Quinoxalines X [1]. A New and Convenient Synthesis of 1*H*-Pyrazolo[3,4-*b*]quinoxalines (Flavazoles)

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Dedicated to Professor Gerhard Kempter on the occasion of his 70th birthday

Quinoxaline-2-aldoximes and -ketoximes (**6**) react with hydrazine, alkylhydrazines or arylhydrazines under acidic conditions to afford 1*H*-pyrazolo[3,4-*b*]quinoxalines (flavazoles) (**1**). Since the oximes (**6**) are easily available from phenylenediamine, the herein described methodology provides a convenient two step entry to various functionalized flavazoles. Furthermore, acylation and alkylation of the 1-unsubstituted 1*H*-pyrazolo[3,4-*b*]quinoxalines **7** proceeds smoothly and in good yield to afford 31 different flavazoles **11** and **12**.

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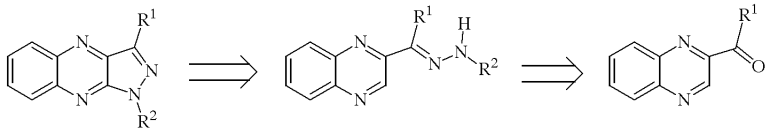
1*H*-Pyrazolo[3,4-*b*]quinoxalines (flavazoles) (**1**) are a group of heterocyclic compounds, which are of great biological interest. In early studies they were used for the characterization of carbohydrates [2]. More recently, flavazoles were found to exhibit a high antibacterial activity [3], significant diuretic and antiinflammatory properties [4], antifungal activity [5], as well as cytotoxic effects [6].

Structures **1-3**



1 **2** **3**

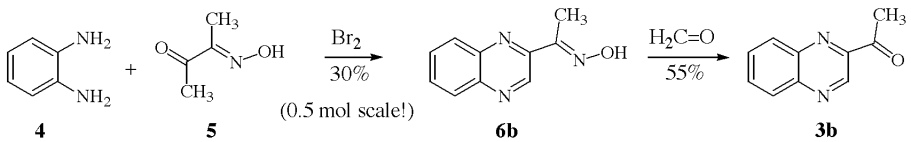
Besides a few examples of pyrazine cyclizations [7], the most common synthesis of the flavazole system start from quinoxaline hydrazones **2** by dehydrogenation [8], dehydration [9], or dehydrochlorination [3,6,10]. However, expensive reagents like azobenzene were used for the dehydrogenations. Furthermore, the requisite hydrazones **2** had to be synthesized from carbonyl compounds **3**, which are oxidation labile and were only available in small amounts [11].

To overcome this problem, we developed a convenient one-pot synthesis of 2-acetylquinoxaline (**3b**) starting from 1,2-phenylenediamine (**4**) and 2,3-butanedione monoxime (**5**) *via* the oxime **6b** on a large scale (Scheme 1) [12]. Since oximes can be directly transformed into hydrazones, we became interested in a new synthesis of flavazoles in only a few steps starting from 1,2-phenylenediamine (**4**).

In our initial experiments, we focused on the simple reaction of the oximes **6** with hydrazine hydrate under acidic conditions. After optimization, cheap hydrochloric acid was found to give the best results. Indeed, the desired flavazoles **7** were isolated in only one step in high yield (Scheme 2). In the first step of the reaction, hydrazones **8** were obviously formed *in situ* by the elimination of hydroxylamine. Acid catalyzed protonation of one ring nitrogen induced directly the cyclization to the dihydroflavazoles **9**, which were readily oxidized to the aromatic system. This mechanistic proposal is in accordance with literature known reactions of flavazole derivatives derived from sugars [13]. Furthermore, it seems to provide an explanation, why a similar acid catalyzed cyclization of quinoline hydrazones fails [14], since there is not the second ring nitrogen. Finally, the advantage of our strategy described herein is not only the direct one-step synthesis of flavazoles **7**, but also the liberation of hydroxylamine, acting as the oxidant in the last step. Thus, neither expensive co-oxidants like azobenzene nor an excess of hydrazine should be necessary for the reaction sequence.

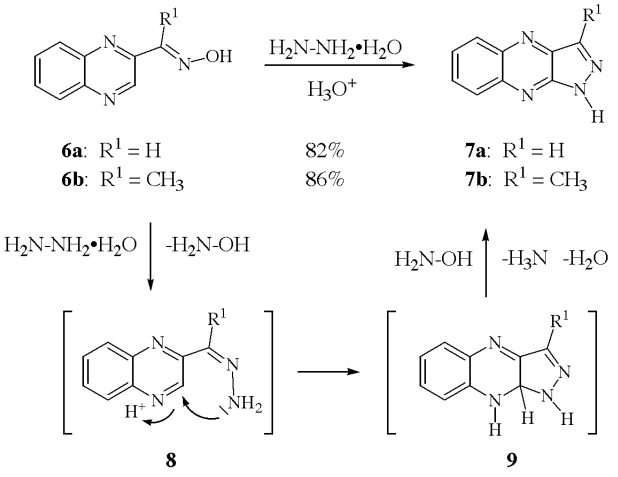
To prove this hypothesis further and to evaluate the scope and limitations of this new flavazole synthesis, we investigated the one-pot reaction of the oximes **6** with a

Scheme 1



4 **5** **6b** **3b**

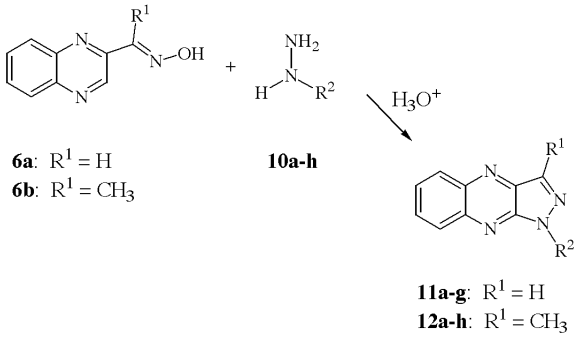
Scheme 2



broad variety of alkyl and aryl substituted hydrazines **10** (Scheme 3). Indeed, only 1.1 equivalent of hydrazine was required for the complete conversion of the oximes **6**, indicating that hydrazine does not act as the oxidant. Thus, the direct synthesis of flavazoles from oximes does not only reduce the number of steps, but also no external oxidant is necessary. This new strategy allowed the synthesis of 15 different flavazoles **11** and **12** in moderate to good yields (Table 1), and some of them showed promising antifungal and antibacterial activity [3,15].

Interestingly, benzohydrazides **10** (R^2 = COAr) did not react with oximes **6** to the desired products under acidic conditions, even after prolonged reaction times. To investigate the reason for this behavior, we synthesized the acylhydrazones **2i-k** independently and treated these compounds with strong acids. However, even under such drastic conditions no cyclization occurred (Scheme 4). Obviously, the acylated nitrogen atom is not nucleophilic enough to attack the protonated quinoxaline ring. To overcome this problem, the acylhydrazones **2** were cylized in the presence of *p*-chloranil. This reagent induces radical reactions by H-atom abstraction. Indeed, the so formed aza radicals attack the quinoxaline ring intramoleculary to afford the desired benzoyl flavazoles **12i-k** after oxidation to the aromatic system. However, due to side reactions only moderate yields were achieved (Scheme 4).

Scheme 3



Scheme 4

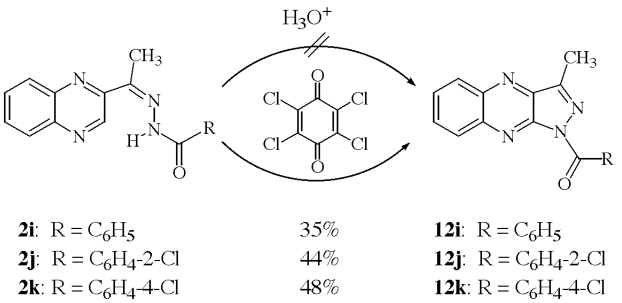


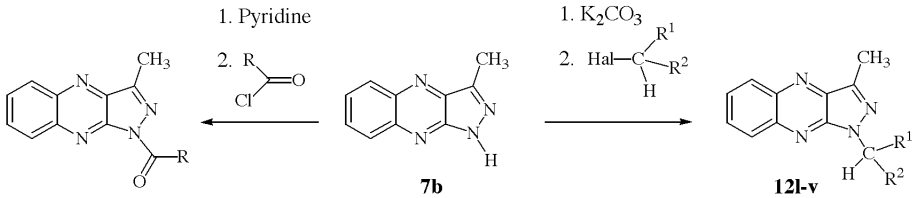
Table 1

Flavazole	R^1	R^2	Yield (%)
11a	H	CH_3	72
11b	H	$C(CH_3)_3$	77
11c	H	C_6H_5	53
11d	H	C_6H_4-2-Cl	36
11e	H	C_6H_4-3-Cl	44
11f	H	C_6H_4-4-Cl	62
11g	H	C_6H_4-4-NO_2	48
12a	CH_3	CH_3	73
12b	CH_3	$C(CH_3)_3$	81
12c	CH_3	C_6H_5	73
12d	CH_3	C_6H_4-2-Cl	54
12e	CH_3	C_6H_4-3-Cl	62
12f	CH_3	C_6H_4-4-Cl	58
12g	CH_3	C_6H_4-4-NO_2	76
12h	CH_3	C_6H_4-4-Br	77

To obtain higher yields of benzoyl flavazoles **12i-k** and to introduce various other substituents at N-1 of the flavazole system, we became finally interested in the acylation and alkylation of the unsubstituted flavazole **7b**. Thus, a broad variety of 11 additional flavazoles **12l-v** were synthesized in moderate to good yields (Scheme 5, Table 2).

In conclusion, we developed a new and convenient synthesis of various flavazoles in only few steps starting from phenylenediamine. The key step is the one-pot transformation of oximes into the corresponding flavazoles. The advantage of this strategy consists in the elimination of hydroxylamine, which acts as the oxidant for the final aromatization. Furthermore, acylation and alkylation of the unsubstituted nitrogen offered an entry to functionalized derivatives. Since many of such compounds exhibit promising biological activities, the methodology described herein would be applicable for the synthesis of other flavazoles.

Scheme 5



12i: R = C_6H_5 (55%)
12j: R = C_6H_4-2-Cl(58%)
12k: R = C_6H_4-4-Cl(46%)

Table 2

Flavazole	R^1	R^2	Yield (%)
12a	H	H	65
12l	CH_3	H	59
12m	CH_3	CH_3	76
12n	$CH_2CH_2CH_3$	H	48
12o	$CH(CH_3)_2$	H	42
12p	Vinyl	H	65
12q	$CO_2CH_2CH_3$	H	78
12r	$CO_2CH_2CH_3$	CH_3	69
12s	C_6H_5	H	37
12t	C_6H_4-4-Cl	H	52
12u	C_6H_5	CH_3	45
12v		H	40

EXPERIMENTAL

All melting points were determined on a Boetius micro hotstage microscope (Fa. Analytik Dresden). The ir spectra (potassium bromide) were recorded with a Perkin Elmer FTIR 1600 spectrometer (cm^{-1}). The mass spectra (ms) were obtained on a Finnigan-MAT SSQ 710 (70 eV). Elemental analyses were performed on the autanalyser CHNS-932 (Fa. Leco instruments GmbH); satisfactory microanalyses were obtained for all new substances (C, H, N +/-0,3%). The ^1H and ^{13}C nmr spectra were determined for solution in deuteriochloroform or deuteriodimethyl sulfoxide on a Bruker ARX 300 NMR spectrometer at 300.13 MHz and 75.47 MHz, respectively; the chemical shifts are given in the δ scale (ppm) downfield from tetramethyl silane (TMS) as internal standard.

1*H*-Pyrazolo[3,4-*b*]quinoxaline (**7a**).

Aqueous 20% hydrazine hydrate 7.5 ml (30 mmoles) and 5 ml of 37% hydrochloric acid were added to a hot solution of 1.73 g (10 mmoles) of oxime **6a** in 75 ml of ethanol. The mixture was heated at reflux for 4 hours, concentrated *in vacuo* and neutralized with a 5% aqueous solution of sodium carbonate. The solid was collected by filtration, washed with water and recrystallized from toluene to yield 1.40 g (82%) of **7a**, mp 280-282 °C; ms: m/z 170 (M^+); ir: 3120, 3085, 3045, 2905, 2834, 1615, 1590, 1560, 1510, 1470, 1415, 1340, 1215, 1175, 1120, 1050, 920, 850, 755, 600, 550, 420; ^1H nmr (deuteriodimethyl sulfoxide): δ 13.13 (br, 1H, NH), 8.77 (s, 1H, 3-H), 8.27-7.82 (m, 4H, aromatic); ^{13}C nmr (deuteriodimethyl sulfoxide): δ 143.2, 141.1, 140.7, 136.5, 134.5, 130.9, 130.0, 128.5, 128.0.

Anal. Calcd. for $C_9H_6N_4$: C, 63.52; H, 3.55; N, 32.92. Found: C, 63.80; H, 3.61; N, 33.26.

3-Methyl-1*H*-pyrazolo[3,4-*b*]quinoxaline (**7b**).

Aqueous 20% hydrazine hydrate 7.5 ml (30 mmoles) and 5 ml of 37% hydrochloric acid were added to a hot solution of 1.87 g (10 mmoles) of oxime **6b** in 75 ml of ethanol. The mixture was heated at reflux for 4 hours, concentrated *in vacuo* and neutralized with a 5% aqueous solution of sodium carbonate. The solid was collected by filtration, washed with water and was recrystallized from dioxane to yield 1.58 g (86%) of **7b**, mp 224-226 °C; ms: m/z 184 (M^+); ir: 3114, 3024, 2864, 2798, 1624, 1594, 1562, 1506, 1480, 1436, 1382, 1344, 1300, 1244, 1212, 1138, 1092, 980, 916, 814, 750, 650, 610, 590, 420; ^1H nmr (deuteriodimethyl sulfoxide): δ 13.64 (s, 1H, NH), 8.26-7.79 (m, 4H, aromatic), 2.73 (s, 3H, 3-CH_3); ^{13}C nmr (deuteriodimethyl sulfoxide): δ 143.8, 142.3, 141.0, 139.9, 135.7, 130.5, 129.1, 128.2, 127.3, 11.51.

Anal. Calcd. for $C_{10}H_8N_4$: C, 65.21; H, 4.38; N, 30.42. Found: C, 65.45; H, 4.67; N, 30.19.

General Procedure for the Reaction of Oximes **6a** and **6b** with Alkylhydrazines **10a** and **10b**.

A solution of the appropriate alkylhydrazine **10a** or **10b** (15 mmoles) in hot ethanol was added to a solution of 1.73 g (10 mmoles) of oxime **6a** or 1.83 g (10 mmoles) of oxime **6b** in 100 ml of hot ethanol. After the addition of 5 ml of 37% hydrochloric acid the mixture was heated at reflux for 5 hours. The solution was concentrated *in vacuo* to 30 ml and was neutralized with a 5% aqueous solution of sodium carbonate. The mixture was kept in a refrigerator overnight and the precipitate was collected by filtration, washed with water and recrystallized.

1-Methyl-1*H*-pyrazolo[3,4-*b*]quinoxaline (**11a**).

This compound was obtained from **6a** and methylhydrazine sulphate (**10a**) in 72% yield as colorless needles (ethanol), mp 123.5-124.5 °C; ms: m/z 184 (M^+); ir: 3095, 3060, 2920, 1615, 1575, 1485, 1435, 1405, 1355, 1330, 1200, 1150, 1095, 920, 905, 845, 810, 755, 740, 730, 650, 600; ^1H nmr (deuteriochloroform): δ 8.42 (s, 1H, 3-H), 8.18-7.64 (m, 4H, aromatic), 4.20 (s, 3H,

1-CH_3); ^{13}C nmr (deuteriochloroform): δ 141.9, 141.3, 140.9, 136.5, 132.9, 130.5, 130.0, 128.4, 127.5, 34.1.

Anal. Calcd. for $C_{10}H_8N_4$: C, 65.20; H, 4.38; N, 30.41. Found: C, 65.40; H, 4.42; N, 30.34.

1-*tert*-Butyl-1*H*-pyrazolo[3,4-*b*]quinoxaline (**11b**).

This compound was obtained from **6a** and *tert*-butylhydrazine hydrochloride (**10b**) in 77% yield as colorless needles (methanol), mp 79-80 °C; ms: m/z 226 (M^+); ir: 3100, 3060, 2980, 2925, 2905, 2825, 1560, 1495, 1480, 1415, 1390, 1355, 1350, 1300, 1235, 1170, 1110, 1035, 1000, 905, 845. 830, 780, 605, 420; ^1H nmr (deuteriochloroform): δ 8.44 (s, 1H, 3-H), 8.17-7.67 (m, 4H, aromatic), 1.92 (s, 9H, *tert*-butyl-H); ^{13}C nmr (deuteriochloroform): δ 142.2, 140.8, 140.6, 137.4, 131.7, 130.0, 129.9, 129.1, 127.5, 60.69, 28.90 (3).

Anal. Calcd. for $C_{13}H_{14}N_4$: C, 69.00; H, 6.24; N, 24.76. Found: C, 69.07; H, 6.30; N, 25.04.

1,3-Dimethyl-1*H*-pyrazolo[3,4-*b*]quinoxaline (**12a**).

This compound was obtained from **6b** and methylhydrazine sulphate (**10a**) in 73% yield as yellow needles (cyclohexane), mp 137-138 °C; ms: m/z 198 (M^+); ir: 2930, 1620,1580,1510, 1500, 1400, 1380, 1350, 1260, 1245, 1185, 1125, 1050, 960, 900, 845, 765, 725, 655, 630, 605, 420; ^1H nmr (deuteriochloroform): δ 8.19-7.63 (m, 4H, aromatic), 4.12 (s, 3H, 1-CH_3), 2.75 (s, 3H, 3-CH_3); ^{13}C nmr (deuteriochloroform): δ 142.7, 141.8, 141.4, 140.3, 136.0, 130.4, 130.1, 128.3, 127.0, 33.60, 11.47.

Anal. Calcd. for $C_{11}H_{10}N_4$: C, 66.65; H, 5.08; N, 28.26. Found: C, 66.43; H, 5.38; N, 28.35.

1-*tert*-Butyl-3-methyl-1*H*-pyrazolo[3,4-*b*]quinoxaline (**12b**).

This compound was obtained from **6b** and *tert*-butylhydrazine hydrochloride (**10b**) in 81% yield as yellow needles (ethanol), mp 159.5-160.5 °C; ms: m/z 240 (M^+); ir: 3070, 2980, 2930, 2870, 1960, 1620, 1515, 1500, 1475, 1425, 1375, 1310, 1395, 1310, 1240, 1205, 1150, 1130, 1205, 995, 805, 755, 725, 665, 615, 600, 620, 415; ^1H nmr (deuteriochloroform): δ 8.22-7.65 (m, 4H, aromatic), 2.80 (s, 3H, 3-CH_3), 1.90 (s, 9H, *tert*-butyl); ^{13}C nmr (deuteriochloroform): δ 143.0, 141.0, 140.4, 140.0, 136.9, 129.9, 129.9, 129.0, 127.0, 60.04, 29.02, 11.61.

Anal. Calcd. for $C_{14}H_{16}N_4$: C, 69.97; H, 6.71; N, 23.31. Found: C, 69.81; H, 6.50; N, 23.57.

General Procedure for the Reaction of Oxime **6a** with Arylhydrazines **10c-g**.

A solution of the appropriate arylhydrazine **10c-g** (11 mmoles) or corresponding hydrochloride in acetic acid was added to a solution of 1.73 g (10 mmoles) of oxime **6a** in 100 ml of acetic acid at 80 °C. After the addition of 5 ml of a 60% aqueous solution of perchloric acid, the mixture was heated at reflux for 30-60 minutes. The products, precipitate directly at room temperature or after the addition of water, were collected by filtration and washed with water.

1-Phenyl-1*H*-pyrazolo[3,4-*b*]quinoxaline (**11c**).

This compound was obtained from **10c** in 53% yield as yellow needles (50% aqueous acetic acid), mp 147-149 °C; ms: m/z 246 (M^+); ir: 3090, 3063, 1700, 1652, 1599, 1576, 1501, 1427, 1391, 1360, 1214, 1166, 1120, 1088, 1055, 1009, 970, 905, 850, 804, 750, 689, 672, 608, 532, 500, 421; ^1H nmr (deuteriochloroform): δ 8.47 (s, 1H, C^3-H), 8.30-7.98 (m, 4H, aromatic/quinoxaline), 7.67-7.14 (m, 5H, aromatic/ phenyl); ^{13}C nmr (deuteriochloroform): δ 141.7, 141.4, 141.1, 139.2, 137.8, 135.0, 130.9, 130.0, 129.1 (2), 129.0, 128.2, 125.8, 119.8 (2).

Anal. Calcd. for $C_{15}H_{10}N_4$: C, 73.16; H, 4.09; N, 22.75. Found: C, 73.27; H, 4.13; N, 22.98.

1-(2-Chlorophenyl)-1*H*-pyrazolo[3,4-*b*]quinoxaline (**11d**).

This compound was obtained from **10d** in 36% yield as yellow needles (ethanol), mp 133.5-134.5 °C; ms: m/z 280 (M^+), 282 (M^++2); ir: 3080, 3066, 1588, 1575, 1565, 1490, 1470, 1380, 1350, 1225, 1205, 1125, 1095, 1070, 1045, 990, 835, 750, 730, 660, 600, 420; ^1H nmr (deuteriochloroform): δ 8.73 (s, 1H, 3-H), 8.30-7.48 (m, 8H, aromatic); ^{13}C nmr (deuteriochloroform): δ 142.9, 141.9, 141.7, 137.0, 135.8, 135.4, 132.3, 131.1, 130.8, 130.4, 130.3, 129.7, 128.9, 128.3, 127.7.

Anal. Calcd. for $C_{15}H_9ClN_4$: C, 64.18; H, 3.23; N, 19.96. Found: C, 64.31; H, 3.28; N, 19.93.

1-(3-Chlorophenyl)-1*H*-pyrazolo[3,4-*b*]quinoxaline (**11e**).

This compound was obtained from **10e** in 44% yield as yellow needles (1,2-dimethoxyethane), mp 152-153 °C; ms: m/z280 (M^+), 282 (M^++2); ir: 3100, 3030, 1600, 1590, 1570, 1560, 1540, 1520, 1485, 1465, 1415, 1380, 1350, 1250, 1220, 1120, 1100, 1075, 945, 855, 770, 755, 735, 670, 660, 420; ^1H nmr (deuteriochloroform): δ 8.57 (s, 1H, 3-H), 8.48-7.23 (m, 8H,aromatic); ^{13}C nmr (deuteriochloroform): δ 141.9, 141.3, 140.2, 138.0, 135.7, 134.9, 131.2, 130.1 (3), 129.1, 128.6, 125.7, 119.5, 117.4.

Anal. Calcd. for $C_{15}H_9ClN_4$: C, 64.18; H, 3.23; N, 19.96. Found: C, 64.30; H, 3.27; N, 19.68.

1-(4-Chlorophenyl)-1*H*-pyrazolo[3,4-*b*]quinoxaline (**11f**).

This compound was obtained from **10f** in 62% yield as yellow needles (dimethylformamide), mp 197-198 °C; ms: m/z280 (M^+), 282 (M^++2); ir: 3110, 3060, 1600, 1580, 1570, 1560, 1540, 1500, 1430, 1380, 1330, 1250, 1220, 1120, 1105, 1065, 970, 905, 855, 750, 730, 685, 665, 605, 420; ^1H nmr (deuteriochloroform): δ 8.93 (s, 1H, 3-H), 8.55-7.47 (m, 8H, aromatic).

Anal. Calcd. for $C_{15}H_9ClN_4$: C, 64.18; H, 3.23; N, 19.96. Found: C, 63.99; H, 3.07; N, 19.63.

1-(4-Nitrophenyl)-1*H*-pyrazolo[3,4-*b*]quinoxaline (**11g**).

This compound was obtained from **10g** in 48% yield as yellow needles (pyridine), mp 310-311 °C; ms: m/z 291 (M^+); ir: 3080, 1596, 1564, 1548, 1518, 1504, 1482, 1430, 1388, 1334, 1236, 1216, 1166, 1148, 1114, 1068, 970, 908, 804, 850, 766, 748, 730, 684, 608, 548, 528, 496, 422.

Anal. Calcd. for $C_{15}H_9N_5O_2$: C, 61.86; H, 3.11; N, 24.04. Found: C, 61.74; H, 3.05; N, 24.25.

General Procedure for the Reaction of Oxime **6b** with Arylhydrazines **10c-h**.

A solution of the appropriate arylhydrazines **10c-h** (10.5 mmoles) or corresponding hydrochloride in acetic acid was added to a solution of 1.87 g (10 mmoles) of oxime **6b** in 30 ml of acetic acid at 80 °C. After the addition of 5 ml of 37% hydrochloric acid, the mixture was heated at reflux for 15-30 minutes. The products, precipitated directly at room temperature or after the addition of water, were collected by filtration and washed with water.

3-Methyl-1-phenyl-1*H*-pyrazolo[3,4-*b*]quinoxaline (**12c**).

This compound was obtained from **10c** in 73% yield as yellow needles (ethanol), mp 134-135 °C; ms: m/z 260 (M^+); ir: 3065, 2950, 2920, 1600, 1570, 1505, 1480, 1450, 1380, 1355, 1335, 1250, 1240, 1200, 1130, 1115, 1075, 1060, 1035, 1000, 900, 840, 750, 740, 690, 675, 660, 600, 500, 460, 402; ^{1}H nmr (deuteriochloroform): δ 8.39-7.25 (m, 9H, aromatic), 2.80 (s, 3H, Me); ^{13}C nmr (deuteriochloroform): δ 144.1, 142.3, 141.3, 140.5, 139.3, 137.5, 130.6, 130.0, 129.0 (2), 128.8, 127.7, 125.1, 119.3 (2), 11.6.

Anal. Calcd. for $C_{16}H_{12}N_4$: C, 73.83; H, 4.64; N, 21.53. Found: C, 73.54; H, 4.74; N, 21.42.

1-(2-Chlorophenyl)-3-methyl-1*H*-pyrazolo[3,4-*b*]quinoxaline (**12d**).

This compound was obtained from **10d** in 54% yield as yellow needles (cyclohexane), mp 155-156 °C; ms: m/z 293 (M^+), 295 (M^++2); ir: 3060, 2985, 2955, 1590, 1565, 1495, 1475, 1450, 1380, 1355, 1270, 1240, 1200, 1130, 1100, 1080, 1050, 1000, 840, 720, 660, 610, 600; ^{1}H nmr (deuteriochloroform): δ 8.28-7.44 (m, 8H, aromatic), 2.89 (s, 3H, CH_3); ^{13}C nmr (deuteriochloroform): δ 144.7, 143.5, 141.7, 140.9, 136.7, 135.5, 132.1, 130.8, 130.7, 130.2, 130.0, 129.6, 128.7, 127.7, 127.6, 11.7.

Anal. Calcd. for $C_{16}H_{11}ClN_4$: C, 65.21; H, 3.76; N, 19.01. Found: C, 65.14; H, 3.88; N, 19.08.

1-(3-Chlorophenyl)-3-methyl-1*H*-pyrazolo[3,4-*b*]quinoxaline (**12e**).

This compound was obtained from **10e** in 62% yield as yellow needles (*n*-heptane), mp 138-140 °C; ms: m/z 293 (M^+), 295 (M^++2); ir: 3100, 3075, 1595, 1560, 1515, 1485, 1380, 1355, 1235, 1200, 1125, 1105, 1070, 940, 860, 770, 750, 740, 725, 670, 600; ^{1}H nmr (deuteriochloroform): δ 8.33-7.14 (m, 8H, aromatic), 2.71 (s, 3H, CH_3); ^{13}C nmr (deuteriochloroform): δ 144.6, 142.1, 140.9, 140.4, 140.1, 137.4, 134.6, 130.7, 129.9, 129.9, 128.7, 127.9, 124.7, 118.6, 116.5, 11.5.

Anal. Calcd. for $C_{16}H_{11}ClN_4$: C, 65.21; H, 3.76; N, 19.01. Found: C, 65.23; H, 3.79; N, 19.12.

1-(4-Chlorophenyl)-3-methyl-1*H*-pyrazolo[3,4-*b*]quinoxaline (**12f**).

This compound was obtained from **10f** in 58% yield as yellow needles (toluene), mp 236-236.5 °C; ms: m/z 293 (M^+), 295 (M^++2); ir: 3116, 3058, 2920, 1594, 1564, 1524, 1496, 1478, 1448, 1414, 1384,1356, 1240, 1200, 1122, 1092, 1062, 1012, 830, 760, 604, 506, 422.

Anal. Calcd. for $C_{16}H_{11}ClN_4$: C, 65.21; H, 3.76; N, 19.01. Found: C, 65.22; H, 3.80; N, 18.91.

3-Methyl-1-(4-nitrophenyl)-1*H*-pyrazolo[3,4-*b*]quinoxaline (**12g**).

This compound was obtained from **10g** in 76% yield as yellow needles (toluene), mp 242-243 °C; ms: m/z 305 (M^+); ir: 3116, 1596, 1568, 1505, 1480, 1444, 1418, 1382, 1333, 1259, 1238, 1203, 1120, 1112, 1092, 1064, 1008, 852, 832, 764, 748, 732, 603, 499, 420.

Anal. Calcd. for $C_{16}H_{11}N_5O_2$: C, 62.95; H, 3.63; N, 22.94. Found: C, 62.29; H, 3.54; N, 23.18.

1-(4-Bromophenyl)-3-methyl-1*H*-pyrazolo[3,4-*b*]quinoxaline (**12h**).

This compound was obtained from **10h** in 77% yield as yellow needles (butanol), mp 241-242 °C; ms: m/z 338 (M^+), 340 (M^++2); ir: 3112, 3060, 2905, 1586, 1568, 1526, 1494, 1448, 1410, 1384, 1356, 1240, 1200, 1122, 1090, 1064, 1010, 926, 826, 764, 732, 672, 602, 504, 476, 422.

Anal. Calcd. for $C_{16}H_{11}BrN_4$: C, 56.66; H, 3.27; N, 16.52. Found: C, 56.28; H, 3.20; N, 16.71.

General Procedure for the Synthesis of the Acylhydrazones **2i-k**.

A solution of the appropriate benzohydrazides **10i-k** (22 mmoles) was added to a solution of 3.44 g (20 mmoles) of 2-sacetylquinoxaline (**3b**) in 50 ml of hot ethanol. The mixture was heated at reflux until thin layer chromatography indicated complete conversion, kept in a refrigerator overnight, and the precipitate was collected by filtration.

N'-[1-(Quinoxalin-2-yl)ethylidene]benzohydrazide (**2i**).

This compound was obtained from benzohydrazide (**10i**) in 88% yield as colorless needles (toluene), mp 230-231 °C; ms: m/z 290 (M^+); ir: 3185, 3060, 1665, 1605, 1550, 1485, 1430, 1380, 1310, 1230, 1150, 1080, 1050, 955, 940, 790, 755, 735, 630, 600; ^{1}H nmr (deuteriochloroform): δ 9.30 (s, 1H, 3-H), 8.19-7.50 (m, 9H, aromatic).

Anal. Calcd. for $C_{17}H_{14}N_4O$: C, 70.33; H, 4.86; N, 19.30. Found: C, 70.43; H, 4.70; N, 19.48.

N'-[1-(Quinoxalin-2-yl)ethylidene]-2-chlorobenzohydrazide (**2j**).

This compound was obtained from 2-chlorobenzohydrazide (**10j**) in 63% yield as colorless needles (ethanol), mp 197-198 °C; ms: m/z 324 (M^+), 326 (M^++2);. ir: 3185, 3060, 1665, 1605, 1550, 1485, 1430, 1380, 1310, 1230, 1150, 1080, 1050, 955, 940, 790, 755, 735, 630, 600;^{1}H nmr (deuteriochloroform): δ 10.23 (s, 1H, N-H), 9.01 (s, 1H, 3-H), 8.14-7.37 (m, 8H, aromatic), 2.59 (s, 3H, CH_3); ^{13}C nmr (deuteriochloroform): δ 149.1, 143.4, 141.7, 141.2, 134.8, 131.2, 130.9, 130.4, 130.1, 130.0 (2), 129.5 (2), 128.9, 128.8, 126.6, 10.5.

Anal. Calcd. for $C_{17}H_{13}ClN_4O$: C, 62.87; H, 4.03; N, 17.25. Found: C, 63.03; H, 4.20; N, 17.50.

N'-[1-(Quinoxalin-2-yl)ethylidene]-4-chlorobenzohydrazide (**2k**).

This compound was obtained from 4-chlorobenzhydrazide (**10k**) in 54% yield as colorless needles (dimethylformamide), mp 238-240 °C; ms: m/z 324 (M^+), 326 (M^++2); ir: 3365, 3050, 3030, 1675, 1590, 1515, 1485, 1430, 1400, 1355, 1255, 1150, 1120, 1095, 1010, 950, 830, 750, 680, 565, 520, 495; ^{1}H nmr (deuteriochloroform): δ 9.23 (s, 1H, 3-H), 8.12-7.49 (m, 8H, aromatic), 2.60 (s, 3H, CH_3).

Anal. Calcd. for $C_{17}H_{13}ClN_4O$: C, 62.87; H, 4.03; N, 17.25. Found: C, 62.72; H, 4.09; N, 17.46.

General Procedure for the Cyclization of the Acylhydrazones **2i-k** with *p*-Chloranil.

A mixture of 2.70 g (11 mmoles) of *p*-chloranil and of the appropriate acylhydrazones **2i-k** (10 mmoles) in 200 ml of *p*-xylene was heated at reflux for 12 hours. The solvent was removed *in vacuo* and the residue was washed with methanol, two times with 1 *N* potassium hydroxide solution, with water and again with methanol and recrystallized.

1-Benzoyl-3-methyl-1*H*-pyrazolo[3,4-*b*]quinoxaline (**12i**).

This compound was obtained from **2i** in 36% yield as colorless needles (butanol), mp 201-201.5 °C; ms: m/z 288 (M^+); ir: 3058, 2917, 1704, 1598, 1576, 1534, 1496, 1450, 1416, 1388, 1344, 1308, 1228, 1184, 1164, 1130, 1112, 1036, 992, 904, 874, 850, 828, 798, 768, 716, 698, 670, 618, 602, 500, 560, 418; ^{1}H nmr (deuteriochloroform): δ 8.34-7.53 (m, 9H, aromatic), 2.80 (s, 3H, 3-CH_3); ^{13}C nmr (deuteriochloroform): δ 166.2, 148.5, 144.6, 141.7, 141.7, 138,2, 132.7, 132.5, 131.5, 131.0 (2), 130.0, 129.7, 129.4, 127.9 (2), 11.8.

Anal. Calcd. for $C_{17}H_{12}N_4O$: C, 70.82; H, 4.19; N,19.43.Found: C, 70.77; H, 4.15; 19.29.

1-(2-Chlorobenzoyl)-3-methyl-1*H*-pyrazolo[3,4-*b*]quinoxaline (**12j**).

This compound was obtained from **2j** in 44% yield as colorless needles (butanol), mp 192-194 °C; ms: m/z 322 (M^+), 324 (M^++2); ir: 3068, 2928, 1716, 1618, 1590, 1572, 1542, 1502, 1474, 1440, 1414, 1392, 1348, 1312, 1286, 1260, 1172, 1112, 1064, 1024, 1000, 906, 866, 852, 826, 768, 732, 716, 674, 650, 608, 442, 416; ^{1}H nmr (deuteriochloroform): δ 8.28-7.46 (m, 8H, aromatic), 2.74 (s, 3H, 3-CH_3); ^{13}C nmr (deuteriochloroform): δ 164.6, 149.8, 143.8, 141.7, 141.5, 138.5, 134.3, 131.6, 131.6, 131.5, 129.8, 129.6, 129.5 (2), 129.3, 126.6, 11.7.

Anal. Calcd. for $C_{17}H_{11}ClN_4O$: C, 63.26; H, 3.43; N, 17.36. Found: C, 63.43; H, 3.49; N, 17.28.

1-(4-Chlorobenzoyl)-3-methyl-1*H*-pyrazolo[3,4-*b*]quinoxaline (**12k**).

This compound was obtained from **2k** in 48% yield as colorless needles (2-methoxyethanol), mp 197.5-198.5 °C; ms: m/z 322 (M^+), 324 (M^++2); ir: 3060, 2922, 1712, 1618, 1586, 1536, 1486, 1416, 1346, 1308, 1228, 1166, 1112, 1084, 1030, 994, 906, 828, 768, 740, 676, 622, 600, 574, 530, 482, 418;^{1}H nmr (deuteriochloroform): δ 8.34-7.49 (m, 8H, aromatic), 2.80 (s, 3H, 3-CH_3); ^{13}C nmr (deuteriochloroform): δ 165.0, 148.9, 144.6, 141.8 (2), 139.0, 138.2, 132.5 (2), 131.7, 131.0, 130.0, 129.7, 129.5, 128.3, 11.8.

Anal. Calcd. for $C_{17}H_{11}ClN_4O$: C, 63.26; H, 3.43; N, 17.36. Found: C, 63.18; H, 3.48; N, 17.43.

General Procedure for the Acylation of the 1-Unsubstituted Flavazole **7b**.

The appropriate benzoyl chloride 25 mmoles was added dropwise to a solution of 1.84 g (10 mmoles) of the flavazole **7b** in 40 ml of pyridine at – 15 °C. The mixture was stirred and heated slowly during 30 minutes until reflux. Reflux was continued for 5 minutes, and the solution was cooled to room temperature and poured onto 100 g of ice. After one hour the product was collected by filtration, washed with 40 ml of water and 20 ml of ethanol and recrystallized.

1-Benzoyl-3-methyl-1*H*-pyrazolo[3,4-*b*]quinoxaline (**12i**).

This compound was obtained from benzoyl chloride in 55% yield as colorless needles (butanol), mp 201-201.5 °C; ms: m/z 288 (M^+); ir: 3058, 2917, 1704, 1598, 1576, 1534, 1496, 1450, 1416, 1388, 1344, 1308, 1228, 1184, 1164, 1130, 1112, 1036, 992, 904, 874, 850, 828, 798, 768, 716, 698, 670, 618, 602, 500, 560, 418; ^{1}H nmr (deuteriochloroform): δ 8.34-7.53 (m, 9H, aromatic), 2.80 (s, 3H, 3-CH_3); ^{13}C nmr (deuteriochloroform): δ 166.2, 148.5, 144.6, 141.7, 141.7, 138,2, 132.7, 132.5, 131.5, 131.0 (2), 130.0, 129.7, 129.4, 127.9 (2), 11.8.

Anal. Calcd. for $C_{17}H_{12}N_4O$: C, 70.82; H, 4.19; N, 19.43. Found: C, 71.01; H, 4.15; N, 19.31.

1-(2-Chlorobenzoyl)-3-methyl-1*H*-pyrazolo[3,4-*b*]quinoxaline (**12j**).

This compound was obtained from 2-chlorobenzoyl chloride in 58% yield as colorless needles (butanol), mp 192-194 °C; ms: m/z 322 (M^+), 324 (M^++2); ir: 3068, 2928, 1716, 1618, 1590, 1572, 1542, 1502, 1474, 1440, 1414, 1392, 1348, 1312, 1286, 1260, 1172, 1112, 1064, 1024, 1000, 906, 866, 852, 826, 768, 732, 716, 674, 650, 608, 442, 416; ^{1}H nmr (deuteriochloroform): δ 8.28-7.46 (m, 8H, aromatic), 2.74 (s, 3H, 3-CH_3); ^{13}C nmr (deuteriochloroform): δ 164.6, 149.8, 143.8, 141.7, 141.5, 138.5, 134.3, 131.6, 131.6, 131.5, 129.8, 129.6, 129.5 (2), 129.3, 126.6, 11.7.

Anal. Calcd. for $C_{17}H_{11}ClN_4O$: C, 63.26; H, 3.43; N, 17.36. Found: C, 63.43; H, 3.49; N, 17.28.

1-(4-Chlorobenzoyl)-3-methyl-1*H*-pyrazolo[3,4-*b*]quinoxaline (**12k**).

This compound was obtained from 4-chlorobenzoyl chloride in 46% yield as colorless needles (2-methoxyethanol), mp 197.5-198.5 °C; ms: m/z 322 (M^+), 324 (M^++2); ir: 3060, 2922, 1712, 1618, 1586, 1536, 1486, 1416, 1346, 1308, 1228, 1166, 1112, 1084, 1030, 994, 906, 828, 768, 740, 676, 622, 600, 574, 530, 482, 418;^{1}H nmr (deuteriochloroform): δ 8.34-7.49 (m, 8H, aromatic), 2.80 (s, 3H, 3-CH_3); ^{13}C nmr (deuteriochloroform): δ 165.0, 148.9, 144.6, 141.8 (2), 139.0, 138.2, 132.5 (2), 131.7, 131.0, 130.0, 129.7, 129.5, 128.3 (2), 11.8.

Anal. Calcd. for $C_{17}H_{11}ClN_4O$: C, 63.26; H, 3.43; N, 17.36. Found: C, 63.11; H, 3.39; N, 17.22.

General Procedure for the Alkylation of the 1-Unsubstituted Flavazole **7b**.

A mixture of 1.84 g (10 mmoles) of the flavazole **7b**, 15 mmoles of the appropriate halogen compound and 2.76 g (20 mmoles) of anhydrous potassium carbonate in 50 ml of 2-butanone was heated at reflux for 8 hours. The hot solution was filtered and the residue was washed two times with 30 ml of hot 2-butanone. The filtrates were combined, concentrated *in vacuo* and 60 ml of 10% sodium hydroxide solution was added to the residue. The product was collected by filtration, washed with water and recrystallized.

1,3-Dimethyl-1*H*-pyrazolo[3,4-*b*]quinoxaline (**12a**).

This compound was obtained from the reaction of compound **7b** with methyl iodide in 65% yield as yellow needles (cyclohexane), mp 137-138 °C; ms: m/z 198 (M^+); ir: 2930, 1620,1580,1510, 1500, 1400, 1380, 1350, 1260, 1245, 1185, 1125, 1050, 960, 900, 845, 765, 725, 655, 630, 605, 420;^{1}H nmr (deuteriochloroform): δ 8.19-7.63 (m, 4H, aromatic), 4.12 (s, 3H, 1-CH_3), 2.75 (s, 3H, 3-CH_3); ^{13}C nmr (deuteriochloroform): δ 142.7, 141.8, 141.4, 140.3, 136.0, 130.4, 130.1, 128.3, 127.0, 33.60, 11.47.

Anal. Calcd. for $C_{11}H_{10}N_4$: C, 66.65; H, 5.08; N, 28.26. Found: C, 66.43; H, 5.38; N, 28.35.

1-Ethyl-3-methyl-1*H*-pyrazolo[3,4-*b*]quinoxaline (**12l**).

This compound was obtained from the reaction of compound **7b** with ethyl iodide in 59% yield as yellow needles (cyclohexane), mp 97-98 °C; ms: m/z 212 (M^+); ir: 3036, 2972, 2932, 1950, 1734, 1618, 1580, 1514, 1482, 1464, 1376, 1356, 1324, 1302, 1248, 1230, 1182, 1124, 1086, 1058, 994, 970, 932, 844, 864, 726, 656, 626, 608, 558, 426; ^{1}H nmr (deuteriochloroform): δ 8.23-7.64 (m, 4H, aromatic), 4.59 (q, J = 7.2 Hz, 2H, CH_3-CH_2), 2.80 (s, 3H, 3-CH_3), 1.58 (t, J = 7.2 Hz, 3H, CH_3-CH_2); ^{13}C nmr (deuteriochloroform): δ 142.2, 141.8, 141.4, 140.5, 136.3, 130.4, 130.1, 128.3, 127.0, 41.85, 14.71, 11.60.

Anal. Calcd. for $C_{12}H_{12}N_4$: C, 67.91; H, 5.10; N, 26.39. Found: C, 67.73; H, 5.15; N, 26,24.

1-Isopropyl-3-methyl-1*H*-pyrazolo[3,4-*b*]quinoxaline (**12m**).

This compound was obtained from the reaction of compound **7b** with 2-iodopropane in 76% yield as yellow needles (hexane), mp 102-103.5 °C; ms: m/z 226 (M^+); ir: 3068, 2974, 2930, 2874, 1572, 1500, 1482, 1456, 1382, 1364, 1350, 1312, 1234, 1198, 1136, 1114, 1060, 970, 906, 842, 758, 730, 676, 622, 608, 542, 466, 422; ^{1}H nmr(deuteriochloroform): δ 8.25-7.64 (m, 4H, aromatic), 5.34 (qu, J = 6.7 Hz, 1H, H_3C-C*H*-CH_3), 2.82 (s, 3H, 3-CH_3), 1.64 (d, J = 6.7 Hz, 6H, *H*$_3$C-CH-C*H*$_3$); ^{13}C nmr (deuteriochloroform): δ 142.0, 141.7, 141.4, 140.6, 136.5, 130.3, 130.1, 128.4, 127.0, 48.5, 21.8 (2), 11.7.

Anal. Calcd. for $C_{13}H_{14}N_4$: C, 69.00; H, 6.24; N, 24.76. Found: C, 69.14; H, 6.28; N, 24.64.

1-Butyl-3-methyl-1*H*-pyrazolo[3,4-*b*]quinoxaline (**12n**).

This compound was obtained from the reaction of compound **7b** with 1-iodobutane in 48% yield as yellow needles (hexane), mp 57-60 °C; ms: m/z 240 (M^+); ir: 3058, 2952, 2928, 2868, 1618, 1578, 1560, 1498, 1482, 1464, 1414, 1376, 1350, 1324, 1242, 1222, 1182, 1122, 1070, 1012, 976, 922, 758, 726, 694, 638, 602, 422; ^{1}H nmr (deuteriochloroform): δ 8.25-7.66 (m, 4H, aromatic), 4.54 (t, J =7.2 Hz, 2H, N-CH_2), 1.99 (q, J = 7.4 Hz, 2H, CH_3-CH_2-CH_2-CH_2), 1.39 (sx, J = 7.5 Hz, 2H, CH_3-CH_2-CH_2-CH_2), 0.97 (t, J = 7.4 Hz, 3H, CH_3-CH_2-CH_2-CH_2); ^{13}C nmr (deuteriochloroform): δ 142.6, 141.8, 141.6, 140.5, 136.2, 130.3, 130.1, 128.4, 127.0, 46.67, 31.51, 19.91, 13.59, 11.61.

Anal. Calcd. for $C_{14}H_{16}N_4$: C, 69.97; H, 6.71; N, 23.31. Found: C, 70.21; H, 6.85; N, 23.19.

1-Isobutyl-3-methyl-1*H*-pyrazolo[3,4-*b*]quinoxaline (**12o**).

This compound was obtained from the reaction of compound **7b** with 2-bromobutane in 42% yield as yellow needles (hexane), mp 81-83 °C; ms: m/z 240 (M^+); ir: 3044, 2960, 2926, 2872, 2360, 1940, 1844, 1734, 1618, 1576, 1560, 1510, 1498, 1484, 1466, 1430, 1404, 1386, 1352, 1320, 1286, 1246, 1226, 1182, 1122, 1072, 986, 942, 880, 842, 764, 7289, 708, 642, m 622, 600;^{1}H nmr (deuteriochloroform): δ 8.25-7.66 (m, 4H, aromatic), 4.35 (d, J = 7.4 Hz, 2H, N-CH_2), 2.81 (s, 3H, 3-CH_3), 2.47 (m, 1H, isobutyl-CH), 0.97 (d, J = 6.7, 6H, isobutyl-CH_3); ^{13}C nmr (deuteriochloroform): δ 143.0, 141.7, 141.7, 140.6, 136.1, 130.3, 130.1, 128.5, 127.0, 54.19, 28.93, 20.25, 20.02, 11.63.

Anal. Calcd. for $C_{14}H_{16}N_4$: C, 69.97; H, 6.71; N, 23.31. Found: C, 70.13; H, 6.81; N, 23.25.

1-Allyl-3-methyl-1*H*-pyrazolo[3,4-*b*]quinoxaline (**12p**).

This compound was obtained from the reaction of compound **7b** with allyl bromide in 65% yield as yellow needles (hexane), mp 88-90 °C; ms: m/z 224 (M^+); ir: 3084, 3018, 2918, 1646, 1618, 1582, 1560ß, 1514, 1498, 1482, 1464, 1416, 1388, 1350, 1320, 1286, 1246, 1224, 1184, 1122, 1062, 996, 932, 842, 766, 714, 648, 602, 562, 532, 424;^{1}H nmr (deuteriochloroform): δ 8.24-7.65 (m, 4H, aromatic), 6.12 (m, 1H, CH_2-C*H*=CH_2), 5.29-5.15 (m, 4H, CH_2-CH=CH_2), 2.81 (s, 3H, 3-CH_3).

Anal. Calcd. for $C_{13}H_{12}N_4$: C, 69.62; H, 5.39; N, 24.98. Found: C, 69.48; H, 5.44; N, 25.21.

Ethyl (3-methyl-1*H*-pyrazolo[3,4-*b*]quinoxalin-1-yl)acetate (**12q**).

This compound was obtained from ethyl bromoacetate in 78% yield as yellow needles (ethanol), mp 164-165.5 °C; ms: m/z 270 (M^+); ir: 2988, 2938, 1748, 1580, 1500, 1474, 1460, 1378, 1348, 1322, 1286, 1218, 1184, 1122, 1028, 902, 932, 874, 774, 743, 728, 684, 646, 602, 568, 426; ^{1}H nmr (deuteriochloroform): δ 8.27-7.68 (m, 4H, aromatic), 5.32 (s, 2H, N-CH_2), 4.23 (qu, J = 7.14 Hz, 2H, CH_3-CH_2), 2.81 (s, 3H, 3-CH_3), 1.27 (t, J = 7.14, 3H, CH_3-CH_2); ^{13}C nmr (deuteriochloroform): δ 168.0, 143.7, 143.4, 141.5, 140.8, 136.6, 130.7, 130.2, 128.4, 127.5, 61.73, 47.97, 14.02, 11.69.*Anal.* Calcd. for $C_{14}H_{14}N_4O_2$: C, 62.21; H, 5.22; N, 20.73. Found: C, 62.14; H, 5.31; N, 20.65.

Ethyl 2-(3-methyl-1*H*-pyrazolo[3,4-*b*]quinoxalin-1-yl)propionate (**12r**).

This compound was obtained from the reaction of compound **7b** with ethyl 2-bromopropionate in 69% yield as yellow needles (ethanol), mp 87-89 °C; ms: m/z 284 (M^+); ir: 2986, 2916, 1578, 1500, 1480, 1452, 1386, 1348, 1294, 1210, 1196, 1156, 1136, 1122, 1086, 1034, 964, 890, 864, 766, 728, 702, 670, 638, 600, 540, 464, 424; ^{1}H nmr (deuteriochloroform): δ 8.28-7.69 (m, 4H, aromatic), 5.78 (q, J = 7.4 Hz, 1H, N-C-H), 4.18 (q, J = 7.1 Hz, 2H, Ester-CH_2), 2.83 (s, 3H, 3-CH_3) 2.02 (d, J = 7.4, 3H, CH_3-CH-), 1.18 (t, J = 7.1, 3H, Ester-CH_3); ^{13}C nmr (deuteriochloroform): δ 181.7, 170.5, 143.2, 141.4, 140.9, 136.7, 130.6, 130.2, 128.4, 127.3, 61.61, 54.39, 16.13, 13.96, 11.71.

Anal. Calcd. for $C_{15}H_{16}N_4O_2$: C, 63.37; H, 5.67; N, 19.71. Found: C, 63.47; H, 5.76; N, 19.55.

1-Benzyl-3-methyl-1*H*-pyrazolo[3,4-*b*]quinoxaline (**12s**).

This compound was obtained from the reaction of compound **7b** with benzyl bromide in 37% yield as yellow needles (hexane), mp 156-158 °C; ms: m/z 274 (M^+); ir: 3064, 2918, 1684, 1604, 1578, 1512, 1498, 1480, 1456, 1382, 1352, 1316, 1266, 1240, 1206, 1178, 1120, 1104, 1072, 982, 930, 904, 842, 760, 730, 712, 680, 638, 618, 604, 576, 422; ^{1}H nmr (deuteriochloroform): δ 8.20-7.58 (m, 4H, aromatic/quinoxaline) 7.37-7.17 (m, 5H, aromatic/phenyl), 5.68 (s, 2H, benzyl-CH_2), 2.75 (s, 3H, 3-CH_3); ^{13}C nmr (deuteriochloroform): δ 143.1, 142.9, 141.9, 140.9, 137.0, 136.6, 130.7, 130.4, 128.8, 128.2, 128.2, 128.1, 128.0, 127.9 , 127.4,50.81, 11.95.

Anal. Calcd. for $C_{17}H_{14}N_4$: C, 74.43; H, 5.14; N, 20.42. Found: C, 74.51; H, 5.18; N, 20.38.

1-(4-Chlorobenzyl)-3-methyl-1*H*-pyrazolo[3,4-*b*]quinoxaline (**12t**).

This compound was obtained from the reaction of compound **7b** with 4-chlorobenzyl chloride in 52% yield as yellow needles (ethanol), mp 170-171 °C; ms: m/z 308 (M^+), 310 (M^++2); ir: 3052, 2920, 1576, 1562, 1516, 1492 1464, 1420, 1408, 1386, 1352, 1320, 1302, 1286, 1244, 1224, 1196, 1180, 1120, 1094, 1012, 988, 928, 904, 814, 770, 718, 692, 642, 602, 556, 482, 462, 422; ^{1}H nmr (deuteriochloroform): δ 8.24-7.22 (m, 8H, aromatic), 5.65 (s, 2H, CH_2), 2.77 (s, 3H, 3-CH_3); ^{13}C nmr (deuteriochloroform): δ 142.9, 142.8, 141.7, 140.8, 136.4, 135.2, 133.6, 130.6, 130.2, 129.4 (2), 128.7 (2), 128.5, 127.3, 49.9, 11.6.

Anal. Calcd. for $C_{17}H_{13}ClN_4$: C, 66.13; H, 4.24; N, 18.15. Found: C, 66.19; H, 4.28; N, 18.06.

3-Methy1-1-(1-phenylethyl)-1*H*-pyrazolo[3,4-*b*]quinoxaline (**12u**).

This compound was obtained from the reaction of compound **7b** with (1-bromoethyl)benzene in 45% yield as yellow needles (heptane), mp 116-118 °C; ms: m/z 288 (M^+); ir: 3060, 2976, 2926, 1618, 1574, 1510, 1498, 1478, 1458, 1382, 1348, 1310, 1280, 1240, 1206, 1180, 1144, 1134, 1122, 1090, 1054, 1030, 992, 954, 918, 842, 760, 730, 710, 634, 616, 588, 560, 636, 422; ^{1}H nmr (deuteriochloroform): δ 8.23-7.20 (m, 9H, arom.), 6.35 (q, 1H, H_3C-C*H*),2.81 (s, 3H, 3-CH_3), 2.08 (d, 3H, *H*$_3$C-CH); ^{13}C nmr (deuteriochloroform): δ 142.6, 142.3, 141.7, 141.6, 140.8, 136.7, 130.3, 130.2, 128.6, 128.4 (2), 127.5, 127.1, 126.8 (2), 55.5, 20.4, 11.8.

Anal. Calcd. for $C_{18}H_{16}N_4$: C, 74.98; H, 5.59; N, 19.43. Found: C, 75.11; H, 5.64; N, 19.25.

1-(2-Chloropyridin-5-ylmethyl)-3-methyl-1*H*-pyrazolo[3,4-*b*]-quinoxaline (**12v**).

This compound was obtained from the reaction of compound **7b** with 2-chloro-5-chloromethylpyridine in 40% yield as yellow needles (ethanol), mp 163-164 °C; ms: m/z 309 (M^+), 311 (M^++2);ir: 3050, 2920, 1738, 1620, 1566, 1498, 1484, 1424, 1394, 1352, 1318, 1290, 1242, 1224, 1180, 1110, 1020, 986, 950, 834, 764, 732, 712, 642, 602, 494, 496, 422; ^{1}H nmr (deuterio-chloroform): δ 8.54-7.23 (m, 7H, aromatic), 5.69 (s, 2H, N-CH_2), 2.78 (s, 3H, 3-CH_3); ^{13}C nmr (deuteriochloroform): δ 151.0, 149.4, 143.5, 142.8, 141.6, 140.9, 138.7, 136.5, 131.2, 130.8, 130.3, 128.5, 127.5, 124.2, 47.4, 11.6.

Anal. Calcd. for $C_{16}H_{12}ClN_5$: C, 62.04; H, 3.90; N, 22.61. Found: C, 61.98; H, 3.95; N, 22.53.

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