Supporting Materials to

Ru-Catalyzed Asymmetric Hydrogenation of α-Ketoesters with $CeCl_3 \cdot 7H_2O$ as Additive

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Page

General: All reactions were carried out under inert atmosphere of dry argon or nitrogen. THF and toluene were freshly distilled from sodium/benzophenone ketyl, while CH_2Cl_2 was distilled from P_2O_5 under argon atmosphere. EtOH for catalyst preparation or hydrogenation was distilled from magnesium under atmosphere. The preparation of samples and the setup of high-pressure reactor were either carried out in a glovebox or using standard Schlenk-type techniques. ^{1}HNMR (300 MHz), ^{13}CNMR (75.4 MHz) were registered on 300M spectrometers with $CDCl_3$ as solvent and tetramethylsilane (TMS) as internal standard. Chemical shifts are reported in units (ppm) by assigning TMS resonance in the ^{1}H spectrum as 0.00 ppm and $CDCl_3$ resonance in the ^{13}C spectrum as 77.0 ppm. All coupling constants (*J* values) were reported in Hertz (Hz). Column chromatography was performed on silica gel 300-400 mesh.

Experiment: asymmetric hydrogenation of *α*-ketoesters[1,2]

To a 20 mL Schlenk tube were added $[Ru(benzene)Cl_2]_2$ (10 mg, 0.02 mmol) and (*S*)-**3** (30 mg, 0.045 mmol). The tube was purged with Argon three times before addition of freshly distilled and degassed EtOH/CH_2Cl_2 (3 mL/3 mL). The resulting mixture was heated at 50 °C for 1 h. The catalyst was dried under reduced pressure and was taken into a glove box in a dry nitrogen atmosphere and dissolved in degassed ethanol (8 mL) which was then put into 4 vials equally. To these vials *α*-ketoester (1 mmol) was introduced, and then the vials were taken into an autoclave. The autoclave was purged three times with H_2, and the pressure of H_2 was set to 50 atm. before it was placed in an oil bath at designed temperature for 20h. Cooled to ambient temperature and the hydrogen was released carefully. The solvent was removed and the residue was passed through a silica gel column to give the product. Enantiomeric purity of the product was determined by HPLC.

Asymmetric hydrogenation of benzoylformic acid methyl ester (1a) with S/C: 10000

The preparation of catalyst ([Ru(benzene)Cl_2]$_2$ (10 mg, 0.02 mmol) and (*S*)-**3** (30 mg, 0.045 mmol)) was same as above. In a glove box, the catalyst and $CeCl_3 \cdot 7H_2O$ (75 mg, 0.2 mmol) were dissolved in 80 mL of MeOH in an autoclave, then to this freshly distilled and degassed methyl benzoylformate (**1a**) (65.6 g, 400 mmol) was introduced. The autoclave was purged three times with H_2, and the pressure of H_2 was set to 60 atm. The autoclave was placed to an oil bath at 100°C for 10h. Work up was same as above to give 66.0 g white solid (**2a**, 99.3% yield, 92% ee). The product was hydrolyzed by heating it in a 5% NaOH aqueous solution at 40°C for 1h, acidified with diluted HCl solution and then extracted with ethyl acetate to give the mandelic acid **4a**. Recrystallization of **4a** (50 g) in 200 mL $ClCH_2CH_2Cl$ gave 41.4g white flakes (**4a**). After transferring **4a** to **2a** in refluxing MeOH with a drop of concentrated sulfuric acid, the ee value of the recrystallized product (**4a**) was determined to be higher than 99%.

Methyl-mandelate (2a)[3] ^{1}HNMR (300 MHz, $CDCl_3$) δ 3.47 (d, *J* = 4.2 Hz, 1H), 3.76 (s, 3H), 5.18 (d, J = 6.9 Hz, 1H), 7.33-7.44 (m, 5H); ^{13}CNMR (75.4MHz, $CDCl_3$) δ 52.9, 72.9, 126.5, 128.4, 128.5, 138.2,174.0.

Ethyl-4-mandelate (2b)[4] ^{1}HNMR (300 MHz, $CDCl_3$) δ 1.23 (t, *J*= 7.2 Hz, 3H), 3.51 (d, *J* = 6.0 Hz, 1H), 4.17-4.26 (m, 2H), 5.16 (d, *J* = 6.0 Hz, 1H), 7.33-7.44 (m, 5H); ^{13}CNMR (75.4MHz, $CDCl_3$) δ 13.9, 62.0, 72.8, 126.4, 128.2, 128.4, 138.3, 173.5.

Ethyl-4-methylmandelate (2c)[5] ^{1}HNMR (300 MHz, $CDCl_3$) δ 1.23 (t, *J*= 7.2 Hz, 3H), 2.35(s, 3H), 3.44 (d, *J* = 6.0 Hz, 1H), 4.13-4.30 (m, 2H), 5.12 (d, *J* = 6.0 Hz, 1H), 7.16 (d, *J*= 8.1 Hz, 2H), 7.30 (d, *J*= 8.1 Hz, 2H); ^{13}CNMR (75.4MHz, $CDCl_3$) δ 14.0, 21.2, 62.2, 72.7, 126.4, 129.2, 135.5, 138.2, 173.8.

Ethyl-4-methoxylmandelate (2d)[6] ^{1}HNMR (300 MHz, $CDCl_3$) δ 1.23 (t, *J*= 7.2 Hz, 3H), 3.43 (d, *J* = 5.4 Hz, 1H), 3.81(s, 3H), 4.17-4.26 (m, 2H), 5.11 (d, *J* = 5.4 Hz, 1H), 6.88-7.35 (m, 4H); ^{13}CNMR (75.4MHz, $CDCl_3$) δ 14.0, 56.3, 62.2, 72.4, 113.9, 127.8, 130.6, 159.6, 173.9.

Ethyl-2-methylmandelate (2e)[4] ^{1}HNMR (300 MHz, $CDCl_3$) δ 1.22 (t, *J*= 7.2 Hz, 3H), 2.44(s, 3H), 3.47 (d, *J* = 4.8 Hz, 1H), 4.14-4.30 (m, 2H), 5.36 (d, *J* = 4.8 Hz, 1H), 7.18-7.31 (m, 4H); ^{13}CNMR (75.4MHz, $CDCl_3$) δ 13.9, 19.3, 62.1, 70.3, 126.2, 126.6, 128.3, 130.7, 136.3, 136.7, 174.1.

Ethyl-4-fluoromandelate (2f) [4] ^{1}HNMR (300 MHz, $CDCl_3$) δ 1.23 (t, *J*= 7.2 Hz, 3H), 3.49 (d, *J* = 5.4 Hz, 1H), 4.18-4.28 (m, 2H), 5.14 (d, *J* = 5.4 Hz, 1H), 7.03- 7.08 (m, 2H), 7.38-7.42 (m, 2H) ; ^{13}CNMR (75.4MHz, $CDCl_3$) δ 13.9, 62.3, 72.1, 115.5(d), 128.2(d), 134.1(d), 161.0(d), 173.4.

Ethyl-4-chloromandelate (2g) [4] ^{1}HNMR (300 MHz, $CDCl_3$) δ 1.23 (t, *J*= 7.2 Hz, 3H), 3.54 (d, *J* = 5.4 Hz, 1H), 4.15-4.30 (m, 2H), 5.13 (d, *J* = 5.4 Hz, 1H), 7.32- 7.39

(m, 4H); ^{13}CNMR (75.4MHz, $CDCl_3$) δ 14.0, 62.5, 72.1, 127.9, 128.7, 134.2, 136.8, 173.3.

Ethyl-4-bromomandelate (2h) [4] ^{1}HNMR (300 MHz, $CDCl_3$) δ 1.23 (t, *J*= 7.2 Hz, 3H), 3.53 (d, *J* = 5.4 Hz, 1H), 4.14-4.30 (m, 2H), 5.13 (d, *J* = 5.4 Hz, 1H), 7.27- 7.33 (m, 2H), 7.48- 7.51 (m, 2H); ^{13}CNMR (75.4MHz, $CDCl_3$) δ 14.0, 62.5, 72.1, 122.4, 128.2, 131.6, 137.3, 173.2.

Ethyl-2-chloromandelate (2i) [4] ^{1}HNMR (300 MHz, $CDCl_3$) δ 1.23 (t, *J*= 7.2 Hz, 3H), 3.59 (d, *J* = 5.4 Hz, 1H), 4.21-4.27 (m, 2H), 5.55 (d, *J* = 5.4 Hz, 1H), 7.27- 7.41 (m, 4H); ^{13}CNMR (75.4MHz, $CDCl_3$) δ 13.9, 62.4, 70.3, 127.1, 128.7, 129.7, 129.9, 133.5, 136.1, 173.2.

Ethyl- 2-Hydroxy-propionic acid ethyl ester (2j)[6] ^{1}HNMR (300 MHz, $CDCl_3$) ^{1}H NMR (300 MHz, $CDCl_3$): 1.26(t, *J*= 7.2Hz, 3H), 1.38(d, *J*= 6.9Hz, 3H), 4.22(m,4H); ^{13}CNMR (75.4MHz, $CDCl_3$) δ 14.1, 20.4, 61.7, 66.7, 175.7.

Reference

1 Mashima, K.; Kusano, K.; Sate, N.; Matsumura, Y.; Nozaki, K.; Kumobayashi, H.; Sayo, N.; Hori, Y.; Ishizaki, T.; Akutagawa, S.; Takaya, H. *J. Org. Chem.* **1994**, *59*, 3064.

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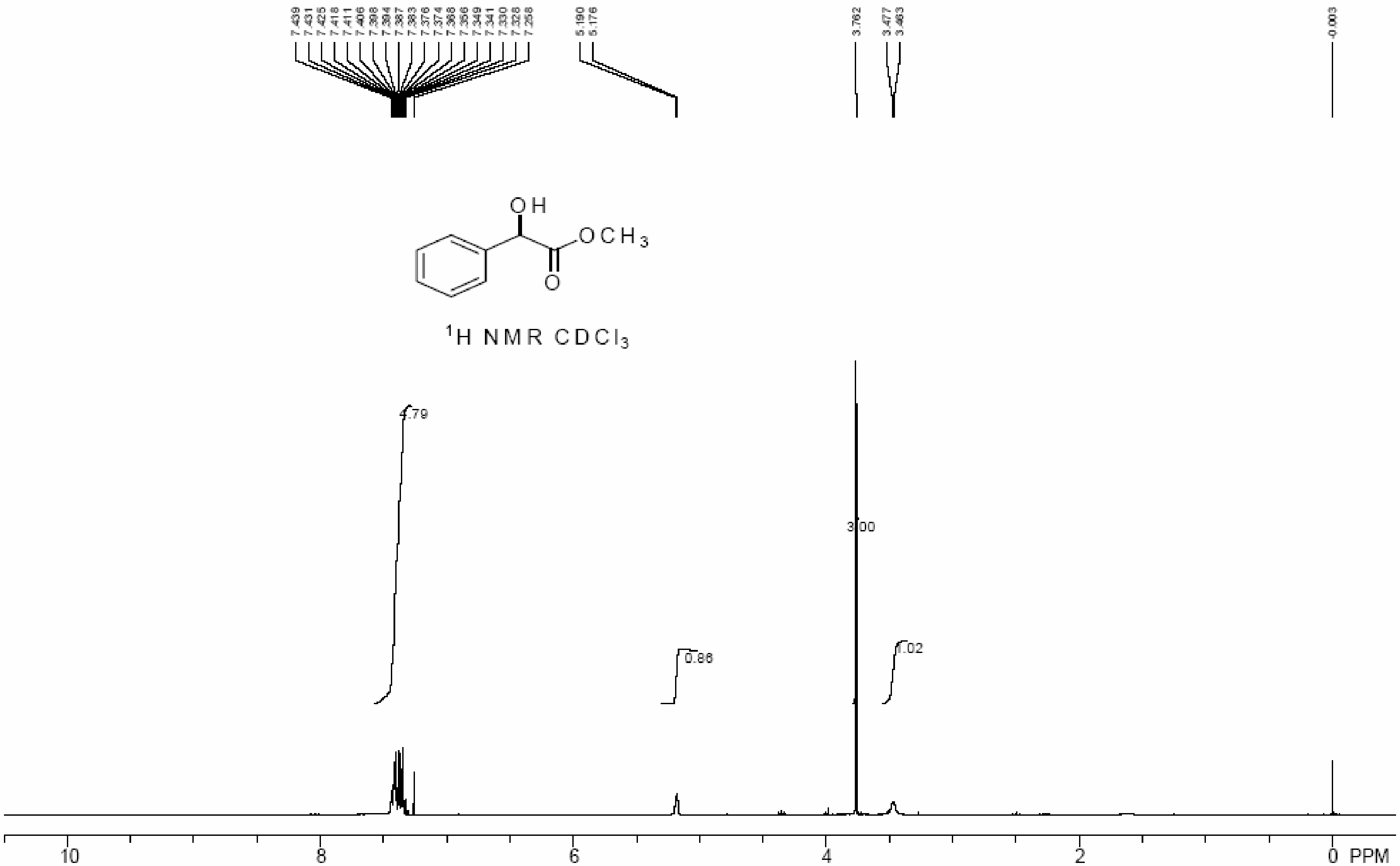
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7.356
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7.341
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7.328
7.258
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5.176
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3.463
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6
4
2
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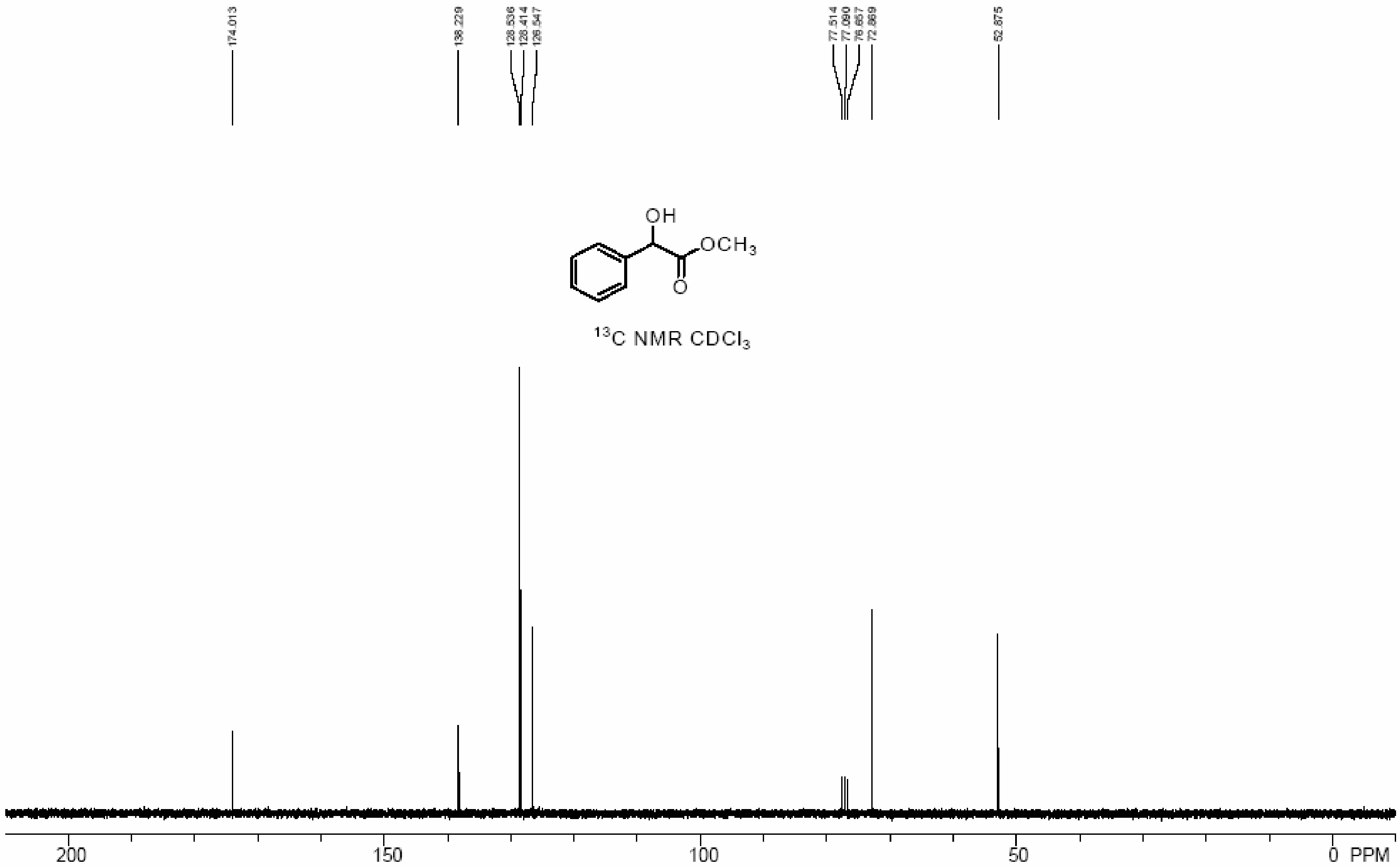
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50
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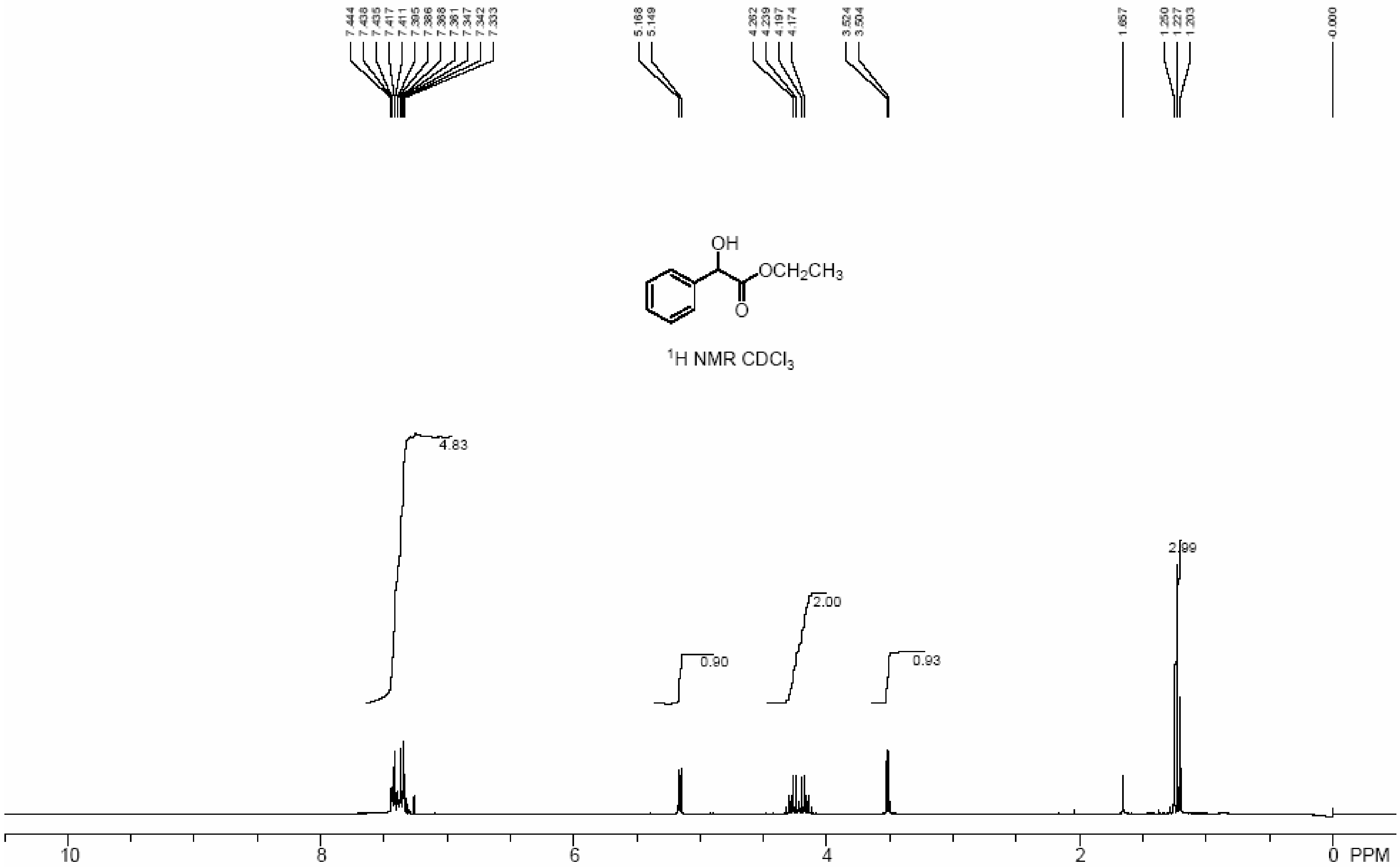

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3.524 3.504
1.657
1.250 1.227 1.203
-0.000
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2.99
10
8
6
4
2
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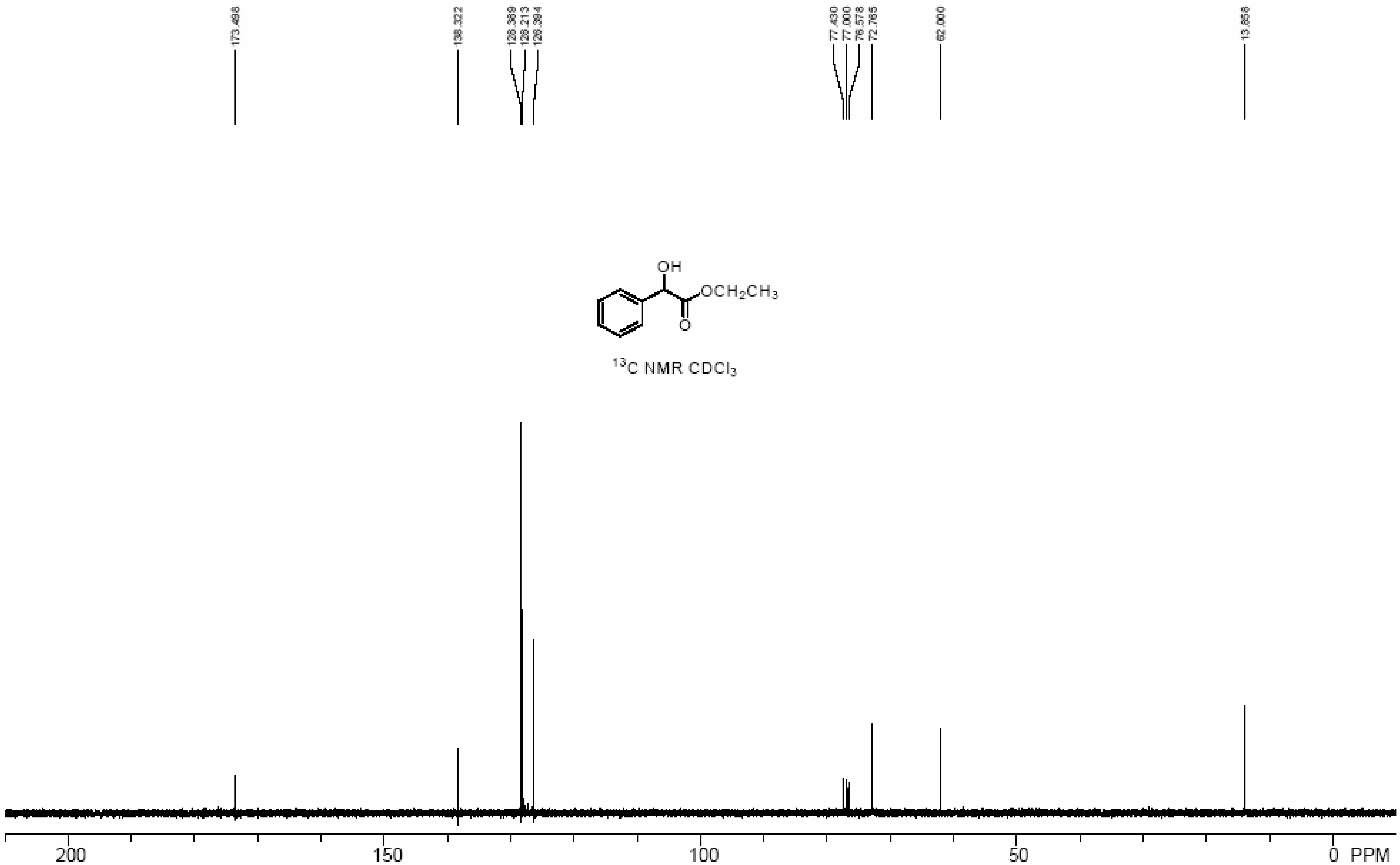
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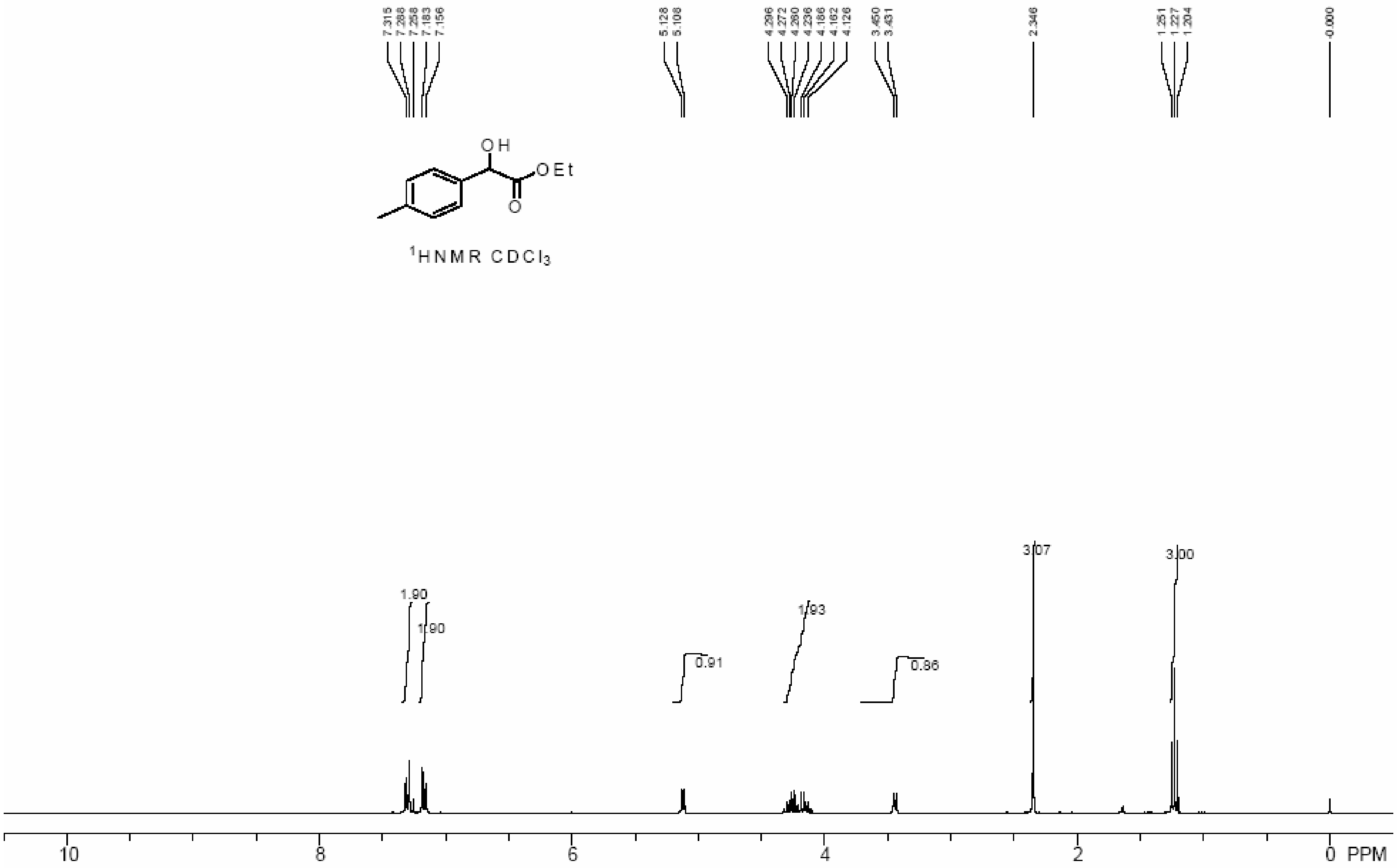
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4.126
3.450
3.431
2.346
1.251
1.227
1.204
0.000
OH
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O
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10
8
6
4
2
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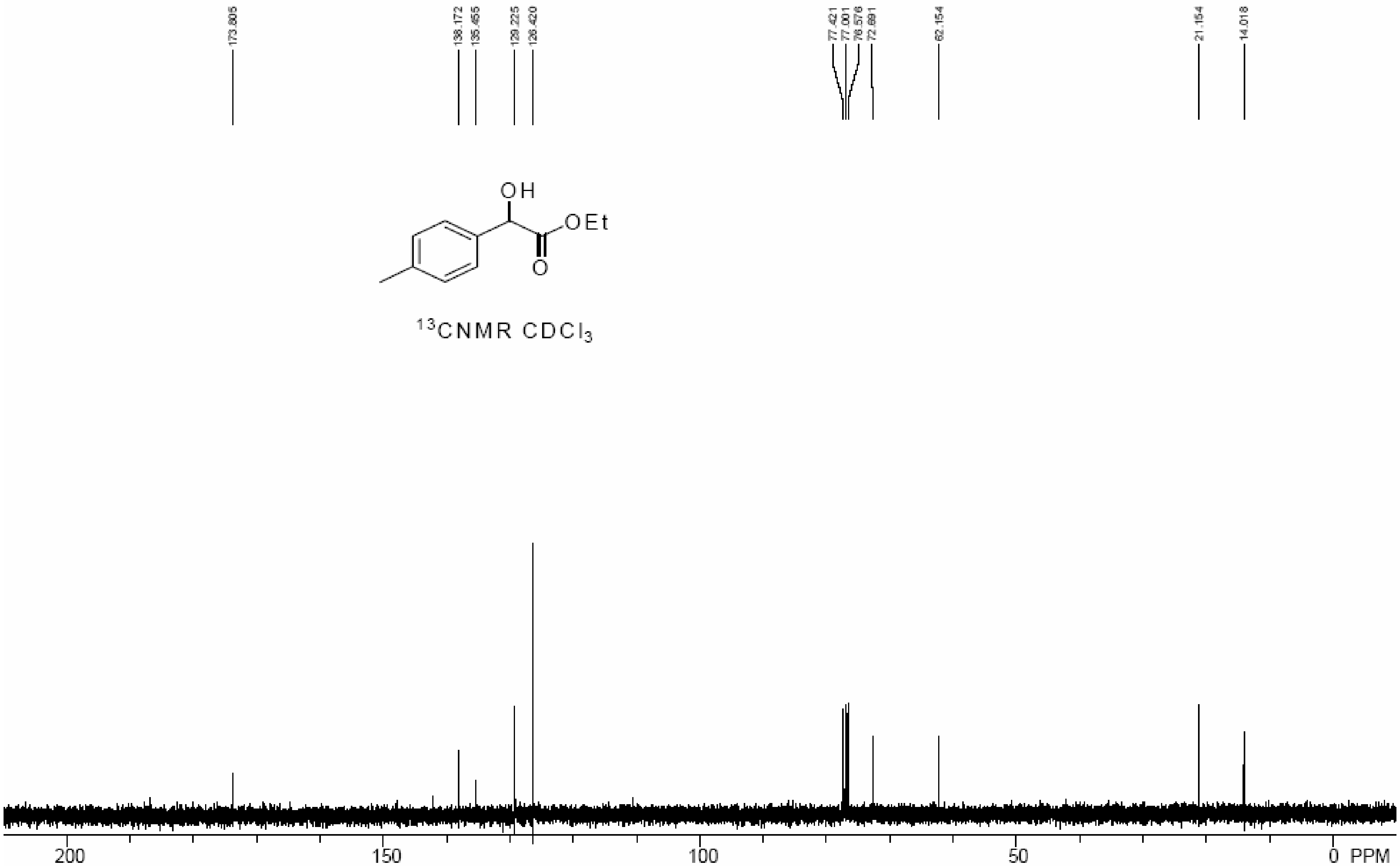

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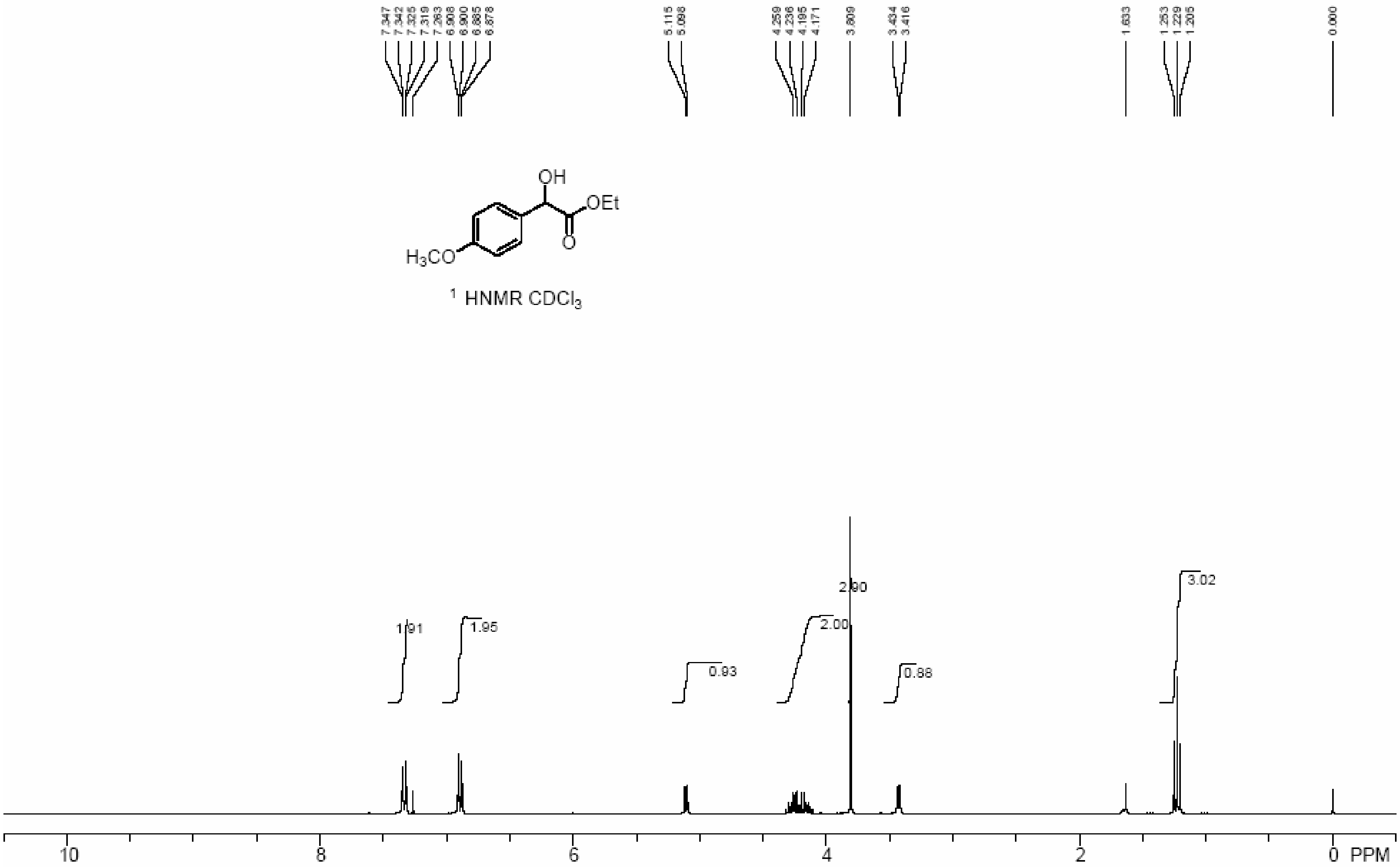
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4.195
4.171
3.809
3.434
3.416
1.633
1.253
1.229
1.205
0.000
OH
OEt
O
H_3CO
1.91
1.95
0.93
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10
8
6
4
2
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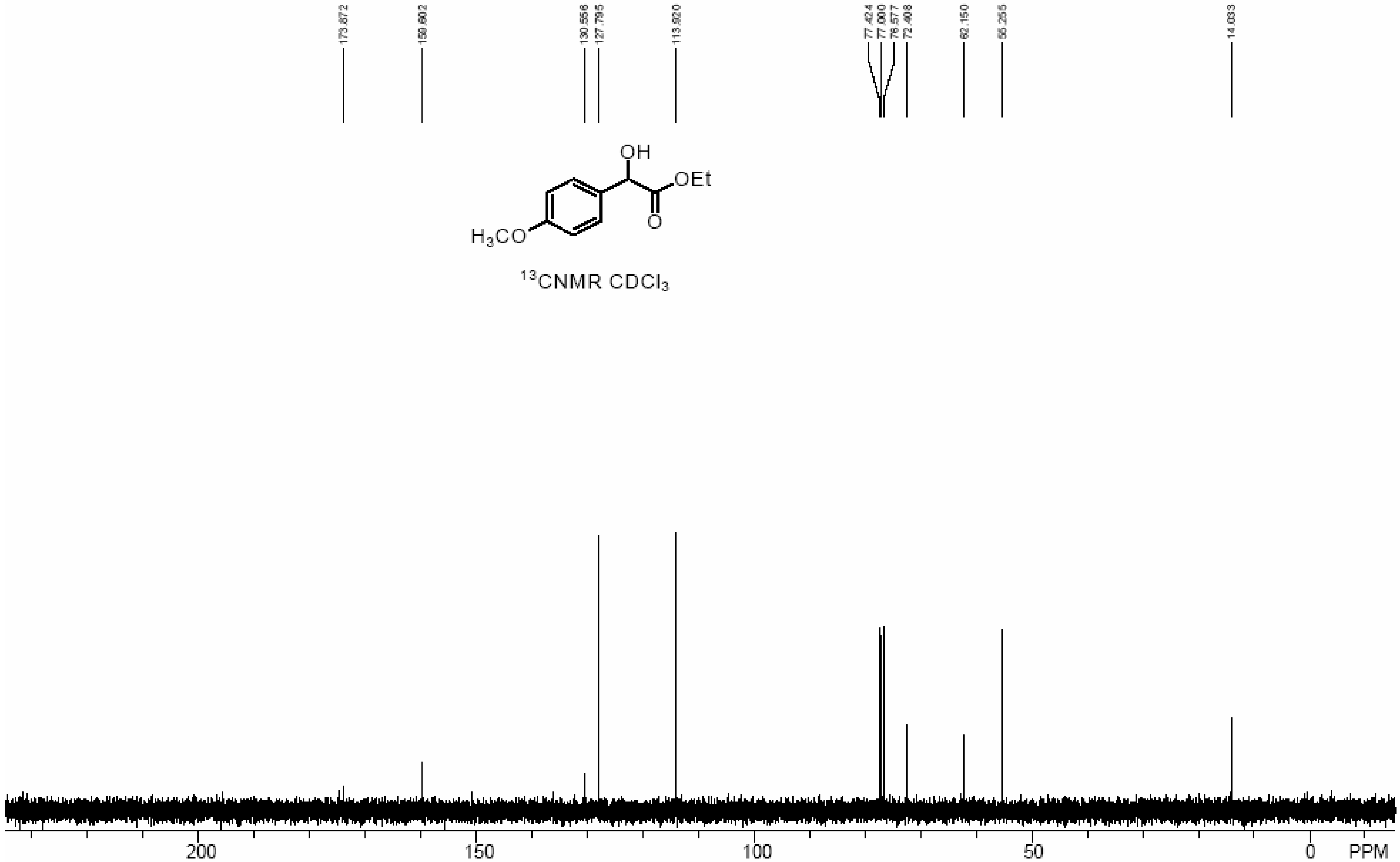
^{1} HNMR $CDCl_3$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OEt
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H_3CO
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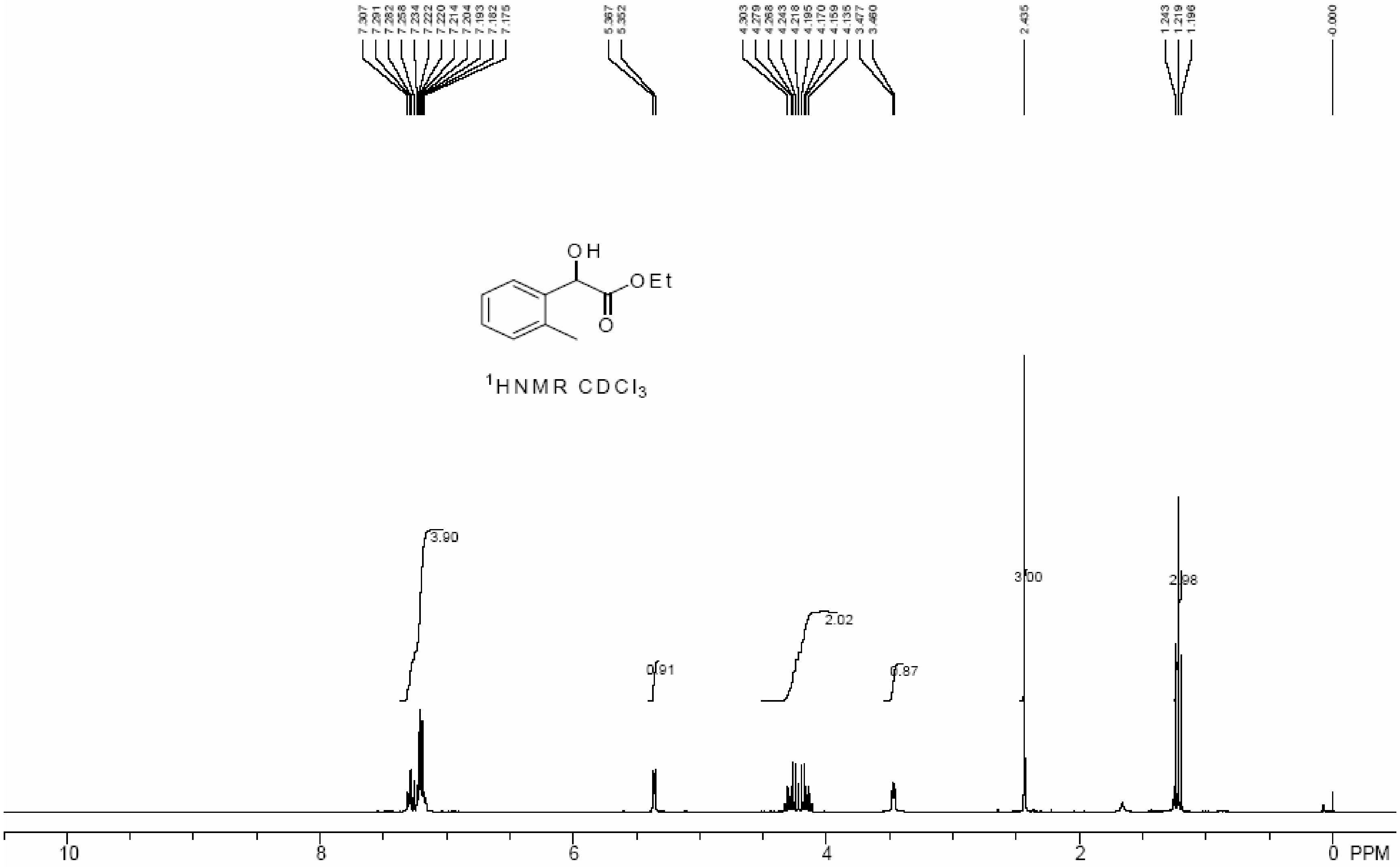
150
100
50
0
PPM



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5.352
4.303
4.279
4.268
4.243
4.218
4.195
4.170
4.159
4.135
3.477
3.460
2.435
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1.219
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OH
OEt
O
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6
4
2
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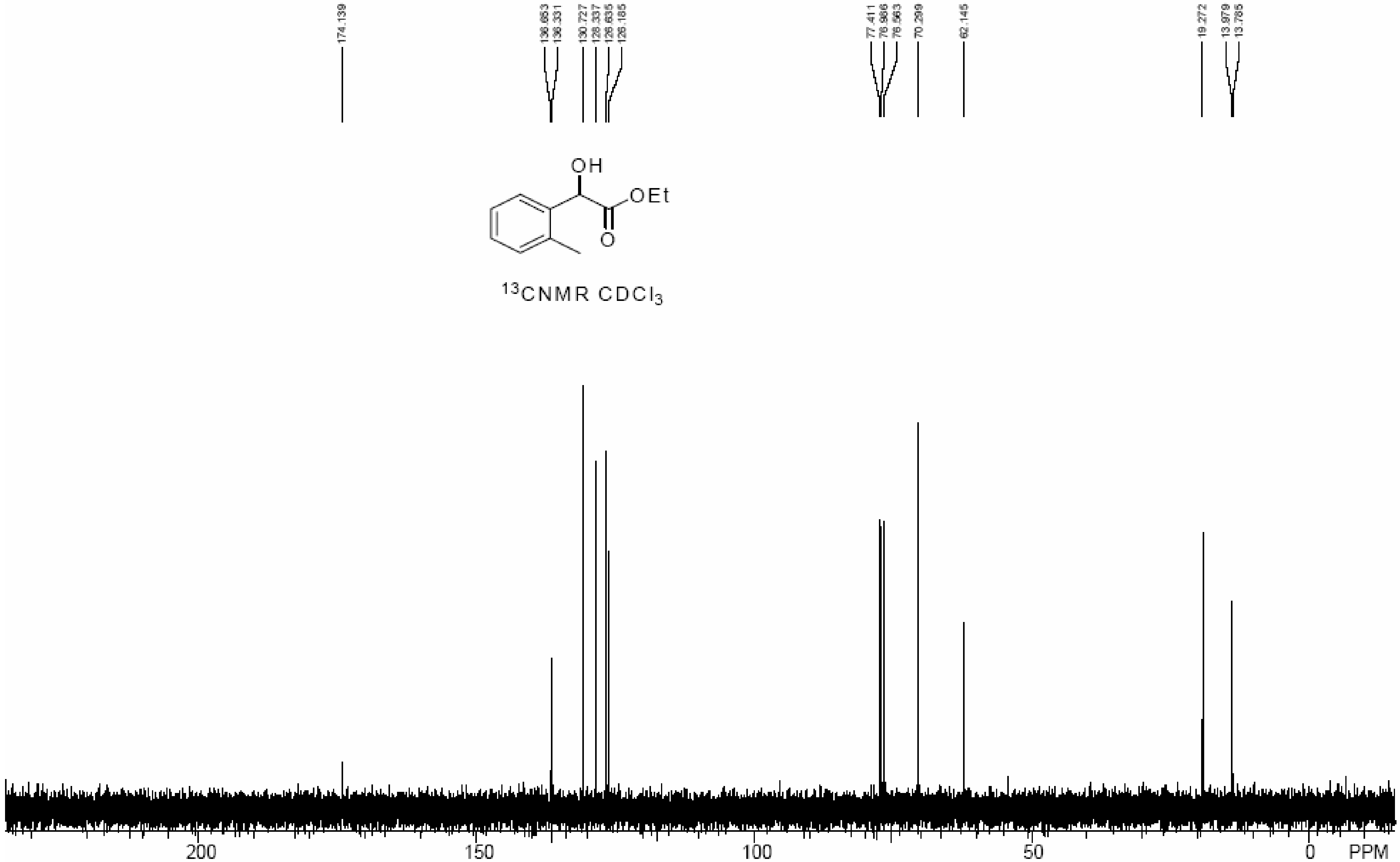
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O
^{13}CNMR CDCl$_3$
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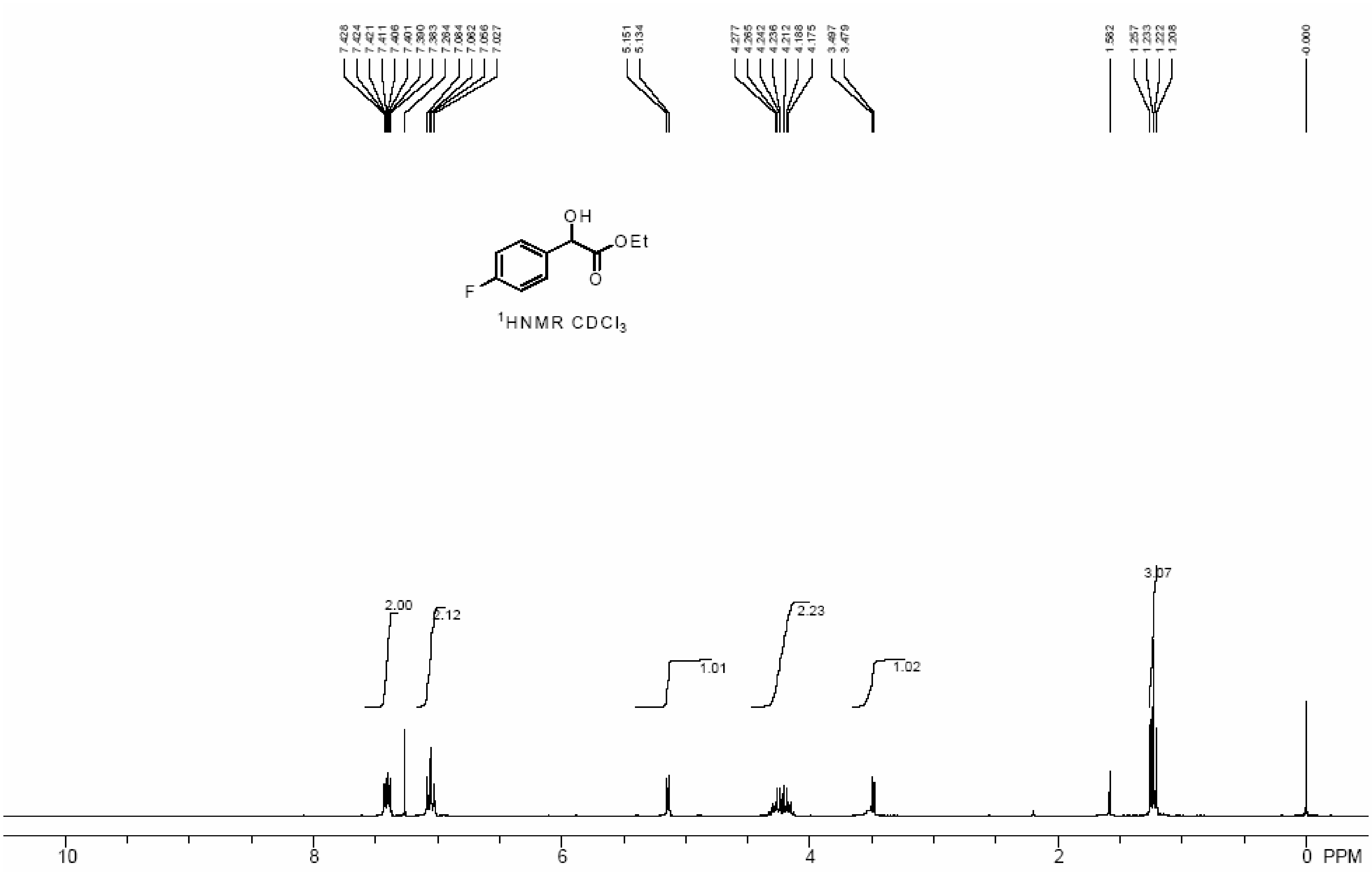
150
100
50
0
PPM



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OEt
O
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4
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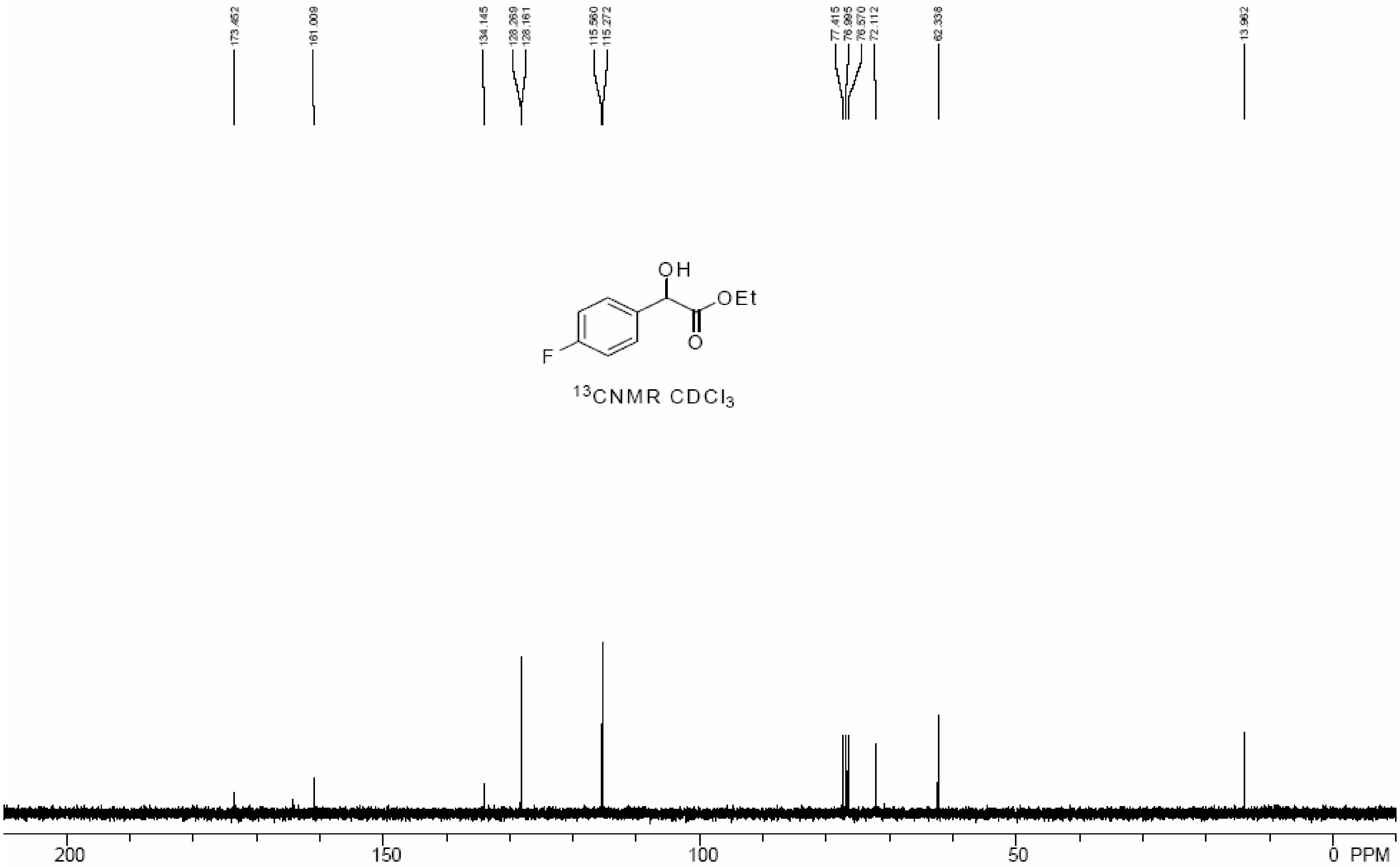
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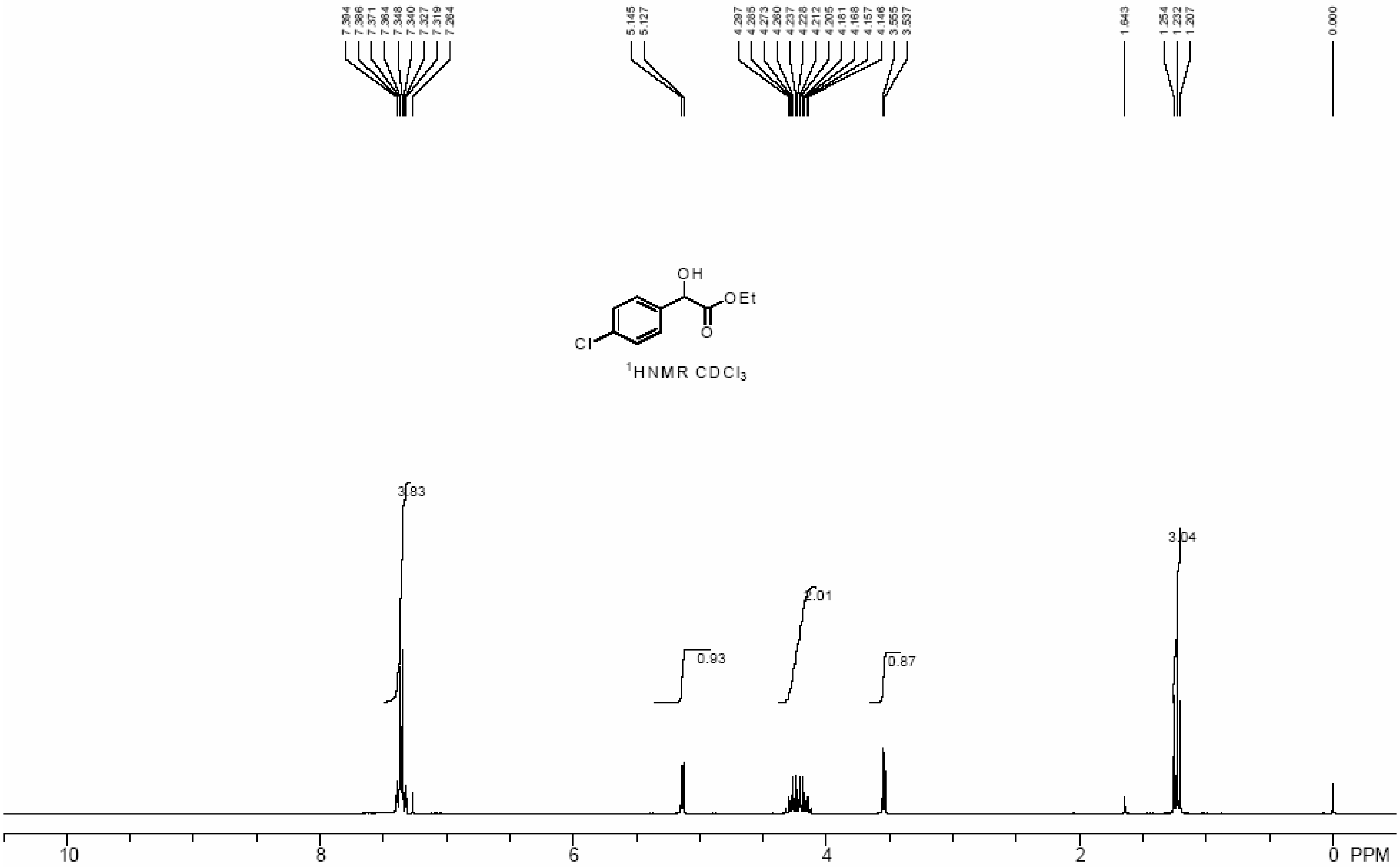

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1.254 1.232 1.207
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OEt
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6
4
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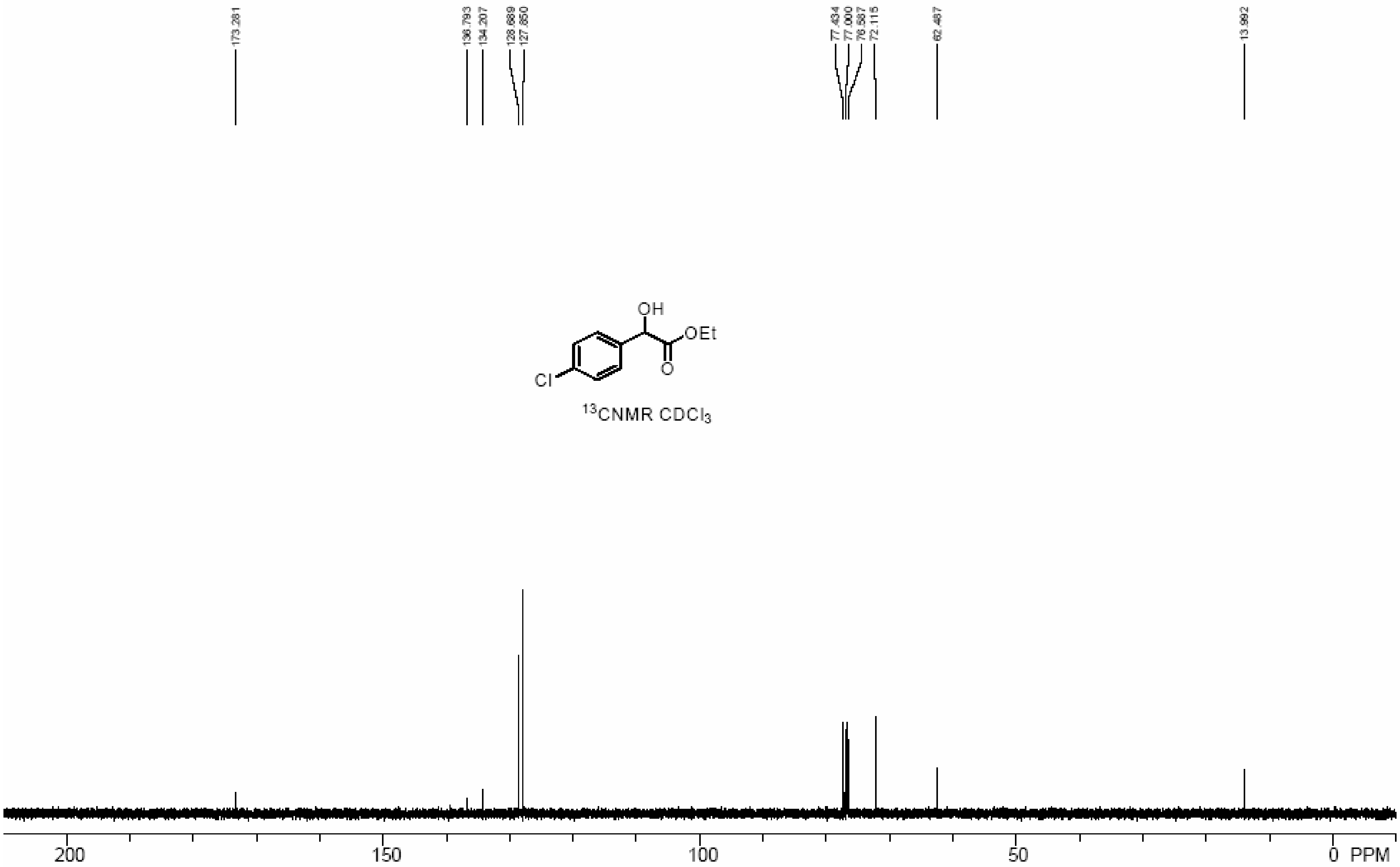

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50
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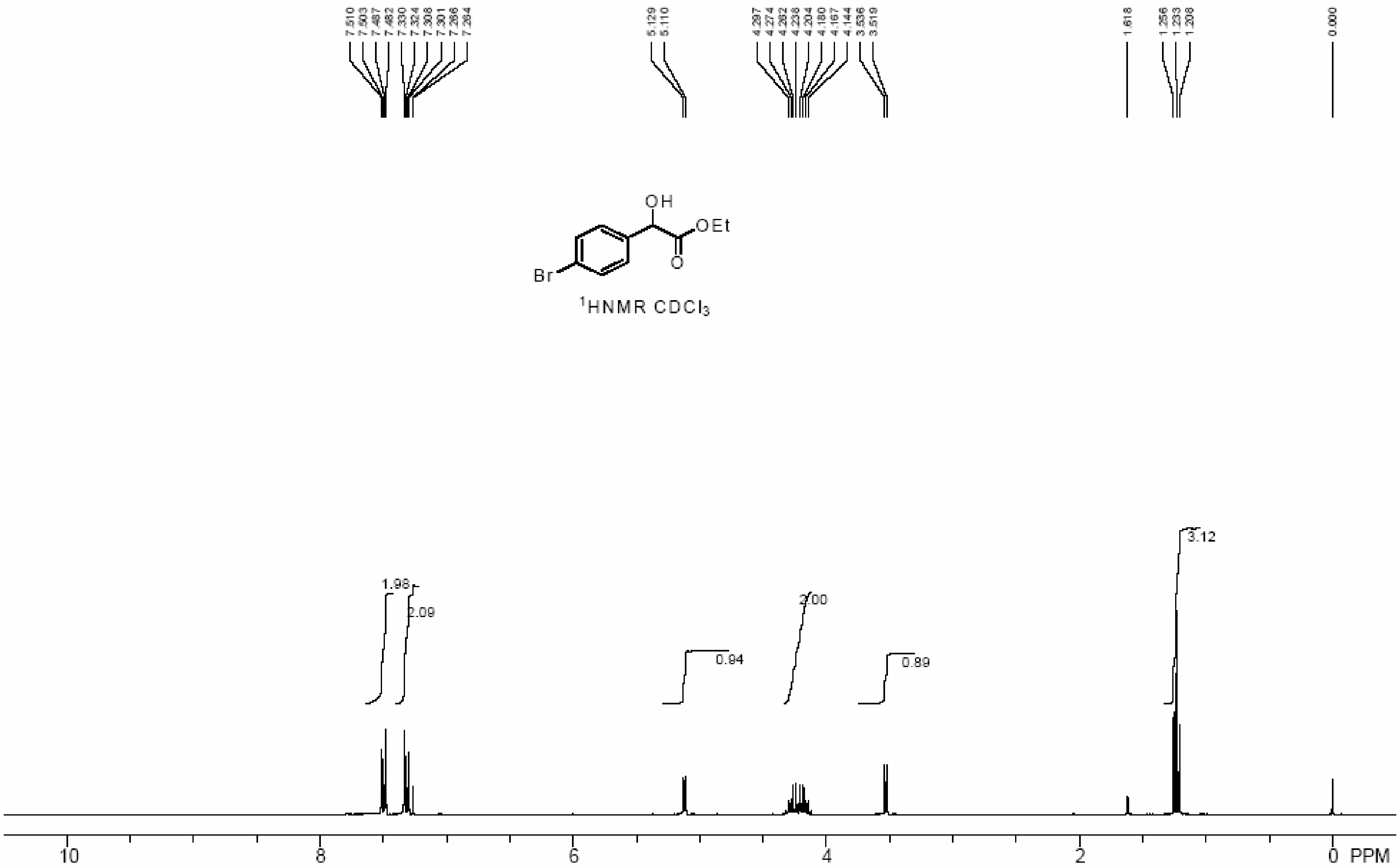

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Br
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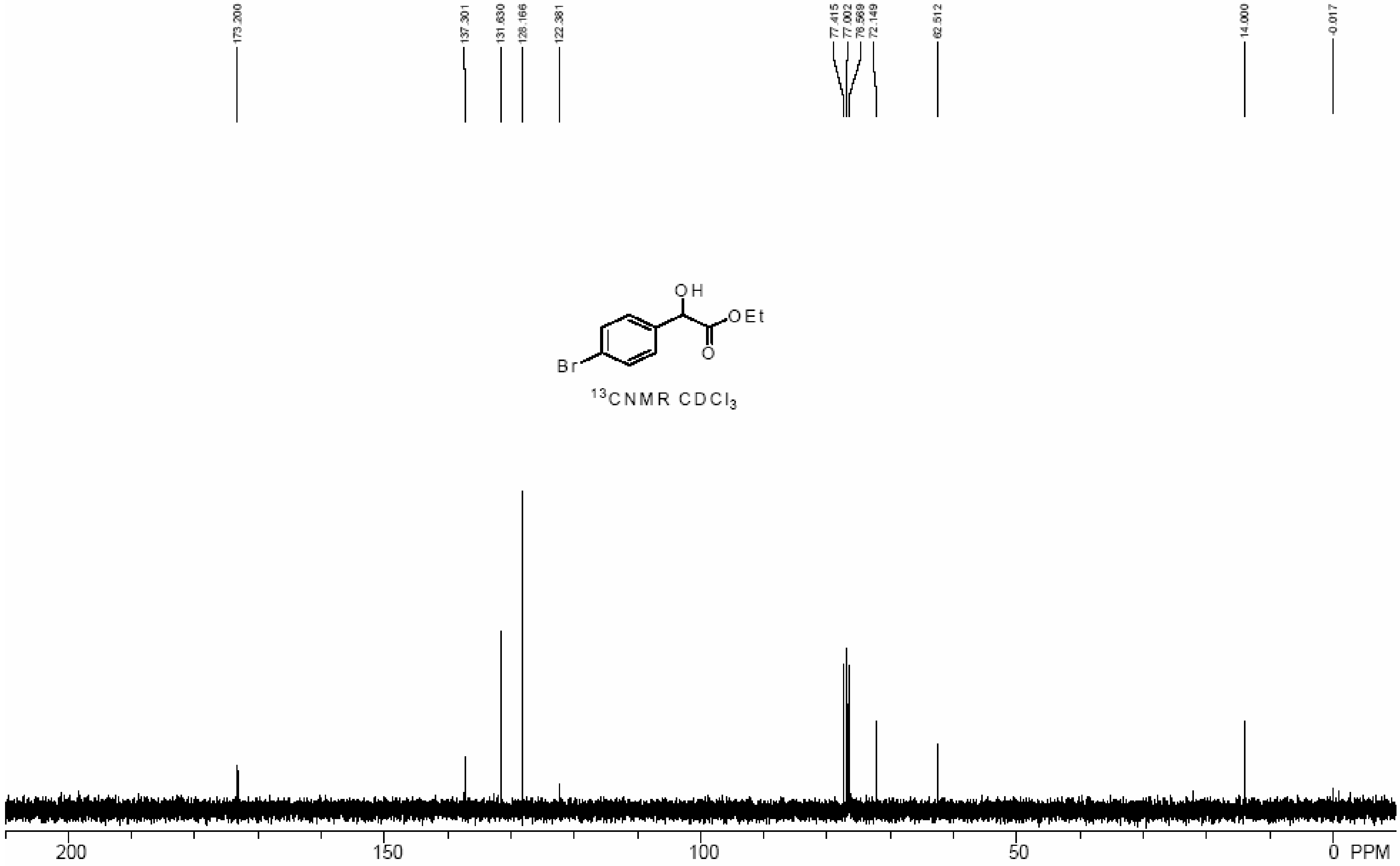
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100
50
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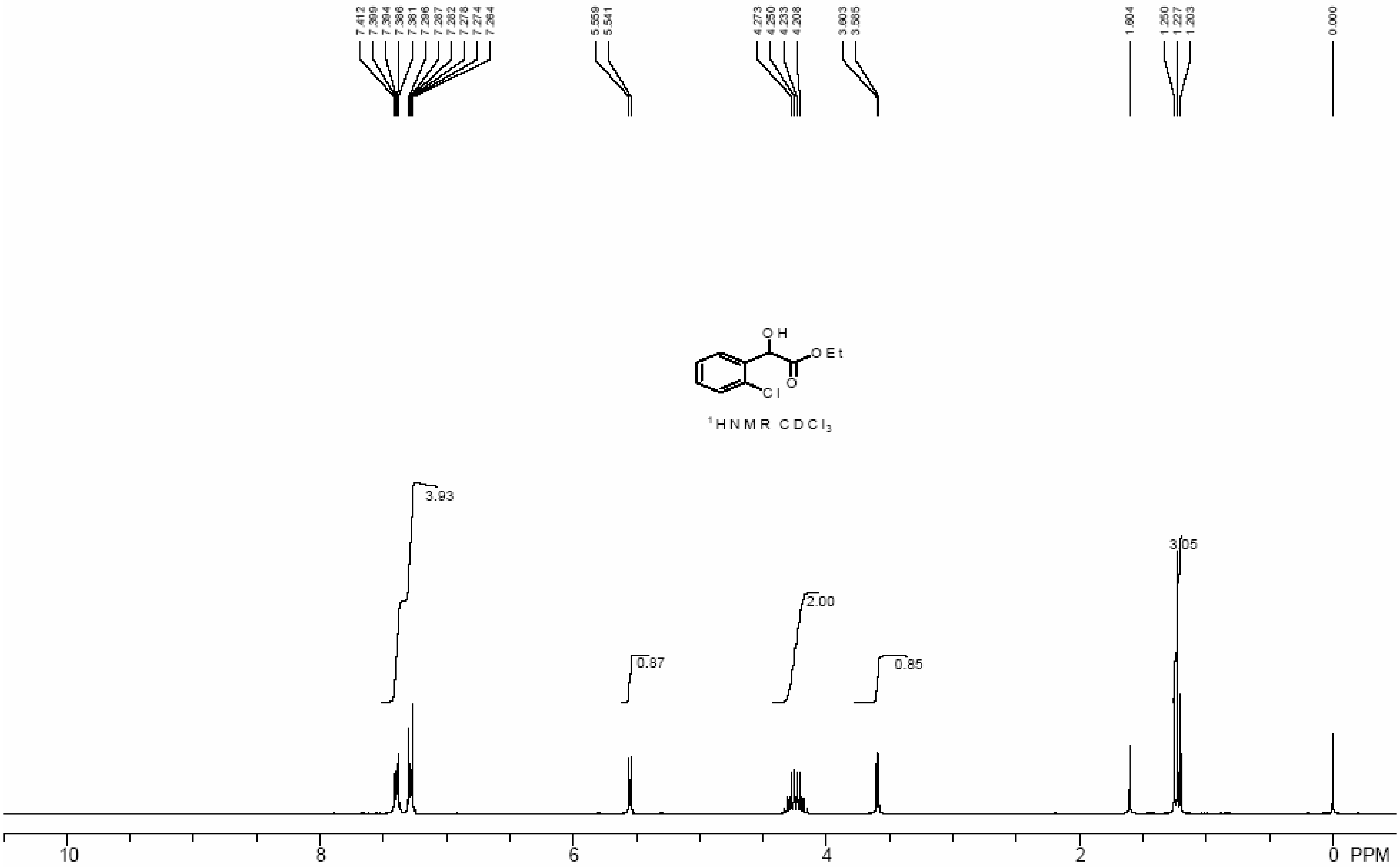

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4.233
4.208
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1.604
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OH
OEt
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0.85
10
8
6
4
2
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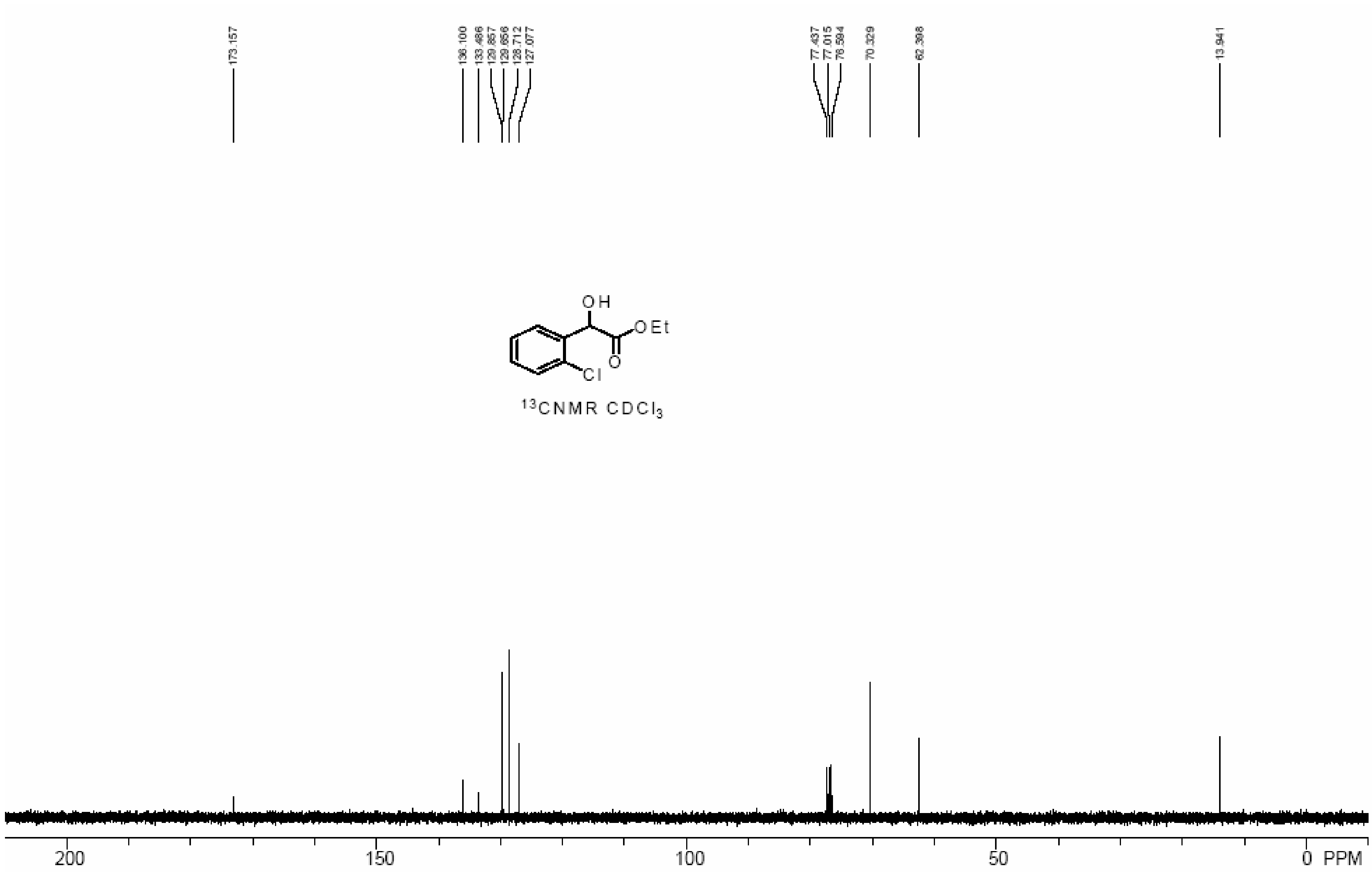
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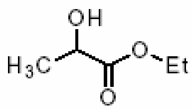
150
100
50
0 PPM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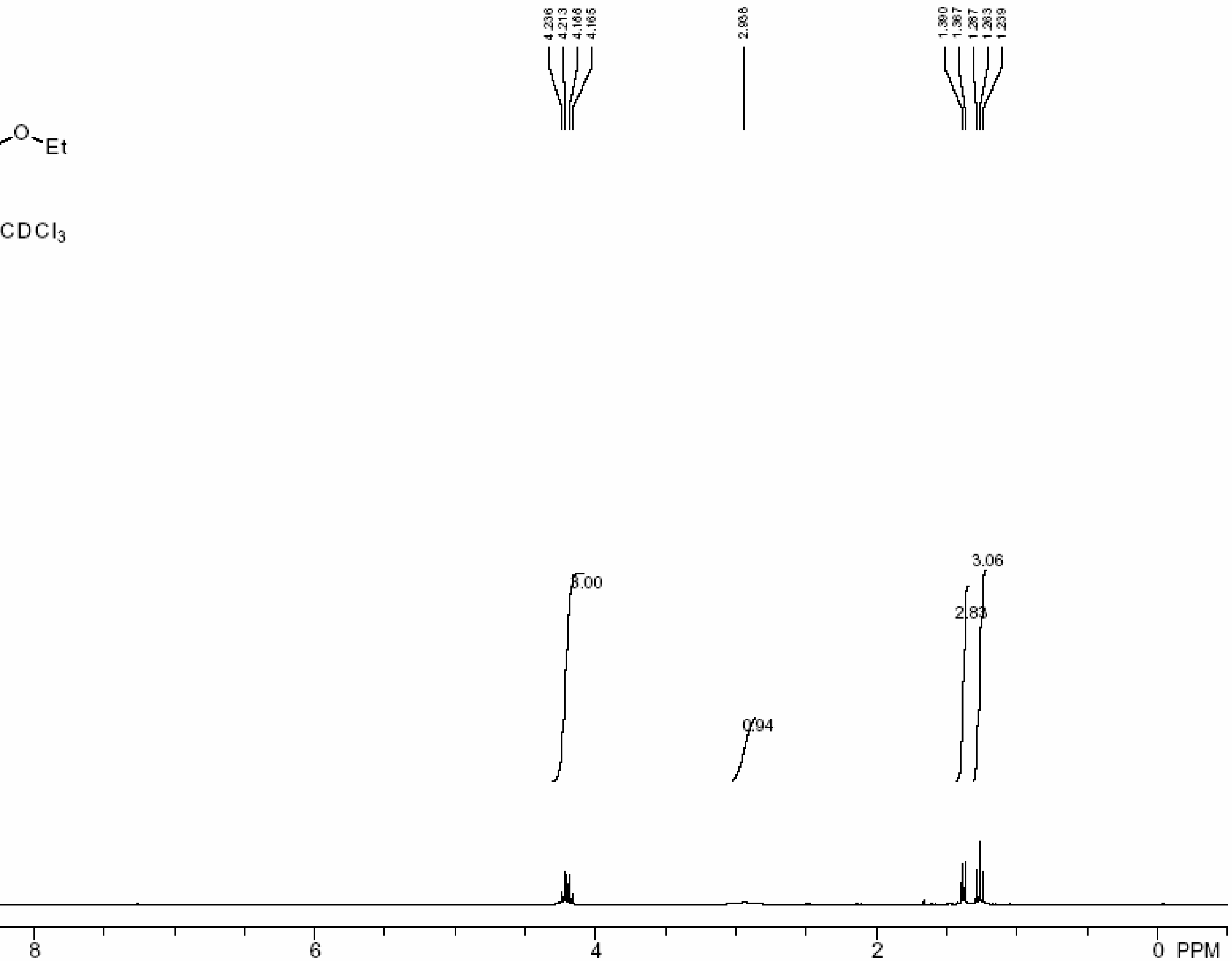
Et
O

^{1}HNMR $CDCl_3$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3.06
10
8
6
4
2
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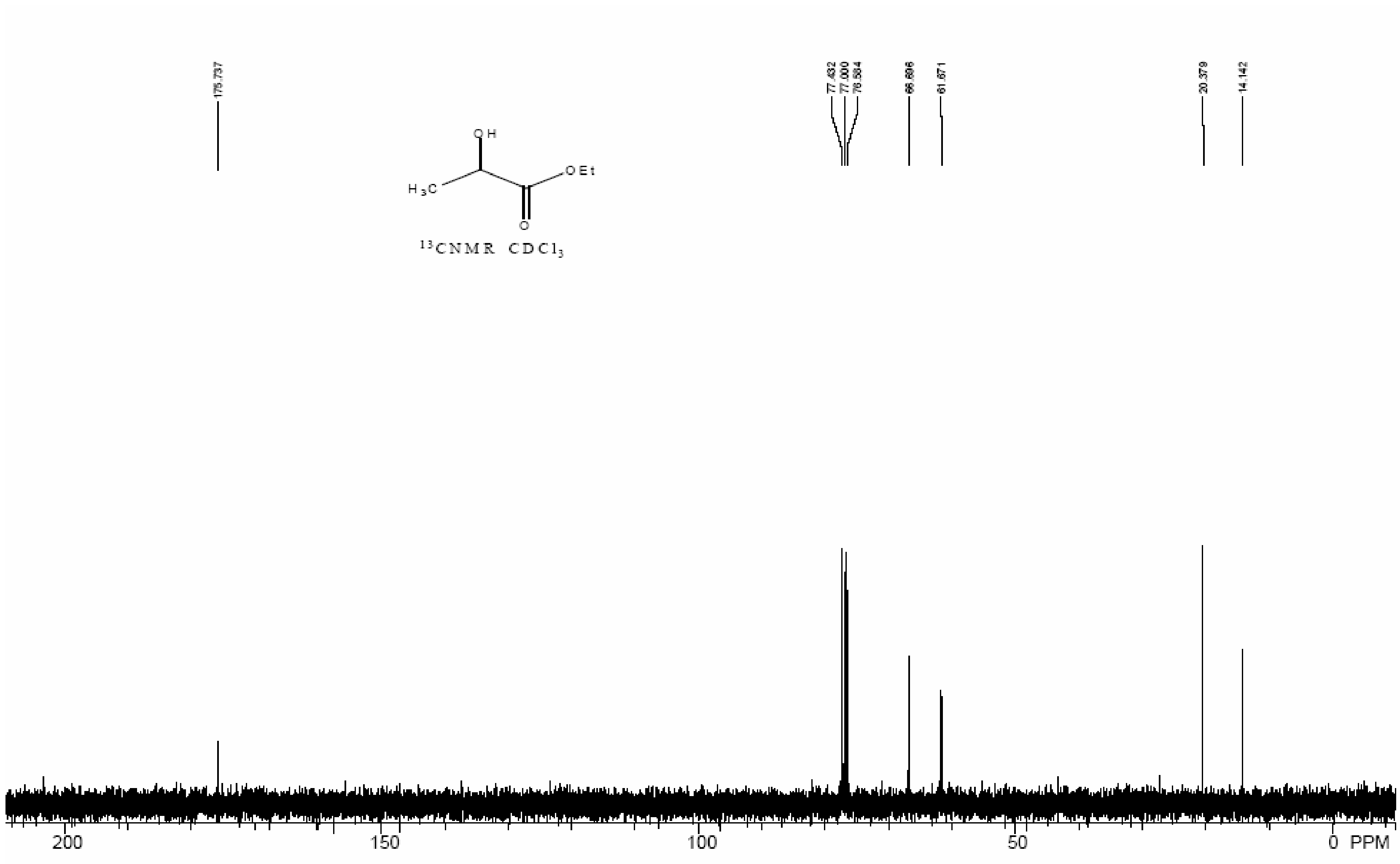

175.737
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77.000
76.584
66.696
61.671
20.379
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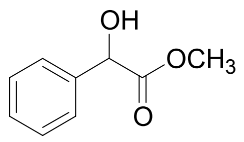
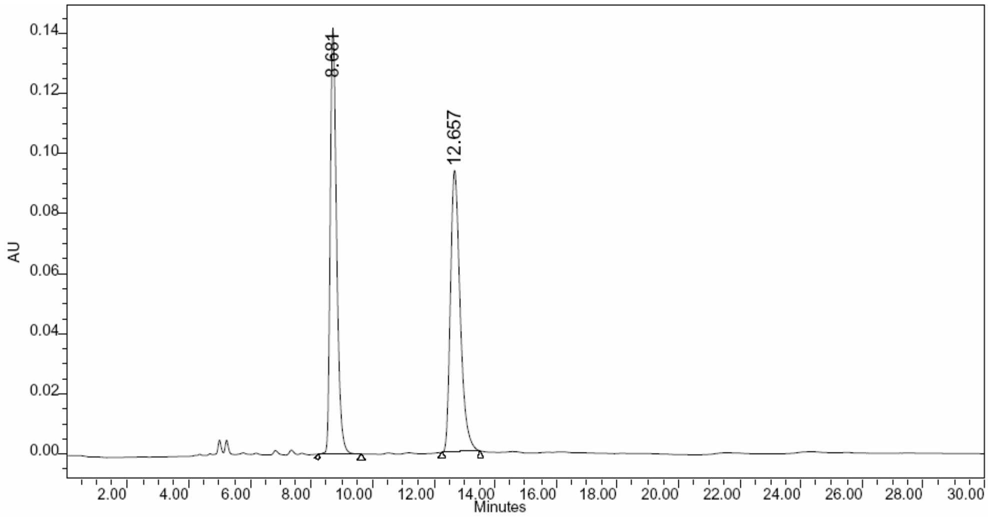
OH
H_3C
OEt
O
^{13}CNMR $CDCl_3$
200
150
100
50
0 PPM



2a racemate



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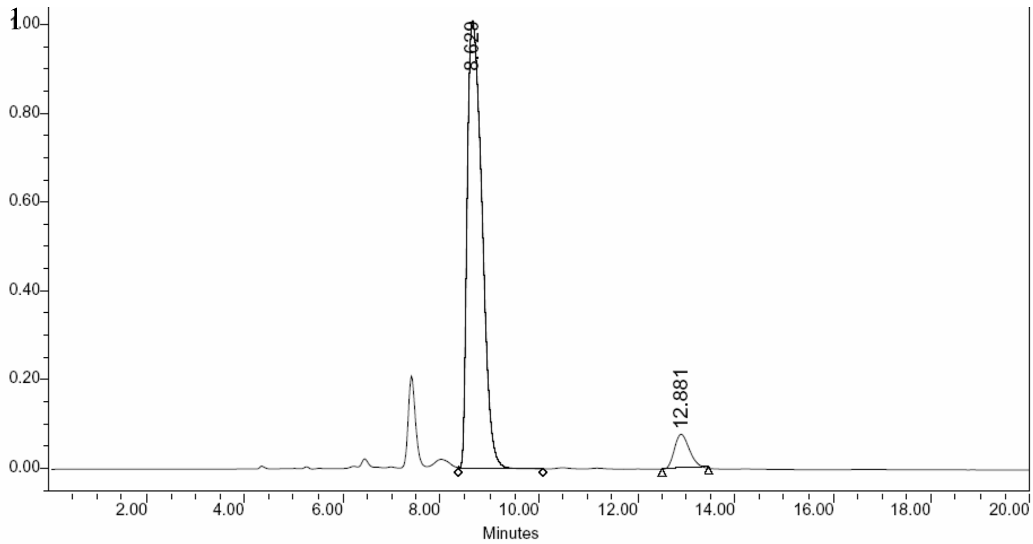
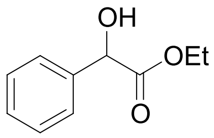
2	12.657	2070074	50.07	93629	39.77

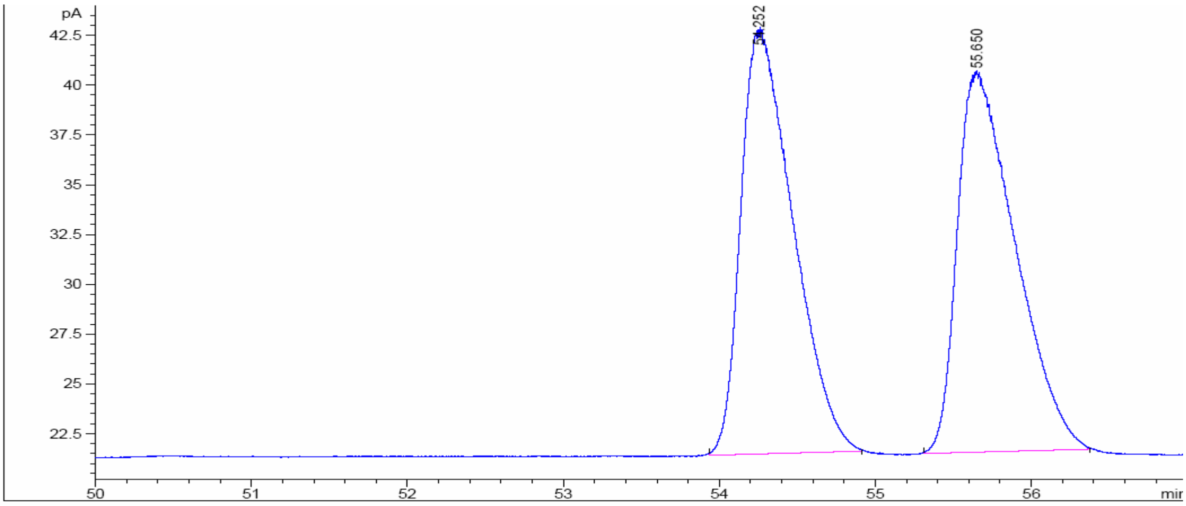
Table 1 entry1



	RT (min)	Area (V*sec)	% Area	Height (V)	% Height
1	8.629	21188307	92.62	1011092	92.85
2	12.881	1688857	7.38	77911	7.15

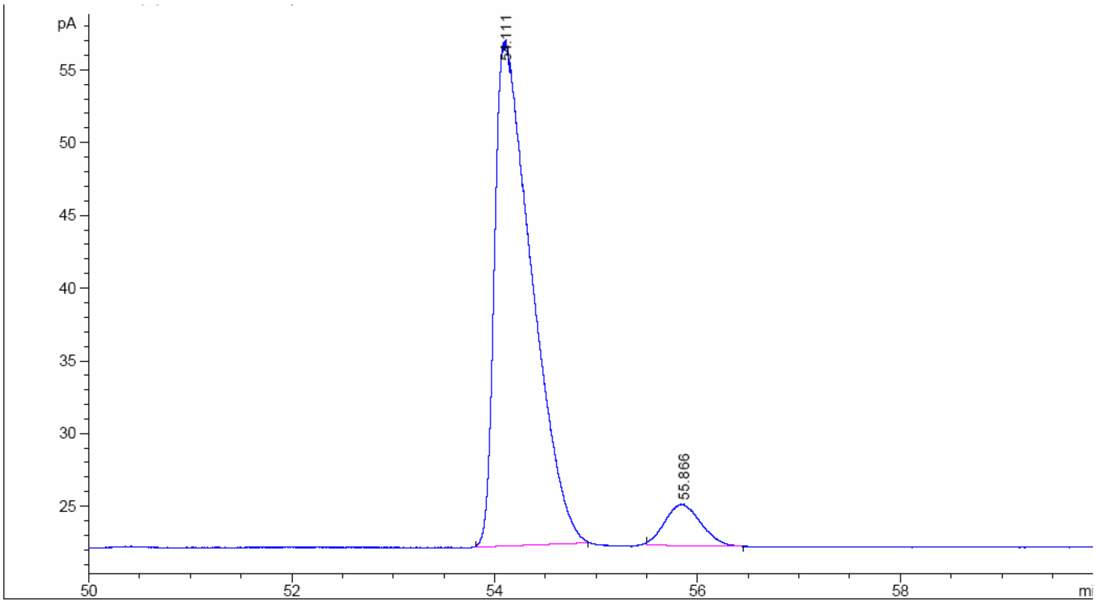


2b racemate
GC on a β-DEX 325 capillary column



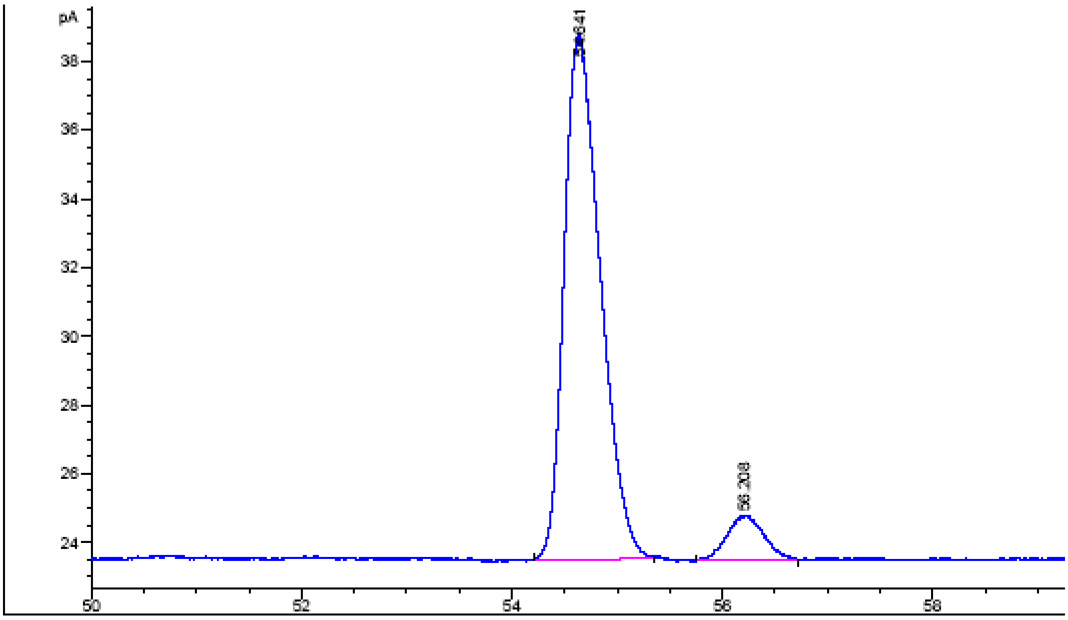

```
=====================================================================
                        Area Percent Report
=====================================================================

Sorted By             :      Signal
Multiplier            :      1.0000
Dilution              :      1.0000
Sample Amount         :      1.00000  [ng/ul]   (not used in calc.)

Signal 1: FID1 A,

Peak RetTime Type  Width     Area      Height     Area
  #   [min]        [min]   [pA*s]      [pA]        %
----|-------|----|-------|----------|----------|--------|
   1  54.252 BB    0.2830  495.81268   21.26423 50.13688
   2  55.650 BB    0.3043  493.10550   19.09515 49.86312

Totals :                   988.91818   40.35938

 Results obtained with enhanced integrator!
=====================================================================
                          *** End of Report ***
```

Table 1 entry 2



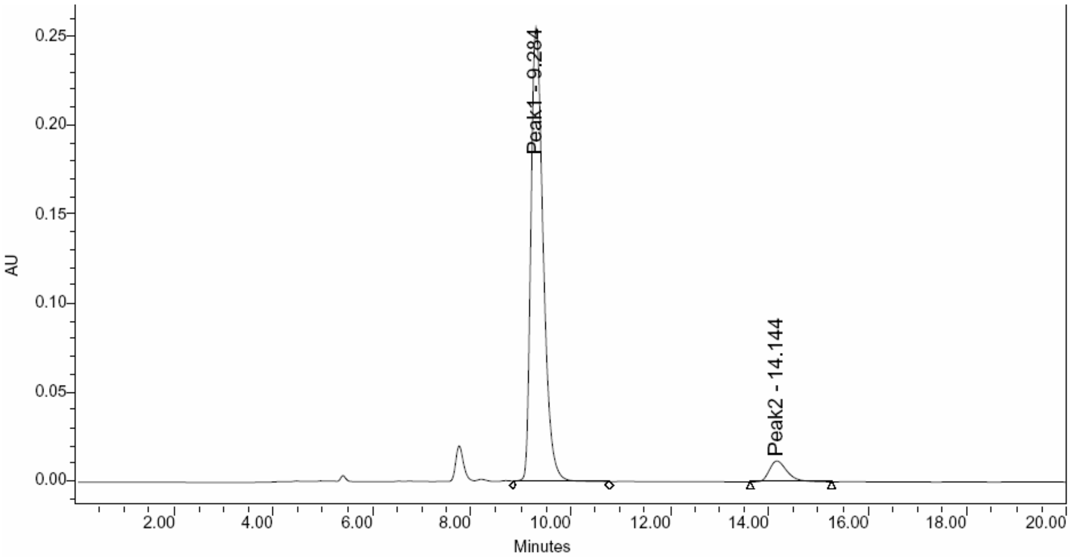

```
=====================================================================
                         Area Percent Report
=====================================================================

Sorted By             :      Signal
Multiplier            :      1.0000
Dilution              :      1.0000
Sample Amount         :      1.00000  [ng/ul]   (not used in calc.)


Signal 1: FID1 A,

Peak RetTime Type  Width     Area      Height     Area
  #   [min]        [min]   [pA*s]      [pA]         %
----|-------|----|-------|----------|----------|--------|
   1  54.111 BB    0.3015  878.98462   34.69747 92.66794
   2  55.866 BB    0.2931   69.54691    2.82568  7.33206

Totals :                   948.53152   37.52315

 Results obtained with enhanced integrator!
=====================================================================
                          *** End of Report ***
```

Table 1 entry 3



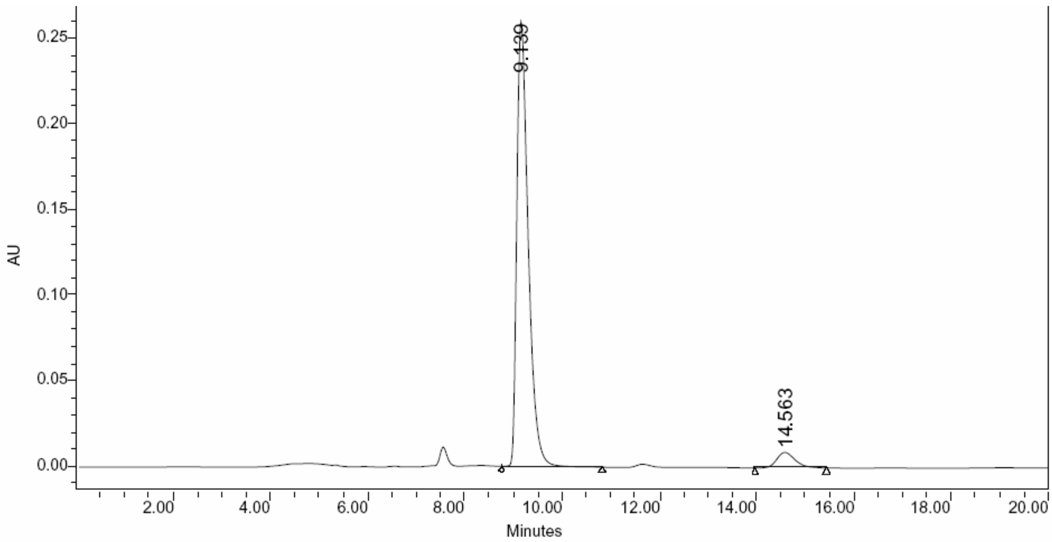

```
=====================================================================
                          Area Percent Report
=====================================================================

Sorted By             :      Signal
Multiplier            :      1.0000
Dilution              :      1.0000
Sample Amount         :      1.00000  [ng/ul]   (not used in calc.)


Signal 1: FID1 A,

Peak RetTime Type  Width     Area      Height     Area
  #   [min]        [min]    [pA*s]      [pA]       %
----|-------|----|-------|----------|----------|--------|
   1  54.641 BB    0.2861  365.06741   15.26147 91.94329
   2  56.208 PV    0.2909   31.98973    1.30084  8.05671

Totals :                   397.05714   16.56231

 Results obtained with enhanced integrator!
=====================================================================
                          *** End of Report ***
```

Table 1 entry 5



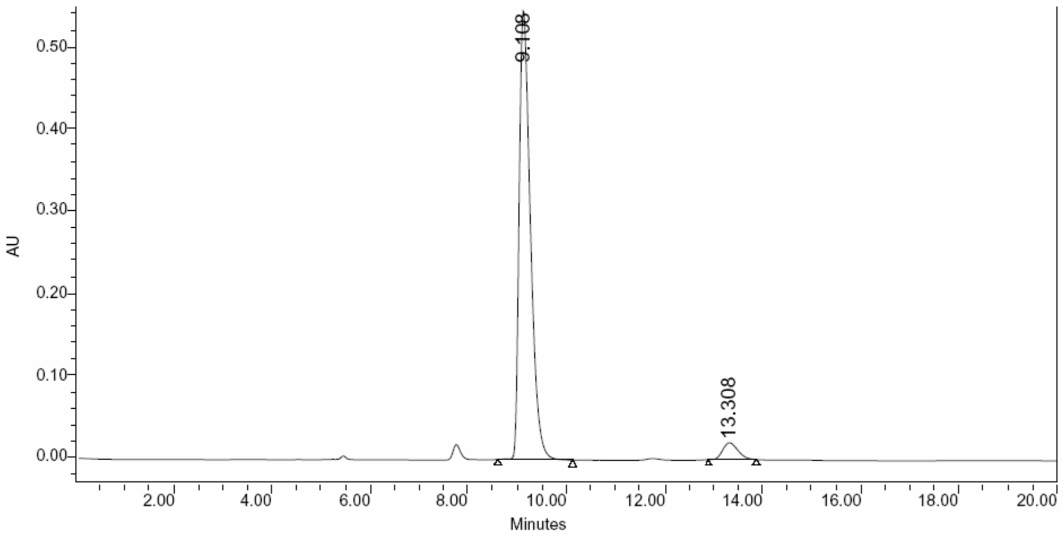
	Peak Name	RT (min)	Area (V*sec)	% Area	Height (V)	% Height
1	Peak1	9.284	4398532	93.71	255108	95.60
2	Peak2	14.144	295204	6.29	11743	4.40

Table 1 entry 6



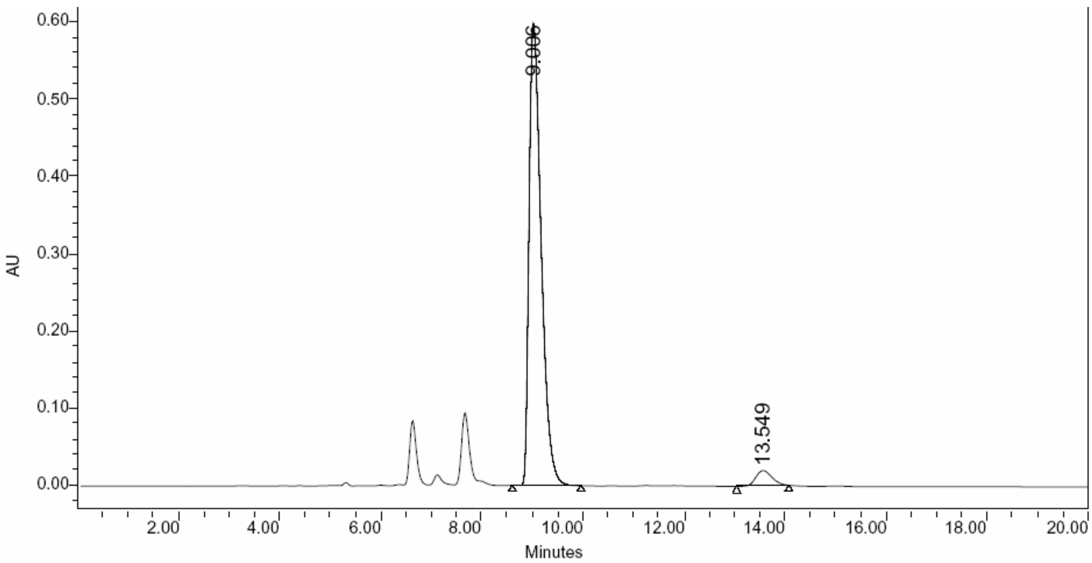
	RT (min)	Area (V*sec)	% Area	Height (V)	% Height
1	9.139	4275203	94.76	260468	96.65
2	14.563	236556	5.24	9023	3.35

Table 1 entry 7



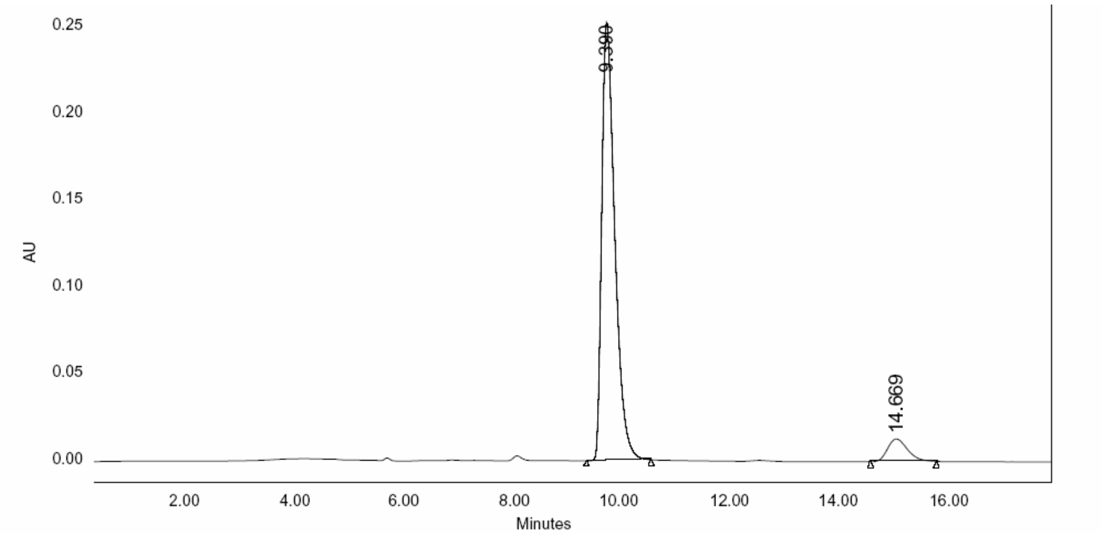
	RT (min)	Area (V*sec)	% Area	Height (V)	% Height
1	9.108	8699575	95.12	547327	96.38
2	13.308	446191	4.88	20573	3.62

Table 1 entry 8



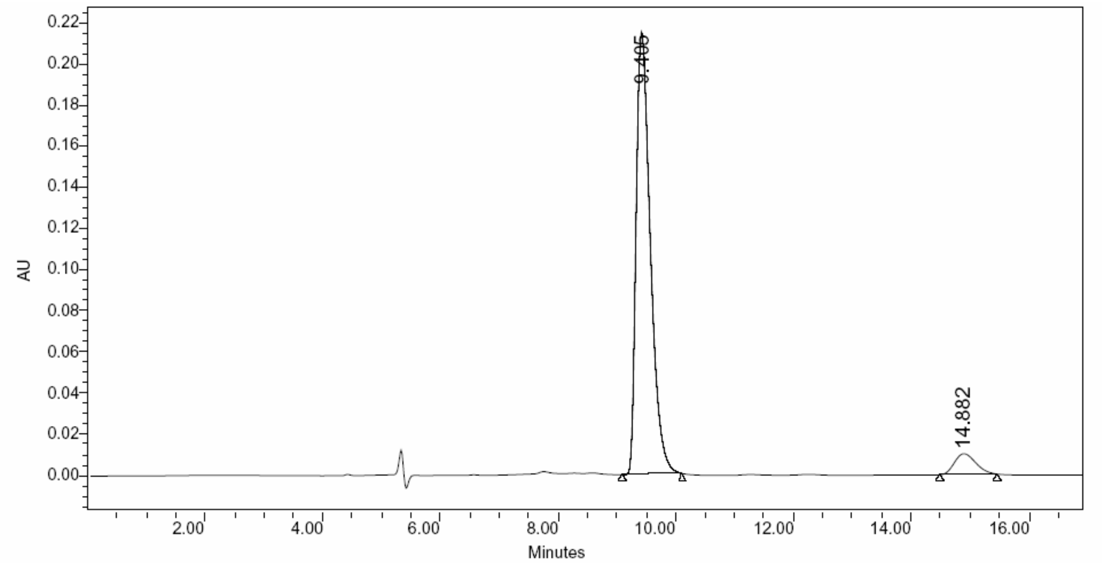
	RT (min)	Area (V*sec)	% Area	Height (V)	% Height
1	9.006	9959719	95.76	599169	96.80
2	13.549	440687	4.24	19780	3.20

Table 1 entry 9



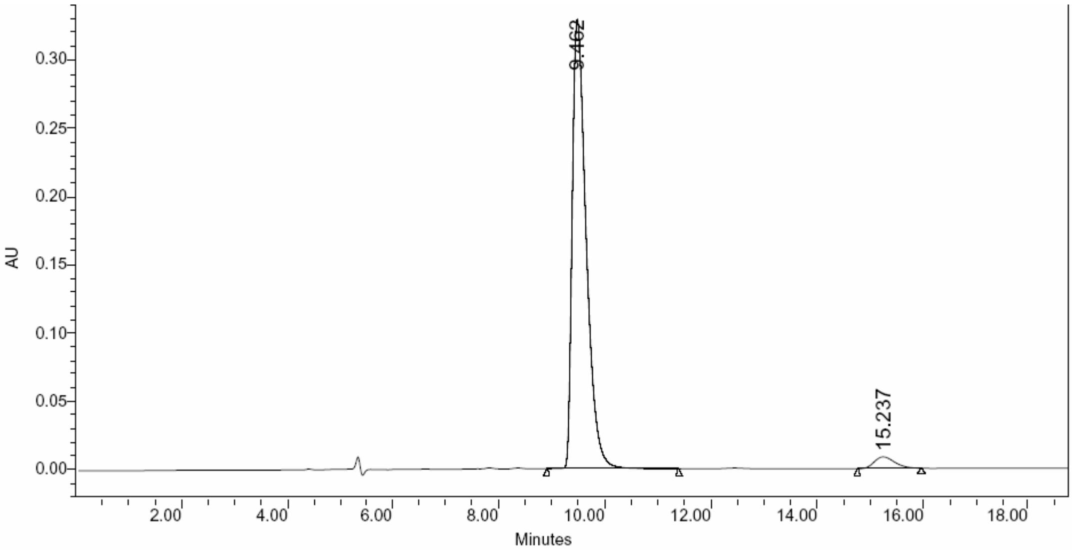
	RT (min)	Area (V*sec)	% Area	Height (V)	% Height
1	9.390	4163648	92.66	252439	95.11
2	14.669	329630	7.34	12987	4.89

Table 1 entry 10



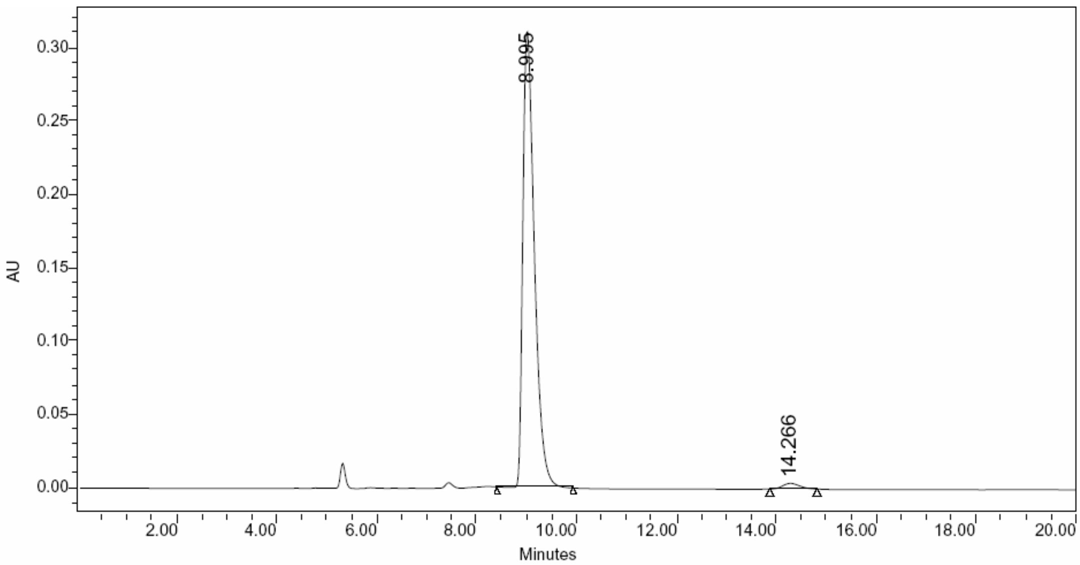
	RT (min)	Area (V*sec)	% Area	Height (V)	% Height
1	9.405	3611984	93.39	215496	95.51
2	14.882	255799	6.61	10122	4.49

Table 1 entry 11



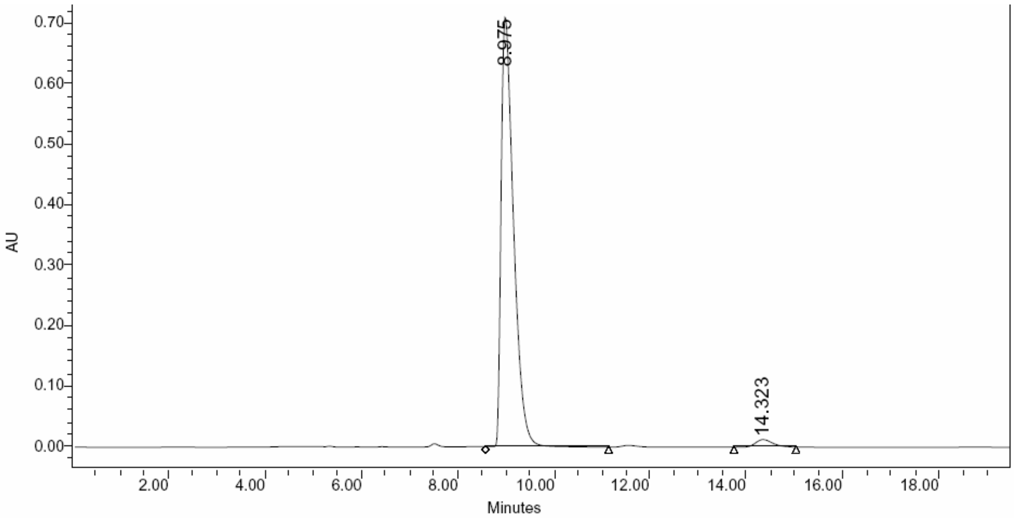
	RT (min)	Area (V*sec)	% Area	Height (V)	% Height
1	9.462	6017788	96.28	329006	97.46
2	15.237	232659	3.72	8584	2.54

Table 1 entry 12



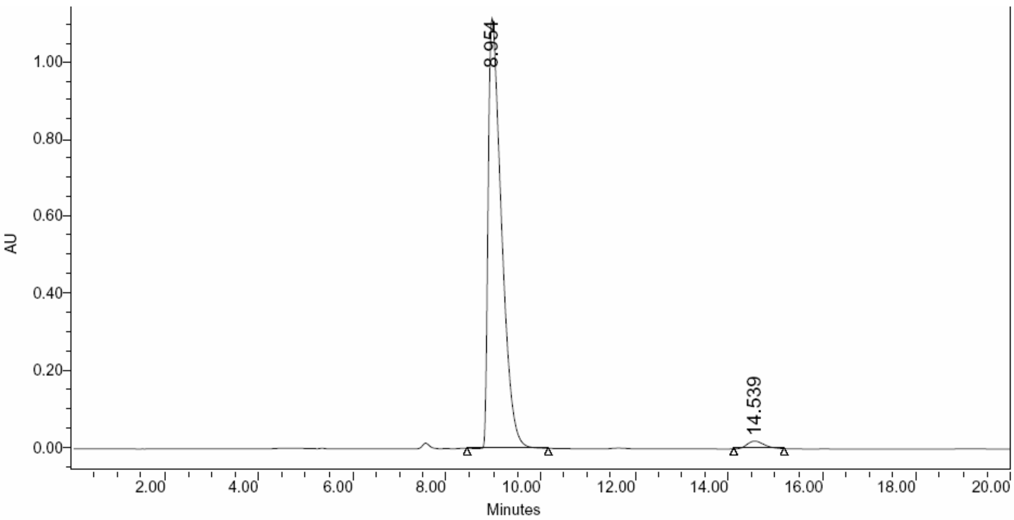
	RT (min)	Area (V*sec)	% Area	Height (V)	% Height
1	8.995	5004223	98.16	310965	98.76
2	14.266	93700	1.84	3893	1.24

Table 1 entry 13



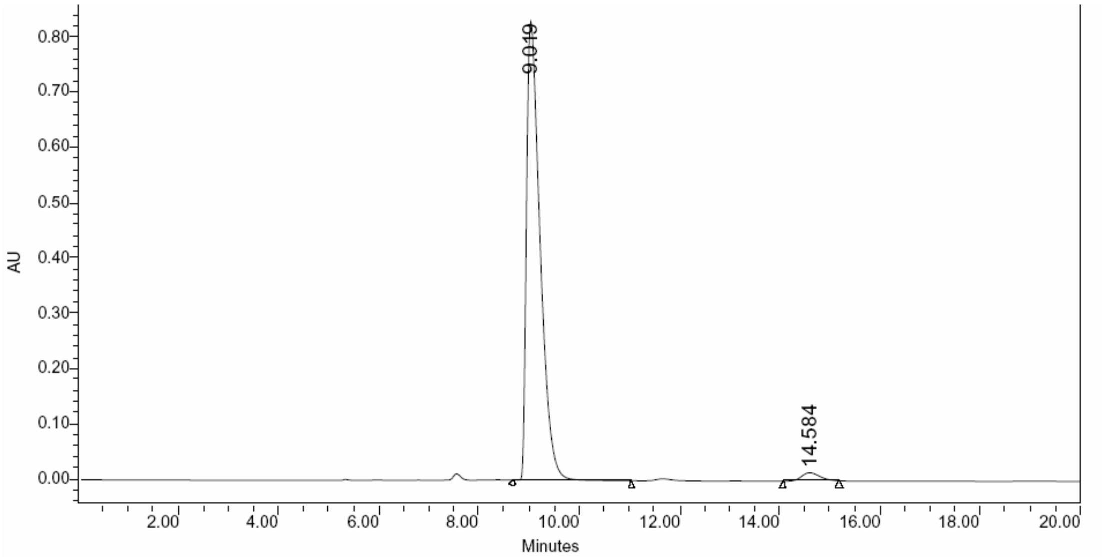
	RT (min)	Area (V*sec)	% Area	Height (V)	% Height
1	8.975	12745283	97.65	712351	98.28
2	14.323	306233	2.35	12438	1.72

Table 1 entry 14



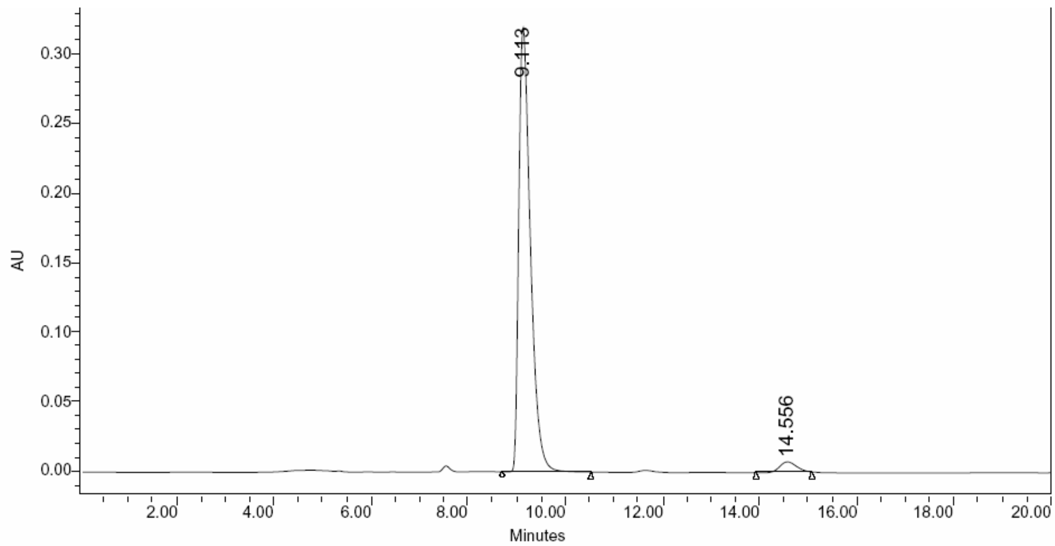
	RT (min)	Area (V*sec)	% Area	Height (V)	% Height
1	8.954	21910690	97.77	1114474	98.25
2	14.539	499547	2.23	19832	1.75

Table 1 entry 15

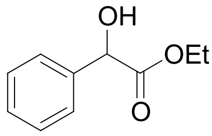


	RT (min)	Area (V*sec)	% Area	Height (V)	% Height
1	9.019	15655044	97.64	830213	98.22
2	14.584	378585	2.36	15011	1.78

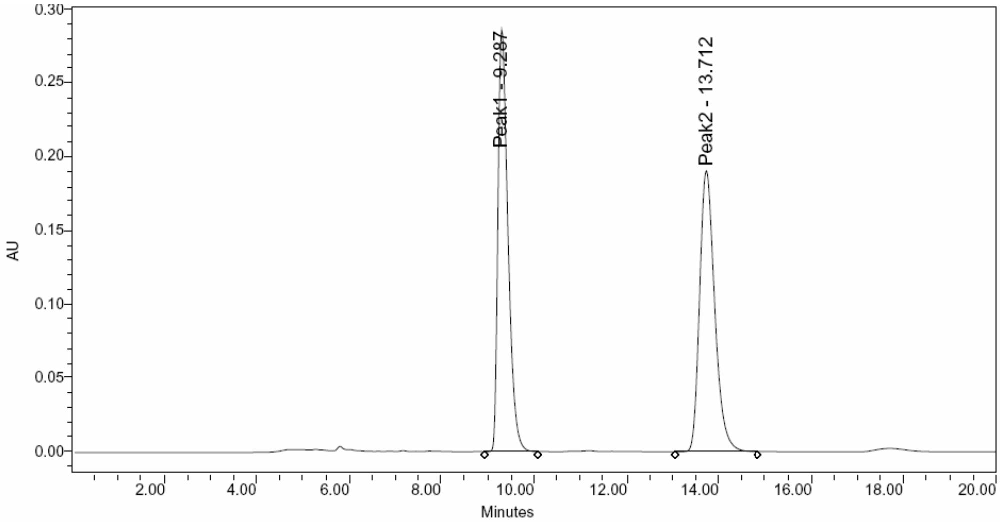
Table 1 entry 16



	RT (min)	Area (V*sec)	% Area	Height (V)	% Height
1	9.113	5345784	96.69	319803	97.70
2	14.556	182734	3.31	7541	2.30

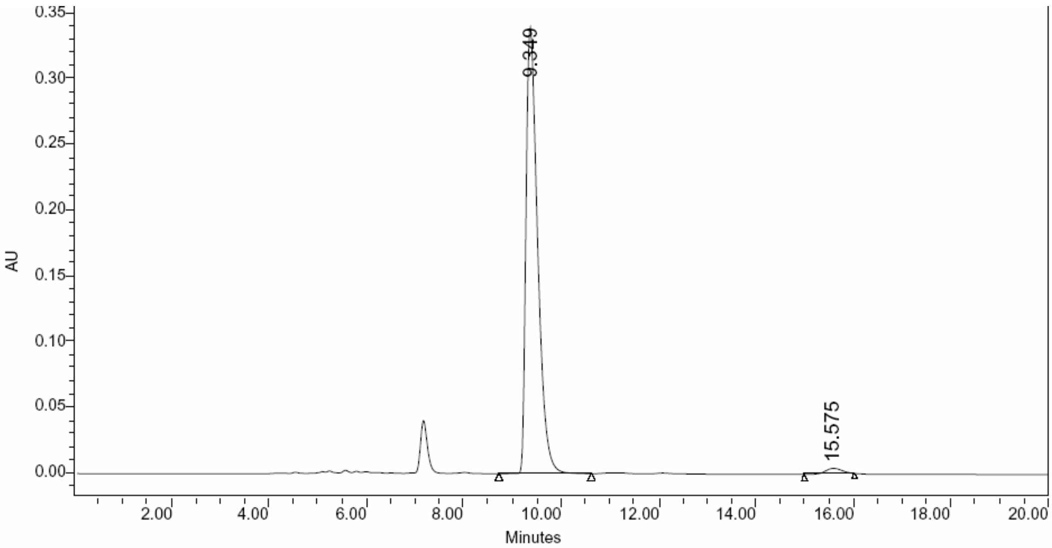


2b racemate



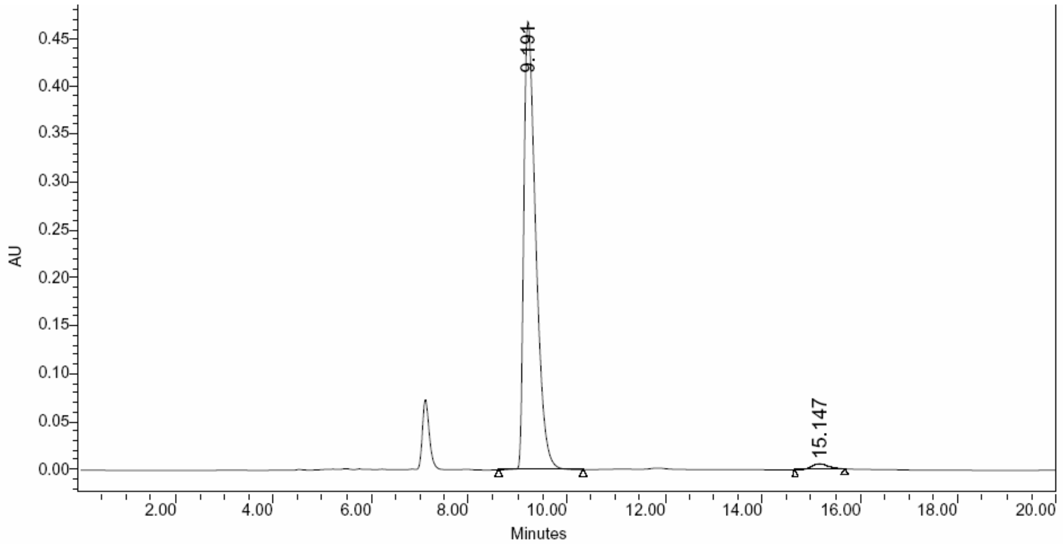
	Peak Name	RT (min)	Area (V*sec)	% Area	Height (V)	% Height
1	Peak1	9.287	4329437	49.93	286644	60.04
2	Peak2	13.712	4341260	50.07	190817	39.96

Table 1 entry 17



	RT (min)	Area (V*sec)	% Area	Height (V)	% Height
1	9.349	5626248	98.28	339385	98.78
2	15.575	98345	1.72	4197	1.22

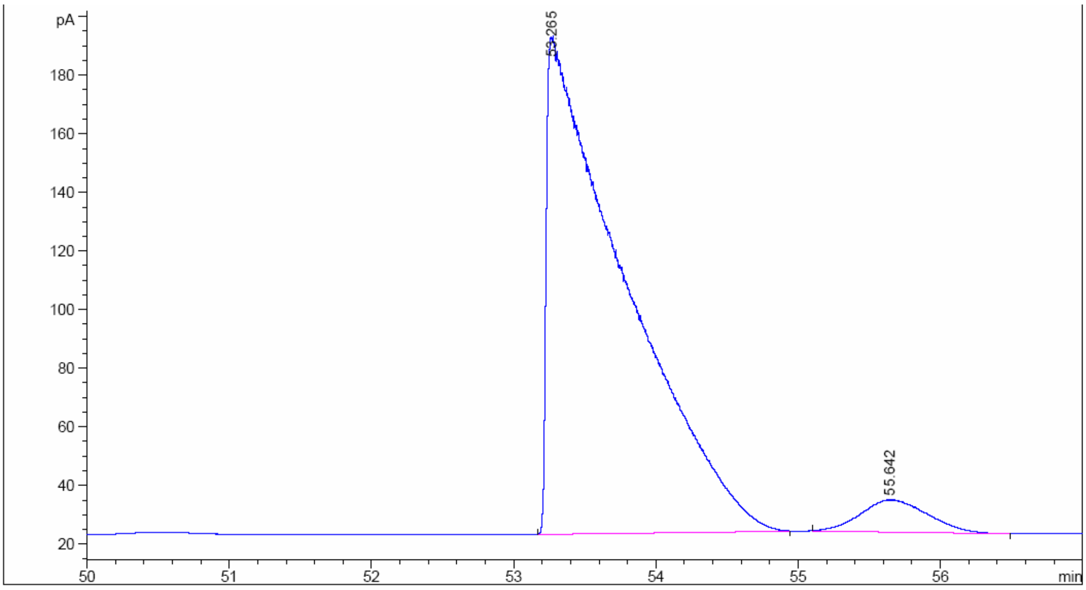
Table 1 entry 18



	RT (min)	Area (V*sec)	% Area	Height (V)	% Height
1	9.191	7962527	98.28	470324	98.77
2	15.147	139104	1.72	5835	1.23

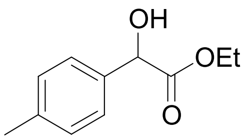
Table 2 entry 1 A
same to **Table 1** entry 2

Table 2 entry 1 B

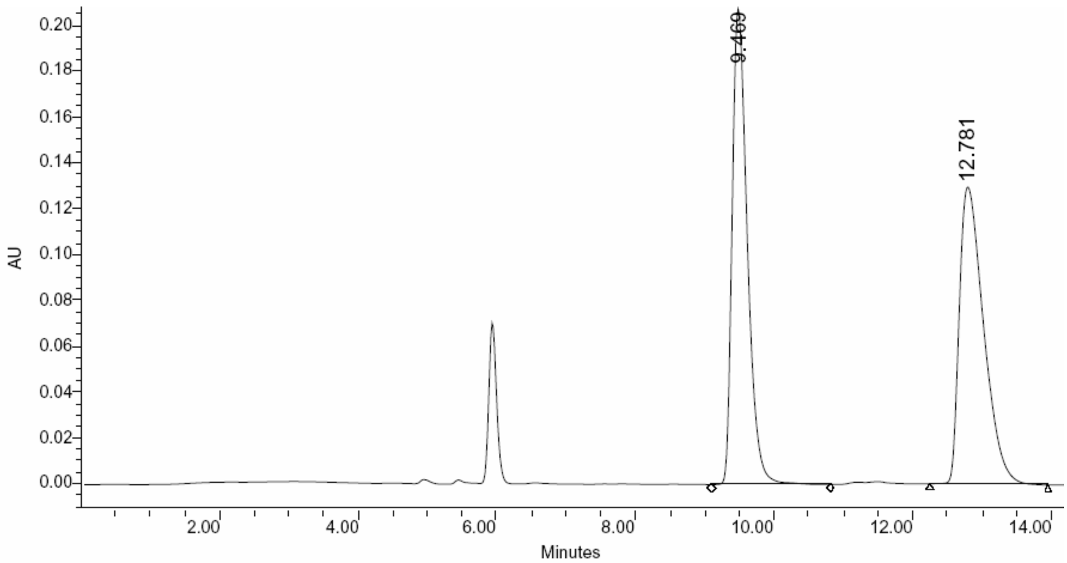



```
=====================================================================
                         Area Percent Report
=====================================================================

Sorted By             :      Signal
Multiplier            :      1.0000
Dilution              :      1.0000
Sample Amount         :      1.00000  [ng/ul]   (not used in calc.)


Signal 1: FID1 A,

Peak RetTime Type  Width      Area       Height      Area
  #   [min]        [min]    [pA*s]       [pA]         %
----|-------|----|-------|----------|----------|--------|
   1  53.265 BB    0.4551 6447.95752  169.78192 94.68195
   2  55.642 BP    0.3856  362.16608   11.04379  5.31805

Totals :                  6810.12360  180.82572

 Results obtained with enhanced integrator!
=====================================================================
                          *** End of Report ***
```

Table 2 entry 1 C
same to **Table 1** entry 17

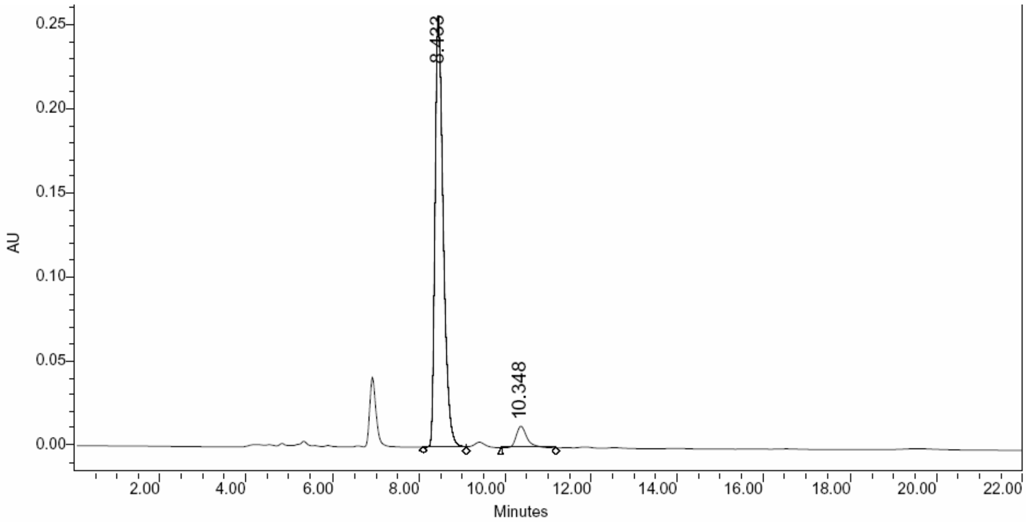


2c racemate



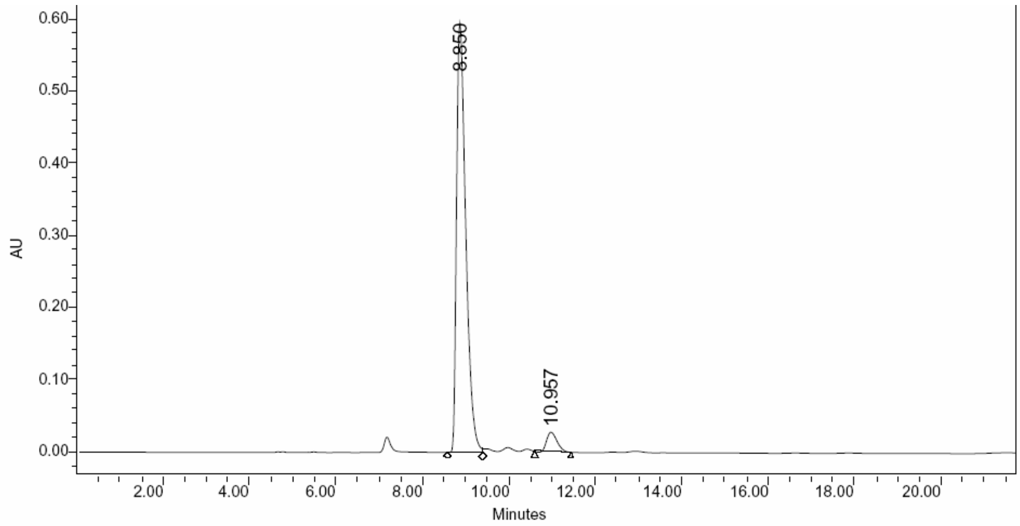
	RT (min)	Area (V*sec)	% Area	Height (V)	% Height
1	9.469	3161370	50.03	207658	61.56
2	12.781	3157190	49.97	129680	38.44

Table 2 entry 2 A



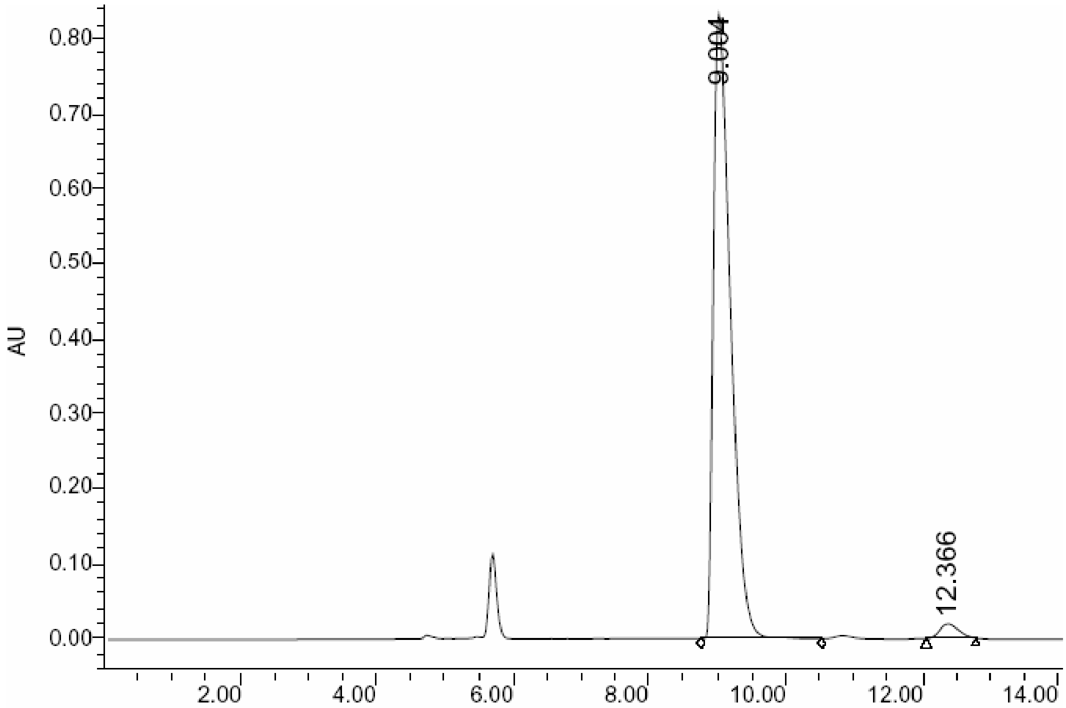
	RT (min)	Area (V*sec)	% Area	Height (V)	% Height
1	8.433	3417858	93.60	257154	95.21
2	10.348	233727	6.40	12935	4.79

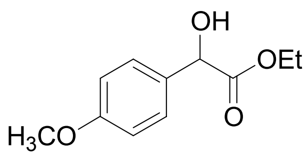
Table 2 entry 2 B



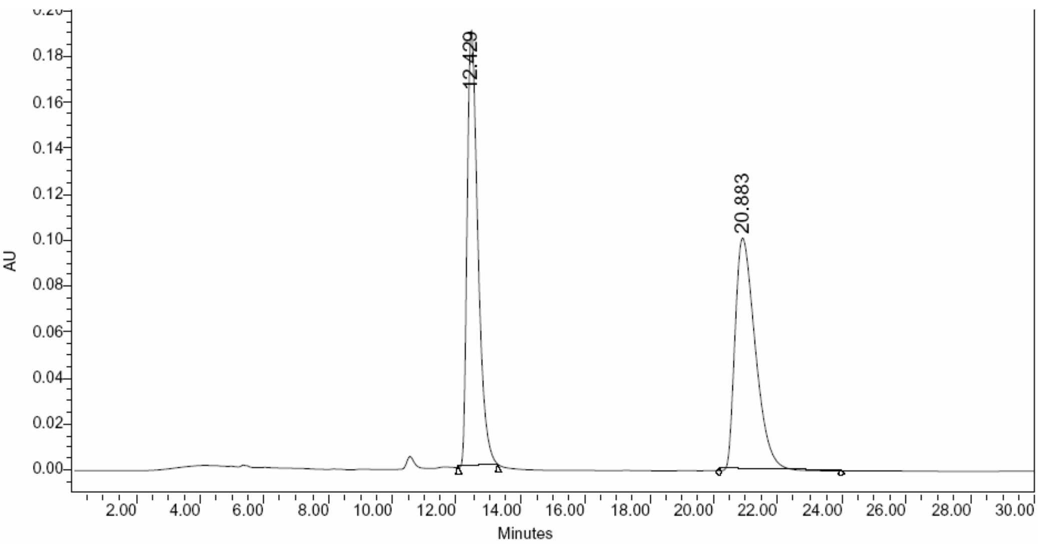
	RT (min)	Area (V*sec)	% Area	Height (V)	% Height
1	8.850	8865592	95.03	595994	95.59
2	10.957	463644	4.97	27467	4.41

Table 2 entry 2 C



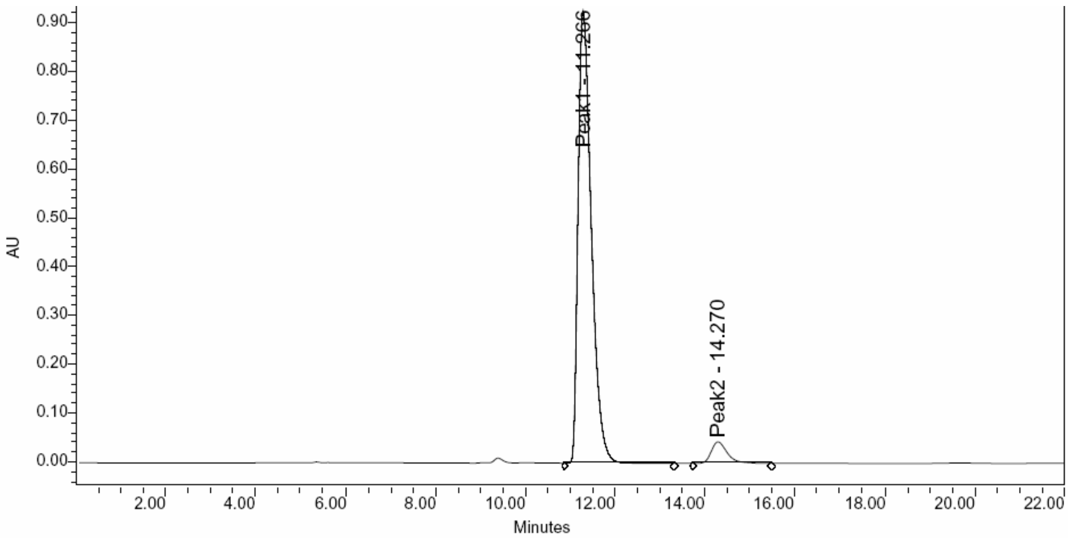


2d racemate



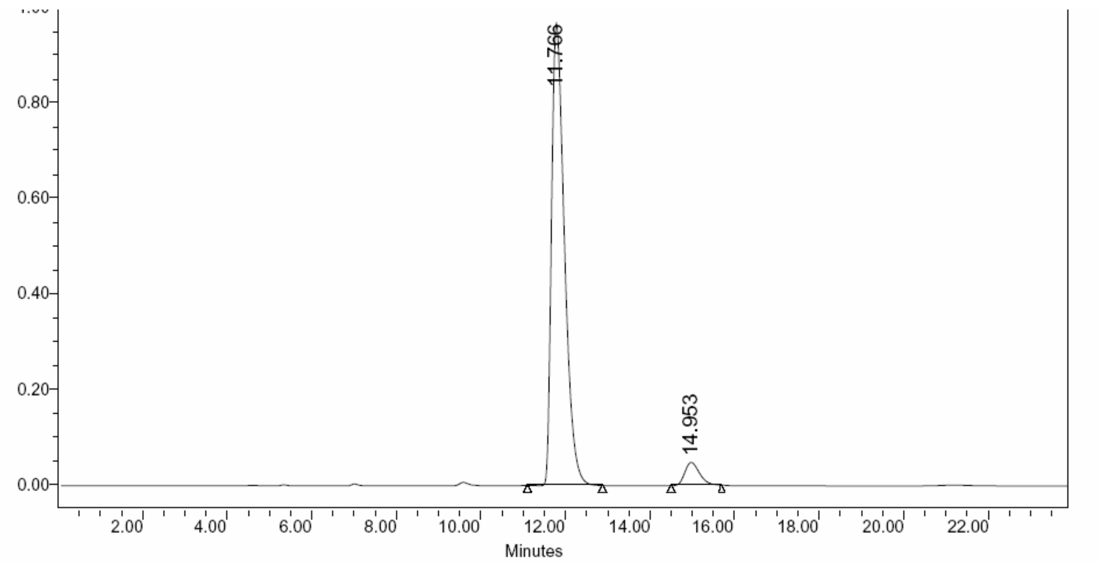
	RT (min)	Area (V*sec)	% Area	Height (V)	% Height
1	12.429	4444519	50.05	189948	65.33
2	20.883	4435081	49.95	100816	34.67

Table 2 entry 3 A



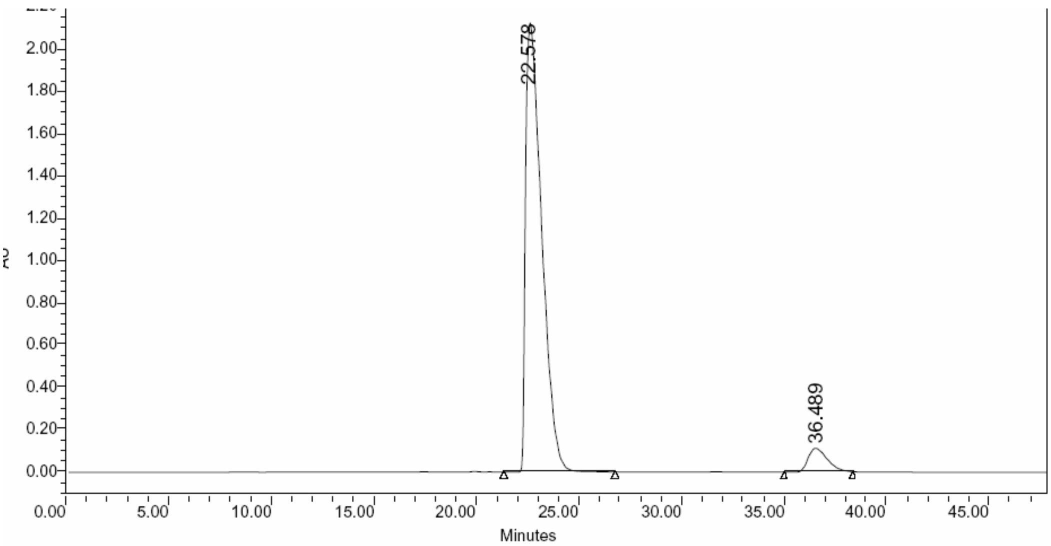
	Peak Name	RT (min)	Area (V*sec)	% Area	Height (V)	% Height
1	Peak1	11.266	18931703	94.61	927286	95.49
2	Peak2	14.270	1078313	5.39	43788	4.51

Table 2 entry 3 B

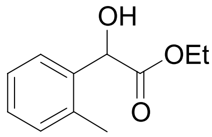


	RT (min)	Area (V*sec)	% Area	Height (V)	% Height
1	11.766	20562370	94.57	967531	95.24
2	14.953	1180574	5.43	48370	4.76

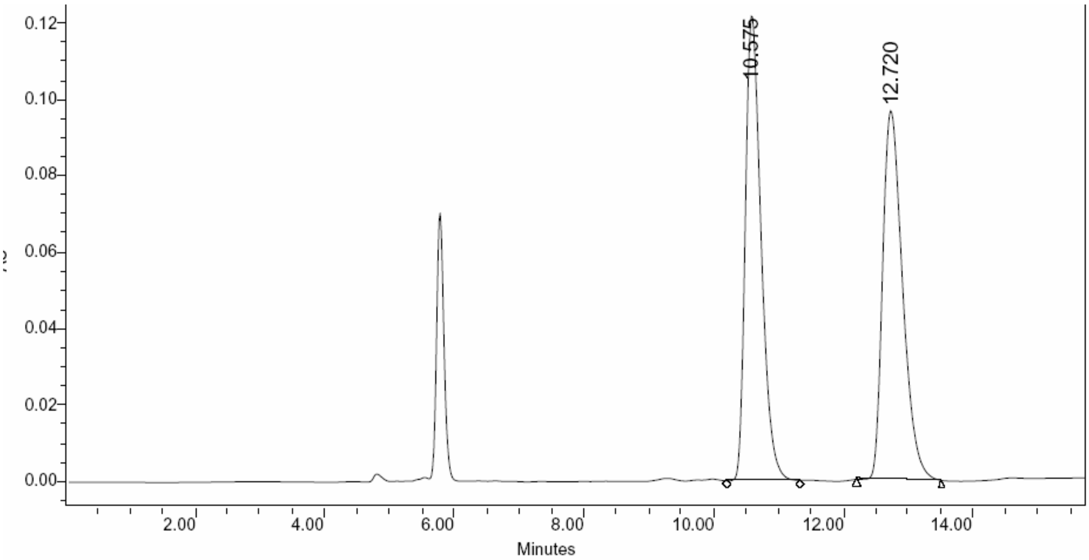
Table 2 entry 3 C



	RT (min)	Area (V*sec)	% Area	Height (V)	% Height
1	22.578	116472800	94.13	2126795	94.99
2	36.489	7264045	5.87	112115	5.01

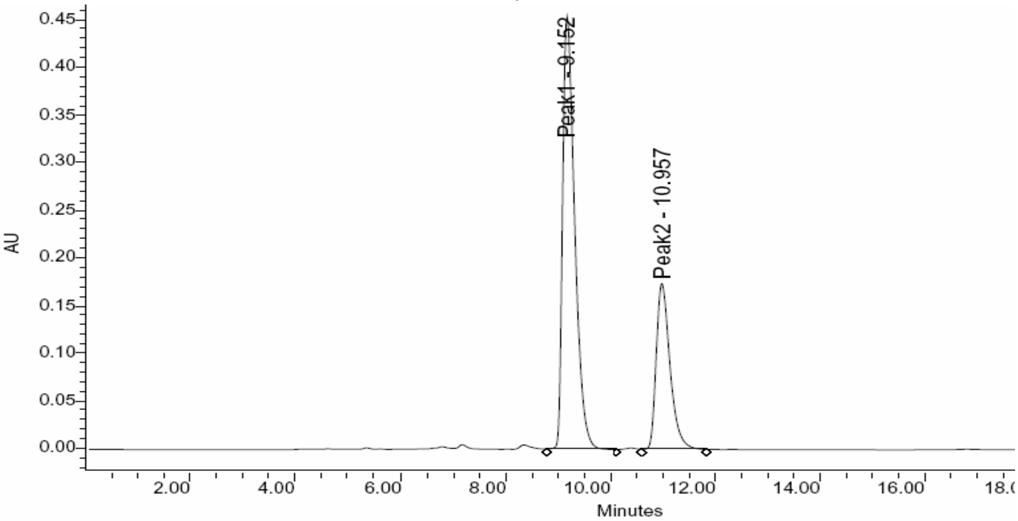


2e racemate



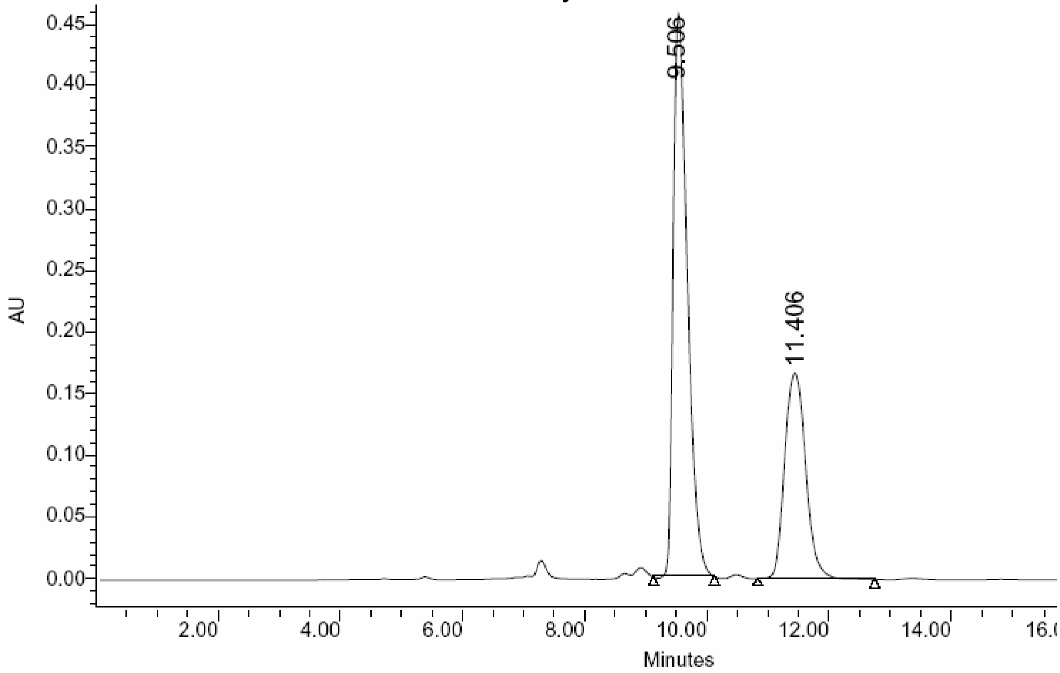
	RT (min)	Area (V*sec)	% Area	Height (V)	% Height
1	10.575	2073555	50.07	122178	55.83
2	12.720	2067581	49.93	96655	44.17

Table 2 entry 4 A



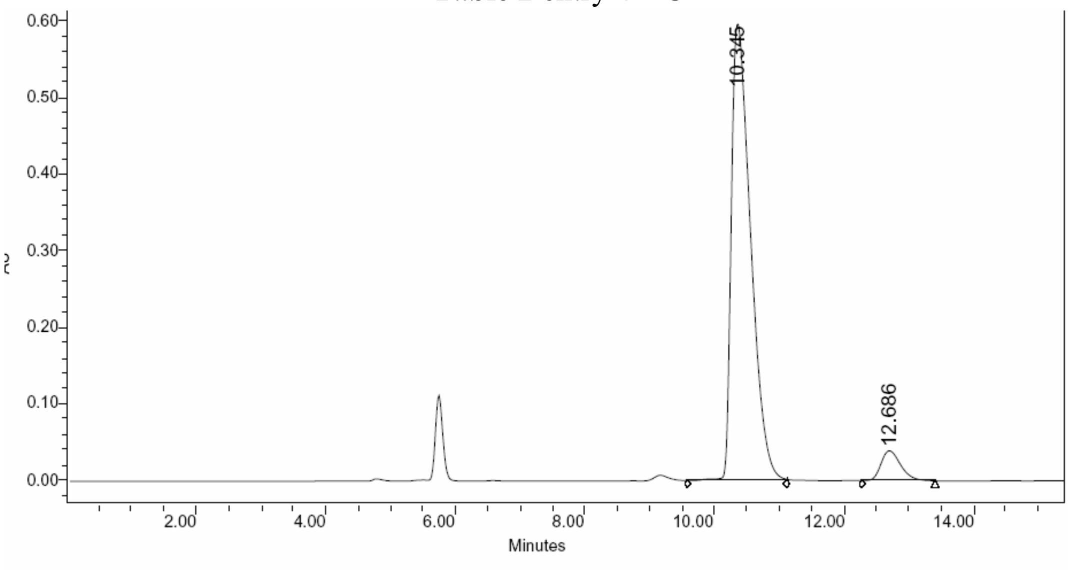
	Peak Name	RT (min)	Area (V*sec)	% Area	Height (V)	% Height
1	Peak1	9.152	7276340	69.54	454444	72.26
2	Peak2	10.957	3187270	30.46	174421	27.74

Table 2 entry 4 B

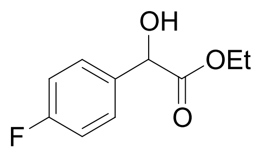


	RT (min)	Area (V*sec)	% Area	Height (V)	% Height
1	9.506	7360108	64.86	457102	73.28
2	11.406	3987812	35.14	166701	26.72

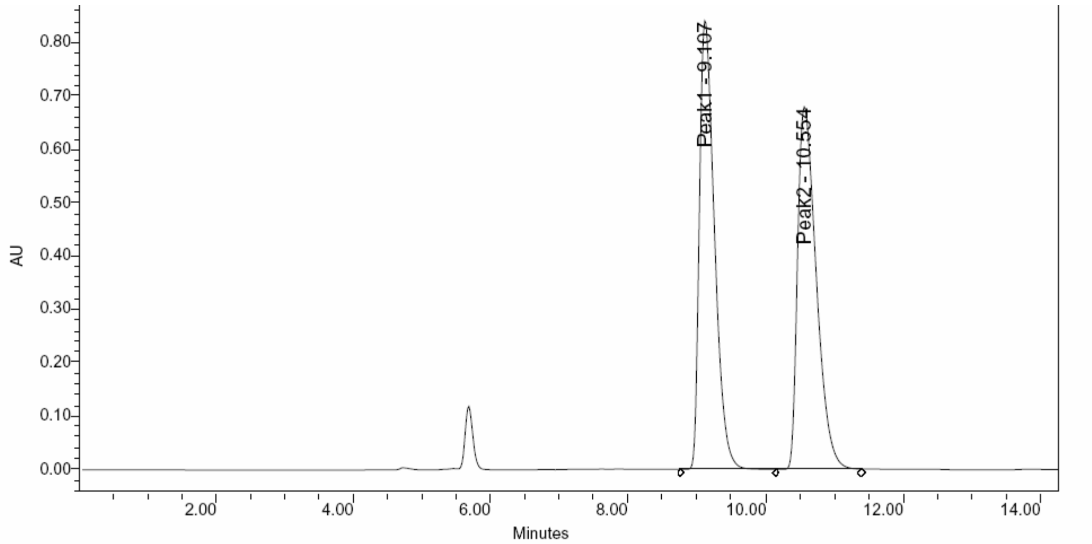
Table 2 entry 4 C



	RT (min)	Area (V*sec)	% Area	Height (V)	% Height
1	10.345	12391456	93.66	597278	93.82
2	12.686	838654	6.34	39353	6.18

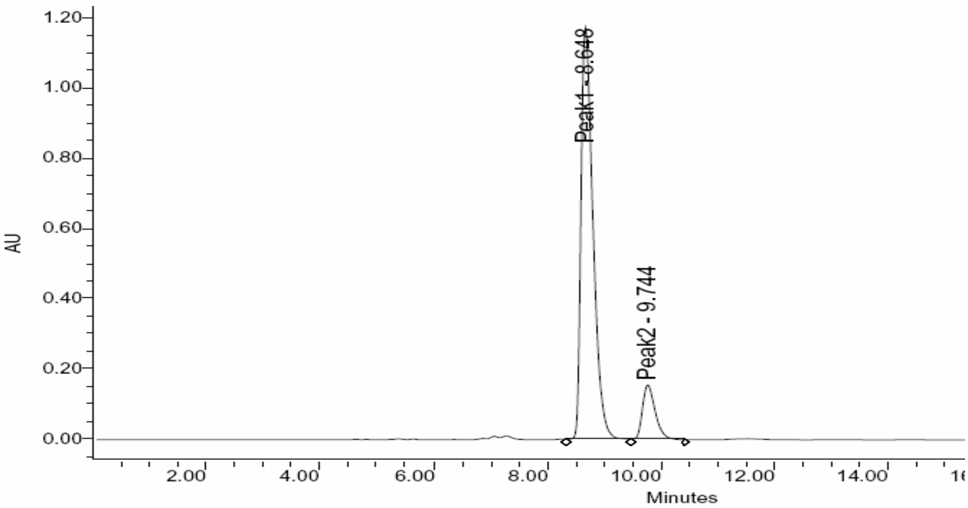


2f racemate



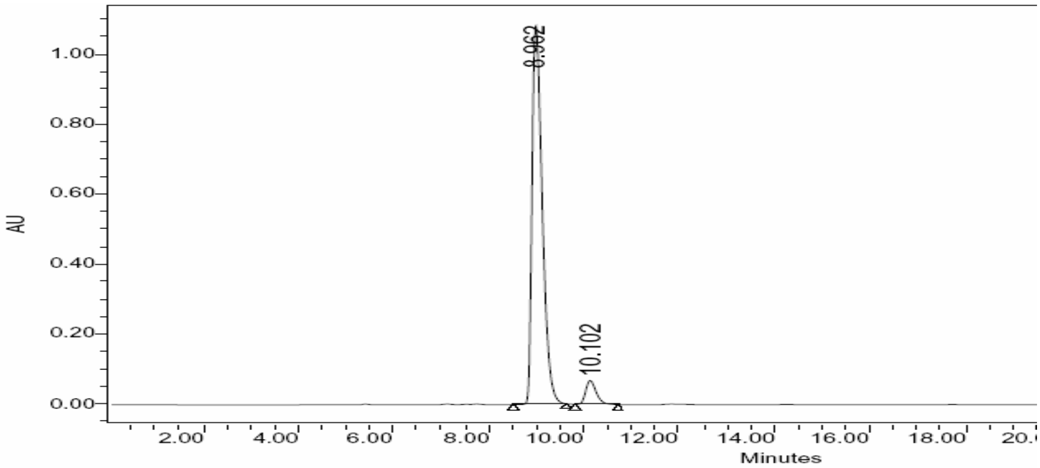
	Peak Name	RT (min)	Area (V*sec)	% Area	Height (V)	% Height
1	Peak1	9.107	12888183	49.96	845822	55.35
2	Peak2	10.554	12908873	50.04	682367	44.65

Table 2 entry 5 A



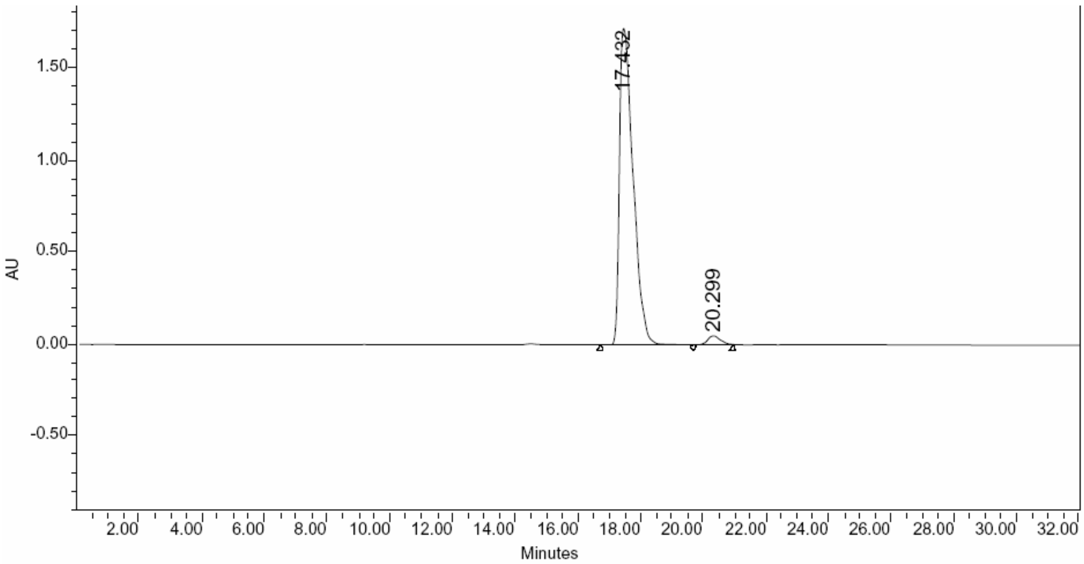
	Peak Name	RT (min)	Area (V*sec)	% Area	Height (V)	% Height
1	Peak1	8.648	17275823	87.56	1175638	88.27
2	Peak2	9.744	2454594	12.44	156301	11.73

Table 2 entry 5   B

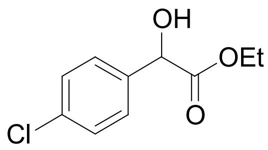


	RT (min)	Area (V*sec)	% Area	Height (V)	% Height
1	8.962	16177274	93.98	1083260	94.07
2	10.102	1036772	6.02	68278	5.93

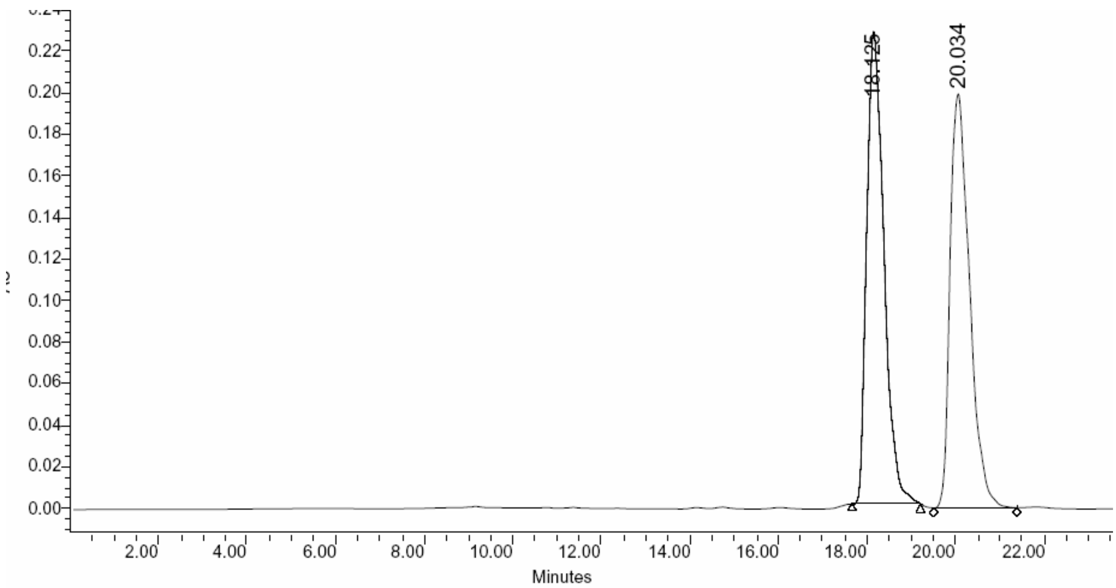
Table 2 entry 5   C



	RT (min)	Area (V*sec)	% Area	Height (V)	% Height
1	17.432	52090045	97.54	1720869	97.34
2	20.299	1311643	2.46	46938	2.66

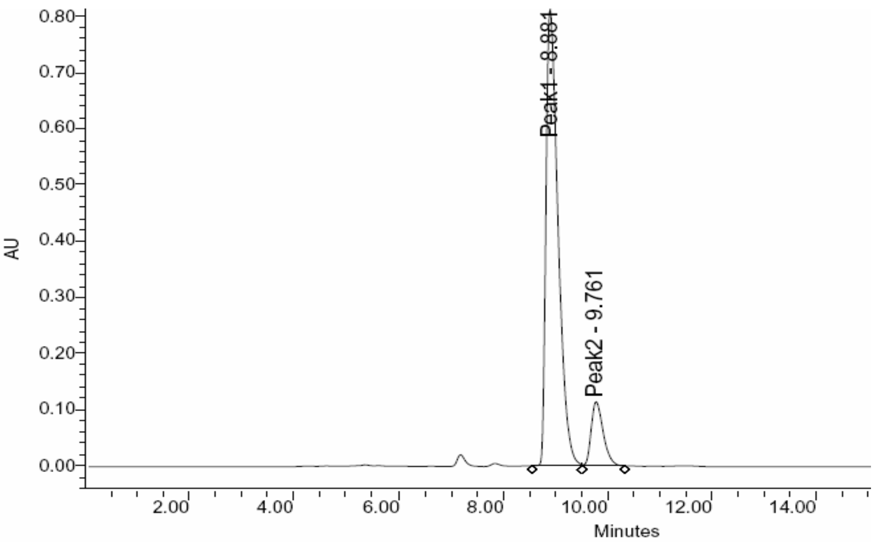


2g racemate



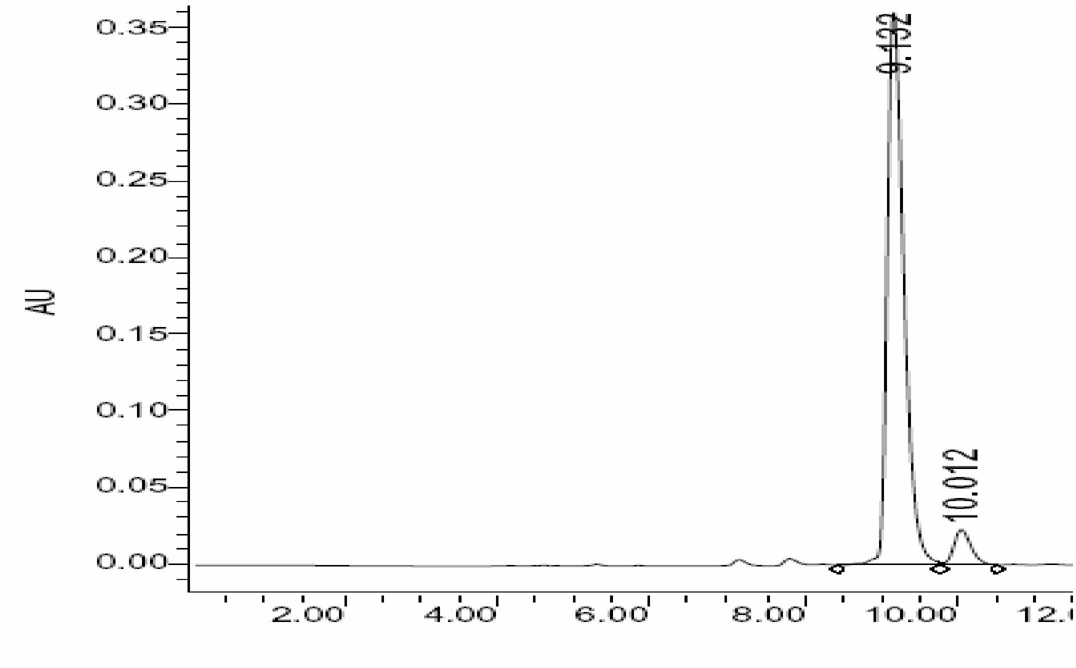
	RT (min)	Area (V*sec)	% Area	Height (V)	% Height
1	18.125	6164480	50.05	227842	53.28
2	20.034	6151184	49.95	199792	46.72

Table 2 entry 6 A



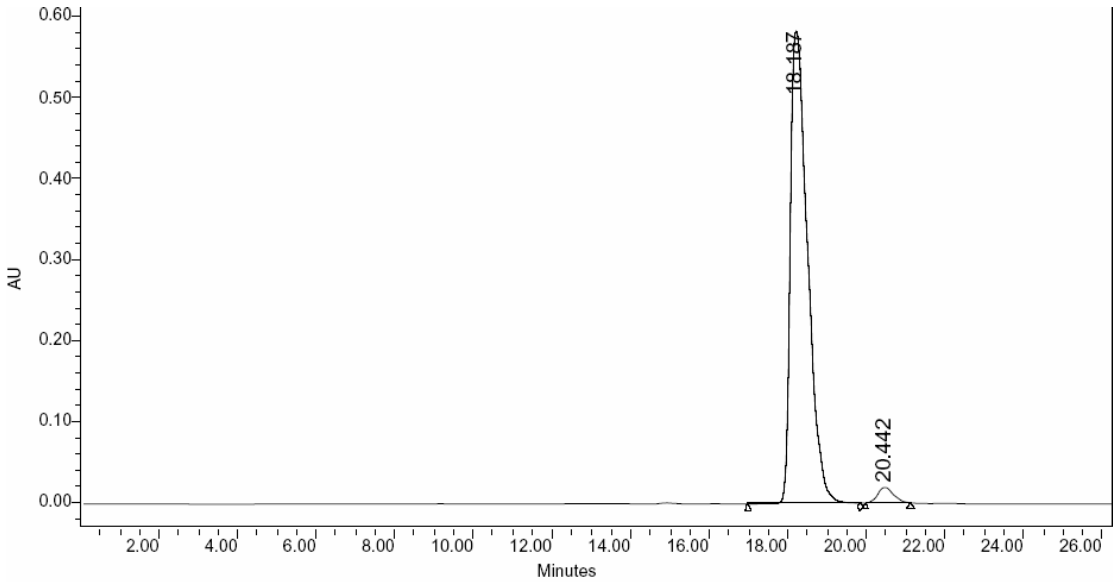
	Peak Name	RT (min)	Area (V*sec)	% Area	Height (V)	% Height
1	Peak1	8.881	13167841	87.41	813937	87.55
2	Peak2	9.761	1897327	12.59	115752	12.45

Table 2 entry 6 B

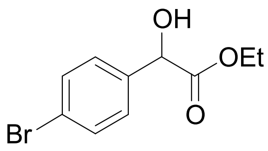


	RT (min)	Area (V*sec)	% Area	Height (V)	% Height
1	9.132	5502861	93.50	361300	93.88
2	10.012	382505	6.50	23565	6.12

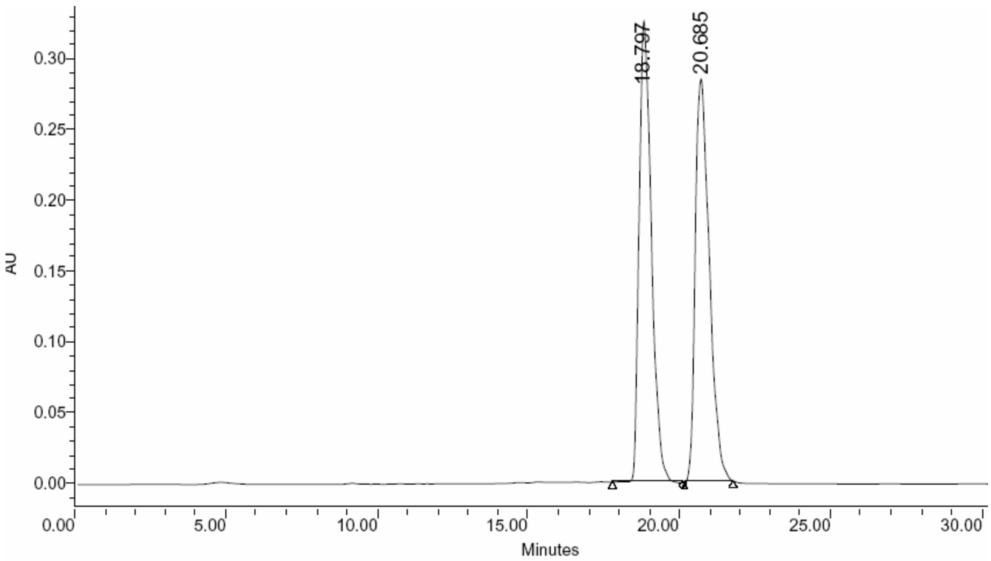
Table 2 entry 6 C



	RT (min)	Area (V*sec)	% Area	Height (V)	% Height
1	18.187	17814839	97.07	583264	96.84
2	20.442	538640	2.93	19033	3.16

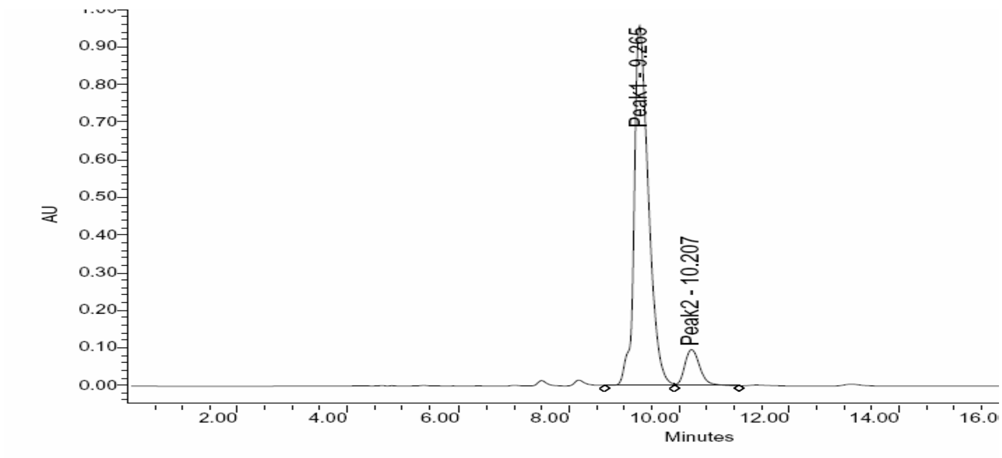


2h racemate



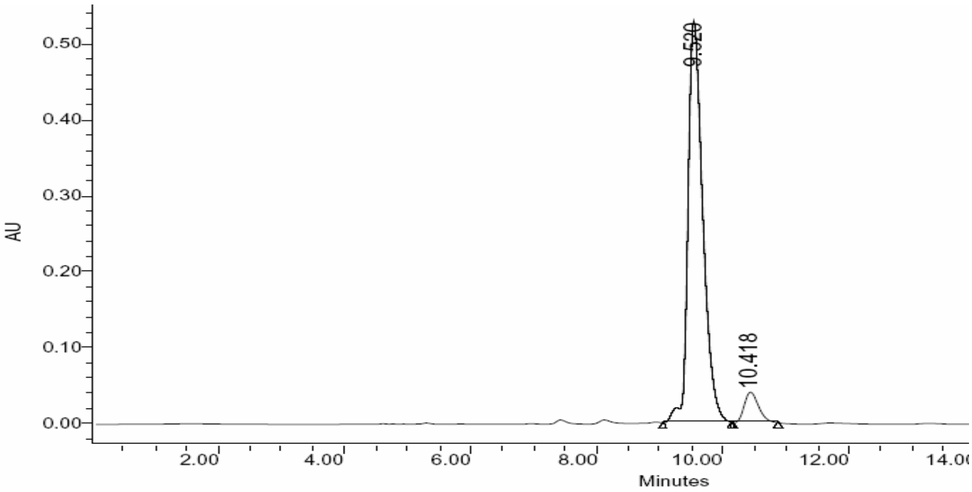
	RT (min)	Area (V*sec)	% Area	Height (V)	% Height
1	18.797	9229315	49.93	325992	53.38
2	20.685	9254949	50.07	284754	46.62

Table 2 entry 7　A



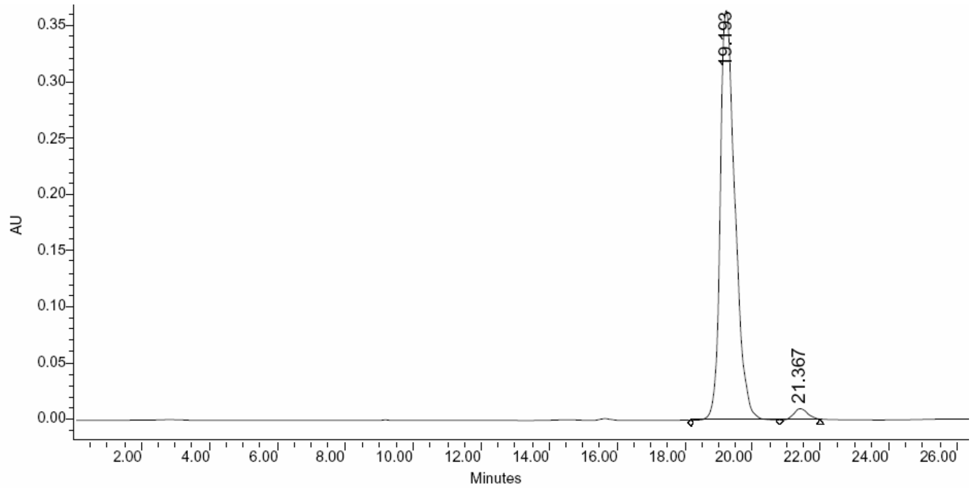
	Peak Name	RT (min)	Area (V*sec)	% Area	Height (V)	% Height
1	Peak1	9.265	17366725	90.14	957816	90.78
2	Peak2	10.207	1899808	9.86	97277	9.22

Table 2 entry 7 B

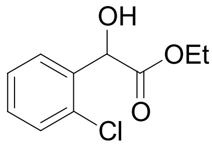


	RT (min)	Area (V*sec)	% Area	Height (V)	% Height
1	9.520	8648017	93.14	529673	92.93
2	10.418	637310	6.86	40279	7.07

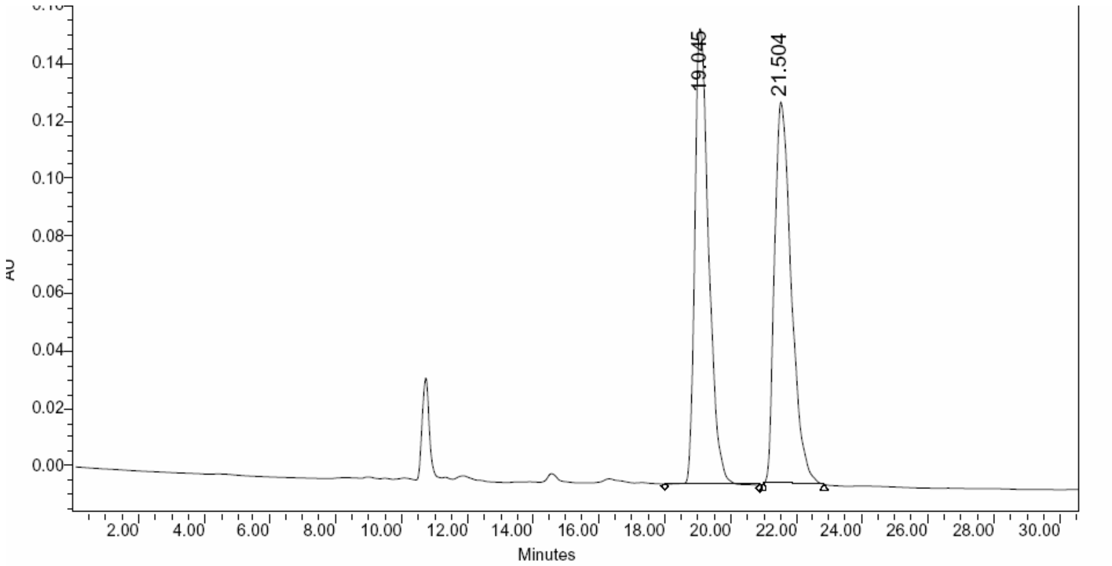
Table 2 entry 7 C



	RT (min)	Area (V*sec)	% Area	Height (V)	% Height
1	19.193	11030938	97.66	363688	97.49
2	21.367	264627	2.34	9378	2.51

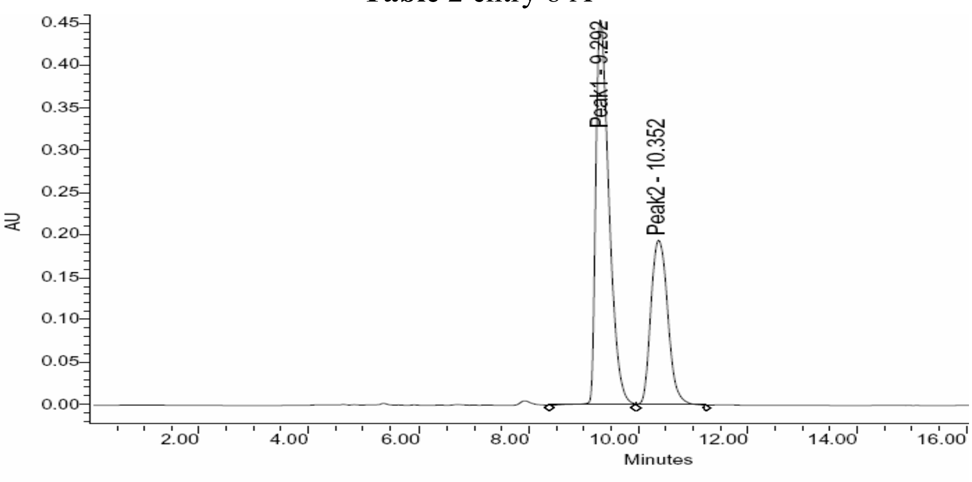


2i racemate



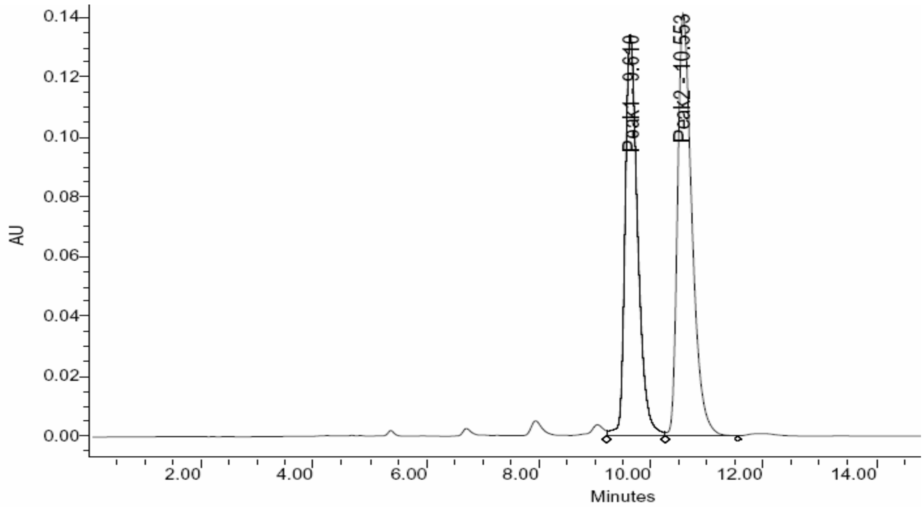
	RT (min)	Area (V*sec)	% Area	Height (V)	% Height
1	19.045	4678298	49.77	158615	54.45
2	21.504	4720705	50.23	132687	45.55

Table 2 entry 8 A



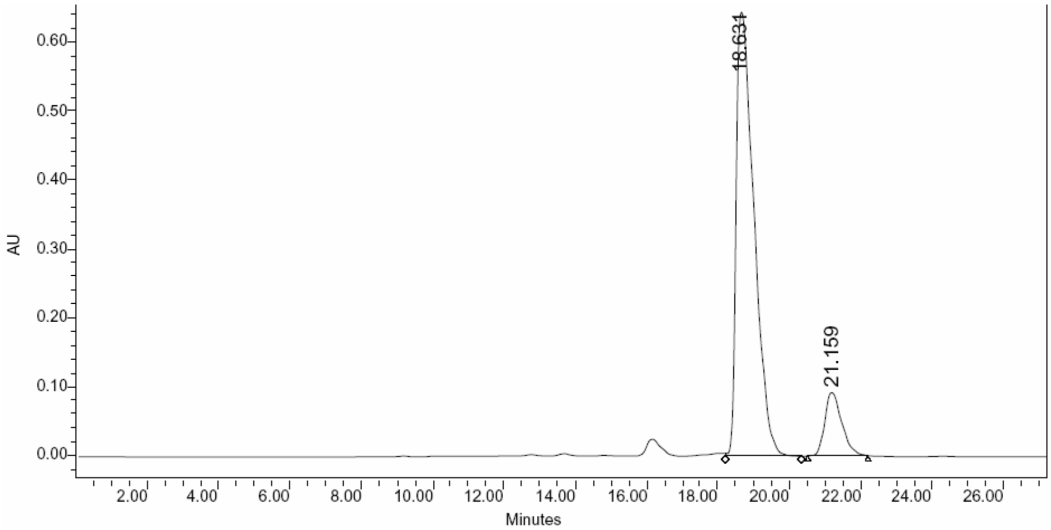
	Peak Name	RT (min)	Area (V*sec)	% Area	Height (V)	% Height
1	Peak1	9.292	7678215	64.56	455955	70.07
2	Peak2	10.352	4215429	35.44	194787	29.93

Table 2 entry 8 B

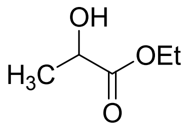


	Peak Name	RT (min)	Area (V*sec)	% Area	Height (V)	% Height
1	Peak1	9.610	2098508	45.45	134619	48.80
2	Peak2	10.553	2518374	54.55	141247	51.20

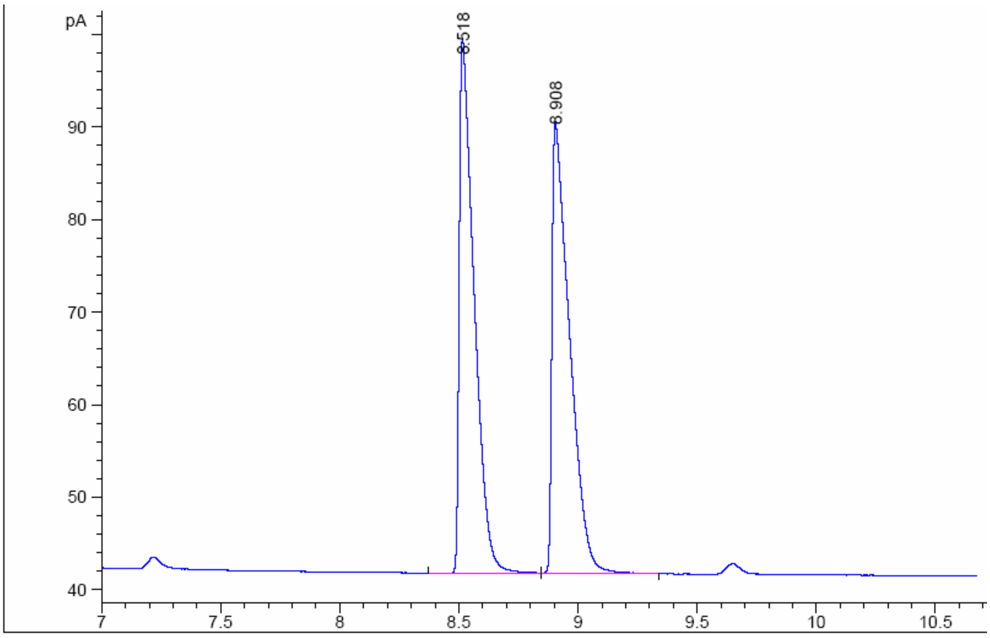
Table 2 entry 8 C



	RT (min)	Area (V*sec)	% Area	Height (V)	% Height
1	18.631	22405259	88.03	644867	87.55
2	21.159	3047734	11.97	91669	12.45

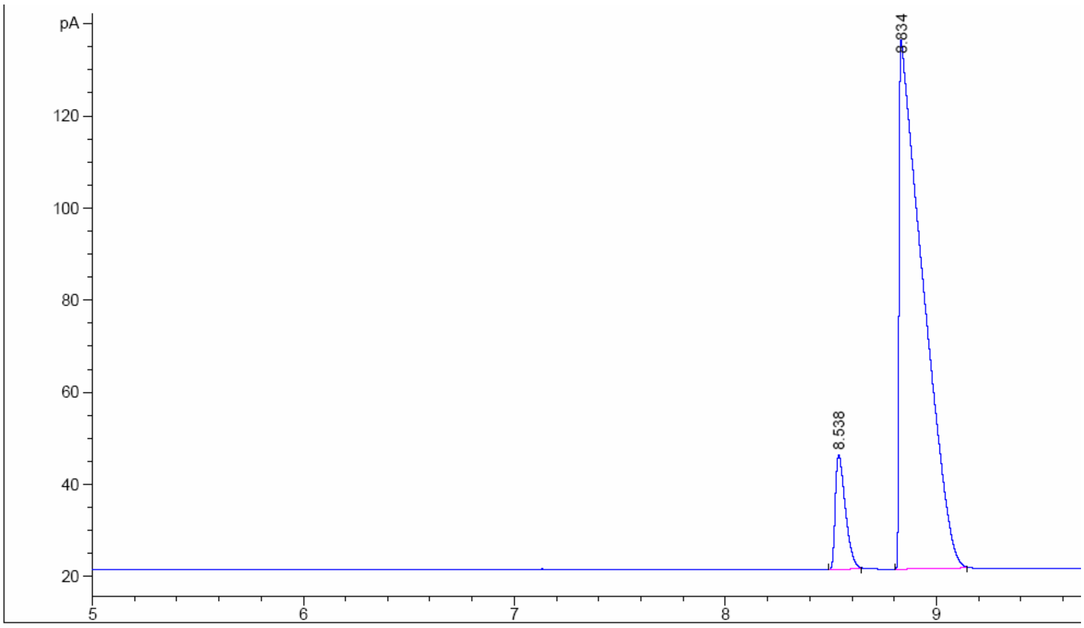


2j racemate



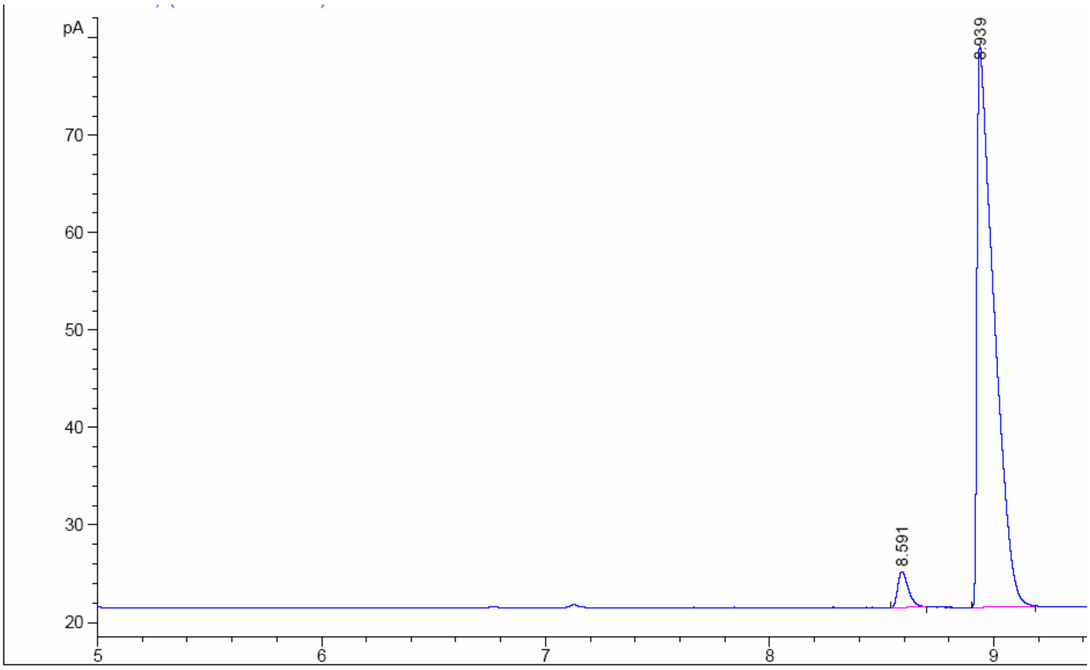

```
=====================================================================
                        Area Percent Report
=====================================================================

Sorted By             :      Signal
Multiplier            :      1.0000
Dilution              :      1.0000


Signal 1: FID1 A,

Peak RetTime Type  Width     Area      Height     Area
  #   [min]        [min]   [pA*s]      [pA]         %
----|-------|----|-------|----------|----------|--------|
   1   8.518 PV     0.0645  249.63239   57.62408 49.91093
   2   8.908 VB     0.0750  250.52341   47.92484 50.08907

Totals :                    500.15579  105.54891

 Results obtained with enhanced integrator!
=====================================================================
                          *** End of Report ***
```

Table 2 entry 9   A



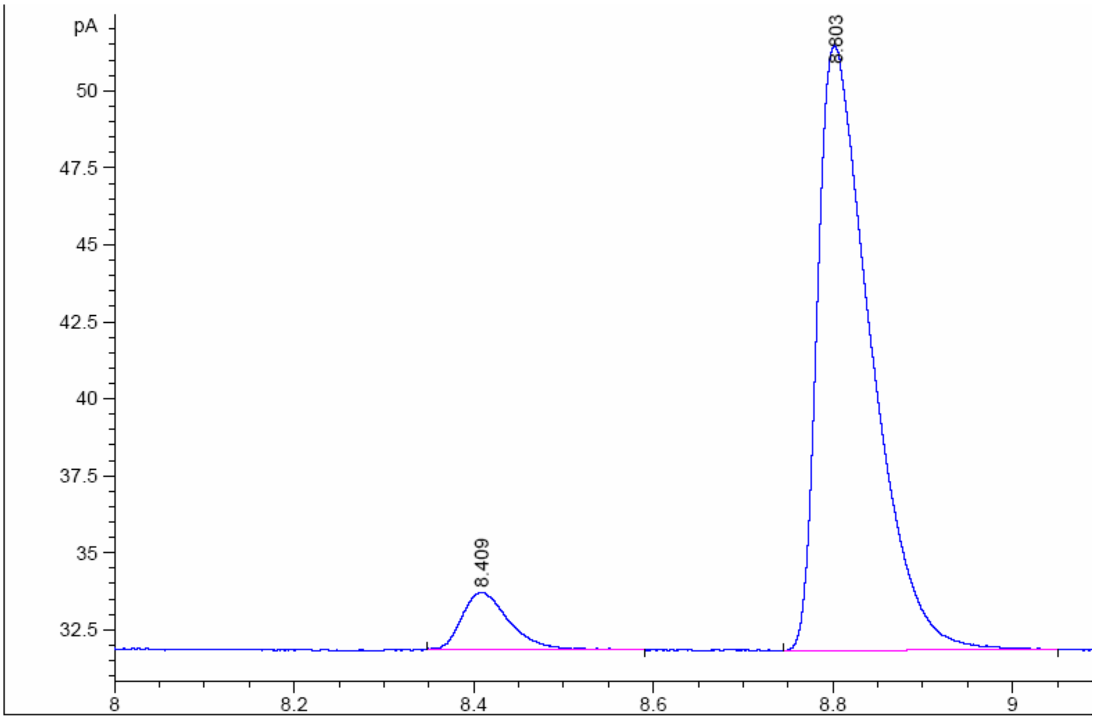

```
=====================================================================
                         Area Percent Report
=====================================================================

Sorted By             :      Signal
Multiplier            :      1.0000
Dilution              :      1.0000
Sample Amount         :      1.00000  [ng/ul]    (not used in calc.)


Signal 1: FID1 A,

Peak RetTime Type  Width     Area      Height     Area
  #   [min]        [min]   [pA*s]       [pA]        %
----|-------|----|-------|----------|----------|--------|
   1   8.538 PB    0.0508   82.58672   24.83826  8.44882
   2   8.834 PB    0.0971  894.90698  114.55589 91.55118

Totals :                   977.49371  139.39414

 Results obtained with enhanced integrator!
=====================================================================
                          *** End of Report ***
```

Table 2 entry 9 B



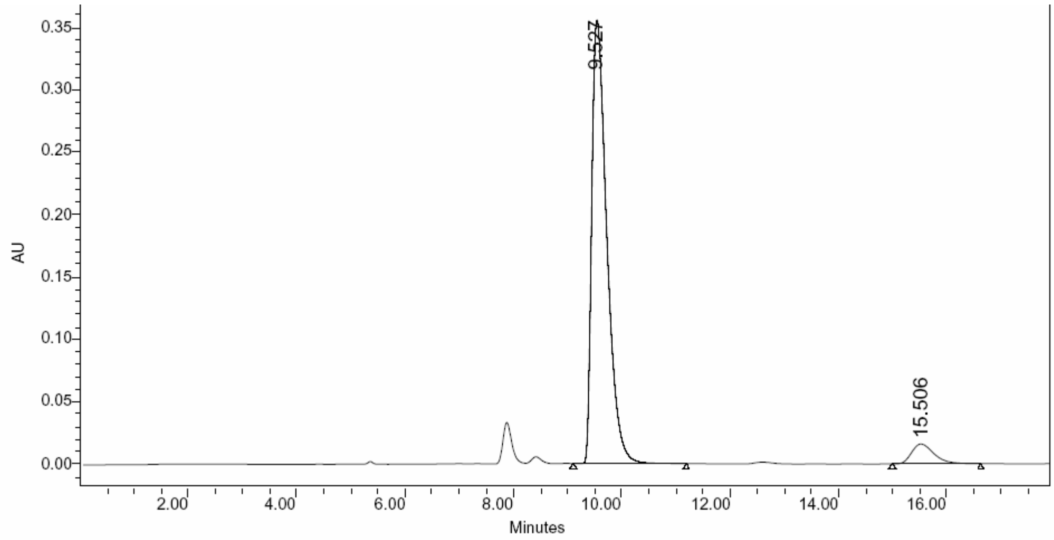

```
=====================================================================
                       Area Percent Report
=====================================================================

Sorted By             :      Signal
Multiplier            :      1.0000
Dilution              :      1.0000
Sample Amount         :      1.00000  [ng/ul]   (not used in calc.)


Signal 1: FID1 A,

Peak RetTime Type  Width     Area      Height     Area
  #   [min]        [min]   [pA*s]      [pA]        %
----|-------|----|-------|----------|----------|--------|
   1   8.591 PB    0.0516   12.05946    3.64666  3.85637
   2   8.939 PB    0.0678  300.65540   57.68548 96.14363

Totals :                   312.71485   61.33214

 Results obtained with enhanced integrator!
=====================================================================
                         *** End of Report ***
```

Table 2 entry 9 C



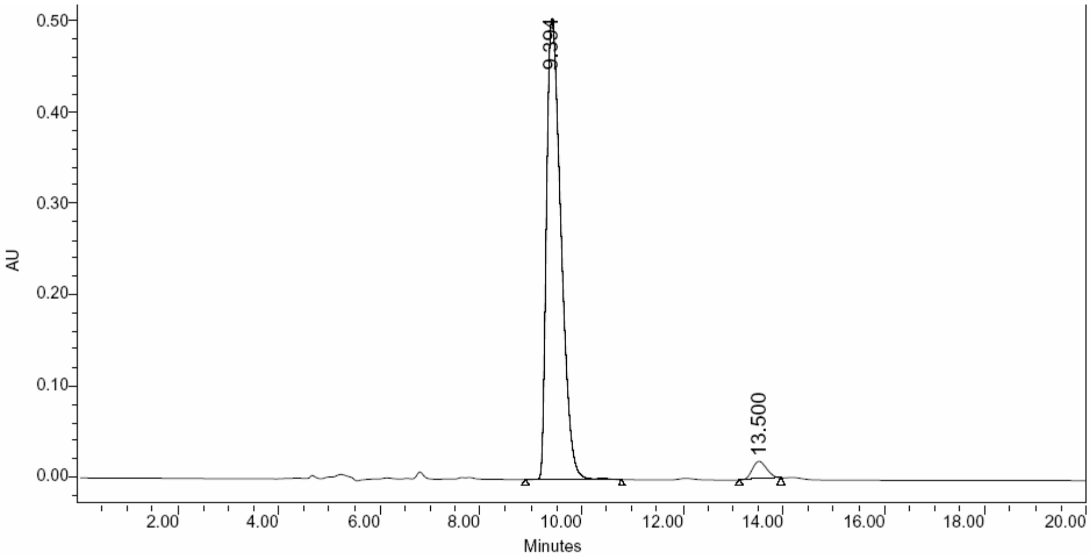

```
=====================================================================
                         Area Percent Report
=====================================================================

Sorted By             :      Signal
Multiplier            :      1.0000
Dilution              :      1.0000


Signal 1: FID1 A,

Peak RetTime Type  Width     Area      Height     Area
  #   [min]        [min]   [pA*s]      [pA]         %
----|-------|----|-------|----------|----------|--------|
   1   8.409 BB    0.0574    6.88861    1.85360  7.84896
   2   8.803 PB    0.0623   80.87600   19.54976 92.15104

Totals :                    87.76461   21.40336

 Results obtained with enhanced integrator!
=====================================================================
                         *** End of Report ***
```

After the catalyst in MeOH solution with 5eq. of catalyst $CeCl_3 \cdot 7H_2O$ was stirred in air for 10 days, and hydrogenation of **1a** with this solution under the standard condition



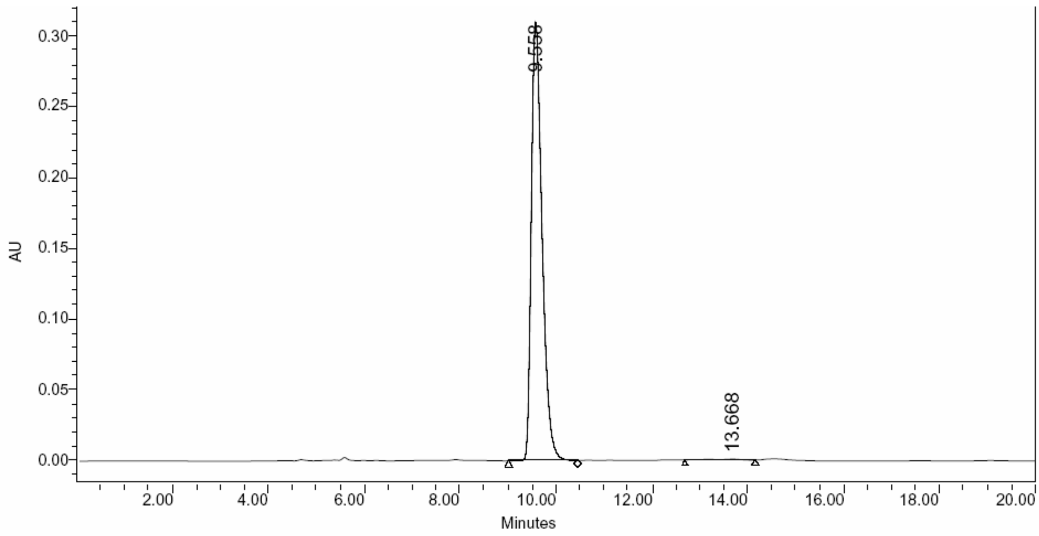
	RT (min)	Area (V*sec)	% Area	Height (V)	% Height
1	9.527	6868367	93.74	356003	95.71
2	15.506	458424	6.26	15964	4.29

(**1a**)(S/C: 1/10,000) was hydrogenated



	RT (min)	Area (V*sec)	% Area	Height (V)	% Height
1	9.394	10080834	96.29	506459	96.29
2	13.500	388101	3.71	19502	3.71

Enantiomeric purity of the product after recrystallization



	RT (min)	Area (V*sec)	% Area	Height (V)	% Height
1	9.558	4839848	99.54	311380	99.81
2	13.668	22134	0.46	582	0.19