



# Highly stereoselective and catalytic desulfitative C–O and C–I dienylation with sulfolenes: The importance of basic additives

Hang T. Dang, Viet D. Nguyen, Hoang H. Pham, Hadi D. Arman, Oleg V. Larionov\*

Department of Chemistry, The University of Texas at San Antonio, San Antonio, TX 78249, United States

## ARTICLE INFO

### Article history:

Received 1 February 2019

Received in revised form

29 March 2019

Accepted 2 April 2019

Available online 8 April 2019

### Keywords:

Cross-coupling

Desulfitation

Dienes

Palladium catalysis

Polyenes

Sulfinates

Sulfolenes

## ABSTRACT

Conjugated dienes and polyenes are central structural motifs of natural products, and key synthetic intermediates in organic synthesis and materials science. We describe herein a palladium-catalyzed dienylation of aryl, heteroaryl, and vinyl triflates, nonaflates and iodides that were previously identified as recalcitrant substrates for the sulfolene-mediated catalytic dienylation. The method has now been successfully expanded to C–O and C–I dienylation, demonstrating broad scope with respect to sulfoxides, iodides and sulfolenes. The reactions proceed with high regio- and stereoselectivity, and efficiency that are strongly influenced by basic additives, whose influence on the reaction performance was systematically studied.

© 2019 Elsevier Ltd. All rights reserved.

## 1. Introduction

Conjugated dienes play increasingly important roles in organic synthesis. The reactive diene moiety offers a plethora of opportunities for functionalization at one, two, or all four carbon atoms in a regio- and stereoselective manner, and significant efforts have recently been directed towards the development of catalytic methods of diene functionalization [1], in addition to the well-established cycloaddition approaches [2]. Conjugated dienes are also important precursors to functional materials and polymers [3]. More extended conjugated polyene units are common structural motifs of natural products, some of which have been used for treatment of infectious diseases and cancer (Fig. 1) [4]. Given the importance of conjugated dienes and polyenes, several general approaches were developed to access them, including olefination reactions with ylides [5] and transition metal-catalyzed vinylation procedures [6,7], including methods that allow for construction of dienes and polyenes in iterative fashion [8]. While these methods have significantly improved synthetic access to conjugated dienes and polyenes, a dienylation approach that takes advantage of appropriately designed four-carbon atom reagents can enable

direct installation of a dienyl unit. However, this approach would require development of a catalytic system that could control the stereoselectivity of formation of both C=C bonds in the diene unit, and the dienylation reagents have to be readily available in a variety of substitution patterns. Given these challenges, until recently, this approach remained unexplored. In 2018, our group disclosed the highly stereo- and regioselective palladium-catalyzed dienylation of aryl, heteroaryl, and vinyl chlorides and bromides with sulfolenes as four-carbon dienylation reagents (Fig. 2) [9]. The use of sulfolenes is advantageous, because they are readily accessible by means of scalable procedures in a variety of substitution patterns from simple precursors, or are industrially produced bulk chemicals [10]. The dienylation reaction is catalyzed by palladium, and the use of dppbz (1,2-bis(phenylphosphino)benzene) as a ligand is required to achieve high *E*- and *Z*-stereoselectivity. The regioselectivity of the dienylation is determined by the base-mediated ring opening of sulfolenes that is structure-dependent. For example, 2-substituted sulfolenes **1** produce 4-substituted dienesulfonates **2**, while 3-substituted sulfolenes **3** produce 2-substituted dienesulfonates **4**. The ring-opening is also highly stereoselective: *Z*-C=C bond is formed adjacent to the sulfonate group, while the distal C–C bond has the *E*-configuration. The 1*Z*-configuration predisposes the ensuing dienylation to produce 1*Z*-dienes that are indeed observed for the majority of substituted sulfinates.

\* Corresponding author.

E-mail address: [oleg.larionov@utsa.edu](mailto:oleg.larionov@utsa.edu) (O.V. Larionov).

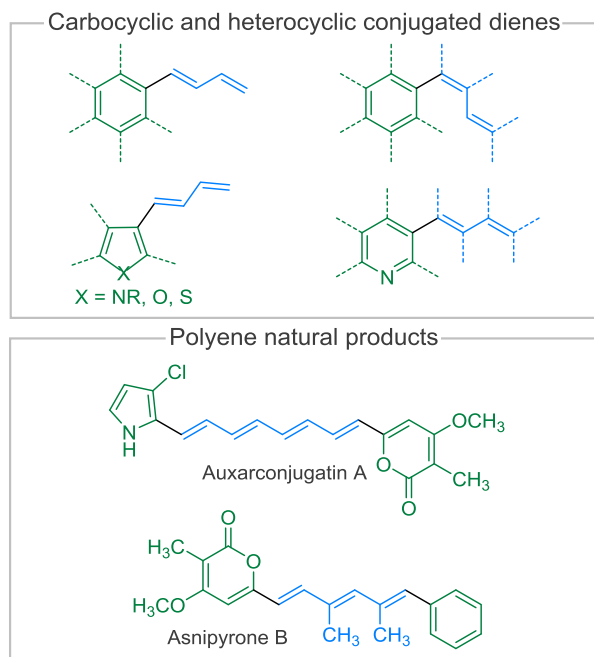


Fig. 1. Conjugated dienes and polyenes.

However, highly stereoselective formation of 1*E*-dienes was observed for some sulfolenes. These results point to the isomerization of the dienesulfinate moiety either at the stage of dienesulfinate salts **5**, or at the stage of arylpalladium(II) sulfinate intermediate **6**. Both isomerization processes can be catalyzed by basic reagents that are present in the reaction mixture, for example, potassium carbonate, as was previously shown for salts of type **5**.

Indeed, presence of potassium carbonate as a basic additive was crucial for achieving high stereoselectivity and high yields. Carbonates are known to rapidly react with sulfur dioxide [11] that is produced in the desulfitation of arylpalladium sulfinate **6** en route to arylidenepalladium **7**. The role of potassium carbonate can therefore be twofold: it can catalyze the isomerization of sulfinate salts **5** and **6**, and remove the sulfur dioxide from the reaction mixture, thus facilitating the potentially reversible desulfitation step [12].

## 2. Results and discussion

Although the dienylation reaction exhibited a broad substrate scope with respect to aryl, heteroaryl and vinyl halides, as well as various substituted sulfolenes, the reaction was incompatible with aryl triflates. For example, an attempted dienylation of triflate **8** with sulfolene **9** produced diene **10** in only 9% yield and with 1 : 1 *E*/*Z* ratio (Scheme 1). In addition, phenol **11** was formed in 49% yield, indicating that a base-mediated cleavage of the base-labile triflate group can be responsible for the incompatibility of aryl triflates.

Aryl sulfonates, particularly triflates, are key synthetic intermediates that are used to convert C(sp<sup>2</sup>)-O bonds to C-C bonds by a variety of catalytic transformations. The synthetic importance of the C(sp<sup>2</sup>)-O bond stems from the abundance of phenols among synthetic precursors of industrial and biological origin, and the ready availability of vinyl triflates from carbonyl compounds. The incompatibility of the dienylation reaction with sulfonates is, therefore, a serious impediment for its synthetic application in the areas that capitalize on the availability of efficient and stereoselective C(sp<sup>2</sup>)-O functionalization reactions, e.g., natural product synthesis and medicinal chemistry. In addition, by extending the

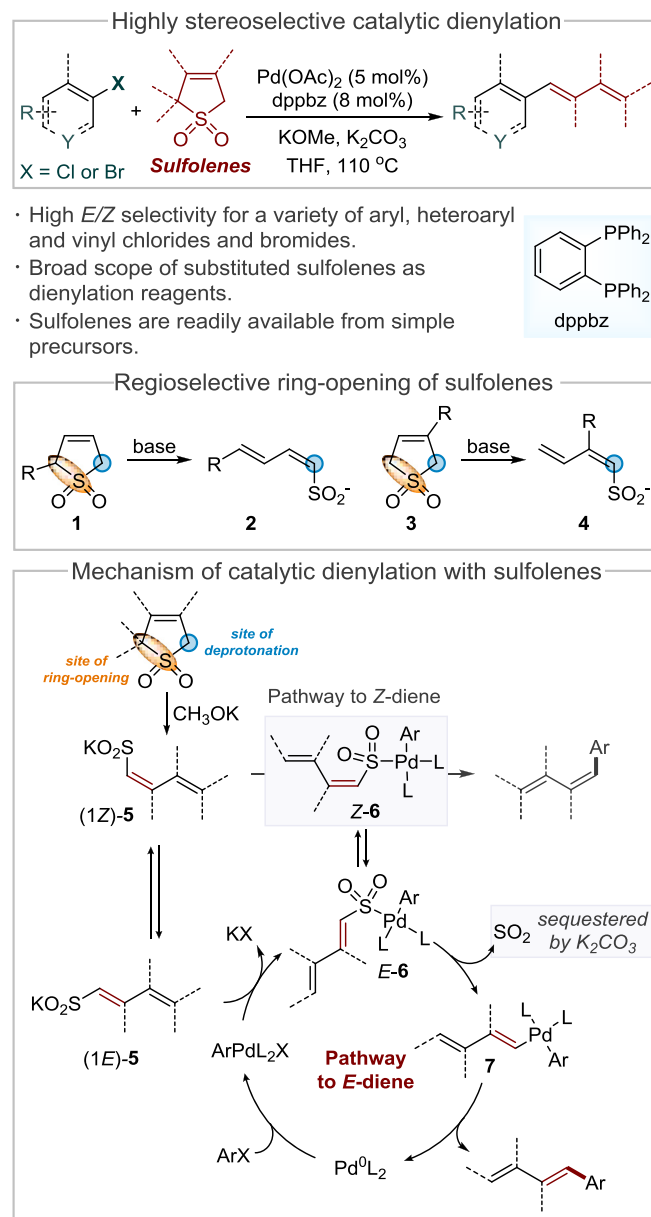
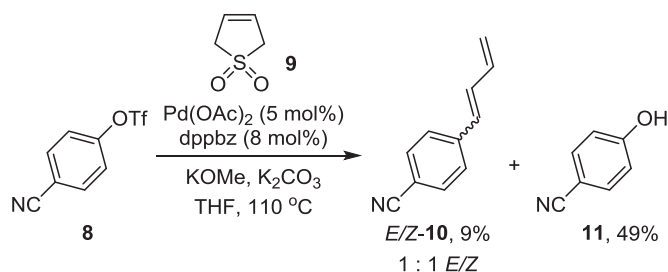


Fig. 2. Palladium-catalyzed dienylation.

scope of the dienylation reaction to these substrates, we hoped to gain better understanding of the roles of the reagents that are used in the reaction. Given that both potassium methoxide and potassium carbonate can have deleterious effects on the stability of triflate substrates, we first embarked on the study of the influence of basic additives on the stereoselectivity and efficiency of the dienylation reaction with dienesulfinate salt **12**, thus excluding potassium methoxide from the reaction mixture (Table 1). Interestingly, the reaction with potassium carbonate resulted in 84% yield of diene **10** with a 1.5 : 1 *E/Z* ratio (entry 1), confirming that the basic additive is responsible for the low stereoselectivity in THF.

This result highlights the important role that the basic additive plays in determining the stereoselectivity of the dienylation reaction. Replacement of THF with dioxane as a solvent had a detrimental effect (entry 2), favoring triflate cleavage. The reaction proceeded substantially better in toluene (entry 3), although the

Scheme 1. Attempted dienylation of triflate **8**.

**Table 1**  
Optimization of C–O dienylation<sup>a</sup>.

Entry	Basic additive	Solvent	Yield, % <sup>b</sup>	E/Z ratio
1	K <sub>2</sub> CO <sub>3</sub>	THF	84	1.5:1
2	K <sub>2</sub> CO <sub>3</sub>	Dioxane	0 <sup>c</sup>	–
3	K <sub>2</sub> CO <sub>3</sub>	Toluene	68	21:1
4	Cs <sub>2</sub> CO <sub>3</sub>	THF	13 <sup>d</sup>	>30:1
5	Li <sub>2</sub> CO <sub>3</sub>	THF	47	>30:1
6	Na <sub>2</sub> CO <sub>3</sub>	THF	92	5.7:1
7	K <sub>3</sub> PO <sub>4</sub>	THF	55	22:1
8	K <sub>2</sub> HPO <sub>4</sub>	THF	40	>30:1
9	KH <sub>2</sub> PO <sub>4</sub>	THF	49	>30:1
10	Na <sub>2</sub> HPO <sub>4</sub>	THF	35	>30:1
11	Li <sub>3</sub> PO <sub>4</sub>	THF	71	>30:1
12	KHCO <sub>3</sub>	THF	81 <sup>e</sup>	>30:1

<sup>a</sup> Reaction conditions: triflate **8** (1 mmol), sulfonate **12** (2 mmol), Pd(OAc)<sub>2</sub> (5 mol %), dppbz (8 mol %), basic additive (2 mmol), solvent (9 mL), 100 °C, 18 h.

<sup>b</sup> Determined by <sup>1</sup>H NMR spectroscopy with 1,4-dimethoxybenzene as an internal standard.

<sup>c</sup> Phenol **11** was produced in 67% yield.

<sup>d</sup> Phenol **11** was produced in 85% yield.

<sup>e</sup> Isolated yield.

stereoselectivity was not as high as for the dienylation of aryl halides. Carbonates of other alkali metals showed disparate but overall unsatisfactory performance. While low yields and high stereoselectivity were observed for cesium and lithium carbonates (entries 4 and 5), high yield and low stereoselectivity was observed for sodium carbonate (entry 6).

We then proceeded to investigate the influence of other basic salts on the reaction performance. Although the reaction with potassium phosphate afforded diene **10** in a fairly good yield, the *E*-stereoselectivity was below 30 : 1 (entry 7). On the other hand, both potassium hydrogen phosphate and dihydrogen phosphate gave rise to diene **10** with very high *E/Z* ratio, albeit at the expense of the yield (entries 8, 9). Various sodium and lithium phosphate salts were also investigated (e.g., entries 10 and 11). In both cases high stereoselectivity was observed, but the yield remained unsatisfactory. Gratifyingly, when potassium hydrogen carbonate was used, diene **10** was produced essentially as a single *E*-isomer, and in 81% yield. With this result in hand, we proceeded to test the dienylation reaction with potassium hydrogen carbonate as a basic additive and potassium methoxide as a base. Surprisingly, the reaction did not produce any dienylation product, instead affording a mixture of products of triflate cleavage and substitution with methoxide

(phenol **11** and 4-methoxybenzonitrile). This result indicated that in addition to the carbonate-induced cleavage of the triflate group, the reaction also suffered from the deleterious effects of the nucleophilicity of potassium methoxide.

Our prior experiments showed that although the methoxide-induced ring opening of sulfone **9** is completed within 10 min at 110 °C it is very slow at room temperature, thus leaving ample time for the unproductive triflate cleavage by the methoxide. On the other hand, potassium *tert*-butoxide effects a fast sulfone ring opening even at room temperature. We therefore tested the two-flask procedure, wherein sulfone **9** and potassium *tert*-butoxide were allowed to react separately at room temperature for 1 h, before being added to the reaction vessel with the catalyst. This procedure afforded diene **10** with the same high *E*-stereoselectivity and 81% yield. With this simple procedure in hand we proceeded to test the scope of the triflate dienylation with sulfone **9** (Fig. 3). A variety of products (**13–32**) bearing cyano (**10**, **13**), halogen (**14–16**), alkyl (**17**), alkylthio (**18**), methoxy (**19**), and fluorinated groups (**20**, **21**) were tolerated. Keto and ester groups (**23** and **24**) were suitable, as well bicyclic aromatic substrates (**25–27**). All substitution patterns (ortho, meta and para) were well-tolerated. Heteroaryl triflates of the pyridine and quinoline series and the estrone-derived triflate also afforded the corresponding dienes **28–33** in synthetically useful yields.

We also tested the triflate dienylation protocol with various natural product-derived vinyl triflates. Despite the pronounced propensity for polymerization, polyenes **34–37** derived from cholesterol, stigmaterol, diosgenin, and ergosterol were readily obtained from the corresponding triflates. The newly-established synthetic access to the highly air-sensitive ergosterol-derived pentaene **37** highlights the potential of the triflate dienylation procedure for preparation of polyenes. Conversion of unsaturated ketones to conjugated polyenyl triflates typically proceeds under milder conditions than conversion to the corresponding bromides. Hence, the new triflate dienylation procedure can be particularly useful for the synthesis of polyenes with labile vinyl bromide precursors.

Nonaflates (nonafluorobutanesulfonates, RONf) are cost-effective and reactive electrophiles that have found use in C–C bond-forming cross-coupling reactions and other synthetic applications [13]. Nonaflates can be readily accessed from the inexpensive and bench-stable nonafluoride (Nff), and their use can be particularly advantageous in large-scale C–O functionalization applications. We, therefore, tested the performance of a series of aryl nonaflates in the newly-developed dienylation protocol. In all of the cases, dienes **10**, **19**, **24** and **31** were produced in good yields, indicating that nonaflates are also suitable substrates for the dienylation protocol.

We further proceeded to test the triflate dienylation procedure with substituted sulfones (Fig. 4). 2,4-Substituted sulfone **38** reacted smoothly with aryl and heteroaryl triflates, producing dienes **39** and **40** with >30 : 1 stereoselectivity and in excellent yields. The dienes share the 1*Z*,2*E* configuration in line with the reactivity observed for aryl halides and as predicted by the stereo- and regiochemical model of the sulfone ring-opening process. The desulfative coupling with sulfone **38** was 1*Z*-selective. Substituted polyenes **41–42** were also prepared from stigmaterol and cholesterol-derived vinyl triflates, confirming applicability of the dienylation procedure for polyene synthesis. Estrone-derived diene **43** was also prepared in a good yield. The structure of heterocyclic diene **40** was confirmed by single crystal X-ray crystallographic analysis (Fig. 5a). Trisubstituted sulfone **44** also reacted with high stereoselectivity, affording diversely substituted 1*Z*-dienes **45–48** in good yields. Similarly, 3-substituted myrcene-derived sulfone **49** produced 1*Z*-dienes **50–52** with >30 : 1 *Z*-

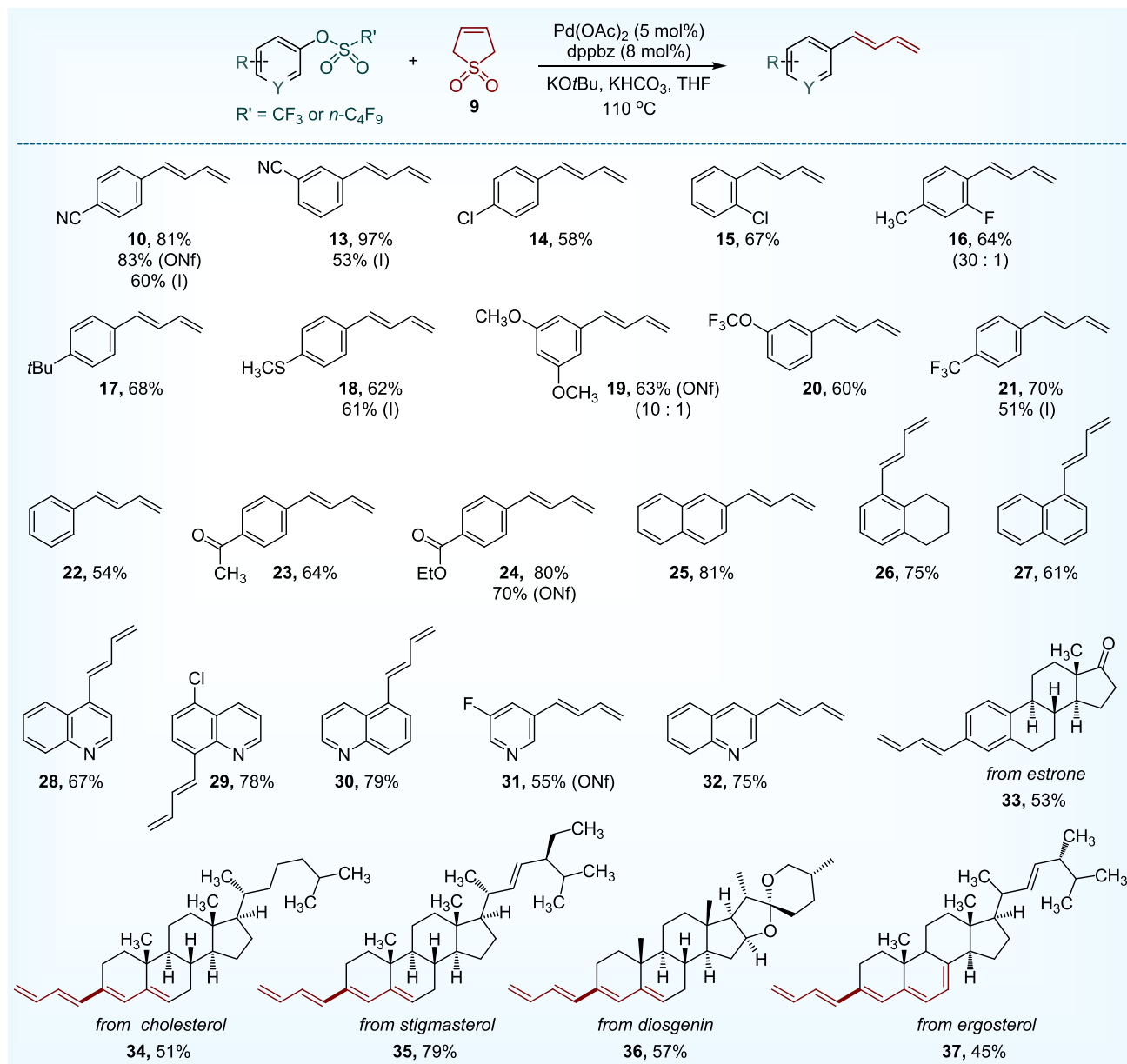
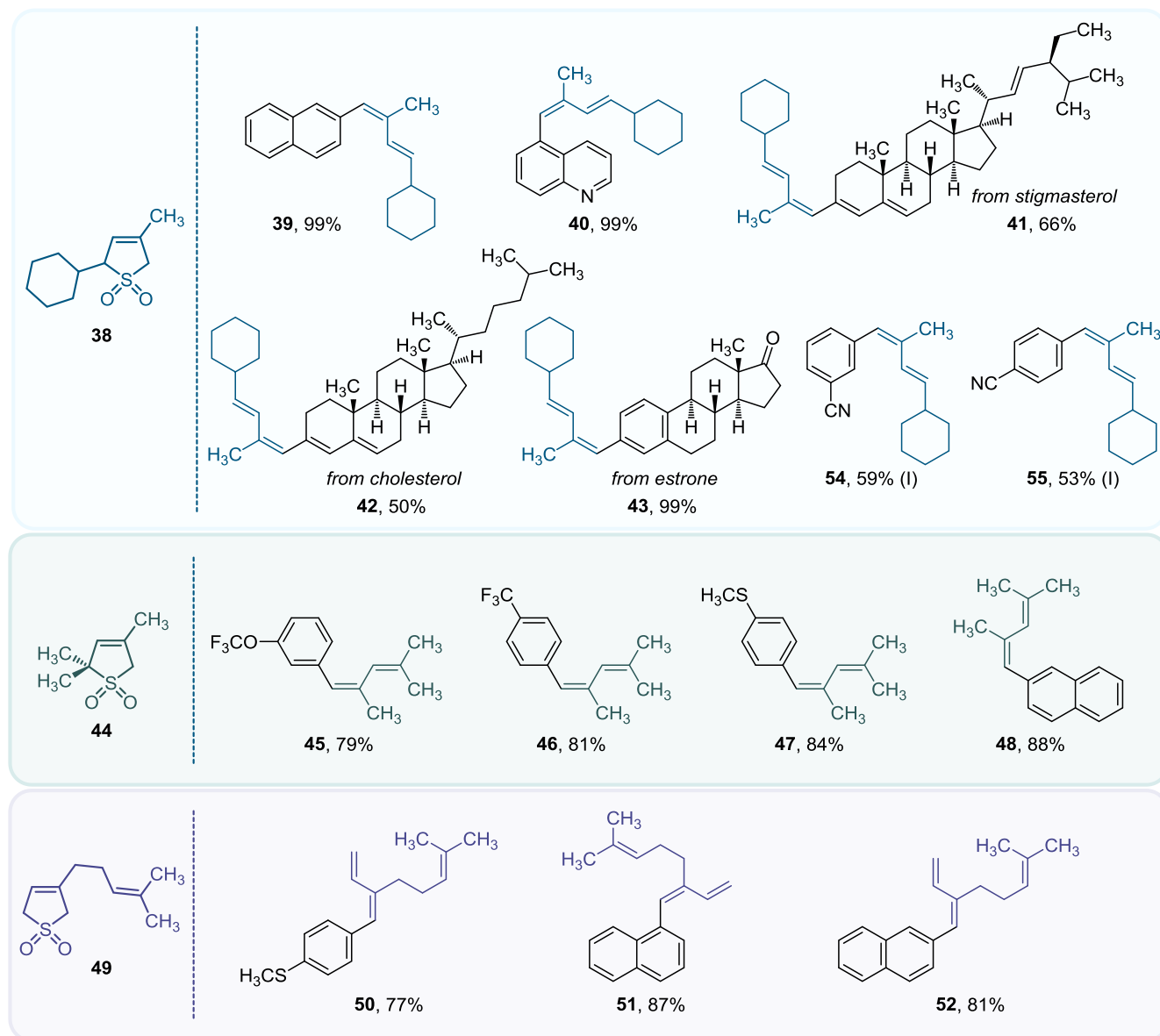


Fig. 3. Conjugated dienes and polyenes obtained with sulfolene **9**. Aryl and vinyl triflates were used, and *E/Z* ratio >30:1 unless otherwise specified.

selectivity and in good yields. The results with substituted sulfolenes **9**, **38**, **44** and **49** confirm broad scope of the triflate dienylation procedure with a variety of sulfolenes and triflates. In all of the cases, only the dienylation products were formed, and diensulfones that may be produced by a reaction of halo(hetero)arenes with diensulfate salts **5** were not observed [14]. The success of the present study hinged on identification of potassium hydrogen carbonate as a basic additive that can efficiently sequester sulfur dioxide and catalyze the *Z/E*-isomerization of the diensulfate unit (in the case of sulfolene **9**), but that is not basic enough to cleave labile aryl sulfonates. Use of strongly basic potassium *tert*-butoxide to accelerate the ring-opening of sulfolenes allowed for by-passing potassium methoxide that was also responsible for the unproductive cleavage of triflate esters.

With the catalytic dienylation of triflates and nonaflates secured, we proceeded with the study of the dienylation of iodides that were also found to be resistant to the reaction conditions

developed for bromide and chloride substrates. The behavior of the catalytic dienylation system stands in stark contrast to the majority of other palladium-catalyzed cross-coupling reactions, for which aryl iodides are typically the most reactive electrophiles [15]. Aryl iodides are less cost-effective and less readily available than aryl bromides, chlorides and sulfonates, and they are typically only used when the more readily obtainable electrophiles do not show satisfactory performance. We were, however, intrigued by the challenge of circumventing the lack of reactivity of iodides in the catalytic dienylation and endeavored to extend the scope of the dienylation reaction to  $\text{C}(\text{sp}^2)\text{--I}$  bonds. Our initial attempts to effect conversion of iodide **53** to diene **10** confirmed that alkali carbonate and phosphate salts were not suitable as basic additives for  $\text{C}\text{--I}$  dienylation (Table 2, entries 1–3). Prompted by our earlier research on Pd-catalyzed functionalization of heterocyclic *N*-oxides [16] that showed the superior performance of basic silver salts, especially with aryl iodides as electrophiles, we employed silver oxide



**Fig. 4.** Dienylation products obtained with substituted sulfolenes **38**, **44** and **49**. Aryl and vinyl triflates were used, and *E/Z* ratio >30:1 unless otherwise specified.

as a basic additive and observed a much improved catalytic performance and stereoselectivity (entry 4). Interestingly, the rate-enhancing effect was limited to silver oxide, while reactions with copper(I) oxide, as well as other basic silver salts (e.g., carbonate and phosphate) did not produce diene **10** (entries 5–7). Replacing potassium methoxide with potassium *tert*-butoxide resulted in higher stereoselectivity, albeit at the expense of lower yield. Further improvement in yield was achieved by reducing concentration of the reactants, likely due to improved mixing (entry 9). Increased loading of potassium *tert*-butoxide and sulfolene **9** further improved the yield and stereoselectivity, although, even after further optimization, the performance of the C–I dienylation could not achieve the levels of C–Br and C–O dienylation. Several aryl iodides were evaluated in the dienylation reaction with sulfolenes **9** and **38** (Figs. 3 and 4). Dienes **10**, **13**, **18**, **21** (Fig. 3) and **54**, **55** (Fig. 4) were obtained with high stereoselectivities, confirming that C–I dienylation can be used to directly access conjugated dienes from aryl iodides. The structure of diene **55** was confirmed by

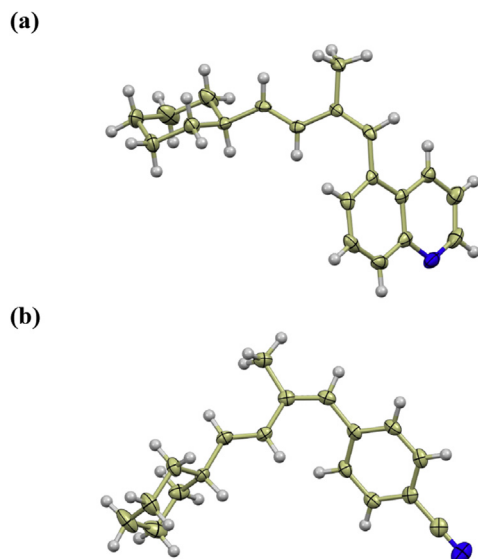
single crystal X-ray crystallographic analysis (Fig. 5b).

The beneficial role of silver oxide may be explained by facilitation of the anion metathesis en route to arylpalladium sulfinate intermediate **6** (Fig. 2) that may be sluggish in the case of the iodide.

### 3. Conclusion

In summary, we developed a simple procedure for the palladium-catalyzed, highly stereoselective dienylation of triflates, nonaflates and iodides that are not compatible with the dienylation method developed for chlorides and bromides. The new protocol allows for efficient and highly stereoselective conversion of triflates and nonaflates to substituted dienes and polyenes. The development of this protocol was enabled by a study of the influence of basic additives on the stereoselectivity and efficiency of dienylation. Potassium hydrogen carbonate was found to be the basic additive of choice for sulfonates, while silver oxide was the optimal





**Fig. 5.** X-Ray crystallographic structure of dienes **40** (a) and **55** (b) with ellipsoids shown at the 65% probability level.

**Table 2**

Optimization of C–I dienylation<sup>a</sup>.

Entry	Basic additive	Base	Yield, % <sup>b</sup>	E/Z ratio
1	K <sub>2</sub> CO <sub>3</sub>	KOMe	9%	1:1
2	K <sub>3</sub> PO <sub>4</sub>	KOMe	12%	1:1.7
3	CS <sub>2</sub> CO <sub>3</sub>	KOMe	15%	1.5:1
4	Ag <sub>2</sub> O	KOMe	59%	15:1
5	Cu <sub>2</sub> O	KOMe	—	—
6	Ag <sub>2</sub> CO <sub>3</sub>	KOMe	—	—
7	Ag <sub>3</sub> PO <sub>4</sub>	KOMe	—	—
8	Ag <sub>2</sub> O	KOrBu	45%	>30:1
9 <sup>c</sup>	Ag <sub>2</sub> O	KOrBu	55%	27:1
10 <sup>c,d</sup>	Ag <sub>2</sub> O	KOrBu	60%	>30:1

<sup>a</sup> Reaction conditions: iodide **53** (1 mmol), sulfolene **9** (2 mmol), Pd(OAc)<sub>2</sub> (5 mol %), ligand (8 mol%), base (1.6 mmol), basic additive (2 mmol), THF (10 mL), 16 h.

<sup>b</sup> Determined by <sup>1</sup>H NMR spectroscopy with 1,4-dimethoxy-benzene as an internal standard.

<sup>c</sup> 15 mL of THF was used.

<sup>d</sup> 2 equiv. of KOrBu and 2.2 equiv. of sulfolene **9** were used.

reagent for iodides. The scope of the reaction was found to encompass a variety of functional groups. Aryl, heteroaryl and vinyl triflates were readily converted to conjugated dienes and polyenes in good to excellent yields and with high regio- and stereo-selectivity. In addition, several substituted sulfolenes were successfully used as dienylation reagents, indicating that the reaction can be used to prepare substituted dienes, in particular, the more synthetically challenging Z-dienes with a variety of substitution patterns.

## Acknowledgments

Financial support by the Welch Foundation (AX-1788), the NSF

(CHE-1455061 and CHE-1625963), NIGMS (SC3GM105579), Max and Minnie Tomerlin Voelcker Fund, and the Brown Foundation is gratefully acknowledged.

## Appendix A. Supplementary data

Supplementary data to this article can be found online at <https://doi.org/10.1016/j.tet.2019.04.012>.

## References

- [1] (a) G.L.J. Bar, G.C. Lloyd-Jones, K.I. Booker-Milburn, *J. Am. Chem. Soc.* 127 (2005) 7308; (b) H. Du, B. Zhao, Y. Shi, *J. Am. Chem. Soc.* 129 (2007) 762; (c) L. Liao, R. Jana, K.B. Urkalan, M.S. Sigman, *J. Am. Chem. Soc.* 133 (2011) 5784; (d) M.A. Bohn, A. Schmidt, G. Hilt, M. Dindaroglu, H.-G. Schmalz, *Angew. Chem. Int. Ed.* 50 (2011) 9689; (e) J.C. Leung, L.M. Geary, T.-Y. Chen, J.R. Zbieg, M.J. Krische, *J. Am. Chem. Soc.* 134 (2012) 15700; (f) E. McNeill, T. Ritter, *Acc. Chem. Res.* 48 (2015) 2330; (g) Y.N. Timsina, R.K. Sharma, T.V. RajanBabu, *Chem. Sci.* 6 (2015) 3994; (h) X.-H. Yang, V.M. Dong, *J. Am. Chem. Soc.* 139 (2017) 1774; (i) S.R. Sardini, M.K. Brown, *J. Am. Chem. Soc.* 139 (2017) 9823; (j) A. Tortajada, R. Ninokata, R. Martin, *J. Am. Chem. Soc.* 140 (2018) 2050; (k) X. Wu, L.Z. Gong, *Synthesis* 51 (2019) 122.
- [2] (a) E.J. Corey, *Angew. Chem. Int. Ed.* 41 (2002) 1650; (b) F. Fringuelli, A. Taticchi, *The Diels-Alder Reaction: Selected Practical Methods*, John Wiley & Sons, Ltd, Chichester, 2002; (c) Y. Yamamoto, H. Yamamoto, *Eur. J. Org. Chem.* 9 (2006) 2031.
- [3] (a) M.D. Beery, M.K. Rath, V.V. Sheares, *Macromolecules* 34 (2001) 2469; (b) L. Li, S. Li, D. Cui, *Macromolecules* 49 (2016) 1242.
- [4] (a) S. Hanessian, *Natural Products in Medicinal Chemistry*, Wiley-VCH, Weinheim, 2014; (b) S.D. Rychnovsky, *Chem. Rev.* 95 (1995) 2021; (c) C. Thirsk, A. Whiting, *J. Chem. Soc., Perkin Trans. 1* (8) (2002) 999; (d) H. Inano, K. Suzuki, H. Ishii-Ohba, H. Yamanouchi, M. Takahashi, K. Wakabayashi, *Carcinogenesis* 14 (1993) 2157; (e) I.H. Paik, S.J. Xie, T.A. Shapiro, T. Labonte, A.A.N. Sarjeant, A.C. Baegle, G.H. Posner, *J. Med. Chem.* 49 (2006) 2731.
- [5] (a) G. Mehta, H.S. Prakash Rao (Eds.), *John Wiley & Sons, Ltd, Chichester*, 1997; (b) M. De Paolis, I. Chataigner, J. Maddaluno, *Top. Curr. Chem.* 327 (2012) 87.
- [6] (a) A.L. Hansen, J.P. Ebran, M. Ahlquist, P.O. Norrby, T. Skrydstrup, *Angew. Chem. Int. Ed.* 45 (2006) 3349; (b) E.-I. Negishi, Z. Huang, G. Wang, S. Mohan, C. Wang, H. Hattori, *Acc. Chem. Res.* 41 (2008) 1474; (c) C. Zheng, D. Wang, S.S. Stahl, *J. Am. Chem. Soc.* 134 (2012) 16496.
- [7] (a) S.L. Buchwald, R.B. Nielsen, *J. Am. Chem. Soc.* 111 (1989) 2870; (b) J. Ryan, G.C. Micalizio, *J. Am. Chem. Soc.* 128 (2006) 2764; (c) I.T. Crouch, T. Dreier, D.E. Frantz, *Angew. Chem. Int. Ed.* 50 (2011) 6128; (d) X.-H. Hu, J. Zhang, X.-F. Yang, Y.H. Xu, T.-P. Loh, *J. Am. Chem. Soc.* 137 (2015) 3169; (e) A.M. Olivares, D.J. Weix, *J. Am. Chem. Soc.* 140 (2018) 2446; (f) M. Liu, P. Yang, M.K. Karunananda, Y. Wang, P. Liu, K.M. Engle, *J. Am. Chem. Soc.* 140 (2018) 5805.
- [8] (a) S.J. Lee, K.C. Gray, J.S. Paek, M.D. Burke, *J. Am. Chem. Soc.* 130 (2008) 466; (b) S.J. Lee, T.M. Anderson, M.D. Burke, *Angew. Chem. Int. Ed.* 49 (2010) 8860; (c) E.M. Woerly, J. Roy, M.D. Burke, *Nat. Chem.* 6 (2014) 484; (d) J. Li, A.S. Grillo, M.D. Burke, *Acc. Chem. Res.* 48 (2015) 2297.
- [9] (a) V.T. Nguyen, H.T. Dang, H.H. Pham, V.D. Nguyen, C. Flores-Hansen, H.D. Arman, O.V. Larionov, *J. Am. Chem. Soc.* 140 (2018) 8434; (b) For a Pd-catalyzed dienylation with cyclobutene, see: N.J. McAlpine, L. Wang, B. Carrow, *J. Am. Chem. Soc.* 140 (2018) 13634.
- [10] (a) L. Martial, L. Bischoff, *Synlett* 26 (2015) 1225; (b) H.T. Dang, V.T. Nguyen, V.D. Nguyen, H.D. Arman, O.V. Larionov, *Org. Biomol. Chem.* 16 (2018) 3605.
- [11] (a) T.C. Keener, W.T. Davis, *JAPCA* 34 (1984) 651; (b) S. Kimura, J.M. Smith, *AIChE J.* 33 (1987) 1522; (c) E. Lippert, K. Mocek, E. Erdős, *Collect. Czechoslov. Chem. Commun.* 59 (1994) 2357.
- [12] (a) G. Pelzer, J. Herwig, W. Keim, R. Goddard, *Russ. Chem. Bull.* 47 (1998) 904; (b) S.R. Dubbaka, P. Vogel, *Angew. Chem. Int. Ed.* 44 (2005) 7674; (c) S.G. Modha, V.P. Mehta, E.V. Van der Eycken, *Chem. Soc. Rev.* 42 (2013) 5042; (d) K. Yuan, J.-F. Soule, H. Doucet, *ACS Catal.* 5 (2015) 978; (e) D.H. Ortgies, A. Hassanpour, F. Chen, S. Woo, P. Forgione, *Eur. J. Org. Chem.* 3 (2016) 408.
- [13] (a) J. Hoegermeier, H.U. Reissig, *Adv. Synth. Catal.* 351 (2009) 2747; (b) H. Vorbruggen, *Synthesis* 8 (2008) 1165; (c) R. Zimmer, M. Weibel, H.-U. Reissig, *J. Prakt. Chem.* 340 (1998) 274.
- [14] V.D. Nguyen, V.T. Nguyen, G.C. Haug, H.T. Dang, H.D. Arman, W.C. Ermler,

- O.V. Larionov, ACS Catal. (9) (2019) 4015–4024.
- [15] A. de Meijere (Ed.), Handbook of Organopalladium Chemistry for Organic Synthesis by E.-i. Negishi, John Wiley & Sons, Inc., Hoboken, 2002.
- [16] (a) D.E. Stephens, J. Lakey-Beitia, A.C. Atesin, T.A. Ateşin, G. Chavez, H.D. Arman, O.V. Larionov, ACS Catal. 5 (2015) 167;  
(b) D.E. Stephens, J. Lakey-Beitia, G. Chavez, C. Ilie, H.D. Arman, O.V. Larionov, Chem. Commun. 51 (2015) 9507;  
(c) D.E. Stephens, O.V. Larionov, Tetrahedron 71 (2015) 8683.