Continuous Flow Coupling and Decarboxylation Reactions Promoted by Copper Tubing

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I. General Information: All flow experiments were performed using Vapourtec R4/R2 plus chemistry system (Figure 1). All reagents and solvents were used as supplied. ^{1}H NMR spectra were recorded using an internal deuterium lock at ambient temperature on a Varian 400 MHz spectrometer. An internal reference of δ_H 7.26 was used for $CDCl_3$. Data are presented as follows: chemical shift (in ppm on the δ scale relatively to δ_{TMS} = 0), multiplicity (s = singlet, d = doublet, t = triplet, q = quartet, quint. = quintuplet, m = mutiplet, br = broad, dd = doublet of doublet, dt = doublet of triplet, dq = doublet of quartet), coupling constant (*J*/Hz) and integration. ^{13}C NMR spectra were recorded on a Varian 400 MHz spectrometer. An internal reference of δ_C 77.0 was used for $CDCl_3$. Melting points were recorded on a Mel-Temp (Laboratory Devices). High resolution mass spectra were recorded using a Agilent 6220 mass spectrometer with electrospray ionization source and Agilent 1200 liquid chromatograph. The resolution of the MS system was approximately 11000 (FWHM definition).

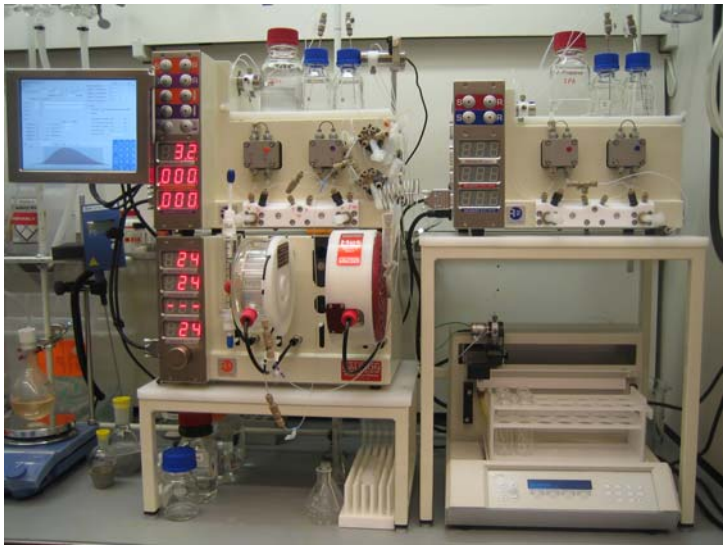
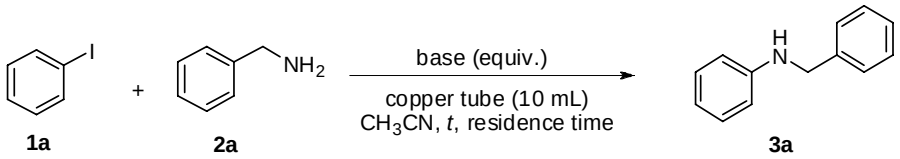


Figure 1. Vapourtec R4/R2 plus flow chemistry system

II. Reaction optimization for Ullmann coupling of 1a and 2a.



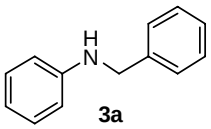
1a **2a** **3a**

entry[a]	base (equiv.)	*t* (°C)	residence time (min)	flow rate (mL/min)	conversion[b]
1	pyridine (5.0)	150	30	0.33	< 5%
2	DIPEA (5.0)	150	30	0.33	< 5%
3	Et_3N (5.0)	150	30	0.33	< 5%
4	DBU (3.0)	150	30	0.33	0%
5	TBAA (1.1)	120	30	0.33	0%
6	TBAA (1.1)	150	30	0.33	65%
7	TBAA (1.1)	200	30	0.33	80%
8[c]	TBAA (1.1)	150	60	0.33	85%
9[c]	TBAA (1.1)	150	100	0.33	95%
10[c]	TBAA (1.1)	150	120	0.17	100%
11[d]	TBAA (1.1)	150	30	0.33	0%
12[e]	TBAA (1.1)	150	30	-	50%
13[f]	TBAA (1.1)	150	30	-	31%
13[g]	TBAA (1.1)	90	960	-	40%

[a] Reaction conditions: **1a** (2 mmol, 1 M), **2a** (2.4 mmol, 1.2 M), entries 1-9 were carried out in CTFR; [b] Conversion is based on ^{1}H NMR analysis of crude materials; [c] Two 10 mL CTFRs were connected in series; [d] Reaction was carried out in PFA tube reactor; [e] Batch reaction, μwave, 400 W, CuI (10 mol %), CH_3CN (1.0 M); [f] Batch reaction, μwave, 400 W, Cu powder (10 mol %), CH_3CN (1.0 M); [g] Batch reaction, oil bath, CuI (10 mol %).

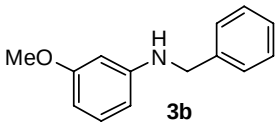
III. Ullmann coupling in CTFR.

General procedure: A solution of **1a** (2.0 mmol, 1 M), **2a** (2.40 mmol, 1.2 M) and tetrabutylammonium acetate (2.2 mmol, 2.2 M) in dry CH_3CN (2 mL) was injected into a injection loop of the R2 unit of the Vapourtec flow system. The flow stream was pumped at 0.167 mL/min equating to a residence time of 120 min. The reagent stream was directed into CTFRs (two reactors were connected in series using 1.0 mm i.d. PFA tubing, each reactor has 10 mL internal volume, a 250 psi BPR was connected after CTFRs) heated at 150 ºC using R4 unit of the Vapourtec system. After leaving flow reactors, the crude reaction solution was collected by fraction collector into 20 mL glass vials. The leached copper was then removed by stirring the crude reaction mixture with QuadraPure™ TU resins (1.5 mmol/g loading, 2g) at room temperature for 2 h. Filter off the resin, evaporation of the solvent and flash chromatography on silica gel (0% - 10% EtOAc/heptane eluant) afforded the desired product as a pale yellow oil (273 mg, 74%).



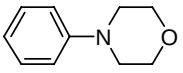
3a

***N*-benzylaniline (3a).** ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.35 - 7.45 (m, 4H), 7.35 - 7.28 (m, 1H), 7.26 - 7.18 (m, 2H), 6.77 (t, *J* = 7.33 Hz, 1H), 6.69 (d, *J* = 7.58 Hz, 2H), 4.38 (s, 2H), 4.07 - 4.34 (m, 1H); ^{13}C NMR (100MHz, $CDCl_3$) δ 129.2, 128.6, 127.5, 127.2, 117.6, 112.9, 48.3.



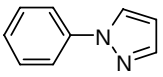
3b

***N*-benzylaniline (3b).** (334 mg, 78%), pale yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.42 - 7.31 (m, 4 H), 7.27 - 7.31 (m, 1H), 7.09 (t, *J* = 8.0 Hz, 1H), 6.31 (td, *J* = 8.0, 1.89 Hz, 2H), 6.23 (t, *J* = 2.15 Hz, 1H), 4.52 - 4.83 (brs, NH), 4.32 (s, 2H), 3.75 (s, 3H); ^{13}C NMR (100MHz, $CDCl_3$) δ 160.7, 149.4, 139.2, 129.9, 128.5, 127.4, 127.1, 105.9, 102.5, 98.8, 54.9, 48.1.



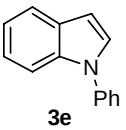
3c

4-phenylmorpholine (3c). (247 mg, 76%), light brown solid. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.31 - 7.19 (m, 2 H), 7.09 - 6.79 (m, 3H), 3.88 (t, *J* = 4.5 Hz, 4H), 3.17 (t, *J* = 4.0 Hz, 4 H); ^{13}C NMR (100MHz, CDCl3) δ 151.2, 129.1, 120.0, 115.6, 66.9, 49.3.



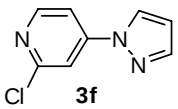
3d

1-phenyl-1*H*-pyrazole (3d) (264 mg, 92%), colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.92 (d, *J* = 2.5 Hz, 1H), 7.73 - 7.68 (m, 3H), 7.48 - 7.43 (m, 2H), 7.31 - 7.27 (m, 1H), 6.47 (t, *J* = 2.0 Hz, 1H). ^{13}C NMR (100 MHz, CDCl3) δ 141.0, 140.1, 129.4, 126.7, 126.4, 119.2, 107.5.



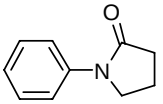
3e

1-phenyl-1*H*-indole (3e). (322 mg, 83%), colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.44 (d, *J* = 7.6 Hz, 1H), 7.34 - 7.30 (m, 1H), 7.30 - 7.24 (m, 4 H), 7.15 - 7.07 (m, 2 H), 7.00 - 6.89 (m, 2 H), 6.44 (d, 1 H); ^{13}C NMR (100 MHz, CDCl3) δ 139.8, 135.8, 129.6, 129.3, 127.9, 126.4, 124.3, 122.3, 121.1, 120.3, 110.5, 103.5.



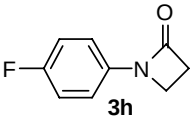
3f

2-chloro-4-(1*H*-pyrazol-1-yl)pyridine (3f). (155 mg, 53%), white solid. ^{1}H NMR (400 MHz, $CDCl_3$) δ δ 8.42 (d, *J* = 4.0 Hz, 1H), 8.01 (d, *J* = 2.0 Hz, 1H) 7.79 (s, 1H), 7.72 (d, *J* = 2.0 Hz, 1H), 7.57 (dd, *J* = 2.0, 4.0 Hz), 6.56 (dd, *J* = 2.8, 1.8 Hz). ^{13}C NMR (100 MHz, CDCl3) δ 152.9, 150.7, 147.8, 143.0, 126.8, 112.7, 111.3, 109.6; HRMS (Cl/NH_3) *m/z* calcd for $C_8H_6ClN_3$ $[M+H]^+$ 179.0250 found 179.0253.



3g

1-phenylpyrrolidin-2-one (3g). (305 mg, 95%), white solid. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.61 (d, *J* = 8.8 Hz, 2H), 7.43 - 7.31 (m, 2H), 7.20 - 7.08 (m, 1 H), 3.87 (t, *J* = 6.9 Hz, 2H), 2.62 (t, *J* = 8.0 Hz, 2H), 2.17 (quint., 2 H); ^{13}C NMR (100 MHz, CDCl3) δ 174.2, 139.3, 128.7, 124.4, 119.9, 48.7, 32.7, 18.0.

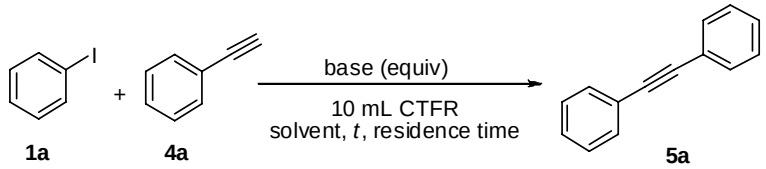


3h

1-(4-fluorophenyl)azetidin-2-one (3h). (280 mg, 85%), white solid. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.43 - 7.30 (m, 2H), 7.11 - 6.95 (m, 2H), 3.62 (t, *J* = 4.4 Hz, 2H), 3.13 (t, *J* = 4.0 Hz, 2 H); ^{13}C NMR (100 MHz, CDCl3) δ 164.1, 160.2, 157.7, 134.8, 117.5, 117.4, 116.0, 115.8,

38.2, 36.2; HRMS (Cl/NH_3) *m/z* calcd for C_9H_8FNO $[M+H]^+$ 165.0590 found 165.0591; m.p. 81 °C - 83 °C.

IV. Reaction optimization for Sonogashira coupling of 1a and phenylacetylene



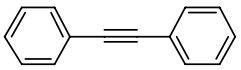
1a **4a** **5a**

entry[a]	base (equiv.)	*t* (°C)	solvent	residence time (min)	flow rate (mL/min)	conversion[b]
1	n-$BuNH_2$ (5.0)	150	DMF	20 min	0.50	10%
2	DIPEA (5.0)	150	DMF	20 min	0.50	< 5%
3	Et_3N (5.0)	150	DMF	20 min	0.50	< 5%
4	TBAA (1.5)	150	DMF	20 min	0.50	72%
5	TBAA (1.1)	170	DMF	30 min	0.33	96%
6[c]	TBAA (1.1)	170	CH_3CN	30 min	0.33	87%
7[c]	TBAA (1.1)	170	EtOAc	30 min	0.33	75%
8[c]	TBAA (1.1)	170	EtOH	30 min	0.33	70%
9[d]	TBAA (1.1)	170	DMF	20 min	0.50	0%
10[e]	TBAA (1.1)	170	DMF	30 min	-	84%
11[f]	TBAA (1.1)	170	DMF	30 min	-	10%

[a] Reaction conditions: **1a** (1.0 mmol, 1 M), **4a** (1.2 mmol, 1.2 M), entries 1-8 were experiments carried out in CTFR; [b] Conversion is based on ^1H NMR analysis of crude materials; [c] Precipitations were observed and caused subsequent system clogging; [d] Reaction was carried out in PFA tube reactor; [e] μwave, 400 W, CuI (10 mol %), DMF (0.5 M); [f] μwave, 400 W, Cu powder (10 mol %), DMF (0.5 M).

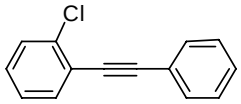
V. Sonogashira coupling in CTFR.

General procedure: A solution of **1a** (1.0 mmol, 1 M) in dry DMF (1.0 mL) and a solution of phenylacetylene (1.20 mmol, 1.2 M) and tetrabutylammonium acetate (1.1 mmol, 1.1 M) in dry DMF (1.0 mL) were injected into separate injection loops of the R2 unit of the Vapourtec flow system. Each channel containing the flow stream was pumped at 0.167 mL/min (at a total rate of 0.333 mL/min, equating 30 min residence time). The two streams were then mixed in a T-mixer before being directed into the a 10 mL CTFR heated at 170 ºC (a 100 psi BPR was connected after the reactor). After leaving the flow reactor, the crude reaction solution was collected by fraction collector into 20 mL glass vials. The leached copper was then removed by stirring the crude reaction mixture with QuadraPure™ TU resins (1.5 mmol/g loading, 2g) at room temperature for 2 h. Filter off the resin, evaporation of the solvent in Genervac and flash chromatography on silica gel (0% - 5% CH_2Cl_2/heptane eluant) afforded the desired product as a pale yellow oil (273 mg, 74%).



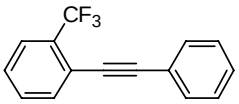
5a

1,2-diphenylethyne (5a). (161 mg, 90%), white solid. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.40 – 7.20 (m, 6H), 7.58 - 7.50 (m, 4H).



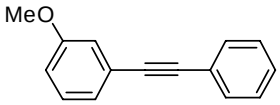
5b

1-chloro-2-(phenylethynyl)benzene (5b). (186 mg, 87%), colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.63 - 7.53 (m, 2 H), 7.46 - 7.42 (m, 1 H), 7.39 - 7.33 (m, 2 H), 7.30 - 7.21 (m, 3 H). ^{13}C NMR (100 MHz, CDCl3) δ 135.9, 133.2, 131.7, 129.3, 129.2, 128.6, 128.3, 126.4, 123.2, 122.9, 94.5, 86.1.



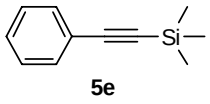
5c

1-(phenylethynyl)-2-(trifluoromethyl)benzene (5c). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.68 (t, *J* = 7.4 Hz, 2H), 7.60 - 7.49 (m, 3H), 7.45 - 7.34 (m, 4H).



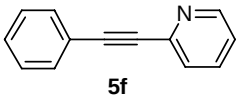
5d

1-methoxy-3-(phenylethynyl)benzene (5d). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.57 - 7.50 (m, 2H), 7.39 - 7.31 (m, 3H), 7.29 - 7.23 (m, 1H), 7.13 (d, *J* = 7.6 Hz, 1H), 7.07 (dd, *J* = 2.5, 1.3 Hz, 1H), 6.87 - 6.93 (m, 1H), 3.83 (s, 3H). ^{13}C NMR (100 MHz, CDCl3) δ 159.3, 131.6, 129.4, 128.32, 128.27, 124.2, 124.1, 123.1, 116.3, 114.9, 89.4, 89.1, 55.2.



5e

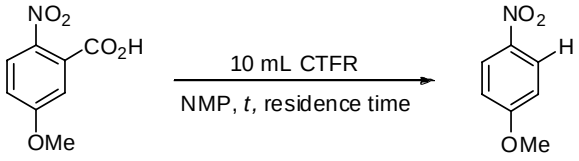
trimethyl(phenylethynyl)silane (5e). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.50 - 7.43 (m, 2H), 7.32 – 7.28 (m, 3H), 0.25 (s, 9H).



5f

2-(phenylethynyl)pyridine (5f). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.63 (d, *J* = 4.2 Hz, 1H), 7.68 (td, *J* = 7.8, 1.8 Hz, 1H), 7.65 - 7.56 (m, 2H), 7.53 (d, *J* = 7.8 Hz, 1H), 7.41 - 7.31 (m, 3H), 7.24 (dd, J = 4.0, 8.0 Hz, 1H). ^{13}C NMR (100 MHz, CDCl3) δ 150.0, 143.4, 136.1, 132.0, 128.9, 128.3, 127.1, 122.7, 122.2, 89.2, 88.5.

VI. Reaction optimization for decarboxylation of 5-methoxy-2-nitrobenzoic acid.



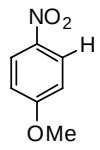
6a **7a**

entry[a]	*t* (°C)	residence time (min)	flow rate (mL/min)	conversion[b]
1	170	30 min	0.33	40%
2	180	30 min	0.33	72%
3	190	30 min	0.33	100%
4	250	15 min	0.67	100%
5[c]	190	30 min	0.33	0%
6[d]	190	30 min	-	77%
7[e]	190	30 min	-	53%

[a] Reaction conditions: **6a** (2 mmol, 1 M), entries 1-4 were carried out in CTFR; [b] Conversion is based on ^{1}H NMR analysis of crude materials; [c] Reaction was carried out in a stainless steel tube reactor; [d] μwave, 400 W, Cu_2O (10 mol %), NMP (1.0 M); [e] μwave, 400 W, Cu powder (1.0 equiv), NMP (1.0 M).

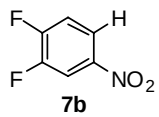
VII. Decarboxylation in CTFR.

General procedure: A solution of **6a** (2.0 mmol, 1 M) in dry NMP (2 mL) was injected into a injection loop of the R2 unit of the Vapourtec flow system. The flow stream was pumped at 0.667 mL/min equating to a residence time of 15 min. The reagent stream was directed into a 10 mL CTFR (a 250 psi BPR was connected after CTFR) heated at 250 ºC using R4 unit of the Vapourtec system. After leaving flow reactor, the crude reaction solution was collected by fraction collector into 20 mL glass vials. The leached copper was then removed by stirring the crude reaction mixture with QuadraPure™ TU resins (1.5 mmol/g loading, 2g) at room temperature for 2 h. The resin was filtered off and the remaining solution was diluted with 20 mL methyl tert-butyl ether, and the organic phase was washed with half saturated sodium chloride solution (4 x) to remove NMP, and then dried over $MgSO_4$. Evaporation of the solvent afforded the desired product as a white solid, no additional purification needed (290 mg, 95%).



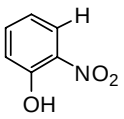
7a

1-methoxy-4-nitrobenzene (7a). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.21 (d, *J* = 4.0 Hz, 2H), 6.96 (d, *J* = 4.0 Hz, 2H), 3.91 (s, 3H).



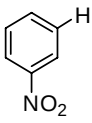
7b

1,2-difluoro-4-nitrobenzene (7b). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.19 - 8.02 (m, 1H), 7.44 - 7.29 (m, 2H).



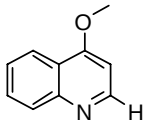
7c

2-nitrophenol (7c). ^{1}H NMR (400 MHz, $CDCl_3$) δ 10.6 (s, 1H), 8.1 (dd, J = 8.6, 1.5 Hz, 1H), 7.67 - 7.50 (m, 1H), 7.17 (dd, J = 8.5, 1.1 Hz, 1H), 7.07-6.87 (m, 1H).



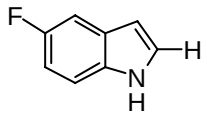
7d

nitrobenzene (7d). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.31 - 8.19 (m, 1H), 7.80 - 7.65 (m, 1H), 7.63 - 7.46 (m, 1H).



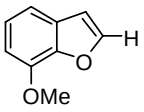
7e

4-methoxyquinoline (7e). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.76 (d, *J* = 5.0 Hz, 1H), 8.21 (d, *J* = 7.6 Hz, 1H), 8.05 (d, *J* = 8.6 Hz, 1H), 7.80 - 7.65 (m, 1H), 7.59 - 7.45 (m, 1H), 6.75 (d, *J* = 5.3 Hz, 1H), 4.06 (s, 3H); ^{13}C NMR (100 MHz, CDCl3) δ 162.3, 151.2, 148.9, 129.7, 128.7, 125.6, 121.7, 121.3, 100.0, 55.6.



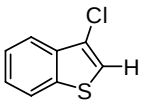
7f

5-fluoro-1H-indole (7f). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.13 (brs, 1H), 7.33 - 7.23 (m, 3H), 6.95 (td, *J* = 9.0, 2.4 Hz, 1H), 6.60 - 6.43 (m, 1H); ^{13}C NMR (100 MHz, CDCl3) δ 159.1, 156.8, 132.3, 128.2 (128.1), 125.8, 111.6 (111.5), 110.5 (110.3), 105.5, (105.3), 102.8 (102.8).



7g

7-methoxybenzofuran (7g). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.62 (d, *J* = 2.0 Hz, 1H), 7.23 - 7.12 (m, 2H), 6.81 (dd, *J* = 7.6, 1.3 Hz, 1H), 6.77 (d, 1H) 4.02 (s, 3H). ^{13}C NMR (100 MHz, CDCl3) δ 145.5, 145.0, 144.3, 129.1, 123.4, 113.5, 106.9, 106.2, 56.0.



7h

3-chlorobenzo[b]thiophene (7h). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.94 - 7.77 (m, 2H), 7.55 - 7.38 (m, 2H), 7.32 (s, 1H). ^{13}C NMR (100 MHz, CDCl3) δ 138.3, 136.0, 125.3, 124.8, 122.8, 121.8, 121.0, 120.7.

VIII. Selected ^{1}H and ^{13}C NMR spectra.

11/4/2010 9:32:49 AM

Acquisition Time (sec)	3.9584	*Comment*	Notebook U-13020-EXP085-ISO Name ZHANGYUT Project FLOW			*Date*	24 Sep 2010 20:41:36
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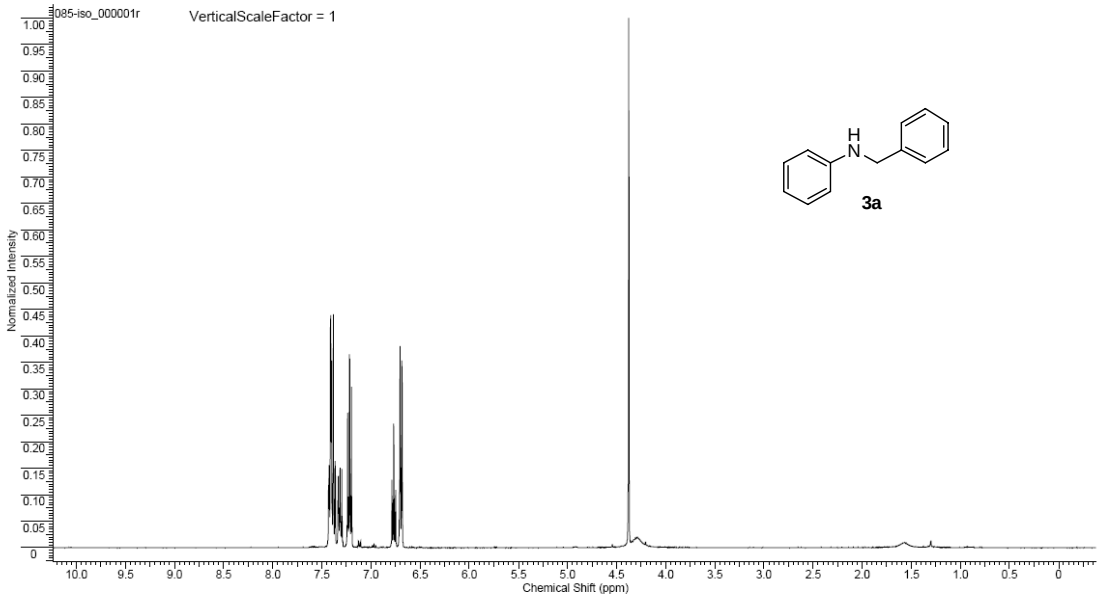
Sweep Width (Hz)	8277.89	*Temperature (degree C)*	27.000				



3a

11/29/2010 6:47:28 PM

Acquisition Time (sec)	3.9584	*Comment*	Notebook U-13020-EXP115-ISO Name ZHANGYUT Project FLOW			*Date*	29 Nov 2010 23:00:16
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Original Points Count	32768	*Owner*	av400b	*Points Count*	32768	*Pulse Sequence*	zg30
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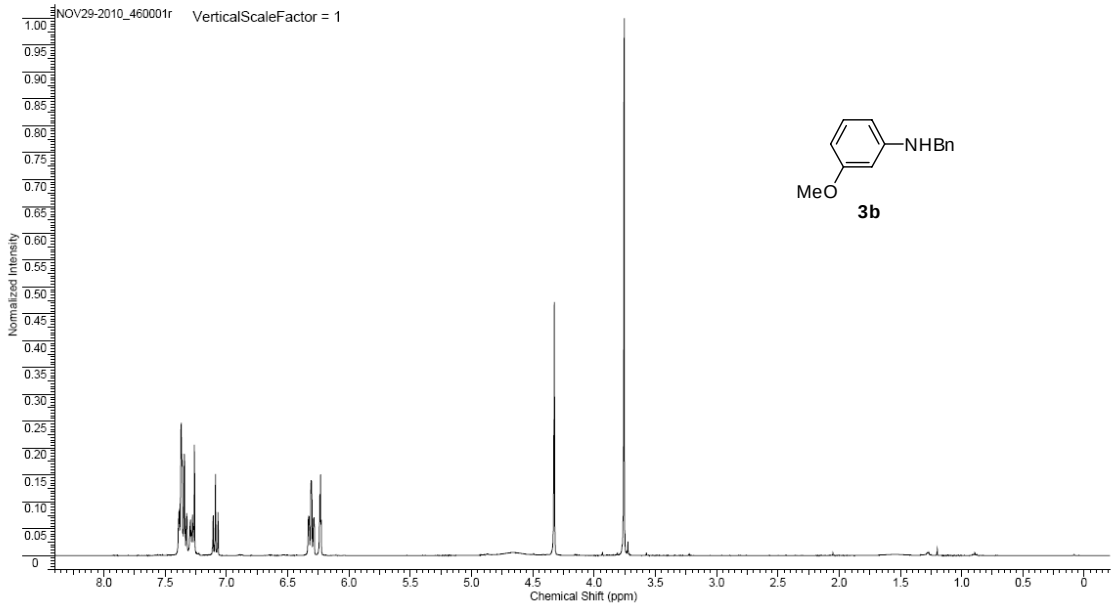
Sweep Width (Hz)	8277.89	*Temperature (degree C)*	27.000				



3b

11/4/2010 9:36:55 AM

Acquisition Time (sec)	3.9584	*Comment*	Notebook U-13020-EXP091-ISO Name ZHANGYUT Project FLOW	*Date*	27 Sep 2010 13:58:24		
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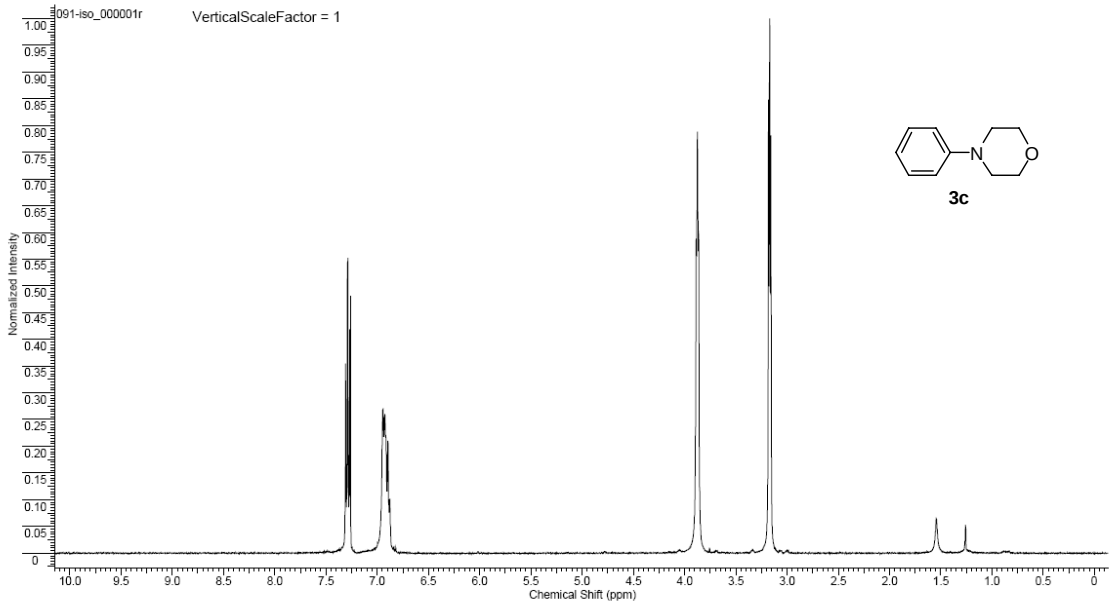
Original Points Count	32768	*Owner*	av400b	*Points Count*	32768	*Pulse Sequence*	zg30
Receiver Gain	574.70	*SW(cyclical) (Hz)*	8278.15	*Solvent*	CHLOROFORM-d	*Spectrum Offset (Hz)*	2457.9258
Sweep Width (Hz)	8277.89	*Temperature (degree C)*	27.000				



3c

11/4/2010 9:39:44 AM

Acquisition Time (sec)	3.9584	*Comment*	Notebook U-13020-EXP096-ISO Name ZHANGYUT Project FLOW	*Date*	24 Sep 2010 21:05:04		
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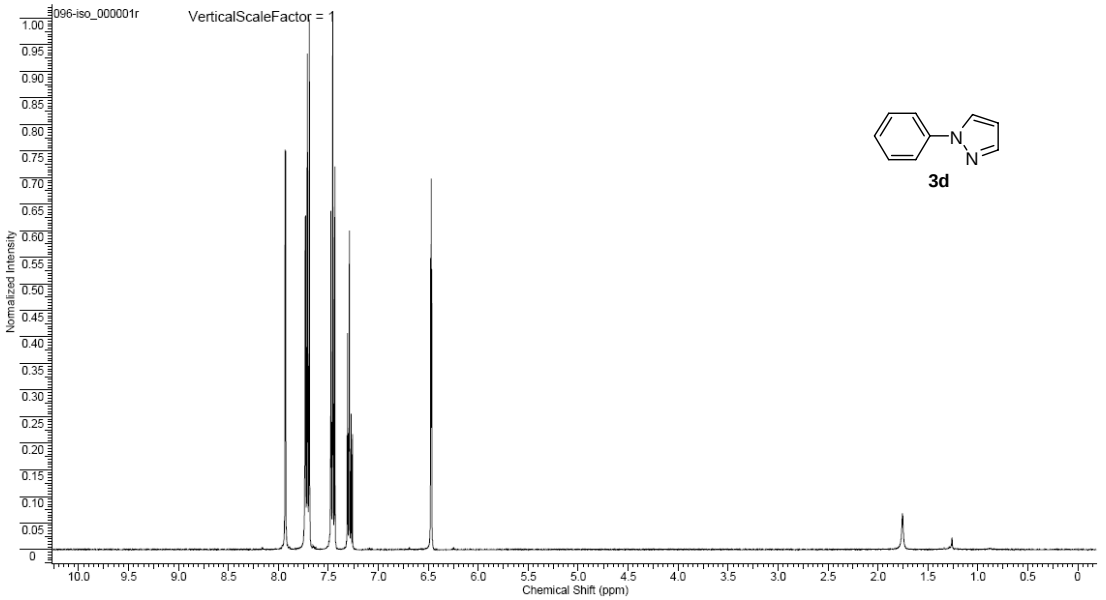
Original Points Count	32768	*Owner*	av400b	*Points Count*	32768	*Pulse Sequence*	zg30
Receiver Gain	574.70	*SW(cyclical) (Hz)*	8278.15	*Solvent*	CHLOROFORM-d	*Spectrum Offset (Hz)*	2457.9258
Sweep Width (Hz)	8277.89	*Temperature (degree C)*	27.000				



3d

11/4/2010 9:42:31 AM

Acquisition Time (sec)	3.9584	***Comment***	Notebook U-13020-EXP098-ISO Name ZHANGYUT Project FLOW			***Date***	27 Sep 2010 20:33:04
Date Stamp	27 Sep 2010 20:33:04			***File Name***	C:\Documents and Settings\zhangyut\Desktop\Local NMR\U-13020\Paper\098-iso_000001r		
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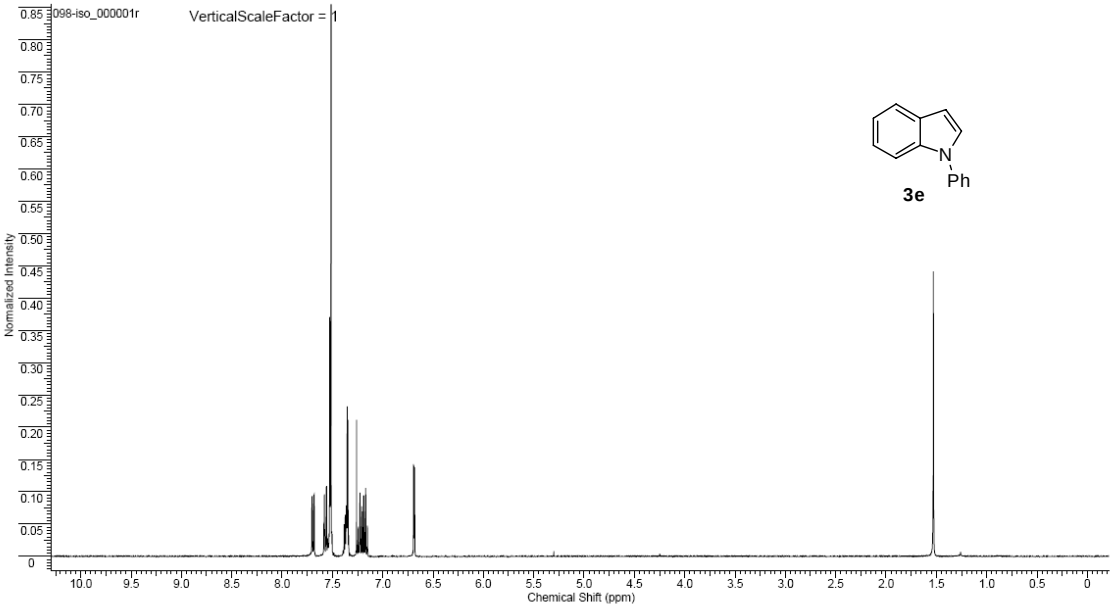
Original Points Count	32768	***Owner***	av400b	***Points Count***	32768	***Pulse Sequence***	zg30
Receiver Gain	812.70	***SW(cyclical) (Hz)***	8278.15	***Solvent***	CHLOROFORM-d	***Spectrum Offset (Hz)***	2457.9258
Sweep Width (Hz)	8277.89	***Temperature (degree C)***	27.000				



3e

11/4/2010 9:46:03 AM

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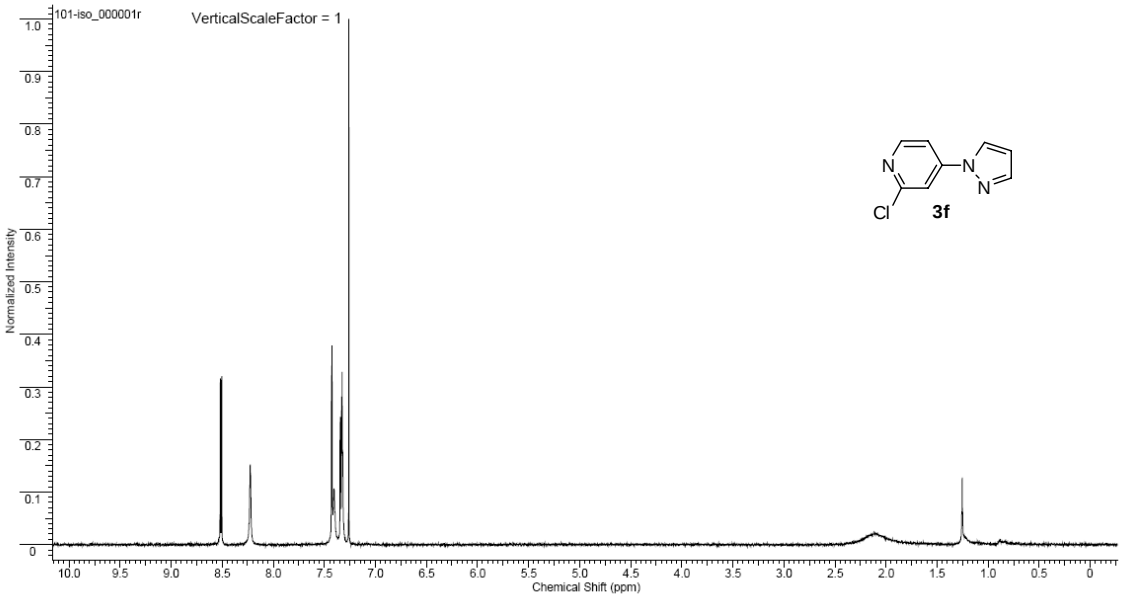
Owner	av400b	***Points Count***	32768	***Pulse Sequence***	zg30	***Receiver Gain***	1149.40
SW(cyclical) (Hz)	8278.15	***Solvent***	CHLOROFORM-d	***Spectrum Offset (Hz)***	2457.9258	***Sweep Width (Hz)***	8277.89
Temperature (degree C)	27.000						



3f

11/4/2010 9:50:09 AM

Acquisition Time (sec)	3.9584	*Comment*	Notebook U-13020-EXP100-ISO Name ZHANGYUT Project FLOW			*Date*	28 Sep 2010 19:58:56
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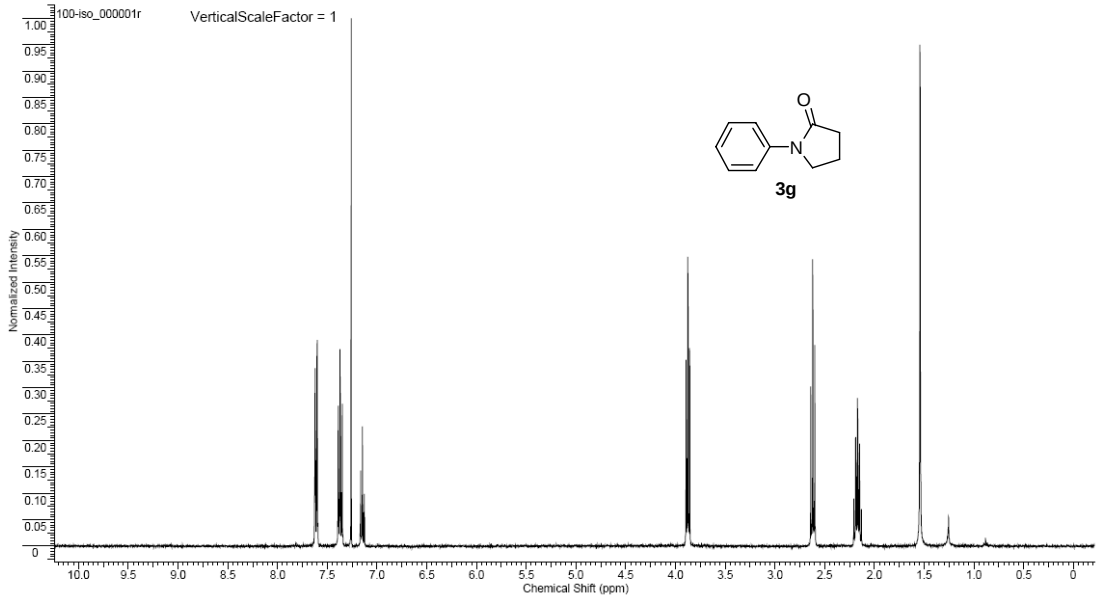
Frequency (MHz)	400.34	*Nucleus*	1H	*Number of Transients*	32	*Origin*	av400b
Original Points Count	32768	*Owner*	av400b	*Points Count*	32768	*Pulse Sequence*	zg30
Receiver Gain	1024.00	*SW(cyclical) (Hz)*	8278.15	*Solvent*	CHLOROFORM-d	*Spectrum Offset (Hz)*	2457.9258
Sweep Width (Hz)	8277.89	*Temperature (degree C)*	26.900				



3g

11/4/2010 9:53:13 AM

Acquisition Time (sec)	3.9584	*Comment*	Notebook U-13020-EXP102-ISO Name ZHANGYUT Project FLOW			*Date*	08 Oct 2010 18:37:52
Date Stamp	08 Oct 2010 18:37:52			*File Name*	C:\Documents and Settings\zhangyut\Desktop\Local NMR\U-13020\Paper\102-iso_000001r		
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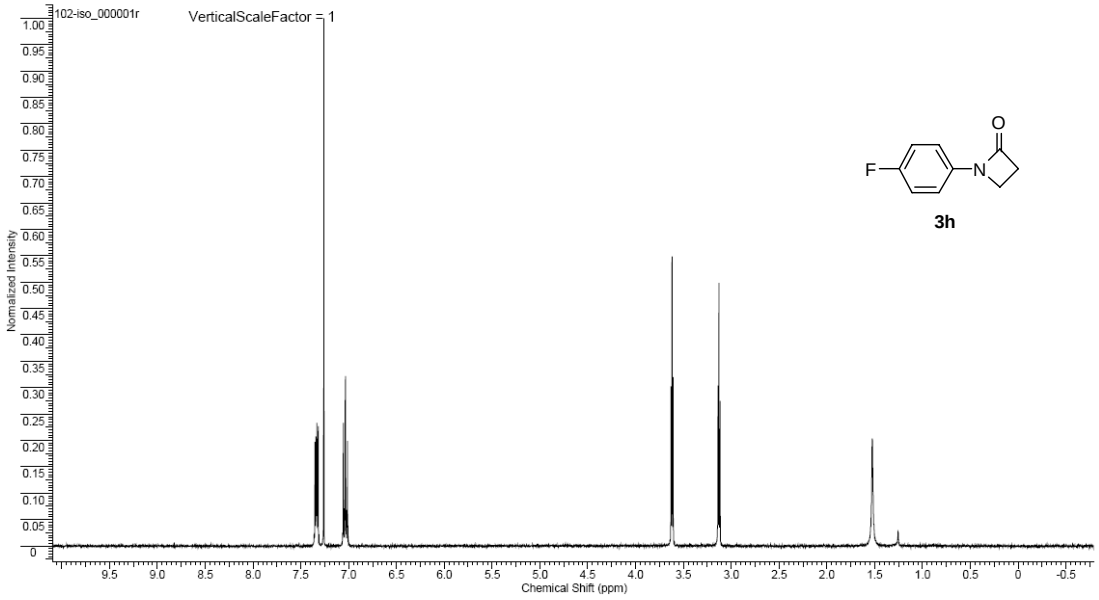
Original Points Count	32768	*Owner*	av400b	*Points Count*	32768	*Pulse Sequence*	zg30
Receiver Gain	1149.40	*SW(cyclical) (Hz)*	8278.15	*Solvent*	CHLOROFORM-d	*Spectrum Offset (Hz)*	2457.9258
Sweep Width (Hz)	8277.89	*Temperature (degree C)*	27.000				



3h

11/4/2010 9:05:25 AM

Acquisition Time (sec)	3.9584	*Comment*	Notebook U-13020-EXP082-4-ISO Name ZHANGYUT Project FLOW				
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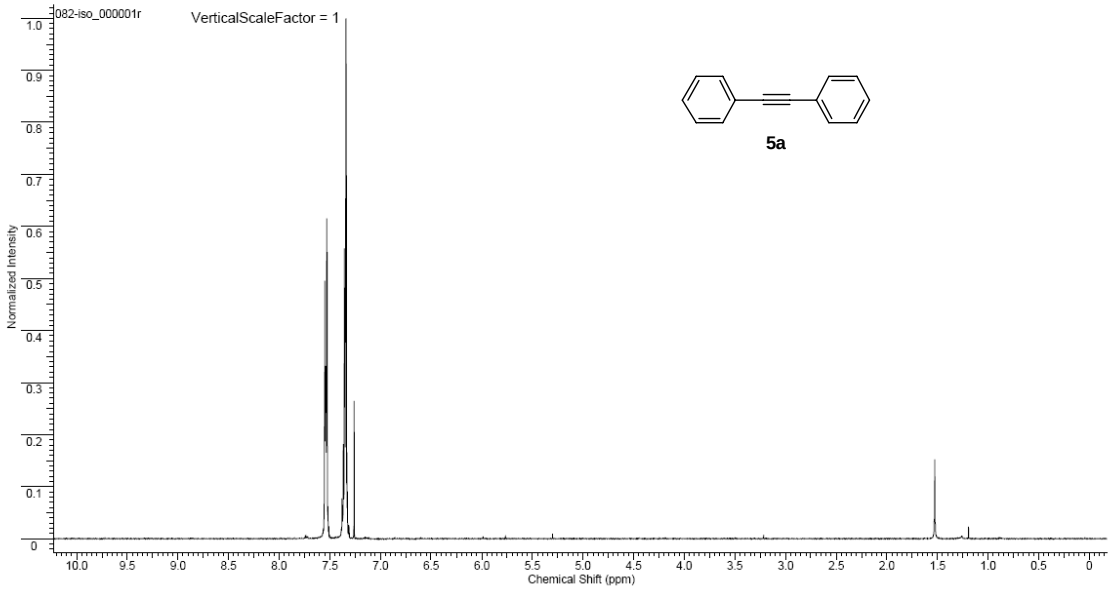
SW(cyclical) (Hz)	8278.15	*Solvent*	CHLOROFORM-d	*Spectrum Offset (Hz)*	2457.9258	*Sweep Width (Hz)*	8277.89
Temperature (degree C)	27.000						



5a

11/4/2010 9:10:26 AM

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Date Stamp	09 Sep 2010 12:56:32			*File Name*	C:\Documents and Settings\zhangyut\Desktop\Local NMR\U-13020\Paper\084-iso_000001r		
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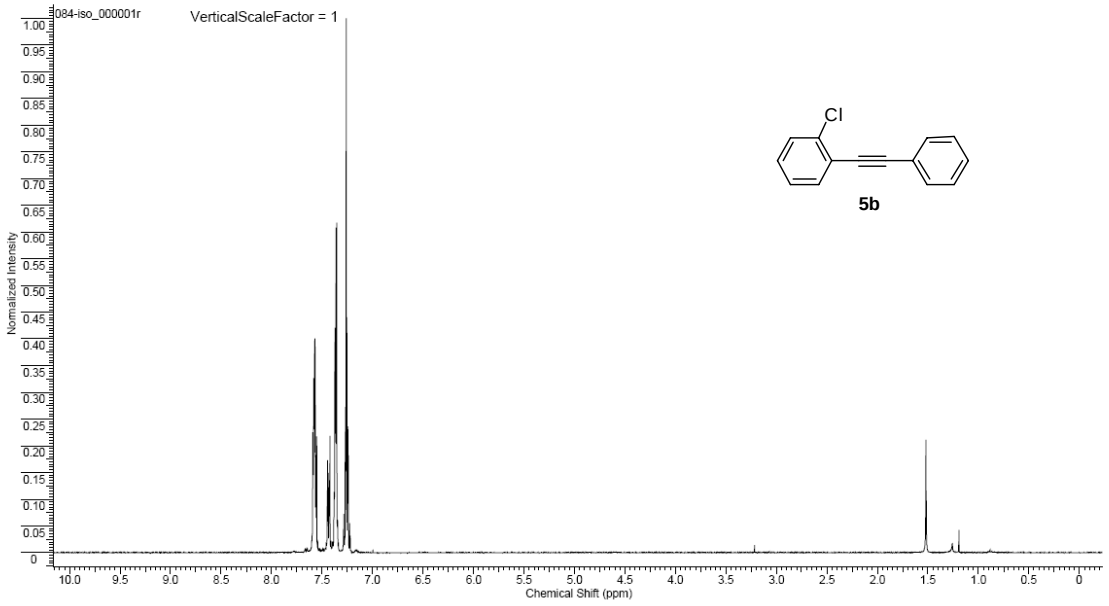

5b

11/4/2010 9:15:02 AM

Acquisition Time (sec)	3.9584	*Comment*	Notebook U-13020-EXP097-ISO Name ZHANGYUT Project FLOW	*Date*	24 Sep 2010 21:49:52		
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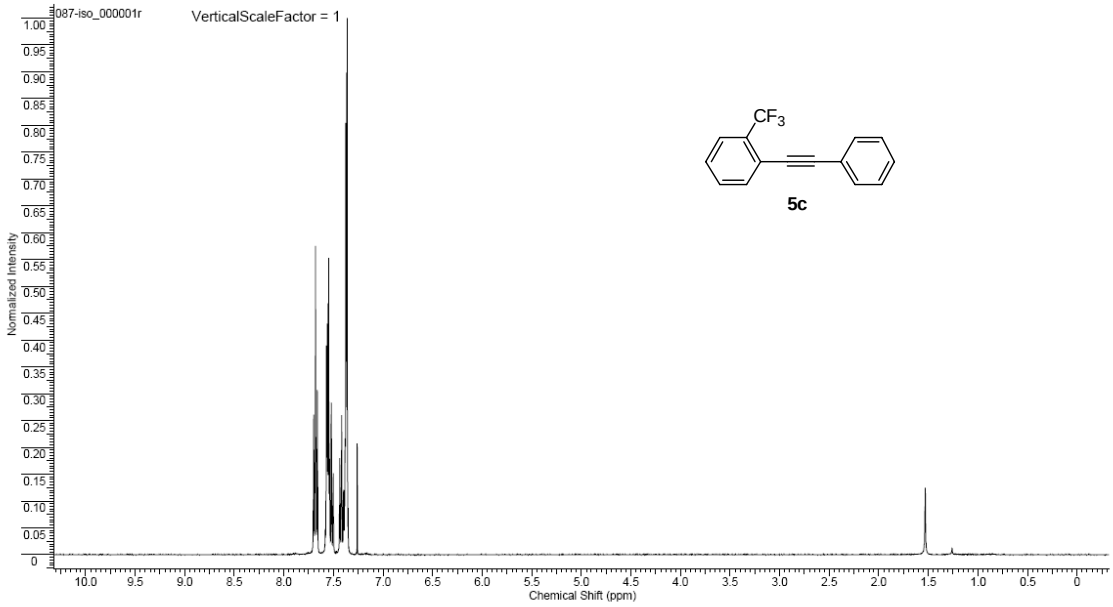
Receiver Gain	574.70	*SW(cyclical) (Hz)*	8278.15	*Solvent*	CHLOROFORM-d	*Spectrum Offset (Hz)*	2457.9258
Sweep Width (Hz)	8277.89	*Temperature (degree C)*	27.000				



5c

11/4/2010 9:19:18 AM

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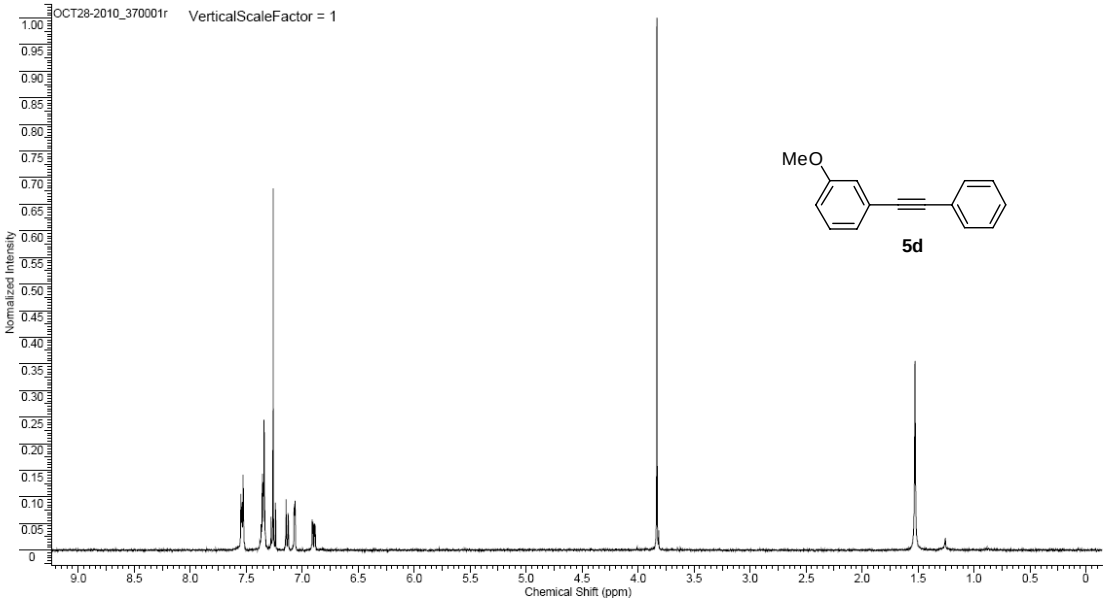
Sweep Width (Hz)	8277.89	*Temperature (degree C)*	27.000				



5d

11/4/2010 9:22:11 AM

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Date Stamp	24 Aug 2010 18:18:40			*File Name*	C:\Documents and Settings\zhangyut\Desktop\Local NMR\U-13020\Paper\084-4_000001r		
Frequency (MHz)	400.34	*Nucleus*	1H	*Number of Transients*	32	*Origin*	av400b
Original Points Count	32768	*Owner*	av400b	*Points Count*	32768	*Pulse Sequence*	zg30
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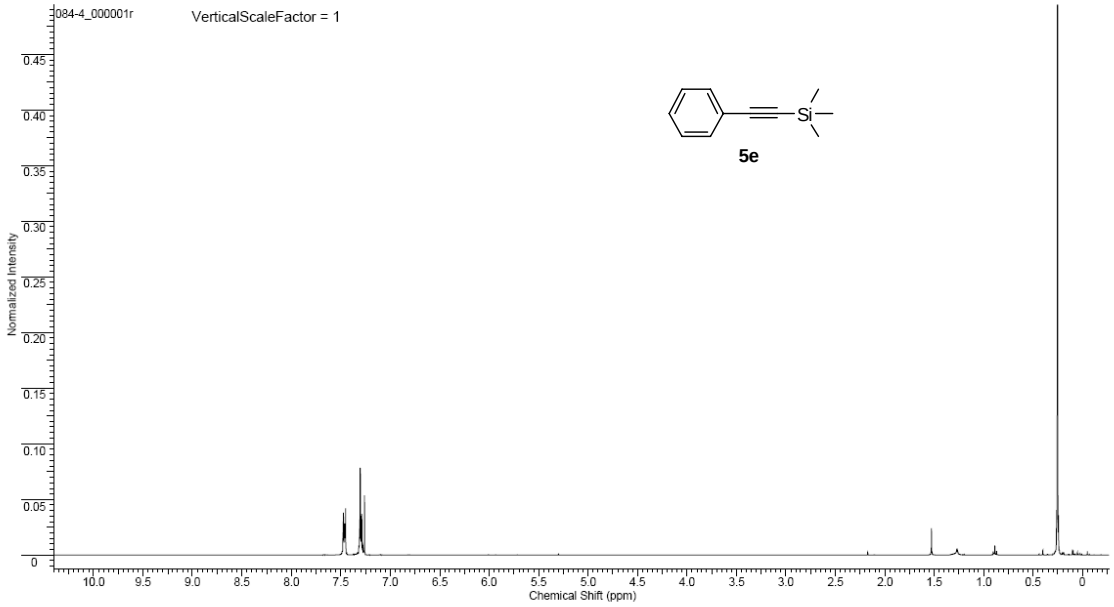

5e

11/4/2010 9:26:31 AM

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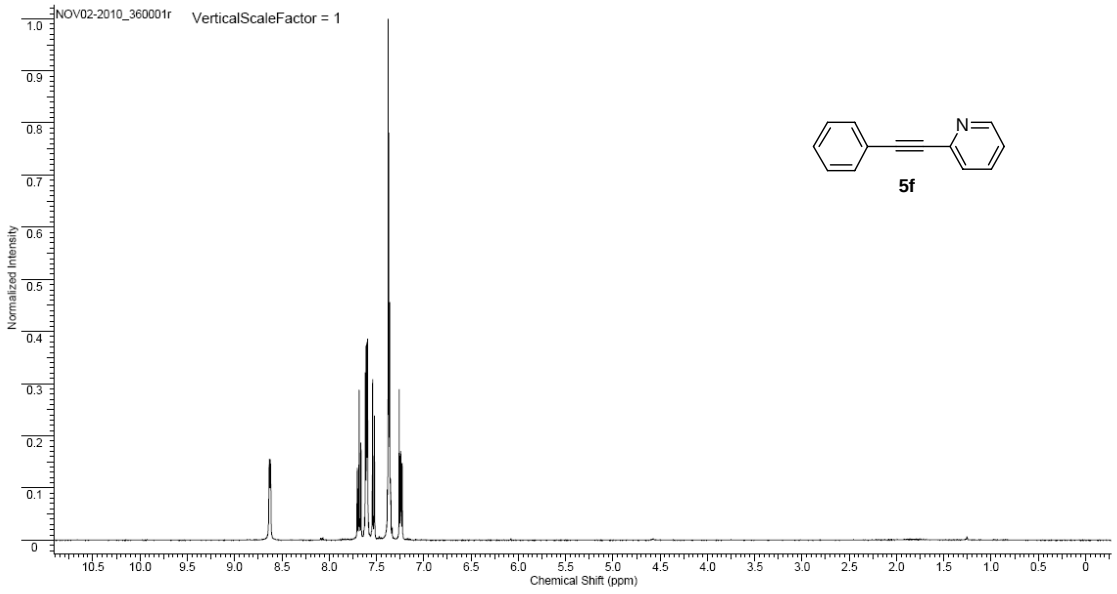
Owner	av400b	*Points Count*	32768	*Pulse Sequence*	zg30	*Receiver Gain*	574.70
SW(cyclical) (Hz)	8278.15	*Solvent*	CHLOROFORM-d	*Spectrum Offset (Hz)*	2457.9258	*Sweep Width (Hz)*	8277.89
Temperature (degree C)	27.000						



5f

11/4/2010 9:56:43 AM

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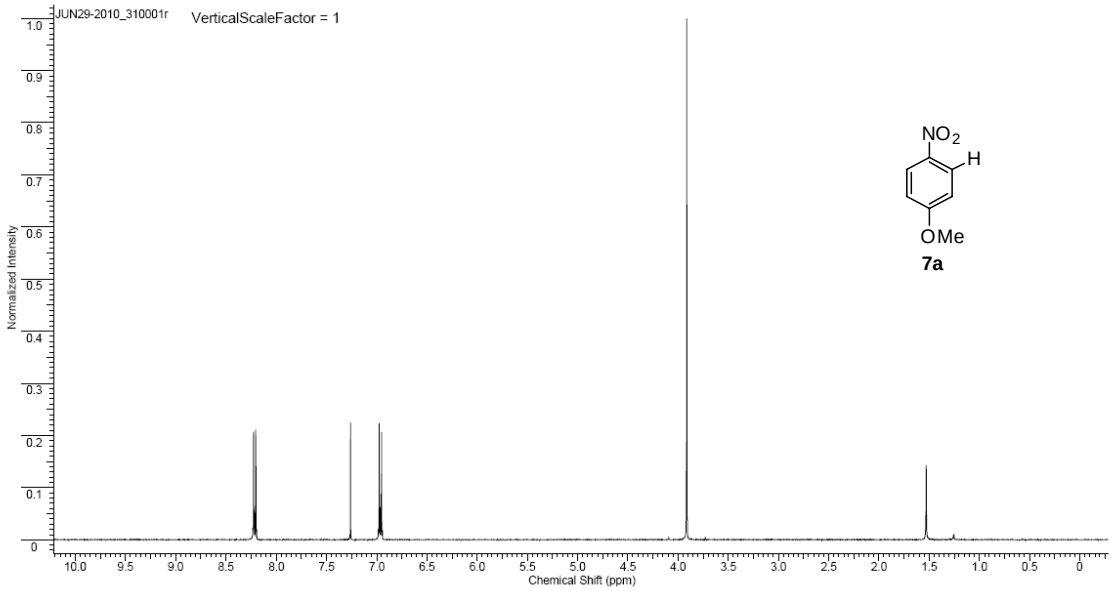
Owner	av400b	*Points Count*	32768	*Pulse Sequence*	zg30	*Receiver Gain*	1149.40
SW(cyclical) (Hz)	8278.15	*Solvent*	CHLOROFORM-d	*Spectrum Offset (Hz)*	2457.9258	*Sweep Width (Hz)*	8277.89
Temperature (degree C)	27.000						



7a

11/4/2010 10:02:44 AM

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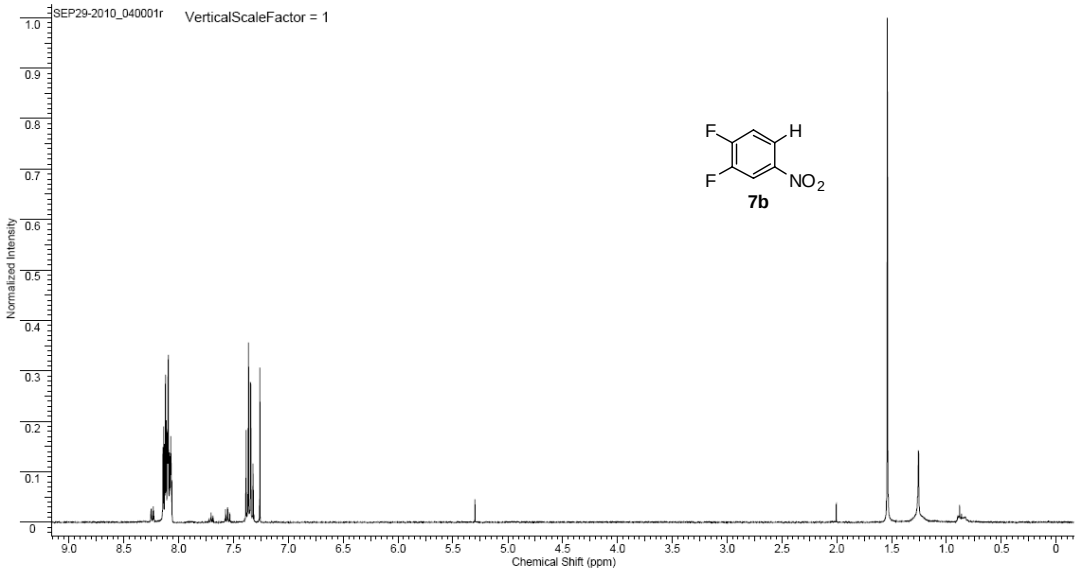
Owner	av400b	*Points Count*	32768	*Pulse Sequence*	zg30	*Receiver Gain*	812.70
SW(cyclical) (Hz)	8278.15	*Solvent*	CHLOROFORM-d	*Spectrum Offset (Hz)*	2457.9258	*Sweep Width (Hz)*	8277.89
Temperature (degree C)	27.000						



7b

11/4/2010 10:10:28 AM

Acquisition Time (sec)	3.9584	*Comment*	Notebook U-13020-EXP095-ISO Name ZHANGYUT Project FLOW	*Date*	24 Sep 2010 21:43:28		
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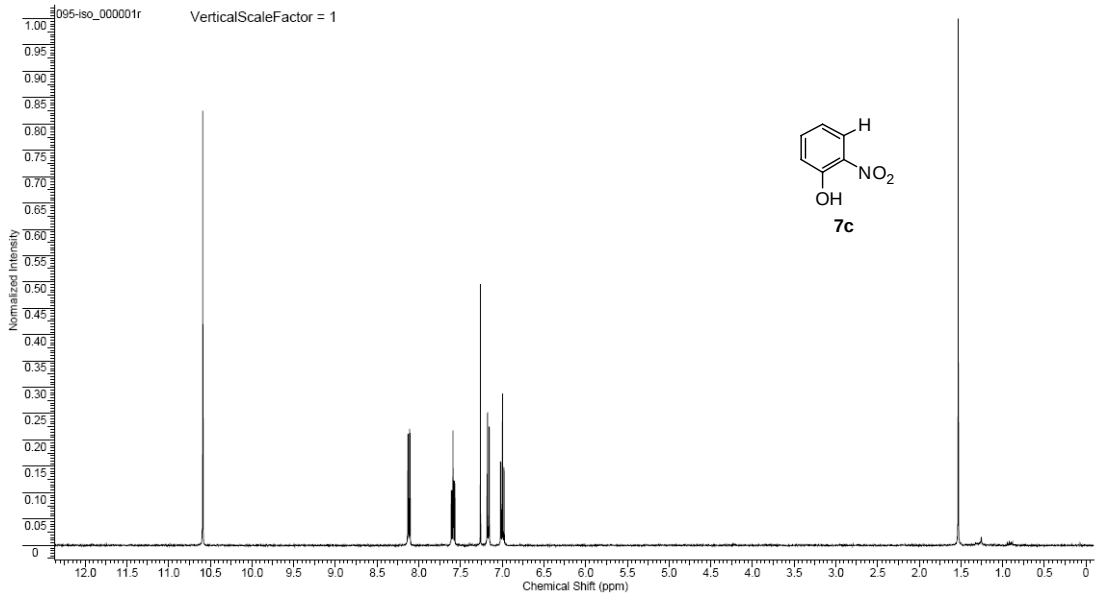
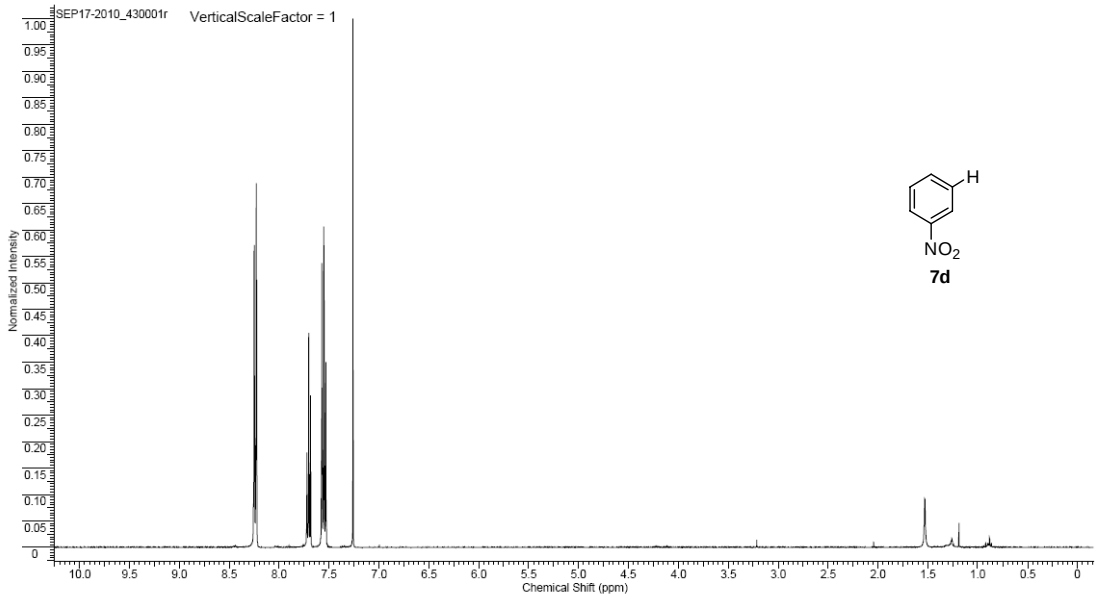
Original Points Count	32768	*Owner*	av400b	*Points Count*	32768	*Pulse Sequence*	zg30
Receiver Gain	1024.00	*SW(cyclical) (Hz)*	8278.15	*Solvent*	CHLOROFORM-d	*Spectrum Offset (Hz)*	2457.9258
Sweep Width (Hz)	8277.89	*Temperature (degree C)*	27.000				



7c

11/4/2010 10:13:48 AM

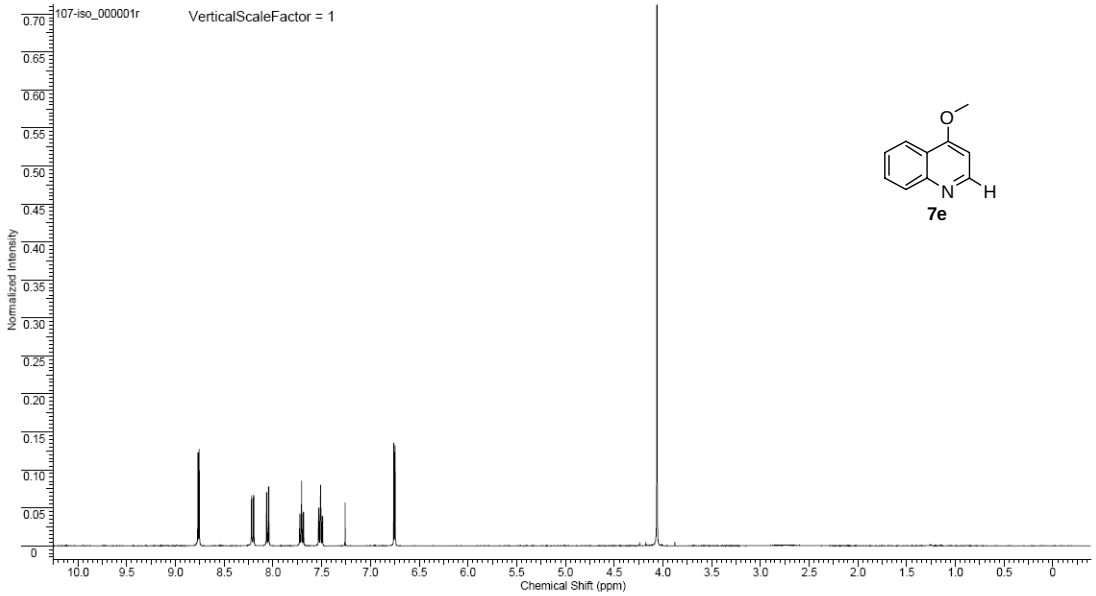
Acquisition Time (sec)	3.9584	*Comment*	Notebook U-13020-EXP092-ISO Name ZHANGYUT Project FLOW	*Date*	17 Sep 2010 21:47:44		
Date Stamp	17 Sep 2010 21:47:44			*File Name*	C:\DOCUME~1\ZHANGYUT\LOCALS~1\TEMP\AWM_TEMP\451666\SEP17-2010_430001r		
Frequency (MHz)	400.34	*Nucleus*	1H	*Number of Transients*	32	*Origin*	av400b
Original Points Count	32768	*Owner*	av400b	*Points Count*	32768	*Pulse Sequence*	zg30
Receiver Gain	645.10	*SW(cyclical) (Hz)*	8278.15	*Solvent*	CHLOROFORM-d	*Spectrum Offset (Hz)*	2457.9258
Sweep Width (Hz)	8277.89	*Temperature (degree C)*	27.000				



7d

11/4/2010 10:16:24 AM

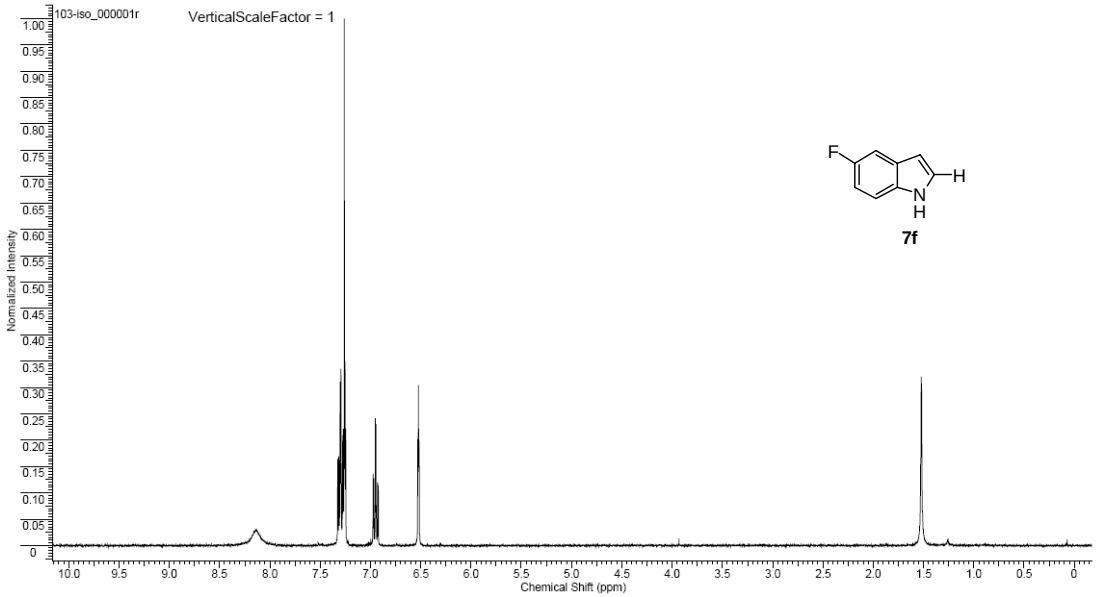
Acquisition Time (sec)	3.9584	*Comment*	Notebook U-13020-EXP107-ISO Name ZHANGYUT Project FLOW	*Date*	07 Oct 2010 13:39:12		
Date Stamp	07 Oct 2010 13:39:12			*File Name*	C:\Documents and Settings\zhangyut\Desktop\Local NMR\U-13020\Paper\107-iso_000001r		
Frequency (MHz)	400.34	*Nucleus*	1H	*Number of Transients*	32	*Origin*	av400b
Original Points Count	32768	*Owner*	av400b	*Points Count*	32768	*Pulse Sequence*	zg30
Receiver Gain	574.70	*SW(cyclical) (Hz)*	8278.15	*Solvent*	CHLOROFORM-d	*Spectrum Offset (Hz)*	2457.9258
Sweep Width (Hz)	8277.89	*Temperature (degree C)*	27.000				



7e

11/4/2010 10:19:01 AM

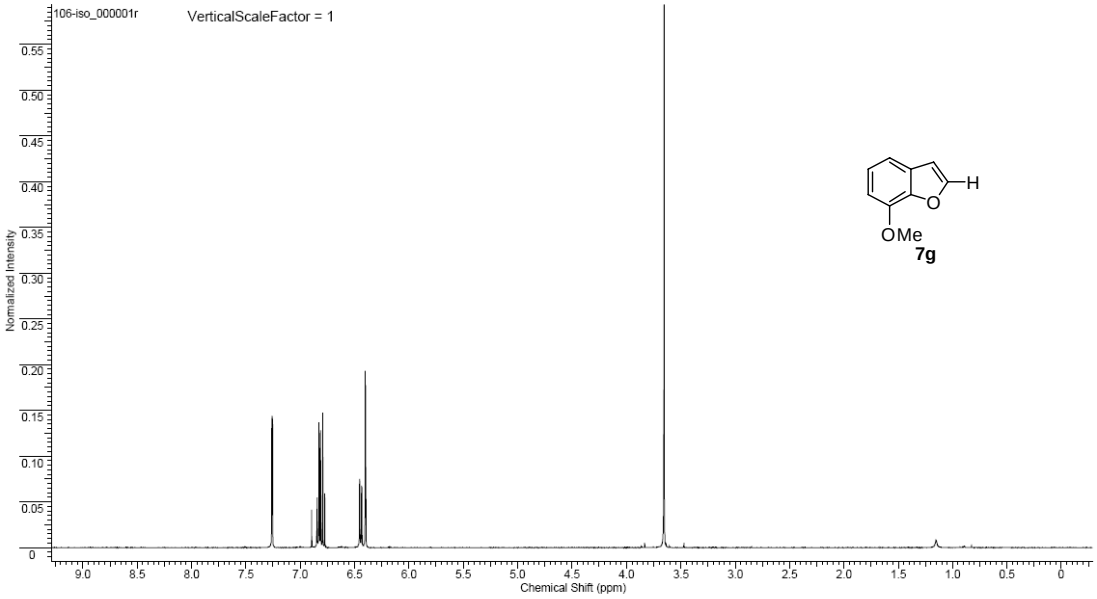
Acquisition Time (sec)	3.9584	*Comment*	Notebook U-13020-EXP103-ISO Name ZHNAGYUT Project FLOW	*Date*	06 Oct 2010 18:48:32		
Date Stamp	06 Oct 2010 18:48:32			*File Name*	C:\Documents and Settings\zhangyut\Desktop\Local NMR\U-13020\Paper\103-iso_000001r		
Frequency (MHz)	400.34	*Nucleus*	1H	*Number of Transients*	32	*Origin*	av400b
Original Points Count	32768	*Owner*	av400b	*Points Count*	32768	*Pulse Sequence*	zg30
Receiver Gain	1024.00	*SW(cyclical) (Hz)*	8278.15	*Solvent*	CHLOROFORM-d	*Spectrum Offset (Hz)*	2457.9263
Sweep Width (Hz)	8277.89	*Temperature (degree C)*	27.000				



7f

11/4/2010 10:27:00 AM

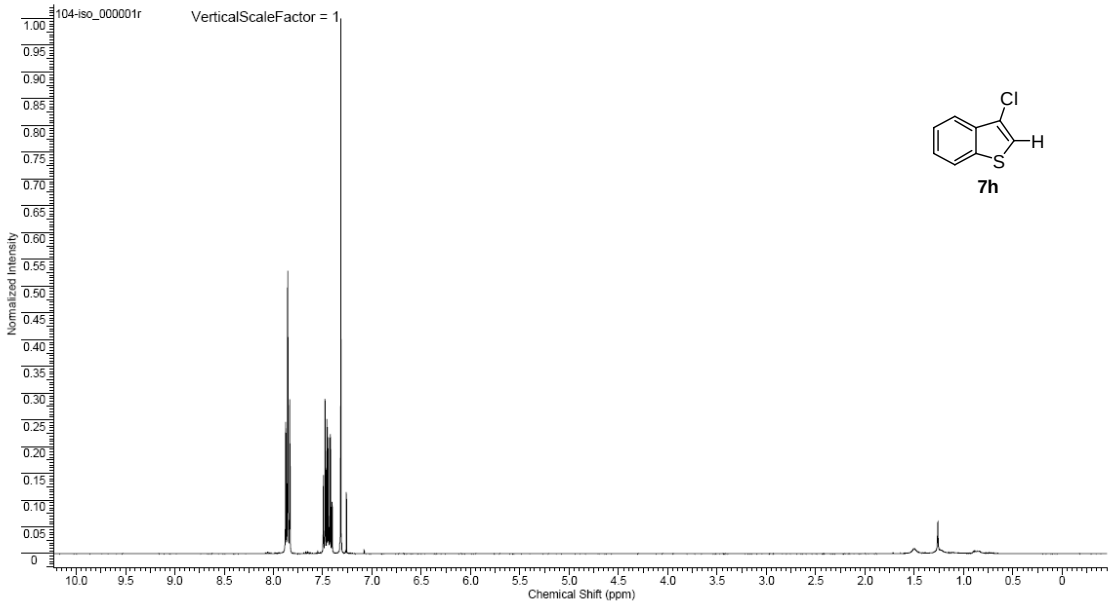
Acquisition Time (sec)	3.9584	*Comment*	Notebook U-13020-EXP106-ISO Name ZHANGYUT Project FLOW	*Date*	07 Oct 2010 13:30:40		
Date Stamp	07 Oct 2010 13:30:40			*File Name*	C:\Documents and Settings\zhangyut\Desktop\Local NMR\U-13020\Paper\106-iso_000001r		
Frequency (MHz)	400.34	*Nucleus*	1H	*Number of Transients*	32	*Origin*	av400b
Original Points Count	32768	*Owner*	av400b	*Points Count*	32768	*Pulse Sequence*	zg30
Receiver Gain	574.70	*SW(cyclical) (Hz)*	8278.15	*Solvent*	CHLOROFORM-d	*Spectrum Offset (Hz)*	2311.1484
Sweep Width (Hz)	8277.89	*Temperature (degree C)*	27.000				



7g

11/4/2010 10:33:17 AM

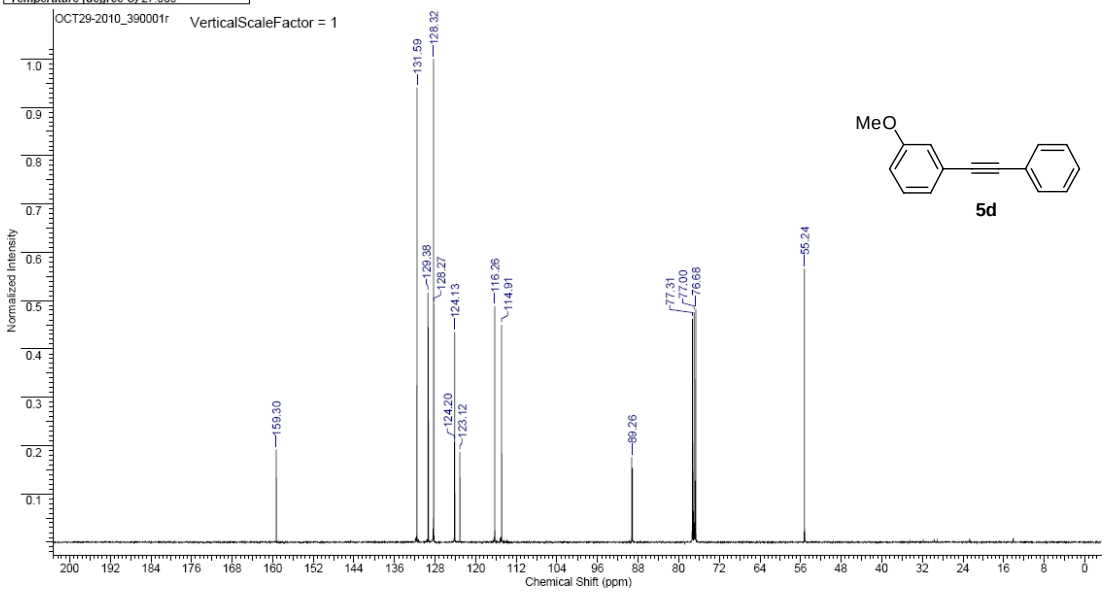
Acquisition Time (sec)	3.9584	*Comment*	Notebook U-13020-EXP104-ISO Name ZHNAGYUT Project FLOW	*Date*	06 Oct 2010 18:57:04		
Date Stamp	06 Oct 2010 18:57:04			*File Name*	C:\Documents and Settings\zhangyut\Desktop\Local NMR\U-13020\Paper\104-iso_000001r		
Frequency (MHz)	400.34	*Nucleus*	1H	*Number of Transients*	32	*Origin*	av400b
Original Points Count	32768	*Owner*	av400b	*Points Count*	32768	*Pulse Sequence*	zg30
Receiver Gain	574.70	*SW(cyclical) (Hz)*	8278.15	*Solvent*	CHLOROFORM-d	*Spectrum Offset (Hz)*	2457.9258
Sweep Width (Hz)	8277.89	*Temperature (degree C)*	27.000				



7h

11/4/2010 3:33:57 PM

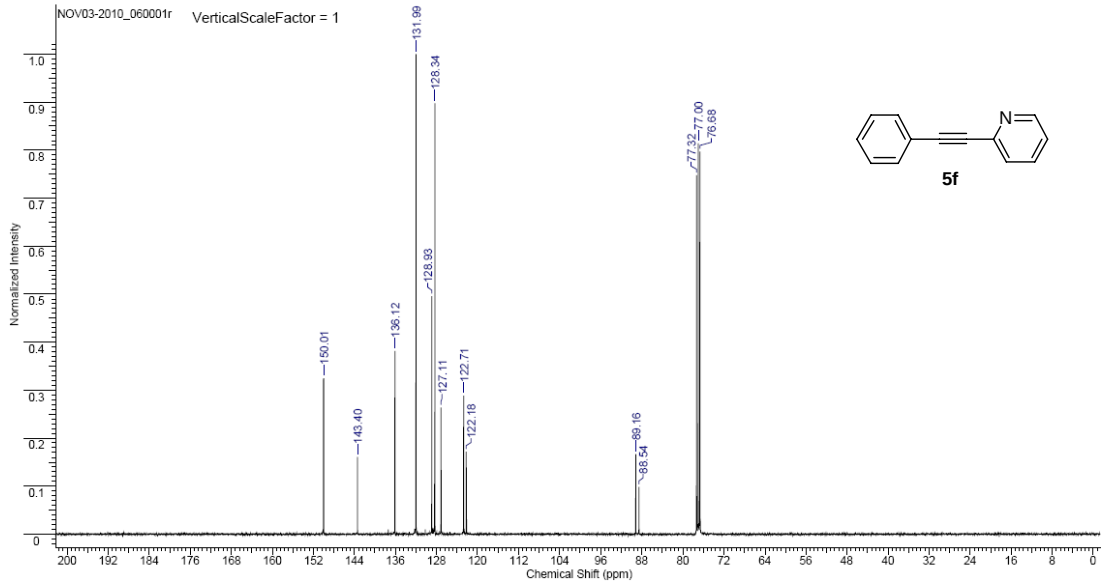
Acquisition Time (sec)	1.3664	*Comment*	Notebook U-13020-EXP110-CARBON Name ZHANGYUT Project FLOW				
Date	29 Oct 2010 21:20:00			*Date Stamp*	29 Oct 2010 21:20:00		
File Name	C:\DOCUME~1\ZHANGYUT\LOCALS~1\TEMP\AWM_TEMP\553375\OCT29-2010_390001r					*Frequency (MHz)*	100.61
Nucleus	13C	*Number of Transients*	256	*Origin*	av400a	*Original Points Count*	32768
Owner	av400a	*Points Count*	32768	*Pulse Sequence*	zgpg30	*Receiver Gain*	9195.20
SW(cyclical) (Hz)	23980.81	*Solvent*	CHLOROFORM-d	*Spectrum Offset (Hz)*	10052.8330	*Sweep Width (Hz)*	23980.08
Temperature (degree C)	27.000						



5d

11/4/2010 3:26:49 PM

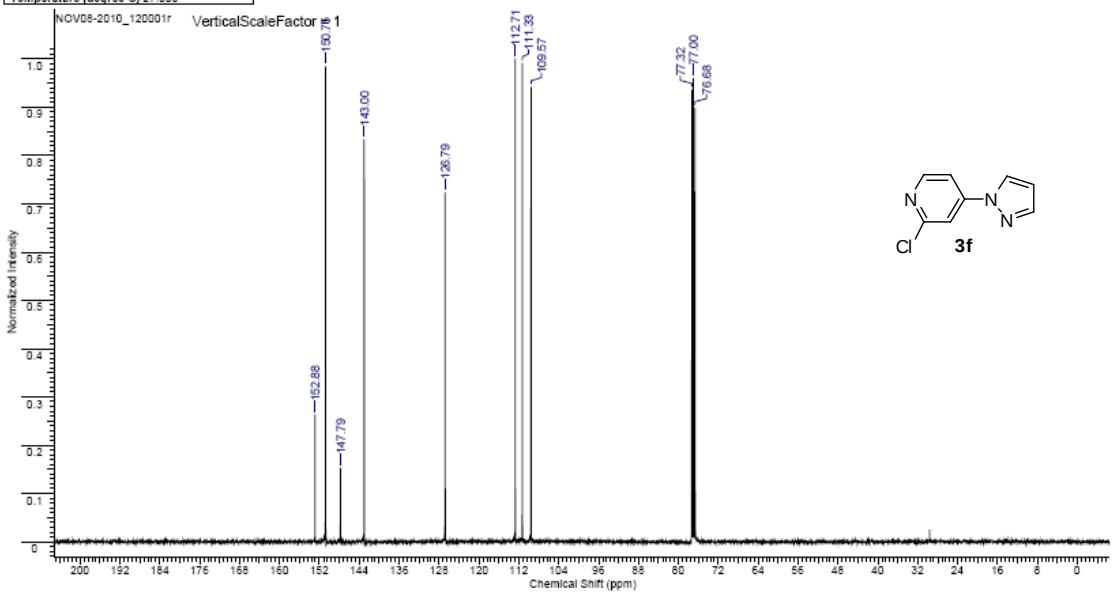
Acquisition Time (sec)	1.3664	*Comment*	Notebook U-13020-EXP109-7-CARBON Name ZHANGYUT Project FLOW				
Date	03 Nov 2010 13:30:40			*Date Stamp*	03 Nov 2010 13:30:40		
File Name	C:\DOCUME~1\ZHANGYUT\LOCALS~1\TEMP\AWM_TEMP\560687\NOV03-2010_060001r					*Frequency (MHz)*	100.61
Nucleus	13C	*Number of Transients*	256	*Origin*	av400a	*Original Points Count*	32768
Owner	av400a	*Points Count*	32768	*Pulse Sequence*	zgpg30	*Receiver Gain*	9195.20
SW(cyclical) (Hz)	23980.81	*Solvent*	CHLOROFORM-d	*Spectrum Offset (Hz)*	10053.5654	*Sweep Width (Hz)*	23980.08
Temperature (degree C)	27.000						



5f

11/8/2010 10:32:18 AM

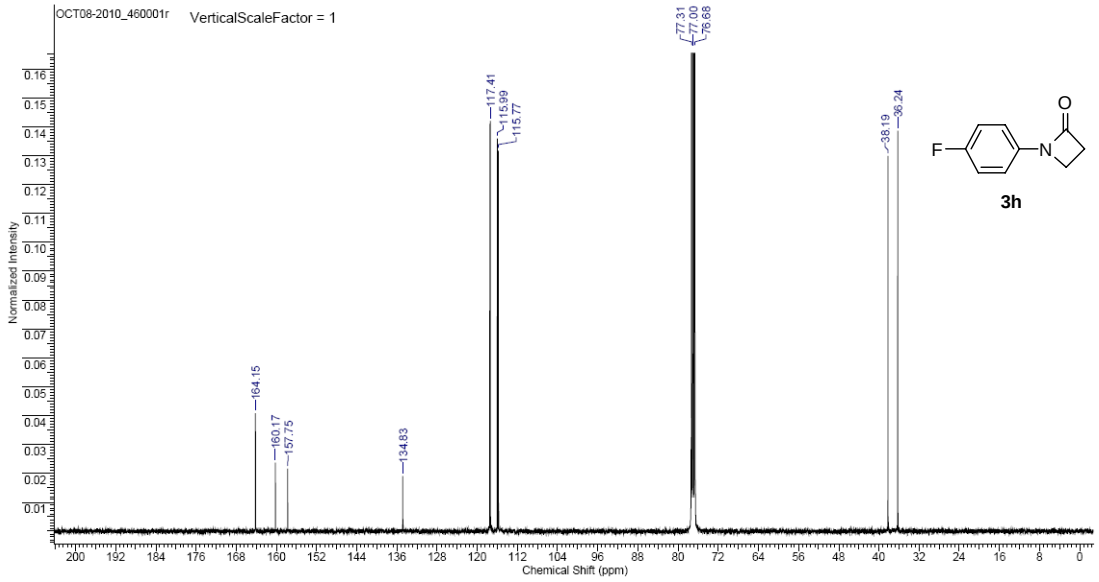
Acquisition Time (sec)	1.3664	Comment	Notebook U-13020-EXP101-2-CARBON Name ZHANGYUT Project FLOW				
Date	08 Nov 2010 14:11:12			Date Stamp	08 Nov 2010 14:11:12		
File Name	C:\DOCUME~1\ZHANGYUT\LOCALS~1\TEMP\AWM_TEMP\570069\NOV08-2010_120001r					Frequency (MHz)	100.61
Nucleus	13C	Number of Transients	256	Origin	av400a	Original Points Count	32768
Owner	av400a	Points Count	32768	Pulse Sequence	zgpg30	Receiver Gain	18390.40
SW(cyclical) (Hz)	23980.81	Solvent	CHLOROFORM-d	Spectrum Offset (Hz)	10055.0293	Sweep Width (Hz)	23980.08
Temperature (degree C)	27.000						



3f

11/4/2010 3:36:53 PM

Acquisition Time (sec)	1.3664	Comment	Notebook U-13020-EXP102-CARBON Name ZHANGYUT Project FLOW				
Date	09 Oct 2010 13:17:52			Date Stamp	09 Oct 2010 13:17:52		
File Name	C:\DOCUME~1\ZHANGYUT\LOCALS~1\TEMP\AWM_TEMP\502864\OCT08-2010_460001r					Frequency (MHz)	100.61
Nucleus	13C	Number of Transients	1024	Origin	av400a	Original Points Count	32768
Owner	av400a	Points Count	32768	Pulse Sequence	zgpg30	Receiver Gain	14596.50
SW(cyclical) (Hz)	23980.81	Solvent	CHLOROFORM-d	Spectrum Offset (Hz)	10057.9561	Sweep Width (Hz)	23980.08
Temperature (degree C)	27.000						



3h

IX. Trace copper analysis.

The amount of leached copper was determined through Graphite Furnace atomic absorption of crude reaction samples.

Sample 082-1 (without using copper scavengers): The sample was obtained by Sonogashira reaction of iodobenzene and phenylacetylene using our general flow conditions described in the Supporting Information, and without using any metal scavenger. After the reaction, the solvent was removed under reduced pressure and the sample was used immediately for trace copper analysis.

Sample 082-2 (after using copper scavenger): The sample was obtained by Sonogashira reaction of iodobenzene and phenylacetylene using our general flow conditions described in the Supporting Information, and the leached copper was then removed by stirring the crude reaction mixture with QuadraPure™ TU resins (1.5 mmol/g loading, 1g) at room temperature for 2 h. After filtering off the resin and evaporation of the solvent, the sample was used immediately for trace copper analysis.

Experimental procedures for determining copper: Approx 5mg of sample was weighed into a quartz vessel and digested in an Anton Paar Microwave 3000 with 5.0ml conc nitric acid using the following program. A blank a was also run . The sample solutions were analysed using a Thermo Solaar graphite furnace atomic absorption against copper standards of between 5ppb and 50ppb. The standard solutions were obtained using the auto dilute function from a 100ppb stock standard and the samples were auto diluted until they contained less than 50ppb Pd. The instrument will attempt 4 autodilutions, with a max dilution of 50x. If the results are still not within range the result will be quoted as a minimum value.

Results

Sample	Cu ppm	rsd
BLANK	0.0	15.3
YZ-082-1 A 9 (autodiluted 50x)	3858	0.9
YZ-082-1 B (autodiluted 50x)	2906	0.5
YZ-082-2 A (autodiluted 3.636x)	49	5.7
YZ-082-2 B (autodiluted 2.985x)	39	3.2

Summary

Sample	Cu (ppm) Result A	Cu (ppm) Result B	Cu (ppm) Average
YZ-082-1	3858	2906	3382
YZ-082-2	49	39	44

The average leached copper for sample 082-1 is 3382 ppm and the average leached copper for sample 082-2 is 44 ppm.

Full details of copper analysis parameters and results (SOLAAR AA Report):

SOLAAR AA Report

Operator Name: PENNY
Results File: C:\SOLAARM\DATA\RESULTS.SLR

Report Date: 30/09/2010 14:25:55

General Parameters

Method : Cu_cofa
Autosampler : FS95/97
Operator : penny
Instrument Mode: Furnace

Description

Main Cu method

Analysis Details

Analysis Name: Analysis 187 30/09/2010
Operator Name: PENNY
Spectrometer: M Series 651026 v1.27

Lamp Information

Element(s)	Serial Number	mA Hours
Cu Ni	n/a	n/a

Deuterium Lamp Hours: 142.28

Sequence Table

Shared Standards: Yes

Action	Cu
Calibration	✓
Sample Blank	✓
YZ-082-1A	✓
YZ-082-1 B	✓
YZ-082-2 A	✓
YZ-082-2 B	✓

Sample Details

Nominal Mass: 1.0000

No.	Sample Id	Sample Mass	Dilution Ratio
1	YZ-082-1A	6.2120	5.0000
2	YZ-082-1 B	7.9910	5.0000
3	YZ-082-2 A	7.4530	5.0000
4	YZ-082-2 B	7.5930	5.0000

Spectrometer Parameters - Cu

Element: Cu
Wavelength: 217.9nm
Background Correction: D2
Signal Type: Transient
Measurement Time: 3.0secs
Measure Peak From: 0.00
Use RSD Test: No
Measurement Mode: Absorbance
Bandpass: 0.5nm
High Resolution: Off
Transient Type: Height
Flier Mode: No
To: 3.00secs
Lamp Current: 80%
Optimise Spectrometer Parameters: No
Number Of Resamples: 3

Furnace Parameters - Cu

Cuvette Type: ELC
Clean Cuvette if sample greater than: 0.001Abs
Injection Temperature: 0°C

Furnace Programme (74.0secs)

Phase	Temp (°C)	Time (sec)	Ramp (°C/sec)	Gas Type	Gas Flow	Commands
1	100	30.0	10	2	0.2L/min	
2	850	20.0	150	2	0.2L/min	
3	2100	3.0	0	2	Off	RD TC
4	2500	3.0	0	2	0.2L/min	TC
5	2700	3.0	0	2	0.2L/min	TC

Sampling Parameters - Cu

Sampling: FS95/97
Working Volume: 20.0µL
Automatic Spike Prep: No
Sample Volume: 20.0µL

Matrix Modifiers

Modifier	Method	Volume	Order
1 Modifier	Wet-mixed	1.0µL	1
2	None	20.0µL	2
3	None	20.0µL	3
4	None	20.0µL	4
5	None	20.0µL	5
6	None	20.0µL	6

Sample Preparation: Int. Dilution
Standard Preparation: Fixed
Slow Solution Uptake: No
Sampling Delay: No
Wash Autosampler if sample greater than: 0.001Abs
Intelligent Dilution Threshold: 100%
Std Additions: None
Slow Injection: No
Number Of Washes: 1

SOLAAR AA Report

Operator Name: PENNY
Results File: C:\SOLAARM\DATA\RESULTS.SLR

Report Date: 30/09/2010 14:25:55

Calibration Parameters - Cu

Calibration Mode: Normal
Concentration Units: µg/L
Excess Curvature Limits: -10% to +40%
Master Standard: 100.0000

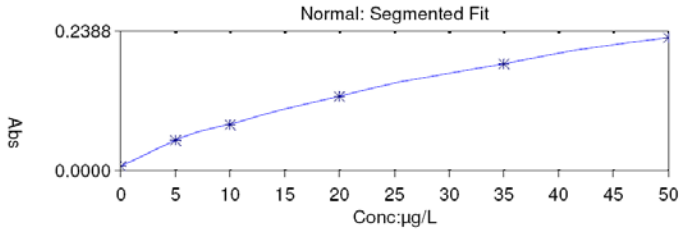
Line Fit: Segmented Curve
Scaled Units: µg/L
Rescale Limit: 10.0%

Use Stored Calibration: No
Scaling Factor: 1.0000
Failure Action: Flag and Continue

Standard 1	5.0000	Standard 4	35.0000
Standard 2	10.0000	Standard 5	50.0000
Standard 3	20.0000		

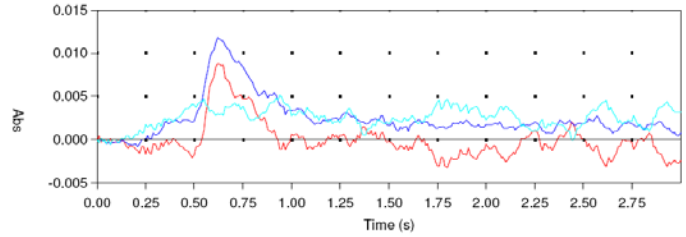
Solution Results - Cu

Min Curvature: 0%
Max Curvature: 34%
Characteristic Conc: 0.4867

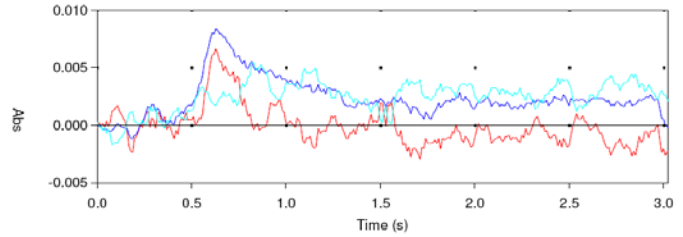


Sample ID	Signal	Rsd	Conc	Corrected Conc	Auto Dilution
	Abs (Height)	%	µg/L	µg/L	
Cu Blank	**0.007**	**36.2**	**0.0000**		

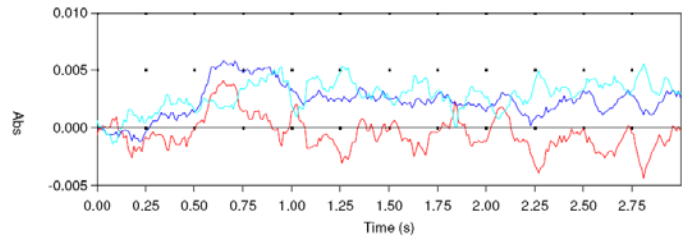
Resample: 1
Height: 0.009
Background: 0.003
Area: -0.000
Background: 0.008
30/09/2010 11:44:51



Resample: 2
Height: 0.007
Background: 0.002
Area: -0.000
Background: 0.007
30/09/2010 11:46:45



Resample: 3
Height: 0.004
Background: 0.002
Area: -0.002
Background: 0.008
30/09/2010 11:48:40



SOLAAR AA Report

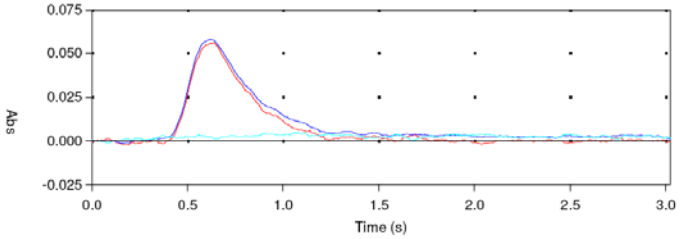
Operator Name: PENNY
Results File: C:\SOLAARM\DATA\RESULTS.SLR

Report Date: 30/09/2010 14:25:55

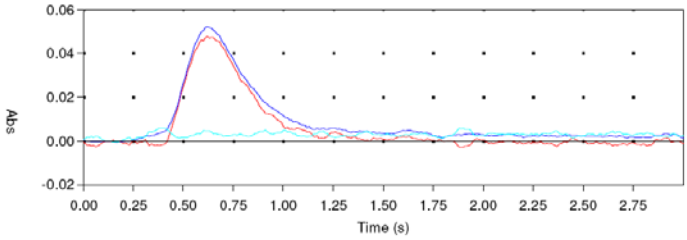
Solution Results - Cu

Sample ID	Signal	Rsd	Conc	Corrected Conc	Auto Dilution
	Abs (Height)	%	µg/L	µg/L	
Cu Standard 1	**0.052**	**8.3**	**5.0000**		

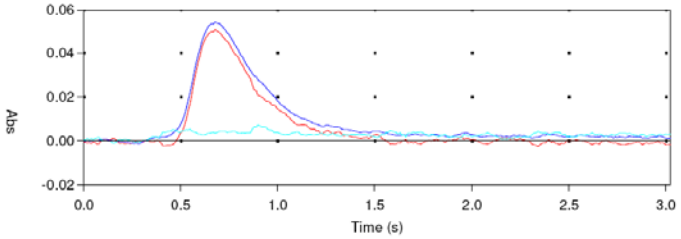
Resample: 1
Height: 0.056
Background: 0.001
Area: 0.020
Background: 0.007
30/09/2010 11:52:37



Resample: 2
Height: 0.048
Background: 0.004
Area: 0.016
Background: 0.009
30/09/2010 11:54:32

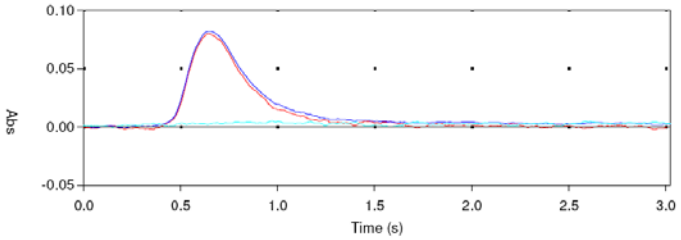


Resample: 3
Height: 0.051
Background: 0.004
Area: 0.017
Background: 0.008
30/09/2010 11:56:27

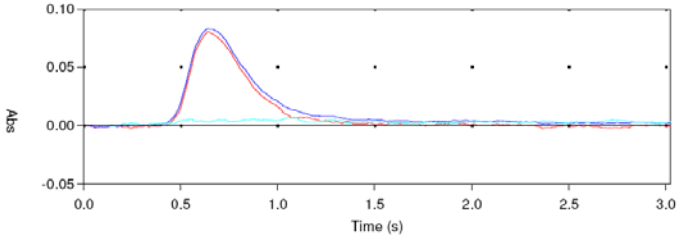


Sample ID	Signal	Rsd	Conc	Corrected Conc	Auto Dilution
	Abs (Height)	%	µg/L	µg/L	
Cu Standard 2	**0.078**	**3.0**	**10.0000**		

Resample: 1
Height: 0.079
Background: 0.002
Area: 0.029
Background: 0.007
30/09/2010 12:00:24



Resample: 2
Height: 0.080
Background: 0.003
Area: 0.027
Background: 0.009
30/09/2010 12:02:19



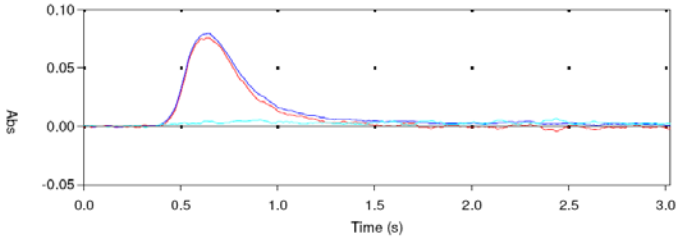
SOLAAR AA Report

Operator Name: PENNY
Results File: C:\SOLAARM\DATA\RESULTS.SLR

Report Date: 30/09/2010 14:25:55

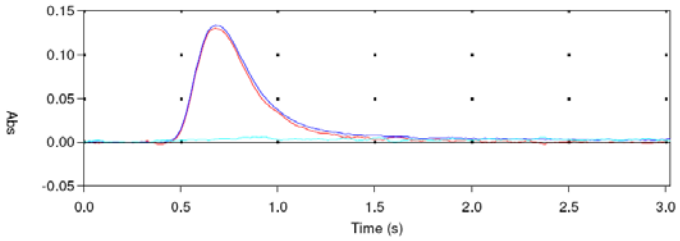
Solution Results - Cu

Resample: 3
Height: 0.076
Background: 0.004
Area: 0.027
Background: 0.008
30/09/2010 12:04:14



Sample ID	Signal	Rsd	Conc	Corrected Conc	Auto Dilution
	Abs (Height)	%	µg/L	µg/L	
Cu Standard 3	**0.126**	**2.4**	**20.0000**		

Resample: 1
Height: 0.130
Background: 0.004
Area: 0.049
Background: 0.008
30/09/2010 12:08:11



Resample: 2
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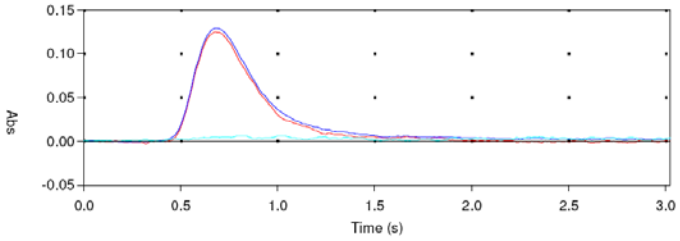
Area: 0.048
Background: 0.008
30/09/2010 12:10:06



Resample: 3
Height: 0.125
Background: 0.003
Area: 0.049
Background: 0.008
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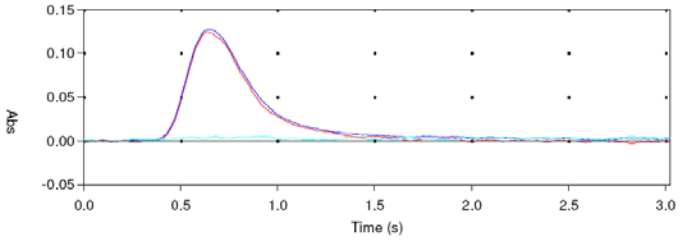
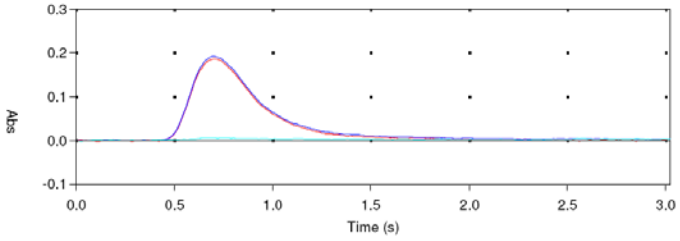


Sample ID	Signal	Rsd	Conc	Corrected Conc	Auto Dilution
	Abs (Height)	%	µg/L	µg/L	
Cu Standard 4	**0.182**	**2.1**	**35.0000**		

Resample: 1
Height: 0.186
Background: 0.005
Area: 0.077
Background: 0.008
30/09/2010 12:15:59



SOLAAR AA Report

Operator Name: PENNY
Results File: C:\SOLAARM\DATA\RESULTS.SLR

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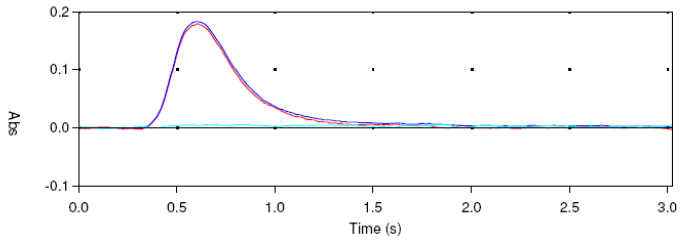
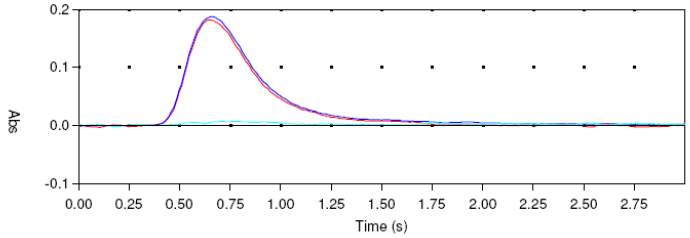
Solution Results - Cu

Resample: 2
Height: 0.179
Background: 0.004
Area: 0.073
Background: 0.009
30/09/2010 12:17:54

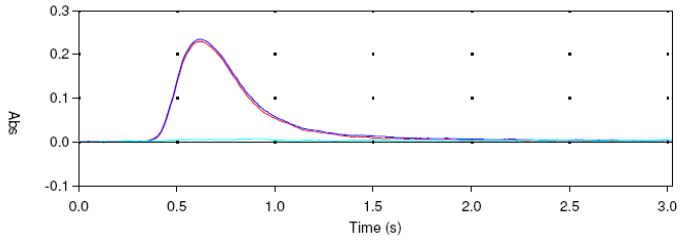


Resample: 3
Height: 0.181
Background: 0.005
Area: 0.074
Background: 0.009
30/09/2010 12:19:50

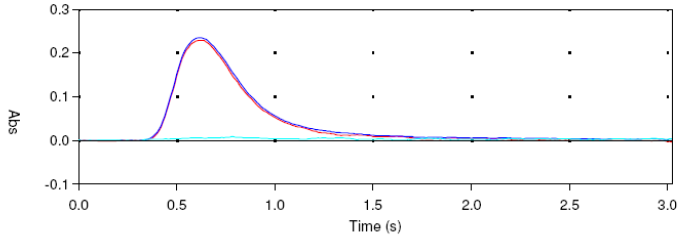


Sample ID	Signal	Rsd	Conc	Corrected Conc	Auto Dilution
	Abs (Height)	%	µg/L	µg/L	
Cu Standard 5	**0.228**	**1.2**	**50.0000**		

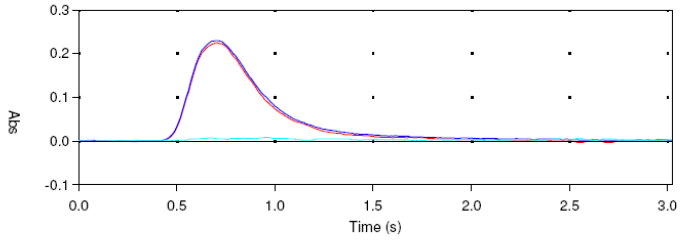
Resample: 1
Height: 0.229
Background: 0.005
Area: 0.099
Background: 0.009
30/09/2010 12:23:46



Resample: 2
Height: 0.229
Background: 0.005
Area: 0.100
Background: 0.009
30/09/2010 12:25:42



Resample: 3
Height: 0.225
Background: 0.006
Area: 0.097
Background: 0.009
30/09/2010 12:27:37



SOLAAR AA Report

Operator Name: PENNY
Results File: C:\SOLAARM\DATA\RESULTS.SLR

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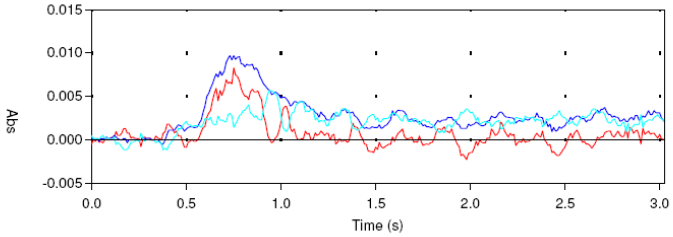
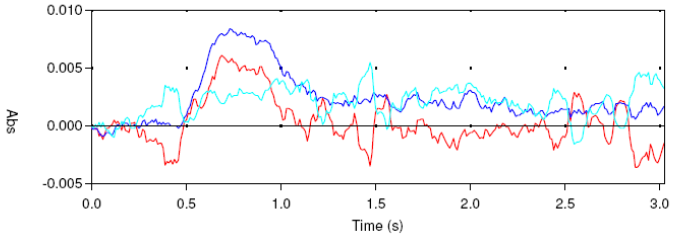
Solution Results - Cu

Sample ID	Signal	Rsd	Conc	Corrected Conc	Auto Dilution
	Abs (Height)	%	µg/L	µg/L	
Cu Sample Blank	**0.007**	**15.3**	**0.0774**	**0.0000**	**1.000**

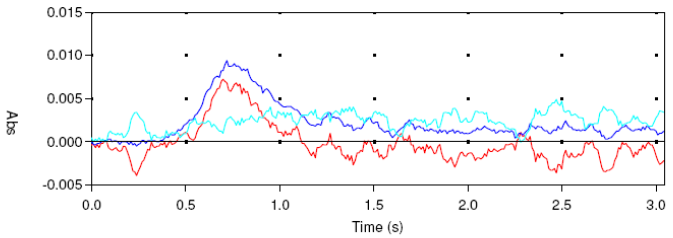
Resample: 1
Height: 0.008
Background: 0.001
Area: 0.002
Background: 0.006
30/09/2010 12:31:23



Resample: 2
Height: 0.006
Background: 0.002
Area: 0.001
Background: 0.006
30/09/2010 12:33:18

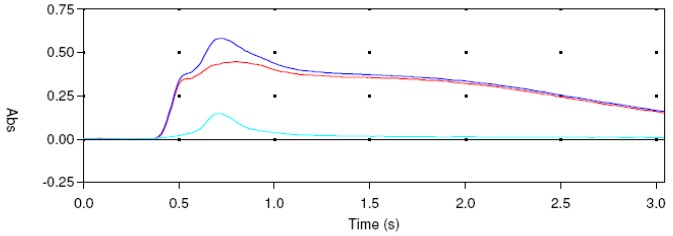


Resample: 3
Height: 0.007
Background: 0.001
Area: -0.000
Background: 0.007
30/09/2010 12:35:13

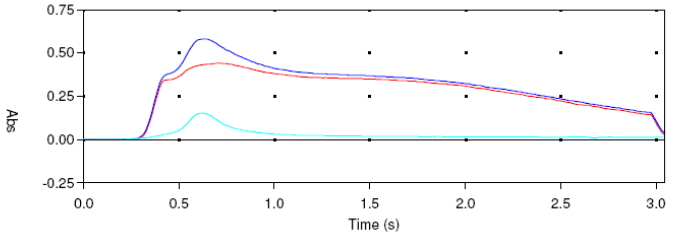


Sample ID	Signal	Rsd	Conc	Corrected Conc	Auto Dilution
	Abs (Height)	%	µg/L	µg/L	
Cu YZ-082-1A	**0.443**	**0.4**	**120.8961 C**	**97.2462 C**	**1.000**

Resample: 1
Height: 0.445
Background: 0.091
Area: 0.817
Background: 0.068
30/09/2010 12:39:00



Resample: 2
Height: 0.441
Background: 0.105
Area: 0.823
Background: 0.079
30/09/2010 12:40:55



SOLAAR AA Report

Operator Name: PENNY
Results File: C:\SOLAARM\DATA\RESULTS.SLR

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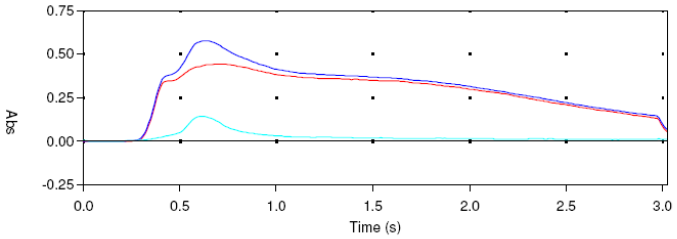
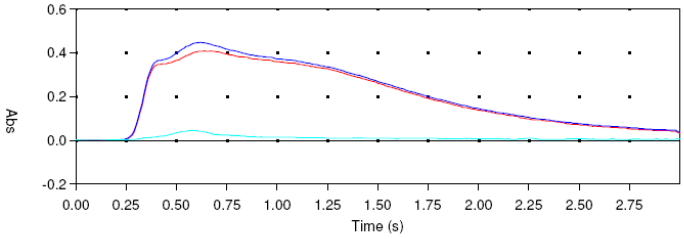
Solution Results - Cu

Resample: 3
Height: 0.443
Background: 0.103
Area: 0.814
Background: 0.076
30/09/2010 12:42:50

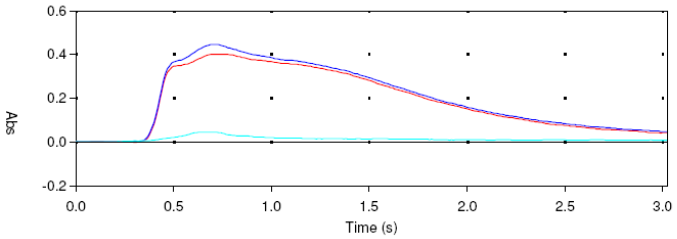


Sample ID	Signal	Rsd	Conc	Corrected Conc	Auto Dilution
	Abs (Height)	%	µg/L	µg/L	
Cu YZ-082-1A	0.403 I	1.2	107.6518 C	360.9720 C	4.167

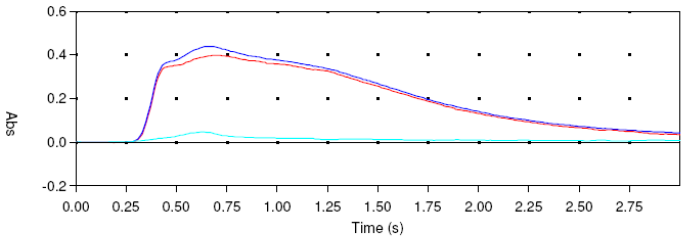
Resample: 1
Height: 0.408
Background: 0.031
Area: 0.586
Background: 0.031
30/09/2010 12:46:46



Resample: 2
Height: 0.402
Background: 0.044
Area: 0.570
Background: 0.038
30/09/2010 12:48:41

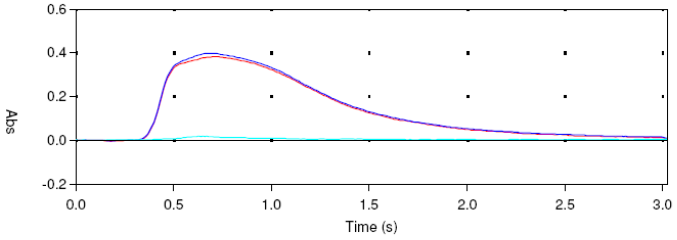


Resample: 3
Height: 0.399
Background: 0.038
Area: 0.557
Background: 0.037
30/09/2010 12:50:36



Sample ID	Signal	Rsd	Conc	Corrected Conc	Auto Dilution
	Abs (Height)	%	µg/L	µg/L	
Cu YZ-082-1A	0.383 I	0.1	101.0790 C	1251.597 C	15.385

Resample: 1
Height: 0.383
Background: 0.015
Area: 0.380
Background: 0.015
30/09/2010 12:54:33



SOLAAR AA Report

Operator Name: PENNY
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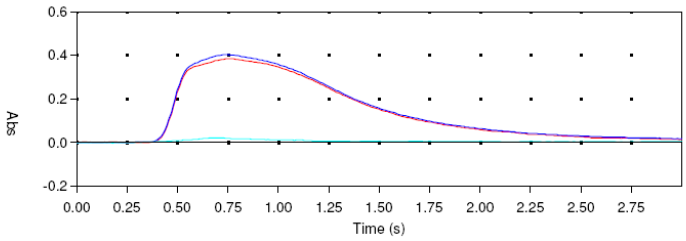
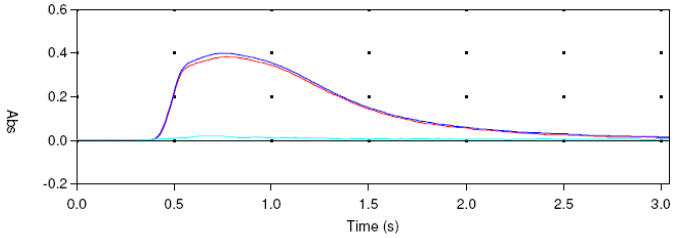
Solution Results - Cu

Resample: 2
Height: 0.383
Background: 0.019
Area: 0.391
Background: 0.019
30/09/2010 12:56:28

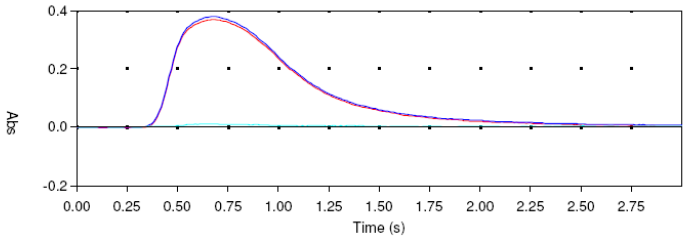


Resample: 3
Height: 0.382
Background: 0.016
Area: 0.378
Background: 0.019
30/09/2010 12:58:23

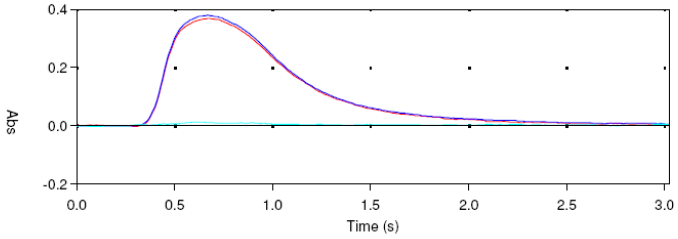


Sample ID	Signal	Rsd	Conc	Corrected Conc	Auto Dilution
	Abs (Height)	%	µg/L	µg/L	
Cu YZ-082-1A	0.367 I	0.9	95.8559 C	3857.627 C	50.000

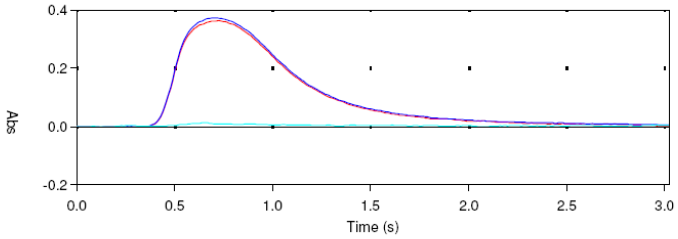
Resample: 1
Height: 0.369
Background: 0.011
Area: 0.268
Background: 0.011
30/09/2010 13:02:19



Resample: 2
Height: 0.369
Background: 0.011
Area: 0.276
Background: 0.012
30/09/2010 13:04:14



Resample: 3
Height: 0.363
Background: 0.009
Area: 0.257
Background: 0.011
30/09/2010 13:06:09



SOLAAR AA Report

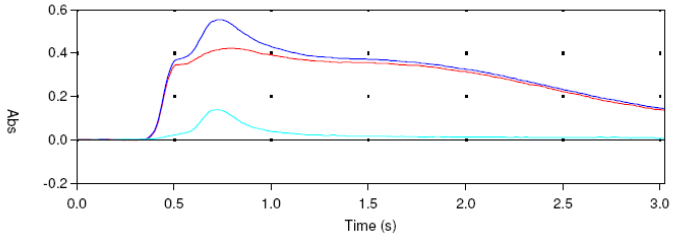
Operator Name: PENNY
Results File: C:\SOLAARM\DATA\RESULTS.SLR

Report Date: 30/09/2010 14:25:55

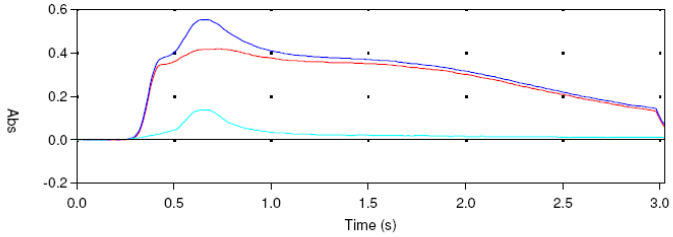
Solution Results - Cu

Sample ID	Signal	Rsd	Conc	Corrected Conc	Auto Dilution
	Abs (Height)	%	µg/L	µg/L	
Cu YZ-082-1 B	0.419	0.8	113.0066 C	70.6602 C	1.000

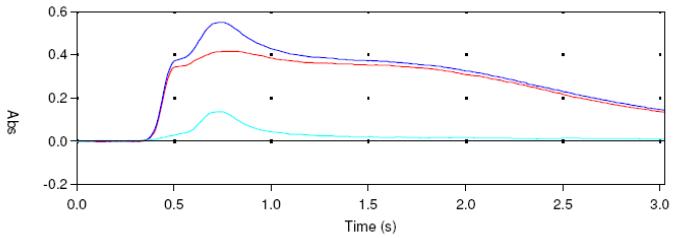
Resample: 1
Height: 0.423
Background: 0.122
Area: 0.796
Background: 0.069
30/09/2010 13:09:57



Resample: 2
Height: 0.418
Background: 0.111
Area: 0.802
Background: 0.078
30/09/2010 13:11:52

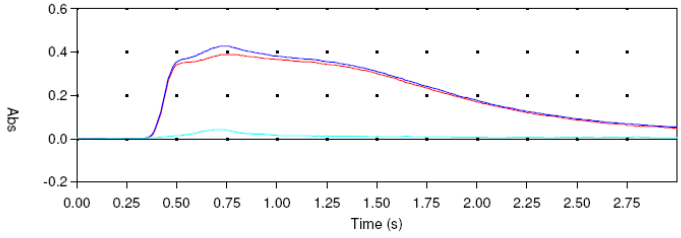


Resample: 3
Height: 0.416
Background: 0.120
Area: 0.788
Background: 0.077
30/09/2010 13:13:47

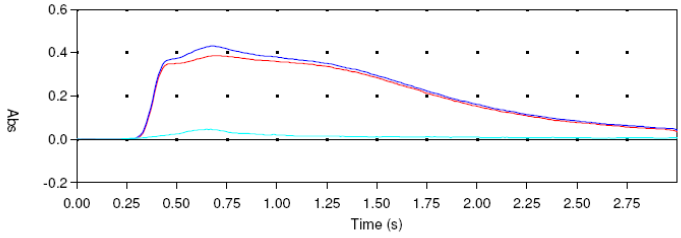


Sample ID	Signal	Rsd	Conc	Corrected Conc	Auto Dilution
	Abs (Height)	%	µg/L	µg/L	
Cu YZ-082-1 B	0.387 I	0.2	102.4616 C	251.3657 C	3.922

Resample: 1
Height: 0.387
Background: 0.037
Area: 0.589
Background: 0.030
30/09/2010 13:17:44



Resample: 2
Height: 0.386
Background: 0.042
Area: 0.585
Background: 0.037
30/09/2010 13:19:39



SOLAAR AA Report

Operator Name: PENNY
Results File: C:\SOLAARM\DATA\RESULTS.SLR

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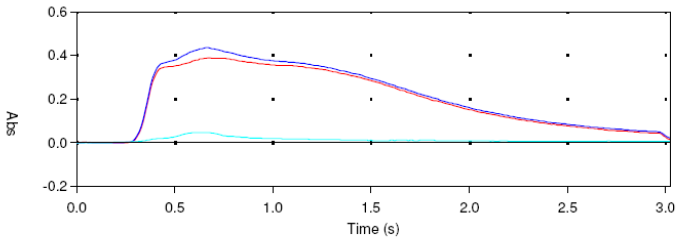
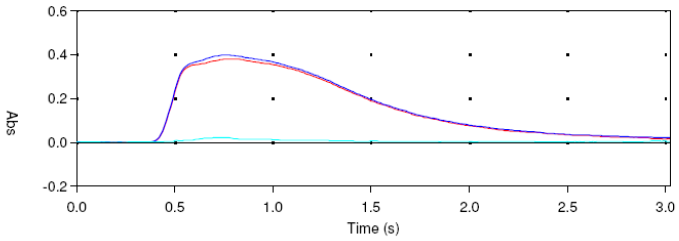
Solution Results - Cu

Resample: 3
Height: 0.388
Background: 0.047
Area: 0.591
Background: 0.039
30/09/2010 13:21:33

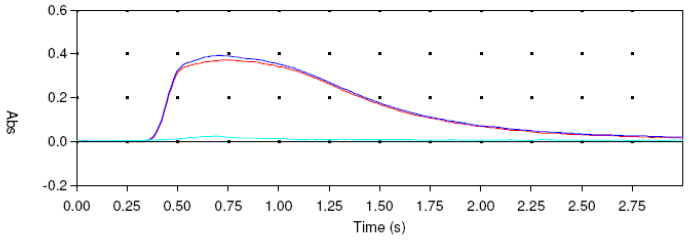


Sample ID	Signal	Rsd	Conc	Corrected Conc	Auto Dilution
	Abs (Height)	%	µg/L	µg/L	
Cu YZ-082-1 B	0.375 I	1.2	98.5333 C	880.7037 C	14.286

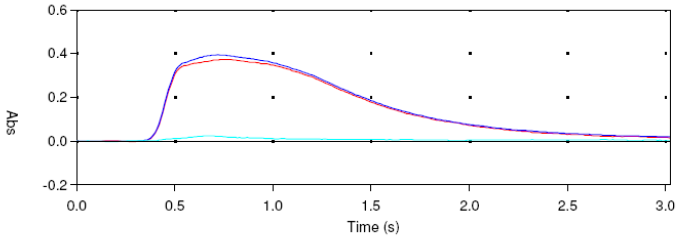
Resample: 1
Height: 0.380
Background: 0.017
Area: 0.429
Background: 0.017
30/09/2010 13:25:32



Resample: 2
Height: 0.371
Background: 0.020
Area: 0.416
Background: 0.020
30/09/2010 13:27:26

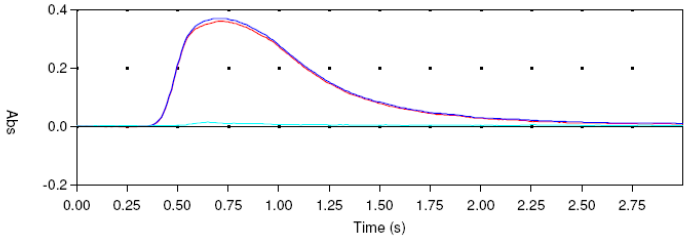


Resample: 3
Height: 0.374
Background: 0.018
Area: 0.425
Background: 0.020
30/09/2010 13:29:22



Sample ID	Signal	Rsd	Conc	Corrected Conc	Auto Dilution
	Abs (Height)	%	µg/L	µg/L	
Cu YZ-082-1 B	0.358 I	0.5	92.8822 C	2905.790 C	50.000

Resample: 1
Height: 0.360
Background: 0.010
Area: 0.288
Background: 0.011
30/09/2010 13:33:19



SOLAAR AA Report

Operator Name: PENNY
Results File: C:\SOLAARM\DATA\RESULTS.SLR

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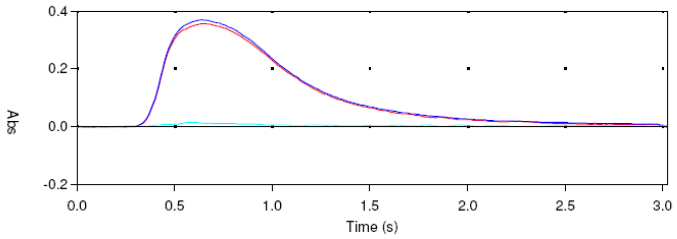
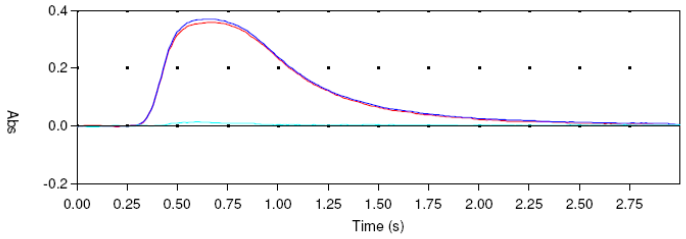
Solution Results - Cu

Resample: 2
Height: 0.356
Background: 0.012
Area: 0.279
Background: 0.013
30/09/2010 13:35:14

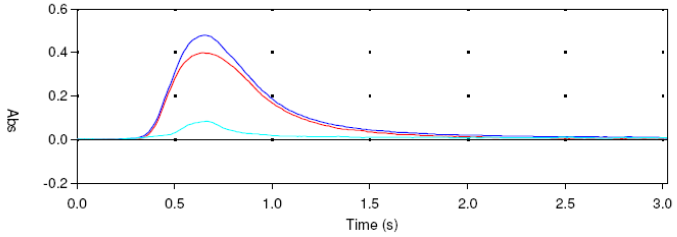


Resample: 3
Height: 0.358
Background: 0.012
Area: 0.287
Background: 0.012
30/09/2010 13:37:09

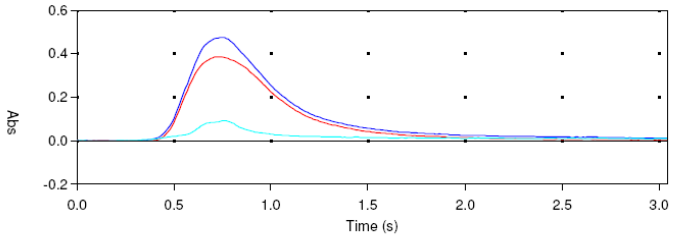


Sample ID	Signal	Rsd	Conc	Corrected Conc	Auto Dilution
	Abs (Height)	%	µg/L	µg/L	
Cu YZ-082-2 A	0.389	2.0	102.9663 C	69.0252 C	1.000

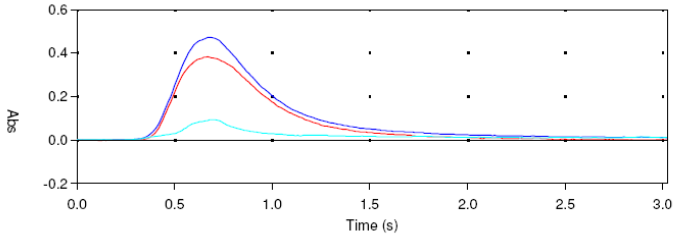
Resample: 1
Height: 0.397
Background: 0.082
Area: 0.234
Background: 0.044
30/09/2010 13:40:57



Resample: 2
Height: 0.387
Background: 0.089
Area: 0.227
Background: 0.056
30/09/2010 13:42:52



Resample: 3
Height: 0.382
Background: 0.090
Area: 0.221
Background: 0.062
30/09/2010 13:44:46



SOLAAR AA Report

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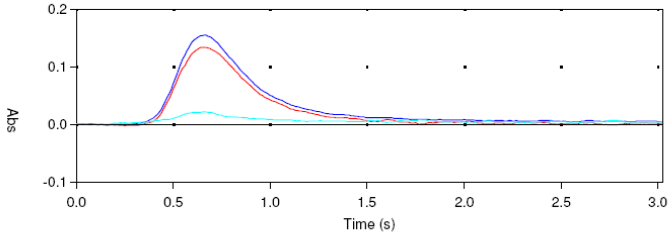
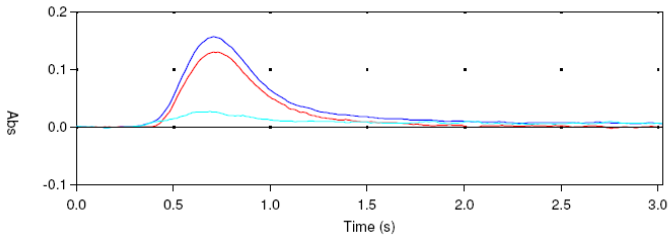
Solution Results - Cu

Sample ID	Signal	Rsd	Conc	Corrected Conc	Auto Dilution
	Abs (Height)	%	µg/L	µg/L	
Cu YZ-082-2 A	**0.128 I**	**5.7**	**20.2298**	**49.2993**	**3.636**

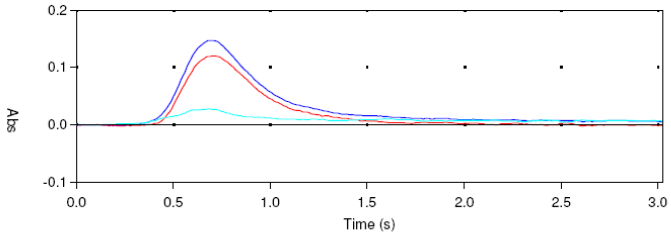
Resample: 1
Height: 0.134
Background: 0.021
Area: 0.063
Background: 0.018
30/09/2010 13:48:43



Resample: 2
Height: 0.130
Background: 0.025
Area: 0.064
Background: 0.027
30/09/2010 13:50:38

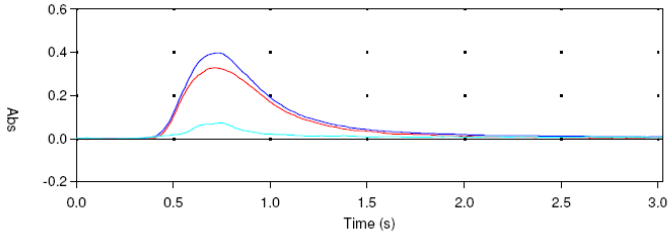


Resample: 3
Height: 0.120
Background: 0.027
Area: 0.057
Background: 0.027
30/09/2010 13:52:33

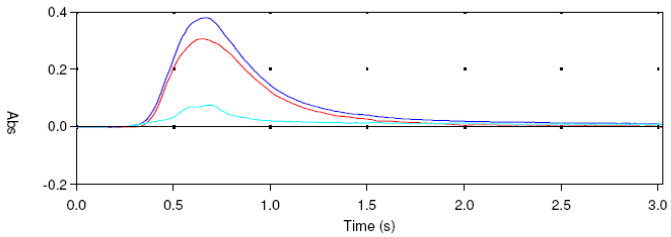


Sample ID	Signal	Rsd	Conc	Corrected Conc	Auto Dilution
	Abs (Height)	%	µg/L	µg/L	
Cu YZ-082-2 B	**0.316**	**3.2**	**79.0344 C**	**51.9932 C**	**1.000**

Resample: 1
Height: 0.327
Background: 0.068
Area: 0.187
Background: 0.041
30/09/2010 13:56:22



Resample: 2
Height: 0.307
Background: 0.072
Area: 0.175
Background: 0.052
30/09/2010 13:58:17



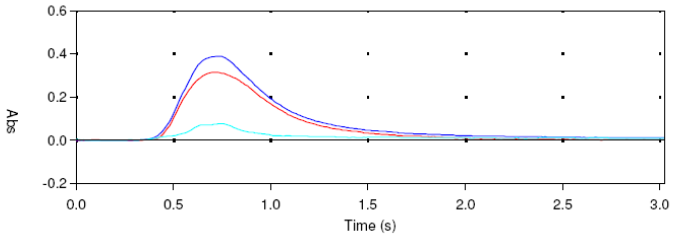
SOLAAR AA Report

Operator Name: PENNY
Results File: C:\SOLAARM\DATA\RESULTS.SLR

Report Date: 30/09/2010 14:25:55

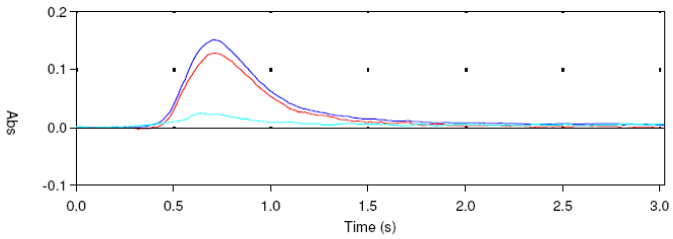
Solution Results - Cu

Resample: 3
Height: 0.315
Background: 0.074
Area: 0.183
Background: 0.052
30/09/2010 14:00:11

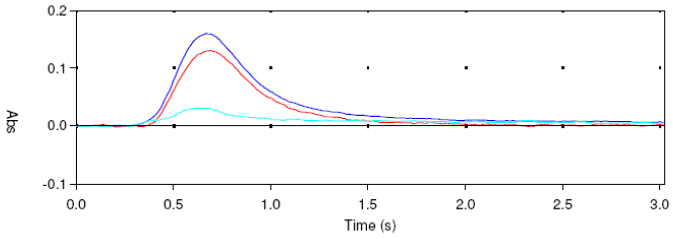


Sample ID	Signal	Rsd	Conc	Corrected Conc	Auto Dilution
	Abs (Height)	%	µg/L	µg/L	
Cu YZ-082-2 B	**0.127 I**	**3.2**	**20.0842**	**39.4280**	**2.985**

Resample: 1
Height: 0.128
Background: 0.022
Area: 0.063
Background: 0.019
30/09/2010 14:04:02



Resample: 2
Height: 0.131
Background: 0.029
Area: 0.067
Background: 0.028
30/09/2010 14:05:58



Resample: 3
Height: 0.123
Background: 0.030
Area: 0.063
Background: 0.027
30/09/2010 14:07:52