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The Generation of Iminium Ions Using Chlorosilanes and their Reactions with Electron Rich Aromatic Heterocycles

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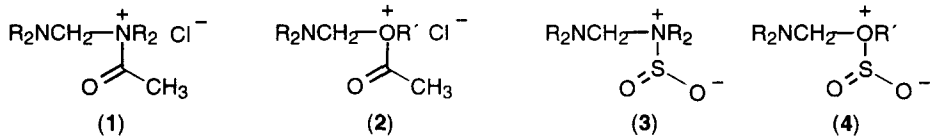
Abstract: Dichlorodimethylsilane and trichloromethylsilane have been used to generate iminium ions from aminals and aminol ethers derived from secondary alkylamines , including glycine derivatives, in aprotic media which were shown to undergo reactions with electron rich aromatic heterocycles, including furan, to give mono-aminoalkylation products in good yields. Whereas chlorotrimethylsilane has been shown to generate iminium ions from aminol ethers, no evidence was adduced for the involvement of iminium ions using aminals. 2,5-Disubstitution of *N*-methylpyrrole was the major result in reactions of *N*-methylpyrrole with aminals in the presence of chlorotrimethylsilane where no build up of hydrogen chloride occurs and where chlorotrimethylsilane can function catalytically. Experimental results, including the use of bis(trimethylsilyl)acetamide as a proton scavenger, and some relative rate data, are presented that allow possible mechanisms to be evaluated.

INTRODUCTION

Mannich reactions carried out under classical aqueous reaction conditions may proceed *via* a number of mechanistic pathways depending on the nucleophilicity of the substrate and more particularly on the pH of the solvent system.[1] The general consensus is that iminium salts are the electrophiles under acidic conditions but that aminals may be involved at high pH's and aminol ethers are possible intermediates in alcoholic media. The failure of an attempted Mannich reaction may be attributed either to the weak electrophilicity of the particular intermediate involved or conversely to the low nucleophilicity of the substrate. *N*-Methylpyrrole does not react with formaldehyde and free amines at room temperature[2] but when amine hydrochlorides are used Mannich bases are formed rapidly.[3] Similarly, although 2-methylfuran affords good yields of Mannich bases, furan does not react under aqueous acidic conditions.[4] Iminium salts may be prepared by a number of methods including the reactions of acetyl chloride with aminals,[5] or trifluoroacetic anhydride with *N*-oxides,[6] and trichloromethylsilane with aminol ethers,[7] and we showed that preformed iminium salts give good yields of Mannich bases with both furan and 2-methylfuran in acetonitrile at room temperature.[8]

As part of our investigation of new protocols we concentrated on Mannich reactions carried out in aprotic solvents without the isolation of reactive intermediates. We suggested that the acyl "onium" salts (**1**) and (**2**), rather than free iminium ions, are potential reactive intermediates in "one pot" reactions of *N*-methylpyrrole with aminals or aminol ethers activated by acetyl chloride.[9] We also argued that when strongly nucleophilic aromatic heterocycles are allowed to react with aminals or aminol ethers in the presence of sulphur dioxide, the dipolar species (**3**) and (**4**) respectively, may be the electrophilic intermediates. Intermediates such as (**4**) are evidently weaker than iminium species in that no Mannich base was formed in an attempted reaction of furan with ethoxy-*N*-pyrrolidinylmethane in the presence of sulphur dioxide.[9]



(1) (2) (3) (4)

A number of nucleophilic aromatic heterocycles are unstable in the presence of mineral acids and in order to improve the applicability of the aminoalkylation of aromatic heterocycles in "one-pot" systems, we set ourselves an objective to devise reaction conditions in which strong acids, such as hydrogen chloride, were not produced. The use of iodotrimethylsilane for the generation of Eschenmoser's salt[10] from bis(dimethylamino)methane[11] and the preparation of iminium chlorides from aminol ethers and trichloromethylsilane,[7] suggested that it would be profitable to use chlorosilane derivatives as mild acid chlorides. The present paper gives a detailed account of our work on *in situ* Mannich reactions using aminals and aminol ethers in the presence of chlorosilanes,[12] and provides further evidence for the involvement of different reactive intermediates when aminals are activated by chlorotrimethylsilane. The catalytic effect of chlorotrimethylsilane in this system is further substantiated.

RESULTS AND DISCUSSION

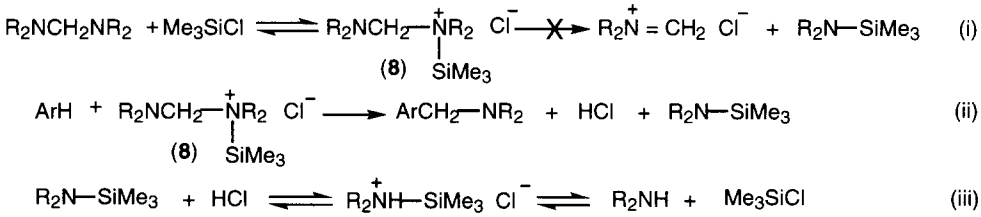
We prepared the aminals (**5a-e**)[13] by the condensation of secondary amines and aqueous formaldehyde as well as a series of aminol ethers (**6a-h**),[8] by the condensation of secondary amines and paraformaldehyde in dry alcohols in the presence of anhydrous potassium carbonate. Higher boiling products were formed in the latter reactions which resulted in the reduction of the yields of the desired products. In two cases the alkoxymethoxy-*N,N*-dialkylaminomethanes (**7a**) and (**7b**) were isolated and characterised. Like previous workers,[14] we were not able to prepare the corresponding aminal from di-isopropylamine. However, the aminol ether (**6h**) was isolated in 67% yield from di-isopropylamine, ethanol, and paraformaldehyde.

$R_2NCH_2NR_2$	R_2NCH_2OR'	$R_2NCH_2OCH_2OR'$
(**5 a**) $R_2 = Me_2$	(**6 a**) $R_2 = Me_2$; $R' = Et$	(**7 a**) $R_2 = Et_2$; $R' = Et$
(**5 b**) $R_2 = Et_2$	(**6 b**) $R_2 = Me_2$; $R' = {}^iPr$	(**7 b**) $R_2 = Et_2$; $R' = {}^iPr$
(**5 c**) $R_2 = (CH_2)_4$	(**6 c**) $R_2 = Et_2$; $R' = Et$	
(**5 d**) $R_2 = (CH_2)_5$	(**6 d**) $R_2 = Et_2$; $R' = {}^iPr$	
(**5 e**) $R_2 = O(CH_2CH_2)_2$	(**6 e**) $R_2 = (CH_2)_4$; $R' = Et$	
	(**6 f**) $R_2 = (CH_2)_5$; $R' = Et$	
	(**6 g**) $R_2 = O(CH_2CH_2)_2$; $R' = Et$	
	(**6 h**) $R_2 = {}^iPr_2$; $R' = Et$	

Nmr spectroscopy indicated that iminium salts are formed when solutions of aminol ethers in deuterio-acetonitrile-sulphur dioxide were treated with trichloromethylsilane, dichlorodimethylsilane, and chlorotrimethylsilane. The methylene carbon signal was typically observed as a triplet in the broad band ^1H-decoupled spectrum due to spin-spin coupling to ^{14}N. Thus, when a solution of ethoxy-*N,N*-(diethylamino)methane in deuterio-acetonitrile-sulphur dioxide was treated with 1 mol. equivalent of dichlorodimethylsilane, the broad band decoupled spectrum was immediately changed and showed three resonances at δ_C = 12.5 (s), 55.0 (t, J = 3.5 Hz) and 165.4 (t, J = 13.5 Hz) ppm. On the other hand, although the formation of iminium salts was indicated when aminals were treated with either trichloromethylsilane or dichlorodimethylsilane, iminium ions were not

observed when using chlorotrimethylsilane. However, the addition of 1 mol. equivalent of *N*-methylpyrrole to the nmr solutions resulted in the rapid appearance of absorptions due to the related 2-(dialkylaminomethyl)-1-methylpyrrole, even when using mixtures of aminals and chlorotrimethylsilane.

It is well known that secondary amines can be protected as their trialkylsilyl derivatives and like the trialkylsilyl derivatives of hydroxy compounds can be regenerated by reaction with a nucleophile in the presence of a proton source. The important difference between silylated amines and the analogous silyl ethers relates to the strength of Si-O and Si-N bonds. The lack of iminium salt formation in the reactions of aminals with chlorotrimethylsilane suggests that low equilibrium concentrations of quaternary silylammonium salts (**8**) are formed which may not break down to the iminium salts [reaction (i)]. In the presence of a nucleophile the unstable quaternary silylammonium salts (**8**) react rapidly forming Mannich bases and trialkylsilylamines. The hydrogen chloride generated in the reaction mixture is captured by trialkylsilylamines which then collapse to the free amines and regenerate chlorotrimethylsilane [reactions (ii) and (iii)]. It is known that the majority of quaternary silylammonium salts are unstable,[15] except those possessing non-nucleophilic counter ions such as $[Co(CO)_4]^-$.[16]

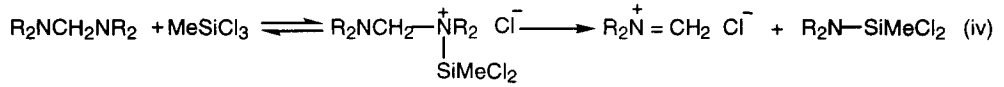


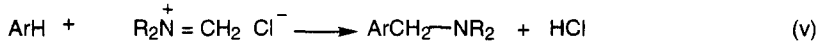
If the above mechanism operates the reaction should be catalytic with respect to chlorotrimethylsilane. Our initial investigations were carried out using equimolar amounts of *N*-methylpyrrole, bis(dimethylamino)methane, and chlorotrimethylsilane in acetonitrile at room temperature. It was found, however, that the predominant product was the disubstitution material, 2,5-bis-(dimethylaminomethyl)-1-methylpyrrole (**10a**). Subsequent reactions using other aminals under various lengths of time gave also the 2,5-disubstitution products (**10b-e**) exclusively or predominantly. We argued that the amount of chlorotrimethylsilane in the reaction should not be critical and we therefore used catalytic amounts. The yields of both products obtained in room temperature reactions were lower but they were significantly improved when the reaction mixtures were heated under reflux.

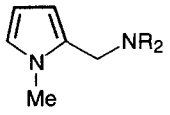
We also carried out reactions of *N*-methylpyrrole with aminals in the presence of trichloromethylsilane and dichlorodimethylsilane which gave the monosubstitution products (**9a-e**) almost exclusively. In these reactions iminium salts are involved and the monosubstitution products are formed as amine hydrochlorides which must be significantly less nucleophilic than the starting materials. However, in the cases using chlorotrimethylsilane, a build up of free hydrogen chloride does not occur and the initial products are formed as free amines. These are more nucleophilic than the starting material and therefore react further affording the 2,5-disubstitution products. This methodology was also applied in the preparation of 2-dialkylaminomethyl derivatives of furan (**11a-b**) and 2-methylfuran (**12a-b**), 2,5-bis(dimethylaminomethyl)pyrrole (**13**), 3-dimethylaminomethylindole (**14**), and 3-dialkylaminomethyl derivatives of 1-methylindole (**15a-c**). The results obtained are recorded in Table 1.

In the reactions in which we used dichlorodimethylsilane or trichloromethylsilane we conclude that the fragmentation that is presumed not to occur as shown in equation (i), is facilitated by the presence of chlorine

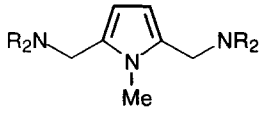
atoms on silicon which render the silicon more electrophilic and hence weaken the nitrogen to carbon bond in the chlorosilylated aminal, as shown in equation (iv). By similar reasoning we also conclude that a dichloromethylsilylamine will be less basic than a trimethylsilylamine and so will not function to remove hydrogen chloride as shown in equation (iii). Thus a build up of hydrogen chloride will occur as the aminoalkylation reactions proceed and protonation of the Mannich base will occur as shown in equation (vi). Any catalytic effect that might be observed would, no doubt, relate to the presence of hydrogen chloride in the reaction mixtures.



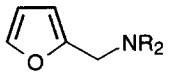




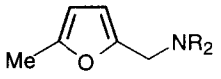
(**9 a**) $R_2 = Me_2$ (**9 d**) $R_2 = (CH_2)_5$
(**9 b**) $R_2 = Et_2$ (**9 e**) $R_2 = O(CH_2CH_2)_2$
(**9 c**) $R_2 = (CH_2)_4$ (**9 f**) $R_2 = {}^iPr_2$



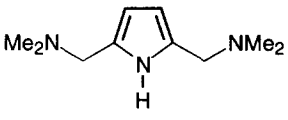
(**10 a**) $R_2 = Me_2$ (**10 d**) $R_2 = (CH_2)_5$
(**10 b**) $R_2 = Et_2$ (**10 e**) $R_2 = O(CH_2CH_2)_2$
(**10 c**) $R_2 = (CH_2)_4$ (**10 f**) $R_2 = {}^iPr_2$



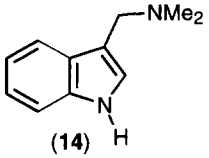
(**11 a**) $R_2 = (CH_2)_4$
(**11 b**) $R_2 = (CH_2)_5$



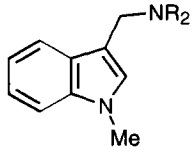
(**12 a**) $R_2 = (CH_2)_4$
(**12 b**) $R_2 = (CH_2)_5$



(**13**)



(**14**)



(**15 a**) $R_2 = Me_2$ (**15 b**) $R_2 = Et_2$ (**15 c**) $R_2 = O(CH_2CH_2)_2$

As indicated from our preliminary investigations, aminol ethers form iminium salts in reactions with all the chlorosilane derivatives mentioned above. *In situ* reactions were also carried out with a variety of aromatic heterocycles using aminol ethers in the presence of chlorosilanes in acetonitrile at room temperature. The results obtained are given in Table 2. In contrast to the results using aminals, it was noted that in a number of the reactions the mono-aminoalkylation product was predominant in the reactions using *N*-methylpyrrole. These

results reinforce the argument that using aminol ethers the reactions proceed through iminium salts and afford the products as the amine hydrochlorides.

TABLE 1. *In Situ* Reactions of Aminals with Heterocycles and Chlorosilanes

Heterocycle	Aminal	Silane[a] (mol%)	Time (h)	Product(s)	Yield (%)[b]
1-Me-pyrrole	$(Me_2N)_2CH_2$	Me_3SiCl (100)	2	**9a**	20
				10a	40
		Me_3SiCl (100)	24	**10a**	66
		$MeSiCl_3$ (100)	20	**9a**	52
		Me_3SiCl (5)	24	**10a**	63
	$(Et_2N)_2CH_2$	Me_3SiCl (12.5)	24	**10b**	78
	$[(CH_2)_4N]_2CH_2$	$MeSiCl_3$ (100)	116	**9c**	75
		Me_3SiCl (5)	24	**9c**	17
				10c	61
	$[(CH_2)_5N]_2CH_2$	Me_3SiCl (100)	120	**10d**	90
	$[O(CH_2CH_2)_2N]_2CH_2$	Me_3SiCl (12.5)	24	**9e**	24
				10e	40
Furan	$[(CH_2)_5N]_2CH_2$	$MeSiCl_3$ (100)	72	**11b**	18
2-Me-furan	$[(CH_2)_4N]_2CH_2$	$MeSiCl_3$ (100)	48	**12a**	64
		Me_3SiCl (100)	48	**12a**	0
	$(CH_2)_5N]_2CH_2$	$MeSiCl_3$ (100)	72	**12b**	65
Pyrrole	$(Me_2N)_2CH_2$	Me_3SiCl (100)	24	**13**	54
Indole	$(Me_2N)_2CH_2$	Me_3SiCl (100)	65	**14**	73
1-Me-indole	$(Me_2N)_2CH_2$	Me_3SiCl (100)	48	**15a**	63

(a) 100 mol% at room temperature and using catalytic amounts under reflux. (b) Yields based on aminal-heterocycle ratio = 1:1.

It is of interest to note that furan, the least nucleophilic substrate, afforded 18% of the Mannich base (**11b**) from a reaction of di-*N*-piperidinylmethane and trichloromethylsilane, but 2-methylfuran, albeit being a stronger nucleophile, gave no Mannich base in a reaction with di-*N*-pyrrolidinylmethane and chlorotrimethylsilane. However, when trichloromethylsilane was used in the latter reaction 64% of the Mannich base (**12a**) was obtained. On the other hand both furan and 2-methylfuran gave good yields of Mannich bases in reactions of

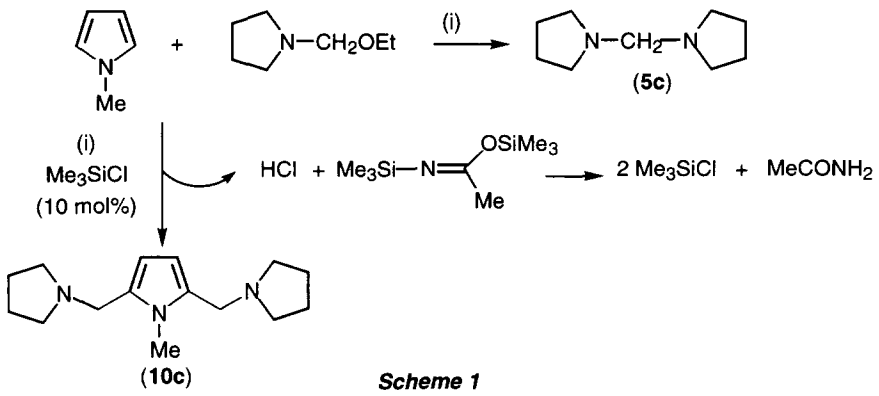
aminol ethers and chlorosilanes. This suggests that the weak nucleophiles only form Mannich bases in systems that proceed *via* the iminium species whereas stronger nucleophiles such as pyrroles and indoles react, even with less electrophilic intermediates, to give good yields of Mannich bases. These observations strengthen the argument that different mechanisms operate in the reactions involving aminals and chlorosilanes.

TABLE 2. *In Situ* Reactions of Aminol Ethers with Heterocycles and Chlorosilanes

Heterocycle	Aminol Ether	Silane[a]	Time (h)	Product(s)	Yield (%)[b]
1-Me-pyrrole	Me_2NCH_2OEt	Me_3SiCl	24	**9a**	21.5
				10a	18.5
	Et_2NCH_2OEt	Me_3SiCl	24	**9b**	23
				10b	49
	$Et_2NCH_2OPr^i$	$MeSiCl_3$	17	**9b**	67
				10b	20
	$Et_2NCH_2OCH_2OPr^i$	$MeSiCl_3$	24	**9b**	55
				10b	25
	$(CH_2)_5NCH_2OEt$	Me_3SiCl	24	**9d**	47
				10d	43
	$^iPr_2NCH_2OEt$	$MeSiCl_3$	68	**9f**	42
				10f	28
Furan	$(CH_2)_4NCH_2OEt$	Me_2SiCl_2	48	**11a**	67
2-Me-furan	$(CH_2)_4NCH_2OEt$	Me_3SiCl	48	**12a**	86
1-Me-indole	$Et_2NCH_2O^iPr$	$MeSiCl_3$	20	**15b**	89
	$O(CH_2CH_2)_2NCH_2OEt$	$MeSiCl_3$	20	**15c**	93

(a) Equimolar amount of silane was used. (b) Yields based on heterocycle-aminol ether ratio = 1:1

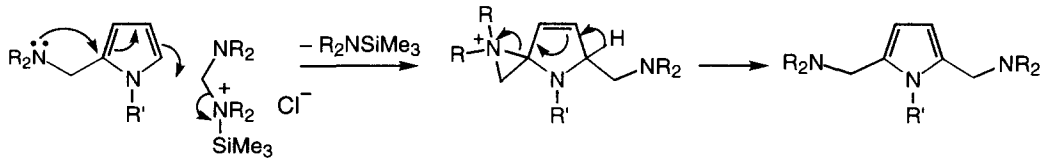
It was possible that the hydrogen chloride generated in the reaction mixtures, as shown in equation (ii), was directly responsible for the propagation of the reactions and hence for the (apparent) catalysis in the reactions in which we used chlorotrimethylsilane. In order to exclude that possibility we carried out reactions in the presence of the proton scavenger bis(trimethylsilyl)acetamide. Duplicate reactions of *N*-methylpyrrole and ethoxy-*N*-pyrrolidinylmethane with a half mole equivalent of bis(trimethylsilyl)acetamide in acetonitrile at room temperature were carried out, as shown in Scheme 1. In the first reaction 10 mol% of chlorotrimethylsilane was also added and gave the disubstitution product 2,5-bis(pyrrolidinylmethyl)-1-methylpyrrole (**10c**) in 52% yield. In the other reaction no chlorotrimethylsilane was added and no Mannich base was isolated. The latter result showed that the powerful silylating agent bis(trimethylsilyl)acetamide did not react with the aminol ether.



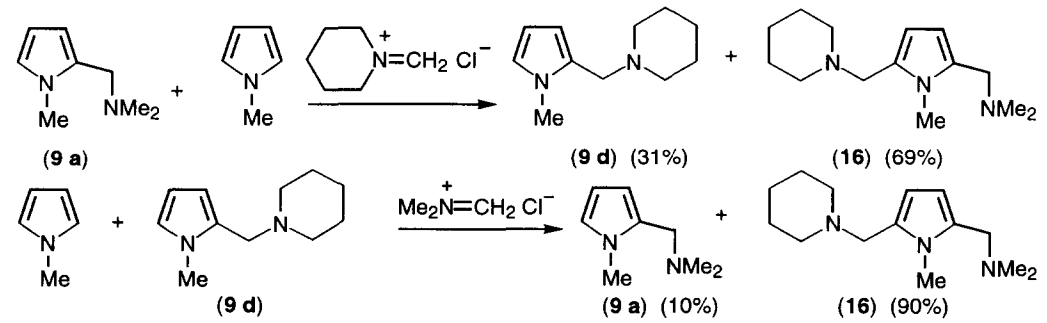
Scheme 1

(i) bis(trimethylsilyl)acetamide (0.5 mol%), MeCN, RT, N_2

It is known that alkyl pyrroles are more reactive towards electrophiles than pyrrole itself.[17] Whereas the nitrogen atom in a protonated Mannich base would have a net electron withdrawing effect on the electron density in the pyrrole ring, it is possible that the aminomethyl moiety of 2-dialkylaminomethylpyrroles, in the free base form, exerts a homoconjugative mesomeric effect increasing the electron density of the ring as shown below.



We also sought estimates of the relative rates of the reactions of 1-methylpyrrole and 2-aminoalkylated-1-methylpyrrole towards iminium salts. Thus, a 50 molar excess of *N*-methylpyrrole and a mono-substituted Mannich base were allowed to compete for a preformed iminium salt and the ratio of products isolated was determined by gas chromatography. The results suggest that the Mannich base (**9d**) is about 9 times more reactive than *N*-methylpyrrole. Although these findings support the results obtained from the preparative scale reactions they should be treated with caution as any mixing effect could not be taken into account. The mixed aminoalkylated *N*-methylpyrrole (**16**) was prepared from the Mannich base (**9a**) and the appropriate preformed iminium salt in 85% yield.



Different nucleophilicities of aromatic heterocycles have been established using a number of electrophilic systems. Thus, competition data for trifluoroacetylation using trifluoroacetic anhydride at 75 °C gave the relative rates thiophene (1.0), furan (1.4 x 10^2), 2-methylfuran (1.2 x 10^5), 2-methoxythiophene (9.1 x 10^5), pyrrole (5.3 x 10^7), and *N*-methylpyrrole (1.0 x 10^8).[18] Similar values were also obtained for reactions of thiophene (1.0), furan (3.0 x 10^3), and pyrrole (5.0 x 10^5) with $[C_6H_7Fe(CO)_3]^+$.[19]

We also carried out competition experiments of heterocycles with electrophilic intermediates generated *in situ* in order to avoid mixing problems that may have been involved in the earlier experiments. Replicate experiments were performed using a 50 molar excess of two different heterocycles using an aminol ether and trichloromethylsilane or an aminal with chlorotrimethylsilane. The reactions were carried out by adding the silicon reagent to the mixture of the other reactants which were then allowed to react in acetonitrile at room temperature for two hours. The ratio of products formed was determined by gas chromatography. A number of combinations of heterocycles gave results that were unsatisfactory because of the very large differences in the apparent relative rates of the reactions and we record in Table 3 two sets of results. Unfortunately no firm conclusion can be drawn from these results. The most interesting pair of heterocycles used was 2-methoxythiophene and 2-methylfuran. The values quoted for trifluoroacetylation showed that 2-methoxythiophene is about 8 times more reactive than 2-methylfuran. In the experiments reported now, using much weaker electrophiles, the reactivity difference increases to about 110 times in one set of experiments and to about 23 times using the other system.

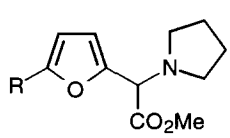
TABLE 3. Ratio of Products in Competition Experiments

Heterocycle Pair	Reagents*	Product Ratio (%)
1-Me-pyrrole : 1-Me-indole	I	58.5 : 41.5
	II	63.5 : 36.5
2-MeO-thiophene : 2-Me-furan	I	99.1 : 0.9
	II	95.9 : 4.1

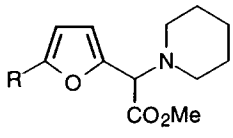
*Reagents: (I) $Me_2NCH_2O^iPr$ / $MeSiCl_3$; (II) $Me_2NCH_2NMe_2$ / Me_3SiCl

That few examples of Mannich reactions have been reported that are based on reactions of aldehydes other than formaldehyde undoubtedly relates to the reduction in reactivity of the already weakly electrophilic iminium species when the methylene group is substituted by an alkyl or aryl residue. On the other hand, a suitably positioned electron withdrawing substituent would result in an increase in reactivity of the type that is well known with acyliminium ions.[20] The presence of a carboxyl group on the iminium carbon atom constitutes such an electron withdrawing group and it is therefore of interest to establish whether Mannich reactions can be used in the synthesis of derivatives of α-amino acids. We report in this paper some preliminary experiments using aminol ethers that were made by reactions of methyl chloromethoxyacetate with secondary amines[21] in order to establish whether arylglycine derivatives could be prepared using our chlorosilane "*in situ*" technology. Some reactions of ketones have already been reported using iminium chlorides which were generated from dialkylaminomethoxyacetamide derivatives by interaction with thionyl chloride.[22] We carried out "*in situ*"

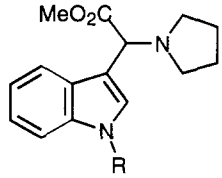
reactions where furan and 2-methylfuran and indole and *N*-methylindole were allowed to react with methyl methoxypyrrolidinylacetate and the piperidinyl analogue in the presence of trichloromethylsilane. We chose to use the monomethyl substituted chlorosilane which was the strongest Lewis acid because we anticipated that the methoxycarbonylmethyleneiminium ions would be at higher energy, and hence more difficult to access, than the other iminium species that we had investigated. We were pleased to obtain yields that were gratifyingly high which suggests that with appropriate changes these reactions could be used to prepare optically pure, non-racemic, arylglycine derivatives. The yields of the eight compounds that we prepared are shown against the structures of the products (**17** - **24**).



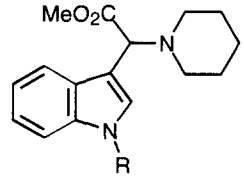
(**17**) R = H; 47%
(**18**) R = Me; 64%



(**19**) R = H; 58%
(**20**) R = Me; 91%



(**21**) R = H; 80%
(**22**) R = Me; 88%



(**23**) R = H; 97%
(**24**) R = Me; 86%

The results reported in this paper confirm that Mannich reactions of derivatives of pyrrole, furan, and indole can be carried out efficiently under aprotic reaction conditions using a wide range of aminals and aminol ethers, including those aminol ethers that generate substituted glycinyl cations. In particular, the anomaly of the apparent failure[4,8] of furan to undergo Mannich reactions is also resolved by the present study.

Acknowledgements
We thank the University for research training awards (to G.P. and R.F.W.) and Dr D.W. Payling (the former Fisons plc) for help in obtaining elemental analyses and some mass spectra.

EXPERIMENTAL

Infrared spectra were recorded on a Perkin-Elmer 257 spectrophotometer. ^{1}H nmr Spectra were recorded on Varian EM 360 A (60 MHz) or Bruker AC-250 (250 MHz) spectrometers and ^{13}C nmr spectra were recorded on Bruker WP 80 (20.1 MHz) together with off resonance decoupling, or Bruker ACF-250 (62.9 MHz) spectrometers in $CDCl_3$ using TMS as reference. *J* Values are given in Hz. Multiplicities are reported as singlet (s), doublet (d), triplet (t), quartet (q), septet (sept.), multiplet (m). Mass spectra were recorded by electron impact using a Kratos (M.S.80) spectrometer or by fast atom bombardment (FAB) using a V.G.70-250 S spectrometer. Melting Points were recorded using a Kofler hot stage apparatus and are uncorrected. Microanalyses were carried out by the former Fisons plc, (Pharmaceutical Division, Loughborough). Gas Chromatography was carried out using a Carlo Erba GC 6000 instrument fitted with a 12 m BPI capillary column at 80 °C using naphthalene as an internal standard.

Preparation of Aminals (**5**) – *General Procedure*

Dialkylamine (2 mol, 40% aqueous solution) was added dropwise to stirred ice-cooled formaldehyde (1 mol, 36% aqueous solution). The mixture was allowed to stand overnight and then saturated with solid potassium

hydroxide. The upper layer was separated, dried over potassium hydroxide pellets and the residual liquid was fractionally distilled.

The following aminals were prepared:

Bis(N,N-dimethylamino)methane (**5a**). Yields (89-92%), b.p. 82-83 °C, (lit.[13] 81.5-83 °C); δ_H (60 MHz) 2.19 (12H, s, CH_3), and 2.66 (2H, s, CH_2) ppm.

Bis(N,N-diethylamino)methane (**5b**). Yields (82-90%), b.p. 47-48 °C/7.5 mmHg, (lit.[23], 166-67 °C); δ_H (60 MHz) 1.00 (12H, t, *J* 7.5, CH_2CH_3), 2.62 (8H, q, *J* 7.5, CH_2CH_3), and 3.05 (2H, s, NCH_2N) ppm; (m/z) 158 (M^+, 0.39%), 86 (100), M^+ measured 158.1765; Calc. for $C_9H_{22}N_2$ 158.1783.

Di(N-pyrrolidinyl)methane (**5c**). Yields (72-85%), b.p. 70 °C/7 mmHg, (lit.[24], 60 °C/3.5 mmHg); δ_H (60 MHz) 1.57-1.98 (8H, m, 3-H and 4-H), 2.38-2.81, (8H, m, 2-H and 5-H), and 3.23 (2H, s, CH_2) ppm; (m/z) 154 (M^+, 59%), 84 (100), M^+ measured 154.1447; Calc. for $C_9H_{19}N_2$ 154.1470.

Di(N-piperidinyl)methane (**5d**). Yields (76-93%), b.p. 100 °C/10 mmHg, (lit.[25], 103-4 °C/14 mmHg); δ_H (60 MHz) 1.39-1.73 (12H, m, 3-H, 4-H, and 5-H), 2.23-2.53 (8H, m, 2-H and 6-H), and 2.77 (2H, s, CH_2) ppm.

Di(N-morpholinyl)methane (**5e**). Yield 76%, b.p. 110 °C/10 mmHg (lit.[26], 99-107 °C/2 mmHg); δ_H (60 MHz) 2.40-2.60 (8H, m, 2-H and 6-H), 2.87 (2H, s, CH_2), and 3.58-3.80 (8H, m, 3-H and 5-H) ppm.

Preparation of Aminol Ethers (**6**)*—General Procedure*

Anhydrous dialkylamine (1 mol), dry alcohol (4 mol), and anhydrous potassium carbonate (1.0 mol) were stirred at 0 °C for 15 minutes. Paraformaldehyde (1.0 mol equiv.) was added in one portion and the mixture was stirred at room temperature for two days. The solid was filtered, washed with dry ether and the filtrate fractionally distilled through an 18" Vigreux column.

The following aminol ethers were prepared:

Ethoxy-N,N-dimethylaminomethane (**6a**). Yield (6.87 g, 15%), b.p. 95 °C, (lit.[27], 123 °C/760 mmHg); δ_H (60 MHz) 1.23 (3H, t, *J* 7.5, OCH_2CH_3), 2.30 (6H, s, NCH_3), 3.43 (2H, q, *J* 7.5, OCH_2CH_3), and 4.13 (2H, s, NCH_2O) ppm.

Isopropoxy-N,N-dimethylaminomethane (**6b**). Yield (25.61 g, 15%), b.p. 98-101 °C; δ_H (60 MHz) 1.17 (6H, d, *J* 6, $CH(CH_3)_2$), 2.33 (6H, s, NCH_3), 3.37-3.93 (1H, sept., *J* 6, $CHMe_2$), and 4.03 (2H, s, NCH_2O) ppm; δ_C (20.1 MHz) 22.5 (q, $CH[CH_3]_2$), 41.6 (q, NCH_3), 69.6 (d, $CHMe_2$), and 87.4 (d, OCH_2N) ppm; (m/z) 117 (M^+, 4.1%), 45 (100), M^+ measured 117.1144; $C_6H_{15}NO$ requires 117.1153.

Ethoxy-N,N-diethylaminomethane (**6c**). First fraction *title compound* (140.2 g, 54%), b.p. 76-78 °C/80 mmHg, (lit.[23] 132-134 °C/756 mmHg); δ_H (60 MHz) 1.10 (6H, t, *J* 7.5, NCH_2CH_3), 1.27 (3H, t, *J* 7.5, OCH_2CH_3), 2.73 (4H, q, *J* 7.5, NCH_2CH_3), 3.43 (2H, q, *J* 7.5, OCH_2CH_3), and 4.23 (2H, s, NCH_2O) ppm; δ_C (20.1 MHz) 13.4 (q, NCH_2CH_3), 15.5 (q, OCH_2CH_3), 46.6 (t, NCH_2CH_3), 63.3 (t, OCH_2CH_3), and 84.4 (t, NCH_2O) ppm; (m/z) 131(M^+, 18.55%), 86 (100), M^+ measured 131.1298; $C_7H_{17}NO$ requires 131.1310. Second fraction *ethoxymethoxy-N,N-diethylaminomethane* (**7a**) (67.5 g, 19%), b.p. 67-69 °C/20 mmHg; δ_H (60 MHz) 1.10 (6H, t, *J* 7.5, NCH_2CH_3), 1.23 (3H, t, *J* 7.5, OCH_2CH_3), 2.77 (4H, q, *J* 7.5, NCH_2CH_3),

3.63 (2H, q, *J* 7.5, OCH_2CH_3) 4.43 (2H, s, NCH_2O), and 4.73 (2H, s, OCH_2O) ppm; δ_C (20.1 MHz) 13.5 (q, NCH_2CH_3), 15.3 (q, OCH_2CH_3), 45.6 (t, NCH_2CH_3), 63.2 (t, OCH_2CH_3), 82.3 (t, NCH_2O), and 93.3 (t, OCH_2O) ppm.

Isopropoxy-N,N-diethylaminomethane (**6d**). First fraction *title compound* (39.89 g, 55%), b.p. 62-64 °C / 43 mmHg; δ_H (60 MHz) 1.07 (6H, t, *J* 7.5, NCH_2CH_3), 1.13 (6H, d, *J* 6, $CH[CH_3]_2$), 2.70 (4H, q, *J* 7.5, NCH_2CH_3), 3.60 (1H, sept., *J* 6, $CHMe_2$), and 4.20 (2H, s, NCH_2O) ppm; δ_C (20.1 MHz) 13.3 (q, NCH_2CH_3), 22.5 (q, $CH[CH_3]_2$), 45.5 (t, NCH_2CH_3), 68.8 (d, $CHMe_2$), and 82.2 (t, NCH_2O) ppm; (m/z) 145 (M^+, 4.2%), 86 (100), M^+ measured 145.1460; $C_8H_{19}NO$ requires 145.1462. Second fraction, *isopropoxymethoxy-N,N-diethylaminomethane* (**7b**) (20.56 g, 23%), b.p. 78 °C/20 mmHg; δ_H (60 MHz) 1.08 (6H, t, *J* 7.5, NCH_2CH_3), 1.13 (6H, d, *J* 6, $CH[CH_3]_2$), 2.67 (4H, q, *J* 7.5, NCH_2CH_3), 3.87 (1H, sept., $CHMe_2$), 4.37 (2H, s, NCH_2O), and 4.70 (2H, s, OCH_2O) ppm; δ_C (20.1 MHz) (13.3, q, NCH_2CH_3), 22.6 (q, $CH[CH_3]_2$), 45.4 (t, NCH_2CH_3), 68.7 (d, $CHMe_2$), 82.1 (t, NCH_2O), and 91.3 (t, OCH_2O) ppm; (m/z) 175 (M^+, 0.11%), 86 (100), M^+ measured 175.1555; $C_9H_{21}NO$ requires 175.1567.

Ethoxy-N-pyrrolidinylmethane (**6e**). Yield (168.9 g, 66%), b.p. 42-44 °C/16 mmHg; δ_H (60 MHz) 1.23 (3H, *J* 7.5, CH_2CH_3), 1.55-1.92 (4H, m, 3-H and 4-H), 2.56-2.94 (4H, m, 2-H and 5-H), 3.53 (2H, q, *J* 7.5, CH_2CH_3), and 4.24 (2H, s, OCH_2) ppm; (m/z) 129 (M^+, 10.9%), 84 (100) M^+ measured 129.1125; $C_7H_{15}NO$ requires 129.1154.

Ethoxy-N-piperidinylmethane (**6f**). Yield (81.66 g, 57%), b.p. 62-64 °C /10 mmHg, (lit.[27], b.p. 101 °C/25 mmHg); δ_H (60 MHz) 1.17 (3H, t, *J* 7.5, CH_2CH_3), 1.37-1.63 (6H, m, 3-H, 4-H, and 5-H), 2.27-2.80 (4H, m, 2-H and 6-H), 3.37 (2H, q, *J* 7.5, OCH_2CH_3), and 3.95 (2H, s, NCH_2O) ppm; (m/z) 143 (M^+, 9.9%), 98 (100), M^+ measured 143.1279; Calc. for $C_8H_{17}NO$ 143.1310.

Ethoxy-N-morpholinylmethane (**6g**). Yield (181.54 g, 61%), b.p. 72-74 °C /9 mmHg, (lit.[28], b.p. 58-63 °C/6 mmHg); δ_H (250 MHz) 1.20 (3H, t, *J* 6.97, CH_2CH_3), 2.48-2.52 (4H, m, C-2 and 6-H), 3.52 (2H, q, *J* 6.97, OCH_2CH_3), 3.68-3.77 (4H, m, C-3 and 5-H), and 4.04 (2H, s, NCH_2O) ppm.

Ethoxy-N,N-di-iso-propylaminomethane (**6h**). Yield (42.69 g, 67%) b.p. 42 °C/5 mmHg, (lit.[27], b.p. 81 °C/25 mmHg); δ_H (60 MHz) 1.11 (12H, d, *J* 6, $CH[CH_3]_2$), 1.17 (3H, t, *J* 7.5, CH_2CH_3), 3.15 (2H, sept., *J* 6, $CHMe_2$), 3.37 (q, *J* 7.5, CH_2CH_3), and 4.23 (2H, s, NCH_2O) ppm; δ_C (20.1 MHz) 15.5 (q, CH_2CH_3), 22.3 (q, $CH[CH_3]_2$), 48.7 (d, $CHMe_2$), 61.4 (t, CH_2CH_3), and 79.6 (t, NCH_2O) ppm; (m/z) M^+ measured 159.1612; Calc. for $C_9H_{21}NO$ 159.1623.

In Situ Reactions of Aminals or Aminol Ethers with Heterocycles and Chlorosilanes—General Method

A chlorosilane derivative (1 equiv. or a catalytic amount) was added to a mixture of a heterocycle (1 equiv.) and an aminal or aminol ether (1 equiv.) in acetonitrile at 0 °C under dry nitrogen. The reaction mixture was stirred at room temperature (1 equiv. of chlorosilane) or heated under reflux (catalytic amount of chlorosilane) for a specified length of time, quenched with water and concentrated *in vacuo* . The residue was acidified to pH2 with 2M HCl when necessary, washed with dichloromethane (3x30 ml) and then basified to pH14 with 4M NaOH and washed with dichloromethane (4x40 ml). The combined organic extracts from the basic solution were dried ($MgSO_4$), concentrated *in vacuo*, and the residue was distilled (Kugelrohr) or recrystallised from a suitable solvent.

Reaction of N-Methylpyrrole with Bis(N,N-dimethylamino)methane and Chlorotrimethylsilane

Chlorotrimethylsilane (2.99 g, 27.5 mmol), *N*-methylpyrrole (2.23 g, 27.5 mmol) and bis(*N,N*-dimethylamino)-methane (2.56 g, 25 mmol) in acetonitrile (150 ml) for 2 h gave after Kugelrohr distillation two fractions. The first fraction was shown to be 2-(N,N-dimethylaminomethyl)-1-methylpyrrole (**9a**) (0.69 g, 20%) b.p. 58 °C / 5 mmHg, (lit.[3], 53-54 °C/6 mmHg); ν_{max} (film) 1635 (aromatic ring) cm^{-1}; δ_H (60 MHz) 2.16 (6H, s, $N[CH_3]_2$), 3.29 (2H, s, CH_2), 3.57 (3H, s, NCH_3), 5.96-6.07 (2H, m, 3-H and 4-H), and 6.45-6.56 (1H, m, 5-H) ppm; δ_C (20.1 MHz) 33.5 (q, NCH_3), 44.7 (q, $N[CH_3]_2$), 55.7 (t, CH_2), 106.4 (d, C-3), 109.3 (d, C-4), 122.4 (d, C-5), and 129.8 (s, C-2) ppm; (m/z) M^+ 138.1149; Calc. for $C_8H_{14}N_2$ 138.1157. The second fraction was shown to be 2,5-bis(N,N-dimethylaminomethyl)-1-methylpyrrole (**10a**) (0.98 g, 40%), b.p. 87 °C/3.5 mmHg, (lit.[3], 87-88 °C/3.5 mmHg); δ_H (60 MHz) 2.21 (12H, s, $N[CH_3]_2$), 3.39 (4H, s, NCH_2), 3.67 (3H, s, NCH_3), and 5.87 (2H, s, 3-H and 4-H) ppm; δ_C (20.1 MHz) 30.2 (q, NCH_3), 44.8 (q, $N[CH_3]_2$), 56.1 (t, CH_2), 107.7 (d, C-3 and C-4), and 130.3 (s, C-2 and C-5) ppm; (m/z) M^+ 195.1731, Calc. for $C_{11}H_{21}N_3$ 195.1735.

Reaction of N-methylpyrrole with Isopropoxy-N,N-diethylaminomethane and Trichloromethylsilane

Trichloromethylsilane (4.11 g, 27.5 mmol), *N*-methylpyrrole (2.23 g, 27.5 mmol) and isopropoxy-*N,N*-diethyl-aminomethane (3.63g, 25 mmol) in acetonitrile (125 ml) for 17 h afforded after Kugelrohr distillation two fractions. The first fraction was shown to be 2-(N,N-diethylaminomethyl)-1-methylpyrrole (**9b**) (2.79 g, 67%), b.p. 70 °C/3.5 mmHg, (lit.[3] 77-77 °C/6 mmHg); δ_H (60 MHz) 0.99 (6H, t, *J* 7.5, $N[CH_2CH_3]_2$), 2.51 (4H, q, *J* 7.5, $N[CH_2CH_3]_2$), 3.49 (2H, s, NCH_2), 3.63 (3H, s, NCH_3), 5.98-6.09 (2H, m, 3-H and 4-H), and 6.50-6.67 (1H, m, 5-H) ppm; δ_C (20.1 MHz) 11.8 (q, NCH_2CH_3), 33.7 (q NCH_3), 46.5 (t, NCH_2CH_3), 50.0 (t, CH_2N), 106.3 (d, C-3), 109.3 (d, C-4), 122.2 (d, C-5), and 130.1 (s, C-2) ppm; (m/z) M^+166.1462; Calc. for $C_{10}H_{18}N_2$ 166.1470. The second fraction was shown to be *2,5-bis(N,N-diethylaminomethyl)-1-methylpyrrole* (**10b**) (0.63 g, 20%), b.p. 100 °C/0.2 mmHg; δ_H (60 MHz) 0.99 (12H, t, *J* 7.5, $N[CH_2CH_3]_2$), 2.49 (8H, q, *J* 7.5, $N[CH_2CH_3]_2$), 3.50 (4H, s, NCH_2), 3.63 (3H, s, NCH_3), and 5.83 (2H, s, 3-H and 4-H) ppm; δ_C (20.1 MHz) 11.8 (q, NCH_2CH_3), 30.7 (q, NCH_3), 46.6 (t, NCH_2CH_3), 50.4 (t, CH_2N), 107.6 (d, C-3 and C-4), and 130.6 (s, C-2 and C-5) ppm; (m/z) M^+ 251.2355; $C_{15}H_{29}N_3$ requires 251.2361.

Reaction of N-methylpyrrole with Di(N- pyrrolidinyl)methane and Chlorotrimethylsilane

Chlorotrimethylsilane (0.22 g, 2 mmol), *N*-methylpyrrole (3.24g, 40 mmol) and di(*N*-pyrrolidinyl)methane (6.17g, 40 mmol) in acetonitrile (150 ml) under reflux for 24 h afforded after Kugelrohr distillation two fractions. First fraction *2-(N-pyrrolidinylmethyl)- 1-methylpyrrole* (**9c**) (1.12 g, 17%), b.p. 100 °C/4 mmHg; δ_H (60 MHz) 1.50-1.87 (4H, m, 3′-H and 4′-H), 2.30-2.70 (4H, m, 2′-H and 5′-H), 2.55 (2H, s, NCH_2), 2.63 (3H, s, NCH_3), 5.93-6.06 (2H, m, 3-H and 4-H), and 6.47-6.60 (1H, m, 5-H) ppm; δ_C (20.1 MHz) 23.6 (t, C-3′and C-4′), 33.5 (q, NCH_3), 51.8 (t, NCH_2), 53.8 (t, C-2′ and C-5′), 106.3 (d, C-3), 108.4 (d, C-4), 121.9 (d, C-5), and 130.4 (s, C-2) ppm; (m/z) 164 (M^+, 11.6%), 94 (100), M^+ 164.1300; $C_{10}H_{16}N_2$ requires 164.1313. Second fraction *2,5-Di(N-pyrrolidinylmethyl)- 1-methylpyrrole* (**10c**) (2.17 g, 70%), b.p. 125 °C/0.5 mmHg; δ_H (60 MHz) 1.57-2.03 (8H, m, 3′-H and 4′-H), 2.23-2.70 (8H, m, 2′-H and 5′-H), 3.55 (4H, s, NCH_2), 3.65 (3H, s, NCH_3), and 5.92 (2H, s, 3-H and 4-H) ppm; δ_C (20.1 MHz) 23.5 (t, C-3′ and C-4′), 30.3 (q, NCH_3), 52.2 (t, NCH_2), 53.8 (t, C-2′ and C-5′), 106.7 (d, C-3 and C-4), and 130.5 (s, C-2 and C-5) ppm; (m/z) 247 (M^+, 21.8%), 177 (100), M^+ 247.2039; $C_{15}H_{25}N_3$ requires 247.2048.

Reaction of N-methylpyrrole with Ethoxy-N-piperidinylmethane and Chlorotrimethylsilane

Chlorotrimethylsilane (2.99 g, 27.5 mmol), *N*-methylpyrrole (3.24g, 40 mmol) and ethoxy-*N*-piperidinyl-methane (3.58 g, 25 mmol) in acetonitrile (125 ml) for 24 h gave after Kugelrohr distillation two fractions. First

fraction *2-(N-piperidinylmethyl)-1-methylpyrrole* (**9d**) (2.09 g, 47%), b.p. 120 °C/5 mmHg, (lit.[3], 97 °C/5 mmHg); δ_H (60 MHz) 1.29-1.70 (6H, m, 3-H′, 4′-H, and 5′-H), 2.22-2.42 (4H, m, 2′-H and 6′-H), 3.32 (2H, s, CH_2), 3.58 (3H, s, NCH_3), 5.86-6.01 (2H, m, 3-H and 4-H), and 6.42-6.52 (1H, m, 5-H) ppm; δ_C (20.1 MHz) 24.7 (t, C-4′), 26.2 (t, C-3′and C-5′), 33.6 (q, NCH_3), 54.3 (t, C-2′ and C-6′), 55.3 (t, CH_2), 106.2 (d, C-3), 109.3 (d, C-4), 122.2 (d, C-5), and 129.4 (s, C-2) ppm; (m/z) M^+ 178.1473; Calc. for $C_{11}H_{18}N_2$ 178.1470. Second fraction *2,5-di(N-piperidinylmethyl)-1-methylpyrrole* (**10d**) (1.48 g, 43%), b.p. 150 °C/0.4 mmHg, (lit.[3], 165-167 °C/3 mmHg); δ_H (250 MHz)1.40-1.56 (12H, m, 3′-H, 4′-H, and 5′-H), 2.30-2.32 (8H, m, 2′-H and 6′-H), 3.36 (4H, s, NCH_2), 3.60 (3H, s, NCH_3), and 5.87 (2H, s, 3-H and 4-H) ppm; δ_C (62.9 MHz) 24.6 (C-4′), 26.1 (C-3′and 5′), 30.6 (NCH_3), 54.2 (C-2′and C-6′), 55.5 (NCH_2), 107.4 (C-3 and C-4), and 129.9 (C-2 and C-5) ppm; (m/z) 275 (M^+, 22.8%), 191 (100), M^+ 275.2363; Calc. for $C_{17}H_{29}N_3$ 275.2361.

Reaction of N-Methylpyrrole with Di(N-morpholinyl)methane and Chlorotrimethylsilane

Chlorotrimethylsilane (0.54g, 5 mmol), *N*-methylpyrrole (3.24 g, 40 mmol) and di(*N*-morpholinyl)methane (7.45 g, 40 mmol) in acetonitrile (150 ml) under reflux for 24 h gave after Kugelrohr distillation *2-(N-morpholinylmethyl)-1-methylpyrrole* (**9e**) (1.71 g, 24%), b.p. 110 °C/3.5 mmHg, (lit.[3], 113-114 °C/5 mmHg); ν_{max} (film) 1630 (aromatic ring) cm^{-1}; δ_H (60 MHz) 2.17-2.46 (4H, m, 3′-H and 5′-H), 3.37 (2H, s, NCH_2), 3.60 (3H, s, NCH_3), 3.44-3.73 (4H, m, 2′-H and 6′-H), 5.87-6.02 (2H, m, 3-H and 4-H), and 6.40-6.55 (1H, m, 5-H) ppm; δ_C (20.1 MHz) 33.0 (q, NCH_3), 52.7 (t, C-3′and C-5′), 54.1 (t, C-2′and C-6′), 66.3 (t, NCH_2O), 105.7 (d, C-3), 109.1 (d, C-4), 121.9 (d, C-5), and 127.5 (s, C-2) ppm; (m/z) M^+ 180.1258; Calc. for $C_{10}H_{16}N_2O$ 180.1263.. The residue was recrystallised from ethyl acetate, giving *2,5-di(N-morpholinylmethyl)-1-methylpyrrole* (**10e**) (2.23 g, 40%), m.p. 70-72 °C; δ_H (60 MHz) 2.24-2.60 (8H, m, 3′-H and 5′-H), 3.41 (4H, s, NCH_2), 3.52-3.86 (8H, m, 2′-H and 6′-H), 3.64 (3H, s, NCH_3), and 5.90 (2H, s, 3-H and 4-H) ppm; δ_C (20.1 MHz) 30.7 (q, NCH_3), 53.4 (t, C-3′and C-5′), 55.2 (t, NCH_2), 67.2 (t, C-2′and C-6′), 108.2 (d, C-3 and C-4), and 129.3 (s, C-2 and C-5) ppm; (m/z) M^+ 279.1951; $C_{15}H_{25}N_3O_2$ requires 279.1947.

Reaction of N-methylpyrrole with ethoxy-N,N-di-isopropylaminomethane and trichloromethylsilane

Trichloromethylsilane (4.11 g, 27.5 mmol), *N*-methylpyrrole (2.23g, 27.5 mmol) and ethoxy-*N,N*-di-isopropylaminomethane (3.98 g, 25 mmol) in acetonitrile (125 ml) for 24 h gave after Kugelrohr distillation two products. The first product *2-(N,N-di-isopropylaminomethyl)-1-methylpyrrole* (**9f**) (2.05 g, 42%), b.p. (90 °C/0.5 mmHg); δ_H (250 MHz) 1.00 (12H, d, *J* 6.8, $CH[CH_3]_2$), 3.01 (2H, sept., *J* 6.8, $CHMe_2$), 3.62 (2H, s, CH_2N), 3.65 (3H, s, NCH_3), 5.96-6.02 (2H, m, 3-H and 4-H), and 6.54-6.55 (1H, m, 5-H) ppm; δ_C (62.9 MHz) 20.3 ($CH[CH_3]_2$), 33.9 (NCH_3), 41.3 (CH_2N), 46.9 ($CHMe_2$, 106.0 (C-3), 109.1 (C-4), 122.1 (C-5), and 130.9 (C-2) ppm; (m/z) 194 (M^+, 6.8%), 94 (100), M^+ 194.1778; $C_{12}H_{22}N_2$ requires 194.1783. The second product *2,5-bis(N,N-di-isopropylaminomethyl)-1-methylpyrrole* (**10f**) (1.17 g, 28%), b.p. 140 °C/0.03 mmHg which crystallised in the Kugelrohr bulb, m.p. 61 °C; δ_C (250 MHz) 0.99 (24H, d, *J* 6.7, $CH[CH_3]_2$), 3.00 (4H, sept. *J* 6.7, $CHMe_2$), 3.61 (4H, s, CH_2N), 3.65 (3H, s, NCH_3), and 5.86 (2H, s, 3-H and 4-H) ppm; δ_C (62.9 MHz) 20.3 ($CH[CH_3]_2$), 30.8 (NCH_3), 41.7 (CH_2N), 46.9 ($CHMe_2$), 107.3 (C-3 and C-4), and 131.2 (C-2 and C-5) ppm; (m/z) 307 (M^+, 15.6%), 207 (100), M^+ 307.2984; $C_{19}H_{37}N_3$ requires 307.2987.

2-(N-pyrrolidinylmethyl)furan (**11a**)

Dichlorodimethylsilane (4.26 g, 33 mmol), furan (2.25g, 33 mmol) and ethoxy-*N*-pyrrolidinylmethane (4.26 g, 30 mmol) in acetonitrile (100 ml) for 48 h gave after Kugelrohr distillation the *title compound* (3.03, 67%), b.p.

67-68 °C/ 3.5 mmHg; δ_H (60 MHz) 1.61-1.96 (4H, m, 3′-H and 4′-H), 2.34-2.71 (4H, m, 2′-H and 5′-H), 3.63 (2H, s, NCH_2), 6.07-6.35 (2H, m, 3-H and 4-H), and 7.27-7.41 (1H, m, 5-H) ppm; δ_C (20.1 MHz) 23.4 (t, C-3′and C-4′), 52.1 (t, NCH_2), 53.9 (t, C-2′and C-5′), 107.5 (d, C-3), 110.0 (d, C-4), 141.8 (d, C-5), and 153.1 (s, C-2) ppm.

2-(N-piperidinylmethyl)furan (**11b**)

Trichloromethylsilane (4.11 g, 25 mmol), furan (1.87g, 27.5 mmol) and di-(*N*-piperidinyl)methane (4.56g, 25 mmol) in acetonitrile (60 ml) for 72 h gave after Kugelrohr distillation the *title compound* (0.74 g, 18%), b.p. 67-68 °C/1 mmHg; δ_H (60 MHz) 1.25-1.79 (6H, m, 3′-H, 4′-H, and 5′-H), 2.25-2.56 (4H, m, 2′-H and 6′-H), 3.49 (2H, s, NCH_2), 6.08-6.38 (2H, m, 3-H and 4-H), and 7.26-7.45 (1H, m, 5-H) ppm; δ_C (20.1 MHz) 24.3 (t, C-4′), 25.9 (t, C-3′and C-5′), 54.2 (t, C-2′ and C-6′), 55.7 (t, NCH_2), 108.5 (d, C-3), 110.0 (d, C-4), 141.9 (d, C-5), and 152.2 (s, C-2) ppm.; (m/z) M^+ 165.1145, $C_{10}H_{15}NO$ requires 165.1154.

5-Methyl-2-(N-pyrrolidinylmethyl)furan (**12a**)

Chlorotrimethylsilane (3.59 g, 33 mmol), 2-methylfuran (2.71g, 33 mmol) and ethoxy-*N*-pyrrolidinyl-methane (4.26g, 30 mmol) in acetonitrile (100 ml) for 48 h gave after Kugelrohr distillation the *title compound* (4.27 g, 86%), b.p. 72-74 °C/2.8 mmHg; δ_H (60 MHz) 1.63-1.95 (4H, m, 3′-H and 4′-H), 2.24 (3H, s, NCH_3), 2.33-2.71 (4H, m, 2′-H and 5′-H), 3.53 (2H, s, NCH_2), 5.71-5.91 (1H, m, 4-H), and 6.00 (1H, d, J_{AB} 3, 3-H) ppm; δ_C (20.1 MHz) 13.5 (q, NCH_3), 23.5 (t, C-3′and C-4′), 52.3 (t, NCH_2), 53.9 (t, C-2′and C-5′), 105.9 (d, C-3), 108.4 (d, C-4), and 151.3 (s, C-2 and C-5) ppm; (m/z) M^+ 165.1145, Calc. for $C_{10}H_{15}NO$ 165.1154.

5-Methyl-2-(N-piperidinylmethyl)furan (**12b**)

Trichloromethylsilane (4.11 g, 27.5 mmol), 2-methylfuran (2.26g, 27.5 mmol) and di-(*N*-piperidinyl)-methane (4.56 g, 25 mmol) in acetonitrile (100 ml) for 72 h gave after Kugelrohr distillation the *title compound* (2.39 g, 67%), b.p. 126-29 °C/4 mmHg (lit.[29], 88-89 °C/6 mmHg); δ_H (60 MHz) 1.27-1.78 (6H, m, 3′-H, 4′-H, and 5′-H), 2.30 (3H, s, NCH_3), 2.30-2.57 (4H, m, 2′-H and 6′-H), 3.42 (2H, s, NCH_2), 5.79-5.96 (1H, m, 4-H), and 6.01 (1H, d, J_{AB} 3, 3-H) ppm.; δ_C (20.1 MHz) 13.6 (q, CH_3), 24.3 (t, C-4′), 25.9 (t, C-3′and C-5′), 54.2 (t, C-2′and C-6′), 55.9 (t, NCH_2), 106.0 (d, C-3), 109.5 (d, C-4), and 150.4 and 151.6 (s, C-2 and C-5) ppm; (m/z) M^+ 179.1298, Calc. for $C_{11}H_{17}NO$ 179.1310.

2,5-Bis(N,N-dimethylaminomethyl)pyrrole (**13**)

Chlorotrimethylsilane (4.89 g, 45 mmol), pyrrole (3.02g, 45 mmol) and bis(*N,N*-dimethylamino)methane (4.60g, 45 mmol) in acetonitrile (150 ml) for 24 h gave after Kugelrohr distillation the *title compound* (4.39 g, 54%), b.p. 95 °C/0.7 mmHg, (lit.[2], 56-8 /2 mmHg); ν_{max} (film) 3140 (NH), 1606 (aromatic ring) cm^{-1}; δ_H (60 MHz) 2.18 (12H, s, $N[CH_3]_2$), 3.38 (4H, s, NCH_2), 5.88 (2H, d, *J* 3, 3-H and 4-H), and 9.80 (1H, br.s, D_2O ex. NH) ppm; δ_C (20.1 MHz) 44.2 (q, $N[CH_3]_2$), 52.3 (t, NCH_2), 107.0 (d, C-3 and C-4), and 128.4 (s, C-2 and C-5) ppm; (m/z) 181 (M^+, 13.9%), 58 (100), M^+ 181.1569; Calc. for $C_{10}H_{19}N_3$ 181.1579.

3-(N,N-Dimethylaminomethyl)indole (**14**)

Chlorotrimethylsilane (2.72 g, 25 mmol), indole (3.22g, 27.5 mmol) and bis(*N,N*-dimethylamino)methane (2.56g, 25 mmol) in acetonitrile (125 ml) for 65 h gave the *title compound* (3.18g, 73%), m.p. 134-135 °C (from acetone) (8.36 g, 96%), (lit.[30] m.p. 134 °C); ν_{max} (Nujol) 3136 (NH), 1616 (aromatic ring) cm^{-1}; δ_H (60 MHz) 2.33 (6H, s, $N[CH_3]_2$), 3.62 (2H, s, CH_2), 6.78-6.89 (1H, m, 2-H), 6.93-7.24 (3H, m, 4-H, 5-H, and

6-H), 7.49-7.80 (1H, m,7-H), and 8.93 (1H, br.s, D_2O ex., NH) ppm; (m/z) 174 (M^+, 25.3%), 130 (100), M^+ 174.1141; Calc. for $C_{11}H_{14}N_2$ 174.1157.

3-(N,N-Dimethylaminomethyl)-1-methylindole (**15a**)

Chlorotrimethylsilane (2.39 g, 22 mmol), *N*-methylindole and bis(*N,N*-dimethylamino)methane (2.04g, 20 mmol) in acetonitrile (120 ml) for 48 h gave after Kugelrohr distillation the *title compound* (2.37 g, 63%) b.p. 98 °C/0.2 mmHg, (lit.[31] b.p. 94-96 °C/0.2 mmHg); δ_H (60 MHz) 2.27 (6H, s, $N[CH_3]_2$), 3.60 (2H, s, NCH_2), 3.63 (3H, s, NCH_3), 6.90 (1H, s, 2-H), 7.00-7.33 (3H, m, 4-H, 5-H, and 6-H), and 7.60-7.83 (1H, m, 7-H) ppm; δ_C (20.1 MHz) 31.5 (q, NCH_3), 44.7 (q, $N[CH_3]_2$), 54.0 (t, NCH_2), 108.5 (d, C-7), 111.3 (s, C-3), 118.4 (d, C-4), 118.9 (d, C-6), 120.9 (d, C-5), 127.5 (d, C-2), 128.8 (s, C-3a), and 136.5 (s, C-7a) ppm; (m/z) 188 (M^+, 19%), 144 (100), M^+ 188.1316; Calc. for $C_{12}H_{16}N_2$ 188.1313.

3-(N,N-diethylaminomethyl)-1-methylindole (**15b**)

Trichloromethylsilane (4.93 g, 33 mmol), *N*-methylindole (3.94 g, 30 mmol) and isopropoxy-*N,N*-diethylaminomethane (4.79 g, 33 mmol) in acetonitrile (150 ml) for 20 h gave after Kugelrohr distillation the *title compound* (5.71 g, 89%), b.p. 126 °C/0.07 mmHg, (lit.[32], hydrochloride salt, m.p. 174 °C); δ_H (60 MHz) 1.07 (6H, t, *J* 7.5, $N[CH_2CH_3]_2$), 2.53 (4H, q, *J* 7.5, $N[CH_2CH_3]_2$), 3.56 (3H, s, NCH_3), 3.73 (2H, s, CH_2N), 6.83 (1H, s, 2-H), 6.92-7.30 (3H, m, 4-H, 5-H, and 6-H), and 7.50-7.80 (1H, m,7-H) ppm; δ_C (20.1 MHz) 12.1 (q, $N[CH_2CH_3]_2$), 32.4 (q, NCH_3), 46.7 (t, $N[CH_2CH_3]_2$), 48.0 (t, CH_2N), 109.0 (d, C-7), 112.3 (s, C-3), 118.9 (d, C-4), 119.7 (d, C-6), 121.5 (d, C-5), 128.1 (d, C-2), 128.6 (s, C-3a), and 137.1 (s, C-7a) ppm; (m/z) 216 (M^+, 17.0%), 144 (100), M^+ 216.1626; Calc. for $C_{14}H_{20}N_2$ 216.1625.

3-(N,N-morpholinylmethyl)-1-methylindole (**15c**)

Trichloromethylsilane (4.11 g, 27.5 mmol), *N*-methylindole (3.28g, 25 mmol) and ethoxy-*N*-morpholinylmethane in acetonitrile (150 ml) for 20 h gave after Kugelrohr distillation the *title compound* (5.36 g, 93%), b.p. 140 °C/0.02 mmHg; δ_H (60 MHz) 2.33-2.57 (4H, m, 2′-H and 6′-H), 3.53-3.83 (4H, m, 3′-H and 5′-H), (3H, s, NCH_3) and (2H, s, CH_2N), 6.90 (1H, s, 2-H), 6.93-7.30 (3H, m, 4-H, 5-H, and 6-H), and 7.53-7.67 (1H, m, 7-H) ppm; δ_C (20.1 MHz) 32.3 (q, NCH_3), 53.5 (t, C-3′and C-5′), 53.9 (t, CH_2N), 67.0 (t, C-2′and C-6′), 109.0 (d, C-8), 110.7 (s, C-3), 119.0 (d, C-4), 119.6 (d, C-6), 121.5 (d, C-5), 128.3 (d, C-2), and s, C-3a), and 137.1 (s, C-7a) ppm; (m/z) 230 (M^+, 11.6%), 144 (100), M^+ 230.1416; $C_{14}H_{18}N_2O$ requires 230.1419.

2-(N,N-Dimethylaminomethyl)-5-(N′-piperidinylmethyl)-1-methylpyrrole (**16**)

Preformed *N*-piperidinyl(methylene)iminium chloride (2.20 g, 16.5 mmol) was added to a solution of 2-(*N,N*-dimethylaminomethyl)-1-methylpyrrole (**9a**) (2.10 g, 15 mmol) in acetonitrile (100 ml) and the mixture was stirred at room temperature under nitrogen for 24 h. After work-up and Kugelrohr distillation the *title compound* was isolated (3.00 g, 85%), b.p. 110 °C/5 mmHg; Found: C, 71.20; H, 10.71; N, 18.15. $C_{14}H_{25}N_3$ requires: C, 71.42; H 10.73; N 17.85%; δ_H (60 MHz) 1.30-1.67 (6H, m, 3′-H, 4′-H, and 5′-H), 2.15 (6H, s, $N[CH_3]_2$), 2.22-2.31 (4H, m, 2′-H and 6′-H), 3.27 (2H, s, CH_2N), 3.31 (2H, s, CH_2N), 3.55 (3H, s, NCH_3), and 5.79 (2H, s, 3-H and 4-H) ppm; δ_C (20.1 MHz) 24.7 (t, C-4′), 26.2 (t, C-3′and C-5′), 30.5 (q, NCH_3), 45.0 (q, $N[CH_3]_2$), 54.3 (t, C-2′and C-6′), 55.7 (t, CH_2NMe_2), 56.1 (t, CH_2N), 107.6 and 107.7 (d, C-3 and C-4), 130.2 and 130.3 (s, C-2 and C-5) ppm; (m/z) 235 (M^+, 8.6%), 151 (100), M^+ 235.2033; $C_{14}H_{25}N_3$ requires 235.2048.

2-(N,N-Dimethylaminomethyl)-5-methoxythiophene

Preformed *N,N*-dimethyl(methylene)iminium chloride (1.03 g, 11 mmol) was added to a solution of 2-methoxythiophene in acetonitrile (50 ml) and the mixture was stirred at room temperature for 20 h. After work-up and Kugelrohr distillation the *title compound* was isolated (1.60 g, 93%), b.p. 105 °C/18 mmHg (lit [33] b.p. 106 °C/15 mmHg). δ_H (250 MHz) 2.25 (6H, s, $N[CH_3]_2$), 3.47 (2H, s, CH_2N), 3.65 (3H, s, OCH_3), 6.0 (1H, d, *J* 3.7), and 6.5 (1H, d, *J* 3.7) ppm; δ_C (62.9 MHz) 44.9 ($N[CH_3]_2$), 59.2 (CH_2N), 60.0 (OCH_3), 102.6 (CH), 123.0 (CH), 128.6 (C), and 165.9 (C) ppm; (m/z) 171 (M^+, 18.7%), 127 (100), M^+ 171.0703; Calc. for $C_8H_{16}NOS$ 171.0718.

Methyl 2-furylpyrrolidinylacetate (**17**)

Trichloromethylsilane (0.82 g, 5.5 mmol), furan (0.37 g, 5.5 mmol), and methyl methoxypyrrolidinylacetate (0.87 g, 5.5 mmol) in acetonitrile (30 ml) for 48 h gave after Kugelrohr distillation the *title compound* (0.49 g, 47%), b.p. 70-73 °C/0.01 mmHg; ν_{max} 2808, 1752 cm^{-1}; δ_H (60 MHz) 1.44 - 2.02 (4H, m, 3′-H and 4′-H), 2.30-2.88 (4H, m, 2′-H and 5′-H), 3.75 (3H, s, OMe), 4.31 (1H, s), 6.24-6.46 (2H, m, 3-H and 4-H), and 7.31-7.47 (1H, m, 5-H) ppm; (m/z) M^+ 209.1059; $C_{11}H_{15}NO_3$ requires 209.1052.

Methyl 5-methyl-2-furylpyrrolidinylacetate (**18**)

Trichloromethylsilane (0.82 g, 5.5 mmol), 2-methylfuran (0.45 g, 5.5 mmol), and methyl methoxypyrrolidinylacetate (0.87 g, 5.5 mmol) in acetonitrile (30 ml) for 48 h gave after Kugelrohr distillation the *title compound* (0.72 g, 64%), b.p. 98-100 °C/0.01 mmHg; ν_{max} 2800, 1752 cm^{-1}; δ_H (60 MHz) 1.58-1.96 (4H, m, 3′-H and 4′-H), 2.27 (3H, ArMe), 2.36-2.78 (4H, m, 2′-H and 5′-H), 3.70 (3H, s, OMe), 4.18 (1H, s), 5.80-5.99 (1H, m, 3-H and 4-H), and 6.22 (1H, d, *J* 3, 3-H) ppm; (m/z) M^+ 223.1210; $C_{12}H_{17}NO_3$ requires 223.1208.

Methyl 2-furylpiperidinylacetate (**19**)

Trichloromethylsilane (1.15 g, 7.7 mmol), furan (0.52 g, 7 mmol), and methyl methoxypiperidinylacetate (1.31 g, 7.7 mmol) in acetonitrile (15 ml) for 39 h gave after Kugelrohr distillation the *title compound* (0.92 g, 58%), b.p. 82-85 °C/0.01 mmHg; ν_{max} 2808, 1738 cm^{-1}; δ_H (60 MHz) 1.19-1.83 (6H, m, 3′-H , 4′-H, and 5′-H), 2.28-2.65 (4H, m, 2′-H and 6′-H), 3.72 (3H, s, OMe), 4.28 (1H, s), 6.24-6.42 (2H, m, 3-H and 4-H), and 7.29-7.46 (1H, m, 5-H) ppm; δ_C (20.1 MHz) 24.4 (t, C-4′), 26.2 (t, C-3′and C-5′), 51.7 (m, OCH_3 and C-2′and C-6′), 67.0 (d, CH), 110.3 (d, C-3 and C-4), 142.6 (d, C-5) 149.7 (s, C-2), and 169.8 (C=O) ppm; (m/z) 235 (M^+, 8.6%), 151 (100), M^+ 223.1212; $C_{12}H_{17}NO_3$ requires 223.1208.

Methyl 5-methyl-2-furylpiperidinylacetate (**20**)

Trichloromethylsilane (0.99 g, 6.6 mmol), 2-methylfuran (0.54 g, 6.6 mmol), and methyl methoxypiperidinylacetate (1.12 g, 6 mmol) in acetonitrile (30 ml) for 48 h gave after Kugelrohr distillation the *title compound* (1.29 g, 91%), b.p. 112-115 °C/0.01 mmHg; ν_{max} 2808, 1740 cm^{-1}; δ_H (60 MHz) 1.13-1.87 (6H, m, 3′-H, 4′-H, and 5′-H), 2.24-2.64 (4H, m, 2′-H and 6′-H), 2.26 (3H, s, ArMe), 3.71 (3H, s, OMe), 4.17 (1H, s), 5.77-5.96 (1H, m, 4-H), and 6.19 (1H, d, *J* 3, 3-H) ppm; δ_C (20.1 MHz) 13.4 (q, ArMe), 24.5 (t, C-4′), 26.1 (t, C-3′and C-5′), 51.7 (m, OCH_3 and C-2′and C-6′), 67.3 (d, CH), 106.4 (d, C-3),110.7 (d, C-4), 147.5 and 152.4 (s, C-2 and C-5), and 170.0 (C=O) ppm; (m/z) 235 (M^+, 8.6%), 151 (100), M^+ 237.1367; $C_{13}H_{19}NO_3$ requires 237.1365.

Methyl 3-indolylpyrrolidinylacetate (**21**)

Trichloromethylsilane (0.82 g, 5.5 mmol), indole (0.64 g, 5.5 mmol), and methyl methoxypyrrolidinyl-acetate (0.87 g, 5.5 mmol) in acetonitrile (30 ml) for 48 h gave the *title compound* (1.03 g, 80%), a pale yellow solid, R_f = 0.44 (ethyl acetate-light petroleum [1:4]), R_f = 0.54 (ethyl acetate-light petroleum [2 : 3]); ν_{max} 3404, 2852, 1734 cm^{-1}; δ_H (60 MHz) 1.49-1.91 (4H, m, 3′-H and 4′-H), 2.34-2.83 (4H, m, 2′-H and 5′-H), 3.64 (3H, s, OMe), 4.42 (1H, s), 6.88-7.45 (4H, m, 2-H, 5H, 6H, and 7H), 7.58-7.92 (1H, m, 4H), and 9.41 (1H, br, NH); δ_C (20.1 MHz) 23.5 (t, C-3′ and C-4′), 51.9 (q, OCH_3), 52.4 (t, C-2′ and C-5′), 64.9 (d, CH), 111.4 (s, C-3),111.6 (d, C-7), 119.2 (d, C-6), 119.7 (d, C-4), 122.0 (d, C-5), 124.4 (d, C-2), 125.3 (s, C-3a), 136.2 (s, C-7a), and 173.1 (C=O) ppm; (m/z) M^+ 258.1372 $C_{15}H_{18}N_2O_2$ requires 258.1368.

Methyl 1-methyl-3-indolylpyrrolidinylacetate (**22**)

Trichloromethylsilane (0.95 g, 6.3 mmol), 1-methylindole (0.83 g, 6.3 mmol), and methyl methoxypyrrolidinyl-acetate (1.00 g, 5.77 mmol) in acetonitrile (40 ml) for 48 h gave the *title compound* (1.38 g, 88%), a pale yellow oil, R_f = 0.38 (ethyl acetate-light petroleum [1 : 4]), R_f = 0.67 (ethyl acetate-light petroleum [2 : 3]); ν_{max} 2876, 1744 cm^{-1}; δ_H (60 MHz) 1.53-1.97 (4H, m, 3′-H and 4′-H), 2.30-2.78 (4H, m, 2′-H and 5′-H), 3.55 (3H, NMe), 3.59 (3H, s, OMe), 4.37 (1H, s), 6.93-7.27 (4H, m, 2-H, 5H, 6H, and 7H), and 7.63-7.94 (1H, m, 4H); δ_C (20.1 MHz) 23.4 (t, C-3′ and C-4′), 32.6 (q, NMe), 51.7 (q, OCH_3), 52.2 (t, C-2′ and C-5′), 64.7 (d, CH), 109.3 (d, C-7), 110.5 (s, C-3), 119.5 (d, C-6), 119.6 (d, C-4), 121.8 (d, C-5), 127.4 (s, C-3a), 128.3 (d, C-2), 136.9 (s, C-7a), and 172.7 (C=O) ppm; (m/z) M^+ 272.1514 $C_{16}H_{20}N_2O_2$ requires 272.1525.

Methyl 3-indolylpiperidinylacetate (**23**)

Trichloromethylsilane (0.99 g, 6.6 mmol), indole (0.77 g, 6.6 mmol), and methyl methoxypiperidinylacetate (1.12 g, 6 mmol) in acetonitrile (30 ml) for 48 h gave the *title compound* (1.03 g, 80%), a white solid, R_f = 0.22 (ethyl acetate-light petroleum [1 : 4]), R_f = 0.67 (ethyl acetate-light petroleum [2 : 3]); ν_{max} 3396, 2852, 1732 cm^{-1}; δ_H (60 MHz) 1.09-1.78 (6H, m, 3′-H,4′-H and 5′-H), 2.21-2.77 (4H, m, 2′-H and 5′-H), 3.63 (3H, s, OMe), 4.41 (1H, s), 6.87-7.45 (4H, m, 2-H, 5H, 6H, and 7H), 7.60-7.95 (1H, m, 4H), and 9.19 (1H, br, NH); δ_C (20.1 MHz) 24.4 (t, C-4′), 25.8 (t, C-3′ and C-5′), 51.7 (q, OCH_3), 52.3 (t, C-2′ and C-6′), 66.6 (d, CH), 110.1 (s, C-3),111.6 (d, C-7), 119.5 (d, C-6), 119.7 (d, C-4), 122.0 (d, C-5), 124.7 (d, C-2), 127.4 (s, C-3a), 136.2 (s, C-7a), and 173.1 (C=O) ppm; (m/z) M^+ 272.1500 $C_{16}H_{20}N_2O_2$ requires 258.1525.

Methyl 1-methyl-3-indolylpiperidinylacetate (**24**)

Trichloromethylsilane (1.15 g, 7.7 mmol), 1-methylindole (1.01 g, 7.7 mmol), and methyl methoxypiperidinyl-acetate (1.31 g, 7.7 mmol) in acetonitrile (40 ml) for 39 h gave the *title compound* (1.38 g, 88%), a pale yellow oil, R_f = 0.62 (ethyl acetate-light petroleum [1 : 4]), R_f = 0.81 (ethyl acetate-light petroleum [2 : 3]); ν_{max} 2852, 1734 cm^{-1}; δ_H (60 MHz) 1.21-1.82 (4H, m, 3′-H, 4-H, and 5′-H), 2.27-2.75 (4H, m, 2′-H and 6′-H), 3.59 (3H, NMe), 3.63 (3H, s, OMe), 4.39 (1H, s), 6.92-7.28 (4H, m, 2-H, 5H, 6H, and 7H), and 7.64-7.93 (1H, m, 4H); δ_C (20.1 MHz) 24.5 (t, C-4′), 26.1 (t, C-3′ and C-5), 32.5 (q, NMe), 51.4 (q, OCH_3), 52.0 (t, C-2′ and C-6′), 66.5 (d, CH), 109.2 (s, C-3), 109.2 (d, C-7), 119.4 (d, C-6), 120.0 (d, C-4), 121.8 (d, C-5),

127.9 (s, C-3a), 128.7 (d, C-2), 137.0 (s, C-7a), and 172.6 (C=O) ppm; (m/z) M^+ 286.1673 $C_{17}H_{22}N_2O_2$ requires 286.1681.

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