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Synthetic Methods

Enantioselective Transformation of Allyl Carbonates into Branched Allyl Carbamates by Using Amines and Recycling CO_2 under Iridium Catalysis

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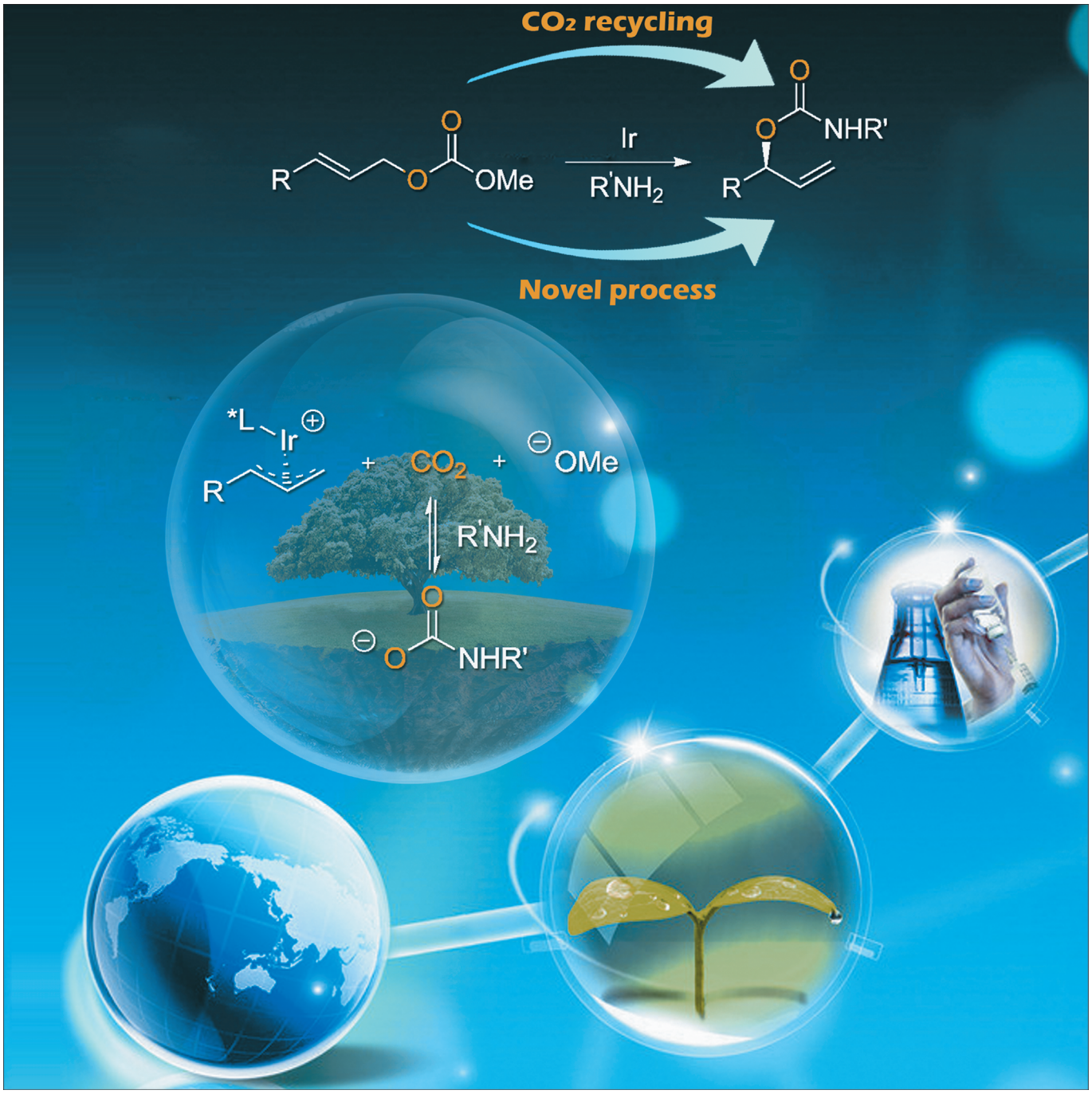
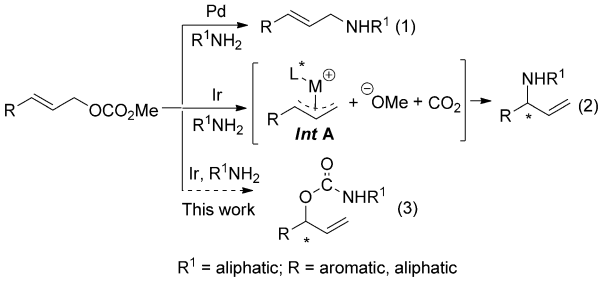


Abstract: Enantioselective transformation of allyl carbonates into branched allyl carbamates by using amines and recycling CO_2 in the presence of an Ir complex and K_3PO_4 was accomplished. This provided branched allyl carbamates in fair to excellent yields with up to 98:2 regioselectivity and 93% *ee*. The role of CO_2 in this transformation is discussed as well.

Transition-metal-mediated allylation has emerged as a powerful method for the regio-, diastereo-, and enantioselective formation of carbon–carbon[1] or carbon–heteroatom[2] bonds. However, the selectivities depends on various factors such as the nature of the metal complex, the substitution pattern of the substrate, the nucleophile, the leaving group, the solvent, and the temperature.[3] When allylic carbonates are employed as substrates, linear products are preferentially obtained with Pd catalysts[4] (Scheme 1, reaction 1); however, branched products



Scheme 1. Transition-metal-catalyzed allylation of allyl carbonates with amines.

are favored in the presence of other transition metals, such as iridium[5] and ruthenium.[6] Detailed mechanistic studies on the Ir-catalyzed allylic substitution have been carried out by several research groups.[7] The essential step is the formation of a π-allyl–iridium complex through decarboxylation, an intermediate that then undergoes various transformations. In these reactions, CO_2 is produced as a co-product in the decarboxylation step (Scheme 1, reaction 2).[7a] The conversion of CO_2 into useful chemicals has gained great attention from the viewpoint of carbon resources and environmental issues.[8] We speculated that CO_2 may be recycled by an attack of a nucleophile, such as an amine, that is, an amidation reaction, followed by an Ir-catalyzed allylation reaction to give a branched allylic carbamate (Scheme 1, reaction 3). To the best of our knowledge, such a reaction has not been explored despite its potential in both atom-economic synthesis and our mechanistic understanding of π-allyl–metal chemistry. Allyl carbamates are an important class of compounds; there is a broad interest in them with regards to both synthetic intermediates[9] and biologically active molecules.[10] Allyl carbamates are generally synthesized from the reaction of allyl alcohols with isocyanates.[11] Therefore, a new synthetic method for the preparation of chiral allyl carbamates is highly desirable. Furthermore, we are confronted with an additional issue; the branched allyl carbamate is a good substrate for Ir-catalyzed allylic aminations as well.[12] Herein, we report the first enantioselective transformation of allyl carbonates into branched allyl carbamates in the presence of amines.

In an initial test of our hypothesis, we explored a model reaction of (*E*)-cinnamyl methyl carbonate **2a** with *n*-propylamine in the presence of different types of bases and a well-known iridacycle,[5b] which is generated from 2 mol% of [{Ir(cod)Cl}$_2$] and 4 mol% of ligand **1a**,[13–14] under various reaction conditions. We found that employing propyl amine **3a** in this reaction in *N*,*N*-dimethylformamide (DMF)[15] at 35 °C led to **6a** as the sole amination product in 32% yield (Table 1, entry 1). Surprisingly, in the presence of CsF, a trace amount of the branched carbamate **4a**[16] was obtained (Table 1, entry 2). Significant improvement in efficiency, regioselectivity, and enantioselectivity (55% yield, **4a**/**5a** 81:19, 88% *ee*) was achieved when Cs_2CO_3 was employed; 15% of **6a** and a minor allylic alcohol were obtained as well (Table 1, entry 3). These results strongly suggest that the domino reaction occurred as speculated and that the nature of the base exerts a significant effect on this reaction. As a result, a range of bases were investigated. Among these bases, K_3PO_4 gave **4a** in fair yield with **4a**/**5a** 90:10 and 85% *ee* (Table 1, entry 5), whereas the remaining bases gave rise to poor results (Table 1, entries 4, 6–8). Examination of a range of solvents revealed that DMSO is the optimum solvent (Table 1, entries 5, 9–11).

In terms of transition-metal-catalyzed allylic substitution, elevated reaction temperatures promotes the reductive elimination process.[17] Indeed, a change of the reaction temperature has a dramatic influence on efficiency and enantioselectivity (Table 1, entries 11–13). The reaction at room temperature[18] gave **4a** in 43% yield with **4a**/**5a** 94:6 with 93% ee; 13% of amination product **6a** was obtained as well (Table 1, entry 12). Upon raising the temperature to 35 °C, the yield of **4a** was improved to 80%; however, the *ee* value of **4a** was reduced to 86% while the regioselectivity was maintained at 94:6 (Table 1, entry 11). Upon further elevating the reaction temperature to 50 °C, both regio- and enantioselectivity were reduced; 5% of amination product **6a** was obtained (Table 1, entry 13).

A set of chiral ligands, including Feringa's ligand, **1a**, **1b**,[14] **1c**,[13] **1d**,[14] **1e**,[19] and PHOX ligand **1f**[20] (Figure 1), was evaluated. The reaction with **1a** at 25 °C gave superior results; 7% yield of **6a** was obtained as well (Table 1, entry 11). Ligand **1d**, which bears a simple biphenyl backbone, afforded the product in good yield (69%) and regioselectivity (86:14), albeit with slightly lower enantioselectivity (80% *ee*, Table 1, entry 16). The use of ligands **1b** and **1c**, which have bulky groups on the

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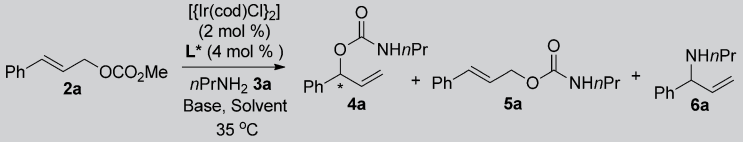
Table 1. Optimization of the reaction conditions.[a]



Entry	L*	Base	Solvent	**4a/5a**[c]	Yield **6a** [%][c]	Yield **4** [%][b]	*ee*[d]
1	**1a**	–	DMF	--	32	–[e]	–
2	**1a**	CsF	DMF	n.d.[f]	–	Trace	n.d.
3	**1a**	Cs_2CO_3	DMF	85:15	15	55	88
4	**1a**	K_2CO_3	DMF	n.d.	n.d.	25	n.d.
5	**1a**	K_3PO_4	DMF	90:10	12	46	85
6	**1a**	KOAc	DMF	90:10	trace	28	n.d.
7	**1a**	DABCO	DMF	83:17	trace	39	28
8	**1a**	DBU	DMF	55:45	25	29	78
9	**1a**	K_3PO_4	THF	--	38	–	–
10	**1a**	K_3PO_4	CH_2Cl_2	--	21	–	–
11	**1a**	K_3PO_4	DMSO	94:6	7	80	86
12[g]	**1a**	K_3PO_4	DMSO	94:6	13	43	93
13[h]	**1a**	K_3PO_4	DMSO	89:11	5	73	80
14	**1b**	K_3PO_4	DMSO	85:15	11	23	90
15	**1c**	K_3PO_4	DMSO	57:43	15	18	79
16	**1d**	K_3PO_4	DMSO	86:14	11	69	80
17	**1e**	K_3PO_4	DMSO	n.d.	–	Trace	n.d.
18	**1f**	K_3PO_4	DMSO	n.d.	–	Trace	n.d.

[a] All the reactions were carried out on a 0.2 mmol reaction scale by using 2 mol% of $[\{Ir(cod)Cl\}_2]$, 4 mol% of **1a–f**, 120 mol% of base, 120 mol% of **2a**, and 100 mol% of **3a** (0.1 M). [b] Yields of isolated product. [c] Determined by ^{1}H NMR analysis of the crude reaction mixture. [d] Determined by HPLC analysis by using a chiral column (Chiralcel OD-H column). [e] Not detected. [f] n.d. = not determined. [g] At room temperature. [h] At 50 °C.

nation products **6a–e** were obtained in 8–15% yields (Table 2, entries 1–5). Lower reaction temperatures led to improved levels of enantioselectivity (Table 2, entry 1 and entry 4, 93% and 90% *ee*, respectively, at 25 °C). A range of amines, including *n*-butylamine, isopropylamine, and allylamine, were explored by using (*E*)-methyl 5-phenylpent-2-enyl carbonate (**2f**) as the substrate and the corresponding products, **4f**[21] and **4g–i**, were obtained in good to excellent yields (70–94%) with excellent levels of regioselectivity (95:5–98:2) and 76–80% *ee*; a trace amount of **6f–i**, respectively, was found in these cases (Table 2, entries 6–9). Alkyl-substituted allylic carbonates, such as **2g** and **2h**, were well tolerated, providing the branched carbamates **4j** and **4k** in 88 and 78% yield, with the same excellent regioselectivity (96:4) and 88 and 78% *ee*, respectively (Table 2, entries 10 and 11).

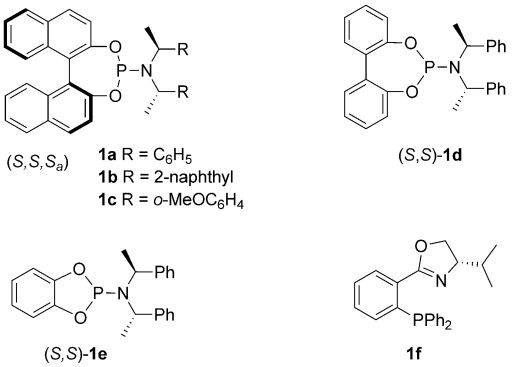
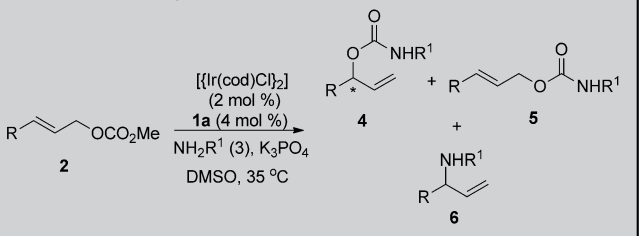


Figure 1. Chiral ligands **1a–f**.

phenyl ring of the amine moiety, resulted in poor yields (18–23%, Table 1, entries 14 and 15). Notably, the reaction completely failed when both **1e** and **1f** were employed (Table 1, entries 17 and 18).

We further examined the scope and generality of this reaction. Aryl-substituted substrates, such as (*E*)-cinnamyl methyl carbonate **2a** and allylic carbonates (**2b–e**), with either electron-withdrawing groups (4-Cl and 4-Br) or electron-donating groups (3-OCH_3 and 4-CH_3) gave the respective products in moderate to high yields (52–80%) with high levels of regioselectivity (89:11—96:4) and enantioselectivity (88–93% *ee*); ami-

Table 2. Scope of allyl carbonates **2** and amines **3**.[a]



Entry	**2**	R	R^1	**4/5**[c]	Yield **6** [%][c]	Yield **4** [%][b]	*ee* [%][d]
1[e]	**2a**	Ph	*n*Pr	94:6	**6a**, 13	**4a**, 43	93
2	**2b**	4-ClC_6H_4	*n*Pr	94:6	**6b**, 9	**4b**, 77	90
3	**2c**	4-BrC_6H_4	*n*Pr	96:4	**6c**, 8	**4c**, 80	87
4[e]	**2d**	3-$MeOC_6H_4$	*n*Pr	93:7	**6d**, 15	**4d**, 54	90
5	**2e**	4-MeC_6H_4	*n*Pr	89:11	**6e**, 11	**4e**, 52	88
6	**2f**	$PhCH_2CH_2$	*n*Pr	95:5	**6f**, trace	**4f**, 94	77
7	**2f**	$PhCH_2CH_2$	*i*Pr	98:2	**6g**, trace	**4g**, 80	76
8	**2f**	$PhCH_2CH_2$	*n*Bu	97:3	**6h**, trace	**4h**, 70	76
9	**2f**	$PhCH_2CH_2$	allyl	97:3	**6i**, trace	**4i**, 75	80
10	**2g**	*n*Pr	*n*Pr	96:4	**6j**, trace	**4j**, 88	88
11	**2h**	Et	*n*Pr	96:4	**6k**, trace	**4k**, 78	78
12	**2c**	4-BrC_6H_4	*i*Pr	85:15	**6l**, 7	**4l**, 58	94

[a] Reaction conditions as in Table 1, entry 12 at either 25 °C or 35 °C. [b] Yield of isolated products. [c] Determined by ^{1}H NMR analysis of the crude reaction mixture. [d] Determined by HPLC analysis by using a chiral column or GC. [e] The reaction was performed at room temperature.

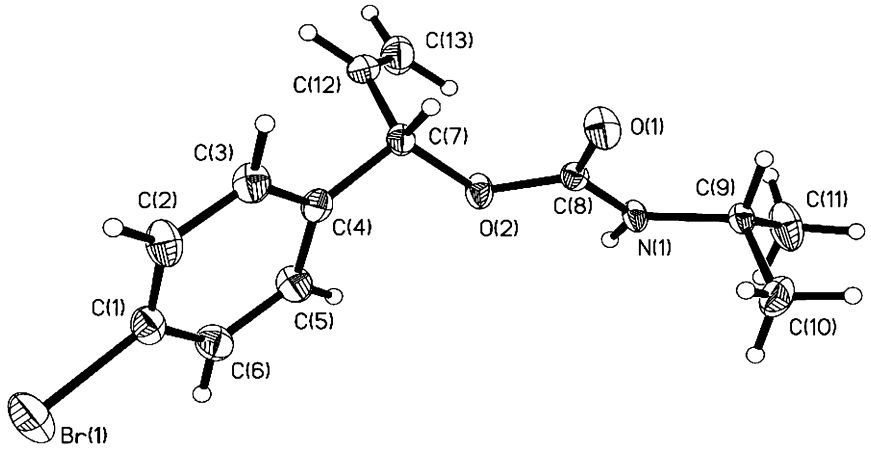
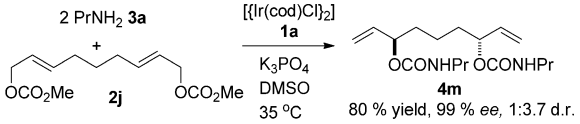


Figure 2. X-ray structure of (*S*)-**4l**.

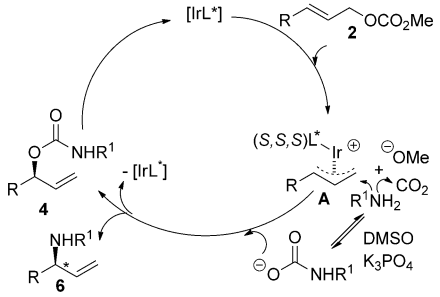
X-ray analysis of **4l**[22] revealed that its absolute configuration is *S* (Figure 2).

This methodology was extended to bis(allylcarbonates) and the synthesis of (3*R*,7*R*)-nona-1,8-diene-3,7-diyl bis(propylcarbamate) (**4m**) was demonstrated (Scheme 2). The domino reaction of the bis(allylcarbonate) **2j** under the optimal reaction conditions occurred twice to give the corresponding product **4m** in 80% yield with 99% *ee* and 1:3.7 d.r.



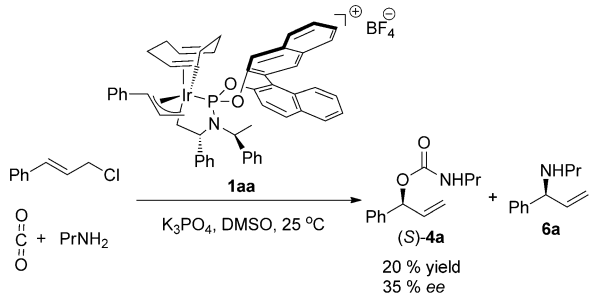
Scheme 2. Domino amidation—allylation reaction of **2j**.

For the mechanism, we propose that it begins by insertion of iridium into the allyl–oxygen bond to liberate an ionized π-allyl–Ir complex (**Int A**), methoxide, and CO_2. Subsequently, an amidation reaction between CO_2 and an amine occurs to form a carbamate ion[23] ($^-$OCONHR), which in turn attacks **Int A** to yield an allyl carbamate **4** and regenerating the catalyst. In the presence of K_3PO_4, **Int A** is directly attacked by the amine to give an extrusion product, allylamine **6** (Scheme 3).



Scheme 3. Proposed mechanism.

We present three piece of experimental evidence for the above mechanistic hypothesis: 1) a domino reaction of (*E*)-(3-chloroprop-1-enyl)benzene,[24] CO_2, and *n*PrNH$_2$ occurred in the presence of π-allyl–Ir complex (**1aa**, 0.20 mol%, prepared according to Helmchen's method)[7d] and K_3PO_4 in DMSO at 25 °C, providing the same *S* product **4a** (Scheme 4) as that for entry 1 of Table 2; 2) under the optimized conditions, using **4a**/**2a** (1:2) as the reactants, isomerization of **4a** into thermodynamically stable **5a** (**4a**/**5a** 94:6)



Scheme 4. Domino reaction of (*E*)-(3-chloroprop-1-enyl)benzene, propylamine, and CO_2.

was confirmed through ^{1}H NMR analysis of the crude products; the branched allylic alcohol,[25] but not amine **6a**, was observed as well; 3) using **5a** as the reactant, no reaction occurred (see the Supporting Information).

In summary, we have developed a domino reaction of allyl carbonate, amine, and recycling CO_2, a reaction that occurs in the presence of K_3PO_4 and DMSO with the assistance of an iridium complex and provides the branched allyl carbamates **4** in good yields with excellent levels of regioselectivity and good to excellent levels of enantioselectivity. Essential for the success of the reaction was the role of CO_2, which is generated in the course of this reaction and then recycled.

Experimental Section

General procedure

The yellow iridacycle[5b] made from [{Ir(cod)Cl}$_2$] (0.004 mmol, 2 mol%) and phosphoramidite ligand **1a** (0.008 mmol, 4 mol%) was placed in a dry Schlenk tube filled with argon. Then, allylic carbonate **2** (0.24 mmol, 120 mol%), K_3PO_4 (0.24 mmol, 120 mol%), amine **3** (0.20 mmol, 100 mol%), and DMSO (2.0 mL) were added. The reaction mixture was stirring at 35 °C. After the completion of the reaction, the crude reaction mixture was diluted with water and extracted with ethyl acetate. The crude residue was purified

by flash column chromatography (petroleum ether/ethyl acetate) to give the desired products **4**.

Acknowledgements

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Keywords: allylcarbamates · carbon dioxide · domino reactions · enantioselectivity · iridium

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[25] Branched allylic alcohols were observed as products in the iridium-catalyzed allylic hydroxylation of allylic carbonates in the presence of either H_2O or $KHCO_3$; see ref. [2o].

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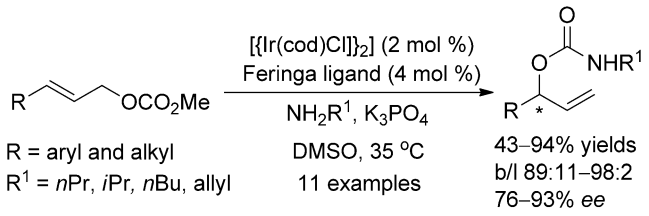


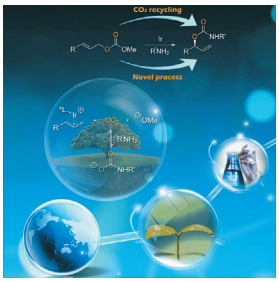
Branching out: Allyl carbonates can be enantioselectively transformed into branched allyl carbamates by using amines and recycling CO_2 in the presence of an Ir complex and K_3PO_4. Branched allylcarbamates are obtained in fair to excellent yields, up to 98:2 regioselectivity, and up to 93% *ee* (see scheme; cod = 1,4-cyclooctadiene).

Synthetic Methods

*S.-C. Zheng, M. Zhang, X.-M. Zhao**

■■ – ■■

Enantioselective Transformation of Allyl Carbonates into Branched Allyl Carbamates by Using Amines and Recycling CO_2 under Iridium Catalysis



Iridium Catalysis

In their Communication on page ■■ ff., X.-M. Zhao et al. show that allyl carbonates can be enantioselectively transformed into branched allyl carbamates in the presence of an iridium catalyst and an amine. CO_2, which is initially expelled upon oxidative addition, is recycled by being trapped by the amine, the resulting carboxylate adduct undergoing nucleophilic addition with the allyl–iridium intermediate.