

Pd(0)-Catalyzed Sequential C–N Bond Formation via Allylic and Aromatic C–H Amination of α -Methylstyrenes with Diaziridinone

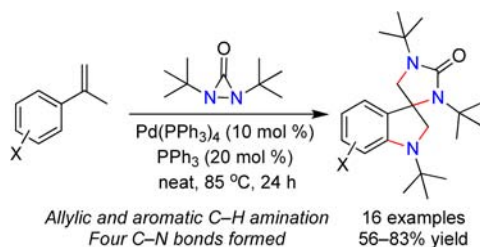
Thomas A. Ramirez, Qian Wang, Yingguang Zhu, Huaiji Zheng, Xingao Peng, Richard G. Cornwall, and Yian Shi*

Department of Chemistry, Colorado State University, Fort Collins, Colorado 80523, United States

yian@lamar.colostate.edu

Received July 10, 2013

ABSTRACT



A novel Pd(0)-catalyzed sequential C–N bond formation process via allylic and aromatic C–H amination of α -methylstyrenes with di-*tert*-butyldiaziridinone, giving spirocyclic indolines in good yields, is described. Four C–N bonds and one spiro quaternary carbon are generated in a single operation.

C–N bond formation is very important in organic synthesis, and various effective methods have been developed.¹

(1) For leading reviews, see: (a) Osborn, H. M. I.; Sweeney, J. *Tetrahedron: Asymmetry* **1997**, 8, 1693. (b) Lucet, D.; Le Gall, T.; Mioskowski, C. *Angew. Chem., Int. Ed.* **1998**, 37, 2580. (c) Wolfe, J. P.; Wagaw, S.; Marcoux, J.-F.; Buchwald, S. L. *Acc. Chem. Res.* **1998**, 31, 805. (d) Hartwig, J. F. *Acc. Chem. Res.* **1998**, 31, 852. (e) Ley, S. V.; Thomas, A. W. *Angew. Chem., Int. Ed.* **2003**, 42, 5400. (f) Hultsch, K. C. *Adv. Synth. Catal.* **2005**, 347, 367. (g) Muzart, J. *Tetrahedron* **2005**, 61, 4179. (h) Kotti, S. R. S.; Timmons, C.; Li, G. *Chem. Biol. Drug Des.* **2006**, 67, 101. (i) Singh, G. S.; D'hooghe, M.; De Kimpe, N. *Chem. Rev.* **2007**, 107, 2080. (j) Beccalli, E. M.; Brogini, G.; Martinelli, M.; Sottocornola, S. *Chem. Rev.* **2007**, 107, 5318. (k) Jensen, K. H.; Sigman, M. S. *Org. Biomol. Chem.* **2008**, 6, 4083. (l) Lin, G.-Q.; Xu, M.-H.; Zhong, Y.-W.; Sun, X.-W. *Acc. Chem. Res.* **2008**, 41, 831. (m) de Figueiredo, R. M. *Angew. Chem., Int. Ed.* **2009**, 48, 1190. (n) Cardona, F.; Goti, A. *Nat. Chem.* **2009**, 1, 269. (o) Fischer, C.; Koenig, B. *Beilstein J. Org. Chem.* **2011**, 7, 59. (p) Chemler, S. R. *J. Organomet. Chem.* **2011**, 696, 150. (q) De Jong, S.; Nosal, D. G.; Wardrop, D. J. *Tetrahedron* **2012**, 68, 4067. (r) Song, G.; Wang, F.; Li, X. *Chem. Soc. Rev.* **2012**, 41, 3651.

(2) For leading reviews on C–H amination, see: (a) Katsuki, T. *Synlett* **2003**, 281. (b) Müller, P.; Fruit, C. *Chem. Rev.* **2003**, 103, 2905. (c) Davies, H. M. L.; Long, M. S. *Angew. Chem., Int. Ed.* **2005**, 44, 3518. (d) Li, Z.; He, C. *Eur. J. Org. Chem.* **2006**, 4313. (e) Fantauzzi, S.; Caselli, A.; Gallo, E. *Dalton Trans.* **2009**, 5434. (f) Collet, F.; Dodd, R. H.; Dauban, P. *Chem. Commun.* **2009**, 5061. (g) Zalatan, D. N.; Du Bois, J. *Top. Curr. Chem.* **2010**, 292, 347. (h) Driver, T. G. *Org. Biomol. Chem.* **2010**, 8, 3831. (i) Cho, S. H.; Kim, J. Y.; Kwak, J.; Chang, S. *Chem. Soc. Rev.* **2011**, 40, 5068. (j) Ramirez, T. A.; Zhao, B.; Shi, Y. *Chem. Soc. Rev.* **2012**, 41, 931. (k) Gephart, R. T., III; Warren, T. H. *Organometallics* **2012**, 31, 7728. (l) Roizen, J. L.; Harvey, M. E.; Du Bois, J. *Acc. Chem. Res.* **2012**, 45, 911.

Direct C–H amination presents an attractive approach to construct C–N bonds and remains an active area.² In our previous studies on the Pd(0)-catalyzed diamination^{3,4} of olefins with di-*tert*-butyldiaziridinone (**1**),^{5,6} we have found that terminal olefins **2** (R = CH₂CH₂R²) can be aminated at allylic and homoallylic carbons to give diamination products **3** (Scheme 1).⁴ This diamination process likely proceeds via a diene intermediate, generated from the terminal olefin via allylic C–H activation to form a π -allyl Pd complex and subsequent β -hydride elimination.⁴ In our efforts to further explore the reactivity of diaziridinone, we have investigated terminal olefins which lack homoallylic

(3) For examples of Pd(0)-catalyzed diamination of conjugated dienes using **1**, see: (a) Du, H.; Zhao, B.; Shi, Y. *J. Am. Chem. Soc.* **2007**, 129, 762. (b) Zhao, B.; Du, H.; Cui, S.; Shi, Y. *J. Am. Chem. Soc.* **2010**, 132, 3523.

(4) For examples of Pd(0)-catalyzed allylic and homoallylic C–H diamination of terminal olefins using **1**, see: (a) Du, H.; Yuan, W.; Zhao, B.; Shi, Y. *J. Am. Chem. Soc.* **2007**, 129, 7496. (b) Du, H.; Zhao, B.; Shi, Y. *J. Am. Chem. Soc.* **2008**, 130, 8590.

(5) For a leading review on diaziridinones, see: Heine, H. W. In *The Chemistry of Heterocyclic Compounds*; Hassner, A., Ed.; John Wiley & Sons, Inc: New York, 1983; p 547.

(6) For the preparation of di-*tert*-butyldiaziridinone (**1**), see: (a) Greene, F. D.; Stowell, J. C.; Bergmark, W. R. *J. Org. Chem.* **1969**, 34, 2254. (b) Du, H.; Zhao, B.; Shi, Y. *Org. Synth.* **2009**, 86, 315.

Scheme 1

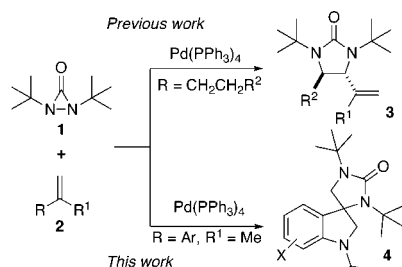
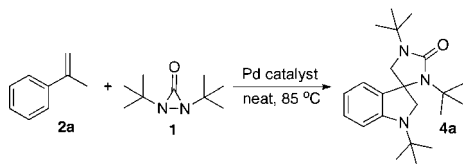


Table 1. Studies on Reaction Conditions^a



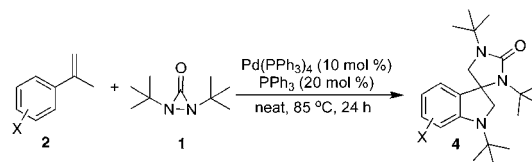
entry	catalyst	ligand (x mol %)	yield ^b (%)
1	Pd(PPh ₃) ₄		18
2	Pd(PPh ₃) ₄		51
3	Pd(PPh ₃) ₄	PPh ₃ (10 mol %)	58
4	Pd(PPh₃)₄	PPh₃ (20 mol %)	75
5	Pd(PPh ₃) ₄	PPh ₃ (30 mol %)	62
6	—	PPh ₃ (60 mol %)	0
7	Pd ₂ (dba) ₃		0
8	Pd ₂ (dba) ₃	PPh ₃ (60 mol %)	65
9	Pd ₂ (dba) ₃	P(<i>p</i> -MeO-Ph) ₃ (60 mol %)	36
10	Pd ₂ (dba) ₃	P(<i>p</i> -tolyl) ₃ (60 mol %)	51
11	Pd ₂ (dba) ₃	P(<i>o</i> -tolyl) ₃ (60 mol %)	0
12	Pd ₂ (dba) ₃	P(<i>p</i> -F ₃ C-Ph) ₃ (60 mol %)	35
13	Pd ₂ (dba) ₃	dppp (30 mol %)	0
14	Pd ₂ (dba) ₃	BINAP (30 mol %)	0

^a All reactions were carried out with olefin **2a** (0.40 mmol), di-*tert*-butyldiaziridinone (**1**) (1.60 mmol), Pd(PPh₃)₄ (0.040 mmol) or Pd₂(dba)₃ (0.020 mmol), and appropriate phosphine ligand at 85 °C under Ar for 24 h unless otherwise stated. For entry 1, di-*tert*-butyldiaziridinone (**1**) was added in one portion. For entries 2–14, di-*tert*-butyldiaziridinone (**1**) was slowly added over 10 h via syringe pump. ^b Isolated yield based on olefin **2a**.

hydrogens and thus cannot form dienes under the reaction conditions. During such studies, it has been found that spirocyclic indolines **4** can be obtained when α -methylstyrenes were treated with di-*tert*-butyldiaziridinone (**1**) and a Pd(0) catalyst (Scheme 1).⁷ The reaction likely proceeds via

(7) For leading references on indolines derived from Pd-catalyzed C–H activation: (a) Watanabe, T.; Oishi, S.; Fujii, N.; Ohno, H. *Org. Lett.* **2008**, *10*, 1759. (b) Houlden, C. E.; Bailey, C. D.; Ford, J. G.; Gagné, M. R.; Lloyd-Jones, G. C.; Booker-Milburn, K. I. *J. Am. Chem. Soc.* **2008**, *130*, 10066. (c) Mei, T.-S.; Wang, X.; Yu, J.-Q. *J. Am. Chem. Soc.* **2009**, *131*, 10806. (d) Neumann, J. J.; Rakshit, S.; Dröge, T.; Glorius, F. *Angew. Chem., Int. Ed.* **2009**, *48*, 6892. (e) Nakanishi, M.; Katayev, D.; Besnard, C.; Küding, E. P. *Angew. Chem., Int. Ed.* **2011**, *50*, 7438. (f) He, G.; Zhao, Y.; Zhang, S.; Lu, C.; Chen, G. *J. Am. Chem. Soc.* **2012**, *134*, 3. (g) He, G.; Lu, C.; Zhao, Y.; Nack, W. A.; Chen, G. *Org. Lett.* **2012**, *14*, 2944. (h) Saget, T.; Lemouzy, S. J.; Cramer, N. *Angew. Chem., Int. Ed.* **2012**, *51*, 2238. (i) Mei, T.-S.; Leow, D.; Xiao, H.; Laforteza, B. N.; Yu, J.-Q. *Org. Lett.* **2013**, *15*, 3058.

Table 2. Substrate Scope^a



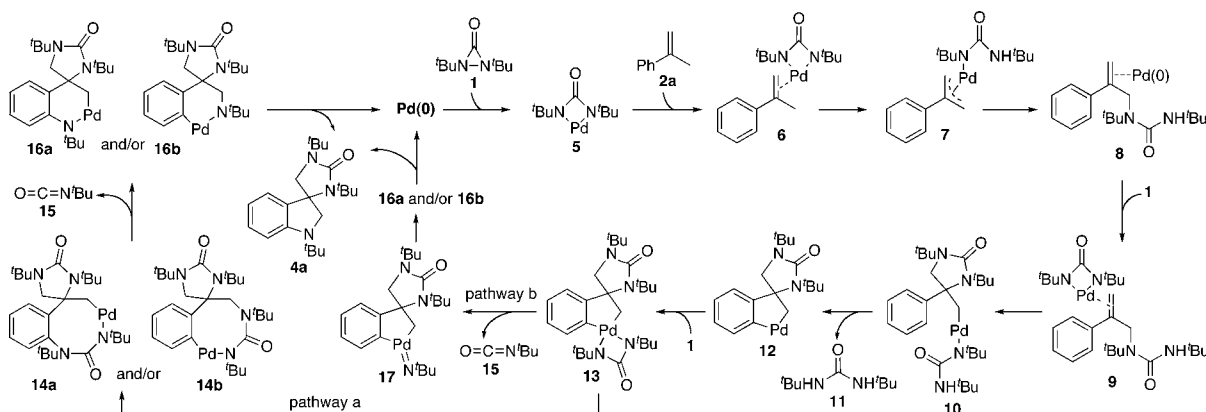
entry	substrate (2)	product (4)	yield (%) ^b
1	2a , X = H	4a	75
2	2b , X = OMe	4b	81
3	2c , X = Me	4c	71
4	2d , X = <i>i</i> -Pr	4d	70
5	2e , X = <i>t</i> -Bu	4e	61
6	2f , X = F	4f	73
7	2g , X = Cl	4g	69
8	2h , X = Br	4h	63
9	2i , X = CO ₂ Me	4i	81
10	2j , X = OMe	4j	79
11	2k , X = Me	4k	74
12	2l , X = Cl	4l	68
13	2m , X = Br	4m	64
14	2n	4n	70
15	2o	4o	56
16	2p	4p	83

^a All reactions were carried out with olefin **2** (0.40 mmol), di-*tert*-butyldiaziridinone (**1**) (1.60 mmol) (added over 10 h via syringe pump), Pd(PPh₃)₄ (0.040 mmol), and PPh₃ (0.080 mmol) at 85 °C under Ar for 24 h (total). ^b Isolated yield. The ratio of the regioisomers was determined to be > 20:1 (for entries 10, 11, 13, and 15), 8:1 (for entry 12), and 10:1 (for entry 14) by ¹H NMR analysis of the crude reaction mixture.

a novel C–H activation and C–N bond formation process. Herein, we report our preliminary studies on this subject.

Our initial studies were carried out with α -methylstyrene (**2a**) as the test substrate. Treating **2a** with di-*tert*-butyldiaziridinone (**1**) and 10 mol % of Pd(PPh₃)₄ under neat conditions at 85 °C for 24 h gave spirocyclic indoline **4a** in

Scheme 2. Proposed Catalytic Cycle



18% yield (Table 1, entry 1). The yield was increased to 51% when di-*tert*-butyldiaziridinone (**1**) was added slowly over 10 h via syringe pump (Table 1, entry 2). The yield was further improved with addition of PPh_3 ligand to the reaction system, with 20 mol % of PPh_3 being optimal (Table 1, entries 3–5). No reaction was observed with PPh_3 alone (Table 1, entry 6). The reaction was also investigated with $\text{Pd}_2(\text{dba})_3$ as catalyst (Table 1, entries 7–14). No product was formed without additional ligand (Table 1, entry 7). The nature of the ligand has a dramatic effect on the product yield. Among the ligands examined, PPh_3 gave the highest yield (Table 1, entry 8), and essentially no product was obtained with $\text{P}(o\text{-tolyl})_3$, dppp , or BINAP (Table 1, entries 11, 13, and 14).

As shown in Table 2, the reaction process can be extended to various *para*-, *meta*-, di-, and trisubstituted α -methylstyrenes **2b–p**, giving the corresponding spirocyclic indoline products **4b–p** in 56–83% yield (Table 2, entries 2–16). For entries 10–15, the reaction generally occurred at the less sterically hindered position (for the X-ray data of **4j** and **4n**, see the Supporting Information). In the cases of entries 10, 11, 13, and 15, the reactions proceeded with high regioselectivity (> 20:1).

While a precise understanding of the reaction mechanism awaits further study, a plausible catalytic pathway is proposed in Scheme 2. The $\text{Pd}(0)$ first inserts into the

N–N bond of di-*tert*-butyldiaziridinone (**1**) to give four-membered $\text{Pd}(\text{II})$ species **5**, which then forms complex **6** with α -methylstyrene (**2a**). Abstraction of an allylic hydrogen from **6** leads to π -allyl Pd complex **7**,^{8,9} which affords allyl urea-ligated $\text{Pd}(0)$ intermediate **8** via reductive elimination.¹⁰ Reaction of intermediate **8** with another equivalent of **1** provides **9**, which undergoes a $\text{Pd}(\text{II})$ -catalyzed cyclization to give **10**.^{11,12} Subsequently, **10** undergoes an intramolecular aromatic C–H activation to form urea **11** and pallada(II)cycle **12**,¹³ which inserts into the N–N bond of **1** to give pallada(IV)cycle **13**. Reductive elimination of pallada(IV)cycle **13** leads to eight-membered pallada(II)cycle **14a** and/or **14b** (pathway a), which is transformed to **16a** and/or **16b** by releasing *tert*-butyl isocyanate (**15**).¹⁴ Upon reductive elimination, **16a** and/or **16b** is converted to spirocyclic indoline **4a** with the regeneration of the $\text{Pd}(0)$ catalyst. Alternatively,

(11) For leading reviews on $\text{Pd}(\text{II})$ -catalyzed cyclization of olefins with N and O nucleophiles, see: (a) Hegedus, L. S. *Tetrahedron* **1984**, *40*, 2415. (b) Müller, T. E.; Beller, M. *Chem. Rev.* **1998**, *98*, 675. (c) Stoltz, B. M. *Chem. Lett.* **2004**, *33*, 362. (d) Sigman, M. S.; Schultz, M. J. *Org. Biomol. Chem.* **2004**, *2*, 2551. (e) Wolfe, J. P.; Thomas, J. S. *Curr. Org. Chem.* **2005**, *9*, 625. (f) Zeni, G.; Larock, R. C. *Chem. Rev.* **2006**, *106*, 4644. (g) Minatti, A.; Muñoz, K. *Chem. Soc. Rev.* **2007**, *36*, 1142. (h) Kotov, V.; Scarborough, C. C.; Stahl, S. S. *Inorg. Chem.* **2007**, *46*, 1910.

(12) For Pd -catalyzed allylic C–H amination and subsequent cyclization using *N,N*-di-*tert*-butylthiadiaziridine 1,1-dioxide, see: Wang, B.; Du, H.; Shi, Y. *Angew. Chem., Int. Ed.* **2008**, *47*, 8224.

(13) For leading reviews on palladacycles derived from C–H activation, see: (a) Dyker, G. *Angew. Chem., Int. Ed.* **1999**, *38*, 1698. (b) Kakiuchi, F.; Chatani, N. *Adv. Synth. Catal.* **2003**, *345*, 1077. (c) Catellani, M. *Synlett* **2003**, 298. (d) Alberico, D.; Scott, M. E.; Lautens, M. *Chem. Rev.* **2007**, *107*, 174. (e) Catellani, M.; Motti, E.; Della Ca', N. *Acc. Chem. Res.* **2008**, *41*, 1512. (f) Kakiuchi, F.; Kochi, T. *Synthesis* **2008**, 3013. (g) Muñoz, K. *Angew. Chem., Int. Ed.* **2009**, *48*, 9412. (h) Ackermann, L.; Vicente, R.; Kapdi, A. R. *Angew. Chem., Int. Ed.* **2009**, *48*, 9792. (i) Jazsar, R.; Hitce, J.; Renaudat, A.; Sofack-Kreutzer, J.; Baudoin, O. *Chem.—Eur. J.* **2010**, *16*, 2654. (j) Xu, L.-M.; Li, B.-J.; Yang, Z.; Shi, Z.-J. *Chem. Soc. Rev.* **2010**, *39*, 712. (k) Sehnaal, P.; Taylor, R. J. K.; Fairlamb, I. J. S. *Chem. Rev.* **2010**, *110*, 824. (l) Shi, F.; Larock, R. C. *Top. Curr. Chem.* **2010**, *292*, 123. (m) Martins, A.; Mariampillai, B.; Lautens, M. *Top. Curr. Chem.* **2010**, *292*, 1. (n) McMurray, L.; O'Hara, F.; Gaunt, M. J. *Chem. Soc. Rev.* **2011**, *40*, 1885. (o) Wencel-Delord, J.; Dröge, T.; Liu, F.; Glorius, F. *Chem. Soc. Rev.* **2011**, *40*, 4740. (p) Malinakova, H. C. *Top. Organomet. Chem.* **2011**, *35*, 85.

(14) (a) Komatsu, M.; Tamabuchi, S.; Minakata, S.; Ohshiro, Y. *Heterocycles* **1999**, *50*, 67. (b) Bocelli, G.; Catellani, M.; Cugini, F.; Ferraccioli, R. *Tetrahedron Lett.* **1999**, *40*, 2623. (c) Paul, F.; Fischer, J.; Ochsenbein, P.; Osborn, J. A. *C. R. Chimie* **2002**, *5*, 267.

(8) For leading reviews on the generation of π -allyl Pd complexes from olefins with PdX_2 , see: (a) Trost, B. M. *Acc. Chem. Res.* **1980**, *13*, 385. (b) Åkermark, B.; Zetterberg, K. In *Handbook of Organopalladium Chemistry for Organic Synthesis*; Negishi, E.-I., Ed.; Wiley: New York, 2002; p 1875. (c) Trost, B. M. *J. Org. Chem.* **2004**, *69*, 5813.

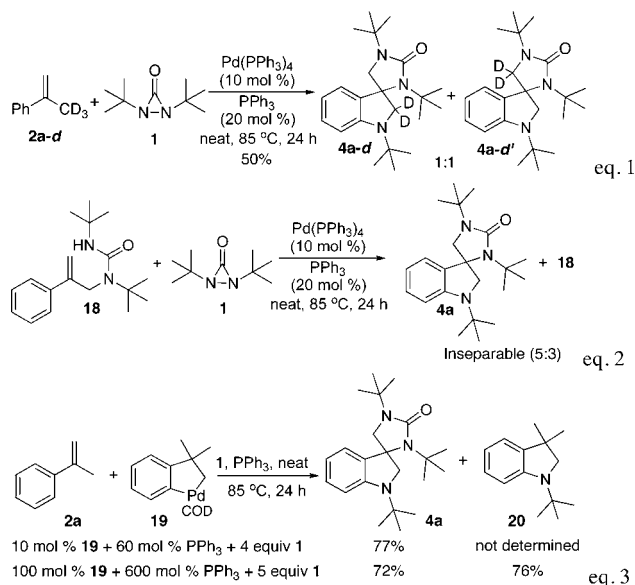
(9) For a book on Pd chemistry, see: Tsuji, J. *Palladium Reagents and Catalysts: New Perspective for the 21st Century*; Wiley: New York, 2004.

(10) For leading references on Pd -promoted or catalyzed allylic C–H amination, see: (a) Heathcock, C. H.; Stafford, J. A.; Clark, D. L. *J. Org. Chem.* **1992**, *57*, 2575. (b) van der Schaaf, P. A.; Sutter, J.-P.; Grellier, M.; van Mier, G. P. M.; Spek, A. L.; van Koten, G.; Pfeiffer, M. J. *Am. Chem. Soc.* **1994**, *116*, 5134. (c) Larock, R. C.; Hightower, T. R.; Hasvold, L. A.; Peterson, K. P. *J. Org. Chem.* **1996**, *61*, 3584. (d) Fraunhoffer, K. J.; White, M. C. *J. Am. Chem. Soc.* **2007**, *129*, 7274. (e) Liu, G.; Yin, G.; Wu, L. *Angew. Chem., Int. Ed.* **2008**, *47*, 4733. (f) Wasa, M.; Yu, J.-Q. *J. Am. Chem. Soc.* **2008**, *130*, 14058. (g) Rice, G. T.; White, M. C. *J. Am. Chem. Soc.* **2009**, *131*, 11707. (h) Reed, S. A.; Mazzotti, A. R.; White, M. C. *J. Am. Chem. Soc.* **2009**, *131*, 11701. (i) Wu, L.; Qiu, S.; Liu, G. *Org. Lett.* **2009**, *11*, 2707. (j) Yin, G.; Wu, Y.; Liu, G. *J. Am. Chem. Soc.* **2010**, *132*, 11978.

pallada(IV)cycl Pd(IV) cycle **13** releases a molecule of *tert*-butyl isocyanate (**15**) to form Pd(IV) -nitrene **17**¹⁵ (pathway b), which undergoes two consecutive reductive eliminations to give product **4a** via **16a** and/or **16b** and to regenerate the Pd(0) catalyst.

To gain some insight into the reaction mechanism, additional experiments were performed (Schemes 3).

Scheme 3



When deuterium-labeled α -methylstyrene **2a-d** was subjected to the standard reaction conditions, equal amounts of indoline products **4a-d** and **4a-d'** were obtained in 50% yield (Scheme 3, eq 1). This result suggests that π -allyl Pd

(15) For leading references on Pd -nitrene species, see: (a) Reference 2g. (b) Migita, T.; Hongoh, K.; Naka, H.; Nakaido, S.; Kosugi, M. *Bull. Chem. Soc. Jpn.* **1988**, *61*, 931. (c) Abboud, K. A.; Villanueva, L. A.; Boncella, J. M. *Acta Crystallogr.* **1993**, *C49*, 1848. (d) Besenyei, G.; Párkányi, L.; Foch, I.; Simándi, L. I.; Kálmán, A. *Chem. Commun.* **1997**, 1143. (e) Foch, I.; Párkányi, L.; Besenyei, G.; Simándi, L. I.; Kálmán, A. *J. Chem. Soc., Dalton Trans.* **1999**, 293. (f) Stromnova, T. A.; Orlova, S. T.; Kazyul'kin, D. N.; Stolyarov, I. P.; Eremenko, I. L. *Russ. Chem. Bull.* **2000**, *49*, 150. (g) Thu, H.-Y.; Yu, W.-Y.; Che, C.-M. *J. Am. Chem. Soc.* **2006**, *128*, 9048. (h) Ng, K.-H.; Chan, A. S. C.; Yu, W.-Y. *J. Am. Chem. Soc.* **2010**, *132*, 12862. (i) Chiba, S.; Zhang, L.; Sanjaya, S.; Ang, G. Y. *Tetrahedron* **2010**, *66*, 5692. (j) Ng, K.-H.; Ng, F.-N.; Yu, W.-Y. *Chem. Commun.* **2012**, *48*, 11680.

complex **7** is very likely to be involved in this process. Attempts to isolate any reaction intermediates were unsuccessful. Allyl urea **18** was subsequently prepared and subjected to the reaction conditions. It was found that **18** did cyclize to provide indoline **4a** (eq 2), which is also in agreement with the reaction mechanism described in Scheme 2. A known palladacycle **19**¹⁶ was also prepared and was found to be catalytically active. Treating α -methylstyrene (**2a**) with di-*tert*-butyldiaziridinone (**1**) in the presence of 10 mol % of **19** and 60 mol % of PPh_3 at 85 °C for 24 h gave indoline **4a** in 77% yield along with small amounts of indoline **20** (eq 3). When stoichiometric amounts of **19** were used, indolines **4a** and **20** were obtained in 72% and 76% yield, respectively. These results suggest that palladacycle **12** is a likely intermediate in the catalytic cycle and can be converted into the indoline **4a**.

In summary, we have discovered a novel Pd(0) -catalyzed C–N bond formation process of α -methylstyrenes with di-*tert*-butyldiaziridinone (**1**) via sequential allylic and aromatic C–H amination. Various α -methylstyrenes can be converted to spirocyclic indolines in good yields with the generation of four C–N bonds and one spiro quaternary carbon in a single operation. The ability of di-*tert*-butyldiaziridinone to be oxidatively inserted into a $\text{R}_2\text{Pd(II)}$ species further illustrates its versatile reactivity and opens up more opportunities for new reaction development with this class of compounds. Such studies are currently underway.

Acknowledgment. We are grateful for the generous financial support from the General Medical Sciences of the National Institutes of Health (GM083944-06).

Supporting Information Available. Experimental procedure, characterization of all compounds, and crystallographic information file for compounds **4a,j,n**, and **19**. This material is available free of charge via the Internet at <http://pubs.acs.org>.

(16) For the preparation of palladacycle **19**, see: (a) Cámpora, J.; López, J. A.; Palma, P.; del Rio, D.; Carmona, E.; Valerga, P.; Graiff, C.; Tiripicchio, A. *Inorg. Chem.* **2001**, *40*, 4116. (b) Cámpora, J.; López, J. A.; Palma, P.; Valerga, P.; Spillner, E.; Carmona, E. *Angew. Chem., Int. Ed.* **1999**, *38*, 147.

The authors declare no competing financial interest.