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Novel one-pot synthesis of (4 or 5)-aryl-2-aryloyl-(1*H*)-imidazoles in water and tauto-isomerization study using NMR

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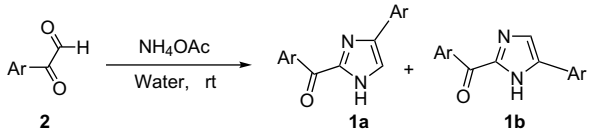
ABSTRACT

A simple and green route to synthesis of (4 or 5)-aryl-2-aryloyl-(1*H*)-imidazoles is described. Two isomers can tautomerize to each other by the heat absorption. The tauto-isomerization process was studied by NMR technique. Acidity and stability of products were studied using B3LYP method.

1. Introduction

As an important member of the five-membered ring heterocycles, the imidazole moiety is present in a wide range of naturally occurring molecules.[1] It is a common scaffold in highly significant biomolecules, including biotin, the essential amino acid histidine, histamine, and the pilocarpine alkaloids.[2] Imidazoles also have an ability to behave as ligands in metalloenzymes and non-natural metal complexes.[3] The use of imidazoles and their derivatives in chemical processes, especially in pharmaceuticals, is becoming increasingly important, because of the possibility of hydrogen bond formation.[4] Compounds with an imidazole moiety have many pharmaceutical activities, several of which have been incorporated in marketed drugs such as cimetidine and losartan.[5] The biological importance of the imidazole ring system has made it a common structure in numerous synthetic compounds, such as fungicides,[6] herbicides,[6] plant growth regulators[7] and therapeutic agents.[8] Recently, advances in green chemistry and organometallic chemistry have extended the boundary of imidazoles to the synthesis and application of a large class of imidazoles such as ionic liquid and imidazole[9] related *N*-heterocyclic carbenes.[10] Due to their wide range of biological, industrial and synthetic applications, these compounds have recently received a great deal of attention. There are several methods reported in the literature for the synthesis of imidazoles, such as hetero-cope rearrangement,[11] four component condensation of aryl glyoxals, primary amines, carboxylic acids and isocyanides on Wang resin,[12] reaction of *N*-(2-oxo)amides with ammonium trifluroacetate,[13] 1,2-aminoalcohols in the presence of PCl_5,[14] diketones, aldehydes, amine and ammonium acetate[15]; from α-aminonitriles,[16] Palladium-catalysed[17] cyclisation of o-pentafluorobenzoylamidoximes,[18] from keto-oxime, aldehydes and ammonium acetate.[19] To the best of our knowledge, there are no reports in the literature on the formation of (4 or 5)-aryl-2-aryloyl-(1*H*)-imidazole derivatives via condensation of arylglyoxals with ammonium acetate. In this paper, we describe the one-pot reaction between arylglyoxals **2** and excess amount of ammonium acetate in water to give (4 or 5)-aryl-2-aryloyl-(1*H*)-imidazoles (**1a** or **1b**) (Scheme 1).



Scheme 1. Synthesis of (4 or 5)-aryl-2-aryloyl-(1*H*)-imidazole.

2. Results and discussion

During our latest work describing the synthesis of new pyrole derivatives,[20] we found that in some cases 1,3-dicarbonyl compounds did not react and were recovered. Therefore the reactions were repeated without using 1,3-dicarbonyl compounds to give new compounds which were characterized as imidazole derivatives. For example, the reaction of 4-methoxyphenylglyoxal in the presence of an excess amount of ammonium acetate in ethanol at room temperature was carried out. ^{1}H NMR gave two signals for NH with different intensities (13.4 ppm with high intensity and 13.5 ppm with low intensity), two singlet signals for the CH of imidazole ring (7.90 ppm with high intensity and 7.64 ppm with low intensity), two different signals for phenyl groups, and two different signals for both methyl groups (Figs. 1a–c in Supplementary data). These results show that there are two isomeric 2-aryloylimidazoles. The signal for NH of 4-aryl-2-aryloyl-(1*H*)-imidazole (isomer **1a**) has a lower chemical shift (ppm) than 5-aryl-2-aryloyl-(1*H*)-imidazole (isomer **1b**). The **a**/**b** ratio was determined by ^{1}H NMR, using the intensities of the NH of the imidazole rings of two isomers. Two isomers (**a** and **b**) can be generated via a [1,5]-hydrogen shift as shown in Scheme 2. According

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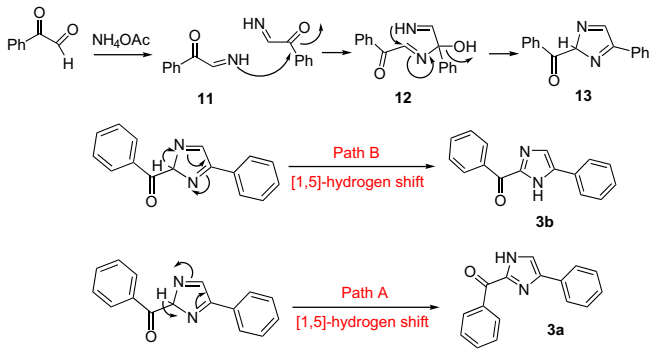


Scheme 2. Plausible mechanism for imidazole synthesis.

the path A and B in which **a** and **b** isomers can be generated respectively. In path A hydrogen shift begins through No.1 nitrogen atom while in path B it begins through No.3 nitrogen atom. To examine the solvent effect on [1,5]-hydrogen shift regioselectivity (**a**/**b** ratio), different solvents were used. Results are summarized in Table 1.

Table 1
Solvent effect on yield (%) and **a**/**b** ratio of products

Solvent	Yield (%) for compd (**3**), (**4**), (**6**)	**a**/**b** ratio for compd (**3**), (**4**), (**6**)
H_2O	69, 59, 71	3.70, 5.90, 4.80
EtOH	71, 87, 83	3.90, 6.00, 4.30
EtOAC	56, 68, 80	1.10, 1.85, 4.16
CH_3CN	48, 63, 62	1.00, 6.25, 2.87
$CHCl_3$	65, 77, 83	1.13, 2.00, 2.93
DMSO	67, 65, 84	1.94, 6.60, 2.92

Based on the data from Table 1 and the friendly environmental nature of water, it was chosen as solvent for these reactions. From experimental and theoretical data we found that aryl groups including electron withdrawing substituents show higher [1,5]-hydrogen shift regioselectivity. The results are summarized in Table 2.

The proposed mechanism involves an attack of (in situ) generated aldimine **11** onto another aldimine molecule with the elimination of one H_2O molecule from **12** to give compound **13** (Scheme 2).

According to paths A and B with a [1,5]-hydrogen shift, **3a** and **3b** can be generated respectively. we tried to isolate these two isomers (**a** and **b**) but since the isomers are converting rapidly to each other therefore we could not isolate them. For the determination of product percentage and spectral data assignment, theoretical methods were used which optimized stabilization energy for two isomers using the B3LYP method on the basis set of (6-311++G d,p) and GAMESS program package.[21] The equilibrium constant from theoretical data was calculate using Eq. 1. Data from this calculation for compounds **3**, **4**, **5**, **6** and **8** are shown in Table 3.

$$\begin{aligned} \Delta G &= G_{\mathbf{b}} - G_{\mathbf{a}} \\ \Delta G &= -RT \ln K \\ K &= [\mathbf{b}]/[\mathbf{a}] \\ K &= e^{-\Delta G/RT} \end{aligned} \qquad (1)$$

The position of the NH signal of imidazole ring in ^{1}H NMR spectra verified our initial suposition that intra molecular hydrogen bonding may be formed between the NH and the carbonyl group of the aryloyl substitution. The obtained data from IR spectroscopy in KBr and CCl_4 showed no differences in the position of NH peaks. Comparison of the ^{1}H NMR spectra in methanol proved hydrogen bonding with imidazole derivatives which was not observed in acetone. This intra molecular hydrogen bonding limited the free rotation of carbon-carbon single bond within the carbonyl group and imidazole ring, that led to existence of two isomeric 2-aryloyl imidazole structures. Two isomers can be tautomerized to each other with [1,3]-hydrogen shifts which was investigated by NMR method. We found that these two isomers can be interchanged with thermal energy. We obtained thermodynamic data for this interchange process with NMR technique.

Variable-temperature ^{1}H NMR spectroscopy was used to investigate the barrier of H–N tauto-isomerization in the case of compound **8** (Scheme 3).

Table 2
Synthesis of (4 or 5)-aryl-2-aryloyl-(1*H*)-imidazoles in water

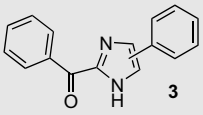
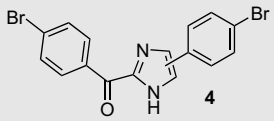
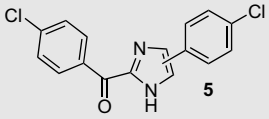
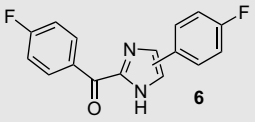
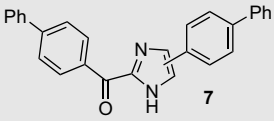
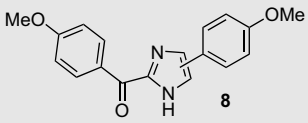
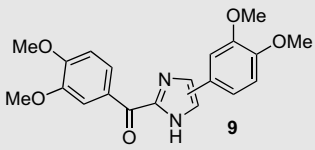
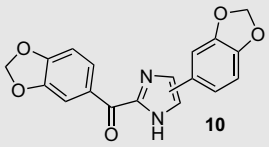
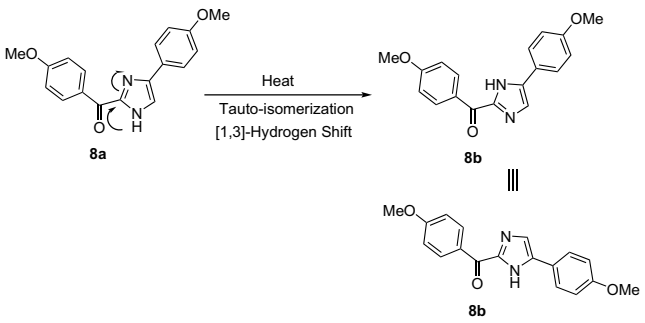
Entry	Imidazole	Yield (%)	**a**/**b** Ratio
1	 **3**	69	3.7
2	 **4**	59	5.6
3	 **5**	75	6.5
4	 **6**	55	4.8
5	 **7**	48	7.5
6	 **8**	79	3.0
7	 **9**	86	2.8
8	 **10**	76	2.9

Table 3
Calculated optimized stabilization energy and equilibrium constant for compounds **3**, **4**, **5**, **6** and **8** [$\Delta E = E_{\mathbf{a}} - E_{\mathbf{b}}$ (kcal)]

Compd	$E_{\mathbf{a}}$ (kcal)	$E_{\mathbf{b}}$ (kcal)	ΔE(kcal)	K
3	−503,188.2520	−503,187.8446	−0.4074	0.0594
4	−3,733,035.6128	−3,733,034.7928	−0.8199	0.2506
5	−1,080,024.2923	−1,080,023.5374	−0.7549	0.0256
6	−627,772.8164	−627,772.0698	−0.7466	0.3206
8	−646,960.6730	−646,960.5844	−0.0886	0.5659



Scheme 3.

^{1}H NMR study of compound **8** in DMSO solvent showed four distinct singlet signals for the hydrogens of the two methyl groups at 298 K. ^{1}H NMR study of these protons shows two distinct singlet signals at 376 K. Figure 1 shows the temperature-dependent ^{1}H NMR spectra of these compounds exhibiting exchange broadening of the two inner short peaks. Four separate signals can be observed for hydrogens of two methyl groups below 320 K, while above 376 K, only two signals can be observed.

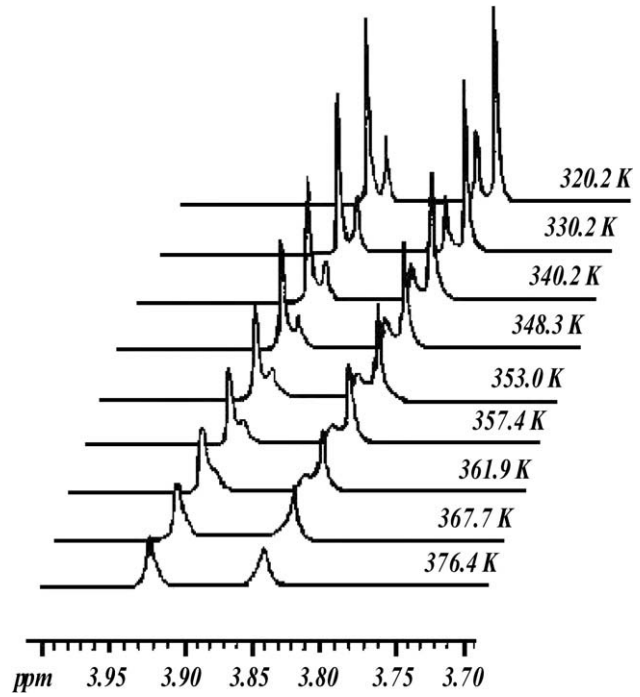


Figure. 1. Temperature-dependent 500 MHz ^{1}H NMR spectra of compd **8**. Only protons attached to methyl groups represented.

Table 4 lists the experimental rate constants characterizing tauto-isomerization of compound **8**.

Eyring and Arrhenius plot from the rate constants extracted using total line-shape analysis of compound **8**, is presented in Figures 2 and 3 respectively.

Table 4
Experimental rate constants

T (K)	k	$1/T$	k/T	$\ln(k/T)$	$\ln(k)$
340.2	1.90	0.002939	0.005585	−5.18768	0.64185
348.3	3.50	0.002871	0.010049	−4.60030	1.25276
353.0	5.10	0.002833	0.014448	−4.23723	1.62924
357.4	7.10	0.002798	0.019866	−3.91876	1.96009
361.9	10.9	0.002763	0.030119	−3.50261	2.38876
367.7	16.0	0.002720	0.043514	−3.13468	2.77258
375.4	24.1	0.002664	0.064198	−2.74578	3.18221

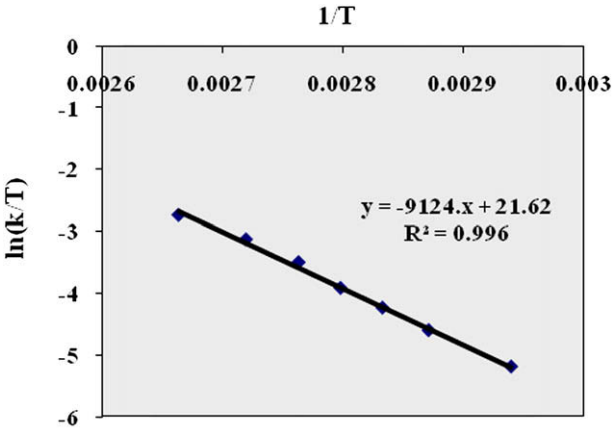


Figure 2. Eyring plot for tauto-isomerization study of compd **8**.

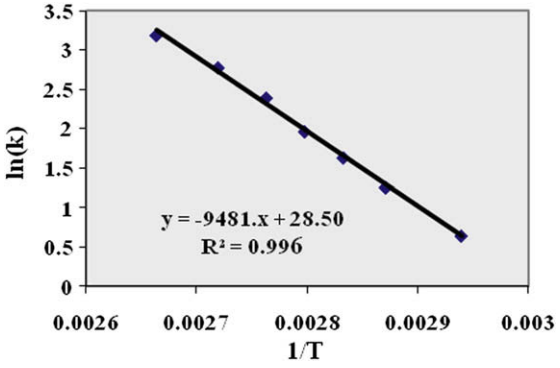


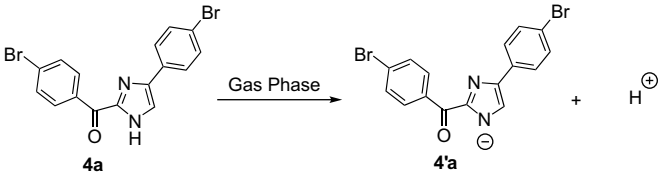
Figure 3. Arrhenius plot for tauto-isomerization study of compd **8**.

Table 5 shows the values of the experimental kinetic parameters for compound **8** obtained from its rate constants.

The B3LYP method with the basis set of (6-311++G d,p) for calculating acidity ($\Delta H_{acidity}$) of these compounds in the gas and solution phase with the use of compound **4** and an imaginary reaction (Scheme 4) was used.

Table 5
Kinetic experimental parameters for compd **8**

Kinetic parameter	Experimental value
$\Delta G^{\#}_{298}$ (kJ/mol)	81.13
$\Delta H^{\#}_{298}$ (kJ/mol)	75.86
$\Delta S^{\#}_{298}$ (J/mol)	−17.72
$\Delta E^{\#}_{298}$ (kJ/mol)	78.83



Scheme 4.

Based on this imaginary reaction the acidity of this compound was calculated using Eq. 2:

$$\left(\Delta H_{acidity}\right) = \Delta U + \Delta(PV) = U[\mathbf{4'a}] + U\left[\mathbf{H}^+\right] - U[\mathbf{4a}] + 2.5RT \quad (2)$$

In Eq. 2, U is the calculated absolute energy and $2.5RT$ is the kinetic energy contribution from H^+ at 298 K. $U[H^+]$=0 because H^+ has no

electron. This contribution is zero at 0 K. In progress for comparison of acidity in gas and solution phase we calculate acidity of compound **4** in water using PCM model. The resulets are given in Table 6. From these data the acidity in water phase is higher than gas phase. We think that this difference resulted from water solvation which is higher in the case of ionic than nutral parts and absend in gas phase.

Table 6
Data for acidity of compd **4**

Parameter	Value (kcal/mol)
$\Delta H^{*}=\Delta H_{(acidity)}$ in gas phase	326.16
$\Delta H^{**}=\Delta H_{(acidity)}$ in water phase	302.73
$\Delta H^{***}=\Delta H^{*}-\Delta H^{**}$	23.43

Finally, Figure 4 shows the optimized geometry for the ground state of compounds **8a** (lower) and **8b** (upper) by B3LYP method in (6-311++G d,p) basis set.

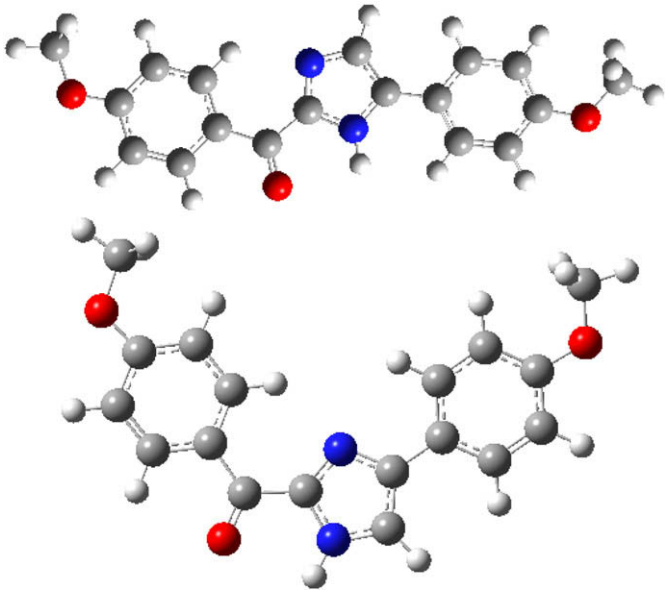


Figure 4. Optimized geometry of compounds **8a** and **8b**.

In conclusion, we report an efficient, novel, and entirely green procedure for the synthesis of new imidazole derivatives in water without using any catalyst at room temperature. In addition, a very easy workup, short reaction time and obtaining pure products directly by filtration, washing the filtrate with water and crystalization from ethanol are some advantages of this new method.

3. Experimental section

3.1. General procedure for synthesis of (4 or 5)-aryl-2-aryloyl-(1*H*)-Imidazole derivatives

To arylglyoxal[22] compound (1 mmol) in water (10 ml), was added ammonium acetate (5 mmol), successively at room temperature (20–25 °C) and stirred at the same temperature for the 30–45 min. After appropriate time the reaction mixture was concentrated, then the obtained solid was filtrated, washed with water (3×15 mL), and the crude was purified by crystallization from ethanol.

3.2. Sample preparation for tauto-isomerization study

Solution-phase NMR samples for ^{1}H NMR was prepared with 0.1 M concentration. Deuteriated solvent was obtained from Merck. DMSO-d_6 were 99.5 atoms% D and contained 1% of TMS.

3.3. NMR measurements for tauto-isomerization study

^{1}H NMR measurements were performed on a Bruker AMX500 using 5 mm variable temperatures (VT) probe with proton observation at 500.13 MHz. All measurements were made on spinning samples in the locked mode. In all measurements, acquisition time was 1.58 s/scan, (with a) pulse length of 9.65 ls, and pulse delay time of 10 s. Typically 16 scans were collected at each temperature and stored in 32k of memory. Sweep width was 10,330.58 Hz for all spectra, giving a digital resolution of 0.316 Hz/point. The resulting solution spectra for all compounds had typical S/N ratios greater than 500:1. The spectra line-width parameter, T2nat, was determined for each spectrum by measuring the line width of the TMS. Probe temperatures (±0.5) were measured with a calibrated, digital thermocouple.

3.4. Computational methods

All computations were carried out with the GAMESS program package. The energies and geometries were calculated with B3LYP method and 6-311++G(d,p) basis set. Harmonic vibrational frequencies were computed to confirm an optimized geometry corresponds to local minimum that has only real frequencies. Rate constants were calculated for exchange spectra using the MEXICO[23] program, which uses an iterative nonlinear least squares regression analysis to obtain the best fit of the experimental spectrum.

4. Characterization of compounds 3–10

4.1. Phenyl-(5-phenyl-1*H*-imidazol-2-yl)ketone (3a) and phenyl-(4-phenyl-1*H*-imidazol-2-yl)ketone (3b)

A yellow solid, ^{1}H NMR (500 MHz, DMSO-d_6): δ 13.80 (0.25H, s, NH), 13.63 (1H, s, NH), 8.60 (2H, d, *J* 7.76 Hz), 8.47 (0.5H, d, *J* 7.7 Hz), 8.08 (1H, s), 7.97 (0.5H, d, *J* 7.95 Hz), 7.94 (2H, d, *J* 7.64 Hz), 7.79 (0.25H, s), 7.69 (1H, t, *J* 7.1 Hz), 7.66 (0.25H, t, *J* 7.6 Hz), 7.60 (2H, t, *J* 7.6 Hz), 7.57 (0.5H, t, *J* 8.1 Hz), 7.47 (0.5H, t, *J* 7.55 Hz), 7.42 (2H, t, *J* 7.7 Hz), 7.37 (0.25H, t, *J* 7.1 Hz), 7.28 (1H, t, *J* 7.3 Hz). ^{13}C NMR (125 MHz, DMSO-d_6): δ 181.6, 179.2, 146.6, 145.5, 143.7, 137.0, 136.8, 136.6, 134.5, 133.9, 133.7, 131.5, 131.4, 129.8, 129.5, 129.1, 129.0, 128.0, 126.5, 125.7, 119.5. IR (neat, cm^{-1}): 3270, 1621, 1454, 1280, 1164, 906, 771, 687. Anal. Calcd for $C_{16}H_{12}N_2O$: C, 77.40; H, 4.87; N, 11.28. Found: C, 77.39; H, 4.73; N, 11.17.

4.2. 4-Fluorophenyl-[5-(4-fluorophenyl)-1*H*-imidazol-2-yl]ketone (6a) and 4-fluorophenyl-[4-(4-fluorophenyl)-1*H*-imidazol-2-yl]ketone (6b)

A yellow solid, ^{1}H NMR (500 MHz, DMSO-d_6): δ 13.81 (0.2H, s, NH), 13.64 (1H, s, NH), 8.70 (2H, dd, *J* 5.89, 8.64 Hz), 8.58 (0.4H, dd, *J* 5.15, 8.07 Hz), 8.07 (1H, s), 8.01 (0.4H, dd, *J*=5.01, 8.16 Hz), 7.95 (2H, dd, *J* 5.74, 8.31 Hz), 7.76 (0.2H, s), 7.43 (2H, t, *J* 8.82 Hz), 7.39 (0.4H, t, *J* 8.83 Hz), 7.31 (0.4H, t, *J* 8.74 Hz), 7.25 (2H, t, *J* 8.8 Hz). ^{13}C NMR (125 MHz, DMSO-d_6): δ 179.9, 179.8, 166.9, 164.9, 163.3, 161.4, 145.3, 145.2, 142.8, 134.5, 134.5, 133.3, 131.0, 131.0, 128.7, 128.7, 127.6, 127.6, 119.4, 116.7, 116.4, 116.3, 116.2, 116.2. IR (neat, cm^{-1}): 3282, 3129, 3096, 1623, 1595, 1514, 1450, 1245, 1160, 906, 838, 774, 649. Anal. Calcd for $C_{16}H_{10}F_2N_2O$: C, 67.60; H, 3.55; N, 9.85. Found: C, 67.59; H, 3.68; N, 10.02.

4.3. 4-Chlorophenyl-[5-(4-chlorophenyl)-1*H*-imidazol-2-yl]ketone (5a) and 4-chlorophenyl-[4-(4-chlorophenyl)-1*H*-imidazol-2-yl]ketone (5b)

An orange solid, ^{1}H NMR (500 MHz, DMSO-d_6): δ 13.91 (0.15H, s, NH), 13.73 (1H, s, NH), 8.60 (2H, d, *J* 8.5 Hz), 8.50 (0.3H, d, *J* 8.2 Hz),

8.15 (1H, s), 7.99 (0.3H, d, *J* 8.7 Hz), 7.95 (2H, d, *J* 8.4 Hz), 7.84(0.15H, s), 7.68 (2H, d, *J* 8.5 Hz), 7.65 (0.3H, d, *J* 8.25 Hz), 7.54 (0.3H, d, *J* 7.55 Hz), 7.49 (2H, d, *J* 8.4 Hz). ^{13}C NMR (125 MHz, DMSO-d_6): δ 181.6, 179.7, 147.9, 146.3, 143.7, 137.0, 136.8, 136.6, 134.5, 133.9, 133.7, 131.5, 131.4, 129.8, 129.5, 129.1, 129.0, 128.0, 126.5, 125.7, 119.5. IR (neat, cm^{-1}): 3277, 3112, 3096, 1619, 1539, 1514, 1445, 1293, 1172, 1100, 1019, 906, 834, 770. Anal. Calcd for $C_{16}H_{10}Cl_2N_2O$: C, 60.59; H, 3.18; N, 8.83. Found: C, 60.58; H, 3.10; N, 8.61.

4.4. 4-Bromophenyl-[5-(4-bromophenyl)-1*H*-imidazol-2-yl]ketone (4a)and 4-bromophenyl-[4-(4-bromophenyl)-1*H*-imidazol-2-yl]ketone (4b)

A yellowish brown solid, ^{1}H NMR (500 MHz, DMSO-d_6): δ 13.91 (0.16H, s, NH), 13.73 (1H, s, NH), 8.51 (2H, d, *J* 8.4 Hz), 8.42 (0.32H, d, *J* 8.3 Hz), 8.16 (1H, s), 7.93 (0.32H, d, *J* 8.15 Hz), 7.89 (2H, d, *J* 8.35 Hz), 7.83 (2H, d, *J* 8.45 Hz), 7.80 (0.32H, d, *J* 8.4 Hz), 7.79 (0.16H, s), 7.67 (0.32H, d, *J* 8.05 Hz), 7.62 (2H, d, *J* 8.35 Hz). ^{13}C NMR (125 MHz, DMSO-d_6): δ 181.6, 179.7, 145.8, 144.3, 143.7, 137.0, 136.8, 136.6, 134.5, 133.9, 133.7, 131.5, 131.4, 129.8, 129.5, 129.1, 129.0, 128.0, 126.5, 125.7, 119.5. IR (neat, cm^{-1}): 3269, 3025, 1612, 1579, 1557, 1451, 1292, 1171, 1073, 1012, 901, 833, 767, 707, 644, 513. Anal. Calcd for $C_{16}H_{10}Br_2N_2O$: C, 47.32; H, 2.48; N, 6.90. Found: C, 47.30; H, 2.56; N, 6.82.

4.5. 4-Methoxyphenyl-[5-(4-methoxyphenyl)-1*H*-imidazol-2-yl]ketone (8a) and 4-methoxy phenyl-[4-(4-methoxyphenyl)-1*H*-imidazol-2-yl]ketone (8b)

A yellow solid, ^{1}H NMR (500 MHz, DMSO-d_6): δ 13.52 (0.37H, s, NH), 13.40 (1H, s, NH), 8.67 (2H, d, *J* 9 Hz), 8.54 (0.74H, d, *J* 8.9 Hz), 7.90 (1H, s), 7.89 (0.74H, d, *J* 8.16 Hz), 7.84 (2H, d, *J* 8.65 Hz), 7.64 (0.37H, s), 7.13 (2H, d, *J* 8.9 Hz), 7.09 (0.74H, d, *J* 8.85 Hz), 7.01 (0.74H, d, *J* 8.9 Hz), 6.99 (2H, d, *J* 8.75 Hz), 3.88 (3H, s), 3.87 (1.11H, s), 3.80 (1.11H, s), 3.78 (3H, s). ^{13}C NMR (125 MHz, DMSO-d_6): δ 179.9, 179.8, 164.1, 163.9, 161.0, 159.4, 146.4, 145.5, 143.5, 136.2, 133.9, 133.8, 129.7, 129.5, 128.5, 128.0, 127.3, 127.0, 122.1, 117.8, 115.2, 114.9, 114.5, 114.4, 56.4, 56.3, 56.0, 55.9. IR (neat, cm^{-1}): 3266, 1611, 1598, 1455, 1289, 1250, 1163, 1028, 905, 832, 774, 643. Anal. Calcd for $C_{18}H_{16}N_2O_3$: C, 70.12; H, 5.23; N, 9.09. Found: C, 70.12; H, 5.27; N, 8.91.

4.6. 3,4-Dimethoxyphenyl-[5-(3,4-dimethoxyphenyl)-1*H*-imidazol-2-yl]ketone (9a) and 3,4-dimethoxyphenyl-[4-(3,4-dimethoxyphenyl)-1*H*-imidazol-2-yl]ketone (9b)

A yellow solid, ^{1}H NMR (500 MHz, DMSO-d_6): δ 13.57 (0.35H, s, NH), 13.41 (1H, s, NH), 8.47 (1H, d, *J* 1.5 Hz), 8.38 (1.35H, m), 8.07 (0.35H, d, *J* 1.61 Hz), 7.97 (1H, s), 7.70 (0.35H, s), 7.62 (0.35H, s), 7.51 (1H, s), 7.48 (1.35H, m), 7.18 (1H, d, *J* 8.55 Hz), 7.14 (0.35H, d, *J* 8.59 Hz), 7.01 (1.35H, m), 3.91 (3H, s), 3.90 (3H, s), 3.88 (1.05H, s), 3.86 (1.05H, s), 3.85 (1.05H, s), 3.83 (3H, s), 3.79 (1.05H, s), 3.76 (3H, s). ^{13}C NMR (125 MHz, DMSO-d_6): δ 179.6, 179.4, 154.0 153.9, 149.9, 149.8, 149.0, 148.9, 145.5, 143.5, 129.6, 129.3, 128.7, 127.6, 126.6, 126.2, 119.1, 118.1, 117.9, 114.4, 113.8, 112.9, 111.8, 111.6, 110.2, 109.5, 56.61, 56.58, 56.43, 56.40, 56.30, 56.28, 56.17, 56.14. IR (neat, cm^{-1}): 3431, 2922, 1627, 1513, 1469, 1378, 1270, 1137, 1022, 853, 768, 608, 452. Anal. Calcd for $C_{20}H_{20}N_2O_5$: C, 65.21; H, 5.47; N, 7.60. Found: C, 65.20; H, 5.50; N, 7.57.

4.7. Benzo[*d*][1,3]dioxol-5-yl-[5-(benzo[*d*][1,3]dioxol-5-yl)-1*H*-imidazol-2-yl]ketone (10a)and benzo[*d*][1,3]dioxol-5-yl-[4-(benzo[*d*][1,3]dioxol-5-yl)-1*H*-imidazol-2-yl]ketone (10b)

A yellowish green solid, ^{1}H NMR (500 MHz, DMSO-d_6): δ 13.52. (0.3H, s, NH), 13.44 (1H, s, NH), 8.45 (1H, d, *J* 8.19 Hz), 8.28 (0.3H, d, *J* 8.13 Hz), 8.16 (1H, s), 8.01 (0.3H, s), 7.94 (1H, s), 7.68 (0.3H, s), 7.58 (0.3H, s), 7.48–7.44 (2.3H, m), 7.14 (1H, d, *J* 8.24 Hz), 7.10 (0.3H, d, *J* 8.22 Hz), 7.01–6.97 (1.3H, m), 6.18 (2H, s), 6.17 (0.6H, s), 6.07 (0.6H, s), 6.04 (2H, s). ^{13}C NMR (125 MHz, DMSO-d_6): δ 182.2, 179.2, 152.4, 148.53, 148.25, 148.1, 147.2, 145.2, 143.4, 130.9, 128.8, 128.4, 128.1, 120.6, 119.2, 118.4, 110.7, 109.6, 109.4, 108.9, 108.7, 106.9, 106.2, 102.8, 102.1, 101.8. IR (neat, cm^{-1}): 3444, 3285, 1622, 1500, 1460, 1245, 1099, 1039, 935, 812, 770, 457. Anal. Calcd for $C_{18}H_{12}N_2O_5$: C, 64.29; H, 3.60; N, 8.33. Found: C, 64.10; H, 3.65; N, 8.40.

4.8. Biphenyl-4-yl-[5-(biphenyl-4-yl)-1*H*-imidazol-2-yl]ketone (11a) and biphenyl-4-yl-[4-(biphenyl-4-yl)-1*H*-imidazol-2-yl]ketone (11b)

A yellow solid, ^{1}H NMR (500 MHz, DMSO-d_6): δ 13.81 (0.3H, s, NH), 13.69 (1H, s, NH), 8.74 (2H, d, *J* 7.95 Hz), 8.60 (0.6H, d, *J* 7.95 Hz), 8.16 (1H, s), 8.08 (0.6H, d, *J* 7.2 Hz), 8.05 (2H, d, *J* 7.8 Hz), 7.94 (2.3H, m), 7.88 (0.6H, d, *J* 7.9 Hz), 7.82 (2H, d, *J* 7.55 Hz), 7.79 (0.6H, d, *J* 6.35 Hz), 7.74 (5.2H, m), 7.52 (3H, m), 7.48 (3H, m), 7.45 (0.9H, m), 7.37 (0.9H, m). ^{13}C NMR (125 MHz, DMSO-d_6): δ 180.9, 179.8, 145.7, 145.3, 144.5, 143.4, 140.6, 139.8, 139.6, 135.6, 133.7, 133.0, 132.3, 132.2, 130.0, 129.9, 129.9, 129.9, 129.8, 129.8, 129.8, 129.7, 129.3, 129.2, 129.1, 128.2, 127.9, 127.9, 127.8, 127.7, 127.7, 127.4, 127.3, 127.3, 126.3, 119.8, 119.7. IR (neat, cm^{-1}): 3270, 3055, 3032, 1615, 1453, 1286, 1169, 906, 839, 755. Anal. Calcd for $C_{28}H_{20}N_2O$: C, 83.98; H, 5.03; N, 7.00. Found: C, 83.99; H, 5.00; N, 6.00.

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Supplementary data

Supplementary data associated with this article can be found in the online version, at doi:10.1016/j.tet.2009.06.082.

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