DOI: 10.1002/ejoc.201000665

Copper-Catalyzed Double *N*-Vinylation of Aromatic Amines: An Efficient Synthesis of Various Substituted *N*-Arylpyrroles

Qian Liao,[a] Liyun Zhang,[a] Fei Wang,[a] Shutao Li,[a] and Chanjuan Xi*[a]

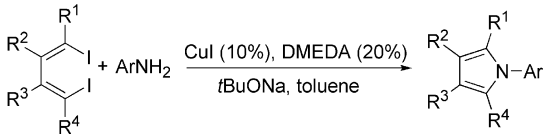
Keywords: Nitrogen heterocycles / Vinylation / Amines / Copper iodide

A simple and efficient approach to various substituted *N*-arylpyrroles has been developed. The method is based on the copper-catalyzed sequential inter- and intramolecular *N*-vinylation of aromatic amines. The reactions proceed to afford substituted *N*-arylpyrroles in good-to-excellent yields using CuI as the precatalyst, *t*BuONa as the base, and N^1,N^2-dimethylethane-1,2-diamine (DMEDA) as the ligand. Anilines with electron-donating and -withdrawing substituents as well as a heteroaromatic amine performed very well under the conditions used. Tri- and tetrasubstituted dienyl diiodides also performed well under the reaction conditions and afforded the corresponding substituted *N*-arylpyrroles in good yields. Products were also obtained in high yields with CuBr or CuCl as precatalyst.

Introduction

Pyrroles are one of the most important classes of heterocyclic compounds as they are the key structural subunits in numerous natural products that exhibit interesting biological activities[1] and contribute to a variety of applications in pharmaceutical use.[2] In addition, substituted pyrroles are of significant interest because they are useful and versatile synthetic intermediates for further structural elaboration.[3] Consequently, much attention has been paid to the preparation of pyrrole derivatives. Classic methods for their preparation include the Knorr,[4] Hantzsch,[5] and Paal–Knorr condensation reactions.[1e,6,7] However, these methods have some limitations with respect to regioselectivity and substitution patterns. Recently, great advances have been made, particularly in transition-metal-catalyzed multicomponent processes and domino reactions.[8,9] In the past few years, copper-catalyzed aryl C–N bond-forming reactions through the coupling of aryl halides and N-nucleophiles have attracted considerable attention[10] and complement Pd-catalyzed reactions very well.[11] More recently, coupling reactions between vinyl halides and amides have also been reported.[12]

Accordingly, the reactions of dienyl dihalides with amides have provided a straightforward method for the construction of *N*-acylpyrroles in a tandem process.[13,14] Nonetheless, access to substituted *N*-arylpyrroles, as an important class of pyrrole, has rarely been reported.[15] Herein we would like to report a copper-catalyzed double *N*-vinylation of aromatic amines for the synthesis of a wide range of structurally diverse pyrroles based on the reaction of (1*Z*,3*Z*)-1,4-diiodo-1,3-dienes with aromatic amines (Scheme 1), which includes *N*-vinylation of amines, which is rarely described in the literature to the best of our knowledge.



Scheme 1.

Results and Discussion

The requisite 1,4-diiodo-1,3-dienes were conveniently prepared in high yields by the iodination of zirconacyclopentadienes derived from intermolecular coupling of two alkynes according to reported methods.[16] We began our initial investigation with (3*Z*,5*Z*)-4,5-diethyl-3,6-diiodoocta-3,5-diene (**1a**) and *p*-methylaniline (**2a**), which was selected as a typical case to screen the experimental conditions. Stimulated by Buchwald and Li and their co-workers' observations,[13,14,17] CuI, DMEDA, Cs_2CO_3 or K_3PO_4, and toluene were selected as the catalytic system at 110 °C. Unfortunately, no desired product was detected by GC analysis (Table 1, entries 1 and 2). We thought that because aniline is a weaker acid than amides, a stronger base should be employed to deprotonate the amino group. When a stronger base, *t*BuOK, was used, the reaction gave a messy mixture (entry 3). When *t*BuONa was used, the desired product was obtained in 32% yield (by NMR; entry 4). Gratifyingly, when the reaction temperature was raised to 140 °C, the yield dra-

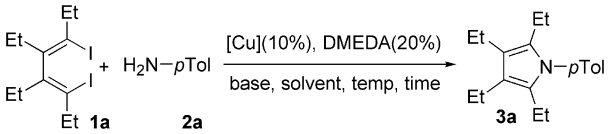
[a] Key Lab of Organic Optoelectronics & Molecular Engineering of Ministry of Education, Department of Chemistry, Tsinghua University,
Beijing, 100084, China
E-mail: cjxi@tsinghua.edu.cn

Supporting information for this article is available on the WWW under http://dx.doi.org/10.1002/ejoc.201000665.

View this journal online at wileyonlinelibrary.com

© 2010 Wiley-VCH Verlag GmbH & Co. KGaA, Weinheim

Table 1. Optimization of base, solvent, copper salt, and temperature in the reaction of **1a** and **2a**.



Entry	[Cu]	Base	Solvent	Temp. /°C	Time /h	Yield /%[a]
1	CuI	Cs_2CO_3	toluene	110	48	n.r.
2	CuI	K_3PO_4	toluene	110	48	n.r.
3	CuI	*t*BuOK	toluene	110	48	–
4	CuI	*t*BuONa	toluene	110	48	32
5	CuI	*t*BuONa	1,4-dioxane	140	48	trace
6	CuI	*t*BuONa	DMF	140	48	–
7	CuI	*t*BuONa	NMP	140	48	–
8	CuI	*t*BuONa	toluene	140	24	63
9	CuI	*t*BuONa	toluene	140	48	92 (88)
10	–	*t*BuONa	toluene	140	48	0
11	CuBr	*t*BuONa	toluene	140	48	73
12	CuCl	*t*BuONa	toluene	140	48	89

[a] ^{1}H NMR yield using Cl_2C=CHCl as the internal standard; isolated yield is given in parentheses.

matically increased to 92% (entry 9). We also tested other commonly used solvents in the copper-catalyzed C–N coupling reactions. The results proved that 1,4-dioxane, DMF, and NMP were not appropriate solvents for this reaction (entries 5–7). A controlled experiment showed that copper is indispensable to the reaction (entry 10). The effect of other copper salts was also examined in the test reaction: CuBr and CuCl as precatalyst gave the product in 73 and 89% yields, respectively (entries 11 and 12).

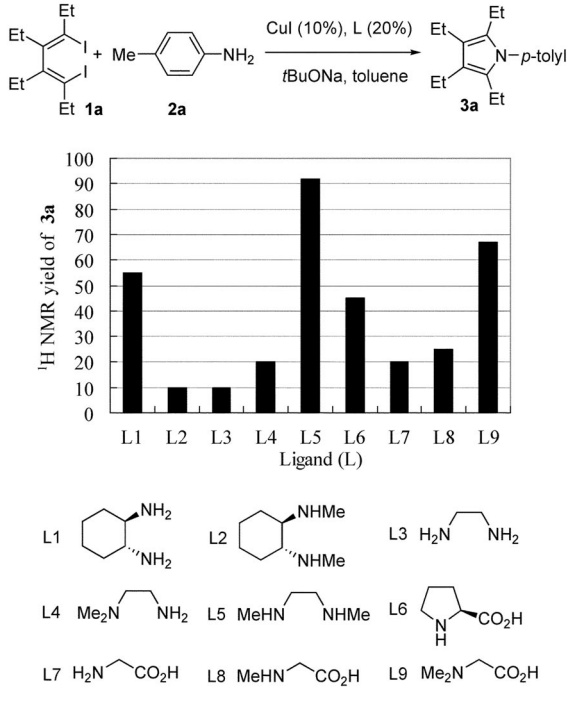
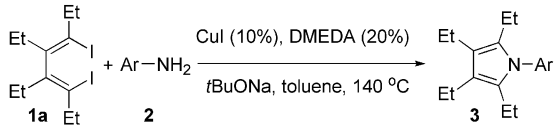


Figure 1. Comparison of ligands in the CuI-catalyzed double *N*-vinylation of aromatic amines.

It has been demonstrated that certain ligands play important roles in rate acceleration in copper-catalyzed C–N coupling reactions.[10d,18] Next, the applicability of other ligands was screened under the optimized conditions. The results are shown in Figure 1. DMEDA is the best ligand in this reaction.

To investigate the scope of the reaction, other aromatic amines were used in the reaction with (3*Z*,5*Z*)-4,5-diethyl-3,6-diiodoocta-3,5-diene (**1a**) under the optimized conditions. The reaction is applicable to various aromatic amines and the results are summarized in Table 2. The reactions

Table 2. Reaction of (3*Z*,5*Z*)-4,5-diethyl-3,6-diiodoocta-3,5-diene (**1a**) with aromatic amines.[a]



Entry	Ar-NH_2	Time /h	Product	Yield /%[b]
1	Me–NH_2 **2a**	48	**3a**	92 (88)
2	MeO–NH_2 **2b**	60	**3b**	78 (70)
3	NH_2 **2c**	48	**3c**	82 (65)
4	F–NH_2 **2d**	48	**3d**	88 (83)
5	Cl–NH_2 **2e**	50	**3e**	91 (87)
6	NH_2 (N) **2f**	48	**3f**	95 (91)
7	Me, NH_2 **2g**	72	**3g**	63 (58)
8	NH_2 **2h**	72	**3h**	59 (53)

[a] Reaction conditions: 1,4-diiodo-1,3-diene (1.0 equiv.), aromatic amine (1.5 equiv.), CuI (10 mol-%), DMEDA (20 mol-%), *t*BuONa (3 equiv.), toluene (2 mL), 140 °C. [b] ^{1}H NMR yields using Cl_2C=CHCl as the internal standard; the isolated yields are given in parentheses.

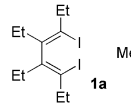
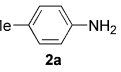
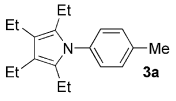
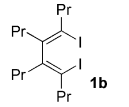
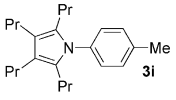
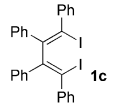
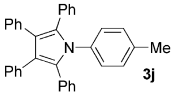
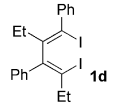
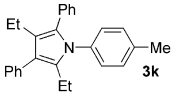
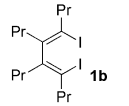
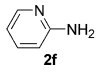
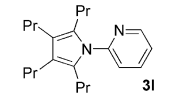
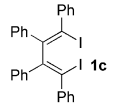
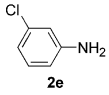
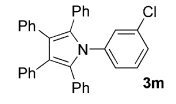
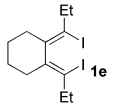
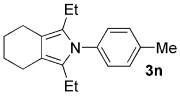
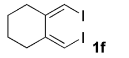
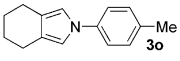
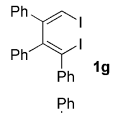
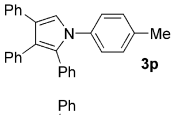
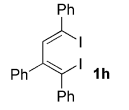
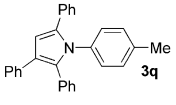
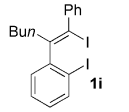
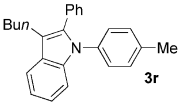
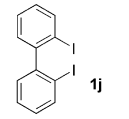
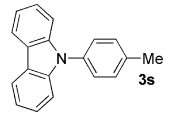
 © 2010 Wiley-VCH Verlag GmbH & Co. KGaA, Weinheim

of anilines with both electron-donating and -withdrawing substituents proceeded very well. For example, the reaction of **1a** with 4-methoxyaniline (**2b**) gives **3b** in 78% yield by NMR (70% isolated yield; entry 2). Similarly, the reaction of **1a** with 4-fluoroaniline (**2d**) gives the desired product in high yield (entry 4). A Cl-substituted aniline is also a good reagent for this reaction (entry 5). The heteroaromatic amine 2-aminopyridine (**2f**) also performs well under the conditions, giving a high yield of more than 95% (entry 6). When 2,5-dimethylaniline (**2g**) and 1-naphthylamine (**2h**), both of which have a large substituent at the *ortho*position, are used, the desired products are formed in moderate yields after 72 h (entries 7 and 8). This may be attributed to the steric hindrance effect of the bulky ethyl groups on the pyrrole ring and the *ortho* substituent on the phenyl ring. When alkyl-substituted amines, such as butyl- and hexylamine were treated with **1a** under similar reaction conditions, the desired products were not observed.

Having established an effective catalytic system for the coupling reactions, we next synthesized a variety of diiododienes[16] to explore the scope of double alkenylation under the optimized conditions. The results are summarized in Table 3.

As well as alkyl-substituted dienyl diiodides, aryl-substituted dienyl diiodides were also found to be suitable substrates. The corresponding products were formed in high yields (entries 3, 4, and 6). When a diiododiene fused with a six-membered ring (**1e**) was used, the reaction proceeded smoothly to afford bicyclic pyrrole **3n** in 86% yield (entry 7). Diiodide **1f** reacted with **2a** to give the pyrrole **3o** in only 35% isolated yield after 48 h (entry 8). Furthermore, this method is also effective for trisubstituted dienyl diiodide compounds. The reaction of (1*Z*,3*Z*)-1,4-diiodo-1,2,3-triphenylbuta-1,3-diene (**1g**) with **2a** led to the formation of **3p** in 79% isolated yield (entry 9). The substrate **1h** also reacted with **2a** to give the trisubstituted arylpyrrole **3q** in moderate yield (entry 10). When 1,4-diiodo-1,4-diphenylbuta-1,3-diene was treated with *p*-methylaniline under the same reaction conditions, the desired product was not observed: A small amount of diyne was observed by GC–MS, which underwent an E2-type elimination. The reactions of (*Z*)-1-iodo-2-(1-iodo-1-phenylhex-1-en-2-yl)benzene (**1i**) and 2,2′-diiodobiphenyl (**1j**) were also examined. Both of them proceeded smoothly under the conditions to afford indole and carbazole in good yields, respectively (entries 11 and 12). Although the coupling reactions of these two substrates with aniline are not tandem vinylations in the strictest sense of the term, they still demonstrate the generality of our catalytic system.

Table 3. Reaction of dienyl diiodide derivatives with aromatic amines.[a]

Entry	Dienyl diiodide	Ar-NH_2	Time /h	Product	Yield /%[b]
1	 **1a**	 **2a**	48	 **3a**	92 (88)
2	 **1b**	**2a**	60	 **3i**	83 (71)
3	 **1c**	**2a**	48	 **3j**	85 (76)
4	 **1d**	**2a**	48	 **3k**	– (60)
5	 **1b**	 **2f**	72	 **3l**	72 (63)
6	 **1c**	 **2e**	48	 **3m**	– (76)
7	 **1e**	**2a**	48	 **3n**	86 (80)
8	 **1f**	**2a**	48	 **3o**	41 (35)
9	 **1g**	**2a**	48	 **3p**	– (79)
10	 **1h**	**2a**	48	 **3q**	– (43)
11	 **1i**	**2a**	48	 **3r**	95 (94)
12	 **1j**	**2a**	48	 **3s**	88 (72)

[a] Reaction conditions: 1,4-diiodo-1,3-diene (1.0 equiv.), aromatic amine (1.5 equiv.), CuI (10 mol-%), DMEDA (20 mol-%), *t*BuONa (3 equiv.), toluene (2 mL) at 140 °C. [b] ^{1}H NMR yields, using Cl_2C=CHCl as internal standard, the isolated yields are given in parentheses.

Conclusions

We have described an efficient copper-catalyzed tandem vinylation of anilines with dienyl diiodides. The methodology provides a facile route to di-, tri-, and tetrasubstituted *N*-arylpyrroles in good-to-excellent yields. It is vital to use a copper salt as the precatalyst with the assistance of an appropriate base and diamine ligand to achieve reasonable yields. The optimized reaction conditions are CuI as the precatalyst, *t*BuONa as the base, and N^1,N^2-dimethylethane-1,2-diamine (DMEDA) as the ligand. Further application of the system to the synthesis of various heterocycles is under progress.

 © 2010 Wiley-VCH Verlag GmbH & Co. KGaA, Weinheim

Experimental Section

General: All *N*-vinylation reactions were carried out in pre-dried screw-capped test-tubes fitted with a Teflon®-lined septum. Toluene and 1,4-dioxane were distilled and stored over sodium. DMF and NMP were freshly distilled. 1,4-Diiodo-1,3-dienes,[16a] 2,2′-diiodobiphenyl,[19] and (*Z*)-1-iodo-2-(1-iodo-1-phenylhex-1-en-2-yl) benzene[20] were prepared according to literature procedures. Other materials were commercially available and were used without further purification. Thin-layer chromatography (TLC) was carried out on silica gel purchased from commercial sources and components were located by observation under UV light. ^{1}H and ^{13}C NMR spectra were recorded with a JEOL AL-300 NMR spectrometer at ambient temperature with $CDCl_3$ as the solvent and TMS as the internal standard. GC–MS spectra were recorded with a Hewlett–Packard GC–MS system.

General Procedure for the Synthesis of 1-Aryl-1*H*-pyrroles: CuI (19 mg, 0.1 mmol), 1,4-diiodo-1,3-diene (1.0 mmol), aniline (1.5 mmol), and *t*BuONa (288 mg, 3.0 mmol) were added to a screw-capped test-tube fitted with a Teflon®-lined septum. The tube was then evacuated and backfilled with N_2 (3 cycles). Aniline (1.5 mmol), DMEDA (21.5 μL, 0.2 mmol), and toluene (2.0 mL) were added by syringe at room temperature. The tube was then sealed and the reaction mixture was stirred at 140 °C for the indicated time. The reaction was cooled to room temperature. Ethyl acetate (3 mL) was added and stirred for 15 min. The deposit was separated and washed with ethyl acetate (3 mL × 3). The organic phase was combined. The solvent was removed under vacuum and the residue was analyzed by ^{1}H NMR spectroscopy. The crude product was purified by column chromatography to give the corresponding products.

2,3,4,5-Tetraethyl-1-(*p*-tolyl)-1*H*-pyrrole (3a): The crude product was purified by column chromatography on basic alumina with petroleum ether to give the desired product as colorless crystals (237 mg, 88%). R_f = 0.6 (petroleum ether). ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.21 (d, $^3J_{HH}$ = 7.9 Hz, 2 H), 7.13 (d, $^3J_{HH}$ = 7.9 Hz, 2 H), 2.47 (q, $^3J_{HH}$ = 7.6 Hz, 4 H), 2.40 (s, 3 H), 2.36 (q, $^3J_{HH}$ = 7.6 Hz, 4 H), 1.17 (t, $^3J_{HH}$ = 7.6 Hz, 6 H), 0.85 (t, $^3J_{HH}$ = 7.6 Hz, 6 H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 137.3, 137.0, 130.2, 129.5, 129.0, 119.2, 21.3, 18.1, 18.0, 17.1, 15.8 ppm. GC–MS (EI): *m*/*z* (%) = 269 (41) $[M]^+$, 254 (100), 224 (20). HRMS: calcd. for $C_{19}H_{27}N$ 269.2143; found 269.2153.

2,3,4,5-Tetraethyl-1-(*p*-methoxyphenyl)-1*H*-pyrrole (3b): The crude product was purified by column chromatography on basic alumina with petroleum ether/EtOAc (10:1) to give the desired product as a pale-yellow oil (201 mg, 70%). R_f = 0.3 (petroleum ether/EtOAc = 50:1). ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.19–7.16 (m, 2 H), 6.96–6.92 (m, 2 H), 3.85 (s, 3 H), 2.46 (q, $^3J_{HH}$ = 7.6 Hz, 4 H), 2.35 (q, $^3J_{HH}$ = 7.6 Hz, 4 H), 1.16 (t, $^3J_{HH}$ = 7.4 Hz, 6 H), 0.86 (t, $^3J_{HH}$ = 7.5 Hz, 6 H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 158.8, 132.4, 130.4, 130.2, 119.1, 113.9, 55.5, 18.1, 18.0, 17.1, 15.8 ppm. GC–MS (EI): *m*/*z* (%) = 285 (29) $[M]^+$, 270 (100). HRMS: calcd. for $C_{19}H_{27}NO$ 285.2093; found 285.2090.

2,3,4,5-Tetraethyl-1-phenyl-1*H*-pyrrole (3c): The crude product was purified by column chromatography on silica gel with petroleum ether to give the desired product as a colorless oil (165 mg, 65%). R_f = 0.4 (petroleum ether). ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.43–7.35 (m, 3 H), 7.26–7.24 (m, 2 H), 2.47 (q, $^3J_{HH}$ = 7.6 Hz, 4 H), 2.38 (q, $^3J_{HH}$ = 7.6 Hz, 4 H), 1.17 (t, $^3J_{HH}$ = 7.6 Hz, 6 H), 0.84 (t, $^3J_{HH}$ = 7.5 Hz, 6 H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 139.7, 130.1, 129.2, 128.8, 127.5, 119.4, 18.05, 17.96, 17.1, 15.7 ppm. GC–MS (EI): *m*/*z* (%) = 255 (31) $[M]^+$, 240 (100), 210 (13). HRMS: calcd. for $C_{18}H_{25}N$ 255.1987; found 255.1982.

2,3,4,5-Tetraethyl-1-(*p*-fluorophenyl)-1*H*-pyrrole (3d): The crude product was purified by column chromatography on basic alumina with petroleum ether to give the desired product as a pale-yellow oil (227 mg, 83%). R_f = 0.5 (petroleum ether). ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.25–7.21 (m, 2 H), 7.13–7.08 (m, 2 H), 2.46 (q, $^3J_{HH}$ = 7.6 Hz, 4 H), 2.36 (q, $^3J_{HH}$ = 7.4 Hz, 4 H), 1.17 (t, $^3J_{HH}$ = 7.6 Hz, 6 H), 0.84 (t, $^3J_{HH}$ = 7.6 Hz, 6 H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 161.9 (d, $^1J_{FC}$ = 247.1 Hz), 135.7 (d, $^4J_{FC}$ = 2.9 Hz), 130.8 (d, $^3J_{FC}$ = 8.7 Hz), 130.3, 119.6, 115.7 (d, $^2J_{FC}$ = 23.1 Hz), 18.0, 17.9, 17.1, 15.7 ppm. GC–MS (EI): *m*/*z* (%) = 273 (29) $[M]^+$, 258 (100), 228 (13). HRMS: calcd. for $C_{18}H_{24}FN$ 273.1893; found 273.1900.

1-(*m*-Chlorophenyl)-2,3,4,5-tetraethyl-1*H*-pyrrole (3e): The crude product was purified by column chromatography on basic alumina with petroleum ether to give the desired product as a pale-yellow oil (251 mg, 87%). R_f = 0.5 (petroleum ether). ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.36–7.34 (m, 2 H), 7.28 (s, 1 H), 7.20–7.16 (m, 1 H), 2.45 (q, $^3J_{HH}$ = 7.6 Hz, 4 H), 2.38 (q, $^3J_{HH}$ = 7.4 Hz, 4 H), 1.16 (t, $^3J_{HH}$ = 7.6 Hz, 6 H), 0.85 (t, $^3J_{HH}$ = 7.4 Hz, 6 H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 141.0, 134.4, 130.1, 129.8, 129.4, 127.8, 127.4, 120.0, 18.0, 17.9, 17.0, 15.7 ppm. GC–MS (EI): *m*/*z* (%) = 289 (29) $[M]^+$, 274 (100), 207 (11). HRMS: calcd. for $C_{18}H_{24}ClN$ 289.1597; found 289.1587.

2,3,4,5-Tetraethyl-1-(2-pyridyl)-1*H*-pyrrole (3f): The crude product was purified by column chromatography on silica gel with petroleum ether/EtOAc (15:1) to give the desired product as a pale-yellow oil (234 mg, 91%). R_f = 0.8 (petroleum ether/EtOAc = 5:1). ^{1}H NMR (300 MHz, $CDCl_3$): δ = 8.60–8.57 (m, 1 H), 7.80 (td, $^3J_{HH}$ = 7.9, $^4J_{HH}$ = 2.1 Hz, 1 H), 7.30–7.25 (m, 2 H), 2.48 (q, $^3J_{HH}$ = 7.4 Hz, 4 H), 2.45 (q, $^3J_{HH}$ = 7.6 Hz, 4 H), 1.14 (t, $^3J_{HH}$ = 7.6 Hz, 6 H), 0.81 (t, $^3J_{HH}$ = 7.5 Hz, 6 H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 152.8, 149.2, 137.7, 129.6, 122.4, 122.1, 120.4, 17.8, 17.7, 16.8, 15.2 ppm. GC–MS (EI): *m*/*z* (%) = 256 (41) $[M]^+$, 241 (100), 227 (20). HRMS: calcd. for $C_{17}H_{24}N_2$ 256.1939; found 256.1933.

1-(2,5-Dimethylphenyl)-2,3,4,5-tetraethyl-1*H*-pyrrole (3g): The crude product was purified by column chromatography on basic alumina with petroleum ether to give the desired product as a colorless oil (163 mg, 58%). R_f = 0.5 (petroleum ether). ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.14 (d, $^3J_{HH}$ = 7.6 Hz, 1 H), 7.01 (d, $^3J_{HH}$ = 7.9 Hz, 1 H), 7.06 (s, 1 H), 2.45 (q, $^3J_{HH}$ = 7.4 Hz, 4 H), 2.40–2.30 (m, 2 H), 2.33 (s, 3 H), 2.18–2.06 (m, 2 H), 1.82 (s, 3 H), 1.15 (t, $^3J_{HH}$ = 7.5 Hz, 6 H), 0.84 (t, $^3J_{HH}$ = 7.5 Hz, 6 H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 138.7, 135.8, 134.4, 130.4, 130.2, 129.2, 128.8, 119.3, 21.0, 18.1, 18.0, 17.3, 16.9, 15.7 ppm. GC–MS (EI): *m*/*z* (%) = 283 (34) $[M]^+$, 268 (100), 254 (13). HRMS: calcd. for $C_{20}H_{29}N$ 283.2300; found 283.2301.

2,3,4,5-Tetraethyl-1-(1-naphthyl)-1*H*-pyrrole (3h): The crude product was purified by column chromatography on silica gel with petroleum ether to give the desired product as colorless crystals (162 mg, 53%). R_f = 0.5 (petroleum ether). ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.87 (d, $^3J_{HH}$ = 7.6 Hz, 2 H), 7.54–7.36 (m, 4 H), 7.05 (d, $^3J_{HH}$ = 8.6 Hz, 1 H), 2.53 (q, $^3J_{HH}$ = 7.6 Hz, 4 H), 2.39–2.27 (m, 2 H), 2.15–2.02 (m, 2 H), 1.22 (t, $^3J_{HH}$ = 7.4 Hz, 6 H), 0.72 (t, $^3J_{HH}$ = 7.4 Hz, 6 H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 136.6, 134.1, 133.0, 131.1, 128.3, 127.9, 127.1, 127.0, 126.5, 125.3, 124.1, 119.5, 18.3, 18.1, 17.3, 16.1 ppm. GC–MS (EI): *m*/*z* (%) = 305 (48) $[M]^+$, 290 (100), 246 (23). HRMS: calcd. for $C_{22}H_{27}N$ 305.2143; found 305.2142.

2,3,4,5-Tetrapropyl-1-(*p*-tolyl)-1*H*-pyrrole (3i): The crude product was purified by column chromatography on basic alumina with petroleum ether to give the desired product as a pale-yellow oil

 © 2010 Wiley-VCH Verlag GmbH & Co. KGaA, Weinheim

(230 mg, 71%). R_f = 0.6 (petroleum ether). ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.18 (d, $^3J_{HH}$ = 8.2 Hz, 2 H), 7.08 (d, $^3J_{HH}$ = 8.3 Hz, 2 H), 2.39–2.34 (m, 7 H), 2.29 (t, $^3J_{HH}$ = 7.9 Hz, 4 H), 1.52 (sext, $^3J_{HH}$ = 7.9 Hz, 4 H), 1.20 (sext, $^3J_{HH}$ = 7.9 Hz, 4 H), 0.98 (t, $^3J_{HH}$ = 7.4 Hz, 6 H), 0.70 (t, $^3J_{HH}$ = 7.4 Hz, 6 H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 137.2, 137.0, 129.4, 129.0, 128.9, 118.4, 27.6, 27.3, 25.6, 24.1, 21.3, 14.9, 14.3 ppm. GC–MS (EI): *m*/*z* (%) = 325 (23) $[M]^+$, 296 (100), 238 (10). HRMS: calcd. for $C_{23}H_{35}N$ 325.2770; found 325.2781.

2,3,4,5-Tetraphenyl-1-(*p*-tolyl)-1*H*-pyrrole (3j): CH_2Cl_2 was used to dilute the reaction mixture and wash the deposit. The crude product was purified by column chromatography on silica gel with petroleum ether/CH_2Cl_2 (10:1) to give the desired product as colorless crystals (352 mg, 76%). R_f = 0.7 (petroleum ether/CH_2Cl_2 = 5:1). ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.10–7.01 (m, 12 H), 6.95–6.89 (m, 10 H), 6.80 (d, $^3J_{HH}$ = 8.2 Hz, 2 H), 2.25 (s, 3 H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 136.6, 136.1, 135.5, 132.5, 131.8, 131.5, 131.2, 129.03, 128.96, 127.7, 127.6, 126.5, 125.4, 122.8, 21.2 ppm. GC–MS (EI): *m*/*z* (%) = 461 (100) $[M]^+$, 281 (22), 165 (25). HRMS: calcd. for $C_{35}H_{27}N$ 461.2143; found 461.2156.

3,5-Diethyl-2,4-diphenyl-1-(*p*-tolyl)-1*H*-pyrrole (3k): The crude product was purified by column chromatography on silica gel with petroleum ether/EtOAc (25:1) to give the desired product as a yellow oil (223 mg, 60%). R_f = 0.4 (petroleum ether/EtOAc = 50:1). ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.41–7.05 (m, 14 H), 2.55–2.48 (m, 4 H), 2.31 (s, 3 H), 0.85 (t, $^3J_{HH}$ = 7.5 Hz, 3 H), 0.77 (t, $^3J_{HH}$ = 7.4 Hz, 3 H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 137.4, 136.9, 136.8, 133.5, 133.1, 130.7, 130.5, 130.1, 129.3, 128.7, 128.1, 127.7, 126.1, 125.9, 122.5, 122.2, 21.2, 18.4, 18.2, 16.2, 15.2 ppm. GC–MS (EI): *m*/*z* (%) = 365 (73) $[M]^+$, 350 (100), 320 (13). HRMS: calcd. for $C_{27}H_{27}N$ 365.2143; found 365.2131.

2,3,4,5-Tetrapropyl-1-(2-pyridyl)-1*H*-pyrrole (3l): The crude product was purified by column chromatography on silica gel with petroleum ether/EtOAc (50:1) to give the desired product as a pale-yellow oil (198 mg, 63%). R_f = 0.7 (petroleum ether/EtOAc = 20:1). ^{1}H NMR (300 MHz, $CDCl_3$): δ = 8.59–8.57 (m, 1 H), 7.78 (td, $^3J_{HH}$ = 7.7, $^4J_{HH}$ = 2.0 Hz, 1 H), 7.29–7.23 (m, 2 H), 2.50–2.33 (m, 8 H), 1.50 (sext, $^3J_{HH}$ = 7.6 Hz, 4 H), 1.12 (sext, $^3J_{HH}$ = 7.6 Hz, 4 H), 0.97 (t, $^3J_{HH}$ = 7.2 Hz, 6 H), 0.69 (t, $^3J_{HH}$ = 7.4 Hz, 6 H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 153.0, 149.1, 137.6, 128.5, 122.4, 122.0, 119.5, 27.2, 26.9, 25.2, 23.7, 14.7, 14.1 ppm. GC–MS (EI): *m*/*z* (%) = 312 (31) $[M]^+$, 283 (100), 225 (20). HRMS: calcd. for $C_{21}H_{32}N_2$ 312.2565; found 321.2555.

1-(*m*-Chlorophenyl)-2,3,4,5-tetraphenyl-1*H*-pyrrole (3m): CH_2Cl_2 was used to dilute the reaction mixture and wash the deposit. The crude product was purified by column chromatography on silica gel with petroleum ether/CH_2Cl_2 (5:1) to give the desired product as colorless crystals (365 mg, 76%). R_f = 0.4 (petroleum ether/CH_2Cl_2 = 5:1). ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.11–6.78 (m, 24 H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 139.7, 134.9, 133.7, 131.7, 131.5, 131.3, 131.0, 129.3, 129.1, 127.7, 127.6, 127.3, 127.0, 126.7, 125.5, 123.1 ppm. HRMS: calcd. for $C_{34}H_{24}ClN$ 481.1597; found 481.1602.

1,3-Diethyl-4,5,6,7-tetrahydro-2-(*p*-tolyl)-2*H*-isoindole (3n): The crude product was purified by column chromatography on basic alumina with petroleum ether to give the desired product as a pale-yellow oil (214 mg, 80%). R_f = 0.5 (petroleum ether). ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.22 (d, $^3J_{HH}$ = 8.1 Hz, 2 H), 7.13 (d, $^3J_{HH}$ = 8.4 Hz, 2 H), 2.55 (m, 4 H), 2.41 (s, 3 H), 2.34 (q, $^3J_{HH}$ = 7.5 Hz, 4 H), 1.78 (m, 4 H), 0.88 (t, $^3J_{HH}$ = 7.5 Hz, 6 H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 137.2, 136.5, 129.4, 128.6, 128.5, 114.6, 24.1, 21.7, 21.2, 18.1, 14.6 ppm. GC–MS (EI): *m*/*z* (%) = 267 (33) $[M]^+$, 252 (100). HRMS: calcd. for $C_{19}H_{25}N$ 267.1987; found 267.1996.

4,5,6,7-Tetrahydro-2-(*p*-tolyl)-2*H*-isoindole (3o):[21] The crude product was purified by column chromatography on basic alumina with petroleum ether to give the desired product as a colorless crystal. (74 mg, 35%) R_f = 0.5 (petroleum ether). ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.22 (d, $^3J_{HH}$ = 8.2 Hz, 2 H), 7.17 (d, $^3J_{HH}$ = 8.2 Hz, 2 H), 6.76 (s, 2 H), 2.64 (br., 4 H), 2.34 (s, 3 H), 1.76 (br., 4 H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 138.8, 134.6, 130.1, 121.9, 120.0, 114.8, 24.2, 22.2, 20.9 ppm. GC–MS (EI): *m*/*z* (%) = 211 (66) $[M]^+$, 183 (100), 168 (13). HRMS: calcd. for $C_{15}H_{17}N$ 211.1361; found 211.1352.

2,3,4-Triphenyl-1-(*p*-tolyl)-1*H*-pyrrole (3p): CH_2Cl_2 was used to dilute the reaction mixture and wash the deposit. The crude product was purified by column chromatography on silica gel with petroleum ether/CH_2Cl_2 (7:1) to give the desired product as yellow crystals (305 mg, 79%). R_f = 0.5 (petroleum ether/CH_2Cl_2 = 5:1). ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.20–6.94 (m, 20 H), 2.30 (s, 3 H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 137.7, 136.5, 135.6, 135.5, 132.1, 131.6, 131.2, 129.6, 128.5, 128.2, 127.9, 127.8, 126.7, 125.9, 125.8, 124.7, 122.9, 121.5, 21.1 ppm. GC–MS (EI): *m*/*z* (%) = 385 (100) $[M]^+$, 267 (18), 252 (7). HRMS: calcd. for $C_{29}H_{23}N$ 385.1830; found 385.1817.

2,3,5-Triphenyl-1-(*p*-tolyl)-1*H*-pyrrole (3q):[22] CH_2Cl_2 was used to dilute the reaction mixture and wash the deposit. The crude product was purified by column chromatography on basic alumina with petroleum ether/CH_2Cl_2 (10:1) to give the desired product as a white solid (165 mg, 43%). R_f = 0.45 (petroleum ether/CH_2Cl_2 = 5:1). ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.26–7.03 (m, 15 H), 6.95 (d, $^3J_{HH}$ = 7.9 Hz, 2 H), 6.85 (d, $^3J_{HH}$ = 7.9 Hz, 2 H), 6.69 (s, 1 H), 2.26 (s, 3 H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 137.0, 136.35, 136.30, 134.9, 133.1, 132.9, 132.4, 131.6, 129.2, 128.9, 128.7, 128.3, 128.2, 128.1, 128.0, 127.0, 126.4, 125.5, 123.5, 110.0, 21.2 ppm. GC–MS (EI): *m*/*z* (%) = 385 (100) $[M]^+$, 267 (8), 165 (15). HRMS: calcd. for $C_{29}H_{23}N$ 385.1830; found 385.1824.

3-Butyl-2-phenyl-1-(*p*-tolyl)-1*H*-indole (3r): The crude product was purified by column chromatography on silica gel with petroleum ether/EtOAc (100:1) to give the desired product as a colorless oil (320 mg, 94%). R_f = 0.5 (petroleum ether/EtOAc = 50:1). ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.69 (dd, $^3J_{HH}$ = 5.9, $^4J_{HH}$ = 3.1 Hz, 1 H), 7.30–7.15 (m, 8 H), 7.10 (d, $^3J_{HH}$ = 8.3 Hz, 2 H), 7.03 (d, $^3J_{HH}$ = 8.3 Hz, 2 H), 2.81 (t, $^3J_{HH}$ = 7.9 Hz, 2 H), 2.32 (s, 3 H), 1.70 (qui, $^3J_{HH}$ = 7.7 Hz, 2 H), 1.36 (sext, $^3J_{HH}$ = 7.4 Hz, 2 H), 0.88 (t, $^3J_{HH}$ = 7.4 Hz, 3 H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 137.9, 137.2, 136.4, 136.1, 132.5, 130.7, 129.7, 128.4, 128.0, 127.8, 127.3, 122.3, 119.9, 119.3, 115.8, 110.7, 33.5, 24.6, 23.0, 21.2, 14.1 ppm. GC–MS (EI): *m*/*z* (%) = 339 (33) $[M]^+$, 296 (100), 207 (18). HRMS: calcd. for $C_{25}H_{25}N$ 339.1987; found 339.1997.

1-(*p*-Tolyl)carbazole (3s):[23] The crude product was purified by column chromatography on silica gel with petroleum ether/CH_2Cl_2 (30:1) to give the desired product as colorless crystals (186 mg, 72%). R_f = 0.45 (petroleum ether). ^{1}H NMR (300 MHz, $CDCl_3$): δ = 8.09 (d, $^3J_{HH}$ = 7.9 Hz, 2 H), 7.37–7.33 (m, 6 H), 7.29–7.19 (m, 4 H), 2.37 (s, 3 H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 141.1, 137.4, 135.1, 130.5, 127.0, 126.0, 123.3, 120.4, 119.8, 109.9, 21.3 ppm. Our NMR spectroscopic data were consistent with the corresponding literature.

Supporting Information (see also the footnote on the first page of this article): NMR spectra for **3a**–**3r**.

 © 2010 Wiley-VCH Verlag GmbH & Co. KGaA, Weinheim

Acknowledgments

This work was supported by the National Natural Science Foundation of China (20872076 and 20972085).

[1] a) R. J. Sundberg in *Compr. Heterocycl. Chem. II* (Eds.: A. R. Katritzky, C. W. Rees, E. F. V. Scriven), Pergamon Press, Oxford, **1996**, vol. 2, p. 119; for selected examples, see: b) A. Aiello, M. D′Esposito, E. Fattorusso, M. Menna, W. E. G. Müeller, S. Perović-Ottstadt, H. C. Schröder, *Bioorg. Med. Chem.* **2006**, *14*, 17–24; c) P. Lewer, E. L. Chapin, P. R. Graupner, J. R. Gilbert, C. Peacock, *J. Nat. Prod.* **2003**, *66*, 143–145; d) A. Fürstner, *Angew. Chem. Int. Ed.* **2003**, *42*, 3582–3603; e) G. Balme, *Angew. Chem. Int. Ed.* **2004**, *43*, 6238–6241; f) D. E. N. Jacquot, M. Zöllinger, T. Lindel, *Angew. Chem. Int. Ed.* **2005**, *44*, 2295–2298; g) H. Garrido-Hernandez, M. Nakadai, M. Vimolratana, Q. Li, T. Doundoulakis, P. G. Harran, *Angew. Chem. Int. Ed.* **2005**, *44*, 765–769; h) J. M. Gottesfeld, L. Neely, J. W. Trauger, E. E. Baird, P. B. Dervan, *Nature* **1997**, *387*, 202–205.

[2] For selected examples, see: a) B. R. Clark, R. J. Capon, E. Lacey, S. Tennant, J. H. Gill, *Org. Lett.* **2006**, *8*, 701–704; b) H. B. Bode, H. Irschik, S. C. Wenzel, H. Reichenbach, R. Müller, G. Höfle, *J. Nat. Prod.* **2003**, *66*, 1203–1206; c) J. W. Huffman, *Curr. Med. Chem.* **1999**, *6*, 705–720.

[3] For example, see: D. L. Boger, C. W. Boyce, M. A. Labroli, C. A. Sehon, Q. Jin, *J. Am. Chem. Soc.* **1999**, *121*, 54–62.

[4] a) L. Knorr, *Ber. Dtsch. Chem. Ges.* **1884**, *17*, 1635–1642; for recent examples, see: b) C. M. Shiner, T. D. Lash, *Tetrahedron* **2005**, *61*, 11628–11640; c) R. K. Bellingham, J. S. Carey, N. Hussain, D. O. Morgan, P. Oxley, L. C. Powling, *Org. Process Res. Dev.* **2004**, *8*, 279–282; d) J. M. Manley, M. J. Kalman, B. G. Conway, C. C. Ball, J. L. Havens, R. Vaidyanathan, *J. Org. Chem.* **2003**, *68*, 6447–6450.

[5] a) A. Hantzsch, *Ber. Dtsch. Chem. Ges.* **1890**, *23*, 1474–1476; for recent examples, see: b) V. S. Matiychuk, R. L. Martyak, N. D. Obushak, Y. V. Ostapiuk, N. I. Pidlypnyi, *Chem. Heterocycl. Compd.* **2004**, *40*, 1218–1219; c) L. Calvo, A. Gonzalez-Ortega, M. C. Saòudo, *Synthesis* **2002**, 2450–2456; d) A. W. Trautwein, R. D. Süßmuth, G. Jung, *Bioorg. Med. Chem. Lett.* **1998**, *8*, 2381–2384.

[6] a) C. Paal, *Ber. Dtsch. Chem. Ges.* **1885**, *18*, 367–371; b) L. Knorr, *Ber. Dtsch. Chem. Ges.* **1885**, *18*, 299–311; for recent examples, see: c) J. Chen, H. Wu, Z. Zheng, C. Jin, X. Zhang, W. Su, *Tetrahedron Lett.* **2006**, *47*, 5383–5387; d) G. Minetto, L. F. Raveglia, A. Sega, M. Taddei, *Eur. J. Org. Chem.* **2005**, 5277–5288; e) B. K. Banik, I. Banik, M. Renteria, S. K. Dasgupta, *Tetrahedron Lett.* **2005**, *46*, 2643–2645.

[7] For areview on the synthesis of pyrroles, see: V. F. Ferreira, M. C. B. V. de Souza, A. C. Cunha, L. O. R. Pereira, M. L. G. Ferreira, *Org. Prep. Proced. Int.* **2001**, *33*, 411–454.

[8] For recent reviews, see: a) A. de Meijere, P. von Zezschwitz, S. Bräse, *Acc. Chem. Res.* **2005**, *38*, 413–422; b) I. Nakamura, Y. Yamamoto, *Chem. Rev.* **2004**, *104*, 2127–2198; c) L. F. Tietze, *Chem. Rev.* **1996**, *96*, 115–136.

[9] For recent syntheses of pyrroles, see: a) Y. Lu, X. Fu, H. Chen, X. Du, X. Jia, Y. Liu, *Adv. Synth. Catal.* **2009**, *351*, 129–134; b) M. R. Rivero, S. L. Buchwald, *Org. Lett.* **2007**, *9*, 973–976; c) R. Martín, M. R. Rivero, S. L. Buchwald, *Angew. Chem. Int. Ed.* **2006**, *45*, 7079–7082; d) K. Hiroya, S. Matsumoto, M. Ashikawa, K. Ogiwara, T. Sakamoto, *Org. Lett.* **2006**, *8*, 5349–5352; e) C. Dong, G. Deng, J. Wang, *J. Org. Chem.* **2006**, *71*, 5560–5564; f) T. J. Harrison, J. A. Kozak, M. Corbella-Pané, G. R. Dake, *J. Org. Chem.* **2006**, *71*, 4525–4529; g) J. T. Binder, S. F. Kirsch, *Org. Lett.* **2006**, *8*, 2151–2153; h) L. Lu, G. Chen, S. Ma, *Org. Lett.* **2006**, *8*, 835–838; i) M. Blangetti, A. Deagostino, C. Prandi, S. Tabasso, P. Venturello, *Org. Lett.* **2009**, *11*, 3914–3917.

[10] For reviews, see: a) G. Evano, N. Blanchard, M. Toumi, *Chem. Rev.* **2008**, *108*, 3054–3131; b) F. Monnier, M. Taillefer, *Angew. Chem. Int. Ed.* **2008**, *47*, 3096–3099; c) I. P. Beletskaya, A. V. Cheprakov, *Coord. Chem. Rev.* **2004**, *248*, 2337–2364; d) S. V. Ley, A. W. Thomas, *Angew. Chem. Int. Ed.* **2003**, *42*, 5400–5449; e) Y. Wang, J. Zeng, X. Cui, *Chin. J. Org. Chem.* **2010**, *30*, 181–199.

[11] For reviews, see: a) J. F. Hartwig, in:*Handbook of Organopalladium Chemistry for Organic Synthesis* (Ed.: E.-I. Negishi), Wiley, Hoboken, NJ, **2002**, vol. 1, p. 1051; b) L. Jiang, S. L. Buchwald in *Metal-Catalyzed Cross-Coupling Reactions* (Eds.: A. de Meijere, F. Diederich), Wiley-VCH, Weinheim, **2004**, vol. 2, p. 699; c) T. Kitawaki, Y. Hayashi, A. Ueno, N. Chida, *Tetrahedron* **2006**, *62*, 6792–6801; d) A. J. Fletcher, M. N. Bax, M. C. Willis, *Chem. Commun.* **2007**, 4764–4766; e) M. C. Willis, G. N. Brace, T. J. K. Findlay, I. P. Holmes, *Adv. Synth. Catal.* **2006**, *348*, 851–856; f) M. C. Willis, G. N. Brace, I. P. Holmes, *Angew. Chem. Int. Ed.* **2005**, *44*, 403–406.

[12] a) Q. Liao, Y. Wang, L. Zhang, C. Xi, *J. Org. Chem.* **2009**, *74*, 6371–6373; b) L. Jiang, G. E. Job, A. Klapars, S. L. Buchwald, *Org. Lett.* **2003**, *5*, 3667–3669; c) Y. Wang, Q. Liao, C. Xi, *Org. Lett.* **2010**, DOI: 10.1021/ol1009416.

[13] R. Martín, C. H. Larsen, A. Cuenca, S. L. Buchwald, *Org. Lett.* **2007**, *9*, 3379–3382.

[14] a) X. Yuan, X. Xu, X. Zhou, J. Yuan, L. Mai, Y. Li, *J. Org. Chem.* **2007**, *72*, 1510–1513; b) X. Zhou, H. Zhang, J. Yuan, L. Mai, Y. Li, *Tetrahedron Lett.* **2007**, *48*, 7236–7239; c) E. Li, X. Xu, H. Li, H. Zhang, X. Xu, X. Yuan, Y. Li, *Tetrahedron* **2009**, *65*, 8961–8968.

[15] R. C. Hodgkinson, J. Schulz, M. C. Willis, *Org. Biomol. Chem.* **2009**, *7*, 432–434.

[16] a) C. Xi, S. Huo, T. H. Afifi, R. Hara, T. Takashashi, *Tetrahedron Lett.* **1997**, *38*, 4099–4102; b) Z. Xi, Z. Song, G. Liu, X. Liu, T. Takahashi, *J. Org. Chem.* **2006**, *71*, 3154–3158; c) Z. Xi, X. Liu, J. Lu, F. Bao, H. Fan, Z. Li, T. Takahashi, *J. Org. Chem.* **2004**, *69*, 8547–8549; d) T. Takahashi, D. Y. Kondakov, Z. Xi, N. Suzuki, *J. Am. Chem. Soc.* **1995**, *117*, 5871–5872; e) T. Takahashi, W.-H. Sun, C. Xi, H. Ubayama, Z. Xi, *Tetrahedron* **1998**, *54*, 715–726; f) H. Ubayama, W.-H. Sun, T. Takahashi, Z. Xi, *Chem. Commun.* **1998**, 1931–1932.

[17] a) T. Hu, C. Li, *Org. Lett.* **2005**, *7*, 2035–2038; b) H. Lu, X. Yuan, S. Zhu, C. Sun, C. Li, *J. Org. Chem.* **2008**, *73*, 8665–8668.

[18] a) K. Kunz, U. Scholz, D. Ganzer, *Synlett* **2003**, 2428–2439; b) F. Monnier, M. Taillefer, *Angew. Chem. Int. Ed.* **2009**, *48*, 6954–6971.

[19] W. Neugebauer, A. J. Kos, P. R. von Schleyer, *J. Organomet. Chem.* **1982**, *228*, 107–118.

[20] M. D. Rausch, L. P. Klemann, *J. Am. Chem. Soc.* **1967**, *89*, 5732–5733.

[21] A. A. Ponomarev, I. A. Markushina, G. E. Marinicheva, *Khim. Geterotsikl. Soedin.* **1970**, 1443–1445.

[22] L. Goldman, J. W. Marsico, R. B. Angier, *J. Am. Chem. Soc.* **1956**, *78*, 4173–4175.

[23] a) K.-T. Wong, S.-Y. Ku, F.-W. Yen, *Tetrahedron Lett.* **2007**, *48*, 5051–5054; b) K. Suzuki, Y. Hori, T. Kobayashi, *Adv. Synth. Catal.* **2008**, *350*, 652–656.

Received: May 10, 2010
Published Online: August 16, 2010

 © 2010 Wiley-VCH Verlag GmbH & Co. KGaA, Weinheim