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Homogeneous catalytic aminocarbonylation of nitrogen-containing iodo-heteroaromatics. Synthesis of *N*-substituted nicotinamide related compounds

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Abstract—Various primary and secondary amines, including amino acid methyl esters, were used as nucleophiles in palladium-catalysed aminocarbonylation of 2-iodopyridine, 3-iodopyridine and iodopyrazine. *N*-Substituted nicotinamides and 3-pyridyl-glyoxylamides (2-oxo-carboxamide type derivatives) of potential biological importance can be obtained from 3-iodopyridine as a result of simple and double carbon monoxide insertions, respectively. The latter examples can be obtained in synthetically acceptable yields by using elevated carbon monoxide pressure. On the contrary, *N*-alkyl/aryl-carboxamides were obtained exclusively in the whole pressure range by using 2-iodopyridine and iodopyrazine.

1. Introduction

Palladium-catalysed carbonylation reactions including amino- and alkoxycarbonylation and carbonylative coupling reactions are widely used in synthetic chemistry.[1] There are a number of applications concerning the synthesis of simple building blocks and the functionalisation of biologically important skeletons.[2] Aminocarbonylation of iodoarenes, iodoalkenes (and that of the corresponding aryl- and enol-triflates) plays a special role among these reactions. Even carboxamides with bulky *N*-substituents are available via this methodology from easily available starting materials. The synthesis of aryl carboxamides and 2-oxo-carboxamides with various structures by using aryl-triflates or aryl halides has been already published.[3]

Our research on homogeneous aminocarbonylation of iodo-heteroaromatics was encouraged by two facts. On one hand, among the application of amines as nucleophiles, that of the amino acid esters as *N*-nucleophiles in aminocarbonylation could be of great importance for two reasons: (i) amino acid derivatives or (oligo)peptides can be marked at the N-termini by the desired aromatic groups and (ii) skeletons of practical importance can be functionalised by amino acids protected at the carboxyl termini. Although the N-acylation of amino acids is widely used in synthetic chemistry, to the best of our knowledge, sporadic examples were published only for the use of homogeneous aminocarbonylation of aryl halides as a tool for the introduction of a carboxamide moiety.[4,5] We found recently[6] that homogeneous catalytic aminocarbonylation of steroidal substrates can be effectively carried out in ionic liquids as solvents even at atmospheric CO pressure using various palladium–phosphine catalytic systems.

On the other hand, the facile synthesis of nicotinic acid derivatives (nicotinamides and the corresponding ketocarboxamides, 3-pyridyl-glyoxylamides) of practical importance might be available via aminocarbonylation of 3-iodopyridine. The biological importance of nicotinamide type derivatives including their evident importance as cofactors, the role of nicotinamide as NAD^+ and $NADP^+$ building block has been reviewed even recently.[7–9]

Encouraged by the increasing importance of the selective synthesis of heterocyclic amides possessing amino acid moieties in the amide functionality, we decided to investigate the possibility of extending the scope of this method to the functionalisation of heterocyclic iodoaryl substrates. To the best of our knowledge, only a few papers are available on the palladium-catalysed carbonylation of pyridyl-halides. The synthesis of ^{11}C-containing nicotinamide and nicotinhydrazide was carried out by amino- and hydrazinocarbonylation, respectively.[10] Heteroaryl bromides, among them 2,5-dibromo-pyridine derivatives, were carbonylated with methanol, piperidine and related nucleophiles in the presence of palladacycle[11] or palladium–2,2′-bypiridine catalysts.[12]

Accordingly, the facile, high-yielding palladium-catalysed aminocarbonylation of 2-iodopyridine, 3-iodopyridine and

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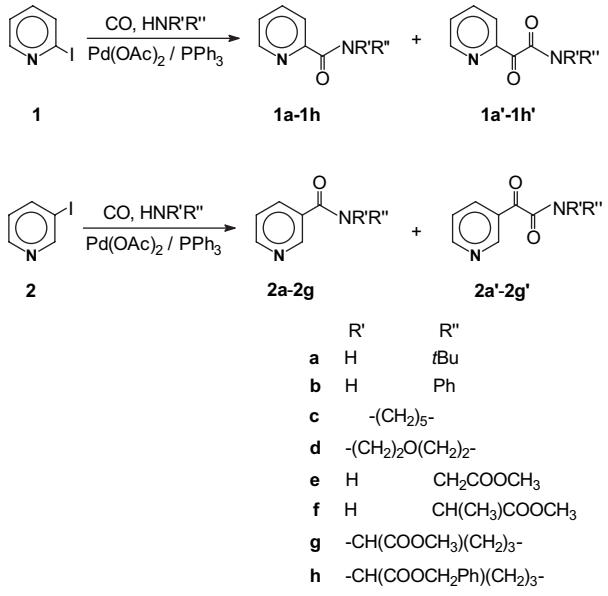
iodopyrazine with various *N*-nucleophiles is published in the present paper.

2. Results and discussion

2-Iodopyridine (**1**), 3-iodopyridine (**2**) and iodopyrazine (**3**) were reacted with *tert*-butylamine (**a**), aniline (**b**), piperidine (**c**), morpholine (**d**), methyl glycinate (**e**), methyl alaninate (**f**), methyl prolinate (**g**) and benzyl prolinate (**h**) under atmospheric and elevated (20–60 bar) carbon monoxide pressures in the presence of in situ generated palladium(0)–triphenylphosphine catalysts (Scheme 1). Palladium(II) acetate was used as catalytic precursor (the formation of Pd(0) species from the generally used $Pd(OAc)_2$–PPh_3 system has been proved by cyclic voltammetry and ^{31}P NMR).[13,14] The reduction of Pd(II) to Pd(0) is due to PPh_3, which is itself oxidised to triphenylphosphine oxide.



	R'	R''
a	H	*t*Bu
b	H	Ph
c	-$(CH_2)_5$-	
d	-$(CH_2)_2O(CH_2)_2$-	
e	H	CH_2COOCH_3
f	H	$CH(CH_3)COOCH_3$
g	-$CH(COOCH_3)(CH_2)_3$-	
h	-$CH(COOCH_2Ph)(CH_2)_3$-	

Scheme 1. Aminocarbonylation of 2-iodopyridine (**1**) and 3-iodopyridine (**2**).

Similar reactivities have been obtained for the two iodopyridines, **1** and **2**. The use of unfunctionalised amines (except for aniline) resulted in nearly complete conversion even under atmospheric carbon monoxide pressure in 24 h. However, decreased reactivity has been observed with amino acid methyl esters (as hydrochloride salts) as nucleophiles. Due to their in situ dehydrochlorination and the presence of triethylamine hydrochloride in the reaction mixture, the target compounds were formed in substantially lower yields. In order to achieve higher conversion and yields of preparative interest for amino acid derivatives, higher carbon monoxide pressure (above 40 bar) was necessary (Table 1).

The chemoselectivity of the aminocarbonylation reaction is strikingly different for **1** and **2**. While carboxamides (**1a–h**) have been formed almost exclusively when **1** has been used as a substrate, the mixture of carboxamides (**2a–h**) and ketocarboxamides (**2a′–h′**) have been obtained by using **2** with varying carbon monoxide pressures.

By using **1** as substrates possessing a 2-iodo-substituent adjacent to nitrogen, traces of ketocarboxamides have been detected only in the case of secondary amines (**c** and **d**). It means that the simple and double carbon monoxide insertions are influenced mainly by the structure of the substrate itself. The resulting carboxamides have been obtained in good isolated yields with **a**, **c** and **d** as nucleophiles. However, **1** shows rather poor reactivity towards amino acid derivatives (**f–h**) (except for **e**) and aniline (**b**) resulting in

Table 1. Aminocarbonylation of 2-iodopyridine (**1**) and 3-iodopyridine (**2**) with primary and secondary amines[a]

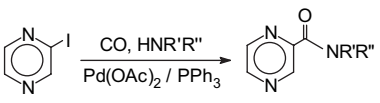
Substrate	Amine	Reaction time [h]	*p*(CO) [bar]	Conversion [%]	Ratio of the carbonylated products;[b] (isolated yields)[c] [%]	
					Carboxamide	Ketocarboxamide
1	^{t}BuNH$_2$	24	1	89	100 (**1a**); (70)	0
1	^{t}BuNH$_2$	6	20	>98	100 (**1a**); (82)	0
1	^{t}BuNH$_2$	6	40	>98	100 (**1a**); (78)	0
1	^{t}BuNH$_2$	6	60	>98	100 (**1a**); (80)	0
1	Aniline	72	1	27	100 (**1b**); (20)	0
1	Piperidine	22	1	>98	98 (**1c**); (83)	2 (**1c′**)
1	Morpholine	72	1	>98	98 (**1d**); (80)	2 (**1d′**)
1	GlyOMe	72	1	93	100 (**1e**); (61)	0
1	AlaOMe	22	1	16	100 (**1f**); (12)	0
1	ProOMe	22	1	27	100 (**1g**); (20)	0
1	ProOBn	22	1	30	100 (**1h**); (23)	0
2	^{t}BuNH$_2$	24	1	>98	48 (**2a**); (34)	52 (**2a′**); (44)
2	^{t}BuNH$_2$	70	40	>98	9 (**2a**)	91 (**2a′**); (76)
2	Aniline	66	40	10	100 (**2b**); (7)	0
2	Piperidine	24	1	>98	69 (**2c**); (60)	31 (**2c′**); (22)
2	Morpholine	24	1	>98	47 (**2d**); (32)	53 (**2d′**); (43)
2	GlyOMe	24	40	20	10 (**2e**); (7)	90 (**2e′**); (71)
2	AlaOMe	22	40	80	20 (**2f**); (15)	80 (**2f′**); (68)
2	AlaOMe	40	90	96	17 (**2f**)	83 (**2f′**); (72)
2	ProOMe	24	40	80	70 (**2g**); (59)	30 (**2g′**); (24)

[a] Reaction conditions: 0.025 mmol $Pd(OAc)_2$; 0.05 mmol PPh_3; 1 mmol **1** (or **2**); 3 mmol *tert*-butylamine (or 1.1 mmol amino acid methyl ester hydrochloride); 0.5 ml triethylamine; 10 ml DMF.
[b] Determined by GC–MS.
[c] Isolated yields are based on the amount of the starting material (**1** or **2**).

conversions up to 30%. This way, in spite of the excellent chemoselectivity towards carboxamides, lower isolated yields have been obtained.

The substrate possessing 3-iodo-substituent (**2**) behaves like the 'hydrocarbon-based' iodo-aromatics (iodobenzene and iodonaphthalene) investigated previously. These substrates tend to undergo double carbon monoxide insertion and the formation of the corresponding ketocarboxamides is favoured. It is worth noting that the double carbonylation of **2** is comparable to monocarbonylation even under atmospheric carbon monoxide pressure, as has been shown for *tert*-butylamine, piperidine and morpholine. The chemoselectivity towards ketocarboxamides is favoured by the increased carbon monoxide pressure, e.g., under 40 bar carbon monoxide pressure the 2-oxo-carboxamide **2a′** is dominating. Although the formation of the 2-oxo-carboxamides is influenced by the structure of the amine nucleophile and lower chemoselectivity towards double carbonylation has been observed, e.g., in case of **c**, they were formed in isolable amounts in all cases except for **2b′**. The use of aniline as less basic nucleophile favours the formation of the corresponding carboxamide (**2b**).

The aminocarbonylation of iodopyrazine (**3**) resulted in the exclusive formation of carboxamides (Scheme 2, Table 2). Even trace amounts of ketocarboxamides could not be determined by GC–MS. Nearly complete conversions and excellent isolated yields have been obtained by using all amine nucleophiles except for **b**. The chemospecific reaction, similar to **1**, can be explained by the close proximity of one of the two aromatic nitrogens (vide infra). As for the positions of the nitrogens related to the iodoaryl functionality, **3** can be considered as a 'hybrid' of **1** and **2**. However, the much higher reactivity of **3** towards amino acid derivatives shows the importance of the electronic parameters as well.



3 **3a-3g**

	R'	R"
a	H	*t*Bu
b	H	Ph
c	-(CH$_2$)$_5$-	
d	-(CH$_2$)$_2$O(CH$_2$)$_2$-	
e	H	CH$_2$COOCH$_3$
f	H	CH(CH$_3$)COOCH$_3$
g	-CH(COOCH$_3$)(CH$_2$)$_3$-	

Scheme 2. Aminocarbonylation of iodopyrazine (**3**).

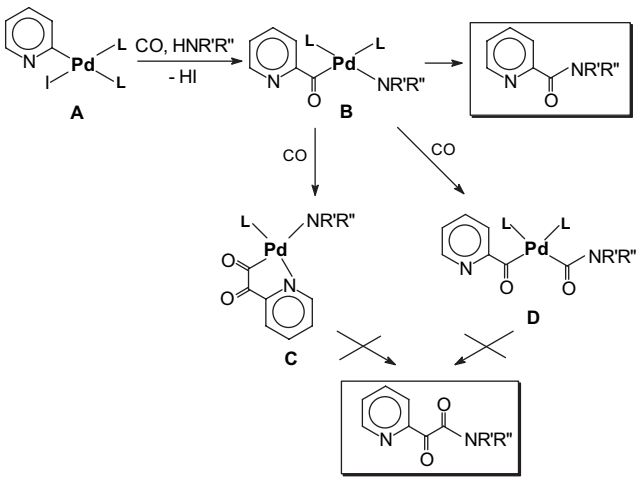
Although the formation of 2-oxo-carboxamide can be explained in two ways, namely both the 'glyoxyl route' and the 'acyl-aminocarbonyl route' can be operative, detailed mechanistic studies revealed that the latter is responsible for the double carbonylation.[15,16] This way, the iodo-substrates are oxidatively added to in situ formed palladium(0) complexes. Carbon monoxide is coordinated to palladium and its insertion to Pd–C bond takes place. While nicotinoyl–palladium complexes (formed from 3-pyridyl–palladium intermediate) might lead to the corresponding nicotinoyl-aminocarbonyl complex, which results in ketocarboxamides by reductive elimination, the corresponding picolinoyl–palladium species (**B**) (formed from 2-pyridyl–palladium intermediate (**A**)) react directly with the amine nucleophile providing the corresponding carboxamide (Scheme 3).

Table 2. Aminocarbonylation of iodopyrazine (**3**) with primary and secondary amines[a]

Amine	Reaction time [h]	*p*(CO) [bar]	Conversion[b] [%]	Isolated yield of the carboxamide[c] [%]
^{t}BuNH$_2$	22	40	>98	82 (**3a**)
^{t}BuNH$_2$	22	20	>98	80 (**3a**)
^{t}BuNH$_2$	22	1	>98	85 (**3a**)
Aniline	22	1	10	8 (**3b**)
Aniline	137	40	21	16 (**3b**)
Piperidine	22	1	>98	81 (**3c**)
Morpholine	22	1	>98	83 (**3d**)
GlyOMe	24	40	92	78 (**3e**)
AlaOMe	24	40	>98	82 (**3f**)
ProOMe	137	40	>98	74 (**3g**)

[a] Reaction conditions: 0.025 mmol Pd(OAc)$_2$; 0.05 mmol PPh$_3$; 1 mmol iodopyrazine; 3 mmol *tert*-butylamine (or 1.1 mmol amino acid methyl ester hydrochloride); 0.5 ml triethylamine; 10 ml DMF.
[b] Determined by GC–MS.
[c] Isolated yields are based on the amount of the starting material (**3**). Carboxamide type products were formed exclusively (no double carbonylation occurred).

Although similarities in the aminocarbonylation of iodo-aromatics and iodoalkenes have been observed, the exclusive carboxamide formation with **1** and **3** is quite unexpected. Mechanistically two explanations can be rationalised: (i) the catalytic transformation of **1** (and similarly that of **3**) is blocked at the stage of the reductive elimination of ketocarboxamide type products from the acyl-aminocarbonyl–palladium intermediate (**D**), and even more probably, (ii) the palladium–arylglyoxyl derivative (**C**) (aryl=2-pyridyl or 2-pyrazyl) is stabilised by N-coordination of the heteroaryl moieties (Scheme 3). Therefore, product formation can be expected from the aminolysis of the palladium–acyl complex (**B**) exclusively.



Scheme 3. Possible intermediates in the aminocarbonylation of 2-iodopyridine (**1**) and 3-iodopyridine (**2**).

3. Conclusions

Palladium-catalysed aminocarbonylation proved to be an efficient, highly reproducible method for the functionalisation of *N*-containing iodo-heteroaromatics in the presence of simple primary and secondary amines as well as amino acid methyl esters as amine nucleophiles. The position of the iodo-substituent related to nitrogen determines the chemoselectivity towards mono- and di-carbonylated products. This way, carboxamide type derivatives have been isolated as a result of chemoselective carbon monoxide insertion by using 2-iodopyridine and iodopyrazine, while the mixture of carboxamides and 2-keto-carboxamides were obtained in the whole pressure range using 3-iodopyridine.

4. Experimental

4.1. General procedures

^{1}H and ^{13}C NMR spectra were recorded in $CDCl_3$ on a Varian Inova 400 spectrometer at 400.13 MHz and 100.62 MHz, respectively. Chemical shifts δ are reported in parts per million relative to $CHCl_3$ (7.26 and 77.00 ppm for ^{1}H and ^{13}C, respectively). Elemental analyses were performed on a 1108 Carlo Erba apparatus. Samples of the catalytic reactions were analysed with a Hewlett Packard 5830A gas chromatograph fitted with a capillary column coated with OV-1. IR spectra were recorded on a Nicolet 5700 FT-IR spectrometer.

4.2. Aminocarbonylation experiments at normal pressure

In a typical experiment a solution of $Pd(OAc)_2$ (5.6 mg, 0.025 mmol), PPh_3 (13.1 mg, 0.05 mmol), 0.5 mmol iodo-substrate (**1**, **2** or **3**), 1.5 mmol *tert*-butylamine (**a**) (or 0.55 mmol amino acid methyl ester hydrochloride (**e**–**h**)) was dissolved in 10 ml DMF under argon. Triethylamine (0.5 ml) was added to the homogeneous yellow solution and the atmosphere was changed to carbon monoxide. The colour changed to dark red. The reaction was conducted for the given reaction time at 50 °C. Some metallic palladium was formed at the end of the reaction, which was filtered. (A sample of this solution was immediately analysed by GC–MS.) The mixture was then concentrated by distillation and evaporated to dryness. The residue was dissolved in chloroform (20 ml) and washed with water (twice 20 ml). The organic phase was dried over Na_2SO_4 and concentrated to a yellow waxy material or a thick oil. Chromatography (silica, chloroform, then chloroform/ethanol=1/1) yielded the desired compounds as yellow solids.

4.3. Aminocarbonylation experiments at high pressure

The DMF solution of the catalyst precursor and reactants (amounts given in Section 4.2.) was transferred under argon into a 100 ml stainless steel autoclave. The reaction vessel was pressurised up to 60 bar total pressure with carbon monoxide and the magnetically stirred mixture was heated in an oil bath at 50 °C for the given reaction time. The workup procedure is identical with that given above.

4.4. Characterisation of the products

4.4.1. 2-(*N*-*tert*-Butyl-carboxamido)-pyridine (1a). ^{1}H NMR ($CDCl_3$) δ: 8.49 (d, 4.8 Hz, 1H, Py); 8.16 (d, 7.6 Hz, 1H, Py); 7.97 (br s, 1H, NH); 7.80 (dt, 7.6 Hz, 1.6 Hz, 1H, Py); 7.36 (dt, 4.8 Hz, 1.2 Hz, 1H, Py); 1.46 (s, 9H, $C(CH_3)_3$). ^{13}C NMR ($CDCl_3$) δ: 163.6; 151.1; 147.9; 137.5; 126.0; 121.9; 51.1; 29.0. IR (KBr (cm^{-1})): 3375 (NH); 1681 (CON). MS *m*/*z* (rel int. %): 178 (22), 163 (90), 106 (86), 78 (100). Analysis calculated for $C_{10}H_{14}N_2O$ (178.23): C, 67.39; H, 7.92; N, 15.72. Found: C, 67.55; H, 8.12; N, 15.46. Yield: 82%.

4.4.2. 2-(*N*-Phenyl-carboxamido)-pyridine (1b). ^{1}H NMR ($CDCl_3$) δ: 9.98 (br s, 1H, NH); 8.58 (d, 4.8 Hz, 1H, Py); 8.28 (d, 7.6 Hz, 1H, Py); 7.90 (dt, 7.6 Hz, 1.6 Hz, 1H, Py); 7.75 (d, 7.8 Hz, 2H, Ph-*ortho*); 7.46 (m, 1H, Ph-*para*); 7.40 (m, 2H, Ph-*meta*); 7.12 (dt, 4.8 Hz, 1.4 Hz, 1H, Py). ^{13}C NMR ($CDCl_3$) δ: 161.9; 149.9; 147.9; 137.7; 137.6; 129.0; 126.3; 124.3; 122.4; 119.7. IR (KBr (cm^{-1})): 3336 (NH); 1671 (CON). MS *m*/*z* (rel int. %): 198 (68), 106 (12), 79 (100), 78 (86). Analysis calculated for $C_{12}H_{10}N_2O$ (198.22): C, 72.71; H, 5.08; N, 14.13. Found: C, 72.90; H, 5.22; N, 13.98. Yield: 20%.

4.4.3. 2-(*N*,*N*-Penta-1,5-diyl-carboxamido)-pyridine (1c). ^{1}H NMR ($CDCl_3$) δ: 8.41 (d, 4.8 Hz, 1H, Py); 7.60 (t, 7.6 Hz, 1H, Py); 7.37 (d, 7.6 Hz, 1H, Py); 7.15 (dt, 7.6 Hz, 1.6 Hz, 1H, Py); 3.58 (br s, 2H, NCH_2); 3.25 (br s, 2H, NCH_2); 1.50 (br s, 4H, $2\times CH_2$); 1.40 (br s, 2H, CH_2). ^{13}C NMR ($CDCl_3$) δ: 167.4; 155.6; 148.3; 136.8; 124.0; 123.0; 48.1; 43.1; 26.3; 25.4; 24.4. IR (KBr (cm^{-1})): 1620 (CON). MS *m*/*z* (rel int. %): 190 (6), 106 (8), 84 (100), 78 (30). Analysis calculated for $C_{11}H_{14}N_2O$ (190.24): C, 69.45; H, 7.42; N, 14.72. Found: C, 69.62; H, 7.60; N, 14.48. Yield: 83%.

4.4.4. 2-(*N*,*N*-Penta-1,5-diyl-glyoxylamido)-pyridine (1c′). MS *m*/*z* (rel int. %): 218 (34), 189 (6), 149 (11), 112 (100), 78 (60), 69 (91).

4.4.5. 2-(*N*,*N*-Penta-3-oxa-1,5-diyl-carboxamido)-pyridine (1d). ^{1}H NMR ($CDCl_3$) δ: 8.42 (d, 4.8 Hz, 1H, Py); 7.68 (t, 7.6 Hz, 1H, Py); 7.50 (d, 7.6 Hz, 1H, Py); 7.21 (dt, 7.6 Hz, 1.6 Hz, 1H, Py); 3.70 (br s, 4H, $2\times OCH_2$); 3.5–3.6 (m, 4H, $2\times NCH_2$). ^{13}C NMR ($CDCl_3$) δ: 167.4; 153.6; 148.2; 137.1; 124.6; 124.0; 66.9; 66.7; 47.7; 42.7. IR (KBr (cm^{-1})): 1621 (CON). MS *m*/*z* (rel int. %): 192 (26), 106 (32), 86 (100), 78 (61). Analysis calculated for $C_{10}H_{12}N_2O_2$ (192.22): C, 62.49; H, 6.29; N, 14.57. Found: C, 62.37; H, 6.32; N, 14.29. Yield: 80%.

4.4.6. 2-(*N*,*N*-Penta-3-oxa-1,5-diyl-glyoxylamido)-pyridine (1d′). MS *m*/*z* (rel int. %): 220 (20), 114 (58), 106 (18), 86 (30), 78 (67).

4.4.7. 2-(*N*-(Methoxycarbonylmethyl)-carboxamido)-pyridine (1e). ^{1}H NMR ($CDCl_3$) δ: 8.58 (d, 4.4 Hz, 1H, Py); 8.45 (br s, 1H, NH); 8.16 (d, 7.6 Hz, 1H, Py); 7.80 (dt, 7.6 Hz, 1.4 Hz, 1H, Py); 7.40 (dt, 4.4 Hz, 1.4 Hz, 1H, Py); 4.24 (d, 8.4 Hz, 1H, CH_2); 3.83 (s, 3H, OCH_3). ^{13}C NMR ($CDCl_3$) δ: 170.1; 164.6; 149.3; 148.2; 137.2; 126.3; 122.2; 52.3; 41.2. IR (KBr (cm^{-1})): 3384 (NH); 1752 (COO); 1673 (CON). MS *m*/*z* (rel int. %): 194 (8), 162

(34), 135 (98), 106 (81), 78 (100). Analysis calculated for $C_9H_{10}N_2O_3$ (194.19): C, 55.67; H, 5.19; N, 14.43. Found: C, 55.62; H, 5.33; N, 14.28. Yield: 61%.

4.4.8. 2-(*N*-(1′-Methoxycarbonyl-ethyl)-carboxamido)-pyridine (1f). ^{1}H NMR ($CDCl_3$) δ: 8.55 (d, 4.4 Hz, 1H, Py); 8.46 (br s, 1H, NH); 8.16 (d, 7.6 Hz, 1H, Py); 7.82 (dt, 7.6 Hz, 1.4 Hz, 1H, Py); 7.40 (dt, 4.4 Hz, 1.4 Hz, 1H, Py); 4.78 (qi, 7.0 Hz, 1H, C*H*(CH_3)); 3.85 (s, 3H, OCH_3); 1.51 (d, 7.0 Hz, 3H, CH(C*H*$_3$)). ^{13}C NMR ($CDCl_3$) δ: 173.1; 163.9; 149.4; 148.2; 137.2; 126.3; 122.2; 52.4; 48.1; 18.4. IR (KBr (cm^{-1})): 3382 (NH); 1744 (COO); 1674 (CON). MS *m*/*z* (rel int. %): 208 (3), 149 (100), 106 (54), 78 (80). Analysis calculated for $C_{10}H_{12}N_2O_3$ (208.22): C, 57.69; H, 5.81; N, 13.45. Found: C, 57.85; H, 5.94; N, 13.26. Yield: 12%.

4.4.9. 2-(*N*-(1′-Methoxycarbonyl-butan-1,4-diyl)-carboxamido)-pyridine (1g). ^{1}H NMR ($CDCl_3$) δ: 8.58; 8.40 (d, 4.4 Hz, 1H, Py); 8.00; 7.86 (d, 7.6 Hz, 1H, Py); 7.70–7.76 (m, 1H, Py); 7.25–7.32 (m, 1H, Py); 5.12; 4.65 (m, 1H, NC*H*); 3.7–4.00 (m, 2H, NCH_2); 3.70; 3.59 (s, 3H, OCH_3); 1.9–2.3 (m, 4H, CH_2CH_2). ^{13}C NMR ($CDCl_3$) δ: 173.4; 172.6; 166.2; 165.5; 153.4; 152.8; 147.8; 147.1; 136.8; 136.7; 125.0; 124.5; 61.6; 60.1; 52.1; 51.9; 49.7; 48.2; 31.8; 28.8; 25.4; 22.0. IR (KBr (cm^{-1})): 1744 (COO); 1631 (CON). MS *m*/*z* (rel int. %): 234 (11), 175 (38), 128 (100), 106 (51), 78 (84). Analysis calculated for $C_{12}H_{14}N_2O_3$ (234.25): C, 61.53; H, 6.02; N, 11.96. Found: C, 61.63; H, 6.14; N, 11.80. Yield: 20%.

4.4.10. 2-(*N*-(1′-Benzyloxycarbonyl-butan-1,4-diyl)-carboxamido)-pyridine (1h). ^{1}H NMR ($CDCl_3$) δ: 8.58; 8.18 (d, 4.4 Hz, 1H, Py); 7.97; 7.88 (d, 7.6 Hz, 1H, Py); 7.70 (m, 1H, Py); 7.20–7.45 (m, 6H, Py+Ph); 5.0–5.25 (m, 2H, C*H*$_2$Ph); 5.15; 4.72 (m, 1H, NCH); 3.75–4.05 (m, 2H, NCH_2); 1.85–2.3 (m, 4H, CH_2CH_2). ^{13}C NMR ($CDCl_3$) δ: 172.7; 172.0; 166.3; 165.5; 153.5; 152.7; 147.9; 147.0; 136.7; 135.8; 135.7; 128.5; 128.3; 128.2; 124.9; 124.5; 124.3; 66.7; 66.5; 61.7; 60.2; 49.6; 48.3; 31.8; 28.8; 25.4; 21.9. IR (KBr (cm^{-1})): 1743 (COO); 1632 (CON). MS *m*/*z* (rel int. %): 310 (8), 219 (20), 204 (81), 175 (76), 106 (80), 91 (83), 78 (100). Analysis calculated for $C_{18}H_{18}N_2O_3$ (310.35): C, 69.66; H, 5.85; N, 9.03. Found: C, 69.82; H, 5.97; N, 8.90. Yield: 23%.

4.4.11. 3-(*N*-*tert*-Butyl-carboxamido)-pyridine (2a). ^{1}H NMR ($CDCl_3$) δ: 8.9 (br s, 1H, Py); 8.7 (br s, 1H, Py); 8.06 (d, 4.8 Hz, 1H, Py); 7.42 (m, 1H, Py); 5.95 (br s, 1H, NH); 1.42 (s, 9H, C(CH_3)$_3$). ^{13}C NMR ($CDCl_3$) δ: 165.0; 151.8; 147.7; 134.9; 132.1; 123.3; 51.8; 28.8. IR (KBr (cm^{-1})): 3370 (NH); 1673 (CON). MS *m*/*z* (rel int. %): 178 (12), 163 (30), 123 (28), 106 (100), 78 (45). Analysis calculated for $C_{10}H_{14}N_2O$ (178.23): C, 67.39; H, 7.92; N, 15.72. Found: C, 67.27; H, 8.08; N, 15.50. Yield: 34%.

4.4.12. 3-(*N*-*tert*-Butyl-glyoxylamido)-pyridine (2a′). ^{1}H NMR ($CDCl_3$) δ: 9.45 (s, 1H, Py); 8.78 (d, 3.6 Hz, 1H, Py); 8.62 (d, 8.0 Hz, 1H, Py); 7.40 (m, 1H, Py); 7.00 (br s, 1H, NH); 1.46 (s, 9H, C(CH_3)$_3$). ^{13}C NMR ($CDCl_3$) δ: 187.4; 160.2; 153.8; 152.1; 138.5; 129.2; 123.2; 51.8; 28.3. IR (KBr (cm^{-1})): 3357 (NH); 1655 (br, CO, CON). MS *m*/*z* (rel int. %): 206 (2), 107 (40), 106 (42), 78 (76), 57 (100). Analysis calculated for $C_{11}H_{14}N_2O_3$ (206.24): C, 64.06; H, 6.84; N, 13.58. Found: C, 64.01; H, 6.97; N, 13.38. Yield: 44%.

4.4.13. 3-(*N*-Phenyl-carboxamido)-pyridine (2b). ^{1}H NMR ($CDCl_3$) δ: 9.05 (d, 1.8 Hz, 1H, Py); 8.69 (dd, 3.6 Hz, 1.8 Hz, 1H, Py); 8.50 (br s, 1H, NH); 8.16 (d, 8.0 Hz, 1.8 Hz, 1H, Py); 7.62 (d, 7.6 Hz, 2H, Ph); 7.30–7.40 (m, 3H, Ph+Py); 7.16 (t, 7.2 Hz, 1H, Ph). ^{13}C NMR ($CDCl_3$) δ: 164.1; 152.2; 148.0; 137.6; 135.4; 130.9; 129.1; 125.0; 123.6; 120.6. IR (KBr (cm^{-1})): 3351 (NH); 1655 (CON). MS *m*/*z* (rel int. %): 198 (68), 106 (100), 78 (63). Analysis calculated for $C_{12}H_{10}N_2O$ (198.22): C, 72.71; H, 5.08; N, 14.13. Found: C, 72.64; H, 5.21; N, 14.01. Yield: 7%.

4.4.14. 3-(*N*,*N*-Penta-1,5-diyl-carboxamido)-pyridine (2c). ^{1}H NMR ($CDCl_3$) δ: 8.50 (m, 2H, Py); 7.60 (d, 7.4 Hz, 1H, Py); 7.22 (dt, 7.4 Hz, 1.6 Hz, 1H, Py); 3.60 (br s, 2H, NCH_2); 3.24 (br s, 2H, NCH_2); 1.60 (br s, 4H, 2×CH_2); 1.48 (br s, 2H, CH_2). ^{13}C NMR ($CDCl_3$) δ: 164.3; 154.7; 151.3; 136.7; 134.8; 123.9; 47.1; 42.4; 26.3; 25.4; 24.3. IR (KBr (cm^{-1})): 1635 (CON). MS *m*/*z* (rel int. %): 190 (100), 106 (72), 78 (49). Analysis calculated for $C_{11}H_{14}N_2O$ (190.24): C, 69.45; H, 7.42; N, 14.72. Found: C, 69.60; H, 7.52; N, 14.49. Yield: 60%.

4.4.15. 3-(*N*,*N*-Penta-1,5-diyl-glyoxylamido)-pyridine (2c′). ^{1}H NMR ($CDCl_3$) δ: 9.10 (br s, 1H, Py); 8.80 (br s, 1H, Py); 8.22 (d, 7.6 Hz, 1H, Py); 7.42 (dt, 7.6 Hz, 1.6 Hz, 1H, Py); 3.65 (br s, 2H, NCH_2); 3.30 (br s, 2H, NCH_2); 1.65 (br s, 4H, 2×CH_2); 1.60 (br s, 2H, CH_2). ^{13}C NMR ($CDCl_3$) δ: 190.3; 167.5; 150.4; 147.6; 134.7; 132.1; 123.3; 47.0; 42.3; 26.2; 25.4; 24.3. IR (KBr (cm^{-1})): 1672 (br, CO, CON). MS *m*/*z* (rel int. %): 218 (3), 190 (42), 112 (100), 69 (70). Analysis calculated for $C_{12}H_{14}N_2O_2$ (206.24): C, 64.06; H, 6.84; N, 13.58. Found: C, 64.22; H, 6.99; N, 13.29. Yield: 22%.

4.4.16. 3-(*N*,*N*-Penta-3-oxa-1,5-diyl-carboxamido)-pyridine (2d). ^{1}H NMR ($CDCl_3$) δ: 8.45 (m, 2H, Py); 7.58 (d, 7.2 Hz, 1H, Py); 7.20 (dt, 7.4 Hz, 1.6 Hz, 1H, Py); 3.60 (br s, 4H, 2×CH_2); 3.45 (t, 2H, CH_2); 3.22 (t, 2H, CH_2). ^{13}C NMR ($CDCl_3$) δ: 167.4; 151.4; 148.0; 135.1; 132.3; 123.4; 66.7; 66.6; 46.3; 41.8. MS *m*/*z* (rel int. %): 192 (20), 191 (63), 177 (28), 106 (100), 86 (30), 78 (79). Analysis calculated for $C_{10}H_{12}N_2O_2$ (192.22): C, 62.49; H, 6.29; N, 14.57. Found: C, 62.56; H, 6.11; N, 14.45. Yield: 32%.

4.4.17. 3-(*N*,*N*-Penta-3-oxa-1,5-diyl-glyoxylamido)-pyridine (2d′). ^{1}H NMR ($CDCl_3$) δ: 9.08 (br s, 1H, Py); 8.78 (d, 4.2 Hz, 1H, Py); 8.20 (d, 7.4 Hz, 1H, Py); 7.40 (dt, 7.4 Hz, 4.2 Hz, 1H, Py); 3.70 (br s, 4H, 2×CH_2); 3.60 (t, 2H, CH_2); 3.33 (t, 2H, CH_2). ^{13}C NMR ($CDCl_3$) δ: 189.4; 164.2; 154.8; 151.2; 148.0; 136.7; 128.8; 123.8; 66.7; 66.5; 46.3; 41.8. IR (KBr (cm^{-1})): 1684 (CO); 1646 (CON). MS *m*/*z* (rel int. %): 220 (4), 192 (61), 114 (94), 106 (52), 78 (51), 70 (100). Analysis calculated for $C_{11}H_{12}N_2O_3$ (220.23): C, 59.99; H, 5.49; N, 12.72. Found: C, 59.82; H, 5.60; N, 12.51. Yield: 43%.

4.4.18. 3-(*N*-(Methoxycarbonylmethyl)-carboxamido)-pyridine (2e). ^{1}H NMR ($CDCl_3$) δ: 9.00 (s, 1H, Py); 8.70

(d, 1.8 Hz, 1H, Py); 8.12 (d, 7.6 Hz, 1H, Py); 7.40 (dt, 7.6 Hz, 1.8 Hz, 1H, Py); 6.92 (br s, 1H, NH); 4.30 (d, 7.2 Hz, 2H, CH_2); 3.75 (s, 3H, OCH_3). ^{13}C NMR ($CDCl_3$) δ: 170.2; 165.6; 152.4; 148.0; 135.2; 123.5; 52.5; 41.6. IR (KBr (cm^{-1})): 3356 (NH); 1751 (COO); 1675 (CON). MS *m/z* (rel int. %): 194 (50), 163 (21), 135 (20), 106 (100), 78 (83). Analysis calculated for $C_9H_{10}N_2O_3$ (194.19): C, 55.67; H, 5.19; N, 14.43. Found: C, 55.50; H, 5.33; N, 14.28. Yield: 7%.

4.4.19. 3-(*N*-(Methoxycarbonylmethyl)-glyoxylamido)-pyridine (2e′). ^1H NMR ($CDCl_3$) δ: 9.48 (s, 1H, Py); 8.82 (d, 2.0 Hz, 1H, Py); 8.61 (d, 7.6 Hz, 1H, Py); 7.70 (br s, 1H, NH); 7.40 (dt, 7.6 Hz, 2.0 Hz, 1H, Py); 4.20 (d, 8.4 Hz, 1H, CH_2); 3.80 (s, 3H, OCH_3). ^{13}C NMR ($CDCl_3$) δ: 185.6; 169.1; 160.8; 154.3; 152.2; 138.4; 123.3; 52.6; 41.0. MS *m/z* (rel int. %): 222 (3), 163 (10), 135 (3), 106 (100), 78 (68). Analysis calculated for $C_{10}H_{10}N_2O_4$ (222.20): C, 54.05; H, 4.54; N, 12.61. Found: C, 54.24; H, 4.71; N, 12.39. Yield: 71%.

4.4.20. 3-(*N*-(1′-Methoxycarbonyl-ethyl)-carboxamido)-pyridine (2f). ^1H NMR ($CDCl_3$) δ: 9.02 (s, 1H, Py); 8.72 (d, 2 Hz, 1H, Py); 8.13 (d, 7.6 Hz, 1H, Py); 7.40 (dt, 7.6 Hz, 2.0 Hz, 1H, Py); 6.78 (br s, 1H, NH); 4.80 (qi, 7.4 Hz, 1H, NHCH); 3.80 (s, 3H, OCH_3); 1.58 (d, 7.4 Hz, $CHCH_3$). IR (KBr (cm^{-1})): 3400 (NH); 1743 (COO); 1657 (CON). MS *m/z* (rel int. %): 208 (4), 149 (73), 106 (100), 78 (38). Analysis calculated for $C_{10}H_{12}N_2O_3$ (208.22): C, 57.69; H, 5.81; N, 13.45. Found: C, 57.79; H, 5.90; N, 13.26. Yield: 15%.

4.4.21. 3-(*N*-(1′-Methoxycarbonyl-ethyl)-glyoxylamido)-pyridine (2f′). ^1H NMR ($CDCl_3$) δ: 9.48 (s, 1H, Py); 8.80 (d, 2.2 Hz, 1H, Py); 8.60 (d, 7.4 Hz, 1H, Py); 7.70 (br s, 1H, NH); 7.40 (dt, 7.4 Hz, 2.2 Hz, 1H, Py); 4.64 (qi, 7.4 Hz, 1H, CH); 3.73 (s, 3H, OCH_3); 1.52 (d, 7.4 Hz, $CHCH_3$). ^{13}C NMR ($CDCl_3$) δ: 185.9; 172.2; 160.2; 154.2; 152.1; 138.4; 129.0; 123.3; 52.7; 48.2; 17.9. IR (KBr (cm^{-1})): 3280 (NH); 1744 (COO); 1673 (br, CO, CON). MS *m/z* (rel int. %): 236 (2), 177 (17), 106 (100), 78 (85). Analysis calculated for $C_{11}H_{12}N_2O_4$ (236.23): C, 55.93; H, 5.12; N, 11.86. Found: C, 55.80; H, 5.23; N, 11.70. Yield: 68%.

4.4.22. 3-(*N*-(2′-Methoxycarbonyl-butan-1,4-diyl)-carboxamido)-pyridine (2g). ^1H NMR ($CDCl_3$) δ: 8.84 (s, 1H, Py); 8.62 (d, 1.8 Hz, Py); 7.90 (d, 7.4 Hz, 1H, Py); 7.32 (dt, 7.4 Hz, 1.8 Hz, 1H, Py); 4.66 (m, 1H, NCH); 3.78 (s, 3H, OCH_3); 3.5–3.7 (m, 2H, NCH_2); 1.8–2.4 (m, 4H, CH_2CH_2). ^{13}C NMR ($CDCl_3$) δ: 172.3; 167.1; 151.1; 148.2; 135.1; 131.9; 123.2; 59.2; 52.3; 49.8; 29.2; 25.3. IR (KBr (cm^{-1})): 1743 (COO); 1632 (CON). MS *m/z* (rel int. %): 234 (7), 175 (61), 106 (100), 78 (34). Analysis calculated for $C_{12}H_{14}N_2O_3$ (234.25): C, 61.53; H, 6.02; N, 11.96. Found: C, 61.58; H, 5.93; N, 11.71. Yield: 59%.

4.4.23. 3-(*N*-(2′-Methoxycarbonyl-butan-1,4-diyl)-glyoxylamido)-pyridine (2g′). ^1H NMR ($CDCl_3$) δ: 9.12 (s, 1H, Py); 8.22 (br s, 1H, Py); 7.55 (m, 1H, Py); 7.25 (m, 1H, Py); 4.70 (m, 1H, NCH); 3.76 (s, 3H, OCH_3); 3.5–3.7 (m, 2H, NCH_2); 1.8–2.4 (m, 4H, CH_2CH_2). ^{13}C NMR ($CDCl_3$) δ: 189.5/188.7 (two isomers due to C(O)–N hindered rotation); 172.3/172.0; 163.7; 154.5/153.9; 151.8/151.3; 148.1; 137.6; 132.0/131.9; 123.6; 59.3; 52.4; 47.3; 30.8; 24.6. IR (KBr (cm^{-1})): 1744 (COO); 1683 (CO); 1643 (CON). MS *m/z* (rel int. %): 262 (2), 234 (14), 203 (6), 175 (3), 156 (13), 128 (100), 106 (35), 78 (22). Analysis calculated for $C_{13}H_{14}N_2O_4$ (262.27): C, 59.54; H, 5.38; N, 10.68. Found: C, 59.74; H, 5.42; N, 10.55. Yield: 24%.

4.4.24. (*N*-*tert*-Butyl-carboxamido)-pyrazine (3a). ^1H NMR ($CDCl_3$) δ: 9.4 (br s, 1H, Pyr); 8.68 (br s, 1H, Pyr); 8.44 (br s, 1H, Pyr); 7.65 (br s, 1H, NH); 1.48 (s, 9H, $C(CH_3)_3$). ^{13}C NMR ($CDCl_3$) δ: 162.0; 146.9; 145.2; 144.0; 142.1; 51.2; 28.7. IR (KBr (cm^{-1})): 3350 (NH); 1665 (CON). MS *m/z* (rel int. %): 179 (46), 164 (100), 107 (87), 79 (89). Analysis calculated for $C_9H_{13}N_3O$ (179.22): C, 60.32; H, 7.31; N, 23.45. Found: C, 60.17; H, 7.46; N, 23.30. Yield: 82%.

4.4.25. (*N*-Phenyl-carboxamido)-pyrazine (3b). ^1H NMR ($CDCl_3$) δ: 9.65 (br s, 1H, NH); 9.50 (br s, 1H, Pyr); 8.78 (br s, 1H, Pyr); 8.57 (br s, 1H, Pyr); 7.75 (d, 7.6 Hz, 2H, Ph); 7.35 (t, 7.6 Hz, 2H, Ph); 7.15 (t, 7.2 Hz, 1H, Ph). ^{13}C NMR ($CDCl_3$) δ: 160.6; 147.5; 144.7; 144.4; 142.3; 137.2; 129.1; 124.8; 119.8. IR (KBr (cm^{-1})): 3350 (NH); 1679 (CON). MS *m/z* (rel int. %): 199 (100), 107 (15), 80 (63), 79 (68). Analysis calculated for $C_{11}H_9N_3O$ (199.21): C, 66.32; H, 4.55; N, 21.09. Found: C, 66.46; H, 4.75; N, 20.96. Yield: 16%.

4.4.26. (*N*-Penta-1,5-diyl-carboxamido)-pyrazine (3c). ^1H NMR ($CDCl_3$) δ: 8.74 (br s, 1H, Py); 8.50 (br s, 1H, Py); 8.42 (br s, 1H, Py); 3.60 (br s, 2H, NCH_2); 3.30 (br s, 2H, NCH_2); 1.60 (br s, 4H, $2\times CH_2$); 1.50 (br s, 2H, CH_2). ^{13}C NMR ($CDCl_3$) δ: 165.3; 150.2; 145.0; 145.1; 143.0; 48.4; 43.6; 26.6; 25.7; 24.5. IR (KBr (cm^{-1})): 1635 (CON). MS *m/z* (rel int. %): 191 (3), 107 (5), 84 (100), 79 (14). Analysis calculated for $C_{10}H_{13}N_3O$ (191.23): C, 62.81; H, 6.85; N, 21.97. Found: C, 62.84; H, 6.96; N, 21.70. Yield: 81%.

4.4.27. (*N*-Penta-3-oxa-1,5-diyl-carboxamido)-pyrazine (3d). ^1H NMR ($CDCl_3$) δ: 8.89 (br s, 1H, Py); 8.54 (br s, 1H, Py); 8.42 (br s, 1H, Py); 3.70 (br s, 4H, $2\times CH_2$); 3.50 (br s, 4H, $2\times CH_2$). ^{13}C NMR ($CDCl_3$) δ: 165.2; 149.1; 146.0; 145.5; 142.6; 67.1; 66.9; 47.9; 43.1. IR (KBr (cm^{-1})): 1636 (CON). MS *m/z* (rel int. %): 193 (8), 107 (16), 86 (100), 79 (30). Analysis calculated for $C_9H_{11}N_3O_2$ (193.21): C, 55.95; H, 5.74; N, 21.75. Found: C, 55.80; H, 5.85; N, 21.64. Yield: 83%.

4.4.28. (*N*-(Methoxycarbonylmethyl)-carboxamido)-pyrazine (3e). ^1H NMR ($CDCl_3$) δ: 9.30 (s, 1H, Pyr); 8.67 (s, 1H, Pyr); 8.42 (s, 1H, Pyr); 8.25 (br s, 1H, NH); 4.20 (br s, 2H, CH_2); 3.68 (s, 3H, OCH_3). ^{13}C NMR ($CDCl_3$) δ: 169.8; 163.2; 147.4; 144.3; 143.9; 142.7; 52.3; 41.1. IR (KBr (cm^{-1})): 3322 (NH); 1747 (COO); 1660 (CON). MS *m/z* (rel int. %): 195 (7), 163 (34), 136 (100), 107 (72), 79 (70). Analysis calculated for $C_8H_9N_3O_3$ (195.18): C, 49.23; H, 4.65; N, 21.53. Found: C, 49.01; H, 4.82; N, 21.30. Yield: 78%.

4.4.29. (*N*-(1′-Methoxycarbonyl-ethyl)-carboxamido)-pyrazine (3f). ^1H NMR ($CDCl_3$) δ: 9.28 (s, 1H, Pyr); 8.66 (s, 1H, Pyr); 8.46 (s, 1H, Pyr); 8.20 (br s, 1H, NH); 4.70 (m, 1H, NHC*H*); 3.68 (s, 3H, OCH_3); 1.46 (d, 7.2 Hz, $CHCH_3$). IR (KBr (cm^{-1})): 3388 (NH); 1744 (COO); 1677

(CON). MS *m*/*z* (rel int. %): 209 (2), 150 (100), 107 (40), 79 (41). Analysis calculated for $C_9H_{11}N_3O_3$ (209.20): C, 51.67; H, 5.30; N, 20.09. Found: C, 51.49; H, 5.12; N, 19.85. Yield: 82%.

4.4.30. (*N*-(2′-Methoxycarbonyl-butan-1,4-diyl)-carboxamido)-pyrazine (3g). ^{1}H NMR ($CDCl_3$) δ: 9.10/9.22 (s, 1H, Pyr); 8.58 (br s, 1H, Pyr); 8.35/8.50 (s, 1H, Pyr); 4.60/5.04 (br s, 1H, NCH); 3.60–3.90 (m, 2H, NCH_2); 3.58/3.71 (s, 3H, OCH_3); 1.8–2.4 (m, 4H, CH_2CH_2). ^{13}C NMR ($CDCl_3$) δ: 172.9/172.2 (two isomers due to C(O)–N hindered rotation); 164.1/163.8; 148.4/147.7; 146.2/146.5; 145.6/145.7; 142.2/141.4; 61.2/60.2; 52.2/52.1; 49.6/48.3; 31.8/28.7; 25.4/21.8. IR (KBr (cm^{-1})): 1745 (COO); 1635 (CON). MS *m*/*z* (rel int. %): 235 (8), 176 (94), 128 (100), 107 (71), 79 (77). Analysis calculated for $C_{11}H_{13}N_3O_3$ (235.24): C, 56.16; H, 5.57; N, 17.86. Found: C, 56.02; H, 5.73; N, 17.61. Yield: 74%.

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