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2-Pyridin-3-ylbenzoxazoles were synthesized by the reaction between 3-pyridinecarboxaldehyde and substituted *o*-aminophenols in the presence of iodobenzene diacetate. The resulting benzoxazoles **3** were treated with methyl iodide to give the corresponding pyridinium salts **4** which underwent the hydride reduction with sodium borohydride or sodium cyanoborohydride to produce 2-(1-methyl-1,2,5,6-tetrahydro-*pyridin*-3-yl)benzoxazole borane complex derivatives.

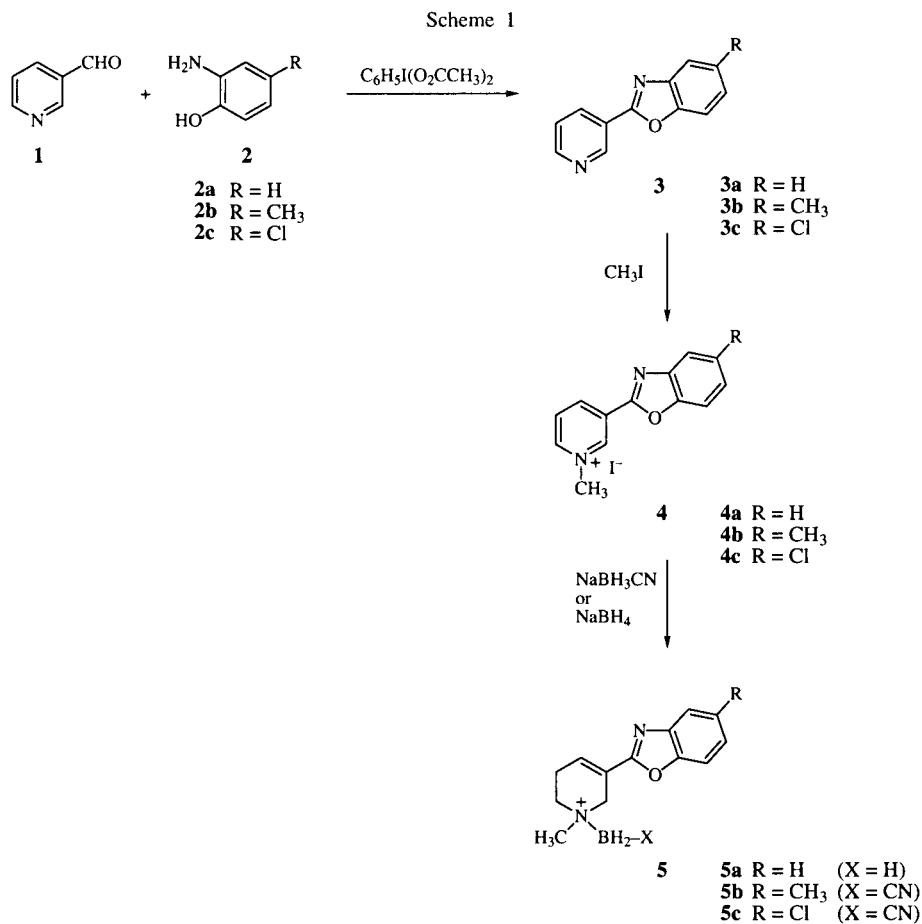
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Both benzoxazoles and tetrahydropyridines are important structural units found in a variety of natural products with interesting biological activities [1]. Benzoxazole rings have attracted synthetic interests for being an essential structure in many agrochemicals as well as in medicines [2-6]. Also, many tetrahydropyridines are being prepared as biologically active compounds in the field of medicinal chemistry.

We wish in this paper to describe the preparation of tetrahydropyridinylbenzoxazole borane complex derivatives featuring the tetrahydropyridine ring connected at the 2-position

of the benzoxazole derivatives. In general, pyridinylbenzoxazoles are prepared from the reactions between pyridinecarboxylic acids and aminophenols [7]. However, in the present study, pyridinylbenzoxazoles were obtained from 3-pyridinecarboxaldehyde (nicotinaldehyde) and *o*-aminophenols in the presence of iodobenzene diacetate.

Thus, 3-pyridinecarboxaldehyde **1** in alcohol was allowed to react with substituted *o*-aminophenols **2** at room temperature. The resultant Schiff's bases were subsequently treated with iodobenzene diacetate utilizing the



hypervalent iodine oxidative intramolecular cyclization to afford 2-pyridin-3-ylbenzoxazoles **3** in excellent yields. This method provided a mild and high-yielding procedure for the synthesis of the oxazole ring in a very short period of reaction time. The completion of the reaction was characterized by the typical fluorescent spot on thin-layer chromatography. The results of the reactions are summarized in Table 1.

Table 1


Chemical Shifts of Pyridine Protons and Physical Properties of Pyridinyl Benzoxazoles

Compound	mp (°C)	Yield (%)	¹ H NMR (δ, ppm)			
			Position of Pyridine Protons			
			2'	4'	5'	6'
3a	104-106	31.9	9.48	8.50	7.50	8.76
3b	98-100	48.2	9.47	8.46	7.47	8.75
3c	147-148	41.7	9.43	7.74	7.50	8.76

The formation of the quaternary salts was confirmed by treating compounds **3** with a large excess of methyl iodide in acetone. The quaternization occurred only at the pyridine nitrogens due to their higher basicity over those of benzoxazoles [8-9]. It required 7 to 8 equivalents of methyl iodide and up to 17 hours of reaction time for the complete quaternization. The spectral data and the yields of quaternary salts are summarized in Table 2.

Table 2

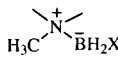
Chemical Shifts of Pyridinium Protons and Physical Properties of Pyridinium Benzoxazoles

Compound	mp (°C)	Yield (%)	¹ H NMR (δ, ppm)				
			Position of Pyridinium Protons				
			2'	4'	5'	6'	
4a	252-254	83.2	9.87	8.34	9.20	9.20	4.51
4b	226-227	82.6	9.83	8.34	9.17	9.17	4.51
4c	237-240	63.8	9.85	8.38	9.20	9.20	4.52

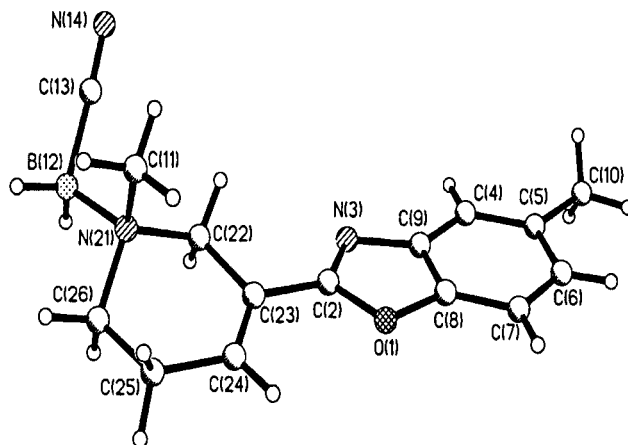
Finally, the pyridinium methiodides **4** were treated with sodium borohydride or sodium cyanoborohydride in tetrahydrofuran to yield the borane or cyanoborane complex of tetrahydropyridines **5**, respectively. The results of

Table 3

Chemical Shifts of Tetrahydropyridine Protons and Physical Properties of Tetrahydropyridinyl-Benzoxazole Borane Complexes

Compound	mp (°C)	Yield (%)	¹ H NMR (δ, ppm)				
			Position of Tetrahydropyridine Protons				
			2'	4'	5'	6'	
5a	116-118	36.5	3.90	7.13	2.59	3.07	2.68
5b	160-162	38.5	3.99	7.12	2.65	3.21	2.78
5c	196-198	46.2	4.02	7.18	2.68	3.22	2.80

the partial reduction and spectral data are shown in Table 3. The structures were determined by X-ray crystallography (for compound **5b**, Figure 1, Tables 4-8) and ir (see the experimental for detailed spectral data).

Figure 1. Molecular Structure of **5b**.

In conclusion, iodobenzene diacetate was utilized for the synthesis of 2-pyridinylbenzoxazoles *via* oxidative intramolecular cyclization of aromatic Schiff's bases which produced from 3-pyridinecarboxaldehyde and substituted *o*-aminophenols. The resulting 2-pyridinylbenzoxazoles were converted to pyridinium methiodides

Table 4

Crystal Data and Structure Refinement for **5b**

Identification code	b
Empirical formula	C ₁₅ H ₁₈ BN ₃ O
Formula weight	267.13
Temperature	294(2) K
Wavelength	0.71073 Å
Crystal system	Monoclinic
Space group	P2 ₁ /n
Unit cell dimensions	a = 7.1147(13) Å α = 90° b = 11.6718(13) Å β = 90.606(13)° c = 17.338(2) Å γ = 90°
Volume, Z	1439.7(3) Å ³ , 4
Density (calculated)	1.232 Mg/m ³
Absorption coefficient	0.078 mm ⁻¹
F(000)	568
Crystal size	0.05 x 0.4 x 0.3 mm
θ range for data collection	2.10 to 25.00°
Limiting indices	-1 ≤ h ≤ 8, -1 ≤ k ≤ 13, -20 ≤ l ≤ 20
Reflections collected	3542
Independent reflections	2545 [R _{int} = 0.0361]
Absorption correction	Semi-empirical from psi-scans
Maximum and minimum transmission	0.2647 and 0.2406
Refinement method	Full-matrix least-squares on F ²
Data/restraints/parameters	2545/0/182
Goodness-of-fit on F ²	1.025
Final R indices [I > 2σ(I)]	R1 = 0.0692, wR2 = 0.1611
R indices (all data)	R1 = 0.1414, wR2 = 0.1950
Extinction coefficient	0.009(3)
Largest diff. peak and hole	0.231 and -0.184 eÅ ⁻³

Table 5
Atomic Coordinates ($\times 10^4$) and Equivalent Isotropic Displacement
Parameters ($\text{\AA}^2 \times 10^3$) for **5b**

	x	y	z	U(eq)
O(1)	293(3)	6164(2)	6167(1)	52(1)
C(2)	-336(6)	5060(3)	6065(2)	47(1)
N(3)	-2034(4)	4969(2)	5791(2)	46(1)
C(4)	-4341(5)	6547(3)	5449(2)	48(1)
C(5)	-4570(6)	7729(3)	5456(2)	51(1)
C(6)	-3090(6)	8425(3)	5711(2)	57(1)
C(7)	-1394(6)	8000(3)	5953(2)	59(1)
C(8)	-1234(6)	6824(3)	5941(2)	47(1)
C(9)	-2641(5)	6102(3)	5709(2)	44(1)
C(10)	-6406(6)	8256(4)	5184(2)	70(1)
C(11)	1049(6)	2472(4)	7636(2)	68(1)
B(12)	402(7)	868(4)	6669(3)	61(1)
C(13)	-1659(7)	754(4)	6989(2)	60(1)
N(14)	-3140(6)	616(4)	7205(3)	87(1)
N(21)	1152(4)	2152(2)	6802(2)	43(1)
C(22)	40(6)	2981(3)	6332(2)	55(1)
C(23)	942(6)	4138(3)	6286(2)	46(1)
C(24)	2739(6)	4300(3)	6431(2)	53(1)
C(25)	4024(6)	3364(3)	6646(2)	60(1)
C(26)	3136(6)	2185(4)	6539(2)	63(1)

*U(eq) is defined as one third of the trace of the orthogonalized U_{ij} tensor.

which were easily converted to tetrahydropyridinylbenzoxazole borane complexes *via* hydride partial reduction in tetrahydrofuran. This method can provide a pathway to the polyheterobicyclic compounds starting from aromatic aldehydes and *o*-aminophenols.

EXPERIMENTAL

Melting points were determined on a Thomas-Hoover apparatus and are uncorrected. Infrared spectra were recorded on a Shimadzu 435 spectrometer. Nuclear magnetic resonance spectra were measured on a Bruker AM-300 spectrometer.

2-Pyridine-3-ylbenzoxazole (**3a**).

2-Aminophenol (2.04 g, 18.70 mmoles) and 2.00 g (18.70 mmoles) of 3-pyridinecarboxaldehyde were stirred in 50 ml of absolute ethanol for 2 hours, then to this was added 6.62 g (20.54 mmoles) of iodobenzene diacetate. After stirring for 10 minutes, the solvent was evaporated and the residue was diluted with ethyl acetate then washed with aqueous sodium hydrogencarbonate solution. The organic layer was separated, washed with brine, dried over anhydrous magnesium sulfate, and then evaporated *in vacuo*. The residue was purified by chromatography on silica gel

Table 6
Bond lengths [\AA] and Angles [$^\circ$] for **5b**

O(1)-C(2)	1.374(4)	O(1)-C(8)	1.385(4)
C(2)-N(3)	1.298(4)	C(2)-C(23)	1.458(5)
N(3)-C(9)	1.397(5)	C(4)-C(9)	1.387(5)
C(4)-C(5)	1.389(5)	C(4)-H(4A)	0.93
C(5)-C(6)	1.398(5)	C(5)-C(10)	1.515(5)
C(6)-C(7)	1.367(5)	C(6)-H(6A)	0.93
C(7)-C(8)	1.377(5)	C(7)-H(7A)	0.93
C(8)-C(9)	1.366(5)	C(10)-H(10A)	0.96
C(10)-H(10B)	0.96	C(10)-H(10C)	0.96
C(11)-N(21)	1.497(4)	C(11)-H(11A)	0.96
C(11)-H(11B)	0.96	C(11)-H(11C)	0.96
B(12)-C(13)	1.579(7)	B(12)-N(21)	1.606(5)
B(12)-H(12A)	0.97	B(12)-H(12B)	0.97
C(13)-N(14)	1.134(5)	N(21)-C(22)	1.487(4)
N(21)-C(26)	1.488(5)	C(22)-C(23)	1.497(5)
C(22)-H(22A)	0.97	C(22)-H(22B)	0.97
C(23)-C(24)	1.315(5)	C(24)-C(25)	1.470(5)
C(24)-H(24A)	0.93	C(25)-C(26)	1.524(5)
C(25)-H(25A)	0.97	C(25)-H(25B)	0.97
C(26)-H(26A)	0.97	C(26)-H(26B)	0.97
C(2)-O(1)-C(8)	103.4(3)	N(3)-C(2)-O(1)	115.1(3)
N(3)-C(2)-C(23)	127.7(3)	O(1)-C(2)-C(23)	117.2(3)
C(2)-N(3)-C(9)	104.2(3)	C(9)-C(4)-C(5)	118.1(4)
C(9)-C(4)-H(4A)	121.0(2)	C(5)-C(4)-H(4A)	121.0(2)
C(4)-C(5)-C(6)	119.5(4)	C(4)-C(5)-C(10)	120.1(4)
C(6)-C(5)-C(10)	120.4(4)	C(7)-C(6)-C(5)	123.1(4)
C(7)-C(6)-H(6A)	118.5(2)	C(5)-C(6)-H(6A)	118.5(2)
C(6)-C(7)-C(8)	115.4(4)	C(6)-C(7)-H(7A)	122.3(2)
C(8)-C(7)-H(7A)	122.3(3)	C(9)-C(8)-C(7)	124.0(4)
C(9)-C(8)-O(1)	108.1(3)	C(7)-C(8)-O(1)	127.9(4)
C(8)-C(9)-C(4)	119.9(3)	C(8)-C(9)-N(3)	109.2(3)
C(4)-C(9)-N(3)	130.9(3)	C(5)-C(10)-H(10A)	109.5(2)
C(5)-C(10)-H(10B)	109.5(2)	H(10A)-C(10)-H(10B)	109.5
C(5)-C(10)-H(10C)	109.5(2)	H(10A)-C(10)-H(10C)	109.5

Table 6 (continued)

N(21)-C(11)-H(11B)	109.5(2)	H(11A)-C(11)-H(11B)	109.5
N(21)-C(11)-H(11C)	109.5(2)	H(11A)-C(11)-H(11C)	109.5
H(11B)-C(11)-H(11C)	109.5	C(13)-B(12)-N(21)	109.6(3)
C(13)-B(12)-H(12A)	109.7(2)	N(21)-B(12)-H(12A)	109.7(2)
C(13)-B(12)-H(12B)	109.7(2)	N(21)-B(12)-H(12B)	109.7(2)
C(22)-N(21)-C(26)	108.5(3)	C(22)-N(21)-C(11)	109.6(3)
C(26)-N(21)-C(11)	110.2(3)	C(22)-N(21)-B(12)	110.8(3)
C(26)-N(21)-B(12)	107.2(3)	C(11)-N(21)-B(12)	110.6(3)
N(21)-C(22)-C(23)	113.0(3)	N(21)-C(22)-H(22A)	109.0(2)
C(23)-C(22)-H(22A)	109.0(2)	N(21)-C(22)-H(22B)	109.0(2)
C(23)-C(22)-H(22B)	109.0(2)	H(22A)-C(22)-H(22B)	107.8
C(24)-C(23)-C(2)	123.1(4)	C(24)-C(23)-C(22)	122.4(4)
C(2)-C(23)-C(22)	114.4(3)	C(23)-C(24)-C(25)	122.9(4)
C(23)-C(24)-H(24A)	118.6(2)	C(25)-C(24)-H(24A)	118.6(2)
C(24)-C(25)-C(26)	112.6(3)	C(24)-C(25)-H(25A)	109.1(2)
C(26)-C(25)-H(25A)	109.1(2)	C(24)-C(25)-H(25B)	109.1(2)
C(26)-C(25)-H(25B)	109.1(2)	H(25A)-C(25)-H(25B)	107.8
N(21)-C(26)-C(25)	112.3(3)	N(21)-C(26)-H(26A)	109.1(2)
C(25)-C(26)-H(26A)	109.1(2)	N(21)-C(26)-H(26B)	109.1(2)
C(25)-C(26)-H(26B)	109.1(2)	H(26A)-C(26)-H(26B)	107.9

Table 7

Anisotropic Displacement Parameters ($\text{\AA}^2 \times 10^3$) for **5b**

	U11	U22	U33	U23	U13	U12
O(1)	53(2)	38(1)	65(2)	0(1)	-11(1)	-6(1)
C(2)	58(3)	39(2)	43(2)	3(2)	0(2)	-7(2)
N(3)	55(2)	36(2)	47(2)	4(1)	-11(2)	-3(2)
C(4)	51(2)	48(2)	45(2)	1(2)	-4(2)	-6(2)
C(5)	60(3)	47(2)	47(2)	6(2)	1(2)	6(2)
C(6)	74(3)	38(2)	60(2)	1(2)	-2(2)	1(2)
C(7)	64(3)	41(2)	72(3)	-2(2)	-9(2)	-8(2)
C(8)	52(2)	41(2)	47(2)	3(2)	-9(2)	0(2)
C(9)	57(3)	38(2)	37(2)	1(2)	-4(2)	-5(2)
C(10)	67(3)	68(3)	76(3)	3(2)	-4(2)	13(3)
C(11)	87(3)	69(3)	48(2)	-3(2)	3(2)	-3(3)
B(12)	71(4)	47(3)	64(3)	2(2)	-6(3)	6(3)
C(13)	68(3)	49(2)	62(3)	5(2)	-7(2)	-6(2)
N(14)	74(3)	85(3)	103(3)	5(2)	6(3)	-8(3)
N(21)	48(2)	42(2)	39(2)	1(1)	-4(1)	5(2)
C(22)	54(2)	46(2)	64(2)	6(2)	-12(2)	-1(2)
C(23)	51(2)	41(2)	46(2)	2(2)	-5(2)	0(2)
C(24)	55(3)	51(2)	52(2)	2(2)	-1(2)	-4(2)
C(25)	48(2)	60(3)	70(3)	4(2)	-5(2)	0(2)
C(26)	60(3)	61(3)	68(3)	4(2)	6(2)	9(2)

*The anisotropic displacement factor exponent takes the form:
 $-2\pi^2[(ha^*)^2U_{11} + \dots + 2hka^*b^*U_{12}]$

Table 8

Hydrogen Coordinates ($\times 10^4$) and Isotropic Displacement Parameters ($\text{\AA}^2 \times 10^3$) for **5b**

	x	y	z	U(eq)
H(4A)	-5301(5)	6068(3)	5275(2)	58
H(6A)	-3268(6)	9214(3)	5716(2)	69
H(7A)	-414(6)	8472(3)	6115(2)	71
H(10A)	-6330(6)	9075(4)	5226(2)	105
H(10B)	-7414(6)	7980(4)	5497(2)	105
H(10C)	-6637(6)	8048(4)	4655(2)	105

Table 8

	x	y	z	U(eq)
H(11A)	1768(6)	1936(4)	7938(2)	101
H(11B)	-237(6)	2457(4)	7797(2)	101
H(11C)	1551(6)	3229(4)	7708(2)	101
H(12A)	407(7)	687(4)	6123(3)	73
H(12B)	1225(7)	330(4)	6934(3)	73
H(22A)	-1198(6)	3062(3)	6555(2)	66
H(22B)	-121(6)	2678(3)	5815(2)	66
H(24A)	3219(6)	5039(3)	6396(2)	63
H(25A)	4403(6)	3455(3)	7181(2)	71
H(25B)	5144(6)	3413(3)	6334(2)	71
H(26A)	3177(6)	1977(4)	5998(2)	76
H(26B)	3864(6)	1624(4)	6827(2)	76

(hexane:ethyl acetate = 4:1), yield 1.17 g (32%), mp 104-106°; ir (potassium bromide): 3050, 1620, 1570, 740 cm^{-1} ; ^1H -nmr (deuteriochloroform): δ 9.48 (s, 1 H, C2'-H), 8.76 (dd, 1 H, C6'-H), 8.50 (m, 1 H, C4'-H), 7.84-7.40 (m, 5 H, aromatic H, C5'-H); ^{13}C -nmr (deuteriochloroform): δ 160.7 (C-2), 152.0 (C-6'), 150.7 (C-8), 148.7 (C-2'), 141.7 (C-9), 134.7 (C-4'), 123.5 (C-3'), 125.7, 124.9, 123.7, 120.2, 110.7 (C-5', aromatic C).

Anal. Calcd. for $\text{C}_{12}\text{H}_8\text{N}_2\text{O}$: C, 73.46; H, 4.11; N, 14.28. Found: C, 73.12; H, 4.28; N, 14.31.

5-Methyl-2-pyridine-3-ylbenzoxazole (**3b**).

Compound **3b** was prepared from 2-amino-*p*-cresol and 3-pyridinecarboxaldehyde by the above procedure and purified chromatographically on silica gel (hexane:ethyl acetate = 4:1), yield 48%, mp 98-100°; ir (potassium bromide): 3050, 3000, 1600, 1410, 1070 cm^{-1} ; ^1H -nmr (deuteriochloroform): δ 9.47 (s, 1 H, C2'-H), 8.75 (dd, 1 H, C6'-H), 8.46 (m, 1 H, C4'-H), 7.57 (s, 1 H, C4-H), 7.48-7.17 (m, 3 H, aromatic H, C5'-H), 2.49 (s, 3 H, CH₃); ^{13}C -nmr (deuteriochloroform): δ 160.3 (C-2), 152.1 (C-6'), 148.4 (C-8), 147.8 (C-2'), 141.4 (C-9), 134.5 (C-4'), 134.4 (C-5), 122.8 (C-3'), 126.9, 124.2, 123.7, 119.7, 110.4 (C-5', aromatic C), 20.9 (CH₃).

Anal. Calcd. for $\text{C}_{13}\text{H}_{10}\text{N}_2\text{O}$: C, 74.21; H, 4.79; N, 13.33. Found: C, 73.90; H, 4.87; N, 13.34.

5-Chloro-2-pyridine-3-ylbenzoxazole (3c).

Compound **3c** was prepared from 2-amino-4-chlorophenol and 3-pyridinecarboxaldehyde according to the procedure for **3a**, and purified chromatographically on silica gel (hexane:ethyl acetate = 4:1), yield 42%, mp 147-148°; ir (potassium bromide): 3080, 3020, 1610, 1590, 1550 cm^{-1} ; $^1\text{H-nmr}$ (deuteriochloroform): δ 9.43 (s, 1 H, C2'-H), 8.76 (dd, 1 H, C6'-H), 8.46 (m, 1 H, C4'-H), 7.74 (s, 1 H, C4-H), 7.49-7.26 (m, 3 H, aromatic H, C5'-H); $^{13}\text{C-nmr}$ (deuteriochloroform): δ 162.0 (C-2), 152.4 (C-6'), 149.3 (C-8), 148.8 (C-2'), 142.8 (C-9), 134.8 (C-4'), 130.4 (C-5), 123.0 (C-3'), 126.0, 123.7, 120.2, 111.4 (C-5', aromatic C).

Anal. Calcd. for $\text{C}_{12}\text{H}_7\text{N}_2\text{OCl}$: C, 62.49; H, 3.06; N, 12.15. Found: C, 62.09; H, 3.06; N, 12.02.

2-(1-Methyl)pyridinium-3-ylbenzoxazole Iodide (4a).

To a stirred solution of 1.17 g (5.95 mmoles) **3a** in 30 ml of acetone was added a solution of 6.77 g (47.68 mmoles) of iodomethane in 10 ml acetone, then the mixture was stirred for 20 hours at room temperature. The precipitate was filtered, the filter cake was washed with acetone, then dried under reduced pressure, yield 1.68 g (83%), mp 252-254°; ir (potassium bromide): 3000, 1640, 1490, 760 cm^{-1} ; $^1\text{H-nmr}$ (deuteriodimethyl sulfoxide): δ 9.87 (s, 1 H, C2'-H), 9.20 (m, 2 H, C5', C6'-H), 8.34 (dd, 1 H, C4'-H), 7.98-7.50 (m, 4 H, C4, 5, 6, 7-H), 4.51 (s, 3 H, CH_3); $^{13}\text{C-nmr}$ (deuteriodimethyl sulfoxide): δ 157.1 (C-2), 150.3 (C-8), 147.3 (C-6'), 144.5 (C-2'), 142.1 (C-5'), 140.7 (C-9), 126.3 (C-3'), 128.2, 127.1, 125.8, 120.3, 111.4 (C-4', aromatic C), 48.7 (CH_3).

Anal. Calcd. for $\text{C}_{13}\text{H}_{11}\text{N}_2\text{OI}$: C, 46.18; H, 3.28; N, 8.28. Found: C, 46.37; H, 3.27; N, 8.28.

5-Methyl-2-(1-methyl)pyridinium-3-ylbenzoxazole Iodide (4b).

The title compound **4b** was prepared from **3b** according to the procedure described for **4a**, yield 83%; mp 226-227°; ir (potassium bromide): 3050, 3000, 1640, 1490 cm^{-1} ; $^1\text{H-nmr}$ (deuteriodimethyl sulfoxide): δ 9.83 (s, 1 H, C2'-H), 9.17 (m, 2 H, C5', C6'-H), 8.34 (dd, 1 H, C4'-H), 7.77-7.37 (m, 3 H, C4, 6, 7-H), 4.51 (s, 3 H, NCH_3), 2.46 (s, 3 H, aromatic CH_3); $^{13}\text{C-nmr}$ (deuteriodimethyl sulfoxide): δ 158.3 (C-2), 150.7 (C-8), 148.1 (C-6'), 145.7 (C-2'), 143.5 (C-5'), 142.8 (C-9), 137.3 (C-5), 129.2 (C-3'), 129.7, 129.6, 121.5, 111.8 (C-4', aromatic C), 49.7 (NCH_3), 21.5 (aromatic CH_3).

Anal. Calcd. for $\text{C}_{14}\text{H}_{13}\text{N}_2\text{OI}$: C, 47.75; H, 3.72; N, 7.95. Found: C, 47.97; H, 3.69; N, 7.97.

5-Chloro-2-(1-methyl)pyridinium-3-ylbenzoxazole Iodide (4c).

Compound **4c** was prepared from **3c** by the procedure described for **4a**, yield 64%; mp 237-240°; ir (potassium bromide): 3500, 3100, 1640, 1440 cm^{-1} ; $^1\text{H-nmr}$ (deuteriodimethyl sulfoxide): δ 9.85 (s, 1 H, C2'-H), 9.20 (m, 2 H, C5', C6'-H), 8.38 (dd, 1 H, C4'-H), 8.05-7.56 (m, 3 H, C4, 6, 7-H), 4.52 (s, 3 H, CH_3); $^{13}\text{C-nmr}$ (deuteriodimethyl sulfoxide): δ 158.6 (C-2), 149.2 (C-8), 147.7 (C-6'), 144.7 (C-2'), 142.4 (C-5'), 142.0 (C-9), 126.0 (C-3'), 129.9, 128.3, 127.2, 120.2, 112.9 (C-4', aromatic C), 48.5 (CH_3).

Anal. Calcd. for $\text{C}_{13}\text{H}_{10}\text{N}_2\text{OICl}$: C, 41.91; H, 2.71; N, 7.52. Found: C, 41.87; H, 2.65; N, 7.38.

2-(1-Methyl-1,2,5,6-tetrahydropyridin-3-yl)benzoxazole-trihydroborane (5a).

To a cooled (-10°) and stirred suspension of 0.87 g (2.57 mmoles) of **4a** in 30 ml of methanol was added portionwise

0.19 g (5.14 mmoles) of sodium borohydride. After stirring at 0° for 1 hour, the solvent was evaporated. The residue was dissolved in ethyl acetate and washed with aqueous sodium hydrogencarbonate solution. The organic layer was washed with brine, dried over anhydrous magnesium sulfate, and then evaporated *in vacuo*. The residue was purified chromatographically on silica gel (hexane:ethyl acetate = 4:1), yield 0.20 g (37%), mp 116-118°; ir (potassium bromide): 3500, 3000, 2350 (borane), 1660, 1450 cm^{-1} ; $^1\text{H-nmr}$ (deuteriochloroform): δ 7.71-7.30 (m, 4 H, aromatic H), 7.13 (m, 1 H, C4'-H), 3.90 (m, 2 H, C2'-H), 3.07 (m, 2 H, C6'-H), 2.68 (s, 3 H, CH_3), 2.59 (m, 2 H, C5'-H); $^{13}\text{C-nmr}$ (deuteriochloroform): δ 160.5 (C-2), 150.2 (C-8), 141.4 (C-9), 122.1 (C-3'), 130.3, 125.6, 124.7, 120.1, 110.4 (C-4', aromatic C), 57.3 (C-2'), 55.2 (C-6'), 48.7 (C-5'), 22.5 (CH_3).

Anal. Calcd. for $\text{C}_{13}\text{H}_{17}\text{BN}_2\text{O}$: C, 68.45; H, 7.51; N, 12.28. Found: C, 68.50; H, 7.68; N, 12.18.

5-Methyl-2-(1-methyl-1,2,5,6-tetrahydropyridine-3-yl)benzoxazole Cyanodihydroborane Complex (5b).

To a cooled (-10°) and stirred suspension of 0.60 g (1.70 mmoles) of **4b** in 30 ml of tetrahydrofuran was added portionwise 0.16 g (2.56 mmoles) sodium cyanoborohydride. After stirring at room temperature for 2 hours, the solvent was evaporated. The residue was dissolved in ethyl acetate and washed with aqueous sodium hydrogencarbonate solution. The organic layer was washed with brine, dried over anhydrous magnesium sulfate, and then evaporated *in vacuo*. The residue was purified chromatographically on silica gel (hexane:ethyl acetate = 4:1), yield 0.15 g (39%), mp 160-162°; ir (potassium bromide): 2900, 2400 (nitrile), 1660, 1520 cm^{-1} ; $^1\text{H-nmr}$ (deuteriochloroform): δ 7.47-7.14 (m, 3 H, aromatic H), 7.12 (m, 1 H, C4'-H), 3.99 (m, 2 H, C2'-H), 3.21 (m, 2 H, C6'-H), 2.78 (s, 3 H, NCH_3), 2.65 (m, 2 H, C5'-H), 2.46 (s, 3 H, CH_3); $^{13}\text{C-nmr}$ (deuteriochloroform): δ 159.8 (C-2), 148.3 (C-8), 141.3 (C-9), 134.6 (C-5), 121.2 (C-3'), 129.4, 126.9, 120.0, 109.8 (C-4', aromatic C), 56.2 (C-2'), 53.9 (C-6'), 46.8 (C-5'), 21.7 (NCH_3), 21.4 (CH_3).

Anal. Calcd. for $\text{C}_{15}\text{H}_{18}\text{BN}_3\text{O}$: C, 67.44; H, 6.79; N, 15.73. Found: C, 67.25; H, 6.84; N, 15.59.

5-Chloro-2-(1-methyl-1,2,5,6-tetrahydropyridine-3-yl)benzoxazole Cyanodihydroborane Complex (5c).

Compound **5c** was prepared from **4c** by the procedure described for **5a**, yield 46%; mp 196-198°; ir (potassium bromide): 3100, 2400 (nitrile), 1660, 1530, 1450 cm^{-1} ; $^1\text{H-nmr}$ (deuteriochloroform): δ 7.67-7.33 (m, 3 H, aromatic H), 7.18 (m, 1 H, C4'-H), 4.02 (m, 2 H, C2'-H), 3.22 (m, 2 H, C6'-H), 2.80 (s, 3 H, NCH_3), 2.68 (m, 2 H, C5'-H); $^{13}\text{C-nmr}$ (deuteriochloroform): δ 161.4 (C-2), 149.2 (C-8), 142.8 (C-9), 130.7 (C-5), 121.4 (C-3'), 131.3, 126.5, 120.6, 111.7 (C-4', aromatic C), 56.6 (C-2'), 54.4 (C-6'), 47.5 (C-5'), 22.3 (CH_3).

Anal. Calcd. for $\text{C}_{14}\text{H}_{15}\text{BN}_3\text{OCl}$: C, 58.48; H, 5.26; N, 14.61. Found: C, 58.47; H, 5.34; N, 14.51.

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