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PALLADIUM-CATALYZED CYCLOCARBONYLATION OF UNSATURATED ALCOHOLS AND AMINES. CHEMOSELECTIVE SYNTHESIS OF HETEROCYCLE-SUBSTITUTED γ- AND δ-LACTONES AND LACTAMS

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Abstract – Unsaturated alcohols and amines react with carbon monoxide and hydrogen, in the presence of a catalytic amount of palladium acetate and a phosphine ligand, to afford selectively heterocycle-substituted γ- and δ-lactones and lactams. The distribution of five- and six-membered ring compounds can be modulated by an appropriate combination of solvent and phosphine ligand. The five-membered products are formed in two isomeric forms *trans* and *cis* with a modest diasteroselectivity (*trans*>*cis*).

INTRODUCTION

Carbonylation reactions of unsaturated alcohols[1-9] and amines[10,11] catalysed by transition metals are an efficient entry to heterocyclic ring systems of wide pharmaceutical interest and of special importance as biologically active compounds. β-Lactams of pharmaceutical interest are also synthesized by stereospecific carbonylations of aminovinyl halides,[12-14] imines,[15,16] aziridines,[17-21] and tiazines.[22]

A possible synthetic pathway concerning the cyclocarbonylation reactions, as a particular class of carbonylations, is the cyclization of unsaturated alcohols and amines in the presence of carbon monoxide (CO) and hydrogen (H_2) to give lactones and lactams, using an appropriate palladium(II) catalyst with phosphine ligands.[22] Alper and co-workers have extensively studied this methodology, which is applied to allylphenols and allylanilines and leads to bicyclic and policyclic lactones and lactams, respectively, containing five, six, or seven members.[22] On the other hand, the same procedure applied to allylic[23,24] and propargylic[25] alcohols leads exclusively to γ-butyrolactones. The use of steroids as substrate for this

reaction allows the regioselective insertion of the lactonic seven-membered function to the steroid moiety.[26,27] The interest towards the selective synthesis of lactones and lactams is increasing, probably because of the widespread presence of these functions in compounds showing biological and pharmacological activity. Moreover, these compounds are extremely useful intermediates in organic synthesis opening elegant synthetic pathways to other chemical functions.

To our knowledg, cyclocarbonylation of unsaturated (heteroaryl) alcohols and amines to give lactones and lactams, respectively, have not been reported. The presence of an heterocycle as substituent of these structures is potentially useful for subsequent synthetic modifications, such as freeing the acyl groups masked by some of the heterocycles.[28-31]

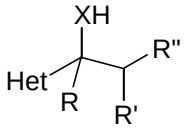
In this paper, we describe the highly regioselective synthesis of five- and six-membered ring lactones and lactams by cyclocarbonylation of homoallylic, propargylic and allenic α-heteroaryl substituted alcohols and amines, under pressure of CO and H_2, catalysed by Pd(II) complexed with phosphine ligands. The influence of gases relative pressure, solvent, temperature, and phosphine ligand nature on the regiochemical control of these reactions is also investigated and discussed.

RESULTS AND DISCUSSION

A number of unsaturated (heteroaryl) alcohols and amines (**1a-1o**) (Chart 1), substrates of cyclocarbonylation reactions, were prepared by reported synthetic routes, as detailed in the EXPERIMENTAL.

Treatment of **1a-1o** in toluene or dichloromethane (CH_2Cl_2) with a mixture of CO and H_2 (600 psi), a catalytic amount of palladium acetate [$Pd(AcO)_2$] and a phosphine ligand, at 70-120°C, for 16-72 h, afforded five- and six-membered ring lactones and lactams. Table 1 collects the results of α-(heteroaryl)homoallylic alcohols (**1a-1f**) cyclocarbonylation leading to the formation of five- and six-membered lactones (**2a-2f**) and (**3a-3f**), respectively, in moderate to good yields (55-92%). The reactions were carried out in toluene under pressure of 300 psi of CO and 300 psi of H_2, using 1,4-bis(diphenylphosphino)butane (DPPB) as ligand, for 16-24 h. The lower yield observed for the oxazolinyl heterocycle (Entry 6) could be due to ring-opening decomposition during the chromatographic purification.[28] Except the 4-pyridinyl derivative (**1e**), a good regioselectivity was found towards the δ-lactone. This latter become the only reaction product (**3f**) when the heterocycle is the 4,4-dimethyl-4,5-dihydrooxazole, in fact, no product (**2f**) was observed. The γ-lactones (**2a-2e**), instead, were formed in two isomeric form *trans* and *cis* with a certain diastereoselectivity towards the *trans* isomer. Table 2 reports the results of the cyclocarbonylation performed on *N*-phenyl substituted α-(heteroaryl)homoallylic amines (**1g-1i**), in analogous reaction conditions reported above and for 36-48 h.

Chart 1



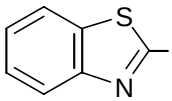
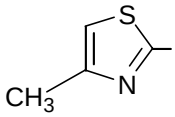
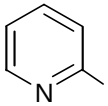
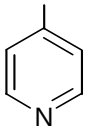
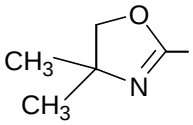
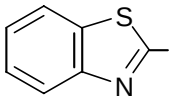
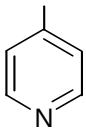
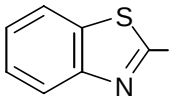
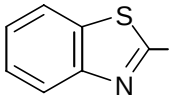
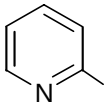
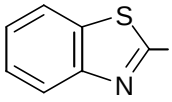
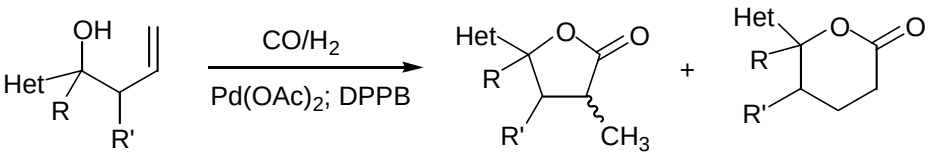
Substrate	Het	R	R’	R”	X
1a:		H	H	═	O
1b:		Ph	H	“	“
1c:		H	H	“	“
1d:		H	H	“	“
1e:		H	H	“	“
1f:		H	Ph	“	“
1g:		Ph	H	“	NPh
1h:		Ph	H	“	“
1i:		H	H	“	“
1l:		CH_3	CH_3	═•═	O
1m:		H	CH_3	“	“
1n:		H	CH_3	“	“
1o:		Ph	H	≡—CH_3	NPh

Table 1. Cyclocarbonylation of α-(heteroaryl)homoallylic alcohols by Pd(II)/DPPB/CO/H_2 in toluene



1a-1f **2a-2f** **3a-3f**

Entry	Substrate	Total yield [%]	Product distribution[a] [%]	
			2 (*trans*/*cis*)[b]	**3**
1	**1a**	75	25 (3/2)	75
2	**1b**	88	40 (3/2)	60
3	**1c**	82	30 (1/1)	70
4	**1d**	92	40 (3/2)	60
5	**1e**	60	50 (4/3)	50
6	**1f**	55	–	100

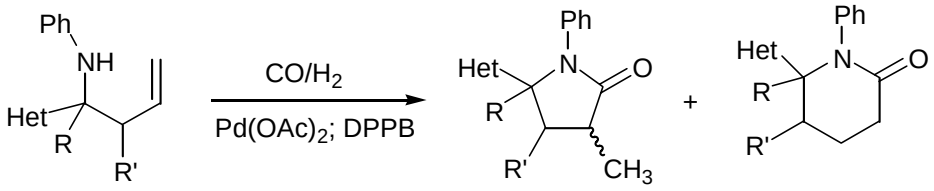
[a]**2** and **3** distribution was measured on isolated products and by GC and ^{1}H NMR spectroscopy. [b]Mixture of diastereoisomers (*trans*/*cis*) measured by GC and ^{1}H NMR spectroscopy.

Five- and six-membered lactams (**2g-2i**) and (**3g-3i**) were isolated with moderate to good yields (40-85%). A good regioselectivity was again observed towards the δ-lactams (Entries 1 and 2) excluding the 4-pyridinyl derivative (**1i**) (Entry 3). The γ-lactams were formed in two isomeric form *trans* and *cis* with a certain diasteroselectivity (*trans*>*cis*). The relative configurations *trans* and *cis* were assigned on the basis of 2D-NOESY correlations. The NOE interactions between the CH_3, bonded to the lactonic or lactamic C-3, and the two different protons linked to the vicinal C-4 were evaluated.

Since **2**/**3** ratio changes using different heterocycles, it can be argued that the heterocycle enters in the coordination sphere of the catalyst at some key point of the reaction, influencing the cyclization reaction. Indeed, when the heteroatom of the heterocycle is located on the 4-position, *para*-like, distant from the reaction centre, very poor influence on the isomeric distribution was noticed (ratio **2**/**3**~1, Entry 5, Table 1, and Entry 3, Table 2). In the other cases, where the heteroatom is on *orto*-like position, **2**/**3** ratios become remarkably different.

In order to investigate better the regiochemistry of these reactions, the effects of solvent, ligands, temperature, gas relative pressure and reaction times, have been evaluated with the substrate (**1c**). The obtained results are collected in Table 3. The use of dichloromethane as solvent led to an increase of the relative yield of the five-membered lactone affording **2c**/**3c** ratio approximately unitary (Entry 4).

Table 2. Cyclocarbonylation of *N*-phenyl substituted α-(heteroaryl)homoallylic amines by Pd(II)/DPPB/CO/H_2 in toluene



1g-1i **2g-2i** **3g-3i**

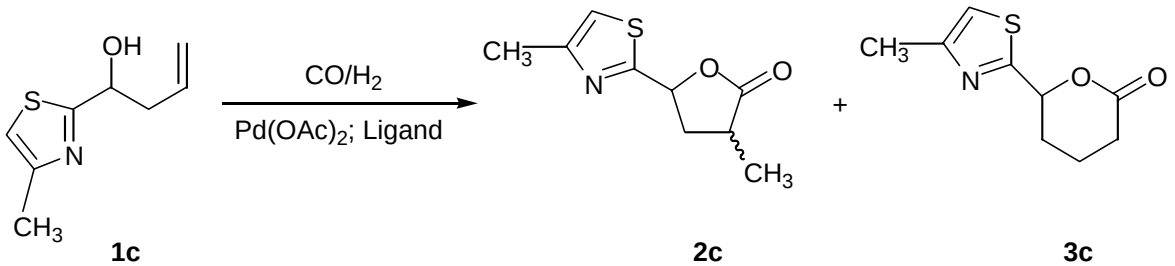
Entry	Substrate	Total yield [%]	Product distribution[a] [%]	
			2 (*trans*/*cis*)[b]	**3**
1	**1g**	85	9 (3/2)	91
2	**1h**	71	22 (5/4)	78
3	**1i**	40	46 (3/2)	54

[a]**2** and **3** distribution was measured on isolated products and by GC and ^{1}H NMR spectroscopy. [b]Mixture of diastereoisomers (*trans*/*cis*) measured by GC and ^{1}H NMR spectroscopy.

A similar increase in **2c**/**3c** ratio was observed keeping the toluene as solvent and using the R(+)-2,2'bis(diphenilphosphino)-1,1'-binaphtalene (BINAP) as ligand instead of DPPB (Entry 6). As expected, the combined use of dichloromethane as solvent and BINAP as ligand led to a strong selectivity towards the five-membered lactone (Entry 7). Changing the temperature, the reaction time (Entry 5), and the gas relative pressures (Entries 2 and 3), we did not notice particularly relevant results. Different chiral ligands have been tested (Entries 8 and 9) without appreciable enantiomeric enrichments of the new stereocenter generated on the compound (**2c**). Moreover, the diastereomeric ratios (*trans*/*cis*) of the five-membered isomer were not influenced by the different reaction conditions.

A similar investigation was carried out on the amine (**1g**) which gave the lactams (**2g**) and (**3g**). Analysing the results reported in Table 4 we observed that the regioselectivity is mainly influenced by the solvent and the catalyst ligand. As in the previous case, the relative yield of the five-membered lactam was increased by the use of dichloromethane as solvent (Entry 2), and BINAP as ligand (Entry 6). As expected, the combined use of dichloromethane as solvent and BINAP as ligand led to a strong selectivity towards the five-membered lactams (Entries 7-9). No variation of **2g**/**3g** ratio was observed changing the temperature and the reaction time (Entry 10), while increasing the gas relative pressures ratio, P_{CO}/P_{H_2}, a further increasing of the five-membered lactam was observed (**2g**/**3g** = 98/2, Entry 8). The use of different chiral ligands did not produce any enantiomeric enrichment (Entries 3-5). Finally, the reaction conditions changing did not influence the diastereomeric ratios (*trans*/*cis*) of the compound (**2g**).

Table 3. Cyclocarbonylation of (**1c**) in various reaction conditions



1c **2c** **3c**

Entry	*T* [°C]	Ligand	P_{CO} [psi]	P_{H_2} [psi]	Solvent	Product distribution[a] [%]		Reaction time [h]
						2c (*trans*/*cis*)[b]	**3c**	
1	120	DPPB[c]	300	300	Toluene	30 (1/1)	70	16
2	120	DPPB	100	500	Toluene	21 (3/1)	79	16
3	120	DPPB	500	100	Toluene	15 (2/1)	85	16
4	120	DPPB	300	300	CH_2Cl_2	45 (2/1)	55	16
5	70	DPPB	300	300	Toluene	25 (1/1)	75	24
6	120	BINAP[d]	300	300	Toluene	40 (2/1)	60	16
7	120	BINAP	300	300	CH_2Cl_2	92 (2/1)	8	16
8	120	DIOP[e]	300	300	Toluene	22 (3/2)	78	20
9	120	BPPM[f]	300	300	Toluene	20 (2/1)	80	18

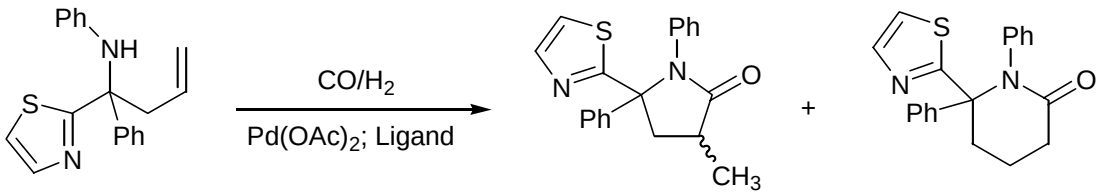
[a]**2c** and **3c** distribution was measured on isolated products and by GC and ^{1}H NMR spectroscopy. They are referred to a total yield of 61-92%. [b]Mixture of diastereoisomers (*trans*/*cis*) measured by GC and ^{1}H NMR spectroscopy. [c]1,4-Bis(diphenylphosphino)butane (DPPB). [d]R(+)-2,2'-Bis(diphenylphosphino) -1,1'-binaphthalene (BINAP). [e](+)-1,4-Bis(diphenylphosphino)-1,4-dideoxy-2,3-O-isopropylidene-D-threitol (DIOP). [f](2S,4S)-1-*tert*-Butoxycarbonyl-4-diphenylphosphino-2-(diphenylphosphinomethyl) pyrrolidine (BPPM).

According to the cyclization mechanism, suggested by Alper and co-workers,[24] we could assume that the different percentage of the five or six-membered ring products is probably related to the different percentage of formation of the two possible palladium coordination forms, before the CO insertion (Scheme 1).

The solvent, the catalyst ligand and the heterocyclic moiety can influence the palladium coordination and could then generate a different percentage of the five- and six-membered ring compounds.

α-(Heteroaryl)allenyl alcohols (**1l-1n**) have been cyclocarbonylated, in toluene at 120°C, using DPPB as catalyst ligand, under pressures of 300 psi of CO and 300 psi of H_2, for 24 h. Six-membered lactones β,γ-unsaturated (**3l-3n**) were mostly isolated, while the α,β-unsaturated five-membered lactones (**2l-2n**) were isolated as minor products. The results obtained (yields 50-70%) are collected in Table 5.

Table 4. Cyclocarbonylation of **1g** in various reaction conditions



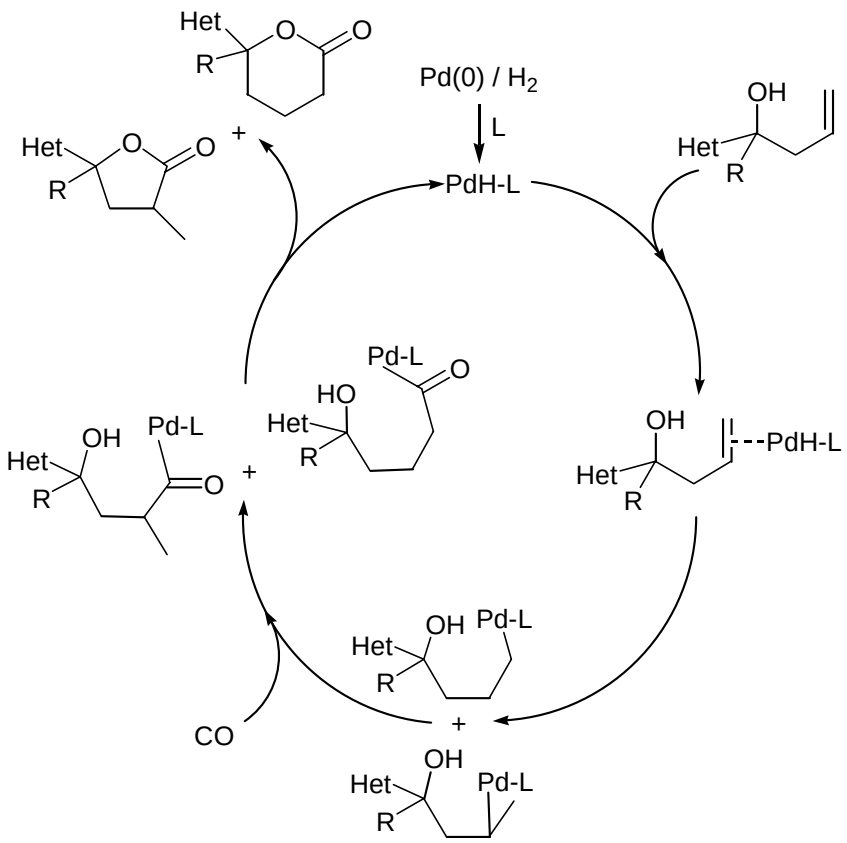
1g **2g** **3g**

Entry	*T* [°C]	Ligand	P_{CO} [psi]	P_{H_2} [psi]	Solvent	Product distribution[a] [%]		Reaction time [h]
						2g (*trans*/*cis*)[b]	**3g**	
1	120	DPPB[c]	300	300	Toluene	9 (3/2)	91	48
2	120	DPPB	300	300	CH_2Cl_2	56 (3/2)	44	48
3	120	DIOP[d]	300	300	Toluene	27 (3/2)	73	48
4	120	DIOP	300	300	CH_2Cl_2	52 (3/2)	48	48
5	120	BPPM[e]	300	300	Toluene	25 (3/2)	75	48
6	120	BINAP[f]	300	300	Toluene	37 (3/2)	63	48
7	120	BINAP	300	300	CH_2Cl_2	90 (5/3)	10	48
8	120	BINAP	500	100	CH_2Cl_2	98 (5/3)	2	48
9	120	BINAP	100	500	CH_2Cl_2	90 (5/3)	10	48
10	70	DPPB	300	300	Toluene	10 (3/2)	90	72

[a]**2g** and **3g** distribution was measured on isolated products and by GC and ^{1}H NMR spectroscopy. They are referred to a total yield of 83-92%. [b]Mixture of diastereoisomers (*trans*/*cis*) measured by GC and ^{1}H NMR spectroscopy. [c]1,4-Bis(diphenylphosphino)butane (DPPB). [d](+)-1,4-Bis(diphenylphosphino)-1,4-dideoxy-2,3-O-isopropylidene-D-threitol (DIOP). [e](2S,4S)-1-*tert*-Butoxycarbonyl-4-diphenylphosphino-2-(diphenylphosphinomethyl)pyrrolidine (BPPM). [f]R(+)-2,2'-Bis(diphenylphosphino)-1,1'-binaphthalene (BINAP).

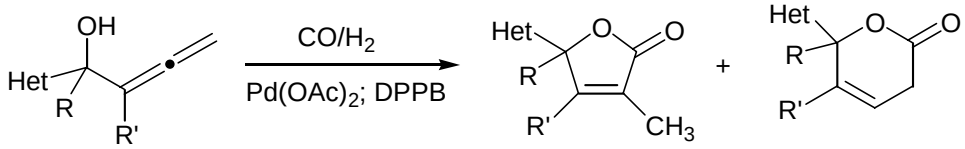
An attempt was made to carry out the reaction with a different solvent and catalyst ligand: in CH_2Cl_2, using BINAP as ligand, the α,β-unsaturated five-membered ring product became the major compound isolated (Entry 3).

Finally, the cyclocarbonylation has been carried out with the alkinylamine (**1o**), in analogous conditions described for (**1g**-**1i**), for 48 h (Scheme 2). Five- and six-membered α,β-unsaturated lactams (**2o**) and (**3o**) have been isolated with a total yield of 55%, and with a ratio of **2o**:**3o** = 2:3. The compound (**2o**) was obtained as a sole isomer, whose relative configuration was not assigned.



Scheme 1

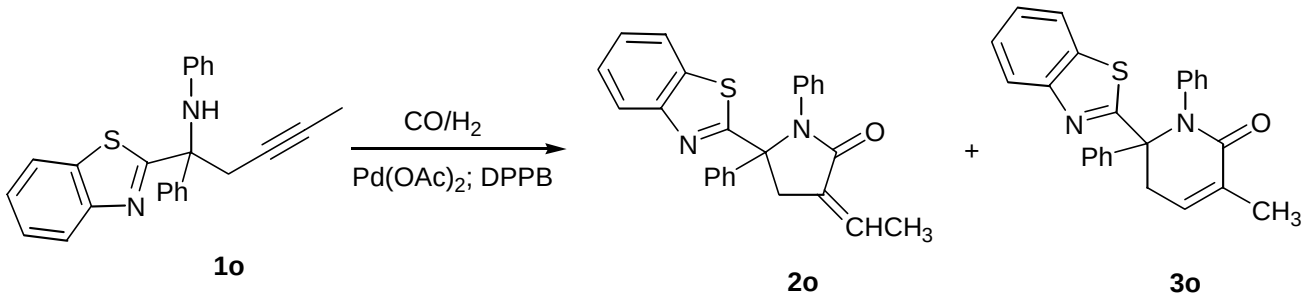
Table 5. Cyclocarbonylation of α-(heteroaryl)allenyl alcohols (**1l-1n**) by Pd(II)/DPPB/CO/H_2 in toluene



1l-1n **2l-2n** **3l-3n**

Entry	Substrate	Total yield [%]	Product distribution[a] [%]	
			2	**3**
1	**1l**	69	traces	95
2	**1m**	55	20	80
3	**1m**[b]	50	95	traces
4	**1n**	70	traces	95

[a]**2** and **3** distribution was measured on isolared products by GC and ^{1}H NMR spectroscopy. [b]Reaction carried out in CH_2Cl_2 using BINAP as catalyst ligand.



1o **2o** **3o**

Scheme 2

In conclusion, we have found that unsaturated (heteroaryl) alcohols and amines undergo palladium-catalyzed cyclocarbonylation reactions to give five- and six-membered lactones and lactams in moderate to good yields. The reactions are regioselective towards the six-membered ring products, excluding the 4-pyridinyl derivatives, using toluene as solvent and DPPB as ligand. In these conditions, the five-membered ring products are formed in two isomeric form *trans* and *cis* with a certain diastereoselectivity (*trans*>*cis*). In order to better investigate the regiochemistry of the reaction, the operating conditions were changed. Using CH_2Cl_2 as solvent and BINAP as ligand the reaction become regioselective towards the five-membered ring products. Change of temperature, reaction time, and gas relative pressures did not afford particularly relevant results. Testing different chiral ligands did not produce any enantiomeric enrichment. The diastereomeric ratios (*trans*/*cis*) of the five-membered ring isomers were not influenced by the different reaction conditions. Finally, lactones and lactams α,β-unsaturated and β,γ-unsaturated can be synthesized by cyclocarbonylation of allenyl and propargyl substrates.

EXPERIMENTAL

General Remarks: Toluene, dichloromethane, allylmagnesium bromide, allyl bromide, 1-bromo-2-butyne, palladium(II) acetate, 1,4-bis(diphenylphosphino)butane (DPPB), R(+)-2,2'-bis(diphenylphosphino)-1,1'-binaphthalene (BINAP), (+)-1,4-bis(diphenylphosphino)-1,4-dideoxy-2,3-O-isopropylidene-D-threitol (DIOP), (2S,4S)-1-*tert*-butoxycarbonyl-4-diphenylphosphino-2-(diphenylphosphinomethyl)pyrrolidine (BPPM), and all other chemicals were of commercial grade (Aldrich), and they were used without further purification. Petroleum ether refers to the 40-60°C boiling fraction. The ^1H and the ^{13}C NMR spectra were recorded on a Bruker Avance 400 apparatus (400.13 MHz and 100.62 MHz, for ^1H and ^{13}C, respectively), with $CDCl_3$ as solvent and TMS as internal standard (δ = 7.24 ppm for ^1H spectra; δ = 77.0 ppm for ^{13}C spectra). The IR spectra were recorded on a Perkin Elmer spectrophotometer Model 283. GC-MS spectral analyses were performed with a Shimadzu GC-17A gas chromatograph (5% diphenyl/95% dimethylpolysiloxane capillary column, 30 m, 0.25 mm *i.d.*) equipped with a Shimadzu GCMS-QP5050A

mass-selective detector operating at 70 eV (EI). Microanalyses were performed on a Carlo Erba C, H, N analyser. Melting points were determined using an electrothermal melting point apparatus and are uncorrected. TLC were performed on Merck silica gel plates with F-254 indicator; viewing was performed by UV light (254 nm). Column chromatographies were performed on silica gel (63-200 mm) using petroleum ether/ether (EP/Et_2O) mixtures as eluents.

General Procedure for the preparation of (heteroaryl) alcohols and amines (1a-1o): All the substrates were prepared according to reported procedures. The homoallylic and allenic alcohols (**1a**, **1b**, **1d**, **1f**, and **1l-1n**) were prepared by [1,2] and [2,3] Wittig rearrangements of the corresponding ethers.[32,33] Alcohols (**1c**) and (**1e**) were prepared by Grignard reaction of allylmagnesium bromide with 4-methylthiazolyl-2-carbaldehyde and pyridinyl-4-carbaldehyde, respectively. Analogously, **1i** was prepared by Grignard reaction of the corresponding imine with allylmagnesium bromide. The amines (**1g**, **1h**, and **1o**) were prepared by nucleophilic substitution of the corresponding amines with allyl bromide or 1-bromo-2-butyne.

General Procedure for the preparation of γ- and δ-lactones and lactams (2a-2o), (3a-3o): A mixture of 1.0 mmol of (**1a-o**), 0.04 mmol (9 mg) of $Pd(AcO)_2$, and 0.1 mmol of ligand was dissolved in 5 mL of solvent and placed in a 45 mL autoclave. The autoclave was purged, pressurized (600 psi of CO + H_2), and then heated (for each case see Results and Discussion section for temperature, gas relative pressure and reaction time). The reaction was then cooled to rt, and worked up by addition of water (5 mL) and extraction with Et_2O (3 × 5 mL). The combined organic layers were dried (Na_2SO_4) and concentrated in vacuo. The crude products were purified by column chromatography (silica gel, petroleum ether/Et_2O in the appropriate ratio) to afford the pure γ and δ-lactones and lactams; overall yields: 40-92%.

5-Benzothiazol-2-yl-3-methyldihydrofuran-2-one (2a): Yield: 44 mg (19%), oil, inseparable diastereomeric mixture *trans*/*cis* in a ratio of 3/2 measured by GC. ^{1}H NMR (400.13 MHz): δ = 1.36 (d, *J* = 7.0 Hz, 3H), 2.10-2.30 (m, 1H), 2.80-3.10 (m, 2H), 5.74 (dd, *J* = 6.0, 10.0 Hz, 1H), 7.34-7.60 (m, 2H), 7.90-8.0 (m, 2H). ^{13}C NMR (100.62 MHz): δ = 15.1, 35.3, 37.5, 76.3, 121.8, 123.1, 125.5, 126.3, 134.5, 152.5, 169.2, 172.0. GC-MS (70 eV); *m/z* (%): 233 (100) [M^+], 205 (15), 188 (40), 176 (68), 162 (40), 149 (61), 136 (65), 108 (27). IR (film): 3060, 2960, 2920, 1780, 1520, 1450, 1150, 1030, 930, 760, 730 cm^{-1}. *Anal*. Calcd for $C_{12}H_{11}NO_2S$: C, 61.78; H, 4.75; N, 6.00; S, 13.74. Found: C, 61.59; H, 4.69; N, 6.05; S, 13.70. Chromatographic eluent: Et_2O/EP = 6/4.

6-Benzothiazol-2-yltetrahydropyran-2-one (3a): Yield: 131 mg (56%), oil. ^{1}H NMR (400.13 MHz): δ = 2.00-2.31 (m, 3H), 2.46-2.70 (m, 3H), 5.79 (dd, *J* = 4.0, 9.0 Hz, 1H), 7.30-7.50 (m, 2H), 7.90 (dd, *J* = 1.6, 7.9 Hz, 1H), 8.00 (d, *J* = 8.1 Hz, 1H). ^{13}C NMR (100.62 MHz): δ = 18.0, 28.4, 29.6, 79.4, 121.8, 123.0, 125.3, 126.2, 134.7, 152.8, 169.4, 171.0. GC-MS (70 eV); *m/z* (%): 233 (96) [M^+], 165 (100), 149 (80), 136 (61), 135 (52). IR (film): 3060, 2960, 2920, 1730, 1510, 1440, 1240, 1150, 1050, 930, 760, 730 cm^{-1}. *Anal*. Calcd for $C_{12}H_{11}NO_2S$: C, 61.78; H, 4.75; N, 6.00; S, 13.74. Found: C, 61.61; H, 4.71; N, 6.08; S, 13.69. Chromatographic eluent: Et_2O/EP = 6/4.

3-Methyl-5-phenyl-5-thiazol-2-yldihydrofuran-2-one (2b): Yield: 91 mg (35%), oil, inseparable diastereomeric mixture *trans*/*cis* in a ratio of 3/2 measured by GC. ^{1}H NMR (400.13 MHz): δ = 1.25-1.32 (m, 3H), 2.60-3.20 (m, 3H), 7.30-7.80 (m, 7H). ^{13}C NMR (100.62 MHz): δ = 15.1, 35.3, 37.5, 76.3, 121.8, 123.1, 125.5, 126.3, 134.5, 152.5, 169.2, 172.0. GC-MS (70 eV); *m/z* (%): 259 (90) [M^+], 190 (50), 161 (42), 105 (100). IR ($CHCl_3$): 3060, 2960, 1780, 1600, 1500, 1450, 1140 cm^{-1}. *Anal*. Calcd for $C_{14}H_{13}NO_2S$: C, 64.86; H, 5.05; N, 5.40; S, 12.34. Found: C, 64.59; H, 5.15; N, 5.30; S, 12.30. Chromatographic eluent: Et_2O/EP = 4/6.

6-Phenyl-6-thiazol-2-yltetrahydropyran-2-one (3b): Yield: 137 mg (53%), solid, mp 159-160°C (from *n*-hexane). ^{1}H NMR (400.13 MHz): δ = 1.70-1.90 (m, 2H), 2.40-2.60 (m, 3H), 2.85-3.00 (m, 1H), 7.27-7.80 (m, 7H). ^{13}C NMR (100.62 MHz): δ = 18.0, 28.4, 29.6, 79.4, 121.8, 123.0, 125.3, 126.2, 134.7, 152.8, 169.4, 171.0. GC-MS (70 eV); *m/z* (%): 259 (90) [M^+], 190 (100), 186 (86), 162 (50), 105 (76). IR (film): 3060, 2960, 1745, 1600, 1500, 1450, 1240, 1140 cm^{-1}. *Anal*. Calcd for $C_{14}H_{13}NO_2S$: C, 64.86; H, 5.05; N, 5.40; S, 12.34. Found: C, 64.65; H, 5.18; N, 5.35; S, 12.35. Chromatographic eluent: Et_2O/EP = 4/6.

3-Methyl-5-(4-methylthiazol-2-yl)dihydrofuran-2-one (2c): Yield 49 mg (25%), oil, diastereomeric mixture *trans*/*cis* in a ratio of 1/1 measured on isolated products. (*trans*-***2c***): ^{1}H NMR (400.13 MHz): δ = 1.33 (d, *J* = 6.5 Hz, 3H), 2.35-2.40 (m, 1H), 2.44 (d, *J* = 0.7 Hz, 3H), 2.80-2.92 (m, 2H), 5.69 (d, *J* = 6.5 Hz, 1H), 7.27 (q, *J* = 0.7 Hz, 1H). ^{13}C NMR (100.62 MHz): δ = 15.1, 16.9, 33.0, 36.5, 75.7, 114.3, 152.0, 166.0, 170.5. GC-MS (70 eV); *m/z* (%): 197 (30) [M^+], 169 (30), 152 (35), 128 (64), 126 (35), 100 (52), 71 (100). IR ($CHCl_3$): 3020, 2920, 2850, 1775, 1440, 1340, 1290, 1150 cm^{-1}. *Anal*. Calcd for $C_9H_{11}NO_2S$: C, 54.78; H, 5.62; N, 7.10; S, 16.25. Found: C, 54.90; H, 5.65; N, 7.05; S, 16.20. (*cis*-***2c***): ^{1}H NMR (400.13 MHz): δ = 1.34 (d, J = 6.7 Hz, 3H), 2.10-2.22 (m, 1H), 2.45 (s, 3H), 2.77-2.99 (m, 2H), 5.53-5.63 (m, 1H), 6.92 (s, 1H). ^{13}C NMR (100.62 MHz): δ = 15.1, 16.9, 31.9, 35.6, 37.8, 75.7, 114.3, 152.5, 166.3, 171.1. GC-MS (70 eV); *m/z* (%): 197 (30) [M^+], 169 (25), 152 (50), 138 (33), 128 (30), 126 (35), 100 (75). IR ($CHCl_3$): 3020,

2920, 2840, 1775, 1440, 1335, 1145 cm^{-1}. *Anal*. Calcd for $C_9H_{11}NO_2S$: C, 54.78; H, 5.62; N, 7.10; S, 16.25. Found: C, 54.82; H, 5.72; N, 7.01; S, 16.29. Chromatographic eluent: Et_2O/EP = 7/3.

6-(4-Methylthiazol-2-yl)tetrahydropyran-2-one (3c): Yield: 112 mg (57%), oil. ^{1}H NMR (400.13 MHz): δ = 1.93-2.12 (m, 3H), 2.35-2.45 (m, 1H), 2.42 (s, 3H), 2.62 (q, *J* = 7.3 Hz, 2H), 5.62 (dd, *J* = 4.1, 9.0 Hz, 1H), 6.88 (s, 1H). ^{13}C NMR (100.62 MHz): δ = 16.9, 18.0, 28.8, 29.7, 79.2, 114.2, 152.9, 168.3, 169.7. GC-MS (70 eV); *m/z* (%): 197 (29) [M^+], 169 (7), 152 (9), 129 (34), 128 (34), 113 (38), 100 (47), 72 (50), 71 (67), 55 (26), 45 (44), 42 (100). IR (film): 3025, 2930, 2840, 1725, 1520, 1440, 1220, 1040 cm^{-1}. *Anal*. Calcd for $C_9H_{11}NO_2S$: C, 54.78; H, 5.62; N, 7.10; S, 16.25. Found: C, 54.85; H, 5.70; N, 7.13; S, 16.28. Chromatographic eluent: Et_2O/EP = 7/3.

3-Methyl-5-pyridin-2-yldihydrofuran-2-one (2d): Yield 65 mg (37%), oil, diastereomeric mixture *trans*/*cis* in a ratio of 3/2 measured on isolated products. (*trans*-***2d***): ^{1}H NMR (400.13 MHz): δ = 1.30 (d, *J* = 6.7 Hz, 3H), 2.30-2.45 (m, 1H), 2.65-2.80 (m, 2H), 5.55 (dd, *J* = 2.6, 6.7 Hz, 1H), 7.19-7.25 (m, 1H), 7.37 (d, *J* = 7.7 Hz, 1H), 7.7 (dt, *J* = 1.7, 7.7 Hz, 1H), 8.56 (d, *J* = 6.0 Hz, 1H). ^{13}C NMR (100.62 MHz): δ = 15.3, 33.2, 36.3, 78.5, 120.1, 123.1, 136.9, 149.6, 158.5, 179.1. GC-MS (70 eV); *m/z* (%): 177 (9) [M^+], 162 (18), 149 (48), 133 (69), 132 (74), 120 (83), 93 (58), 79 (100). IR (film): 3050, 2920, 2840, 1770, 1590, 1430, 1160, 1020 cm^{-1}. *Anal*. Calcd for $C_{10}H_{11}NO_2$: C, 67.78; H, 6.26; N, 7.90. Found: C, 67.95; H, 6.24; N, 7.95. (*cis*-***2d***): ^{1}H NMR (400.13 MHz): δ = 1.30 (d, *J* = 6.7 Hz, 3H), 1.90-2.00 (m, 1H), 2.70-3.00 (m, 2H), 5.40 (dd, *J* = 5.5, 6.1 Hz, 1H), 7.24 (t, *J* = 4.6 Hz, 1H), 7.45 (d, *J* = 7.6 Hz, 1H), 7.73 (t, *J* = 7.6 Hz, 1H), 8.56 (d, *J* = 4.0 Hz, 1H). ^{13}C NMR (100.62 MHz): δ = 15.1, 35.8, 37.7, 79.2, 120.0, 123.2, 137.1, 149.3, 158.5, 179.1. GC-MS (70 eV); *m/z* (%): 177 (9) [M^+], 162 (18), 149 (48), 133 (69), 132 (74), 120 (83), 93 (58), 79 (100). IR (film): 3060, 2920, 2840, 1770, 1590, 1450, 1160, 1020, 930, 770, 740, 720 cm^{-1}. *Anal*. Calcd for $C_{10}H_{11}NO_2$: C, 67.78; H, 6.26; N, 7.90. Found: C, 67.90; H, 6.30; N, 7.88. Chromatographic eluent: Et_2O/EP = 1/1.

6-Pyridin-2-yltetrahydropyran-2-one (3d): Yield: 97 mg (55%), oil. ^{1}H NMR (400.13 MHz): δ = 1.90-2.04 (m, 3H), 2.37-2.43 (m, 1H), 2.58-2.76 (m, 2H), 5.49 (dd, *J* = 3.5, 9.2 Hz, 1H), 7.26 (m, 1H), 7.52 (d, *J* = 7.9 Hz, 1H), 7.77 (dt, *J* = 1.8, 7.9 Hz, 1H), 8.59(d, *J* = 4.3 Hz, 1H). ^{13}C NMR (100.62 MHz): δ = 13.5, 18.5, 41.3, 72.3, 120.1, 123.2, 137.0, 149.0, 158.8, 172.3. GC-MS (70 eV); *m/z* (%): 177 (4) [M^+], 148 (7), 132 (26), 109 (71), 108 (100), 93 (54), 79 (60). IR (film): 3060, 2920, 2840, 1740, 1590, 1450, 1150, 1040 cm^{-1}. *Anal*. Calcd for $C_{10}H_{11}NO_2$: C, 67.78; H, 6.26; N, 7.90. Found: C, 67.85; H, 6.28; N, 7.83. Chromatographic eluent: Et_2O/EP = 1/1.

3-Methyl-5-pyridin-4-yldihydrofuran-2-one (2e): Yield 53 mg (30%), oil, diastereomeric mixture *trans*/*cis* in a ratio of 4/3 measured on isolated products. (*trans*-***2e***): ^{1}H NMR (400.13 MHz): δ = 1.33 (d, *J* = 6.9 Hz, 3H), 2.35-2.45 (m, 1H), 2.60-2.85 (m, 2H), 5.55 (dd, *J* = 6.3, 6.4 Hz, 1H), 7.27 (d, *J* = 5.7 Hz, 2H), 8.52 (d, *J* = 5.7 Hz, 2H). ^{13}C NMR (100.62 MHz): δ = 14.9, 33.0, 37.7, 76.5, 119.7, 149.5, 150.1, 179.1. GC-MS (70 eV); *m/z* (%): 177 (67) [M^+], 148 (20), 132 (90), 118 (72), 42 (100). IR ($CHCl_3$): 3020, 2960, 2920, 2850, 1775, 1600, 1410, 1150 cm^{-1}. *Anal*. Calcd for $C_{10}H_{11}NO_2$: C, 67.78; H, 6.26; N, 7.90. Found: C, 67.85; H, 6.30; N, 7.87. (*cis*-***2e***): ^{1}H NMR (400.13 MHz): δ = 1.35 (d, *J* = 6.6 Hz, 3H), 1.70-1.90 (m, 1H), 2.75-2.90 (m, 2H), 5.35 (dd, *J* = 5.6, 10.5 Hz, 1H), 7.27 (d, *J* = 5.7 Hz, 2H), 8.52 (d, *J* = 5.7 Hz, 2H). ^{13}C NMR (100.62 MHz): δ = 15.2, 35.9, 39.2, 77.1, 119.6, 149.5, 150.1, 179.1. GC-MS (70 eV); *m/z* (%): 177 (61) [M^+], 148 (20), 132 (75), 118 (40), 42 (100). IR ($CHCl_3$): 3020, 2960, 2920, 2850, 1775, 1600, 1410, 1150 cm^{-1}. *Anal*. Calcd for $C_{10}H_{11}NO_2$: C, 67.78; H, 6.26; N, 7.90. Found: C, 67.91; H, 6.31; N, 7.93. Chromatographic eluent: petroleum ether.

6-Pyridin-4-yltetrahydropyran-2-one (3e): Yield: 53 mg (30%), oil. ^{1}H NMR (400.13 MHz): δ = 1.60-1.80 (m, 3H), 2.50-2.70 (m, 3H), 4.70 (dd, *J* = 4.9, 5.0 Hz, 1H), 7.27 (dd, *J* = 1.0, 5.7 Hz, 2H), 8.50 (dd, *J* = 1.3, 5.7 Hz, 2H). ^{13}C NMR (100.62 MHz): δ = 13.8, 18.6, 41.0, 72.7, 120.8, 149.5, 154.0, 172.1. GC-MS (70 eV); *m/z* (%): 177 (22) [M^+], 148 (10), 132 (35), 118 (12), 44 (100). IR ($CHCl_3$): 3060, 2930, 2840, 1720, 1600, 1450, 1230, 1110, 1030 cm^{-1}. *Anal*. Calcd for $C_{10}H_{11}NO_2$: C, 67.78; H, 6.26; N, 7.90. Found: C, 67.92; H, 6.33; N, 7.92. Chromatographic eluent: petroleum ether.

6-(4,4-Dimethyl-4,5-dihydrooxazol-2-yl)-5-phenyltetrahydropyran-2-one (3f): Yield: 158 mg (55%), oil. ^{1}H NMR (400.13 MHz): δ = 1.18 (s, 3H), 1.25 (s, 3H), 1.57 (s, 3H), 1.91-1.97 (m, 1H), 2.53-2.92 (m, 3H), 3.08 (dd, *J* = 3.5, 12.5 Hz, 1H), 3.85 (d, *J* = 8.2 Hz, 1H), 3.95 (d, *J* = 8.2 Hz, 1H), 7.14-7.31 (m, 5H). ^{13}C NMR (100.62 MHz): δ = 23.8, 25.6, 27.9, 30.1, 49.0, 67.7, 79.6, 82.9, 127.8, 128.2, 128.7, 138.0, 163.2, 170.4. GC-MS (70 eV); *m/z* (%): 287 (0) [M^+], 244 (17), 216 (13), 142 (55), 104 (100). IR ($CHCl_3$): 3025, 2960, 2880, 1730, 1660, 1450, 1380, 1370, 1335, 1260, 1200, 1080 cm^{-1}. *Anal*. Calcd for $C_{17}H_{21}NO_3$: C, 71.06; H, 7.36; N, 4.87. Found: C, 71.40; H, 7.25; N, 4.86. Chromatographic eluent: Et_2O/EP = 7/3.

3-Methyl-1,5-diphenyl-5-thiazol-2-ylpyrrolidin-2-one (2g): Yield 27 mg (8%), oil, diastereomeric mixture *trans*/*cis* in a ratio of 3/2 measured on isolated products. (*trans*-***2g***): ^{1}H NMR (400.13 MHz): δ = 1.37 (d, *J* = 6.9 Hz, 3H), 2.51 (dd, *J* = 9.6, 12.5 Hz, 1H), 2.80-2.86 (m, 1H), 3.32 (dd, *J* = 8.0, 12.5 Hz, 1H), 7.06-7.60 (m, 11H), 7.70 (d, *J* = 3.3 Hz, 1H). ^{13}C NMR (100.62 MHz): δ = 15.7, 35.9, 48.0, 71.3, 120.9, 125.9, 126.1, 126.6, 127.5, 128.1, 128.2, 128.3, 128.4, 142.2, 171.0, 173.2. GC-MS (70 eV); *m/z* (%): 334 (75) [M^+], 292 (10), 250 (40), 215 (40), 214 (40), 77 (100). IR ($CHCl_3$): 3060, 3000, 2960, 2860, 1680,

1485, 1445, 1350, 1330, 1120 cm^{-1}. *Anal*. Calcd for $C_{19}H_{18}N_2OS$: C, 70.78; H, 5.63; N, 8.69; S, 9.94. Found: C, 70.65; H, 5.53; N, 8.66; S, 9.86. (*cis*-***2g***): ^1H NMR (400.13 MHz): δ = 1.36 (d, *J* = 7.1 Hz, 3H), 2.64-2.70 (m, 1H), 2.80-2.86 (m, 1H), 3.05 (dd, *J* = 12.1, 12.2 Hz, 1H), 7.06-7.60 (m, 11H), 7.89 (d, *J* = 3.3 Hz, 1H). ^{13}C NMR (100.62 MHz): δ = 15.1, 34.8, 49.1, 70.8, 119.9, 125.8, 126.0, 127.2, 127.9, 128.1, 128.2, 128.3, 128.4, 141.9, 171.1, 173.3. GC-MS (70 eV); *m/z* (%): 334 (75) [M^+], 292 (11), 250 (40), 215 (51), 214 (48), 77 (100). IR ($CHCl_3$): 3060, 3000, 2960, 2860, 1680, 1485, 1445, 1350, 1330, 1120 cm^{-1}. *Anal*. Calcd for $C_{19}H_{18}N_2OS$: C, 70.78; H, 5.63; N, 8.69; S, 9.94. Found: C, 70.60; H, 5.55; N, 8.39; S, 9.90. Chromatographic eluent: Et_2O/EP = 9/1.

1,6-Diphenyl-6-thiazol-2-ylpiperidin-2-one (3g): Yield: 257 mg (77%), oil. ^1H NMR (400.13 MHz): δ = 1.60-1.80 (m, 2H), 2.50-2.80 (m, 3H), 3.10-3.25 (m, 1H), 6.90-7.10 (m, 5H), 7.18 (d, *J* = 3.1 H, 1H), 7.30–7.50 (m, 5H), 7.66 (d, *J* = 3.1 Hz, 1H). ^{13}C NMR (100.62 MHz): δ = 16.4, 31.4, 39.5, 72.0, 120.8, 126.8, 127.9, 128.1, 128.2, 128.4, 129.5, 140.3, 141.6, 142.1, 171.5, 173.3. GC-MS (70 eV); *m/z* (%): 334 (30) [M^+], 241 (25), 214 (52), 77 (33), 44 (100). IR ($CHCl_3$): 3060, 2960, 2920, 2840, 1640, 1480, 1440, 1360, 1330, 1200, 1110 cm^{-1}. *Anal*. Calcd for $C_{19}H_{18}N_2OS$: C, 70.78; H, 5.63; N, 8.69; S, 9.94. Found: C, 71.02; H, 5.51; N, 8.66; S, 9.81. Chromatographic eluent: Et_2O/EP = 9/1.

5-Benzothiazol-2-yl-3-methyl-1,5-diphenylpyrrolidin-2-one (2h): Yield 43 mg (11%), oil, diastereomeric mixture *trans*/*cis* in a ratio of 5/4 measured on isolated products. (*trans*-***2h***): ^1H NMR (400.13 MHz): δ = 1.39 (d, *J* = 7.2 Hz, 3H), 2.62-2.76 (m, 1H), 2.84-2.94 (m, 1H), 3.06 (dd, *J* = 12.1, 12.1 Hz, 1H), 7.06-7.74 (m, 12H), 7.86 (dd, *J* = 0.6, 7.5 Hz, 1H), 8.14 (dd, *J* = 0.7, 8.4 Hz, 1H). ^{13}C NMR (100.62 MHz): δ = 16.0, 36.1, 49.5, 73.7, 121.9, 124.0, 126.0, 126.1, 126.4, 126.7, 127.5, 128.6, 128.7, 128.8, 136.2, 137.6, 141.3, 153.3, 173.2, 178.1. GC-MS (70 eV); *m/z* (%): 384 (8) [M^+], 281 (9), 250 (12), 207 (20), 44 (100). IR ($CHCl_3$): 3045, 2940, 1690, 1592, 1490, 1445, 1350, 1310, 1200 cm^{-1}. *Anal*. Calcd for $C_{24}H_{20}N_2OS$: C, 74.97; H, 5.24; N, 7.28; S, 8.34. Found: C, 74.77; H, 5.20; N, 7.25; S, 8.25. (*cis*-***2h***): ^1H NMR (400.13 MHz): δ = 1.41 (d, *J* = 7.5 Hz, 3H), 2.62-2.76 (m, 1H), 2.84-2.94 (m, 1H), 3.32 (dd, *J* = 7.9, 12.6 Hz, 1H), 7.06-7.74 (m, 12H), 7.73 (dd, *J* = 0.7, 8.0 Hz, 1H) 8.02 (dd, *J* = 0.7, 8.3 Hz, 1H). ^{13}C NMR (100.62 MHz): δ = 15.7, 35.5, 47.8, 73.4, 121.8, 123.9, 125.9, 126.0, 126.4, 126.7, 127.5, 128.2, 128.6, 128.8, 135.9, 137.6, 141.3, 152.3, 173.2, 177.4. GC-MS (70 eV); *m/z* (%): 384 (7) [M^+], 281 (9), 250 (12), 207 (21), 44 (100). IR ($CHCl_3$): 3045, 2940, 1690, 1592, 1490, 1445, 1350, 1310, 1200 cm^{-1}. *Anal*. Calcd for $C_{24}H_{20}N_2OS$: C, 74.97; H, 5.24; N, 7.28; S, 8.34. Found: C, 74.70; H, 5.26; N, 7.20; S, 8.28. Chromatographic eluent: Et_2O/EP = 1/1.

6-Benzothiazol-2-yl-1,6-diphenylpiperidin-2-one (3h): Yield: 230 mg (60%), oil. ^{1}H NMR (400.13 MHz): δ = 1.73-1.78 (m, 2H), 2.77-2.89 (m, 3H), 3.10-3.15 (m, 1H), 6.99-7.50 (m, 12H), 7.77 (d, *J* = 7.9 Hz, 1H), 8.10 (dd, *J* = 0.5, 8.1 Hz, 1H). ^{13}C NMR (100.62 MHz): δ = 17.2, 31.8, 39.5, 72.3, 121.8, 124.1, 126.0, 126.2, 127.4, 128.3, 128.6, 128.7, 129.4, 130.4, 136.4, 140.7, 141.5, 152.5, 172.3, 174.9. GC-MS (70 eV); *m/z* (%): 384 (44) [M^+], 291 (12), 264 (100), 236 (25), 77 (52). IR ($CHCl_3$): 3040, 2970, 1645, 1490, 1435, 1365, 1330, 1280, 1200, 1110, 1070 cm^{-1}. *Anal*. Calcd for $C_{24}H_{20}N_2OS$: C, 74.97; H, 5.24; N, 7.28; S, 8.34. Found: C, 74.66; H, 5.22; N, 7.30; S, 8.41.Chromatographic eluent: Et_2O/EP = 1/1.

3-Methyl-1-phenyl-5-pyridin-4-ylpyrrolidin-2-one (2i): Yield 44 mg (18%), oil, diastereomeric mixture *trans*/*cis* in a ratio of 3/2 measured on isolated products. (*trans*-***2i***): ^{1}H NMR (400.13 MHz): δ = 1.31 (d, *J* = 7.1 Hz, 3H), 2.19-2.26 (m, 1H), 2.26-2.35 (m, 1H), 2.77 (sextet, *J* = 9.1 Hz, 1H), 5.18 (d, *J* = 8.1 Hz, 1H), 7.02-7.30 (m, 5H), 7.49 (d, *J* = 7.8 Hz, 2H), 8.55 (d, *J* = 4.8 Hz, 2H). ^{13}C NMR (100.62 MHz): δ = 15.7, 35.7, 37.0, 60.4, 120.8, 122.5, 124.8, 128.9, 138.3, 150.3, 150.6, 176.8. GC-MS (70 eV); *m/z* (%): 242 (1) [M^+], 122 (100), 78 (80). IR ($CHCl_3$): = 3045, 2940, 2900, 1660, 1590, 1490, 1200 cm^{-1}. *Anal*. Calcd for $C_{16}H_{16}N_2O$: C, 76.16; H, 6.39; N, 11.10. Found: C, 75.86; H, 6.28; N, 11.06. (*cis*-***2i***): ^{1}H NMR (400.13 MHz): δ = 1.36 (d, *J* = 6.8 Hz, 3H), 2.20-2.25 (m, 1H), 2.26-2.36 (m, 1H), 2.80 (sextet, *J* = 9.0 Hz, 1H), 5.19 (d, *J* = 8.0 Hz, 1H), 7.05-7.31 (m, 5H), 7.49 (d, *J* = 8.1 Hz, 2H), 8.56 (d, *J* = 4.8 Hz, 2H). ^{13}C NMR (100.62 MHz): δ = 16.4, 37.5, 38.1, 60.6, 121.3, 122.5, 125.2, 128.7, 138.1, 150.3, 150.4, 176.5. GC-MS and IR data are the same of those reported for the *trans* isomer. *Anal*. Calcd for $C_{16}H_{16}N_2O$: C, 76.16; H, 6.39; N, 11.10. Found: C, 75.90; H, 6.37; N, 10.90. Chromatographic eluent: petroleum ether.

1-Phenyl-6-pyridin-4-ylpiperidin-2-one (3i): Yield: 53 mg (22%), oil. ^{1}H NMR (400.13 MHz): δ = 1.84-1.87 (m, 2H), 1.96-2.01 (m, 1H), 2.33-2.41 (m, 1H), 2.66-2.73 (m, 2H), 5.02 (t, *J* = 5.0 Hz, 1H), 7.12-7.28 (m, 7H), 8.53 (d, *J* = 4.8 Hz, 2H). ^{13}C NMR (100.62 MHz): δ = 17.5, 31.6, 32.4, 64.0, 121.9, 126.9, 127.0, 128.7, 128.9, 141.7, 149.9, 170.4. GC-MS (70 eV); *m/z* (%): 242 (2) [M^+], 122 (100), 78 (70), 77 (30). IR ($CHCl_3$): 3040, 2950, 2900, 1690, 1590, 1495, 1310, 1200 cm^{-1}. *Anal*. Calcd for $C_{16}H_{16}N_2O$: C, 76.16; H, 6.39; N, 11.10. Found: C, 76.33; H, 6.25; N, 11.05. Chromatographic eluent: petroleum ether.

5-Benzothiazol-2-yl-3,4,5-trimethyl-5*H*-furan-2-one (2l): Traces measured by GC-MS (70 eV); *m/z* (%): 259 (76) [M^+], 244 (15), 214 (100), 178 (72). Chromatographic eluent: Et_2O/EP = 1/1.

6-Benzothiazol-2-yl-5,6-dimethyl-3,6-dihydropyran-2-one (3l): Yield: 169 mg (65%), oil. ^{1}H NMR (400.13 MHz): δ = 1.95 (d, *J* = 2.0 Hz, 3H), 2.05 (s, 3H), 3.20-3.22 (m, 2H), 5.66 (m, 1H), 7.43 (t, J = 7.2 Hz, 1H), 7.51 (t, *J* = 6.1 Hz, 1H), 8.05 (d, *J* = 7.8 Hz, 1H), 8.88 (d, *J* = 7.5 Hz, 1H). ^{13}C NMR (100.62 MHz):

δ = 18.7, 26.1, 30.3, 86.8, 117.8, 117.9, 121.7, 123.6, 125.5, 126.2, 135.1, 150.0, 170.0. GC-MS (70 eV); *m/z* (%): 259 (3) [M^+], 244 (4), 214 (100), 200 (30), 188 (62), 108 (93). IR ($CHCl_3$): 3060, 2920, 1735, 1505, 1435, 1375, 1265, 1060, 810, 760, 730 cm^{-1}. *Anal*. Calcd for $C_{14}H_{13}NO_2S$: C, 64.84; H, 5.05; N, 5.40; S, 12.36. Found: C, 65.11; H, 5.20; N, 5.25; S, 12.40. Chromatographic eluent: Et_2O/EP = 1/1.

5-Benzothiazol-2-yl-3,4-dimethyl-5*H*-furan-2-one (2m): Yield 27 mg (11%), solid, mp 44-46°C (from *n*-hexane). ^1H NMR (400.13 MHz): δ = 1.90 (s, 3H), 2.10 (d, *J* = 1.0 Hz, 1H), 6.07 (q, *J* = 1.0 Hz, 3H), 7.40-7.55 (m, 2H), 7.87 (dd, *J* = 1.6, 8.8 Hz, 1H), 8.04 (dd, *J* = 1.2, 7.6 Hz, 1H). ^{13}C NMR (100.62 MHz): δ = 8.7, 29.7, 81.8, 117.0, 117.3, 121.9, 123.4, 125.7, 126.4, 142.0, 154.0, 169.2, 170.0. GC-MS (70 eV); *m/z* (%): 245 (100) [M^+], 200 (90), 164 (31), 135 (10), 111 (21). IR (film): 3050, 2920, 2850, 1766, 1680, 1515, 1460, 1435, 1385, 1316, 1168, 1083, 1030, 760, 730 cm^{-1}. *Anal*. Calcd for $C_{13}H_{11}NO_2S$: C, 63.65; H, 4.49; N, 5.71; S, 13.07. Found: C, 63.80; H, 4.52; N, 5.65; S, 13.02. Chromatographic eluent: Et_2O/EP = 1/1.

6-Benzothiazol-2-yl-5-methyl-3,6-dihydropyran-2-one (3m): Yield: 108 mg (44%), solid, mp 56-60°C (from *n*-hexane). ^1H NMR (400.13 MHz): δ = 1.95 (s, 3H), 3.40-3.45 (m, 2H), 5.72-5.75 (m, 2H), 7.40-7.55 (m, 2H), 7.87 (dd, *J* = 1.6, 8.8 Hz, 1H), 8.04 (dd, *J* = 1.2, 7.6 Hz, 1H). ^{13}C NMR (100.62 MHz): δ = 18.6, 26.1, 86.8, 117.0, 117.8, 121.5, 123.5, 125.3, 126.2, 135.1, 150.0, 169.2, 170.0. GC-MS (70 eV); *m/z* (%): 245 (5) [M^+], 239 (4), 200 (100). IR (film): 3060, 2920, 1735, 1505, 1270, 1060 cm^{-1}. *Anal*. Calcd for $C_{13}H_{11}NO_2S$: C, 63.65; H, 4.49; N, 5.71; S, 13.07. Found: C, 63.85; H, 4.58; N, 5.69; S, 12.98. Chromatographic eluent: Et_2O/EP = 1/1. The same reaction carried out in CH_2Cl_2 and with BINAP as ligand afforded **2m** in a yield of 115 mg (47%) and **3m** in traces.

3,4-Dimethyl-5-pyridin-2-yl-5*H*-furan-2-one (2n): Traces measured by GC-MS (70 eV); *m/z* (%): 189 (100) [M^+], 144 (90), 130 (31), 78 (21). Chromatographic eluent: Et_2O/EP = 1/1.

5-Methyl-6-pyridin-2-yl-3,6-dihydropyran-2-one (3n): Yield: 125 mg (66%), oil. ^1H NMR (400.13 MHz): δ = 1.73 (s, 3H), 3.15 (d, *J* = 11.5 Hz, 1H), 3.36 (d, *J* = 11.5 Hz, 1H), 5.60-5.80 (m, 2H), 7.25-7.35 (m, 2H), 7.70 (t, *J* = 7.7 Hz, 1H), 8.55 (d, *J* = 6.5 Hz, 1H). ^{13}C NMR (100.62 MHz): δ = 19.3, 30.8, 85.5, 117.7, 120.8, 122.0, 123.9, 132.3, 137.3, 150.3, 170.0. GC-MS (70 eV); *m/z* (%): 189 (2) [M^+], 144 (100), 130 (16), 78 (20). IR (film): 3060, 2960, 2920, 1735, 1590, 1430, 1370, 1160 cm^{-1}. *Anal*. Calcd for $C_{11}H_{11}NO_2$: C, 69.83; H, 5.86; N, 7.40. Found: C, 69.98; H, 5.85; N, 7.29. Chromatographic eluent: Et_2O/EP = 1/1.

5-Benzothiazol-2-yl-3-ethylidene-1,5-diphenylpyrrolidin-2-one (2o): Yield 87 mg (22%), solid, mp 63-66°C (from *n*-hexane). ^{1}H NMR (400.13 MHz): δ = 1.78 (dt, *J* = 1.5, 7.2 Hz, 3H), 3.42 (dquintet, J = 1.5, 16.6 Hz, 1H), 3.96 (dquintet, J = 1.5, 16.6 Hz, 1H), 6.84 (m, 1H), 7.10-7.55 (m, 12H), 7.74 (d, J = 7.7 Hz, 1H), 8.05 (d, J = 8.4 Hz, 1H). ^{13}C NMR (100.62 MHz): δ = 14.9, 44.3, 72.2, 121.5, 123.6, 125.6, 126.2, 126.3, 126.4, 127.4, 128.2, 128.4, 128.5, 128.9, 129.7, 131.5, 135.5, 142.3, 152.2, 168.4, 173.4. GC-MS (70 eV); *m/z* (%): 396 (80) [M^+], 303 (20), 261 (70), 77 (100). IR ($CHCl_3$): 3060, 3020, 2920, 2840, 1690, 1670, 1590, 1485, 1440, 1350, 1310 cm^{-1}. *Anal*. Calcd for $C_{25}H_{20}N_2OS$: C, 75.73; H, 5.08; N, 7.06; S, 8.08. Found: C, 75.50; H, 4.98; N, 7.01; S, 8.05. Chromatographic eluent: Et_2O/EP = 1/1.

6-Benzothiazol-2-yl-3-methyl-1,6-diphenyl-5,6-dihydro-1*H*-pyridin-2-one (3o): Yield: 131 mg (33%), solid, mp 85-88°C (from *n*-hexane). ^{1}H NMR (400.13 MHz): δ = 1.98 (s, 3H), 2.90-3.10 (m, 2H), 6.54 (d, J = 7.8 Hz, 2H), 6.67 (t, J = 7.6 Hz, 1H), 7.05-8.10 (m, 12H). ^{13}C NMR (100.62 MHz): δ = 28.7, 30.4, 65.2, 115.8, 118.4, 122.1, 123.6, 124.0, 125.7, 126.0, 126.6, 127.3, 128.3, 129.38, 129.39, 136.5, 143.6, 144.7, 152.5, 172.0, 177.0. GC-MS (70 eV); *m/z* (%): 396 (0) [M^+], 368 (10), 276 (100), 238 (13), 233 (21). IR (film): 3059, 2940, 2927, 1715, 1600, 1500, 1315, 910, 760, 730, 700 cm^{-1}. *Anal*. Calcd for $C_{25}H_{20}N_2OS$: C, 75.73; H, 5.08; N, 7.06; S, 8.08. Found: C, 75.47; H, 5.15; N, 7.09; S, 8.16. Chromatographic eluent: Et_2O/EP = 1/1.

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