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Asymmetric synthesis of optically active 2-vinylpyrrolidines and 2-vinylpiperidines by palladium-catalysed cyclisation of amino allylic carbonates

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ABSTRACT

Optically active 2-vinylpyrrolidines and 2-vinylpiperidines were synthesised from the corresponding amino allylic carbonates via palladium-catalysed cyclisation. The use of chiral ligands gave the corresponding pyrrolidine and piperidine derivatives having er values from low to moderate.

Saturated nitrogen heterocycles, such as pyrrolidines, piperidines and isoxazolidines, appear as subunits in a broad array of biologically active and medicinally significant molecules.[1] For these reasons, the synthesis of these compounds has been of long-standing interest. Many classical approaches to their construction involve the use of C–N bond-forming reactions such as reductive amination, nucleophilic substitution or dipolar cycloaddition.[2] Although these methods have proved to be quite useful, their substrate scope and functional group tolerance are often limited. In recent years, several powerful new transformations have been developed that involve the use of palladium-catalysed C–N bond-forming reactions for construction of heterocyclic rings.[3]

These transformations frequently occur under mild conditions, tolerate a broad array of functional groups and proceed with high stereoselectivity.

The synthesis of saturated nitrogen heterocycles via Pd-catalysed and other C–N bond-forming reactions can be broadly classified into four categories: (i) amination reactions of alkenes, alkynes and allenes;[2a,2f,4] (ii) 1,3-dipolar cycloadditions;[5] (iii) carbonylation processes;[6] and (iv) intramolecular addition of nitrogen nucleophiles to intermediate π-allylpalladium complexes.[7] A number of different strategies have been employed for the generation of reactive intermediate π-allylpalladium complexes, such as oxidative addition of alkenyl epoxides,[8] allylic acetates[9] and related electrophiles to Pd^0. An important improvement in π-allylpalladium chemistry was achieved by the introduction of allylic carbonates. Carbonates are highly reactive, and more importantly, their reactions can be carried out under neutral conditions.[10]

Extending our previous work on the use of allyl carbonates in the synthesis of *O*-heterocycles,[11] herein we describe our preliminary results obtained on enantioselective Pd-catalysed allylic aminations.

Experiments were performed with methyl and isobutyl carbonates **5a–c** (Scheme 1) using commercially available ligands (Fig. 1).

Substrates **5a–c** were prepared by reduction of bromoesters **1a**,**b** to the corresponding aldehydes[12] followed by elongation of the chain *via* Wittig reaction,[13] reduction to the alcohol **3a**,**b**,[14] condensation with methyl or isobutyl chloroformate and, finally, substitution of the bromine atom with a 4-methylbenzenesulfonamide group (tosyl group).

The cyclisation was first studied with methyl carbonate **5a** as the substrate.[15] Ring-closure of **5a** occurred slowly (48 h) at room temperature in the presence of a catalytic amount of $Pd_2(dba)_3$ associated with the (*R*,*R*)-Trost ligand, providing 2-vinylpyrrolidine **6a**[15,16] as a 45:55 mixture of enantiomers in 94% overall yield (Table 1, entry 1).

Isobutyl carbonate **5b** was more reactive under the same conditions (Table 1, entry 2) and gave product **6a** with the highest yield (98%) and stereoselectivity (40:60 er) in 24 h. Longer chain isobutyl carbonate **5c** was also submitted to this cyclisation procedure in the presence of the (*R*,*R*)-Trost ligand. Pyrrolidine **6b**[15,17] was

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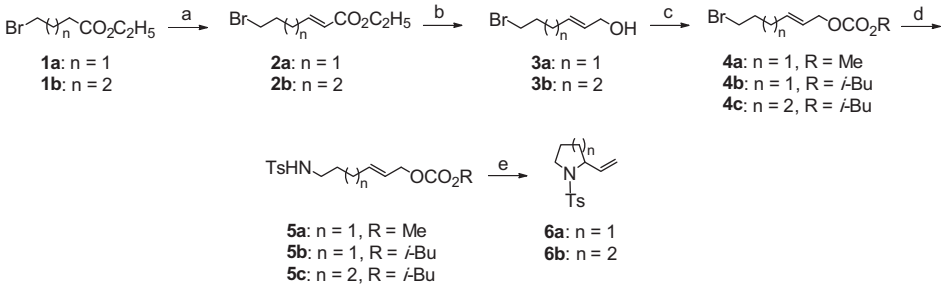

Scheme 1. Pd^0-catalysed synthesis of heterocycles **6a**,**b**; reagents and conditions: (a) 1. DIBAL-H, CH_2Cl_2, −78 °C, 2. $Ph_3P{=}CHO_2C_2H_5$, CH_2Cl_2, rt; (b) DIBAL-H, Et_2O, 0 °C; (c) ROCOCl, C_5H_5N, CH_2Cl_2, 0 °C→rt; (d) TsNHNa, $TsNH_2$, DMSO, 60 °C; (e) [Pd], ligand.

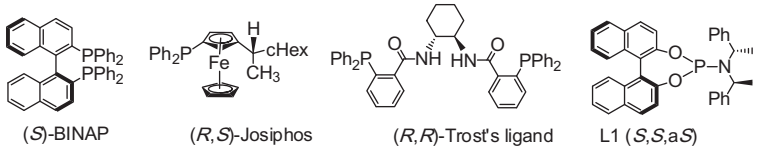

Figure 1. Ligands used in this work.

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

Entry	Substrate	Ligand	Product	Temp (°C)	Time (h)	Yield (%)[b]	er (%)[c]
1	**5a**	(*R*,*R*)-Trost	**6a**	20	48	94	45:55
2	**5b**	(*R*,*R*)-Trost	**6a**	20	24	98	40:60
3	**5c**	(*R*,*R*)-Trost	**6b**	20	24	99	61:39
4	**5a**	(*S*)-BINAP	**6a**	20	48	97	41:59
5	**5b**	(*S*)-BINAP	**6a**	20	48	97	36:64
6	**5c**	(*S*)-BINAP	**6b**	20	48	45	65:35
7	**5a**	(*R*,*S*)-Josiphos	**6a**	20	96	73	47:53
8	**5a**	(*R*,*S*)-Josiphos	**6a**	60	96	78	46:54
9	**5b**	(*R*,*S*)-Josiphos	**6a**	20	48	87	41:59
10	**5b**	(*R*,*S*)-Josiphos	**6a**	60	48	96	50:50
11	**5c**	(*R*,*S*)-Josiphos	**6b**	20	48	10	66:34
12	**5c**	(*R*,*S*)-Josiphos	**6b**	20	168	82	65:35
13	**5c**	(*R*,*S*)-Josiphos	**6b**	60	72	92	53:47
14	**5a**	L1	**6a**	20	24	0	—
15	**5a**	L1	**6a**	60	24	44	22:78
16	**5b**	L1	**6a**	20	24	99	22:78
17	**5c**	L1	**6b**	20	24	99	90:10

[a] [**5**]:[$Pd_2(dba)_3$]:[ligand] = 40:1:2.2 (4.4), THF.
[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 **6b**; the first value corresponds to the enantiomer being eluted first.

obtained in a very good yield (99%) and in a 61:39 ratio (Table 1, entry 3). This Pd^0-catalysed cyclisation was extended to other ligands. Reactions with (*S*)-BINAP required longer reaction times and were characterised by moderate er values of 41:59, 36:64 and 65:35 (**5a**, **5b** and **5c**, respectively), affording quantitative yields of pyrrolidine **6a** (97%) and a moderate yield of piperidine **6b** (45%) (Table 1, entries 4–6). The use of (*R*,*S*)-Josiphos as the chiral ligand and carbonate **5a** afforded **6a** in a good yield of 73% after 96 h but with a very low er value of 47:53 (Table 1, entry 7). Increasing the temperature to 60 °C did not improve the selectivity of the reaction and resulted in only a slight increase in the yield (Table 1, entry 8). Isobutyl carbonate **5b** in the presence of the Josiphos ligand, similar to the results observed in the case of the Trost ligand, gave pyrrolidine **6a** in less time and with a better yield, but with poor enantioselectivity 41:59 (Table 1, entry 9). The same reaction at 60 °C afforded a 1:1 mixture of enantiomers (Table 1, entry 10). Isobutyl carbonate **5c** was less reactive and required a much longer reaction times (Table 1, entries 11–13). Piperidine **6b** was obtained in 10% yield after 48 h and 82% after 168 h as a 65:35 mixture, while at 60 °C, **6b** was obtained in 92% yield after 72 h (53:47 er).

Finally, the asymmetric cyclisation of allylic carbonates **5a–c** was performed in the presence of the phosphorus amidite ligand, L1. The cyclisation of compound **5a** at room temperature did not give the expected product **6a**, but at 60 °C the same reaction afforded a 22:78 mixture of enantiomers in 44% yield after 24 h (Table 1, entries 14–15). The more reactive carbonate **5b**, at room temperature gave quantitatively pyrrolidine **2a** with good selectivity (22:78 er) (Table 1, entry 16). Piperidine **6b** was obtained in 99% yield under the same conditions with an er value of 90:10 starting from allylic carbonate **5c** (Table 1, entry 17).

Table 2 illustrates the influence of the solvent on these intramolecular aminations. The best results were obtained for the reaction carried out in THF. Similar results were observed in toluene.

Table 2
Effect of solvent on the asymmetric allylic amination of substrate **5c** using ligand L1[a]

Entry	Solvent	Yield (%)	er (%)
1	THF	99	90:10
2	CH_2Cl_2	98	75:25
3	Toluene	99	89:11
4	CH_3CN	43	55:45

[a] [**5c**]:[$Pd_2(dba)_3$]:[ligand] = 40:1:4.4, 20 °C, 24 h.

Table 3
Effect of the palladium precursor on the asymmetric allylic amination of substrate **5c**[a]

Entry	[Pd] precursor	Ligand	Time (h)	Yield (%)	er (%)
1	Pd_2dba_3	(*S*)-BINAP	48	45	65:35
2	$[PdCl(C_3H_5)]_2$	(*S*)-BINAP	24	89	56:44
3	$Pd(OAc)_2$	(*S*)-BINAP	24	83	40:60
4	Pd_2dba_3	(*R*,*S*)-Josiphos	48	10	66:34
5	$[PdCl(C_3H_5)]_2$	(*R*,*S*)-Josiphos	24	50	61:39
6	$Pd(OAc)_2$	(*R*,*S*)-Josiphos	24	95	54:46
7	Pd_2dba_3	L1	24	99	90:10
8	$[PdCl(C_3H_5)]_2$	L1	24	0	—
9	$Pd(OAc)_2$	L1	24	80	83:17

[a] [**5c**]:[$Pd_2(dba)_3$]:[ligand] = 40:1:2.2 (4.4); [**5c**]:[$PdCl(C_3H_5)]_2$:[ligand] = 50:1:2.2 (4.4); [**5c**]:[$Pd(OAc)_2$]:[ligand] = 40:1:2.2 (4.4); THF, 20 °C.

In CH_2Cl_2, product **6b** was obtained in an excellent yield but somewhat lower enantioselectivity. The use of CH_3CN resulted in a significant decrease in both the yield and selectivity.

We also investigated the effect of the palladium precursor on this cyclisation reaction (Table 3).[15]

The reaction using $[PdCl(C_3H_5)]_2$ or $Pd(OAc)_2$ as the palladium precursor provided good yields of **6b** (Table 3, entries 2, 3, 5 and 6), but the enantioselectivity decreased. Cyclisation of **5c** in the presence of $Pd(OAc)_2$ and ligand L1 gave a product with a lower yield and selectivity than for the reaction catalysed by $Pd_2(dba)_3$ and L1 (Table 3, entries 7 and 9). It should also be noted that no cyclisation product was observed with the use of $[PdCl(C_3H_5)]_2$ and ligand L1 (Table 3, entry 8).

2-Vinylpyrrolidine and 2-vinylpiperidines were obtained in relatively good yields and with enantiomeric ratios of up to 90:10 via the Pd^0-catalysed cyclisation of the corresponding amino allylic carbonates. The highest enantioselectivities were obtained using the phosphorus amidite ligand L1; some of the yields were very good with Josiphos, but the enantioselectivities were lower.

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Supplementary data

Supplementary data associated with this article can be found, in the online version, at http://dx.doi.org/10.1016/j.tetlet.2012.10.014.

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15. *General 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 tosylamino carbonate **5a–c** (1 mmol) in an appropriate anhydrous solvent (3 mL). The solution was stirred at 25 °C (or 60 °C). After 24 h, removal of the solvent followed by column chromatography using a mixture of hexanes/EtOAc (2:1) as the eluent gave the corresponding product.
General procedure for the Pd^{II}-Catalysed Reaction: A solution of $[PdCl(C_3H_5)]_2$ (5.5 mg, 0.015 mmol) and ligand (0.033 mmol or 0.066 mmol) or $Pd(OAc)_2$ (3.4 mg, 0.015 mmol) and ligand (0.033 mmol or 0.066 mmol) in anhydrous THF (3 mL) was added to unsaturated tosylamino carbonate **5a–c** {0.75 mmol for $[PdCl(C_3H_5)]_2$ or 0.6 mmol for $Pd(OAc)_2$} in THF (3 mL) under an argon atmosphere. The mixture was stirred at room temperature for 24 h. The solvent was evaporated and the residue was purified by column chromatography (hexanes/EtOAc 2:1).
*1-Tosyl-2-vinylpyrrolidine (**6a**).* ^{1}H NMR (600 MHz, $CDCl_3$): δ = 1.50–1.95 (m, 4H, 2H-3, 2H-4), 2.43 (s, 3H, CH_3), 3.24 (ddd, 1H, *J* = 9.8, 7.1, 4.5 Hz, H-5), 3.44 (ddd, 1H, *J* = 9.8, 6.8, 4.5 Hz, H-5), 4.08–4.20 (m, 1H, H-2), 5.12 (dd, 1H, *J* = 10.2, 1.1 Hz, CH=CH_2), 5.27 (dd, 1H, *J* = 17.0, 1.1 Hz, CH=CH_2), 5.82 (ddd, 1H, *J* = 17.0, 10.2, 6.1 Hz, CH=CH_2), 7.30 (d, 2H, *J* = 8.0 Hz, C_6H_4), 7.30 (d, 2H, *J* = 8.0, C_6H_4). ^{13}C NMR (150 MHz, $CDCl_3$): δ = 21.4 (CH_3), 23.6 (C-4), 32.2 (C-3), 48.7 (C-5), 61.8 (C-2), 115.2 (CH=CH_2), 127.5, 129.3 (C_6H_4), 138.7 (CH=CH_2), 135.0, 143.2 (C_6H_4); EI-MS *m/z* 251.1 (14%, M^+), 91.1 (100), 224.1 (65), 155.0 (63), 96.1 (59); HRMS (EI) Calcd for $C_{13}H_{17}NO_2S$ (M^+) 251.0980. Found 251.0975.

*1-Tosyl-2-vinylpiperidine (**6b**).* ^{1}H NMR (600 MHz, $CDCl_3$):δ = 1.30–1.75 (m, 6H, 2H-3, 2H-4, 2H-5), 2.43 (s, 3H, CH_3), 2.94 (ddd, 1H, *J* = 13.5, 12.8, 2.4 Hz, H-6), 3.68 (d, 1H, *J* = 13.5 Hz, H-6), 4.59 (br s, 1H, H-2), 5.10 (d, 1H, *J* = 10.6 Hz, CH=CH_2), 5.17 (d, 1H, *J* = 17.4 Hz, CH=CH_2), 5.70 (ddd, 1H, *J* = 17.4, 10.6, 5.2 Hz, CH=CH_2), 7.28 (d, 2H, *J* = 8.3 Hz, C_6H_4), 7.69 (d, 2H, *J* = 8.3 Hz, C_6H_4). ^{13}C NMR (150 MHz, $CDCl_3$): δ = 19.0 (C-4), 21.4 (CH_3), 24.9 (C-5), 29.6 (C-3), 41.6 (C-2), 55.0 (C-6), 117.0 (CH=CH_2), 127.2, 129.4 (C_6H_4), 135.4 (CH=CH_2), 137.8, 143.3 (C_6H_4); EI-MS *m*/*z* 265.1 (11%, M^+), 91.1 (100), 155.0 (95), 110.1 (67), 238.1 (50); HRMS (EI) Calcd for $C_{14}H_{19}NO_2S$ (M^+) 265.1137. Found 265.1140.

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