Allylic Compounds

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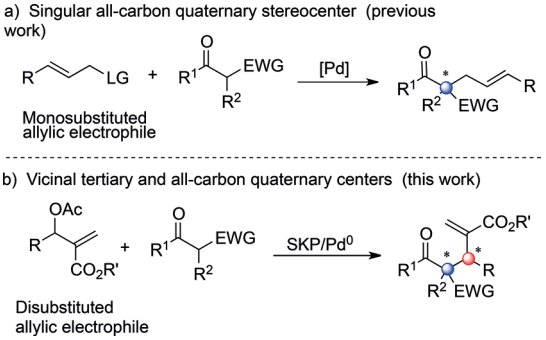
# Palladium-Catalyzed Asymmetric Construction of Vicinal Tertiary and All-Carbon Quaternary Stereocenters by Allylation of β-Ketocarbonyls with Morita–Baylis–Hillman Adducts

*Jiawang Liu, Zhaobin Han, Xiaoming Wang, Fanye Meng, Zheng Wang,* and Kuiling Ding**

***Abstract:*** *Palladium-catalyzed regio-, diastereo-, and enantioselective allylic alkylation of β-ketocarbonyls with Morita–Baylis–Hillman adducts has been developed using a spiroketal-based diphosphine (SKP) as the ligand, thus affording a range of densely functionalized products bearing vicinal tertiary and all-carbon quaternary stereodyad in high selectivities. The utility of the protocol was demonstrated by the facile synthesis of some complex molecules by simple product transformations.*

Although substantial progress has been made in the synthesis of singular all-carbon quaternary stereocenters,[1] catalytic construction of contiguous stereodyads proves far more difficult because of the increased steric demands and the stereochemical control in the C–C bond formation.[2] Among the limited methods for building such a motif, some recent developments involve the use of transition-metal-catalyzed asymmetric allylic alkylations (AAA)[3] as a versatile tool for this challenging C–C bond formation. In this context, several chiral transition-metal catalysts, largely based on either Ir[4] or Mo,[5] have recently been demonstrated as effective for the construction of vicinal stereodyads by stereoselective reactions of a prochiral nucleophile with a prochiral allyl electrophile. Despite that palladium-catalyzed AAA has been utilized in the synthesis of singular all-carbon quaternary stereocenters, for example, by alkylation of a prochiral enolate with an allylic electrophile (Scheme 1 a),[6] however, to our knowledge only a few examples have been documented on their use in the construction of such vicinal stereodyads bearing a quaternary carbon center.[6b] This deficit, presumably owing to the generally preferential formation of the linear product in palladium-catalyzed allylation, constitutes a major limitation in palladium-catalyzed AAA reactions.[7]




***Scheme 1.*** Palladium-catalyzed AAA reactions for the construction of a) singular all-carbon quaternary stereocenters and b) vicinal stereodyads. EWG = electron-withdrawing group.

Herein, we report the first palladium-catalyzed AAA of β-ketocarbonyl compounds, both cyclic and acyclic, with modified MBH adducts.[8,9] With a spiroketal-based diphosphine (SKP)[10] as the chiral ligand, a wide range of densely functionalized products, bearing congested vicinal tertiary and all-carbon quaternary stereodyads, were obtained with high branched regioselectivities, and good to excellent diastereo- and enantioselectivities (Scheme 1 b).

The research was inspired by the unique behavior of SKPs in palladium-catalyzed asymmetric allylic aminations of MBH adducts, wherein the ligand plays a bifunctional role and allows excellent control over both the branched regio- and enantioselectivities.[11] We envisioned that SKP/Pd-catalyzed AAA of MBH adducts with nucleophiles of β-ketocarbonyl compounds[12] might provide an excellent approach for the construction of vicinal chiral tertiary and quaternary centers. Accordingly, the reaction of the MBH adduct **1a** and β-ketoester **2a** was taken for a proof-of-concept prototype to survey the reaction conditions (Table 1). A preliminary investigation (for details, see the Supporting Information) revealed that the reaction proceeds smoothly in the presence of $[Pd_2(dba)_3]$/(*S*,*S*,*S*)-SKP (**L1**) in $CH_2Cl_2$ at −20 °C, thus affording **3aa** in 90 % yield with a high branched/linear selectivity (b/l = 91:9), good diastereoselectivity (12:1 d.r.), and nearly perfect enantioselectivity (> 99 % *ee*; entry 1). The diastereoselectivity was further improved to 17:1 and 16:1 (d.r.) by adding a 2.5 volume % of EtOH and $H_2O$, respectively, to the reaction system without any loss of regio- or enantioselectivity (entries 2 and 3; hereafter designated as reaction conditions A and B, respectively). Subsequently, a SKP ligand series (**L1**–**L6**) and several privileged chiral ligands[13] [(*R*)-BINAP (**L7**), (*R*)-SegPhos (**L8**), (*R*)-SDP (**L9**), and (*R*,*R*)-Trost ligand (**L10**)] were screened in the

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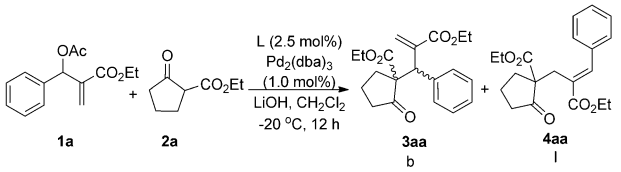
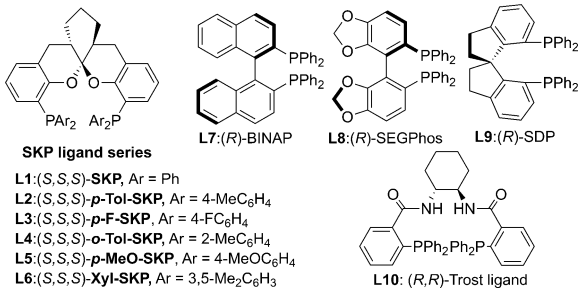
***Table 1:*** Optimization of the reaction conditions.[a]




1a 2a 3aa b 4aa l

| Entry | L | Add.[b] | 3aa/4aa[c] | d.r.[c] | Yield [%][d] | *ee* [%][e] |
|---|---|---|---|---|---|---|
| 1 | **L1** | none | 91:9 | 12:1 | 90 | >99 |
| 2 | **L1** | EtOH | 91:9 | 17:1 | 90 | >99 |
| 3 | **L1** | $H_2O$ | 93:7 | 16:1 | 93 | >99 |
| 4 | **L2** | $H_2O$ | 94:6 | 20:1 | 87 | 98 |
| 5 | **L3** | $H_2O$ | 90:10 | 10:1 | 75 | >99 |
| 6 | **L4** | $H_2O$ | | | 0 | – |
| 7 | **L5** | $H_2O$ | 90:10 | 14:1 | 72 | >99 |
| 8 | **L6** | $H_2O$ | 82:18 | 4:1 | 58 | 97 |
| 9[f] | **L7** | $H_2O$ | – | – | n.o. | – |
| 10[f] | **L8** | $H_2O$ | – | – | n.o. | – |
| 11[g] | **L9** | $H_2O$ | – | – | n.o. | – |
| 12[f] | **L10** | $H_2O$ | – | – | n.o. | – |

[a] Unless otherwise noted, all reactions were performed in $CH_2Cl_2$ (2.0 mL) at −20 °C for 12 h, in the presence of **1a** (0.2 mmol), **2a** (0.22 mmol), [$Pd_2(dba)_3$] (0.002 mmol), the ligand (**L**; 0.005 mmol), and solid LiOH (0.6 mmol). [b] Add. = additive, EtOH or $H_2O$ as the additive (50 μL). [c] The values of **3aa**/**4aa** (b/l) and diastereomeric ratios (d.r.) of **3aa** were determined by $^1$H NMR analysis. [d] Yield of isolated **3aa**. [e] The *ee* values of **3aa** were determined by HPLC analysis on a chiral column. [f] **1a** was fully recovered after the reaction. [g] About 30% of **1a** was isomerized during the reaction. dba = dibenzylideneacetone, n.o. = not observed.



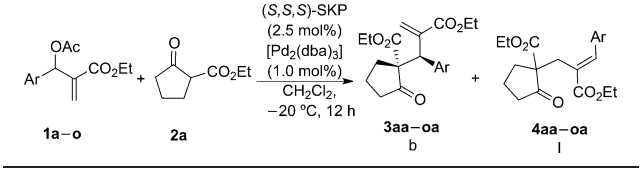

**SKP ligand series**

**L1**:(*S*,*S*,*S*)-**SKP,** Ar = Ph
**L2**:(*S*,*S*,*S*)-***p*-Tol-SKP,** Ar = 4-$MeC_6H_4$
**L3**:(*S*,*S*,*S*)-***p*-F-SKP**, Ar = 4-$FC_6H_4$
**L4**:(*S*,*S*,*S*)-***o*-Tol-SKP,** Ar = 2-$MeC_6H_4$
**L5**:(*S*,*S*,*S*)-***p*-MeO-SKP**, Ar = 4-$MeOC_6H_4$
**L6**:(*S*,*S*,*S*)-**Xyl-SKP,** Ar = 3,5-$Me_2C_6H_3$

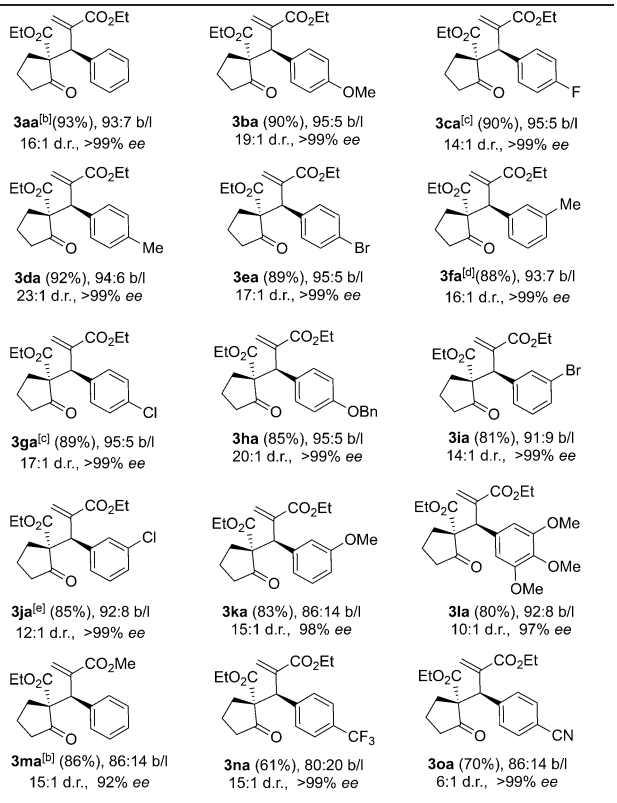
**L7**:(*R*)-BINAP **L8**:(*R*)-SEGPhos **L9**:(*R*)-SDP

**L10**: (*R*,*R*)-Trost ligand

***Table 2:*** Substrate scope with respect to the MBH adducts.[a]




1a–o 2a 3aa–oa b 4aa–oa l




**3aa**[b](93%), 93:7 b/l, 16:1 d.r., >99% *ee*
**3ba** (90%), 95:5 b/l, 19:1 d.r., >99% *ee*
**3ca**[c] (90%), 95:5 b/l, 14:1 d.r., >99% *ee*
**3da** (92%), 94:6 b/l, 23:1 d.r., >99% *ee*
**3ea** (89%), 95:5 b/l, 17:1 d.r., >99% *ee*
**3fa**[d](88%), 93:7 b/l, 16:1 d.r., >99% *ee*
**3ga**[c] (89%), 95:5 b/l, 17:1 d.r., >99% *ee*
**3ha** (85%), 95:5 b/l, 20:1 d.r., >99% *ee*
**3ia** (81%), 91:9 b/l, 14:1 d.r., >99% *ee*
**3ja**[e] (85%), 92:8 b/l, 12:1 d.r., >99% *ee*
**3ka** (83%), 86:14 b/l, 15:1 d.r., 98% *ee*
**3la** (80%), 92:8 b/l, 10:1 d.r., 97% *ee*
**3ma**[b] (86%), 86:14 b/l, 15:1 d.r., 92% *ee*
**3na** (61%), 80:20 b/l, 15:1 d.r., >99% *ee*
**3oa** (70%), 86:14 b/l, 6:1 d.r., >99% *ee*

[a] Unless otherwise noted, the reactions were performed under condition A. The data within parentheses are the yields of isolated **3**. The b/l ratios (**3**:**4**), d.r. and *ee* values of **3** were determined following the methods shown in footnotes of Table 1. The structure of **3ja** was unambiguously established by X-ray diffraction, while the absolute configurations of the other products were assigned by comparing the Cotton effect of their CD spectra with that of **3ja**. [b] Conditions B. [c] −25 °C, 24 h. [d] 18 h. [e] 24 h.

reaction with $H_2O$ as the additive. Except for **L4**, all SKP ligands furnished the branched product **3aa** in good yields (58–93%) with high branched regioselectivity (b/l = 82:18–94:6) and excellent *ee* values (97–>99% *ee*), albeit with d.r. values which varied (entries 3–8). Intriguingly, none of the well-established chiral diphosphine ligands, **L7**–**L10**, delivered **3aa**. Such a sharp contrast in reactivity profile between SKPs and **L7**–**L10** probably reflects a fundamental difference in the substrate activation using the corresponding palladium complexes, hence attesting to the unique role and the superior performance of SKP ligands in this reaction.

With the optimized reaction conditions in hand, we proceeded to explore the substrate scope with regard to racemic MBH adducts using **2a** as the nucleophile (Table 2). In most cases, the reactions were conducted under reaction conditions A. As shown in Table 2, a wide range of functional groups on the phenyl rings of MBH adducts (**1a**–**o**), either electron-donating (MeO, Me, BnO) or electron-withdrawing (Br, Cl, F, $CF_3$, CN), were well tolerated in the reaction, to give a wide range of densely functionalized products (**3aa**–**oa**). They contained well-defined contiguous stereodyads bearing an all-carbon quaternary center adjacent to a tertiary chiral carbon, and were delivered in good to excellent yields (61–93%) with high branched regioselectivities (b/l = 80:20 to 95:5), good diastereoselectivities (6.4:1 to >20:1), and excellent enantioselectivities (92 to >99% *ee*). The MBH substrates with haloaryl moieties, which might be sensitive to palladium catalysis, also worked well, without adverse effect on the reaction (**3ea**, **3ga**, **3ia**, **3ja**). It is interesting to note that the ester moiety on the MBH adduct exhibited a significant effect on the catalysis (especially the enantioselectivity), as shifting from **1a** (ethyl ester) to **1m** (methyl ester) resulted in a decline of the *ee* value from greater than 99% to 92% (**3aa** versus **3ma**).

The scope, with respect to prochiral nucleophiles reacting with **1a**, was then explored in the catalysis. As shown in

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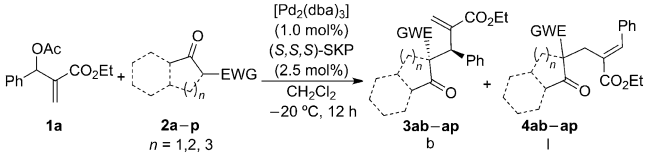
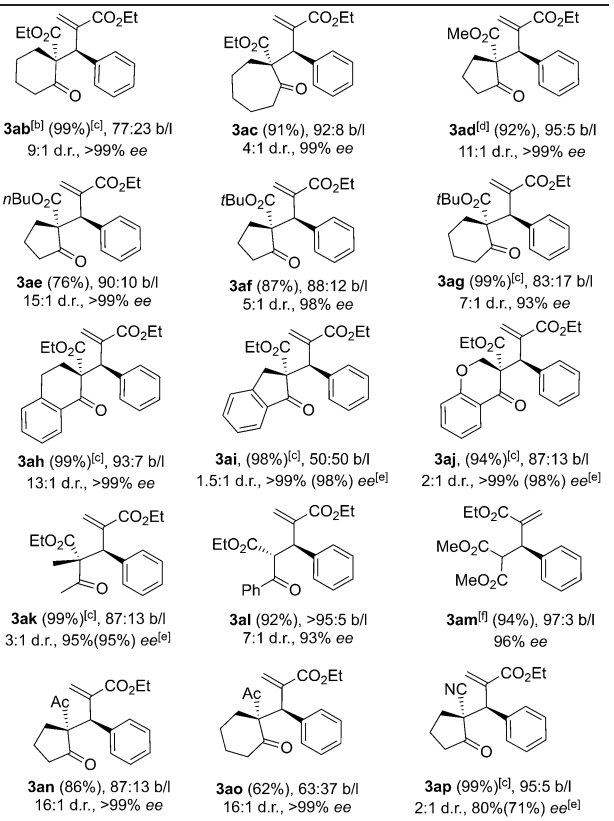
***Table 3:*** Substrate scope with respect to β-ketocarbonyl nucleophiles.[a]

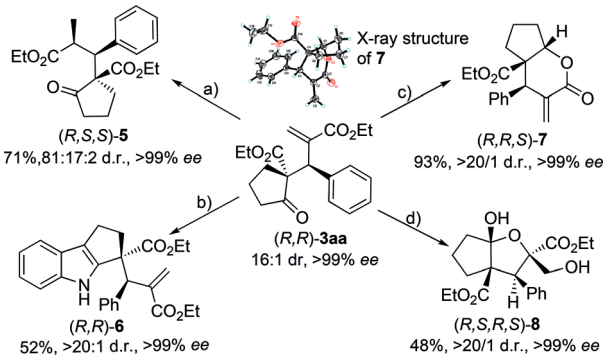



[a] Unless otherwise noted, the reactions were performed under conditions B. The data within parentheses are the yields of isolated **3**. In each case, the b/l and d.r. values were determined by $^1$H NMR analysis, and the *ee* values for **3** was determined by HPLC using a chiral column. [b] −25 °C, 24 h. [c] Yield of isolated **3** and **4**. [d] Conditions A. [e] Data within parentheses are *ee* values for the minor diastereomer. [f] RT, 12 h, aqueous $K_2CO_3$ (1.0 M, 3.0 equiv) as the base.

Table 3, a large variety of β-ketocarbonyl compounds, including cyclic and acyclic β-ketoesters (**2a–l**), dimethyl malonate (**2m**), β-diketones (**2n**, **2o**), and α-cyanoketone (**2p**) were found to be compatible with the procedure (conditions B), thus affording the corresponding products **3aa–ap** in good to high yields (62–99%). Except for **3ap**, all the products (**3aa–ao**) were obtained in excellent enantioselectivities (93–>99% *ee*). In contrast, the regio- and diastereoselectivities of **3aa–ap** were found to vary significantly (b/l = 50:50 to 97:3, d.r. = 1.5:1 to 16:1), depending on the ring size as well as the α-EWG of the nucleophile in a subtle way. The d.r. values of **3aa–ac** (16:1 to 4:1) declined gradually with an increase in the ring size of the cyclic ketone moiety on the corresponding β-ketoesters **2a–c**. The reactions of cyclopentanone-based β-ketoesters (**2a** and **2d–f**) afforded the corresponding products (**3aa**, **3ad, 3ae** and **3af**) with b/l ratios ranging from 88:12 to 95:5, apparently affected by their distinct ester moieties. The reactions of α-carboxyethyl tetralone (**2h**), α-carboxyethyl indanone (**2i**), and α-carboxyethyl chroman-4-one (**2j**) afforded the corresponding products **3ah–aj** with high yields and excellent *ee* values, though in some cases a modest regioselectivity (**3ai**) and diastereoselectivity (**3ai**, **3aj**) were obtained. The reactions of the challenging acyclic β-ketoesters **2k** and **2l** also proceeded smoothly to give the branched products **3ak** and **3al**, respectively, with high b/l ratios and excellent *ee* values, albeit in a moderate diastereoselectivity. The reaction of enolate of malonate (**2m**), generated in situ with aqueous $K_2CO_3$ (3 equiv), gave the allylation product **3am** with an excellent b/l ratio and 96% *ee*. In addition to the β-ketoesters, β-diketones (**2n**, **2o**) also proved to be viable substrates for the reaction, thus affording the desired products **3an** and **3ao** in good yields with high d.r. values and greater than 99% *ee*, though with moderate b/l ratios. The reaction involving α-cyanocyclopentone (**2p**) provided the corresponding product **3ap** with high branched regioselectivity and good *ee* values, albeit with a modest d.r. value. Finally, under reaction conditions B **3aa** and **3ah** were readily synthesized on gram-scale with extremely high optical purities (>99% *ee*; see the Supporting Information), thus attesting to the practicality of the protocol.

The synthetic utility of the method was demonstrated in a number of transformations on the highly functionalized allylation product **3aa** (Scheme 2). Pd/C-catalyzed hydrogenation of **3aa** gave **5**, bearing three contiguous stereocenters, in good yield with greater than 99% *ee* for the major diastereomer. Treatment of **3aa** with phenylhydrazine under acidic conditions provided rapid access to the tricyclic indole derivative **6** in 52% yield without loss of enantioselectivity. Borohydride reduction of **3aa** furnished the bicyclic lactone **7**, bearing an *exo*-methylene moiety, in 93% yield with greater than 20:1 d.r. and greater than 99% *ee*. Finally, dihydroxylation of **3aa** followed by acidic workup provided the hemiketal **8** with greater than 20:1 d.r. and greater than 99% *ee*.




***Scheme 2.*** Synthetic transformations of the allylation product **3aa.** a) Pd/C, $H_2$, EtOH, RT, 24 h. b) $PhNHNH_2$, TFA, DCE, 50 °C, 72 h. c) 1.) $NaBH_4$, MeOH, −65 °C, 6 h; 2.) aq. HCl, RT, 2 h. d) 1.) NMO, $OsO_4$, acetone/$H_2O$ (9:1), RT,12 h; 2.) $Na_2S_2O_3$, HCl, RT, 6 h. Thermal ellipsoids shown at 30% probability. DCE = 1,2-dichloroethane, NMO = *N*-methyl morpholine N-oxide, TFA = trifluoroacetic acid.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Considering the bifunctional role of SKPs in the allylic substitution of MBH acetates,[11] as well as the sense of asymmetric induction in the titled reaction, a schematic representation of the stereocontrol model is proposed in Figure 1. In the key intermediate,[11b] one of the phenyl rings

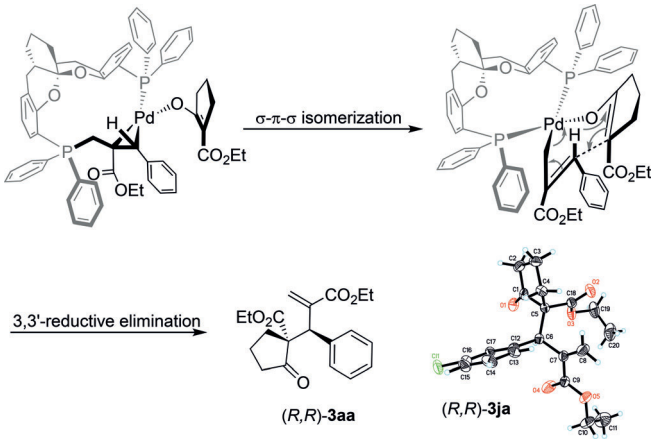


***Figure 1.*** Stereoselectivity control model and X-ray structure for (*R*,*R*)-**3ja**. Thermal ellipsoids shown at 30% probability.

on the phosphonium moiety effectively blocks the backside of the $\eta^2$-Pd-allyl moiety, thus suggesting that the outer-sphere mechanism is unlikely to be feasible. The stereochemical outcome can be explained by a σ-π-σ isomerization of the complex, followed by an inner-sphere 3,3′-reductive elimination[14] of the resulting $\eta^1$-allyl-$\eta^1$-enolatopalladium, thus yielding (*R*,*R*)-**3aa** as the major isomer.[15]

In summary, we have developed the first palladium-catalyzed asymmetric construction of the vicinal tertiary and all-carbon quaternary stereocenters by allylic alkylation of β-dicarbonyl compounds with MBH adducts. The SKP ligand turns out to be critically important in the catalysis, thus affording a wide variety of densely functionalized products in high yields with excellent enantioselectivities, and good to high regio- and diastereoselectivities. The synthetic utility of the protocol was exemplified in a number of transformations which allow rapid access to a variety of polyfunctionalized structures with rich stereocenters.

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## Conflict of interest

The authors declare no conflict of interest.

**Keywords:** allylic compounds · asymmetric catalysis · palladium · P ligands · spiro compounds

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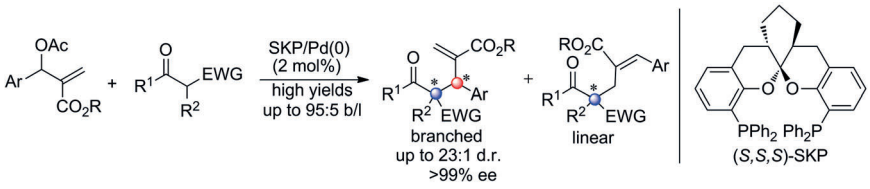
# Communications

## Allylic Compounds

J. Liu, Z. Han, X. Wang, F. Meng, Z. Wang,* K. Ding* ——— ■■■■–■■■■

Palladium-Catalyzed Asymmetric Construction of Vicinal Tertiary and All-Carbon Quaternary Stereocenters by Allylation of β-Ketocarbonyls with Morita–Baylis–Hillman Adducts




**SKP/Pd systems go**: An SKP/Pd system demonstrates unique catalytic performance in construction of vicinal tertiary and all-carbon quaternary stereodyads by allylic alkylation of β-ketocarbonyls with Morita–Baylis–Hillman adducts. Thus a wide range of densely functionalized products are delivered with high regio-, diastereo-, and enantioselectivities.

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