Supplementary Material (ESI) for Organic & Biomolecular Chemistry

Chiral 1-phenylethylamine-derived phosphine-phosphoramidite ligands for highly enantioselective Rh-catalyzed hydrogenation of β-(acylamino)acrylates: significant effect of substituents on 3,3'-positions of binaphthyl moiety

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Supporting Information

General Methods.

All reactions and manipulations were performed in a nitrogen-filled glove box or under nitrogen using Schlenk techniques unless otherwise noted. All solvents were distilled under argon in the presence of the following desiccants: sodium-benzophenone for diethyl ether (Et_2O), tetrahydrofuran (THF) and toluene, CaH_2 for dichloromethane (CH_2Cl_2). (S_c)-DPPNHCH$_3$ **3**[1] and (*S*)-**4**[2] were prepared according to the literature methods. NMR spectra were obtained on Bruker DRX 400 spectrometers. ^{31}P NMR shifts were referenced to external 85% H_3PO_4, while ^{13}C and ^{1}H NMR shifts were referenced to the residual signals of deuterated solvents. Enantiomeric excesses for **6a-e** and **6i-k** were determined by GC performed with HP4890 on a chiral select 1000 capillary column. Enantiomeric excesses for **6f-h** were determined by HPLC performed with an Agilent 1100 series instrument on a chiralpak AD-H column.[3] Optical rotations were measured on a JASCO P-1020 high sensitive polarimeter.

General precodure for preparation of phosphine-phosphoramidite ligand 2.

(S_a)-4-chloro-3,5-dioxa-4-phosphacyclohepta[2,1-α';3,4-α']dinaphthalene (1.0 mmol) was dissolved in 4.0 mL of dried toluene, and cooled to 0 ^{o}C. A solution of (S_c)-DPPNHCH$_3$ **3** (319 mg, 1.0 mmol) and Et_3N (0.38 mL) in 4.0 mL of toluene was added to the above solution within 30 minutes. The resulting mixture was left stirring at room temperature overnight. After filtering off the precipitate, the filtrate was collected and concentrated under reduced pressure. The residue was purified by column chromatography (silica, hexanes/Et_3N = 10/1) to give 548 mg (82.9% yield) of (S_c,S_a)-**2a**, as a white solid. M.p.: 136-138^{o}C; $[\alpha]_D^{25}$ = +67.2 (c 0.42, $ClCH_2CH_2Cl$); ^{1}H NMR (400 MHz, $CDCl_3$): δ 1.58-1.60 (m, 3H), 2.05-2.06 (m, 3H), 2.44 (s, 1H), 2.60 (s, 3H), 5.28-5.30 (m, 1H), 7.12-7.80 (m, 24H); ^{31}P NMR (162 MHz, $CDCl_3$): δ -17.4, 144.7; ^{13}C NMR (100 MHz, $CDCl_3$): δ 17.9, 21.8, 29.4, 56.5, 124.3, 124.9, 126.9, 127.1, 127.2, 128.5, 128.6, 128.7, 128.9, 129.0, 129.6, 133.8, 134.0, 148.9, 150.1; HR-MS (EI): m/z = 661.2310, calcd. for $C_{43}H_{37}NO_2P_2$ {M^+}: 661.2300.

In a similar procedure, (S_c,S_a)-**2b** in 88.1% yield as a white solid. M.p.: 142-144^{o}C; $[\alpha]_D^{25}$ = +275 (c 0.23, $ClCH_2CH_2Cl$); ^{1}H NMR (400 MHz, $CDCl_3$): δ 1.32 (d, 3H), 1.79 (s, 3H), 4.77 (m, 1H), 6.76-7.99 (m, 34H); ^{31}P NMR ($CDCl_3$): δ -17.53, 148.20; ^{13}C NMR: δ 21.7, 30.6, 57.1, 123.5, 125.9, 127.0, 127.1, 127.3, 127.5, 128.1, 128.3, 128.4, 128.5, 128.6, 130.0, 130.1, 133.6, 133.8, 134.0, 138.5, 147.3, 148.0; HR-MS (EI): m/z = 785.2619, calcd. for $C_{53}H_{41}NO_2P_2$ {M^+}: 785.2613.

General procedure for asymmetric hydrogenation

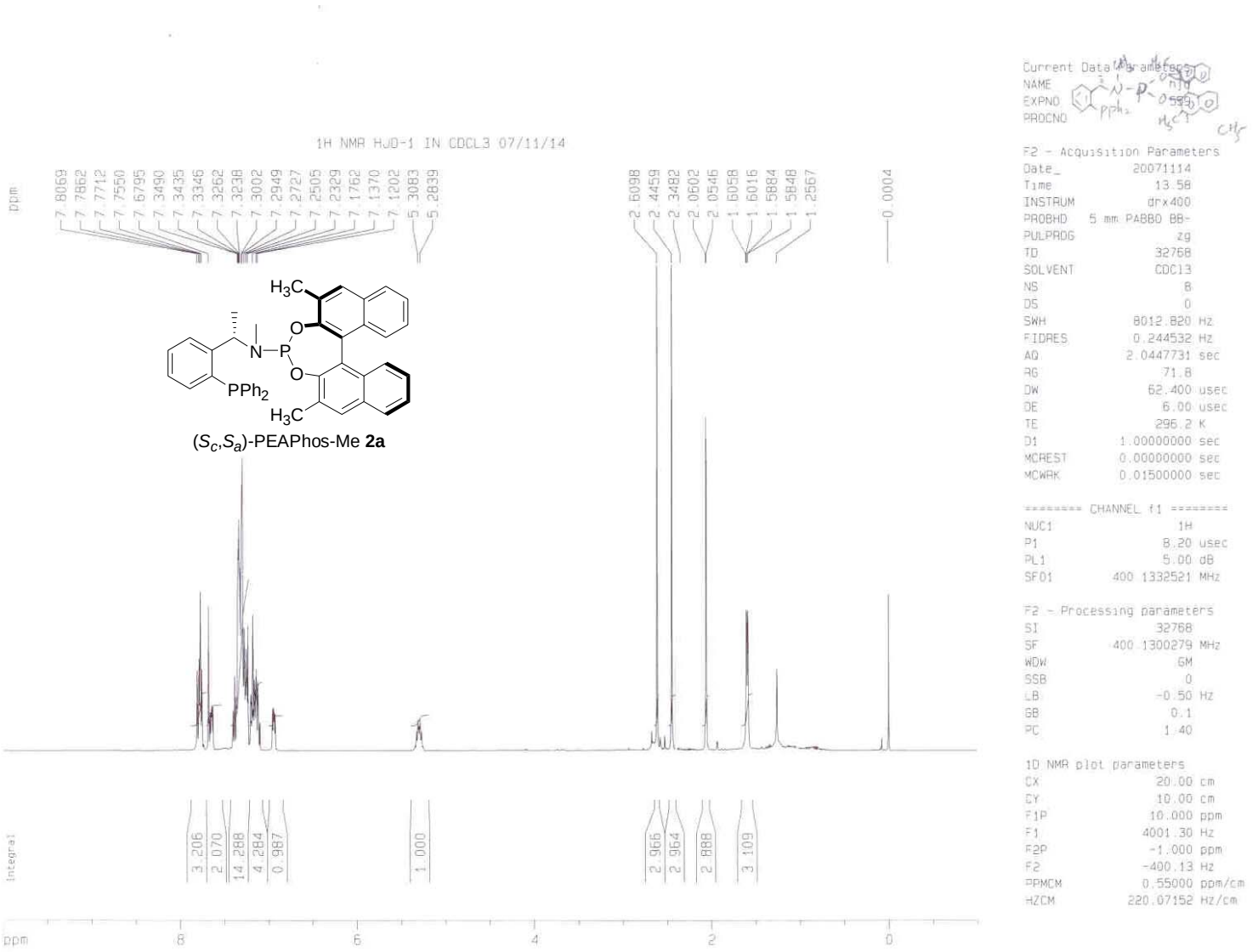
In a nitrogen-filled glovebox, $[Rh(COD)_2]BF_4$ (1.0 mg, 0.0025 mmol) and (S_c,S_a)-**2b** (1.8 mg, 0.00275 mmol) were dissolved in degassed MeOH (1 mL) in a 5 mL of vial. After stirring at room temperature for 15 minutes, a solution of (*Z*)-β-phenyl-β-(acetylamino)acrylate **5a** (58 mg, 0.25 mmol, S/C 100:1) in 1 mL of degassed MeOH was added. The resulting mixture was transferred to an autoclave, which was then charged with H_2 (10 bar). The hydrogenation was performed at room temperature for 24 h. After carefully releasing the hydrogen gas, the reaction mixture was concentrated under reduced pressure. The residue was purified through a plug of silica gel (eluting with a mixture of hexanes/EtOAc, 2/1) to afford **6a**. The enantiomeric excess was determined by chiral GC on chiral select 1000 (30 m x 0.25 mm).

References

1. J.-D. Huang, X.-P. Hu, Z.C. Duan, Q.-H. Zeng, S.-B. Yu, J. Deng, D.-Y. Wang and Z. Zheng, *Org. Lett.*, 2006, **8**, 4367.

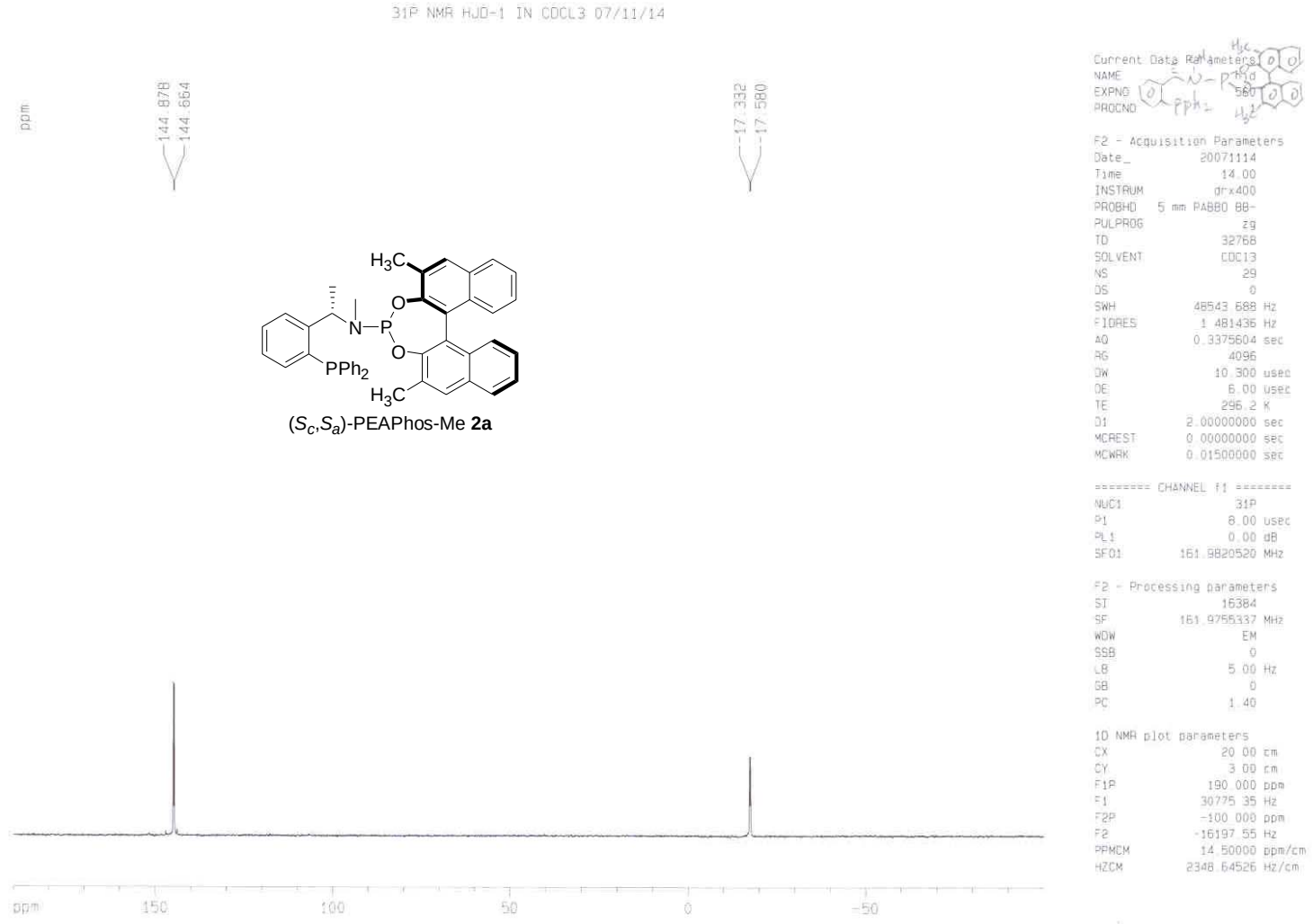
2. (a) T. R. Wu, L. Shen and J. M. Chong, *Org. Lett.*, 2004, **6**, 2701; (b) G. Franciò, C. G. Arena, F. Faraone, C. Graiff, M. Lanfranchi and A. Tiripicchio, *Eur. J. Inorg. Chem.*, 1999, 1219.

3. (a) G. Zhu, Z. Chen, X. Zhang, *J. Org. Chem.*, 1999, **64**, 6907; (b) W. Tang, W. Wang, Y. Chi, X. Zhang, *Angew. Chem. Int. Ed.*, 2003, **42**, 3509.



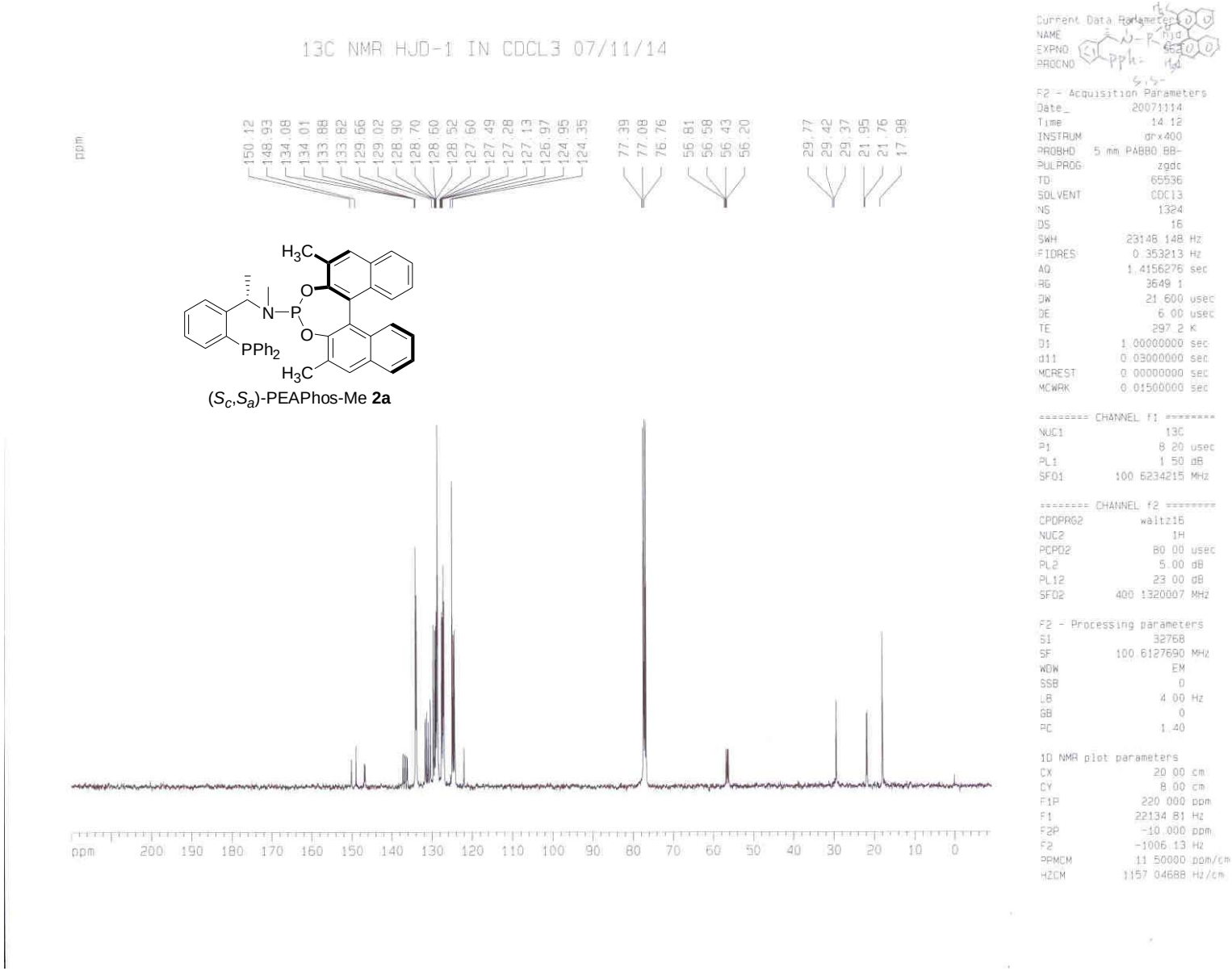
(S_c,S_a)-PEAPhos-Me **2a**

^{1}H NMR of (S_c,S_a)-PEAPhos-Me **2a**



(S_c,S_a)-PEAPhos-Me **2a**

^{31}P NMR of (S_c,S_a)-PEAPhos-Me **2a**



(S_c,S_a)-PEAPhos-Me **2a**

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EXPNO
PROCNO

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TE                297.2 K
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1D NMR plot parameters
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F2              -1006.13 Hz
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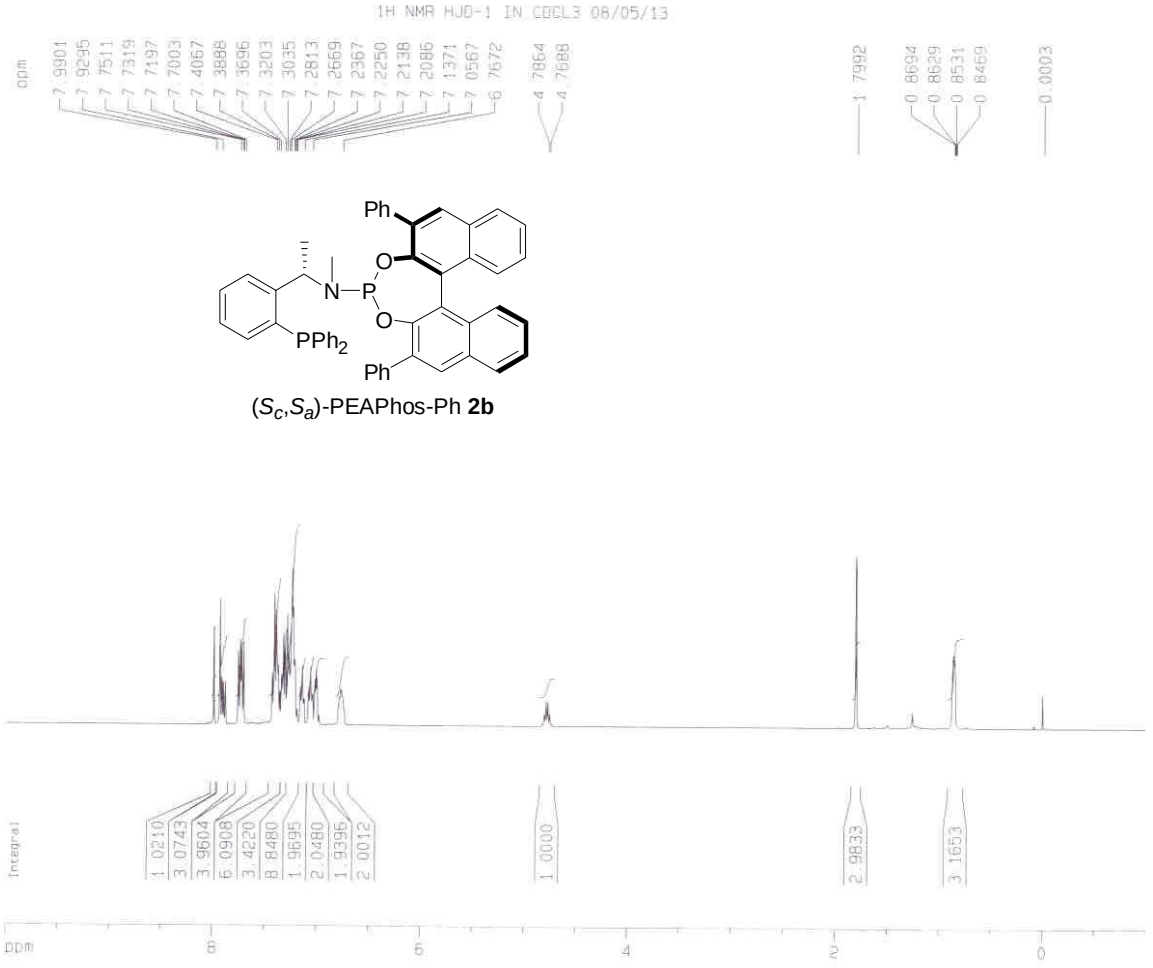
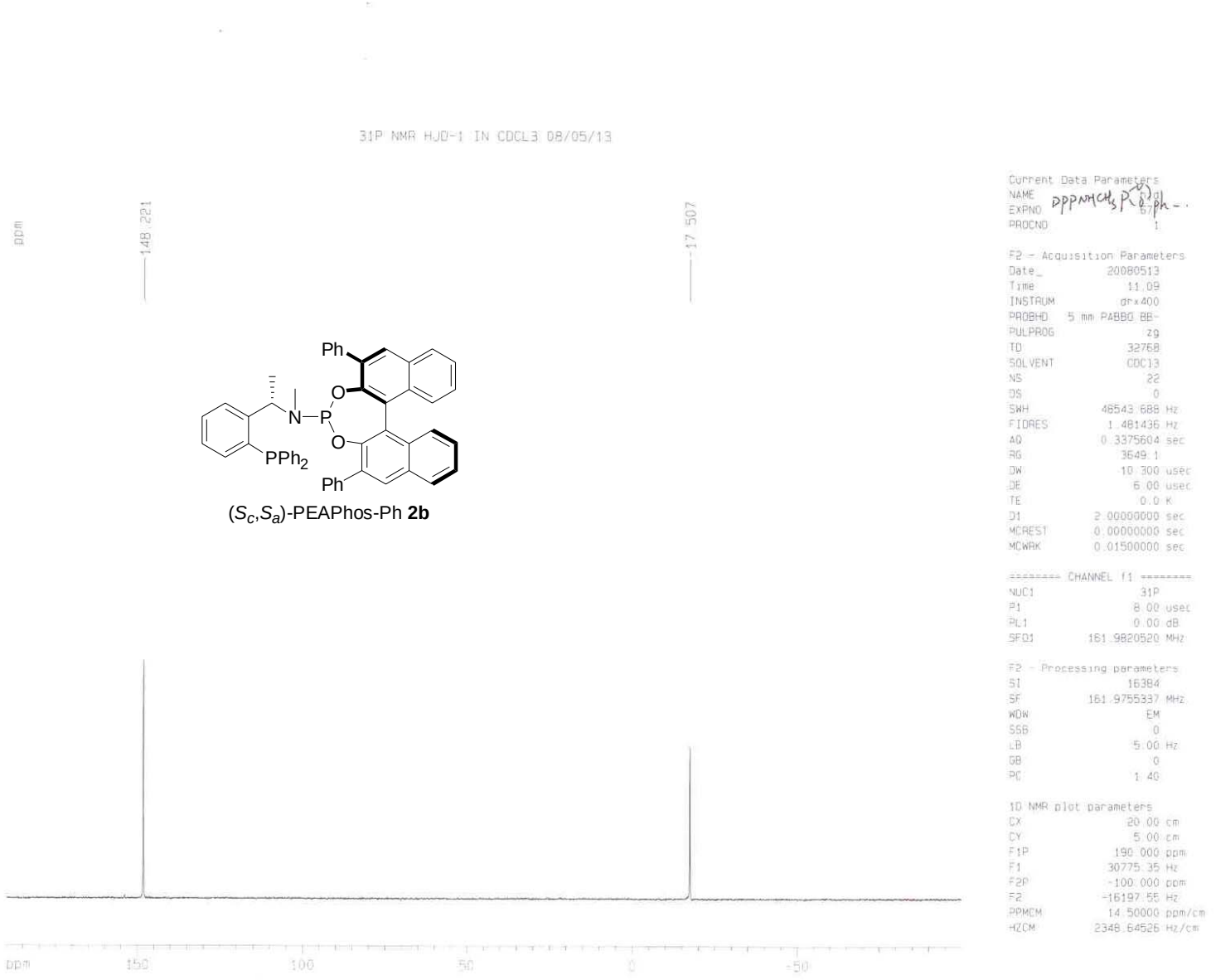
^{13}C NMR of (S_c,S_a)-PEAPhos-Me **2a**



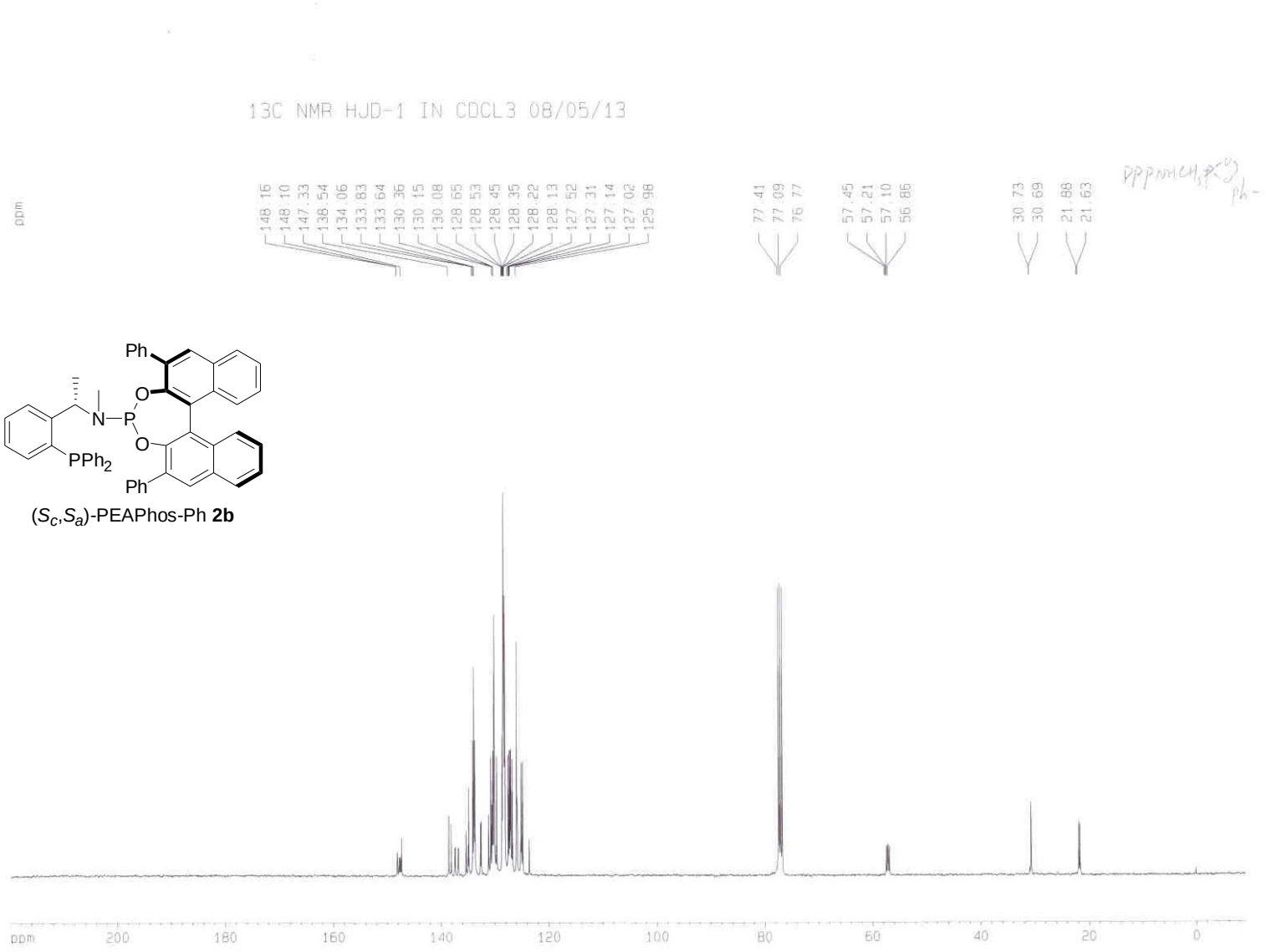
(S_c,S_a)-PEAPhos-Ph **2b**

^{1}H NMR of (S_c,S_a)-PEAPhos-Ph **2b**



(S_c,S_a)-PEAPhos-Ph **2b**

^{31}P NMR of (S_c,S_a)-PEAPhos-Ph **2b**



(S_c,S_a)-PEAPhos-Ph **2b**

^{13}C NMR of (S_c,S_a)-PEAPhos-Ph **2b**

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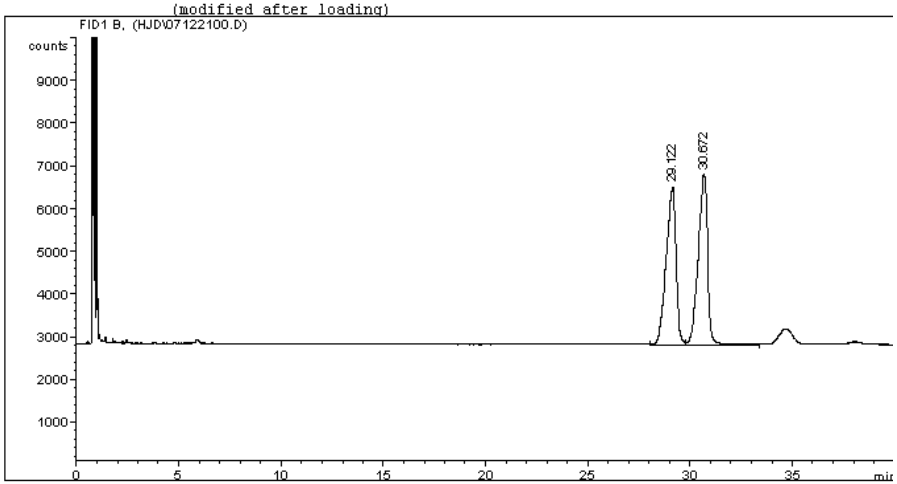

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   2  30.672 VV    0.5061 1.29551e5  3997.09595 50.77165

Totals :                  2.55165e5  7697.56714

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

Instrument 1 12/25/2009 11:27:34 PM hcj

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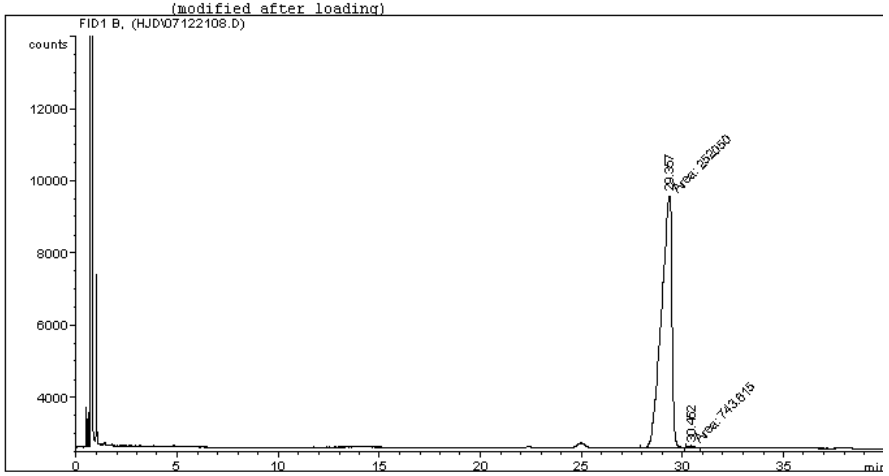

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Totals :                  2.52794e5  7025.25599

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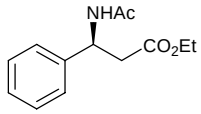
*** End of Report ***



6a

Instrument 1 12/25/2009 11:35:13 PM hcj

Data File C:\HPCHEM\1\DATA\HJD\08042213.D Sample Name: 0420-lxxt

Injection Date : 4/25/2008 3:16:58 AM
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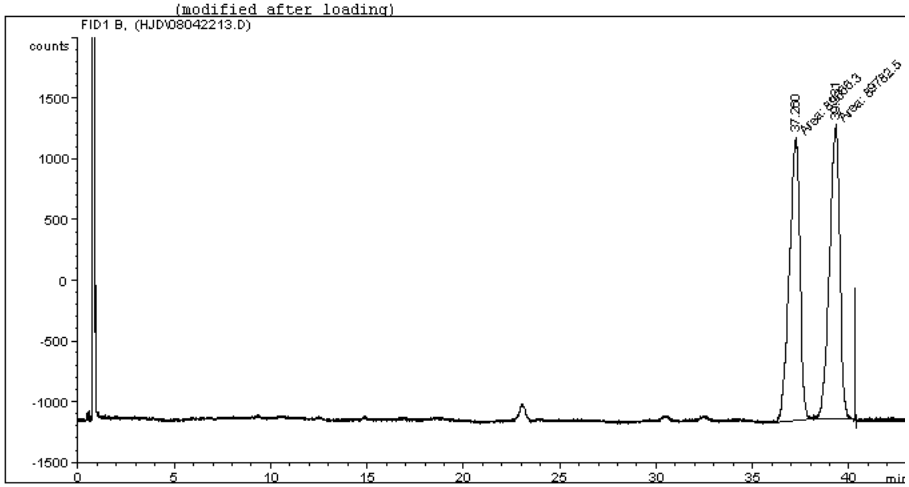

Area Percent Report

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1	37.260	MM	0.6392	8.96663e4	2337.83813	49.96760
2	39.331	MM	0.6158	8.97825e4	2430.00879	50.03240

Totals : 1.79449e5 4767.84692

Results obtained with enhanced integrator!

*** End of Report ***

Instrument 1 12/25/2009 9:28:51 PM hcj Page 1 of 1

Data File C:\HPCHEM\1\DATA\HJD\08042201.D Sample Name: 0420-1

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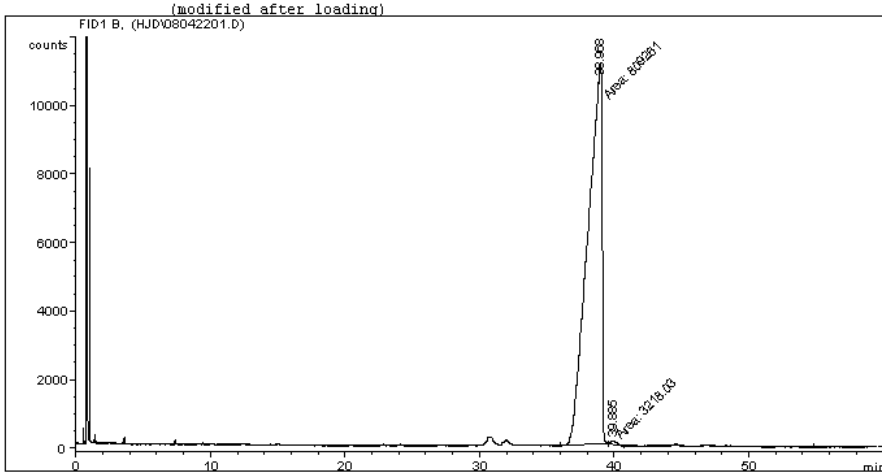

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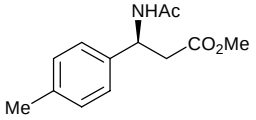
2	39.885	MM	0.5416	3218.03003	99.02280	0.39608

Totals : 8.12479e5 1.11387e4

Results obtained with enhanced integrator!

*** End of Report ***



6b

Instrument 1 12/25/2009 9:32:07 PM hcj Page 1 of 1

Data File C:\HPCHEM\1\DATA\HJD\08042212.D Sample Name: 0420-2xxt

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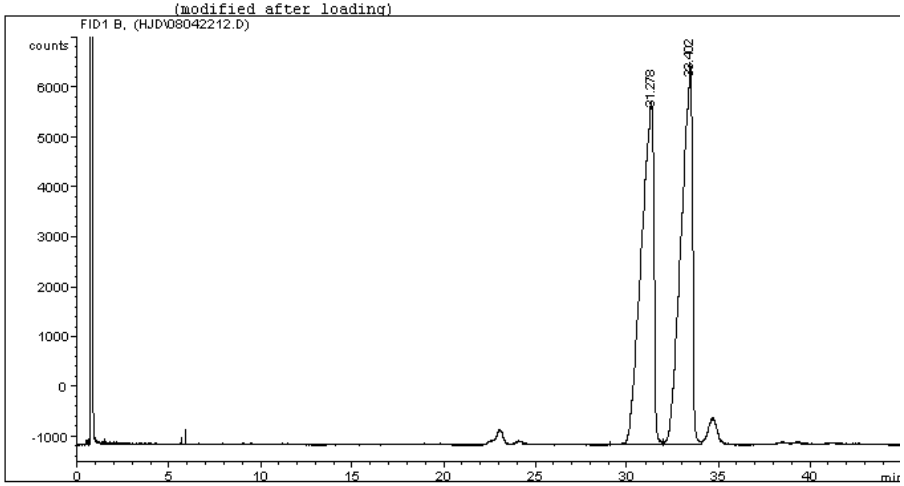


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Dilution              :      1.0000

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   2  33.402 VV    0.6792 3.28464e5  7381.09229 50.07296

Totals :                  6.55971e5  1.40611e4

 Results obtained with enhanced integrator!
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Instrument 1 12/25/2009 9:35:13 PM hcj Page 1 of 1

Data File C:\HPCHEM\1\DATA\HJD\08042208.D Sample Name: 0420-2

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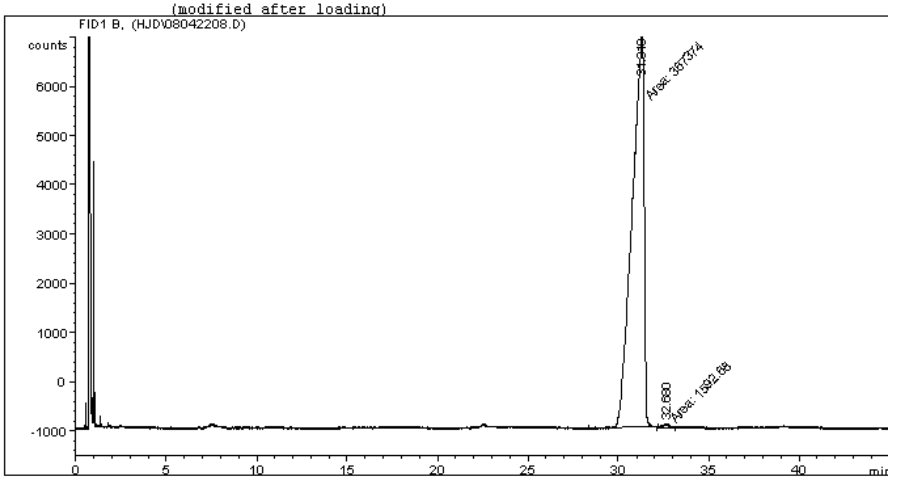


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   2  32.680 MM    0.4853 1592.67651   54.69570  0.43166

Totals :                  3.68966e5  8234.30508

 Results obtained with enhanced integrator!
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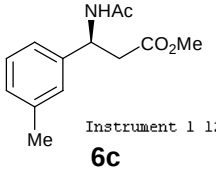

6c

Instrument 1 12/25/2009 9:38:27 PM hcj Page 1 of 1

Data File C:\HPCHEM\1\DATA\HJD\08030601.D Sample Name: 4-CH3 xxt

160,10psi

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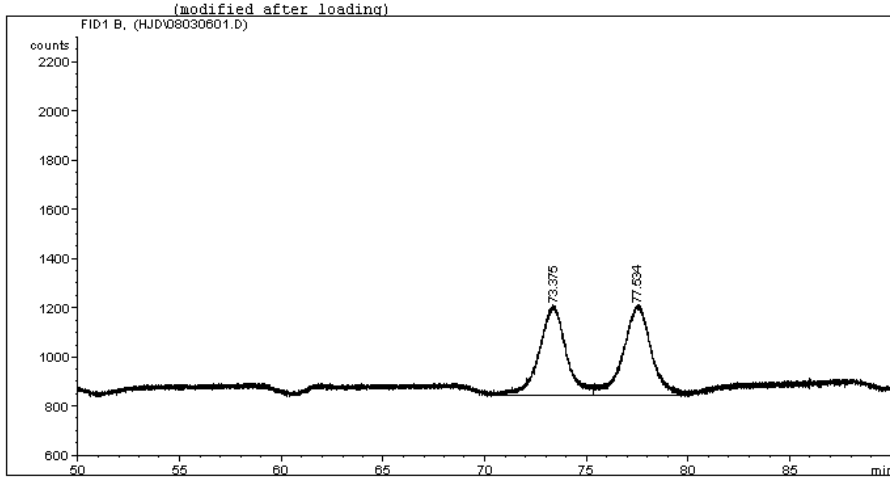


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Dilution              :      1.0000

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   2  77.534 VV    1.4450 3.44035e4   356.76950 50.43673

Totals :                  6.82112e4   715.12137

 Results obtained with enhanced integrator!
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Instrument 1 12/25/2009 9:42:44 PM hcj

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160,10psi

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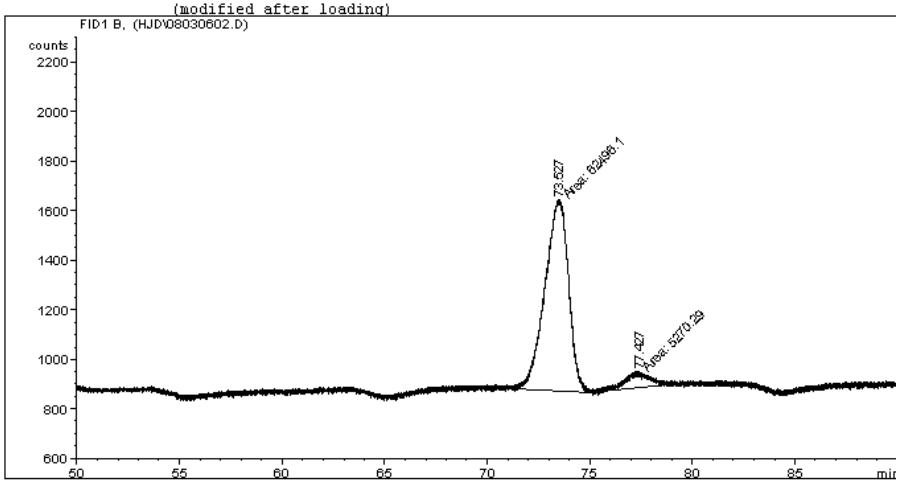


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   1  73.527 MM    1.3598 6.24961e4   765.99634 92.22285
   2  77.427 MM    1.5413 5270.29004   56.98990  7.77715

Totals :                  6.77664e4   822.98624

 Results obtained with enhanced integrator!
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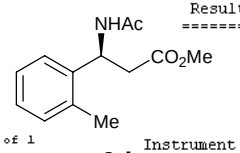

6d

Instrument 1 12/25/2009 9:46:11 PM hcj

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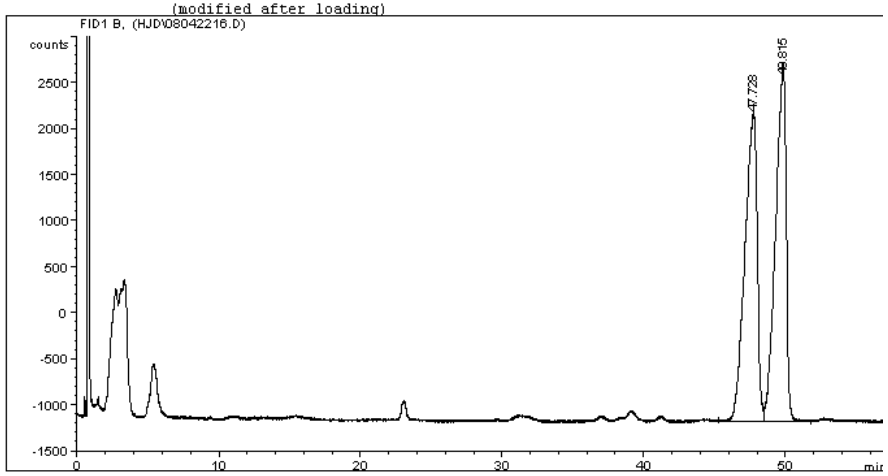
==================================================================
Injection Date  : 4/25/2008 7:07:01 AM
Sample Name     : 0420-8xxt                    Location : Vial 1
Acq. Operator   : hjd                        Inj Volume : Manually
Acq. Method     : C:\HPCHEM\1\METHODS\DEF GC1.M
Last changed    : 4/25/2008 7:05:32 AM by hjd
                  (modified after loading)
Analysis Method : C:\HPCHEM\1\METHODS\DEF GC1.M
Last changed    : 12/25/2009 9:52:27 PM by hcj
                  (modified after loading)
```




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

Sorted By             :      Signal
Multiplier            :      1.0000
Dilution              :      1.0000

Signal 1: FID1 B,

Peak RetTime Type  Width     Area      Height     Area
  #   [min]       [min]  counts*s   [counts]      %
----|-------|----|-------|----------|----------|--------|
   1  47.728 VV    0.9841 2.02987e5  3325.58740 50.05802
   2  49.815 VV    0.7997 2.02517e5  3888.12378 49.94198

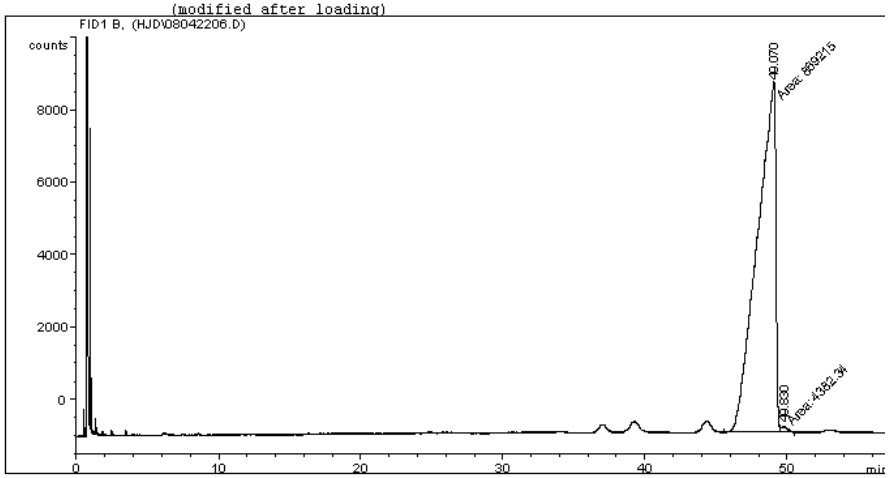
Totals :                  4.05504e5  7213.71118

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

Instrument 1 12/25/2009 9:56:05 PM hcj Page 1 of 1

Data File C:\HPCHEM\1\DATA\HJD\08042206.D Sample Name: 0420-8

```
==================================================================
Injection Date  : 4/24/2008 5:06:06 AM
Sample Name     : 0420-8                       Location : Vial 1
Acq. Operator   : hjd                        Inj Volume : Manually
Acq. Method     : C:\HPCHEM\1\METHODS\DEF GC1.M
Last changed    : 4/24/2008 3:49:15 AM by hjd
                  (modified after loading)
Analysis Method : C:\HPCHEM\1\METHODS\DEF GC1.M
Last changed    : 12/25/2009 9:56:06 PM by hcj
                  (modified after loading)
```




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

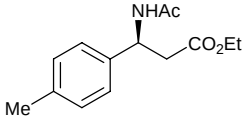
Sorted By             :      Signal
Multiplier            :      1.0000
Dilution              :      1.0000

Signal 1: FID1 B,

Peak RetTime Type  Width     Area      Height     Area
  #   [min]       [min]  counts*s   [counts]      %
----|-------|----|-------|----------|----------|--------|
   1  49.070 MF    1.5058 8.69215e5  9621.00586 99.49836
   2  49.830 FM    0.5204 4382.34473  140.35803  0.50164

Totals :                  8.73597e5  9761.36389

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



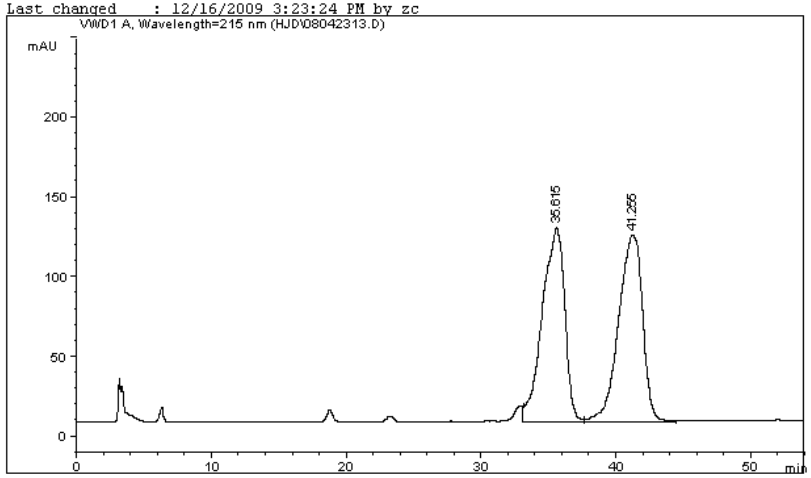
6e

Instrument 1 12/25/2009 9:59:50 PM hcj Page 1 of 1

Data File C:\HPCHEM\2\DATA\HJD\08042313.D Sample Name: 0420-4XXT

AD-H,90:10 230nm

```
==========================================================================
Injection Date  : 4/24/2008 3:58:53 PM
Sample Name     : 0420-4XXT                    Location : Vial 1
Acq. Operator   : HJD
Acq. Method     : C:\HPCHEM\2\METHODS\DZC-P.M
Last changed    : 4/24/2008 3:40:30 PM by HJD
                  (modified after loading)
Analysis Method : C:\HPCHEM\2\METHODS\DEF1 LC.M
Last changed    : 12/16/2009 3:23:24 PM by zc
```




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

Sorted By             :      Signal
Multiplier            :      1.0000
Dilution              :      1.0000

Signal 1: VWD1 A, Wavelength=215 nm

Peak RetTime Type  Width     Area      Height     Area
  #   [min]       [min]  mAU   *s   [mAU   ]      %
----|-------|----|-------|----------|----------|--------|
   1  35.615 VV    1.5964 1.41891e4   122.20000  49.1237
   2  41.255 VB    1.6171 1.46953e4   117.43892  50.8763

Totals :                  2.88844e4   239.63892

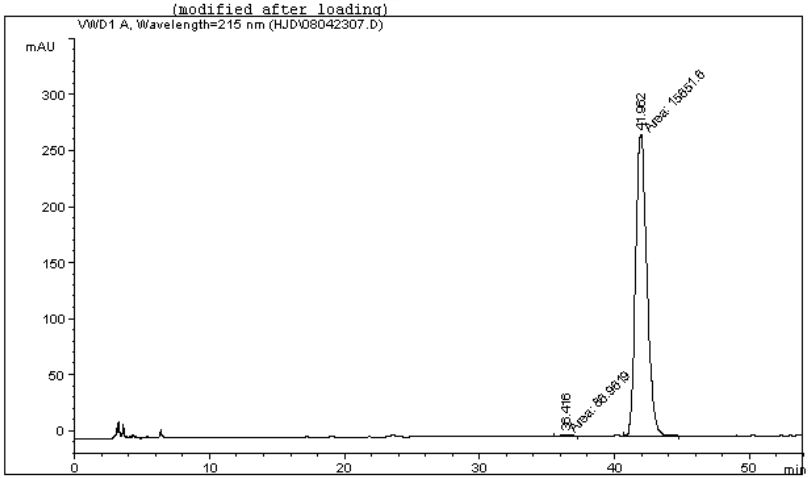
 Results obtained with enhanced integrator!
==========================================================================
                        *** End of Report ***
```

Instrument 2 12/25/2009 11:12:44 AM zc

Data File C:\HPCHEM\2\DATA\HJD\08042307.D Sample Name: 0420-4

AD-H,90:10 230nm

```
==========================================================================
Injection Date  : 4/23/2008 9:01:08 PM
Sample Name     : 0420-4                       Location : Vial 1
Acq. Operator   : HJD
Acq. Method     : C:\HPCHEM\2\METHODS\DZC-P.M
Last changed    : 4/23/2008 9:53:55 PM by HJD
                  (modified after loading)
Analysis Method : C:\HPCHEM\2\METHODS\DEF1 LC.M
Last changed    : 12/25/2009 11:15:13 AM by zc
                  (modified after loading)
```




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

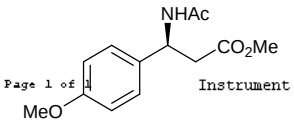
Sorted By             :      Signal
Multiplier            :      1.0000
Dilution              :      1.0000

Signal 1: VWD1 A, Wavelength=215 nm

Peak RetTime Type  Width     Area      Height     Area
  #   [min]       [min]  mAU   *s   [mAU   ]      %
----|-------|----|-------|----------|----------|--------|
   1  36.416 MM    0.8268   86.96188    1.75292   0.5525
   2  41.962 MM    0.9689 1.56516e4   269.22040  99.4475

Totals :                  1.57385e4   270.97332

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



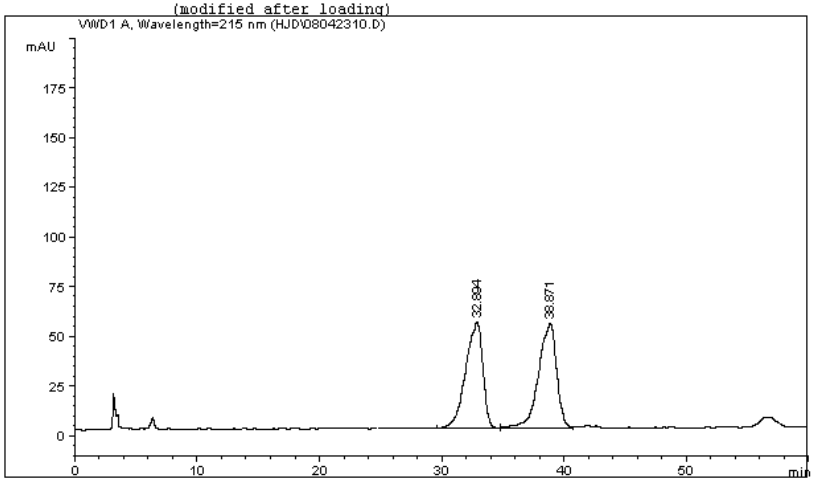
6f

Instrument 2 12/25/2009 11:16:04 AM zc

Data File C:\HPCHEM\2\DATA\HJD\08042310.D Sample Name: 0420-5xxt

AD-H,90:10 230nm

```
==========================================================================
Injection Date  : 4/24/2008 12:22:46 PM
Sample Name     : 0420-5xxt                    Location : Vial 1
Acq. Operator   : HJD
Acq. Method     : C:\HPCHEM\2\METHODS\DZC-P.M
Last changed    : 4/24/2008 9:38:18 AM by HJD
                  (modified after loading)
Analysis Method : C:\HPCHEM\2\METHODS\DEF1 LC.M
Last changed    : 12/25/2009 11:16:05 AM by zc
                  (modified after loading)
```




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

Sorted By             :      Signal
Multiplier            :      1.0000
Dilution              :      1.0000

Signal 1: VWD1 A, Wavelength=215 nm

Peak RetTime Type  Width     Area      Height     Area
  #   [min]        [min]  mAU   *s   [mAU   ]      %
----|-------|----|-------|----------|----------|--------|
   1  32.894 BV    1.3329 5245.17871   53.23633  49.1091
   2  38.871 VV    1.3948 5435.49658   52.60138  50.8909

Totals :                  1.06807e4   105.83771

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

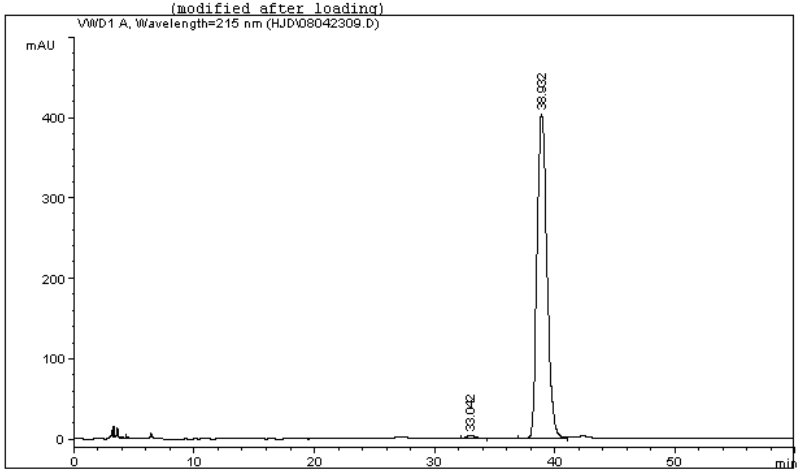
Instrument 2 12/25/2009 11:18:04 AM zc

Page 1 of 1

Data File C:\HPCHEM\2\DATA\HJD\08042309.D Sample Name: 0420-5

AD-H,90:10 230nm

```
==========================================================================
Injection Date  : 4/24/2008 10:35:23 AM
Sample Name     : 0420-5                       Location : Vial 1
Acq. Operator   : HJD
Acq. Method     : C:\HPCHEM\2\METHODS\DZC-P.M
Last changed    : 4/24/2008 9:38:18 AM by HJD
                  (modified after loading)
Analysis Method : C:\HPCHEM\2\METHODS\DEF1 LC.M
Last changed    : 12/25/2009 11:18:05 AM by zc
                  (modified after loading)
```




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

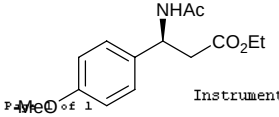
Sorted By             :      Signal
Multiplier            :      1.0000
Dilution              :      1.0000

Signal 1: VWD1 A, Wavelength=215 nm

Peak RetTime Type  Width     Area      Height     Area
  #   [min]        [min]  mAU   *s   [mAU   ]      %
----|-------|----|-------|----------|----------|--------|
   1  33.042 BP    0.7106  152.37654    3.22963   0.6545
   2  38.932 VV    0.8912 2.31279e4   402.77917  99.3455

Totals :                  2.32802e4   406.00880

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



6g

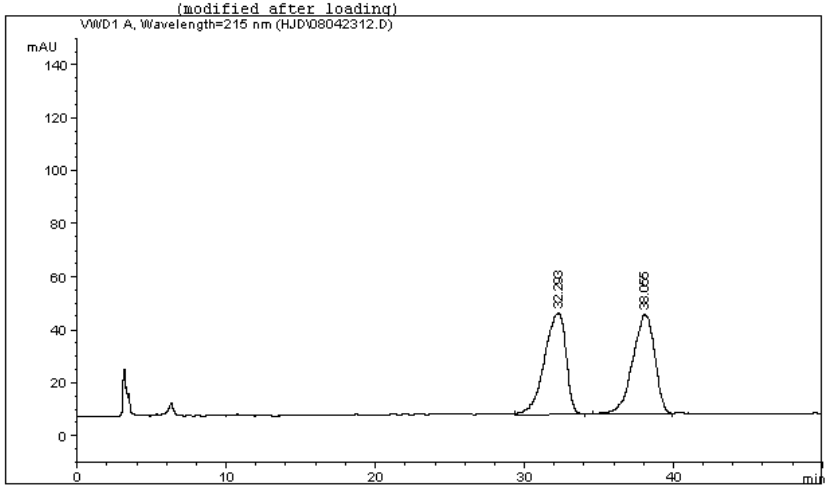
Instrument 2 12/25/2009 11:20:40 AM zc

Page 1 of 1

Data File C:\HPCHEM\2\DATA\HJD\08042312.D Sample Name: 0420-6xxt

AD-H,90:10 230nm

```
==========================================================================
Injection Date  : 4/24/2008 3:07:02 PM
Sample Name     : 0420-6xxt                    Location : Vial 1
Acq. Operator   : HJD
Acq. Method     : C:\HPCHEM\2\METHODS\DZC-P.M
Last changed    : 4/24/2008 3:40:30 PM by HJD
                  (modified after loading)
Analysis Method : C:\HPCHEM\2\METHODS\DEF1 LC.M
Last changed    : 12/25/2009 11:20:41 AM by zc
                  (modified after loading)
```




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

Sorted By             :      Signal
Multiplier            :      1.0000
Dilution              :      1.0000

Signal 1: VWD1 A, Wavelength=215 nm

Peak RetTime Type  Width     Area      Height     Area
  #   [min]        [min]  mAU   *s   [mAU   ]      %
----|-------|----|-------|----------|----------|--------|
   1  32.293 VV    1.4289 3869.19189   38.21138  49.8653
   2  38.055 VV    1.3954 3890.09155   37.53797  50.1347

Totals :                  7759.28345   75.74934

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

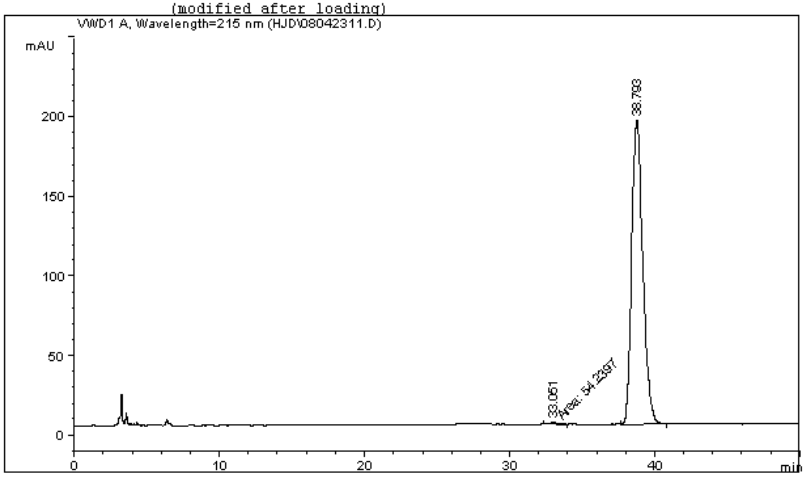
Instrument 2 12/25/2009 11:22:35 AM zc

Page 1 of 1

Data File C:\HPCHEM\2\DATA\HJD\08042311.D Sample Name: 0420-6xxt

AD-H,90:10 230nm

```
==========================================================================
Injection Date  : 4/24/2008 2:07:50 PM
Sample Name     : 0420-6xxt                    Location : Vial 1
Acq. Operator   : HJD
Acq. Method     : C:\HPCHEM\2\METHODS\DZC-P.M
Last changed    : 4/24/2008 9:38:18 AM by HJD
                  (modified after loading)
Analysis Method : C:\HPCHEM\2\METHODS\DEF1 LC.M
Last changed    : 12/25/2009 11:24:39 AM by zc
                  (modified after loading)
```




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

Sorted By             :      Signal
Multiplier            :      1.0000
Dilution              :      1.0000

Signal 1: VWD1 A, Wavelength=215 nm

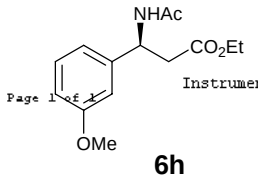
Peak RetTime Type  Width     Area      Height     Area
  #   [min]        [min]  mAU   *s   [mAU   ]      %
----|-------|----|-------|----------|----------|--------|
   1  33.051 MM    0.7036   54.23972    1.28475   0.5283
   2  38.793 VB    0.8022 1.02124e4   190.76672  99.4717

Totals :                  1.02666e4   192.05148

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

Instrument 2 12/25/2009 11:25:07 AM zc

Page 1 of 1

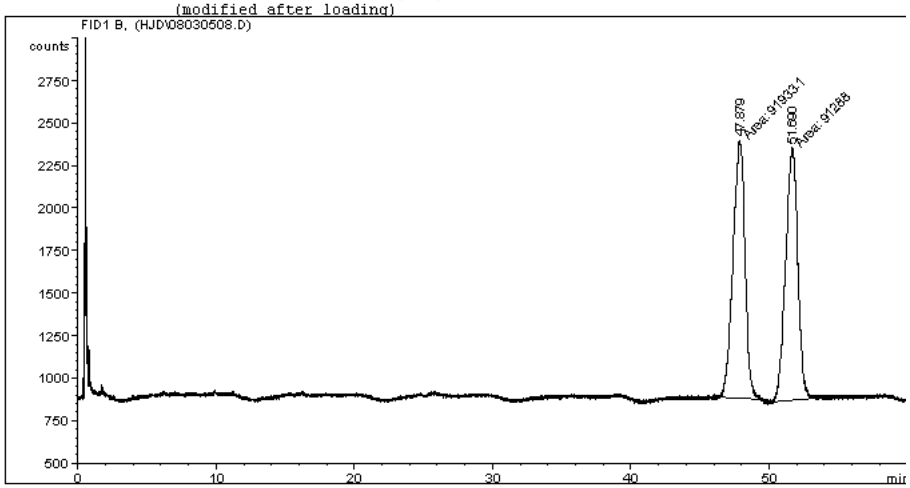


6h

Data File C:\HPCHEM\1\DATA\HJD\08030508.D Sample Name: 4-Cl xxt

160,10psi

```
==========================================================================
Injection Date  : 3/6/2008 7:38:04 AM
Sample Name     : 4-Cl xxt                        Location : Vial 1
Acq. Operator   : hjd                          Inj Volume : Manually
Acq. Method     : C:\HPCHEM\1\METHODS\DEF GC1.M
Last changed    : 3/6/2008 4:36:19 AM by hjd
                  (modified after loading)
Analysis Method : C:\HPCHEM\1\METHODS\DEF GC1.M
Last changed    : 12/25/2009 10:08:43 PM by hcj
                  (modified after loading)
```




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

Sorted By             :      Signal
Multiplier            :      1.0000
Dilution              :      1.0000

Signal 1: FID1 B,

Peak RetTime Type  Width     Area      Height     Area
  #   [min]        [min]  counts*s   [counts]      %
----|-------|----|-------|----------|----------|--------|
   1  47.879 MM    1.0138 9.19331e4  1511.39600 50.17605
   2  51.690 MM    1.0320 9.12880e4  1474.31091 49.82395

Totals :                  1.83221e5  2985.70691

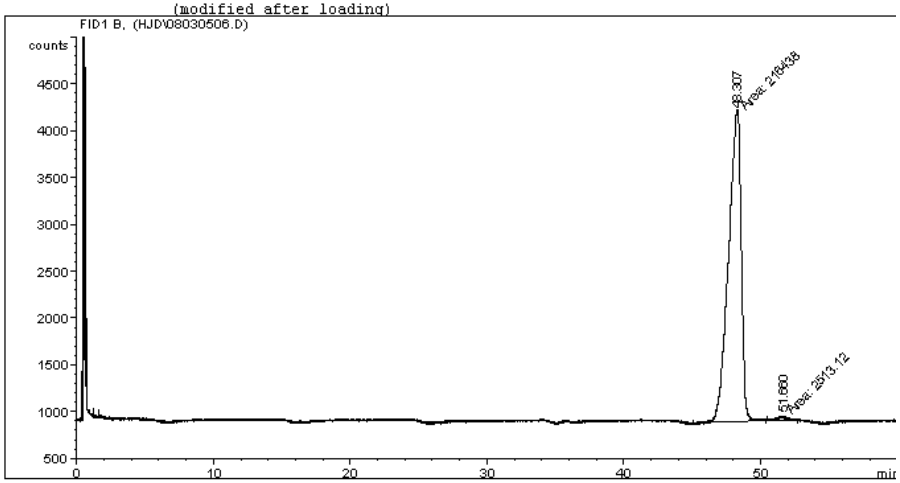
 Results obtained with enhanced integrator!
==========================================================================
                          *** End of Report ***
```

Instrument 1 12/25/2009 10:11:35 PM hcj Page 1 of 1

Data File C:\HPCHEM\1\DATA\HJD\08030506.D Sample Name: 4-Cl

160,10psi

```
==========================================================================
Injection Date  : 3/6/2008 4:34:39 AM
Sample Name     : 4-Cl                            Location : Vial 1
Acq. Operator   : hjd                          Inj Volume : Manually
Acq. Method     : C:\HPCHEM\1\METHODS\DEF GC1.M
Last changed    : 3/6/2008 4:36:19 AM by hjd
                  (modified after loading)
Analysis Method : C:\HPCHEM\1\METHODS\DEF GC1.M
Last changed    : 12/25/2009 10:11:35 PM by hcj
                  (modified after loading)
```




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

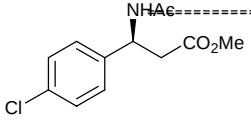
Sorted By             :      Signal
Multiplier            :      1.0000
Dilution              :      1.0000

Signal 1: FID1 B,

Peak RetTime Type  Width     Area      Height     Area
  #   [min]        [min]  counts*s   [counts]      %
----|-------|----|-------|----------|----------|--------|
   1  48.307 MM    1.0918 2.16438e5  3304.12085 98.85220
   2  51.660 MM    1.0846 2513.11646   38.61885  1.14780

Totals :                  2.18951e5  3342.73970

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

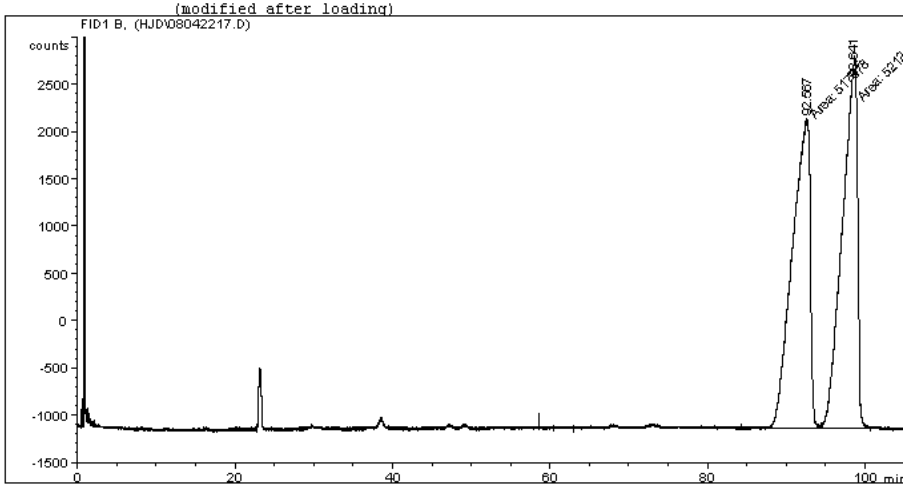


6i

Instrument 1 12/25/2009 10:16:06 PM hcj Page 1 of 1

Data File C:\HPCHEM\1\DATA\HJD\08042217.D Sample Name: 0420-7xxt

```
==================================================================
Injection Date  : 4/25/2008 9:04:19 PM
Sample Name     : 0420-7xxt                    Location : Vial 1
Acq. Operator   : hjd
                                             Inj Volume : Manually
Acq. Method     : C:\HPCHEM\1\METHODS\DEF GC1.M
Last changed    : 4/25/2008 8:46:47 PM by hjd
                  (modified after loading)
Analysis Method : C:\HPCHEM\1\METHODS\DEF GC1.M
Last changed    : 12/25/2009 9:49:21 PM by hcj
                  (modified after loading)
```




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

Sorted By             :      Signal
Multiplier            :      1.0000
Dilution              :      1.0000

Signal 1: FID1 B,

Peak RetTime Type  Width     Area      Height     Area
  #   [min]        [min]  counts*s   [counts]      %
----|-------|----|-------|----------|----------|--------|
   1  92.567 MM    2.6524 5.17678e5  3252.91260 49.83003
   2  98.641 MM    2.2205 5.21209e5  3912.09985 50.16997

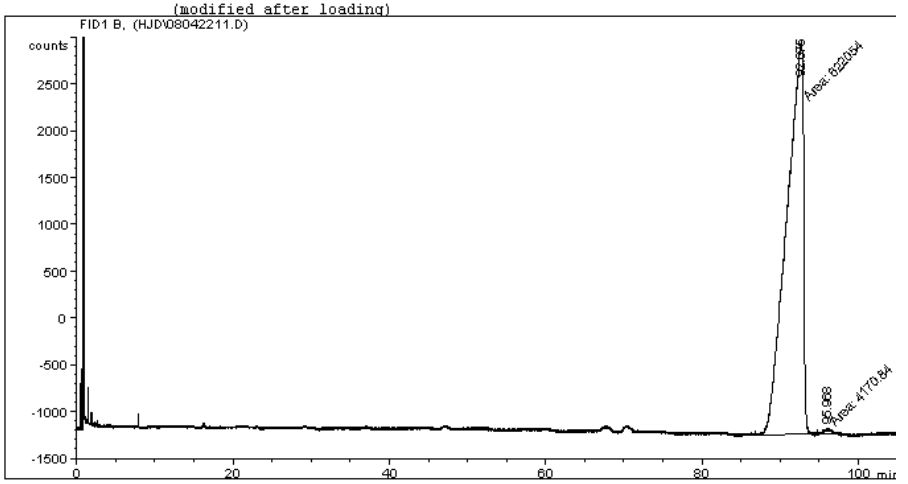
Totals :                  1.03889e6  7165.01245

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

Instrument 1 12/25/2009 9:50:12 PM hcj

Data File C:\HPCHEM\1\DATA\HJD\08042211.D Sample Name: 0420-1xxt

```
==================================================================
Injection Date  : 4/24/2008 11:39:30 PM
Sample Name     : 0420-1xxt                    Location : Vial 1
Acq. Operator   : hjd
                                             Inj Volume : Manually
Acq. Method     : C:\HPCHEM\1\METHODS\DEF GC1.M
Last changed    : 4/24/2008 9:21:49 PM by hjd
                  (modified after loading)
Analysis Method : C:\HPCHEM\1\METHODS\DEF GC1.M
Last changed    : 12/25/2009 9:50:13 PM by hcj
                  (modified after loading)
```




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

Sorted By             :      Signal
Multiplier            :      1.0000
Dilution              :      1.0000

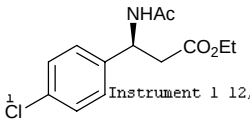
Signal 1: FID1 B,

Peak RetTime Type  Width     Area      Height     Area
  #   [min]        [min]  counts*s   [counts]      %
----|-------|----|-------|----------|----------|--------|
   1  92.675 MM    2.4698 6.22054e5  4197.69092 99.33397
   2  95.968 MM    1.2924 4170.83740   61.50812  0.66603

Totals :                  6.26225e5  4259.19904

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

Instrument 1 12/25/2009 9:52:26 PM hcj

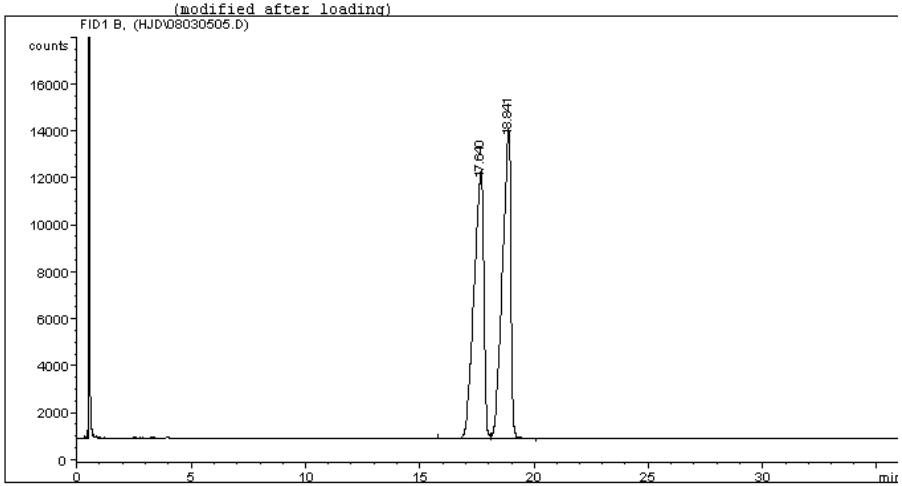


6j

Data File C:\HPCHEM\1\DATA\HJD\08030505.D Sample Name: 4-Fxxt

160,10psi

```
==========================================================================
Injection Date  : 3/6/2008 3:54:12 AM
Sample Name     : 4-Fxxt                          Location : Vial 1
Acq. Operator   : hjd                          Inj Volume : Manually
Acq. Method     : C:\HPCHEM\1\METHODS\DEF GC1.M
Last changed    : 3/6/2008 3:18:06 AM by hjd
                  (modified after loading)
Analysis Method : C:\HPCHEM\1\METHODS\DEF GC1.M
Last changed    : 12/25/2009 9:59:51 PM by hcj
                  (modified after loading)
```




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

Sorted By             :      Signal
Multiplier            :      1.0000
Dilution              :      1.0000

Signal 1: FID1 B,

Peak RetTime Type  Width     Area      Height     Area
  #   [min]       [min]  counts*s   [counts]      %
----|-------|----|-------|----------|----------|--------|
   1  17.640 VV    0.4953 3.42831e5  1.08889e4  50.02874
   2  18.841 VV    0.4253 3.42437e5  1.27506e4  49.97126

Totals :                  6.85268e5  2.36395e4

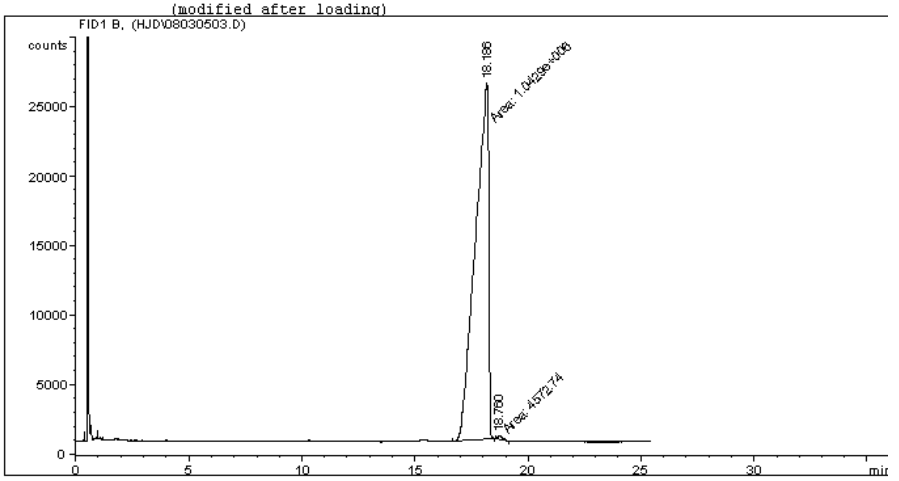
 Results obtained with enhanced integrator!
==========================================================================
                          *** End of Report ***
```

Instrument 1 12/25/2009 10:03:41 PM hcj Page 1 of 1

Data File C:\HPCHEM\1\DATA\HJD\08030503.D Sample Name: 4-F

160,10psi

```
==========================================================================
Injection Date  : 3/6/2008 2:51:42 AM
Sample Name     : 4-F                             Location : Vial 1
Acq. Operator   : hjd                          Inj Volume : Manually
Acq. Method     : C:\HPCHEM\1\METHODS\DEF GC1.M
Last changed    : 3/6/2008 12:49:57 AM by hjd
                  (modified after loading)
Analysis Method : C:\HPCHEM\1\METHODS\DEF GC1.M
Last changed    : 12/25/2009 10:07:45 PM by hcj
                  (modified after loading)
```




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

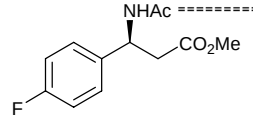
Sorted By             :      Signal
Multiplier            :      1.0000
Dilution              :      1.0000

Signal 1: FID1 B,

Peak RetTime Type  Width     Area      Height     Area
  #   [min]       [min]  counts*s   [counts]      %
----|-------|----|-------|----------|----------|--------|
   1  18.186 MM    0.6791 1.04290e6  2.55967e4  99.56345
   2  18.760 MM    0.2598 4572.73682  293.32980  0.43655

Totals :                  1.04747e6  2.58900e4

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



6k

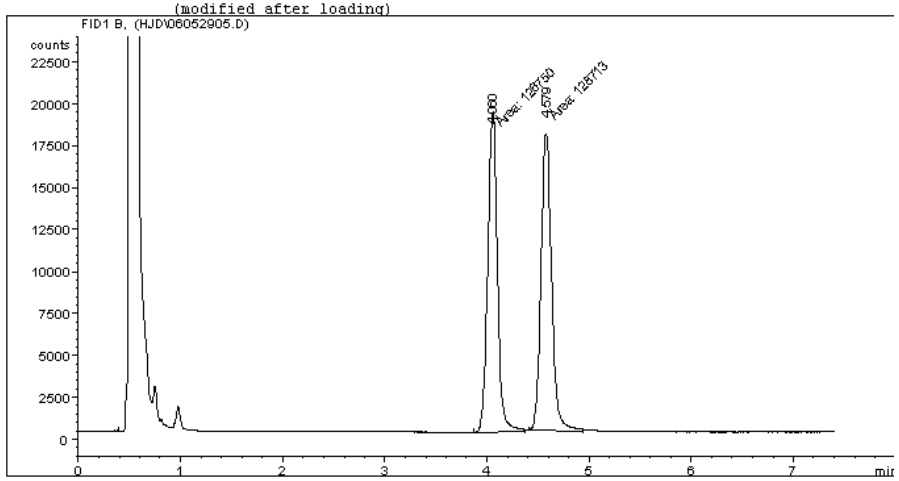
Instrument 1 12/25/2009 10:08:42 PM hcj Page 1 of 1

Data File C:\HPCHEM\1\DATA\HJD\06052905.D Sample Name: B-3

B-390,130 C, 15spi

```
==========================================================================
Injection Date  : 5/31/2006 2:57:40 PM
Sample Name     : B-3                          Location : Vial 1
Acq. Operator   : WDY                        Inj Volume : Manually

Acq. Method     : C:\HPCHEM\1\METHODS\DEF GC1.M
Last changed    : 5/31/2006 2:29:33 PM by WDY
                  (modified after loading)
Analysis Method : C:\HPCHEM\1\METHODS\DEF GC1.M
Last changed    : 12/26/2009 2:12:58 AM by hcj
                  (modified after loading)
```




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

Sorted By             :      Signal
Multiplier            :      1.0000
Dilution              :      1.0000

Signal 1: FID1 B,

Peak RetTime Type  Width     Area      Height     Area
  #   [min]        [min]  counts*s   [counts]      %
----|-------|----|-------|----------|----------|--------|
   1   4.060 MM    0.1166 1.26750e5  1.81169e4  49.61575
   2   4.579 MM    0.1166 1.28713e5  1.83987e4  50.38425

Totals :                  2.55462e5  3.65156e4

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

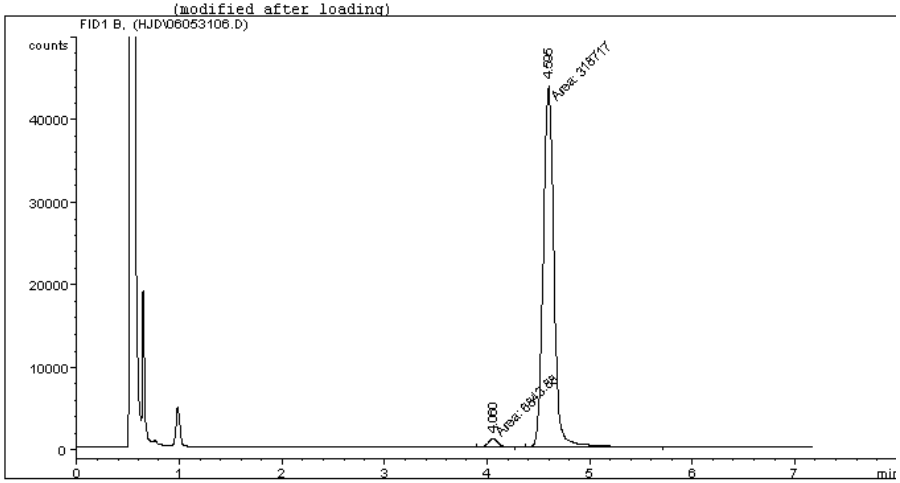
Instrument 1 12/26/2009 2:13:21 AM hcj Page 1 of 1

Data File C:\HPCHEM\1\DATA\HJD\06053106.D Sample Name: A-4

B-390,130 C, 15spi

```
==========================================================================
Injection Date  : 5/31/2006 3:36:54 PM
Sample Name     : A-4                          Location : Vial 1
Acq. Operator   : WDY                        Inj Volume : Manually

Acq. Method     : C:\HPCHEM\1\METHODS\DEF GC1.M
Last changed    : 5/31/2006 2:29:33 PM by WDY
                  (modified after loading)
Analysis Method : C:\HPCHEM\1\METHODS\DEF GC1.M
Last changed    : 12/26/2009 2:18:14 AM by hcj
                  (modified after loading)
```




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

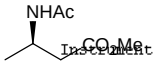
Sorted By             :      Signal
Multiplier            :      1.0000
Dilution              :      1.0000

Signal 1: FID1 B,

Peak RetTime Type  Width     Area      Height     Area
  #   [min]        [min]  counts*s   [counts]      %
----|-------|----|-------|----------|----------|--------|
   1   4.060 MM    0.1020 6843.87500 1117.74878  2.10218
   2   4.595 MM    0.1206 3.18717e5  4.40393e4  97.89782

Totals :                  3.25560e5  4.51570e4

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



8

Instrument 1 12/26/2009 2:18:32 AM hcj Page 1 of 1