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Enantioselective Synthesis of Vicinal All-Carbon Quaternary Centers via Iridium-Catalyzed Allylic Alkylation

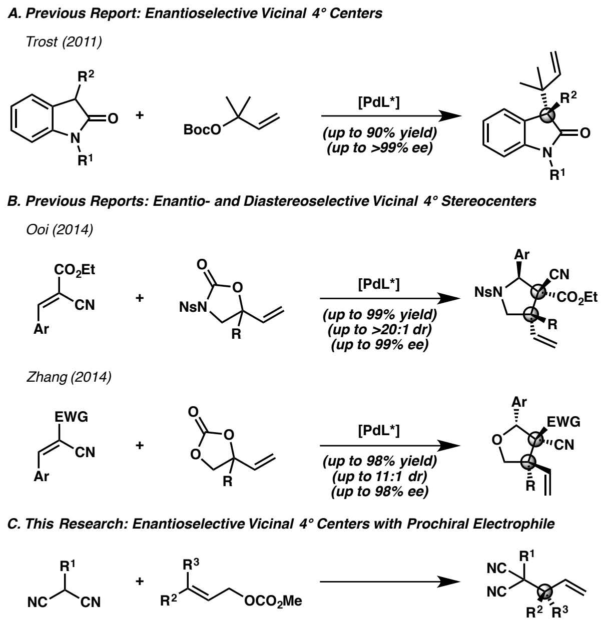
J. Caleb Hethcox,[‡] Samantha E. Shockley,[‡] and Brian M. Stoltz*

Abstract: The development of the first enantioselective transition metal-catalyzed allylic alkylation providing access to acyclic products bearing vicinal all-carbon quaternary centers is disclosed. The iridium-catalyzed allylic alkylation reaction proceeds with excellent yields and selectivities for a range of malononitrile-derived nucleophiles and trisubstituted allylic electrophiles. The utility of these sterically congested products is explored through a series of diverse chemo- and diastereoselective product transformations to afford a number of highly valuable, densely functionalized building blocks, including those containing vicinal all-carbon quaternary stereocenters.

The enantioselective preparation of singular all-carbon quaternary stereocenters has been a persistent challenge in the synthetic community and a topic of great interest to our research group.[1] However, due to significant progress in this area over recent decades,[2] the more formidable challenge of constructing vicinal all-carbon quaternary centers has become the forefront of investigation. A limited number of organic[3] and transition metal-catalyzed[4,5] methods for the enantioselective preparation of vicinal all-carbon quaternary stereocenters have been reported,[6] with enantioselective transition metal-catalyzed allylic alkylation strategies remaining underexplored.

In 2011, Trost reported an enantioselective palladium-catalyzed allylic alkylation of oxindoles to provide reverse prenylated products containing a homoallylic quaternary stereocenter vicinal to an all-carbon quaternary center (Figure 1A).[5a,b] In 2014, Ooi[5c] and Zhang[5d] each disclosed examples of enantio- and diastereoselective palladium-catalyzed allylic alkylation reactions to form cyclic products bearing vicinal all-carbon quaternary stereocenters (Figure 1B). To date, these three methods represent the only enantioselective transition metal-catalyzed allylic alkylation protocols for the synthesis of vicinal all-carbon quaternary centers[7,8] – none of these reports provide access to acyclic products.

Recently, our group reported the first iridium-catalyzed allylic alkylation method to allow for the synthesis of highly enantioenriched allylic quaternary stereocenters.[9] Given that iridium-catalyzed allylic alkylation is well known to facilitate the synthesis of vicinal stereocenters (3°/3° and 3°/4°),[10] we hypothesized that we could utilize our newly developed technology to prepare vicinal all-carbon quaternary centers, with the use of appropriately designed nucleophiles.[11] Herein, we report the first enantioselective transition metal-catalyzed allylic alkylation to form acyclic products bearing vicinal all-carbon quaternary centers (Figure 1C).


A. Previous Report: Enantioselective Vicinal 4° Centers

B. Previous Reports: Enantio- and Diastereoselective Vicinal 4° Stereocenters

C. This Research: Enantioselective Vicinal 4° Centers with Prochiral Electrophile

Figure 1. State-of-the-art in the enantioselective synthesis of vicinal all-carbon quaternary centers via transition metal-catalyzed allylic alkylation

Preliminary studies focused on identifying a suitable catalyst system to promote the reaction of nucleophile **1** and trisubstituted allylic electrophile **2** (Table 1). In designing our optimal nucleophile for the allylic alkylation reaction, we imagined that methylmalononitrile (**1**) would mimic both the acidity and steric bulk of the previously utilized masked acyl cyanide (MAC) nucleophile[9] (Figure 1C, R^1 = OMOM) as well as provide versatile functional handles for derivatizations of product **3**. We were pleased to find that our hypothesis was valid, and when utilizing our optimized conditions for the iridium-catalyzed allylic alkylation of MAC reagents[9] with nucleophile **1**, product **3** was obtained in nearly quantitative yield, though in only a moderate 73% ee (Table 1, entry 1). In an effort to improve the enantioselectivity of the transformation we investigated a range of basic additives, as bases have been reported to have a pronounced effect on selectivity in allylic alkylation reactions.[12] While addition of LiO*t*-Bu provided only a slight enhancement in enantioselectivity to 81% ee (entry 2), we were delighted to find that the amine base DABCO afforded product **3** in 92% yield and an excellent 95% ee (entry 3). At this time, the specific role of

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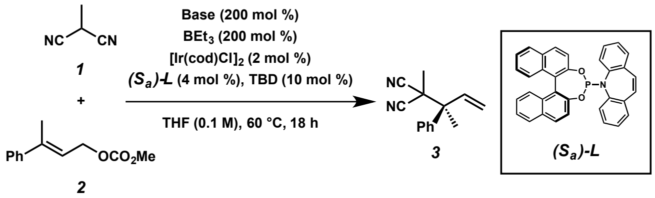
DABCO remains unknown; however, due to the additive's drastic effect on enantioselectivity, we hypothesize that DABCO allows for increased equilibration between diastereomers of an iridium π-allyl complex by slowing the rate of nucleophilic attack.[13,14] Moreover, while we observed the highest yield for the allylic alkylation reaction using a 1:2 nucleophile to electrophile ratio, the nucleophile and electrophile stoichiometry can be varied (1:1 or 2:1) without affecting reaction selectivity, though yields are diminished (entries 4 and 5).[15]

Table 1. Optimization of reaction parameters[a]

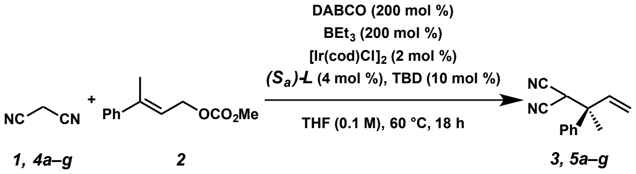


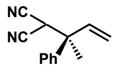
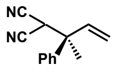
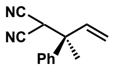
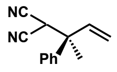
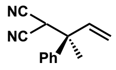
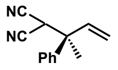
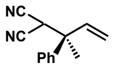
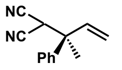
Entry	*Nuc:Elec*	Base	Yield (%)[b]	ee (%)[c]
1	1:2	–	>99	73
2	1:2	LiO*t*-Bu	>99	81
3	**1:2**	**DABCO**	**92**	**95**
4	1:1	DABCO	67	95
5	2:1	DABCO	41	94

[a] Reactions performed on 0.1 mmol scale. [b] ^{1}H NMR yield based on internal standard. [c] Determined by chiral SFC analysis. [d] TBD = 1,3,4-triazabicyclo[4.4.0]dec-5-ene, DABCO = 1,4-diazabicyclo[2.2.2]octane.

With the optimal conditions identified (Table 1, entry 3), we explored the substrate scope for this new transformation. With respect to nucleophile **4**, the process is tolerant of a wide variety of substituted malononitrile derivatives (Table 2).[16] Specifically, we were pleased to find that increasing the steric bulk on the nucleophile results in formation of the corresponding ethyl-substituted **5a** and benzyl-substituted **5b** products in only slightly decreased yields (76% and 69%, respectively) and no significant loss in enantioselectivity.[17] Interestingly, phenyl-substituted nucleophile **4c** gives full conversion to the linear product (**SI-1**)[18] in the allylic alkylation reaction rather than branched product **5c**. Additionally, olefinic substituents on the nucleophile are tolerated under the reaction conditions provided the olefin is at least di-substituted;[19] methallyl-substituted product **5d** can be prepared in 33% yield and 92% ee while prenyl-substituted product **5e** can be constructed in an excellent 92% yield with 96% ee. We reason that increased olefin substitution decreases the affinity of the olefin to bind to the catalyst,[20] thus leading to increased yields. Furthermore, we were delighted to discover that carbonyl-containing product **5f** can be obtained in a moderate 52% yield with an excellent 96% ee. However, we noted that other Lewis basic functionalities, specifically heteroaromatic substituents, are not tolerated on nucleophile **4**. Finally, fluorinated product **5g** can be accessed in a moderate 50% yield with 91% ee.

Table 2. Nucleophile substrate scope[a]

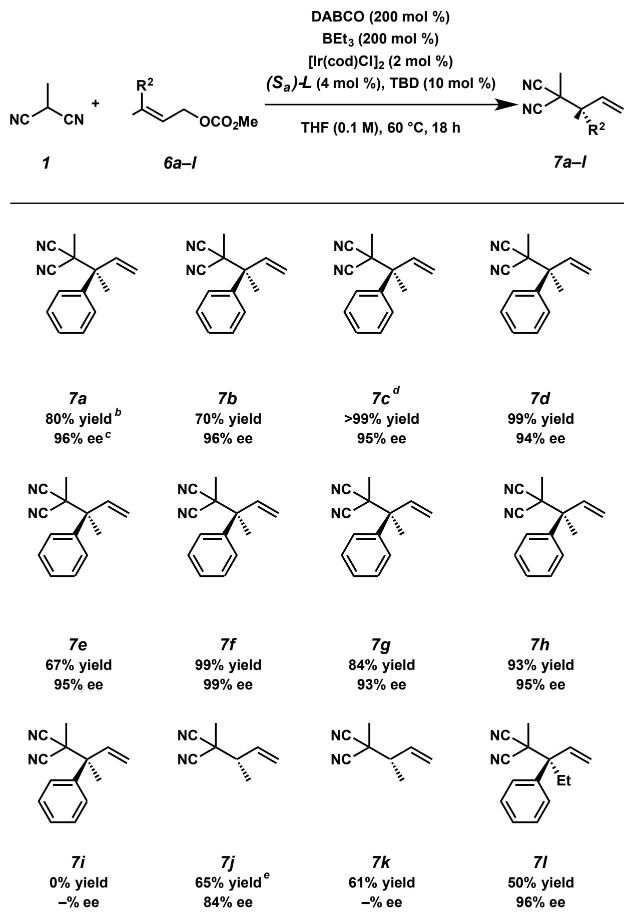


 *3* 89% yield[b] 95% ee[c]	 *5a* 76% yield 95% ee	 *5b* 69% yield 93% ee	 *5c* 0% yield[d] –% ee
 *5d* 33% yield 92% ee	 *5e* 92% yield 96% ee	 *5f* 52% yield 96% ee	 *5g* 50% yield 91% ee

[a] Reactions performed on 0.2 mmol scale. [b] Isolated yield. [c] Determined by chiral SFC. [d] 99% conversion by ^{1}H NMR to linear product **SI-1**.

Pleased to find the reaction amenable to a range of nucleophilic substrates, we sought to further examine the scope of the transformation by exploring the diversity of substitution permitted on trisubstituted allylic electrophile **6** (Table 3). Gratifyingly, we observed that a series of *para*-substituted allylic electrophiles bearing both electron-donating (–*p*-Me, –*p*-OMe) and withdrawing groups (–*p*-Ph, –*p*-F) on the aromatic ring furnish the corresponding products **7a–d** in consistently excellent enantioselectivities (>94% ee) when subjected to the reaction conditions utilizing methylmalononitrile (**1**) as the nucleophile. In evaluating the effect of *meta*-substitution, we found that products **7e–h** (–*m*-Me, –*m*-Cl, –*m*-NO_2, 2-Np) can be obtained with similarly high enantiocontrol (>93% ee). Generally, we noted that electron-rich electrophiles (i.e., **6a**, **6b**, **6e**) provide the corresponding allylic alkylation products in slightly diminished yields (67–80% versus 84–99%) as compared to electron-poor electrophiles (i.e., **6c**, **6d**, **6f**, **6g**). At this time, *ortho*-substitution (i.e., –*o*-Me) is not tolerated under the reaction conditions and no conversion to product **7i** is observed. However, we were pleased to discover that the reaction is amenable to bis-alkyl-substitution on the allylic electrophile allowing for access to product **7j** in 65% yield and 84% ee, though as an inseparable mixture (1:1.5) of branched and linear isomers. Additionally, reverse prenylation can be effected to produce achiral product **7k** in 61% yield. Finally, extension of the alkyl chain on the allylic electrophile to an ethyl group leads to a decreased yield with **7l** isolated in 50% yield but with no loss in selectivity (96% ee).

Table 3. Electrophile substrate scope[a]



[a] Reactions performed on 0.2 mmol scale. [b] Isolated yield. [c] Determined by chiral HPLC or SFC. [d] Absolute stereochemistry determined by single-crystal X-ray analysis; the absolute stereochemistry of all other compounds was assigned by analogy. [e] Combined isolated yield of inseparable linear and branched products (1:1.5 ratio).

With the general reactivity trends for the allylic alkylation reaction explored, we sought to demonstrate the utility of these sterically congested products (Figure 2). Though hydrogenation of the olefin in allylic alkylation product **3** using palladium catalysis proved problematic due to competing reduction of the nitrile groups, we found that treatment of **3** with Wilkinson's catalyst under a hydrogen atmosphere chemoselectively reduces the olefin to furnish **8** in 92% yield. Additionally, ozonolysis of olefin **3** proceeds smoothly to give enantioenriched aldehyde **9** in 93% yield,[21] wherein the aldehyde moiety can serve as a valuable functional handle for further manipulation (e.g., reductive aminations, allylations, and olefinations). Allylic alkylation product **5f** was subjected to a two-step ozonolysis/aldol condensation process to deliver a densely functionalized, enantioenriched cyclopentene in 43% yield, which can then undergo diastereoselective hydration of the bis-nitrile functionality to provide amide **10** in 1:11 dr. Chiral cyclopentenes have been demonstrated to be key building blocks in a number of complex molecule total syntheses.[22] Finally, enantioenriched lactone **11** bearing vicinal all-carbon quaternary stereocenters can be accessed in 65% yield and 1:2.5 dr from allylic alkylation product **3** via ozonolysis followed by reductive quenching. The transformations forming products **10** and **11** showcase that the diastereotopic nitrile functionalities of the allylic alkylation products are amenable to diastereoselective differentiation to afford vicinal all-carbon quaternary stereocenters, which are otherwise difficult to prepare.

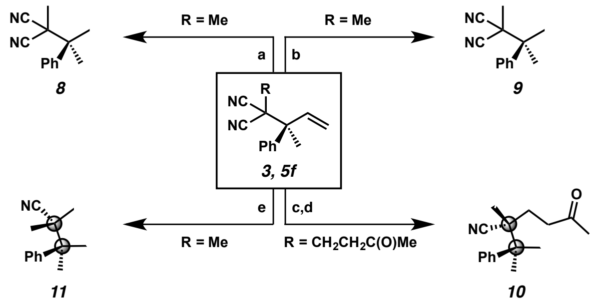


Figure 2. (a) $RhCl(PPh_3)_3$, H_2 (balloon), benzene, 23 °C, 18 h, 92% yield; (b) O_3, pyridine, CH_2Cl_2, –78 °C, 4 min, 93% yield; (c) i. O_3, pyridine, CH_2Cl_2, –78 °C, 4 min, ii. *p*-TsOH, benzene, reflux, 18 h, 47% yield; (d) NaOH, $EtOH/H_2O$ (1:1), 60 °C, 18 h, 38% yield. 1:11 dr; (e) i. O_3, MeOH, –78 °C, 0.5 h, ii. $NaBH_4$, 0 °C, 3 h, 65% yield, 1:2.5 dr.

In conclusion, we have developed the first enantioselective transition metal-catalyzed allylic alkylation reaction for the preparation of acyclic products bearing vicinal all-carbon quaternary centers. Key to the success of this new reaction is the use of DABCO in combination with triethylborane and our unique catalyst prepared from $[Ir(cod)Cl]_2$, (*S*$_a$)-**L**, and TBD. The developed method proceeds with moderate to excellent yields and high levels of enantioselectivity for a wide range of substitution on both the malononitrile-derived nucleophile and the trisubstituted allylic electrophile. Furthermore, the allylic alkylation products can be transformed by chemo- and diastereoselective methods to a number of highly valuable, densely functionalized building blocks, including those containing vicinal all-carbon quaternary stereocenters. Further exploration of this catalyst system is underway and will be reported in due course.

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Keywords: allylic alkylation • quaternary stereocenter • vicinal all-carbon quaternary centers • enantioselective synthesis • iridium

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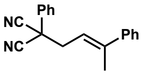
[15] Excess electrophile is unable to be quantitatively recovered as a competing elimination reaction takes place to form a diene byproduct.

[16] To date, only functionalized malononitrile nucleophiles have been successfully utilized in the reported allylic alkylation reaction, despite studies into other bis-electron-withdrawing group-functionalized nucleophiles (e.g., malonates and 1,3-diketones).

[17] Branched substitution is not tolerated in the allylic alkylation reaction as isopropyl-substituted **4** returns only starting material.

[18] Linear product (SI-1):



[19] Allyl-substituted **4** returns only starting material.

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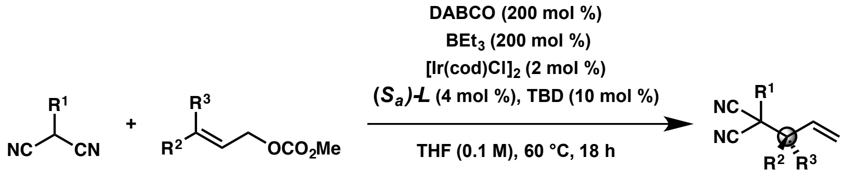

Enantioenriched Vicinal All-Carbon Quaternary Centers

High enantioselectivities (up to 99%) · High yields (up to 99%)

Won't you be my neighbor: The first enantioselective transition metal-catalyzed allylic alkylation providing access to acyclic products bearing vicinal all-carbon quaternary centers has been developed. The iridium-catalyzed reaction proceeds with excellent yields and selectivities for a range of malononitrile-derived nucleophiles and trisubstituted allylic electrophiles. The utility of these sterically congested products is explored through a series of diverse chemoselective and diastereoselective product transformations to afford a number of highly valuable, densely functionalized building blocks, including those containing vicinal all-carbon quaternary stereocenters.

*J. Caleb Hethcox,[‡] Samantha E. Shockley,[‡] and Brian M. Stoltz**

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Enantioselective Synthesis of Vicinal All-Carbon Quaternary Centers via Iridium-Catalyzed Allylic Alkylation