Advanced Synthesis & Catalysis

DOI: 10.1002/adsc.201401020

Rhodium-Catalyzed Decarbonylative Direct Olefination of Arenes with Vinyl Carboxylic Acids

Ruiying Qiu,[a] Lingjuan Zhang,[a] Conghui Xu,[a] Yixiao Pan,[a] Hongze Pang,[a] Lijin Xu,[a,*] and Huanrong Li[a,*]

[a] Department of Chemistry, Renmin University of China, Beijing 100872, People's Republic of China
Fax: (+86)-10-6251-6444; phone: (+86)-10-6251-1528; e-mail: xulj@chem.ruc.edu.cn or hrli@chem.ruc.edu.cn

Received: October 27, 2014; Revised: January 15, 2015; Published online: ■■ ■■, 0000

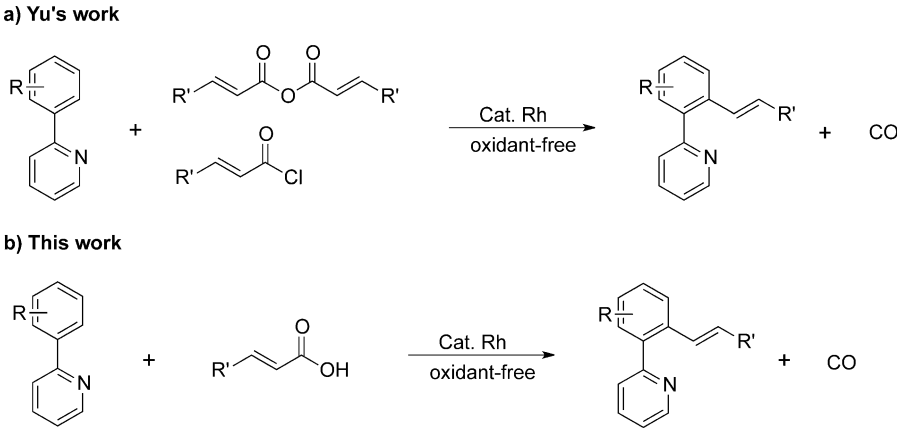
Supporting information for this article is available on the WWW under http://dx.doi.org/10.1002/adsc.201401020.

Abstract: A rhodium(I)-catalyzed direct C–H bond olefination of pyridyl-substituted arenes with readily available vinyl carboxylic acids has been realized. This reaction occurred efficiently without the need for any external oxidant, affording the *ortho*-olefinated products in high yields and excellent regioselectivities. Diversely substituted vinyl carboxylic acids behaved as efficient olefination reagents under the reaction conditions, and a range of functional groups in both coupling partners was well tolerated. Mechanistic studies indicated that a decarbonylation step is involved in this catalytic process, and pivalic anhydride [$(t\text{-BuCO})_2O$] acts as the activator of the carboxylic acids for the *in situ* generation of highly active anhydrides.

Keywords: anhydrides; decarbonylation; olefination; rhodium; vinyl carboxylic acids

Introduction

Within the last decade the transition metal-catalyzed dehydrogenative coupling reaction of simple arenes with olefins has been highlighted as a powerful alternative to the traditional Pd-catalyzed Mirozoki–Heck reaction.[1] This process obviates the requirement of a tedious and costly halogenation step, allowing the normally unreactive arene C–H bonds to undergo direct coupling with olefins to produce the arylated olefins. Fujiwara and Moritani first revealed that simple arenes could serve as useful coupling partners to react directly with olefins under palladium catalysis.[2] Following this significant lead, extensive efforts have been made in the development of more active and selective transition metal catalytic systems. Consequently, recent studies have shown that the presence of a suitable directing group could greatly facilitate the regioselective direct C–H *ortho*-olefination of arenes, and the catalysts derived from palladium,[3] ruthenium[4] and rhodium complexes[5] proved to be highly effective. Despite these spectacular advances,



Scheme 1.

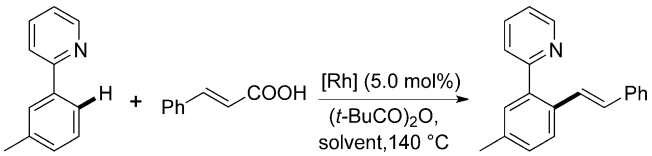
there is still much room for improvement, particularly in terms of substrate scope and catalytic efficiency.

Owing to their easy availability, structural diversity and safety, carboxylic acids and their derivatives have been recently recognized as reliable coupling partners in transition metal-catalyzed decarboxylative or decarbonylative cross-coupling reactions.[6] In this context, using vinyl carboxylic acids and their derivatives as the olefin sources has drawn increasing attention, and a number of useful protocols are known in the literature.[7,8] In the hope of further improving the atom economy and catalytic efficiency, chemists became interested in the combination of decarbonylation or decarboxylation of vinyl carboxylates with direct functionalization of C–H bonds, and exciting progress has been accomplished.[9] Notably, Yu and co-workers demonstrated that, in the presence of a Rh(I) catalyst and a suitable base, the direct olefination of arene C–H bonds *via* decarbonylation of cinnamoyl chlorides and cinnamic anhydrides could be readily realized to give the olefinated products in high yields with good functional group tolerance (Scheme 1, a).[9a–c] Importantly, unlike the decarboxylation process, no external oxidant is required in these reactions. However, this chemistry is plagued by the necessity of prior preparation of cinnamoyl chlorides and cinnamic anhydrides from the parent vinyl carboxylic acids *via* tedious operations. Very recently we reported that vinyl carboxylic acids could serve as effective olefination reagents in Rh(I)-catalyzed decarbonylative direct olefination of indoles.[10] Following this success, herein we report that, in the presence of a Rh(I) catalyst and an appropriate activator, arylpyridines could undergo highly efficient and selective decarbonylative olefination with various vinyl carboxylic acids in the absence of any external oxidants under relatively mild conditions (Scheme 1, b).

Results and Discussion

We initiated our investigations by choosing the coupling reaction of 2-(*meta*-tolyl)pyridine (**1a**) with cinnamic acid (**2a**) as our model system for the optimization studies. Using $(t\text{-BuCO})_2O$ as the additive and toluene as the reaction medium, we first examined the catalytic performance of different rhodium complexes. It was found that $[Rh(COD)_2]OTf$ displayed the highest catalytic activity, affording the desired product (*E*)-2-(5-methyl-2-styrylphenyl)pyridine (**3aa**) in 95% yield (Table 1, entry 1). Comparable catalytic efficiency was observed with $[Rh(NBD)_2]BF_4$ and $[Rh(CO)_2Cl]_2$ (Table 1, entries 5 and 12), but switching to other rhodium complexes led to either diminished yields or no reactivity (Table 1, entries 2–4 and 6–11). Further studies indicated that, when the reaction time was shortened to 12 h, $[Rh(COD)_2]OTf$ remained efficient (Table 1, entry 13), but $[Rh(NBD)_2]BF_4$ and $[Rh(CO)_2Cl]_2$ turned out to be ineffective (Table 1, entries 14 and 15). With

Table 1. Screening conditions for direct olefination of 2-(*meta*-tolyl)pyridine (**1a**) with cinnamic acid (**2a**).[a]

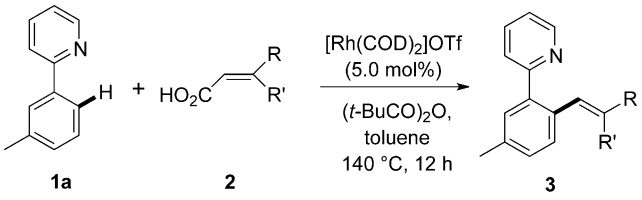


1a **2a** **3aa**

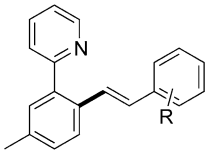
Entry	[Rh]	Solvent	Time [h]	Yield [%][b]
1	$[Rh(COD)_2]OTf$	toluene	24	95
2	$[Rh(COD)Cl]_2$	toluene	24	30
3	$[Rh(COD)_2]BF_4$	toluene	24	54
4	$[Rh(NBD)Cl]_2$	toluene	24	0
5	$[Rh(NBD)_2]BF_4$	toluene	24	89
6	$[Rh(1,5\text{-HD})Cl]_2$	toluene	24	46
7	$[Rh(C_2H_4)_2Cl]_2$	toluene	24	8
8	$[Rh(acac)(C_2H_4)_2]$	toluene	24	0
9	$[Rh(PPh_3)_3Cl]$	toluene	24	0
10	$[Rh(acac)(CO)_2]$	toluene	24	60
11	$[RhCp^*Cl_2]_2$	toluene	24	0
12	$[Rh(CO)_2Cl]_2$	toluene	24	91
13	**$[Rh(COD)_2]OTf$**	toluene	12	95
14	$[Rh(NBD)_2]BF_4$	toluene	12	65
15	$[Rh(CO)_2Cl]_2$	toluene	12	71
16	$[Rh(COD)_2]OTf$	PhCl	12	77
17	$[Rh(COD)_2]OTf$	*p*-xylene	12	72
18	$[Rh(COD)_2]OTf$	anisole	12	89
19	$[Rh(COD)_2]OTf$	DMF	12	67
20	$[Rh(COD)_2]OTf$	DMSO	12	21
21[c]	$[Rh(COD)_2]OTf$	toluene	12	67
22[d]	$[Rh(COD)_2]OTf$	toluene	12	7
23[e]	$[Rh(COD)_2]OTf$	toluene	12	29
24[f]	$[Rh(COD)_2]OTf$	toluene	12	0
25[g]	$[Rh(COD)_2]OTf$	toluene	12	0
26[h]	$[Rh(COD)_2]OTf$	toluene	12	70
27[i]	$[Rh(COD)_2]OTf$	toluene	12	35
28[j]	$[Rh(COD)_2]OTf$	toluene	12	87
29	none	toluene	12	0
30[k]	$[Rh(COD)_2]OTf$	toluene	12	0

[a] *Reaction conditions:* **1a** (0.5 mmol), **2a** (0.75 mmol), [Rh] (5.0 mol%), $(t\text{-BuCO})_2O$ (0.75 mmol), solvent (3.0 mL), 140 °C. COD = cyclooctadiene; NBD = norbornadiene; acac = acetylacetonate; HD = hexadiene; Cp* = pentamethylcyclopentadiene.
[b] Isolated yields reported.
[c] Boc_2O was used to replace $(t\text{-BuCO})_2O$. Boc = *tert*-butyloxycarbonyl.
[d] Ac_2O was used to replace $(t\text{-BuCO})_2O$.
[e] *t*-BuCOCl was used to replace $(t\text{-BuCO})_2O$.
[f] $(CF_3CO)_2O$ was used to replace $(t\text{-BuCO})_2O$.
[g] $(MeOCO)_2O$ was used to replace $(t\text{-BuCO})_2O$.
[h] Reaction temperature 120 °C.
[i] $[Rh(COD)_2]OTf$ (2.5 mol%) was used.
[j] $(t\text{-BuCO})_2O$ (0.5 mmol) was used.
[k] No $(t\text{-BuCO})_2O$ was added.

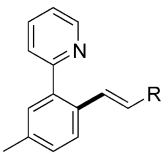
Table 2. Rh-catalyzed direct olefination of **1a** with β-substituted acrylic acids.[a,b]



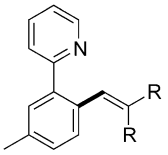
1a 2 3



3ab (R = 4-Me), 97%
3ac (R = 4-OMe), 96%
3ad (R = 2-Me), 95%
3ae (R = 3-OMe), 95%
3af (R = 2,3-$(OMe)_2$), 85%
3ag (R = 3,4,5-$(OMe)_3$), 92%
3ah (R = 4-F), 95%
3ai (R = 4-Br), 85%
3aj (R = 4-Cl), 87%
3ak (R = 2-Cl), 95%
3al (R = 3-Br), 92%
3am (R = 2-Br), 90%
3an (R = 4-pinacolboryl), 79%
3ao (R = 2,3,4,5,6-F_5), 93%
3ap (R = 4-CF_3),95%
3aq (R =4-CO_2Me), 89%
3ar (R = 4-CN),82%



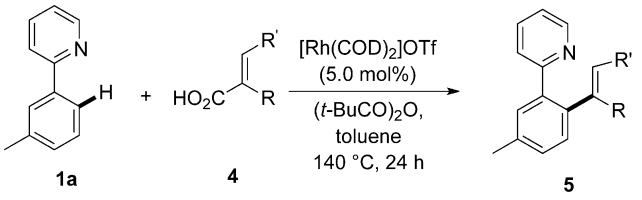
3as (R =2-naphth), 94%
3at (R= 2-thienyl), 72%
3au (R = 2-furyl), 97%
3av (R = Me), 94%
3aw (R = *n*-Pr), 95%



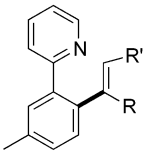
3ax (R = Me), 94%
3ay (R = Ph), 91%

[a] *Reaction conditions*: **1a** (0.5 mmol.), **2** (0.75 mmol), $[Rh(COD)_2]OTf$ (5.0 mol%), $(t\text{-BuCO})_2O$ (0.75 mmol), toluene (3.0 mL), 140 °C, 12 h.
[b] Isolated yields reported.

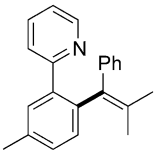
Table 3. Rh-catalyzed direct olefination of **1a** with α-substituted acrylic acids.[a,b]



1a 4 5



5aa (R = Ph, R' = H), 78%
5ab (R = 4-*i*-BuPh, R' = H), 85%
5ac (R = 6-OMe-2-naphthyl, R' = H), 71%
5ad (R = Me, R' = H), 78%
5ae (R = R' = Me), 88%
5af (R = Me, R' = Ph), 92%
5ag (R = Et, R' = 3-NO_2Ph), 85%



5ah, 92%

[a] *Reaction conditions*: **1a** (0.5 mmol), **4** (0.75 mmol), $[Rh(COD)_2]OTf$ (5.0 mol%), $(t\text{-BuCO})_2O$ (0.75 mmol) in 3.0 mL toluene, 140 °C, 24 h.
[b] Isolated yields reported.

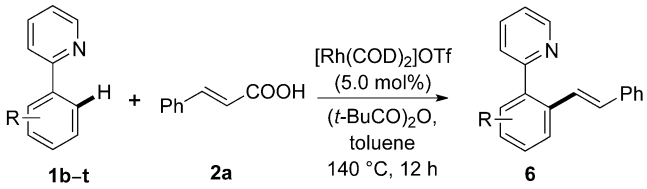
$[Rh(COD)_2]OTf$ as the catalyst, subsequent optimization revealed that toluene was the optimal choice, and reduced yields were obtained in other solvents, such as PhCl, *para*-xylene, anisole, DMF and DMSO (Table 1, entries 16–20). The performance of other additives was also evaluated, but they were all inferior to $(t\text{-BuCO})_2O$ (Table 1, entries 21–25). Lowering the reaction temperature retarded the reaction as the yield of **3aa** dropped to 70% at 120 °C (Table 1, entry 26). When the catalyst loading or the amount of additive was reduced, the yield decreased as well (Table 1, entries 27 and 28). The control experiments showed that no reaction occurred in the absence of either $[Rh(COD)_2]OTf$ or $(t\text{-BuCO})_2O$ (Table 1, entries 29 and 30). Thus the optimal reaction conditions were finally determined as follows: $[Rh(COD)_2]OTf$ (5 mol%) and $(t\text{-BuCO})_2O$ (1.5 equiv.) in toluene at 140 °C for 12 h.

Having the optimized conditions in hand, we then explored the vinylation of **1a** with a range of electronically and sterically diverse vinyl carboxylic acids. As shown in Table 2, cinnamic acids with a wide range of substituents on the benzene ring were effectively converted to the expected products (**3ab**–**3as**) in good to excellent yields with exclusive *E* stereochemistry, and various functional groups could well survive under the reaction conditions regardless of their electronic properties and substitution positions. Notably, the sensitive halogen (**3ai**–**3am**) and pinacolboryl (**3an**) substitutuents were tolerated, providing useful handles for further elaboration. Furthermore, the heteroaryl-substituted acrylic acids could furnish the desired *E*-configurated products (**3at** and **3au**) in excellent yields. More than 90% yields and excellent *E* stereoselectivity (**3av** and **3aw**) were also observed in the reactions of (*E*)-but-2-enoic acid (**2v**) and (*E*)-hex-2-enoic acid (**2w**). The β,β-disubstituted acrylic acids exhibited excellent reactivity, delivering the products **3ax** and **3ay** in 94% and 95% yields, respectively.

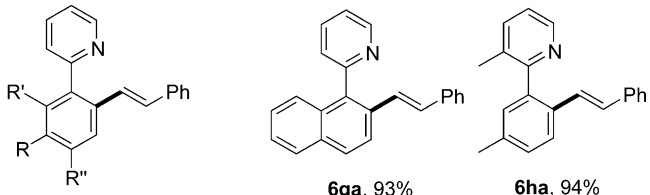
The reaction is not limited to β-substituted acrylic acids only, and α-substituted acrylic acids also participated well although a longer reaction time was required. As shown in Table 3, the α-substituted acrylic acids **4a**–**d** successfully engaged in the coupling reaction, affording the corresponding *E*-configurated products **5aa–5ad** in good yields. The α,β-trisubstituted acrylic acids **4e**–**g** reacted smoothly to give the desired products (**5ae**–**5ag**) in 85–92% yields with excellent *E* stereoselectivity. Noteworthy is that the challenging tetra-substituted acrylic acid **4h** underwent clean conversion to furnish **5ah** in 92% yield.

This cross-coupling reaction was further extended to other 2-arylpyridine derivatives as shown in Table 4. Similar to arene **1a**, 2-arylpyridines (**1b**–**h**)

Table 4. Rh-catalyzed direct olefination of arenes with cinnamic acid (**2a**).[a,b,c]



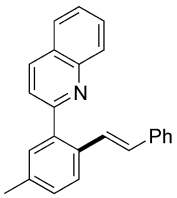
1b–t **2a** **6**



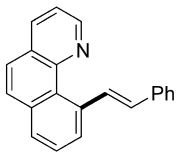
6ba, (R = Ph, R' = R'' = H), 87%
6ca, (R = Me, R' = H, R'' = F), 89%
6da, (R = OMe, R' = H, R'' = OMe), 85%
6ea, (R = H, R' = OMe, R'' = H) 86%
6fa, (R = H, R' = CF_3, R'' = H) 92%

6ga, 93%

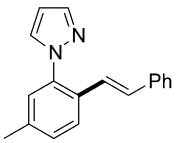
6ha, 94%



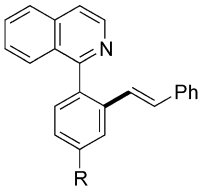
6ia, 86%



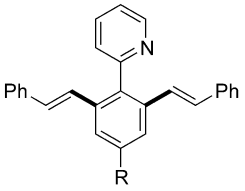
6ja, 90%



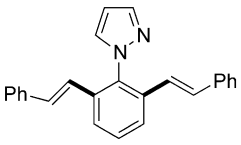
6ka, 90%



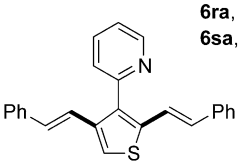
6la, (R = H), 93%
6ma, (R = Me), 90%
6na, (R = F), 88%



6oa, (R = H), 95%
6pa, (R = OMe), 90%
6qa, (R = F), 93%
6ra, (R = Br), 91%
6sa, (R = CF_3), 93%



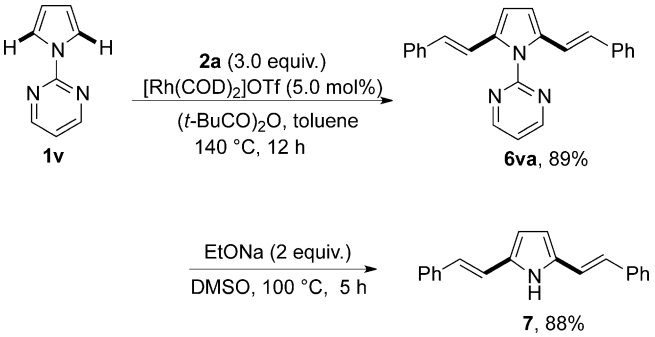
6ta, 89%



6ua, 92%

[a] *Reaction conditions*: **1** (0.5 mmol), **2a** (0.75 mmol), $[Rh(COD)_2]OTf$ (5.0 mol%), $(t\text{-}BuCO)_2O$ (0.75 mmol) in 3.0 mL toluene, 140 °C, 12 h.
[b] Isolated yields reported.
[c] For arenes **1o–u**, 3.0 equiv. of **2a** and $(t\text{-}BuCO)_2O$ were employed.

bearing *meta*- or *ortho*-substituents on the aryl ring could efficiently couple with **2a** to form the desired *ortho*-alkenylated products (**6ba–6ha**). 2-(*meta*-Tolyl)-quinoline (**1i**), benzo[*h*]quinoline (**1j**) and 1-(*meta*-tolyl)-1*H*-pyrazole (**1k**) could also be smoothly olefinated, and high isolated yields (**6ia–6ka**) were achieved. Likewise, this protocol worked well for the direct olefination of 1-arylisoquinolines (**1l–n**), giving



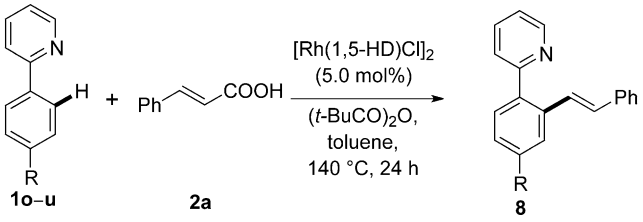
1v **6va**, 89% **7**, 88%

Scheme 2. Olefination of 2-(1*H*-pyrrol-1-yl)pyrimidine (**1v**) with **2a** and removal of the directing group.

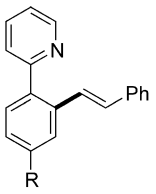
the target products (**6la–6na**) in 88–93% yields. However, when 2-phenylpyridine (**1o**) was employed, a 2:1 mixture of mono- and diolefinated products was observed. Using 2-arylpyridines bearing *para*-substituents on the aryl ring (**1p–s**), 1-phenyl-1*H*-pyrazole (**1t**) and 2-(thiophen-3-yl)pyridine (**1u**) led to similar results. To our delight, increasing the amount of **2a** and $(t\text{-}BuCO)_2O$ to 3.0 equivalents led to the exclusive formation of diolefinated products (**6oa–6ua**) in excellent yields. It is noteworthy that 2-(1*H*-pyrrol-1-yl)pyrimidine (**1v**) was also effective in this reaction, and the pyrimidyl group could be readily removed (Scheme 2).[10] It should be noted that only the *E*-configurated products were obtained in all cases studied.

Unexpectedly, in the case of using $[Rh(1,5\text{-}HD)Cl]_2$ as the catalyst, the coupling reaction of 2-phenylpyridine (**1o**) with **2a** primarily provided the mono-olefi-

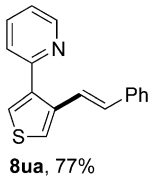
Table 5. Rh-catalyzed direct mono-olefination of arenes with **2a**.[a,b]



1o–u **2a** **8**



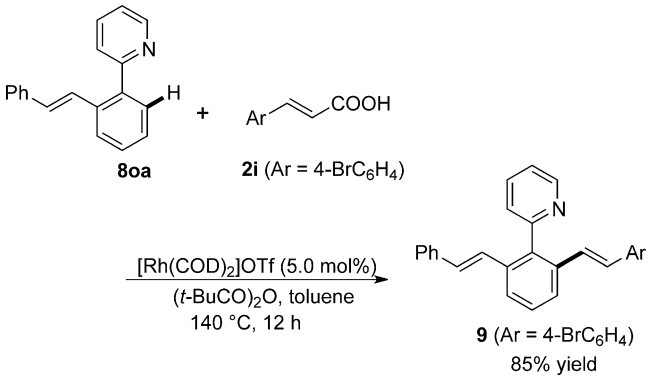
8ta, 69%



8ua, 77%

8oa,(R = H), 62%
8pa, (R = OMe), 55%
8qa, (R = F), 68%
8ra, (R = Br), 65%
8sa, (R = CF_3), 73%

[a] *Reaction conditions*: **1** (0.5 mmol), **2a** (0.6 mmol), $[Rh(1,5\text{-}HD)Cl]_2$ (5.0 mol%), $(t\text{-}BuCO)_2O$ (0.6 mmol) in 3.0 mL toluene, 140 °C, 24 h.
[b] Isolated yields reported.

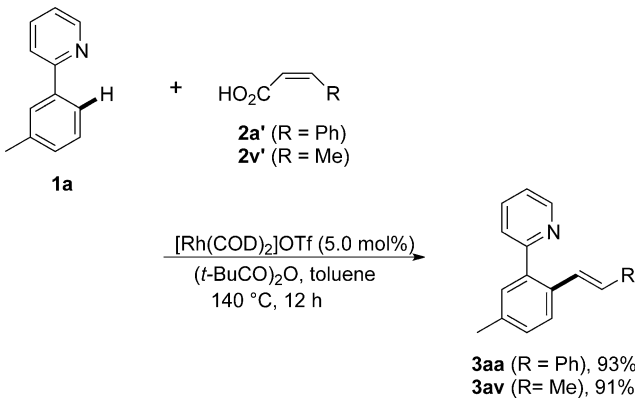


Scheme 3. Reaction of (*E*)-2-(2-styrylphenyl)pyridine (**8oa**) with (*E*)-3-(4-bromophenyl)acrylic acid (**2i**).

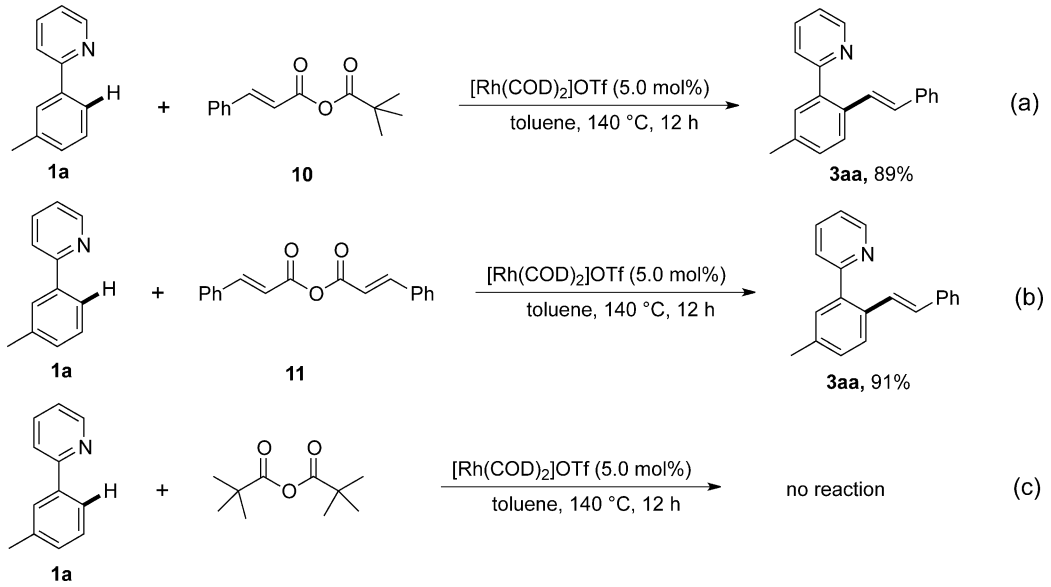
nation product **8oa**, and the diolefinated product **6oa** was only isolated in 11% yield. Encouraged by this finding, we then examined the mono-olefination of other arenes (**1p**–**u**), and satisfactory results (**8pa**–**8ua**) were achieved (Table 5). As exemplified in Scheme 3, the mono-olefinated arylpyridine **8oa** could be further olefinated with **2i** to afford the diolefinated product **9**.

In order to obtain mechanistic insights, a mixture of equimolar amounts of **2a** and $(t\text{-BuCO})_2O$ in toluene was stirred at 140 °C for 1 h, and subsequent analysis by ^{1}H NMR revealed the existence of three anhydrides, *trans*-cinnamic pivalic anhydride **10**, *trans*-cinnamic anhydride **11** and $(t\text{-BuCO})_2O$, in a ratio of 1:0.36:0.83. After overnight stirring, the ratio became 1:0.45:0.41 with the mixed anhydride **10** present in the largest amount. We then examined the coupling reaction of these anhydrides with **1a** under the catalysis of $[Rh(COD)_2]OTf$. Both anhydrides **10** and **11** were smoothly coupled to exclusively provide the product **3aa** in high yields in 12 h (Scheme 4, a and b), but $(t\text{-BuCO})_2O$ was totally unreactive under otherwise identical conditions (Scheme 4, c). These results clearly indicated that the *in situ* generated anhydrides did contribute to the formation of the olefinated product **3aa**. This is consistent with the previous reports by Yamamoto,[11] Goossen,[12] Ryu,[13] and Shi.[14] Analyzing the gas phase of the reaction mixture with GC-TCD confirmed the generation of CO during the reaction, clearly suggesting that a decarbonylation step is involved in the current transformation.

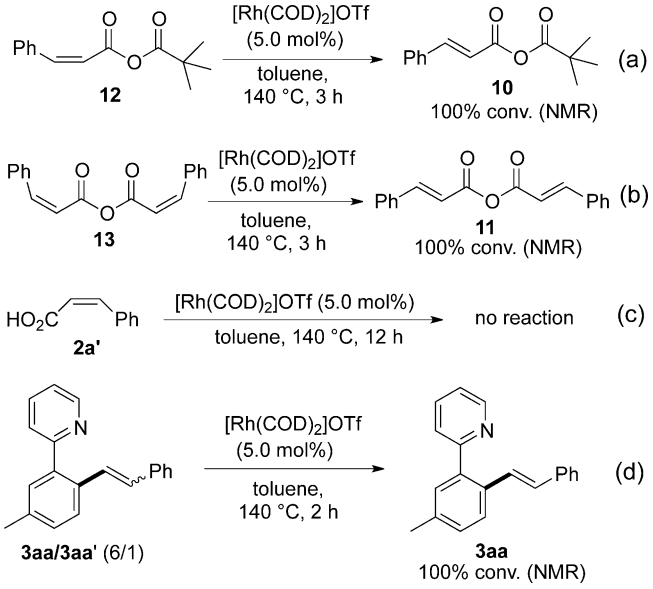
To explore the stereochemistry of this transformation, we next investigated the coupling reaction of **1a** with *cis*-cinnamic acid (**2a′**) and *cis*-crontonic acid (**2v′**). To our surprise, only the *E*-configurated products were obtained (Scheme 5). It is likely that a *cis-trans* isomerization of the olefin took place in the course of the reaction. In an effort to elucidate this process, we carried out experiments with **2a′** moni-



Scheme 5. Direct olefination of **1a** with *cis*-cinnamic acid (**2a′**)and *cis*-crotonic acid (**2v′**).



Scheme 4. The coupling reaction of anhydrides with **1a**.



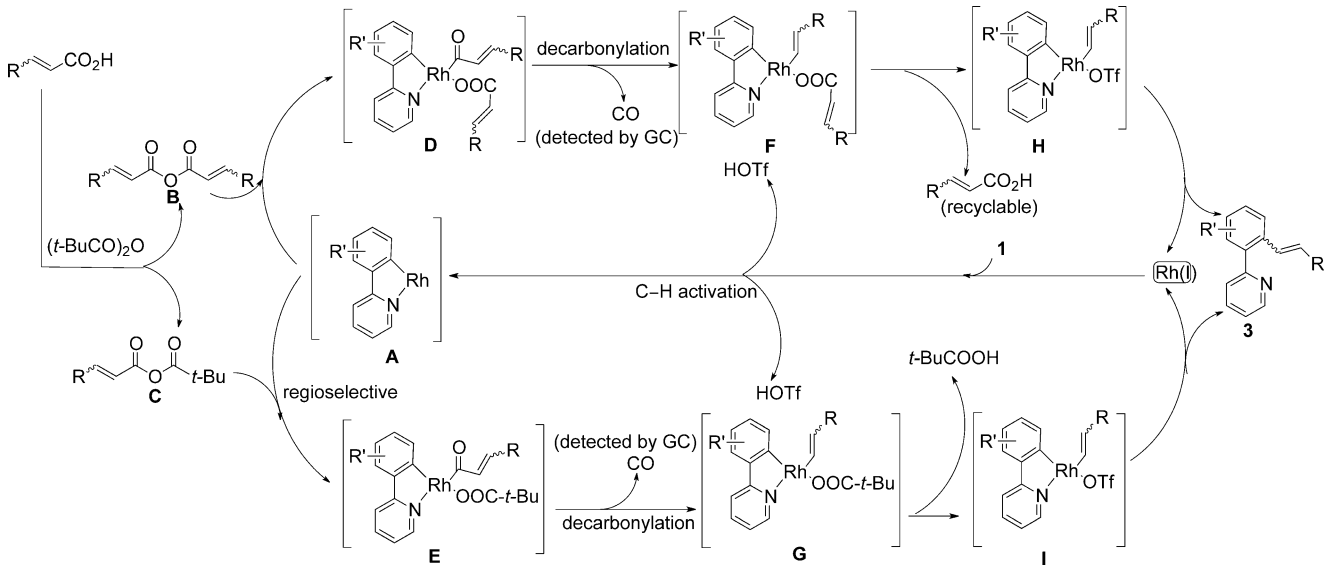
Scheme 6. Rh(I)-catalyzed *cis-trans* isomerization of olefins.

tored by NMR, and three important pieces of information were obtained: (a) **2a′** was *in situ* activated by $(t\text{-BuCO})_2O$ to generate *cis*-cinnamic pivalic anhydride **12** and *cis*-cinnamic anhydride **13**, and $[Rh(COD)_2]OTf$ could efficiently catalyze the isomerization of **12** and **13** to their *trans* analogues **10** and **11** in 3 h (Scheme 6, a, b), but no isomerization could be detected in the absence of $[Rh(COD)_2]OTf$ catalyst; (b) **2a′** could not be isomerized under the catalysis of $[Rh(COD)_2]OTf$ even after overnight stirring (Scheme 6, c); (c) because the catalytic isomerization of *cis*-anhydrides was not very rapid, it is possible that the *cis*-anhydride might react with **1a** to give the *cis*-product; indeed, the coupling reaction of **2a′** with **1a** for 3 h afforded a 6:1 mixture of *trans*-product **3aa** and *cis*-product **3aa′**, which could be totally converted to the *trans* isomer in 2 h in the presence of the $[Rh(COD)_2]OTf$ catalyst (Scheme 6, d). Based on these results, it is clear that this olefination is stereospecific, and the Rh(I)-catalyzed *cis-trans* isomerization of olefins should be responsible for the stereochemistry observed.

On the basis of the above studies, a plausible mechanism is suggested (Scheme 7). First, the arylpyridine **1** reacted with the rhodium(I) species to give the cyclorhodium intermediate **A** *via* the pyridyl nitrogen-assisted C–H activation. The anhydrides **B** and **C** derived from the reaction of vinyl carboxylic acid and $(t\text{-BuCO})_2O$ underwent reaction with **A** to selectively deliver the intermediates **D** and **E**, which produced the intermediates **F** and **G** through the loss of CO. With treatment of HOTf, intermediates **H** and **I** were generated with the release of carboxylic acids. The following reductive elimination of **H** and **I** liberated the desired product **3**. Finally, the rhodium(I) was reformed to finish the catalytic cycle. In the case of *cis* vinyl carboxylic acid, the Rh(I)-catalyzed *cis-trans* isomerization was involved to convert the *in situ* generated *cis* anhydrides and the *cis* olefination product to their *trans* isomers.

Conclusions

In summary, a protocol for the direct olefination of arylpyridines employing vinyl carboxylic acids as the vinyl sources has been developed, providing a general and convenient way to access various olefinated arenes. A range of functional groups survived this new transformation, and differently substituted vinyl



Scheme 7. Proposed mechanism for the decarbonylative direct olefination of arylpyridines.

carboxylic acids proved to be effective. In view of its simplicity, broad substrate scope and the easy availability of vinyl carboxylic acids, this protocol is expected to become an attractive complement to the existing direct C–H olefination of arenes known in the literature. Further studies to expand the substrate scope and synthetic application of this catalytic process are currently underway in this lab, and will be reported in due course.

Experimental Section

General Methods

Unless otherwise noted, all experiments were carried out under a nitrogen atmosphere. ^{1}H NMR and ^{13}C NMR spectra were recorded on a Bruker Model Avance DMX 400 Spectrometer (^{1}H 400 MHz and ^{13}C 106 MHz, respectively). Chemical shifts (δ) are given in ppm and are referenced to residual solvent peaks, and coupling constants (*J*) are reported in Hertz. The commercially available chemicals were used as received without further purification.

General Procedure for Decarbonylative Direct Olefination of Arenes with Vinyl Carboxylic Acids

To an oven-dried pressure tube were sequentially added the arene **1** (0.5 mmol), acrylic acid **2** (0.75 mmol), $[Rh(COD)_2]OTf$ (11.7 mg, 5 mol%), $(t\text{-}BuCO)_2O$ (139.5 mg, 0.75 mmol) and toluene (3.0 mL). After being degassed three times, the tube was heated and stirred vigorously at 140 °C for 12 h in an oil bath under a nitrogen atmosphere. Then the tube was removed from the oil bath and cooled to room temperature. The solvent was removed by vacuum evaporation, and the residue was purified by column chromatography on silica gel using a mixture of ethyl acetate and hexane to give the pure product.

Acknowledgements

Financial support from the National Natural Science Foundation of China (21372258, 21072225, 21172258 and 91127039) is greatly acknowledged.

References

[1] For recent selected reviews, see a) S. I. Kozhushkov, L. Ackermann, *Chem. Sci.* **2013**, *4*, 886; b) J. Wencel-Delord, F. Glorius, *Nat. Chem.* **2013**, *5*, 369; c) G. Song, F. Wang, X. Li, *Chem. Soc. Rev.* **2012**, *41*, 3651; d) N. Kuhl, M. N. Hopkinson, J. Wencel-Delord, F. Glorius, *Angew. Chem.* **2012**, *124*, 10382; *Angew. Chem. Int. Ed.* **2012**, *51*, 10236; e) P. B. Arockiam, C. Bruneau, P. H. Dixneuf, *Chem. Rev.* **2012**, *112*, 5879; f) B.-J. Li, Z.-J. Shi, *Chem. Soc. Rev.* **2012**, *41*, 5588; g) S. R. Neufeldt, M. S. Sanford, *Acc. Chem. Res.* **2012**, *45*, 936; h) K. M. Engle, T.-S. Mei, M. Wasa, J.-Q. Yu, *Acc. Chem. Res.* **2012**, *45*, 788; i) J. Wencel-Delord, T. Droge, F. Liu, F. Glorius, *Chem. Soc. Rev.* **2011**, *40*, 4740; j) S. H. Cho, J. Y. Kim, J. Kwak, S. Chang, *Chem. Soc. Rev.* **2011**, *40*, 5068; k) J. Le Bras, J. Muzart, *Chem. Rev.* **2011**, *111*, 1170; l) T. W. Lyons, M. S. Sanford, *Chem. Rev.* **2010**, *110*, 1147; m) T. Satoh, M. Miura, *Chem. Eur. J.* **2010**, *16*, 11212; n) X. Chen, K. M. Engle, D. H. Wang, J. Q. Yu, *Angew. Chem.* **2009**, *121*, 5196; *Angew. Chem. Int. Ed.* **2009**, *48*, 5094.

[2] For some recent examples, see: a) I. Moritani, Y. Fujiwara, *Tetrahedron Lett.* **1967**, *8*, 1119; b) Y. Fujiwara, I. Moritani, M. Matsuda, *Tetrahedron* **1968**, *24*, 4819; c) Y. Fujiwara, I. Moritani, S. Danno, R. Asano, S. Teranishi, *J. Am. Chem. Soc.* **1969**, *91*, 7166.

[3] For selected papers concerning Pd-catalyzed direct olefination reactions employing directing groups, see: a) M. D. K. Boele, G. P. F. van Strijdonck, A. H. M. de Vries, P. C. J. Kamer, J. G. de Vries, P. W. N. M. van Leeuwen, *J. Am. Chem. Soc.* **2002**, *124*, 1586; b) G. Cai, Y. Fu, Y. Li, X. Wan, Z. Shi, *J. Am. Chem. Soc.* **2007**, *129*, 7666; c) J.-J. Li, T.-S. Mei, J.-Q. Yu, *Angew. Chem.* **2008**, *120*, 6552; *Angew. Chem. Int. Ed.* **2008**, *47*, 6452; d) S. H. Cho, S. J. Hwang, S. Chang, *J. Am. Chem. Soc.* **2008**, *130*, 9254; e) J. Wu, X. Cui, L. Chen, G. Jiang, Y. Wu, *J. Am. Chem. Soc.* **2009**, *131*, 13888; f) A. Garcia-Rubia, R. G. Arrayas, J. C. Carretero, *Angew. Chem.* **2009**, *121*, 6633; *Angew. Chem. Int. Ed.* **2009**, *48*, 6511; g) W. Rauf, A. L. Thompson, J. M. Brown, *Chem. Commun.* **2009**, 3874; h) D.-H. Wang, K. M. Engle, B.-F. Shi, J.-Q. Yu, *Science* **2010**, *327*, 315; i) B.-F. Shi, Y.-H. Zhang, J. K. Lam, D.-H. Wang, J.-Q. Yu, *J. Am. Chem. Soc.* **2010**, *132*, 460; j) T. Nishikata, B. H. Lipshutz, *Org. Lett.* **2010**, *12*, 1972; k) C. Zhu, J. R. Falck, *Org. Lett.* **2011**, *13*, 1214; l) Y.-H. Xu, Y. K. Chok, T.-P. Loh, *Chem. Sci.* **2011**, *2*, 1822; m) H.-X. Dai, A. F. Stepan, M. S. Plummer, Y.-H. Zhang, J.-Q. Yu, *J. Am. Chem. Soc.* **2011**, *133*, 7222; n) L.-Y. Jiao, M. Oestreich, *Org. Lett.* **2013**, *15*, 5374; o) H.-L. Wang, R.-B. Hu, H. Zhang, A.-X. Zhou, S.-D. Yang, *Org. Lett.* **2013**, *15*, 5302; p) H.-X. Dai, G. Li, X.-G. Zhang, A. F. Stepan, J.-Q. Yu, *J. Am. Chem. Soc.* **2013**, *135*, 7567; q) T. Wesch, F. R. Leroux, F. Colobert, *Adv. Synth. Catal.* **2013**, *355*, 2139; r) S. Li, G. Chen, C.-G. Feng, W. Gong, J.-Q. Yu, *J. Am. Chem. Soc.* **2014**, *136*, 5267; s) B. Wang, C. Shen, J. Yao, H. Yin, Y. Zhang, *Org. Lett.* **2014**, *16*, 46; t) X. Ye, X. Shi, *Org. Lett.* **2014**, *16*, 4448.

[4] For selected papers concerning Ru-catalyzed direct olefination reactions employing directing groups, see: a) Y. Matsuura, M. Tamura, T. Kochi, M. Sato, N. Chatani, F. Kakiuchi, *J. Am. Chem. Soc.* **2007**, *129*, 9858; b) T. Ueyama, S. Mochida, T. Fukutani, K. Hirano, T. Satoh, M. Miura, *Org. Lett.* **2011**, *13*, 706; c) L. Ackermann, J. Pospech, *Org. Lett.* **2011**, *13*, 4153; d) K. Padala, M. Jeganmohan, *Org. Lett.* **2011**, *13*, 6144; e) L. Ackermann, L. Wang, R. Wolfram, A. V. Lygin, *Org. Lett.* **2012**, *14*, 728; f) B. Li, J. Ma, N. Wang, H. Feng, S. Xu, b. Wang, *Org. Lett.* **2012**, *14*, 736; g) K. Padala, M. Jeganmohan, *Org. Lett.* **2012**, *14*, 1134; h) K. Graczyk, W. Ma, L. Ackermann, *Org. Lett.* **2012**, *14*, 4006; i) V. Lanke, K. R. Prabhu, *Org. Lett.* **2013**, *15*, 2818; j) V. Lanke, K. R. Prabhu, *Org. Lett.* **2013**, *15*, 6262; k) K. Padala, S. Pimparkar, P. Madasamy, M. Jeganmohan,

Chem. Commun. **2012**, *48*, 7140; l) J. Li, C. Kornhaab, L. Ackermann, *Chem. Commun.* **2012**, *48*, 11343; m) W. Ma, L. Ackermann, *Chem. Eur. J.* **2013**, *19*, 13925; n) P. B. Arockiam, C. Fischmeister, C. Bruneau, P. H. Dixneuf, *Green Chem.* **2011**, *13*, 3075; o) H. Li, X. Xie, L. Wang, *Chem. Commun.* **2014**, *50*, 4218; p) M. R. Yadav, R. K. Rit, M. Shankar, A. K. Sahoo, *J. Org. Chem.* **2014**, *79*, 6123.

[5] For selected papers concerning Rh-catalyzed direct olefination reactions employing directing groups, see: a) K. Ueura, T. Satoh, M. Miura, *Org. Lett.* **2007**, *9*, 1407; b) S. Mochida, K. Hirano, T. Satoh, M. Miura, *J. Org. Chem.* **2009**, *74*, 6295; c) N. Umeda, K. Hirano, T. Satoh, M. Miura, *J. Org. Chem.* **2009**, *74*, 7094; d) S. Mochida, K. Hirano, T. Satoh, M. Miura, *Org. Lett.* **2010**, *12*, 5776; e) N. Guimond, C. Gouliaras, K. Fagnou, *J. Am. Chem. Soc.* **2010**, *132*, 6908; f) A. S. Tsai, M. Brasse, R. G. Bergman, J. A. Ellman, *Org. Lett.* **2011**, *13*, 540; g) F. W. Patureau, F. Glorius, *Angew. Chem.* **2011**, *123*, 1096; *Angew. Chem. Int. Ed.* **2011**, *50*, 1064; h) S. Rakshit, C. Grohmann, T. Besset, F. Glorius, *J. Am. Chem. Soc.* **2011**, *133*, 2350; i) C. Wang, H. Chen, Z. Wang, J. Chen, Y. Huang, *Angew. Chem.* **2012**, *124*, 7354; *Angew. Chem. Int. Ed.* **2012**, *51*, 7242; j) Z. Shi, N. Schroder, F. Glorius, *Angew. Chem.* **2012**, *124*, 8216; *Angew. Chem. Int. Ed.* **2012**, *51*, 8092; k) W. Zhen, F. Wang, M. Zhao, Z. Du, X. Li, *Angew. Chem.* **2012**, *124*, 11989; *Angew. Chem. Int. Ed.* **2012**, *51*, 11819; l) C. Feng, D. Feng, T.-P. Loh, *Org. Lett.* **2013**, *15*, 3670; m) X. Huang, J. Huang, C. Du, X. Zhang, F. Song, J. You, *Angew. Chem.* **2013**, *125*, 13208; *Angew. Chem. Int. Ed.* **2013**, *52*, 12970; n) B. Li, J. Ma, W. Xie, H. Song, S. Xu, B. Wang, *Chem. Eur. J.* **2013**, *19*, 11863; o) B. Gong, J. Shi, X. Wang, Y. Yan, Q. Li, Y. Meng, H. E. Xu, W. Yi, *Adv. Synth. Catal.* **2014**, *356*, 137; p) J. Zhou, B. Li, Z.-C. Qian, B.-F. Shi, *Adv. Synth. Catal.* **2014**, *356*, 1038; q) K. Parthasarathy, C. Bolm, *Chem. Eur. J.* **2014**, *20*, 4896; r) N. K. Mishra, J. Park, S. Sharma, S. Han, M. Kim, Y. Shin, J. Jang, J. H. Kwak, Y. H. Jung, I. S. Kim, *Chem. Commun.* **2014**, *50*, 2350; s) K. Nobushige, K. Hirano, T. Satoh, M. Miura, *Org. Lett.* **2014**, *16*, 1188; t) J. Karthikeyan, N. Yoshikai, *Org. Lett.* **2014**, *16*, 4224.

[6] For selected reviews, see: a) O. Baudoin, *Angew. Chem.* **2007**, *119*, 1395; *Angew. Chem. Int. Ed.* **2007**, *46*, 1373; b) L. J. Goossen, N. Rodriguez, K. Goossen, *Angew. Chem.* **2008**, *120*, 3144; *Angew. Chem. Int. Ed.* **2008**, *47*, 3100; c) L. J. Goossen, K. Goossen, N. Rodríguez, M. Blanchot, C. Linder, B. Zimmermann, *Pure Appl. Chem.* **2008**, *80*, 1725; d) T. Satoh, M. Miura, *Synthesis* **2010**, 3395; e) N. Rodriguez, L. J. Goossen, *Chem. Soc. Rev.* **2011**, *40*, 5030; f) J. Cornella, I. Larrosa, *Synthesis* **2012**, *44*, 653; g) R. Shang, L. Liu, *Sci. China Chem.* **2011**, *54*, 1670; h) J. D. Weaver, A. Recio, A. J. Grenning, J. A. Tunge, *Chem. Rev.* **2011**, *111*, 1846; i) W. I. Dzik, P. P. Lange, L. J. Goossen, *Chem. Sci.* **2012**, *3*, 2671; j) A. Dermenci, G. Dong, *Sci. China Chem.* **2013**, *56*, 685.

[7] For recent papers on decarbonylative coupling reactions with vinyl carboxylic acid derivatives, see: a) L. J. Goossen, J. Paetzold, *Angew. Chem.* **2002**, *114*, 1285; *Angew. Chem. Int. Ed.* **2002**, *41*, 1237; b) L. J. Goossen, J. Paetzold, *Angew. Chem.* **2004**, *116*, 1115; *Angew. Chem. Int. Ed.* **2004**, *43*, 1095; c) J. J. Goossen, J. Paetzold, *Adv. Synth. Catal.* **2004**, *346*, 1665.

[8] For recent papers on decarboxylative coupling reactions with vinyl carboxylic acids, see: a) L. J. Goossen, N. Rodriguez, B. Melzer, C. Linder, G. Deng, L. M. Levy, *J. Am. Chem. Soc.* **2007**, *129*, 4824; b) Z. Wang, Q. Ding, X. He, J. Wu, *Org. Biomol. Chem.* **2009**, *7*, 863; c) M. Yamashita, K. Hirano, T. Satoh, M. Miura, *Chem. Lett.* **2010**, *39*, 68; d) M. Yamashita, K. Hirano, T. Satoh, M. Miura, *Org. Lett.* **2010**, *12*, 592; e) J. Hu, N. Zhao, B. Yang, G. Wang, L.-N. Guo, Y.-M. Liang, S.-D. Yang, *Chem. Eur. J.* **2011**, *17*, 5516; f) Z. He, T. Luo, M. Hu, Y. Cao, J. Hu, *Angew. Chem.* **2012**, *124*, 4010; *Angew. Chem. Int. Ed.* **2012**, *51*, 3944; g) Y. Yang, C. Xie, Y. Xie, Y. Zhang, *Org. Lett.* **2012**, *14*, 957; h) Z. Li, Z. Cui, Z. Liu, *Org. Lett.* **2013**, *15*, 406; i) B. V. Rokade, K. R. Prabhu, *Org. Biomol. Chem.* **2013**, *11*, 6713; j) W.-P. Mai, G. Song, G.-C. Sun, L.-R. Yang, J.-W. Yuan, Y.-M. Xiao, P. Mao, L.-B. Qu, *RSC Adv.* **2013**, *3*, 19264; k) P. Xu, A. Abdukader, K. Hu, Y. Cheng, C. Zhu, *Chem. Commun.* **2014**, *50*, 2308.

[9] a) X. D. Zhao, Z. Yu, *J. Am. Chem. Soc.* **2008**, *130*, 8136; b) W, Jin, Z. Yu, W. He, W. Ye, W.-J. Xiao, *Org. Lett.* **2009**, *11*, 1317; c) W. Ye, N. Luo, Z. Yu, *Organometallics* **2010**, *29*, 1049; d) H. Yang, P. Sun, Y. Zhu, H. Yan, L. Lu, X. Qu, T. Li, J. Mao, *Chem. Commun.* **2012**, *48*, 7847; e) Z. Cui, X. Shang, X.-F. Shao, Z.-Q. Liu, *Chem. Sci.* **2012**, *3*, 2853; f) Y. Yang, J. Yao, Y. Zhang, *Org. Lett.* **2013**, *15*, 3206; g) J. Zhao, W. Zhou, J. Han, G. Li, Y. Pan, *Tetrahedron Lett.* **2013**, *54*, 6507; h) H. Yang, H. Yan, P. Sun, Y. Zhu, L. Lu, D. Liu, G. Rong, J. Mao, *Green Chem.* **2013**, *15*, 976; i) J. M. Neely, T. Rovis, *J. Am. Chem. Soc.* **2014**, *136*, 2735; j) H. Yan, L. Lu, G. Rong, D. Liu, Y. Zheng, J. Chen, J. Mao, *J. Org. Chem.* **2014**, *79*, 7103; k) G. Rong, D. Liu, L. Lu, H. Yan, Y. Zheng, J. Chen, J. Mao, *Tetrahedron* **2014**, *70*, 5033.

[10] L. Zhang, R. Qiu, X. Xue, Y. Pan, C. Xu, D. Wang, X. Wang, L. Xu, H. Li, *Chem. Commun.* **2014**, *50*, 12385.

[11] a) K. Nagayama, I. Shimizu, A. Yamamoto, *Chem. Lett.* **1998**, 1143; b) R. Kakino, H. Narahashi, I. Shimizu, A. Yamamoto, *Chem. Lett.* **2001**, 1242; c) K. Nagayama, I. Shimizu, A. Yamamoto, *Bull. Chem. Soc. Jpn.* **2001**, *74*, 1803; d) R. Kakino, S. Yasumi, I. Shimizu, A. Yamamoto, *Bull. Chem. Soc. Jpn.* **2002**, *75*, 137; e) R. Kakino, H. Narahashi, I. Shimizu, A. Yamamoto, *Bull. Chem. Soc. Jpn.* **2002**, *75*, 1333.

[12] a) L. J. Goossen, K. Ghosh, *Chem. Commun.* **2001**, 2084; b) L. J. Goossen, K. Ghosh, *Angew. Chem.* **2001**, *113*, 3566; *Angew. Chem. Int. Ed.* **2001**, *40*, 3458; c) L. J. Goossen, K. Ghosh, *Eur. J. Org. Chem.* **2002**, 3254; d) L. J. Goossen, N. Rodriguez, *Chem. Commun.* **2004**, 724; e) L. J. Goossen, B. A. Khan, T. Fett, M. Treu, *Adv. Synth. Catal.* **2010**, *352*, 2166.

[13] a) S. Maetani, T. Fukuyama, N. Suzuki, D. Ishihara, I. Ryu, *Chem. Commun.* **2012**, *48*, 2552; b) S. Maetani, T. Fukuyama, I. Ryu, *Org. Lett.* **2013**, *15*, 2754.

[14] F. Pan, Z.-Q. Lei, H. Wang, H. Li, J. Sun, Z.-J. Shi, *Angew. Chem.* **2013**, *125*, 2117; *Angew. Chem. Int. Ed.* **2013**, *52*, 2063.

Rhodium-Catalyzed Decarbonylative Direct Olefination of Arenes with Vinyl Carboxylic Acids

Adv. Synth. Catal. **2015**, *357*, 1 – 9

Ruiying Qiu, Lingjuan Zhang, Conghui Xu, Yixiao Pan, Hongze Pang, Lijin Xu,* Huanrong Li*