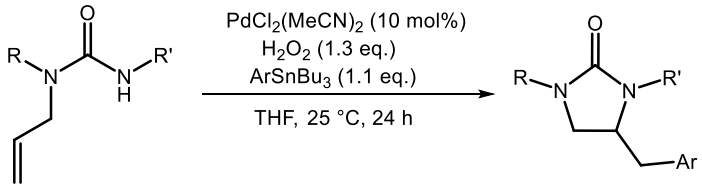
Chemo- and regioselective Pd(II)-catalyzed aminoarylation of *N*-allylureas providing 4-arylmethyl imidazolidinones



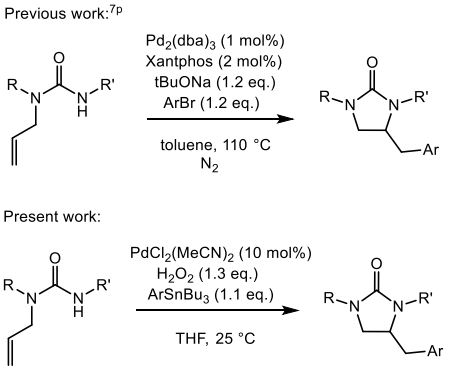
Abstract The aminoarylation reaction of *N*-allylureas under oxidative palladium catalysis, in the absence of ligands and by using the inexpensive H_2O_2 as the sole oxidant, occurred in chemo- and regioselective way. The intramolecular process, through a 5-*exo*-*trig* cyclization provided an easy approach to 4-arylmethyl imidazolidinones.

Key words palladium catalysis, aminoarylation, hydrogen peroxide, imidazolones, ureas, domino reaction

The obtainment of complex molecules through the formation of more than one bond in a single step represents a powerful tool for organic chemists.[1] Among the transition metal-catalyzed reactions the double functionalization of unsaturated systems under palladium catalysis represents a rapid and economical method to obtain functionalized substrates. In particular, when the domino process involved the formation of an intramolecular C-N bond on alkenes, alkynes or allenes combined to a new C-C, C-O or C-N bond formation, the result was the synthesis of functionalized (poly)heterocyclic systems.[2] The synthetic strategies involving the palladium catalyst in oxidative conditions,[3] represent a complementary reactivity to the Pd(0)-catalyzed reactions of aryl(alkyl) halides, offering the possibility of alternative regioselectivity in the bonds formation. In this contest, the use of hydrogen peroxide as the sole oxidant is quite rare.[4]

Following our continuing interest in the difunctionalization reactions of alkenes, we have applied palladium-catalyzed reactions in arylation/halogenation, arylation/esterification, aminohalogenation and diamination processes.[5] Recently we focused our attention on oxyarylation studies, reporting oxazepanes formation through a selective 7-*endo*-cyclization process.[6]

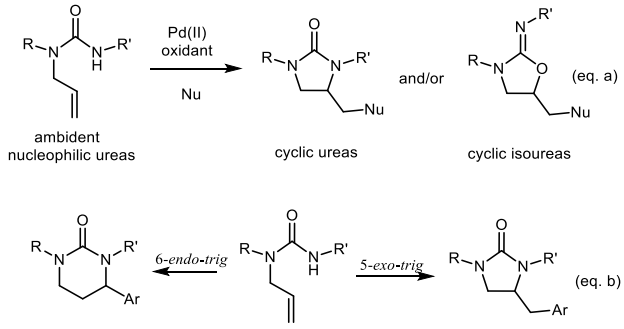
Based on the literature data the aminoarylation reactions are of great interest, as intra- or intermolecular processes, providing heterocyclic systems.[7] In particular, 4-arylmethyl imidazolidinones have been obtained by reaction of *N*-allylureas and arylbromides, performing the reaction under Pd(0) catalysis in the presence of ligand and a base, in toluene at 110°C under N_2 (Scheme 1).



Scheme 1 Aminoarylation of secondary *N*-allylureas.

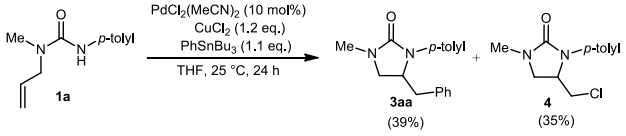
In the present work we are interested to extend the arylation processes combined with the formation of new bonds, with the purpose of: a) to search new conditions for the difunctionalization of alkenes and heterocyclization, b) to investigate in depth the chemo- and regioselectivity of the process, c) to achieve mild reaction conditions.

To this aim we have envisaged the reactivity of *N*-allylureas as ambident nucleophiles showing the possibility of C-N *vs* C-O bond formation, allowing the construction of cyclic ureas or isoureas.[8] The presence of a second nucleophile among the reagents paved the way for a difunctionalization process (Scheme 2, eq. *a*). More over these substrates offered the double possible regioselective 5-*exo-trig*/6-*endo trig* cyclization in the amination step and the presence of an aryl nucleophile resulted in the aminoarylation reaction, involving the C-N and C-C bonds formation (Scheme 2, eq. *b*).



Scheme 2 Chemo- and regioselectivity of secondary *N*-allylureas.

The substrate **1a** selected for this study arises in quantitative yield, from the simple one step reaction between the *p*-tolylisocyanate and methylallylamine performed at r.t. in acetonitrile as solvent. Initially we tested the use of catalytic 10 mol% of $PdCl_2(MeCN)_2$ in the presence of a slightly excess of both $CuCl_2$ as oxidant, and phenyltributylstannane (**2a**) as nucleophile. The complete conversion of the substrate afforded the aminoarylation product **3aa**, isolated in 39% yield, and also the 4-chloromethyl-imidazolidinone **4** (35% yield), arising from an aminohalogenation process, due to the double action of the copper salt as oxidant and as nucleophile (Scheme 3).



Scheme 3 Aminoarylation reaction of the substrate **1a**.

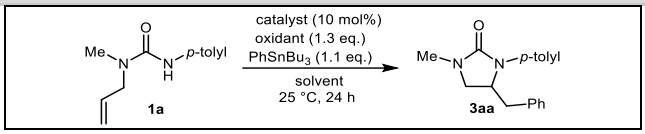
The observed cyclization was totally chemoselective due to the addition of the nitrogen to the double bond with the obtainment of cyclic urea. Moreover, the reaction gave exclusive 5-*exo-trig* cyclization, showing total regioselectivity with the formation of the 4-substituted imidazolidinones. The selective formation of imidazolinone scaffold is a valuable goal because of the wide presence of this heterocycle in natural products[9a] and in a wide range of pharmaceuticals including anti-inflammatory,[9b] anti-infective,[9c] antibacterial[9d] and antitumoral.[9e-g]

It is worth noting the *exo*-cyclization process. In fact, even if *exo*-cyclizations on protected aminoalkenes have been reported,[10] generally palladium-catalyzed difunctionalization of 4-pentenyl-amides in oxidative conditions afforded hexatomic rings, a result which was never observed in our experiments (see Table 1).[4a,4b,7q,11] Moreover, palladium-catalyzed oxidative oxyarylation reactions highlighted the preference for the *endo*-cyclization.[6]

To improve the yield of the reaction, and to exclude the formation of the by-product 4-chloromethylimidazolidinone, we tested different reaction conditions by changing the oxidant reagent and the solvent (Table 1). The use of $Cu(OAc)_2$ as oxidant was unfruitful (entry 2), as well as the silver salt (entry 3) and 1,4-benzoquinone (entry 4). Positive results were reported with the inexpensive H_2O_2 as the sole oxidant (entry 5). The palladium catalyst was essential for the outcome of the reaction (entry 6), whereas different solvents than THF didn't afford the formation of the product (entries 7, 8).

The use of different aryl nucleophiles such as aryl boronic acids, Grignard reagents and arylzinc bromide didn't provide any addition. To exploit the central role of the arylstannane reagents, the 4-benzyloxyphenyltributylstannane (**2b**) was also tested with various *N*-allylureas (**1b-h**). Using the optimized conditions (Table 1, entry 5), the reactions proceeded smoothly providing the exclusive formation of the 4-substituted imidazolidinones **3**, confirming the selective 5-*exo* cyclization (Table 2). Only in two cases (reaction of substrates **1a** and **1g** with the arylstannanes **2b** and **2a** accordingly), the corresponding products were not isolated from the reaction mixture.

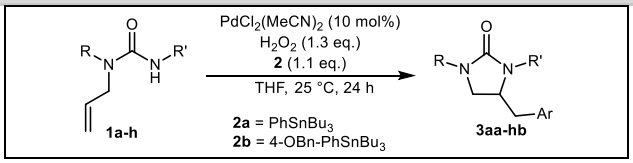
Table 1 Optimization conditions for aminoarylation reaction of *N*-allyl-urea **1a**[a]



Entry	Catalyst	Oxidant	Solvent	**3aa**(%)[b]
1	$PdCl_2(MeCN)_2$	$CuCl_2$	THF	39[c]
2	$PdCl_2(MeCN)_2$	$Cu(OAc)_2$	THF	--
3	$PdCl_2(MeCN)_2$	$AgCO_3$	THF	traces
4	$PdCl_2(MeCN)_2$	BQ	THF	traces
5	$PdCl_2(MeCN)_2$	H_2O_2	THF	59
6	-	H_2O_2	THF	SM
7	$PdCl_2(MeCN)_2$	H_2O_2	MeCN	traces
8	$PdCl_2(MeCN)_2$	H_2O_2	DMF	traces

[a] Reaction conditions: **1a** (0.25 mmol), catalyst (10 mol%), oxidant (1.3 equiv), arylating agent (1.1 equiv), solvent (5 mL). [b] Yield of isolated products. [c] Compound **4** was also isolated (35% yield).

Table 2 Aminoarylation process of *N*-allylureas **1a-h.**



Substrate	R	R'	$ArSnBu_3$	Product	Yield (%)
1a	Me	*p*-tolyl	**2a**	**3aa**	73
1a	Me	p-tolyl	**2b**	**3ab**	--
1b	Me	Ts	**2a**	**3ba**	59
1b	Me	Ts	**2b**	**3bb**	48
1c	Me	4-Cl-Ph	**2a**	**3ca**	66
1c	Me	4-Cl-Ph	**2b**	**3cb**	51
1d	cyclohexyl	Ts	**2a**	**3da**	62
1d	cyclohexyl	Ts	**2b**	**3db**	71
1e	cyclohexyl	4-Cl-Ph	**2a**	**3ea**	58
1e	cyclohexyl	4-Cl-Ph	**2b**	**3eb**	50
1f	Ph	4-Cl-Ph	**2a**	**3fa**	38
1f	Ph	4-Cl-Ph	**2b**	**3fb**	56
1g	Ph	Ts	**2a**	**3ga**	--
1g	Ph	Ts	**2b**	**3gb**	55
1h	Ph	4-Me-Ph	**2a**	**3ha**	59
1h	Ph	4-Me-Ph	**2b**	**3hb**	54

The ring structure was unambiguously confirmed by single crystal X-ray diffraction analysis of the product **3ea** (Fig. 1).[12]

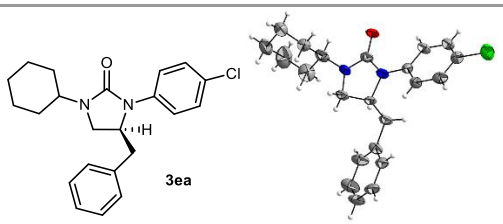
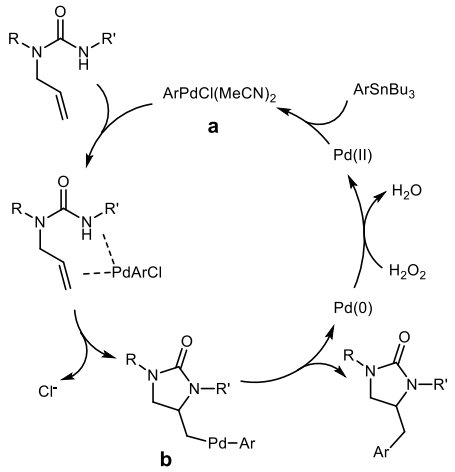


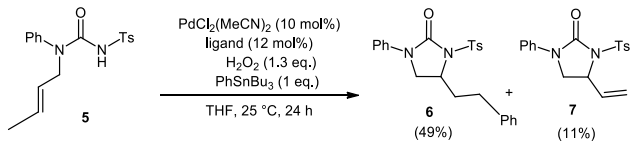
Figure 1 Left: Molecular structure of the S-enantiomer of the compound **3ea**, as determined by single crystal X-ray diffraction. Right: ORTEP scheme showing the corresponding in-crystal molecular conformation of (*S*)-**3ea** at r.t. Thermal ellipsoids are drawn at the 25 % probability level. C: gray; H: white; O: red; N: blue; Cl: green.

On the basis of the previously results reported on the aminoarylation of alkenes, under Pd(II) catalysis,[7e,i,r,s] a plausible mechanism is shown in Scheme 4. Arylpalladium(II) species (**a**) was first formed by transmetalation of arylstannane, followed by insertion of the double bond generating the σ-alkyl-Pd(II) intermediate(**b**). Reductive elimination of the metal and oxidation of Pd(0) to Pd(II) by H_2O_2 completed the catalytic cycle.



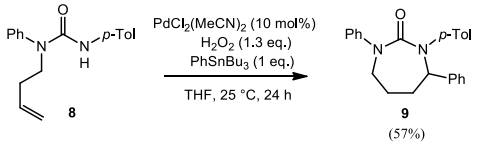
Scheme 4 Proposed mechanism for the 5-*exo-trig* cyclization of the substrates **1**.

The aminoarylation process was applied also on a non-terminal alkene. The *N*-2-butenyl-*N*-phenyl-*N'*-tosylurea **5** afforded as aminoarylation product the 4-(2-phenylethyl)-imidazolidinone **6** (Scheme 5). In this case the process was improved by using the Pd-complex in the presence of the (*S*)-4-tert-butyl-2-(2-pyridyl)oxazoline ligand. The product obtained could be justified through the isolation of the 4-vinyl-imidazolidinone **7** as result of the amination step only. The subsequent step of aryl insertion with reverse regiochemistry, afforded the aminoarylation product 6.



Scheme 5 Aminoarylation reaction of the substrate **5**.

Considering the reaction of the *N*-homoallylic substituted urea **8**, in the presence of phenyltributylstannane under the same reaction conditions, we reported the formation of the 4-phenyl-1,3-diazepan-2-one **9** through a 7-*endo-trig* cyclization (Scheme 6). This result supported a similar mechanism suggested in Scheme 4.[6] Initially, the double bond of the substrate **8** underwent arylation step (through the insertion of PhPdCl arising from transmetalation) with the formation of the σ-alkyl-Pd(II) intermediate. β-Hydride elimination and subsequent amination step with reverse regiochemistry, involving the benzylic position provided the 4-phenyl-1,3-diazepane **9**.



Scheme 6 Aminoarylation reaction of the substrate **8**.

In summary, we have developed an aminoarylation process of *N*-allylureas in the presence of aryltributylstannanes, performed under ligand-free Pd-catalysis, by using the H_2O_2 as oxidant. The reaction was chemo- and regioselective, affording the imidazolidinones as exclusive ring obtained.

Melting points were determined by the capillary method with a Büchi B-540 apparatus and are uncorrected. IR spectra were measured with a Jasco FT/IR 5300 spectrometer. ^{1}H NMR and ^{13}C NMR spectra were recorded with: AVANCE 400 Bruker spectrometer at 400 and 100 MHz, Varian Oxford 300 MHz spectrometer at 300 and 75 MHz and AVANCE 500 Bruker spectrometer at 500 and 125 MHz respectively. Chemical shifts are given as δ values in ppm relative to residual solvent peaks ($CHCl_3$) as the internal reference. ^{13}C NMR spectra are ^{1}H-decoupled and the determination of the multiplicities was achieved by the APT pulse sequence. Mass spectra were determined with a LCQ Advantage Thermo Finningan. Elemental analyses were executed on Perkin-Elmer CHN Analyzer Series II 2400. Thin-layer chromatographic separations were performed on Merck silica-gel 60-F_{254} precoated. Preparative separations were performed by flash chromatography by using Merck silica gel 0.035-0.070 mm.

Procedures

***N*-protected allyl urea: General Procedure**

To a solution of allyl amine (4 mmol) in acetonitrile (40 mL), the isocyanate (4 mmol) was added dropwise at 0 °C under inert atmosphere. The reaction mixture was allowed to warm to room temperature and it was stirred for 24 h. The solvent was evaporated under reduced pressure and the crude product was used without any further purification.

***N*-Allyl-*N*-methyl-*N*-tosyl-urea (1a)**[13]

Colorless oil, yield: 1040 mg (97%). ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.93 (d, *J* = 8.3 Hz, 2H), 7.38 – 7.27 (m, 3H), 5.72 (ddt, *J* = 15.8, 10.5, 5.3 Hz, 1H), 5.17 (dd, *J* = 20.5, 13.7 Hz, 2H), 3.83 (d, *J* = 5.3 Hz, 2H), 2.86 (s, 3H), 2.43 (s, 3H).

***N*-Allyl-*N*-methyl-*N'*-tolyl-urea (1b)**[14]

White solid, yield: 620 mg (76%): mp 110° C (hexane-Et_2O). ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.35 – 7.19 (m, 2H), 7.09 (d, *J* = 8.2 Hz, 2H), 6.73 (br s, 1H), 6.10 – 5.66 (m, 1H), 5.43 – 5.15 (m, 2H), 3.96 (d, *J* = 5.4 Hz, 2H), 3.00 (s, 3H), 2.29 (s, 3H).

***N*-Allyl-*N*-methyl-*N'*-(4-chlorophenyl)urea (1c)**[14]

White solid, yield: 842 mg (94%); mp 115° C (hexane-Et_2O). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.32 (d, *J* = 8.8 Hz, 2H), 7.23 (d, *J* = 8.8 Hz, 2H), 6.45 (br s, 1H), 5.76-5.94 (m, 1H), 5.25-5.30 (m, 2H), 3.97 (d, *J* = 5.2 Hz, 2H), 3.01 (s, 3H).

***N*-Allyl-*N*-cyclohexyl-*N'*-tosyl-urea (1d)**

Yellow oil, yield: 1317 mg (98%). IR: 1658 cm^{-1}. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.79 (d, *J* = 8.1 Hz, 2H), 7.26 (d, *J* = 8.5 Hz, 2H), 5.99 – 5.84 (m, 1H), 5.35 – 5.18 (m, 2H), 3.52 (d, *J* = 6.7 Hz, 2H), 2.91 – 2.72 (m, 1H), 2.40 (s, 3H), 1.98 – 0.96 (m, 10H).^{13}C NMR (101 MHz, $CDCl_3$) δ 155.3 (s), 143.4 (s), 142.5 (s), 139.3 (s), 129.9 (d), 129.6 (d), 126.4 (d), 121.7 (t), 55.7 (d) , 47.0 (t), 29.5 (t), 25.9 (t), 25.1 (t), 24.6 (t), 21.5 (q). MS: *m/z* 337.26 $(M+H)^+$.

***N*-Allyl-*N*-cyclohexyl-*N'*-(4-chlorophenyl)urea (1e)**

White solid; yield: 1113 mg (95%); mp 122° C (hexane-Et_2O); IR: 1663 cm^{-1} .^{1}H NMR (300 MHz, $CDCl_3$) δ 7.31 – 7.23 (m, 2H), 7.23 – 7.15 (m, 2H), 6.52 (br s, 1H), 5.90 (ddt, *J* = 17.3, 10.1, 5.0 Hz, 1H), 5.54 – 5.14 (m, 2H), 4.23 (tt, *J* = 11.5, 3.4 Hz, 1H), 3.83 (dt, *J* = 4.8, 1.8 Hz, 2H), 1.95 – 0.90 (m, 10H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 155.4 (s), 138.1 (s), 136.2 (d), 128.7 (d), 127.5 (s), 120.6 (d), 117.2 (s), 54.2 (d), 45.1 (t), 31.0 (t), 25.8 (t), 25.5 (t). MS: *m/z* 293.75 $(M+H)^+$. Anal. Calcd $C_{16}H_{21}ClN_2O$: C, 65.63; H, 7.23; N, 9.57. Found: C, 65.55; H, 7.29; N, 9.69.

***N*-Allyl-*N*-phenyl-*N'*-(4-chlorophenyl)urea (1f)**

White solid; yield: 1098 mg (96%); mp 75-76° C (hexane-Et_2O); IR: 1670 cm^{-1}. ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.62 – 7.07 (m, 9H), 6.19 (br s, 1H), 6.08 – 5.76 (m, 1H), 5.29 – 5.05 (m, 2H), 4.35 (d, *J* = 6.1 Hz, 2H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 153.8 (s), 141.1 (s), 137.4 (s), 133.9 (d), 130.3 (d), 128.7 (d), 128.5 (d) , 128.3 (d), 127.8 (s), 120.4 (d), 117.6 (t), 52.3 (t). MS: *m/z* 287.54 $(M+H)^+$. Anal. Calcd $C_{16}H_{15}ClN_2O$: C, 67.02; H, 5.27; N, 9.77. Found: C, 66.96; H, 5.36; N, 9.81.

***N*-Allyl-*N*-phenyl-*N'*-tosyl-urea (1g)**

Orange solid, yield: 1293 mg (98%); mp 74-76° C (hexane-Et_2O); IR: 1696 cm^{-1}. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.93 (d, *J* = 8.3 Hz, 2H), 7.53 – 7.38 (m, 3H), 7.38 – 7.26 (m, 2H), 7.19 (d, *J* = 7.2 Hz, 2H), 7.09 (br s, 1H), 5.79 (ddt, *J* = 16.7, 10.2, 6.4 Hz, 1H), 5.13 – 4.97 (m, 2H), 4.18 (d, *J* = 6.3 Hz, 2H), 2.46 (s, *J* = 5.4 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 150.1 (s), 144.6 (s), 139.3 (s), 136.1 (s), 132.4 (d), 130.6 (d), 129.5 (d), 129.1 (d), 128.4 (d), 128.3 (d), 118.7 (t), 52.4 (t), 21.7 (q). MS: (ESI) 353.67 *m/z* $(M+Na)^+$. Anal. Calcd for $C_{17}H_{18}N_2O_3S$: C, 61.80; H, 5.49; N, 8.48. Found: C, 61.66; H, 5.67; N, 8.31.

***N*-Allyl-*N*-phenyl-*N'*-tolyl-urea (1h)**

Pale-yellow solid; yield: 1000 mg (94%); mp 83-84° C (hexane-Et_2O); IR: 1660 cm^{-1}.^{1}H NMR (300 MHz, $CDCl_3$) δ 7.69 – 7.24 (m, 5H), 7.24 – 7.16 (m, 2H), 7.06 (d, *J* = 8.3 Hz, 2H), 6.15 (br s, 1H), 5.97 (ddt, *J* = 17.4, 9.8, 6.1 Hz, 1H), 5.27 – 4.96 (m, 2H), 4.37 (dt, *J* = 6.1, 1.2 Hz, 2H), 2.29 (s, 3H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 154.1 (s), 141.5 (s), 136.2 (s), 134.2 (d), 132.5 (s), 130.2 (d), 129.3 (d), 128.5 (d), 128.0 (d), 119.4 (d), 117.4 (t), 52.3 (t), 20.7 (q). MS: *m/z* 267.27 $(M+H)^+$, 289.29 $(M+Na)^+$. Anal. Calcd $C_{17}H_{18}N_2O$: C, 76.66; H, 6.81; N, 10.52. Found: C, 76.54; H, 6.90; N, 10.57.

***(E)*-*N*-But-2-en-1-yl-*N*-phenyl-*N'*-tosyl-urea (5)**

White solid; yield: 1087 mg (79%); mp: 104-107° C (decomp.); IR: 1690 cm^{-1}.^{1}H NMR (300 MHz, $CDCl_3$) δ 8.01 – 7.85 (m, 2H), 7.50 – 7.26 (m, 5H), 7.19 – 7.11 (m, 2H), 6.93 (br s, 1H), 5.46 – 5.36 (m, 2H), 4.12 – 4.01 (m, 2H), 2.44 (s, 3H), 1.58 (ddd, *J* = 4.0, 2.0, 1.0 Hz, 3H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 149.9 (s), 144.5 (s), 139.4 (s), 136.2 (s), 130.4 (d), 130.2 (d), 129.4 (d), 129.0 (d), 128.4 (d), 128.3 (d), 125.1 (d), 51.7 (t), 21.6 (q), 17.6 (q). MS: *m/z* 345.62 $(M+H)^+$. Anal. Calcd $C_{18}H_{20}N_2O_3S$: C, 62.77; H, 5.85; N, 8.13. Found: C, 62.86; H, 5.79; N, 8.04.

1-(But-3-en-1-yl)-1-phenyl-3-(*p*-tolyl)urea (8)

Pale-yellow oil; yield: (89%); IR: 1678 cm^{-1}. ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.49 (t, *J* = 7.4 Hz, 2H), 7.38 (dd, *J* = 15.1, 7.7 Hz, 1H), 7.32 (d, *J* = 7.2 Hz, 2H), 7.15 (d, *J* = 8.4 Hz, 2H), 7.03 (d, *J* = 8.3 Hz, 2H), 6.03 (s, 1H), 5.80 (ddt, *J* = 17.0, 10.2, 6.8 Hz, 1H), 5.06 (dd, *J* = 21.0, 5.3 Hz, 2H), 3.92 – 3.73 (m, 2H), 2.39 – 2.28 (m, 2H), 2.26 (s, 3H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 154.2 (s), 141.4 (s), 136.3 (s), 135.4 (d), 132.4 (s)l, 130.3 (d), 129.2 (d), 128.8 (d), 128.1 (d), 119.4 (d), 116.6 (t), 48.7 (t), 32.9 (t), 20.7 (q). MS: *m/z* 190.24 $(M+H)^+$. Anal. Calcd $C_{11}H_{13}N_2O$: C, 69.82; H, 6.92; N, 14.80. Found: C, 69.78; H, 6.99; N, 14.90.

Aminoarylation reaction of *N*-allyl urea: General procedure

A mixture of *N*-allylurea 1 (0.25 mmol.), $PdCl_2(CH_3CN)_2$ (10 mol%), H_2O_2 (0.33 mmol), and $PhSnBu_3$ (0.25 mmol.) in THF (0.2 M) was stirred at room temperature. In the case of the substrate **5**, also (*S*)-4-tert-butyl-2-(2-pyridyl)oxazoline ligand (12 mol%) was added to the reaction mixture. After 24 h the solvent was evaporated under reduced pressure and water (10 mL) was added. The aqueous layer was extracted with CH_2Cl_2 (3 x 10 mL), then the organic layers were dried over Na_2SO_4 and concentrated under reduced pressure. The crude product was purified by silica gel column chromatography to afford the corresponding imidazolidinone 3.

4-Benzyl-1-methyl-3-tolyl-imidazolidin-2-one (3aa)

Yellow oil, yield: 51 mg (73%); R_f 0.37 (n-Hex/EtOAc 3:1); IR: 1680 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.34 (d, *J* = 8.3 Hz, 2H), 7.30 – 7.03 (m, 7H), 4.40 – 4.29 (m, 1H), 3.27 (t, *J* = 8.7 Hz, 1H), 3.14 – 3.00 (m, 2H), 2.72 (s, 3H), 2.59 (dd, *J* = 13.6, 9.7 Hz, 1H), 2.27 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 136.7 (s), 136.2 (s), 133.4 (s), 129.6 (d), 129.2 (d), 128.7 (d), 126.8 (d), 121.4 (d), 54.8 (d), 49.4 (t), 38.1 (t), 31.1 (q), 20.8 (q). MS: *m/z* 281.51 $(M+H)^+$. Anal. Calcd $C_{18}H_{20}N_2O$: C, 77.11; H, 7.19; N, 9.99. Found: C, 77.22; H, 7.12; N, 9.91.

4-(chloromethyl)-1-methyl-3-(p-tolyl)imidazolidin-2-one (4)

Yellow oil, yield: 54 mg (35%); R_f 0.39 (n-Hex/EtOAc 3:1); IR: 1696 cm^{-1} ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.32 (d, *J* = 8.2 Hz, 2H), 7.17 (d, *J* = 8.0 Hz, 2H), 4.60 – 4.27 (m, 1H), 3.70 – 3.59 (m, 2H), 3.56 – 3.38 (m, 2H), 2.90 (s, 3H), 2.34 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 158.1 (s), 135.5 (s), 134.2 (s), 129.8 (d), 121.7

(d), 54.5 (d), 48.4 (t), 43.8 (t), 31.0 (q), 20.8 (q). MS: *m/z* 239.34 $(M+H)^+$. Anal. Calcd $C_{12}H_{15}ClN_2O$: C, 60.38; H, 6.33; N, 11.74. Found: C, 60.49; H, 6.30; N, 11.68.

4-Benzyl-1-methyl-3-tosyl-imidazolidin-2-one (3ba)

Yellow oil, yield: 52 mg (59%); R_f 0.43 (n-Hex/EtOAc 3:1); IR: 1690 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$) δ 7.91 (d, *J* = 8.2 Hz, 2H), 7.29 – 7.07 (m, 7H), 4.54 – 4.34 (m, 1H), 3.43 (dd, *J* = 13.0, 3.6 Hz, 1H), 3.19 (t, *J* = 9.0 Hz, 1H), 2.98 (dd, *J* = 9.2, 3.4 Hz, 1H), 2.71 (dd, *J* = 13.2, 9.9 Hz, 1H), 2.58 (s, 3H), 2.35 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 153.9 (s), 144.6 (s), 136.6 (s), 135.7 (s), 129.6 (d), 129.5 (d), 128.8 (d), 128.2 (d), 127.2 (d), 115.2 (d), 54.9 (d), 48.7 (t), 40.8 (t), 30.5 (q), 21.7 (q). MS: *m/z* 345.32 $(M+H)^+$. Anal. Calcd $C_{18}H_{20}N_2O_3S$: C, 62.77; H, 5.85; N, 8.13. Found: C, 62.83; H, 5.80; N, 8.17.

4-(4-Benzyloxyphenyl)methyl-1-methyl-3-tosylimidazolidin-2-one (3bb)

Yellow oil, yield: 54 mg (48%); R_f 0.39 (n-Hex/EtOAc 3:1); IR: 1696 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$) δ 7.89 (dd, *J* = 18.8, 8.3 Hz, 2H), 7.43 – 7.20 (m, 7H), 7.04 (d, *J* = 8.4 Hz, 2H), 6.85 (d, *J* = 8.4 Hz, 2H), 4.97 (s, 2H), 4.46 – 4.26 (m, 1H), 3.34 (dd, *J* = 13.5, 3.3 Hz, 1H), 3.19 (t, *J* = 9.0 Hz, 1H), 2.97 (dd, *J* = 9.4, 3.2 Hz, 1H), 2.66 (dd, *J* = 13.4, 9.7 Hz, 1H), 2.57 (s, 3H), 2.35 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 158.0 (s), 153.9 (s), 144.5 (s), 136.9 (s), 136.6 (s), 130.5 (d), 129.6 (d), 128.6 (d), 128.2 (d), 128.0 (d), 127.9 (s), 127.5 (d), 70.1 (t), 55.0 (d), 48.7 (t), 39.9 (t), 30.5 (q), 21.7 (q). MS: *m/z* 451.39 $(M+H)^+$. Anal. Calcd $C_{25}H_{26}N_2O_4S$: C, 66.65; H, 5.82; N, 6.22. Found: C, 66.51; H, 5.89; N, 6.20.

4-Benzyl-1-methyl-3-(4-chlorophenyl)imidazolidin-2-one (3ca)

White solid, yield: 50 mg (66%); mp 90° C (hexane-Et_2O); R_f 0.41 (n-Hex/EtOAc 3:1); IR: 1651 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 7.53 (d, *J* = 8.8 Hz, 2H), 7.42 – 7.21 (m, 5H), 7.16 (d, *J* = 7.2 Hz, 2H), 4.45 (ddd, *J* = 12.9, 8.6, 4.1 Hz, 1H), 3.40 (t, *J* = 8.8 Hz, 1H), 3.23 (dd, *J* = 8.9, 4.7 Hz, 1H), 3.12 (dd, *J* = 13.8, 3.1 Hz, 1H), 2.82 (s, 3H), 2.72 (dd, *J* = 13.7, 9.4 Hz, 1H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 137.5 (s), 136.2 (s), 131.3 (s), 129.2 (d), 129.0 (d), 128.8 (d), 128.5 (s), 127.0 (d), 121.7 (d), 54.3 (d), 49.1 (t), 37.9 (t), 31.0 (q). MS: *m/z* 301.79 $(M+H)^+$. Anal. Calcd $C_{17}H_{17}ClN_2O$: C, 67.88; H, 5.70; N, 9.31. Found: C, 67.97; H, 5.62; N, 9.36.

4-(4-Benzyloxyphenyl)methyl-1-methyl-3-(4-chlorophenyl)imidazolidin-2-one (3cb)

Yellow oil, yield: 52 mg (51%); R_f 0.38 (n-Hex/EtOAc 3:1); IR: 1646 cm^{-1} . ^1H NMR (400 MHz, $CDCl_3$) δ 7.59 – 7.28 (m, 10H), 7.03 (d, *J* = 8.3 Hz, 2H), 6.91 (d, *J* = 8.3 Hz, 2H), 5.04 (s, 2H), 4.43 – 4.28 (m, 1H), 3.37 (t, *J* = 8.7 Hz, 1H), 3.18 (dd, *J* = 8.5, 4.4 Hz, 1H), 3.00 (d, *J* = 13.9 Hz, 1H), 2.78 (s, 3H), 2.65 (dd, *J* = 13.7, 9.2 Hz, 1H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 158.0 (s), 157.9 (s), 137.5 (s), 136.9 (s), 130.2 (d), 129.1 (d), 129.0 (d), 128.6 (d), 128.4 (s), 128.0 (d), 127.5 (d), 121.8 (d), 115.2 (d), 70.1 (t), 54.4 (d), 49.1 (t), 37.00 (t), 31.0 (q). MS: *m/z* 407.85 $(M+H)^+$. Anal. Calcd $C_{24}H_{23}ClN_2O_2$: C, 70.84; H, 5.70; N, 6.88. Found: C, 70.95; H, 5.63; N, 6.79.

4-Benzyl-1-cyclohexyl-3-tosyl-imidazolidin-2-one (3da)

Yellow oil, yield: 64 mg (62%); R_f 0.44 (n-Hex/EtOAc 3:1); IR: 1658 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$) δ 7.93 (d, *J* = 8.1 Hz, 2H), 7.31 – 7.16 (m, 5H), 7.10 (d, *J* = 7.2 Hz, 2H), 4.54 – 4.37 (m, 1H), 3.58 – 3.42 (m, 1H), 3.31 (dd, *J* = 13.4, 3.4 Hz, 1H), 3.17 (t, *J* = 9.0 Hz, 1H), 2.95 (dd, *J* = 9.3, 2.6 Hz, 1H), 2.70 (dd, *J* = 13.3, 9.4 Hz, 1H), 2.35 (s, 3H), 1.79 – 0.62 (m, 10H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 152.9 (s), 144.5 (s), 136.7 (s), 135.7 (s), 129.6 (d), 129.5 (d), 128.8 (d), 128.2 (d), 127.1 (d), 55.0 (d), 51.4 (d), 42.1 (t), 40.4 (t), 30.0 (t), 29.7 (t), 25.3 (t), 25.2 (t), 21.7 (q). MS: *m/z* 413.26 $(M+H)^+$. Anal. Calcd $C_{23}H_{28}N_2O_3S$: C, 66.96; H, 6.84; N, 6.79. Found: C, 66.89; H, 6.92; N, 6.69.

4-(4-Benzyloxyphenyl)methyl-1-cyclohexyl-3-tosylimidazolidin-2-one (3db)

Yellow oil, yield: 92 mg (71%); R_f 0.36 (n-Hex/EtOAc 2:1); IR: 1692 cm^{-1}.^1H NMR (400 MHz, $CDCl_3$) δ 8.01 (d, *J* = 8.2 Hz, 2H), 7.47 – 7.28 (m, 7H), 7.11 (d, *J* = 8.4 Hz, 2H), 6.94 (d, *J* = 8.4 Hz, 2H), 5.06 (s, 2H), 4.61 – 4.44 (m, 1H), 3.69 – 3.52 (m, 1H), 3.46 – 3.23 (m, 2H), 3.04 (dd, *J* = 9.2, 2.6 Hz, 1H), 2.75 (dd, *J* = 13.5, 9.3 Hz, 1H), 2.44 (s, 3H), 1.92 – 0.87 (m, 10H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 158.0 (s), 152.9 (s), 144.4 (s), 137.0 (s), 136.8 (s), 130.6 (d), 129.5 (d), 128.6 (d), 128.3 (d), 128.1 (d), 128.0 (d), 127.9 (s), 127.4 (d), 115.2 (d), 70.1 (t), 55.1 (d), 51.4 (d), 42.2 (t), 39.5 (t), 30.1 (t), 29.7 (t), 25.3 (t), 25.2 (t), 21.7 (q). MS: *m/z* 519.67 $(M+H)^+$. Anal. Calcd $C_{30}H_{34}N_2O_4S$: C, 69.47; H, 6.61; N, 5.40. Found: C, 69.55; H, 6.69; N, 5.34.

4-Benzyl-1-cyclohexyl-3-(4-chlorophenyl)imidazolidin-2-one (3ea)

White solid, yield: 54 mg (58%); mp: 76° C, R_f 0.43 (n-Hex/EtOAc 3:1); IR: 1698 cm^{-1}. ^1H NMR (300 MHz, $CDCl_3$) δ 7.55 (d, *J* = 8.7 Hz, 2H), 7.42 – 7.23 (m, 5H), 7.13 (d, *J* = 6.8 Hz, 2H), 4.51 – 4.32 (m, 1H), 3.81 – 3.62 (m, 1H), 3.38 (t, *J* = 8.7 Hz, 1H), 3.17 (dd, *J* = 8.8, 3.9 Hz, 1H), 3.04 (dd, *J* = 14.0, 2.7 Hz, 1H), 2.71 (dd, *J* = 13.8, 8.8 Hz, 1H), 1.88 – 0.98 (m, 10H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 156.7 (s), 137.7 (s), 136.2 (s), 129.2 (d), 129.0 (d), 128.7 (d), 128.0 (s), 126.9 (d), 121.3 (d), 54.3 (d), 51.2 (d), 42.1 (t), 37.6 (t), 30.2 (t), 29.9 (t), 25.5 (t), 25.5 (t). MS: *m/z* 369.45 $(M+H)^+$. Anal. Calcd $C_{22}H_{25}ClN_2O$: C, 71.63; H, 6.83; N, 7.59. Found: C, 71.58; H, 6.80; N, 7.66.

Single crystal X-ray diffraction analysis. See the Supporting Information for more details. The data collection was carried out on a Bruker AXS Smart APEX 3-circle diffractometer with graphite-monochromated Mo Kα radiation (λ = 0.71073 Å) at a nominal power of the source of 50 kV x 30 mA. A 100 % complete full sphere of reflections was measured up to a resolution of $\sin\theta/\lambda = 0.45$ $Å^{-1}$ by means of 5 ω–scans of the reciprocal lattice. The Saint+ [] and SADABS [] programs were employed to account for systematic errors, including absorption and beam anisotropy corrections. The compound crystallizes in a $P2_1/c$ centric lattice (a = 11.1136(19) Å, b = 12.867(2) Å, c = 29.058(5) Å, β = 94.558(11)º) as a 1:1 racemate, with two molecules with inverse handedness per asymmetric unit and a total of 8 molecules per cell. The molecular structure was solved through the charge flipping method [] and least-squares refined within the Independent Atom Model approximation implemented in Shelx. [] 23311 individual structure factor amplitudes, corresponding to 3255 independent observations, entered the fitting, giving a final agreement factor R1(F) of 0.1064 for 1758 $F_o > 4\sigma(F_o)$ in conjunction with a goodness-of-fit of 1.040 and largest Fourier residuals of +0.40 / –0.31 e/$Å^3$, both close to the chlorine heavy atom.

4-(4-Benzyloxyphenyl)methyl-1-cyclohexyl-3-(4-chlorophenyl)imidazolidin-2-one (3eb)

Pale-yellow oil, yield: 59 mg (50%); R_f 0.32 (n-Hex/EtOAc 3:1); IR: 1698 cm^{-1}. ^1H NMR (300 MHz, $CDCl_3$) δ 7.60 – 7.51 (m, 2H), 7.49 – 7.30 (m, 7H), 7.10 – 7.00 (m, 2H), 6.98 – 6.89 (m, 2H), 5.07 (s, 2H), 4.40 (ddd, *J* = 12.5, 8.6, 3.9 Hz, 1H), 3.74 (tt, *J* = 12.1, 3.9 Hz, 1H), 3.39 (t, *J* = 8.8 Hz, 1H), 3.17 (dd, *J* = 8.9, 4.3 Hz, 1H), 2.98 (dd, *J* = 13.9, 3.3 Hz, 1H), 2.68 (dd, *J* = 13.9, 8.7 Hz, 1H), 1.93 – 0.95 (m, 10H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 157.9 (s), 156.7 (s), 137.8 (s), 137.0 (s), 130.3 (d), 129.0 (d), 128.6 (d), 128.5 (s), 128.0 (d), 127.4 (d), 121.3 (d), 115.1 (d), 70.1 (t), 54.4 (d), 51.2 (d), 42.1 (t), 36.8 (t), 30.3 (t), 29.9 (t), 25.5 (t), 25.5 (t). MS: *m/z* 475.56 $(M+H)^+$, 498.03 $(M+Na)^+$. Anal. Calcd $C_{29}H_{31}ClN_2O_2$: C, 73.33; H, 6.58; N, 5.90. Found: C, 73.46; H, 6.50; N, 5.84.

4-benzyl-3-(4-chlorophenyl)-1-phenylimidazolidin-2-one (3fa)

Colorless oil, yield: 34 mg (38%); R_f 0.31 (n-Hex/EtOAc 4:1); IR: 1690 cm^{-1}. ^1H NMR (300 MHz, $CDCl_3$) δ 7.61 – 7.53 (m, 2H), 7.51 – 7.44 (m, 2H), 7.43 – 7.13 (m, 8H), 7.11 – 7.02 (m, 2H), 4.67 – 4.51 (m, 1H), 3.90 (t, *J* = 9.0 Hz, 1H), 3.67 (dd, *J* = 9.3, 4.8 Hz, 1H), 3.18 (dd, *J* = 13.8, 3.4 Hz, 1H), 2.77 (dd, *J* = 13.8, 9.4 Hz, 1H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 154.8 (s), 139.7 (s), 136.8 (s), 135.7 (s), 129.4 (s), 129.1 (d), 128.9 (d), 128.8 (d), 127.2 (d), 123.2 (d), 122.7 (d), 118.2 (d), 53.9 (d), 47.0 (t), 38.3 (t). MS: *m/z* 363.17 $(M+H)^+$. Anal. Calcd $C_{22}H_{19}ClN_2O$: C, 72.82; H, 5.28; N, 7.72. Found: C, 72.76; H, 5.25; N, 7.79.

4-(4-Benzyloxyphenyl)methyl-1-phenyl-3-(4-chlorophenyl) imidazolidin-2-one (3fb)

Yellow oil, yield: 66 mg (56%); R_f 0.34 (n-Hex/EtOAc 4:1); IR: 1688 cm^{-1}. ^1H NMR (300 MHz, $CDCl_3$) δ 7.62 – 7.28 (m, 13H), 7.15 – 7.03 (m, 3H), 6.97 – 6.84 (m, 2H), 5.04 (s, 2H), 4.62 – 4.46 (m, 1H), 3.90 (t, *J* = 9.0 Hz, 1H), 3.66 (dd, *J* = 9.2, 4.9 Hz, 1H), 3.10 (dd, *J* = 13.9, 3.4 Hz, 1H), 2.73 (dd, *J* = 13.9, 9.1 Hz, 1H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 158.0 (s), 154.9 (s), 139.7 (s), 136.9 (s), 130.2 (d), 129.4 (s), 129.1 (d), 128.8 (d), 128.6 (d), 128.0 (d), 127.9 (s), 127.4 (d), 123.1 (d), 122.6 (d), 118.2 (d), 115.3 (d), 70.1 (t), 53.9 (d), 47.0 (t), 37.4 (t). MS: *m/z* 469.57 $(M+H)^+$. Anal. Calcd $C_{29}H_{25}ClN_2O_2$: C, 74.27; H, 5.37; N, 5.97. Found: C, 74.36; H, 5.31; N, 5.94.

4-(4-Benzyloxyphenyl)methyl-1-phenyl-3-tosylimidazolidin-2-one (3gb)

Yellow oil, yield: 71 mg (55%); R_f 0.36 (n-Hex/EtOAc 3:1); IR: 1695 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$) δ 7.96 (d, *J* = 8.2 Hz, 2H), 7.41 – 7.15 (m, 11H), 7.08 (d, *J* = 8.4 Hz, 2H), 7.00 (t, *J* = 7.1 Hz, 1H), 6.86 (d, *J* = 8.5 Hz, 2H), 4.97 (s, 2H), 4.65 – 4.41 (m, 1H), 3.72 (t, *J* = 9.1 Hz, 1H), 3.50 – 3.37 (m, 2H), 2.76 (dd, *J* = 13.4, 9.8 Hz, 1H), 2.36 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 158.1 (s), 151.4 (s), 144.9 (s), 138.4 (s), 136.9 (s), 136.3 (s), 130.6 (d), 129.6 (d), 128.9 (d), 128.6 (d), 128.4 (d), 128.0 (d), 127.7 (s), 127.5 (d), 124.3 (d), 118.8 (d), 115.3 (d), 70.1 (t), 54.5 (d), 47.2 (t), 40.0 (t), 21.7 (q). MS: *m/z* 513.43 $(M+H)^+$. Anal. Calcd $C_{30}H_{28}N_2O_4S$: C, 70.29; H, 5.51; N, 5.46. Found: C, 70.38; H, 5.43; N, 5.43.

4-benzyl-1-phenyl-3-(p-tolyl)imidazolidin-2-one (3ha)

Colorless oil, yield: 50 mg (59%); R_f 0.38 (n-Hex/EtOAc 4:1); IR: 2921, 1705, 1404, 1292 cm^{-1}. ^1H NMR (300 MHz, $CDCl_3$) δ 7.55 – 7.44 (m, 4H), 7.37 – 7.13 (m, 9H), 7.10 – 7.01 (m, 1H), 4.64 – 4.51 (m, 1H), 3.85 (t, *J* = 9.0 Hz, 1H), 3.65 (dd, *J* = 9.2, 5.3 Hz, 1H), 3.20 (dd, *J* = 13.7, 3.3 Hz, 1H), 2.74 (dd, *J* = 13.7, 9.6 Hz, 1H), 2.36 (d, *J* = 8.2 Hz, 3H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 155.3 (s), 140.1 (s), 136.1 (s), 135.5 (s), 134.3 (s), 129.7 (d), 129.4 (d), 129.2 (d), 128.8 (d), 128.8 (d), 127.0 (d), 122.8 (d), 122.3 (d), 118.0 (d), 54.3 (d), 47.1 (t), 38.5 (t), 20.9 (q). MS: *m/z* 343.60$(M+H)^+$. Anal. Calcd $C_{23}H_{22}N_2O$: C, 80.67; H, 6.48; N, 8.18. Found: C, 80.75; H, 6.54; N, 8.11.

4-(4-Benzyloxyphenyl)methyl-1-phenyl-3-tolylimidazolidin-2-one (3hb)

Colorless oil, yield: 61 mg (54%); R_f 0.40 (n-Hex/EtOAc 4:1); IR: 1690 cm^{-1}. ^1H NMR (300 MHz, $CDCl_3$) δ 7.57 – 7.19 (m, 13H), 7.12 – 7.04 (m, 3H), 6.97 – 6.88 (m, 2H), 5.04 (s, *J* = 7.3 Hz, 2H), 4.59 – 4.45 (m, 1H), 3.86 (t, *J* = 8.9 Hz, 1H), 3.64 (dd, *J* = 9.2, 5.3 Hz, 1H), 3.12 (dd, *J* = 13.8, 3.3 Hz, 1H), 2.69 (dd, *J* = 13.8, 9.5 Hz, 1H), 2.37 (s, 3H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 157.9 (s), 155.3 (s), 140.1 (s), 136.9 (s), 135.5 (s), 134.2 (s), 130.2 (d), 129.7 (d), 128.7 (d), 128. 6 (d), 128.3 (s), 128.0 (d), 127.4 (d), 122.7 (d), 122.2 (d), 118.0 (d), 115.2 (d), 70.1 (t), 54.3 (d), 47.1 (t), 37.5 (t), 20.9 (q). MS: *m/z* 449.48 $(M+H)^+$, 471.52 $(M+Na)^+$. Anal. Calcd $C_{30}H_{28}N_2O_2$: C, 80.33; H, 6.29; N, 6.25. Found: C, 80.26; H, 6.28; N, 6.28.

4-phenethyl-1-phenyl-3-tosylimidazolidin-2-one (6)

Colorless oil, yield: 52 mg (49%); R_f 0.29 (n-Hex/EtOAc 4:1); IR: 1695 cm^{-1}. ^1H NMR (300 MHz, $CDCl_3$) δ 8.00 (d, *J* = 8.3 Hz, 2H), 7.50 – 7.08 (m, 12H), 4.57 – 4.46 (m, 1H), 4.03 (t, *J* = 9.1 Hz, 1H), 3.56 (dd, *J* = 9.2, 3.4 Hz, 1H), 2.77 – 2.64 (m, 2H), 2.50 – 2.37 (m, 4H), 2.28 – 2.15 (m, 1H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 144.8 (s), 140.0 (s), 138.3 (s), 136.1 (s), 129.6 (d), 129.0 (d), 128.6 (d), 128.3 (d), 128.3 (d), 126.4 (d), 124.4 (d), 119.5 (s), 118.7 (d), 53.1 (d), 48.1 (t), 36.3 (t), 30.3 (t), 21.7 (q). MS: *m/z* 420.90 $(M+H)^+$. Anal. Calcd $C_{24}H_{24}N_2O_3S$: C, 68.55; H, 5.75; N, 6.66. Found: C, 68.63; H, 5.71; N, 6.60.

4-vinyl-1-phenyl-3-tosylimidazolidin-2-one (7)

Colorless oil, yield: 10 mg (11%); R_f 0.19 (n-Hex/EtOAc 4:1); IR: 1689 cm^{-1}. ^1H NMR (500 MHz, $CDCl_3$) δ 8.02 – 7.97 (m, 2H), 7.48 – 7.43 (m, 2H), 7.38 – 7.31 (m, 4H), 7.14 (d, *J* = 7.4 Hz, 1H), 5.95 (ddd, *J* = 17.0, 10.1, 8.0 Hz, 1H), 5.53 (d, *J* = 17.0 Hz, 1H), 5.38 (d, *J* = 10.2 Hz, 1H), 4.94 (td, *J* = 8.8, 3.4 Hz, 1H), 4.15 (t, *J* = 9.1 Hz, 1H), 3.58 (dd, *J* = 9.3, 3.4 Hz, 1H), 2.45 (s, 3H). ^{13}C NMR (126 MHz, CDCl3) δ 151.3 (s), 144.7 (s), 138.4 (s), 136.2 (s), 135.2 (d), 129.5 (d), 129.0 (d), 128.6 (d), 124.4 (d), 119.4 (t), 118.7 (d), 55.8 (d), 49.2 (t), 21.7 (q). MS: *m/z* 365.22 $(M+Na)^+$.

1,4-diphenyl-3-(*p*-tolyl)-1,3-diazepan-2-one (9)

Colorless oil, yield: 51 mg (57 %); R_f 0.37 (n-Hex/EtOAc 3:1); IR: 1694 cm^{-1}. ^1H NMR (300 MHz, $CDCl_3$) δ 7.62 – 7.11 (m, 28H), 7.05 (d, *J* = 8.4 Hz, 5H), 4.93 (dd, *J* = 8.1, 6.2 Hz, 2H), 3.82 (td, *J* = 7.3, 2.0 Hz, 4H), 2.28 (s, 7H), 2.24 – 2.02 (m, 4H), 1.90 – 1.49 (m, 5H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 154.4 (s), 141.7 (s), 141.1 (s), 136.2 (s), 132.5 (s), 130.4 (d), 129.3 (d), 128.7 (d), 128.6 (d), 128.3 (d), 128.2 (d), 126.9 (d), 119.5 (d), 63.4 (d), 48.3 (t), 37.1 (t), 26.0 (t), 20.7 (q). MS: *m/z* 379.81 $(M+Na)^+$. Anal. Calcd $C_{35}H_{37}N_4O_2$: C, 77.03; H, 6.83; N, 10.27. Found: C, 77.12; H, 6.78; N, 10.21.

Acknowledgment

Università degli Studi di Milano is acknowledged for financial support. Support through CMST COST Action, CA15106 (CHAOS) is also gratefully acknowledged.

Supporting Information

YES (this text will be updated with links prior to publication)

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