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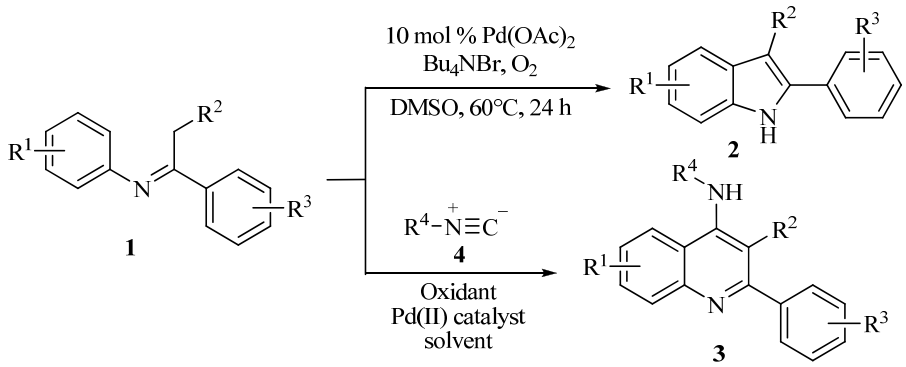
SYNTHESIS OF 4-AMINOQUINOLINES BY AEROBIC OXIDATIVE PALLADIUM-CATALYZED DOUBLE C–H ACTIVATION AND ISOCYANIDE INSERTION

An unprecedented aerobic oxidative Pd-catalyzed imidoylative coupling of two C–H fragments furnishing medicinally valuable 4-aminoquinolines is reported. Optimization studies are described and several analogs were successfully prepared.

Keywords: isocyanides, palladium, quinolines, catalysis, C–H bond activation, imidoylative cross-coupling.

Isocyanides are important reagents that have found various applications in different fields of organic chemistry (*e. g.* multicomponent reactions and cycloadditions) [1–6]. They were recently identified as versatile C_1 building blocks in palladium catalysis and readily undergo 1,1-migratory insertion similar to carbon monoxide*. This strategy has been applied in the synthesis of important functional groups [7–9] and heterocycles [10–19], predominantly by amidination of aryl halides by imidoylative cross-coupling with amines. The selective catalytic activation of C–H bonds, rather than preactivation as halides, offers substantial advantages, like improved atom and step economy, and is therefore a more environmentally benign alternative [20–23]. Indeed, C–H activation has been combined with isocyanide insertion in the synthesis of amidine-containing heterocycles [24, 25], but also imine/enamine-containing heterocycles are accessible by imidoylative cross-coupling of aryl halides and C–H fragments [26–29]. In light of our interest in Pd-catalyzed cascade reactions [29] and imidoylative cross-couplings** [11, 16, 19], we became intrigued by the potential of an imidoylative double C–H activation cascade. Imidoylative coupling of two C–H fragments is unprecedented and would yield valuable imine/enamine products in a highly sustainable manner.

Glorius recently reported an elegant synthesis of indoles **2** by Pd-catalyzed oxidative cyclization of *N*-arylimines **1**, although an activating electron-withdrawing



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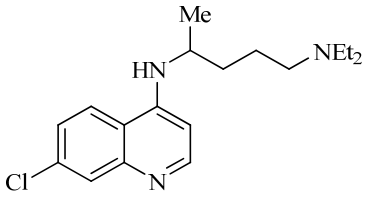
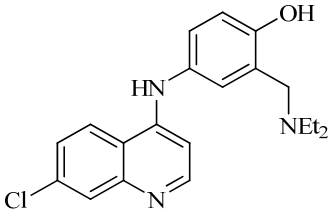
group was required on the R^2 position [30, 31]. However, Yoshikai subsequently reported modified conditions that overcame this limitation [32]. We therefore chose to evaluate the potential use of our envisioned double C–H activation reaction with this system. An imidoylative Pd-catalyzed oxidative cyclization of *N*-aryl imines **1** provides straightforward access to valuable 4-aminoquinolines **3**, the structures of which are found in some important antimalarial drugs, like chloroquine and amodiaquine.



Chloroquine

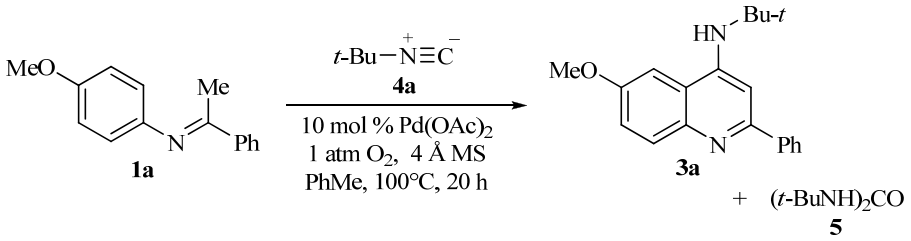


Amodiaquine

We started our investigations by studying the reaction between *N*-arylimine **1a** and *tert*-butyl isocyanide (**4a**) (Table 1). We first tested the conditions developed by Yoshikai, but no detectable amount of the desired product **3a** was formed. We were pleased to find conversion to 4-aminoquinoline **3a** using $Pd(OAc)_2$ (10 mol %) in the presence of molecular sieves (MS) in toluene at 100°C under oxygen atmosphere, although the conversion was poor (Table 1, Entry 1). The black reaction mixture, which was observed after a few hours, indicated formation of palladium black. We screened several other oxidants ($CuCl_2$, $Cu(OAc)_2$, AgOAc, benzoquinone, $K_2S_2O_8$), solvents (THF, DMSO, DMF, MeCN, *t*-BuOH, dioxane, DCE, DME), and palladium catalysts ($PdCl_2$, $Pd(O_2CCF_3)_2$, $Pd(MeCN)_2Cl_2$), but no improvement was achieved. We argued that palladium black formation could be retarded by addition of more *tert*-butyl isocyanide, which coordinates to palladium(0) species. Indeed, a higher yield was obtained when three equivalents of

Table 1

Optimization of the reaction conditions*



Entry	Equivalents of **4a**	Additive	Conversion**, %	Yield**, %
1	1.5	none	20	8
2	3.0	none	31	15
3	3.0	1,10-Phenanthroline (20 mol %)	30	12
4	3.0	Pyridine (1 equiv.)	31	12
5	3.0	PivOH (10 mol %)	40	24
6	3.0	PivOH (20 mol %)	42	25
7	3.0	PivOH (30 mol %)	64	46
8	3.0	PivOH (40 mol %)	48	19
9	3.0	PivOH (60 mol %)	40	6

* Standard conditions: imine **1a** (0.5 mmol), $Pd(OAc)_2$ (10 mol %), 4 Å MS (150 mg), PhMe (2.5 ml), 100°C under O_2 atmosphere for 20 h.

** Determined by GC analysis using dodecane as internal standard.

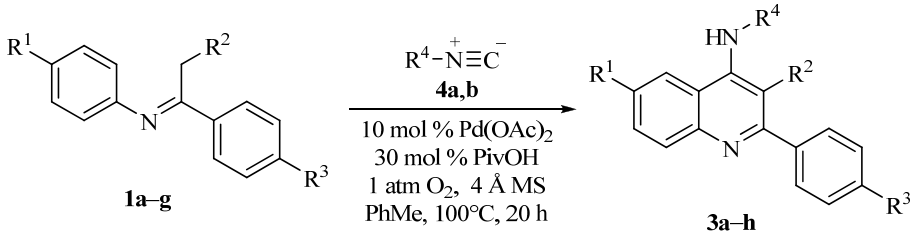
isocyanide **4a** were used (Entry 2). Coordinating additives, such as 1,10-phenanthroline and pyridine, gave no further improvement (Entries 3 and 4), and varying the temperature did also not improve the yield. Finally, we found that a catalytic amount of pivalic acid is beneficial to the reaction (Entries 5–9). The reaction is highly sensitive to the amount of pivalic acid used, with 30 mol % giving the optimal result. It is, however, important to note that the yields varied between individual experiments using identical reaction conditions, and only the relative trend shown in Table 1 is of value. Surprisingly, the unreacted starting compound **1a** remained intact under the optimal conditions (Entry 7), suggesting only catalyst deactivation hampers the reaction. We were unfortunately not able to further improve the conversion of this transformation. The only side product we identified was *N*,*N*'-di-*tert*-butylurea (**5**), which we have encountered previously in aerobic oxidative Pd-catalyzed imidoylation reactions [19].

We then evaluated the scope of the Pd-catalyzed coupling of various *N*-arylimines **1a**–**g** and isocyanides **4a**,**b** in order to find a more suitable substrate (Table 2). In the event, electron-withdrawing and -donating substituents on both aromatic rings had only minor influence on the course of the reaction. Working with isocyanide **4a** in all cases a similar isolated yield (15–27%) was observed. In some cases removal of urea **5**, forming as the side product, was problematic and the target product was isolated as a mixture. Isopropyl isocyanide (**4b**) was readily converted to 4-aminoquinoline **3g** in reaction with imine **1a** under the same conditions. We also installed an electron-withdrawing ester group on the *N*-arylimine **1g** to activate the C–H bond of the methylene group, but surprisingly in this case product **3h** was not observed in an appreciable quantity.

A plausible mechanism, based on previous literature reports [30–32], is depicted below (possible additional ligands on palladium are omitted for clarity). Nucleophilic attack of enamine **1'** on palladium and elimination of carboxylic acid leads

Table 2

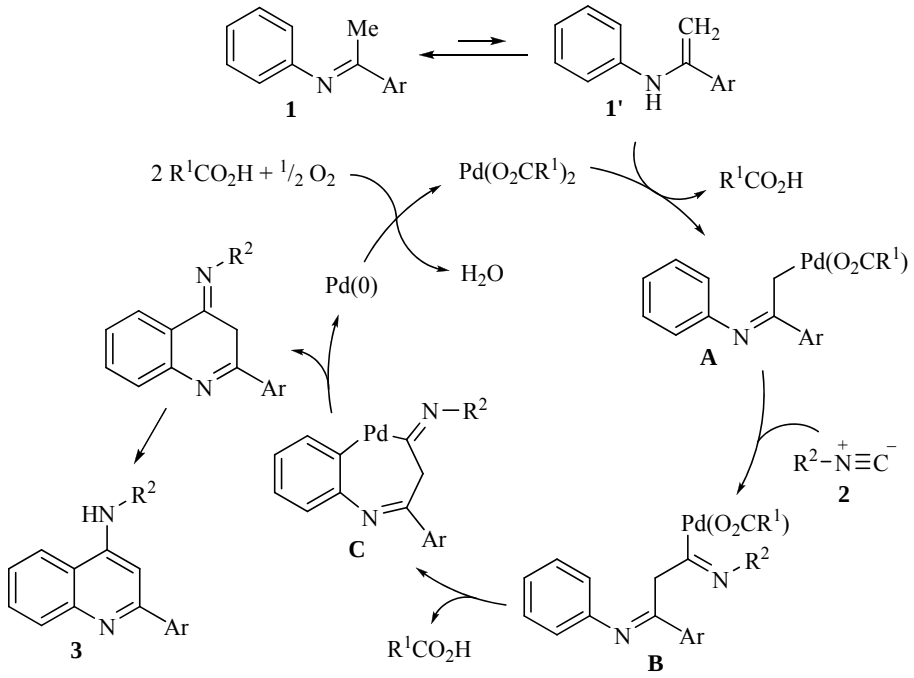
Scope of the reaction towards 4-aminoquinolines*



Imine	Isocyanide	R^1	R^2	R^3	R^4	Product	Yield, %
1a	**4a**	OMe	H	H	*t*-Bu	**3a**	21
1b	**4a**	OMe	H	Me	*t*-Bu	**3b**	23
1c	**4a**	OMe	H	Cl	*t*-Bu	**3c**	22
1d	**4a**	OMe	H	OMe	*t*-Bu	**3d**	19
1e	**4a**	Me	H	H	*t*-Bu	**3e**	27
1f	**4a**	Cl	H	H	*t*-Bu	**3f**	15
1a	**4b**	OMe	H	H	*i*-Pr	**3g**	13
1g	**4a**	OMe	COOEt	H	*t*-Bu	**3h**	–

* Yields refer to isolated material and are corrected for contamination with $(t\text{-BuNH})_2CO$.

to α-palladated imine **A**. Migratory insertion of isocyanide followed by intramolecular C–H bond activation provides palladium species **C**, which undergoes reductive elimination to afford the product and palladium(0). Alternatively, the second C–H bond activation event could occur prior to isocyanide insertion. Finally, palladium is reoxidized by molecular oxygen.



R^1 = *t*-Bu, Me; R^2 = *t*-Bu, *i*-Pr

In summary, we have reported the first example of an imidoylative coupling of two C–H fragments using aerobic oxidative palladium catalysis. The reaction produces valuable 4-aminoquinolines from readily available starting materials, although yields are still modest and need further optimization. We believe imidoylative C–H bond activation offers various opportunities for the efficient synthesis of fine chemicals with nitrogen functionality, as illustrated by this preliminary work.

EXPERIMENTAL

^{1}H and ^{13}C NMR spectra were recorded on a Bruker Avance 500 spectrometer (500 and 125 MHz, respectively) in DMSO-d_6, using the residual solvent as internal standard (δ 2.50 ppm for ^{1}H nuclei, δ 39.5 ppm for ^{13}C nuclei). Electrospray ionization high-resolution mass spectrometry was carried out using a Bruker micrOTOF-Q instrument in positive ion mode (capillary potential 4500 V). Melting points were determined on a Buchi M-565 apparatus. The obtained compounds were purified by flash chromatography using Silicycle Silia-P Flash silica gel (particle size 40–63 μm, pore diameter 60 Å), eluent – $CHCl_3$–MeOH (gradient). TLC analysis was performed using Merck TLC plates (SiO_2, Kieselgel 60 F254 neutral, on aluminium with fluorescence indicator), spots of the compounds were visualized by UV detection (254 nm).

***N*-arylimines 1a–g** were prepared by condensation of the corresponding aniline and acetophenone derivatives according to literature procedure and purified by vacuum distillation or crystallization from EtOH, Et_2O, or EtOAc [33]. ^{1}H NMR spectra of imines **1a**–**h** were in good agreement with literature data [33–38].

Synthesis of 4-aminoquinolines 3a–g (General Method). *N*-Arylimine **1a–g** (0.5 mmol), $Pd(OAc)_2$ (11.2 mg, 10 mol %), pivalic acid (15.3 mg, 30 mol %), and activated powdered 4Å molecular sieves (150 mg) were added to a Schlenk tube. Vacuum was applied, and the vessel was backfilled with O_2 three times. Toluene (2.5 ml) was added, followed by isocyanide **4a**,**b** (1.5 mmol). The resulting mixture was stirred vigorously at 100°C for 20 h under O_2 atmosphere (balloon). Then, the mixture was cooled, filtered over Celite, concentrated, and purified by flash chromatography. Products were isolated in reasonable purity (>90% by ^{1}H NMR spectroscopy), or along with *N*,*N*'-di-*tert*-butylurea (**5**) in some cases (compounds **3c**,**f**). Using imine **1g**, the corresponding 4-aminoquinoline **3h** was not isolated.

***N*-(*tert*-Butyl)-6-methoxy-2-phenylquinolin-4-amine (3a)**. Yield 32 mg (21%), brownish oil. ^{1}H NMR spectrum, δ, ppm (*J*, Hz): 8.07 (2H, d, *J* = 7.5, H-2,6 Ph); 7.81 (1H, d, *J* = 9.1, H-8); 7.58 (1H, d, *J* = 2.4, H-5); 7.52 (2H, t, *J* = 7.4, H-3,5 Ph); 7.45 (1H, t, *J* = 7.3, H-4 Ph); 7.32 (1H, dd, *J* = 9.0, *J* = 2.5, H-7); 7.09 (1H, s, H-3); 6.30 (1H, br. s, NH); 3.93 (3H, s, OCH_3); 1.57 (9H, s, $C(CH_3)_3$). ^{13}C NMR spectrum, δ, ppm: 156.2 (C); 153.5 (C); 148.6 (C); 143.2 (C); 139.7 (C); 130.3 (CH); 128.9 (CH); 128.7 (CH); 126.9 (CH); 120.8 (CH); 119.3 (C); 101.5 (CH); 98.2 (CH); 55.9 (CH_3); 51.4 (C); 29.0 (CH_3). Found, *m*/*z*: 307.1812. $C_{20}H_{23}N_2O$ $[M+H]^+$. Calculated, *m*/*z*: 307.1805.

***N*-(*tert*-Butyl)-6-methoxy-2-(4-methylphenyl)quinolin-4-amine (3b)**. Yield 37 mg (23%), off-white oil. ^{1}H NMR spectrum, δ, ppm (*J*, Hz): 8.07 (2H, d, *J* = 8.0, H-2,6 Ar); 7.80 (1H, d, *J* = 9.1, H-8); 7.57 (1H, d, *J* = 2.0, H-5); 7.34–7.29 (3H, m, H-7, H-3,5 Ar); 7.07 (1H, s, H-3); 6.28 (1H, br. s, NH); 3.93 (3H, s, OCH_3); 2.37 (3H, s, $ArC\underline{H}_3$); 1.56 (9H, s, $C(CH_3)_3$). ^{13}C NMR spectrum, δ, ppm: 156.1 (C); 153.4 (C); 148.6 (C); 143.1 (C); 138.4 (C); 136.8 (C); 130.2 (CH); 129.3 (CH); 126.8 (CH); 120.7 (CH); 119.2 (C); 101.5 (CH); 98.0 (CH); 55.9 (CH_3); 51.4 (C); 29.0 (CH_3); 20.9 (CH_3). Found, *m*/*z*: 321.1976. $C_{21}H_{25}N_2O$ $[M+H]^+$. Calculated, *m*/*z*: 321.1961.

***N*-(*tert*-Butyl)-2-(4-chlorophenyl)-6-methoxyquinolin-4-amine (3c)**. Isolated as mixture with *N*,*N*'-di-*tert*-butylurea (**5**) in a 4:1 ratio (determined by ^{1}H NMR spectrum). Yield 22% (after correction for impurities), yellowish oil. ^{1}H NMR spectrum, δ, ppm (*J*, Hz): 8.11 (2H, d, *J* = 8.4, H-2,6 Ar); 7.80 (1H, d, *J* = 9.1, H-8); 7.58 (1H, d, *J* = 2.4, H-5); 7.56 (2H, d, *J* = 8.5, H-3,5 Ar); 7.32 (1H, dd, *J* = 9.1, *J* = 2.3, H-7); 7.08 (1H, s, H-3); 6.31 (1H, br. s, NH); 3.93 (3H, s, OCH_3); 1.56 (9H, s, $C(CH_3)_3$). ^{13}C NMR spectrum, δ, ppm: 156.3 (C); 152.2 (C); 148.7 (C); 143.3 (C); 138.5 (C); 133.6 (C); 130.4 (CH); 128.6 (CH); 128.6 (CH); 120.9 (CH); 119.3 (C); 101.5 (CH); 97.9 (CH); 55.9 (CH_3); 51.4 (C); 29.0 (CH_3). Found, *m*/*z*: 341.1428. $C_{20}H_{22}ClN_2O$ $[M+H]^+$. Calculated, *m*/*z*: 341.1415.

***N*-(*tert*-Butyl)-6-methoxy-2-(4-methoxyphenyl)quinolin-4-amine (3d)**. Yield 32 mg (19%), off-white solid, mp 67–81°C. ^{1}H NMR spectrum, δ, ppm (*J*, Hz): 8.03 (2H, d, *J* = 8.7, H-2,6 Ar); 7.79 (1H, d, *J* = 9.1, H-8); 7.57 (1H, d, *J* = 2.4, H-5); 7.31 (1H, dd, *J* = 9.1, *J* = 2.4, H-7); 7.07 (2H, d, *J* = 8.7, H-3,5 Ar); 7.04 (1H, s, H-3); 6.32 (1H, br. s, NH); 3.93 (3H, s, OCH_3); 3.83 (3H, s, OCH_3); 1.45 (9H, s, $C(CH_3)_3$). ^{13}C NMR spectrum, δ, ppm: 160.1 (C); 156.0 (C); 153.0 (C); 148.7 (C); 142.8 (C); 131.7 (C); 129.8 (CH); 128.3 (CH); 120.8 (CH); 119.0 (C); 114.1 (CH); 101.6 (CH); 97.7 (CH); 55.9 (CH_3); 55.3 (CH_3); 51.5 (C); 29.0 (CH_3). Found, *m*/*z*: 337.1925. $C_{21}H_{25}N_2O_2$ $[M+H]^+$. Calculated, *m*/*z*: 337.1911.

***N*-(*tert*-Butyl)-6-methyl-2-phenylquinolin-4-amine (3e)**. Yield 39 mg (27%), off-white solid, mp 128–132°C. ^{1}H NMR spectrum, δ, ppm (*J*, Hz): 8.11–8.05 (3H, m, H-5, H-2,6 Ph); 7.75 (1H, d, *J* = 8.5, H-8); 7.53–7.42 (4H, m, H-7, H-3,4,5 Ph); 7.05 (1H, s, H-3); 6.34 (1H, br. s, NH); 2.47 (3H, s, 6-CH_3); 1.53 (9H, s, $C(CH_3)_3$). ^{13}C NMR spectrum, δ, ppm: 158.8 (C); 149.0 (C); 146.0 (C); 139.7 (C); 133.5 (C); 131.3 (CH); 129.0 (CH); 128.7 (CH); 128.5 (CH); 127.0 (CH); 120.8 (CH); 118.4 (C); 97.9 (CH); 51.4 (C); 28.9 (CH_3); 21.2 (CH_3). Found, *m*/*z*: 291.1867. $C_{20}H_{23}N_2$ $[M+H]^+$. Calculated, *m*/*z*: 291.1856.

***N*-(*tert*-Butyl)-6-chloro-2-phenylquinolin-4-amine (3f)**. Isolated as mixture with *N*,*N*'-di-*tert*-butylurea (**5**) in a 5:8 ratio (determined by ^{1}H NMR spectrum). Yield 15% (after correction for impurities), yellowish-brown solid. ^{1}H NMR spectrum, δ, ppm (*J*, Hz): 8.52 (1H, d, *J* = 1.9, H-5); 8.09 (2H, d, *J* = 7.3, H-2,6 Ph); 7.86 (1H, d, *J* = 8.9, H-8); 7.64

(1H, dd, *J* = 8.9, *J* = 1.9, H-7); 7.53 (2H, t, *J* = 7.1, H-3,5 Ph); 7.48 (1H, t, *J* = 7.1, H-4 Ph); 7.12 (1H, s, H-3); 6.61 (1H, br. s, NH); 1.55 (9H, s, $C(CH_3)_3$). ^{13}C NMR spectrum, δ, ppm: 156.2 (C); 148.9 (C); 146.5 (C); 139.4 (C); 130.9 (CH); 129.8 (CH); 129.3 (CH); 128.7 (CH); 128.6 (C); 127.1 (CH); 121.4 (CH); 119.5 (C); 98.5 (CH); 51.6 (C); 28.8 (CH_3). Found, *m*/*z*: 311.1320. $C_{19}H_{20}ClN_2$ $[M+H]^+$. Calculated, *m*/*z*: 311.1310.

***N*-Isopropyl-6-methoxy-2-phenylquinolin-4-amine (3g)**. Yield 19 mg (13%), brown oil. ^1H NMR spectrum, δ, ppm (*J*, Hz): 8.13 (2H, d, *J* = 7.5, H-2,6 Ph); 7.81 (1H, d, *J* = 9.1, H-8); 7.66 (1H, d, *J* = 2.4, H-5); 7.51 (2H, t, *J* = 7.5, H-3,5 Ph); 7.45 (1H, t, *J* = 7.2, H-4 Ph); 7.32 (1H, dd, *J* = 9.1, *J* = 2.4, H-7); 6.96 (1H, s, H-3); 6.88 (1H, br. s, NH); 4.12 (1H, octet, *J* = 6.6, $C\underline{H}Me_2$); 3.93 (3H, s, OCH_3); 1.34 (6H, d, *J* = 6.3, $CH(C\underline{H}_3)_2$). ^{13}C NMR spectrum, δ, ppm: 156.2 (C); 153.9 (C); 149.7 (C); 143.0 (C, only observed in ^1H–^{13}C HMBC); 139.4 (C); 129.8 (CH); 128.9 (CH); 128.5 (CH); 127.1 (CH); 121.1 (CH); 118.4 (C); 101.3 (CH); 95.7 (CH); 55.9 (CH_3); 43.5 (CH); 22.0 (CH_3). Found, *m*/*z*: 293.1661. $C_{19}H_{21}N_2O$ $[M+H]^+$. Calculated, *m*/*z*: 293.1648.

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