Palladium-catalyzed domino Heck/ring opening of sulfolenes/desulfitative coupling: regio- and stereoselective synthesis of alkylated conjugated dienes

Journal:	*Organic Chemistry Frontiers*
Manuscript ID	QO-RES-05-2020-000615.R2
Article Type:	Research Article
Date Submitted by the Author:	30-Jul-2020
Complete List of Authors:	Wu, Xin-Xing; Nantong University, College of Chemistry and Chemical Engineering Ye, Hao; Nantong University, College of Chemistry and Chemical Engineering Dai, Hong; Nantong University, College of Chemistry and Chemical Engineering Yang, Bing; Nantong University, College of Chemistry and Chemical Engineering Wang, Yang; Nantong University, School of Chemistry and Chemical Engineering Chen, Shufeng; Inner Mongolia University, Department of Chemistry and Chemical Engineering Hu, Lanping; Nantong University

Journal Name

ARTICLE

Received 00th January 20xx,
Accepted 00th January 20xx

DOI: 10.1039/x0xx00000x

www.rsc.org/

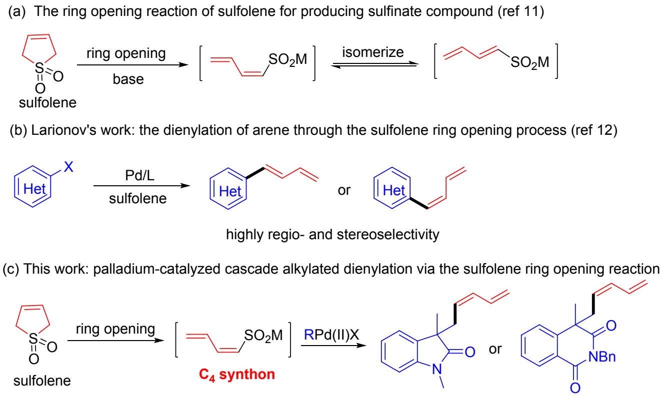
Palladium-catalyzed domino Heck/ring opening of sulfolenes/desulfitative coupling: regio- and stereoselective synthesis of alkylated conjugated dienes

Xin-Xing Wu,*[a] Hao Ye,[a] Hong Dai,[a] Bing Yang,[a] Yang Wang,[a] Shufeng Chen[b] and Lanping Hu*[a]

A novel palladium-catalyzed regio- and stereoselective dienylation via a combination of cascade carbopalladation and a subsequent desulfitative coupling after the base-induced ring opening of sulfolenes has been described. In this reaction, a range of *Z*-selective conjugated dienes bearing oxindoles or isoquinolinediones are obtained in moderate yields.

Introduction

Compounds incorporating conjugated dienes found in a wide array of both natural products and pharmaceuticals.[1] Diene motifs are important synthetic building blocks that are commonly used in chemical transformations, such as difunctionalizations,[2] hydrofunctionalizations,[3] and cycloaddition reactions.[4] In view of its important application value, great extensive effort has been devoted to developing efficient protocols for preparing conjugated diene compounds. The most common method is based on C_2 and C_2 coupling (e.g. Mizoroki-Heck reaction, Suzuki coupling reaction) through a central sigma bond formation.[5] Furthermore, reacting C_3 with C_1 synthon (e.g. Wittig-type olefination) is also an alternative approach to realize dienylation.[6] For instance, the group of Stahl developed aerobic oxidative Heck reactions for synthesis of branched conjugated dienes.[7] Engle and co-workers realized substituted 1,3-dienes via six-membered palladacycles.[8] The Wang group reported palladium-catalyzed oxidative cross-coupling to form furyl substituted conjugated dienes.[9] The Carrow group has recently made an impressive breakthrough to generate substituted 1,3-dienes and 1,3,5-trienes by a mild palladium-catalyzed aerobic coupling of boronic acids with cyclobutene.[10] However, among these established methods, the vast majority of reported methods were limited to synthesis of aryl substituted conjugated dienes, relatively few studies devoted to the synthesis of alkylated conjugated dienes. Moreover, due to the less stability than *E*-configuration, the research of conjugated dienes with *Z*-configuration is relatively rare. Therefore, efficient and convenient synthetic methods to furnish alkylated conjugated 1,3-dienes in a regio- and *Z*-stereoselective fashion need to be further developed.



Scheme 1. Synthesis of conjugated 1,3-dienes.

On the other hand, the salt of dienylsulfinic acids can be prepared through the ring opening reaction of sulfolene compounds that are stable and readily accessible from simple precursors.[11] Based on the above synthetic property, the pioneering work was reported by Larionov and co-workers to achieve palladium-catalyzed dienylation of arenes enabled by a regioselective base-induced ring opening of readily available sulfolenes.[12] However, alkylated conjugated dienylation has never been realized via a similar strategy. Inspired by previous works[13] and our research interest in domino carbopalladation reactions,[14] we envision that sulfolenes could be suitable dienylation reagents applying in transient σ-alkylpalladium(II) catalyzed domino reaction. Herein, we developed a palladium catalyzed regio- and stereoselective dienylation through an intramolecular domino cyclization/ring opening of sulfolenes/desulfitative coupling pathway to provide a range of alkylated conjugated diene compounds by introducing C_4 unit directly (Scheme 1). Notably, due to the possible isomerization of dienylsulfinate salts at higher temperatures or with catalytic amounts of base,[15] controlling the stereoselectivity of dienylation still remains a challenging task.

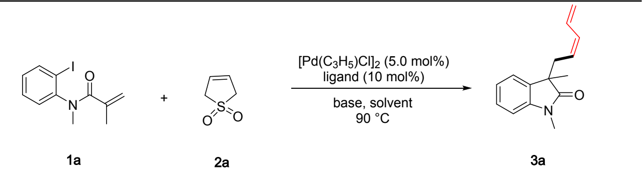
[a] College of Chemistry and Chemical Engineering, Nantong University, Nantong 226019, P. R. China
E-mail: wuxinxng@163.com; hlp@ntu.edu.cn
[b] Inner Mongolia Key Laboratory of Fine Organic Synthesis, College of Chemistry and Chemical Engineering, Inner Mongolia University, Hohhot 010021, P. R. China.

† Electronic supplementary information (ESI) available. CCDC 1975373 (**3i**). For ESI and crystallographic data in CIF or electronic format see DOI: 10.1039/c000000x/

Results and discussion

We commenced our studies using *N*-(2-iodophenyl)-*N*-methylmethacrylamide (**1a**) and 2,5-dihydrothiophene 1,1-dioxide (**2a**) for optimization of the reaction conditions (Table 1). An initial test led to the target product **3a** in 32% isolated yield and with 12:1 *Z*/*E* ratio in the presence of PPh_3 and ^tBuOK in dioxane at 90 ° C for 12 h (entry 1). The influence of the base was examined. Lower yields and diastereoselectivity were observed in the case of CH_3OK and K_2CO_3 (entries 2 and 3). Other bases, including ^tBuOLi, ^tBuONa and Cs_2CO_3, failed to give the target product. It should be noted that combination of K_2CO_3 and ^tBuOK as the base could significantly facilitate the transformation, affording the desired product 3a in 54% isolated yield with high *Z*-diastereoselectivity (>20:1, entry 4). In the following optimization, A series of ligands were also screened, and P(*p*-tolyl)$_3$ proved to be the most competent ligand providing the target product in 71% yield with >20:1(21:1) *Z*/*E* ratio (entries 5-11). Solvent screening indicated that the yields were dramatically reduced by replacing dioxane with toluene or 1,2-dichloroethane (DCE). 1,2-dimethoxyethane (DME) and trahydrofuran (THF) were also inferior to dioxane (entries 12-16). Finally, investigation of the reaction temperature showed that increasing and reducing temperature had a negative effect on the reaction (entries 17 and 18).

Table 1. Optimization of the reaction conditions[a]

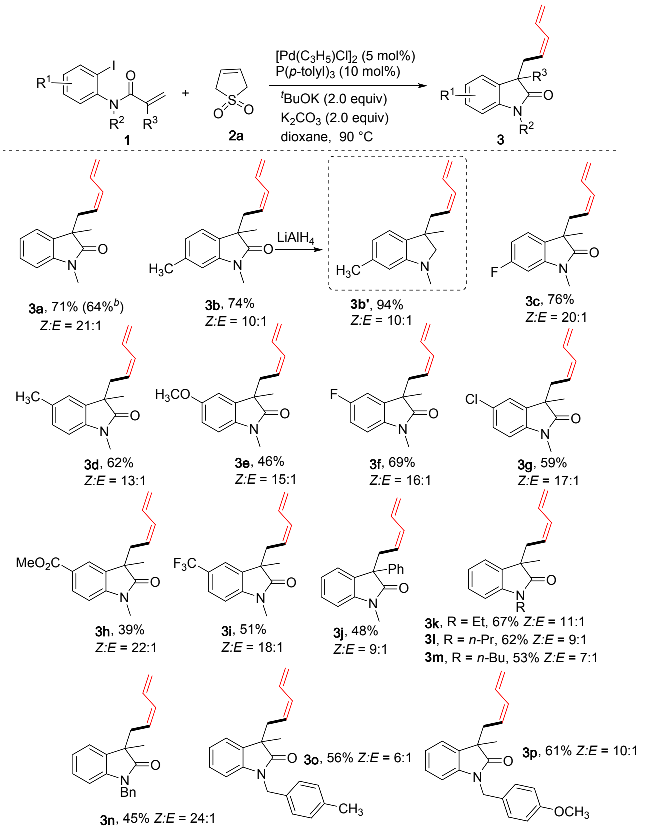


Entry	Ligand	Base	Solvent	Yield (%)	Z/E Ratio[d]
1	PPh_3	^tBuOK	dioxane	32	12:1
2	PPh_3	CH_3OK	dioxane	<10	3:1
3	PPh_3	K_2CO_3	dioxane	21	1.8:1
4	PPh_3	$^tBuOK/K_2CO_3$	dioxane	54	>20:1
5	P(2-furyl)$_3$	$^tBuOK/K_2CO_3$	dioxane	27	8:1
6	Sphos	$^tBuOK/K_2CO_3$	dioxane	<10	5:1
7	DPEphos	$^tBuOK/K_2CO_3$	dioxane	<10	3:1
8	dppb	$^tBuOK/K_2CO_3$	dioxane	19	1:1
9	P(*p*-FC$_6$H$_5$)$_3$	$^tBuOK/K_2CO_3$	dioxane	39	>20:1
10	**P(*p*-tolyl)$_3$**	**$^tBuOK/K_2CO_3$**	**dioxane**	**71**	**>20:1**
11	P(*p*-MeOC$_6$H$_5$)$_3$	$^tBuOK/K_2CO_3$	dioxane	66	>20:1
12	P(*p*-tolyl)$_3$	$^tBuOK/K_2CO_3$	MeCN	14	>20:1
13	P(*p*-tolyl)$_3$	$^tBuOK/K_2CO_3$	toluene	<10	>20:1
14	P(*p*-tolyl)$_3$	$^tBuOK/K_2CO_3$	DCE	<10	>20:1
15	P(*p*-tolyl)$_3$	$^tBuOK/K_2CO_3$	DME	55	>20:1
16	P(*p*-tolyl)$_3$	$^tBuOK/K_2CO_3$	THF	40	13:1
17[b]	P(*p*-tolyl)$_3$	$^tBuOK/K_2CO_3$	dioxane	62	>20:1
18[c]	P(*p*-tolyl)$_3$	$^tBuOK/K_2CO_3$	dioxane	58	>20:1

[a]Reaction conditions unless otherwise noted: **1a** (0.2 mmol), **2a** (0.4 mmol), $[Pd(C_3H_5)Cl]_2$ (5 mol%), ligand (10 mol%), base (0.4 mmol), solvent (2.0 mL, 0.1 M), 90 °C, 12 h under argon atmosphere conditions. [b]80 °C. [c]100 °C. [d]Determined by GC-MS.

Under the conditions established above, the substrate scope of this palladium-catalyzed intramolecular domino Heck/ring opening of sulfolenes/desulfitative coupling reaction was then investigated. As shown in Table 2. The acrylamide substrates **1b**-**1i** bearing a range of functional groups, including electron-donating groups (-Me and -OMe) and electron-withdrawing groups (-F, -Cl, -CO_2Me and -CF_3), at the different positions on the benzene ring were tested, and the corresponding products **3b**-**i** were achieved with *Z*/*E* ratio values (from 10:1 to 22:1) in 39%-76% yields. The exact structure of **3i** was further unambiguously elucidated by single crystal X-ray crystallography (see the Supporting Information)[16]. Note that 2-phenylacrylamide could also be converted to the dienylation product **3j**, albeit in a lower yield of 48% with a *Z*/*E* ratio value. Several substituents, namely Et, *n*-Pr and *n*-Bu on the nitrogen atom were also well tolerated under the optimal reaction conditions. Additionally, various *N*-benzyl groups (Bn, 4-MeBn, and 4-OCH$_3$Bn) were investigated, giving access to the desired products **3n**-**p** in 45-61% yields with moderate to high selectivity. Furthermore, synthetic transformation of **3b** in the presence of $LiAlH_4$ were explored, the reduction of product **3b'** was obtained in 94% yield. Finally, methylacrylamide **1a** (2 mmol) and sulfolene **2a** (4 mmol) were employed to examine the scability and desired product **3a** was formed in 64% yield with similar selectivity under the standard reaction conditions.

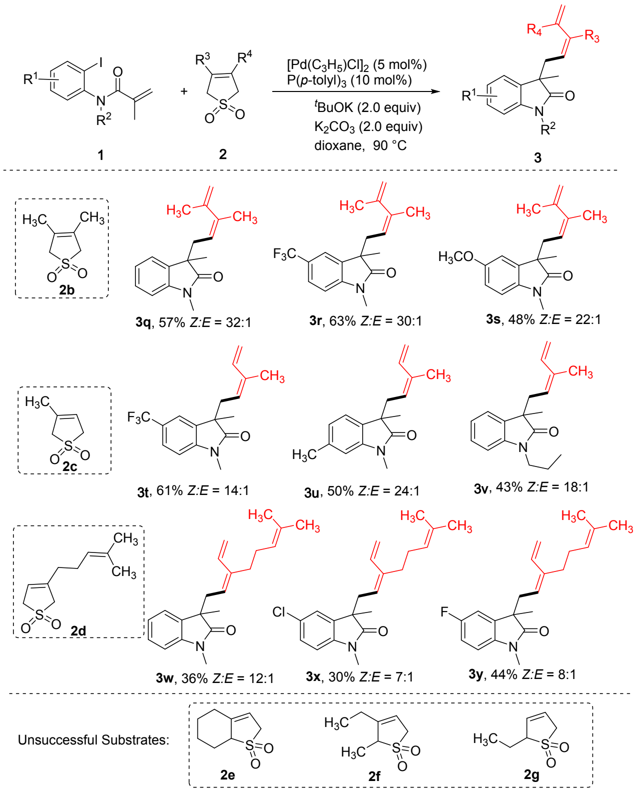
Table 2. Results of the reaction of acrylamide and sulfolene[a]



[a]Reaction conditions unless otherwise noted: **1** (0.2 mmol), **2a** (0.4 mmol), $[Pd(C_3H_5)Cl]_2$ (5 mol%), P(*p*-tolyl)$_3$ (10 mol%), K_2CO_3 (0.4 mmol), ^tBuOK (0.4 mmol), dioxane (2.0 mL, 0.1 M), 90 °C, 12 h under argon atmosphere conditions. [b]**1a** (2.0 mmol).

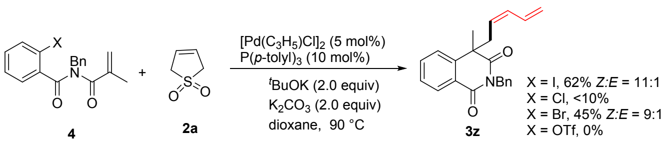
Next, the regio- and stereoselectivity of dienylation with different sulfolenes were investigated (Table 3). The desired conjugated dienes were produced in all these cases. For example, substituted conjugated dienes **3q**-**s** were produced in moderate yields and satisfactory stereoselectivity with 3,4-dimethyl sulfolene (**2b**) as substrate. Similarly, isoprene- and myrcene-derived sulfolenes (**2c** and **2d**) gave the corresponding products **3t**-**y** in acceptable yields. The *Z*-diastereoselectivity of **3q**, **3t** and **3y** were further confirmed by the NOE analysis (see the Supporting Information). Unfortunately, when performing this dienylation with substrates **2e**-**g**, all of them did not work.[17]

Table 3. Substrate scope[a]



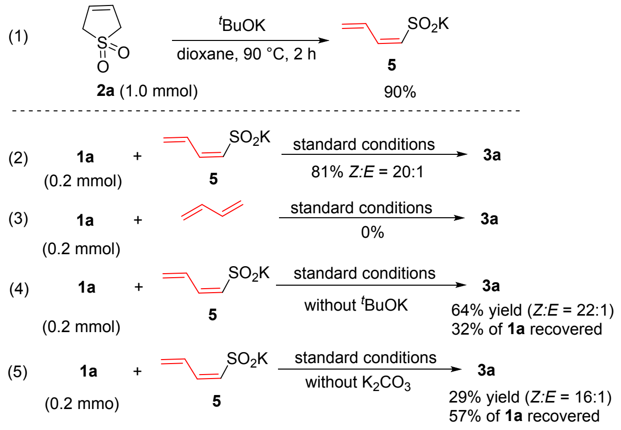
[a]Reaction conditions unless otherwise noted: **1** (0.2 mmol), **2** (0.4 mmol), $[Pd(C_3H_5)Cl]_2$ (5 mol%), P(*p*-tolyl)$_3$ (10 mol%), K_2CO_3 (0.4 mmol), ^{t}BuOK (0.4 mmol), dioxane (2.0 mL, 0.1 M), 90 °C, 12 h under argon atmosphere conditions.

To ascertain further the scope of this method, reactions with *N*-methacryloylbenzamide **4** and sulfolene **2a** was conducted under the standard conditions (Scheme 2). The conjugated dienes bearing isoquinolinedione **3z** was obtained in reasonable yield and selectivity. As a comparison, a lower yield was obtained for the reaction of aryl chloride or bromide and no product was observed when using aryltriflate as the substrate, which showed that the disconnection of C-X bonds of different substrates have a great effect on this cascade dienylation reaction.

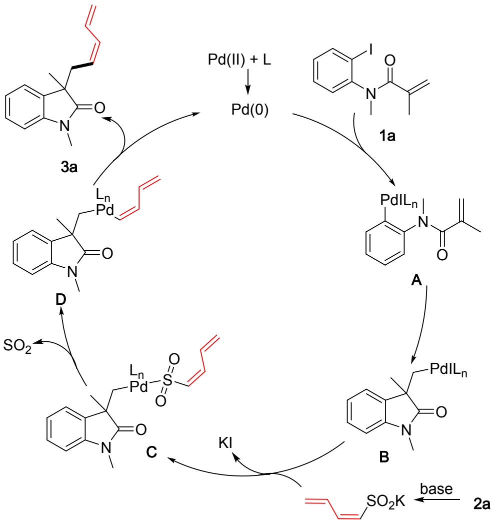


Scheme 2. Synthesis of conjugated dienes bearing iso-quinolinedione

A number of control experiments were conducted to shed light on the reaction mechanism (Scheme 3). Sulfolene **2a** can be rapid transformed into potassium sulfinate **5** in the presence of potassium *tert*-butoxide at 90 °C in dioxane. When treated **5** with acrylamide **1a** under standard reaction conditions, the target product **3a** was obtained in 81% yield with good selectivity, while no reaction was observed when 1,3-butadiene was applied. From this result, it was reasonable to infer that dienylsulfinates are the intermediates of the dienylation reaction. In additionally, without *tert*-butoxide or potassium carbonate under standard conditions, the reaction could not proceed completely and only 64% and 29% yields of **3a** were obtained, respectively. These outcomes indicate that dual-base system is crucial for the dienylation process.



Scheme 3. Mechanistic Studies.



Scheme 4. Proposed reaction mechanism.

On the basis of the above experimental results and literature reports,[18] a mechanistic pathway is proposed in Scheme 4. Oxidative addition of Pd(0) to the carbon-halogen bond followed by intramolecular carbopalladation to generate a primary $C(sp^3)$-Pd(II) species **B**. Assisted by base, the potassium dienylsulfinate generated by the ring opening of sulfolene **2a** undergoes cross-coupling with alkylpalladium **B** to afford intermediate **C**. Subsequently, The elimination of sulfur dioxide generates intermediate **D**, which undergoes reductive elimination to produce product **3a** and meanwhile regenerate Pd(0) species for the catalytic cycle.

Conclusions

In summary, we have established an efficient palladium-catalyzed domino cyclization for accessing a series of alkylated conjugated dienes. The reaction proceeds through a sequence of Heck cyclization, ring opening of sulfolenes and subsequent desulfitative coupling. Importantly, the developed dienylation method shows good regio- and stereoselectivity and compatibility of substrates. Further investigations toward exploring this type of domino reaction are still in progress in our laboratory.

Conflicts of interest

The authors declare no competing financial interest.

Acknowledgements

Generous financial support from the Program of High-level Talents (03083031) of Nantong University and the National Science Foundation (NSF 21662025) is gratefully acknowledged.

Notes and references

1 (a) *Natural Products in Medicinal Chemistry*; S. Hanessian, Ed.;Wiley-VCH: Weinheim, 2014; (b) I. H. Paik, S. J. Xie, T. A. Shapiro, T. Labonte, A. A. N. Sarjeant, A. C. Baege and G. H. Posner, Second Generation, Orally Active, Antimalarial, Artemisinin-Derived Trioxane Dimers with High Stability, Efficacy, and Anticancer Activity, *J. Med. Chem.,* 2006, **49**, 2731-2734; (c) S. D. Rychnovsky, Oxo Polyene Macrolide Antibiotics, *Chem. Rev.,* 1995, **95**, 2021-2040.

2 For selected examples: (a) S. R. Sardini and M. K. Brown, Catalyst Controlled Regiodivergent Arylboration of Dienes, *J. Am. Chem. Soc.,* 2017, **139**, 9823-9826; (b) X. Wu, H.-C. Lin, M.-L. Li, L.-L. Li, Z.-Y. Han and L.-Z. Gong, Enantioselective 1,2-Difunctionalization of Dienes Enabled by Chiral Palladium Complex-Catalyzed Cascade Arylation/Allylic Alkylation Reaction, *J. Am. Chem. Soc.,* 2015, **137**, 13476-13479; (c) Y. Huang, K. B. Smith and M. K. Brown, Copper-Catalyzed Borylacylation of Activated Alkenes with Acid Chlorides, *Angew. Chem., Int. Ed.,* 2017, **56**, 13314-13318; (d) Y. Liu, Y. Xie, H. Wang and H. Huang, Enantioselective Aminomethylamination of Conjugated Dienes with Aminals Enabled by Chiral Palladium Complex-Catalyzed C-N Bond Activation, *J. Am. Chem. Soc.,* 2016, **138**, 4314-4317; (e) G. L. J. Bar and G. C. Lloyd-Jones, Pd(II)-Catalyzed Intermolecular 1,2-Diamination of Conjugated Dienes, *J. Am. Chem. Soc.,* 2005, **127**, 7308-7309.

3 (a) Y.-Y. Gui, N. Hu, X.-W. Chen, L. L. Liao, T. Ju, J.-H. Ye, Z. Zhang, J. Li and D.-G. Yu, Highly Regio- and Enantioselective Copper-Catalyzed Reductive Hydroxymethylation of Styrenes and 1,3-Dienes with CO_2, *J. Am. Chem. Soc.,* 2017, **139**, 17011-17014; (b) V. Saini, M. O'Dair and M. S. Sigman, Synthesis of Highly Functionalized Tri- and Tetrasubstituted Alkenes via Pd-Catalyzed 1,2-Hydrovinylation of Terminal 1,3-Dienes, *J. Am. Chem. Soc.,* 2015, **137**, 608-611; (c) X. H. Yang and V.M. Dong, Rhodium-Catalyzed Hydrofunctionalization: Enantioselective Coupling of Indolines and 1,3-Dienes, *J. Am. Chem. Soc.,* 2017, **139**, 1774-1777; (d) N. J. Adamson, K. C. E. Wilbur and S. J. Malcolmson, Enantioselective Intermolecular Pd-Catalyzed Hydroalkylation of Acyclic 1,3-Dienes with Activated Pronucleophiles, *J. Am. Chem. Soc.,* 2018, **140**, 2761-2764.

4 (a) J. M. Hoyt, V. A. Schmidt, A. M. Tondreau and P. J. Chirik, Iron-Catalyzed Intermolecular [2+2] Cycloadditions of Unactivated Alkenes, *Science*, 2015, **349**, 960-963; (b) S. Kim, H. Kim, K. Um and P. H. Lee, Synthesis of Azepinoindoles via Rhodium-Catalyzed Formal Aza-[4+3] Cycloaddition Reaction of 3-Diazoindolin-2-imines with 1,3-Dienes in One-Pot, *J. Org. Chem.*, 2017, **82**, 9808-9815; (c) H. Kim, S. Kim, J. Kim, J. Y. Son, Y. Baek, K. Um and P. H. Lee, One-Pot Synthesis of Indolizines via Sequential Rhodium-Catalyzed [2+1]-Cyclopropanation, Palladium-Catalyzed Ring Expansion, and Oxidation Reactions from Pyridotriazoles and 1,3-Dienes, *Org. Lett.*, 2017, **19**, 5677-5680; (d) B. Lang, H. Zhu, C. Wang, P. Lu and Y. Wang, Rhodium-Catalyzed Cycloadditions between 3-Diazoindolin-2-imines and 1,3-Dienes, *Org. Lett.*, 2017, **19**, 1630-1633.

5 For selected examples: (a) P. Zhou, H. Jiang, L. Huang and X. Li, Acetoxypalladation of Unactivated Alkynes and Capture with Alkenes to give 1-Acetoxy-1,3-Dienes Taking Dioxygen as Terminal Oxidant, *Chem.Commun.*, 2011, **47**, 1003-1005; (b) M. Yamashita, K. Hirano, T. Satoh and M. Miura, Synthesis of α,ω-Diarylbutadienes and -Hexatrienes via Decarboxylative Coupling of Cinnamic Acids with Vinyl Bromides under Palladium Catalysis, *Org. Lett.*, 2010, **12**, 592-595; (c) A. L. Krasovskiy, S. Haley, K. Voigtritter and B. H. Lipshutz, Stereoretentive Pd-Catalyzed Kumada-Corriu Couplings of Alkenyl Halides at Room Temperature, *Org. Lett.,* 2014, **16**, 4066-4069; (d) X.-H. Hu, J. Zhang, X.-F. Yang, Y. H. Xu and T.-P. Loh, Stereo- and Chemoselective Cross-Coupling between Two Electron-Deficient Acrylates: An Efficient Route to (*Z,E*)-Muconate Derivatives, *J. Am. Chem. Soc.,* 2015, **137**, 3169-3172; (e) L. K. G. Ackerman, M. W. Lovell and D. J. Weix, Multimetallic Catalysed Cross-Coupling of Aryl Bromides with Aryl Triflates, *Nature*, 2015, **524**, 454-457;. (f) A. M. Olivares and D. J. Weix, Multimetallic Ni- and Pd-Catalyzed Cross-Electrophile Coupling To Form Highly Substituted 1,3-Dienes, *J. Am. Chem. Soc.*, 2018, **140**, 2446-2449.

6 (a) J. Barluenga, F. Rodríguez, L. Álvarez-Rodrigo and F. J. Fañanás, Zirconium-Mediated Cross-Coupling of Terminal Alkynes and Vinyl Bromides: Selective Synthesis of Cyclobutene and 1,3-Diene Derivatives, *Chem. Eur. J.*, 2004, **10**, 101-108; (b) S. F. Justyna, R. Aline, F. Adrian, W. Jędrzej, K. Maciej and P. Piotr, A highly Selective Synthesis of 1-Substituted (*E*)-Buta-1,3-Dienes with 4,4,5,5-Tetramethyl-2-Vinyl-1,3,2-Dioxaborolane as Building Block, *Appl. Organomet. Chem.*, 2014, **28**, 137-139.

7 C. Zheng, D. Wang and S. S. Stahl, Catalyst-Controlled Regioselectivity in the Synthesis of Branched Conjugated Dienes via Aerobic Oxidative Heck Reactions, *J. Am. Chem. Soc.*, 2012, **134**, 16496-16499.

8 M. Liu, P. Yang, M. K. Karunananda, Y. Wang, P. Liu and K. M. Engle, C(alkenyl)-H Activation via Six-Membered Palladacycles: Catalytic 1,3-Diene Synthesis, *J. Am. Chem. Soc.*, 2018, **140**, 5805-5813.

9 Y. Ping, S. Zhang, T. Chang and J. Wang, Palladium-Catalyzed Oxidative Cross-Coupling of Conjugated Enynones with Allylarenes: Synthesis of Furyl-Substituted 1,3-Dienes, *J. Org. Chem.*, 2019, **84**, 8275-8283.

10 N J. McAlpine, L. Wang and B P. Carrow, A Diverted Aerobic Heck Reaction Enables Selective 1,3Diene and 1,3,5-Triene Synthesis Through C-C Bond Scission, *J. Am. Chem. Soc.,* 2018, **140**, 13634-13639.

11 (a) R. C. Krug J. A. Rigney and G. R. Tichelaar, Unsaturated Cyclic Sulfones. VI. Benzylsulfonyldienes via Ring Cleavage, *J. Org. Chem.*, 1962, **27**, 1305-1309; (b) Y. S. Lee, E. K. Ryu, K.-Y. Yun and Y. H. Kim, Novel One-Pot Synthesis of Substituted 1,3-Butadiene-1-sulfonyl Chlorides from 3-Sulfolenes, *Synlett*, 1996, **1996**, 247-248; (c) Y. Gaoni, 1,3- and 1,4-Dienylic Sulfoxides by Reaction of Sulfolenes and Bicyclic Sulfones with Grignard Reagents, *Tetrahedron Lett.*, 1977, **18**, 4521-4524; (d) J.-E. Bäckvall, R. Chinchilla, C. Nájera and M. Yus, The Use of Sulfonyl 1,3-Dienes in Organic Synthesis, *Chem. Rev.*, 1998, **98**, 2291-2312; (e) N.-W. Liu, S. Liang and G. Manolikakes, Recent Advances in the Synthesis of Sulfones, *Synthesis,* 2016, **48**, 1939-1973; (f) H. T. Dang, V. T. Nguyen, V. D. Nguyen, H. D. Arman and O. V. Larionov, Efficient Synthesis of 3-Sulfolenes from Allylic Alcohols and 1,3-Dienes enabled by Sodium Metabisulfite as a Sulfur Dioxide Equivalent, *Org. Biomol. Chem.*, 2018, **16**, 3605-3609.

12 (a) V. T. Nguyen, H. T. Dang, H. H. Pham, V. D. Nguyen, C. Flores-Hansen, H. D. Arman and O. V. Larionov, Highly Regio- and Stereoselective Catalytic Synthesis of Conjugated Dienes and Polyenes *J. Am. Chem. Soc.,* 2018, **140**, 8434-8438; (b) H. T. Dang, V. T. Nguyen, H. H. Pham, H. D. Arman and O. V. Larionov, Highly Stereoselective and Catalytic Desulfitative C-O and C-I Dienylation with Sulfolenes: The Importance of Basic Additives, *Tetrahedron*, 2019, **75**, 3258-3264.

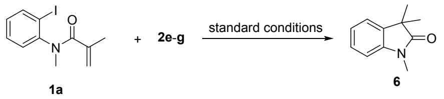
13 (a) B. Ju, S. Chen and W. Kong, Pd-Catalyzed Enantioselective Double Heck Reaction, *Org. Lett.,* 2019, **21**, 9343-9347; (b) R.-X. Liang, K. Wang, Q. Wu, W.-J. Sheng and Y.-X. Jia, Palladium-Catalyzed Dearomative Arylvinylation Reaction of Indoles with N-Arylsulfonylhydrazones, *Organometallics*, 2019, **38**, 3927-3930; (c) R.-R. Liu, T.-F. Xu, Y.-G. Wang, B. Xiang, J.-R. Gao and Y.-X. Jia, Palladium-Catalyzed Dearomative Arylalkynylation of Indoles, *Chem. Commun.*, 2016, **52**, 13664-13667; (d) C. Shen, R. Liu, R. Fan, Y. Li, T. Xu, J. Gao and Y.-X. Jia, Enantioselective Arylative Dearomatization of Indoles via Pd-Catalyzed Intramolecular Reductive Heck Reactions, *J. Am. Chem. Soc.*, 2015, **137**, 4936-4939; (e) A. D. Marchese, L. Kersting and M. Lautens, Diastereoselective Nickel-Catalyzed Carboiodination Generating Six-Membered Nitrogen-Based Heterocycles, *Org. Lett.*, 2019, **21**, 7163-7168; (f) H. Yoon, A D. Marchese and M. Lautens, Carboiodination Catalyzed by Nickel, *J. Am. Chem. Soc.*, 2018, **140**, 10950-10954; (g) W. Kong, Q. Wang and J. Zhu, Palladium-Catalyzed Enantioselective Domino Heck/Intermolecular C-H Bond Functionalization: Development and Application to the Synthesis of (+)-Esermethole, *J. Am. Chem. Soc.*, 2015, **137**, 16028-16031; (h) K. Wang, Z. Ding, Z. Zhou and W. Kong, Ni-Catalyzed Enantioselective Reductive Diarylation of Activated Alkenes by Domino Cyclization/Cross-Coupling, *J. Am. Chem. Soc.*, 2018, **140**, 12364-12368; (i) R.-X. Liang, R.-Y. Chen, C. Zhong, J.-W. Zhu, Z.-Y. Cao and Y.-X. Jia, 3,3'-Disubstituted Oxindoles Formation via Copper-Catalyzed Arylboration and Arylsilylation of Alkenes, *Org. Lett.*, 2020, **22**, 3215-3218.

14 (a) X.-X. Wu, W.-L. Chen, Y. Shen, S. Chen, P.-F. Xu and Y.-M. Liang, Palladium-Catalyzed Domino Heck/Intermolecular C-H Bond Functionalization: Efficient Synthesis of Alkylated Polyfluoroarene Derivatives, *Org. Lett.*, 2016, **18**, 1784-1787; (b) X.-X. Wu, A. Liu, S. Xu, J. He, W. Sun and S. Chen, Palladium-Catalyzed Domino Cyclization/Alkylation of Terminal Alkynes: Synthesis of Alkynyl-Functionalized Azaindoline Derivatives, *Org. Lett.*, 2018, **20**, 1538-1541; (c) X.-X. Wu, A. Liu, M. Mou, H. Chen and S. Chen, Palladium-Catalyzed Cascade Carbopalladation/Phenol Dearomatization Reaction: Construction of Diversely Functionalized Spirocarbocyclic Scaffolds, *J. Org. Chem.*, 2018, **83**, 14181-14194; (d) X.-X. Wu, H. Tian, Y. Wang, A. Liu, H. Chen, Z. Fan, X. Li and S. Chen, A Facile Approach to Synthesize Azaindoline Functionalized Spirocarbocyclic Scaffolds via a Pd-Catalyzed Cascade Cyclization/Dearomatization Process, *Org. Chem. Front.*, 2018, **5**, 3310-3314.

15 P. Gamero-Melo, M. Villanueva-García, J. Robles, R. Contreras and M. A. Paz-Sandoval, A Combined Experimental and Theoretical Study of Metallic Salts of Thiapentadienyl, Sulfinylpentadienyl and Butadienesulfonyls, *J. Organomet. Chem.*, 2005, **690**, 1379-1395.

16 CCDC 1975373 (**3i**) contains the supplementary crystallographic data for this paper. See the supplementary information for additional details.

17 When using **2e**-**g** as the substrates, no desired product was obtained, and the directing intramolecular heck reduction reaction of **1a** occurred:



18 (a) S G. Newman and M. Lautens, Palladium-Catalyzed Carboiodination of Alkenes: Carbon−Carbon Bond Formation with Retention of Reactive Functionality, *J. Am. Chem. Soc.*, 2011, **133**, 1778-1780; (b) H. Yoon, D A. Petrone and M. Lautens, Diastereoselective Palladium-Catalyzed Arylcyanation/Heteroarylcyanation of Enantioenriched N-Allylcarboxamides, *Org. Lett.*, 2014, **16**, 6420-6423.