A convenient access to 1-substituted-2-azinyl-1-ethanones *via* acylation of alkylated azines with *N*-acylbenzotriazoles

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Abstract
Reactions of alkylazines **9a–f** (2-methylpyridine, 2-benzylpyridine, 4-benzylpyridine, 2-methylquinoline, 4-methylquinoline or 4-methylpyrimidine) with readily available *N*-acylbenzotriazoles **8a–j** produced 1-substituted-2-azinyl-1-ethanones **10a–p** in 50–95% yields.

Keywords: *N*-Acylbenzotriazoles, alkylated azines, 1-substituted-2-azinyl-1-ethanones

Introduction

1,2-Disubstituted-1-ethanones (X-CH_2CO-Y) play an important role in organic synthesis.[1] Among such derivatives, 1-substituted-2-azin-2-yl-1-ethanones (Het-CH_2COY) find important and widespread uses as ligands to chelate transition metals[2] and medically important gallium ^{66}Ga, ^{67}Ga, and ^{68}Ga radioisotopes.[3] Compounds of this class are also useful as synthetic templates in the preparation of chiral building blocks[4] for a wide variety of alkaloids, e.g., hydrangea **1**,[5] lamellarins **2**,[6] sedamines **3**[7] and lobelines **4** and **5**[8] as well as steroid-like compounds such as azasteroids **6**.[9] These systems have long been recognized as bioactive natural products.[10] For example, early findings on the biological properties of lobelines (also known as Indian tobacco) support their potential ability to exhibit agonist activity[8] and enhance latent inhibition[11] at nicotinic receptors, stimulate autonomic ganglia,[12] and improve memory.[10a]

Moreover, certain 1-substituted-2-azinyl-1-ethanone derivatives exhibit biological activities as potential hypocholesteremic agents having minimal estrogenic activity[13] and others are valuable synthons in the development of various pharmaceutically important molecules[1a,14] and in the preparation of chiral nematic materials.[15]

Previous protocols for syntheses of 1-substituted-2-azinyl-1-ethanones (Scheme 1) include: (i) from 1-substituted-2-azinylethynes by hydration in 2N H_2SO_4 in the presence of $HgCl_2$;[16] (ii) reactions of organometallic reagents with aldehyde followed by Swern oxidation;[17] (iii) radical

nucleophilic substitution reactions ($S_{RN}1$) of haloazines with ketone enolates;[18] (iv) reactions of α-haloazinium salts (pseudo-Vilsmeier reagents) with *N,N*-disubstituted enamines followed by acidic hydrolysis and dequaternization;[19] and (v) acylation of methylated azines.

Approaches of type (v) are the most commonly used and include treatment of methlyazines with carbonitriles[20] or with activated derivatives of carboxylic acids, especially acid chlorides,[21] esters,[13,22] and amides.[23]

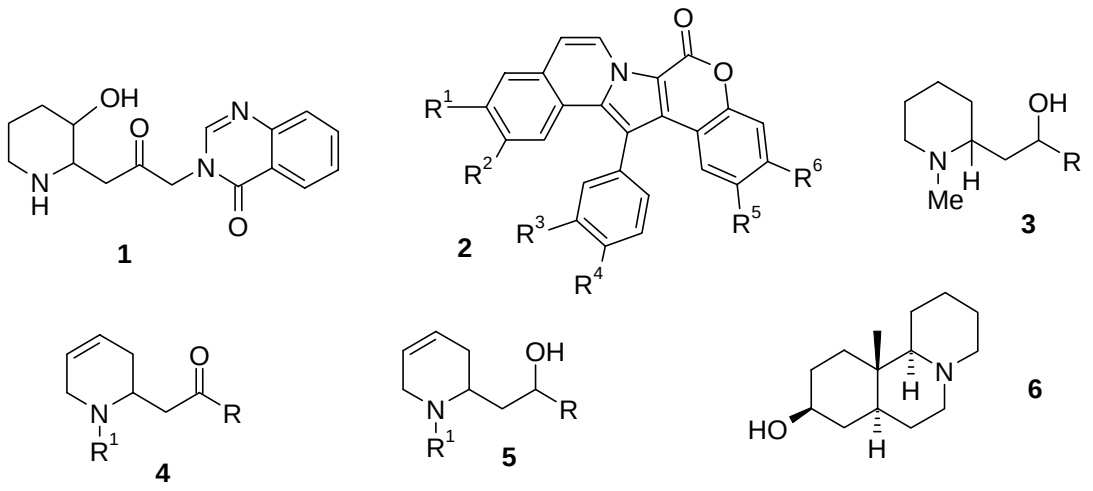


Figure 1

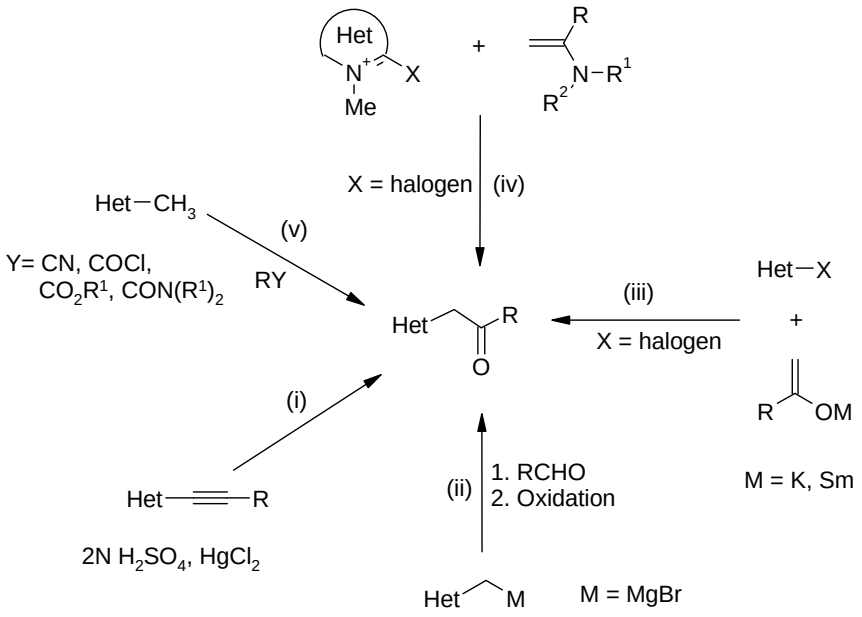
Claisen-type condensation methods in refs[22a–c] require either a 2:1 molar ratio of metallated alkylazine:acylating ester or 2 molar equivalents of base that might cause ester self-condensation prior to the lateral acylation. Among the conventional methods available for the synthesis of 1-substituted-2-azinyl-1-ethanones, approaches based on the use of amides as acylating reagents are scarce.

We have reported earlier the use of *N*-acylbenzotriazoles in the syntheses of amides,[24] esters,[25] β-keto sulfones[26] and β-keto nitriles.[27] In view of our previous results, we now describe a further application of *N*-acylbenzotriazoles in a general and convenient access to a variety of 1-substituted-2-azinyl-1-ethanones in satisfactory to excellent yields by the acylation of alkylated azines.

Results and Discussion

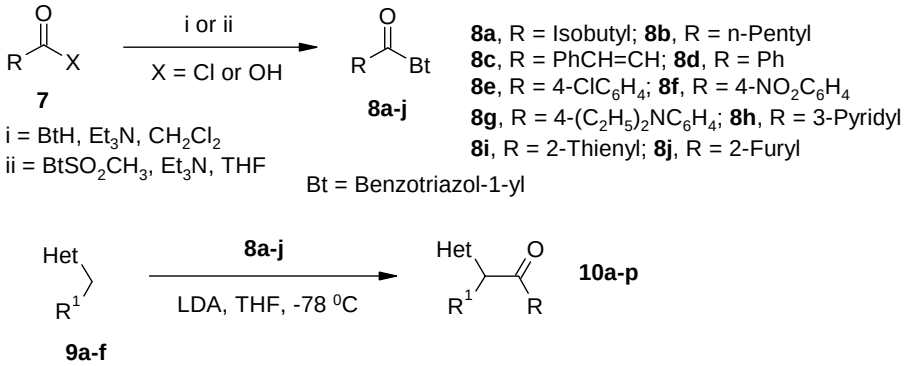
The starting *N*-acylbenzotriazoles **8a–f** with alkyl, alkenyl or aryl substituents (R = isobutyl, *n*-butyl, cinnamyl, phenyl, 4-chlorophenyl or 4-nitrophenyl) were prepared by stirring acid chlorides in CH_2Cl_2 with benzotriazole in the presence of Et_3N at room temperature[28] while **8g–j** (R = 4-diethylaminophenyl, 3-pyridyl, 2-thienyl or 2-furyl) were readily prepared by refluxing

the corresponding carboxylic acids in THF with 1-(methansulfonyl)-1*H*-benzotriazole in the presence of Et_3N.[24a]



Scheme 1

The acylation reactions were accomplished by treatment of alkylazines **9a–f** (1.0 equivalent) in THF at -78 ^oC with LDA (2.0 equivalents), itself prepared *in situ* from *n*-butyllithium and diisopropylamine), followed by the addition, at -78 ^oC, of a THF solution of the appropriate *N*-acylbenzotriazole **8a–j** (1.0 equivalent). The solution was allowed to warm up to room temperature overnight. After aqueous workup, 1-substituted-2-azinyl-1-ethanones **10a–p** were isolated as the only products in good to excellent yields (Scheme 2, Table 1). This approach provided known compounds **10a,d,i**[22a] and **10b**[29] in yields comparable with those reported in the literature and dramatically improved the previous yields of **10f**, **10g**, **10h**, and **10j** from 12%,[13] 41%,[22d] 58%[22a] and 50.3%[22b] to 91%, 95%, 84% and 72% yield, respectively.



For designation of R, $R^1$and Het in **10** see Table 1

Scheme 2

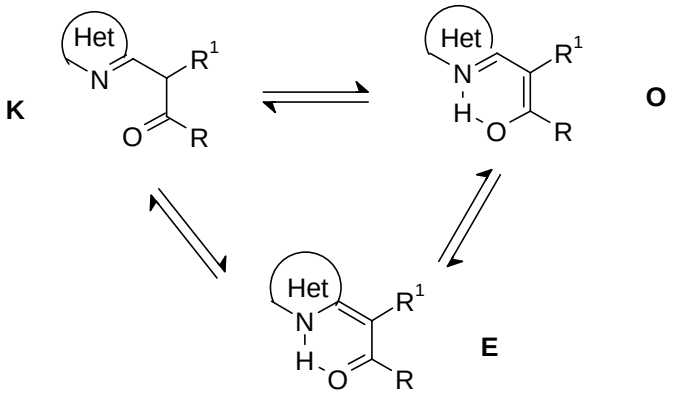
Table 1. Preparation of 1-Substituted–2-azinyl-1-ethanones **10a–p**

Entry	Het	R of RCOBt **8**	R^1 of $HetCH_2R^1$ **9**	Yield (%)[a] (keto +enol)	Keto/ enol (%)[b]
10a	Pyrid-2-yl	$(CH_3)_2CHCH_2$	H	65 (60[22a])[c]	95/ 5
10b	Pyrid-2-yl	$CH_3(CH_2)_3CH_2$	H	60 (52[29])[c]	100/ 0
10c	Pyrid-2-yl	PhCH=CH	H	65	27/ 73
10d	Pyrid-2-yl	Ph	H	78 (82[22a])[c]	59/ 41
10e	Pyrid-2-yl	4-ClC_6H_4	H	83	38/ 62
10f	Pyrid-2-yl	4-ClC_6H_4	Ph	95 (12[13])[c]	58/ 42
10g	Quinolin-2-yl	Ph	H	91 (41[22d])[c]	8/ 92
10h	Pyrid-2-yl	Fur-2-yl	H	84 (58[22a])[c]	68/ 32
10i	Pyrid-2-yl	Thien-2-yl	H	68 (73[22a])[c]	85/ 15
10j	Pyrid-2-yl	Pyrid-3-yl	H	72 (50[22b])[c]	16/ 84
10k	Pyrimidin-4-yl	Fur-2-yl	H	50	50/ 50
10l	Quinolin-4-yl	Thien-2-yl	H	66	100/ 0
10m	Pyrid-4-yl	4-ClC_6H_4	Ph	63	100/ 0
10n	Pyrid-4-yl	4-$(C_2H_5)_2NC_6H_4$	Ph	67	100/ 0
10o	Quinolin-4-yl	4-ClC_6H_4	H	87	100/ 0
10p	Quinolin-4-yl	4-$NO_2C_6H_4$	H	72	100/ 0

[a] Products were recovered as mixture of keto/enol tautomers as evidenced by ^{1}H NMR in $CDCl_3$ with the exceptions of **10b,l–p**, where the percentage of the keto form was 100%. [b] Determined by ^{1}H NMR of products **10**. [c] Literature yield.

The structures of the novel condensation products **10c,e,k–p** are supported by their spectroscopic data together with microanalyses and known compounds **10a,b,d,f–j** by comparison of their melting points and spectroscopic data with the literature reports together with microanalyses in some cases. In nearly all cases, the acylated products derived from 2-alkylazines exist in $CDCl_3$ solution as tautomeric mixtures. Their ^{1}H NMR spectra display two closely overlapping sets of signals and their proton-decoupled ^{13}C NMR spectra generally show two sets of lines. By comparison of the magnitudes of the enolic and ketonic shifts to values from the literature,[30] they were identified as the ketone and enol forms **K** and **O**; enaminone tautomers **E** were not observed (Scheme 3). The integrated intensities of the side-chain methylene and vinyl protons in the ^{1}H NMR spectra of $CDCl_3$ solutions of **10a–k** indicated a predominance of the **O** forms in **10c,e,g,j** 62**–**92% while **K** forms predominated in **10a,d,f,h,i** 58–95%. Although ^{1}H NMR spectra showed a tautomeric mixture of about 1:1 for **10k**, **10b** was observed exclusively in the K form. This finding is in accord with the facts that hydrogen-bonding reinforces tautomeric effects[31] and tautomer ratio is crucially dependent on both steric and polar effects of the substituents attached to the carbonyl group[30] (Scheme 3). However, the

condensation products **10l–p** derived from 4-benzylpyridine and 4-methylquinoline exist predominantly in the ketonic form.



Scheme 3

This new synthetic procedure for the preparation of 1-substituted-2-azinyl-1-ethanones offers several advantages. Good generality has been demonstrated since a variety of alkyated azines can be acylated with aliphatic (to give **10a,b**), alkenyl (to give **10c**), benzenoid (to give **10d–g,m–p**) and heterocyclic acylation reagents (to give **10h–l**). The high average yield for the 8 previously known examples (78%) compared to the reported (47%) and the overall average yield for 16 examples (73%), confirm once again the superiority of *N*-acylbenzotriazoles as an alternative class of acylating reagents, which extend and complement the arsenal of reagents for acylations of alkylated heterocycles. Compared with acid chlorides, the advantage of *N*-acylbenzotriazoles resides in their neutral character and high stability. While *N*,*N*-dimethylamides[23] have been used successfully for the synthesis of 1-alkyl-2-pyridin-2-yl-1-ethanones, they are not as easily accessible as the corresponding *N*-acylbenzotriazoles.

In summary, we have developed a convenient and quite general method for the synthesis of 1,2-disubstituted-1-ethanones having a pyridyl, quinolyl or pyrimidyl moiety that describes the potentiality of *N*-acylbenzotriazoles as valuable acylating agents of alkyated azines.

Experimental Section

General Procedures. All reactions were carried out under an atmosphere of nitrogen, unless otherwise specified. Glassware was routinely oven-dried at 160 ^{o}C for a minimum of 4 h and then connected to a vacuum line before assembling under a dry argon stream. Anhydrous solvents were obtained by distillation immediately prior to use, from sodium benzophenone ketyl (tetrahydrofuran). Melting points were uncorrected. ^{1}H NMR (300 MHz) and ^{13}C NMR (75 MHz) spectra were recorded using deuteriochloroform ($CDCl_3$) as solvent. Column chromatography was carried out on silica gel (230–400 mesh).

General procedure for the preparation of 1-substituted-2-azinyl-1-ethanones 10a–p

To a solution of LDA (4.0 mmol) (prepared *in situ* from diisopropylamine and *n*-butyllithium in THF at –78 ^{o}C), a solution of the alkylated heterocycle **9** (2.0 mmol) in dry THF (15 mL) was added dropwise under argon. After stirring the resulting mixture for 1 h at this temperature to ensure complete carbanion formation, a solution of *N*-acylbenzotriazole **8** (2.0 mmol) in dry THF (10 mL) was added dropwise at –78 ^{o}C. The reaction mixture was allowed to warm to rt overnight before quenching with water (50 mL) and extraction with EtOAc (3 x 30 mL). The combined organic layers were washed with water (50 mL), dried over $MgSO_4$. The solvent was removed under vacuum and the residue was placed in a silica-gel column and eluted with hexanes/EtOAc 10:1 followed by recrystallization from CH_2Cl_2/ hexanes for solid products to give the pure 1-substituted-2-azinyl-1-ethanones **10**. All ^{1}H and ^{13}C NMR signals for tautomeric compounds are for [keto + enol] unless otherwise specified.

3-Methyl-1-(pyrid-2-yl)-2-pentanone (10a). Colorless oil[22a] (65%). ^{1}H NMR [keto + enol] δ 8.54 (dd, *J* = 4.8, 1.0 Hz, 1H), 8.20 (br d, 5.0 Hz, 1H), 7.64 (dt, *J* = 7.6, 1.8 Hz, 1H), 7.52 (td, *J* = 7.5, 1.5 Hz, 1H), 7.23–7.15 (m, 2H), 6.92–6.86 (m, 2H), 5.30 (enol s, 0.05H), 3.92 (keto s, 1.9H), 2.47 (d, J = 6.7 Hz, 2H), 2.16 (septet, *J* = 6.6 Hz, 1H), 0.89 (d, *J* = 6.6 Hz, 6H). ^{13}C NMR [keto + enol] δ 200.9, 169.2, 158.5, 154.7, 149.3, 144.2, 136.7, 136.4, 124.0, 121.7, 120.2, 117.8, 95.9, 52.6, 51.4, 45.4, 26.2, 24.2, 22.3 (2C). Anal. Calcd. For $C_{11}H_{15}NO$: N, 8.48. Found: N, 8.22.

1-(Pyrid-2-yl)-2-heptanone (10b). Colorless oil[29] (60%). ^{1}H NMR δ 8.57 (d, *J* = 4.8 Hz, 1H), 7.66 (td, *J* = 7.7, 1.8 Hz, 1H), 7.25–7.18 (m, 2H), 3.94 (s, 2H), 2.53 (t, *J* = 7.4 Hz, 2H), 1.34–1.19 (m, 6H), 0.86 (t, *J* = 7.1 Hz, 3H). ^{13}C NMR δ 207.6, 154.7, 149.2, 136.7, 124.2, 121.9, 52.0, 42.7, 31.1, 23.3, 22.3, 13.8.

(E)-4-Phenyl-1-pyrid-2-yl-but-3-en-2-one (10c). Yellow prisms (65%), mp 90–92 °C. ^{1}H NMR [keto + enol] δ 14.6 (enol br s, 0.73H), 8.58 (d, *J* = 8.1 Hz, 1H), 8.43 (d, *J* = 8.1 Hz, 1H), 8.35 (d, *J* = 5.0 Hz, 1H), 8.16 (d, *J* = 7.2 Hz, 1H), 8.15 (s, 1H), 7.78–7.47 (m, 8H), 7.40–7.26 (m, 5H), 7.05–6.97 (m, 2H), 6.84 (d, *J* = 16.2 Hz, 1H), 6.59 (d, *J* = 15.9 Hz, 1H), 5.60 (enol s, 0.73H), 4.18 (keto s, 0.54H). ^{13}C NMR [keto + enol] δ 190.1, 158.7, 148.8, 145.5, 137.0, 136.6, 132.0, 131.5, 130.3, 129.1, 129.0, 128.9, 128.7, 128.4, 128.2, 127.1, 126.2, 124.5, 121.6, 120.2, 119.0, 116.1, 114,8, 100.6, 100.3, 50.7. HRMS For $C_{15}H_{13}NO$: 223.2743. Found: 223.1006

1-Phenyl-2-(pyrid-2-yl)-1-ethanone (10d). Yellow needles (78%), mp 67–69 °C (lit.[22a] 52.5–54.0 ^{0}C). ^{1}H NMR [keto + enol] δ 8.56 (d, *J* = 4.3 Hz, 1H), 8.28 (d, *J* = 4.9 Hz, 1H), 8.07 (d, *J* = 7.1 Hz, 2H), 7.85 (dd, *J* = 8.0, 2.1 Hz, 2H), 7.66–7.52 (m, 3H) 7.47–7.38 (m, 4H), 7.30 (d, *J* = 7.8 Hz, 2H), 7.18–7.14 (m, 1H), 7.06 (d, *J* = 8.1 Hz, 1H), 6.99–6.95 (m, 1H), 6.8 (enol s, 0.41 H), 4.50 (keto s, 1.18 H). ^{13}C NMR [keto + enol] δ 196.8 164.3, 158.5, 155.2, 149.5, 144.2, 138.8, 137.1, 136.5, 136.4, 133.2, 129.3, 128.7, 128.6, 128.3, 125.4, 124.2, 121.9, 121.5, 118.4, 94.1, 48.4. Anal. Calcd. For $C_{13}H_{11}NO$: C, 79.16; H, 5.62; N, 7.10. Found: C, 79.15; H, 5.63; N, 7.08.

1-(4-Chlorophenyl)-2-(pyrid-2-yl)-1-ethanone (10e). Yellow needles (83%), mp 96–97 °C. ^{1}H NMR [keto + enol] δ 8.45 (d, *J* = 4.4 Hz, 1H), 8.27 (d, *J* = 4.8 Hz, 1H), 8.01 (d, *J* = 8.4 Hz, 2H),

7.77 (d, *J* = 8.5 Hz, 2H), 7.66–7.58 (m, 2H), 7.42 (d, *J* = 8.6 Hz, 2H), 7.36 (d, *J* = 8.4 Hz, 2H), 7.29 (d, *J* = 7.8 Hz, 1H), 7.19–7.15 (m, 1H), 7.05 (d, *J* = 8.1 Hz, 1H), 7.00–6.98 (m, 1H), 6.03 (enol s, 0.62H), 4.45 (keto s, 0.76H). ^{13}C NMR [keto + enol] δ 195.7, 163.5, 158.2, 154.9, 149.6, 144.0, 139.7, 137.2, 136.6, 135.1, 135.0, 130.2, 128.9, 128.5, 126.8, 124.1, 122.0, 121.6, 11.6, 100.2, 94.1, 48.5. Anal. Calcd. For $C_{13}H_{10}ClNO$: C, 67.40; H, 4.35; N, 6.05. Found: C, 67.38; H, 4.30; N, 5.93.

1-(4-Chlorophenyl)-2-phenyl-2-(pyrid-2-yl)-1-ethanone (10f). Yellow prisms (95%), mp 90–92 °C (lit.[13] 95–98 °C). ^{1}H NMR [keto + enol] δ 8.54 (d, *J* = 4.8 Hz, 1H), 8.34 (d, *J* = 5.1 Hz, 1H), 7.95 (d, *J* = 8.5 Hz, 2H), 7.64–7.50 (m, 2H), 7.37 –6.99 (m, 19 H), 6.84 (d, *J* = 8.4 Hz, 1H), 6.21 (keto s, 0.58H). ^{13}C NMR [keto + enol] δ 196.3, 163.3, 159.8, 159.0, 149.3, 143.0, 139.5, 137.7, 137.3, 137.2, 136.7, 136.5, 134.9, 133.7, 132.5, 130.4, 130.3, 129.1, 129.0, 128.9, 128.8, 127.6, 127.5, 127.0, 123.8, 122.1, 120.8, 118.7, 109.0, 62.1. Anal. Calcd. For $C_{19}H_{14}ClNO$: C, 74.15; H, 4.58; N, 4.55. Found: C, 74.23; H, 4.56; N, 4.59.

(Z)-1-Phenyl-2-quinolin-2-ylethanol (10g). Yellow needles (91%), mp 114–116 °C (lit.[22d] 115.5–117.0 °C). ^{1}H NMR δ 15.78 (enol br s, 0.92H), 8.02 (dd, *J* = 5.9, 2.2 Hz, 2H), 7.69 (d, *J* = 9.0 Hz, 1H), 7.61–7.49 (m, 6H), 7.30 (dd, *J* = 6.8, 2.0 Hz, 1H), 6.91 (d, *J* = 9.0 Hz, 1H), 6.1 (enol s, 0.92H). ^{13}C NMR δ 184.0, 154.0, 139.7, 137.7, 136.1, 130.9, 130.3, 128.2, 127.5, 126.6, 123.6, 123.2, 122.2, 118.1, 89.8.

1-Fur-2-yl-2-(pyrid-2-yl)-1-ethanone (10h). Yellow needles (84%), mp 54–55 °C (lit.[22a] 49.5–51.0 °C). ^{1}H NMR [keto + enol] δ 8.55 (d, *J* = 4.4 Hz, 1H), 8.18 (d, *J* = 5.1 Hz,1H), 7.67–7.55 (m, 3H), 7.46 (s, 1H), 7.35–7.31 (m, 2H), 7.19–7.15 (m, 1H), 7.03 (d, *J* = 8.2 Hz, 1H), 6.92 (t, *J* = 6.0 Hz, 1H), 6.84 (d, *J* = 3.3 Hz, 1H), 6.54 (br s, 1H), 6.49 (br s, 1H), 6.03 (enol s, 0.32H), 4.34 (keto s, 1.36H). ^{13}C NMR [keto + enol] δ 185.4, 169.9, 152.3, 151.3, 149.5 (2C), 146.8 (2C), 143.0, 137.2, 136.5, 132.3, 124.1, 122.0, 121.6, 118.5, 117.7, 112.4, 111.7, 109.4, 92.4, 48.0. Anal. Calcd. For $C_{11}H_9NO_2$: C, 70.58; H, 4.85; N, 7.48. Found: C, 70.51; H, 4.91; N, 7.36.

2-(Pyrid-2-yl)-1-(thien-2-yl)-1-ethanone (10i). Pale yellow oil[22a] (68%). ^{1}H NMR [keto + enol] δ 8.58 (ddd, *J* = 4.9, 1.8, 0.8 Hz, 1H), 8.06 (ddd, *J* = 4.9, 1.7, 0.9 Hz, 1H), 7.87 (dd, *J* = 3.9, 1.3 Hz, 1H), 7.66 (td, *J* = 7.6, 1.8 Hz, 1H), 7.63 (dd, *J* = 4.9, 1.2 Hz, 1H), 7.57 (d, *J* = 1.8 Hz, 1H), 7.55 (dd, *J* = 2.9, 1.1 Hz, 1H), 7.52 (dd, *J* = 3.9, 1.3 Hz, 1H), 7.34–7.43 (m, 1H), 7.19 (ddd, *J* = 8.9, 5.1, 1.2 Hz, 1H), 7.11 (dd, *J* = 5.1, 3.9 Hz, 1H), 7.05 (dd, *J* = 5.1, 3.6 Hz, 1H), 6.98 (dt, *J* = 8.4, 0.9 Hz, 1H), 6.84 (ddd, *J* = 7.2, 5.4, 1.2 Hz, 1H), 5.95 (enol s, 0.15H), 4.45 (keto s, 1.7H). ^{13}C NMR [keto+enol] δ 189.6, 157.5, 154.7, 149.4, 143.7, 141.3, 137.4, 136.7, 134.3, 133.4, 128.2, 127.6, 127.1, 125.4, 125.3, 124.2, 122.1, 121.4, 116.7, 115.0, 91.5, 48.9.

2-(Pyrid-2-yl)-1-(pyrid-3-yl)-1-ethanone (10j). Yellow prisms (72%), mp 70–71 °C (lit.[22b] 69–70 °C). ^{1}H NMR [keto + enol] δ 15.80 (s, 1H), 9.27 (dd, *J* = 2.4, 0.9 Hz, 1H), 9.07 (dd, *J* = 2.4, 0.9 Hz, 1H), 8.76 (dd, *J* = 4.8, 1.5 Hz, 1H), 8.60 (dd, *J* = 4.8, 1.5 Hz, 1H), 8.34 (dt, *J* = 9.9, 2.4 Hz, 1H), 8.29 (d, *J* = 5.1 Hz, 1H), 8.11 (dt, *J* = 8.4, 1.8 Hz, 1H), 7.67 (d, *J* = 1.8 Hz, 1H), 7.64 (dd, *J* = 1.8, 0.9 Hz, 1H), 7.62 (d, *J* = 1.5 Hz, 1H), 7.40 (ddd, *J* = 7.8, 4.8, 0.9 Hz, 1H), 7.34 (ddd, *J* = 7.8, 4.8, 0.9 Hz, 1H), 7.30 (br s, 1H), 7.19 (ddd, *J* = 7.5, 5.4, 1.2 Hz, 1H), 7.10 (dd, *J* =

8.1, 0.9 Hz, 1H), 7.02 (ddd, *J* = 7.5, 5.4, 1.2 Hz, 1H), 6.09 (enol s, 0.84H), 4.50 (keto s, 0.32H). ^{13}C NMR [keto + enol] δ 195.6, 162.3, 158.0, 154.4, 153.5, 150.0, 150.0, 149.7, 147.1, 143.9, 137.4, 136.6, 136.0, 132.8, 132.2, 131.8, 124.1, 123.5, 123.1, 122.1, 121.7, 118.9, 94.8, 48.6.

1-(Fur-2-yl)-2-(pyrimidin-4-yl)-1-ethanone (10k). Yellow prisms (50%), mp128–130 °C. ^{1}H NMR [keto + enol] δ 9.16 (d, *J* = 1.2 Hz, 1H), 8.70 (s, 1H), 8.68 (s, 1H), 8.31 (d, *J* = 5.7 Hz, 1H), 7.63 (dd, *J* = 1.8, 0.7 Hz, 1H), 7.51 (br s, 1H), 7.39 (dd, *J* = 5.1, 1.5 Hz, 1H), 7.34 (d, *J* = 3.6 Hz, 1H), 6.96 (br d, *J* = 3.3 Hz, 1H), 6.86 (br d, *J* = 5.7 Hz, 1H), 6.58 (dd, *J* = 3.6, 1.8 Hz, 1H), 6.50–6.53 (m, 1H), 5.97 (enol s, 0.5H), 4.33 (keto s, 1H). ^{13}C NMR [keto + enol] δ 183.7, 163.4, 163.0, 161.4, 158.8, 156.9, 154.7, 153.1, 150.6, 147.1, 144.3, 121.8, 118.7, 117.1, 112.6, 112.0 (2C), 112.0, 91.0, 47.1. Anal. Calcd. For $C_{10}H_8N_2O_2$: C, 63.82; H, 4.28; N, 14.89. Found: C, 63.81; H, 4.22; N, 14.85.

2-(Quinolin-4-yl)-1-(thien-2-yl)-1-ethanone (10l). Yellow prisms (66%), mp 66–68 °C. ^{1}H NMR δ 8.34 (d, *J* = 4.5 Hz, 1H), 8.12 (dd, *J* = 7.9, 0.7 Hz, 1H), 7.94 (dd, *J* = 8.5, 0.9 Hz, 1H), 7.84 (dd, *J* = 3.9, 0.9 Hz, 1H), 7.73–7.67 (m, 2H), 7.54 (ddd, *J* = 8.2, 6.9, 1.3 Hz, 1H), 7.30 (d, *J* = 4.5 Hz, 1H), 7.14 (dd, *J* = 4.9, 3.9 Hz, 1H), 4.64 (s, 2H). ^{13}C NMR δ 188.6, 150.0, 148.4, 143.3, 140.5, 134.5, 132.6, 130.2, 129.3, 128.3, 127.6, 126.8, 123.6, 122.7, 42.8. Anal. Calcd. For $C_{15}H_{11}NOS$: C, 71.12; H, 4.38; N, 5.53. Found: C, 70.73; H, 4.29; N, 5.42.

1-(4-Chlorophenyl)-2-phenyl-2-(pyrid-4-yl)-1-ethanone (10m). Oil (63%). ^{1}H NMR δ 8.50 (dd, *J* = 6.1 Hz, 2H), 7.90 (dd, *J* = 8.7 Hz, 2H), 7.36 (dd, *J* = 8.7 Hz, 2H), 7.25-7.33 (m, 5H), 7.14 (dd, *J* = 6.1 Hz, 2H), 5.94 (s, 1H). ^{13}C NMR δ 195.4, 149.7, 147.7, 139.8, 136.7, 134.3, 130.2, 129.2, 128.9, 128.8, 127.8, 124.2, 58.5. Anal. Calcd. For $C_{19}H_{14}ClNO$: N, 4.55. Found: N, 4.61.

1-[4-(Diethylamino)phenyl]-2-phenyl-2-(pyrid-4-yl)-1-ethanone (10n). Colorless prisms (67%), mp 134–136 °C. ^{1}H NMR δ 8.50 (dd, *J*= 6.1 Hz, 2H), 7.89 (d, *J* = 9.2 Hz, 2 H), 7.24-7.33 (m, 6H), 7.21 (dd, *J*= 6.1 Hz, 2H), 6.57 (d, *J* = 9.2 Hz, 2H), 3.36 (q, *J* = 7.1 Hz, 4H), 1.16 (t, *J* = 7.1 Hz, 6H). ^{13}C NMR δ 193.9, 151.3, 149.7, 149.0, 138.2, 131.5, 128.9, 128.8, 128.7, 127.3, 124.6, 110.2, 57.5, 44.4, 12.4. Anal. Calcd For $C_{23}H_{24}N_2O$: C, 80.20; H, 7.02; N, 8.13. Found: C, 80.54; H, 7.26; N, 8.25.

1-(4-Chlorophenyl)-2-(quinolin-4-yl)-1-ethanone (10o). Colorless plates (87%), mp 138–139 °C. ^{1}H NMR δ 8.84 (d, *J* = 4.3 Hz, 1H), 8.14 (d, *J* = 8.4 Hz, 1H), 7.97 (d, *J* = 8.5 Hz, 2H), 7.82 (d, *J* = 8.2 Hz, 1H), 7.70 (t, *J* = 7.1, 1H), 7.53 (t, *J* = 7.1 Hz, 1H), 7.45 (d, *J* = 8.5 Hz, 2H), 7.23 (d, *J* = 4.3 Hz, 1H), 4.67 (s, 2H). ^{13}C NMR δ 194.7, 150.0, 148.3, 140.6, 140.1, 134.4, 130.3, 129.7, 129.3, 129.1, 127.5, 126.8, 123.4, 122.7, 42.0. Anal. Calcd. For $C_{17}H_{12}ClNO$: C, 72.47; H, 4.29; N, 4.97. Found: C, 72.30; H, 4.34; N, 4.87.

1-(4-Nitrophenyl)-2-(quinolin-4-yl)-1-ethanone (10p). Pink prisms (72%), mp 127–128 °C. ^{1}H NMR δ 8.88 (d, *J* = 4.3 Hz, 1H), 8.35 (d, *J* = 8.1 Hz, 2H), 8.22 (d, *J* = 8.1 Hz, 2H), 8.16 (s, 1H), 7.83 (d, *J* = 8.1 Hz, 1H), 7.75 (t, *J* = 8.1 Hz, 1H), 7.58 (t, *J* = 7.6 Hz, 1H), 7.28 (d, *J* = 4.3 Hz, 1H), 4.79 (s, 2H). ^{13}C NMR δ 194.0, 163.0, 150.0, 140.6, 139.9, 130.5, 129.6, 129.5, 127.2, 124.1, 123.3, 122.8, 113.1, 42.7. Anal. Calcd. For $C_{17}H_{12}N_2O_3$: N, 9.58. Found: N, 9.43.

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