Supporting Information

One Pot Synthesis of Azaindoles via Palladium-catalyzed α-heteroarylation of ketone enolates

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Supporting Information-Table of Contents

I. General Methods

Commercially available reagents and solvents* were utilized as received unless otherwise noted. All reactions were performed in dry glassware, under a nitrogen atmosphere. ^{1}H NMR and ^{13}C NMR were recorded in the solvent noted ($CDCl_3$ or DMSO-D_6), using a 400 MHz spectrometer unless otherwise stated. The NMR chemical shifts are reported in ppm relative to tetramethylsilane.

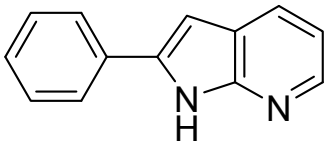
*The THF used was DrySolve® THF, purchased from EMD and was used without further drying.

II. General Procedure

Sodium bis(trimethylsilyl)amide, 1.0M in THF (1.5 mL, 1.5 mmol) was added to a solution of allyl(1,3-bis(2,6-diisopropylphenyl)imidazolidin-2-ylidene)palladium(IV) chloride **6** (28.7 mg, 0.05 mmol) and ketone (1.0 mmol) in THF (1 mL) at rt. After stirring 5 minutes at rt, *o*-bromoaminoheterocycle (0.25 mmol) was added as a solution in THF (0.2 ml) and the reaction was heated to 100-105 ºC in a pressure tube for 4 hrs. After cooling to rt, the reaction mixture was partitioned between EtOAc (30 ml) and saturated NH_4Cl solution (30 ml). The organic layer was washed with saturated NH_4Cl solution (30 ml) and the combined aqueous layers were back extracted with EtOAc (15 ml). After drying ($MgSO_4$) and filtration, the combined organic layer was concentrated to afford a residue that was chromatographed on a silica gel, eluting with an EtOAc/Hex gradient. Concentration of the pure fractions afforded the product.

III. Compound Characterization

2-phenyl-1H-pyrrolo[2,3-b]pyridine (9)[1,2]



Following general procedure on 3-bromopyridin-2-amine (43 mg; 0.25 mmol), followed by trituration with heptane.

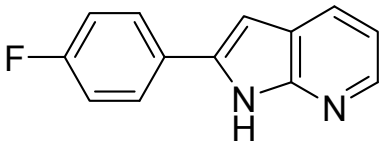
Yield: 36 mg (74%), tan powder.

^{1}H NMR (400 MHz, $CDCl_3$) δ ppm 6.79 (d, *J*= 1.5 Hz, 1 H), 7.10 (dd, *J*= 7.8, 4.8 Hz, 1 H), 7.40 (t, *J*= 7.4 Hz, 1 H), 7.52 (t, *J*= 7.6 Hz, 2 H), 7.88 (d, *J*= 7.1 Hz, 2 H), 7.96 (dd, *J*= 7.8, 1.3 Hz,1 H), 8.30 (dd, *J*= 4.8, 1.3 Hz, 1 H), 12.31 (s, 1 H).

^{13}C NMR (101 MHz, $CDCl_3$) δ ppm 97.40, 116.13, 122.42, 125.97 (2 C), 128.24, 128.77, 129.08 (2 C), 132.51, 139.66, 142.12, 150.06.

HRMS: Calculated for $C_{13}H_{11}N_2$ $[M+H]^+$: 195.09168, Found: 195.09173.

2-(4-fluorophenyl)-1H-pyrrolo[2,3-b]pyridine (11)[4]



Following general procedure on 3-bromopyridin-2-amine (43 mg; 0.25 mmol).

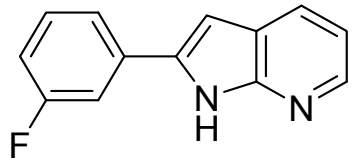
Yield: 50 mg (94%), tan powder.

^{1}H NMR (400 MHz, DMSO-D_6) δ ppm 6.89 (d, *J*=2.0 Hz, 1 H), 7.05 (dd, *J*=7.8, 4.8 Hz, 1 H), 7.31 (t, *J*=8.9 Hz, 2 H), 7.92 (dd, *J*=7.8, 1.3 Hz, 1 H), 7.95 - 8.01 (m, 2 H), 8.20 (dd, *J*=4.8, 1.5 Hz, 1 H), 12.14 (s, 1 H).

^{13}C NMR (101 MHz, DMSO-D_6) δ ppm 97.07, 115.76, 115.98, 116.06, 120.90, 127.35, 127.43, 127.81, 128.23, 128.26, 137.27, 142.81, 149.65, 160.67, 163.11.

HRMS: Calculated for $C_{13}H_{10}FN_2$ $[M+H]^+$: 213.08225, Found: 213.08231.

2-(3-fluorophenyl)-1H-pyrrolo[2,3-b]pyridine (13)[4]



Following general procedure on 3-bromopyridin-2-amine (43 mg; 0.25 mmol), followed by trituration with heptane.

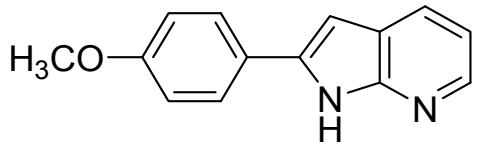
Yield: 31 mg (58%), off-white powder.

^{1}H NMR (400 MHz, $CDCl_3$) δ ppm 6.81 (s, 1 H), 7.06 - 7.15 (m, 2 H), 7.48 (td, *J*=7.8, 5.9 Hz, 1 H), 7.61 (dt, *J*=9.9, 2.0 Hz, 1 H), 7.67 (d, *J*=7.8 Hz, 1 H), 7.98 (dd, *J*=7.8, 1.5 Hz, 1 H), 8.34 (dd, *J*=4.8, 1.5 Hz, 1 H), 12.76 (s, 1 H).

^{13}C NMR (101 MHz, $CDCl_3$) δ ppm 98.20, 112.71, 112.93, 114.84, 115.05, 116.36, 121.57, 121.60, 122.29, 129.18, 130.57, 130.65, 134.66, 138.40, 142.47, 150.02, 162.12, 164.56.

HRMS: Calculated for $C_{13}H_{10}FN_2$ $[M+H]^+$: 213.08225, Found: 213.08231.

2-(4-methoxyphenyl)-1H-pyrrolo[2,3-b]pyridine (15)[5]



Following general procedure on 3-bromopyridin-2-amine (43 mg; 0.25 mmol).

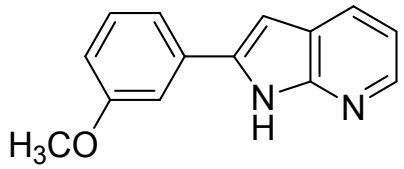
Yield: 49 mg (87%), Light orange powder.

^{1}H NMR (400 MHz, DMSO-D_6) δ ppm 3.80 (s, 3 H), 6.78 (d, *J*=2.3 Hz, 1 H), 6.94 - 7.03 (m, 3 H), 7.87 (d, *J*=8.8 Hz, 3 H), 8.15 (dd, *J*=4.7, 1.39 Hz, 1 H), 12.02 (s, 1 H).

^{13}C NMR (101 MHz, DMSO-D_6) δ ppm 55.22, 95.65, 114.34, 115.86, 121.13, 124.18, 126.72, 127.25, 138.37, 142.14, 149.58, 159.20.

HRMS: Calculated for $C_{14}H_{13}N_2O$ $[M+H]^+$: 225.10224, Found: 225.10237 .

2-(3-methoxyphenyl)-1H-pyrrolo[2,3-b]pyridine (17)



Following general procedure on 3-bromopyridin-2-amine (43 mg; 0.25 mmol), except that two chromatographies were required.

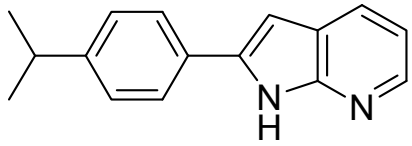
Yield: 27 mg (48%), Light yellow powder.

^{1}H NMR (400 MHz, DMSO-D_6) δ ppm 3.85 (s, 3 H), 6.89 (m, 1 H), 6.94 (d, *J*= 2.0 Hz, 1H), 7.07 (dd, *J*=7.8, 4.5 Hz, 1 H), 7.37 (t, *J*=8.1 Hz, 1 H), 7.52 (s, 1 H), 7.54 (d, *J*=1.5 Hz, 1 H), 7.93 (dd, *J*= 7.8,1.3 Hz, 1H), 8.22 (dd, *J*=4.78, 1.51 Hz, 1 H), 12.15 (s, 1 H).

^{13}C NMR (101 MHz, DMSO-D_6) δ ppm 55.23, 97.38, 110.54, 113.80, 116.02, 117.72, 120.83, 127.84, 129.96, 132.90, 138.07, 142.88, 149.57, 159.72.

HRMS: Calculated for $C_{14}H_{13}N_2O[M+H]^+$:225.10224, Found: 225.10238 .

2-(4-isopropylphenyl)-1H-pyrrolo[2,3-b]pyridine (19)



Following general procedure on 3-bromopyridin-2-amine (43 mg; 0.25 mmol).

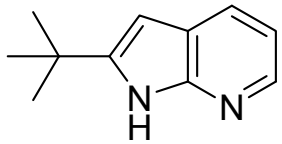
Yield: 48 mg (81%), Light yellow powder.

^{1}H NMR (400 MHz, $CDCl_3$) δ ppm 1.32 (d, *J*= 6.8 Hz, 6 H), 2.93 - 3.03 (m, 1 H), 6.75 (s, 1 H), 7.10 (dd, *J*=7.8, 4.8 Hz, 1 H), 7.37 (d, *J*=8.3 Hz, 2 H), 7.78 (d, *J*=8.3 Hz, 2 H), 7.93 (dd, *J*=7.8, 1.5 Hz, 1 H), 8.29 (dd, *J*=4.9, 1.4 Hz, 1 H), 11.78 (s, 1 H).

^{13}C NMR (101 MHz, $CDCl_3$) δ ppm 23.94, 33.97, 96.74, 115.95, 122.52, 125.83, 127.07, 128.55, 129.89, 139.76, 141.56, 149.14, 149.80.

HRMS: Calculated for $C_{16}H_{17}N_2$ $[M+H]^+$:237.13863, Found: 237.13879.

2-tert-butyl-1H-pyrrolo[2,3-b]pyridine (21)[6]



Following general procedure on 3-bromopyridin-2-amine (43 mg; 0.25 mmol).

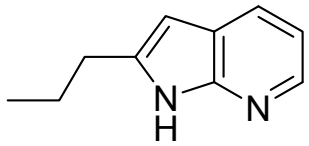
Yield: 38 mg (87%), Light yellow powder.

^{1}H NMR (400 MHz, $CDCl_3$) δ ppm 1.47 (s, 9 H), 6.20 (d, *J*=2.3 Hz, 1 H), 7.04 (dd, *J*=7.8, 4.3 Hz, 1 H), 7.84 (d, *J*=7.1 Hz, 1 H), 8.27 (dd, *J*=4.8, 1.5 Hz, 1 H), 11.21 (s, 1 H).

^{13}C NMR (101 MHz, $CDCl_3$) δ ppm 30.05, 32.30, 94.42, 115.34, 121.44, 127.82, 141.00, 149.47, 150.84.

HRMS: Calculated for $C_{11}H_{15}N_2$ $[M+H]^+$: 175.12298, Found: 175.12309.

2-propyl-1H-pyrrolo[2,3-b]pyridine (23)[2]



Following general procedure on 3-bromopyridin-2-amine (43 mg; 0.25 mmol), except that two chromatographies were required.

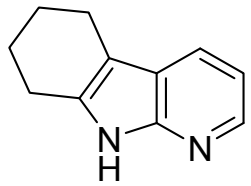
Yield: 24 mg (60%), Tan powder.

^{1}H NMR (400 MHz, $CDCl_3$) δ ppm 1.03 (t, *J*=7.4 Hz, 3 H), 1.76 - 1.86 (m, 2 H), 2.81 (t, *J*=7.6 Hz, 2 H), 6.19 (s, 1 H), 7.02 (dd, *J*=7.8, 4.8 Hz, 1 H), 7.81 (dd, *J*=7.8, 1.3 Hz, 1 H), 8.19 (dd, *J*=4.8, 1.5 Hz, 1 H), 10.59 (s, 1 H).

^{13}C NMR (101 MHz, $CDCl_3$) δ ppm 13.93, 22.37, 30.72, 97.24, 115.43, 121.77, 127.54, 140.42, 141.46, 149.10.

HRMS: Calculated for $C_{10}H_{13}N_2$ $[M+H]^+$: 161.10733, Found: 161.10748.

6,7,8,9-tetrahydro-5H-pyrido[2,3-b]indole (25)[7]



Following general procedure on 3-bromopyridin-2-amine (43 mg; 0.25 mmol).

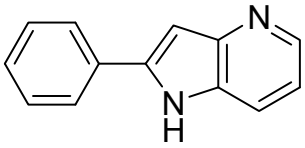
Yield: 22 mg (51%), Tan powder.

^{1}H NMR (400 MHz, $CDCl_3$) δ ppm 1.84 - 1.96 (m, 4 H), 2.67 (t, *J*=5.9 Hz, 2 H), 2.78 (t, *J*=5.9 Hz, 2 H), 6.99 (dd, *J*=7.7, 4.9 Hz, 1 H), 7.73 (d, *J*=7.8 Hz, 1 H), 8.16 (d, *J*=3.8 Hz, 1 H). 9.35 (s, 1 H).

^{13}C NMR (101 MHz, $CDCl_3$) δ ppm 20.64, 22.94, 23.11, 23.17, 108.20, 114.90, 120.69, 125.62, 135.25, 140.52, 148.64.

HRMS: Calculated for $C_{11}H_{13}N_2$ $[M+H]^+$: 173.10733, Found: 173.10746.

2-phenyl-1H-pyrrolo[3,2-b]pyridine (27)[1]



Following general procedure on 2-bromopyridin-3-amine (43 mg; 0.25 mmol), followed by trituration with heptane.

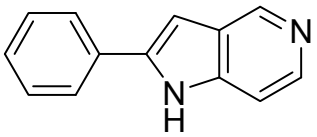
Yield: 10 mg (20%), tan powder.

^{1}H NMR (400 MHz, DMSO-D_6) δ ppm 7.05 (d, *J*=1.5 Hz, 1 H), 7.10 (dd, *J*=8.2, 4.6 Hz, 1 H), 7.37 (t, *J*=7.4 Hz, 1 H), 7.49 (t, *J*=7.7 Hz, 2 H), 7.75 (d, *J*=8.0 Hz, 1 H), 7.87 - 7.96 (m, 2 H), 8.30 (dd, *J*=4.6, 1.4 Hz, 1 H), 11.78 (s, 1 H).

^{13}C NMR (101 MHz, DMSO-D_6) δ ppm 98.96, 116.63, 118.28, 125.41, 128.31, 129.00, 129.96, 131.52, 141.01, 142.62, 146.63.

HRMS: Calculated for $C_{13}H_{11}N_2$ $[M+H]^+$: 195.09168, Found: 195.09176.

2-phenyl-1H-pyrrolo[3,2-c]pyridine (29)[1]



Following general procedure on 3-bromopyridin-4-amine (43 mg; 0.25 mmol), except heating fro 6 hr, followed by trituration with ethyl ether.

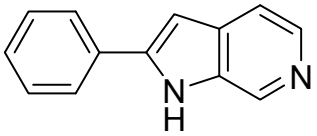
Yield: 20 mg (41%), tan powder.

^{1}H NMR (400 MHz, DMSO-D_6) δppm 7.04 (s, 1 H), 7.36 (d, *J*=6.0 Hz, 2 H), 7.48 (t, *J*=7.2 Hz, 2 H), 7.89 (d, *J*=7.3 Hz, 2 H), 8.16 (s, 1 H), 8.81 (s, 1 H), 11.98 (s, 1 H).

^{13}C NMR (101 MHz, DMSO-D_6) δ ppm 97.55, 106.58, 125.33, 125.70, 128.05, 128.98, 131.38, 138.84, 140.33, 140.40, 142.89.

HRMS: Calculated for $C_{13}H_{11}N_2$ $[M+H]^+$: 195.09168, Found: 195.09175.

2-phenyl-1H-pyrrolo[2,3-c]pyridine (31)[1]



Following general procedure on 4-bromopyridin-3-amine (43 mg; 0.25 mmol), followed by reverse phase preparative HPLC using a C-18 column and a water/MeOH + 0.1%TFA gradient and subsequent free-basing.

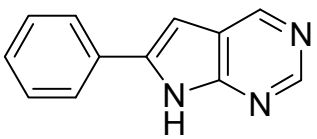
Yield: 7 mg (14%), tan powder.

^{1}H NMR (400 MHz, DMSO-D_6) δ ppm 6.98 (s, 1 H), 7.40 (t, *J*=7.3 Hz, 1 H), 7.47 - 7.57 (m, 3 H), 7.93 (d, *J*=7.3 Hz, 2 H), 8.09 (d, *J*=5.3 Hz, 1 H), 8.74 (s, 1 H), 12.05 (s, 1 H).

^{13}C NMR (101 MHz, DMSO-D_6) δ ppm 97.96, 114.44, 125.78, 128.59, 129.02, 131.20, 132.86, 133.95, 134.12, 137.92, 141.50.

HRMS: Calculated for $C_{13}H_{11}N_2$ $[M+H]^+$: 195.09168, Found: 195.09175.

6-phenyl-7H-pyrrolo[2,3-d]pyrimidine (33)[6]



Following general procedure on 5-bromopyrimidin-4-amine (43 mg; 0.25 mmol), except that the reaction was heated for 6 hr.

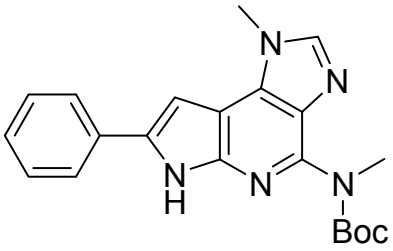
Yield: 30 mg (60%), tan powder.

^{1}H NMR (400 MHz, DMSO-D_6) δ ppm 7.06 (s, 1 H), 7.39 (t, *J*=7.3 Hz, 1 H), 7.49 (t, *J*=7.6 Hz, 2 H), 7.96 (d, *J*=7.3 Hz, 2 H), 8.74 (s, 1 H), 8.97 (s, 1 H), 12.61 (s, 1 H).

^{13}C NMR (101 MHz, DMSO-D6) δ ppm 96.21, 119.42, 125.70, 128.69, 129.02, 130.76, 139.33, 148.63, 151.15, 152.45.

HRMS: Calculated for $C_{12}H_{10}N_3$ $[M+H]^+$: 196.08692, Found: 196.08696.

tert-butyl methyl(1-methyl-7-phenyl-1,6-dihydroimidazo[4,5-d]pyrrolo[2,3-b]pyridin-4-yl)carbamate (34)[8]



Following general procedure on tert-butyl 6-amino-7-iodo-1-methyl-1H-imidazo[4,5-c]pyridin-4-yl(methyl)carbamate (40 mg; 0.10 mmol), substituting lithium bis(trimethylsilyl)amide, 1.0M in THF for sodium bis(trimethylsilyl)amide, 1.0M in THF.

Yield: 21 mg (56%), Off-white powder.

^{1}H NMR (400 MHz, $CDCl_3$) δ ppm 1.42 (s, 9 H), 3.46 (s, 3 H), 4.11 (s, 3 H), 6.99 (d, *J*=2.26 Hz, 1 H), 7.34 (t, *J*=7.40 Hz, 1 H), 7.43 - 7.51 (m, 2 H), 7.67 (dd, *J*=8.41, 1.13 Hz, 2 H), 7.80 (s, 1 H), 9.10 (s, 1 H).

^{13}C NMR (101 MHz, $CDCl_3$) δ ppm 28.22, 32.59, 36.16, 80.31, 94.01, 105.63, 124.81, 127.87, 129.16, 131.00, 131.73, 134.68, 136.23, 141.39, 143.27 143.31, 154.94.

HRMS: Calculated for $C_{21}H_{24}N_5O_2$ $[M+H]^+$: 378.19245, Found: 378.19278.

IV. NMR Spectra

3/3/2009 2:29 PM

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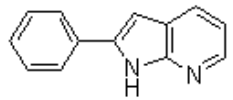
2-phenyl-1H-pyrrolo[2,3-b]pyridine



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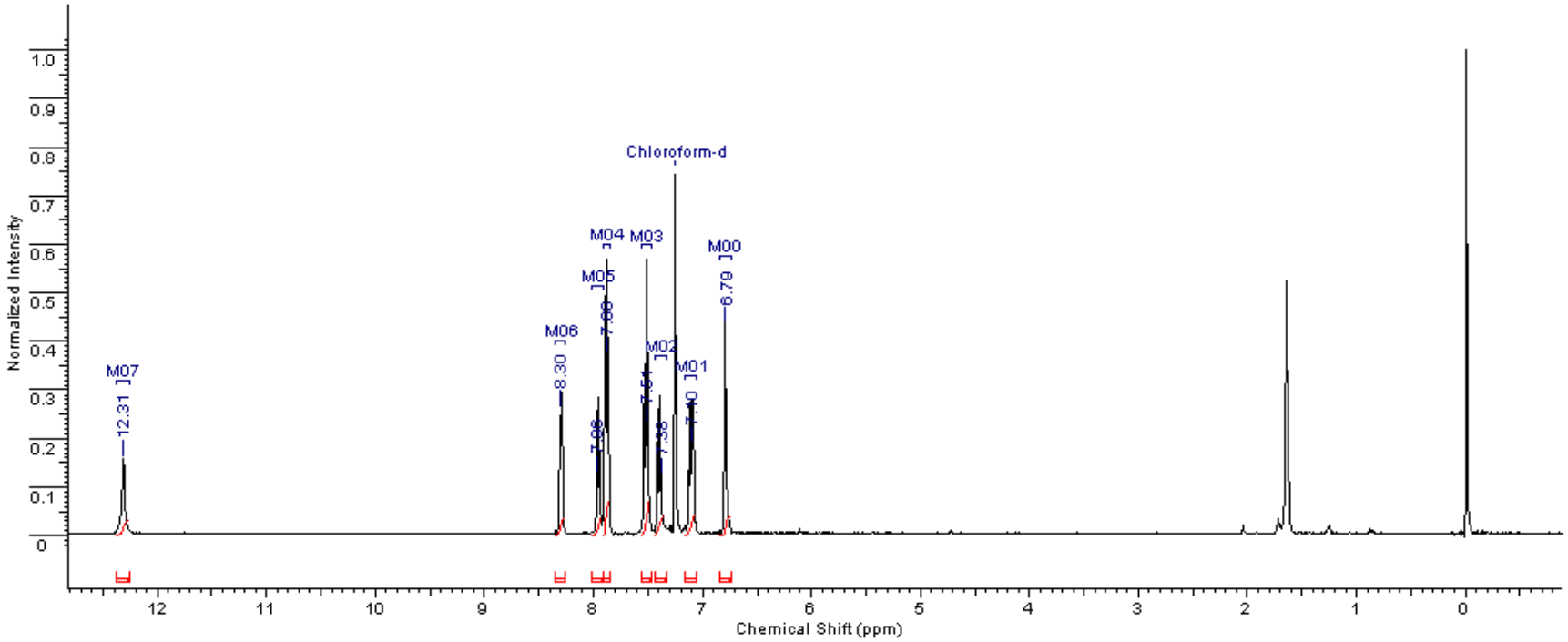

3/3/2009 2:03 PM

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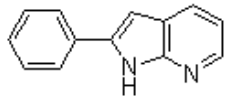
2-phenyl-1H-pyrrolo[2,3-b]pyridine



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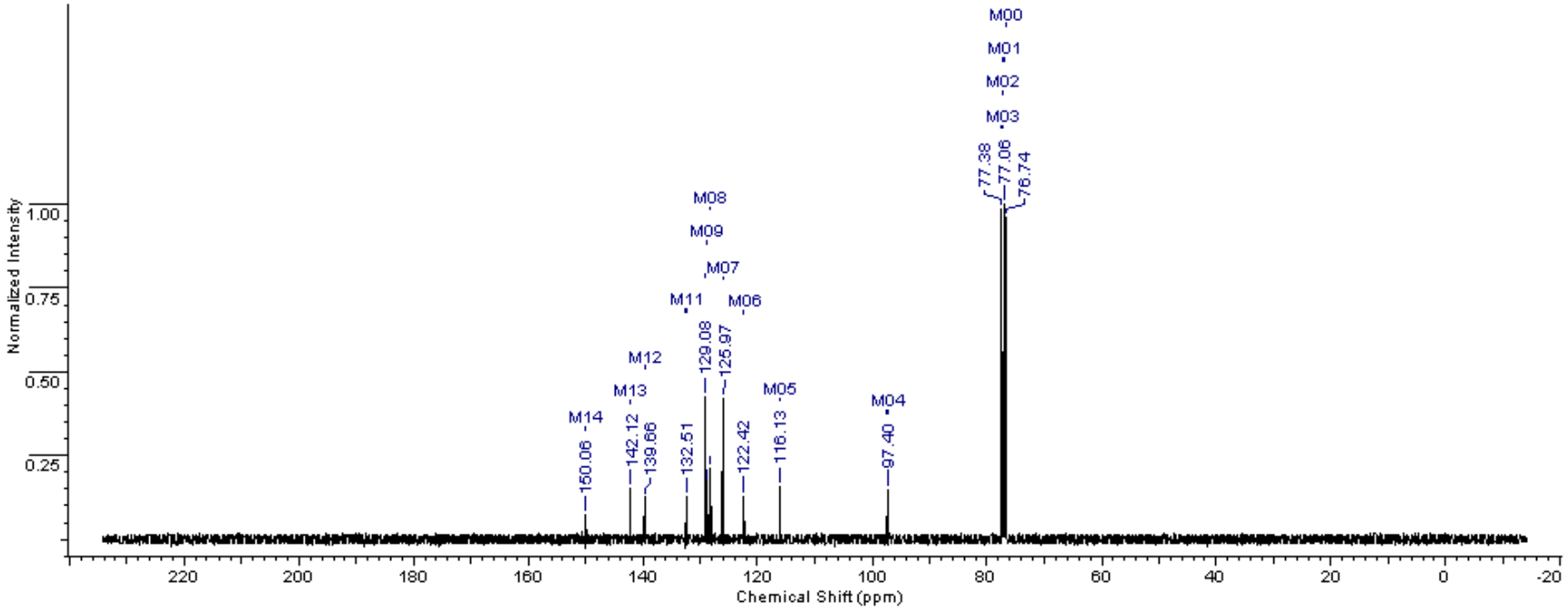

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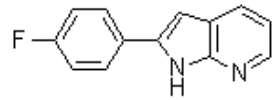
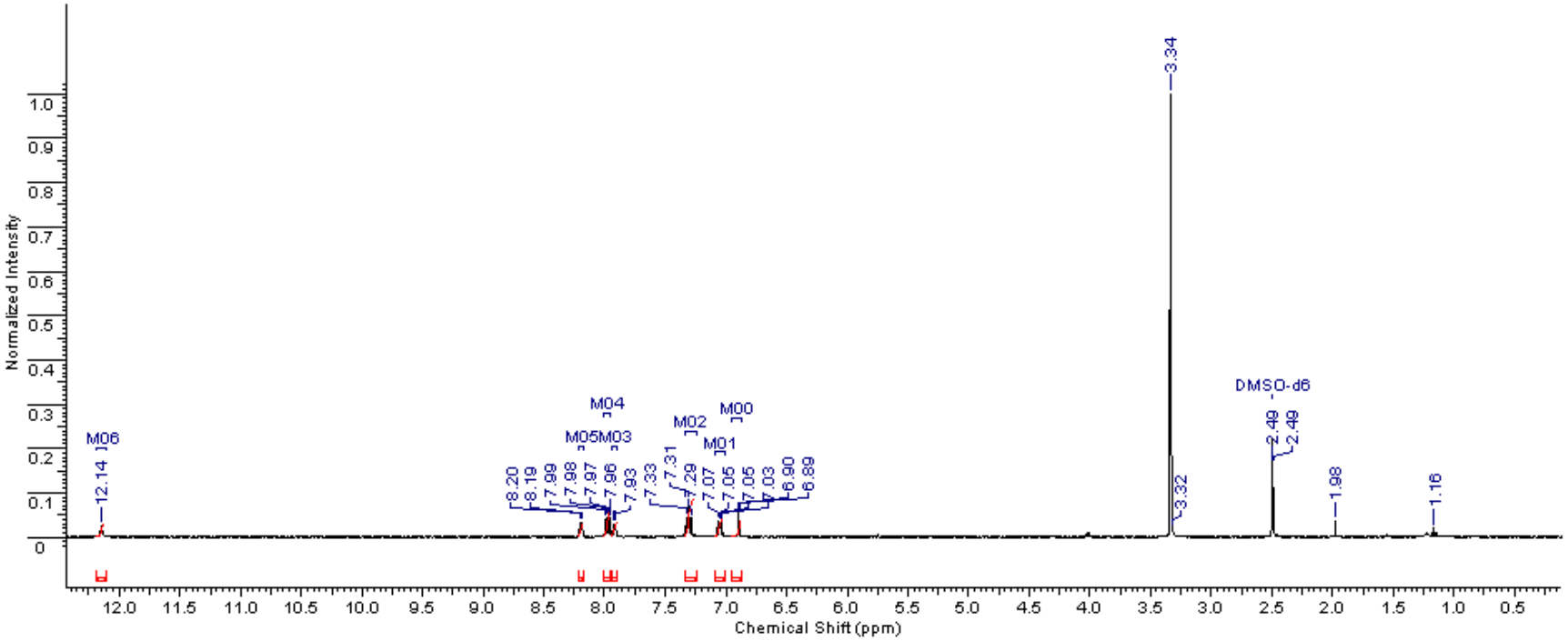
2-(4-fluorophenyl)-1H-pyrrolo[2,3-b]pyridine

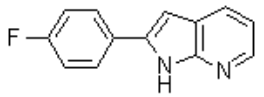


11



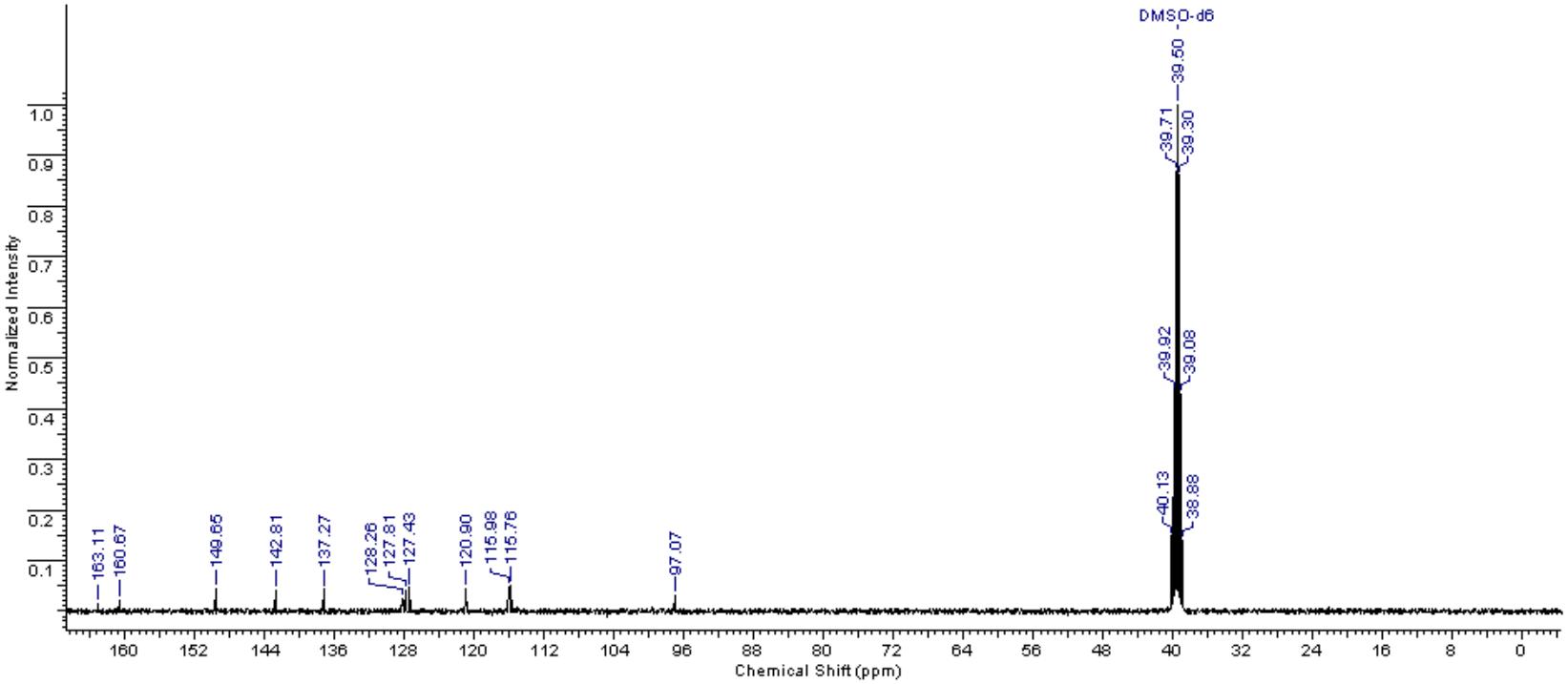
3/4/2009 7:51 AM

Acquisition Time (sec)	1.3108	*Comment*	Spergel 79036-070-01 68778-223-01			*Date*	04 Mar 2009 00:49:26
File Name	C:\DOCUME~1\SPERGELS\LOCALS~1\TEMP\ACR45.TMP\79036-070-02_10.JDX					*Frequency (MHz)*	100.62
Nucleus	13C	*Number of Transients*	1024	*Origin*	79036-070-02	*Original Points Count*	32768
Owner	spergels	*Points Count*	32768	*Solvent*	CHLOROFORM-D	*Spectrum Offset (Hz)*	10543.9316
Sweep Width (Hz)	24999.24	*Temperature (degree C)*	21.100				



11

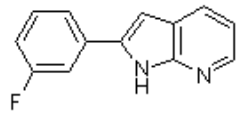
2-(4-fluorophenyl)-1H-pyrrolo[2,3-b]pyridine



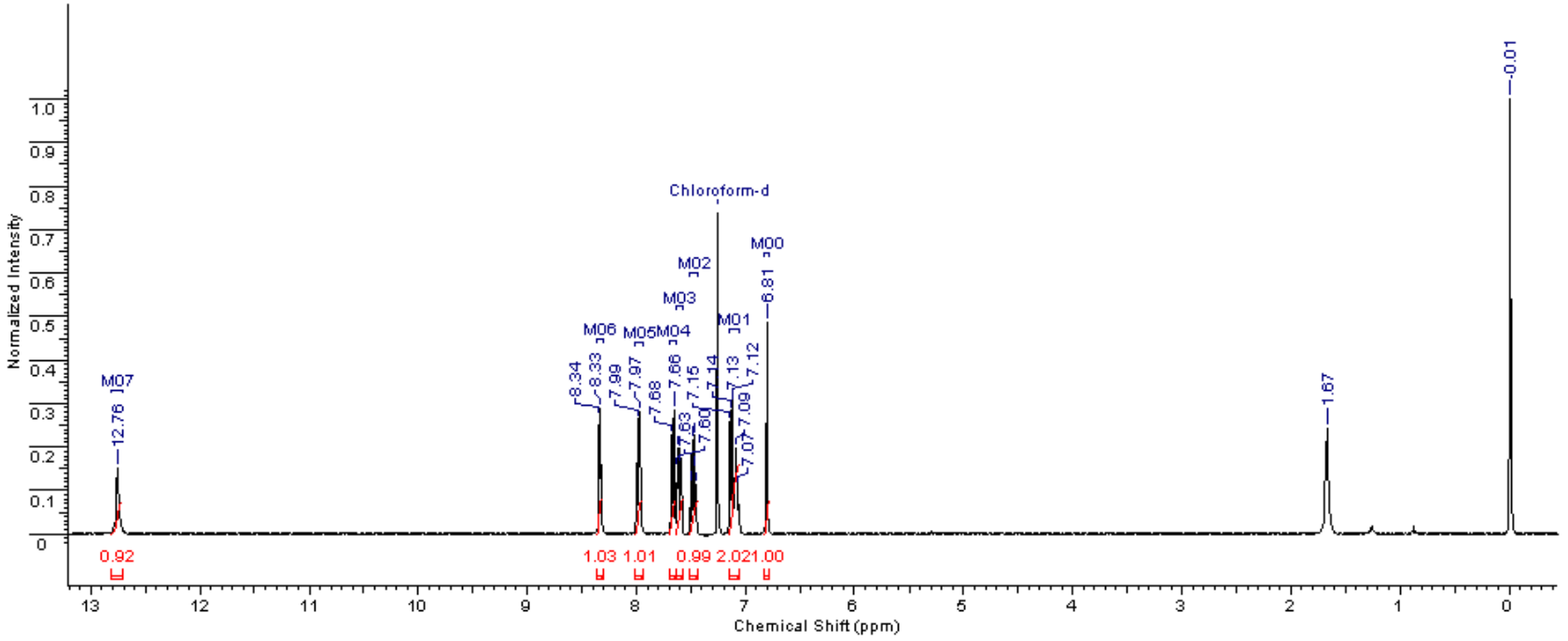
3/3/2009 4:42 PM

Acquisition Time (sec)	3.9715	*Comment*	Spergel 68778-225-01			*Date*	23 Jul 2007 15:05:53
File Name	C:\DOCUME~1\SPERGELS\LOCALS~1\TEMP\68778-225-01_20.JDX					*Frequency (MHz)*	400.13
Nucleus	1H	*Number of Transients*	16	*Origin*	nmrl2b	*Original Points Count*	32768
Owner	spergels	*Points Count*	32768	*Solvent*	CHLOROFORM-D		
Spectrum Offset (Hz)	2457.4097	*Sweep Width (Hz)*	8250.83	*Temperature (degree C)*	27.000		

2-(3-fluorophenyl)-1H-pyrrolo[2,3-b]pyridine



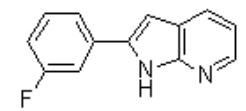
13



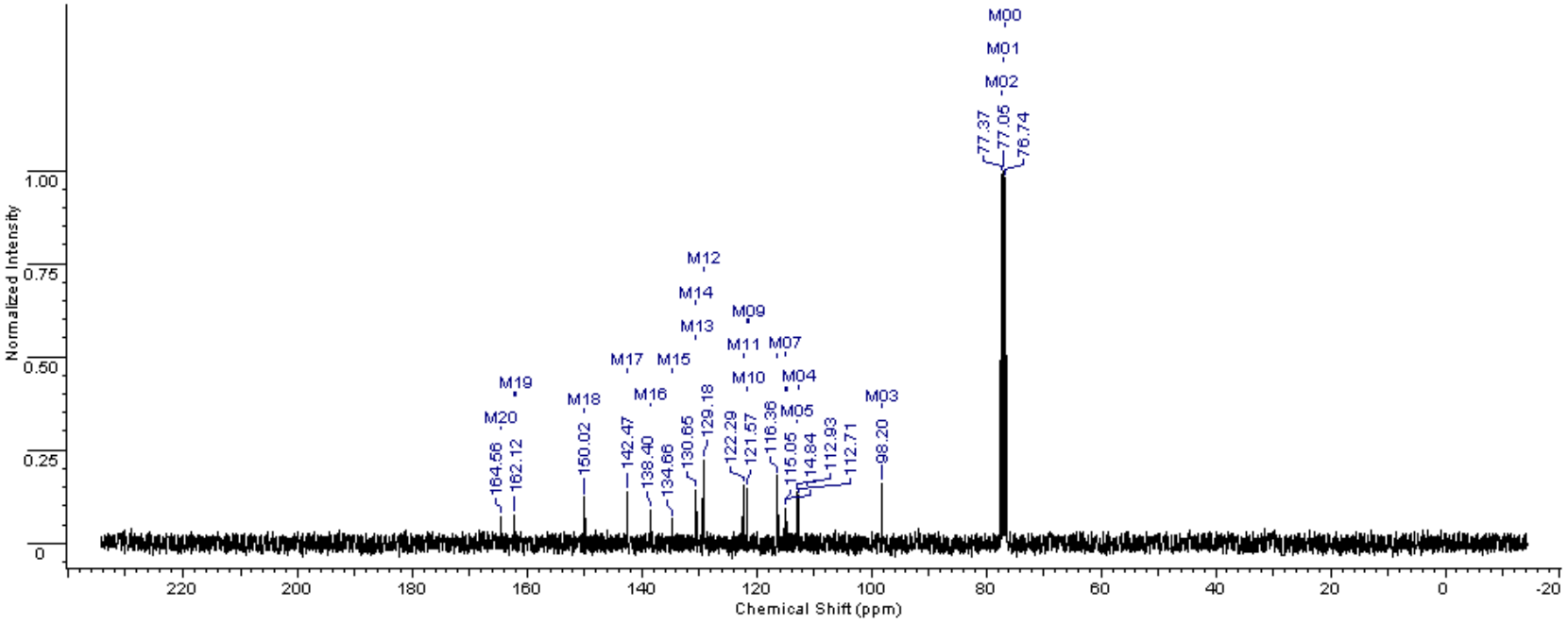
3/3/2009 5:03 PM

Acquisition Time (sec)	1.3108	*Comment*	Spergel 79036-071-01 68778-225-01			*Date*	03 Mar 2009 20:17:12
File Name	C:\DOCUME~1\SPERGELS\LOCALS~1\TEMP\ACRCO.TMP\79036-071-01_10.JDX					*Frequency (MHz)*	100.62
Nucleus	13C	*Number of Transients*	256	*Origin*	79036-071-01	*Original Points Count*	32768
Owner	spergels	*Points Count*	32768	*Solvent*	CHLOROFORM-D	*Spectrum Offset (Hz)*	11070.3760
Sweep Width (Hz)	24999.24	*Temperature (degree C)*	20.900				

2-(3-fluorophenyl)-1H-pyrrolo[2,3-b]pyridine



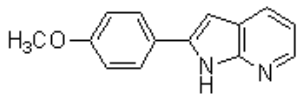
13



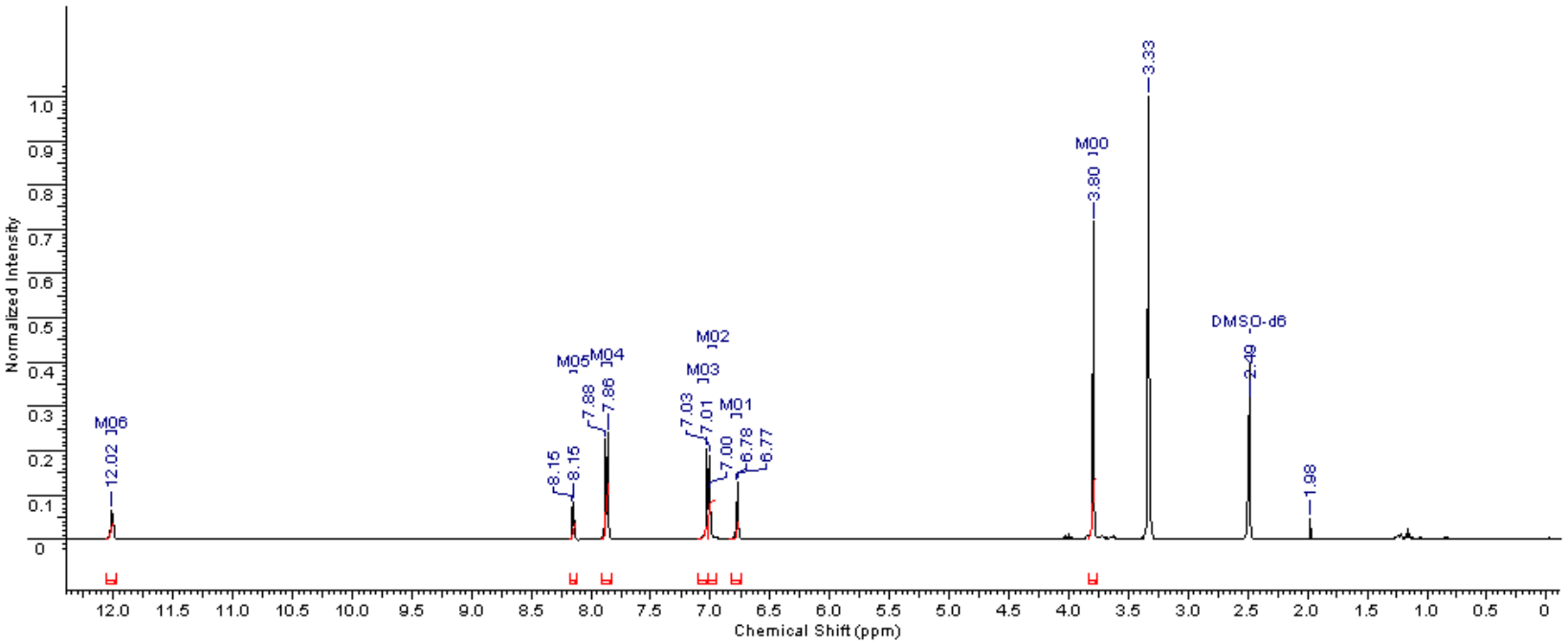
3/5/2009 8:00 AM

Acquisition Time (sec)	3.9715	*Comment*	Spergel 68778-226-01			*Date*	23 Jul 2007 18:58:00
File Name	C:\DOCUME~1\SPERGELS\LOCALS~1\TEMP\68778-226-01_10.JDX					*Frequency (MHz)*	400.13
Nucleus	1H	*Number of Transients*	16	*Origin*	nmr2b	*Original Points Count*	32768
Owner	spergels	*Points Count*	32768	*Solvent*	DMSO-D6	*Spectrum Offset (Hz)*	2464.2148
Sweep Width (Hz)	8250.83	*Temperature (degree C)*	27.000				

2-(4-methoxyphenyl)-1H-pyrrolo[2,3-b]pyridine



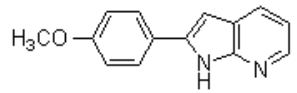
15



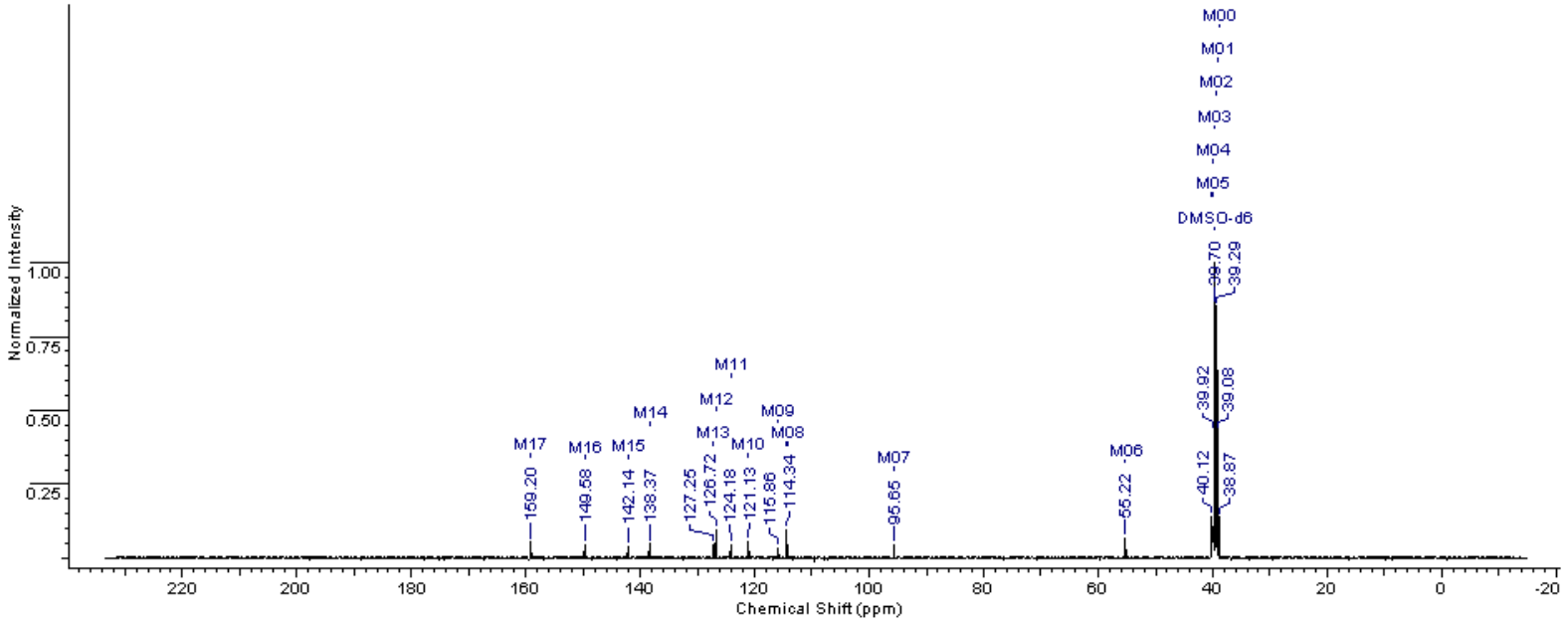
3/5/2009 7:43 AM

Acquisition Time (sec)	1.3108	*Comment*	Spergel 79036-072-01			*Date*	05 Mar 2009 01:35:47
File Name	C:\DOCUME~1\SPERGELS\LOCALS~1\TEMP\ACR4B.TMP\79036-072-01_10.JDX					*Frequency (MHz)*	100.62
Nucleus	13C	*Number of Transients*	2048	*Origin*	79036-072-01	*Original Points Count*	32768
Owner	spergels	*Points Count*	32768	*Solvent*	DMSO-D6	*Spectrum Offset (Hz)*	11021.5313
Sweep Width (Hz)	24999.24	*Temperature (degree C)*	20.900				

2-(4-methoxyphenyl)-1H-pyrrolo[2,3-b]pyridine



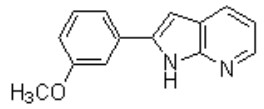
15



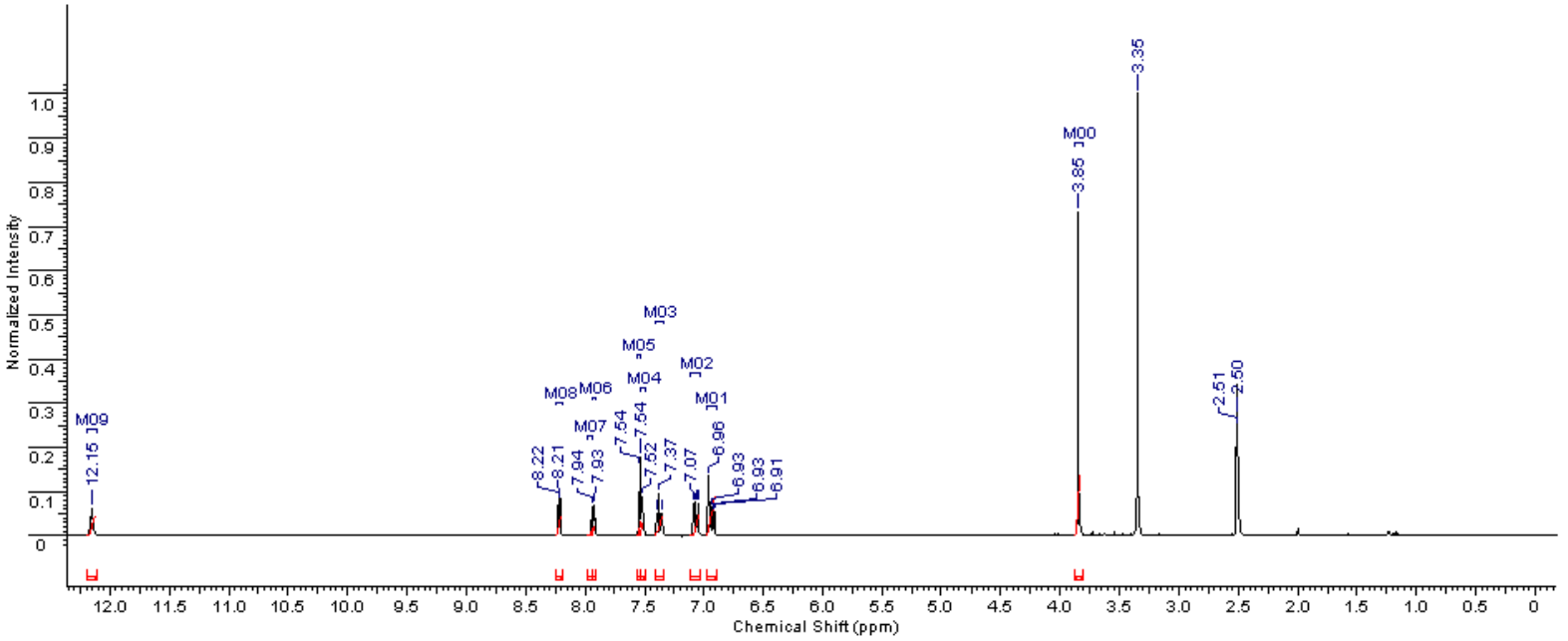
3/5/2009 8:11 AM

Acquisition Time (sec)	3.9715	*Comment*	Spergel 68778-227-01			*Date*	25 Jul 2007 14:51:45
File Name	C:\DOCUME~1\SPERGELS\LOCALS~1\TEMP\68778-227-01_10.JDX					*Frequency (MHz)*	400.13
Nucleus	1H	*Number of Transients*	16	*Origin*	nmrl2b	*Original Points Count*	32768
Owner	spergels	*Points Count*	32768	*Solvent*	DMSO-D6	*Spectrum Offset (Hz)*	2471.0171
Sweep Width (Hz)	8250.83	*Temperature (degree C)*	27.000				

2-(3-methoxyphenyl)-1H-pyrrolo[2,3-b]pyridine



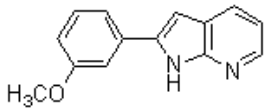
17



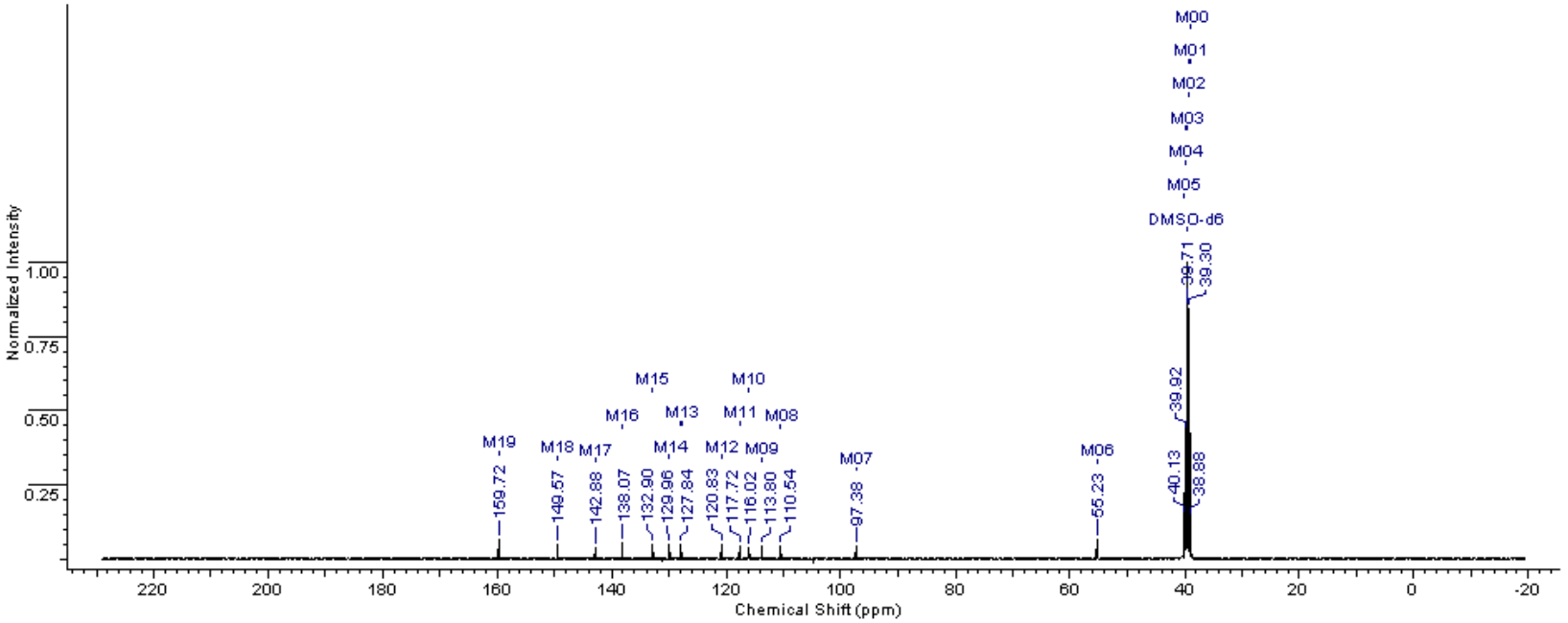
3/5/2009 7:48 AM

Acquisition Time (sec)	1.3108	*Comment*	Spergel 79036-073-01 68778-227-01			*Date*	05 Mar 2009 03:12:11
File Name	C:\DOCUME~1\SPERGELS\LOCALS~1\TEMP\ACR51.TMP\79036-073-01_10.JDX					*Frequency (MHz)*	100.62
Nucleus	13C	*Number of Transients*	2048	*Origin*	79036-073-01	*Original Points Count*	32768
Owner	spergels	*Points Count*	32768	*Solvent*	DMSO-D6	*Spectrum Offset (Hz)*	10543.9316
Sweep Width (Hz)	24999.24	*Temperature (degree C)*	20.900				

2-(3-methoxyphenyl)-1H-pyrrolo[2,3-b]pyridine



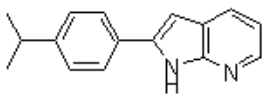
17



3/4/2009 8:52 AM

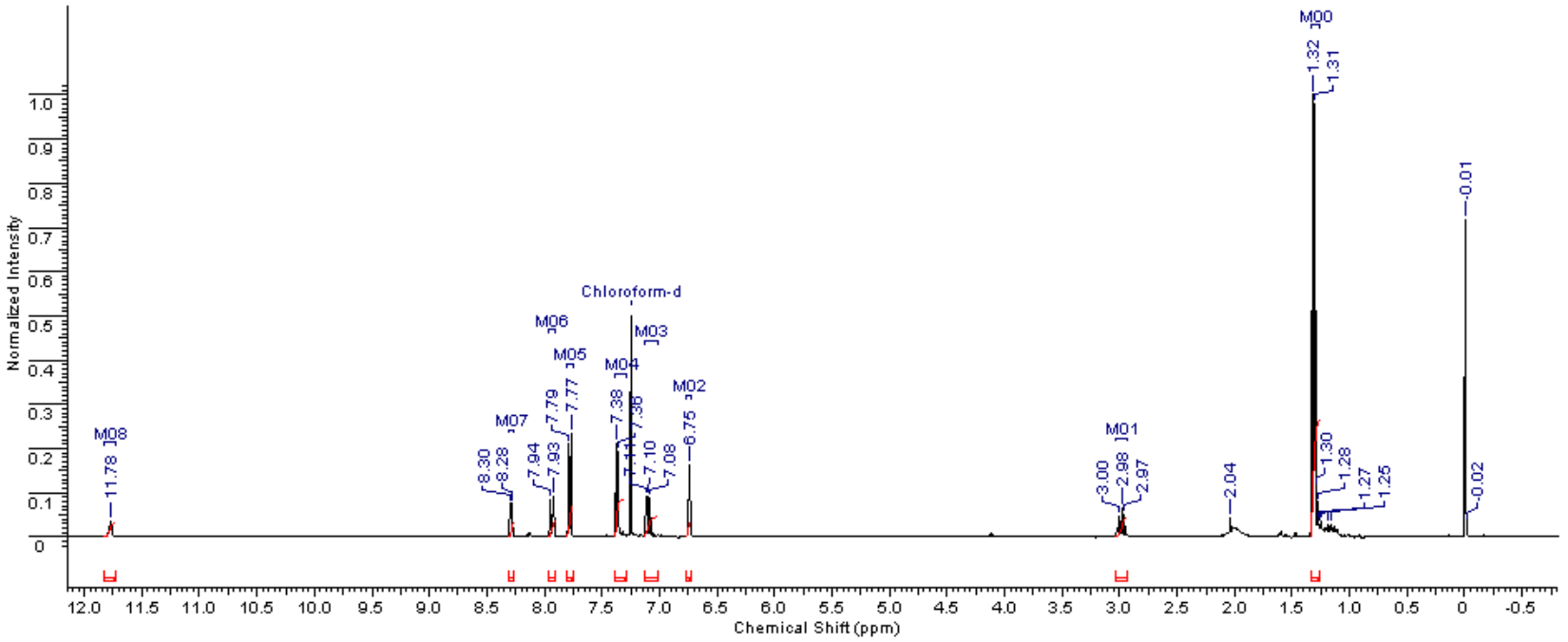
Acquisition Time (sec)	3.9715	*Comment*	Spergel 68778-222-01			*Date*	17 Jul 2007 19:39:28
File Name	C:\DOCUME~1\SPERGELS\LOCALS~1\TEMP\68778-222-01_10.JDX					*Frequency (MHz)*	400.13
Nucleus	1H	*Number of Transients*	16	*Origin*	nmr2b	*Original Points Count*	32768
Owner	spergels	*Points Count*	32768	*Solvent*	CHLOROFORM-D		
Spectrum Offset (Hz)	2467.6614	*Sweep Width (Hz)*	8250.83	*Temperature (degree C)*	27.000		

VerticalScaleFactor = 1



19

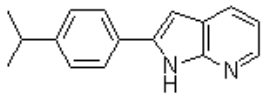
2-(4-isopropylphenyl)-1H-pyrrolo[2,3-b]pyridine



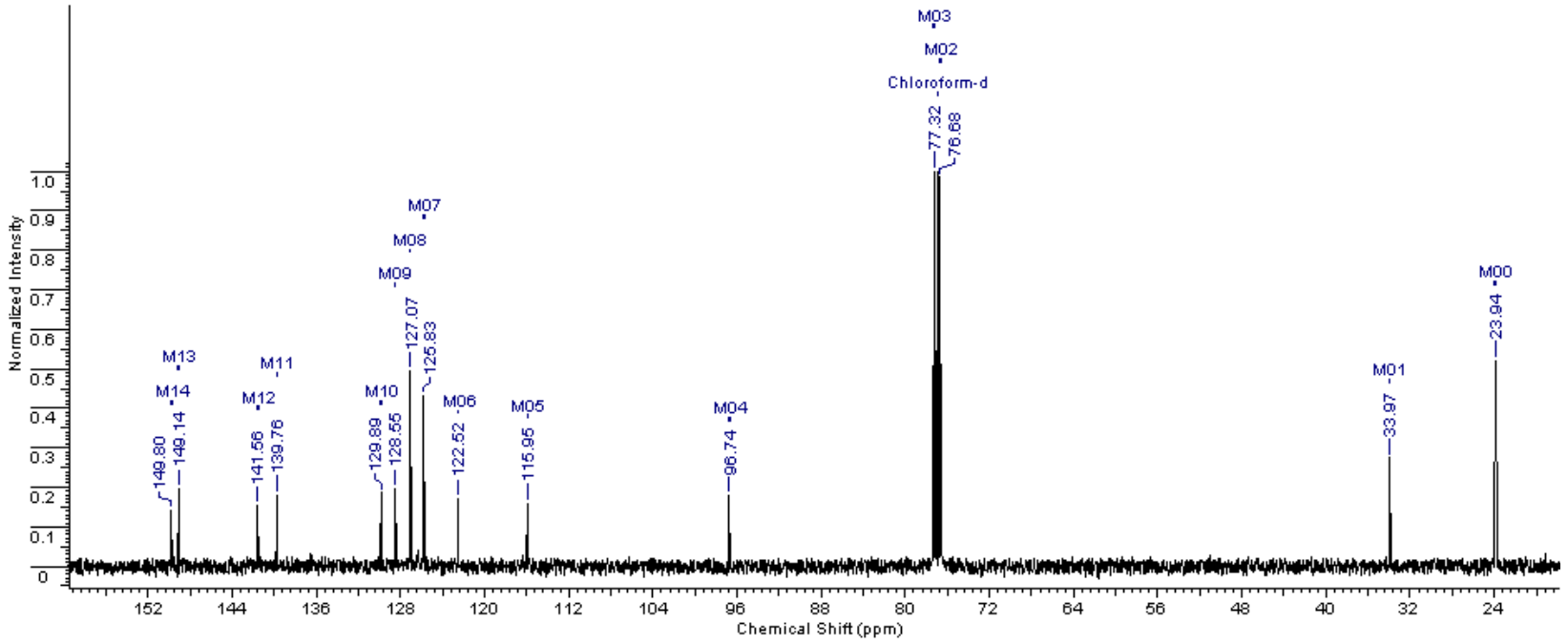
3/4/2009 8:16 AM

Acquisition Time (sec)	1.3108	*Comment*	Spergel 79036-074-01 68778-222-01			*Date*	04 Mar 2009 12:52:12
File Name	C:\DOCUME~1\SPERGELS\LOCALS~1\TEMP\ACR48.TMP\79036-074-01_10.JDX					*Frequency (MHz)*	100.62
Nucleus	13C	*Number of Transients*	256	*Origin*	79036-074-01	*Original Points Count*	32768
Owner	spergels	*Points Count*	32768	*Solvent*	CHLOROFORM-D	*Spectrum Offset (Hz)*	11062.6250
Sweep Width (Hz)	24999.24	*Temperature (degree C)*	22.500				

2-(4-isopropylphenyl)-1H-pyrrolo[2,3-b]pyridine



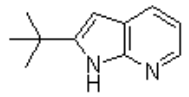
19



3/4/2009 3:36 PM

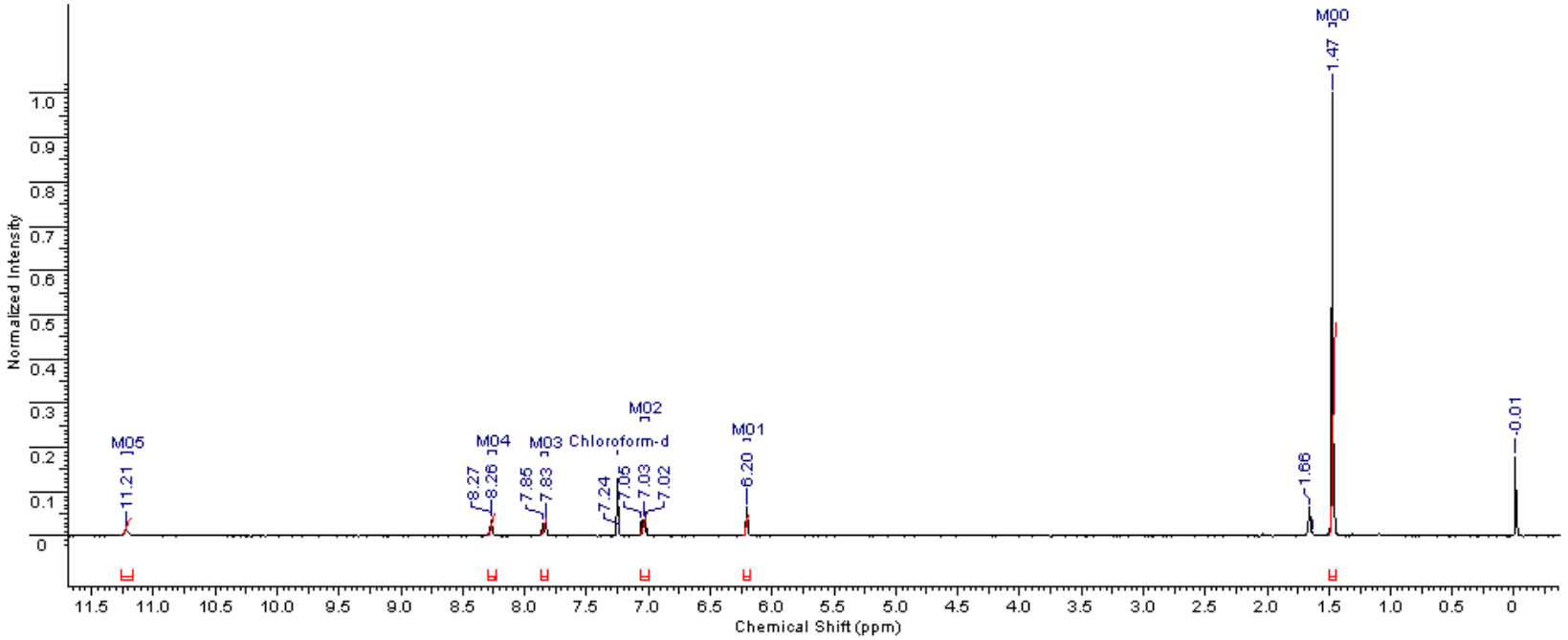
Acquisition Time (sec)	3.9715	*Comment*	Spergel 68778-229-01			*Date*	26 Jul 2007 15:42:40
File Name	C:\DOCUME~1\SPERGELS\LOCALS~1\TEMP\68778-229-01_10.JDX					*Frequency (MHz)*	400.13
Nucleus	1H	*Number of Transients*	16	*Origin*	nmrf2b	*Original Points Count*	32768
Owner	spergels	*Points Count*	32768	*Solvent*	CHLOROFORM-D		
Spectrum Offset (Hz)	2457.6614	*Sweep Width (Hz)*	8250.83	*Temperature (degree C)*	27.000		

VerticalScaleFactor = 1



21

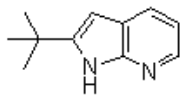
2-tert-butyl-1H-pyrrolo[2,3-b]pyridine



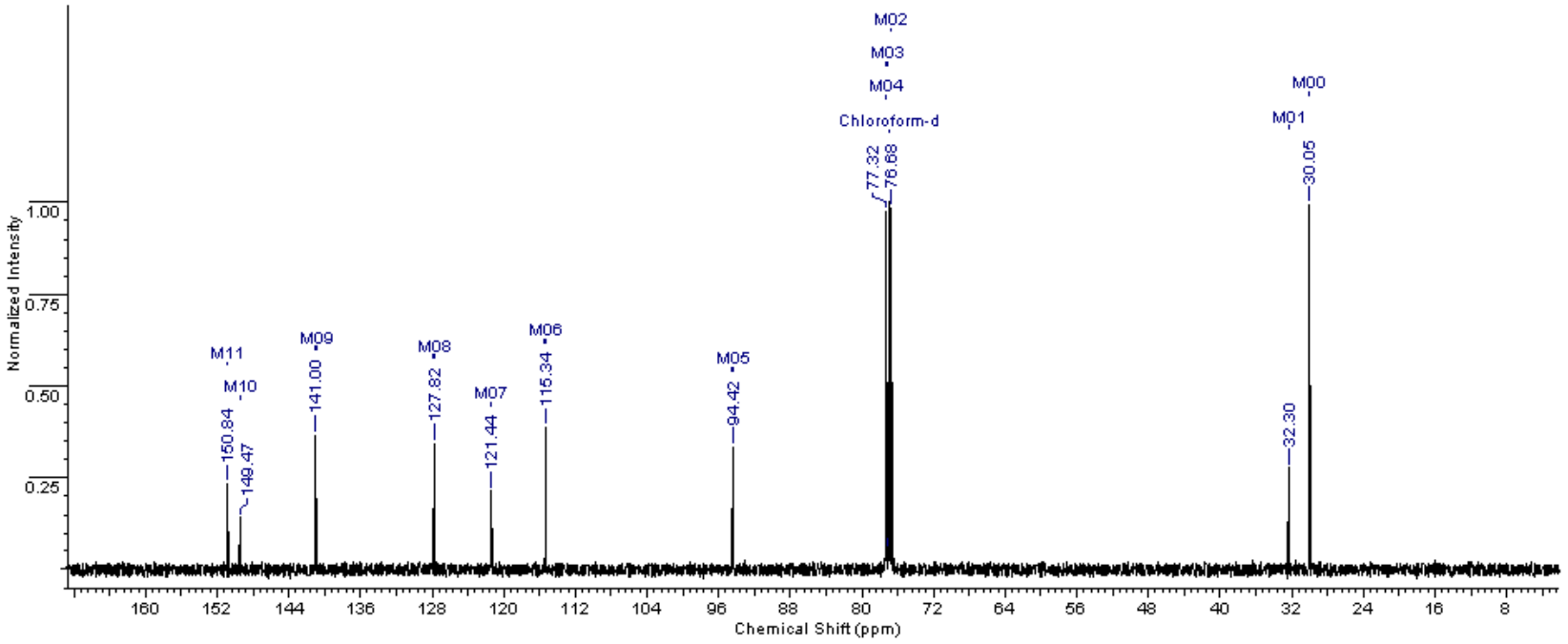
3/4/2009 3:05 PM

Acquisition Time (sec)	1.3108	*Comment*	Spergel 79036-075-01 68778-229-01			*Date*	04 Mar 2009 19:25:42
File Name	C:\DOCUME~1\SPERGELS\LOCALS~1\TEMP\ACR78.TMP\79036-075-01_10.JDX					*Frequency (MHz)*	100.62
Nucleus	13C	*Number of Transients*	256	*Origin*	79036-075-01	*Original Points Count*	32768
Owner	spergels	*Points Count*	32768	*Solvent*	CHLOROFORM-D	*Spectrum Offset (Hz)*	11064.9150
Sweep Width (Hz)	24999.24	*Temperature (degree C)*	21.100				

2-tert-butyl-1H-pyrrolo[2,3-b]pyridine



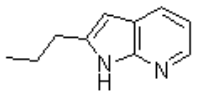
21



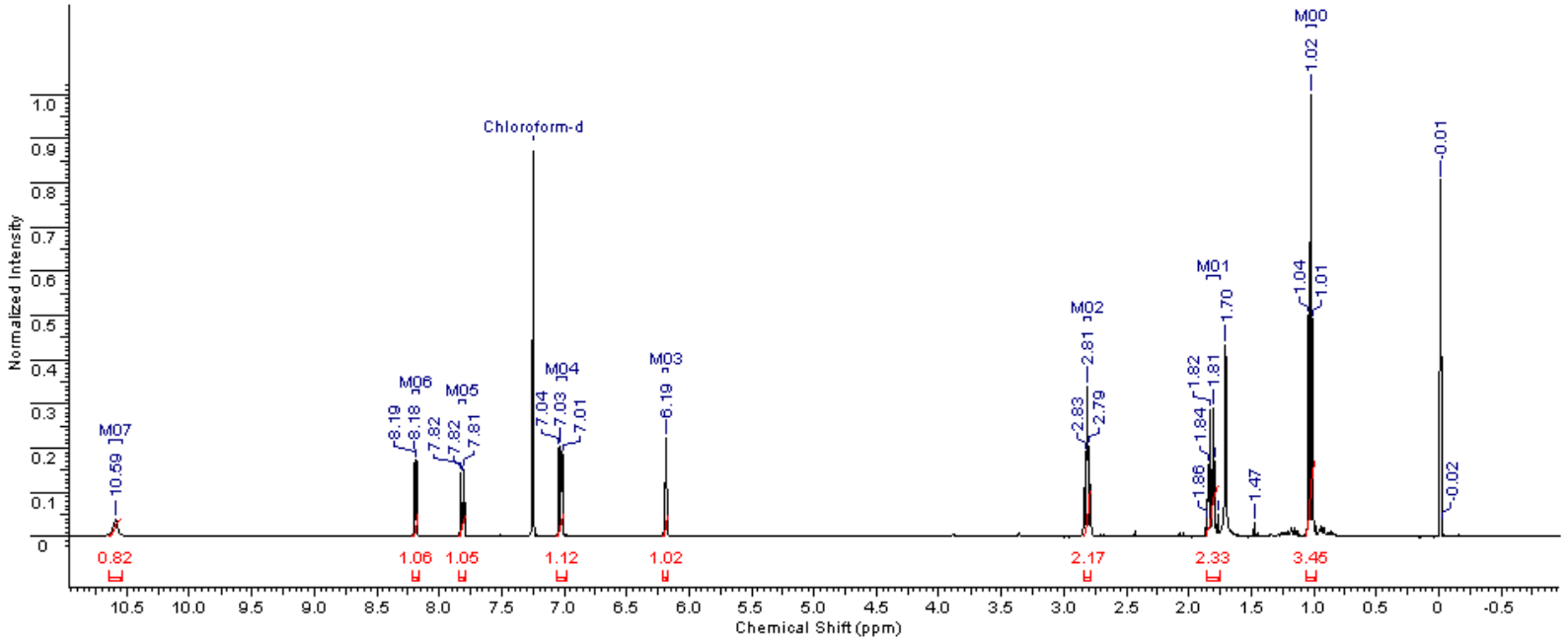
3/4/2009 3:44 PM

Acquisition Time (sec)	3.9715	*Comment*	Spergel 74581-016-01			*Date*	19 Sep 2007 15:56:02
File Name	C:\DOCUME~1\SPERGELS\LOCALS~1\TEMP\74581-016-01_10.JDX					*Frequency (MHz)*	400.13
Nucleus	1H	*Number of Transients*	16	*Origin*	nmr2b	*Original Points Count*	32768
Owner	spergels	*Points Count*	32768	*Solvent*	CHLOROFORM-D		
Spectrum Offset (Hz)	2467.6614	*Sweep Width (Hz)*	8250.83	*Temperature (degree C)*	27.000		

2-propyl-1H-pyrrolo[2,3-b]pyridine

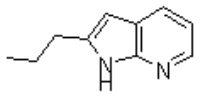


23



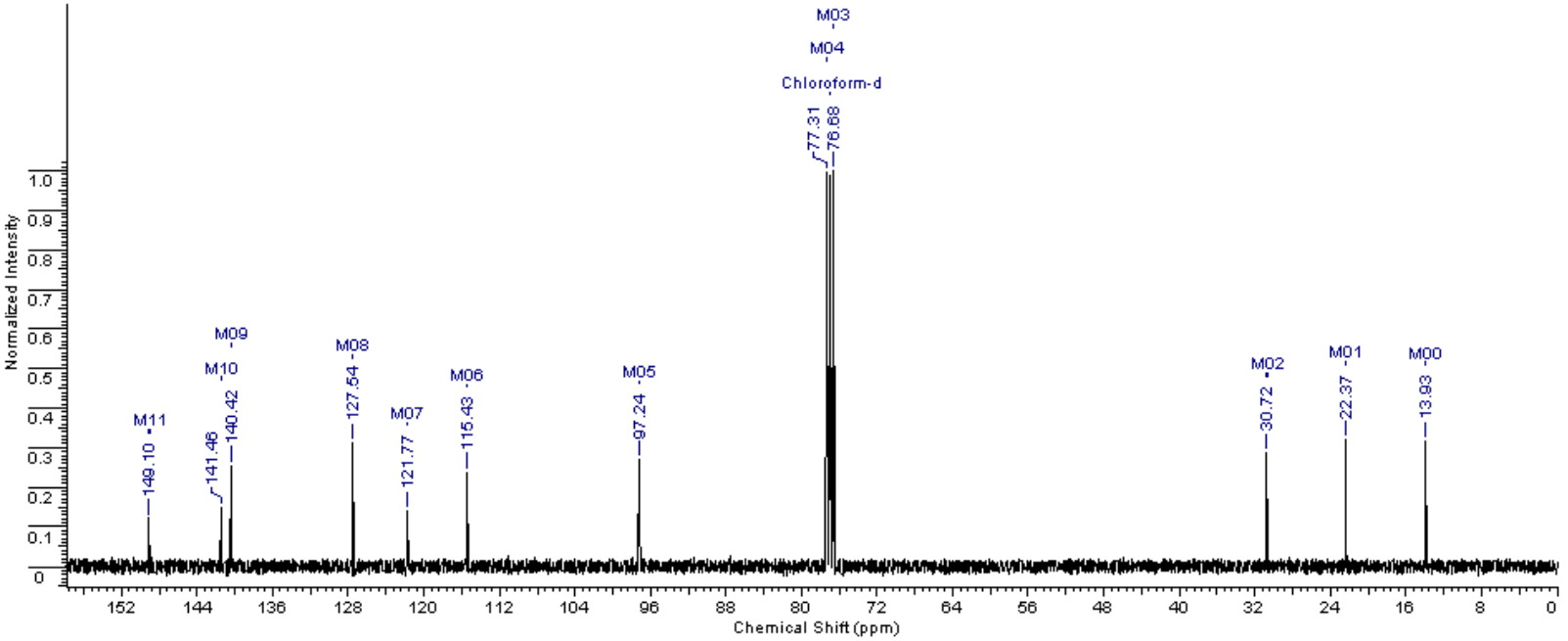
3/4/2009 3:16 PM

Acquisition Time (sec)	1.3108	*Comment*	Spergel 79036-076-01 74581-016-01			*Date*	04 Mar 2009 19:58:29
File Name	C:\DOCUME~1\SPERGELS\LOCALS~1\TEMP\ACR81.TMP\79036-076-01_10.JDX					*Frequency (MHz)*	100.62
Nucleus	13C	*Number of Transients*	256	*Origin*	79036-076-01	*Original Points Count*	32768
Owner	spergels	*Points Count*	32768	*Solvent*	CHLOROFORM-D	*Spectrum Offset (Hz)*	11064.1514
Sweep Width (Hz)	24999.24	*Temperature (degree C)*	21.100				



23

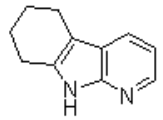
2-propyl-1H-pyrrolo[2,3-b]pyridine



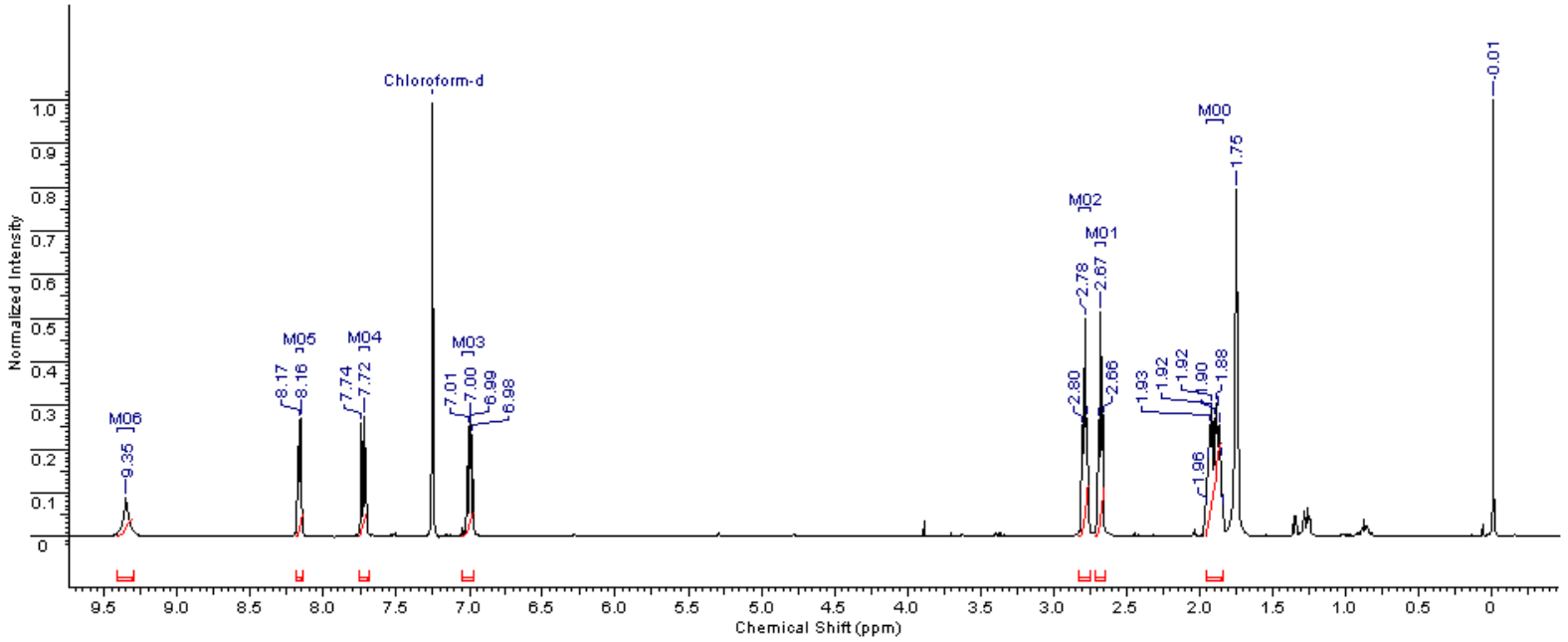
3/5/2009 10:38 AM

Acquisition Time (sec)	3.9715	*Comment*	Spergel 74581-011-01			*Date*	07 Sep 2007 17:14:45
File Name	C:\DOCUME~1\SPERGELS\LOCALS~1\TEMP\74581-011-01_10.JDX					*Frequency (MHz)*	400.13
Nucleus	1H	*Number of Transients*	16	*Origin*	nmrl2b	*Original Points Count*	32768
Owner	spergels	*Points Count*	32768	*Solvent*	CHLOROFORM-D		
Spectrum Offset (Hz)	2457.6614	*Sweep Width (Hz)*	8250.83	*Temperature (degree C)*	27.000		

6,7,8,9-tetrahydro-5H-pyrido[2,3-b]indole



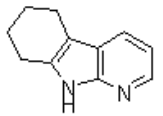
25



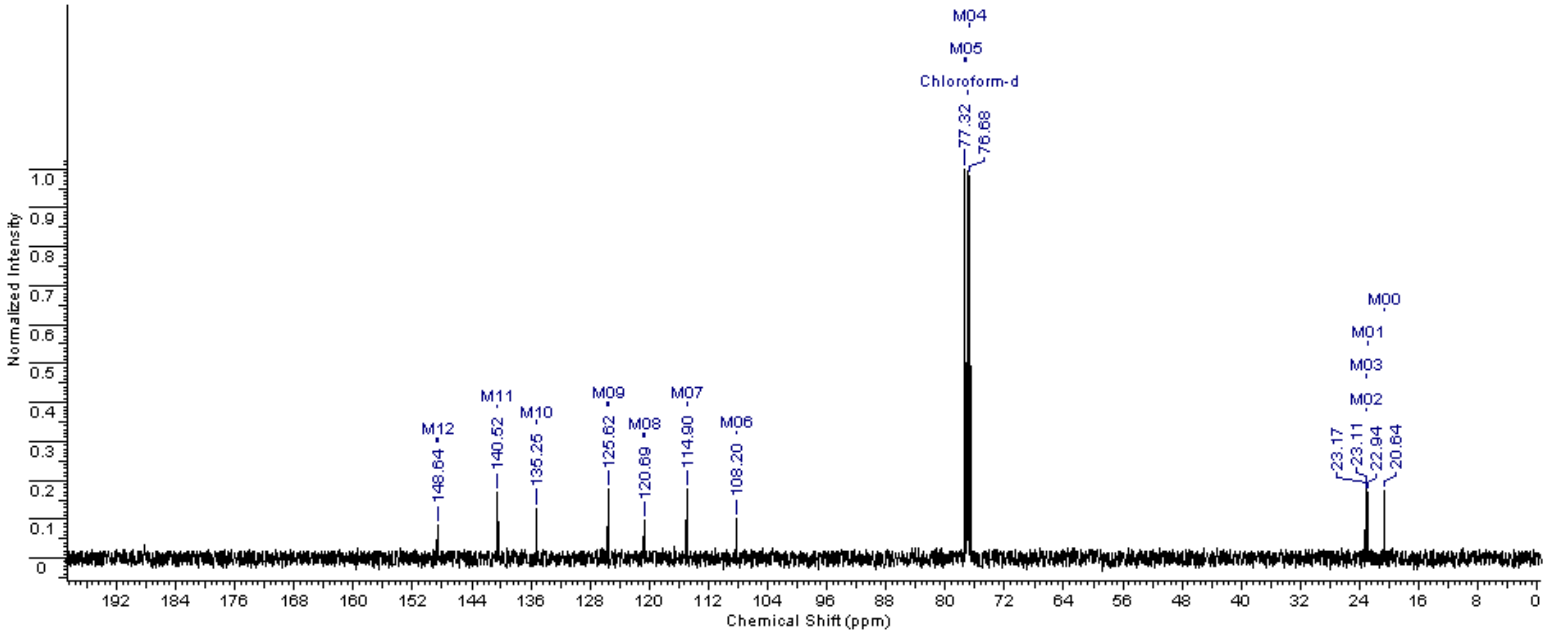
3/5/2009 10:17 AM

Acquisition Time (sec)	1.3108	*Comment*	Spergel 79036-077-01 74581-011-01			*Date*	05 Mar 2009 14:53:53
File Name	C:\DOCUME~1\SPERGELS\LOCALS~1\TEMP\ACR70.TMP\79036-077-01_10.JDX					*Frequency (MHz)*	100.62
Nucleus	13C	*Number of Transients*	256	*Origin*	79036-077-01	*Original Points Count*	32768
Owner	spergels	*Points Count*	32768	*Solvent*	CHLOROFORM-D	*Spectrum Offset (Hz)*	11064.1514
Sweep Width (Hz)	24999.24	*Temperature (degree C)*	21.900				

6,7,8,9-tetrahydro-5H-pyrido[2,3-b]indole



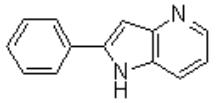
25



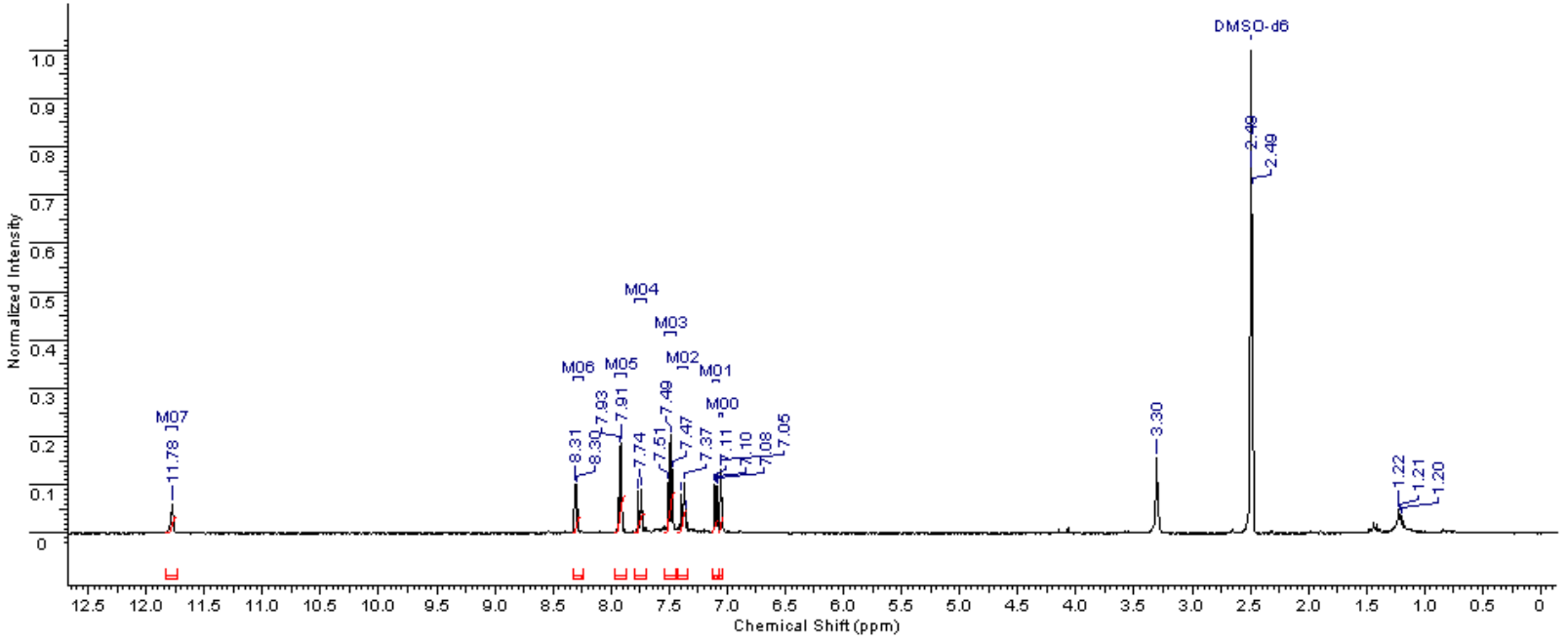
3/17/2009 1:30 PM

Acquisition Time (sec)	3.9847	*Comment*	Spergel 79036-082-01 DMSO			*Date*	17 Mar 2009 17:14:30
File Name	C:\DOCUME~1\SPERGELS\LOCALS~1\TEMP\ACR57.TMP\79036-082-10_10.JDX					*Frequency (MHz)*	400.13
Nucleus	1H	*Number of Transients*	16	*Origin*	79036-082-10	*Original Points Count*	32768
Owner	spergels	*Points Count*	32768	*Solvent*	DMSO-D6	*Spectrum Offset (Hz)*	2463.8589
Sweep Width (Hz)	8223.43	*Temperature (degree C)*	25.000				

2-phenyl-1H-pyrrolo[3,2-b]pyridine



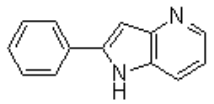
27



3/18/2009 8:34 AM

Acquisition Time (sec)	1.3108	*Comment*	Spergel 79036-082-01			*Date*	18 Mar 2009 05:16:21
File Name	C:\DOCUME~1\SPERGELS\LOCALS~1\TEMP\ACR51.TMP\79036-082-11_10.JDX					*Frequency (MHz)*	100.62
Nucleus	13C	*Number of Transients*	8192	*Origin*	79036-082-11	*Original Points Count*	32768
Owner	spergels	*Points Count*	32768	*Solvent*	DMSO-D6	*Spectrum Offset (Hz)*	11020.0059
Sweep Width (Hz)	24999.24	*Temperature (degree C)*	21.800				

2-phenyl-1H-pyrrolo[3,2-b]pyridine



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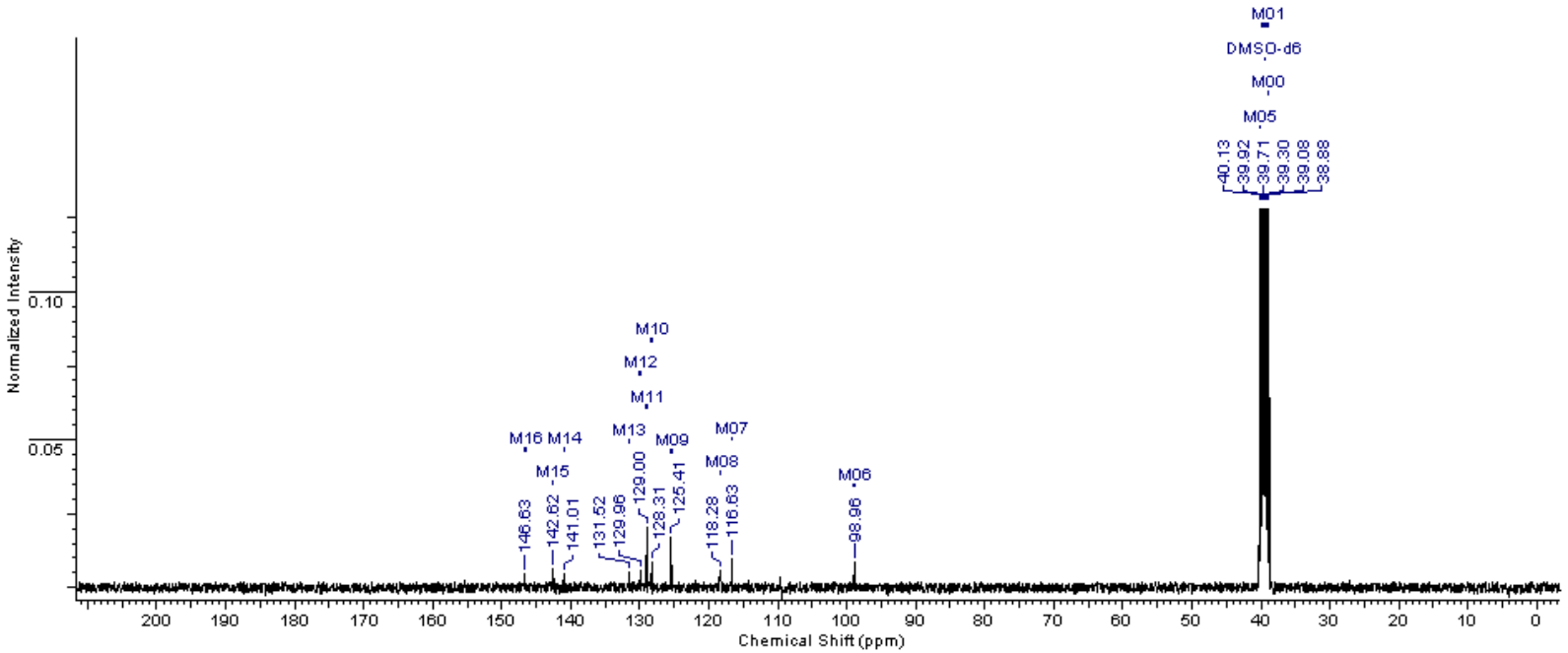
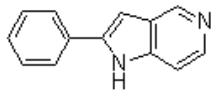


3/9/2009 1:54 PM

Acquisition Time (sec)	3.9847	*Comment*	Spergel 79036-084-01 68778-233-01			*Date*	09 Mar 2009 17:18:18
File Name	C:\DOCUME~1\SPERGELS\LOCALS~1\TEMP\ACR9B.TMP\79036-084-01_20.JDX					*Frequency (MHz)*	400.13
Nucleus	1H	*Number of Transients*	16	*Origin*	79036-084-01	*Original Points Count*	32768
Owner	spergels	*Points Count*	32768	*Solvent*	DMSO-D6	*Spectrum Offset (Hz)*	2464.8630
Sweep Width (Hz)	8223.43	*Temperature (degree C)*	21.500				

2-phenyl-1H-pyrrolo[3,2-c]pyridine



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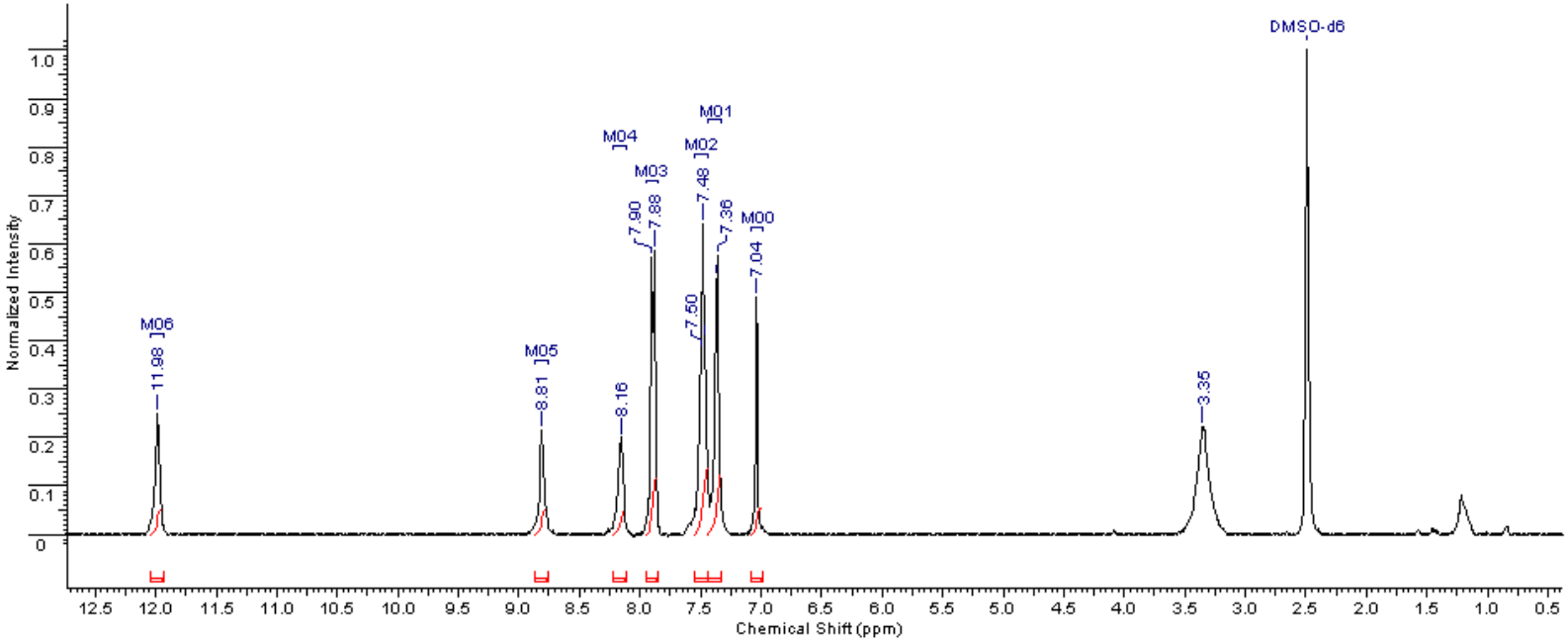
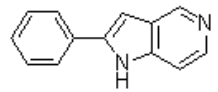


3/10/2009 7:50 AM

Acquisition Time (sec)	1.3108	*Comment*	Spergel 79036-084-01 68778-223-01			*Date*	09 Mar 2009 21:19:48
File Name	C:\DOCUME~1\SPERGELS\LOCALS~1\TEMP\ACR1A.TMP\79036-084-01_10.JDX					*Frequency (MHz)*	100.62
Nucleus	13C	*Number of Transients*	8192	*Origin*	79036-084-01	*Original Points Count*	32768
Owner	spergels	*Points Count*	32768	*Solvent*	DMSO-D6	*Spectrum Offset (Hz)*	11015.8857
Sweep Width (Hz)	24999.24	*Temperature (degree C)*	25.300				

2-phenyl-1H-pyrrolo[3,2-c]pyridine



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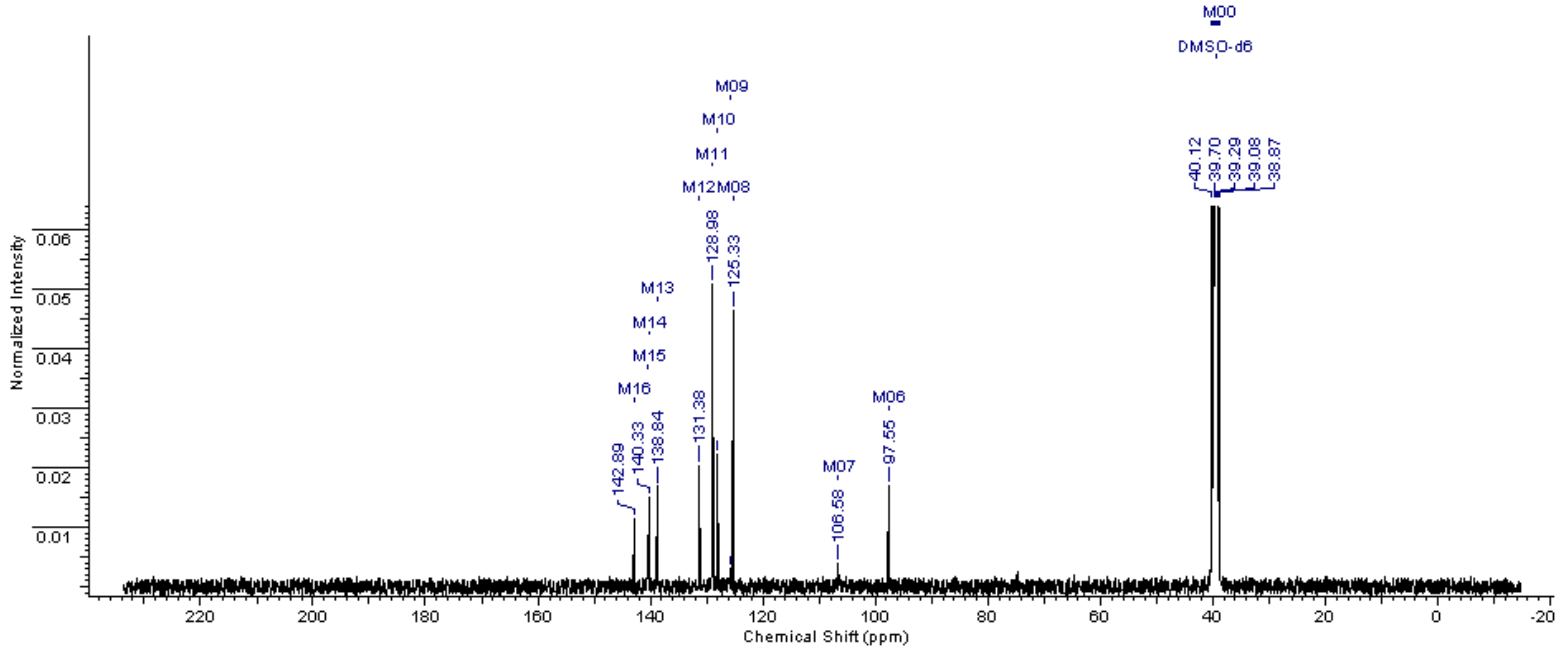
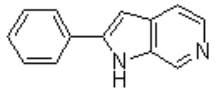


3/16/2009 2:51 PM

Acquisition Time (sec)	3.9847	*Comment*	Spergel 79036-090-01 79036-083-01			*Date*	16 Mar 2009 17:53:11
File Name	C:\DOCUME~1\SPERGELS\LOCALS~1\TEMP\ACR75.TMP\79036-090-01_10.JDX					*Frequency (MHz)*	400.13
Nucleus	1H	*Number of Transients*	16	*Origin*	79036-090-01	*Original Points Count*	32768
Owner	spergels	*Points Count*	32768	*Solvent*	DMSO-D6	*Spectrum Offset (Hz)*	2463.8591
Sweep Width (Hz)	8223.43	*Temperature (degree C)*	25.000				

2-phenyl-1H-pyrrolo[2,3-c]pyridine



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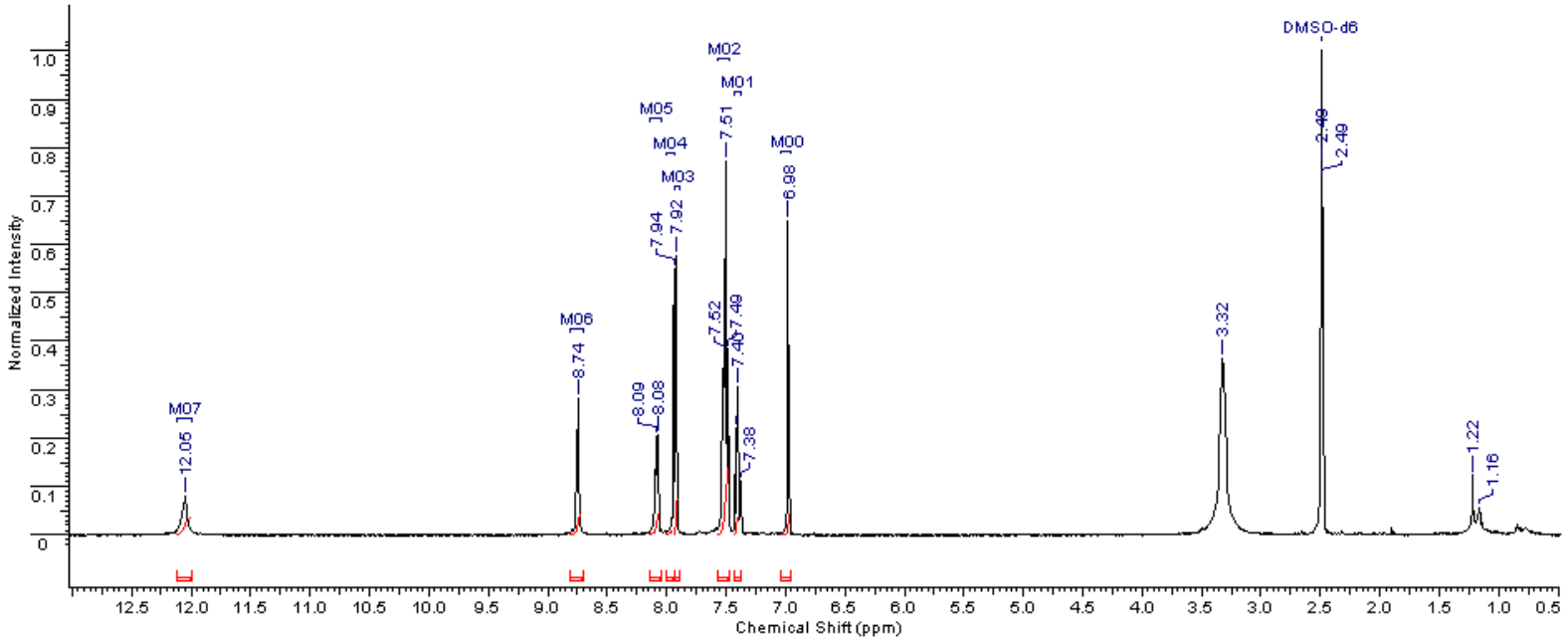
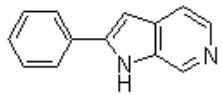


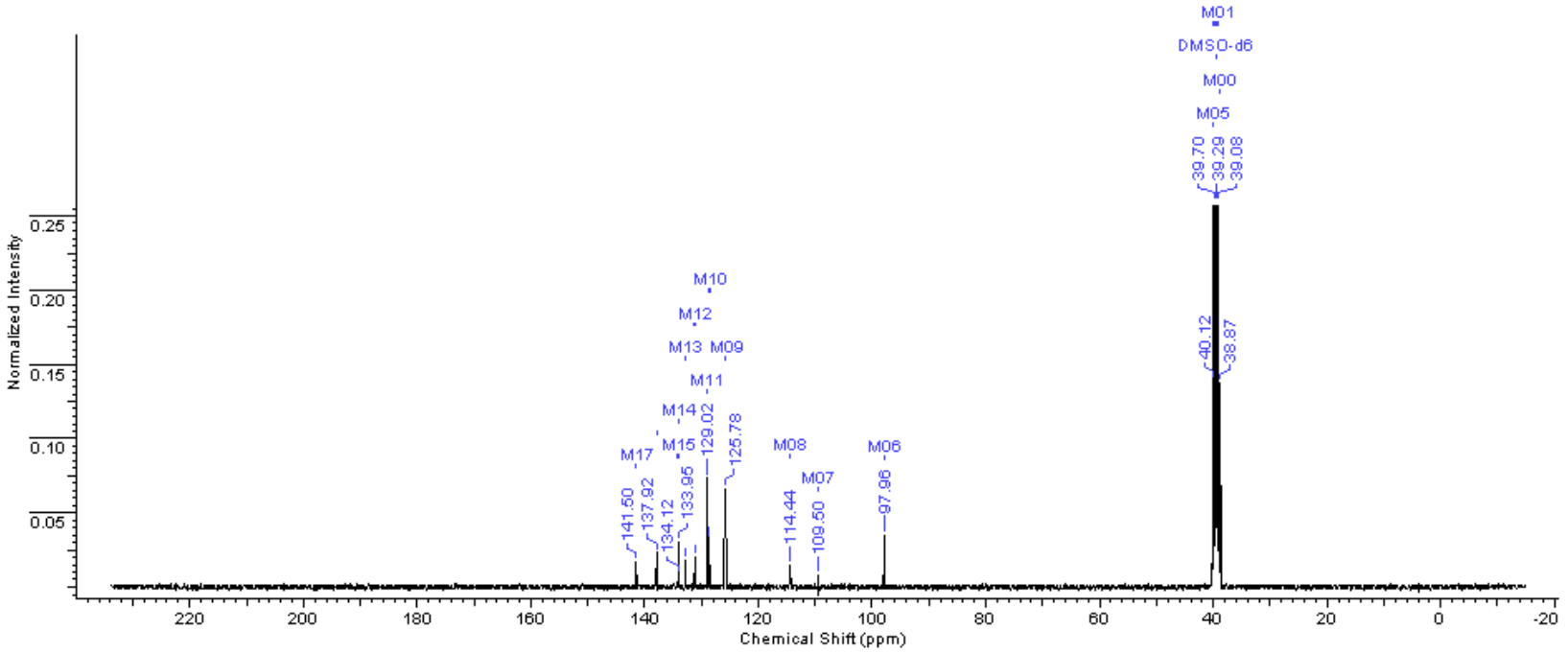
3/17/2009 8:54 AM

Acquisition Time (sec)	1.3108	*Comment*	Spergel 79036-090-01 79036-083-01			*Date*	17 Mar 2009 05:14:57
File Name	C:\DOCUME~1\SPERGELS\LOCALS~1\TEMP\ACR49.TMP\79036-090-02_10.JDX					*Frequency (MHz)*	100.62
Nucleus	13C	*Number of Transients*	8192	*Origin*	79036-090-02	*Original Points Count*	32768
Owner	spergels	*Points Count*	32768	*Solvent*	DMSO-D6	*Spectrum Offset (Hz)*	11017.7168
Sweep Width (Hz)	24999.24	*Temperature (degree C)*	25.000				



2-phenyl-1H-pyrrolo[2,3-c]pyridine

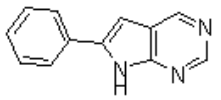
31



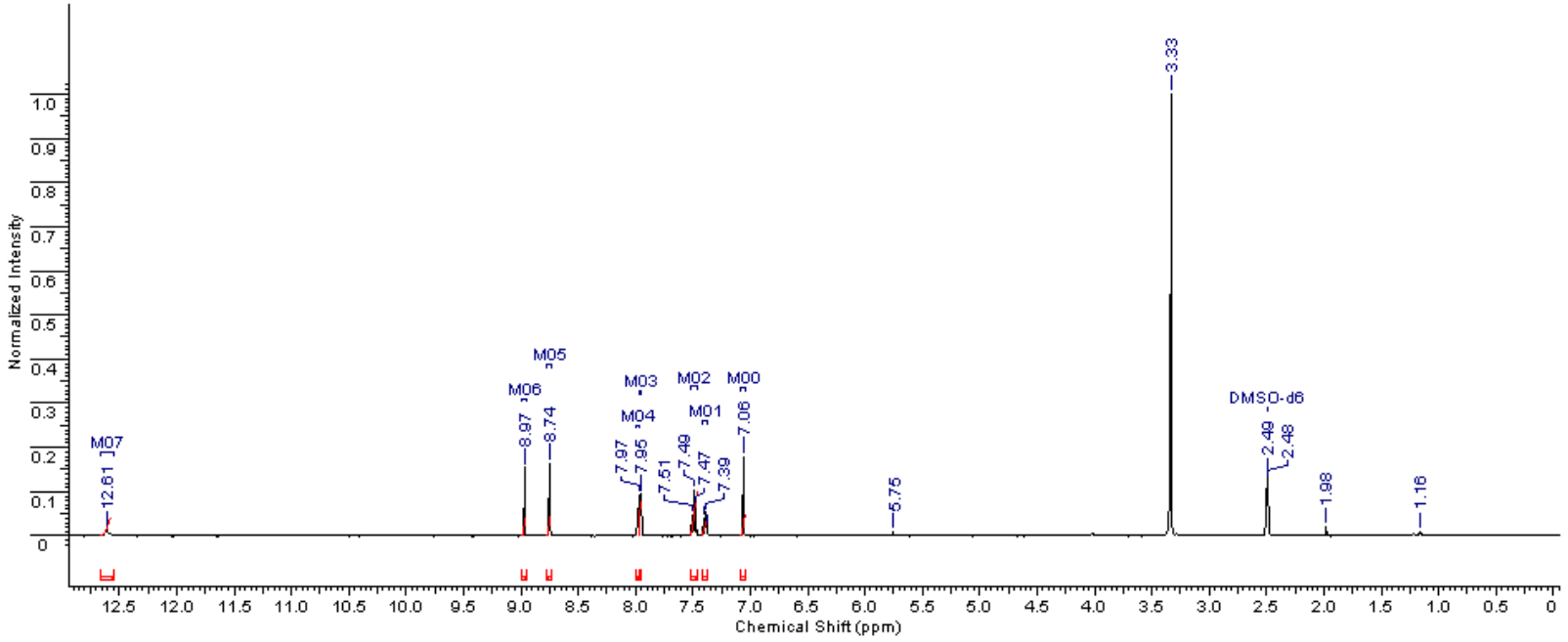
3/5/2009 3:53 PM

Acquisition Time (sec)	3.9715	*Comment*	Spergel 74581-023-01			*Date*	26 Sep 2007 15:52:35
File Name	C:\DOCUME~1\SPERGELS\LOCALS~1\TEMP\74581-023-01_10.JDX					*Frequency (MHz)*	400.13
Nucleus	1H	*Number of Transients*	16	*Origin*	nmrf2b	*Original Points Count*	32768
Owner	spergels	*Points Count*	32768	*Solvent*	DMSO-D6	*Spectrum Offset (Hz)*	2464.4666
Sweep Width (Hz)	8250.83	*Temperature (degree C)*	27.000				

6-phenyl-7H-pyrrolo[2,3-d]pyrimidine



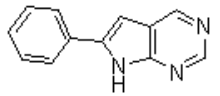
33



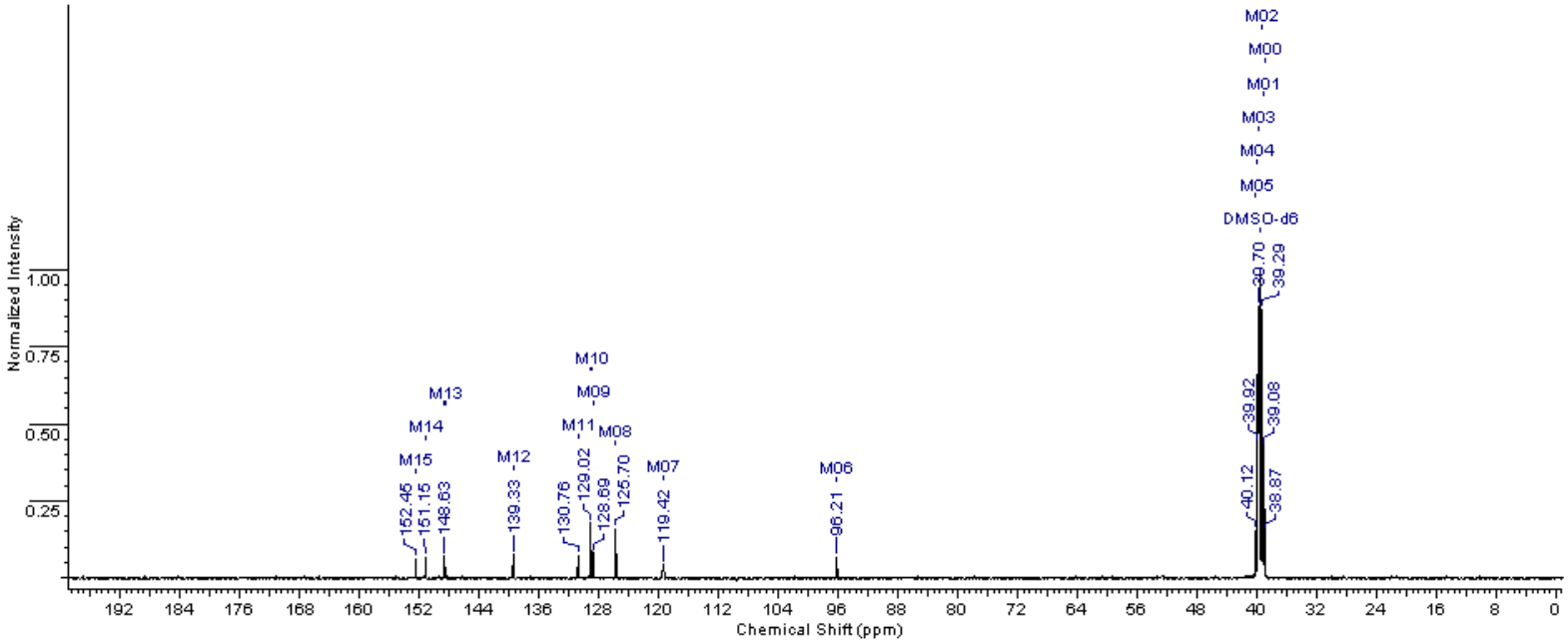
3/6/2009 7:37 AM

Acquisition Time (sec)	1.3108	*Comment*	Spergel 79036-080-01 74581-023-01			*Date*	06 Mar 2009 03:12:48
File Name	C:\DOCUME~1\SPERGELS\LOCALS~1\TEMP\ACR34.TMP\79036-080-01_10.JDX					*Frequency (MHz)*	100.62
Nucleus	13C	*Number of Transients*	2048	*Origin*	79036-080-01	*Original Points Count*	32768
Owner	spergels	*Points Count*	32768	*Solvent*	DMSO-D6	*Spectrum Offset (Hz)*	11021.5313
Sweep Width (Hz)	24999.24	*Temperature (degree C)*	21.100				

6-phenyl-7H-pyrrolo[2,3-d]pyrimidine



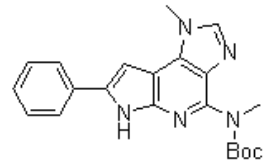
33



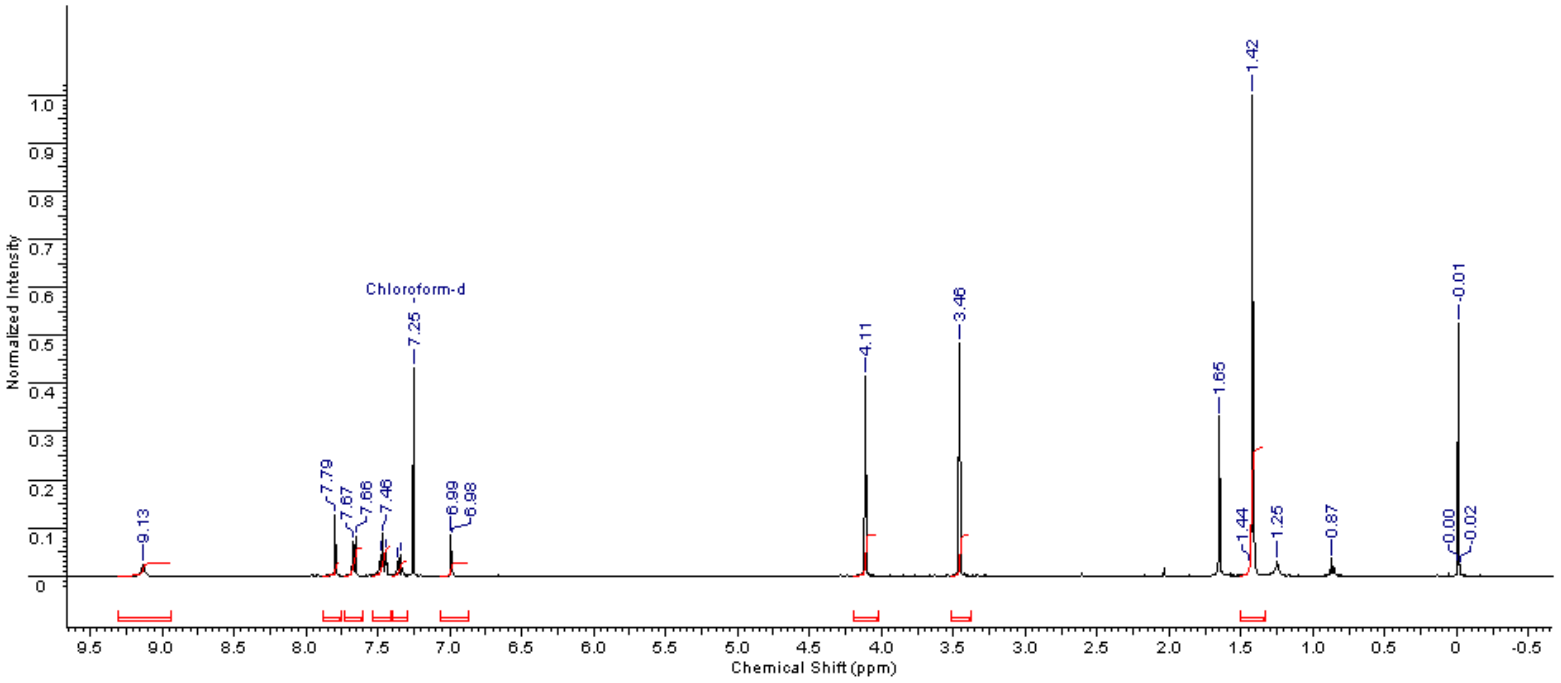
3/5/2009 4:23 PM

Acquisition Time (sec)	3.9847	*Comment*	Spergel 79036-054-01			*Date*	19 Feb 2009 13:56:23
File Name	C:\DOCUME~1\SPERGELS\LOCALS~1\TEMP\ACRC7.TMP\79036-054-01_10.JDX					*Frequency (MHz)*	400.13
Nucleus	1H	*Number of Transients*	16	*Origin*	79036-054-01	*Original Points Count*	32768
Owner	spergels	*Points Count*	32768	*Solvent*	CHLOROFORM-D		
Spectrum Offset (Hz)	2457.3765	*Sweep Width (Hz)*	8223.43	*Temperature (degree C)*	21.700		

tert-butyl methyl(1-methyl-7-phenyl-1,6-dihydroimidazo[4,5-d]pyrrolo[2,3-b]pyridin-4-yl)carbamate



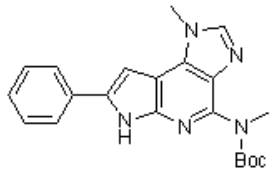
34



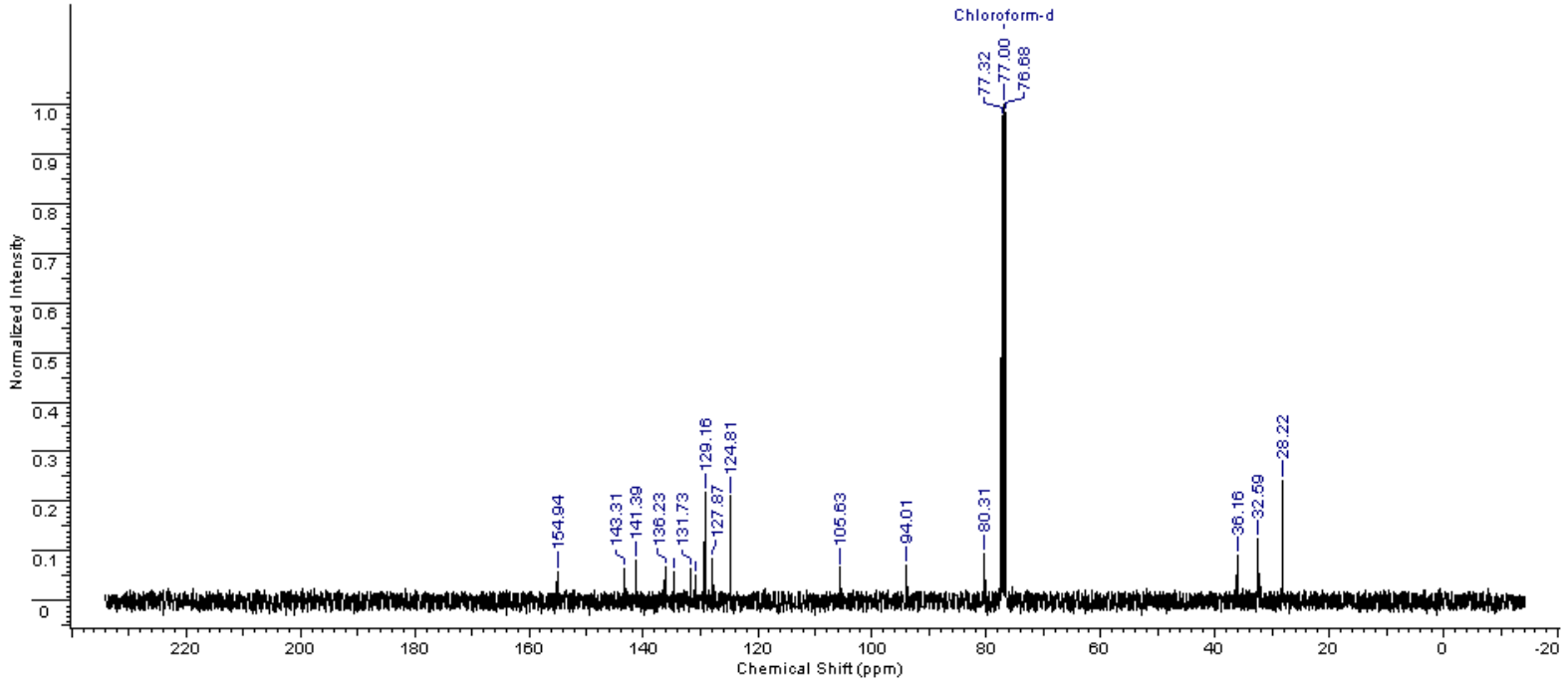
3/6/2009 8:46 AM

Acquisition Time (sec)	1.3108	*Comment*	Spergel 79036-079-01 79036-054-01			*Date*	06 Mar 2009 12:37:10
File Name	C:\DOCUME~1\SPERGELS\LOCALS~1\TEMP\ACR56.TMP\79036-079-01_20.JDX					*Frequency (MHz)*	100.62
Nucleus	13C	*Number of Transients*	256	*Origin*	79036-079-01	*Original Points Count*	32768
Owner	spergels	*Points Count*	32768	*Solvent*	CHLOROFORM-D	*Spectrum Offset (Hz)*	11064.1514
Sweep Width (Hz)	24999.24	*Temperature (degree C)*	22.900				

tert-butyl methyl(1-methyl-7-phenyl-1,6-dihydroimidazo[4,5-d]pyrrolo[2,3-b]pyridin-4-yl)carbamate



34



V. References

[1] Kuzmich, Daniel; Mulrooney, Carol *Synthesis* **2003**, *11,* 1671-1678.

[2] Carlos de Matos, Marcos; Alatorre-Santamaria, Sergio; Gotor-Fernandez, Vicente; Gotor, Vicente *Synthesis* **2007**, *14,* 2149-2152.

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[4] Graczyk, P. Patent WO 013139, 2004.

[5] Mettey, Yvette; Gompel, Marie; Thomas, Virginia; Garnier, Matthieu; Leost, Maryse; Ceballos-Picot, Irne; Noble, Martin; Endicott, Jane; Vierfond, Jean-michel; Meijer, Laurent *J. Med. Chem.* **2003**, *2,* 222-236.

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[8] Pitts, W. J.; Kempson, J.; Guo, J.; Das, J.; Langevine, C. M.; Spergel, S. H.; Watterson, S. H. Patent WO 122137, 2006.