Synthesis of Cyclopropanes by Intramolecular Attack of *N*-Nucleophiles on the Central Carbon of (π-Allyl)palladium Complexes

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Professor Gurnos Jones on the occasion of his 70th birthday

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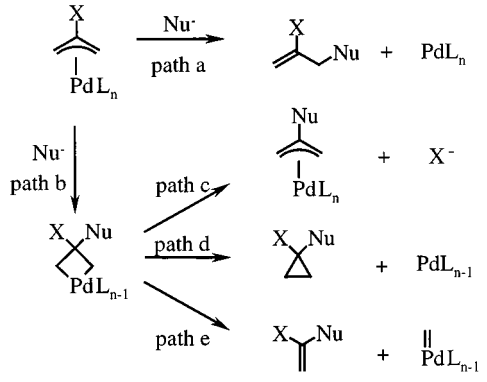
ortho-Halobenzamides such as compound **1a** react in the presence of allene and base with catalytic amounts of palladium(0) complexes to form cyclopropanes such as **3a**. This reaction is believed to proceed via an intermediate palladacyclobutane and is the first example of a noncarbon nucleophile attack on the centre carbon of an (η^3-allyl)palladium complex leading, by reductive elimination, to cyclopropanes. The regiochemistry of the nucleophilic attack (central versus terminal carbon) depends on the nature of ligand and solvent as electron rich palladium complexes favour central carbon attack.

Introduction

The reaction of nucleophiles with (η^3-allyl)palladium complexes is one of the most important palladium(II)-catalyzed reactions and proceeds generally with high regioselectivity by path a (Scheme 1).[1,2] In the case of alkylation, for instance, the attack of stabilized carbanions such as malonate derivatives occurs predominantly at the sterically less-hindered terminal carbon atom of the allylic moiety. In contrast unstabilized carbanions such as Grignard reagents react initially at the electron-deficient metal centre by formation of a σ-alkyl palladium species. Subsequent reductive elimination leads to terminal substitution products.



Scheme 1. Possible reaction pathways of nucleophilic attack on (η^3-allyl)palladium complexes

Attack of nucleophiles at the central carbon atom (C_c) of (η^3-allyl)palladium complexes is much less common and leads initially to the formation of a palladacyclobutane (path b, Scheme 1). Depending on the nature of the centre carbon substituent X this metallacycle may undergo rearrangement to a centre substituted (η^3-allyl)palladium complex (Scheme 1, path c).[3,4] In the absence of a good leaving group, however, reductive elimination with formation of a cyclopropane moiety is possible (path d). A further conceivable pathway (path e) involving a palladium carbene has not been reported so far.

The formation of cyclopropanes from (η^3-allyl)palladium complexes was first observed by Hegedus.[5] The existence of an intermediate palladocyclobutane was subsequently confirmed by isolation and X-ray structure determination[6] and additional experimental[7] and theoretical[8,9] studies concerning central versus terminal attack have been reported. The formation of cyclopropanes seems mainly restricted to nonstabilized carbon nucleophiles such as enolates of amides, esters, ketones and sulfonamides; all these substrates require stoichiometric amounts of (η^3-allyl)palladium(II) complexes.[10−12] Musco et al. reported a process catalytic in palladium involving ketene silyl acetals as nucleophiles in the presence of thallium(I) acetate leading, in low yields, to cyclopropane products.[13,14] Recently Satake et al. reported a substantial improvement in this reaction for special ketene silyl acetals by variation of palladium ligand and base.[15,16]

All these examples, however, are restricted to carbon nucleophiles. We now report the first examples of the attack of nitrogen nucleophiles on the centre carbon atom of (η^3-allyl)palladium(II) complexes with formation of cyclopropanes. This reaction is catalytic in palladium.

Results and Discussion

In contrast to the previously reported reactions, the (η^3-allyl)palladium(II) complexes are formed by addition of aryl palladium halides generated in situ to allene[17] instead of oxidative addition of palladium(0) to an allyl acetate/

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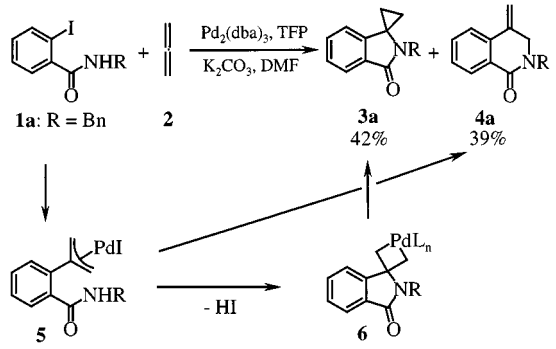
halide. The former process is known to proceed by regioselective addition of the aryl moiety at the centre carbon of the allene moiety.[18] Reacting **1a** with allene **2** (1 atm.) in the presence of K_2CO_3 (2.0 equiv.) and a catalyst comprising $Pd_2(dba)_3$ (5 mol-% Pd) and tri-2-furylphosphane (TFP, 10 mol-%) in DMF (c = 0.17 mol/l) at 80 °C in a Schlenk tube afforded a ca. 1:1 mixture of cyclopropane **3a** and the allylation product **4a** (Scheme 2).



Scheme 2.

The structure of compound **3a** was confirmed by X-ray crystallography.[19] The central attack can either occur with the lone pair of the neutral secondary amide, as the reaction is also observed when the base K_2CO_3 is substituted by sodium azide,[20] or with the amide anion, as the acidity of nitrogen-bound protons is assumed to increase in the coordination sphere of palladium complexes.[21] The formation of the cyclopropane moiety is probably facilitated by conjugation of the e_A Walsh orbital of the cyclopropane with a π-orbital of the adjacent aryl group, as the plane of the three-membered ring in **3a** is almost parallel to its axis[22] (which may also explain the "aryl effect" described by Hoffmann[11]). An enabling feature is the kinetically favoured formation of a five-membered ring rather than the six-membered ring **4a** which results from terminal substitution. In a control experiment, pure allyl amide **4a** was subjected to the same reaction conditions for a second time. No interconversion with **3a** was observed and **4a** was recovered in almost quantitative yield. Therefore **4a** is neither in equilibrium with, nor a precursor of, cyclopropane **3a**.

Further substrates were investigated as shown in Table 1 under the same reaction conditions. The formation of a cyclopropane moiety seems to be restricted to secondary *ortho*-halobenzamides and a contributing factor may be the pK_a of these substrates.

All the successful substrates have calculated pK_a′s in the range of 14.0 ± 0.5,[23] whilst the sulfonamide **13** (pK_a ≈ 10.8) and the amine **15** (pK_a ≈ 8.2) gave exclusively the allylation products. The homologous amide **18** (pK_a ≈ 15.5) gave exclusively the seven-membered ring product **19**, and the primary amide **1g** (pK_a ≈ 15.5) gave a mixture of unidentifiable products. In the cases of the secondary amides (**1a−f**) the ratio of terminal to central product seems to be determined by two effects. Increasing steric bulk favours the allylation product **4** whereas electron-donating groups either on the aryl halide or on the *N*-benzyl group favour

Table 1. Reaction of various substrates with allene and K_2CO_3 in presence of $Pd_2(dba)_3$/TFP in DMF

Nucleophile[a]	t [h]	Yield [%] (3)	Yield [%] (4)
1a: R = Bn	16	42	39
b: R = Me	16	68	5
c: R = *p*MeOBn	40	48	28
d: R = 2,4-di-MeO-Bn	22	53	26
e: R = iPr	22	38	35
f: R = *t*Bu	87	–	75
g: R = H	46	–	–
		(8)	(9)
7a: R = Bn	110	61	14
b: R = *p*MeOBn	86	61	–
		(11)	(12)
10a: R = Bn	92	65	4
b: R = *p*OMeBn	140	62	–
(13)	50	–	(14) 73
(15)	19	–	(16) 80
(17)	21	–	–
(18)	120	–	(19) 84

[a] Amounts of catalyst used: **1a,b**: 5 mol-% "Pd"/10 mol-% TFP; **1c,e,g**: 10 mol-% "Pd"/20 mol-% TFP; **1d,f** and **7a,b**, **10**, **13**, **15**, **17**: 20 mol-% "Pd"/30 mol-% TFP.

cyclopropane formation **3**. The rate-limiting step is probably the oxidative addition, as bromides (**7**, **10**) required longer reaction times and higher amounts of catalyst. Within the iodides **1a−f** the reaction time increases with increasing steric demand of the amide substituent.

It has been reported for carbon nucleophile attack on (π-allyl)palladium complexes that the regiochemistry (central C_c versus terminal C_t) can be controlled by proper choice of the ligand.[5−7] Thus, ligands with at least partial π-acceptor properties like phosphanes give predominantly the product of terminal substitution, whereas strongly σ-donating ligands favour central attack. TMEDA (*N*,*N*,*N*′,*N*′-tetramethylethylendiamine) was found to promote central attack most strongly. The reason for this trend seems to be a decreasing carbenium ion character of the allyl moiety of the

Table 2. Ligand and solvent effects observed with amide **1a**

Entry	"Pd"[a] (mol-%)	Ligand (mol-%)	Solvent	*T* [°C]	*t* [h]	**3a**:**4a**:**20**:**1a**[b]
1	A (0.1)	PPh_3 (0.2)	DMF	80−90	16	35:65:0:0
2	B (0.05)	TFP (0.1)	DMF	80−90	16	50:50:0:0
3	A (0.1)	TMEDA (2.0)	DMF	80−90	16	48:4:0:48
4	A (0.1)	TMEDA (2.0)	DMF	100	40	62:7:0:0[c]
5	B (0.1)	TFP (0.2)	THF	80−90	16	45:4:3:48
6	B (0.1)	TFP (0.2)	dioxane	80−90	16	32:2:3:63
7	B (0.2)	TFP (0.3)	dioxane	100	45	62:7:24:7
8	B (0.2)	TFP (0.3)	dioxane	110	120	73:7:0[d]:0[e]
9	B (0.1)	TFP (0.2)	toluene	80−90	16	6:1:5:88
10	B (0.2)	TFP (0.3)	toluene	100	45	12:0[e]:50:38

[a] A: $Pd(OAc)_2$; B: $Pd_2(dba)_3$. − [b] Ratio of compounds assigned from ^1H NMR spectra of reaction mixture. − [c] Isolated yields. − [d] Compound **20** was detected in the ^1H NMR spectrum of the reaction mixture but not isolated due to decomposition on silica. − [e] Only traces were detected.

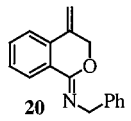
intermediate palladium complex. In such situations, as the predicted difference of the LUMO coefficients of C_c and C_t is rather small,[7] central attack of suitable nucleophiles becomes possible assuming the reaction is frontier-orbital controlled.

This encouraged us to investigate the influence of ligands and solvents on the reaction of **1a** (Table 2). We observed similar effects to those reported for carbon nucleophiles. The less-strongly σ-donating ligand triphenylphosphane (Entry 1) gave less cyclopropane product **3a** than the $Pd_2(dba)_3$/TFP system. In contrast, TMEDA increases the amount of cyclopropane (Entries 3 and 4). However, the increase in central attack was accompanied by increased reaction times from π-acceptor ligands to σ-donor ligands,[24] and as a consequence polymerization of excess allene occurred as a side reaction.

An interesting effect was observed by varying the solvent. In THF and dioxane (Entries 5−8) the formation of cyclopropane was favoured, but the reaction became even slower than with TMEDA/DMF. The palladium catalyst was stable over a period of a few days at 80−90 °C in DMF, whilst it decomposed in dioxane after three days at the same temperature, as indicated by the formation of metallic palladium. Surprisingly, the catalyst seemed to be more stable in dioxane at higher temperature (110 °C, Entry 8) to give total consumption of **1a** before decomposition. At this elevated temperature, however, polymerization of the excess allene again became noticeable. The isolated yields of cyclopropane **3a** (and allyl compound **4a**) were in both cases good (TMEDA/DMF [Entry 4]: 62% **3a**; 7% **4a**; TFP/1,4-dioxane [Entry 8]: 73% **3a;** 7% **4a**).[25]

Another effect was observed with toluene as solvent (Entries 9−10) where traces of another product detected in the reactions in THF or dioxane became the main product after (incomplete) reaction over three days. This additional compound was unstable. Rapid flash chromatography on silica gel resulted in almost total decomposition. However, a small sample was isolated (m/z = 249) and its NMR spectrum suggested it was the (*Z*)-imino ester **20** (Figure 1).

Such imino esters are known to hydrolyse quite quickly either by acid or base catalysis.[26]



20

Figure 1. Main product obtained in toluene as solvent

A feasible explanation for the formation of the imino ester **20** is a change from frontier orbital to charge controlled reaction.

Conclusion

All these observations seem to support the conclusions of studies made with carbon nucleophiles that the regiochemistry of nucleophilic attack on (η^3-allyl)palladium complexes depend on the latter's electronic character: central carbon attack is favoured when the ionic character is reduced. π-Donor ligands, electron donating substituents on the substrate as well as stabilizing solvents with donor properties like 1,4-dioxane favour central attack on (η^3-allyl)palladium complexes.

Experimental Section

General Remarks: Melting points (uncorrected) were determined on a Reichert hot-stage apparatus. − IR: Nicolet Avatar 360 FT-IR spectrometer. − ^1H NMR spectra were recorded with a Bruker DPX 300 (300 MHz) spectrometer and chemical shift values are reported in ppm relative to TMS (δ = 0.00). − ^{13}C NMR spectra were recorded with a Bruker DPX 300 (75.5 MHz) or a Bruker DRX 500 (125 MHz) and chemical shift values are reported in ppm relative to $CDCl_3$ (δ = 77.0). The DEPT-135 pulse sequence was used for the determination of signal types, cPr refers to signals for the cyclopropanyl ring. − MS: VG-AutoSpec spectrometer. *m*-Nitrobenzyl alcohol (*m*NBA) was used as the matrix in the FAB experiments. − Microanalyses were obtained using a Carlo Erba Elemental Analyser MOD 1106 instrument. − Preparative flash column chromatography was performed on Merck silica gel 60 (230−400 mesh). − R_f values were determined by thin layer chromatography (TLC) on Merck silica gel 60 F_{254} and spots were visu-

alized with UV light. − Light petroleum refers to the fraction with boiling range 40−60 °C. − The amides **1a−g**, **13** and **17** were prepared by aminolysis of their commercially available acid chlorides. Compounds **7a**,**b**, **10a**,**b** and **18** were prepared in a similar fashion by converting commercially available acids into the corresponding acid chlorides with thionyl chloride according to standard procedures. Amine **15** was prepared according to a literature procedure.[27] − The expression "Schlenk tube" is used for a 100 mL one-neck pressure dram vessel.

General Procedure: A Schlenk tube dried under vacuum was filled under a slow stream of nitrogen with the corresponding halide (1.00 mmol), potassium carbonate (276 mg, 2.0 equiv.), $Pd_2(dba)_3$ (5−20 mol-%), tri-2-furylphosphane (10−30 mol-%, see footnote in Table 1) and dry DMF (6 mL). The reaction mixture was cooled in vacuo to −196 °C and allene gas was added (1 atm.). Then the reaction mixture was heated to 80−90 °C for the time given in Table 2. After cooling to room temperature excess allene gas was carefully released, the reaction mixture poured into water (100 mL) and extracted with ether (300 mL). After washing with a second portion of water (50 mL) the combined aqueous phases were extracted with diethyl ether (100 mL) and the combined organic phases dried over magnesium sulfate. The solvent was removed in vacuo and the residue purified by column chromatography. When THF, 1,4-dioxane or toluene were used as solvents (Table 2, Entries 5−10) the crude reaction mixture was filtered through a celite plug without aqueous work up. The following results relate to reactions carried out in DMF, unless otherwise noted.

Compound 3a: Colourless solid, 42% yield (105 mg, eluent: light petroleum/diethyl ether 1:2, $R_f = 0.23$), crystallized from diethyl ether, m.p. 116 °C. − ^{1}H NMR ($CDCl_3$): δ = 1.20−1.48 (m, 4 H, cPr-H), 4.61 (s, 2 H, NCH_2Ph), 7.02 (d, J = 7.6 Hz, 1 H, Ar-H), 7.20−7.65 (m, 7 H, Ar-H), 7.95 (d, J = 7.6 Hz, 1 H, Ar-H). − ^{13}C NMR (75.5 MHz, $CDCl_3$): δ = 11.4 (2 × cPr-C), 42.4 (NCH_2Ph), 45.3 (C_{quat}, cPr-C), 118.0 (+), 124.2 (+), 127.4 (+), 127.7 (+), 129.1 (+), 129.2 (+), 131.6 (C_{quat}), 132.0 (+), 138.0 (C_{quat}), 148.0 (C_{quat}), 168.9 (C=O). − IR (nujol): $\tilde{\nu}$ = 1683 cm^{-1}, 1474, 1456, 759, 689. − MS (70 eV): *m/z* (%) = 249 (55) [M^+], 158 (45) [M^+ − Bn], 91 (100) [Bn^+]. − $C_{17}H_{15}NO$ (249.3): calcd. C 81.90, H 6.06, N 5.62; found C 81.75, H 6.15, N 5.40.

Compound 4a: Pale yellow oil, 39% yield (98 mg, eluent: light petroleum/diethyl ether 1:2, $R_f = 0.68$). − ^{1}H NMR ($CDCl_3$): δ = 4.13 (s, 2 H, 3-H), 4.83 (s, 2 H, NCH_2Ph), 5.15 (s, 1 H, =CH_2), 5.56 (s, 1 H, =CH_2), 7.57−7.27 (m, 8 H, Ar-H), 8.29 (d, 1 H, J = 7.5 Hz, Ar-H). − ^{13}C NMR (75.5 MHz, $CDCl_3$): δ = 50.6 (NCH_2Ph), 52.2 (C-3), 112.7 (=CH_2), 123.5 (+), 127.9 (+), 128.1 (+), 128.4 (+), 129.1 (2 × C, +), 132.5 (+), 136.1 (C_{quat}), 137.0 (C_{quat}), 137.2 (C_{quat}), 163.9 (C=O). − IR (neat): $\tilde{\nu}$ = 1652 cm^{-1}, 1602, 1572, 1480, 1453, 1298, 1162, 902, 734, 707. − MS (70 eV): *m/z* (%) = 249 (80) [M^+], 158 (75) [M^+ − Bn], 145 (60) [M^+ − NBn + H], 91 (100) [Bn^+]. − $C_{17}H_{15}NO$ (249.3): calcd. C 81.90, H 6.06, N 5.62; found C 81.60, H 6.10, N 5.35.

Compound 20: The reaction in toluene (Table 2, Entry 10) resulted in a mixture of **3a**, **20** and starting material **1a**. Rapid flash chromatography on silica gel gave **20** (20 mg) as a pale yellow oil (8% yield, eluent: light petroleum/diethyl ether 4:1, $R_f = 0.31$). − ^{1}H NMR (75.5 MHz, $CDCl_3$): δ = 4.70 (s, 2 H, NCH_2Ph), 4.81 (s, 2 H, OCH_2), 5.30 (s, 1 H, =CH_2), 5.66 (s, 1 H, =CH_2) 7.22−7.56 (m, 8 H, Ar-H), 8.26 (d, J = 7.5 Hz, 1 H, Ar-H). − ^{13}C NMR ($CDCl_3$): δ = 50.3 (NCH_2Ph), 70.8 (OCH_2), 111.9 (=CH_2), 126.7 (+), 128.1 (+), 128.4 (+), 128.6 (+), 129.3 (+), 130.0 (C_{quat}) 130.9 (+), 131.1 (+), 134.4 (C_{quat}), 137.2 (C_{quat}), 141.7 (C_{quat}), 153.5 (C=N). − MS (70 eV): *m/z* (%) = 249 (95) [M^+], 248 (90) [M^+ − H], 144 (100) [M^+ − NBn], 115 (75) [$C_9H_7^+$], 91 (95) [Bn^+].

Compound 3b: Pale yellow needles, 68% yield (117 mg, eluent: diethyl ether, $R_f = 0.12$), crystallized from diethyl ether, m.p. 84 °C. − ^{1}H NMR ($CDCl_3$): δ = 1.32−1.37 (m_c, 2 H, cPr-H), 1.56−1.60 (m, 2 H, cPr-H), 2.87 (s, 3 H, NMe), 7.06 (d, J = 7.5 Hz, 1 H, Ar-H), 7.42 (dd, J^1 = 7.5 Hz, J^2 = 7.5 Hz, 1 H, Ar-H), 7.51 (dd, J^1 = 7.5 Hz, J^2 = 7.5 Hz, 1 H, Ar-H), 7.88 (dd, J^1 = 7.5 Hz, J^2 = 7.5 Hz, 1 H, Ar-H). − ^{13}C NMR (75.5 MHz, $CDCl_3$): δ = 10.5 (2 × cPr-C), 24.3 (NMe), 45.4 (C_{quat}, cPr-C), 118.0 (+), 123.8 (+), 125.9 (+), 131.7 (+), 132.1 (C_{quat}), 147.5 (C_{quat}), 168.4 (C=O). − IR (nujol): $\tilde{\nu}$ = 1668 cm^{-1}, 1539, 1475, 1425, 758, 693. − FAB-MS (*m*NBA): *m/z* (%) = 174 (100) [M^+ + H], 173 (50) [M^+], 158 (45) [M^+ − CH_3], 144 (20) [M^+ − NCH_3], 130 (15) [M^+ − C_3H_7]. − $C_{11}H_{11}NO$ (173.2): calcd. C 76.28, H 6.40, N 8.09; found C 76.35, H 6.40, N 7.80.

Compound 4b: Yellow oil, 5% yield (9 mg, eluent: diethyl ether, R_f = 0.38). − ^{1}H NMR ($CDCl_3$): δ = 3.09 (s, 3 H, NMe), 4.16 (s, 2 H, 3-H), 5.17 (s, 1 H, =CH_2), 5.53 (s, 1 H, =CH_2), 7.32−7.52 (m, 3 H, Ar-H), 8.08 (d J = 7.4 Hz, 1 H, Ar-H). − ^{13}C NMR (75.5 MHz, $CDCl_3$): δ = 35.1 (Me), 54.8 (C-3), 112.5 (=CH_2), 123.4 (+), 128.2 (C_{quat}), 128.8 (+), 129.2 (+), 132.2 (+), 136.0 (C_{quat}), 137.0 (C_{quat}), 164.0 (C=O). − IR (neat): $\tilde{\nu}$ = 1647 cm^{-1}, 1600, 1570, 1496, 1436, 1400, 906, 778, 708. − MS (70 eV): *m/z* (%) = 173 (100) [M^+], 158 (10) [M^+ − CH_3], 144 (35) [M^+ − NCH_3]. − $C_{11}H_{11}NO$ (173.2): calcd. C 76.28, H 6.40, N 8.09; found C 76.05, H 6.55, N 8.05.

Compound 3c: Colourless solid, 48% yield (133 mg, eluent: light petroleum/diethyl ether 1:1, $R_f = 0.13$), crystallized from diethyl ether, m.p. 132 °C. − ^{1}H NMR ($CDCl_3$): δ = 1.24 (m_c, 2 H, cPr-H), 1.47 (m_c, 2 H, cPr-H), 3.77 (s, 3 H, OMe), 4.55 (s, 2 H, NCH_2Ph), 6.82 (d, J = 8.5 Hz, 2 H, Ar-H), 7.02 (d, J = 7.5 Hz, 1 H, Ar-H), 7.17 (d, J = 8.5 Hz, 2 H, Ar-H), 7.45 (dd, J^1 = J^2 = 7.5 Hz, 1 H, Ar-H), 7.53 (dd, J^1 = J^2 = 7.5 Hz, 1 H, Ar-H), 7.95 (d, J = 7.5 Hz, 1 H, Ar-H). − ^{13}C NMR (75.5 MHz, $CDCl_3$): δ = 11.4 (2 × cPr-C), 41.9 (NCH_2), 45.3 (C_{quat}, cPr-C), 55.7 (OMe), 114.4 (+), 117.9 (+), 124.2 (+), 127.7 (+), 128.7 (+), 130.1 (C_{quat}), 131.6 (C_{quat}), 131.9 (+), 148.0 (C_{quat}), 159.2 (C_{quat}), 168.8 (C=O). − IR (nujol): $\tilde{\nu}$ = 1670 cm^{-1}, 1497, 813, 742, 699. − MS (70 eV): *m/z* (%) = 279 (30) [M^+], 264 (15) [M^+ − CH_3], 158 (10) [M^+ − *p*MeOBn], 121 (100) [*p*MeOBn$^+$]. − $C_{18}H_{17}NO_2$ (279.3): calcd. C 77.40, H 6.13, N 5.01; found C 77.40, H 6.25, N 5.10.

Compound 4c: Pale yellow oil, 28% yield (78 mg, eluent: light petroleum/diethyl ether 1:1, $R_f = 0.31$). − ^{1}H NMR ($CDCl_3$): δ = 3.80 (s, 3 H, OMe), 4.11 (s, 2 H, 3-H), 4.76 (s, 2 H, NCH_2Ph), 5.15 (s, 1 H, =CH_2), 5.55 (s, 1 H, =CH_2), 6.87 (d, J = 7.5 Hz, 2 H, Ar-H), 7.27 (d, J = 7.5 Hz, 2 H, Ar-H), 7.41−7.56 (m, 3 H, Ar-H), 8.22 (d, J = 7.6 Hz, 1 H, Ar-H). − ^{13}C NMR (75.5 MHz, $CDCl_3$): δ = 50.0 (NCH_2), 52.0 (NCH_2), 55.7 (OMe), 112.6 (=CH_2), 114.4 (+), 123.5 (+), 128.2 (C_{quat}), 129.1 (+), 129.2 (+), 129.3 (C_{quat}), 129.9 (+), 132.4 (+), 136.1 (C_{quat}), 137.0 (C_{quat}), 159.4 (C_{quat}), 163.8 (C=O). − IR (neat): $\tilde{\nu}$ = 1651 cm^{-1}, 1514, 1299, 1174, 1109, 1034, 906, 816, 777, 707. − MS (70 eV): *m/z* (%) = 279 (50) [M^+], 158 (10) [M^+ − *p*MeOBn], 121 (100) [*p*MeOBn$^+$]. − $C_{18}H_{17}NO_2$ (279.3): calcd. C 77.40, H 6.13, N 5.01; found C 77.10, H 6.25, N 4.75.

Compound 3d: Colourless solid, 53% yield (163 mg, eluent: light petroleum/diethyl ether 1:2, R_f = 0.18), crystallized from diethyl ether, m.p. 115 °C. − ^{1}H NMR ($CDCl_3$): δ = 1.24 (m_c, 2 H, cPr-H), 1.52 (m_c, 2 H, cPr-H), 3.76 (s, 3 H, OMe), 3.83 (s, 3 H, OMe), 4.53 (s, 2 H, NCH_2), 6.35−6.43 (m, 2 H, Ar-H), 7.01−7.09 (m, 2 H, Ar-H), 7.40−7.54 (m, 2 H, Ar-H), 7.94 (d, J = 7.1 Hz, 1 H, Ar-

H). − ^{13}C NMR (125 MHz, $CDCl_3$): δ = 11.0 (2 × cPr-C), 35.6 (NCH_2), 44.8 (C_{quat}, cPr-C), 55.4 (2 × OMe), 98.3 (+), 104.4 (+), 117.5 (+), 118.0 (C_{quat}), 123.6 (+), 127.2 (+), 129.1 (+), 131.4 (+), 131.5 (C_{quat}), 147.7 (C_{quat}), 157.4 (C_{quat}), 160.1 (C_{quat}), 168.5 (C=O). − IR (nujol): $\tilde{\nu}$ = 1683 cm^{-1}, 1619, 1588, 844, 791, 758, 691. − FAB-MS (*m*NBA): *m/z* (%) = 310 (85) [M^+ + H], 294 (5) [M^+ − OMe], 266 (2) [$M^+ - C_3H_7$], 151 (100) [di-OMeBn$^+$]. − $C_{19}H_{19}NO_3$ (309.4): calcd. C 73.77, H 6.19, N 4.53; found C 73.55, H 6.20, N 4.25.

Compound 4d: Colourless solid, 26% yield (79 mg, eluent: light petroleum/diethyl ether 1:2, R_f = 0.33), crystallized from diethyl ether, m.p. 113 °C. − ^{1}H NMR ($CDCl_3$): δ = 3.79 (s, 3 H, OMe), 3.83 (s, 3 H, OMe), 4.18 (s, 2 H, NCH_2), 4.75 (s, 2 H, NCH_2), 5.16 (s, 1 H, =CH_2), 5.54 (s, 1 H, =CH_2), 6.46 (s, 2 H, Ar-H), 7.26 (m_c, 1 H, Ar-H), 7.40−7.55 (m, 3 H, Ar-H), 8.18 (dd, J^1 = 7.5, J^2 = 1.6 Hz, 1 H, Ar-H). − ^{13}C NMR (75.5 MHz, $CDCl_3$): δ = 45.1 (NCH_2), 52.5 (NCH_2), 55.8 (2 × OMe), 98.8 (+), 104.2 (+), 112.3 (=CH_2), 117.8 (C_{quat}), 123.4 (+), 128.5 (C_{quat}), 128.9 (+), 129.2 (+), 131.0 (+), 132.2 (+), 136.2 (C_{quat}), 137.5 (C_{quat}), 159.0 (C_{quat}), 160.7 (C_{quat}), 163.9 (C=O). − IR (nujol): $\tilde{\nu}$ = 1645 cm^{-1}, 1489, 911, 826, 799, 782, 711. − FAB-MS (*m*NBA): *m/z* (%) = 310 (100) [M^+ + H], 309 (30) [M^+], 172 (23 [M^+ − di-MeOPh], 151 (100) [di-MeOBn$^+$]. − $C_{19}H_{19}NO_3$ (309.4): calcd. C 73.77, H 6.19, N 4.53; found C 73.55, H 6.15, N 4.30.

Compound 3e: Pale yellow oil, 38% yield (76 mg, eluent: light petroleum/diethyl ether 1:1, R_f = 0.20). − ^{1}H NMR ($CDCl_3$): δ = 1.34 (m_c, 2 H, cPr-H), 1.48−1.53 [m, 8 H, cPr-H, $CH(CH_3)_2$], 3.08 [sept, J = 6.8 Hz, 1 H, $CH(CH_3)_2$], 7.00 (d, J = 7.5 Hz, 1 H, Ar-H), 7.40 (dd, J^1 = 7.5 Hz, J^2 = 7.5 Hz, 1 H, Ar-H), 7.48 (dd, J^1 = 7.5, J^2 = 7.5 Hz, 1 H, Ar-H), 7.83 (d, J = 7.5 Hz, 1 H, Ar-H). − ^{13}C NMR (75.5 MHz, $CDCl_3$): δ = 11.1 (2 × cPr-C), 20.4 [$C(CH_3)_2$], 44.1 [$C(CH_3)_2$], 44.3 (C_{quat}, cPr-C), 117.9 (+), 123.5 (+), 127.6 (+), 131.5 (+), 132.9 (C_{quat}), 147.4 (C_{quat}), 168.4 (C=O). − IR (neat): $\tilde{\nu}$ = 2973 cm^{-1}, 2937, 1682, 1472, 1453, 1380, 1363, 1322, 947, 757, 732, 695. − MS (70 eV): *m/z* (%) = 201 (60) [M^+], 186 (50) [$M^+ - CH_3$], 172 (20) [$M^+ - NCH_3$], 158 (100) [$M^+ - NCH(CH_3)_2$]. − HRMS calcd. for $C_{13}H_{15}NONa$ [M + Na^+]: 224.1051; found 224.1054.

Compound 4e: Yellow oil, 35% yield (71 mg, eluent: light petroleum/diethyl ether 1:1, R_f = 0.27). − ^{1}H NMR ($CDCl_3$): δ = 1.22 [d, J = 6.8 Hz, 6 H, $CH(CH_3)_2$], 4.06 (s, 2 H, CH_2N), 5.11 [sept, 1 H, $CH(CH_3)_2$], 5.26 (s, 1 H, =CH_2), 5.56 (s, 1 H, =CH_2), 7.39−7.55 (m, 3 H, Ar-H), 8.15 (d, 1 H, Ar-H). − ^{13}C NMR (75.5 MHz, MHz, $CDCl_3$): δ = 19.9 [$CH(CH_3)_2$], 44.4 [$CH(CH_3)_2$], 45.9 (CH_2N), 112.2 (=CH_2), 123.3 (+), 128.9 (C_{quat}), 129.0 (+), 129.2 (+), 132.1 (+), 135.8 (C_{quat}), 137.8 (C_{quat}), 163.1 (C=O). − IR (neat): $\tilde{\nu}$ = 2975 cm^{-1}, 1644, 1599, 1570, 1475, 1302, 1213, 1179, 905, 777, 709. − MS (70 eV): *m/z* (%) = 201 (75) [M^+], 186 (100) [$M^+ - CH_3$], 159 (50) [$M^+ - C(CH_3)_2$], 145 (55) [$M^+ - NC(CH_3)_2$]. − HRMS calcd. for $C_{13}H_{15}NONa$ [M + Na^+]: 224.1051; found 224.1043.

Compound 4f: Pale yellow needles, 75% yield (161 mg, eluent: light petroleum/diethyl ether 4:1, R_f = 0.33), crystallized from diethyl ether, m.p. 90 °C. − ^{1}H NMR ($CDCl_3$): δ = 1.56 [s, 9 H, $C(CH_3)_3$], 4.20 (s, 2 H, 3-H), 5.23 (s, 1 H, =CH_2), 5.53 (s, 1 H, =CH_2), 7.38−7.42 (m, 2 H, Ar-H), 7.50 (m_c, 1 H, Ar-H), 8.14 (d, J = 7.4 Hz, 1 H, Ar-H). − ^{13}C NMR (75.5 MHz, $CDCl_3$): δ = 29.3 [$C(CH_3)_3$], 49.5 (C-3), 58.3 [$C(CH_3)_3$], 112.1 (=CH_2), 123.2 (+), 129.1 (+), 129.4 (+), 129.6 (+), 132.2 (C_{quat}), 136.1 (C_{quat}), 138.9 (C_{quat}), 165.2 (C=O). − IR (neat): $\tilde{\nu}$ = 2974 cm^{-1}, 1651, 1463, 1295, 1200, 1140, 902, 775, 710. − MS (70 eV): *m/z* (%) = 215 (50) [M^+], 200 (90) [$M^+ - CH_3$], 172 (13) [$M^+ - C_3H_7$], 159 (100) [$M^+ - C_4H_8$], 115 (35) [$C_9H_7^+$].

Compound 8a: Colourless oil, 61% yield (169 mg, eluent: light petroleum/diethyl ether 1:2, R_f = 0.20). − ^{1}H NMR ($CDCl_3$): δ = 1.19 (m_c, 2 H, cPr-H), 1.41 (m_c, 2 H, cPr-H), 3.88 (s, 3 H, OMe), 4.59 (s, 2 H, NCH_2Ph), 6.92 (d, J = 7.6 Hz, 1 H, Ar-H), 7.08−7.45 (m, 7 H, Ar-H). − ^{13}C NMR (75.5 MHz, $CDCl_3$): δ = 10.9 (2 × cPr-C), 42.5 (NCH_2Ph), 45.1 (C_{quat}, cPr-C), 56.2 (OMe), 106.7 (+), 120.8 (+), 127.3 (+), 127.7 (+), 129.1 (+), 132.7 (+), 138.0 (C_{quat}), 140.2 (C_{quat}), 160.0 (C_{quat}), 168.8 (C=O). − IR (neat): $\tilde{\nu}$ = 1699 cm^{-1}, 1515, 1475, 1175, 1034, 756. − MS (70 eV): *m/z* (%) = 279 (75) [M^+], 264 (15) [$M^+ - CH_3$], 236 (60) [$M^+ - C_3H_7$], 188 (50) [M^+ − Bn], 91 (100) [Bn^+]. − $C_{18}H_{17}NO_2$ (279.3): calcd. C 77.40, H 6.13, N 5.01; found C 77.40, H 6.10, N 5.00.

Compound 9a: Colourless oil, 14% yield (39 mg, eluent: light petroleum/diethyl ether 1:2, R_f = 0.42). − ^{1}H NMR ($CDCl_3$): δ = 3.89 (s, 3 H, OMe), 4.12 (s, 2 H, CH_2N), 4.81 (s, 1 H, =CH_2), 5.43 (s, 1 H, =CH_2), 7.03−7.73 (m, 8 H, Ar-H). − ^{13}C NMR (75.5 MHz, $CDCl_3$): δ = 50.8 (NCH_2Ph), 52.3 (CH_2N), 56.0 (OMe), 110.5 (=CH_2), 111.5 (+), 120.5 (+), 125.1 (+), 127.9 (+), 128.4 (+), 129.0 (C_{quat}), 129.1 (+), 129.4 (C_{quat}), 136.4 (C_{quat}), 137.2 (C_{quat}), 160.6 (C_{quat}), 163.8 (C=O). − IR (neat): $\tilde{\nu}$ = 1651 cm^{-1}, 1606, 1505, 1454, 1266, 736, 702. − MS (70 eV): *m/z* (%) = 279 (55) [M^+], 264 (13) [$M^+ - CH_3$], 236 (40) [$M^+ - C_3H_7$], 188 (30) [M^+ − Bn], 91 (55) [Bn^+]. − $C_{18}H_{17}NO_2$ (279.3): calcd. C 77.40, H 6.13, N 5.01; found C 77.65, H 6.10, N 4.90.

Compound 8b: Colourless solid, 61% yield (190 mg, eluent: light petroleum/diethyl ether 1:1, R_f = 0.12), crystallized from diethyl ether, m.p. 114 °C. − ^{1}H NMR ($CDCl_3$): δ = 1.18 (m_c, 2 H, cPr-H), 1.42 (m_c, 2 H, cPr-H), 3.76 (s, 3 H, OMe), 3.87 (s, 3 H, OMe), 4.53 (s, 2 H, NCH_2), 6.81−7.17 (m_c, 6 H, Ar-H), 7.44 (d, J = 2.4 Hz, 1 H, Ar-H). − ^{13}C NMR (75.5 MHz, $CDCl_3$): δ = 10.9 (2 × cPr-C), 41.9 (NCH_2), 45.0 (C_{quat}, cPr-H), 55.6 (OMe), 56.2 (OMe), 106.7 (+), 114.4 (+), 119.0 (+), 120.7 (+), 128.7 (+), 130.1 (C_{quat}), < cPr-H)132.8 (C_{quat}), 140.2 (C_{quat}), 159.2 (C_{quat}), 160.0 (C_{quat}), 168.8 (C=O). − IR (nujol): $\tilde{\nu}$ = 1682 cm^{-1}, 1608, 1515, 1434, 830, 807, 782. − FAB-MS (*m*NBA): *m/z* (%) = 309 (70) [M^+], 293 (10) [$M^+ - CH_4$], 266 (10) [$M^+ - C_3H_7$], 202 (12) [M^+ − *p*OMePh], 188 (10) [M^+ − *p*OMeBn], 121 (100) [*p*OMeBn$^+$]. − $C_{19}H_{19}NO_3$ (309.4): calcd. C 73.77, H 6.19, N 4.53; found C 73.80, H 6.25, N 4.35.

Compound 11a: Colourless solid, 65% yield (201 mg, eluent: diethyl ether, R_f = 0.16), crystallized from diethyl ether, m.p. 123 °C. − ^{1}H NMR ($CDCl_3$): δ = 1.19 (m_c, 2 H, cPr-H), 1.43 (m_c, 2 H, cPr-H), 3.92 (s, 3 H, OMe), 3.97 (s, 3 H, OMe), 4.59 (s, 2 H, NCH_2Ph), 6.45 (s, 1 H, Ar-H), 7.20−7.32 (m, 5 H, Ph-H), 7.43 (s, 1 H, Ar-H). − ^{13}C NMR (75.5 MHz, $CDCl_3$): δ = 11.1 (2 × cPr-C), 42.4 (NCH_2Ph), 45.1 (C_{quat}, cPr-C), 56.7 (2 × OMe), 100.3 (+), 105.8 (+), 123.7 (C_{quat}), 127.3 (+), 127.6 (+), 129.0 (+),138.2 (C_{quat}), 141.5 (C_{quat}), 143.4 (C_{quat}), 149.8 (C_{quat}), 169.0 (C=O). − IR (nujol): $\tilde{\nu}$ = 1645 cm^{-1}, 1505, 827, 799, 782, 743. − MS (70 eV): *m/z* (%) = 309 (100) [M^+], 294 (50) [$M^+ - CH_3$], 266 (30) [$M^+ - C_3H_7$], 218 (85) [M^+ − Bn], 91 (70) [Bn^+]. − $C_{19}H_{19}NO_3$ (309.4): calcd. C 73.77, H 6.19, N 4.53; found C 73.60, H 6.25, N 4.30.

Compound 12a: Pale yellow oil, 4% yield (12 mg, eluent: diethyl ether, R_f = 0.43) − ^{1}H NMR ($CDCl_3$): δ = 3.89 (s, 3 H, OMe), 3.90 (s, 3 H, OMe), 4.05 (s, 2 H, 3-H), 4.73 (s, 2 H, NCH_2Ph), 5.00 (s, 1 H, =CH_2), 5.34 (s, 1 H, =CH_2), 6.90 (s, 1 H, Ar-H), 7.2−7.3 (m, 5 H, Ar-H), 7.63 (s, 1 H, Ar-H). − ^{13}C NMR (75.5 MHz, $CDCl_3$): δ = 50.7 (NCH_2), 52.4 (NCH_2), 56.5 (OMe), 56.6 (OMe), 105.3 (+), 110.6 (=CH_2), 110.8 (+), 121.5 (C-4), 127.9 (+), 128.4

(+), 129.1 (+), 129.9 (C_{quat}), 136.9 (C_{quat}), 137.4 (C_{quat}), 150.2 (C_{quat}), 152.6 (C_{quat}), 163.9 (C=O). − IR (neat): $\tilde{\nu}$ = 1651 cm^{-1}, 1602, 1510, 737, 703. − MS (70 eV): *m/z* (%) = 309 (100) [M^+], 218 (55) [M^+ − Bn], 91 (90) [Bn^+]. − $C_{19}H_{19}NO_3$ (309.4): calcd. C 73.77, H 6.19, N 4.53; found C 73.55, H 6.35, N 4.25.

Compound 11b: Colourless solid, 62% yield (212 mg, eluent: diethyl ether, R_f = 0.13), crystallized from diethyl ether, m.p. 129 °C. − ^{1}H NMR ($CDCl_3$): δ = 1.18 (m_c, 2-H, cPr-H), 1.44 (m_c, 2 H, cPr-H), 3.77 (s, 3 H, OMe), 3.92 (s, 3 H, OMe), 3.96 (s, 3 H, OMe), 4.53 (s, 2 H, NCH_2), 6.44 (s, 1 H, Ar-H), 6.82 (d, *J* = 11.0 Hz, 2 H, Ar-H), 7.15 (d, *J* = 11.0 Hz, 2 H, Ar-H), 7.42 (s, 1 H, Ar-H). − ^{13}C NMR (75.5 MHz, $CDCl_3$): δ = 11.1 (2 × cPr-C), 41.9 (NCH_2), 45.1 (C_{quat}, cPr-C), 55.7 (OMe), 56.6 (OMe), 56.7 (OMe), 100.2 (+), 105.8 (+), 114.4 (+), 123.8 (C_{quat}), 128.6 (+), 130.3 (C_{quat}), 149.8 (C_{quat}), 153.4 (C_{quat}), 159.2 (C_{quat}), 169.0 (C_{quat}). − IR (nujol): $\tilde{\nu}$ = 1665 cm^{-1}, 1505, 1062, 1007, 779, 755, 693. − FAB-MS (*m*NBA): *m/z* (%) = 340 (80) [M^+ + H], 324 (10) [M^+ − CH_3], 232 (10) [M^+ − *p*OMePh], 218 (10) [M^+ − *p*OMeBn], 121 (100) [*p*OMeBn$^+$]. − $C_{20}H_{21}NO_4$ (339.4): calcd. C 70.78, H 6.24, N 4.13; found C 70.80, H 6.40, N 4.00.

Compound 14: Pale yellow oil, 73% yield (208 mg, eluent: light petroleum/diethyl ether 4:1, R_f = 0.17). − ^{1}H NMR ($CDCl_3$): δ = 4.22 (s, 2 H, NCH_2), 4.28 (s, 2 H, NCH_2), 5.20 (s, 1 H, C=CH_2), 5.94 (s, 1 H, C=CH_2), 7.36 (m_c, 5 H, Ar-H), 7.53 (m_c, 2 H, Ar-H), 7.83 (m_c, 2 H, Ar-H). − ^{13}C NMR (75.5 MHz, $CDCl_3$): δ = 42.2 (2 × NCH_2), 116.5 (=CH_2), 125.2 (+), 125.7 (+), 128.5 (+), 129.1 (+), 129.2 (+), 130.0 (+), 132.7 (+), 132.7 (C_{quat}), 132.8 (C_{quat}), 134.4 (C_{quat}), 135.4 (C_{quat}). − IR (nujol): $\tilde{\nu}$ = 1470 cm^{-1}, 1455, 1337, 1167. − MS (70 eV): *m/z* (%) = 285 (13) [M^+], 234 (25) [M^+ − C_4H_3], 194 (55) [M^+ − Bn], 91 (100) [Bn^+].

Compound 16: Yellow oil, 80% yield (188 mg, eluent: light petroleum/diethyl ether 1:1, R_f = 0.54) − ^{1}H NMR ($CDCl_3$): δ = 3.40 (s, 2 H, 1-H), 3.66 (s, 2 H, NCH_2), 3.71 (s, 2 H, NCH_2), 4.94 (s, 1 H, =CH_2), 5.60 (s, 1 H, =CH_2), 7.00−7.70 (m, 9 H, Ar-H). − ^{13}C NMR (75.5 MHz, $CDCl_3$): δ = 56.8 (NCH_2), 58.5 (NCH_2), 61.9 (NCH_2), 108.4 (=CH_2), 123.9 (+), 127.0 (+), 127.4 (+), 127.7 (+), 128.8 (+), 128.9 (+), 130.0 (+), 132.6 (C_{quat}), 135.1 (C_{quat}), 138.4 (C_{quat}), 139.7 (C_{quat}). − MS (70 eV): *m/z* (%) = 235 (35) [M^+], 234 (35) [M^+ − H], 144 (45 [M^+ − Bn], 115 [$C_9H_7^+$], 91 (100) [Bn^+]. − HRMS calcd. for $C_{17}H_{18}N$ [M + H^+]: 236.1439; found 236.1433.

Compound 19: Colourless solid, 84% yield (222 mg, eluent: diethyl ether, R_f = 0.38), crystallized from diethyl ether, m.p. 92 °C. − ^{1}H NMR ($CDCl_3$): δ = 4.00 (s, 2 H, CH_2), 4.20 (s, 2 H, CH_2), 4.61 (s, 2 H, NCH_2Ph), 4.98 (s, 1 H, =CH_2), 5.54 (s, 1 H, =CH_2), 7.18−7.62 (m, 9 H, Ar-H). − ^{13}C NMR (75.5 MHz, $CDCl_3$): δ = 44.6 (C-1), 49.1 (NCH_2), 53.4 (NCH_2), 113.8 (=CH_2), 127.0 (+), 127.9 (+), 128.6 (+), 129.0 (+), 129.1 (+),131.6 (+), 132.2 (C_{quat}), 135.4 (C_{quat}), 137.5 (C_{quat}), 140.9 (C_{quat}), 172.4 (C=O). − IR (nujol): $\tilde{\nu}$ = 1659 cm^{-1}, 1539, 1454, 776, 750. − MS (70 eV): *m/z* (%) = 263 (40) [M^+], 158 (25) [M^+ − NBn], 129 (70) [M^+ − CONHBn], 115 (55) [M^+ − CH_2CONHBn], 91 (100) [Bn^+]. − $C_{18}H_{17}NO$ (263.3): calcd. C 82.10, H 6.51, N 5.32; found C 81.95, H 6.60, N 5.20.

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[1] A. Heumann, M. Réglier, *Tetrahedron* **1995**, *51*, 975−1015.
[2] B. M. Trost, D. L. van Vranken, *Chem. Rev.* **1996**, *96*, 395−422.
[3] M. G. Organ, M. Miller, Z. Konstantinou, *J. Am. Chem. Soc.* **1998**, *120*, 9283−9290.
[4] K. Ohe, H. Matsuda. T. Morimoto, S. Ogoshi, N. Chatani, S. Murai, *J. Am. Chem. Soc.* **1994**, *116*, 4125−4126.
[5] L. S. Hegedus, W. H. Darlington, C. E. Russell, *J. Org. Chem.* **1980**, *45*, 5193−5196.
[6] H. M. R. Hoffmann, A. R. Otte, A. Wilde, S. Menzer, D. J. Williams, *Angew. Chem.* **1995**, *107*, 73−76; *Angew. Chem. Int. Ed. Engl.* **1995**, *34*, 100−102.
[7] A. M. Castaño, A. Aranyos, K. J. Szabó, J.-E. Bäckvall, *Angew. Chem.* **1995**, *107*, 2767−2769; *Angew. Chem. Int. Ed. Engl.* **1995**, *34*, 2551−2553.
[8] K. J. Szabó, *Organometallics* **1996**, *15*, 1128−1133.
[9] A. Aranyos. K. J. Szabó, A. M. Castaño, J.-E. Bäckvall, *Organometallics* **1997**, *16*, 1058−1064.
[10] H. M. R. Hoffmann, A. R. Otte, A. Wilde, *Angew. Chem.* **1992**, *104*, 224−225; *Angew. Chem. Int. Ed. Engl.* **1992**, *31*, 234−236.
[11] A. Wilde, A. R. Otte, H. M. R. Hoffmann, *J. Chem. Soc., Chem. Commun.* **1993**, 615−616.
[12] A. R. Otte, A. Wilde, H. M. R. Hoffmann, *Angew. Chem.* **1994**, *106*, 1352−1354; *Angew. Chem. Int. Ed. Engl.* **1994**, *33*, 1280−1282.
[13] C. Carfagna, L. Mariani, A. Musco, G. Sallese, *J. Org. Chem.* **1991**, *56*, 3924−3927.
[14] M. Formica, A. Musco, R. Pontellini, K. Linn, C. Mealli, *J. Organomet. Chem.* **1993**, *448*, C6−C9, and cited references.
[15] A. Satake, T. Nakata, *J. Am. Chem. Soc.* **1998**, *120*, 10391−10396.
[16] A. Satake, H. Koshino, T. Nakata, *Chem. Lett.* **1999**, 49−50.
[17] For a recent review on palladium-catalyzed reations of allenes see: R. Zimmer, C. U. Dinesh, E. Nandanan, F. A. Khan, *Chem. Rev.* **2000**, *100*, 3067−3125.
[18] R. Grigg, V. Sridharan, *J. Organomet. Chem.* **1999**, *576*, 65−87.
[19] Crystallographic data (excluding structure factors) for the structure reported in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication no. CCDC-146113. Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK [Fax: (internat.) + 44(1223)336−033; E-mail: deposit@ccdc.cam.ac.uk].
[20] Sodium azide is used in anion capture processes of palladium catalyzed cascade reactions not only as the anion capture reagent but also as the base to regenerate Pd(0) from the intermediate H−Pd−halide species: M. Gardiner, R. Grigg, V. Sridharan, N. Vicker, *Tetrahedron Lett.* **1998**, *39*, 435−438.
[21] J. F. Hartwig, *Angew. Chem.* **1998**, *110*, 2154−2177; *Angew. Chem. Int. Ed.* **1998**, 2046−2067.
[22] A. de Meijere, *Angew. Chem.* **1979**, *90*, 867−869; *Angew. Chem. Int. Ed. Engl.* **1979**, *18*, 809−826.
[23] The pK_a values were calculated using the ACD/I-Lab service (www.acdlabs.com).
[24] This is in accordance with competition experiments between π-acceptor and σ-donor ligands in substitution reactions at the centre carbon atom of (η^3-allyl)palladium complexes reported by Bäckvall et al.[7]
[25] The ^{1}H NMR spectra of crude products indicated nearly identical yields in both cases. The lower isolated yield with TMEDA/DMF may be due to the loss of product during aqueous work up, which is not necessary if dioxane is the solvent.
[26] T. Okuyama, G. L. Schmir, *J. Am. Chem. Soc.* **1972**, *94*, 8805−8811.
[27] M. Mori, K. Chiba, Y. Ban, *J. Org. Chem.* **1978**, *43*, 1684−1687.

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