

Supporting Information for

Highly Enantioselective Hydrogenation of Enamides Catalyzed by

Chiral Phosphoric Acids

Guilong Li and Jon C. Antilla*

Department of Chemistry, University of South Florida,
4202 East Fowler Avenue CHE205A, Tampa, Florida 33620

jantilla@cas.usf.edu

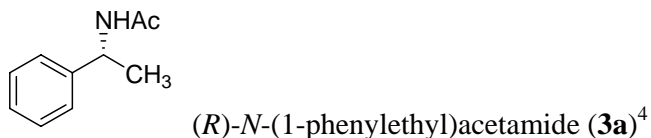
General Considerations	S2
Experimental section	S3
Compound Characterization data.....	S3-S7
References	S7
Spectra Copies of chiral HPLC.....	S8-37

General Considerations: All reactions were carried out in flame-dried or oven-dried screw-cap test tubes with magnetic stirring. All solvents (toluene, dichloromethane, and THF) were purified by passing through a column of activated alumina under a dry argon atmosphere. Ethyl acetate was purchased from Aldrich and dried with molecular sieves (4Å). Additional solvents (acetonitrile and chloroform) were purchased anhydrous from commercial sources and transferred under an argon atmosphere. VAPOL phosphoric acid was synthesized according to the literature procedure.¹ Chiral BINOL was purchased from commercial sources and used without further purification. Substituted BINOL phosphoric acids (**A3**, and **A4**) were prepared from chiral BINOL according to the known literature procedures.² Phenylphosphinic acid was purchased from commercial sources and used without further purification. Thin layer chromatography was performed on Merck TLC plates (silica gel 60 F254). Flash column chromatography was performed with Merck silica gel (230-400 mesh). Enantiomeric excess (ee) was determined using a Varian Prostar HPLC with a 210 binary pump and a 335 diode array detector. Column conditions are reported in the experimental section below. Melting points were determined using a MEL-TEMP 3.0 instrument and are uncorrected. Optical rotations were performed on a Rudolph Research Analytical Autopol IV polarimeter (λ 589) using a 700- L cell with a path length of 1-dm. ¹H NMR and ¹³C NMR were recorded on a Bruker Avance DPX-250 (250 MHz) instrument with chemical shifts reported relative to tetramethylsilane (TMS). Compounds described in the literature were characterized by comparing their ¹H NMR, ¹³C NMR chemical shift and melting points to the reported values.

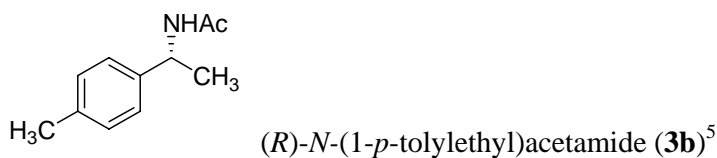
All enamides were prepared according to the reported procedures except that the purification of the enamides was by flash column chromatography (EtOAc / hexane) and followed by recrystallization from EtOAc/hexane.³

All racemic amide products were prepared by hydrogenation of the corresponding enamide with 10% Pd/C as the catalyst and by using EtOAc as the solvent.

Typical procedure for the asymmetric hydrogenation of enamide catalyzed by a dual-catalytic system of a chiral Brønsted acid and acetic acid (Method B): To a flame-dried reaction tube was added enamide **1** (0.2 mmol), Hantzsch ester **2** (55.7 mg, 0.22 mmol) and catalyst **A4** (1.4 mg, 0.002 mmol). The mixture was purged with argon, then acetic acid (1.0 μ L, 0.02 mmol) and toluene (1.2 mL) were added. The suspension was heated to 50°C with stirring. The crude product was purified by flash column chromatography (EtOAc/hexane) after the reaction was completed (monitored by TLC) to provide pure product amide **3**. ee values were measured on HPLC with a suitable chiral column.

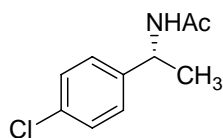


The product was obtained by flash chromatography (hexane: EtOAc = 1:1 to EtOAc) as a white solid, 31.4 mg, 97% yield, 91% ee. HPLC analysis: Chiralcel AD-H (hexane/iPrOH = 95/5, 1.0 mL/min), $t_{r-major}$ 9.12 min, $t_{r-minor}$ 11.60 min. Melting point: 89-91 °C. $[\alpha]_D^{20}$ = 109.3 (c = 1.49, EtOH). ¹H NMR (250MHz, CDCl₃): δ 1.46 (d, J =6.8 Hz, 3H), 1.94 (s, 3H), 5.04-5.15 (m, 1H), 6.09 (br, 1H), 7.27-7.30 (m, 5H). ¹³C NMR (62.5 MHz, CDCl₃): δ 21.8, 23.4, 48.8, 126.2, 127.3, 128.7, 143.3, 169.2.



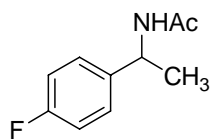
This reaction was performed in 0.1 mmol scale. The product was obtained by flash

chromatography (hexane: EtOAc = 1:1 to EtOAc) as a white solid, 16.5 mg, 93% yield, 90% ee. HPLC analysis: Chiralcel AD-H (hexane/iPrOH = 95/5, 1.0 mL/min), $t_{\text{r-major}}$ 9.99 min, $t_{\text{r-minor}}$ 13.03 min. Melting point: 80-82°C. $[\alpha]_{\text{D}}^{20} = +135.7$ (c = 0.715, EtOH). ^1H NMR (250 MHz, CDCl_3): δ 1.46 (d, J = 6.8 Hz, 3H), 1.96 (s, 3H), 2.32 (s, 3H), 5.03-5.14 (m, 1H), 5.78 (br, 1H), 7.17 (dd, J = 7.8, 9.0 Hz, 4H). ^{13}C NMR (62.5 MHz, CDCl_3): δ 21.1, 21.7, 23.5, 48.6, 126.2, 129.3, 137.1, 140.2, 169.0.



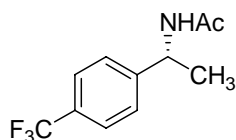
(*R*)-*N*-(1-(4-chlorophenyl)ethyl)acetamide (**3c**)⁶

The product was obtained by flash chromatography (hexane: EtOAc = 1:1 to EtOAc) as a white solid, 34.6 mg, 88% yield, 91% ee. HPLC analysis: Chiralcel AD-H (hexane/iPrOH = 95/5, 1.0 mL/min), $t_{\text{r-major}}$ 10.71 min, $t_{\text{r-minor}}$ 14.21 min. Melting point: 97-99 °C. $[\alpha]_{\text{D}}^{20} = +122.3$ (c = 1.38, EtOH). ^1H NMR (250 MHz, CDCl_3): δ 1.43 (d, J = 6.8 Hz, 3H), 1.95 (s, 3H), 4.99-5.11 (m, 1H), 6.02 (br, 1H), 7.25 (dd, J = 8.8, 6.8 Hz, 4H). ^{13}C NMR (62.5 MHz, CDCl_3): δ 21.7, 23.3, 48.2, 127.6, 128.7, 133.0, 141.9, 169.2.



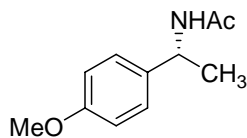
N-(1-(4-fluorophenyl)ethyl)acetamide (**3d**)⁷

The product was obtained by flash chromatography (hexane: EtOAc = 1:1 to EtOAc) as a white solid, 34.9 mg, 96% yield, 89% ee. HPLC analysis: Chiralcel AD-H (hexane/iPrOH = 95/5, 1.0 mL/min), $t_{\text{r-major}}$ 9.88 min, $t_{\text{r-minor}}$ 12.65 min. Melting point: 118-120 °C. $[\alpha]_{\text{D}}^{20} = +105.2$ (c = 1.60, EtOH). ^1H NMR (250 MHz, CDCl_3): δ 1.44 (d, J = 7.0 Hz, 3H), 1.95 (s, 3H), 5.01-5.13 (m, 1H), 6.11 (br, 1H), 6.99 (t, J = 8.6, 2H), 7.24-7.29 (m, 2H). ^{13}C NMR (62.5 MHz, CDCl_3): δ 21.8, 23.3, 48.2, 115.3 (d, J = 21.3 Hz), 127.8 (d, J = 8.0 Hz), 139.2 (d, J = 3.1 Hz), 161.9 (d, J = 243.8 Hz), 169.2.



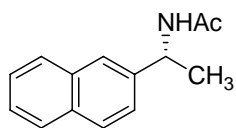
(*R*)-*N*-(1-(4-(trifluoromethyl)phenyl)ethyl)acetamide (**3e**)⁵

The product was obtained by flash chromatography (hexane: EtOAc = 1:1 to EtOAc) as a white solid, 44.3 mg, 96% yield, 87% ee. Melting point: 101-102 °C. HPLC analysis: Chiralcel AD-H (hexane/iPrOH = 95/5, 1.0 mL/min), $t_{r\text{-major}}$ 8.71 min, $t_{r\text{-minor}}$ 11.63 min. $[\alpha]_D^{20} = +85.8$ ($c = 1.62$, EtOH). ^1H NMR (250 MHz, CDCl_3): δ 1.44(d, $J = 7.0$ Hz, 3H), 1.96 (s, 3H), 5.05-5.16 (m, 1H), 6.18 (br, 1H), 7.34 (d, $J = 8.0$, 2H), 7.56(d, $J = 8.0$, 2H). ^{13}C NMR (62.5 MHz, CDCl_3): δ 21.8, 23.2, 48.6, 124.1 (d, $J = 270.3$ Hz), 125.6 (q, $J = 4.0$ Hz), 126.4, 129.5 (d, $J = 32.1$ Hz), 147.5, 169.4.



(*R*)-*N*-(1-(4-methoxyphenyl)ethyl)acetamide (**3f**)⁵

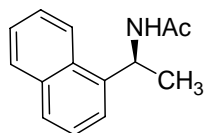
No cocatalyst acetic acid was used in this case. The product was obtained by flash chromatography (hexane: EtOAc = 1:1 to EtOAc) as a white solid, 37.1 mg, 96% yield, 95% ee. Melting point: 84-85 °C. HPLC analysis: Chiralcel AD-H (hexane/iPrOH = 95/5, 1.0 mL/min), $t_{r\text{-minor}}$ 16.48 min, $t_{r\text{-major}}$ 18.64 min. $[\alpha]_D^{20} = +140.9$ ($c = 1.475$, EtOH). ^1H NMR (250 MHz, CDCl_3): δ 1.45(d, $J = 7.0$ Hz, 3H), 1.94 (s, 3H), 3.78(s, 3H), 4.99-5.11(m, 1H), 5.93 (br, 1H), 6.85(d, $J = 8.8$, Hz, 2H), 7.23(d, $J = 8.8$, Hz, 2H). ^{13}C NMR (62.5 MHz, CDCl_3): δ 21.7, 23.4, 48.2, 114.0, 127.4, 135.4, 158.8, 169.1.



(*R*)-*N*-(1-(naphthalen-2-yl)ethyl)acetamide (**3g**)⁸

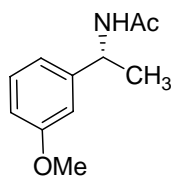
The product was obtained by flash chromatography (hexane: EtOAc = 1:1 to EtOAc) as a white solid, 43.0 mg, 99% yield, 92% ee. Melting point: 108-109 °C. HPLC analysis: Chiralcel AD-H (hexane/iPrOH = 95/5, 1.0 mL/min), $t_{r\text{-major}}$ 13.12 min, $t_{r\text{-minor}}$ 19.56 min. $[\alpha]_D^{20} = +102.0$ ($c = 1.97$, EtOH). ^1H NMR (250 MHz, CDCl_3): δ 1.54(d, $J = 7.0$ Hz, 3H), 1.97 (s, 3H), 5.21-5.32 (m, 1H), 6.21 (d, $J = 6.5$ Hz, 1H),

7.40-7.48 (m, 3H), 7.73-7.81 (m, 4H). ^{13}C NMR (62.5 MHz, CDCl_3): δ 21.7, 23.4, 48.9, 124.6, 124.8, 125.9, 126.3, 127.6, 127.9, 128.5, 132.7, 133.4, 140.7, 169.3.



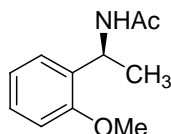
(*S*)-*N*-(1-(naphthalen-1-yl)ethyl)acetamide (**3h**)^{5,9}

The product was obtained by flash chromatography (hexane: EtOAc = 1:1 to EtOAc) as a white solid, 18.2 mg, 43% yield, 78% ee. Melting point: 147-149 °C. HPLC analysis: Chiralcel AS-H (hexane/iPrOH = 95/5, 1.0 mL/min), $t_{\text{r-major}}$ 29.43 min, $t_{\text{r-minor}}$ 36.89 min. $[\alpha]_{\text{D}}^{20} = -47.9$ ($c = 0.82$, EtOH). ^1H NMR (250 MHz, CDCl_3): δ 1.66 (d, $J = 6.5$ Hz, 3H), 1.94 (s, 3H), 5.83-5.94 (m, 2H), 7.44-7.55 (m, 4H), 7.78-8.12 (m, 3H). ^{13}C NMR (62.5 MHz, CDCl_3): δ 20.7, 23.4, 44.7, 122.6, 123.5, 125.2, 125.9, 126.6, 128.4, 128.8, 131.2, 134.0, 138.3, 168.9.



(*R*)-*N*-(1-(3-methoxyphenyl)ethyl)acetamide (**3i**)¹⁰

The product was obtained by flash chromatography (hexane: EtOAc = 1:1 to EtOAc) as an oil, 38.0 mg, 98% yield, 71% ee. HPLC analysis: Chiralcel AD-H (hexane/iPrOH = 95/5, 1.0 mL/min), $t_{\text{r-major}}$ 13.40 min, $t_{\text{r-minor}}$ 16.69 min. $[\alpha]_{\text{D}}^{20} = +93.8$ ($c = 1.58$, EtOH). ^1H NMR (250 MHz, CDCl_3): δ 1.44 (d, $J = 7.0$ Hz, 3H), 1.94 (s, 3H), 3.78 (s, 3H), 5.00-5.11 (m, 1H), 6.09 (br, 1H), 6.76-6.89 (m, 3H), 7.23 (t, $J = 7.8$ Hz, 1H). ^{13}C NMR (62.5 MHz, CDCl_3): δ 21.8, 23.4, 55.2, 112.3, 112.4, 118.4, 129.7, 145.0, 159.8, 169.2.



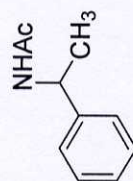
(*S*)-*N*-(1-(2-methoxyphenyl)ethyl)acetamide (**3j**)^{10b}

The product was obtained by flash chromatography (hexane: EtOAc = 1:1 to EtOAc) as a white solid, 36.9 mg, 96% yield, 41% ee. HPLC analysis: Chiralcel AD-H

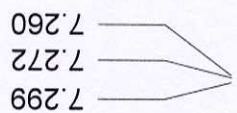
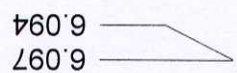
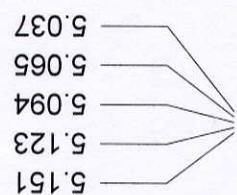
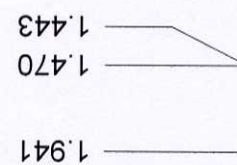
(hexane/iPrOH = 95/5, 1.0 mL/min), $t_{\text{r-minor}}$ 11.97 min, $t_{\text{r-major}}$ 16.69 min. Melting point: 142-144 °C. $[\alpha]_{\text{D}}^{20} = -38.3$ ($c = 1.69$, EtOH). ^1H NMR (250 MHz, CDCl_3): δ 1.41(d, $J = 7.0$ Hz, 3H), 1.95 (s, 3H), 3.86 (s, 3H), 5.20-5.32 (m, 1H), 6.50 (d, $J = 6.8$ Hz, 1H), 6.90 (t, $J = 7.5$ Hz, 2H), 7.19-7.25 (m, 2H). ^{13}C NMR (62.5 MHz, CDCl_3): δ 21.5, 23.6, 55.4, 111.1, 120.9, 128.0, 128.4, 131.0, 157.0, 168.8.

References:

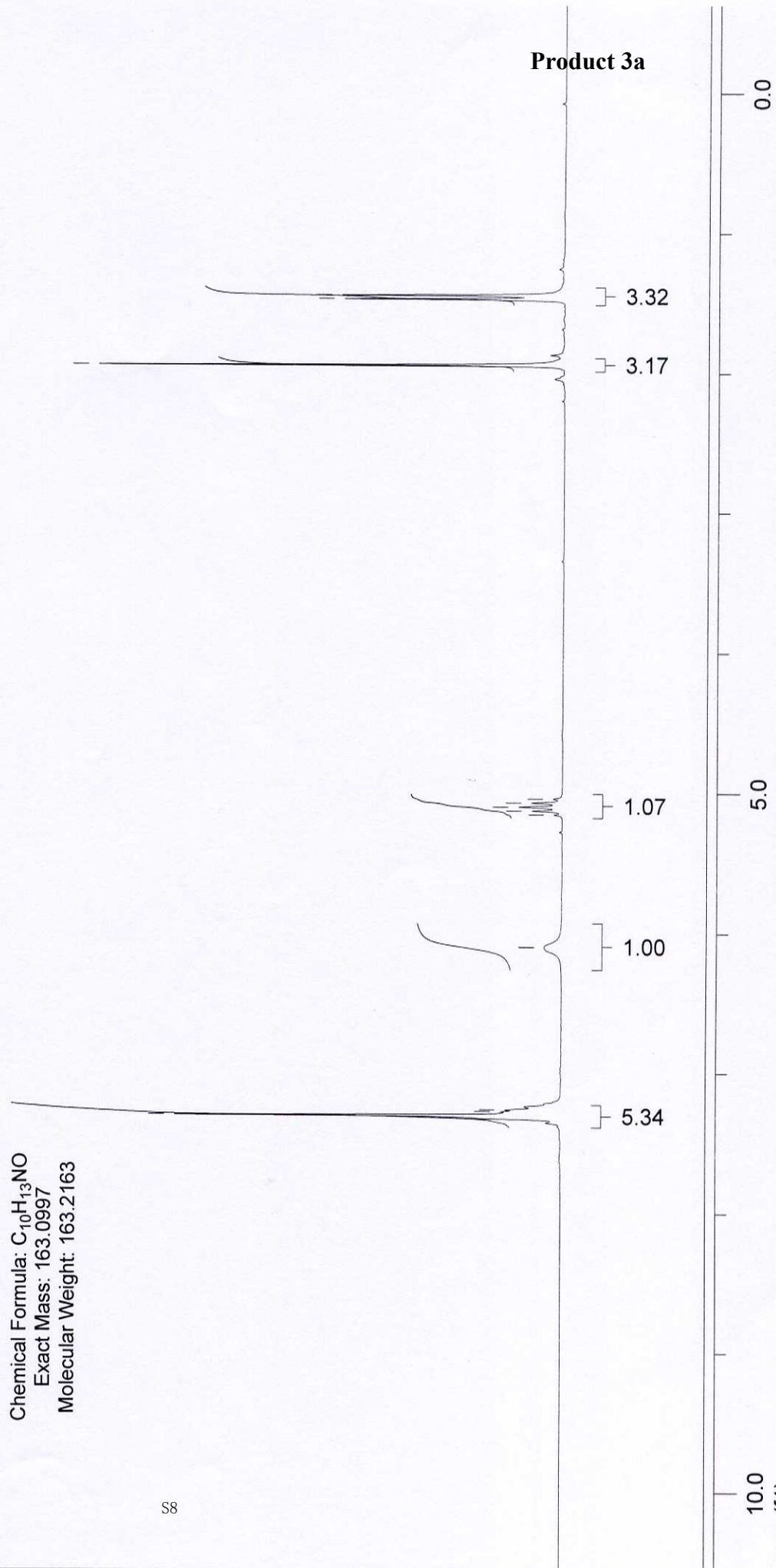
1. (a) Bao J.; Wulff, W. D.; Dominy, J. B.; Fumo, M. J.; Grant, E. B.; Rob, A. C.; Whitcomb, M. C.; Yeung, S.-M.; Ostrander, R. L.; Rheingold, A. L. *J. Am. Chem. Soc.* **1996**, *118*, 3392. (b) Rowland, G. B.; Zhang, H.; Rowland, E. B.; Chennamadhavuni, S.; Wang, Y.; Antilla, J. C. *J. Am. Chem. Soc.* **2005**, *127*, 15696.
2. For procedures, see: (a) Storer, R. I.; Carrera, D. E.; Ni, Y.; MacMillan, D. W. C. *J. Am. Chem. Soc.* **2006**, *128*, 84. For characterization data, see: (b) Inanaga, J. EP 1134209 A1, **2001**, 16 pp. (c) Toh, J.; Fuchibe, K.; Akiyama, T. *Angew. Chem., Int. Ed.* **2006**, *45*, 4796.
3. Burk, M. J.; Casy, G.; Johnson, N. B. *J. Org. Chem.* **1998**, *63*, 6084.
4. Zhao, D.; Wang, Z.; Ding, K. *Tetrahedron Lett.* **2007**, *48*, 5095.
5. Kim, M.-J.; Kim, W.-H.; Han, K.; Choi, Y. K.; Park, *Org. Lett.* **2007**, *9*, 1157.
6. Zhang, Q.; Takacs, J. M. *Org. Lett.* **2008**, *10*, 545.
7. Hu, X.-P.; Zheng, Z. *Org. Lett.* **2004**, *6*, 3585.
8. (a) Paetzold, J.; Baeckvall, J. E. *J. Am. Chem. Soc.* **2005**, *127*, 17620. (b) Hansen, A.L.; Skrydstrup, T. *J. Org. Chem.* **2005**, *70*, 5997.
9. Hamersak, Z.; Roje, M.; Hollosi, M.; Majer, Z.; Sunjic, V. *Spectroscopy Letters*, **2002**, *35*, 73.
10. (a) Sanz, R.; Martinez, A.; Guilarte, V.; Alvarez-Gutierrez, J. M.; Rodriguez, F. *Eur. J. Org. Chem.* **2007**, *28*, 4642. (b) Horiba, M.; Yamamoto, S.; Oi, N.; *Agricultural and Biological Chemistry*, **1982**, *46*, 1219.



Chemical Formula: $C_{10}H_{13}NO$
 Exact Mass: 163.0997
 Molecular Weight: 163.2163

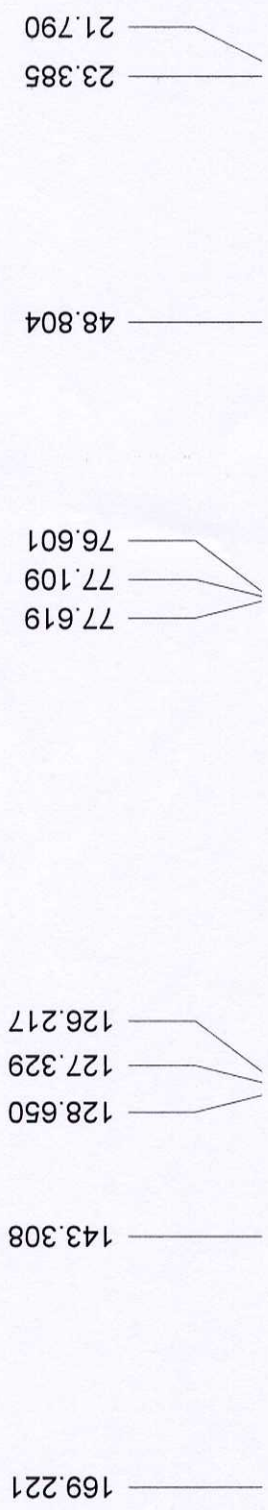
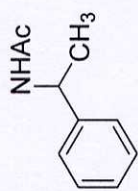


Product 3a



Product 3a

Chemical Formula: $C_{10}H_{13}NO$
 Exact Mass: 163.0997
 Molecular Weight: 163.2163

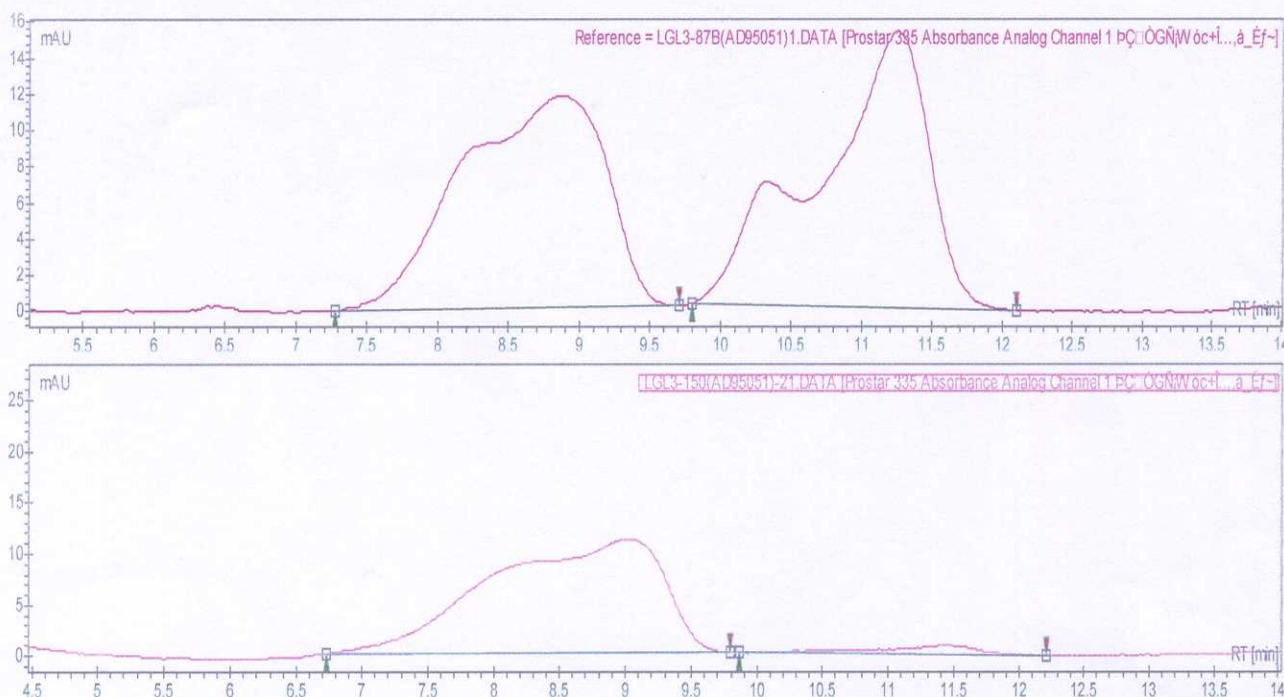


Chromatogram : LGL3-150(AD95051)-21_channel1

Product 3a

System : HPLC
Method : LGL
User : Gerald Rowland

Acquired : 11/13/2008 10:33:03 AM
Processed : 11/13/2008 4:14:15 PM
Printed : 11/13/2008 4:15:03 PM



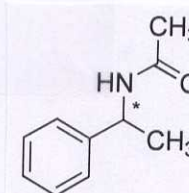
Peak results :

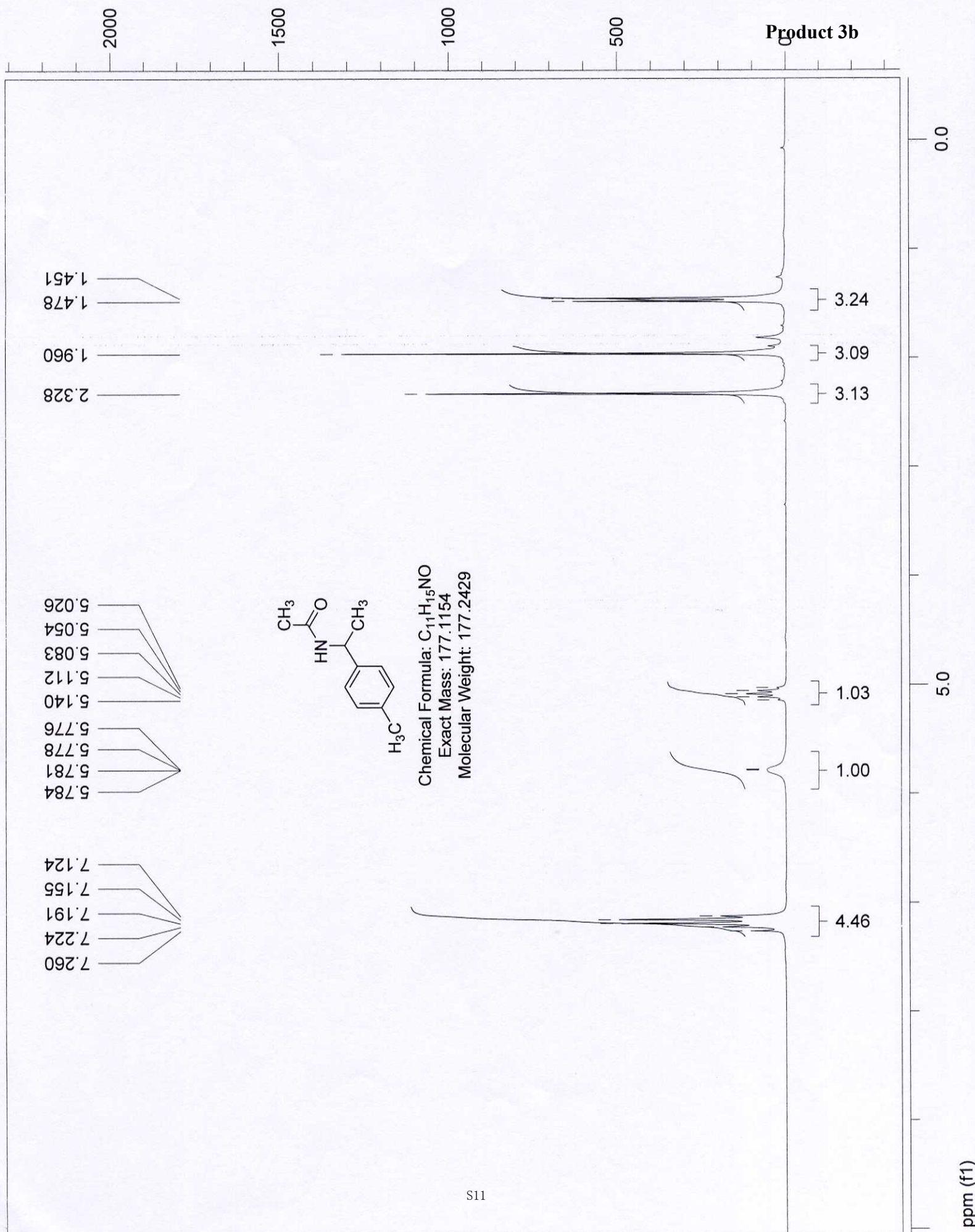
LGL3-87B(AD95051)1.D [Prostar 335 Absorbance Analog Channel 1] CC(C)C(=O)Nc1ccccc1

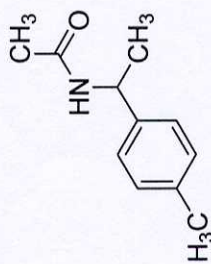
Index	Name	Time [Min]	Quantity [% Area]	Height [mAU]	Area [mAU.Min]	Area % [%]
1	UNKNOWN	8.88	50.13	11.7	13.9	50.130
2	UNKNOWN	11.25	49.87	15.3	13.8	49.870
Total			100.00	27.0	27.7	100.000

LGL3-150(AD95051)-21.D [Prostar 335 Absorbance Analog Channel 1] CC(C)C(=O)Nc1ccccc1

Index	Name	Time [Min]	Quantity [% Area]	Height [mAU]	Area [mAU.Min]	Area % [%]
1	UNKNOWN	9.03	95.44	11.1	16.8	95.442
2	UNKNOWN	11.47	4.56	0.9	0.8	4.558
Total			100.00	12.0	17.6	100.000

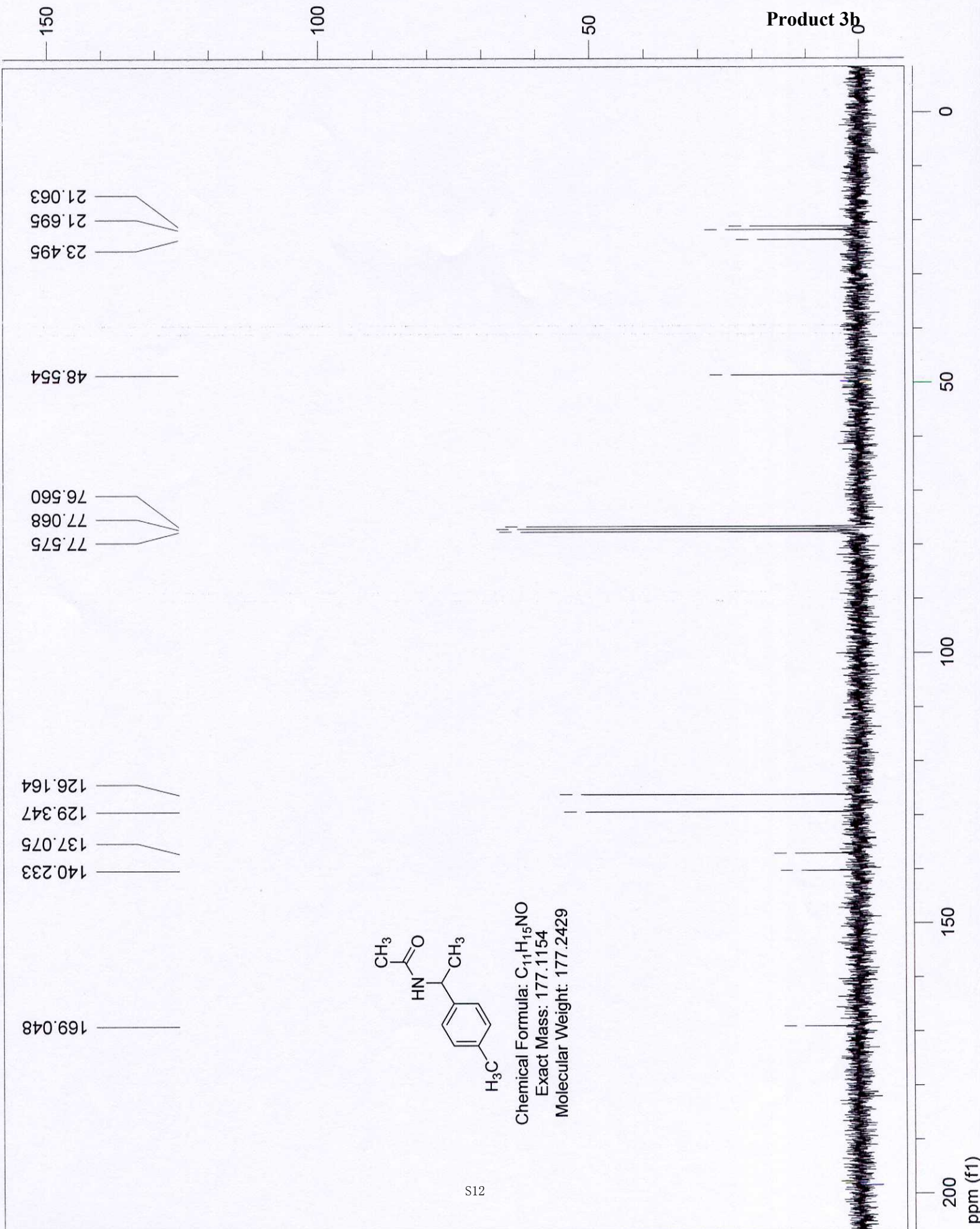






Chemical Formula: C₁₁H₁₅NO
 Exact Mass: 177.1154
 Molecular Weight: 177.2429

S12

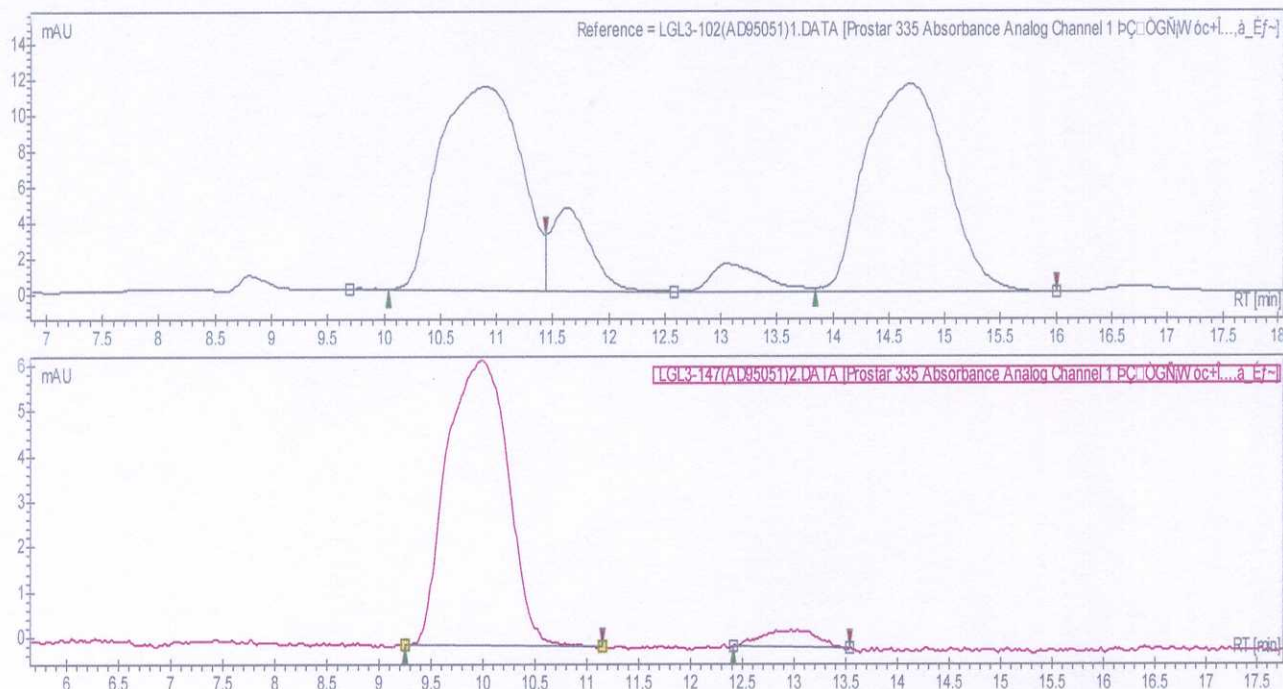


Chromatogram : LGL3-147(AD95051)2_channel1

Product 3b

System : HPLC
Method : LGL
User : Gerald Rowland

Acquired : 7/9/2008 3:33:32 PM
Processed : 7/9/2008 3:59:08 PM
Printed : 11/7/2008 2:52:45 PM



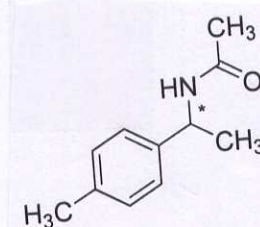
Peak results :

LGL3-102(AD95051)1.DATA [Prostar 335 Absorbance Analog Channel 1]

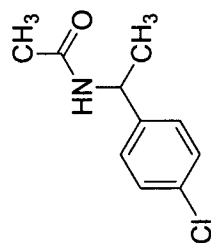
Index	Name	Time [Min]	Quantity [% Area]	Height [mAU]	Area [mAU.Min]	Area % [%]
1	UNKNOWN	10.89	49.45	11.4	9.6	49.449
2	UNKNOWN	14.69	50.55	11.6	9.8	50.551
Total			100.00	23.0	19.4	100.000

LGL3-147(AD95051)2.DATA [Prostar 335 Absorbance Analog Channel 1]

Index	Name	Time [Min]	Quantity [% Area]	Height [mAU]	Area [mAU.Min]	Area % [%]
1	UNKNOWN	9.99	95.02	6.3	4.3	95.023
2	UNKNOWN	13.03	4.98	0.4	0.2	4.977
Total			100.00	6.7	4.5	100.000



Product 3c



Chemical Formula: $C_{10}H_{12}ClNO$
 Exact Mass: 197.0607
 Molecular Weight: 197.6614

1.415
1.442

1.948

4.991
5.020
5.049
5.078
5.106

6.019

7.198
7.233
7.260
7.295

3.28

3.30

1.07

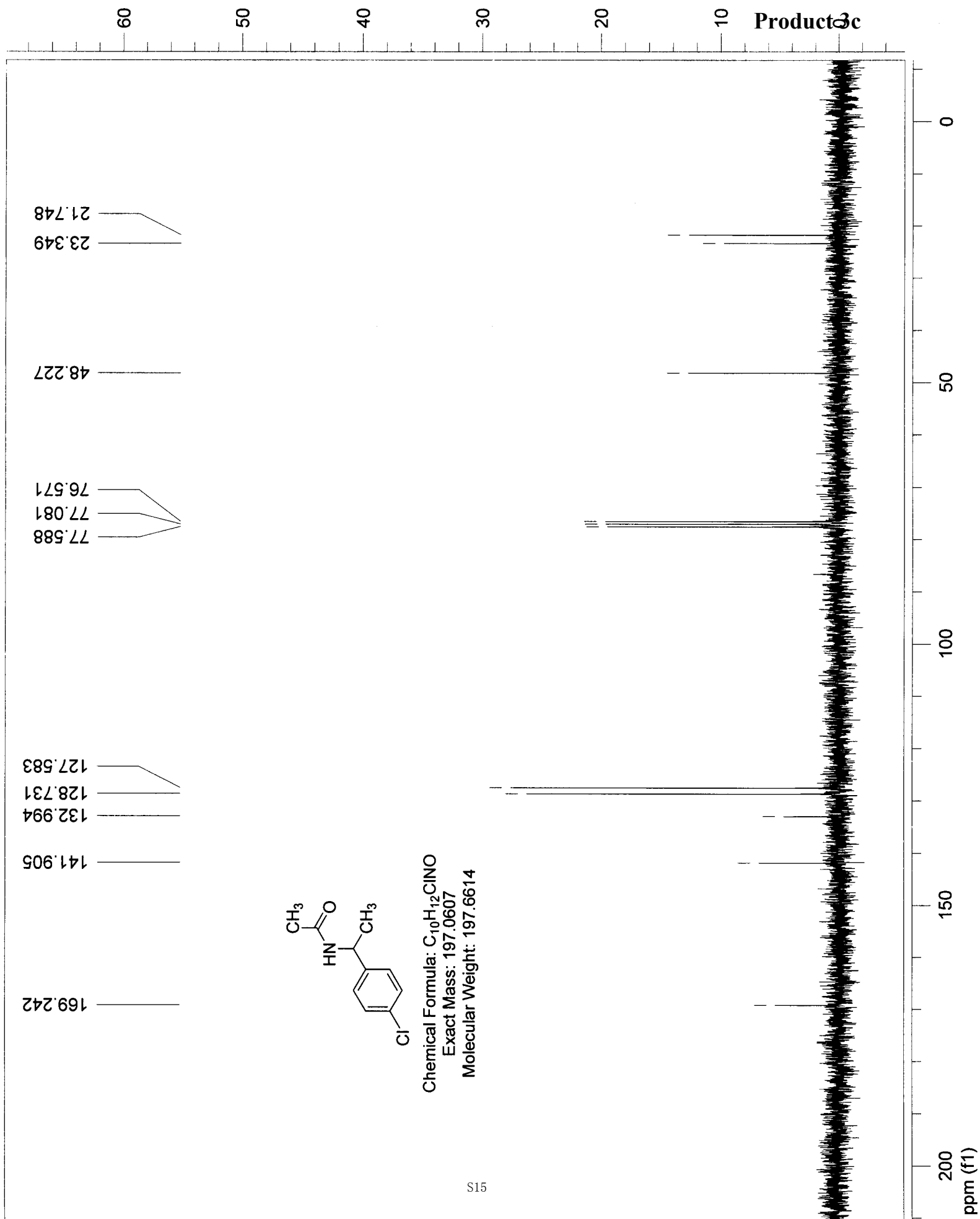
1.00

4.48

0.0

5.0

10.0
ppm (f1)

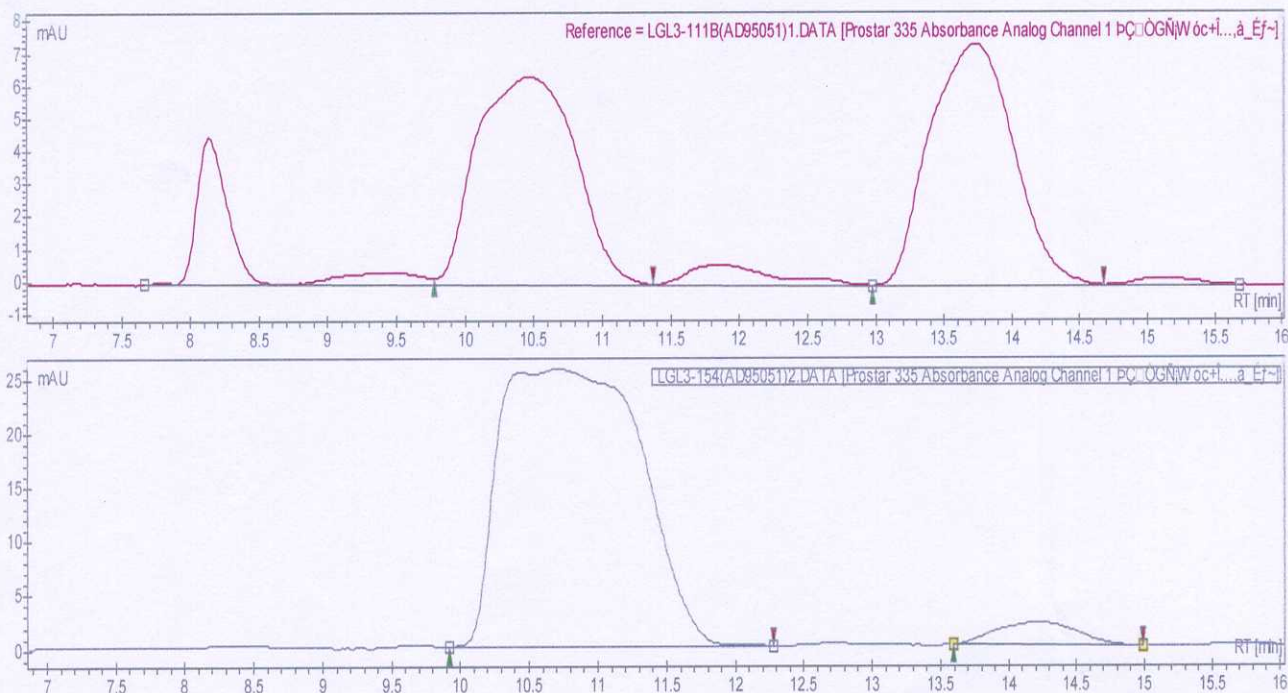


Chromatogram : LGL3-154(AD95051)2_channel1

Product 3c

System : HPLC
Method : LGL
User : Gerald Rowland

Acquired : 7/15/2008 4:50:18 PM
Processed : 7/15/2008 5:12:32 PM
Printed : 10/29/2008 2:23:08 PM



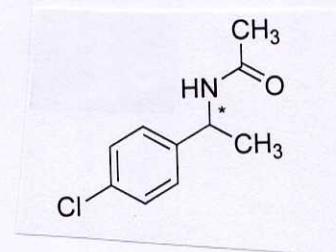
Peak results :

LGL3-111B(AD95051)1.DATA [Prostar 335 Absorbance Analog Channel 1 bC OGÑjW óc+Î...à_Éf~]

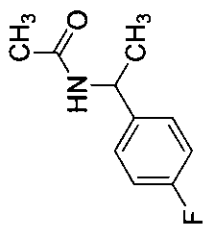
Index	Name	Time [Min]	Quantity [% Area]	Height [mAU]	Area [mAU.Min]	Area % [%]
1	UNKNOWN	10.47	50.22	6.4	5.3	50.222
2	UNKNOWN	13.73	49.78	7.4	5.3	49.778
Total			100.00	13.8	10.6	100.000

LGL3-154(AD95051)2.DATA [Prostar 335 Absorbance Analog Channel 1 bC OGÑjW óc+Î...à_Éf~]

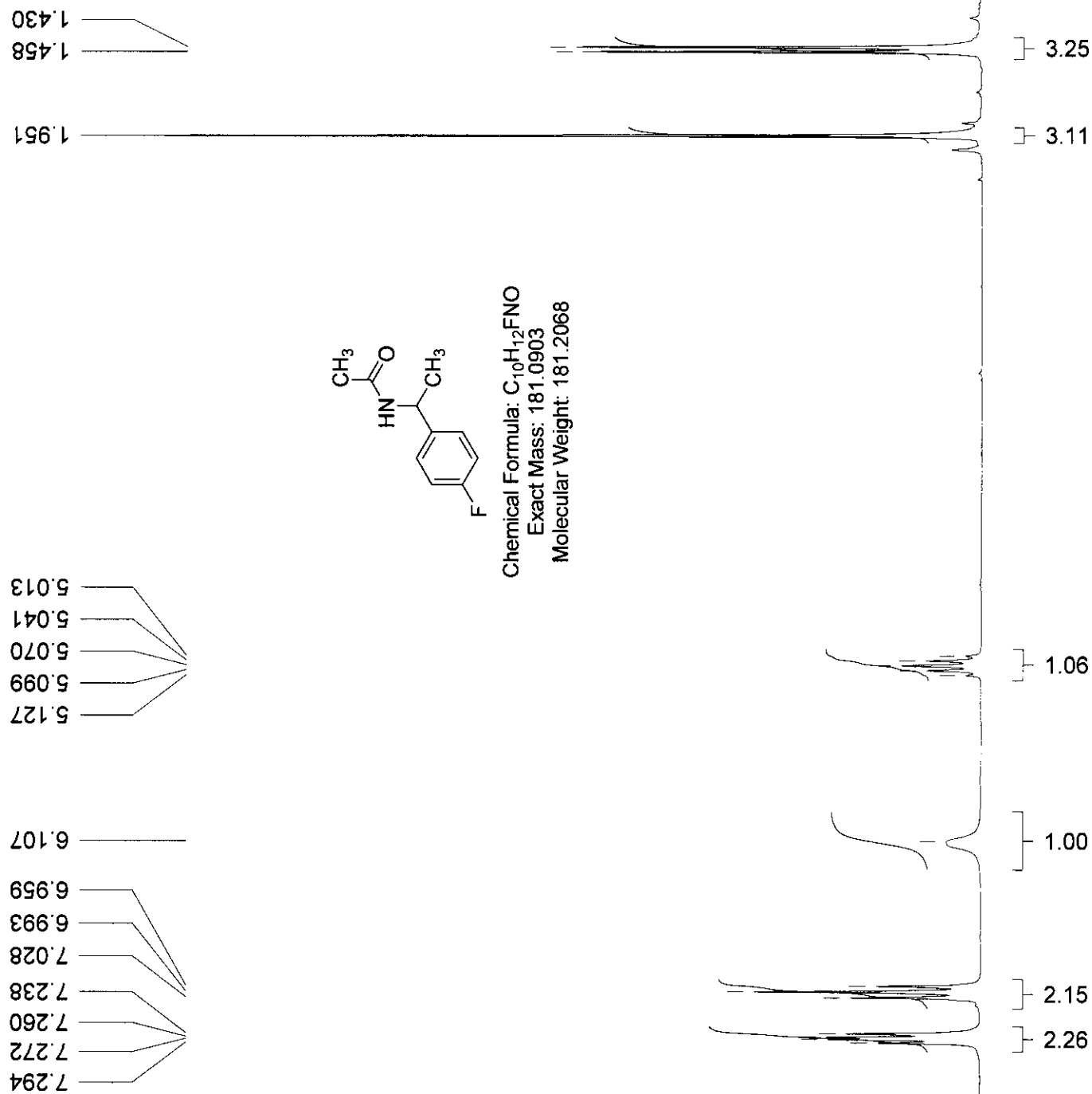
Index	Name	Time [Min]	Quantity [% Area]	Height [mAU]	Area [mAU.Min]	Area % [%]
2	UNKNOWN	10.71	95.49	25.7	30.8	95.490
1	UNKNOWN	14.21	4.51	2.1	1.5	4.510
Total			100.00	27.8	32.3	100.000

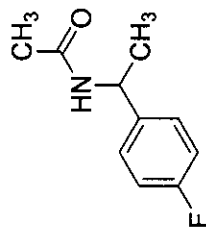


Product 3d

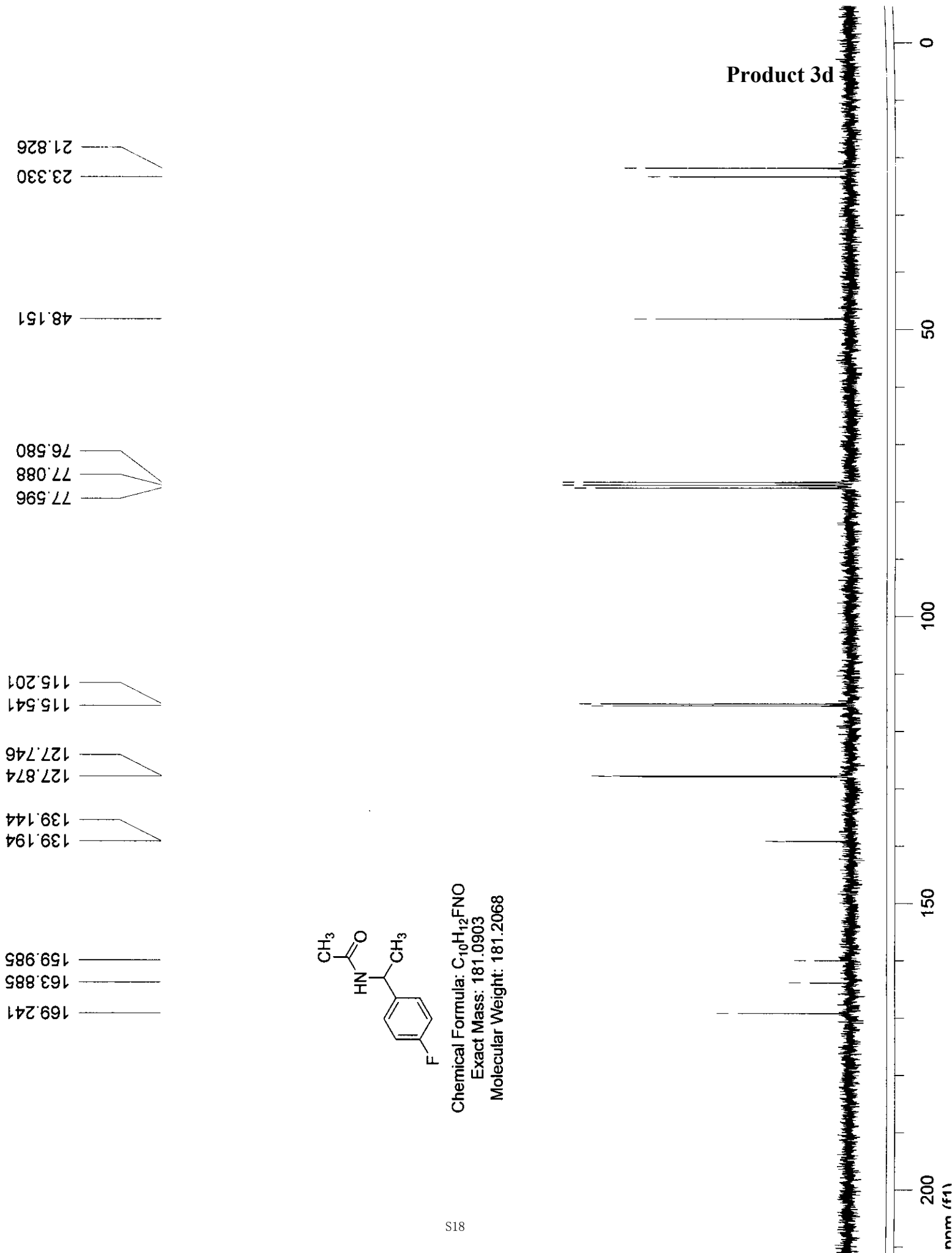


Chemical Formula: $C_{10}H_{12}FNO$
 Exact Mass: 181.0903
 Molecular Weight: 181.2068





Chemical Formula: $C_{10}H_{12}FNO$
Exact Mass: 181.0903
Molecular Weight: 181.2068

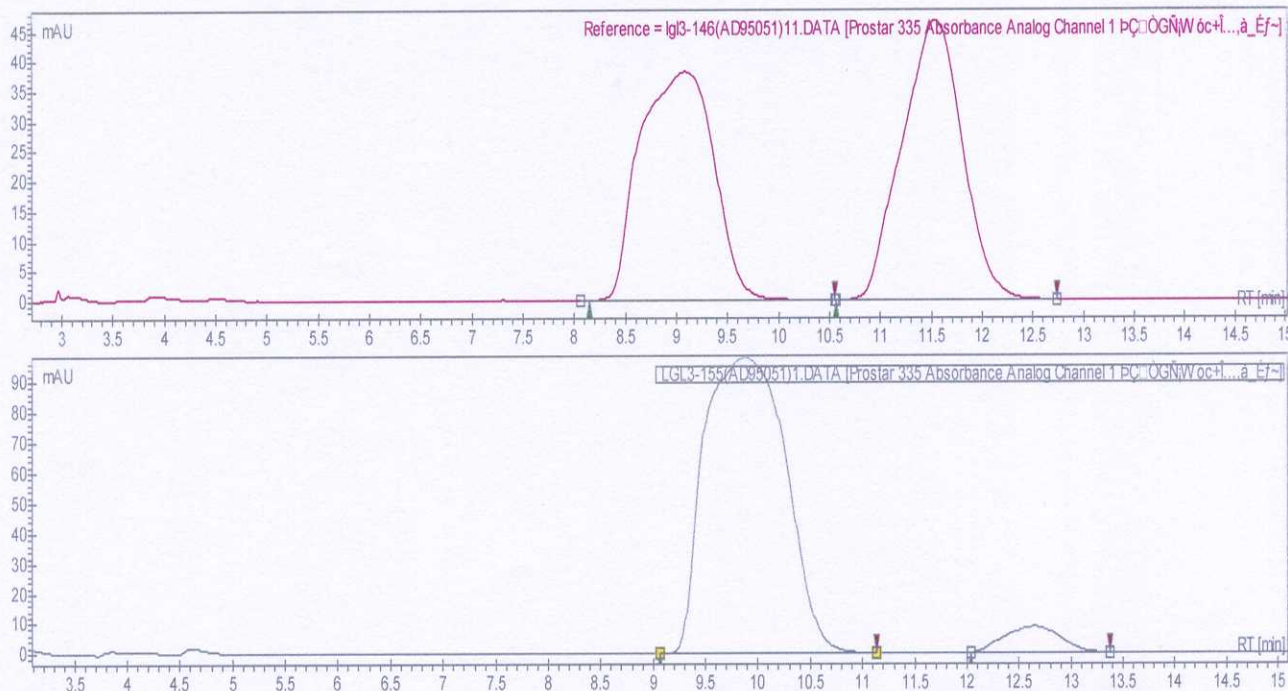


Chromatogram : LGL3-155(AD95051)1_channel1

Product 3d

System : HPLC
Method : LGL
User : Gerald Rowland

Acquired : 7/15/2008 5:12:23 PM
Processed : 7/15/2008 5:32:59 PM
Printed : 10/29/2008 4:18:57 PM



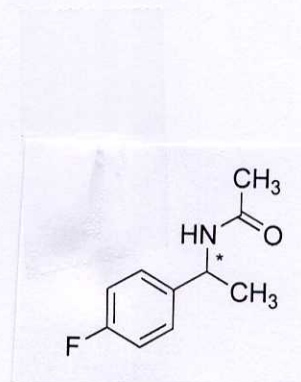
Peak results :

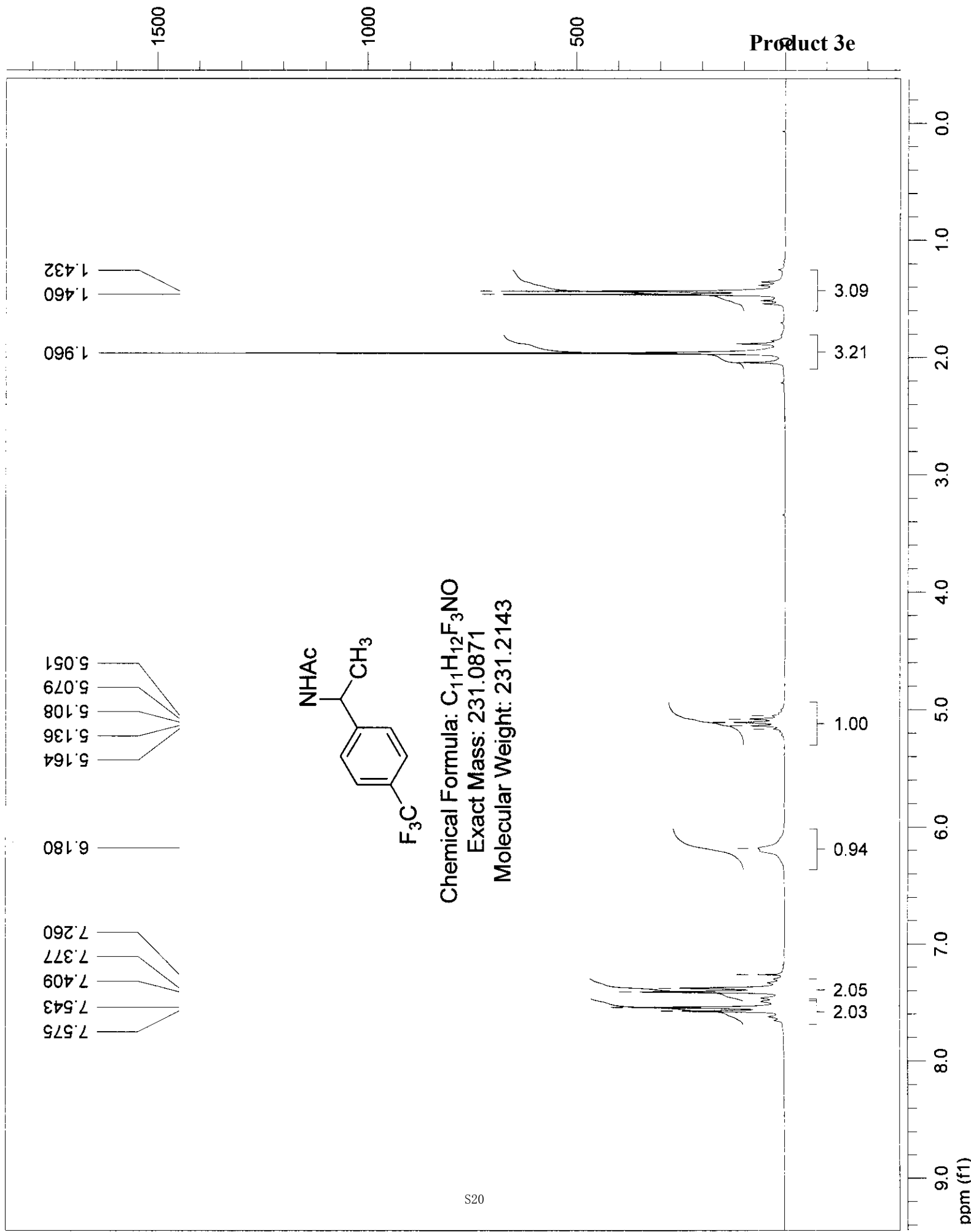
Igl3-146(AD95051)11.DAT [Prostar 335 Absorbance Analog Channel 1 bÇ□ÖGÑjW óc+Î....à_Éf~]

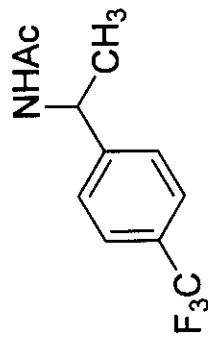
Index	Name	Time [Min]	Quantity [% Area]	Height [mAU]	Area [mAU.Min]	Area % [%]
1	UNKNOWN	9.08	50.04	38.0	31.9	50.037
2	UNKNOWN	11.55	49.96	46.6	31.9	49.963
Total			100.00	84.7	63.8	100.000

LGL3-155(AD95051)1.DAT [Prostar 335 Absorbance Analog Channel 1 bÇ□ÖGÑjW óc+Î....à_Éf~]

Index	Name	Time [Min]	Quantity [% Area]	Height [mAU]	Area [mAU.Min]	Area % [%]
1	UNKNOWN	9.88	94.38	97.7	88.5	94.375
2	UNKNOWN	12.65	5.62	8.5	5.3	5.625
Total			100.00	106.2	93.7	100.000







Chemical Formula: $C_{11}H_{12}F_3NO$
 Exact Mass: 231.0871
 Molecular Weight: 231.2143

Product 3a

21.833
23.239

48.586

76.560
77.068
77.576

121.946
125.484
125.544
125.604
125.663
126.271
126.441
129.226
129.740

147.519

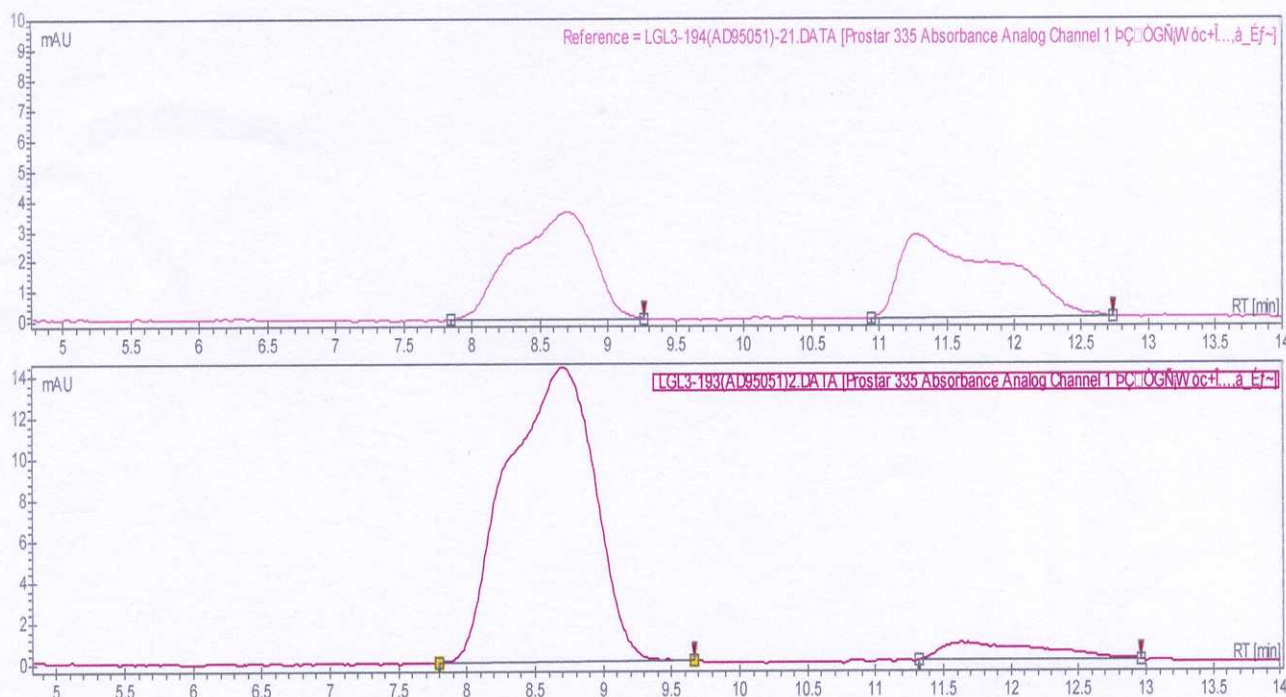
169.414

Chromatogram : LGL3-193(AD95051)2_channel1

Product 3e

System : HPLC
Method : LGL
User : Gerald Rowland

Acquired : 8/26/2008 4:54:24 PM
Processed : 8/26/2008 5:18:19 PM
Printed : 8/26/2008 6:02:25 PM



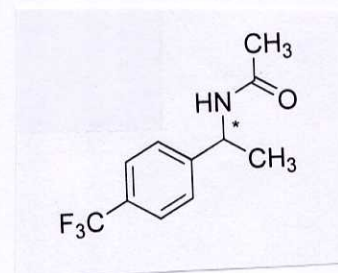
Peak results :

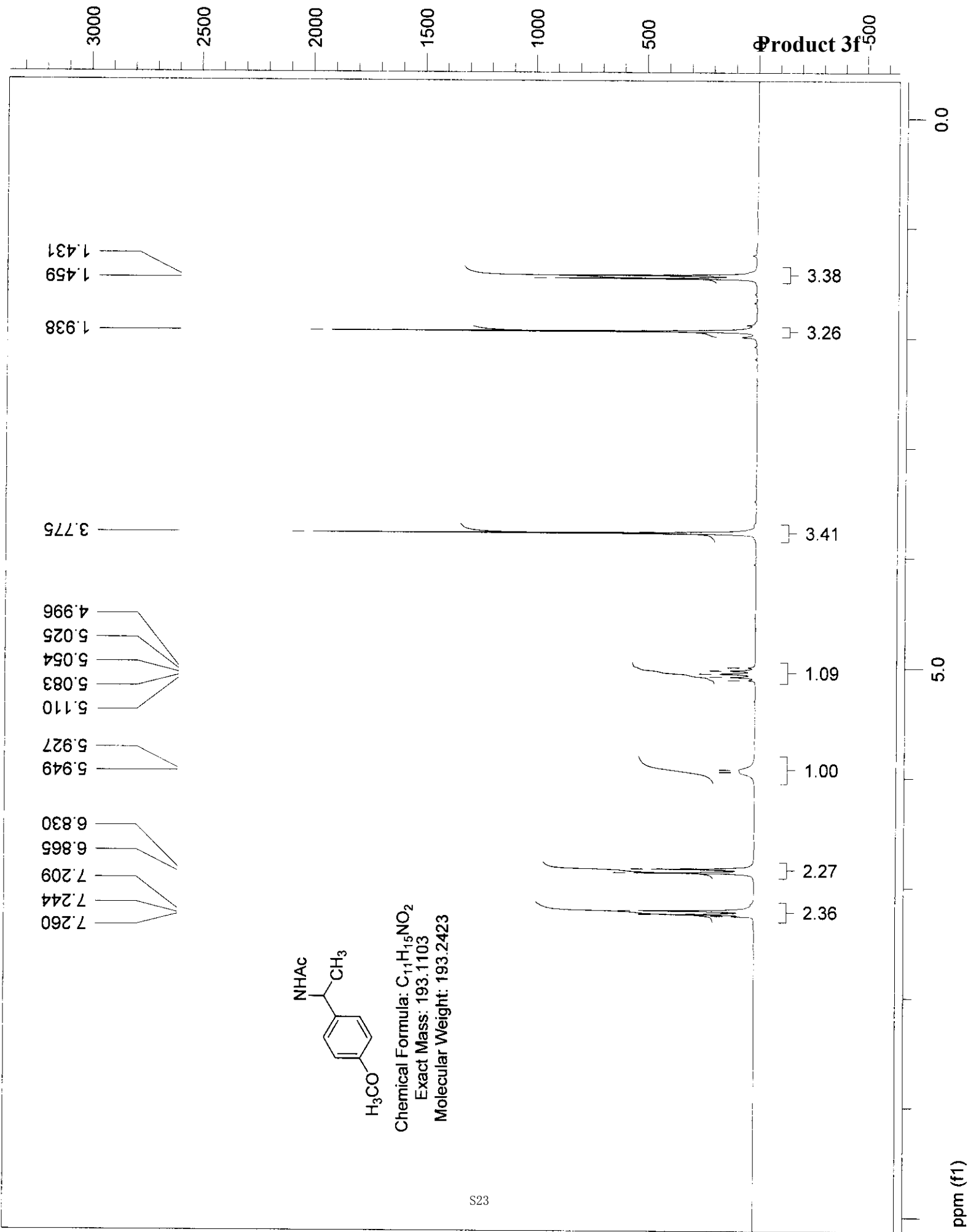
LGL3-194(AD95051)-21.D [Prostar 335 Absorbance Analog Channel 1]

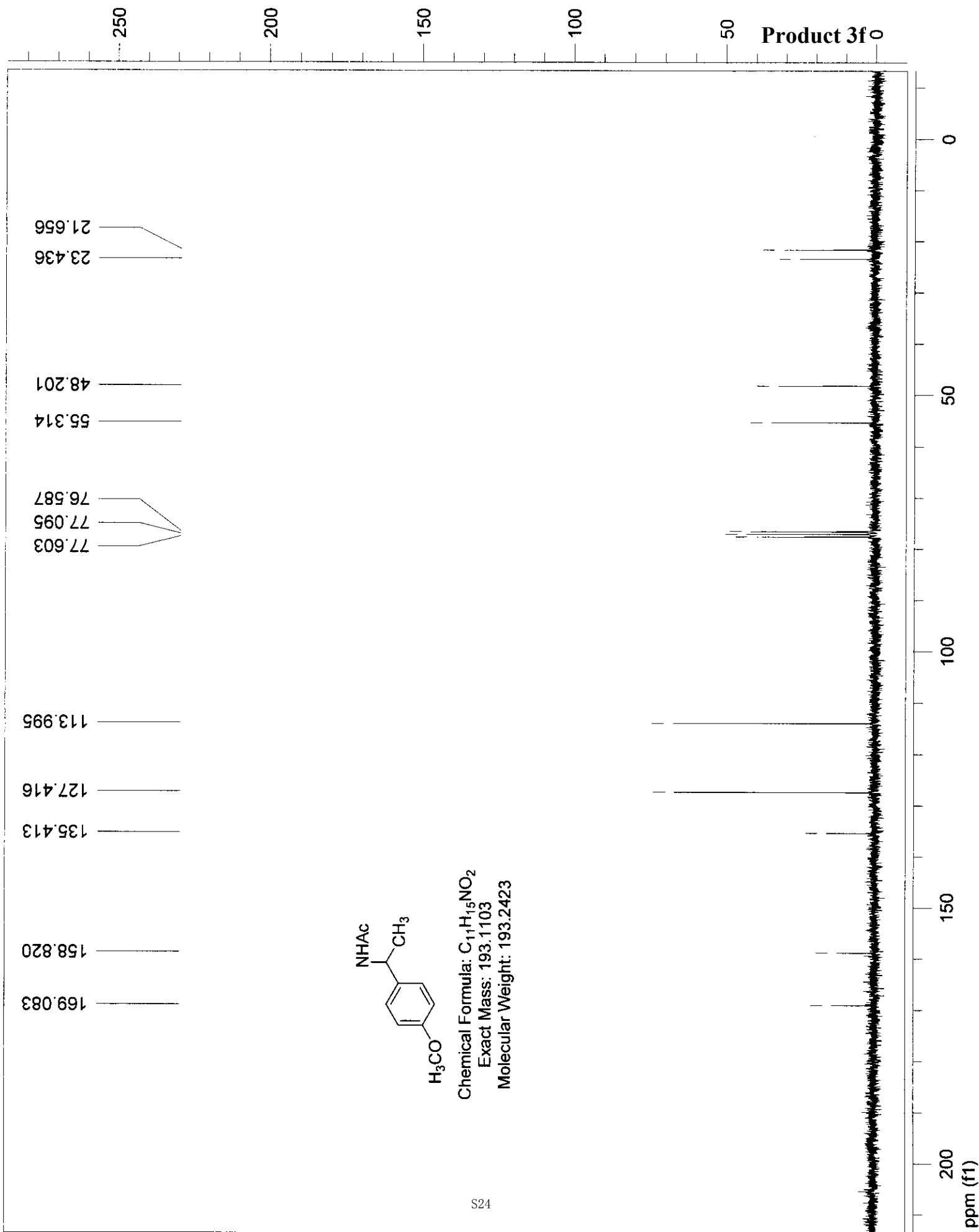
Index	Name	Time [Min]	Quantity [% Area]	Height [mAU]	Area [mAU.Min]	Area % [%]
1	UNKNOWN	8.71	50.12	3.5	2.4	50.123
2	UNKNOWN	11.27	49.88	2.8	2.4	49.877
Total			100.00	6.3	4.8	100.000

LGL3-193(AD95051)2.D [Prostar 335 Absorbance Analog Channel 1]

Index	Name	Time [Min]	Quantity [% Area]	Height [mAU]	Area [mAU.Min]	Area % [%]
1	UNKNOWN	8.71	93.64	14.3	10.7	93.639
2	UNKNOWN	11.63	6.36	0.8	0.7	6.361
Total			100.00	15.1	11.4	100.000





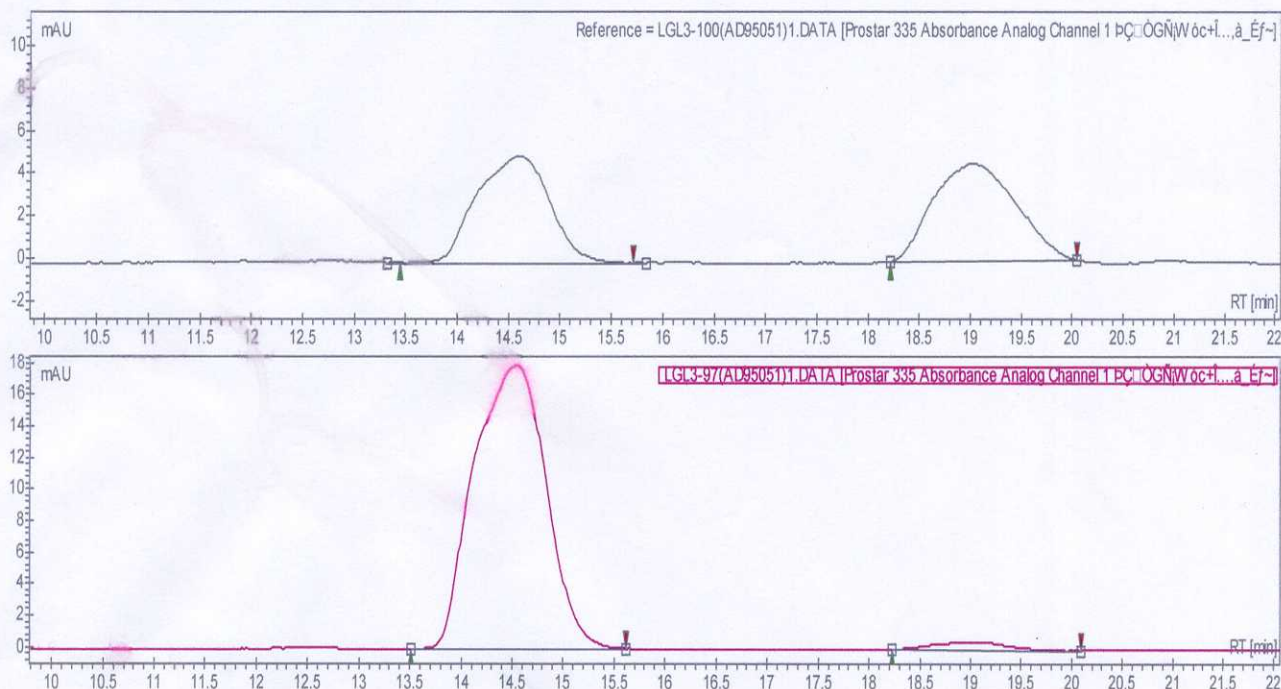


Chromatogram : LGL3-97(AD95051)1_channel1

Product 3f

System : HPLC
Method : LGL
User : Gerald Rowland

Acquired : 5/30/2008 11:14:04 AM
Processed : 5/30/2008 12:13:47 PM
Printed : 5/30/2008 12:14:52 PM



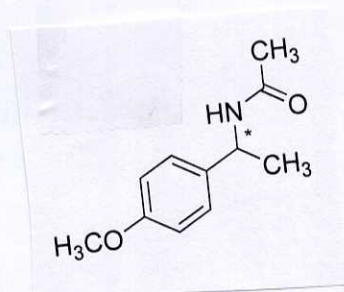
Peak results :

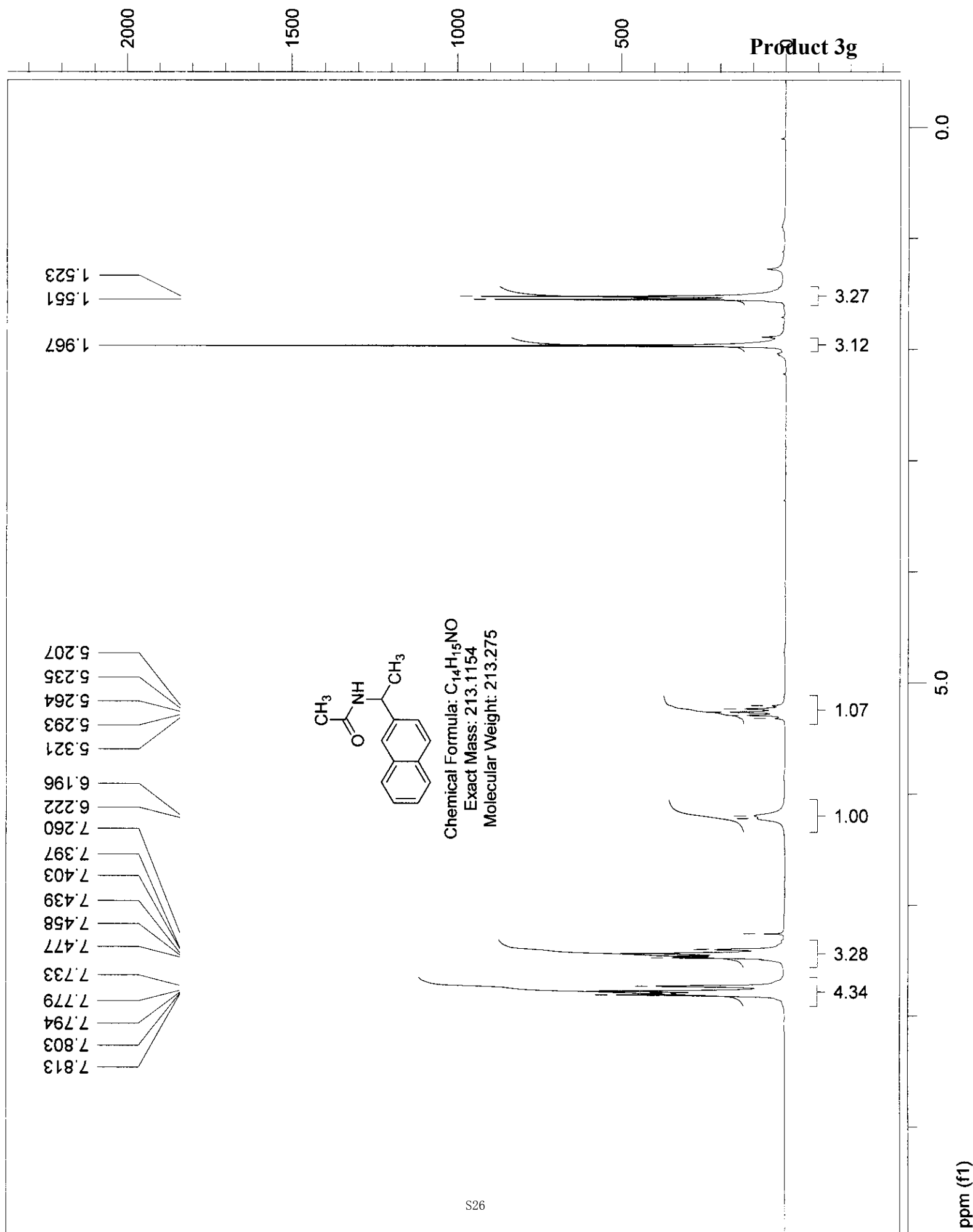
LGL3-100(AD95051)1.DAT [Prostar 335 Absorbance Analog Channel 1 bÇÖGÑjW óc+Î...â_Éf~]

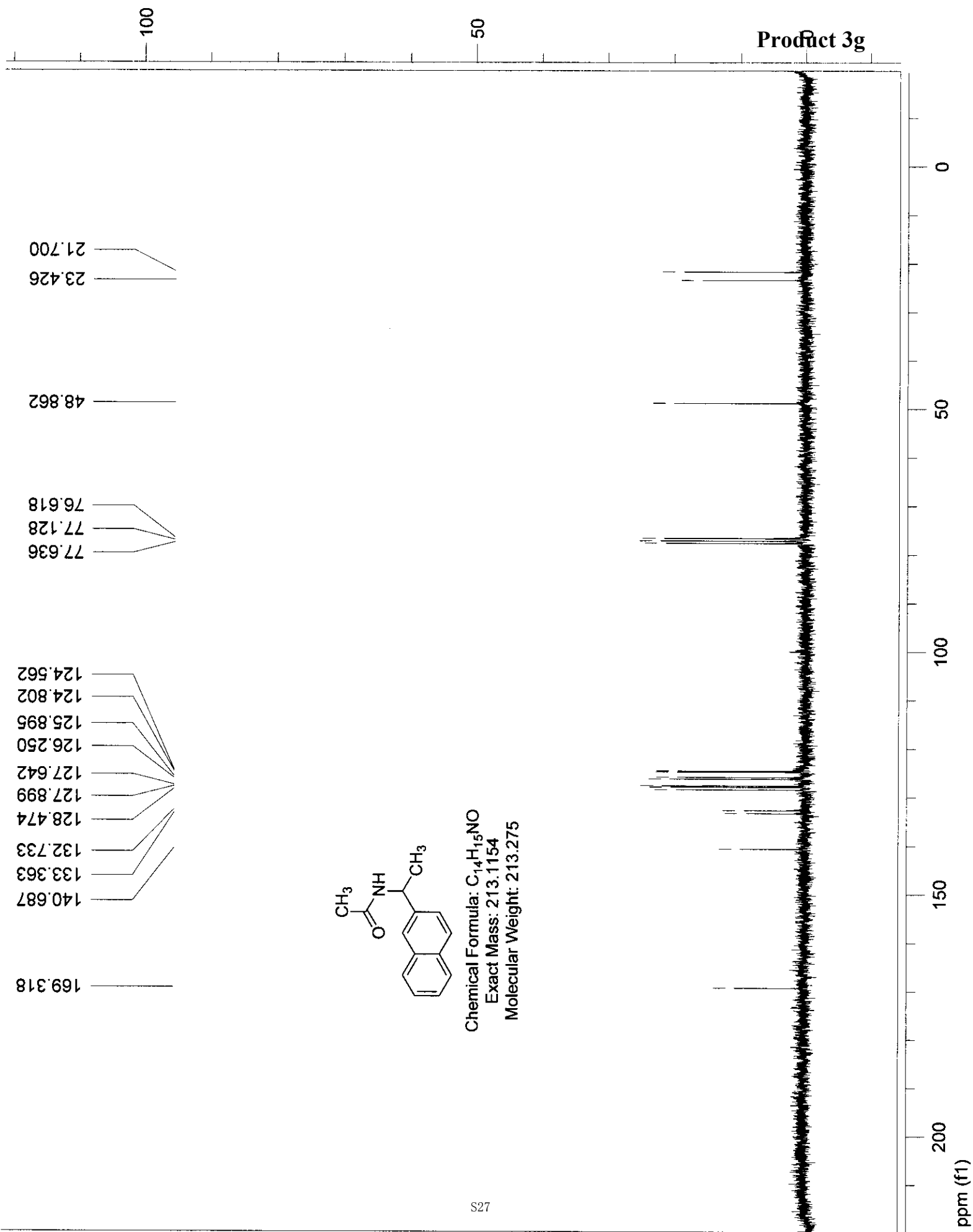
Index	Name	Time [Min]	Quantity [% Area]	Height [mAU]	Area [mAU.Min]	Area % [%]
1	UNKNOWN	14.61	48.89	5.0	4.1	48.893
2	UNKNOWN	19.04	51.11	4.6	4.3	51.107
Total			100.00	9.6	8.4	100.000

LGL3-97(AD95051)1.DAT [Prostar 335 Absorbance Analog Channel 1 bÇÖGÑjW óc+Î...â_Éf~]

Index	Name	Time [Min]	Quantity [% Area]	Height [mAU]	Area [mAU.Min]	Area % [%]
1	UNKNOWN	14.53	97.44	18.0	14.7	97.436
2	UNKNOWN	19.00	2.56	0.5	0.4	2.564
Total			100.00	18.4	15.1	100.000





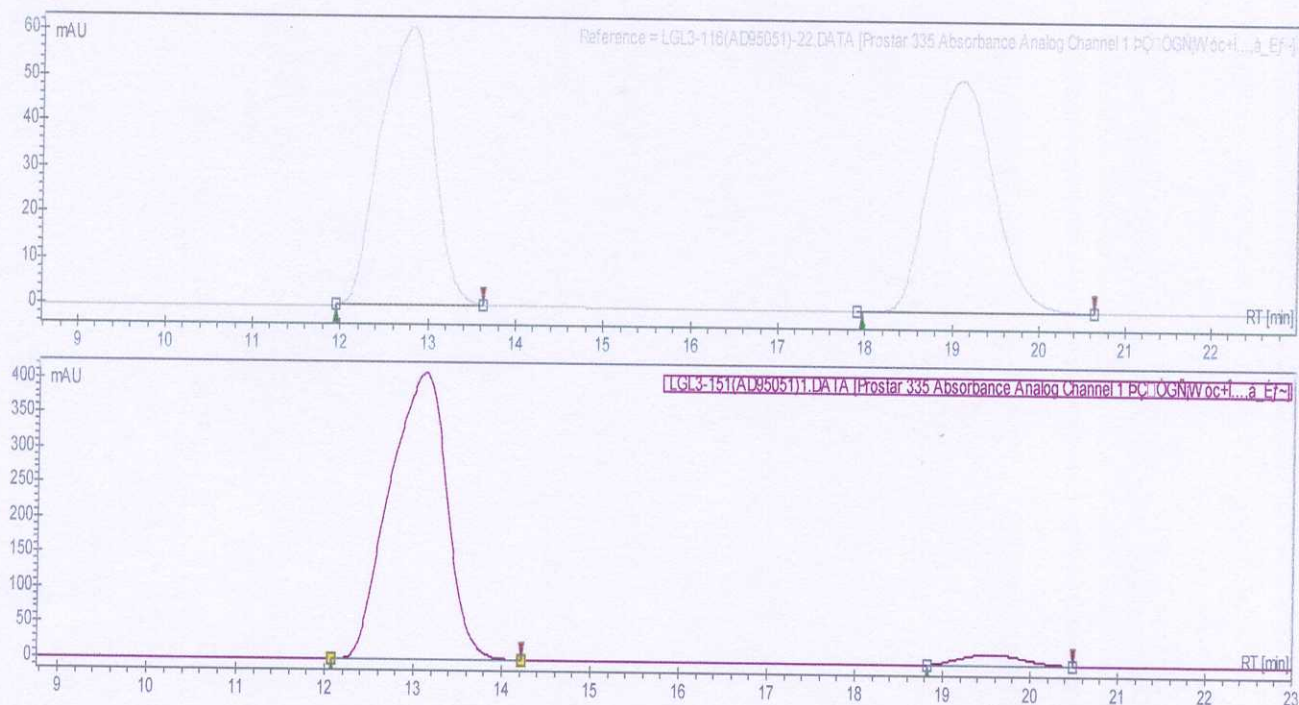


Chromatogram : LGL3-151(AD95051)1_channel1

Product 3g

System : HPLC
Method : LGL
User : Gerald Rowland

Acquired : 7/11/2008 11:47:20 AM
Processed : 7/11/2008 12:16:32 PM
Printed : 10/30/2008 9:51:23 AM



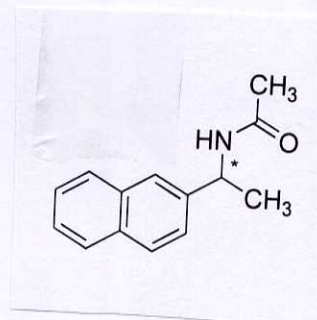
Peak results :

LGL3-116(AD95051)-22.DAT [Prostar 335 Absorbance Analog Channel 1 PQ:OGN\W oc+I....a_Ef~]

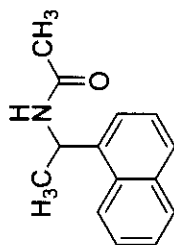
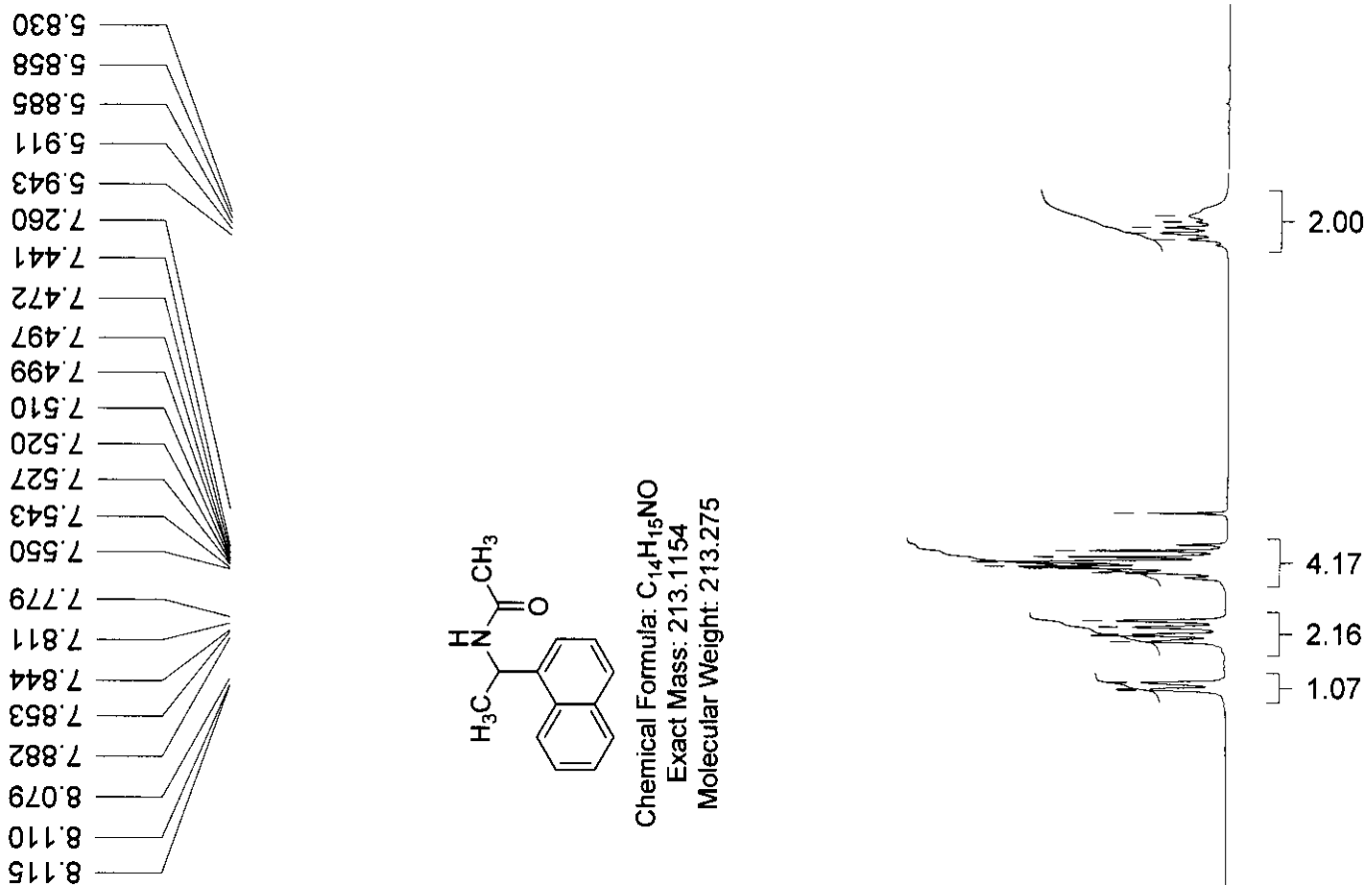
Index	Name	Time [Min]	Quantity [% Area]	Height [mAU]	Area [mAU.Min]	Area % [%]
2	UNKNOWN	12.80	49.69	60.8	42.6	49.694
1	UNKNOWN	19.09	50.31	50.5	43.2	50.306
Total			100.00	111.3	85.8	100.000

LGL3-151(AD95051)1.DAT [Prostar 335 Absorbance Analog Channel 1 PQ:OGN\W oc+I....a_Ef~]

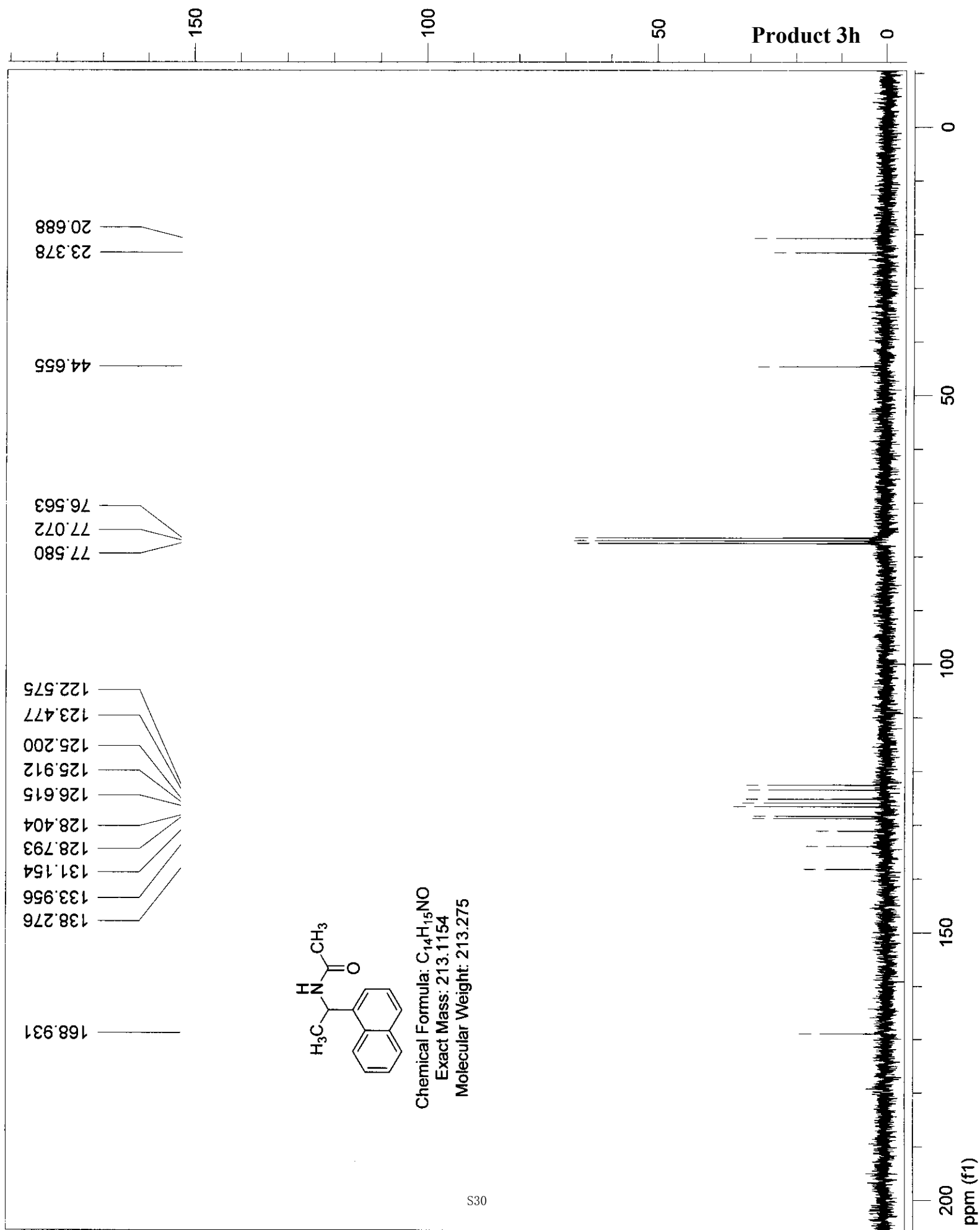
Index	Name	Time [Min]	Quantity [% Area]	Height [mAU]	Area [mAU.Min]	Area % [%]
1	UNKNOWN	13.12	95.96	410.1	306.2	95.959
2	UNKNOWN	19.56	4.04	15.5	12.9	4.041
Total			100.00	425.6	319.0	100.000



Product 3h



Chemical Formula: C₁₄H₁₅NO
Exact Mass: 213.1154
Molecular Weight: 213.275

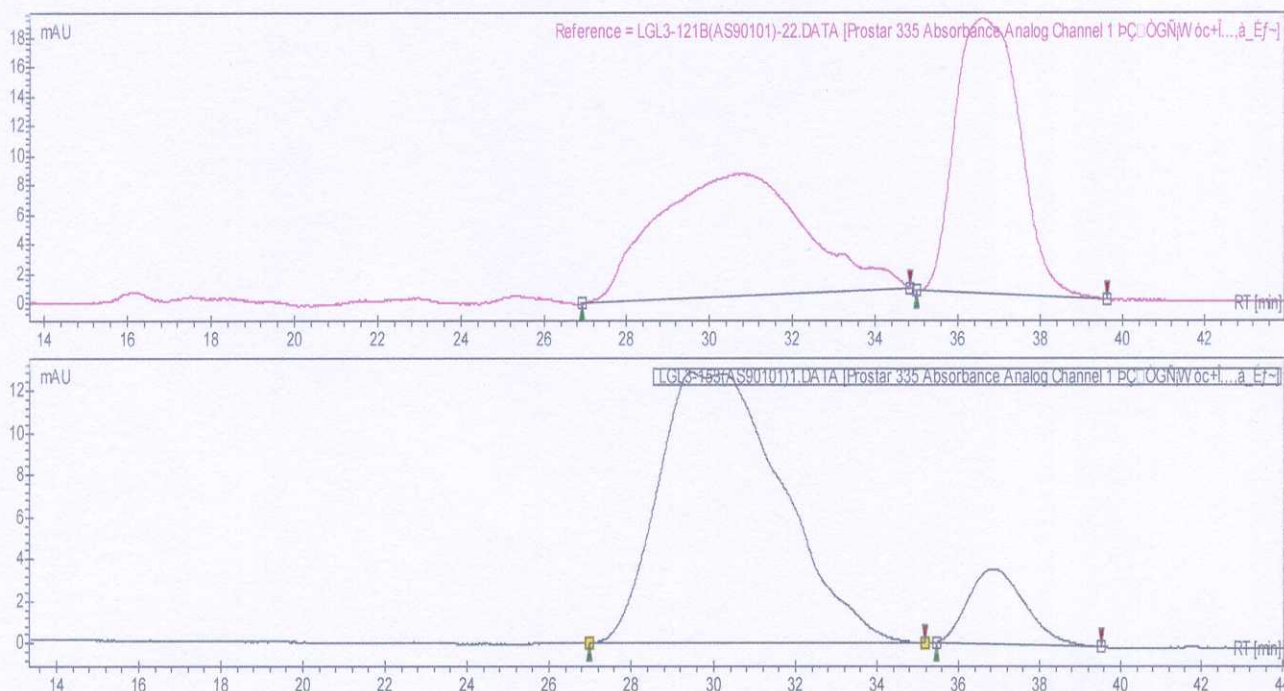


Chromatogram : LGL3-153(AS90101)1_channel1

Product 3h

System : HPLC
Method : LGL
User : Gerald Rowland

Acquired : 7/16/2008 10:03:47 AM
Processed : 7/16/2008 12:11:46 PM
Printed : 10/30/2008 11:11:26 AM



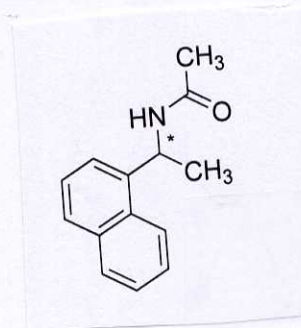
Peak results :

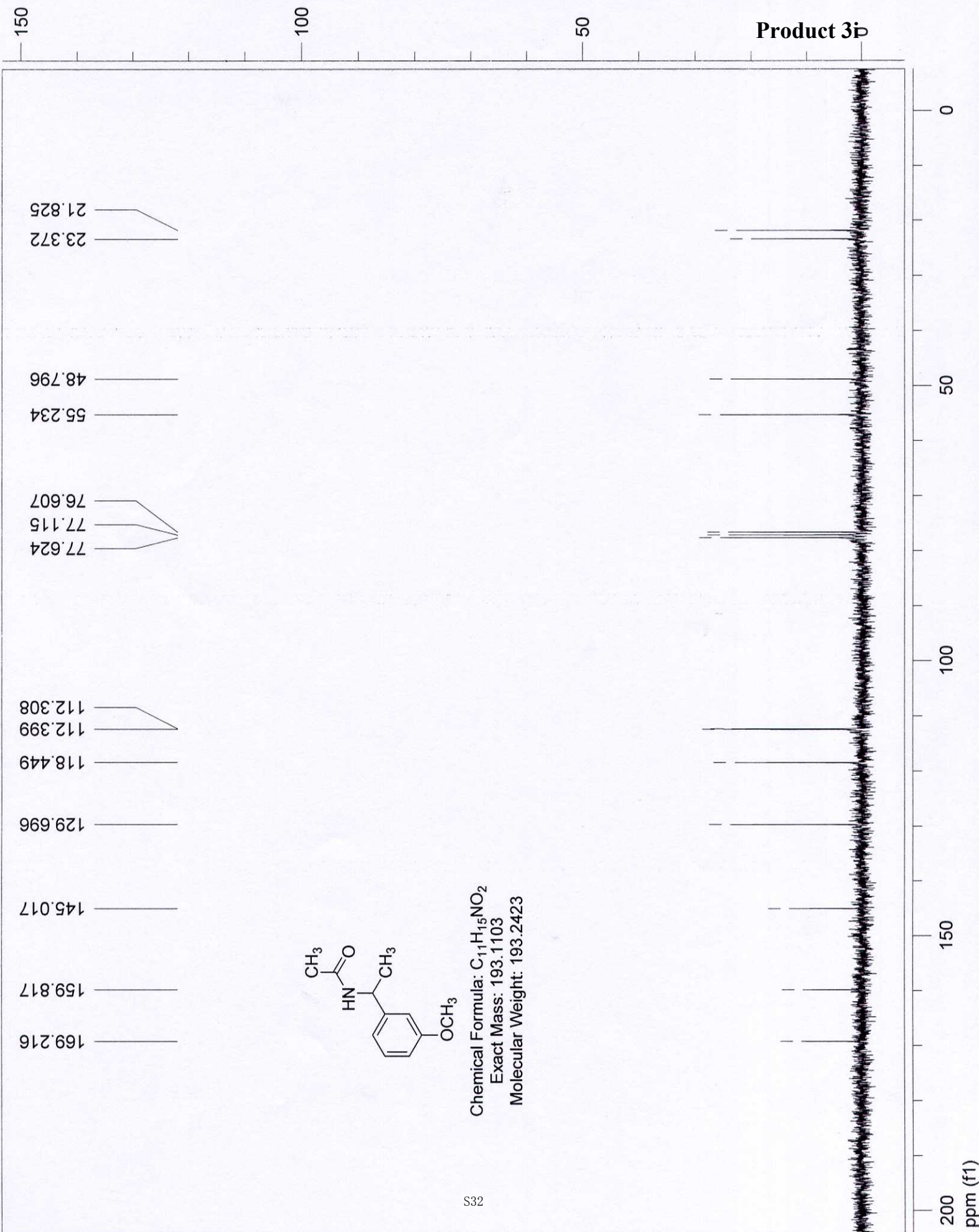
LGL3-121B(AS90101)-22.D [Prostar 335 Absorbance Analog Channel 1] CC(=O)N[C@H](C)c1ccc2ccccc2c1

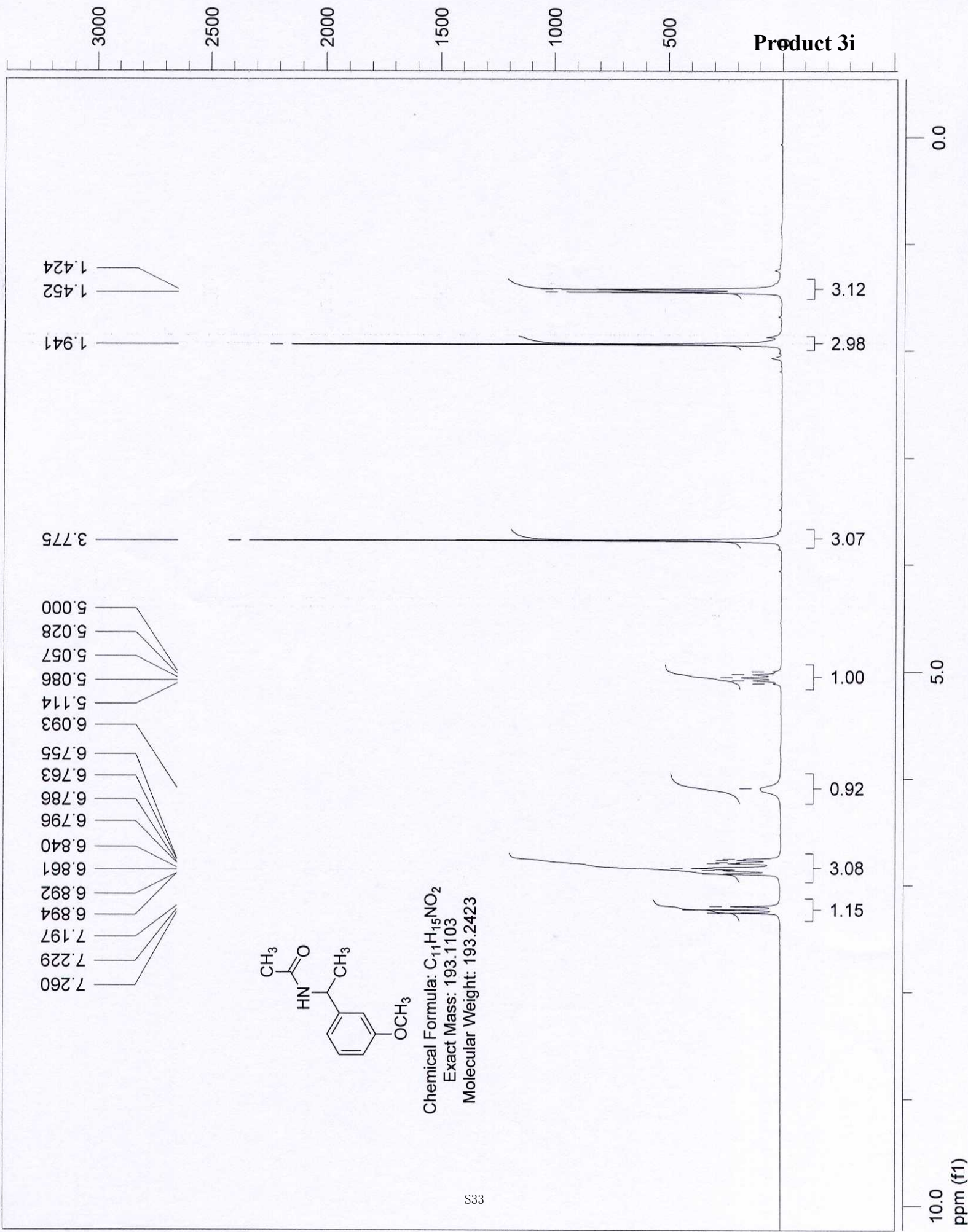
Index	Name	Time [Min]	Quantity [% Area]	Height [mAU]	Area [mAU.Min]	Area % [%]
2	UNKNOWN	30.73	50.42	8.2	34.5	50.424
1	UNKNOWN	36.57	49.58	18.7	34.0	49.576
Total			100.00	26.9	68.5	100.000

LGL3-153(AS90101)1.D [Prostar 335 Absorbance Analog Channel 1] CC(=O)N[C@H](C)c1ccc2ccccc2c1

Index	Name	Time [Min]	Quantity [% Area]	Height [mAU]	Area [mAU.Min]	Area % [%]
1	UNKNOWN	29.43	88.79	12.9	45.2	88.790
2	UNKNOWN	36.89	11.21	3.6	5.7	11.210
Total			100.00	16.4	50.9	100.000





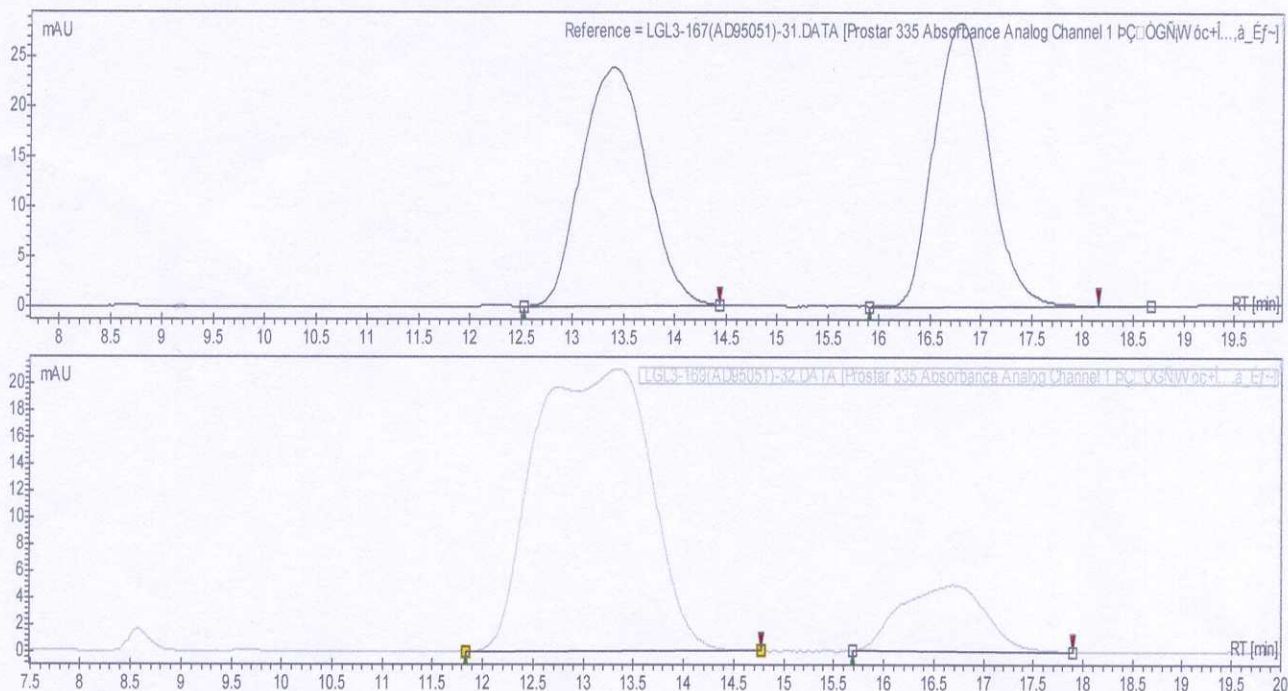


Chromatogram : LGL3-169(AD95051)-32_channel1

Product 3i

System : HPLC
Method : LGL
User : Gerald Rowland

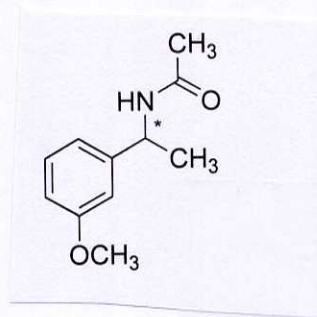
Acquired : 7/30/2008 2:37:24 PM
Processed : 8/1/2008 11:03:37 AM
Printed : 8/1/2008 11:09:51 AM



Peak results :

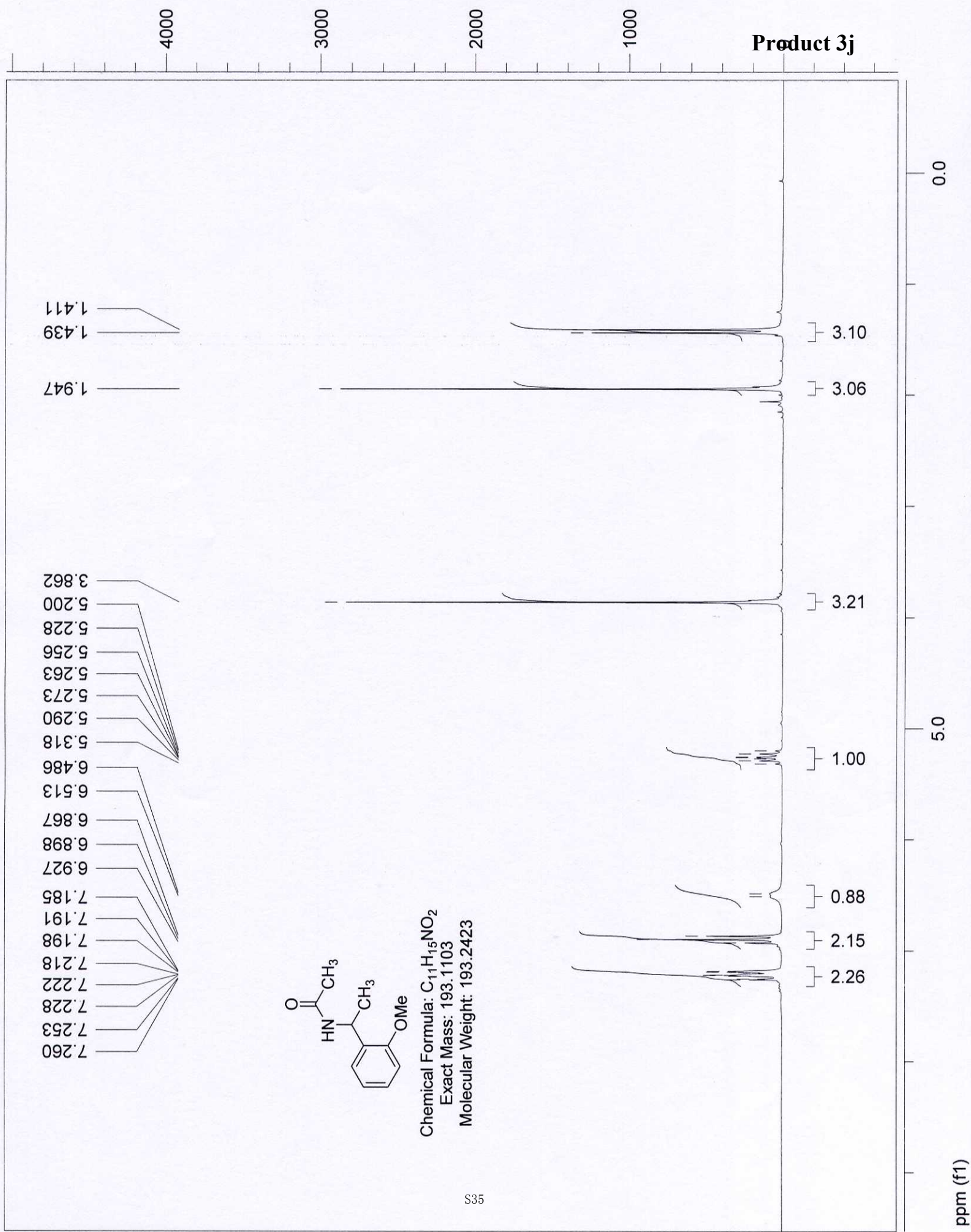
LGL3-167(AD95051)-31.DAT [Prostar 335 Absorbance Analog Channel 1 PÇ□ÖGÑ;W óc+Î...,à_Éf~]

Index	Name	Time [Min]	Quantity [% Area]	Height [mAU]	Area [mAU.Min]	Area % [%]
1	UNKNOWN	13.40	49.74	23.8	17.6	49.739
2	UNKNOWN	16.80	50.26	28.4	17.8	50.261
Total			100.00	52.2	35.4	100.000

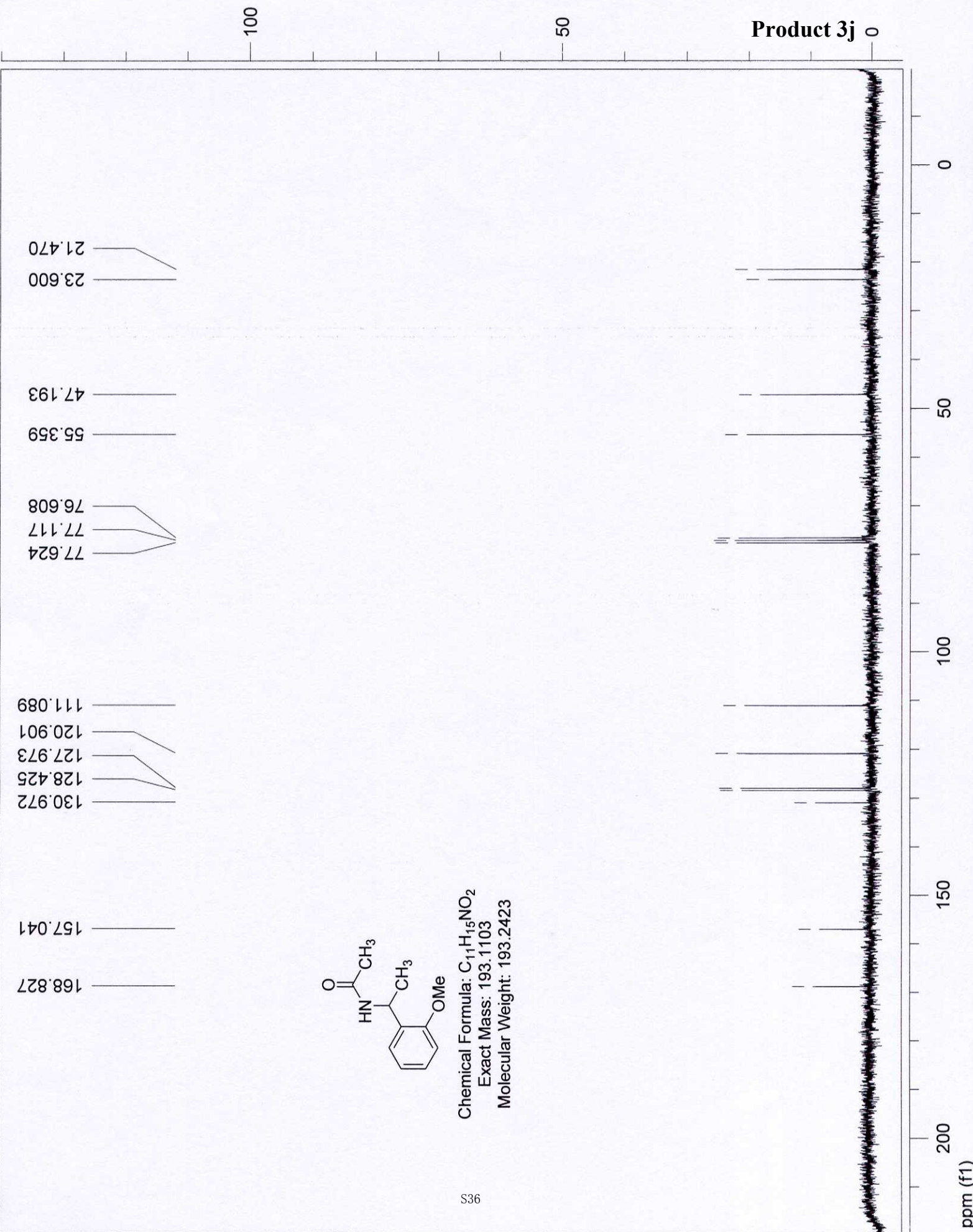


LGL3-169(AD95051)-32.DAT [Prostar 335 Absorbance Analog Channel 1 PÇ□ÖGÑ;W óc+Î...,à_Éf~]

Index	Name	Time [Min]	Quantity [% Area]	Height [mAU]	Area [mAU.Min]	Area % [%]
1	UNKNOWN	13.33	85.35	21.0	28.1	85.346
2	UNKNOWN	16.65	14.65	4.9	4.8	14.654
Total			100.00	25.9	32.9	100.000



Product 3j 0

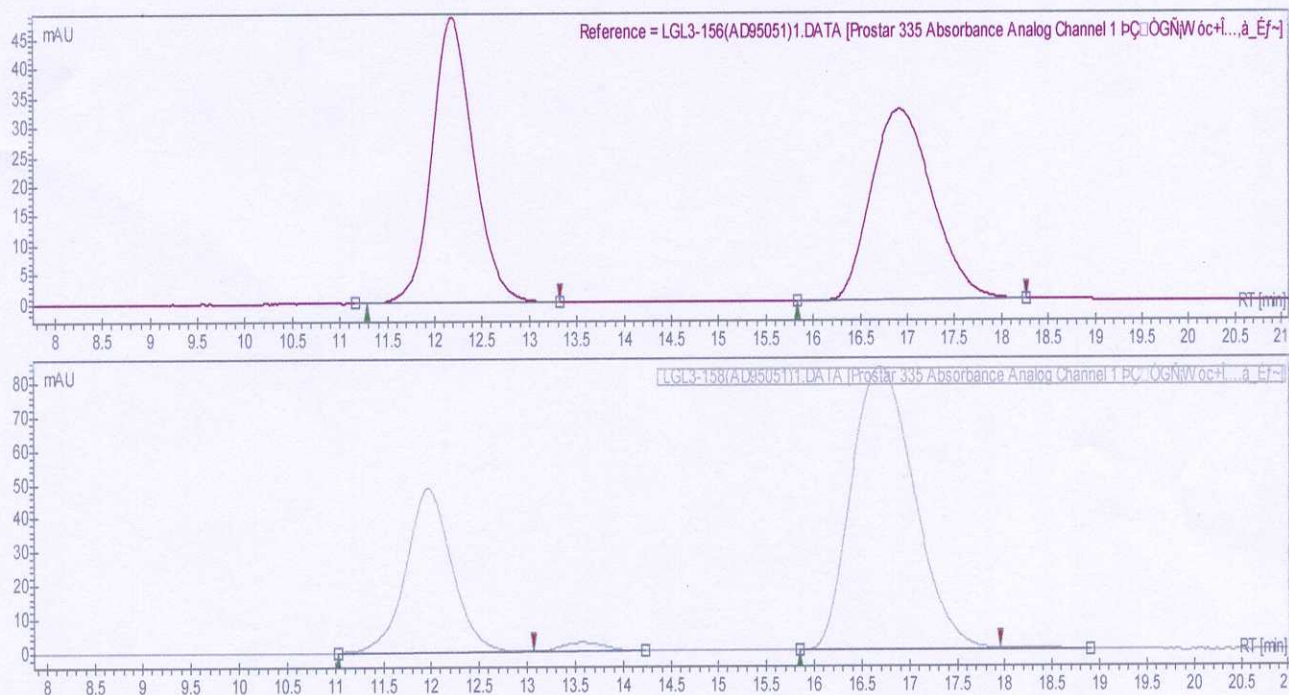


Chromatogram : LGL3-158(AD95051)1_channel1

Product 3j

System : HPLC
Method : LGL
User : Gerald Rowland

Acquired : 7/16/2008 2:39:21 PM
Processed : 7/16/2008 3:01:45 PM
Printed : 10/30/2008 4:20:21 PM



Peak results :

LGL3-156(AD95051)1.D [Prostar 335 Absorbance Analog Channel 1]

Index	Name	Time [Min]	Quantity [% Area]	Height [mAU]	Area [mAU.Min]	Area % [%]
1	UNKNOWN	12.17	50.11	48.5	24.5	50.109
2	UNKNOWN	16.92	49.89	32.3	24.4	49.891
Total			100.00	80.8	48.9	100.000

LGL3-158(AD95051)1.D [Prostar 335 Absorbance Analog Channel 1]

Index	Name	Time [Min]	Quantity [% Area]	Height [mAU]	Area [mAU.Min]	Area % [%]
1	UNKNOWN	11.97	29.45	48.7	26.9	29.450
2	UNKNOWN	16.69	70.55	84.1	64.5	70.550
Total			100.00	132.8	91.5	100.000

