

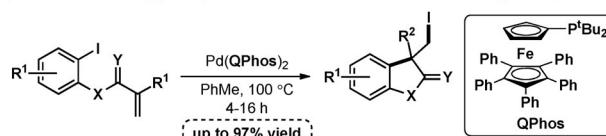
Additive Effects in the Palladium-Catalyzed Carboiodination of Chiral *N*-Allyl Carboxamides**

David A. Petrone, Hyung Yoon, Harald Weinstabl, and Mark Lautens*

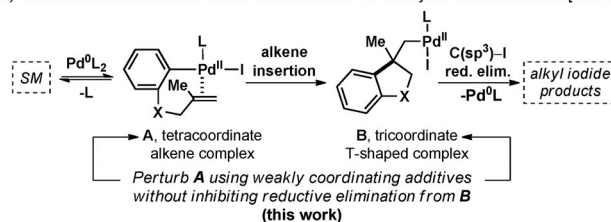
Abstract: The use of Pd catalysis as a means to synthesize organic halides has recently received increased attention. Among the reported methods is the Pd-catalyzed carboiodination, which uses extremely bulky ligands to facilitate carbon–halogen reductive elimination from Pd^{II} as the key catalytic step. When approaching substrates exhibiting low stereoselectivity, catalyst troubleshooting becomes difficult as there are few ligands known to promote the key reductive elimination. Herein, we present our finding that tertiary amines act as weakly coordinating ligands which significantly enhance diastereoselectivity in the Pd/QPhos-catalyzed carboiodination of chiral *N*-allyl carboxamides. This methodology allows efficient access to enantioenriched and densely functionalized dihydroisoquinolinones, and has been applied toward the asymmetric formal synthesis of (+)-corynoline.

We have been investigating the synthetic potential of reversible oxidative addition^[1] in catalytic processes since our first report in 2010.^[2a] Our group subsequently developed an olefin carboiodination process^[3] by reacting an aryl iodide containing a tethered alkene in the presence of sterically hindered ligands and a palladium catalyst (Scheme 1a).^[2b] Tong et al. found similar reactivity with alkenyl iodides containing tethered alkenes using palladium and a large excess of a bidentate ligand.^[2c] We have broadened the scope of the carboiodination process by demonstrating that aryl bromides could serve as precursors in the presence of added iodide,^[2d] and investigated the selective carboiodination of polyhalogenated starting materials.^[2e] Diastereoselective processes were also probed by studying substrates with pre-existing stereocenters. All of these studies employ QPhos or

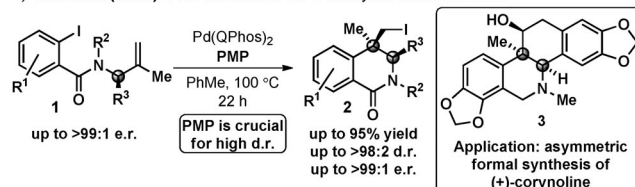
a) Lautens 2011: Pd(0)-catalyzed intramolecular olefin carboiodination [Ref. 2a]



b) Lautens and Houk 2012: On the mechanism of Pd-catalyzed carboiodination [Ref. 3]



c) This work (cont.): PMP as additive in Pd-catalyzed carboiodination



Scheme 1. Development of Pd⁰-catalyzed alkene carboiodination. SM = starting material; L = QPhos.

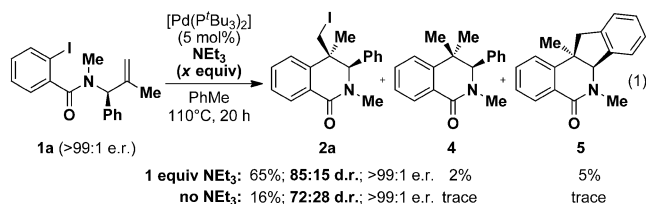
PrBu₃ as ligands. A computational study undertaken with Houk found that ArI oxidative addition occurs from a four-coordinate ArPd^{II}I species **A** which contains a single phosphine ligand and a bound olefin. Alkene insertion ensues to form T-shaped tricoordinate species **B**, which undergoes turnover-limiting reductive elimination to form the desired alkyl iodide (Scheme 1b). The use of less bulky phosphines leads to tetracoordinate Pd species, which fail to undergo reductive elimination.^[4] In substrates which give lower selectivity, a dilemma arises when seeking to improve the diastereoselectivity of carbopalladation, since there is currently a limited number of suitable bulky phosphines that trigger the necessary reductive elimination. The ligands found to promote high selectivity during alkene insertion (**A** to **B**) were found to be significantly different than those needed to go from **B** to the final product. Herein, we report a solution to this dilemma by using weakly binding amine additives^[5] in the diastereoselective synthesis of enantioenriched dihydroquinolinones^[5] from chiral *N*-allyl carboxamides. The optimal amine (1,2,2,6,6-pentamethylpiperidine, PMP) has the correct balance of enhancing diastereoselectivity and chemoselectivity while only minimally reducing the reaction rate (Scheme 1c). This highly stereoselective transformation was required for our asymmetric formal synthesis of (+)-corynoline **3**,^[7–10] a member of the phenanthridine alkaloids.

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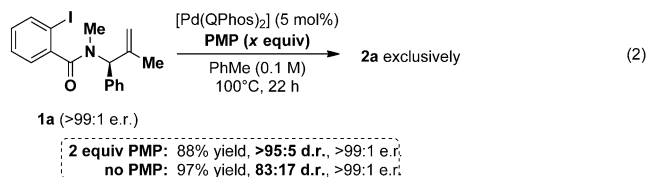
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Our study commenced by preparing enantioenriched *N*-allyl carboxamide **1a** (>99:1)^[10] by a 5-step route employing Ellman's auxiliary in order to test the subsequent carboiodination. When **1a** was subjected to the previously developed conditions of [Pd(PtBu₃)₂] (5 mol %) and NEt₃ (1 equiv)^[12] in PhMe (0.05 M) at 110 °C,^[2e] **2** was obtained in 65 % yield with 85:15 d.r. (**2a:2a'**) and no erosion of e.r. Two by-products in **4** (2 %) and **5** (5 %) were observed which likely form by a reduction of the Pd^{II} species resulting from alkene insertion,^[13] or a C–H functionalization of the aromatic ring oriented *cis* to this species,^[14] respectively. In the absence of amine base the yield and diastereoselectivity of **2a** decreased to 16 % and 72:28, respectively, when using this catalyst [Eq. (1)]. After screening various reaction parameters, the



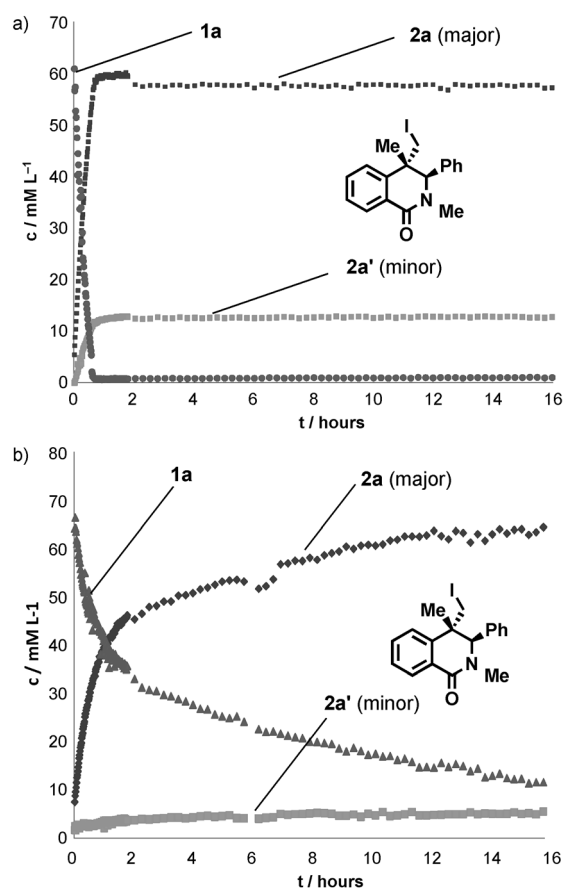
optimal conditions were found to be [Pd(QPhos)₂] (5 mol %) and PMP (2 equiv) in PhMe (0.1 M), at 100 °C for 22 h.^[15] Under these conditions, **2a** was isolated in 88 % yield with >95:5 d.r., whereas in the absence of PMP, **2a** was afforded in 97 % yield with 83:17 d.r. [Eq. (2)]. The positive influence of



amine base addition on the selectivity became clear and was general across a series of tertiary amines, however, PMP provided superior yields and selectivities.

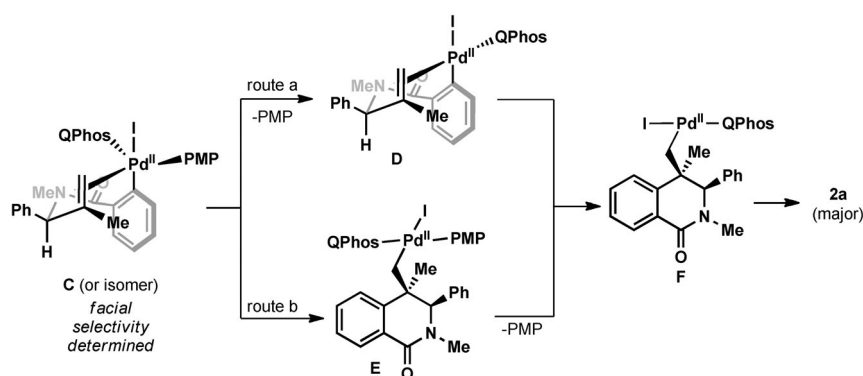
One possible explanation for the change in d.r. is the selective decomposition under the reaction conditions, but this proved to not be the case. Alternatively, the bulky and basic tertiary amine PMP^[16] may alter the geometry of the active catalyst by weak coordination, thus making the carbopalladation more selective. We believed that a deeper understanding of these results could be gained by in situ NMR reaction monitoring (Scheme 2).^[15,17] Therein, we found that the reaction had reached full conversion after 35 min in the absence of PMP (Scheme 2a), whereas ca. 60 % conversion had been reached after the same time frame in the presence of PMP (Scheme 2b). The possibility of selective decomposition was contradicted by observing the consistent production of both diastereomers with no observable diminution of yield. Conversely, these experiments support the notion of amine coordination, as its presence attenuates the overall reaction rate, while imparting nearly a fivefold increase in selectivity.

Based on earlier studies,^[18] the facial selectivity of olefin coordination, and subsequent carbopalladation will deter-



Scheme 2. In situ reaction monitoring for the intramolecular carboiodination of **1a**. a) Reaction conditions: Pd(QPhos)₂ (0.05 equiv), [1a]₀ = 0.1 M, [D₈]PhMe, 368 K, 600 MHz. b) Reaction conditions: Pd(QPhos)₂ (0.05 equiv), PMP (2 equiv), [1a]₀ = 0.1 M, [PMP] = 0.2 M, [D₈]PhMe, 368 K, 600 MHz.

mine the diastereoselectivity.^[19] Therefore, it appears that the added amine is interacting with the catalyst in this step. However, in order to have all three substrate-derived ligands (aryl, halide, and alkene) as well as both, QPhos and PMP, bound during this step, a pentacoordinate Pd^{II} intermediate would need to exist,^[20] and olefin insertion reactions of pentacoordinate Pd^{II} species are energetically unfavorable.^[21] Overman reported that a pentacoordinate Pd^{II} intermediate undergoes associative ionization to form a cationic tetracoordinate Pd^{II}-BINAP species in polar solvents like DMA during the asymmetric Heck reaction.^[22] However, our use of a nonpolar solvent (PhMe) casts a level of doubt on a similar cationic process occurring here. Mikami et al. reported that either four- or five-coordinate species can undergo carbopalladation during Pd^{II}-catalyzed cyclization of 1,6-enynes, when a polar (DMSO) or nonpolar solvent (PhH) is used, respectively.^[23] Two options are: 1) an associative mechanism involving olefin-assisted ligand dissociation of **C**, thereby creating a neutral four-coordinate species **D** which undergoes carbopalladation (Scheme 3, route a), or 2) a neutral five-coordinate complex containing both, QPhos and PMP, ligands directly undergoes olefin carbopalladation to form **E** (Scheme 3, route b). Both routes ultimately lead to a tricoor-



Scheme 3. Possible fates of the proposed pentacoordinate $\text{ArPd}^{\text{II}}\text{X}$ -olefin intermediate **C**.

dinate neopentyl Pd^{II} complex **F** which undergoes reductive elimination to form product.

The effect of added amine on the d.r. was explored for a variety of substrates and was found to provide a straightforward route to dihydroisoquinolinones (Table 1). In all cases, enantioenriched carboxamides (**1a–o**) were cyclized to the corresponding products (**2a–o**) with no erosion of e.r. Furthermore, either starting material enantiomer is accessible with nearly complete enantioenrichment. For instance, *ent*-**1a** was prepared and reacted to give *ent*-**2a** in 90% yield with > 95:5 d.r. Electron-rich aryl iodides (**1b–c**, **1g**) participated under the standard reaction conditions to provide the desired dihydroisoquinolinones (**2b–c**, **2g**) in good yields (82 to 88%) and selectivities (93:7 to 94:6 d.r.). Electron-deficient aryl iodides **1d** and **1e** underwent cyclization to the corresponding products **2d** and **2e** with identical levels of selectivity (97:3 d.r.) in 54% and 76% yields, respectively. The former required a 7.5 mol% [Pd] to avoid a sluggish and low yielding reaction. When the N-protecting group on nitrogen was converted from Me to Bn (**1h–j**), the highest selectivities were observed (> 98:2) with comparable product yields (87–95%) in substrates possessing an allylic aromatic group (**2h–j**). Substitution on the noniodinated aromatic ring appeared to have no serious deleterious effects on yield, and **1k** and **1l** were efficiently cyclized to the desired products (**2k** and **2l**) in 76% and 82% yield with 93:7 and 94:6 d.r., respectively.

PMB ether **1m** was efficiently cyclized to the corresponding orthogonally protected product **2m** in 91% yield with 80:20 d.r. Ether **2m** could be deprotected using DDQ to afford alcohol **6**, which underwent smooth cyclization to pyrano-fused tricycle **7** (Scheme 4). When **1f** containing an N-Bz group was subjected to the reaction conditions using 7.5 mol% [Pd], the corresponding product **2f** was obtained in 61% yield after 48 h, albeit with a decreased diastereoselectivity of 65:35 d.r. Finally, the robustness of this reaction was highlighted by highly electron-rich substrates **1n** and **1o** undergoing cyclization to the corresponding products **2n** and **2o** in 84% and 91% yield with 92:8 and 87:13 d.r., respectively, when 7.5 mol% [Pd] was used. It should be noted that products arising from β -hydrogen elimination were isolated exclusively when starting materials containing mono-substituted olefins were employed.^[15]

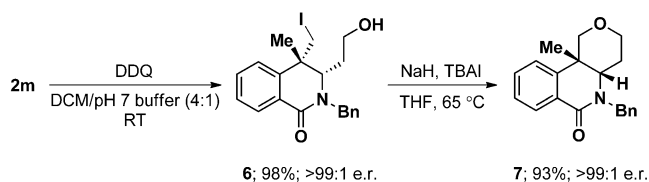
This methodology was used to achieve the asymmetric formal synthesis of (+)-corynoline **3** (Scheme 5). Hexacycle **3** has exhibited diverse pharmacological effects including inhibition of cell adhesion^[8a] and acetylcholinesterase,^[8b] as well as fungi- and cytotoxicity,^[8c] yet only a limited number of total syntheses of this molecule have been reported.^[9,10] We achieved the diastereoselective carbiodination of **1n** on a 5 gram scale under slightly modified conditions,^[15] to afford **2n** in 84% yield in 91:9 d.r.

Cyanide displacement of the hindered neopentyl iodide afforded nitrile **8** in 67% yield, which was not susceptible to

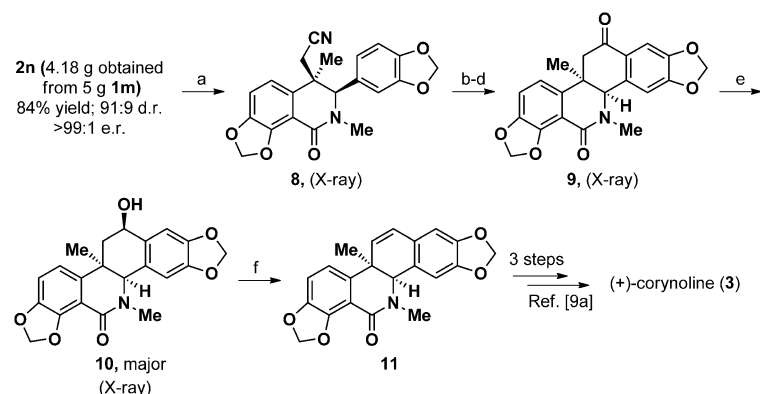
Table 1: Reaction scope.^[a–d]

	R = H; 88% yield; >95:5 d.r.; >99:1 e.r. (2a) ^[e] 5-Me ; 88% yield; 94:6 d.r.; >99:1 e.r. (2b) 4,5-OMe ; 82% yield; 93:7 d.r.; >99:1 e.r. (2c) 4,5-F ; 54% yield; 97:3 d.r.; >99:1 e.r. (2d) ^[f] 4-Cl ; 76% yield; 97:3 d.r.; >99:1 e.r. (2e)
	2g , 82% yield 94:6 d.r.; >99:1 e.r.
	2h 95% yield 98:2 d.r.; >99:1 e.r.
	R = F; 87% yield; 98:2 d.r.; >99:1 e.r. (2i) OMe ; 90% yield; 98:2 d.r.; >99:1 e.r. (2j)
	R ¹ =R ² =OMe 76% yield; 93:7 d.r.; >99:1 e.r. (2k) R ¹ =Cl; R ² =H; 82% yield; 94:6 d.r.; >99:1 e.r. (2l)
	2m , 91% yield 80:20 d.r.; >99:1 e.r.
	2n , 84% yield ^[f] 92:8 d.r.; >99:1 e.r.
	X-ray structure of 2n
	2o , 69% yield 90:10 d.r.; 87:13 d.r.; >99:1 e.r.

[a] 0.2 mmol scale. [b] All yields shown are yields of the combined isolated diastereomers. [c] D.r. values determined by ¹H NMR analysis of the crude reaction mixture. [d] E.r. values determined by HPLC using a chiral stationary phase. [e] 7.5 mol% [Pd(QPhos)₂], PMP (3.5 equiv). [f] The reaction was run for 48 h. [g] Both diastereomers were found to be present in > 99:1 e.r.



Scheme 4. Synthesis of fused pyran **6** from **2l**. DDQ: 2,3-dichloro-5,6-dicyano-1,4-benzochinone; TBAI: tetrabutylammonium iodide.



Scheme 5. Asymmetric formal synthesis of **3**. Reaction conditions: a) KCN (7.5 equiv), 18-C-6 (7.5 equiv), DMF, 100 °C, 67%; b) DIBAL (4 equiv), DCM, -78 °C, 51%; c) NaOCl₂ (10 equiv), NaH₂PO₄ (8.4 equiv), 2-methyl-2-butene (15 equiv), tBuOH:H₂O, 0 °C, 79%; d) Eaton's Reagent (neat), 0 °C, 66%; e) NaBH₄ (10 equiv), MeOH:THF, 0 °C, 91% (95:5 d.r.); f) NEt₃ (30 equiv), MsCl (15 equiv), DCM, 0 °C, 99%.

the desired acid in 40% after two steps, which was transformed to the fused polycyclic ketone **9** by using Eaton's reagent under conditions developed by Cushman.^[9b] Diastereoselective reduction of **9** afforded benzylic alcohol **10** in 91% yield as a 95:5 mixture of diastereomers, which were eliminated to the corresponding *cis*-alkene **11** in 99% yield using MsCl/NEt₃. Alkene **11** intersects Naito's racemic synthesis which provides access to the natural product in three steps.^[9a]

In conclusion, we have developed a diastereoselective Pd⁰-catalyzed carboiodination of enantioenriched *N*-allyl carboxamides which allows convenient access to enantioenriched dihydroisoquinolinones. We have found that added PMP significantly increases the diastereoselectivity of this transformation. On the basis of this finding, the involvement of a pentacoordinate palladium species during selectivity-determining carbopalladation has been proposed. In all examples good to excellent yields and diastereoselectivities are obtained under these conditions. Finally, we have applied this methodology to the asymmetric formal synthesis of (+)-corynoline which represents the first application of the carboiodination methodology towards the synthesis of a natural product. Studies regarding the mechanism of this effect are ongoing in our laboratory and will be reported in due course.

Experimental Section

A dry 2 dram vial was charged with **1b** (81.0 mg, 0.2 mmol, 1 equiv) and [Pd(QPhos)₂] (15.3 mg, 0.01 mmol, 5 mol %), and purged with argon. The contents of the vial were taken up in PhMe (2 mL), and PMP (72.4 μL, 0.4 mmol, 2 equiv) was added to the mixture. The reaction vial was fitted with a Teflon lined screw cap, sealed with Teflon tape, and placed into a preheated oil bath (100 °C). After 22 h the reaction was cooled, filtered through a short pad of silica gel eluting with EtOAc, and concentrated. The d.r. was determined by ¹H NMR analysis of the crude reaction mixture, which was subsequently purified by silica gel flash column chromatography using hexanes/EtOAc (3:1 v/v) as the mobile phase to give **2b** as a white solid (71.6 mg, 0.177 mmol, 88%).

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