Synthesis of Benzimidazoles by Phosphine-Mediated Reductive Cyclisation of *ortho*-Nitro-anilides

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Heating *ortho*-nitro-anilides **1**–**3** and 2-methyl-*N*-(3-nitropyridin-2-yl)propanamide (**5**) with 4 equiv. of a phosphine led to the 2-substituted benzimidazoles **6**–**8** and to the imidazo[4,5-*b*]pyridine **10**, respectively, in yields between 45 and 85%. Heating **1** with $(EtO)_3P$ effected cyclisation and *N*-ethylation, leading to the 1-ethylbenzimidazole **6b**. The slow cyclisation of the *N*-pivaloylnitroaniline **2b** allowed isolation of the intermediate phosphine imide **11** that slowly transformed into the 1*H*-benzimidazole **7b**. The structure of **11** was established by crystal-structure analysis. While the *N*-methylated *ortho*-nitroacetanilide **3** cyclised to the 1,2-dimethyl-1*H*-benzimidazole (**8**), the 2-methylpropananilide **4** was transformed into 1-methyl-3-(1-methylethyl)-2*H*-benzimidazol-2-one (**9**).

Introduction. – The reductive cyclisation of 6-(acylamino)-5-nitrosopyrimidines using triaryl- or trialkylphosphines leads in high yields to 8-substituted guanines [1][2]. This robust method has, to the best of our knowledge, only be used for the cyclisation of the above mentioned nitrosopyrimidines [3]. We became interested in the analogous reductive cyclisation of *N*-acyl-2-nitroanilines and similar heteroaromatic compounds, considering the practically limited access to nitroso arenes [4][5] and the much easier synthesis of *N*-acyl-2-nitroanilines. The cyclisation is expected to lead to annulated imidazoles, and would be particularly attractive if phosphites could be used besides phosphines. We decided to test this reductive cyclisation by transforming a few *ortho*-nitro-anilides, notwithstanding the many known methods for the synthesis of benzimidazoles[1]) [7]. The first synthesis of a benzimidazole was reported in 1872 by *Hobrecker* who treated 4-methyl-2′-nitroacetanilide with Sn/HCl and isolated 2,5-dimethylbenzimidazole [8]. Since then, *ortho*-nitro-anilides were transformed to benzimidazoles in reducing media such as Zn/AcOH and Fe/HCl, by catalytic or electrochemical reduction, or by treatment with ferrous oxalate. Stepwise procedures, *i.e.*, cyclisation of intermediate *ortho*-amino-anilides or reduction of intermediate benzimidazole *N*-oxides are also well-known. All of the mentioned methods, as well as other ones used for the synthesis of benzimidazoles, were thoroughly reviewed [9–14].

Results and Discussion. – The starting known *ortho*-nitro-anilides **1**–**4** [15] were prepared from the commercially available 2-nitroaniline and *N*-methyl-2-nitroaniline. *N*-(3-Nitropyridin-2-yl)isobutyramide was prepared by acylating the commercially available 3-nitropyridin-2-amine with isobutyryl chloride in the presence of *Hünig*'s

[1]) For selected recent syntheses, see [6].

base at room temperature that resulted in a mixture of **5** (61%) and the *N*,*N*-diacylated product (35%). The ^{1}H-NMR spectra of the *N*-methyl anilides **3** and **4** in $CDCl_3$ display two sets of signals, evidencing a mixture of (*E*)- and (*Z*)-rotamers. Due to the deshielding by the C=O group, the *N*-Me group of the (*E*)-rotamer resonates at lower field than that of the (*Z*)-rotamer ($\Delta\delta = 0.2$ ppm). The nitro-anilides **1** and **2** and the pyridine-derived nitro-anilide **5** in $CDCl_3$ solution are (*E*)-configured single rotamers, due to the intramolecular H-bond between NH and the NO_2 group, as evidenced by the chemical shift of the N*H* signal (δ 10.27–11.36 for **1** and **2**, and 9.82 ppm for **5**)[2]).

The 6-(acylamino)-5-nitrosopyrimidines had been cyclised to guanines by treatment with 2 equiv. of Ph_3P in boiling xylene [1]. The *ortho*-nitro-anilides **1**–**3** and the pyridine derivative **5** were unreactive under these conditions, while cyclisation in the presence of 4 equiv. of Ph_3P in boiling decane (174°) effected the desired transformation. The expected 2-substituted benzimidazoles **6**–**8** (*Table*) and the imidazopyridine **10** were isolated in yields between 45 and 85% (*Entries 1*, *4*, *7*, *8*, *10*, *12*, and *14*, in the *Table*).

A scouting experiment suggested that replacing Ph_3P by 1,2-bis(diphenylphosphino)ethane (DPPE) has only a small effect on yields [19].

Replacing xylene by *p*-cymene, 1,2-dichlorobenzene, ethoxybenzene, or diethyleneglycol diethyl ether provided the benzimidazoles in similar yields, while treating **5** with Ph_3P in boiling DMF led to a mixture of products. The reaction proceeded faster at the higher temperature of boiling diethylene glycol diethyl ether (190°), but yields were not improved (*Entries 2* and *5*). Microwave heating of solutions in 1,2-dichlorobenzene/DMF 10:1 to 250° in a sealed vessel (*Entries 6*, *9*, and *11*) shortened the reaction time considerably. The cyclisations were completed within 30 min, with yields comparable to those resulting from conventional heating.

Heating **1** with $(EtO)_3P$ in decane (*Entry 3*) led to cyclisation and to *N*-ethylation, yielding 42% of the 1*H*-benzimidazole **6b**. *N*-Alkylation was also observed when $(BuO)_3P$ was used instead of $(EtO)_3P$. A scouting experiment showed that $(PhO)_3P$ transformed **1** slowly into **6a**, as inferred from TLC.

The reaction of the *N*-pivaloyl-2-nitroaniline (**2b**) in boiling decane proceeded more slowly than the one of the less bulky anilides, requiring several days to form **7b**. This allowed identifying an intermediate. Monitoring the reaction by TLC showed the initial appearance of a less polar compound that was slowly converted to **7b**. Interrupting the reaction after 12 h allowed isolation of the 1*H*-benzimidazole **7b** (15%) and a less polar intermediate (59%) that was identified as the phosphine imide **11** [34] by crystal-structure analysis[3]) (*Fig. 1*).

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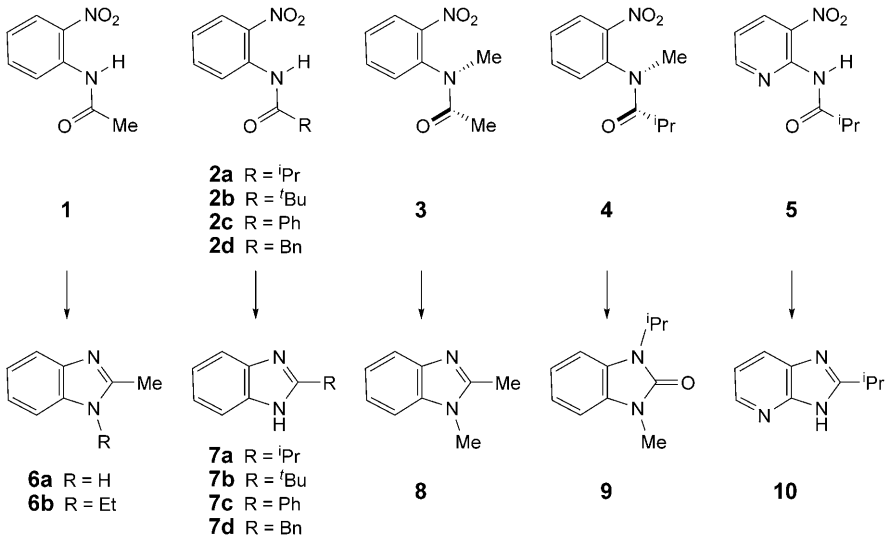
[2]) A similar H-bond was observed between neighbouring C(O)NH and NO groups [2][16]. Its effect on the acylation of 2,4-diamino-5-nitrosopyrimidines and 2-amino-4-(methylamino)-5-nitrosopyrimidines was discussed [17]. N*H* of *N*-(pyridin-2-yl)isobutyramide in $CDCl_3$ solution resonates at δ 8.06 ppm [18].

[3]) The crystallographic data have been deposited with the *Cambridge Crystallographic Data Centre,* with deposition No. CCDC-807072 for **11** and CCDC-807073 for **9**. Copies of the data can be obtained free of charge *via* http://www.ccdc.cam.ac.uk/data_request/cif.

Table. *Reductive Cyclisation of 2-Nitroanilides* **1**–**4** *and* N-*(3-Nitropyridin-2-yl) Amide* **5** *with Phosphines or Phosphites*



Entry	Starting material		Conditions[a])	Product		Yield [%]
1	**1**	[20][15a]	*A* (12 h)	**6a**	[21][6q]	85
2	**1**		*B*	**6a**		70
3	**1**		*C*	**6b**	[22][6z][6aa][7b]	42
4	**2a**	[23][15a]	*A* (12 h)	**7a**	[24][25]	74
5	**2a**		*B*	**7a**		70
6	**2a**		*D*	**7a**		69
7	**2b**	[26][15a]	*A* (144 h)	**7b**	[27][6l]	49
8	**2c**	[28][15b]	*A* (12 h)	**7c**	[21][6c]	62
9	**2c**		*D*	**7c**		76
10	**2d**	[29][15b]	*A* (12 h)	**7d**	[30][6b]	64
11	**2d**		*D*	**7d**		53
12	**3**	[31][15b]	*A* (12 h)	**8**	[32][33]	45
13	**4**	[15c]	*A* (12 h)	**9**		49
14	**5**		*A* (12 h)	**10**		63

[a]) *A:* PPh_3, decane, reflux ($T_{reflux} = 168–178°$); *B:* 1,2-bis(diphenylphosphino)ethane (DPPE), diethylene glycol diethyl ether, reflux ($T_{reflux} = 180–190°$), 2 h; *C:* $P(OEt)_3$, decane, reflux, 12 h; *D:* PPh_3, 1,2-dichlorobenzene/DMF, microwave irradiation, 250°, 1 bar, 30 min.

In the solid state of **11**, the acylamino group adopts the s-*cis*-configuration. The torsion angle C(1)–N(7)–C(8)–O(9) is −7.3°, with the C=O group turned away from to the phosphine imide moiety, the torsion angle C(8)–N(7)–C(1)–C(2) being −175.3°. In solution in $CDCl_3$, **11** forms an intramolecular NH···N=P H-bond, as evidenced by the chemical shift of the N*H* signal, resonating at 9.70 ppm. Although the position of the corresponding H-atom in the solid state of **11** could not be determined,

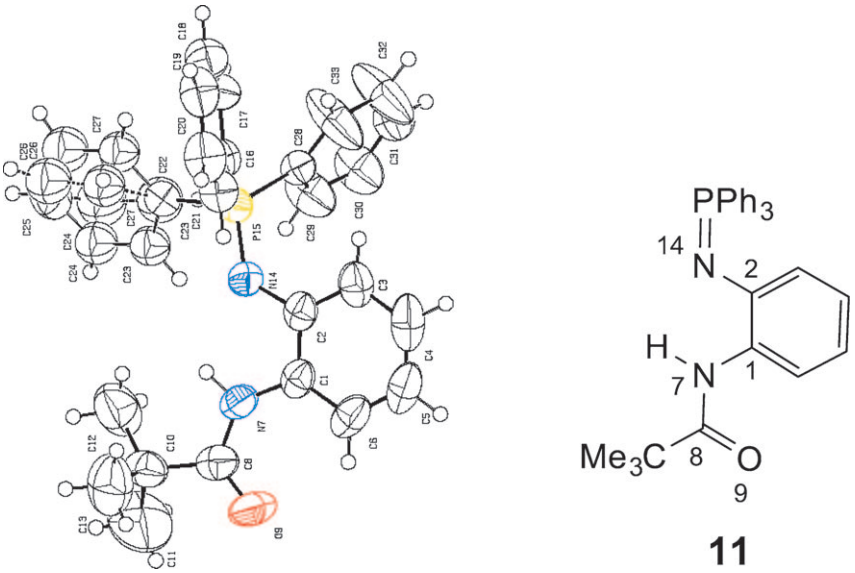


Fig. 1. *Crystal structure of the phosphine imide* **11**

the distance N(7)···N(14) is 2.58 Å, with a calculated N(7)*H*···*N*(14) distance of *ca.* 2.16 Å. No intermolecular H-bonds are detectable in the solid state of **11**[4]).

Surprisingly, heating the *N*-methylated isobutyramide **4** and Ph_3P in boiling decane (*Entry 13*) led to a product (49%) that could not be the expected benzimidazole, the C*H* group of the isopropyl group resonating at an unexpectedly low field (4.74 ppm), and the IR spectrum showing a strong (C=O) band at 1688 cm^{-1}. The structure of the benzimidazolone **9** was established by crystal structure analysis[3]) (*Fig. 2*).

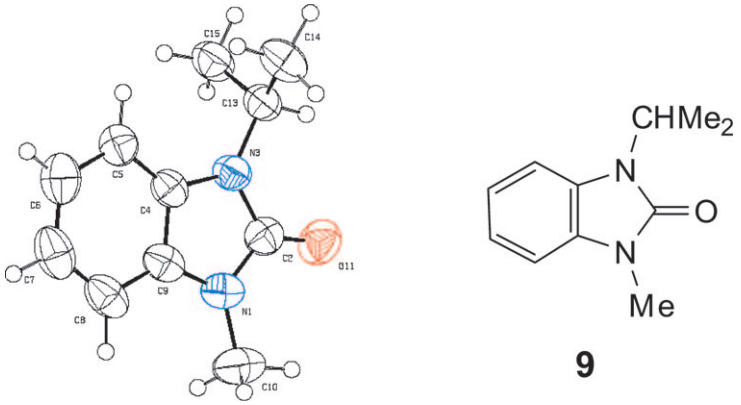


Fig. 2. *Crystal structure of the rearrangement product* **9**

[4]) A considerable number of crystal structure analyses of phosphine imides were found in the *Cambridge Data File*, many of them as metal complexes. For representative references, see [35].

The formation of the phosphine imide **11** and, particularly, the contrast between the formation of the benzimidazole **8** from **3**, but of the benzimidazolone **9** from **4**, were surprising. We had expected the reaction mechanism for the cyclisation of the nitro-anilides **1**–**4** to be similar to the one suggested for the cyclisation of 4-(acylamino)-5-nitrosopyrimidines [1], *i.e.*, reduction of the NO_2 to the NO group, followed by addition of the phosphine to the NO group, and formation of an aza-*Wittig* reagent[5]) *via* a nitrene or nitrenoid intermediate. Surprisingly, however, no intermediate phosphine imide was observed during the formation, under milder reaction conditions, of an 8-(*tert*-butyl)guanine from a 4-(pivaloylamino)-5-nitrosopyrimidine [1]. The addition of a phosphine to the NO_2 group[6]) is thought to occur more slowly than that to the NO group, due to the different formal negative charge on the O-atoms [39], the relative stability of NO_2 and NO compounds, and – for nitrosopyrimidines – also to the effect of the electronegative properties of the heteroaromatic ring[7]). For the anilides **1** and **2**, and for **5**, the nucleophilic attack of the phosphine may also occur more readily than onto the *N*-alkylated nitro-anilide **3**, on account of the intramolecular H-bond. This difference of reactivity of the nitro-anilides is, however, not expected to affect the outcome of the reaction, and the lower yields for the cyclisation of **3** to **8** must reflect the different reactivity of the *bona fide* NO intermediate, or one of the subsequently formed reactive intermediates.

A reaction mechanism rationalising the observations is depicted in the *Scheme 2*. Starting material (SM) for the discussion of the reaction mechanism are the *bona fide* intermediate nitrosoamides. Addition of Ph_3P to the nitrosoamides possessing an NH group is expected to lead to an intermediate **12**, which is stabilized by an intramolecular N*H*$\cdots$N H-bond. Elimination of Ph_3PO then generates the H-bond-stabilised nitrenoid intermediate **13** [40]. Reaction with Ph_3P forms the phosphine imide **14**, which is also stabilized by an intramolecular H-bond. As a consequence of this H-bond, the phosphine imide moiety and the C=O group of **14** are too far away from each other to undergo an intramolecular aza-*Wittig* reaction[8]). However, at the high temperature of the reaction, conformers **14** and **15** will (partially) equilibrate. The ensuing aza-*Wittig* reaction of conformer **15** leads to the observed benzimidazoles **6** and **7**.

The aza-*Wittig* reaction of the pivaloyl amide is sufficiently slow to allow isolating the phosphine imide **11**, since addition of the phosphine imide moiety to the C=O group generates an intermediate with two adjacent tetrahedral centres.

In the absence of the NH group, elimination of Ph_3PO from the addition product **16** may lead to the nitrene **17**, as there is no configurational bias by a H-bond.

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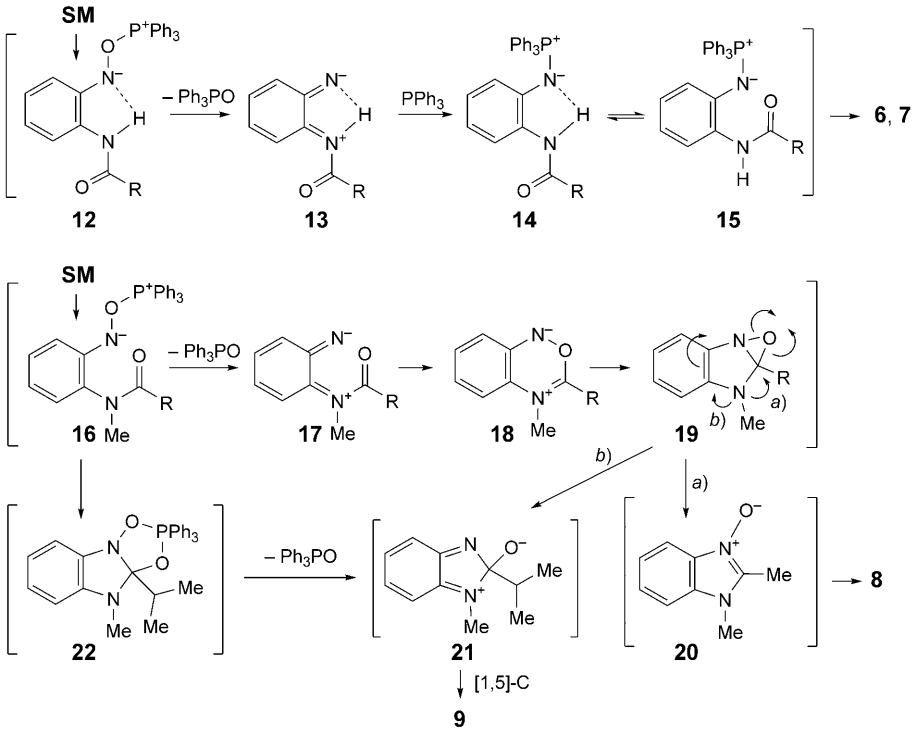
5) For the formation of indoles by intramolecular *Wittig* reaction, see [36]. For a review about phosphine imides in the synthesis of heterocycles, see [37].

6) A single-electron transfer (SET) to the NO_2 group cannot be excluded on the basis of our experiments. For a reaction of a phosphite anion that leads to a SET to a shielded NO_2 compound and to a nucleophilic attack on a less shielded analogue, see [38].

7) The consequence, *i.e.*, the expectation that the cyclisation of *ortho*-nitro-anilides possessing acceptor substituents and of heteroaromatic analogues will give the best results, has not yet been checked.

8) A similar effect of an intramolecular H-bond stabilizing the starting material was observed for the intramolecular [4 + 2] cycloaddition of 6-(dienoylamino)-5-nitrosopyrimidines [2][41] and for the nitroso-ene reaction of 4-(alkenoylamino)-5-nitrosopyrimidines [16].

Scheme. *Reaction Mechanism Rationalising the Transformation of the Intermediate Nitrosoanilines* (SM = Starting Material) *to the Products* **6**–**8** *of Cyclisation and to the Rearrangement Product* **9**



Electrocyclisation of **17** forms **18** that may evolve towards the oxaziridine **19**. Oxaziridine intermediates were considered before as intermediates in related reactions [42]. The N–O bond of **19** may open either to generate the *N*-oxide **20** that will be deoxygenated by Ph_3P, leading to the dimethylbenzimidazole **8**, or to the *ortho*-diazaquinoid intermediate **21** that will generate the rearranged product **9** either by a [1,5] sigmatropic rearrangement [43], or by a 1,2 pinacol–pinacolone type migration of the i-Pr group. It is, however, not clear why there should be such a dichotomy in the opening of the oxaziridine substituted by either a Me, or an i-Pr group, so that one oxaziridine will react while maintaining the aromatic ring intact, and the other one lead to dearomatization. It is more likely that the isobutyrylamino group of **16** (R = 1-methylethyl = isopropyl) is more strongly turned out of the plane of the aromatic ring than the one of the analogous acetamido derivative, and directly attacked by the negatively charged N-centre to generate the phosphorane **22** and hence **21**, while the acetamido analogue may evolve *via* **17**–**20**, and result in the benzimidazole **8**.

Thus, *ortho*-nitro-anilides are converted by reaction with phosphines in one pot to form annulated imidazoles or imidazolones in non-optimized yields between 45 and 85%, with intramolecular H-bonds and conformational aspects strongly influencing the course of the transformation.

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Experimental Part

General. Solvents were distilled. Commercially available reagents were used as supplied. The reactions were carried out in oven-dried glassware, under N_2 or Ar, unless stated otherwise. Qual. TLC: precoated silica-gel plates (*Merck* silica gel *60 F_{254}*); detection by UV. Flash chromatography (FC): silica gel *Fluka 60* (0.04–0.063 mm) or alumina under slightly elevated pressure (0.1–0.4 bar). M.p.: uncorrected. IR Spectra: *ca.* 2% soln. in $CHCl_3$; absorptions in cm^{-1}. NMR Spectra: chemical shifts δ in ppm rel. to TMS as external standard or to a solvent peak; multiplicities of ^{13}C-signals determined by DEPT (distortionless enhancement of polarisation transfer). HR-MS-MALDI: in gentisic acid (=2,5-dihydroxybenzoic acid, DHB) or 3-hydroxypicolinic acid (3-HPA) matrix. For elemental analysis, samples were sublimed or dried for at least 3 d at $< 10^{-4}$ Torr.

General Procedure for the Synthesis of Anilides **1** *and* **2**. The acyl chloride (1.5 equiv.) was added over 30 min to a cold (4°) orange soln. of 2-nitroaniline (3–4 mmol) and DMAP (=4-(dimethylamino)pyridine; 0.03 equiv.) in a 1:1 mixture of pyridine (12–15 equiv.) and CH_2Cl_2. The mixture was stirred, until TLC indicated the disappearance of the starting material, diluted with CH_2Cl_2, washed with 2M HCl, sat. aq. $NaHCO_3$ soln., and brine, dried ($MgSO_4$), and evaporated. FC afforded the desired anilides.

General Procedure for the Synthesis of Anilides **3** *and* **4**. A dark ocre soln. of *N*-methyl-2-nitroaniline (4–5 mmol) in an acyl chloride (10–20 equiv.) was treated with *Hünig*'s base (1.3–1.5 equiv.) at 25°. The mixture was stirred at the indicated temp., until TLC indicated the disappearance of the starting material, and poured into 10% aq. Na_2CO_3 soln. The mixture was vigorously stirred for 1 h and extracted with CH_2Cl_2. The combined org. layers were washed with brine, dried ($MgSO_4$), and evaporated. FC afforded the desired anilides.

General Procedure A for the Synthesis of Benzimidazoles. A soln. of an anilide (0.5 mmol) in decane (5 ml) was treated with Ph_3P (4 equiv.). The mixture was heated to reflux, until TLC indicated the disappearance of the starting material, left to reach 25°, diluted with $CHCl_3$, and purified by FC and/or crystallisation to obtain the desired benzimidazoles.

General Procedure B for the Synthesis of Benzimidazoles. A soln. of an anilide (0.1 mmol) in 1,2-dichlorobenzene (1.5 ml) and DMF (0.15 ml) was treated with Ph_3P (4 equiv.). The mixture was heated to 250° at 1 bar in the microwave oven for 30 min. FC afforded the desired benzimidazoles.

Acylation of 3-Nitropyridin-2-amine. According to the general procedure for **3** and **4** at 25°. FC (silica gel, cyclohexane/AcOEt 6:1 → 3:1 → 1:1) gave 61% of compound **5** and 35% of 2-methyl-*N*-(2-methylpropanoyl)-*N*-(3-nitropyridin-2-yl)propanamide.

2-Methyl-N-*(3-nitropyridin-2-yl)propanamide* (**5**). Yellow solid. M.p. 132–133.5°. R_f (cyclohexane/AcOEt 1:1) 0.28. ^{1}H-NMR (300 MHz, $CDCl_3$): 9.82 (br. *s*, exchange with D_2O, NH); 8.70 (*dd*, *J* = 4.7, 1.7, H–C(6′)); 8.47 (*dd*, *J* = 8.2, 1.7, H–C(4′)); 7.23 (*dd*, *J* = 8.2, 4.7, H–C(5′)); 2.78 (*sept.*, *J* = 6.9, Me_2CH); 1.31 (*d*, *J* = 6.9, Me_2CH). HR-EI-MS: 209.0794 (8, M^+, $C_9H_{11}N_3O_3^+$; calc. 209.0800), 163.0865 (14, $[M - NO_2]^+$, $C_9H_{11}N_2O^+$; calc. 163.0871), 70.0331 (69), 43.0575 (100).

2-Methyl-N-*(2-methylpropanoyl)*-N-*(3-nitropyridin-2-yl)propanamide.* Ocre solid. M.p. 67.5–69.5°. R_f (cyclohexane/AcOEt 1:1) 0.53. ^{1}H-NMR (300 MHz, $CDCl_3$): 8.79 (*dd*, *J* = 4.8, 1.7, H–C(6′)); 8.46 (*dd*, *J* = 8.2, 1.7, H–C(4′)); 7.59 (*dd*, *J* = 8.2, 4.8, H–C(5′)); 2.91 (*sept.*, *J* = 6.7, 2 Me_2CH); 1.20 (*d*, *J* = 6.7, 2 Me_2CH). HR-EI-MS: 279.1214 (0.27, M^+, $C_{13}H_{17}N_3O_4^+$; calc. 279.1219), 236.0668 (4, $[M - C_3H_7]^+$, $C_{10}H_{10}N_3O_4^+$; calc. 236.0671), 71.0487 (63), 43.0722 (100).

*2-(1-Methylethyl)-3*H-*imidazo[4,5*-b*]pyridine* (**10**). General procedure *A* (12 h at reflux). FC (silica gel; cyclohexane/AcOEt/MeOH 1:1:0 → 1:3:0 → 1:3:0.05), followed by FC ($CHCl_3$/AcOEt 2:1 → 1:4), gave **10** (63%). Colourless solid. M.p. 149–151.5° (sublimed). R_f (AcOEt) 0.21. IR ($CHCl_3$): 3451*w*, 3223*m*, 3154*m*, 3089*s*, 2972*s*, 2876*m*, 2776*m*, 2747*m*, 1924*w*, 1887*w*, 1851*w*, 1729*w*, 1615*m*, 1598*m*, 1520*m*, 1485*w*, 1460*m*, 1432*s*, 1418*s*, 1391*m*, 1305*m*, 1280*m*, 1264*s*, 1161*w*, 1115*w*, 1093*m*, 1066*w*, 1050*w*, 980*w*, 917*w*. ^{1}H-NMR (300 MHz, $CDCl_3$): 13.87 (br. *s*, exchange with D_2O, NH); 8.36 (*dd*, *J* = 5.0, 1.4, H–C(5)); 8.07 (br. *d*, *J* = 7.9, H–C(7)); 7.26 (*dd*, *J* = 8.0, 5.0, H–C(6)); 3.39 (*sept.*, *J* = 7.0, Me_2CH); 1.58

(*d*, *J* = 7.0, *Me*$_2$CH). ^{13}C-NMR (300 MHz, $CDCl_3$): 162.50 (*s*, C(2)); 149.38 (*s*, C(3a)); 141.85 (*d*, C(5)); 136.30 (*s*, C(7a)); 127.35 (*d*, C(7)); 117.90 (*d*, C(6)); 29.87 (*d*, Me$_2$*C*H); 21.48 (*q*, *Me*$_2$CH). HR-EI-MS: 161.0946 (40, M^+, $C_9H_{11}N_3^+$; calc. 161.0953), 160.0870 (25, $[M-H]^+$, $C_9H_{10}N_3^+$; calc. 160.0875), 146.0708 (100, $[M-Me]^+$, $C_8H_8N_3^+$; calc. 146.0718). LR-ESI-MS: 213.2 (100, $[M+Na]^+$). Anal. calc. for $C_9H_{11}N_3$ (161.20): C 67.06, H 6.88, N 26.07; found: C 67.16, H 6.76, N 26.08.

*1,3-Dihydro-1-methyl-3-(1-methylethyl)-2*H*-benzimidazol-2-one* (**9**). General procedure *A*. FC (cyclohexane/AcOEt 1:1) gave **9** (49%). Colourless solid. M.p. 104–106°. R_f (cyclohexane/AcOEt 2:1) 0.32. IR ($CHCl_3$): 3067*w*, 3031*w*, 3007*m*, 2983*m*, 2938*w*, 2881*w*, 1916*w*, 1866*w*, 1812*w*, 1688*s*, 1620*w*, 1606*w*, 1496*s*, 1458*w*, 1436*m*, 1398*m*, 1390*m*, 1372*w*, 1362*w*, 1324*w*, 1218*w*, 1161*w*, 1129*w*, 1093*w*, 1084*w*, 1048*w*, 1021*w*, 951*w*, 910*w*. ^{1}H-NMR (300 MHz, $CDCl_3$): 7.16–6.94 (*m*, 4 arom. H); 4.74 (*sept.*, *J* = 7.0, Me$_2$C*H*); 3.40 (*s*, MeN); 1.53 (*d*, *J* = 7.0, *Me*$_2$CH). ^{13}C-NMR (300 MHz, $CDCl_3$): 154.05 (*s*, C=O); 130.43, 128.39 (2*s*, C(3a), C(7a)); 120.98, 120.81 (2*d*, C(5), C(6)); 109.02, 107.56 (2*d*, C(4), C(7)); 45.18 (*d*, Me$_2$*C*H); 27.12 (*q*, MeN); 20.45 (*q*, *Me*$_2$CH). HR-EI-MS: 190.1097 (58, M^+, $C_{11}H_{14}N_2O^+$; calc. 190.1106), 175.0858 (27, $[M-Me]^+$, $C_{10}H_{11}N_2O^+$; calc. 175.0871), 148.0630 (100, $[M-C_3H_6]^+$, $C_8H_8N_2O^+$; calc. 148.0637). LR-ESI-MS: 213.2 (100, $[M+Na]^+$). Anal. calc. for $C_{11}H_{14}N_2O \cdot 1/8\ H_2O$ (192.49): C 68.63, H 7.46, N 14.55; found: C 68.69, H 7.44, N 14.35.

Crystal Structure of **9**. $C_{11}H_{14}N_2O$ (190.246), Monoclinic $P2_1/n$, $a = 9.0169$ (10) Å, $b = 9.9103$ (12), $c = 12.030$ (2) Å, $\beta = 105.013$ (7)°, $V = 1038.3$ (2) Å^3, $Z = 4$, $D_{calc} = 1.217$ Mg/m^3, F(000) = 408.0. The reflexions were measured on a *Bruker Nonius Kappa CCD* diffractometer with MoK_α radiation $\lambda = 0.71073$ at 223 K, θ range = 2.753–24.108°. Refinement on F^2 (full-matrix least-squares refinement), R(all) = 0.0809, R(gt) = 0.0563. All the calculations were performed using maXus. The programme SHELXS-97 was used to solve the structure, and the programme SHELXL-97 was used to refine the structure.

2,2-Dimethyl-N-*{2-[(triphenylphosphoranylidene)amino]phenyl}propanamide* (**11**). General procedure *A* (12 h at reflux). FC (alumina B, act. III; cyclohexane/AcOEt 5:1 → 3:1); gave **11** (59%) and **7b** (15%).

Data of **11**. Colourless solid. M.p. 180–181.5° (Et_2O/hexane). R_f (cyclohexane/AcOEt 2:1) 0.45. IR ($CHCl_3$): 3336*w*, 3079*w*, 3061*w*, 3007*m*, 2965*w*, 2870*w*, 1983*w*, 1963*w*, 1916*w*, 1895*w*, 1818*w*, 1775*w*, 1655*m*, 1592*m*, 1574*m*, 1517*s*, 1483*m*, 1469*m*, 1446*s*, 1437*s*, 1398*w*, 1345*s*, 1309*s*, 1257*w*, 1162*w*, 1116*s*, 1050*w*, 1020*m*, 999*w*, 923*w*. ^{1}H-NMR (300 MHz, $CDCl_3$): 9.70 (br. *s*, exchange with CD_3OD, NH); 8.45 (*ddd*, *J* = 8.0, 2.7, 1.8, H–C(6)); 7.79–6.69 (*m*, 6 arom. H); 7.60–7.42 (*m*, 9 arom. H); 6.69 (*td*, *J* = 7.6, 1.3), 6.59 (*td*, *J* = 7.6, 1.8) (H–C(4), H–C(5)); 6.42 (*dt*, *J* ≈ 7.8, 1.3, H–C(3)); 1.32 (*s*, *t*-Bu). ^{13}C-NMR ($CDCl_3$, 75 MHz): 176.35 (*s*, C=O); 139.73 (*s*, C(2)); 133.25 (*d*, ^3J(C,P) = 19.8, C(1)); 132.60 (*dd*, ^2J(C,P) = 9.7, 3 C(2′) and 3 C(6′)); 132.14 (*dd*, ^4J(C,P) = 2.7, 3 C(4′)); 130.60 (*d*, ^1J(C,P) = 100.1, 3 C(1′)); 128.86 (*dd*, ^3J(C,P) = 12.1, 3 C(3′) and 3 C(5′)); 122.54 (*d*, C(5)); 119.34 (*dd*, ^4J(C,P) = 9.4, C(6)); 118.08 (*dd*, ^3J(C,P) ≈ ^4J(C,P) ≈ 2.6, C(3) and C(4)); 40.09 (*s*, Me_3C); 28.06 (*q*, *Me*$_3$C). HR-MALDI-MS: 453.2097 (100, $[M+H]^+$, $C_{29}H_{30}N_2OP^+$; calc. 453.2096). Anal. calc. for $C_{29}H_{30}N_2OP$ (752.53): C 76.80, H 6.67, N 6.18, P 6.83; found: C 76.54, H 6.63, N 6.24, P 6.81.

Crystal Structure of **11**. $C_{29}H_{29}N_2OP$ (452.538), Monoclinic $P2_1/c$, $a = 9.0471$ (2), $b = 14.3479$ (4), $c = 19.6929$ (5) Å, $\beta = 102.671$ (2)°, $V = 2494.02$ (11) Å^3, $Z = 4$, $D_{calc} = 1.205$ Mg/m^3, F(000) = 960.0. The reflexions were measured on a *Bruker Nonius Kappa CCD* diffractometer with MoK_α radiation $\lambda = 0.71073$ at 298 K, θ range = 2.425–27.485 °. Refinement on F^2 (full-matrix least-squares refinement), R(all) = 0.1318, R(gt) = 0.0848. All calculations were performed using maXus. The programme SIR97 was used to solve the structure, and the programme SHELXL-97 was used to refine the structure.

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