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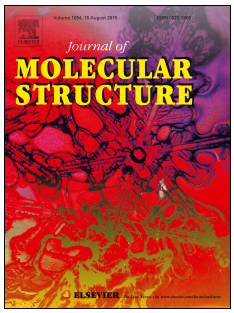

Tautomer-selective derivatives of enolate, ketone and enaminone by addition reaction of picolyl-type anions with nitriles

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Tautomer-selective derivatives of enolate, ketone and enaminone by addition reaction of picolyl-type anions with nitriles

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ABSTRACT

We describe an efficient for the synthesis of compounds of tautomeric β-pyridyl/quinolyl-enol, -ketone, -enaminone , which were finally characterized by standard methods like NMR, IR or SCXRD. The addition reaction of lithiated intermediates of picoline, 2-ethylpyridine and 2-methylquinoline, respectively, with nitriles followed by acid hydrolysis afforded the corresponding tautomeric compounds of enol, ketone and emaminone. Interestingly, treatment of 2-methylpyridine or 2-ethylpyridine with nitriles, respectively, yielded mostly β-pyridyl ketone and enol tautomers without enaminones, while 2-methylquinoline with nitriles gave β-quinolyl ketone and enaminone tautomers without enols. The reaction of 2-benzylpyridine with nitriles was not available under the same conditions.

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Keywords: Pyridyl/Quinolyl; Nitriles; Addition reaction; Ketone; Enol; Enaminones.

1. Introduction

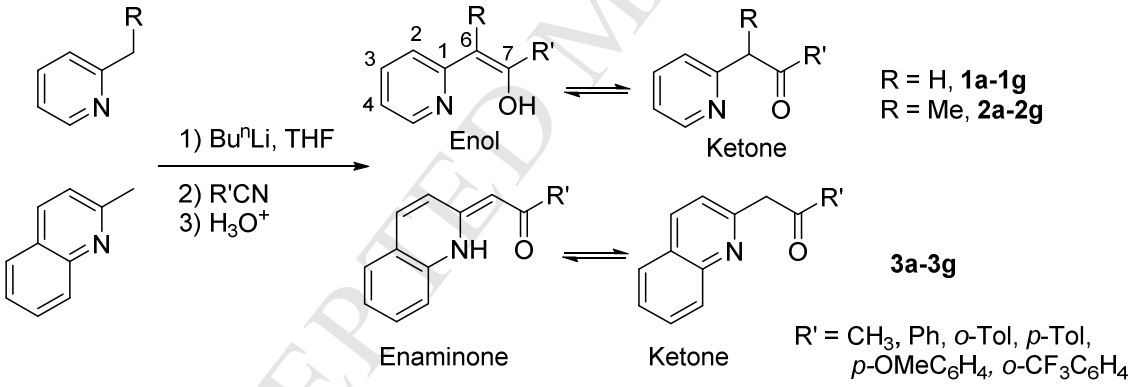
The methods to prepare heterocyclic ketones or enols should be available by the base-promoted condensation of methyl-heterocycle compounds with the appropriate esters, nitriles or carboxylic acid chlorides. Although the addition of Grignard reagents to nitriles has been known for a long time [1], some useful preparations with bulky reactants are usually required harsh conditions such as refluxing in high boiling solvents (toluene) for a extended period or large excesses of the Grignard reagents [2].

The addition reactions of nitriles to carbanions have been extensively investigated to form 1-azaallyls and β-diketiminates [3], after hydrolysis, to afford ketone compounds [4]. The formation of 1-azaallyls and β-diketiminates involves nucleophilic attack of carbanion on nitriles to form C-C bond [5]. We have reported the addition of picolyl/lutidyl lithium with α-hydrogen-free nitriles gave the pyridyl-substituted 1-azaallyl lithium and their corresponding metal complexes [6]; moreover, the addition reactions of lithium silylquinolylamide with dimethylcyanamide resulted in quinolylguanidinates [7]. In comparison, little attention has been devoted to their hydrolysis products which possess a nitrogen heterocyle aromatic ring as the chelating [N,O] ligands of pyridyl/quinolyl-enolates [8].

In fact, the most straightforward way to prepare heterocyclic ketones was the reaction of heterocyclic lithium salt with nitriles followed by acidic hydrolysis [9]. In

this manner, Bildstein and coworkers reported four compounds of pyridyl/quinolyl-enolates by addition of α-picolyl/quinolyl-lithium with acetonitrile or benzonitrile followed by acidic hydrolysis [9b]. These [N,O] ligands exist in three tautomers: enol, ketone and enaminone, depending on the substituent pattern in the molecule [9b,10].

To evaluate the scope of the addition and hydrolysis products, a series of aliphatic and aromatic nitriles were reacted with pyridyl- and quinolyl lithium reagents. Herein, we report a simple and efficient one pot synthesis of pyridyl/quinolyl ketone and describe the substituent effect on the tautomeric equilibrium between enol, keton and enaminone (Scheme 1).



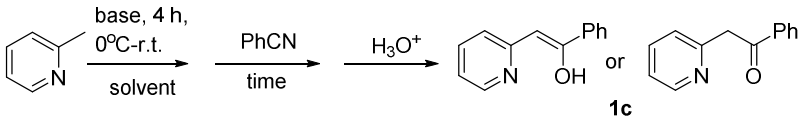
Scheme 1. The reaction of *o*-substituted pyridine/quinoline with nitriles.

2. Results and discussion

Initially the model reaction of picoline with PhCN was examined under different conditions (Table 1). As expected, in the solvents like Et_2O, hexane and THF, **1c** could be obtained in good yields (Table 1, entries 1-5). Among all the solvents tested, THF proved to be the most efficient. In this case, the mixture of picoline, BuLi with

PhCN afforded compound **1c** in 80% yield within 6 hours (Table 1, entry 5). Except BuLi, other types of base reagents were also investigated. Bu^tOK and NaH gave relatively lower efficiency compared to Bu^nLi (Table 1, entries 6-7).

Table 1. Optimization of the reaction conditions for the synthesis of **1c**[a]



Entry	base	solvent	Time	Yield[b] %
1	Bu^nLi	Et_2O	12 h	71
2	Bu^nLi	Et_2O	6 h	72
3	Bu^nLi	Hexane	12 h	45
4	Bu^nLi	THF	12 h	80
5	**Bu^nLi**	**THF**	**6 h**	**80**
6	Bu^tOK	THF	12 h	32
7	NaH	THF	12 h	38

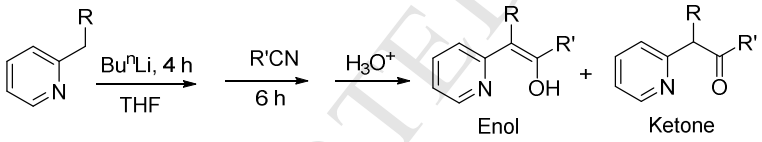
[a] Reaction conditions: picoline (3.0 mmol), base (3.0 mmol), anhydrous solvent (6 mL), PhCN (3.0 mmol), room temperature.

[b] Isolated yield.

Under the conditions as for **1c** in entry 5 (Table 1), a series of reaction of lithiated 2-substituted pyridine/quinoline with nitriles were carried out, and some of the results are summarized in Table 2 and Table 3. It was found that different heterocyclic substrates reacted with nitriles to yield selective tautomeric compounds of enol, ketone and enaminone under the same reaction conditions (Scheme 1). The reaction of 2-methylpyridyl anion with RCN gave the tautomeric mixtures of enol and ketone (**1a-1g**, Table 2, entries 1-7). However, when the addition of pyridine-2-ylethyl lithium with nitriles was carried out, ketone forms (**2c-2g**, Table 2, entries 10-14))

were found to be dominant in solution or solid. Compound **2c** was also obtained by coupling of 2-bromopyridine and propiophenone using di-tert-butylneopentylphosphine and palladium (II) as a catalyst [11]. Thereby, while reaction of pyridine-2-ylethyl lithium with aliphatic CH_3CN and Bu^tCN, respectively, were proven to be inert under identical conditions, so products **2a** and **2b** were not obtained which may be due to the electron-donating group decreasing the C-eletrophilicity (Table 2, entries 8 and 9). Enaminone tautomers (**3a-3f**) were more prominent for 2-sustituted quinolines (Table 3, entries 15-20). **3g** could not undergo the insertion under the identical conditions, which might be attributed to the strong electron-withdrawing group and steric effects at the ortho benzene ring (Table 3, entry 21).

Table 2. Synthesis of **1** and **2** and their tautomeric compositions

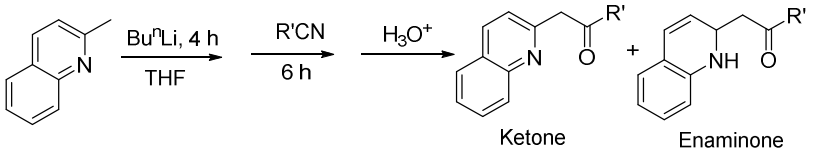


Entry	R	R'	Products	Yield[a] %	Enol[b] %	Ketone[b] %
1	H	Me	**1a**	72	8	92
2	H	Bu^t	**1b**	83	12	88
3	H	Ph	**1c**	80	60	40
4	H	*o*-Tol	**1d**	84	59	41
5	H	*p*-Tol	**1e**	90	27	73
6	H	*p*-$OMeC_6H_4$	**1f**	93	16	84
7	H	*o*-$CF_3C_6H_4$	**1g**	69	84	16
8	Me	Me	**2a**	NA	–	–
9	Me	Bu^t	**2b**	NA	–	–
10	Me	Ph	**2c**	73	0	>99

11	Me	*o*-Tol	**2d**	76	16	84
12	Me	*p*-Tol	**2e**	93	0	>99
13	Me	*p*-$OMeC_6H_4$	**2f**	84	0	>99
14	Me	*o*-$CF_3C_6H_4$	**2g**	85	47	53

[a] Isolated yield. [b]Determined by ^1H NMR ($CDCl_3$)

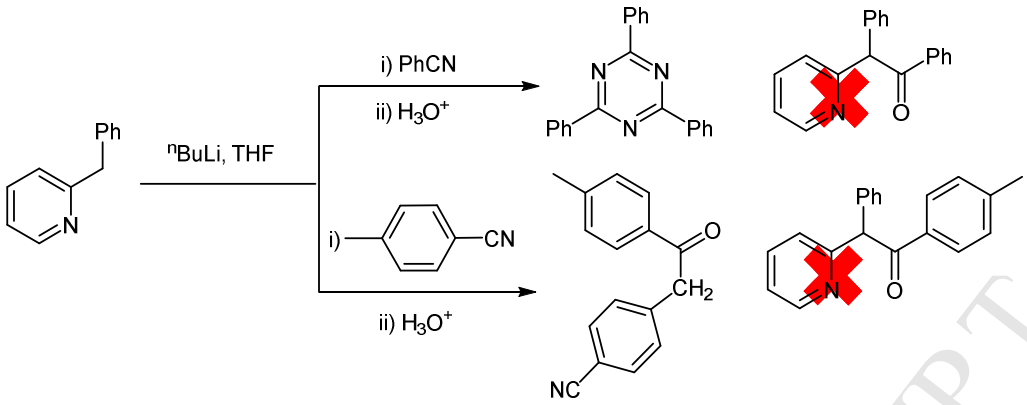
Table 3. Synthesis of **3** and their tautomeric compositions



Entry	R'	Products	Yield[a] %	Ketone[b] %	Enaminone[b] %
15	Me	**3a**	62	18	82
16	Bu^t	**3b**	69	15	85
17	Ph	**3c**	84	4	96
18	*o*-Tol	**3d**	87	3	97
19	*p*-Tol	**3e**	89	7	93
20	*p*-$OMeC_6H_4$	**3f**	91	9	91
21	*o*-$CF_3C_6H_4$	**3g**	NA	–	–

[a] Isolated yield. [b]Determined by ^1H NMR ($CDCl_3$)

When 2-benzylpyridine was used, the reaction did not lead to the formation of the addition products, excluding a competitive cross-coupling product produced by the nitriles alone (Scheme 2). The oligomerization of benzonitrile in the presence of alkyllithium is known reaction [12], and dimerization of methyl-substituted benzonitrile was reported by Petty [13].



Scheme 2. The reaction of 2-benzylpyridine with nitriles

The tautomers of enol and ketone were identified by the presence of the H6 signals (usually in $CDCl_3$) in ^1H NMR spectra and an unconjugated keto group in the IR spectra. Figure 1 depicts an overlay of ^1H NMR spectra (300 MHz, $CDCl_3$) of **1c**, **2f** and **3d**.

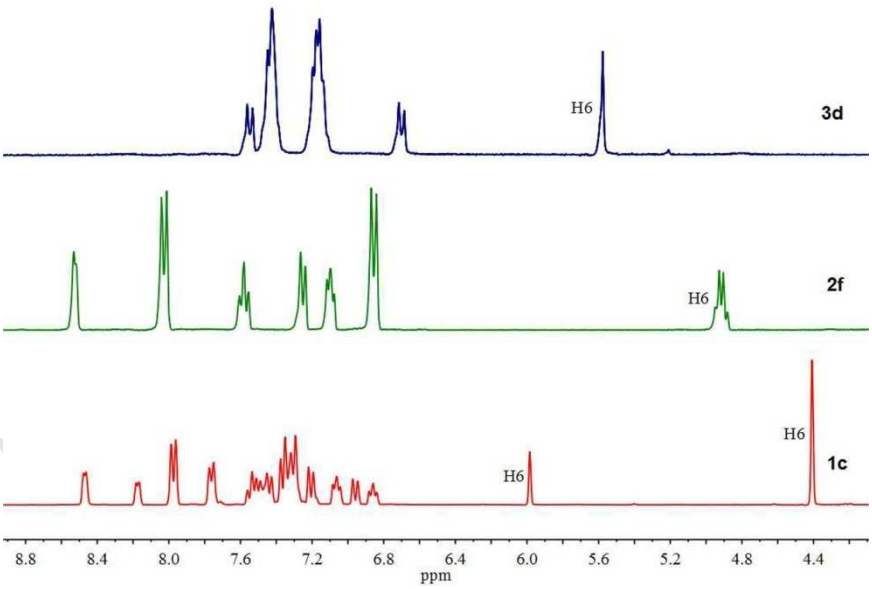


Figure 1. Overlay of ^1H NMR spectra (300 MHz, $CDCl_3$) of **1c**, **2f** and**3d**

As it can be seen, singlets in the range 3.79-4.54 ppm were assigned to CH_2 group of the ketone and signals in the range 5.27-6.37 were attributed to the CH of the enol for **1a-1g**. Quartets in the range 4.58-5.03 were observed to CH group in **2a-2g**, and singlets in the range of 5.51-6.02 were assigned to CH group in **3a-3f**. However, it is difficult to distinguish the enol and enaminone by comparing their ^{1}H NMR spectra [8c]. For distinguishing enol and enaminone, ^{13}C NMR spectra would be the best method based on the difference in carbon chemical shift between C of the enol (=C-OH) and enaminone (C=O). The values of δ_c fall in the ranges 185-201 ppm for the enaminones **3a-3f** and156-170 ppm for the enol tautomers **1a-1g**. In general, δ_c values increase when R becomes more electron-withdrawing for the carbonyl C of enaminones and enols. The large down-field shift of OH and NH protons at 15-16 ppm was attributed to the strong intramolecular hydrogen bond, in which these protons are also broadened and that indicated the presence of intermolecular hydrogen bonds in enols and enaminones.

The proportions of tautomers were determined by integration of the H6 signals (Figuer 1). It can be seen that the ratios of three forms were sensitive to the heterocycle and substituent in the molecule. In general, only two of tautomers were observed in the mixture of respective pyridines (ketone and enol) and quinolines (ketone and enaminone) [10c]. The strong electron-withdrawing group in the molecule such as **1g** and **2g** resulted in more enol form, in contrast, electron-donating group produced more ketone form.

IR absorption spectra were in accordance with the assignments of ^{1}H and ^{13}C NMR shifts. Broad absorption bands were observed in the frequency range 3300-3600 cm^{-1} due to the strong intramolecular hydrogen bonding interactions of **1a-1g** and **3a-3f**.

The structures of **1e**, **2e** and **3d** have been confirmed by X-ray single-crystal diffraction. The different tautomeric equilibria are often paid attention in solution. However, the molecular structures showed that there was only one tautomer can be seen in the solid state. The molecular geometries of **1e**, **2e** and **3d** are illustrated in Figure 2-4 and their selected bond lengths and angles are presented in Table 4.

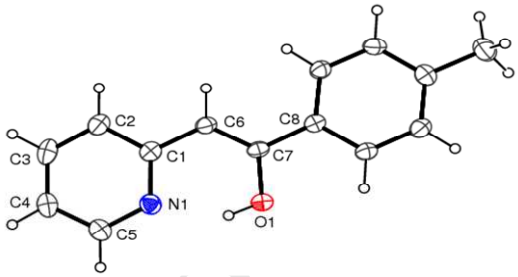


Figure 2. Molecular structure of **1e**.Thermal ellipsoids are drawn at the 30% probability level.

Comparison of their crystal structures, it can be seen that their molecular geometries are significantly different from each other. For enol **1e** and enaminone **3d**, the N1C1C6C7O1 backbone is almost planar and is coplanar with the pyridine (**1e**) and quinoline (**3d**) ring respectively. Their torsion angles of N1,O1-C1-C6-C7 are 4.3(3) and -0.9(4)º for compound **1e**, and 4.5(2) and -5.7(2)º for compound **3d**, respectively. However, the N1C1C6C7O1 backbone in ketone **2e** is strongly twisted with the N1,O1-C1-C6-C7 torsion angles being -34.82(17) and 116.08(16)º. In the N1C1C6C7O1 moiety, the bond lengths N1-C1, C1-C2 and C7-O in **1e** and **3d** are

longer and C1-C6 and C6-C7 are shorter compared to those in **2e**. That indicates the π-electron delocalization is present in N1C1C6C7O1 fragment in **1e** and **3d**. On the other hand, the C6-C7 bond in **1e** is shorter than that in **2e** and **3d**, forming an obvious conjugated system between N1C1C6C7O1 and benzene ring. The benzene ring is almost coplanar with the pyridine ring in **1e**, while it is twisted around the C7-C8 bond in **3d**. It can be seen the twisting depends on the substituents rather than type of compound [14]. The intramolecular hydrogen bond O-H···N in **1e** is almost as long as that N-H···O=C in **3d**. Intramolecular hydrogen bonding in **1e** and **3d** leads to the formation of a six-membered quasi-ring.

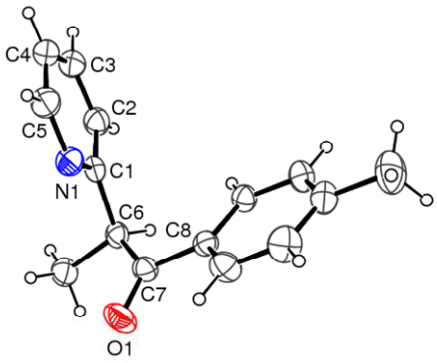


Figure 3. Molecular structure of **2e**.Thermal ellipsoids are drawn at the 30% probability level.

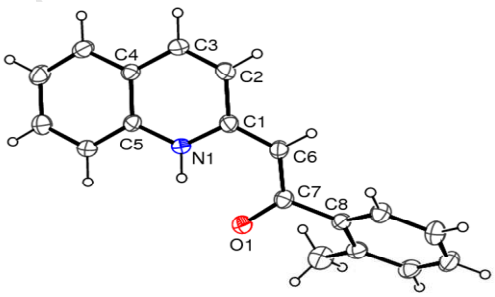


Figure 4. Molecular structure of **3d**.Thermal ellipsoids are drawn at the 30% probability level.

Table 4. Selected bond lengths [Å], angles [º] H-bonds [Å]and torsion angles [º] for **1e**, **2e** and **3d**

Geometric parameters	**1e**	**2e**	**3d**
Bond lengths [Å]			
C1－N1	1.354(3)	1.3317(19)	1.3505(15)
C1－C2	1.399(3)	1.380(2)	1.4304(17)
C2－C3	1.380(3)	1.383(3)	1.3402(18)
C3－C4	1.371(4)	1.362(3)	1.4208(18)
C4－C5	1.383(4)	1.363(3)	1.4027(16)
C1－C6	1.446(3)	1.514(2)	1.3908(17)
C6－C7	1.355(3)	1.518(2)	1.4307(17)
C7－O1	1.351(2)	1.2164(18)	1.2685(15)
C7－C8	1.470(3)	1.492(2)	1.5062(17)
H-bonds [Å]			
O1···H	0.839	-	-
N1－H	-	-	0.860
N1···H	1.817	-	-
N1··· O1	2.567	-	2.615
Bond angles [º]			
N1HO1	147.90	-	132.60
N1C1C6	117.6(2)	115.98(14)	120.60(12)
C1C6C7	124.6(2)	109.93(12)	123.44(12)
C6C7O1	121.4(2)	120.44(15)	122.61(12)
C8C7O1	113.6(2)	119.94(15)	118.36(12)
Torsion angles [º]			
N1C1C6C7	4.3(3)	-34.82(17)	4.5(2)
O1C1C6C7	-0.9(4)	116.08(16)	-5.7(2)

3. Conclusions

In conclusion, we have developed an efficient insertion reaction of pyridyl-/quinolyl-lithium with nitriles for preparing pyridyl-/quinolyl-ketone compounds. These heterocyclic ketones exist in three tautomers of enol, ketone and enaminone. The tautomeric equilibria are affected by the substituent in the molecule. The tautomeric species have been identified from NMR and IR spectra. We noticed that **1a-1g** was in the tautomeric equilibrium with ketone and enol, however, the ketone was more stable than enol for **2c-2g**, and the enaminone was found to be predominant for **3a-3f**. Both enol and enaminone derivatives were stabilized by an intramolecular hydrogen bond which formed a six-membered quasi-ring. Their anions are expected to be good σ- and π-donors, like cyclopentadienyl ligands. Based on above, further studies on the coordination chemistry of this class of ketone ligands with tautomeric equilibrium and the application of their metal complexes are presently underway.

4. Experimental

General Information:

All sensitive manipulations were carried out under dry N_2 using standard Schlenk techniques. All reagents purchased from commercial sources were purified by standard techniques prior to use. Tetrahydrofuran was dried by distilling from sodium/benzophenone. The compounds 1-(2-Pyridinyl)-2-propanone (**1a**) [9b], 1-Phenyl-2-(2-pyridinyl)-ethanone (**1c**) [9b], 1-(2-Quinolinyl)-2-propanone (**3a**) [10e]

and 1-Phenyl-2-(2-quinolinyl)-ethanone (**3c**) [10e] were reported in published papers. Herein we added some data for future reference. NMR spectra were recorded on a Bruker AVANCE 600 (^{1}H 600 MHz, ^{13}C 150 MHz) or Bruker AVANCE 300 (^{1}H 300 MHz, ^{13}C 75 MHz) at room temperature. The chemical shifts of ^{1}H and ^{13}C were referenced to TMS or residual solvent resonances. IR spectra of the compounds were recorded with a Bruker Tensor 27 ATR-FTIR spectrometer using KBr pellets. Elemental analyses were performed on an Vario EL III instrument.

Typical procedure for the synthesis of 1a

To a solution of 2-methylpyridine (2.79 g, 30 mmol) in 35 mL THF, ^{n}BuLi (12.4 mL, 2.5 M solution in hexane, 30 mmol) was slowly added at 0 °C with stirring. The mixture was allowed to warm to room temperature for 4 h, after which acetontrile (1.61 mL, 31 mmol) was added at 0 °C and then stirred for 6 h at room temperature. A sulfuric acid of 60% aqueous solution was then added dropwise until a PH of 1 was reached, and was stirred for 1 d to complete acidic hydrolysis, then neutralized with saturated aqueous KOH solution. The organic layer was extracted with CH_2Cl_2 (50 mL×3), then dried over $MgSO_4$ and concentrated by rotary evaporator. This compound was purified by reduced pressure distillation, resulting in yellow oil of **1a**. **1b**-**2g** were purified by reduced pressure distillation. **3a**-**3f** were purified by recrystallization and chromatography.

1-(2-Pyridinyl)-2-propanone (1a)：

This compound was reported by a published paper [9b]. Because no data of enol have been reported, we include different data here for future reference. Yield: 2.92 g

(72%). Bp 45 °C at 3 mbar. ^{1}H NMR (600 MHz, $CDCl_3$, 298 K): δ 2.20 (s, 3H, CH_3), 3.89 (s, 2H, CH_2), 5.27 (s, 1H, =CH), 6.83-6.92 (m, 2H, pyridyl), 7.16-7.19 (m, 2H, pyridyl), 7.44-7.52 (m, 1H, pyridyl), 7.63 (d, *J* = 6.0 Hz 1H, pyridyl), 8.17 (d, *J* = 8.4 Hz, 1H, pyridyl), 8.54 (d, *J* = 8.4 Hz, 1H, pyridyl), 14.71 (s, 1H, OH). ^{13}C NMR (150 MHz, $CDCl_3$, 298 K): δ 22.5, 29.9, 53.0, 95.3, 117.8, 120.2, 121.9, 124.1, 136.6, 144.0, 149.4, 154.7, 167.3 (C-OH), 205.2 (C=O). ν_{max} (KBr): 3418 (OH), 3075, 2912, 2842, 1714 (C=O), 1644 (C=N), 1583 (C=N), 1468, 1432, 1355, 1148, 746 cm^{-1}. Anal. Calcd for C_8H_9NO: C, 71.09; H, 6.71; N, 10.36. Found: C, 71.11; H, 6.78; N, 10.42.

3,3-Dimethyl-1-(2-pyridinyl)-2-butanone (1b)：

Yellow oil. Yield: 4.41 g (83%). Bp 121 °C at 3 mbar. ^{1}H NMR (300 MHz, $CDCl_3$, 298 K): δ 1.20 (s, 9H, CH_3), 4.01 (s, 2H, CH_2), 5.37 (s, 1H, =CH), 6.85-6.91 (m, 2H, pyridyl), 7.10-7.20 (m, 2H, pyridyl), 7.48 (t, *J* = 7.8 Hz, 1H, pyridyl), 7.57 (t, *J* = 7.5 Hz, 1H, pyridyl), 8.15 (d, *J* = 4.8 Hz, 1H, pyridyl), 8.49 (d, *J* = 4.5Hz, 1H, pyridyl), 15.14 (s, 1H, OH). ^{13}C NMR (75 MHz, $CDCl_3$, 298 K): 27.0, 28.8, 45.4, 46.7, 91.9, 118.7, 121.6, 122.4, 125.2, 137.0, 137.6, 144.9, 156.3, 212.9 (C=O). ν_{max} (KBr): 3404 (OH), 3034, 2969, 2855, 1717 (C=O), 1635 (C=N), 1603 (C=N), 1480, 1431, 1365, 1275, 1120, 1054, 890, 801, 735 cm^{-1}. Anal. Calcd for $C_{11}H_{15}NO$: C, 74.54; H, 8.53; N, 7.90. Found: C, 74.48; H, 8.55; N, 7.92.

1-Phenyl-2-(2-pyridinyl)-ethanone (1c)：

Red oil but slowly solidified. Yield: 4.73 g (80%). Bp 117 °C at 3 mbar. Mp 56-58 °C. ^{1}H NMR (300 MHz, $(CD_3)_2SO$, 298 K): 4.54 (s, 2H, CH_2), 6.37 (s, 1H, =CH),

7.12-7.22 (m, 1H, ArH), 7.24-7.30 (m, 1H, ArH), 7.36-7.44 (m, 2H, ArH), 7.49 (t, *J* = 7.5 Hz, 2H, ArH), 7.61-7.75 (m, 1H, ArH), 7.77-7.85 (m, 1H, ArH), 8.01 (d, *J* = 7.8 Hz, 2H, ArH), 8.39 (d, *J* = 3.9 Hz, 1H, ArH), 8.46 (d, *J* = 3.3 Hz, 1H, ArH), 15.38 (s, 1H, OH). ^{1}H NMR (300 MHz, $CDCl_3$, 298 K): δ 4.40 (s, 2H, CH_2), 5.98 (s, 1H, =CH), 6.84 (t, *J* = 6.0 Hz, 1H, ArH), 6.94 (d, *J* = 8.1 Hz, 1H, ArH), 7.04 (t, *J* = 6.0 Hz, 1H, ArH), 7.19 (d, *J* = 7.8 Hz, 1H, ArH), 7.29-7.37 (m, 5H, ArH), 7.42-7.56 (m, 3H, ArH), 7.75 (d, *J* = 6.9 Hz, 2H, ArH), 7.96 (d, *J* = 7.8 Hz, 2H, ArH), 8.16 (d, *J* = 4.8 Hz, 1H, ArH), 8.46 (d, *J* = 4.2 Hz, 1H, ArH), 15.23 (s, 1H, OH). ^{13}C NMR (75 MHz, $(CD_3)_2SO$, 298 K): δ 48.5, 94.6, 119.9, 122.7, 126.0, 128.3, 129.3, 129.6, 130.1, 130.3, 134.1, 136.8, 137.3, 137.4, 138.9, 145.1, 149.9 , 156.6, 158.6, 164.0 (C-OH), 197.9 (C=O). ν_{max} (KBr): 3420 (OH), 1648 (C=O), 1590 (C=N), 1545 (C=N), 1420, 1378, 1280, 1144, 806, 751, 678 cm^{-1}. Anal. Calcd for $C_{13}H_{11}NO$: C, 79.16; H, 5.62; N, 7.10. Found: C, 79.07; H, 5.71; N, 7.04.

1-(2-Methylphenyl)-2-(2-pyridinyl)-ethanone (1d)：

Yellow oil but slowly solidified. Yield: 5.32 g (84%). Bp 135 °C at 3 mbar. ^{1}H NMR (300 MHz, $(CD_3)_2SO$, 298 K): δ 2.39 (s, 3H, CH_3), 2.50 (s, 3H, CH_3), 4.45 (s, 2H, CH_2), 5.76 (s, 1H, =CH), 7.09-7.11 (m, 1H, ArH), 7.12-7.14 (m, 1H, ArH), 7.20-7.32 (m, 4H, ArH), 7.35-7.45 (m, 4H, ArH), 7.69-7.76 (m, 2H, ArH), 7.79-7.92 (m, 2H, ArH), 8.37 (d, *J* = 5.1 Hz, 1H, ArH), 8.46 (d, *J* = 5.1 Hz, 1H, ArH), 15.25 (s, 1H, OH). ^{13}C NMR (75 MHz, $(CD_3)_2SO$, 298 K): δ 19.6, 20.0, 49.7, 96.6, 118.1, 120.8, 121.1, 123.7, 125.0, 125.1, 127.3, 128.0, 128.3, 130.0, 130.6, 130.9, 134.8, 135.8, 136.6, 136.8, 137.2, 143.3, 148.4, 155.0, 157.0, 166.8 (C-OH), 200.1 (C=O). ν_{max}

(KBr): 3422 (OH), 3002, 2933, 2870, 1644 (C=O), 1593 (C=N), 1564 (C=N), 1508, 1442, 1163, 1054, 948, 847, 728 cm^{-1}. Anal. Calcd for $C_{14}H_{13}NO$: C, 79.59; H, 6.20; N,6.63. Found: C,79.64; H, 6.27; N, 6.68.

1-(4-Methylphenyl)-2-(2-pyridinyl)-ethanone (1e)：

Yellow oil but slowly solidified. Yield: 5.70 g (90%). Bp 142 °C at 3 mbar. Mp 66-69 °C. ^{1}H NMR (300 MHz, $CDCl_3$, 298 K): δ 2.32 (s, 3H, $ArCH_3$), 4.41 (s, 2H, CH_2), 5.96 (s, 1H, =CH), 6.85-6.89 (m, 1H, ArH), 6.95 (d, *J* = 8.1 Hz, 1H, ArH), 7.07-7.25 (m, 4H, ArH), 7.49-7.59 (m, 1H, ArH), 7.65 (d, *J* = 7.8 Hz, 1H, ArH), 7.88 (d, *J* = 8.1 Hz, 1H, ArH), 8.18 (d, *J* = 4.8 Hz, 1H, ArH), 8.48 (d, *J* = 4.5 Hz, 1H, ArH), 15.32 (s, 1H, OH). ^{13}C NMR (75 MHz, $CDCl_3$, 298 K): δ 22.1, 22.4, 49.0, 94.2, 118.9, 122.2, 122.6, 125.0, 126.2, 129.6, 130.1, 134.8, 137.4, 137.8, 144.9, 150.1, 156.1, 197.2 (C=O). ν_{max} (KBr): 3428 (OH), 2929, 2855, 1643 (C=O), 1586 (C=N), 1537 (C=N), 1513, 1455, 1382, 940, 808, 735 cm^{-1}. Anal. Calcd for $C_{14}H_{13}NO$: C, 79.59; H, 6.20; N, 6.63. Found: C, 79.48; H, 6.33; N, 6.74.

1-(4-Methoxyphenyl)-2-(2-pyridinyl)-ethanone (1f)：

Yellow oil but slowly solidified. Yield: 6.33 g (93%). Bp 153 °C at 3 mbar. Mp 85-87 °C. ^{1}H NMR (300 MHz, $CDCl_3$, 298 K): δ 3.71 (s, 3H, OCH_3), 4.33 (s, 2H, CH_2), 5.86 (s, 1H, =CH), 6.78 (d, *J* = 8.4 Hz, 2H, ArH), 6.88 (d, *J* = 8.1 Hz, 2H, ArH), 7.04 (t, *J* = 6.0 Hz, 1H, ArH), 7.17 (d, *J* = 7.8 Hz, 1H, ArH), 7.41 (d, *J* = 7.8 Hz, 1H, ArH), 7.48-7.53 (m, 2H, ArH), 7.66 (d, *J* = 8.4 Hz, 2H, ArH), 7.92 (d, *J* = 8.4 Hz, 1H, ArH), 8.09 (d, *J* = 4.8 Hz, 1H, ArH), 8.44-8.53(m, 1H, ArH), ^{13}C NMR (150 MHz, $CDCl_3$, 298 K): δ 51.0, 58.1, 58.3, 95.5, 116.2, 120.8, 124.2, 124.7, 127.1,

129.8, 131.9, 132.4, 133.8, 134.7, 139.4, 139.9, 146.7, 152.3, 158.4, 161.5, 163.5, 166.5 (C-OH), 198.2 (C=O) ppm. ν_{max} (KBr): 3424 (OH), 2978, 2912, 2847, 1627 (C=O), 1584 (C=N), 1546 (C=N), 1504, 1455, 1234, 1177, 1054, 874, 792, 726 cm^{-1}. Anal. Calcd for $C_{14}H_{13}NO_2$: C, 73.99; H, 5.77; N,6.16. Found: C, 74.12; H, 5.68; N, 6.14.

2-(2-Pyridinyl)-1-[2-(trifluoromethyl)pheny- l]-ethanone (1g):

Red oil. Yield: 5.48 g (69%). Bp 135 °C at 3 mbar. ^{1}H NMR (300 MHz, $CDCl_3$, 298 K): δ 4.16 (s, 2H, CH_2), 5.39 (s, 1H, =CH), 6.69 (d, *J* = 7.5Hz, 2H, ArH), 6.92 (d, *J* = 6.6 Hz, 1H, ArH), 7.05 (d, *J* = 6.0 Hz, 1H, ArH), 7.20 (d, *J* = 6.9 Hz, 1H, ArH), 7.29 (d, *J* = 6.0 Hz, 1H, ArH), 7.35 (d, *J* = 7.2 Hz, 1H, ArH), 7.46 (d, *J* = 6.9 Hz, 1H, ArH), 7.91 (d, *J* = 6.9 Hz, 1H, ArH), 8.23-8.32 (m, 1H, ArH), 15.33 (s, 1H, OH). ^{13}C NMR (150 MHz, $CDCl_3$, 298 K): δ 32.6, 54.9, 100.2, 100.5, 120.5, 121.2, 124.3, 125.1, 129.2, 129.3, 130.4, 130.6, 131.3, 131.6, 133.0, 133.2, 134.5, 134.6, 138.5, 139.5, 140.3, 141.8, 142.4, 145.6, 150.4, 152.2, 156.8, 160.5, 162.5, 170.7 (C-OH), 203.4 (C=O). ν_{max} (KBr): 3420 (OH), 1645 (C=O), 1594 (C=N), 1568 (C=N), 1472, 1357, 1264, 1080, 937, 807, 735 cm^{-1}. Anal. Calcd for $C_{14}H_{10}F_3NO$: C, 63.40; H, 3.80; N, 5.28. Found: C, 63.32; H, 3.77; N, 5.33.

1-Phenyl-2-(2-pyridinyl)-1-propanone (2c):

Yellow oil but slowly solidified. Yield: 4.62 g (73%). Bp 123 °C at 3 mbar. Mp 65-68 °C. ^{1}H NMR (300 MHz, $(CD_3)_2SO$, 298 K): δ 1.41 (d, J = 6.9 Hz, 3H, CH_3), 5.03 (m, 1H, CH), 7.14-7.16 (m, 1H, ArH), 7.18-7.43 (m, 3H, ArH), 7.48-7.53 (m, 1H, ArH), 7.53-7.74 (m, 1H, ArH), 8.38 (m, 1H, ArH). ^{13}C NMR (75 MHz, $(CD_3)_2SO$, 298 K): δ

16.8, 48.6, 121.1, 121.8, 127.6, 132.1, 135.6, 136.4, 148.5, 160.4, 198.3 (C=O). ν_{max} (KBr): 3051, 2994, 2929, 1685 (C=O), 1594 (C=N), 1578 (C=N), 1431, 1325, 1226, 1071, 956, 792, 743, 702 cm^{-1}. Anal. Calcd for $C_{14}H_{13}NO$: C, 79.59; H, 6.20; N, 6.63. Found: C,79.44; H, 6.14; N, 6.74.

1-(2-Methylphenyl)-2-(2-pyridinyl)-1-propanone (2d):

Yellow oil. Yield: 5.13 g (76%). Bp 138 °C at 3 mbar. ^{1}H NMR (300 MHz, $CDCl_3$, 298 K): δ 1.48 (d, *J* = 6.9 Hz, 3H, CH_3), 1.68 (s, 3H, CH_3), 2.27 (s, 3H, $ArCH_3$), 2.36 (s, 3H, $ArCH_3$), 4.70 (m, 1H, CH), 6.95-7.19 (m, 6H, ArH), 7.46 (t, *J* = 7.5 Hz, 1H, ArH), 7.60 (d, *J* = 6.9 Hz, 1H, ArH), 8.27 (s, 1H, ArH), 8.40 (d, *J* = 3.9 Hz, 1H, ArH), 15.96 (s, 1H, OH). ^{13}C NMR (75 MHz, $CDCl_3$, 298 K): δ 15.5, 18.6, 20.4, 22.2, 54.1,118.2,118.7,119.3, 119.8, 120.1, 122.9, 123.4, 126.6, 129.3, 129.7,131.2, 132.1, 137.8, 138.5, 139.1, 139.5, 145.5, 150.6, 161.8, 164.2 (C-OH), 204.6 (C=O). ν_{max} (KBr): 3418 (OH), 2908, 1658 (C=O), 1621 (C=N), 1586 (C=N), 1460, 1311, 1048, 947, 792, 743, 686 cm^{-1}. Anal. Calcd for $C_{15}H_{15}NO$: C, 79.97; H, 6.71; N, 6.22. Found: C, 79.75; H, 6.59; N, 6.18.

1-(4-Methylphenyl)-2-(2-pyridinyl)-1-propanone (2e):

Yellow oil but slowly solidified. Yield: 6.28 g (93%). Bp 144 °C at 3 mbar. Mp 70-71 °C. ^{1}H NMR (300 MHz, $CDCl_3$, 298 K): δ 1.47 (d, J = 6.9 Hz, 3H, CH_3), 2.18 (s, 3H, $ArCH_3$), 4.86 (m, 1H, CH), 6.92 (d, J = 5.1 Hz, 1H, ArH), 7.01 (d, J = 7.8 Hz, 2H, ArH), 7.13 (d, J = 7.8 Hz, 1H, ArH), 7.41 (m, 1H, ArH), 7.85 (d, J = 7.8 Hz, 1H, ArH), 8.40 (d, J = 5.1 Hz, 1H, ArH). ^{13}C NMR (75 MHz, $CDCl_3$, 298 K): δ 18.3, 21.8, 50.8,

122.1, 122.2, 129.4, 134.2, 137.2, 143.9, 161.5, 199.2 (C=O) ppm. v_{max} (KBr): 2929, 1685 (C=O), 1603 (C=N), 1562 (C=N), 1431, 1341, 1234, 1054, 956, 850, 801, 759 cm^{-1} . Anal. Calcd for $C_{15}H_{15}NO$: C, 79.97; H, 6.71; N, 6.22. Found: C, 79.81; H, 6.63; N, 6.31.

1-(4-Methoxyphenyl)-2-(2-pyridinyl)-1-propanone (2f):

Yellow oil. Yield: 6.08 g (84%). Bp 158 °C at 3 mbar. ^{1}H NMR (300 MHz, $CDCl_3$, 298 K): δ 1.56 (d, J = 6.9Hz, 3H, CH_3), 3.79 (s, 3H, OCH_3), 4.90 (m, 1H, CH), 6.84 (d, J = 8.7 Hz, 2H, ArH), 7.07 (t, J = 6.0 Hz,1H, ArH), 7.23 (d, J = 7.8 Hz,1H, ArH), 7.55 (t,J = 7.8 Hz,1H, ArH), 8.01 (d, J = 8.7 Hz, 2H, ArH), 8.53 (d, J = 5.1 Hz, 1H, ArH). ^{13}C NMR (75 MHz, $CDCl_3$, 298 K): δ 18.2, 50.6, 55.6, 114.0, 122.1, 129.7, 131.5, 137.1, 149.8, 161.7, 163.6, 198.2 (C=O). v_{max} (KBr): 2912, 1705 (C=O), 1635 (C=N), 1594 (C=N), 1471, 1322, 1128, 848, 752, 712 cm^{-1}. Anal. Calcd for $C_{15}H_{15}NO_2$: C, 74.67; H, 6.27; N, 5.81. Found: C, 74.45; H, 6.22; N, 5.77.

2-(2-Pyridinyl)-1-[2-(trifluoromethyl)phenyl]-1-propanone (2g):

Red oil but slowly solidified. Yield: 7.12 g (85%). Bp 138 °C at 3 mbar. Mp 72-74 °C. ^{1}H NMR (300 MHz, $CDCl_3$, 298 K): δ 1.56 (d, J = 7.2 Hz, 3H, CH_3), 1.66 (s, 3H, CH_3), 4.56-4.63 (m, 1H, CH), 7.03-7.07 (m, 2H, ArH), 7.09-7.13 (m, 2H, ArH), 7.13-7.55 (m, 3H, ArH), 7.58 (d, J = 8.1 Hz, 2H, ArH), 7.70 (t, J = 8.1 Hz, 2H, ArH), 8.31 (d, J = 4.8 Hz, 1H, ArH), 8.47 (d, J = 4.5 Hz, 1H, ArH), 16.32 (s, 1H, OH). ^{13}C NMR (150 MHz, $CDCl_3$, 298 K): δ 17.6, 19.9, 57.0, 103.3, 121.6, 122.0, 124.8, 125.6, 127.4, 127.8, 129.1, 129.5, 130.9, 131.3, 132.9, 133.5, 134.6, 134.9, 140.5, 146.9, 152.3, 162.6, 164.1 (C-OH), 206.3 (C=O). v_{max} (KBr): 3436 (OH), 2936, 1643

(C=O), 1603 (C=N), 1553 (C=N), 1488, 1316, 1177, 1005, 931, 792, 768 cm^{-1}. Anal. Calcd for $C_{15}H_{12}F_3NO$: C, 64.51; H, 4.33; N, 5.02. Found: C, 64.65; H, 4.38; N, 4.96.

1-(2-Quinolinyl)-2-propanone (3a):

Yellow powder. Yield: 3.44 g (62%). NMR spectra data is consistent with literature values.[2] v_{max} (KBr): 3354 (OH), 2912, 2855, 1635 (C=O), 1586 (C=N), 1563 (C=N), 1455, 1414, 1357, 1217, 1177, 1152, 940, 833, 726 cm^{-1}.

3,3-Dimethyl-1-(2-quinolinyl)-2-butanone (3b):

This was recrystallized from (CH_2Cl_2/Hexane=1/1) then purified by chromatography (petroleum ether/ethyl acetate=8/1) to afford a yellow powder. Yield: 4.70 g (69%). Mp 71-72 °C. ^{1}H NMR (300 MHz, $CDCl_3$, 298 K): δ 1.24 (s, 9H, CH_3), 5.51 (s, 1H, CH), 6.72 (d, *J* = 9.0 Hz, 1H, ArH), 7.21 (t, *J* = 7.5 Hz, 1H, ArH), 7.37 (d, *J* = 8.1 Hz, 2H, ArH), 7.47 (t, *J* = 7.5 Hz, 1H, ArH), 7.56 (d, *J* = 9.0 Hz, 1H, ArH), 15.28 (s, lH, NH) (enaminone-form). ^{13}C NMR (150 MHz, $CDCl_3$, 298 K): δ 28.1, 40.7, 88.1, 117.9, 122.4, 123.0, 123.2, 127.5, 130.7, 135.6, 137.9, 153.8, 200.5 (C=O) (enaminone-form). δ 26.4, 44.9, 47.2, 122.3, 126.2, 126.9, 127.6, 129.0, 129.4, 136.1, 147.9, 156.2, 212.4 (C=O) (ketone-form). v_{max} (KBr): 3421 (NH), 3044, 2962, 1635 (C=O), 1578(C=N), 1553 (C=N), 1471, 1406, 1357, 1210, 1136, 883, 808, 743 cm^{-1}. Anal. Calcd for $C_{15}H_{17}NO$: C, 79.26; H, 7.54; N, 6.16. Found: C, 79.02; H, 7.66; N, 6.08.

1-(2-Methylphenyl)-2-(2-quinolinyl)-ethanone (3d):

Yellow powder. Yield: 6.81 g (87%). Mp 140-141°C. ^{1}H NMR (300 MHz, $CDCl_3$, 298 K): δ 2.46 (s, 3H, $ArCH_3$), 5.58 (s, 1H, CH), 6.72 (d, J = 9.3 Hz, 1H, ArH),

7.16-7.20 (m, 4H, ArH), 7.45 (d, J = 7.2 Hz, 4H, ArH), 7.56 (d, J = 9.0 Hz, 1H, ArH), 15.34 (s, lH, NH) (enaminone-form).^{13}C NMR (150 MHz, $CDCl_3$, 298 K): δ 20.3, 93.8, 118.1, 122.1, 123.2, 123.6, 125.4, 127.6, 128.8, 130.8, 130.9, 135.7, 136.1, 137.7, 141.6, 153.6, 189.3 (C=O) (enaminone-form) . v_{max} (KBr): 3428 (NH), 3060, 2962, 2929, 1635 (C=O), 1578 (C=N), 1546 (C=N), 1447, 1406, 1341, 1217, 1185, 1071, 980, 817, 751 cm^{-1}. Anal. Calcd for $C_{18}H_{15}NO$: C, 82.73; H, 5.79; N, 5.36. Found: C, 82.58; H, 5.87; N, 5.28.

1-(4-Methylphenyl)-2-(2-quinolinyl)-ethanone (3e)：

Yellow powder. Yield: 6.97 g (89%). Mp 173-175 °C. ^{1}H NMR (300 MHz, $CDCl_3$, 298 K): δ 2.41 (s, 3H, $ArCH_3$), 6.05 (s, 1H, CH), 6.86 (d, J = 6.9Hz, 1H, ArH), 7.25 (d, J = 7.2 Hz, 3H, ArH), 7.44-7.55 (m, 3H, ArH), 7.64 (d, J = 9.3 Hz, 1H, ArH), 7.87(d, J = 7.8 Hz, 2H, ArH), 15.65 (s, lH, NH) (enaminone-form). ^{13}C NMR (75 MHz, $CDCl_3$, 298 K): δ 21.6, 89.7, 118.1, 122.5, 123.3, 123.7, 126.8, 127.7, 129.1, 129.6, 131.1, 136.1, 137.2, 137.9, 140.9, 154.1, 184.5 (C=O) (enaminone-form). v_{max}(KBr): 3411 (NH), 3051, 2929, 1627 (C=O), 1578 (C=N), 1546 (C=N), 1455, 1414, 1332, 1185, 1136, 964, 817,735 cm^{-1}. Anal. Calcd for $C_{18}H_{15}NO$: C, 82.73; H, 5.79; N, 5.36. Found: C, 82.86; H, 5.64; N, 5.38.

1-(4-Methoxyphenyl)-2-(2-quinolinyl)-ethanone (3f)：

Yellow powder. Yield: 7.60 g (91%). Mp 156-157 °C. ^{1}H NMR (300 MHz, $CDCl_3$, 298 K): δ 3.86 (s, 3H, OCH_3), 6.02 (s, 1H, CH), 6.84 (d, J = 9.3 Hz, 1H, ArH), 6.96 (d, J = 8.1 Hz, 2H, ArH), 7.20-7.26 (m, 2H, ArH), 7.42-7.61 (m, 4H, ArH), 7.95 (d, J = 9.0 Hz, 1H, ArH), 15.54 (s, lH, NH) (enaminone-form). ^{13}C NMR (75 MHz, $CDCl_3$,

298 K): δ 55.4, 89.2, 113.6, 117.8, 122.5, 123.5, 127.6, 128.5, 131.0, 132.7, 135.9, 137.8, 153.8, 161.7, 169.6, 184.2 (C=O) (enaminone-form). v_{max} (KBr): 3420 (NH), 3011, 2978, 2929, 1635 (C=O), 1594 (C=N), 1546 (C=N), 1455, 1420, 1325, 1250, 1168, 1022, 956, 817,743 cm^{-1}. Anal. Calcd for $C_{18}H_{15}NO_2$: C, 77.96; H, 5.45; N, 5.05. Found: C, 77.82; H, 5.38; N, 4.98.

X-ray crystallography:

X-ray diffraction data were collected on a Bruker D8 Venture CCD diffractometer using graphite-monochromated Mo Kα radiation (λ = 0.71073 Å). The structures were solved by direct methods [15]. All non-H atoms were refined anisotropically and the H atoms were included in calculated positions [15]. CCDC 1437358 (**1e**), 1437359 (**2e**) and 1411757 (**3d**) contains the supplementary crystallographic data which can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif. Crystallographic data for compounds **1e**, **2e** and **3d** are summarized in Table 5.

Table 5. Details of the X-ray structure determinations of compounds **1e, 2e** and **3d**

Compound	**1e**	**2e**	**3d**
Formula	$C_{14}H_{13}NO$	$C_{15}H_{15}NO$	$C_{18}H_{15}NO$
Formula weight	211.25	225.28	261.31
Crystal system	Orthorhombic	Orthorhombic	Monoclinic
Space group	$P2_12_12_1$	$P2_12_12_1$	$P2_1/c$
Colour of crystal	Yellow	Yellow	Yellow
a(Å)	7.4849(3)	6.8411(4)	7.6693(3)
b(Å)	11.7102(5)	10.6073(7)	14.5236(5)
c(Å)	25.6784(11)	17.5834(11)	12.2223(4)
α(°)	90	90	90
β(°)	90	90	92.0500(10)
γ(°)	90	90	90
V(Å^3)	2250.70(16)	1275.95(14)	1360.52(8)
Temperature (K)	200(2)	282(2)	296(2)
Z	8	4	4
D(gcm^{-3})	1.247	1.173	1.276
Crystal size (mm)	0.30×0.18×0.15	0.30×0.25×0.18	0.48×0.40×0.28
μ (mm^{-1})	0.079	0.073	0.079

θ range (°)	2.83-25.04	3.01-25.05	2.18-25.05
Reflections collected	17446	9682	7684
Number of parameters	293	157	183
F(000)	896	480	552
Goodness-of-fit on F^2	1.037	1.067	1.069
Final R indices [$I>2\sigma(I)$]			
R_1	R_1 = 0.0464	R_1 = 0.0322	R_1 = 0.0352
wR_2	wR_2 = 0.0958	wR_2 = 0.0707	wR_2 = 0.0949
R indices (all data)			
R_1	R_1 = 0.0768	R_1 = 0.0411	R_1 = 0.0407
wR_2	wR_2 = 0.1085	wR_2 = 0.0762	wR_2 = 0.1001

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Highlights

An efficient insertion reaction of pyridyl-/quinolyl-lithium with nitriles for preparing pyridyl-/quinolyl-ketone compounds was reported.

The tautomeric equilibria were affected by the substituent in the molecule.

A useful way to determine the structures of β-pyridyl-/quinolyl-enol, -ketone, -enaminone tautomers have been described.