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Highly regio- and stereoselective palladium-catalyzed allylic carbonate amination. A practical route to dehydro-β-amino esters

Giuliana Cardillo [a,*], Luca Gentilucci [a], Elisa Mosconi [a], Alessandra Tolomelli [a,*], Stefano Troisi [a], Eusebio Juaristi [b]

[a] Department of Chemistry 'G.Ciamician', University of Bologna, Via Selmi 2, 40126 Bologna, Italy
[b] Departamento de Química, Centro de Investigación y de Estudios Avanzados del Instituto Politécnico Nacional, Col. San Pedro Zacatenco, Apartado Postal 14-740, 07000 Mexico

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ABSTRACT

A pratical, highly enantioselective method for the synthesis of dehydro-β-amino acids was developed starting from easily accessible enantiopure allylic carbonates. The substitution with amines for C–N bond formation on these substrates bearing substituents on the Cα, Cβ, and Cγ position of the allylic system has received, until now, little attention. The reactions, carried out under palladium-catalyzed conditions, resulted in good yields and complete regioselectivity. Moreover, starting from enantiopure carbonates, complete retention of the configuration could be observed, affording enantiopure allylic amines.

1. Introduction

The C–N bond formation is one of the most important linkages in organic chemistry and allows the preparation of unusual amino acids. The substitution of allylic acetates or carbonates is a powerful method for the preparation of allylic amines and represents one of the most attractive procedures for their asymmetric synthesis.[1] While primary allylic carbonates have been widely studied, the substrates bearing substituents in Cα, Cβ, and Cγ have received less attention. Recently, we reported a pratical regio- and stereoselective synthesis of dehydro-β-amino esters via amination of racemic and enantiomerically pure allylic carbonates.[2] Dehydro-β-amino esters are interesting precursors of unsaturated or saturated β-amino acids and also β-lactams.[3] In an ongoing project dealing with the use of the α,β′-unsaturated β-amino acids, we envisaged their insertion as a rigid core in small constrained non-peptidic molecules mimicking the RGD motif. This sequence is present in a wide number of extracellular matrix proteins like fibronectin, fibrinogen, vitronectin capable of the inhibition of integrin subtypes such as $\alpha_v\beta_3$ and $\alpha_5\beta_1$.[4]

2. Results and discussion

In our previous work we reported that the uncatalyzed reaction proceeds via an S_N2' mechanism affording exclusively the regioisomer A (Fig. 1).[5] On the other hand, under palladium-catalyzed conditions,[2,6] the substitution of carbonates with benzylamine showed a strong solvent-dependent regiocontrol affording almost exclusively one of the two possible regioisomers.[7] In particular, regioisomer B, which is the object of this study, is preferentially obtained when the reaction is performed in CH_3CN. In both cases, we observed a complete transfer of chirality from the starting substrate to the products.

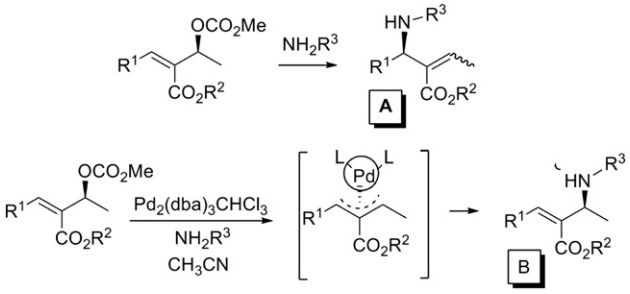

Figure 1. Allylic carbonate substitution.

* Corresponding authors. E-mail address: giuliana.cardillo@unibo.it (G. Cardillo).

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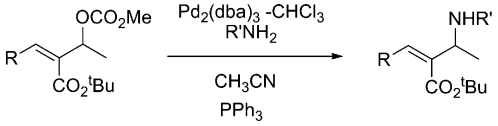
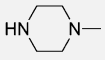
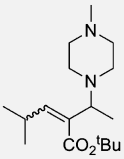
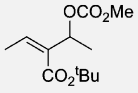
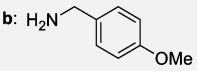
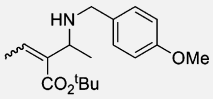
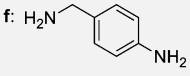
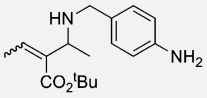
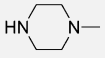
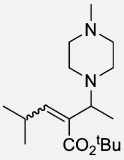
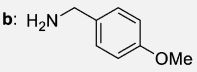
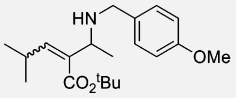
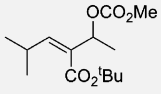
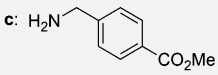
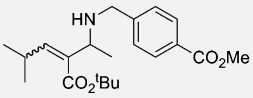
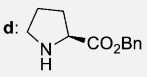
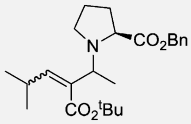
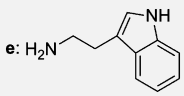
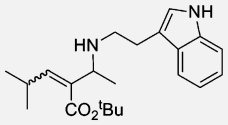
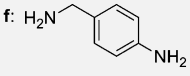
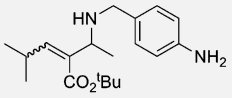
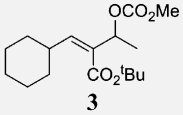
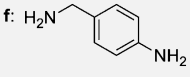
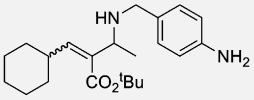
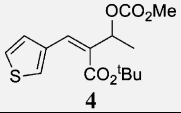
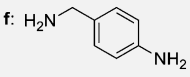
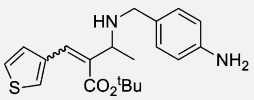
To complete our work, we present here the development of previously reported results under Pd catalyzed conditions using the carbonates **1**–**4** and a variety of amines as nucleophiles.[2] The reaction was carried out in CH_3CN. Initially, a series of experiments was performed using racemic carbonates **1**–**4** with bifunctionalized amines in the presence of 2.5 mol % $Pd_2(dba)_3/CHCl_3$.

The usual work-up[2] and purification by column chromatography provided the products (Table 1).

Table 1
Pd-catalyzed substitution on racemic carbonates **1**–**4**



Entry	Reagent	Amine	Product		Yield[a] (%)	*Z*/*E*
1		**a**: 		**5a**	40 35[b]	50/50
2	 **1**	**b**: 		**5b**	35[b]	20/80
3		**f**: 		**5f**	60	30/70
4		**a**: 		**6a**	47	95/5
5		**b**: 		**6b**	45	95/5
6	 **2**	**c**: 		**6c**	40	95/5
7		**d**: 		**6d**	60	95/5
8		**e**: 		**6e**	60	92/8
9		**f**: 		**6f**	65	95/5
10	 **3**	**f**: 		**7f**	70	90/10
11	 **4**	**f**: 		**8f**	87	20/80

[a] All experiments were performed using racemic carbonates **1**–**4** with bifunctionalized amines in the presence of 2.5% $Pd_2(dba)_3/CHCl_3$ and refluxing in CH_3CN for 12 h. Yields were calculated after purification of the products by flash chromatography on silica gel.

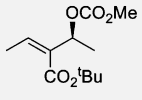
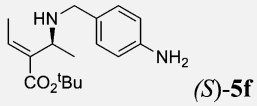
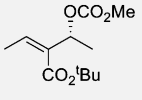
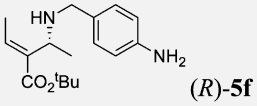
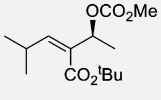
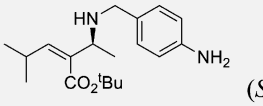
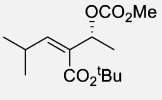
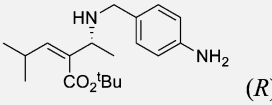
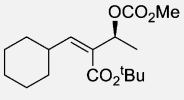
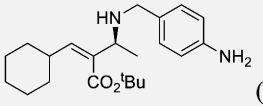
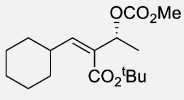
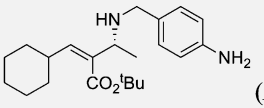
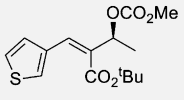
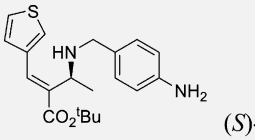
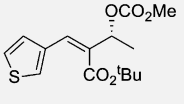
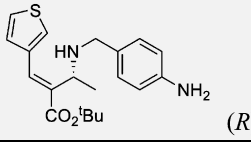
[b] The reaction was conducted with 5 mol % PPh_3 as additive.

Carbonate **1** reacted with *N*-methylpiperazine in the presence, or in the absence, of PPh_3[8] giving the expected regioisomer **5a** in low yield and in both cases with complete isomerization of the double bond (*E*/*Z* ratio 1:1, Table 1 entry 1).[9] Similar results have been obtained in the reaction of **1** with *p*-methoxybenzylaniline and **5b** was isolated in moderate yield as a mixture 80:20 of *E*/*Z* isomers (entry 2). The configuration of the double bond was attributed on the basis of the vinyl proton ^{1}H NMR chemical shift and confirmed by NOE experiments.[3b,10a,10b,10c] On reaction of **1** with 4-aminomethylaniline as a nucleophile, **5f** was obtained in higher yield, in a 70:30 *E*/*Z* ratio of geometrical isomers (Table 1 entry 3).

The carbonate **2** also provided the corresponding products in good yield, but in this case with preferential formation of the *Z* isomer (*Z*/*E* ratio from 92:8 to 95:5). No trace of the regioisomer deriving from the S_N2' mechanism was detected in the ^{1}H NMR of the crude, while traces of about 10–20% of the unreacted starting material were observed (Table 1 entries from 4–6, 8, and 9). The benzyl L-proline (Table 1 entry 7) underwent substitution giving 4-aminomethylaniline acting as the nucleophile gave the corresponding compounds **7f** and **8f**, isolated in good yield by flash chromatography on silica gel. The 4-aminomethylaniline exclusively reacted at the benzylamine function to give complete regioselectivity (Table 1 entries 10 and 11). A good *Z*/*E* ratio could be observed for **7f** (90/10), while for **8f** the preferential formation of the *E* isomer was obtained (*Z*/*E* ratio 20:80), as already observed for **5b** and **5f**.

We focused our attention on the products derived by the substitution reactions with 4-aminomethyaniline as they are interesting intermediates for the synthesis of potential RGD mimetics. Therefore, with these results in hand, we investigated this reaction on enantiomerically pure carbonates. Resolution of racemic allylic alcohols via *Pseudomonas Cepacia* lipase acetylation afforded enantiomerically pure *Z*-(*S*)-allylic alcohols and *Z*-(*R*)-acetates that were easily converted into the corresponding carbonates.[11] The results obtained on treating optically active carbonates **1**–**4** with 4-aminomethylaniline are reported in Table 2.

Table 2
Reaction of enantiomerically pure carbonates **1**–**4** with 4-aminomethylaniline

Entry	Substrate	Product[a]	ee[b](%)	Yield (%)
1	 (*S*)-**1**	 (*S*)-**5f**	>99	72
2	 (*R*)-**1**	 (*R*)-**5f**	>99	58
3	 (*S*)-**2**	 (*S*)-**6f**	>99	61
4	 (*R*)-**2**	 (*R*)-**6f**	>99	59
5	 (*S*)-**3**	 (*S*)-**7f**	>99	68
6	 (*R*)-**3**	 (*R*)-**7f**	>99	60
7	 (*S*)-**4**	 (*S*)-**8f**	>99	85
8	 (*R*)-**4**	 (*R*)-**8f**	>99	78

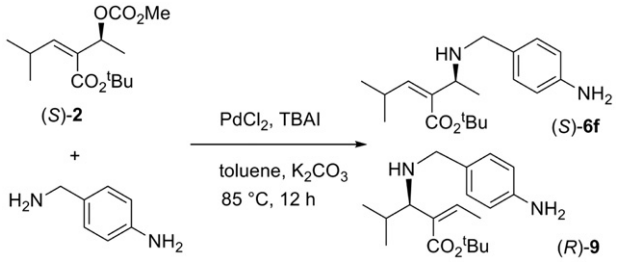
[a] Reaction carried out in the presence of 2.5 mol % $Pd_2(dba)_3/CHCl_3$ in refluxing CH_3CN.
[b] Determined by HPLC on chiral column on isolated pure compounds (Chiralcel AD column for **5f** and **7f**, Chiralcel IA column for **6f**, Chiralcel OJ column for **8f**).

almost exclusively the corresponding dehydro-β-amino esters with the *Z* geometry of the double bond (*Z*/*E* ratio 95:5) but as a 1:1 mixture of diastereoisomers, with respect to the newly formed C–N bond. Finally the reaction of carbonates **3** and **4** with

The enantiomeric excess of isolated products were determined by HPLC on chiral column, after separation of the *Z* isomer from the *E* isomer. The configuration of the newly created stereocentre was unequivocally attributed on the basis of previously reported

research[2] and on the basis of mechanistic considerations. In fact, the mechanism for the palladium-catalyzed allylic amination is generally accepted to proceed via a palladium/allyl complex that in the second step is attacked directly by the amine nucleophile, in analogy with the reaction mechanism for soft carbon nucleophiles. Since both the oxidative addition leading to palladium complex and the nucleophilic attack occur with inversion of configuration at the reacting allylic carbon atom, the overall process proceeds with retention of configuration.[12]

Finally, in order to verify the usefulness of our procedure and to optimize our methodologies on the basis of modern techniques, we tested palladium nanoparticles as catalysts. In a recent paper Ranu and co-workers[13] explored the efficient allylic amination of allyl alcohol derivatives catalyzed by palladium nanoparticles in the presence of a base. This research group described a new protocol that gave good yields of allylated amines. On the basis of the considerable interest in the metal nanoparticles,[14] we applied the Ranu's protocol to our substrate. The reaction was first performed on the racemic **2**, then on the (*S*)-**2** carbonate. After the period of time required for completion, the reaction was worked-up as usual (Scheme 1).



Scheme 1. Pd-nanoparticles catalyzed reaction.

The regioisomers (*S*)-**6f** and (*R*)-**9**[5] were obtained in 60:40 ratio and were separated by flash chromatography. The ^{1}H NMR spectrum of (*S*)-**6f** showed the exclusive presence of the *Z* isomer and the chiral HPLC analysis showed only the (*S*) enantiomer. On the contrary, (*R*)-**9** was isolated as a 1:1 mixture of *Z*/*E* isomers. This protocol lacked in regioselectivity, affording both **6f** and **9**, but a high stereoselectivity could be observed in the double bond and the stereocentre formation of **6f**.

In conclusion, we have reported herein some examples on the substitution of bifunctionalized amines on allylic carbonates via a regio- and stereoselective Pd-catalyzed reaction. Optimized conditions gave access to dehydro-β-amino esters generally in good yields. Starting from enantiopure derivatives, we observed complete retention of the initial stereochemistry. A new procedure, taking advantage of Pd-nanoparticles technology was also tested, showing unfortunately a lack of regioselectivity.

3. Experimental section

3.1. General

All chemicals were purchased from commercial suppliers and used without further purification. Anhydrous solvents were purchased in Sure/Seal bottles (250 mL) over molecular sieves and used without further drying. Flash chromatography was performed on silica gel (230–400 mesh). NMR Spectra were recorded with Varian Gemini 200, Mercury Plus 400 or Unity Inova 600 MHz spectrometers. Chemical shifts were reported as δ values (ppm) relative to the solvent peak of $CDCl_3$ set at δ=7.27 (^{1}H NMR) or δ=77.0 (^{13}C NMR). Coupling constants are given in hertz. The enantiomeric excesses of products were determined by HPLC analyses performed an HP1100 instrument with UV/vis detector and equipped with chiral column (Chiralcel AD, OJ or IA columns) eluted with *n*-hexane/2-propanol. Optical rotations were measured in a Perkin/Elmer 343 polarimeter using a 1 dm cuvette and are referenced to the Na-D line value at 25 °C. Melting points were determined on a Stuart Scientific SMP3 apparatus and are uncorrected.

3.2. General procedure for the preparation of the carbonates 1–4

To a solution of the *Z*-allylic alcohol (1 mmol) in dry THF (10 mL), under an inert atmosphere at −78 °C, LiHMDS (1.5 equiv, 1.5 mL 1 M solution in THF) was added dropwise. The solution was stirred for 30 min and then methyl chloroformate (2 equiv, 2 mmol) was added in one portion. After 40 min, the mixture was quenched with water (2 mL) and THF removed under reduced pressure. The residue was diluted with ethylacetate (10 mL) and washed twice with water (5 mL). The two phases were separated, the organic layer was dried over Na_2SO_4, and solvent was removed under reduced pressure. Carbonates **1**–**4** were isolated by flash chromatography on silica gel (cyclohexane/ethylacetate 95/5 as eluant).

*3.2.1. Compound **1**.* Yellow oil; R_f (30% ethylacetate/70% cyclohexane) 0.64; ^{1}H NMR ($CDCl_3$, 200 MHz) δ 1.45 (d, *J*=6.6 Hz, 3H, CH_3CHO), 1.51 (s, 9H, OC(CH_3)$_3$), 1.99 (d, *J*=7.2 Hz, 3H, CH_3CHC), 3.76 (s, 3H, CH_3OCO), 5.48 (q, *J*=6.6 Hz, 1H, CH_3CHO), 6.23 (q, *J*=7.2 Hz, 1H, CH_3CHC); ^{13}C NMR ($CDCl_3$, 75 MHz) δ_C 15.3, 20.0, 28.3 (3C), 54.6, 74.1, 81.3, 134.4, 135.8, 155.0, 165.5; IR (neat, cm^{-1}) 792, 852, 941, 1047, 1155, 1264, 1368, 1443, 1725, 1751, 2976. (*S*) Enantiomer: $[\alpha]_D$ −24.6 (*c* 1 in $CHCl_3$); (*R*) enantiomer: $[\alpha]_D$ +25.0 (*c* 1 in $CHCl_3$); LC-ESI-MS rt 9.77 min, *m*/*z* 244 (M), 267 (M+Na). Anal. Calcd for $C_{12}H_{20}O_5$(244.13): C 59.00, H 8.25; found C 59.09, H 8.28.

*3.2.2. Compound **2**.* Pale yellow oil; R_f (30% ethylacetate/70% cyclohexane) 0.78; ^{1}H NMR ($CDCl_3$, 200 MHz) δ 1.01 (d, *J*=6.6 Hz, 6H, CH_3CHCH_3), 1.42 (d, *J*=6.6 Hz, 3H, CH_3CHO), 1.50 (s, 9H, OC(CH_3)$_3$), 3.02–3.17 (m, 1H, CH_3CHCH_3), 3.77 (s, 3H, CH_3OCO), 5.46 (q, *J*=6.6 Hz, 1H, CH_3CHO), 5.84 (d, *J*=9.6 Hz, 1H, CHC*H*C); ^{13}C NMR ($CDCl_3$, 75 MHz) δ_C 19.8, 22.5 (2C), 26.2, 28.1 (3C), 54.5, 74.0, 81.2, 131.3, 146.7, 155.0, 165.6; IR (neat, cm^{-1}) 792, 941, 1047, 1154, 1269, 1344, 1368, 1442, 1717, 1750, 2871, 2975. (*S*) Enantiomer: $[\alpha]_D$ −30.0 (*c* 1 in $CHCl_3$); (*R*) enantiomer: $[\alpha]_D$ +28.9 (*c* 1 in $CHCl_3$); LC-ESI-MS rt 11.82 min, *m*/*z* 272 (M), 295 (M+Na). Anal. Calcd for $C_{14}H_{24}O_5$(272.16): C 61.74, H 8.88; found C 61.76, H 8.86.

*3.2.3. Compound **3**.* Pale yellow oil; R_f (30% ethylacetate/70% cyclohexane) 0.81; ^{1}H NMR ($CDCl_3$, 200 MHz) δ 0.86–1.30 (m, 6H, *cyclohexyl*), 1.39 (d, *J*=6.2 Hz, 3H, CH_3CHO), 1.47 (s, 9H, OC(CH_3)$_3$), 1.66–1.79 (m, 4H, *cyclohexyl*), 2.78 (bq, *J*=10.4 Hz 1H, C*H* cyclohexyl), 3.74 (s, 3H, CH_3OCO), 5.43 (q, *J*=6.2 Hz, 1H, CH_3CHO), 5.83 (d, *J*=9.4 Hz, 1H, CHC*H*C); ^{13}C NMR ($CDCl_3$, 75 MHz) δ_C 19.9, 25.5, 25.8, 28.1 (3C), 32.4 (2C), 37.7 (2C), 54.5, 74.0, 81.0, 131.5, 145.4, 154.8, 165.5; IR (neat, cm^{-1}) 734, 791, 846, 941, 966, 1003, 1848, 1086, 1153, 1223, 1265, 1368, 1393, 1448, 1718, 1751, 2852, 2926. (*S*) Enantiomer: $[\alpha]_D$ −25.2 (*c* 1 in $CHCl_3$); (*R*) enantiomer: $[\alpha]_D$ +26.7 (*c* 1 in $CHCl_3$); LC-ESI-MS rt 10.81 min, *m*/*z* 312 (M), 335(M+Na). Anal. Calcd for $C_{17}H_{28}O_5$(312.19): C 65.36, H 9.03; found C 65.51, H 9.05.

*3.2.4. Compound **4**.* Yellow oil; R_f (30% ethylacetate/70% cyclohexane) 0.70; ^{1}H NMR ($CDCl_3$, 200 MHz) δ 1.49 (s, 9H, OC(CH_3)$_3$), 1.53 (d, *J*=6.6 Hz, 3H, CH_3CHO), 3.78 (s, 3H, CH_3OCO), 5.51 (q, *J*=6.6 Hz, 1H, CH_3CHO), 6.72 (s, 1H, CC*H*C), 7.14–7.31 (m, 3H, *thiophenyl*); ^{13}C NMR ($CDCl_3$, 75 MHz) δ_C 20.1, 28.0 (3C), 54.8, 75.3, 82.1, 125.3, 126.5, 126.7, 128.2, 133.2, 136.1, 155.0, 166.6; IR (neat, cm^{-1}) 790, 845, 937, 986, 1008, 1049, 1086, 1146, 1268, 1367, 1406, 1442, 1647, 1716, 2552, 2932, 2980, 3101, 3362. (*S*) Enantiomer: $[\alpha]_D$ +46.0 (*c* 1 in $CHCl_3$); (*R*)

enantiomer: $[\alpha]_D$ −42.0 (*c* 1 in $CHCl_3$); LC-ESI-MS rt 10.59 min, *m*/*z* 312 (M), 335(M+Na). Anal. Calcd for $C_{15}H_{20}O_5S$(312.1): C 57.67, H 6.45, S 10.26; found C 57.85, H 6.44, S 10.29.

3.3. General procedure for the preparation of the dehydro-β-amino esters

To a solution of the carbonate **1**–**4** (0.2 mmol) in dry CH_3CN (2 mL), under nitrogen atmosphere, $Pd_2(dba)_3/CHCl_3$ (2.5%, 0.005 mmol) was added in one portion. After stirring the solution at room temperature for 30 min, the amine (1.2 equiv) was added. The solution was refluxed for 12 h and then the mixture was filtered through a Celite pad and concentrated under reduced pressure. The dehydro-β-amino ester was isolated by flash chromatography on silica gel.

3.3.1. Compound ***5a***. Orange oil (40%), (1:1 *E*/*Z* mixture); R_f (30% ethylacetate/70% cyclohexane) 0.10; ^{1}H NMR (200 MHz, $CDCl_3$) (*E*) δ 1.09 (d, *J*=6.6 Hz, 3H, CH_3CHN), 1.46 (s, 9H, OC(CH_3)$_3$), 1.84 (d, *J*=7.4 Hz, 3H, CH_3CHC), 2.44 (s, 3H, CH_3N), 2.50–2.80 (m, 8H, *piperazine*), 3.42 (q, *J*=7.4 Hz, 1H, CH_3CHN), 6.63 (q, *J*=6.6 Hz, 1H, CH_3CHC); (*Z*) δ 1.26 (d, *J*=6.6 Hz, 3H, CH_3CHN), 1.42 (s, 9H, OC(CH_3)$_3$), 1.78 (d, *J*=7.4 Hz, 3H, CH_3CHC), 2.44 (s, 3H, CH_3N), 2.50–2.80 (m, 8H, *piperazine*), 3.42 (q, *J*=7.4 Hz, 1H, CH_3CHN), 5.70 (q, *J*=6.6 Hz, 1H, CH_3CHC);^{13}C NMR (75 MHz, $CDCl_3$) δ 15.6, 17.7, 28.3 (3C), 47.6, 55.8, 57.0 (2C), 57.4 (2C), 90.0, 132.3, 135.9, 164.3; IR (neat, cm^{-1}) 696, 721, 802, 1014, 1119, 1152, 1261, 1367, 1392, 1454, 1622, 1712, 2795, 2852, 2930, 2964, 3364. Anal. Calcd for $C_{15}H_{28}N_2O_2$ (268.4): C 67.13, H 10.52, N 10.44; found C 67.07, H 10.52, N 10.46.

3.3.2. Compound ***5b***. Yellow oil (35%), (80:20 *E*/*Z* mixture); R_f (30% ethylacetate/70% cyclohexane) 0.10; ^{1}H NMR (200 MHz, $CDCl_3$) (*E*) δ 1.34 (d, *J*=6.6 Hz, 3H, CH_3CHN), 1.52 (s, 9H, OC(CH_3)$_3$), 1.74 (d, *J*=7.4 Hz, 3H, CH_3CHC), 2.58 (br s, 1H, N*H*), 3.53 (d, *J*=12.4 Hz, 1H, HNCH_2), 3.69 (d, *J*=12.4 Hz, 1H, HNCH_2), 3.73 (q, *J*=6.6 Hz, 1H, CH_3CHN), 3.81 (s, 3H, OCH_3), 6.80–6.86 (m, 1H, CH_3CHC), 6.85 (d, *J*=8.4 Hz, 2H, *phenyl*), 7.24 (d, *J*=8.4 Hz, 2H, *phenyl*); ^{13}C NMR (75 MHz, $CDCl_3$) δ 13.8, 20.6, 28.3 (3C), 50.0, 50.7, 55.3, 80.7, 113.8 (2C), 129.5 (2C), 132.0, 135.9, 137.9, 151.1, 166.7; IR (neat, cm^{-1}) 699, 766, 832, 1031, 1097, 1160, 1258, 1339, 1449, 1511, 1577, 1604, 1651, 1698, 2850, 2926, 2961, 3366. Anal. Calcd for $C_{18}H_{27}NO_3$ (305.4): C 70.79, H 8.91, N 4.59; found C 70.52, H 8.94, N 10.47.

3.3.3. Compound ***5f***. Yellow oil (60%), (70:30 *E*/*Z* mixture); R_f (50% ethylacetate/50% cyclohexane on alumina plates) 0.23; ^{1}H NMR ($CDCl_3$, 200 MHz) (*E*) δ 1.31 (d, *J*=7 Hz, 3H, CH_3CHN), 1.50 (s, 9H, OC(CH_3)$_3$), 1.72 (d, *J*=7.4 Hz, 3H, CH_3CHC), 3.43 (d, *J*=12.4 Hz, 1H, HNCH_2), 3.60 (d, *J*=12.4 Hz, 1H, HNCH_2), 3.72 (q, *J*=6.6 Hz, 1H, CH_3CHN), 6.63 (d, *J*=8 Hz, 2H, *phenyl*), 6.81 (q, *J*=7.4 Hz, 1H, CH_3CHC), 7.08 (d, *J*=8 Hz, 2H, *phenyl*); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 13.8, 20.7, 28.4 (3C), 49.9, 51.0, 80.5, 115.2 (2C), 129.4 (2C), 130.6, 136.3, 137.7, 145.2, 166.7; IR (neat, cm^{-1})1141, 1278, 1367, 1392, 1453, 1517, 1632, 1695, 2929, 2975, 3216, 3368, 3445. LC-ESI-MS rt 8.39 min, *m*/*z* 290 (M), 313 (M+Na). Chiral HPLC analysis 99:1 to 96:4 *n*-hexane/2-propanol in 30 min, 1.0 mL/min, AD column, rt 23.52 min for [*E*-(*R*)-**5f**] and 26.12 min [*E*-(*S*)-**5f**]; *E*-(*S*)-**5f** $[\alpha]_D$ −14.0 (*c* 1 in $CHCl_3$); *E*-(*R*)-**5f** $[\alpha]_D$ +14.0 (*c* 1 in $CHCl_3$). Anal. Calcd for $C_{17}H_{26}N_2O_2$ (290.2): C 70.31, H 9.02, N 9.65; found C 70.08, H 9.00, N 9.65.

3.3.4. Compound ***6a***. Orange oil (47%), (95:5 *Z*/*E* mixture); R_f (40% ethylacetate/60% cyclohexane) 0.12; ^{1}H NMR (200 MHz, $CDCl_3$) (*Z*): δ 0.96 (d, *J*=6.6 Hz, 3H, CH_3CHCH_3), 0.99 (d, *J*=6.6 Hz, 3H, CH$_3$CHCH_3), 1.09 (d, *J*=7 Hz, 3H, CH_3CHN), 1.49 (s, 9H, OC(CH_3)$_3$), 2.24 (s, 3H, CH_3N), 2.25–2.40 (m, 8H, *piperazine*), 2.65–2.83 (m, 1H, CH$_3$C*H*CH$_3$), 3.40 (q, *J*=7 Hz, 1H, CH_3CHN), 5.33 (d, *J*=9.6 Hz, 1H, CHC*H*C); ^{13}C NMR (75 MHz, $CDCl_3$) δ 12.8, 22.9 (2C), 28.4 (3C), 28.6, 46.1, 55.7 (4C), 60.9, 80,3, 135.6, 140.4, 167.2; IR (neat, cm^{-1}) 1014, 1148, 1239, 1322, 1366, 1455, 1716, 2793, 2869, 2935, 2969. LC-MS-ESI rt 1.73, 297 (M+1). Anal. Cacld for $C_{17}H_{32}N_2O_2$ (296.4): C 68.88, H 10.88, N 9.45; found C 68.93, H 10.89, N 9.43.

3.3.5. Compound ***6b***. Yellow oil (45%), (95:5 *Z*/*E* mixture); R_f (30% ethylacetate/70% cyclohexane) 0.33; ^{1}H NMR (200 MHz, $CDCl_3$) (*Z*): δ 1.03 (d, *J*=6.6 Hz, 3H, CH_3CHCH_3), 1.07 (d, *J*=6.6 Hz, 3H, CH$_3$CHCH_3), 1.25 (d, *J*=6.6 Hz, 3H, CH_3CHN), 1.53 (s, 9H, OC(CH_3)$_3$), 1.82 (br s, 1H, N*H*), 2.84–3.06 (m, 1H, CH$_3$C*H*CH$_3$), 3.32 (q, *J*=6.6 Hz, 1H, CH_3CHN), 3.53 (d, *J*=12.6 Hz, 1H, HNCH_2), 3.73 (d, *J*=12.6 Hz, 1H, HNCH_2), 3.80 (s, 3H, OCH_3), 5.55 (d, *J*=10.0 Hz, 1H, CHC*H*C) 6.86 (d, *J*=8.8 Hz, 2H, *phenyl*), 7.25 (d, *J*=8.8 Hz, 2H, *phenyl*); ^{13}C NMR (75 MHz, $CDCl_3$) δ 21.4, 22.8, 23.2, 28.4 (3C), 28.7, 50.5, 55.3, 57.0, 80.9, 113.8 (2C), 129.5 (2C), 132.9, 133.7, 144.4, 158.6, 167.9; IR (neat, cm^{-1}) 829, 848, 1037, 1152, 1246, 1300, 1320, 1367, 1392, 1465, 1512, 1611, 1707, 2834, 2868, 2932, 2966. LC-MS-ESI rt 4.13, 334 (M+1). Anal. Calcd for $C_{20}H_{31}NO_3$ (333.4): C 72.04, H 9.37, N 4.20; found C 71.95, H 9.40, N 4.18.

3.3.6. Compound ***6c***. Yellow oil (40%), (95:5 *Z*/*E* mixture); R_f (30% ethylacetate/70% cyclohexane) 0.35; ^{1}H NMR (200 MHz, $CDCl_3$) (*Z*): δ 0.98 (d, *J*=6.2 Hz, 3H, CH$_3$CHCH_3), 1.04 (d, *J*=6.2 Hz, 3H, CH_3CHCH$_3$), 1.24 (d, *J*=6.6 Hz, 3H, CH_3CHN), 1.51(s, 9H, OC(CH_3)$_3$), 1.77 (br s, 1H, N*H*), 2.86–3.02 (m, 1H, CH$_3$C*H*CH$_3$), 3.27 (q, *J*=6.6 Hz, 1H, CH_3CHN), 3.65 (d, *J*=13.4 Hz, 1H, HNCH_2), 3.84 (d, *J*=13.4 Hz, 1H, HNCH_2), 3.92 (s, 3H, OCH_3), 5.51 (d, *J*=9.8 Hz, 1H, CHC*H*C), 7.40 (d, *J*=8.4 Hz, 2H, *phenyl*), 7.99 (d, *J*=8.4 Hz, 2H, *phenyl*); ^{13}C NMR (75 MHz, $CDCl_3$) δ 21.2, 22.7, 23.2, 28.4, 28.6, 50.7, 52.1, 57.4, 81.1, 128.1, 128.2 (2C), 128.8, 129.7 (2C), 144.8, 146.0, 163.5, 164.2; IR (neat, cm^{-1}) 699, 759, 1019, 1151, 1278, 1367, 1435, 1615, 1656, 1683, 1722, 2868, 2930, 2965. LC-MS-ESI rt 5.33, 362 (M+1). Anal. Calcd for $C_{21}H_{31}NO_4$ (361.4): C 69.78, H 8.64, N 3.87; found C 69.52, H 8.63, N 3.87.

3.3.7. Compound ***6d***. Yellow oil (60%); (95:5 *Z*/*E* mixture; 1:1 diastereomeric mix); R_f (30% ethylacetate/70% cyclohexane) 0.40; *Z*-isomer A; ^{1}H NMR (200 MHz, $CDCl_3$) δ 0.92–1.00 (m, 6H, CH_3CHCH_3), 1.25 (d, *J*=7 Hz, 3H, CH_3CHN), 1.48 (s, 9H, OC(CH_3)$_3$), 1.76–1.92 (m, 4H, NCH$_2$CH_2CH_2), 2.63–2.83 (m, 2H, NCH_2), 3.00–3.10 (m, 1H, CH$_3$C*H*CH$_3$), 3.54–3.68 (m, 2H, CH$_3$C*H*N, NC*H*CO), 5.12 (s, 2H, CH_2Ph), 5.48 (d, *J*=9.8 Hz, 1H, CHC*H*C), 7.28–7.41 (m, 5H, *phenyl*); *Z*-isomer B: ^{1}H NMR (200 MHz, $CDCl_3$) δ 0.94 (m, 6H, CH_3CHCH_3), 1.18 (d, *J*=7 Hz, 3H, CH_3CHN), 1.50 (s, 9H, OC(CH_3)$_3$), 1.76–1.92 (m, 4H, NCH$_2$CH_2CH_2), 2.63–2.83 (m, 2H, NCH_2), 3.00–3.10 (m, 1H, CH$_3$C*H*CH$_3$), 3.54–3.68 (m, 2H, CH$_3$C*H*N, NC*H*CO), 5.12 (s, 2H, CH_2Ph), 5.55 (d, *J*=9.8 Hz, 1H, CHC*H*C), 7.28–7.41 (m, 5H, *phenyl*); ^{13}C NMR (75 MHz, $CDCl_3$) δ 17.8, 22.8, 23.4, 27.0, 28.3, 28.6, 30.1, 49.2, 59.1, 62.3, 66.0, 80.7, 128.1 (2C), 128.2(2C), 128.6(2C), 136.2, 143.3, 168.4, 175.1; IR (neat, cm^{-1}) 697, 750, 1149, 1241, 1270, 1367, 1392, 1455, 1732, 2869, 2971; LC-MS-ESI rt 5.57, 402 (M+1). LC-MS-ESI rt 5.61, 402 (M+1). Anal. Calcd for $C_{24}H_{35}NO_4$ (401.5): C 71.79, H 8.79, N 3.49; found C 72.03, H 8.78, N 3.48.

3.3.8. Compound ***6e***. Brown oil (60%) (95:5 *Z*/*E* mixture); R_f (30% ethylacetate/70% cyclohexane) 0.12; ^{1}H NMR (200 MHz, $CDCl_3$) (*Z*) δ 0.97 (d, *J*=6.6 Hz, 3H, CH_3CHCH_3), 0.98 (d, *J*=6.6 Hz, 3H, CH$_3$CHCH_3), 1.23 (d, *J*=6.6 Hz, 3H, CH_3CHN), 1.41 (s, 9H, OC(CH_3)$_3$), 1.98 (br s, 1H, N*H*), 2.79–3.00 (m, 5H, NCH_2CH_2, CH$_3$C*H*CH$_3$), 3.37 (q, *J*=6.6 Hz, 1H, CH_3CHN), 5.52 (d, *J*=9.4 Hz, 1H, CHC*H*C), 7.01 (s, 1H, NC*H aromatic*), 7.01–7.21 (m, 2H, *phenyl*), 7.34 (d, *J*=7.4 Hz, 1H, *phenyl*), 7.61 (d, *J*=7.8 Hz, 1H, *phenyl*), 8.29 (br s, 1H, N*H aromatic*); ^{13}C NMR (75 MHz, $CDCl_3$) δ 21.4, 22.8, 23.1, 26.1, 28.2 (3C), 28.5, 47.3, 57.5, 81.0, 111.2, 114.2, 119.0, 119.2, 121.9, 128.5, 128.8, 132.1, 136.5, 144.8, 167.7; IR (neat, cm^{-1}) 739, 1120, 1152, 1244, 1367, 1455, 1703,

2868, 2927, 2971, 3057, 3408; LC-MS-ESI rt 5.57, 357 (M+1). Anal. Calcd for $C_{22}H_{32}N_2O_2$ (356.5): C 74.12, H 9.05, N 7.86; found C 73.84, H 9.02, N 7.86.

3.3.9. Compound ***6f****.* Yellow oil (65%), (95:5 *Z*/*E* mixture); R_f (40% ethylacetate/60% cyclohexane) 0.14; ^{1}H NMR ($CDCl_3$, 200 MHz) (*Z*): δ 1.02 (d, *J*=5.4 Hz, 3H, CH_3CHCH$_3$), 1.05 (d, *J*=5.4 Hz, 3H, CH$_3$CHCH_3), 1.23 (d, *J*=7.8 Hz, 3H, CH_3CHN), 1.51 (s, 9H, OC(CH_3)$_3$), 2.86–3.02 (m, 1H, CH$_3$C*H*CH$_3$), 3.31 (q, *J*=6.6 Hz, 1H, CH$_3$C*H*N), 3.46 (d, *J*=12.6 Hz, 1H, HNCH_2), 3.66 (d, *J*=12.6 Hz, 1H, HNCH_2), 5.55 (d, *J*=9.6 Hz, 1H, CHC*H*C), 6.63 (d, *J*=7.8 Hz, 2H, *phenyl*), 7.10 (d, *J*=7.8 Hz, 2H, *phenyl*); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 21.5, 22.8, 23.3, 28.4 (3C), 28.6, 50.6, 56.9, 80.9, 115.2 (2C), 129.4 (2C), 130.7, 133.7, 144.5, 145.3, 167.9; IR (neat, cm^{-1}) 1152, 1241, 1277, 1367, 1392, 1454, 1518, 1622, 1700, 2868, 2929, 2969, 3218, 3372. LC-MS-ESI: rt 2.9 min 319 (M+1); [*Z*-(*R*)-**6f**]: $[\alpha]_D$ −4.8 (*c* 1 in $CHCl_3$); [*Z*-(*S*)-**6f**]: $[\alpha]_D$ +6.6 (*c* 1 in $CHCl_3$). Chiral HPLC analysis 98:2 to 90:10 *n*-hexane/2-propanol in 25 min, 0.8 mL/min, IA column, rt 15.10 min for [*Z*-(*R*)-**6f**] and 15.61 min for [*Z*-(*S*)-**6f**]. Anal. Calcd for $C_{19}H_{30}N_2O_2$ (318.4): C 71.66, H 9.50, N 8.80; found C 71.69, H 9.46, N 8.82.

3.3.10. Compound ***7f****.* Yellow oil (70%), (90:10 *Z*/*E* mixture); R_f (30% ethylacetate/70% cyclohexane) 0.13; ^{1}H NMR ($CDCl_3$, 200 MHz) (*Z*): δ 1.00–1.10, (m, 6H, *cyclohexyl*), 1.25 (d, *J*=Hz, 3H, CH_3CHN), 1.52 (s, 9H, OC(CH_3)$_3$), 1.60–1.80 (m, 4H, *cyclohexyl*), 2.52–2.68 (m, 1H, C*H* cyclohexyl), 3.31 (q, *J*=6.6 Hz, 1H, CH$_3$C*H*N),3.45 (d, *J*=13 Hz, 1H, HNCH_2), 3.65 (d, *J*=13 Hz, 1H, HNCH_2), 5.57, (d, *J*=9.6 Hz, 1H, CHC*H*C), 6.63 (d, *J*=7.8 Hz, 2H, *phenyl*), 7.09 (d, *J*=7.8 Hz, 2H, *phenyl*); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 21.5, 25.8, 28.4 (3C), 32.9 (2C), 33.3 (2C), 38.3, 50.6, 56.9, 80.8, 115.2 (2C), 129.4 (2C), 130.7, 134.1, 142.9, 145.3, 167.9; IR (neat, cm^{-1}) 826, 489, 1111, 1152, 1221, 1252, 1267, 1367, 1392, 1448, 1518, 1622, 1698, 2850, 2925, 2974, 3218, 3372. [*Z*-(*R*)-**7f**]: $[\alpha]_D$ −6.1 (*c* 1 in $CHCl_3$); [*Z*-(*S*)-**7f**]: $[\alpha]_D$ +7.8 (*c* 1 in $CHCl_3$), LC-MS-ESI rt 5.56, 359 (M+1). Chiral HPLC analysis 95:5 to 90:10 *n*-hexane/2-propanol in 25 min, 1.0 mL/min, AD column, rt 11.10 min for [*Z*-(*R*)-**7f**] and 14.08 min for [*Z*-(*S*)-**7f**]. Anal. Calcd for $C_{22}H_{34}N_2O_2$ (358.5): C 73.70, H 9.56, N 7.81; found C 73.77, H 9.53, N 7.82.

3.3.11. Compound ***8f****.* Orange oil (87%), (80:20 *E*/*Z* mixture); R_f (40% ethylacetate/60% cyclohexane) 0.12; ^{1}H NMR ($CDCl_3$, 200 MHz) (*E*): δ 1.32 (d, *J*=7 Hz, 3H, CH_3CHN), 1.57 (s, 9H, OC(CH_3)$_3$), 3.42 (d, *J*=12 Hz, 1H, HNCH_2), 3.60 (d, *J*=12 Hz, 1H, HNCH_2), 4.10 (q, *J*=7 Hz, 1H, CH$_3$C*H*N), 6.57 (d, *J*=8.4 Hz, 2H, *phenyl*), 6.66 (d, *J*=7.6 Hz, 1H, *thiophenyl*), 6.99 (d, *J*=8.4 Hz, 2H, *phenyl*), 7.08–7.19 (m, 1H, *thiophenyl*), 7.28–7.34 (m, 1H, *thiophenyl*), 7.61 (s, 1H, CC*H*C); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 20.6, 28.3 (3C), 50.6, 50.9, 81.0, 115.1 (2C), 125.7, 126.4, 128.7, 129.3 (2C), 130.3, 133.4, 135.9, 136.4, 145.2, 166.9; IR (neat, cm^{-1}) 729, 793, 841, 1163, 1249, 1306, 1392, 1455, 1519, 1568, 1593, 1699, 2851, 2925, 2974, 3371. [*E*-(*R*)-**8f**]: $[\alpha]_D$ +5.0 (*c* 1 in $CHCl_3$); [*E*-(*S*)-**8f**]: $[\alpha]_D$ −4.2 (*c* 1 in $CHCl_3$), LC-MS-ESI rt 2.77, 359 (M+1). Chiral HPLC analysis 95:5 to 90:10 *n*-hexane/2-propanol in 20 min, 0.8 mL/min, OJ column, rt 35.80 min for [*E*-(*S*)-**8f**] and 38.58 min for [*E*-(*R*)-**8f**]. Anal. Calcd for $C_{20}H_{26}N_2O_2S$ (358.5): C 67.01, H 7.31, N 7.81; found C 66.83, H 7.28, N 7.81.

3.4. Representative procedure for Pd-nanoparticles catalyzed reaction

A mixture of amine (1 mmol), allyl carbonate (3 mmol), $PdCl_2$ (0.045 mmol), tetrabutylammonium iodide (1 mmol), and K_2CO_3 (2 mmol) in toluene (3 mL) was stirred at 85 °C for 10 h. The reaction was monitored by TLC and quenched with water upon disappearance of the starting carbonate. The reaction mixture was extracted with Et_2O (3×10 mL). The extract was washed with water and brine then dried (Na_2SO_4). Evaporation of solvent afforded the crude products, which were purified by column chromatography on silica [hexane/ethylacetate (70:30)–(50:50)] to provide products. The remaining black Pd nanoparticles, after extraction with ether, were further washed with ether and dried for reuse.

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Supplementary data

Supplementary data associated with this article can be found in online version at doi:10.1016/j.tet.2010.05.022.

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