increase of reaction rate. Steric effects are also evident. When the trifluoromethyl substituent is located in the *ortho* position (**1e**) only low-molecular-weight oligomers are obtained in a very low yield. Thus, placing the CF_3 group in the phenyl *meta* or *para* positions (**1b–d**) does not drastically influence the steric properties of the ligands and constitutes the modification of choice for the formation of highly efficient systems for the CO/propene copolymerization reaction.

Whereas electronic effects on the stereoselectivity of several different catalytic asymmetric reactions have been observed before,[21, 22, 27–29] a comparable influence on the catalytic activity has been reported in particular for Rh-catalyzed hydroformylation.[30–33] Because of the C_1 symmetry of the ligands, we believe that the isomeric intermediates containing CO and/or the olefin coordinated to Pd display significantly different reactivities. When the complex $[(\mathbf{1d})PdMe]^+$ is placed under a CO atmosphere the product $[(\mathbf{1d})Pd(CO)COMe]^+$ is formed through a highly regioselective coordination of the acyl moiety *trans* to the PAr_2 group.[16] The electrophilicity of the metal center, and hence that of the coordinated substrates should be higher in the case of the ligands bearing more electron-withdrawing PAr_2 groups. This also should coincide with a lower binding energy of the substrate. In contrast to other catalytic systems,[34] in fact, the kinetic order of the copolymerization with respect to carbon monoxide is positive. The crucial assumption sustaining the electronic effect on activity is that the configurational isomers in which the monomers are coordinated *trans* to the PAr_2 groups should be more reactive by virtue of their increased electrophilicity in this position. Furthermore, it has to be noted that in catalytic polyketone synthesis the electrophilicity of the metal center needs to be carefully balanced in order for olefins to compete with CO as ligands. Thus, for ligands containing a basic PAr_2 group, such as **1f**, CO is likely to bind more strongly to the Pd^{II} center, leading to a drastic decrease of the overall rate.

In conclusion, Pd^{II} systems combined with sterically very similar chiral ferrocenyl ligands **1a–g** (except **1e**) produce almost completely isotactic copolymers from propene and CO in a highly enantioselective fashion. Only small variations in enantioface discrimination were observed, whereas drastic changes in catalytic activity were noted by changing the electronic properties of the PAr_2 substituent.

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Versatile Indole Synthesis by a 5-*endo-dig* Cyclization Mediated by Potassium or Cesium Bases[**]

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The addition of heteroatomic nucleophiles to triple bonds is an important reaction that often requires a high activation energy.[1] Intramolecular additions proceed more readily and a recent hydroamination of *o*-chlorostyrenes followed by

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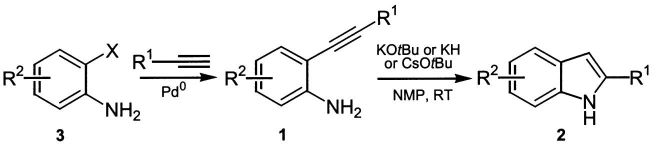
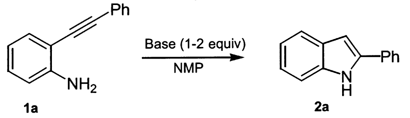
cyclization has provided an elegant access to indolines.[2] The palladium-catalyzed synthesis of indoles starting from 2-alkynylanilines of type **1**[3] or more frequently from their corresponding trifluoroacetamides has been well studied.[4] A molybdemum(0)-catalyzed cyclization of compounds **1** to indoles **2** has been reported.[5] Recently,[6] we have reported the high catalytic activity of $CsOH \cdot H_2O$[7] for promoting the addition of anilines or alcohols to alkynes or styrenes. Herein, we report a new mild synthesis of 2-substituted indoles of type **2** mediated by potassium or cesium bases in *N*-methylpyrrolidinone (NMP; Scheme 1).



Scheme 1. Base-mediated indole synthesis.

The scope of the reaction is broad and most of these ring closures are complete within a few hours at room temperature. Initial studies have shown that the strong base $CsOH \cdot H_2O$ is an effective base for the cyclization of 2-(2-phenylethynyl)aniline (**1a**); however, a reaction temperature of 90 °C was required for the completion of the reaction (Table 1). Similarly finely powdered KOH or NaOEt[8] led only to sluggish reactions below 80 °C. In strong contrast, soluble potassium or cesium alkoxides such as KO*t*Bu[9] or CsO*t*Bu[10] as well as KH[11] in NMP led to a fast reaction at room temperature (3–12 h). These mild reaction conditions allow the presence of various functionalities in the starting (2-alkynyl)anilines of type **1** and enables the preparation of a range of polyfunctional indoles (Table 2).

Table 1. Na, K, Cs base-mediated cyclizations.

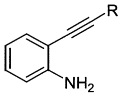
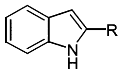
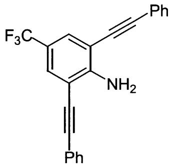
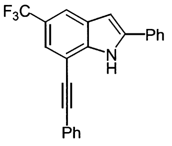
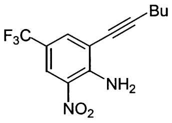
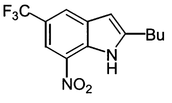
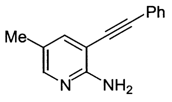
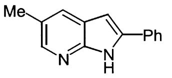
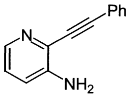
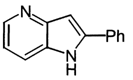
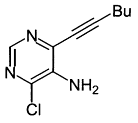
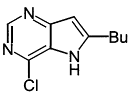
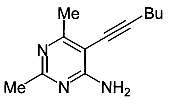
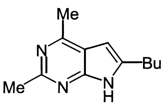
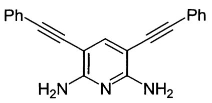
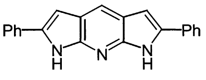
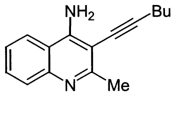
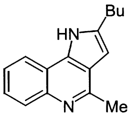


Base	*T* [°C]	*t* [h]	Yield [%][a]
NaH	60	8	< 5
NaOEt	80	15	66
KO*t*Bu	25	4	79
KH	25	5	72
CsOH	90	5	68
CsO*t*Bu	25	5	71

[a] Yield of isolated analytically pure **2a**.

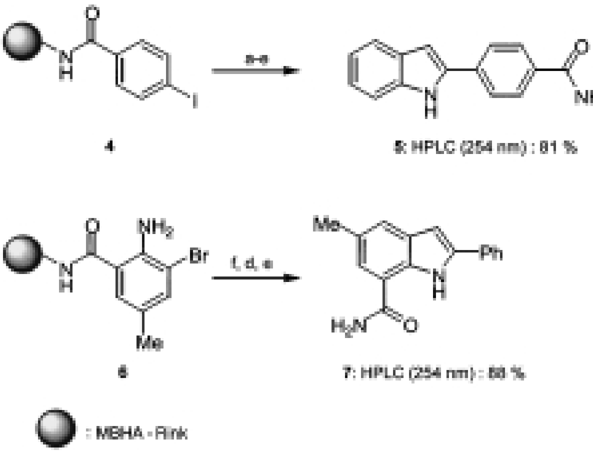
The precursors **1** were prepared by the Sonogashira cross-coupling[12] of the corresponding (2-iodo- or 2-bromoanilines **3** with 1-alkynes in satisfactory to excellent yields. Various 2-substituted indoles are conveniently prepared either by using KH (1.3–2.1 equiv; Method A) or KO*t*Bu (1.3–1.7 equiv; Method B). An excess of base is necessary in these cyclizations since the final product is an unreactive potassium salt of indoles **2**. It is not basic enough to deprotonate a further molecule of starting material **1**. Several functional groups such as a hydroxy (entry 5; Table 2), an acetal (entry 6;

Table 2. Functionalized indoles **2a–r** obtained by the cyclization of the aniline derivatives **1a–r** in the presence of KH (Method A) or KO*t*Bu (Method B) at room temperature.

Entry	Aniline **1**	Indole **2**	Method[a]	Yield [%][b]
				
1	**1a**: R = Ph	**2a**: R = Ph	A (B)	72 (79)
2	**1b**: R = Bu	**2b**: R = Bu	A (B)	76 (78)
3	**1c**: R = 1-cyclohexenyl	**2c**: R = 1-cyclohexenyl	A	67
4	**1d**: R = H	**2d**: R = H	B	62
5	**1e**: R = $(CH_2)_2OH$	**2e**: R = $(CH_2)_2OH$	A	61
6	**1f**: R = $CH(OEt)_2$	**2f**: R = $CH(OEt)_2$	B	81
7	**1g**: R = 2-thienyl	**2g**: R = 2-thienyl	A	70
8	**1h**: R = 2-thiazolyl	**2h**: R = 2-thiazolyl	A	61
9	**1i**: R = 3-chloropropyl	**2i**: R = cyclopropyl	A	75
10	**1j**: R = 2-aminophenyl	**2j**: R = 2-aminophenyl	A	82
11	 **1k**	 **2k**	A	80
12	 **1l**	 **2l**	B	77
13	 **1m**	 **2m**	A	72
14	 **1n**	 **2n**	A	74
15	 **1o**	 **2o**	B	78
16	 **1p**	 **2p**	B	61[c]
17	 **1q**	 **2q**	B	80[d]
18	 **1r**	 **2r**	B	90[d]

[a] Method A: KH (1.3–1.7 equiv), NMP, room temperature, 3–12 h. Method B: KO*t*Bu (1.3–2.1 equiv), NMP, room temperature, 3–12 h. [b] Yields of isolated analytically pure products. [c] *T* = 60 °C, *t* = 5 h. [d] *T* = 80 °C, *t* = 6 h.

Table 2), an additional amino group (entry 10; Table 2), an alkyne (entry 11; Table 2), or a nitro group (entry 12; Table 2) are tolerated. When the alkyne bears a 3-chloropropyl substituent (entry 9; Table 2), a cyclopropanation occurs after cyclization providing 2-cyclopropylindole (**2i**) in 75% yield. Remarkably, this cyclization reaction can be extended to various heterocyclic precusors such as the aminopyridines **1m** and **1n** (entries 15 and 16; Table 2). In all cases, a smooth cyclization occurs under similar reaction conditions (Method A or Method B) providing new types of heterocycles of interest for pharmaceutical applications. It was also possible to perform this ring closure on solid phase. Thus, 4-iodobenzamide attached to a Rink–MBHA resin **4** undergoes a smooth Sonogashira reaction[13] with (trimethylsilyl)acetylene. After desilylation a second cross-coupling with 2-iodoaniline provides the expected precursor for cyclization. Treatment with KO*t*Bu (15 equiv) in NMP (25 °C, 24 h) affords the indole **5** in 81% purity after cleavage from the resin. Similarly, the Rink–MBHA resin attached 2-bromoaniline derivative **6** was converted to the 2-phenyl-substituted indole **7** (88% purity after cleavage from the resin) using an analogeous reaction sequence (Scheme 2).



Scheme 2. Solid-phase synthesis of indoles.

In summary, the combination of KO*t*Bu, KH, or CsO*t*Bu with the polar solvent NMP allows a smooth preparation of various indoles and azaindoles by a 5-*endo-dig* cyclization.[14, 15]

Experimental Section

Typical procedure for the preparation of 2-phenylindole (**2a**): Method A: To a stirred solution of potassium hydride (42 mg, 1.05 mmol) in NMP (4 mL) was added under argon (2-phenylethynyl)aniline (**1a**) (97 mg, 0.50 mmol) in NMP (1 mL). The reaction mixture was vigorously stirred for 5 h at room temperature. Water (1 mL) and dichloromethane (50 mL) were added, and the resulting solution was washed with a saturated NaCl solution, dried ($MgSO_4$), and concentrated under reduced pressure. The residue was purified by flash chromatography (silica gel, dichloromethane/pentane 7/3) to give 2-phenylindole (**2a**) (73 mg, 0.36 mmol, 72% yield; m.p. 171–175 °C).

Method B: The reaction was carried out as above using potassium *tert*-butoxide (73 mg, 0.65 mmol) instead of potassium hydride. The reaction was stirred for 4 h at room temperature. After the same workup procedure as described for method A, the product **2a** (76 mg, 0.39 mmol) was obtained in 79% yield.

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[10] Cesium *tert*-butoxide is conveniently prepared by the addition of *t*BuOH to cesium in toluene at 0 °C (15 min).

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