Supporting Information for

D-Camphor-derived Triazolium Salts for Catalytic Intramolecular Crossed Aldehyde-Ketone Benzoin Reactions

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General Methods.

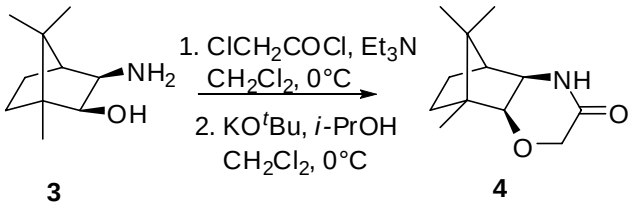
All reactions utilizing air- or moisture-sensitive reagents were carried out in flame-dried glassware under a dry Ar atmosphere. All solvents were purified and dried according to standard methods prior to use.

^{1}H NMR spectra were recorded on a VARIAN Mercury 300 MHz spectrometer in chloroform-d_3. Chemical shifts are reported in ppm with the internal TMS signal at 0.0 ppm as a standard. The data is being reported as (s = singlet, d = doublet, t = triplet, m = multiplet or unresolved, brs = broad singlet, coupling constant(s) in Hz, integration). ^{13}C NMR spectra were recorded on a VARIAN Mercury 75 MHz spectrometer in chloroform-d_3. Chemical shifts are reported in ppm with the internal chloroform signal at 77.0 ppm as a standard. ^{19}F NMR spectra were recorded on a VARIAN Mercury 282 MHz spectrometer. Chemical shifts are reported in ppm with CCl_3F signal at 0.00 ppm as an external standard.

Optical rotation ($[\alpha]_D$) were measured on a Perkin-Elmer785A UV/VIS Detector polarimeter. Enantiomeric excesses were assesses by HPLC analysis on a chiral stationary phase, CHIRALPAK AD-H or CHIRALCEL OD-H or CHIRALPAK AS-H (Daicel Chemical Ind., Ltd., Φ 0.46mm × 25 cm).

Keto-aldehydes **5j**[1] and **5l**[2] were synthesized according to the literature.

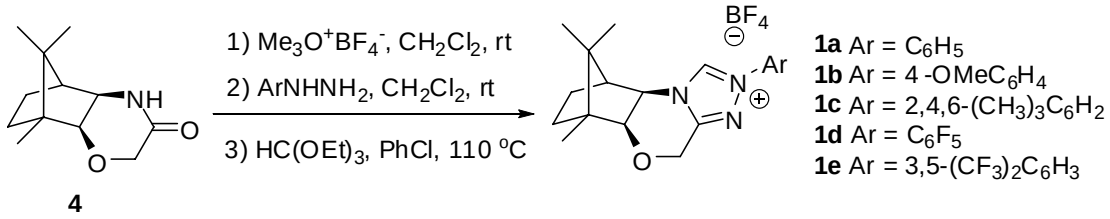
Preparation[3] of the lactam 4.



3 **4**

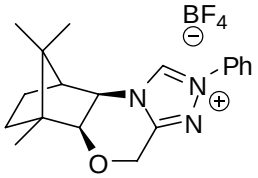
To a solution of **3**[4] (6.0 g, 36.4 mmol) and triethylamine (11.2 mL, 80 mmol) in CH_2Cl_2 (200 mL) at 0℃ was slowly added chloroacetyl chloride (3.2 mL, 40 mmol) over 20 min. The mixture was allowed to warm to ambient temperature and stirred for about 6 h. The solution was then cooled to 0℃ and potassium *tert*-butoxide (13.1 g, 153 mmol) in 2-propanol (100 mL) was added dropwise over 30 min. The mixture was allowed to warm to ambient temperature and stirred for about 2 d. After completion (monitored by TLC), the solvent was removed under reduced pressure. Water (50 mL) was added to the residue, and the mixture was extracted with ethyl acetate (50 mL × 3). The combined ethyl acetate extract was washed with brine, dried over anhydrous Na_2SO_4 and then concentrated under reduced pressure. The crude product was purified by flash column chromatography to afford the title compound **4** as a white solid (3.6 g, yield 66%): R_f (1:1 petro-ether to ethyl acetate) = 0.3; $[\alpha]_D^{20}$ = +97.1^o (c = 1.00, $CHCl_3$). **^{1}H NMR** (300 MHz, $CDCl_3$) δ 0.85 (s, 3 H), 1.00 (s, 3 H), 1.08 (m, 1 H), 1.13 (s, 3 H), 1.53-1.74 (m, 4 H), 3.37 (d, *J* = 6.6 Hz, 1 H), 3.66 (d, *J* = 6.9 Hz, 1 H), 3.77 (d, *J* = 15.3 Hz, 1 H), 4.12 (d, *J* = 15 Hz, 1 H), 6.38 (brs, 1 H); **^{13}C NMR** (75 MHz, $CDCl_3$) δ 10.9, 20.3, 21.8, 25.7, 32.7, 47.2, 48.9, 50.0, 57.9, 65.8, 83.4, 171.1; **IR** (KBr): ν_{max} (cm^{-1}) = 3178, 3066, 2955, 2873, 1688, 1429, 1353, 1114, 830, 807, 446; **MS** (EI, *m/*z, rel. intensity) 209 (M^+, 19), 95 (100); **HRMS** (EI) calcd for $C_{12}H_{19}NO_2$ (M^+): 209.1416; Found: 209.1423.

Preparation[5] of triazolium salts 1.



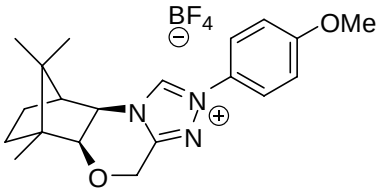
4

A flamed-dried 50 mL round bottom flask was charged with lactam **4** (0.50 g, 2.4 mmol) and CH_2Cl_2 (15 mL). Trimethyloxonium tetrafluoroborate (0.43 g, 2.9 mmol) was added and the mixture was stirred for about 1 d at rt. The corresponding aryl hydrazine (2.4 mmol) was added and stirred for another 1 d. The solvent was evaporated and chlorobenzene (25 mL) was added, followed by triethyl orthoformate (2.5 mL / day, 15 mmol). The mixture was then heated to 110℃ and stirred at this temperature for about 3 d. After completion (monitored by NMR), the solvent was removed under reduced pressure. The crude product was purified by flash column chromatography and further purified by recrystallization in hexane/ethyl acetate. All the yields indicated below refer to those obtained after recrystallization.

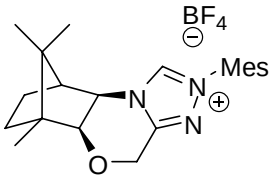


1a: white solid, yield 35%. $[\alpha]_D^{20}$ = +29.4° (c = 1.00, $CHCl_3$). **^{1}H NMR** (300 MHz, $CDCl_3$) δ 0.66 (s, 3 H), 0.86 (s, 3 H), 1.00 (s, 3 H), 1.19-1.28 (m, 2 H), 1.55-1.59 (m, 1 H), 1.79-1.82 (m, 1 H), 2.65 (d, *J* = 4.8 Hz, 1 H), 4.07 (d, *J* = 7.2 Hz, 1 H), 4.46 (d, *J* = 6.9 Hz, 1 H), 4.72 (d, *J* = 15.3 Hz, 1 H), 5.03 (d, *J* = 15 Hz, 1 H), 7.46-7.53 (m, 3 H), 7.85-7.88 (m, 2 H), 10.26 (s, 1 H); **^{13}C NMR** (75 MHz, $CDCl_3$) δ 11.0, 20.2, 21.2, 25.4, 32.4, 48.2, 49.6, 50.0, 58.7, 60.8, 83.8, 120.5, 130.1, 130.6, 134.9, 139.0, 151.2; **IR** (KBr): ν_{max} (cm^{-1}) =3104, 2879, 1594, 1394, 1227, 1104, 1063, 975, 805,

764, 688, 521; **MS** (ESI, *m/z*, rel. intensity) 310.2 (M-BF_4); **HRMS** (ESI) calcd for $C_{19}H_{24}N_3O$ (M-BF_4): 310.1914; Found: 310.1914.

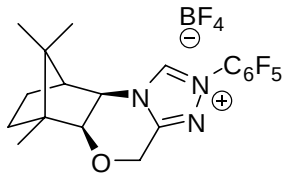


1b: pale yellow solid, yield 30%. $[\alpha]_D^{20}$ = +31.7° (c = 1.00, $CHCl_3$). **^{1}H NMR** (300 MHz, $CDCl_3$) δ 0.67 (s, 3 H), 0.87 (s, 3 H), 1.01 (s, 3 H), 1.25-1.29 (m, 2 H), 1.61-1.68 (m, 1 H), 1.80-1.90 (m, 1 H), 2.64 (d, *J* = 4.8 Hz, 1 H), 3.83 (s, 3 H), 4.08 (d, *J* = 6.9 Hz, 1 H), 4.44 (d, *J* = 6.9 Hz, 1 H), 4.70 (d, *J* = 15.3 Hz, 1 H), 5.03 (d, *J* = 15.3 Hz, 1 H), 6.94 (d, *J* = 9.0 Hz, 2 H), 7.77 (d, *J* = 9.3 Hz, 2 H), 10.13 (s, 1 H); **^{13}C NMR** (75 MHz, $CDCl_3$) δ 11.0, 20.2, 21.2, 25.4, 32.4, 48.2, 49.6, 49.9, 55.7, 58.7, 60.7, 83.8, 115.0, 122.2, 128.0, 138.2, 151.0, 161.1; **IR** (KBr): ν_{max} (cm^{-1}) = 3154, 2947, 1590, 1514, 1459, 1261, 1110, 1062, 977, 827, 522; **MS** (ESI, *m/z*, rel. intensity) 340.2 (M-BF_4); **HRMS** (ESI) calcd for $C_{20}H_{26}N_3O_2$ (M-BF_4): 340.2020; Found: 340.2014.

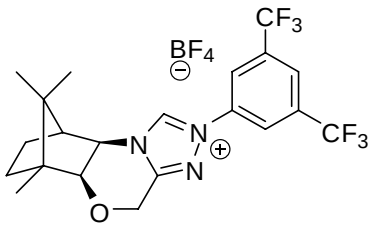


1c: colorless crystalline, yield 25%. $[\alpha]_D^{20}$ = +6.6° (c = 1.00, $CHCl_3$). **^{1}H NMR** (300 MHz, $CDCl_3$) δ 0.67 (s, 3 H), 0.88 (s, 3 H), 1.02 (s, 3 H), 1.22-1.25 (m, 2 H), 1.58-1.66 (m, 1 H), 1.82-1.85 (m, 1 H), 2.01 (s, 6 H), 2.37 (s, 3 H), 2.65 (d, *J* = 4.2 Hz, 1 H), 4.12 (d, *J* = 6.9 Hz, 1 H), 4.55 (d, *J* = 7.2 Hz, 1 H), 4.74 (d, *J* = 15.0 Hz, 1 H), 5.02 (d, *J* = 15.0 Hz, 1 H), 7.00 (s, 2 H), 9.80 (s, 1 H); **^{13}C NMR** (75 MHz, $CDCl_3$) δ 11.1, 17.0, 20.1, 21.1, 21.2, 25.3, 32.6, 48.2, 49.6, 50.0, 58.7, 60.7, 84.0, 129.6, 131.1, 141.8, 143.1, 151.1; **IR** (KBr): ν_{max} (cm^{-1}) =3141, 2951, 2927, 1589,

1458, 1222, 1105, 1060, 976, 805, 647, 522; **MS** (ESI, *m/z*, rel. intensity) 352.2 (M-BF_4); **HRMS** (ESI) calcd for $C_{22}H_{30}N_3O$ (M-BF_4): 352.2383; Found: 352.2400.



1d: white solid, yield 35%. $[\alpha]_D^{20}$ = +29.0° (c = 1.00, $CHCl_3$). **^{1}H NMR** (300 MHz, $CDCl_3$) δ 0.64 (s, 3 H), 0.91 (s, 3 H), 1.03 (s, 3 H), 1.24-1.39 (m, 2 H), 1.67-1.71 (m, 1 H), 1.93-1.97 (m, 1 H), 2.46 (d, *J* = 4.2 Hz, 1 H), 4.14 (d, *J* = 6.6 Hz, 1 H), 4.55 (d, *J* = 6.9 Hz, 1 H), 4.75 (d, *J* = 15.0 Hz, 1 H), 5.05 (d, *J* = 15.0 Hz, 1 H), 10.14 (s, 1 H); **^{13}C NMR** (75 MHz, $CDCl_3$) δ 10.9, 19.8, 21.0, 25.1, 32.4, 48.4, 49.5, 50.1, 58.5, 60.9, 83.8, 110.7, 136.2, 139.0, 141.7, 142.2, 145.3, 152.2; **IR** (KBr): ν_{max} (cm^{-1}) =3134, 2967, 1608, 1531, 1517, 1394, 1215, 1076, 1004, 987, 852, 800, 628, 524, 462; **MS** (ESI, *m/z*, rel. intensity) 400.2 (M-BF_4); **HRMS** (ESI) calcd for $C_{19}H_{19}N_3O$ (M-BF_4): 400.1443; Found: 400.1436.

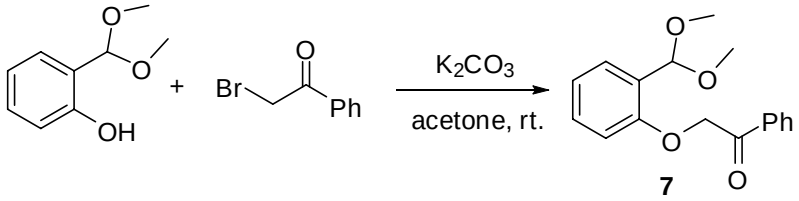


1e: white solid. yield 25%. **^{1}H NMR** (300 MHz, $CDCl_3$) δ 0.66 (s, 3 H), 0.85 (s, 3 H), 1.02 (s, 3 H), 1.17-1.27 (m, 2 H), 1.58-1.60 (m, 1 H), 1.79-1.83 (m, 1 H), 2.64 (d, *J* = 4.5 Hz, 1 H), 4.11 (d, *J* = 6.9 Hz, 1 H), 4.53 (d, *J* = 6.9 Hz, 1 H), 4.77 (d, *J* = 15.0 Hz, 1 H), 5.10 (d, *J* = 15.3 Hz, 1 H), 7.95 (s, 1 H), 8.44 (s, 2 H), 10.47 (s, 1 H); **^{19}F NMR** (282 MHz, $CDCl_3$): δ -63.3, -151.5, -151.6. **^{13}C NMR** (75 MHz, $CDCl_3$) δ 11.0, 20.3, 21.0, 25.4, 29.7, 32.3, 48.3, 49.6, 49.9, 58.7, 61.2, 83.8, 120.3, 121.2, 124.0 (m), 133.8 (q, *J* = 34.8 Hz), 136.0, 140.5, 160.0; **IR** (KBr): ν_{max} (cm^{-1}) =3134, 2967, 1608, 1531, 1517, 1394, 1215, 1076, 1004, 987, 852, 800, 628, 524, 462; **MS** (ESI, *m/z*, rel.

intensity) 446.2 (M-BF_4); **HRMS** (ESI) calcd for $C_{21}H_{22}N_3OF_6$ (M-BF_4): 446.1672; Found: 446.1662.

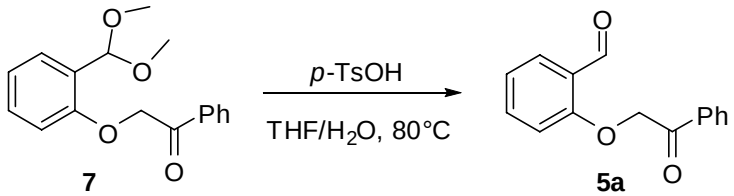
General procedure for the preparation of keto-aldehydes (5a-i, 5k)

The preparation of keto-aldehyde **5a** is representative.



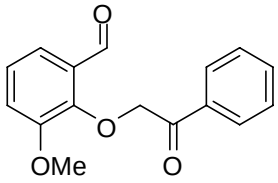
To a solution of the acetal[6] (1.1 g, 6 mmol) in acetone (5 mL) was added K_2CO_3 (0.7 g, 5 mmol). After stirring for 0.5 h, ω-bromoacetophenone (1 g, 5 mmol) was added and the mixture was stirred at room temperature overnight. After completion (monitored by TLC), water was added to the solution, and the mixture was extracted with ethyl acetate. The combined ethyl acetate extract was washed with brine, dried over anhydrous Na_2SO_4 and then concentrated under reduced pressure. The crude product was purified by flash column chromatography (hexane/EtOAc = 10/1).

7: yellow solid, yield 70%. **^{1}H NMR** (300 MHz, $CDCl_3$) δ 3.38 (s, 6 H), 5.31 (s, 2 H), 5.77 (s, 1 H), 6.82 (d, *J* = 8.4 Hz, 1 H), 7.02 (t, *J* = 7.5 Hz, 1 H), 7.26 (dd, *J* = 1.8, 15.6 Hz, 1 H), 7.47-7.62 (m, 4 H), 8.00 (d, *J* = 8.4 Hz, 2 H).

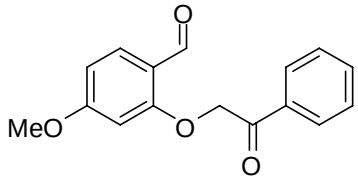


To a solution of **7** (0.27 g, 1 mmol) in THF (4 mL) /H_2O (1 mL) was added *p*-TsOH (0.028 g, 0.1 mmol), and the solution was heated at 80℃ for 2h. After completion (monitored by TLC), the mixture was cooled to room temperature and extracted with CH_2Cl_2. The combined organic layers were washed successively with saturated $NaHCO_3$, brine, dried over anhydrous Na_2SO_4 and then concentrated under reduced pressure. This material was suitable for the next reaction. The compound could be further purified by recrystallization in hexane/ethyl acetate.

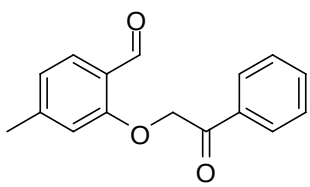
5a [7] (entry 1, Table 2): white solid, yield 100%. **^{1}H NMR** (300 MHz, $CDCl_3$) δ 5.44 (s, 2 H), 6.86 (d, *J* = 8.1 Hz, 1 H), 7.07 (t, *J* = 7.8 Hz, 1 H), 7.48-7.55 (m, 3 H), 7.66 (t, *J* = 7.5 Hz, 1 H), 7.89 (dd, *J* = 1.5, 7.8 Hz, 1 H), 8.01 (d, *J* = 7.8 Hz, 2 H), 10.59 (s, 1 H).



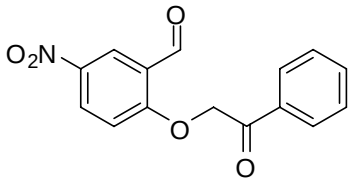
5b[8] (entry 2, Table 2): white solid, yield 40%, 2 steps. **^{1}H NMR** (300 MHz, $CDCl_3$) δ 3.86 (s, 3 H), 5.52 (s, 2 H), 7.14 (d, *J* = 4.8 Hz, 1 H), 7.46 (m, 3 H), 7.60 (m, 1 H), 7.92 (d, *J* = 7.2 Hz, 2 H), 10.66 (s, 1 H); **^{13}C NMR** (75 MHz, $CDCl_3$) δ 56.1, 74.8, 118.0, 119.3, 124.2, 127.7, 128.8, 129.7, 133.7, 134.4, 150.4, 151.8, 190.6, 194.4.



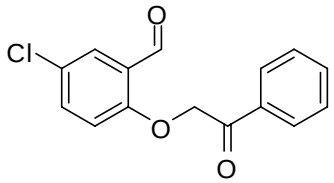
5c (entry 3, Table 2): white solid, yield 77%, 2 steps. **^{1}H NMR** (300 MHz, $CDCl_3$) δ 3.80 (s, 3 H), 5.37 (s, 2 H), 6.32 (s, 1 H), 6.56 (d, *J* = 8.7 Hz, 1 H), 7.49 (t, *J* = 7.5 Hz, 2 H), 7.62 (t, *J* = 7.5 Hz, 1 H), 7.83 (d, *J* = 8.7 Hz, 1 H), 7.97 (d, *J* = 7.5 Hz, 2 H), 10.38 (s, 1 H); **^{13}C NMR** (75 MHz, $CDCl_3$) δ 55.6, 70.7, 99.2, 106.5, 119.3, 128.0, 128.9, 130.7, 134.0, 134.1, 161.9, 165.9, 188.1, 193.4; **IR** (KBr): ν_{max} (cm^{-1}) = 3064, 2910, 1705, 1668, 1601, 1401, 1263, 1211, 1107, 1066, 983, 838, 765, 690, 660, 583, 449; **MS** (EI, *m/*z, rel. intensity) 270 (M^+, 2), 151 (100); **HRMS** (EI) calcd for $C_{16}H_{14}O_4$ (M^+): 270.0892; Found: 270.0888.



5d (entry 4, Table 2): yellow solid, yield 40%, 2 steps. **^{1}H NMR** (300 MHz, $CDCl_3$) δ 2.33 (s, 3 H), 5.40 (s, 2 H), 6.65 (s, 1 H), 6.85 (d, *J* = 7.8 Hz, 1 H), 7.50 (t, *J* = 7.5 Hz, 2 H), 7.63 (t, *J* = 7.5 Hz, 1 H), 7.74 (d, *J* = 7.8 Hz, 1 H), 7.97 (d, *J* = 7.8 Hz, 1 H), 10.49 (s, 1 H); **^{13}C NMR** (75 MHz, $CDCl_3$) δ 22.2, 70.7, 113.2, 122.6, 123.0, 128.0, 128.5, 128.9, 134.1, 147.3, 160.3, 189.2, 193.5; **IR** (KBr): ν_{max} (cm^{-1}) = 3059, 2909, 1707, 1681, 1608, 1403, 1259, 1211, 981, 813, 761, 687, 666, 591, 453; **MS** (EI, *m/z*, rel. intensity) 254 (M^+, 1), 105 (100); **HRMS** (EI) calcd for $C_{16}H_{14}O_3$ (M^+): 254.0943; Found: 254.0946.

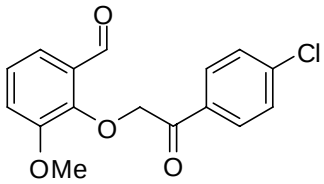


5e (entry 5, Table 2): yellow solid, yield 70%, 2 steps. **^{1}H NMR** (300 MHz, DMSO-d_6) δ 6.06 (s, 2 H), 7.47 (dd, *J* = 2.4, 7.8 Hz, 1 H), 7.60 (t, *J* = 7.5 Hz, 2 H), 7.73 (t, *J* = 7.5 Hz, 1 H), 8.04 (d, *J* = 7.2 Hz, 2 H), 8.44 (dd, *J* = 2.4, 7.8 Hz, 2 H), 10.46 (s, 1 H); **^{13}C NMR** (75 MHz, DMSO-d_6) δ 72.4, 116.2, 124.1, 124.7, 128.7, 129.6, 131.3, 134.5, 134.9, 141.8, 165.3, 188.6, 193.8; **IR** (KBr): ν_{max} (cm^{-1}) = 3114, 2885, 1917, 1702, 1688, 1611, 1586, 1430, 1341, 1285, 1228, 1081, 975, 763, 679, 559; **MS** (EI, *m/z*, rel. intensity) 267 (M^+-H_2O, 12), 105 (100); **Anal.** calcd for $C_{15}H_{11}NO_5$: C, 63.16; H, 3.89, N, 4.91; Found: C, 62.98; H, 3.95, N, 4.83.

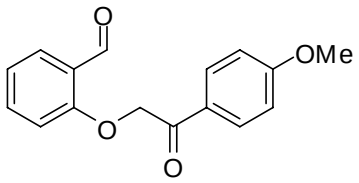


5f (entry 6, Table 2): yellow solid, yield 94%, 2 steps. **^{1}H NMR** (300 MHz, $CDCl_3$) δ 5.47 (s, 2 H), 6.81 (d, *J* = 8.7 Hz, 1 H), 7.42 (d, *J* = 8.7 Hz, 1 H), 7.52 (t, *J* = 7.5 Hz, 2 H), 7.66 (t, *J* = 7.2 Hz, 1 H), 7.79 (s, 1 H), 7.97 (d, *J* = 7.5 Hz, 2 H), 10.51 (s, 1 H); **^{13}C NMR** (75 MHz, $CDCl_3$) δ 70.8, 114.4, 126.0, 127.2, 127.8, 128.0, 129.0, 133.8, 134.3, 135.1, 158.7, 188.2, 192.9; **IR** (KBr): ν_{max} (cm^{-1}) = 1708, 1677, 1598, 1401,

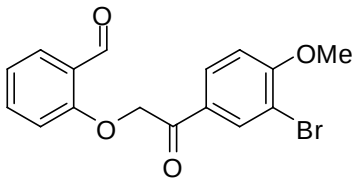
1277, 1230, 1186, 973, 815, 755, 685, 584, 552; **MS** (EI, *m/*z, rel. intensity) 274 (M^+, 1), 105 (100); **Anal.** calcd for $C_{15}H_{11}ClO_3$: C, 65.58; H, 4.04; Found: C, 65.49; H, 4.27.



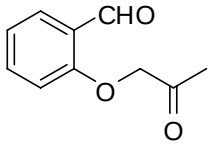
5g (entry 7, Table 2): white solid, yield 71%, 2 steps. **^{1}H NMR** (300 MHz, $CDCl_3$) δ 3.84 (s, 3 H), 5.46 (s, 2 H), 7.12 (d, *J* = 3.9 Hz, 2 H), 7.42 (m, 1 H), 7.43 (d, *J* = 8.4 Hz, 2 H), 7.87 (d, *J* = 8.4 Hz, 2 H), 10.62 (s, 1 H); **^{13}C NMR** (75 MHz, $CDCl_3$) δ 56.0, 74.7, 117.9, 119.2, 124.2, 129.0, 129.1, 129.5, 132.6, 140.0, 150.1, 151.7, 190.4, 193.3; **IR** (KBr): ν_{max} (cm^{-1}) = 2928, 1705, 1685, 1587, 1481, 1396, 1259, 1204, 1091, 1064, 965, 915, 777, 745, 653, 579, 535; **MS** (EI, *m/*z, rel. intensity) 304 (M^+, 3), 139 (100); **Anal.** calcd for $C_{16}H_{13}ClO_4$: C, 63.06; H, 4.30; Found: C, 62.82; H, 4.54.



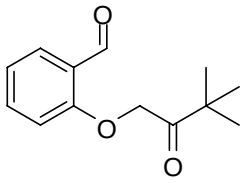
5h (entry 8, Table 2): white solid, yield 45%, 2 steps. **^{1}H NMR** (300 MHz, $CDCl_3$) δ 3.89 (s, 3 H), 5.38 (s, 2 H), 6.86 (d, *J* = 8.7 Hz, 1 H), 6.98 (m, 2 H), 7.06 (t, *J* = 3.6 Hz, 1 H), 7.49 (td, *J* = 1.8, 7.8 Hz, 1 H), 7.86 (dd, *J* = 1.8, 7.8 Hz, 1 H), 7.98 (d, *J* =8.4 Hz, 2 H), 10.58 (s, 1 H); **^{13}C NMR** (75 MHz, $CDCl_3$) δ 55.5, 70.6, 112.7, 114.1, 121.5, 125.2, 127.1, 128.5, 130.4, 135.7, 160.4, 164.2, 189.6, 192.0; **IR** (KBr): ν_{max} (cm^{-1}) = 2960, 2867, 1683, 1599, 1305, 1225, 1174, 975, 834, 757, 651, 589, 499, 441; **MS** (EI, *m/*z, rel. intensity) 270 (M^+, 1), 135 (100); **HRMS** (EI) calcd for $C_{16}H_{14}O_4$ (M^+): 270.0892; Found: 270.0885.



5i[11] (entry 9, Table 2): pale reddish powder, yield 65%, 2 steps. **^{1}H NMR** (300 MHz, acetone-d_6) δ 4.02 (s, 3 H), 5.75 (s, 2 H), 7.10 (t, *J* = 7.2 Hz, 1 H), 7.25 (q, *J* = 8.7 Hz, 2 H), 7.60 (td, *J* = 1.8, 8.1 Hz, 1 H), 7.77 (dd, *J* = 1.8, 7.5 Hz, 1 H), 8.12 (dd, *J* = 2.1, 9.0 Hz, 1 H), 8.26 (d, *J* = 2.1 Hz, 1 H), 10.62 (s, 1 H); **^{13}C NMR** (75 MHz, DMSO-d_6) δ 56.8, 70.5, 111.0, 112.5, 114.1, 121.1, 124.4, 127.5, 128.1, 129.6, 132.7, 136.2, 159.6, 160.4, 189.2, 191.7; **IR** (KBr): ν_{max} (cm^{-1}) = 2974, 2867, 1702, 1665, 1594, 1481, 1406, 1300, 1257, 1205, 992, 763, 680, 578, 443; **MS** (EI, *m/z*, rel. intensity) 348 (M^+, 1), 215 (100); **HRMS** (EI) calcd for $C_{16}H_{11}BrO_3$ (M^+-H_2O): 329.9897; Found: 329.9892.

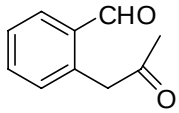


5j[1] (entry 10, Table 2): pale yellow crystalline. **^{1}H NMR** (300 MHz, $CDCl_3$) δ 2.34 (s, 3 H), 4.68 (s, 2 H), 6.81 (d, *J* = 8.7 Hz, 1 H), 7.11 (t, *J* = 7.5 Hz, 1 H), 7.55 (dt, *J* = 1.8, 7.8 Hz, 1 H), 7.88 (dd, *J* = 1.8, 7.8 Hz, 1 H), 10.58 (s, 1 H).



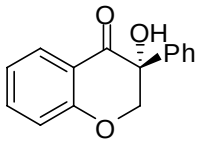
5k (entry 11, Table 2): white solid, yield 80%, 2 steps. **^{1}H NMR** (300 MHz, $CDCl_3$) δ 1.26 (s, 9 H), 5.03 (s, 2 H), 6.72 (d, *J* = 8.7 Hz, 1 H), 7.05 (t, *J* = 7.5 Hz, 1 H), 7.49 (dt, *J* = 1.8, 8.1 Hz, 1 H), 7.85 (dd, *J* = 1.8, 7.8 Hz, 1 H), 10.57 (s, 1 H); **^{13}C NMR** (75 MHz, $CDCl_3$) δ 26.2, 43.1, 68.8, 112.4, 121.4, 125.2, 128.5, 135.6, 160.3, 189.6, 208.6; **IR** (KBr): ν_{max} (cm^{-1}) = 2981, 2870, 1716, 1684, 1598, 1481, 1233, 989, 757,

648, 503; **MS** (EI, *m/*z, rel. intensity) 220 (M^+, 1), 57 (100); **HRMS** (EI) calcd for $C_{13}H_{16}O_3$ (M^+): 220.1099; Found: 220.1095.



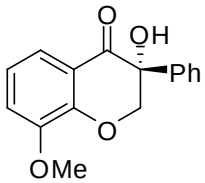
5l[2]: pale yellow oil. **^{1}H NMR** (300 MHz, $CDCl_3$) δ 2.33 (s, 3 H), 4.14 (s, 2 H), 7.21 (d, *J* = 6.6 Hz, 1 H), 7.48-7.59 (m, 2 H), 7.82 (dd, *J* = 1.8, 6.9 Hz, 1 H), 10.01 (s, 1 H).

General Procedure for Intramolecular Crossed Aldehyde-Ketone Benzoin Reactions



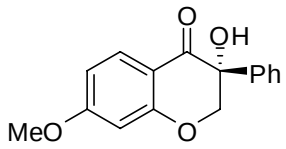
The reaction of keto-aldehyde **5a** is representative (entry 1, Table 2). A flame dried Schlenk tube was cooled to room temperature and filled with argon. To this flask were added triazolium salt **1d** (3.2 mg, 0.006 mmol, 6 mol %), DBU (0.76 μL, 0.005 mmol, 5 mol %), THF (1 mL). The mixture was stirred for 0.5 h at room temperature, keto-aldehyde **5a** (26 mg, 0.1 mmol) was added. After the reaction was complete (monitored by TLC), the reaction was cooled to 0℃, and water was added. The product was extracted with CH_2Cl_2 (5 mL ×3). The combined organic layers were dried over anhydrous Na_2SO_4, concentrated under reduced pressure, and then purified by silica-gel column chromatography (hexane/EtOAc = 10/1) to afford benzoin product **6a** as a white solid.

6a[7] (entry 1, Table 2): white solid, 93% yield, 84% ee [Daicel Chiralpak AD-H, hexanes/2-propanol = 90/10, v = 1.0 mL/min^{-1}, λ = 230 nm, t (minor) = 13.64 min, t (major) = 16.65 min]. **^{1}H NMR** (300 MHz, $CDCl_3$) δ 4.23 (s, 1 H), 4.47 (d, *J* = 11.1 Hz, 1 H), 4.85 (d, *J* = 11.7 Hz, 1 H), 6.96 (d, *J* = 8.1 Hz, 1H), 7.07 (t, *J* = 7.5 Hz, 1 H), 7.03-7.36 (m, 3 H), 7.44-7.54 (m, 3 H), 7.93 (dd, *J* = 1.5, 8.1 Hz, 1 H).

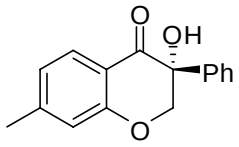


6b (entry 2, Table 2): white solid, 96% yield, 76% ee [Daicel Chiralcel OD-H, hexanes/2-propanol = 75/25, v = 0.5 mL · min^{-1}, λ = 230 nm, t (major) = 16.77 min, t (minor) = 19.95 min]; $[\alpha]_D^{20}$ = +41.7^o (c = 1.45, $CHCl_3$). **^{1}H NMR** (300 MHz, $CDCl_3$) δ 3.85 (s, 3 H), 4.30 (s, 1 H), 4.48 (d, *J* = 11.7 Hz, 1 H), 4.99 (d, *J* = 11.7 Hz, 1 H), 6.95-7.05 (m, 2 H), 7.26-7.33 (m, 3 H), 7.45-7.53 (m, 3 H); **^{13}C NMR** (75 MHz,

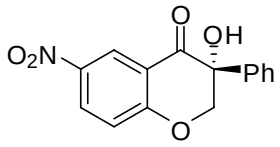
$CDCl_3$) δ 56.1, 73.2, 74.0, 117.2, 118.5, 119.7, 121.6, 126.0, 128.6, 128.7, 138.1, 148.6, 151.3, 194.5; **IR** (KBr): ν_{max} (cm^{-1}) = 3398, 3002, 2872, 1679, 1489, 1440, 1272, 11443, 1028, 973, 767, 694, 636, 558, 470; **MS** (EI, *m/*z, rel. intensity) 270 (M^+, 12), 151 (100); **Anal**. calcd for $C_{16}H_{14}O_4$: C, 71.10; H, 5.22; Found: C, 70.83; H, 5.43.



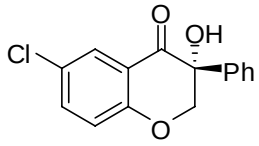
6c[9] (entry 3, Table 2): white solid, 99% yield, 87% ee [Daicel Chiralcel OD-H, hexanes/2-propanol = 90/10, v = 0.5 mL · min^{-1}, λ = 230 nm, t (major) = 25.88 min, t (minor) = 28.79 min]; $[\alpha]_D^{20}$ = -7.0° (c = 1.35, $CHCl_3$). **^{1}H NMR** (300 MHz, $CDCl_3$) δ 3.82 (s, 3 H), 4.26 (s, 1 H), 4.46 (d, *J* = 11.4 Hz, 1 H), 4.81 (d, *J* = 11.7 Hz, 1 H), 6.39 (d, *J* = 2.1 Hz, 1 H), 6.62 (dd, *J* = 2.1, 8.7 Hz, 1 H), 7.30-7.35 (m, 3 H), 7.45-7.48 (m, 2 H), 7.86 (d, *J* = 8.7 Hz, 1 H); **^{13}C NMR** (75 MHz, $CDCl_3$) δ 55.7, 72.9, 74.2, 100.8, 110.9, 112.8, 125.9, 128.6, 129.3, 139.0, 163.7, 166.8, 192.9.



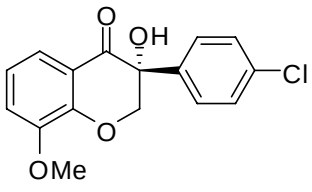
6d (entry 4, Table 2): white solid, 92% yield, 78% ee [Daicel Chiralcel OD-H, hexanes/2-propanol = 98/2, v = 0.8 mL · min^{-1}, λ = 230 nm, t (major) = 21.15 min, t (minor) = 24.13 min]; $[\alpha]_D^{20}$ =+28.5° (c = 1.20, $CHCl_3$). **^{1}H NMR** (300 MHz, $CDCl_3$) δ 2.35 (s, 3 H), 4.26 (s, 1 H), 4.45 (d, *J* = 11.4 Hz, 1 H), 4.82 (d, *J* = 11.4 Hz, 1 H), 6.77 (s, 1 H), 6.88 (d, *J* = 7.8 Hz, 1 H), 7.29-7.33 (m, 3 H), 7.45-7.48 (m, 2 H), 7.82 (d, *J* = 8.4 Hz, 1 H); **^{13}C NMR** (75 MHz, $CDCl_3$) δ 22.0, 73.2, 73.8, 116.8, 118.0, 123.4, 126.0, 127.4, 128.6, 128.7, 138.7, 148.6, 161.6, 194.1; **IR** (KBr): ν_{max} (cm^{-1}) = 3396, 3057, 2879, 1678, 1619, 1450, 1349, 1261, 1263, 1100, 1041, 950, 757, 699, 643, 551, 495; **MS** (EI, *m/*z, rel. intensity) 254 (M^+, 2), 135 (100); **Anal**. calcd for $C_{16}H_{14}O_3$: C, 75.57; H, 5.55; Found: C, 75.59; H, 5.71.



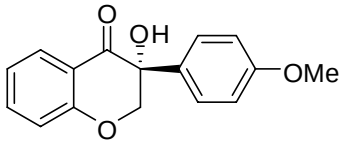
6e (entry 5, Table 2): white solid, 95% yield, 93% ee [Daicel Chiralpak AS-H, hexanes/2-propanol = 95/5, v = 1.0 mL · min^{-1}, λ = 230 nm, t (major) = 70.75 min, t (minor) = 76.28 min]; $[\alpha]_D^{20}$ =+288.4^o (c = 1.25, $CHCl_3$). **^{1}H NMR** (300 MHz, $CDCl_3$) δ 4.21 (s, 1 H), 4.59 (d, *J* = 12.0 Hz, 1 H), 5.04 (d, *J* = 12.0 Hz, 1 H), 7.11 (d, *J* = 9.1 Hz, 1H), 7.35-7.37 (m, 3 H), 7.44-7.47 (m, 2 H), 8.35 (dd, *J* = 3.3, 9.6 Hz, 1 H), 8.82 (d, *J* = 3.0 Hz, 1 H); **^{13}C NMR** (75 MHz, $CDCl_3$) δ 73.5, 73.6, 118.8, 119.3, 124.1, 125.9, 129.0, 129.4, 131.0, 136.9, 142.5, 165.0, 192.8; **IR** (KBr): ν_{max} (cm^{-1}) = 3422, 1698, 1619, 1527, 1482, 1338, 1076, 1014, 846, 752, 700, 615, 551, 499; **MS** (EI, *m/*z, rel. intensity) 285 (M^+, 3), 166 (100); **Anal**. calcd for $C_{15}H_{11}NO_5$: C, 63.16; H, 3.89, N, 4.91; Found: C, 63.27; H, 4.13, N, 4.91.



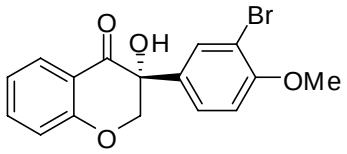
6f (entry 6, Table 2): yellow solid, 94% yield, 90% ee [Daicel Chiralcel OD-H, hexanes/2-propanol = 90/10, v = 1.0 mL · min^{-1}, λ = 230 nm, t (major) = 9.23 min, t (minor) = 10.33 min]; $[\alpha]_D^{20}$ =+96.2^o (c = 2.23, $CHCl_3$). **^{1}H NMR** (300 MHz, $CDCl_3$) δ 4.19 (s, 1 H), 4.45 (d, *J* = 12.0 Hz, 1 H), 4.86 (d, *J* = 11.7 Hz, 1 H), 6.91 (d, *J* = 9.0 Hz, 1 H), 7.31-7.33 (m, 3 H), 7.41-7.45 (m, 3 H), 7.88 (d, *J* = 2.7 Hz, 1 H); **^{13}C NMR** (75 MHz, $CDCl_3$) δ 73.4, 73.7, 119.7, 119.9, 125.9, 126.8, 127.5, 128.8, 129.0, 136.6, 137.9, 159.9, 193.6; **IR** (KBr): ν_{max} (cm^{-1}) = 3418, 1684, 1605, 1479, 1423, 1279, 1106, 1031, 974, 827, 754, 698, 618, 497; **MS** (EI, *m/*z, rel. intensity) 274 (M^+, 10), 155 (100); **Anal**. calcd for $C_{15}H_{11}ClO_3$: C, 65.58; H, 4.04; Found: C, 65.76; H, 4.22.



6g (entry 7, Table 2): white solid, 96% yield, 74% ee [Daicel Chiralpak AD-H, hexanes/2-propanol = 80/20, v = 1.0 mL · min^{-1}, λ = 230 nm, t (major) = 36.12 min, t (minor) = 38.28 min]; $[\alpha]_D^{20}$ =+14.2° (c = 1.57, $CHCl_3$). **^{1}H NMR** (300 MHz, $CDCl_3$) δ 3.87, (s, 3 H), 4.29 (br, 1 H), 4.48 (d, *J* = 11.7 Hz, 1 H), 4.95 (d, *J* = 11.7 Hz, 1 H), 6.98-7.09 (m, 2 H), 7.26 (d, *J* = 7.2 Hz, 2 H), 7.40 (d, *J* = 8.4 Hz, 2 H), 7.49 (d, *J* = 8.1 Hz, 1 H); **^{13}C NMR** (75 MHz, $CDCl_3$) δ 56.1, 72.8, 73.9, 117.4, 118.5, 119.4, 121.8, 127.5, 128.9, 134.7, 136.6, 148.6, 151.2, 194.1; **IR** (KBr): ν_{max} (cm^{-1}) = 3449, 1685, 1607, 1491, 1299, 1257, 1042, 904, 839, 760, 728, 625, 527, 487, 404; **MS** (EI, *m/*z, rel. intensity) 304 (M^+, 14), 151 (100); **Anal**. calcd for $C_{16}H_{13}ClO_4$: C, 63.06; H, 4.30; Found: C, 63.11; H, 4.46.

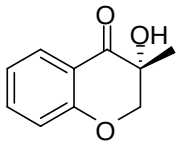


6h (entry 8, Table 2): white solid, 93% yield, 90% ee [Daicel Chiralpak AD-H, hexanes/2-propanol = 75/25, v = 0.5 mL · min^{-1}, λ = 230 nm, t (minor) = 25.54 min, t (major) = 31.13 min]; $[\alpha]_D^{20}$ =+74.3° (c = 1.00, $CHCl_3$). **^{1}H NMR** (300 MHz, $CDCl_3$) δ 3.73 (s, 3 H), 4.27 (s, 1 H), 4.43 (d, *J* = 11.4 Hz, 1 H), 4.83 (d, *J* = 12.0 Hz, 1 H), 6.82 (d, *J* = 7.2 Hz, 2 H), 6.94 (d, *J* = 8.4 Hz, 1 H), 7.03 (t, *J* = 7.2 Hz, 1 H), 7.39 (m, 2 H), 7.48 (m, 1 H), 7.91 (dd, *J* = 1.5, 7.8 Hz, 1 H); **^{13}C NMR** (75 MHz, $CDCl_3$) δ 55.1, 73.0, 73.5, 114.0, 117.9, 119.1, 121.8, 127.4, 127.5, 130.2, 136.6, 159.8, 161.3, 194.6; **IR** (KBr): ν_{max} (cm^{-1}) = 3429, 2968, 2839, 1687, 1608, 1516, 1479, 1261, 1017, 829, 758, 602, 553, 495, 410; **MS** (EI, *m/*z, rel. intensity) 270 (M^+, 2), 135 (100); **Anal**. calcd for $C_{16}H_{14}O_4$: C, 71.10; H, 5.22; Found: C, 70.75; H, 5.41.

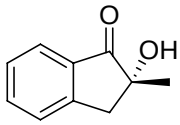


6i (entry 9, Table 2): white solid, 99% yield, 87% ee [Daicel Chiralpak AD-H, hexanes/2-propanol = 90/10, v = 1.0 mL · min^{-1}, λ = 230 nm, t (minor) = 30.81 min, t

(major) = 35.33 min]; $[\alpha]_D^{20}$ =+36.3° (c = 1.85, $CHCl_3$). **^{1}H NMR** (300 MHz, $CDCl_3$) δ 3.83 (s, 3 H), 4.27 (s, 1 H), 4.43 (d, *J* = 11.7 Hz, 1 H), 4.79 (d, *J* = 11.7 Hz, 1 H), 6.79 (d, *J* = 8.4 Hz, 1 H), 6.97 (d, *J* = 11.7 Hz, 1 H), 7.06 (t, *J* = 8.1 Hz, 1 H), 7.32 (dd, *J* = 2.4, 8.4 Hz, 1 H), 7.49-7.54 (m, 1 H), 7.70 (d, *J* = 2.4 Hz 1 H), 7.91 (dd, *J* = 1.8, 7.8 Hz, 1 H); **^{13}C NMR** (75 MHz, $CDCl_3$) δ 56.2, 72.6, 73.4, 111.6, 112.0, 118.0, 118.8, 122.1, 126.3, 127.7, 131.2, 131.8, 136.9, 156.1, 161.3, 194.0; **IR** (KBr): ν_{max} (cm^{-1}) = 3420, 3387, 1683, 1603, 1500, 1477, 1458, 1266, 1016, 948, 817, 754, 680, 625, 507; **MS** (EI, *m/z*, rel. intensity) 348 (M^+, 2), 121 (100); **Anal**. calcd for $C_{16}H_{13}BrO_4$: C, 55.04; H, 3.75; Found: C, 55.04; H, 4.03.



6j[7] (entry 10, Table 2): white solid, 94% yield, 2% ee [Daicel Chiralpak AD-H, hexanes/2-propanol = 98/2, v = 1.0 mL · min^{-1}, λ = 230 nm, t (major) = 22.57 min, t (minor) = 27.78 min]; $[\alpha]_D^{20}$ =+0.2° (c = 1.05, $CHCl_3$). **^{1}H NMR** (300 MHz, $CDCl_3$) δ 1.44 (s, 3 H), 3.89 (s, 1 H), 4.19 (d, *J* = 11.1 Hz, 1 H), 4.28 (d, *J* = 11.4 Hz, 1 H), 6.96 (d, *J* = 8.1 Hz, 1 H), 7.03 (t, *J* = 7.5 Hz, 1 H), 7.49 (t, *J* = 7.8 Hz, 1 H), 7.86 (d, *J* = 7.8 Hz, 1 H); **^{13}C NMR** (75 MHz, $CDCl_3$) δ 22.3, 70.6, 74.5, 117.8, 118.1, 121.8, 127.6, 136.5, 161.2, 196.5.



6l[10]: colorless oil, 87% yield, 48% ee [Daicel Chiralpak AS-H, hexanes/2-propanol = 90/10, v = 0.7 mL · min^{-1}, λ = 230 nm, t (major) = 13.38 min, t (minor) = 25.63 min]; $[\alpha]_D^{20}$ =+26.4° (c = 0.60, $CHCl_3$). **^{1}H NMR** (300 MHz, $CDCl_3$) δ 1.45 (s, 3 H), 3.22 (s, 1 H), 3.23 (d, *J* = 16.8 Hz, 1 H), 3.29 (d, *J* = 16.8 Hz, 1 H), 7.38 (d, *J* = 7.5 Hz, 1 H), 7.43 (d, *J* = 8.1 Hz, 1 H), 7.64 (dt, *J* = 1.2, 7.5 Hz, 1 H), 7.77 (d, *J* = 8.1 Hz, 1 H), .

Referance

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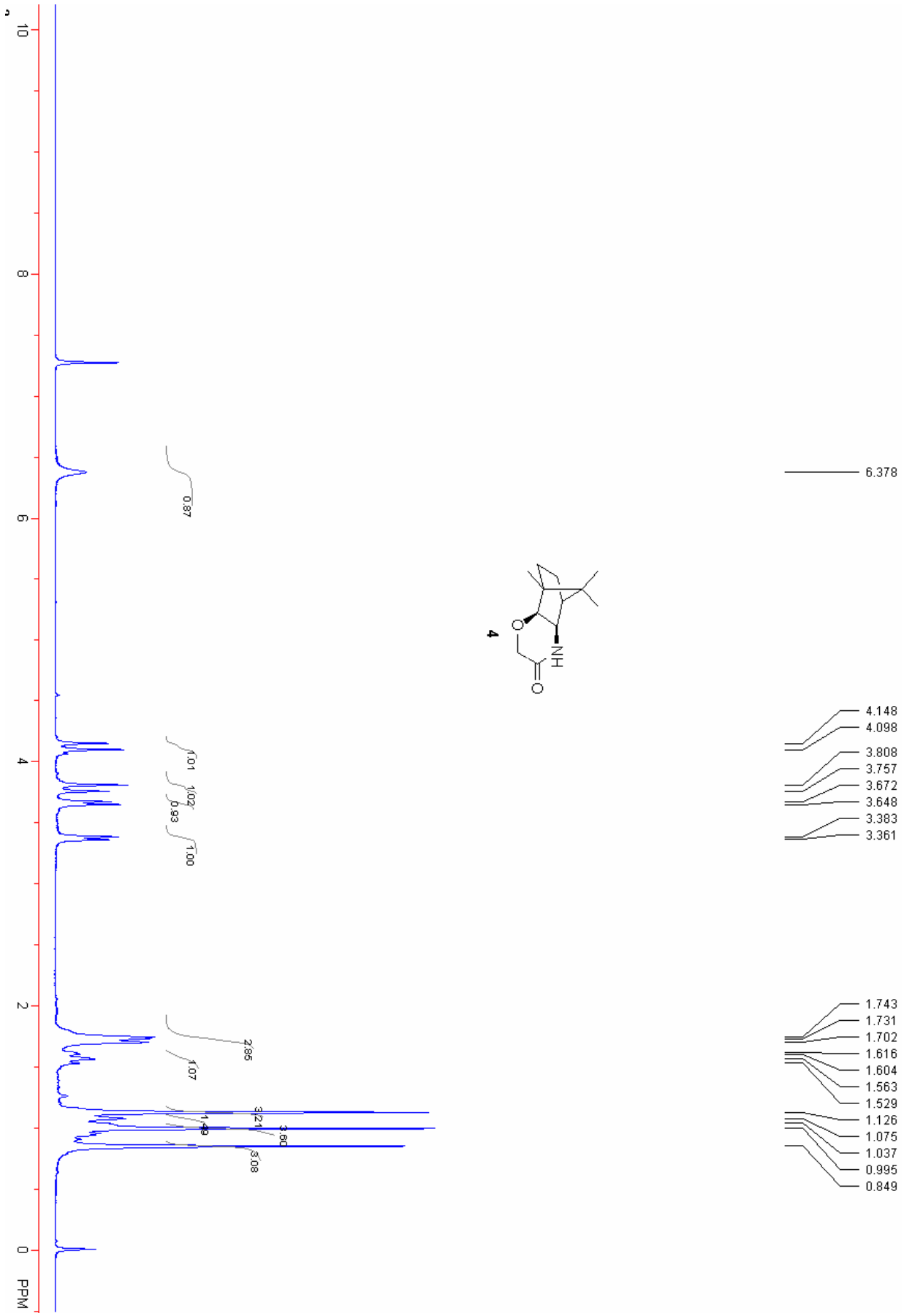
[11] The compound **5i** has poor solubility in various solvents such as THF, acetone, DMSO. It deposited easily during the hydrolysis of the corresponding acetal, and simply filtration of the reaction mixture afforded the compound which was pure enough for the next reaction.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4
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1.02
0.93
1.00
2.85
1.07
3.21
1.49
3.60
3.08
4
O
NH
O
6.378
4.148
4.098
3.808
3.757
3.672
3.648
3.383
3.361
1.743
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1.616
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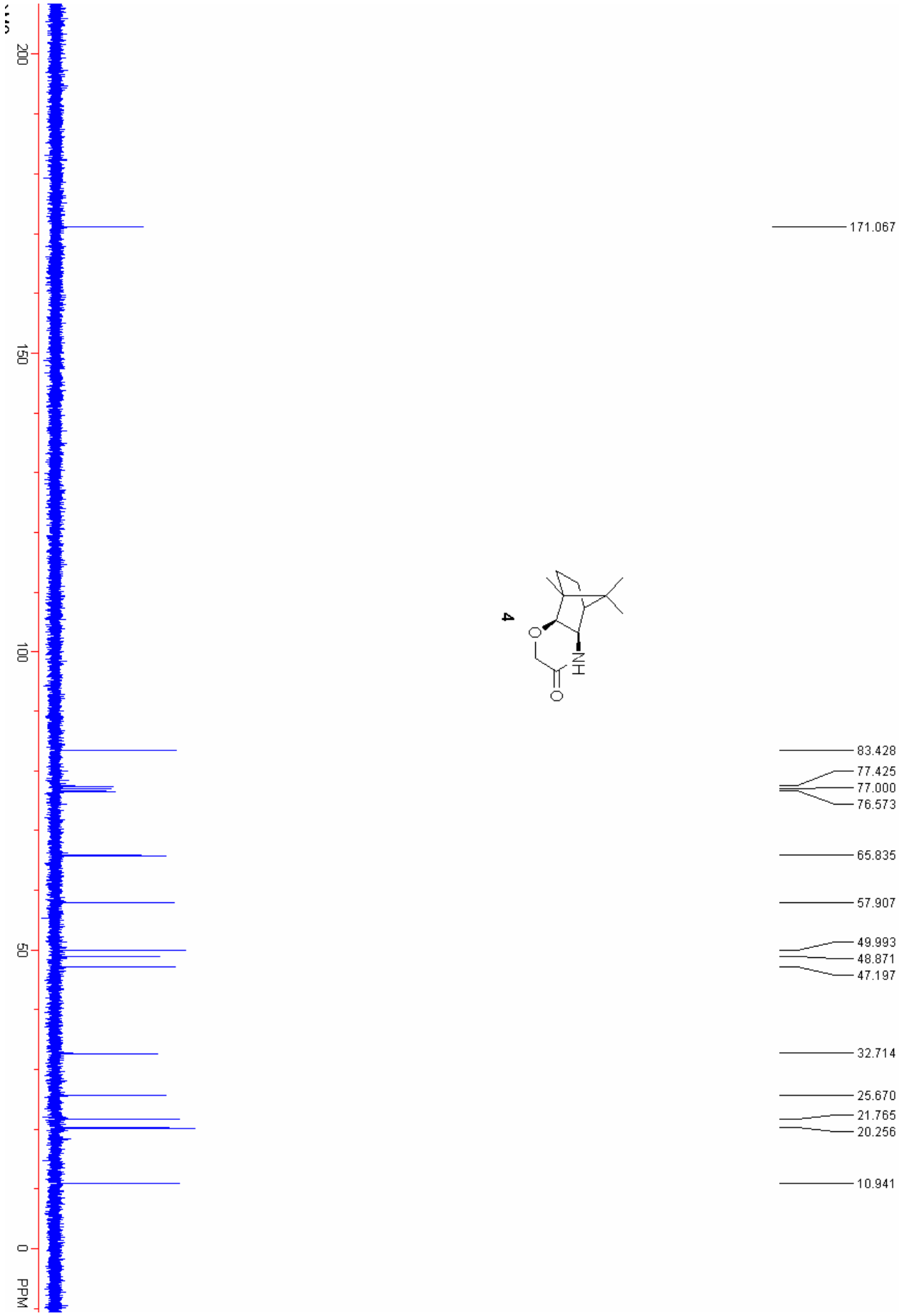
1.563
1.529
1.126
1.075
1.037
0.995
0.849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NH
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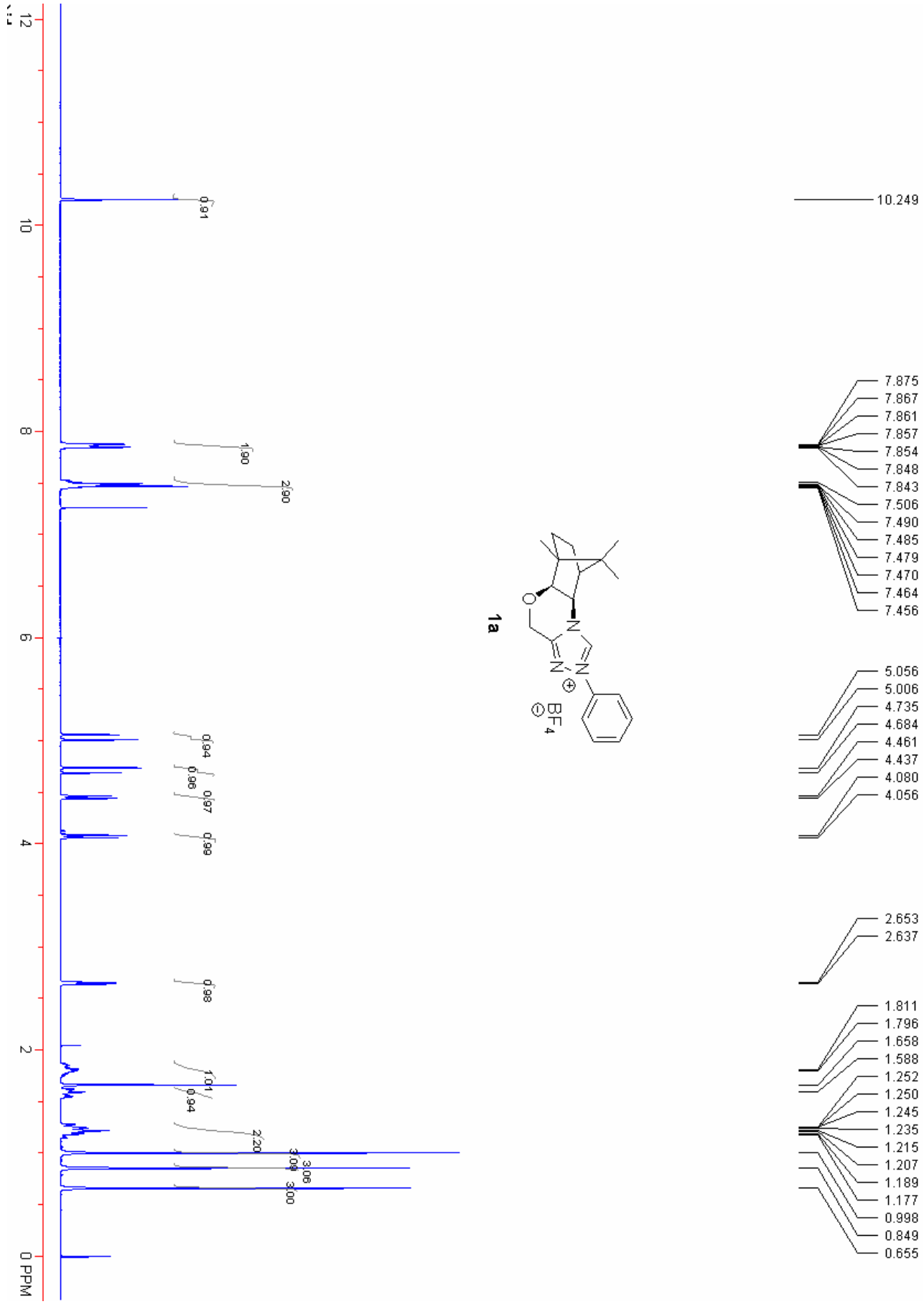
21.765
20.256
10.941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8
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4
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2.90
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0.96
0.97
0.99
0.98
1.01
0.94
2.20
3.09
3.06
3.00
1a
BF4
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7.875
7.867
7.861
7.857
7.854
7.848
7.843
7.506
7.490
7.485
7.479
7.470
7.464
7.456
5.056
5.006
4.735
4.684
4.461
4.437
4.080
4.056
2.653
2.637
1.811
1.796
1.658
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1.245
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1.215
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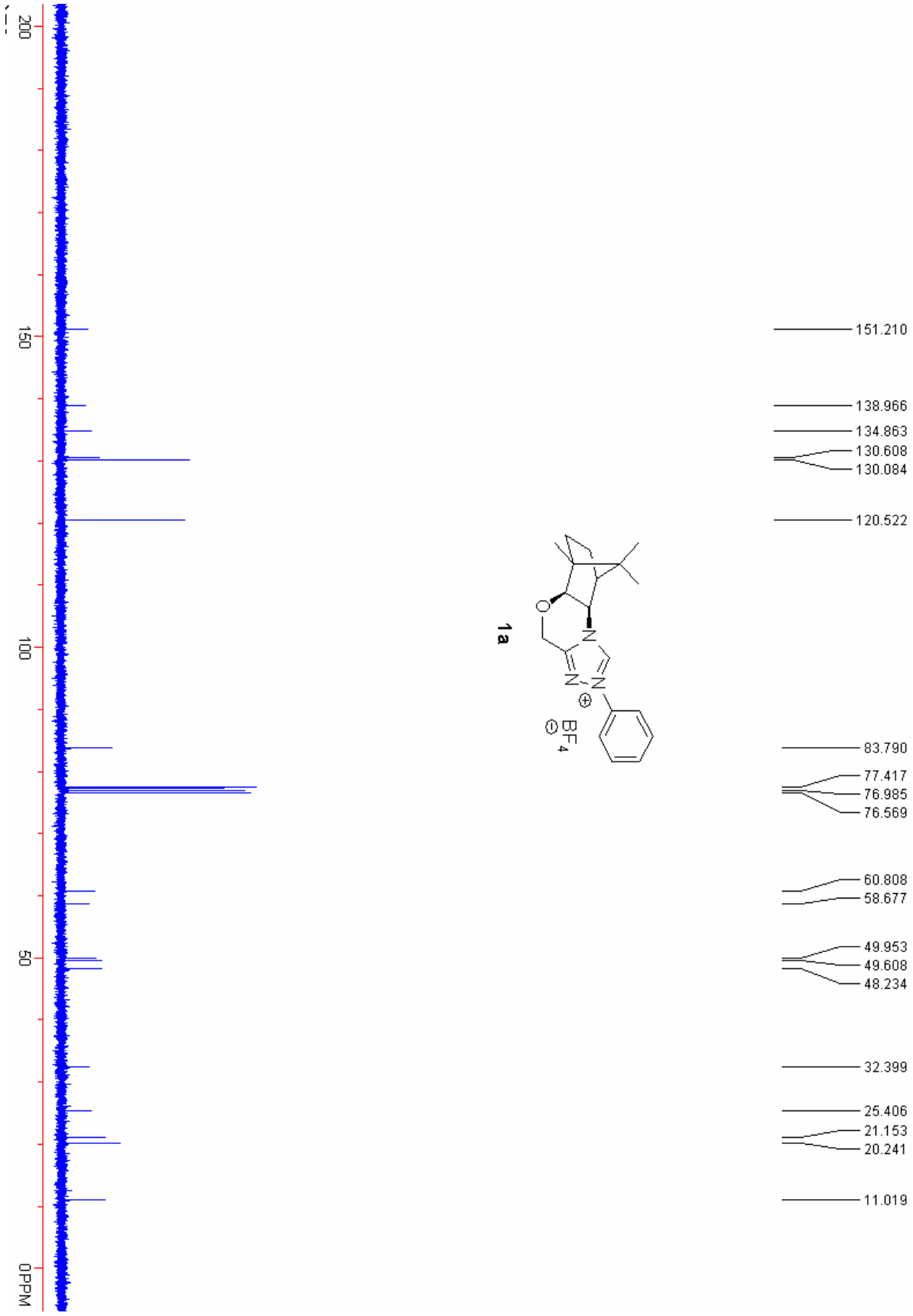
0.849
0.655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120.522
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77.417
76.985
76.569
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49.608
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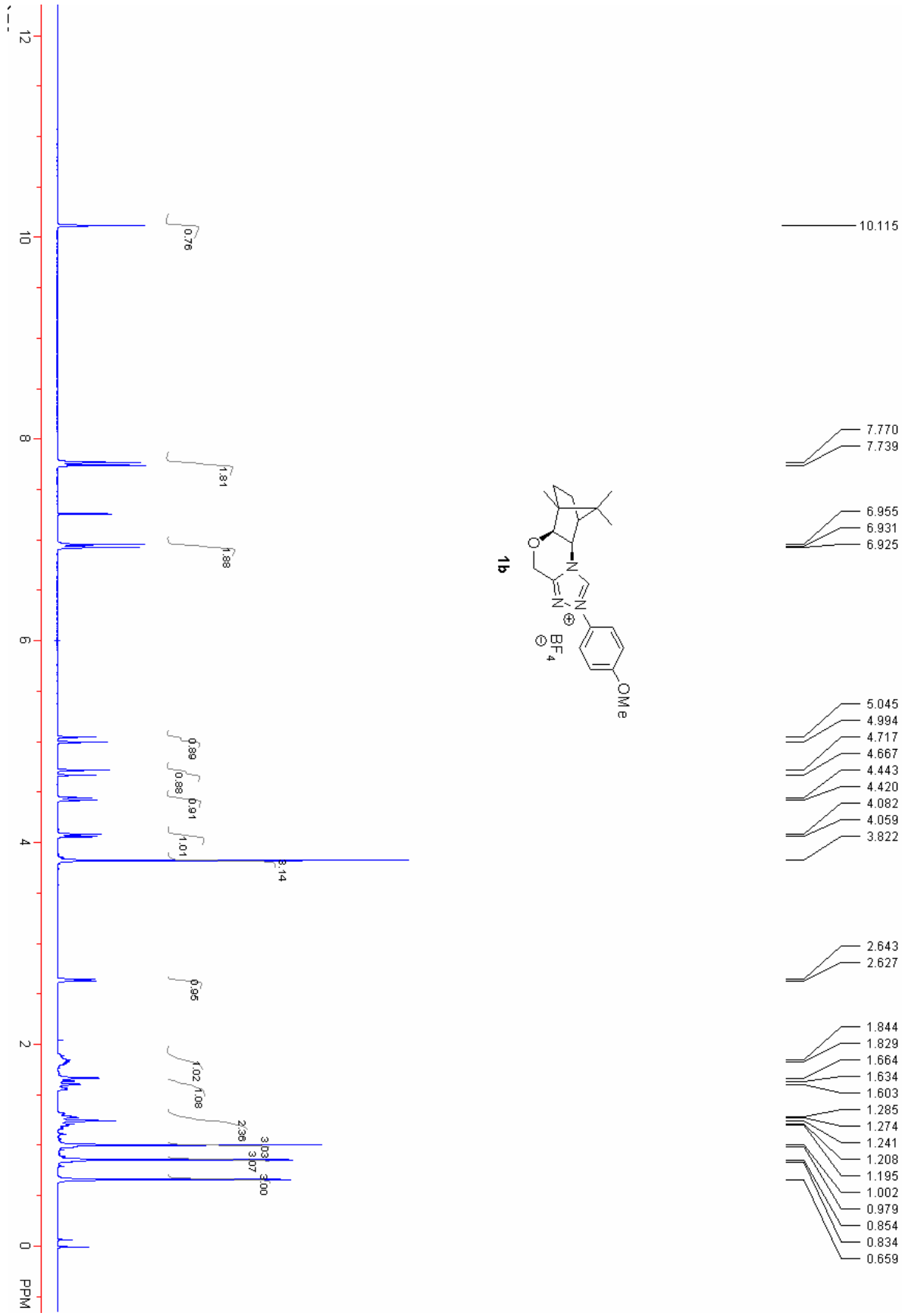
BF4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0.88
0.91
1.01
8.14
0.95
1.02
1.08
2.36
3.03
3.07
3.00
1b
BF4
OMe
10.115
7.770
7.739
6.955
6.931
6.925
5.045
4.994
4.717
4.667
4.443
4.420
4.082
4.059
3.822
2.643
2.627
1.844
1.829
1.664
1.634
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1.208
1.195
1.002
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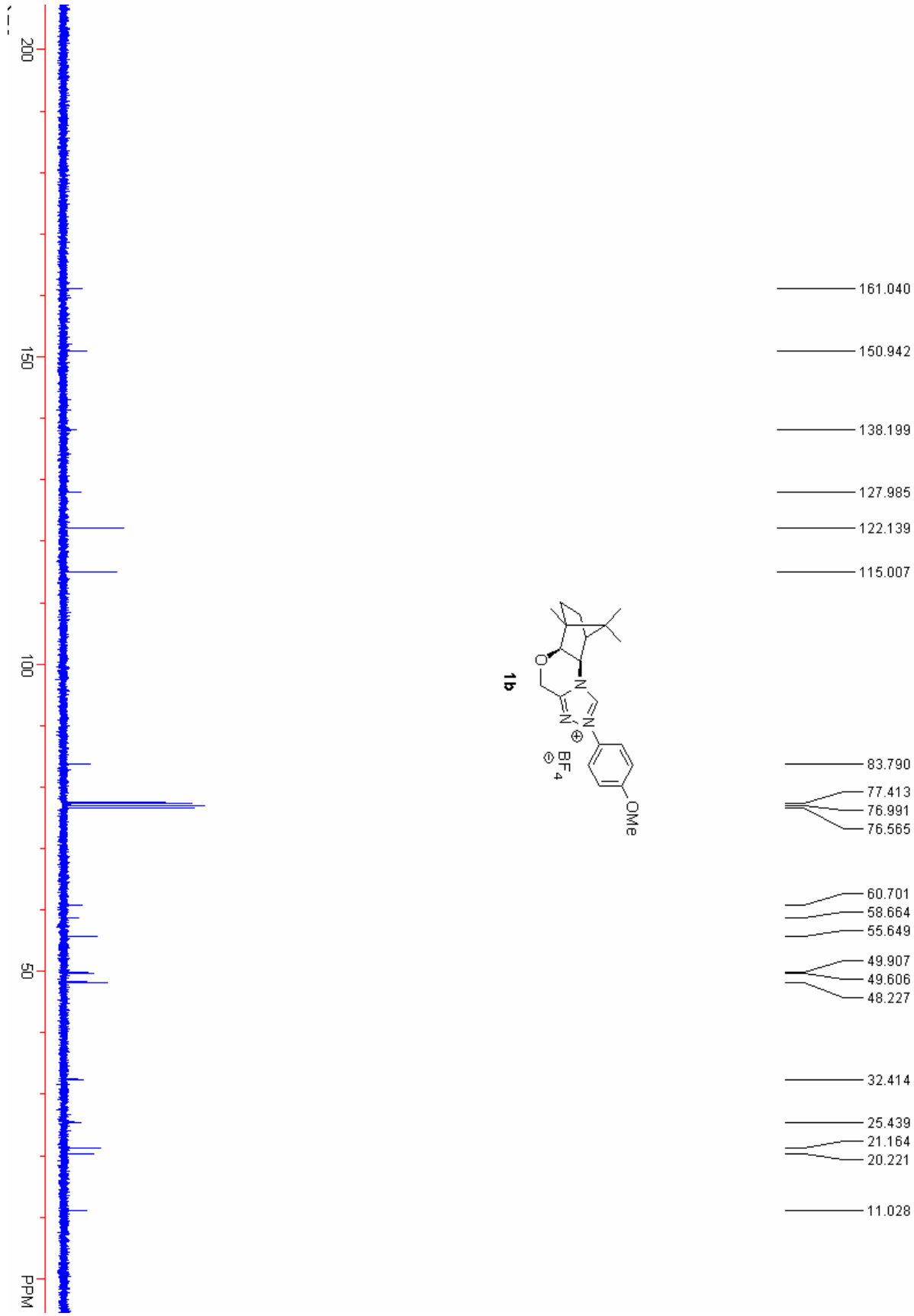
0.834
0.659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76.991
76.565
60.701
58.664
55.649
49.907
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25.439
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1b
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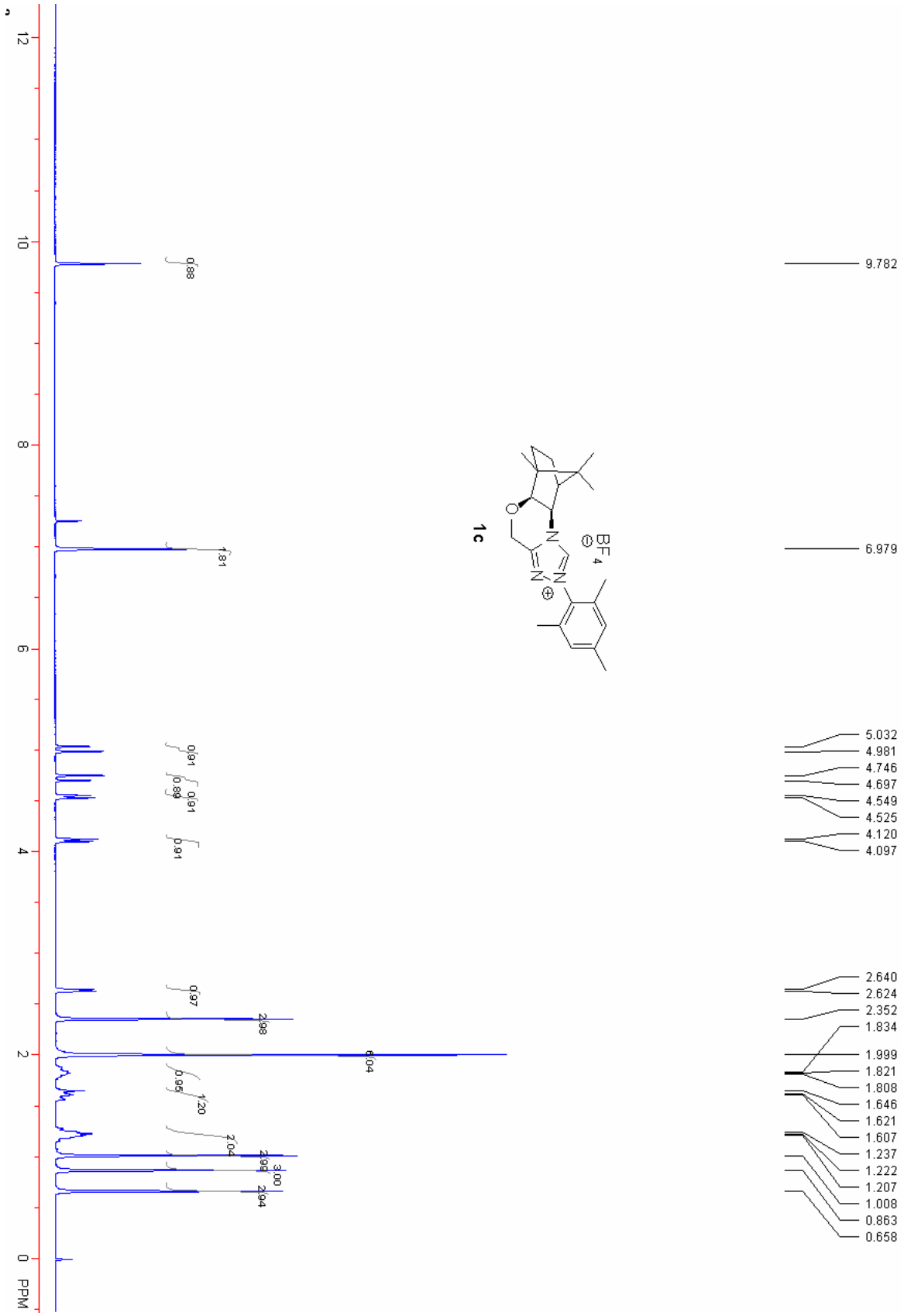
N
N
N
BF4
OMe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0.95
1.20
2.04
2.99
3.00
2.94
PPM
9.782
6.979
5.032
4.981
4.746
4.697
4.549
4.525
4.120
4.097
2.640
2.624
2.352
1.834
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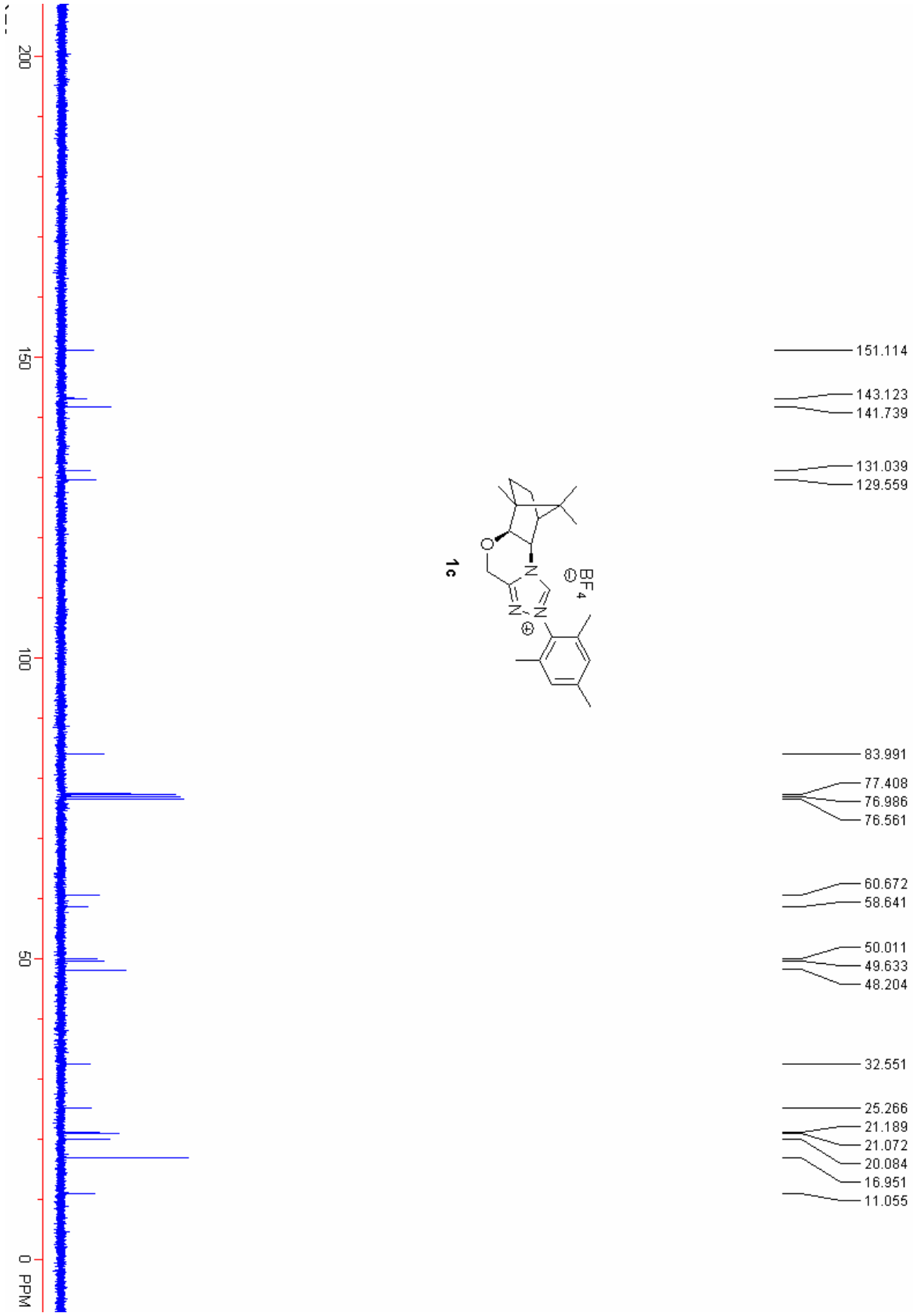
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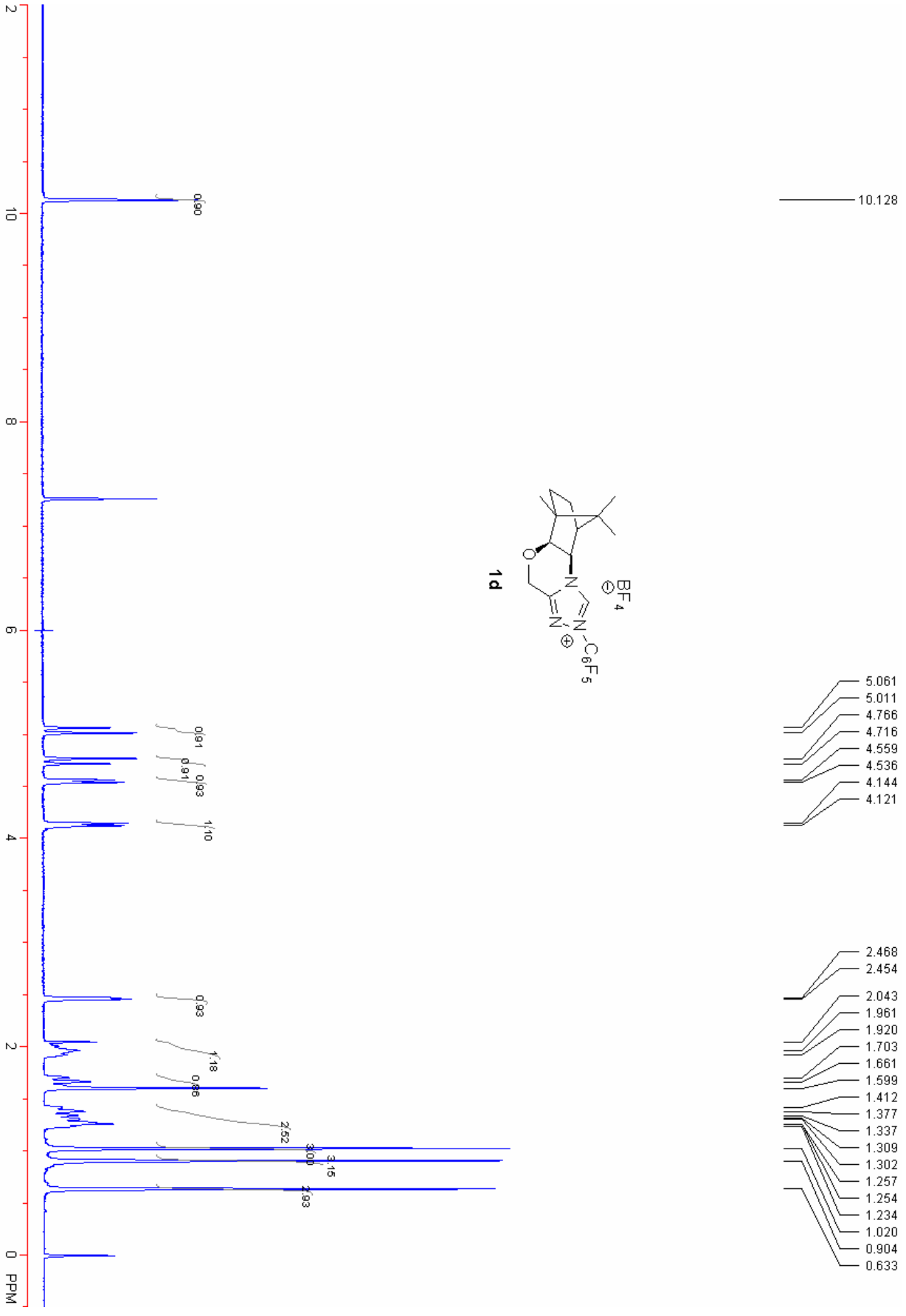
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4.716
4.559
4.536
4.144
4.121
2.468
2.454
2.043
1.961
1.920
1.703
1.661
1.599
1.412
1.377
1.337
1.309
1.302
1.257
1.254
1.234
1.020
0.904
0.633
0.90
0.91
0.91
0.93
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0.93
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3.15
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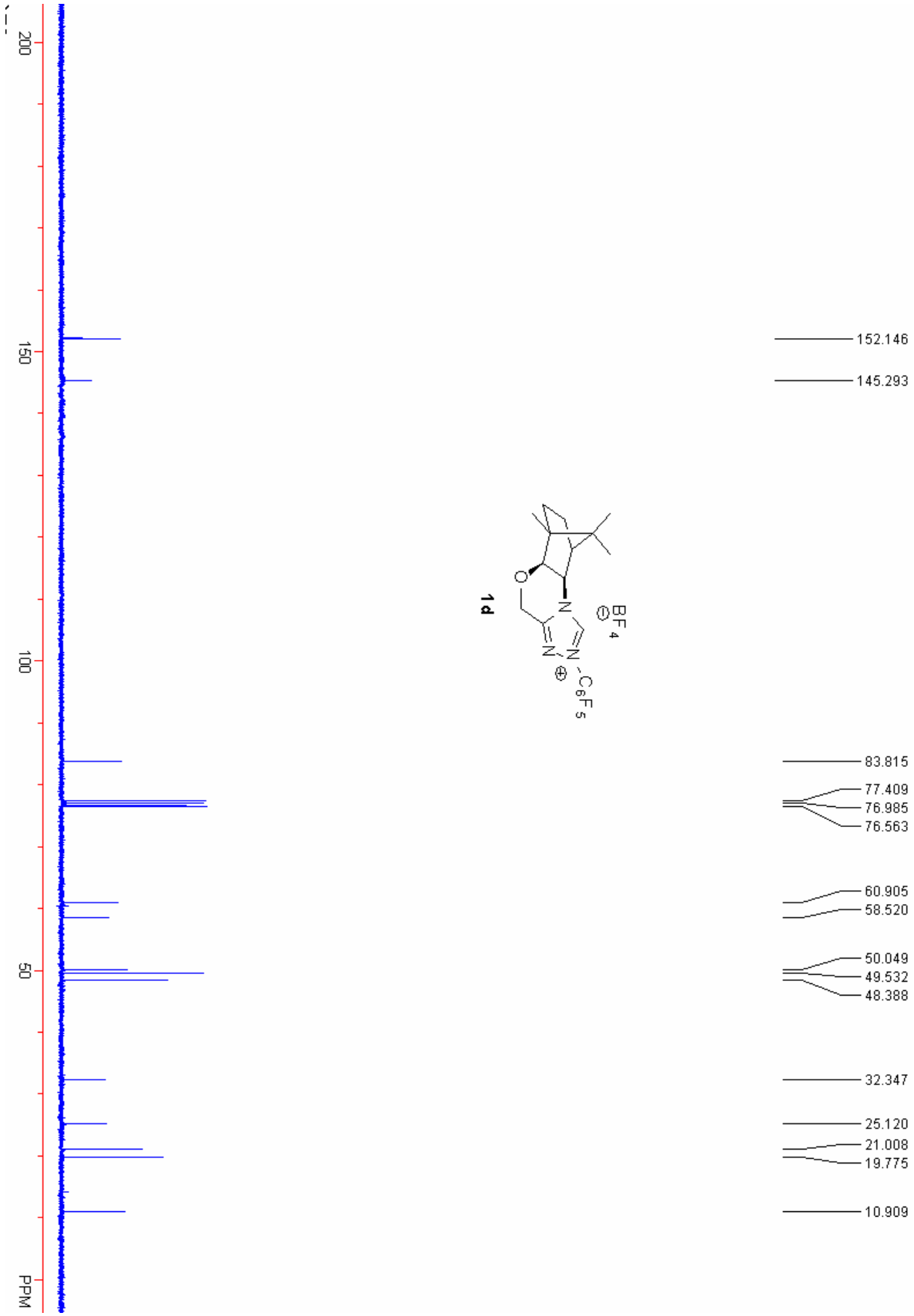
1d
BF4
PPM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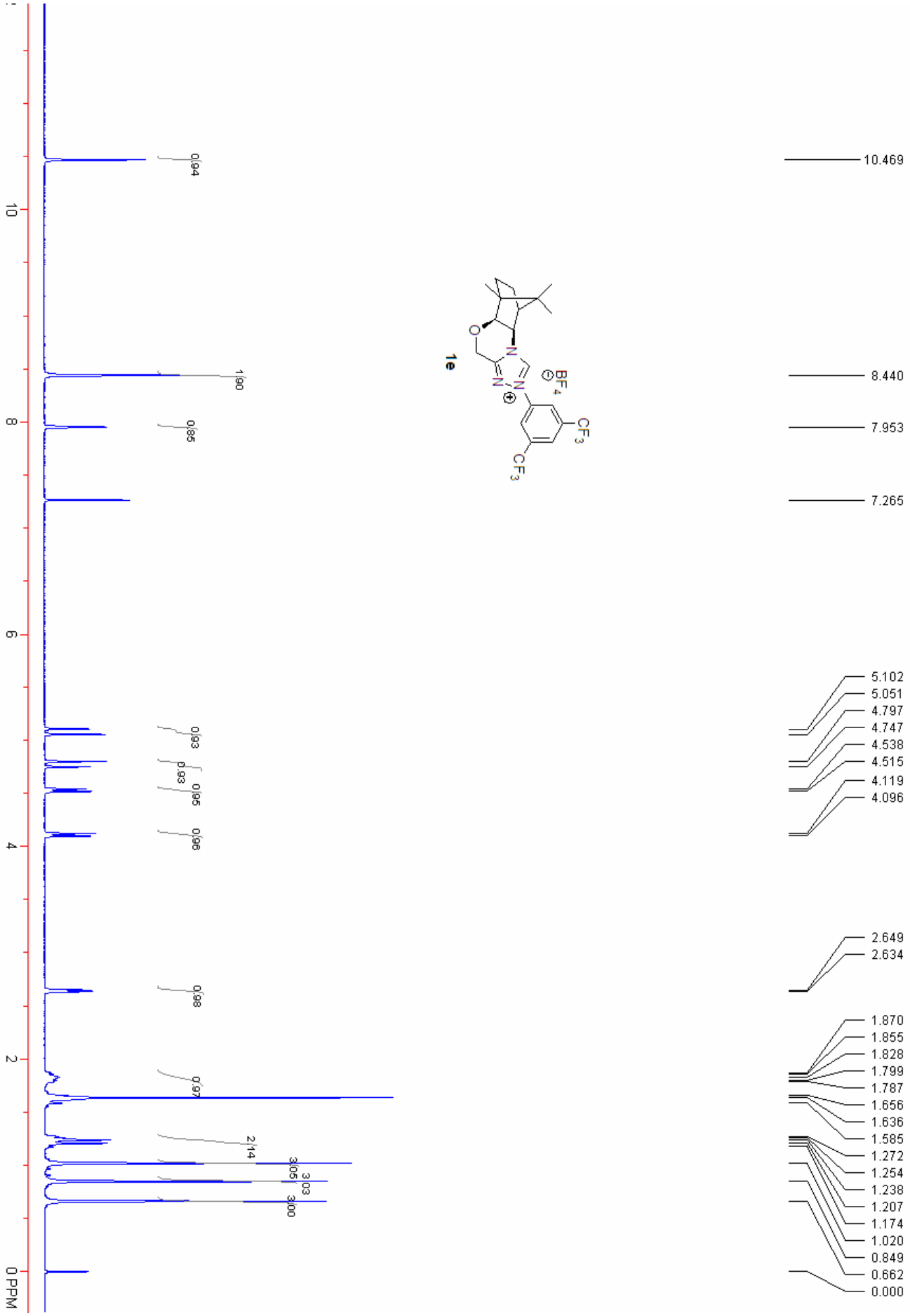
19.775
10.909
1d
BF4
C6F5


10
8
6
4
2
0 PPM
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1.90
0.85
0.93
0.93
0.95
0.96
0.98
0.97
2.14
3.05
3.03
3.00
1e
BF4
CF3
CF3
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7.265
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4.747
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4.515
4.119
4.096
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2.634
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1.799
1.787
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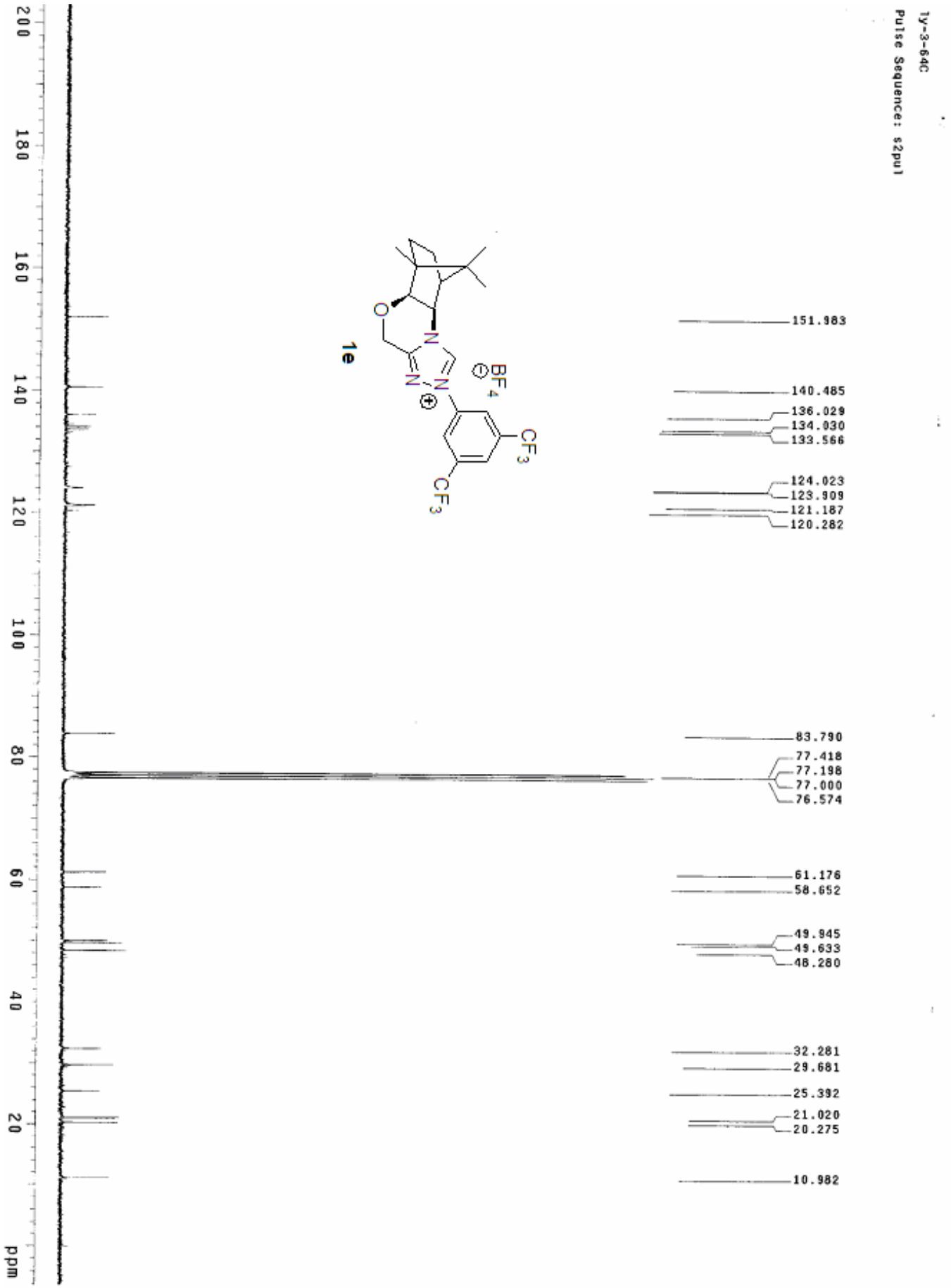
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123.909
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77.198
77.000
76.574
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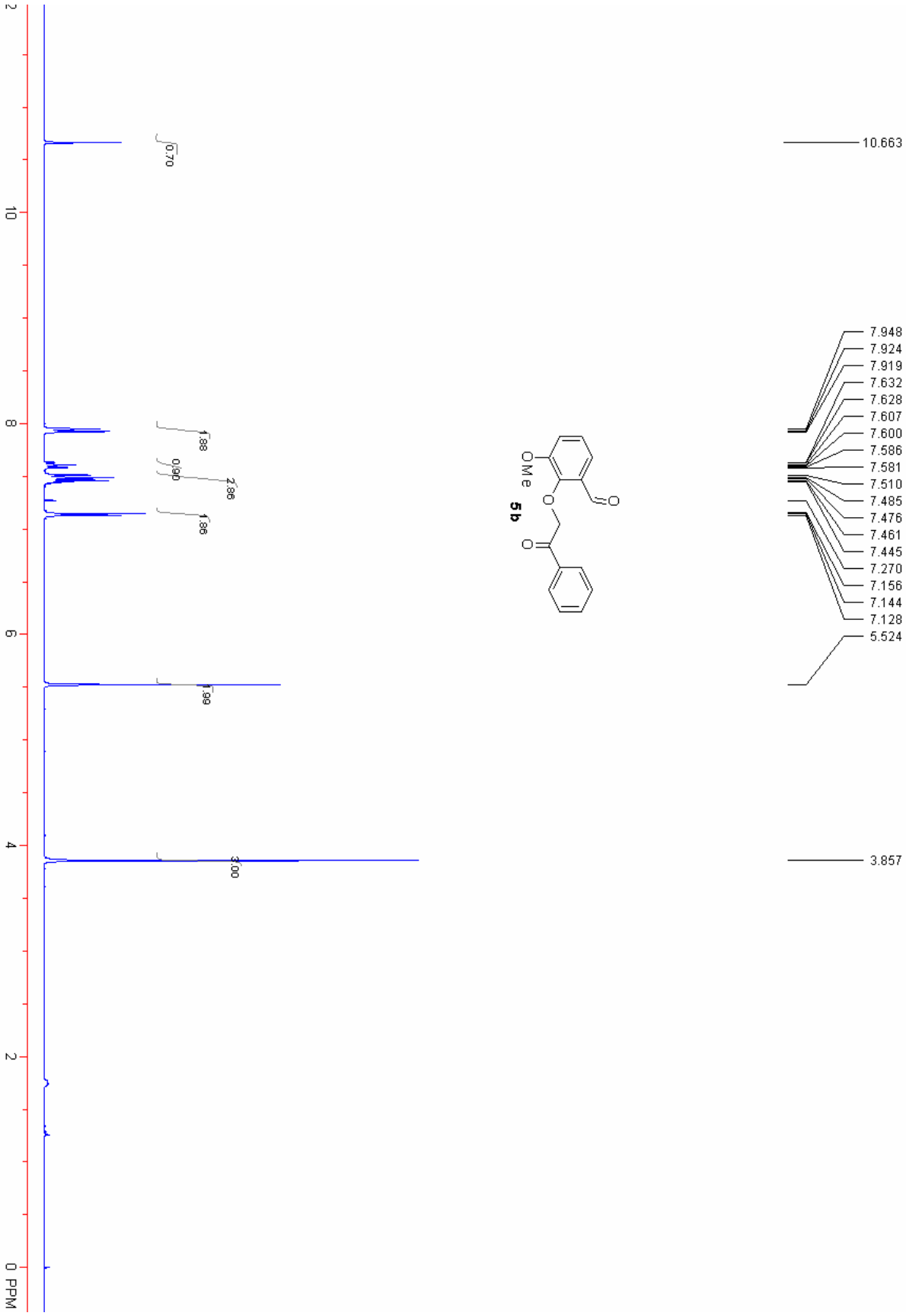
ppm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7.485
7.476
7.461
7.445
7.270
7.156
7.144
7.128
5.524
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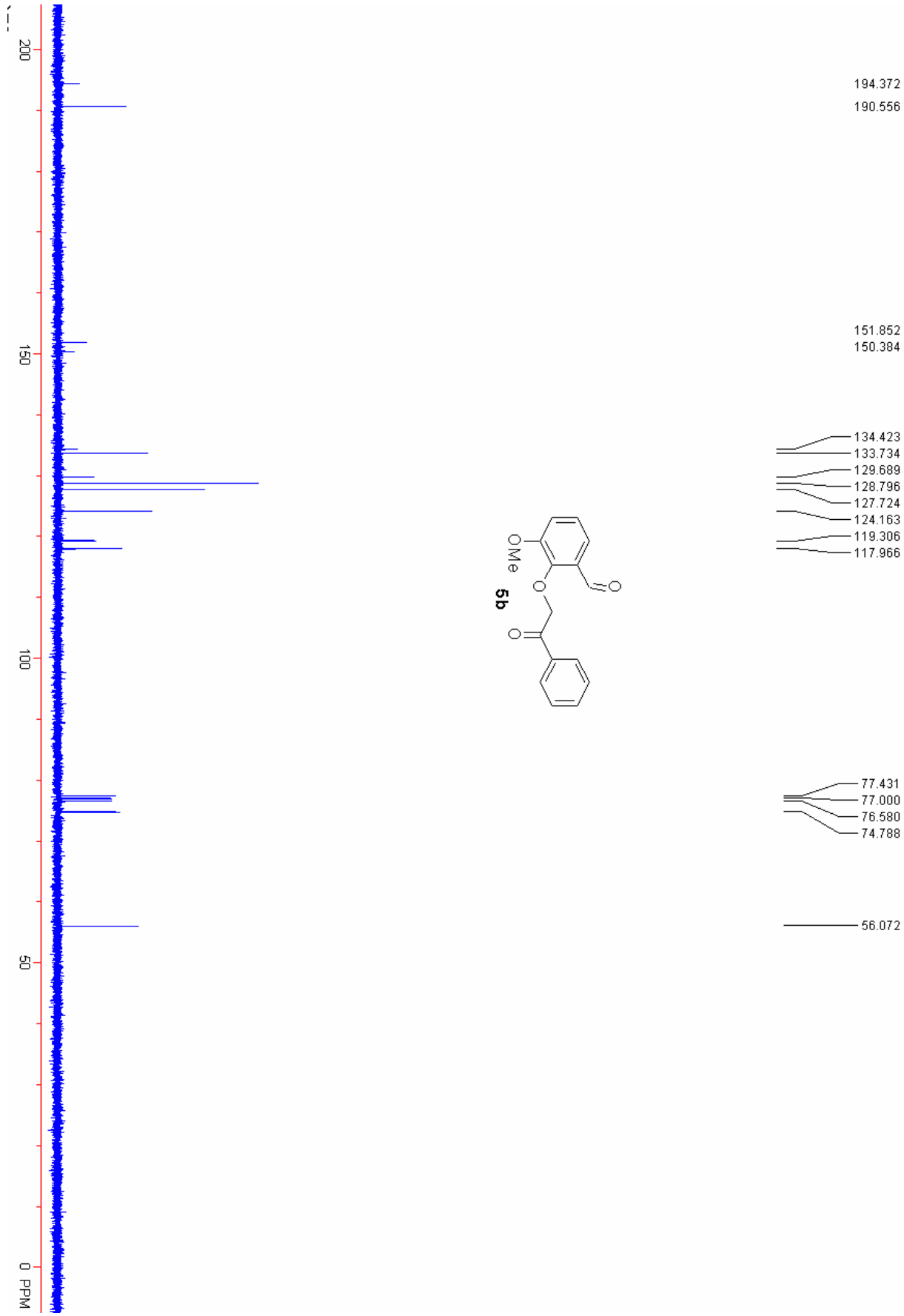
1.86
1.99
3.00
OMe
O
O
O
5g
PPM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129.689
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127.724
124.163
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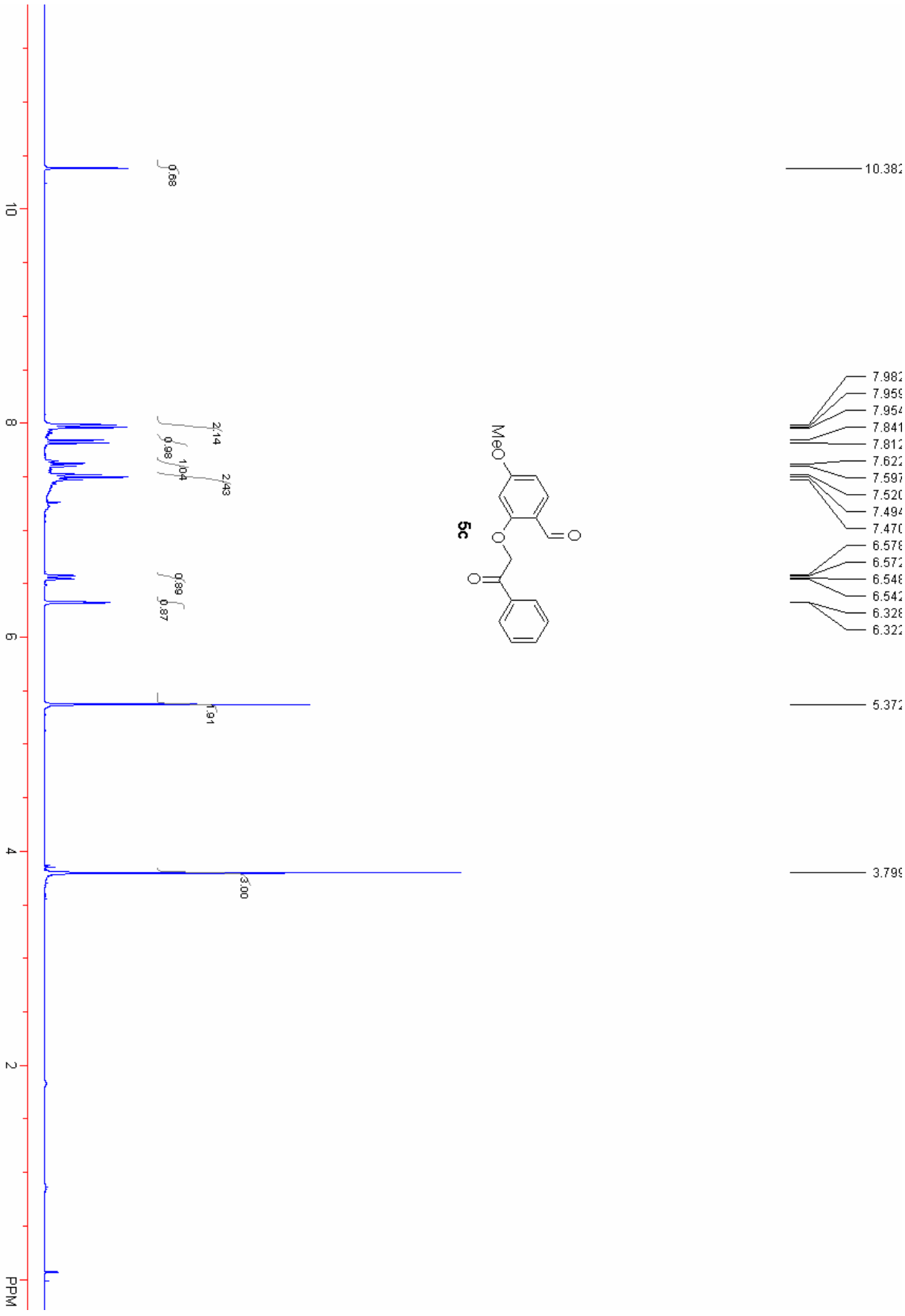
74.788
56.072
OMe
5b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7.597
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7.494
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6.572
6.548
6.542
6.328
6.322
5.372
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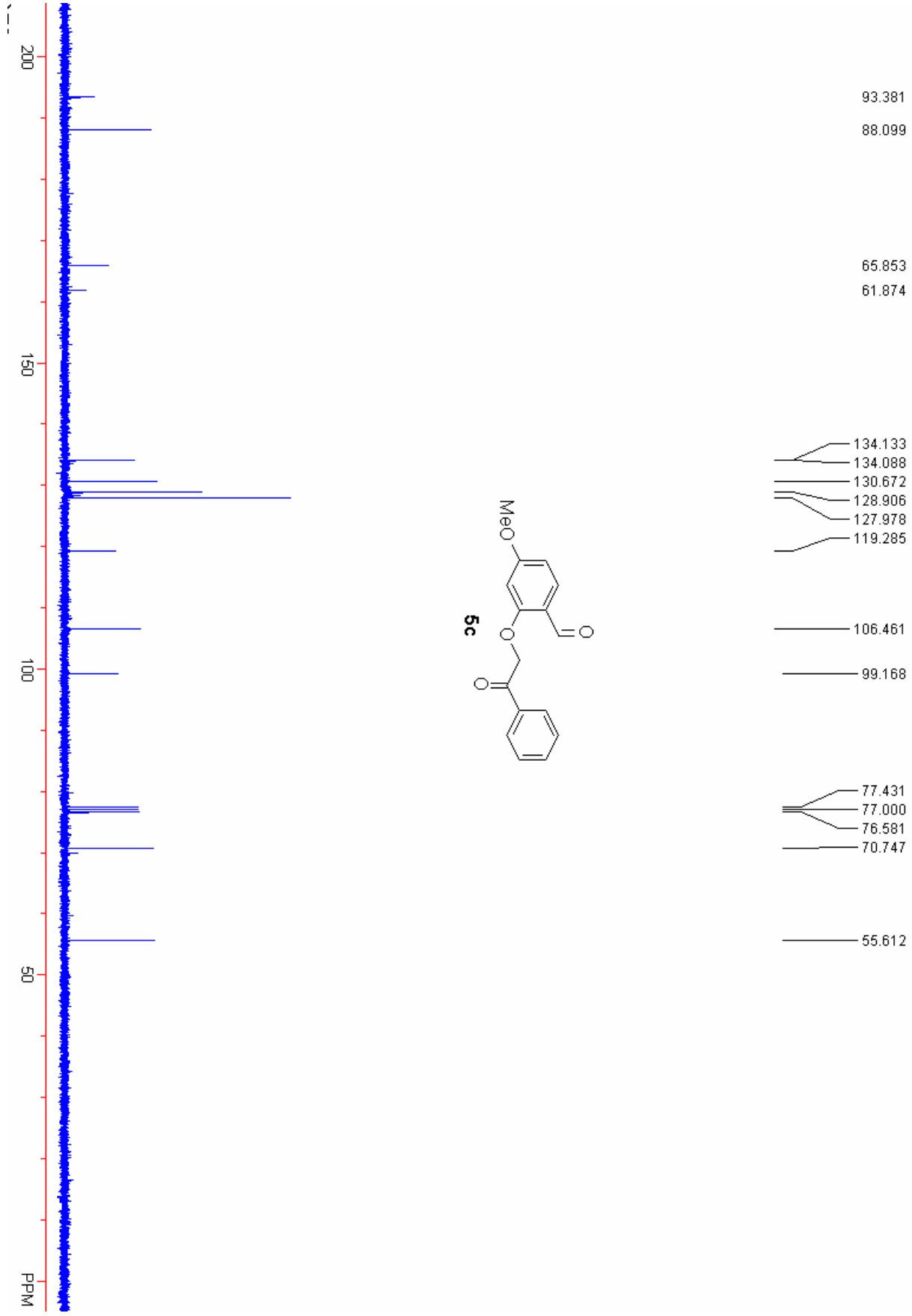
MeO
5c
PPM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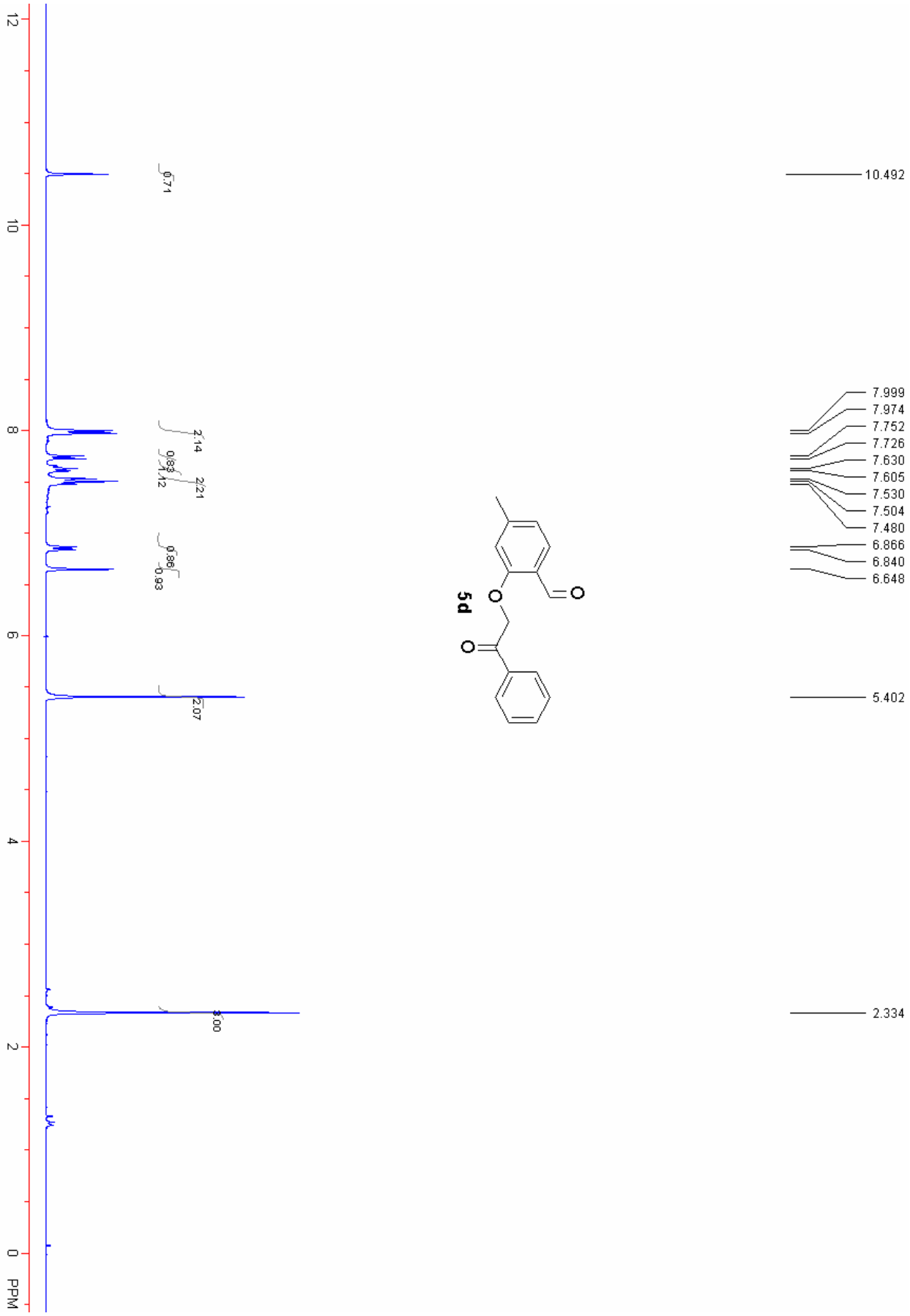
MeO
O
O
O
5c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0.93
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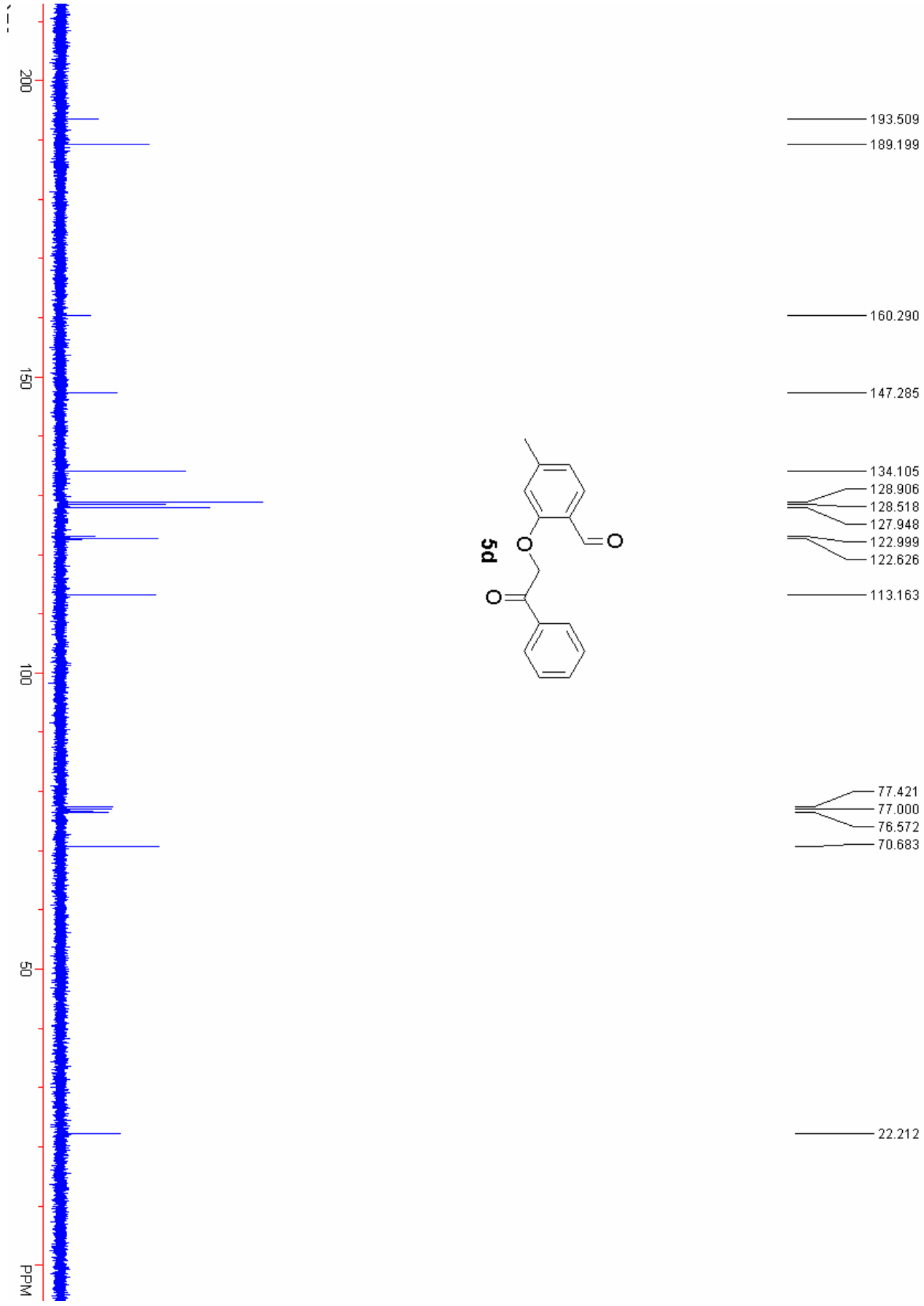
5d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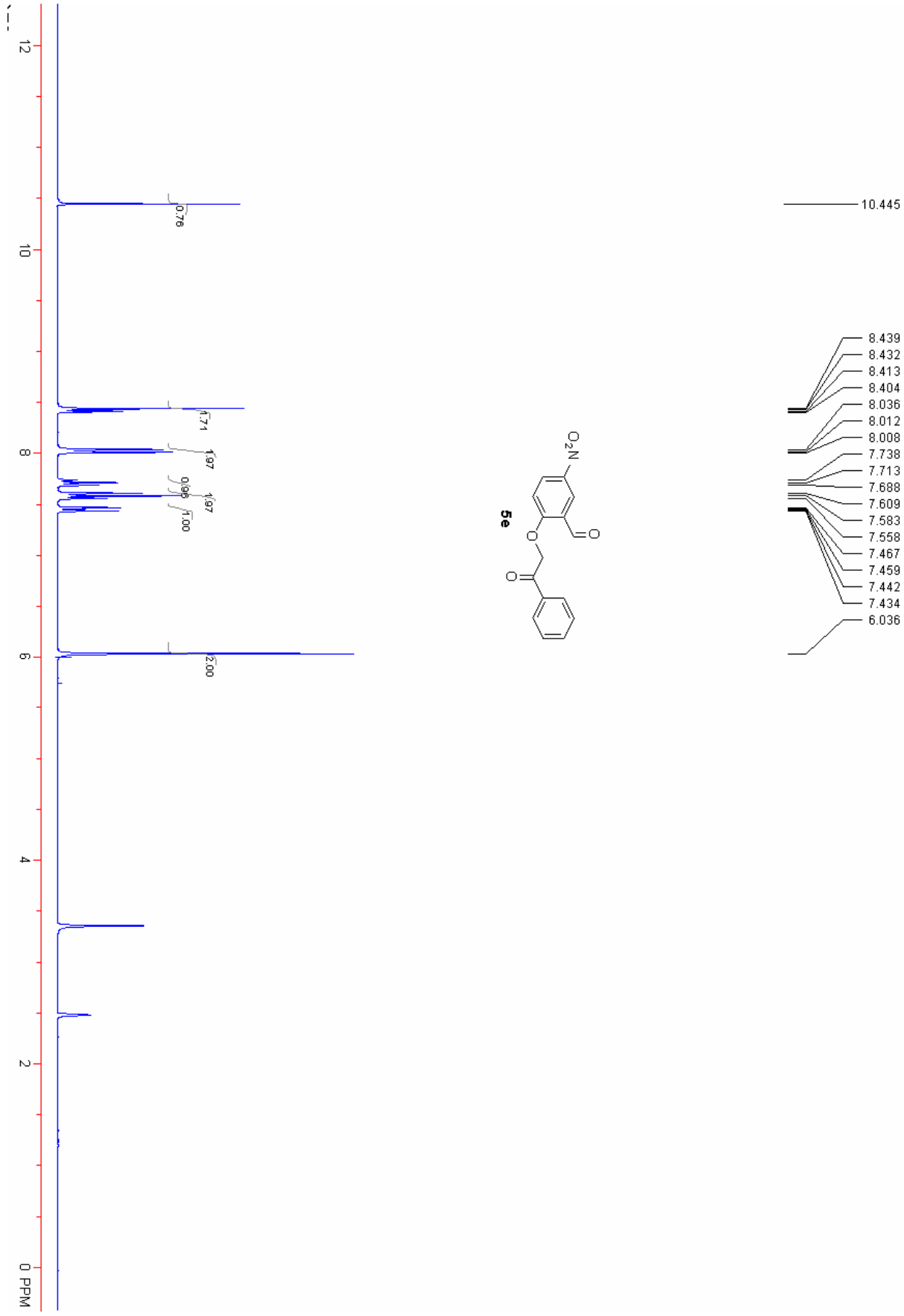
5d
O
O
O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O
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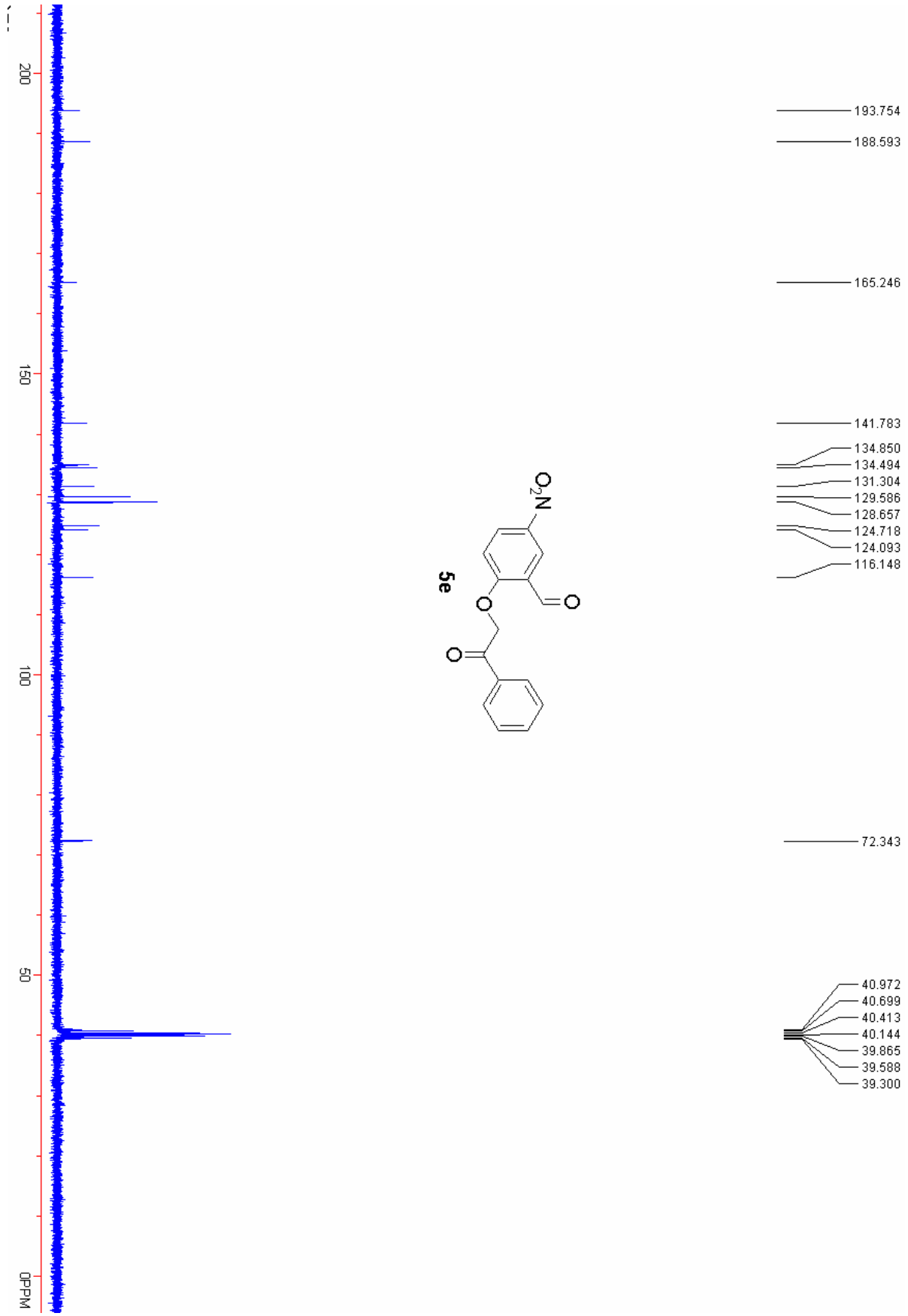
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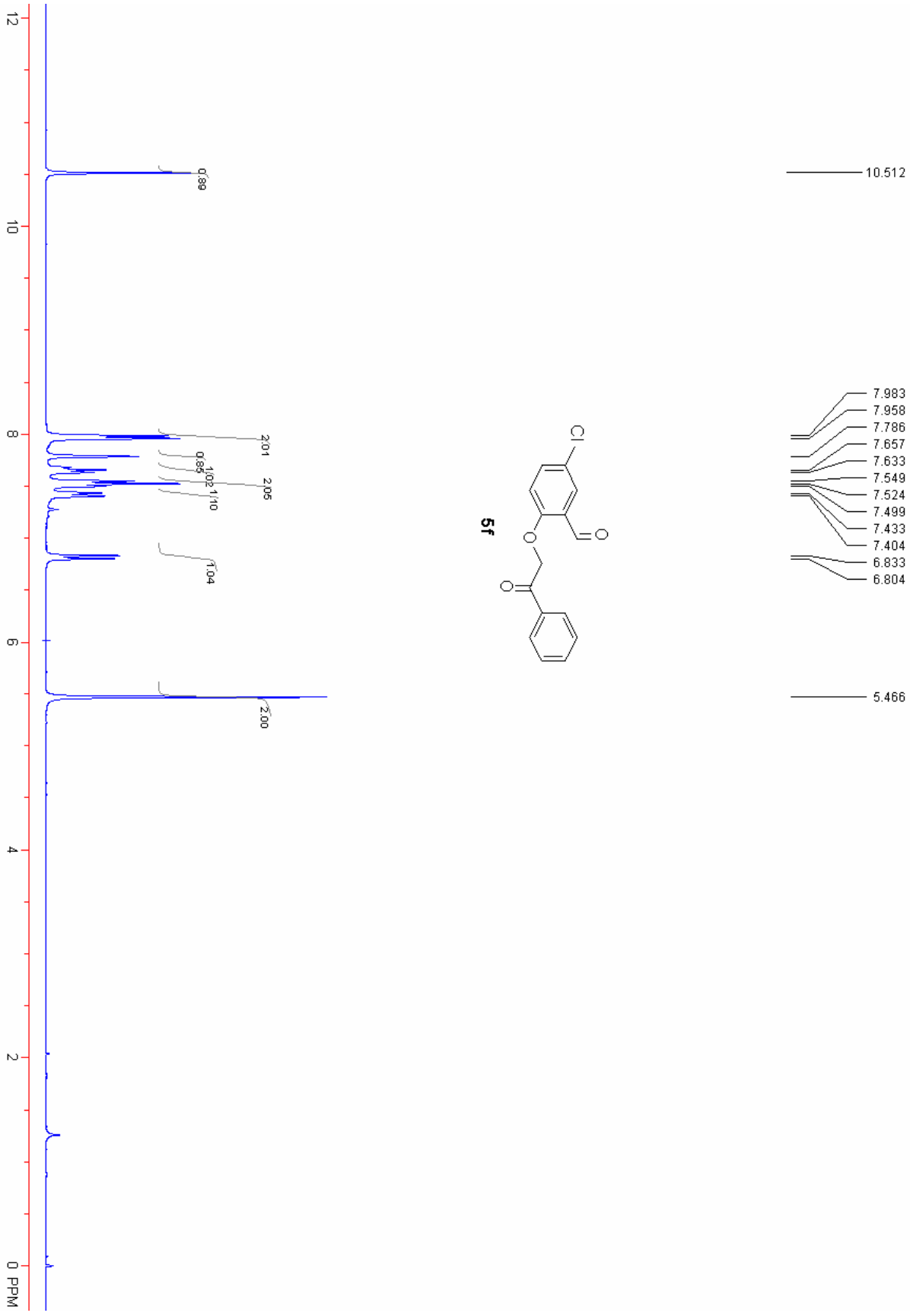
O
O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8
6
4
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0.85
1.02
1.10
2.05
1.04
2.00
Cl
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O
O
5f
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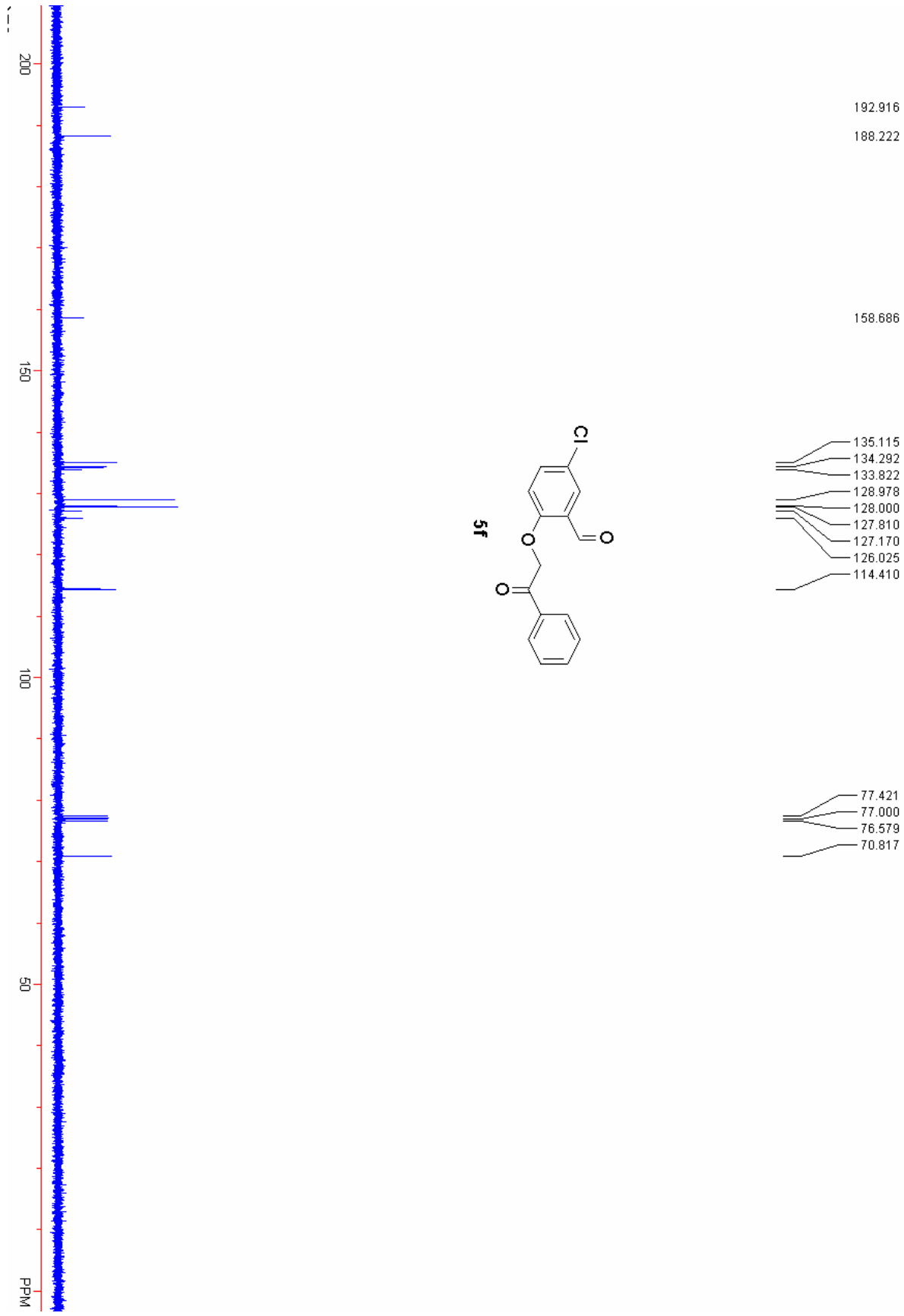
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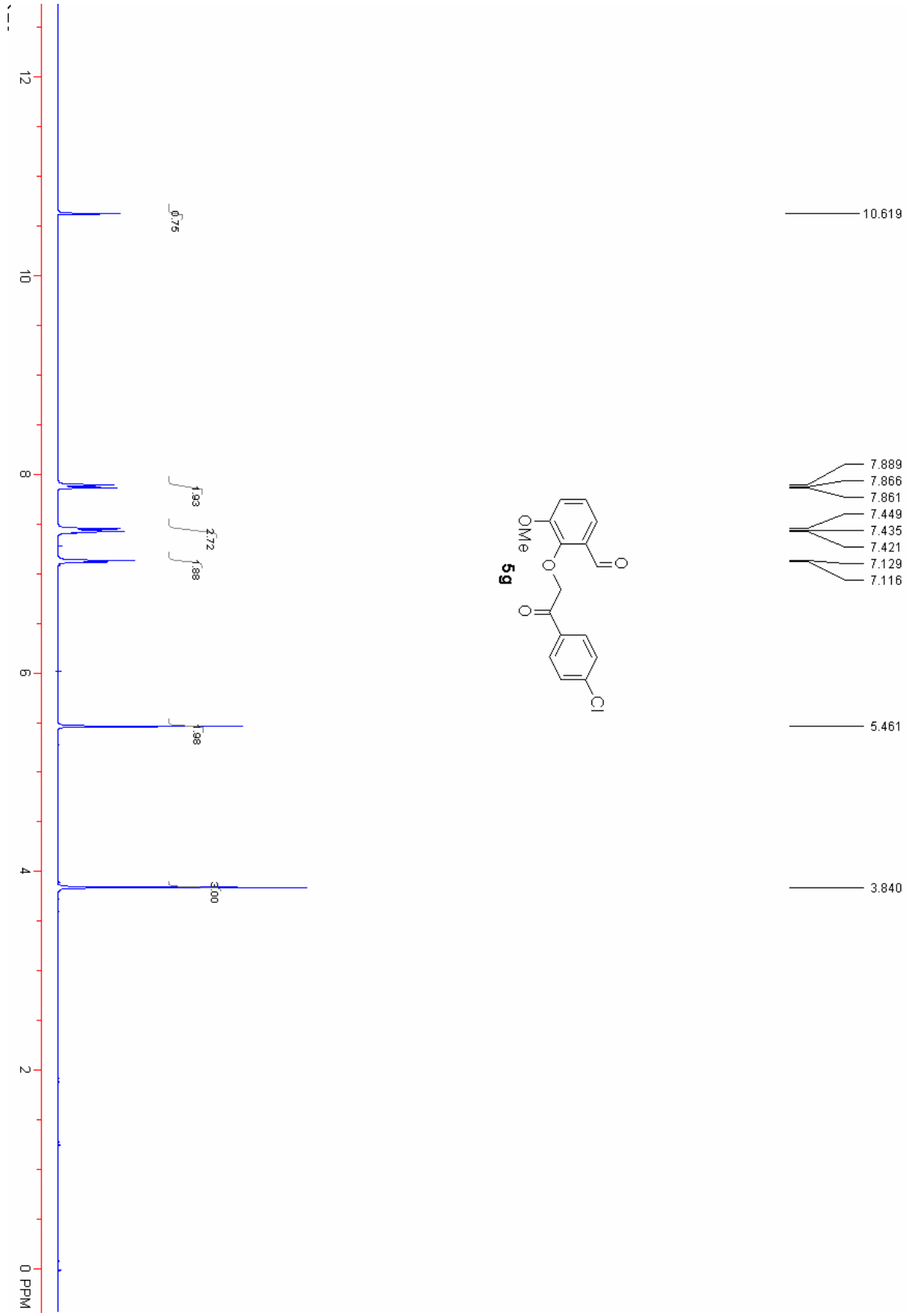
O
O
5f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O
O
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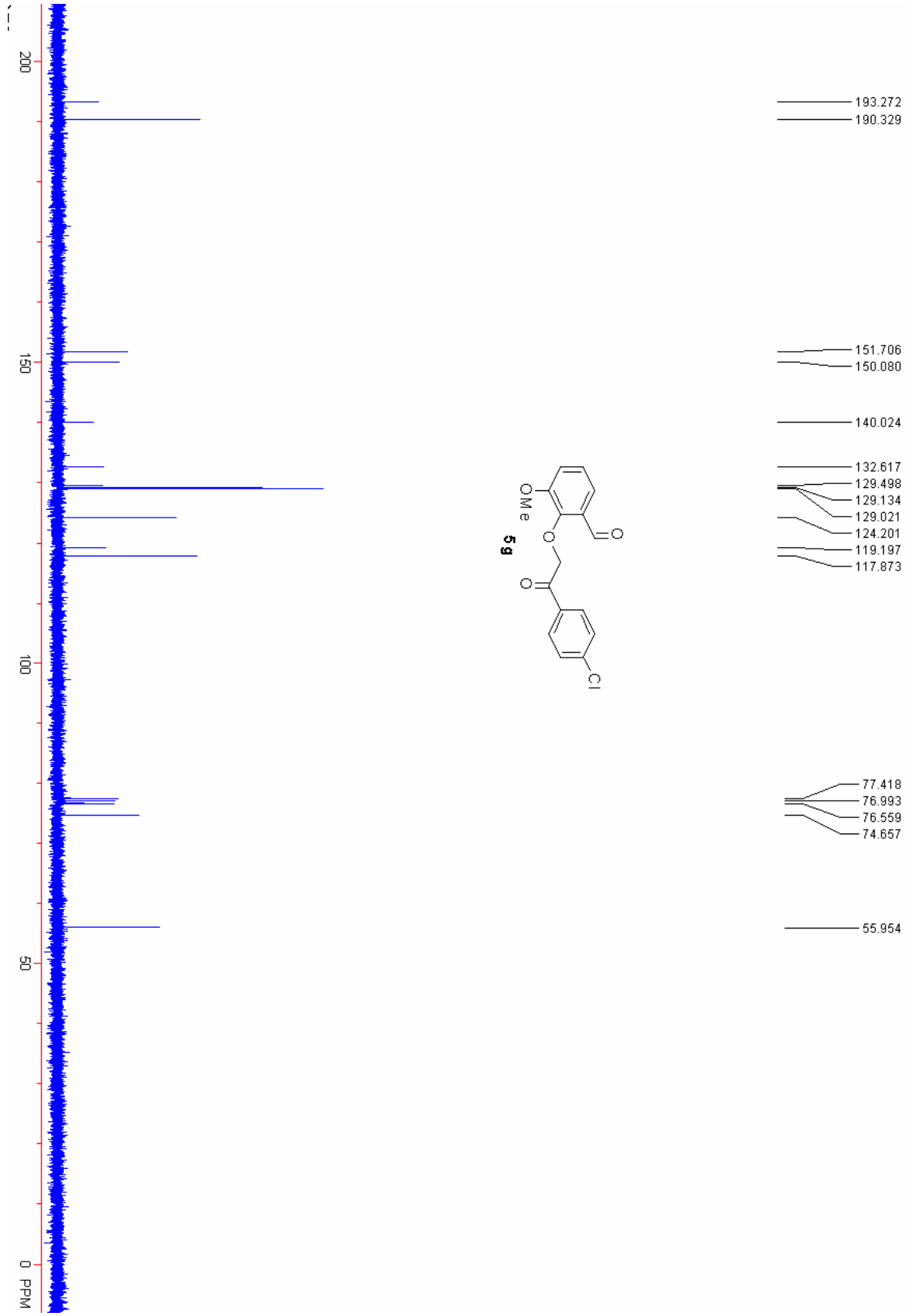
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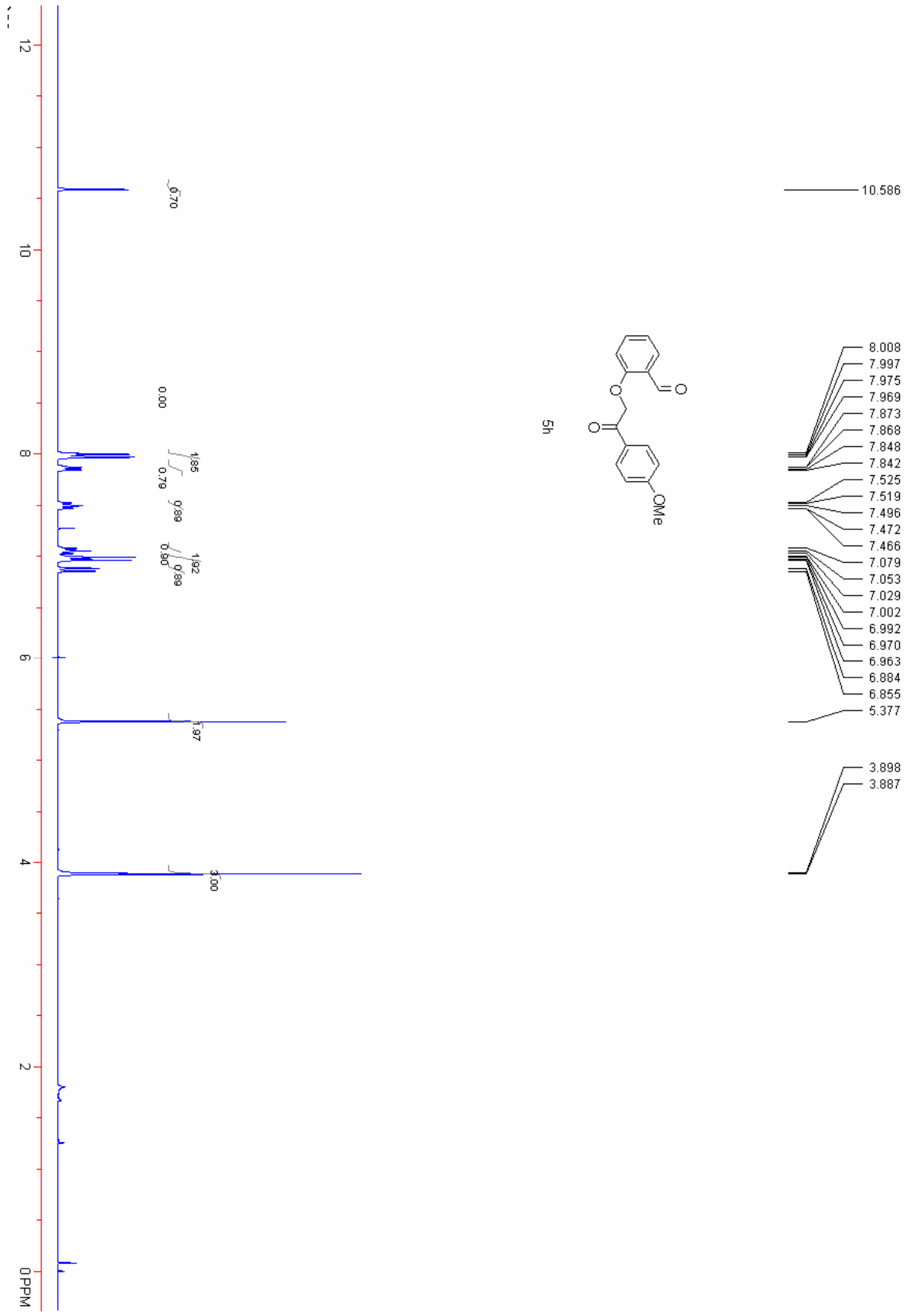
Cl
5g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0.89
1.97
3.00
5h
O
O
O
OMe
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7.997
7.975
7.969
7.873
7.868
7.848
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7.525
7.519
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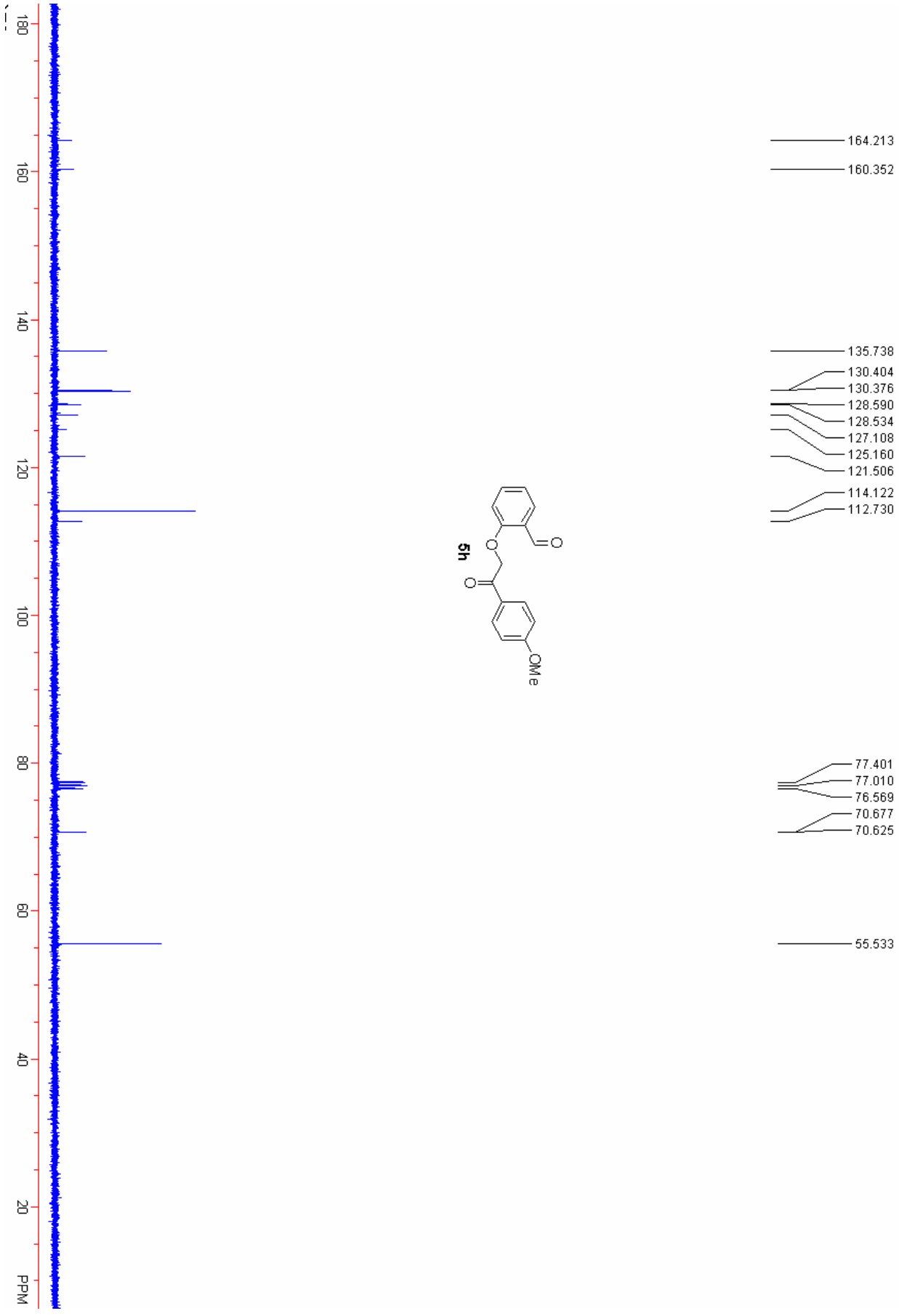
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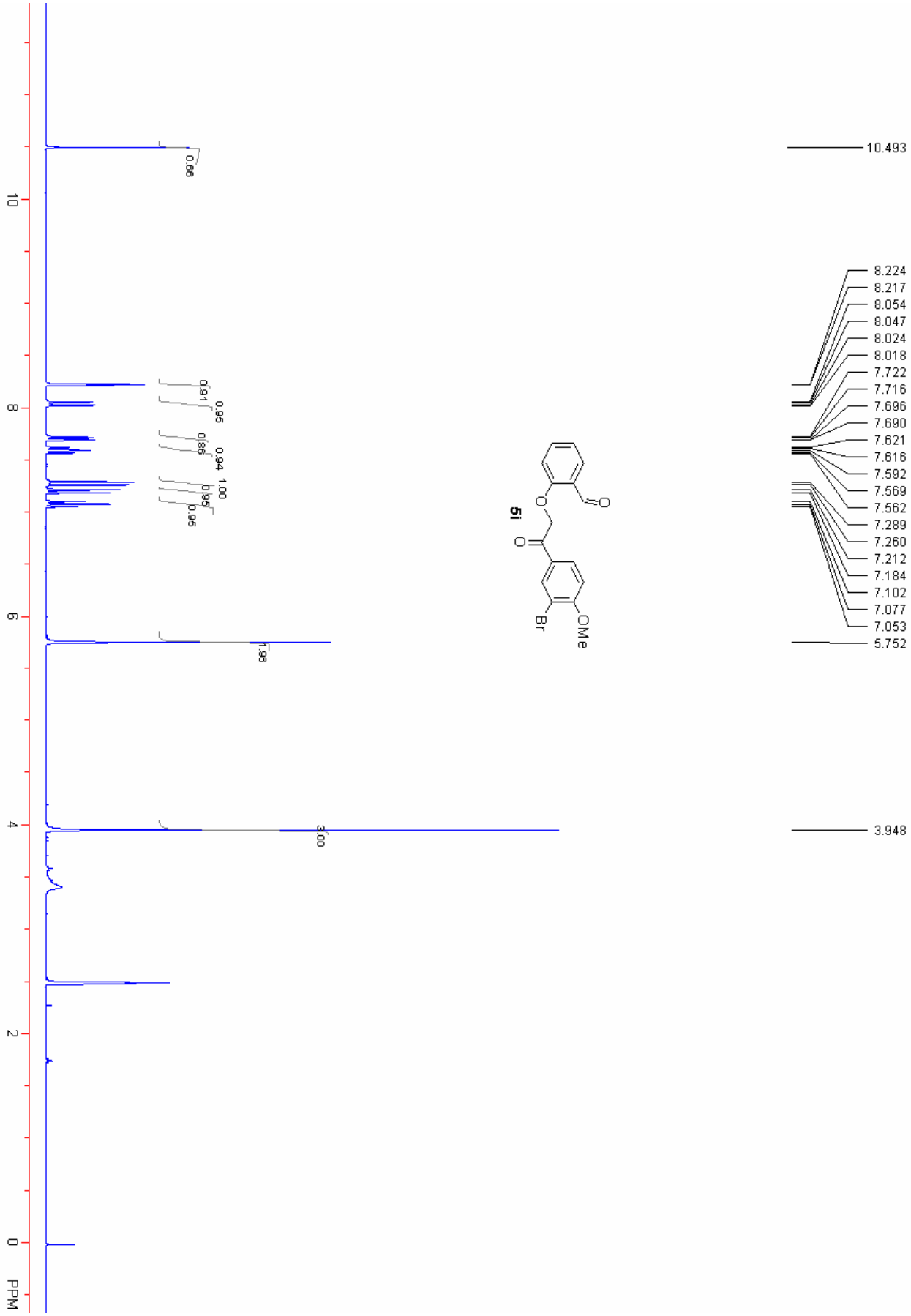
5h
OMe
PPM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7.102
7.077
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0.95
0.86
0.94
1.00
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5i
O
O
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OMe
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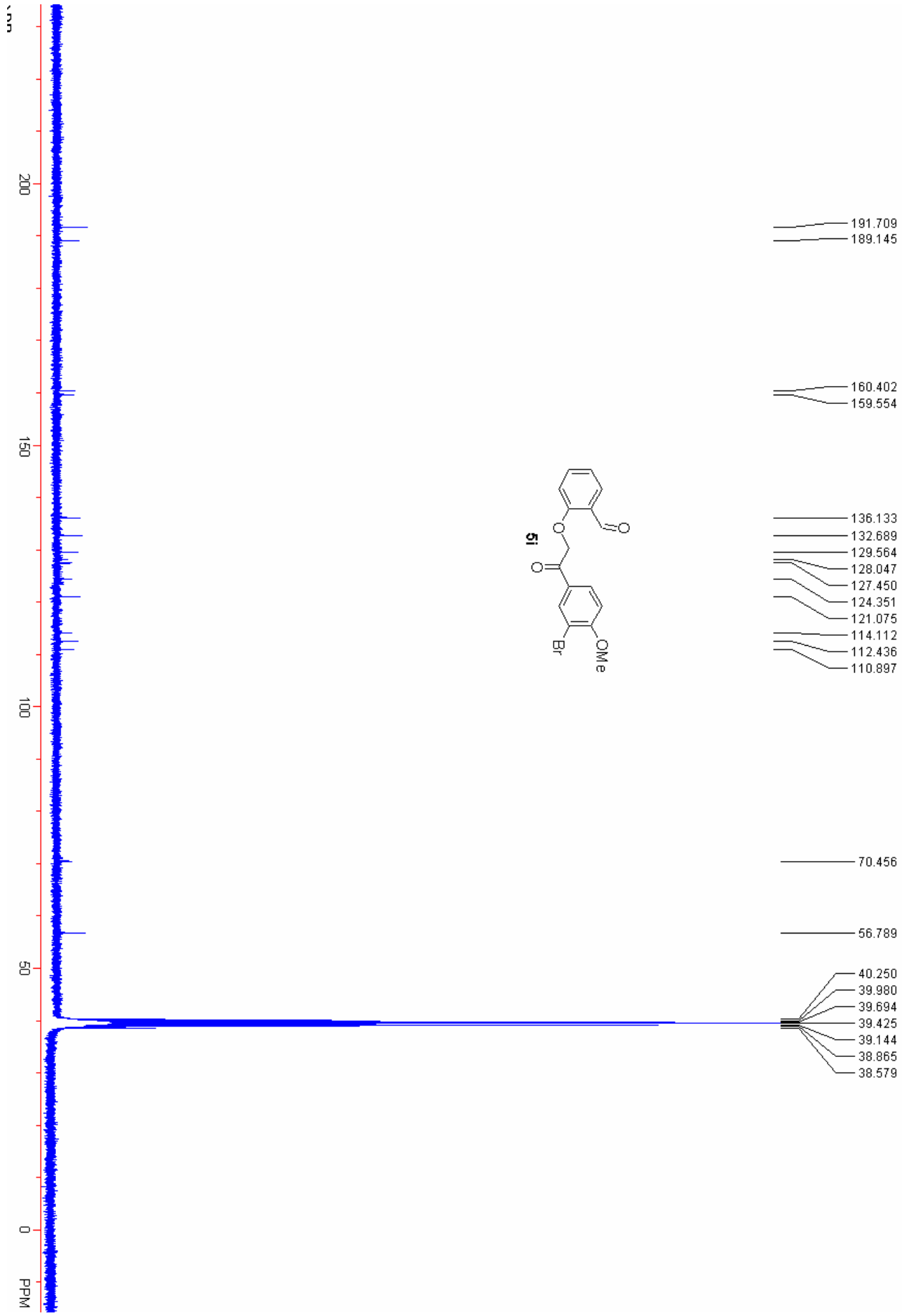
PPM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70.456
56.789
40.250
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5i
Br
OMe
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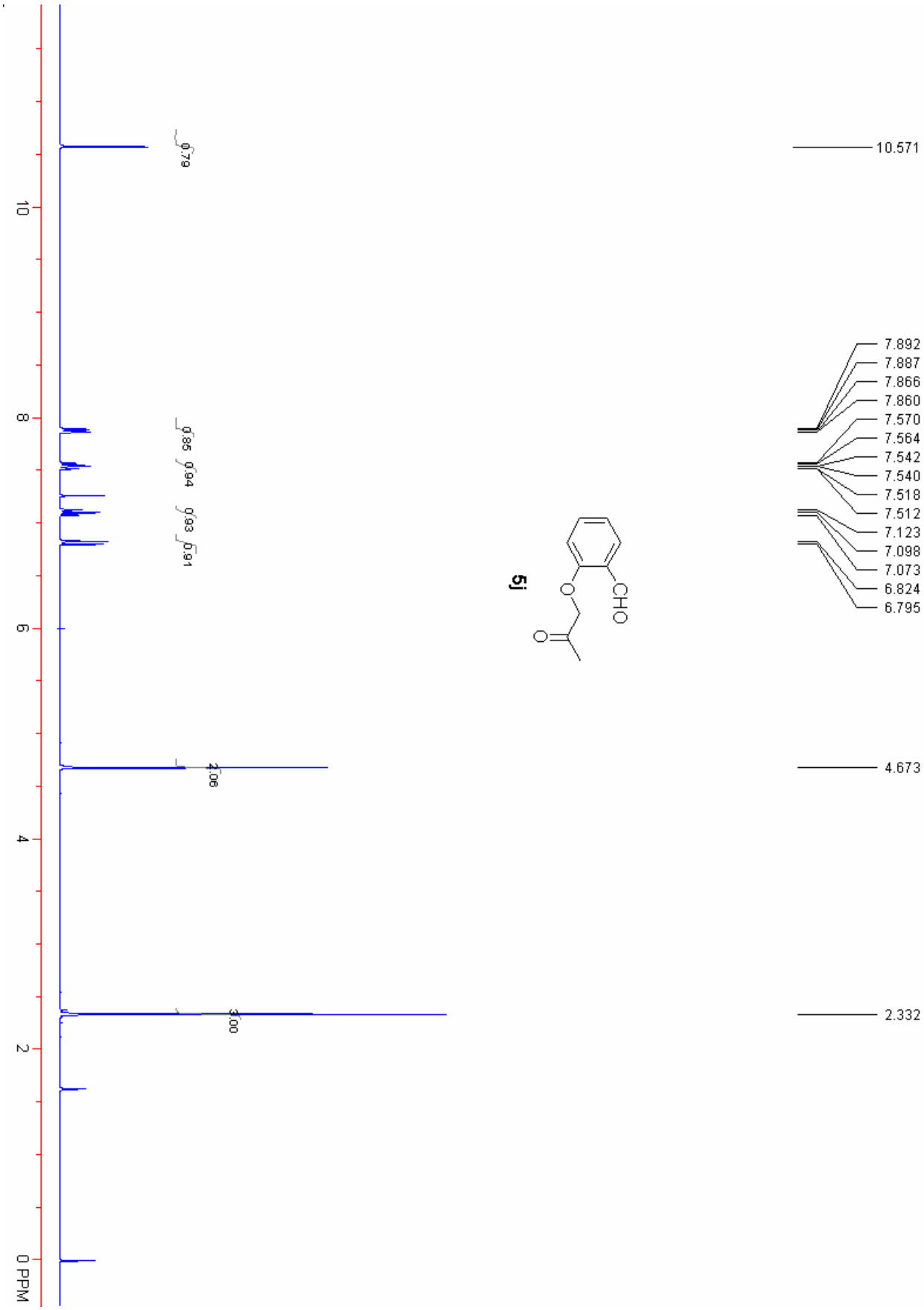
100
50
0
PPM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4.673
2.332
0.79
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3.00
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O
O
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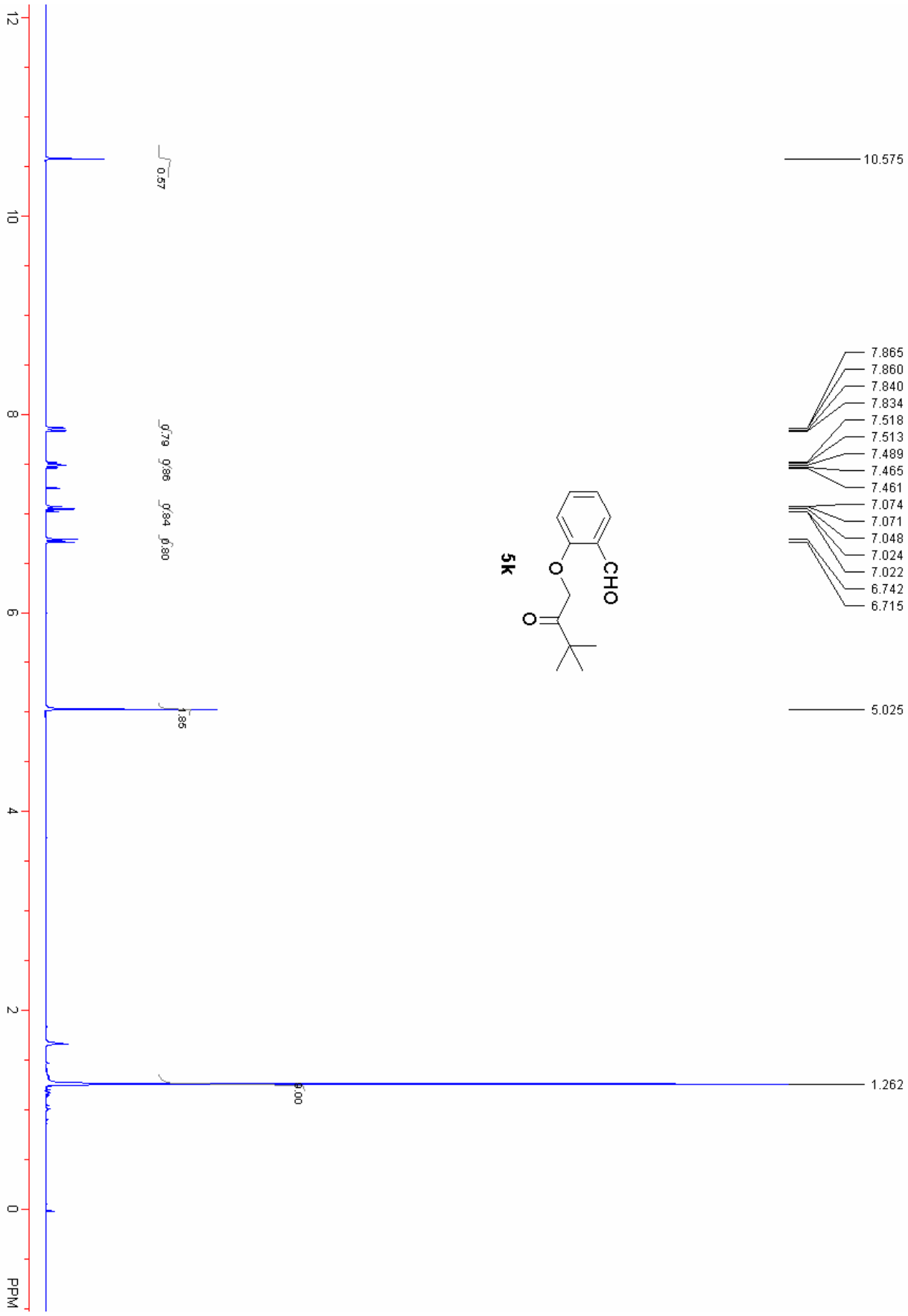
8
6
4
2
0 PPM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7.489
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7.074
7.071
7.048
7.024
7.022
6.742
6.715
5.025
1.262
0.57
0.79
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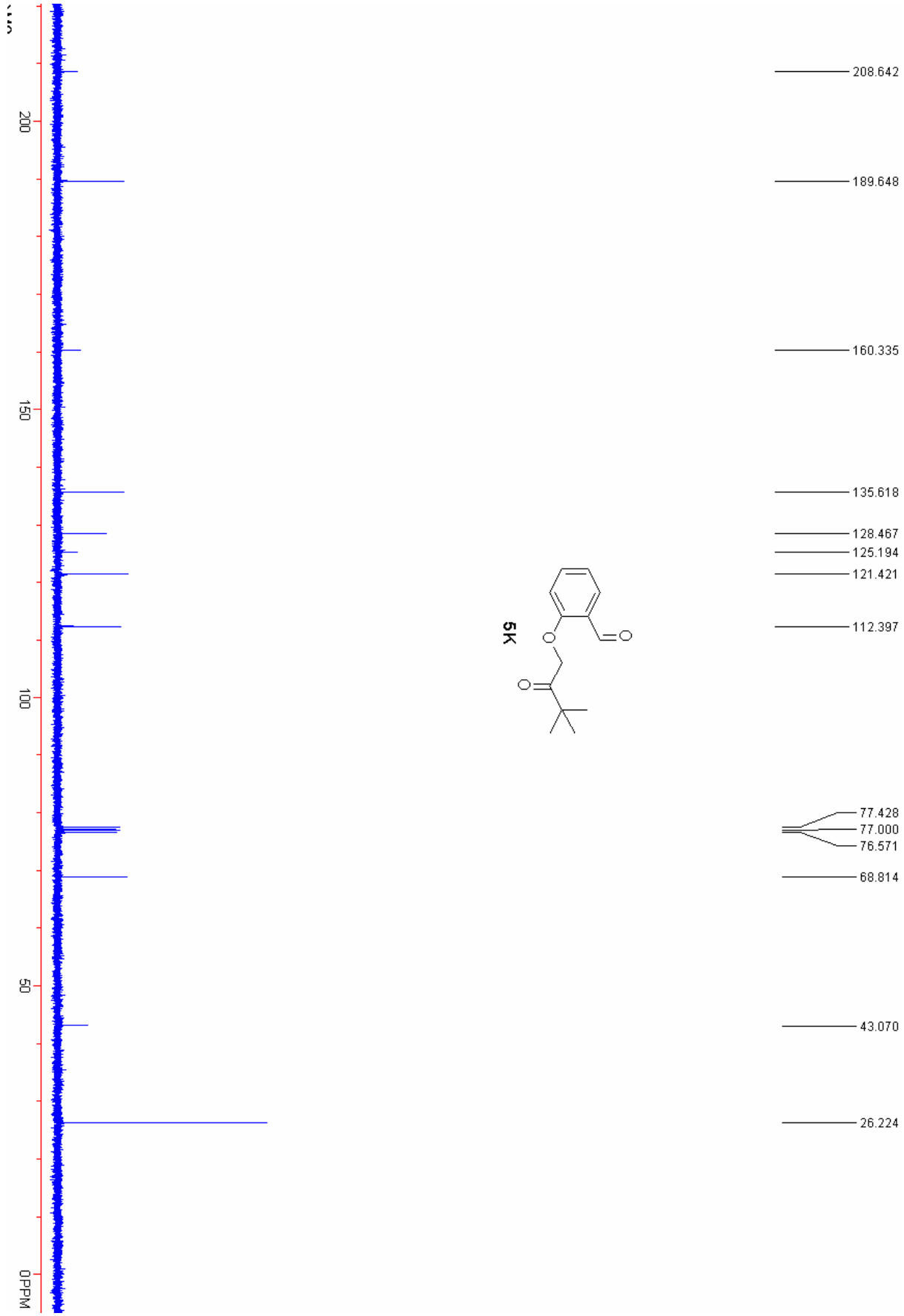
1.85
9.00
5k
CHO
O
O
PPM
12
10
8
6
4
2
0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200
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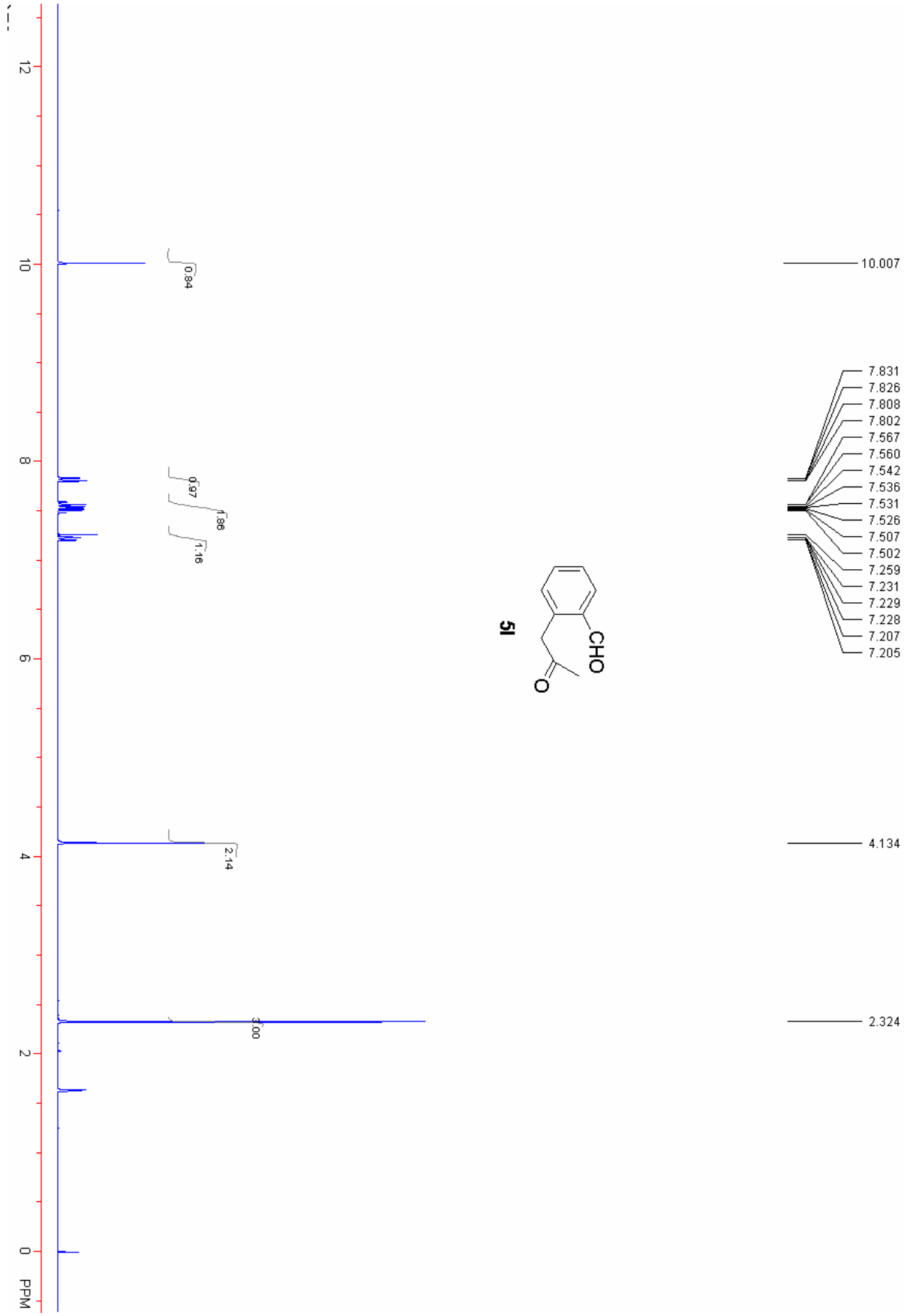
100
50
0PPM
5K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5l
CHO
O
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7.536
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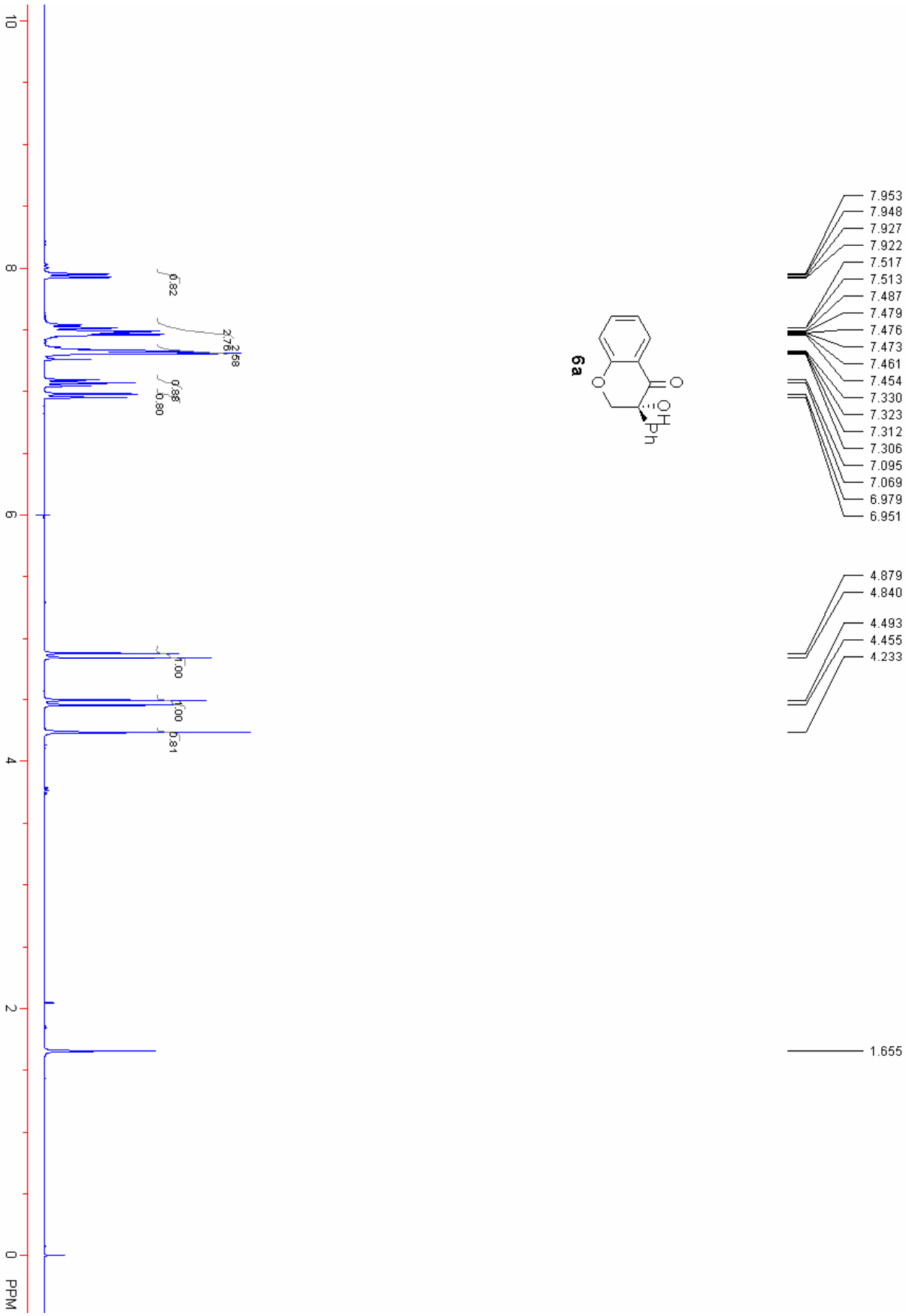
4.134
2.324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0.80
1.00
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0.81
6a
OH
Ph
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7.927
7.922
7.517
7.513
7.487
7.479
7.476
7.473
7.461
7.454
7.330
7.323
7.312
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1.655

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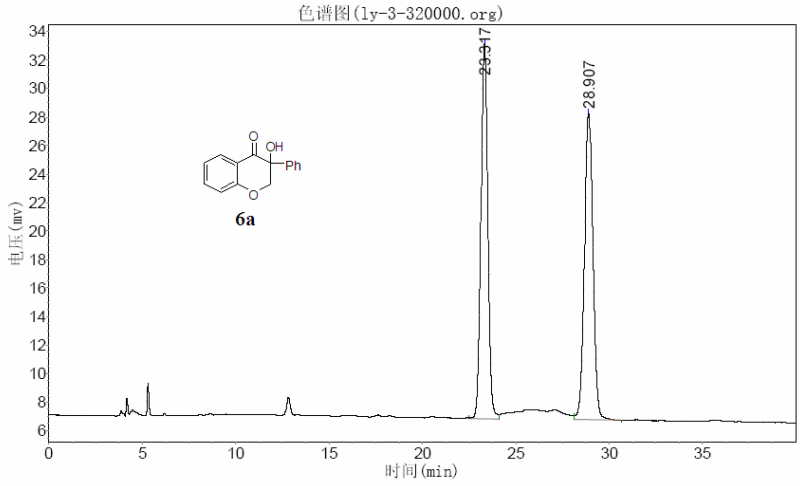
实验者：ly
报告时间：2007-06-22,13:54:20



No.	R. Time	Peak Height	Peak Area	Percent
1	23.317	26322.977	671239.438	49.3902
2	28.907	21531.582	687813.938	50.6098
总计		47854.559	1359053.375	100.0000

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实验者：ly
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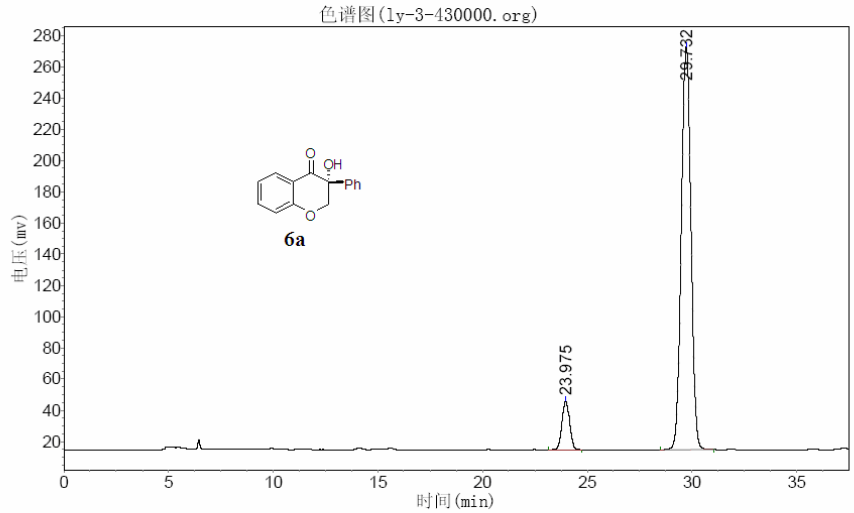
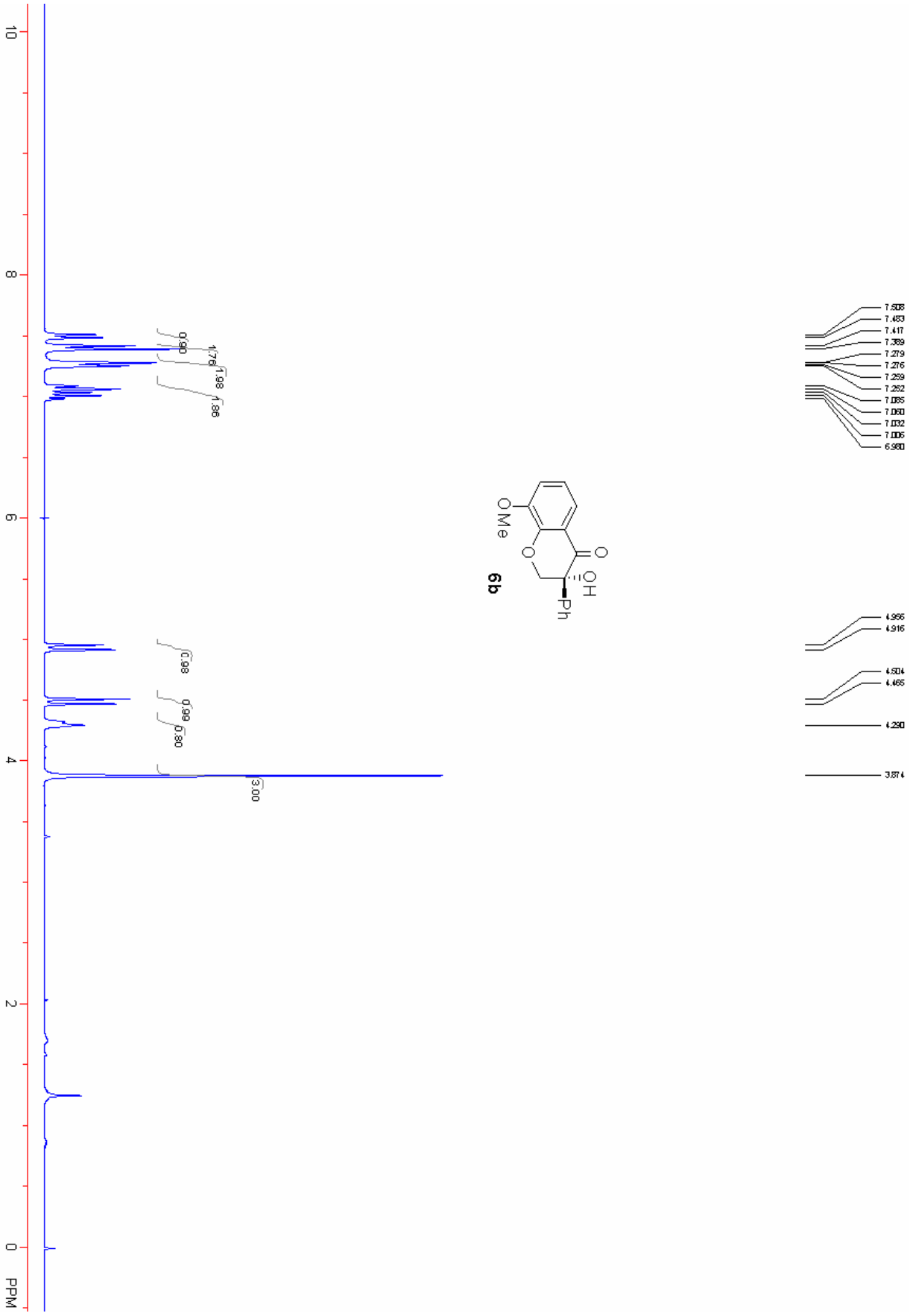


No.	R. Time	Peak Height	Peak Area	Percent
1	23.975	8887.660	189315.172	7.7224
2	29.732	85025.695	2262203.750	92.2776
总计		93913.355	2451518.922	100.0000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8
6
4
2
0
PPM
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1.78
1.88
1.86
0.98
0.99
0.80
3.00
OMe
O
O
OH
Ph
6b
7.508
7.483
7.417
7.389
7.279
7.276
7.259
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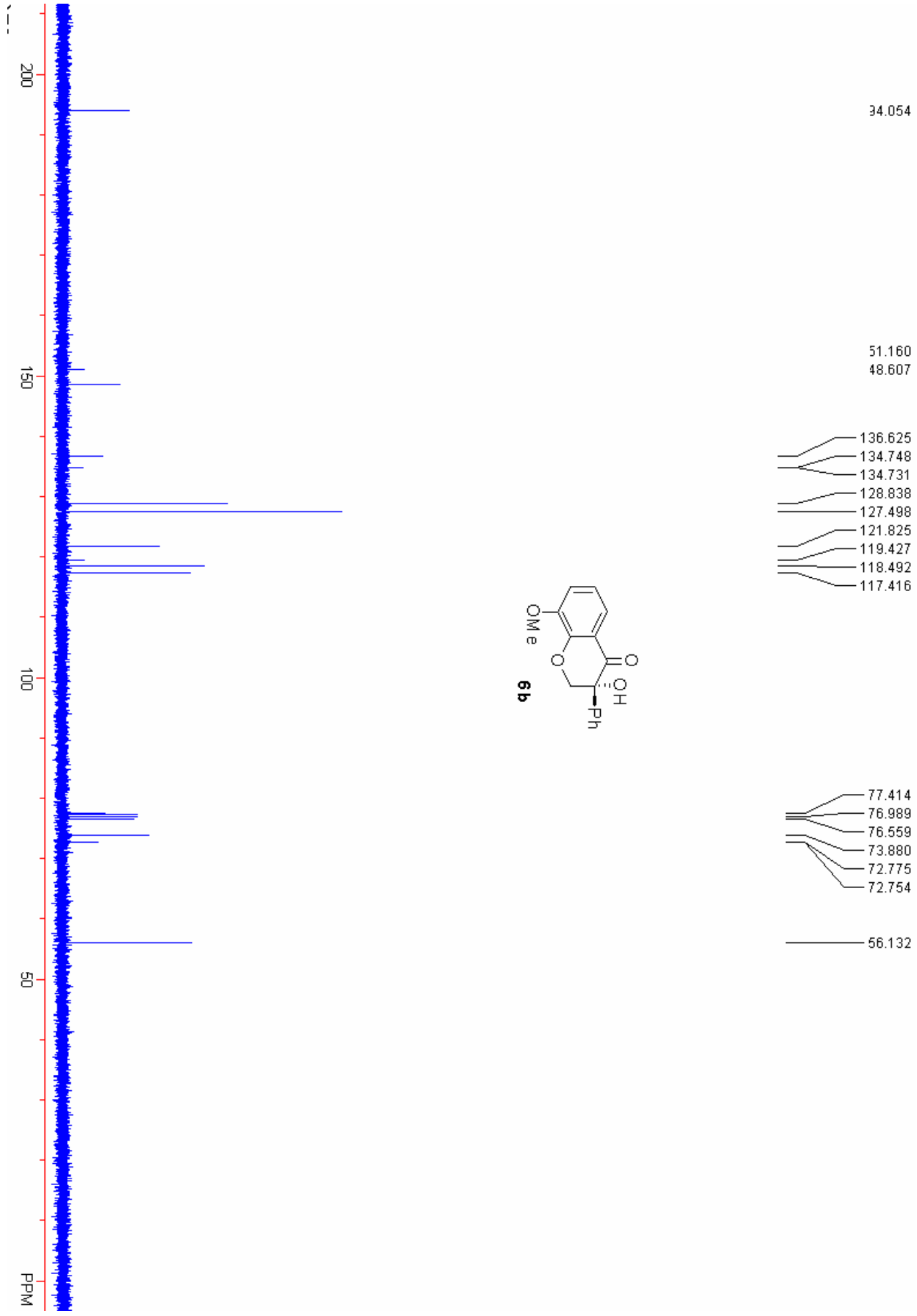
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118.492
117.416
77.414
76.989
76.559
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72.775
72.754
56.132
OMe
O
O
OH
Ph
6b

实验时间：2066-11-16,17:00:13
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实验者：ly
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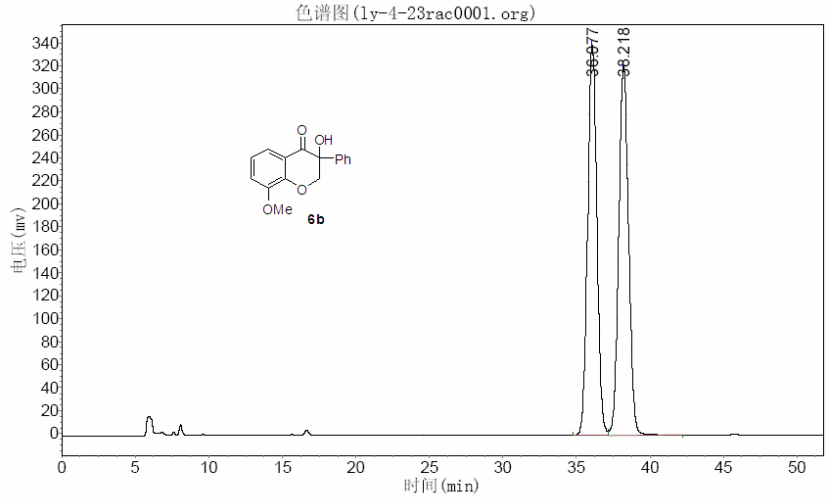

No.	R. Time	PeakHeight	PeakArea	PerCent
1	36.077	340200.094	14889927.000	49.7251
2	38.218	321910.063	15054571.000	50.2749
总计		662110.156	29944498.000	100.0000

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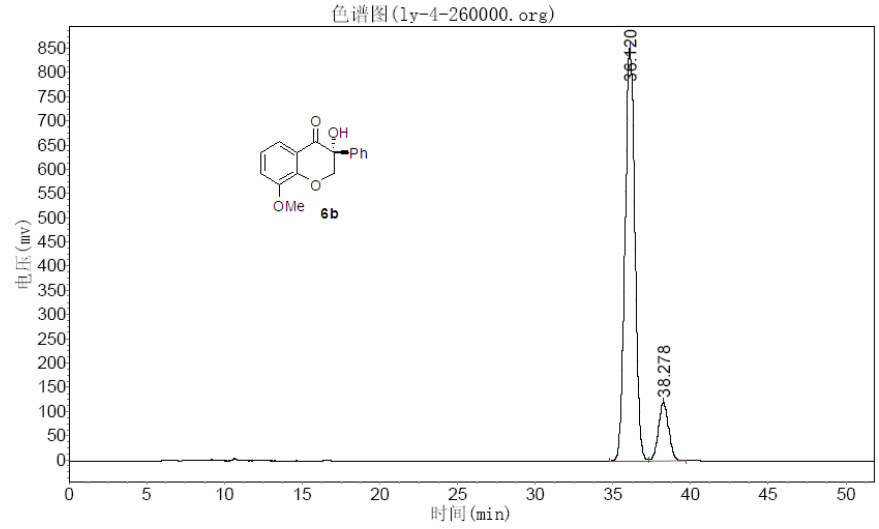
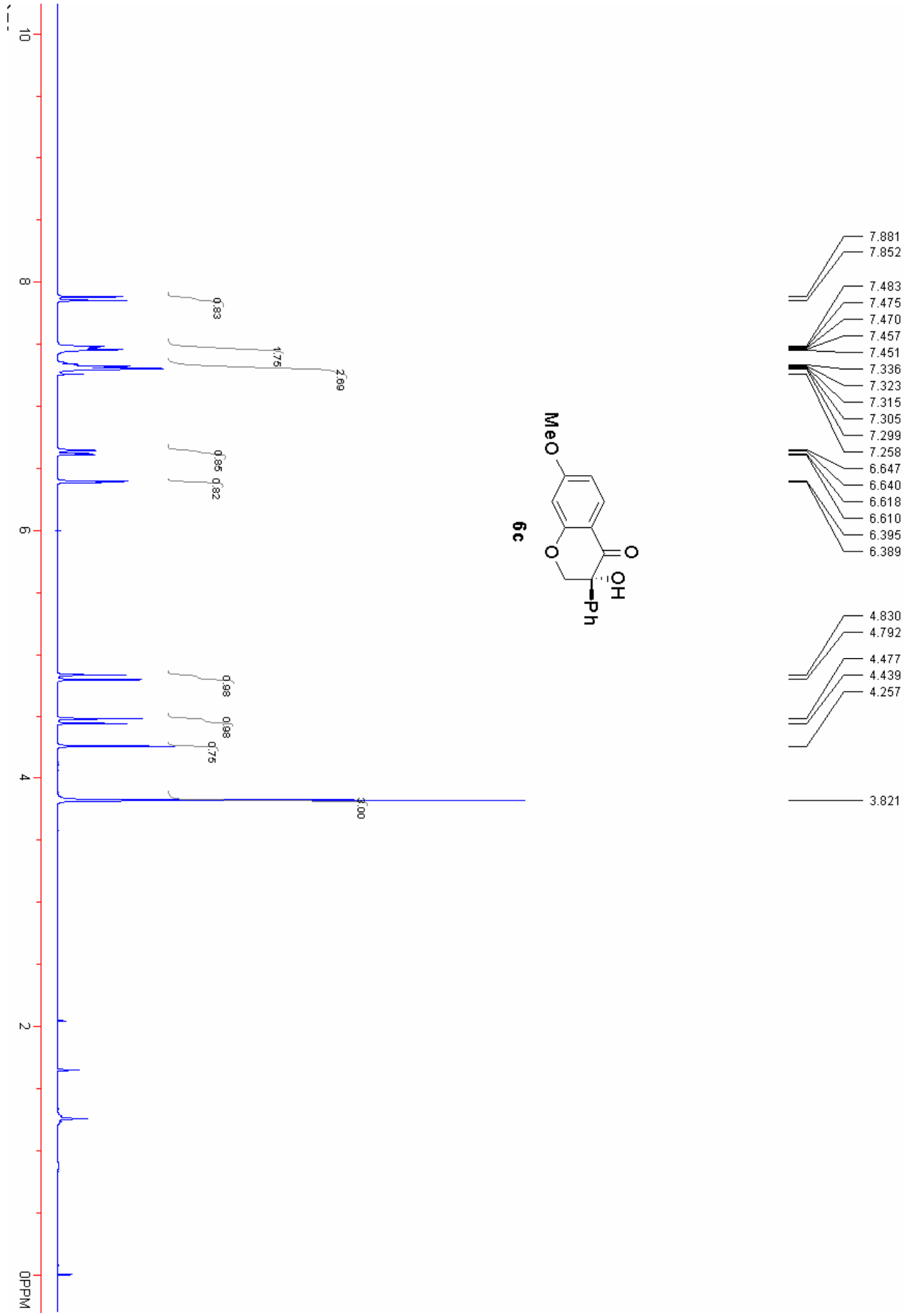
实验者：ly
报告时间：2066-11-16,19:17:44



No.	R. Time	PeakHeight	PeakArea	PerCent
1	36.120	854128.000	37443528.000	87.1682
2	38.278	120049.547	5511970.000	12.8318
总计		974177.547	42955498.000	100.0000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6
4
2
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1.75
2.69
0.85
0.82
0.98
0.98
0.75
3.00
MeO
O
O
OH
Ph
6c
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7.852
7.483
7.475
7.470
7.457
7.451
7.336
7.323
7.315
7.305
7.299
7.258
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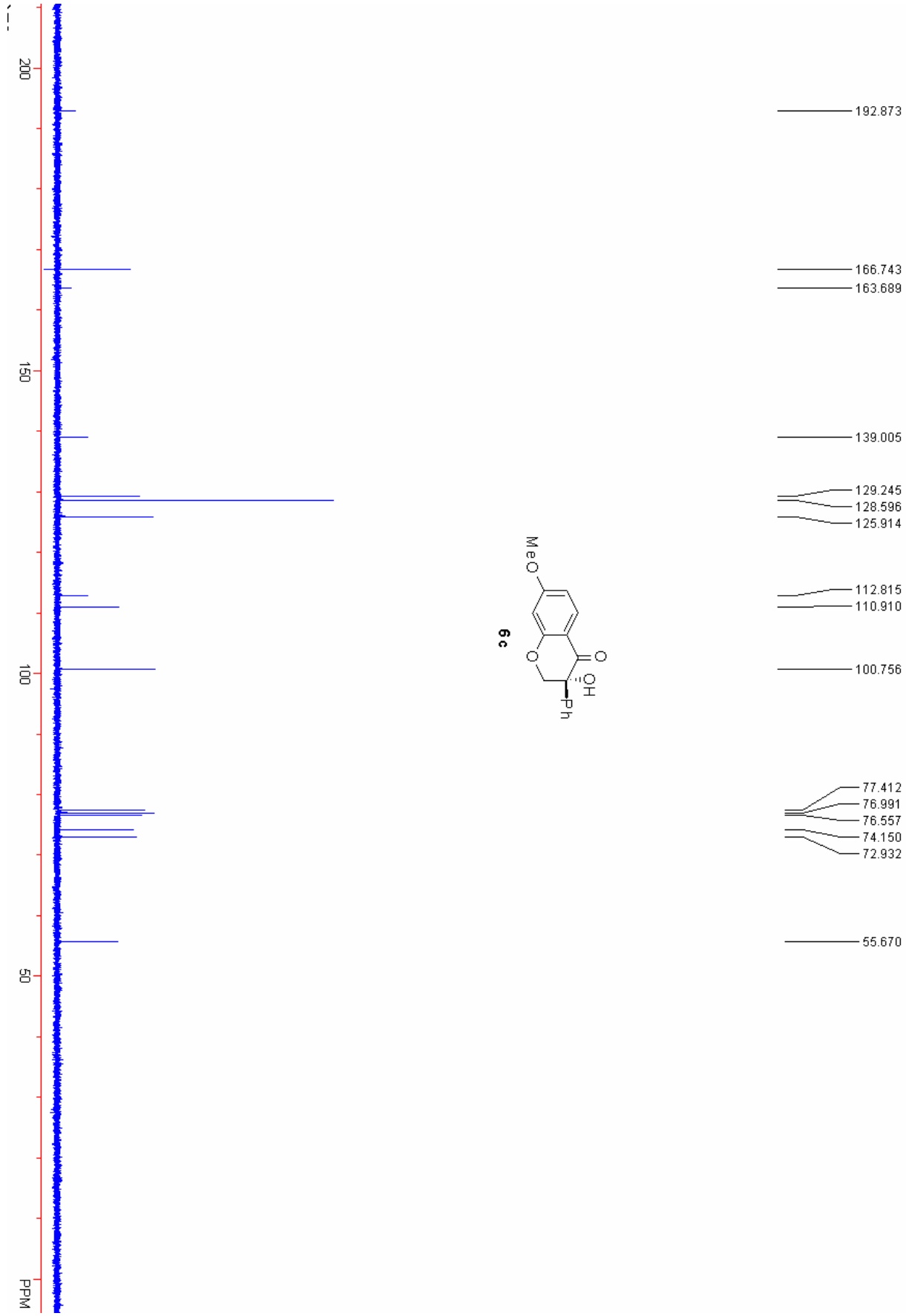
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74.150
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MeO
O
O
OH
Ph
6c

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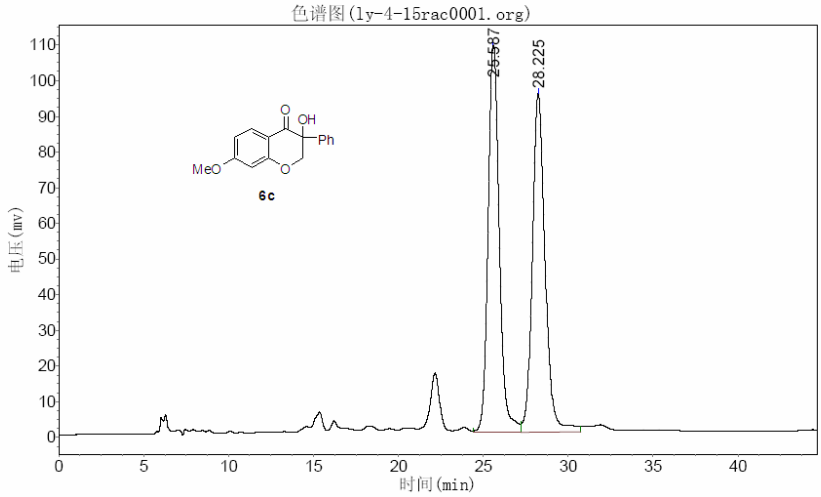
实验者：ly
报告时间：2066-11-07,8:37:00



No.	R. Time	PeakHeight	PeakArea	PerCent
1	25.587	108605.430	4915090.500	49.6039
2	28.225	95013.914	4993597.000	50.3961
总计		203619.344	9908687.500	100.0000

实验时间：2066-11-07,9:04:38
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实验者：ly
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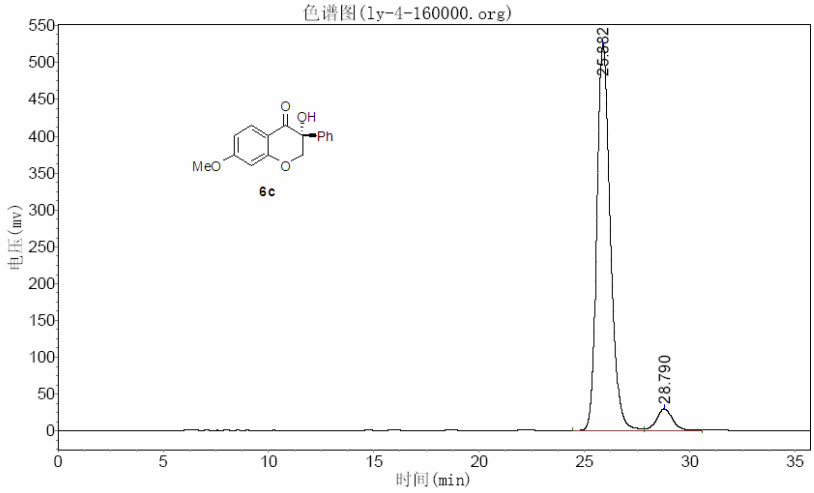
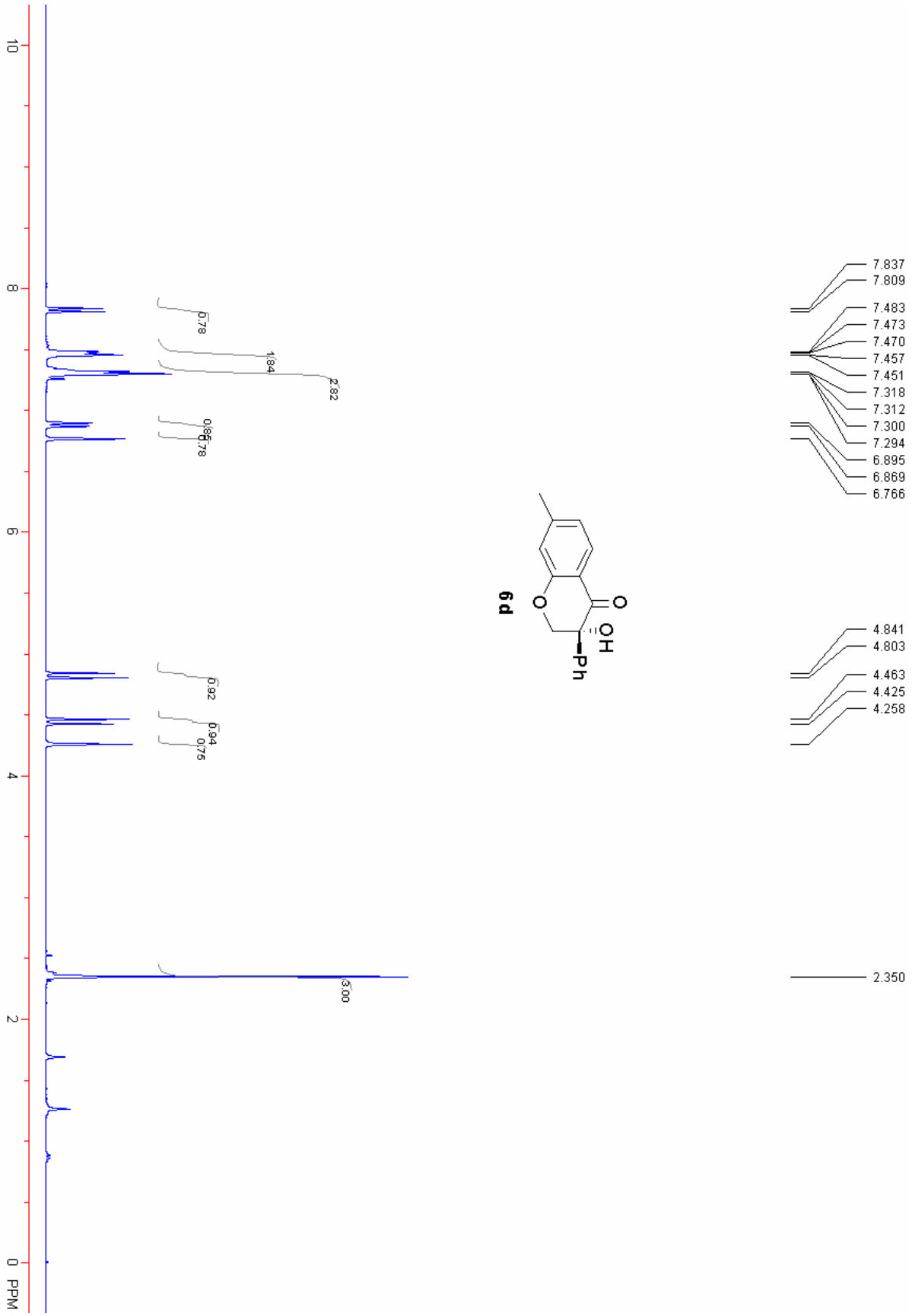


No.	R. Time	PeakHeight	PeakArea	PerCent
1	25.882	524444.813	23268358.000	93.6954
2	28.790	29491.820	1565683.375	6.3046
总计		553936.633	24834041.375	100.0000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0.85
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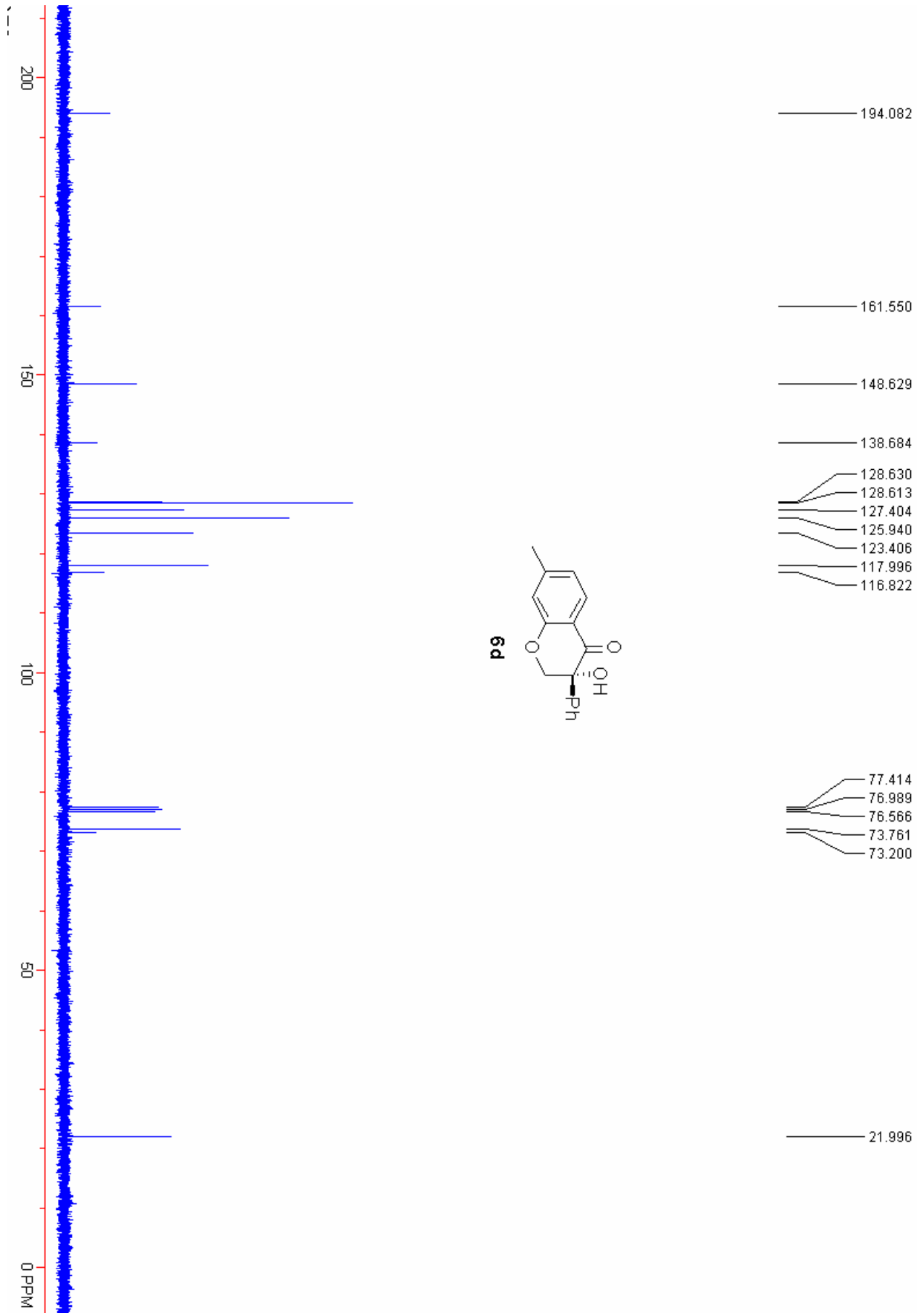
0.94
0.75
3.00
7.837
7.809
7.483
7.473
7.470
7.457
7.451
7.318
7.312
7.300
7.294
6.895
6.869
6.766
4.841
4.803
4.463
4.425
4.258
2.350
6g
O
OH
Ph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128.613
127.404
125.940
123.406
117.996
116.822
77.414
76.989
76.566
73.761
73.200
21.996
9d
O
OH
Ph

实验时间：2066-11-07,12:09:26
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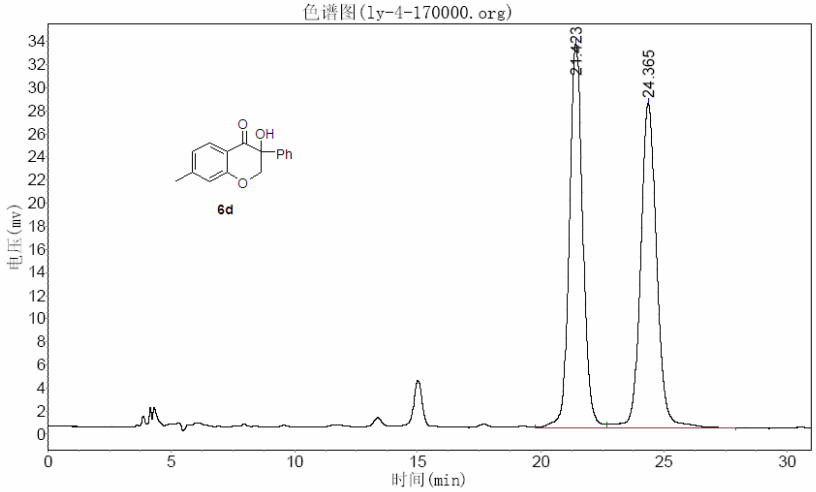
实验者：ly
报告时间：2066-11-07,12:11:33



No.	R. Time	PeakHeight	PeakArea	PerCent
1	21.423	33252.121	1265080.625	49.7774
2	24.365	28119.863	1276394.750	50.2226
总计		61371.984	2541475.375	100.0000

实验时间：2066-11-07,13:01:59
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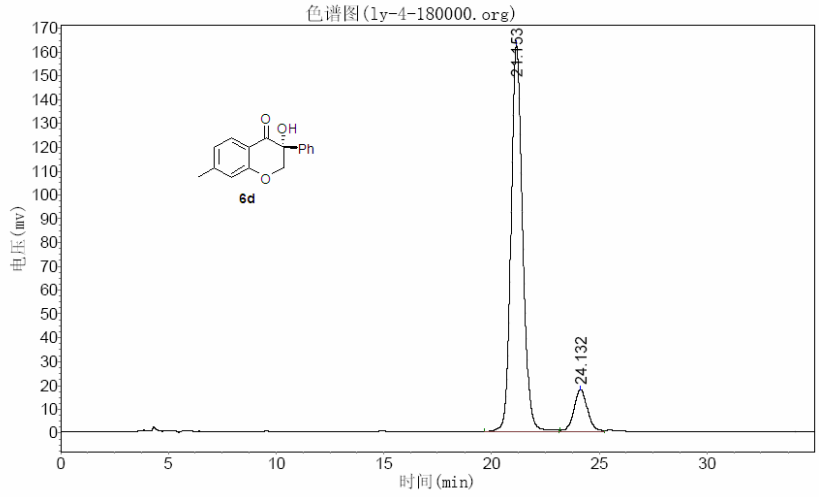
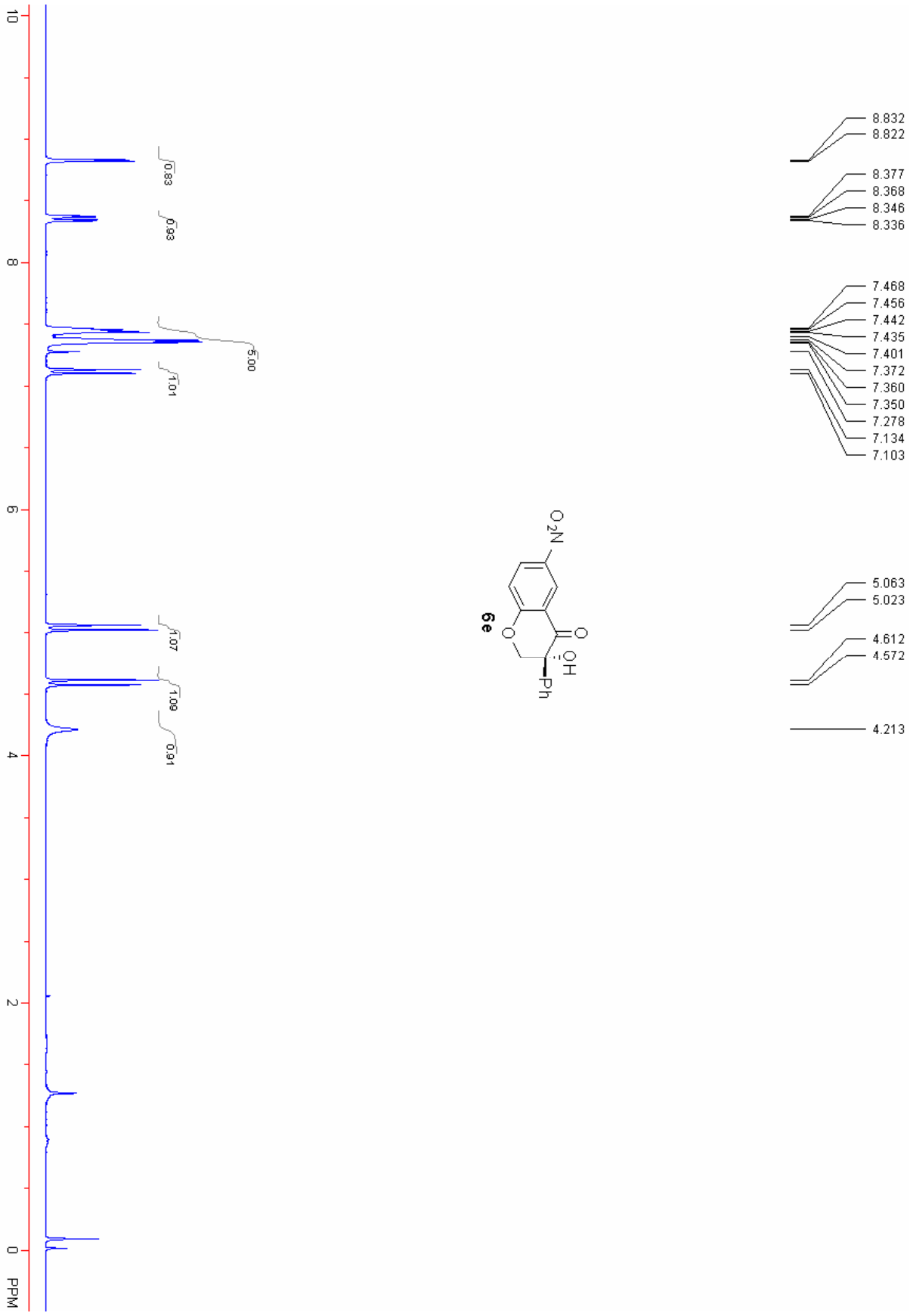
实验者：ly
报告时间：2066-11-07,13:47:04



No.	R. Time	PeakHeight	PeakArea	PerCent
1	21.153	162376.297	6095815.500	88.7660
2	24.132	17508.912	771472.625	11.2340
总计		179885.209	6867288.125	100.0000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6
4
2
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1.09
0.91
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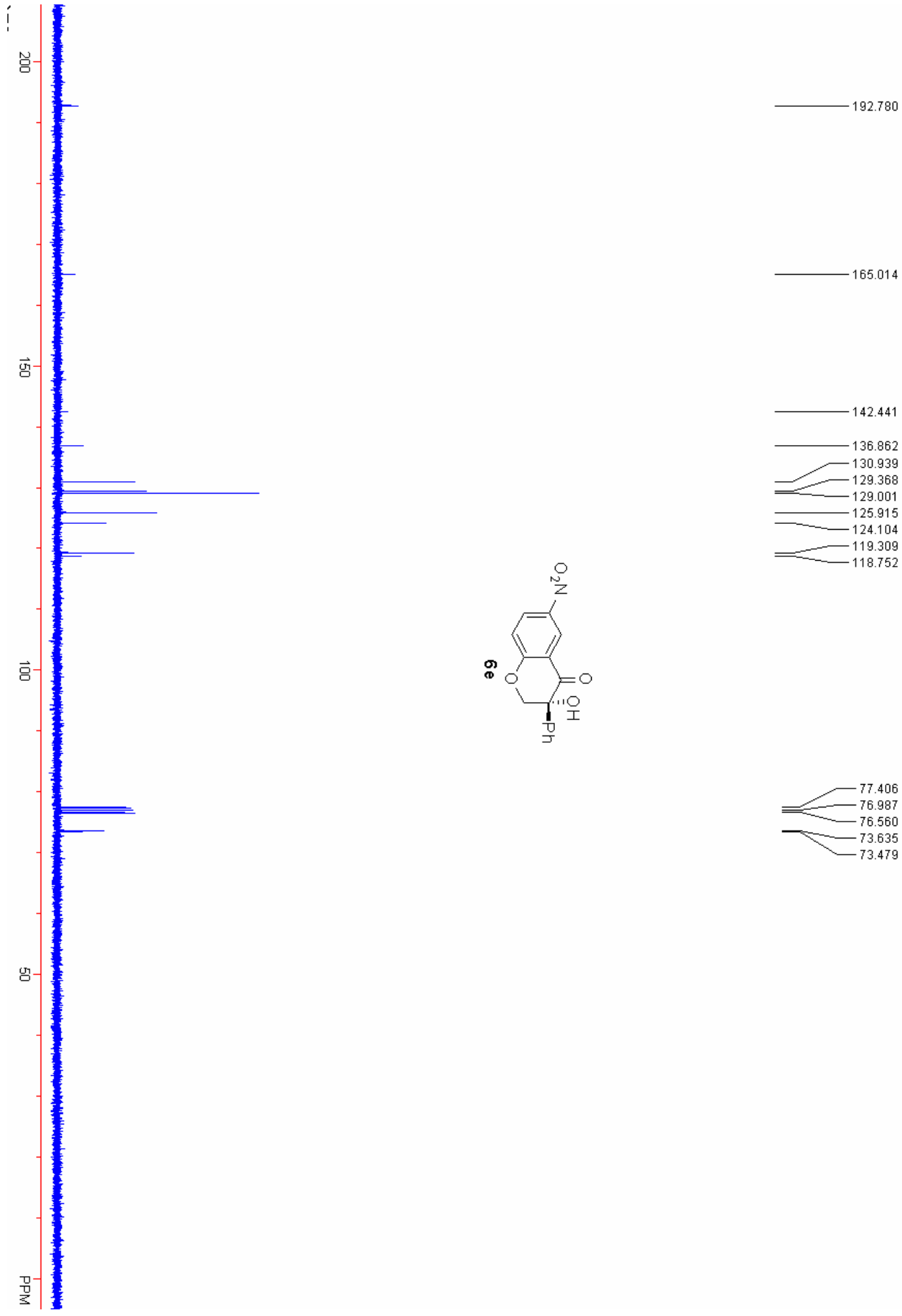
8.822
8.377
8.368
8.346
8.336
7.468
7.456
7.442
7.435
7.401
7.372
7.360
7.350
7.278
7.134
7.103
5.063
5.023
4.612
4.572
4.213
O2N
O
O
OH
Ph
6e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124.104
119.309
118.752
77.406
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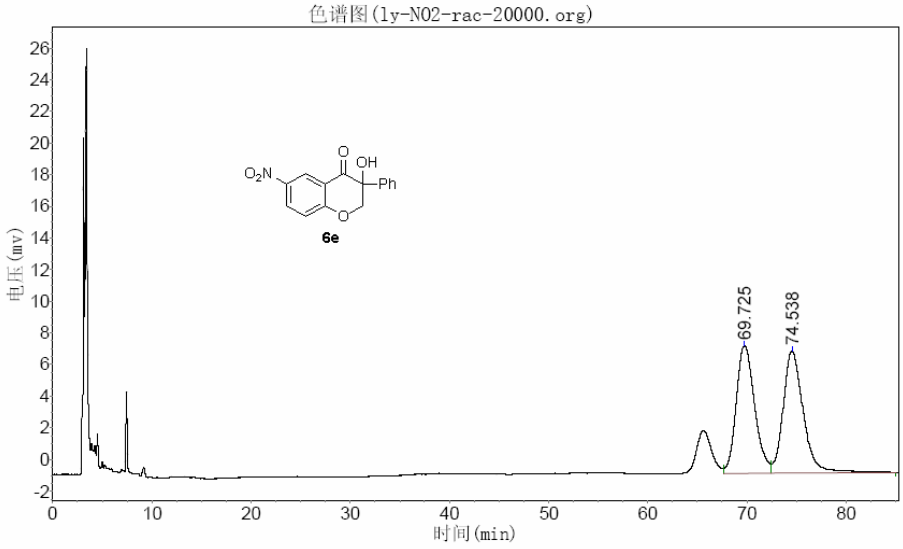
73.635
73.479
O2N
O
O
OH
Ph
6e

谱图文件:D:\date\ly\样品\ly-N02-rac-20000.org

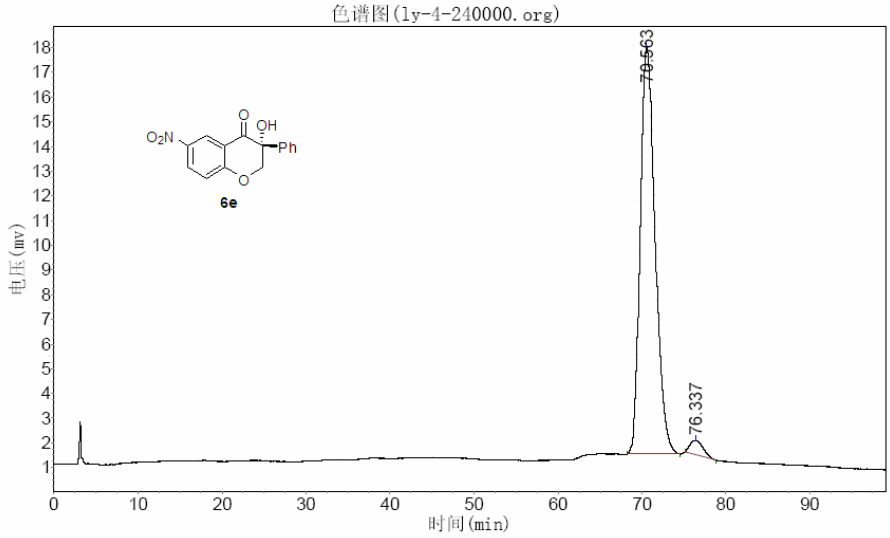
报告时间：2066-12-20,15:42:16
积分方法:面积归一法



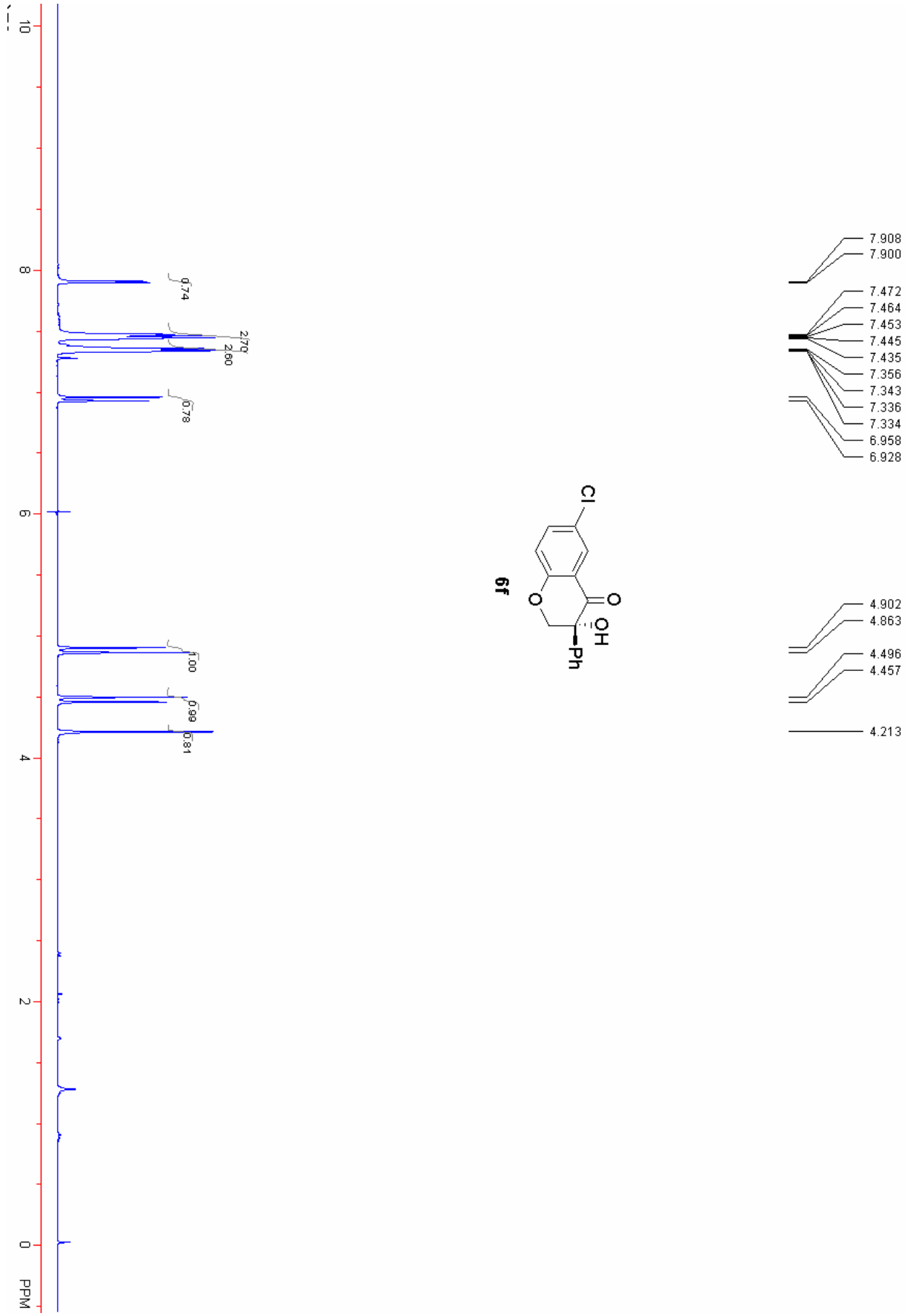
No.	R. Time	PeakHeight	PeakArea	PerCent
1	69.725	8066.171	1041452.188	48.7254
2	74.538	7725.981	1095938.875	51.2746
总计		15792.152	2137391.063	100.0000

实验时间：2066-11-30,12:10:18
谱图文件:D:\date\ly\样品\ly-4-240000.org

实验者：liyi
报告时间：2066-11-30,12:11:54



No.	R. Time	PeakHeight	PeakArea	PerCent
1	70.563	16450.930	2032654.125	96.9959
2	76.337	583.583	62953.688	3.0041
总计		17034.513	2095607.813	100.0000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0.99
0.81
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7.900
7.472
7.464
7.453
7.445
7.435
7.356
7.343
7.336
7.334
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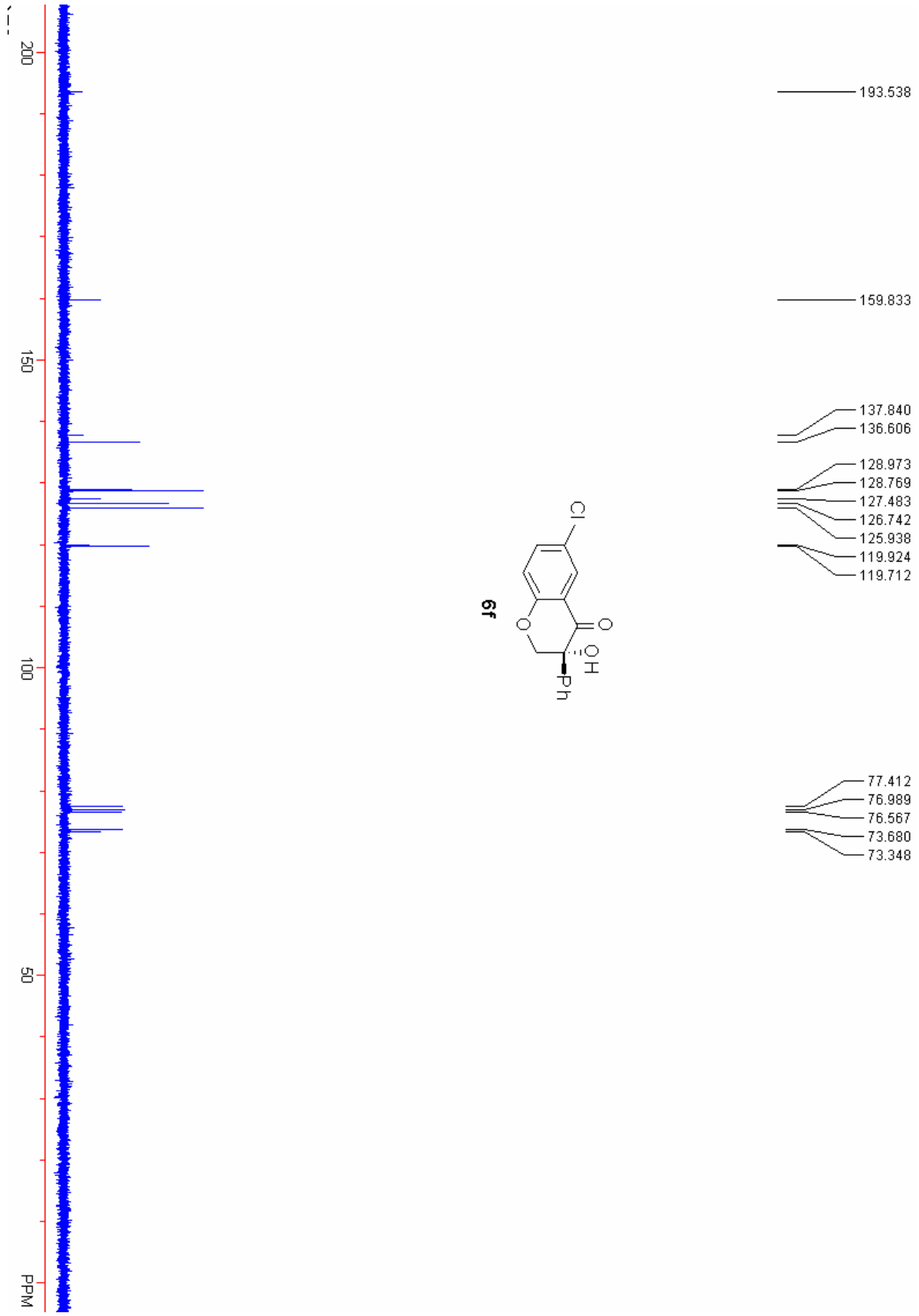
4.863
4.496
4.457
4.213
Cl
O
O
OH
Ph
6f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128.973
128.769
127.483
126.742
125.938
119.924
119.712
77.412
76.989
76.567
73.680
73.348
6f
Cl
O
O
OH
Ph

实验时间：2066-11-30,15:15:34
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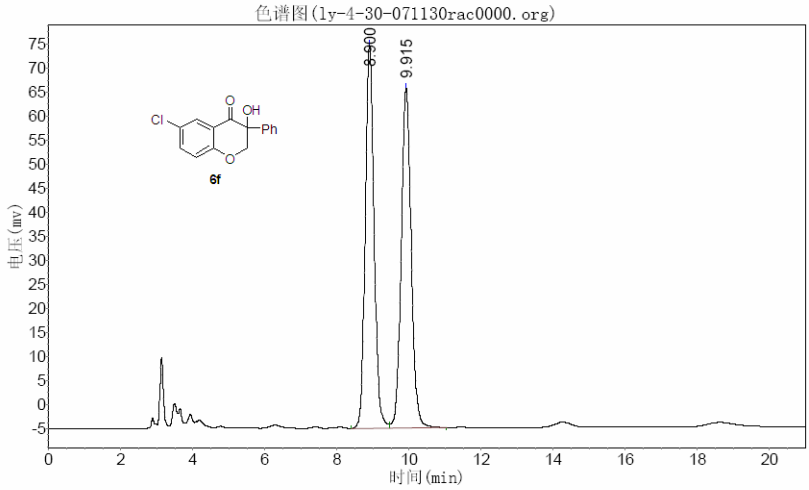
实验者：liyi
报告时间：2066-11-30,15:17:12



No.	R. Time	PeakHeight	PeakArea	PerCent
1	8.900	79883.523	1361480.625	49.9449
2	9.915	70743.773	1364483.875	50.0551
总计		150627.297	2725964.500	100.0000

实验时间：2066-11-30,15:55:19
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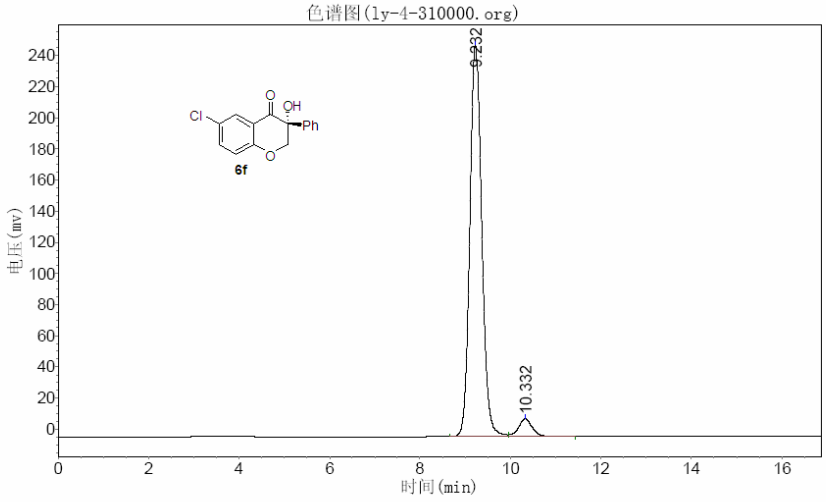
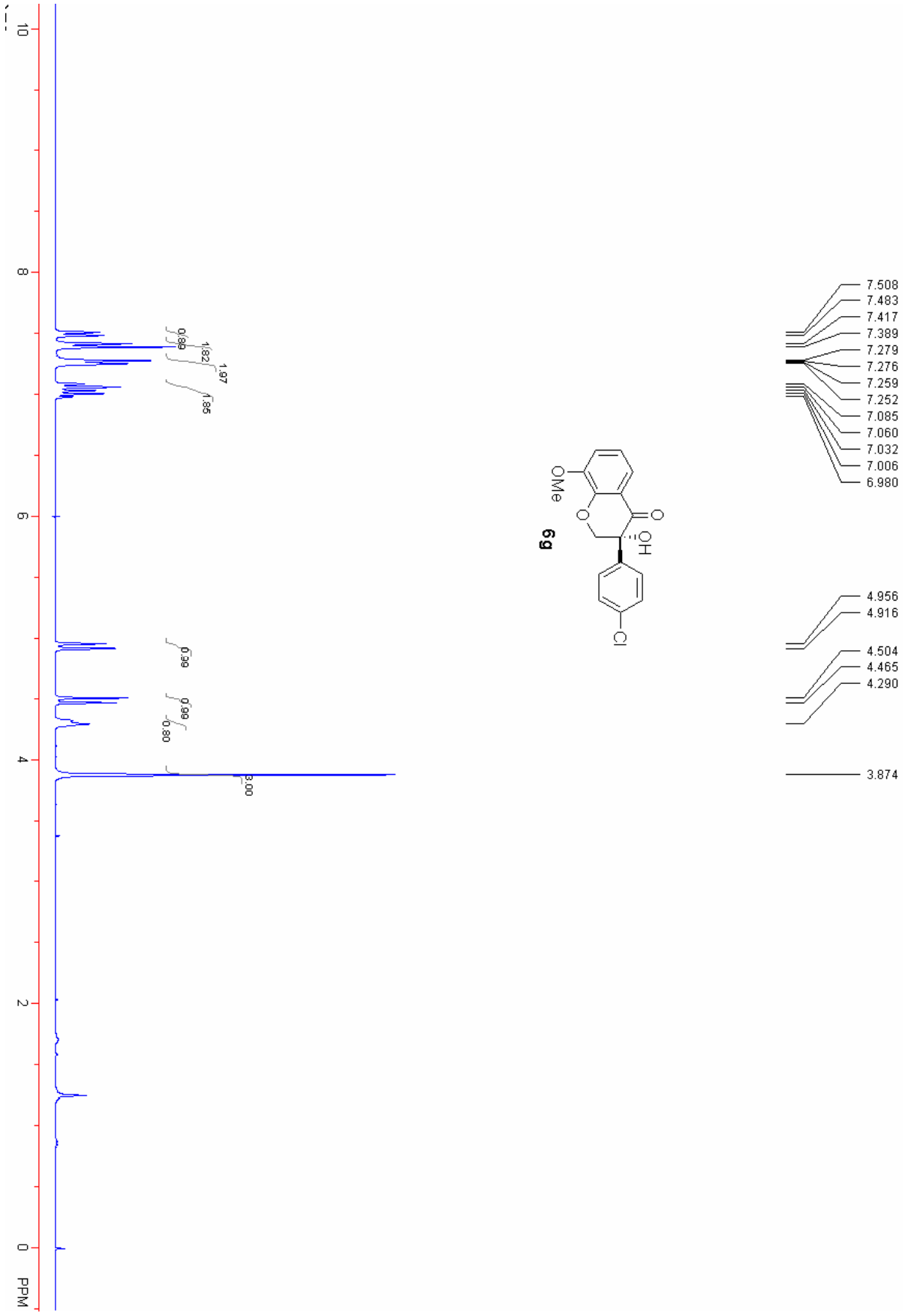
实验者：liyi
报告时间：2066-11-30,16:08:12



No.	R. Time	PeakHeight	PeakArea	PerCent
1	9.232	251650.609	4573684.500	94.8920
2	10.332	11406.304	246200.156	5.1080
总计		263056.913	4819884.656	100.0000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6
4
2
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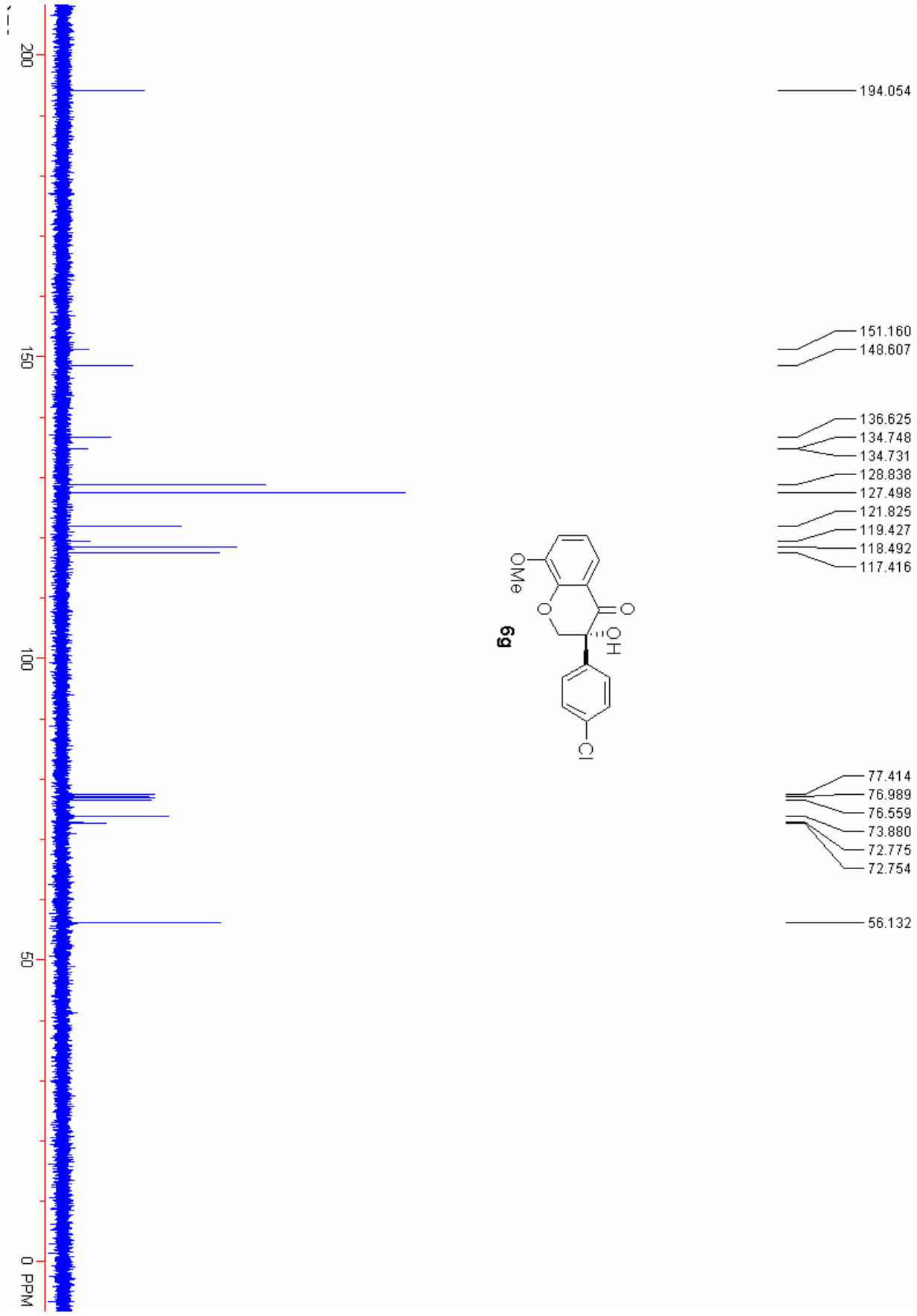
1.82
1.97
1.85
0.99
0.99
0.80
3.00
OMe
O
O
OH
Cl
6g
7.508
7.483
7.417
7.389
7.279
7.276
7.259
7.252
7.085
7.060
7.032
7.006
6.980
4.956
4.916
4.504
4.465
4.290
3.874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0 PPM
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134.748
134.731
128.838
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121.825
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118.492
117.416
77.414
76.989
76.559
73.880
72.775
72.754
56.132
OMe
O
O
OH
Cl
6g

实验时间：2066-11-16,17:00:13
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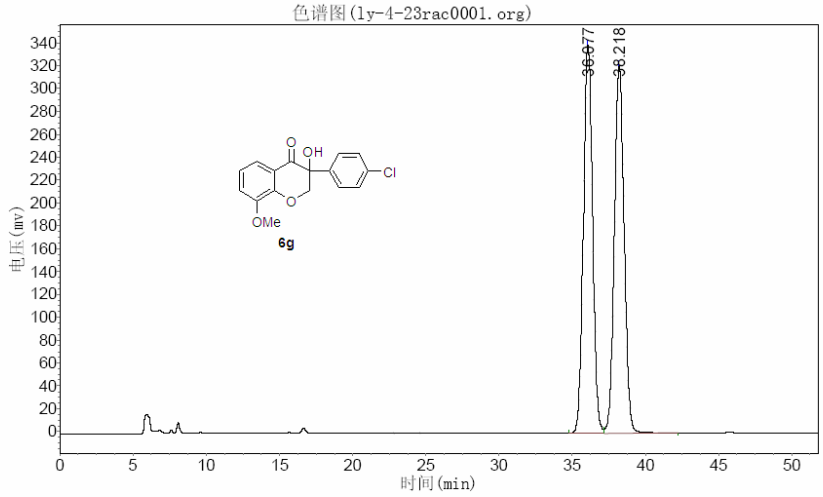
实验者：ly
报告时间：2066-11-16,17:53:46



No.	R. Time	PeakHeight	PeakArea	PerCent
1	36.077	340200.094	14889927.000	49.7251
2	38.218	321910.063	15054571.000	50.2749
总计		662110.156	29944498.000	100.0000

实验时间：2066-11-16,19:13:29
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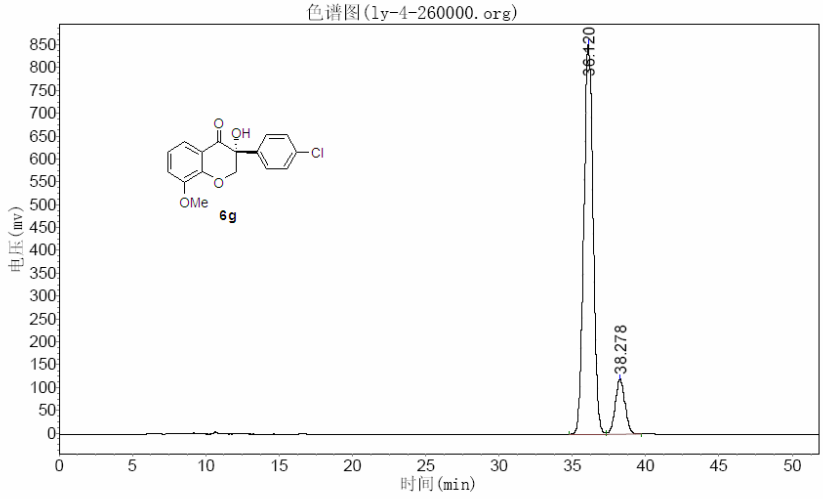
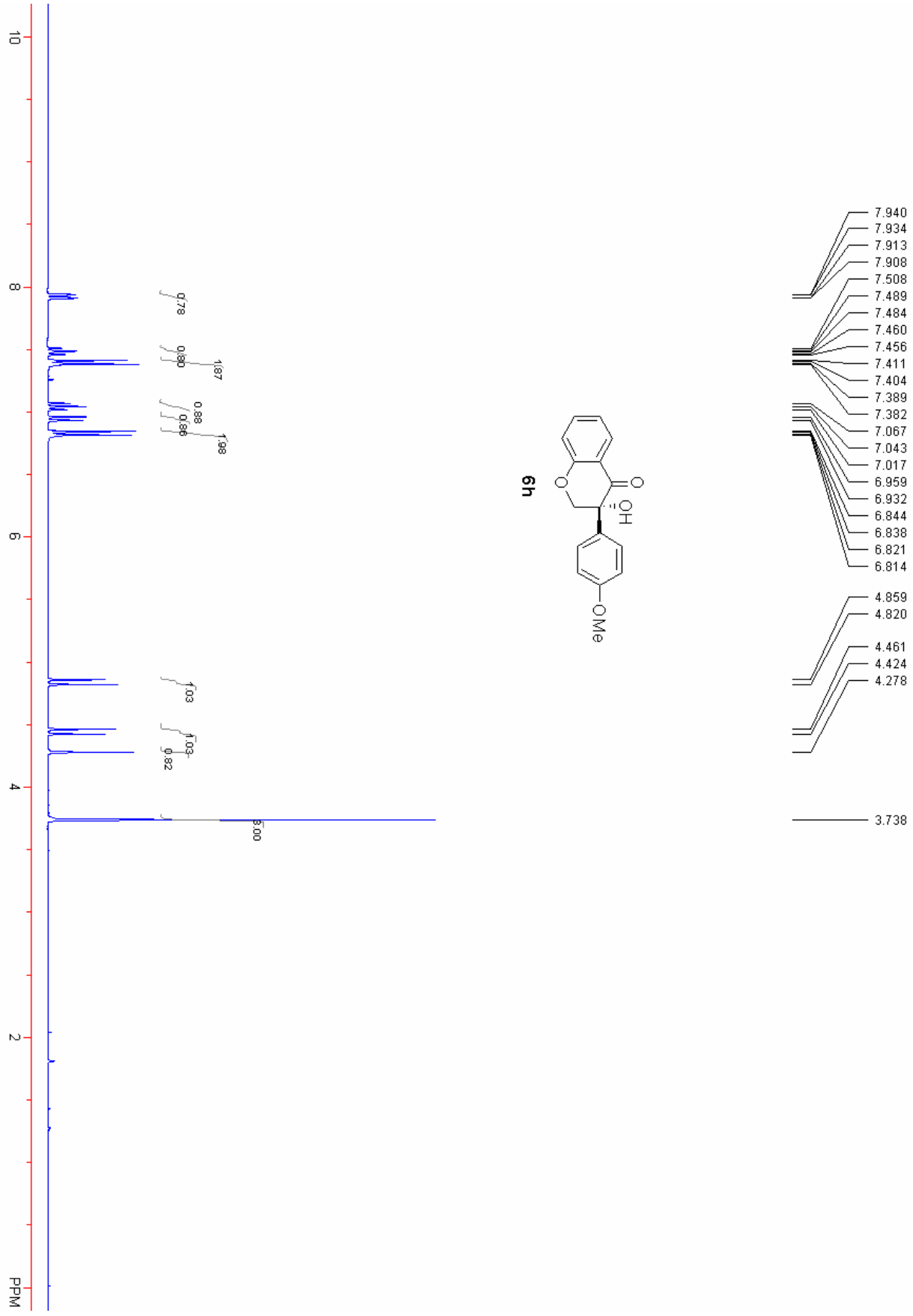
实验者：ly
报告时间：2066-11-16,19:17:44



No.	R. Time	PeakHeight	PeakArea	PerCent
1	36.120	854128.000	37443528.000	87.1682
2	38.278	120049.547	5511970.000	12.8318
总计		974177.547	42955498.000	100.0000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6
4
2
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0.86
1.98
1.03
1.03
0.82
5.00
6h
OH
O
OMe
7.940
7.934
7.913
7.908
7.508
7.489
7.484
7.460
7.456
7.411
7.404
7.389
7.382
7.067
7.043
7.017
6.959
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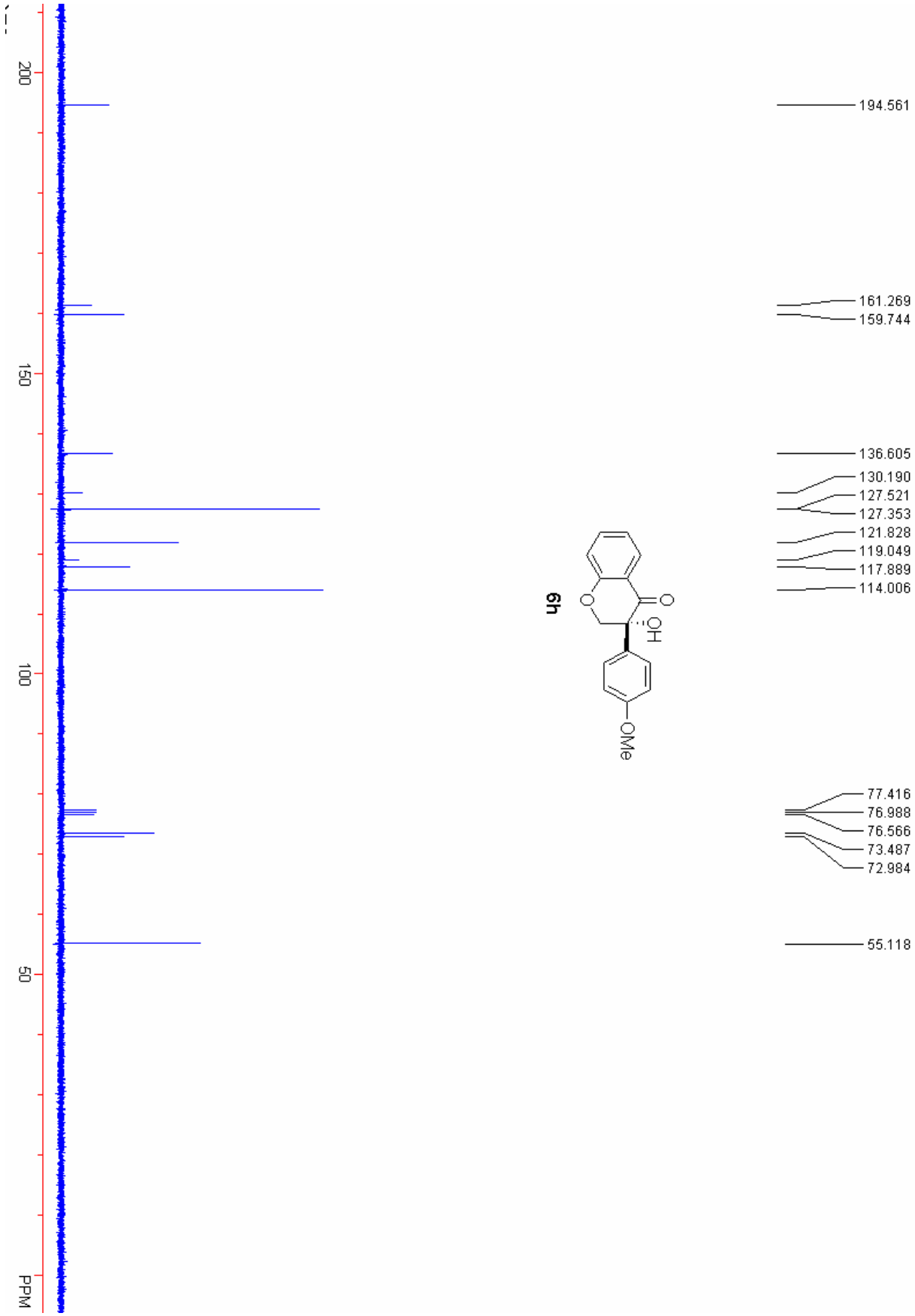
3.738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100
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130.190
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127.353
121.828
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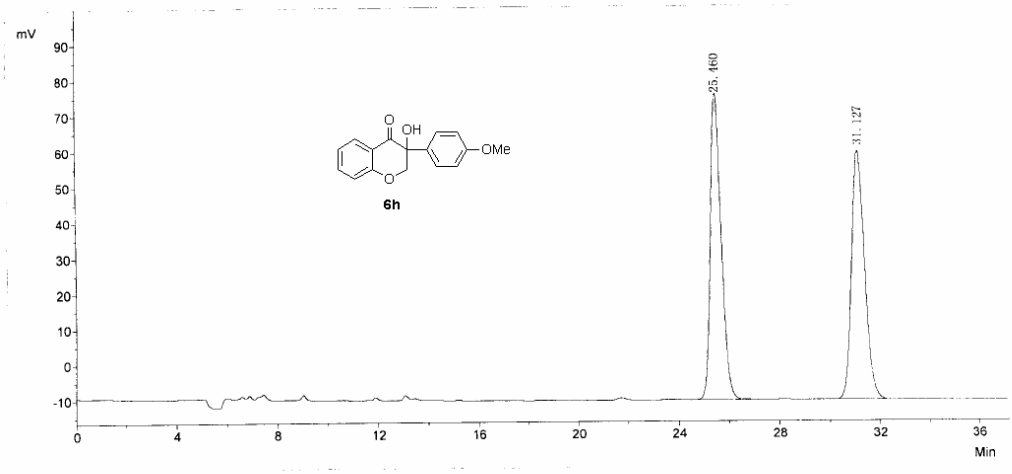
117.889
114.006
77.416
76.988
76.566
73.487
72.984
55.118
6h
O
OH
OMe

样品名称:分析谱图
分析日期:2007-10-23
色谱柱:
流速:

样品文件名:3-78.che
分析时间:10:00
流动相:
检测波长:



No.	PeakNo	R.Time	PeakHeight	PeakArea	PerCent
1	1	25.460	84451.4	2530307.5	49.9939
2	2	31.127	69722.1	2530921.1	50.0061
Total			154173.5	5061228.6	100.0000

样品名称:分析谱图
分析日期:2007-10-23
色谱柱:
流速:

样品文件名:3-79.che
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流动相:
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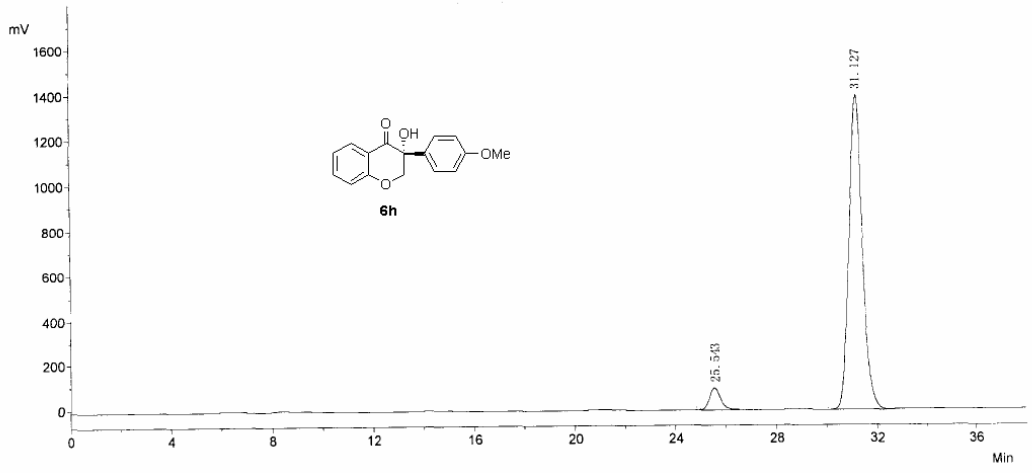
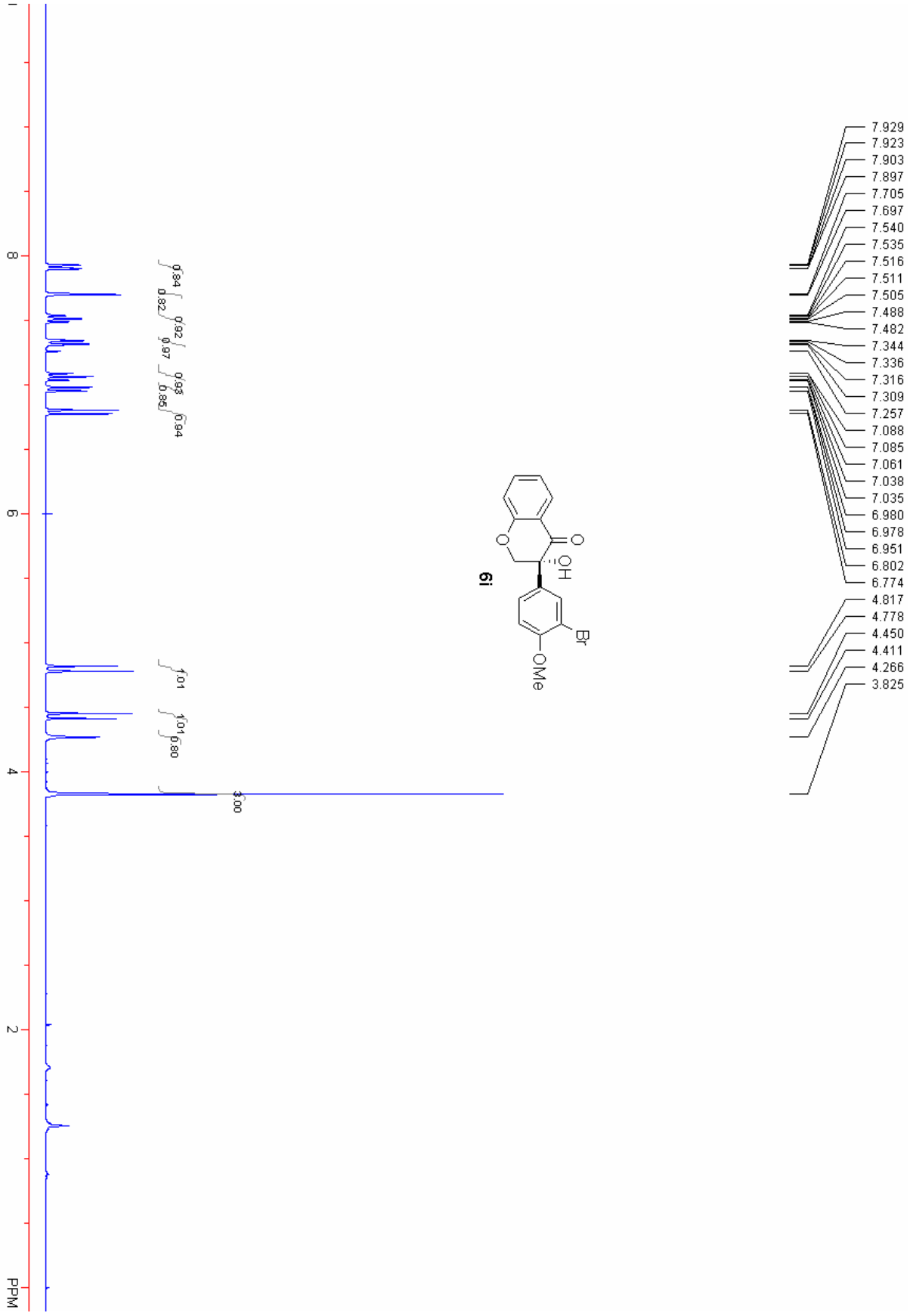


No.	PeakNo	R.Time	PeakHeight	PeakArea	PerCent
1	1	25.543	95376.0	2881659.4	5.2274
2	2	31.127	1387070.0	52244432.9	94.7726
Total			1482446.0	55126092.3	100.0000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6.978
6.951
6.802
6.774
4.817
4.778
4.450
4.411
4.266
3.825
0.84
0.82
0.92
0.97
0.93
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1.01
0.80
3.00
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O
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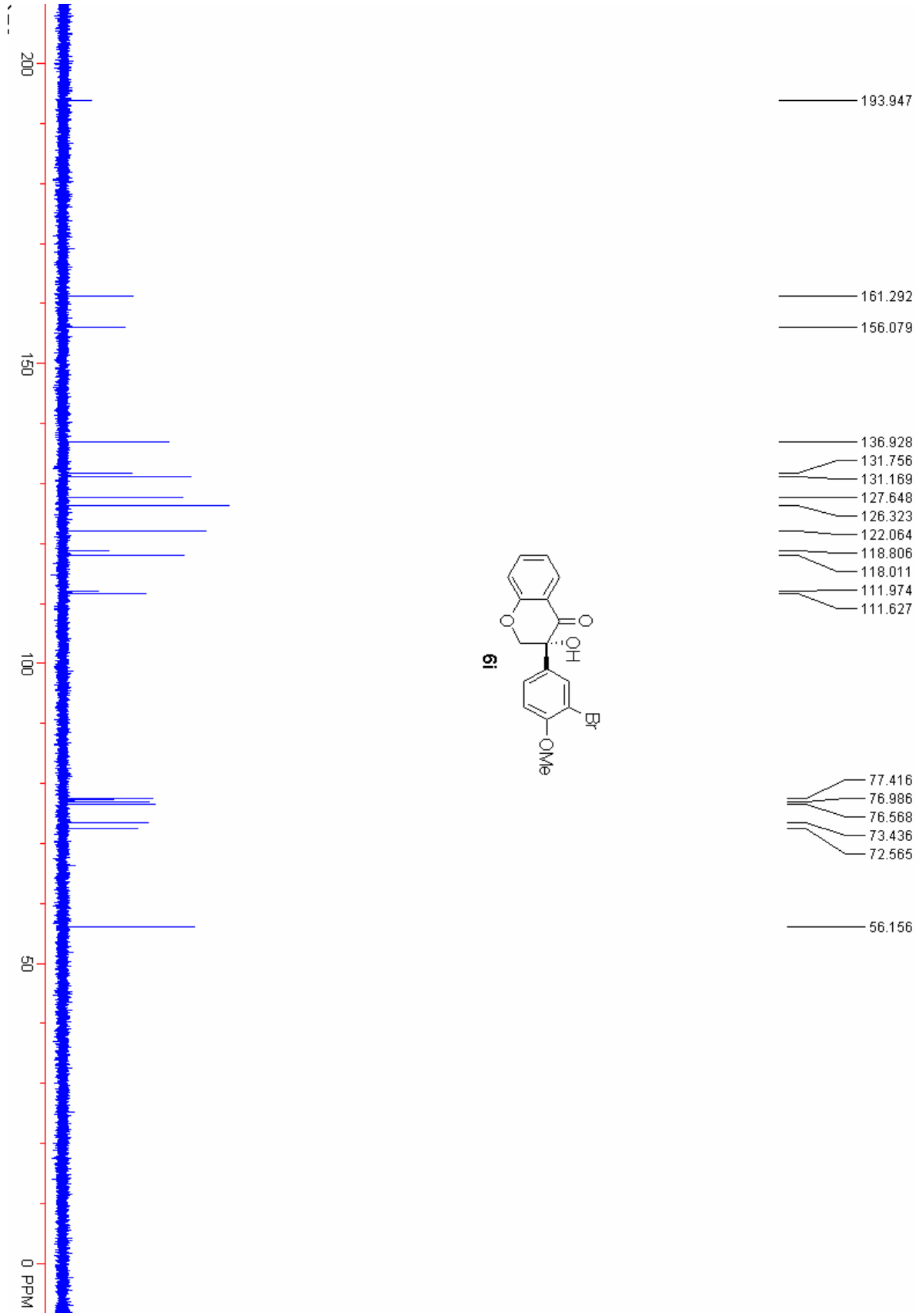
Br
OMe
8
6
4
2
PPM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118.806
118.011
111.974
111.627
77.416
76.986
76.568
73.436
72.565
56.156
6i
OH
Br
OMe

实验时间：2066-10-24,9:30:49
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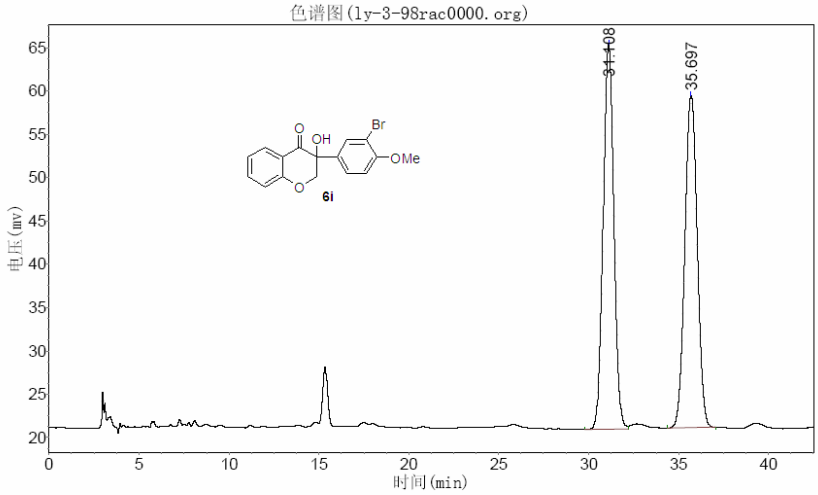
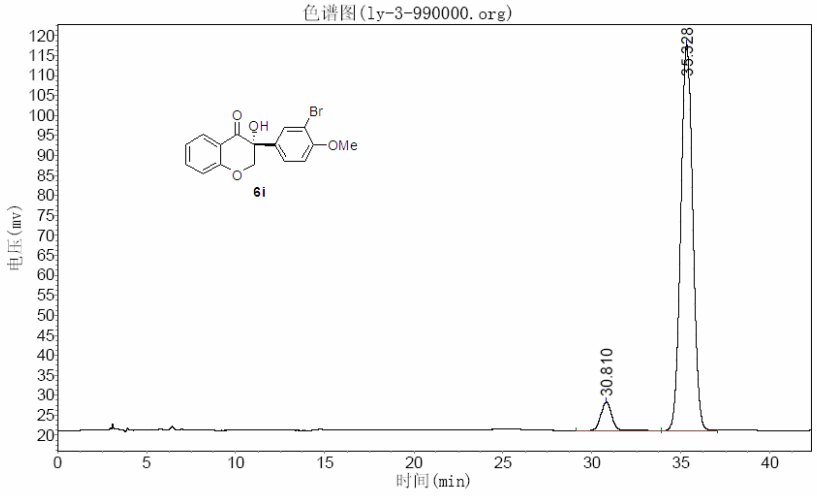
实验者：ly
报告时间：2066-10-24,9:43:25



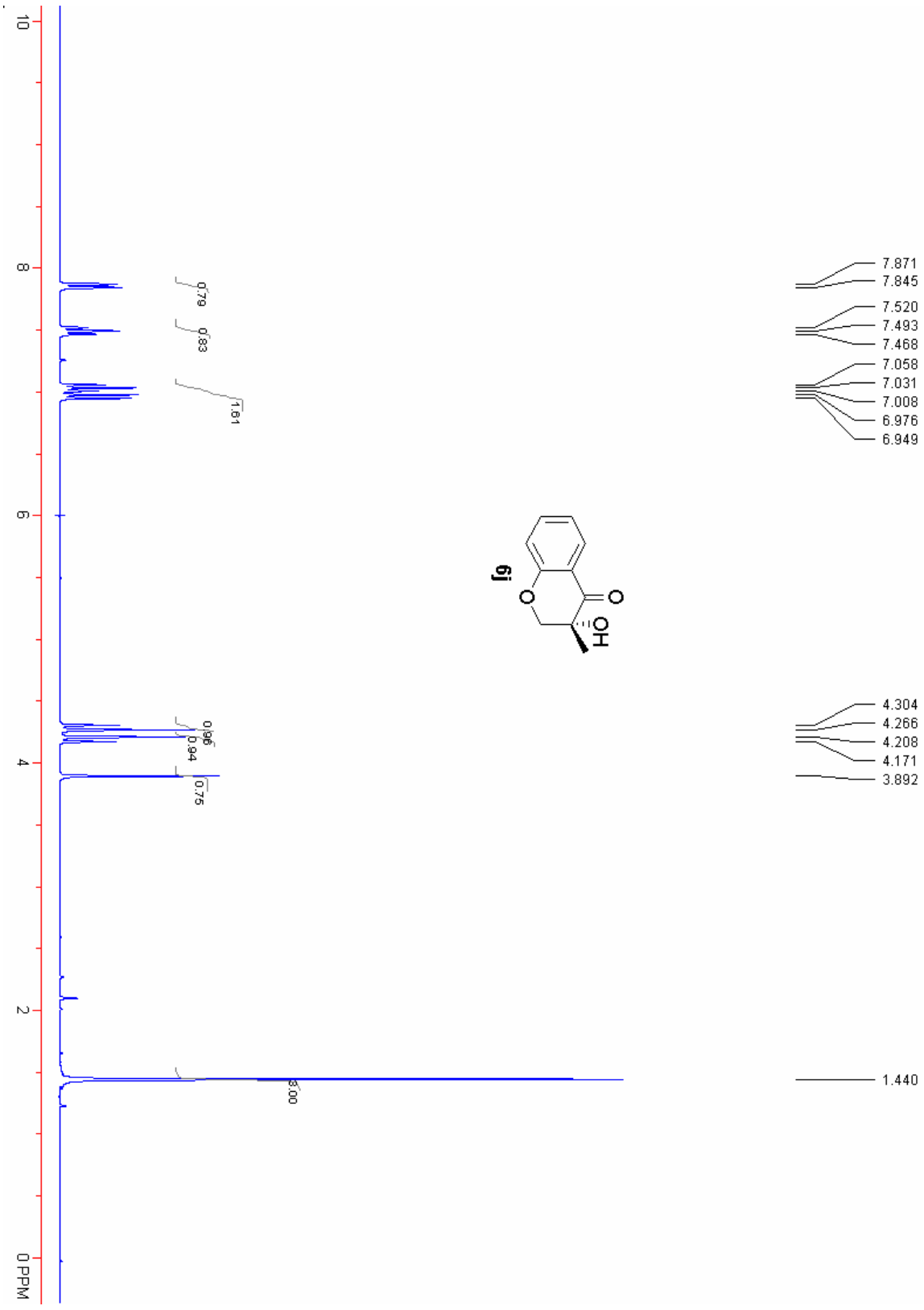
No.	R. Time	PeakHeight	PeakArea	PerCent
1	31.108	44420.879	1839343.875	50.1847
2	35.697	38339.938	1825807.750	49.8153
总计		82760.816	3665151.625	100.0000

实验时间：2066-10-24,10:20:45
谱图文件:D:\date\ly\样品\ly-3-990000.org

实验者：ly
报告时间：2066-10-24,10:22:19



No.	R. Time	PeakHeight	PeakArea	PerCent
1	30.810	7224.182	315866.063	6.5184
2	35.328	96721.672	4529857.500	93.4816
总计		103945.854	4845723.563	100.0000


10
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6
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0.96
0.94
0.75
3.00
6j
O
O
HO
7.871
7.845
7.520
7.493
7.468
7.058
7.031
7.008
6.976
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实验时间：2066-11-27,17:10:02
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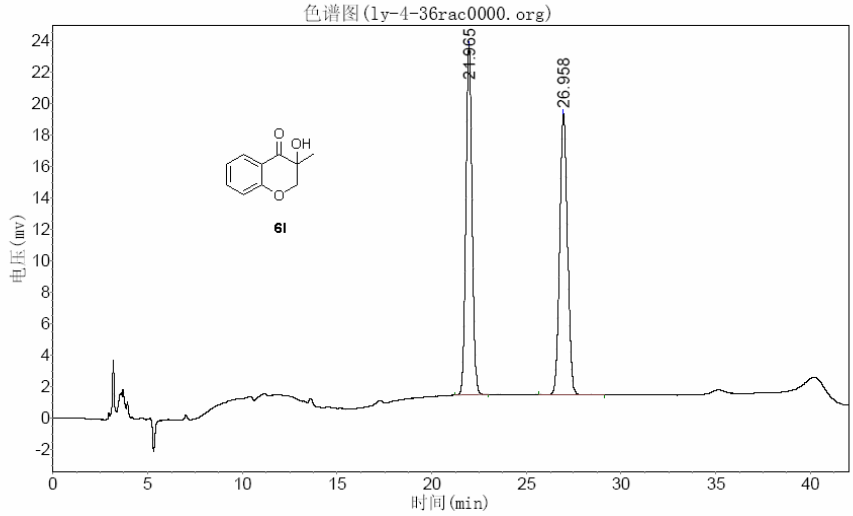
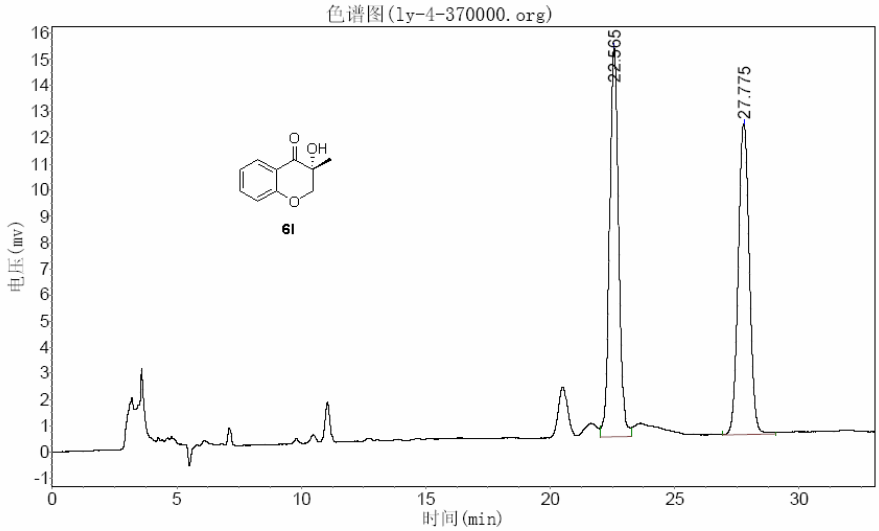
实验者：liyi
报告时间：2066-12-14,8:54:47



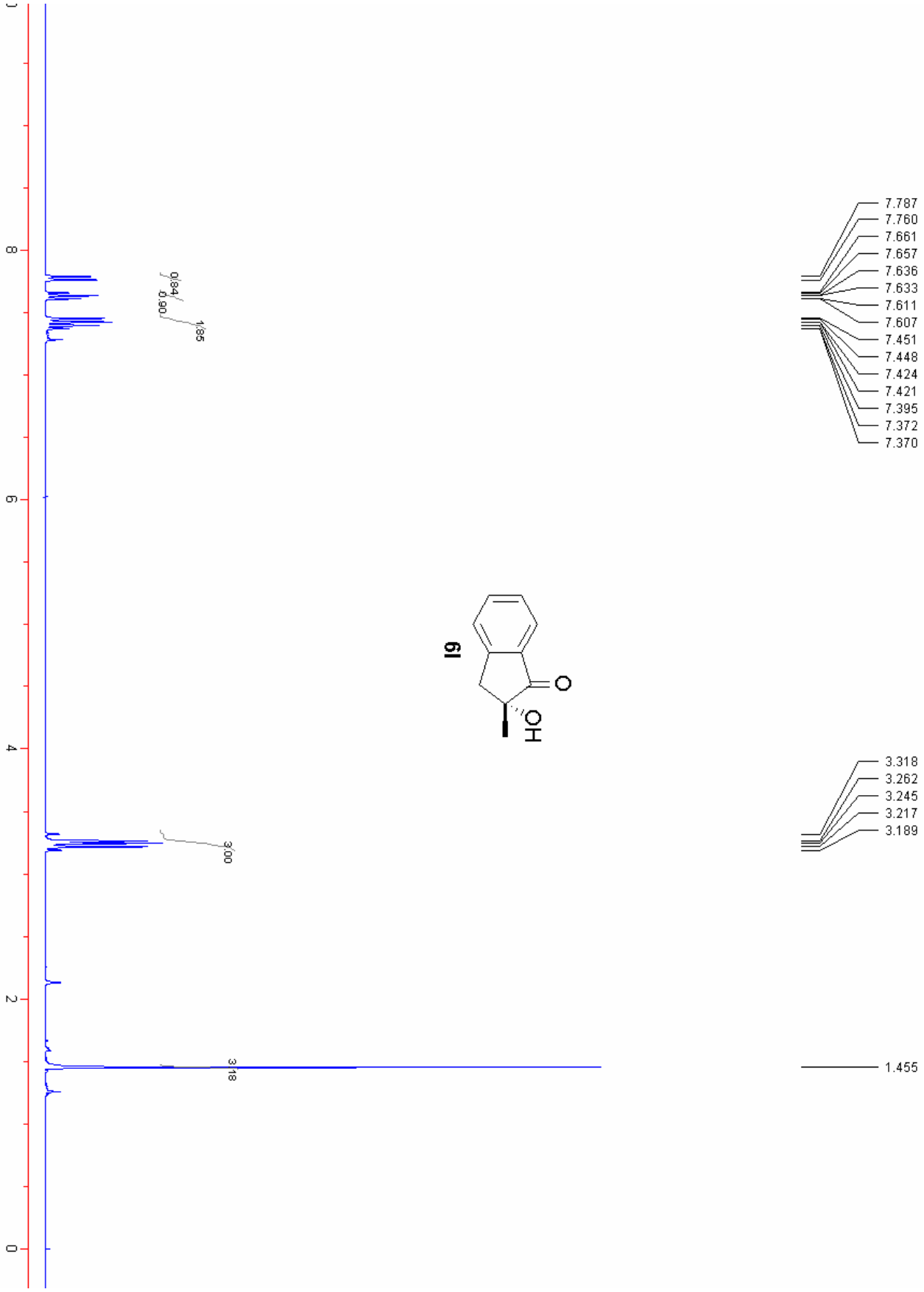
No.	R. Time	PeakHeight	PeakAera	PerCent
1	21.965	22188.908	514523.844	49.7751
2	26.958	17880.012	519173.563	50.2249
总计		40068.920	1033697.406	100.0000

实验时间：2066-11-27,18:05:50
谱图文件:D:\date\ly\样品\ly-4-370000.org

实验者：liyi
报告时间：2066-11-27,18:10:36



No.	R. Time	PeakHeight	PeakArea	PerCent
1	22.565	14862.074	379236.469	51.1234
2	27.775	11859.028	362570.000	48.8766
总计		26721.103	741806.469	100.0000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7.370
3.318
3.262
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3.217
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0.90
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3.00
3.18
8
6
4
2
0
6l
O
OH

样品名称:分析谱图
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分析日期:2007-10-25
分析时间:09:17
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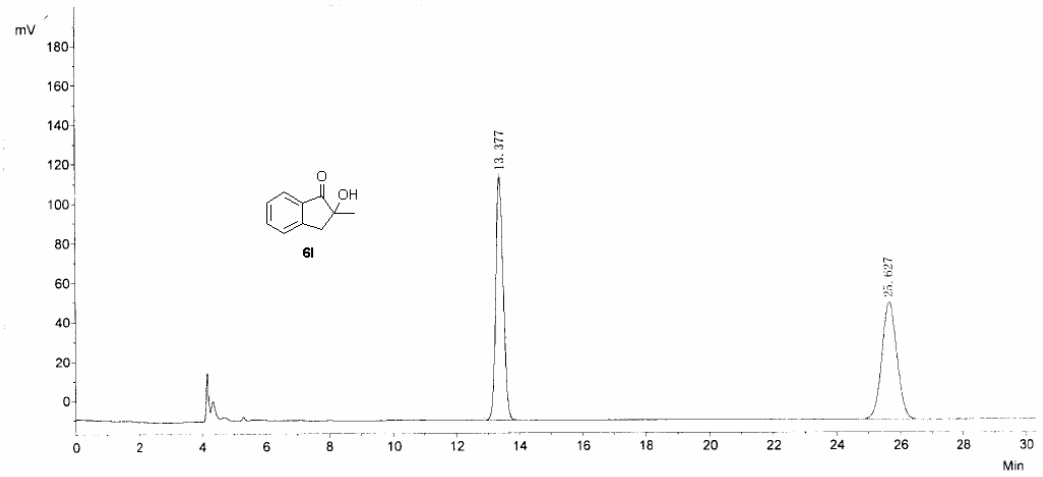
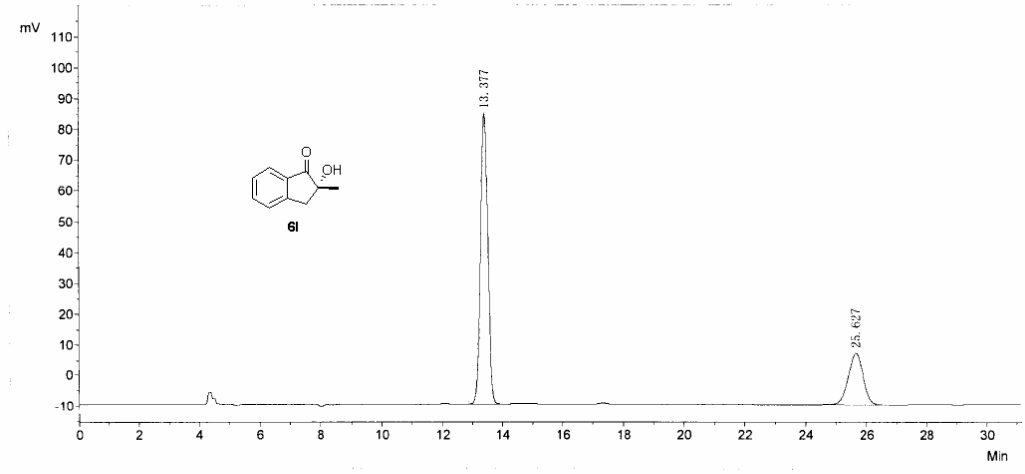
流动相:
流速:
检测波长:



No.	PeakNo	R.Time	PeakHeight	PeakArea	PerCent
1	1	13.377	123298.8	1995873.1	50.0510
2	2	25.627	58660.1	1991807.3	49.9490
Total			181958.9	3987680.4	100.0000

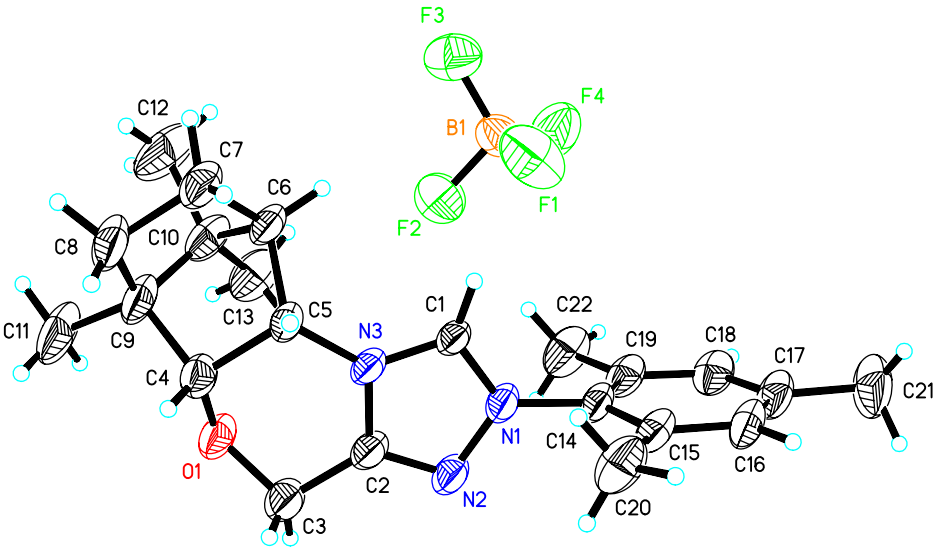
样品名称:分析谱图
样品文件名:ly-3-96.che
分析日期:2007-10-25
分析时间:09:49
色谱柱:
流动相:
流速:
检测波长:

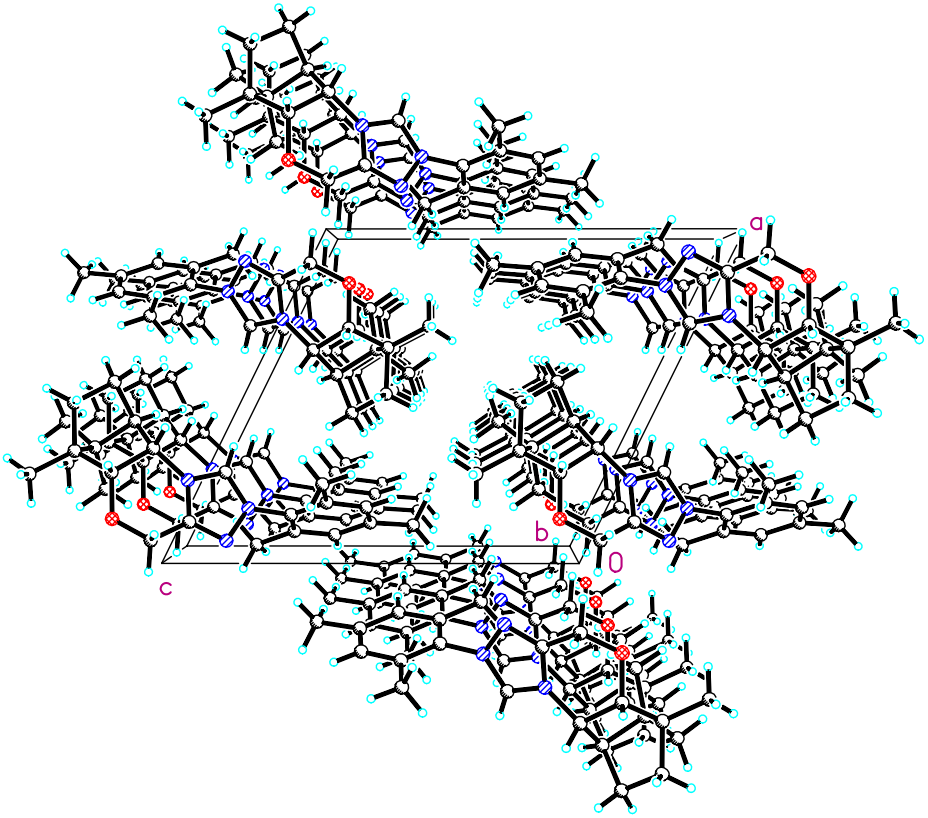


No.	PeakNo	R.Time	PeakHeight	PeakArea	PerCent
1	1	13.377	94012.0	1585212.1	73.7905
2	2	25.627	16721.8	563047.1	26.2095
Total			110733.8	2148259.2	100.0000

Table 1. Crystal data and structure refinement for Triazolium Salt **1c**.

Identification code	cd27300
Empirical formula	C22 H30 B F4 N3 O
Formula weight	439.30
Temperature	293(2) K
Wavelength	0.71073 A
Crystal system, space group	Monoclinic, P2(1)
Unit cell dimensions	a = 12.0906(18) A alpha = 90 deg.
	b = 7.9338(12) A beta = 116.257(2) deg.
	c = 13.540(2) A gamma = 90 deg.
Volume	1164.8(3) A^3
Z, Calculated density	2, 1.252 Mg/m^3
Absorption coefficient	0.099 mm^-1
F(000)	464
Crystal size	0.497 x 0.205 x 0.181 mm
Theta range for data collection	1.68 to 25.50 deg.
Limiting indices	-11<=h<=14, -9<=k<=9, -16<=l<=16
Reflections collected / unique	6146 / 2332 [R(int) = 0.1465]
Completeness to theta = 25.50	99.5 %
Absorption correction	Empirical
Max. and min. transmission	1.00000 and 0.75123
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	2332 / 1 / 287
Goodness-of-fit on F^2	0.948
Final R indices [I>2sigma(I)]	R1 = 0.0626, wR2 = 0.1517
R indices (all data)	R1 = 0.0821, wR2 = 0.1626
Absolute structure parameter	-10(10)
Extinction coefficient	0.010(4)
Largest diff. peak and hole	0.249 and -0.211 e.A^-3


F3
F4
B1
F2
F1
C12
C7
C6
C8
C10
C13
C5
C1
C22
C11
C9
N3
C19
C18
C17
C21
C4
N1
C14
C15
C16
O1
C2
N2
C20
C3


a
b
0
c