Palladium(0)-Catalyzed Reaction of Acidic Anilines with (*Z*)-2-Butene-1,4-diyl Dicarbonate – Preparation of *N*-Aryl-4-vinyloxazolidin-2-ones

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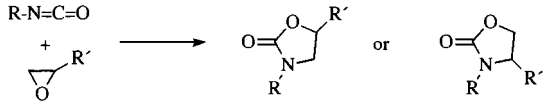
Palladium-catalyzed reaction of acidic anilines with (*Z*)-2-butene-1,4-diyl dicarbonate affords *N*-aryl-4-vinyloxazolidin-2-ones. The success of the reaction depends on the acidity of the aniline and requires in situ conversion of the dicarbonate into carbamate carbonate by nucleophilic attack of the aniline conjugate base followed by palladium-catalyzed intramolecular cyclization.

Introduction

Oxazolidin-2-ones are masked amino alcohols which have attracted a great deal of interest.[1] Oxazolidin-2-ones can be prepared by thermal or catalytic reaction of oxiranes with isocyanates (Scheme 1). For monosubstituted oxiranes this method produces in general 5-substituted oxazolidin-2-ones,[2] although certain catalysts favor the 4-substituted isomers.[3] Trost[4a,4b] and Alper[4c] have reported the formation of *N*-aryl-4-vinyloxazolidin-2-ones by palladium-catalyzed reaction of vinyloxiranes with isocyanates[4] but the method failed in the case of 4-nitrophenyl isocyanate.[4c] Related work by Hayashi[5a] and by Trost[5b–f] consists of the palladium(0)-catalyzed cyclization of 2-alkene-1,4-diyl dicarbamates to 4-vinyloxazolidinones. Other recent preparations of oxazolidin-2-ones under palladium catalysis are the cyclization of propargyl tosylcarbamates[6] and of allenyl tosylcarbamates.[7]



Scheme 1. Oxazolidin-2-ones by reaction of oxiranes with isocyanates

Palladium-catalyzed allylation of nucleophiles (the Tsuji–Trost reaction) is a synthetic method highly accepted due to its broad applicability and facile experimental procedure.[8] Moreover, for most usual nucleophiles the Tsuji–Trost reaction takes place with overall retention of configuration at the electrophilic center thus offering a stereochemical complement to the noncatalyzed substitutions. We have reported the palladium-catalyzed allylation of acidic anilines[9] and of other acidic nitrogen nucleophiles,[10] which occurs with overall stereochemical retention of configuration.

However, unexpected results were obtained when acidic anilines **1** reacted with (*Z*)-2-butene-1,4-diyl dicarbonate (**2**) in the presence of Pd^0 species and these results will be presented here.

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Pd^0-catalyzed allylation of nucleophiles with butene-1,4-diol derivatives produces cyclic products. Thus, dinucleophiles of type 1,1 (doubly nucleophilic reagents with a nucleophilic atom which may react twice, such as $R-NH_2$, $RCO-CH_2-COR$, etc.) produce three- or five-membered rings. In a mechanistically related work Ibuka and co-workers have reported the Pd^0-catalyzed isomerization of *cis*- and *trans*-2-alkyl-*N*-alkyl(or -aryl)sulfonyl-3-vinylaziridines[11] without formation of five-membered rings. In contrast, Oshima described the isomerization of 2-(1,3-butadienyl)-*N*-tosylaziridines into 2,5-dihydro-*N*-tosyl-2-vinylpyrroles.[12] Strong electron-attracting *N*-sulfonyl groups are required in both cases for isomerization to occur through aziridine opening. In contrast, five-membered pyrroles and derivatives are directly formed from 1,4-difunctionalized butenes under Pd catalysis.[13] Dinucleophiles of type 1,4 (Y–C–C–X) produce upon reaction with 2-butene-1,4-diol derivatives, vinyl-substituted 6-membered rings where X = Y = NHR,[14,15,16a] X = NHR and Y = OH,[14,15,16b,16c] and X = Y = OH.[17] This includes highly acidic arenesulfonamide nucleophiles.[14,15,16c] However, the reactions of dinucleophiles of types 1,5 and 1,6 [$TsNH(CH_2)_nNHTs$ (n = 3,4)] with butene-1,4-diyl dicarbonate afford 8- and 9-membered rings instead of vinyl substituted 6- and 7-membered rings.[14]

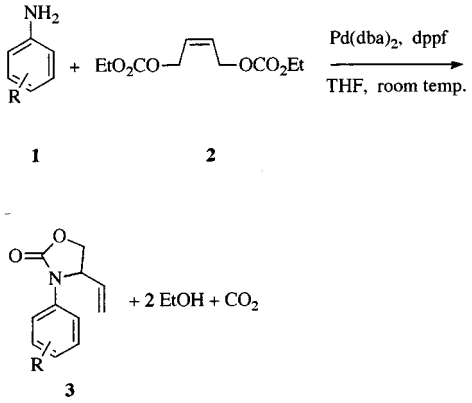
The 4-membered ring *N*-(trifluoromethanesulfonyl)-2-vinylazetidine opens under Pd^0 catalysis and dimerizes to the corresponding twelve-membered ring instead to recyclize to the 6-membered ring.[18]

Results and Discussion

With the above precedents in mind we were surprised to find the results of Scheme 2 and Table 1. The reactions of anilines **1** with dicarbonate **2** produce *N*-aryl-4-vinyloxazolidin-2-ones **3** in excellent yields. The precatalytic system [bis(dibenzylidene)acetone]palladium/1,1′-bis(diphenylphosphanyl)ferrocene was used. The bidentate phosphane 1,1′-bis(diphenylphosphanyl)ethane gave also good results, but with $Pd(PPh_3)_4$ the reaction failed and the anilines were not consumed. The IR ($\tilde{\nu}$ in the range 1749–1758 cm^{-1})

  1434–193X/99/0101–0181 $ 17.50+.50/0

and NMR spectra as well as analytical data are in agreement with the proposed structures (see Experimental Section). NOE experiments were performed in order to ascertain the position of the vinyl chain. In some cases minor isomers very similar to **3** in their general structure could be isolated (see experiments 1, 4, and 5 of Table 1). They were characterized as *N*-aryl-5-vinyl-1,3-oxazolidin-2-ones **14** by NOE experiments and X-ray diffraction (for **14a**, full details on X-ray diffraction will be published elsewhere in due time). Thus, for 4-vinyloxazolidinone **3a** irradiation at δ = 8.76 (aromatic H *ortho* to the oxazolidinone ring) produces NOE enhancements at the 4-H signal at δ = 5.06 (2.9%) and also at the terminal vinylic protons signals (0.8%); for the regioisomeric compound **14a**, by irradiation at δ = 8.77 (aromatic H *ortho* to the oxazolidinone ring) NOE enhancements were observed for 4-H and 4′-H at δ = 3.95 (0.9%) and 4.37 (1.9%). Similar results were also obtained for **3b**. Also, DEPT experiments performed on **3a**, **14a** and **3b** confirmed the position of the vinyl group in the oxazolidinone ring.



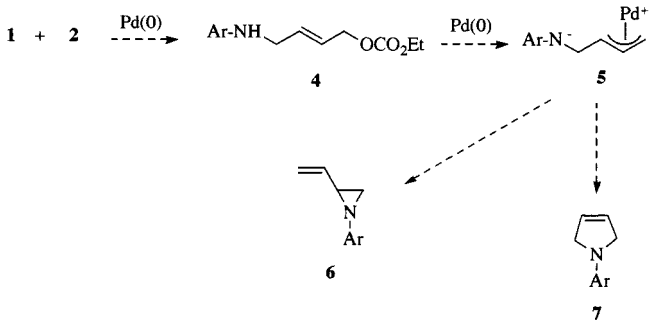
Scheme 2. Pd^0-catalyzed formation of *N*-aryl-4-vinyloxazolidin-2-ones

Table 1. Palladium-catalyzed reactions of anilines **1** with dicarbonate **2**[a]

entry	**1**, R	[**1**]	**2**:**1**[b]	time [h]	**3** (%)[c]
1	**1a**, 3,5-$(NO_2)_2$	0.2 M	2:1	7	**3a** (52)[d,e]
2	**1b**, 4-(NO_2)	0.3 M	2:1	48	**3b** (81)
3	**1c**, 4-NC	0.6 M	2:1	24	**3c** (80)
4	**1d**, 3,5-$(CF_3)_2$	0.2 M	2:1	48	**3d** (93)[d]
5	**1e**, 3,5-$(Cl)_2$	0.2 M	2:1	36	**3e** (80)[d]
6	**1f**, 3-NO_2	0.5 M	2:1	7	**3f** (74)
7	**1g**, 4-MeOCO	0.5 M	1.5:1	24	**3g** (83)
8	**1h**, 3-Cl, 4-F	0.5 M	2:1	24	**3h** (47)
9	**1i**, 4-CF_3	0.4 M	2:1	6	**3i** (73)
10	**1j**, 4-I	0.3 M	1.5:1	24	**3j** (60)
11	**1k**, 4-Cl	0.6 M	1.5:1	24	**3k** (50)
12	**1l**, H	0.5 M	2:1	48	**3l** (22)
13	**1m**, 4-MeO	0.3 M	1.5:1	48	**3m** (15)

[a] All reactions were carried out in THF at room temp. for the indicated non-optimized time in the presence of 5% $Pd(dba)_2$ and 15% dppf unless otherwise stated. – [b] Yields of **3** were somehow dependent on this molar excess of **2**. – [c] Isolated yields. – [d] 3-Aryl-5-vinyloxazolidin-2-one **14** were also isolated: **14a** (15%), **14d** (4%), and **14e** (5%). – [e] When bis(1,2-diphenylphosphanyl)ethane (dppe) was used in the place of dppf, **3a** (27%) and **14a** (35%) were isolated after 24 h.

An examination of Table 1 reveals that at least moderate electron-withdrawing groups are required for the success of the reaction. The experiments of Table 1 are ordered by decreasing σ^- values and it is evident that results synthetically useful are not achieved for substituents H and 4-OMe. Nevertheless, experiments with *ortho*-substituted anilines bearing electron-withdrawing groups (i.e. 2-nitroaniline, 2,4-dinitroaniline, 2,6-dichloro-4-nitroaniline, 2,3,4,5,6-pentafluoroaniline) failed to give oxazolidinones, thus pointing out that *ortho* positions must be free. In no case vinylaziridines **6** or dihydropyrroles **7** were isolated. The formation of these compounds was a priori possible as depicted in Scheme 3.



Scheme 3. Alternative pathway leading to vinylaziridines **6** and dihydropyrroles **7**

All experimental facts can be explained by the sequence of events of Scheme 4.

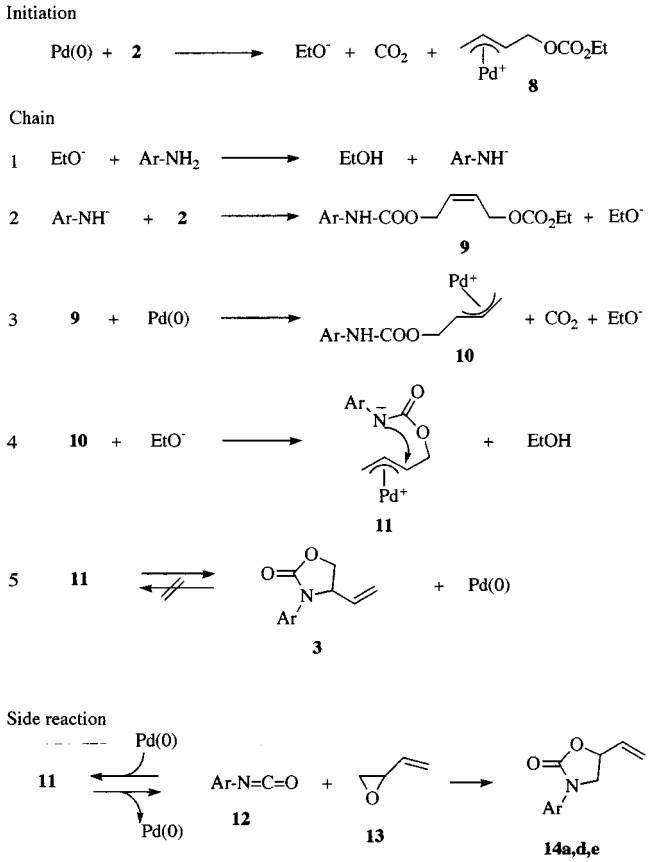
Step 0 is the initiation step according to the well-known reaction of Pd^0 species with allylic carbonates.[19] The ethoxide anion thus formed triggers the cycle of reactions 1−5, the net result of which is shown in Scheme 2.

Step 1 is quantitatively shifted to the right in all experiments except for 12 and 13 (R = H and 4-OMe). The order of acidities in THF is assumed to be the same as in DMSO, but different from the order in water.[20] Bordwell has published lists of acidities of proton-active compounds in DMSO and the following values are relevant:[20] pK_a (DMSO): 4-nitroaniline (**1b**): 20.9; methanol: 29.0; aniline (**1l**): 30.6. Therefore, according to σ^- values all or nearly all anilines of Table 1 should be more acidic than ethanol (about the same pK_a value than methanol) with the only exceptions of **1l** and **1m** (experiments 12 and 13).

Step 2 is a transamidation which probably does not require palladium in a specific form, but only the base (anion ethoxide) generated in situ from allylic dicarbonate **2** and the Pd^0 species. Bäckvall has reported a close precedent[21], the formation of the *N*-benzylcarbamate of *cis*-4-acetoxy-2-cyclohexen-1-ol by reaction of its methylcarbonate with benzylamine in the presence of Pd^0,[21] although oxazolidinone formation was not observed.

Step 3 is again a straightforward reaction of an allylic carbonate with the Pd^0 species to afford intermediate **10**; *anti-syn* isomerization might occur at this level as it is usual for cationic (η^3-allyl)palladium complexes.

Step 4 is the straightforward formation of the required zwitterionic intermediate **11**.



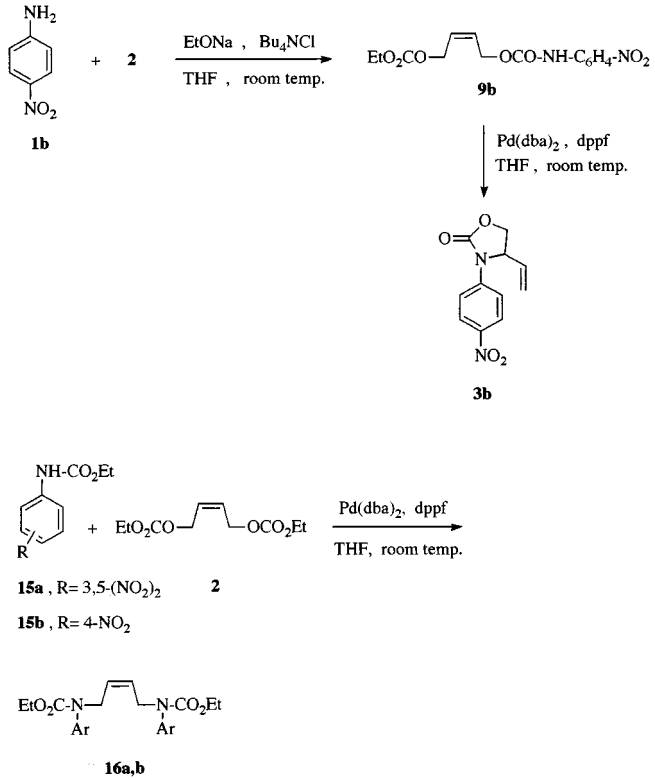
Scheme 4. Sequence of events leading to *N*-aryloxazolidin-2-ones **3** and **14**

Step 5 is the intramolecular cyclization of intermediate **11** to *N*-aryloxazolidin-2-ones **3** with recovery of the catalytic species.

Long-lived zwitterions **11** are anticipated for strong electron-withdrawing substituents R. In such cases **11** can also deliver aryl isocyanates **12** and vinyloxirane **13**. We have no direct evidence for the formation of **12** and/or **13**, but their noncatalyzed reaction explains the formation of minor quantities of 5-vinyloxazolidinones **14** sometimes isolated.[2]

Further experiments were performed to gain better mechanistic insight. Thus, *N*-(3,5-dinitrophenyl)-4-vinyloxazolidin-2-one (**3a**) was recovered after standard treatment with the catalytic system for seven days, no isomerization to the 5-isomer being observed. Thus, cyclization of **11** into **3a** is not reversible under the reaction conditions (Scheme 4). 4-Nitroaniline (**1b**) reacts with **2** in the presence of sodium ethoxide and a phase-transfer agent to afford carbamate **9b**, which cyclizes to **3b** under Pd^0 catalysis (Scheme 5). Reaction of arylcarbamates **15a** and **15b** with **2** under palladium catalysis affords only the disubstitution compounds **16** (undetermined stereochemistry), thus ruling out the intervention of **15** in the formation of oxazolidinones.

Finally, we examined by GLC-MS analysis the crude product of the reaction of 4-methoxyaniline (**1m**) and dicarbonate **2** (experiment 13 in Table 1) and peaks were observed attributable to the following compounds: 4-Me-



Scheme 5. Complementary experiments

$OC_6H_4-NH-CH_2CH=CH-CH_2-OEt$ [*m/z* (%): 221 (49) $[M^+]$, 122 (100)]; 4-$MeOC_6H_4-NHCO_2-CH_2CH=CH-CH_2-OCO_2Et$ {*m/z* (%): 309 (6) $[M^+]$, 135 (100)}; oxazolidinone **3m** {*m/z* (%): 219 (100) $[M^+]$, see Scheme 2}; mixed carbonate **4m** {*m/z* (%): 265 (9) $[M^+]$, 162 (100), see Scheme 3}; vinylaziridine **6m** or dihydropyrrole **7m** {*m/z* (%): 175 (100) $[M^+]$, see Scheme 3}.

In summary, an efficient method to prepare *N*-aryl-4-vinyloxazolidin-2-ones is reported as a consequence of an unprecedented reactivity of 2-butene-1,4-diyl dicarbonate. Indeed, the experimental results require that the conjugate base of the arylamine reacts faster with dicarbonate **2** (uncatalyzed reaction 2 of Scheme 4) than with the cationic (η^3-allyl)palladium complex **8** to afford products **4** of Scheme 3.

Experimental Section

General: All reactions under Pd catalysis were performed under inert atmosphere with anhydrous solvents using standard Schlenk techniques. Syringes or cannulae were used for transfer of solutions. Carbamates **15a**,**b** were prepared by standard procedures by reaction of corresponding anilines **1a**,**b** with ethyl chloroformate or diethyl carbonate and they have been reported in the literature.[22] Oxazolidinones **3k**[4c] and **3l**[3] had been described in the literature. THF was distilled from sodium benzophenone ketyl. All solutions were concentrated under reduced pressure in a rotary evaporator. – Melting points were determined with a Kofler apparatus and are uncorrected. – IR spectra were recorded with a Nicolet FT-IR 510 ZDX. – NMR spectra were recorded with a Bruker AC250 or a Bruker AM400. ^{1}H-NMR (250 MHz) chemical shifts are reported

relative to $CHCl_3$ at δ = 7.26 and tetramethylsilane at δ = 0.00. Coupling constants are reported in Hz. ^{13}C-NMR (62.5 MHz) chemical shifts are expressed relative to $CDCl_3$ at δ = 77.00 and tetramethylsilane at δ = 0.00. − Mass spectra (EIMS) were obtained with a Hewlett-Packard 5989A spectrometer and determined at an ionizing voltage of 70 eV; relevant data are listed as *m/z* (%). − Elemental analyses were performed at Servei d'Anàlisi Química de la Universitat Autònoma de Barcelona.

Reaction of 3,5-Dinitroaniline (1a) with Dicarbonate 2 under Pd^0 Catalysis (Entry 1, Table 1). − Formation of 3a and 14a. − General Procedure for the Formation of *N*-Aryl-4-vinyl-1,3-oxazolidin-2-ones 3: A degassed solution of **2** (1.267 g, 5.47 mmol) in anhydrous THF (5 mL) was added to a stirred and degassed mixture of **1a** (0.50 g, 2.73 mmol), $Pd(dba)_2$ (0.070 g, 0.137 mmol), 1,1′-bis(diphenylphosphanyl)ferrocene (0.227 g, 0.409 mmol), and anhydrous THF (10 mL). The reaction mixture was stirred at room temp. under argon for 7 h (GLC monitoring). The solvent was evaporated to dryness and the residue was chromatographed on silica gel (230−400 mesh), eluting with hexanes and hexanes/ethyl acetate mixtures of increasing polarity. The following compounds were obtained in the given order.

Dibenzylideneacetone: 0.077 g.

***N*-(3,5-Dinitrophenyl)-5-vinyl-1,3-oxazolidin-2-one (14a):** 0.107 g, 15% yield, m.p. 121−123°C (dichloromethane/pentane). − IR (KBr): $\tilde{\nu}$ = 1760 cm^{-1} (C=O) . − ^{1}H NMR ($CDCl_3$): δ = 3.95 (dd, *J* = 8.8 and 7.3 Hz, 1 H, 4-H), 4.37 (apparent t, *J* = 8.8 Hz, 1 H, 4-H), 5.24 (m, 1 H, 5-H), 5.50 (d, *J* = 10.2 Hz, 1 H, vinylic H), 5.60 (d, *J* = 17.5 Hz, 1 H, vinylic H), 6.02 (ddd, *J* = 16.8, 10.2 and 6.6 Hz, 1 H, vinylic H), 8.77 (s, 3 H, aromatic H). − ^{13}C NMR ($CDCl_3$): δ = 50.1 (C-4), 73.8 (C-5), 113.1, 117.2, 120.9, 132.8, 140.6, 148.9, 153.8 (C=O). − MS (70 eV, EI); *m/z* (%): 279 (17) [M$^+$], 235 (60) [M$^+$ − CO_2], 234 (73), 194 (100) [M$^+$ − $C_3H_3NO_2$], 148 (61), 75 (64), 63 (39). − $C_{11}H_9N_3O_6$ (279.2): calcd. C 47.30, H 3.25, N 15.05; found C 47.62, H 3.49, N 15.09.

***N*-(3,5-Dinitrophenyl)-4-vinyl-1,3-oxazolidin-2-one (3a):** 0.393 g, 52%, m.p. 128−130°C (dichloromethane/pentane). − IR (KBr): $\tilde{\nu}$ = 1753 cm^{-1} (C=O). − ^{1}H NMR ($CDCl_3$): δ = 4.26 (dd, *J* = 8.7 and 5.8 Hz, 1 H, 5-H), 4.74 (apparent t, *J* = 8.7 Hz, 1 H, 5-H), 5.06 (m, 1 H, 4-H), 5.54 (d, *J* = 10.2 Hz, 1 H, vinylic H), 5.60 (d, *J* = 16.8 Hz, 1 H, vinylic H), 5.87 (ddd, *J* = 17.5, 10.2 and 8.02 Hz, 1 H, vinylic H), 8.76 (s, 3 H, aromatic H). − ^{13}C NMR ($CDCl_3$): δ = 59.0 (C-4), 67.3 (C-5), 113.5, 119.3, 122.5, 132.8, 139.7, 148.7, 154.4 (C=O). − MS (70 eV, EI); *m/z* (%): 279 (58) [M$^+$], 234 (52), 220 (51), 194 (100) [M$^+$ − $C_3H_3NO_2$], 148 (51), 75 (98), 63 (61). − $C_{11}H_9N_3O_6$ (279.2): calcd. C 47.30, H 3.25, N 15.05; found C 47.66, H 3.43, N 14.85.

***N*-(4-Nitrophenyl)-4-vinyl-1,3-oxazolidin-2-one (3b; Entry 2, Table 1):** 0.686 g, 81% yield, m.p. 78.5−80°C (dichloromethane/hexane). − IR (KBr): $\tilde{\nu}$ = 1756 cm^{-1} (C=O). − ^{1}H NMR ($CDCl_3$): δ = 4.16 (dd, *J* = 8.8 and 5.4 Hz, 1 H, 5-H), 4.63 (apparent t, *J* = 8.8 Hz, 1 H, 5-H), 4.88−4.99 (m, 1 H, 4-H), 5.41 (d, *J* = 9.9 Hz, 1 H, vinylic H), 5.42 (d, *J* = 17.2 Hz, 1 H, vinylic H), 5.82 (ddd, *J* = 17.2, 9.9 and 7.5 Hz, 1 H, vinylic H), 7.66 (d, *J* = 9.3 Hz, 2 H, aromatic H), 8.19 (d, *J* = 9.3 Hz, 2 H, aromatic H). − ^{13}C NMR ($CDCl_3$): δ = 58.8 (C-4), 67.2 (C-5), 119.5, 121.0, 124.6, 133.7, 142.9, 143.5, 154.6 (C=O). − MS (70 eV, EI); *m/z* (%): 234 (98) [M$^+$], 189 (29), 175 (47), 149 (100) [M$^+$ - $C_3H_3NO_2$], 144 (20), 143 (26), 129 (54), 117 (45), 103 (58), 90 (24), 76 (59), 77 (23), 75 (21), 64 (29), 63 (28), 50 (29), 44 (30). − $C_{11}H_{10}N_2O_4$ (234.2): calcd. C 56.41, H 4.30, N 11.96; found C 56.41, H 4.27, N 11.78.

***N*-(4-Cyanophenyl)-4-vinyl-1,3-oxazolidin-2-one (3c; Entry 3, Table 1):** 1.010 g, 80% yield, m.p. 104−106°C (dichloromethane/pentane). − IR (KBr): $\tilde{\nu}$ = 2223 cm^{-1} (CN), 1749 (C=O). − ^{1}H NMR ($CDCl_3$): δ = 4.16 (dd, *J* = 8.7 and 5.1 Hz, 1 H, 5-H), 4.63 (apparent t, *J* = 8.7 Hz, 1 H, 5-H), 4.93 (m, 1 H, 4-H), 5.41 (d, *J* = 10.2 Hz, 1 H, vinylic H), 5.43 (d, *J* = 16.0 Hz, 1 H, vinylic H), 5.83 (ddd, *J* = 17.5, 10.2 and 7.3 Hz, 1 H, vinylic H), 7.63 (s, 4 H, aromatic H). − ^{13}C NMR ($CDCl_3$): δ = 58.6 (C-4), 67.1 (C-5), 117.8, 118.5, 120.0, 120.8, 132.8, 133.8, 141.1, 154.6 (C=O). − MS (70 eV, EI); *m/z* (%): 214 (47) [M$^+$], 169 (26), 155 (62), 143 (24), 129 (88) [M$^+$ − $C_3H_3NO_2$], 102 (100) [M$^+$ − $C_5H_6NO_2$], 75 (31), 51 (26). − $C_{11}H_{10}N_2O_4$ (214.2): calcd. C 67.28, H 4.70, N 13.08; found C 67.78, H 4.86, N 12.38.

Reaction of 3,5-Bis(trifluoromethyl)aniline (1d) with Dicarbonate 2 (Entry 4, Table 1). − Formation of 3d and 14d: The reaction was carried out according to the general procedure (see above).

***N*-[3,5-Bis(trifluoromethyl)phenyl]-4-vinyl-1,3-oxazolidin-2-one (3d):** 0.922 g, 93% yield, colorless oil. − IR (film): $\tilde{\nu}$ = 1764 cm^{-1} (C=O). − ^{1}H NMR ($CDCl_3$): δ = 4.19 (dd, *J* = 8.8 and 6.6 Hz, 1 H, 5-H), 4.67 (apparent t, *J* = 8.8 Hz, 1 H, 5-H), 4.96 (m, 1 H, 4-H), 5.46 (d, *J* = 10.2 Hz, 1 H, vinylic H), 5.48 (d, *J* = 18.3 Hz, 1 H, vinylic H), 5.82 (ddd, *J* = 16.8, 10.2 and 8.0 Hz, 1 H, vinylic H), 7.63 (s, 1 H, aromatic H), 7.99 (s, 2 H, aromatic H). − MS (70 eV, EI); *m/z* (%): 325 (71) [M$^+$], 280 (28), 266 (77), 254 (23), 240 (100) [M$^+$ − $C_3H_3NO_2$], 213 (86) [M$^+$ − $C_5H_6NO_2$], 163 (22). − $C_{13}H_9F_6NO_2$ (324.6): calcd. C 47.99, H 2.79, N 4.31; found 48.40, H 3.06, N 4.27.

***N*-[3,5-Bis(trifluoromethyl)phenyl]-5-vinyl-1,3-oxazolidin-2-one (14d):** 0.039 g, 4% yield, oil. − ^{1}H NMR ($CDCl_3$): δ = 3.84 (dd, *J* = 8.8 and 7.3 Hz, 1 H, 4-H), 4.25 (apparent t, *J* = 8.8 Hz, 1 H, 4-H), 5.16 (m, 1 H, 5-H), 5.51 (d, *J* = 10.2 Hz, 1 H, vinylic H), 5.57 (d, *J* = 16.8 Hz, 1 H, vinylic H), 6.00 (ddd, *J* = 16.8, 10.2 and 6.6 Hz, 1 H, vinylic H), 7.64 (s, 1 H, aromatic H), 8.03 (s, 2 H, aromatic H). − MS (70 eV, EI); *m/z* (%): 325 (65) [M$^+$], 280 (26), 266 (71), 240 (100) [M$^+$ − $C_3H_3NO_2$], 213 (86) [M$^+$ − $C_5H_6NO_2$], 163 (25).

Reaction of 3,5-Dichloroaniline (1e) with Dicarbonate 2 (Entry 5, Table 1). − Formation of 3e and 14e: The reaction was carried out according to the general procedure (see above).

***N*-(3,5-Dichlorophenyl)-4-vinyl-1,3-oxazolidin-2-one (3e):** 0.640 g, 80% yield, colorless oil. − IR (film): $\tilde{\nu}$ = 1756 cm^{-1} (C=O). − ^{1}H NMR ($CDCl_3$): δ = 4.13 (dd, *J* = 8.8 and 5.1 Hz, 1 H, 5-H), 4.60 (apparent t, *J* = 8.8 Hz, 1 H, 5-H), 4.82 (m, 1 H, 4-H), 5.41 (d, *J* = 10.2 Hz, 1 H, vinylic H), 5.42 (d, *J* = 16.8 Hz, 1 H, vinylic H), 5.80 (ddd, *J* = 17.5, 10.2 and 8.0 Hz, 1 H, vinylic H), 7.12 (s, 1 H, aromatic H), 7.42 (s, 2 H, aromatic H). − ^{13}C NMR ($CDCl_3$): δ = 58.8 (C-4), 67.1 (C-5), 118.7, 120.9, 124.4, 133.8, 135.1, 138.9, 154.7 (C=O). − MS (70 eV, EI); *m/z* (%): 261/259/257 (6/57/87) [M$^+$], 258 (13), 212 (27), 200 (37), 198 (57), 178 (39), 176/174/172 (11/63/100) [M$^+$ − $C_3H_3NO_2$], 149/147/145 (9/49/76) [M$^+$ − $C_5H_6NO_2$], 109 (37). − $C_{11}H_9Cl_2NO_2$ (257.9): calcd. C 51.36, H, 3.53, N 5.45; found C 51.23, H 3.79, N 5.14.

***N*-(3,5-Dichlorophenyl)-5-vinyl-1,3-oxazolidin-2-one (14e):** 0.039 g, 5% yield, oil. − ^{1}H NMR ($CDCl_3$): δ = 3.73 (dd, *J* = 8.8 and 6.6 Hz, 1 H, 4-H), 4.13 (apparent t, *J* = 8.8 Hz, 1 H, 4-H), 5.09 (m, 1 H, 5-H), 5.43 (d, *J* = 10.2 Hz, 1 H, vinylic H), 5.53 (d, *J* = 16.8 Hz, 1 H, vinylic H), 5.97 (ddd, *J* = 16.8, 10.2 and 6.6 Hz, 1 H, vinylic H), 7.12 (s, 1 H, aromatic H), 7.49 (s, 2 H, aromatic H). − MS (70 eV, EI); *m/z* (%): 261/259/257 (3/18/27) [M$^+$], 258 (4), 212 (41), 176/174/172 (11/65/100) [M$^+$ − $C_3H_3NO_2$], 149/147/145 (6/26/41) [M$^+$ − $C_5H_6NO_2$].

***N*-(3-Nitrophenyl)-4-vinyl-1,3-oxazolidin-2-one (3f; Entry 6, Table 1):** 0.873 g, 74% yield, m.p. 76−77°C (*tert*-butyl methyl ether/pen-

tane). − IR (KBr): $\tilde{\nu}$ = 1758 cm^{-1} (C=O). − ^1H NMR ($CDCl_3$): δ = 4.19 (dd, *J* = 8.8 and 5.8 Hz, 1 H, 5-H), 4.67 (apparent t, *J* = 8.8 Hz, 1 H, 5-H), 4.97 (m, 1 H, 4-H), 5.43 (d, *J* = 10.2 Hz, 1 H, vinylic H), 5.48 (d, *J* = 16.8 Hz, 1 H, vinylic H), 5.83 (ddd, *J* = 17.5, 10.2 and 8.0 Hz, 1 H, vinylic H), 7.54 (apparent t, *J* = 8.0 Hz, 1 H, aromatic H), 7.97 (m, 2 H, aromatic H), 8.27 (apparent t, *J* = 2.2 Hz, 1 H, aromatic H). − ^{13}C NMR ($CDCl_3$): δ = 59.0 (C-4), 67.1 (C-5), 115.0, 119.0, 121.3, 126.3, 129.7, 133.7, 138.3, 148.4, 155.0 (C=O). − MS (70 eV, EI); *m/z* (%): 234 (80) [M^+], 190 (25) [$M^+ - CO_2$], 175 (49), 149 (100) [$M^+ - C_3H_3NO_2$], 143 (28), 129 (40), 117 (39), 103 (38), 76 (58), 63 (35). − $C_{11}H_{10}N_2O_4$ (234.2): calcd. C 56.41, H 4.30, N 11.96; found C 56.69, H 4.29, N 11.64.

***N*-(4-Methoxycarbonylphenyl)-4-vinyl-1,3-oxazolidin-2-one (3g; Entry 7, Table 1):** 1.145 g, 83% yield, m.p. 83−84°C (dichloromethane/pentane). − IR (KBr): $\tilde{\nu}$ = 1757 cm^{-1} (C=O), 1707 (C=O). − ^1H NMR ($CDCl_3$): δ = 3.89 (s, 3 H, CH_3), 4.14 (dd, *J* = 8.8 and 5.1 Hz, 1 H, 5-H), 4.60 (apparent t, *J* = 8.8 Hz, 1 H, 5-H), 4.92 (m, 1 H, 4-H), 5.37 (d, *J* = 10.2 Hz, 1 H, vinylic H), 5.40 (d, *J* = 17.5 Hz, 1 H, vinylic H), 5.82 (ddd, *J* = 17.5, 10.2 and 8.0 Hz, 1 H, vinylic H), 7.57 (dt, *J* = 8.7 and 2.9 Hz, 2 H, aromatic H), 8.02 (dt, *J* = 8.7 and 2.9 Hz, 2 H, aromatic H). − ^{13}C NMR ($CDCl_3$): δ = 51.8 (CH_3), 58.8 (C-4), 67.1 (C-5), 119.5, 120.4, 125.8, 130.4, 134.2, 141.2, 154.9 (C=O), 166.4 (C=O ester). − MS (70 eV, EI); *m/z* (%): 247 (100) [M^+], 216 (26) [$M^+ - OCH_3$), 188 (38) [$M^+ - COOCH_3$], 162 (43) [$M^+ - C_3H_3NO_2$], 135 (27) [$M^+ - C_5H_6NO_2$]. − $C_{13}H_{13}NO_4$ (247.2): calcd. C 63.15, H 5.30, N 5.66; found C 63.20, H 5.27, N 5.46.

***N*-(3-Chloro-4-fluorophenyl)-4-vinyl-1,3-oxazolidin-2-one (3h; Entry 8, Table 1):** 0.485 g, 47% yield, b.p. 170°C (oven temp.)/0.08 Torr. − IR (film): $\tilde{\nu}$ = 1755 cm^{-1} (C=O). − ^1H NMR ($CDCl_3$): δ = 4.11 (dd, *J* = 8.7 and 6.6 Hz, 1 H, 5-H), 4.60 (apparent t, *J* = 8.8 Hz, 1 H, 5-H), 4.81 (m, 1 H, 4-H), 5.37 (d, *J* = 10.2 Hz, 1 H, vinylic H), 5.38 (d, *J* = 16.8 Hz, 1 H, vinylic H), 5.78 (ddd, *J* = 17.5, 10.2 and 8.0 Hz, 1 H, vinylic H), 7.11 (apparent t, *J* = 8.8 Hz, 1 H, aromatic H), 7.29 (m, 1 H, aromatic H), 7.55 (apparent dd, *J* = 6.6 and 2.9 Hz, 1 H, aromatic H). − ^{13}C NMR ($CDCl_3$): δ = 59.6 (C-4), 67.0 (C-5), 116.3, 116.7, 120.9, 121.1, 123.5, 134.0, 153.2, 155.3, 157.1. − MS (70 eV, EI); *m/z* (%): 241 (90) [M^+], 196 (22), 158 (31), 156 (100) [$M^+ - C_3H_3NO_2$], 135 (22), 131 (22), 129 (68) [$M^+ - C_5H_6NO_2$]. − $C_{11}H_9ClFNO_2$ (241.6): calcd. C 54.67, H 3.75, N 5.79; found C 54.42, H 3.69, N 5.63.

***N*-(4-Trifluoromethylphenyl)-4-vinyl-1,3-oxazolidin-2-one (3i; Entry 9, Table 1):** 0.815 g, 73% yield, oil. − IR (film): $\tilde{\nu}$ = 1758 cm^{-1} (C=O). − ^1H NMR ($CDCl_3$): δ = 4.14 (dd, *J* = 8.8 and 5.8 Hz, 1 H, 5-H), 4.61 (apparent t, *J* = 8.8 Hz, 1 H, 5-H), 4.91 (m, 1 H, 4-H), 5.38 (d, *J* = 10.2 Hz, 1 H, vinylic H), 5.41 (d, *J* = 16.8 Hz, 1 H, vinylic H), 5.80 (ddd, *J* = 17.5, 10.2 and 8.0 Hz, 1 H, vinylic H), 7.60 (s, 4 H, aromatic H). − MS (70 eV, EI); *m/z* (%): 258 (11) [M+1], 257 (69) [M^+], 238 (9) [$M^+ - F$], 212 (25), 198 (59), 172 (68) [$M^+ - C_3H_3NO_2$], 145 (100) [$M^+ - C_5H_6NO_2$]. − $C_{12}H_{10}F_3NO_2$ (257.2): calcd. C 56.04, H 3.92, N 5.44; found C 56.18, H 4.03, N 5.37.

***N*-(4-Iodophenyl)-4-vinyl-1,3-oxazolidin-2-one (3j; Entry 10, Table 1):** 0.570 g, 60% yield; m.p. 66−68°C (diethyl ether/pentane). − IR (KBr): $\tilde{\nu}$ = 1753 cm^{-1} (C=O). − ^1H NMR ($CDCl_3$): δ = 4.10 (dd, *J* = 8.8 and 5.8 Hz, 1 H, 5-H), 4.58 (apparent t, *J* = 8.8 Hz, 1 H, 5-H), 4.82 (m, 1 H, 4-H), 5.35 (d, *J* = 10.2 Hz, 1 H, vinylic H), 5.37 (d, *J* = 17.5 Hz, 1 H, vinylic H), 5.77 (ddd, *J* = 17.5, 10.2 and 8.0 Hz, 1 H, vinylic H), 7.22 (d, *J* = 8.7 Hz, 2 H, aromatic H), 7.65 (d, *J* = 8.7 Hz, 2 H, aromatic H). − ^{13}C NMR ($CDCl_3$): δ = 59.2 (C-4), 67.1 (C-5), 88.6, 120.7, 122.8, 134.3, 136.8, 137.8, 159.5 (C=O). − MS (70 eV, EI); *m/z* (%): 316 (14) [M+1], 315 (100) [M^+], 256 (16), 230 (37) [$M^+ - C_3H_3NO_2$], 203 (24) [$M^+ - C_5H_6NO_2$], 76 (20). − $C_{11}H_{10}INO_2$ (315.1): calcd. C 41.93, H 3.20, N 4.44; found C 42.48, H 3.13, N 4.19.

***N*-(4-Methoxyphenyl)-4-vinyl-1,3-oxazolidin-2-one (3m; Entry 13, Table 1):** 0.187 g, 15% yield; oil. − IR (film): $\tilde{\nu}$ = 1750 cm^{-1} (C=O). − ^1H NMR ($CDCl_3$): δ = 3.80 (s, 3 H, CH_3O), 4.09 (dd, *J* = 8.7 and 6.6 Hz, 1 H, 5-H), 4.57 (apparent t, *J* = 8.7 Hz, 1 H, 5-H), 4.75 (m, 1 H, 4-H), 5.28 (d, *J* = 10.2 Hz, 1 H, vinylic H), 5.31 (d, *J* = 16.8 Hz, 1 H, vinylic H), 5.78 (ddd, *J* = 16.8, 10.2 and 8.0 Hz, 1 H, vinylic H), 6.88 (d, *J* = 8.7 Hz, 2 H, aromatic H), 7.29 (d, *J* = 8.7 Hz, 2 H, aromatic H). − MS (70 eV, EI); *m/z* (%): 219 (100) [M^+], 160 (28), 134 (51) [$M^+ - C_3H_3NO_2$], 107 (14) [$M^+ - C_5H_6NO_2$], 77 (14).

Reaction of 4-Nitroaniline (1b) with Dicarbonate 2 in the Presence of Sodium Ethoxide and in the Absence of Pd^0. − Formation of Carbamate 9b: A mixture of **1b** (0.600 g, 4.344 mmol), sodium ethoxide (0.295 g, 4.344 mmol), *n*-tetrabutylammonium chloride (1.18 g, 4.344 mmol), and anhydrous THF (5 mL) was stirred at room temp. for 20 min. Then, a solution of **2** (2.017 g, 8.688 mmol) in anhydrous THF (5 mL) was added and the stirred mixture was left at room temp. for 5 d. The solvent was evaporated to dryness and the residue was chromatographed on silica gel (230−400 mesh), eluting with hexanes and mixtures of hexanes/ethyl acetate of increasing polarity. The following compounds were obtained in that order.

Carbamate 9b: 0.703 g, 50%, m.p. 107−108°C (dichloromethane/pentane). − IR (film): $\tilde{\nu}$ = 3260 cm^{-1} (N−H), 1741 (br., C=O). − ^1H NMR ($CDCl_3$): δ = 1.33 (t, *J* = 6.6 Hz, 3 H, CH_3), 4.27 (q, *J* = 6.6 Hz, 2 H, CH_2OCO), 4.75 (m, 4 H, 2 OCH_2C=), 5.80 (m, 2 H, CH=CH), 7.02 (br. s, 1 H, NH), 7.56 (d, *J* = 8.7 Hz, 2 H, aromatic H), 8.21 (d, *J* = 8.7 Hz, 2 H, aromatic H).

4-Nitroaniline (1b): 0.168 g, 28% recovery.

Formation of Oxazolidinone 3b from Carbamate 9b under Pd^0 Catalysis: A degassed and stirred solution of **9b** (0.400 g, 1.234 mmol), $Pd(dba)_2$ (0.034 g, 0.062 mmol), and 1,1′-bis(diphenylphosphanyl)-ferrocene (0.102 g, 0.185 mmol) in anhydrous THF (10 mL) was left at room temp. under argon for 2 d. GLC, TLC and ^1H-NMR monitoring showed the disappearance of **9b** and the formation of **3b**.

Reaction of Carbamate 15a with Dicarbonate 2 under Pd^0 Catalysis. − Formation of 16a: A degassed solution of **2** (0.382 g, 1.646 mmol) in anhydrous THF (5 mL) was added to a stirred and degassed mixture of **15a** (0.35 g, 1.372 mmol), $Pd(dba)_2$ (0.036 g, 0.069 mmol), 1,1′-bis(diphenylphosphanyl)ferrocene (0.114 g, 0.206 mmol), and anhydrous THF (5 mL). The reaction mixture was stirred at room temp. under argon for 24 h (GLC monitoring). The solvent was evaporated to dryness and the residue was chromatographed on silica gel (230−400 mesh), eluting with hexanes and hexanes/ethyl acetate mixtures of increasing polarity. The following compounds were obtained in that order.

Dibenzylideneacetone: 0.037 g.

Dicarbamate 16a: 0.182 g, 47% with respect to **15a**, m.p. 171−172°C (dichloromethane/pentane). − IR (KBr): $\tilde{\nu}$ = 1717 cm^{-1} (C=O). − ^1H NMR ($CDCl_3$): δ = 1.30 (t, *J* = 7.3 Hz, 6 H, 2 CH_3), 4.28 (q, *J* = 7.3 Hz, 4 H, 2 CH_2OCO), 4.48 (m, 4 H, 2 NCH_2C=), 5.86 (m, 2 H, CH=CH), 8.50 (s, 4 H, aromatic H), 8.84 (s, 2 H, aromatic H). − ^{13}C NMR ($CDCl_3$): δ = 14.1 (CH_3), 50.9, 63.2, 115.1, 124.8, 128.4, 144.2, 148.3, 154.0 (C=O). − $C_{22}H_{22}N_6O_{12}$ (562.45): calcd. C 46.96, H 3.94, N 14.95; found C 47.99, H 4.12, N 14.11.

Reaction of Carbamate 15b with Dicarbonate 2 under Pd^0 Catalysis. – Formation of 16b: Obtained in 85% yield (0.115 g) from **15b** according to an analogous procedure as described for **16a**. M.p. 125–126°C (dichloromethane/pentane). – IR (KBr): $\tilde{\nu}$ = 1717 cm^{-1} (C=O). – ^1H NMR ($CDCl_3$): δ = 1.25 (t, *J* = 7.3 Hz, 6 H, 2 CH_3), 4.21 (q, *J* = 7.3 Hz, 4 H, 2 CH_2OCO), 4.35 (m, 4 H, 2 NCH_2C=), 5.70 (m, 2 H, CH=CH), 7.35 (d, *J* = 8.7 Hz, 4 H, aromatic H), 8.17 (d, *J* = 8.7 Hz, 4 H, aromatic H). – ^{13}C NMR ($CDCl_3$): δ = 14.4 (CH_3), 51.2, 62.5, 124.2, 125.5, 128.3, 144.8, 147.8, 154.4 (C=O). – $C_{22}H_{24}N_4O_8$ (472.1): calcd. C 55.91, H 5.12, N 11.86; found C 56.32, H 5.37, N 11.32.

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[1] [1a] M. E. Dyen, D. Swern, *Chem. Rev.* **1967**, *67*, 197–246. – [1b] D. J. Ager, I. Prakash, D. R. Schaad, *Chem. Rev.* **1996**, *96*, 835–875.
[2] [2a] J. E. Herweh, T. A. Foglia, D. Swern, *J. Org. Chem*. **1968**, *33*, 4029–4033. – [2b] D. Braun, J. Weinert, *Liebigs Ann. Chem*. **1976**, 221–224. – [2c] D. Braun, J. Weinert, *Liebigs Ann. Chem*. **1979**, 200–209. – [2d] W. A. Gregory, D. R. Brittelli, C.-L. J. Wang, M. A. Wuonola, R. J. McRipley, D. C. Eustice, V. S. Eberly, P. T. Bartholomew, A. M. Slee, M. Forbes, *J. Med. Chem*. **1989**, *32*, 1673–1681.
[3] M. Fujiwara, A. Baba, H. Matsuda, *J. Heterocycl. Chem*. **1988**, *25*, 1351–1357.
[4] [4a] B. M. Trost, A. R. Sudhakar, *J. Am. Chem. Soc*. **1988**, *110*, 7933–7935. – [4b] B. M. Trost, A. R. Sudhakar, *J. Am. Chem. Soc.* **1987**, *109*, 3792–3794. – [4c] C. Larksarp, H. Alper, *J. Am. Chem. Soc*. **1997**, *119*, 3709–3715.
[5] [5a] T. Hayashi, A. Yamamoto, Y. Ito, *Tetrahedron Lett*. **1988**, *29*, 99–102. – [5b] B. M. Trost, D. L. Van Vranken, *J. Am. Chem. Soc.* **1990**, *112*, 1261–1263. – [5c] B. M. Trost, D. L. Van Vranken, *Angew. Chem. Int. Ed. Engl*. **1992**, *31*, 228–230. – [5d] B. M. Trost, D.L. Van Vranken, C. Bingel, *J. Am. Chem. Soc*. **1992**, *114*, 9327–9343. – [5e] B. M. Trost, D. L. Van Vranken, *J. Am. Chem. Soc*. **1993**, *115*, 444–458. – [5f] B. M. Trost, D. E. Patterson, *J. Org. Chem*. **1998**, *63*, 1339–1341.
[6] [6a] A. Arcadi, *Synlett* **1997**, 941–943. – [6b] D. Bouyssi, M. Cavicchioli, G. Balme, *Synlett* **1997**, 944–946.
[7] [7a] M. Kimura, K. Fugami, S. Tanaka, Y. Tamaru, *J. Org. Chem*. **1992**, *57*, 6377–6379. – [7b] M. Kimura, S. Tanaka, Y. Tamaru, *J. Org. Chem*. **1995**, *60*, 3764–3772.
[8] For reviews see: [8a] B. M. Trost, T. R. Verhoeven, "Organopalladium Compounds in Organic Synthesis and in Catalysis" in *Comprehensive Organometallic Chemistry* (Eds.: G. Wilkinson, F. G. A. Stone, E. W. Abel), Pergamon Press, New York, **1982**, vol. 8, chapter 57. – [8b] B. M. Trost, *Acc. Chem. Res.* **1980**, *13*, 385–393. – [8c] B. M. Trost, *Chemtracts: Org. Chem*. **1988**, *1*, 415–435. – [8d] B. M. Trost, *Angew. Chem. Int. Ed. Engl*. **1989**, *28*, 1173–1192. – [8e] S. A. Godleski, "Nucleophiles with Allyl-Metal Complexes" in *Comprehensive Organic Synthesis* (Eds.: B. M. Trost, I. Fleming), Pergamon Press, New York, **1991**, vol. 4, chapter 3.3. – [8f] J. Tsuji, I. Minami, *Acc. Chem. Res.* **1987**, *20*, 140–145. – [8g] J. Tsuji, *Tetrahedron* **1986**, *42*, 4361–4401. – [8h] R. F. Heck, *Palladium Reagents in Organic Synthesis*, Academic Press, London, **1985**. – [8i] G. Consiglio, R. M. Waymouth, *Chem. Rev.* **1989**, *89*, 257–276. – [8j] C. G. Frost, J. Howarth, J. M. J. Williams, *Tetrahedron: Asymmetry* **1992**, *3*, 1089–1122. – [8k] J. Tsuji, *Palladium Reagents and Catalysis*, John Wiley and Sons, Chichester, **1995**. – [8l] P. J. Harrington, "Transition Metal Allyl Complexes: Pd, W, Mo-assisted Nucleophilic Attack" in *Comprehensive Organometallic Chemistry II* (Eds.: E. W. Abel, F. G. A. Stone, G. Wilkinson), Pergamon Press, New York, **1995**, vol. 12, chapter 8.2. – [8m] M. Moreno-Mañas, R. Pleixats, *Adv. Heterocycl. Chem*. **1996**, *96*, 73–129.
[9] M. Moreno-Mañas, L. Morral, R. Pleixats, *J. Org. Chem*. **1998**, *63*, 6160–6166.
[10] [10a] S. Cerezo, J. Cortés, M. Moreno-Mañas, R. Pleixats, A. Roglans, *Tetrahedron*, in press. – [10b] S. Cerezo, J. Cortés, J.-M. López, M. Moreno-Mañas, R. Pleixats, A. Roglans, *Tetrahedron*, in press.
[11] [11a] T. Ibuka, N. Mimura, H. Aoyama, M. Akaji, H. Ohno, Y. Miwa, T. Taga, K. Nakai, H. Tamamura, N. Fujii, *J. Org. Chem*. **1997**, *62*, 999–1015. – [11b] T. Ibuka, N. Mimura, H. Ohno, K. Nakai, M. Akaji, H. Habashita, H. Tamamura, Y. Miwa, T. Taga, N. Fujii, Y. Yamamoto, *J. Org. Chem*. **1997**, *62*, 2982–2991.
[12] K. Fugami, Y. Morizawa, K. Oshima, H. Nozaki, *Tetrahedron Lett*. **1985**, *26*, 857–860.
[13] [13a] S.-I. Murahashi, T. Shimamura, I. Moritani, *J. Chem. Soc., Chem. Commun*. **1974**, 931–932. – [13b] J.-E. Bäckvall, J.E. Nyström, *J. Chem. Soc., Chem. Commun*. **1981**, 59–61.
[14] T. Tsuda, T. Kiyoi, T. Saegusa, *J. Org. Chem*. **1990**, *55*, 3388–3390.
[15] Y. Uozumi, A. Tanahashi, T. Hayashi, *J. Org. Chem*. **1993**, *58*, 6826–6832.
[16] [16a] A. Yamazaki, K. Achiwa, *Tetrahedron: Asymmetry* **1995**, *6*, 1021–1024. – [16b] C. Thorey, J. Wilken, F. Hénin, J. Martens, T. Mehler, J. Muzart, *Tetrahedron Lett*. **1995**, *36*, 5527–5530. – [16c] P. Lhoste, M. Massacret, D. Sinou, *Bull. Soc. Chim. Fr.* **1997**, *134*, 343–347.
[17] [17a] M. Massacret, C. Goux, P. Lhoste, D. Sinou, *Tetrahedron Lett*. **1994**, *35*, 6093–6096. – [17b] C. Goux, M. Massacret, P. Lhoste, D. Sinou, *Organometallics* **1995**, *14*, 4585–4593.
[18] A. Satake, H. Ishii, I. Shimizu, Y. Inoue, H. Hasegawa, A. Yamamoto, *Tetrahedron* **1995**, *51*, 5331–5340.
[19] J. Tsuji, I. Shimizu, I. Minami, Y. Ohashi, T. Sugiura, K. Takahashi, *J. Org. Chem*. **1985**, *50*, 1523.
[20] [20a] F. G. Bordwell, *Acc. Chem. Res.* **1988**, *21*, 456–463. – [20b] F. G. Bordwell, D. J. Algrim, *J. Am. Chem. Soc*. **1988**, *110*, 2964–2968. – [20c] F. G. Bordwell, X.-M. Zhang, J.-P. Cheng *J. Org. Chem*. **1993**, *58*, 6410–6416.
[21] R. G. P. Gatti, A. L. E. Larsson, J.-E. Bäckvall, *J. Chem. Soc., Perkin Trans. 1* **1997**, 577–584.
[22] For **15a** see: [22a] J. J. Blanksma, G. Verberg, *Recl. Trav. Chim. Pays-Bas* **1934**, *53*, 1037–1046. –
For **15b** see: [22b] E. Angeles, A. Santillan, I. Martínez, A. Ramírez, E. Moreno, M. Salmon, R. Martínez, *Synth. Commun.* **1994**, *24*, 2441–2447. – [22c] R. Leardini, G. Zanardi, *Synthesis* **1982**, 225–227.

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