Asymmetric Catalysis

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Palladium-Catalyzed Asymmetric Allylic Allylation of Racemic Morita–Baylis–Hillman Adducts

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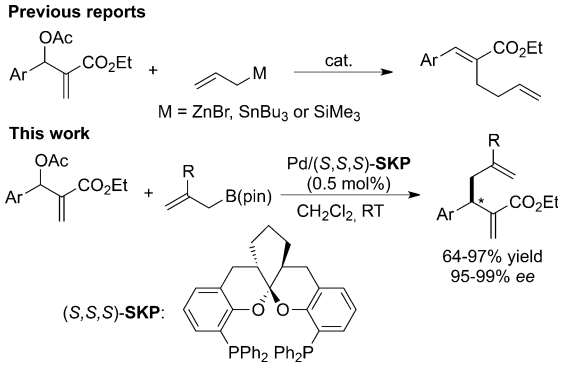
Abstract: *A palladium-catalyzed asymmetric allyl–allyl cross-coupling of acetates of racemic Morita–Baylis–Hillman adducts and allylB(pin) has been developed using a spiroketal-based bis(phosphine) as the chiral ligand, thus affording a series of chiral 1,5-dienes bearing a vinylic ester functionality in good yields, high branched regioselectivities, and uniformly excellent enantioselectivities (95–99% ee). Further synthetic manipulations of the allylation products provided novel ways for rapid access to a range of chiral polycyclic lactones and polycyclic lactams, as well as the antidepressant drug (−)-Paroxetine, in high optical purities.*

Transition metal catalyzed asymmetric allylic substitution reactions play an important role in modern organic synthesis.[1] Of great value is the allylic allylation, often through cross-coupling[2] of an allylmetal reagent and an allyl electrophile to give 1,5-dienes which are versatile synthetic intermediates.[3] A breakthrough in the field of asymmetric allyl–allyl cross-coupling was made in 2010, when Morken and co-workers reported the reaction of allylic carbonates with allyl boronates in the presence of a chiral diphospine/palladium catalyst, to provide the branched chiral 1,5-dienes with high regio- and enantioselectivities.[4] Feringa and co-workers later reported a phosphoramidite/Cu catalyst for asymmetric synthesis of branched chiral 1,5-dienes from allylic bromides and allyl Grignard reagents.[5] Very recently, Carreira and co-workers disclosed first examples on the enantioselective cross-coupling reactions of racemic branched allylic alcohols with allylsilanes and 1,1-disubstituted terminal alkenes using an Ir/(P,olefin) complex.[6] Despite the fact that Morita–Baylis–Hillman (MBH) adducts, a type of functionalized allylic compounds, have been widely used in numerous synthetic applications,[7] thus far their allyl–allyl cross-coupling reactions invariably afford achiral linear products,[8] and the corresponding asymmetric version has not yet been realized. Herein we report the first example of the enantioselective allylic allylation of acetates of MBH adducts using the palladium complex of a spiroketal-based chiral diphosphine (SKP)[9,10] as the catalyst. The resultant densely functionalized chiral 1,5-dienes turned out to be a versatile synthetic handle for a number of important transformations.



The study was inspired by our recent disclosure of the unique bifunctional role of spiroketal-based bis(phosphine) ligand (SKP) for the control of regioselectivity in palladium-catalyzed asymmetric allylic aminations of acetates of MBH adducts.[11,12] The initial attempts using either allyl stannanes or allyl silianes to react with the acetates of the MBH adducts in the presence of a Pd/SKP catalyst system did not afford any desired allyl–allyl cross-coupling products (see the Supporting Information). Gratifyingly, allylic pinacolatoboronate, [allylB(pin)] (**2a**), proved to be an effective nucleophile for allyl–allyl cross-coupling with the MBH adduct acetate **1a** (see Table 1). A preliminary survey of reaction parameters for SKP/[$Pd_2(dba)_3$]-catalyzed cross-coupling of **1a** and allyl-B(pin) revealed that the reaction was best performed in dichloromethane at room temperature for 17 hours with CsF as an additive, thereby affording the branched allylation product **3a** in 92% yield with excellent chemo-, regio-, and enantioselectivities (B/L = 92:8, 97% *ee*; see the Supporting Information). Under the optimized reaction conditions, the impact of the palladium precursors and chiral ligands on the outcomes of the cross-coupling were further evaluated and the results are summarized in Table 1. While the reactivity and/or the branched/linear regioselectivity (**3a**/**4a**) varied significantly from case to case, excellent *ee* values (96–97%) of the branched product **3a** were attained using the (*S*,*S*,*S*)-SKP series of ligands (entries 1–4). In contrast, (*R*)-furyl-BIPHEP, which performed well in Morken's catalyst system,[4] provided moderate enantioselectivity (60% *ee*) albeit with high branched regioselectivity (**3a**/**4a** = 92:8; entry 5). Unfortunately, several privileged chiral ligands[13] such as (*R*)-BINAP, (*R*)-SDP, and (*R*,*R*)-Trost ligand, only afforded unsatisfactory results (entry 6–8). With (*S*,*S*,*S*)-SKP as the ligand, use of other palladium salts, for example,

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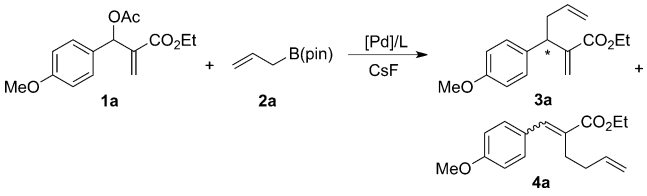
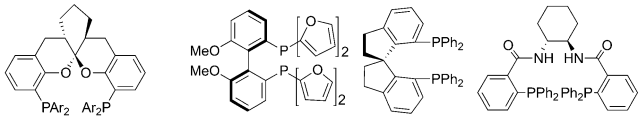
Table 1: Catalyst survey for asymmetric allyl–allyl cross-coupling of **1a** with allylB(pin).[a]



	Pd salt (mol%)	Ligand[b]	**3a**/**4a**[c]	Yield [%][d]	*ee* [%][e]
1	$[Pd_2(dba)_3]$ (1)	SKP	92:8	92	97
2	$[Pd_2(dba)_3]$ (1)	*o*-Tol-SKP	20:80	13	97
3	$[Pd_2(dba)_3]$ (1)	*p*-Tol-SKP	>20:1	19	97
4	$[Pd_2(dba)_3]$ (1)	xyl-SKP	88:12	41	96
5	$[Pd_2(dba)_3]$ (1)	furyl-BIPHEP	92:8	76	60
6	$[Pd_2(dba)_3]$ (1)	BINAP	92:8	85	25
7	$[Pd_2(dba)_3]$ (1)	Trost ligand	66:34	60	15
8	$[Pd_2(dba)_3]$ (1)	SDP	87:13	12	52
9	$[\{Pd(C_3H_5)Cl\}_2]$ (1)	SKP	92:8	91	97
10	$Pd(OAc)_2$(2)	SKP	90:10	90	96
11	$[Pd(CH_3CN)_2Cl_2]$ (2)	SKP	94:6	94	94
12	$PdCl_2$(2)	SKP	79:21	12	–
13	$[Pd_2(dba)_3]$ (0.5)	SKP	92:8	72	97
14	$[Pd_2(dba)_3]$ (0.2)	SKP	87:13	61	97
15	$[\{Pd(C_3H_5)Cl\}_2]$ (0.5)	SKP	92:8	91	97
16	$[\{Pd(C_3H_5)Cl\}_2]$ (0.2)	SKP	89:11	33	97

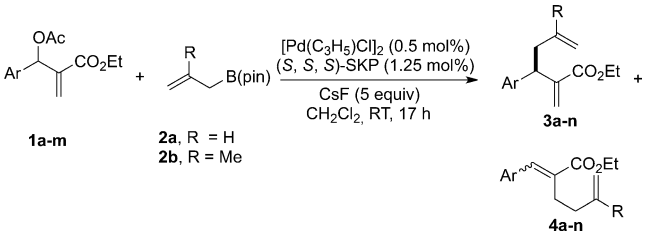
[a] Unless otherwise noted, all reactions were performed with **1a** (0.2 mmol), **2a** (0.24 mmol), CsF (1.0 mmol), and the specified catalyst in CH_2Cl_2 (2.5 mL) at RT for 17 h. [b] In each case, the ligand loading was 1.25 molar equiv relative to that of Pd. [c] Determined by ^{1}H NMR spectroscopy. [d] Yield of the isolated **3a** and **4a**. [e] The *ee* value of **3a** was determined by HPLC on a chiral stationary phase. dba = dibenzylideneacetone.

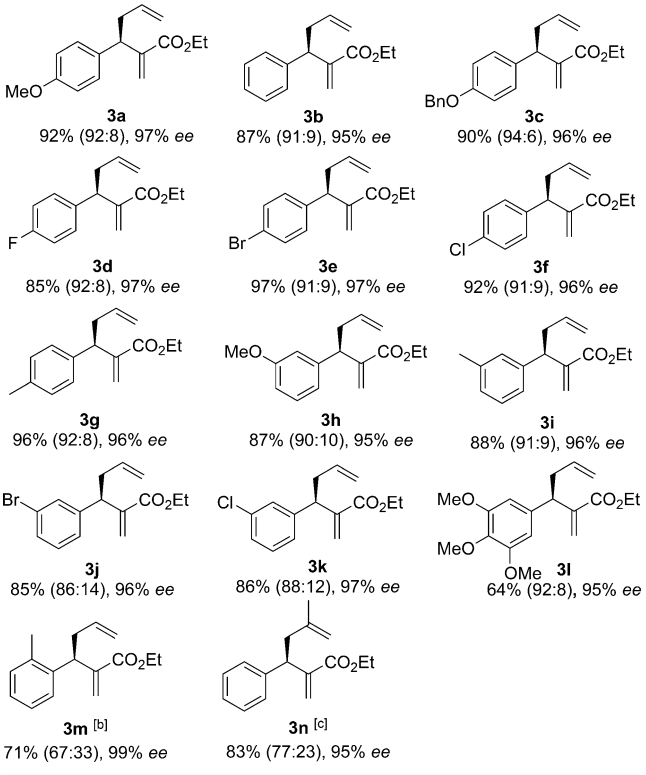


$[Pd(\eta^3\text{-}C_3H_5)Cl]_2$, $Pd(OAc)_2$, or $[Pd(CH_3CN)_2Cl_2]$, as catalyst precursors also delivered excellent results, mostly comparable to those of $[Pd_2(dba)_3]$ (entries 9–11 versus 1), except for the case using $PdCl_2$ (entry 12). Further trials to lower the catalyst loadings were thus performed using either $[\{Pd(\eta^3\text{-}C_3H_5)Cl\}_2]$ or $[Pd_2(dba)_3]$ along with a SKP ligand as the catalyst, and $[\{Pd(\eta^3\text{-}C_3H_5)Cl\}_2]$ turned out to be superior in this context (entries 15 and 16 versus 13 and 14).

With the optimized reaction conditions in hand, we proceeded to examine the reaction scope, and the results are summarized in Table 2. By using the unsubstituted allylboronate **2a** as the nucleophile, both electron-donating and electron-withdrawing groups on the phenyl rings of MBH adducts **1a**–**m** were well tolerated, and the corresponding cross-coupling products **3a**–**m** were obtained in good yield with consistently excellent enantioselectivities (95–99% *ee*). The branched/linear regioselectivities (**3**/**4**) for the allylation of **1a**–**l** were generally high (>86:14), with the exception of **1m**, which afforded more of the linear coupling product (**3m**/**4m** = 67:33), probably because of the sterically congested *o*-

Table 2: Substrate scope for the asymmetric allyl–allyl cross-couplings.[a]



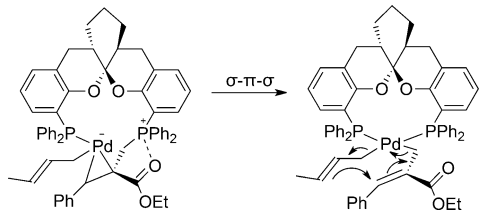


[a] For reaction conditions, see entry 15 in Table 1. Substrate scale of 0.4 mmol. The absolute configurations were assigned by CD spectra. [b] $[\{Pd(C_3H_5)Cl\}_2]$ (0.008 mmol), and (*S*,*S*,*S*)-SKP (0.02 mmol). [c] **1b** (0.2 mmol), **2b** (0.3 mmol), CsF (2 mmol), $[\{Pd(C_3H_5)Cl\}_2]$ (0.01 mmol) and (*S*,*S*,*S*)-SKP (0.025 mmol) in CH_2Cl_2 (2.5 mL), 17 h, 40 °C.

tolyl group in **1m**. In contrast, the reactivity and selectivity control in the reactions of substituted allylboronates proved to be more demanding. For the reaction of **1b** with 2-methyl-substituted allyl boronate, methallylB(pin) (**2b**), higher loadings of both the catalyst (5 mol% $[\{Pd(\eta^3\text{-}C_3H_5)Cl\}_2]$, 12.5 mol% SKP) and the CsF activator (10 molar equiv), as well as a slightly elevated temperature (40 °C), were required for a smooth catalysis, to give the corresponding allylation product **3n** in good yield (83%) with excellent regio- and enantioselectivity (**3n**/**4n** = 77:23, 95% *ee*).

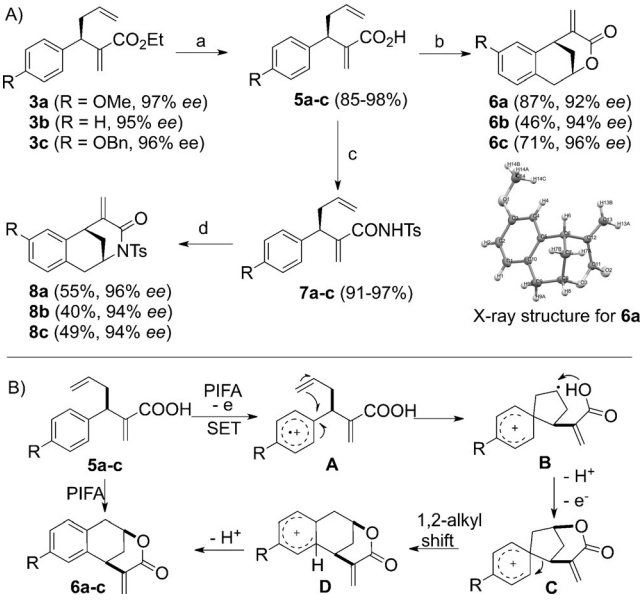
A preliminary study on the reaction mechanism was carried out by varying the structure of substrates, using either linear or branched, and including enantioenriched allyl acetates and several isomeric allylic boronates (see Scheme S2 in the Supporting Information). The observation of the branched allyl–allyl cross-coupling product being the major isomer, and essentially identical asymmetric induction suggests that an inner-sphere 3,3′-reductive elimination might be operative, analogous to that disclosed by Morken and co-

workers.[4] Considering the known bifunctional role of spiroketal-based bis(phosphine) (SKP) ligands in the allylic substitution of acetates of MBH adducts,[12] as well as the outcomes of these reactions (see Scheme S2), the key intermediates involved in inner-sphere 3,3′-reductive elimination[4,14] were thus proposed (Scheme 1) to illustrate the high regio- and stereoselectivity in the present allyl–allyl cross-coupling.



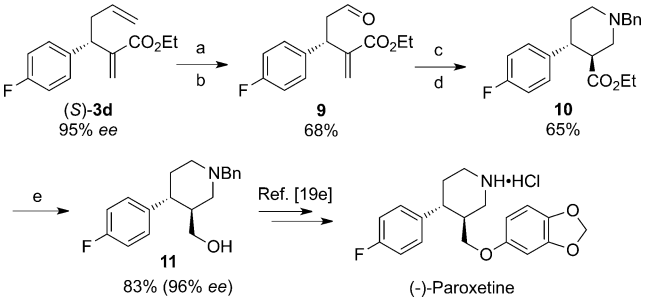
Scheme 1. Proposed model for inner-sphere 3,3′-reductive elimination in allyl–allyl cross-coupling.

The resultant enantioenriched products (**3**), bearing an ester group in proximity to the 1,5-diene moiety, proved to be versatile building blocks for the synthesis of some useful complex molecules in a number of interesting transformations. The practical utility of the reaction was first showcased in the rapid construction of some important chiral polycyclic lactones and lactams, as shown in Scheme 2. Treatment of **5a–c**, the hydrolytic products of **3a–c**, with phenylliodine(III) bis(trifluoroacetate) (PIFA) and a catalytic amount of Sc(OTf)$_3$ at 0 °C delivered the polycyclic lactones **6a–c** in good yields with excellent optical purities (92–96% *ee*). The structure of the polycyclic molecule **6a** was unambiguously established by X-ray diffraction analysis (Scheme 2 A). Extension of the PIFA/Sc(OTf)$_3$-mediated oxidative cyclization to the *p*-toluensulfonyl (Ts) modified amides **7a–c** provided a one-step synthesis of the polycyclic lactams **8a–c** (94–96% *ee*) under similarly mild reaction conditions (Scheme 2 A). It is noteworthy that the structures of the polycyclic lactams **8a–c** incorporate a benzomorphan core[15] (benzobicyclo[3.3.1]) as the scaffold, which has been recognized as the key subunit in a wide range of biologically active natural products such as morphine, codeine, and pentazoine, as well as a variety of artificial analgesics.[16] In addition, the exocyclic C=C bond in **8a–c** might also serve as a handle for further synthetic manipulations. Thus, this new transformation provides a simple and useful tool for the efficient construction of the synthetically challenging chiral polycyclic structures from open-chain precursors. While the mechanistic details for the novel oxidative cyclization of either **5a–c** or **7a–c** are still unclear at present, a plausible pathway is tentatively proposed in Scheme 2 B. PIFA can induce a single-electron-transfer (SET)[17] from the electron-rich aryl rings of **5** to produce an arene radical cation of the type **A**, as has been demonstrated in the elegant studies by Kita and co-workers.[18] Subsequently, the electrophilic radical **A** may undergo an intramolecular 5-*endo-trig* cyclization by addition to the terminal olefinic carbon atom, to generate the secondary C-centered radical species **B**. Further oxidative lactonization and deprotonation of **B** gives the carbocation **C**, which can rearrange to an arenium ion **D** by an intramolecular 1,2-alkyl shift. Further deprotonation of **D** leads to rearomatization to afford the polycyclic lactones **6a–c** as the final products. The PIFA-promoted oxidative cyclization of **7a–c** to **8a–c** seems likely to follow an analogous mechanism.



Scheme 2. A) Synthetic utility of the cross-coupling products in the preparation of the polycyclic lactones **6a-c** and polycyclic lactams **8a–c**. Reaction conditions: a) **3a–c**, LiOH, THF/H_2O (1:1), reflux, 24 h; b) **5a–c**, PIFA, Sc(OTf)$_3$, CH_3CN, 0 °C, 12 h; c) **5a–c**, *p*-toluenesulfonyl isocyanate (PTSI), Et_3N, THF, 60 °C, 3 h; d) **7a–c**, PIFA, Sc(OTf)$_3$, CH_3CN, 0 °C, 12 h. X-ray structure of **6a** is shown with thermal ellipsoids at 50% probability.[20] B) Proposed mechanism for PIFA-mediated oxidative cyclizations of **5**. PIFA = phenyliodine bis(trifluoroacetate), THF = tetrahydrofuran, Ts = 4-toluenesulfonyl.

The synthetic utility of the titled catalysis was further explored in the formal synthesis of (−)-Paroxetine, a potent serotonin reuptake inhibitor widely used in the treatment of depression, anxiety, and panic disorders.[19] The reaction sequence is shown in Scheme 3, with the fluorine-containing cross-coupling product (*S*)-**3d** as the starting material, which was readily obtained in high optical purity (95% *ee*) under reaction conditions illustrated in Table 2 using (*R*,*R*,*R*)-SKP as the chiral ligand. The key intermediate, 3-hydroxymethyl 4-



Scheme 3. Formal synthesis of (−)-Paroxetine. Reaction conditions: a) *m*CPBA (1.5 equiv), CH_2Cl_2, 0 °C–RT, 17 h; b) HIO_5 (1.2 equiv), THF/H_2O (3:1), 0 °C, 1 h; c) $BnNH_2$ (3 equiv), $NaBH_3CN$ (5 equiv), AcOH (6 equiv), MeOH, RT, 17 h; d) *t*BuOK (3 equiv), *t*BuOH (1.5 equiv), toluene, RT, 1 h; e) $LiAlH_4$ (10 equiv), THF, 0 °C, 1 h. *m*CPBA = *m*-chloroperbenzoic acid.

arylpiperidine (**11**), for synthesis of (−)-Paroxetine[19e] can be readily obtained in a five-step procedure in 36% yield.

In summary, an efficient and mild asymmetric allyl–allyl cross-coupling reaction of acetates of MBH adducts and allylboronates has been developed using a SKP/palladium complex as the catalyst, to afford a range of highly functionalized chiral 1,5-dienes in good yields, high regioselectivities, and excellent enantioselectivities (95–99% *ee*). Synthetic utilities were demonstrated in a number of simple but powerful transformations involving the resultant 1,5-dienes, which provided versatile scaffolds for rapid access to a number of complex molecules, including some polycyclic lactones and biologically interesting polycyclic lactams, as well as the *anti*-depression drug (−)-Paroxetine.

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Conflict of interest

The authors declare no conflict of interest.

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[20] CCDC 1423316 (**6a**) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre.

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