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Enantioselective and Regioselective Ruthenium-Catalyzed Decarboxylative Etherification of Allyl Aryl Carbonates

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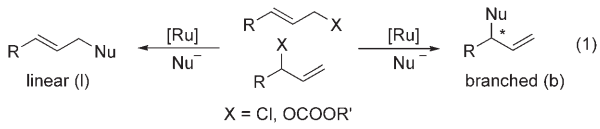
Among the large variety of synthetic methods yielding non-racemic products, one of the most documented is the attack of nucleophiles onto allyl–metal intermediates yielding chiral allylic products in high enantiomeric purity.[1] With unsymmetrical allyl–metal intermediates, the regioselectivity of the reaction is of central importance and it can be controlled by the metal at-play.[2] In this respect, several ruthenium derivatives have proven to be largely effective for the introduction of nucleophiles at the more substituted position leading to branched (b) rather than linear (l) products [Eq. (1)].[3] Cp*Ru derivatives, and Cp′Ru moeties that contain cyclopentadienyl rings with tethered ligands, are generally preferred over CpRu compounds (Cp* = C_5Me_5, Cp = C_5H_5).[4–9]



Typical substrates are primary or secondary allyl carbonates and chlorides, and effective allylic alkylation, amination, and etherification reactions have been developed.[4–10] If non-racemic secondary allyl carbonates are used, the reactions proceed stereospecifically with, possibly, complete transfer of chirality.[4] Recently, it was shown that allyl β-keto esters[10] and alcohols[11] can also be employed as substrates in related processes.

Efficient Ru-catalyzed enantioselective allylic substitutions of linear unsymmetrical substrates are nevertheless rare. Only two types of successful transformations have been reported so far. The first concerns the etherification of allyl chlorides with phenols. Bruneau and Renaud and coworkers have first shown that combinations of Cp*Ru **1a** and box-type ligands (e.g. **1**, Figure 1) afford allyl aryl ethers

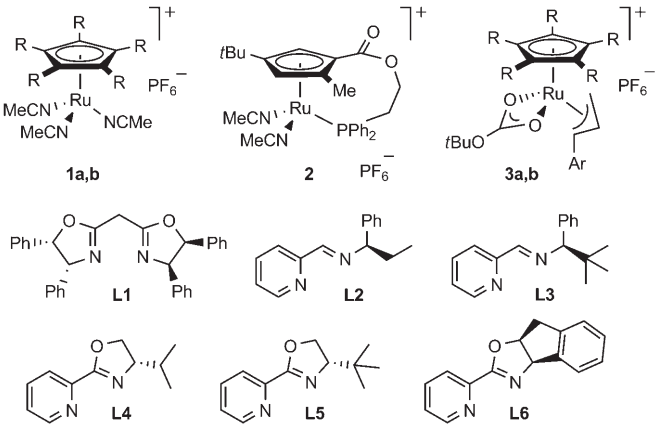


Figure 1. Ruthenium complexes **a**: R = Me, **b**: R = H and chiral diimine ligands.

in good enantioselectivity and decent regioselectivity (up to 82% *ee*, b/l 1.6:1 to 6.5:1).[12] Very recently, Onitsuka et al. have reported excellent results for this reaction using planar-chiral Cp′Ru **2** as mediator (up to 95% *ee* and, b/l > 20:1) and shown that only allyl halides provide high selectivity in this reaction.[13] The second kind of transformation concerns the decarboxylative rearrangement of allyl β-keto esters. Recently, our group has shown that CpRu **1b** and pyridine–imine ligands (e.g. **L2** and **L3**, Figure 1) afford non-racemic γ,δ-unsaturated ketones through regio- and enantioselective C–C bond forming reactions (up to 85% *ee* and, b/l > 20:1).[14] However, none of these transformations have used allyl carbonates as starting materials. The lack of any examples of this process was striking as these moieties are very common starting materials in asymmetric metal-catalyzed processes.[1,15] A possible reason is the facile reaction of these substrates with Cp*Ru **1a** and CpRu **1b** to

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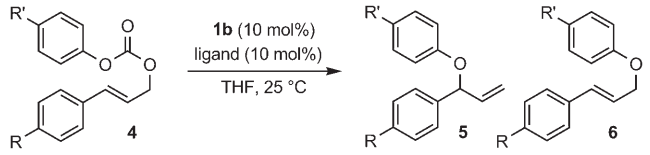
form Ru^{IV} allyl carbonate complexes of type **3a** and **3b** (Figure 1).[8e,g] The derived complexes are more catalytically-active than **1a** and **1b** and lead to racemic products only.

The development of an efficient enantioselective allylation reaction using allyl carbonates as substrates and ruthenium catalysts was then worth studying. Herein we report that allyl aryl carbonates can be used. They react in the presence of CpRu **1b** and easy-to-prepare pyridylmonooxazoline (pymox) ligands to afford branched allyl aryl ethers in high enantiomeric purity and excellent regioselectivity (up to 87% *ee* and, b/l > 20:1).[16] This transformation is, to our knowledge, the first example of an effective enantioselective decarboxylative etherification.

In view of the successful results with aryloxides as nucleophiles in *intermolecular* Ru-catalyzed displacement reactions,[13,14] we reasoned that allyl aryl carbonates of type **4** (Table 1) ought to be ideal substrates as, after carbon dioxide extrusion, the resulting aryloxides could react directly with allyl fragments.[17] Surprisingly, only few reports have been devoted to the formation of allyl aryl ethers by metal-catalyzed, intramolecular decarboxylation of allyl aryl carbonates.[18,19] To our knowledge a single attempt has been reported at developing an enantioselective version of this transformation (up to 24% *ee*).[20] This lack of examples was making the study even more interesting.

Table 1. Ligand screening for allyl carbonate **4a**.[a]



a: R = H, R' = H **d:** R = H, R' = Me
b: R = Cl, R' = H **e:** R = Cl, R' = Me
c: R = NO_2, R' = H **f:** R = H, R' = NO_2

Allyl	Ligand	*t* [h]	Conversion [%]	*ee*[b]	Configuration[c]	b/l ratio[d]
4a	–	24	34	–	–	83:17
4a	bpy	2	37	–	–	93:7
4a	L2	2	24	60	(−)	93:7
4a	L3	2	14	73	(−)	93:7
4a	L4	2	74	56	(−)	91:9
4a	L5	2	<10	–	–	–
4a	L6	2	100	84	(+)	>95:5
4a	L6	12	100	78	(+)	91:9

[a] **1b** (10 mol%), ligand (10 mol%), THF, 25°C, c = 0.5 M; the results being the average of at least two runs. [b] Determined by CSP-HPLC. [c] Sign of the optical rotation. [d] Ratios of branched (**5a**) to linear (**6a**) products determined by ^{1}H NMR spectroscopy (400 MHz).

Initial experiments were conducted using conditions similar to that of the enantioselective rearrangement of allyl β-keto esters.[15] Allyl carbonate **4a** (Table 1, R, R′ = H) was treated with catalytic amounts of **1b** (10 mol%) in THF at room temperature (Table 1).[21] Importantly, without ligand, little reactivity was observed (34% conversion after 24 h); the presence of 2,2′-bipyridine (bpy)[5] accelerating the reaction and improving the regioselectivity. In presence of **L2** and **L3** (10 mol%),[15] the reaction proceeded but modest results were obtained (conversion up to 24% after 2 h, up to 73% *ee*). A screening of chiral ligands was then performed, and of pymox derivatives in particular.[22] A selection is presented in Figure 1. Ligands **L4** to **L6** were synthesized following the procedure of Bolm et al. by condensing commercially available enantiopure 1,2-aminoalcohols onto 2-cyanopyridine with a catalytic amount of $ZnCl_2$.[23,24] Whereas ligand **L4** allowed the reaction to proceed with decent conversion (2 h, 74%) and moderate enantioselectivity (**5a**: 56% *ee*), essentially no reaction was observed with more sterically hindered, *tert*-butyl substituted **L5**. With ligand **L6**, derived from (1*R*,2*S*)-*cis*-1-amino-2-indanol, the reaction was the fastest (2 h, 100% conversion) and the desired branched adduct **5a** afforded with good overall selectivity (84% *ee*, b/l > 95:5).[25] The results are summarized in Table 1. Interestingly, longer reaction times (12 h) leads to a small but definite decrease in both, *ee* and, b/l values. This result will be explained later in the course of the study.

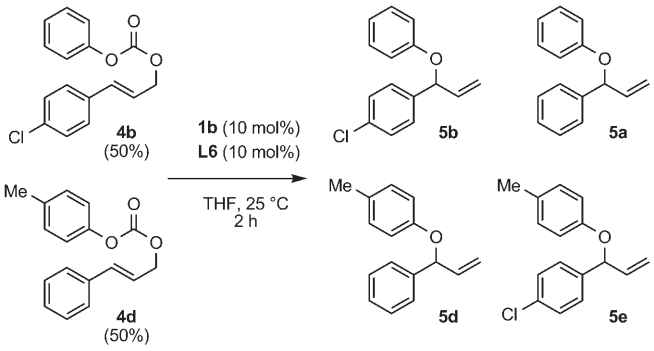
With the improved conditions at hand (THF, 25°C, **L6** 10 mol%), the scope of the asymmetric protocol was studied with allyl carbonates **4b–f** (Table 2). At first substituents were introduced on the aromatic nucleus of the cinnamyl fragment (**4b**: R = *p*-Cl, **4c**: R = *p*-NO_2). From **4a–c**, a gradual decrease in the reactivity of the allylic substitution was noticed. In terms of regioselectivity, whereas no change was observed with **4b**, a sharp decrease proceeded with **4c** (b/l **4b**: >95:5 and **4c**: 75:25). These variations resulting from the presence of an electron-withdrawing atom or group are in line with a previous result in this field.[8a] Interestingly, in terms of enantioselectivity, little difference is observed with these three substrates which would tend to indicate that the enantio- and the regiodetermining steps of this reaction are distinct and independent. A series of allyl carbonates with substituents on the aryloxy moiety (**4d–f**) was also prepared. Their structures are detailed in Tables 1and 2. Not surprisingly, slower reactions resulted from the introduction of electron-donating, *p*-Me on the "leaving-group" (**4d** and **4e**) with, however, little effect on the regioselectivity (b/l 90:10) and enantiomeric purity of the branched products (84–85% *ee*). With **4f**, a clear activation resulted from the presence of the electron-withdrawing, *p*-NO_2 group, however, at the expense of the enantiomeric purity of **5f** (34% *ee*).

Table 2. Ru-catalyzed etherification of allyl carbonates **4a** to **4f**.[a]

Allyl	R	R′	*t* [h]	Conversion [%]	*ee*[b]	Configuration[c]	b/l ratio[d]
4a	H	H	2.0	100	84	(+)	>95:5
4b	Cl	H	2.5	92	87	(+)	>95:5
4c	NO_2	H	7.0	87	85	(−)	75:25
4d	H	Me	2.5	90	84	(−)	90:10
4e	Cl	Me	3.5	90	85	(−)	90:10
4f	H	NO_2	0.5	94	34	(−)	87:13

[a] **1b** (10 mol%), **L6** (10 mol%), THF, 25°C, c = 0.5 M; the results being the average of at least two runs. [b] Determined by CSP-HPLC. [c] Sign of the optical rotation. [d] Ratios of branched (**5**) to linear (**6**) products determined by ^{1}H NMR spectroscopy (400 MHz).

To gain some insight on the nature of the asymmetric transformation, a series of experiments was performed. First, a 1:1 mixture of allyl carbonates **4b** and **4d** was treated under the standard conditions (Scheme 1) and ^{1}H NMR analysis (500 MHz) of the resulting mixture indicated the presence of products **5b** and **5d**, and cross-over products **5a** and **5e** in a 1.4:2.0:1.0:1.4 ratio, respectively. This result indicates that the etherification reaction proceeds through a state where in situ generated nucleophilic and electrophilic fragments are separated in solution resulting in a complete cross-over.



Scheme 1. -Reactions of **4b** and **4d**.

At that stage, we considered the result of the decarboxylative etherification of **4a** for which, after 12 h of reaction time at 25 °C, lower levels of enantio- and regioselectivity were obtained (78 % *ee*, b/l 91:9). We wondered if an equilibration between products **5a** and **6a** did not occur under the reaction conditions at the expense of the selectivity. Preliminary experiments performed at 25 °C seemed to validate this hypothesis, but these studies were hampered by slow kinetics. The decarboxylative etherification of **4a** was thus performed at 60 °C. The results are detailed in Table 3. Clearly, full conversion was achieved rapidly at this higher temperature. A result similar to that of the reaction at 25 °C after 12 h was obtained after only 45 min at 60 °C (Table 3, entry 1). Longer reaction times (Table 3, entries 2–6) resulted, as hypothesized, in a progressive loss of enantiomeric purity and in an increase of the b/l ratio. Branched adduct **5a** disappeared in favor of linear compound **6a** which became the exclusive product after reaction at 60 °C for 22 h.

Table 3. Etherification of allyl carbonate **4a**.[a]

Entry	*t* [h]	Conversion [%]	*ee*[b]	Configuration[c]	b/l ratio[d]
1	0.75	100	80	(+)	92:8
2	1.5	100	74	(+)	89:11
3	2.5	100	64	(+)	80:20
4	3.5	100	50	(+)	69:31
5	8.0	100	2	(+)	33:66
6	22	100	–	–	<5:95

[a] **1b** (10 mol %), **L6** (10 mol %), THF, 60 °C, $c = 0.5$ M. [b] Determined by CSP-HPLC. [c] Sign of the optical rotation. [d] Ratios of branched (**5a**) to linear (**6a**) determined by NMR spectroscopy (^{1}H NMR, 400 MHz).

To further characterize the **5**→**6** transformation, experiments were performed under the following conditions: 60 °C, THF, **1b** and **L6** 10 mol % each. A mixture of *rac*-**5a** and **6a** (b/l 92:08) was heated for 4 h. The, b/l ratio gradually changed in favor of the linear product to reach a 80:20 value. Importantly, a small enantiomeric excess could be detected for the remaining branched substrate in favor of (−)-**5a** (9 % *ee*; see the Supporting Information for details). This means that, out of the racemic mixture the (+)-**5a** enantiomer has reacted to some extent faster than (−)-**5a** during this branched to linear transformation. As the dextrorotatory enantiomer is the one preferentially formed during the enantioselective etherification with **L6** as ligand, this explains why longer reaction times are detrimental for the enantiomeric excess.

A 1:1 mixture of allyl ethers **5b** and **5d** was also heated (60 °C) in the presence of the catalytic combination and the reaction was monitored by ^{1}H NMR (400 MHz). After 7 h, all possible branched and linear products compatible with intermolecular processes were observed (**5b**, **5d**, **6b**, **6d** and cross-over **5a**, **5e**, **6a**, **6e**). A prolonged reaction time of 24 h leads to the quasi exclusive formation of the linear products (**6a**, **6b**, **6d**, and **6e**) in approximately equal amounts. These results indicate that aryloxides can act as leaving groups[26] under the reactions conditions if care is not taken to avoid a displacement (lower temperature, short reaction time).[27] Equilibration between branched and linear products occurs, via a dissociative, intermolecular mechanism leading to a loss of enantiomeric purity of the initial branched allyl aryl ethers and, finally, to the exclusive formation of the linear thermodynamically more-stable isomers. The enantioselectivity observed during the reaction probably results from the initial oxidative addition step; the regioselectivity being then dictated by the structure of the π-allyl complex.[5g,8g]

In conclusion, we have just described the first effective decarboxylative etherification of allyl aryl carbonates using a readily-prepared (one step from commercial sources) pymox ligand **L6** and readily available CpRu complex **1b**. Reaction conditions are most simple as only these two reagents are necessary. We have also characterized an equilibration reaction that must be taken into consideration for any asymmetric development. Further studies are performed to understand the intricate details of this transformation and extend the results to other useful processes.

Experimental Section

General procedure for catalytic etherification of the allyl carbonates: In a 1 mL vial under dinitrogen atmosphere, [RuCp(MeCN)$_3$][PF$_6$] (**1b**; 6.3 mg, 14.4 μmol, 10 mol %) and pymox **L6** ligand (3.4 mg, 10 mol %) were dissolved in distilled anhydrous THF (300 μL). The resulting deep red solution was stirred for 5 min at room temperature before the addition of the allyl aryl carbonates **4** (0.144 mmol). The reaction was stirred under N_2 at 25 °C until no trace of the starting material could be seen on TLC (silica gel, Et$_2$O/pentane 8:2). The reaction mixture was diluted with Et$_2$O/pentane 8:2 (1.5 mL). The precipitated metal salts were fil-

tered on a short silica gel column (0.5 cm × 4 cm, Et_2O/pentane 8:2): The solvents were evaporated under reduced pressure to afford the crude reaction mixture as a pale yellow oil which was analyzed by ^1H NMR spectroscopy and CSP-HPLC.

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Keywords: allylic compounds · C–O bond formation · enantioselectivity · N ligands · ruthenium

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