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Regio and Enantioselective Allylation of Phenols via Decarboxylative Allylic Etherification of Allyl Aryl Carbonates Catalyzed by (Cyclopentadienyl)ruthenium(II) Complexes and Pyridine-Hydrazone Ligands

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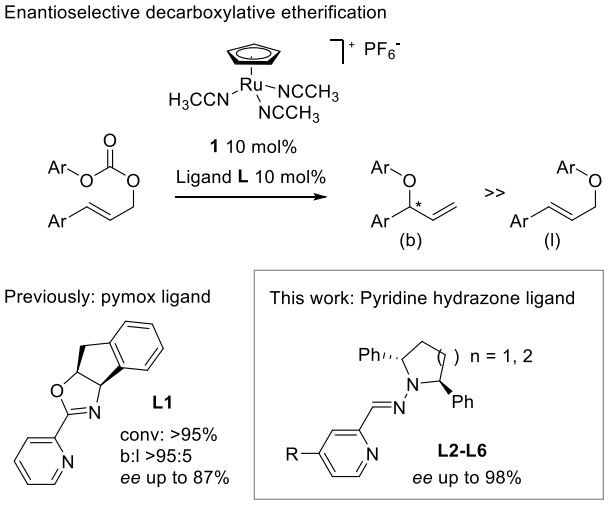
Abstract. (Cyclopentadienyl)tris(acetonitrile)ruthenium hexafluorophosphate $[CpRu(CH_3CN)_3][PF_6]$ in combination with pyridine-hydrazone ligands efficiently catalyzes the asymmetric decarboxylative allylic rearrangement of allyl aryl carbonates. Formations of C–O bonds with high regio- and enantioselectivity ratios (up to 95:5 and 98% *ee*) are obtained. Good stereocontrol of the pseudotetrahedral geometry of the CpRu moiety is achieved by the hydrazone ligand and its "electron-poor" nature is evidenced through the epimerization of hexacoordinated TRISPHAT-N anion.

Keywords: allylic compounds; enantioselective catalysis; etherification; ruthenium catalysts

The nucleophilic attack onto electrophilic allyl metal intermediates is a general tool in organometallic chemistry.[1] This methodology allows the formation of C–H, C–O, C–N, C–S and C–C bonds using the appropriate nucleophiles.[2]. Several allylic building blocks for natural product synthesis have been made through this methodology.[3] Moreover the nature of the metal center plays a significant role in the control of the regio- and enantioselectivity of the transformations. Metals including Cu,[4] Fe,[5] Ir,[6] Mo,[7] Pd,[8] Rh [9] and Ru [10] have been utilized and display high levels of enantioselectivity or enantiospecificity, in addition to regioselectivity.

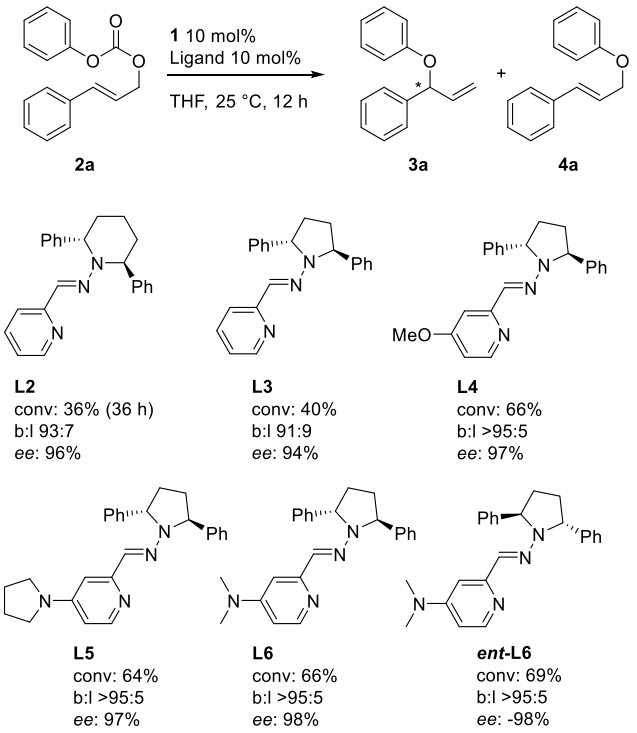
As just mentioned, ruthenium complexes are able to promote the regioselective attack of nucleophiles onto unsymmetrical π-allyl fragments and lead to the preferred formation of branched (b) over linear (l) products.[10] In addition, stereogenic centers are usually created during the formation of the adducts. Electron rich complexes such as Cp*Ru (Cp* = C_5Me_5)[10-11] or Cp'Ru (planar chiral complexes)[12] are generally preferred to the corresponding CpRu (Cp = C_5H_5) complexes[13] due to their higher reactivity. Various substrates can be used but the most common are primary or secondary allyl chlorides and carbonates. From the point of view of selectivity, enantiopure complexes of Cp*Ru developed by Bruneau gave high enantioselectivity but modest regioselectivity for the allylic etherification of allyl chlorides.[14] These Cp*Ru complexes were generally used in combination with bis(oxazoline) ligands. Cp'Ru complexes can also induce stereogenic information. They were found to be very efficient using allylic chloride or bromide producing excellent regio- and enantioselectivities either with a tethered phosphane[12b] or sulfoxide ligand.[12a]



Scheme 1. Decarboxylative allylic etherification with CpRu catalysts.

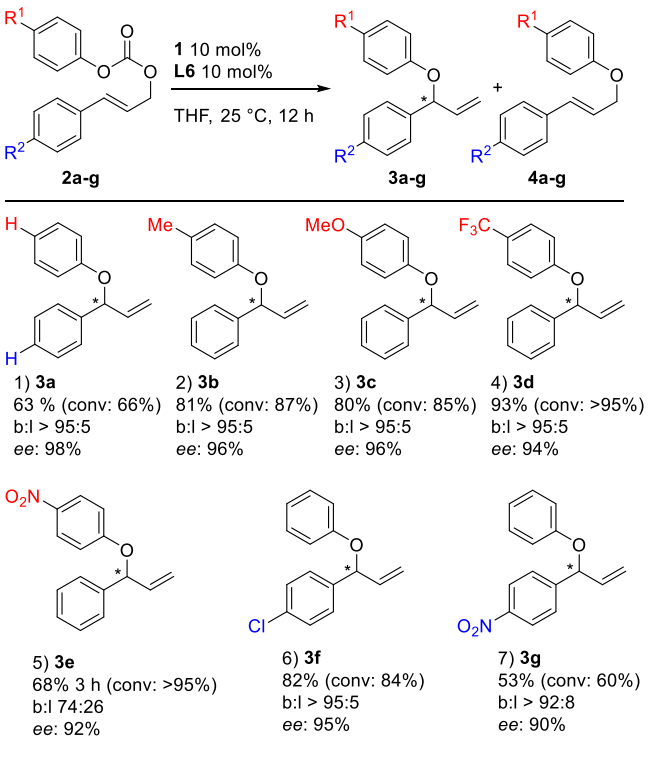
Previously, our group has shown that combinations of $[CpRu(CH_3CN)_3][PF_6]$ **1** (10 mol%) and enantiopure pyridine monooxazoline ligands can be efficient for the stereocontrol of such transformations.[13d-g] Using pymox **L1** in particular, decarboxylative allylic substitution of allyl aryl carbonates gave for instance relatively high enantiomeric excesses and regioselectivity (up to 87% *ee* and b:l >20:1, Scheme 1).[13g] In this process, it was however necessary to monitor the reactions carefully as branched products (b) were shown to racemize and isomerize to the more thermodynamically stable linear products (l), conducting overtime to a net loss of both enantio- and regioselectivities. Since electronic and steric properties of the *N*,*N*-bidentate ligands **L** are crucial for both reactivity and asymmetric induction,[13b] the literature was surveyed for "diimine" structures that could improve the situation. The recent family of pyridine-hydrazone ligands developed by Lassaletta and co–workers was deemed particularly interesting. Achiral picolinaldehyde *N*,*N*-dialkylhydrazones are effective in Ir–catalyzed nitrogen–directed borylation of arenes,[15] while the chiral pyrrolidine derivative **L3** is also a suitable catalyst in enantioselective 1,2-addition of boronic acids to cyclic sulfonimines and Suzuki–Miyaura cross-coupling to biaryls.[16] Their use in allylic substitutions was however unknown and care was thus taken to attempt the decarboxylative etherification reaction in their presence. The key structural elements that make these ligands appealing for this purpose are the strong conjugation along the hydrazone system and the C_2-symmetry at the pyrrolidine terminus, making the rotation around N-N bonds inconsequential and always maintaining the chiral environment in close proximity to the metal center.[17]

Using conditions developed previously for ligand **L1** (dry THF, freshly distilled,[18] 25 °C), combinations of pyridine-hydrazones **L2** to **L6** and $[CpRu(CH_3CN)_3][PF_6]$ **1** (10 mol% each) were thus evaluated. To our satisfaction, all ligands allowed the reaction to occur and afforded satisfactory results in the first experiments. In details, using piperidine-derived **L2**, interesting levels of regio- and enantioselectivities were achieved (b:l 93:7 and *ee* 96%, Scheme 2). However, only a moderate reactivity was afforded in particular in comparison with **L1** (conv 36% in 36 h *vs.* > 98% in 2 h respectively). With pyrrolidine **L3**, reactivity was improved (40% conv after 12 h) while obtaining comparable regio- and enantioselectivities. It was thus decided to retain the 2,5-diphenylpyrrolidine motif and investigate the influence of functional groups on the pyridine ring. As it could be expected, the presence of electron donating groups increased reactivity to afford conversions up to 69% in 12 hours (**L4**–**L6,** Scheme 2). Satisfactorily, improvements in regio- and enantioselectivity were also achieved with these three ligands. **L6** (or its antipode *ent*-**L6**), giving rise to the highest *ee* value, was selected for the remainder of this study.



Scheme 2. Ligands screening (THF, 25 °C, 12 h unless otherwise noted).

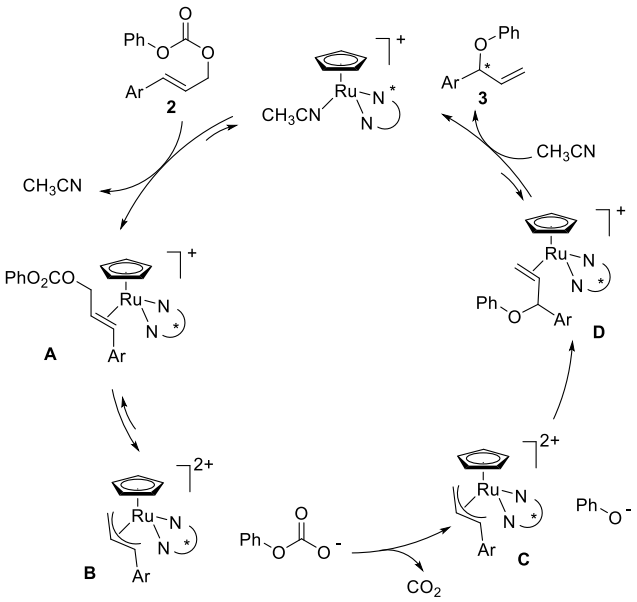
Table 1. Substrate scope [a)]



[a] Reaction conditions: **1** (10 mol%), **L6** (10 mol%), THF, 25 °C, 12 h unless otherwise noted, *c* = 0.5 M; b:l ratios and conversions (conv) determined by ^{1}H NMR (400 MHz); *ee* determined by CSP-HPLC or CSP-SFC.

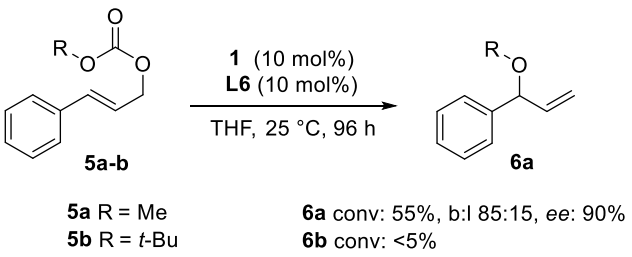
The scope of the reaction was then explored. First, the influence of substituents of the aryloxy moiety was evaluated. Surprisingly, an increased reactivity was noticed with electron-donating groups on the phenol unit (*p*-Me or *p*-OMe) leading however to a slightly lower enantiomeric excesses (Table 1, entries 2 and 3). As expected, electron withdrawing groups such as CF_3 or NO_2 highly increased the rate of the reaction (entries 4 and 5). For instance, after only 3 h, complete conversion and good level of enantiomeric excess were obtained with the nitro substituent at the expense of b:l ratio nevertheless. After 12 h of reaction with this substrate, a sharp decrease of both b:l ratio and enantiomeric excess were noted (b:l 57:43. 80% ee). This is explained by the better leaving group ability of the corresponding nitro-phenoxide leading to a faster isomerization and racemization.[13d] On the other hand, substitutions on the cinnamyl part of electron withdrawing groups led to good selectivity levels but lower conversions (entries 6 and 7). As an example, the nitro group was found to have a negative effect on both enantiomeric excess and reactivity. Clearly, its presence induces a destabilization of the cationic π-allyl complex (see below, intermediates **B** and **C**) and hence a slower formation. Cross-over experiments were further performed (Supporting Information) and confirmed, with **L6**, the dissociative nature of the transformation.[13d] A rather classical mechanistic rationale can be thus proposed (Scheme 3). After the ruthenium-olefin complex formation, the oxidative addition occurs to form the π-allyl intermediate (**A→B**). At this step, decarboxylation of the leaving group occurs to generate a nucleophilic phenoxide. Its subsequent attack on the allylic complex occurs regio- and stereoselectively at the most substituted (branched) position.[19],[11j,20] After decomplexation, the allylic ether product is obtained. The asymmetric induction is likely determined during the **C→D** elemental step. All ligands **L2** to **L6** provide a more effective discrimination than pymox **L1**. In addition, the donor amino groups on **L5** and **L6** are favorable for the reactivity promoting probably a faster oxidative addition (**A→B**) which is believed to be the rate-determining step.

Moreover, it was shown in previous studies that allyl aryl ethers **3** continue to react under the [CpRu]/**L1** catalysis.[13d,13g] In fact, both *in-situ* racemization of the products and isomerization to linear (thermodynamically preferred) regioisomers **4** happen via oxidative addition and reformation of π-allyl intermediates. These unwanted pathways occur concomitantly to the main reaction. However, with ligand **L6**, these side reactions are clearly slower allowing the isolation of products **3** with high enantiomeric purity levels (*ee* up to 98%) and good regioselectivity.[21]



Scheme 3. Mechanistic proposal.

At that stage, it was deemed interesting to prepare allyl alkyl carbonates **5a** and **5b** and a couple of experiments were performed under standard reaction conditions to estimate, in the presence of **L6**, the difference of reactivity of these substrates with that of the aryl derivatives (Scheme 4). While a much longer reaction time (96 h) was necessary for the partial conversion of **5a** (55%), a total lack of reactivity was observed with **5b** after four days.[22] In the case of **5a**, the expected product **6a** was formed with good enantioselectivity (*ee* 90% *vs* 70% with **L1**) and a moderate branched to linear ratio of 85:15.



Scheme 4. Decarboxylative allylic etherification of allyl alkyl carbonates

Finally, our group has previously reported the synthesis and resolution of TRISPHAT-N, a

hexacoordinated phosphorus anion (**TTN**, Figure 1). This anion can be isolated in racemic and enantiopure forms; the Δ enantiomer being easier to separate by precipitation than the Λ antipode.[23],[24] Importantly, **TTN** efficiently coordinates to metal centers thanks to the pyridine moiety. The resulting zwitterionic species are air and moisture stable. Associated with CpRu and **phen**/**L1** ligands,[13b] the TTN zwitterions become lipophilic and are readily isolated by column chromatography over silica gel.

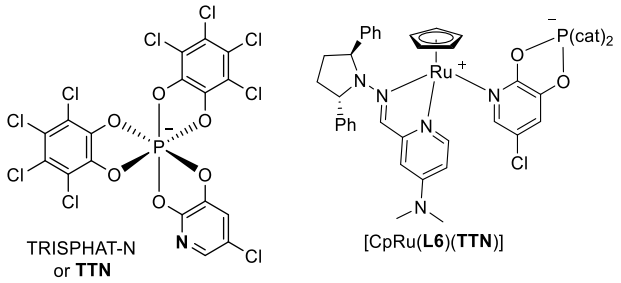
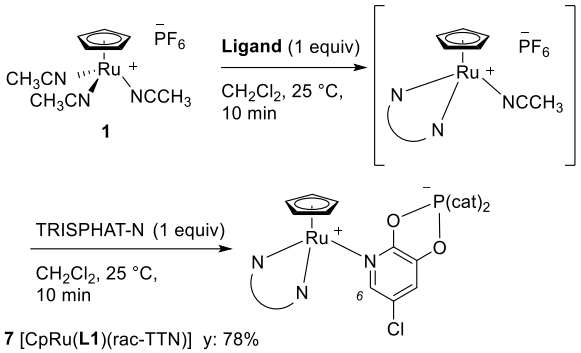


Figure 1. TRISPHAT-N (Δ enantiomer shown) as counterion/ligand for CpRu complexes. cat = tetrachlorocatecholate.

To gain some insight on the higher asymmetric induction with **L6** over **L1**, the preparation of **TTN** complexes was considered even if it was clear that this study could be challenging in regards of the presence of three stereogenic elements within the complexes. In fact, the pseudo-tetrahedral Ru center, the three-bladed propeller geometry of the anion, and the enantiopure ligand **L6** (or *ent*-**L6**) concur to generate up to four equilibrating diastereomers in solution.[13c,23] In view of this situation, and hoping to simplify it, care was taken to utilize not only the racemic but also the available Δ source of the anion (*rac*- and Δ-**TTN** respectively) and this in combination with both **L6** and *ent*-**L6** forms of the ligand.[25] In terms of synthesis, the complexes were prepared by the reaction of equimolar amounts of **1**, ligands **L1** or **L6**/*ent*-**L6** and [Bu_3NH][*rac*-**TTN**] or [*N*-benzylcinchonidinium][*Δ*-**TTN**] salts in CH_2Cl_2 at 25 °C followed by a chromatographic separation. The procedure and resulting complexes **7**, **8**, **9**, **10** and **11** are detailed on Scheme 5.



7 [CpRu(**L1**)(rac-TTN)] y: 78%
8 [CpRu(*R*-*R*,**ent-6**))(Δ-TTN)] y: 42%
9 [CpRu(*R*-*R*,**ent-6**))(*rac*-TTN)] y: 46%
10 [CpRu(*S*-*S*,**L6**))(Δ-TTN)] y: 46%
11 [CpRu(*S*-*S*,**L6**))(*rac*-TTN)] y: 64%

Scheme 5. Synthesis of [CpRu(**L**)(**TTN**)] complexes. cat = tetrachlorocatecholate.

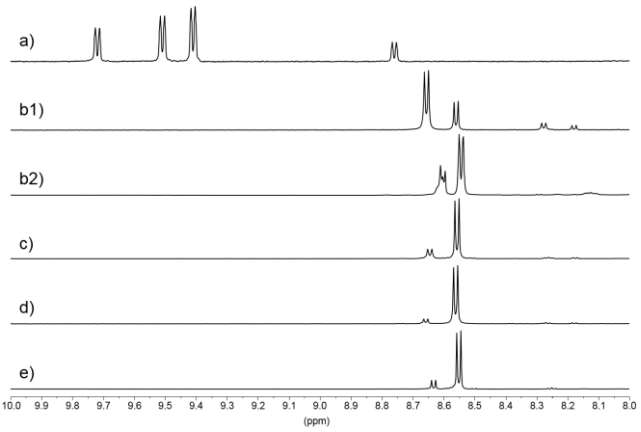


Figure 2. ^{1}H NMR spectra (500 MHz, $CDCl_3$, 10.0 to 8.0 ppm): a) complex **7** (**L1**, *rac*-**TTN**); b1) complex **8** (*ent*-**L6**, Δ-**TTN**) immediately after dissolution; b2) complex **8** after 12 h; c) complex **9** (*ent*-**L6**, *rac*-**TTN**); d) complex **10** (**L6**, Δ-**TTN**); e) complex **11** (**L6**, *rac*-**TTN**).

First, for comparison purposes, the complex made of pymox **L1** and *rac*-**TTN** was analyzed by ^{1}H NMR spectroscopy and, as expected, signals corresponding to the pyridine protons H6 (TRISPHAT) of the four possible diastereomers were distinguishable (complex **5**, spectrum a, Figure 2).[13g],[26] Then, derivative **8** made of *ent*-**L6** and Δ-**TTN** was monitored and two major peaks were observed for this proton immediately after the dissolution of the complex in $CDCl_3$ (spectrum b1, Figure 2).[27] However, to our surprise, it was found that the composition of the mixture was changing over time (spectrum b2). Knowing from previous studies[23] that the equilibrium among the diastereomeric species is reached rapidly with CpRu moieties, an epimerization of the TRISPHAT anion was considered. This was readily tested and confirmed with complexes **9**, **10** and **11** that afforded the same spectra despite their different origin (spectra c, d and e, Figure 1). In these

three instances, only two signals were obtained with the same intensities (~86:14 ratio) irrelevant of the racemic or Δ nature of the anion or of the *ent*-**L6** or **L6** character of the ligand. Normally, with the racemic anion, one would have expected to see four pics and not two (see spectrum a for instance). Exchanging *ent*-**L6** to **L6** in the complexes made with the enantiopure anion, one would have expected to observe two new signals at different chemical shifts which was not the case (spectra b2 and d). As mentioned, the most logical explanation of this unexpected phenomenon is a racemization of the anion induced its binding to the Lewis acidic Ru moiety. In fact, in the field of chiral hexacoordinated phosphate chemistry, it is known that Brønsted or Lewis acids provoke an equilibrium between the Δ and Λ forms through partially dissociative mechanisms.[28] The fact that complexes made of **L6** appear to be more *Lewis* acidic than that derived from **L1** can be explained by the more electron-poor nature of **L6**,[21] and the higher steric strain induced onto the anion by the bulkier ligand. These results also indicate that **L6** (or *ent*-**L6**) leads to a better stereocontrol of the pseudo-tetrahedral CpRu geometry than ligand **L1**,[29] and this might be the reason for the higher asymmetric induction in the etherification. Accordingly, the predicted geometries for the diastereomeric pseudo–tetrahedral [(R_{Ru})-CpRu**L6**(CH_3CN)] and [(S_{Ru})-CpRu**L6**(CH_3CN)] complexes[30] suggest that a considerable steric repulsion between the Cp ring and one of the phenyl groups of the diphenylpyrrolidine terminus in the latter might be responsible for a much favored formation of the (R_{Ru}) isomer (Figure 3).

In conclusion, novel combinations of [$CpRu(CH_3CN)_3$][PF_6] and pyridine-hydrazone ligands (**L2** to **L6**) are described and applied in decarboxylative allylic substitution reactions. High values are obtained for the regio- and enantioselectivity ratios (up to 95:5 and 98% *ee*). Other applications of these ligands in enantioselective catalysis are looked for.

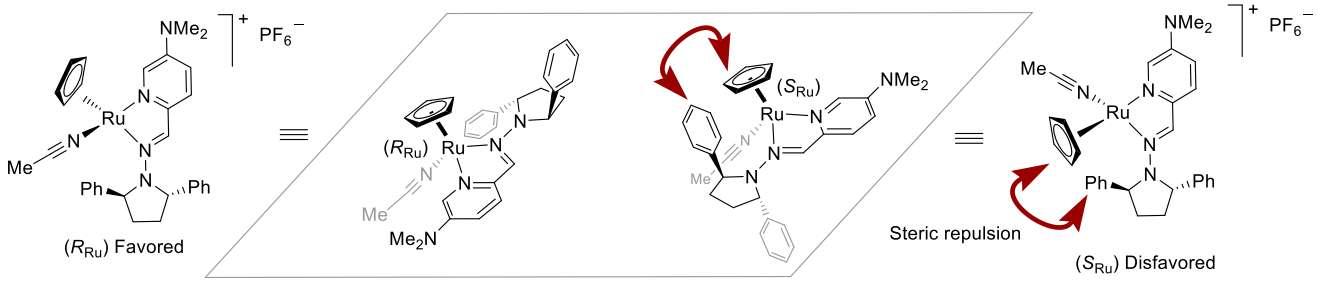


Figure 3. Proposed geometries of the diastereomeric pseudo–tetrahedral [(R_{Ru})-CpRu**L6**(CH_3CN)] and [(S_{Ru})-CpRu**L6**(CH_3CN)] complexes.

Experimental Section

General procedure: In a 2 mL vial under N_2 atmosphere, [Ru(η^5-C_5H_5)(CH_3CN)$_3$][PF_6] **1** (6.3 mg, 14.4 µmol, 0.1 equiv) and ligand (14.4 µmol, 0.1 equiv) were dissolved in 0.3 mL of anhydrous freshly distilled THF. The resulting deep red solution was stirred for 5 minutes at 25 °C before the addition of the allyl aryl carbonates (0.144 mmol, 1 equiv). The reaction was stirred under N_2 at 25 °C until no trace of the starting material could be detected on TLC (SiO_2, Et_2O:Pentane 8:2). The reaction mixture was diluted with 1 mL of a 8:2 mixture of ether and pentane. The precipitated metal salts were filtered on a short SiO_2 column (0.5 cm x 4 cm, elution 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 ^{1}H NMR and CSP-HPLC or CSP-SFC.

Acknowledgements

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[26] The diastereomeric ratio was constant over time in this case (1.0:0.75:0.55:0.35, ^{1}H NMR, 400 MHz).

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COMMUNICATION

Regio and Enantioselective Allylation of Phenols via Decarboxylative Allylic Etherification of Allyl Aryl Carbonates Catalyzed by (Cyclopentadienyl)ruthenium(II) Complexes and Pyridine-Hydrazone Ligands

Adv. Synth. Catal. **2015**, *Volume*, Page – Page

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