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Palladium-Catalyzed Intramolecular Mizoroki-Heck-Type Reaction of Diarylmethyl Carbonates

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Abstract. A palladium-catalyzed intramolecular Mizoroki-Heck-type reaction of diarylmethyl *tert*-butyl carbonates has been developed. The reaction proceeds under external base-free, neutral conditions to form the corresponding methyleneindane in good yields only with liberation of CO₂ and *t*BuOH. The resulting *exo*-methylene moiety is reactive and thus a good synthetic handle for further manipulations. Additionally, the asymmetric synthesis is also possible through a Pd/chiral Mandyphos ligand-mediated kinetic resolution. To the best of our knowledge, this is the first successful example of catalytic enantioselective Mizoroki-Heck-type reaction of secondary benzyl electrophiles.

Keywords: asymmetric catalysis; indanes; kinetic resolution; Mizoroki-Heck reaction; palladium

The transition-metal-catalyzed Mizoroki-Heck-type reaction is now one of the indispensable carbon-carbon bond forming reactions in modern organic synthesis. In particular, the intramolecular variants can construct unique cyclic frameworks, which are frequently occurring in natural products and bioactive molecules.^[1] Under traditional conditions, C_{sp2}-hybridized organic halides are usually employed as the carbon electrophiles, but recent progress allows C_{sp3}-hybridized alkyl electrophiles as well as less toxic and more readily available phenol and alcohol derivatives to be adopted in the Mizoroki-Heck-type reactions.^[2] Moreover, the asymmetric catalysis were also developed by several research groups.^[1b,d,2e,3] Despite the aforementioned certain advances, the enantioselective Mizoroki-Heck-type reaction with racemic secondary alkyl electrophiles still remains a great challenge. In 2014, Jarvo reported a nickel-catalyzed enantiospecific intramolecular Mizoroki-Heck-type reaction of secondary benzyl ethers to from the optically active methylenecyclopentanes.^[4] This reaction can successfully control the point chirality at the benzylic position, which stems from the electrophile. However, the strong external reductant, MeMgI, was inevitable for the catalyst turnover. Additionally, the tedious preparation of optically

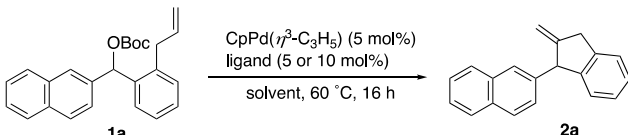
active starting substrates was necessary for obtaining the targeted chiral products. Thus, further development of Mizoroki-Heck-type reaction of secondary alkyl electrophiles, particularly, its enantioselective version is highly appealing. Here, we report a palladium-catalyzed intramolecular Mizoroki-Heck-type reaction of diarylmethyl *tert*-butyl carbonates. The reaction proceeds well under external base-free conditions, and the corresponding methyleneindanes are obtained in good yields. Furthermore, the catalytic enantioselective synthesis is possible through kinetic resolution using an optically active Mandyphos ligand. To the best of our knowledge, this is the first successful example of catalytic enantioselective Mizoroki-Heck-type reaction of secondary benzyl electrophiles.

During our recent studies on the palladium-catalyzed benzylic substitution reactions of diarylmethyl electrophiles,^[5,6] we envisioned the intramolecular Mizoroki-Heck-type reaction of diarylmethyl *tert*-butyl carbonate **1a** (Table 1). On the basis of our previous results, we initially investigated some bidentate bisphosphine ligands with relatively large bite angles, in conjunction with the CpPd(η^3 -C₃H₅) catalyst and MeCN solvent, but the low conversion was generally observed (entries 1–4). On the other hand, the more common dppe and dppp ligands with smaller bite angles showed good reactivity (entries 5 and 6). Moreover, several monodentate phosphine ligands, particularly, Buchwald biarylphosphine ligands, were found to be more effective (entries 7–12), with 2-dicyclohexylphosphino-2',4',6'-triisopropylbiphenyl (XPhos) proving to be best (100% ¹H NMR and 91% isolated yield; entry 9). Additional solvent screening were performed, but the reaction proceeded uniquely in only MeCN solvent (entries 13–16).^[7]

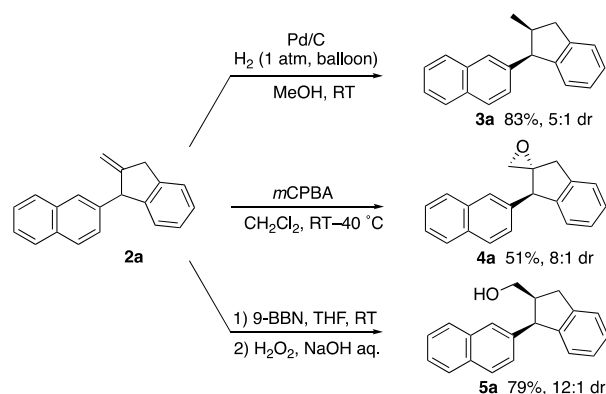
The *exo*-methylene moiety in methyleneindane **2a** was reactive and thus readily elaborated (Scheme 1). The hydrogenation under standard Pd/C catalysis afforded the 1,2-disubstituted indane **3a** with a 5:1 *cis/trans* ratio. The epoxidation with *m*CPBA was also possible with the same diastereoselection, and the corresponding epoxide **4a** was obtained. Moreover,

the hydroboration/oxidation sequence provided the primary alcohol **5a** with high *cis* selectivity.^[8]

Table 1. Optimization Studies for Palladium-Catalyzed Intramolecular Mizoroki-Heck-Type Reaction of Diarylmethyl *tert*-Butyl Carbonate **1a**.^[a]

			
Entry	Ligand	Solvent	Yield [%] ^[b]
1	<i>rac</i> -binap	MeCN	0
2	dppf	MeCN	13
3	DPEphos	MeCN	0
4	xantphos	MeCN	24
5	dppe	MeCN	74
6	dppp	MeCN	79
7	PPh ₃	MeCN	35
8	PPhCy ₂	MeCN	57
9	XPhos	MeCN	>99 (91)
10	SPhos	MeCN	96
11	RuPhos	MeCN	91
12	Cy-JohnPhos	MeCN	96
13	XPhos	1,4-dioxane	0
14	XPhos	DMF	28
15	XPhos	DMSO	9
16	XPhos	toluene	0

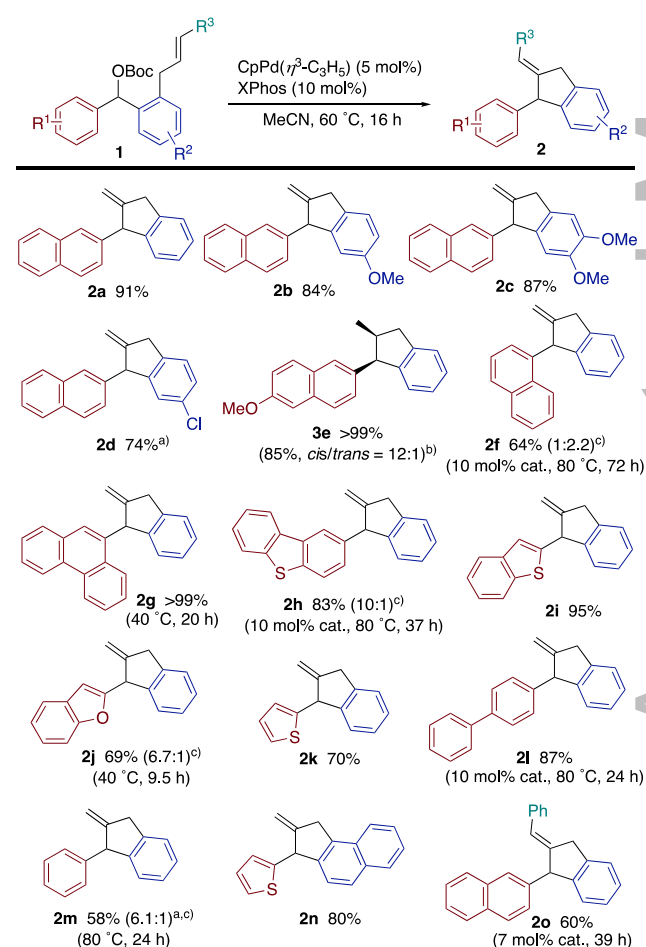
a) Conditions: **1a** (0.20 mmol), CpPd(η^3 -C₃H₅) (0.010 mmol), ligand (0.010 mmol for bidentate ligands and 0.020 mmol for monodentate ligands), and solvent (1.5 mL), 60 °C, 16 h, N₂. b) Estimated by ¹H NMR using CH₂Br₂ as an internal standard. Isolated yield in parentheses. Boc = *tert*-butoxycarbonyl.



Scheme 1. Synthetic Elaborations of **2a**.

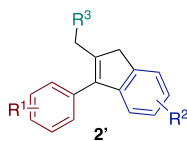
We then examined the scope and limitation of the present palladium catalysis with conditions of entry 9 in Table 1 (Scheme 2). The electron-donating MeO-substituted substrates **1b** and **1c** were successfully converted under the standard conditions, and the corresponding methyleneindanes **2b** and **2c** were isolated in 84% and 87% yields, respectively. In the case of the Cl-substituted **1d**, the reaction was completely shut down. However, given the facile

oxidative addition of aryl-Cl to XPhos-ligated Pd⁰ species, the use of dppp instead of XPhos successfully delivered the desired **2d** in 74% yield. When the MeO group was introduced on the naphthalene ring, the reaction itself proceeded smoothly, but the corresponding methyleneindane **2e** was unstable for silica gel column purification and thus isolated in the saturated form **3e** after the hydrogenation as shown in Scheme 1. The 2-naphthalene substituent could be replaced with 1-naphthalene (**2f**) and more condensed phenanthrene (**2g**) and dibenzothiophene (**2h**). The reaction was compatible with five-membered heteroaromatic systems such as benzothiophene (**2i**) and benzofuran (**2j**). Moreover, the monocyclic thienyl-, biphenyl-, and even simple phenyl-substituted substrates underwent the Mizoroki-Heck reaction to produce **2k–2m** in acceptable yields. Additionally notable is the successful access to the cyclopentanaphthalene scaffold (**2n**). Furthermore, the internal olefin **1o** was also viable to furnish the benzyldieneindane **2o** with high *E* selectivity. Although in some cases (**2f**, **2h**, **2j**, and **2m**) the olefin migration isomers **2'** were also detected, various substituted indane derivatives were successfully prepared under neutral conditions only with liberation of CO₂ and *t*BuOH.^[9,10]

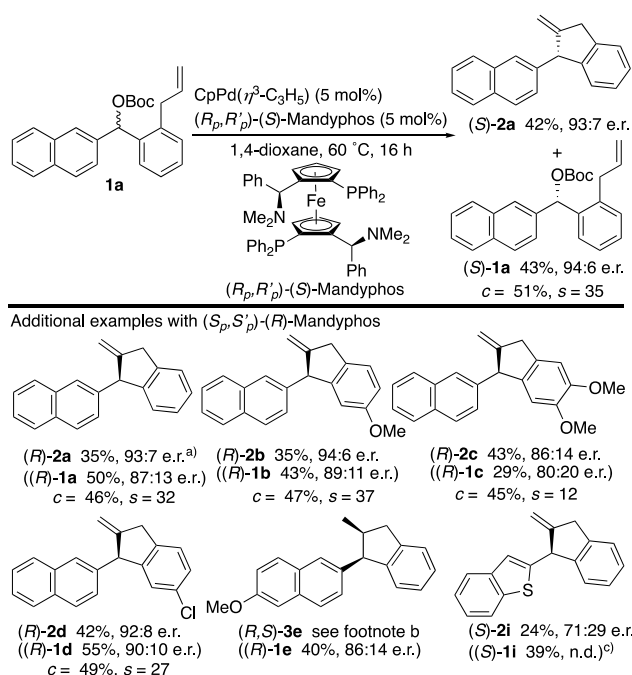


Scheme 2. Palladium-Catalyzed Intramolecular Mizoroki-Heck-Type Reaction of Various Diarylmethyl *tert*-Butyl Carbonates **1**. Standard conditions: **1** (0.20 mmol),

CpPd(η^3 -C₃H₅) (0.010 mmol), XPhos (0.020 mmol), and MeCN (1.5 mL), 60 °C, 16 h, N₂. Isolated yields are shown. The minor modifications from the standard conditions are in parentheses. ^{a)} With 10 mol % of CpPd(η^3 -C₃H₅) and dppp. ^{b)} ¹H NMR yield of **2e** using CH₂Br₂ as an internal standard. The isolated yield and *cis/trans* ratio of hydrogenated **3e** are shown in parentheses. ^{c)} The ratio of **2** and olefin migration isomer **2'** is shown in parentheses. See the Supporting Information for details.

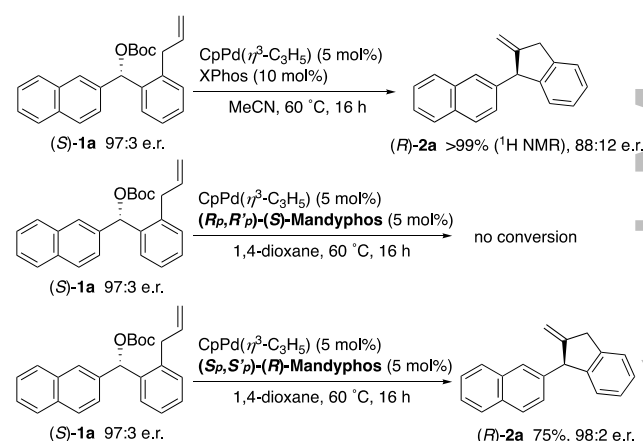


The prevalence of optically active indane structures in biologically active compounds and natural products^[11] prompted us to develop the catalytic enantioselective Mizoroki-Heck-type reaction of **1a**. After the extensive screening of various chiral phosphine ligands, we were pleased to find that the combination of CpPd(η^3 -C₃H₅) and (*R_p*,*R'_p*)-(*S*)-Mandyphos ligand in 1,4-dioxane successfully induced the enantioselectivity (Scheme 3): the enantioenriched (*S*)-**2a** was obtained in 42% yield with 93:7 enantiomeric ratio (e.r.). The reaction occurred in a kinetic resolution manner, and thus the unreactive starting substrate (*S*)-**1a** was recovered also in an enantioenriched form (43%, 94:6 e.r., *c* = 51%, *s* = 35).^[12] Additional examples with the (*S_p*,*S'_p*)-(*R*)-Mandyphos ligand were also illustrated. The racemic **1b–e** were catalytically converted to the optically active methyleneindanes (*R*)-**2b–e** with 85:15–94:6 e.r. Again, the kinetic resolution was observed, and the remaining substrates were enantiomerically enriched (*c* = 45–49%, *s* = 12–37). On the other hand, the benzothiophene substrate **1i** decreased the reactivity and enantioselectivity ((*S*)-**2i**). The reaction could also be performed on a 1.0 mmol scale, thus indicating the good reproducibility of the asymmetric catalysis ((*R*)-**2a**).



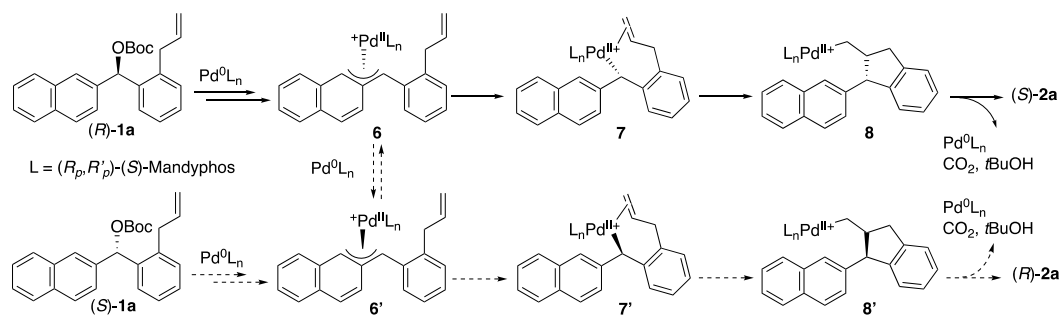
Scheme 3. Enantioselective Mizoroki-Heck-Type Reaction of Diarylmethyl *tert*-Butyl Carbonate **1**. Conversion *c* = (e.e. of **1**)/(e.e. of **1** + e.e. of **2**). Selectivity *s* = ln[(1 - *c*)(1 - e.e. of **1**)]/ln[(1 - *c*)(1 + e.e. of **1**)]. Conditions: **1** (0.20 mmol), CpPd(η^3 -C₃H₅) (0.010 mmol), Mandyphos (0.010 mmol), and 1,4-dioxane (1.5 mL), 60 °C, 16 h, N₂. ^{a)} On a 1.0 mmol scale. ^{b)} In methyl *tert*-butyl ether (MTBE) instead of 1,4-dioxane. Isolated as indane **3e** in 36% yield (*cis/trans* = 7:1) after the hydrogenation. 85:15 and 92:8 e.r. for *cis*- and *trans*-isomers, respectively. ^{c)} The starting **1i** was unstable for chromatographic purification and analysis, and thus the e.r. could not be determined.

To get insight into the stereochemical course, we implemented some control experiments with the independently prepared (*S*)-**1a** (97:3 e.r.; Scheme 4). The reaction under non-enantioselective conditions with XPhos afforded (*R*)-**2a** with a drop of e.r. but with inversion of configuration. Subsequent investigations under asymmetric catalysis showed the significant match/mismatch phenomena: the Pd/(*R_p*,*R'_p*)-(*S*)-Mandyphos catalyst resulted in no conversion, whereas the optically active (*R*)-**2a** was readily formed with 98:2 e.r. under Pd/(*S_p*,*S'_p*)-(*R*)-Mandyphos catalysis. This outcome is consistent with the kinetic resolution mechanism.



Scheme 4. Control Experiments with (*S*)-**1a**.

On the basis of the above findings and literature information, we attempted to propose that the mechanism of the reaction of **1a** is as follows (Scheme 5). The initial stereoinvertive S_N2-type oxidative addition^[13] of Pd⁰L_n [L = (*R_p*,*R'_p*)-(*S*)-Mandyphos] to (*R*)-**1a** and (*S*)-**1a** can form the corresponding π -benzylpalladium^[14] intermediates **6** and **6'**, respectively. However, in this step the kinetic resolution occurs to generate one diastereomer **6** selectively. Subsequent olefin coordination and insertion provide the alkylpalladium species (**6** to **7** to **8**). The observed (*S*)-**2a** then follows from β -H elimination. The catalytic cycle is completed with concomitant elimination of CO₂ and *t*BuOH. Given the results in Scheme 3, the conceivable stereochemical erosion through the equilibrium^[15]



Scheme 5. Plausible reaction mechanism of **1a** with (R_p,R'_p) -(*S*)-Mandyphos ligand.

between **6** and **6'** is almost negligible under the enantioselective conditions but somewhat competitive under nonenantioselective conditions using the XPhos ligand (Scheme 4).

In conclusion, we have developed a palladium-catalyzed intramolecular Mizoroki-Heck-type reaction of diarylmethyl carbonates to form the corresponding methyleneindanes in good yields under external base-free, neutral conditions. Additionally, the asymmetric synthesis is possible through the kinetic resolution with the chiral Mandyphos ligand. To the best of our knowledge, this is the first successful example of catalytic enantioselective Mizoroki-Heck-type reaction of secondary benzylic electrophiles. Further improvement of enantioselectivity and development of related asymmetric benzylic substitution reactions are currently underway.

Experimental Section

$\text{CpPd}(\eta^3\text{-C}_3\text{H}_5)$ (2.1 mg, 0.010 mmol) and (R_p,R'_p) -(*S*)-Mandyphos (8.2 mg, 0.010 mmol) were placed in a 4 mL screw cap vial in a glovebox filled with nitrogen. 1,4-Dioxane (0.5 mL) was added to the vial, and suspension was stirred for 10 min. The mixture was transferred to another 4 mL screw cap vial containing (2-allylphenyl)(naphthalen-2-yl)methyl *tert*-butyl carbonate (**1a**; 74.9 mg, 0.20 mmol) with additional 1,4-dioxane (1.0 mL). The vial was sealed with a cap and taken out of the glovebox. The suspension was stirred for 16 h at 60 °C. The resulting mixture was filtered through a short pad of activated alumina and sodium sulfate. Concentration in vacuo and subsequent purification by column chromatography on neutral silica gel with hexane/ethyl acetate (40/1 to 20/1 v/v) as an eluent gave (*S*)-2-(2-methylene-2,3-dihydro-1*H*-inden-1-yl)naphthalene [(*S*)-**2a**; 22 mg, 8.4×10^{-2} mmol, 93:7 e.r.] in 42% yield: enantiomeric ratio was determined by HPLC analysis in comparison with authentic racemic sample (CHIRALPAK AD-H column, *n*-hexane/isopropyl alcohol = 99.7/0.3, 0.5 mL/min, major isomer: t_R = 11.8 min, minor isomer: t_R = 12.7 min, UV detection at 275.0 nm, 30 °C). The unreacted (*S*)-(2-allylphenyl)(naphthalen-2-yl)methyl *tert*-butyl carbonate [(*S*)-**1a**; 32 mg, 8.6×10^{-2} mmol, 94:6 e.r.] was also recovered in 43% yield: the enantiomeric ratio was determined by HPLC analysis in comparison with authentic racemic sample (CHIRALCEL OJ-H column, *n*-hexane/isopropyl alcohol = 97/3, 0.5 mL/min, major isomer: t_R = 13.6 min, minor isomer: t_R = 10.1 min, UV detection at 256.0 nm).

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COMMUNICATION

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