

REACTION OF METHOXY-N-HETEROAROMATICS WITH PHENYLACETONITRILE
UNDER BASIC CONDITIONS

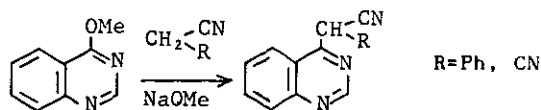
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Abstract — The monomethoxyl derivatives of various π -electron-deficient *N*-heteroaromatics reacted with phenylacetonitrile in tetrahydrofuran in the presence of sodium hydride to give α -phenyl-*N*-heteroareneacetonitriles in the yields ranging from 45 to 78%. On the contrary, the reaction of these methoxyl derivatives with ethyl cyanoacetate or malononitrile under similar conditions was restricted within narrow limits. The synthesis of benzoyl-*N*-heteroaromatics by the air-oxidation of α -phenyl-*N*-heteroareneacetonitriles was described additionally.

In nucleophilic substitution at the α - and γ -positions (active positions) of π -electron-deficient *N*-heteroaromatic compounds, alkoxy groups are recognized to be very weak leaving groups, so that the reaction of the alkoxy derivatives with nucleophilic reagents, particularly with carbanions generated from active methylene compounds, is not well investigated.¹ The reaction of 4-methoxyquinazoline with nitrile-stabilized carbanions is an exceptional example, and the corresponding 4-substituted products obtained.²

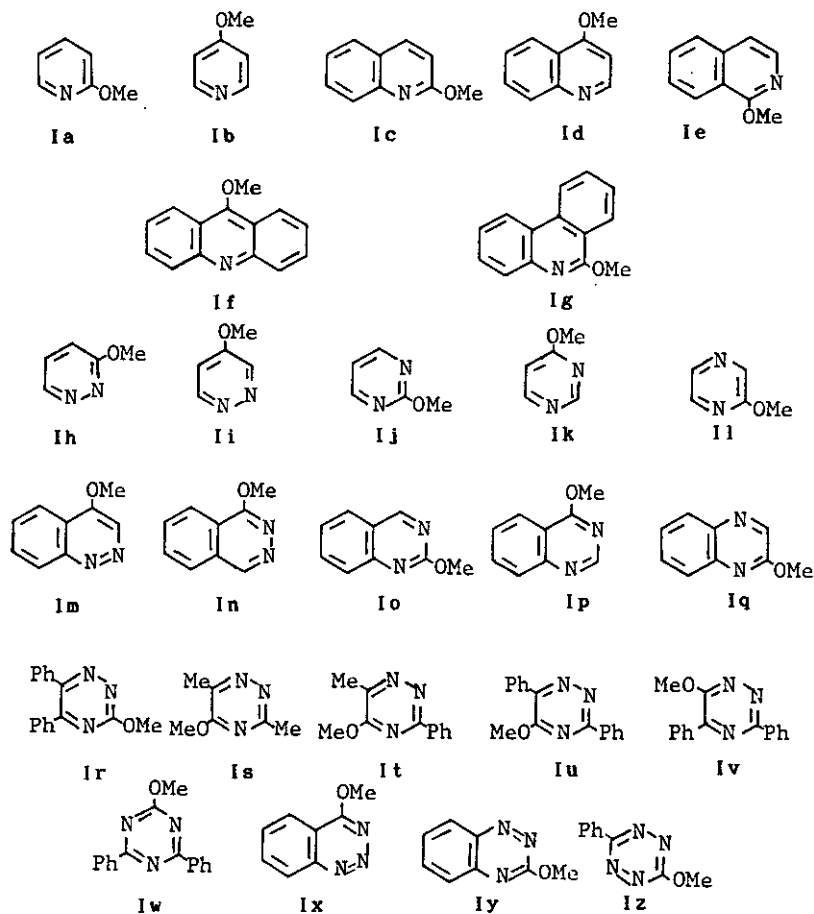
As illustrated in Scheme 1, it was suggested that at the highly active position of π -electron-deficient *N*-heteroaromatics, even alkoxy groups might be replaced with nucleophilic reagents.



Scheme 1

On the other hands, in 1954, Mizuno *et al.* have reported that phenylacetonitrile widely reacted with various chloro-*N*-heteroaromatics under basic conditions, and the α -phenyl-*N*-heteroareneacetonitriles were obtained in the yields ranging from 43 to 100%.³ Further, Panizzon has presented that phenylacetonitrile smoothly reacted with 2-chloropyridine which is known to be an inactive heteroaryl chloride, although it has a chlorine substituent at the α -position.⁴ These findings demonstrate that phenylacetonitrile is an extremely powerful reagent comparing with other active methylene compounds such as ethyl cyanoacetate, malononitrile, diethyl malonate, and acetylacetone.

From these points of view, we investigated the reaction of various π -electron-deficient *N*-heteroaromatics containing a methoxyl group at their active position with phenylacetonitrile under basic conditions in order to compare the reactivity of π -electron-deficient *N*-heteroaromatics for addition-elimination type nucleophilic substitutions.



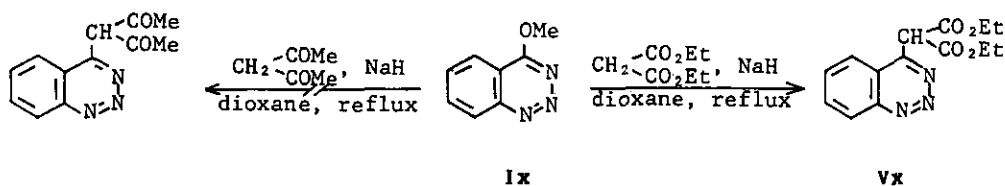
Scheme 2

In the present investigation, sodium hydride and tetrahydrofuran (THF) were used as a base and a solvent, because such reaction conditions were confirmed to give the best yield of the product (IIC) on the trial of 4-methoxyquinoline (Ic) with phenylacetonitrile.

As shown in Table I, all the tested methoxyl derivatives (Ia-z) underwent the substitution to give α -phenyl-N-heteroareneacetonitriles (IIa-z). Out of our initial expectation, fundamental difference of reactivity among the substrates was not observed, but a wide range of successful results shows the excellent ability of phenylacetonitrile carbanion as described by Mizuno, *et al.*³

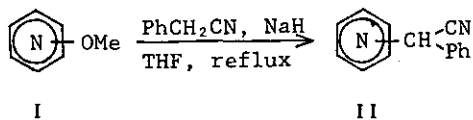
On the contrary, when the compounds Ia-z were treated with ethyl cyanoacetate or with malononitrile under similar conditions (dioxane was used as solvent instead of THF), only nine kinds of methoxyl derivatives (If, Im, Ip, Is, It, Iu, Iw, Ix, and Iz) were converted into the desired compounds (II and III).⁵ The results are listed in Table II.

It should be noted that compound Ix is the most reactive among the substrates employed. The reaction of Ia-z with diethyl malonate or with acetylacetone failed, except for that of Ix with diethyl malonate. Namely, Ix reacted with diethyl malonate to give diethyl 1,2,3-benzotriazine-4-malonate (Vx) in 49% yield, while Ix was unchanged by the reaction with acetylacetone.



On the basis of these results, it is clear that a methoxyl group on the active position of acridine (the 9-position), quinazoline (the 4-position), 1,2,4-triazine (the 5-position), 1,3,5-triazine, 1,2,3-benzotriazine (the 4-position), and 1,2,4,5-tetrazine, can act as an effective leaving group in the reaction with nitrile-stabilized carbanions. These results has also demonstrated that the reactivity of carbanions derived from active methylene compounds can be arranged in order of $\text{^-CH(CN)Ph} \gg \text{^-CH(CN)}_2 > \text{^-CH(CN)CO}_2\text{Et} \gg \text{^-CH(CO}_2\text{Et)}_2 > \text{^-CH(COMe)}_2$.

Table I. Reaction of Methoxy-N-heteroaromatics (I) with Phenylacetonitrile

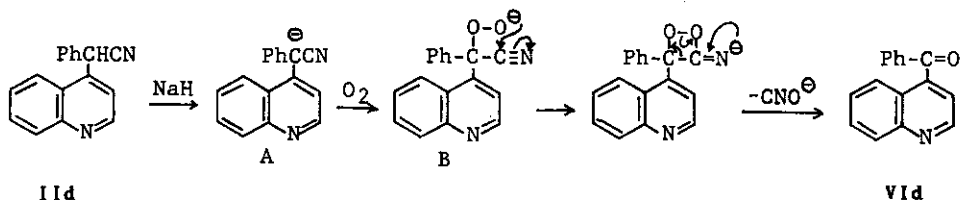


NO. ^a	mp (°C) [Lit. mp (°C)]	Recryst. solvent	Yield (%)	NO. ^a	mp (°C) [Lit. mp (°C)]	Recryst. solvent	Yield (%)
IIa	84-86 [85 ⁴]	hexane-Et ₂ O	39	IIm	195-197 [197-198 ³]	AcOEt	62
IIb	77-78 [76-77 ⁴]	hexane-Et ₂ O	43	II n	136-138 [138-139 ³]	AcOEt	46
IIc	91-93 [92-93 ³]	hexane-AcOEt	53	IIo	119-121	AcOEt	57
II d	89-90 [88.5-90 ⁶]	hexane-AcOEt	51	IIp	111-112 [112 ³]	AcOEt	78
IIe	139-141 [143-145 ⁷]	hexane-AcOEt	41	IIq	111-112 [111-112 ³]	AcOEt	39
II f	206-208 [210 ³]	AcOEt	78	IIr	138-140	hexane-AcOEt	41
IIg	153-155	AcOEt	36	II s	185-186	AcOEt	71
IIh	138-140 [136-137 ⁸]	hexane-Et ₂ O	58	II t	220-221	AcOEt	49
II i	146-148	AcOEt	62	II u	245-246	AcOEt	68
II j	50-62 ^b [90-91 ⁹]	hexane-Et ₂ O	47 56	II v	154-155	AcOEt	46
II k	117-118	hexane-AcOEt	62	II w	177-178 [177-178 ¹¹]	AcOEt	45
II l	134-135 [132-134 ¹⁰]	hexane-AcOEt	46	II x	144-145	AcOEt	71
				II y	140-142	AcOEt	61
				II z	149-151	AcOEt	77

a) In all the cases, the ring systems are corresponding to Ia-z shown in Scheme 2.

b) The observed melting point of IIj is quite different from the reported value, but the structure of our sample is well supported by elemental analysis and spectroscopies.

probably, highly π -electron-deficient rings attract the negative charge formed on the methine group and decrease the susceptibility of the substrates to air-oxidation (A \rightarrow B).



Scheme 3

Table III. *N*-Heteroaryl Phenyl Ketones (VI)

No. ^a	mp (°C) [Lit. mp (°C)]	Recryst. solvent	Yield (%)	No. ^a	mp (°C) or bp (°C/mmHg) [Lit. mp (°C)] or [Lit. bp (°C)/(mmHg)]	Recryst. solvent	Yield (%)
VIa	40-42 [44-46 ¹⁴]	hexane	94	VIi	104-106	AcOEt	93
VIb	70-71 [71-72 ¹⁵]	hexane	94	VIj	84-85 [85-85.5 ⁹]	hexane	90
VIc	108-110 [111 ¹⁶]	hexane	93	VIk	103-105	hexane	90
VI d	60-62 [59-60 ¹⁷]	hexane	93	VI l	155/3 [99-200/20 ²¹]		93
VI e	75-76 [76-77 ¹⁸]	hexane	93	VI m	99-100	AcOEt	94
VI f	217-218 [217.5 ¹⁹]	AcOEt	92	VI n	122-123 [123-124 ²²]	hexane-AcOEt	92
VI g	152-154	AcOEt	92	VI o	100-102	hexane-AcOEt	91
VI h	68-69 [70-72 ²⁰]	hexane	93	VI p	96-98 [97-98 ²³]	AcOEt	92
				VI q	78-80 [80-81 ²⁴]	hexane-AcOEt	91

a) In all the cases, the ring systems are corresponding to Ia-q shown in Scheme 2.

During our investigations, Hermann, *et al.*, reported a new synthesis of aryl heteroaryl ketones via $S_{RN}1$ reaction of halo-*N*-heteroaromatics with potassium phenylacetonitrile followed by phase transfer catalyzed decyanation.⁹ Their procedure on the decyanation is essentially the same to our oxidative transformation.

In this connection, it has been reported that VII, VI_m, VI_q, and VI_r could not be synthesized by the Grignard reaction of the corresponding nitriles with phenylmagnesium bromide.²⁵ Thus, the air-oxidation of α -phenyl-*N*-heteroareneacetonitriles provides a method for the preparation of *C*-benzoyl-*N*-heteroaromatics.

EXPERIMENTAL

All melting points were determined by capillary method and are uncorrected. Proton magnetic resonance (¹H-nmr) spectra were recorded at either 60 MHz on a JEOL JNM-PMX 60 spectrometer or 100 MHz on a FX-100 spectrometer. Chemical shifts are quoted in δ value (ppm) with tetramethylsilane (TMS) or 2,2-dimethyl-2-silapentanesulfonic acid sodium salt (DSS) as an internal standard, and coupling constants (*J*) are given in hertz (Hz). The following abbreviations are used: s=singlet, d=doublet, t=triplet, q=quartet, m=multiplet, and br=broad. Infrared (ir) spectra were produced on a JASCO IR 810 spectrometer. Column chromatography was carried out on silica gel (NAKARAI CHEMICALS, Ltd. silica gel 60 or KATAYAMA CHEMICALS, Ltd. silica gel 60).

6-Methoxy-3,6-diphenyl-1,2,4-triazine (IV) ——— 6-Chloro-3,6-diphenyl-1,2,4-triazine²⁶ (0.53 g, 2 mmol) was added to a methanolic solution of NaOMe prepared from metallic Na (0.05 g, 2.2 mgatom) and dry MeOH (20 ml), and the mixture was stirred at room temperature for 18 h. After evaporation of the solvent, the residue was diluted with H₂O, and the mixture was extracted with Et₂O. The ethereal solution was dried over Na₂SO₄. Evaporation of Et₂O followed by recrystallization of the residue from hexane to give pale yellow needles, mp 104-105°C. Yield 0.51 g (97%). ¹H-Nmr (CCl₄): 8.6-8.2 (m, 4H), 7.7-7.3 (m, 6H), 4.26 (s, 3H).

2-Methoxy-4,6-diphenyl-1,3,5-triazine (I_w) ——— 2-Chloro-4,6-diphenyl-1,3,5-triazine²⁷ (0.53 g, 2 mmol) was added to a methanolic solution of NaOMe prepared from metallic Na (0.05 g, 2.2 mgatom) and dry MeOH (20 ml). The mixture was stirred at room temperature for 30 min. After removal of MeOH, a small amount of H₂O was added to the residue, and the mixture was extracted with Et₂O. The ethereal

solution was dried over K_2CO_3 and evaporated. Recrystallization of the residue from hexane gave colorless needles, mp 112-113°C. Yield 0.49 g (93%). ^1H-Nmr (CCl_4): 8.8-8.4 (m, 4H), 7.6-7.3 (m, 6H), 4.12 (s, 3H).

3-Methoxy-1,2,4-benzotriazine (Iy) ——— 3-Methylthio-1,2,4-benzotriazine²⁸ (0.35 g, 2 mmol) was added to a methanolic solution of NaOMe prepared from metallic Na (0.05 g, 2.2 mgatom) and dry MeOH (20 ml). The mixture was stirred at room temperature for 2 h. After removal of MeOH, a small amount of H_2O was added to the residue, and the mixture was extracted with Et_2O . The ethereal solution was dried over K_2CO_3 and evaporated. Recrystallization of the residue from hexane gave yellow needles (0.29 g, 91%). mp 104-105 °C (lit.²⁹ mp 106 °C).

3-Methoxy-6-phenyl-1,2,4,5-tetrazine (Iz) ——— 3-Bromo-6-phenyl-1,2,4,5-tetrazine³⁰ (0.48 g) was treated with NaOMe, prepared from a 60% oil dispersion of NaH (0.09 g, 2.2 mmol) and dry MeOH (0.1 g, 3 mmol), in dry Et_2O (20 ml). Recrystallization from Et_2O gave red scales (0.33 g, 89%). mp 88-89 °C. ^1H-Nmr (CCl_4): 8.7-8.7 (m, 2H), 7.7-7.4 (m, 3H), 4.37 (s, 3H).

General Procedure for the Reaction of Methoxy-N-heteroaromatics (I) with Phenylacetonitrile ——— A 60% oil dispersion of NaH (0.18 g, 4.5 mmol) was washed with hexane, to which phenylacetonitrile (0.49 g, 4 mmol) in dry THF (20 ml) was added, and the mixture was refluxed for 30 min. Then a methoxy-N-heteroarene(I) (2 mmol) was added, and the mixture was refluxed under a nitrogen atmosphere until I was disappeared on tlc. After removal of THF under reduced pressure, the residue was diluted with H_2O . The aqueous solution was neutralized with 5% AcOH and extracted with $CHCl_3$. The $CHCl_3$ solution was washed with sat. NaCl, dried over $MgSO_4$, and evaporated. Unreacted phenylacetonitrile was removed by distillation at 80 °C (2 mmHg) to give the residue which was chromatographed on silica gel column. Recrystallization from an appropriate solvent shown in Table I gave a pure product (II). The yields, the melting points, and spectral data are shown in Tables I and IV.

Table IV. Spectral Data for II

No.	I _r (CHCl ₃) cm ⁻¹	¹ H-Nmr (CDCl ₃)	
		δ	(ppm)
IIa	2260	8.52 (dd, <u>J</u> =5, <u>J</u> =2, 1H), 7.7-6.9 (m, 8H), 5.20 (s, 1H)	
IIb	2260	8.54 (d, <u>J</u> =6, 2H), 7.5-7.0 (m, 7H), 5.02 (s, 1H)	
IIc	2260	8.13 (d, <u>J</u> =8, 1H), 7.9-7.2 (m, 10H), 5.47 (s, 1H)	
IId	2250	9.00 (d, <u>J</u> =5, 1H), 8.4-7.3 (m, 10H), 5.83 (s, 1H)	
IIe	2250	8.53 (d, <u>J</u> =5, 1H), 8.2-7.2 (m, 10H), 5.86 (s, 1H)	
II f	3440, 2200	8.53 (dd, <u>J</u> =8, <u>J</u> =2, 1H), 7.4-6.5 (m, 12H), 1.6-1.5 (br, 1H)	
IIg	2200	8.7-7.0 (m, 13H), 6.09 (s, 1H)	
IIh	2260	9.16 (dd, <u>J</u> =5, <u>J</u> =2, 1H), 7.7-7.3 (m, 7H), 5.70 (s, 1H)	
IIi	3440, 2190	12.7-12.4 (br, 1H), 8.01 (dd, <u>J</u> =3, 1H), 7.6-7.2 (m, 6H), 6.7-6.3 (m, 1H)	
IIj	2260	8.65 (d, <u>J</u> =5, 2H), 7.7-7.0 (m, 6H), 5.27 (s, 1H)	
IIk	2150	9.25 (d, <u>J</u> =1, 1H), 8.77 (d, <u>J</u> =5, 1H), 7.7-7.3 (m, 6H), 5.24 (s, 1H)	
IIl	2260	8.67 (s, 1H), 8.56 (s, 2H), 7.7-7.3 (m, 5H), 5.35 (s, 1H)	
II m	2190	9.3-9.0 (br, 1H), 8.93 (dd, <u>J</u> =7, <u>J</u> =2, 1H), 7.7-6.8 (m, 9H)	
II n	3400, 2170	9.50 (s, 1H), 8.2-7.3 (m, 9H), 6.13 (s, 1H)	
II o	3380, 2250	8.3-8.0 (br, 1H), 7.7-7.0 (m, 10H)	
II p	3380, 2190	12.0-11.5 (br, 1H), 8.85 (dd, <u>J</u> =7, <u>J</u> =2, 1H) 8.1-7.3 (m, 8H), 7.1-6.8 (m, 1H)	
II q	2250	8.76 (s, 1H), 8.2-7.2 (m, 9H), 5.49 (s, 1H)	
II r	2250	7.9-7.3 (m, 15H), 5.83 (s, 1H)	
II s	3420, 2190	13.0-12.7 (br, 1H), 7.9-7.7 (m, 2H), 7.5-7.2 (m, 3H)	
II t	2180	13.4-13.1 (br, 1H), 8.3-7.1 (m, 10H)	
II u	2190	13.7-13.5 (br, 1H), 8.4-6.9 (m, 15H)	
II v	2240	8.8-8.5 (m, 2H), 7.8-7.4 (m, 8H), 7.4-7.2 (m, 5H), 5.74 (s, 1H)	
II w	2240	8.9-8.6 (m, 4H), 7.9-7.3 (m, 11H), 5.41 (s, 1H)	
II x	2200	9.2-8.9 (m, 1H), 7.9-7.3 (m, 9H)	
II y	2250	8.7-8.4 (m, 1H), 8.3-8.0 (m, 3H), 8.0-7.6 (m, 3H) 7.5-7.3 (m, 3H), 6.00 (s, 1H)	
II z	2260	8.7-8.5 (m, 2H), 7.8-7.3 (m, 8H), 5.90 (s, 1H)	

General Procedure for the Reaction of Methoxy-N-heteroaromatics (I) with Ethyl Cyanoacetate — A 60% oil dispersion of NaH (0.18 g, 4.5 mmol) was washed with hexane, to which ethyl cyanoacetate (0.45 g, 4 mmol) in dry dioxane (20 ml) was added, and the mixture was stirred for 30 min at room temperature. A methoxy-N-heteroarene (I) (2 mmol) was treated as described above. After neutralization with 5% AcOH, precipitated crystals were collected by suction, washed well with H₂O, dried in air, and recrystallized from AcOEt to give the product (III). The yields, the melting points, and the spectral data are shown in Tables II and V.

Table V. Spectral Data for III

No.	Ir (CHCl ₃) cm ⁻¹	¹ H-Nmr (CDCl ₃)
		δ (ppm)
III f	2170, 1630	12.9-12.5 (br, 1H), 8.25 (dd, $J=5, J=2$, 2H), 8.0-7.0 (m, 1H), 4.12 (q, $J=7$, 2H), 1.12 (t, $J=7$, 3H)
III p	2200, 1650	14.7-13.8 (br, 1H), 9.22 (dd, $J=5, J=2$, 1H), 8.10 (s, 1H), 7.9-7.3 (m, 3H), 4.36 (q, $J=7$, 2H), 1.39 (t, $J=7$, 3H)
III s	2210, 1670	14.7-13.7 (br, 1H), 4.35 (q, $J=7$, 2H), 2.92 (s, 3H), 2.56 (s, 3H), 1.37 (t, $J=7$, 3H)
III t	2200, 1660	14.9-14.4 (br, 1H), 8.2-7.9 (m, 2H), 7.6-7.3 (m, 3H), 4.41 (q, $J=7$, 2H), 2.97 (s, 3H), 1.41 (t, $J=7$, 3H)
III u	2200, 1650	15.0-14.7 (br, 1H), 8.7-8.5 (m, 2H), 8.4-7.9 (m, 2H), 7.9-7.3 (m, 6H), 4.35 (q, $J=7$, 2H), 1.37 (t, $J=7$, 3H)
III w	2180, 1630	14.5-14.0 (br, 1H), 8.7-8.5 (m, 2H), 8.3-8.1 (m, 2H), 7.8-7.3 (m, 6H), 4.18 (q, $J=7$, 2H), 1.48 (t, $J=7$, 3H)
III x	2210, 1670	9.5-9.3 (m, 1H), 8.3-7.7 (m, 3H), 4.61 (s, 1H), 4.37 (q, $J=7$, 2H), 1.40 (t, $J=7$, 3H)
III z	2250, 1670	9.5-8.7 (br, 1H), 8.4-8.1 (m, 2H), 7.8-7.6 (m, 3H), 4.24 (q, $J=7$, 2H), 1.27 (t, $J=7$, 3H)

General Procedure for the Reaction of Methoxy-N-heteroaromatics (I) with Malonitrile — A 60% oil dispersion of NaH (0.18 g, 4.5 mmol) washed with hexane, malonitrile (0.26 g, 4 mmol), and I (2 mmol) in dry dioxane (20 ml) were treated as described above. After neutralization with 5% AcOH, precipitated crystals were collected by suction, washed well with H₂O, dried in air, and recrystallized from AcOEt to give the product (IV). The yields, the melting points, and the spectral data are shown in Tables III and VI.

Table VI. Spectral Data for IV

No.	Ir (KBr) cm ⁻¹	1H-Nmr (DMSO-d ₆)	
		δ	(ppm)
IVf	3270, 2210, 2190	12.5 (br, 1H), 8.56 (dd, $J=8, J=1$, 2H), 7.8-7.2 (m, 6H)	
IVm	3270, 2210, 2190	14.8-14.0 (br, 1H), 8.72 (d, $J=8$, 1H), 8.28 (s, 1H), 8.0-7.5 (m, 3H)	
IVp	3280, 2210, 2190	13.4 (br, 1H), 8.63 (d, $J=9$, 1H), 8.47 (s, 1H), 8.0-7.4 (m, 3H)	
IVs	3200, 2220, 2200	14.5-14.4 (br, 1H), 2.56 (s, 3H), 2.42 (s, 3H)	
IVt	3200, 2220, 2200	15.0-14.5 (br, 1H), 7.8-7.6 (m, 2H), 7.5-7.1 (m, 3H), 2.25 (s, 3H)	
IVu	3200, 2220, 2200	8.4-8.1 (m), 7.8-7.6 (m) ^a	
IVw	3200, 2220, 2200	8.4-8.1 (m, 4H), 7.8-7.4 (m, 7H)	
IVx	3200, 2250, 2200	8.58 (dd, $J=8, J=1$, 1H), 8.2-7.6 (m, 3H)	

a The integrated ratio is 1:4.

Diethyl 1,2,3-Benzotriazine-4-malonate (Vx) — A 60% oil dispersion of NaH (0.18 g, 4.5 mmol), diethyl malonate (0.64 g, 4 mmol), and 4-methoxy-1,2,3-benzotriazine (Ix) (0.32 g, 2 mmol) were treated as described above. After neutralization with 5% AcOH, the mixture was extracted with CHCl₃. The CHCl₃ solution was washed with sat. NaCl, dried over MgSO₄, and evaporated. The residue was recrystallized from hexane-AcOEt to give pale yellow prisms (0.28 g, 49%). mp 127-128 °C. ¹H-Nmr (CDCl₃-TMS): 15.3-14.8 (br, 1H), 8.3-7.6 (m, 4H), 4.41 (q, $J=7$, 4H), 1.40 (t, $J=7$, 6H). Ir (CHCl₃): 1720, 1660 cm⁻¹.

General Procedure for the Preparation of *N*-Heteroaryl Phenyl Ketones (VI) — A 60% oil dispersion of NaH (0.04 g, 1 mmol) was washed with hexane, to which II (1 mmol) in dry THF (10 ml) was added, and the mixture was stirred for 5 min, until the evolution of hydrogen was ceased. The color of the solution turned to reddish yellow. A current of oxygen was passed into the solution until the color turned to colorless. The solvent was removed under reduced pressure to give the residue, which was diluted with H₂O (10 ml) and the mixture was extracted with CHCl₃. The CHCl₃ solution was dried over MgSO₄ and evaporated. The residue was recrystallized from an appropriate solvent shown in Table III or distilled under reduced pressure to give product (VI). The yields, the melting points, and the spectral data are shown in Tables IV and VII.

Table VII. Spectral Data for VI

No.	Ir (CHCl ₃) cm ⁻¹	¹ H-Nmr (CDCl ₃)	
		δ	(ppm)
VIa	1665	8.74(dd, <i>J</i> =5, <i>J</i> =2, 1H), 8.4-8.0(m, 3H), 7.82(dd, <i>J</i> =7, <i>J</i> =2, 1H), 7.7-7.3(m, 4H)	
VIb	1670	8.77(d, <i>J</i> =6, 2H), 8.0-7.7(m, 2H), 7.5-7.3(m, 5H)	
VIc	1660	8.5-7.3(m)	
VId	1670	8.92(d, <i>J</i> =4, 1H), 8.15(dd, <i>J</i> =5, <i>J</i> =2, 1H), 8.0-7.2(m, 8H), 7.30(d, <i>J</i> =4, 1H)	
VIe	1675	8.44(d, <i>J</i> =6, 1H), 8.4-7.1(m, 10H)	
VI f	1670	8.37(d, <i>J</i> =8, 2H), 8.0-7.1(m, 11H)	
VIg	1680	8.8-8.5(m, 2H), 8.5-7.2(m, 11H)	
VIh	1670	9.27(dd, <i>J</i> =5, <i>J</i> =2, 1H), 8.5-8.0(m, 3H), 7.8-7.0(m, 4H)	
VIi	1675	9.53(s, 1H), 9.50(d, <i>J</i> =2, 1H), 8.0-7.5(m, 6H)	
VIj	1680	8.89(d, <i>J</i> =5, 2H), 8.1-7.9(m, 2H), 7.6-7.2(m, 4H)	
VIk	1680	9.32(d, <i>J</i> =2, 1H), 8.96(d, <i>J</i> =5, 1H), 8.3-8.1(m, 2H), 7.91(dd, <i>J</i> =5, <i>J</i> =2, 1H), 7.7-7.4(m, 3H)	
VIl	1670	9.22(d, <i>J</i> =2, 1H), 8.72(d, <i>J</i> =3, 1H), 8.57(dd, <i>J</i> =3, <i>J</i> =2, 1H), 8.3-8.0(m, 2H), 7.6-7.3(m, 3H)	
VI m	1670	9.36(s, 1H), 8.8-8.6(m, 1H), 8.1-7.3(m, 8H)	
VI n	1670	9.66(s, 1H), 8.4-7.8(m, 6H), 7.7-7.3(m, 3H)	
VI o	1680	9.76(s, 1H), 8.6-7.2(m, 9H)	
VI p	1675	9.33(s, 1H), 8.3-7.1(m, 9H)	
VI q	1660	9.50(s, 1H), 8.4-7.5(m, 9H)	

Table VIII. Analytical Data for All New Compounds

No.	Formula	Analysis (%)			No.	Formula	Analysis (%)		
		Calcd (Found)					Calcd (Found)		
		C	H	N			C	H	N
IV	$C_{16}H_{13}N_3O$	72.99 (73.17)	4.98 (4.87)	15.96 (15.79)	IIz	$C_{16}H_{11}N_5$	70.32 (70.37)	4.06 (3.92)	25.63 (25.45)
Iw	$C_{16}H_{13}N_3O$	72.99 (73.26)	4.98 (4.96)	15.96 (16.09)	IIIs	$C_{10}H_{12}N_4O_2$	54.54 (54.27)	5.49 (5.29)	25.44 (25.25)
Iz	$C_9H_8N_4O$	57.44 (57.66)	4.28 (4.19)	29.77 (30.01)	IIIx	$C_{12}H_{10}N_4O_2$	59.50 (59.36)	4.16 (3.95)	23.13 (23.07)
IIg	$C_{21}H_{14}N_2$	85.69 (85.41)	4.79 (4.72)	9.52 (9.35)	IIIz	$C_{13}H_{11}N_5O_2$	57.99 (57.90)	4.12 (4.14)	26.01 (26.15)
IIIi	$C_{12}H_9N_3$	73.83 (73.73)	4.65 (4.63)	21.53 (21.61)	IVs	$C_8H_7N_5$	55.48 (55.24)	4.07 (4.25)	40.44 (40.19)
IIIj	$C_{12}H_9N_3$	73.83 (74.11)	4.65 (4.65)	21.53 (21.29)	IVt	$C_{13}H_9N_5$	66.37 (66.40)	3.86 (3.74)	29.77 (30.02)
IIIk	$C_{12}H_9N_3$	73.83 (73.98)	4.65 (4.57)	21.53 (21.36)	IVu	$C_{18}H_{11}N_5$	72.72 (72.60)	3.73 (3.56)	23.56 (23.35)
IIIo	$C_{16}H_{11}N_3$	78.35 (78.34)	4.52 (4.46)	17.13 (17.12)	IVw	$C_{18}H_{11}N_5$	72.72 (72.67)	3.73 (3.56)	23.56 (23.42)
IIIr	$C_{23}H_{16}N_4$	79.29 (79.12)	4.63 (4.42)	16.08 (16.05)	IVx	$C_{10}H_{10}N_5$	61.54 (61.13)	2.58 (2.78)	35.88 (35.92)
IIIs	$C_{13}H_{12}N_4$	69.62 (69.82)	5.39 (5.28)	24.99 (24.94)	Vx	$C_{14}H_{15}N_3O_4$	58.13 (58.09)	5.23 (5.28)	14.53 (14.43)
IIIt	$C_{18}H_{14}N_4$	75.50 (75.79)	4.93 (4.89)	19.57 (19.63)	VIg	$C_{20}H_{13}NO$	84.78 (84.76)	4.62 (4.48)	4.94 (4.94)
IIU	$C_{23}H_{16}N_4$	79.29 (78.87)	4.63 (4.56)	16.08 (15.77)	VIi	$C_{11}H_8N_2O$	71.73 (71.94)	4.38 (4.30)	15.21 (15.22)
IIv	$C_{23}H_{16}N_4$	79.29 (79.22)	4.63 (4.46)	16.08 (16.27)	VIk	$C_{11}H_8N_2O$	71.73 (71.88)	4.38 (4.34)	15.21 (14.97)
IIx	$C_{15}H_{10}N_4$	73.15 (73.04)	4.09 (4.03)	22.75 (22.30)	VIIm	$C_{15}H_{10}N_2O$	76.91 (77.04)	4.30 (4.05)	11.96 (11.78)
IIy	$C_{15}H_{10}N_4$	73.15 (72.97)	4.09 (4.06)	22.75 (22.72)	VIo	$C_{15}H_{10}N_2O$	76.91 (76.98)	4.30 (4.34)	11.96 (11.82)

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