

Palladium-Catalyzed Suzuki-Miyaura Coupling of Pyridyl-2-Boronic Esters with Aryl Halides

Using Highly Active and Air-Stable Phosphine Chloride and Oxide Ligands

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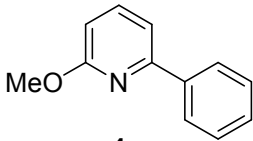
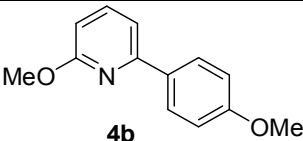
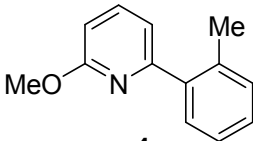
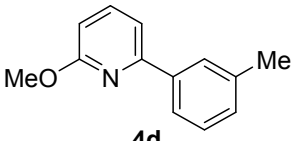
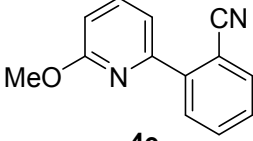
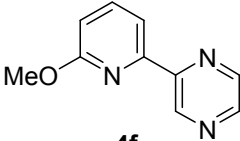
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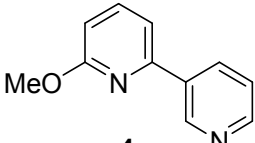
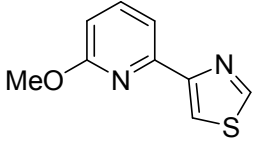
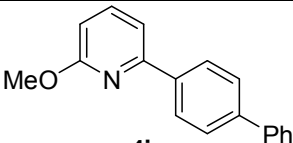
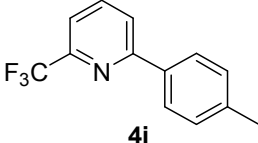
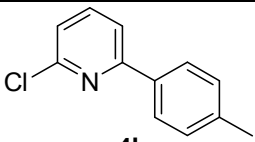
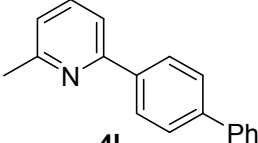
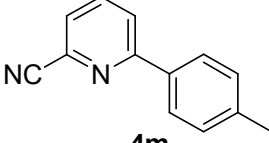
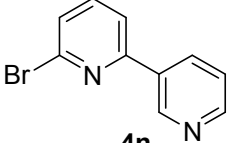
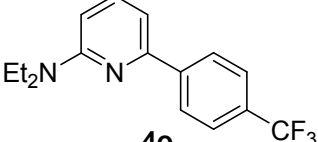
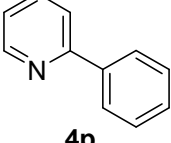
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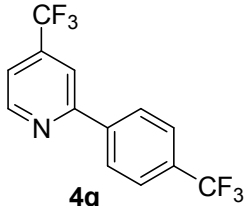
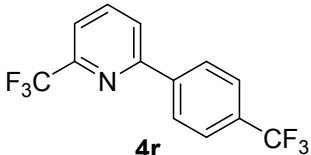
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Flash chromatography was performed using Si 25 S/M cartridges. Analytical thin layer chromatography (TLC) was performed with 0.25 mm silica gel 60-F commercial silica gel plates. Visualization was accomplished with UV light.

LC/MS solvent was acetonitrile/water with 0.05% formic acid.

^1H and ^{13}C nuclear magnetic resonance (NMR) spectra were recorded on a 500 or 600 MHz spectrometer.

General Procedure: To a sealed tube was added aryl bromide (1 eq.), boronic ester (1.2 eq.), base (2 eq.), solvent and catalyst (3 mol%). The sealed tube was then heated at 90 °C over 18 h. After 1 h, to the mixture was added dichloromethane and water. The organic layer was concentrated and purified by silica gel chromatography eluting with ethyl acetate and hexanes to give the desired product.

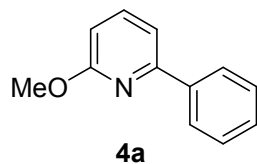
Representative procedure: To a solution of **2a** (56 mg, 37 μL , 0.36 mmol) and **3a** (100 mg, 0.43 mmol) in 4 mL of 2-propanol was added **1a** (6 mg, 0.011 mmol) and cesium fluoride (108 mg, 0.71 mmol) and flushed with nitrogen. The resulting mixture was stirred at 100 °C overnight, cooled to room temperature, concentrated, and purified by biotage with 2-5% ethyl acetate in hexanes to give **4a** (42 mg, 0.23 mmol, 64%) as a pale yellow oil.

Scale-up procedure: To a solution of **3b** (1000 mg, 3.66 mmol) and **2k** (687 mg, 3.05 mmol) in 10 mL of isopropanol was added **1c** (7.7 mg, 0.015 mmol) and cesium fluoride (928 mg, 6.1 mmol) and flushed with nitrogen. The resulting mixture was stirred at 90 °C overnight, cooled to room temperature, diluted with ethyl acetate (200 mL), and washed with water (100 mL). The aqueous layer was extracted with additional 200 mL of ethyl acetate. The combined organic layers were dried with sodium sulfate and then concentrated in vacuo. The resulting residue was purified by biotage with 2-5% ethyl acetate in hexanes to give **4r** (879 mg, 3.02 mmol, 99%) as a white crystalline solid. (The first time the same reaction gave a yield of 93%).

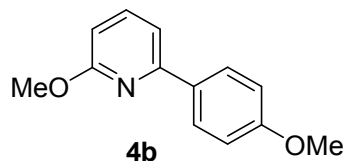
***i*-PrOLi additive procedure:** To a solution of **2k** (41 mg, 0.18 mmol), **3i** (100 mg, 0.37 mmol), CsF (84 mg, 0.55 mmol), PXPd (**1a**) (3 mg, 0.0056 mmol) in dioxane (3 mL) was added lithium isopropoxide (0.18 mL, 0.36 mmol, THF solution, 2 M). The resulting mixture was heated at 90 °C overnight. The same work-up and column purification procedures as the aforementioned scale-up protocol yielded the desired product **4q** as a colorless oil (26 mg, 0.095 mmol, 52%).

***t*-BuOLi additive procedure:** (Table 3, entry 10) Pyridine-2-boronic acid pinacol ester **3h** (1.58 g, 7.64 mmol) and bromobenzene **2a** (1.0 g, 6.37 mmol) were dissolved in isopropanol (5 mL) before being added to a mixture of the POPd-mix catalyst (0.096 g, 0.191 mmol) and lithium tert-butoxide (1.02 g, 13 mmol) in isopropanol (10 mL). The reaction mixture was stirred at room temperature for 30 min and then heated to 90 °C for 12 h. After the reaction mixture was cooled down to room temperature, it was filtered through celite. The filtrate was collected and the solvents were removed by rotary evaporation. The crude product was purified by silica gel column chromatography eluting with 5% ethyl acetate in hexanes to afford the 2-phenylpyridine as a pale yellow liquid (0.49 g, 3.16 mmol, 50%).

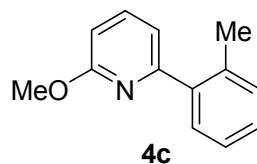
Appendix: (The ¹H-NMR, ¹³C-NMR and LC/MS)



4a: ¹H-NMR (500 MHz, CDCl₃): δ 8.14 (m, 2 H), 7.67 (t, *J*=7.5 Hz, 1H), 7.53 (m, 2H), 7.47 (m, 1H), 7.39 (d, *J*=7.5 Hz, 1H), 6.76 (d, *J*=8.0 Hz, 1H), 4.12 (s, 3H); ¹³C-NMR (150 MHz, CDCl₃): δ 163.7, 154.6, 139.13, 139.05, 128.8, 128.6, 126.7, 112.8, 109.2, 53.2. LC/MS *m/z*: 186.12 (M+H).

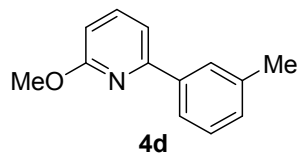


4b: ¹H-NMR (500 MHz, CDCl₃): δ 8.08 (dd, *J*=2.0, 7.0 Hz, 2H), 7.62 (t, *J*=7.5 Hz, 1H), 7.31 (d, *J*=7.0 Hz, 1H), 7.04 (dd, *J*=2.0, 7.0 Hz, 2H), 6.69 (d, *J*=8.0 Hz, 1H), 4.10 (s, 3H), 3.89 (s, 3H); ¹³C-NMR (125 MHz, CDCl₃): δ 163.9, 160.6, 154.7, 139.4, 132.0, 128.2, 114.2, 112.2, 108.6, 55.6, 53.4. LC/MS *m/z*: 216.10 (M+H).

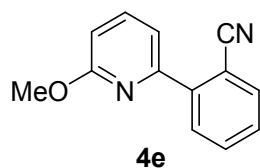


4c: ¹H-NMR (500 MHz, CDCl₃): δ 7.67 (t, *J*=8.0 Hz, 1H), 7.51 (d, *J*=6.5 Hz, 1H), 7.34 (m, 3H), 7.05 (d, *J*=7.0 Hz, 1H), 6.76 (d, *J*=8.0 Hz, 1H), 4.03 (s, 3H), 2.52 (s, 3H); ¹³C-NMR (125 MHz, CDCl₃): δ

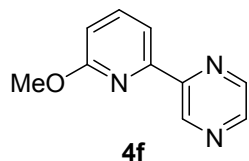
163.5, 157.9, 140.4, 138.9, 136.5, 131.2, 130.0, 128.4, 126.1, 117.0, 109.0, 53.6, 21.1. LC/MS m/z: 200.18 (M+H).



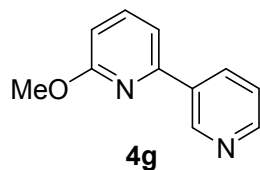
4d: $^1\text{H-NMR}$ (500 MHz, CDCl_3): δ 7.94 (s, 1H), 7.91 (d, $J=8.0$ Hz, 1H), 7.66 (t, $J=8.0$ Hz, 1H), 7.41 (m, 2H), 7.27 (d, $J=7.0$ Hz, 1H), 6.74 (d, $J=8.0$ Hz, 1H), 4.12 (s, 3H), 2.51 (s, 3H); $^{13}\text{C-NMR}$ (125 MHz, CDCl_3): δ 163.7, 154.8, 139.0, 138.1, 129.5, 128.4, 127.3, 123.8, 112.8, 109.0, 53.1, 29.7, 21.5. LC/MS m/z: 200.19 (M+H).



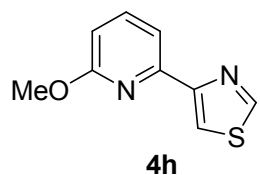
4e: $^1\text{H-NMR}$ (500 MHz, CDCl_3): δ 7.81 (m, 2H), 7.68 (m, 2H), 7.46 (t, $J=7.5$ Hz, 1H), 7.31 (d, $J=7.5$ Hz, 1H), 6.79 (d, $J=8.5$ Hz, 1H), 4.10 (s, 3H); $^{13}\text{C-NMR}$ (125 MHz, CDCl_3): δ 163.6, 152.3, 142.7, 139.0, 134.5, 132.4, 129.2, 128.4, 119.1, 115.1, 110.8, 53.8. LC/MS m/z: 211.15 (M+H).



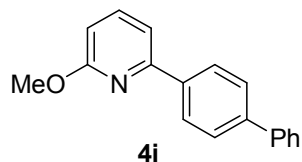
4f: $^1\text{H-NMR}$ (500 MHz, CDCl_3): δ 9.59 (d, $J=1.5$ Hz, 1H), 8.55 (m, 2H), 7.93 (d, $J=7.5$ Hz, 1H), 7.68 (t, $J=8.0$ Hz, 1H), 6.79 (d, $J=8.5$ Hz, 1H), 4.02 (s, 3H); $^{13}\text{C-NMR}$ (125 MHz, CDCl_3): δ 163.8, 151.6, 151.2, 144.4, 143.7, 143.5, 139.6, 114.4, 112.4, 53.6. LC/MS m/z: 188.15 (M+H).



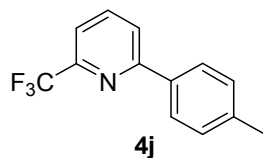
4g: $^1\text{H-NMR}$ (500 MHz, CDCl_3): δ 9.22 (s, 1H), 8.58 (d, $J=4.5$ Hz, 1H), 8.28 (dt, $J=2.0, 8.0$ Hz, 1H), 7.60 (t, $J=7.5$ Hz, 1H), 7.33 (m, 2H), 6.70 (d, $J=8.5$ Hz, 1H), 3.99 (s, 3H); $^{13}\text{C-NMR}$ (125 MHz, CDCl_3): δ 164.2, 152.1, 149.9, 148.4, 139.5, 134.7, 134.2, 123.7, 113.1, 110.5, 53.5. LC/MS m/z: 187.19 (M+H).



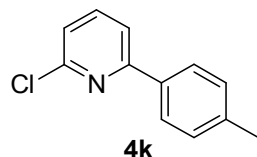
4h: $^1\text{H-NMR}$ (600 MHz, CDCl_3): δ 8.85 (d, $J=2.4$ Hz, 1H), 8.10 (d, $J=1.8$ Hz, 1H), 7.74 (d, $J=7.8$ Hz, 1H), 7.66 (t, $J=7.8$ Hz, 1H), 6.70 (d, $J=7.8$ Hz, 1H), 4.01 (s, 3H); $^{13}\text{C-NMR}$ (150 MHz, CDCl_3): δ 163.6, 156.4, 152.8, 149.7, 139.4, 116.5, 113.7, 110.2, 53.1. LC/MS m/z : 193.12 (M+H).



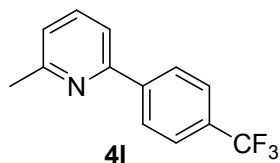
4i: $^1\text{H-NMR}$ (500 MHz, CDCl_3): δ 8.17 (d, $J=8.5$ Hz, 2H), 7.70 (m, 6H), 7.52 (m, 2H), 7.42 (m, 2H), 4.10 (s, 3H); $^{13}\text{C-NMR}$ (125 MHz, CDCl_3): δ 164.1, 154.6, 141.9, 141.0, 139.5, 138.3, 129.2, 127.8, 127.6, 127.45, 127.40, 113.1, 109.6, 53.5. LC/MS m/z : 262.18 (M+H).



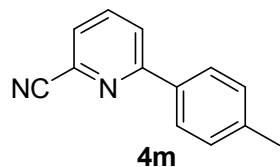
4j: $^1\text{H-NMR}$ (500 MHz, CDCl_3): δ 8.01 (d, $J=8.0$ Hz, 2H), 7.90 (d, $J=3.5$ Hz, 2H), 7.60 (t, $J=4.5$ Hz, 1H), 7.33 (d, $J=8.0$ Hz, 2H), 2.46 (s, 3H); $^{13}\text{C-NMR}$ (125 MHz, CDCl_3): δ 157.7, 147.9, 139.9, 137.9, 134.9, 129.5, 126.9, 122.3, 118.05, 118.03, 21.1. LC/MS m/z : 238.02 (M+H).



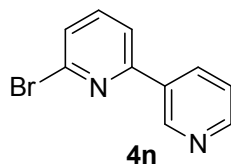
4k: $^1\text{H-NMR}$ (500 MHz, CDCl_3): δ 7.92 (d, $J=8.0$ Hz, 2H), 7.70 (t, $J=8.0$ Hz, 1H), 7.64 (d, $J=7.5$ Hz, 1H), 7.29 (d, $J=8.0$ Hz, 2H), 7.26 (d, $J=7.5$ Hz, 1H), 2.43 (s, 3H); $^{13}\text{C-NMR}$ (150 MHz, CDCl_3): δ 158.1, 139.7, 139.2, 134.9, 129.5, 126.8, 124.8, 122.1, 118.2, 21.3. LC/MS m/z : 204.19 (M+H).



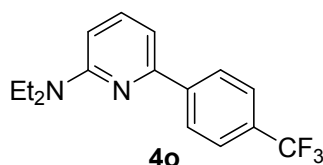
4l: $^1\text{H-NMR}$ (600 MHz, CDCl_3): δ 8.10 (d, $J=7.8$ Hz, 2H), 7.71 (d, $J=8.4$ Hz, 2H), 7.67 (t, $J=7.8$ Hz, 1H), 7.54 (d, $J=7.8$ Hz, 1H), 7.16 (d, $J=7.8$ Hz, 1H); $^{13}\text{C-NMR}$ (150 MHz, CDCl_3): δ 159.0, 155.6, 143.3, 137.3, 130.7, 127.5, 125.9, 125.8, 122.7, 118.2, 24.9. LC/MS m/z : 238.17 (M+H).



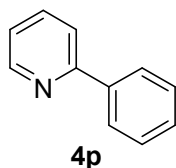
4m: $^1\text{H-NMR}$ (500 MHz, CDCl_3): δ 7.96 (m, 3H), 7.90 (t, $J=7.5$ Hz, 1H), 7.62 (d, $J=7.5$ Hz, 1H), 7.33 (d, $J=8.0$ Hz, 2H), 2.46 (s, 3H); $^{13}\text{C-NMR}$ (125 MHz, CDCl_3): δ 158.9, 140.4, 137.5, 134.3, 133.6, 129.7, 126.9, 126.2, 123.1, 117.4, 21.3. LC/MS m/z : 195.02 (M+H).



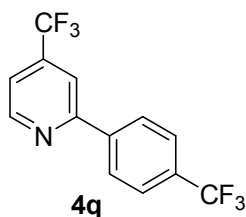
4n: $^1\text{H-NMR}$ (600 MHz, CDCl_3): δ 9.14 (d, $J=1.8$ Hz, 1H), 8.64 (m, 1H), 8.30 (m, 1H), 7.69 (d, $J=7.8$ Hz, 1H), 7.62 (t, $J=7.8$ Hz, 1H), 7.45 (d, $J=7.8$ Hz, 1H), 7.38 (dd, $J=4.8, 7.8$ Hz, 1H); $^{13}\text{C-NMR}$ (150 MHz, CDCl_3): δ 156.1, 150.7, 148.3, 142.8, 139.5, 134.8, 133.5, 127.4, 123.9, 119.3. LC/MS m/z : 237.04(M+H).



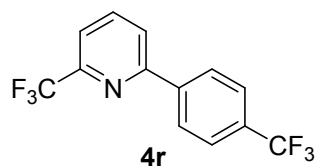
4o: $^1\text{H-NMR}$ (600 MHz, CDCl_3): δ 8.14 (d, $J=8.4$ Hz, 2H), 7.68 (d, $J=8.4$ Hz, 2H), 7.51 (t, $J=7.8$ Hz, 1H), 7.01 (d, $J=7.2$ Hz, 1H), 6.49 (d, $J=8.4$ Hz, 1H), 3.61 (q, $J=7.2$ Hz, 4H), 1.24 (t, $J=6.9$ Hz, 6H); $^{13}\text{C-NMR}$ (150 MHz, CDCl_3): δ 157.5, 153.8, 143.9, 138.1, 130.2, 127.1, 125.6, 125.5, 107.8, 105.2, 42.8, 13.2. LC/MS m/z : 295.18 (M+H).



4p: $^1\text{H-NMR}$ (500 MHz, CDCl_3): δ 8.72 (d, $J=4.5$ Hz, 1H), 8.03 (d, $J=7.0$ Hz, 2H), 7.73 (d, $J=3.5$ Hz, 2H), 7.50 (t, $J=7.0$ Hz, 2H), 7.44 (t, $J=7.0$ Hz, 1H), 7.22 (q, $J=4.5$ Hz, 1H); $^{13}\text{C-NMR}$ (150 MHz, CDCl_3): δ 157.7, 149.9, 139.7, 137.0, 129.2, 129.0, 127.2, 122.4, 120.8. LC/MS m/z : 156.17 (M+H).



4q: $^1\text{H-NMR}$ (500 MHz, CDCl_3): δ 8.89 (d, $J=2.5$ Hz, 1H), 8.14 (d, $J=8.0$ Hz, 2H), 7.95 (s, 1H), 7.74 (d, $J=8.5$ Hz, 2H), 7.51 (d, $J=2.5$ Hz, 1H); $^{13}\text{C-NMR}$ (150 MHz, CDCl_3): δ 157.2, 150.9, 141.2, 139.4, 131.6, 127.4, 125.94, 125.89, 125.87, 118.4, 116.3; LC/MS m/z : 292.12 (M+H).

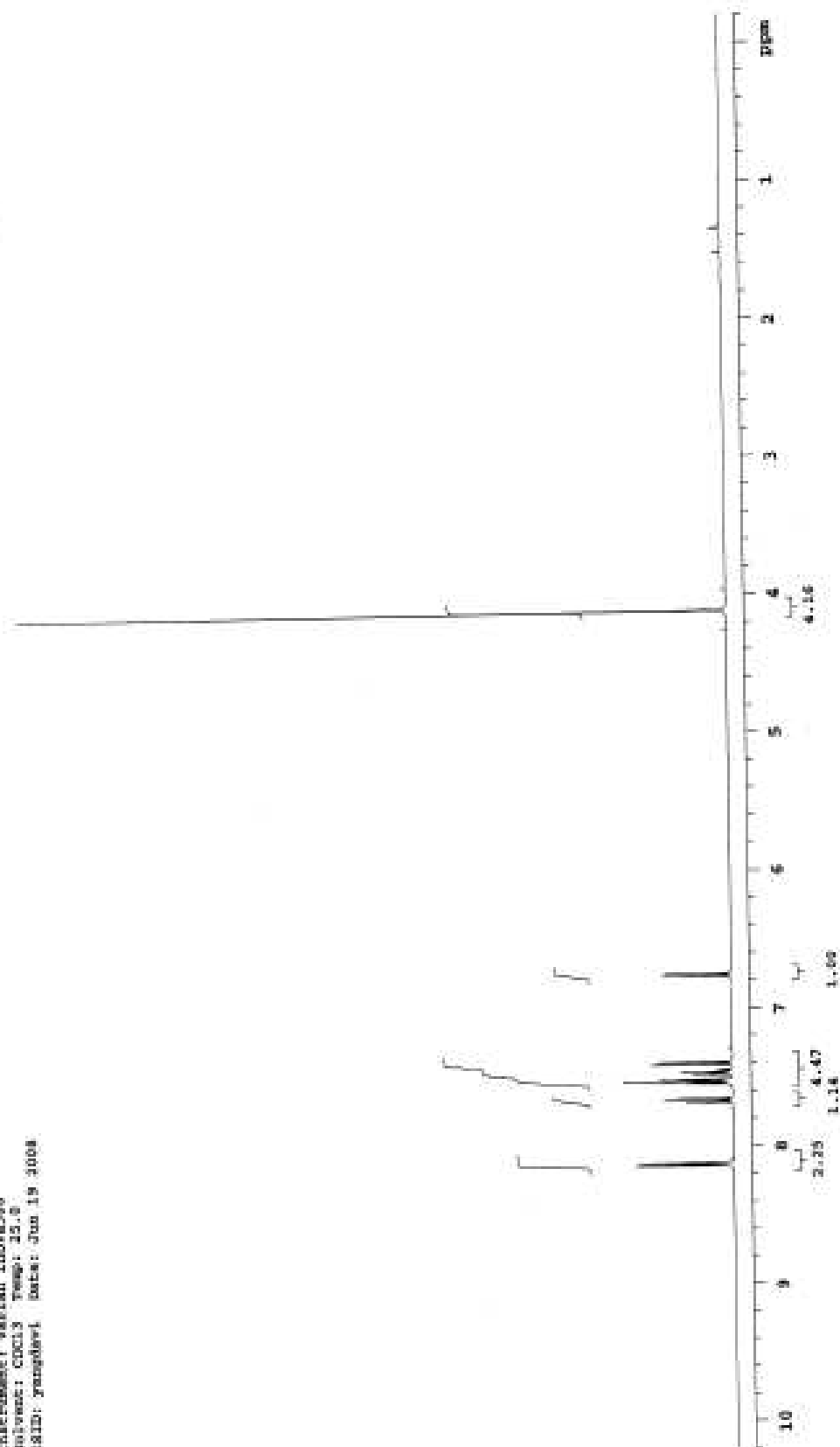


4r: ^1H -NMR (600 MHz, CDCl_3): δ 8.18 (d, $J=7.8$ Hz, 2H), 7.97 (m, 2H), 7.75 (d, $J=7.8$ Hz, 2H), 7.68 (m, 1H); ^{13}C -NMR (150 MHz, CDCl_3): δ 156.5, 148.7, 141.2, 138.7, 131.8, 127.7, 126.1, 126.0, 123.3, 119.64, 119.63. LC/MS m/z : 292.19 (M+H).

Appendix: (^1H - and LC/MS spectra)

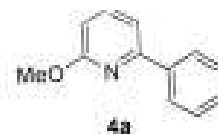


400. Spectrus: xl
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 FID: yangdavi Date: Jun 19 2008



Openlynx Report - Yang, David x47098 (yangdavi)
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ID:1
 Time:09:02

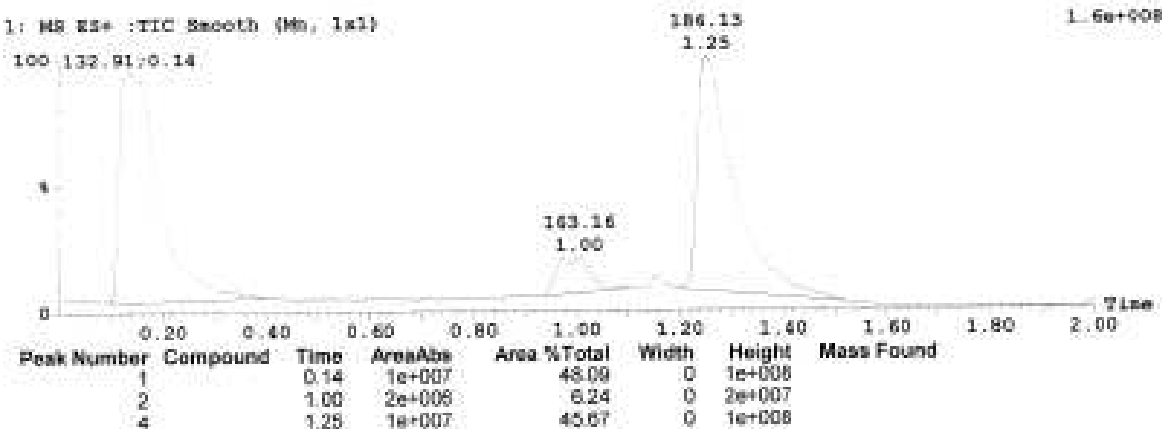


Printed: Thu Jun 19 09:15:23 2008

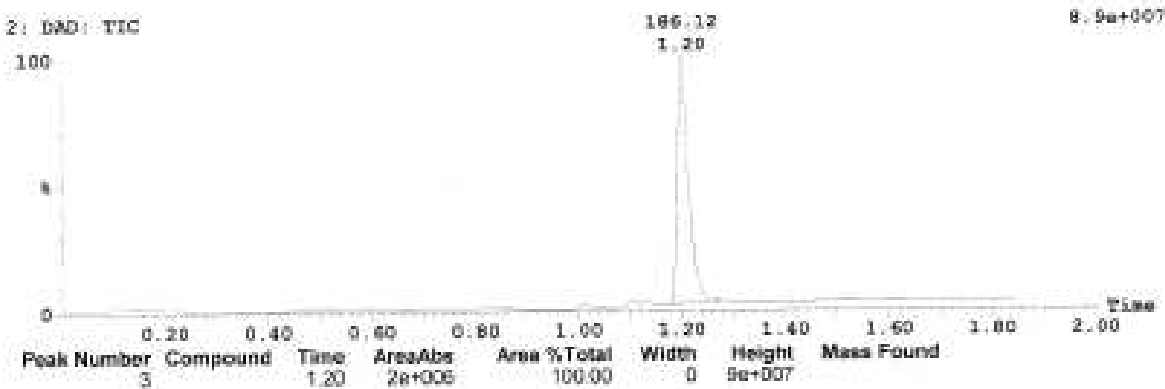
Sample Report (continued):

Sample 2 Vial 1:57 ID:1 File 20082Q_15268 Date 19-Jun-2008 Time 09:02:28 Description

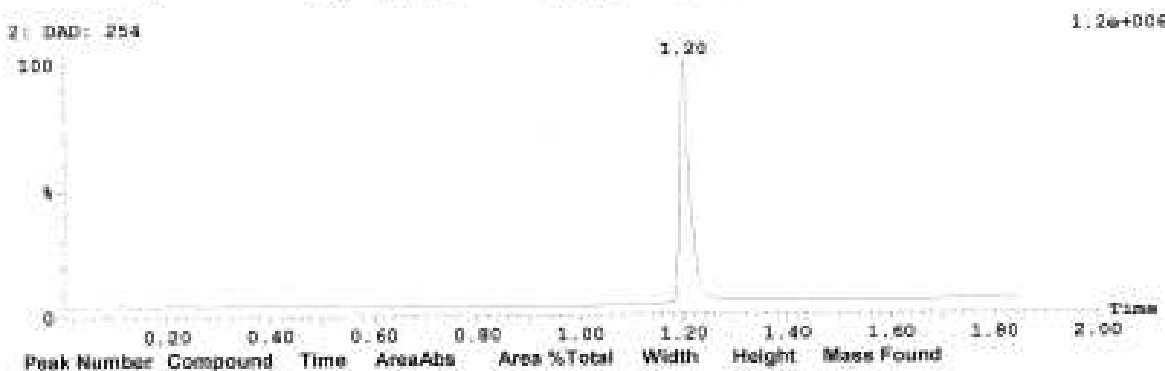
1: MS ES+ :TIC Smooth (Mn, 1x1)



2: DAD: TIC

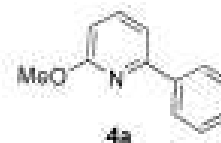


3: DAD: 254



Openlynx Report - Yang, David x47096 (yangdavi)
Sample: 2 Vial: 167
File: 200820_15268 Date: 19-Jun-2008
Description:

ID: 1
Time: 09:02:28



Printed: Thu Jun 19 09:15:23 2008

Sample Report (continued):

Peak ID	Compound	Time	Mass Found
1		0.14	

(Time: 0.14) Combine (21:37) 1:MS ES+ 9.7e+007



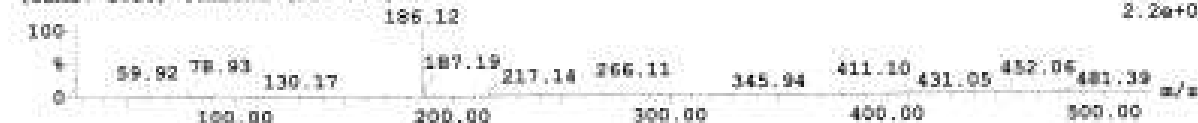
Peak ID	Compound	Time	Mass Found
2		1.00	

(Time: 1.00) Combine (192:208) 1:MS ES+ 4.3e+006



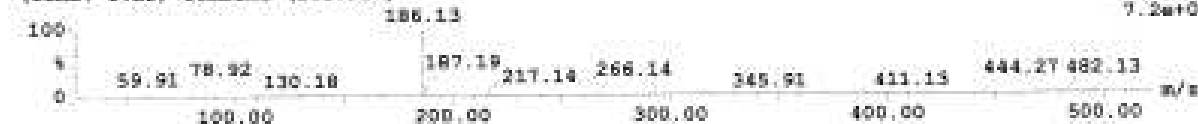
Peak ID	Compound	Time	Mass Found
3		1.20	

(Time: 1.20) Combine (231:246) 1:MS ES+ 2.2e+007

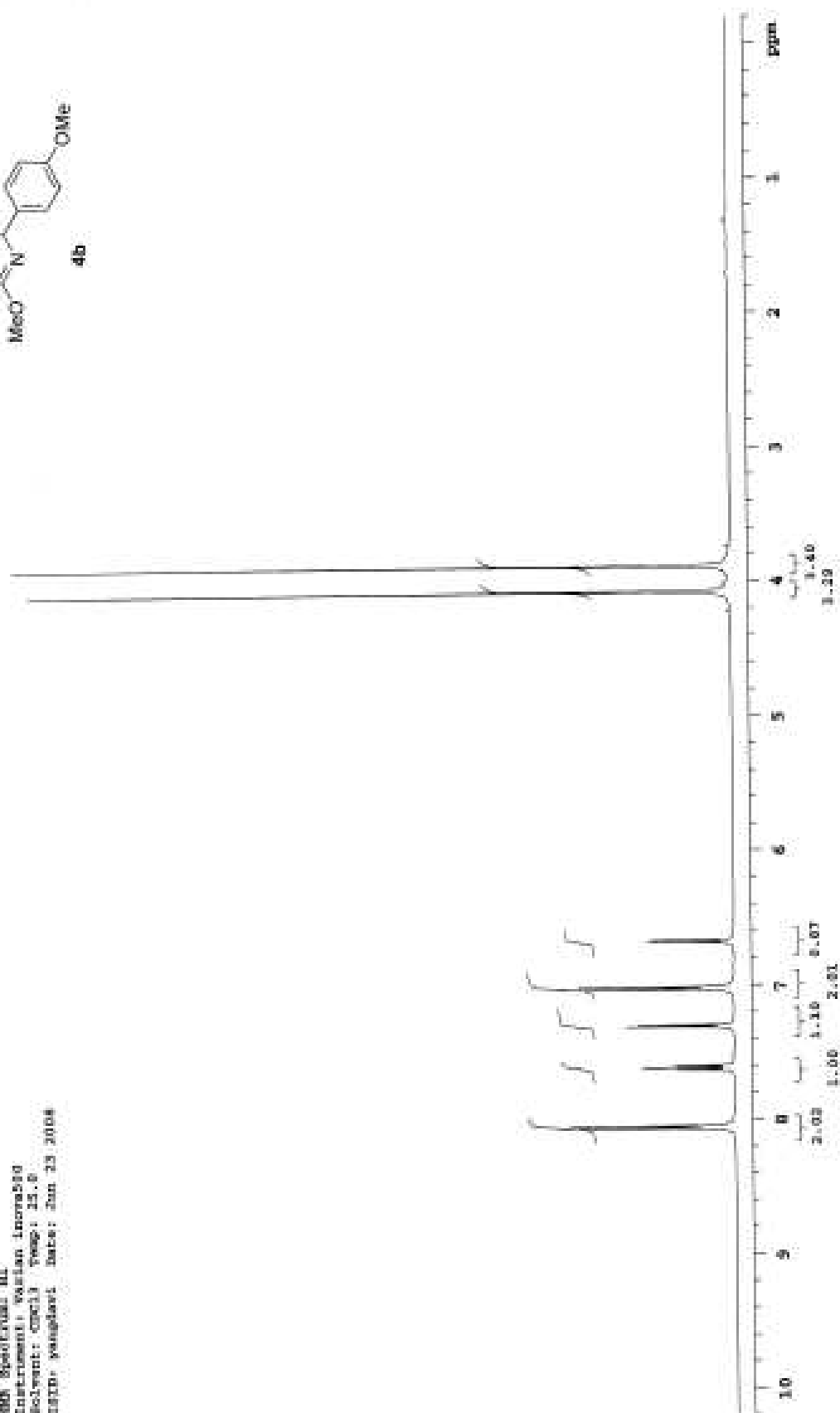
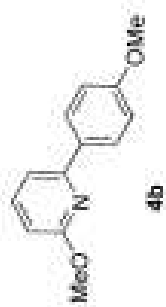


Peak ID	Compound	Time	Mass Found
4		1.25	

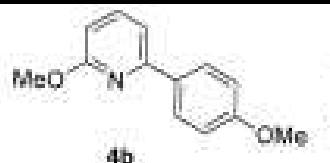
(Time: 1.25) Combine (241:257) 1:MS ES+ 7.2e+007



1H NMR Spectrum: H1
Instrument: Varian Inova500
Solvent: CDCl3 Tmp: 25.0
1370- yanglavl Date: Jun 23 2008



Openlynx Report - Yang, David x47996 (yangdavi)
 Sample: 1 Vial: 122
 File: 20082Q_15323 Date: 20-Jun-2008
 Description:



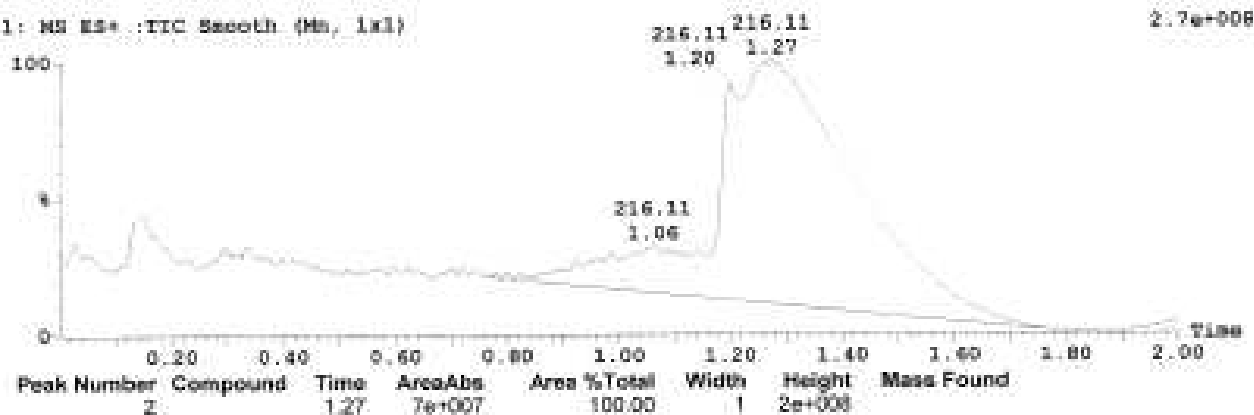
Page 1

Printed: Fri Jun 20 13:30:52 2008

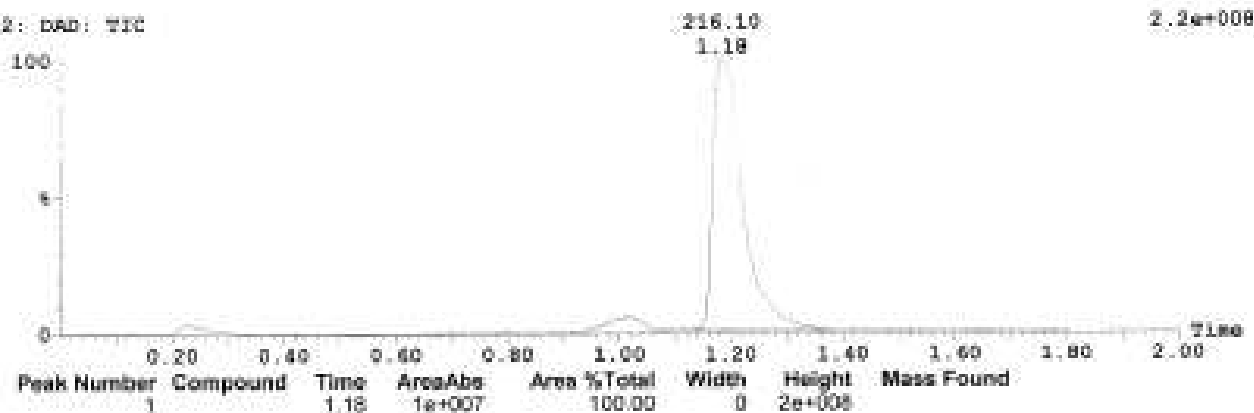
Sample Report:

Sample 1 Vial 1:22 ID RY800-C304_13888-1 File 20082Q_15323 Date 20-Jun-2008 Time 10:57:02 Description

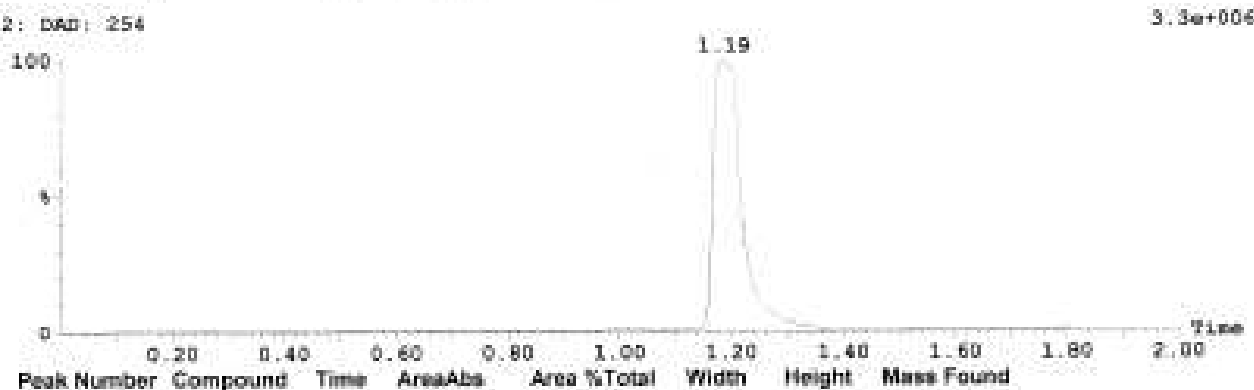
1: MS MS+ :TIC Smooth (Ms, 1x1)



2: DAD: TIC



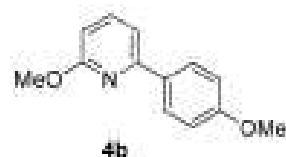
2: DAD: 254



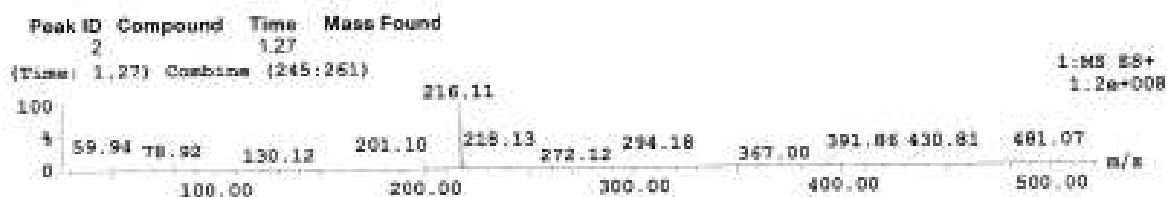
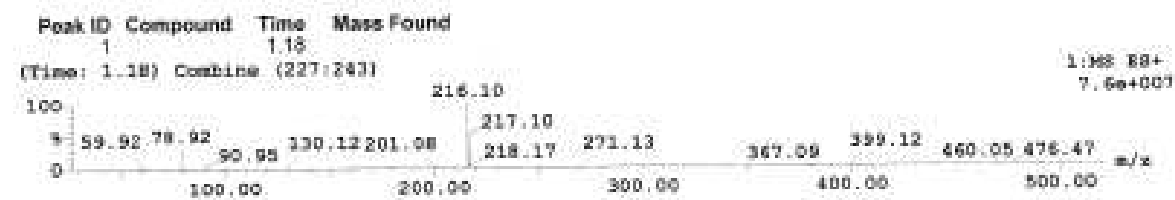
Openlynx Report - Yang, David x47096 (yangdavi)
Sample: 1
File 200820_15323
Description:
Vial 1:22
Date 20-Jun-2008

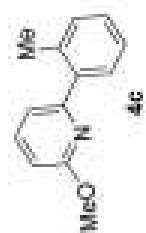
Page 2

Printed: Fri Jun 20 13:30:52 2008

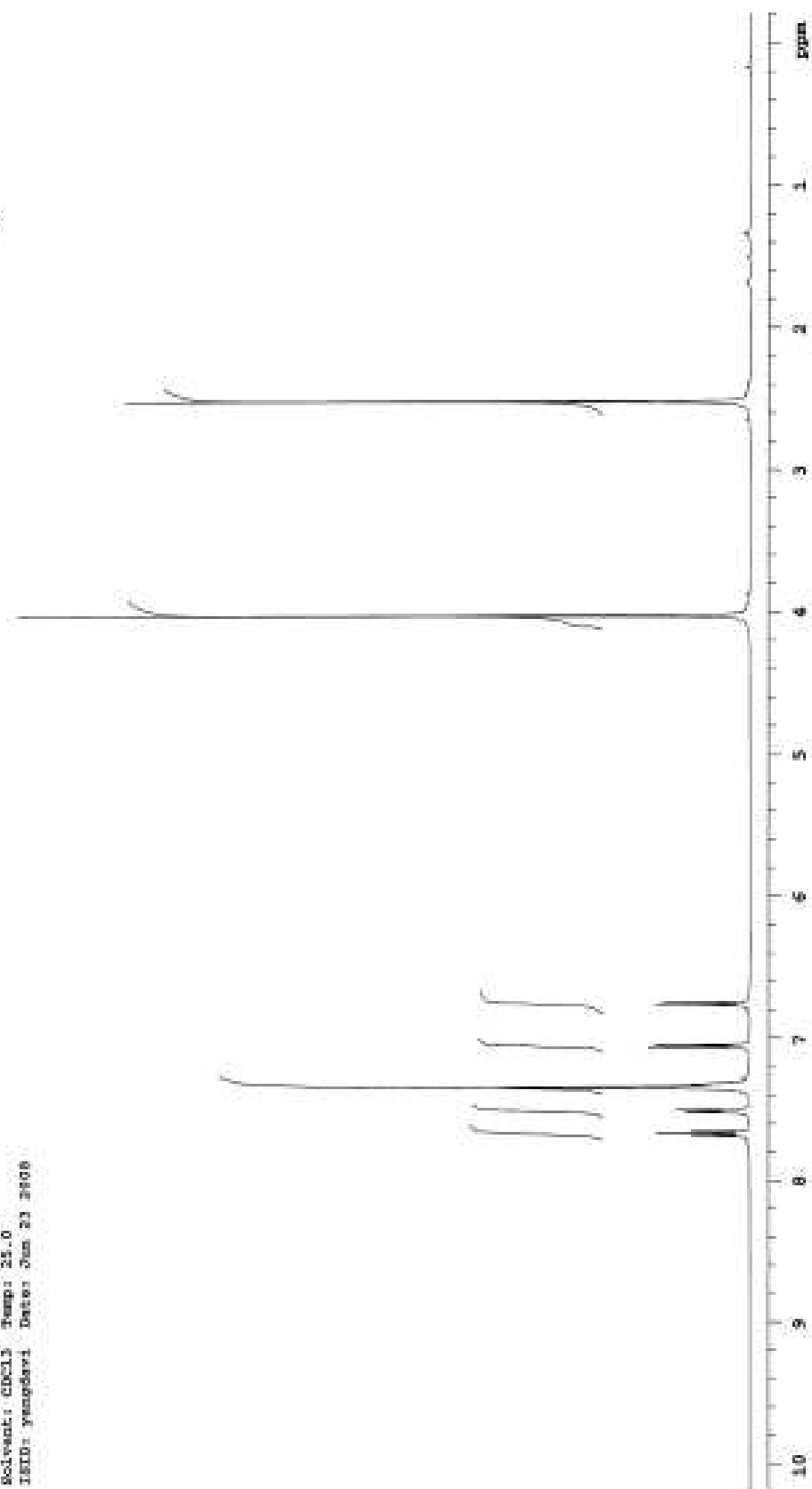


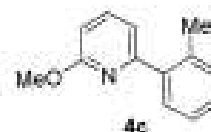
Sample Report (continued):





1H NMR Spectrum: 81
 Instrument: Varian Inova500
 Solvent: CDCl3 Temp: 25.0
 FID: yangdavi Date: Jun 23 2008



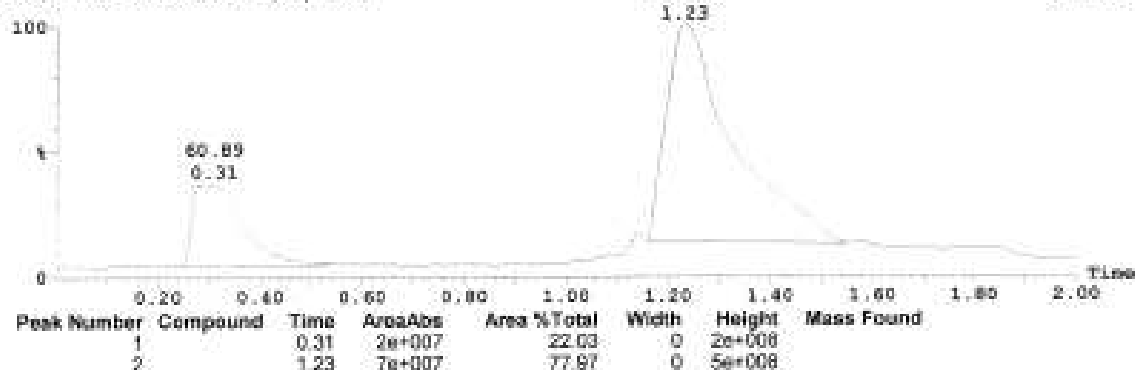


Printed: Fri Jun 20 13:31:09 2008

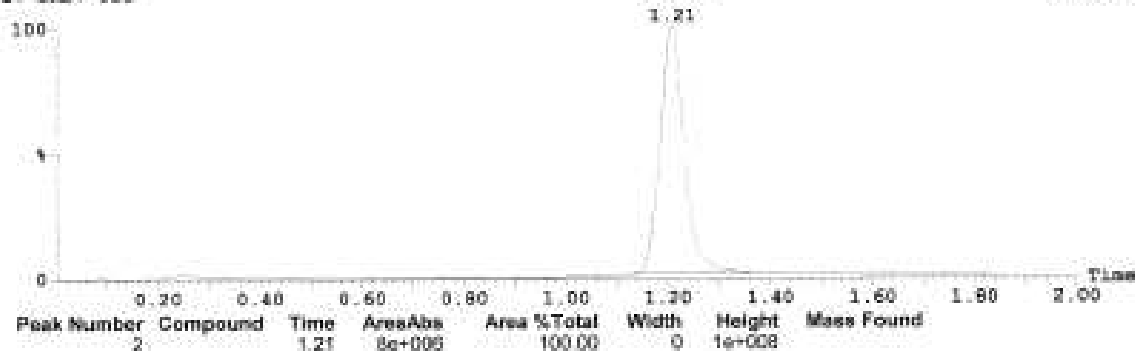
Sample Report:

Sample 1 Vial 1:26 ID RY800-C304_13851-1 File 20082Q_15327 Date 20-Jun-2008 Time 11:39:55 Description

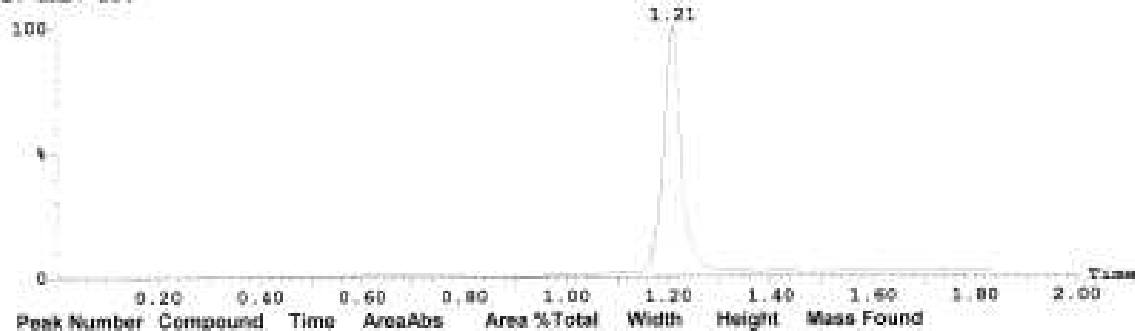
1: MS ES+ :TIC Smooth (Mn, 1x1) 200.18 5.7e+008



2: DAD: TIC 200.18 1.4e+008

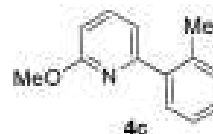


2: DAD: 254 1.21 1.6e+006



Openlynx Report - Yang, David x47096 (yangdevi)
 Sample: 1
 File: 200820_15327
 Description:

Vol: 128
 Date: 20-Jun-2008



Page 2

Printed: Fri Jun 20 13:31:09 2008

Sample Report (continued):

Peak ID	Compound	Time	Mass Found
1		0.31	

(Time: 0.31) Combine (55:71)

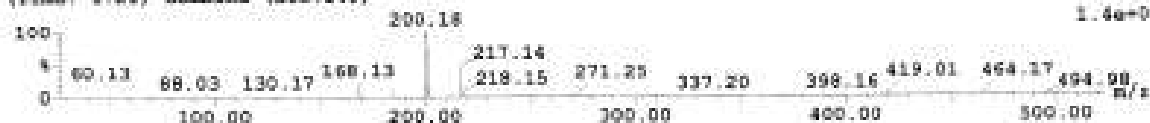
1:MS ES+
1.5e+008

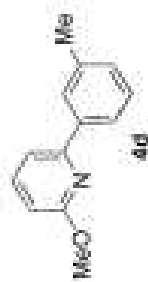


Peak ID	Compound	Time	Mass Found
2		1.23	

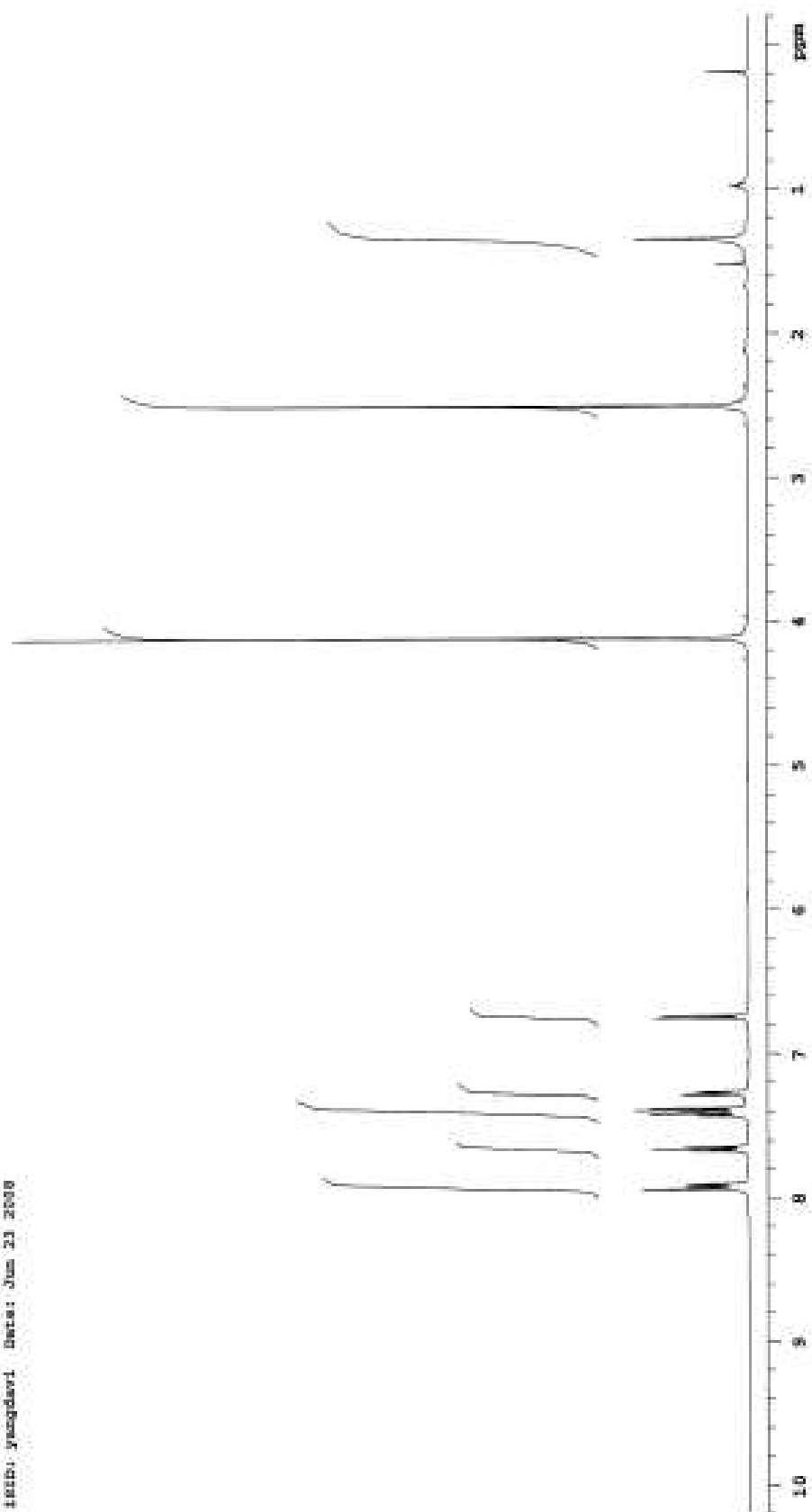
(Time: 1.21) Combine (232:248)

1:MS ES+
1.4e+008

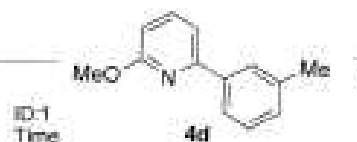




NMR Spectrum: 31
 Instrument: Varian Inova500
 Solvent: CDCl₃ Temp: 25.0
 Date: Jun 23 2008



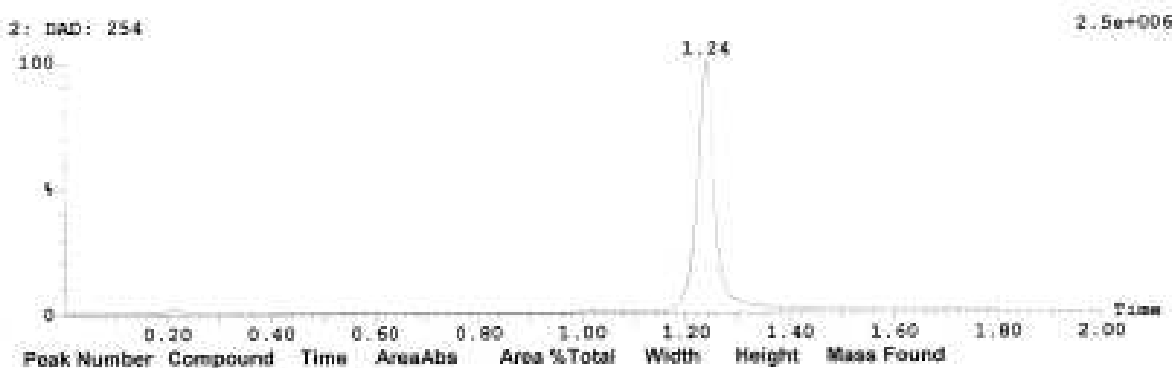
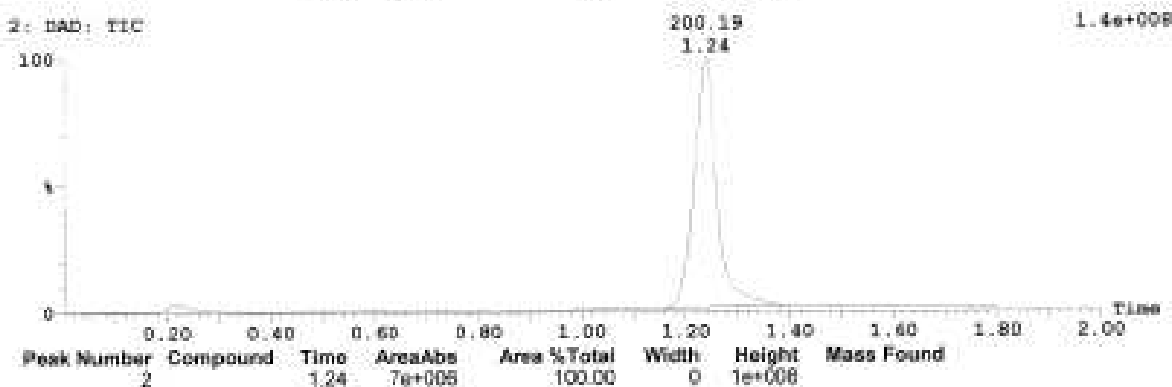
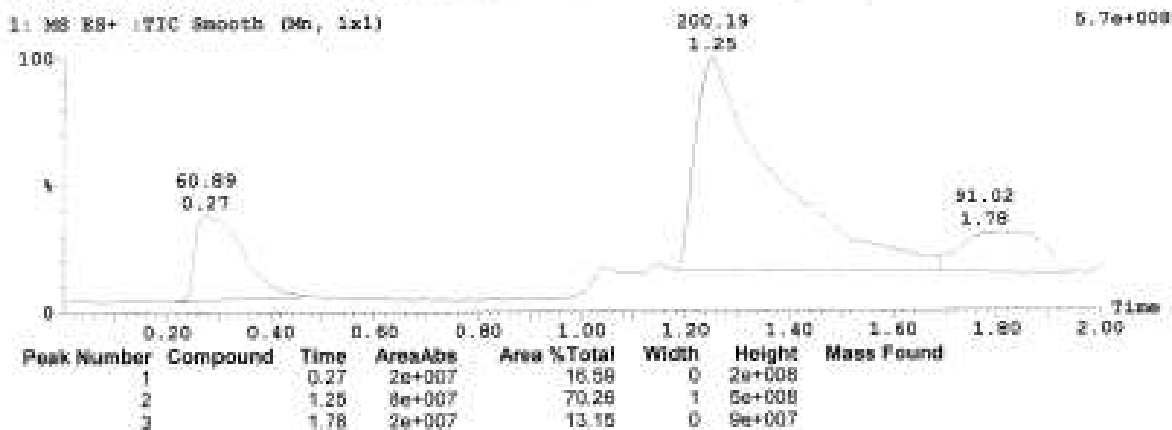
Openlynx Report - Yang, David x47096 (yangdavi)
 Sample: 2 Vial: 1-33
 File: 20082Q_15334 Date: 20-Jun-2008
 Description:



Printed: Fri Jun 20 13:32:29 2008

Sample Report:

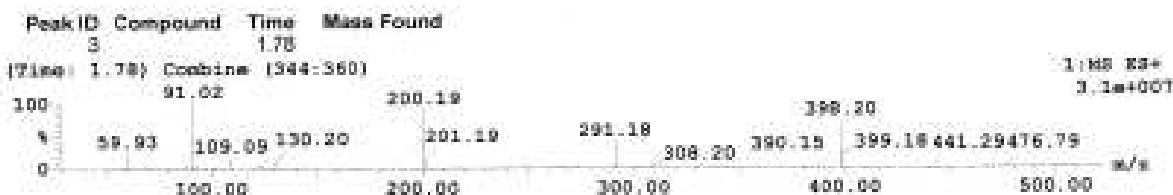
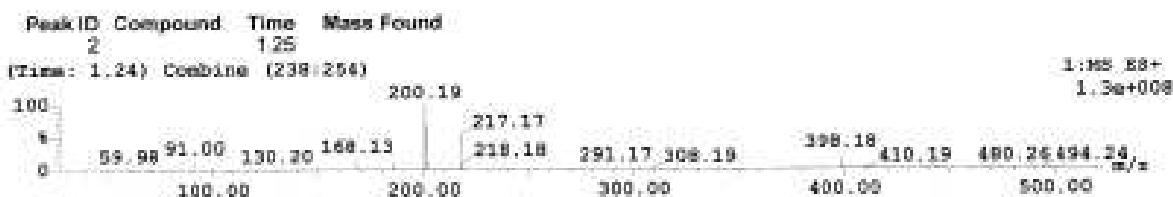
Sample 2 Vial 1:33 ID 1 File 20082Q_15334 Date 20-Jun-2008 Time 12:26:00 Description

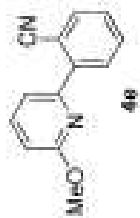




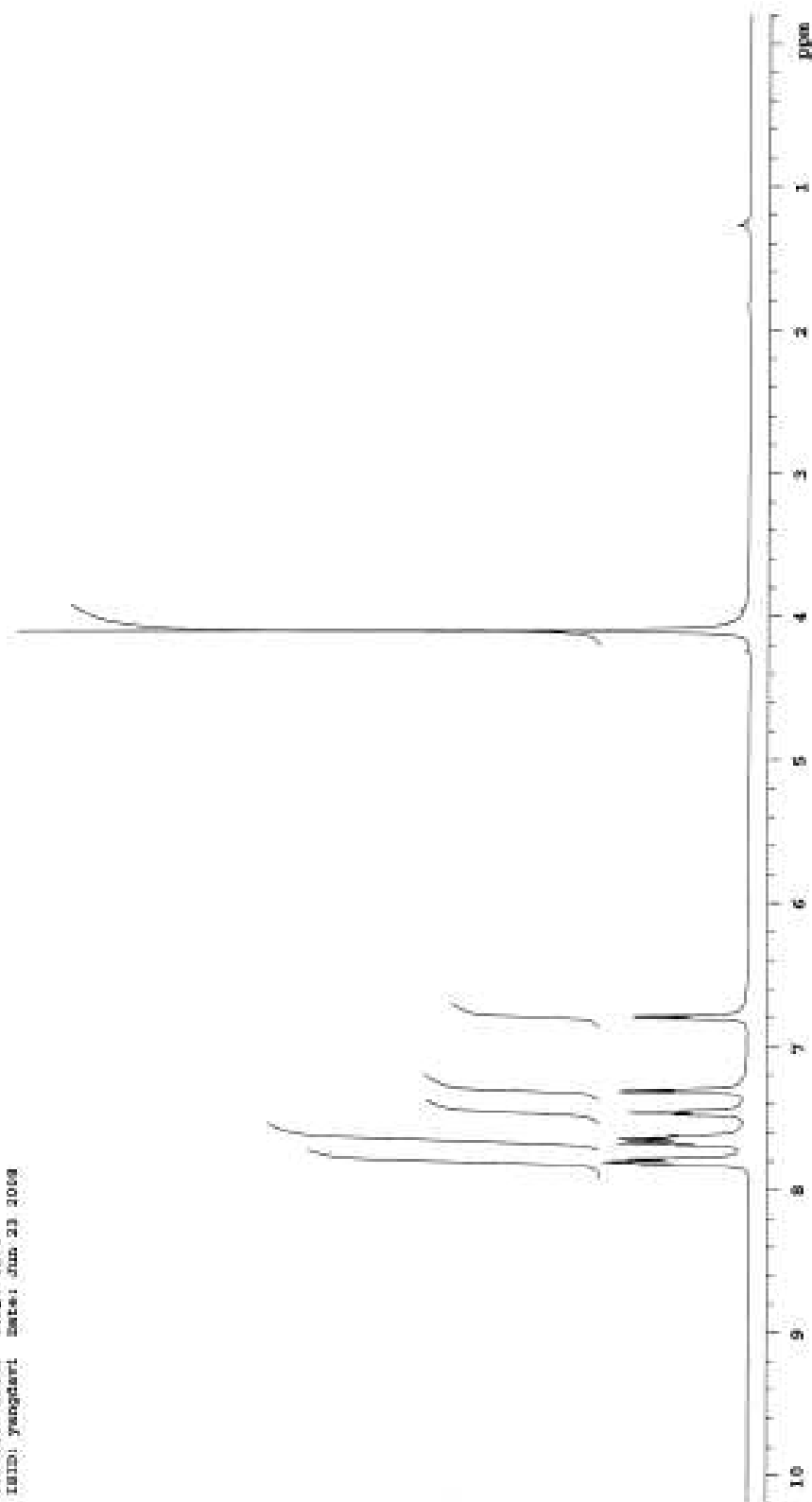
Printed: Fri Jun 20 13:32:29 2008

Sample Report (continued):





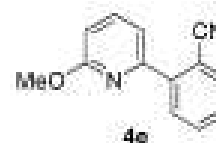
FID Spectrum: III
 Instrument: Varian Inova400
 Solvent: CDCl₃ Temp: 25.5
 ESI: yangdari Date: Jun 23 2009



Openlynx Report - Yang, David x47096 (yangdavi)
 Sample: 1
 File: 20082Q_15343
 Description:

Vial: 1:42
 Date: 20-Jun-2008

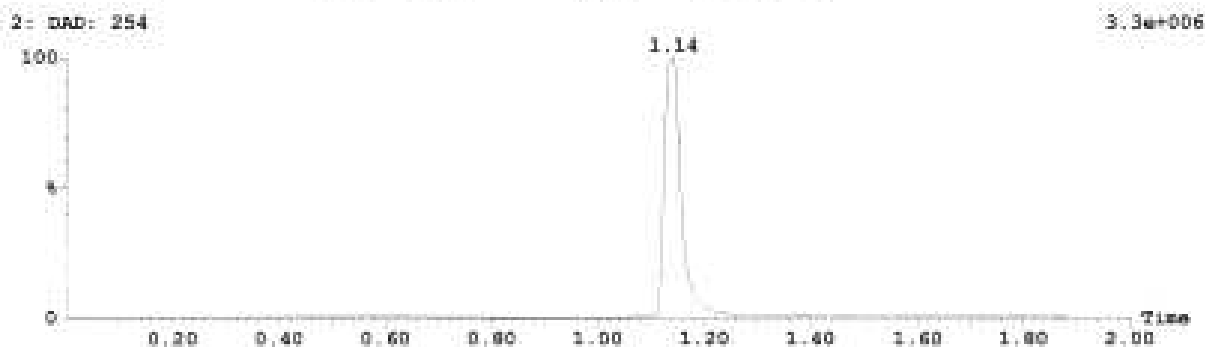
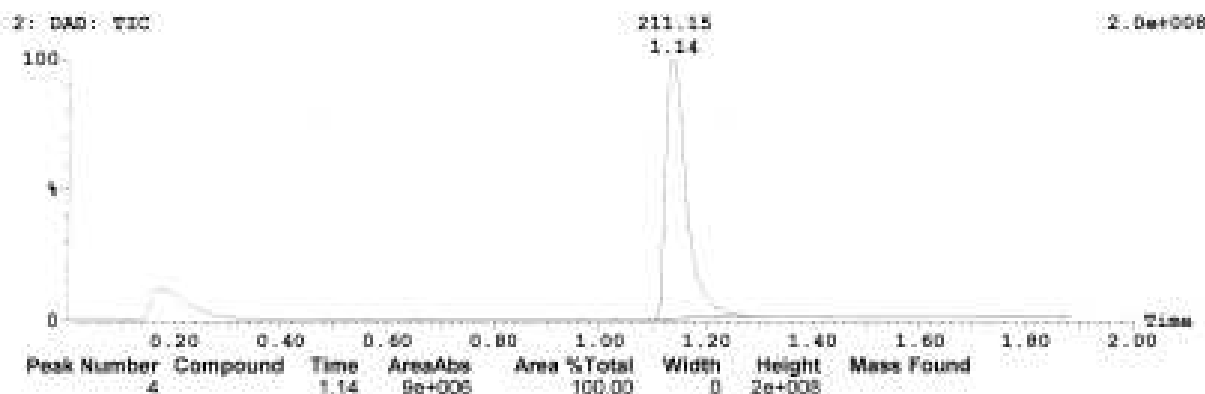
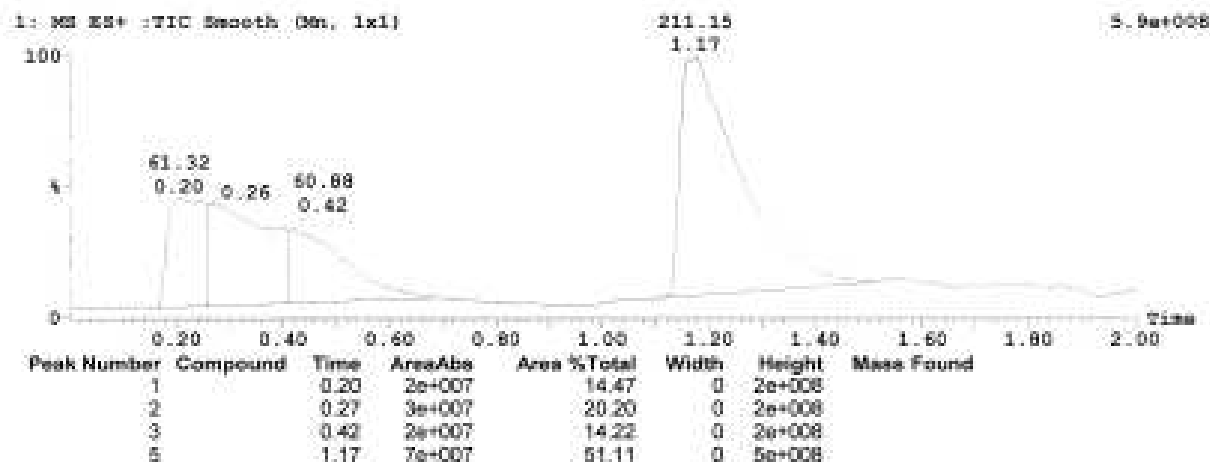
ID: RY800-C304_1
 Time: 13:44:54

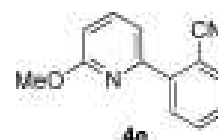


Printed: Fri Jun 20 13:51:50 2008

Sample Report:

Sample 1 Vial 1:42 ID RY800-C304_13873-1 File 20082Q_15343 Date 20-Jun-2008 Time 13:44:54 Description





Printed: Fri Jun 20 13:51:50 2008

Sample Report (continued):

Peak Number	Compound	Time	AreaAbs	Area %Total	Width	Height	Mass Found
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Peak ID	Compound	Time	Mass Found
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1		0.20	
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(Time: 0.20) Combine (34:50)

1:MS ES+

8.3e+007



Peak ID	Compound	Time	Mass Found
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2		0.27	
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(Time: 0.27) Combine (48:64)

1:MS ES+

9.3e+007



Peak ID	Compound	Time	Mass Found
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3		0.42	
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(Time: 0.42) Combine (76:92)

1:MS ES+

1.5e+008



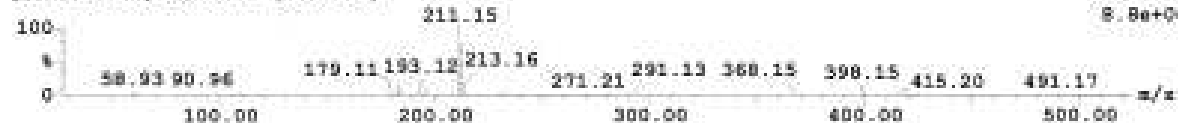
Peak ID	Compound	Time	Mass Found
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4		1.14	
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(Time: 1.14) Combine (218:234)

1:MS ES+

8.8e+007



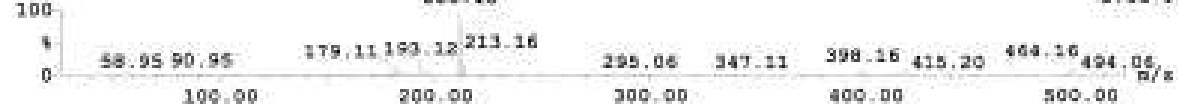
Peak ID	Compound	Time	Mass Found
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5		1.17	
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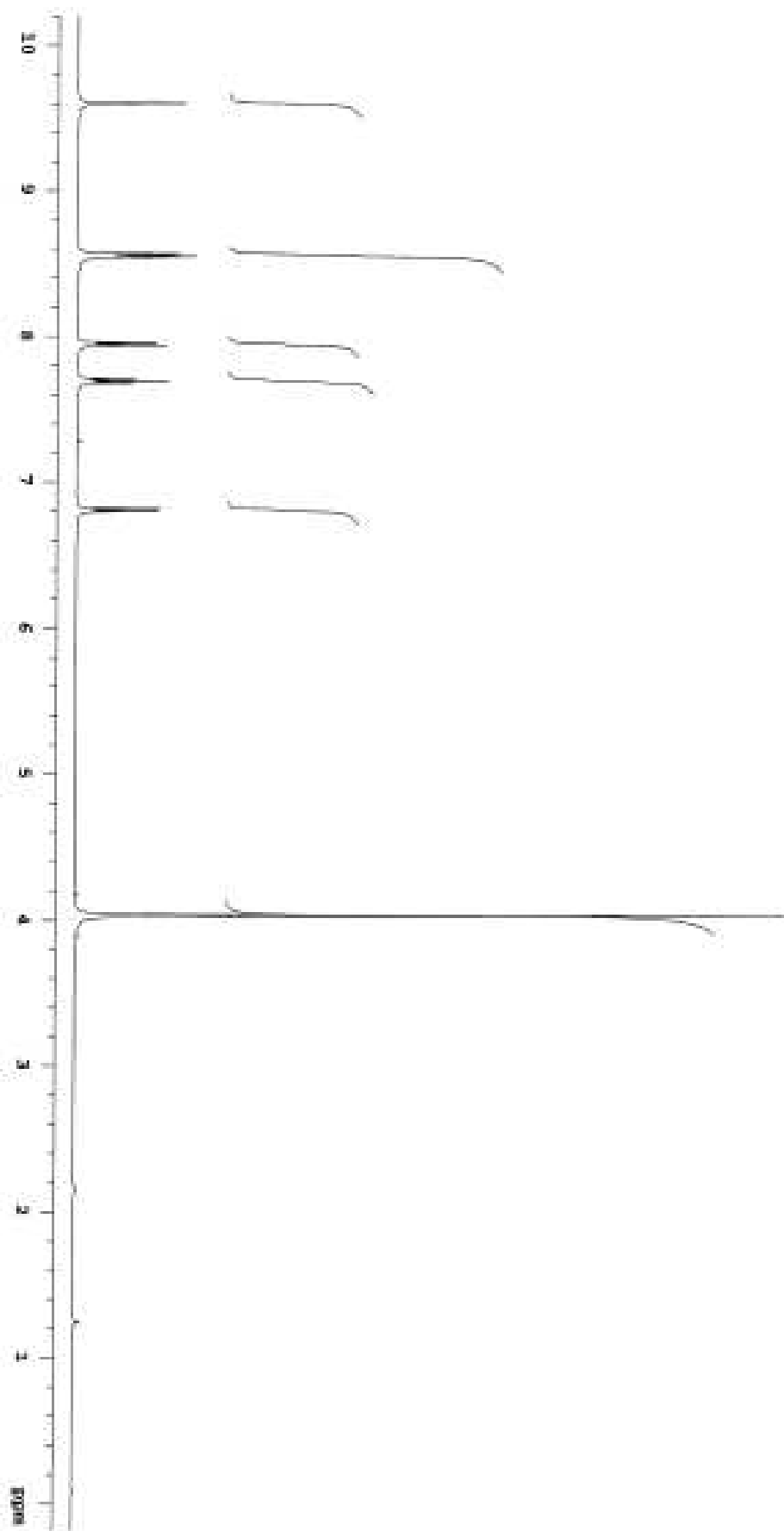
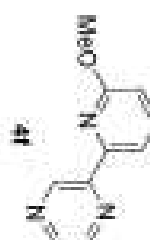
(Time: 1.17) Combine (225:241)

1:MS ES+

1.5e+008

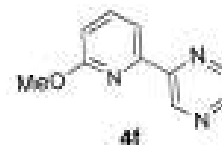


100% Spectrum: 41
 Instrument: Varian Inova500
 Solvent: CDCl₃ Temp: 25.0
 Date: September 16th 2010



Openlynx Report - Yang, David x47096 (yangdavi)
 Sample: 1 Vial: 155
 File: 20082Q_15356 Date: 20-Jun-2008
 Description:

ID: RY800-C304_13881
 Time: 14:44:51

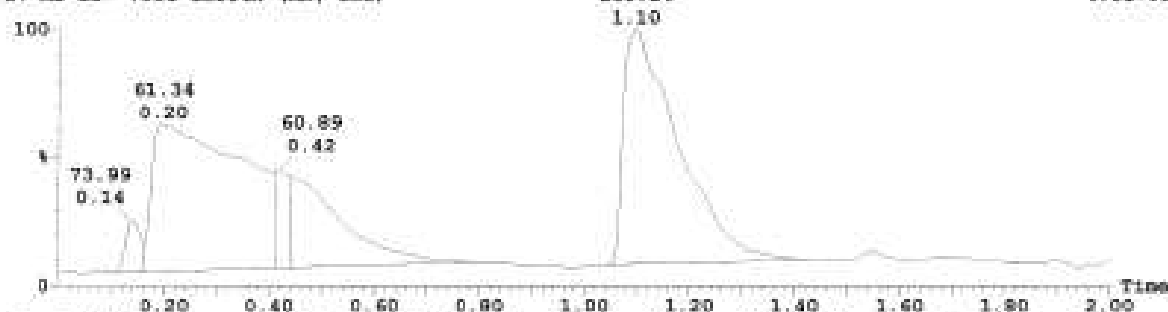


Printed: Fri Jun 20 14:49:04 2008

Sample Report:

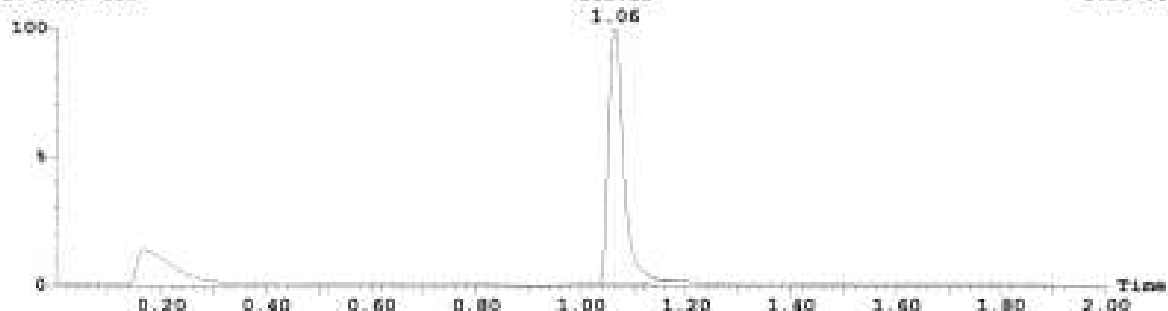
Sample 1 Vial: 155 ID: RY800-C304_13881-1 File: 20082Q_15356 Date: 20-Jun-2008 Time: 14:44:51 Description:

1: MS ES+ (TIC Smooth (Ms, 1x1)) 188.14 4.6e+008



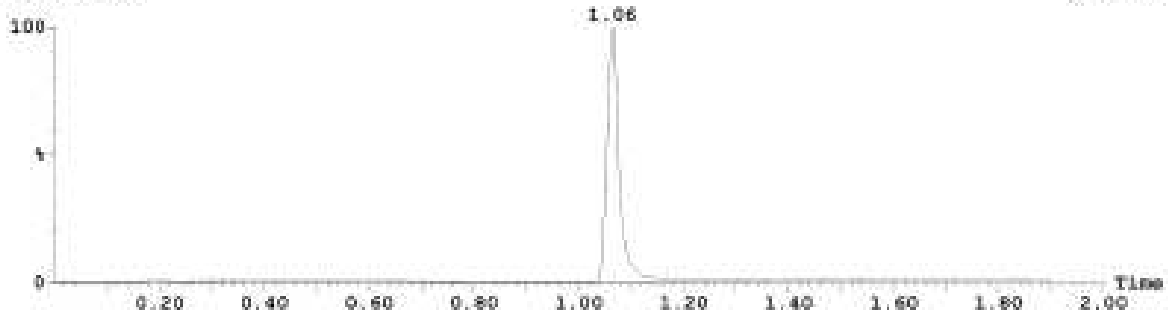
Peak Number	Compound	Time	AreaAbs	Area %Total	Width	Height	Mass Found
1		0.14	3e+006	2.29	0	9e+007	
2		0.20	5e+007	39.39	0	3e+008	
3		0.42	5e+006	4.03	0	2e+008	
4		0.44	2e+007	14.93	0	2e+008	
5		1.10	5e+007	39.35	0	4e+008	

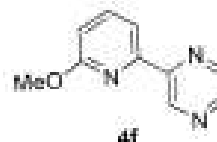
2: DAD: TIC 188.15 1.6e+008



Peak Number	Compound	Time	AreaAbs	Area %Total	Width	Height	Mass Found
5		1.06	6e+006	100.00	0	2e+008	

3: DAD: 254 1.06 2.1e+006





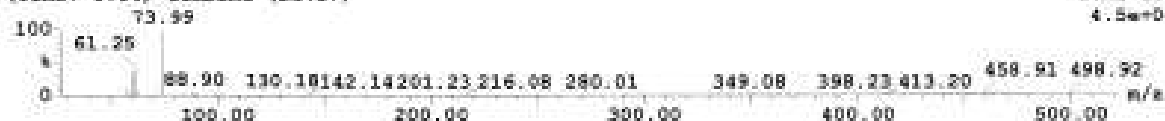
Sample Report (continued):

Peak Number	Compound	Time	AreaAbs	Area %Total	Width	Height	Mass Found
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Peak ID	Compound	Time	Mass Found
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(Time: 0.14) Combine (21:37)

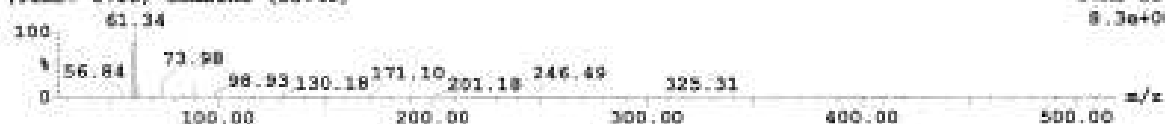
1:MS ES+
4.5e+007



Peak ID	Compound	Time	Mass Found
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(Time: 0.20) Combine (33:49)

1:MS ES+
8.3e+007



Peak ID	Compound	Time	Mass Found
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(Time: 0.42) Combine (77:93)

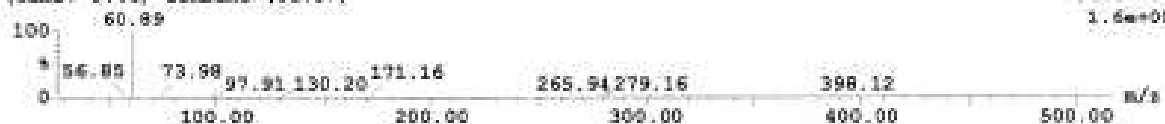
1:MS ES+
1.6e+008



Peak ID	Compound	Time	Mass Found
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(Time: 0.44) Combine (81:97)

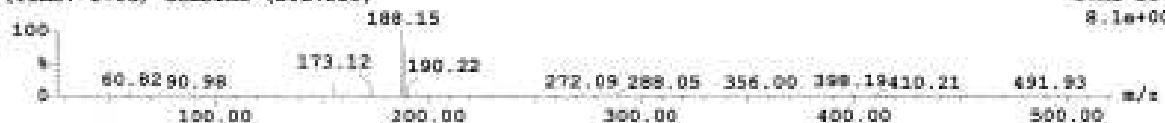
1:MS ES+
1.6e+008



Peak ID	Compound	Time	Mass Found
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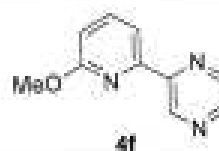
(Time: 1.06) Combine (203:219)

1:MS ES+
8.1e+007



Openlynx Report - Yang, David x47098 (yangdavi)
Sample: 1
File 200820_15356
Description:

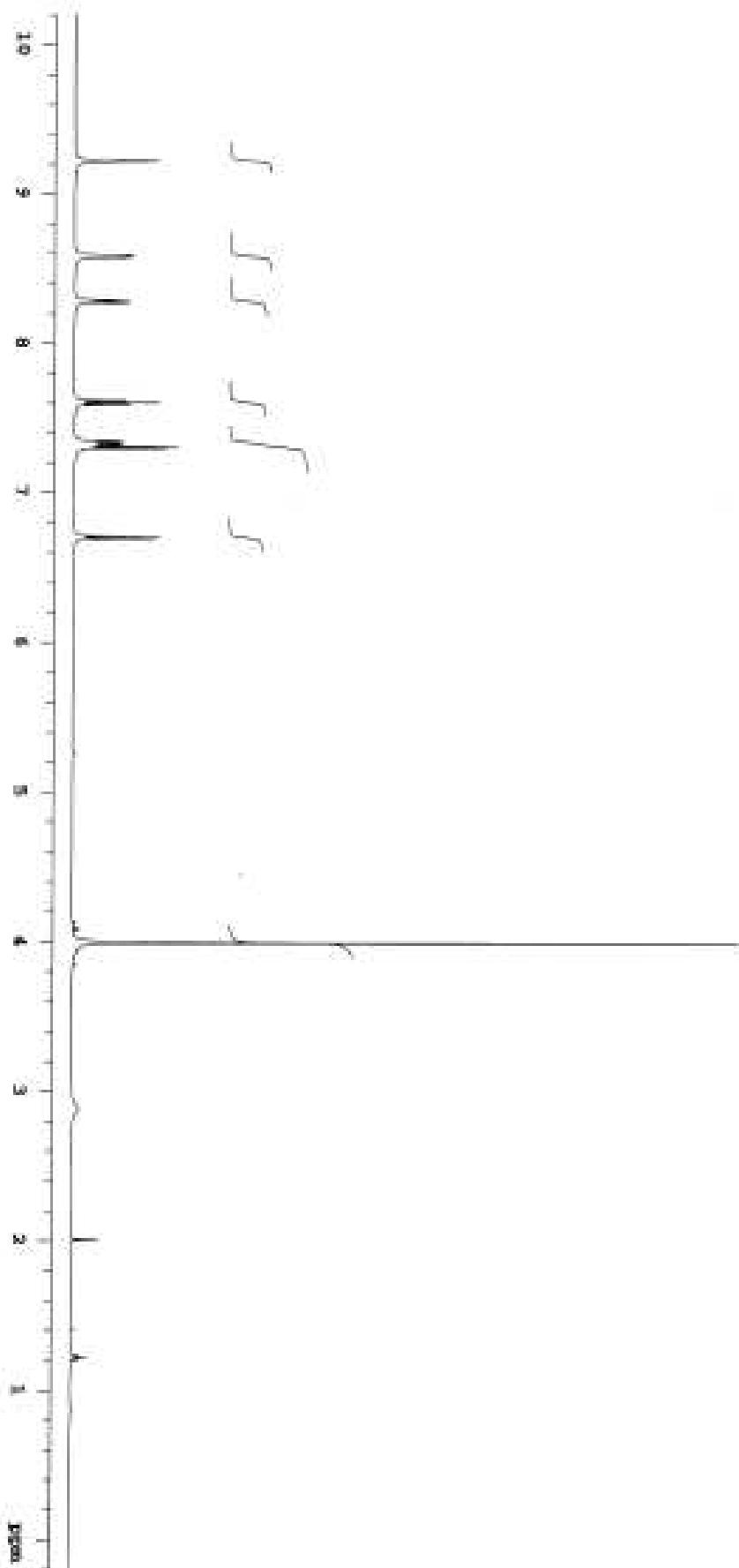
Page 3



Printed: Fri Jun 20 14:48:04 2008

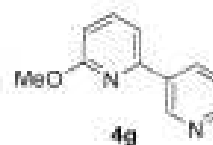
Sample Report (continued):



COC1=CC=C(C=C1)N2C=CC=CC=C2N3C=CC=CC=C3

Openlynx Report - Yang, David x47096 (yangdavi)
 Sample: 1
 File: 2008ZQ_15370
 Description:

ID: RY800-C304
 Time: 16:15:08



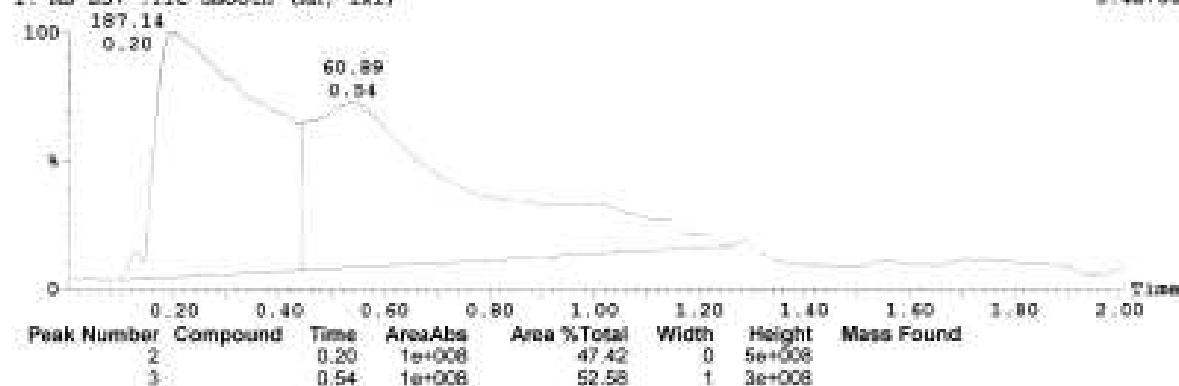
Printed: Fri Jun 20 16:18:28 2008

Sample Report:

Sample 1 Vial 1:69 ID RY800-C304_13890-1 File 2008ZQ_15370 Date 20-Jun-2008 Time 16:15:08 Description

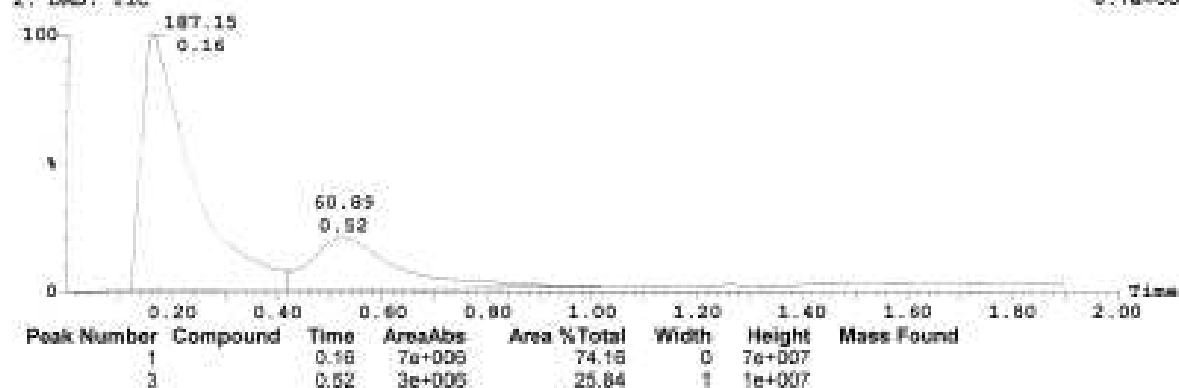
1: MS ES+ :TIC Smooth (Mn, 1x1)

5.4e+008



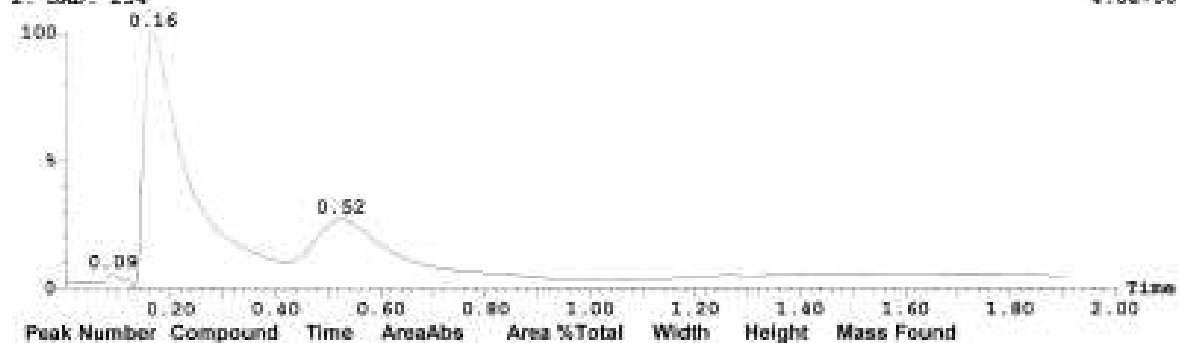
2: DAD: TIC

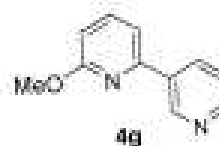
6.7e+007



2: DAD: 254

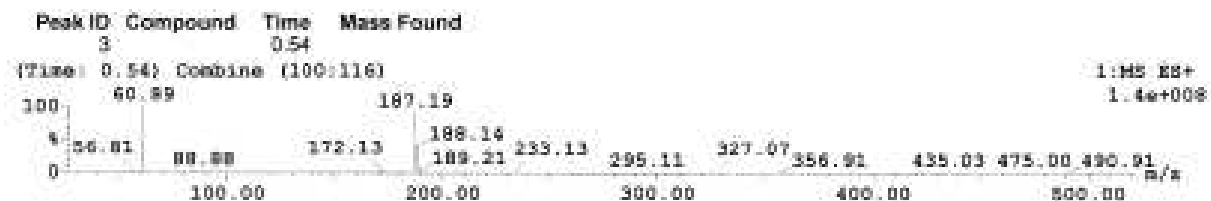
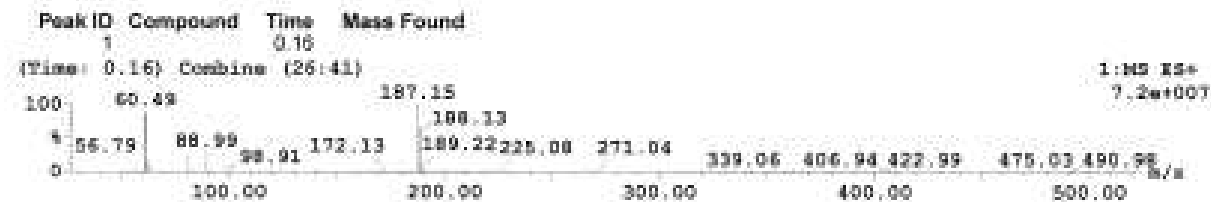
4.8e+005



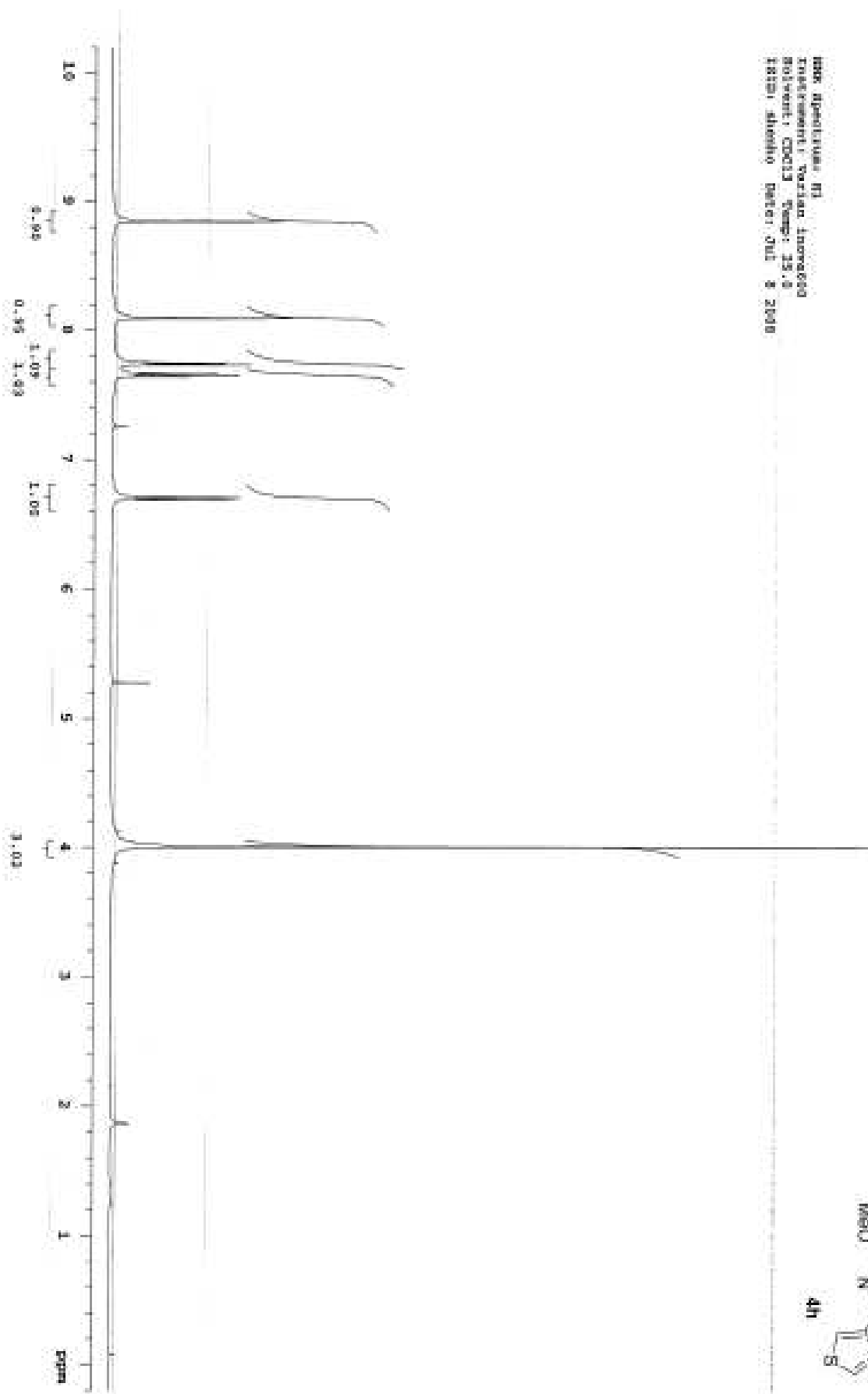
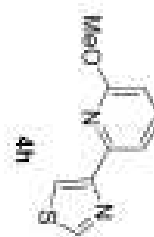


Printed: Fri Jun 20 16:19:28 2008

Sample Report (continued):

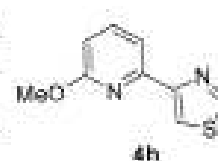


1H NMR Spectrum (400 MHz, CDCl₃)
 Solvent: CDCl₃ Temp: 25.0
 1H NMR Spectrum Date: 01/18/2018



Openlynx Report - Yang, David x47096 (yangdavi)
 Sample: 1 Vial: 1-98
 File: 20082Q_16397 Date: 09-Jul-2008
 Description:

ID: RY800-C304_14533-
 Time: 13:45:13

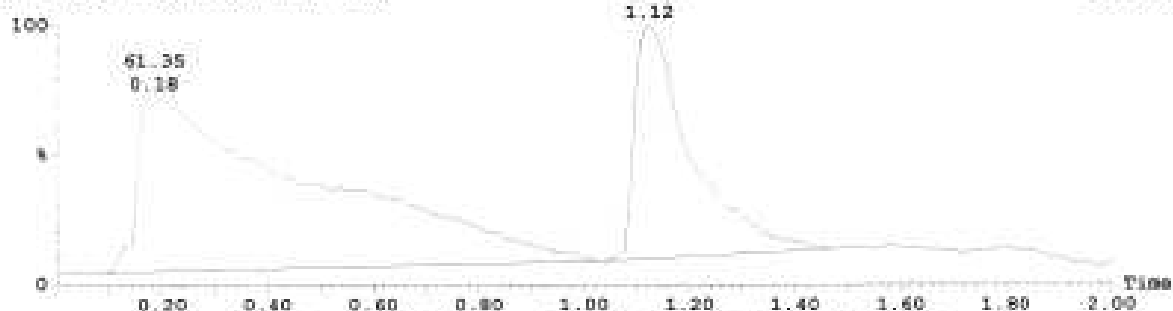


Printed: Wed Jul 09 13:51:50 2008

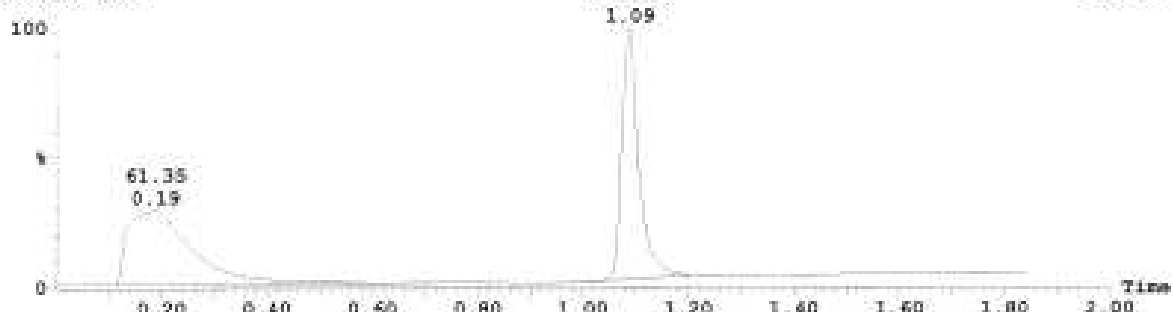
Sample Report:

Sample 1 Vial 1:96 ID RY800-C304_14533-1 File 20082Q_16397 Date 09-Jul-2008 Time 13:45:13 Description

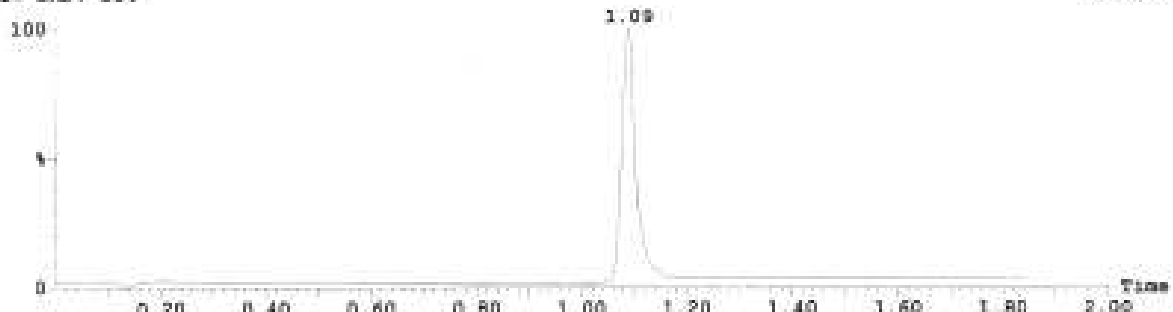
1: MS ES+ :TIC Smooth (Mn, 1x1) 193.11 5.8e+008

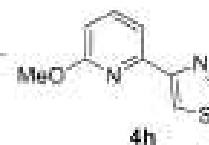


2: DAD: TIC 193.12 1.5e+008



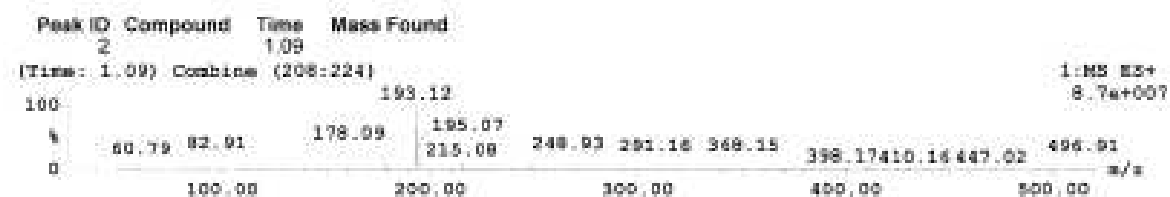
2: DAD: 254 1.09 2.5e+006



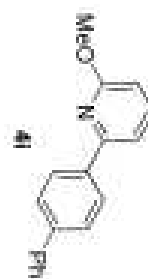
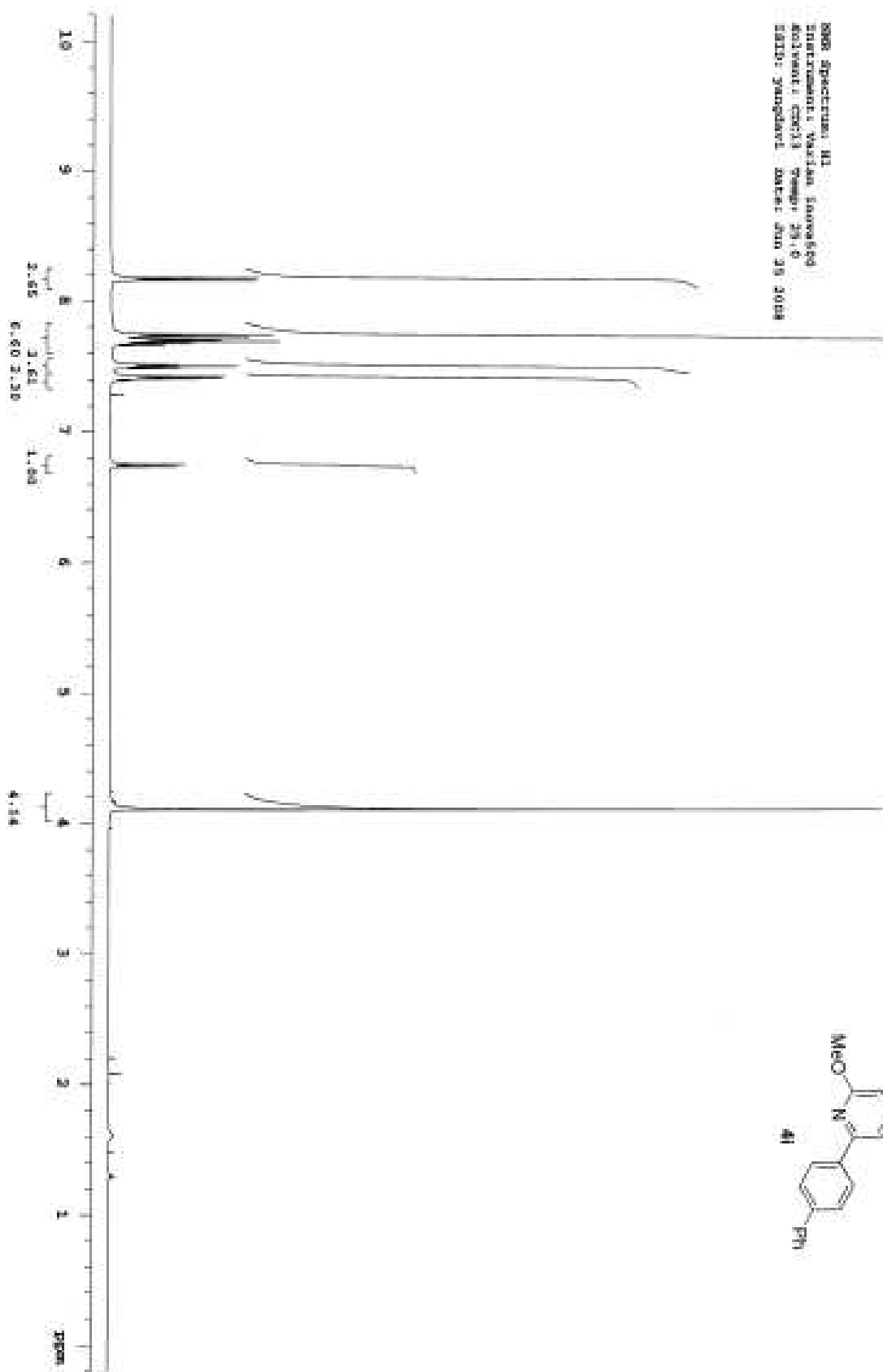


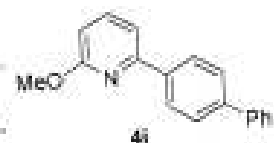
Printed: Wed Jul 09 13:51:50 2008

Sample Report (continued):



8008 Spectrum: 41
 Instrument: Varian Inova500
 Solvent: CDCl₃ Temp: 25.0
 Date: jangdaei Date: Jun 28 2014



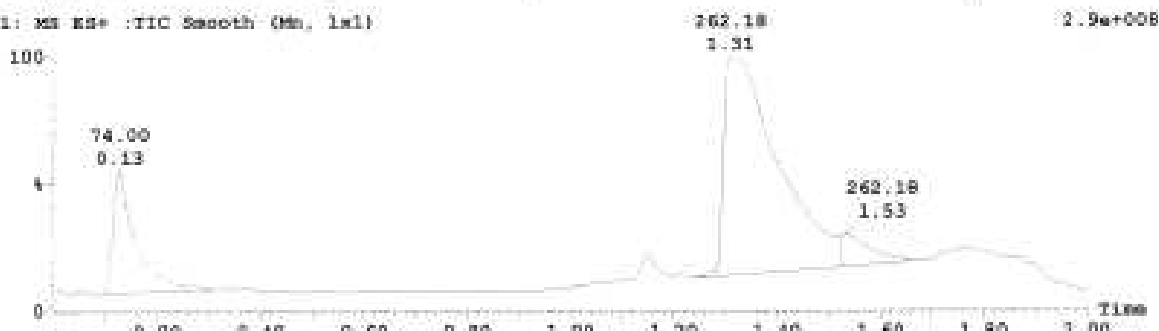


Printed: Wed Jun 25 08:11:21 2008

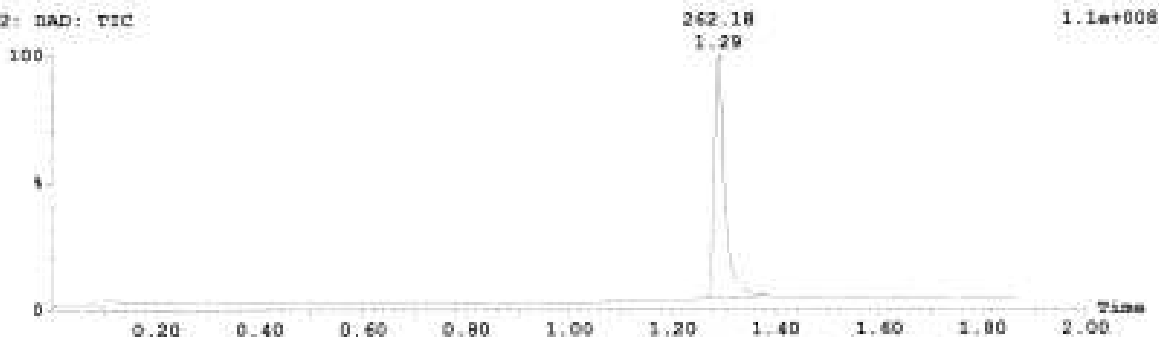
Sample Report:

Sample 1 Vial 1:74 ID RY800-C304_14021-1 File 2008ZQ_15575 Date 24-Jun-2008 Time 17:52:33 Description:

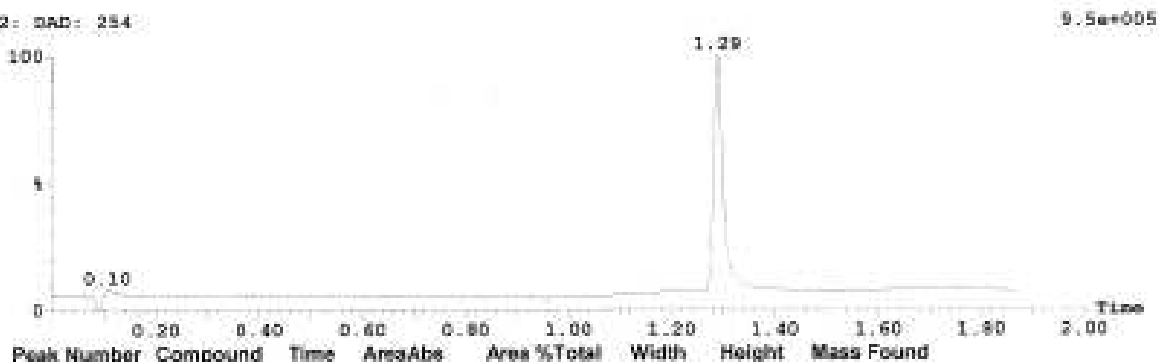
1: MS ES+ :TIC Smooth (Min, 1s1)



2: DAD: TIC

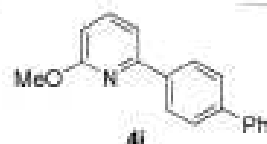


2: DAD: 254



Openlynx Report - Shen, Hong x1755 (SHENHO)
 Sample: 1 Vial: 174
 File: 20082Q_15575 Date: 24-Jun-2008
 Description:

Page 2

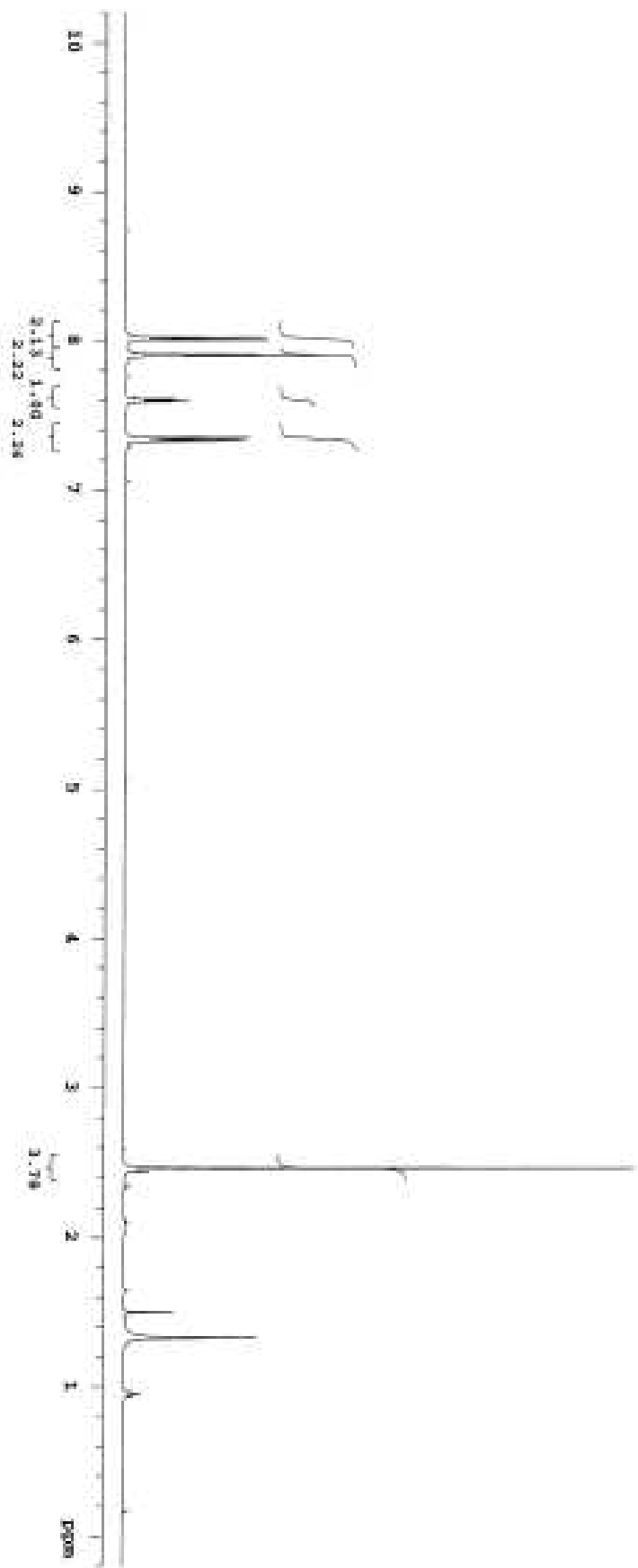
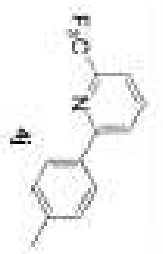


Printed: Wed Jun 25 08:11:21 2008

Sample Report (continued):



100% Spectrum: XL
 Instrument: Varian 1000/500
 Solvent: CDCl₃ Temp: 25.0
 T1: 1.00 s Relax: 2.00 s
 T2: 1.00 s Relax: 2.00 s





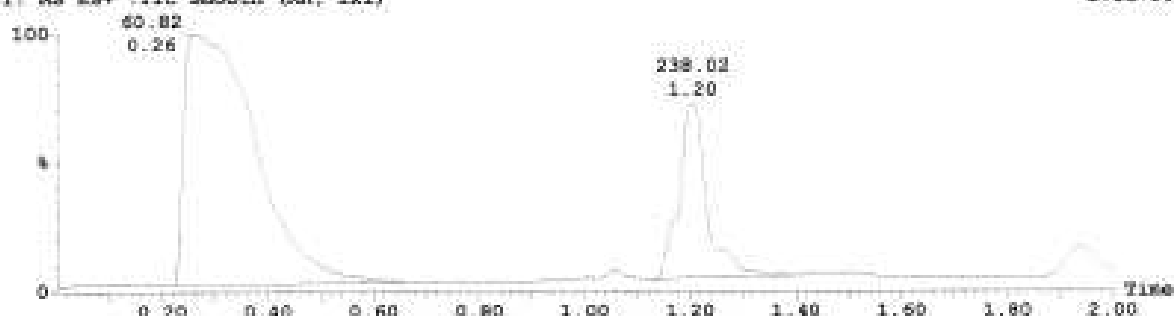
Printed: Mon Jun 30 11:34:32 2008

Sample Report:

Sample: 1 Vial: 1:75 ID: 800-C303_5616-1 File: 2006ZQ_8174 Date: 30-Jun-2008 Time: 11:27:18 Description:

1: MS ES+ :TIC Smooth (Mn, 1x1)

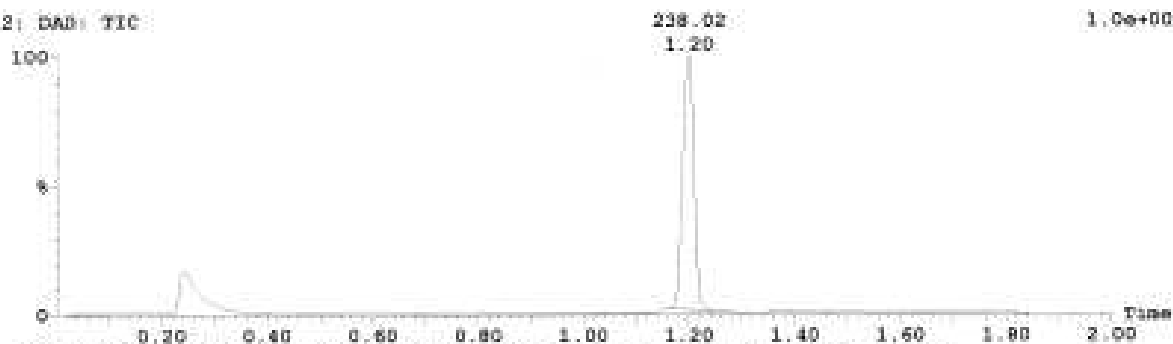
2.3e+008



Peak Number	Compound	Time	AreaAbs	Area %Total	Width	Height	Mass Found
1		0.26	4e+007	78.88	0	2e+008	
2		1.20	1e+007	21.14	0	2e+008	

2: DAD: TIC

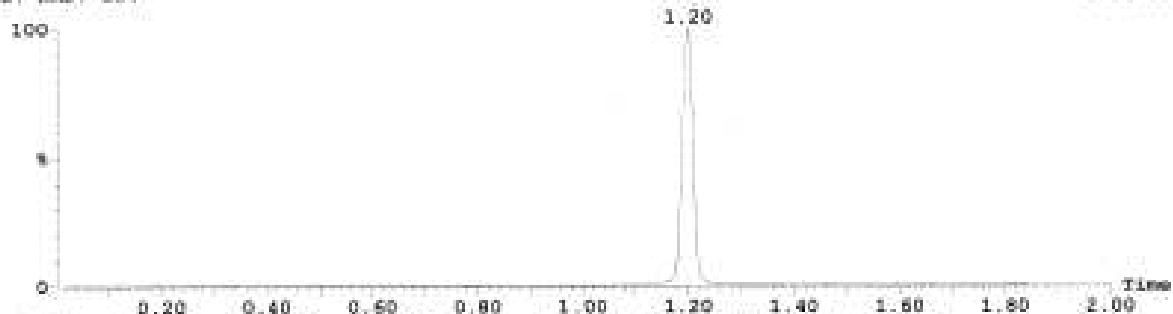
1.0e+008



Peak Number	Compound	Time	AreaAbs	Area %Total	Width	Height	Mass Found
2		1.20	2e+006	100.00	0	1e+008	

2: DAD: 254

2.3e+008

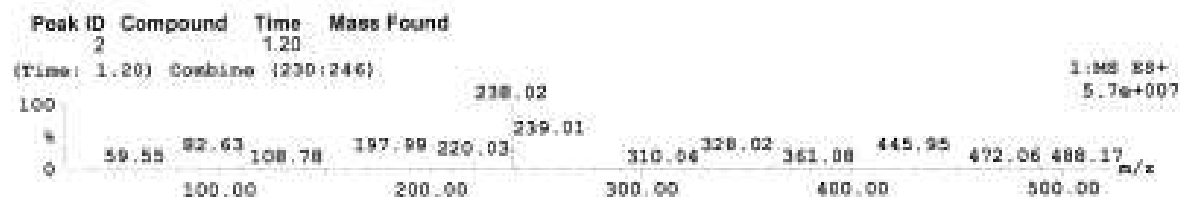
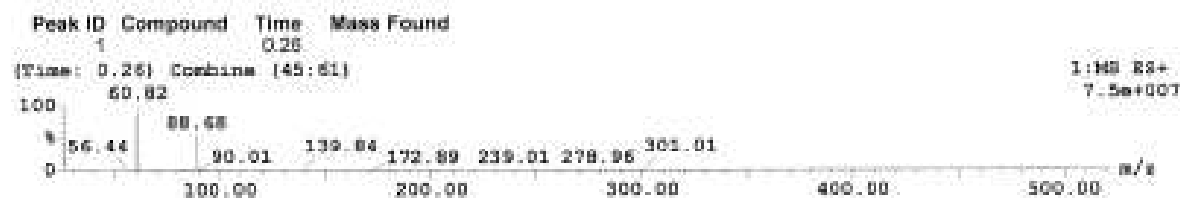


Peak Number	Compound	Time	AreaAbs	Area %Total	Width	Height	Mass Found
2		1.20	2e+006	100.00	0	1e+008	

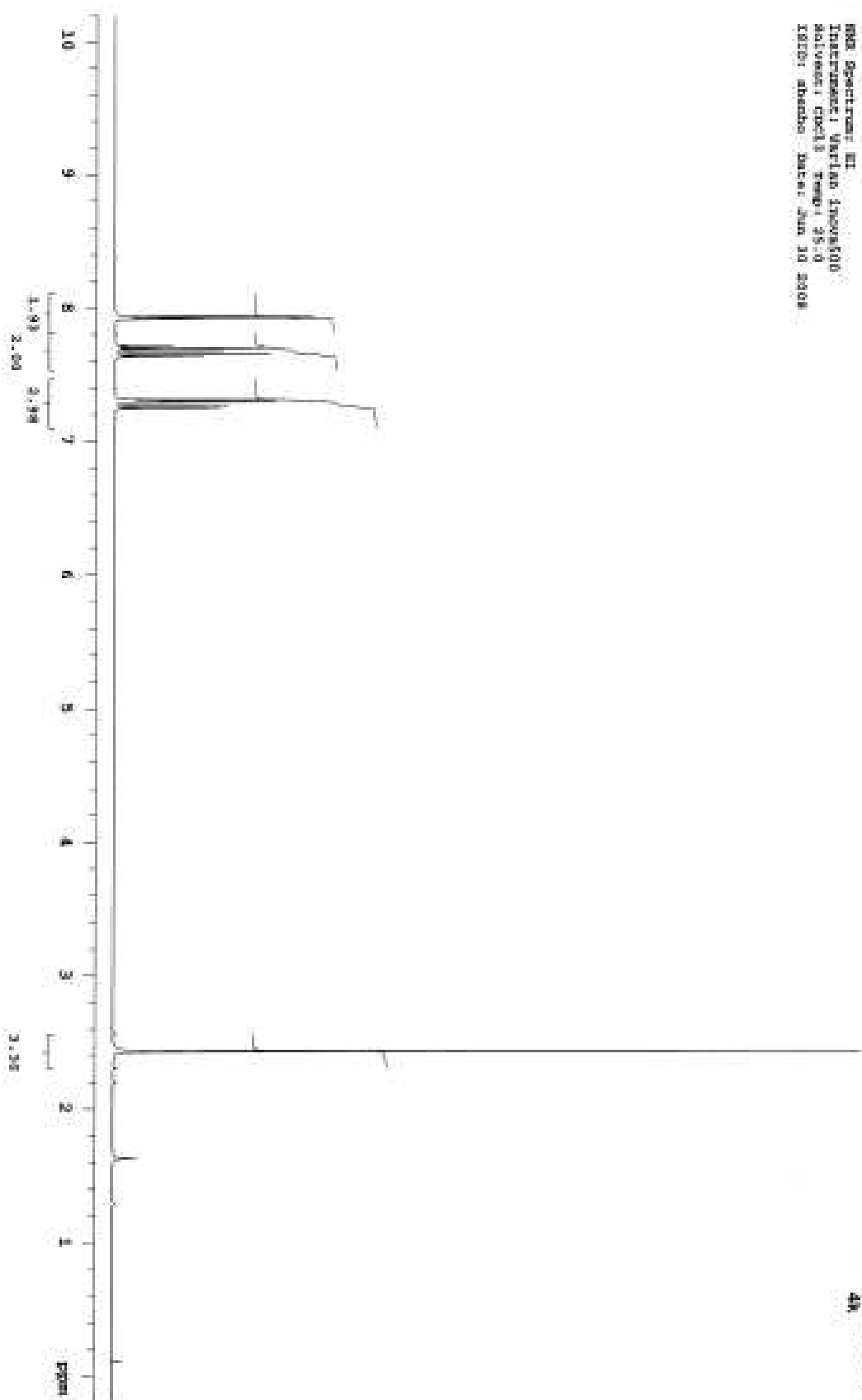


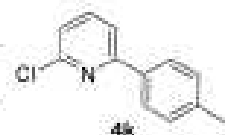
Printed: Mon Jun 30 11:34:32 2008

Sample Report (continued):



NMR Spectrum: ¹H
 Instrument: Varian 1H/500
 Solvent: CDCl₃ Temp: 25.0
 FID: 400000 Date: Jun 10 2008





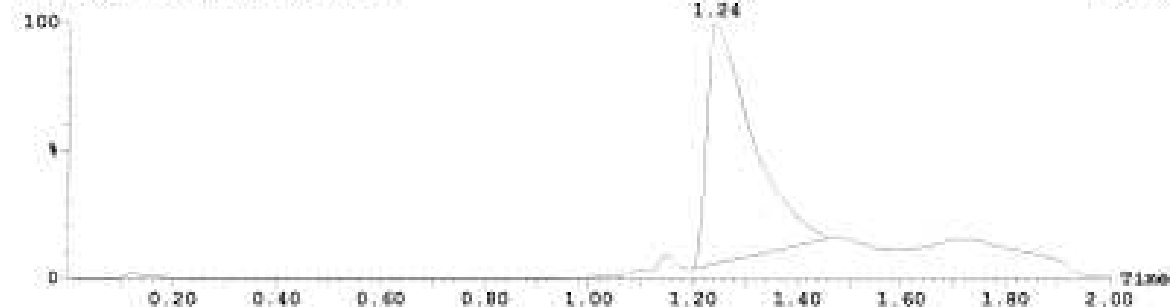
Printed: Mon Jun 30 15:22:14 2008

Sample Report:

Sample 1 Vial 1:49 ID: RY800-C304_14236-1 File: 2008ZQ_15950 Date: 30-Jun-2008 Time: 14:56:21 Description:

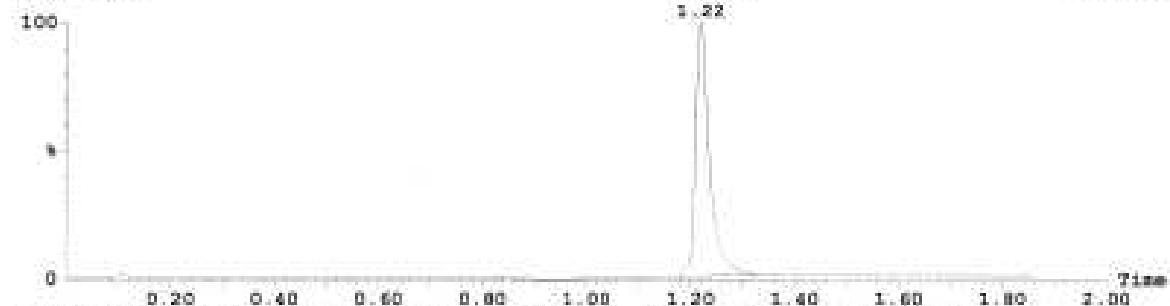
1: MS ES+ (TIC Smooth (Ms, 1x1))

204.18 5.2e+008
1.24



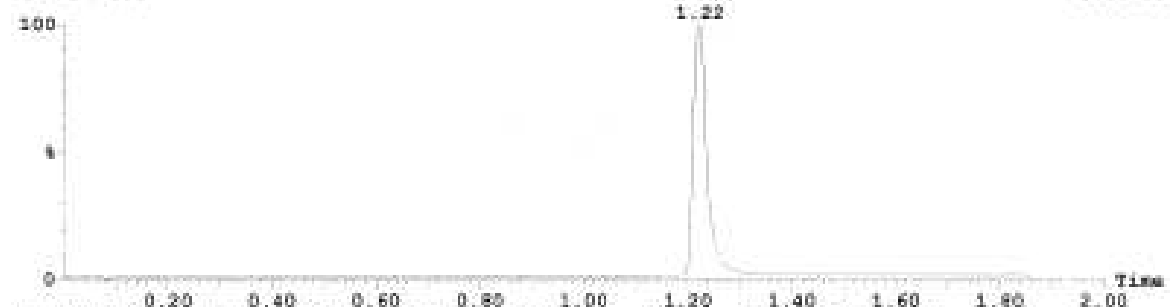
2: DAD: TIC

204.19 1.7e+008
1.22



2: DAD: 254

1.22 3.3e+006



Openlynx Report - Shen, Hong x1755 (SHENHO)

Sample: 1

File:200820_15950

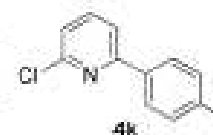
Description:

Val:1.49

Date:30-Jun-2008

ID:RY800-C304_14236

Time:14:56:21

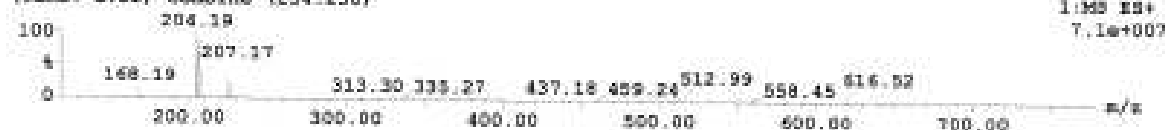


Printed: Mon Jun 30 15:22:14 2008

Sample Report (continued):

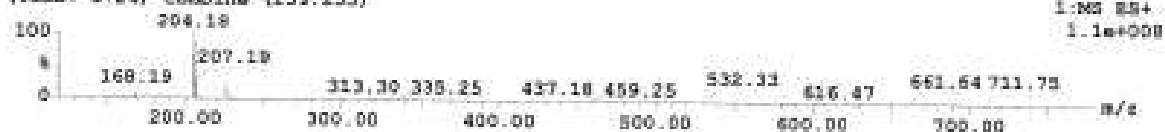
Peak ID	Compound	Time	Mass Found
1		1.22	

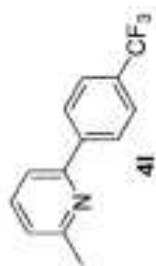
(Time: 1.22) Combine (234:250)



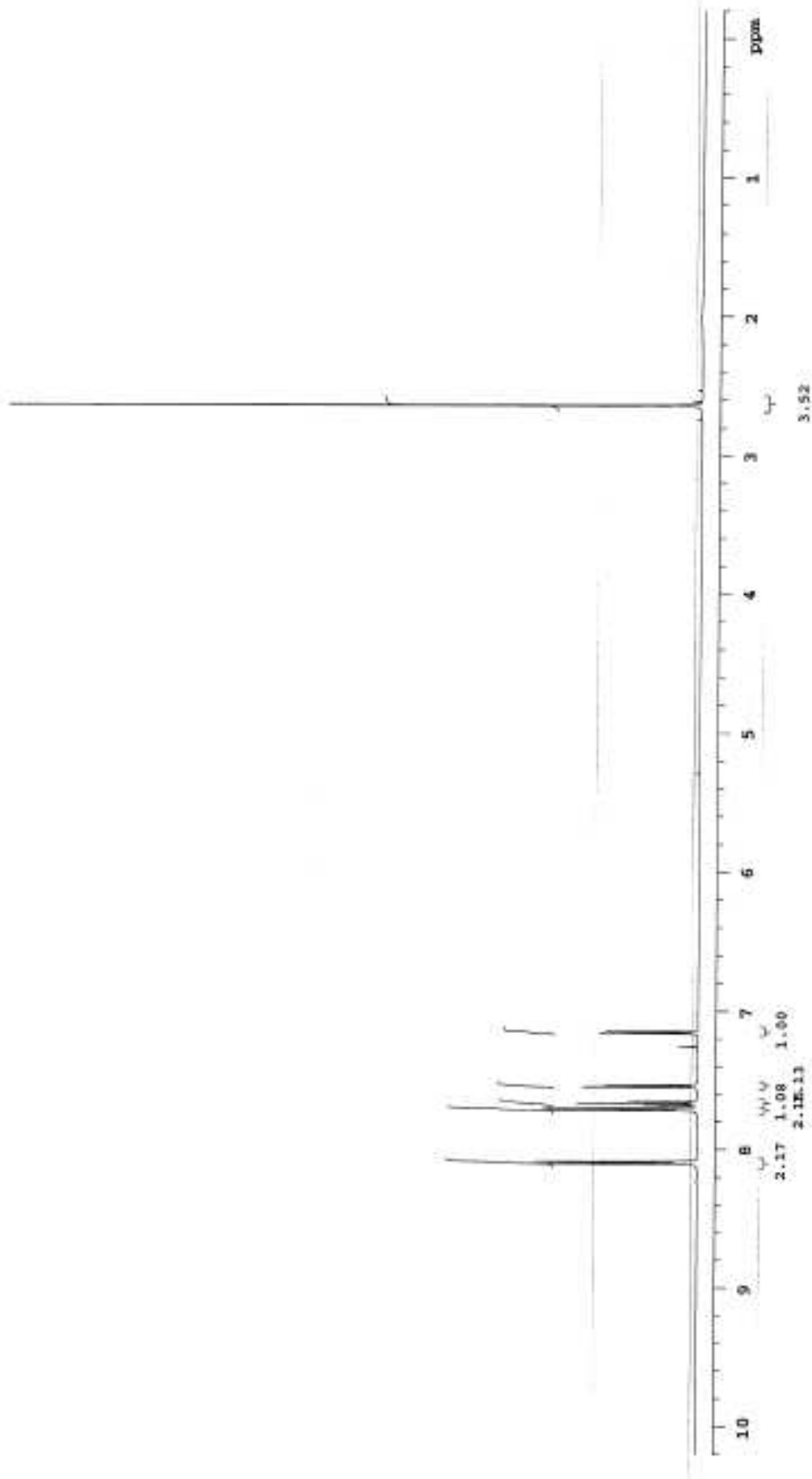
Peak ID	Compound	Time	Mass Found
2		1.24	

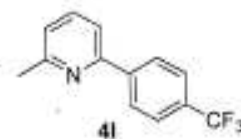
(Time: 1.24) Combine (239:255)





NMR Spectrum: M1
 Instrument: Varian inova600
 Solvent: CDCl₃ Temp: 25.0
 IRID: yangdavi Date: Jul 16 2008



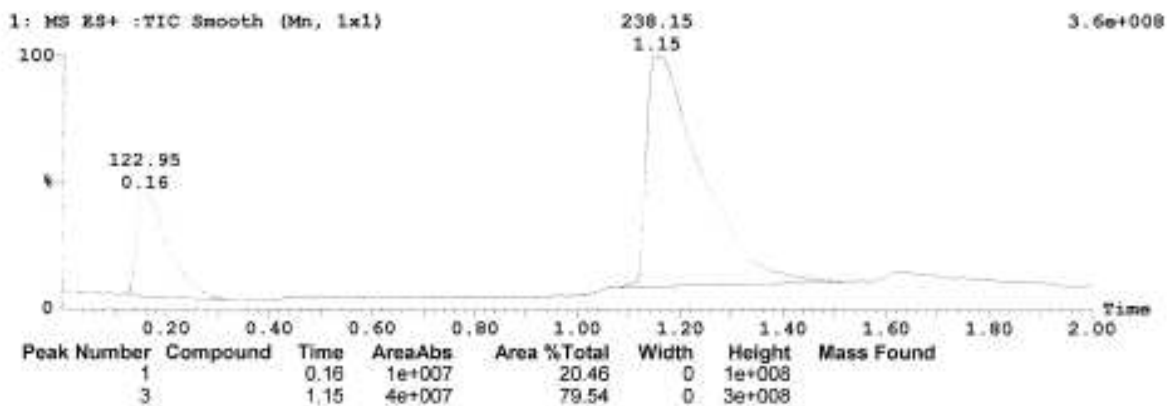


Printed: Wed Jul 16 14:06:52 2008

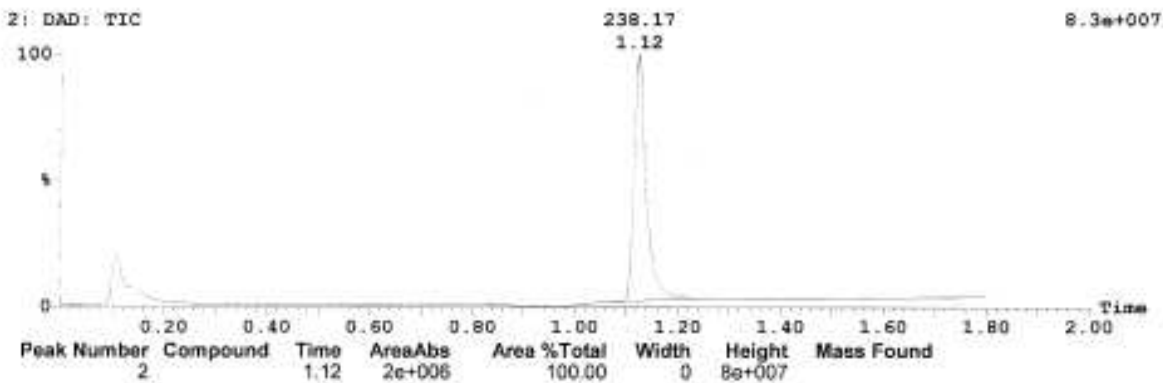
Sample Report:

Sample 1 Vial 1:85 ID RY800-C304_14736-1 File 2008ZQ_16686 Date 16-Jul-2008 Time 13:52:04 Description

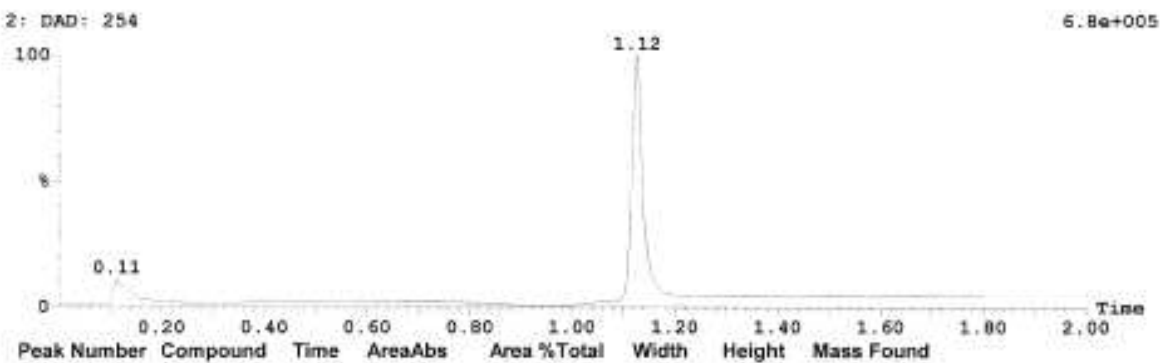
1: MS 29+ :TIC Smooth (Mn, 1x1)



2: DAD: TIC



2: DAD: 254



Openlynx Report - Yang, David x47096 (yangdavi)

Sample: 1

File: 2008ZQ_16688

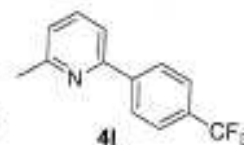
Description:

Vial: 1:85

Date: 16-Jul-2008

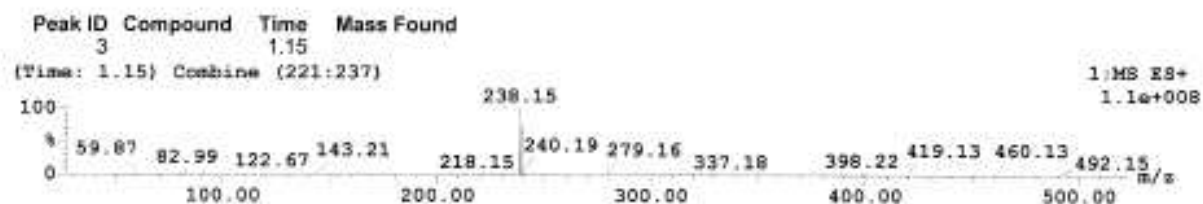
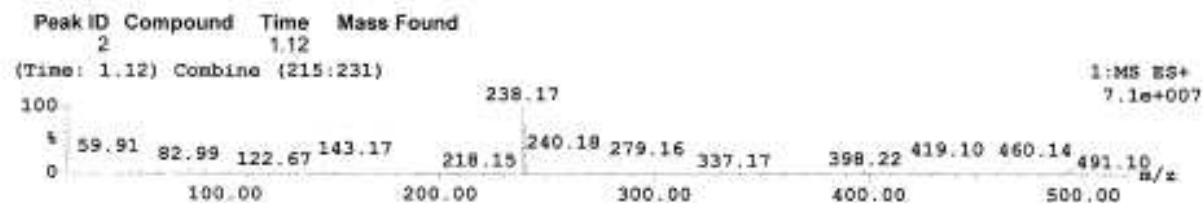
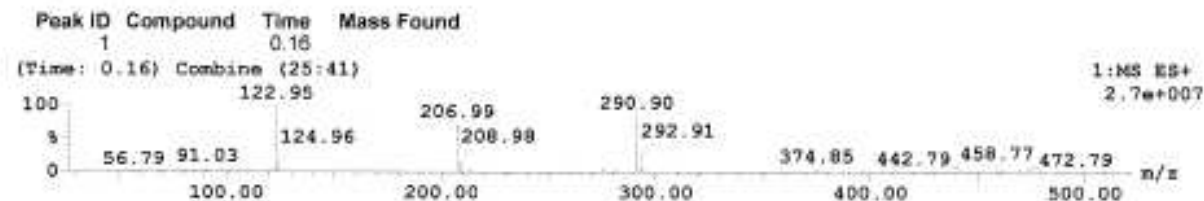
ID: RY800-C304_14736-1

Time: 13:52:04



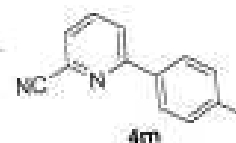
Printed: Wed Jul 16 14:06:52 2008

Sample Report (continued):



Openlynx Report - Shen, Hong x1755 (SHENHO)
 Sample: 1 Vial: 1:35
 File: 20082Q_8334 Date: 02-Jul-2008
 Description:

ID: 800-C303_5731-1
 Time: 17:38:21

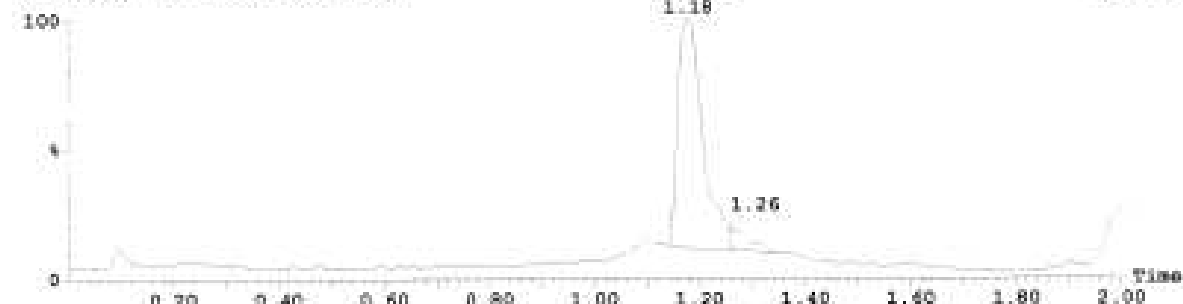


Printed: Thu Jul 03 08:28:25 2008

Sample Report:

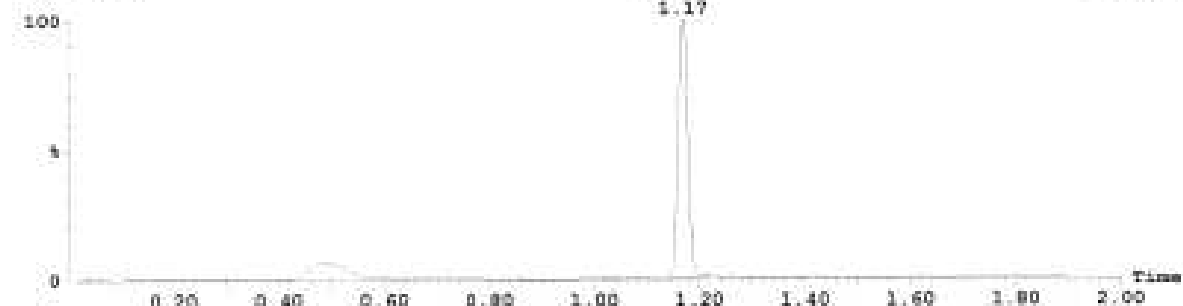
Sample 1 Vial 1:35 ID 800-C303_5731-1 File 20082Q_8334 Date 02-Jul-2008 Time 17:38:21 Description

1: MS ES+ (TIC Smooth (Mn, 1x1)) 195.02 2.1e+008
 1.18



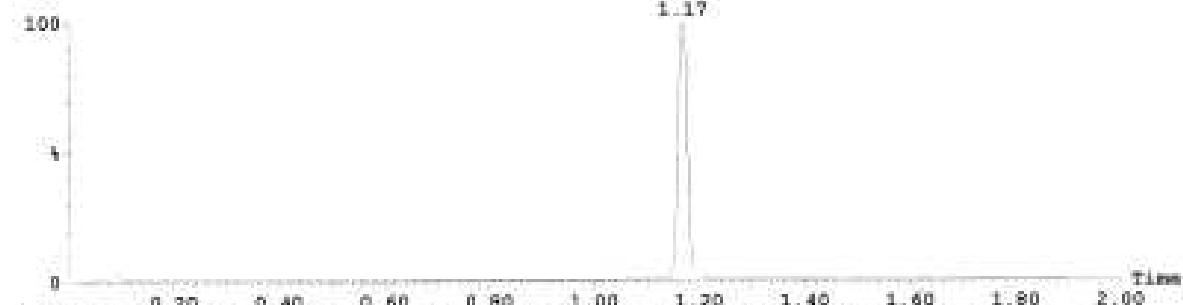
Peak Number	Compound	Time	AreaAbs	Area %Total	Width	Height	Mass Found
1		1.18	1e+007	94.73	0	2e+008	
2		1.27	6e+005	5.27	0	2e+007	

2: DAD: TIC 195.02 1.7e+008
 1.17



Peak Number	Compound	Time	AreaAbs	Area %Total	Width	Height	Mass Found
1		1.17	4e+006	100.00	0	2e+008	

2: DAD: 254 1.17 3.1e+006



Peak Number	Compound	Time	AreaAbs	Area %Total	Width	Height	Mass Found
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Openlynx Report - Shen, Hong x1755 (SHENHO)

Sample: 1

File:2008ZQ_8334

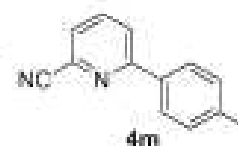
Description:

Vial:1-35

Date:02-Jul-2008

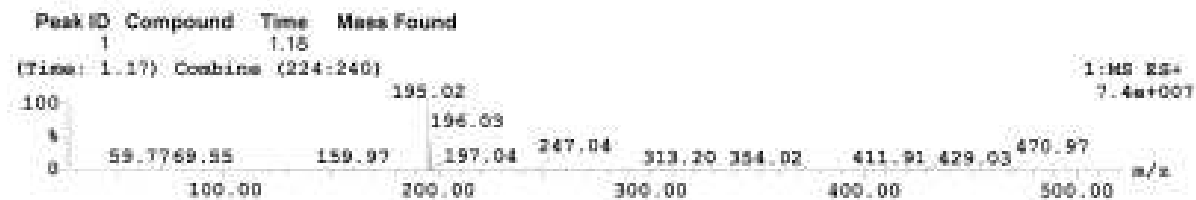
ID:800-C303_5731-1

Time:17:38:21

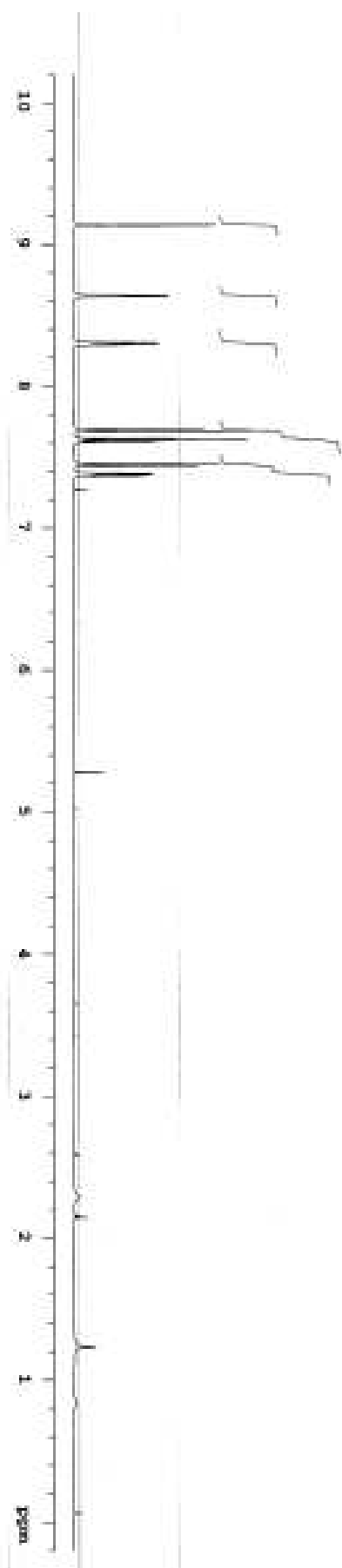
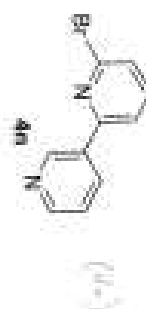


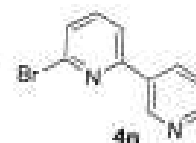
Printed: Thu Jul 03 08:28:25 2008

Sample Report (continued):



0000 Spectrum: 01
 Instrument: Varian Inova400
 Solvent: CDCl₃ Temp: 25.0
 L810: jangshen Date: Jul 14 2008



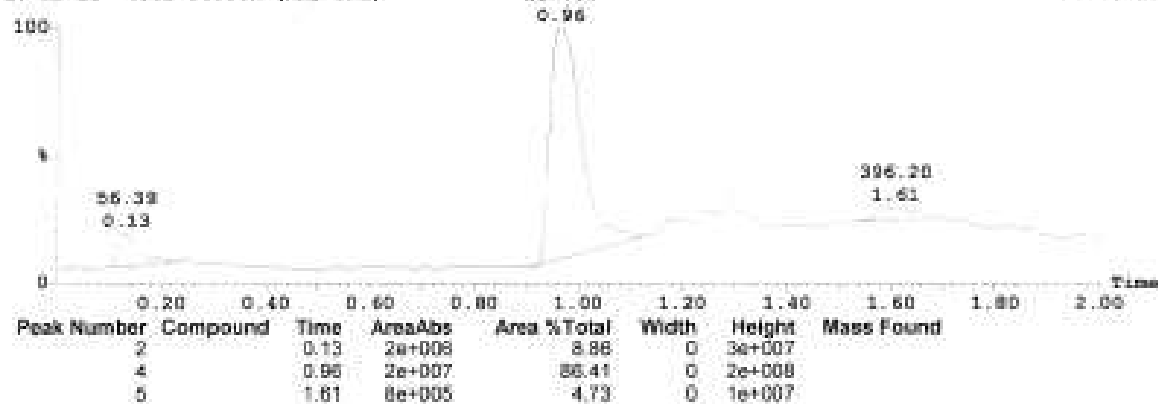


Printed: Mon Jul 14 17:59:17 2008

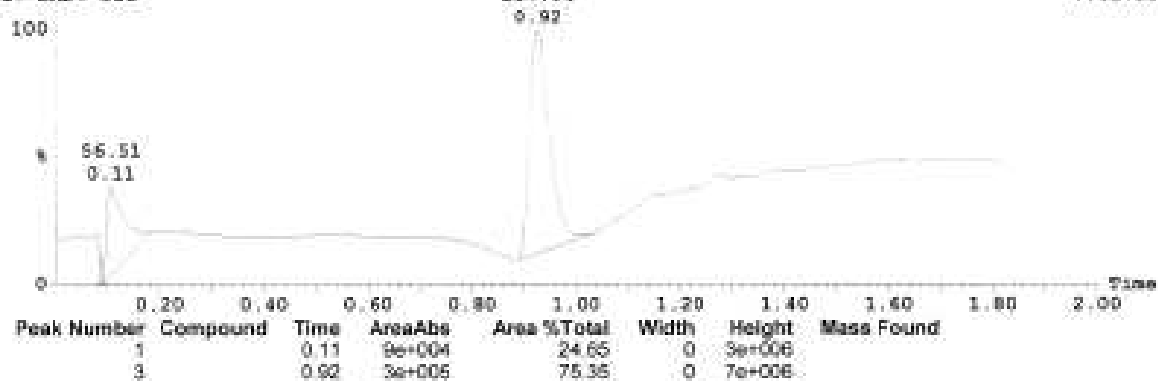
Sample Report:

Sample 1 Vial 1:70 ID RY800-C304_14662-1 File 20082Q_16571 Date 14-Jul-2008 Time 17:24:33 Description

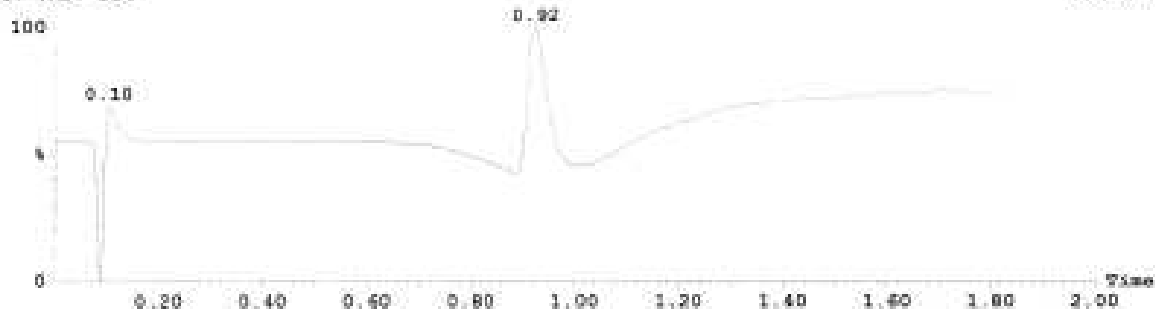
1: MS ES+ :TIC Smooth (Ms, 1x1) 237.04 2.4e+008



2: DAD: TIC 237.04 7.4e+006

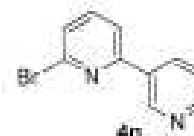


3: DAD: 254 0.92 7.8e+004



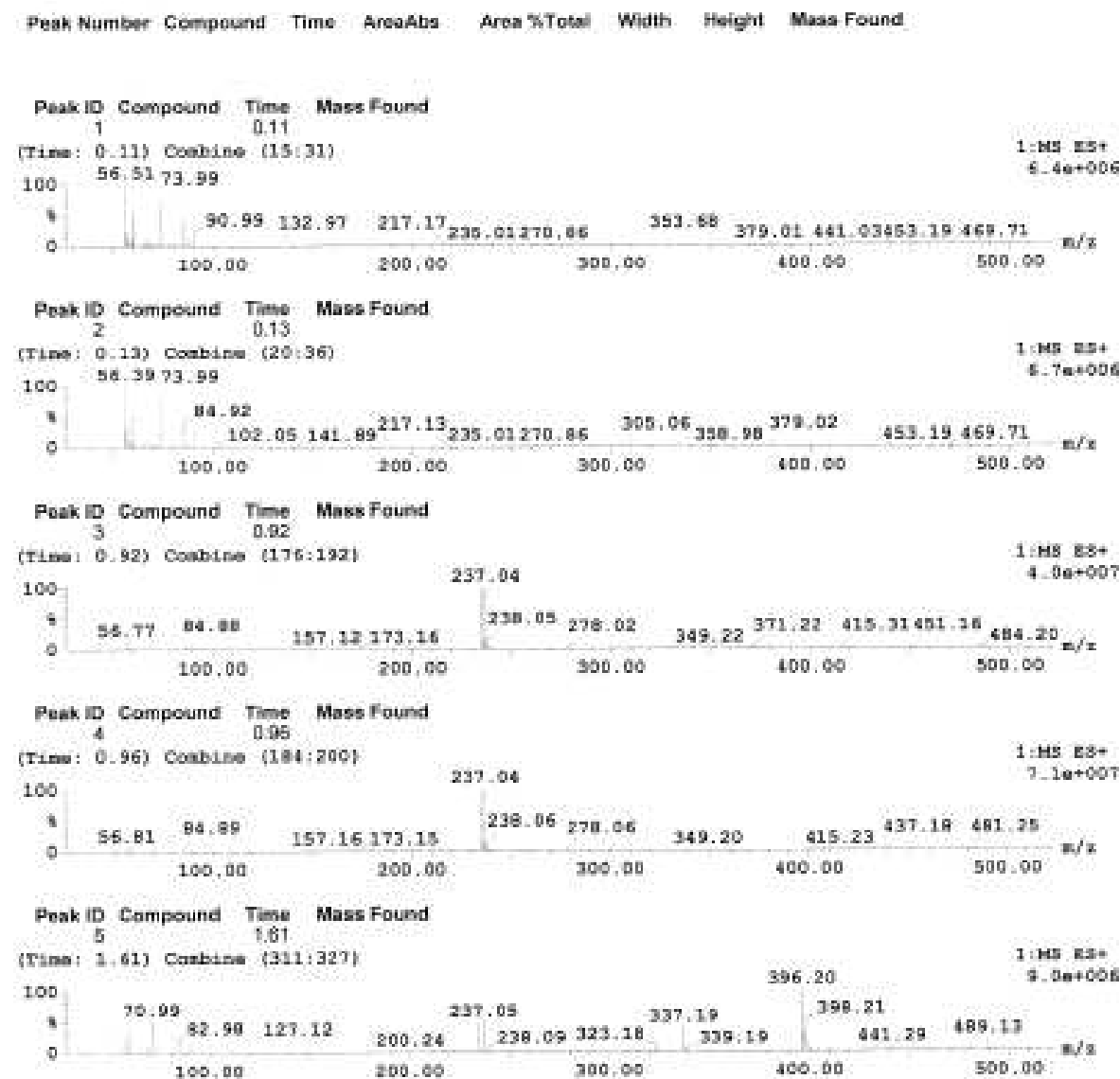
Openlynx Report - Yang, David x47096 (yangdavi)
 Sample: 1
 File: 200820_16571
 Description:

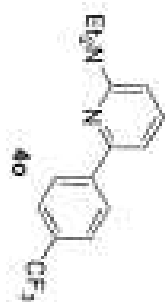
ID: RY800-C304_146
 Time: 17:24:35



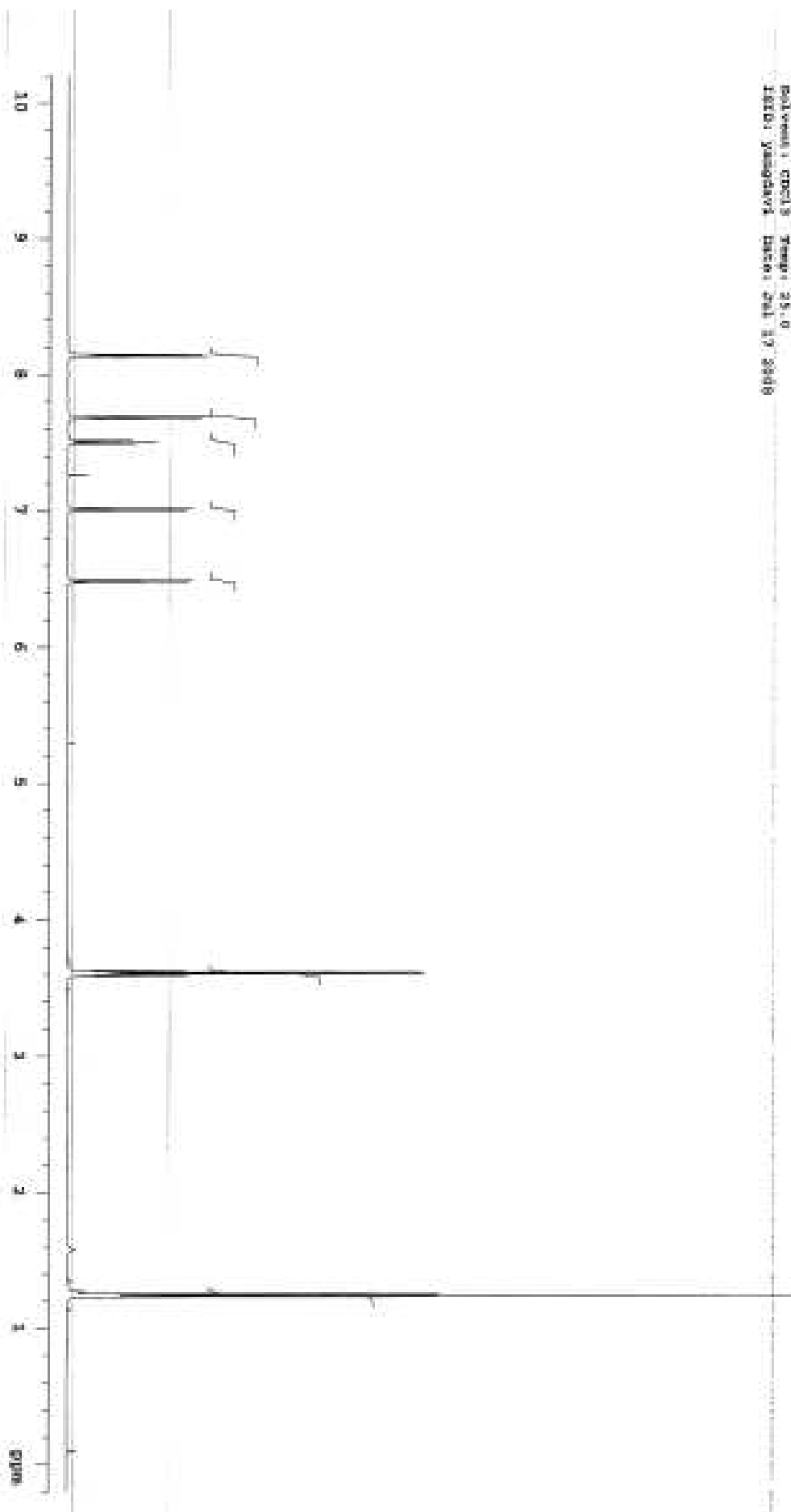
Printed: Mon Jul 14 17:58:17 2008

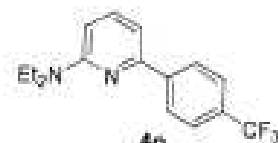
Sample Report (continued):





Name: Spectrum: 41
 Instrument: Varian Inova400
 Solvent: CDCl₃ Temp: 25.0
 100% yield: 100% 1H 13C 200



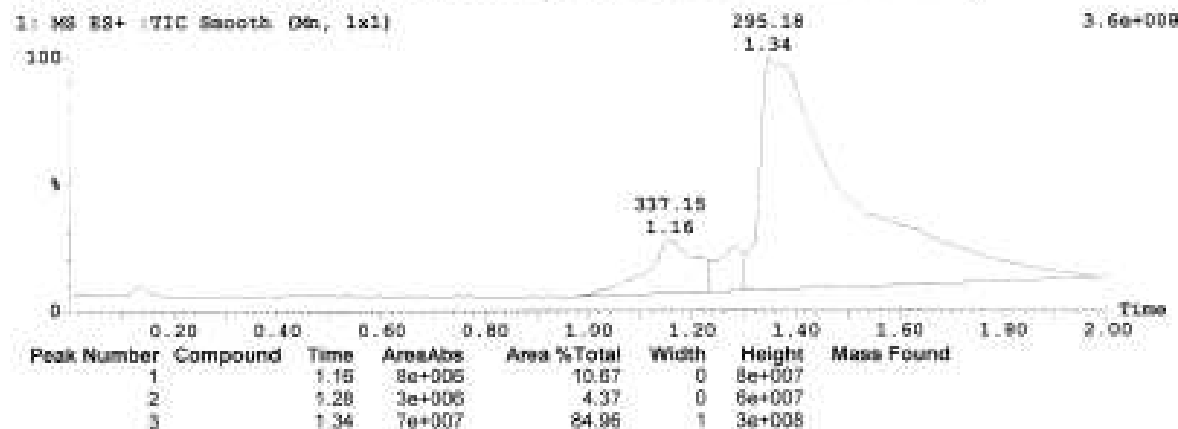


Printed: Wed Jul 16 17:58:37 2008

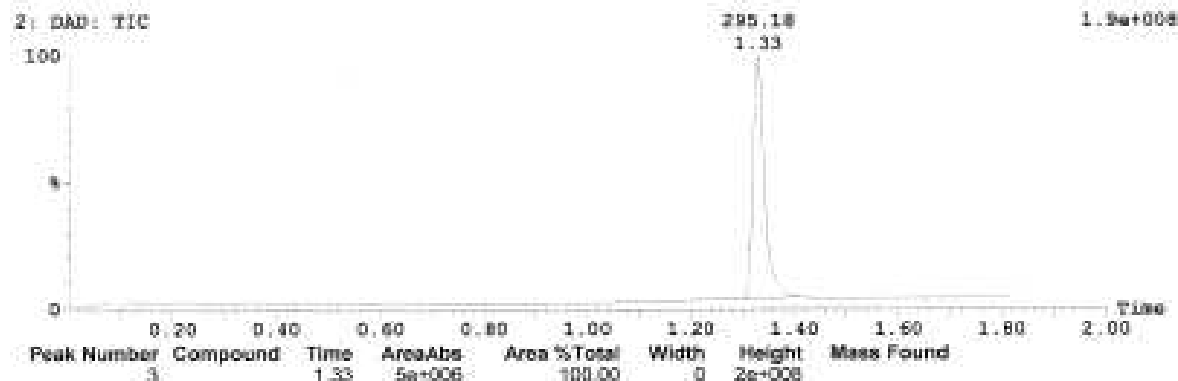
Sample Report:

Sample 1 Vial 1-1 ID: RY800-C304_14745-1 File: 2008ZQ_16702 Date: 16-Jul-2008 Time: 17:21:02 Description:

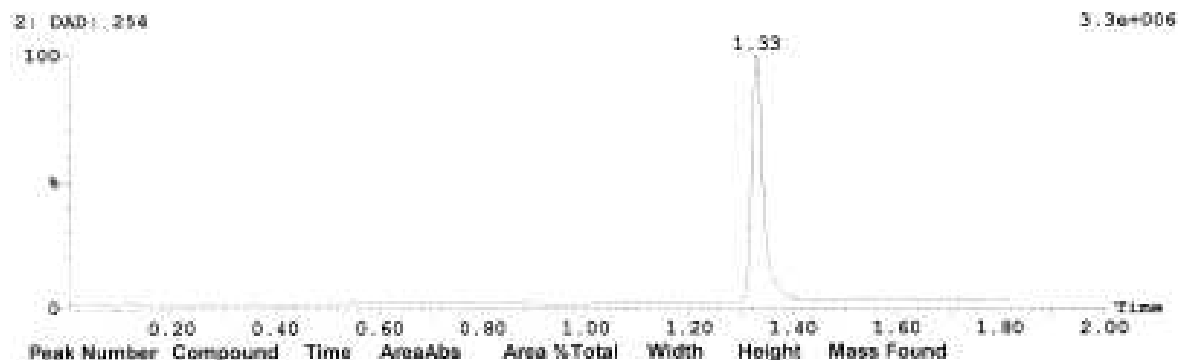
1: MS ES+ :TIC Smooth (Mn, 1x1)



2: DAD: TIC

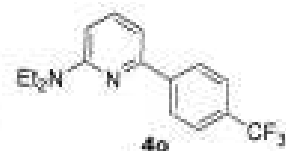


2: DAD: 254



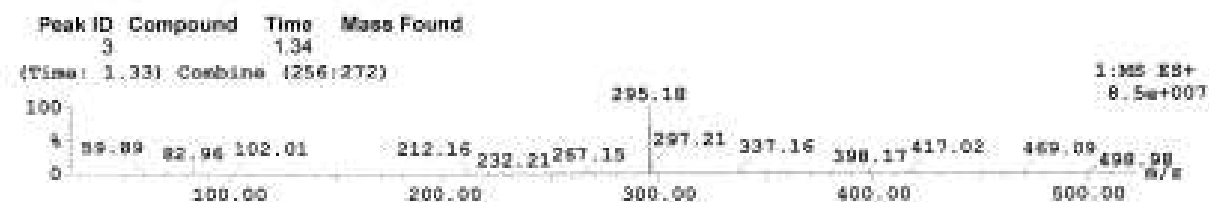
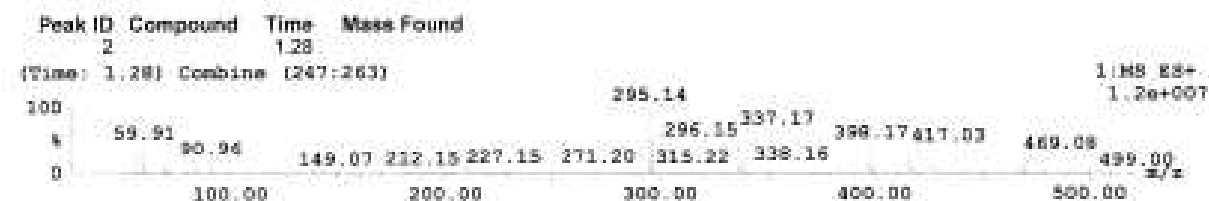
Openlynx Report - Yang, David x47096 (yangdavi)
 Sample: 1
 File: 200820_16702
 Description:

ID: RY800-C304_14
 Time: 17:21:02

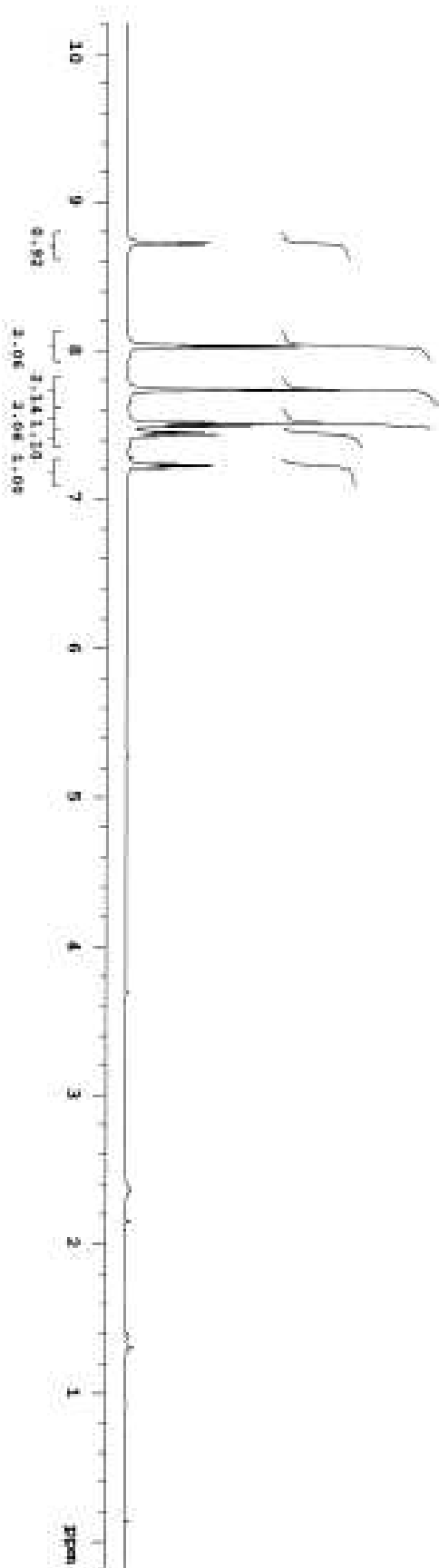
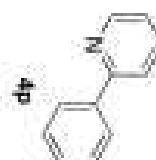


Printed: Wed Jul 16 17:58:37 2008

Sample Report (continued):

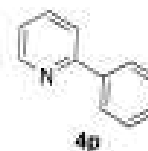


Name: Naphthalene, 2H
 Date Acquired: 12/10/2010
 Solvent: CDCl₃ Temp: 25.0
 Ref: Yonkers Date: Jul 28 2008



Openlynx Report - Yang, David x47098 (yangdavi)
 Sample: 1 Vial: 1:35
 File: 2008ZQ_17138 Date: 29-Jul-2008
 Description:

ID: RY800-C304_15072-
 Time: 11:38:38



Printed: Tue Jul 29 11:48:45 2008

Sample Report:

Sample 1 Vial 1:35 ID RY800-C304_15072-1 File 2008ZQ_17138 Date 29-Jul-2008 Time 11:38:38 Description

1: MS ES+ (TIC Smooth (No. 1x1)) 1.9e+008
 100 156.17
 0.45



Peak Number	Compound	Time	AreaAbs	Area %Total	Width	Height	Mass Found
1		0.13	3e+006	15.72	0	7e+007	
3		0.45	2e+007	84.28	0	2e+008	

2: DAD: TIC 156.17 1.1e+007
 100 0.42



Peak Number	Compound	Time	AreaAbs	Area %Total	Width	Height	Mass Found
1		0.11	1e+006	9.16	0	3e+006	
2		0.42	1e+006	90.84	0	9e+006	

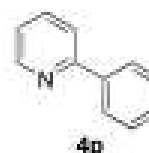
2: DAD: 254 1.1e+005
 100 0.42



Peak Number	Compound	Time	AreaAbs	Area %Total	Width	Height	Mass Found
		0.11					

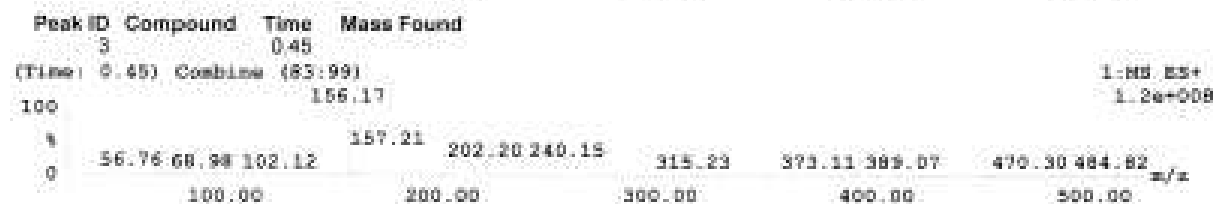
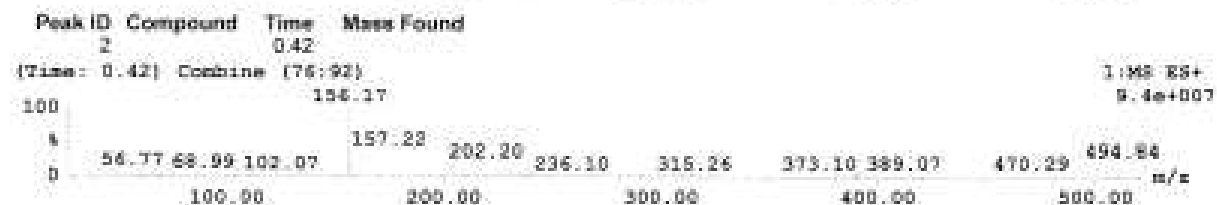
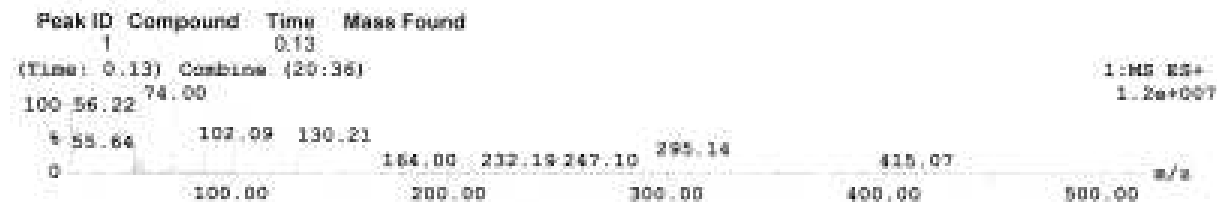
Openlynx Report - Yang, David x47098 (yangdavi)
 Sample: 1 Vial: 1/35
 File: 200620_17136 Date: 29-Jul-2008
 Description:

ID: RY800-C304_15072-1
 Time: 11:38:38

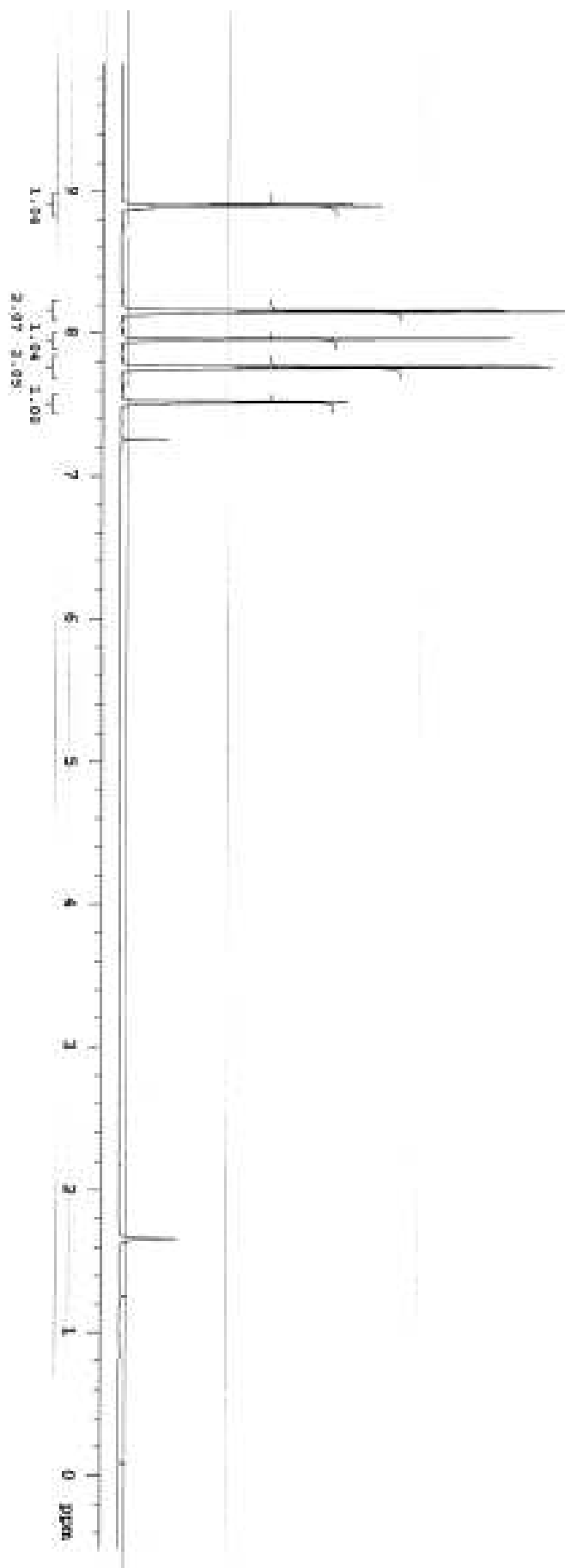
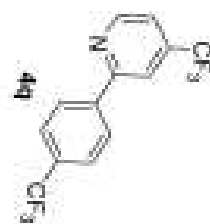


Printed: Tue Jul 29 11:48:45 2008

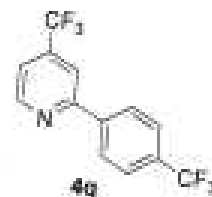
Sample Report (continued):



8008 Spectrum: 4E
 Instrument: Varian Inova400
 Solvent: CDCl₃ Temp: 25.5
 1H NMR (400 MHz, CDCl₃)



Printed: Wed Jul 30 14:09:58 2008



Sample Report:

Sample 1 Vial 1:25 ID RY800-C304_15135-1 File 2008ZQ_17226 Date 30-Jul-2008 Time 14:05:52 Description

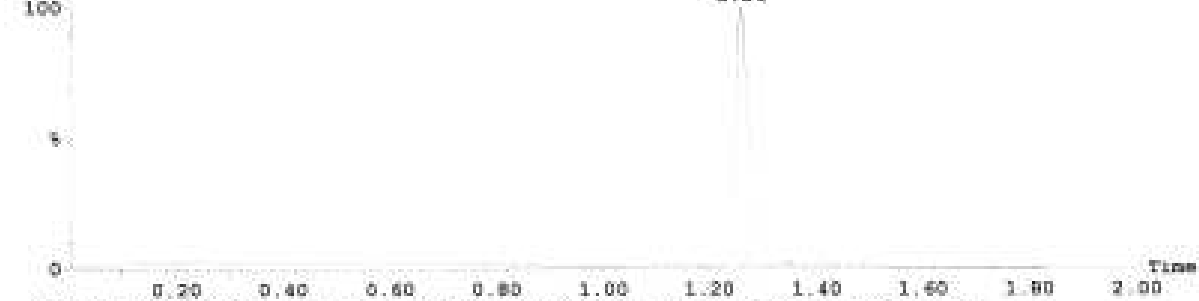
1: MS ES+ :TIC Smooth (Mn, 1x1)

292.12 3.4e+008
1.28



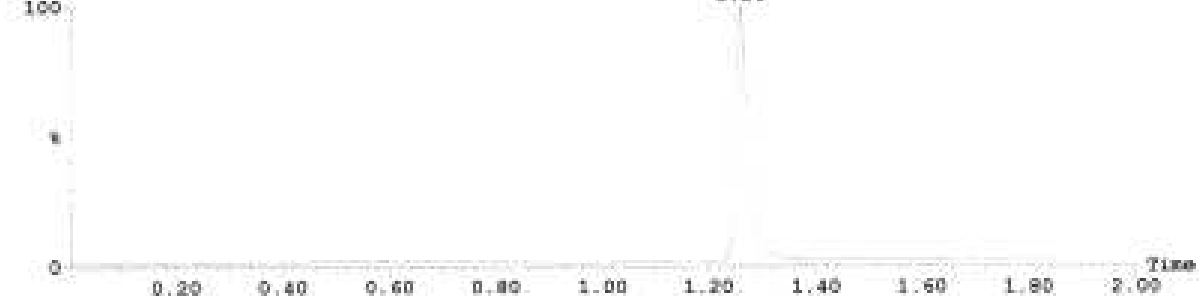
2: DAD: TIC

292.12 1.3e+008
1.26



2: DAD: 254

1.26 2.8e+008



Openlynx Report - Yang, David x47056 (yangdavi)

Sample: 1

Val:1.25

ID:RY800-C304_1

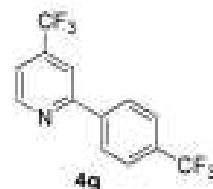
File:20082Q_17226

Date:30-Jul-2008

Time:14:00:52

Description:

Printed: Wed Jul 30 14:09:56 2008



Sample Report (continued):

Peak Number	Compound	Time	AreaAbs	Area %Total	Width	Height	Mass Found
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Peak ID	Compound	Time	Mass Found
1		0.15	

(Time: 0.15) Combine (23:39)

1:MS ES+
6.6e+006



Peak ID	Compound	Time	Mass Found
2		0.29	

(Time: 0.29) Combine (51:67)

1:MS ES+
1.6e+008



Peak ID	Compound	Time	Mass Found
3		0.31	

(Time: 0.31) Combine (55:71)

1:MS ES+
1.6e+008



Peak ID	Compound	Time	Mass Found
4		0.53	

(Time: 0.53) Combine (98:114)

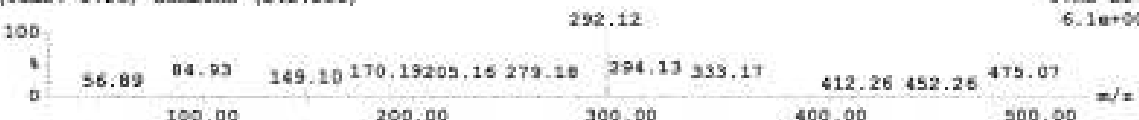
1:MS ES+
2.3e+007

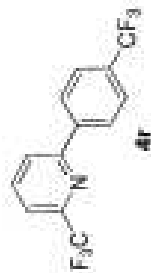


Peak ID	Compound	Time	Mass Found
5		1.28	

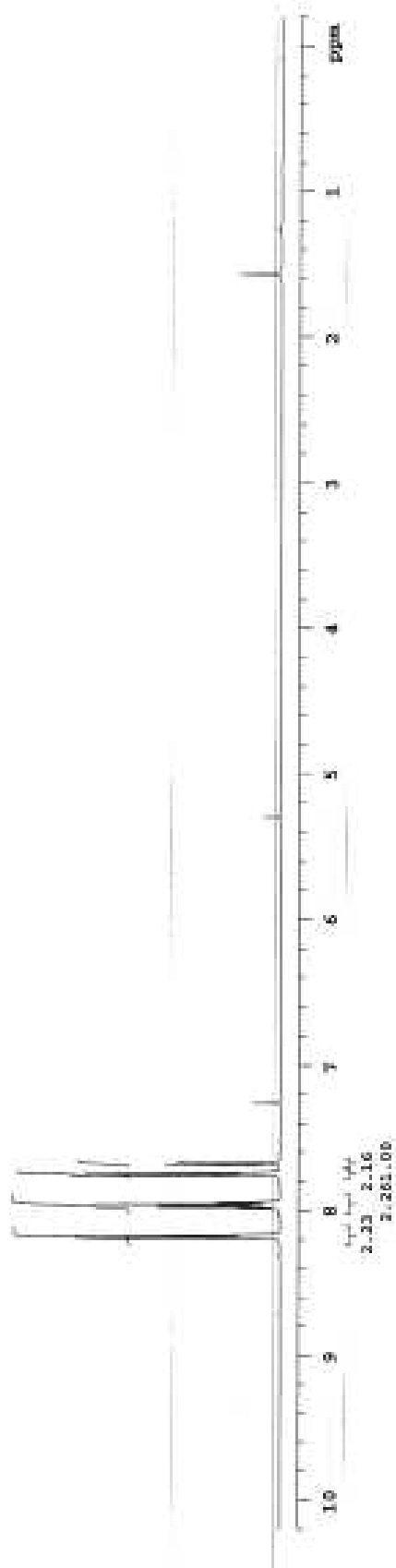
(Time: 1.26) Combine (242:258)

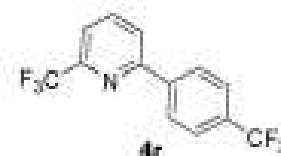
1:MS ES+
6.1e+007





NMR Spectrum: H1
 Instrument: Varian innox600
 Solvent: cdcl3 Temp: 25.9
 ID10: yangdani Date: Jul 14 2008





Printed: Tue Jul 15 12:37:18 2008

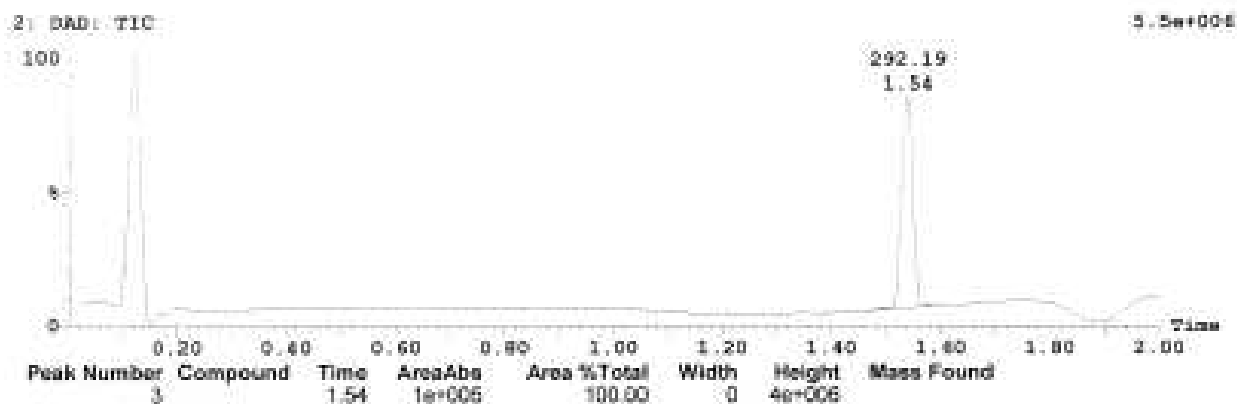
Sample Report:

Sample 1 Vial 1: 43 ID: RY800_C307_20456-1 File: 2008ZQ_24183 Date: 15-Jul-2008 Time: 12:31:30 Description:

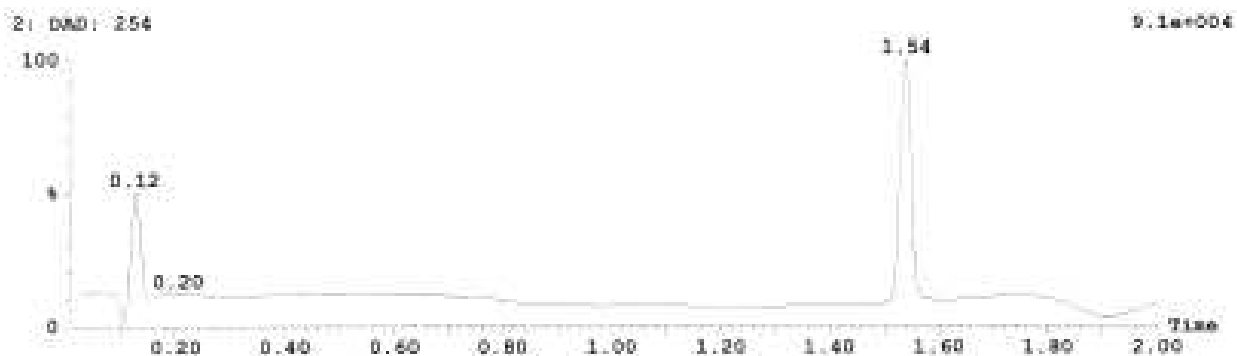
1: MS E8+ (TIC Smooth (Mn, 1x1))

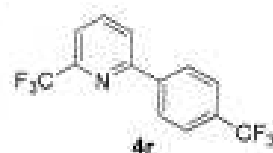


2: DAD: TIC



2: DAD: 254





Printed: Tue Jul 15 12:37:18 2008

Sample Report (continued):

Peak Number	Compound	Time	AreaAbs	Area %Total	Width	Height	Mass Found
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Peak ID	Compound	Time	Mass Found
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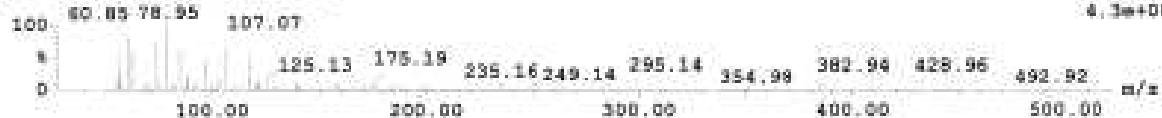
1

0.13

(Time: 0.13) Combine (20:36)

1:MS: ES+

4.3e+005



Peak ID	Compound	Time	Mass Found
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2

1.50

(Time: 1.50) Combine (290:306)

1:MS: ES+

6.8e+005



Peak ID	Compound	Time	Mass Found
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3

1.54

(Time: 1.54) Combine (297:313)

1:MS: ES+

1.0e+006



Peak ID	Compound	Time	Mass Found
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4

1.67

(Time: 1.67) Combine (323:339)

1:MS: ES+

3.1e+005

