DIRECT PREPARATION OF *N*-(ALK-1-EN-1-YL)CARBAMATES FROM CYCLIC KETONES AND UNSUBSTITUTED CARBAMATES

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N-(Alk-1-en-1-yl)carbamates bearing an endocyclic carbon-carbon double bond have been prepared by the reaction of unsubstituted carbamates with tetrahydronaphthalen-2-one and chroman-2-one derivatives in the presence of a catalytic amount of 4-methylbenzene-1-sulfonic acid.

Keywords: *N*-(Alk-1-en-1-yl)carbamates; Cyclic ketones; Chromenes; Dihydronaphthalenes; Amines; Acid catalysis; Enantioselective hydrogenation.

N-(Alk-1-en-1-yl)carbamates are a class of compounds with potential in organic synthesis. They can easily be acylated *via* Friedel–Crafts and Vilsmeier reactions, they produce β-amino alcohol derivatives *via* hydroboration[1], and they have recently been involved in the modification of *N*-protected dehydroamino acids *via* oxidation of their C=C double bonds[2,3] to produce functionalized α-amino acid derivatives. Their activated double bond has been used to perform [2+2] cycloaddition with heteroallenes, namely dichloroketene, to give modified proline compounds[4], and to react with chromium alkoxycarbenes to produce optically active spiroketals[5]. The stereoselective palladium-catalyzed Heck-type reaction of endocyclic *N*-(alk-1-en-1-yl)carbamates with diazonium tetrafluoroborate has been used as a key step in the synthesis of pyrrolidine alkaloids[6].

The double bond of dehydro-*N*-carbamoyl-α-amino acids[7], and dehydro-*N*-carbamoyl-β-amino alcohols, acetates and oximes[8], all of them bifunctional compounds containing two potential chelating groups, has been enantioselectively hydrogenated in the presence of rhodium catalysts to afford optically active acyclic α-amino acid[7], and β-amino alcohol and 1,2-diamine[8] derivatives. The enantioselective hydrogenation of the C=C

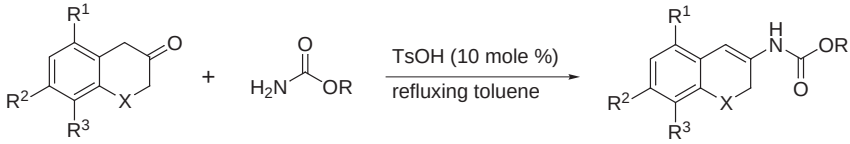
bond of a cyclic *N*-(alk-1-en-1-yl)carbamate was also performed in the presence of a ruthenium(binap) precursor to generate optically active pyrrolidine derivatives with moderate enantioselectivity[9]. We have also shown that 4-methylene-*N*-acyloxazolidinones, which are members of the cyclic *N*-(alk-1-en-1-yl)carbamate family with the nitrogen atom in the ring, were hydrogenated in the presence of ruthenium complexes with very high enantioselectivity[10] providing a straightforward access to both *R*- and *S*-enantiomers of the very useful acyloxazolidinone chiral auxiliaries[11]. More recently, cyclic *N*-(alk-1-en-1-yl)carbamates bearing an endocyclic C=C bond were also enantioselectively hydrogenated using ruthenium catalysis in a three-step conversion of cyclic ketones into optically active amines[12].

The preparation of *N*-(alk-1-en-1-yl)carbamates was initially based on acylation of enamines or imines with chloroformates in the presence of a base[4a,13]. The dehydration of cyclic *N*-(1-hydroxyalkyl)carbamates promoted by trifluoroacetic anhydride/2,6-lutidine[4a,6,14], and the sodium perrhenate-catalyzed reaction of α-azido ketones with chloroformate[15] afford cyclic carbamates bearing an endocyclic carbon–carbon double bond. Cyclic and acyclic *N*-(alk-1-en-1-yl)carbamates have been obtained by elimination of methanol from *N*-(1-methoxyalkyl)carbamates in the presence of ammonium chloride as acid catalyst[1]. *N*-(1-Alkoxycarbonyl-1-en-1-yl)carbamates have been obtained in good yields from α-ketoesters by the acid-catalyzed reaction of primary carbamates in the presence of $POCl_3$ (ref.[16]), TsOH (refs[7b,17]) or HCl (ref.[7c]).

Following our objective to transform cyclic ketones into optically active amines[12,18], we were interested in simple preparations of *N*-(alk-1-en-1-yl)carbamates. We report here a straightforward acid-catalyzed synthesis of new *N*-(alk-1-en-1-yl)carbamates by direct condensation of unsubstituted carbamates with the unactivated cyclic ketones **1**, **2** and **3** according to Scheme 1.

RESULTS AND DISCUSSION

As mentioned in the introduction, the acid-catalyzed condensation of unsubstituted carbamates with activated ketones, such as α-ketoesters has been known, but the reaction with unactivated cyclic ketones has not yet been reported. Due to the necessity of the presence of an acid catalyst in this reaction and with the goal of an easy removal of the catalyst, we first tested the activity of the acid ion-exchange resin Amberlyst 15, which was used in the formation of enamides from primary amide and cyclic ke-



4-18

	X	R^1	R^2	R^3
1	CH_2	H	H	H
2	CH_2	H	CH_3	CH_2CH_2COOH
3	O	OCH_3	H	H

SCHEME 1

TABLE I
Preparation of *N*-(alk-1-en-1-yl)carbamates **4**–**18**[a]

X	R^1	R^2	R^3	R	Carbamate	Yield, %
CH_2	H	H	H	Et	**4**	90
				Me	**5**	93[b]
				Bu	**6**	78
				i-Bu	**7**	85
				t-Bu	**8**	55
				Ph	**9**	50
				$PhCH_2$	**10**	60
				CCl_3CH_2	**11**	68
CH_2	H	Me	$CH_2CH_2CO_2H$	Et	**12**	66
				t-Bu	**13**	60
				$PhCH_2$	**14**	60
O	OMe	H	H	Et	**15**	50
				t-Bu	**16**	65
				$PhCH_2$	**17**	50
				CH_2=$CHCH_2$	**18**	64

[a] General conditions: ketone (10 mmol), carbamate (25 mmol), TsOH (1 mmol), refluxing toluene, Dean–Stark apparatus, inert atmosphere, 20 h. [b] Carbamate (50 mmol).

tones[19], but without success. The activation with a Lewis acid such as $BF_3 \cdot Et_2O$ also proved to be inefficient. Finally, an efficient direct preparation was achieved when 4-methylbenzene-1-sulfonic acid was used in refluxing toluene.

Thus, when 10 mmol of 1,2,3,4-tetrahydronaphthalen-2-one **1** and 25 mmol of ethyl carbamate were heated for 20 h under inert atmosphere in the presence of 1 mmol of TsOH in refluxing toluene in a Dean–Stark apparatus, the corresponding *N*-(alk-1-en-1-yl)carbamate **4** was isolated in 90% yield after chromatography over silica gel.

Under similar conditions, the *N*-(alk-1-en-1-yl)carbamates **5**–**11** were prepared in good yields from primary alkyl and aryl carbamates (Table I). It was important to perform the reaction under an inert atmosphere of nitrogen and to continuously remove water from the reaction mixture. In the case of methyl carbamate, 5 equivalents were used because of its sublimation inside the apparatus. The condensation reaction was also performed in satisfactory yields with the related tetralone **2**, which contains a carboxylic group as substituent of the aromatic ring, and the *N*-(alk-1-en-1-yl)carbamates **12**–**14** were isolated in 66, 60 and 60% yield, respectively (Table I). The generality of the reaction was shown by the synthesis of the *N*-(alk-1-en-1-yl)carbamates **15**–**18** from the chroman-2-one derivative **3** (Table I).

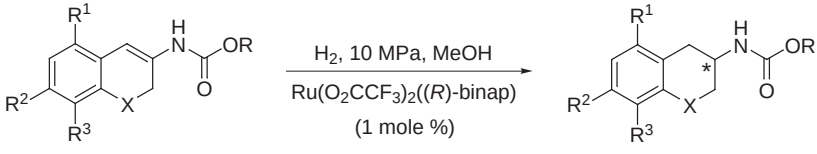
It is noteworthy that only the *N*-(alk-1-en-1-yl)carbamates with the carbon–carbon double bond conjugated with the aromatic ring were formed.

These *N*-(alk-1-en-1-yl)carbamates could be isolated as colorless oils or white solids, but they were very air and moisture-sensitive and had to be kept at 6 °C in a refrigerator, or used as soon as they were produced. They showed a ^{1}H NMR signal for the vinylic proton in the range 6.5–6.8 ppm. The characteristic HC=C–NH–CO_2 structure led to three signals in the ^{13}C spectra at 100–110 (HC=), 127–133 (C–N) and 151–154 (C=O) ppm.

The carbamates were tested in enantioselective hydrogenation with the goal of producing optically active amines. The well-known $Ru(O_2CCF_3)_2$-((*R*)-binap) complex was inactive in the hydrogenation of the *N*-(alk-1-en-1-yl)carbamates **4**–**10** derived from 2-tetralin. On the other hand, the *N*-(alk-1-en-1-yl)carbamates **15**–**18** were hydrogenated in methanol at 60 °C under 10 MPa of hydrogen in the presence of 1 mole % of $Ru(O_2CCF_3)_2$-((*R*)-binap) as catalyst precursor (Scheme 2), but the enantiomeric excesses were not satisfactory (<25%). The best results were obtained with the *N*-(alk-1-en-1-yl)carbamates **12**–**14**, which under similar conditions gave the corresponding carbamates derived from 2-tetralin in 65–88% enantiomeric excesses[12] (Table II). The results show that the presence of

functional groups on the bicyclic structure makes the hydrogenation possible yielding in dependance on their nature and position, optically-enriched amine derivatives. As expected, the amine hydrochlorides were obtained by appropriate deprotection methods under mild conditions without racemization[12].

In conclusion, we have shown that the acid-catalyzed condensation of unsubstituted carbamates with cyclic ketones provides a straightforward and selective route to *N*-(alk-1-en-1-yl)carbamates. These compounds are suitable precursors for enantioselective hydrogenation affording optically active carbamates, which can easily be deprotected by well-known methods to produce optically active amines.



12-15 **19-22**

	X	R^1	R^2	R^3	R
15, 19	O	OCH_3	H	H	Et
12, 20	CH_2	H	CH_3	CH_2CH_2COOH	Et
13, 21	CH_2	H	CH_3	CH_2CH_2COOH	*t*-Bu
14, 22	CH_2	H	CH_3	CH_2CH_2COOH	$PhCH_2$

SCHEME 2

TABLE II
Enantioselective hydrogenation of *N*-(alk-1-en-1-yl)carbamates **12**–**15**[a]

Enecarbamate	Reaction time, h	Carbamate	Yield[b], %	e.e., %
12	20	**20**	80	75
13	48	**21**	94	65
14	60	**22**	95	88
15	20	**19**	90	22

[a] General conditions: carbamate (1 mmol), H_2 (10 MPa), MeOH (10 ml), catalyst $Ru(O_2CCF_3)_2$((*R*)-binap) (0.01 mmol), 50 °C. [b] Isolated yield.

EXPERIMENTAL

Preparation of *N*-(Alk-1-en-1-yl)carbamates

Into a 250 ml flask equipped with a Dean–Stark apparatus, 10 mmol of ketone, 25 mmol of a carbamate and 1 mmol (192 mg) of 4-methylbenzene-1-sulfonic acid monohydrate were introduced under an inert atmosphere of nitrogen. Toluene (60 ml) was then added and the mixture was refluxed for 20 h. After cooling, 40 ml of toluene was added and the organic phase was washed three times with 100 ml of water. The organic phase was then evaporated to dryness and the *N*-(alk-1-en-1-yl)carbamates were purified by flash chromatography on silica gel with a diethyl ether–pentane mixture as eluent (4 : 1 for **4**–**11**, 2 : 1 for **12**–**18**). The isolated *N*-(alk-1-en-1-yl)carbamates were very air-sensitive and stored under nitrogen at 6 °C.

Ethyl N-(3,4-dihydro-2-naphthyl)carbamate (**4**). Colorless oil, yield 90%. ^{1}H NMR (200.130 MHz, $CDCl_3$): 1.27 (t, J = 7.1, 3 H, CH_3); 2.40 (t, J = 8.2, 2 H, ring CH_2); 2.86 (t, J = 8.2, 2 H, ring CH_2); 4.17 (q, J = 7.1, 2 H, OCH_2); 6.02 (broad s, 1 H, NH); 6.76 (s, 1 H, CH=); 6.90–7.15 (m, 4 H arom.). ^{13}C NMR {^{1}H} (50.323 MHz, $CDCl_3$): 14.63 (CH_3), 27.42 (ring CH_2), 28.06 (ring CH_2), 52.4 (OCH_2), 108.67 (CH=), 125.44 (CH arom.), 125.76 (CH arom.), 126.74 (CH arom.), 127.05 (CH arom.), 132.44 (C quat. =CN), 135.04 (C quat. arom.), 135.31 (C quat. arom.), 153.46 (CO carbamate). HRMS: calculated for $C_{13}H_{15}NO_2$ $[M]^+$ 217.11028, found 217.1119.

Methyl N-(3,4-dihydro-2-naphthyl)carbamate (**5**). Colorless oil, yield 93%. ^{1}H NMR (200.130 MHz, $CDCl_3$): 2.40 (t, J = 8.1, 2 H, ring CH_2); 2.86 (t, J = 8.1, 2 H, ring CH_2); 3.72 (s, 3 H, OCH_3); 6.03 (broad s, 1 H, NH); 6.76 (s, 1 H, CH=); 6.90–7.20 (m, 4 H arom.). ^{13}C NMR {^{1}H} (50.323 MHz, $CDCl_3$): 27.39 (ring CH_2), 28.04 (ring CH_2), 61.3 (OCH_3), 108.82 (CH=), 125.52 (CH arom.), 125.79 (CH arom.), 126.75 (CH arom.), 127.06 (CH arom.), 132.44 (C quat. =CN), 134.94 (C quat. arom.), 135.13 (C quat. arom.), 153.85 (CO carbamate). HRMS: calculated for $C_{12}H_{13}NO_2$ $[M]^+$ 203.09463, found 203.0940.

Butyl N-(3,4-dihydro-2-naphthyl)carbamate (**6**). Colorless oil, yield 78%. ^{1}H NMR (200.130 MHz, $CDCl_3$): 0.93 (t, J = 7.3, 3 H, CH_3); 1.20–1.50 (m, 2 H, CH_2); 1.50–1.80 (m, 2 H, CH_2); 2.40 (t, J = 8.2, 2 H, ring CH_2); 2.86 (t, J = 8.2, 2 H, ring CH_2); 4.12 (q, J = 7.3, 2 H, OCH_2); 6.05 (broad s, 1 H, NH); 6.77 (s, 1 H, CH=); 6.90–7.15 (m, 4 H arom.). HRMS: calculated for $C_{15}H_{19}NO_2$ $[M]^+$ 245.14158, found 245.1409.

Isobutyl N-(3,4-dihydro-2-naphthyl)carbamate (**7**). Colorless oil, yield 85%. ^{1}H NMR (200.130 MHz, $CDCl_3$): 0.94 (d, J = 6.8, 6 H, 2 CH_3); 1.94 (hept, J = 6.8, 1 H, CH); 2.41 (t, J = 8.2, 2 H, ring CH_2); 2.86 (t, J = 8.2, 2 H, ring CH_2); 3.90 (d, J = 6.8, 2 H, OCH_2); 6.05 (broad s, 1 H, NH); 6.76 (s, 1 H, CH=); 7.25–7.40 (m, 4 H arom.). ^{13}C NMR {^{1}H} (50.323 MHz, $CDCl_3$): 19.12 (2 CH_3), 27.58 (ring CH_2), 27.98 (CH), 28.00 (ring CH_2), 71.44 (OCH_2), 108.63 (CH=), 125.43 (CH arom.), 125.77 (CH arom.), 126.72 (CH arom.), 126.99 (CH arom.), 132.35 (C quat. =CN), 134.93 (C quat. arom.), 135.00 (C quat. arom.), 153.35 (CO carbamate). HRMS: calculated for $C_{15}H_{19}NO_2$ $[M]^+$ 245.14158, found 245.1409.

tert-Butyl N-(3,4-dihydro-2-naphthyl)carbamate (**8**). Colorless oil, yield 55%. ^{1}H NMR (200.130 MHz, $CDCl_3$): 1.48 (s, 9 H, *t*-Bu); 2.36 (t, J = 8.2, 2 H, ring CH_2); 2.85 (t, J = 8.2, 2 H, ring CH_2); 5.87 (broad s, 1 H, NH); 6.76 (s, 1 H, CH=); 6.90–7.20 (m, 4 H arom.). HRMS: calculated for $C_{15}H_{19}NO_2$ $[M]^+$ 245.14158, found 245.1409.

Phenyl N-(3,4-dihydro-2-naphthyl)carbamate (**9**). White solid, yield 50%. ^{1}H NMR (200.130 MHz, $CDCl_3$): 2.49 (t, J = 8.2, 2 H, ring CH_2); 2.91 (t, J = 8.2, 2 H, ring CH_2); 6.36

(broad s, 1 H, NH); 6.82 (s, 1 H, CH=); 6.90–7.30 (m, 7 H arom.); 7.30–7.50 (m, 2 H arom.). ^{13}C NMR {^{1}H} (50.323 MHz, $CDCl_3$): 27.19 (ring CH_2), 28.04 (ring CH_2), 109.95 (CH=), 121.78 (2 × CH arom.), 125.84 (CH arom.), 125.86 (CH arom.), 126.03 (CH arom.), 126.84 (CH arom.), 127.15 (CH arom.), 129.54 (2 × CH arom.), 132.58 (C quat. =CN), 134.70 (2 × C quat. arom.), 150.62 (C quat. arom.), 151.48 (CO carbamate). For $C_{17}H_{15}NO_2$ (265.3) calculated: 76.96% C, 5.70% H, 5.28% N; found: 76.85% C, 5.81% H, 5.35% N.

Benzyl N-(3,4-dihydro-2-naphthyl)carbamate (**10**). Colorless oil, yield 60%. ^{1}H NMR (200.130 MHz, $CDCl_3$): 2.39 (t, *J* = 8.2, 2 H, ring CH_2); 2.86 (t, *J* = 8.2, 2 H, ring CH_2); 5.15 (s, 2 H, OCH_2); 6.08 (broad s, 1 H, NH); 6.79 (s, 1 H, CH=); 6.90–7.15 (m, 4 H arom.); 7.25–7.40 (m, 5 H arom.). ^{13}C NMR {^{1}H} (50.323 MHz, $CDCl_3$): 27.49 (ring CH_2), 28.01 (ring CH_2), 67.09 (OCH_2), 108.95 (CH=), 125.55 (CH arom.), 125.84 (CH arom.), 126.76 (CH arom.), 127.04 (CH arom.), 128.43 (2 × CH arom.), 128.48 (CH arom.), 128.72 (2 × CH arom.), 132.40 (C quat. =CN), 134.85 (2 × C quat. arom.), 136.05 (C quat. arom.), 152.94 (CO carbamate). HRMS: calculated for $C_{18}H_{17}NO_2$ $[M]^+$ 279.12593, found 279.1262.

2,2,2-Trichloroethyl N-(3,4-dihydro-2-naphthyl))carbamate (**11**). Colorless oil, yield 68%. ^{1}H NMR (200.130 MHz, $CDCl_3$): 2.46 (t, *J* = 8.2, 2 H, ring CH_2); 2.89 (t, *J* = 8.2, 2 H, ring CH_2); 4.77 (s, 2 H, OCH_2); 6.31 (broad s, 1 H, NH); 6.79 (s, 1 H, CH=); 6.90–7.15 (m, 4 H arom.). ^{13}C NMR {^{1}H} (50.323 MHz, $CDCl_3$): 27.21 (ring CH_2), 27.98 (ring CH_2), 74.57 (OCH_2), 95.36 (C quat. CCl_3), 110.33 (CH=), 125.99 (CH arom.), 126.04 (CH arom.), 126.85 (CH arom.), 127.17 (CH arom.), 132.54 (C quat. =CN), 134.32 (C quat. arom.), 134.44 (C quat. arom.), 151.21 (CO carbamate). HRMS: calculated for $C_{13}H_{12}NO_2Cl_3$ $[M]^+$ 318.99336, found 318.9946.

3-[6-(Ethoxycarbonamido)-2-methyl-7,8-dihydro-1-naphthyl]propanoic acid (**12**). White solid, yield 66%. ^{1}H NMR (200.130 MHz, $CDCl_3$): 1.27 (t, *J* = 7.1, 3 H, CH_3 carbamate); 2.29 (s, 3 H, CH_3); 2.30–2.60 (m, 4 H, ring CH_2 + CH_2); 2.80–3.10 (m, 4 H, ring CH_2 + CH_2); 4.17 (q, *J* = 7.1, 2 H, OCH_2); 6.13 (broad s, 1 H, NH); 6.69 (s, 1 H, CH=); 6.81 (d, *J* = 7.7, 1 H arom.); 6.93 (d, *J* = 7.7, 1 H arom.). ^{13}C NMR {^{1}H} (50.323 MHz, $CDCl_3$): 14.61 (CH_3 carbamate), 19.91 (CH_3), 24.45 (2 × CH_2), 27.41 (ring CH_2), 33.73 (ring CH_2), 61.52 (OCH_2), 109.40 (CH=), 124.55 (CH arom.), 128.56 (CH arom.), 130.51 (C quat. =CN), 133.26 (C quat. arom.), 133.79 (C quat. arom.), 133.98 (C quat. arom.), 135.16 (C quat. arom.), 153.76 (CO carbamate), 179.01 (COOH). For $C_{17}H_{21}NO_4$ (303.4) calculated: 67.31% C, 6.98% H, 4.62% N; found: 67.21% C, 6.89% H, 4.70% N.

3-[6-(tert-Butoxycarbonamido)-2-methyl-7,8-dihydro-1-naphthyl]propanoic acid (**13**). White solid, yield 60%. ^{1}H NMR (200.130 MHz, $CDCl_3$): 1.48 (s, 9 H, *t*-Bu); 2.28 (s, 3 H, CH_3); 2.32–2.47 (m, 4 H, ring CH_2 + CH_2); 2.81–3.05 (m, 4 H, ring CH_2 + CH_2); 6.17 (broad s, 1 H, NH); 6.68 (s, 1 H, CH=); 6.78 (d, *J* = 8.0, 1 H arom.); 6.91 (d, *J* = 8.0, 1 H arom.). For $C_{19}H_{25}NO_4$ (331.4) calculated: 68.86 % C, 7.60% H, 4.23 % N; found: 69.05% C, 7.65% H, 4.15% N.

3-[6-(Benzyloxycarbonamido)-2-methyl-7,8-dihydro-1-naphthyl]propanoic acid (**14**). White solid, yield 60%. ^{1}H NMR (200.130 MHz, $CDCl_3$): 2.29 (s, 3 H, CH_3); 2.34–2.50 (m, 4 H, ring CH_2 + CH_2); 2.80–3.05 (m, 4 H, ring CH_2 + CH_2); 5.15 (s, 2 H, OCH_2); 6.26 (broad s, 1 H, NH); 6.71 (s, 1 H, CH=); 6.81 (d, *J* = 7.7, 1 H arom.); 6.94 (d, *J* = 7.7, 1 H arom.); 7.36 (broad s, 5 H arom.). ^{13}C NMR {^{1}H} (50.323 MHz, $CDCl_3$): 19.91 (CH_3), 24.42 (2 × CH_2), 27.41 (ring CH_2), 33.68 (ring CH_2), 67.22 (OCH_2), 109.53 (CH=), 124.60 (CH arom.), 128.40 (2 × CH arom.), 128.48 (CH arom.), 128.60 (CH arom.), 128.71 (2 × CH arom.), 130.50 (C quat. =CN), 133.16 (C quat. arom.), 133.74 (C quat. arom.), 133.89 (C quat. arom.), 135.15 (C quat. arom.), 135.99 (C quat. arom.), 153.24 (CO carbamate), 178.98 (COOH). For

$C_{22}H_{23}NO_4$ (365.4) calculated: 72.31% C, 6.34% H, 3.83% N; found: 72.05% C, 6.25% H, 3.85% N.

Ethyl N-(5-methoxychromen-3-yl)carbamate (**15**). White solid, yield 50%. ^{1}H NMR (200.130 MHz, $CDCl_3$): 1.26 (t, *J* = 7.1, 3 H, CH_3); 3.78 (s, 3 H, OCH_3); 4.15 (q, *J* = 7.1, 2 H, OCH_2 carbamate); 4.83 (s, 2 H, ring CH_2); 6.25 (broad s, 1 H, NH); 6.43 (d, *J* = 8.2, 1 H arom.); 6.46 (d, *J* = 8.2, 1 H arom.); 6.54 (s, 1 H, CH=); 6.96 (t, *J* = 8.2, 1 H arom.). For $C_{13}H_{15}NO_4$ (249.3) calculated: 62.64% C, 6.07% H, 5.62% N; found: 62.80% C, 6.12% H, 5.78% N.

tert-Butyl N-(5-methoxychromen-3-yl)carbamate (**16**). White solid, yield 65%. ^{1}H NMR (200.130 MHz, $CDCl_3$): 1.46 (s, 9 H, *t*-Bu); 3.78 (s, 3 H, OCH_3); 4.78 (s, 2 H, OCH_2); 6.03 (broad s, 1 H, NH); 6.43 (d, *J* = 8.2, 1 H arom.); 6.45 (d, *J* = 8.2, 1 H arom.); 6.54 (s, 1 H, CH=); 6.95 (t, *J* = 8.2, 1 H arom.). ^{13}C NMR {^{1}H} (50.323 MHz, $CDCl_3$): 28.28 (3 × CH_3, *t*-Bu), 55.67 (OCH_3), 65.36 (OCH_2), 81.10 (C quat. *t*-Bu), 100.10 (CH=), 104.05 (CH arom.), 108.46 (CH arom.), 112.44 (C quat. arom.), 126.96 (CH arom.), 128.31 (C quat. =CN), 152.42 (C quat. arom.), 152.69 (CO carbamate), 154.86 (C quat. arom.). HRMS: calculated for $C_{15}H_{19}NO_4$ $[M]^+$ 277.13141, found 277.1303.

Benzyl N-(5-methoxychromen-3-yl)carbamate (**17**). White solid, yield 50%. ^{1}H NMR (200.130 MHz, $CDCl_3$): 3.78 (s, 3 H, OCH_3); 4.83 (s, 2 H, ring CH_2); 5.13 (s, 2 H, OCH_2 carbamate); 6.26 (broad s, 1 H, NH); 6.43 (d, *J* = 8.2, 1 H arom.); 6.46 (d, *J* = 8.2, 1 H arom.); 6.56 (s, 1 H, CH=); 6.97 (t, *J* = 8.2, 1 H arom.); 7.35 (broad s, 5 H arom.). ^{13}C NMR {^{1}H} (50.323 MHz, $CDCl_3$): 55.69 (OCH_3), 65.18 (OCH_2), 67.29 (OCH_2), 100.86 (CH=), 104.19 (CH arom.), 108.62 (CH arom.), 112.50 (C quat. arom.), 127.23 (CH arom.), 127.91 (C quat. =CN), 128.25 (CH arom.), 128.40 (2 × CH arom.), 128.71 (2 × CH arom.), 136.06 (C quat. arom.), 152.59 (C quat. arom.), 153.63 (CO carbamate), 155.04 (C quat. arom.). For $C_{15}H_{19}NO_4$ (277.3) calculated: 64.97% C, 6.91% H, 5.05% N; found 65.11% C, 6.82% H, 4.98% N.

Allyl N-(5-methoxychromen-3-yl)carbamate (**18**). White solid, yield 64%. ^{1}H NMR (200.130 MHz, $CDCl_3$): 3.78 (s, 3 H, OCH_3); 4.59 (dt, *J* = 6.1 and 1.4, 2 H, allyl OCH_2); 4.83 (s, 2 H, OCH_2); 5.20–5.36 (m, 2 H, $=CH_2$); 5.60–5.80 (m, 1 H, allyl CH=); 6.25 (broad s, 1 H, NH); 6.43 (d, *J* = 8.2, 1 H arom.); 6.45 (d, *J* = 8.2, 1 H arom.); 6.55 (s, 1 H, CH=); 6.97 (t, *J* = 8.2, 1 H arom.). For $C_{14}H_{15}NO_4$ (261.3) calculated: 64.36% C, 5.79% H, 5.36% N; found: 64.51% C, 5.65% H, 5.22% N.

Procedure for Enantioselective Hydrogenation

In a 125 ml stainless steel autoclave were introduced under inert atmosphere 1 mmol of *N*-(alk-1-en-1-yl)carbamate, 0.01 mmol of $Ru(O_2CCF_3)_2$((*R*)-binap) and 10 ml of methanol. The autoclave was then flushed three times with hydrogen and pressurized to 10 MPa. After reaction, the crude mixture was evaporated and the conversion was determined by ^{1}H NMR. After removal of the organometallic residues, by filtration on silica gel, the enantiomeric excess was measured by HPLC with a chiral column (Chiralcel OD 25 cm) with a hexane–isopropanol (85 : 15) mixture as eluent.

Ethyl N-(5-methoxychromen-3-yl)carbamate (**19**). White solid, yield 90%. ^{1}H NMR (200.130 MHz, $CDCl_3$): 1.25 (t, *J* = 7.1, 3 H, CH_3); 2.66 (d, *J* = 17.4, 1 H, ring CH_2); 2.85 (dd, *J* = 17.4 and 5.6, 1 H, CH_2) ; 3.78 (s, 3 H, OCH_3); 4.02–4.25 (m, 5 H, ring OCH_2 + $OC\mathbf{H}_2Me$); 4.81 (broad s, 1 H, NH); 6.42 (d, *J* = 8.3, 1 H arom.); 6.47 (d, *J* = 8.3, 1 H arom.); 7.07 (t, *J* =

8.3, 1 H arom.). For $C_{13}H_{17}NO_4$ (251.3) calculated: 62.14% C, 6.82% H, 5.57% N; found: 62.00% C, 6.75% H, 5.68% N.

3-[6-(Ethoxycarbonamido)-2-methyl-5,6,7,8-tetrahydro-1-naphthyl]propanoic acid (**20**). White solid, yield 80%. ^{1}H NMR (200.130 MHz, $CDCl_3$): 1.22 (t, *J* = 7.1, 3 H, CH_3); 1.65–1.90 (m, 1 H, ring CH_2); 195–2.20 (m, 1 H, ring CH_2); 2.29 (s, 3 H, CH_3); 2.35–2.52 (m, 2 H, CH_2); 2.66 (dd, *J* = 16.0 and 8.1, 1 H, ring CH_2); 2.72–3.00 (m, 4 H, ring CH_2 + CH_2); 3.07 (dd, *J* = 16 and 4.8, 1 H, ring CH_2); 3.76–4.02 (m, 1 H, CHN); 4.10 (q, *J* = 7.1, OCH_2); 4.66 (broad s, 1 H, NH); 6.83 (d, *J* = 8.0, 1 H arom.); 6.94 (d, *J* = 8.0, 1 H arom.). ^{13}C NMR {^{1}H} (50.323 MHz, $CDCl_3$): 14.67 (CH_3), 19.54 (CH_3), 24.42 (2 × CH_2), 29.24 (ring CH_2), 33.13 (ring CH_2), 36.49 (ring CH_2), 46.20 (CHN), 60.80 (OCH_2), 127.89 (CH arom.), 136.73 (C quat. arom.), 156.31 (CO carbamate), 178.30 (COOH). For $C_{17}H_{23}NO_4$ (305.4) calculated: 66.86% C, 7.59% H, 4.59% N; found: 66.65% C, 7.65% H, 4.48% N.

3-[6-(tert-Butoxycarbonamido)-2-methyl-5,6,7,8-tetrahydro-1-naphthyl]propanoic acid (**21**). White solid, yield 94%. ^{1}H NMR (200.130 MHz, $CDCl_3$): 1.42 (s, 9 H, *t*-Bu); 1.70–1.90 (m, 1 H, ring CH_2); 198–2.15 (m, 1 H, ring CH_2); 2.29 (s, 3 H, CH_3); 2.38–2.50 (m, 2 H, CH_2); 2.64 (dd, *J* = 16.0 and 7.8, 1 H, ring CH_2); 2.75–3.00 (m, 4 H, ring CH_2 + CH_2); 3.07 (dd, *J* = 16.0 and 4.8, 1 H, ring CH_2); 3.80–4.05 (m, 1 H, CHN); 4.70 (broad s, 1 H, NH); 6.83 (d, *J* = 8.0, 1 H arom.); 6.94 (d, *J* = 8.0, 1 H arom.). For $C_{19}H_{27}NO_4$ (333.4) calculated: 68.44% C, 8.16% H, 4.20% N; found: 68.40% C, 8.25% H, 4.17% N.

3-[6-(Benzyloxycarbonamido)-2-methyl-5,6,7,8-tetrahydro-1-naphthyl]propanoic acid (**22**). White solid, yield 95%. ^{1}H NMR (200.130 MHz, $CDCl_3$): 1.72–1.87 (m, 1 H, ring CH_2); 2.01–2.13 (m, 1 H, ring CH_2); 2.28 (s, 3 H, CH_3); 2.40–2.49 (m, 2 H, CH_2); 2.63 (dd, *J* = 16.1 and 7.7, 1 H, ring CH_2); 2.77–2.99 (m, 4 H, ring CH_2 + CH_2); 3.07 (dd, *J* = 16.1 and 4.9, 1 H, ring CH_2); 3.90–4.10 (m, 1 H, CHN); 4.79 (broad s, 1 H, NH); 5.09 (s, 2 H, OCH_2); 6.83 (d, *J* = 8.0, 1 H arom.); 6.94 (d, *J* = 8.0, 1 H arom.); 7.33 (m, 5 H arom.). For $C_{22}H_{25}NO_4$ (367.4) calculated: 71.91% C, 6.86% H, 3.81% N; found: 72.04% C, 6.91% H, 3.77% N.

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