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Palladium-catalysed selective aminocarbonylation of 1′,4-diiodostyrene

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ABSTRACT

1′,4-Diiodostyrene possessing both iodo-aryl and iodo-alkenyl functionalities was prepared and used as substrate in palladium-catalysed aminocarbonylation. The corresponding dicarboxamides were obtained as major products in high yields by using several amine nucleophiles including amino acid methyl esters. Due to the highly different reactivity of the two iodo-functionalities, the selective aminocarbonylation of the iodo-vinyl moiety was carried out at atmospheric carbon monoxide pressure resulting in the formation of 4-iodo-phenyl-acrylamides. The latter amides were used as substrates in high pressure aminocarbonylation resulting in amide–ketocarboxamide type products. The latter functionality was formed via double carbon monoxide insertion into the iodo–aryl bond.

1. Introduction

Although palladium-catalysed carbonylations are not as widely used as direct coupling reactions, such as Heck, Suzuki, Kumada, Stille and Sonogashira reactions, are among the most favoured ones due to their simplicity of introducing a carbonyl moiety.[1] In the presence of various nucleophiles such as amines and alcohols, the synthesis of amides and esters was carried out. Several applications were aimed at the synthesis of simple building blocks and at the functionalisation of biologically important skeletons.[2] Homogeneous aminocarbonylation plays a special role among such carbonylations, since the highly active palladium-acyl intermediates, formed under catalytic conditions, act as efficient acylation agents even in the case of amines with low basicity. Similarly, amines with bulky substituents adjacent to the amine functionality can be transformed efficiently to carboxamides. In this way, the conventional methodology based on the carboxylic acid–carboxylic halide–carboxamide route can be substituted for a single catalytic reaction.[3] Although the enol triflates and aryl triflates were the most favoured substrates in palladium-catalysed aminocarbonylation, recently, the corresponding iodo analogues, i.e., the iodo-alkenes and iodo-aromatics, provided clean, high-yielding synthetic procedure towards carboxamides.[4] The homogeneous catalytic synthesis of unsaturated carboxamides or aryl carboxamides with various structures has been published also in our group.[5,6]

Iodostyrenes possessing the iodo substituent in the aromatic ring (2-iodo- and 4-iodostyrene) are known starting materials in polymer chemistry[7–9] and in cross-coupling.[10] Iodostyrenes possessing the iodo substituent in the unsaturated side chain ((*E*)-β-iodostyrene and α-iodostyrene) are also known as reactive substrates in Stille cross-coupling,[11] and Heck-[12] and Stille-coupling[13] reactions, respectively.

It is worth noting that in spite of their lower reactivity, the more easily available bromo analogues ((*E*)-β-bromostyrene[14–18] and α-bromostyrene[19,20]) were used preferentially in various transition metal-catalysed reactions.

Encouraged by the increasing importance of unsaturated carboxamides, we decided to investigate the possibility of extending the scope of aminocarbonylation to a substrate possessing both 'iodo-vinyl' and iodo-aryl functionalities. Accordingly, a systematic investigation of the aminocarbonylation of 1′,4-diiodostyrene with simple primary and secondary amines, as well as with amino acid methyl esters is reported here.

2. Results and discussion

2.1. Synthesis of 1′,4-diiodostyrene (3)

The above diiodo substrate (**3**) has been synthesised according to some analogous examples described in the seminal work of Barton et al.[21] Although the conventional ketone–hydrazone–iodo-alkene route has been used, some modifications already published for iodo-alkenes of similar structure have been carried out[22] (see Experimental). Accordingly, 4-iodoacetophenone (**1**) has been converted to the corresponding hydrazone (**2**) by using barium

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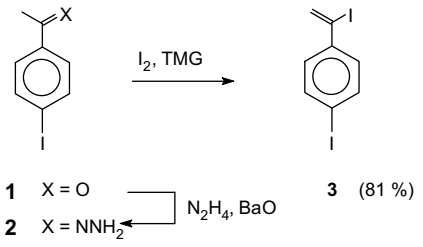
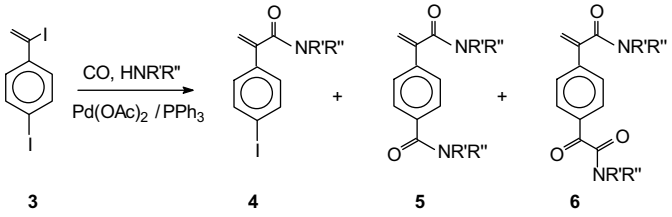
oxide. Hydrazone **2** gave the target compound **3** in 81% yield upon addition of iodine in the presence of a base (TMG=*N*,*N*,*N*′,*N*′-tetramethylguanidine) (Scheme 1). The last step had to be carried out under argon providing strictly moisture- and oxygen-free conditions. The diiodo substrate (**3**) must be kept under argon in a refrigerator protected from light. Under these conditions it can be stored for months without any sign of decomposition.



Scheme 1. Synthesis of **3** from the corresponding ketone (**1**) via its hydrazone (**2**).

2.2. Aminocarbonylation of 1′,4-diiodostyrene (3)

1′,4-Diiodostyrene (**3**) was reacted with *tert*-butylamine (**a**), aniline (**b**), piperidine (**c**), morpholine (**d**), methyl glycinate (**e**), methyl alaninate (**f**), methyl valinate (**g**) and methyl prolinate (**h**). All reactions were carried out both under atmospheric and under high pressure (40 bar) carbon monoxide in the presence of in situ generated palladium(0)-triphenylphosphine catalysts (Scheme 2). Palladium(II) acetate was used as catalytic precursor and reduced to Pd(0) as described previously in detail.[23,24]



	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	H	$CH(CH(CH_3)_2)COOCH_3$
h	-$CH(COOCH_3)(CH_2)_3$-	

Scheme 2. Palladium-catalysed aminocarbonylation of **3**.

The reactivity of the iodo-alkene moiety of **3**, compared to cyclic[6] and open-chain aliphatic iodo-alkenes,[25] was found to be exceptionally high. This functionality was transferred to the corresponding carboxamide functionality in all cases. In this way, 2-(4-iodo-phenyl)-acrylamides (**4**), 2-(4-carboxamido-phenyl)-acrylamides (**5**) and 2-(4-glyoxylamido-phenyl)-acrylamides (**6**) were formed depending on the type of the amines and on the reaction conditions.

The mixture of **5** and **6** was obtained by using simple primary (**a**) and secondary amines (**c**,**d**) even at atmospheric carbon monoxide pressure. The dicarboxamide-type products (**5**) were formed as the major ones under all reaction conditions and the yields of synthetic importance were obtained especially with secondary amines (entries 5–8). The reaction could be shifted slightly towards the formation of 'tricarbonylated' **6** at 40 bar CO pressure (compare entries 1 and 2, 5 and 6, 7 and 8). While good to excellent yields were obtained for **5**, the yields of **6** fall typically below 20% except for **a** (entry 2). Both types of compounds were isolated by column chromatography. It is worth noting that aniline (**b**), the amine of the lowest basicity in the series of amines used, resulted in substantially lower yields (entries 3 and 4) and the products could not be isolated as highly pure compound for full characterisation.

Surprisingly, the application of amino acid ester hydrochlorides (**e**–**h**) resulted in rather different product distribution. The monocarboxamide derivatives (**4**), i.e., those compounds containing an unreacted iodo-arene functionality, were formed with high chemoselectivity at atmospheric carbon monoxide pressure (entries 9, 11, 13 and 15). The formation of dicarboxamide-type products (**5**) was highly favoured towards **6** at high CO pressure (entries 10, 12 and 14). The carboxamide–ketocarboxamide products (**6**) were obtained in low yields. Only **6f** and **6h** could be isolated as pure products and fully characterised.

2.3. Aminocarbonylation of *N*-(methoxycarbonylmethyl)-2-(4-iodo-phenyl)-acrylamide (4e)

The easy availability of 4-iodo-phenyl-acrylamides enabled the synthesis of **7** and **8** containing different *N*-substituents in the amide functionalities. The aminocarbonylation of **4e** resulted in almost exclusive formation of **8a**, **8c** and **8f** (Scheme 3). These target compounds were isolated in high yields (78–88%) and fully characterised. The 'mixed' dicarboxamides (**7a**, **7c** and **7f**) were formed only in traces (<5%) and could be detected by ^{1}H and ^{13}C NMR only.

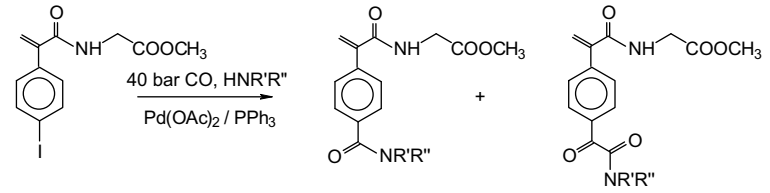
2.4. Alkoxycarbonylation of 1′,4-diiodostyrene (3)

1′,4-Diiodostyrene (**3**) was also reacted with methanol under high pressure (60 bar) carbon monoxide in the presence of in situ palladium(0)-triphenylphosphine catalysts (Scheme 4). Complete conversion but a low isolated yield of 23% for **9** was obtained. It is worth noting that with other alcohols (benzyl alcohol, *tert*-butanol) the isolation of the corresponding esters failed.

The low yields of esters could be explained by two side reactions observed already for iodo-alkene derivatives. On one hand, some carboxylic acid and anhydride formation was detected with low-reactivity nucleophiles such as benzyl alcohol and especially *tert*-butanol, due to the presence of traces of H_2O in the solvent and adsorbed on the wall of the glassware.[26] Thus, hydroxycarbonylation instead of alkoxycarbonylation might take place. On the other hand, the iodo-alkene functionality of **3** underwent hydrolysis under the severe reaction conditions, resulting in the starting acetophenone derivative (**1**) via its enol form.

3. Conclusions

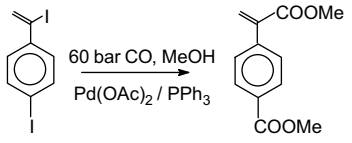
In summary, amino- and alkoxycarbonylation of 1′,4-diiodostyrene, possessing two iodo substituents with different reactivity, were carried out. Both types of palladium-catalysed carbonylations proved to be efficient method for the functionalisation of α-iodo-vinyl and iodo-aryl functionalities. Dicarboxamide and carboxamide-ketocarboxamide derivatives were synthesised by using the variety of amine nucleophiles. The arylacrylamide-type products could serve as intermediates of chiral building blocks, such as 2-aryl-propionic amides, available, e.g., via asymmetric hydrogenation. Furthermore, the application of iodo-alkenes/iodo-arenes, as synthetic surrogates of the corresponding enol-triflate/aryl triflate analogues in palladium-catalysed carbonylations, is supported by green chemistry principles such as high yields and selectivities obtained in clean homogeneous catalytic reactions.



4e 7 8

	R'	R"	
a	H	*t*-Bu	(88 %)
c	-$(CH_2)_5$-		(82 %)
f	H	$CH(CH_3)COOCH_3$	(78 %)

Scheme 3. Palladium-catalysed aminocarbonylation of **4e**.



3 **9** (23 %)

Scheme 4. Palladium-catalysed alkoxycarbonylation of **3**.

4. Experimental

4.1. General procedures

^1H 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 residual $CHCl_3$ (7.26 and 77.00 ppm for ^1H and ^{13}C, respectively). Elemental analyses were measured 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. TLC analyses were carried out with Merck TLC sheets (Silica gel 60 F_{254}) and chloroform/ethyl acetate or dichloromethane/ethyl acetate mixtures as appropriate eluents.

4.2. Synthesis of 1′,4-diiodostyrene (3)

4-Iodoacetophenone (**1**) (10.01 g, 40.7 mmol), freshly distilled hydrazine hydrate (98%, 2.24 g, 44.8 mmol) and barium oxide (1.63 g) in absolute ethanol (50 mL) were heated for 3 days at 90 °C. After completion of the reaction, iced water (200 mL) and dichloromethane (130 mL) were added, and the white precipitate was filtered. The organic phase was separated and dried over sodium sulfate for 1 day. (It is worth noting that the hydrazone derivative can be stored over sodium sulfate for several days without decomposition.) At last it was evaporated to give the hydrazone (**2**) derivative. The product was used in the next step without further purification.

To a stirred solution of iodine (18.19 g, 71.7 mmol) in dichloromethane (50 mL) the mixture of 1,1,3,3-tetramethylguanidine (TMG, 11.96 g, 103.8 mmol) and 4-iodoacetophenone hydrazone (**2**) (9 g, 34.6 mmol) in dichloromethane (30 mL) was added dropwise between 0 and 12 °C, cooled in an iced-water bath during the addition. After the addition was complete, the mixture was stirred for half an hour. Then the solvent was evaporated and the residue was heated at 90 °C under argon atmosphere for 2 h. The mixture was poured into water (300 mL) and extracted with dichloromethane (4×50 mL). The combined organic layer was washed successively with 1 N aqueous HCl (3×50 mL), water (50 mL), 5% aqueous $NaHCO_3$ (2×50 mL), water (50 mL), saturated aqueous $Na_2S_2O_3$ (10 mL) and water (3×50 mL) again, dried over sodium sulfate and evaporated. The iodo-alkene (**3**) was obtained as a red-brown viscous material and used for carbonylation experiments without further purification.

*4.2.1. 1′,4-Diiodostyrene (**3**)*

δ_H (400 MHz, $CDCl_3$) 7.62 (d, 8.1 Hz, 2H, Ph), 7.23 (d, 8.1 Hz, 2H, Ph), 6.45 (br s, 1H, =CH), 6.07 (br s, 1H, =CH). δ_C (100.6 MHz, $CDCl_3$) 141.3, 137.3, 129.8, 127.9, 105.9, 94.8. IR (KBr, cm^{-1}): 1602 (C=C). MS *m*/*z* (rel int. %): 356 (22), 229 (100), 102 (47). Analysis calculated for $C_8H_6I_2$ (355.94): C, 27.00; H, 1.70. Found: C, 27.22; H, 1.86. R_f (petroleum ether (40–70)) 0.58; brown viscous material. Yield: 10.02 g, 81%.

4.3. Aminocarbonylation of 3 at normal pressure

In a typical experiment $Pd(OAc)_2$ (5.6 mg, 0.025 mmol), PPh_3 (13.1 mg, 0.05 mmol), 0.5 mmol diiodo substrate (**3**), and 3.0 mmol non-functionalized amine (**a**–**d**) (or 1.1 mmol amino acid methyl ester (**e**–**h**) hydrochloride) were dissolved in 10 mL of 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 a given reaction time (see Table 1) at 50 °C. Some metallic palladium was formed and precipitated at the end of the reaction, which was filtered off. (A sample of this solution was immediately analysed by GC–MS and TLC.) The mixture was then concentrated and evaporated to dryness. The residue was dissolved in chloroform (20 mL) and washed in turn with water (20 mL). The organic phase was thoroughly washed with 5% HCl (2×20 mL), saturated $NaHCO_3$ (20 mL), brine (20 mL), dried over Na_2SO_4 and concentrated to a yellow waxy material or a thick oil. The chemically pure products (2-(4-iodo-phenyl)-acrylamides (**4**), 2-(4-carboxamido-phenyl)-acrylamides (**5**), 2-(4-glyoxylamido-phenyl)-acrylamides (**6**)) were isolated from the reaction mixtures by column chromatography (silica, chloroform/ethyl acetate or dichloromethane/ethyl acetate mixtures) yielding the desired compounds typically as yellow solids.

4.4. Aminocarbonylation of 3 at high pressure

The DMF solution of the catalyst precursor and reactants (amounts as given above) was transferred under argon into a 100 mL stainless steel autoclave. The reaction vessel was pressurised up to 40 bar total pressure with carbon monoxide and the magnetically stirred mixture was heated in an oil bath at 50 °C for 22 h. The work-up procedure is identical with that given above.

Table 1
Palladium-catalysed aminocarbonylation of 1′,4-diiodostyrene (**3**)[a]

Entry	Amine	Retention time (h)	*p*(CO) (bar)	Composition of the reaction mixture (%)[b] (isolated yield, %)		
				4	**5**	**6**
1	^{t}BuNH$_2$ (**a**)	24	1	0	71 (55)	29 (n.d.)[c]
2	^{t}BuNH$_2$ (**a**)	24	40	0	51 (42)	49 (40)
3	Aniline (**b**)	90	1		31 (n.d.)	4 (n.d.)
4	Aniline (**b**)	90	40		30 (n.d.)	32 (n.d.)
5	Piperidine (**c**)	24	1	0	95 (84)	5 (n.d.)
6	Piperidine (**c**)	24	40	0	80 (72)	20 (16)
7	Morpholine (**d**)	45	1	0	96 (88)	4 (n.d.)
8	Morpholine (**d**)	45	40		92 (86)	8 (6)
9	GlyOMe (**e**)	24	1	>96 (89)	<2	<2
10	GlyOMe (**e**)	24	40	30 (n.d.)	68 (56)	<2
11	AlaOMe (**f**)	24	1	>98 (90)	<2	0
12	AlaOMe (**f**)	24	40	<2	70 (64)	28 (20)
13	ValOMe (**g**)	24	1	85 (77)	15 (n.d.)	0
14	ValOMe (**g**)	24	40	<2	78 (61)	20 (n.d.)
15	ProOMe (**h**)	24	1	>98 (90)	<2	
16	ProOMe (**h**)	24	40	0	60 (55)	40 (31)

[a] Reaction conditions: 0.025 mmol Pd(OAc)$_2$, 0.05 mmol PPh$_3$, 1 mmol 1′,4-diiodo-styrene (**3**), 3 mmol non-functionalised amine (or 1.1 mmol amino acid methyl ester hydrochloride), 10 mL DMF.
[b] Practically complete conversion (>98%) has been obtained in all cases except for aniline (35% and 62% at 1 bar and 40 bar CO pressure, respectively).
[c] n.d.=not determined (not isolated as pure products in the given run).

4.5. Aminocarbonylation of 4e at high pressure

In a typical experiment Pd(OAc)$_2$ (5.6 mg, 0.025 mmol), PPh$_3$ (13.1 mg, 0.05 mmol), 0.5 mmol iodoaromatic substrate (**4e**), 1.5 mmol non-functionalized amine (**a** or **c**) (or 0.55 mmol alanine methyl ester (**f**)) were dissolved in 10 mL of DMF under argon. Triethylamine (0.5 mL) was added to the homogeneous yellow solution and this mixture was transferred under argon into a 100 mL stainless steel autoclave. The reaction vessel was pressurised to 40 bar total pressure with carbon monoxide and the magnetically stirred mixture was heated in an oil bath at 50 °C for 24 h. Some metallic palladium was formed and precipitated at the end of the reaction, which was filtered off. (A sample of this solution was immediately analysed by GC–MS and TLC.) The mixture was then concentrated and evaporated to dryness. The residue was dissolved in chloroform (20 mL) and washed in turn with water (20 mL). The organic phase was thoroughly washed with 5% HCl (2×20 mL), saturated NaHCO$_3$ (20 mL), brine (20 mL), dried over Na$_2$SO$_4$ and concentrated to a yellow waxy material or a thick oil. The chemically pure products (**8**) were isolated from the reaction mixtures by column chromatography (silica, dichloromethane/ethyl acetate 1/1).

4.6. Alkoxycarbonylation of 3 at high pressure

A mixture of **3** (398 mg, 1 mmol), palladium(II) acetate (5.6 mg, 0.025 mmol), and PPh$_3$ (13.1 mg, 0.05 mmol) was dissolved in 10 mL of DMF (or, in parallel experiments, 20 mL of methyl ethyl ketone) under argon, and NEt$_3$ (0.5 mL) and methanol (0.13 mL, 5 mmol) as *O*-nucleophile were added. The reaction mixture was then transferred under argon into a 100 mL stainless steel autoclave, which was pressurised to 60 bar with CO and the magnetically stirred mixture was heated in an oil bath at 50 °C for 70 h. The work-up procedure was identical with that given above for the carboxamides.

4.7. Characterisation of the products

*4.7.1. 2-(4-N-tert-Butylcarboxamido-phenyl)-N-tert-butyl-acrylamide (**5a**)*

δ_H (400 MHz, CDCl$_3$) 7.70 (d, 8.3 Hz, 2H, Ar), 7.39 (d, 8.3 Hz, 2H, Ar), 5.98 (br s, 2H, =CH+NH), 5.56 (br s, 1H, =CH), 5.48 (br s, 1H, NH), 1.45 (s, 9H, ^{t}Bu), 1.34 (s, 9H, ^{t}Bu). δ_C (100.6 MHz, CDCl$_3$) 166.5, 166.3, 145.4, 139.9, 135.8, 127.9, 127.1, 121.2, 51.7, 51.6, 28.7, 28.6. IR (KBr, cm^{-1}): 3301 (NH), 1661 (CON), 1644 (CON). MS *m*/*z* (rel int. %): 302 (44), 287 (26), 230 (100), 202 (35), 174 (23), 102 (30). Analysis calculated for $C_{18}H_{26}N_2O_2$ (302.42): C, 71.49; H, 8.67; N, 9.26. Found: C, 71.25, H, 8.82; N, 9.01; R_f (50% EtOAc/CHCl$_3$) 0.67; off-white, mp 173–176 °C. Yield: 83 mg, 55%.

*4.7.2. 2-(4-N-tert-Butylglyoxylamido-phenyl)-N-tert-butyl-acrylamide (**6a**)*

δ_H (400 MHz, CDCl$_3$) 8.32 (d, 8.3 Hz, 2H, Ar), 7.47 (d, 8.3 Hz, 2H, Ar), 6.95 (br s, 1H, NH), 6.03 (br s, 1H, =CH), 5.65 (br s, 1H, =CH), 5.47 (br s, 1H, NH), 1.44 (s, 9H, ^{t}Bu), 1.37 (s, 9H, ^{t}Bu). δ_C (100.6 MHz, CDCl$_3$) 187.8, 166.2, 160.9, 145.3, 142.7, 133.1, 131.5, 127.7, 121.9, 51.7, 51.6, 28.6, 28.3. IR (KBr, cm^{-1}): 3289 (NH), 1679 (CO), 1659 (CON), 1644 (CON), 1604 (C=C). MS *m*/*z* (rel int. %): 330 (1), 230 (100), 203 (58), 102 (22). Analysis calculated for $C_{19}H_{26}N_2O_3$ (330.43): C, 69.06; H, 7.93; N, 8.48. Found: C, 68.85; H, 8.12; N, 8.19; R_f (33% EtOAc/CH$_2$Cl$_2$) 0.85; pale-yellow, mp 138–142 °C. Yield: 40 mg, 66%.

*4.7.3. 2-(4-N-Phenylcarboxamido-phenyl)-N-phenyl-acrylamide (**5b**)*

δ_H (400 MHz, CDCl$_3$) 7.95 (d, 8.2 Hz, 2H, Ar), 7.72 (d, 7.3 Hz, 2H, *o*-Ph), 7.68 (d, 7.3 Hz, 2H, *o*-Ph), 7.58 (d, 8.2 Hz, 2H, Ar), 7.02 (t, 7.3 Hz, 2H, *p*-Ph), 6.90 (t, 7.3 Hz, 4H, *m*-Ph), 5.93 (br s, 1H, =CH), 5.86 (br s, 1H, =CH). IR (KBr, cm^{-1}): 3329 (NH), 1650 (CON), 1597 (C=C).

*4.7.4. 2-(4-N-Phenylglyoxylamido-phenyl)-N-phenyl-acrylamide (**6b**)*

δ_H (400 MHz, CDCl$_3$) 7.10–7.92 (m, 14H, Ar), 6.65 (br s, 2H, NH), 6.26 (br s, 1H, =CH), 5.83 (br s, 1H, =CH).

*4.7.5. 2-(4-N,N-Pentan-1,5-diyl-carboxamido-phenyl)-N,N-pentan-1,5-diyl-acrylamide (**5c**)*

δ_H (400 MHz, CDCl$_3$) 7.42 (d, 8.3 Hz, 2H, Ar), 7.32 (d, 8.3 Hz, 2H, Ar), 5.71 (br s, 1H, =CH), 5.34 (br s, 1H, =CH), 3.65 (br s, 4H, N(CH$_2$)$_2$), 3.30 (br s, 4H, N(CH$_2$)$_2$), 1.30–1.70 (m, 12H, 2×(CH$_2$)$_3$). δ_C (100.6 MHz, CDCl$_3$) 169.7, 168.8, 144.5, 136.7, 136.5, 127.3, 125.7, 114.1, 49.0 (br), 48.0, 43.2 (br), 42.4, 26.4, 25.6, 24.5, 24.4. IR (KBr, cm^{-1}): 1677 (CON), 1635 (CON). MS *m*/*z* (rel int. %): 326 (55), 325 (100), 282 (9), 242 (41), 215 (22), 102 (21). Analysis calculated for $C_{20}H_{26}N_2O_2$ (326.44): C, 73.59; H, 8.03; N, 8.58. Found: C, 73.65; H, 8.22; N, 8.44. R_f (50% EtOAc/CHCl$_3$) 0.45; pale-brown highly viscous material. Yield: 138 mg, 84%.

*4.7.6. 2-(4-N,N-Pentan-1,5-diyl-glyoxylamido-phenyl)-N,N-pentan-1,5-diyl-acrylamide (**6c**)*

δ_H (400 MHz, CDCl$_3$) 7.88 (d, 8.3 Hz, 2H, Ar), 7.50 (d, 8.3 Hz, 2H, Ar), 5.80 (br s, 1H, =CH), 5.42 (br s, 1H, =CH), 3.63 (br s, 4H, N(CH$_2$)$_2$), 3.25 (br s, 4H, N(CH$_2$)$_2$), 1.40–1.70 (m, 12H, 2×(CH$_2$)$_3$). δ_C (100.6 MHz, CDCl$_3$) 191.1, 168.2, 165.2, 144.2, 141.6, 133.0, 130.1, 126.3, 116.4, 48.0, 47.1, 42.2, 41.7, 26.4, 26.2, 25.4, 25.3, 24.4, 24.3. IR (KBr, cm^{-1}): 1678 (CO), 1638 (br, CON). Analysis calculated for $C_{21}H_{26}N_2O_3$ (354.45): C, 71.16; H, 7.39; N, 7.90. Found: C, 71.02; H, 7.42; N, 7.72. R_f (50% EtOAc/CHCl$_3$) 0.60; brown viscous material. Yield: 29 mg, 16%.

*4.7.7. 2-(4-N,N-3-Oxapentan-1,5-diyl-carboxamido-phenyl)-N,N-3-oxapentan-1,5-diyl-acrylamide (**5d**)*

δ_H (400 MHz, CDCl$_3$) 7.45 (d, 8.2 Hz, 2H, Ar), 7.36 (d, 8.2 Hz, 2H, Ar), 5.78 (br s, 1H, =CH), 5.39 (br s, 1H, =CH), 3.30–3.76 (m, 16H, 2×(CH$_2$)$_2$O(CH$_2$)$_2$). δ_C (100.6 MHz, CDCl$_3$) 169.7, 168.8, 143.5, 136.8, 135.5, 127.7, 125.8, 115.6, 66.7 (2C), 47.3 (br), 41.9 (br). IR (KBr, cm^{-1}): 1636 (br, 2×CON). MS *m*/*z* (rel int. %): 330 (38), 329 (36), 244

(100), 217 (16), 159 (37), 102 (41). Analysis calculated for $C_{18}H_{22}N_2O_4$ (330.38): C, 65.44; H, 6.71; N, 8.48. Found: C, 65.30; H, 6.88; N, 8.26. R_f (3% EtOH/CH_2Cl_2) 0.48; highly viscous yellow material. Yield: 146 mg, 88%.

4.7.8. 2-(4-N,N-3-Oxapentan-1,5-diyl-glyoxylamido-phenyl)-N,N-3-oxapentan-1,5-diyl-acrylamide (**6d**)

δ_H (400 MHz, $CDCl_3$) 7.90 (d, 8.1 Hz, 2H, Ar), 7.52 (d, 8.1 Hz, 2H, Ar), 5.73 (br s, 1H, =CH), 5.49 (br s, 1H, =CH), 3.25–3.75 (m, 16H, 2×$(CH_2)_2O(CH_2)_2$). δ_C (100.6 MHz, $CDCl_3$) 190.4, 168.6, 165.3, 143.5, 141.7, 133.2, 130.5, 126.5, 117.9, 67.0 (2C), 66.9 (2C), 47.6, 46.5, 42.2, 41.9. IR (KBr, cm^{-1}): 1675 (CO), 1630 (CON). Analysis calculated for $C_{19}H_{22}N_2O_5$ (358.39): C, 63.68; H, 6.19; N, 7.82. Found: C, 63.50; H, 6.02; N, 7.55. R_f (3% EtOAc/CH_2Cl_2) 0.47; off-white crystals, mp 135–140 °C. Yield: 11 mg, 6%.

4.7.9. 2-(4-Iodo-phenyl)-N-methoxycarbonylmethyl-acrylamide (**4e**)

δ_H (400 MHz, $CDCl_3$) 7.69 (d, 8.3 Hz, 2H, Ar), 7.14 (d, 8.3 Hz, 2H, Ar), 6.28 (br s, 1H, NH), 6.07 (br s, 1H, =CH), 5.66 (br s, 1H, =CH), 4.09 (d, 5.4 Hz, 2H, CH_2COO), 3.73 (s, 3H, OCH_3). δ_C (100.6 MHz, $CDCl_3$) 170.1, 167.2, 143.5, 137.8, 136.0, 129.8, 122.5, 94.6, 52.4, 41.5. IR (KBr, cm^{-1}): 3295 (NH), 1754 (COO), 1644 (CON). MS *m*/*z* (rel int. %): 345 (43), 257 (32), 229 (100), 159 (16), 102 (76). Analysis calculated for $C_{12}H_{12}NO_3$ (345.14): C, 41.76; H, 3.50; N, 4.06. Found: C, 41.51; H, 3.39; N, 3.86. R_f (20% EtOAc/$CHCl_3$) 0.56; off-white solid, mp 90–92 °C. Yield: 154 mg, 89%.

4.7.10. 2-(4-N-(Methoxycarbonylmethyl)-carboxamido-phenyl)-N-methoxycarbonylmethyl-acrylamide (**5e**)

δ_H (400 MHz, $CDCl_3$) 7.71 (d, 8.3 Hz, 2H, Ar), 7.38 (d, 8.3 Hz, 2H, Ar), 7.18 (br s, 1H, NH), 6.61 (br s, 1H, NH), 6.03 (br s, 1H, =CH), 5.65 (br s, 1H, =CH), 4.12 (d, 5.6 Hz, 2H, CH_2COO), 4.06 (d, 5.6 Hz, 2H, CH_2COO), 3.72 (s, 3H, CH_3), 3.70 (s, 3H, CH_3). δ_C (100.6 MHz, $CDCl_3$) 170.4, 170.1, 167.6, 167.0, 143.5, 139.7, 133.4, 128.0, 127.5, 122.6, 52.3, 52.2, 41.6, 41.4. IR (KBr, cm^{-1}): 1751 (COO), 1662 (br, CON). Analysis calculated for $C_{16}H_{18}N_2O_6$ (334.33): C, 57.48; H, 5.43; N, 8.38. Found: C, 57.40; H, 5.32; N, 8.19. R_f (40% EtOAc/CH_2Cl_2) 0.25; highly viscous yellow material. Yield: 94 mg, 56%.

4.7.11. 2-(4-Iodo-phenyl)-N-(1-methoxycarbonylethyl)-acrylamide (**4f**)

δ_H (400 MHz, $CDCl_3$) 7.67 (d, 8.4 Hz, 2H, Ar), 7.11 (d, 8.4 Hz, 2H, Ar), 6.30 (br s, 1H, NH), 6.01 (br s, 1H, =CH), 5.62 (br s, 1H, =CH), 4.61 (quint., 7.2 Hz, 1H, CHCOO), 3.70 (s, 3H, OCH_3), 1.39 (d, 7.3 Hz, 3H, $CHCH_3$). δ_C (100.6 MHz, $CDCl_3$) 173.2, 166.6, 143.7, 137.8, 136.0, 129.8, 122.1, 94.6, 52.5, 48.4, 18.2. IR (KBr, cm^{-1}): 3275 (NH), 1745 (COO), 1646 (CON). MS *m*/*z* (rel int. %): 359 (17), 300 (80), 257 (38), 229 (100), 102 (71). Analysis calculated for $C_{13}H_{14}NO_3I$ (359.16): C, 43.47; H, 3.93; N, 3.90. Found: C, 43.28; H, 4.10; N, 3.77. R_f (10% EtOAc/$CHCl_3$) 0.52; pale-brown solid, mp 73–77 °C. Yield: 162 mg, 90%.

4.7.12. 2-(4-N-(1-Methoxycarbonylethyl)-carboxamido-phenyl)-N-(1-methoxycarbonylethyl)-acrylamide (**5f**)

δ_H (400 MHz, $CDCl_3$) 7.78 (d, 8.2 Hz, 2H, Ar), 7.42 (d, 8.2 Hz, 2H, Ar), 7.00 (br d, 6.8 Hz, 1H, NH), 6.41 (br d, 6.8 Hz, 1H, NH), 6.07 (br s, 1H, =CH), 5.67 (br s, 1H, =CH), 4.75 (quint., 7.2 Hz, 1H, CHCOO), 4.64 (quint., 7.2 Hz, 1H, CHCOO), 3.75 (s, 3H, OCH_3), 3.71 (s, 3H, OCH_3), 1.49 (d, 7.3 Hz, 3H, $CHCH_3$), 1.40 (d, 7.3 Hz, 3H, $CHCH_3$). δ_C (100.6 MHz, $CDCl_3$) 173.6, 173.2, 166.6, 166.3, 143.7, 139.7, 133.8, 128.1, 127.4, 122.7, 52.5, 52.4, 48.5, 48.3, 18.3, 18.0. IR (KBr, cm^{-1}): 3365 (NH), 1745 (COO), 1646 (br, 2×CON), 1611 (C=C). Analysis calculated for $C_{18}H_{22}N_2O_6$ (362.38): C, 59.66; H, 6.12; N, 7.73. Found: C, 59.50; H, 6.01; N, 7.48. R_f (50% EtOAc/CH_2Cl_2) 0.45; brown highly viscous solid. Yield: 117 mg, 64%.

4.7.13. 2-(4-N-(1-Methoxycarbonylethyl)-glyoxylamido-phenyl)-N-(1-methoxycarbonylethyl)-acrylamide (**6f**)

δ_H (400 MHz, $CDCl_3$) 8.33 (d, 8.3 Hz, 2H, Ar), 7.52 (d, 8.3 Hz, 2H, Ar), 6.23 (br s, 2H, NH), 6.13 (br s, 1H, =CH), 5.75 (br s, 1H, =CH), 4.60–4.73 (m, 2H, CHCOO), 3.77 (s, 3H, OCH_3), 3.73 (s, 3H, OCH_3), 1.49 (d, 7.3 Hz, 3H, $CHCH_3$), 1.42 (d, 7.3 Hz, 3H, $CHCH_3$). δ_C (100.6 MHz, $CDCl_3$) 186.2, 173.1, 172.3, 166.5, 166.2, 142.4, 133.0, 131.5, 128.0, 127.3, 123.5, 52.6, 52.5, 48.4, 48.1, 18.1, 18.0. IR (KBr, cm^{-1}): 3282 (NH), 1742 (COO), 1660 (CO), 1647 (CON), 1608 (C=C). Analysis calculated for $C_{19}H_{22}N_2O_7$ (390.39): C, 58.46; H, 5.68; N, 7.18; Found: C, 58.28; H, 5.56; N, 5.41. R_f (50% EtOAc/CH_2Cl_2) 0.67; brown highly viscous solid. Yield: 39 mg, 20%.

4.7.14. 2-(4-Iodo-phenyl)-N-(1-methoxycarbonyl-2-methylpropyl)-acrylamide (**4g**)

δ_H (400 MHz, $CDCl_3$) 7.69 (d, 8.4 Hz, 2H, Ar), 7.13 (d, 8.4 Hz, 2H, Ar), 6.15 (br s, 1H, NH), 6.02 (br s, 1H, =CH), 5.63 (br s, 1H, =CH), 4.59–4.64 (m, 1H, CHCOO), 3.72 (s, 3H, OCH_3), 0.92 (d, 6.5 Hz, 3H, $CHCH_3$), 0.84 (d, 6.5 Hz, 3H, $CHCH_3$). δ_C (100.6 MHz, $CDCl_3$) 172.3, 166.9, 143.8, 137.8, 136.0, 129.7, 122.2, 94.6, 57.4, 52.2, 31.2, 19.1, 17.8. IR (KBr, cm^{-1}): 3301 (NH), 1744 (COO), 1645 (CON). MS *m*/*z* (rel int. %): 387 (9), 328 (51), 273 (53), 229 (100), 102 (67). Analysis calculated for $C_{15}H_{18}NO_3I$ (387.22): C, 46.53; H, 4.69; N, 3.62. Found: C, 46.39; H, 4.77; N, 3.40. R_f (40% EtOAc/$CHCl_3$) 0.87; pale-brown solid, mp 60–64 °C. Yield: 148 mg, 77%.

4.7.15. 2-(4-N-(1-Methoxycarbonyl-2-methylpropyl)-carboxamido-phenyl)-N-(1-methoxycarbonyl-2-methylpropyl)-acrylamide (**5g**)

δ_H (400 MHz, $CDCl_3$) 7.81 (d, 8.1 Hz, 2H, Ar), 7.50 (d, 8.1 Hz, 2H, Ar), 6.66 (br d, 8.5 Hz, 1H, NH), 6.18 (br d, 8.5 Hz, 1H, NH), 6.12 (br s, 1H, =CH), 5.72 (br s, 1H, =CH), 4.76–4.79 (m, 1H, CHCOO), 4.63–4.67 (m, 1H, CHCOO), 3.75 (s, 3H, OCH_3), 3.72 (s, 3H, OCH_3), 2.15–2.30 (m, 2H, 2×$CH(CH_3)_2$), 1.01 (d, 6.9 Hz, 3H, $CH(CH_3)$), 0.99 (d, 6.9 Hz, 3H, $CH(CH_3)$), 0.93 (d, 6.9 Hz, 3H, $CH(CH_3)$), 0.84 (d, 6.9 Hz, 3H, $CH(CH_3)$). δ_C (100.6 MHz, $CDCl_3$) 172.6, 172.2, 166.9, 166.7, 143.9, 139.9, 134.2, 128.2, 127.5, 123.0, 57.5, 57.4, 52.2 (2C), 31.6, 31.2, 19.1, 19.0, 18.0, 17.8. IR (KBr, cm^{-1}): 3277 (NH), 1744 (COO), 1646 (CON). Analysis calculated for $C_{22}H_{30}N_2O_6$ (418.49): C, 63.14; H, 7.23; N, 6.69. Found: C, 63.25; H, 7.37; N, 6.50. R_f (40% EtOAc/$CHCl_3$) 0.57; brown viscous solid. Yield: 128 mg, 61%.

4.7.16. 2-(4-Iodo-phenyl)-N,N-(1-methoxycarbonyl-1,4-butanediyl)-acrylamide (**4h**)

δ_H (400 MHz, $CDCl_3$) 7.62 (d, 7.8 Hz, 2H, Ar), 7.21 (d, 7.8 Hz, 2H, Ar), 5.71 (br s, 1H, =CH), 5.42 (br s, 1H, =CH), 4.60–4.54 (m, 1H, CHCOO), 3.72 (s, 3H, OCH_3), 3.26–3.30 (m, 2H, CH_2), 0.76–1.22 (m, 4H, CH_2CH_2). δ_C (100.6 MHz, $CDCl_3$) 172.4, 168.7, 144.5, 137.9, 134.8, 127.9, 115.8, 94.4, 58.4, 52.3, 48.6, 29.4, 24.8. IR (KBr, cm^{-1}): 1744 (COO), 1639 (CON). MS *m*/*z* (rel int. %): 385 (17), 326 (91), 257 (33), 229 (100), 102 (66). Analysis calculated for $C_{15}H_{16}NO_3I$ (385.20): C, 46.77; H, 4.19; N, 3.64. Found: C, 46.60; H, 4.01; N, 3.40. R_f (10% EtOAc/$CHCl_3$) 0.50; red-brown highly viscous solid. Yield: 173 mg, 90%.

4.7.17. 2-(4-N,N-(1-Methoxycarbonyl-1,4-butanediyl)-carboxamido-phenyl)-N,N-(1-methoxycarbonyl-1,4-butanediyl)-acrylamide (**5h**)

δ_H (400 MHz, $CDCl_3$) 7.50 (br s, 4H, Ar), 5.76 (br s, 1H, =CH), 5.47 (br s, 1H, =CH), 4.50–4.63 (m, 2H, 2×CHCOO), 3.70 (s, 3H, OCH_3), 3.68 (s, 3H, OCH_3), 3.20–3.65 (m, 4H, 2×NCH_2), 1.70–2.25 (m, 8H, 2×CH_2CH_2). δ_C (100.6 MHz, $CDCl_3$) 172.6, 172.4, 168.9, 168.8, 144.7, 137.1, 136.0, 127.9, 125.9, 116.4, 59.1, 58.5, 52.2 (2C), 49.9, 48.6, 29.4, 29.3, 25.4, 24.8. IR (KBr, cm^{-1}): 1744 (COO), 1638 (CON). MS *m*/*z* (rel int. %): 414 (3), 355 (34), 286 (100), 258 (24), 102 (29). Analysis calculated for $C_{22}H_{26}N_2O_6$ (414.46): C, 63.76; H, 6.32; N, 6.76.

Found: C, 63.55; H, 6.42; N, 6.53. R_f (50% EtOAc/$CHCl_3$) 0.26; golden highly viscous solid. Yield: 114 mg, 55%.

*4.7.18. 2-(4-N,N-(1-Methoxycarbonyl-1,4-butanediyl)-glyoxylamido-phenyl)-N,N-(1-methoxycarbonyl-1,4-butanediyl)-acrylamide (**6h**)*

δ_H (400 MHz, $CDCl_3$) 8.03 (d, 7.8 Hz, 2H, Ar), 7.63 (d, 7.8 Hz, 2H, Ar), 5.88 (br s, 1H, =CH), 5.62 (br s, 1H, =CH), 4.56–4.70 (m, 2H, CHCOO), 3.77 (s, 3H, OCH_3), 3.74 (s, 3H, OCH_3), 3.30–3.60 (m, 4H, 2×NCH_2), 1.80–2.35 (m, 8H, 2×CH_2CH_2). δ_C (100.6 MHz, $CDCl_3$) 190.4, 172.3, 171.8, 168.4, 165.1, 144.6, 141.3, 132.6, 132.0, 126.6, 118.2, 58.5, 58.3, 52.5, 52.3, 48.6, 47.2, 29.4, 29.1, 24.8, 24.6. IR (KBr, cm^{-1}): 1752 (COO), 1681 (CO), 1646 (CON), 1604 (C=C). Analysis calculated for $C_{23}H_{26}N_2O_7$ (442.47): C, 62.43; H, 5.92; N, 6.33. Found: C, 62.57; H, 5.80; N, 6.18. R_f (50% EtOAc/$CHCl_3$) 0.38; golden highly viscous solid. Yield: 68 mg, 31%.

*4.7.19. 2-(4-(N-tert-Butylglyoxylamido)-phenyl)-N-(methoxycarbonylmethyl)-acrylamide (**8a**)*

δ_H (400 MHz, $CDCl_3$) 8.32 (d, 8.3 Hz, 2H, Ar), 7.53 (d, 8.3 Hz, 2H, Ar), 6.93 (br s, 1H, NH), 6.24 (br s, 1H, NH), 6.19 (br s, 1H, =CH), 5.77 (br s, 1H, =CH), 4.10 (d, 5.4 Hz, 2H, CH_2COO), 3.74 (s, 3H, OCH_3), 1.45 (s, 9H, ^{t}Bu). δ_C (100.6 MHz, $CDCl_3$) 187.8, 170.0, 166.9, 160.9, 143.5, 142.0, 133.3, 131.5, 127.9, 123.7, 52.3, 51.7, 41.5, 28.3. IR (KBr, cm^{-1}): 3358 (NH), 1751 (COO), 1666 (br, 2×CON), 1604 (C=C). Analysis calculated for $C_{18}H_{21}N_2O_5$ (345.38): C, 62.60; H, 6.13; N, 8.11. Found: C, 62.73; H, 6.30; N, 7.90. R_f (50% EtOAc/CH_2Cl_2) 0.67; yellow solid, mp 69–73 °C. Yield: 153 mg, 88%.

*4.7.20. 2-(4-(N,N-1,5-Pentandiylglyoxylamido)-phenyl)-N-(methoxycarbonylmethyl)-acrylamide (**8c**)*

δ_H (400 MHz, $CDCl_3$) 7.91 (d, 8.2 Hz, 2H, Ar), 7.55 (d, 8.2 Hz, 2H, Ar), 6.41 (br s, 1H, NH), 6.11 (br s, 1H, =CH), 5.78 (br s, 1H, =CH), 4.10 (d, 5.5 Hz, 2H, CH_2COO), 3.74 (s, 3H, OCH_3), 3.20–3.70 (m, 4H, 2×NCH_2), 1.50–1.70 (m, 6H, 3×CH_2). δ_C (100.6 MHz, $CDCl_3$) 191.0, 170.0, 167.0, 165.1, 143.5, 142.5, 133.0, 129.8, 128.5, 123.3, 52.3, 47.0, 41.4, 26.3, 26.1, 24.3. IR (KBr, cm^{-1}): 3422 (NH), 1753 (COO), 1676 (CO), 1640 (br, 2×CON). Analysis calculated for $C_{18}H_{20}N_2O_5$ (344.37): C, 62.78; H, 5.85; N, 8.13. Found: C, 62.61; H, 5.72; N, 7.88. R_f (50% EtOAc/CH_2Cl_2) 0.50; pale-brown viscous material. Yield: 142 mg, 82%.

*4.7.21. 2-(4-(N-1-Methoxycarbonylethyl-glyoxylamido)-phenyl)-N-(methoxycarbonylmethyl)-acrylamide (**8f**)*

δ_H (400 MHz, $CDCl_3$) 8.30 (d, 8.3 Hz, 2H, Ar), 7.49 (d, 8.3 Hz, 2H, Ar), 6.26 (br s, 2H, 2×NH), 6.15 (br s, 1H, =CH), 5.76 (br s, 1H, =CH), 4.62 (quint., 5.5 Hz, 2H, CHCOO), 3.74 (s, 3H, OCH_3), 3.70 (s, 3H, OCH_3), 1.48 (d, 3H, $CHCH_3$). δ_C (100.6 MHz, $CDCl_3$) 186.5, 172.3, 170.0, 167.0, 161.0, 143.5, 133.0, 131.5, 128.5, 128.0, 123.7, 52.6, 52.3, 48.1, 41.4, 17.9. IR (KBr, cm^{-1}): 3355 (NH), 1747 (COO), 1716 (CO), 1667 (br, 2×CON), 1605 (C=C). Analysis calculated for $C_{18}H_{20}N_2O_7$ (376.37): C, 57.44; H, 5.36; N, 7.44. Found: C, 57.31; H, 5.50; N, 7.17. R_f (50% EtOAc/CH_2Cl_2) 0.51; pale-brown, mp 207–210 °C (decomposed). Yield: 146 mg, 78%.

*4.7.22. Methyl 2-(4-methoxycarbonylphenyl)-acrylate (**9**)*

δ_H (400 MHz, $CDCl_3$) 8.00 (d, 7.8 Hz, 2H, Ar), 7.47 (d, 7.8 Hz, 2H, Ar), 6.43 (br s, 1H, =CH), 5.95 (br s, 1H, =CH), 3.92 (s, 3H, OCH_3), 3.81 (s, 3H, OCH_3). IR (KBr, cm^{-1}): 1725 (COO), 1609 (C=C). MS *m*/*z* (rel int. %): 220 (48), 189 (100), 181 (47), 129 (13), 102 (23). Analysis calculated for $C_{12}H_{12}O_4$ (220.22): C, 65.45; H, 5.49. Found: C, 65.28; H, 5.59. R_f (2% EtOAc/$CHCl_3$) 0.80; pale-yellow viscous material. Yield: 26 mg, 23%.

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