

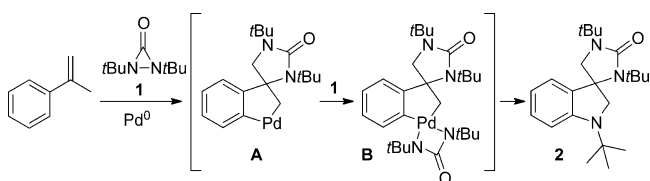
Palladium(0)-Catalyzed Heck Reaction/C–H Activation/Amination Sequence with Diaziridinone: A Facile Approach to Indolines**

Huaiji Zheng, Yingguang Zhu, and Yian Shi*

Abstract: Indolines are important moieties present in various biologically significant molecules and have attracted considerable attention in synthetic chemistry. This paper describes a Heck reaction/C–H activation/amination sequence for forming indolines using di-*tert*-butyldiaziridinone. The reaction process likely proceeds via a pallada(II)cycle, which is converted into an indoline by oxidative addition to the diaziridinone and two subsequent C–N bond formations.

Indolines are important moieties contained in various biologically and pharmaceutically active compounds,^[1] and their syntheses have attracted considerable attention. The cyclization involving replacement of a leaving group by a nitrogen atom is among the widely used methods to synthesize indolines.^[2,3] Direct C–H amination presents an attractive strategy for the construction of this class of molecules and has become an active area of research in recent years.^[4–6]

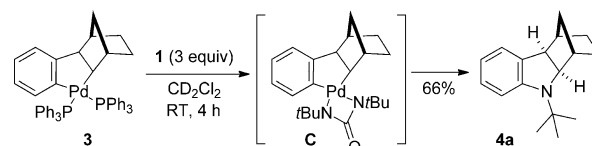
Recently, we reported that α -methylstyrene can be efficiently transformed into spirocyclic indolines by a palladium(0)-catalyzed sequential C–N bond formation involving allylic and aromatic C–H amination with di-*tert*-butyldiaziridinone (**1**; Scheme 1).^[7] This reaction process likely proceeds



Scheme 1. The formation of spirocyclic indolines from α -methylstyrene.

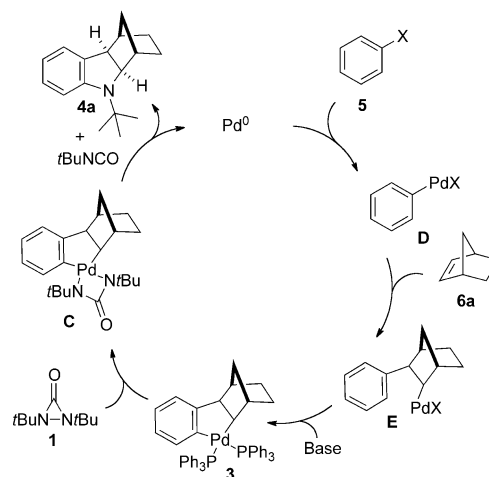
via the pallada(II)cycle **A**, which oxidatively inserts into the diaziridinone to form the pallada(IV)cycle **B**.^[8] Upon release of *tert*-butyl isocyanate (*t*BuNCO), **B** is converted into the spirocyclic indoline **2** through two consecutive reductive eliminations.

Previously, we have shown that palladium(0) can readily insert into the N–N bond of **1**, and the resulting four-membered palladium(II) species reacts with dienes to form diamination products.^[9] The oxidative insertion of a pallada(II)cycle into **1** is mechanistically interesting. To further probe this process, the known pallada(II)cycle **3**^[10] was thus prepared^[11] and reacted with **1** (Scheme 2). The palladacycle



Scheme 2. Synthesis of the indoline **4a** from the pallada(II)cycle **3**.

was indeed smoothly transformed into the indoline **4a** in 66 % yield at room temperature.^[12] This result prompted us to investigate if the indoline could be directly formed from an aryl halide (**5**), norbornene (**6a**), and **1** with catalytic amounts of palladium(0) by in situ formation of **3** by a Heck reaction and subsequent C–H activation (Scheme 3). The key issue for



Scheme 3. Proposed catalytic cycle.

such a transformation is whether the aryl halide can compete with the diaziridinone for the oxidative addition by the palladium(0) catalyst to initiate the catalytic cycle. Herein, we report our preliminary studies on this subject.

Initial studies were carried out with *p*-iodoanisole (**5b**) as a test substrate under various reaction conditions. As shown in Table 1, the base had a significant effect on the reaction efficiency. No products were isolated with K_2CO_3 , Na_2CO_3 ,

[*] Dr. H. Zheng, Dr. Y. Zhu, Prof. Dr. Y. Shi
Department of Chemistry, Colorado State University
Fort Collins, CO 80523 (USA)
E-mail: yian@lamar.colostate.edu

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Table 1: Studies on the reaction conditions.^[a]

Entry	Solvent	Base	Catalyst	Ligand	Yield [%] ^[b]
1	PhMe	K ₂ CO ₃	[Pd(PPh ₃) ₄]	–	0
2	PhMe	Na ₂ CO ₃	[Pd(PPh ₃) ₄]	–	0
3	PhMe	Et ₃ N	[Pd(PPh ₃) ₄]	–	0
4	PhMe	K ₃ PO ₄	[Pd(PPh ₃) ₄]	–	79
5	PhMe	NaOtBu	[Pd(PPh ₃) ₄]	–	82
6	PhMe	CS ₂ CO ₃	[Pd(PPh ₃) ₄]	–	90
7	DMF	CS ₂ CO ₃	[Pd(PPh ₃) ₄]	–	70
8	MeCN	CS ₂ CO ₃	[Pd(PPh ₃) ₄]	–	84
9	THF	CS ₂ CO ₃	[Pd(PPh ₃) ₄]	–	76
10	1,4-dioxane	CS ₂ CO ₃	[Pd(PPh ₃) ₄]	–	74
11 ^[c]	PhMe	CS ₂ CO ₃	[Pd(PPh ₃) ₄]	–	89
12	PhMe	CS ₂ CO ₃	[Pd ₂ (dba) ₃]	–	0
13	PhMe	CS ₂ CO ₃	[Pd ₂ (dba) ₃]	PPh ₃	84
14	PhMe	CS ₂ CO ₃	[Pd ₂ (dba) ₃]	P(<i>p</i> -MeOC ₆ H ₅) ₃	81
15	PhMe	CS ₂ CO ₃	[Pd ₂ (dba) ₃]	P(<i>p</i> -CF ₃ C ₆ H ₅) ₃	90
16	PhMe	CS ₂ CO ₃	[Pd ₂ (dba) ₃]	binap	0

[a] All reactions were carried out with *p*-iodoanisole (**5b**; 0.30 mmol), norbornene (**6a**; 0.60 mmol), di-*tert*-butyldiaziridinone (**1**; 0.45 mmol), Pd (0.030 mmol; Pd/P=1/4), base (0.60 mmol), and solvent (0.30 mL) at 80 °C under Ar for 36 h unless otherwise stated. For entry 4, the reaction time was 72 h. [b] Yield of isolated product. [c] The reaction was carried out with [Pd(PPh₃)₄] (0.015 mmol) and **1** (0.35 mmol) at 80 °C for 48 h. binap = 2,2'-bis(diphenylphosphino)-1,1'-binaphthyl, dba = dibenzylideneacetone, DMF = *N,N*-dimethylformamide, THF = tetrahydrofuran.

and Et₃N (entries 1–3). To our delight, the reaction proceeded efficiently with bases such as K₃PO₄, NaOtBu, and CS₂CO₃ (entries 4–6). For example, treating **5b** and **6a** with 1.5 equivalents of **1**, 10 mol % [Pd(PPh₃)₄], and 2.0 equivalents of CS₂CO₃ in toluene at 80 °C gave **4b** in 90 % yield (entry 6). Polar solvents such as DMF, MeCN, THF, and 1,4-dioxane gave lower yields as compared to toluene (entries 7–10). A similar yield (89 %) was obtained when the amount of [Pd(PPh₃)₄] was reduced from 10 mol % to 5 mol % (entries 6 and 11). The effect of the ligand was also briefly investigated with [Pd₂(dba)₃] as a catalyst (entries 12–16). No product was formed with [Pd₂(dba)₃] alone (entry 12). PPh₃, P(*p*-MeOC₆H₅)₃, and P(*p*-CF₃C₆H₅)₃ were shown to be effective ligands for the reaction, thus giving **4b** in 81–90 % yield (entries 13–15). However, no desired product was obtained with binap (entry 16).

As shown in Table 2, the reaction process can be extended to various *para*-, *meta*-, *ortho*-, and disubstituted iodobenzenes, thus giving the corresponding indoline products in 67–97 % yield (entries 1–19). The Heck reaction occurred from the *exo* face of norbornene as indicated by the X-ray structure of **4g** (see the Supporting Information). For the bromo-substituted iodobenzenes **5d** and **5n**, the reaction selectively occurred at iodide to give the indolines **4d** and **4n**, respectively, in good yields (entries 4 and 14). For *meta*-substituted iodobenzenes (entries 9–12 and entry 18), the C–H amination regioselectively occurred at the sterically less hindered position. Good yields (72–96 %) were also obtained for the

Table 2: Substrate scope.^[a]

Entry	5	4	Yield [%] ^[b]
1	5a , R = H	4a	90
2	5b , R = OMe	4b	89
3	5c , R = <i>n</i> Bu	4c	91
4	5d , R = Br	4d	68
5	5e , R = F	4e	72
6	5f , R = CF ₃	4f	78
7	5g , R = CO ₂ Me	4g (X-ray)	93
8	5h , R = NO ₂	4h	84
9	5i , R = OMe	4i	82
10	5j , R = CH ₂ OTBS	4j	97
11	5k , R = CO ₂ Me	4k	85
12	5l	4l	84
13	5m , R = OMe	4m	90 ^[c]
14	5n , R = Br	4n	81 ^[c]
15	5o , R = NO ₂	4o	88 ^[c]
16	5p , R = OMe	4p	94 ^[c]
17	5q , R = NO ₂	4q	80 ^[c]
18	5r	4r	93
19	5s	4s	67

[a] All reactions were carried out with the iodobenzene **5** (0.30 mmol), norbornene (**6a**; 0.60 mmol), di-*tert*-butyldiaziridinone (**1**; 0.35 mmol), [Pd(PPh₃)₄] (0.015 mmol), CS₂CO₃ (0.60 mmol), and toluene (0.30 mL) at 80 °C under Ar for 48 h unless otherwise stated. [b] Yield of isolated product based on **5**. [c] Reaction time, 72 h. TBS = *tert*-butyldimethylsilyl.

corresponding indolines (**7–9**)^[13] when **6b** and the bridged olefins **6c,d** were used (Figure 1).^[14] For the indoline **7b**, the reaction process is amenable to gram scale. The indoline **7b** can be converted into the *N*-*tert*-butyl indole **10** in 79 % yield

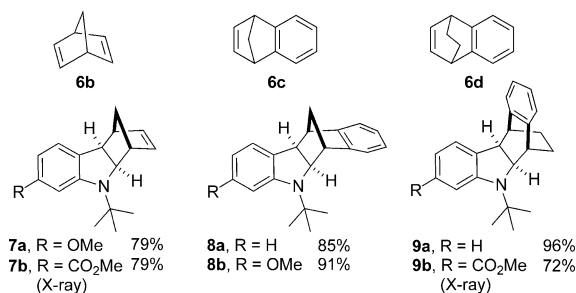
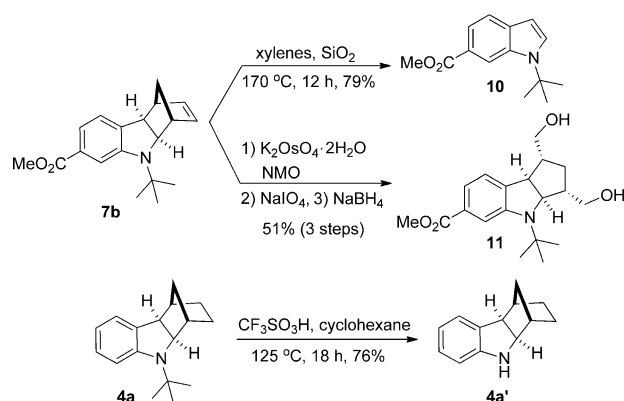


Figure 1. Indolines from other bridged olefins.

with SiO₂ in xylenes by a retro-Diels–Alder reaction, and into the tricyclic indoline **11** in 51 % yield over three steps involving dihydroxylation, oxidative diol cleavage, and reduction (Scheme 4).^[15] As shown in the case of **4a**, the removal of the *tert*-butyl group was accomplished with CF₃SO₃H/cyclohexane, thus giving the deprotected indoline **4a'** in 76 % yield (Scheme 4).



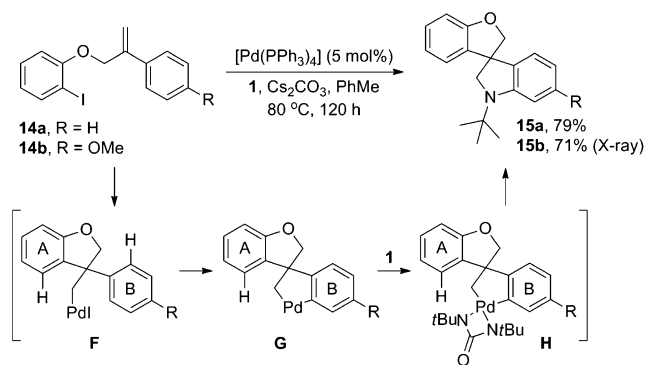
Scheme 4. Synthetic transformations of **7b** and **4a**. NMO = *N*-methylmorpholine *N*-oxide.

The intramolecular reaction process was also found to be feasible with alkene-tethered iodobenzenes.^[16] As shown in Table 3, polycyclic fused indolines (**13a–e**)^[13] were readily obtained in 62–93 % yield (entries 1–5). Iodobenzenes bearing nonbridged 1,1-disubstituted olefins were also effective substrates for the reaction (entries 2–5). When *o*-iodophenyl allyl ethers (**14**) with phenyl substituents on the olefins were subjected to the reaction conditions, the polycyclic spiroindolines **15** were obtained in 71–79 % yield (Scheme 5). In these cases, the C–H activation occurred selectively at the phenyl group **B** rather than phenyl group **A** to reduce the ring strain. The pentacyclic indoline **17** was obtained in 90 % yield when the iodobenzene **16**, containing an exocyclic olefin, was used as substrate (Scheme 6).^[17]

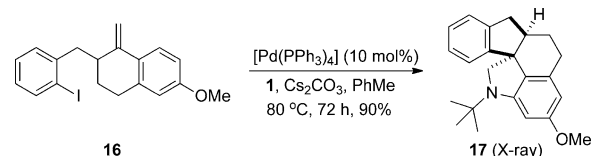
Table 3: Intramolecular process.^[a]

Entry	12	13	Yield [%] ^[b]
1			93
2			75
3			65 ^[c,d]
4			81 ^[c]
5			62 ^[c]

[a] All reactions were carried out with the iodobenzene **12** (0.30 mmol), di-*tert*-butyldiaziridine (**1**; 0.35 mmol), [Pd(PPh₃)₄] (0.015 mmol), Cs₂CO₃ (0.60 mmol), and toluene (0.30 mL) at 80 °C under Ar for 72 h unless otherwise stated. [b] Yield of the isolated product based on **12**. [c] Used 0.030 mmol of [Pd(PPh₃)₄]. [d] Reaction time, 120 h.



Scheme 5. Synthesis of the polycyclic spiroindoline **15**.



Scheme 6. Synthesis of the pentacyclic indoline **17**.

In summary, we have developed a novel palladium(0)-catalyzed Heck reaction/C–H activation/amination sequence with iodobenzenes, olefins, and di-*tert*-butyldiaziridinone (**1**), thus providing a variety of polycyclic indolines in good yields. The reaction process likely proceeds via a pallada(II)cycle, which is intercepted by the diaziridinone through oxidative addition (Scheme 3). The resulting pallada(IV)cycle is transformed into the indoline product after release of *tert*-butyl isocyanate and subsequent reductive elimination. The current work not only provides a new approach to indolines, which are contained in various biologically important molecules, but also further illustrates the versatile reactivity and synthetic utility of diaziridinone, and may open up new opportunities for the development of other reaction processes.

Experimental Section

Representative procedure for intermolecular process (Table 2, entry 1): Iodobenzene (**5a**; 0.0612 g, 0.30 mmol), norbornene (**6a**; 0.0564 g, 0.60 mmol), di-*tert*-butyldiaziridinone (**1**; 0.0595 g, 0.35 mmol), [Pd(PPh₃)₄] (0.0173 g, 0.015 mmol), Cs₂CO₃ (0.1956 g, 0.60 mmol), and toluene (0.30 mL, distilled from sodium) were added to a 1.5 mL vial equipped with a magnetic stir bar. The vial was flushed with argon for 20 s, sealed, and then immersed into an oil bath (80 °C). The reaction mixture was vigorously stirred at 80 °C for 48 h, cooled to room temperature, and purified by flash chromatography on silica gel (hexanes/ethyl acetate = 100:1) to give the indoline **4a** (0.065 g, 90 %).

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- [1] For selected examples, see: a) J. Bermudez, S. Dabbs, K. A. Joiner, F. D. King, *J. Med. Chem.* **1990**, *33*, 1929; b) J. M. Ontoria, S. D. Marco, I. Conte, M. E. D. Francesco, C. Gardelli, U. Koch, V. G. Matassa, M. Poma, C. Steinkühler, C. Volpari, S. Harper, *J. Med. Chem.* **2004**, *47*, 6443; c) A. H. Abdel-Rahman, E. M. Keshk, M. A. Hanna, Sh. M. El-Bady, *Bioorg. Med. Chem.* **2004**, *12*, 2483; d) J. M. Bentley, D. R. Adams, D. Bebbington, K. R. Benwell, M. J. Bickerdike, J. E. P. Davidson, C. E. Dawson, C. T. Dourish, M. A. J. Duncton, S. Gaur, A. R. George, P. R. Giles, R. J. Hamlyn, G. A. Kennett, A. R. Knight, C. S. Malcolm, H. L. Mansell, A. Misra, N. J. T. Monck, R. M. Pratt, K. Quirk, J. R. A. Roffey, S. P. Vickers, I. A. Cliffe, *Bioorg. Med. Chem. Lett.* **2004**, *14*, 2367; e) T. Noguchi, N. Tanaka, T. Nishimata, R. Goto, M. Hayakawa, A. Sugidachi, T. Ogawa, F. Asai, T. Ozeki, K. Fujimoto, *Chem. Pharm. Bull.* **2007**, *55*, 393; f) M. A. Rode, S. S. Rindhe, B. K. Karale, *J. Serb. Chem. Soc.* **2009**, *74*, 1377; g) R. R. Poondra, N. N. Kumar, K. Bijian, M. Prakesch, V. Campagna-Slater, A. Reayi, P. T. Reddy, A. Choudhry, M. L. Barnes, D. M. Leek, M. Daroszewska, C. Loughheed, B. Xu, M. Schapira, M. A. Alaoui-Jamali, P. Arya, *J. Comb. Chem.* **2009**, *11*, 303; h) S. C. Annedi, J. Ramnauth, S. P. Maddaford, P. Renton, S. Rakhit, G. Mladenova, P. Dove, S. Silverman, J. S. Andrews, M. D. Felice, F. Porreca, *J. Med. Chem.* **2012**, *55*, 943.
- [2] For leading reviews on the synthesis of indolines, see: a) S. Anas, H. B. Kagan, *Tetrahedron: Asymmetry* **2009**, *20*, 2193; b) D. Liu, G. Zhao, L. Xiang, *Eur. J. Org. Chem.* **2010**, 3975; c) D. Zhang, H. Song, Y. Qin, *Acc. Chem. Res.* **2011**, *44*, 447.
- [3] For leading reviews on C–N bond formation, see: a) J. F. Hartwig, *Angew. Chem.* **1998**, *110*, 2154; *Angew. Chem. Int. Ed.* **1998**, *37*, 2046; b) J. P. Wolfe, S. Wagaw, J.-F. Marcoux, S. L. Buchwald, *Acc. Chem. Res.* **1998**, *31*, 805; c) B. H. Yang, S. L. Buchwald, *J. Organomet. Chem.* **1999**, *576*, 125; d) S. V. Ley, A. W. Thomas, *Angew. Chem.* **2003**, *115*, 5558; *Angew. Chem. Int. Ed.* **2003**, *42*, 5400; e) G. Evano, N. Blanchard, M. Toumi, *Chem. Rev.* **2008**, *108*, 3054; f) S. R. Chemler, *J. Organomet. Chem.* **2011**, *696*, 150.
- [4] For recent leading reviews on C–H amination, see: a) D. N. Zalatan, J. Du Bois, *Top. Curr. Chem.* **2010**, *292*, 347; b) T. G. Driver, *Org. Biomol. Chem.* **2010**, *8*, 3831; c) S. H. Cho, J. Y. Kim, J. Kwak, S. Chang, *Chem. Soc. Rev.* **2011**, *40*, 5068; d) T. A. Ramirez, B. Zhao, Y. Shi, *Chem. Soc. Rev.* **2012**, *41*, 931; e) R. T. Gephart III, T. H. Warren, *Organometallics* **2012**, *31*, 7728; f) J. L. Roizen, M. E. Harvey, J. Du Bois, *Acc. Chem. Res.* **2012**, *45*, 911; g) L. Zhang, L. Deng, *Chin. Sci. Bull.* **2012**, *57*, 2352; h) J. L. Jeffrey, R. Sarpong, *Chem. Sci.* **2013**, *4*, 4092.
- [5] For leading references on synthesis of indolines by C(sp²)–H activation, see: a) C. E. Houlden, C. D. Bailey, J. G. Ford, M. R. Gagné, G. C. Lloyd-Jones, K. I. Booker-Milburn, *J. Am. Chem. Soc.* **2008**, *130*, 10066; b) J.-J. Li, T.-S. Mei, J.-Q. Yu, *Angew. Chem.* **2008**, *120*, 6552; *Angew. Chem. Int. Ed.* **2008**, *47*, 6452; c) M. Wasa, J.-Q. Yu, *J. Am. Chem. Soc.* **2008**, *130*, 14058; d) T.-S. Mei, X. Wang, J.-Q. Yu, *J. Am. Chem. Soc.* **2009**, *131*, 10806; e) G. He, Y. Zhao, S. Zhang, C. Lu, G. Chen, *J. Am. Chem. Soc.* **2012**, *134*, 3; f) G. He, C. Lu, Y. Zhao, W. A. Nack, G. Chen, *Org. Lett.* **2012**, *14*, 2944; g) E. T. Nades, O. Daugulis, *J. Am. Chem. Soc.* **2012**, *134*, 7; h) T.-S. Mei, D. Leow, H. Xiao, B. N. Laforteza, J.-Q. Yu, *Org. Lett.* **2013**, *15*, 3058.
- [6] For leading references on synthesis of indolines by C(sp³)–H activation, see: a) R. C. Larock, T. R. Hightower, L. A. Hasvold, K. P. Peterson, *J. Org. Chem.* **1996**, *61*, 3584; b) T. Watanabe, S. Oishi, N. Fujii, H. Ohno, *Org. Lett.* **2008**, *10*, 1759; c) J. J. Neumann, S. Rakshit, T. Dröge, F. Glorius, *Angew. Chem.* **2009**, *121*, 7024; *Angew. Chem. Int. Ed.* **2009**, *48*, 6892; d) K. Sun, R. Sachwani, K. J. Richert, T. G. Driver, *Org. Lett.* **2009**, *11*, 3598; e) S. Rousseaux, M. Davi, J. Sofack-Kreutzer, C. Pierre, C. E. Kefalidis, E. Clot, K. Fagnou, O. Baudoin, *J. Am. Chem. Soc.* **2010**, *132*, 10706; f) M. Nakanishi, D. Katayev, C. Besnard, E. P. Kündig, *Angew. Chem.* **2011**, *123*, 7576; *Angew. Chem. Int. Ed.* **2011**, *50*, 7438; g) Q. Nguyen, K. Sun, T. G. Driver, *J. Am. Chem. Soc.* **2012**, *134*, 7262; h) T. Saget, S. J. Lemouzy, N. Cramer, *Angew. Chem.* **2012**, *124*, 2281; *Angew. Chem. Int. Ed.* **2012**, *51*, 2238.
- [7] T. A. Ramirez, Q. Wang, Y. Zhu, H. Zheng, X. Peng, R. G. Cornwall, Y. Shi, *Org. Lett.* **2013**, *15*, 4210.
- [8] For leading reviews on palladacycles derived from C–H activation, see: a) G. Dyker, *Angew. Chem.* **1999**, *111*, 1808; *Angew. Chem. Int. Ed.* **1999**, *38*, 1698; b) F. Kakiuchi, N. Chatani, *Adv. Synth. Catal.* **2003**, *345*, 1077; c) M. Catellani, *Synlett* **2003**, 298; d) D. Alberico, M. E. Scott, M. Lautens, *Chem. Rev.* **2007**, *107*, 174; e) M. Catellani, E. Motti, N. Della Cá, *Acc. Chem. Res.* **2008**, *41*, 1512; f) K. Muñiz, *Angew. Chem.* **2009**, *121*, 9576; *Angew. Chem. Int. Ed.* **2009**, *48*, 9412; g) L. Ackermann, R. Vicente, A. R. Kapdi, *Angew. Chem.* **2009**, *121*, 9976; *Angew. Chem. Int. Ed.* **2009**, *48*, 9792; h) R. Jazsar, J. Hitce, A. Renaudat, J. Sofack-Kreutzer, O. Baudoin, *Chem. Eur. J.* **2010**, *16*, 2654; i) L.-M. Xu, B.-J. Li, Z. Yang, Z.-J. Shi, *Chem. Soc. Rev.* **2010**, *39*, 712; j) P. Sehnal, R. J. K. Taylor, I. J. S. Fairlamb, *Chem. Rev.* **2010**, *110*, 824; k) F. Shi, R. C. Larock, *Top. Curr. Chem.* **2010**, *292*, 123; l) L. McMurray, F. O'Hara, M. J. Gaunt, *Chem. Soc. Rev.* **2011**, *40*, 1885; m) J. Wencel-Delord, T. Dröge, F. Liu, F. Glorius, *Chem. Soc. Rev.* **2011**, *40*, 4740; n) H. C. Malinakova, *Top. Organomet. Chem.* **2011**, *35*, 85.
- [9] a) H. Du, B. Zhao, Y. Shi, *J. Am. Chem. Soc.* **2007**, *129*, 762; b) H. Du, W. Yuan, B. Zhao, Y. Shi, *J. Am. Chem. Soc.* **2007**, *129*, 7496;

- c) H. Du, W. Yuan, B. Zhao, Y. Shi, *J. Am. Chem. Soc.* **2007**, *129*, 11688; d) H. Du, B. Zhao, Y. Shi, *J. Am. Chem. Soc.* **2008**, *130*, 8590; e) B. Zhao, H. Du, S. Cui, Y. Shi, *J. Am. Chem. Soc.* **2010**, *132*, 3523.
- [10] a) M. Catellani, L. Ferioli, *Synthesis* **1996**, 769; b) M. Catellani, F. Frignani, A. Ragoni, *Angew. Chem.* **1997**, *109*, 142; *Angew. Chem. Int. Ed. Engl.* **1997**, *36*, 119.
- [11] D. I. Chai, P. Thansandote, M. Lautens, *Chem. Eur. J.* **2011**, *17*, 8175.
- [12] For leading references on indoline formation from a nickel(II)-cycle and an azide, see: a) K. Koo, G. L. Hillhouse, *Organometallics* **1995**, *14*, 4421; b) K. Koo, G. L. Hillhouse, *Organometallics* **1996**, *15*, 2669.
- [13] The stereochemistry of **8** and **13a** were tentatively assigned by analogy to **7** and **4**.
- [14] No reactions were observed when styrene and α -methylstyrene were used. It appears that the reaction might be facilitated by the strain of bicyclic olefins.
- [15] P. Thansandote, D. G. Hulcoop, M. Langer, M. Lautens, *J. Org. Chem.* **2009**, *74*, 1673.
- [16] For leading references on tandem intramolecular Heck reaction/C–H activation processes, see: a) Q. Huang, A. Fazio, G. Dai, M. A. Campo, R. C. Larock, *J. Am. Chem. Soc.* **2004**, *126*, 7460; b) R. T. Ruck, M. A. Huffman, M. M. Kim, M. Shevlin, W. V. Kandur, I. W. Davies, *Angew. Chem.* **2008**, *120*, 4789; *Angew. Chem. Int. Ed.* **2008**, *47*, 4711; c) Z. Lu, C. Hu, J. Guo, J. Li, Y. Cui, Y. Jia, *Org. Lett.* **2010**, *12*, 480.
- [17] Bridged and 1,1-disubstituted olefins were used to avoid the β -hydride elimination.