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The Nafion-H Catalysed Cyclization of α-Carbomethoxy-α-Diazoacetanilides. Synthesis of 3-Unsubstituted-2-Indolinones.

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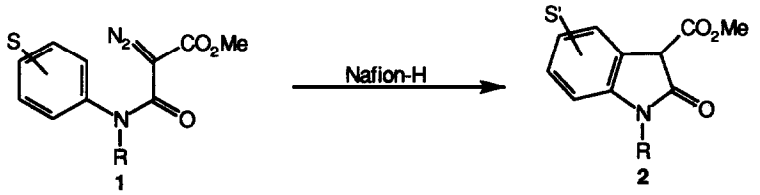
Abstract: Diazoanilides of type **4** were found to undergo Nafion-H catalysed cyclization onto the aromatic ring and concomitant decarboxylation, under optimal conditions, to give 3-unsubstituted 2-indolinones **5** in moderate yields. Diazoanilides that possess electron-donating substituents in the aromatic moiety gave higher yields of **5** and, in one case, the presence of an electron-withdrawing group in the aromatic moiety did not impede the cyclization. In the case of the diazoanilides that possess a N-butenyl group, preferential 1,3-dipolar cycloaddition of the diazo unit onto the butenyl double bond occurred to give an unstable 1-pyrazoline which was converted, by loss of nitrogen accompanied by hydrogen migration, to dihydro-2-pyridinone derivatives. It was also found that substituents *ortho* to the amido group and/or the site of cyclization sterically retarded the cyclization.

The rhodium(II) catalysed cyclization reactions of α-diazoamides and α-diazoanilides have been the subject of much investigation in recent years from a synthetic and mechanistic point of view.[1] In comparison, however, the acid-catalysed cyclization of α-diazoamides and α-diazoanilides have attracted far less attention; only two studies have so far been reported. Doyle and coworkers first demonstrated[2] that Nafion-H®,[3] was as effective as rhodium(II) acetate in catalysing the cyclization of N-aryl-α-diazoanilides to give good yields of 2-indolinones. Interestingly, they also noted that the cyclization reaction of diazoanilides such as the N-aryl-α-diazoacetamides to give the 3-acetyl-2-indolinones were only marginally catalysed by Nafion-H. Uncatalysed cyclization, presumably via a carbene aromatic C-H insertion pathway, also occurred. In another area of heterocyclic synthesis, Rishton and Schwartz showed[4] that the cyclization of N-benzyl- and N-phenethyl- α-diazoacetamides was smoothly catalysed by trifluoroacetic acid to give good yields of 1,4-dihydro-3-isoquinolinones and 1,4,5-trihydro-3-benzazepin-2-ones, respectively.

Recently we showed[5] that the rhodium(II) acetate catalysed cyclization of α-carbomethoxy-α-diazoanilides **1** resulted in preferential C-H insertion at the N-alkyl substituent to give either 2-azetidinones or 2-pyrrolidinones as major products. No 2-indolinone products, arising from C-H insertion into the N-aryl moiety, were detected. This result was attributed to the lower electrophilicity of the transient rhodium carbenoid whereby C-H insertion is preferred over electrophilic aromatic substitution-type reaction. Therefore, we became interested in examining whether diazoanilides such as **1** would undergo cyclization onto the aromatic ring to give the 2-indolinone **2** (Eq. 1) under the influence of Nafion-H since Doyle had shown that this acid catalysed the intramolecular electrophilic aromatic substitution in N-aryl-α-diazoacetamides. The diazoanilides being studied have different substitution pattern in the aromatic ring, and possess different electron-donating and electron-withdrawing groups in the aromatic moiety. They also have different N-"alkyl" substituents, some of which have functional groups. These attributes would allow us to assess: 1) the influence



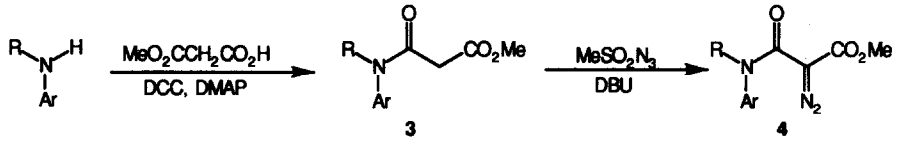
(Eq. 1)

of electronic factors and/or steric factors on the efficiency of the cyclization reaction, 2) the possible involvement of carbene intermediates during the reaction (the N-alkyl substituents would serve to compete with the aromatic ring for the carbene intermediates), and 3) the tolerance of the reaction conditions to some functional groups. We report, here, the details of our work.[6]

RESULTS AND DISCUSSIONS

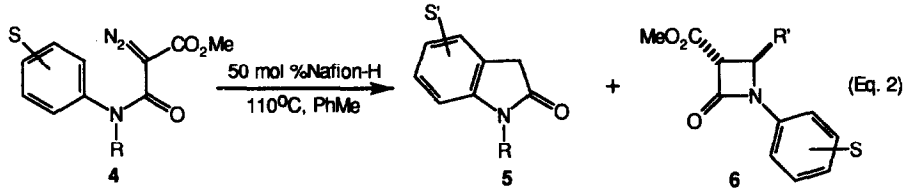
The α-diazoanilides used in this study were readily prepared from the appropriate N-substituted anilines, as outlined in Scheme I, using our previously established methodology.[5] Acylation of the appropriate N-substituted anilines with α-carbomethoxyacetic acid/DCC[7] resulted in the corresponding amides **3** (90-95%), which were then treated with methanesulfonyl azide[8] in the presence of DBU to give the α-diazoanilides **4** (60-70%).

Scheme I



	Ar	R		Ar	R
a	4-MeOPh	Me	**i**	4-MePh	CH_2Ph
b	3,4-DiMeOPh	CH_2Ph	**j**	4-MeO_2CPh	Bu
c	3,4-DiMeOPh	Bu	**k**	Ph	Et[5]
d	4-MeOPh	Bu[5]	**l**	2-Br-4-MePh	Et
e	4-MeOPh	$(CH_2)_2CO_2Me$	**m**	4-MePh	$(CH_2)_2CH{=}CH_2$
f	3,4-DiMeOPh	$(CH_2)_3OSiMe_2Bu$-t	**n**	2-Br-4-MePh	$(CH_2)_2CH{=}CH_2$
g	2,5-DiMeOPh	$(CH_2)_2CO_2Me$			
h	2,5-DiMeOPh	$(CH_2)_3OSiMe_2Bu$-t			

***Optimization Studies on Diazoanilide* 4a.** We began our studies by first examining the cyclization reaction of the diazoanilide **4a** (S= 4-OMe, R= Me, Eq. 2) under different conditions in order to define the optimum reaction conditions. The results are shown in Table I. It is evident that cyclization was slow (2.5 d) when the reaction was conducted in toluene at 92°C and in the absence of Nafion-H (Run 1). 2-Indolinone **5a** (S'=



5-OMe, R= Me; 49%) and 2-azetidinone **6a** (S= 4-OMe, R'= H; 19%) were obtained, and starting diazoanilide (25%) was recovered. Although the starting material was completely consumed at a higher temperature (20 h, 110° C, Run 2), there was an increase in the amount of the 2-azetidinone **6a** (25%) being formed and only 37% of **5a** was obtained. Conducting the cyclization reaction in refluxing toluene (110°C) but in the presence

Table I. Optimization Studies Using Diazoanilide **4a**.

Run	Nafion-H mol %	Conditions[a]	**5** (%, S'= 5-MeO R= Me)	**6** (%, S= 4-MeO R'= H)	Recovered **4a** (%)
1	0	A	49[b]	19[b]	25
2	0	B	37	25	0
3	10	B	52	19	0
4	50	C	54[b]	8[b]	8
5	50	B	68	13	0

a, Reaction carried out in toluene at specified temperature (°C) / time (h): A, 92/ 60; B, 110°C/ 20 h; C, 92/ 120. b, Yields not based on recovered **4a**.

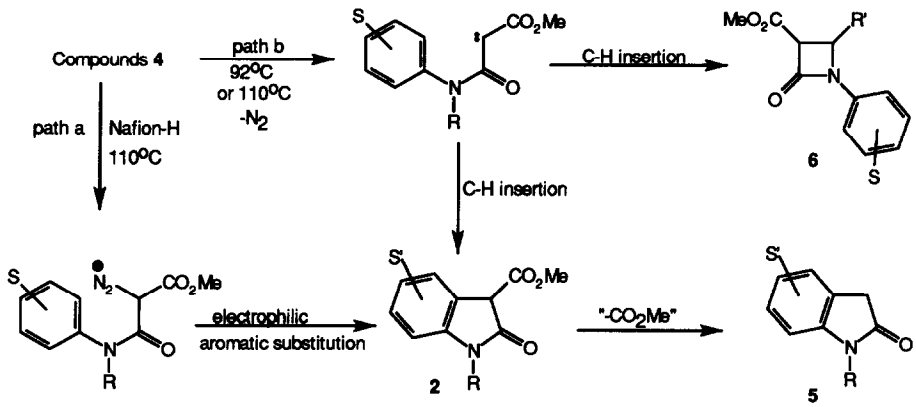
of 10 mol % of Nafion-H resulted in a 52% yield of **5a**. This yield was an improvement over that obtained in Run 2. Exposure of **4a** to 50 mol % of Nafion-H but at a reaction temperature of 92°C (Run 4) resulted in a slower reaction and after 2 d, 8% of starting material was recovered unchanged. The yield of **5a** was 54%

and that of **6a** was 8%. The optimum reaction conditions that we found best suited for effecting cyclization of **4a** entailed the use of 50 mol % Nafion-H and a reaction temperature of 110°C (Run 5). Under these conditions all of **4a** was consumed and **5a** was obtained in 68% yield. The 2-azetidinone **6a** was also formed albeit in 13% yield.

It is also interesting to note that in the above reactions, the expected 3-carbomethoxy-2-indolinone **2a** (S'= 5-OMe, R= Me) was not detected. This suggests that the decarboxylation of **2a** is a facile process, and indeed in all subsequent cyclizations that were examined (*vide infra*) only the decarboxylated 2-indolinones were obtained. This type of Nafion-H catalysed decarboxylation is rare.[9]

Reaction Pathway. The above results indicate that under thermal conditions (92°C or 110°C), the diazoanilide is converted to a carbene intermediate which then undergoes C-H insertion into the aromatic moiety or the N-methyl unit to yield **4a** and **5a**. A generalized pathway is shown in Chart I. However, in the presence of 50

Chart I



mol % of Nafion-H, a diazonium intermediate, formed by the protonation of the diazoanilide, would also be involved. Subsequent intramolecular electrophilic aromatic substitution involving the diazonium intermediate[10] would give **5a**. It is very likely that under the optimized reaction conditions, the primary cyclization pathway is the one that involves a diazonium intermediate (path a); the carbene C-H insertion pathway (path b) would also occur, but to a minor extent. The higher yield obtained for **5a** under the optimized reaction conditions, therefore, reflects the additive contribution of both the diazonium and carbene cyclization pathways.

***Cyclization of Diazoanilides* 4b-l.** We next subjected the diazoanilides **4b-l** to the optimal reaction conditions and the results are summarized in Table II. The structure of the 2-indolinones are readily inferred from their spectroscopic data: The infrared absorption of the carbonyl group occurs in the range 1704–1713 cm^{-1}. In the

^{1}H NMR, the methylene protons at C-3 resonate as a singlet in the range δ 3.45–3.50 and, in the ^{13}C NMR, the C-3 signal appeared in the range δ 34.3–35.7.

It is clear that the compounds with strong electron-donating methoxy groups in the aromatic ring reacted efficiently to give good yields of 2-indolinones (entries 1-4), whereas the compound with a weak electron-donating methyl group (Entry 8) gave a lower yield (52%). In Entries 1 and 2, the corresponding products arising from C-H carbene insertion into the N-butyl and N-benzyl groups were not detected. For the N-butyl diazoanilide (Entry 3), a small amount (8%) of the known *trans*-2-azetidinone **6c**,[5] formed by carbene C-H insertion into the N-butyl group was obtained. Interestingly, the 2-pyrrolidinone product was not detected.

Table II. Cyclization of Diazoanilides **4b-l** Using 50 mol % Nafion-H at 110°C.

Entry		**4**, Ar	R	**5**, S'(%)[a]	**6**, R'(%)[a]
1	**b**	3,4-DiMeOPh	CH_2Ph	5,6-DiMeO (71)	Not detected
	b'			4,5-DiMeO (11)	
2	**c**	3,4-DiMeOPh	n-Bu	5,6-DiMeO (79)	Not detected
	c'			4,5-DiMeO (5)	
3	**d**	4-MeOPh	n-Bu	5-MeO (68)	n-Pr (8)[b]
4	**e**	4-MeOPh	$(CH_2)_2CO_2Me$	5-MeO (67)	CH_2CO_2Me (4)[c]
5	**f**	3,4-DiMeOPh	$(CH_2)_3OSiMe_2Bu^t$	5,6-DiMeO (55)	Not detected
	f'			4,5-DiMeO (7)	
6	**g**	2,5-DiMeOPh	$(CH_2)_2CO_2Me$	4,7-DiMeO (31)	Not detected
7	**h**	2,5-DiMeOPh	$(CH_2)_3OSiMe_2Bu^t$	4,7-DiMeO (39)	Not detected
8	**i**	4-MePh	CH_2Ph	5-Me (52)	Not detected
9	**j**	4-CO_2MePh	n-Bu	5-CO_2Me (50)	n-Pr (10)[d]
10	**k**	Ph	Et	H (28)[e]	Me (7)[b,e]
11	**l**	2-Br-4-MePh	Et	5-Me-7-Br (36)	Not detected

a) Yields refer to isolated yields of chromatographically pure compounds. b) See ref. 5. c) Obtained as a 6.7 : 1.0 *trans-cis* mixture based on the integration of the H-3 doublet–H-3 (trans), δ 3.99 ;H-3 (cis), δ 4.36 . d) Obtained as the *trans* isomer inseparable from starting **4j**; ratio 2.5 : 1. e) Inseparable mixture. Yield was calculated based on a combined isolated yield of 35%; ratio **5k** : **6k** is 2.8 : 1.

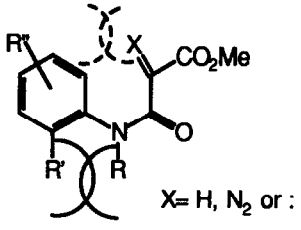
In the reaction of the 3,4-dimethoxy diazoanilides, where attack *ortho* and *para* to an electron-donating methoxy group is possible, it is found that cyclization *para* to the 3-methoxy group is strongly preferred. Thus the ratio of para:ortho isomers in Entry 1 is 15 : 1, in Entry 2 is 5.4 : 1 and in Entry 5 is 17 : 1. These observations are also in agreement with those reported for similar and related processes.[11] The cyclization was found not to be impeded by the presence of an electron-withdrawing ester group in the aromatic ring (Entry 9). This would be expected since the reaction occurred at the position *meta* to the deactivating ester

group. The yield of the 2-indolinone, **5j**, was 50%, which is comparable to that obtained in Entry 8. However, it was found that a longer reaction time (28 h) was required and an inseparable mixture (11 mg) of *trans* **6j** ($J_{3,4}$= 2.6 Hz) and starting diazoanilide **4j** were also isolated. The ratio of **6j** : **4j** is 2.5 : 1 which is based on the integration of the triplet of the methyl moiety (**6j**, δ 1.05; **4j**, δ 0.92) in the N-butyl group. The unsubstituted diazoanilide **4k**[5] (Entry 10) reacted inefficiently and gave **5k** and **6k**[5] in a combined yield of 35% as an inseparable mixture. The ratio of **5k**: **6k** is 2.8 : 1 and is based on the integration of the methyl triplet (δ 1.16) in **5k** and the methyl doublet (δ 1.48) in **6k**.

The ester function is found to be compatible with the present reaction conditions (Entries 4 and 10) and, in the case of the t-butyldimethylsilylether group (Entry 5), a small amount (9%) of desilylated 2-indolinone derivative[12] was also obtained.

It is also found that lower yields of 2-indolinones are obtained in the cyclizations of the diazoanilides possessing either a substituent *ortho* to the amide unit or possessing substituents that are *ortho* to the amide moiety and the site of reaction (compare Entries 4/6, 5/7 and 8/11). The inefficiency of these cyclizations may be due to unfavorable steric interaction between the N-substituent and the *ortho* substituent and/or steric crowding[13] at the site of cyclization (Figure 1). Such interactions would lead to the destabilization of the reactive conformer of the diazonium (major pathway) and carbene (minor pathway) intermediates in the transition state and, therefore, thwarting the cyclization reaction. The reactive intermediates would either decompose or react via other pathways. In the case of a carbene intermediate, it was found that C-H insertion

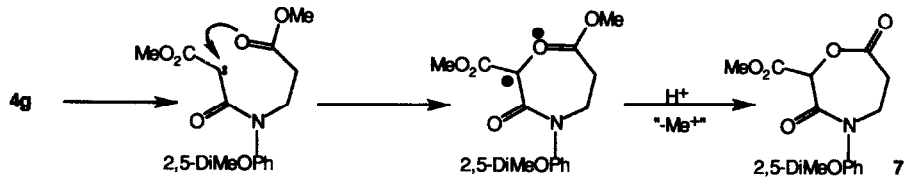
Figure 1



4	R	R'	R''
g	$(CH_2)_2CO_2Me$	MeO	5-MeO
h	$(CH_2)_3OSiMe_2Bu\text{-}t$	MeO	5-MeO
I	Et	Br	4-Me
n	$(CH_2)_2CH{=}CH_2$	Br	4-Me

occurred at the N-alkyl group (Entries 3,4,9 and 10) to give 2-azetidinones and, in the case of **4g** (Entry 6), the 1,4-oxazepine-3,7-dione derivative **7** was isolated in 17% yield. The formation of **7** is attributed to the

Chart II



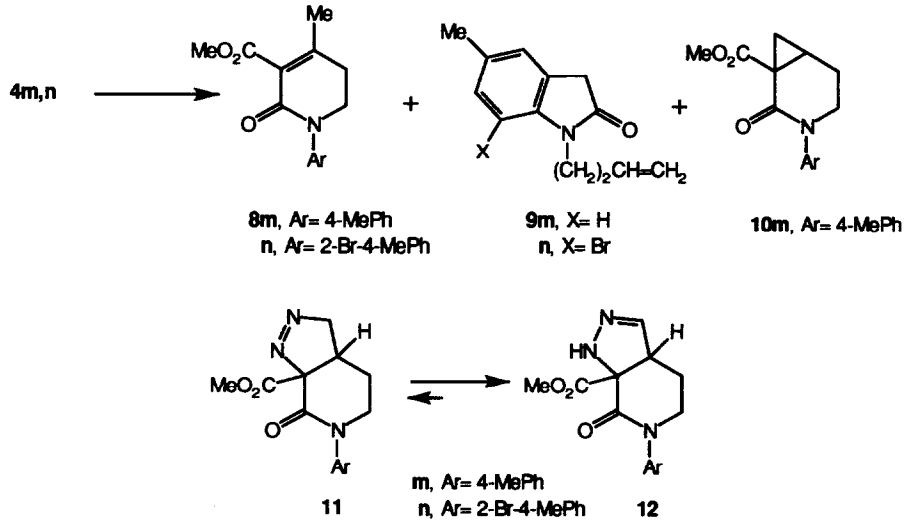
interception of the carbene intermediate by the ester carbonyl oxygen[14] to give a carbonyl ylide (Chart II),

which subsequently collapses to **7**.

***Diazoanilides* 4m,n**. Unlike the diazoanilides **4a-l**, compounds **4m,n** yielded the dihydro-2-pyridinone derivative **8m** (35%) and **8n** (73%) as major products under the optimized reaction conditions (Scheme II). For **4m**, the 2-indolinone **9m** was obtained in 24% yield whereas for **4n**, the 2-indolinone **9n** was formed in only 10% yield. The lower yield of **9n** is as expected on the basis of the steric arguments alluded to earlier (*vide supra*, Fig 1). In addition, a very small amount (7%) of the cyclopropane product **10m** was also isolated from the reaction of **4m**. Such a product was not detected in the reaction of **4n**.

The dihydro-2-pyridinone structure that is common to **8m,n** was readily confirmed by infra-red and nmr spectroscopy. The infra-red spectrum showed amide and ester carbonyl absorptions at 1665 and 1733 cm^{-1}.

Scheme II



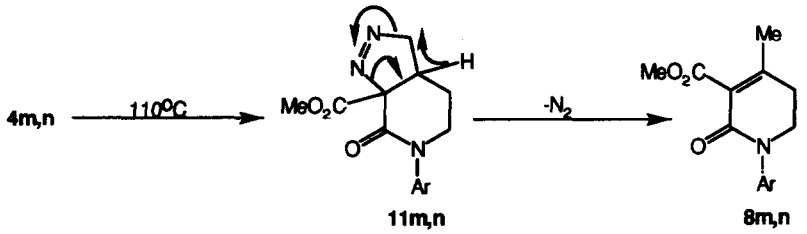
The higher frequency observed for the ester carbonyl absorption is attributed to steric interaction of the ester function with the vicinal C-4 methyl group which caused the ester group to rotate out of conjugation with the double bond. The ^{1}H nmr showed the C-4 methyl singlet at δ 2.06 and, in the ^{13}C nmr, the C-3 and C-4 olefinic carbons resonated at δ 127 - 128 and δ 150 - 152, respectively. The ^{13}C DEPT experiments confirmed the presence of two methylene carbons; the C-5 resonance occurred at δ 30.59 and C-6 resonated at δ 47.41.

The formation of **8m,n** deserves further comment. We found that the diazoanilides **4m,n** undergo facile intramolecular 1,3-dipolar cycloadition to give, initially, the unstable 1-pyrazolines **11m,n**[15] which

tautomerized to the more stable 2-pyrazoline isomers **12m,n** either on prolonged storage or during chromatographic purification.[16] It is, therefore, very likely that **8m,n** are formed from the 1-pyrazolines **11m,n** which, in turn, are generated from the diazoanilides **4m,n** under thermal conditions, and Nafion-H is not required for the formation of **8m,n**. This notion was confirmed by the reaction of **4m** in toluene at 110°C (20 h),[17] which resulted in the formation of **8m** (70%) and **9m** (7%). (A very small amount (< 1%) of the cyclopropane derivative **10m** was detected by t.l.c.) Also, it is interesting to note that the yield of the 2-indolinone **9m** obtained under thermal conditions is much lower than that obtained under the optimized reaction conditions. This result is in accord with our earlier observations (Table I and II) which showed that Nafion-H promoted the formation of 2-indolinone.

It has been demonstrated[18] that 1-pyrazolines possessing geminally disubstituted electron-withdrawing groups are thermally unstable and readily undergo a concerted loss of nitrogen accompanied by hydrogen migration to give olefinic products. Therefore, it is reasonable to suggest that the 1-pyrazolines **11m,n** are also thermally unstable and they undergo facile thermal collapse to give **8m,n**. The mechanism is shown in Chart III.

Chart III



11m,n **8m,n**

The formation of cyclopropanes from pyrazolines has been extensively investigated[19] and is mechanistically more complex. Therefore, we reserve comment on the formation of **10m**.

In summary, the diazoanilides of type **4** have been found to undergo Nafion-H catalysed intramolecular cyclization onto the aromatic moiety to directly give 3-unsubstituted-2-indolinones. Diazoanilides possessing electron-donating groups in the aromatic ring were found to give moderately good yields of 2-indolinones. In one case, it was found that the cyclization was not impeded by the presence of an electron-withdrawing ester group in the aromatic moiety. The cyclization reaction was also found to be sensitive to steric effects; the presence of substituents either *ortho* to the amide group or *ortho* to the site of reaction and the amide moiety resulted in a lower yield of the 2-indolinone product. The results also indicate that carbene intermediates are involved, although to a minor extent and, is evidenced by the entrapment of the carbene intermediates by the N-"alkyl" substituents.

It was found that under the optimized reaction conditions, the diazoanilides **4m,n** yielded the dihydro-2-pyridinones **8m,n** as major products. The formation of **8m,n** is rationalized based on the thermal collapse of

the unstable 1-pyrazolines **11m,n** produced by the intramolecular 1,3-dipolar cycloaddition of **4m,n**.

Together, this method and the recently reported[5] rhodium(II) acetate catalysed cyclization would provide ready access to compounds possessing the 2-azetidinone, 2-pyrrolidinone and 2(3H)-indolinone ring systems from the same diazoanilide precursor.

EXPERIMENTAL

Melting points were recorded on a Kofler hot-stage melting point apparatus and are uncorrected. N.M.R. spectra were obtained at 200.00 MHz on a Bruker AC200 QNP at the University of Regina; chemical shifts are reported in parts per million (δ) relative to the appropriate reference signals. ^{1}H N.M.R. (200 MHz) were recorded in deuteriochloroform ($CDCl_3$) using tetramethylsilane (δ_H 0.00) or residual chloroform (δ_H 7.24) as reference; multiplicities of signals are given as s, singlet; d, doublet; t, triplet; q, quartet; m, multiplet; br, broad and coupling constants are given in Hertz. Proton assignments were based on homonuclear decoupling experiments. ^{13}C and ^{13}C DEPT-135 N.M.R. (50.32 MHz) were recorded in $CDCl_3$ using the $CDCl_3$ signal at δ 77.0 as reference. The ^{13}C DEPT-135 pulse sequence[20] inverted only the CH_2s (designated (-)); the CHs and CH_3s remained upright. Quaternary carbons are not seen. Microanalyses were performed at the Microanalytical Department, University of Alberta and at the University of Regina, Canada. Low resolution electron-impact and chemical ionization (NH_3) mass spectra were recorded at the University of Saskatchewan on an VG-MS-12 spectrometer. Reaction progress was monitored by t.l.c on Merck silica gel 60_{F254} precoated (0.25 mm) on aluminum backed sheets, and reaction products were purified by flash chromatography[21] (Merck silica gel 60, 230-400 mesh). For the purification and/or drying of solvents and reagents see reference 5.

General procedure for the preparation of anilides 3. The appropriate aniline (1 mmol) and α-carbomethoxyacetic acid (1.1 mmol) were dissolved, under Ar, in dry CH_2Cl_2 (5 mL). DMAP (10 mol%) was added, the solution was cooled to 0°C and DCC (1.07 mmol) was added portionwise. The mixture was stirred for 15 min at 0°C and at rt for 5 h. Then 1M HCl (1 mL) was added, the mixture was stirred for 20 min. and the precipitated urea was filtered off. The filtrate was washed with 1M HCl (2x5 mL), satd. $NaHCO_3$ (2x5 mL) and dried (Na_2SO_4). The filtered solution was evaporated and the crude product chromatographed to give **3**. Anilides **3d,k** are known compounds (Ref.5, see Supplementary Material).

N-Methyl-N-(4-methoxyphenyl)-α-carbomethoxyacetamide (3a) ν_{max} (neat): 2954, 2840, 1744, 1666, 1600, 1575, 1513 cm^{-1}. δ_H: 3.21 (s, 2H, CH_2), 3.29 (s, 3H, Me), 3.70 (s, 3H, OMe), 3.83 (s, 3H, OMe), 6.93 (d, 2H, J= 7.6 Hz, ArH), 7.17 (d, 2H, J= 7.6 Hz, ArH). δ_C: 37.37, 41.04, 52.01, 55.30, 114.81, 126.13, 135.98, 159.02, 166.27, 168.01. Anal. Calcd for $C_{12}H_{15}NO_4$: C, 60.75; H, 6.37; N, 5.90. Found: C, 60.49; H, 6.38; N, 5.76.

N-Benzyl-N-(3,4-dimethoxyphenyl)-α-carbomethoxyacetamide (3b) ν_{max} (neat): 3062, 3003, 2951, 2839, 1731, 1650, 1600, 1593 cm^{-1}. δ_H: 3.27 (s, 2H, $CH_2C(O)$), 3.69 (s, 6H, 2xOMe), 3.88 (s, 3H, OMe), 4.90 (s, 2H, NCH_2), 6.41 (d, 1H, J= 2.6 Hz, ArH), 6.59 (dd, 1H, J= 8.5, 2.6 Hz, ArH), 6.78 (d, 1H, J= 8.5 Hz, ArH), 7.26 (br s, 5H, PhH). δ_C: 41.42, 52.24, 53.06, 55.81, 55.90, 111.10, 111.53, 120.43, 127.48, 128.35,

129.05, 134.34, 137.10, 148.85, 149.21, 166.16, 168.33.

N-Butyl-N-(3,4-dimethoxyphenyl)-α-carbomethoxyacetamide (3c) ν_{max} (neat): 2955, 2931, 2871, 1742, 1660, 1593, 1512 cm^{-1}. δ_H: 0.91 (t, 3H, J= 7.0 Hz, Me), 1.23-1.61 (m, 4H, $(CH_2)_2$), 3.20 (s, 2H, $CH_2C(O)$), 3.68 (s, 3H, OMe), 3.70 (t, 2H, J= 7.0 Hz, NCH_2), 3.89 (s, 3H, OMe), 3.91 (s, 3H, OMe), 6.71-6.81 (m, 2H, ArH), 6.89 (d, 1H, J=8.5 Hz, ArH). δ_C: 13.63, 19.76, 29.56, 41.37, 48.96, 52.01, 55.84, 111.10, 120.21, 134.66, 148.70, 149.41, 165.71, 168.29. Anal. Calcd for $C_{16}H_{23}NO_5$: C, 62.10; H, 7.50; N, 4.53. Found: C, 62.21; H, 7.58; N, 4.39.

N-(Methoxycarbonylethyl)-N-(4-methoxyphenyl)-α-carbomethoxyacetamide (3e) ν_{max}(neat): 2999, 2953, 1738, 1662, 1607 cm^{-1}. δ_H 2.62 (t, 2H, J= 6.4 Hz, CH_2), 3.19 (s, 2H, $CH_2C(O)$), 3.62 (s, 3H, OMe), 3.68 (s, 3H, OMe), 3.82 (s, 3H, OMe), 4.00 (t, 2H, J= 6.0 Hz, NCH_2), 6.92 (d, 2H, J= 8.1 Hz, ArH), 7.12, 2H, J= 8.1 Hz, ArH). δ_C: 32.34, 41.40, 45.40, 51.60, 52.15, 55.41, 114.93, 129.21, 134.03, 159.38, 166.15, 167.96, 171.65. EIMS (m/z, rel. intensity): 309 (M, 30), 278 (M-OMe, 9), 209 (M- $MeO_2CCH{=}C{=}O$, 37), 136 (M-CH_2CO_2Me- $MeO_2CCH{=}C{=}O$, 100). Calcd for $C_{15}H_{19}NO_6$: 309.1.

N-(*tert*-Butyldimethylsilyloxypropyl)-N-(3,4-dimethoxyphenyl)-α-carbomethoxyacetamide (3f) ν_{max}(neat): 2952, 2932, 2855, 1745, 1661, 1593, 1512 cm^{-1}. δ_H: 0.00 (s, 6H, 2xMeSi), 0.80 (s, 9H, t-Bu), 1.75 (quintet, 2H, J= 6.5 Hz, CH_2), 3.17 (s, 2H, CH), 3.60 (t, 2H, J= 6.5 Hz, NCH_2), 3.62 (s, 3H, OMe), 3.72 (t, 2H, J= 6.5 Hz, OCH_2), 3.82 (s, 3H, OMe), 3.86 (s, 3H, OMe), 6.68 (br s, 11H, ArH), 6.74 (d, 1H, J= 2.6, ArH), 6.74 (d, 1H, J= 8.4 Hz, ArH). δ_C: -5.45, 18.15, 25.79, 30.88, 41.48, 46.89, 52.17, 55.79, 60.74, 111.13, 111.26, 120.28, 134.91, 148.83, 149.56, 165.90, 168.37. EIMS (m/z, rel. intensity): 425 (M, 5), 410 (M-Me, 4), 368 (M- *t*-Bu, 100). Calcd for $C_{21}H_{35}NO_6Si$: 425.3

N-(Methoxycarbonylethyl)-N-(2,5-dimethoxyphenyl)-α-carbomethoxyacetamide (3g) ν_{max} (neat): 2989, 2952, 2839, 1739, 1668, 1612, 1588, 1507 cm^{-1}. δ_H: 2.56-2.68 (m, 2H, CH_2), 3.11 (d, 1H, J= 15.1 Hz, CH(CO)), 3.18 (d, 1H, J= 15.1 Hz, CH(CO)), 3.61 (s, 3H, OMe), 3.67 (s, 3H, OMe), 3.77 (s, 3H, OMe), 3.79 (s, 3H, OMe), 3.95 (t, 2H, J= 7.2 Hz, NCH_2), 6.78 (s, 1H, ArH), 6.90 (s, 2H, ArH). δ_C: 32.28, 41.13, 44.53, 51.46, 52.06, 55.66, 112.37, 114.68, 115.54, 130.08, 149.09, 153.58, 166.45, 167.95, 171.86. EIMS (m/z, rel intensity): 339 (M, 78), 308 (M-OMe, 81), 239 (M-$MeO_2CCH{=}C{=}O$, 49), 166 (M-CH_2CO_2Me-$MeO_2CCH{=}C{=}O$, 92). Calcd for $C_{16}H_{21}NO_7$: 339.1.

N-(*tert*-Butyldimethylsilyloxypropyl)-N-(2,5-dimethoxyphenyl)-α-carbomethoxyacetamide (3h) ν_{max} ($CDCl_3$): 2952, 2856, 1747, 1666, 1610, 1589, 1507 cm^{-1}. δ_H: -0.05 (s, 6H, 2xMeSi), 0.79 (s, 9H, t-Bu), 1.70 (quintet, 2H, J= 6.5 Hz, CH_2), 3.09 (s, 2H, $CH_2C(O)$), 3,57 (t, 2H, J= 2.5 Hz, NCH_2), 3.60 (s, 3H, OMe), 3.70 (t, 2H, J= 6.5 Hz, OCH_2), 3.71 (s, 3H, OMe), 3.73 (s, 3H, OMe),6.70 (s, 1H, ArH), 6.83 (s, 2H, ArH). δ_C: -5.53, 18.07, 25.73, 30.67, 41.18, 46.02, 52.02, 55.67, 60.78, 112.45, 114.32, 115.55, 130.53, 149.12, 153.53, 166.52, 168.15. CIMS (m/z, rel. intensity): 426 (M+H, 100), 369 (M+H-*t*-Bu). Calcd for $C_{21}H_{35}O_6Si$: 425.6.

N-Benzyl-N-(4-methylphenyl)-α-carbomethoxyacetamide (3i) ν_{max} (neat): 3061, 3030, 2950, 1744, 1662, 1604, 1583, 1512 cm^{-1}. δ_H: 2.29 (s, 3H, Me), 3.21 (s, 2H, $CH_2C(O)$), 3.65 (s, 3H, OMe), 4.88 (s, 2H, NCH_2), 6.89 (d, 2H, J= 7.8 Hz, ArH), 7.10 (d, 2H, J= 7.8 Hz, ArH), 7.24 (s, 5H, PhH). δ_C: 20.68, 41.16, 51.82, 52.69, 127.05, 127.64, 128.00, 128.41, 129.94, 136.67, 138.02, 138.69, 165.69, 167.81. EIMS (m/z, rel. intensity): 297 (M, 7), 197 (M-$MeO_2CCH{=}C{=}O$, 11), 91 ($C_7H_7^+$, 100). Calcd for $C_{18}H_{19}NO_3$: 297.3.

N-Butyl-N-(4-methoxycarbonylphenyl)-α-carbomethoxyacetamide (3j) ν_{max}(neat): 2954, 2933, 2873, 1745, 1724, 1666, 1604, 1508 cm^{-1}. δ_H: 0.88 (t, 3H, J= 7.6 Hz, Me), 1.20-1.58 (m, 4H, $(CH_2)_2$), 3.17 (s, 2H, CH_2), 3.65 (s, 3H, OMe), 3.71 (t, 2H, J= 7.6 Hz, NCH_2), 7.29 (d, 2H, J= 8.0 Hz, ArH), 8.10 (d, 2H, J= 8.0 Hz, ArH). δ_C: 13.64, 19.83, 29.63, 41.59, 49.17, 52.27, 52.32, 128.12, 130.00, 131.14, 146.18, 165.00, 166.92, 167.98. EIMS (m/z, rel. intensity): 307 (M, 51), 276 (M-OMe, 27), 251 (M-CH_2=$CHCH_2CH_2$, 100), 207 (M-MeO_2C=CH=C=O, 30). Calcd for $C_{16}H_{21}NO_5$: 307.3.

N-Ethyl-N-(2-bromo-4-methylphenyl)-α-carbomethoxyacetamide (3l) ν_{max} ($CDCl_3$): 2976, 2951, 2874, 1749, 1668 cm^{-1}. δ_H: 1.14 (t, 3H, J= 7.2 Hz, Me), 2.39 (s, 3H, Me), 3.07 (d, 1H, J=15 Hz, CHC(O)), 3.16 (d, 1H, J= 15 Hz, CHC(O)), 3.25-3.46 (m, 1H, NCH), 3.99-4.20 (m, 1H, NCH), 7.19, (s, 2H, ArH), 7.53 (s, 1H, ArH). δ_C: 12.61, 20.72, 41.57, 43.24, 52.14, 123.39, 129.35, 130.53, 134.29, 137.49, 140.63, 165.52, 167.86. CIMS (m/z, rel. intensity): 316 (M(^{81}Br)+H, 98.9), 314 (M(^{79}Br)+H, 100), 234 (M(^{79}Br)-^{79}Br, 98). Calcd for $C_{13}H_{16}{}^{79}BrNO_3$: 313.1

N-(3-Butenyl)-N-(4-methylphenyl)-α-carbomethoxyacetamide (3m) ν_{max}(neat): 3075, 2978, 2950, 2860, 1745, 1664, 1608, 1515 cm^{-1}. δ_H: 2.30 (dt, 2H, J= 6.8, 6.8 Hz, CH_2), 2.40 (s, 3H, Me), 3.18 (s, 2H, $CH_2C(O)$), 3.68 (s, 3H, OMe), 3.80 (t, 2H, J= 6.8 Hz, NCH_2), 4.99 - 5.13 (m, 2H, $=CH_2$), 5.65 - 5.90 (m, 1H, =CH), 7.10 (d, 2H, J= 8.2 Hz, ArH), 7.25 (d, 2H, d= 8.2 Hz, ArH). δ_C: 20.85, 31.72, 41.42, 48.32, 51.95, 116.52, 127.82, 130.24, 134.85, 138.22, 138.93, 165.63, 167.98. EIMS (m/z, rel. intensity): 261 (M, 3), 220 (M-CH_2CH=CH_2, 16), 120 (M-CH_2CH=CH_2- MeO_2CCH=C=O, 100). Calcd for $C_{15}H_{19}NO_3$: 261.4.

N-(3-Butenyl)-N-(2-bromo-4-methylphenyl)-α-carbomethoxyacetamide (3n) ν_{max} (neat): 3075, 2979, 2950, 1744, 1671, 1599, 1493 cm^{-1}. δ_H: 2.25-2.46 (m, 2H, CH_2), 2.40 (s, 3H, Me), 3.07 (d, 1H, J= 13.4 Hz, CHC(O)), 3.17 (d, 1H, J= 13.4 Hz, CHC(O)), 3.18 (dt, 1H, J= 13.8, 7.1 Hz, NCH), 3.69 (s, 3H, OMe), 4.19 (dt, 1H, J= 13.8, 7.1 Hz, NCH), 4.99-5.17 (m, 2H, $=CH_2$), 5.65-5.89 (m, 1H, =CH), 7.20 (s, 2H, ArH), 7.54 (s, 1H, ArH). δ_C: 20.74, 31.78, 41.54, 47.68, 52.15, 116.71, 123.24, 129.37, 130.65, 134.35, 134.96, 137.66, 140.74, 165.84, 167.77. EIMS m/z(rel. intensity): 341 (M(^{81}Br), 1.4), 339 (M(^{79}Br), 1.5), 300 (M(^{81}Br)-CH_2CH=CH_2, 92), 298 (M(^{79}Br)-CH_2CH=CH_2, 100), 260 (M(^{79}Br)-^{79}Br); Calcd for $C_{15}H_{18}{}^{81}BrNO_3$: 341.0 and $C_{15}H_{18}{}^{79}BrNO_3$: 339.1.

General procedure for diazotization The appropriate diazoanilide **3** (1 mmol) was dissolved in dry CH_3CN (2 mL/mmol) under Ar and then cooled to 0°C. $MeSO_2N_3$ (2 mmol) was added followed by dropwise addition of DBU (2 mmol). The mixture was stirred at 0°C for 30 min and at rt (3–6 h). The mixture was diluted with CH_2Cl_2 (4 mL/mL CH_3CN), washed with 10% aq. NaOH (3 x 5 mL) and the organic layer separated. The aq. phase was reextracted once with CH_2Cl_2 (5 mL). The combined organic extracts were washed with water (10 mL), dried (Na_2SO_4), filtered and evaporated. Chromatographic purification of the crude product gave **4** as a pale yellow or yellow-orange oil. Diazoanilides **4d,k** have been reported (Ref. 5, see Supplementary Material).

N-Methyl-N-(4-methoxyphenyl)-α-carbomethoxy-α-diazoacetamide (4a) ν_{max}(neat): 2953, 2802, 2123, 1734, 1681, 1654, 1588, 1508 cm^{-1}. δ_H: 3.35 (s, 3H, Me), 3.65 (s, 3H, OMe), 3.81 (s, 3H, OMe), 6.90 (d, 2H, J= 7.6 Hz, ArH), 7.12 (d, 2H, J= 7.6 Hz, ArH). δ_C: 38.70, 52.11, 55.35, 114.58, 127.09, 136.25, 158.32,

160.47, 162.68. Anal. Calcd for $C_{12}H_{13}N_3O_4$: C, 54.73; H, 4.98; N, 15.97. Found: C, 54.64; H, 5.16; N, 15.83.

N-Benzyl-N-(3,4-dimethoxyphenyl)-α-carbomethoxy-α-diazoacetamide (4b) ν_{max} (neat): 3062, 3027, 3002, 2953, 2839, 2115, 1730, 1691, 1643, 1594, 1513 cm^{-1}. δ_H: 3.64 (s, 3H, OMe), 3.71 (s, 3H, OMe), 3.86 (s, 3H, OMe), 4.92 (s, 2H, NCH_2), 6.50 (d, 1H, J= 2.6 Hz, ArH), 6.61 (dd, 1H, J= 8.5, 2.6 Hz, ArH), 6.78 (d, 1H, J= 8.5 Hz, ArH), 7.17-7.38 (m, 5H, PhH). δ_C: 52.12, 54.15, 55.75, 55.83, 110.43, 110.85, 119.40, 127.37, 128.24, 128.66, 134.49, 136.73, 148.16, 149.10, 160.31, 162.63. Anal. Calcd for $C_{19}H_{19}N_3O_5$: C, 61.76; H, 5.19; N, 11.38. Found: C, 61.86; H, 5.33; N, 11.46.

N-Butyl-N-(3,4-dimethoxyphenyl)-α-carbomethoxy-α-diazoacetamide (4c) ν_{max} (neat): 2956, 2934, 2872, 2114, 1730, 1691, 1643, 1594, 1512 cm^{-1}. δ_H: 0.90 (t, 3H, J= 7.0 Hz, Me), 1.22-1.65 (m, 4H, $(CH_2)_2$), 3.65 (s, 3H, OMe), 3.74 (t, 2H, J= 7.0 Hz, NCH_2), 3.88 (s, 3H, OMe), 3.90 (s, 3H, OMe), 6.70 (s, 1H, ArH), 6.75 (d, 1H, J= 8.5 Hz, ArH), 6.88 (d, 2H, J= 8.5 Hz, ArH). δ_C: 13.45, 19.72, 29.37, 50.43, 51.89, 55.67, 55.82, 110.04, 110.86, 119.11, 134.50, 147.96, 149.20, 159.67, 162.63.

N-(Methoxycarbonylethyl)-N-(4-methoxyphenyl)-α-carbomethoxy-α-diazoacetamide (4e) ν_{max} (neat): 3001, 2953, 2840, 2121, 1730, 1691, 1641, 1584, 1511 cm^{-1}. δ_H: 2.65 (t, 2H, J= 7.2 Hz, CH_2), 3.60 (s, 3H, OMe), 3.63 (s, 3H, OMe), 3.91 (s, 3H, OMe), 4.02 (t, 2H, J= 7.2 Hz, NCH_2), 6.90 (d, 2H, J= 8.5 Hz, ArH), 7.10 (d, 2H, J= 8.5 Hz, ArH). δ_C: 32.19, 47.06, 51.67, 52.24, 55.46, 114.72, 128.15, 134.13, 158.70, 160.69, 162.60, 171.80. EIMS (m/z, rel. intensity): 335 (M, 18), 307 (M-N_2, 14). Calcd for $C_{15}H_{17}N_3O_6$: 335.1

N-(tert-Butyldimethylsilyloxypropyl)-N-(3,4-dimethoxyphenyl)-α-carbomethoxy-α-diazoacetamide (4f) ν_{max} (neat): 2951, 2855, 2115,1729, 1692, 1631, 1594, 1513 cm^{-1}. δ_H: 0.00 (s, 6H, 2xMeSi), 0.80 ((s, 9H, t-Bu), 1.79 (quintet, 2H, J= 6.5 Hz, CH_2), 3.59 (t, 2H, J= 6.5 Hz, OCH_2), 3.60 (s, 3H, OMe), 3.78 (t, 2H, J= 6.5 Hz, NCH_2), 3.80 (s, 3H, OMe), 3.85 (s, 3H, OMe), 6.63 - 6.70 (m, 1H, ArH), 6.72 (d, 1H, J= 2.6 Hz, ArH), 6.79 (d, 1H, J= 8.4 Hz, ArH). δ_C: -5.47, 18.13, 25.78, 30.74, 48.57, 52.21, 55.97, 56.06, 60.52, 110.12, 111.10, 119.22, 135.04, 148.17, 149.49, 160.16, 162.89. Anal. Calcd for $C_{21}H_{33}N_3O_6Si$: C, 55.85; H, 7.37; N, 9.31. Found: C, 55.90; H, 7.55; N, 9.02.

N-(Methoxycarbonylethyl)-N-(2,5-dimethoxyphenyl)-α-carbomethoxy-α-diazoacetamide (4g) ν_{max} (neat): 2999, 2953, 2839, 2117, 1737, 1691, 1657, 1611, 1588, 1509 cm^{-1}. δ_H: 2.67 (t, 2H, J= 7.2 Hz, CH_2), 3.59 (s, 3H, OMe), 3.77 (s, 3H, OMe), 3.81 (s, 3H, OMe), 3.95 (t, 2H, J= 7.2 Hz, NCH_2), 6.73 (d, 1H, J=2.4 Hz, ArH_6), 6.81-6.94 (m, 2H, ArH). δ_C: 31.79, 45.51, 51.30, 51.92, 55.57, 55.70, 112.36, 113.54, 114.99, 129.78, 148.47, 153.43, 161.05, 164.68, 171.71. Anal. Calcd for $C_{16}H_{19}N_3O_7$: C, 52.59; H, 5.24; N, 11.51. Found: C, 52.37; H, 5.22; N, 11.22.

N-(*tert*-Butyldimethylsilyloxypropyl)-N-(2,5-dimethoxyphenyl)-α-carbomethoxy-α-diazoacetamide (4h) ν_{max} (neat): 2953, 2931, 2115, 1730, 1690, 1654, 1610, 1588, 1507 cm^{-1}. -0.05 (s, 6H, 2xMe), 0.80 (s, 9H, t-Bu), 1.76 (quintet, 2H, J= 6.5 Hz, CH_2), 3.58 (t, 2H, J= 6.5 Hz, CH_2), 3.60 (s, 3H, OMe), 3.70 (t, 2H, J= 6.5 Hz, OCH_2), 3.72 (s, 3H, OMe), 3.75 (s, 3H, OMe), 6.69 (d, 1H, J= 2.5 Hz, ArH), 6.80 (m, 2H, ArH). δ_C: -5.48, 18.13, 25.78, 30.51, 47.30, 52.12, 55.79, 55.90, 60.73, 112.51, 113.60, 115.20, 130.68, 148.71, 153.62, 161.09, 163.33. Anal. Calcd for $C_{21}H_{19}N_3O_6Si$: C, 55.84; H, 7.37; N, 9.31. Found: 55.70; H, 7.58; N, 9.12.

N-Benzyl-N-(4-methylphenyl)-α-carbomethoxy-α-diazoacetamide (4i) ν_{max} (neat): 3061, 3030, 2951, 2119, 1729, 1690, 1635, 1607, 1580 cm^{-1}. δ_H: 2.35 (s, 3H, Me), 3.62 (s, 3H, OMe), 5.00 (s, 2H, NCH_2), 7.00 (d,

2H, J= 7.8 Hz, ArH), 7.14 (d, 2H, J= 7.8 Hz, ArH), 7.30 (s, 5H, PhH). δ_C: 20.75, 51.96, 53.99, 126.16, 127.18, 128.15, 128.24, 129.75, 136.67, 136.89, 139.32, 160.37, 162.43. Anal. Calcd for $C_{18}H_{17}N_3O_3$: C, 66.85; H, 5.30; N, 13.00. Found: C, 66.58; H, 5.20; N, 12.88.

N-Butyl-N-(4-methoxycarbonylphenyl)-α-carbomethoxy-α-diazoacetamide (4j) ν_{max} (neat): 2955, 2872, 2127, 1722, 1695, 1634, 1601, 1576, 1509 cm^{-1}. δ_H: 0.90 (t, 3H, J= 7.1 Hz, Me), 1.20-1.65 (m, 4H, $(CH_2)_2$), 3.51 (s, 3H, OMe), 3.84 (t, 2H, J= 7.1 Hz, NCH_2), 3.92 (s, 3H, OMe), 7.29 (d, 2H, J= 8.0 Hz, ArH), 8.05 (d, 2H, J= 8.0 Hz, ArH). δ_C: 13.52, 19.86, 29.77, 50.56, 51.94, 52.05, 125.53, 127.89, 130.52, 146.78, 160.61, 161.62, 165.99. CIMS m/z (rel. intensity): 334 (M+H, 100); Calcd for $C_{16}H_{19}N_3O_5$: 333.1

N-Ethyl-N-(2-bromo-4-methylphenyl)-α-carbomethoxy-α-diazoacetamide (4l) ν_{max} (neat): 2952, 2873, 2123, 1733, 1690, 1654, 1560, 1493 cm^{-1}. δ_H: 1.16 (t, 3H, J= 7.2 Hz, Me), 2.36 (s, 3H, Me), 3.50-3.75 (m, 1H, CH), 3.62 (s, 3H, OMe), 3.80-4.02 (m, 1H, CH), 7.09-7.22 (m, 2H, ArH), 7.48 (s, 1H, ArH). δ_C: 12.28, 20.54, 45.09, 51.99, 122.83, 128.96, 130.18, 134.04, 137.10, 139.63, 160.29, 162.54. Anal. Calcd for $C_{13}H_{14}BrN_3O_3$: C, 45.88; H, 4.15; N, 12.36. Found: C, 45.82; H, 4.08; N, 12.15.

N-(3-Butenyl)-N-(4-methylphenyl)-α-carbomethoxy-α-diazoacetamide (4m) ν_{max} (neat): 3075, 3035, 2979, 2120, 1731, 1693, 1634, 1607, 1580, 1511 cm^{-1}. δ_H: 2.34 (dt, J= 6.8, 6.8 Hz, CH_2), 2.36 (s, 3H, Me), 3.60 (s, 3H, OMe), 3.82 (t, 2H, J= 6.8 Hz, NCH_2), 4.95 - 5.10 (m, 2H, $=CH_2$), 5.62 - 5.89 (m, 1H, =CH), 7.08 (d, 2H, J= 8.2 Hz, ArH), 7.20 (d, 2H, J= 8.2 Hz, ArH). δ_C: 20.78, 31.76, 49.88, 51.94, 116.65, 126.30, 129.88, 134.71, 136.96, 139.07, 160.04, 162.57.

N-(3-Butenyl)-N-(2-bromo-4-methylphenyl)-α-carbomethoxy-α-diazoacetamide (4n) ν_{max} (neat): 2.29-2.49 (m, 2H, CH_2), 2.38 (s, 3H, Me), 3.48-3.69 (m, 1H, NCH), 3.67 (s, 3H, OMe), 3.81-4.07 (m, 1H, NCH), 4.98-5.17 (m, 2H, $=CH_2$), 5.67-5.88 (m, 1H, =CH), 7.18 (s, 2H, ArH), 7.48 (s, 1H, ArH). δ_C: 20.66, 31.50, 49.62, 52.12, 116.77, 122.85, 129.06, 130.31, 134.17, 134.74, 137.40, 139.84, 160.57, 162.60.

General procedure for the Nafion-H catalysed reaction. The diazoanilide **4** (1 mmol) was dissolved in dry toluene (15 mL) and Nafion-H (500 mg, ca. 50 mol % SO_3H) was added. The mixture was refluxed, under argon, for 20 h, then cooled to rt, filtered and concentrated. The product **5** was isolated by column chromatography.

1-Methyl-5-methoxy-2(3H)-indolinone (5a) mp: 97 - 98.5°C. ν_{max} (CH_2Cl_2): 3057, 3004, 2940 1705, 1660, 1633, 1603, 1512 cm^{-1}. δ_H: 3.20 (s, 3H, NMe), 3.50 (s, 2H, $CH_2C(O)$), 3.78 (s, 3H, OMe), 6.68 - 6.95 (m, 3H, ArH). δ_C: 26.20, 36.08, 55.79, 109.22, 111.86, 112.04, 125.79, 138.75, 155.80, 174.67. Anal. Calcd for $C_{10}H_{11}NO_2$: C, 67.77; H, 6.26; N, 7.90. Found: C, 67.84; H, 6.35; N, 7.65.

1-Benzyl-5,6-dimethoxy-2(3H)-indolinone (5b) mp: 118 - 120°C. ν_{max} (nujol): 2925, 2848, 1711, 1617, 1511 cm^{-1}. δ_H: 3.59 (s, 2H, CH_2), 3.75 (s, 3H, OMe), 3.82 (s, 3H, OMe), 4.90 (s, 2H, NCH_2), 6.32 (s, 1H, ArH), 6.89 (s, 1H, ArH), 7.19-7.40 (m, 5H, PhH). δ_C: 35.79, 43.73, 56.20, 56.73, 95.35, 109.64, 115.07, 127.16, 127.55, 128.70, 135.89, 137.92, 144.87, 149.04, 175.44. Anal. Calcd for $C_{17}H_{17}NO_3$: C, 72.05; H, 6.05; N, 4.95. Found: C, 71.77; H, 6.22; N, 4.88.

1-Benzyl-4,5-dimethoxy-2(3H)-indolinone (5b') mp 106 - 109°C. ν_{max} (CH_2Cl_2, film): 3058, 3000, 1707, 1603, 1500, 1490 cm^{-1}. δ_H: 3.68 (s, 2H, CH_2), 3.80 (s, 3H, OMe), 3.92 (s, 3H, OMe), 6.35 (d, 1H, J= 7.8

Hz, ArH), 6.70 (d, 1H, J= 7.8 Hz, ArH), 7.18-7.40 (m, 5H, PhH). δ_C: 34.28(-), 43.90(-), 56.47, 60.04, 103.40, 111.75, 116.01, 127.36, 127.59, 128.74, 135.96, 138.57, 146.01, 148.22, 174.55. EIMS m/z (rel. intensity): 283 (M, 63); Calcd for $C_{17}H_{17}NO_3$: 283.1.

1-Butyl-5,6-dimethoxy-2(3H)-indolinone (5c) ν_{max} (CH_2Cl_2, film): 2956, 2933, 2871, 1707, 1621, 1603, 1510 cm^{-1}. δ_H: 0.96 (t, 3H, J= 7.2 Hz, Me), 1.30-1.50 (m, 2H, CH_2), 1.56-1.75 (m, 2H, CH_2), 3.47 (s, 2H, $CH_2C(O)$), 3.68 (t, 2H, J= 7.2 Hz, NCH_2), 3.85 (s, 3H, OMe), 3.92 (s, 3H, OMe), 6.46 (s, 1H, ArH), 6.89 (s, 1H, ArH). δ_C: 13.72, 20.15, 29.69, 35.83, 39.73, 56.46, 56.82, 94.68, 109.84, 115.40, 138.36, 144.74, 149.20, 175.32. EIMS m/z (rel. intensity): 249 (M, 100), 234 (M-Me, 74), 178 (M-CH_2=$CHCH_2Me$, 47); Calcd for $C_{14}H_{19}NO_3$: 249.1.

1-Butyl-4,5-dimethoxy-2(3H)-indolinone (5c') δ_H: 0.95 (t, 3H, J= 7.2 Hz, Me), 1.30-1.75 (m, 4H, 2xCH_2), 3.55 (s, 2H, $CH_2C(O)$), 3.66 (t, 2H, J= 7.2 Hz, NCH_2), 3.82 (s, 3H, OMe), 3.91 (s, 3H, OMe), 6.48 (d, 1H, J= 7.2 Hz, ArH), 6.80 (d, 1H, J= 7.2 Hz, ArH). EIMS (m/z, rel. intensity): 249 (M, 100), 234 (M-15, 65), 178 (M-15-CH2=CHCH2CH3, 68). Calcd for $C_{14}H_{19}NO_3$: 249.1.

1-Butyl-5-methoxy-2(3H)-indolinone (5d) ν_{max} (CH_2Cl_2): 3053, 2986, 1700, 1601, 1493 cm^{-1}. δ_H: (0.94, t, 3H, J= 6.8 Hz, Me), 1.29 - 1.50 (m, 2H, CH_2), 1.55 - 1.75 (m, 2H, CH_2), 3.49 (s, 2H, $CH_2(CO)$), 3.70 (t, 2H, J= 6.8 Hz, NCH_2), 6.72 (d, 1H, J= 8.2 Hz, ArH), 6.81 (dd, 1H, J= 8.2, 1.8 Hz, ArH), 6.89 (br s, 1H, ArH). δ_C: 13.72, 20.16 (-), 29.44 (-), 36.11(-), 39.80 (-), 55.76, 108.47, 111.87, 112.05, 125.97, 138.21, 155.64, 174.36. EIMS (m/z, rel. intensity): 219 (M, 64), 204 (M-15, 7), 176 (M-$CH_2CH_2CH_3$, 30), 148 (M-15-CH_3CH_2CH=CH_2, 100). Calcd for $C_{13}H_{17}NO_2$: 219.7

5-Methoxy-1-(methoxycarbonylethyl)-2(3H)-indolinone (5e) mp: 51.5 - 53°C. ν_{max}(CH_2Cl_2): 3055, 2999, 2952, 1732, 1704, 1634, 1600, 1494 cm^{-1}. δ_H: 2.70, (t, 2H, J= 7.2 Hz, CH_2), 3.50 (s, 2H, $CH_2C(O)$), 3.68 (s, 3H, OMe), 3.80 (s, 3H, OMe), 4.00 (t, 2H, J= 7.2 Hz, NCH_2), 6.80 (s, 2H, ArH), 6.88 (s, 1H, ArH). δ_C: 32.09, 35.99, 36.03, 51.91, 55.79, 108.54, 112.04, 112.14, 125.83, 137.48, 155.78, 171.66, 174.64. Anal. Calcd for $C_{13}H_{15}NO_4$: C, 62.63; H, 6.07; N, 5.62. Found: 62.41; H, 6.26; N, 5.53.

1-(*tert*-Butyldimethylsilyloxypropyl)-5,6-dimethoxy-2(3H)-indolinone (5f) ν_{max} (neat): 2930, 2856, 1711, 1621, 1603, 1510 cm^{-1}. δ_H: 0.02 (s, 6H, 2xMe), 0.89 (s, 9H, t-Bu), 1.82 (quintet, 2H, J= 6.5 Hz, CH_2), 3.40 (s, 2H, $CH_2C(O)$), 3.62 - 3.79 (m, 4H, NCH_2,OCH_2), 3.82 (s, 3H, OMe), 3.86 (s, 3H, OMe), 6.50 (s, 1H, ArH), 6.82 (s, 1H, ArH). δ_C: -5.38, 18.45, 25.85, 30.78, 35.85, 37.04, 56.37, 56.82, 60.31, 94.67, 109.76, 115.24, 138.46, 144.74, 149.27, 175.38. EIMS m/z (rel. intensity): 365 (M, 28), 308 (M- t-Bu, 100); Calcd for $C_{19}H_{31}NO_4Si$: 365.3.

1-(*tert*-Butyldimethylsilyloxypropyl)-4,5-dimethoxy-2(3H)-indolinone (5f') ν_{max} (neat): 2955, 2930, 2856, 1704, 1643, 1602, 1514 cm^{-1}. δ_H: 0.02 (s, 6H, 2xMeSi), 0.89 (s, 9H, t-Bu), 1.82 (quintet, 2H, J= 6.5 Hz, CH_2), 3.41 (s, 2H, $CH_2C(O)$), 3.60 - 3.80 (m, 4H, NCH_2,OCH_2), 3.81 (s, 3H, OMe), 3.90 (s, 3H, OMe), 6.53 (d, 1H, J= 7.5 Hz, ArH), 6.78 (d, 2H, J= 7.5 Hz, ArH). EIMS m/z (rel. intensity): 365 (M, 15), 308 (M- t-Bu, 100); Calcd for $C_{19}H_{31}NO_4Si$: 365.3.

4,7-Dimethoxy-1-(methoxycarbonylethyl)-2(3H)-indolinone (5g) mp: 108 - 109.5°C. ν_{max} (CH_2Cl_2): 3054, 2953, 1734, 1706, 1614, 1508 cm^{-1}. δ_H: 2.79 (t, 2H, J= 6.5 Hz, CH_2), 3.42 (s, 2H, CH_2), 3.69 (s, 3H, OMe), 3.80 (s, 3H, OMe), 3.81 (s, 3H, OMe), 4.25 (t, 2H, J= 6.5 Hz, NCH_2), 6.51 (d, 1H, J= 8.5 Hz, ArH), 6.80 (d, 1H, J= 8.5 Hz, ArH). δ_C: 33.69, 33.94, 37.84, 51.67, 55.58, 56.42, 104.65, 112.28, 132.84, 139.52,

149.86, 166.96, 171.77, 175.17. EIMS m/z (rel. intensity): 279 (M, 100), 178 (M- 15-CH_2=$CHCO_2Me$, 91), 264 (M-15, 11); Calcd for $C_{14}H_{17}NO_5$: 279.1.

1-(*tert*-Butyldimethylsilyloxypropyl)-4,7-dimethoxy-2(3H)-indolinone (5h) ν_{max} (neat): 2952, 2930, 1712, 1613, 1511 cm^{-1}. δ_H: 0.03 (s, 6H, 2xSiMe), 0.88 (s, 9H, t-Bu), 1.87 (quintet, 2H, J= 6.5 Hz, CH_2), 3.40 (s, 2H, $CH_2C(O)$), 3.66 (t, 2H, J= 6.5 Hz, NCH_2), 3.78 (s, 3H, OMe), 3.90 (s, 3H, OMe), 3.99 (t, 2H, J= 6.5 Hz, OCH_2), 6.48 (d, 1H, J= 8.5 Hz, ArH), 6.78 (d, 1H, J= 8.5 Hz, ArH). δ_C: -5.37, 18.30, 25.91, 32.70, 33.78, 39.72, 55.58, 56.46, 61.22, 104.41, 112.46, 133.31, 139.78, 149.78, 165.55, 175.44. EIMS m/z (rel. intensity): 365 (M, 8), 308 (M- t-Bu, 100); Calcd for $C_{19}H_{31}NO_4Si$: 365.3.

1-Benzyl-5-methyl-2(3H)-indolinone (5i) mp: 65 - 67.5°C. ν_{max} (CH_2Cl_2, film): 3025, 2908, 1710, 1626, 1606, 1500 cm^{-1}. δ_H: 2.30 (s, 3H, Me), 3.58 (s, 2H, $CH_2C(O)$), 4.89 (s, 2H, NCH_2), 6.59 (d, 1H, J= 72 Hz, ArH), 6.96 (d, 1H, J= 7.2 Hz, ArH), 7.09 (br s, 1H, ArH), 7.29 (s, 5H, PhH). δ_C: 20.94, 35.72, 43.65, 108.70, 124.45, 125.22, 127.24, 127.46, 127.89, 128.64, 131.82, 135.91, 141.83, 175.02. Anal. Calcd for $C_{16}H_{15}NO$: C, 80.97; H, 6.38; N, 5.91. Found: C, 80.82; H, 6.41; N, 5.91.

1-Butyl-5-(methoxycarbonyl)-2(3H)-indolinone (5j) mp: 82 - 83.5°C. ν_{max} (CH_2Cl_2, film): 3057, 2957, 2933, 1712, 1618, 1496 cm^{-1}. δ_H: 0.98 (t, 3H, J= 7.1 Hz, Me), 1.30-1.50 (m, 2H, CH_2), 1.58-1.78 (m, 2H, CH_2), 3.55 (s, 2H, $CH_2C(O)$), 3.71 (t, 2H, J= 7.1 Hz, NCH_2), 6.87 (d, 1H, J= 8.6 Hz, ArH), 7.91 (br s, 1H, ArH), 8.01 (d, 1H, J= 8.6 Hz, ArH). δ_C: 13.70, 20.16, 29.49, 35.37, 39.99, 52.00, 107.75, 124.01, 124.44, 125.64, 130.56, 148.82, 166.84, 175.09. Anal. Calcd for $C_{14}H_{17}NO_3$: C, 67.98; H, 6.93; N, 5.67. Found: C, 67.85; H, 7.11; N, 5.56.

1-Ethyl-2(3H)-indolinone (5k) Obtained as an inseparable mixture with the known[5] **6k**. ^1H nmr data for **5k** are quoted for signals that are discernible. ν_{max} (neat): 3054, 1711, 1614 cm^{-1}. δ_H: 1.16 (t, 3H, J= 7.4 Hz, Me), 3.40 (s, 2H, $CH_2C(O)$), 3.67 (q, 2H, J= 7.4 Hz, NCH_2), 6.75 - 7.30 (extensive overlap with ArHs of **6k**). δ_C: 12.63, 34.59, 35.82, 108.15, 122.07, 124.45, 124.73, 127.76, 144.28, 174.67.

7-Bromo-1-ethyl-5-methyl-2(3H)-indolinone (5l) mp: 103.5 - 107°C. ν_{max} (CH_2Cl_2, film): 2977, 2933, 2873, 1714, 1620, 1572 cm-1. δ_H: 1.26 (t, 3H, J= 7.2 Hz, Me), 2.23 (s, 3H, Me), 3.45 (s, 2H, $CH_2C(O)$), 4.11 (q, 2H, J= 7.2 Hz, NCH_2), 6.95 (s, 1H, ArH), 7.19 (s, 1H, ArH). δ_C: 14.89, 20.31, 29.65, 35.70, 36.15, 101.43, 124.41, 127.70, 133.14, 133.51, 175.03. Anal. Calcd for $C_{11}H_{12}BrNO$: C, 51.97; H, 4.76; , 5.51. Found: C, 52.07; H, 4.79; N, 5.38.

3-Carbomethoxy-1-(4-methoxyphenyl)-2-azetidinone (6a) mp: 98–100°C. ν_{max} (nujol): 2921, 2855, 1756, 1729, 1620, 1587, 1517 cm^{-1}. δ_H: 3.74 (t, 1H, J= 5.7 Hz, H-4), 3.78 (s, 3H, OMe), 3.81 (s, 3H, OMe), 3.92 (dd, 1H, J= 5.7, 2.8 Hz, H-3), 4.18 (dd, 1H, J= 5.7, 2.8 Hz, H-4'), 6.88 (d, 2H, J= 7.5 Hz, ArH), 7.30 (d, 2H, J= 7.5 Hz, ArH). δ_C: 41.37, 52.68, 52.89, 55.38, 114.30, 117.63, 131.44, 156.33, 158.24, 167.36. Anal. Calcd for $C_{12}H_{13}NO_4$: C, 61.26; H, 5.96; N, 5.57. Found: C, 60.87; H, 6.00; N, 5.57.

3-Carbomethoxy-4-carbomethoxymethyl-1-(4-methoxyphenyl)-2-azetidinone (6e) ν_{max} (CH_2Cl_2): 3048, 3001, 2954, 1761, 1736, 1665, 1640, 1611, 1585, 1514 cm^{-1}. Data quoted for the major *trans* isomer: (The only signal for the minor *cis* isomer that is well separated is H-3 and is given in parentheses.) δ_H: 2.64 (dd, 1H, J= 16.3, 8.6 Hz, CHC(O)), 3.13 (dd, 1H, J= 16.3, 4.3 Hz, CHC(O)), 3.70 (s, 3H, OMe), 3.79 (s, 3H, OMe), 3.81 (s, 3H, OMe), 3.99 (d, J= 2.1 Hz, H-3) and [4.36 (d, J= 5.3 Hz, H-3)] (1H), 4.61 - 4.71 (m, 1H, H-4), 6.90 (d, 2H, J= 8.5 Hz, ArH), 7.29 (d, 2H, J= 8.5 Hz, ArH). δ_C: 35.90, 51.11, 52.20, 52.85, 55.49,

59.84, 114.57, 119.07, 124.79, 156.78, 158.05, 166.81, 169.92. EIMS m/z (rel. intensity): 307 (M, 70); Calcd for $C_{15}H_{17}NO_6$: 307.1.

1-(4-Carbomethoxyphenyl)-3-carbomethoxy-4-propyl-2-azetidinone (6j) Obtained as an inseparable mixture of **6j** and **4j**. ^{1}H nmr signals of **6j** is derived from the comparison of the ^{1}H nmr of the mixture with that of **4j**. ν_{max} (neat): 3060, 2957, 2894, 1767, 1721, 1605, 1515 cm^{-1}. δ_H: 1.02 (t, 3H, J= 6.9 Hz, Me), 1.40 - 1.60 (m, 3H, CH_2,CH), 2.10 - 2.30 m, 1H, CH), 3.84, s, 3H, OMe), 3.88 (d, 1H, J= 2.6 Hz, H-3), 3.93 (s, 3H, OMe), 4.45 (dt, 1H, J= 8.9, 2.6 Hz, H-4), 7.42 (d, 2H, J= 7.8 Hz, ArH), 8.05 (d, 2H, J= 7.8 Hz, ArH).

2-Carbomethoxy-4-(2,5-dimethoxyphenyl)-1,4-oxazepin-3,7-dione (7) ν_{max} (CH_2Cl_2: 1739, 1692, 1619, 1509 cm^{-1}. δ_H: 2.69 (t, 2H, J= 7.0 Hz, CH_2), 3.69 (s, 3H, OMe), 3.80 (s, 6H, 2xOMe), 4.21 (t, 3H, J= 7.0 Hz, NCH_2), 5.15 (s, 1H, $CH(CO)_2$), 6.56 (dd, 1H, J= 7.2, 2.5 Hz, ArH), 6.61 (s, 1H, ArH), 7.02 (d, 1H, J= 7.2 Hz, ArH). δ_C: 31.61(-), 37.84(-), 51.97, 53.11, 55.76, 76.27, 102.06, 108.17, 118.16, 127.90, 137.69, 155.78, 160.64, 166.24, 171.28. EIMS m/z: 323 (M, 100), 292 (M-OMe, 12), 264 (M-CO_2Me, 33); Calcd for $C_{15}H_{17}NO_7$: 323.1.

3-Carbomethoxy-1-(4-methylphenyl)-4-methyl-5,6-dihydro-2-pyridinone (8m) mp: 154 - 156.5°C. ν_{max} (CH_2Cl_2): 2952, 2928, 2851, 1732, 1666, 1639, 1613, 1512 cm^{-1}. δ_H: 2.03 (s, 3H, C_4-Me), 2.31 (s, 3H, Me), 2.52 (t, 2H, J= 6.3 Hz, CH_2), 3.80 (t, 2H, J= 6.3 Hz, CH_2), 3.82 (s, 3H, OMe), 7.07 - 7.30 (m, 4H, ArH). δ_C: 20.92, 20.99, 3055, 47.53, 52.25, 124.71, 127.61, 129.34, 135.76, 139.54, 150.76, 161.84, 166.80. Anal. Calcd for $C_{15}H_{17}NO_3$: C, 69.47; H, 6.61; N, 5.40. Found: 69.49; H, 6.75; N, 5.39.

1-(2-Bromo-4-methylphenyl)-3-carbomethoxy-4-methyl-5,6-dihydro-2-pyridinone (8n) ν_{max} (neat): 3040, 2949, 2913, 1733, 1665, 1637, 1600, 1556, 1493 cm^{-1}. δ_H: 2.06 (s, 3H, C_4-Me), 2.32 (s, 3H, Me), 2.44 (dt, 1H, J= 17.1, 5.3 Hz, H5), 2.80 (dt, 1H, J= 17.1, 5.3 Hz, H5'), 3.70 (dd, 2H, J= 8.3, 5.3 Hz, NCH_2), 3.82 (s, 3H, OMe), 7.11 (d, 1H, J= 8.7 Hz, ArH), 7.19 (d, 1H, J= 8.7 Hz, ArH), 7.45 (br s, 1H, ArH). δ_C: 20.78, 21.14, 30.59(-), 47.41(-), 52.24, 121.91, 127.02, 129.17, 129.33, 133.76, 138.31, 139.46, 151.83, 161.20, 166.61. Anal. Calcd for $C_{15}H_{16}BrNO_3$: C, 53.25; H, 4.77; N, 4.14. Found: C, 53.44; H, 4.67; N, 4.01.

1-(3-Butenyl)-5-methyl-2(3H)-indolinone (9m) ν_{max} (CH_2Cl_2): 3052, 2979, 2924, 2868, 1707, 1624, 1600 cm^{-1}. δ_H: 2.32 (s, 3H, Me), 2.41 (dt, 2H, J= 6.8, 6.8 Hz, CH_2), 3.49 (s, 2H, $CH_2C(O)$), 3.75 (t, 2H, J= 6.8 Hz, NCH_2), 5.00 - 5.15 (m, 2H, $=CH_2$), 5.70 - 5.95 (m, 1H, =CH), 6.74 (d, 1H, J= 7.8 Hz, ArH), 7.06 (d, 1H, J= 7.8 Hz, ArH), 7.08 (s, 1H, ArH). δ_C: 21.05, 31.82, 35.83, 39.42, 108.07, 117.35, 124.71, 125.41, 127.96, 131.72, 134.61, 142.06, 174.99. Anal. Calcd for $C_{13}H_{15}NO$: C, 77.57; H, 7.52; N, 6.96. Found: C, 77.69; H, 7.86; N, 6.85.

7-Bromo-5-Methyl-1-(3-butenyl)-2(3H)-indolinone (9n) ν_{max} (CH_2Cl_2, film): 3076, 2952, 2921, 2858, 1718, 1641, 1619, 1571 cm^{-1}. δ_H: 2.30 (s, 3H, Me), 2.39-2.59 (m, 2H, CH_2), 3.50 (s, 2H, CH_2), 4.19 (t, 2H, J= 7.6 Hz, NCH_2), 5.00-5.19 (m, 2H, $=CH_2$), 5.71-5.99 (m, 1H, =CH), 7.00 (br s, 1H, ArH), 7.20 (br s, 1H, ArH). EIMS m/z (rel. intensity): 281 (M(^{81}Br), 36), 279 (M(^{79}Br), 36); Calcd for $C_{13}H_{14}{}^{81}BrNO$: 281.1 and $C_{13}H_{14}{}^{79}BrNO$: 279.1.

1-Carbomethoxy-3-(4-methylphenyl)-2-oxo-3-azabicyclo[4.1.0]heptane (10m) mp: 104 - 108.5°C. ν_{max} (CH_2Cl_2): 3053, 2951, 2924, 2858, 1731, 1658, 1612, 1513 cm^{-1}. δ_H: 1.51 ("t", 1H, J= 4.8 Hz, CH), 1.88 - 2.10 (m, 3H, CH_2,CH), 2.31 (s, 3H, Me), 2.35 - 2.49 (m, 1H, CH), 3.40 - 3.69 (m, 2H, NCH_2), 3.79 (s, 3H, OMe), 7.05 - 7.21 (m, 4H, ArH). δ_C: 17.09, 20.94, 22.53, 24.53, 29.14, 47.68, 52.58, 125.59, 129.50, 136.32,

140.20, 166.24, 170.80. CIMS (m/z, rel. intensity): 260 (M+1, 100). Calcd for $C_{15}H_{17}NO_3$: 259.1.

9-Methoxycarbonyl-7-(4-methylphenyl)-8-oxo-1,2,7-triazabicyclo[3.4.0]-2-nonene (12m) mp 125 - 128.5°C ν_{max} (CH_2Cl_2): 3333, 3030, 2952, 1745, 1666, 1606, 1582, 1552, 1513 cm^{-1}. δ_H: 1.85-2.07 (m, 1H, CH), 2.15-2.38 (m, 1H, CH), 2.32 (s, 3H, Me), 3.60-3.90 (m, 3H, NCH_2, CH), 3.83 (s, 3H, OMe), 6.71 (s, 1H, =CH), 6.92 (s, 1H, NH), 7.09 - 7.23 (m, 4H, ArH). δ_C: 20.98, 25.22, 49.00, 49.29, 53.47, 72.12, 125.04, 129.65, 136.84, 139.51, 144.53, 165.51, 171.20. CIMS (m/z, rel. intensity): 288 (M+1, 100), 259 (M-N_2, 52). Calcd for $C_{15}H_{17}N_3O_3$: 287.1

9-Methoxycarbonyl-7-(2-bromo-4-methylphenyl)-8-oxo-1,2,7-triazabicyclo[3.4.0]-2-nonene (12n) mp: 142 - 145°C. ν_{max} (CH_2Cl_2): 3348, 3061, 2955, 1748, 1664, 1601, 1493 cm^{-1}. δ_H: 1.90-2.52 (m, 2H, CH_2), 2.35 (s, 3H, Me), 3.40-3.91 (m, 3H, NCH_2, CH), 3.83 and 3.85 (s, 3H, OMe), 6.75 (s, 1H, =CH), 6.90 and 6.93 (s, 1H, NH), 7.05-7.20 (m, 2H, ArH), 7.49 (br s, 1H, ArH). [This compound showed restricted rotation about the aryl C-N bond. δ_H (DMSO-d_6): 1.79-2.09 (m, 1H, CH), 2.11-2.39 (m, 1H, CH), 2.33 (s, 3H, Me), 3.30-3.81 (m, 3H, NCH_2, CH), 3.70 and 3.74 (s, 3H, OMe), 6.78 (s, 1H, =CH), 7.10-7.40 (m, 3H, NH,2x ArH), 7.55 (br s, 1H, Ar-H). When this sample was heated at 63°C, the signals and in particular the ester methoxy and NH resonances coalesced to give a singlet at δ 3.77 and a broad hump between 7.22 and 7.35, respectively.] EIMS (m/z, rel. intensity): 339 (M(^{81}Br)-N_2, 11.2), 337 (M(^{79}Br)-N_2, 10.7). Calcd for $C_{15}H_{16}{}^{79}BrN_3O_3$: 365.1 and $C_{15}H_{16}{}^{81}BrN_3O_3$: 367.1.

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REFERENCES AND NOTES

1. a) For recent reviews see, a) Padwa, A.; Krumpe, K. E. *Tetrahedron* **1992**, *48*, 5385. b) Davies, H. M. L. *Comprehensive Organic Synthesis*, Trost, B. M.; Fleming, I. ed., Pergamon Press, Oxford, **1991**, vol. *4*, 1052. c) Adams, J.; Spero, D. M. *Tetrahedron* **1991**, *47*, 1765.
2. Doyle, M. P.; Shanklin, M. S.; Pho, H. Q.; Mahapatro, S. N. *J. Org. Chem.* **1988**, *53*, 1017.
3. ®Registered trademark of Dupont Co. a) For a review see Olah, G. A.; Iyer, P. S.; Prakash, G. S. K. *Synthesis* **1986**, 513. b) Purchased from Aldrich Chemical Co., WI and used without further purification.
4. Rishton, M. R.; Schwartz, M. A. *Tetrahedron Lett.* **1988**, *29*, 2613.
5 Wee, A. G. H.; Liu, B-S.; Zhang, L. *J. Org. Chem.* **1992**, *57*, 4404.
6. Preliminary communication: Liu, B-S.; Wee, A. G. *Heterocycles* **1993**, *36*, 455.
7. Neises, B.; Steglich, W. *Angew. Chem., Int. Ed. Engl. 1978*, **17**, 522.
8. Taber, D. F.; Ruckle, R. E. Jr.; Hennessy, M. J. *J. Org. Chem.* **1986**, *51*, 4077.

9. For the Nafion-H catalysed decarboxylation of a β-keto ester, see Shono, T.; Matsumura, Y.; Tsubata, K. *J. Am. Chem. Soc.* **1981**, *103*, 1172.
10. a) Beames, D. J.; Mander, L. N. *Aust. J. Chem.* **1974**, *27*, 1257. b) Beames, D. J.; Klose, T. R.; Mander, L. N. *Aust. J. Chem.* **1974**, *27*, 1269. c) Johnson, D. W.; Mander, L. N. *Aust. J. Chem.* **1974**, *27*, 1287. d) Burke, S. D.; Grieco, P. A. *Org. React.* **1979**, *26*, 383.
11. a) Babu, S. D.; Hrytsak, M. D.; Durst, T. *Can. J. Chem.* **1989**, *67*, 1071. b) See ref. 2.
12. ν_{max} (neat): 3500 - 3300, 3055, 2937, 1701, 1621, 1511 cm^{-1}. δ_H: 1.66 (br s, 1H, OH), 1.82 (quintet, J= 6.5 Hz, CH_2), 3.50 (s, 2H, $CH_2C(O)$), 3.55 (t, 2H, J= 6.5 Hz, OCH_2), 3.81 (s, 3H, OMe), 3.85 (t, 2H, J= 6.5 Hz, NCH_2), 3.89 (s, 3H, OMe), 6.49 (s, 1H, ArH), 6.88 (s, 1H, ArH).
13. This is in analogy to the steric hindrance observed in the electrophilic aromatic substitution reactions of *meta*-disubstituted benzenes; see March, J. *Advanced Organic Chemistry*, 4th ed., Wiley, New York, **1992**, 514.
14. Kirmse, W. *Carbene Chemistry*, 2nd ed. Academic Press, New York, **1971**, pp 430-436. b) The interception of a carbene by an ester carbonyl oxygen is relatively rare when compared to the interception by a ketone and an aldehyde carbonyl oxygen.
15. We have tentatively assigned the *cis* stereochemistry to the ring juncture on account of the fact that the pyrazolines are formed under kinetic control and following a parallel plane *exo* approach.
16. For example, when a sample of **4m** was stored at rt (24°C) 1.3-dipolar cycloaddition occurred to give **11m**. **11m** slowly tautomerized to **12m** over 3 d.
17. The $CuSO_4$ catalysed[9d] decomposition of **4m** only resulted in the formation of **9m** in 21% yield; the cyclopropane derivative **10m** was not obtained.
18. a) Dean, F. M.; Park, K. B. *J. Chem. Soc. Perkin Trans. I* **1976**, 1260 and references cited. b) McGreer, D. E.; Wu, W-S. *Can. J. Chem.* **1967**, *45*, 461.
19. a) For a review: Engel, P. S. *Chem. Rev.* **1980**, *80*, 99. b) Gerth, D. B.; Engel, P. S. *J. Am. Chem. Soc.* **1983**, *105*, 6849.
20. Doddrell, D. M.; Pegg, D. T.; Bendall, M. R. *J. Magn. Reson.* **1982**, *48*, 323.
21. Still, W. C.; Kahn, M.; Mitra, A. *J. Org. Chem.* **1978**, *43*, 2923.

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