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Synthesis of 2-naphthylacrylamides and 2-naphthylacrylates via homogeneous catalytic carbonylation of 1-iodo-1-naphthylethene derivatives

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ABSTRACT

Two highly reactive iodoalkenes (1-iodo-1-(2-naphthyl)ethene and 1-iodo-1-(1-naphthyl)ethene) were prepared from the corresponding acetonaphthone isomers via their hydrazones and used as substrates in palladium-catalysed carbonylations. Both iodoalkenyl substrates proved to be highly reactive in the presence of various *N*-nucleophiles and the corresponding *N*-substituted naphthylacrylamides were formed chemoselectively in nearly quantitative yields. High isolated yields (up to 93%) were achieved with all types of amines under mild reaction conditions. The alkoxycarbonylation of the above iodoalkenes resulted in esters of unexpectedly good isolated yields (up to 77%).

1. Introduction

Conjugated unsaturated carboxamides represent an important family of building blocks in synthetic chemistry.[1] Among them 2-acetamidoacrylamides and 2-acetamidocinnamic amides are widely used substrates in enantioselective hydrogenation for the synthesis of alanine amides and phenylalanine amides, respectively.[2] Their synthetic applicability and chemical properties can be tuned by structural variation both on the amide nitrogen and on the carbon–carbon double bond.

The palladium-catalysed carbonylation reactions of haloaromatics or haloalkenes (preferably iodo derivatives) as well as those of the corresponding triflate surrogates are important and widely used reactions for the synthesis of aromatic or α-unsaturated carboxylic acid derivatives, respectively. For example, in the presence of various nucleophiles such as amines and alcohols the efficient synthesis of carboxamides and esters can be carried out, respectively.[3] The efficacy of these reactions can be demonstrated both by the synthesis of simple model compounds and by the functionalisation of biologically important skeletons.[4] The key to their wide application lies in the fact that even those carboxamides, which are difficult to prepare (or not available in yields of practical importance) via the conventional carboxylic acid–carboxylic halide–carboxamide route can be synthesised from easily available starting materials.[5]

In spite of the close structural relation to phenylacrylic acid derivatives, relatively little is known on synthesis and application of naphthylacrylates and naphthylacrylamides. Conformational studies and photochemical behaviour of ethyl 2-naphthylacrylate and *N*,*N*-dimethyl-2-naphthylacrylamide were carried out.[6]

Encouraged by the fact that the palladium-catalysed aminocarbonylation reaction of the iodoalkene or enol-triflate intermediate might provide an efficient route for the synthesis of 2-naphthylacryloyl amides, we decided to investigate their synthesis by using the corresponding 1-iodo-1-naphthylethene derivatives as substrates. The synthetic utility of the aminocarbonylation reaction for the synthesis of unsaturated carboxamides or aryl carboxamides with various structures has been demonstrated recently also in our group.[7,8] Accordingly, a clean and almost quantitative synthetic methodology is reported here for the aminocarbonylation of 1-iodo-1-naphthylethene isomers with simple primary and secondary amines, as well as with functionalised amines like amino acid methyl esters as *N*-nucleophiles.

2. Results and discussion

2.1. Synthesis of 1-iodo-1-(1-naphthyl)ethene (5) and 1-iodo-1-(2-naphthyl)ethene (7)

The above two iodoalkenes have been synthesised in the conventional ketone–hydrazone–iodo-alkene route by using BaO and

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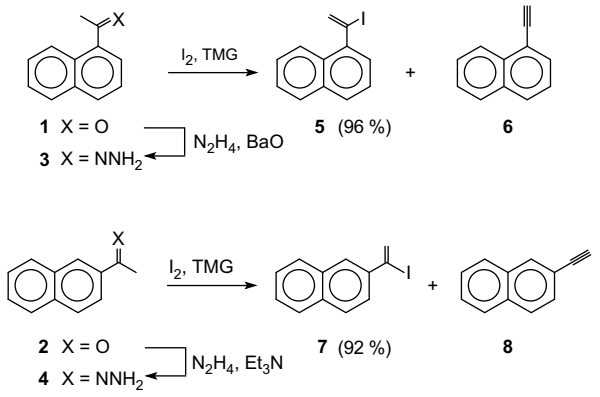
TMG (*N*,*N*,*N*′,*N*′-tetramethylguanidine) in the two consecutive steps (Scheme 1).[9] As in case of previous preparations, the hydrazone derivatives (**3** and **4**) were not isolated. Since 1-ethynyl- and 2-ethynyl-naphthalenes (**6** and **8**, respectively) were formed as undesired side-products in the iodination step aiming at the synthesis of **5** and **7**, respectively, several modifications had to be done concerning the original paper. By using TMG in ninefold excess as usual in case of cyclic ketones, **1** was transformed also to **6** (the ratio of **5**/**6** was ca. 2/1). It was necessary to decrease the TMG/hydrazone ratio to 3/1 in order to obtain the target iodoalkene compounds (**5** and **7**) as major products. The yields of **5** and **7** were also increased by decreasing the reaction temperature of the iodine-TMG step, i.e., the reaction temperature was kept between 5 and 10 °C throughout



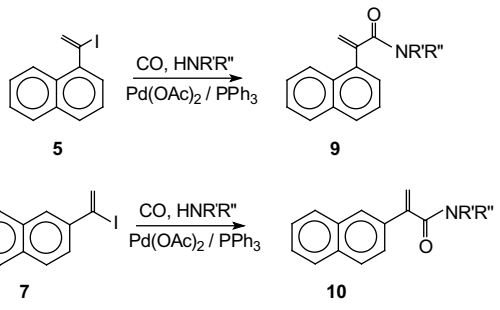
Scheme 1. Synthesis of the iodoalkenes (**5** and **7**) from the corresponding ketones via their hydrazones.

the reaction. When the addition of the hydrazone-TMG mixture to iodine in dichloromethane was completed, the solution was allowed to warm up to room temperature. It has to be noted that the high isolated yields, given for the iodoalkenes in the Experimental section, could be obtained only when the 'iodovinyl' product-forming step was carried out under argon providing strictly moisture- and oxygen-free conditions. Optimised experimental conditions for the synthesis of **5** and **7** are given below in the Experimental section.

2.2. Amino- and alkoxycarbonylation of 5 and 7

The iodo-naphthylethene isomers (1-iodo-1-(1-naphthyl)ethene, **5** and 1-iodo-1-(2-naphthyl)ethene, **7**) were reacted with *tert*-butylamine (**a**), aniline (**b**), piperidine (**c**), morpholine (**d**), methyl glycinate (**e**), methyl alaninate (**f**), methyl valinate (**g**) and methyl prolinate (**h**) under atmospheric carbon monoxide in the presence of in situ generated palladium(0)-triphenylphosphine catalysts (Scheme 2). The palladium(0) complexes, able to activate iodoalkenes, were prepared in situ from palladium(II) acetate as described previously in detail.[10,11]

The reactivity of both iodo-naphthylethene isomers, **5** and **7**, compared to several types of iodoalkenes, such as linear (e.g., 1-iodo-1-dodecene[8]) and cyclic iodoalkenes (e.g., 1-iodo-1-cyclohexene[12] and similar compounds of pharmacological importance[1,5]), proved to be exceptionally high. Due to the presence of an activating aryl-group at the sp^2 carbon atom bearing the iodide as good leaving group, all of the resulting *N*-substituted 2-naphthylacrylamides (**9a**–**h** and **10a**–**h**) have been obtained with practically complete conversion and isolated in 70–93% yields after column chromatography (Experimental) except for **b**. It has to be noted that **10b** could not be isolated as a pure substance for full characterisation. The decreased reactivity of **b** could be explained by its lower basicity compared to the primary and secondary alkylamines used. Even those amines,



	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 **5** and **7**.

such as sterically hindered secondary amines (**h**), which have shown decreased reactivity in aminocarbonylation of various iodoalkenes in previous studies, provided excellent isolated yields (Table 1). It is worth noting that no 2-ketocarboxamide formation, due to double carbon monoxide insertion, was observed.

Detailed GC–MS analyses have shown that high conversions have been obtained with different amines even after a short reaction time. For example, the reaction of **5** with **a** towards **9a** resulted in 70%, 98.7% and 99.6% conversions in 15 min, 30 min and 45 min, respectively. In the same reactions times, the reaction of **5** with **c** towards **9c** resulted in 47%, 76% and 97% conversions, respectively. It is worth noting that the full conversions, obtained in seemingly excessive reaction times, such as 20 h (Table 1), enabled the facile isolation of the amide products.

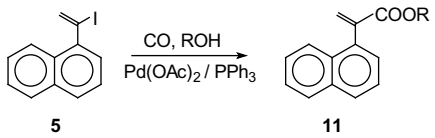
The enhanced reactivity of the substrates was also reflected in alkoxycarbonylation. In addition to the widely used methanol (**i**) even the less reactive alcohols (isopropyl alcohol (**j**) and benzyl alcohol (**l**)) brought about yields of synthetic interest (Scheme 3).

Table 1
Palladium-catalysed aminocarbonylation of **5** and **7**[a]

Entry	Substrate	Amine	Isolated yield[b] (amide) [%]
1	**5**	*t*-BuNH_2 (**a**)	87 (**9a**)
2	**7**	*t*-BuNH_2 (**a**)	85 (**10a**)
3	**5**	Aniline (**b**)	13 (**9b**)
4	**7**	Aniline (**b**)	n.d. (**10b**)
5	**5**	Piperidine (**c**)	93 (**9c**)
6	**7**	Piperidine (**c**)	90 (**10c**)
7	**5**	Morpholine (**d**)	88 (**9d**)
8	**7**	Morpholine (**d**)	85 (**10d**)
9	**5**	GlyOMe (**e**)	80 (**9e**)
10	**7**	GlyOMe (**e**)	77 (**10e**)
11	**5**	AlaOMe (**f**)	80 (**9f**)
12	**7**	AlaOMe (**f**)	75 (**10f**)
13	**5**	ValOMe (**g**)	76 (**9g**)
14	**7**	ValOMe (**g**)	75 (**10g**)
15	**5**	ProOMe (**h**)	70 (**9h**)
16	**7**	ProOMe (**h**)	73 (**10h**)

[a] Reaction conditions: 0.025 mmol $Pd(OAc)_2$; 0.05 mmol PPh_3, 1 mmol substrate (**5** or **7**); 3 mmol non-functionalised amine (or 1.1 mmol amino acid methyl ester hydrochloride); 1 bar CO; 10 mL DMF, reaction time: 20 h.

[b] Practically complete conversion (>99.8%) has been obtained in all cases except for **b** (27% for **9b**, 12% for **10b** (not isolated)). Isolated yields are based on the substrates (**5** and **7**).



R	
i	Me
j	*i*Pr
k	*t*Bu
l	Bn

Scheme 3. Palladium-catalysed alkoxycarbonylation of **5**.

The corresponding esters were produced in 77%, 63% and 69% yields, respectively. The only alcohol resulting in extremely low conversions, and therefore no isolated yields, was *tert*-butanol (**k**).

3. Conclusion

The activated geminally disubstituted iodoalkenes, 1-naphthyl-1-iodoethenes, proved to be excellent substrates in palladium-catalysed aminocarbonylation providing the corresponding naphthylacrylamides in nearly quantitative yields. High tolerance towards *N*-nucleophiles were observed, i.e., even those amines with steric hindrance or less basicity brought about the products in yields of practical importance.

It could be stated, that the exceptional reactivity of the 1-naphthyl-1-iodoethenes, compared to the aliphatic analogues, resulted in 2-naphthylacrylamide type synthetic building blocks in clean aminocarbonylation.

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 residual $CHCl_3$ (7.26 and 77.00 ppm for ^{1}H 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. The amines and amino acid derivatives were purchased from Aldrich.

4.2. Synthesis of 1-iodo-1-(1-naphthyl)ethene (5)

1-Acetonaphthone (**1**) (5 g, 29.4 mmol), freshly distilled hydrazine hydrate (98%, 1.62 g, 32.3 mmol) and barium oxide (1.18 g, 7.7 mmol) in absolute ethanol (50 mL) were heated for 24 h at 90 °C. After completion of the reaction, iced water (200 mL) and dichloromethane (150 mL) were added, and the white precipitate was filtered. The organic phase was separated, dried over sodium sulfate for a day and concentrated to give the hydrazone (**3**) derivative. The product was used in the next step without further purification.

To a stirred solution of iodine (15.43 g, 60.8 mmol) in dichloromethane (50 mL) the mixture of 1,1,3,3-tetramethylguanidine (TMG, 10.15 g, 88.1 mmol) and 1-acetonaphthone hydrazone (**3**) (5.41 g, 29.4 mmol) in dichloromethane (30 mL) was added dropwise between 0 and 15 °C by using an ice-bath. 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 an argon atmosphere for 2 h. The mixture was poured into water (300 mL) and extracted with dichloromethane (3×80 mL). The combined organic layers were washed 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 iodoalkene (**5**) was obtained as a brown viscous material and used for carbonylation experiments without further purification. Yield: 7.86 g; 96%.

4.2.1. 1-Iodo-1-(1-naphthyl)ethene (*5*)

δ_H (400 MHz, $CDCl_3$) 8.21 (dd, 8.4 Hz, 0.8 Hz, 1H, Naph); 7.88 (d, 8.1 Hz, 1H, Naph); 7.83 (d, 8.1 Hz, 1H, Naph); 7.59 (t, 7.2 Hz, 1H, Naph); 7.45–7.54 (m, 2H, Naph); 7.41 (t, 7.2 Hz, 1H, Naph); 6.37 (d, 1.2 Hz, 1H, =CH); 6.33 (d, 1.2 Hz, 1H, =CH). δ_C (100.6 MHz, $CDCl_3$) 141.5; 133.7; 131.1; 129.8; 128.8; 128.2; 126.3; 126.1; 125.7; 125.4; 125.2; 102.3. IR (KBr (cm^{-1})): 1616 (C=C). MS *m*/*z* (rel.int. %): 280 (10), 153 (100), 127 (7). Anal. Calcd for $C_{12}H_9I$ (280.11): C, 51.46; H, 3.24; Found: C, 51.62; H, 3.39; R_f (petroleum ether 40/70) 0.77; brown viscous material.

4.3. Synthesis of 1-iodo-1-(2-naphthyl)ethene (7)

The above protocol described for **5** was followed. A brown solid material with appropriate purity was obtained and used without further purification as a substrate for carbonylation reactions. Yield: 14.79 g; 92%.

4.3.1. 1-Iodo-1-(2′-naphthyl)ethene (*7*)

δ_H (400 MHz, $CDCl_3$) 7.98 (br s, 1H, Naph); 7.80–7.88 (m, 2H, Naph); 7.75 (d, 8.4 Hz, 1H, Naph); 7.64 (dd, 8.6 Hz, 1.9 Hz, 1H, Naph); 7.47–7.52 (m, 2H, Naph); 6.60 (d, 1.8 Hz, 1H, =CH); 6.18 (d, 1.8 Hz, 1H, =CH). δ_C (100.6 MHz, $CDCl_3$) 138.8; 133.4; 132.9; 128.4; 128.3; 127.8; 127.6; 127.5; 126.8; 126.6; 124.9; 107.6. MS *m*/*z* (rel.int. %): 280 (15), 153 (100), 127 (9). Anal. Calcd for $C_{12}H_9I$ (280.11): C, 51.46; H, 3.24; Found: C, 51.57; H, 3.36; R_f (petroleum ether 40/70) 0.60; mp 70–75 °C.

4.4. 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 (**5** or **7**), 1.5 mmol nonfunctionalized amine (**a**–**d**) (or 0.55 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 20 h at 50 °C. Some metallic palladium was formed at the end of the reaction, which was filtered off. A sample of this solution was immediately analysed by GC–MS. The mixture was then concentrated to dryness. The residue was dissolved in chloroform (20 mL) and washed 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. Chromatography (silica, chloroform, then chloroform/ethyl acetate mixtures) yielded the desired compounds typically as pale brown viscous materials or yellow solids.

4.5. Alkoxycarbonylation experiments at high pressure

A mixture of **5** (or **7**) (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 under argon, and NEt_3 (0.5 mL) and methanol (0.13 mL, 5 mmol) or (isopropylalcohol, 0.38 mL, 5 mmol; benzyl alcohol, 0.52 mL, 5 mmol) as *O*-nucleophiles were added. The reaction mixture was then transferred under argon into a 100 mL stainless steel autoclave, which was pressurised to 55 bar with CO and the magnetically stirred mixture was heated in an oil bath at 50 °C for

Table 2
Palladium-catalysed alkoxycarbonylation of **5**[a]

Entry	Alcohol	Conversion [%]	Isolated yield[b] (ester) [%]
1	Methanol (**i**)	>99	77 (**11i**)
2	Isopropyl alcohol (**j**)	>98	63 (**11j**)
3	*tert*-Butanol (**k**)	<2	n.d. (**11k**)
4	Benzyl alcohol (**l**)	>98	69 (**11l**)

[a] Reaction conditions: 0.025 mmol $Pd(OAc)_2$; 0.05 mmol PPh_3, 1 mmol substrate (**5**); 5 mmol alcohol; 55 bar CO; 10 mL DMF; r.time: 66 h.
[b] Isolated yields are based on the substrate (**5**).

the reaction time given in Table 2. The work-up procedure was identical with that given above for the carboxamides.

4.6. Characterisation of the amide and ester products

*4.6.1. N-tert-Butyl-2-(1-naphthyl)acrylamide (**9a**)*

δ_H (400 MHz, $CDCl_3$) 7.80–7.86 (m, 3H, Naph); 7.41–7.46 (m, 3H, Naph); 7.39 (d, 6.8 Hz, 1H, H-2); 6.60 (d, 1.1 Hz, 1H, =CH); 5.58 (d, 1.1 Hz, 1H, =CH); 5.20 (br s, 1H, NH); 1.20 (s, 9H, *t*Bu). δ_C (100.6 MHz, $CDCl_3$) 165.5; 143.9; 135.3; 133.5; 131.5; 128.9; 128.3; 127.3; 126.4; 126.2; 125.6; 125.5; 125.4; 51.2; 28.3. IR (KBr (cm^{-1})): 3262 (NH); 1644 (CON); 1613 (C=C). MS *m*/*z* (rel.int. %): 253 (30), 238 (6), 196 (14), 153 (100), 127 (3). Anal. Calcd for $C_{17}H_{19}NO$ (253.34): C, 80.60; H, 7.56; N, 5.53; Found: C, 80.52, H, 7.75; N, 5.33; R_f (3% EtOAc/$CHCl_3$) 0.64; off-white solid, mp 108–110 °C.

*4.6.2. N-Phenyl-2-(1-naphthyl)acrylamide (**9b**)*

δ_H (400 MHz, $CDCl_3$) 7.90–7.99 (m, 3H, Naph); 7.47–7.59 (m, 4H, Naph); 7.32 (d, 7.9 Hz, 2H, o-Ph); 7.22 (t, 7.9 Hz, 2H, m-Ph); 7.16 (br s, 1H, NH); 7.05 (t, 7.9 Hz, 3H); 6.85 (br s, 1H, =CH); 5.77 (br s, 1H, =CH). δ_C (100.6 MHz, $CDCl_3$) 164.3; 143.0; 137.5; 134.5; 133.8; 131.7; 129.5; 128.8; 128.6; 127.8; 127.7; 127.1; 126.6; 125.6; 125.3; 124.6; 120.1. IR (KBr (cm^{-1})): 1648 (CON). MS *m*/*z* (rel.int. %): 273 (55), 207 (1), 168 (25), 153 (100), 152 (90), 127 (7). Anal. Calcd for $C_{19}H_{15}NO$ (273.33): C, 83.49; H, 5.53; N, 5.12; Found: C, 83.33; H, 5.39; N, 4.94; R_f (5% EtOAc/$CHCl_3$) 0.75; brown solid, mp 75–76 °C.

*4.6.3. 2-(1-Naphthyl)-1-piperidin-1-ylpropenone (**9c**)*

δ_H (400 MHz, $CDCl_3$) 8.26 (d, 7.8 Hz, 1H, Naph); 7.82 (d, 7.8 Hz, 1H, Naph); 7.79 (d, 7.8 Hz, 1H, Naph); 7.40–7.55 (m, 4H, Naph); 5.91 (br s, 1H, =CH); 5.68 (br s, 1H, =CH); 3.55–3.63 (m, 2H, NCH_2); 3.28–3.34 (m, 2H, NCH_2); 1.52 (br s, 4H, $(CH_2)_2$); 1.10 (br s, 2H, CH_2). δ_C (100.6 MHz, $CDCl_3$) 169.5; 145.0; 135.7; 133.9; 130.8; 128.5; 126.4; 126.1; 125.9; 125.2; 125.1; 121.8; 113.6; 47.8; 43.1; 25.7; 25.4; 24.4. IR (KBr (cm^{-1})): 1631 (CON). MS *m*/*z* (rel.int. %): 265 (96), 182 (18), 153 (98), 152 (100), 112 (51). Anal. Calcd for $C_{18}H_{19}NO$ (265.35): C, 81.48; H, 7.22; N, 5.28; Found: C, 81.20; H, 7.03; N, 5.10; R_f (10% EtOAc/$CHCl_3$) 0.56; pale brown viscous material.

*4.6.4. 1-(Morpholin-4-yl)-2-(1-naphthyl)propenone (**9d**)*

δ_H (400 MHz, $CDCl_3$) 8.18 (d, 7.9 Hz, 1H, Naph); 7.81 (d, 7.8 Hz, 1H, Naph); 7.79 (d, 7.8 Hz, 1H, Naph); 7.38–7.51 (m, 4H, Naph); 5.92 (br s, 1H, =CH); 5.72 (br s, 1H, =CH); 3.60 (br s, 2H, OCH_2); 3.55 (br s, 2H, OCH_2); 3.30 (br s, 2H, CH_2); 3.21 (br s, 2H, CH_2). δ_C (100.6 MHz, $CDCl_3$) 169.7; 144.2; 135.3; 133.9; 130.6; 128.9; 128.6; 126.6; 126.1; 125.3; 124.8; 123.2 (double intensity); 66.3 (br, double intensity); 47.1; 42.5. IR (KBr (cm^{-1})): 1636 (CON). MS *m*/*z* (rel.int. %): 267 (57), 180 (18), 153 (100), 152 (80), 127 (6), 114 (24). Anal. Calcd for $C_{17}H_{17}NO_2$ (267.33): C, 76.38; H, 6.41; N, 5.24; Found: C, 76.22; H, 6.55; N, 5.01; R_f (30% EtOAc/$CHCl_3$) 0.43; pale brown viscous material.

*4.6.5. (2-(1-Naphthyl)acryloylamino)acetic acid methyl ester (**9e**)*

δ_H (400 MHz, $CDCl_3$) 7.82–7.91 (m, 3H, Naph); 7.41–7.53 (m, 4H, Naph); 6.72 (br s, 1H, =CH); 5.87 (br s, 1H, NH); 5.69 (br s, 1H, =CH); 3.97 (d, 5.5 Hz, 2H, CH_2); 3.62 (s, 3H, OCH_3). δ_C (100.6 MHz, $CDCl_3$) 169.8; 166.3; 141.8; 134.5; 133.6; 131.7; 129.1; 128.3; 127.5; 127.3; 126.6; 126.3; 125.4; 125.3; 52.1, 41.4. IR (KBr (cm^{-1})): 3411 (NH); 1753 (COO); 1668 (CON); 1612 (C=C). MS *m*/*z* (rel.int. %): 269 (14), 180 (38), 153 (100), 152 (80), 127 (4). Anal. Calcd for $C_{16}H_{15}NO_3$ (269.30): C, 71.36; H, 5.61; N, 5.20; Found: C, 71.12; H, 5.84; N, 5.01; R_f (20% EtOAc/$CHCl_3$) 0.58; pale brown viscous material.

*4.6.6. 2-(2-(1-Naphthyl)acryloylamino)propionic acid methyl ester (**9f**)*

δ_H (400 MHz, $CDCl_3$) 7.82–7.92 (m, 3H, Naph); 7.41–7.52 (m, 4H, Naph); 6.70 (br s, 1H, =CH); 5.93 (br s, 1H, NH); 5.66 (br s, 1H, =CH); 4.61 (quintet, 7.2 Hz, 1H, C*H*CH_3); 3.62 (s, 3H, OCH_3); 1.22 (d, 7.2 Hz, 3H, CHC*H*$_3$). δ_C (100.6 MHz, $CDCl_3$) 172.8; 165.7; 142.2; 134.5; 133.6; 131.6; 129.1; 128.3; 127.5; 127.1; 126.5; 126.3; 125.4 (double intensity); 52.2; 48.3; 17.9. IR (KBr (cm^{-1})): 3331 (NH); 1743 (COO); 1668 (CON); 1613 (C=C). MS *m*/*z* (rel.int. %): 283 (14), 224 (10), 180 (20), 153 (100), 152 (55), 127 (2). Anal. Calcd for $C_{17}H_{17}NO_3$ (283.33): C, 72.07; H, 6.05; N, 4.94; Found: C, 71.90; H, 6.20; N, 4.71; R_f (10% EtOAc/$CHCl_3$) 0.60; pale brown viscous material.

*4.6.7. 3-Methyl-2-(2-(1-naphthyl)acryloylamino)butyric acid methyl ester (**9g**)*

δ_H (400 MHz, $CDCl_3$) 7.78–7.87 (m, 3H, Naph); 7.40–7.50 (m, 4H, Naph); 6.66 (br s, 1H, =CH); 5.80 (br d, 8.4 Hz, 1H, NH); 5.67 (br s, 1H, =CH); 4.50–4.57 (m, 1H, C*H*NH); 3.54 (s, 3H, OCH_3); 1.90–2.00 (m, 1H, C*H*$(CH_3)_2$); 0.73 (d, 6.9 Hz, 3H, CHC*H*$_3$); 0.52 (d, 6.9 Hz, 3H, CHC*H*$_3$). δ_C (100.6 MHz, $CDCl_3$) 171.8; 166.0; 142.4; 134.6; 133.5; 131.6; 129.1; 128.3; 127.4; 126.8; 126.5; 126.3; 125.4; 125.3; 57.3; 51.9; 31.0; 18.8; 17.3. IR (KBr (cm^{-1})): 3420 (NH); 1743 (COO); 1677 (CON; 1615 (C=C)). MS *m*/*z* (rel.int. %): 311 (10), 252 (23), 197 (20), 180 (12), 153 (100), 128 (3). Analysis calculated for $C_{19}H_{21}NO_3$ (311.38): C, 73.29; H, 6.80; N, 4.50; Found: C, 73.19; H, 6.92; N, 4.29; R_f (10% EtOAc/$CHCl_3$) 0.64; pale brown viscous material.

*4.6.8. 1-(2-(1-Naphthyl)acryloyl)pyrrolidine-2-carboxylic acid methyl ester (**9h**, two rotational isomers, 80/20)*

δ_H (400 MHz, $CDCl_3$) 8.12 (d, 7.9 Hz, 1H, Naph); 7.73–7.81 (m, 2H, Naph); 7.38–7.48 (m, 4H, Naph); 6.20/5.97 (major/minor) (br s, 1H, =CH); 5.68/5.60 (major/minor) (br s, 1H, =CH); 4.47–4.52/4.03–4.09 (major/minor) (m, 1H, NCH); 3.70/3.27 (major/minor) (s, 3H, OCH_3); 3.00–3.07 (m, 2H, NCH_2); 1.60–2.08 (m, 4H, $(CH_2)_2$). δ_C (100.6 MHz, $CDCl_3$) 172.4/172.0 (major/minor); 169.5/168.9 (minor/major); 145.5/144.8 (minor/major); 135.3/134.6 (major/minor); 133.7; 131.0; 128.9/128.7 (minor/major); 128.6/128.4 (minor/major); 126.6; 126.4; 126.0; 125.3; 125.1; 124.3/123.8 (major/minor); 59.8/59.4 (minor/major); 52.0/51.8 (major/minor); 48.3/46.7 (major/minor); 31.4/28.8 (minor/major); 25.0/21.8 (major/minor). IR (KBr (cm^{-1})): 1744 (COO); 1637 (CON). MS *m*/*z* (rel.int. %): 309 (14), 250 (22), 181 (9), 153 (100), 152 (45), 128 (10). Anal. Calcd for $C_{19}H_{19}NO_3$ (309.36): C, 73.77; H, 6.19; N, 4.53; Found: C, 73.68; H, 6.34; N, 4.31; R_f (20% EtOAc/$CHCl_3$) 0.53; pale brown viscous material.

*4.6.9. N-tert-Butyl-2-(2-naphthyl)acrylamide (**10a**)*

δ_H (400 MHz, $CDCl_3$) 7.78–7.85 (m, 4H, Naph); 7.43–7.50 (m, 3H, Naph); 6.08 (d, 1.2 Hz, 1H, =CH); 5.68 (d, 1.2 Hz, 1H, =CH); 5.62 (br s, 1H, NH); 1.40 (s, 9H, *t*Bu). δ_C (100.6 MHz, $CDCl_3$) 167.0; 146.1; 134.6; 133.3; 133.1; 128.3; 128.2; 127.7; 127.3; 126.5 (double intensity); 125.5; 121.0; 51.6; 28.8. IR (KBr (cm^{-1})): 3346 (NH); 1647 (CON). MS *m*/*z* (rel.int. %): 253 (47), 238 (10), 196 (42), 153 (100), 127 (8). Anal. Calcd for $C_{17}H_{19}NO$ (253.34): C, 80.60; H, 7.56; N, 5.53; Found: C, 80.45, H, 7.72; N, 5.40; R_f (3% EtOAc/$CHCl_3$) 0.74; R_f (10% EtOAc/$CHCl_3$) 0.84; yellow solid, mp 93–95 °C.

*4.6.10. N-Phenyl-2-(2-naphthyl)acrylamide (**10b**, obtained as impure material not suitable for full characterisation)*

δ_H (400 MHz, $CDCl_3$) 7.05–7.90 (m, 12H, Ar); 6.25 (br s, 1H, NH); 5.82 (br s, 1H, =CH); 5.42 (br s, 1H, =CH). MS *m*/*z* (rel.int. %): 273 (60), 207 (66), 153 (100), 152 (92), 127 (29). R_f (5% EtOAc/$CHCl_3$) 0.75.

*4.6.11. 2-(2-Naphthyl)-1-piperidin-1-ylpropenone (**10c**)*

δ_H (400 MHz, $CDCl_3$) 7.76–7.82 (m, 4H, Naph); 7.60 (d, 8.2 Hz, 1H, Naph); 7.4–7.46 (m, 2H, Naph); 5.80 (br s, 1H, =CH); 5.41 (br s, 1H, =CH); 3.68–3.75 (m, 2H, NCH_2); 3.28–3.33 (m, 2H, NCH_2); 1.60 (br s, 4H, $(CH_2)_2$); 1.34 (br s, 2H, CH_2). δ_C (100.6 MHz, $CDCl_3$) 169.2; 145.3; 133.4; 133.2; 133.0; 128.5; 128.4; 127.6; 126.4; 125.3; 123.1; 113.6; 48.0; 42.5; 26.3; 25.7; 24.5. IR (KBr (cm^{-1})): 1633 (CON). MS *m*/*z* (rel.int. %): 265 (100), 182 (26), 153 (80), 152 (79), 127 (13). Anal. Calcd for $C_{18}H_{19}NO$ (265.35): C, 81.48; H, 7.22; N, 5.28; Found: C, 81.29; H, 7.01; N, 5.05; R_f (10% EtOAc/$CHCl_3$) 0.65; yellow solid, mp 71–72 °C.

*4.6.12. 1-(Morpholin-4-yl)-2-(2-naphthyl)propenone (**10d**)*

δ_H (400 MHz, $CDCl_3$) 7.76–7.82 (m, 4H, Naph); 7.58 (d, 8.2 Hz, 1H, Naph); 7.40–7.46 (m, 2H, Naph); 5.83 (br s, 1H, =CH); 5.42 (br s, 1H, =CH); 3.80 (br s, 2H, OCH_2); 3.71 (br s, 2H, OCH_2); 3.42 (br s, 2H, CH_2); 3.34 (br s, 2H, CH_2). δ_C (100.6 MHz, $CDCl_3$) 169.5; 144.5; 133.4; 133.3; 132.6; 128.8; 128.4; 127.7; 126.7; 126.6; 125.3; 122.9; 114.8; 66.8 (double intensity); 47.4; 42.0. IR (KBr (cm^{-1})): 1623 (CON). MS *m*/*z* (rel.int. %): 267 (70), 182 (20), 153 (100), 152 (81), 127 (11). Anal. Calcd for $C_{17}H_{17}NO_2$ (267.33): C, 76.38; H, 6.41; N, 5.24; Found: C, 76.33; H, 6.28; N, 5.07; R_f (30% EtOAc/$CHCl_3$) 0.54; R_f (10% EtOAc/$CHCl_3$) 0.37; yellow solid, mp 127–128 °C.

*4.6.13. (2-(2-Naphthyl)-acryloylamino)acetic acid methyl ester (**10e**)*

δ_H (400 MHz, $CDCl_3$) 7.80–7.90 (m, 4H, Naph); 7.48–7.53 (m, 3H, Naph); 6.33 (br s, 1H, NH); 6.21 (br s, 1H, =CH); 5.77 (br s, 1H, =CH); 4.12 (d, 5.6 Hz, 2H, CH_2); 3.73 (s, 3H, OCH_3). δ_C (100.6 MHz, $CDCl_3$) 170.2; 167.6; 144.3; 133.9; 133.3; 133.2; 128.4; 128.3; 127.7; 127.6; 126.6; 126.5; 125.6; 122.7; 52.3; 41.5. IR (KBr (cm^{-1})): 3374 (NH); 1751 (COO); 1644 (CON). MS *m*/*z* (rel.int. %): 269 (42), 210 (6), 196 (8), 181 (11), 153 (100), 152 (62), 127 (6). Anal. Calcd for $C_{16}H_{15}NO_3$ (269.30): C, 71.36; H, 5.61; N, 5.20; Found: C, 71.20; H, 5.80; N, 5.03; R_f (10% EtOAc/$CHCl_3$) 0.48; R_f (20% EtOAc/$CHCl_3$) 0.63; yellow solid, mp 147–148 °C.

*4.6.14. 2-(2-(2-Naphthyl)acryloylamino)propionic acid methyl ester (**10f**)*

δ_H (400 MHz, $CDCl_3$) 7.80–7.91 (m, 4H, Naph); 7.48–7.53 (m, 3H, Naph); 6.40 (br s, 1H, NH); 6.18 (br s, 1H, =CH); 5.76 (br s, 1H, =CH); 4.72 (quintet, 7.2 Hz, 1H, C*H*CH_3); 3.72 (s, 3H, OCH_3); 1.41 (d, 7.2 Hz, 3H, CHC*H*$_3$). δ_C (100.6 MHz, $CDCl_3$) 173.2; 167.0; 144.5; 134.0; 133.3; 133.2; 128.4; 128.3; 127.7; 127.5; 126.6; 126.5; 125.5; 122.3; 52.4; 48.4; 18.2. IR (KBr (cm^{-1})): 3302 (NH); 1744 (COO); 1655 (CON). MS *m*/*z* (rel.int. %): 283 (24), 224 (18), 181 (17), 153 (100), 152 (41), 127 (4). Anal. Calcd for $C_{17}H_{17}NO_3$ (283.33): C, 72.07; H, 6.05; N, 4.94; Found: C, 71.88; H, 6.22; N, 4.76; R_f (10% EtOAc/$CHCl_3$) 0.70; golden highly viscous material.

*4.6.15. 3-Methyl-2-(2-(2-naphthyl)acryloylamino)butyric acid methyl ester (**10g**)*

δ_H (400 MHz, $CDCl_3$) 7.80–7.93 (m, 4H, Naph); 7.49–7.54 (m, 3H, Naph); 6.22 (br s, 1H, NH); 6.19 (br s, 1H, =CH); 5.80 (br s, 1H, =CH); 4.70–4.77 (m, 1H, C*H*NH); 3.75 (s, 3H, OCH_3); 2.17–2.24 (m, 1H, C*H*$(CH_3)_2$); 0.98 (d, 6.8 Hz, 3H, CHC*H*$_3$); 0.85 (d, 6.8 Hz, 3H, CHC*H*$_3$). δ_C (100.6 MHz, $CDCl_3$) 172.2; 167.3; 144.6; 134.0; 133.3; 133.2; 128.4; 128.3; 127.7; 127.5; 126.6; 126.5; 125.5; 122.5; 57.5; 52.1; 31.3; 19.1; 17.8. IR (KBr (cm^{-1})): 3334 (NH); 1742 (COO); 1666 (CON). MS *m*/*z* (rel.int. %): 311 (11), 252 (20), 197 (26), 181 (4), 153 (100), 152 (42), 127 (4). Anal. Calcd for $C_{19}H_{21}NO_3$ (311.38): C, 73.29; H, 6.80; N, 4.50; Found: C, 73.10; H, 7.02; N, 4.35; R_f (10% EtOAc/$CHCl_3$) 0.77; R_f (1% EtOAc/$CHCl_3$) 0.54; dark yellow highly viscous material.

*4.6.16. 1-(2-(2-Naphthyl)acryloyl)pyrrolidine-2-carboxylic acid methyl ester (**10h**, two rotational isomers 80/20)*

δ_H (400 MHz, $CDCl_3$) 7.98 (s, 1H, Naph); 7.75–7.85 (m, 3H, Naph); 7.63 (d, 8.1 Hz, 1H, Naph); 7.40–7.46 (m, 2H, Naph); 5.86/5.80 (major/minor) (br s, 1H, =CH); 5.55/5.42 (major/minor) (br s, 1H, =CH); 4.60–4.67/4.23–4.28 (major/minor) (m, 1H, NCH); 3.80 (s, 3H, OCH_3); 3.34 (t, 7.4 Hz, 2H, NCH_2); 1.70–2.30 (m, 4H, $(CH_2)_2$). δ_C (100.6 MHz, $CDCl_3$) 172.6; 169.4; 145.6/145.5 (minor/major); 133.5; 133.3; 132.5; 128.6; 128.5; 127.6; 126.5; 126.4; 125.8; 123.3; 115.6/115.3 (minor/major); 60.4/58.5 (minor/major); 52.3/52.1 (major/minor); 48.6/46.1 (major/minor); 31.2/29.5 (minor/major); 24.9/22.6 (major/minor). IR (KBr (cm^{-1})): 1744 (COO); 1639 (CON). MS *m*/*z* (rel.int. %): 309 (19), 250 (22), 181 (11), 153 (100), 152 (38), 127 (6). Anal. Calcd for $C_{19}H_{19}NO_3$ (309.36): C, 73.77; H, 6.19; N, 4.53; Found: C, 73.60; H, 6.31; N, 4.28; R_f (10% EtOAc/$CHCl_3$) 0.45; R_f (20% EtOAc/$CHCl_3$) 0.65; dark yellow highly viscous material.

*4.6.17. 2-(1-Naphthyl)acryloic acid methyl ester (**11i**)*

δ_H (400 MHz, $CDCl_3$) 7.82–7.90 (m, 2H; Naph); 7.74 (d, 7.1 Hz, 1H, Naph); 7.45–7.51 (m, 3H, Naph); 7.37 (d, 7.0 Hz, 1H, Naph); 6.72 (br s, 1H, =CH); 5.89 (br s, 1H, =CH); 3.72 (s, 3H, OMe). δ_C (100.6 MHz, $CDCl_3$) 167.5; 140.7; 135.3; 133.4; 131.8; 129.9; 128.6; 128.3; 126.9; 126.2; 125.8; 125.2 (double intensity); 52.2. IR (KBr (cm^{-1})): 1721 (CON); 1629 (C=C). MS *m*/*z* (rel.int. %): 212 (23), 197 (3), 153 (100), 128 (6). Anal. Calcd for $C_{14}H_{12}O_2$ (212.25): C, 79.23; H, 5.70; Found: C, 79.05, H, 5.50. R_f ($CHCl_3$) 0.65; highly viscous yellow material.

*4.6.18. 2-(1-Naphthyl)acryloic acid isopropyl ester (**11j**)*

δ_H (400 MHz, $CDCl_3$) 7.72–7.86 (m, 3H, Naph); 7.45–7.50 (m, 3H, Naph); 7.35 (d, 7.0 Hz, 1H, Naph); 6.63 (br s, 1H, =CH); 5.86 (br s, 1H, =CH); 5.09 (heptet, 6.4 Hz, 1H, C*H*$(CH_3)_2$); 1.19 (d, 6.4 Hz, 6H, CH(C*H*$_3)_2$). δ_C (100.6 MHz, $CDCl_3$) 166.7; 141.8; 135.8; 133.6; 132.0; 129.2; 128.6; 128.5; 127.2; 126.2; 125.9; 125.6; 125.4; 68.8; 21.8. IR (KBr (cm^{-1})): 1714 (CON); 1627 (C=C). MS *m*/*z* (rel.int. %): 240 (13), 198 (10), 153 (100), 128 (3). Anal. Calcd for $C_{16}H_{16}O_2$ (240.30): C, 79.97; H, 6.71; Found: C, 79.81, H, 6.88. R_f ($CHCl_3$) 0.59; highly viscous yellow material.

*4.6.19. 2-(1-Naphthyl)acryloic acid benzyl ester (**11l**)*

δ_H (400 MHz, $CDCl_3$) 7.82–7.88 (m, 2H, Naph); 7.72 (d, 7.1 Hz, 1H, Naph); 7.18–7.50 (m, 9H, Naph+Ph); 6.73 (br s, 1H, =CH); 5.92 (br s, 1H, =CH); 5.21 (s, 2H, CH_2Ph). δ_C (100.6 MHz, $CDCl_3$) 167.0; 141.1; 136.1; 135.5; 133.6; 132.0; 130.2; 128.8; 128.6 (double intensity); 128.5; 128.3; 128.1 (double intensity); 127.2; 126.4; 126.0; 125.6; 125.5; 66.9. IR (KBr (cm^{-1})): 1720 (COO). MS *m*/*z* (rel.int. %): 288 (18), 197 (12), 153 (100), 128 (4), 91 (65). Anal. Calcd for $C_{20}H_{16}O_2$ (288.35): C, 83.31; H, 5.59; Found: C, 83.20, H, 5.71. R_f ($CHCl_3$) 0.74; highly viscous yellow material.

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