SUPPORTING INFORMATION

Conformational Control and Photoenolization of Pyridine-3-Carboxaldehydes in the Solid State: Stabilization of Photoenols via Hydrogen-Bonding and Electronic Control

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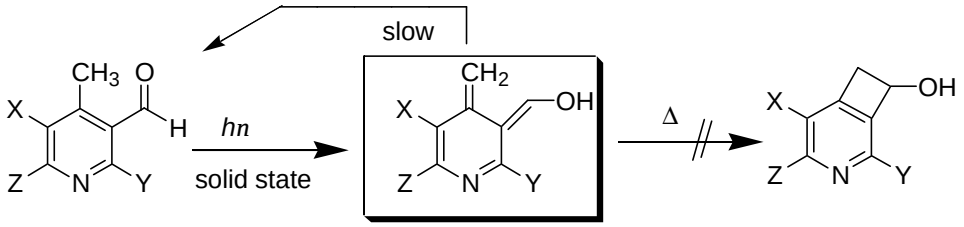
Graphic for TOC



1a-HBF$_4$: X = H; Y = Z = CH_3
1b: X = Br, Y = Z = CH_3
1b-HBF$_4$: X = Br; Y = Z = CH_3
1c: X = CN, Y = Z = CH_3
2b: X = Br, Y = OCH_3, Z = CH_3
2c: X = CN, Y = OCH_3, Z = CH_3
2d: X = CHO, Y = OCH_3, Z = CH_3

Colored
(yellow to Brick-red)

3: X = H, Y = Z = OCH_3
4: X = H, Y = Cl, Z = CH_3
5: X = H, Y = Z = Cl

General Aspects. The melting points were determined with a Perfit Melting Point Apparatus (Perfit, India) and are uncorrected. The solvents were used as received and purified by standard procedures where necessary. Column chromatography was conducted on silica gel (particle size: 60-120 mesh, Acme Synthetic Chemicals, India).

Preparation of 3-Bromo-2,4,6-trimethylpyridine.[1] To a solution of 2,4,6-trimethyl pyridine (1.83 g, 15.14 mmol) in trifluoroacetic acid (3.0 mL) were added conc. H_2SO_4 (4.0 mL) and NBS (5.39 g, 30.28 mmol) and the resultant reaction mixture was stirred for 36 h at room temperature. After this period, the contents were poured into crushed ice and the solution was made alkaline with 2N-NaOH. The organic matter was extracted with ethyl acetate, washed with saturated Na_2SO_4, filtered and the solvent removed in vacuo. The residue was subjected to column chromatography (10 % EtOAc – pet. ether) to obtain 2.9 g (95 %) of a colorless liquid;[2] IR (neat) cm^{-1} 2924, 1587, 1446; ^1H NMR ($CDCl_3$, 400 MHz) ä 2.20 (s, 3H), 2.30 (s, 3H), 2.51 (s, 3H), 6.70 (s, 1H); ^{13}C NMR ($CDCl_3$, 100 MHz) ä 22.8, 23.4, 25.3, 120.9, 122.8, 146.9, 155.2, 156.2.

Preparation of 3,5-Dibromo-2,4,6-trimethylpyridine. A similar procedure as described above with 3.0 molar equivalents of NBS over an extended period (60 h) led to isolation of 3,5-dibromo-2,4,6-trimethylpyridine in 56 % yield, mp 82 °C (lit. 81.5 °C).[2]

Preparation of 3-Cyano-2,4,6-trimethylpyridine.[3] To a solution of 1.29 g (14.4 mmol) of cuprous cyanide in 15 mL of DMF was added 2.40 g (12 mmol) of 3-bromo-2,4,6-trimethylpyridine and the resultant mixture was heated at reflux (150-160 °C) for 18 h. Subsequently, the reaction mixture was cooled to room temperature and a solution of $FeCl_3$ (8 g in 2 mL of conc. HCl and 8 mL of water) was added. The mixture was poured into crushed ice and made alkaline with 2N-NaOH solution. The organic matter was extracted with ethyl acetate, washed with saturated Na_2SO_4, filtered and the solvent removed in vacuo. The residue was subjected to column chromatography (10 % EtOAc-pet. ether) to obtain 1.02 g (65 %) of 3-cyano-2,4,6-trimethylpyridine as a colorless solid, mp 41-42 °C; IR (KBr) cm^{-1} 2960, 2216, 1586; ^1H NMR ($CDCl_3$, 400 MHz) ä 2.38 (s, 3H), 2.40 (s, 3H), 2.56 (s, 3H), 6.85 (s, 1H); ^{13}C NMR ($CDCl_3$, 100 MHz) ä 20.0, 23.4, 24.4, 106.7, 116.2, 121.5, 150.9, 160.8, 161.0.

Preparation of 5-Bromo-3-cyano-2,4,6-trimethylpyridine and 3,5-Dicyano-2,4,6-trimethylpyridine. A similar procedure as described above with 3,5-Dibromo-2,4,6-trimethylpyridine and 1.7 molar equivalents of CuCN led to isolation, subsequent to column chromatography, of 3,5-dicyano-2,4,6-trimethylpyridine and 5-bromo-3-cyano-2,4,6-trimethylpyridine in a ratio of 5.27 : 1 with an overall yield of 69 %, mp 124-126 °C (lit.[4] 124 °C).

5-Bromo-3-cyano-2,4,6-trimethylpyridine. Colorless crystalline powder, mp 105-106 °C; IR (KBr) cm^{-1} 2923, 2222, 1555; ^1H NMR ($CDCl_3$, 400 MHz) δ 2.60 (s, 3H), 2.67 (s, 3H), 2.69 (s, 3 H), ^{13}C NMR ($CDCL_3$, 100 MHz) δ 22.3, 23.4, 26.4, 108.6, 115.9, 121.2, 150.5, 159.2, 160.9.

5-Bromo-3-cyano-2-methoxy-4,6-dimethylpyridine. 3-Cyano-2-methoxy-4,6,-dimethylpyridine was brominated using NBS and trifluoroacetic acid-Conc. H_2SO_4 mixture (following the procedure as that described for 3-bromo-2,4,6-trimethylpyridine) to isolate the required product in 92 % yield, mp 100-101 °C (lit.[5] 95-98 °C).

Preparation of 3-cyano-2-methoxy-4,6,-dimethylpyridine. This compound was prepared by following a procedure reported for analogous compounds.[6] To a solution of 5-cyano-6-hydroxy-2,4-dimethylpyridine (1.78 g, 12 mmol) in 20 mL of dry benzene was added silver carbonate (1.76 g, 6.4 mmol). The flask was stirred in dark and methyl iodide (1.5 mL, 24 mmol) was added in three portions at different intervals. After 48 h, the mixture was filtered and benzene was removed in vacuo. The residue was subjected to column chromatography (10 % EtOAc-pet. ether) to obtain a white solid. Yield 1.31g (67 %), mp 99-100 °C (lit.[7] 98 °C).

Preparation of 3-cyano-2,6-dimethoxy-4-methylpyridine. This compound was prepared from 3-cyano-2,6-dihydroxy-4-methylpyridine by following the procedure described above in 64% yield, mp 115 °C (lit.[7] 114 °C).

Preparation of 3,5-Dicyano-2-methoxy-4,6-dimethylpyridine. Cyanation of 5-bromo-3-cyano-2-methoxy-4,6-dimethylpyridine led to the dicyano compound in 61 % yield using the procedure described above for 3-cyano-2,4,6-trimethylpyridine, colorless crystalline powder, mp 98-99 °C; IR (KBr) cm^{-1} 2227, 1573; ^1H NMR ($CDCl_3$, 400 MHz) δ 2.66 (s, 3H), 2.71 (s, 3H), 4.08 (s, 3H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 19.6, 24.2, 55.3, 95.6, 103.6, 113.1, 115.1, 157.7, 164.8, 165.6.

General Procedure for the Reduction of Cyanopyridines. 2-Chloro-3-formyl-4,6-dimethylpyridine **4** was synthesized from commercially available 2-chloro-4,6-dimethylnicotinonitrile. A 10 mL solution in dichloromethane of 2-chloro-4,6-dimethylnicotinonitrile (0.67g, 4 mmol) in a two-necked round-bottom flask was cooled to 0 °C in an ice bath under N_2 gas atmosphere. After 10 min, 5 mL (5 mmol) of DIBAL (1M in toluene) was slowly added to the flask. The reaction mixture was gradually allowed to attain room temperature. After stirring for 6 h, it was quenched with dil. HCl and the contents were heated at reflux for 30 min. Subsequently, the reaction mixture was made alkaline with 10 % NaOH solution and extracted with ethyl acetate, dried over anhydrous Na_2SO_4, filtered and solvent removed in vacuo. The crude product was submitted to silica-gel column chromatography (10% EtOAc-pet. ether) to obtain 0.50 g (70 %) of product as colorless crystalline powder, mp 57-58 °C; IR (KBr) cm^{-1} 1695, 1593; ^1H NMR ($CDCl_3$, 400 MHz) δ 2.52 (s, 3H), 2.56 (s, 3H), 6.99 (s, 1H), 10.52 (s, 1H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 20.8, 24.3, 124.7, 126.1, 152.9, 154.5, 162.8, 191.6. Anal. Calcd for C_8H_8ClNO (mol wt 169.61) C, 56.65; H, 4.75; N, 8.26. Found: C, 57.08; H, 4.98; N, 8.37.

3-Formyl-2,4,6-trimethylpyridine 1a: Yield 74%, colorless liquid; IR (neat film) cm^{-1} 2970, 1690, 1589; ^1H NMR ($CDCl_3$, 400 MHz) δ 2.53 (s, 3H), 2.57 (s, 3H) 2.80 (s, 3H), 6.92 (s, 1H) 10.59 (s, 1H); ^{13}C NMR ($CDCL_3$, 100 MHz) δ 20.2, 22.8, 24.4, 124.5, 125.8, 150.1, 160.5, 161.7, 192.0.

5-Bromo-3-formyl-2,4,6-trimethylpyridine 1b: Yield 70%, colorless crystalline powder, mp 64-66 °C; IR (KBr) cm^{-1} 2924, 1695, 1554; ^1H NMR ($CDCl_3$, 400 MHz) δ 2.67 (s, 3H), 2.70 (s, 3H) 2.71 (s, 3H), 10.51 (s, 1H); ^{13}C NMR ($CDCL_3$, 100 MHz) δ 19.6, 22.8, 26.8, 123.9, 127.7, 148.7, 157.9, 161.0, 192.1.

5-Cyano-3-formyl-2,4,6-trimethylpyridine 1c: Yield 55%, colorless crystalline powder, mp 93-95 °C; IR (KBr) cm^{-1} 2924, 2223, 1692; ^1H NMR ($CDCl_3$, 400 MHz) δ 2.77 (s, 3H), 2.79 (s, 3H), 2.83 (s, 3H), 10.56 (s, 1H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 18.3, 23.6, 24.4, 110.1, 115.6, 126.0,153.3, 163.2, 164.6, 190.7. Anal. Calcd for $C_{10}H_{10}N_2O$ (mol wt 174.2) C, 68.95; H, 5.79; N, 16.08. Found: C, 68.29; H, 6.23; N, 16.04.

3-Formyl-2-methoxy-4,6-dimethylpyridine 2a: Yield 69%, colorless liquid; IR (neat film) cm^{-1} 2955, 1685, 1597; ^1H NMR ($CDCl_3$, 400 MHz) δ 2.42 (s, 3H), 2.53 (s, 3H), 3.99 (s, 3H), 6.60 (s, 1H) 10.47 (s, 1H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 20.9, 24.5, 53.7, 114.5, 120.1, 152.5, 161.6, 165.5, 191.3.

5-Bromo-3-formyl-4,6-dimethyl-2-methoxypyridine 2b: Yield 71%, colorless crystalline powder, mp 92-94 °C; IR (KBr) cm^{-1} 2951, 1687, 1555; ^1H NMR ($CDCl_3$, 400 MHz) δ 2.60 (s, 3H), 2.66 (s, 3H), 3.98 (s, 3H), 10.38 (s, 1H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 19.9, 26.6, 53.9, 118.1, 151.1, 159.0,160.3, 163.4, 190.7. Anal. Calcd for $C_9H_{10}BrNO_2$ (mol wt 244.09) C, 44.29; H, 4.13; N, 5.74. Found: C, 44.53; H, 4.48; N, 5.94.

5-Cyano-3-formyl-2methoxy-4,6-dimethylpyridine 2c: Yield 66% (including **2d**), colorless crystalline powder, mp 108-110 °C; IR (KBr) cm^{-1} 2956, 2223, 1688, 1563; ^1H NMR ($CDCl_3$, 400 MHz) δ 2.71 (s, 3H), 2.78 (s, 3H), 4.09 (s, 3H), 10.45 (s, 1H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 18.8, 24.4, 54.7, 114.7, 116.1, 124.2, 155.8, 165.9, 166.1, 189.8. Anal. Calcd for $C_{10}H_{10}N_2O_2$ (mol wt 190.2) C, 63.15; H, 5.30; N, 14.73. Found: C, 63.25; H, 5.58; N, 14.67.

3,5-Diformyl -2methoxy-4,6-dimethylpyridine 2d: Yield 66% (including **2c**), colorless crystalline powder, mp 98-99 °C; IR (KBr) cm^{-1} 2961, 1689; ^1H NMR ($CDCl_3$, 400 MHz) δ 2.75 (s, 3H), 2.84 (s, 3H), 4.09 (s, 3H), 10.49 (s, 1H), 10.54 (s, 1H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 15.6, 24.4, 54.4, 115.8, 124.1, 155.0, 165.3,165.8, 191.1, 191.3.

3-Formyl-4-methyl-2,6-dimethoxypyridine 3: Yield 76%, colorless crystalline powder, mp 96-98 °C; IR (KBr) cm^{-1} 2992, 1672; ^1H NMR ($CDCl_3$, 400 MHz) δ 2.54 (s, 3H), 3.95 (s, 3H), 4.01 (s, 3 H), 6.14 (s, 1H), 10.37 (s, 1H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 21.4, 53.8 (×2), 105.3, 110.8, 155.3, 165.6, 166.7, 189.7. Anal. Calcd for $C_9H_{11}NO_3$ (mol wt 181.19) C, 59.66; H, 6.12; N, 7.73. Found: C, 59.65; H, 6.28; N, 7.78.

Preparation of 1a-HBF_4 and 1b-HBF_4: To the dichloromethane solutions of the aldehydes **1a** and **1b** (ca. 200 mg), was added calculated amount of HBF_4 and stirred for about 15 min. Subsequently, the solvent was removed under reduced pressure to obtain a gummy material. Addition of diethyl ether to

this material led to precipitation of white salts, which were collected by filtration which are found to be highly hygroscopic

1a-HBF_4: Yield 55 %, highly hygroscopic colorless powder; ^{1}H NMR (DMSO-d_6, 400 MHz) δ 2.67 (s, 3H), 2.74 (s, 3H), 2.87 (s, 3H), 7.72 (s, 1H), 10.40 (s, 1H); ^{13}C NMR (DMSO-d_6, 100 MHz) δ 18.5, 19.8, 20.5, 128.01, 128.04, 155.55, 155.57, 159.4, 191.6.

1b-HBF_4: Yield 68 %, highly hygroscopic colorless powder; ^{1}H NMR (DMSO-d_6, 400 MHz) δ 2.68 (s, 9H), 10.41 (s, 1H); ^{13}C NMR (DMSO-d_6, 100 MHz) δ 19.8, 21.3, 25.2, 124.0, 128.5, 151.9, 156.1 158.4, 192.9.

References:

1. Duan, J.; Zhang, L. H.; Dolbier, W. J., Jr. *Synlett.* **1999**, 1245.
2. Tomasik, P.; Drzeniek, W. *Rocz. Chem*. **1969**, *43*, 569; *Chem. Abstr*. **1969**, *71*, 12976b.
3. Friedman, L.; Shechter, H. *J. Org. Chem.* **1961**, *26*, 2522.
4. Lukes, R.; Kuthan,J. *J. Collect. Czech. Chem. Commun.* **1961**, *26*, 1422; *Chem. Abstr*. **1961**, *55* 27307i.
5. Thompson, W. J.; Jones, J. H.; Lyle, P. J.; Thies, J. E. *J. Org. Chem.* **1988**, *53*, 2052.
6. Hopkins, G. C.; Jonak, J. P.; Minnemeyer, J.; Tieckelmann, H. *J. Org. Chem*. **1967**, *32*, 4040.
7. Janin, Y. L.; Huel, C.; Flad, G.; Thirot, S. *Eur. J. Org. Chem*. **2002**, 1763.

Table S1. Crystal data and structure refinement for 1c.

Identification code	**1c**	
Empirical formula	$C_{10}\ H_{10}\ N_2\ O$	
Formula weight	174.20	
Temperature	293(2) K	
Diffractometer used	Siemens P4	
Radiation used, Wavelength	MoKα, 0.71073 Å	
Crystal system, Space group	Monoclinic, $P2_1/n$	
Unit cell dimensions	a = 3.980(1) Å	α= 90°.
	b = 16.248(2) Å	β= 93.08(1)°.
	c = 14.228(2) Å	γ = 90°.
Volume	918.8(3) $Å^3$	
Z, Calculated Density	4, 1.259 Mg/m^3	
Absorption coefficient	0.084 mm^{-1}	
F(000)	368	
Crystal size	0.25x 0.19 x 0.18 mm	
Theta range for data collection	1.90 to 22.99°.	
Scan type	2θ-θ	
Scan speed	Variable, 2.0° to 60.0°/min. in ω	
Scan range (ω)	1.18° plus Kα separation	
Background measurement	Stationary crystal and stationary counter at the beginning and end of scan, each for 25.0% of total scan time	
Index ranges	$0\le h\le 4$, $-17\le k\le 0$, $-15\le l\le 15$	
Reflections collected	1674	
Independent reflections	1271 [R(int) = 0.0273]	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	1271 / 0 / 119	
Goodness-of-fit on F^2	1.001	
Weighting scheme	$1/[\sigma^2 (Fo^2)+(0.1056P)^2 +0.02P]$, $P=(\max(F_o^2,0)+2*F_c^2)/3$	
Data to parameter ratio	10.68:1	
Final R indices, 772 reflections [$I>2\sigma(I)$]	R1 = 0.0579, wR2 = 0.1565	
R indices (all data)	R1 = 0.1033, wR2 = 0.1768	
Extinction coefficient	0.013(7)	
Largest diff. peak and hole	0.174 and -0.148 $e.Å^{-3}$	

Table S2. Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters ($Å^2$x 10^3) for 1c. U(eq) is defined as one third of the trace of the orthogonalized U^{ij} tensor.

	x	y	z	U(eq)
O(1)	-3471(9)	2653(2)	3324(3)	131(1)
N(1)	1055(6)	864(2)	1066(2)	62(1)
N(2)	3350(11)	-828(3)	3724(3)	134(2)
C(1)	-880(8)	1664(2)	2353(2)	61(1)
C(2)	92(7)	1049(2)	2998(2)	61(1)
C(3)	1505(7)	340(2)	2627(2)	60(1)
C(4)	1970(8)	265(2)	1661(2)	56(1)
C(5)	-375(8)	1550(2)	1396(2)	61(1)
C(6)	-2427(11)	2438(2)	2650(3)	90(1)
C(7)	-291(10)	1119(2)	4043(2)	90(1)
C(8)	2531(10)	-329(2)	3235(3)	83(1)
C(9)	3415(9)	-489(2)	1240(2)	73(1)
C(10)	-1339(10)	2168(2)	656(2)	87(1)

Table S3. Bond lengths [Å] and angles [°] for 1c.

O(1)-C(6)	1.121(4)	N(1)-C(4)	1.329(4)
N(1)-C(5)	1.347(4)	N(2)-C(8)	1.105(4)
C(1)-C(2)	1.397(4)	C(1)-C(5)	1.400(4)
C(1)-C(6)	1.472(5)	C(2)-C(3)	1.398(4)
C(2)-C(7)	1.508(4)	C(3)-C(4)	1.402(4)
C(3)-C(8)	1.436(5)	C(4)-C(9)	1.492(4)
C(5)-C(10)	1.491(4)		
C(4)-N(1)-C(5)	119.4(2)	C(2)-C(1)-C(5)	119.7(3)
C(2)-C(1)-C(6)	121.9(3)	C(5)-C(1)-C(6)	118.5(3)
C(1)-C(2)-C(3)	116.4(3)	C(1)-C(2)-C(7)	123.7(3)
C(3)-C(2)-C(7)	119.9(3)	C(2)-C(3)-C(4)	121.3(3)
C(2)-C(3)-C(8)	120.3(3)	C(4)-C(3)-C(8)	118.4(3)
N(1)-C(4)-C(3)	121.0(3)	N(1)-C(4)-C(9)	116.4(2)
C(3)-C(4)-C(9)	122.7(3)	N(1)-C(5)-C(1)	122.3(3)
N(1)-C(5)-C(10)	114.1(3)	C(1)-C(5)-C(10)	123.6(3)
O(1)-C(6)-C(1)	133.7(4)	N(2)-C(8)-C(3)	177.9(4)

Table S4. Anisotropic displacement parameters ($Å^2 x\ 10^3$) for 1c. 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}
O(1)	150(3)	111(2)	136(3)	-36(2)	45(2)	15(2)
N(1)	82(2)	48(2)	55(2)	-2(1)	8(1)	-8(1)
N(2)	186(4)	116(3)	100(3)	44(2)	17(3)	50(3)
C(1)	66(2)	52(2)	66(2)	-10(2)	8(2)	-13(2)
C(2)	64(2)	64(2)	57(2)	-14(2)	11(2)	-14(2)
C(3)	65(2)	61(2)	54(2)	1(2)	2(2)	-12(2)
C(4)	66(2)	48(2)	56(2)	-6(2)	8(2)	-13(2)
C(5)	72(2)	47(2)	63(2)	1(2)	3(2)	-13(2)
C(6)	98(3)	79(2)	96(3)	-19(2)	25(2)	-9(2)
C(7)	109(3)	105(3)	57(2)	-16(2)	15(2)	-5(2)
C(8)	99(3)	85(3)	66(2)	11(2)	5(2)	2(2)
C(9)	88(3)	54(2)	77(2)	-7(2)	8(2)	1(2)
C(10)	110(3)	63(2)	89(2)	14(2)	2(2)	1(2)

Table S5. Hydrogen coordinates (x 10^4) and isotropic displacement parameters ($Å^2$x 10^3) for 1c.

	x	y	z	U(eq)
H(6A)	-2568	2834	2177	108
H(7A)	697	1626	4269	135
H(7B)	822	665	4358	135
H(7C)	-2637	1112	4169	135
H(9A)	1676	-893	1137	109
H(9B)	5157	-707	1662	109
H(9C)	4340	-351	651	109
H(10A)	-198	2046	94	131
H(10B)	-714	2708	875	131
H(10C)	-3727	2147	520	131

Table S6. Torsion angles [°] for 1c.

C(5)-C(1)-C(2)-C(3)	-0.7(4)	C(6)-C(1)-C(2)-C(3)	179.5(3)
C(5)-C(1)-C(2)-C(7)	178.9(3)	C(6)-C(1)-C(2)-C(7)	-0.9(5)
C(1)-C(2)-C(3)-C(4)	1.2(4)	C(7)-C(2)-C(3)-C(4)	-178.4(3)
C(1)-C(2)-C(3)-C(8)	-179.0(3)	C(7)-C(2)-C(3)-C(8)	1.3(5)
C(5)-N(1)-C(4)-C(3)	-0.8(4)	C(5)-N(1)-C(4)-C(9)	177.7(2)
C(2)-C(3)-C(4)-N(1)	-0.5(4)	C(8)-C(3)-C(4)-N(1)	179.8(3)
C(2)-C(3)-C(4)-C(9)	-178.9(3)	C(8)-C(3)-C(4)-C(9)	1.4(4)
C(4)-N(1)-C(5)-C(1)	1.3(4)	C(4)-N(1)-C(5)-C(10)	-179.0(3)
C(2)-C(1)-C(5)-N(1)	-0.5(5)	C(6)-C(1)-C(5)-N(1)	179.3(3)
C(2)-C(1)-C(5)-C(10)	179.7(3)	C(6)-C(1)-C(5)-C(10)	-0.4(5)
C(2)-C(1)-C(6)-O(1)	-11.3(7)	C(5)-C(1)-C(6)-O(1)	168.9(5)
C(2)-C(3)-C(8)-N(2)	-36(13)	C(4)-C(3)-C(8)-N(2)	144(13)

Table S7. Crystal data and structure refinement for 2c

Identification code	**2c**	
Empirical formula	$C_{10}\ H_{10}\ N_2\ O_2$	
Formula weight	190.20	
Temperature	293(2) K	
Diffractometer used	Siemens P4	
Radiation used, Wavelength	MoKα, 0.71073 Å	
Crystal system, Space group	Triclinic, $P\ \bar{1}$	
Unit cell dimensions	a = 7.478(1) Å	α= 78.30(1)°.
	b = 7.908(1) Å	β= 86.76(1)°.
	c = 8.284(1) Å	γ = 80.91(1)°.
Volume	473.53(10) $Å^3$	
Z, Calculated Density	2, 1.334 Mg/m^3	
Absorption coefficient	0.095 mm^{-1}	
F(000)	200	
Crystal size	0.27 x 0.23 x 0.16 mm	
Theta range for data collection	2.51 to 23.99°.	
Scan type	2θ-θ	
Scan speed	Variable, 2.0° to 60.0°/min. in ω	
Scan range (ω)	1.20° plus Kα separation	
Background measurement	Stationary crystal and stationary counter at the beginning and end of scan, each for 25.0% of total scan time	
Index ranges	$0\le h\le 8,\ -8\le k\le 8,\ -9\le l\le 9$	
Reflections collected	1607	
Independent reflections	1478 [R(int) = 0.0115]	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	1478 / 0 / 128	
Goodness-of-fit on F^2	1.001	
Weighting scheme	$1/[\sigma^2 (Fo^2)+(0.0755P)^2 +0.13P]$, $P=(\max(F_o^2,0)+2*F_c^2)/3$	
Data to parameter ratio	11.55:1	
Final R indices, 1208 reflections [I>2σ(I)]	R1 = 0.0470, wR2 = 0.1275	
R indices (all data)	R1 = 0.0574, wR2 = 0.1344	
Extinction coefficient	0.012(7)	
Largest diff. peak and hole	0.192 and -0.170 $e.Å^{-3}$	

Table S8. Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters ($Å^2$x 10^3) for 2c. U(eq) is defined as one third of the trace of the orthogonalized U^{ij} tensor.

	x	y	z	U(eq)
O(1)	188(2)	12849(2)	7524(2)	73(1)
O(2)	1850(2)	7850(2)	8378(2)	57(1)
N(1)	3058(2)	7626(2)	5815(2)	45(1)
N(2)	3641(3)	11686(3)	756(3)	80(1)
C(1)	1751(2)	10441(2)	6436(2)	42(1)
C(2)	2112(2)	11279(2)	4827(2)	42(1)
C(3)	2951(2)	10216(2)	3746(2)	42(1)
C(4)	3398(2)	8418(2)	4263(2)	41(1)
C(5)	2256(2)	8615(2)	6838(2)	42(1)
C(6)	872(3)	11360(3)	7712(3)	55(1)
C(7)	1653(3)	13211(3)	4235(3)	59(1)
C(8)	3343(3)	11017(3)	2069(3)	53(1)
C(9)	4249(3)	7270(3)	3117(3)	54(1)
C(10)	2421(3)	6011(3)	8904(3)	65(1)

Table S9. Bond lengths [Å] and angles [°] for 2c.

O(1)-C(6)	1.190(3)	O(2)-C(5)	1.337(2)
O(2)-C(10)	1.434(3)	N(1)-C(5)	1.324(2)
N(1)-C(4)	1.341(2)	N(2)-C(8)	1.136(3)
C(1)-C(2)	1.395(3)	C(1)-C(5)	1.409(3)
C(1)-C(6)	1.469(3)	C(2)-C(3)	1.407(3)
C(2)-C(7)	1.498(3)	C(3)-C(4)	1.391(3)
C(3)-C(8)	1.439(3)	C(4)-C(9)	1.493(3)
C(5)-O(2)-C(10)	118.97(16)	C(5)-N(1)-C(4)	117.53(16)
C(2)-C(1)-C(5)	117.53(17)	C(2)-C(1)-C(6)	123.48(17)
C(5)-C(1)-C(6)	118.98(17)	C(1)-C(2)-C(3)	116.71(16)
C(1)-C(2)-C(7)	123.16(17)	C(3)-C(2)-C(7)	120.13(17)
C(4)-C(3)-C(2)	121.40(16)	C(4)-C(3)-C(8)	119.76(17)
C(2)-C(3)-C(8)	118.84(17)	N(1)-C(4)-C(3)	121.47(17)
N(1)-C(4)-C(9)	116.60(16)	C(3)-C(4)-C(9)	121.93(17)
N(1)-C(5)-O(2)	118.74(16)	N(1)-C(5)-C(1)	125.34(17)
O(2)-C(5)-C(1)	115.91(16)	O(1)-C(6)-C(1)	126.9(2)
N(2)-C(8)-C(3)	178.4(2)		

Table S10. Anisotropic displacement parameters ($Å^2 x\ 10^3$) for 2c. 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}
O(1)	83(1)	61(1)	74(1)	-26(1)	5(1)	5(1)
O(2)	78(1)	48(1)	43(1)	-4(1)	11(1)	-12(1)
N(1)	48(1)	41(1)	45(1)	-7(1)	2(1)	-9(1)
N(2)	103(2)	76(1)	53(1)	3(1)	13(1)	-10(1)
C(1)	38(1)	44(1)	47(1)	-11(1)	-1(1)	-11(1)
C(2)	36(1)	42(1)	48(1)	-6(1)	-4(1)	-10(1)
C(3)	39(1)	47(1)	41(1)	-4(1)	-1(1)	-13(1)
C(4)	36(1)	45(1)	44(1)	-8(1)	0(1)	-11(1)
C(5)	43(1)	44(1)	40(1)	-5(1)	2(1)	-13(1)
C(6)	65(1)	51(1)	52(1)	-14(1)	6(1)	-13(1)
C(7)	67(1)	44(1)	62(1)	-4(1)	-1(1)	-8(1)
C(8)	56(1)	53(1)	48(1)	-4(1)	2(1)	-10(1)
C(9)	59(1)	53(1)	51(1)	-15(1)	7(1)	-9(1)
C(10)	92(2)	49(1)	49(1)	2(1)	2(1)	-13(1)

Table S11. Hydrogen coordinates (x 10^4) and isotropic displacement parameters ($Å^2$x 10^3) for 2c.

	x	y	z	U(eq)
H(6A)	848	10709	8780	66
H(7A)	362	13526	4167	88
H(7B)	2203	13538	3164	88
H(7C)	2099	13808	4992	88
H(9A)	4810	6177	3746	81
H(9B)	5148	7830	2429	81
H(9C)	3336	7065	2441	81
H(10A)	1886	5387	8224	97
H(10B)	2043	5654	10032	97
H(10C)	3717	5762	8808	97

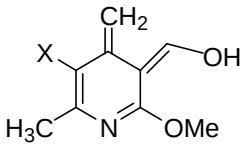
Table S12. Torsion angles [°] for 2c.

C(5)-C(1)-C(2)-C(3)	0.1(2)	C(6)-C(1)-C(2)-C(3)	-179.60(16)
C(5)-C(1)-C(2)-C(7)	-179.84(17)	C(6)-C(1)-C(2)-C(7)	0.5(3)
C(1)-C(2)-C(3)-C(4)	-0.2(2)	C(7)-C(2)-C(3)-C(4)	179.80(17)
C(1)-C(2)-C(3)-C(8)	179.65(16)	C(7)-C(2)-C(3)-C(8)	-0.4(3)
C(5)-N(1)-C(4)-C(3)	0.9(3)	C(5)-N(1)-C(4)-C(9)	-178.07(16)
C(2)-C(3)-C(4)-N(1)	-0.4(3)	C(8)-C(3)-C(4)-N(1)	179.84(16)
C(2)-C(3)-C(4)-C(9)	178.55(16)	C(8)-C(3)-C(4)-C(9)	-1.3(3)
C(4)-N(1)-C(5)-O(2)	177.92(15)	C(4)-N(1)-C(5)-C(1)	-1.0(3)
C(10)-O(2)-C(5)-N(1)	4.8(3)	C(10)-O(2)-C(5)-C(1)	-176.21(17)
C(2)-C(1)-C(5)-N(1)	0.5(3)	C(6)-C(1)-C(5)-N(1)	-179.81(17)
C(2)-C(1)-C(5)-O(2)	-178.46(15)	C(6)-C(1)-C(5)-O(2)	1.3(2)
C(2)-C(1)-C(6)-O(1)	8.8(3)	C(5)-C(1)-C(6)-O(1)	-170.9(2)
C(4)-C(3)-C(8)-N(2)	-173(9)	C(2)-C(3)-C(8)-N(2)	7(9)

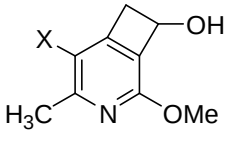
SEMI-EMPIRICAL AM1 CALCULATIONS

All the calculations were run using the MOPAC 6/pc Ver. 6.12. The energies were computed using the key words 'AM1' and 'Precise'. When the Herbert's test was not satisfied, the initial geometries were changed and the energies recomputed until the Peter's and Herbert's tests were satisfied.

The .ARC files of the following compounds as representative cases are collated below.



Enol



CB

2a: X = H
2b: X = Br
2c: X = CN
2d: X = CHO

SUMMARY OF AM1 CALCULATIONS for 2a-CB

MOPAC 6/PC VERSION 6.12

C9 H11 N O2

: 5/11/2002

AM1 PRECISE BONDS VECTORS

HERBERTS TEST WAS SATISFIED IN BFGS
SCF FIELD WAS ACHIEVED

HEAT OF FORMATION	=	-19.129949 KCAL
ELECTRONIC ENERGY	=	-10951.693152 EV
CORE-CORE REPULSION	=	8801.943044 EV
GRADIENT NORM	=	3.623077
DIPOLE	=	1.56712 DEBYE
NO. OF FILLED LEVELS	=	32
IONIZATION POTENTIAL	=	9.197877 EV
MOLECULAR WEIGHT	=	165.191
SCF CALCULATIONS	=	82
COMPUTATION TIME =	27.000 SECONDS	

FINAL GEOMETRY OBTAINED CHARGE

AM1 PRECISE BONDS VECTORS

C	.0000000	0	.000000	0	.000000	0	0	0	0	-.029
C	1.3699567	1	.000000	0	.000000	0	1	0	0	-.192
C	1.4320040	1	115.843441	1	.000000	0	2	1	0	.041
N	1.3479944	1	124.388981	1	-.227602	1	3	2	1	-.210
C	1.4975981	1	117.502755	1	-179.941227	1	3	2	1	-.177
C	1.3727225	1	118.505614	1	.322498	1	4	3	2	.170
C	1.3884255	1	121.133190	1	.177532	1	6	4	3	-.245
O	1.3797469	1	121.465607	1	-179.693025	1	6	4	3	-.208
C	1.5162520	1	148.001878	1	178.104314	1	7	6	4	.094
C	1.4277096	1	117.536920	1	.028295	1	8	6	4	-.063
O	1.4023838	1	116.973588	1	68.244019	1	9	7	6	-.314
C	1.5884519	1	86.816789	1	179.844889	1	9	7	6	-.121
H	1.0956940	1	120.516988	1	179.814992	1	2	3	1	.150
H	1.1085590	1	113.699851	1	117.087960	1	12	9	7	.109
H	1.1100216	1	113.096607	1	-114.641575	1	12	9	7	.126
H	1.1168186	1	110.216461	1	-2.689429	1	5	3	2	.085
H	1.1185455	1	110.286672	1	117.330292	1	5	3	2	.100
H	1.1183092	1	110.606990	1	-122.909950	1	5	3	2	.100
H	1.1195733	1	102.922418	1	179.237007	1	10	8	6	.098
H	1.1158653	1	110.715657	1	60.578766	1	10	8	6	.085
H	1.1161543	1	110.550434	1	-62.299263	1	10	8	6	.084
H	1.1151768	1	114.712562	1	-64.235539	1	9	7	6	.100
H	.9659393	1	106.783460	1	-56.062450	1	11	9	7	.217

0

SUMMARY OF AM1 CALCULATIONS for 2a-Enol

MOPAC 6/PC VERSION 6.12

C9 H11 N O2

: 5/11/2002

AM1 PRECISE BONDS VECTORS

HERBERTS TEST WAS SATISFIED IN BFGS
SCF FIELD WAS ACHIEVED

HEAT OF FORMATION	=	-26.961114 KCAL
ELECTRONIC ENERGY	=	-10937.733781 EV
CORE-CORE REPULSION	=	8787.644089 EV
GRADIENT NORM	=	3.381230
DIPOLE	=	.48591 DEBYE
NO. OF FILLED LEVELS	=	32
IONIZATION POTENTIAL	=	8.152940 EV
MOLECULAR WEIGHT	=	165.191
SCF CALCULATIONS	=	47
COMPUTATION TIME =	16.000 SECONDS	

FINAL GEOMETRY OBTAINED CHARGE

AM1 PRECISE BONDS VECTORS

C	.0000000	0	.000000	0	.000000	0	0	0	0	.000
C	1.4545846	1	.000000	0	.000000	0	1	0	0	-.199
C	1.3631094	1	121.901771	1	.000000	0	2	1	0	.005
N	1.4046001	1	122.021515	1	.969166	1	3	2	1	-.237
C	1.4924401	1	121.372555	1	-179.993447	1	3	2	1	-.165
C	1.3116269	1	117.528581	1	-5.351689	1	4	3	2	.185
C	1.4734127	1	126.415781	1	-1.666231	1	6	4	3	-.217
O	1.3826693	1	120.577880	1	178.190384	1	6	4	3	-.251
C	1.3581269	1	125.599052	1	-165.142249	1	7	6	4	.091
C	1.4288495	1	118.274396	1	.750618	1	8	6	4	-.057
O	1.3521465	1	129.210751	1	-1.906600	1	9	7	6	-.247
C	1.3465155	1	120.444340	1	-169.737071	1	1	2	3	-.240
H	1.0993963	1	121.049364	1	-179.003384	1	2	3	1	.139
H	1.0953497	1	123.495795	1	177.946182	1	12	1	2	.110
H	1.0971551	1	121.472965	1	-1.580954	1	12	1	2	.120
H	1.1197002	1	102.932379	1	-179.891333	1	10	8	6	.095
H	1.1160567	1	110.422037	1	-61.363547	1	10	8	6	.092
H	1.1160081	1	110.509354	1	61.409651	1	10	8	6	.088
H	1.1092241	1	122.276693	1	177.514897	1	9	7	6	.172
H	.9696945	1	111.910255	1	1.210217	1	11	9	7	.247
H	1.1168275	1	110.117761	1	-1.460198	1	5	3	2	.080
H	1.1183892	1	110.534076	1	-121.701003	1	5	3	2	.095
H	1.1184862	1	110.295777	1	118.597833	1	5	3	2	.093

0

SUMMARY OF AM1 CALCULATIONS for 2b-Enol

MOPAC 6/PC VERSION 6.12

C9 H10 N O2 Br

: 8/ 7/2001

AM1 PRECISE BONDS VECTORS

HERBERTS TEST WAS SATISFIED IN BFGS
SCF FIELD WAS ACHIEVED

HEAT OF FORMATION = -19.770341 KCAL
ELECTRONIC ENERGY = -12556.856187 EV
CORE-CORE REPULSION = 10067.259113 EV
WARNING -- GEOMETRY IS NOT AT A STATIONARY POINT
DIPOLE = 1.77212 DEBYE
NO. OF FILLED LEVELS = 35
IONIZATION POTENTIAL = 8.355455 EV
MOLECULAR WEIGHT = 244.088
SCF CALCULATIONS = 54
COMPUTATION TIME = 26.000 SECONDS

FINAL GEOMETRY OBTAINED CHARGE
AM1 PRECISE BONDS VECTORS

C	.0000000	0	.000000	0	.000000	0	0	0	0	.003
C	1.4618104	1	.000000	0	.000000	0	1	0	0	-.244
C	1.3721642	1	120.493518	1	.000000	0	2	1	0	.051
N	1.4022548	1	122.254194	1	-.633683	1	3	2	1	-.240
C	1.4947781	1	121.990335	1	178.494527	1	3	2	1	-.177
C	1.3131672	1	117.717798	1	-8.803296	1	4	3	2	.197
C	1.4691945	1	125.554537	1	-.435739	1	6	4	3	-.225
O	1.3797704	1	121.102410	1	179.634088	1	6	4	3	-.244
C	1.3449478	1	123.550758	1	-159.641678	1	1	2	3	-.221
C	1.3576443	1	125.865018	1	-159.850425	1	7	6	4	.096
C	1.4298630	1	118.232082	1	.023584	1	8	6	4	-.059
O	1.3520301	1	128.659641	1	-2.396993	1	10	7	6	-.244
Br	1.8725047	1	121.215833	1	-179.811818	1	2	3	1	.056
H	1.0971009	1	122.243447	1	176.362096	1	9	1	2	.113
H	1.0971083	1	122.898771	1	-3.207665	1	9	1	2	.135
H	1.1187618	1	109.561353	1	-58.641279	1	5	3	2	.099
H	1.1177708	1	112.239823	1	-178.983401	1	5	3	2	.102
H	1.1187324	1	109.500368	1	60.606268	1	5	3	2	.098
H	1.1091518	1	122.358078	1	176.703517	1	10	7	6	.176
H	1.1195759	1	102.898156	1	-179.840587	1	11	8	6	.099
H	1.1160370	1	110.454452	1	61.570758	1	11	8	6	.090
H	1.1161637	1	110.369629	1	-61.234835	1	11	8	6	.094
H	.9704750	1	111.562218	1	.528535	1	12	10	7	.247
0										

SUMMARY OF AM1 CALCULATIONS for 2b-CB

MOPAC 6/PC VERSION 6.12

C9 H10 N O2 Br

: 8/ 7/2001

AM1 PRECISE BONDS VECTORS

HERBERTS TEST WAS SATISFIED IN BFGS
SCF FIELD WAS ACHIEVED

HEAT OF FORMATION	=	-8.460372 KCAL
ELECTRONIC ENERGY	=	-12665.697437 EV
CORE-CORE REPULSION	=	10176.591994 EV
DIPOLE	=	3.66331 DEBYE
NO. OF FILLED LEVELS	=	35
IONIZATION POTENTIAL	=	9.252038 EV
MOLECULAR WEIGHT	=	244.088
SCF CALCULATIONS	=	59
COMPUTATION TIME =	28.000 SECONDS	

FINAL GEOMETRY OBTAINED CHARGE

AM1 PRECISE BONDS VECTORS

C	.0000000	0	.000000	0	.000000	0	0	0	0	-.001
C	1.3707632	1	.000000	0	.000000	0	1	0	0	-.243
C	1.4418203	1	115.366225	1	.000000	0	2	1	0	.069
N	1.3433229	1	124.153073	1	-.239452	1	3	2	1	-.156
C	1.4981577	1	118.273480	1	179.828467	1	3	2	1	-.186
C	1.3770947	1	119.126765	1	.409042	1	4	3	2	.189
C	1.3862309	1	120.607321	1	-1.003343	1	6	4	3	-.250
O	1.3776191	1	113.734724	1	179.495219	1	6	4	3	-.175
C	1.5164434	1	147.945354	1	-177.465314	1	7	6	4	.086
O	1.4045779	1	112.512922	1	-63.244107	1	9	7	6	-.312
C	1.5902172	1	86.850914	1	-179.527736	1	9	7	6	-.155
C	1.4292503	1	114.269010	1	-175.461927	1	8	6	4	-.083
Br	1.8604395	1	123.127161	1	-179.747923	1	2	3	1	.074
H	1.1159460	1	114.927959	1	65.216295	1	9	7	6	.098
H	.9657318	1	106.507712	1	-159.991137	1	10	9	7	.209
H	1.1092872	1	114.185550	1	-117.344289	1	11	9	7	.115
H	1.1102701	1	113.499165	1	113.811398	1	11	9	7	.121
H	1.1184156	1	109.321310	1	-59.585522	1	5	3	2	.102
H	1.1183549	1	109.355620	1	59.734606	1	5	3	2	.101
H	1.1181985	1	112.183757	1	-179.900147	1	5	3	2	.110
H	1.1187394	1	103.136575	1	173.978618	1	12	8	6	.110
H	1.1170809	1	109.930899	1	-67.403675	1	12	8	6	.072
H	1.1183807	1	110.866965	1	54.581253	1	12	8	6	.104
0										

SUMMARY OF AM1 CALCULATIONS for 2c-Enol

MOPAC 6/PC VERSION 6.12

C10 H10 N2 O2

: 8/ 7/2001

AM1 PRECISE BONDS VECTORS

HERBERTS TEST WAS SATISFIED IN BFGS
SCF FIELD WAS ACHIEVED

HEAT OF FORMATION	=	5.399624 KCAL
ELECTRONIC ENERGY	=	-13098.695074 EV
CORE-CORE REPULSION	=	10628.130457 EV
DIPOLE	=	4.12372 DEBYE
NO. OF FILLED LEVELS	=	36
IONIZATION POTENTIAL	=	8.519930 EV
MOLECULAR WEIGHT	=	190.201
SCF CALCULATIONS	=	79

COMPUTATION TIME = 30.000 SECONDS

FINAL GEOMETRY OBTAINED CHARGE

AM1 PRECISE BONDS VECTORS

C	.0000000	0	.000000	0	.000000	0	0	0	0	.004
C	1.4655384	1	.000000	0	.000000	0	1	0	0	-.096
C	1.3757437	1	120.911073	1	.000000	0	2	1	0	.076
N	1.3993716	1	122.168970	1	-.199023	1	3	2	1	-.250
C	1.4941906	1	122.228279	1	178.862927	1	3	2	1	-.180
C	1.3153899	1	117.814388	1	-6.409001	1	4	3	2	.210
C	1.4691547	1	125.966890	1	-1.860347	1	6	4	3	-.229
O	1.3783298	1	120.723513	1	178.531736	1	6	4	3	-.244
C	1.3451947	1	121.765889	1	-164.548865	1	1	2	3	-.223
C	1.4184760	1	121.693987	1	-178.928155	1	2	3	1	-.077
C	1.3593177	1	125.670476	1	-161.657114	1	7	6	4	.103
C	1.4305499	1	118.401323	1	.157300	1	8	6	4	-.059
O	1.3503831	1	128.946429	1	-2.830656	1	11	7	6	-.241
H	1.0964283	1	122.808289	1	177.010578	1	9	1	2	.114
H	1.0975854	1	122.201281	1	-2.443302	1	9	1	2	.133
H	1.1165216	1	111.006076	1	3.535215	1	5	3	2	.097
H	1.1194701	1	109.976939	1	-116.732612	1	5	3	2	.104
H	1.1190485	1	110.332567	1	124.004867	1	5	3	2	.103
H	1.1098318	1	122.225027	1	176.576690	1	11	7	6	.177
H	1.1196196	1	102.832845	1	-179.968220	1	12	8	6	.100
H	1.1159655	1	110.433942	1	61.325081	1	12	8	6	.092
H	1.1159057	1	110.347358	1	-61.420246	1	12	8	6	.096
H	.9703341	1	111.927635	1	.899044	1	13	11	7	.248
N	1.1646128	1	179.388874	1	-160.159375	1	10	2	3	-.058
0										

SUMMARY OF AM1 CALCULATIONS for 2c-CB

MOPAC 6/PC VERSION 6.12

```
 C10 H10 N2  O2
                                                    : 8/ 7/2001
AM1 PRECISE BONDS VECTORS


    HERBERTS TEST WAS SATISFIED IN BFGS
    SCF FIELD WAS ACHIEVED


         HEAT OF FORMATION       =        18.663619 KCAL
         ELECTRONIC ENERGY       =    -13201.451535 EV
         CORE-CORE REPULSION     =     10731.462088 EV
         GRADIENT NORM           =         2.390663
         DIPOLE                  =         4.02049 DEBYE
         NO. OF FILLED LEVELS    =        36
         IONIZATION POTENTIAL    =         9.540134 EV
         MOLECULAR WEIGHT        =       190.201
         SCF CALCULATIONS        =        57
         COMPUTATION TIME =  24.000 SECONDS


         FINAL GEOMETRY OBTAINED                                    CHARGE
AM1 PRECISE BONDS VECTORS


 C     .0000000  0       .000000  0       .000000  0    0    0    0       .016
 C    1.3773413  1       .000000  0       .000000  0    1    0    0      -.085
 C    1.4438023  1    115.581318  1       .000000  0    2    1    0       .080
 N    1.3441117  1    123.953120  1       .099657  1    3    2    1      -.162
 C    1.4985529  1    118.877471  1   -179.868211  1    3    2    1      -.186
 C    1.3766294  1    119.183586  1      -.085447  1    4    3    2       .199
 C    1.3872601  1    120.735674  1      -.721441  1    6    4    3      -.257
 O    1.3759867  1    113.632594  1    179.650596  1    6    4    3      -.172
 C    1.5170498  1    147.864970  1   -177.555001  1    7    6    4       .087
 O    1.4040778  1    112.426635  1    -63.128593  1    9    7    6      -.311
 C    1.5903187  1     86.889833  1   -179.292634  1    9    7    6      -.160
 C    1.4298923  1    114.368667  1   -175.730980  1    8    6    4      -.084
 C    1.4144502  1    122.219974  1   -179.841240  1    2    3    1      -.079
 H    1.1158783  1    114.910676  1     65.507679  1    9    7    6       .099
 H     .9658713  1    106.555662  1   -162.435832  1   10    9    7       .211
 H    1.1092252  1    114.210035  1   -117.513304  1   11    9    7       .117
 H    1.1103491  1    113.449304  1    113.688628  1   11    9    7       .123
 N    1.1640519  1    178.663216  1    179.820171  1   13    2    3      -.043
 H    1.1158783  1    111.138780  1     -4.265965  1    5    3    2       .097
 H    1.1193954  1    109.913191  1    116.024678  1    5    3    2       .109
 H    1.1193137  1    110.357982  1   -124.740325  1    5    3    2       .110
 H    1.1187787  1    103.099772  1    174.495840  1   12    8    6       .112
 H    1.1183202  1    110.796502  1     55.096352  1   12    8    6       .105
 H    1.1170012  1    109.935001  1    -66.870529  1   12    8    6       .073
 0
```

SUMMARY OF AM1 CALCULATIONS for 2d-Enol

MOPAC 6/PC VERSION 6.12

C10 H11 N O3

: 8/ 7/2001

AM1 PRECISE BONDS VECTORS

HERBERTS TEST WAS SATISFIED IN BFGS
SCF FIELD WAS ACHIEVED

HEAT OF FORMATION	=	-54.227110 KCAL
ELECTRONIC ENERGY	=	-13792.800905 EV
CORE-CORE REPULSION	=	11194.620538 EV
GRADIENT NORM	=	5.620391
DIPOLE	=	3.22860 DEBYE
NO. OF FILLED LEVELS	=	37
IONIZATION POTENTIAL	=	8.344145 EV
MOLECULAR WEIGHT	=	193.202
SCF CALCULATIONS	=	48

COMPUTATION TIME = 20.000 SECONDS

FINAL GEOMETRY OBTAINED CHARGE

AM1 PRECISE BONDS VECTORS

C	.0000000	0	.000000	0	.000000	0	0	0	0	.014
C	1.4603226	1	.000000	0	.000000	0	1	0	0	-.232
C	1.3725703	1	121.065443	1	.000000	0	2	1	0	.057
N	1.3975894	1	122.688618	1	1.277140	1	3	2	1	-.248
C	1.4956533	1	120.744205	1	-178.664800	1	3	2	1	-.181
C	1.3152863	1	117.527185	1	3.322740	1	4	3	2	.207
C	1.4695498	1	126.408159	1	1.302981	1	6	4	3	-.223
O	1.3796796	1	120.110481	1	-178.578581	1	6	4	3	-.249
C	1.3466640	1	121.102861	1	168.179554	1	1	2	3	-.229
C	1.4732382	1	119.395701	1	178.672518	1	2	3	1	.235
C	1.3602607	1	125.314817	1	169.192439	1	7	6	4	.100
C	1.4300861	1	118.493970	1	.033258	1	8	6	4	-.057
O	1.3502949	1	129.448752	1	1.386296	1	11	7	6	-.244
H	1.0953637	1	123.585527	1	-176.876654	1	9	1	2	.112
H	1.0983782	1	121.723522	1	3.640095	1	9	1	2	.132
H	1.1180458	1	109.677385	1	-46.954249	1	5	3	2	.091
H	1.1175133	1	112.349529	1	-167.592090	1	5	3	2	.107
H	1.1192499	1	109.161947	1	72.193578	1	5	3	2	.092
H	1.1100302	1	122.243286	1	-178.017769	1	11	7	6	.176
H	1.1197808	1	102.925686	1	-179.843541	1	12	8	6	.098
H	1.1160887	1	110.251318	1	61.782169	1	12	8	6	.093
H	1.1160226	1	110.463403	1	-61.205533	1	12	8	6	.092
H	.9694465	1	112.319486	1	-2.552279	1	13	11	7	.248
O	1.2315315	1	124.835931	1	128.963135	1	10	2	3	-.282
H	1.1165567	1	114.183376	1	-49.837508	1	10	2	3	.087
0										

SUMMARY OF AM1 CALCULATIONS for 2d-CB

MOPAC 6/PC VERSION 6.12

C10 H11 N O3

: 8/ 7/2001

AM1 PRECISE BONDS VECTORS

HERBERTS TEST WAS SATISFIED IN BFGS
SCF FIELD WAS ACHIEVED

HEAT OF FORMATION = -47.056497 KCAL
ELECTRONIC ENERGY = -13917.341662 EV
CORE-CORE REPULSION = 11319.472235 EV
DIPOLE = .39869 DEBYE
NO. OF FILLED LEVELS = 37
IONIZATION POTENTIAL = 9.639472 EV
MOLECULAR WEIGHT = 193.202
SCF CALCULATIONS = 98
COMPUTATION TIME = 42.000 SECONDS

FINAL GEOMETRY OBTAINED CHARGE

AM1 PRECISE BONDS VECTORS

C	.0000000	0	.000000	0	.000000	0	0	0	0	.040
C	1.3765977	1	.000000	0	.000000	0	1	0	0	-.243
C	1.4431068	1	114.986278	1	.000000	0	2	1	0	.077
N	1.3425556	1	124.480821	1	-.135770	1	3	2	1	-.168
C	1.4995327	1	118.229143	1	179.799513	1	3	2	1	-.188
C	1.3781323	1	119.013157	1	-.199332	1	4	3	2	.203
C	1.3866985	1	120.695029	1	.077688	1	6	4	3	-.326
O	1.3759959	1	113.688363	1	179.471876	1	6	4	3	-.173
C	1.5217065	1	147.993345	1	-178.635833	1	7	6	4	.095
O	1.3958496	1	116.782124	1	-62.488203	1	9	7	6	-.306
C	1.5892434	1	86.665077	1	179.998425	1	9	7	6	-.157
C	1.4300680	1	114.329465	1	176.559783	1	8	6	4	-.083
C	1.4644024	1	122.174116	1	-179.790330	1	2	3	1	.234
H	1.1153378	1	115.700072	1	63.681139	1	9	7	6	.138
H	.9662564	1	107.972787	1	-50.298788	1	10	9	7	.211
H	1.1097157	1	114.162811	1	-116.610882	1	11	9	7	.127
H	1.1102294	1	114.048272	1	115.102434	1	11	9	7	.124
H	1.1180838	1	109.337749	1	59.712217	1	5	3	2	.096
H	1.1185799	1	112.260021	1	179.880858	1	5	3	2	.115
H	1.1180532	1	109.322153	1	-59.906490	1	5	3	2	.096
H	1.1188670	1	103.113416	1	176.109288	1	12	8	6	.113
H	1.1168460	1	110.029326	1	-65.240862	1	12	8	6	.078
H	1.1184080	1	110.793771	1	56.805195	1	12	8	6	.096
O	1.2340503	1	123.533573	1	178.239328	1	13	2	3	-.292
H	1.1141445	1	115.785092	1	-1.800352	1	13	2	3	.094

0

Ab Initio (HF/6-31G**) Calculations

Summary of HF calculations for 2a(E-enol)

Basis set : 6-31G(d,p)

No. of Imaginary frequencies=0

HF=-551.3635713 Hartrees

Final optimized structure in Cartesian coordinates:

C	0.000000	0.000000	0.000000
C	0.000000	0.000000	1.466933
C	1.360782	0.000000	2.065720
C	2.439421	0.421505	1.161083
N	2.342233	0.541835	-0.089120
C	1.104989	0.261266	-0.693341
C	-1.132090	0.025682	2.166471
C	1.582112	-0.461197	3.306031
O	2.716663	-0.507350	3.981664
O	3.611149	0.659893	1.766029
C	4.714580	1.039669	0.959515
C	1.154459	0.311848	-2.191336
H	0.187625	0.098267	-2.630342
H	1.481441	1.293747	-2.520118
H	1.876548	-0.408189	-2.565226
H	-1.153268	0.112676	3.237215
H	-2.083578	-0.026178	1.668824
H	0.770110	-0.877796	3.871050
H	5.540174	1.176537	1.642144
H	4.940661	0.266951	0.239243
H	4.498515	1.960252	0.437793
H	-0.931761	-0.168775	-0.508119
H	3.412972	-0.101115	3.481552

Summary of HF calculations for 2a(Z-enol)

Basis set : 6-31G(d,p)

No. of Imaginary frequencies=0

HF =-551.3574321 Hartrees

Final optimized structure in Cartesian coordinates:

C	0.000000	0.000000	0.000000
C	0.000000	0.000000	1.328863
C	1.239598	0.000000	2.114474
C	2.480031	-0.000071	1.295036
C	2.286031	-0.000038	-0.170045
N	1.175137	-0.000009	-0.766250
C	1.191733	0.000060	3.446495

C	3.738276	-0.000180	1.741272
O	4.069528	-0.000261	3.034506
O	3.418663	-0.000018	-0.872444
C	3.325001	0.000363	-2.282222
C	-1.248323	-0.000022	-0.831395
H	-2.139357	0.000138	-0.215289
H	-1.267002	0.873652	-1.476425
H	-1.267140	-0.873881	-1.476172
H	2.061739	0.000063	4.067363
H	0.235346	0.000125	3.939278
H	4.554651	-0.000254	1.045867
H	4.344022	0.001072	-2.641376
H	2.803368	-0.879623	-2.631558
H	2.802300	0.879902	-2.631042
H	5.005467	-0.000301	3.142053
H	-0.929653	0.000000	1.868111

Summary of HF calculations for 2b(E-enol)

Basis set : 6-31G(d,p)

No. of Imaginary frequencies=0

HF =-3120.6656769 Hartrees

Final optimized structure in Cartesian coordinates:

C	0.000000	0.000000	0.000000
C	0.000000	0.000000	1.334324
C	1.257552	0.000000	2.107310
C	2.431648	-0.410542	1.293234
C	2.287777	-0.205480	-0.148216
N	1.192997	-0.009824	-0.740926
Br	-1.629221	0.072768	2.317847
C	1.356990	0.360887	3.382152
C	3.489518	-1.021563	1.847824
O	4.613083	-1.404489	1.269054
O	3.426437	-0.267471	-0.844501
C	3.359848	-0.116200	-2.255151
C	-1.202719	0.034246	-0.896222
H	-2.133306	0.021320	-0.353025
H	-1.159027	0.927899	-1.510756
H	-1.166640	-0.818080	-1.567343
H	2.313713	0.442595	3.863454
H	0.493589	0.591618	3.972886
H	3.473448	-1.274526	2.890841
H	4.377851	-0.202906	-2.604074
H	2.741103	-0.888162	-2.688763
H	2.953851	0.851793	-2.508371
H	4.628466	-1.130582	0.361001

Summary of HF calculations for 2b(Z-enol)

Basis set : 6-31G(d,p)

No. of Imaginary frequencies=0

HF=-3120.6589243 Hartrees

Final optimized structure in Cartesian coordinates:

C	0.000000	0.000000	0.000000
C	0.000000	0.000000	1.479015
C	1.368852	0.000000	2.063416
C	2.462939	0.338057	1.140373
N	2.348605	0.437602	-0.111535
C	1.105985	0.202374	-0.716518
C	-1.107422	0.016318	2.214956
C	1.707058	-0.313963	3.316166
O	0.838163	-0.674679	4.261302
O	3.642322	0.532438	1.720623
C	4.752168	0.826087	0.893682
C	1.215925	0.232130	-2.212988
Br	-1.674085	-0.279845	-0.870579
H	0.281799	0.034464	-2.712190
H	1.586195	1.205789	-2.518520
H	1.952410	-0.501613	-2.525274
H	-1.070443	0.044536	3.282966
H	-2.074642	0.002079	1.755349
H	1.284452	-0.918816	5.054494
H	2.738507	-0.284982	3.609590
H	5.591624	0.936532	1.564243
H	4.930857	0.021974	0.193794
H	4.585702	1.741638	0.344320

Summary of HF calculations for 2c(E-enol)

Basis set : 6-31G(d,p)

No. of Imaginary frequencies=0

HF=-643.0991304 Hartrees

Final optimized structure in Cartesian coordinates:

C	0.000000	0.000000	0.000000
C	0.000000	0.000000	1.479171
C	1.365906	0.000000	2.060793
C	2.420514	0.492226	1.174987
N	2.311304	0.644200	-0.077495
C	1.106990	0.317810	-0.693085
C	-1.115231	0.026838	2.200401
C	1.610476	-0.517205	3.276436
O	2.747581	-0.557119	3.941405
O	3.578724	0.760616	1.773299

C	4.667764	1.210363	0.975487
C	1.186787	0.380597	-2.188997
C	-1.232999	-0.286792	-0.682565
N	-2.217722	-0.515777	-1.204155
H	0.253095	0.127460	-2.668943
H	1.482441	1.381659	-2.485435
H	1.961511	-0.297790	-2.531672
H	-1.094902	0.115397	3.270648
H	-2.082170	-0.029510	1.737347
H	0.816047	-0.991211	3.820841
H	5.485349	1.360453	1.663873
H	4.922878	0.467166	0.234890
H	4.410939	2.135896	0.482956
H	3.428999	-0.098222	3.467437

Summary of HF calculations for 2c(Z-enol)

Basis set : 6-31G(d,p)

No. of Imaginary frequencies=0

HF=-643.0935903 Hartrees

Final optimized structure in Cartesian coordinates:

C	0.000000	0.000000	0.000000
C	0.000000	0.000000	1.342965
C	1.253579	0.000000	2.132233
C	2.481085	-0.087647	1.299544
C	2.286061	-0.040303	-0.158148
N	1.167284	0.000452	-0.751765
C	-1.248598	0.010157	2.058369
N	-2.228776	0.018758	2.635961
C	1.238931	0.075925	3.460752
C	3.738889	-0.220928	1.733346
O	4.080138	-0.291021	3.017144
O	3.403224	-0.047420	-0.868471
C	3.305729	-0.017213	-2.282086
C	-1.233281	0.004649	-0.853525
H	-2.145369	0.003697	-0.275555
H	-1.215724	0.880369	-1.494258
H	-1.218111	-0.866220	-1.500981
H	2.133907	0.084406	4.043899
H	0.306770	0.132622	3.990473
H	4.543255	-0.278892	1.026527
H	4.324161	-0.031283	-2.640309
H	2.764832	-0.879476	-2.644269
H	2.802155	0.881027	-2.608527
H	5.010128	-0.407258	3.117118

Summary of HF calculations for 2d(E-enol)

Basis set : 6-31G(d,p)

No. of Imaginary frequencies=0

HF=-664.0868893 Hartrees

Final optimized structure in Cartesian coordinates:

C	0.000000	0.000000	0.000000
C	0.000000	0.000000	1.487277
C	1.362707	0.000000	2.078951
C	2.377852	0.643497	1.253018
N	2.254993	0.873783	0.014009
C	1.102011	0.445102	-0.643925
C	-1.088221	0.051464	2.248426
C	1.634536	-0.616354	3.238552
O	2.775882	-0.649544	3.905277
O	3.504297	0.972723	1.881342
C	4.550056	1.574201	1.129593
C	1.298902	0.577745	-2.132052
C	-1.179906	-0.458295	-0.757617
O	-2.206909	-0.843495	-0.284274
H	0.444953	0.319633	-2.735796
H	1.576885	1.604049	-2.345336
H	2.137117	-0.044808	-2.428482
H	-1.001536	0.157627	3.315185
H	-2.072498	-0.011838	1.836117
H	3.421408	-0.094403	3.488683
H	0.869098	-1.187870	3.728265
H	5.349082	1.747175	1.834446
H	4.874483	0.913262	0.339448
H	4.213553	2.506613	0.701888
H	-1.075503	-0.448996	-1.841304

Summary of HF calculations for 2d(Z-enol)

Basis set : 6-31G(d,p)

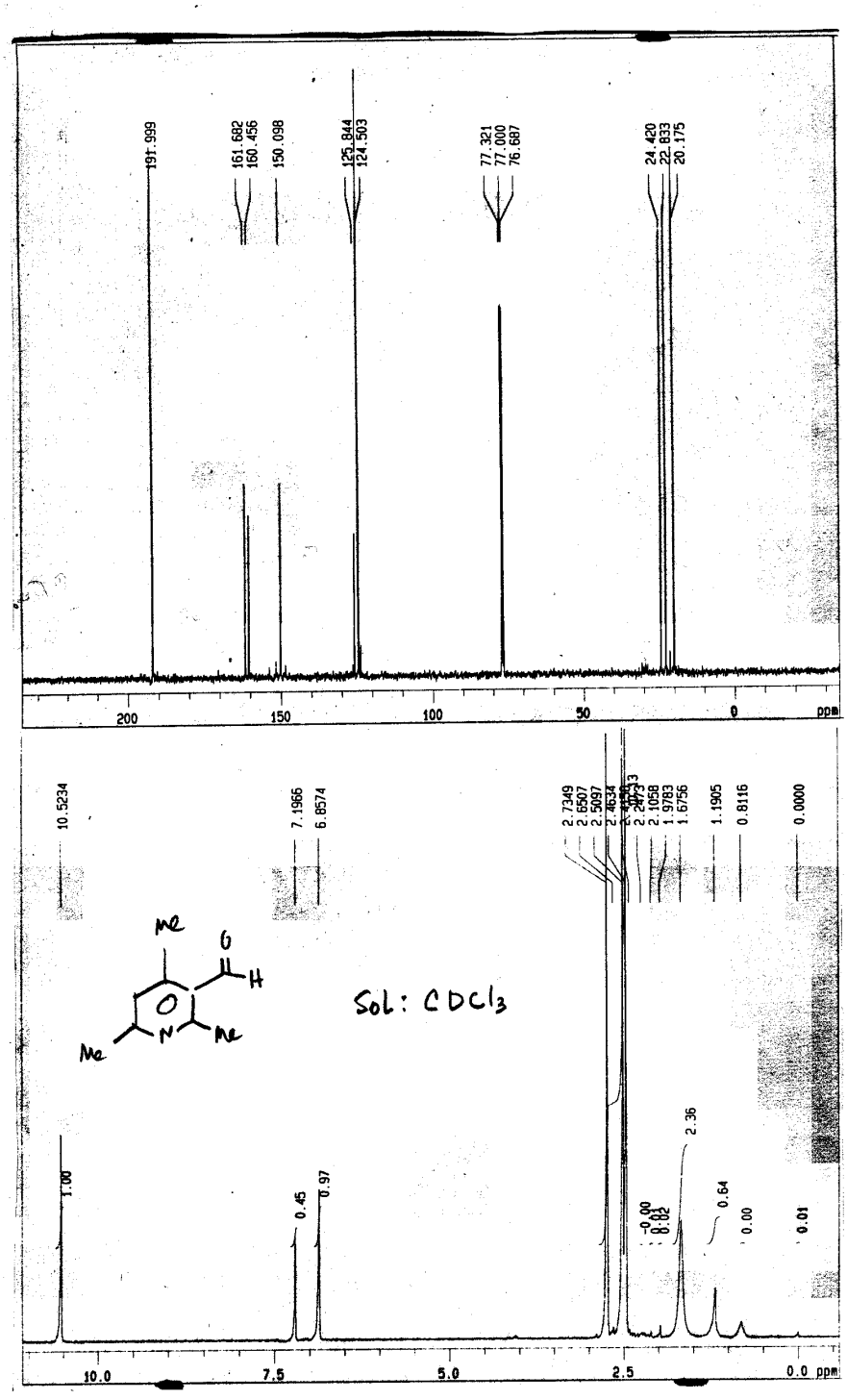
No. of Imaginary frequencies=0

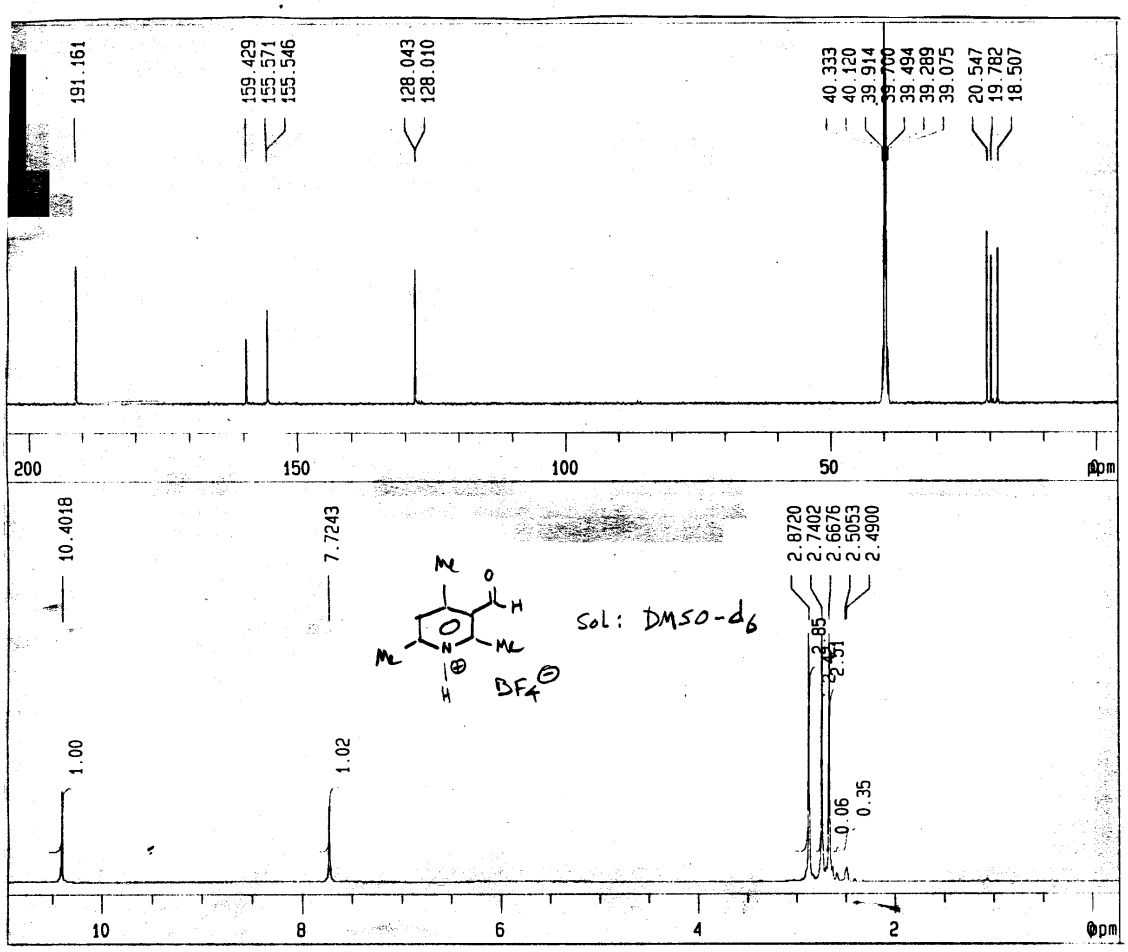
HF=-664.079405 Hartrees

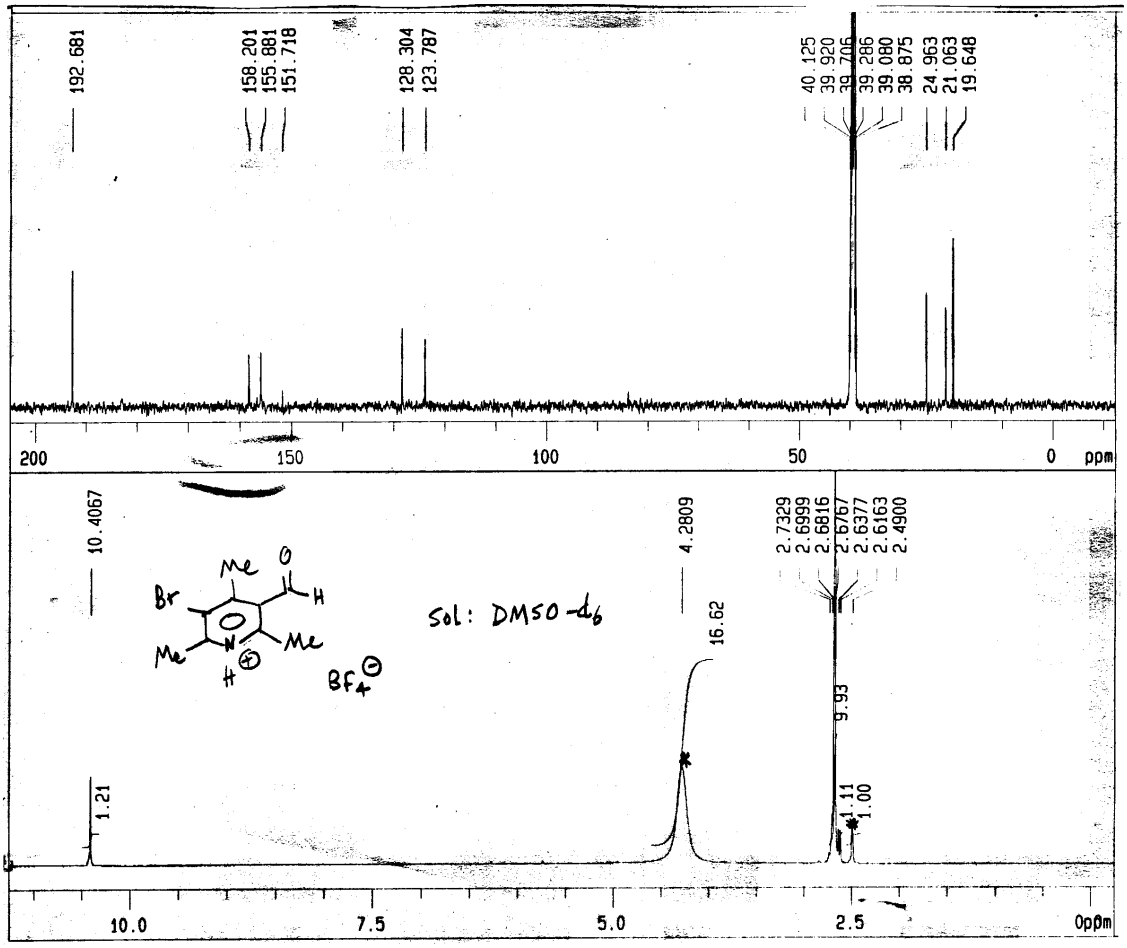
Final optimized structure in Cartesian coordinates:

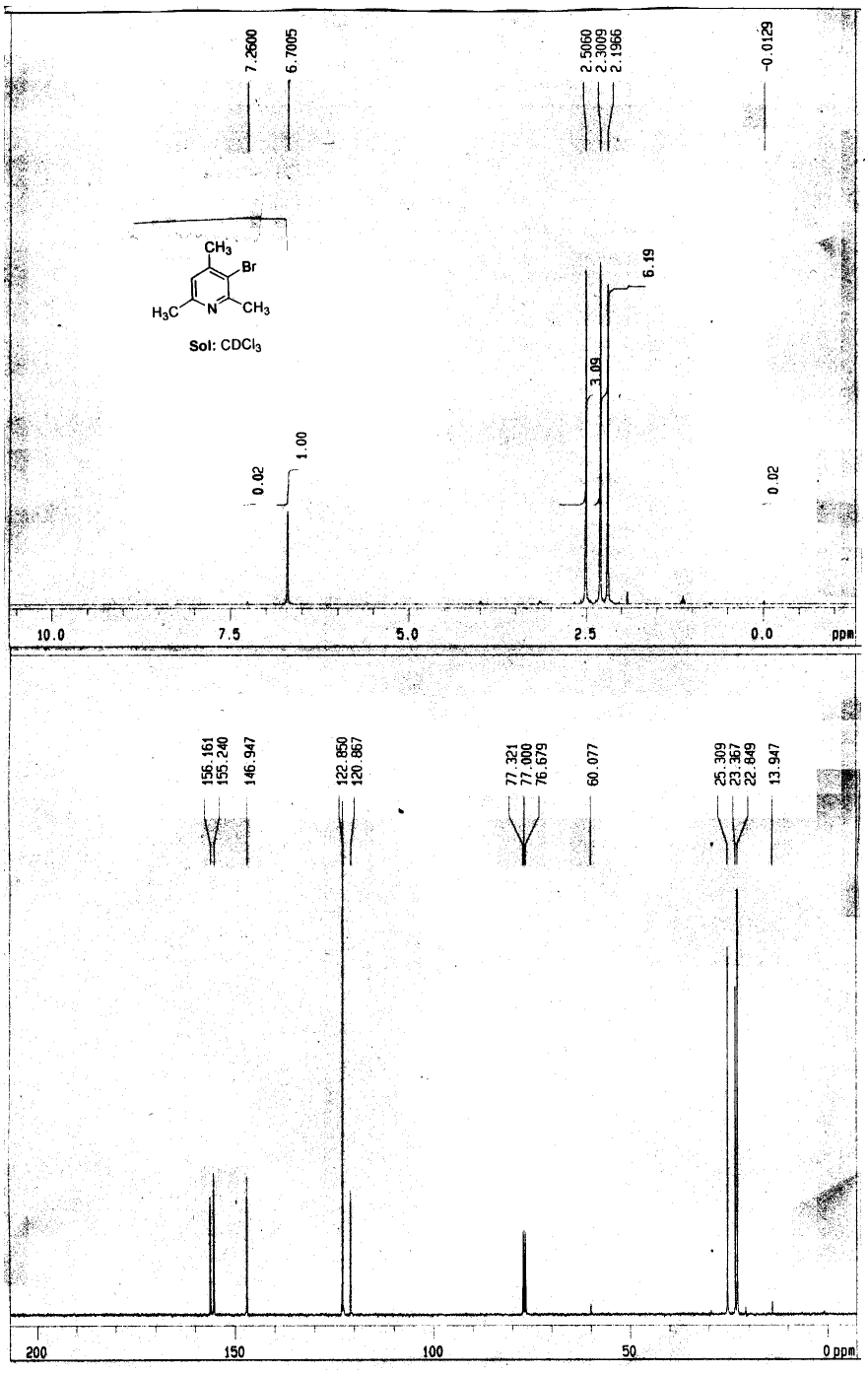
C	0.000000	0.000000	0.000000
C	0.000000	0.000000	1.489426
C	1.360690	0.000000	2.087577
C	2.412780	0.557869	1.233337
N	2.296567	0.754983	-0.013311
C	1.119836	0.377914	-0.656004
C	-1.096885	0.039534	2.238967
C	1.723782	-0.478397	3.278678
O	0.881916	-1.049369	4.141466

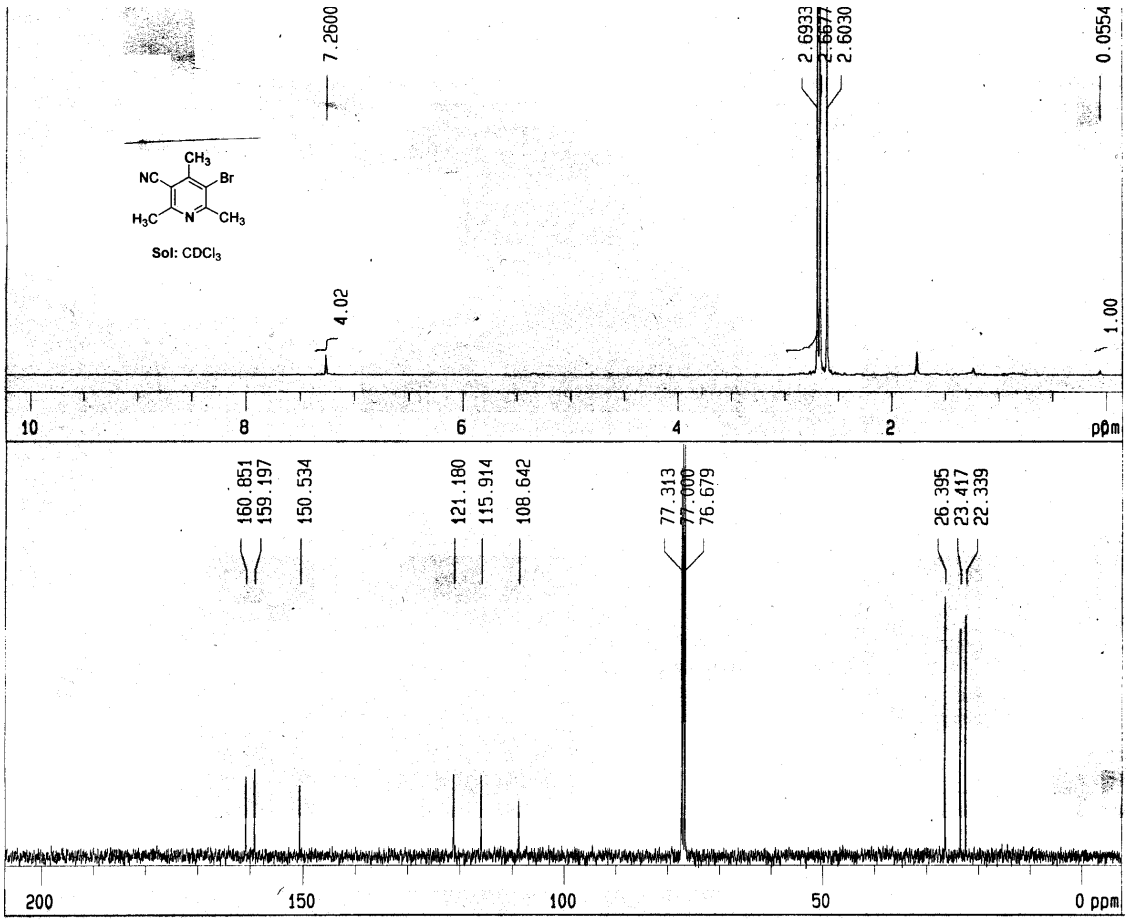
O	3.547606	0.850309	1.848018
C	4.623182	1.352820	1.075647
C	1.319011	0.478987	-2.147135
C	-1.195755	-0.412525	-0.758565
O	-2.245223	-0.749037	-0.296043
H	0.452077	0.263388	-2.748787
H	1.655850	1.484812	-2.372785
H	2.120512	-0.193706	-2.435753
H	-1.028174	0.078257	3.307695
H	-2.071816	0.021668	1.801511
H	1.345062	-1.404093	4.881320
H	2.749651	-0.415715	3.588874
H	5.432223	1.506894	1.773986
H	4.910662	0.642259	0.313752
H	4.348678	2.285590	0.604709
H	-1.082326	-0.415292	-1.841195

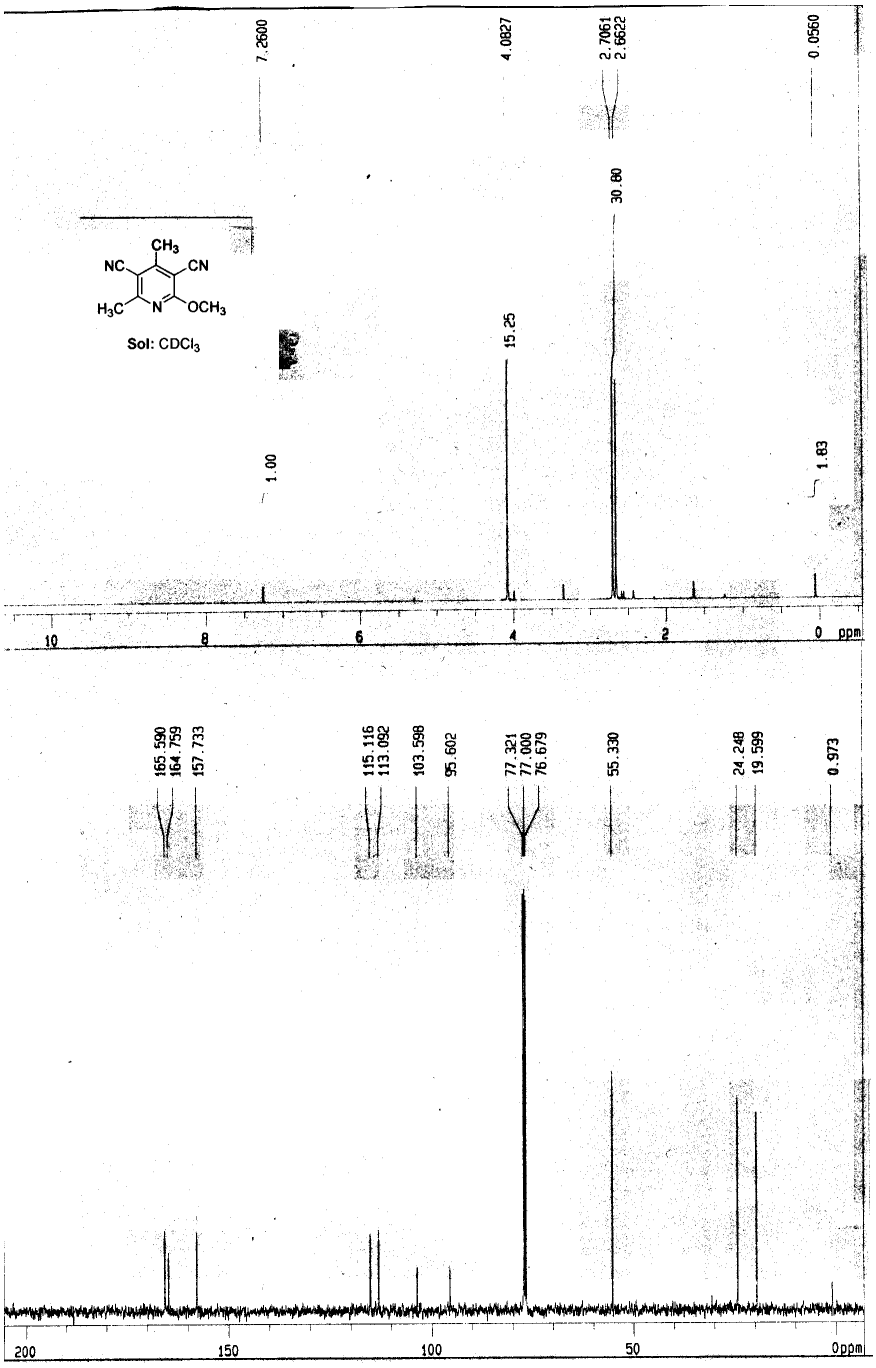

191.999
161.682
160.456
150.098
125.844
124.503
77.321
77.000
76.687
24.420
22.633
20.175
200
150
100
50
0
ppm
10.5234
7.1966
6.8574
2.7349
2.6507
2.5097
2.4634
2.4473
2.4313
2.2473
2.1058
1.9783
1.6756
1.1905
0.8116
0.0000
Me
O
H
N
Me
Me
Sol: CDCl3
1.00
0.45
0.97
2.36
0.64
0.00
0.01
10.0
7.5
5.0
2.5
0.0 ppm

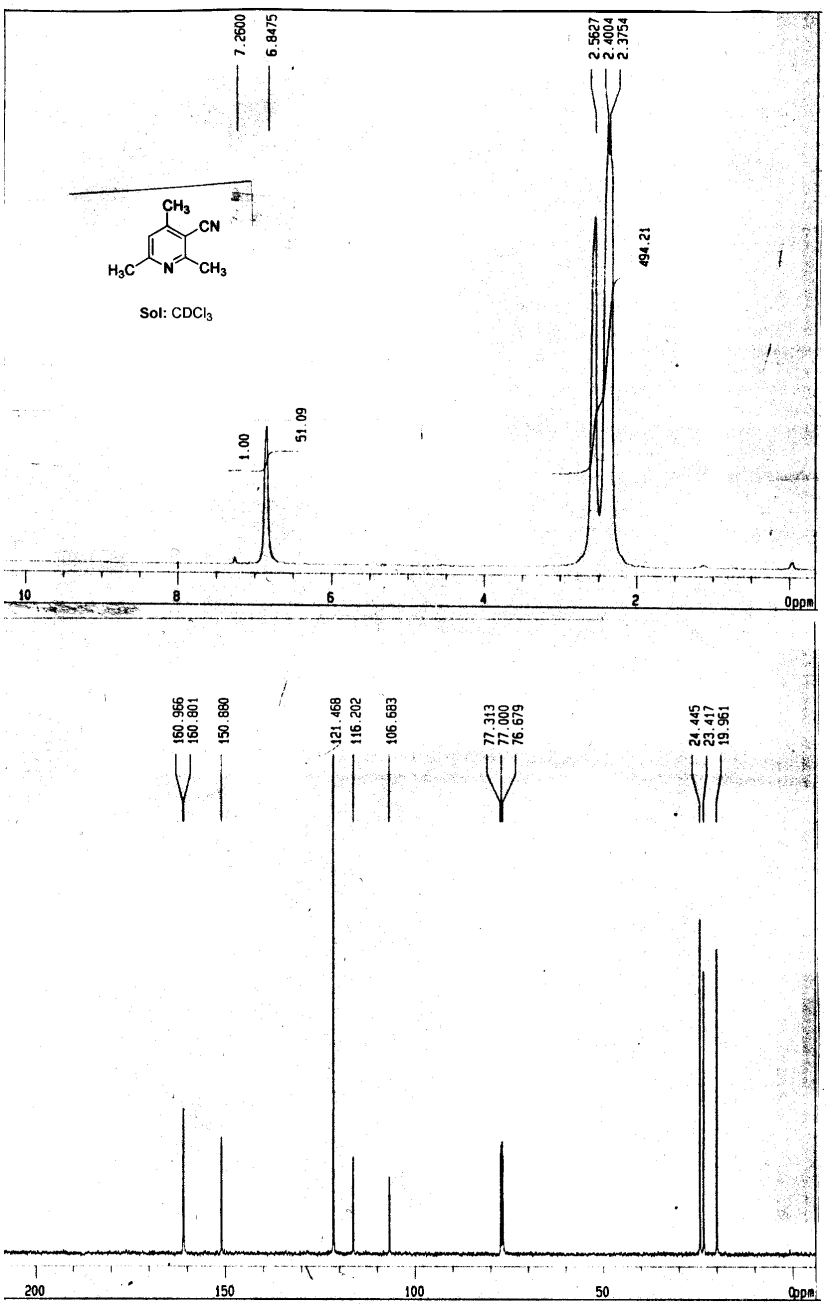

191.161
159.429
155.571
155.546
128.043
128.010
40.333
40.120
39.914
39.700
39.494
39.289
39.075
20.547
19.782
18.507
200
150
100
50
ppm
10.4018
7.7243
2.8720
2.7402
2.6676
2.5053
2.4900
Me
O
H
Me
N
H
Me
BF4
Sol: DMSO-d6
1.00
1.02
0.06
0.35
10
8
6
4
2
ppm

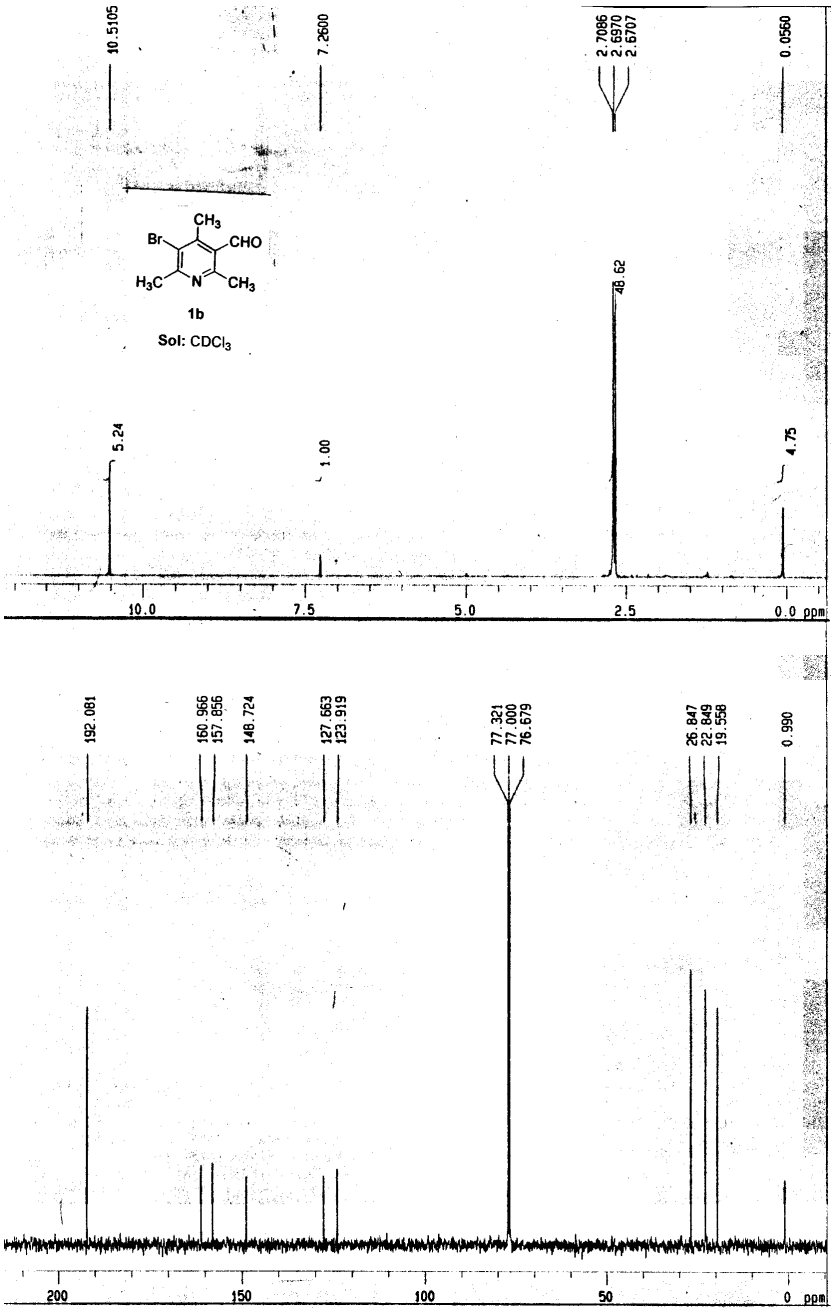

192.681
158.201
155.881
151.718
128.304
123.787
40.125
39.920
39.706
39.286
39.080
38.875
24.963
21.063
19.648
200
150
100
50
0
ppm
10.4067
4.2809
2.7329
2.6999
2.6816
2.6767
2.6377
2.6163
2.4900
Me
O
H
Br
Me
Me
H
BF4
Sol: DMSO-d6
16.62
9.93
1.21
1.11
1.00
10.0
7.5
5.0
2.5
0ppm

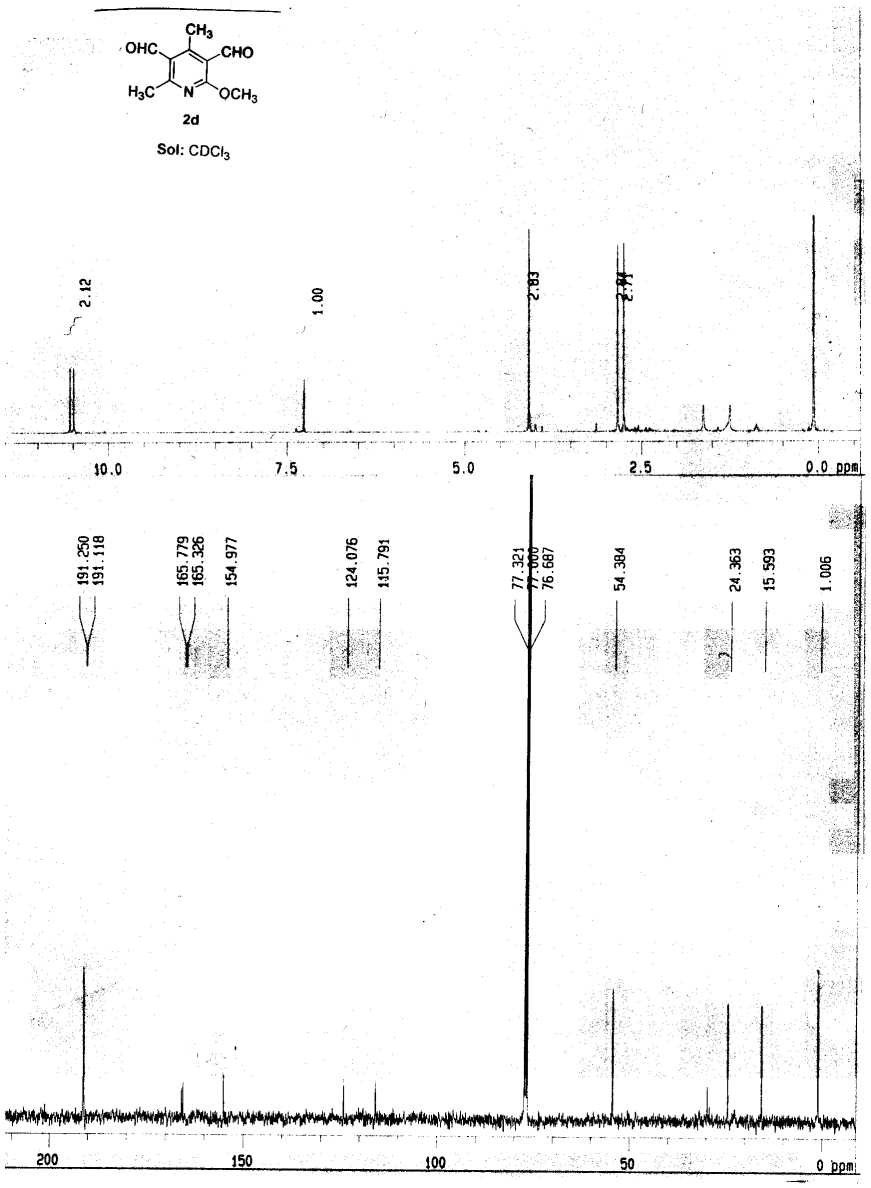

7.2600
6.7005
2.5060
2.3009
2.1966
-0.0129
CH3
Br
H3C
N
CH3
Sol: CDCl3
6.19
3.09
1.00
0.02
0.02
10.0
7.5
5.0
2.5
0.0
ppm
156.161
155.240
146.947
122.850
120.867
77.321
77.000
76.679
60.077
25.309
23.367
22.849
13.947
200
150
100
50
0 ppm

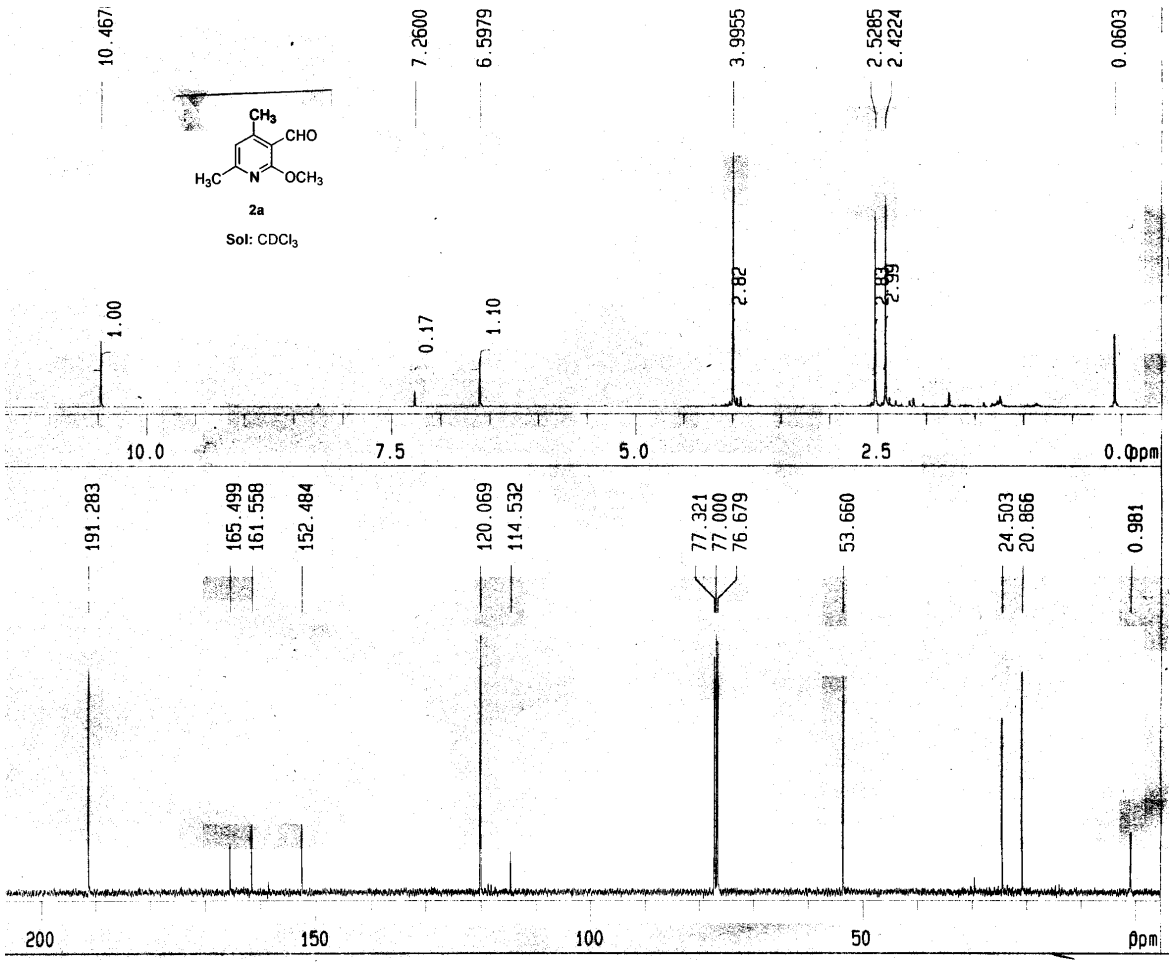

7.2600
2.6933
2.6677
2.6030
0.0554
4.02
1.00
CH3
NC
Br
H3C
N
CH3
Sol: CDCl3
10
8
6
4
2
ppm
160.851
159.197
150.534
121.180
115.914
108.642
77.313
77.000
76.679
26.395
23.417
22.339
200
150
100
50
0 ppm


7.2600
4.0827
2.7061
2.6622
0.0560
30.60
15.25
1.00
1.83
CH3
NC
CN
H3C
N
OCH3
Sol: CDCl3
10
8
6
4
2
0 ppm
165.590
164.759
157.733
115.116
113.092
103.598
95.602
77.321
77.000
76.679
55.330
24.248
19.599
0.973
200
150
100
50
0ppm


7.2600
6.8475
2.5627
2.4004
2.3754
494.21
51.09
1.00
Sol: CDCl3
10
8
6
4
2
0ppm
160.966
160.801
150.880
121.468
116.202
106.683
77.313
77.000
76.679
24.445
23.417
19.961
200
150
100
50
0ppm


10.5105
7.2600
2.7096
2.6970
2.6707
0.0560
CH3
Br
CHO
H3C
N
CH3
1b
Sol: CDCl3
48.62
5.24
1.00
4.75
10.0
7.5
5.0
2.5
0.0 ppm
192.081
160.966
157.856
148.724
127.663
123.919
77.321
77.000
76.679
26.847
22.849
19.558
0.990
200
150
100
50
0 ppm


CH3
OHC
CHO
H3C
N
OCH3
2d
Sol: CDCl3
2.12
1.00
2.83
2.91
10.0
7.5
5.0
2.5
0.0 ppm
191.250
191.118
165.779
165.326
154.977
124.076
115.791
77.321
77.000
76.687
54.384
24.363
15.593
1.006
200
150
100
50
0 ppm


10.467
7.2600
6.5979
3.9955
2.5285
2.4224
0.0603
CH3
CHO
H3C
N
OCH3
2a
Sol: CDCl3
1.00
0.17
1.10
2.82
2.83
2.89
10.0
7.5
5.0
2.5
0.0ppm
191.283
165.499
161.558
152.484
120.069
114.532
77.321
77.000
76.679
53.660
24.503
20.866
0.981
200
150
100
50
0ppm

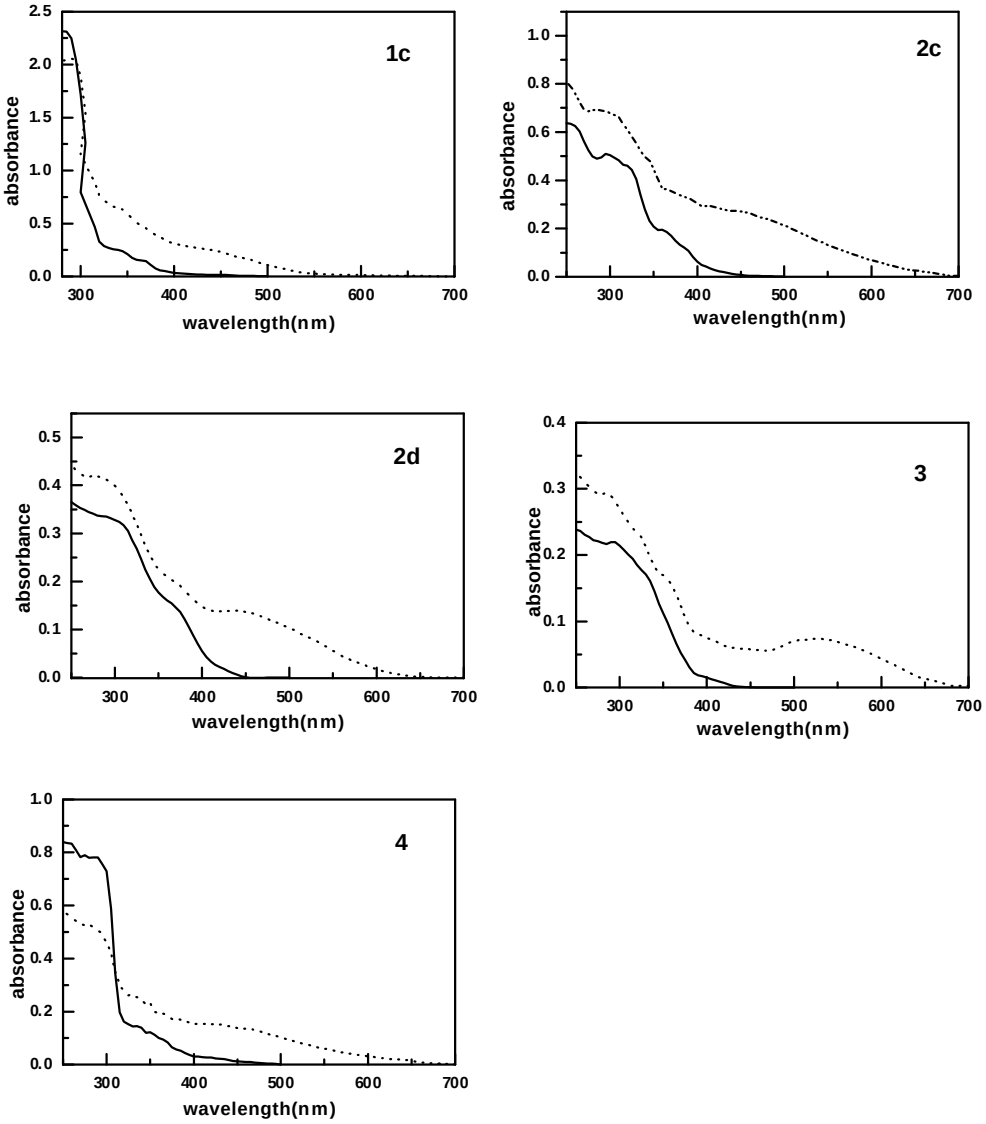


Figure S1. The UV-vis absorption spectra of the solid aldehydes **1c**, **2c**, **2d**, **3** and **4** before (solid line) and after (dotted line) exposure to UV-irradiation (λ >350 nm)