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CYCLOCONDENSATION OF α-OXOKETENE DITHIOACETALS WITH β-LITHIOAMINO-β-SUBSTITUTED ACRYLONITRILES: SYNTHESIS OF 2,6-SUBSTITUTED AND 5,6-ANNELATED 3-CYANO-4-(METHYLTHIO)PYRIDINES

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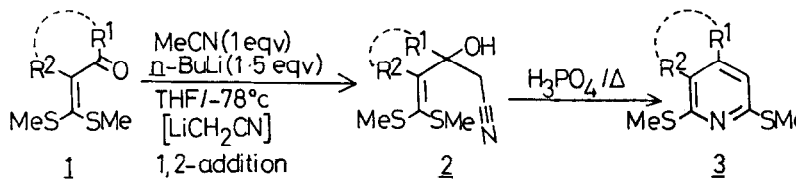
Abstract: *The lithiated β-amino-β-substituted acrylonitriles* 4a-d *generated in situ by reaction of lithioacetonitrile with either acetonitrile or substituted nitriles undergo cyclocondensation with α-oxoketenedithioacetals through 1,4-addition to afford 2,6-substituted and 5,6-annelated-4-(methylthio)-3-cyanopyridines* 6a-m, 11a-h *and* 12a-b *in good yields. A few of the 2,6-diheterylpyridines* 6n-q *were also synthesized following this procedure. The corresponding α-cinnamoyl (*12a-c*) and α-(5-aryl-2,4-pentadienoyl) (*12d*) ketenedithioacetals on the other hand underwent cyclization with* 4a *to afford the corresponding 4-aryl- (or 4-styryl-6-[2-bis (methylthio)ethenyl]-3-cyanopyridines* 14a-d *in good yields. Raney Nickel desulphurization of some of these pyridines afforded products of reductive dethiomethylation and those formed by reductive alkylation of nitrile group.*

In continuation of our programmed studies on aromatic and heteroaromatic annelation involving reactions of α-oxoketene dithioacetals 1 with allyl and azaallyl anions[1], we had recently reported that the lithioacetonitrile generated under controlled conditions undergoes regioselective 1,2-addition with 1 to yield the corresponding carbinolacetals 2, which on treatment with phosphoric acid underwent Ritter type intramolecular ring closure with concomitant methylthio group migration to yield the corresponding 3,4-substituted and fused 2,6-bis(methylthio)pyridines 3 in high yields (Scheme 1)[2-3]. The methylthio group migration was successfully interrupted by incorporating bromide ion as an external nucleophile to afford the corresponding 2-bromopyridines[3]. The lithioacetonitrile can also be made to undergo either self condensation to give the corresponding β-lithioaminocrotononitrile[4] (4a)(Scheme 2) or it can further be reacted with various other substituted nitriles to afford the corresponding β-lithioamino-β-substituted acrylonitriles 4b-e (Scheme 2), a new group of ambident nucleophiles that should display marked difference in regioselectivity towards 1 resulting in clear 1,4-addition and cyclization to give the corresponding 4-(methylthio)-3-cyanopyridine derivatives (Scheme 2). Such a strategy will enhance the scope of our pyridine synthesis since it enables us to manipulate the desired substituents at 2 and 6 positions of pyridine ring. We herein describe our new results on the efficient synthesis of a novel group of pyridine derivatives.

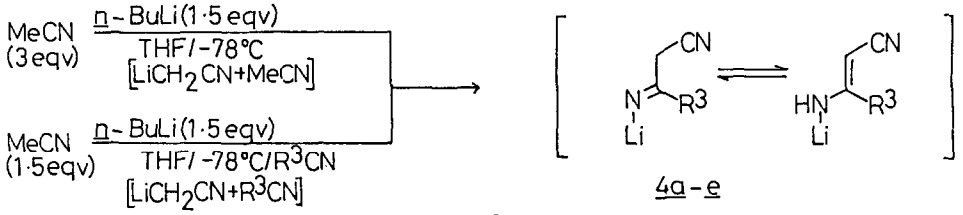


Scheme 1

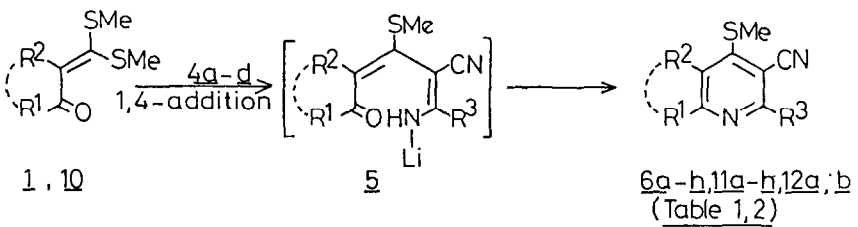
RESULTS AND DISCUSSION

When the β-lithioaminocrotononitrile (4a) generated *in situ* by treating excess of acetonitrile (3 eqv) with *n*-butyllithium (1.5 eqv), was reacted with 1a (R^1 = 4-$MeOC_6H_4$, R^2=H), the product (92%) obtained after work-up was characterized as 3-cyano-2-methyl-4-(methylthio)-6-(4-methoxyphenyl)pyridine (6a) on the basis of its spectral and analytical data (Scheme 2)[5]. The regiochemistry of 6a was further confirmed by its reductive dethiomethylation with W-4 Raney Nickel in ethanol which afforded two products characterized as the substituted pyridines 7(30%) and 8(40%) respectively (Scheme 2). Apparently the nitrile group in 6a has also undergone reductive alkylation under these conditions. In the ^{1}H NMR spectrum(90 MHz)of 7, the H-4 and H-5 protons appeared as characteristic doublets at δ7.65 and 7.90 with a coupling constant of 8.5 Hz which rules out the regioisomeric structure 8A that would be formed by 1,2-addition of the enaminonitrile 4a to 1a. The other acyclic ketene dithioacetals 1b-h similarly reacted with 4a under identical conditions to afford the corresponding pyridines 6b-h in overall high yields (Table 1). Only 6h was obtained in 30% yield probably due to competetive deprotonation of 1h in the basic medium. Similarly, the β-lithioaminocinnamonitrile (4b) generated *in situ* by treating lithioacetonitrile with benzonitrile, also reacted with 1b, 1e and 1h under identical conditions to afford the corresponding 2-phenylpyridines 6i-k in 57-91% overall yields (Table 1). The corresponding β-(2-thienyl)(4c) and β-(2-furyl)(4d) β-lithioaminoacrylonitriles generated *in situ* by reacting lithioacetonitrile with 2-cyanothiophene and 2-cyanofuran respectively, also underwent facile cyclization with 1b under similar conditions to afford the respective 2-(2-thienyl)-(6l) and 2-(2-furyl)-(6m)pyridines in good yields (Table 1). However, the β-(2-pyridyl) derivative 4e failed to react with (1b) under similar conditions and only the starting materials(1b and 9) were recovered unchanged.

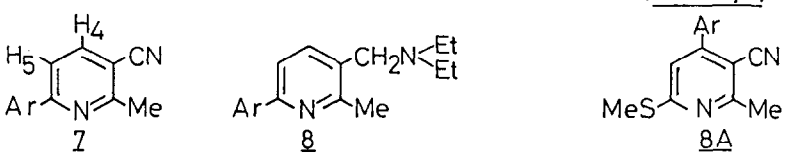
The above reaction strategy was extended for the synthesis of 2,6-diheteryl-3-cyanopyridines which are potential ligands for the chelation of transition metals (Scheme 3)[6]. Thus the substituted pyridines (6n-q) with either (2-furyl) or (2-thienyl) groups in 2- and 6- positions could be obtained in good yields by reacting appropriately substituted α-oxoketene dithioacetals 1e and 1f with either 4c or 4d (Scheme 3). However, the α-(2-pyridinoyl)ketene dithioacetal 1i failed to condense with any one of 4a-e to afford the desired 6-(2-pyridyl)-2-heterylpyridines. The pyridine nitrogen appears to chelate strongly with lithium in 4e thus resulting in the failure of the reaction.



4a, R^3 = Me
4b, R^3 = C_6H_5
4c, R^3 = 2-Thienyl
4d, R^3 = 2-Furyl
4e, R^3 = 2-Pyridyl



1, 10 5 6a-h,11a-h,12a,b (Table 1,2)



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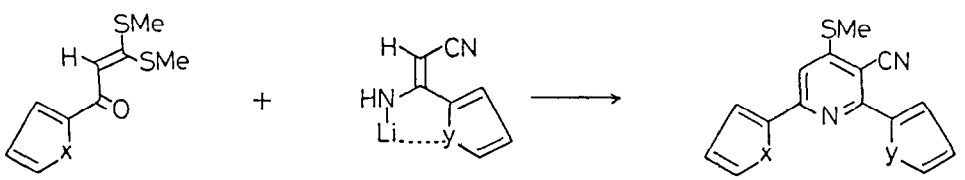
Ar = 4-$MeOC_6H_4$

Scheme 2



1e, x = O
1f, x = S

4c, y = S
4d, y = O

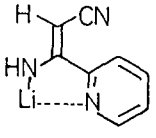
6n, x = O; y = S
6o, x = y = S
6p, x = y = O
6q, x = S; y = O

Scheme 3

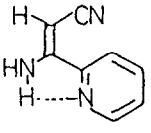
Table 1: Synthesis of 2,6-Substituted-4-(methylthio)-3-cyanopyridines

Entry	1	4	Products	R^1	R^2	R^3	%Yield(6)
1	1a	4a	6a	4-$MeOC_6H_4$	H	Me	92
2	1b	4a	6b	C_6H_5	H	Me	86
3	1c	4a	6c	4-ClC_6H_4	H	Me	90
4	1d	4a	6d	2-Naphthyl	H	Me	92
5	1e	4a	6e	2-Furyl	H	Me	85
6	1f	4a	6f	2-Thienyl	H	Me	82
7	1g	4a	6g	3-Pyridyl	H	Me	62
8	1h	4a	6h	Me	H	Me	30
9	1b	4b	6i	C_6H_5	H	C_6H_5	91
10	1e	4b	6j	2-Furyl	H	C_6H_5	87
11	1h	4b	6k	Me	H	C_6H_5	57
12	1b	4c	6l	C_6H_5	H	2-Thienyl	65
13	1b	4d	6m	C_6H_5	H	2-Furyl	76

1i



4e



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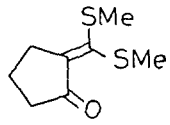
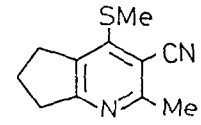
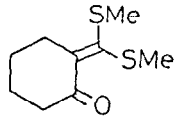
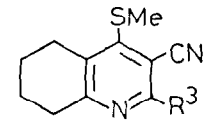
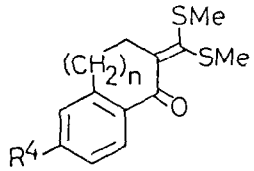
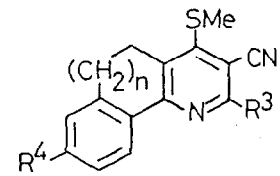
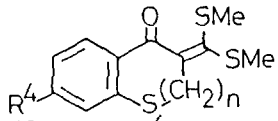
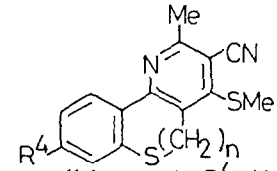
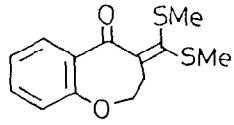
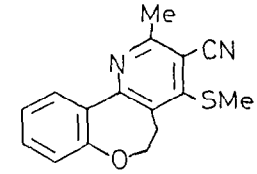
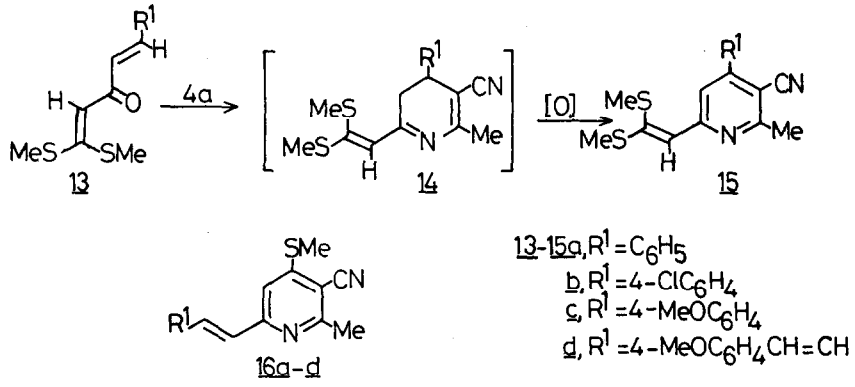
The cyclic α-oxoketene dithioacetals 10a and 10b derived from cyclopentanone and cyclohexanone respectively also reacted with 4a,b under the above reaction conditions to yield the corresponding 5,6-cyclopentanopyridine 11a and 5,6,7,8-tetrahydroquinolines 11b, 12a in good yields(Table 2).Under similar reaction conditions, the annelated pyridines 11c-e and 12b were obtained by reacting the corresponding benzocyclic ketene dithioacetals 10c-e with 4a,b (Table 2). Also the α-oxoketene dithioacetals 10f-h derived from benzocyclic ketones with one heteroatom reacted with 4a to afford the corresponding fused pyridine derivates 11f-h in 83-89% overall yields (Table 2). The structures of all the product pyridines 11a-h and 12a-b were confirmed by their spectral and analytical data.

The reactivity of 4a with α-cinnamoyl ketene dithioacetals 13a-c was next examined. Thus under the described conditions 13a-c reacted with 4a to afford the corresponding 4-aryl-6-[2-bis(methylthio)ethenyl]pyridines 15a-c in 85-89% overall yields (Scheme 4). The pyridines 15a-c are apparently formed by cyclization of 4a on the cinnamoyl group of 13 followed by dehydrogenation of the intermediate dihydropyridines 14a-c under experimental conditions. Similarly 13d reacted with 4a to afford the corresponding 4-styrylpyridine 15d in 84% yield. However the pyridines 16a-d which would have been formed by the attack of 4a on bis(methylthio)-methylene double bond could not be detected in the reaction mixture,thus demonstrating high chemoselectivity of 4a towards 13a-d (Scheme 4).

Table 2 Synthesis of 2-Substituted-5,6-annelated 3-Cyanopyridines

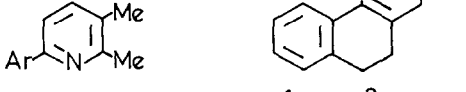
Entry	Starting materials	$NCCH=C(R^3)NHLi$ 4	Products	% yield
1	 10a	4a	 11a	57
2	 10b	4a	 11b, R^3 = Me	62
3	10b	4b	12a, $R^3 = C_6H_5$	82
4	 10c, n = 1, R^4 = H	4a	 11c, n = 1; R^3 = Me; R^4 = H	87
5	10d, n = 1, R^4 = MeO	4a	11d, n = 1; R^3 = Me; R^4 = MeO	86
6	10e, n = 2; R^4 = H	4a	11e, n = 2; R^3 = Me; R^4 = H	84
7	10c, n = 1; R^4 = H	4b	12b, n = 1; $R^3 = C_6H_5$; R^4 = H	83
8	 10f, n = 1; R^4 = H	4a	 11f, n = 1; R^4 = H	83
9	10g, n = 2; R^4 = Me	4a	11g, n = 2; R^4 = Me	89
10	 10h	4a	 11h	87



Scheme 4

A few of the product pyridines were subjected to reductive dethiomethylation with Raney Nickel which was accompanied with concomitant reduction of nitrile group also[7]. Thus the treatment of 6a with W-4 Raney Nickel in ethanol afforded the mixture of 7 and 8 as described earliar (Scheme 1). When 6a was heated with W-4 Raney Nickel in refluxing ethanol, the intermediate 3-(diethylamino)methylpyridine 8 underwent futher hydrogenolysis to afford 2,3-dimethyl-6-(4-methoxyphenyl)pyridine (17) in good yield. Similarly, the fused pyridines 11c and 12b afforded the corresponding 18 and 19 under the described conditions. The nitrile group therefore provides further scope for functional group transformation in these systems. Attempts to selectively dethiomethylate 6a with deactivated Raney Nickel in the presence of aprotic solvents (dioxane, acetone) under various conditions gave either starting material or intractable mixture of several products. Interestingly tetrahydroquinoline 12a underwent selective dethiomethylation to give 20 on treatment with W-4 Raney Nickel at room temperature under similar conditions.

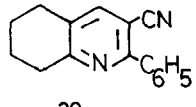
Extensive literature is available on the synthesis of pyridine and its derivatives[8]. Most of the methods generally involve introduction of the desired substituents on a preconstructed pyridine rings or the construction



17, Ar = 4-MeOC6H4

18, R1 = Me; R2 = Et2NCH2

19, R1 = C6H5; R2 = Me



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of these rings from appropriately substituted open-chain precursors. One of the oldest and useful methods which still enjoys synthetic applications belongs to the latter category involving the condensation of the appropriately substituted β-aminoacrylate, β-aminoacrylonitrile or the corresponding enaminones with β-substituted-α,β-unsatuared carbonyl compounds or their equivalents[8]. However, quite often these reactions fail to adhere to the required regioselectivity and thus a regiomixture of substituted pyridines are sometimes obtained. Also most of these enamines have been reacted with only acyclic 1,3-electrophilic components and only a few enaminonitriles and esters with β-methyl substituents have been utilized in reactions thus leading to a limited substituent variation.The present methodology provides an advantage of liberal structural manipulation on both the components. A number of β-substituted β-lithioaminoacrylonitriles can be generated *in situ* by reacting lithioacetonitrile with a number of substituted nitriles. The α-oxoketene dithioacetals, on the other hand, can be derived from a wide structural variants of active methylene ketones. Recently, Potts and co-workers[6] have efficiently utilized the α-oxoketene dithioacetals for the synthesis of 2,6-substituted pyridines by first converting them to 1,5-enediones through the 1,4-addition of potassium enolate anions of active methylene ketones and subsequent cyclization of 1,5-enediones in the presence of ammonium acetate.

EXPERIMENTAL SECTION

Melting points were obtained on a 'Thomas Hoover' capillary melting point apparatus and are uncorrected. Infrared spectra were recorded on a Perkin-Elmer 297 spectrophotometer. ^{1}H NMR spectra were recorded on a Varian EM-390 spectrometer and chemical shift values are expressed in ppm downfield from Me_4Si. The ^{13}C NMR spectra were recorded on a Brucker WM-400 spectrometer. Mass spectra were obtained on a Jeol JMS D-300 spectrometer and elemental analyses were carried out by Heraeus CHN-O-RAPID instrument. Tetrahydrofuran(THF) was distilled under nitrogen from sodium benzophenone ketyl immediately before use.

Commercially available acetonitrile and benzonitrile were dried and distilled before use,while 2-cyanofuran and 2-cyanothiophene were purchased from Aldrich and used as such.2-Cyanopyridine was prepared according to the reported procedure[9].All the oxoketene dithioacetals employed were reported earlier and prepared accordingly[10].

General Procedure for the Reaction of α-Oxoketene Dithioacetals with β-Lithioaminocrotononitrile (4a):

To a stirred solution of freshly distilled acetonitrile (1.23g, 30 mmol) in anhydrous THF (25 mL),*n*-BuLi[11] (15 mmol) was added through syringe via a rubber septum under an efficient atmosphere of nitrogen at -78°C and the reaction mixture was stirred for 0.5 hr at the same temperature. The resulting light reddish suspension of β-lithioaminocrotononitrile was treated (5 min) with a solution of appropriate oxoketene dithioacetal (10 mmol) in THF (50 mL) and the reaction mixture was allowed to warm to room temperature and stirred further for 20 hr. It was then poured into satd. NH_4Cl solution, extracted with ether (2 x 50 mL), washed with water (150 mL),dried (Na_2SO_4) and concentrated *in vacuo* to give crude pyridines 6a-h, 11a-h and 15a-d, which were purified by column chromatography over silica gel using EtOAc-hexane (1:20) as eluent.

General Procedure for the Reaction of α-Oxoketene Dithioacetals with β-lithioamino-β-substituted acrylonitriles (4b-e):

The β-lithioamino-β-substituted acrylonitriles(4b-e)were generated *in situ* and reacted with α-oxoketene dithioacetals by following the above general procedure using equimolar quantities of acetonitrile(0.62g,15mmol),appropriate nitrile(15 mmol),*n*-BuLi(15 mmol)and oxoketene dithioacetals(15mmol).

In the case of pyridines 6k,6l,6n,6o,11a,11b and 12a,the reaction mixture was further refluxed for 12 hrs after stirring at room temperature (20hr) under N_2 atmosphere to ensure completion of reaction.
The spectral and analytical data for the product pyridines 6a-q,11a-h,12a,b,15a-d is given below.

3-Cyano-2-methyl-4-(methylthio)-6-(4'-methoxyphenyl)pyridine (6a)colourless needles (hexane-$CHCl_3$);mp 157-158°C;IR(KBr)2215,1607,1585,1558,1530,1512,1473 cm^{-1};^1H NMR($CDCl_3$) δ 2.60(s,3H,SMe),2.74(s,3H,Me),3.88(s,3H,OMe),6.98(d,2H,J=9.0 Hz,arom),7.28(s,1H,H-5),7.88(d,2H,J=9.0 Hz,arom);^{13}C NMR($CDCl_3$) δ 13.96(S$\underline{C}H_3$),23.70(C$\underline{H}_3$),55.24(O$\underline{C}H_3$),103.6(C≡N),110.81(C-5),114.1(CH,arom),115.61(C-1',arom),128.7(CH,arom), 130.1(C-3), 155.0(C-2,C-6), 157.92(C-4),161.4(C-4');MS m/z 270(M^+,100%),255(12),224(18).Anal.Calcd for $C_{15}H_{14}N_2OS$: C,66.64; H,5.22; N,10.36. Found:C,66.47; H,5.09; N,10.13.

3-Cyano-2-methyl-4-(methylthio)-6-phenylpyridine (6b) colourless crystals (hexane-$CHCl_3$); mp 126-127°C; IR(KBr) 2200,1548,1525,1495,1426 cm^{-1}; ^1H NMR($CDCl_3$) δ 2.60(s,3H,SMe), 2.72(s,3H,Me), 7.26(s,1H,H-5), 7.34-7.52(m,3H, arom), 7.82-8.10(m,2H,arom); MS m/z 240(M^+,100%),194(31),152(8); Anal.Calcd for $C_{14}H_{12}N_2S$:C,69.96; H,5.03; N,11.66. Found:C,69.77; H,5.21; N,11.49.

3-Cyano-2-methyl-4-(methylthio)-6-(4-chlorophenyl)pyridine (6c) colourless crystals(hexane-$CHCl_3$);mp 162-163°C;IR(KBr)2209,1596,1580,1562 cm^{-1},^1H NMR ($CDCl_3$) δ 2.62(s,3H,SMe), 2.74(s,3H,Me), 7.28(s,1H,H-5), 7.44(d,2H,J=9.0 Hz arom),8.00(d,2H,J=9.0 Hz,arom);MS m/z 276(M^+,33%),274(M^+,100),228(26).Anal. Calcd for $C_{14}H_{11}ClN_2S$:C,61.19;H,4.04;N,10.20.Found:C,60.98;H,3.90;N,10.02.

3-Cyano-2-methyl-3-(methylthio)-6-(2-naphthyl)pyridine(6d) colourless needles (hexane-$CHCl_3$); mp 187-188°C; IR(KBr) 2222,1560,1540,1432 cm^{-1}; ^1H NMR($CDCl_3$) δ 2.58(s,3H,SMe), 2.79(s,3H,Me), 7.38(s,1H,H-5), 7.40-7.60(m,3H, arom), 7.74-8.08(m,4H,arom),8.44(s,1H,arom); MS m/z 290 (M^+,100%),244(18). Anal.Calcd for $C_{18}H_{14}N_2S$:C,74.45;H,4.86;N,9.65.Found:C,74.26;H,4.62;N,9.61.

3-Cyano-2-methyl-4-(methylthio)-6-(2-furyl)pyridine (6e) light yellow needles (hexane-$CHCl_3$); mp 159-160°C; IR(KBr)2205,1594,1540,1483,1430cm^{-1}; ^1H NMR($CDCl_3$) δ 2.58(s,3H,SMe), 2.68(s,3H,Me), 6.50-6.58(brs,1H,H-4'furyl), 7.16(d,1H,J=3 Hz,H-3'furyl), 7.28(s,1H,H-5), 7.51(brs,1H,H-5'furyl); MS m/z 230(M^+, 100%), 202(10), 197(9). Anal.Calcd for $C_{12}H_{10}N_2OS$: C,62.58; H,4.38; N,12.17. Found: C,62.37; H,4.26; N,12.02.

3-Cyano-2-methyl-4-(methylthio)-6-(2-thienyl)pyridine(6f) light yellow needles(hexane-$CHCl_3$); mp 155-156°C; IR(KBr)2204,1554,1514,1440,1420 cm^{-1}; ^1H NMR($CDCl_3$) δ 2.47(s,3H,SMe), 2.66(s,3H,Me), 7.08-7.30(m,1H,H-4'thienyl), 7.24(s,1H,H-5), 7.50(brd,1H,J=5 Hz,H-3' thienyl), 7.68(brd,1H,J=4.5 Hz,H-5' thienyl); MS m/z 246(M^+,100%), 213(12), 200(8). Anal.Calcd for $C_{12}H_{10}N_2S_2$: C,58.50; H,4.09; N,11.37. Found: C,58.32; H,3.96; N,11.58.

3-Cyano-2-methyl-4-(methylthio)-6-(3-pyridyl)pyridine(6g) colourless crystals($CHCl_3$);mp 195-196°C;IR(KBr)2210,1580,1558,1528,1445,1425 cm^{-1};^1H NMR ($CDCl_3$) δ2.68(s,3H,SMe),2.80(s,3H,Me),7.34-7.58(m,merged with H-5,1H,H-5' pyridyl),7.34(s,1H,H-5),8.28(dt,1H,J=9,1.5 Hz,H-4'pyridyl),8.74(brd,1H,J=5 Hz,H-6'pyridyl),9.24(brs,1H,H-2'pyridyl);MS m/z 241(M^+,100%),195(26).Anal. Calcd for $C_{13}H_{11}N_3S$:C,64.70;H,4.60;N,17.41.Found:C,64.48;H,4.79;N,17.54.

3-Cyano-4-(methylthio)-2,6-dimethylpyridine(6h)light brown needles(hexane); mp 42-43°C;IR(KBr)2210,1580,1440 cm^{-1};^1H NMR(CCl_4) δ2.42(s,3H,SMe),2.54(s, 3H,Me),2.70(s,3H,Me),6.90(s,1H,H-5);MS m/z 178(M^+,100%),163(6),132(62),104 (13). Anal.Calcd for $C_9H_{10}N_2S$: C,60.64; H,5.65; N,15.72. Found: C,60.88;

H,5.49; N,15.85.

3-Cyano-2,6-diphenyl-4-(methylthio)pyridine (6i) colourless crystals (hexane-$CHCl_3$); mp 145°C; IR(KBr) 2215,1550,1490,1430 cm^{-1}; ^1H NMR($CDCl_3$) δ 2.75(s,3H,SMe),7.42-7.65(m,7H,arom and H-5),7.84-8.20(m,4H,arom); MS m/z 302(M^+,100%), 255(31). Anal. Calcd for $C_{19}H_{14}N_2S$: C,75.46; H,4.67; N,9.27. Found: C,75.54; H,4.59; N,9.14.

3-Cyano-6-(2-furyl)-4-(methylthio)-2-phenylpyridine (6j) colourless crystals (hexane-$CHCl_3$); mp 176-177°C; IR(KBr) 2215,1595,1545,1481 cm^{-1}; ^1H NMR($CDCl_3$) δ2.65(s,3H,SMe), 6.51-6.61(m,1H,H-4' furyl), 7.19-7.30(m,1H,H-3' furyl),7.40-7.62(m,5H,arom,H-5 and H-5' furyl),7.81-8.04(m,2H,arom);MS m/z 292(M^+,100%), 259(58), 246(13). Anal.Calcd for $C_{17}H_{12}N_2OS$: C,69.84; H,4.14; N,9.58. Found: C,69.98, H,4.09; N,9.65.

3-Cyano-6-methyl-4-(methylthio)-2-phenylpyridine (6k) colourless crystals (hexane-$CHCl_3$); mp 133-134°C; IR(KBr)2210,1595,1464,1417 cm^{-1};^1H NMR($CDCl_3$) δ 2.14(s,3H,SMe),2.19(s,3H,Me),7.38-7.52(m,3H,arom),7.62-7.80(m,2H,arom);MS m/z 241(M^++1,100%), 240(M^+,3), 225(21). Anal. Calcd for $C_{14}H_{12}N_2S$: C,69.96; H,5.87; N,11.66. Found: C,69.81; H,5.92; N,11.88.

3-Cyano-2-(2-thienyl)-4-(methylthio)-6-phenylpyridine (6l) colourless crystals(hexane-$CHCl_3$); mp 141-142°C; IR(KBr)2200,1575,1550,1508,1418cm^{-1};^1H NMR($CDCl_3$) δ 2.68(s,3H,SMe),7.11-7.40(m,2H,arom),7.23(s,1H,H-5),7.65(s,5H, arom), 8.38-8.54(brd,1H,thienyl H); MS m/z 308(M^+,100%). Anal.Calcd for $C_{17}H_{12}N_2S_2$: C,66.20; H,3.92; N,9.09; Found: C,66.09; H,4.02; N,9.01.

3-Cyano-2-(2-furyl)-4-(methylthio)-6-phenylpyridine(6m) colourless crystals (hexane-$CHCl_3$); mp 122-123°C;IR(KBr)2200,1584,1540,1510 cm^{-1};^1H NMR($CDCl_3$) δ 2.66(s,3H,SMe),6.60-6.74(dd,1H,J=3.5,2 Hz,H-4'furyl),7.40-7.84(m,5H,arom and furyl),7.40(s,1H,H-5),8.00-8.30(m,2H,arom);MS m/z 292(M^+,100%),263(24), 246(17). Anal.Calcd for $C_{17}H_{12}N_2OS$: C,69.84,H,4.14;N,9.58. Found:C,69.66;H, 3.97; N,9.49.

3-Cyano-6-(2-furyl)-2-(2-thienyl)-4-(methylthio)pyridine (6n) light yellow crystals(hexane-$CHCl_3$); 64%; mp 168-169°C; IR(KBr)2200,1588,1550,1510,1482, 1430 cm^{-1}; ^1H NMR($CDCl_3$) δ 2.61(s,3H,SMe), 6.56-6.66(dd,1H,J=3.5,2 Hz,H-4' furyl), 7.20(dd,1H,J=5,4.5 Hz,H-4'thienyl), 7.28(m,1H,H-3'furyl),7.30(s,1H, H-5),7.48-7.73(m,2H,H-3'furyl and thienyl),8.30(brd,1H,J=5 Hz,H-5 thienyl); MS m/z 298(M^+,100%),252(18). Anal.Calcd for $C_{15}H_{10}N_2OS_2$: C,60.38; H,3.38; N,9.39. Found: C,60.42; H,3.24; N,9.20.

3-Cyano-2,6-bis(2-thienyl)-4-(methylthio)pyridine(6o) light yellow crystals (hexane-$CHCl_3$); 57%; mp 149-150°C; IR(KBr)2200,1560,1422 cm^{-1};^1H NMR($CDCl_3$) δ2.70(s,3H,SMe),7.13-7.42(m,3H,thienyl),7.31(s,1H,H-5),7.62(brd,1H,J=5.5 Hz thienyl),7.74-8.0(m,1H,thienyl), 8.48(brd,1H,J=5.5 Hz,thienyl); MS m/z 314 (M^+,100%). Anal.Calcd for $C_{15}H_{10}N_2S_3$:C,57.29; H,3.21; N,8.97.Found:C,57.11; H,3.09; N,8.85.

3-Cyano-2,6-bis(2-furyl)-4-(methylthio)pyridine (6p) colourless crystals (hexane-$CHCl_3$);85%; mp 151-152°C; IR(KBr)2214,1604,1592,1547,1513,1481cm^{-1}; ^1H NMR($CDCl_3$) δ 2.59(s,3H,SMe),6.40-6.69(dd,1H,J=3.5, 2 Hz,H-4'furyl),7.20 (brd,merged with H-5 signal,1H,J=3.5 Hz,H-3'furyl),7.22(s,1H,H-5),7.40(brd, 1H,J=3.5 Hz,H-3'furyl),7.55(brs,1H,H-5'furyl),7.63(brs,1H,H-5'furyl);MS m/z 282(M^+,100%), 236(7). Anal.Calcd for $C_{15}H_{10}N_2O_2S$: C,63.81; H,3.57; N,9.92. Found: C,63.67; H,3.69; N,9.98.

3-Cyano-2-(2-furyl)-6-(2-thienyl)-4-(methylthio)pyridine (6q) colourless needles(hexane-$CHCl_3$);78%;mp 126-127°C;IR(KBr)2200,1549,1505,1480,1432cm^{-1}; ^1H NMR($CDCl_3$) δ 2.64(s,3H,SMe),6.64(dd,1H,J=3.5, 2 Hz,H-4'furyl),7.18-7.40 (m,1H,H-4'thienyl),7.30(s,1H,H-5),7.60(m,2H,thienyl and furyl),7.76(brs,2H, thienyl and furyl); MS m/z 298(M^+,60%). Anal.Calcd for $C_{15}H_{10}N_2OS_2$:C,60.38; H,3.38; N,9.39.Found: C,60.09; H,3.22; N,9.16.

3-Cyano-2-methyl-4-(methylthio)-6,7-dihydro-*5H*-cyclopenta[*b*]pyridine (11a) yellow oil;IR(KBr)2202,1548,1525 cm^{-1}; ^1H NMR($CDCl_3$) δ 1.66-1.90(m,2H,CH_2),

2.36(s,3H,SMe),2.41(s,3H,Me),2.62-2.97(m,4H,CH_2); Anal.Calcd for $C_{11}H_{12}N_2S$: C,64.67; H,5.92; N,6.86.Found: C,64.59; H,5.78; N,6.64.

3-Cyano-2-methyl-4-(methylthio)-5,6,7,8-tetrahydroisoquinoline (11b) colourless crystals (hexane-$CHCl_3$); mp 71-72°C; IR(KBr)2220,1535,1420 cm^{-1};^1H NMR ($CDCl_3$) δ 1.72-1.99(m,4H,CH_2), 2.62(s,3H,SMe),2.64(s,3H,Me),2.70-2.98(m,4H, CH_2);MS m/z 218(M^+,65%),203(100),170(11).Anal.Calcd for $C_{12}H_{14}N_2S$: C,66.01, H,6.46; N,12.83. Found: C,59.85; H,6.29; N,12.96.

3-Cyano-4-(methylthio)-2-phenyl-5,6,7,8-tetrahydroquinoline (12a) colourless crystals (hexane-$CHCl_3$); mp 127-128°C; IR(KBr) 2205,1579,1550,1446, 1420 cm^{-1}; ^1H NMR($CDCl_3$)δ 1.70-1.98(m,4H,CH_2), 2.60(s,3H,SMe), 2.43-2.66(m, 2H,CH_2),2.74-3.10(m,2H,CH_2),7.32-7.58(m,3H,arom),7.82-8.06(m,2H,arom); MS m/z 280(M^+,100%) 265(23), 247(100). Anal.Calcd for $C_{17}H_{16}N_2S$: C,72.82; H,5.75; N,9.99. Found: C,72.71; H,5.62; N,10.06.

3-Cyano-5,6-dihydro-2-methyl-4-(methylthio)-benzo[*h*]quinoline (11c) light yellow crystals(hexane-$CHCl_3$);mp 131-132°C; IR(KBr)2200,1600,1540,1520,1427 cm^{-1}; ^1H NMR($CDCl_3$) δ 2.62(s,3H,SMe), 2.76(s,3H,Me), 2.87-3.29(m,4H, CH_2), 7.10-7.41(m,3H,arom), 8.18-8.38(m,1H,H-10 arom); MS m/z 266 (M^+,64%), 251(100) 218(27). Anal. Calcd for $C_{16}H_{14}N_2S$: C,72.14; H,5.30; N,10.52. Found: C,72.31; H, 5.11; N, 10.29.

3-Cyano-5,6-dihydro-8-methoxy-2-methyl-4-(methylthio)-benzo[*h*]quinoline (11d) light yellow needles (hexane-$CHCl_3$); mp 170-171°C; IR(KBr)2209,1611, 1575,1540,1515,1440 cm^{-1};^1H NMR($CDCl_3$) δ 2.53(s,3H,SMe),2.74(s,3H,Me),2.81-3.29(m,4H,CH_2),3.84(s,3H,OMe),6.88(d,1H,J=1.5 Hz,H-7 arom),6.92(dd,1H,J=8, 2 Hz,H-9 arom),8.28(d,1H,J=8 Hz,H-10 arom); MS m/z 296(M^+,100%),281(53), 248(84).Anal.Calcd for $C_{17}H_{16}N_2OS$: C,68.87; H,5.44; N,9.45. Found:C,68.66; H,5.27; N,9.59.

3-Cyano-6,7-dihydro-2-methyl-4-(methylthio)-*5H*-benzocyclohepta[1,2-*b*]pyridine (11e) light yellow crystals (hexane-$CHCl_3$); mp 131-132°C; IR(KBr) 2217,1543,1518,1442,1402 cm^{-1}; ^1H NMR($CDCl_3$) δ 2.10-2.40(m,2H,CH_2), 2.66(s,3H,SMe), 2.85(s,3H,Me), 2.40-2.99(m, merged with SMe and Me signals,4H,CH_2), 7.18-7.56(m,3H,arom), 7.73-8.89(m,1H,arom); MS m/z 280(M^+,100%), 265(94). Anal. Calcd for $C_{17}H_{16}N_2S$: C,72.82; H,5.75; N,9.99. Found: C,72.76; H,5.83; N,10.22.

3-Cyano-5,6-dihydro-4-(methylthio)-2-phenylbenzo[*h*]quinoline (12b) colourless needles (hexane-$CHCl_3$); mp 174-175°C; IR(KBr)2218,1604,1535,1518 cm^{-1}; ^1H NMR($CDCl_3$) δ 2.64(s,3H,SMe), 2.84-3.09(m,2H,CH_2), 3.18-3.38(m,2H,CH_2), 7.21-7.61(m,6H,arom), 7.90-8.09(m,2H,arom), 8.38-8.50(m,1H,arom); MS m/z 328(M^+,100%), 327(51), 313(67).Anal. Calcd for $C_{21}H_{16}N_2S$: C,76.79; H,4.91; N,8.53. Found: C,76.66; H,4.88; N,8.47.

3-Cyano-2-methyl-4-(methylthio)-*5H*-[1]benzothiapyrano[4,3-*b*]pyridine (11f) light yellow needles (hexane-$CHCl_3$); mp 182-183°C; IR(KBr)2205,1585,1544, 1520,1430 cm^{-1};^1H NMR($CDCl_3$) δ 2.74(s,3H,SMe), 2.80(s,3H,Me),4.26(s,2H, CH_2),7.18-7.39(m,3H,arom),8.28-8.48(m,1H,H-10 arom); MS m/z 284(M^+,54%), 269(100), 236(46). Anal. Calcd for $C_{15}H_{12}N_2S_2$: C,63.35; H,4.25, N,9.85. Found: C,63.21; H,4.14; N, 9.69.

3-Cyano-5,6-dihydro-2,9-dimethyl-4-(methylthio)-[1]benzothiepino[5,4-*b*]-pyridine (11g) light yellow needles(hexane-$CHCl_3$);mp 182-183°C;IR(KBr)2220, 1600,1550,1526 cm^{-1};^1H NMR($CDCl_3$) δ 2.40(s,3H,Me),2.68(s,3H,SMe),2.80(s,3H, Me),2.97-3.48(m,4H,CH_2),7.32(brd,1H,J=9Hz,H-10 arom),7.48(brs,1H,H-8 arom), 7.64(d,1H,J=8.5 Hz,H-11 arom);MS m/z 312(M^+,100%),297(38),284(54).Anal.Calcd for $C_{17}H_{16}N_2S_2$: C,65.35; H,5.16; N,8.97. Found: C,65.51; H,5.04; N,8.79.

3-Cyano-5,6-dihydro-2-methyl-4-(methylthio)-[1]benzoxepino[5,4-*b*]pyridine (11h) light yellow crystals(hexane-$CHCl_3$); mp 124-125°C; IR(KBr)2224,1604, 1550,1530,1489,1410 cm^{-1};^1H NMR($CDCl_3$) δ 2.62(s,3H,SMe),2.84(s,3H,Me),3.20 (t,2H,J=6.5 Hz,CH_2), 4.52(brt,2H,CH_2), 7.02-7.51(m,3H,arom),7.71-7.90(m,1H, arom);MS m/z 282 (M^+, 58%), 267(100). Anal. Calcd for $C_{16}H_{14}N_2OS$: C,68.06; H,5.00; N,9.92. Found: C,67.88; H,4.72; N,9.64.

β-Amino-β-(2-pyridyl)acrylonitrile (9) colourless crystals ($CHCl_3$); 88%; mp 115-116°C(lit[4c] mp 112-115°); IR(KBr)3440,3320,2195,1660,1610,1588 cm^{-1}; ^1H NMR($CDCl_3$) δ 4.60(s,1H,olefinic),5.70-6.18(brS,2H,NH_2),7.26-7.94(m,3H,pyridyl)8.64(brd,1H,J=6 Hz,H-6 pyridyl). Anal.Calcd for $C_8H_7N_3$: C,66.19;H,4.86; N,28.95. Found: C,66.11; H,4.65; N,28.79.

3-Cyano-2-methyl-4-phenyl-6-[2-bis(methylthio)ethenyl]pyridine (15a) light yellow needles (hexane-$CHCl_3$); 89%; mp 120-121°C; IR(KBr)2200,1565, 1496,1428 cm^{-1}; ^1H NMR($CDCl_3$) δ 2.50(s,6H,SMe),2.83(s,3H,Me),6.43(s,1H,olefinic), 7.40(s,1H,H-5), 7.36-7.69(m,5H,arom); ^{13}C NMR($CDCl_3$) δ 16.33, 17.37 (SMe), 23.95(Me), 116.62(CN), 118.80(olefinic C), 120.196(C-5), 128.36(C-3' and C'-5), 128.75(C-1'), 128.83(C-2'and C-6'), 129-59(C-4'), 137.10(C=SMe), 148.00(C-3), 155.10(C-4), 157.50(C-2), 162.50(C-6); MS m/z 312(M^+,18%),297 (100),265(12),250(20). Anal.Calcd for $C_{17}H_{16}N_2S_2$: C,65.35; H,5.16; N,20.52. Found: C,65.29; H,5.31; N,20.63.

3-Cyano-2-methyl-4-(4-chlorophenyl)-6-[2-bis(methylthio)ethenyl]pyridine (15b) light yellow needles (hexane-$CHCl_3$); 85%; mp 144-145°C; IR(KBr) 2200,1595,1575,1562,1548,1498,1429 cm^{-1}; ^1H NMR($CDCl_3$) δ 2.50(s,6H,SMe), 2.70(s,3H,Me),6.48(s,1H,olefinic), 7.45(s,1H,H-5), 7.60(s,4H,arom); MS m/z 348(30%),346(M^+,60),333(48),331(100). Anal.Calcd for $C_{17}H_{15}ClN_2S_2$: C,58.86; H, 4.36; N,8.08. Found: C, 58.69; H,4.26; N, 8.22.

3-Cyano-2-methyl-4-(4-methoxyphenyl)-6-[2-bis(methylthio)ethenyl]pyridine (15c) light yellow crystals (hexane-$CHCl_3$); mp 155-156°C; IR(KBr) 2200,1610,1570,1550,1510,1495,1430 cm^{-1}; ^1H NMR($CDCl_3$) δ 2.50(s,3H,SMe), 2.81(s,3H,Me),3.88(s,3H,OMe), 6.46(s,1H,olefinic),7.08(d,2H,J=9.0Hz,arom), 7.42(s,1H,H-5),7.63(d,2H,J=9.0 Hz,arom); MS m/z 342(M^+,51%),327(100). Anal. Calcd for $C_{18}H_{18}N_2OS_2$:C,63.13; H,5.30; N,8.18.Found:C,62.98; H,5.12;N,8.01.

3-Cyano-2-methyl-4-(4-methoxylstyryl)-6-[2-bis(methylthio)ethenyl]pyridine (15d) light yellow needles(hexane-$CHCl_3$);84%; mp 139-140°C;IR(KBr)2200, 1606,1574,1512,1504,1430 cm^{-1};^1H NMR($CDCl_3$) δ 2.50(s,3H,SMe),2.72(s,3H,Me), 3.82(s,3H,OMe),6.40(s,1H,CH=C(SMe)$_2$), 6.90(d,2H,J=9.0 Hz,arom),7.26(d,2H,J= 9 Hz,arom),7.48(s,1H,H-5),7.57(s,2H,olefinic); MS m/z 368(M^+,32%),353(100), 335(29),321(18).Anal.Calcd for $C_{20}H_{20}N_2OS_2$; C,65.18; H,5.47; N,7.60. Found: C,65.02; H,5.29, N,7.75.

General Procedure for Reductive Dethiomethylation of 3-Cyano-4-(methylthio)pyridines (6a,11c,12a,b) with Raney Nickel.
A solution of pyridine(5 mmol)in ethanol(80 mL)was stirred with W-4 Raney Nickel[12] (ca. 15-20 times by weight) for 2-4 hr (monitored by TLC)[refluxed for 3 hr(17,19)]. Raney Nickel was separated by filtration and the residue washed with the hot ethanol and the combined filtrate was concentrated *in vacuo*.The residue was extracted with chloroform (30 mL), washed with water (2x30 mL), dried (Na_2SO_4), and evaporated to give the crude products which were purified either by recrystallization from suitable solvent or passing through short length silica gel column using EtOAc-hexane (1:20) as eluent. In the case of 6a, elution with EtOAc-hexane gave first 7 (30%) followed by 8 (40%).

3-Cyano-2-methyl-6-(4-methoxyphenyl)pyridine (7) white crystals (hexane-$CHCl_3$); 30%; mp 94°C; IR (KBr) 2195,1586,1533,1511,1491,1428,1356 cm^{-1}; ^1H NMR($CDCl_3$) δ 2.80(s,3H,Me),3.89(S,3H,OMe),7.06(d,2H,J=9.0 Hz,arom), 7.65(d, 1H,J=8.5 Hz,H-4), 7.90(d,1H,J=8.5,H-5),8.13(d,2H,J=9.0 Hz,arom). Anal.Calcd for $C_{14}H_{12}N_2O$:C,74.98; H,5.40; N,12.49.Found:C,74.77; H,5.18;N,12.35.

3-(N,N-diethylamino)methyl-2-methyl-6-(4-methoxyphenyl)pyridine (8) red oil; 40%;IR(neat)1603,1580,1505 cm^{-1}; ^1H NMR($CDCl_3$) δ1.03(t,6H,J=7.5Hz,Me), 2.50(q,4H,J=7.5Hz,CH_2),2.62(s,3H,Me),3.50(s,2H,CH_2),3.80(s,3H,OMe),6.98(d, 2H,J=9.0 Hz,arom),7.44(d,1H,J=8.0 Hz,H-4), 7.67(d,1H,J=8.0 Hz,H-5), 7.98(d, 2H,J=9.0Hz,arom);MS m/z 284(M^+,36%). Anal. Calcd for $C_{18}H_{24}N_2O$: C,76.02; H, 8.50; N,9.85. Found: C,76.21; H,8.62; N,10.02.

2,3-Dimethyl-6-(4-methoxyphenyl)pyridine (17) colourless crystals (hexane); mp 67-68°C; 65%; IR(KBr) 1612,1589,1516 cm^{-1}; ^1H NMR(CCl_4) δ 2.20(s,3H,Me), 2.48(s,3H,Me),3.72(s,3H,OMe), 6.84(d,2H,J=9Hz,arom), 7.27(brs,2H,H-4 and H-5), 7.86(d,2H,J=9.0Hz,arom); MS m/z 215(M^++2,100%),200(27),172(11). Anal. Calcd for $C_{14}H_{15}NO$:C,78.84; H,7.09; N,6.57.Found: C,78.66; H,6.88; N,6.72.

5,6-Dihydro-3-(N,N-diethylamino)methyl-2-methylbenzo[*h*]quinoline (18) red oil; 76%; IR(CCl_4) 1590,1578,1545,1430 cm^{-1}; ^1H NMR($CDCl_3$) δ 1.06 (t,6H,J=7.5Hz,Me), 2.53(q,4H,J=7.5Hz,CH_2), 2.62(s,3H,Me), 2.90(brs,4H,CH_2), 3.51(s,2H,CH_2),7.06-7.56(m,3H,arom),7.46(s,1H,H-4),8.21-8.46(m,1H,arom); MS m/z 266(M^+,100%), 251(25). Anal. Calcd for $C_{19}H_{24}N$: C,85.66; H,9.08; N,5.26. Found: C,85.73; H,8.91; N,5.09.

5,6-Dihydro-3-methyl-2-phenylbenzo[*h*]quinoline (19) white crystals (hexane); 71%; mp 47-48°C; IR(KBr) 1600,1580,1555 cm^{-1}; ^1H NMR($CDCl_3$) δ2.31(brS,2H,CH_2); 2.49(s,3H,Me), 2.88(brS,2H,CH_2), 7.14-8.10(m,8H,arom), 8.32-8.41(m,1H,arom); MS m/z 271 (M^+,100%); Anal. Calcd for $C_{20}H_{17}N$: C,88.52; H,6.32; N,5.16. Found: C,88.59; H,6.19; N,5.02.

3-Cyano-2-phenyl-5,6,7,8-tetrahydroquinoline(20) white crystals (hexane-$CHCl_3$); 66%; mp 68°C; IR(KBr) 2220,1571,1552,1452,1440,1392 cm^{-1}; ^1H NMR($CDCl_3$) δ1.48-2.04(m,4H,CH_2), 2.42-3.10(m,4H,CH_2), 7.18-7.60(m,3H,arom), 7.65-8.06(m,2H,arom), 8.51(s,1H,H-4); MS m/z 234(M^+,35%). Anal. Calcd for $C_{16}H_{14}N_2$: C,82.02; H,6.02; N,11.96. Found: C,81.88; H,5.95; N,12.05.

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