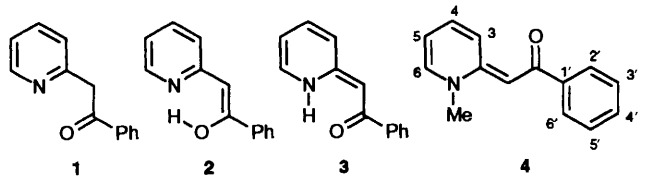
^1H and ^{13}C NMR Spectra of α-Heterocyclic Ketones and Assignment of Keto, Enol and Enaminone Tautomeric Structures

Rory A. More O'Ferrall* and Brian A. Murray
Department of Chemistry, University College, Belfield, Dublin 4, Ireland

A method for distinguishing enol and enaminone tautomers of acylmethyl heterocycles is described based on differences in ^{13}C chemical shift between the carbonyl carbon atom of the enaminone (C=O) and enolic carbon atom of the enol (=C–OH). For 2-, 3- and 4-acetylmethyl, -phenacyl, and -pyridacyl-pyridines, -pyrazines, -quinolines, -quinoxalines, -phenanthrolines, -benzoxazoles and -benzothiazoles (usually in $CDCl_3$ as solvent) measured values of δ_c fall in the non-overlapping ranges 179–191 ppm for the enaminones and 161–171 for the enols. Both sets of chemical shifts depend on the electronegativity of the acyl substituent and for strongly electron-withdrawing groups, such as pyruvate, δ_c for the enaminone does overlap the range for the enol. However the difference in chemical shifts ($\Delta\delta_c \sim 20$) appears to be nearly independent of substituent, and in these cases the value for the enaminone can be predicted from a correlation of δ_c with σ^* for the acyl substituent based on data of Greenhill, Loghmani-Khouzani and Maitland (*J. Chem. Soc., Perkin Trans. 1*, 1991, 2831) for substituted quinolines. No other proton or carbon chemical shift differentiates the tautomers, but the structural assignments are corroborated by (*a*) comparisons with *N*-methyl enaminone models for the enaminone tautomers, (*b*) coupling constants (J_{34}) between 3- and 4-hydrogen atoms of pyridine and quinoline rings and (*c*) allylic coupling between CH_3 and vinyl hydrogens in enols of methyl ketones. With the exception of pyruvates, enols are observed only for 2-substituted heterocycles, usually as mixtures (in $CDCl_3$) with the easily distinguished keto tautomers, but for (2-substituted) quinolines and quinoxalines the enaminone tautomer predominates. Structural assignments in aqueous media or other solvents where solubility precludes NMR measurements follow from correlations of UV–VIS with NMR spectra. NMR and UV–VIS measurements are considered in detail for the example of 2-phenacylpyridine.

Studies of tautomerism of α-heterocyclic ketones seek to distinguish keto, enol and enaminone tautomers[1–6] shown below as **1**, **2** and **3** for the example of 2-phenacylpyridine. The keto tautomer is identified by the presence of a methylene group in the NMR and the appropriate heterocyclic and acyl chromophores in the UV, as well as an unconjugated keto group in the IR. However, more difficult to distinguish are the enol and enaminone.



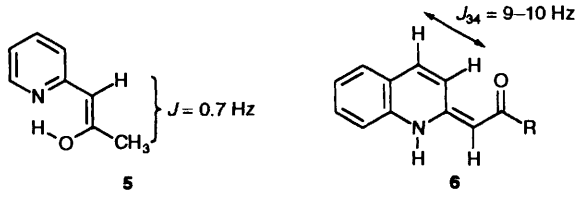
1 **2** **3** **4**

The enaminone tautomer of 2-phenacylpyridine was identified by Katritzky from comparison of its UV spectrum with that of its *N*-methyl enaminone (**4**).[2] Although the latter has an *E* configuration for the exocyclic double bond, whereas the double bond in **3** is probably *Z*,[3,4] both show similar absorptions, with λ_{max}(water) = 400 nm for **3** and 410 nm for **4**. The spectrum of the N–H enaminone is observed directly in aqueous solution as a weak long wavelength absorption[2] corresponding to the presence of 8–9% of this tautomer accompanying the predominant ketone.[4]

In less polar media such as chloroform or dioxane, the keto and enaminone spectra of 2-phenacylpyridine are replaced by a new absorption with λ_{max} = 335 nm.[2,5] ^1H NMR and IR spectra, and the similarity of the UV spectrum to that of its enolate anion, indicate that this represents the enol tautomer **2**, the structure of which is confirmed by NMR measurements of the corresponding (2-pyridyl)acetone (**5**), which shows allylic coupling (0.7 Hz) between the hydrogen and methyl substituents of the enol.[6]

These structural assignments provide a starting point for a wider study of differences in NMR spectra of enol and enaminone tautomers aimed at distinguishing these species in the absence of an *N*-methyl model for the enaminone structure.

Earlier comparisons of ^1H NMR and UV–VIS spectra of enols and enaminones have been discussed by Mondelli and Merlini with reference especially to acylmethyl quinolines and quinoxalines and their 3,4-dihydro-4-oxo derivatives.[6] No clear distinction based on proton chemical shifts could be found, but the diagnostic value of allylic coupling between methyl and vinyl hydrogens in the enol of an actylmethyl heterocycle was clearly established. It was also shown that a difference exists in 3,4-hydrogen coupling constants of 2-quinolylmethyl derivatives between enaminone (J = 9.0–9.5 Hz, *e.g.*, in **6**) and keto or enol tautomers (J = 8.0–8.2 Hz), presumably reflecting the loss of aromaticity in the heterocyclic ring of the enaminone.[6]



5 **6**

Unfortunately, the scope of these criteria is limited. Thus, compounds considered in this paper include arylacylmethyl derivatives of pyrazine, quinoxaline, benzoxazole and benzothiazole, none of which show allylic or heterocyclic ring coupling constants. Recently, Greenhill, Maitland and Loghmani-Khouzani have reported IR, UV and ^1H and ^{13}C NMR spectra for a range of acylmethylquinolines[7–11] and

Table 1 Assignments of peaks in ^1H and ^{13}C NMR spectra of 2-phenacylpyridine and its enol, and the *N*-methyl enaminone model for its enaminone tautomer[a,b]

	Keto		Enol		*N*-Methyl enaminone	
Atom	^1H	^{13}C	^1H	^{13}C	^1H	^{13}C
C~O	—	196.9	15.48	164.4	—	185.1
Cα	4.49	48.5	6.07	94.2	5.58	85.2
N–CH_3	—	—	—	—	3.52	43.0
C2(Cq)	—	155.3	—	158.6	—	154.2
C3	⟨7.59–7.51⟩[c]	124.3	7.66–7.60	121.6	9.23–9.18	110.1
C4	7.31–7.28	136.5	7.07–7.04	137.2	7.24–7.21	135.7[d]
C5	7.18–7.13	121.9	6.99–6.94	118.5	6.28–6.22	122.7
C6	8.57–8.54	149.6	8.28–8.26	144.3	7.24.–7.21	138.7[d]

[a] Chemical shifts in ppm from TMS in $CDCl_3$. [b] Temperature *ca.* 25 °C. [c] The symbols ⟨ ⟩ indicate that the signal is found in the range indicated but its precise limits are obscured by other signals. [d] These signals may be interchanged.

Greenhill has reviewed tautomeric assignments based on these measurements.[7] These authors noted an upfield shift in δ_C for the carbonyl carbon of the enaminone relative to that of the keto-tautomer in the ^{13}C NMR spectrum.[8,9] However as most of the compounds studied were 2-substituted quinolines, for which only keto and enaminone tautomers are observed, the possibility that the carbonyl chemical shift group might also differentiate enol and enaminone tautomers was not pursued. Enol structures were indeed assigned in the case of (4-quinolyl)pyruvic acid esters, but on the basis of IR spectra, which pointed to the presence of an enolic double bond and hydrogen-bonded hydroxy group. In this paper differences in carbon chemical shifts between enols and enaminones are examined by extending measurements of ^{13}C spectra to a range of structures for which the enol isomer is more prominent.

Results

^1H and ^{13}C NMR spectra of more than twenty α-heterocyclic ketones have been measured, together with spectra of several *N*-methyl enaminones, non-heterocyclic ketones such as deoxybenzoin, and simple heterocyclic compounds such as 2- and 4-acetylpyridine and pyridylacetic acid esters. Details of individual spectra are given in the Experimental section. In general, spectra were measured in deuteriochloroform, although some compounds were also studied in other solvents, *e.g.* [$^2H_8$]-dioxane or [$^2H_4$]methanol.

Significant spectral features of keto, enol and enamine tautomers are conveniently illustrated for 2-phenacylpyridine, for which (as described above) independent evidence for the identities of each tautomer exist. In $CDCl_3$ solution keto and enol tautomers are present in a 60 : 40 ratio. Separation of peaks in the proton spectra was facilitated by integration and the availability of spectra in other solvents such as D_2O and dioxane in which either keto or enol forms are dominant. The *N*-methyl enaminone was taken as a model for the enaminone (bearing in mind that the configuration of its double bond is *E* rather than *Z*) and its ^1H and ^{13}C NMR spectra are shown in Fig. 1.

A complete assignment of spectra based on the measurements in $CDCl_3$ and data from the literature[6,12,13] is summarised in Table 1. The numbering of carbon atoms used for all three tautomers is shown in **4**. In the ^{13}C spectra tertiary and quaternary carbon atoms were distinguished from their relative intensities and DEPT spectra. For quaternary carbons only the assignments of C2 (158.6) and C–O (164.4) of the enol were ambiguous. The value of C2 was assigned from its similarity to C2 in the ketone (155.3) and the expectation that there should be only a small difference of acyl from vinyl substituent effects. For tertiary carbons comparisons with other substituted

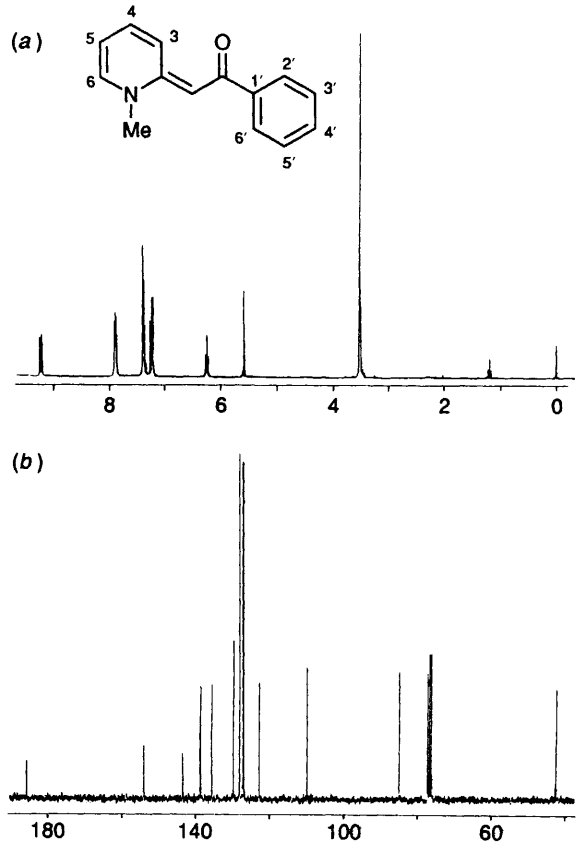


Fig. 1 NMR spectra of 2-phenacylpyridine *N*-methyl enaminone (**4**) (*a*) proton NMR spectrum; (*b*) carbon-13 NMR spectrum

pyridines and (for C3 and C4) with keto and enaminone spectra of acylquinolines[8,9] assisted assignments. Phenyl carbon atoms were easily distinguished by comparison with α-substituted acetophenones.

The main features of the ^1H and ^{13}C NMR spectra may be summarised as follows.

(*a*) The ketone is readily distinguishable by its carbonyl carbon signal at 196.9 (compare acetophenone: 197.6 ppm) and the high-field ^1H-signal for the $-CH_2-$ group at 4.49 ppm.

(*b*) The enol and enaminone tautomers, though easily distinguished from the ketone, are less readily distinguished from each other: thus the =CH– group (Cα in Table 1) shows similar signals in both ^1H (6.07 and 5.58 ppm) and ^{13}C NMR (94.2 and 85.2 ppm). However, the 'carbonyl' carbon shows a significant difference: the enaminone tautomer, which formally retains the carbonyl function, shows this carbon at 185.1 ppm, *ca.* 12 ppm below that of the ketone, while the enol shows the

Table 2 Tautomeric compositions of α-heterocyclic ketones ($HetCH_2COR$) in deuteriochloroform and other solvents[a]

Heterocycle	R[b]	Keto (%)	Enol (%)	Enaminone (%)
2-Pyridyl	Phenyl	60	40	
3-Pyridyl	Phenyl	*c*		
3-Pyridyl$^+$–Me	Phenyl	*c*		
4-Pyridyl	Phenyl	*c*		
2-Pyrazyl	Phenyl	74	26	
2-Pyrazyl	Phenyl[d]	13	87	
2-Quinolyl	Phenyl	*ca.* 5		*ca.* 95
4-Quinolyl	Phenyl	*ca.* 98[e]		
2-Phenanthrolyl	Phenyl			*c*
2-Quinoxalyl	Phenyl	19		81
Benzoxazol-2-yl	Phenyl	50	50	
Benzothiazol-2-yl	Phenyl	40	60	
4-Pyridyl	2-Pyridyl	*c*		
2-Pyrazyl	2-Pyridyl	47	53	
2-Pyrazyl	2-Pyridyl[d]	55	45	
2-Quinolyl	2-Pyridyl			*c*
2-Quinoxalyl	2-Pyridyl	8		92
Benzothiazol-2-yl	2-Pyridyl	19	81	
Benzothiazol-2-yl	2-Pyridyl[f]	< 5	> 95	
2-Pyrazyl	4-Pyridyl	13	87	
2-Pyrazyl	4-Pyridyl[d]	18	82	
2-Quinolyl	4-Pyridyl			*c*
2-Pyridyl	Methyl	*c*, *g*		
Benzothiazol-2-yl	Methyl	78	22	
Benzothiazol-2-yl	Methyl[h]	67	33	
2-Pyridyl	Ethoxycarbonyl		*c*	
2-Quinolyl	Ethoxycarbonyl			*c*
Benzothiazol-2yl	Ethoxycarbonyl		*c*	

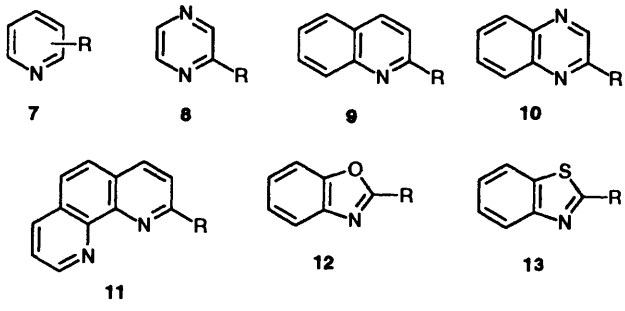
[a] In $CDCl_3$ unless otherwise stated. [b] Group attached to carbonyl. [c] The compound exists exclusively in the form of the tautomer indicated, as determined by NMR (*i.e.*, > 99%). [d] [$^2H_8$]Dioxane. [e] *ca.* 2% of another tautomer present. [f] [$^2H_6$]DMSO. [g] *ca.* 25% of enol tautomer in CCl_4. [h] [$^2H_4$]Methanol.

corresponding carbon at the considerably lower value of 164.4 ppm.

(*c*) The chemical shift of H3 of the *N*-methyl enaminone appears well downfield from other heterocyclic or phenyl hydrogen atoms at 9.2 ppm. This is a well known phenomenon arising from the proximity of the carbonyl group in the *E*-configuration of the *N*-methyl enaminone (**4**) and does not occur in the *Z*-configuration.[3,4]

(*d*) Further differences can be seen in the heterocyclic ring, notably the signal for the C3 carbon of the enaminone (110.1), which occurs at a higher field than all other carbon atoms of the heterocyclic (or phenyl) rings of any of the tautomers, and > 10 ppm upfield from the corresponding carbons of the enol and keto tautomers. C6 also shows some variation with tautomer structure, although the diagnostic value of this difference is limited to pyridyl ketones. Surprisingly, C2 is almost invariant between tautomers, despite the fact that this carbon carries an exocyclic double bond in the non-aromatic enaminone: apparently the conversion of the C2–Cα bond from single to double compensates for the effect of loss of aromaticity on δ_{C2}.

These results, especially the difference in ^{13}C chemical shift of the acyl carbon atom, provide a starting point for assigning ^{13}C and ^1H NMR spectra of other acyl heterocycles to enol, enaminone and (the usually unambiguous) keto tautomers. We have made measurements for pyridine, pyrazine, quinoline, quinoxaline, phenanthroline, benzoxazole and benzothiazole heterocycles with benzoyl, acetyl, pyridacyl and ethoxycarbonyl (EtOOCCO–) acyl substituents. These structures are shown as **7**–**13** below. As in the case of 2-phenacylpyridine, spectra were commonly recorded for mixtures of tautomers, the proportions of which were determined by integration of the ^1H NMR spectrum (*e.g.*, by using the CH_2 signal of the ketone and =CH– signal of the enol). Normally, one tautomer was recognisable as the keto form and, on the basis of the acyl carbon shift (coupled with other evidence noted below), the second was assigned as enol or enaminone (usually the former). These assignments and the proportions of tautomers in $CDCl_3$ or, occasionally, other solvents are recorded in Table 2.



R = (a) CH_2COPh; (b) CH_2COCH_3; (c) CH_2COPy; (d) CH_2CO-COOEt

Selected data for different tautomers are summarised in Tables 3–5. Table 3 shows the carbon and hydrogen chemical shifts assigned to enol tautomers, including vinyl-CH and OH protons and vinyl, enolic and ring carbon atoms. The 'ring' carbon atom is that to which the enol substituent is attached, and is denoted Cq as a reminder that it is a quaternary carbon and that (depending on the heterocycle) it may correspond to positions of the ring other than C2.

For pyridines C2(Cq) is easily distinguished from the tertiary C6 carbon by a DEPT spectrum. However for bicyclic ketones both carbon atoms are quaternary and are distinguished on the basis of the insensitivity of δ_{C2} to substituents and tautomerism and its relatively high-field shift compared with other quaternary ring carbon atoms, *e.g.*, 154.1 compared with 139.8 and 137.7 for 2-phenacylquinoline.

Table 3 Selected ^1H and ^{13}C NMR signals of the enol tautomers [HetCH=C(OH)R] of α-heterocyclic ketones[a]

Heterocycle	R[b]	–C*H*=	–O*H*	–*C*H=	=*C*–OH	Cq[c]
2-Pyridyl	Methyl[d]	5.22	—	95.8	165.7	159.3
2-Pyridyl	Phenyl	6.07	15.48	94.2	164.4	158.6
2-Pyridyl	Ethoxycarbonyl	6.52	13.61	103.1	152.7	156.4[e]
2-Pyrazyl	Phenyl	6.14	13.89	92.1	164.5	154.2
2-Pyrazyl	Phenyl[f]	6.28	13.88	92.6	164.5	154.8
2-Pyrazyl	2-Pyridyl	6.92	13.68	93.9	161.8	*ca.* 152
2-Pyrazyl	2-Pyridyl[f]	7.02	13.65	95.9	163.5	*ca.* 155
2-Pyrazyl	4-Pyridyl	6.27	13.77	94.4	161.0	153.1
2-Pyrazyl	4-Pyridyl[f]	6.45	13.79	94.9	161.7	154.1
Benzoxazol-2-yl	Phenyl	6.20	()[g]	83.7	166.3	160.5
Benzothiazol-2-yl	Phenyl	6.37	*ca* 13.9	90.9	163.5	165.5
Benzothiazol-2-yl	2-Pyridyl	7.11	*ca.* 13.2	92.5	168.0	164.1
Benzothiazol-2-yl	Methyl[h]	5.63	()[g]	92.7	()[g]	()[g]
Benzothiazol-2-yl	Ethoxycarbonyl	6.78	*ca.* 11.8	99.0	153.4	166.1/162.9[i]

[a] In $CDCl_3$ unless otherwise stated. [b] Group attached to enol carbon. [c] Carbon atom of heterocyclic ring at point of sidechain attachment. [d] In CCl_4. [e] Assignment of =C–OH *versus* Cq comes from greater value of Cq for enol than *N*-methyl enaminone for 2-phenacylpyridine. [f] [$^2H_8$]-Dioxane. [g] Not seen. [h] Shows allylic coupling (0.6 Hz) between vinyl hydrogen and methyl group. [i] Cq and ester carbonyl group.

Table 4 Selected ^1H and ^{13}C NMR signals of the enaminone tautomers of α-heterocyclic ketones and some *N*-methyl enaminone models[a]

Heterocycle	R[b]	=C*H*–	–N*H*	=*C*H–	–C=O	*C*q[c]
2-Pyridyl	Phenyl	5.58	[N–Me]	85.2	185.1	154.2
2-Pyridyl	Ethoxycarbonyl	5.90	[N–Me]	85.1	172.5	155.1
2-Quinolyl	Phenyl	6.06	*ca.* 15.7	89.9	184.1	154.1
2-Quinolyl	Phenyl	5.95	[N–Me]	91.2	187.2	153.8
2-Quinolyl	2-Pyridyl	6.09	15.89	90.5	180.2	154.6
2-Quinolyl	4-Pyridyl	6.08	15.89	90.5	180.0	154.6
2-Quinolyl	Ethoxycarbonyl	6.34	Not seen	93.6	170.1	155.0
2-Quinoxalyl	Phenyl	6.22	14.71	91.2	181.8	149.7/147.8
2-Quinoxalyl	2-Pyridyl	6.99	14.62	91.9	178.6	*ca.* 149[d]
2-Phenanthrolyl	Phenyl	6.13	16.42	89.4	185.3	152.6
9-Methyl-2-phenanthrolyl	Phenyl[e]	6.07	[N–Me]	91.9	187.0	156.2
Benzothiazol-2-yl	Phenyl	6.48	[N–Me]	87.1	184.4	—[f]
Benzothiazol-2-yl	Methyl	5.80	[N–Me]	90.4	191.3	—[f]

[a] In $CDCl_3$ unless otherwise stated. [b] R = group attached to carbonyl carbon. [c] Carbon atom of heterocyclic ring at point of sidechain attachment. [d] 149.8/148.3. [e] The 3-hydrogen has a shift of δ 9.23 consistent with an *E*-configuration of the double bond as in *N*-methyl enaminones of 2-phenacyl-pyridine and -quinoline. [f] Not assigned.

The C2 carbon atom must also be differentiated from the enolic carbon atom (=C–OH). Commonly the latter falls 10–20 ppm to lower field and is easily identified. However, for ethyl (2-pyridyl)pyruvate (**7d**) C2 is assigned the higher value, both from the expectation that the electronegative COCOOEt group decreases $\delta_{C\text{-}O}$ (see below) and because analogy with phenacylpyridine suggests that δ_{C2} should be larger for the enol than the *N*-methyl enaminone (155.1). For benzoxazoles and benzothiazoles, where C_2 is flanked by two heteroatoms, the chemical shift also becomes comparable to that of the enolic carbon atoms (δ_C = 161–166 ppm) *except* in the case of ethyl benzothiazolylpyruvate where the shift of the enolic carbon (153.4) is comparable to that of 2-pyridylpyruvate.

Table 4 shows chemical shifts assigned to enaminone tautomers. Compared with Table 3 values for the carbonyl carbon atom replace those for the enolic carbon atom and enolic protons replace those for N–H.

Table 5 shows proton chemical shifts of the methylene group and carbon chemical shifts of the methylene, carbonyl and Cq carbon atoms of keto tautomers, and includes non-heterocyclic compounds for comparison.[12,13]

If the pyruvates are excluded the carbonyl chemical shifts of the enaminones in Table 3 and enols in Table 4 fall into non-overlapping ranges that allow these tautomers to be distinguished. Inspection of Greenhill and Maitland's data[8] for a wider range of quinolyl enaminones, including pyruvates, shown in Table 6, however, reveals a systematic variation of δ_{CO} with the electronegativity of the acyl substituent so that for COCOOEt and other strongly electron-withdrawing groups the ranges of chemical shifts overlap. On the other hand the data of this paper for enol pyruvates (Table 3) suggests that a similar if less pronounced substituent dependence may apply to the enols, with the consequence that for the same acyl substituent the difference in chemical shifts is little affected and the possibility of distinguishing structures is sustained. A limited number of measurements for pyridyl enols are included in Table 6.

A number of factors assist or confirm the assignments of enol or enaminone structures based on enolic *versus* acyl carbon chemical shifts. In some cases, such as 2-phenacylpyridine, the availability of an *N*-methyl enaminone provides a model for the enaminone tautomer, and this is true of 2-phenacylquinoline and 2-phenacylphenanthroline for which the enaminone is itself the stable tautomer.[3] In Table 4 it can be seen that the N–H and *N*-methyl enaminone chemical shifts are in good agreement for 2-phenacylquinoline, with all carbon shifts within ±4 ppm of each other, as earlier reported by Greenhill and Maitland.[8] The ^1H NMR spectra are also similar, with the obvious exception of H3, which in the *N*-methyl enaminone appears 2.3 ppm downfield, due to the difference in configuration of double bonds (*Z versus E*). The same remarks apply to 2-phenacylphenanthroline except that its *N*-methyl enaminone also contains a methyl substituent at the 9-position.

The difference between enol and enaminone tautomers for

Table 5 Selected ^1H and ^{13}C NMR signals of the keto tautomers of substituted ketones ($X-CH_2COR$)[a,b]

X	R[c]	CH_2	CH_2	C=O	Cq[d]
H	Phenyl	2.62[e]	26.3[e]	197.6	—
Phenyl	Phenyl	4.27	45.5	197.7	134.3
2-Pyridyl	Phenyl	4.49	48.5	196.9	155.3
3-Pyridyl	Phenyl	4.30	42.3	196.5	130.2
3-Pyridyl$^+$-Me	Phenyl	4.82	41.8	194.6	135.4
4-Pyridyl	Phenyl	4.29	44.6	195.9	143.7
2-Pyrazyl	Phenyl	4.53	45.4	195.7	151.2
2-Pyrazyl	Phenyl[f]	4.53	45.6	196.0	152.5
2-Quinolyl	Phenyl	4.71	49.5	197.0	()[g]
4-Quinolyl	Phenyl	4.74	42.2	195.9	141.8
2-Quinoxalyl	Phenyl	4.72	46.6	195.8	()[g]
Benzoxazol-2-yl	Phenyl	4.63	39.7	192.5	165.8
Benzothiazol-2-yl	Phenyl	4.83	43.9	194.1	168.1
H	2-Pyridyl	2.73[e]	25.6[e]	199.8	—
4-Pyridyl	2-Pyridyl	4.57	43.4	197.6	144.0
2-Pyrazyl	2-Pyridyl	4.80	44.3	197.4	*ca.* 153[h]
2-Pyrazyl	2-Pyridyl[f]	4.73	46.0	199.1	*ca.* 155[i]
2-Quinoxalyl	2-Pyridyl	4.98	45.4	197.4	()[g]
Benzothiazol-2-yl	2-Pyridyl	5.10	42.7	195.8	()[g]
H	4-Pyridyl	2.64[e]	26.6[e]	197.31	—
2-Pyrazyl	4-Pyridyl	4.54	45.4	195.3	153.1
2-Pyrazyl	4-Pyridyl[f]	4.54	45.7	196.1	151.9
Benzothiazol-2-yl	Methyl	4.24	48.4	196.1	162.8

[a] In $CDCl_3$ unless otherwise stated. [b] Normally heterocyclic but some simple ketones are included for comparison. [c] Group attached to carbonyl. [d] Carbon atom of heterocyclic ring at point of sidechain attachment. [e] CH_3 signal. [f] [$^2H_8$]Dioxane as solvent. [g] Not seen. [h] 153.9 or 152.4. [i] 155.9 or 154.5.

Table 6 Substituent dependence of carbonyl (δ_{CO}) and enolic ($\delta_{=C-OH}$) chemical shifts of enaminone tautomers of 2-acylquinolines (2-RCOQ) and enol tautomers of 2-acylpyridines (2-RCoPy) in $CDCl_3$[a]

R	σ_R^*	δ_{CO}[b]	$\delta_{=C-OH}$
Bu^t	−0.30	200.5	
Pr^i	−0.19	198.5	
Et	−0.10	195.7	
Me	0	191.8	165.7[c]
Ph	1.00	184.2	164.4
$BrCH_2$	0.75	184.8	
2-Py	—	181.5	
COOEt	2.26	170.4	152.7
CF_3	2.61	173.6	
CCl_3	2.65	179.3	
CN	3.30	157.1	

[a] Except as indicated. [b] Data from J. V. Greenhill, H. Loghmani-Khouzani and D. J. Maitland, *J. Chem. Soc., Perkin Trans. 1*, 1991, 2831. [c] In CCl_4.

quinolyl, pyridyl and phenanthrolyl derivatives is confirmed by J_{34} coupling constants (**6**) shown in Table 7. Values for pyridines appear not to have been used previously in making this distinction, but they show a sharp divergence between enol or keto and enaminone structures, even though for a wider selection of substituted pyridines[14] the range of J_{34} values for keto and enol tautomers (6.8–9.2 Hz) comes closer to that measured for the single example of an (*N*-methyl)pyridyl enaminone (10 Hz). Further confirmation of enamine structures for the major or minor tautomers of 2-quinolylpyruvates (**9d**) and of pyridacylquinolines (**9c**), and of the enol structure for the corresponding pyridylpyruvate (**7d**) comes from comparisons of UV spectra with those of their phenacyl analogues (**7a** and **9a**), for which *N*-methyl enaminones are available.

For acetylbenzothiazole (**13b**), allylic coupling (0.6 Hz) and the NMR and UV spectra of an *N*-methyl enaminone model point to an enolic structure for the unknown tautomer and, based on similarities of structures and spectra, the same may be inferred for phenacylbenzothiazole (**13a**) and, indeed, also for phenacylbenzoxazole (**12a**) and the corresponding benzothiazole and benzoxazole pyruvates (**13d** and **12d**).[15]

Probably least independent evidence exists for assignment of tautomers in the pyrazyl (**8**) and quinoxalyl (**10**) systems. However, a close correspondence of chemical shifts between pyridyl and pyrazyl and between quinolyl and quinoxalyl structures discernible in Tables 3 and 4 allows little room for doubt that the pyrazyl and quinoxalyl tautomer assignments as enol and enaminone, respectively, are correct.

For the keto tautomers studied, it is noteworthy that the acyl substituent causes a rather constant change in chemical shift upon replacement of hydrogen in the corresponding methyl-substituted heterocycle: 1.98 (± 0.06) ppm for the benzoyl group (based on ten compounds) and 2.17 (± 0.14) ppm for the pyridacyl group (Table 5). There is also a systematic effect of the heterocyclic substituent upon the chemical shift of the methylene group, reflecting its electronegativity. Parallel effects of substituents on corresponding shifts for enol and enaminone tautomers are apparent in Table 8. On the other hand sidechain carbon chemical shifts appear to be quite insensitive to the nature of the heterocycle.

Discussion

The purpose of this study was to seek a criterion for distinguishing enol from enaminone tautomers (**14** and **15**) of α-heterocyclic ketones. Proton chemical shifts are ineffective because even the most sharply differentiated peaks, for the vinylic hydrogens (Hv in **14** and **15**) and the OH and NH hydrogens, are sufficiently similar to yield overlapping ranges for the structures considered. As noted above, allylic coupling constants for enols of methyl ketones (R = CH_3 in **14**) and J_{34} coupling constants between 3- and 4-ring hydrogens of pyridine

Table 7 Coupling constants, J_{34}, between the 3- and 4-hydrogens of the heterocyclic ring of α-(2-pyridyl) and α-(2-quinolyl) ketones[a]

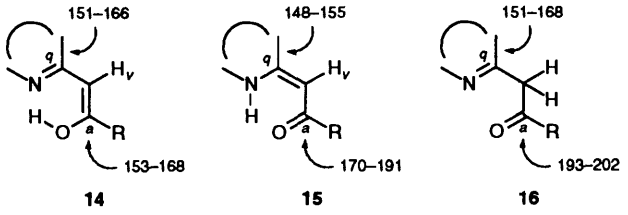
Compound	Keto	Enol	Enaminone
2-Phenacylpyridine	8.1	7.9	
2-Phenacylpyridine *N*-methyl enaminone			10.0
Ethyl 2-pyridylpyruvate		7.9	
Ethyl 2-pyridylpyruvate *N*-methyl enaminone			9.2
2-Phenacylquinoline			9.2
2-Phenacylquinoline N-methyl enaminone			9.5
Ethyl 2-quinolylpyruvate			9.2
2-(2-Pyridacyl)quinoline			9.2
2-(4-Pyridacyl)quinoline			9.2
2-Phenacylphenanthroline			9.2
2-Phenacylphenanthroline 1,9-dimethyl enaminone			8.8

[a] Values in Hz measured in $CDCl_3$ (error *ca.* ± 0.3 Hz); *cf.* structure **6**.

Table 8 Comparison of ^1H shifts at the α-carbon of 2-substituted ketones, X–CH_2–COR, and their tautomers[a]

	R = Phenyl			R = 2′-Pyridacyl		
X	KH	EH	MH	KH	EH	MH
H	2.62[b]		—	2.73[b]		—
2-Pyridyl	4.49	6.07	(5.58)[c]			
2-Pyrazyl	4.53	6.14		4.80	6.92	
Benzoxazol-2-yl	4.63	6.20				
2-Quinolyl	4.71		6.06[d]			6.09
2-Phenanthrolyl			6.07			
2-Quinoxalyl	4.72		6.22	4.98		6.99
Benzothiazol-2-yl	4.83	6.37	(6.48)[c]	5.10	7.11	

[a] Chemical shifts in ppm downfield from TMS in $CDCl_3$. [b] CH_3 shift. [c] Figures in parentheses refer to an *N*-methyl enaminone. [d] Corresponding *N*-methyl enaminone: 5.95 ppm.

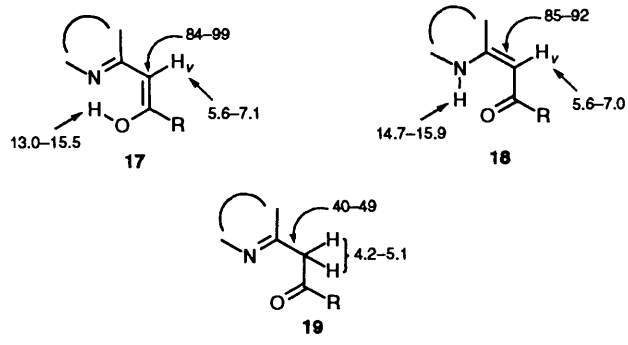


14 **15** **16**

and quinoline heterocycles (**6**) do provide a distinction[6] but these criteria are of too limited application to be generally useful.

Measurements of ^{13}C NMR spectra monitor more radical changes in electronic structure and might be expected to provide a better guide to identities of tautomers. For polycyclic compounds ^{13}C spectra are relatively complex, but the peaks for the acyl or enolic carbon (denoted a in **14–16**), the *ipso* carbon of the heterocyclic ring (q) and the (vinylic) α-carbon atoms (v in **14** and **15**) stand out by virtue of their low- or high-field shifts.

The clearest criterion differentiating enol and enaminone tautomers is an upfield shift of roughly 20 ppm between enolic and carbonyl carbon atoms (a). This is reflected in the observed range of chemical shifts for the three tautomers based on measurements for the acylmethyl heterocycles **7–13** (**a–c**) summarised in structures **14–16**. It can be seen that for the acyl carbon atom (Ca) these ranges are quite broad but do not overlap between enol (153–168) and enaminone (170–191) tautomers. By contrast, for the ring carbon atom to which the sidechain is attached (Cq), the ranges *do* overlap, as they do for the vinylic carbon and proton (Hv) chemical shifts. Chemical shift data for the vinylic carbon and for the vinylic, NH and OH hydrogen atoms are summarised in **17–19**, with details given in Tables 3–5, 7 and 8.



17 **18** **19**

The difference in enolic and acyl carbon chemical shifts can be put on a firmer basis by considering their structural dependence. While our data show that these shifts are relatively insensitive to

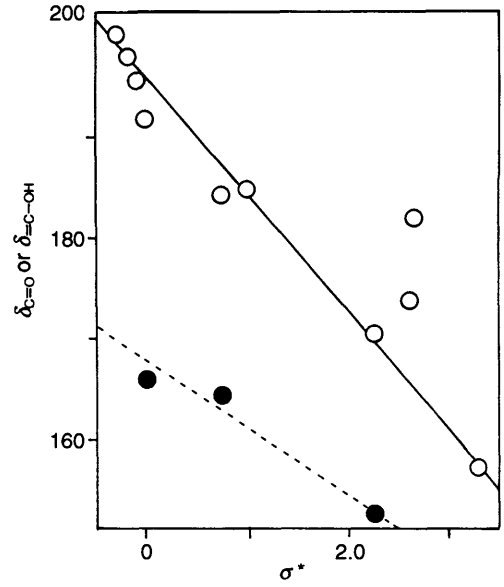
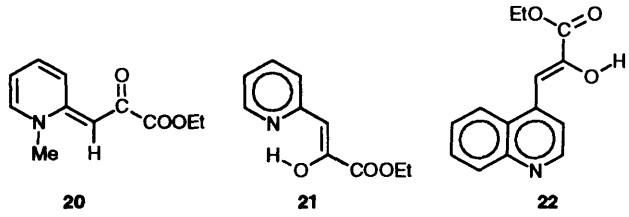


Fig. 2 Plot of ^{13}C chemical shifts for the carbonyl group of the enaminone tautomers of 2-acylquinolines [2-RCOQ (○)] and enolic carbon of 2-acylpyridines [2-RCOPy (●)] against Taft's σ* for the acyl substituent (R)

the nature of the heterocycle, Greenhill *et al.* have demonstrated that for enaminone tautomers of acylquinolines (QCH_2COR) the chemical shift of the carbonyl group depends quite strongly on the electronegativity of the acyl substituent (R), as shown from the plot of δ_c versus Taft's substituent constants σ* in Fig. 2.

Fig. 2 extends the range of chemical shifts for the enaminone shown in **15**. For a sufficiently strongly electron-withdrawing substituent such as CF_3 indeed it can be seen that the shift does overlap the range of enol chemical shifts in **15**. Fortunately, this does not rule out use of the values for assigning tautomer structures because the enols appear to show a similar dependence on substituent electronegativity. Thus for the *N*-methyl enaminone of ethyl (2-pyridyl)pyruvate (**20**) the acyl carbon has a chemical shift δ_c = 172.5 for the carbonyl group (Table 4), close to the value for ethyl (2-quinolyl)pyruvate (170.4), whereas for ethyl (2-pyridyl)pyruvate the corresponding value is δ_c = 152.7 ($CDCl_3$), *i.e.*, at 20 ppm higher field. That the 2-pyridylpyruvate is predominantly enol (**21**) is confirmed by the low intensity of the enaminone peak ($\varepsilon = 0.37 \times 10^4$ dm^3 mol^{-1} cm^{-1} at 401 nm in $CHCl_3$) compared with that of the *N*-methyl enaminone ($\varepsilon = 2.0 \times 10^4$ dm^3 mol^{-1} cm^{-1} at 409 nm in CH_3OH and other solvents) and the appearance of a peak at 317 nm ($\varepsilon = 1.6 \times 10^4$ dm^3 mol^{-1} cm^{-1}) attributable to the enol.

If we apply the same criterion to two further examples of pyruvates for which *N*-methyl enaminones are unavailable, namely the ethyl benzothiazol-2-ylpyruvate (Table 3) and ethyl 4-quinolylpyruvate (**22**) from Greenhill's work,[10] acyl chemical



20 **21** **22**

shifts of 153.4 and 153.2, respectively, strongly indicate enol structures. For the 4-quinolylpyruvate a similar assignment was based on IR measurements.[10] A further small corroboration of

these structures comes from δ_c values for the vinylic α-carbon atoms which are 99 and 101 for the benzothiazolyl- and quinolyl-pyruvates, respectively, compared with 103.1 for the pyridylpyruvate enol and 86 for its *N*-methyl enaminone.

By comparison with enaminones carbon chemical shifts of enols have been measured for only a few substituents, namely phenyl, ethoxycarbonyl and methyl. However, as seen in Fig. 2 these appear to show a similar, if perhaps weaker, dependence upon σ^* to that for the enaminones. Although the enol data are very limited the figure suggests that prediction of an enaminone chemical shift based on σ^* should be effective in distinguishing an enaminone from enol structure, for which δ_c is smaller by between 15 and 25 ppm for chemically accessible variations of acyl substituents. There seems to be no significant dependence on the nature of the heterocycle.

A significant feature of the structural assignments based on the above criterion is that they yield a consistent pattern of tautomer stabilities. Table 2 summarises tautomeric equilibria in (mainly) $CDCl_3$ solutions. In general, enol or enaminone tautomers are seen only for 2-substituted heterocycles (probably because of stabilisation by hydrogen bonding), and enaminones are favoured over enols by benzo annellation. Thus, enols predominate for 2-(acylmethyl)-pyridines and -pyrazines and enaminones for the corresponding quinolines and quinoxalines.

Ethyl (4-quinolyl)pyruvate represents an exception to the rule that enols are not seen for 4-substituted heterocycles. It is possible that here stabilisation by intramolecular hydrogen-bonding is provided by the ethoxycarbonyl group (**22**).[10] For acylpyridines, moreover, the balance between enol and enaminone depends on the solvent with the enol favoured by non-polar solvents.[2,4] Thus ethyl (2-pyridyl)pyruvate shows a strong long wavelength absorption (λ_{max} = 394 nm) similar to that of the *N*-methyl enaminone (409 nm) in methanol but a dominant enol spectrum (λ_{max} = 313 or 317 nm) in cyclohexane or chloroform. It is possible that the same difference applies to **22** for which λ_{max} = 468 nm reported in ethanol[16] presumably implies the presence of enaminone, perhaps (as for the pyridylpyruvate) as a mixture with the enol.

The preference for an enol structure for pyrazines, benzoxazoles and benzothiazoles probably arises because the low basicity of the nitrogen atom is unfavourable to strong conjugation between the nitrogen atom and the carbonyl group, upon which the stability of the enaminone depends. This point is discussed in an accompanying paper.[17]

In conclusion we note that tautomeric equilibria are often of primary interest in aqueous solution.[2-4,18] Although solubility normally precludes NMR measurements in D_2O, tautomeric species in aqueous solution can usually be identified from measurements of UV–VIS spectra. Correlating UV–VIS with NMR measurements in solvents where both are accessible then provides an effective means of establishing structures of species of interest. In general, proportions of keto imine and enaminone tautomers are quite insensitive to the solvent but internally hydrogen-bonded enols of 2-substituted heterocycles are favoured in non-polar solvents relative to water.[2,4] Thus for 2-phenacylpyridine the enaminone is more stable than the enol in water, although the reverse is true in chloroform or dioxane. For 2-phenacylpyrazine on the other hand, the enol is preferred in both aqueous and non-polar media. Again this is probably because the low basicity of the nitrogen atom is less favourable to the enaminone.[17]

Experimental

α-Heterocyclic ketones were normally prepared from the appropriate methylheterocycle and ester by base-catalysed condensation. Details of most of the preparations (and those of the *N*-methyl enaminones) are recorded elsewhere.[3,4,15,16,18-20] Here, we report only the preparation of 4-(2-pyridacyl)pyridine for which Wolfe's method[19] for 4-phenacylpyridine was adapted by replacing methyl benzoate with ethyl picolinate (distilled). The product was purified by flash silica chromatography using chloroform as the eluent and ether–light petroleum (b.p. 40–60 °C) for recrystallisation; the yield was 35% (Found: C, 73.05; H, 5.1; N, 14.3. $C_{12}H_{10}N_2O$ requires C, 72.70; H, 5.08; N, 14.13%.)

Spectra were measured for several commercially available compounds. Deoxybenzoin (Aldrich) was decolourised with activated charcoal and recrystallised from *ca.* 40:60 aqueous ethanol. 2-Acetylpyrazine (Aldrich) was used without further purification. Methyl 2-pyridylacetate (Aldrich) was chromatographed on a silica column using ether as the eluent. Methyl 4-pyridylacetate (Aldrich) was distilled. 2- and 4-Acetylpyridine (Fluka) were purified over KOH pellets overnight followed by distillation under reduced pressure (20 mmHg). Purities of compounds wee checked by NMR spectroscopy.

NMR Spectra.—Preliminary ^1H NMR spectra were run on a Perkin-Elmer R12B instrument operating at 60 MHz. All the spectra reported were measured on a Jeol JNM-GX 270 FT spectrometer operating at 270.05 MHz (^1H) or 67.80 (^{13}C) or a Varian Unity 500 instrument operating at 499.84 MHz (^1H) or 125.70 (^{13}C). Spectra were run for samples in deuteriochloroform using tetramethylsilane (TMS) as an internal reference, unless otherwise stated. ^{13}C NMR were generally referenced to the centre peak of the solvent (77.1 ppm for $CDCl_3$). Spectra were run at constant temperatures between 20 and 25 °C; the resolution was 0.002 ppm (^1H) and 0.02 ppm (^{13}C). To prevent protonation of basic heterocycles by DCl from deuteriochloroform, NMR solutions were filtered through anhydrous sodium carbonate. As well as $CDCl_3$, [$^2H_6$]dichloromethane, [$^2H_8$]dioxane, [$^2H_4$]methanol and D_2O solvents were used; all were of > 99%-atom isotopic purity.

In the ^{13}C spectra not all chemical shifts could be assigned unambiguously. For substituted pyridines there was little difficulty because of the availability of model compounds and because the acyl and Cq carbon atoms of interest are quaternary and distinguishable from all other carbon atoms except the *ipso* carbon atom (Ci) of the aryl ring attached to the carbonyl group. For bicyclic structures, however, the carbon atoms of the ring junctions are also quaternary. For quinoxaline and benzoxazole or benzothiazole these carbons are identified by low-field shifts arising from the presence of two heterocyclic atoms but this is not true of the quinolines. Although Greenhill's study of 2-acylmethylquinolines suggests that the quaternary carbon at the ring fusion next to the nitrogen is *ca.* 10 ppm upfield in the enaminone compared with the keto tautomer further uncertainty attaches to assignment of the six tertiary ring carbon atoms of the enaminones. In principle the chemical shifts of the two carbon atoms of the heterocyclic ring might be used diagnostically, but because of the ambiguity in the assignments, and because these atoms are not present in other benzo fused heterocycles, no attempt was made to characterise the tautomers in this way.

NMR spectra and assignments are given below. In the case of tautomeric ketones, K, E and M are used to indicate keto, enol and enaminone, respectively. Other symbols used include d (doublet), t (triplet), q (quartet, or quaternary in ^{13}C spectra), br (broad), v br (very broad), w (weak; in ^{13}C spectra, < 20% of most intense peak) and ns (not seen). Where q (quaternary) is indicated, this was determined by the DEPT (distortionless enhancement by polarisation transfer)-135 routine; the remaining peaks are all CH, except for the obvious (upfield) CH_2 and CH_3 signals (a question mark indicates uncertainty in an assignment).

2-*Phenacylpyridine*. (60%K/40%E). δ_H 15.48 (OH), 8.56–8.54 (H_{6K}), 8.28–8.26 (H_{6E}), 8.09–8.05 ($H_{2',6'K}$), 7.86–7.82 ($H_{2',6'E}$), 7.66–7.60 (H_{3E}), 7.59–7.51 ($H_{4',3K}$), 7.48–7.36 ($H_{3',5'K,3',4'E}$), 7.18–7.13 (H_{5K}), 7.07–7.04 (H_{4E}), 6.99–6.94 (H_{5E}), 6.07 (CH=), 4.49 (CH_2); δ_C 196.9w (C=O); 164.4w (COH), 158.6w (C_{2E}); 155.3w (C_{2K}), 149.6 (C_{6K}), 144.3 (C_{6E}), 137.2 (C_{4E}), 136.6 ($C_{1'K}$), 136.5w (C_{4K}), 133.3 ($C_{4'K}$), 129.3 ($C_{4'E}$), 128.8 ($C_{3',5'K}$), 128.7 ($C_{2',6'K}$), 128.3 ($C_{3',5'E}$), 125.5 ($C_{2',6'E}$), 124.3 (C_{3K}), 121.9 (C_{5K}), 121.61 (C_{3E}), 118.5 (C_{5E}), 94.2 (CH=); 48.5 (CH_2), ($C_{1'E}$ ns).

2-*Phenacylpyridine* N-*methyl enaminone*. δ_H 9.20 (dd, *J* 10.0, 1.5 Hz, H_3), 7.92–7.86 ($H_{2',6'}$), 7.41–7.34 ($H_{3'-5'}$), 7.24–7.21 (d, *J* 6.7 Hz, $H_{4,6}$), 6.25 (dt, *J* 6.7, 1.5 Hz, H_5), 5.58 (=CH), 3.52 (CH_3); δ_C 185.1w (C=O), 154.2w (C_2), 143.6w ($C_{1'}$), 138.7, 135.7 ($C_{4,6}$), 129.7 ($C_{4'}$), 128.0 ($C_{3',5'}$), 127.0 ($C_{2',6'}$), 122.7 (C_5), 110.1 (C_3), 85.2 (=CH), 43.0 (CH_3).

(2-*Pyridyl*)*acetone*. δ_H of ketone in $CDCl_3$ and of enol in CCl_4 (70% K, 30% E): 8.5–8.7 (H_{6K}); 8.2–8.3 (H_{6E}), 6.8–7.8 ($H_{3,4,5K}$, $H_{3,4,5E}$); 5.22 (CH=), 4.0 (CH_2), 2.24 (CH_{3K}), 2.02 (CH_{3E}); δ_C(CCl_4 with [$^2H_6$]acetone insert: δ_{CCl_4} = 96.7) 205.8 (C=O), 165.7 (=COH), 159.3 (C_{2E}), 157.5 (C_{2K}), 149.5 (C_{6K}), 145.2 (C_{6E}), 136.5, 119.2, 118.0 ($C_{3,4,5E}$), 136.3, 123.8, 121.6 ($C_{3,4,5K}$), 95.8 (=CH), 53.1 (CH_2), 29.5 (CH_{3K}), 22.1 (CH_{3E}).

Ethyl 2-*pyridylpyruvate* (E): δ_H 13.61 (br, OH), 8.39–8.37 (H_6), 7.74–7.67 (H_3), 7.20–7.19 (H_4), 7.17–7.12 (H_5), 6.52 (CH=), 4.34 (q, *J* 7.1 Hz, CH_2), 1.37 (t, *J* 7.1 Hz, CH_3), δ_C 163.8w (*C*OOEt); 156.4w and 152.7w (COH, C_2), 145.2 (C_6), 137.7 (C_4), 123.2 (C_3), 121.0 (C_5), 103.1 (CH=), 61.5 (CH_2), 14.4 (CH_3).

Ethyl 2-*pyridylpyruvate* N-*methyl enaminone*. δ_H 9.17 (d, *J* 9.2 Hz, H_3), 7.5–7.4 ($H_{4,6}$), 6.53 (td, *J* 6.8, 1.6 Hz, H_5), 5.90 (=CH), 4.29 (q, *J* 7.15 Hz, CH_2), 3.68 (CH_3), 1.37 (t, *J* 7.1 Hz, CH_3); δ_C 172.5 (C=O); 166.3 (COOR), 155.1 (C_2), 139.4/137.5 ($C_{4,6}$), 123.6 (C_5), 112.9 (C_3), 85.1 (=CH), 61.4 (CH_2), 43.6 (CH_3), 14.2 (CH_3).

Ethyl 2-*pyridylacetate*. (K): δ_H 8.57–8.56 (H_6), 7.69–7.63 (H_3), 7.31–7.28 (H_4), 7.22–7.17 (H_5), 3.86 (CH_2), 3.73 (CH_3), δ_C 170.9w (C=O), 154.2 (C_2), 149.3 (C_6), 136.5 (C_4), 123.7 and 122.0 ($C_{3,5}$); 52.0 (CH_3), 43.6 (CH_2).

3-*Phenacylpyridine*. (K): δ_H 8.53 ($H_{2,6}$), 8.04–8.00 ($H_{2',6'}$), 7.63–7.5 ($H_{4,4'}$), 7.52–7.46 ($H_{3',5'}$), 7.29–7.25 (H_5), 4.30 (CH_2); δ_C 196.5w (C=O), 150.6 (C_2), 148.3 (C_6), 137.3 (C_4), 136.2w ($C_{1'}$), 133.4 ($C_{4'}$), 130.2w (C_3), 128.8 ($C_{3',5}$), 128.4 ($C_{2',6'}$), 123.4 (C_5), 42.3 (CH_2).

3-*Phenacylpyridine methiodide*. (K): δ_H 9.39 (H_2), 9.06–9.04 (H_6), 8.41–8.39 (H_4), 8.09–8.05 ($H_{2',6'}$), 8.03–8.00 (H_5), 7.64–7.61 ($H_{4'}$), 7.55–7.49 ($H_{3',5}$), 4.82 (CH_2), 4.56 (CH_3); δ_C 194.6 (C=O), 147.3 (C_2), 146.7 (C_6), 143.2 (C_4), 136.5 ($C_{1'}$), 135.4 (C_3), 134.4 ($C_{4'}$), 129.2 ($C_{3',5'}$), 128.7 ($C_{2',6'}$), 127.4 (C_5), 49.2 (CH_3), 41.8 (CH_2).

4-*Phenacylpyridine*. (K): δ_H 8.58–8.55 ($H_{2,6}$), 8.01–7.98 ($H_{2',6'}$), 7.63–7.57 ($H_{4'}$), 7.52–7.46 ($H_{3',5'}$), 7.22–7.20 ($H_{3,5}$), 4.29 (CH_2); δ_C 195.9w (C=O), 143.5w (C_4), 136.2w ($C_{1'}$), 133.7 ($C_{4'}$), 128.8 ($C_{3',5'}$), 128.5 ($C_{2',6'}$); 124.9 ($C_{3,5}$); 44.6 (CH_2).

4-(2'-*Pyridacyl*)*pyridine*. (K): δ_H 8.74–8.71 ($H_{6'}$), 8.56–8.54 ($H_{2,6}$), 8.08–8.04 ($H_{3'}$), 7.89–7.82 ($H_{4'}$), 7.54–7.49 ($H_{5'}$), 7.29–7.27 ($H_{3,5}$), 4.57 (CH_2); δ_C 197.6w (C=O), 152.5w ($C_{2'}$), 149.6 ($C_{2,6}$), 149.0 ($C_{6'}$), 144.0 (C_4), 137.1 ($C_{4'}$), 127.6 ($C_{3'}$), 125.3 ($C_{3,5}$), 122.3 ($C_{5'}$), 44.6 (CH_2).

Ethyl 4-*pyridylacetate*. (K); δ_H 8.56–8.54 (dd, *J* 6.1 Hz, $H_{2,6}$), 7.24–7.22 (d, *J* 6.1 Hz, $H_{3,5}$), 3.71 (CH_3), 3.64 (CH_2); δ_C 170.5w (C=O), 149.9 ($C_{2,6}$), 142.8w (C_4), 124.6 ($C_{3,5}$), 52.3w (CH_3), 40.4 (CH_2).

2-*Phenacylquinoline*. (*ca.* 5%K/95%M): δ_H 15.7 (v br, NH), 7.97–7.93 ($H_{2',6'M}$), 7.60 (d, *J* 9.2 Hz, H_{4M}), 7.50–7.42 ($H_{3',5'M,\ 5-8M}$), 7.25–7.20 ($H_{4'M}$), 6.82 (d, *J* 9.2 Hz, H_{3M}), 6.06 (=CH), 4.71 (CH_2); δ_C 197.0 wq ($C{=}O_K$), 184.1q ($C{=}O_M$), 154.1q (C_{2M}), 139.8q and 137.7q ($C_{1',10M}$), 136.2 (C_{4M}), 131.0, 130.4 ($C_{4'M}$), 128.3 ($C_{3',5'M}$), 127.6, 126.7 ($C_{2',6'M}$), 123.7, 123.3q (C_{9M}), 122.3, 118.1 (C_{3M}), 89.9 (=CH), 49.5w (CH_2).

2-*Phenacylquinoline* N-*methyl enaminone*. δ_H 9.10 (d, *J* 9.5 Hz, H_3), 7.95–7.91 ($H_{2',6'}$), 7.52–7.34 and 7.19 (t, *J* 7.4 Hz) ($H_{4,5-8,\ 3',4',5'}$), 5.95 (=CH), 3.63 (CH_3); δ_C 187.2q (C=O), 153.8q (C_2), 143.1q and 140.1q ($C_{6,1'}$), 133.9 (C_4), 130.7 ($C_{4'}$), 130.4, 128.4, 128.2 ($C_{3',5'}$), 127.3 ($C_{2',6'}$), 123.6q (C_9), 122.6, 122.5, 114.5 (C_3), 91.2 (=CH), 35.2 (CH_3).

2-(2-*Pyridacyl*)*quinoline*. (M): δ_H 15.89 (br, NH), 8.72–8.70 ($H_{3',6'}$), 7.75 (d?, 9.2 Hz, H_4), 7.77–7.74 and 7.61–7.50 ($H_{5-8,4'}$), 7.34–7.28 ($H_{5'}$), 6.92 (d, *J* 9.2 Hz, H_3), 6.09 (=CH); δ_C 180.2w (C=O), 154.6 (C_2), 150.3, 146.5 ($C_{6'}$), 137.7 and 137.1 ($C_{4,10\ or\ 4'}$), 131.4, 127.8, 124.5, 123.7, 121.9 and 120.4 ($C_{5,8-10,3',5'}$), 118.7 (C_3), 90.5 (CH=).

2-(4-*Pyridacyl*)*quinoline*. (M): δ_H 15.89 (NH), 8.70 (d, 6.2 Hz, $H_{2',6'}$), 7.74 (d, *J* 6.2 Hz, $H_{3',5'}$), 7.75–7.72 (1 H) and 7.56–7.50 (3 H) and 7.33–7.27 (1 H) ($H_{5,8-10}$), 6.90 (d, 9.2 Hz, H_3), 6.08 (=CH); δ_C 180.0w (C=O), 154.6w (C_2), 150.2 ($C_{2',6'}$), 146.4 ($C_{4'}$), 137.6 and 137.1 ($C_{4,10}$), 131.3, 127.7, 124.4, 123.7 and 121.8 ($C_{5,8-10}$); 120.4 ($C_{3',5'}$), 118.7 (C_3), 90.5 (CH=).

Ethyl 2-*quinolylpyruvate*. (M): δ_H (NH, ns), 7.87 (d, *J* 9.2 Hz, H_4), 7.64–7.58 (2 H) and 7.54–7.51 and 7.40–7.34 (H_{5-8}), 6.99 (d, 9.2 Hz, H_3), 6.36 (CH=), 4.36 (q, *J* 7.2 Hz, CH_2), 1.41 (t, *J* 7.2 Hz, CH_3); δ_C 170.1 (=CH*C*=O), 164.3 (*C*OOEt), 155.0 (C_2), 137.8 (C_4), 137.6 (C_{10}), 131.5, 127.7, 125.2, 124.2 and 121.7 ($C_{5,8-10}$), 119.3 (C_3), 93.6 (=CH), 61.5 (CH_2), 14.1 (CH_3).

4-*Phenacylquinoline*. (K/*ca.* 2%M): δ_H 9.06–9.04 (d, *J* 4.4 Hz, H_{2M}), 8.86–8.85 (d, *J* 4.4 Hz, H_2), 8.18–8.14 (H_5), 8.08–8.02 ($H_{2',6'}$), 7.88–7.85 (H_8), 7.75–7.69 (H_7), 7.68–7.46 ($H_{3',4',5',6}$), 7.28–7.26 (d, *J* 4.4 Hz, H_3), 4.74 (CH_2); δ_C 195.9w (C=O), 149.7 (C_2), 147.8w (C_6), 141.8 (C_4), 136.2w ($C_{1'}$), 133.8 ($C_{4'}$), 128.9 ($C_{3',5'}$), 128.5 ($C_{2',6'}$), 130.4–122.9 ($C_{3,5-8}$), 44.6 (CH_2).

2-*Phenacylphenanthroline*. (M): δ_H 16.42 (1 H, br s, N–H), 9.08 (1 H, dd, *J* 4.4, 1.9 Hz), 8.09 (1 H, dd, *J* 8.3, 1.9 Hz, H_7), 8.07–8.05 (2 H, m, $H_{2'}$ and $H_{6'}$), 7.60 (1 H, d, *J* 9.2 Hz, H-4), 7.50 (1 H, dd, *J* 8.3, 4.4 Hz), 7.44–7.43 (5 H, m, H_3, H_5, $H_{3'}$, $H_{4'}$ and $H_{5'}$), 6.93 (1 H, dd, *J* 8.9, 1.6 Hz, H_6), 6.13 (1 H, s, =CH–); δ_C 185.3 (C=O), 152.6 (C_2), 150.1 (C_9), 140.4 (C_{10a}), 138.1 ($C_{1'}$), 135.7 (C_7), 135.5 (C_4), 135.2 (C_{10b}), 130.2 ($C_{4'}$), 128.6 (C_{6a}), 128.1 ($C_{3'}$ and $C_{5'}$), 127.0 ($C_{2'}$ and $C_{6'}$), 124.9 (C_3), 123.8 (C_6), 123.1 (C_8), 122.0 (C_5), 121.3 (C_{4a}), 89.4 (=CH–).

(1,9-*Dimethyl*-2-*phenacyl*)*phenanthroline* N-*methyl enaminone*. δ_H 9.25 (1 H, d, *J* 8.8 Hz, H_3), 8.00–7.95 (2 H, m, H_2 and $H_{6'}$), 7.94 (1 H, d, *J* 8.1 Hz, H-7), 7.5–7.4 (5 H, m, $H_{3'}$, $H_{4'}$, $H_{5'}$, H_4, H_5), 7.33 (1 H, d, *J* 8.5 Hz, H_6), 7.26 (1 H, d, *J* 8.1 Hz, H_8), 6.07 (1 H, s, =CH–), 4.23 (3 H, s, N-CH_3), 2.69 (3 H, s, CH_3); δ_C 187.0 (C=O), 156.9 (C_2), 156.2 (Cq), 143.2 (C_{10a}), 139.9 ($C_{1'}$), 138.1 (C_{10b}), 136.5 (C_7), 134.0 (C_4), 130.2 ($C_{4'}$), 128.2 (C-6a), 128.1 ($C_{3'}$ and $C_{5'}$), 127.3 ($C_{2'}$ and $C_{6'}$), 124.9 (C_6), 124.1 (C-4a), 124.0 (C_3), 122.8 (C_5), 122.6 (C_8), 91.9 (=CH–), 46.4 (N-CH_3), 25.4 (CH_3).

2-*Phenacylpyrazine*. (74%K/26%E): δ_H 13.89 (OH), 8.62–8.61 (H_{3K}), 8.54–8.52 (H_{6K}), 8.47–8.45 ($H_{5K,3E}$), 8.26 ($H_{5,6E}$), 8.07–8.03 ($H_{2',6'K}$), 7.86–7.83 ($H_{2',6'E}$), 7.62–7.56 ($H_{4'K}$), 7.51–7.45 ($H_{3',5K}$), 7.43–7.41 ($H_{3',4'5'E}$), 6.14 (CH=), 4.53 (CH_2); δ_C 195.7 (C=O), 164.5w (COH), 154.2w (C_{2E}), 151.2 (C_{2K}), 145.9, 144.2, 142.9; 139.6w and 139.3w (E), 136.2 ($C_{1'K}$), 135.2w ($C_{1'E}$), 133.6 ($C_{4'K}$), 130.0 ($C_{4'E}$), 128.8, 128.6 ($C_{3',5'E}$), 128.5 ($C_{2',6'\ or\ 3',5'K}$), 125.6 ($C_{2',6'E}$), 92.1 (CH=), 45.4 (CH_2).

2-(2-*Pyridacyl*)*pyrazine*. (47%K/53%E): δ_H 13.68 (br, OH), 8.72–8.70 ($H_{6'K}$), 8.66–8.64 ($H_{3K,6'E}$), 8.57–8.53 ($H_{5,6K}$), 8.47–8.46 (H_{3E}), 8.34 ($H_{5,6E}$), 8.10–8.07 ($H_{3'E}$), 7.98–7.95 ($H_{3'K}$), 7.89–7.83 ($H_{4'K}$), 7.83–7.77 ($H_{4'E}$), 7.53–7.48 ($H_{5'E}$), 7.34–7.29 ($H_{5'K}$), 6.92 (CH=), 4.80 (CH_2); δ_C 197.4w (C=O), 161.8 (COH), 153.8, 152.5w, 152.4 and 151.8 ($C_{2,2'K,E}$), 149.1 ($C_{6'K}$), 149.0 ($C_{6'E}$), 146.1 (C_{5E}), 144.9 (C_{5K}), 144.1 (C_{3E}), 142.6 (C_{3K}), 139.9

(C_{6K}), 139.8 (C_{6K}), 137.0 ($C_{4'E}$), 136.9 ($C_{4'K}$), 127.5 ($C_{3'E}$), 124.2 ($C_{3'K}$), 122.2 ($C_{5'E}$), 120.2 ($C_{5'K}$), 93.9 (CH=), 44.3 (CH_2).

2-(4-*Pyridacyl*)*pyrazine*. (13%K/87%E): δ_H 13.77 (OH), 8.85–8.83 ($H_{2',6'K}$), 8.69–8.67 ($H_{2',6'E}$), 8.63–8.62 (H_{3K}), 8.55–8.53 (H_{6K}), 8.52–8.51 (H_{3E}), 8.51–8.50 (H_{5K}), 8.38–8.37 (H_{6E}), 8.33–8.32 (H_{5E}), 7.83–7.81 ($H_{3',5'K}$), 7.68–7.66 ($H_{3',5'E}$), 7.83–7.77 ($H_{4'E}$), 7.53–7.48 ($H_{5'E}$), 7.34–7.29 ($H_{5'K}$), 6.27 (CH=), 4.54 (CH_2); δ_C 195.3w (C=O), 161.0 (COH), 153.1, 151.0w ($C_{2',6'K}$), 150.1 ($C_{2',6'E}$), 145.7w (C_{5K}), 144.4(1) (C_{5E}), 144.3(6) (C_{3K}), 143.2w ($C_{4'K}$), 142.3 ($C_{4'E}$), 141.9w (C_{6K}), 140.5 (C_{3E}), 139.8 (C_{6E}), 121.2w ($C_{3',5'K}$), 119.3 ($C_{3',5'E}$), 94.4 (CH=), 45.4w (CH_2).

2-*Phenacylquinoxaline*. (19%K/81%M): δ_H 14.70 (br, NH), 8.86(s, H_{3K}), 8.41 (s, H_{3M}), 8.10–8.06($H_{2',6'K}$), 8.06–7.96(H_{10K}?), 7.95–7.91($H_{2',6'M}$), 7.82–7.79(H_{10M}), 7.75–7.71($H_{8,9K}$), 7.59–7.34 (remaining quinoxalyl and $H_{3'-5'}$, K and M), 6.22 (=CH), 4.72 (CH_2); δ_C 195.8w (C=O_K), 181.8 (C=O_M), 150.8w (C_{2K}), 149.7 and 147.8 (C_{3M} and C_{5M}), 146.3w (C_{3K}), 142.4w (C_{5K}), 141.3w (C_{6K}), 137.7 and 137.4 (M), 136.2w ($C_{1'K}$), 133.7w ($C_{4'K}$), 132.7 (M), 131.1 and 131.0 ($C_{4'M}$ and C_{9M}), 130.1–128.8 (other aromatics, K), 129.2 (M), 128.5 ($C_{3',5'M}$), 126.6 ($C_{2',6'M}$), 125.7 and 119.8 (M), 91.2 (=CH), 46.4w (CH_2).

2-(2-*Pyridacyl*)*quinoxaline*. (8%K/92%M). δ_H 14.62 (br, NH); 8.92 (s, H_{3K}), 8.66–8.65 ($H_{6'M}$), 8.54 (s, H_{3M}), 8.09–8.07 ($H_{3'M}$), 7.85–7.78 ($H_{4',10M}$), 7.59–7.41 (H_{7-9M}), 7.39–7.32 ($H_{5'M}$), 6.22 (=CH), 4.98 (CH_2); δ_C 197.4w (C=O_K), 178.6 (C=O_M), 153.9, 149.8, 148.8, 148.3, 137.8, 137.0, 133.0, 130.9, 129.3, 126.1, 125.2, 121.0 and 120.3 (M), 91.9 (=CH), 45.4w (CH_2).

2-*Phenacylbenzoxazole*. (50%K/50%E): δ_H 8.06–8.03 ($H_{2',6'K}$), 7.89–7.86 ($H_{2',6'E}$), 7.73–7.70 (H_{6K}), 7.62–7.58 ($H_{4'K,6E}$), 7.54–7.43 ($H_{3',5',9K,E,4'E}$), 7.35–7.24 ($H_{7,8K,E}$), 6.20 (=CH), 4.63 (CH_2); δ_C 192.5w (C=O), 166.3w (COH), 165.8w (C=N_K), 160.5w (C=N_E), 151.3w (C_{4K}), 148.8w (C_{4E}), 141.3w (C_{5E}), 139.9w (C_{5K}), 135.7w ($C_{1'K}$), 134.1 ($C_{1'E}$), 134.0 ($C_{4'K}$), 130.7 ($C_{4'E}$), 129.0 ($C_{3',5'K}$), 128.7 ($C_{3',5'E}$), 128.6 ($C_{2',6'K}$), 125.9 ($C_{2',6'E}$), 125.1, 124.7, 124.4 and 124.2 ($C_{7,8K,E}$), 117.9 and 120.0 ($C_{6K,E}$), 110.7 and 110.3 ($C_{9K,E}$), 83.7 (CH=), 39.7 (CH_2).

Benzothiazol-2-ylacetone. (78%K/22%E): δ_H 8.03–7.99 (H_{6K}), 7.90–7.86 (H_{9K}), 7.76–7.72 (H_{6E}), 7.51–7.45 (H_{7or8K}), 7.42–7.36 (H_{7or8K} and $H_{7,8E}$), 7.26 (t, H_{9E}), 5.63 (d, *J* 0.6 Hz, =CH); 4.23 (CH_2), 2.33 (CH_3, K), 2.10 (d, *J* 0.6 Hz, CH_3, E); δ_C 202.4w (C=O), 162.8w (C=N_K), 152.9w (C_{5K}), 135.8w (C_{4K}), 126.4w (C_{8E}), 126.2 and 126.0 ($C_{7,8K}$), 123.9w (C_{7E}), 123.0 and 121.7w ($C_{6,9K}$), 121.4 and 119.6w ($C_{6,9E}$), 92.7w (CH=), 48.4 (CH_2), 30.0 (CH_3, K), 22.2w (CH_3, E), (COH, $C_{4,5E}$ and C=N_E ns).

Benzothiazol-2-ylacetone N-*methyl enaminone*. δ_H 7.54–7.50 (H_6), 7.14–7.05 (H_9), 7.32–7.26 ($H_{7,8}$), 5.80 (=CH), 3.49 (NCH_3), 2.19 (CH_3); δ_C 191.3w (C=O), 160.5w, 139.8w ($C_{4/5}$), 126.9 and 126.3w ($C_{7,8}$), 122.6 and 122.3 ($C_{6,9}$), 109.6, 90.4 (=CH), 32.3 (NCH_3), 29.0 (CCH_3).

2-*Phenacylbenzothiazole*. (40%K/60%E): δ_H *ca.* 13.9 (v br, OH), 8.10–8.07 (H_{6E}), 8.03–8.00 (H_{6K}), 7.88–7.86 ($H_{2',6',9E}$), 7.64–7.58 (H_{7K}), 7.52–7.47 (H_{9E}?), 7.45–7.41 ($H_{3'-5'}$), 7.38–7.35 (H_{9K}?), 7.32–7.27 (H_{8E}?), 6.37 (=CH), 4.83 (CH_2); δ_C 194.1w (C=O), 168.1w (C=N_K), 165.5w (C=N_E), 163.5w (COH), 152.7w (C_{5K}), 150.4w (C_{5E}), 136.0 and 135.8w ($C_{1',4K}$), 134.8w ($C_{1'E}$), 133.9 ($C_{4'K}$), 131.4w (C_{4E}), 130.4 ($C_{4'E}$), 128.9 ($C_{3',5'K}$), 128.7 ($C_{2',6'K}$), 128.6 ($C_{3',5'E}$), 126.5 and 126.1 ($C_{8K,E}$), 126.0 ($C_{2',6'E}$), 125.1 and 124.2 ($C_{7K,E}$), 122.9 and 121.4 ($C_{9K,E}$), 121.6 and 120.0 ($C_{6K,E}$), 90.9 (CH=), 43.9 (CH_2).

2-*Phenacylbenzothiazole* N-*methyl enaminone*. δ_H 7.99–7.95 ($H_{2',6'}$), 7.57–7.54 (H_6), 7.42–7.38 ($H_{3',4',5'}$), 7.36–7.29 (H_9), 7.17–7.09 ($H_{7,8}$), 5.48 (=CH), 3.58 (CH_3); δ_C 184.4 (C=O), 162.3, 139.9 ($C_{4/5}$), 139.5 ($C_{1'}$), 130.8 ($C_{4'}$), 128.3 ($C_{3',5'}$), 127.1 ($C_{2',6'}$), 127.1 and 126.5 ($C_{7,8}$), 122.8 and 122.3 ($C_{6,9}$), 109.8, 87.1 (=CH), 32.5 (CH_3).

2-(2-*Pyridacyl*)*benzothiazole*. (19%K/81%E): δ_H *ca.* 13.2 (v br, OH), 8.72–8.70 ($H_{6'K}$), 8.64–8.62 ($H_{6'E}$), 8.11–8.09 ($H_{3'K}$), 8.03–8.00 ($H_{3'E}$), 7.87–7.75 ($H_{4',6,9K,E}$), 7.51–7.26 ($H_{5',7,8K,E}$), 7.11 (CH=), 5.10 (CH_2); δ_C 195.8w (C=O), 168.0w (COH), 164.1w (C=N_E), 152.5w (C_{5E}), 152.3w ($C_{2'K}$?), 152.2 ($C_{2'E}$), 150.4w ($C_{6'K}$), 149.2 ($C_{6'E}$), 137.1w (C_{6K}?), 137.0 ($C_{4'E}$), 136.0w (C_{4E}), 132.0w?, 127.7w, 126.5, 125.9w, 125.0, 124.5, 124.4, 122.9w, 122.4w, 121.5, 120.9 and 102.2 (remaining benzo), 92.5 (CH=), 42.7 (CH_2).

Ethyl benzothiazol-2-ylpyruvate. (E): δ_H *ca.* 11.8 (v br, OH), 7.90–7.87 (H_6), 7.85–7.82 (H_9), 7.51–7.45 and 7.40–7.34 ($H_{7,8}$), 6.78 (CH=), 4.38 (q, 7.1 Hz, CH_2), 1.41 (t, *J* 7.1 Hz, CH_3); δ_C 166.1 and 162.9 (C=N and COH), 153.4w (*C*OOEt), 150.1w (C_5), 132.3w (C_4), 126.9 (C_8), 125.3 (C_7), 121.6 and 121.0 ($C_{6,9}$), 99.0 (CH=), 62.1 (CH_2), 14.2 (CH_3).

2-*Acetylpyridine*. δ_H 8.70–8.68 (H_6), 8.06–8.02 (H_3), 7.87–7.81 (H_4), 7.51–7.46 (H_5), 2.73 (CH_3); δ_C 199.8w (C=O), 153.4w (C_2), 148.8 (C_6), 136.7 (C_4), 127.0 and 121.4 ($C_{3,5}$), 25.6 (CH_3).

4-*Acetylpyridine*. δ_H 8.82 (d, *J* 6.1 Hz, $H_{2,6}$), 7.74 (d, *J* 6.1 Hz, $H_{3,5}$), 2.64 (CH_3); δ_C 197.3w (C=O), 150.9 ($C_{2,6}$), 142.6 (C_4), 121.2 ($C_{3,5}$), 26.6 (CH_3).

2-*Acetylpyrazine*. δ_H 9.24 (H_3), 8.77–8.76 (H_5), 8.67–8.66 (H_6), 7.51–7.46 (H_5), 2.73 (CH_3); δ_C 199.4w (C=O), 147.8 ($C_{2,5}$), 143.6 ($C_{3,6}$), 25.8 (CH_3).

Deoxybenzoin (α-*phenylacetophenone*). δ_H 8.02–7.99 ($H_{2,6}$, *Ph*CO), 7.57–7.51 (H_4, *Ph*CO), 7.47–7.41 ($H_{3,5}$, *Ph*CO), 7.35–7.20 (*Ph*CH_2), 4.27 (CH_2); δ_C 197.7w (C=O), 136.6w (C_1, *Ph*CO), 134.6w (C_1,*Ph*CH_2), 133.2 (C_4,*Ph*CO), 129.5 (C_4,*Ph*CH_2), 128.7, 128.6 and 126.9 ($C_{2,3,5}$, Ph), 45.5 (CH_2).

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