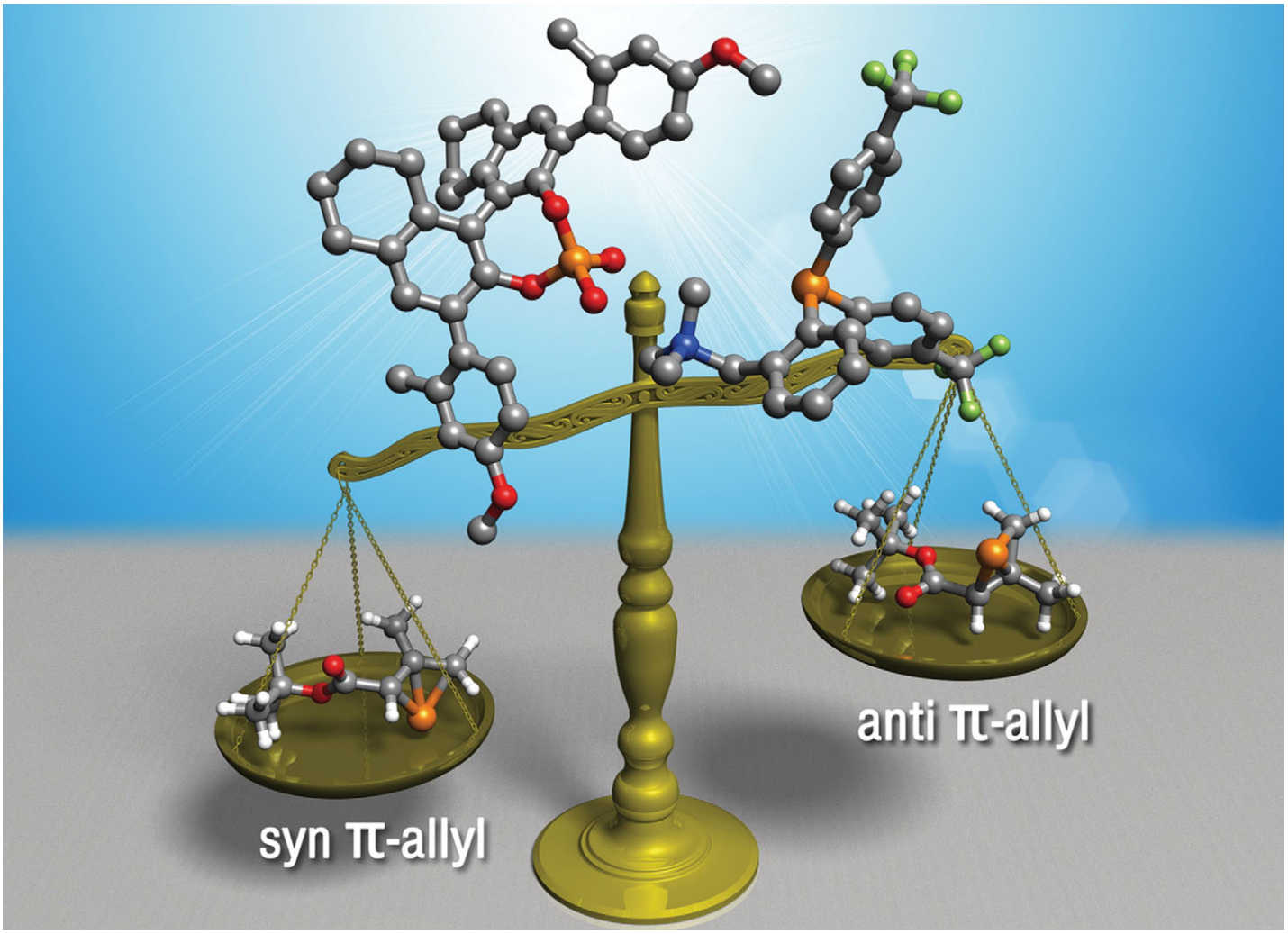

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Ligand-controlled *E*/*Z* selectivity and enantioselectivity in palladium-catalyzed allylation of benzofuranones with 1,2-disubstituted allylic carbonates†

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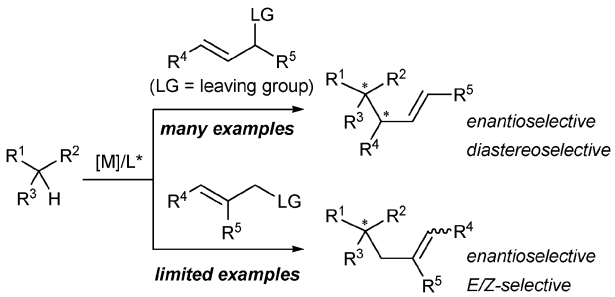
The first highly *E*- and enantioselective allylic alkylation of prochiral carbon nucleophiles with 1,2-disubstituted allylic carbonates is reported. The key to the successful development of this protocol is the ability of modular ion-paired chiral ligands to simultaneously control the *E*/*Z* selectivity and enantioselectivity.

Precise control of stereochemistry in carbon–carbon bond-forming reactions is a subject of fundamental importance in organic synthesis, and has been continuously addressed in the development of a number of synthetically valuable catalytic transformations based on the different strategies. Among them, transition-metal-catalyzed asymmetric allylic alkylations have been extensively studied, rendering them one of the most powerful tools for the stereoselective construction of nascent chiral carbons at prochiral nucleophiles and/or allylic electrophiles.[1] Depending on the substitution patterns of allylic substrates and catalytic systems, this mode of asymmetric C–C bond connection gives rise to the multiple stereochemistries. For instance, the reactions of prochiral nucleophiles with 1-substituted or 1,3-disubstituted allylic substrates generate two adjacent stereocenters in the product incorporating the 3,3-disubstituted or 1,3,3-trisubstituted (branched) allylic unit and hence require the simultaneous enantio- and diastereocontrol. With the aim of controlling these intricate stereochemistries by a catalyst, several reliable methodologies have been developed.[2–4] On the other hand, asymmetric allylations with 1,2-disubstituted allylic substrates lead to the formation of enantiomeric and geometrical isomers of the product having a 1,2,3-trisubstituted (liner) allylic unit (Scheme 1). Despite their potential synthetic relevance, however, catalytic protocols for enabling a highly *E*- and enantioselective allylic alkylation are very limited.[5]



Scheme 1 Transition-metal-catalyzed asymmetric allylic alkylations.

In the palladium-catalyzed allylic alkylation with 1,2-disubstituted allylic substrates, the *E*/*Z* selectivity is strongly influenced by the relative stability of the *syn* and *anti* π-allyl palladium intermediates. The *syn* π-allyl complex is generally more stable than the *anti* counterpart because of the unfavorable 1,3-allylic strain in the *anti* complex.[6] Introduction of a substituent at the 2-position of the allylic moiety, however, destabilizes the *syn* complex through 1,2-steric repulsion (Fig. 1). Therefore, the relative population of each complex is predominantly governed by the nature of the substituents on the allylic component and is difficult to control by a catalyst.[7] This common understanding probably constitutes the prime reason for *E*- or *Z*-selective asymmetric allylic alkylation remaining elusive. Herein, we demonstrate the feasibility of essentially ligand-controlled high *E*- and enantioselectivity for the first time in the palladium-catalyzed allylation of benzofuranones with 1,2-disubstituted allylic carbonates.

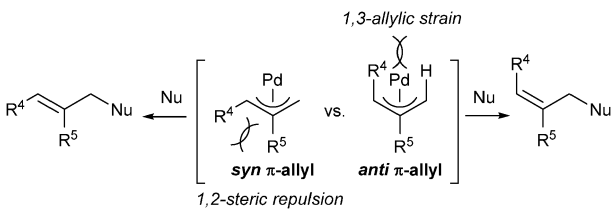


Fig. 1 *syn* and *anti* π-allyl Pd complexes leading to the *E*- or *Z*-product.

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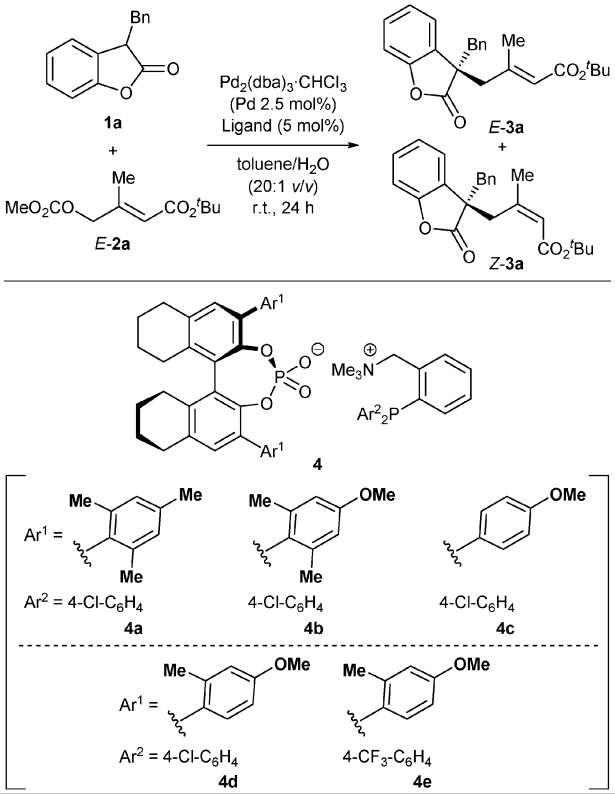
† Electronic supplementary information (ESI) available: Experimental details (including selected NMR spectra) and crystallographic data. CCDC 972631–972633. For ESI and crystallographic data in CIF or other electronic format see DOI: 10.1039/c3cc49338e

Table 1 Optimization of the ligand structure and reaction conditions for asymmetric allylation of benzofuranone **1a** with 1,2-disubstituted allylic carbonate *E*-**2a**[a]



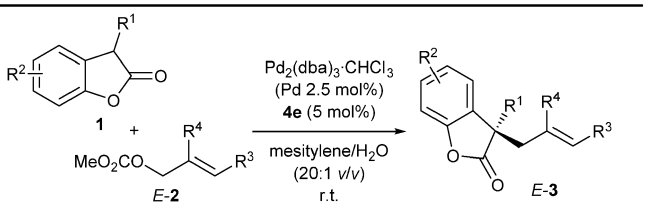
Entry	Ligand	Yield[b] (%)	*E*/*Z*[c]	ee[d] (%)
1	PPh_3	99	1 : 1	—
2	**4a**	88	1.5 : 1	12
3	**4b**	96	2.5 : 1	50
4	**4c**	35	6.7 : 1	79
5	**4d**	44	9.4 : 1	93
6	**4e**	99	11 : 1	92
7[e]	**4e**	99	>20 : 1	94

[a] Unless otherwise noted, reactions were carried out on 0.2 mmol of **1a** with 1.0 equiv. of **2a** under the influence of $Pd_2(dba)_3{\cdot}CHCl_3$ (Pd 2.5 mol%) and ligand (5 mol%) in toluene/H_2O at room temperature for 24 h. [b] Combined yield of *E*-**3a** and *Z*-**3a**. [c] The *E*/*Z* ratio was determined by ^{1}H NMR (400 MHz) analysis of crude product. [d] Enantiomeric excess of the *E*-isomer was indicated, which was analyzed by chiral HPLC. [e] The reaction was performed in mesitylene/H_2O (20 : 1) instead of toluene/H_2O.

Our initial studies focused on examining the effect of a ligand on the stereoselectivity of the alkylation with 1,2-disubstituted allylic electrophiles. For this purpose, 3-benzylbenzofuranone **1a**[8,9] and *E*-1,2-disubstituted allylic carbonate *E*-**2a** were selected as model substrates, and the reaction was attempted in the presence of $Pd_2(dba)_3{\cdot}CHCl_3$ and PPh_3 as a ligand in toluene/H_2O (20 : 1 volume ratio) at room temperature (Table 1, entry 1). After stirring for 24 h, the desired allylated product **3a** was obtained quantitatively in an *E*/*Z* ratio of 1 : 1, revealing the intrinsic geometrical preference of this allylation. Then, the reaction was performed using ion-paired chiral ligands[10–15] **4a** and **4b**, which exhibited high stereocontrolling ability in the previously reported allylation of benzofuranones with simple 1-substituted allylic carbonates;[8] the conversion to **3a** was smooth, with a slight inclination for the formation of the *E*-isomer but with a low to moderate enantiomeric excess (entries 2 and 3). These results prompted us to pursue the modification of the chiral anion component of the ligand **4** with regard to the structural feature of 3,3′-aromatic substitutents (Ar^1). Interestingly, reduction of the steric demand by removal of the 2,6-dimethyl groups from Ar^1 (**4c**) led to a significant improvement in both *E*/*Z*- and enantioselectivities; further, the installation of a 2-methyl-4-methoxyphenyl group (**4d**) enabled even higher levels of geometrical and enantiocontrol, although the chemical yield of **3a** was substantially diminished (entries 4 and 5). This reactivity problem was overcome by switching the 4-chlorophenyl phosphorous substituent (Ar^2) of the ammonium phosphine component of **4d** to a 4-trifluoromethylphenyl group (**4e**) without detrimental impact on the selectivity profile (entry 6). Finally, we succeeded in the quantitative isolation of geometrically almost pure *E*-**3a** with 94% ee by using mesitylene in place of toluene under otherwise identical conditions (entry 7).

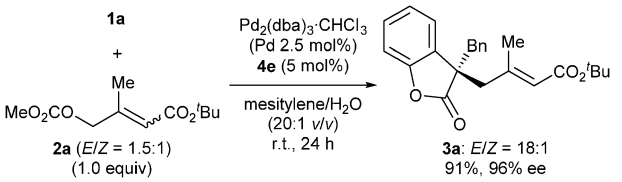
With the optimized ligand structure and reaction conditions in hand, we explored the substrate scope of the present *E*- and enantioselective allylic alkylation of benzofuranones. The representative results are shown in Table 2. The reactions of various 3-substituted benzofuranones with allylic carbonate *E*-**2a** gave the corresponding allylated products (**3b–3e**) in excellent yield with good-to-high *E*- and enantioselectivity (entries 1–4). Introduction of an electron-donating or electron-withdrawing substituent into the 5- or 6-position of benzofuranone did not affect the stereochemical outcome (entries 5–7). The synthetically useful levels of geometrical and enantiocontrol appeared feasible with allylic carbonates possessing other electron-withdrawing substituents such as ethyl ester, dimethyl phosphonate, or nitrile at the

Table 2 Substrate scope[a]



Entry	**1** (R^1, R^2)	**2** (R^3, R^4)	**3**	Yield[b] (%)	*E*/*Z*[c]	ee[d] (%)
1[e,f]	**1b** (Me, H)	**2a** ($CO_2{}^tBu$, Me)	**3b**	90	>20 : 1	91
2	**1c** (^{i}Bu, H)	**2a**	**3c**	93	>20 : 1	90
3	**1d** (CH_2OMe, H)	**2a**	**3d**	90	10 : 1	88
4	**1e** (CH_2CO_2Et, H)	**2a**	**3e**	92	12 : 1	90
5	**1f** (Bn, 5-OMe)	**2a**	**3f**	91	>20 : 1	93
6[e]	**1g** (Bn, 5-Cl)	**2a**	**3g**	99	>20 : 1	97
7	**1h** (Bn, 6-Me)	**2a**	**3h**	90	14 : 1	92
8	**1a** (Bn, H)	**2b** (CO_2Et, Me)	**3i**	76	7.0 : 1	90
9[e]	**1a**	**2c** [$PO(OMe)_2$, Me]	**3j**	88	8.7 : 1	85
10[e]	**1a**	**2d** (CN, Me)	**3k**	89	10 : 1	91
11	**1a**	**2e** ($CO_2{}^tBu$, Et)	**3l**	79	3.8 : 1	45

[a] Unless otherwise noted, reactions were carried out on 0.2 mmol of **1** with 1.0 equiv. of **2** under the influence of $Pd_2(dba)_3{\cdot}CHCl_3$ (Pd 2.5 mol%) and **4e** (5 mol%) in mesitylene/H_2O at room temperature. For reaction time, see ESI. [b] Isolated yield of *E*-**3**. [c] The *E*/*Z* ratio was determined by ^{1}H NMR (400 MHz) analysis of the crude product. [d] Enantiomeric excess of the *E*-**3**, which was analyzed by chiral HPLC. [e] The reaction was conducted at 10 °C. [f] The reaction was performed using $Pd_2(dba)_3{\cdot}CHCl_3$ (Pd 5 mol%) and **4e** (10 mol%).



Scheme 2 Asymmetric allylation of **1a** with an *E*/*Z* mixture of allylic carbonate **2a**.

1-position (entries 8–10). Unfortunately, this system was sensitive to the alteration of the substituent at the 2-position of allylic carbonates, as the reaction of **1a** with 2-ethyl-substituted **2e** furnished **3l** with insufficient stereoselectivity (entry 11). The absolute configuration and olefin geometry of allylated product **3g** were unequivocally determined by X-ray crystallographic analysis. In addition, the predominant formation of *E*-configured **3j** and **3k** was confirmed by X-ray analysis, and the stereochemistries of the remaining examples were assumed by analogy.

To gain insight into the reaction pathway, we examined the reaction of **1a** with an *E*/*Z*-isomeric mixture of **2a** under the optimal conditions, wherein **3a** was obtained in 91% yield with similarly excellent *E*- and enantioselectivity (Scheme 2). This result clearly indicates that the rapid *syn–anti* isomerization of the intermediary π-allyl palladium complex occurred prior to the carbon–carbon bond-forming event, and that ligand **4e** would play a pivotal role in controlling the distribution of these *syn* and *anti* complexes or the relative rate of the bond formation from each complex.

We have developed a palladium-catalyzed highly *E*- and enantioselective allylation of 3-substituted benzofuranones with 1,2-disubstituted allylic carbonates. The judicious utilization of the structural modularity of the ion-paired chiral ligands allowed for rigorous and simultaneous control of *E*/*Z* selectivity and enantioselectivity. We believe that the present study expands the versatility of transition-metal-catalyzed allylic alkylations for the construction of synthetically valuable chiral building blocks.

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