Electronic Supplementary information

Silver(I)-*N*-heterocyclic carbene catalyzed multicomponent reactions: a facile synthesis of multisubstituted pyridines

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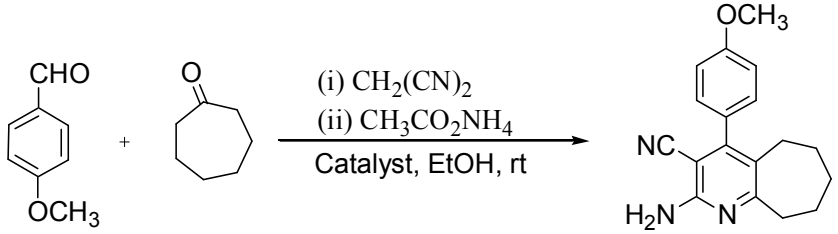
1. Table S1. Optimization of reaction parameters for the synthesis of **3a**.

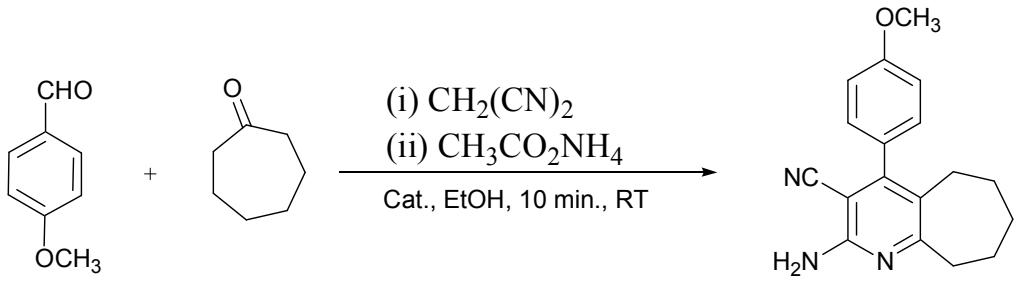


1a **2a** **3a**

Entry	Catalyst	Time (min.)	Yield (%)[a]	
1	No Catalyst	360	--	
2	AgOAc	120	--	
3	AgOTf	120	--	
4	$AgSbF_6$	120	--	
5	$AgNO_3$	120	--	
6	Ag(I)-NHC (**a**)	10	94	
7	Ag(I)-NHC (**b**)	12	86	
8	Ag(I)-NHC (**c**)	10	90	
9	Ag(I)-NHC (**d**)	10	90	
10	Ag(I)-NHC (**e**)	10	88	
11	Ag(I)-NHC (**f**)	15	91	
12	Organo-NHC	40	32	
13	Organo-NHC + AgOAc	15	84	
14	Organo-NHC + AgOTf	15	80	
15	DABCO	30	65	*b*
16	PPh_3	45	50	
17	AgOTf + DABCO	40	74	
18	AgOTf + TEA	40	58	
19	AgOTf + K_2CO_3	40	52	
20	AgOAc + DABCO	40	70	
21	AgOTf + DBU	35	75	
22	AgOAc + NaOAc	35	65	
23	$Cu(OAc)_2$ + DBU	60	55	
24	$Al(OTf)_3$ + DBU	60	45	
25	$Cu(OTf)_2$	120	--	
26	$Ni(OTf)_2$	120	--	
27	Organo-NHC + $Cu(OTf)_2$	30	68	
28	Organo-NHC + $Al(OTf)_3$	30	62	
29	Organo-NHC + $Sc(OTf)_3$	45	70	
30	Organo-NHC + $Ni(OTf)_2$	40	65	

[a] GC Yields. [b] Knoevenagel condensed product.

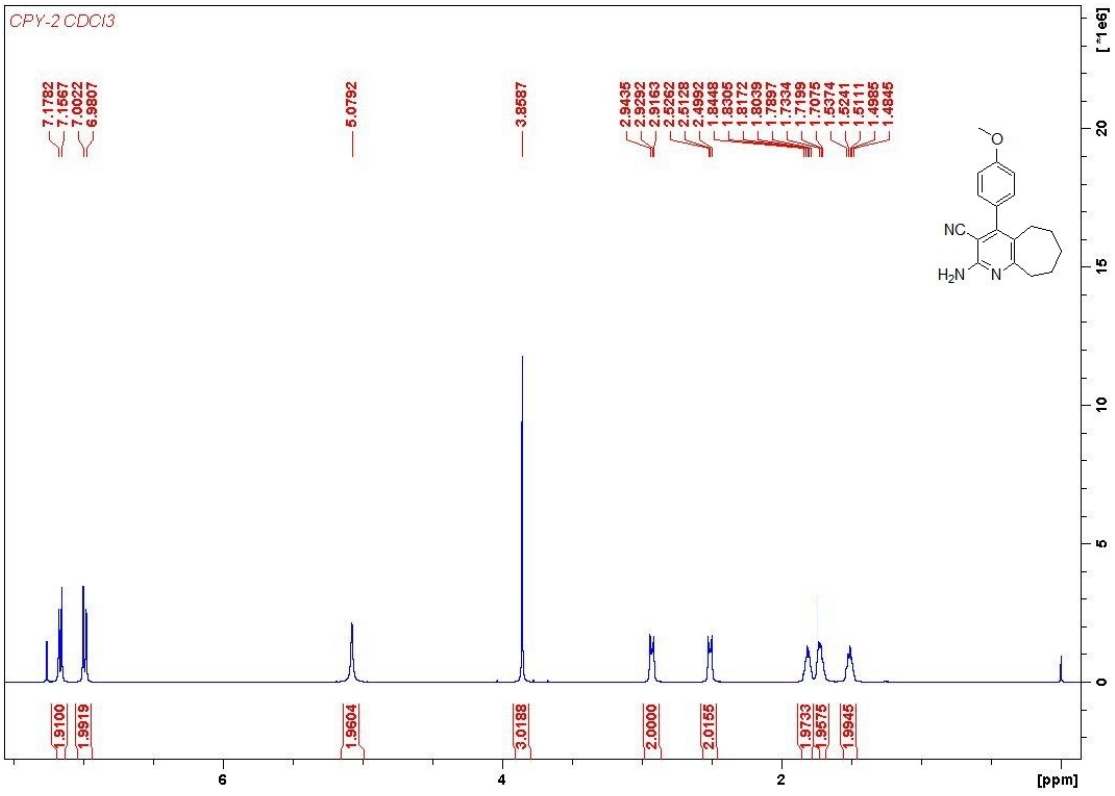
2. **Table S2**. Catalyst load experiment in the multicomponent reaction of **1a** and **2a** catalyzed by Ag(I)-NHC (**i**) catalyst.



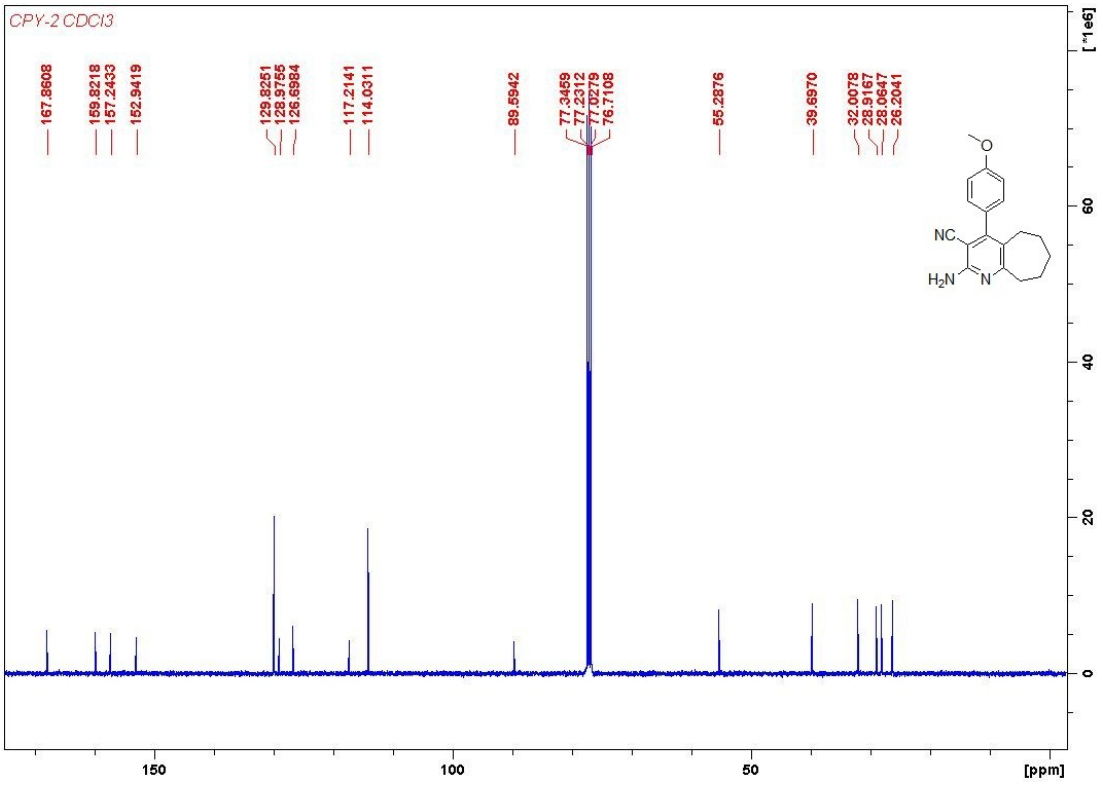
1a **2a** **3a**

Entry	Ag(I)-NHC (**a**)	GC yield (%)
1	2.0 mol%	94
2	3.0 mol%	96
3	3.5 mol%	96
4	4.0 mol%	96

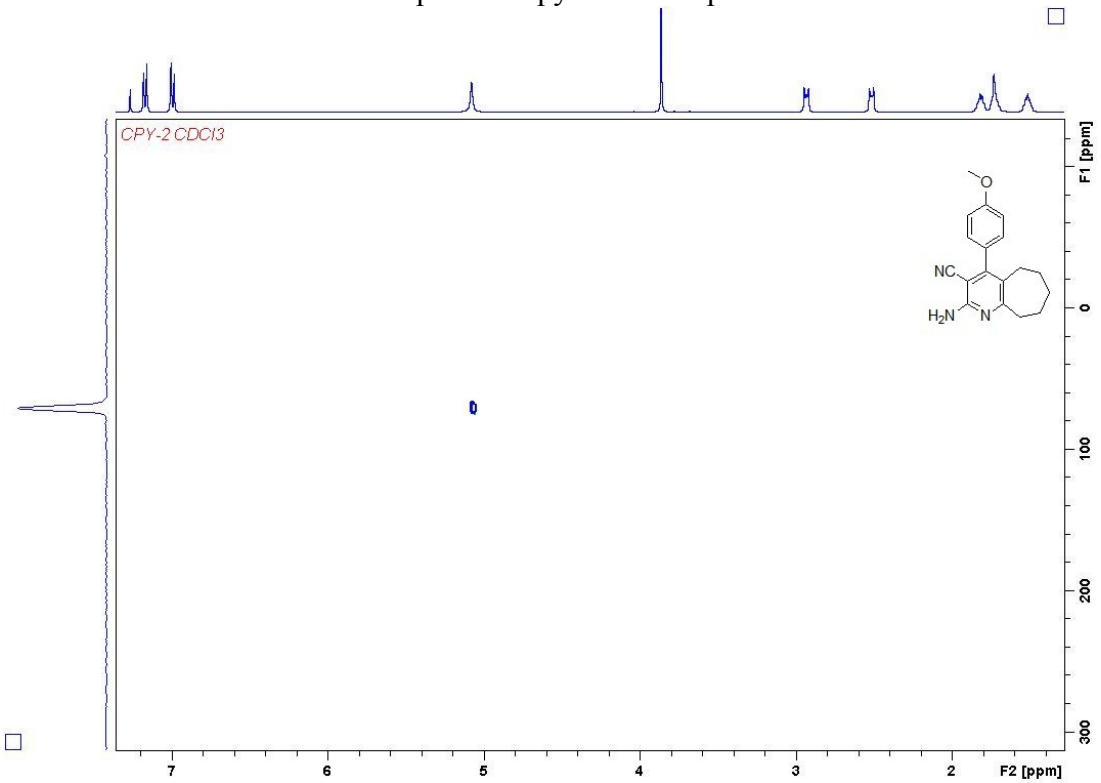
3. **Spectra of pyridine compounds** (**3a-i** & **4a-d**).



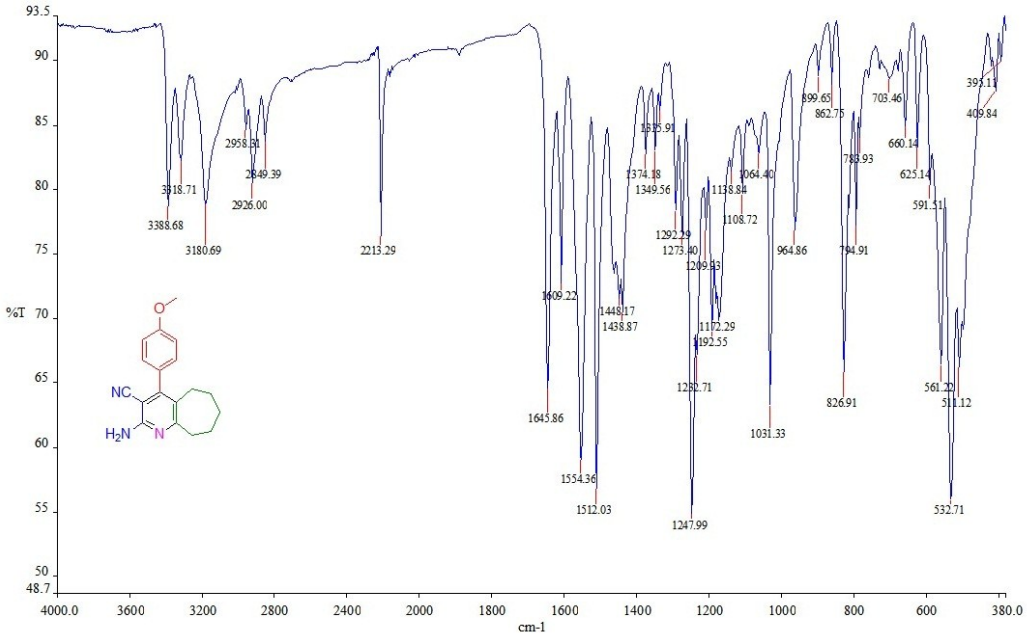
^{1}H NMR spectra of pyridine compound **3a**



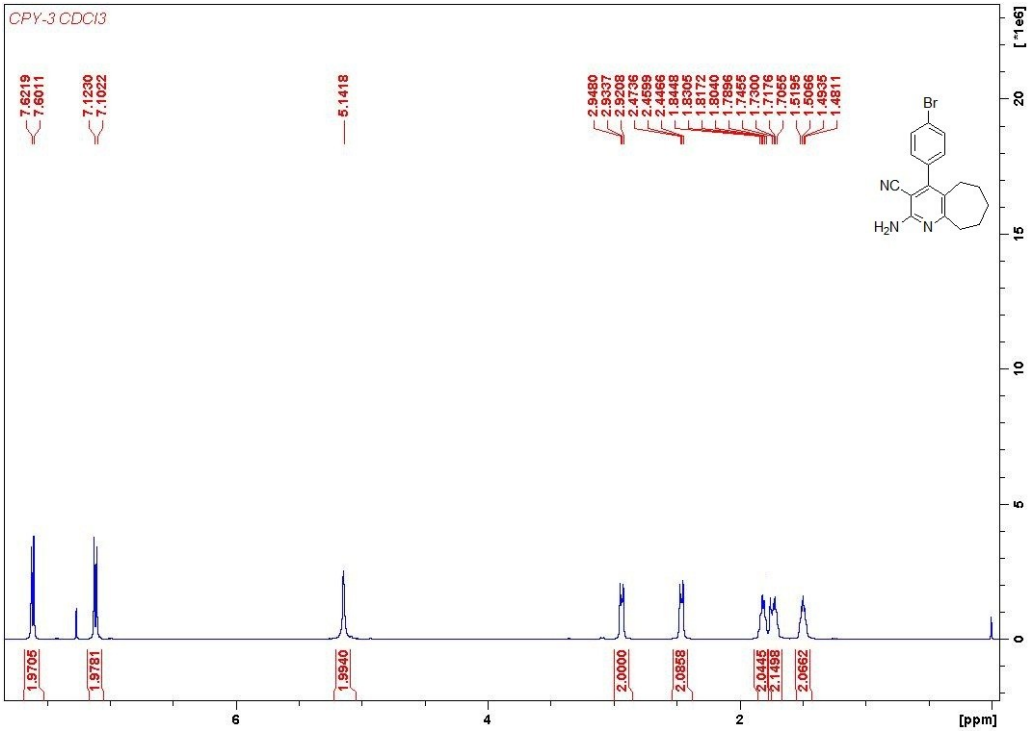
^{13}C NMR spectra of pyridine compound **3a**



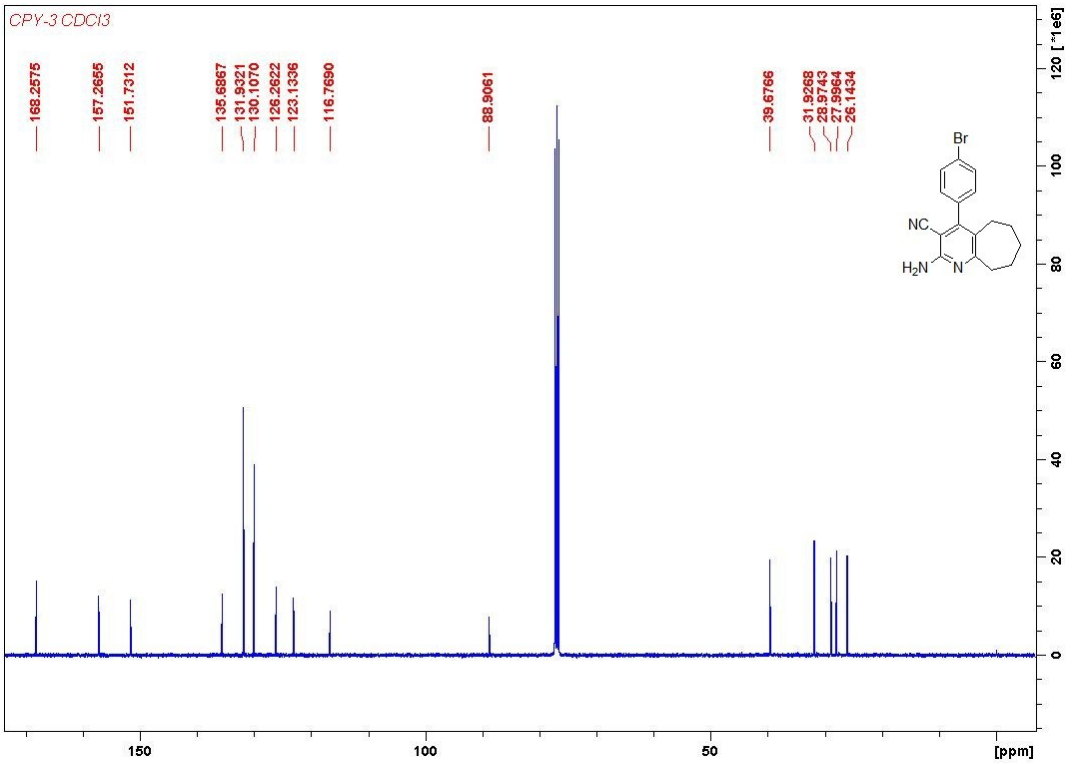
^{15}N NMR (ghsqc) spectra of pyridine compound **3a**



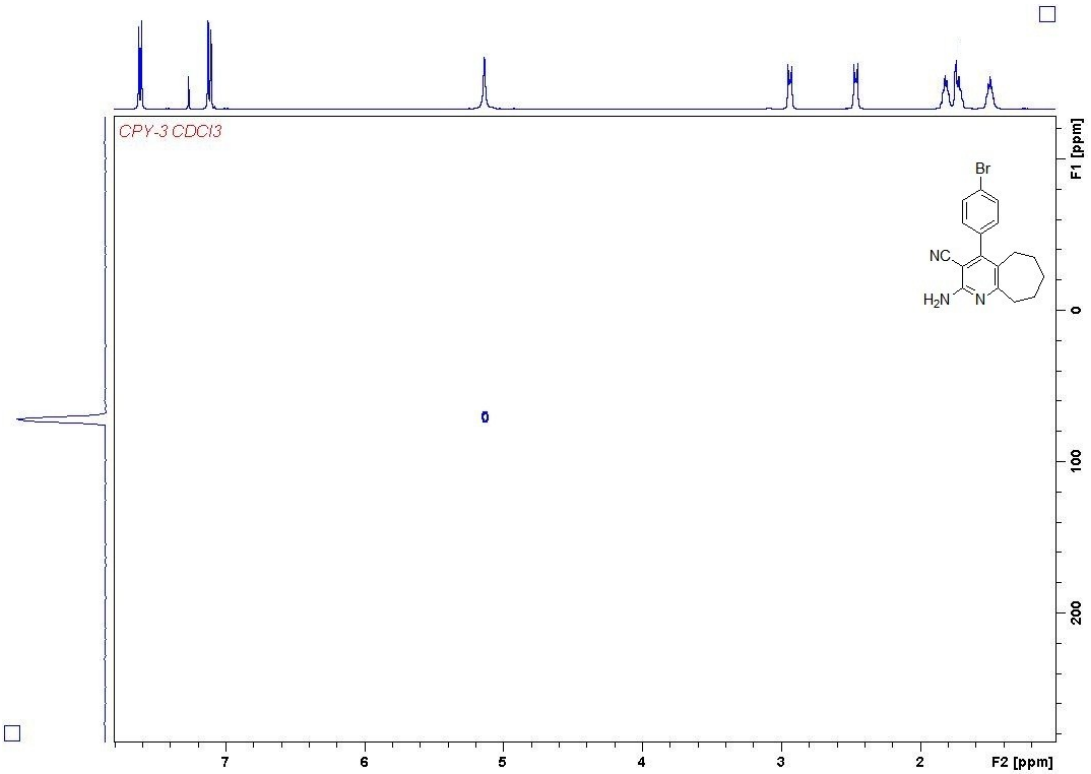
FTIR spectra of pyridine compound **3a**



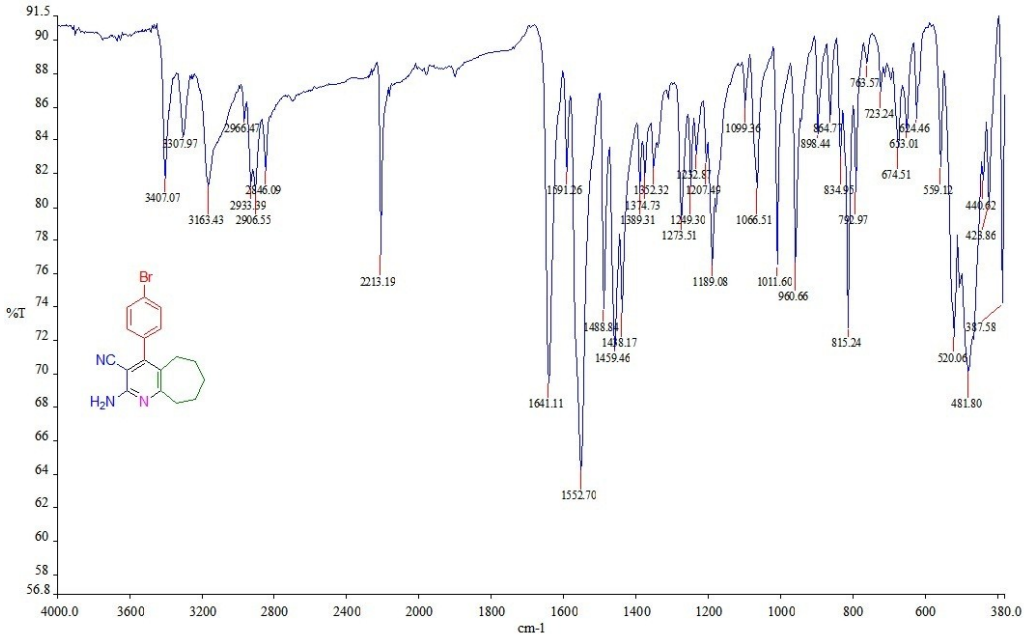
^{1}H NMR spectra of pyridine compound **3b**



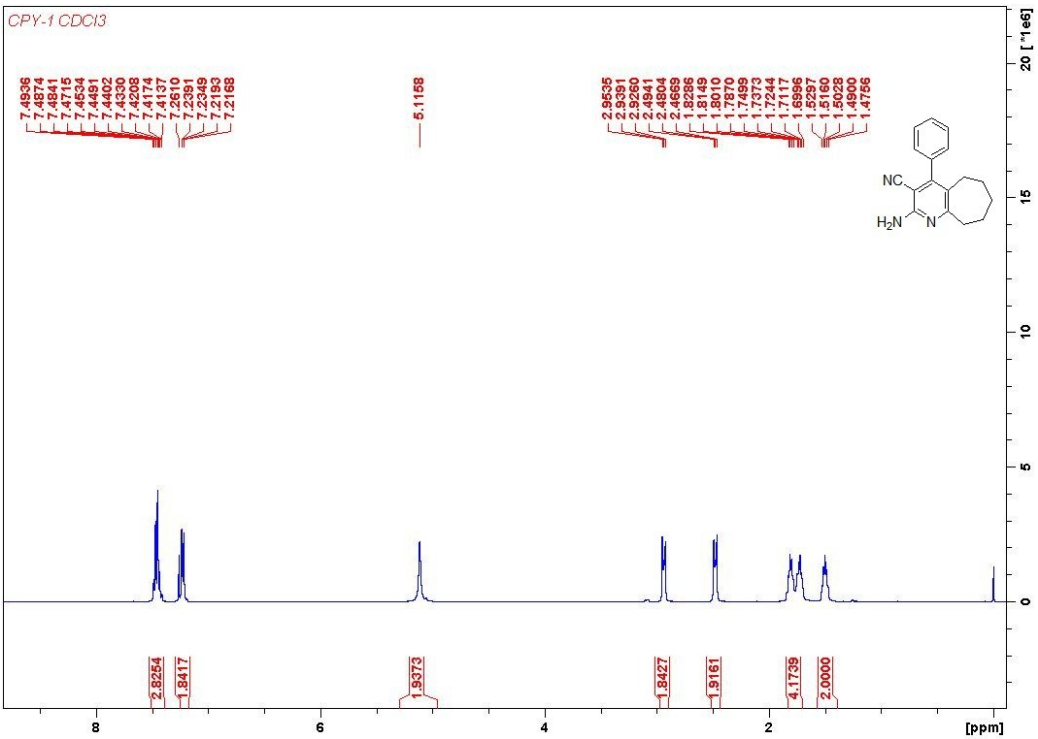
^{13}C NMR spectra of pyridine compound **3b**



^{15}N NMR (ghsqc) spectra of pyridine compound **3b**



FTIR spectra of pyridine compound **3b**



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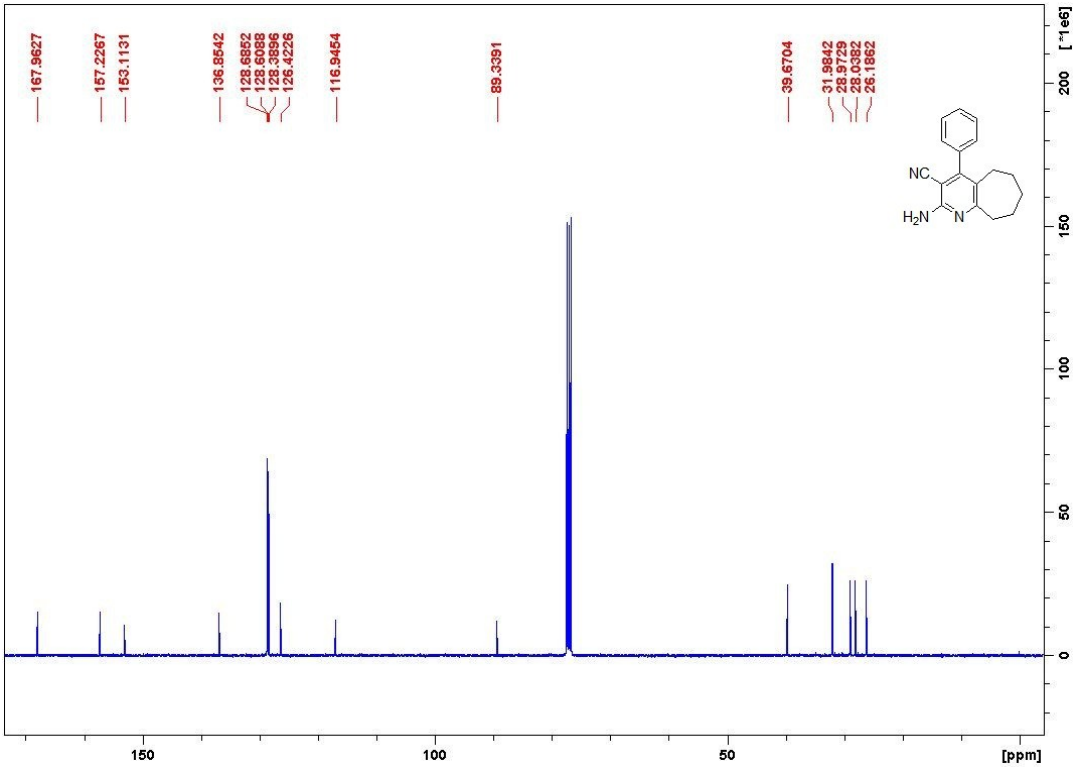
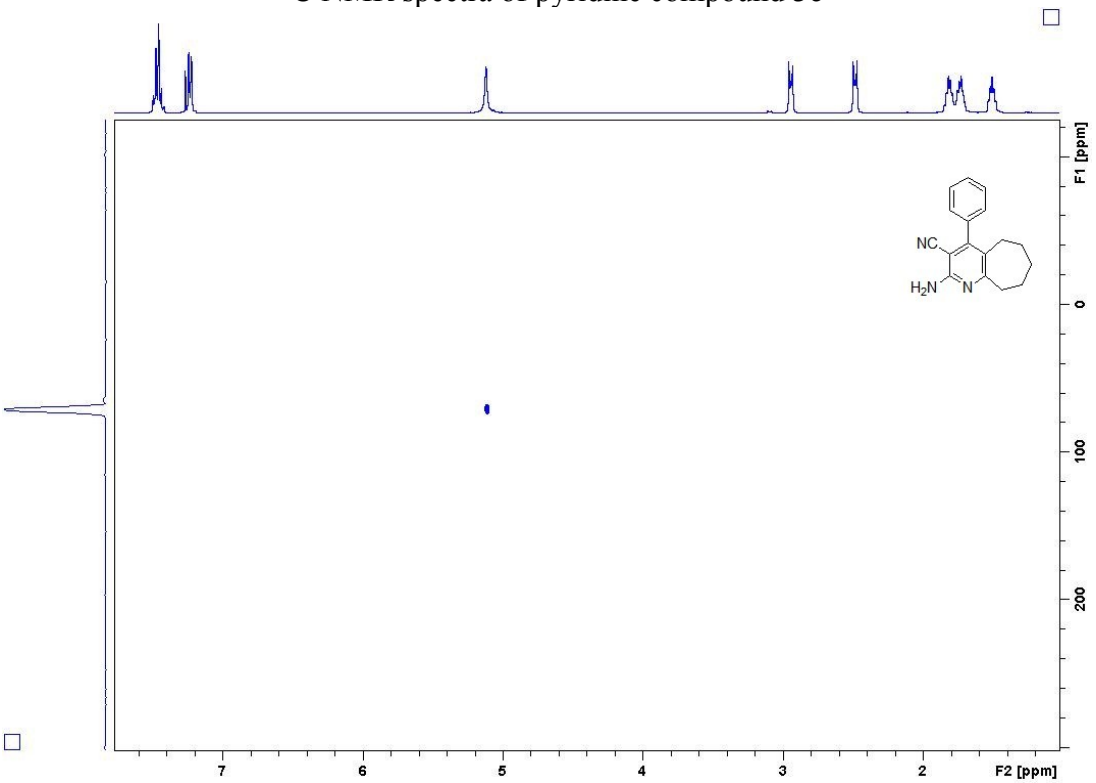
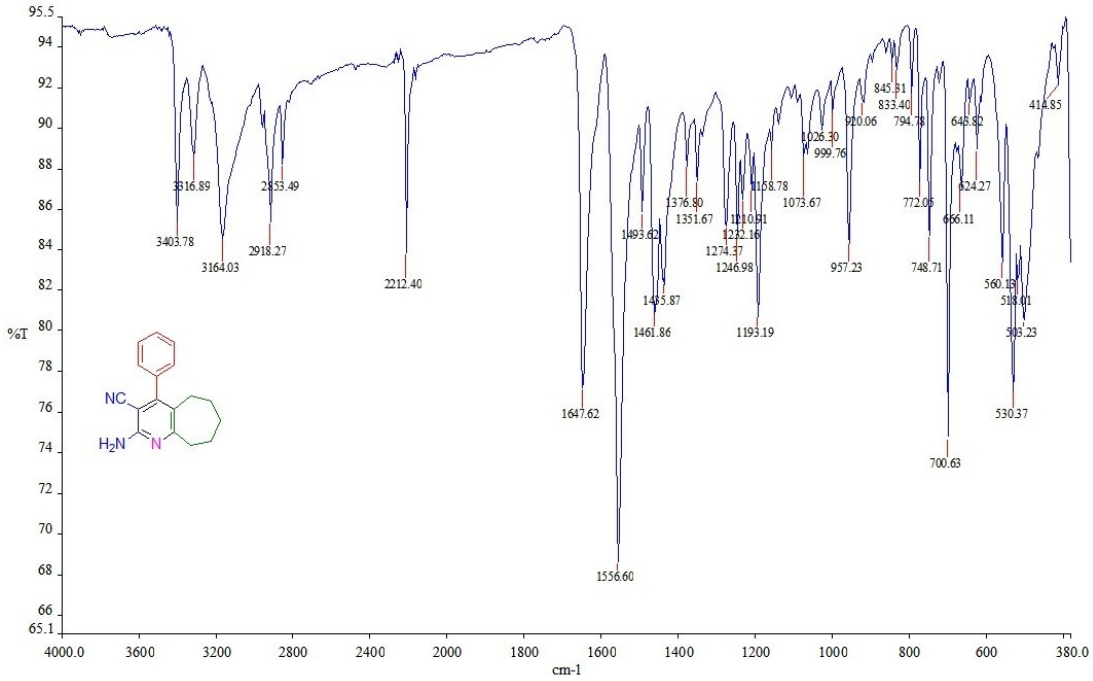


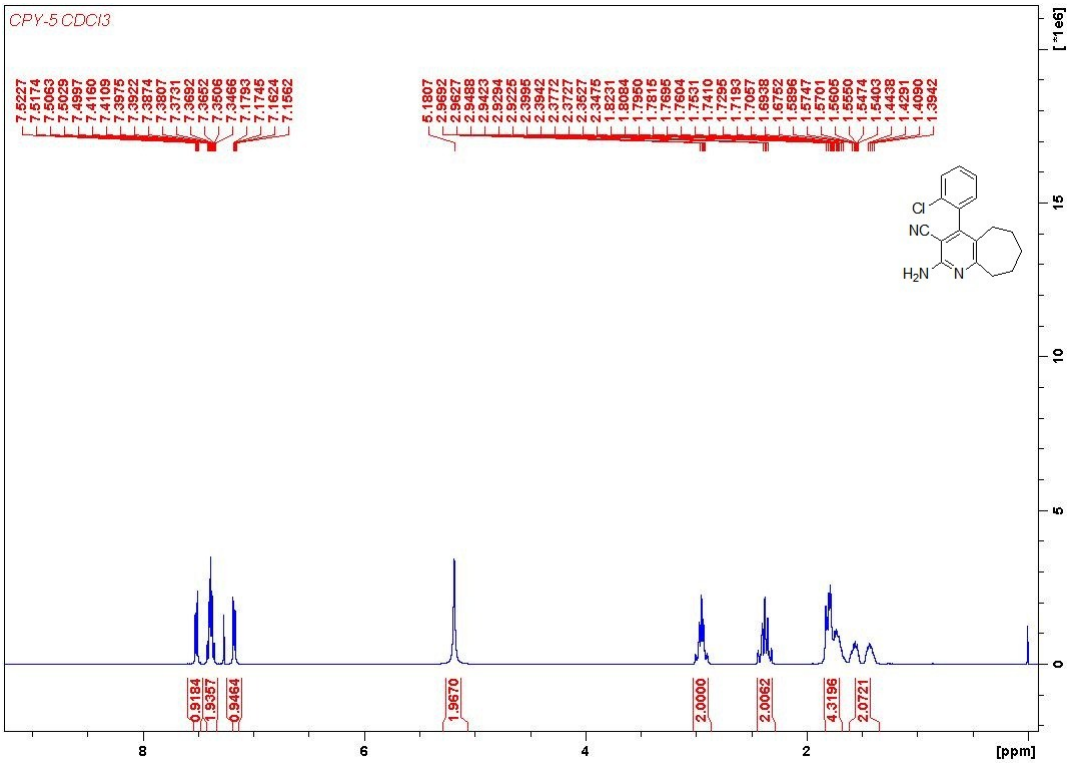
^{13}C NMR spectra of pyridine compound **3c**



^{15}N NMR (ghsqc) spectra of pyridine compound **3c**



FTIR spectra of pyridine compound **3c**



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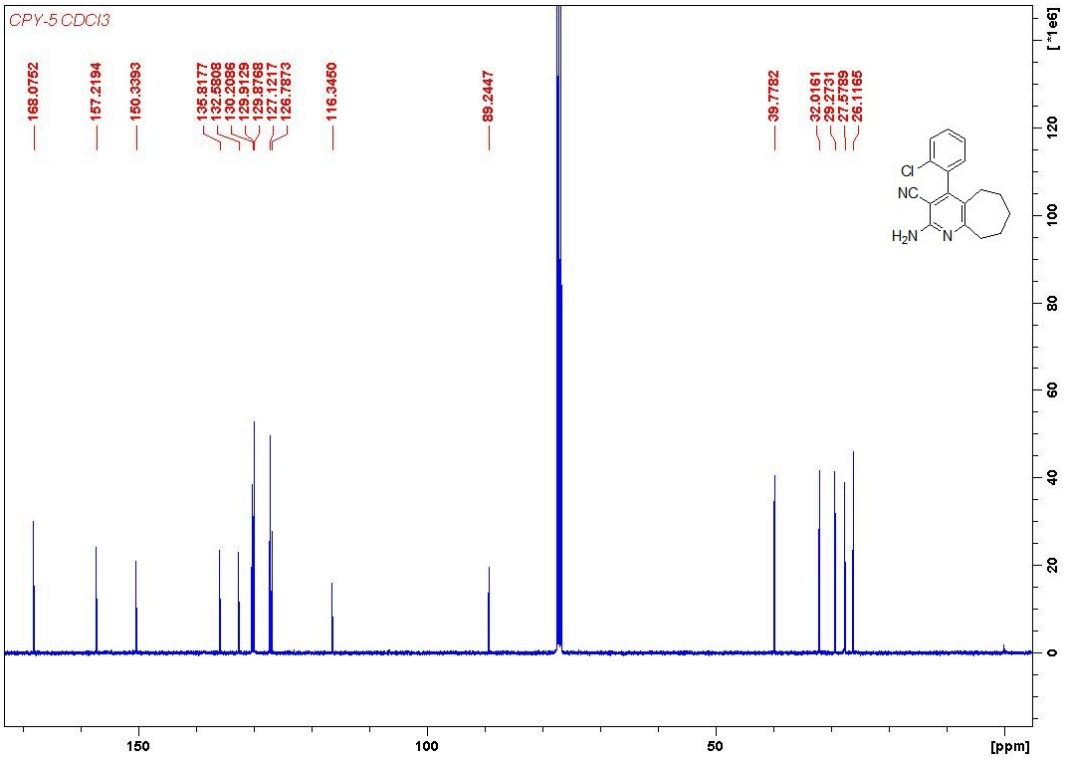
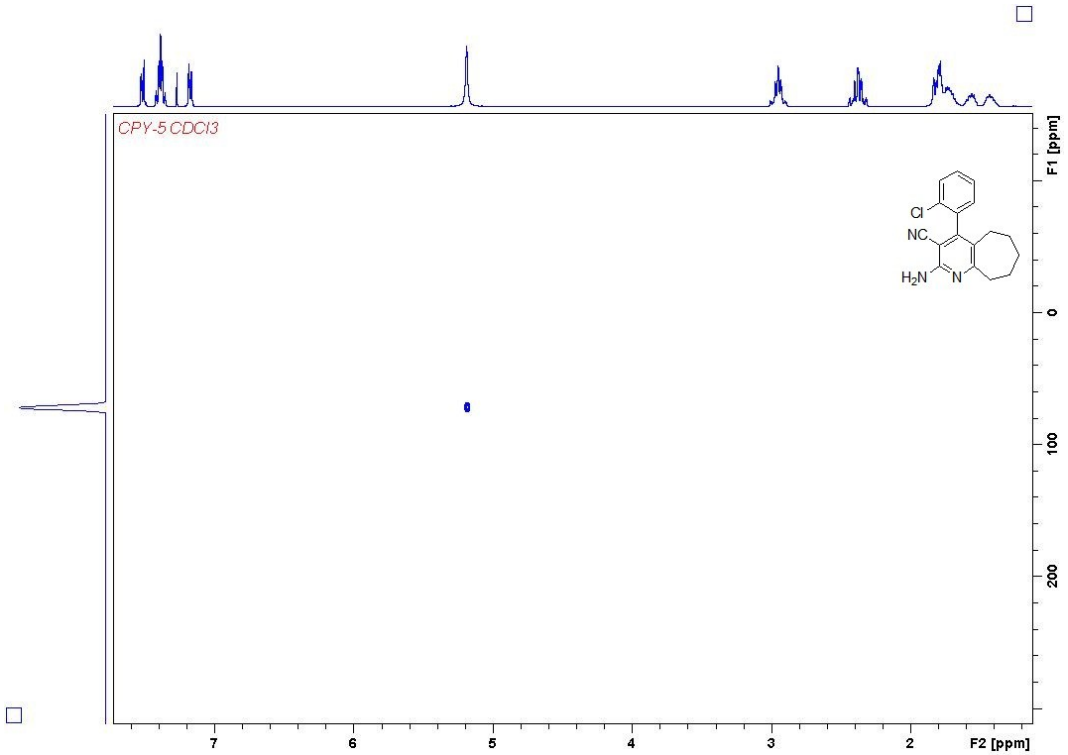
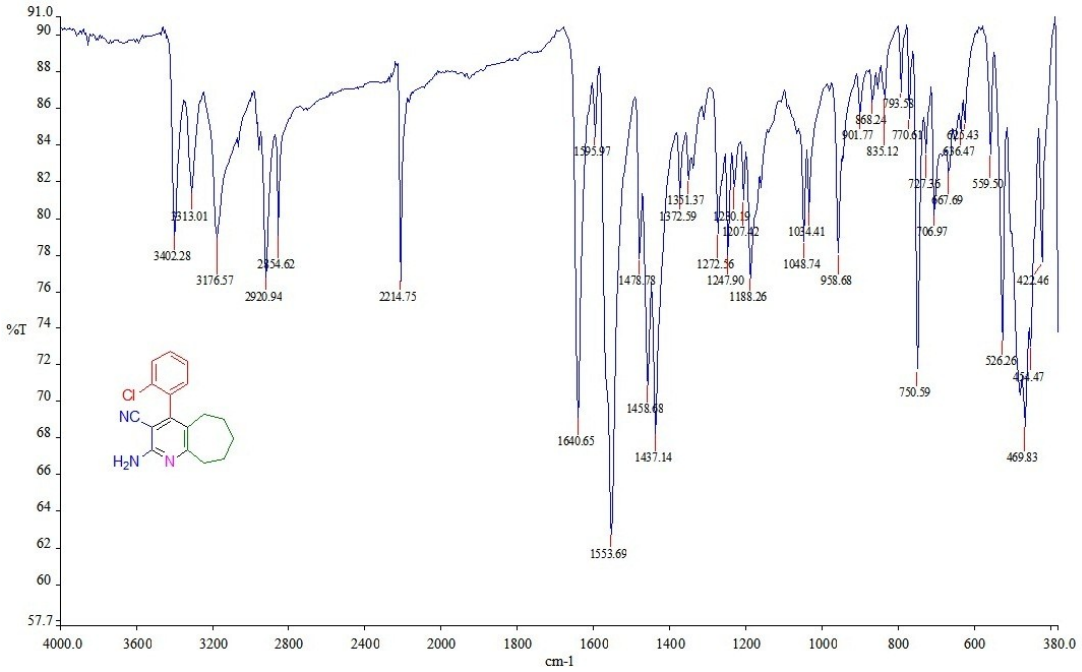


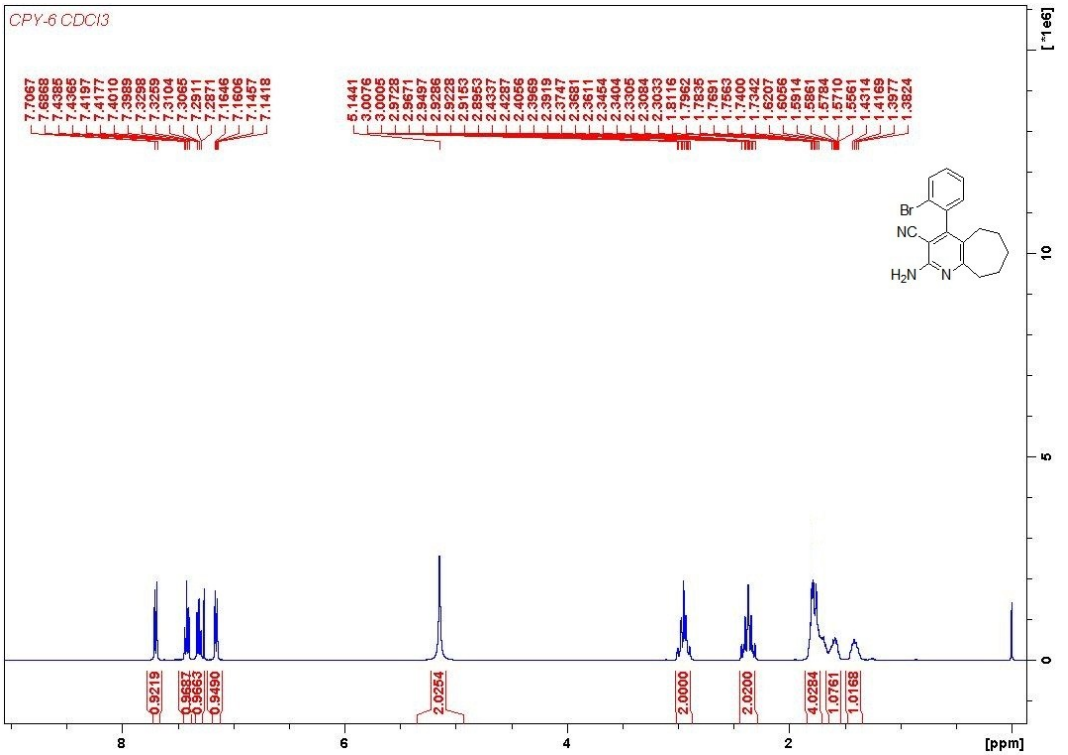
^{13}C NMR spectra of pyridine compound **3d**



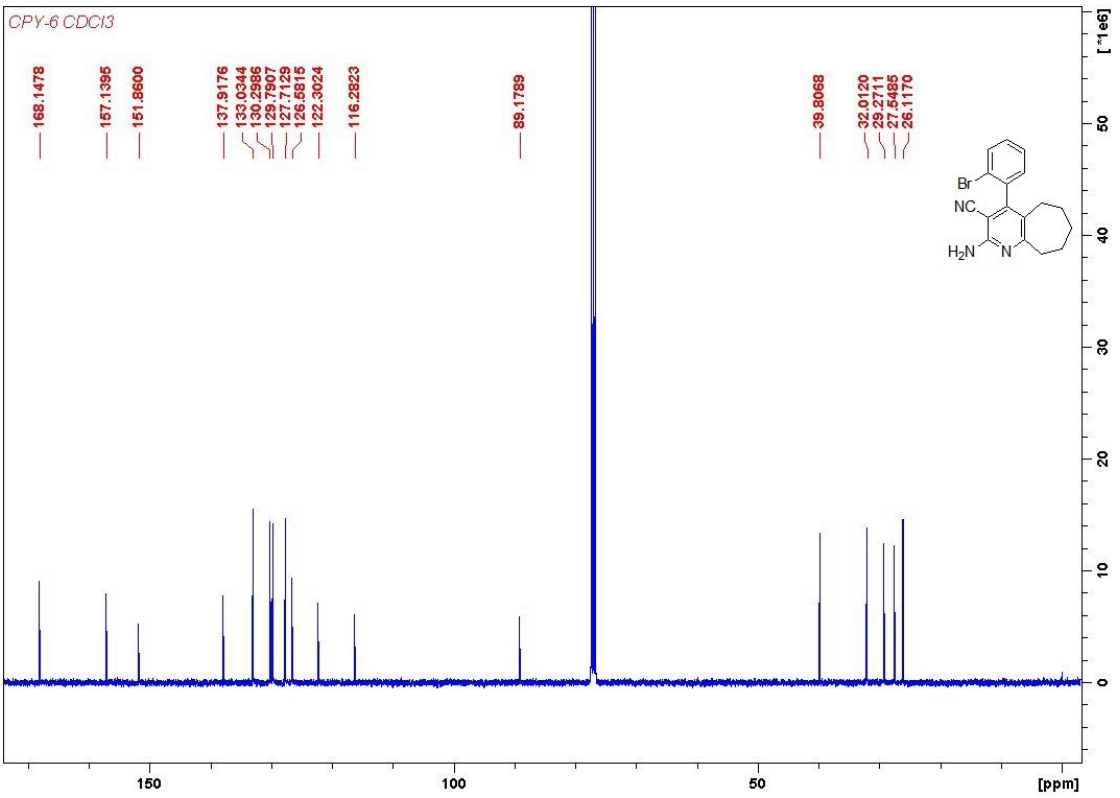
^{15}N NMR (ghsqc) spectra of pyridine compound **3d**



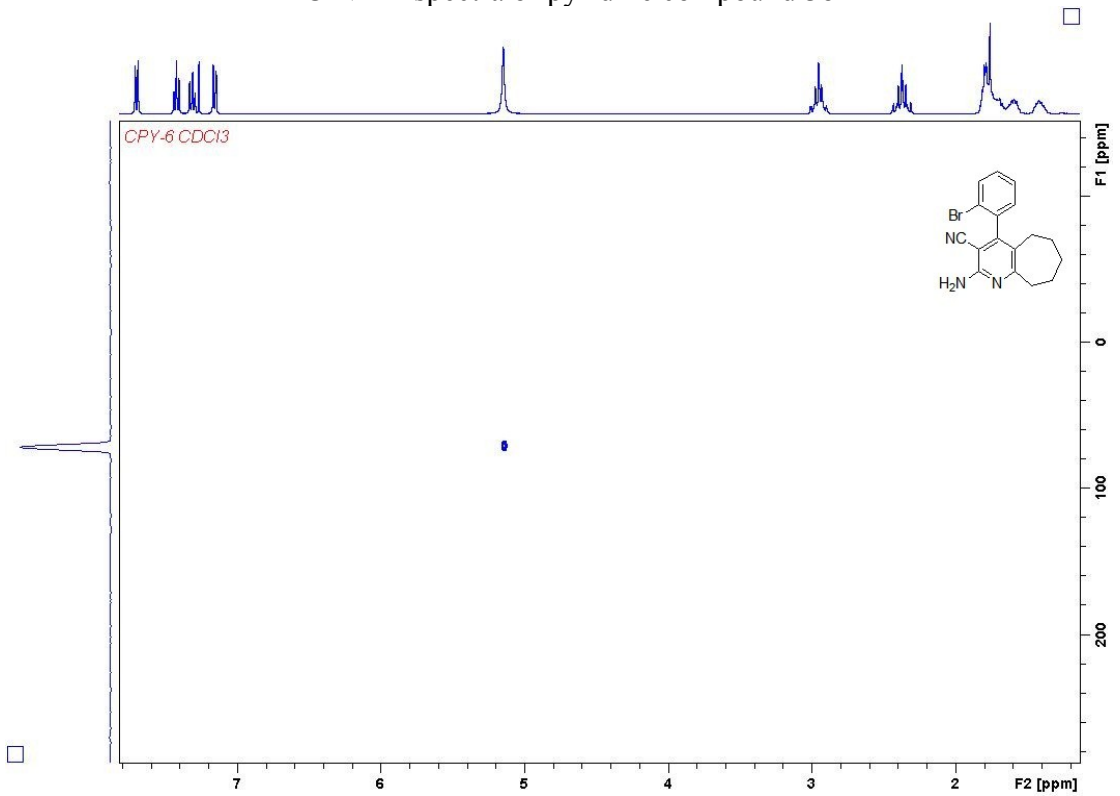
FTIR spectra of pyridine compound **3d**



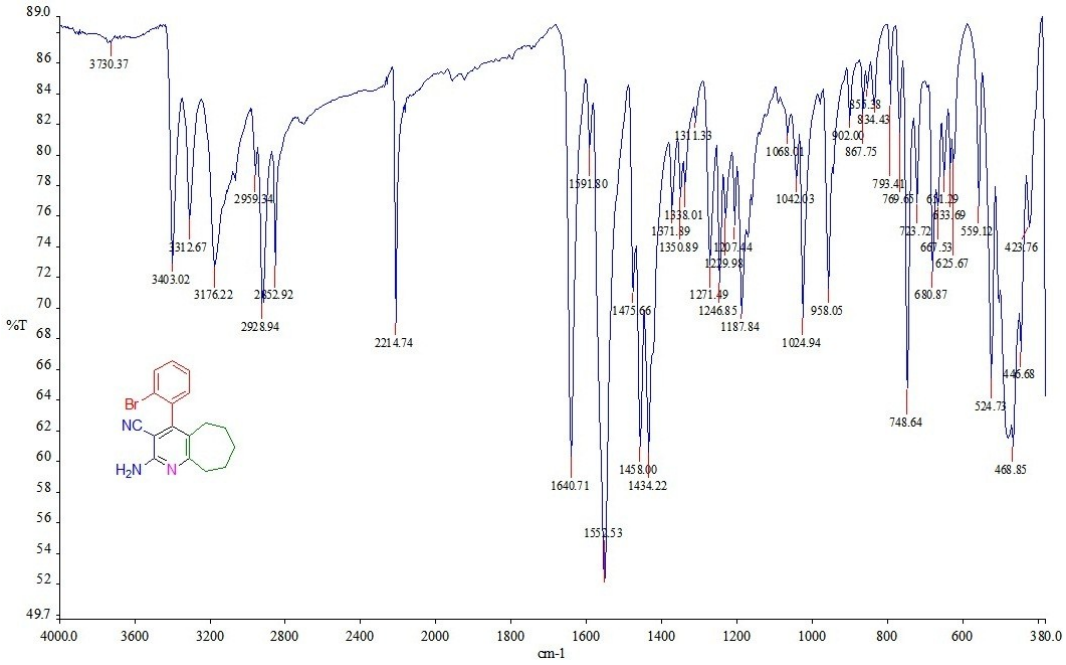
^{1}H NMR spectra of pyridine compound **3e**



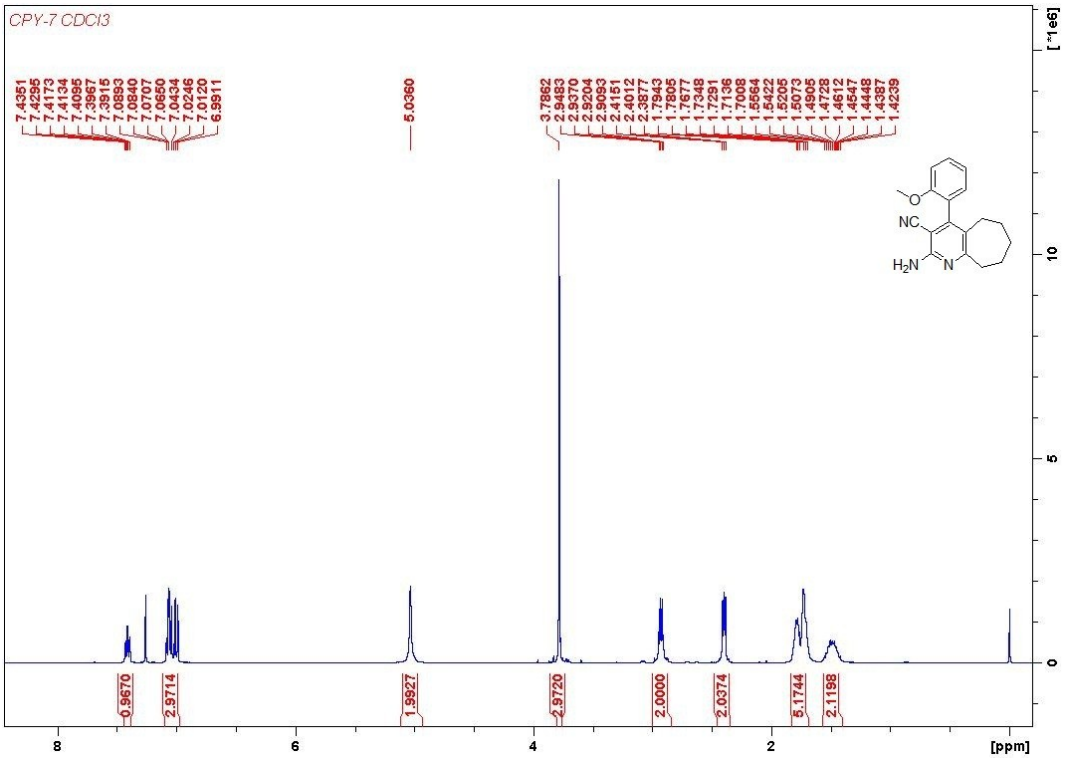
^{13}C NMR spectra of pyridine compound **3e**



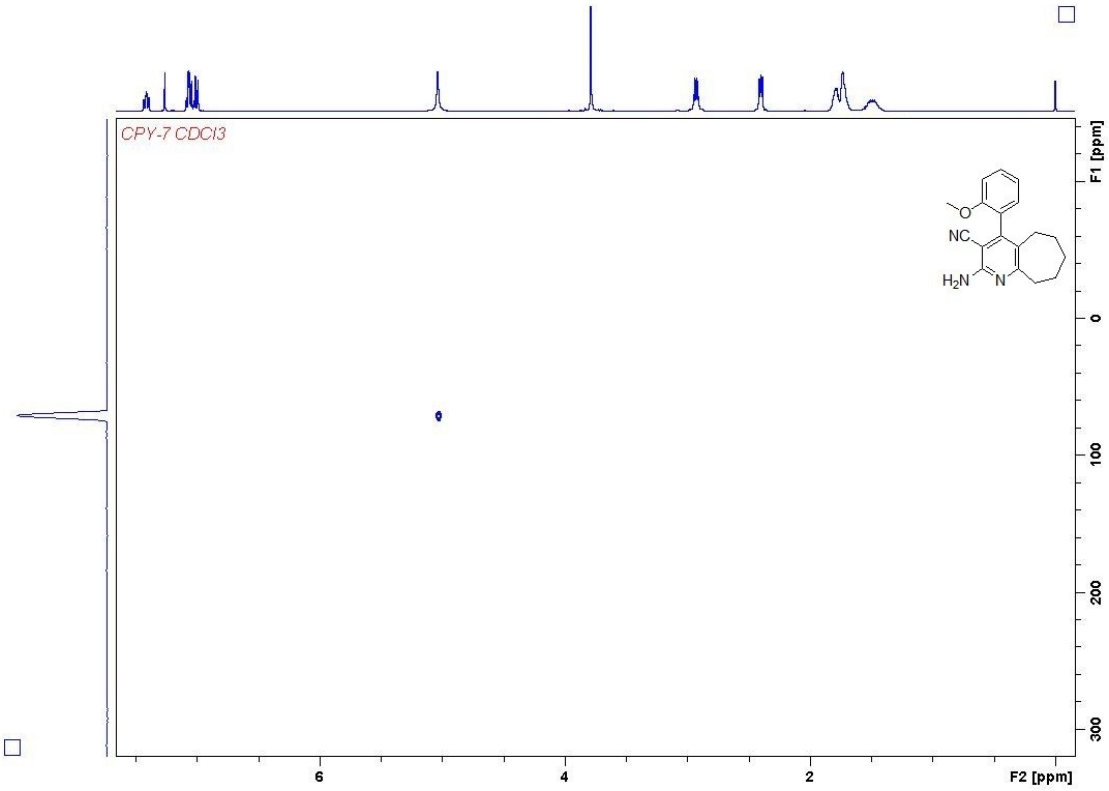
^{15}N NMR (ghsqc) spectra of pyridine compound **3e**



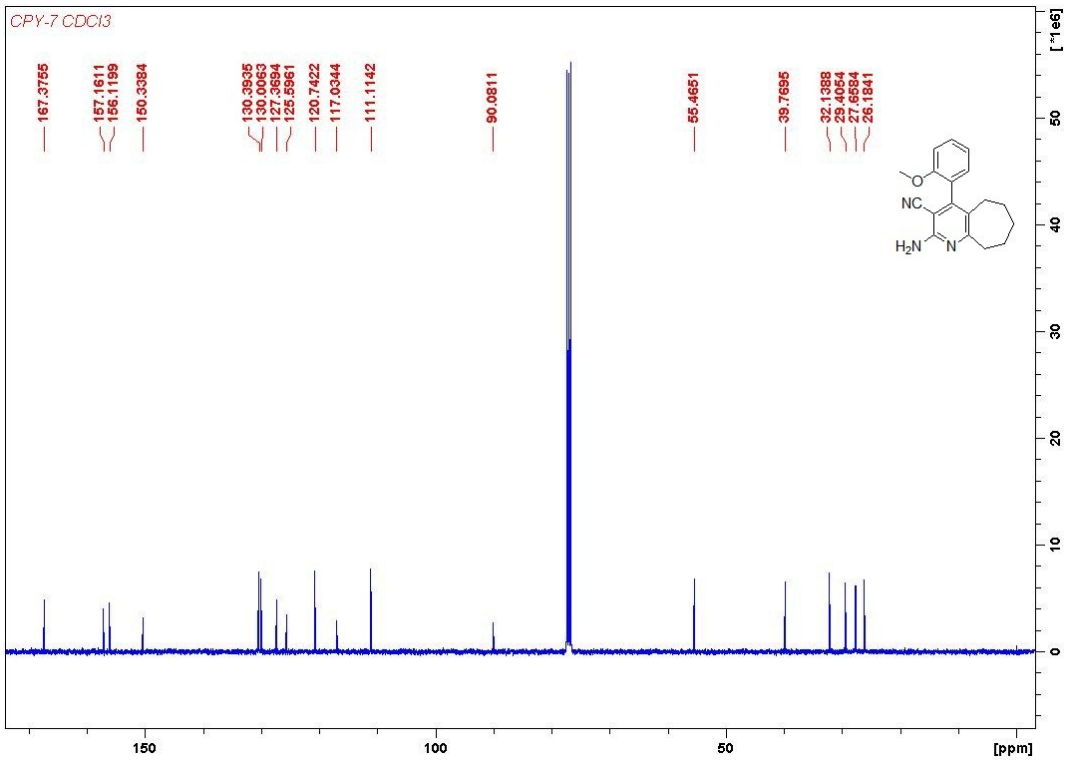
FTIR spectra of pyridine compound **3e**



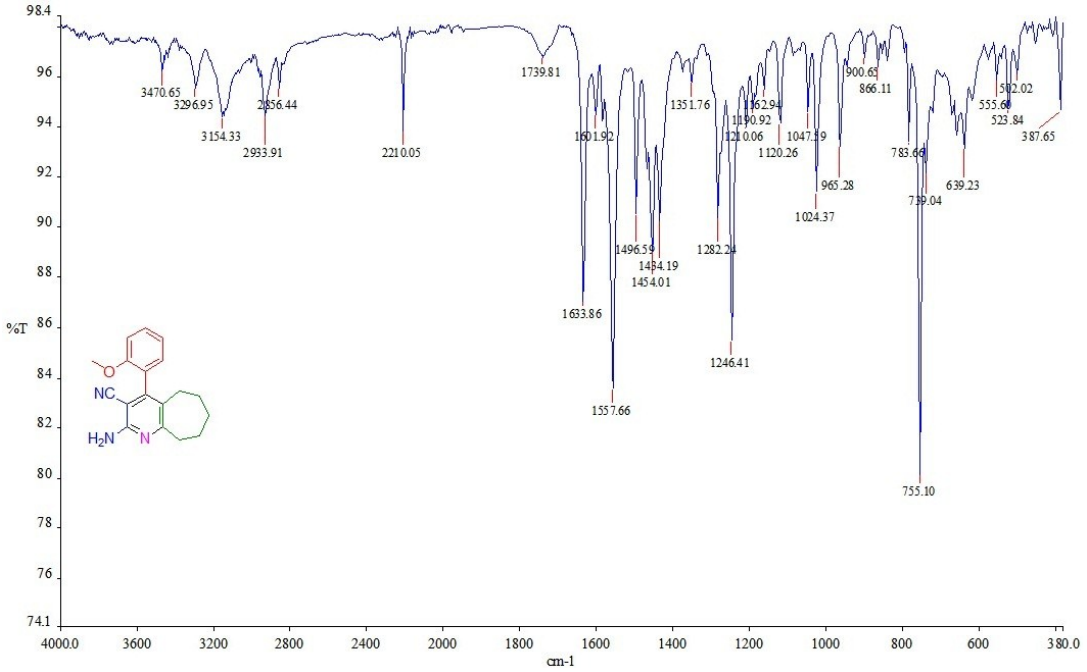
^{1}H NMR spectra of pyridine compound **3f**



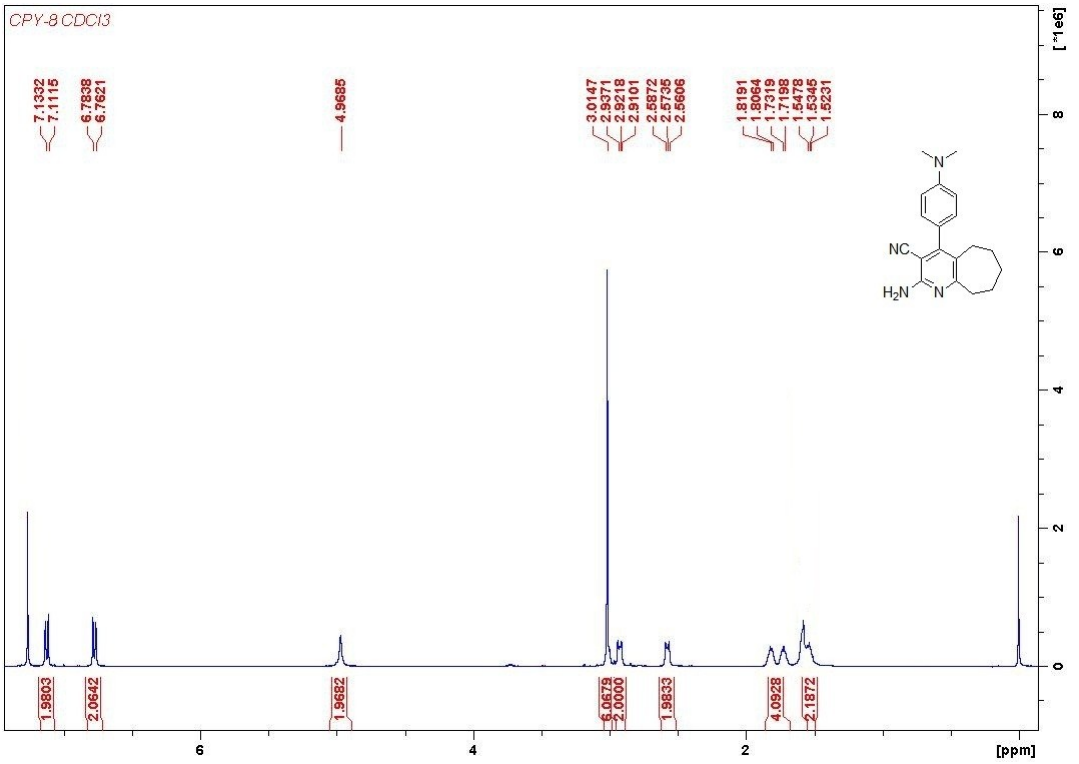
^{15}N NMR (ghsqc) spectra of pyridine compound **3f**



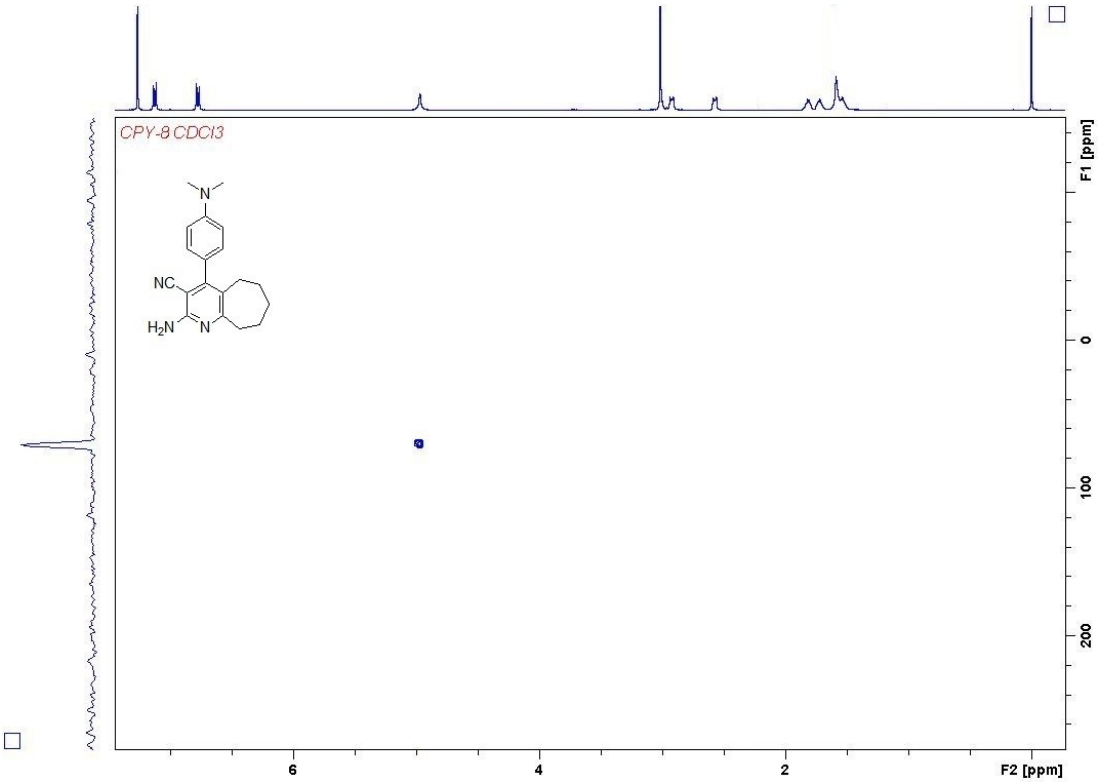
^{13}C NMR spectra of pyridine compound **3f**



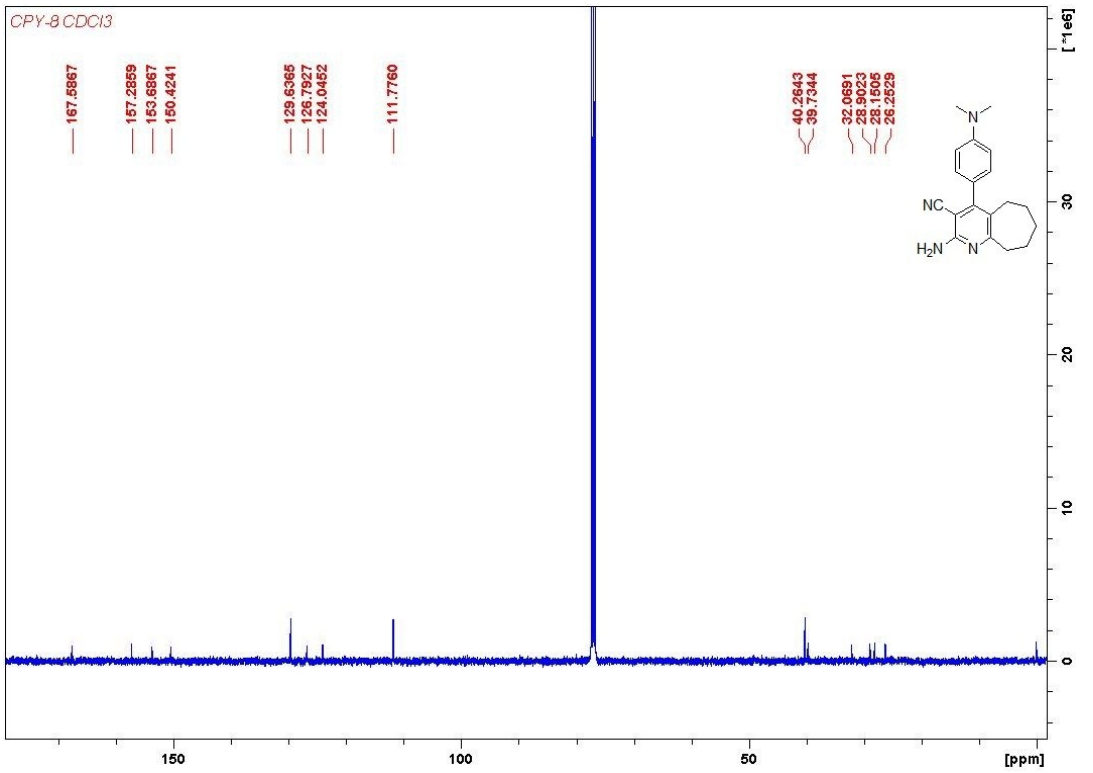
FTIR spectra of pyridine compound **3f**



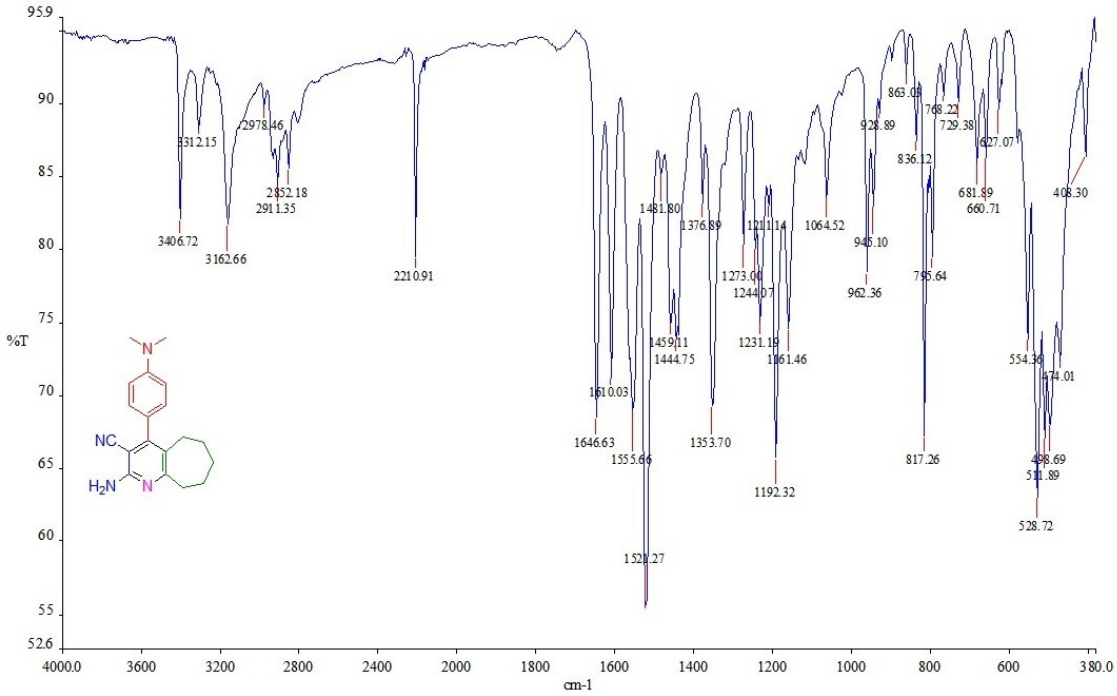
^{1}H NMR spectra of pyridine compound **3g**



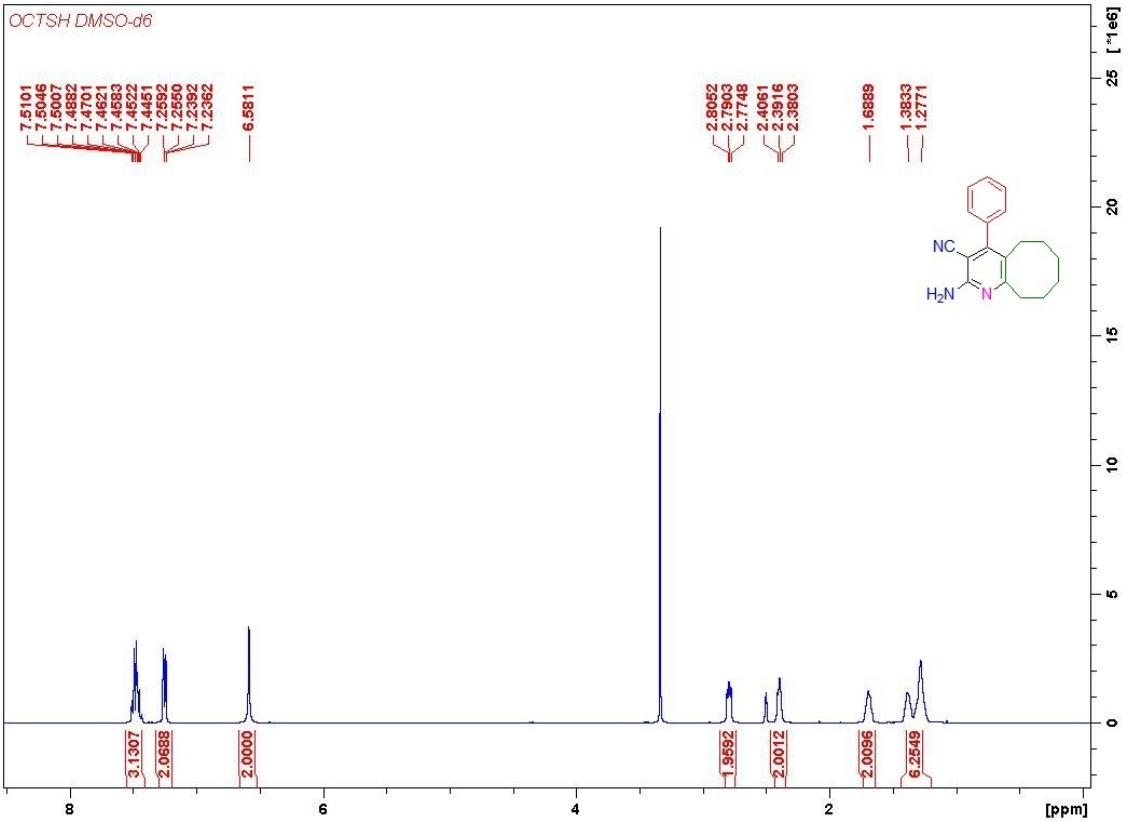
^{15}N NMR (ghsqc) spectra of pyridine compound **3g**



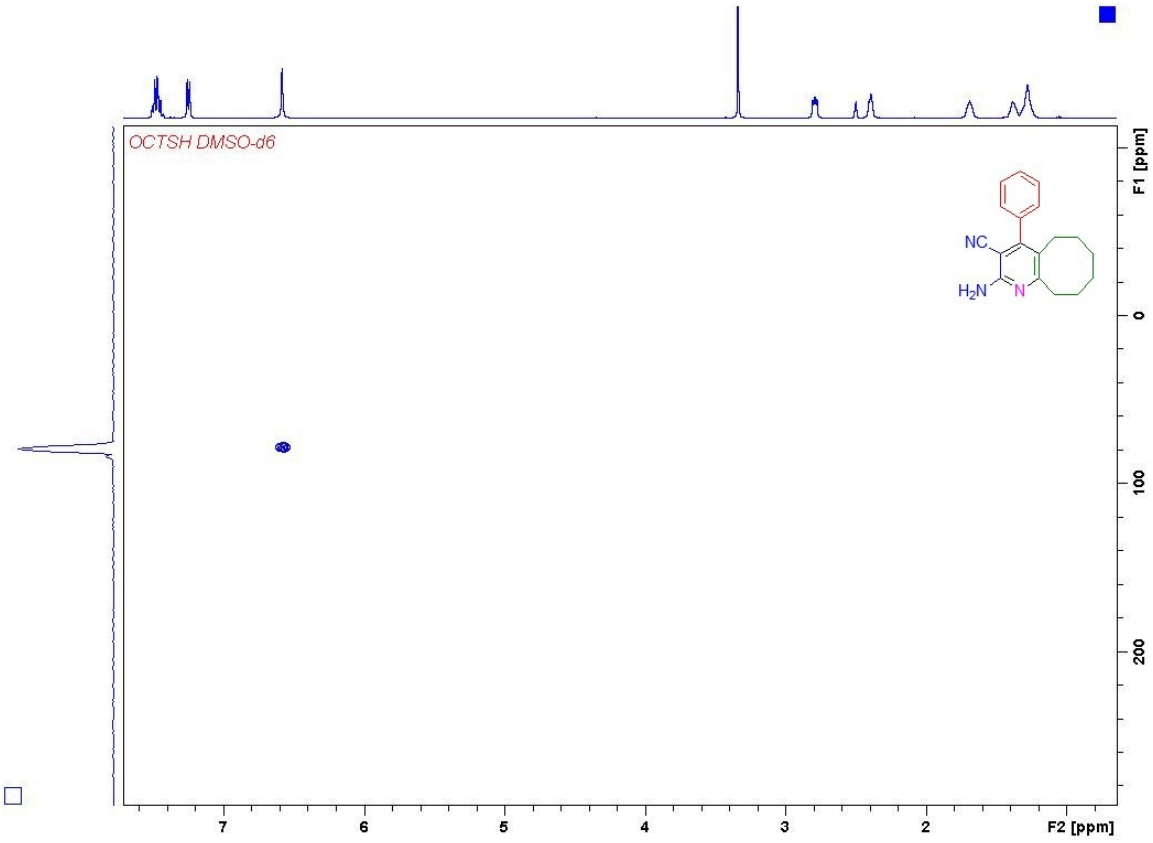
^{13}C NMR spectra of pyridine compound **3g**



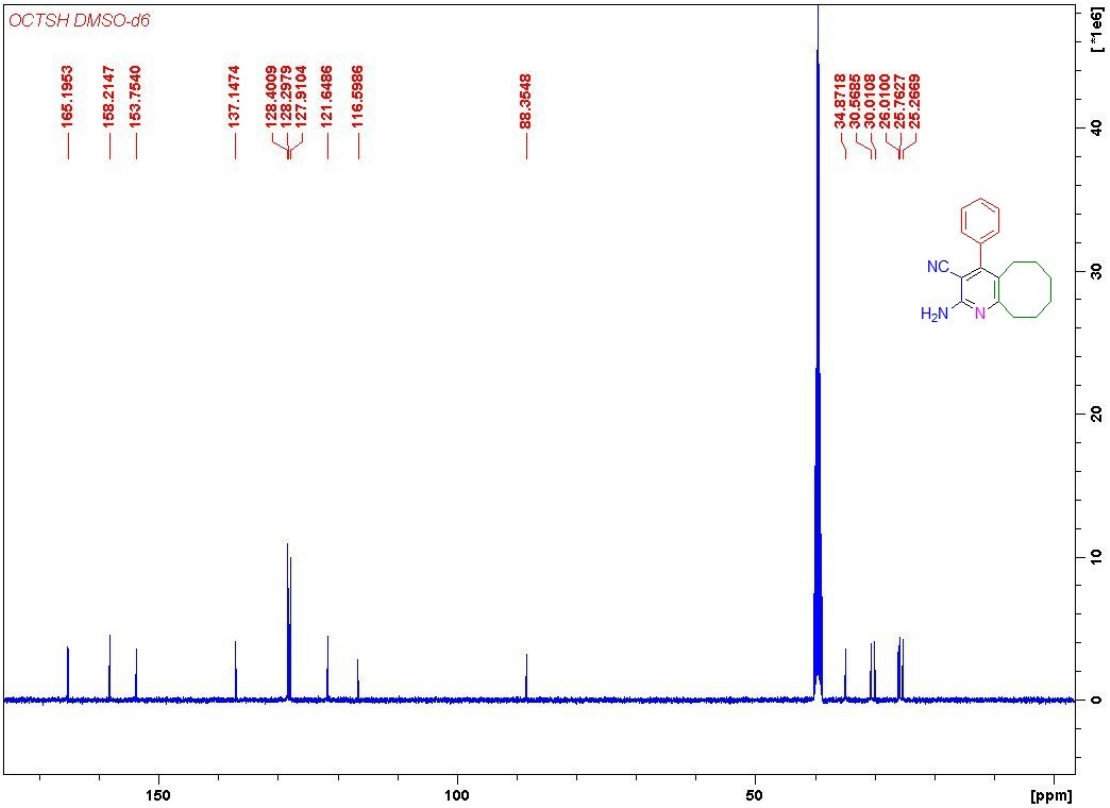
FTIR spectra of pyridine compound **3g**



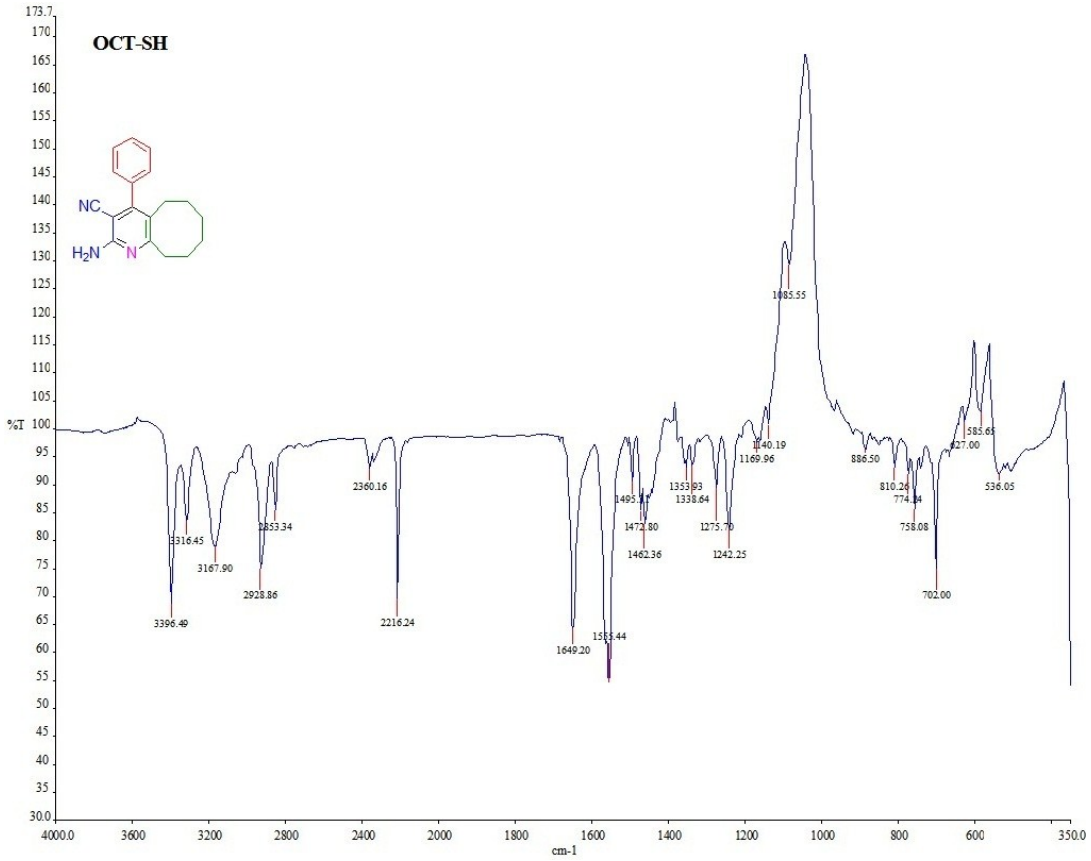
[1]H NMR spectra of pyridine compound **3h**



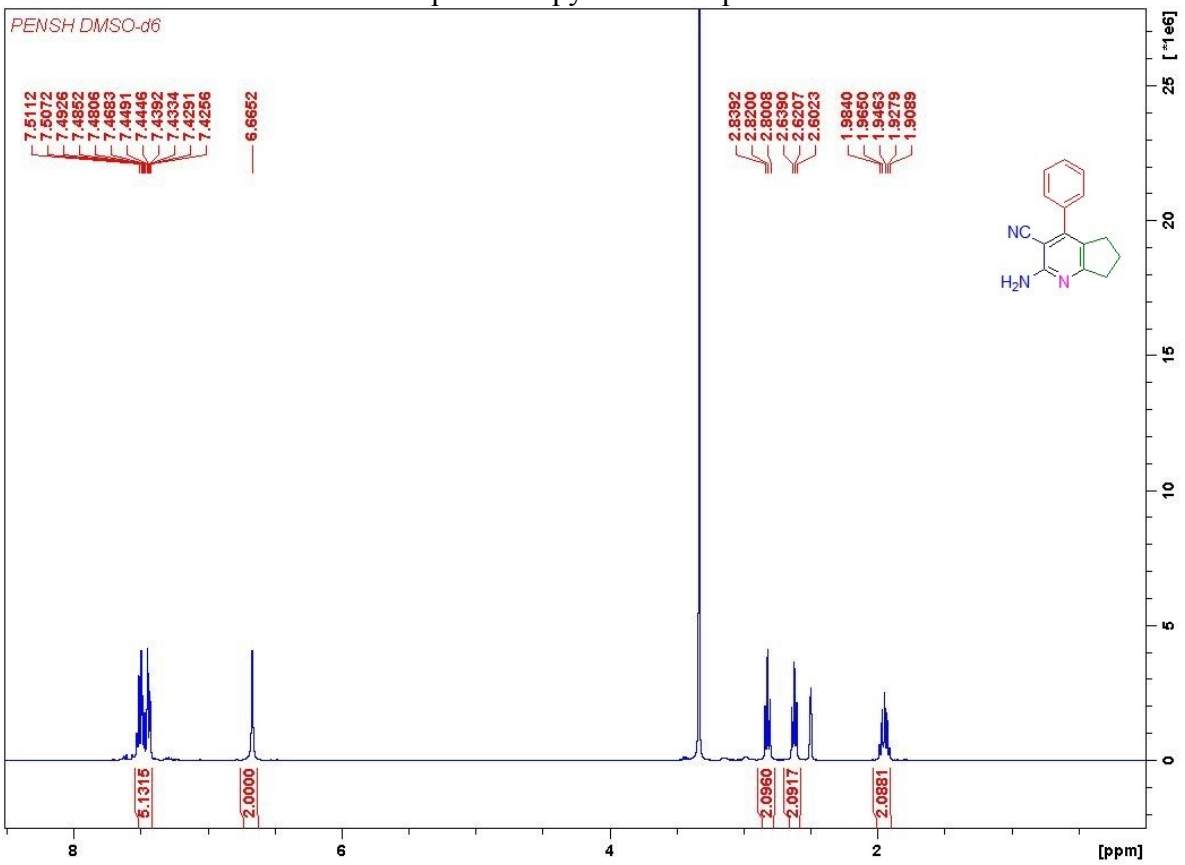
^{15}N NMR (ghsqc) spectra of pyridine compound **3h**



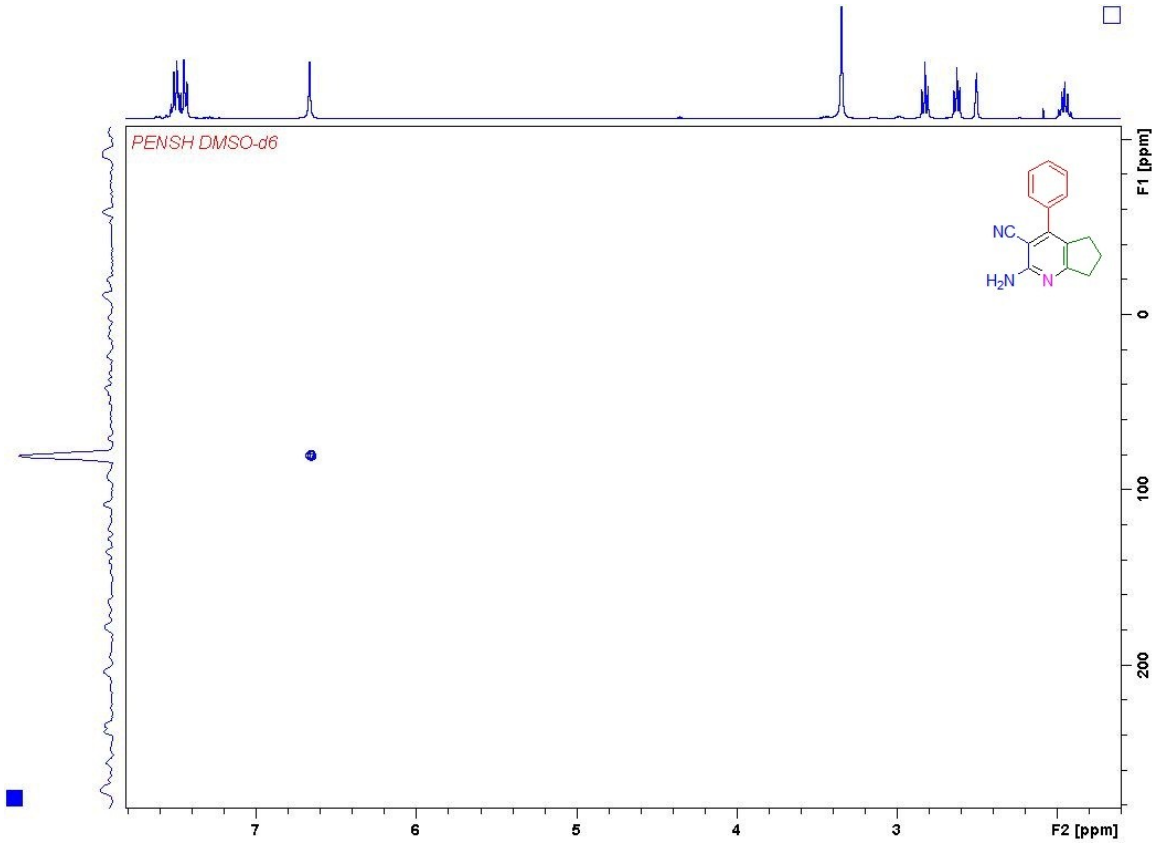
^{13}C NMR spectra of pyridine compound **3h**



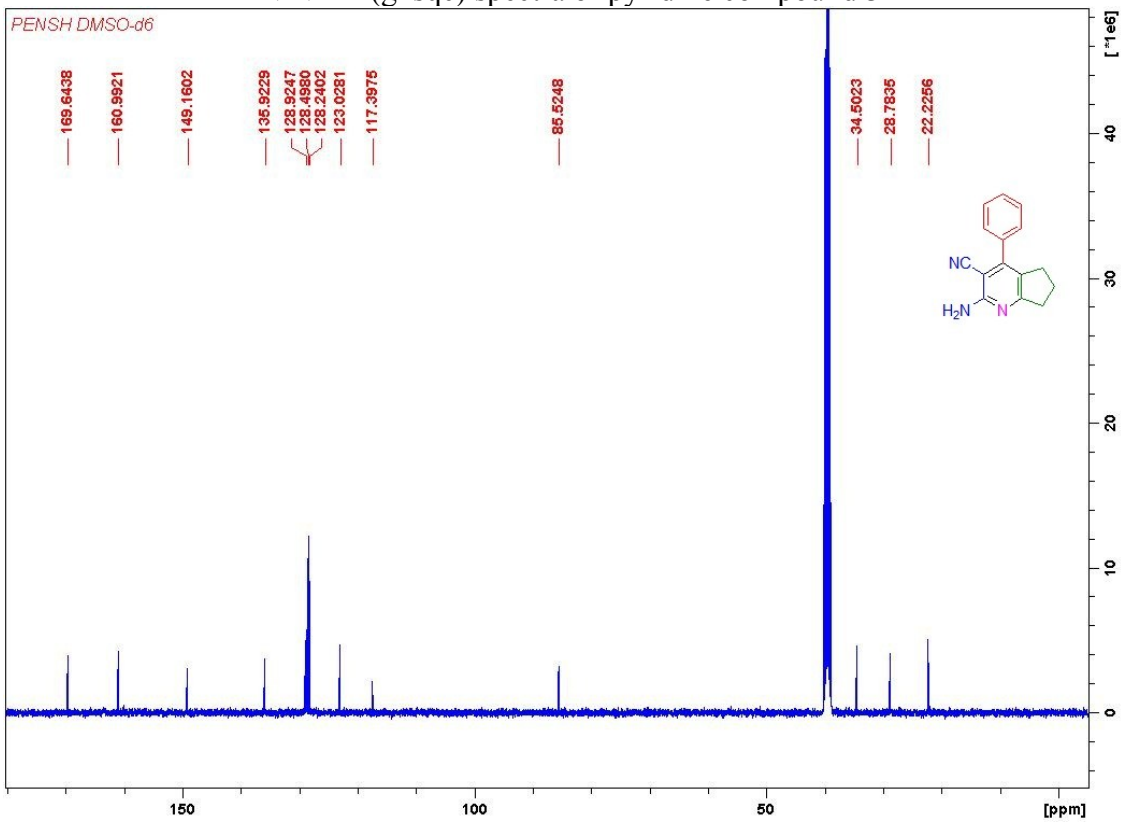
FTIR spectra of pyridine compound **3h**



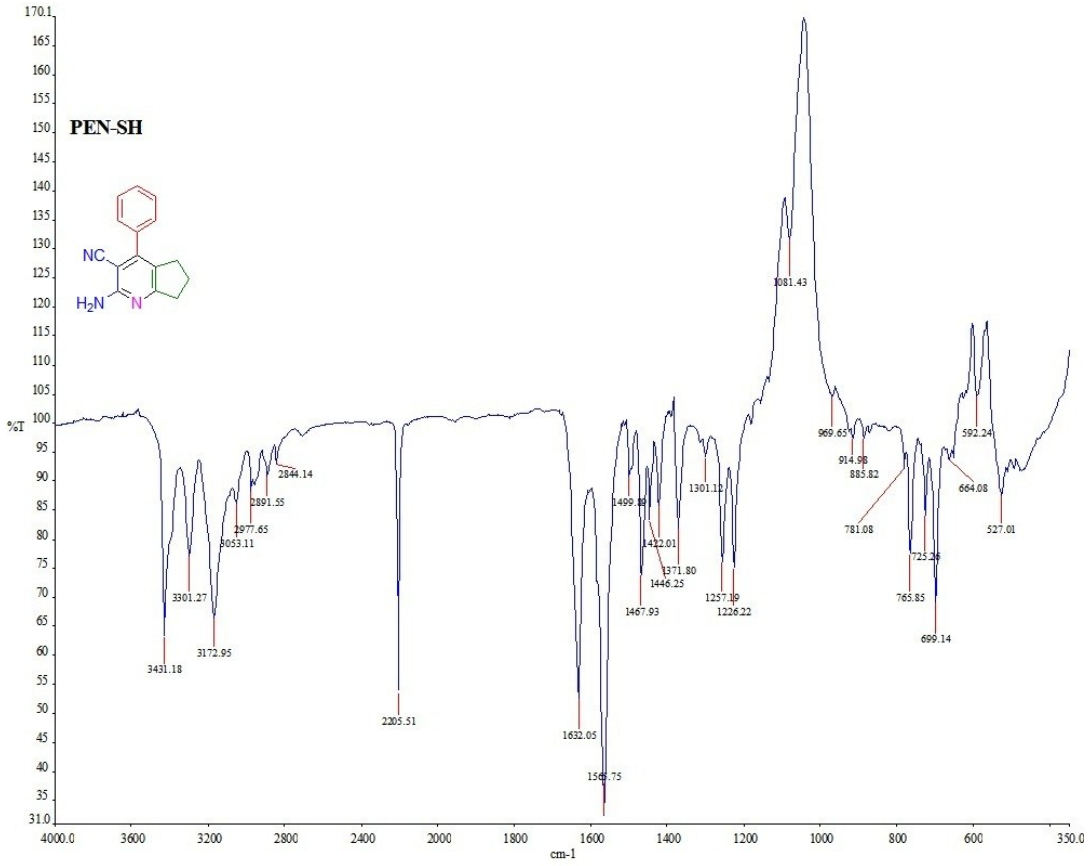
^{1}H NMR spectra of pyridine compound **3i**



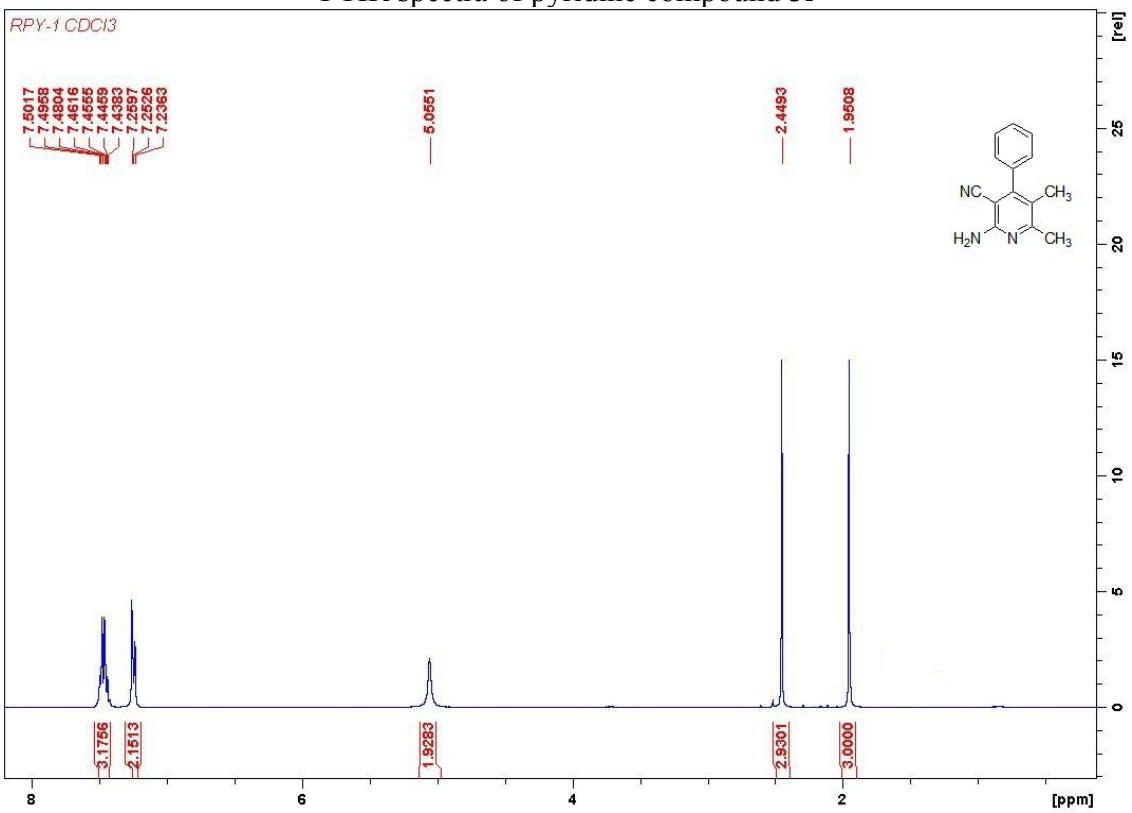
^{15}N NMR (ghsqc) spectra of pyridine compound **3i**



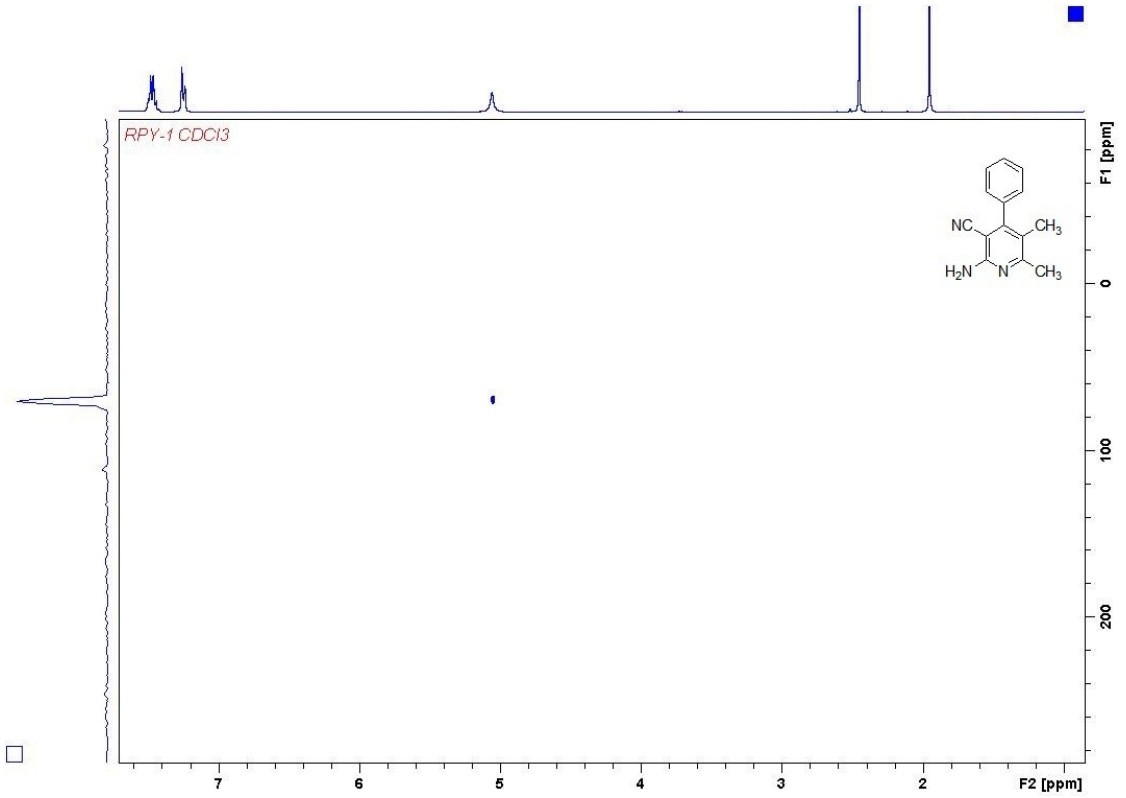
^{13}C NMR spectra of pyridine compound **3i**



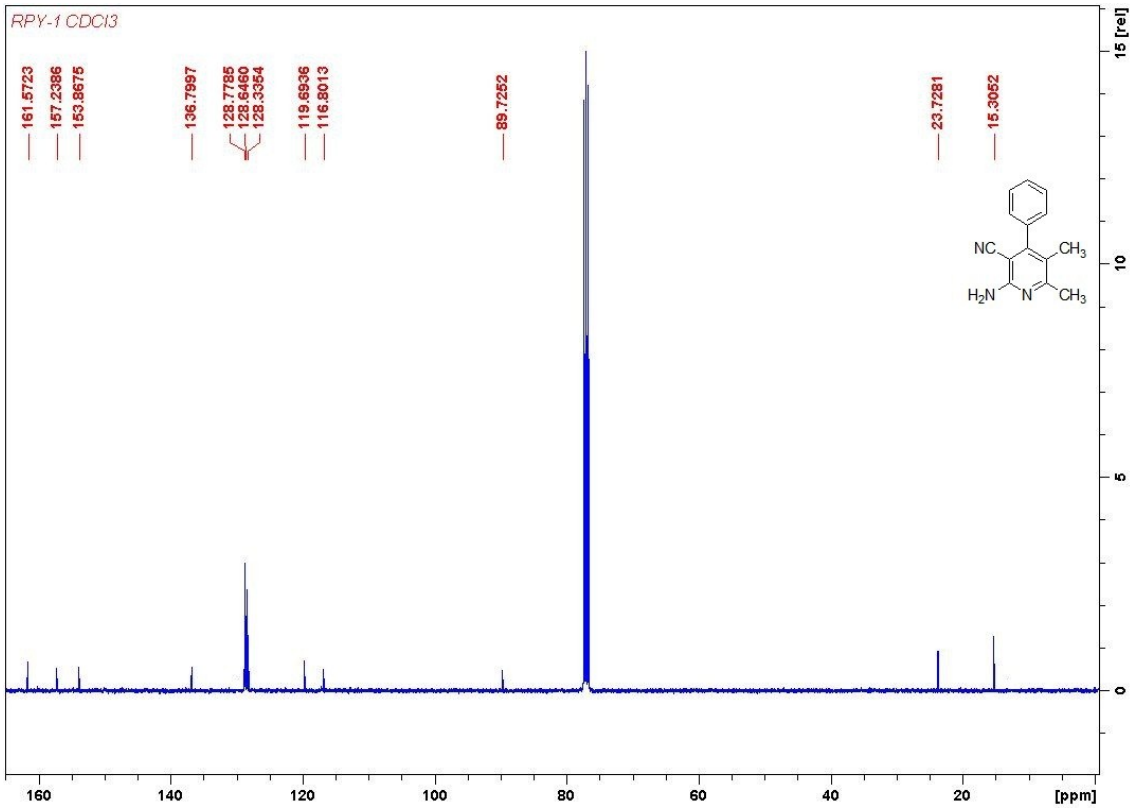
FTIR spectra of pyridine compound **3i**



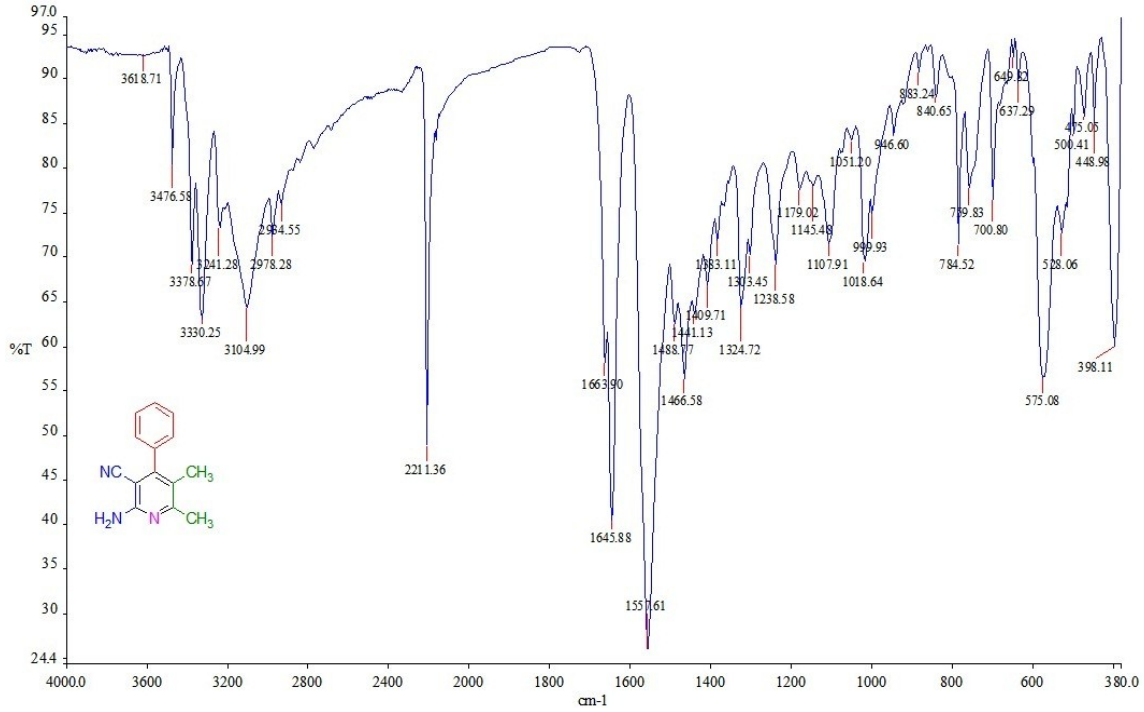
^{1}H NMR spectra of pyridine compound **4a**



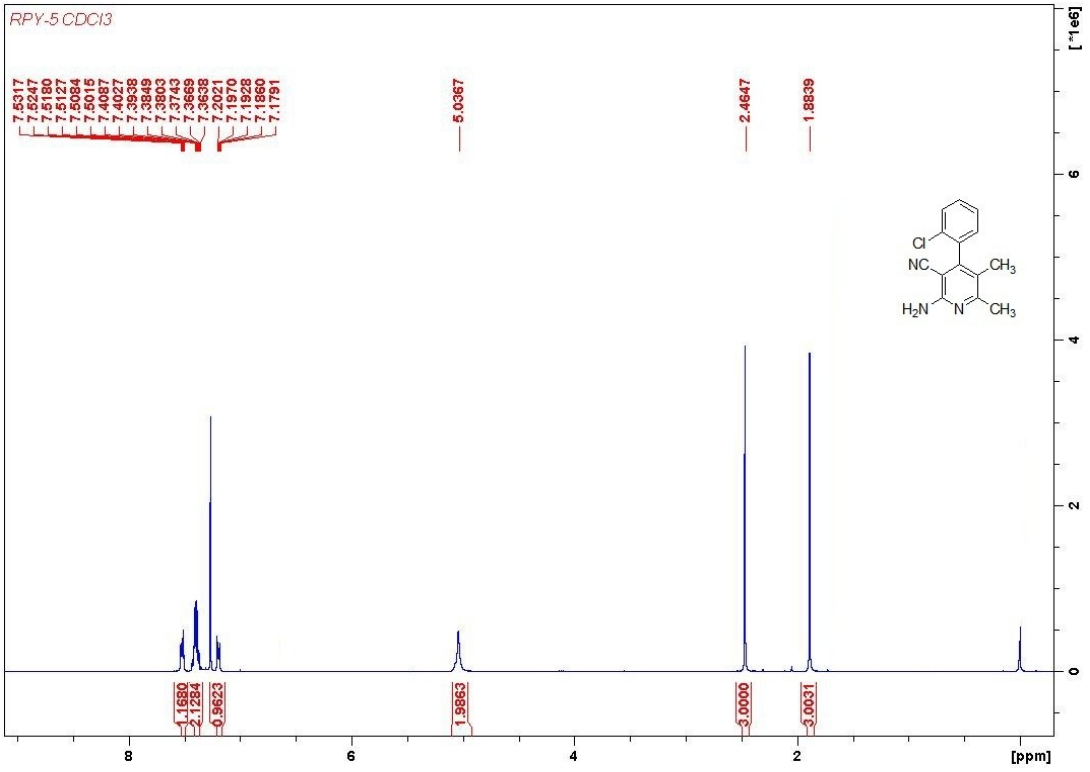
^{15}N NMR (ghsqc) spectra of pyridine compound **4a**



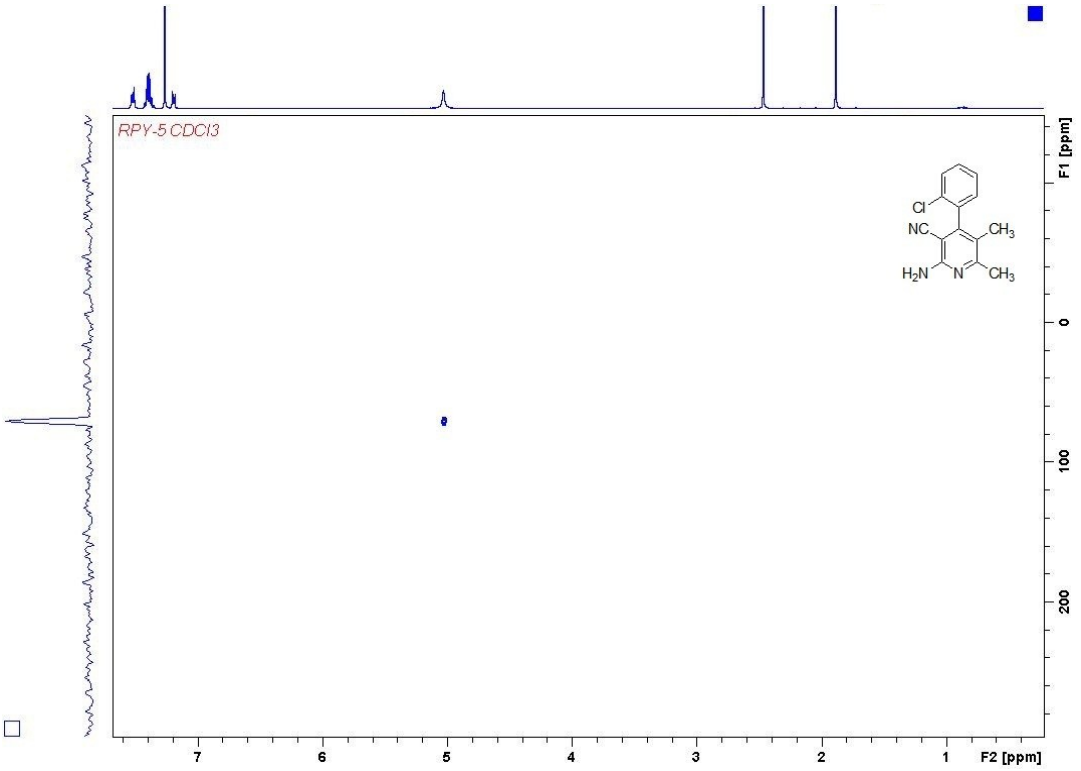
^{13}C NMR spectra of pyridine compound **4a**



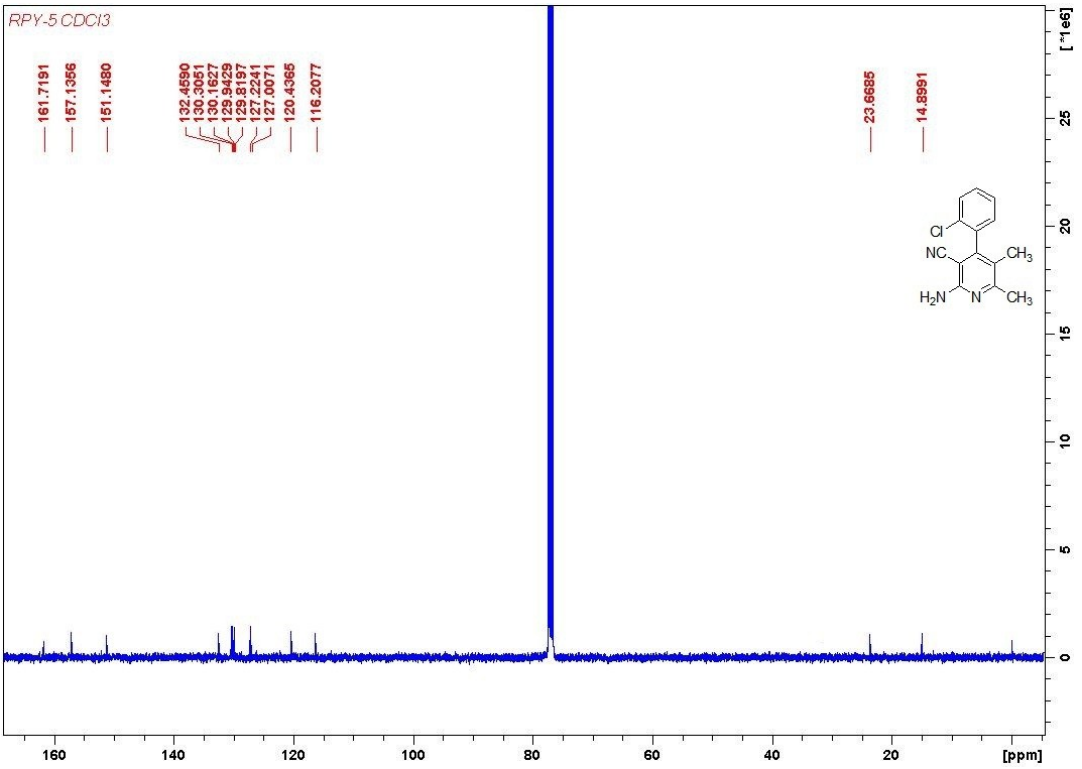
FTIR spectra of pyridine compound **4a**



^{1}H NMR spectra of pyridine compound **4b**



^{15}N NMR (ghsqc) spectra of pyridine compound **4b**



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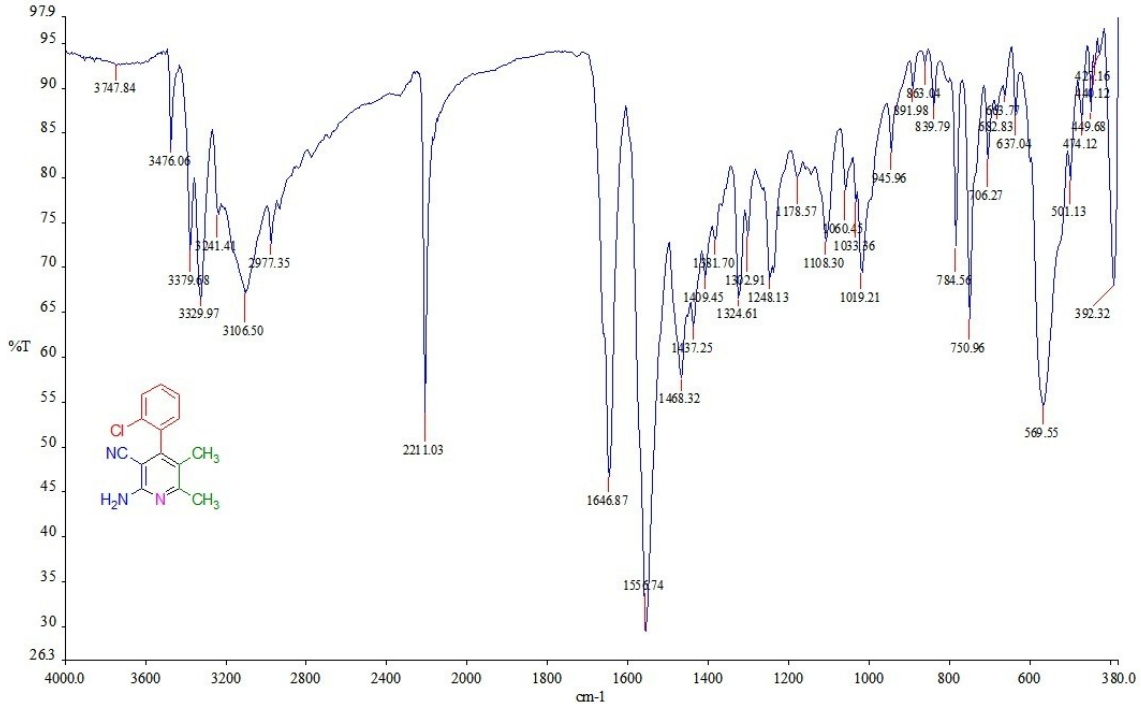
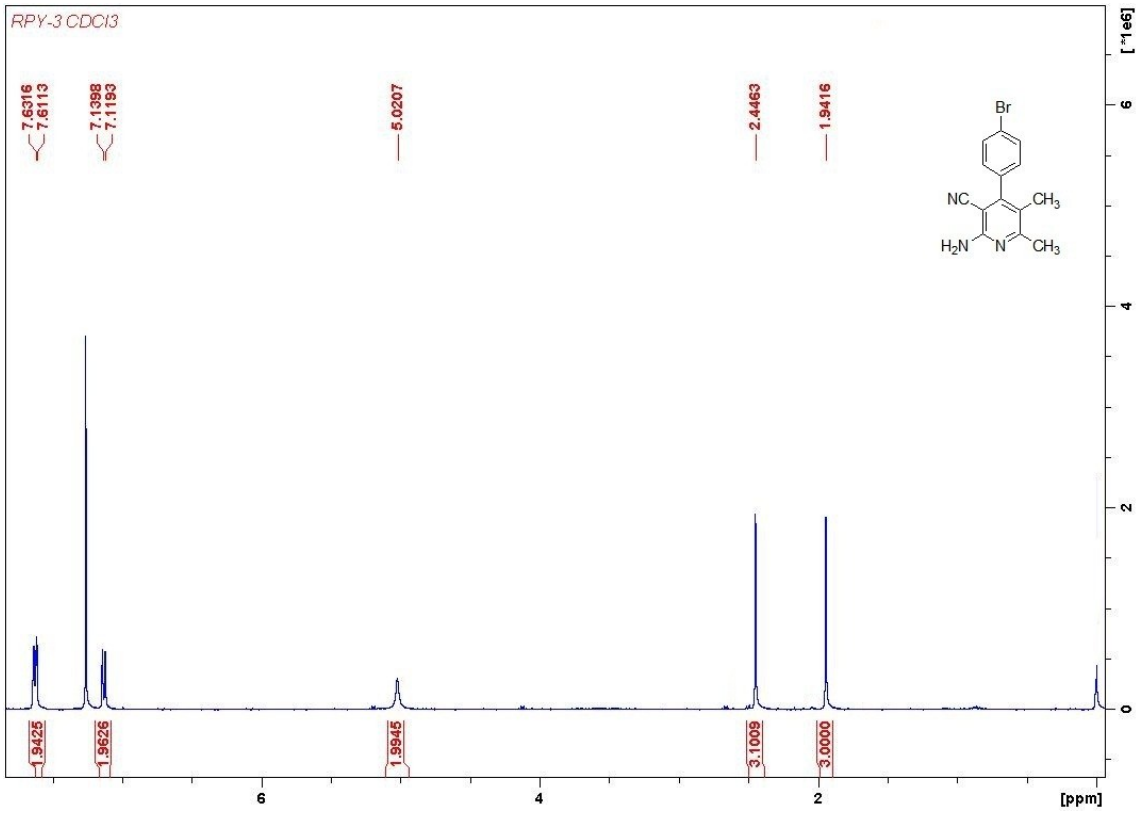
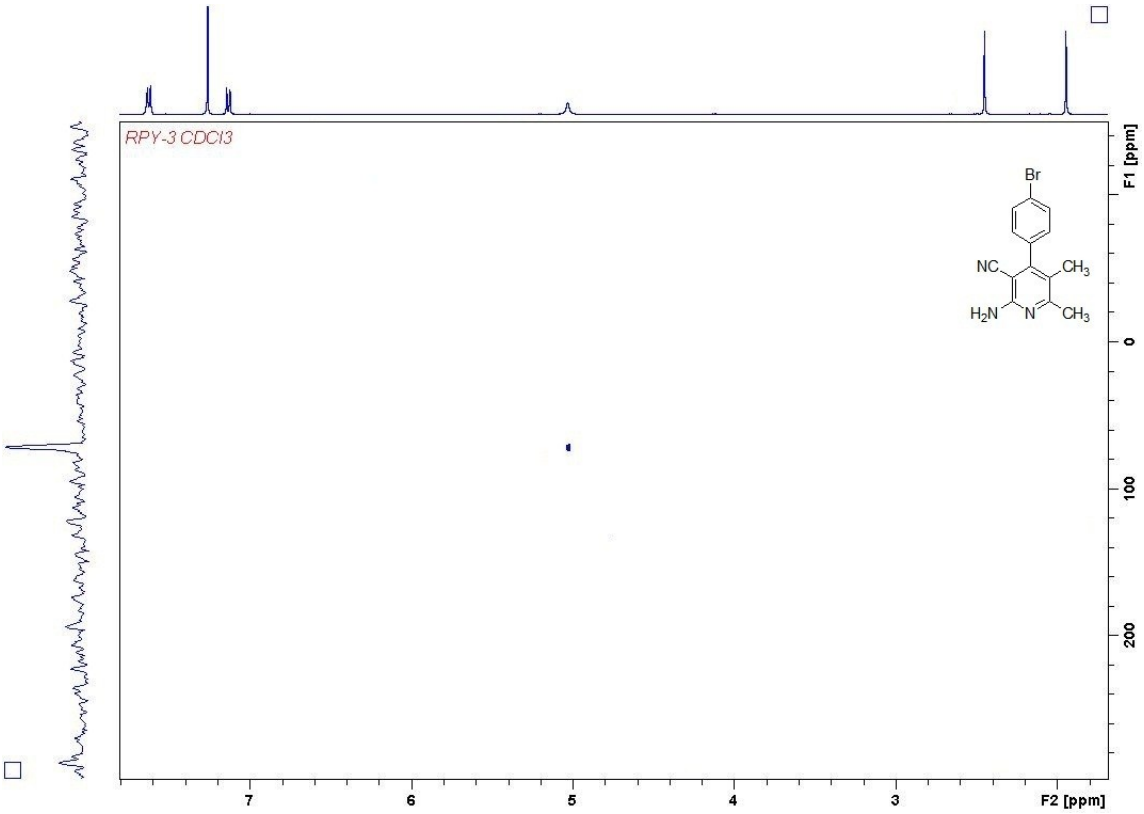


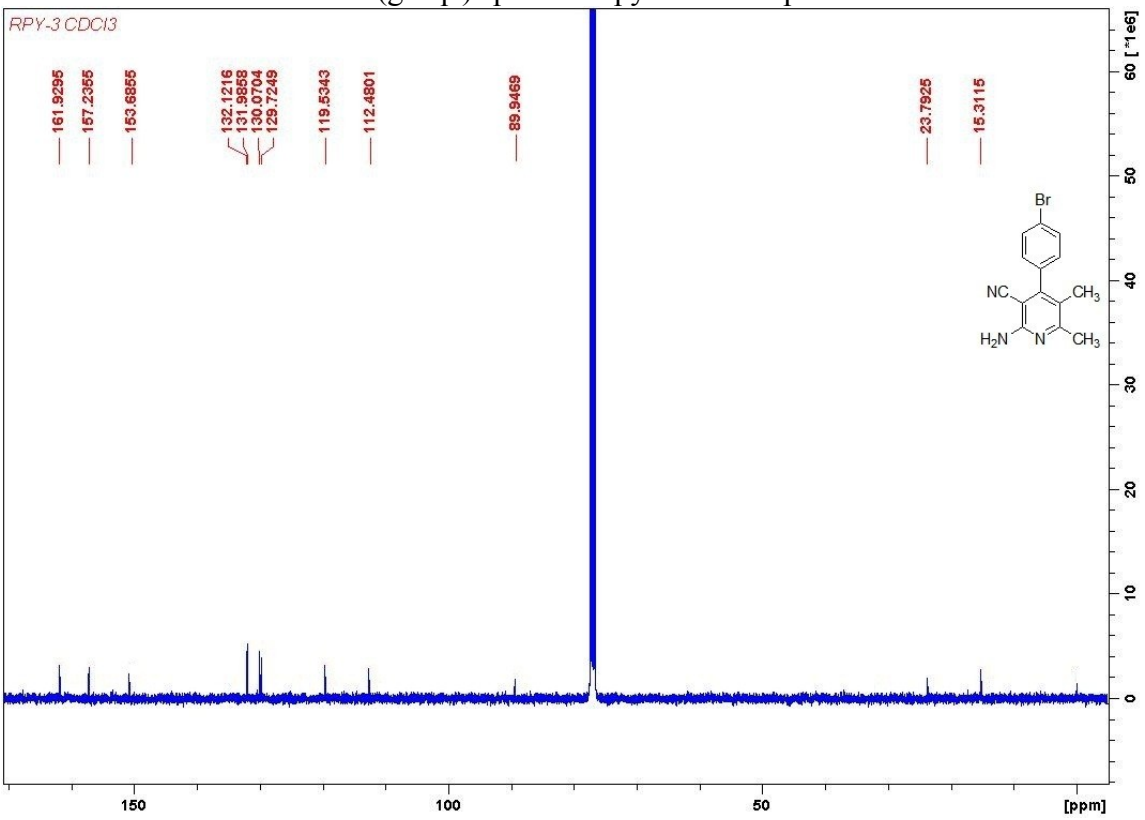
FTIR spectra of pyridine compound **4b**



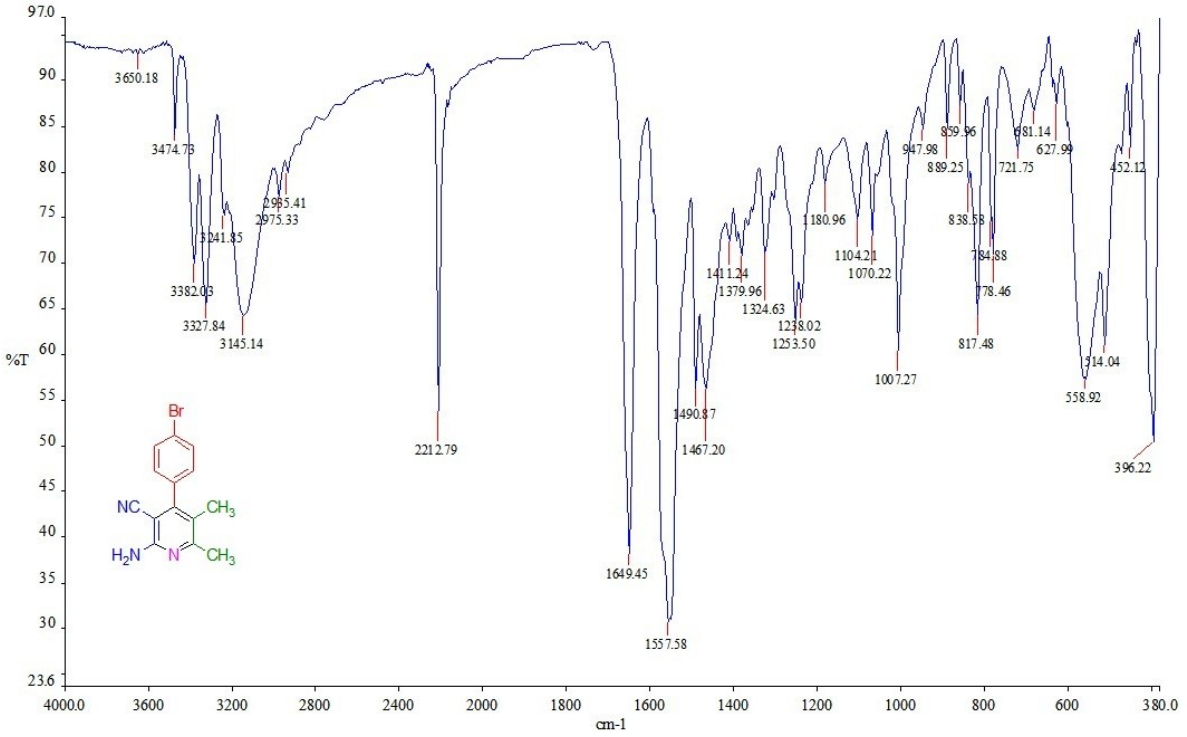
^{1}H NMR spectra of pyridine compound **4c**



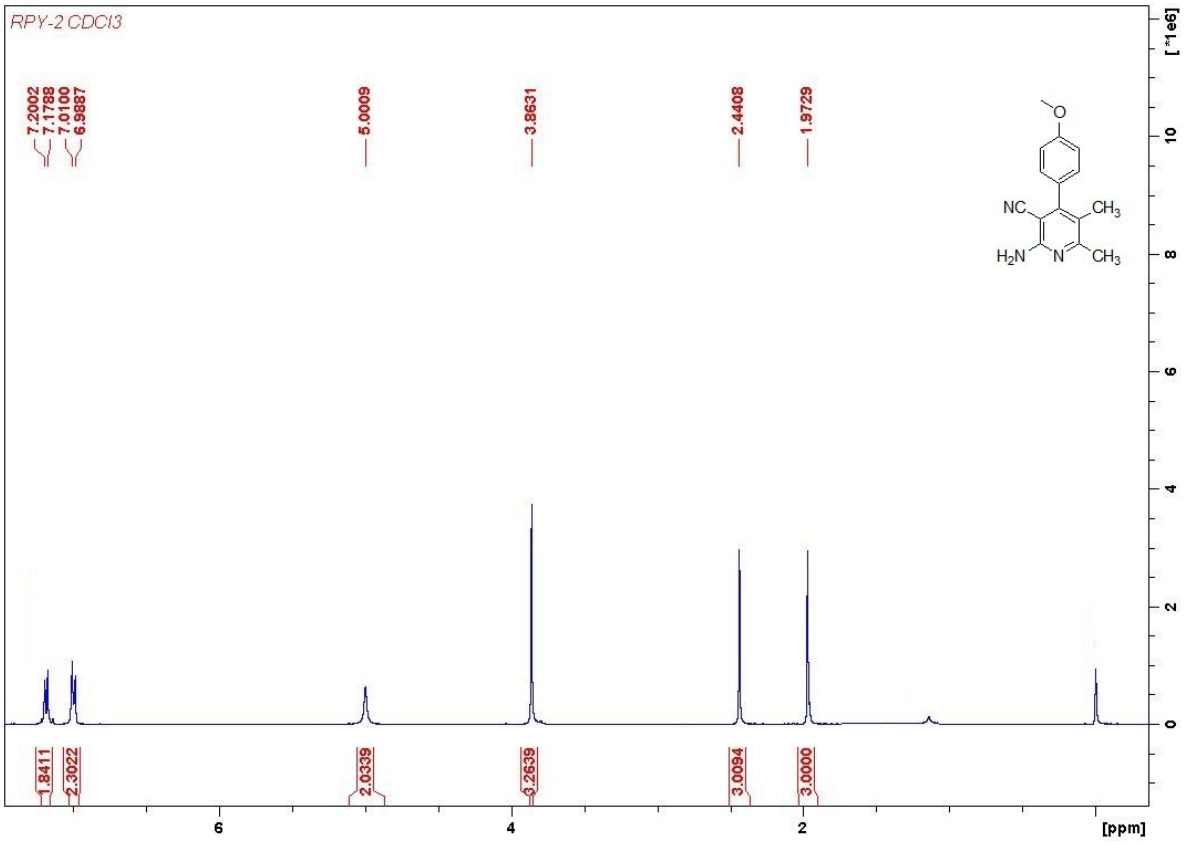
^{15}N NMR (ghsqc) spectra of pyridine compound **4c**



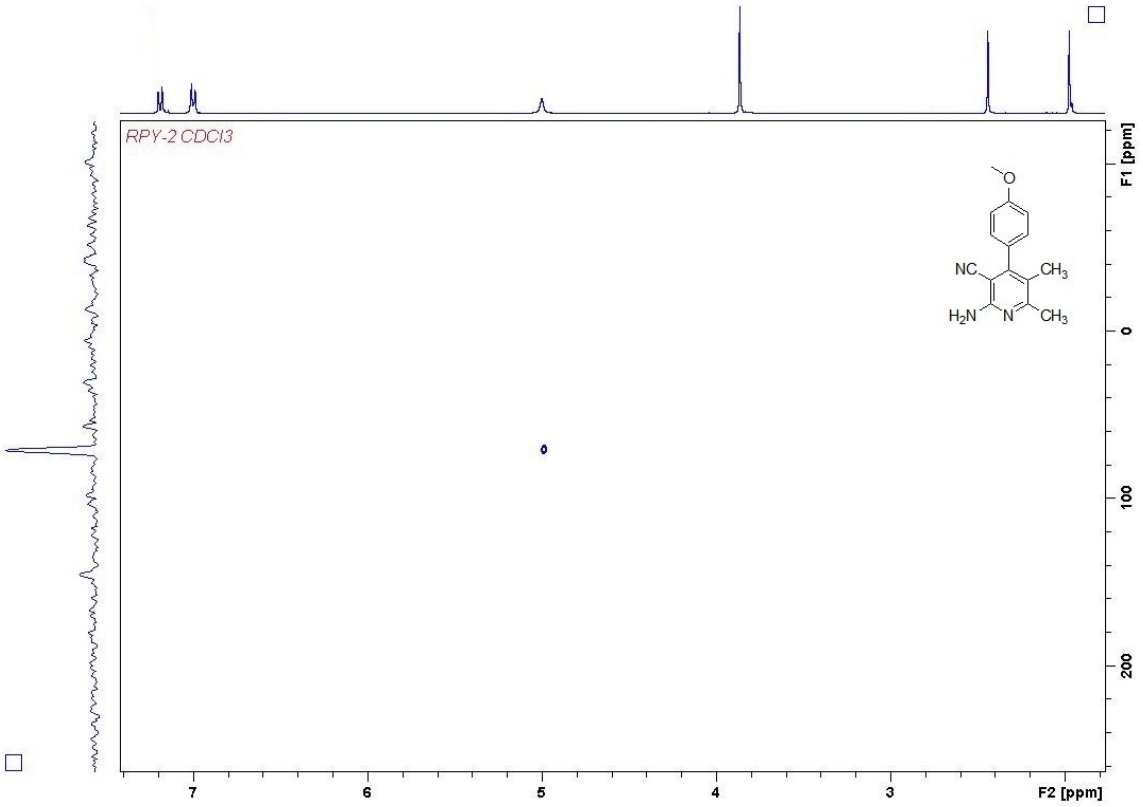
^{13}C NMR spectra of pyridine compound **4c**



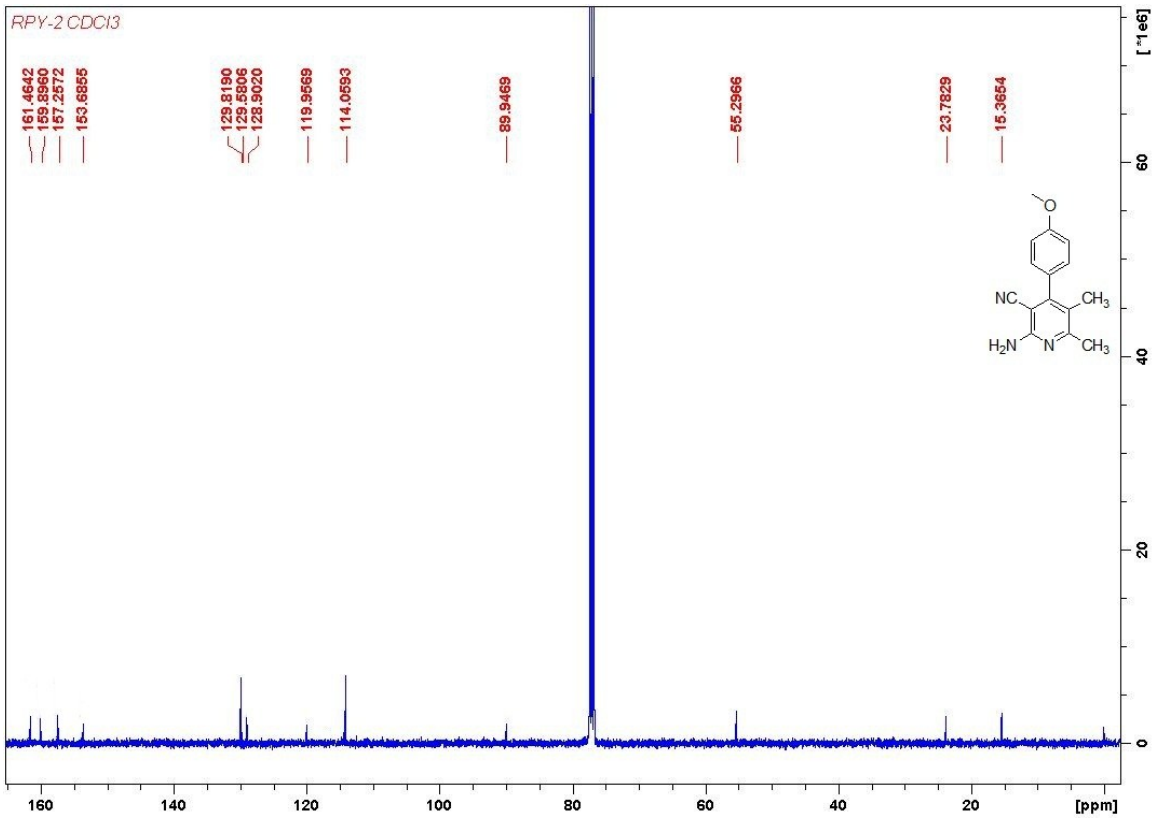
FTIR spectra of pyridine compound **4c**



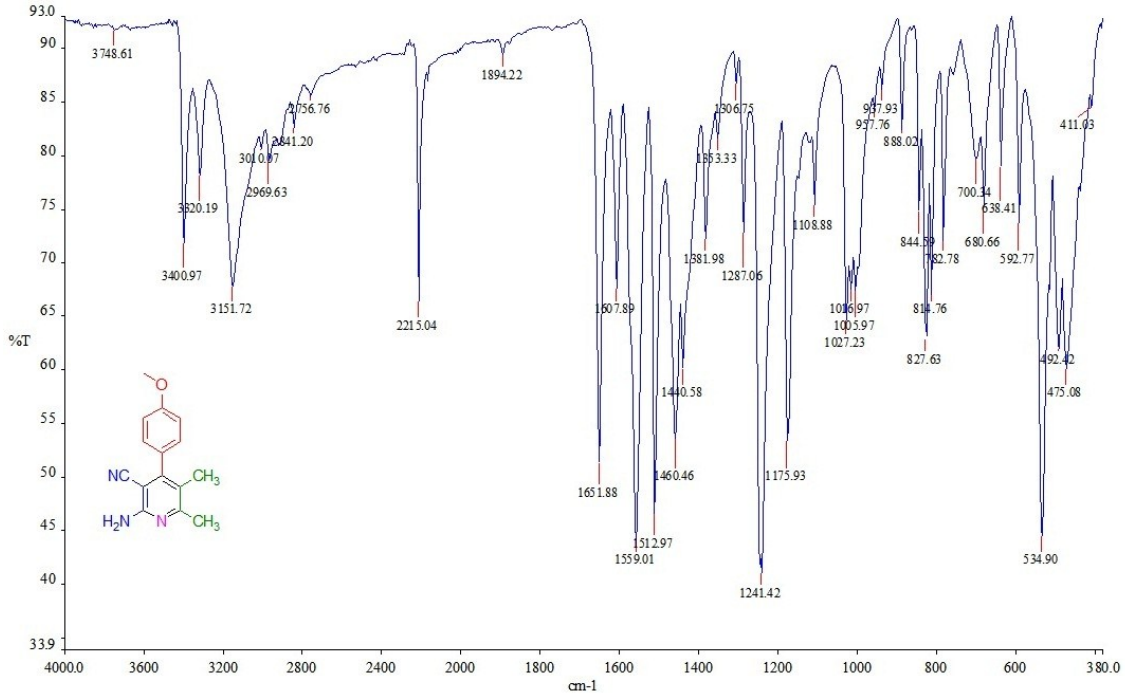
^{1}H NMR spectra of pyridine compound **4d**



^{15}N NMR (ghsqc) spectra of pyridine compound **4d**

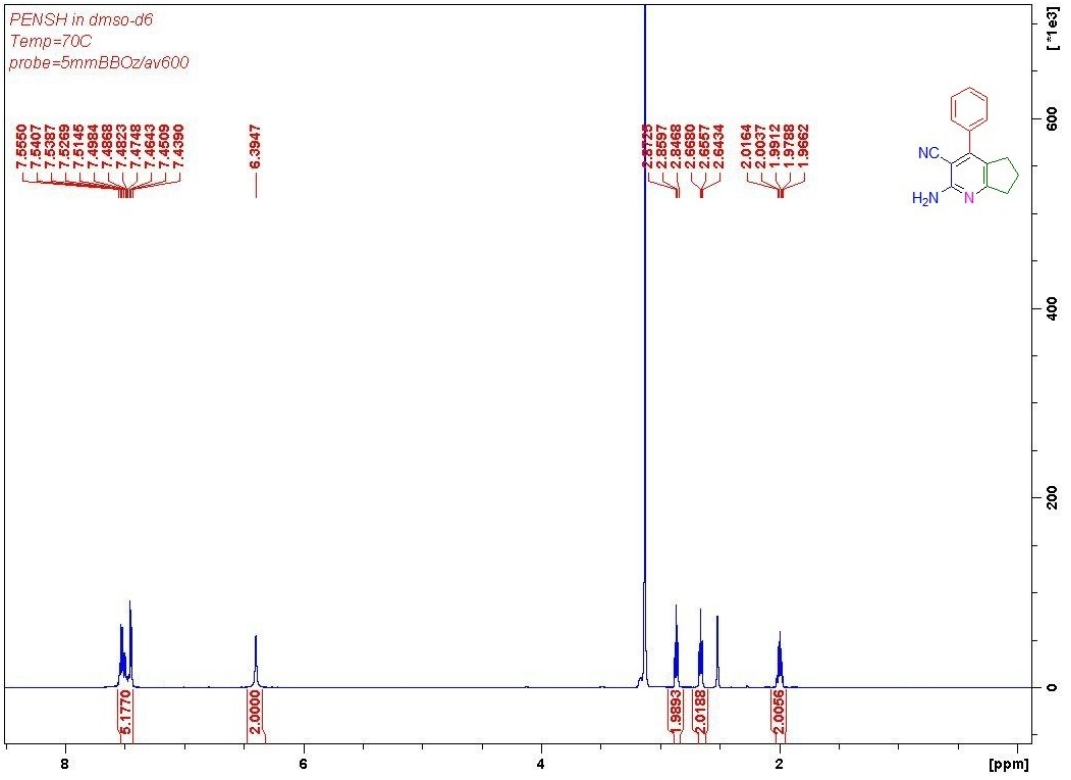


^{13}C NMR spectra of pyridine compound **4d**

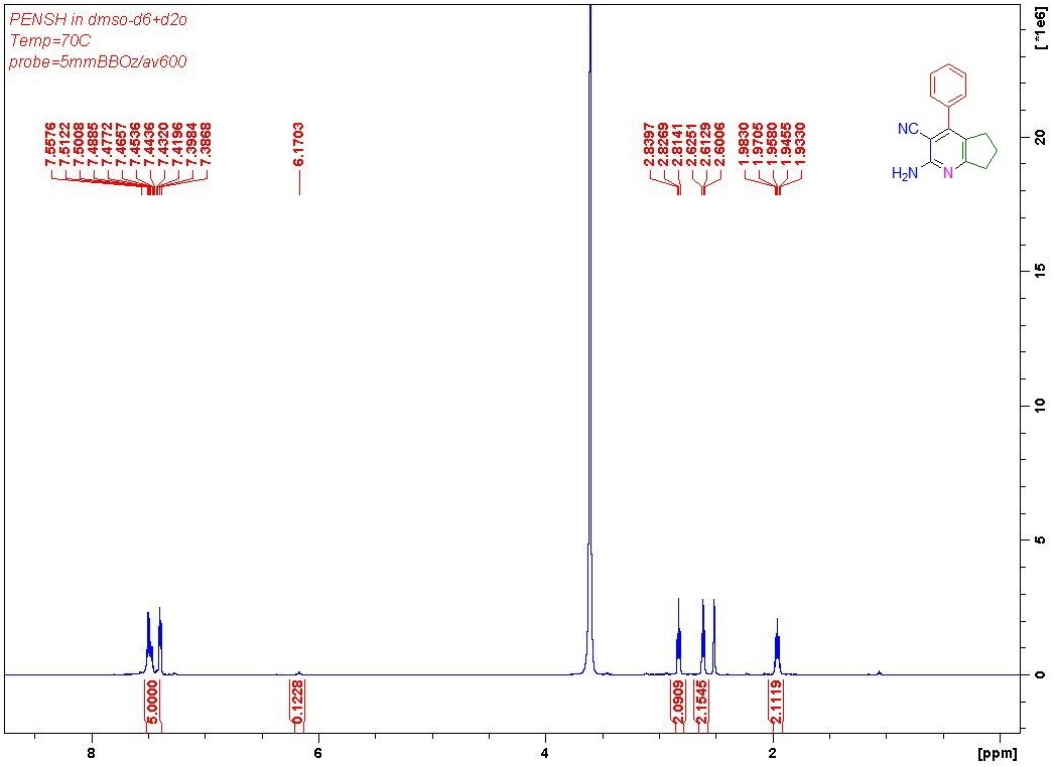


FTIR spectra of pyridine compound **4d**

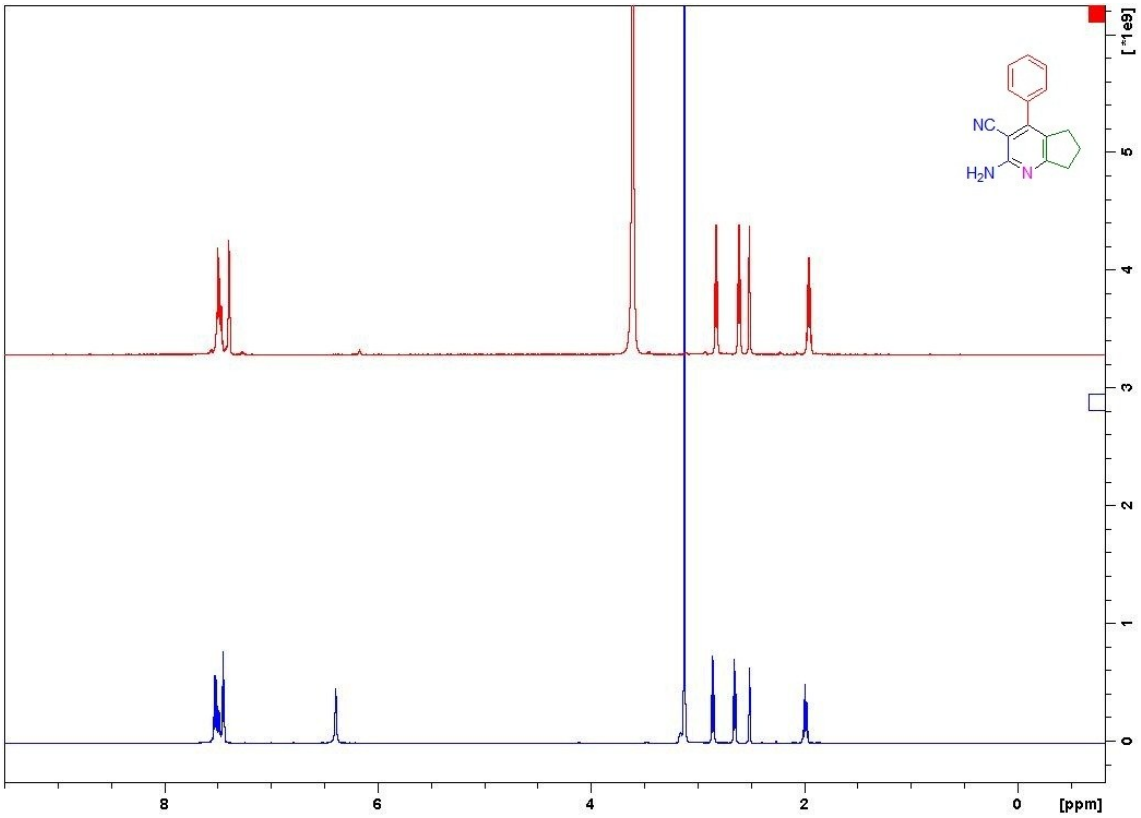
4. D_2O exchange study of compound (**3i**).



^{1}H NMR spectra of compound **3i** (DMSO-d_6)



^{1}H NMR spectra of compound **3i** (DMSO-d_6 + D_2O). Absence of -NH_2 peak



^{1}H NMR comparison spectra of compound **3i** (Blue: DMSO-d_6; Red: DMSO-d_6 + D_2O)

5. Single Crystal X-ray data of compound (**3a**).

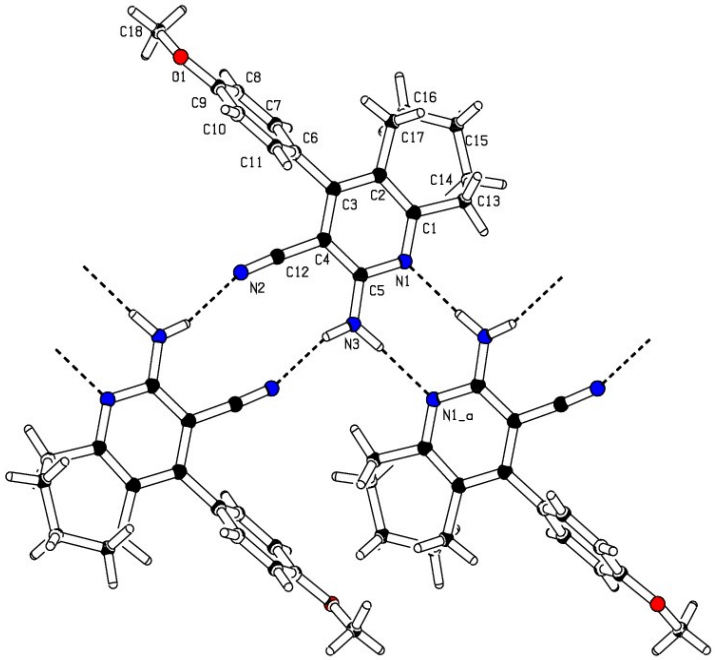


Table 1. Crystal data and structure refinement for 14ub_sbj_sk1a_1_0ma.

Identification code	shelx	
Empirical formula	C18 H19 N3 O	
Formula weight	293.36	
Temperature	173(2) K	
Wavelength	0.71073 Å	
Crystal system	Orthorhombic	
Space group	P b c n	
Unit cell dimensions	a = 15.7449(9) Å	α= 90°.
	b = 10.7620(7) Å	β= 90°.
	c = 18.2213(12) Å	γ = 90°.
Volume	3087.5(3) $Å^3$	
Z	8	
Density (calculated)	1.262 Mg/m^3	
Absorption coefficient	0.080 mm^{-1}	
F(000)	1248	
Crystal size	0.380 x 0.300 x 0.260 mm^3	
Theta range for data collection	2.235 to 27.996°.	
Index ranges	-20<=h<=20, -14<=k<=13, -15<=l<=24	
Reflections collected	37338	
Independent reflections	3725 [R(int) = 0.0484]	
Completeness to theta = 25.242°	100.0 %	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	0.979 and 0.970	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	3725 / 0 / 207	
Goodness-of-fit on F^2	1.130	
Final R indices [I>2sigma(I)]	R1 = 0.0577, wR2 = 0.1617	
R indices (all data)	R1 = 0.0701, wR2 = 0.1728	
Extinction coefficient	n/a	
Largest diff. peak and hole	0.372 and -0.246 $e.Å^{-3}$	

Table 2. Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters ($Å^2$x 10^3) for 14ub_sbj_sk1a_1_0ma. U(eq) is defined as one third of the trace of the orthogonalized U^{ij} tensor.

	x	y	z	U(eq)
C(1)	7988(1)	3498(2)	2588(1)	31(1)
C(2)	7341(1)	3643(2)	3113(1)	31(1)
C(3)	7579(1)	4011(2)	3818(1)	31(1)
C(4)	8446(1)	4210(2)	3963(1)	31(1)
C(5)	9054(1)	4045(2)	3403(1)	31(1)
C(6)	6957(1)	4226(2)	4423(1)	32(1)
C(7)	6479(1)	3258(2)	4715(1)	35(1)
C(8)	5921(1)	3452(2)	5297(1)	39(1)
C(9)	5833(1)	4643(2)	5584(1)	39(1)
C(10)	6289(1)	5614(2)	5286(1)	43(1)
C(11)	6854(1)	5407(2)	4714(1)	40(1)
C(12)	8735(1)	4559(2)	4677(1)	39(1)
C(13)	7780(1)	3126(2)	1811(1)	37(1)
C(14)	7416(1)	1804(2)	1740(1)	46(1)
C(15)	6483(1)	1680(2)	1933(1)	45(1)
C(16)	6261(1)	2017(2)	2720(1)	44(1)
C(17)	6428(1)	3389(2)	2911(1)	37(1)
C(18)	4874(2)	3930(3)	6500(1)	65(1)
N(1)	8815(1)	3680(2)	2724(1)	33(1)
N(2)	9006(1)	4848(2)	5234(1)	59(1)
N(3)	9893(1)	4228(2)	3510(1)	42(1)
O(1)	5313(1)	4929(2)	6157(1)	53(1)

Table 3. Bond lengths [Å] and angles [°] for 14ub_sbj_sk1a_1_0ma.

C(1)-N(1)	1.341(2)
C(1)-C(2)	1.405(2)
C(1)-C(13)	1.507(2)
C(2)-C(3)	1.396(2)
C(2)-C(17)	1.509(2)
C(3)-C(4)	1.407(2)
C(3)-C(6)	1.493(2)
C(4)-C(5)	1.410(2)
C(4)-C(12)	1.428(3)
C(5)-N(3)	1.350(2)
C(5)-N(1)	1.350(2)
C(6)-C(11)	1.388(3)
C(6)-C(7)	1.390(3)
C(7)-C(8)	1.393(3)
C(7)-H(7)	0.9500
C(8)-C(9)	1.392(3)
C(8)-H(8)	0.9500
C(9)-O(1)	1.362(2)
C(9)-C(10)	1.379(3)
C(10)-C(11)	1.388(3)
C(10)-H(10)	0.9500
C(11)-H(11)	0.9500
C(12)-N(2)	1.144(3)
C(13)-C(14)	1.539(3)
C(13)-H(13A)	0.9900
C(13)-H(13B)	0.9900
C(14)-C(15)	1.516(3)
C(14)-H(14A)	0.9900
C(14)-H(14B)	0.9900
C(15)-C(16)	1.519(3)
C(15)-H(15A)	0.9900
C(15)-H(15B)	0.9900
C(16)-C(17)	1.539(3)
C(16)-H(16A)	0.9900
C(16)-H(16B)	0.9900

C(17)-H(17A)	0.9900
C(17)-H(17B)	0.9900
C(18)-O(1)	1.422(3)
C(18)-H(18A)	0.9800
C(18)-H(18B)	0.9800
C(18)-H(18C)	0.9800
N(3)-H(1N)	0.96(3)
N(3)-H(2N)	0.87(3)

N(1)-C(1)-C(2)	124.16(16)
N(1)-C(1)-C(13)	115.07(16)
C(2)-C(1)-C(13)	120.78(15)
C(3)-C(2)-C(1)	117.59(16)
C(3)-C(2)-C(17)	122.09(16)
C(1)-C(2)-C(17)	120.32(16)
C(2)-C(3)-C(4)	118.52(16)
C(2)-C(3)-C(6)	123.21(15)
C(4)-C(3)-C(6)	118.26(15)
C(3)-C(4)-C(5)	120.15(16)
C(3)-C(4)-C(12)	121.39(16)
C(5)-C(4)-C(12)	118.45(15)
N(3)-C(5)-N(1)	116.53(16)
N(3)-C(5)-C(4)	122.72(16)
N(1)-C(5)-C(4)	120.75(15)
C(11)-C(6)-C(7)	118.47(17)
C(11)-C(6)-C(3)	120.06(17)
C(7)-C(6)-C(3)	121.46(16)
C(6)-C(7)-C(8)	121.38(18)
C(6)-C(7)-H(7)	119.3
C(8)-C(7)-H(7)	119.3
C(9)-C(8)-C(7)	119.11(19)
C(9)-C(8)-H(8)	120.4
C(7)-C(8)-H(8)	120.4
O(1)-C(9)-C(10)	116.30(19)
O(1)-C(9)-C(8)	123.8(2)
C(10)-C(9)-C(8)	119.92(18)
C(9)-C(10)-C(11)	120.47(19)

C(9)-C(10)-H(10)	119.8
C(11)-C(10)-H(10)	119.8
C(6)-C(11)-C(10)	120.62(19)
C(6)-C(11)-H(11)	119.7
C(10)-C(11)-H(11)	119.7
N(2)-C(12)-C(4)	176.6(2)
C(1)-C(13)-C(14)	113.98(17)
C(1)-C(13)-H(13A)	108.8
C(14)-C(13)-H(13A)	108.8
C(1)-C(13)-H(13B)	108.8
C(14)-C(13)-H(13B)	108.8
H(13A)-C(13)-H(13B)	107.7
C(15)-C(14)-C(13)	114.98(18)
C(15)-C(14)-H(14A)	108.5
C(13)-C(14)-H(14A)	108.5
C(15)-C(14)-H(14B)	108.5
C(13)-C(14)-H(14B)	108.5
H(14A)-C(14)-H(14B)	107.5
C(14)-C(15)-C(16)	114.93(17)
C(14)-C(15)-H(15A)	108.5
C(16)-C(15)-H(15A)	108.5
C(14)-C(15)-H(15B)	108.5
C(16)-C(15)-H(15B)	108.5
H(15A)-C(15)-H(15B)	107.5
C(15)-C(16)-C(17)	113.80(17)
C(15)-C(16)-H(16A)	108.8
C(17)-C(16)-H(16A)	108.8
C(15)-C(16)-H(16B)	108.8
C(17)-C(16)-H(16B)	108.8
H(16A)-C(16)-H(16B)	107.7
C(2)-C(17)-C(16)	113.00(16)
C(2)-C(17)-H(17A)	109.0
C(16)-C(17)-H(17A)	109.0
C(2)-C(17)-H(17B)	109.0
C(16)-C(17)-H(17B)	109.0
H(17A)-C(17)-H(17B)	107.8
O(1)-C(18)-H(18A)	109.5

O(1)-C(18)-H(18B)	109.5
H(18A)-C(18)-H(18B)	109.5
O(1)-C(18)-H(18C)	109.5
H(18A)-C(18)-H(18C)	109.5
H(18B)-C(18)-H(18C)	109.5
C(1)-N(1)-C(5)	118.82(15)
C(5)-N(3)-H(1N)	119.1(16)
C(5)-N(3)-H(2N)	123.6(18)
H(1N)-N(3)-H(2N)	117(2)
C(9)-O(1)-C(18)	117.25(18)

Symmetry transformations used to generate equivalent atoms:

Table 4. Anisotropic displacement parameters ($Å^2 x\ 10^3$)for 14ub_sbj_sk1a_1_0ma. The anisotropic displacement factor exponent takes the form: $-2\pi^2[\ h^2 a^{*2} U^{11} + ... + 2\ h\ k\ a^*\ b^*\ U^{12}\ ]$

	U^{11}	U^{22}	U^{33}	U^{23}	U^{13}	U^{12}
C(1)	28(1)	35(1)	30(1)	0(1)	-2(1)	-3(1)
C(2)	27(1)	35(1)	31(1)	0(1)	-3(1)	-2(1)
C(3)	26(1)	35(1)	31(1)	-1(1)	-1(1)	-1(1)
C(4)	26(1)	39(1)	28(1)	-2(1)	-2(1)	-3(1)
C(5)	25(1)	38(1)	30(1)	0(1)	-2(1)	-2(1)
C(6)	24(1)	41(1)	29(1)	-2(1)	-3(1)	1(1)
C(7)	32(1)	38(1)	36(1)	-1(1)	3(1)	5(1)
C(8)	34(1)	46(1)	37(1)	5(1)	4(1)	6(1)
C(9)	32(1)	57(1)	29(1)	-3(1)	1(1)	11(1)
C(10)	41(1)	44(1)	44(1)	-12(1)	-3(1)	3(1)
C(11)	32(1)	43(1)	45(1)	-7(1)	-1(1)	-5(1)
C(12)	26(1)	58(1)	33(1)	-3(1)	2(1)	-5(1)
C(13)	34(1)	49(1)	29(1)	-4(1)	0(1)	-9(1)
C(14)	44(1)	48(1)	45(1)	-11(1)	-5(1)	-6(1)
C(15)	46(1)	46(1)	45(1)	-3(1)	-8(1)	-14(1)
C(16)	35(1)	56(1)	41(1)	2(1)	-5(1)	-14(1)
C(17)	25(1)	51(1)	34(1)	-1(1)	-4(1)	0(1)
C(18)	72(2)	74(2)	48(1)	16(1)	26(1)	29(1)
N(1)	26(1)	42(1)	29(1)	-3(1)	0(1)	-3(1)
N(2)	36(1)	105(2)	35(1)	-12(1)	-4(1)	-12(1)
N(3)	24(1)	67(1)	36(1)	-10(1)	-1(1)	-7(1)
O(1)	55(1)	64(1)	40(1)	-2(1)	15(1)	16(1)

Table 5. Hydrogen coordinates (x 10^4) and isotropic displacement parameters ($Å^2$x 10^3) for 14ub_sbj_sk1a_1_0ma.

	x	y	z	U(eq)
H(7)	6535	2448	4513	43
H(8)	5604	2779	5495	46
H(10)	6215	6431	5474	52
H(11)	7173	6081	4521	48
H(13A)	8303	3184	1511	45
H(13B)	7364	3723	1608	45
H(14A)	7498	1519	1228	55
H(14B)	7747	1243	2062	55
H(15A)	6306	811	1843	55
H(15B)	6151	2219	1600	55
H(16A)	6597	1487	3056	53
H(16B)	5653	1832	2805	53
H(17A)	6271	3912	2485	44
H(17B)	6059	3630	3328	44
H(18A)	4523	4253	6900	97
H(18B)	5286	3335	6696	97
H(18C)	4511	3515	6138	97
H(1N)	10278(17)	4080(20)	3115(15)	52(7)
H(2N)	10108(17)	4500(20)	3920(16)	54(7)

Table 6. Torsion angles [°] for 14ub_sbj_sk1a_1_0ma.

N(1)-C(1)-C(2)-C(3)	0.7(3)
C(13)-C(1)-C(2)-C(3)	-178.86(17)
N(1)-C(1)-C(2)-C(17)	-178.63(17)
C(13)-C(1)-C(2)-C(17)	1.8(3)
C(1)-C(2)-C(3)-C(4)	-0.3(3)
C(17)-C(2)-C(3)-C(4)	178.98(17)
C(1)-C(2)-C(3)-C(6)	178.66(17)
C(17)-C(2)-C(3)-C(6)	-2.0(3)
C(2)-C(3)-C(4)-C(5)	0.4(3)
C(6)-C(3)-C(4)-C(5)	-178.63(16)
C(2)-C(3)-C(4)-C(12)	-178.50(18)
C(6)-C(3)-C(4)-C(12)	2.4(3)
C(3)-C(4)-C(5)-N(3)	179.68(18)
C(12)-C(4)-C(5)-N(3)	-1.4(3)
C(3)-C(4)-C(5)-N(1)	-0.8(3)
C(12)-C(4)-C(5)-N(1)	178.11(18)
C(2)-C(3)-C(6)-C(11)	-115.1(2)
C(4)-C(3)-C(6)-C(11)	63.9(2)
C(2)-C(3)-C(6)-C(7)	65.8(2)
C(4)-C(3)-C(6)-C(7)	-115.2(2)
C(11)-C(6)-C(7)-C(8)	-1.4(3)
C(3)-C(6)-C(7)-C(8)	177.75(17)
C(6)-C(7)-C(8)-C(9)	0.9(3)
C(7)-C(8)-C(9)-O(1)	-179.23(18)
C(7)-C(8)-C(9)-C(10)	0.7(3)
O(1)-C(9)-C(10)-C(11)	178.15(18)
C(8)-C(9)-C(10)-C(11)	-1.8(3)
C(7)-C(6)-C(11)-C(10)	0.3(3)
C(3)-C(6)-C(11)-C(10)	-178.85(18)
C(9)-C(10)-C(11)-C(6)	1.3(3)
N(1)-C(1)-C(13)-C(14)	114.29(19)
C(2)-C(1)-C(13)-C(14)	-66.1(2)
C(1)-C(13)-C(14)-C(15)	79.1(2)
C(13)-C(14)-C(15)-C(16)	-61.4(3)
C(14)-C(15)-C(16)-C(17)	63.8(3)

C(3)-C(2)-C(17)-C(16)	-114.2(2)
C(1)-C(2)-C(17)-C(16)	65.1(2)
C(15)-C(16)-C(17)-C(2)	-82.9(2)
C(2)-C(1)-N(1)-C(5)	-1.1(3)
C(13)-C(1)-N(1)-C(5)	178.48(16)
N(3)-C(5)-N(1)-C(1)	-179.33(17)
C(4)-C(5)-N(1)-C(1)	1.2(3)
C(10)-C(9)-O(1)-C(18)	-176.5(2)
C(8)-C(9)-O(1)-C(18)	3.5(3)

Symmetry transformations used to generate equivalent atoms:

Table 7. Hydrogen bonds for 14ub_sbj_sk1a_1_0ma [Å and °].

D-H...A	d(D-H)	d(H...A)	d(D...A)	<(DHA)	Symmetry operations
N(3)—H(1N)…N(1)	0.96(3)	2.14(3)	3.090(2)	177(2)	-x,y,1/2-z
N(3)—H(2N)…N(2)	0.87(3)	2.19(3)	3.038(3)	163(3)	-x,1-y,-z