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Enantioselective synthesis of *N*-heterocycles via intramolecular Pd(0)-catalysed allylic amination

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ABSTRACT

An efficient and stereoselective synthesis of pyrrolidine-, piperidine-, and azepane-type *N*-heterocycles is described by the intramolecular Pd(0)-catalysed cyclisation of amino allylic carbonates. The use of chiral ligands gave the corresponding heterocyclic derivatives having er values that were from moderate to good.

1. Introduction

Nitrogen heterocycles are ubiquitous in natural products, pharmaceuticals, organic materials, and numerous functional molecules.[1] For these reasons the efficient stereoselective construction of these molecules, particularly in a catalytic enantioselective manner, has been of long-standing interest. Several powerful new transformations have been developed that involve the use of transition metal-catalysed *C*–*N* bond-forming reactions for the construction of heterocyclic rings. These transformations frequently occur under mild conditions, tolerate a broad array of functional groups and proceed with high stereoselectivity.

Recently, a variety of late transition metal complexes based on Pt[2] and Rh, in which the enantioselective hydroamination of unactivated alkenes with amines has been presented.[3] Futhermore, Ir,[4] Pd,[5] Au,[6] and Cu[7] based catalysts have been reported as catalysts for intramolecular hydroamination.

Intramolecular cyclisation of allenes with tethered amines in the presence of a transition metal catalyst represents a second route for generating nitrogen-containing heterocycles. These transformations have been developed with metal salts or complexes of Zr, Ti,[8] Cu,[9] lanthanides,[10] Pd,[11] Au,[12] Ag,[13] and Hg.[14]

The intramolecular enantioselective amination of allylic alcohols with amines or carbamates has also attracted attention as a route to functionalised nitrogen heterocycles, and methods employing catalysts based on Au,[15] Bi,[16] Pd,[17] Ru,[18] Hg, Sn, Ga, Bi, and Fe[16,19] have been reported.

The groups of Helmchen have reported enantioselective intramolecular amination of allylic acetates and carbonates catalysed by Ir complexes.[20] This method gave 2-vinylpyrrolidine and 2-vinylpiperidine derivatives in good yields and ee values of >90%.

By extending our previous work on the use of allyl carbonates in the synthesis of *O*- and *N*-heterocycles,[21] in this paper we report results on enantioselective intramolecular Pd(0)-catalysed allylic amination.

2. Results and discussion

2.1. Synthesis of the starting materials

The starting allylic carbonates **5a**–**i** were prepared according to Scheme 1.

The reduction of bromoesters **1a**–**c** to the corresponding aldehydes,[22] followed by elongation of the chain via the Wittig reaction[23] afforded unsaturated esters **2a**–**c** in 75, 72, and 70% yields, respectively. Compounds **3a**–**c** were obtained in 85, 98, and 76% yields, respectively, by the reduction of esters **2a**–**c** with DIBAL–H in diethyl ether.[24]

Condensation of these alcohols with methyl or isobutyl chloroformate at 0 °C afforded allylic carbonates **4a**–**e** in 82–96% yield. Finally, substitution of the bromine atom with a 4-methylbenzenesulfonamide group (tosyl group), benzyl group,

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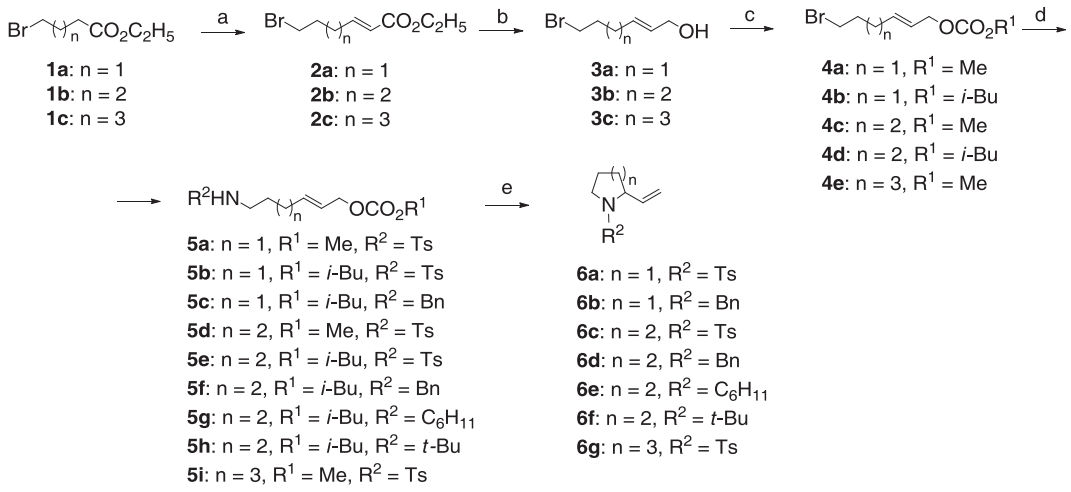

Scheme 1. Pd^0-catalysed synthesis of heterocycles **6a**–**g**. Reagents and conditions: (a) 1. DIBAL–H, CH_2Cl_2, −78 °C, 2. $Ph_3P{=}CHCO_2C_2H_5$, CH_2Cl_2, rt; (b) DIBAL–H, Et_2O, 0 °C; (c) R^1OCOCl, C_5H_5N, CH_2Cl_2, 0 °C→rt; (d) TsNHNa, $TsNH_2$, DMSO, 60 °C or R^2NH_2, *i*-Pr_2EtN, DMF, rt for R^2=Bn, C_6H_{11}, *t*-Bu; (e) $Pd_2(dba)_3$, ligand.

cyclohexyl or *tert*-butyl group gave corresponding amino-carbonates **5a**–**i** (45–85% yield).

2.2. Pd(0)-catalysed cyclisation of allylic carbonates 5a–i

The cyclisation was first studied with methyl carbonate **5a** as the substrate. The ring-closure of **5a** occurred readily in THF at room temperature in the presence of a catalytic amount of $Pd_2(dba)_3$ and PPh_3, which provided exclusively 1-tosyl-2-vinylpyrrolidine **6a**[21b] in 98% yield (Table 1, entry 1). Under the same conditions isobutyl carbonate **5b** quantitatively gave pyrrolidine **6a** (Table 1, entry 2). The cyclisation of *N*-benzyl carbonate **5c** occurred slowly at room temperature and provided 1-benzyl-2-vinylpyrrolidine **6b**[15b,20d,25] in 95% yield (Table 1, entry 3). Longer chain, methyl and isobutyl carbonates **5d** and **5e** were also submitted to this cyclisation procedure, 1-tosyl-2-vinylpiperidine **6c**[21b] was obtained in a very good yield after 30 min in both cases (97 and 98%, respectively, Table 1, entries 4 and 5). The reaction with *N*-benzyl carbonate **5f** required a longer reaction time (48 h) but gave an *N*-benzyl derivative of piperidine **6d**[15b,20d,25] in 98% yield (Table 1, entry 6). The cyclisation of compound **5g** at room temperature did not give the expected product **6e**. The same reaction at 60 °C afforded 1-cyclohexyl-2-vinylpiperidine **6e** in 56% yield after 20 h (Table 1, entries 7 and 8). The formation of *N*-*tert*-butyl-2-vinylpiperidine **6f** was never observed in the cyclisation of allylic carbonate **5h** (Table 1, entries 9 and 10). Finally, we studied the Pd(0)-catalysed cyclisation of allylic carbonate **5i**. Azepane **6g** was obtained in 70% yield after 24 h at 20 °C (Table 1, entry 11).

Table 1
Pd^0-catalysed allylic cyclisation of substrates **5a**–**i** according to Scheme 1[a]

Entry	Substrate	Product	*T* [°C]	Time [h]	Yield[b] [%]
1	**5a**	**6a**	20	0.5	98
2	**5b**	**6a**	20	0.5	99
3	**5c**	**6b**	20	24	95
4	**5d**	**6c**	20	0.5	97
5	**5e**	**6c**	20	0.5	98
6	**5f**	**6d**	20	48	99
7	**5g**	**6e**	20	24	0
8	**5g**	**6e**	60	24	56
9	**5h**	**6f**	20	48	0
10	**5h**	**6f**	60	48	0
11	**5i**	**6g**	20	24	70

[a] [**5**]/[$Pd_2(dba)_3$]/[PPh_3]=40:1:4.4, THF.
[b] Yield refers to isolated pure products after column chromatography.

2.3. Pd(0)-catalysed asymmetric cyclisation

Asymmetric cyclisation was performed only with *N*-tosyl and *N*-benzyl isobutyl carbonates **5b**, **5c**, **5e** and **5f**. The results presented in Table 1 and our previous studies[21b,c] have shown that using isobutyl carbonates as a starting material gave higher reactivities and selectivities in comparison with methyl carbonates. Several types of ligands were selected for testing.

Phosphines were the first class of ligands (Fig. 1) applied to the Pd(0)-catalysed allylic substitutions (Table 2, entries 1–10). Ring-closure of **5b** occurred slowly (48 h) at room temperature in the presence of (*S*)-Binap and provided 1-tosyl-2-vinylpyrrolidine **6a** as a 41:59 mixture of enantiomers in 97% overall yield (Table 2, entry 1). Longer chain isobutyl carbonate **5e** was less reactive under the same conditions and gave piperidine **6c** in 45% yield and in a 65:35 ratio (Table 2, entry 2). Carbonate **5b** in the presence of the Josiphos ligand, similar to the results observed for (*S*)-Binap, gave pyrrolidine **6a** in good yield (87%) and with an enantioselectivity ratio of 41:59 (Table 2, entry 3).

The same reaction at 60 °C afforded a 1:1 mixture of enantiomers (Table 2, entry 4). Isobutyl carbonate **5e** was less reactive and required a much longer reaction time (Table 2, entries 5–7). *N*-Tosyl piperidine **6c** was obtained in 10% yield after 48 h and 82% after 168 h as a 65:35 mixture, while at 60 °C **6c** was obtained in 92% yield after 72 h (53:47 er). The same reaction in the presence of the Walphos–phosphines ligand derived from ferrocene–afforded a 1:1 mixture of enantiomers (Table 2, entry 8). The trifluoromethyl derivative of Walphos was more reactive and gave a product of intramolecular allylic amination **6c** in a higher yield (81%) and was enantioselective (69:31). Asymmetric cyclisation of *N*-tosyl carbonate **5e** was also carried out in the presence of the phosphine-amine ligand PPM. This cyclisation gave piperidine **6c** in 64% yield and a very low er value of 53:47.

Phosphorus amidites were second class of ligands used for the construction of heterocyclic rings (Table 2, entries 11–16). The cyclisation of compounds **5b** at room temperature in the presence of L1(*S*,*S*,a*S*) gave pyrrolidine **6a** (99% yield) with good selectivity (22:78 er) (Table 2, entry 11). Piperidine **6c** was obtained in 99% yield under the same conditions with an er value of 90:10 starting from allyl carbonate **5e** (Table 2, entry 12). Lowering the temperature to 0 °C and −20 °C improved the selectivity of the reaction, and an er of 93:7 and 92:8, respectively (Table 2, entries 13 and 14). We also tried to cyclise **5e** in the presence of phosphorus amidite ligand L2(*R*,*R*,*R*), which is different from the L1(*S*,*S*,a*S*) of 2,5-

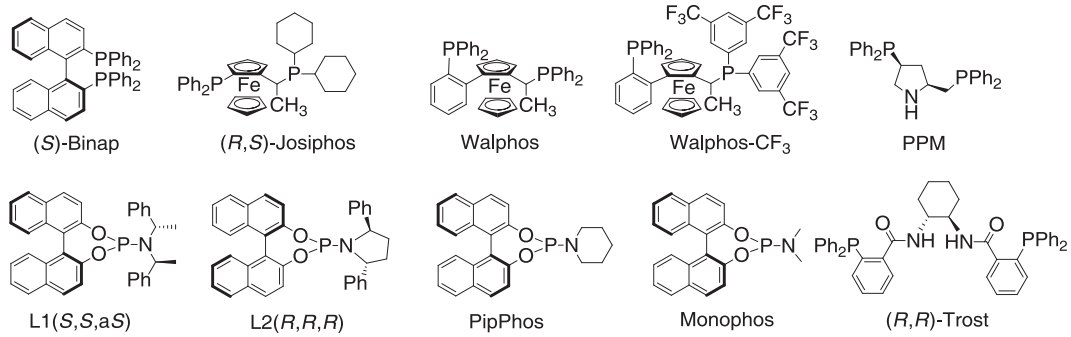

Fig. 1. Ligands used in this work.

Table 2
Pd^0-catalysed asymmetric allylic cyclisation of *N*-tosyl carbonates **5b** and **5e**[a]

Entry	Carbonate	Product	Ligand	*T* [°C]	Time [h]	Yield[b] [%]	er[c]
1	**5b**	**6a**	(*S*)-Binap	20	48	97	41:59
2	**5e**	**6c**	(*S*)-Binap	20	48	45	65:35
3	**5b**	**6a**	(*R*,*S*)-Josiphos	20	48	87	41:59
4	**5b**	**6a**	(*R*,*S*)-Josiphos	60	48	96	50:50
5	**5e**	**6c**	(*R*,*S*)-Josiphos	20	48	10	66:34
6	**5e**	**6c**	(*R*,*S*)-Josiphos	20	168	82	65:35
7	**5e**	**6c**	(*R*,*S*)-Josiphos	60	72	92	53:47
8	**5e**	**6c**	Walphos	20	24	56	50:50
9	**5e**	**6c**	Walphos−CF_3	20	48	81	69:31
10	**5e**	**6c**	PPM	20	24	64	53:47
11	**5b**	**6a**	L1(*S*,*S*,a*S*)	20	24	99	22:78
12	**5e**	**6c**	L1(*S*,*S*,a*S*)	20	24	99	90:10
13	**5e**	**6c**	L1(*S*,*S*,a*S*)	0	24	99	93:7
14	**5e**	**6c**	L1(*S*,*S*,a*S*)	−20	24	99	92:8
15	**5e**	**6c**	L2(*R*,*R*,*R*)	20	48	0	—
16	**5e**	**6c**	PipPhos	20	24	38	58:42
17	**5b**	**6a**	(*R*,*R*)-Trost	20	24	98	40:60
18	**5e**	**6c**	(*R*,*R*)-Trost	20	24	99	61:39
19	**5e**	**6c**	(*R*,*R*)-Trost	0	24	0	—

[a] [**5**]/[$Pd_2(dba)_3$]/[ligand]=40:1:2.2 (4.4), THF; (*S*)-Binap: (*S*)-(−)-(1,1′-binaphthalene-2,2′-diyl)bis(diphenylphosphine), (*R*,*S*)-Josiphos: (*R*)-1-{(*S*)-2-diphenylphosphanyl]ferrocenyl}ethyldicyclohexylphosphane, Walphos: (*R*)-1-{(R_P)-2-[2-(diphenylphosphino)phenyl]ferrocenyl}ethyldiphenylphosphine, Walphos−CF_3: (*R*)-1-{(R_P)-2-[2-(diphenylphosphino)phenyl]ferrocenyl}ethylbis[3,5-bis-(trifluoromethyl)phenyl]phosphine, PPM: (2*S*,4*S*)-(−)-4-diphenylphosphino-2-(diphenylphosphinomethyl)pyrrolidine, L1(*S*,*S*,a*S*): (*S*,*S*,*S*)-(+)-(3,5-dioxa-4-phosphacyclohepta[2,1-*a*:3,4-*a*′]dinaphthalen-4-yl)bis(1-phenylethyl)amine, L2(*R*,*R*,*R*): (*R*,*R*,*R*)-1-(3,5-dioxa-4-phosphacyclohepta[2,1-*a*:3,4-*a*′]dinaphthalen-4-yl)-2,5-diphenylpyrrolidine, PipPhos: (*S*)-(+)-(3,5-dioxa-4-phosphacyclohepta[2,1-*a*:3,4-*a*′]dinaphthalen-4-yl)piperidine, (*R*,*R*)-Trost: (1*R*,2*R*)-1,2-bis[(2-diphenylphosphanyl)benzoylamino]cyclohexane.

[b] Yield refers to isolated pure products after column chromatography.

[c] Enantioselectivity (er) was measured by chiral stationary phase HPLC on a Chiral IA column (25 cm×4.6 mm); *i*-propanol/hexane (99:1), flow rate=0.2 mL min^{-1}, t_R=23.8 min and t_R=24.8 min for **6a**; methanol, flow rate=0.2 mL min^{-1}, t_R=23.6 min and t_R=26.4 min for **6c**; the first value corresponds to the enantiomer being eluted first.

diphenylpyrrolidine substituent [L1(*S*,*S*,a*S*) has a bis(1-phenylethyl) amine substituent]. At room temperature **5e** did not give the expected product **6c** (Table 2, entry 15). The next phosphorus amidite ligand with a piperidine ring (PipPhos) and carbonate **5e** afforded **6c** in 38% yield after 24 h but with a very low er value of 58:42 (Table 2, entry 16).

Finally, the asymmetric cyclisation of carbonates **5b** and **5e** was performed in the presence of the phosphine-amide (*R*,*R*)-Trost ligand. Ring-closure of **5b** gave 2-vinylpyrrolidine **6a** as a 40:60 mixture of enantiomers in 98% overall yield (Table 2, entry 17). Piperidine **6c** was obtained in a very good yield (99%) and with highest stereoselectivity (61:39 er) (Table 2, entry 18). Decreasing the temperature to 0 °C did not improve the selectivity of the reaction, what is more, in these conditions cyclisation did not take place (Table 2, entry 19).

Cyclisation of *N*-benzyl carbonates **5c** and **5f** to pyrrolidine and piperidine derivatives **6b** and **6d**, respectively, also took place in the presence of four classes of ligands (Table 3, entries 1–22). The phosphine ligands proved more effective for *N*-benzyl carbonates than for *N*-tosyl derivatives **5b** and **5e**. When the reaction was performed at 20 °C we observed that the (*S*)-Binap afforded *N*-benzyl pyrrolidine **6b** in 88% yield and with an *S*/*R* enantiomeric ratio[20a,d] of 83:17 (Table 3, entry 1). Under the same conditions *N*-benzyl piperidine **6d** was obtained with an er of 14:86 (*S*/*R*) but in a 14% yield (Table 3, entry 2). Increasing the temperature to 60 °C gave the cyclised product in a 95% yield in less time, but resulted in a decrease in enantioselectivity (Table 3, entry 3). (*R*,*S*)-Josiphos gave good selectivity only for piperidine **6d**. We obtained selectivity *S*/*R* 65:35 for pyrrolidine **6b**, and *S*/*R* 17:83 for **6d** (Table 3, entries 4 and 5).

Table 3
Pd^0-catalysed asymmetric allylic cyclisation of *N*-benzyl carbonates **5c** and **5f**[a]

Entry	Carbonate	Product	Ligand	*T* [°C]	Time [h]	Yield[b] [%]	er[c] (*S*/*R*)
1	**5c**	**6b**	(*S*)-Binap	20	24	88	83:17
2	**5f**	**6d**	(*S*)-Binap	20	48	14	14:86
3	**5f**	**6d**	(*S*)-Binap	60	24	95	28:72
4	**5c**	**6b**	(*R*,*S*)-Josiphos	20	24	50	65:35
5	**5f**	**6d**	(*R*,*S*)-Josiphos	20	48	30	17:83
6	**5f**	**6d**	(*R*,*S*)-Josiphos	60	96	87	63:37
7	**5f**	**6d**	Walphos	20	24	96	50:50
8	**5f**	**6d**	Walphos-CF_3	20	24	99	53:47
9	**5c**	**6b**	PPM	20	24	95	94:6
10	**5f**	**6d**	PPM	20	24	92	56:44
11	**5c**	**6b**	L1(*S*,*S*,a*S*)	20	24	99	27:73
12	**5f**	**6d**	L1(*S*,*S*,a*S*)	20	24	96	3:97
13	**5f**	**6d**	L1(*S*,*S*,a*S*)	0	24	99	87:13
14	**5f**	**6d**	L1(*S*,*S*,a*S*)	−20	120	50	71:29
15	**5f**	**6d**	L2(*R*,*R*,*R*)	20	48	0	—
16	**5f**	**6d**	PipPhos	20	24	93	51:49
17	**5f**	**6d**	Monophos	20	24	92	46:54
18	**5c**	**6b**	(*R*,*R*)-Trost	20	24	99	88:12
19	**5f**	**6d**	(*R*,*R*)-Trost	60	24	96	16:84
20	**5f**	**6d**	(*R*,*R*)-Trost	20	48	86	12:88
21	**5f**	**6d**	(*R*,*R*)-Trost	0	24	84	71:29
22	**5f**	**6d**	(*R*,*R*)-Trost	−20	120	13	68:32
23	**5f**	**6d**	(*R*,*R*)-Trost	−40	120	11	55:45

[a] [**5**]/[$Pd_2(dba)_3$]/[ligand]=40:1:2.2 (4.4), THF; Monophos: (*R*)-(−)-(3,5-dioxa-4-phosphacyclohepta[2,1-*a*:3,4-*a*′]dinaphthalen-4-yl)dimethylamine.

[b] Yield refers to isolated pure products after column chromatography.

[c] Enantioselectivity (er) was measured by chiral stationary phase HPLC on a Chiral OD-H column (25 cm×4.6 mm); hexane/*i*-propanol (99.9:0.1), flow rate=0.5 mL min^{-1}, t_R[(*S*)-**6b**]=8.66 min and t_R[(*R*)-**6b**]=11.31 min; hexane/*i*-propanol (99.9:0.1), flow rate=0.5 mL min^{-1}, t_R[(*S*)-**6d**]=7.41min and t_R[(*R*)-**6d**]=7.95 min.

The Walphos ligands, similarly as for the tosyl derivatives, proved to be completely unselective in this type of cyclisation and

afforded practically a 1:1 mixture of enantiomers (Table 3, entries 7 and 8). The phosphine-amine ligand PPM gave products **6b** and **6d** in a good yield of 95% and 92%, respectively, after 24 h, but the er value of **6d** was very low (*S*/*R* 58:42) while that of **6b** was 94:6 (Table 3, entries 9 and 10). Among the phosphorus amidite ligands, the most effective proved to be L1(*S*,*S*,a*S*) (Table 3, entries 11–17). Both carbonates **5c** and **5f** gave cyclisation products in excellent yields (99% for **6b** and 96% for **6d**) and high enantioselectivity, especially for *N*-benzyl piperidine, 3:97 in favour of (*R*)-**6d** (Table 3, entries 11 and 12). Additionally, lowering the temperature to 0 °C gave **6d** with a reversal of configuration (*S*/*R* 87:13) (Table 3, entry 13). We observed that lowering the temperature to −20 °C resulted in a decrease in both yield and selectivity (er 71:29, 50% yield) (Table 3, entry 14).

Finally, we tested the phosphine-amide (*R*,*R*)-Trost ligand. Cyclisation of **5e** at 20 °C gave an 88:12 (*S*/*R*) mixture of stereoisomers in 99% yield (Table 3, entry 18). The use of longer-chain carbonate **5f** afforded a good yield and stereoselectivity: (*S*)-**6d**/(*R*)-**6d** 16:84 and 12:88 at 60 and 20 °C, respectively (Table 3, entries 19, 20). We also examined the influence of temperature on the asymmetric allylic amination of substrate **5f** using the Trost ligand. Similarly to ligand L1(*S*,*S*,a*S*), lowering the temperature resulted in a decrease in yield and selectivity of the reaction; moreover, *N*-benzyl pyrrolidine **6d** showed the opposite ratio (er values of 71:29 at 0 °C).

3. Conclusion

In conclusion, we have developed a simple and efficient methodology for the synthesis of chiral nitrogen-containing heterocycles via Pd(0)-catalysed cyclisation of amino allylic carbonates. 2-Vinylpyrrolidine and 2-vinylpiperidine were obtained in good yields and with enantiomeric ratios of up to 3:97. The highest enantioselectivites for both *N*-tosyl and *N*-benzyl derivatives were obtained using the phosphorus amidite ligand L1(*S*,*S*,a*S*). (*S*)-Binap and (*R*,*R*)-Trost ligands proved effective only in the synthesis of *N*-benzyl-2-vinylpyrrolidine and piperidine.

4. Experimental

4.1. General

All solvents and reagents were purchased from Sigma–Aldrich and were used as supplied, without additional purification. NMR spectra were recorded in $CDCl_3$ on Varian Gemini 2000 (200 MHz for ^{1}H NMR, 50 MHz for ^{13}C NMR) or Bruker Avance III (600 MHz for ^{1}H NMR, 150 MHz for ^{13}C NMR), coupling constants are reported in hertz (Hz). Chromatographic purification of compounds was achieved with 230–400 mesh size silica gel. The progress of reactions was monitored by silica gel thin layer chromatography plates (Merck TLC Silicagel 60 F_{254}). The enantiomeric ratio was determined by HPLC (ProStar Varian) employing a Chiralpak IA or Kromasil OD-H column (25 cm×4.6 mm).

4.2. Typical procedure for the synthesis of bromocarbonates 4c, 4e (4a,b,d[21b])

A solution of alcohol **3** (22.0 mmol) in CH_2Cl_2 (50 mL) cooled to 0 °C was treated with pyridine (2.2 mL, 27.5 mmol) and methyl chloroformate (2.1 mL, 27.5 mmol). After 2 h at room temperature, the reaction mixture was quenched with water (30 mL) and extracted with CH_2Cl_2 (2×50 mL). The combined organic phases were dried (Na_2SO_4) and evaporated under reduced pressure. The crude product was purified by flash column chromatography on silica gel to give allylic bromocarbonate **4**.

4.2.1. (E)-7-Bromohept-2-en-1-yl methyl carbonate ***4c****.* Colourless oil, 4.8 g, 87% yield; R_f (hexane/EtOAc, 4:1) 0.60; ν_{max} (liquid film) 3002, 1743, 1674, 1266 cm^{-1}; δ_H (200 MHz, $CDCl_3$) 1.59 (quintet, 2H, *J* 6.9, H-6), 1.83 (quintet, 2H, *J* 6.9, H-5), 2.12 (q, 2H, *J* 7.1, H-4), 3.43 (t, 2H, *J* 6.9, H-7), 3.80 (s, 3H, C*H*$_3$), 4.56 (d, 2H, *J* 6.3, H-1), 5.62 (dt, 1H, *J* 15.5, 6.3, H-2), 5.80 (dt, 1H, *J* 15.5, 6.3, H-3); δ_C (50 MHz, $CDCl_3$) 29.7 (C-4), 31.3 (C-5), 32.1 (C-6), 33.5 (C-7), 54.7 (O*C*H$_3$), 68.5 (C-1), 123.9 (C-3), 136.3 (C-2), 155.5 (CO). Found: C, 42.94; H, 6.05. $C_9H_{15}BrO_3$ requires C, 43.05; H, 6.02%.

4.2.2. (E)-8-Bromooct-2-en-1-yl methyl carbonate ***4e****.* Colourless oil, 4.6 g, 82% yield; R_f (hexane/EtOAc, 5:1) 0.80; ν_{max} (liquid film) 3007, 1748, 1673, 1267 cm^{-1}; δ_H (200 MHz, $CDCl_3$) 1.30–1.60 (m, 4H, H-5, H-6), 1.80–2.20 (m, 4H, H-4, H-7), 3.40 (t, 2H, *J* 6.6, H-8), 3.78 (s, 3H, C*H*$_3$), 4.56 (d, 2H, *J* 6.2, H-1), 5.60 (dt, 1H, *J* 15.2, 6.2, H-2), 5.80 (dt, 1H, *J* 15.2, 6.6, H-3); δ_C (50 MHz, $CDCl_3$) 28.5, 29.5 (C-4 and C-5), 32.0 (C-6), 32.4 (C-7), 48.2 (C-8), 62.8 (O*C*H$_3$), 63.7 (C-1), 127.1 (C-3), 129.7 (C-2), 155.5 (CO). Found: C, 45.12; H, 6.48. $C_{10}H_{17}BrO_3$ requires C, 45.30; H, 6.46%.

4.3. Typical procedure for the synthesis of aminocarbonates 5d, 5i (5a, 5b, 5e[21b])

A solution of bromocarbonate **4** (11.0 mmol), $TsNH_2$ (1.9 g, 11.0 mmol), and TsNHNa (2.1 g, 11.0 mmol) in DMSO (60 mL) was stirred for 16 h at 60 °C. Then the reaction mixture was diluted with brine (60 mL) and extracted with diethyl ether (3×30 mL). The combined organic phases were dried (Na_2SO_4) and evaporated under reduced pressure. The crude product was purified by flash column chromatography on silica gel to give allylic aminocarbonate **5**.

4.3.1. (E)-(7-(4-Methylphenylsulfonamido)hept-2-en-1-yl) methyl carbonate ***5d****.* Colourless oil, 2.4 g, 65% yield; R_f (hexane/EtOAc, 4:1) 0.62; ν_{max} (liquid film) 3285, 1748, 1599, 1328, 1161, 1270 cm^{-1}; δ_H (200 MHz, $CDCl_3$) 1.30–1.62 (m, 4H, H-5, H-6), 2.00 (q, 2H, *J* 7.0, H-4), 2.43 (s, 3H, C$_6$H$_4$C*H*$_3$), 2.92 (q, 2H, *J* 6.4, H-7), 3.77 (s, 3H, OC*H*$_3$), 4.53 (d, 2H, *J* 6.0, H-1), 5.15 (s, 1H, *J* 6.2, NH), 5.50 (dt, 1H, *J* 15.4, 6.0, H-2), 5.70 (dt, 1H, *J* 15.4, 7.0, H-3), 7.30 (d, 2H, *J* 8.2, C$_6$*H*$_4$), 7.74 (d, 2H, *J* 8.2, C$_6$*H*$_4$); δ_C (50 MHz, $CDCl_3$) 21.4 (*C*H$_3$C$_6$H$_4$), 25.5 (C-5), 28.8 (C-4), 31.4 (C-6), 42.9 (C-7), 54.6 (O*C*H$_3$), 68.4 (C-1), 123.9, 127.7, 129.7 (*C*$_6$H$_4$, C-2, C-3), 136.3, 143.4 (C$_q$), 155.7 (CO). Found: C, 56.32; H, 6.83; N, 4.28. $C_{16}H_{23}NO_5S$ requires C, 56.29; H, 6.79; N, 4.10%.

4.3.2. (E)-(8-(4-Methylphenylsulfonamido)oct-2-en-1-yl) methyl carbonate ***5i****.* Colourless oil, 2.6 g, 67% yield; R_f (hexane/EtOAc, 2:1) 0.43; ν_{max} (liquid film) 3285, 1746, 1598, 1328, 1160, 1269 cm^{-1}; δ_H (200 MHz, $CDCl_3$) 1.20–1.52 (m, 6H, H-5, H-6, H-7), 2.00 (q, 2H, *J* 6.7, H-4), 2.43 (s, 3H, C$_6$H$_4$C*H*$_3$), 2.91 (q, 2H, *J* 6.6, H-8), 3.77 (s, 3H, OC*H*$_3$), 4.55 (d, 2H, *J* 6.2, H-1), 5.47 (s, 1H, NH), 5.52 (dt, 1H, *J* 15.1, 6.0, H-2), 5.73 (dt, 1H, *J* 15.1, 6.7, H-3), 7.30 (d, 2H, *J* 8.0, C$_6$*H*$_4$), 7.74 (d, 2H, *J* 8.0, C$_6$*H*$_4$); δ_C (50 MHz, $CDCl_3$) 21.5 (*C*H$_3$C$_6$H$_4$), 25.9, 28.1, 29.3, 31.9 (C-4, C-5, C-6, C-7), 43.1 (C-8), 54.7 (O*C*H$_3$), 68.5 (C-1), 123.5, 136.7 (C-2, C-3), 127.0, 129.6 (*C*$_6$H$_4$), 136.9, 143.3 (C$_q$), 155.6 (CO). Found: C, 57.36; H, 7.04; N, 3.82. $C_{17}H_{25}NO_5S$ requires C, 57.44; H, 7.09; N, 3.94%.

4.4. Typical procedure for the synthesis of aminocarbonates 5c, 5f–h

A 1.5 M solution of *i*-Pr$_2$NEt in DMF (5.2 mL *i*-Pr$_2$NEt in 14.8 mL DMF) and the corresponding amine: benzylamine, cyclohexylamine, *tert*-butylamine (33.0 mmol) was added successively to a 0.8 M solution of appropriate bromide **4** (11.0 mmol) in DMF (14 mL). The reaction mixture was stirred at room temperature until the transformation of the bromide was complete (16–24 h), as

indicated by thin layer chromatography. After being diluted with EtOAc (50 mL), the mixture was then washed with H_2O (3×20 mL) and a saturated aqueous solution of NaCl (20 mL). The organic layer was dried on $MgSO_4$, filtered, and concentrated under reduced pressure. The crude product was purified by flash column chromatography on silica gel to give allylic aminocarbonate **5**.

4.4.1. (E)-6-(Benzylamino)hex-2-en-1-yl isobutyl carbonate ***5c***. Yellow oil, 2.0 g, 60% yield; R_f (EtOAc/MeOH, 7:1) 0.63; ν_{max} (liquid film) 3316, 3086, 3062, 3028, 1743, 1679, 1251 cm^{-1}; δ_H (200 MHz, $CDCl_3$) 0.94 (d, 6H, *J* 6.6, $CH_2CH(CH_3)_2$), 1.63 (quintet, 2H, *J* 7.6, H-5), 1.85–2.20 (m, 3H, H-4, $CH_2CH(CH_3)_2$), 2.64 (t, 2H, *J* 7.6, H-6), 3.79 (s, 2H, $CH_2C_6H_5$), 3.91(d, 2H, *J* 6.7, $CH_2CH(CH_3)_2$), 4.55 (d, 2H, *J* 6.2, H-1), 5.62 (dt, 1H, *J* 15.7, 6.2, H-2), 5.77 (dt, 1H, *J* 15.7, 6.4, H-3), 7.21–7.41 (m, 5H, C_6H_5); δ_C (50 MHz, $CDCl_3$) 18.8 ($CH_2CH(CH_3)_2$), 27.6 ($CH_2CH(CH_3)_2$), 28.7 (C-4), 29.8 (C-5), 48.4 (C-6), 53.7 ($CH_2C_6H_5$), 68.3 (C-1), 74.0 ($CH_2CH(CH_3)_2$), 123.8 (C-3), 127.0, 128.3, 128.4 (C_6H_5), 136.5 (C-2), 139.7 (C_q), 155.3 (CO). Found: C, 70.75; H, 8.89; N, 4.72. $C_{18}H_{27}NO_3$ requires C, 70.79; H, 8.91; N, 34.56%.

4.4.2. (E)-7-(Benzylamino)hept-2-en-1-yl isobutyl carbonate ***5f***. Yellow oil, 1.7 g, 48% yield; R_f (EtOAc/MeOH, 7:1) 0.63; ν_{max} (liquid film) 3324, 3086, 3062, 3027, 1744, 1694, 1251 cm^{-1}; δ_H (200 MHz, $CDCl_3$) 0.94 (d, 6H, *J* 6.6, $CH_2CH(CH_3)_2$), 1.34–1.60 (m, 4H, H-5, H-6), 1.86–2.12 (m, 3H, $CH_2CH(CH_3)_2$), 1.65 (s, 1H, NH), 2.06 (q, 2H, *J* 6.4, H-4), 2.60 (t, 2H, *J* 7.1, H-7), 3.80 (s, 2H, $CH_2C_6H_5$), 3.92 (d, 2H, *J* 6.7, $CH_2CH(CH_3)_2$), 4.55 (d, 2H, *J* 6.3, H-1), 5.62 (dt, 1H, *J* 12.7, 6.3, H-2), 5.77 (dt, 1H, *J* 12.7, 6.4, H-3), 7.24–7.35 (m, 5H, C_6H_5); δ_C (50 MHz, $CDCl_3$) 18.9 ($CH_2CH(CH_3)_2$), 26.5 ($CH_2CH(CH_3)_2$), 27.7 (C-4), 29.4 (C-5), 32.0 (C-2), 49.1 (C-7), 53.9 ($CH_2C_6H_5$), 68.4 (C-1), 74.0 ($CH_2CH(CH_3)_2$), 123.5 (C-3), 126.9, 128.1, 128.4 (C_6H_5), 137.0 (C-2), 140.2 (C_q), 155.2 (CO). Found: C, 71.23; H, 9.28; N, 4.42. $C_{19}H_{29}NO_3$ requires C, 71.44; H, 9.15; N, 4.38%.

4.4.3. (E)-7-(Cyclohexylamino)hept-2-en-1-yl isobutyl carbonate ***5g***. Colourless oil, 2.1 g, 62% yield; R_f (EtOAc/MeOH/CH_2Cl_2, 5:3:3) 0.19; ν_{max} (liquid film) 3326, 1745, 1673, 1249 cm^{-1}; δ_H (200 MHz, $CDCl_3$) 0.94 (d, 6H, *J* 6.7, $CH_2CH(CH_3)_2$), 1.04–1.30 (m, 6H, C_6H_{11}), 1.36–1.60 (m, 6H, C_6H_{11}, H-6), 1.70–2.16 (m, 3H, H-5, $CH_2CH(CH_3)_2$), 1.70 (s, 1H, NH), 2.08 (q, 2H, *J* 6.7, H-4), 2.45–2.52 (m, 1H, C_6H_{11}), 2.64 (t, 2H, *J* 6.8, H-7), 3.91 (d, 2H, *J* 6.7, $CH_2CH(CH_3)_2$), 4.55 (d, 2H, *J* 6.3, H-1), 5.65 (dt, 1H, *J* 15.3, 6.3, H-2), 5.77 (dt, 1H, *J* 15.3, 6.5, H-3); δ_C (50 MHz, $CDCl_3$) 18.6 ($CH_2CH(CH_3)_2$), 24.7 (C_6H_{11}), 25.7 (C_6H_{11}), 26.3 (C-5), 27.4 ($CH_2CH(CH_3)_2$), 29.0 (C_6H_{11}), 31.7 (C-4), 32.6 (C-6), 42.0 (C-7), 56.4 (C_6H_{11}), 68.1 (C-1), 73.6 ($CH_2CH(CH_3)_2$), 123.4 (C-3), 136.6 (C-2), 155.0 (CO); EIMS (*m*/*z*): 312.3 $[M+H]^+$. Found: C, 69.12; H, 10.79; N, 4.48. $C_{18}H_{33}NO_3$ requires C, 69.41; H, 10.68; N, 4.50%.

4.4.4. (E)-7-(tert-Butylamino)hept-2-en-1-yl isobutyl carbonate ***5h***. Colourless oil, 2.7 g, 85% yield; R_f (EtOAc/MeOH, 7:1) 0.43; ν_{max} (liquid film) 3430, 1747, 1674, 1261 cm^{-1}; δ_H (200 MHz, $CDCl_3$) 0.95 (d, 6H, *J* 6.6, $CH_2CH(CH_3)_2$), 1.46 (s, 9H, $(CH_3)_3$), 1.36–1.56 (m, 2H, H-6), 1.70–2.14 (m, 5H, H-4, H-5, $CH_2CH(CH_3)_2$), 2.82 (t, 2H, *J* 8.5, H-7), 3.91 (t, 2H, *J* 6.7, $CH_2CH(CH_3)_2$), 4.57 (d, 2H, *J* 6.1, H-1), 5.65 (dt, 1H, *J* 15.6, 6.1, H-2), 5.77 (dt, 1H, *J* 15.6, 6.3, H-3); δ_C (50 MHz, $CDCl_3$) 18.8 ($CH_2CH(CH_3)_2$), 26.0 ($CH_2CH(CH_3)_2$), 26.0 ($C(CH_3)_3$), 26.4 (C-5), 27.7 (C-6), 31.6 (C-4), 41.7 (C-7), 56.5 ($C(CH_3)_3$), 68.2 (C-1), 73.9 ($CH_2CH(CH_3)_2$), 124.0 (C-3), 135.9 (C-2), 155.1 (CO); HRMS (EI): M^+, found 285.23039. $C_{16}H_{31}NO_3$ requires 285.23041.

4.5. Typical procedure for the Pd^0-catalysed reaction

The catalytic system was prepared by stirring $Pd_2(dba)_3$ (22.9 mg, 0.025 mmol) and the ligand (0.055 mmol or 0.11 mmol) in an appropriate anhydrous solvent (3 mL) for 0.5 h in a Schlenk tube under argon. This solution was added, under argon, to a Schlenk tube containing the unsaturated aminocarbonate **5a**–**i** (1 mmol) in an appropriate anhydrous solvent (3 mL). The solution was stirred at 25 °C (or 60 °C). After an appropriate period of time, removal of the solvent followed by column chromatography gave the corresponding product.

Compounds **6a**–**d** are known and described in the literature (**6a**, **6c**[21b] and **6b**, **6d**[20a,d]).

4.5.1. 1-Cyclohexyl-2-vinylpiperidine ***6e***. Yellow oil; R_f (EtOAc/MeOH/CH_2Cl_2, 5:3:3) 0.37; ν_{max} (liquid film) 3076, 1643, 1329, 1160, 1092 cm^{-1}; δ_H (600 MHz, $CDCl_3$) 0.95–1.90 (m, 16H, H-3, H-4, H-5, H-2′, H-3′, H-4′, H-5′, H-6′), 2.16 (dt, 1H, *J* 11.1, 2.5, H-6), 2.73 (dt, 1H, *J* 10.8, 2.6, H-6), 2.84–3.06 (m, 2H, H-1′, H-2), 5.00 (dd, 1H, *J* 10.1, 1.8, $CHCH_2$), 5.13 (dd, 1H, *J* 17.2, 1.8, $CHCH_2$), 5.80 (dt, 1H, *J* 17.2, 10.2, $CHCH_2$); δ_C (150 MHz, $CDCl_3$) 23.5 (C-3′, C-5′), 24.2 (C-4), 25.7 (C-4′), 26.1 (C-5′), 31.5 (C-3), 34.1 (C-2′, C-6′), 45.4 and 59.1 (C-1′ and C-6), 63.8 (C-2), 114.6 ($CHCH_2$), 142.1 ($CHCH_2$); HRMS (EI): M^+, found 193.18305. $C_{13}H_{23}N$ requires 193.18298.

4.5.2. 1-Tosyl-2-vinylazepane ***6g***. Yellow oil; R_f (EtOAc/hexane, 5:1) 0.73; ν_{max} (liquid film) 3063, 3027, 1663, 1335, 1159, 1090 cm^{-1}; δ_H (600 MHz, $CDCl_3$) 1.08–1.60 (m, 8H, H-3, H-4, H-5, H-6), 2.42 (s, 3H, CH_3), 2.90 (dd, 1H, *J* 13.2, 7.2, H-7), 3.68 (dd, 1H, *J* 13.2, 6.6, H-7), 4.59 (m, 1H, H-2), 5.10 (d, 1H, *J* 11.6, $CHCH_2$), 5.17 (d, 1H, *J* 17.0, $CHCH_2$), 5.80 (ddd, 1H, *J* 17.0, 11.6, 5.2, $CHCH_2$), 7.28 (d, 2H, *J* 8.2, C_6H_4), 7.69 (d, 2H, *J* 8.2, C_6H_4); δ_C (150 MHz, $CDCl_3$) 21.4 ($C_6H_4CH_3$), 24.1 (C-4), 25.9 (C-5), 29.4 (C-6), 30.1 (C-3), 43.60 (C-7), 58.9 (C-2), 115.1 ($CHCH_2$), 127.1, 129.6 (C_6H_4), 136.2 ($CHCH_2$); HRMS (EI): M^+, found 279.12930. $C_{15}H_{21}NO_2S$ requires 279.12869.

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