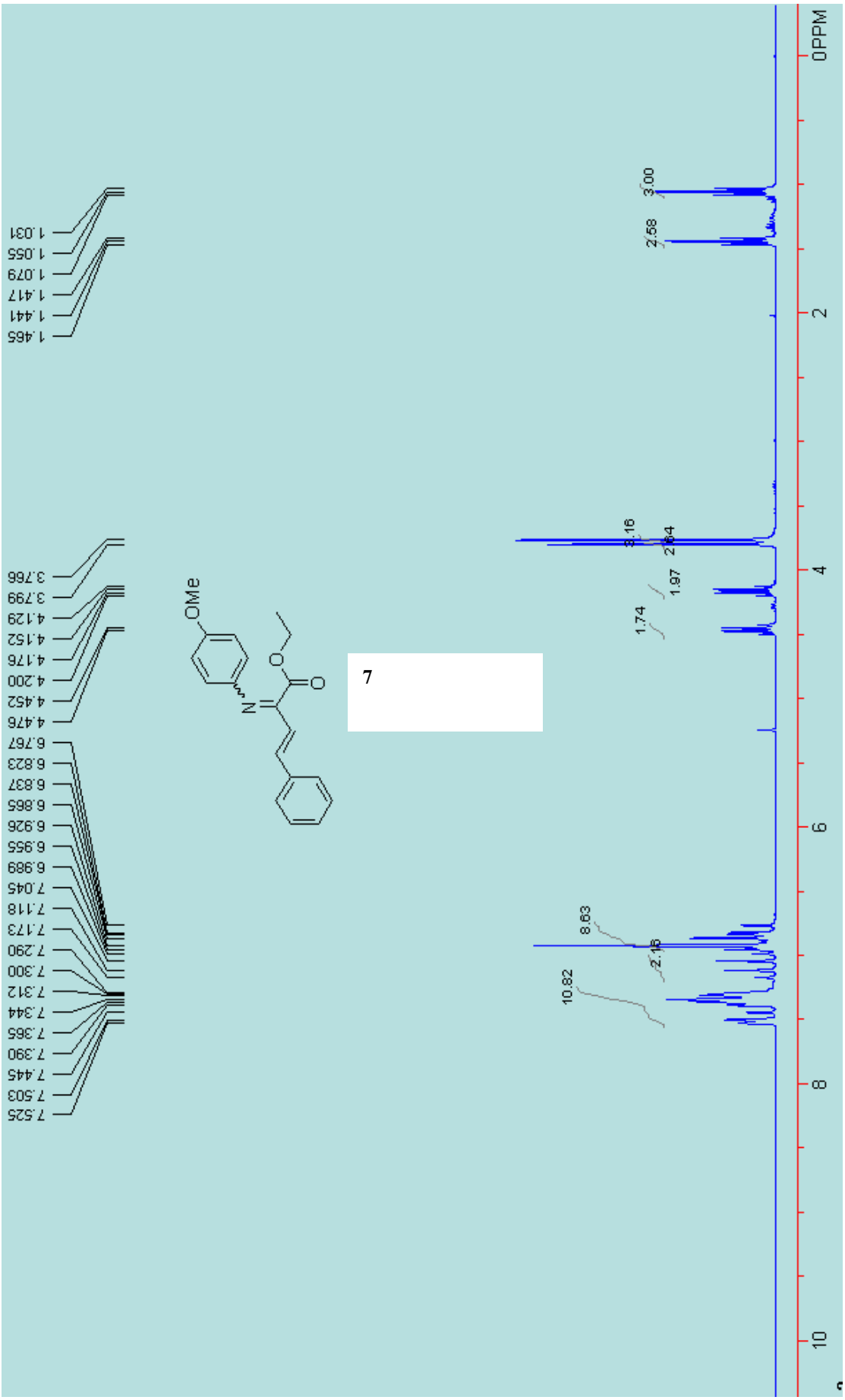
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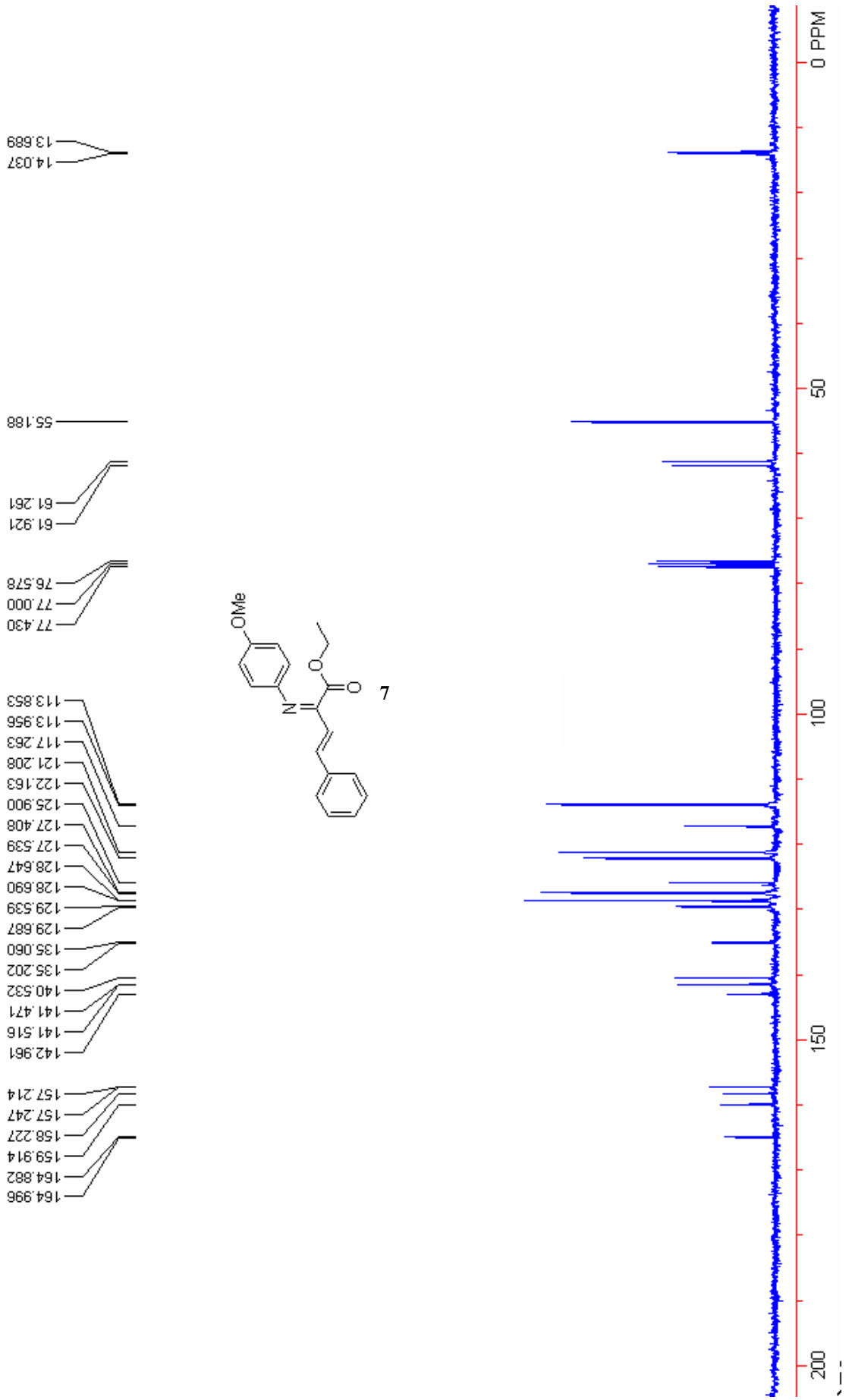
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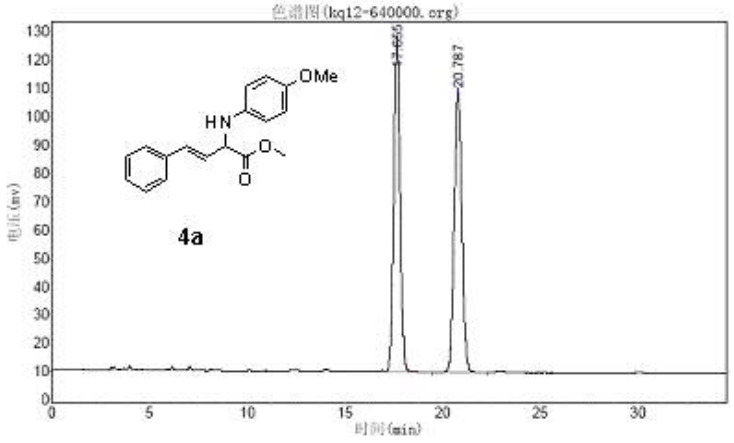
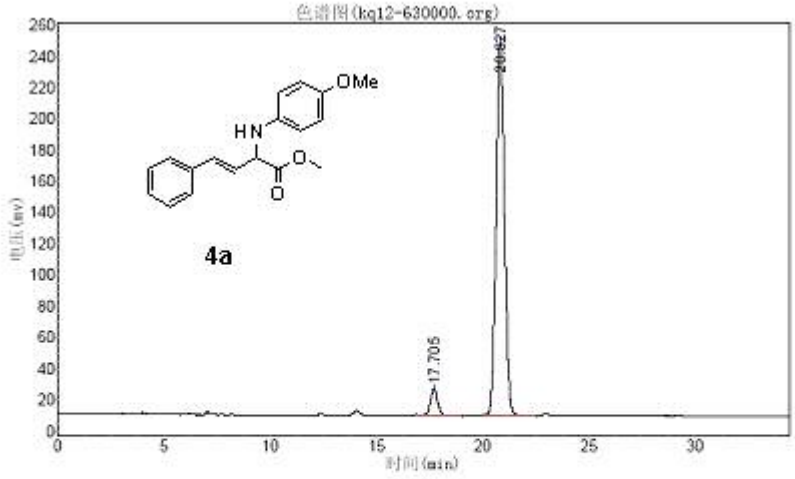
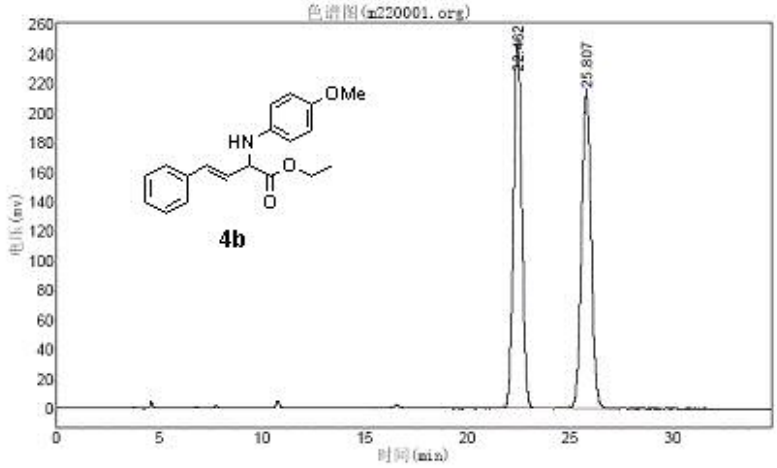


PeakNo	RetTime	PeakHeight	PeakArea	PerCent
1	17.655	117704.555	2663222.250	49.8294
2	20.787	99158.172	2681459.250	50.1706
总计		216862.727	5344681.500	100.0000



PeakNo	RetTime	PeakHeight	PeakArea	PerCent
1	17.705	17195.654	388926.875	5.6408
2	20.827	239232.328	6505980.000	94.3592
总计		256427.982	6894906.875	100.0000



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1	22.462	248739.563	6932001.000	50.0270
2	25.807	213900.625	6924528.000	49.9730
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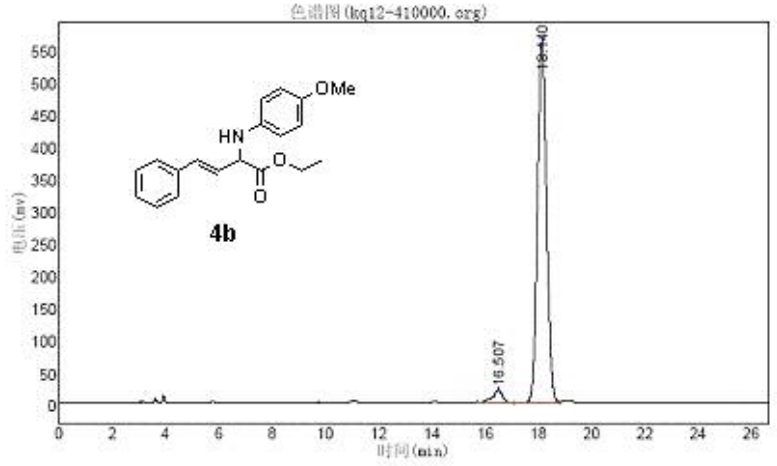

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1	16.507	19027.172	507034.719	3.6658
2	18.140	561016.938	13324363.000	96.3342
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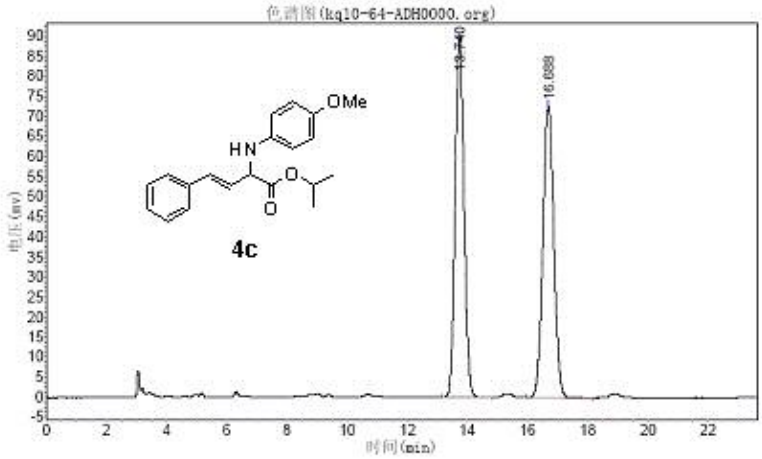

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1	13.740	89654.742	1834734.250	49.9857
2	16.688	73051.898	1835783.875	50.0143
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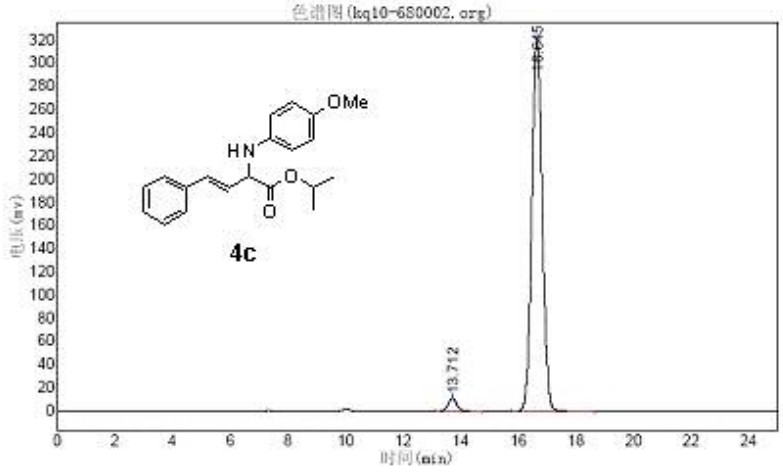

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1	13.712	10917.434	229880.297	2.7758
2	16.645	319135.469	8051725.000	97.2242
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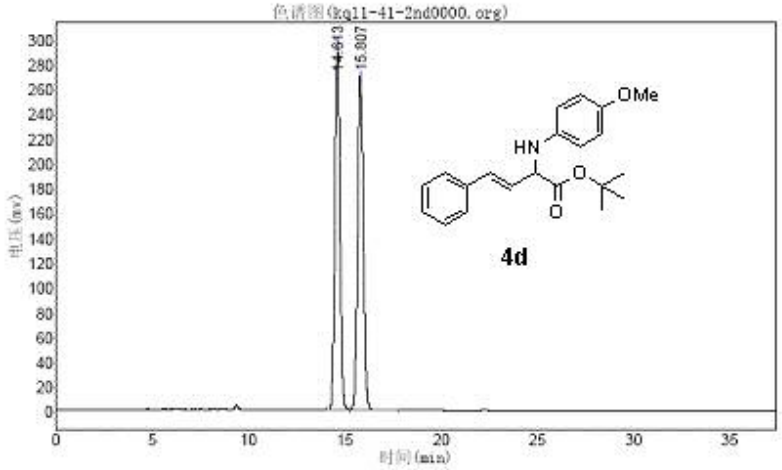

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1	14.613	297759.781	5437764.500	49.6772
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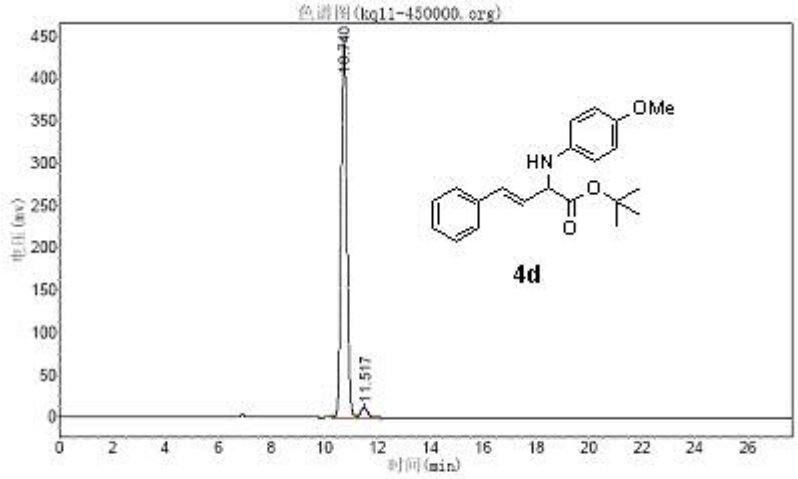

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1	10.740	443061.750	6664058.500	97.0682
2	11.517	11964.155	201281.266	2.9318
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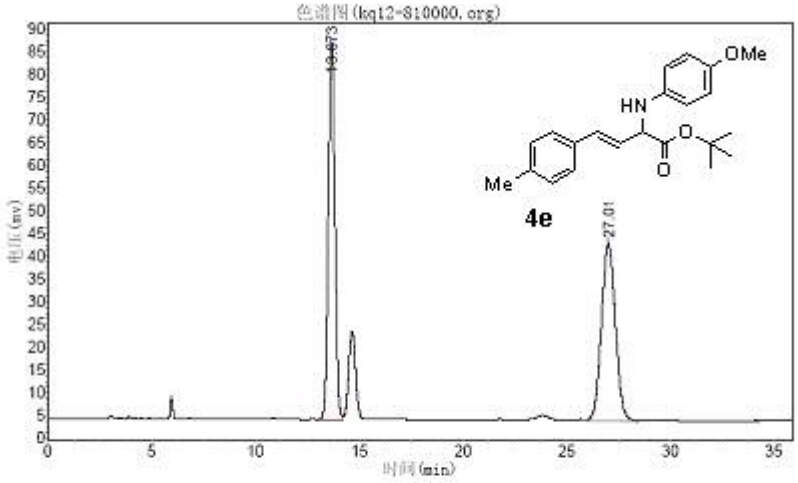

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1	13.673	83138.047	1815180.375	49.9747
2	27.013	39120.477	1817019.500	50.0253
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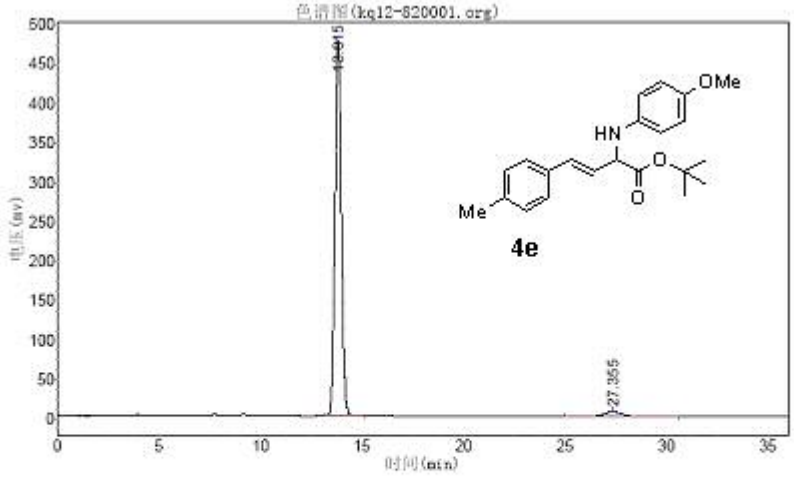

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1	13.815	475309.188	10456626.000	97.3066
2	27.355	5884.919	289430.813	2.6934
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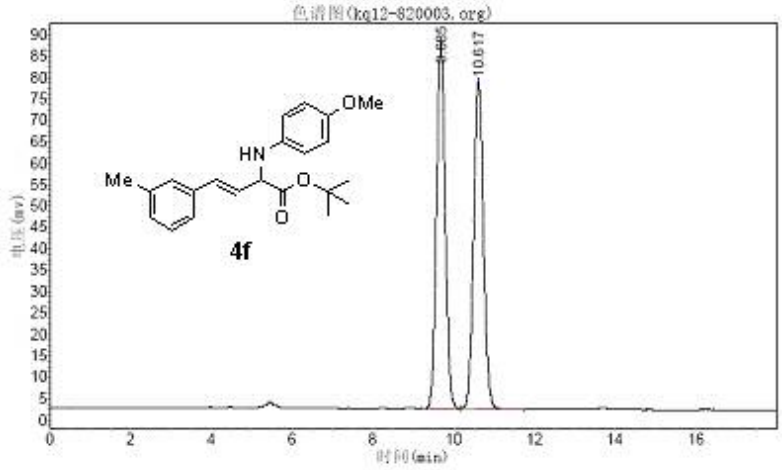

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1	9.685	85805.148	1294153.875	49.7974
2	10.617	76558.336	1304683.875	50.2026
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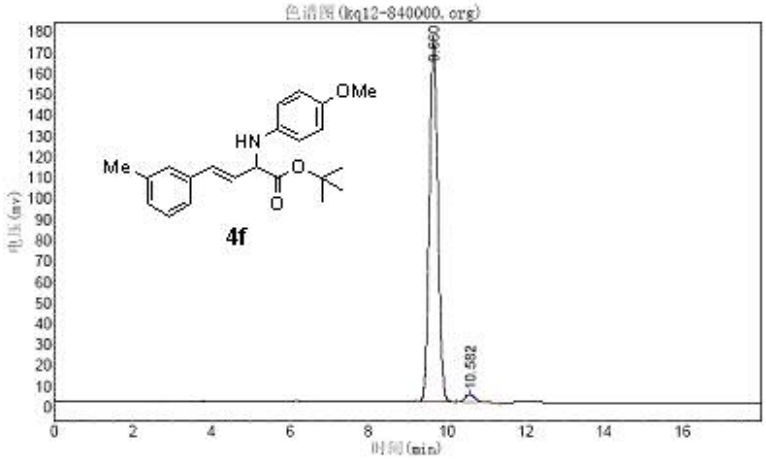

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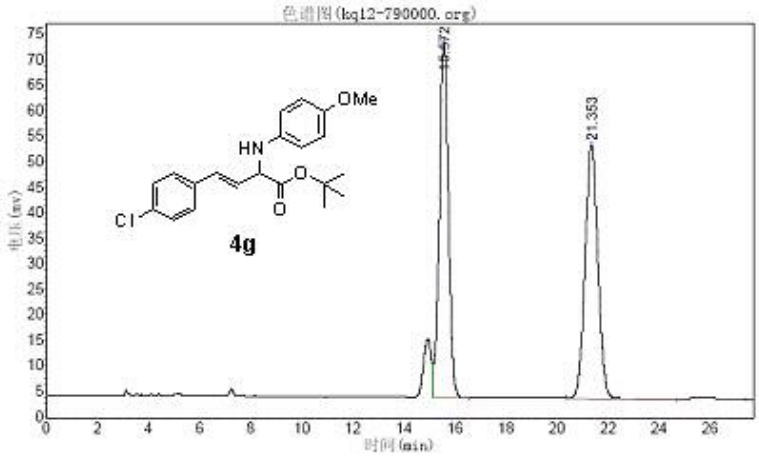
1	9.660	173355.844	2609578.000	97.6182
2	10.582	3719.825	63672.539	2.3818
总计		177075.669	2673250.539	100.0000



PeakNo	RetTime	PeakHeight	PeakArea	PerCent
1	15.572	69802.477	1732521.875	49.8865
2	21.353	49651.332	1740403.500	50.1135
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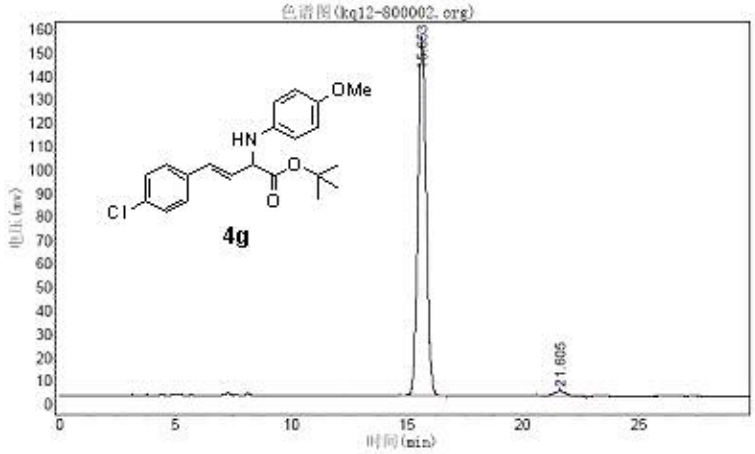
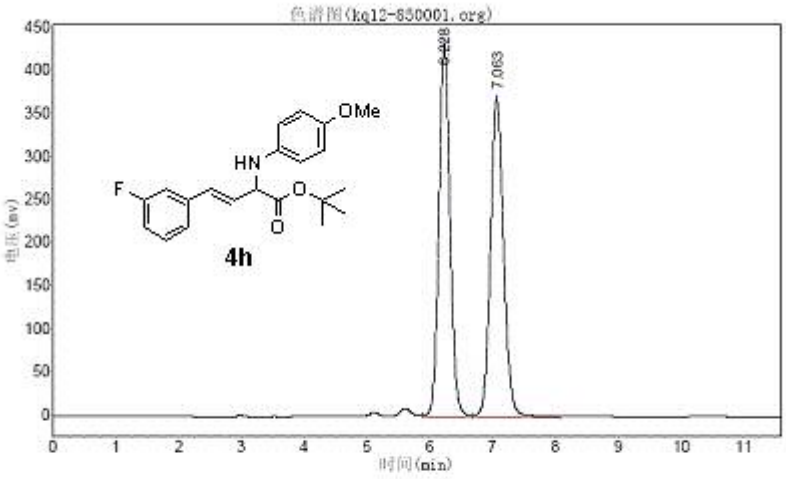
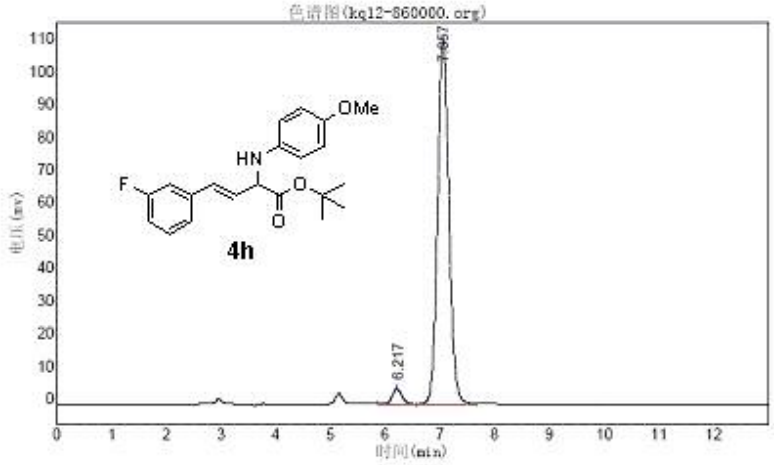


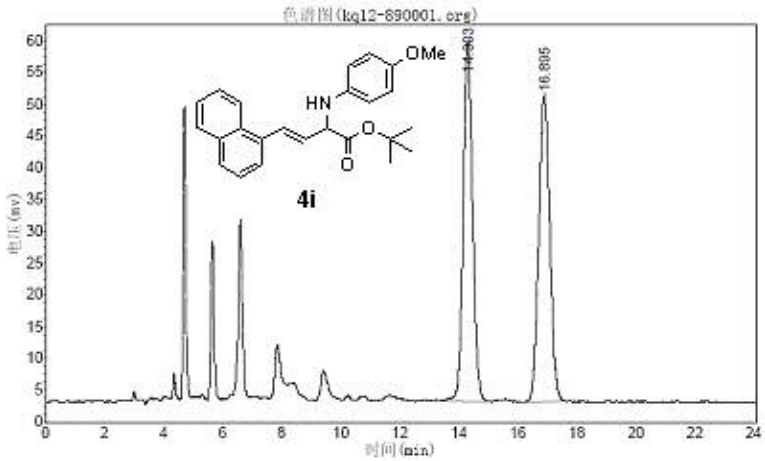
PeakNo	RetTime	PeakHeight	PeakArea	PerCent
1	15.653	151578.531	3795131.250	98.0867
2	21.605	2013.834	74028.156	1.9133
总计		153592.365	3869159.406	100.0000



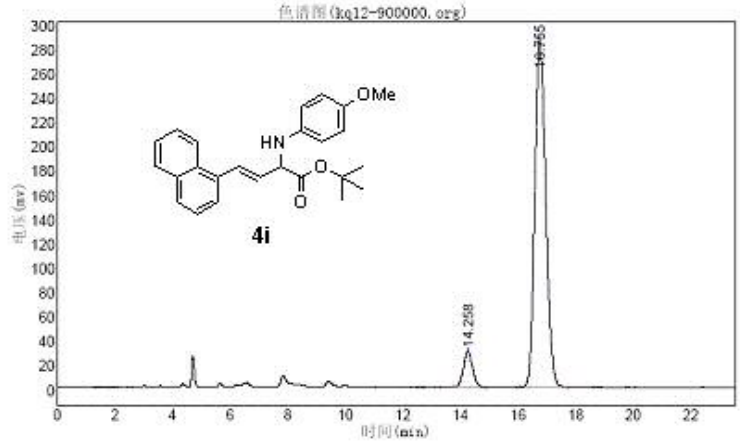
PeakNo	RetTime	PeakHeight	PeakArea	PerCent
1	6.228	433237.906	5317314.000	49.7722
2	7.063	369195.156	5365981.000	50.2278
总计		802433.063	10683295.000	100.0000



PeakNo	RetTime	PeakHeight	PeakArea	PerCent
1	6.217	4778.594	62144.258	3.7153
2	7.057	111130.992	1610503.250	96.2847
总计		115909.586	1672647.508	100.0000



PeakNo	RetTime	PeakHeight	PeakArea	PerCent
1	14.303	56477.969	1273874.750	50.4523
2	16.895	48102.270	1251036.375	49.5477
总计		104580.238	2524911.125	100.0000



PeakNo	RetTime	PeakHeight	PeakArea	PerCent
1	14.258	29239.445	647271.063	7.9205
2	16.755	286091.094	7524815.500	92.0795
总计		315330.539	8172086.563	100.0000