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Carboxylic Acid Promoted, Redox-Neutral Ru-Catalyzed C-H Allylation of Aromatic Ketones

Dattatraya H. Dethe*[a], Nagabhushana C. Beeralingappa[a], and Balu D. Dherange[a]

Abstract: An redox-neutral, carboxylic acid promoted, $[RuCl_2(p\text{-cymene})]_2$ catalyzed weakly coordinating, carbonyl assisted C-H allylation of aromatic ketones has been developed. The beneficial effect of carboxylic acid on ruthenium catalyst towards C-H allylation of aromatic ketones has been further explored, using commercially available allyl acetate under mild reaction conditions. In addition, this method requires redox-neutral reaction conditions, easily accessible starting materials and it shows excellent functional group compatibility.

Transition metal catalyzed aromatic C-H bond activation has become a most fundamental and alternative method to the conventional techniques.[1] Particularly, the directing group-assisted aromatic C-H bond activation and subsequent C−C bond formation process have attracted much attention in terms of synthetic and atom efficiency.[2] Over the past decade, there is a huge advancement in the field of transition metal catalyzed $C(sp^2)$-H allylation reactions[1a,3-4], which accounts for the synthetic and pharmaceutical importance of the allyl group.[5] Generally, various metal catalysts including low abundant and highly expensive rhodium to less expensive Cp*Co(III)-Catalysts showed their reactivity for $C(sp^2)$-H allylation reactions on aromatic rings. Similarly, metal catalyzed weakly coordinating ketone directed aromatic $C(sp^2)$-H functionalization reactions have enormously enhanced the application of ketones in synthetic chemistry[6] but carbonyl directed $C(sp^2)$-H allylation of aromatic ketones are very rare. In particular, a ruthenium-catalysed oxidant-free allylation of aromatic ketoximes has been reported by Jeganmohan group[4b]. Ackermann et al., reported Manganese(I)-catalyzed ketoxime directed substitutive C-H allylation on aromatic ring by carboxylate assistance[4d] and recently, Maji group reported that the ketone-directed Cp*Co(III)-catalyzed C−H allylation using allyl isobutyl carbonate as an allyl source at 100 °C.[7] Although, above methods offers allylated products in good yields but either it requires three steps for achieving allylated ketones (preinstallation, allylation and removal of directing group) or it requires a synthetically prepared allyl source and higher reaction temperature. However, preinstallation and detachment of these directing groups in the course of the reaction are often undesirable and unnecessary. This may hamper the use of C-H functionalization reactions for synthetic applications. It is noteworthy to mention that allylation followed by isomerization of the double bond is a major side reaction for such type of allylation reactions. Furthermore, a reaction at a higher temperature may cause isomerization of double bond.[8] Thus, the development of C-H allylation with functionalizable directing groups under mild reaction conditions is highly desirable. Herein, we report an alternative method, carboxylic acid promoted, redox-neutral, ruthenium catalyzed $C(sp^2)$-H allylation of weakly coordinating aromatic ketones using commercially available allyl acetate as an allyl source (scheme 1).

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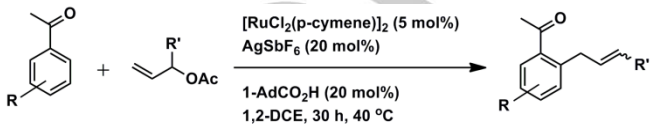
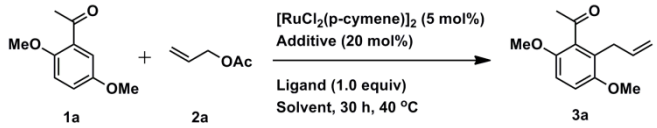
Scheme 1: Ketone Directed $C(sp^2)$-H Allylation of acetophenones



To optimize the reaction conditions, allylation reaction was performed using 2,5-dimethoxy acetophenone **1a** and allyl acetate **2a** in 1,2-dichloroethane at 60 °C for 12 h with 5 mol% $[RuCl_2(p\text{-cymene})]_2$ as the catalyst, 20 mol % $AgSbF_6$ as an additive and 1 equivalent of $Cu(OAc)_2.H_2O$. The desired *ortho*-allylated product **3a** and its olefin isomerized product were obtained in 65% yield in 3:1 ratio respectively (Table 1, entry 1). To achieve the complete conversion, reaction was performed by increasing temperature to 80 °C, which resulted in the formation of the isomerized product as a major product. To avoid such isomerization, we conducted a reaction at lower temperature. When the reaction mixture was allowed to be stirred at room temperature for 30 h, solely *ortho* allylated product **3a** was isolated in 58% yield (entry 2). It confirms that lower reaction temperature and higher reaction time were beneficial in providing allylated product exclusively in better yield. To elevate the reaction efficacy, the catalytic reaction was tested in various solvents such as dichloromethane, *t*-AmOH, acetonitrile, NMP, trifluoroethanol, DMF, and dioxane (entry 3-9). Reaction in dioxane afforded 50% yield whereas dichloromethane and trifluoroethanol were moderately effective in providing **3a** in 38% and 33% yield respectively while other polar solvents were found to be less effective. Also, the replacement of $Cu(OAc)_2.H_2O$ with AgOAc and KOAc resulted in a lower yield of desired product **3a** (entry 10 & 11). The catalytic reaction was screened with various additives such as NH_4PF_6, AgOAc, and Ag_2CO_3 (entry 12-14). Change of additive to NH_4PF_6 afforded the desired product in 45% yield (entry 12) and other additives did not produce any satisfactory results. To our delight, a significant improvement in the yield (72%) was observed, when the reaction was performed by using 20 mol% of 1-$AdCO_2H$ along with $AgSbF_6$ and $Cu(OAc)_2.H_2O$ (entry 15). Similarly, mesitylenecarboxylic acid ($MesCO_2H$) was also found to be an equally efficient ligand in generating desired product **3a** (entry 16) whereas the employment of pivalic acid and acetic acid was found to be ineffective (entry 17-18). Notably, the use of alkyl carboxylic acid as an additive significantly enhances the reactivity of *in situ* generated ruthenium-based catalytic system and is well documented.[9,10] A drastic decrease in the yield was observed when benzoic acid was used as a ligand probably due to competitive reactive sites (entry 19). To our delight, when the reaction was carried out by using 20 mol% of 1-$AdCO_2H$ in the absence of $Cu(OAc)_2.H_2O$, the desired product **3a** was obtained in 75% (entry 20). This clearly showed that, 1-adamantane carboxylate ion acts as a base to remove the proton from the activated C-H bond of the Ru/arene-complex. The reaction follows base-assisted intermolecular electrophilic substitution pathway.[4b,4d] Finally, the allylation reaction was tested using different allyl sources such as allyl alcohol, allyl bromide, and allyl methyl carbonate. It was found that allyl alcohol and allyl bromide didn't form any allylation product under optimized reaction conditions whereas allyl methyl carbonate provided **3a** with 26% of yield (entry 21). Based on these results, allyl acetate was chosen as an allyl source for reaction.

Table 1: Optimization of Reaction Conditions

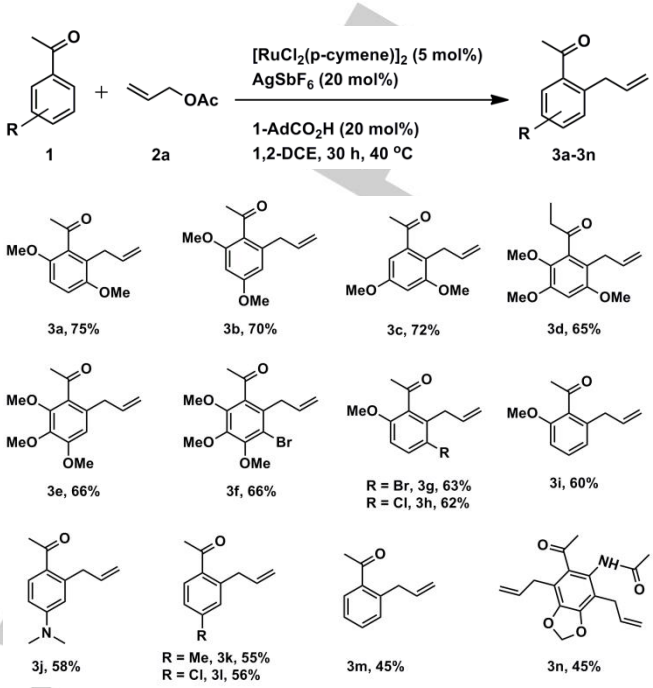


Entry	Solvent	Additive	Ligand	[b]Yield, 3a, (%)
1	DCE	$AgSbF_6$	$Cu(OAc)_2.H_2O$	65
2[a]	DCE	$AgSbF_6$	$Cu(OAc)_2.H_2O$	58
3	DCM	$AgSbF_6$	$Cu(OAc)_2.H_2O$	38
4	t-AmOH	$AgSbF_6$	$Cu(OAc)_2.H_2O$	13
5	CH_3CN	$AgSbF_6$	$Cu(OAc)_2.H_2O$	Trace
6	NMP	$AgSbF_6$	$Cu(OAc)_2.H_2O$	20
7	TFE	$AgSbF_6$	$Cu(OAc)_2.H_2O$	33
8	DMF	$AgSbF_6$	$Cu(OAc)_2.H_2O$	Trace
9	Dioxane	$AgSbF_6$	$Cu(OAc)_2.H_2O$	50
10[c]	DCE	-	AgOAc	16
11	DCE	$AgSbF_6$	KOAc	12
12	DCE	NH_4PF_6	$Cu(OAc)_2.H_2O$	45
13	DCE	AgOAc	$Cu(OAc)_2.H_2O$	<10
14	DCE	Ag_2CO_3	$Cu(OAc)_2.H_2O$	0
15[a,d]	DCE	$AgSbF_6$	$Cu(OAc)_2.H_2O$ + 1-$AdCO_2H$	72
16[a,d]	DCE	$AgSbF_6$	$Cu(OAc)_2.H_2O$ + $MesCO_2H$	70
17[a,d]	DCE	$AgSbF_6$	$Cu(OAc)_2.H_2O$ + PivOH	40
18[a,d]	DCE	$AgSbF_6$	$Cu(OAc)_2.H_2O$ + CH_3CO_2H	20
19[a,d]	DCE	$AgSbF_6$	$Cu(OAc)_2.H_2O$ + $PhCO_2H$	15
20[d]	**DCE**	**$AgSbF_6$**	**1-$AdCO_2H$**	**75**
21[d,e]	DCE	$AgSbF_6$	1-$AdCO_2H$	26
22[d,f]	DCE	$AgSbF_6$	1-$AdCO_2H$	70 & 65
23[d]	DCE	$AgSbF_6$	CH_3CO_2H	25

Reaction conditions: [a]**1a** (0.2 mmol), **2a** (0.4 mmol), $[Ru(p\text{-cymene})Cl_2]_2$ (5 mol %), additive (20 mol %) and ligand (1 equiv.) at 40 °C in a specific solvent (2.0 mL), under argon, 30 h (Note: entry 1 - Reaction carried out at 60 °C). [b]Isolated yields are of product **3a**. [c]The reaction was performed without $AgSbF_6$. [d]20 mol% carboxylic acid was used. [e]Allyl methyl carbonate was used instead of allyl acetate. [f]30 and 50 mol% carboxylic acid was used respectively.

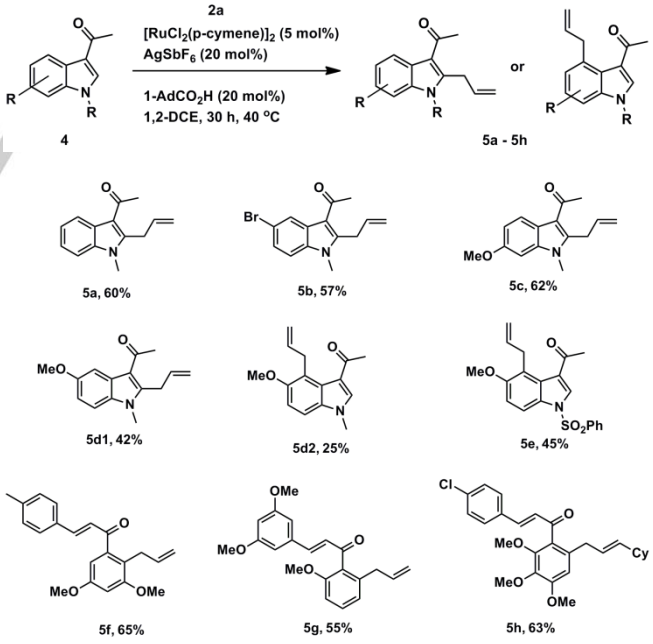
After optimization of the reaction conditions, we next explored the substrate scope of aromatic ketones with allyl acetate (Table 2). It was found that substituents on the aromatic ketones plays a significant electronic effect on their reactivity. As shown in Table 2, electron-rich, methoxy substituted aromatic ketones provided corresponding allylated products in good yields. In addition, the position of methoxy substitution with respect to the directing group showed little effect on their reactivity. Di, trimethoxy substituted acetophenones **1a** - **1f** reacted well with allyl acetate to generate desired products **3a** to **3f** in very good yields. Halogen substituted aromatic ketones such as **1g** and **1h** afforded corresponding allylated products **3g** and **3h** in 63% and 62% yield respectively. Similarly, 2'-methoxy, 4'-(N,N-dimethylamine), 4'-methyl, 4'-chloro substituted acetophenones (**1i - 1l**) independently exhibited their reactivity for allylation reaction to furnish required products

Table 2: Substrate Scope for Aromatic Ketones with Allyl acetate



Reaction conditions: [a]**1a** (0.2 mmol), **2a** (0.4 mmol), $[Ru(p\text{-cymene})Cl_2]_2$ (5 mol %), $AgSbF_6$ (20 mol %) and 1-$AdCO_2H$ (20 mol%) at 40 °C in a 1,2-dichloroethane (2.0 mL), under argon for 30 h. [b]Isolated yields are of product **3**.

Table 3: Substrate Scope for Indoles and Chalcones with Allylacetate



Reaction conditions: [a]**4** (0.2 mmol), **2a** (0.4 mmol), $[Ru(p\text{-cymene})Cl_2]_2$ (5 mol %), $AgSbF_6$ (20 mol %) and 1-$AdCO_2H$ (20 mol%) at 40 °C in a 1,2-dichloroethane (2.0 mL), under argon for 30 h. Cy = cyclohexyl, 2° Cyclohexyl allylacetate was used.

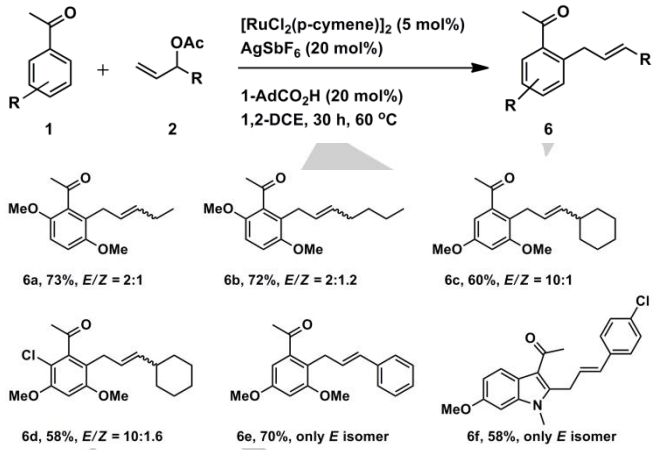
(**3i - 3m**) in moderate yields. Also, acetophenone with bis coordinating groups **1n**, underwent allylation reaction to afford the *bis*-allylated product in 45% yield. No reaction was observed for

aromatic ketones containing electron-withdrawing groups under standard reaction conditions, which limits the scope of this method. Also, no reaction was observed when benzaldehydes were employed as substrates. This may be due to the weak coordinating ability of aldehydes, its susceptibility toward oxidation, and undesired metal insertion into the acyl C-H bond.[11]

The scope of the allylation reaction was further explored with various indole derivatives (Table 3). Allylation of *N*-protected 3-acetylindole generally offers C-2 allylated indole. A simple N-methyl indole **4a** shown its reactivity while generating C-2 allylated product **5a** in 60% yield. Substrate **5b** was also successfully synthesized in moderate yield, showing the tolerance of the bromo group and its scope for further functionalization. Similarly, electron-rich substrate **4c** successfully afforded allylated product **5c** in 62% yield. Lack of selectivity is probably due to electronic effects on 4-methoxy substituted 3-acetylindole ring (**4d**), delivered a mixture of C-2 and C-4 allylated products **5d1** and **5d2** in 67% yield in 2:1.3 ratio respectively. Interestingly, when indole nitrogen was protected with a strong electron-withdrawing benzenesulfonyl group, regioselectivity was completely shifted to C-4 position to afford the product **5e** in 45% yield. Notably, the versatility of this method was further explored to chalcones and generated the corresponding allylation products in good to moderate yields (Table 3, **5f - 5h**).

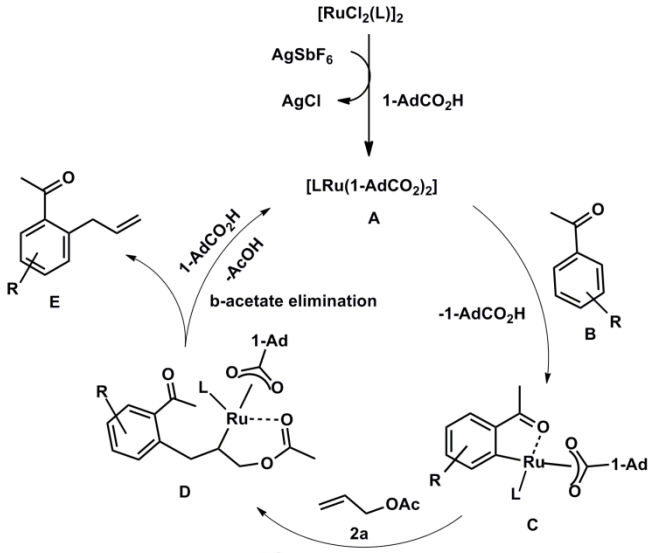
Next, we investigated the reactivity of aromatic ketones with various α-substituted secondary allyl acetates (Table 4). Under optimized conditions, α-ethyl and α-butyl substituted allyl acetates **2b** and **2c** reacted well with 2,5-dimethoxy acetophenone **1a** to afford desired products **6a** and **6b** in 73% and 72% yield respectively. In both cases**,** however a mixture of stereoisomeric products were isolated with an *E/Z* ratio of 2:1 and 2:1.2 respectively. Similarly, substrates **1c** and **1p** exhibited their reactivity with sterically hindered cyclohexyl substituted allyl acetate **2d** to afford desired products **6c** and **6d** in 60% and 58% yield. In this case, due to the steric effect of the cyclohexyl group, both the products **6c** and **6d** were obtained with high stereoselectivity (nearly 90% *E* isomer). The allylation reaction

Table 4: Allylation Reaction of Aromatic Ketones with Secondary Allylic Acetates



Reaction conditions: [a]Aryl ketone **1** (0.2 mmol), 2[o] Allyl acetate **2** (0.24 mmol), $[Ru(p\text{-cymene})Cl_2]_2$ (5 mol %), $AgSbF_6$ (20 mol %) and 1-$AdCO_2H$ (20 mol%) at 60 [o]C in a 1,2-dichloroethane (2.0 mL), under argon for 30 h. The *E/Z* ratios were determined by using a ^1H NMR integration method.

Scheme 2: Plausible Reaction Mechanism



was also compatible with cinnamyl derivatives such as **2e** and **2f**, which on treatment with 3,5-dimethoxy acetophenone and 3-acetyl indole derivative respectively furnished desired products **6e** and **6f** in a highly stereoselective manner. Interestingly, when we performed the C-H allylation reaction of 2,5-dimethoxy acetophenone with branched and linear allyl acetates of same carbon skeleton under standard reaction conditions, we only observed successful transformation for the secondary allyl acetate (branced) substrate while no reaction was observed in case of the corresponding primary allyl acetate (linear).

Based on the previous report,[4b] a possible mechanism for the allylation reaction of aromatic ketones with allyl acetate as shown in scheme 2. The catalytic cycle is commenced with *in situ* generated reactive cationic ruthenium complex $[RuX_n(L)]^+$ **A** from treatment of $[Ru(p\text{-cymene})Cl_2]_2$ with $AgSbF_6$ and 1-adamantane carboxylic acid. Next, ketone **B** coordinates with reactive complex **A** followed by subsequent *ortho*-ruthenation providing a cyclic ruthenacycle **C**. Ruthenium-carbon bond of intermediate **C** could be cleaved by coordinative regioselective insertion of allyl acetate **2a** to generate an intermediate **D**. β-acetate elimination of an intermediate **D** leads to the formation of corresponding *ortho*-allylated aromatic ketone **E** along with regeneration of ruthenium (II) cationic complex **A** for the next catalytic cycle.

Conclusions

We have developed a carboxylic acid promoted and redox-neutral ruthenium-catalyzed *ortho* allylation of aromatic ketones such as substituted acetophenones, 3-acetyl indoles, and chalcones. Weakly coordinating, easily accessible ketone assisted C-H allylation using cheap and commercially available allyl acetate in presence of less expensive $[Ru(p\text{-cymene})Cl_2]_2$ catalyst under mild reaction temperature has been achieved. This method provides an access to various synthetically useful terminal olefin systems in moderate to good yields.

Experimental Section

General procedure for C-H allylation of aromatic ketones

A 8 mL seal tube was fitted with septum and charged with $[RuCl_2(p\text{-cymene})]_2$ (8 mg, 0.012 mmol, 5.0 mol%), $AgSbF_6$ (18 mg, 0.05 mmol, 20 mol%) and 1-adamantane carboxylic acid (10 mg, 0.05 mmol, 20 mol%) under nitrogen atmosphere. To that 1,2-dichloroethane (2 mL) was added and stirred about 5 minutes. Then aromatic ketone or acetyl indole (0.25 mmol, 1.0 equiv) and allyl acetate (0.5 mmol, 2.0 equiv) [Note: 1.2 equiv., of **2b** - **2f** were used] were added into the reaction mixture in sequence *via* syringe. The tube was sealed under N_2 and stirred at 40 °C for 30 h [Note: Reactions between aryl ketones **1** and **2°** allyl acetates were conducted at 60 °C]. After completion of the reaction as indicated by the TLC, the crude mixture was directly purified by silica gel column chromatography.

Conflict of Interest

The authors declare no conflict of interest.

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Keywords: 1-Adamantane carboxylic acid • Allylation • Aromatic ketones • Ketone directed • Ruthenium

References

[1] (a) N. K. Mishra, S. Sharma, J. Park, S. Han, I. S. Kim, *ACS Catal*. **2017**, *7*, 2821-2847; (b) N. H. Frost, H. Leuser, M. I. Calaza, F. F. Kneisel, P. Knochel, *Org. Lett.* **2003**, *5*, 2111−2114; (c) Y. Kiyotsuka, H. P. Acharya, Y. Katayama, T. Hyodo, Y. Kobayashi, *Org. Lett.*, **2008**, *10*, 1719- 1722; (d) H. Ohmiya, Y. Makida, T. Tanaka, M. Sawamura, *J. Am.Chem. Soc.* **2008**, *130*, 17276−17277; (e) P. A. Evans, D. Uraguchi, *J. Am. Chem. Soc.* **2003**, *125*, 7158-7159; (f) D. Polet, X. Rathgeb, C. A. Falciola, J. B. Langlois, S. E. Hajjaji, A. Alexakis, *Chem. - Eur. J.* **2009**, *15*, 1205−1216; (g) M. Kodomari, S. Nawa, T. Miyoshi, *J. Chem. Soc., Chem. Commun.* **1995**, 1895-1896; (h) M. Niggemann, M. J. Meel, *Angew. Chem. Int. Ed.* **2010**, *49*, 3684-3687; (i) T. B. Poulsen, K. A. Jørgensen, *Chem. Rev.* **2008**, *108*, 2903-2915; (j) A. M. Echavarren, J. K. Stille, *J. Am. Chem. Soc.* **1987**, *109*, 5478-5486; (k) K. T. Croset, D. Polet, A. Alexakis. *Angew. Chem. Int. Ed.* **2004**, *43*, 2426-2428.

[2] (a) F. Wang, S. Yu, X. Li, *Chem. Soc. Rev.* **2016**, *45*, 6462-6477; (b) L. Yang, H. Huang, *Chem. Rev.* **2015**, *115*, 3468-3517; (c) G. Song, X. Li, *Acc. Chem. Res.* **2015**, *48*, 1007-1020; (d) S.-S. Li, L. Qin, L. Dong, *Org. Biomol. Chem.* **2016**, *14*, 4554-4570; (e) W.-H. Rao, B.-F. Shi, *Org. Chem. Front.* **2016**, *3*, 1028-1047; (f) P. B. Arockiam, C. Bruneau, P. H. Dixneuf, *Chem. Rev*. **2012**, *112*, 5879-5918; (g) N. Kuhl, M. N. Hopkinson, J. W. Delord, F. Glorius, *Angew. Chem., Int. Ed.* **2012**, *51*, 10236-10254.

[3] (a) S. Debbarma, S. S. Bera, M. S. Maji, *J. Org. Chem.* **2016**, *81*, 11716; (b) B. Ye, N. Cramer, *J. Am. Chem. Soc.* **2013**, *135*, 636; (c) S.-S. Zhang, J.-Q. Wu, X. Liu, H. Wang, *ACS Catal.* **2015**, *5*, 210; (d) J.-Q. Wu, Z.-P. Qiu, S.-S. Zhang, J.-G. Liu, Y.-X. Lao, L.-Q. Gu, Z.-S. Huang, J. Li, H. Wang, *Chem. Commun.* **2015**, *51*, 77; (e) C. Feng, D. Feng, T.-P. Loh, *Chem. Commun.* **2015**, *51*,342; (f) R. Zeng, C. Fu, S. Ma, *J. Am. Chem. Soc.* **2012**, *134*, 9597; (g) Y. Takahama, Y. Shibata, K. Tanaka, *Org. Lett.* **2016**, *18*, 2934; (h) H. Dai, C. Yu, Z. Wang, H. Yan, C. Lu, *Org. Lett.* **2016**, *18*, 3410.

[4] (a) M. Kim, S. Sharma, N. K. Mishra, S. Han, J. Park, M. Kim, Y. Shin, J. H. Kwak, S. H. Han, I. S. Kim, *Chem. Commun.* **2014**, *50*, 11303; (b) R. Manikandan, P. Madasamy, M. Jeganmohan, *Chem. Eur. J.* **2015**, *21*, 13934; (c) Y.-Q. Xia, L. Dong, *Org. Lett.* **2017**, *19*, 2258; (d) W. Liu, S. C. Richter, Y. Zhang, L. Ackermann, *Angew. Chem., Int. Ed.* **2016**, *55*, 7747; (e) Q. Lu, F. J. R. Klauck, F. Glorius, *Chem. Sci.* **2017**, *8*, 3379; (f) X. Cong, Y. Li, Y. Wei, X. Zeng, *Org. Lett.* **2014**, *16*, 3926; (g) N. Barsu, D. Kalsi, B. Sundararaju, *Chem. Eur. J.* **2015**, *21*, 9364; (h) S. Asako, L. Ilies, E. Nakamura, *J. Am. Chem. Soc.* **2013**, *135*, 17755; (i) G. Cera, T. Haven, L. Ackermann, *Angew. Chem., Int. Ed.* **2016**, *55*, 1484; (j) X. Wu, H. Ji, *Org. Lett.*, **2018**, *20*, 2224-2227.

[5] (a) E. M. Mmutlane, J. P. Michael, I. R. Green, C. B. de Koning, *Org. Biomol. Chem.* **2004**, *2*, 2461-2470; (b) C.-K. Chan, Y.-L. Tsai, Y.-L. Chan, M.-Y. Chang, *J. Org. Chem.* **2016**, *81*, 9836; (c) J. L. Farmer, H. N. Hunter, M. G. Organ, *J. Am. Chem. Soc.* **2012**, *134*, 17470; (d) G. Ni, Q. J. Zhang, Z.-F. Zheng, R.-Y. Chen, D.-Q. Yu, *J. Nat. Prod.* **2009**, *72*, 966; (e) J. A. Marshall, *Chem. Rev*. **2000**, *100*, 3163; (f) B. M. Trost, O. R. Thiel, H.-C. Tsui, *J. Am. Chem. Soc.* **2002**, *124*, 11616.

[6] (a) F. W. Patureau, T. Besset, F. Glorius, *Angew. Chem. Int. Ed.* **2011**, *50*, 1064-1067; (b) K. Padala, M. Jeganmohan, *Org. Lett.*, **2011**, *13*, 6144-6147; (b) Q.-Z. Zheng, N. Jiao, *Tetrahedron Lett*. **2014**, *55*, 1121; (c) Z. Huang, H. N. Lim, F. Mo, M. C. Young, G. Dong, *Chem. Soc. Rev.* **2015**, *44*, 7764; (d) Y. Hu, B. Zhou, H. Chen, C. Wang, *Angew.Chem. Int. Ed*. **2018**, *57*, 12071-12075; (d) D. H. Dethe, C. B. Nagabhushana, A. A. Bhat, *J. Org. Chem.* **2020**, *85*, 7565-7575.

[7] M. R. Sk, S. S. Bera, M. S. Maji, *Org. Lett.* **2018**, *20*, 134-137.

[8] (a) R. Manikandan, M. Jeganmohan. *Org. Biomol. Chem.*, **2016**, *14*, 7691-7701; (b) S. Jambu, M. Jeganmohan. *Org. Lett*. **2019**, *21*, 5655-5659; (c) A. S. Trita, A. Biafora, M. P. Drapeau, P. Weber, L. J. Gooßen *Angew. Chem. Int. Ed*. **2018**, *57*, 14580-14584; (d) S. Jambu, M. Tamizmani, M. Jeganmohan. *Org. Lett*. **2018**, *20*, 1982-1986.

[9] (a) L. Ackermann, P. Novak, R. Vicente, N. Hofmann. *Angew. Chem. Int. Ed.* **2009**, *48*, 6045 –6048.; (b) M. Lafrance, K. Fagnou, *J. Am. Chem. Soc*. **2006**, *128*, 16496-16497; (c) M. Lafrance, S. I. Gorelsky, K. Fagnou, *J. Am. Chem. Soc.* **2007**, *129*, 14570 – 14571; (d) L. Ackermann, R. Vicente, R. Born, *Adv. Synth. Catal*. **2008**, *350*, 741-748; (e) L. Ackermann, A. Althammer, S. Fenner, *Angew. Chem. Int. Ed.* **2009**, *48*, 201-204; (f) M. Miura, T. Sato, in Modern Arylation Methods (Ed.: L. Ackermann), Wiley-VCH, Weinheim, **2009**, pp. 335-361; (g) P. de Mendoza, A. M. Echavarren in Modern Arylation Methods (Ed.: L. Ackermann), Wiley-VCH, Weinheim, **2009**, pp. 363- 400.

[10] (a) L. Ackermann, M. Mulzer. *Org. Lett.* **2008**, *10*, 5043-5045; (b) S. Oi, R. Funayama, T. Hattori, Y. Inoue, *Tetrahedron* **2008**, *64*, 6051-6059; (c) L. Ackermann, R. Born, P. A. Bercedo, *Angew. Chem. Int. Ed*. **2006**, *45*, 2619-2622; (d) L. Ackermann, *Org. Lett*. **2005**, *7*, 3123-3125; (e) F. Kakiuchi, Y. Matsuura, S. Kan, N. Chatani, *J. Am. Chem. Soc*. **2005**, *127*, 5936-5945; (f) S. Oi, E. Aizawa, Y. Ogino, Y. Inoue, *J. Org. Chem.* **2005**, *70*, 3113-3119.

10.1002/ejoc.202100717

[11] (a) X.-H. Liu, H. Park, J.-H. Hu, Y. Hu, Q.-L. Zhang, B.-L. Wang, B. Sun, K. S. Yeung, F. L. Zhang, J. Q. Yu, *J. Am. Chem. Soc*, **2017**, *139*, 888-896; (b) K. Fumitoshi, S. Taisuke, I. Kimitaka, C. Naoto, M. Shinji, *Chem. Lett*. **2001**, *30*, *386-387*.

10.1002/ejoc.202100717

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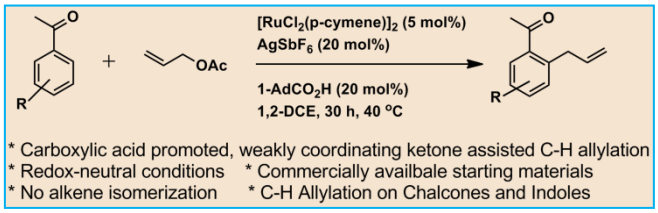
An alternative method for the weakly coordinating, ketone-directed C(sp^2)-H allylation of aromatic ketones such as substituted acetophenones, 3-acetyl indoles, and chalcones has been developed under redox-neutral conditions. 1-Adamantane carboxylic acid plays a crucial role in improving the reactivity of the [$RuCl_2$(p-cymene)]$_2$ catalyst under mild reaction temperature. This method provides an access to various synthetically useful terminal olefin systems in moderate to good yields.



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Carboxylic Acid Promoted, Redox-Neutral Ru-Catalyzed C-H Allylation of Aromatic Ketones

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