Enantioselective Organocatalytic Reductive Amination of Aliphatic Ketones by Benzothiazoline as Hydrogen Donor

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Supporting information

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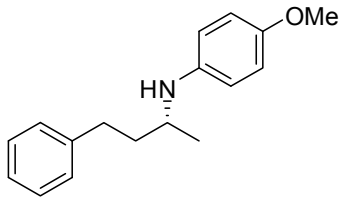
General. NMR spectra were recorded on Unity Inova-400 instrument (Varian Inc., 400 MHz for ^{1}H, 100 MHz for ^{13}C) using $CDCl_3$ as a solvent. Tetramethylsilane (TMS) (δ = 0) or $CHCl_3$ (δ = 7.27) served as an internal standard for ^{1}H NMR, and $CDCl_3$ was used as an internal standard (δ = 77.0) for ^{13}C NMR. Optical rotations were measured on a HORIBA SEPA-500 polarimeter. Purification of the products was performed by preparative TLC on silica gel (Wako gel B-5F). All solvents were purified according to the standard procedures. Benzothiazoline **1a** was synthesized according to our previous report.[1]

1. General procedure for the chiral phosphoric acid catalyzed enantioselective reductive amination using benzothiazoline

A typical procedure for the preparation of **3a** is described for the reaction of 4-phenyl-2-butanone with *p*-anisidine:

A magnetic stirrer bar and powdered molecular sieves 5A (MS 5A) (100 mg) were placed in a test tube under nitrogen atmosphere. The MS 5A were then dried with a heat gun under reduced pressure and the test tube was refilled with nitrogen. *p*-Anisidine

(12.3 mg, 0.100 mmol) , phosphoric acid **2g** (3.60 mg, 5 μmol), and benzothiazoline **1a** (30.0 mg, 0.140 mmol) were added to the test tube successively under nitrogen atmosphere at room temperature. 4-Phenyl-2-butanone (15.0 μL, 0.100 mmol) was added to the test tube using benzene (2 mL) at 20 °C. After being stirred for 2 days at the same temperature, the mixture was filtered and the filtrate was concentrated under reduced pressure, and the residue was purified by preparative thin layer chromatography on silica gel (AcOEt / hexane = 1 / 10) to give 22.1 mg (0.0870 mmol, 87%) of **3a** as pale yellow oil.



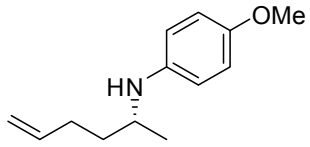
3a (87%, 97% ee)[2]

^{1}H NMR (400 MHz, $CDCl_3$) δ: 1.19 (d, *J* = 6.4 Hz, 3 H), 1.67 – 1.79 (m, 1H), 1.81 – 1.92 (m, 1H), 2.72 (dd, *J* = 8.4, 8.4 Hz, 2 H), 3.39 (ddq, *J* = 6.4, 6.4, 6.4 Hz, 1 H), 3.73 (s, 3H), 6.48 – 6.53 (m, 2 H), 6.72 – 6.78 (m, 2 H), 7.15 – 7.21 (m, 3 H), 7.24 -7.31 (m, 2 H).

^{13}C NMR (100 MHz, $CDCl_3$) δ: 20.8, 32.5, 38.8, 48.9, 55.8, 114.7, 114.9, 125.8, 128.3, 128.4, 141.7, 142.0, 151.9.

HPLC conditions: Daicel CHIRALCEL® OD-H column, hexane/2-propanol = 95/5, flow rate = 0.5 mL min^{-1}, major enantiomer: t_R =21.8 min; minor enantiomer: t_R = 24.4 min.

$[\alpha]_D^{24}$ - 7.0 (c 2.3, $CHCl_3$) [lit., $[\alpha]_D^{27}$ -2.8 (c 1.2, $CHCl_3$)][2]



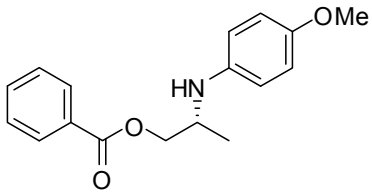
3b (97%, 95% ee)[2]

^{1}H NMR (400 MHz, $CDCl_3$) δ: 1.17 (d, *J* = 6.4 Hz, 3 H), 1.45 – 1.57 (m, 1H), 1.62 – 1.74 (m, 1H), 2.10 – 2.22 (m, 2 H), 3.40 (ddq, *J* = 6.4, 6.4, 6.4 Hz, 1 H), 3.74 (s, 3H), 4.97 (dd, *J* = 10.0, 1.2 Hz, 1 H), 5.02 (ddd, *J* = 16.4, 3.2, 1.6 Hz, 1 H), 5.75 – 5.88 (m, 1 H), 6.59 (d, *J* = 8.8 Hz, 2 H), 6.74 – 6.81 (m, 2 H).

^{13}C NMR (100 MHz, $CDCl_3$) δ: 20.5, 30.4, 36.0, 49.5, 55.8, 114.8, 114.9, 115.2, 138.3, 141.1, 152.2.

HPLC conditions: Daicel CHIRALPAK® IE column, hexane/2-propanol = 20/1, flow rate = 0.5 mL min^{-1}, major enantiomer: t_R =11.1 min; minor enantiomer: t_R = 10.6 min.

$[\alpha]_D^{24}$ - 9.9 (c 1.5, $CHCl_3$) [lit., $[\alpha]_D^{28}$ -3.8 (c 0.4, $CHCl_3$)][2]



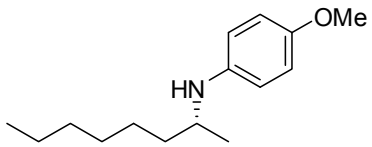
3c (64%, 91% ee)[2]

^{1}H NMR (400 MHz, $CDCl_3$) δ: 1.32 (d, *J* = 6.4 Hz, 3 H), 3.74 (s, 3H), 3.83 (ddq, *J* = 6.4, 5.8, 5.8 Hz, 1 H), 4.21 (dd, *J* = 10.8, 5.8 Hz, 1 H), 4.45 (dd, *J* = 10.8, 5.8 Hz, 1 H), 6.67 (d, *J* = 8.8 Hz, 2 H), 6.75 – 6.81 (m, 2 H), 7.43 (t, *J* = 7.6 Hz, 2 H), 7.53 – 7.59 (m, 1 H), 7.99 -8.04 (m, 2 H).

^{13}C NMR (100 MHz, $CDCl_3$) δ: 18.2, 48.9, 55.7, 67.9, 115.0, 115.1, 128.4, 129.6, 130.0, 133.0, 140.9, 152.4, 166.5.

HPLC conditions: Daicel CHIRALPAK® IE column, hexane/2-propanol = 20/1, flow rate = 1.0 mL min^{-1}, major enantiomer: t_R =22.1 min; minor enantiomer: t_R = 19.0 min.

$[\alpha]_D^{24}$ + 12.0 (c 1.8, $CHCl_3$) [lit., $[\alpha]_D^{26}$ +12.8 (c 0.2, $CHCl_3$)][2]



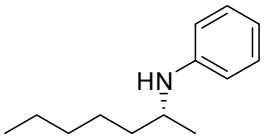
3d (80%, 95% ee)[2]

^{1}H NMR (400 MHz, $CDCl_3$) δ: 0.89 (t, *J* = 6.8 Hz, 3 H), 1.15 (d, *J* = 6.4 Hz, 3 H), 1.24 – 1.45 (m, 9 H), 1.51 – 1.62 (m, 1H), 3.36 (ddq, *J* = 6.4, 6.4, 6.4 Hz, 1 H), 3.75 (s, 3H), 6.54 – 6.60 (m, 2 H), 6.75 – 6.81 (m, 2 H).

^{13}C NMR (100 MHz, $CDCl_3$) δ: 14.1, 20.7, 22.6, 26.1, 29.4, 31.8, 37.2, 49.6, 55.8, 114.8, 114.9, 141.7, 151.8.

HPLC conditions: Daicel CHIRALPAK® IE column, hexane/2-propanol = 20/1, flow rate = 0.5 mL min^{-1}, major enantiomer: t_R =10.6 min; minor enantiomer: t_R = 9.9 min.

$[\alpha]_D^{24}$ - 6.9 (c 1.8, $CHCl_3$) [lit., $[\alpha]_D^{27}$ -8.0 (c 1.1, $CHCl_3$)][2]



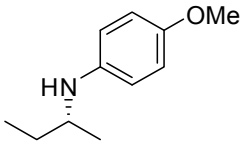
3e (77%, 94% ee)[3]

^{1}H NMR (400 MHz, $CDCl_3$) δ: 0.89 (t, *J* = 6.8 Hz, 3 H), 1.18 (d, *J* = 6.4 Hz, 3 H), 1.24 – 1.48 (m, 7 H), 1.50 – 1.63 (m, 1H), 3.36 (ddq, *J* = 6.4, 6.4, 6.4 Hz, 1 H), 6.55 – 6.61 (m, 2 H), 6.63 – 6.69 (m, 1 H), 7.13 – 7.20 (m, 2 H).

^{13}C NMR (100 MHz, $CDCl_3$) δ: 14.0, 20.7, 22.6, 25.8, 31.9, 37.1, 48.5, 113.1, 116.8, 129.2, 147.6.

HPLC conditions: Daicel CHIRALCEL® OD-H column, hexane/2-propanol = 99/1, flow rate = 0.5 mL min^{-1}, major enantiomer: t_R =11.1 min; minor enantiomer: t_R = 12.1 min.

$[\alpha]_D^{24}$ - 17.2 (c 1.4, $CHCl_3$).



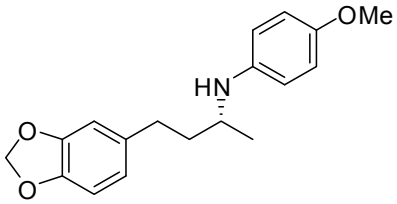
3f (99%, 86% ee)[2]

^{1}H NMR (400 MHz, $CDCl_3$) δ: 0.94 (t, *J* = 7.6 Hz, 3 H), 1.15 (d, *J* = 6.4 Hz, 3 H), 1.38 – 1.50 (m, 1 H), 1.54 – 1.66 (m, 1H), 3.31 (ddq, *J* = 6.4, 6.4, 6.4 Hz, 1 H), 3.74 (s, 3H), 6.55 – 6.61 (m, 2 H), 6.74 – 6.80 (m, 2 H).

^{13}C NMR (100 MHz, $CDCl_3$) δ: 10.3, 20.1, 29.5, 51.0, 55.8, 114.89, 114.94, 141.6, 151.9.

HPLC conditions: Daicel CHIRALCEL® AS-H column, hexane/2-propanol = 95/5, flow rate = 1.0 mL min^{-1}, major enantiomer: t_R =10.5 min; minor enantiomer: t_R = 8.2 min.

$[\alpha]_D^{24}$ - 17.9 (c 1.6, $CHCl_3$) [lit., $[\alpha]_D^{28}$ -25.2 (c 0.2, $CHCl_3$)][5]



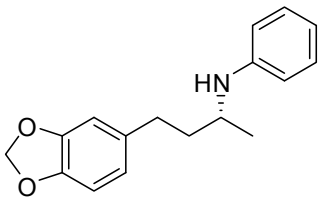
3g (98%, 97% ee)[3]

^{1}H NMR (400 MHz, $CDCl_3$) δ: 1.18 (d, *J* = 6.4 Hz, 3 H), 1.63 – 1.74 (m, 1 H), 1.75 – 1.87 (m, 1H), 2.64 (dd, *J* = 7.8, 7.8 Hz, 2 H), 3.38 (ddq, *J* = 6.4, 6.4, 6.4 Hz, 1 H), 3.74 (s, 3H), 5.91 (s, 2 H), 6.48 – 6.55 (m, 2 H), 6.59 – 6.64 (m, 1 H), 6.65 – 6.68 (m, 1 H), 6.72 (d, *J* = 8.0 Hz, 1 H)), 6.72 – 6.79 (m, 2 H).

^{13}C NMR (100 MHz, $CDCl_3$) δ: 20.8, 32.2, 39.0, 48.9, 55.8, 100.7, 108.1, 108.8, 114.8, 114.9, 121.1, 135.9, 141.6, 145.6, 147.5, 151.9.

HPLC conditions: Daicel CHIRALCEL® OD-H column, hexane/2-propanol = 98/2, flow rate = 1.0 mL min^{-1}, major enantiomer: t_R =32.9 min; minor enantiomer: t_R = 26.9 min.

$[\alpha]_D^{24}$ - 16.2 (c 1.9, $CHCl_3$).



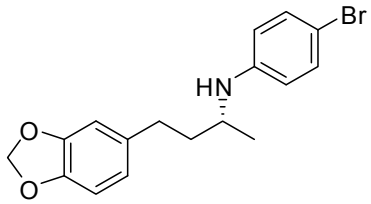
3h (85%, 97% ee)[3]

^{1}H NMR (400 MHz, $CDCl_3$) δ: 1.20 (d, *J* = 6.4 Hz, 3 H), 1.66 – 1.77 (m, 1 H), 1.77 – 1.88 (m, 1H), 2.64 (dd, *J* = 7.8, 7.8 Hz, 2 H), 3.47 (ddq, *J* = 6.4, 6.4, 6.4 Hz, 1 H), 5.91 (s, 2 H), 6.51 – 6.57 (m, 2 H), 6.59 – 6.64 (m, 1 H), 6.64 – 6.70 (m, 2 H), 6.72 (d, *J* = 8.0 Hz, 1 H), 7.11 – 7.18 (m, 2 H).

^{13}C NMR (100 MHz, $CDCl_3$) δ: 20.8, 32.2, 39.0, 47.9, 100.7, 108.1, 108.8, 113.3, 117.1, 121.1, 129.3, 135.8, 145.6, 147.4, 147.5.

HPLC conditions: Daicel CHIRALCEL® OD-H column, hexane/2-propanol = 98/2, flow rate = 1.0 mL min^{-1}, major enantiomer: t_R =22.2 min; minor enantiomer: t_R = 20.2 min.

$[\alpha]_D^{24}$ - 11.4 (c 2.2, $CHCl_3$).



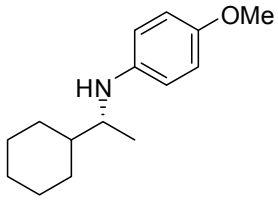
3h (86%, 96% ee)[3]

^{1}H NMR (400 MHz, $CDCl_3$) δ: 1.18 (d, *J* = 6.4 Hz, 3 H), 1.64 – 1.86 (m, 2 H), 2.62 (dd, *J* = 7.8, 7.8 Hz, 2 H), 3.40 (ddq, J = 6.4, 6.4, 6.4 Hz, 1 H), 5.91 (s, 2 H), 6.36 – 6.42 (m, 2 H), 6.57 – 6.62 (m, 1 H), 6.63 – 6.66 (m, 1 H), 6.71 (d, *J* = 7.6 Hz, 1 H), 7.18 – 7.24 (m, 2 H).

^{13}C NMR (100 MHz, $CDCl_3$) δ: 20.6, 32.1, 38.8, 47.8, 100.7, 108.1, 108.4, 108.8, 114.7, 121.1, 131.9, 135.5, 145.6, 146.4, 147.6.

HPLC conditions: Daicel CHIRALCEL® OD-H column, hexane/2-propanol = 99/1, flow rate = 1.0 mL min^{-1}, major enantiomer: t_R =47.3 min; minor enantiomer: t_R = 42.7 min.

$[\alpha]_D^{24}$ - 16.8 (c 2.7, $CHCl_3$).



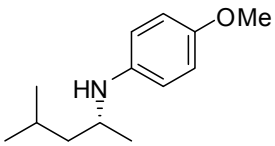
3h (82%, 97% ee)[2]

^{1}H NMR (400 MHz, $CDCl_3$) δ: 1.08 (d, *J* = 6.4 Hz, 3 H), 0.97 – 1.32 (m, 5 H), 1.38 – 1.49 (m, 1 H), 1.62 – 1.85 (m, 5 H), 3.22 (dq, *J* = 6.4, 6.0 Hz, 1 H), 3.74 (s, 3 H), 6.54 (d, *J* = 8.8 Hz, 2 H), 6.76 (d, *J* = 9.2 Hz, 1 H).

^{13}C NMR (100 MHz, $CDCl_3$) δ: 17.3, 26.3, 26.5, 26.6, 28.2, 29.8, 42.8, 54.1, 55.8, 114.5, 114.9, 142.2, 151.6.

HPLC conditions: Daicel CHIRALCEL® OD-H column, hexane/2-propanol = 99/1, flow rate = 0.5 mL min^{-1}, major enantiomer: t_R =13.3 min; minor enantiomer: t_R = 14.8 min.

$[\alpha]_D^{26}$ - 6.9 (c 1.5, $CHCl_3$) [lit., $[\alpha]_D^{28}$ -4.3 (c 1.1, $CHCl_3$)][2]



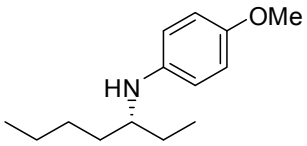
3i (55%, 97% ee)[3]

^{1}H NMR (400 MHz, $CDCl_3$) δ: 0.90 (d, *J* = 6.4 Hz, 3 H), 0.93 (d, *J* = 6.4 Hz, 3 H), 1.13 (d, *J* = 6.4 Hz, 3 H), 1.18 – 1.27 (m, 1 H), 1.41 – 1.50 (m, 1 H), 1.75 (dq, *J* = 6.8, 6.4 Hz, 1 H), 3.43 (ddq, *J* = 6.4, 6.4, 6.4 Hz, 1 H), 3.74 (s, 3 H), 6.53 – 6.59 (m, 2 H), 6.74 – 6.79 (m, 2 H).

^{13}C NMR (100 MHz, $CDCl_3$) δ: 21.0, 22.5, 23.0, 25.1, 46.9, 47.6, 55.8, 114.7, 114.9, 141.8, 151.8.

HPLC conditions: Daicel CHIRALCEL® AS-H column, hexane/2-propanol = 99/1, flow rate = 0.3 mL min^{-1}, major enantiomer: t_R =21.8 min; minor enantiomer: t_R = 23.2 min.

$[\alpha]_D^{24}$ - 12.7 (c 1.1, $CHCl_3$).



3j (35%, 68% ee)[3]

^{1}H NMR (400 MHz, $CDCl_3$) δ: 0.89 (t, *J* = 7.6 Hz, 3 H), 0.91 (t, *J* = 7.6 Hz, 3 H), 1.24 – 1.62 (m, 8 H), 3.10 (brs, 1 H), 3.18 (dddd, *J* = 6.0, 6.0, 6.0, 6.0 Hz, 1 H), 3.73 (s, 3 H), 6.51 – 6.57 (m, 2 H), 6.73 – 6.79 (m, 2 H).

^{13}C NMR (100 MHz, $CDCl_3$) δ: 10.0, 14.1, 22.8, 27.1, 28.1, 34.0, 55.0, 55.8, 114.3, 114.9, 142.4, 151.5.

HPLC conditions: Daicel CHIRALCEL® AS-H column, hexane/2-propanol = 99/1, flow rate = 0.5 mL min^{-1}, major enantiomer: t_R =11.4 min; minor enantiomer: t_R = 10.3 min.

$[\alpha]_D^{24}$ + 11.5 (c 2.5, $CHCl_3$).

2. General procedure for reductive amination (syntheses of racemic products)

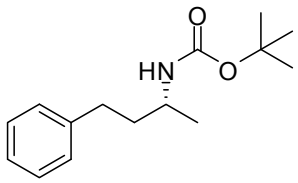
A typical procedure for the preparation of *rac*-**3a** is described for the reaction of 4-phenyl-2-butanone and *p*-anisidine:

A magnetic stirrer bar and powdered molecular sieves 5A (MS 5A) (100 mg) were placed in a test tube under nitrogen atmosphere. The MS 5A were then dried with a heat gun under reduced pressure and the test tube was refilled with nitrogen. *p*-Anisidine (24.6 mg, 0.200 mmol), 4-phenyl-2-butanone (30.0 μL, 0.200 mmol), and benzene (1 mL) were added to the test tube successively under nitrogen atmosphere at room temperature. After the mixture was stirred for 1 days, the mixture was filtered and the filtrate was concentrated under reduced pressure. The residue was diluted by MeOH (2 mL), and $NaBH_4$ (24.0 mg, 0.634 mmol) was added to the mixture at room temperature. After 5 min, AcOH (6.00 μL, 0.105 mmol) was slowly added to the mixture at the same time and stirred for 1 day. Saturated aqueous $NaHCO_3$ solution (5 mL) was added to the mixture and extracted with CH_2Cl_2 (10 mL × 3), dried over anhydrous Na_2SO_4. The filtrate was evaporated under reduced pressure. The residue was purified by preparative thin layer chromatography on silica gel (AcOEt / hexane = 1 / 10) to give 19.0 mg (0.0744 mmol, 37%) of *rac*-**3a** as pale yellow oil.

$NaBH_3CN$ was used instead of $NaBH_4$ for the preparation of *rac*-**3c**.

3. Deprotection of PMP group on **3a**[4]

The reaction was carried out under air. To a solution of **3a** (51.0 mg, 0.200 mmol), MeCN (2 mL), and H_2O (2 mL) were added trichloroisocyanuric acid (TCCA) (0.230 g, 0.100 mmol) and 1 M aqueous H_2SO_4 (0.2 mL). The mixture was stirred for 20 h at room temperature and then washed CH_2Cl_2 (10 mL × 3). The resulting aqueous phase was subsequently brought to pH 10.5 by addition of 5 M aqueous KOH (3 mL) and extracted with AcOEt (15 mL × 4). The combined organic layers were dried over anhydrous Na_2SO_4. The organic material was filtered and the filtrate was concentrated under reduced pressure. The crude material was diluted with CH_2Cl_2 (1 mL), NEt_3 (0.140 mL, 1.0 mmol), and Boc_2O (0.140 mL, 0.6 mmol) successively added to the mixture at room temperature. After 12 h, the mixture was concentrated under reduced pressure. The crude material was purified by preparative thin layer chromatography on silica gel (AcOEt / hexane = 1 / 10) to give 39.1 mg (0.157 mmol, 79%) of **5** as white solid.



5 (79%, 97% ee)[5]

^{1}H NMR (400 MHz, $CDCl_3$) δ: 1.15 (d, *J* = 6.4 Hz, 3 H), 1.45 (s, 9 H), 1.66 – 1.78 (m, 2 H), 2.60 – 2.70 (m, 2 H), 3.71 (brs, 1 H), 4.37 (brs, 1 H), 7.15 – 7.21 (m, 3 H), 7.24 – 7.31 (m, 2 H).

^{13}C NMR (100 MHz, $CDCl_3$) δ: 21.4, 28.4, 32.5, 39.2, 46.4, 79.0, 125.8, 128.3, 128.4, 141.9, 155.3.

HPLC conditions: Daicel CHIRALCEL® OD-H column, hexane/2-propanol = 96/4, flow rate = 0.5 mL min^{-1}, major enantiomer: t_R =14.96 min; minor enantiomer: t_R = 13.6 min.

$[\alpha]_D^{24}$ + 12.0 (c 3.5, $CHCl_3$) [lit., $[\alpha]_D^{25}$ +13.9 (c 0.9, $CHCl_3$)][5]

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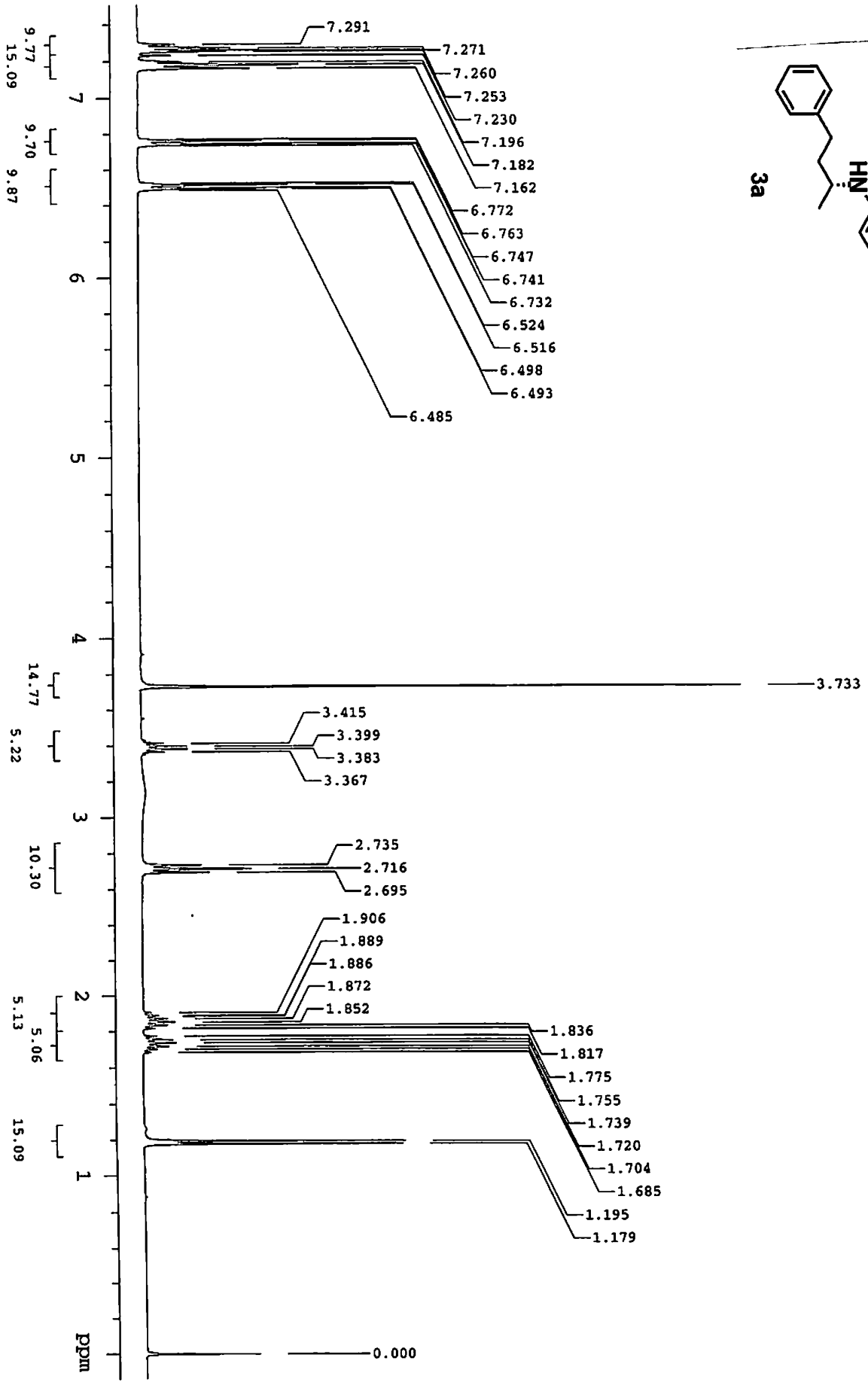
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6.493
6.485
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3.415
3.399
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2.716
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1.179
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ppm
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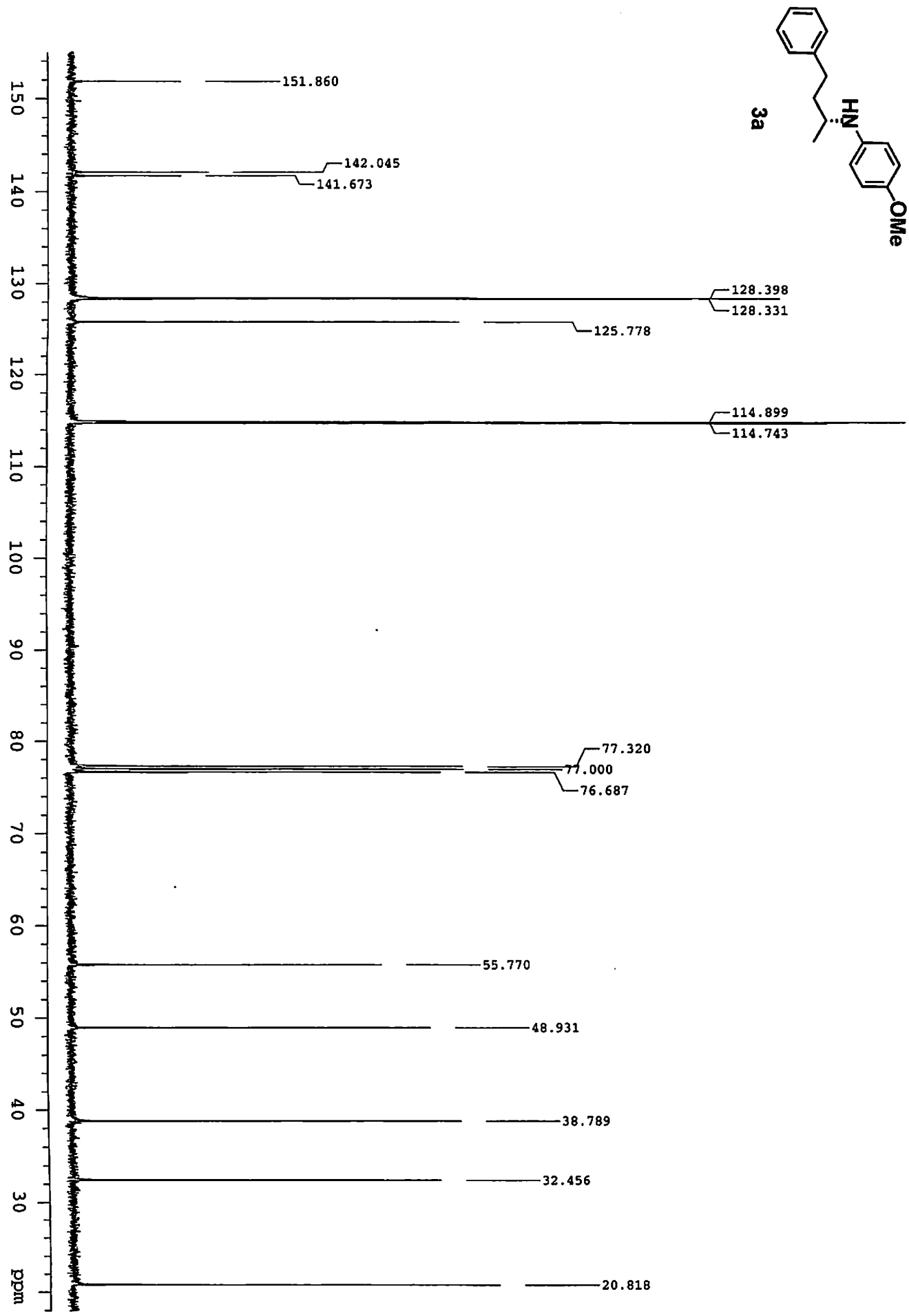
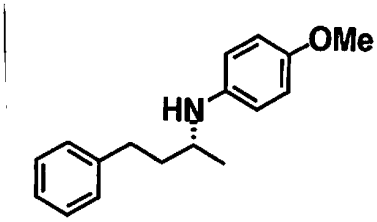
3a
HN
OMe





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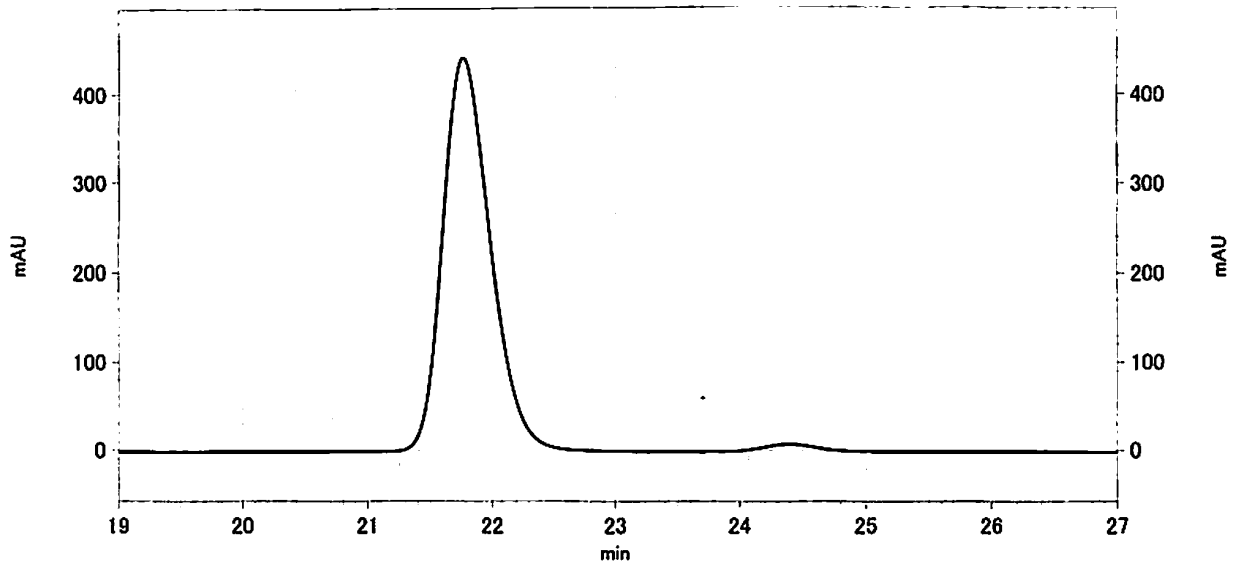

Pk #	Time	Area	Area%	Type
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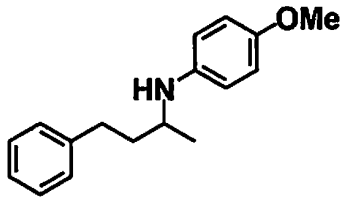
2	24.39	721788	1.514	BI



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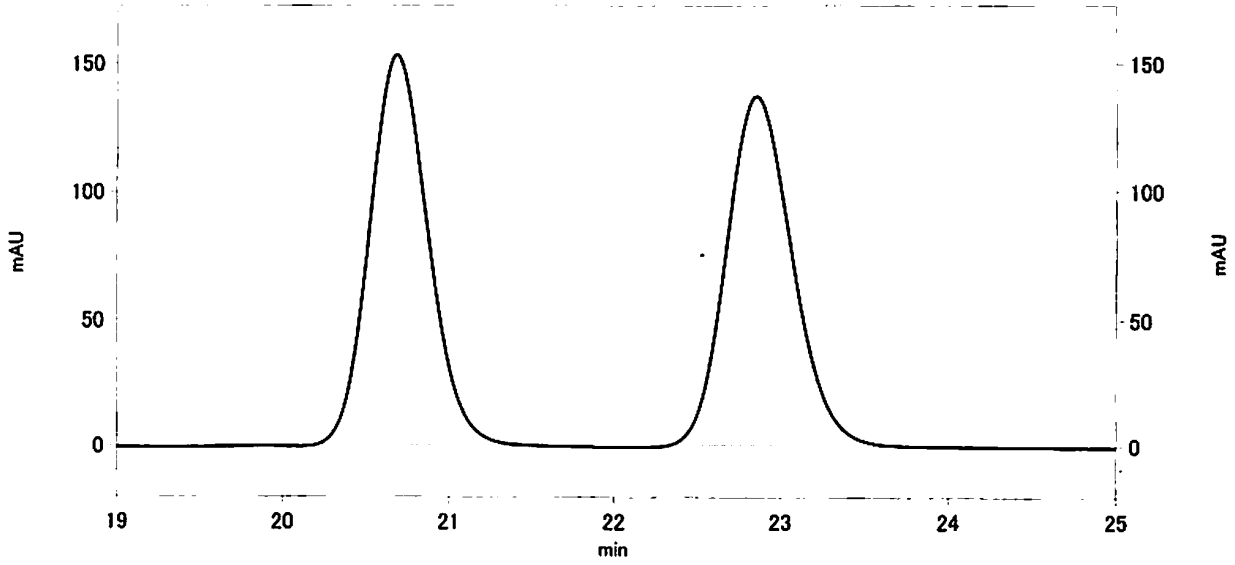

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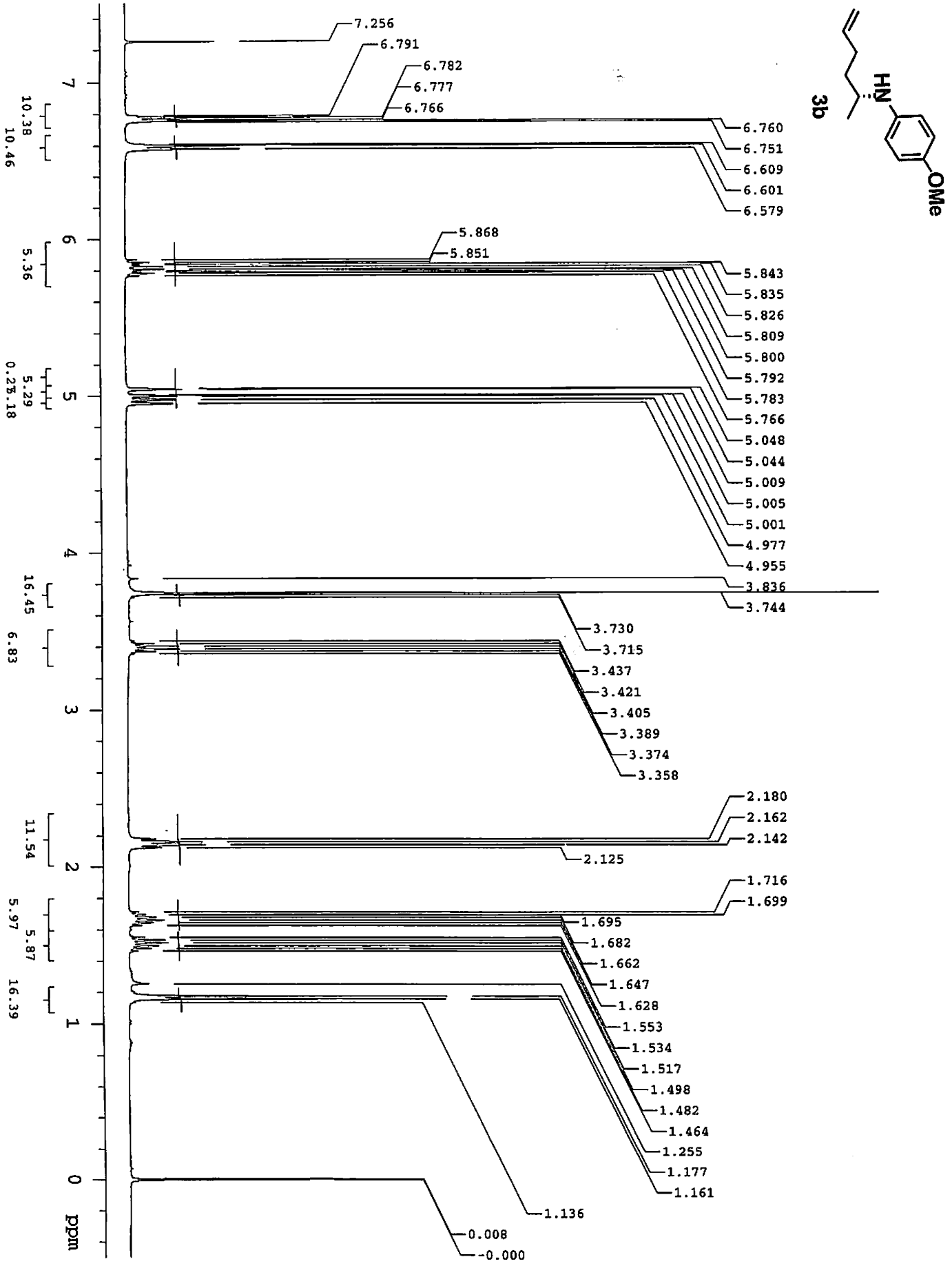
2	22.85	15006321	49.951	BB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6.601
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5.868
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5.826
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5.792
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5.048
5.044
5.009
5.005
5.001
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4.955
3.836
3.744
3.730
3.715
3.437
3.421
3.405
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3.374
3.358
2.180
2.162
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1.699
1.695
1.682
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1.647
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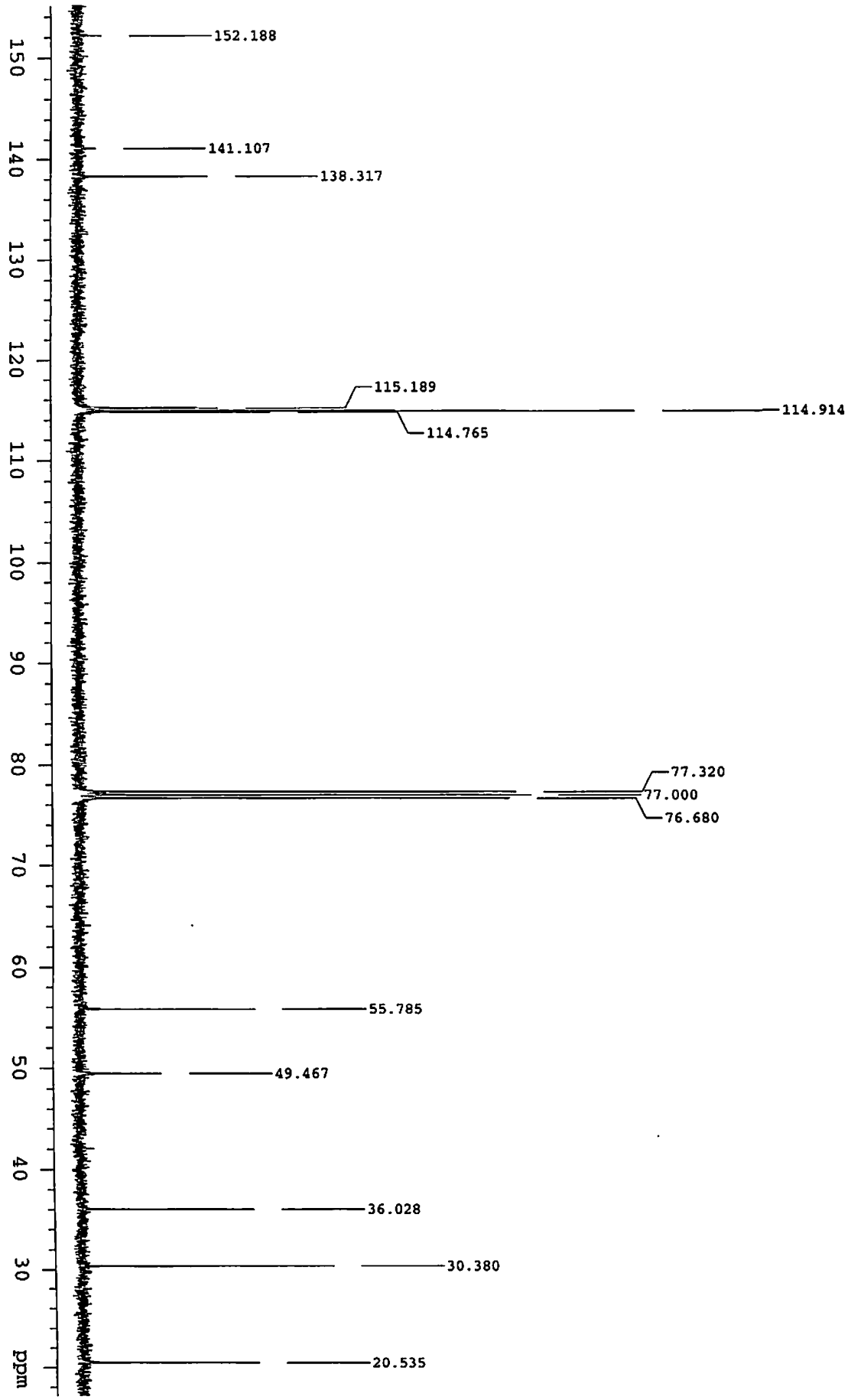

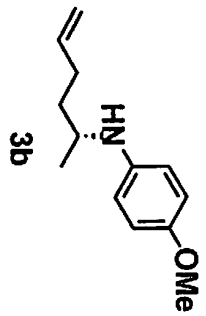

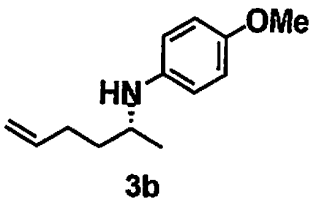

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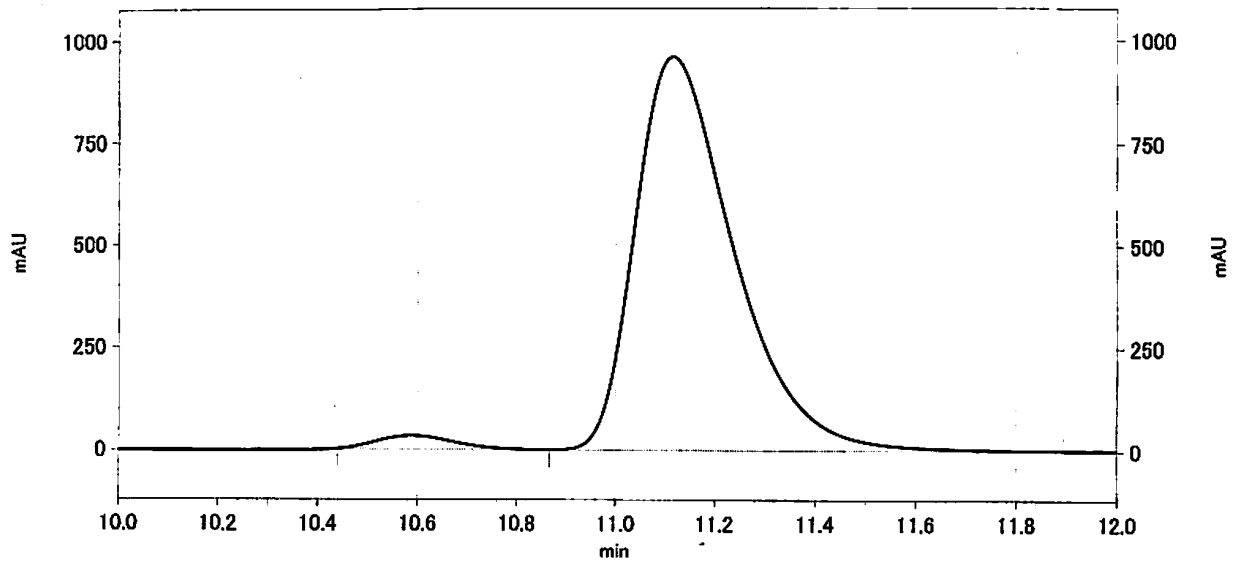
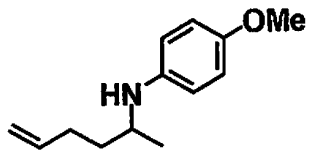


Pk #	Time	Area	Area%	Type
1	10.59	1394269	2.578	BB
2	11.11	52692076	97.422	BB



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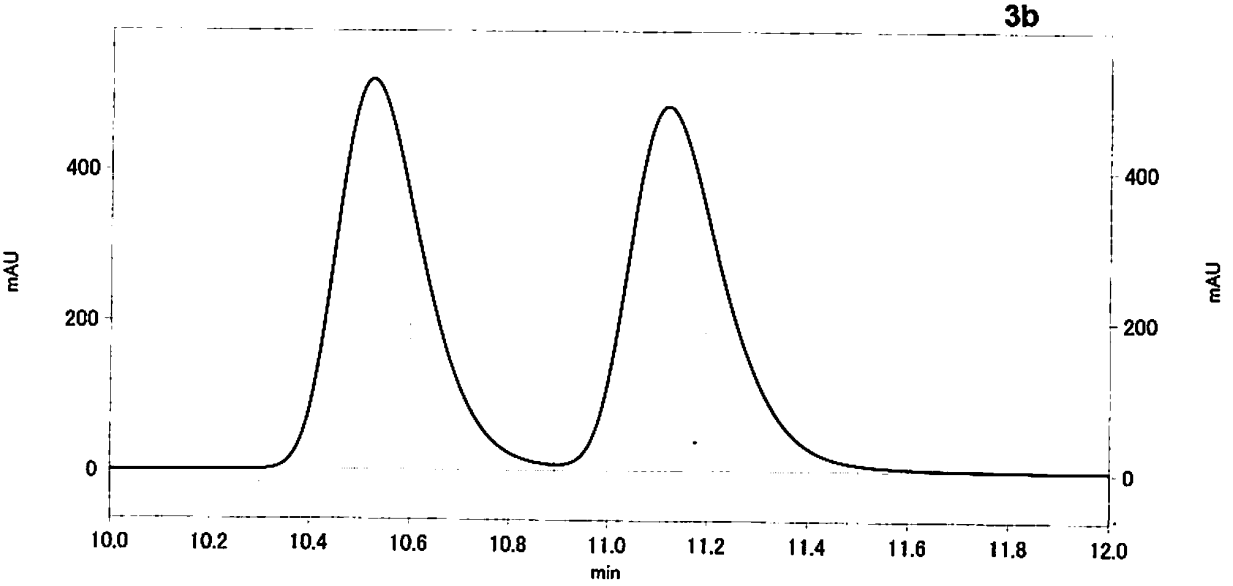
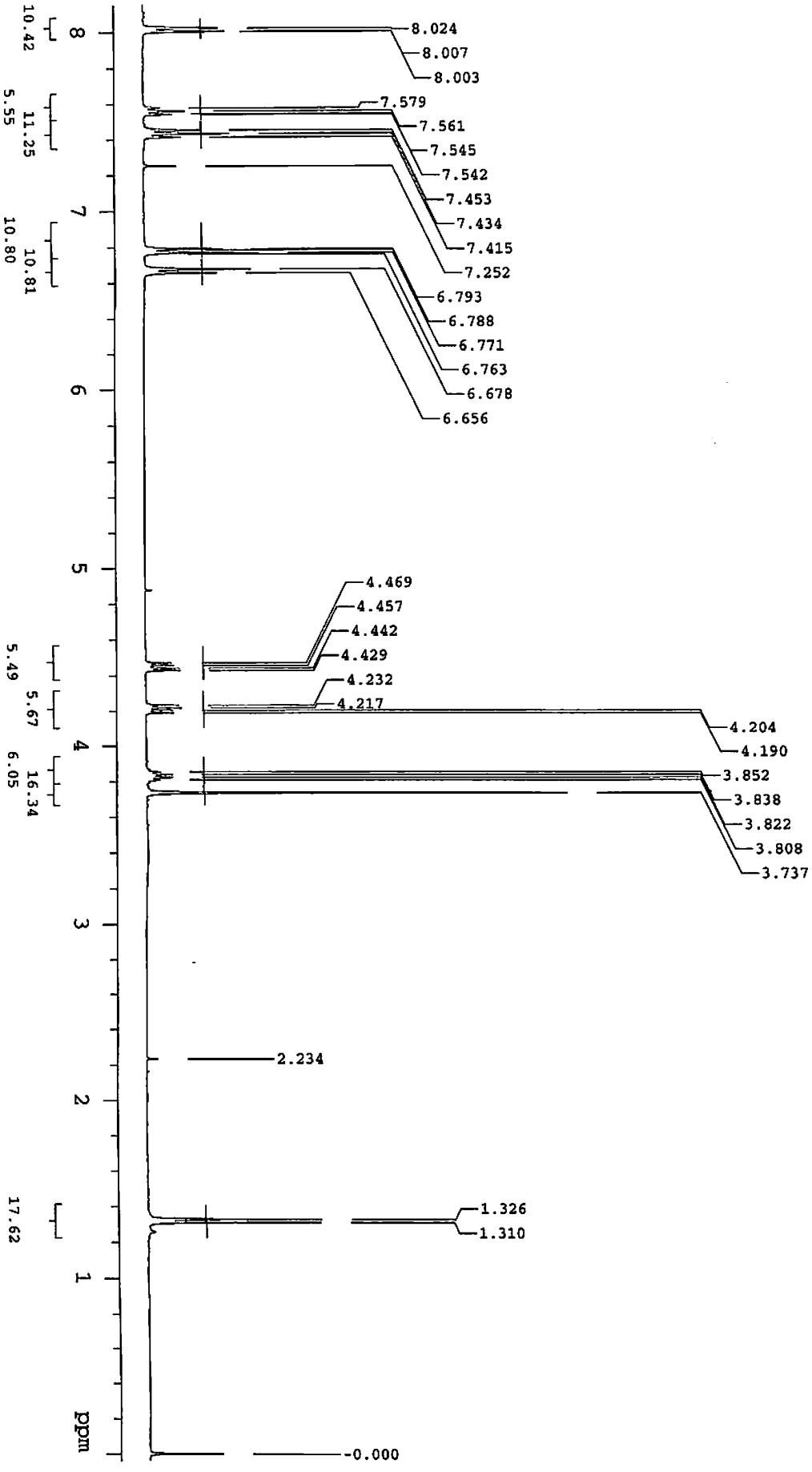
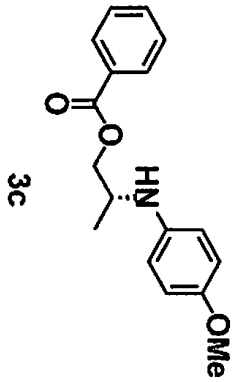
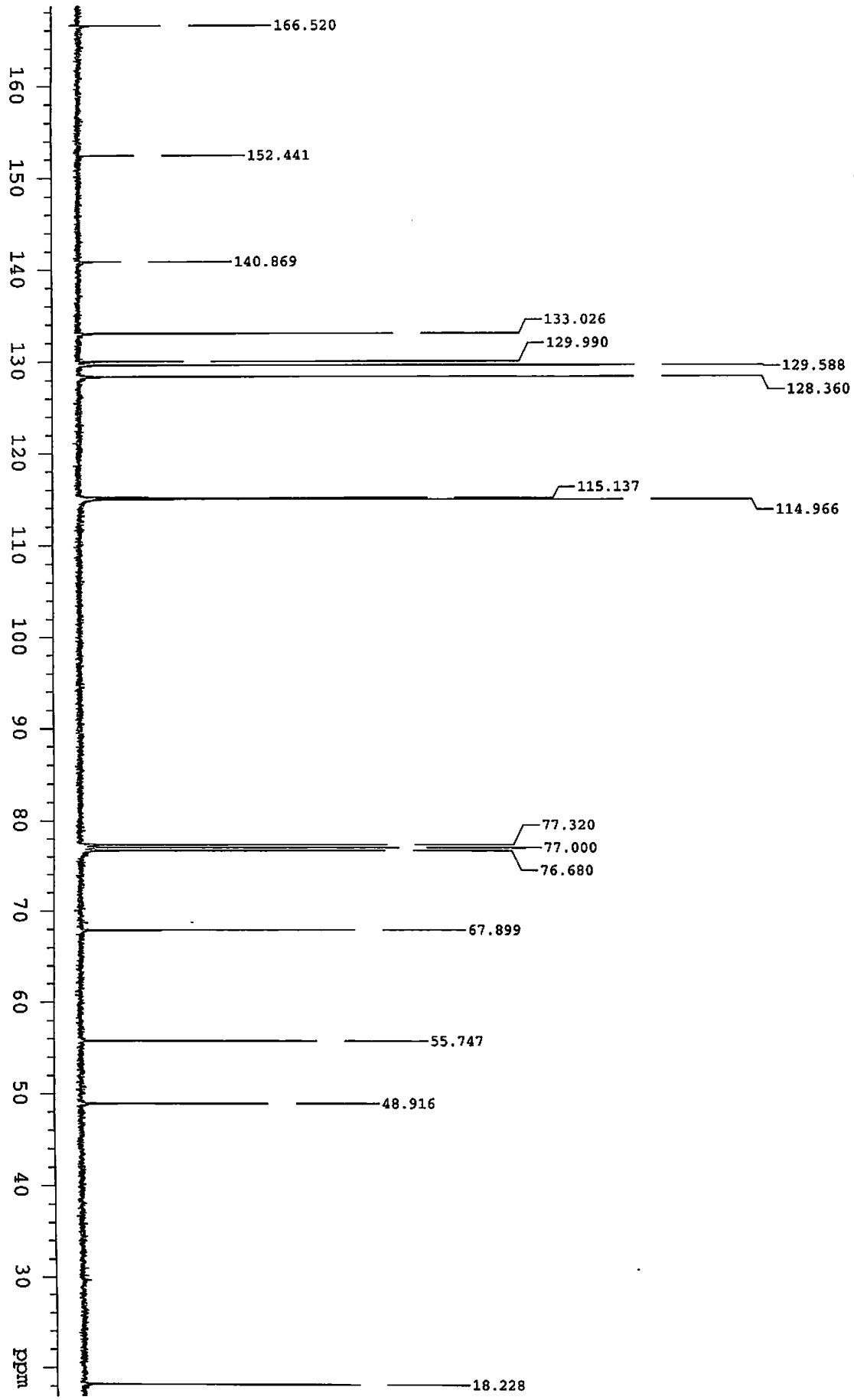


Pk #	Time	Area	Area%	Type
1	10.53	25811929	49.489	BV
2	11.12	26345018	50.511	VI



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67.899
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18.228
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140
130
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50
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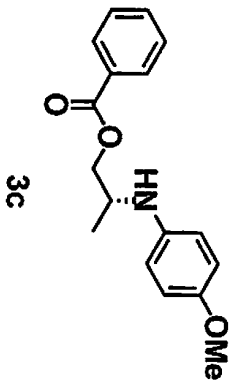
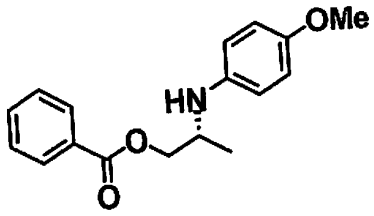
30
ppm


O
O
HN
OMe

3c



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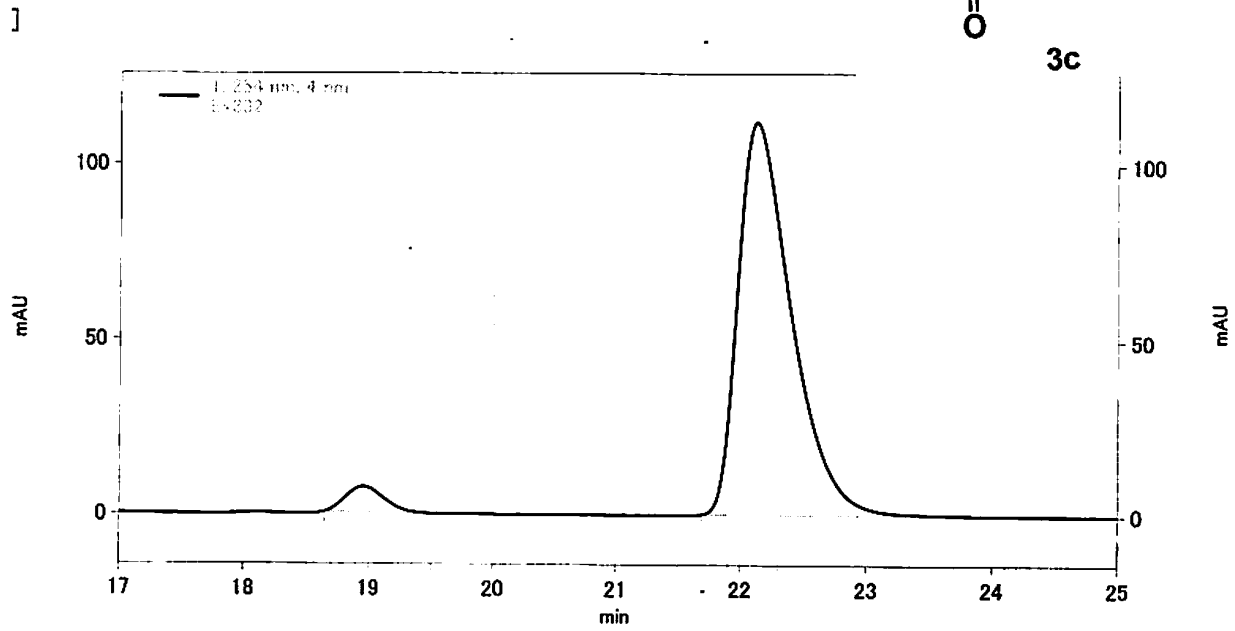

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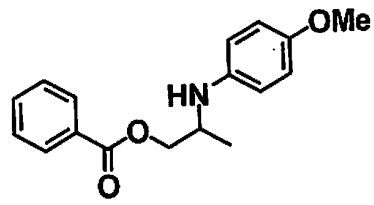
2	22.13	13264246	95.522	BB



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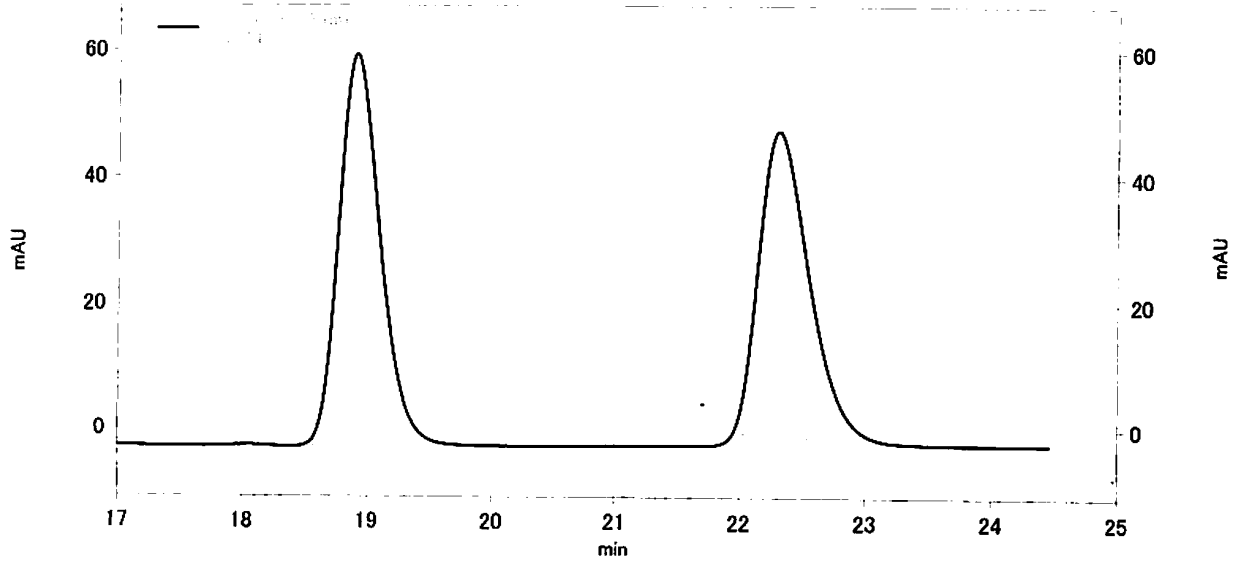

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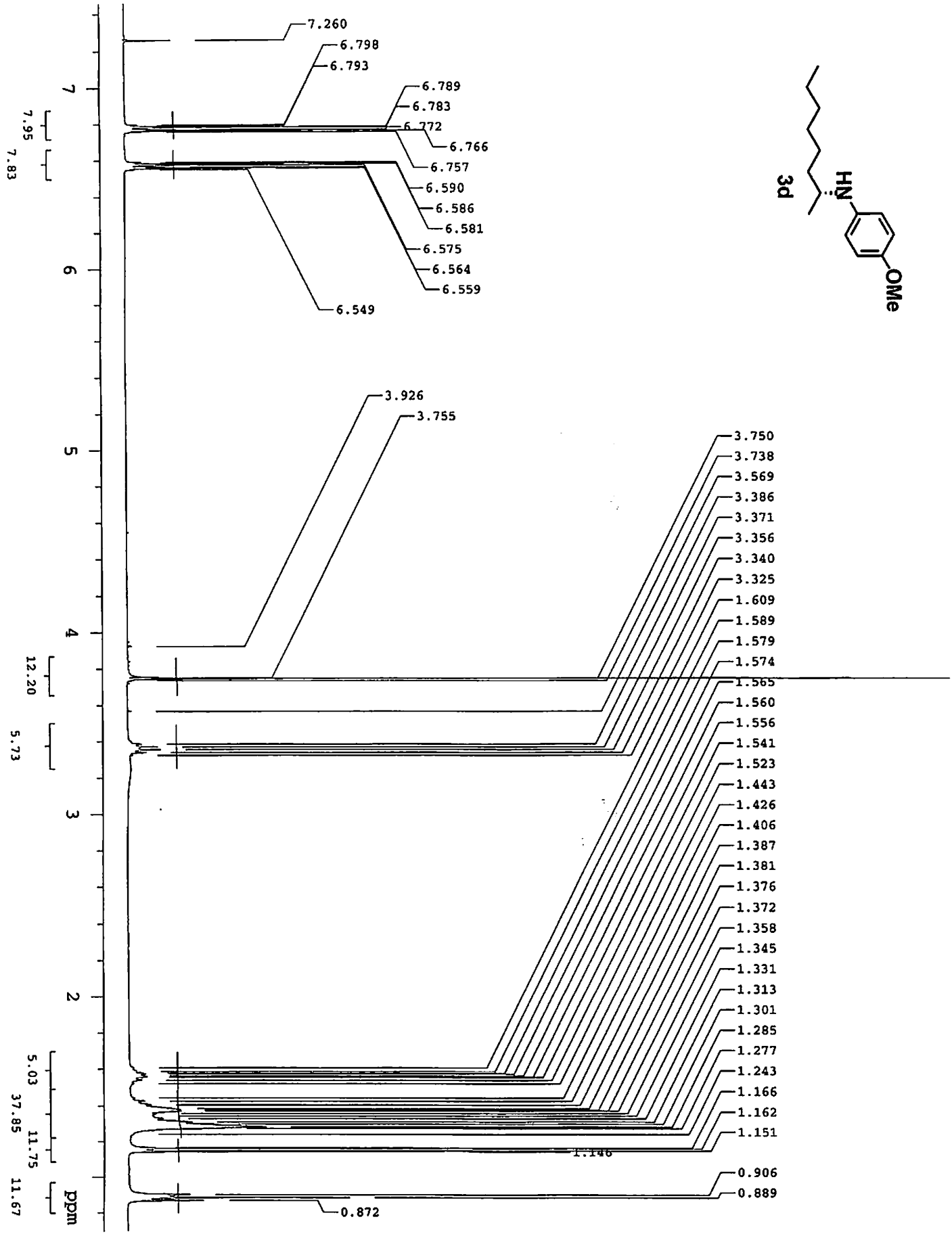
2	22.31	5368637	49.357	BB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6.549
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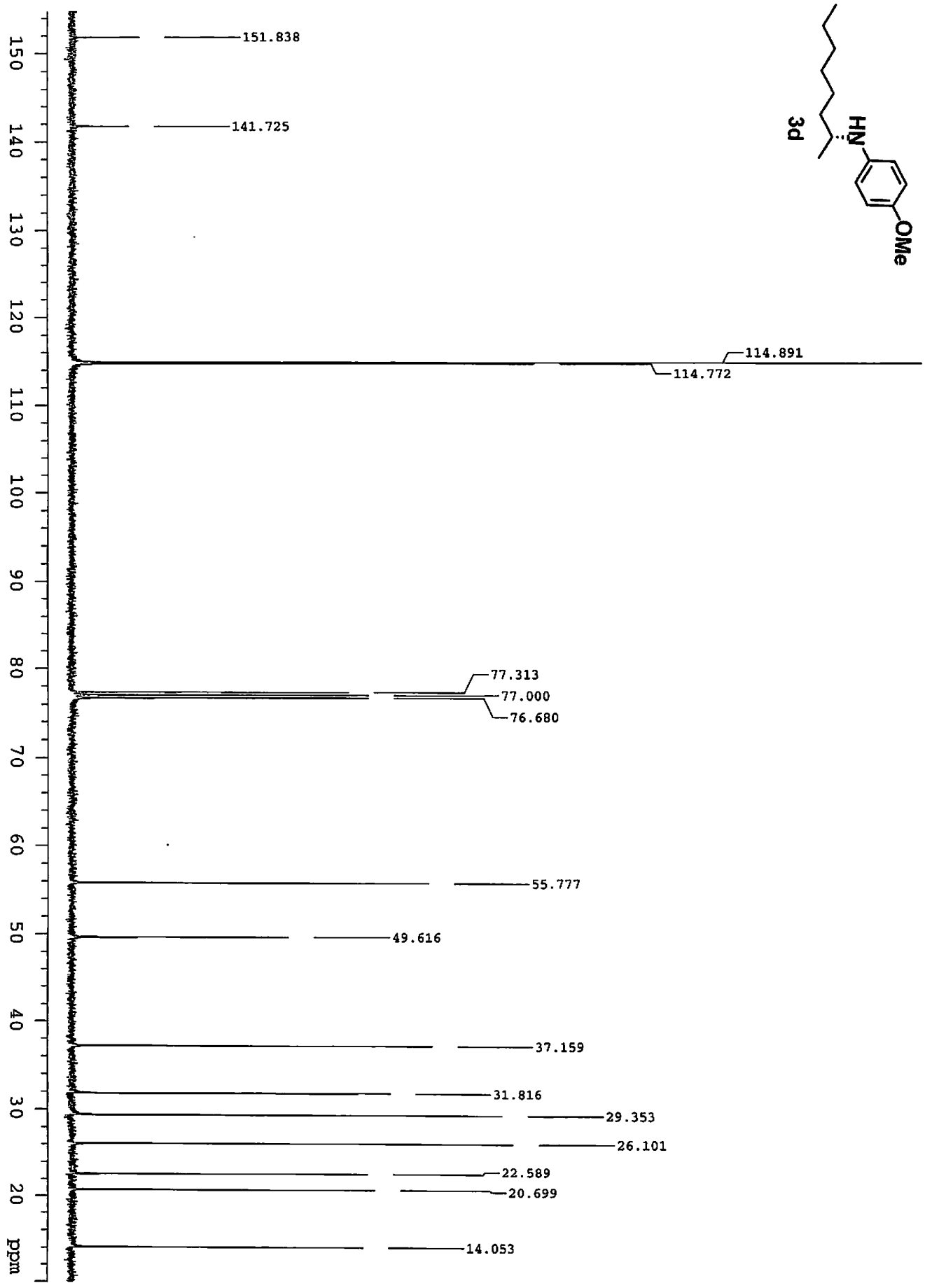
OMe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3d
HN
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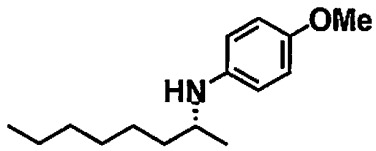

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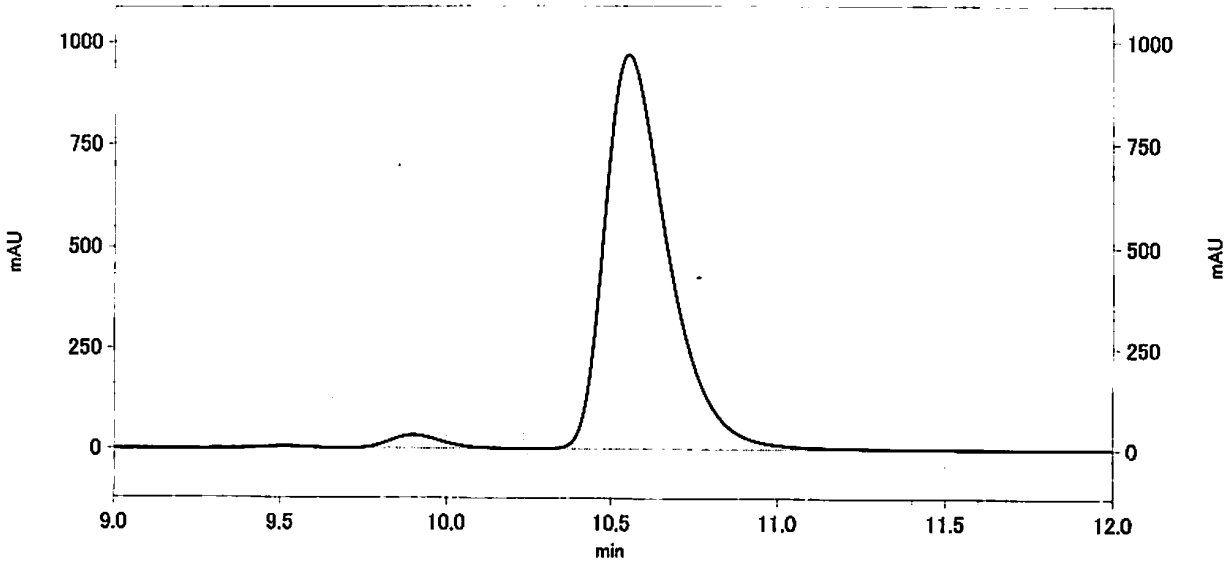

Pk #	Time	Area	Area%	Type
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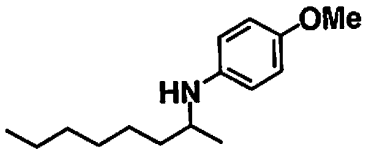

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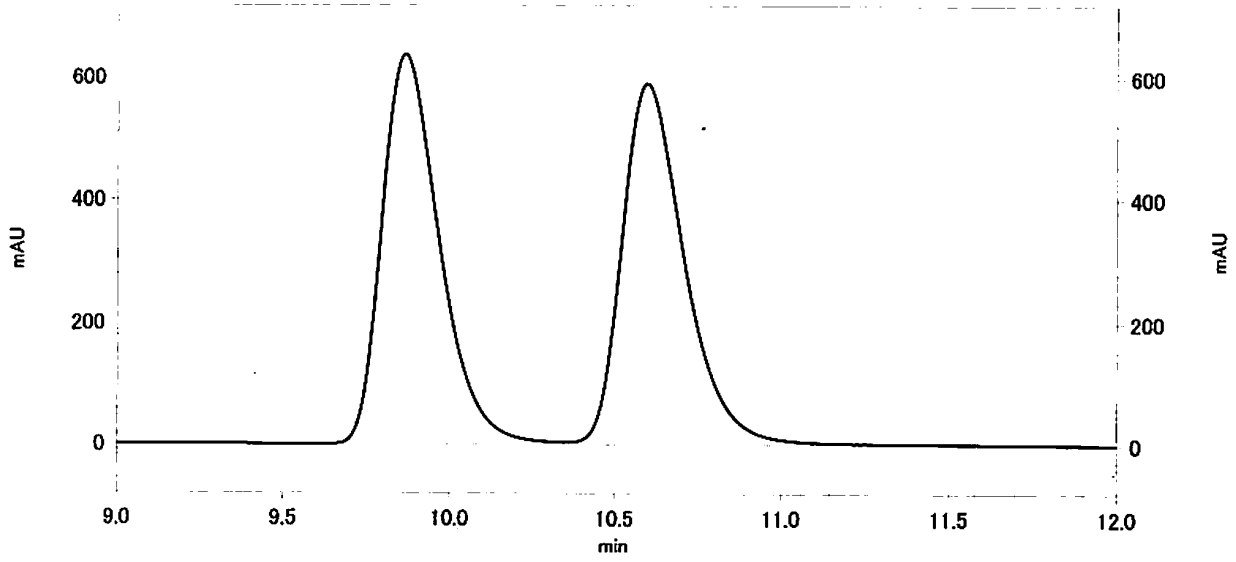

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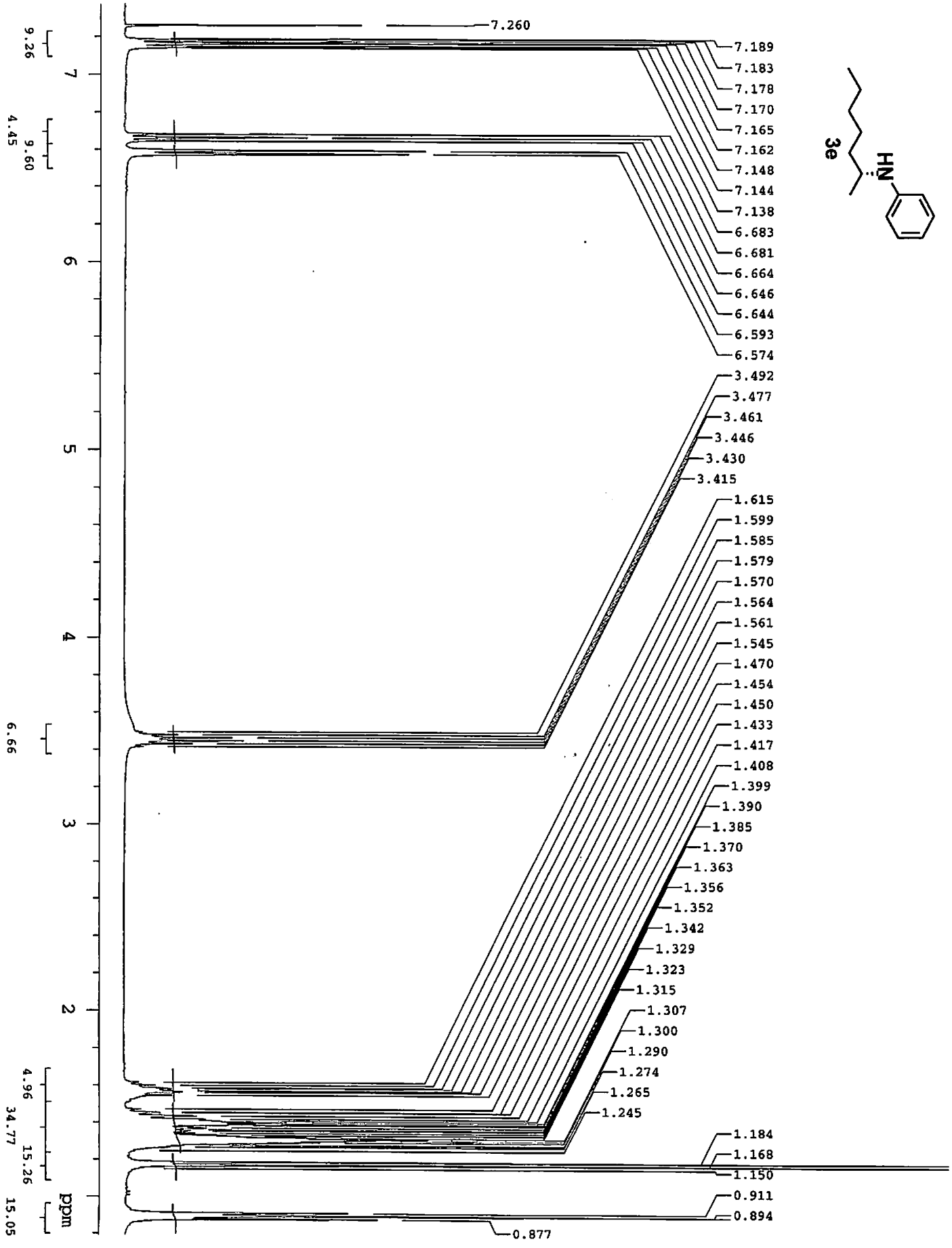
2	10.59	31081718	50.246	VB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3e
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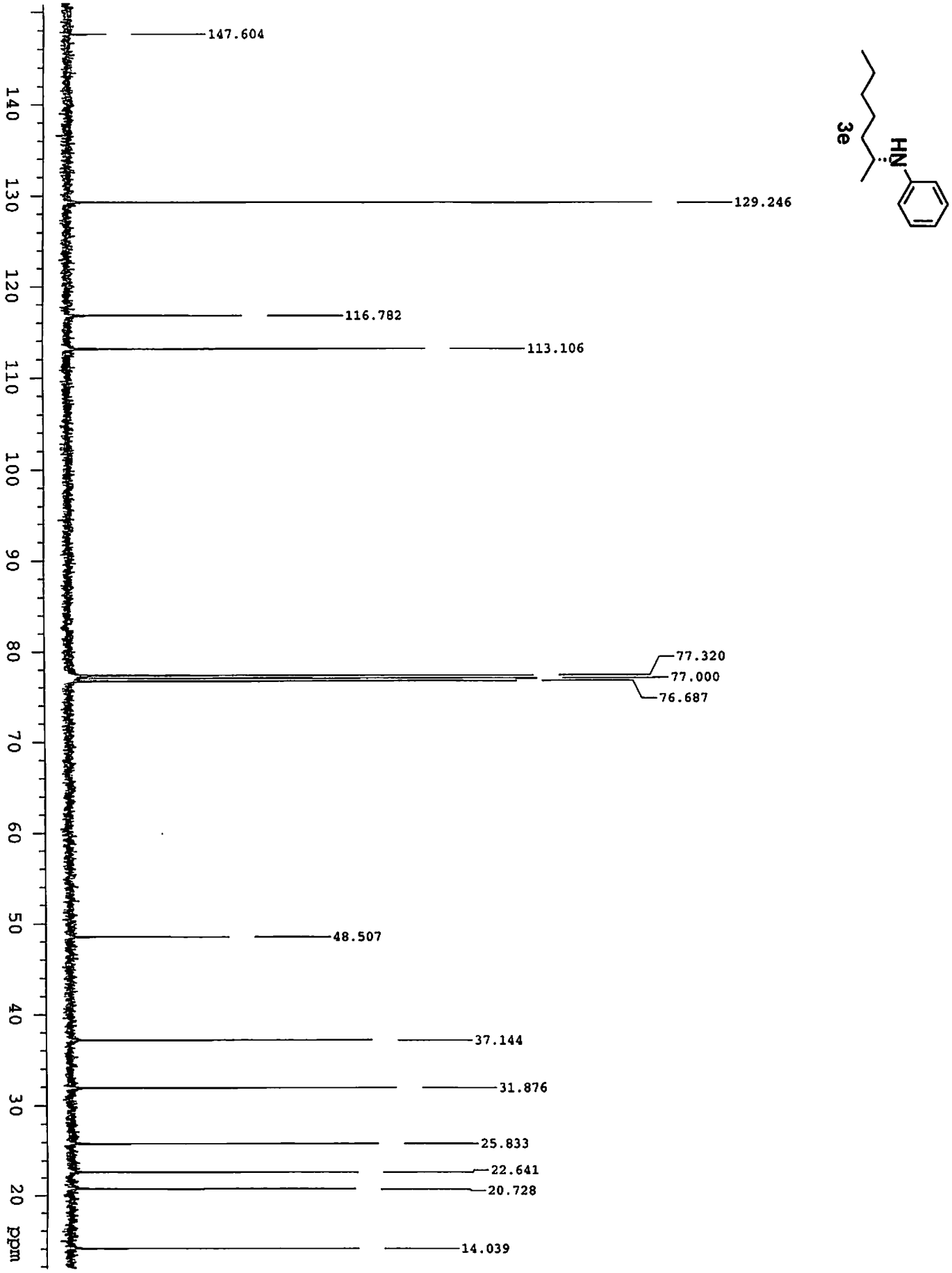
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20
ppm
3e
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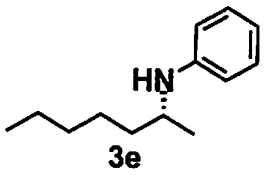

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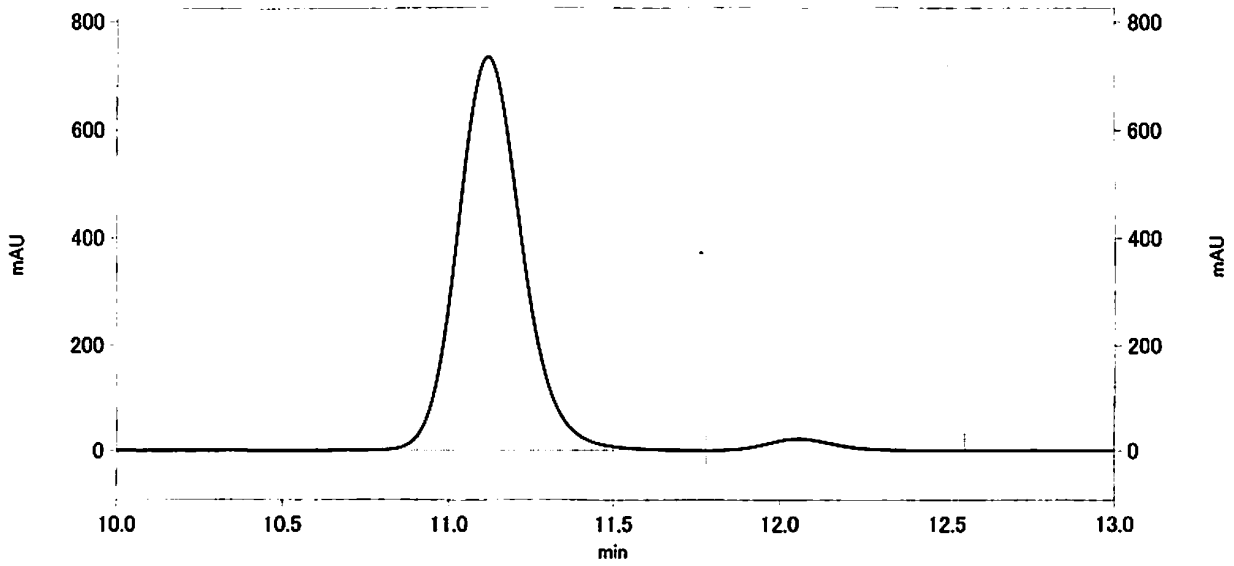

Pk #	Time	Area	Area%	Type
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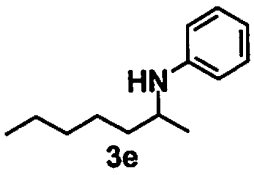
2	12.06	1225786	2.963	BB



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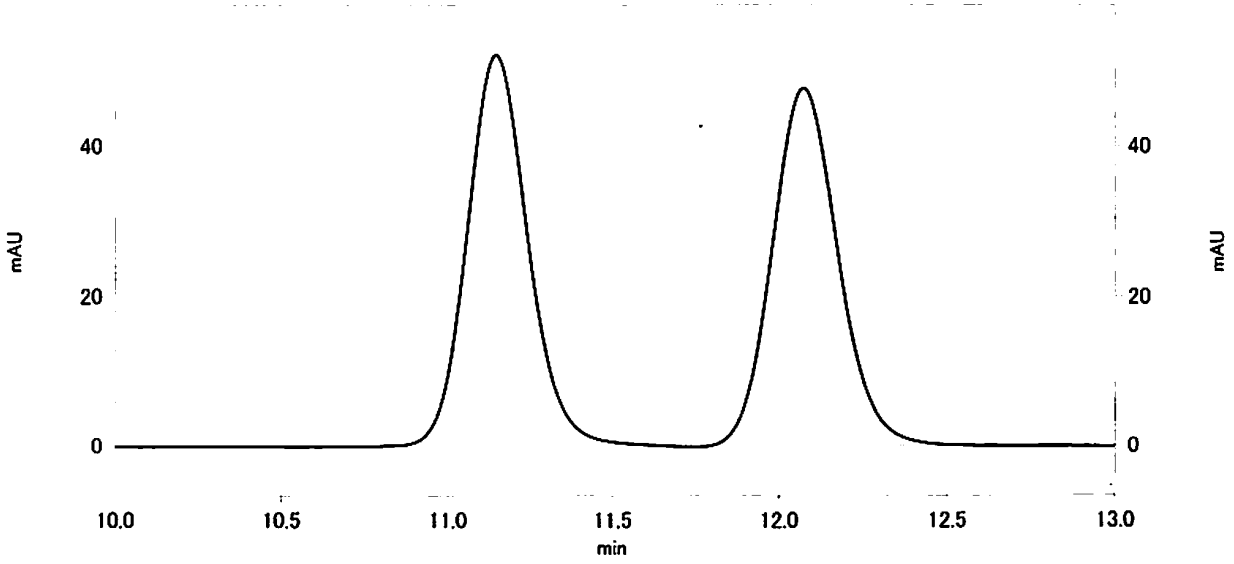

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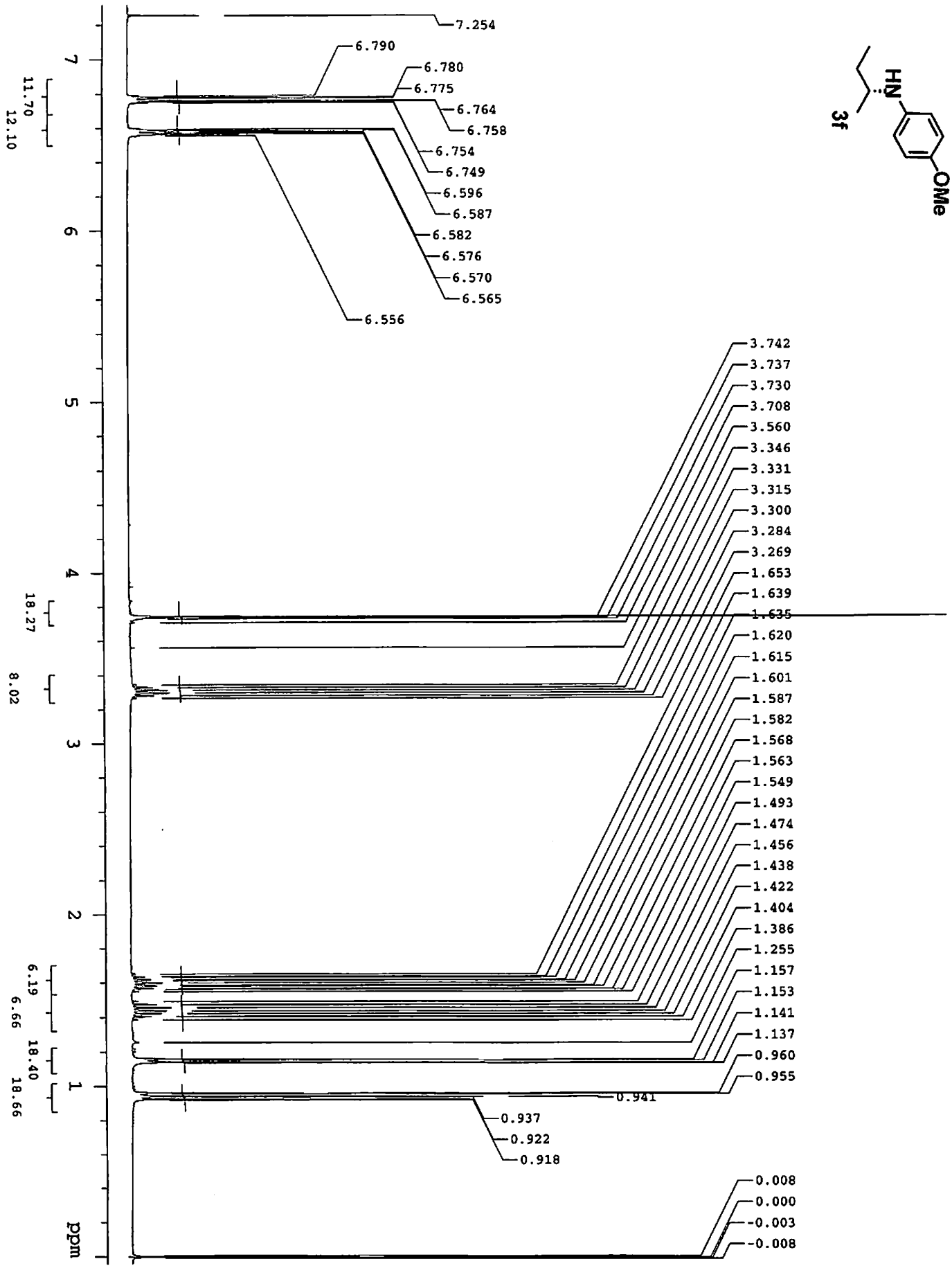
2	12.07	2577190	49.717	BB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1.620
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1.153
1.141
1.137
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0.941
0.937
0.922
0.918
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0.000
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OMe
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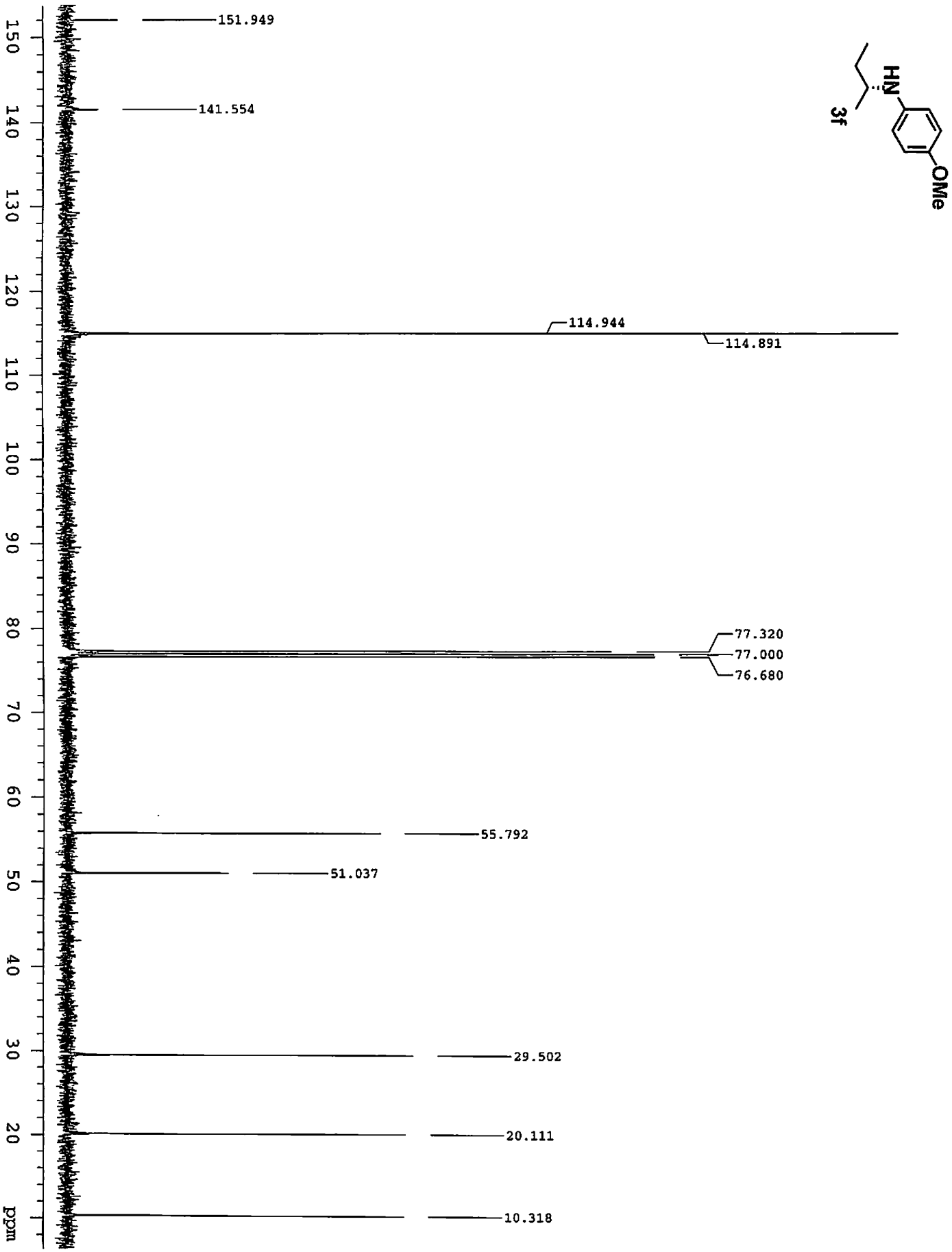
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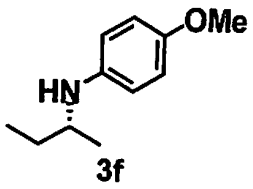
3f
HN
OMe



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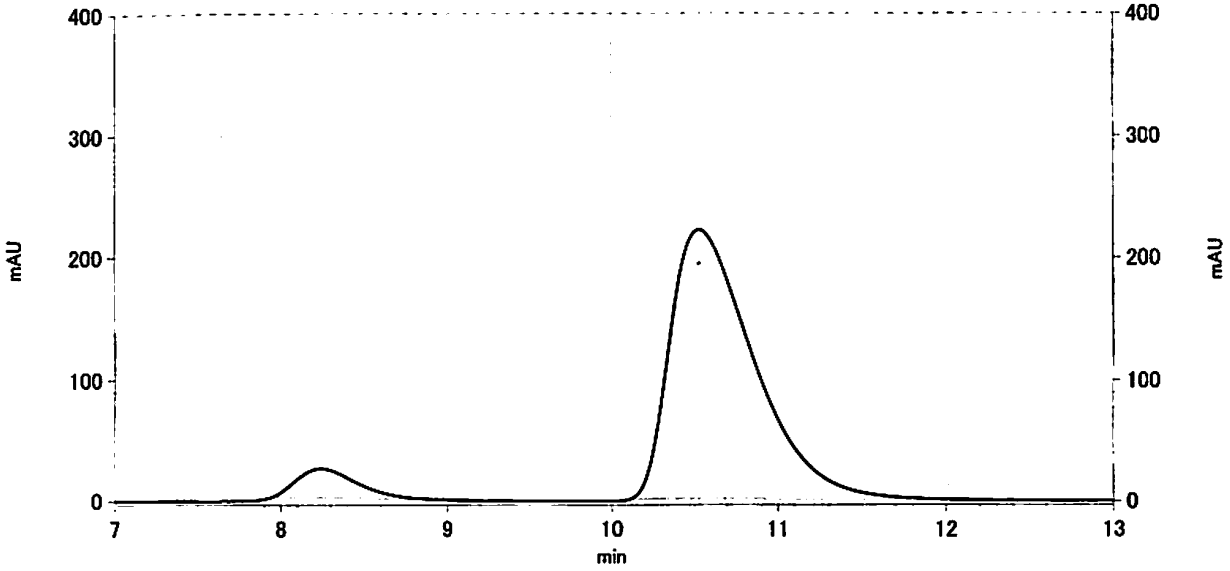
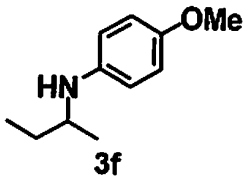


Pk #	Time	Area	Area%	Type
1	8.24	2342360	7.070	BB
2	10.53	30787740	92.930	BB



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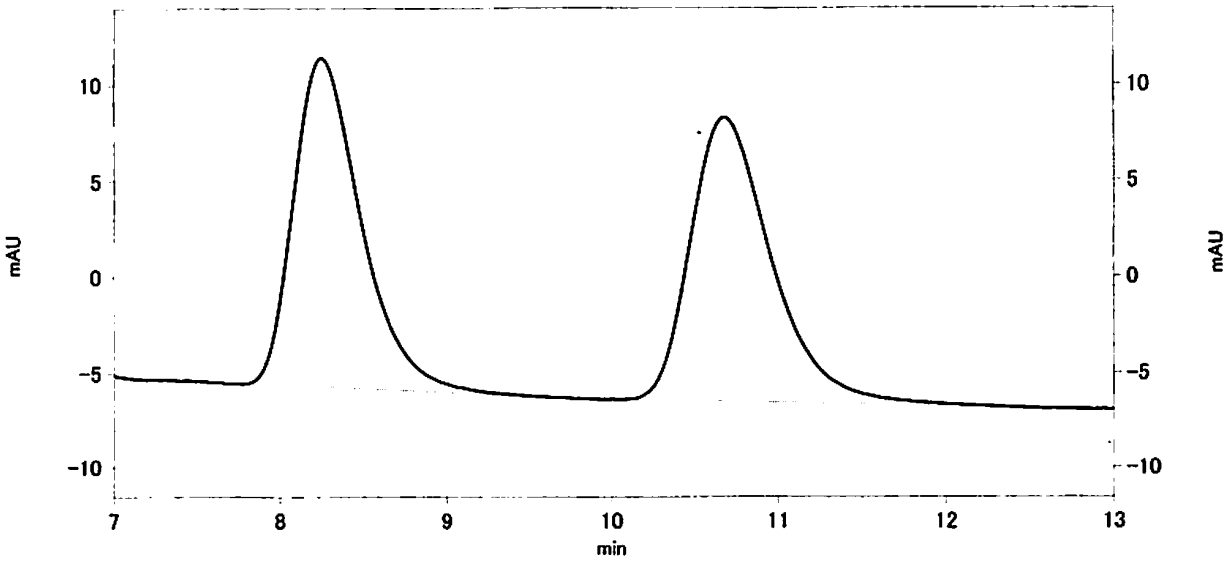
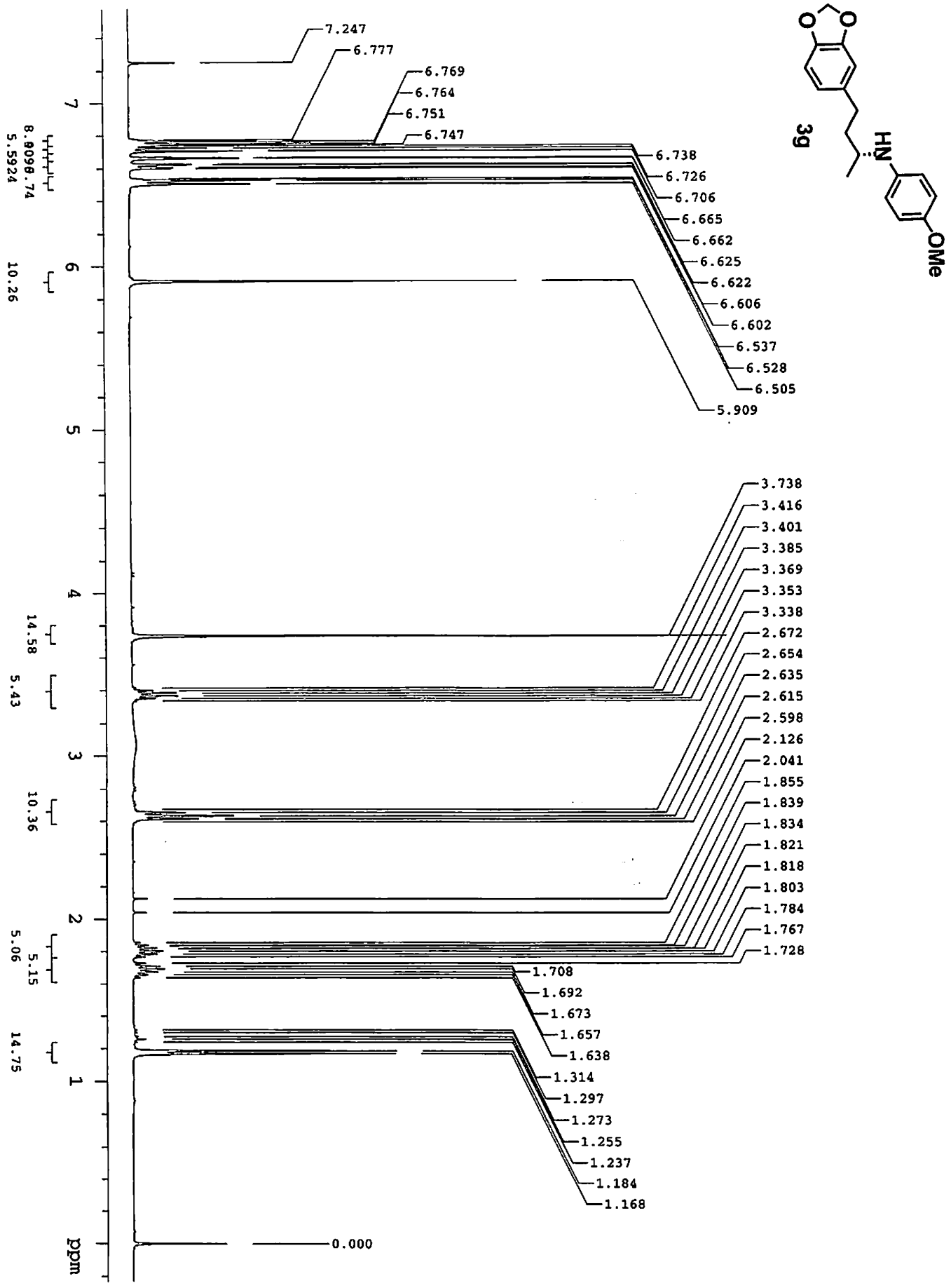


Pk #	Time	Area	Area%	Type
1	8.25	1928126	49.099	BB
2	10.68	1998928	50.901	BB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6.751
6.747
6.738
6.726
6.706
6.665
6.662
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6.622
6.606
6.602
6.537
6.528
6.505
5.909
3.738
3.416
3.401
3.385
3.369
3.353
3.338
2.672
2.654
2.635
2.615
2.598
2.126
2.041
1.855
1.839
1.834
1.821
1.818
1.803
1.784
1.767
1.728
1.708
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1.657
1.638
1.314
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1.273
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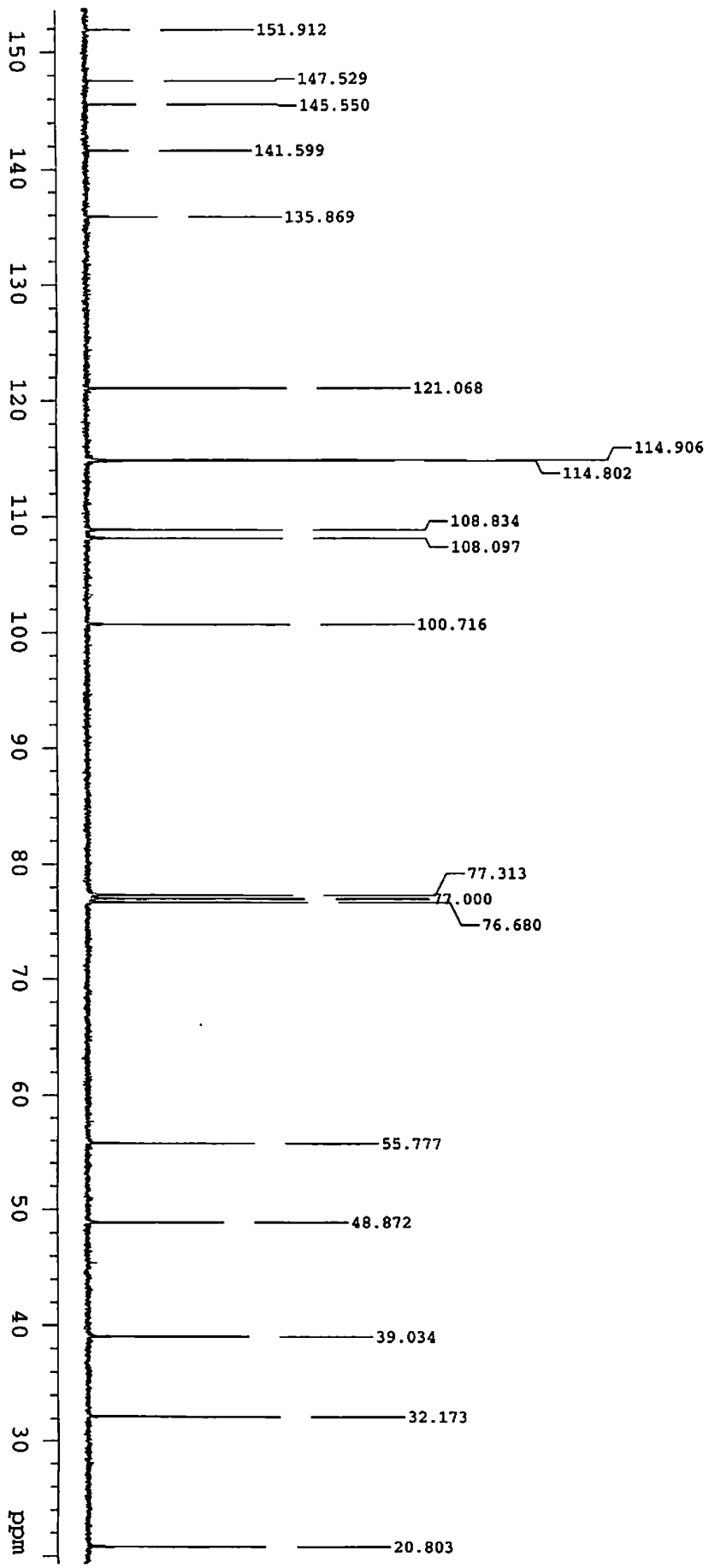
5.15
5.06
14.75
3g
HN
OMe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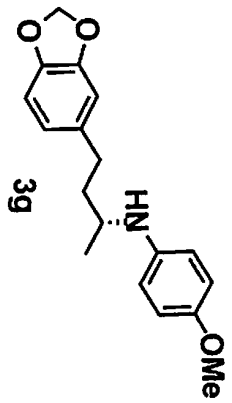
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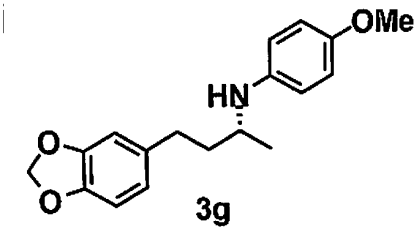
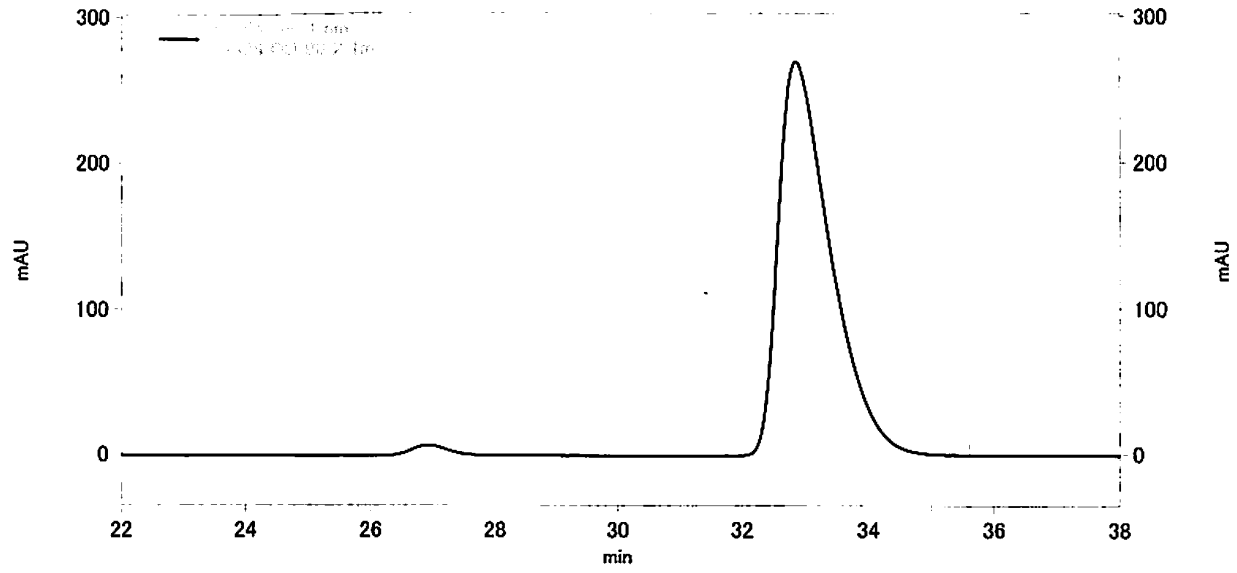
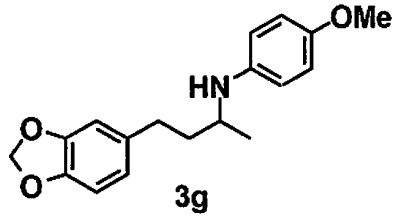
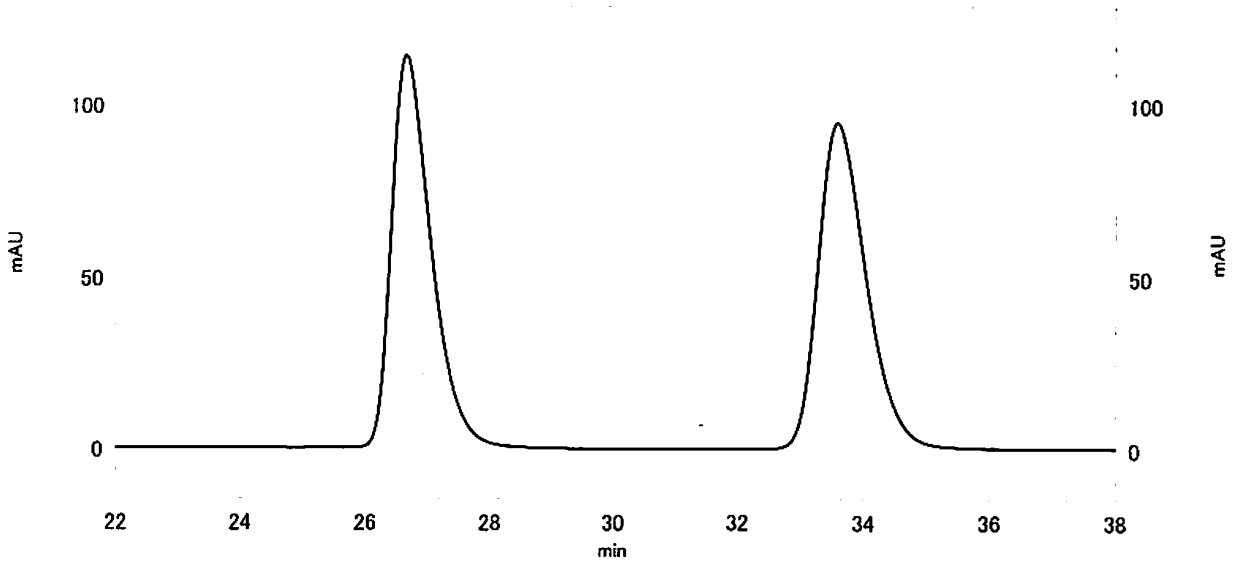
HN
OMe



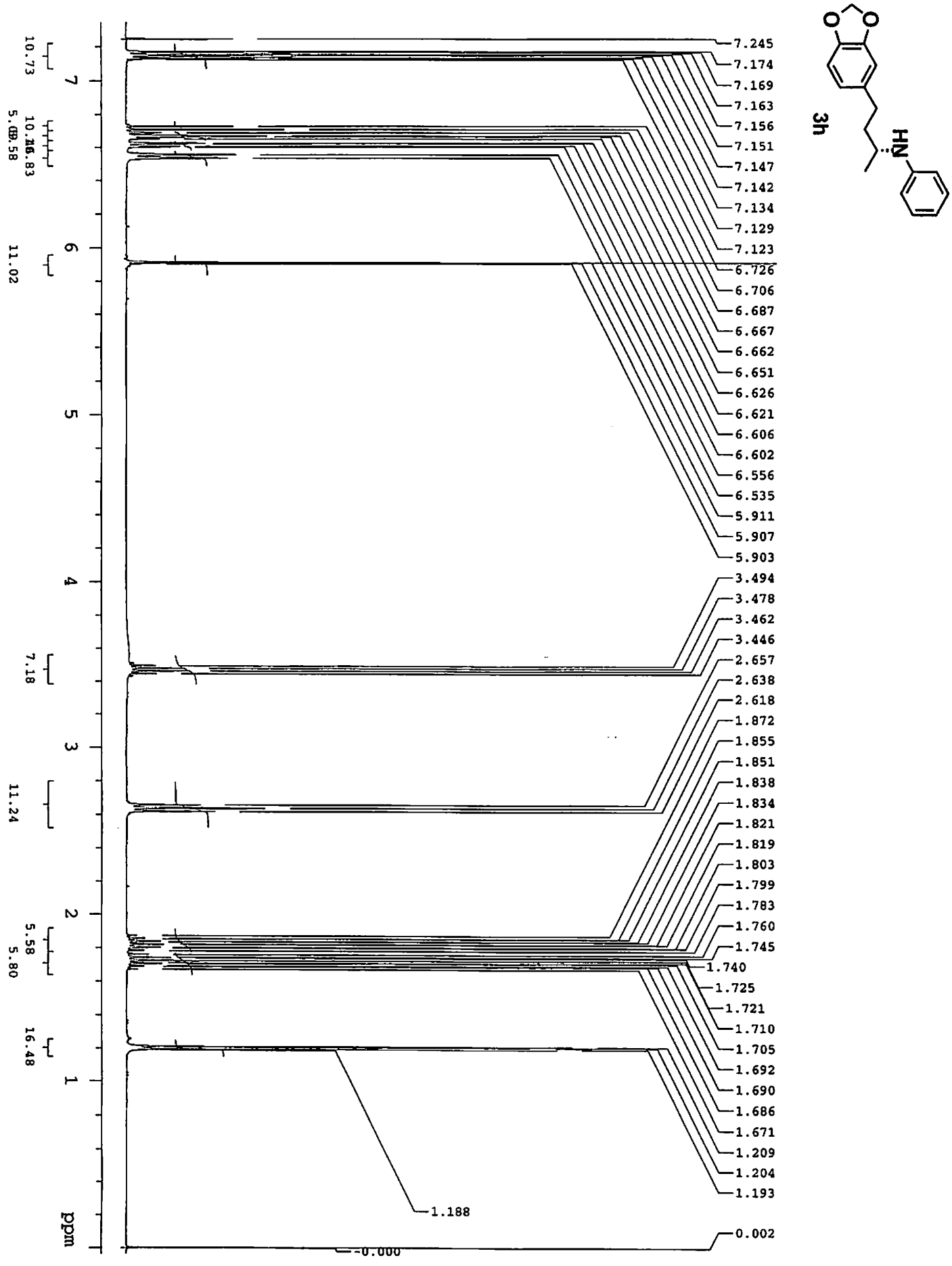


Peak #	Retention time	Type	Area	Area %
1	26.93	BB	916508	1.456
2	32.85	BB	62051487	98.544





Peak #	Retention time	Type	Area	Area %
1	26.65	BB	19887912	50.172
2	33.58	BB	19751502	49.828


3h
HN
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7.174
7.169
7.163
7.156
7.151
7.147
7.142
7.134
7.129
7.123
6.726
6.706
6.687
6.667
6.662
6.651
6.626
6.621
6.606
6.602
6.556
6.535
5.911
5.907
5.903
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3.478
3.462
3.446
2.657
2.638
2.618
1.872
1.855
1.851
1.838
1.834
1.821
1.819
1.803
1.799
1.783
1.760
1.745
1.740
1.725
1.721
1.710
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1.690
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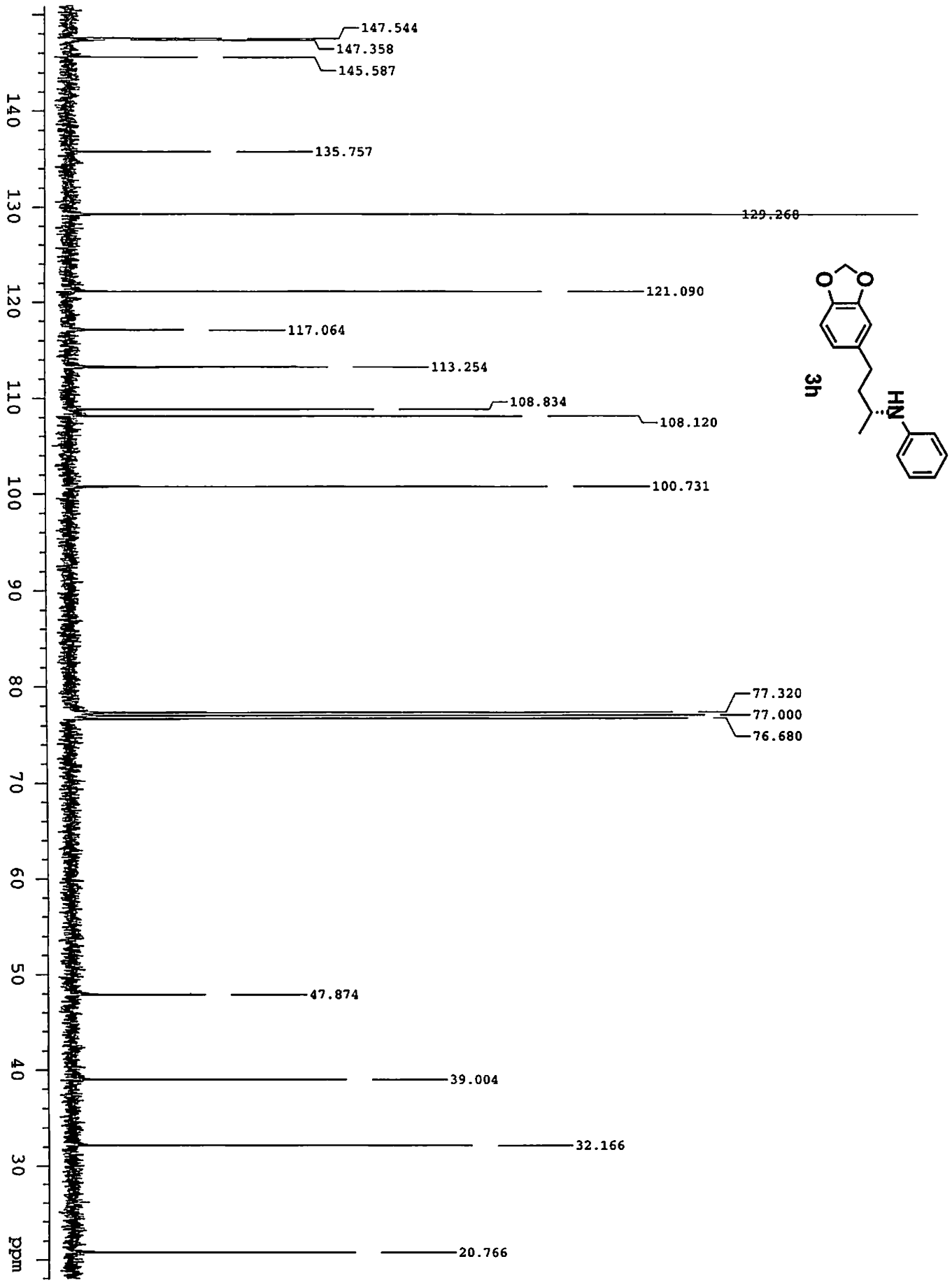
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121.090
117.064
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108.120
100.731
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77.000
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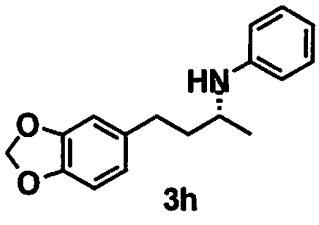
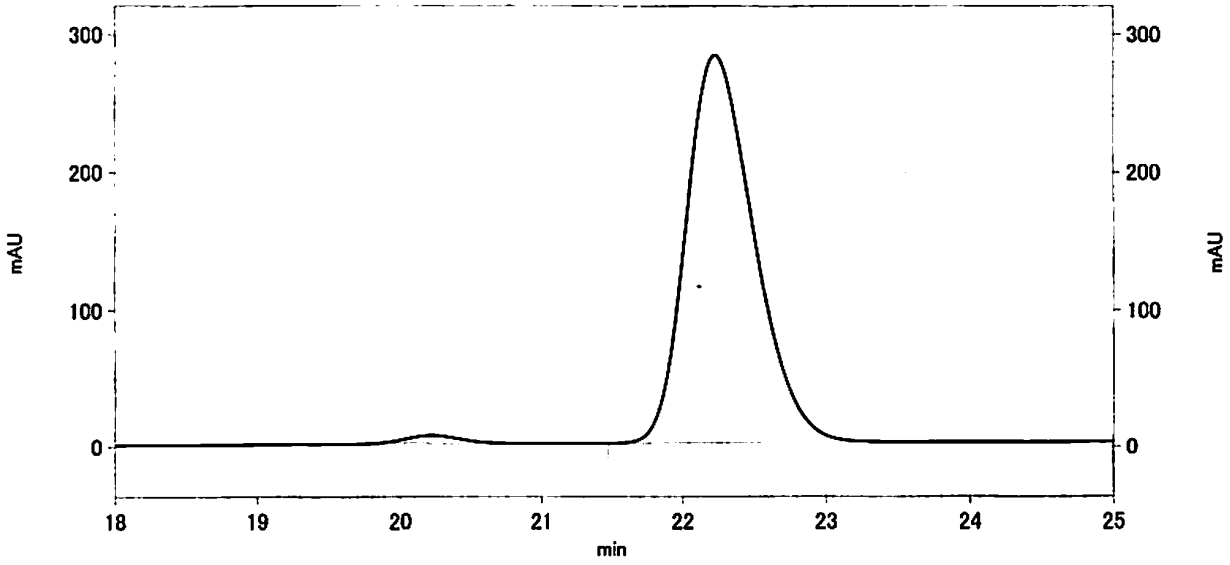
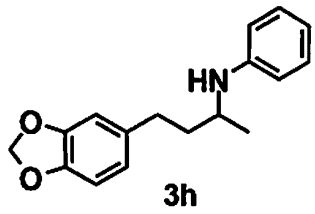
47.874
39.004
32.166
20.766
140
130
120
110
100
90
80
70
60
50
40
30
ppm
3h
HN



3h



Peak #	Retention time	Type	Area	Area %
1	20.23	BB	602109	1.590
2	22.23	BB	37267222	98.410



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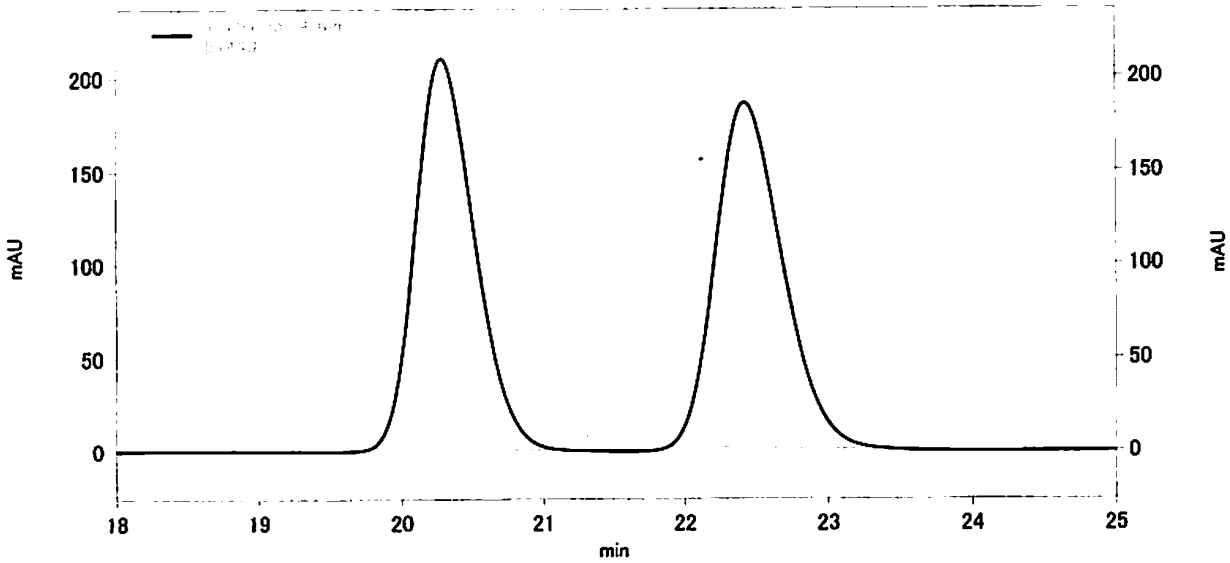
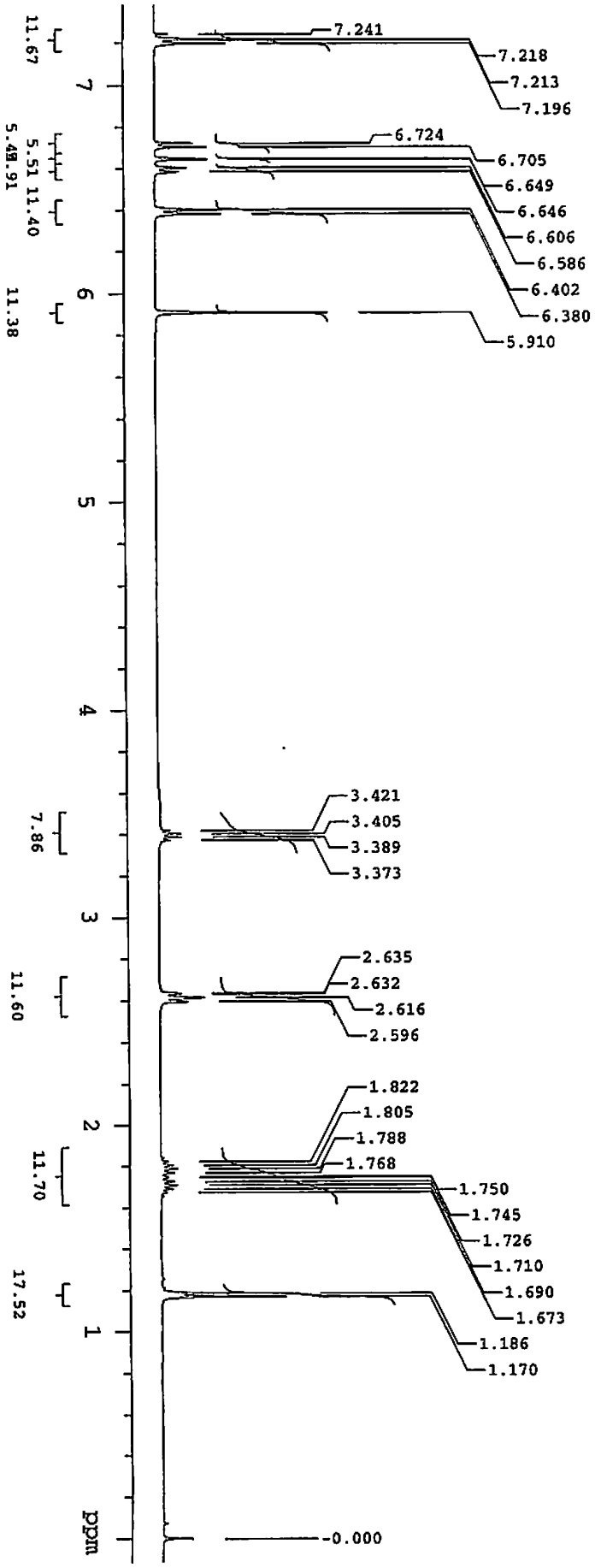
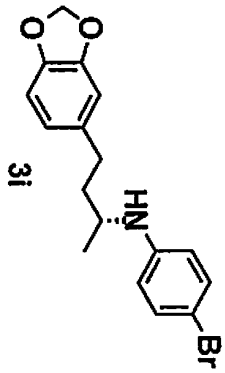
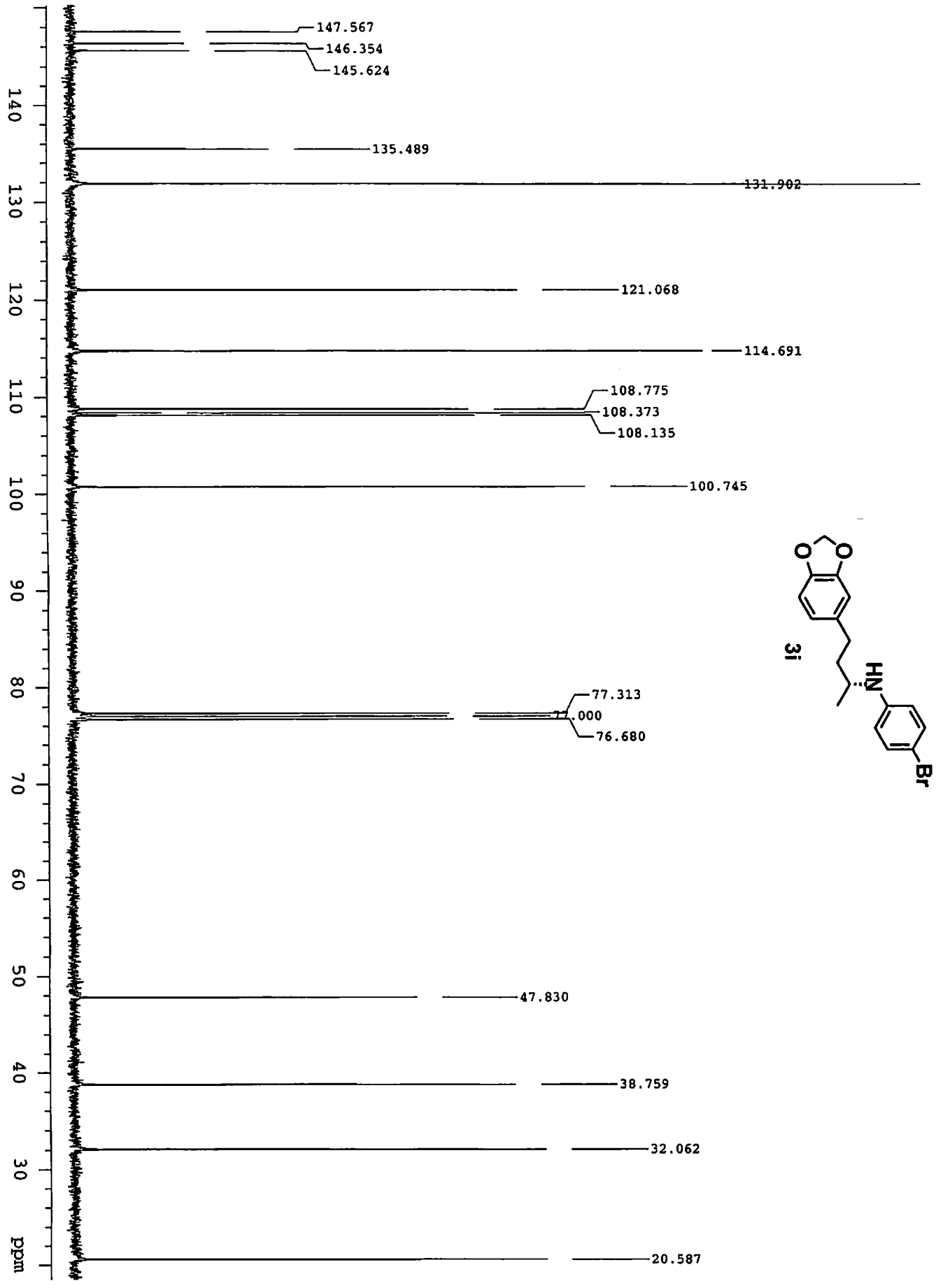


Peak #	Retention time	Type	Area	Area %
1	20.28	BB	24060822	50.037
2	22.42	BB	24025511	49.963



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108.373
108.135
100.745
77.313
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47.830
38.759
32.062
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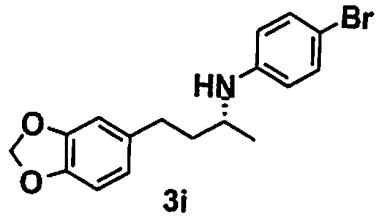
140
130
120
110
100
90
80
70
60
50
40
30
ppm
3i
HN
Br



3i

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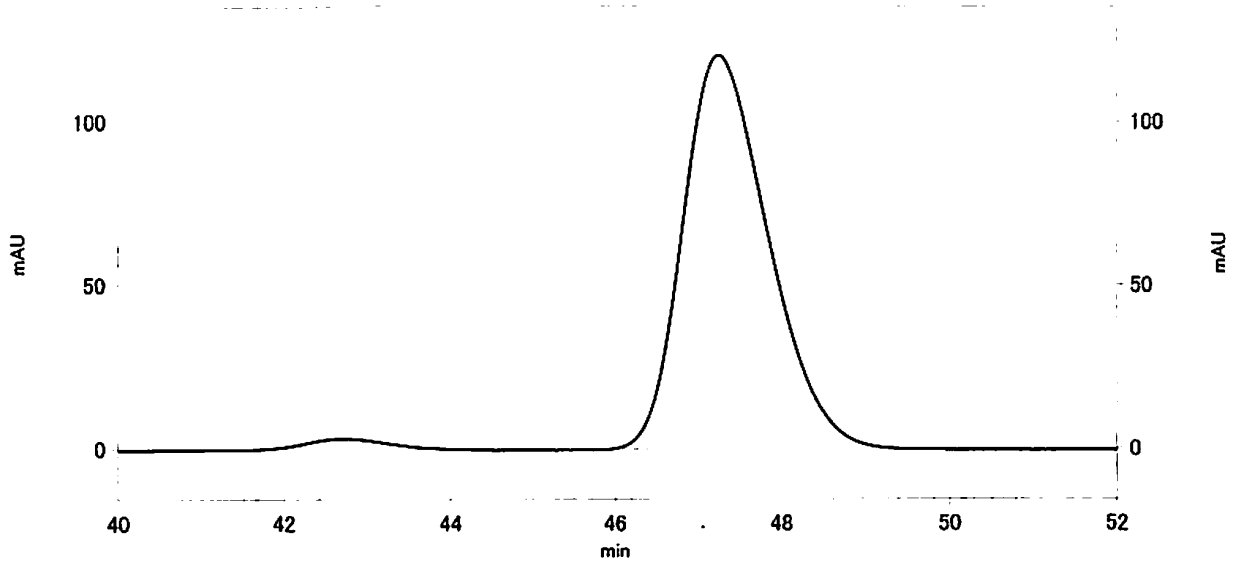
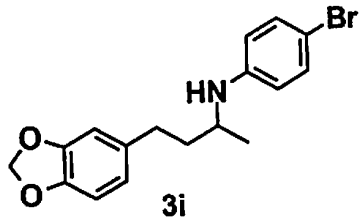


Pk #	Time	Area	Area%	Type
1	42.69	653441	1.871	BB
2	47.25	34274964	98.129	BB



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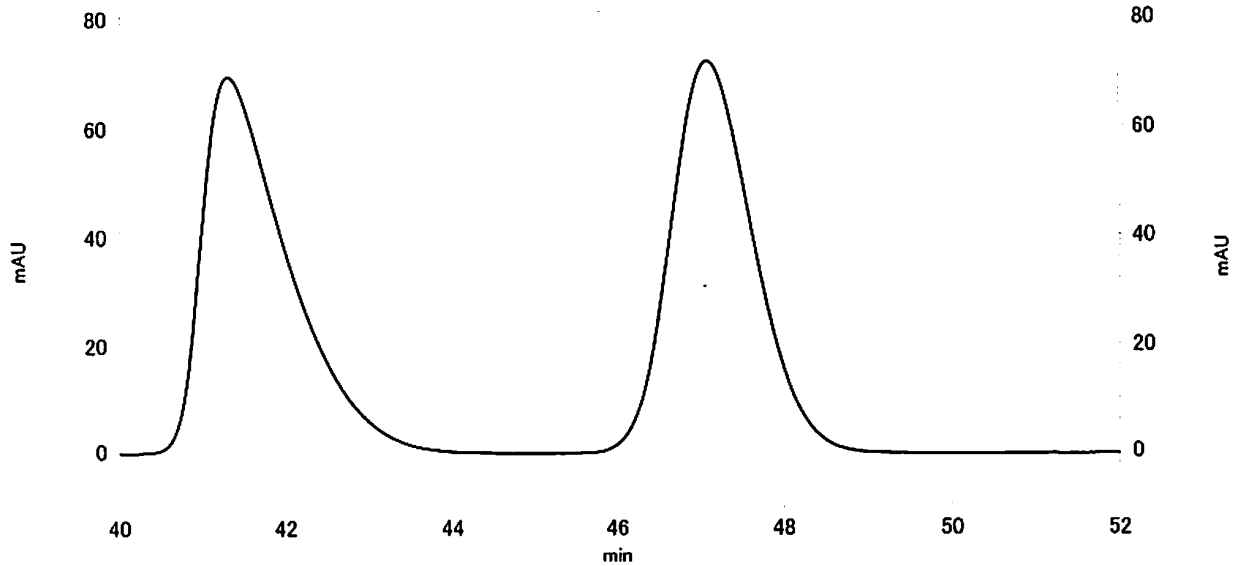
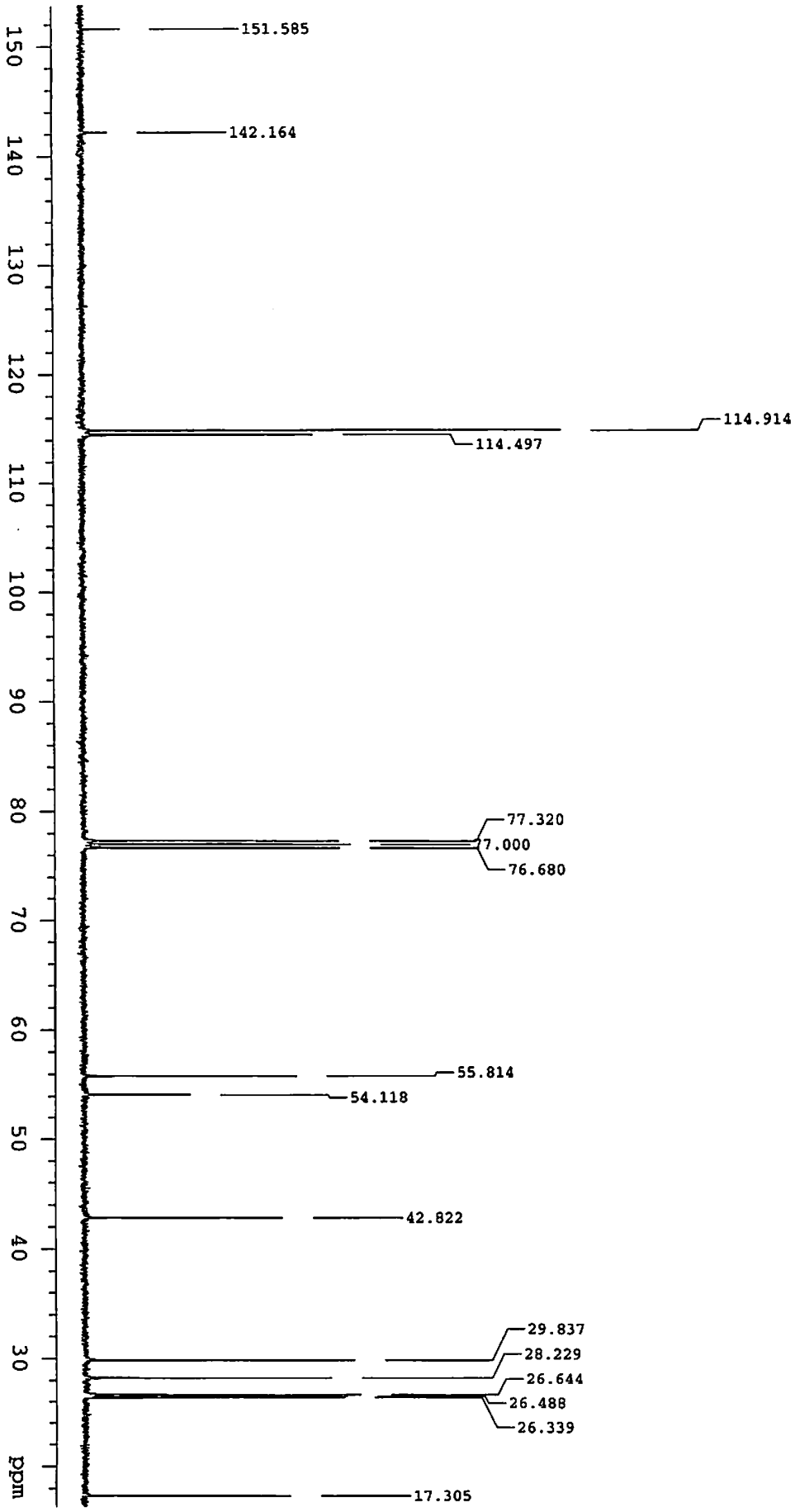


Pk #	Time	Area	Area%	Type
1	41.31	20190162	50.005	BB
2	47.09	20186291	49.995	BB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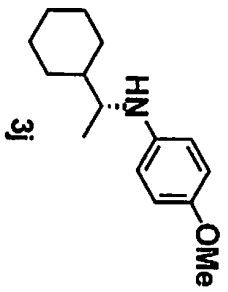
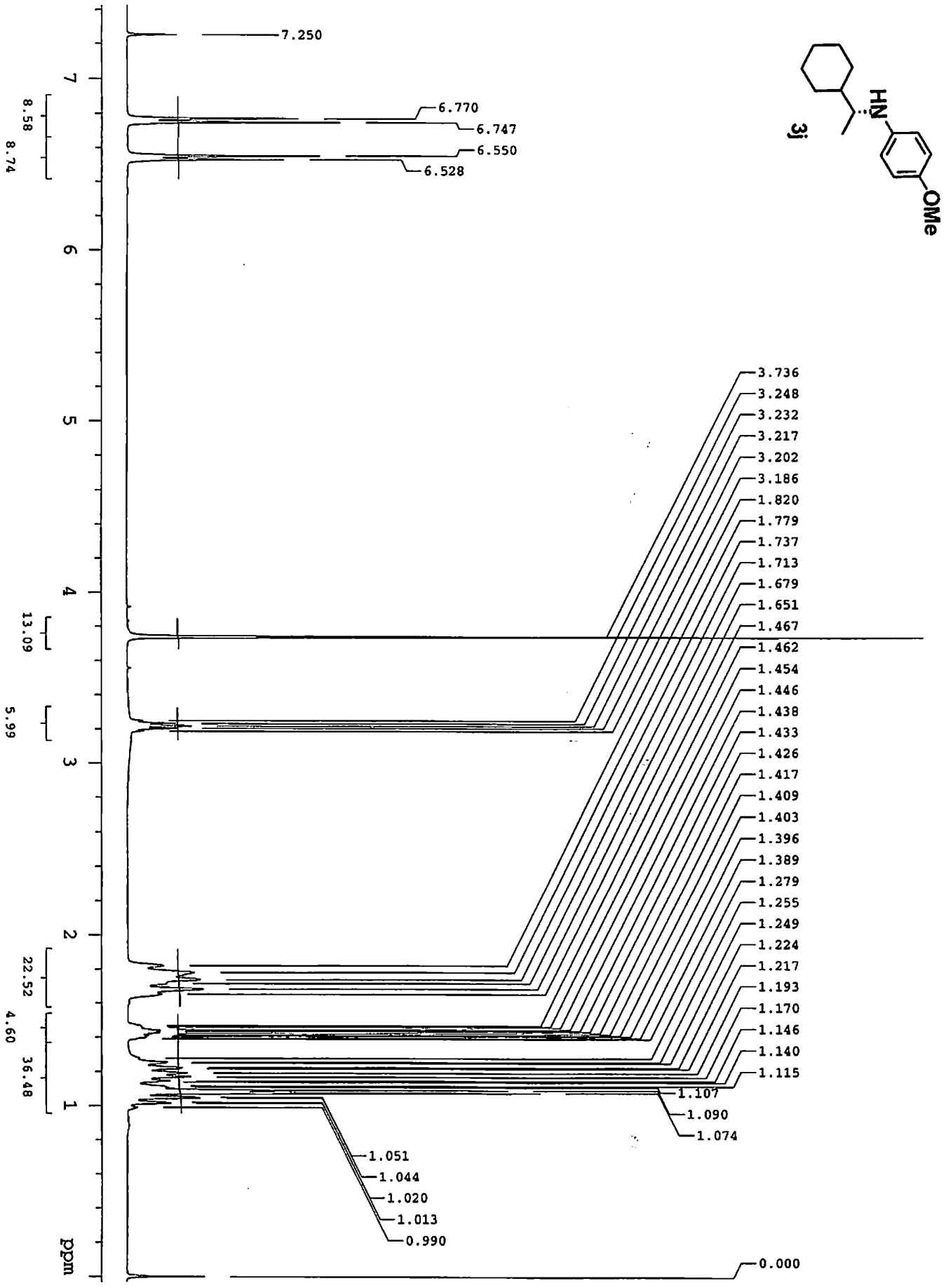
114.497
77.320
7.000
76.680
55.814
54.118
42.822
29.837
28.229
26.644
26.488
26.339
17.305
150
140
130
120
110
100
90
80
70
60
50
40
30
ppm


3j
HN
OMe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6.550
6.528
3.736
3.248
3.232
3.217
3.202
3.186
1.820
1.779
1.737
1.713
1.679
1.651
1.467
1.462
1.454
1.446
1.438
1.433
1.426
1.417
1.409
1.403
1.396
1.389
1.279
1.255
1.249
1.224
1.217
1.193
1.170
1.146
1.140
1.115
1.107
1.090
1.074
1.051
1.044
1.020
1.013
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8.74
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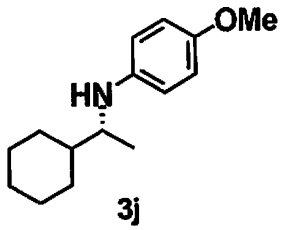
4.60
36.48
ppm
HN
OMe
3j



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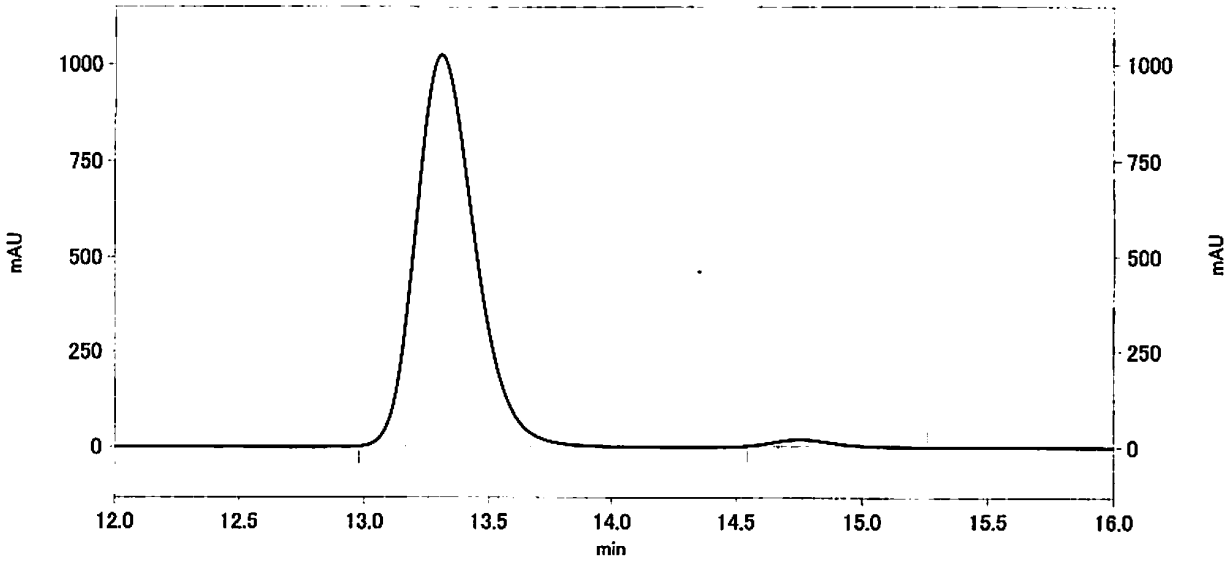
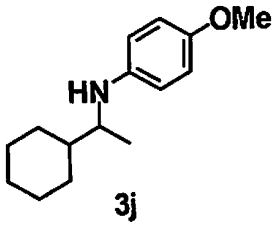


Pk #	Time	Area	Area%	Type
1	13.31	67426367	98.370	BB
2	14.75	1117381	1.630	BB



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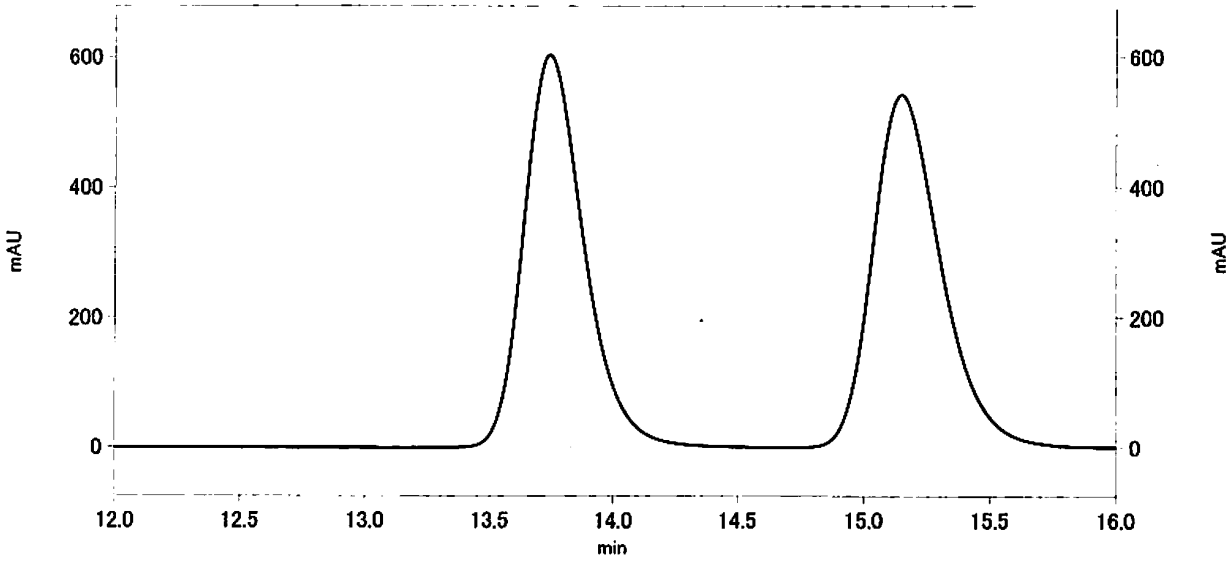
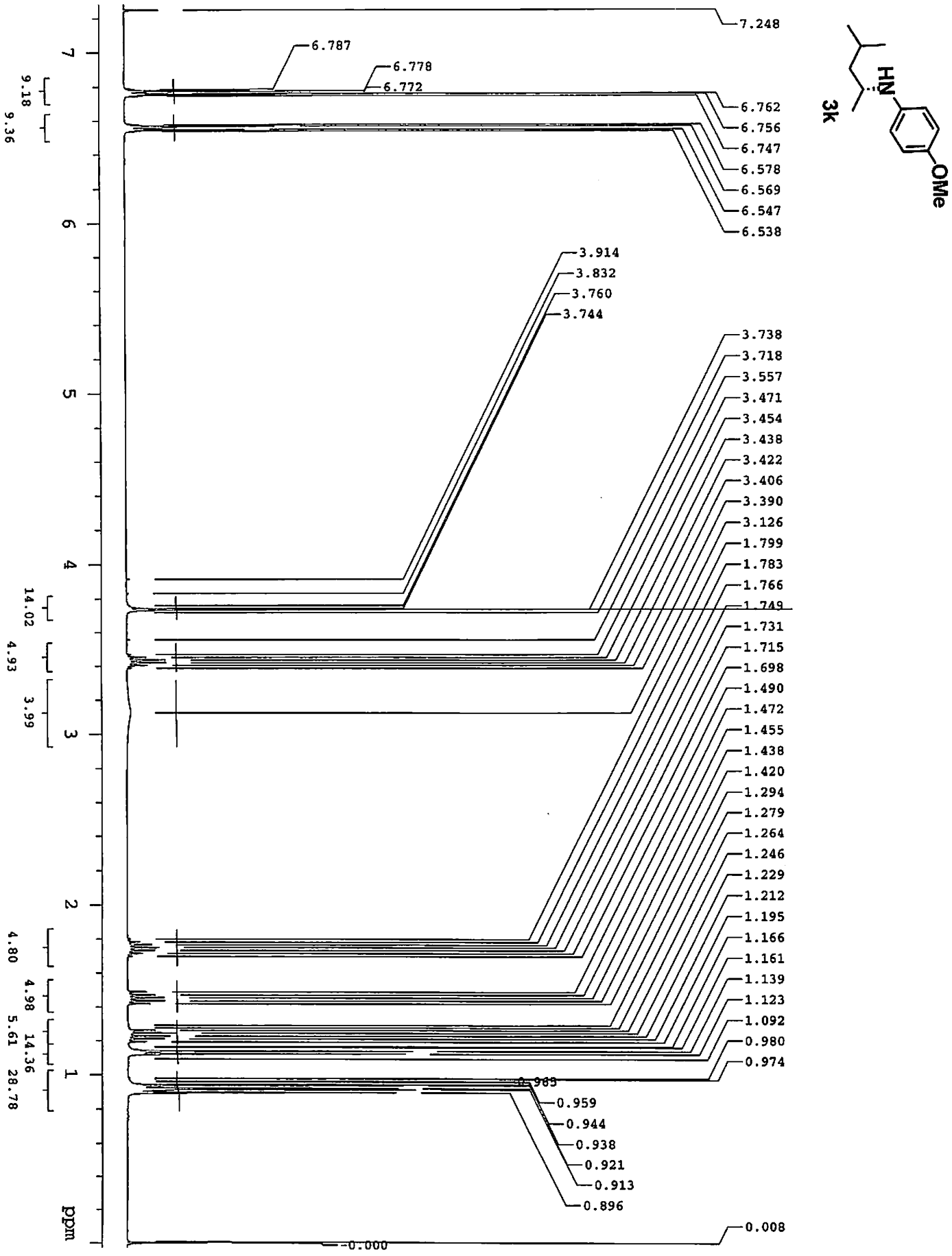


Pk #	Time	Area	Area%	Type
1	13.74	40885266	49.961	BB
2	15.15	40948935	50.039	BB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6.762
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6.547
6.538
3.914
3.832
3.760
3.744
3.738
3.718
3.557
3.471
3.454
3.438
3.422
3.406
3.390
3.126
1.799
1.783
1.766
1.749
1.731
1.715
1.698
1.490
1.472
1.455
1.438
1.420
1.294
1.279
1.264
1.246
1.229
1.212
1.195
1.166
1.161
1.139
1.123
1.092
0.980
0.974
0.963
0.959
0.944
0.938
0.921
0.913
0.896
0.008
0.000
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5.61
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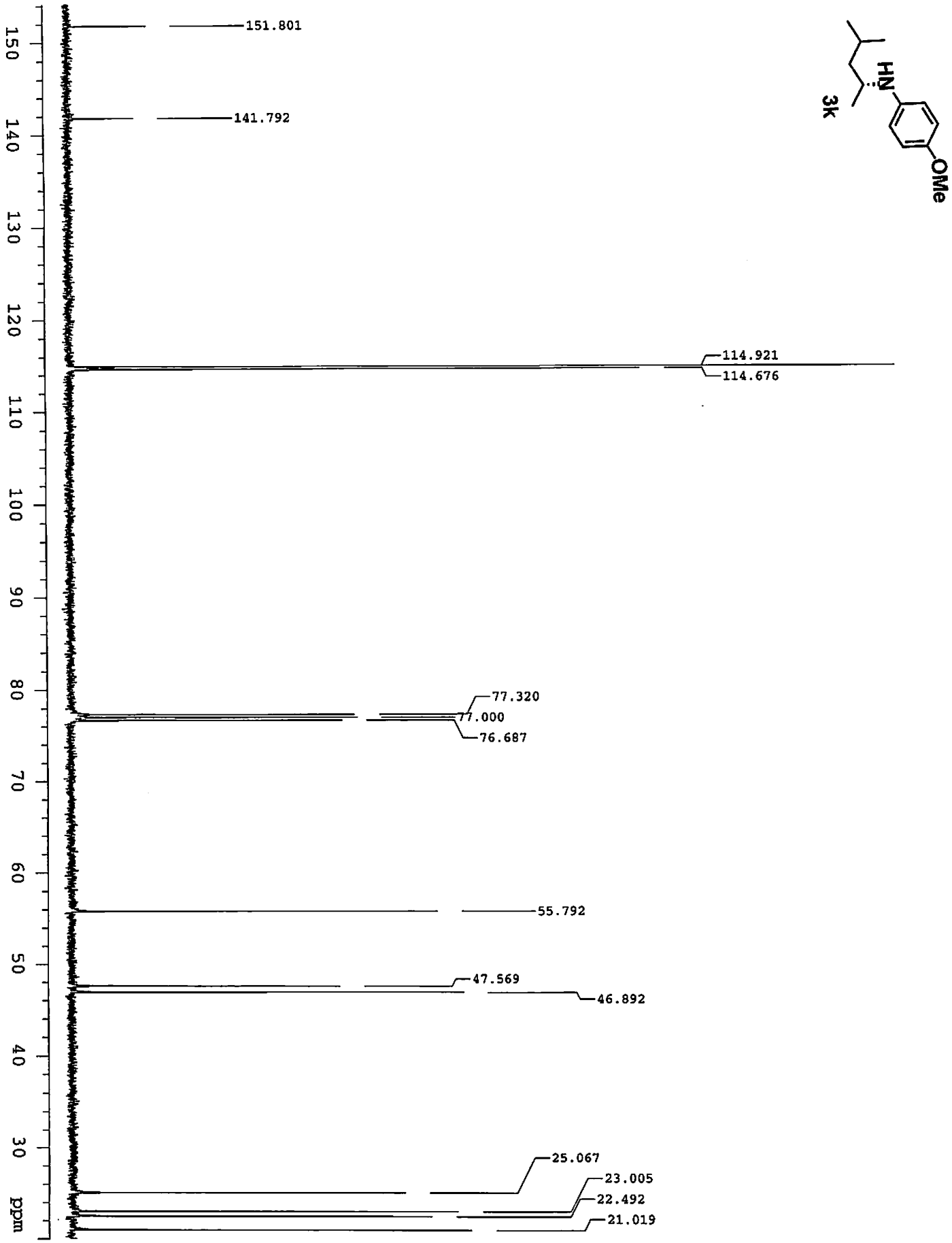
ppm
HN
OMe
3k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120
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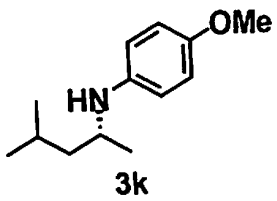
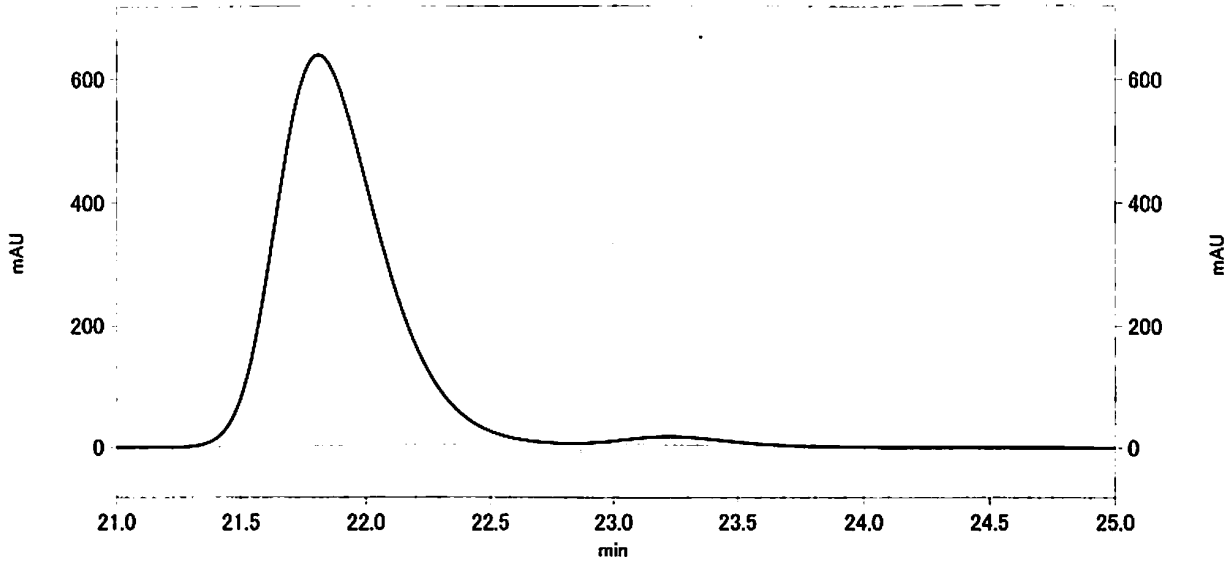
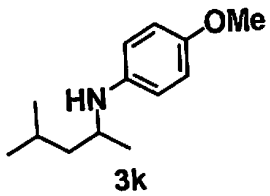
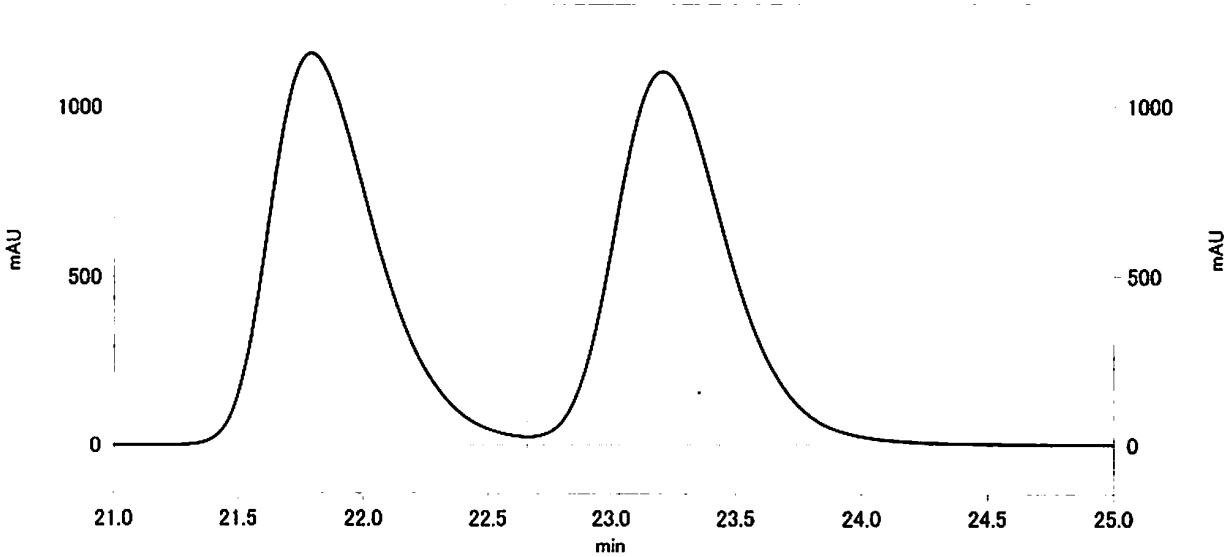
100
90
80
70
60
50
40
30
ppm
HN
OMe
3k



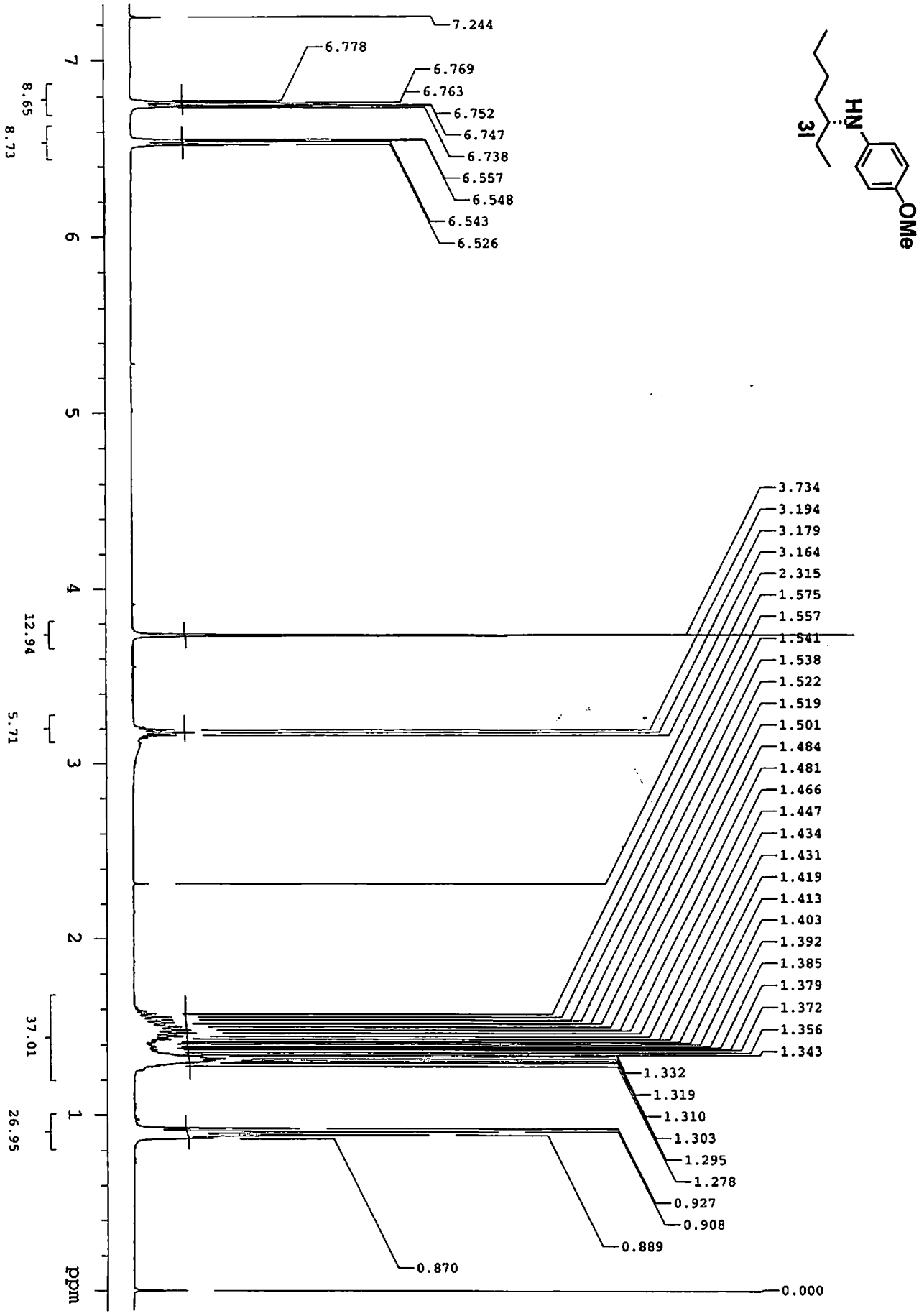


Pk #	Time	Area	Area%	Type
1	21.81	75162416	98.192	BI
2	23.22	1384266	1.808	BB





Pk #	Time	Area	Area%	Type
1	21.79	138582439	49.573	BV
2	23.21	140967394	50.427	VB


7.244
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6.769
6.763
6.752
6.747
6.738
6.557
6.548
6.543
6.526
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3.194
3.179
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1.557
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1.372
1.356
1.343
1.332
1.319
1.310
1.303
1.295
1.278
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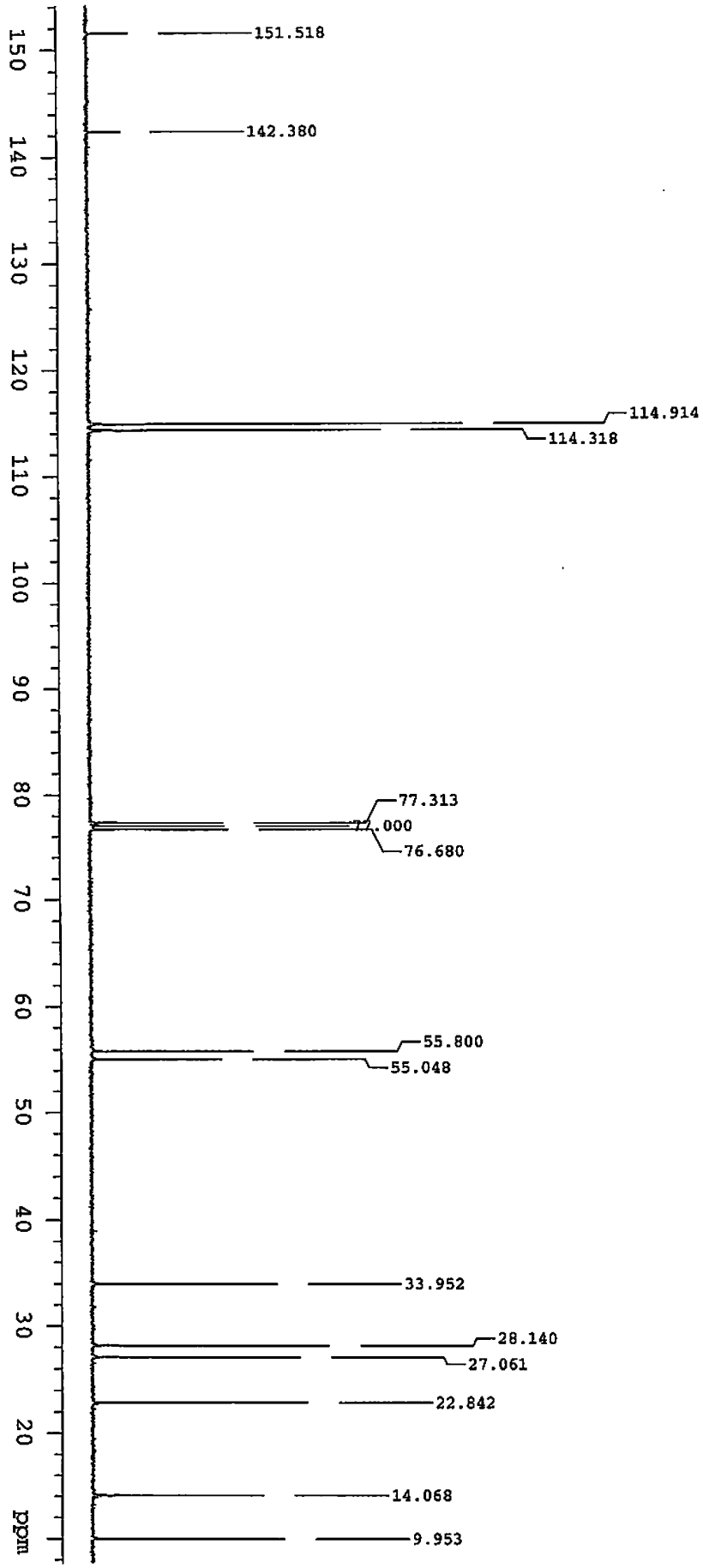
0.889
0.870
0.000
8.65
8.73
12.94
5.71
37.01
26.95
ppm
HN
OMe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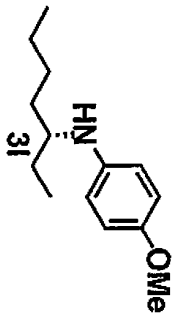
142.380
114.914
114.318
77.313
77.000
76.680
55.800
55.048
33.952
28.140
27.061
22.842
14.068
9.953
150
140
130
120
110
100
90
80
70
60
50
40
30
20
ppm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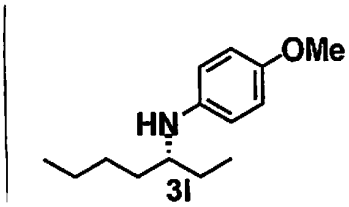
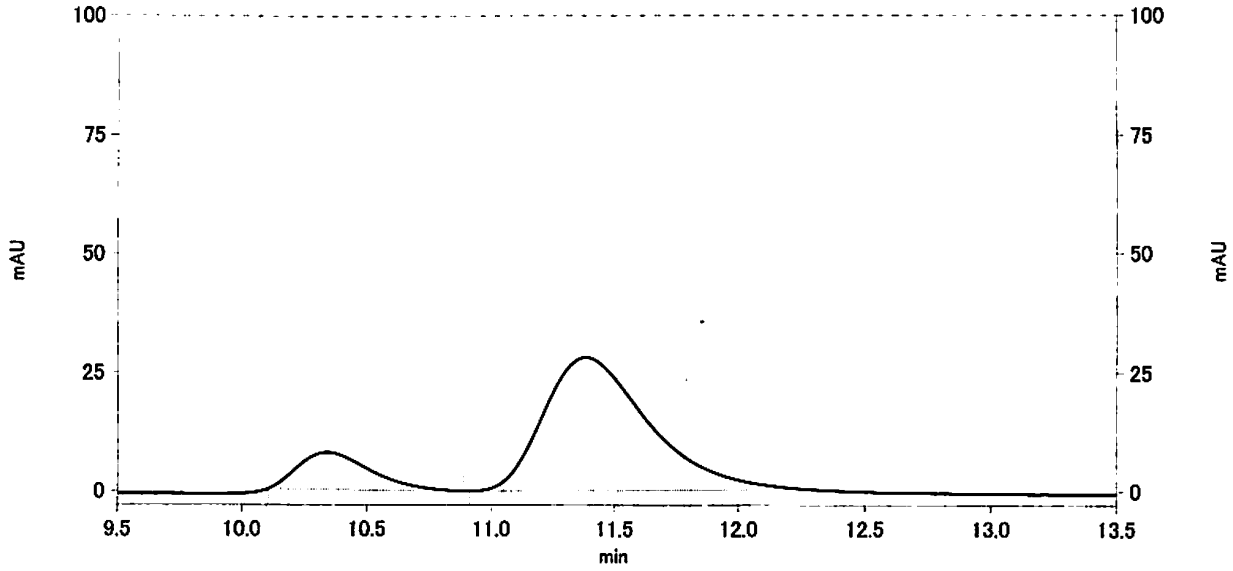
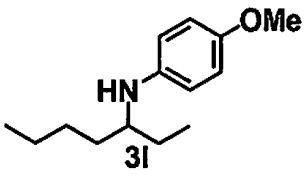
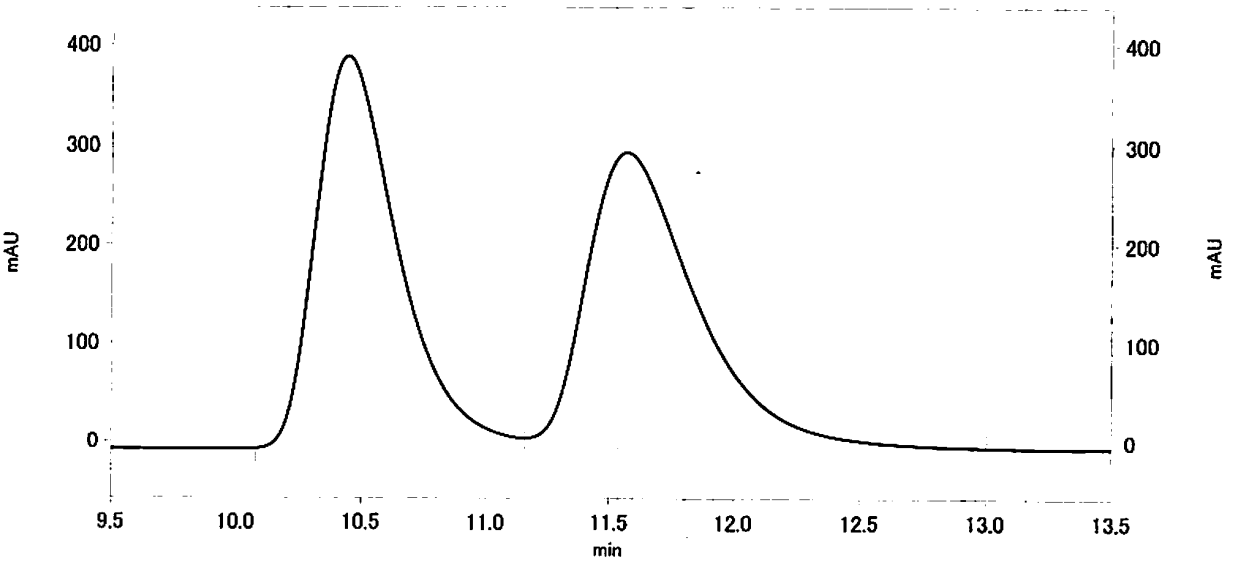
OMe



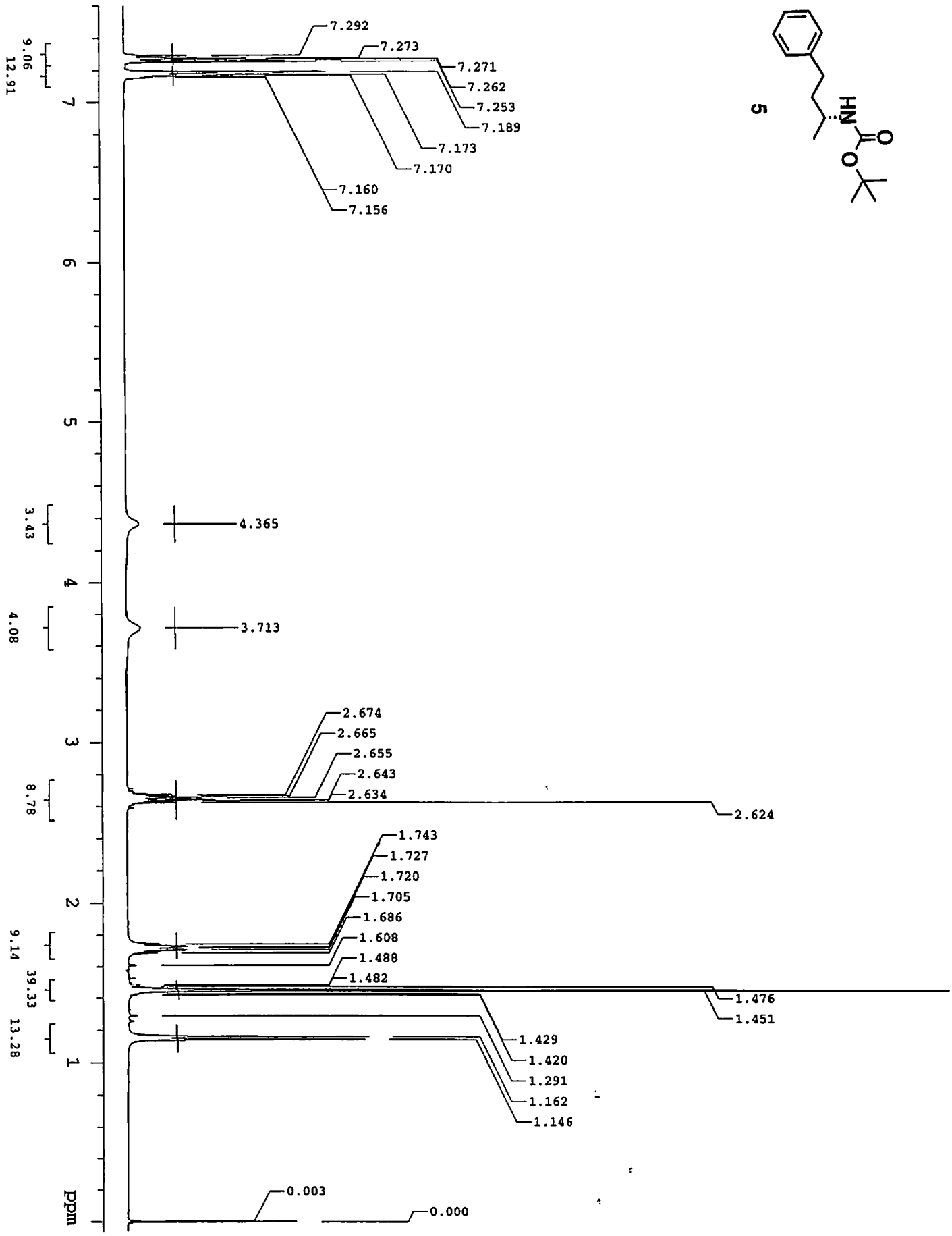


Pk #	Time	Area	Area%	Type
1	10.34	628831	15.970	BB
2	11.38	3308793	84.030	BB





Pk #	Time	Area	Area%	Type
1	10.45	36519251	49.453	BV
2	11.57	37326713	50.547	VB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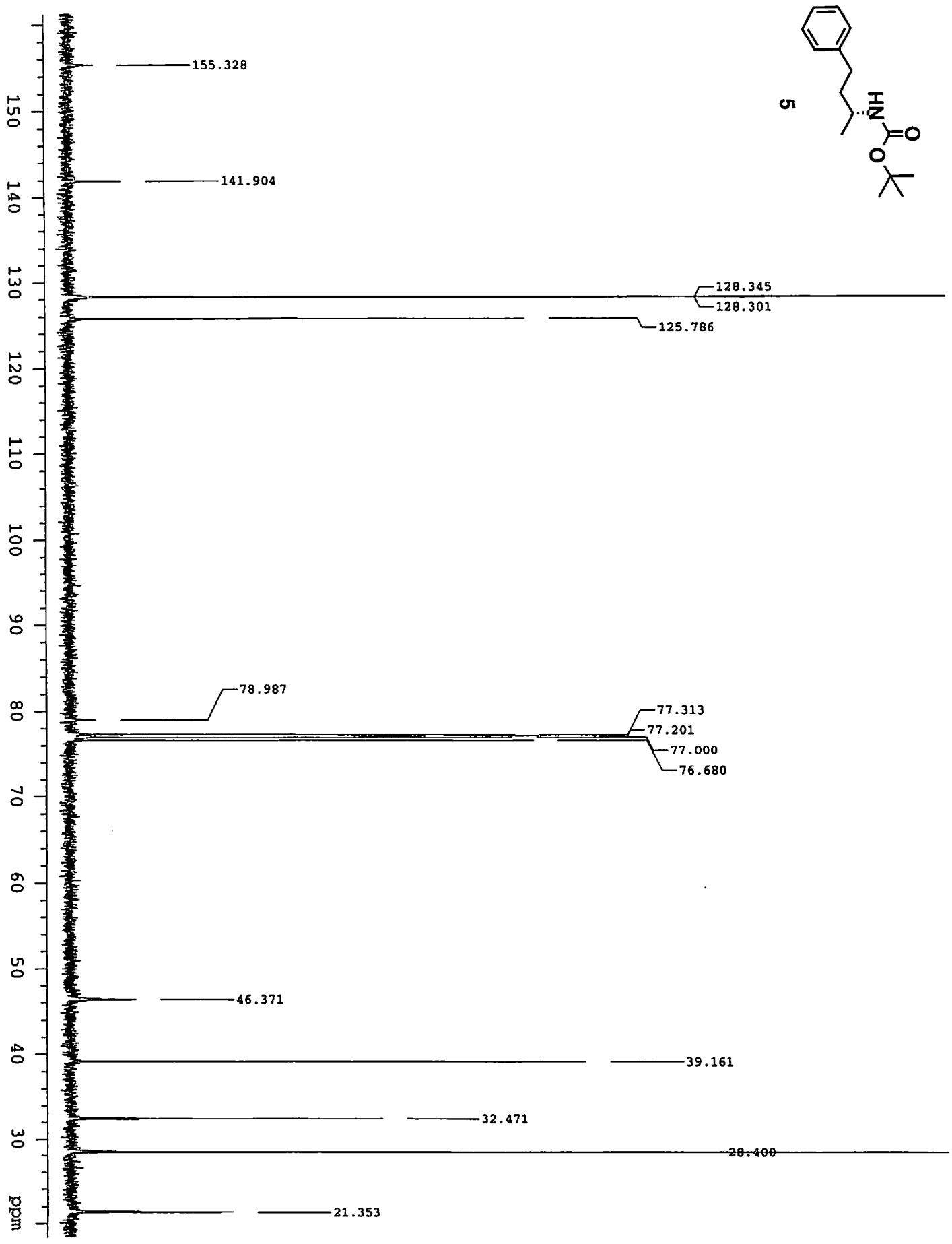
7.271
7.262
7.253
7.189
7.173
7.170
7.160
7.156
4.365
3.713
2.674
2.665
2.655
2.643
2.634
2.624
1.743
1.727
1.720
1.705
1.686
1.608
1.488
1.482
1.476
1.451
1.429
1.420
1.291
1.162
1.146
0.003
0.000
9.06
12.91
3.43
4.08
8.78
9.14
39.33
13.28
ppm
5
HN
O
O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128.301
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77.313
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77.000
76.680
46.371
39.161
32.471
28.400
21.353
ppm
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140
130
120
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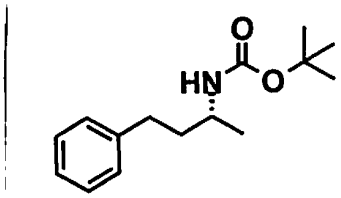
100
90
80
70
60
50
40
30
5
NH
O
O



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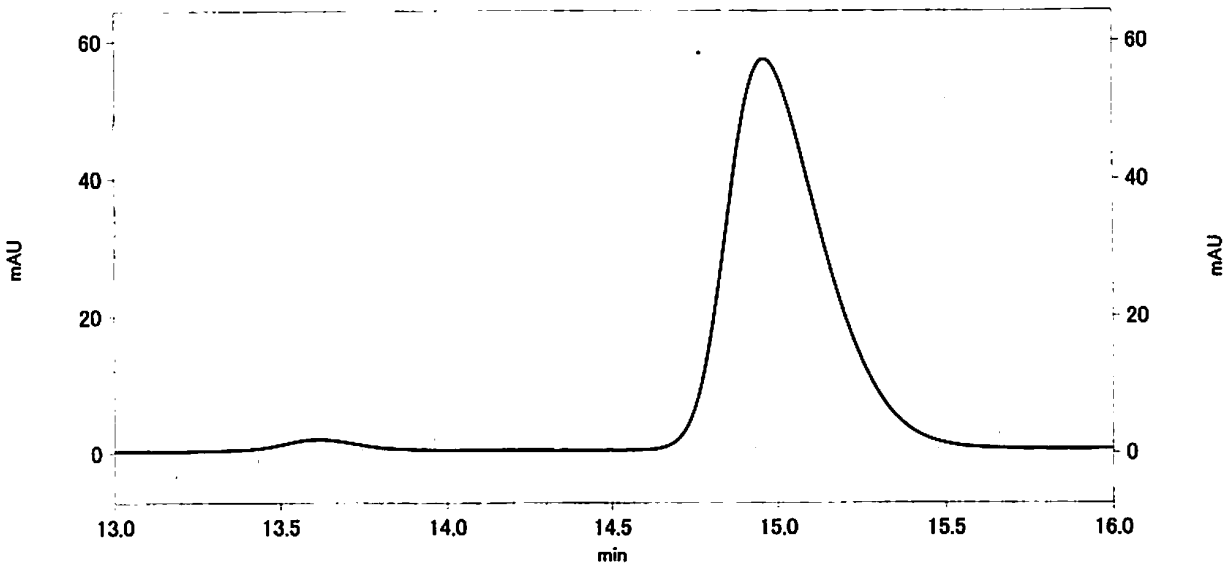
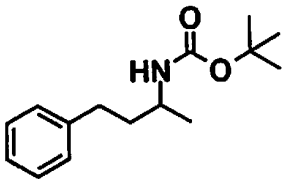
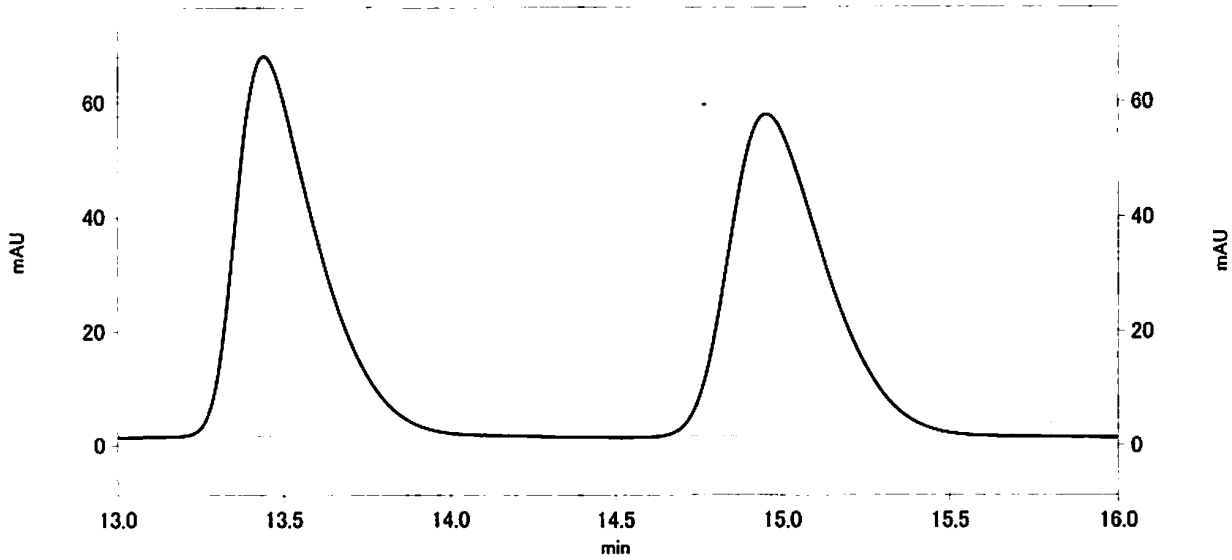


Pk #	Time	Area	Area%	Type
1	13.61	76716	1.654	BB
2	14.96	4561026	98.346	BB



5



Pk #	Time	Area	Area%	Type
1	13.44	4514159	49.912	BB
2	14.95	4529993	50.088	BB