ORGANIC LETTERS

2010
Vol. 12, No. 3
604−607

Ruthenium Catalyzed Directing Group-Free C2-Selective Carbenoid Functionalization of Indoles by α-Aryldiazoesters

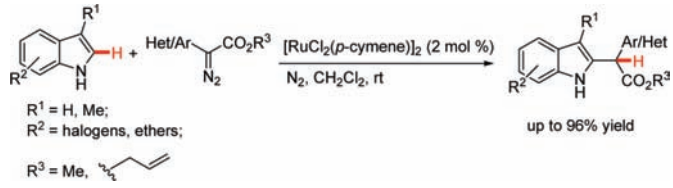
Wai-Wing Chan, Shing-Hin Yeung, Zhongyuan Zhou, Albert S. C. Chan, and Wing-Yiu Yu*

Open Laboratory of Chirotechnology, The Institute of Molecular Technology for Drug Discovery and Synthesis and the Department of Applied Biology and Chemical Technology, The Hong Kong Polytechnic University, Hung Hom, Kowloon, Hong Kong

bcwyyu@inet.polyu.edu.hk

Received December 7, 2009

ABSTRACT



A directing group-free approach for C2-selective carbenoid functionalization of NH-indoles is presented. Using $[RuCl_2(p\text{-cymene})]_2$ as catalyst and α-aryldiazoesters as carbenoid source, 2-alkylated indoles were obtained in up to 96% isolated yield. Similarly, a regioselective carbenoid functionalization of NH-pyrroles was also achieved.

The use of diazo compounds for C−H bond functionalization under transition metal catalysis is a powerful approach for C−C bond formation. While dirhodium (II, II) carboxylates and derivatives are highly successful for catalytic regio- and stereoselective carbenoid C−H insertion to a wide range of hydrocarbons,[1] the analogous functionalization of indole substrates remains relatively unexplored. Synthesis of the indole nucleus has been attracting widespread interest due to its prevalence in many naturally occurring alkaloids and pharmaceutically active compounds;[2] transition metal catalyzed heteroannulation strategies have been extensively exploited for the synthesis of complicated indole structures.[2a,c,3] Yet, direct C−H functionalization of indoles with C−C bond formation should be an appealing strategy, in view of its operational simplicity and seemingly higher overall synthetic efficiency. In 2002, Kerr and co-workers reported the $Rh_2(OAc)_4$-catalyzed reactions of indoles with methyl diazomalonate, and C3- and/or N-alkylated products were formed.[4a] According to this study, N-group protection is critical for achieving the C3-selective carbenoid functionalization. Later, Davies and co-workers, however, observed double cyclopropanation to the aromatic nucleus for the

(1) For comprehensive reviews, see: (a) Doyle, M.; Mckervey, M.; Ye, T. *Modern Catalytic Methods for Organic Synthesis with Diazo Compounds: From Cyclopropanes to Ylides*; John Wiley & Sons Inc.: New York, 1998. For recent reviews on Rh-catalyzed carbenoid C−H insertion reactions, see: (b) Doyle, M. P.; Duffy, R.; Ratnikov, M.; Zhou, L. *Chem. Rev.* DOI: 10.1021/cr900239n. Published Online: Sept 28, 2009 (Review). (c) Davies, H. M. L.; Manning, J. R. *Nature* **2008**, *451*, 417. (d) Davies, H. M. L.; Beckwith, R. E. J. *Chem. Rev.* **2003**, *103*, 2861.

(2) (a) Poulsen, T. B.; Jørgensen, K. A. *Chem. Rev.* **2008**, *108*, 2903. (b) Humphrey, G. R.; Kuethe, J. T. *Chem. Rev.* **2006**, *106*, 2875. (c) Cacchi, S.; Fabrizi, G. *Chem. Rev.* **2005**, *105*, 2873. (d) Bandini, M.; Melloni, A.; Tommasi, S.; Umani-Ronchi, A. *Synlett* **2005**, 1199. (e) Sundberg, R. J. *Indoles*; Academic Press: London, UK, 1996. (f) Sundberg, R. J. *The Chemistry of Indoles*; Academic Press: New York, 1970.

(3) (a) Becclalli, E. M.; Broggini, G.; Martinelli, M.; Sottocornola, S. *Chem. Rev.* **2007**, *107*, 5318. (b) Zeni, G.; Larcok, R. C. *Chem. Rev.* **2006**, *106*, 4644. (c) Witulski, B.; Alayrac, C.; Tevzadze-Saeftel, L. *Angew. Chem., Int. Ed.* **2003**, *42*, 4257. (d) van Esseveldt, B. C. J.; van Delft, F. L.; de Geld, R.; Rutjes, F. P. J. T. *Org. Lett.* **2003**, *5*, 1717.

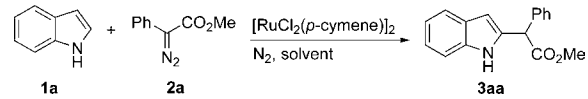
10.1021/ol9028226
Published on Web 12/31/2009

$Rh_2(DOSP)_4$-catalyzed reaction of 2- or 3-methyl-*N*-Boc-indoles with donor−acceptor carbenoids.[5]

Since the pioneering works by Nishiyama and co-workers,[6] Ru-catalyzed alkene cyclopropanation has been extensively investigated.[7] However, there are limited examples on ruthenium-catalyzed carbenoid C−H insertion reactions in the literature. Recently, we showed that $[RuCl_2(p\text{-cymene})]_2$ can effect catalytic stereoselective intramolecular carbenoid C−H insertion reactions, and cis-β-lactams were obtained in excellent yields.[8e] As our continuing interest to develop catalytic C−H bond functionalizations,[8] herein we describe regioselective C2 carbenoid C−H functionalization of NH free indoles using $[RuCl_2(p\text{-cymene})]_2$ as catalyst, and 2-indolyl aryl carboxylic esters were obtained in 80−90% yields. Indeed, direct C3-selective indole functionalizations are well established,[9] the analogous regioselective C2 functionalization remains challenging.[10] A recent work by Carretero and co-workers showed that regioselective Pd-catalyzed C2 alkenylation of indoles and pyrroles can be achieved by employing a *N*-(2-pyridyl)sulfonyl moiety as a directing group.[10i] To date, there are few examples on direct C2-selective functionalization of NH-free indoles.[10d,h,l]

Treatment of indole **1a** (0.5 mmol) with methyl phenyldiazoacetate **2a** (0.25 mmol) and $[RuCl_2(p\text{-cymene})]_2$ (2 mol %) in DCM at room temperature for 0.5 h produced **3aa** in 96% isolated yield (Table 1, entry 1). The molecular structure of a chlorinated derivative **3fa** has been established by X-ray crystallography (see the Supporting Information). In this work, a one-pot protocol was effective for the reactions of diazoesters with indole; no dimer formation was detected by GC-MS analysis. Without the Ru catalyst, no **3aa** was formed with full recovery of the starting materials.

Table 1. Reaction Optimization[a]



1a 2a 3aa

entry	solvent	temp (°C)	time (h)	yield (%)[b]
1	DCM	rt	0.5	96[c]
2[d]	toluene	40	7	60
3[d]	toluene	100	7	18
4	toluene	rt	4	70
5	DCE	rt	1	52
6	CH_3CN	rt	18	trace
7	THF	rt	18	trace
8	MeOH	rt	18	trace
9	dioxane	rt	18	–[e]
10	DMF	rt	18	–[e]

[a] Reaction conditions: **1a** (0.5 mmol), **2a** (0.25 mmol), $[RuCl_2(p\text{-cymene})]_2$ (2.5 mol %), solvent (2 mL). [b] Yields were determined by GC-FID with tetradecane as internal standard. The percentage yield is based on the amount of the limiting reagent. [c] 2 mol % of catalyst was used; isolated yield. [d] **1a**:**2a** = 1:1. [e] No detectable product formation.

For the reaction of **1a** with **2a**, higher reaction temperature (40−100 °C) gave poorer results with some dimer formation (entries 2 and 3). While employing toluene and DCE as solvent for the indole functionalization would give **3aa** in lower yields (entries 4 and 5), little or no product formation was observed if CH_3CN, THF, MeOH, dioxane, or DMF was employed as the solvent (entries 6−10). Moreover, use of exogenous ligands (e.g., pybox, PPh_3, and acetate) led to no product formation based on GC-MS analysis.

To scrutinize for any N−H/C3 alkylation,[11] we undertook GC-MS analysis of the reaction mixture. To our delight, only **3aa** and the unreacted indole were observed, and no N−H and C3 alkylated products were detected. The outcome of the Ru-catalyzed indole functionalization is dependent upon the N-substituents. For example, treatment of *N*-Boc (Boc = *tert*-butoxycarbonyl) or *N*-phenylindole with **2a** under our experimental conditions failed to afford any desired products with complete recovery of the indoles and diazo reagents. Yet, *N*-methylindole reacted with **2a** to give the 3-alkylated product (52%) exclusively without any 2-alkylated products being isolated.

Table 2 depicts the results of the Ru-catalyzed indole functionalization by various aryldiazoesters. The substituted aryldiazoesters **2b**−**g** (substituent = Me, F, Cl, Br, CF_3, NO_2) can effectively transform **1a** to its corresponding 2-alkylated indoles in 48−92% yields (entries 2−7). With the methoxy-substituted diazoesters **2h** and **2i**, the Ru-catalyzed transformations furnished the desired products in 83% and 84%

(4) (a) Gibe, R.; Kerr, M. A. *J. Org. Chem.* **2002**, *67*, 6247. (b) Antos, J. M.; Francis, M. B. *J. Am. Chem. Soc.* **2004**, *126*, 10256.

(5) Hedley, S. J.; Ventura, D. L.; Dominiak, P. M.; Nygren, C. L.; Davies, H. M. L. *J. Org. Chem.* **2006**, *71*, 5349.

(6) (a) Nishiyama, H.; Itoh, Y.; Sugawara, Y.; Matsumoto, H.; Aoki, K.; Itoh, K. *Bull. Chem. Soc. Jpn.* **1995**, *68*, 1247. (b) Nishiyama, H.; Itoh, Y.; Sugawara, Y.; Matsumoto, H.; Park, S.-B.; Itoh, K. *J. Am. Chem. Soc.* **1994**, *116*, 2223.

(7) For a review, see: Lebel, H.; Marcoux, J.-F.; Molinaro, C.; Charette, A. B. *Chem. Rev.* **2003**, *103*, 977.

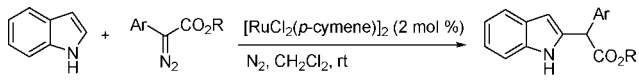
(8) (a) Yu, W.-Y.; Sit, W. N.; Zhou, Z.; Chan, A. S.-C. *Org. Lett.* **2009**, *11*, 3174. (b) Yu, W.-Y.; Tai, Y.-T.; Zhou, Z.; Chan, A. S. C. *Org. Lett.* **2009**, *11*, 469. (c) Yu, W.-Y.; Sit, W. N.; Lai, K.-M.; Zhou, Z.; Chan, A. S. C. *J. Am. Chem. Soc.* **2008**, *130*, 3304. (d) Thu, H.-Y.; Yu, W.-Y.; Che, C.-M. *J. Am. Chem. Soc.* **2006**, *128*, 9048. (e) Choi, M. K.-W.; Yu, W.-Y.; Che, C.-M. *Org. Lett.* **2005**, *7*, 1081. (f) Cheung, W.-H.; Zheng, S.-L.; Yu, W.-Y.; Zhou, G.-C.; Che, C.-M. *Org. Lett.* **2003**, *5*, 2535.

(9) For selected examples of C3-selective alkylations of indoles, see: (a) Hong, L.; Wang, L.; Chen, C.; Zhang, B.; Wang, R. *Adv. Synth. Catal.* **2009**, *351*, 772. (b) Rueping, M.; Nachtsheim, B. J.; Moreth, S. A.; Bolte, M. *Angew. Chem., Int. Ed.* **2008**, *47*, 593. (c) Itoh, J.; Fuchibe, K.; Akiyama, T. *Angew. Chem., Int. Ed.* **2008**, *47*, 4061. (d) Dong, H.-M.; Lu, H.-H.; Lu, L.-Q.; Chen, C.-B.; Xiao, W.-J. *Adv. Synth. Catal.* **2007**, *349*, 1597. (e) Chen, W.; Du, W.; Yue, L.; Li, R.; Wu, Y.; Ding, L.-S.; Chen, Y.-C. *Org. Biomol. Chem.* **2007**, *5*, 816. (f) Blay, G.; Fernández, I.; Pedro, J. R.; Vila, C. *Org. Lett.* **2007**, *9*, 2601. (g) Yang, H.; Hong, Y.-T.; Kim, S. *Org. Lett.* **2007**, *9*, 2281. (h) Li, C.-F.; Liu, H.; Liao, J.; Cao, Y.-J.; Liu, X.-P.; Xiao, W.-J. *Org. Lett.* **2007**, *9*, 1874. (i) Bartoli, G.; Bosco, M.; Carlone, A.; Pesciaioli, F.; Sambri, L.; Melchiorre, P. *Org. Lett.* **2007**, *9*, 1403.

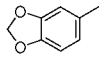
(10) For C2 arylation of indoles, see: (a) Joucla, L.; Djakovitch, L. *Adv. Synth. Catal.* **2009**, *351*, 673. (b) Phipps, R. J.; Grimster, N. P.; Gaunt, M. J. *J. Am. Chem. Soc.* **2008**, *130*, 8172. (c) Lebrasseur, N.; Larrosa, I. *J. Am. Chem. Soc.* **2008**, *130*, 2926. (d) Wang, X.; Gribkov, D. V.; Sames, D. *J. Org. Chem.* **2007**, *72*, 1476. (e) Stuart, D. R.; Villemure, E.; Fagnou, K. *J. Am. Chem. Soc.* **2007**, *129*, 12072. (f) Toure, B. B.; Lane, B. S.; Sames, D. *Org. Lett.* **2006**, *8*, 1979. (g) Lane, B. S.; Sames, D. *Org. Lett.* **2004**, *6*, 2897. (h) Sezen, B.; Sames, D. *J. Am. Chem. Soc.* **2003**, *125*, 5274. For C2 alkenylation of indoles, see: (i) García-Rubia, A.; Arrayás, R. G.; Carretero, J. C. *Angew. Chem., Int. Ed.* **2009**, 48–6511. (j) Maehara, A.; Tsurugi, H.; Satoh, T.; Miura, M. *Org. Lett.* **2008**, *10*, 1159. (k) Capito, E.; Brown, J. M.; Ricci, A. *Chem. Commun.* **2005**, 1854. (l) Grimster, N. P.; Guantlett, C.; Godfrey, C. R. A.; Gaunt, M. J. *Angew. Chem., Int. Ed.* **2005**, *44*, 3125.

(11) Deng, Q.-H.; Xu, H.-W.; Yuen, A. W.-H.; Xu, Z.-J.; Che, C.-M. *Org. Lett.* **2008**, *10*, 1529.

Table 2. Ru-Catalyzed C2-Selective Functionalization of NH-Indole **1a** with Aryldiazoacetates[a]



1a 2 3

entry	Ar	R	product	time (h)	yield (%)[b]
1	Ph	Me (**2a**)	**3aa**	0.5	96
2	4-MeC$_6$H$_4$	Me (**2b**)	**3ab**	0.5	87
3	4-FC$_6$H$_4$	Me (**2c**)	**3ac**	0.5	92
4	4-ClC$_6$H$_4$	Me (**2d**)	**3ad**	0.5	80
5	4-BrC$_6$H$_4$	Me (**2e**)	**3ae**	0.5	90
6	4-CF$_3$C$_6$H$_4$	Me (**2f**)	**3af**	0.5	77
7	4-NO$_2$C$_6$H$_4$	Me (**2g**)	**3ag**	2	48
8	4-MeOC$_6$H$_4$	Me (**2h**)	**3ah**	0.5	83
9	3-MeOC$_6$H$_4$	Me (**2i**)	**3ai**	0.5	84
10	2-MeOC$_6$H$_4$	Me (**2j**)	**3aj**	18	trace[c]
11	4-MeOC$_6$H$_4$	CH$_2$CH=CH$_2$ (**2k**)	**3ak**	2	50
12	2-naphthyl	Me (**2l**)	**3al**	72	74
13	1-naphthyl	Me (**2m**)	**3am**	72	22
14	Ph	*tert*-butyl (**2n**)	**3an**	24	12
15		Me (**2o**)	**3ao**	0.5	65
16		Me (**2p**)	**3ap**	0.5	91
17		Me (**2q**)	**3aq**	18	61

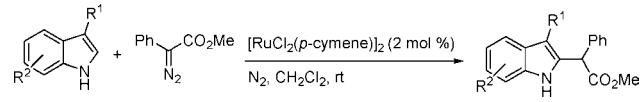
[a] Reaction conditions: **1a** (0.5 mmol), **2** (0.25 mmol), [RuCl$_2$(*p*-cymene)]$_2$ (2 mol %), CH$_2$Cl$_2$ (2 mL) at room temperature. Consumption of **2** was monitored by TLC. [b] Isolated yield. [c] Detected by GC-MS, diazo reagent remained after 18 h.

yields (entries 8 and 9). However, the analogous reaction of the ortho-substituted **2j** was ineffective (entry 10). Performing the reaction at 70 °C gave several undefined products according to GC-MS analysis; only the C3-alkylated product (25%) was successfully isolated. Moreover, no benzofuran formation was observed in our study.[12] Notably, the terminal C═C bond was tolerated versus C−H insertion, and the reaction of indole with diazoester **2k** furnished the C−H insertion product **3ak** selectively in 50% yield (entry 11). Indeed, the analogous Rh-catalyzed reactions with allyl phenyldiazoacetates would proceed preferably via intramolecular cyclopropanation.[13]

The Ru-catalyzed indole functionalization is sensitive to the steric properties of the diazoesters. When diazoester **2*l*** reacted with **1a**, **3a*l*** was formed in 74% yield (entry 12). However, with the 1-naphthyl derivative (**2m**) as the reagent, only 22% product yield was attained (entry 13). Low product yield (12%) was also obtained for the reaction with *tert*-butyl-substituted **2n** (entry 14).

Facile transformations with diazoesters containing heterocyclic moieties were also achieved. By reacting **1a** with the thienyldiazoacetate **2n**, its 2-alkylation product was obtained in 65% yield (entry 15). Likewise, the analogous reactions of diazoesters with bicyclic heterocycles such as **2o** and **2p** also afforded the desired products in 91% and 61% yields (entries 16 and 17).

Table 3. Effect of Indole Structures[a]



1 2a 3

entry	R^1	R^2	product	time (h)	yield (%)[b]
1	CH$_3$	H (**1b**)	**3ba**	0.5	65
2	CH$_2$CO$_2$Me	H (**1c**)	**3ca**	24	—[c]
3	H	7-CH$_3$ (**1d**)	**3da**	0.5	96
4	H	5-F (**1e**)	**3ea**	1	72
5	H	5-Cl (**1f**)	**3fa**	1	69
6	H	5-Br (**1g**)	**3ga**	1	69
7	H	5-I (**1h**)	**3ha**	1	61
8	H	5-OMe (**1i**)	**3ia**	1	75
9	H	5-OCH$_2$Ph (**ij**)	**3ja**	1	87

[a] Reaction conditions: **1** (0.5 mmol), **2a** (0.25 mmol), [RuCl$_2$(*p*-cymene)]$_2$ (2 mol %), CH$_2$Cl$_2$ (2 mL) at room temperature. Consumption of **2a** was monitored by TLC. [b] Isolated yield. [c] No detectable product formation.

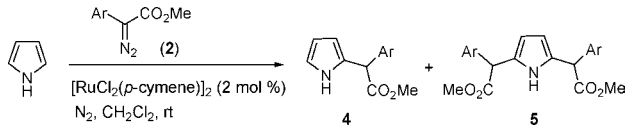
Table 3 shows the effect of the indole structure. Treatment of 3-methylindole **1b** with **2a** afforded **3ba** in 65% yield (Table 3, entry 1). However, **1c** containing a −CH$_2$CO$_2$Me group at the C3 position failed to undergo significant reaction over 24 h and the diazo was largely recovered unchanged. Yet, substituents (e.g., Me) on the 7-position have no effect on the reaction and **3da** was formed in 96% (entry 3). Furthermore, substituents at the 5-position of indoles were all tolerated and the desired 2-alkylation products **3ea**−**3ja** were formed in 61−87% yields (entries 4−9).

The C2 selective pyrrole functionalization has also been pursued; pyrroles are known to be important building blocks for many biologically active compounds. Previously, Davies and co-workers reported the Rh-catalyzed double- and monocyclopropanations of *N*-Boc pyrroles with aryldiazoacetates.[5] Initially, we treated pyrrole (0.5 mmol) with **2a** (0.25 mmol) and [RuCl$_2$(*p*-cymene)]$_2$ (2 mol %) in DCM at room temperature for 1 h, and 2-substituted **4a** and 2,5-disubstituted N−H pyrrole **5a** were obtained in 70% combined yield in a 79:21 ratio (Table 4, entry 1). Notably, GC-MS analysis did not reveal any 3- and *N*-alkylated products. To minimize the degree of double alkylation, 5 equiv of pyrrole was later employed in conjunction with syringe pump addition of **2a** over 10 h, and **4a** and **5a** were produced in 74% combined yield in a 95:5 ratio (entry 2). The reaction of pyrrole and **2** exhibits good tolerance to substituents on the aryl ring of the diazoesters, and combined yields of 84% and 77% were obtained with **2e** and **2h**, respectively (entries 3 and 4). Similarly, the reactions of heterocycle-substituted diazoesters **2p** and **2q** gave the

(12) (a) Reddy, R. P.; Lee, G. H.; Davies, H. M. L. *Org. Lett.* **2006**, *8*, 3437. (b) Davies, H. M. L.; Grazini, M. V. A.; Aouad, E. *Org. Lett.* **2001**, *3*, 1475.

(13) Doyle, M. P.; Hu, W.; Weathers, T. M., Jr. *Chirality* **2003**, *15*, 369.

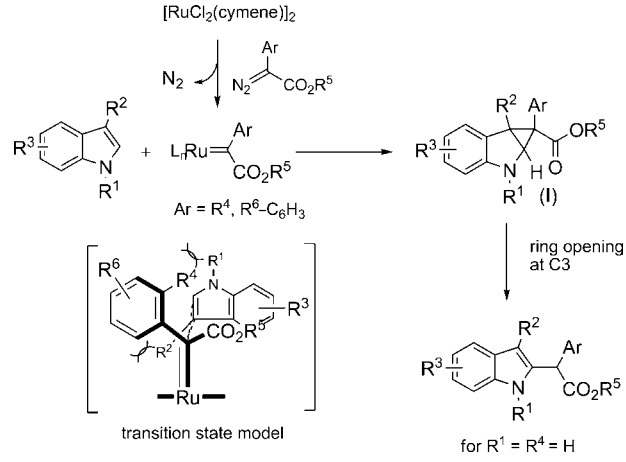
Table 4. Ru-Catalyzed C2-Selective Functionalization of NH-Pyrrole[a]



entry	diazo	product	4:5	combined yield [%][b]
1	**2a**	**4a/5a**	79:21	70
2[c]	**2a**	**4a/5a**	95:5	74
3[c]	**2e**	**4e/5e**	93:7	84
4	**2h**	**4h/5h**	91:9	77
5[c]	**2p**	**4p/5p**	91:9	79
6	**2q**	**4q/5q**	94:<6[d]	89

[a] Reaction conditions: pyrrole (0.5 mmol), **2** (0.25 mmol), $[RuCl_2(p\text{-cymene})]_2$ (2 mol %), CH_2Cl_2 (2 mL) at room temperature. Consumption of **2** was monitored by TLC. [b] Isolated yields. [c] 5 equiv of pyrrole and slow addition of **2** over 10 h were employed. [d] Determined by ^1H NMR.

Scheme 1. Proposed Mechanism and Transition State Model



desired products in 79% and 89% yields (entries 5 and 6). For the reaction involving diazoesters **2k** and **2p**, selective mono versus double alkylation (9:1) was observed even with a single-batch addition protocol being employed.

Mechanistically, we propose that the indole functionalization should involve reactive ruthenium−carbene intermediates derived from the diazoesters (Scheme 1).[6,8e,14] To probe the nature of the functionalization, we performed a kinetic isotope effect (KIE = k_H/k_D) study with deuterium-labeled indoles by competitive experiments. While KIE values >2 were seen in some Rh-catalyzed carbenoid C−H insertions,[15] KIE values of 1.04 (C2) and 1.02 (C3) were observed for this Ru-catalyzed reaction. The small KIE is not compatible with the direct C−H insertion mechanism.

On the basis of the KIE results, the Ru-catalyzed indole C−H functionalization may occur via a cyclopropylindoline intermediate (**I**), its subsequent ring-opening at the C3 position would afford the observed C2-alkylated product (Scheme 1). Cyclopropane intermediates have been isolated in some Rh-catalyzed intramolecular diazo functionalization of indoles.[16] Yet, the factors that favor the C3-selective cyclopropane ring-opening remain uncertain.[17] A transition state model (Scheme 1) anagolous to cyclopropanation may account for the poor reactivity of indoles bearing the N- and C3-substituents due to steric hindrance. Apparently, the diazoesters with bulky ester groups such as $CO_2{}^tBu$ should also exhibit poor reactivity due to steric hindrance (Table 2, entry 14).

In conclusion, we have developed a highly regioselective approach for C2 alkylation of NH-indoles using α-aryldiazoesters as reagent and $[RuCl_2(p\text{-cymene})]_2$ as catalyst; directing groups are not needed for this transformation. Because of easy operation, we anticipate that this Ru-catalyzed reaction would complement other functionalization approaches for selective indole synthesis.

Acknowledgment. We thank the financial support from The Hong Kong Research Grants Council (PolyU 5019/06P, SEG_PolyU01) and The Areas of Excellence Scheme (AoE/P-10-01) administered by the University Research Grants Council (HKSAR, China).

Supporting Information Available: Detail experimental procedures and characterization data. This material is available free of charge via the Internet at http://pubs.acs.org.

OL9028226

(14) Che, C.-M.; Huang, J.-S.; Lee, F.-W.; Li, Y.; Lai, T.-S.; Kwong, H.-L.; Teng, P.-F.; Lee, W.-S.; Lo, W.-C.; Peng, S.-M.; Zhou, Z.-Y. *J. Am. Chem. Soc.* **2001**, *123*, 4119.

(15) (a) Davies, H. M. L.; Hansen, T.; Churchill, M. R. *J. Am. Chem. Soc.* **2000**, *122*, 3063. (b) Demonceau, A.; Moels, A. F.; Costa, J.-L. *J. Mol. Catal.* **1990**, *58*, 21.

(16) (a) Yang, J.; Song, H.; Xiao, X.; Wang, J.; Qin, Y. *Org. Lett.* **2006**, *8*, 2187. (b) Bao, Z.; Wee, A. G. H. *Chem. Commun.* **2008**, 4837.

(17) Cyclopropylindoline is known to ring-open at the C2 position; the C3-selective ring-opening is rare, see for an example: Jung, M. E.; Slowinski, F. *Tetrahedron Lett.* **2001**, *42*, 6835.