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Allylic activation across an Ir–Sn heterobimetallic catalyst: nucleophilic substitution and disproportionation of allylic alcohol

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ABSTRACT

A nucleophilic substitution of allylic alcohols with carbon (arene, heteroarene, allyltrimethylsilane, and 1,3-dicarbonyl compound), sulfur (thiol), oxygen (alcohol), and nitrogen (sulfonamide) nucleophiles has been demonstrated using an in house developed $[Ir(COD)(SnCl_3)l(\mu\text{-}Cl)]_2$ heterobimetallic catalyst in 1,2-dichloroethane to afford the corresponding allylic products in moderate to excellent yields. In 4-hydroxycoumarin, allylation occurs at the 3-position. The diaryl-substituted allylic alcohols undergo disproportionation in presence of the heterobimetallic catalyst to provide the corresponding alkenes and chalcones. An electrophilic mechanism is proposed from Hammett correlation study.

1. Introduction

Notwithstanding the importance of single metal homogeneous catalysis, recent years have been the emergence of newer concepts involving multi-metallic homogeneous catalysis.[1] This is mainly due to the fact that the incorporation of two or more metals in a single scaffold often results in selective substrate binding, dual and synergistic activation, and higher efficiency.[2,3] In the course of our continuing effort to exploit the organic reactivity of a reagent combination involving transition metal and tin as partners,[4] we became attracted to the recent heightened interest in cooperative catalysis in homogeneous regime.[5] Quite recently, we disclosed a novel homogeneous heterobimetallic catalyst $[Ir(\mu\text{-}Cl)(COD)Cl(SnCl_3)]_2$ (hereafter Ir^{III}–$SnCl_3$), which showed remarkable efficiency toward the activation of different electrophiles, for example, π-activated 1°, 2°, and 3° benzylic alcohols and secondary/tertiary propargylic alcohols,[6a–d] ethers,[6e] and aldehydes.[6f] Keeping in view the importance of metal catalyzed activation of allylic substrates (vide infra) and our own enthusiasm,[6a,6g] we were encouraged to study the reactivity of allylic compounds at the Ir^{III}–$SnCl_3$ regime toward C–C, C–S, C–O, and C–N bond formation reaction with various carbon (arene, heteroarene, allyltrimethylsilane, 1,3-dicarbonyl compound), sulfur (thiol), oxygen (alcohol), and nitrogen (sulfonamide) nucleophiles in a regioselective manner. Additionally, disproportionation of allylic alcohols can be achieved by Ir^{III}–$SnCl_3$ catalyst in the absence of nucleophiles to provide alkene and α,β-unsaturated ketones selectively.[7]

As it is considered as an ideal and more efficient way, the direct substitution of allylic alcohols has emerged as a frontier area of research, because the products obtained in these processes are highly interesting building blocks that have been widely used in complex natural product synthesis of great importance. In parallel this protocol will provide an attractive salt-free, environment friendly, and atom-economic technique with water being the only by-product. It has been observed that some allylated aromatic compounds, such as 3-phenylpropenes can be used as a potent inhibitor of the enzyme dopamine β-hydroxylase.[8] Very recently attempts have been carried out to perform the catalytic nucleophilic substitution of allylic alcohols and their derivatives with carbon and heteroatom-centered nucleophiles. A variety of transition metals, such as Ru,[9] Ir,[10] Ni,[11] Mo,[12] Pd,[13] and Cu,[14] several Lewis acids,[15] Brønsted acids,[16] and even molecular iodine[17] can promote these reactions under different conditions. Despite the impressive progress, most of the catalysts are very much specific with respect to nucleophiles. It therefore remains a challenge to develop an alternative catalytic system that will exhibit outstanding versatility for a broad spectrum of

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nucleophiles. Hence we present here for the first time in the literature where a single in house designed catalyst, namely [Ir(μ-Cl)(COD)Cl($SnCl_3$)]$_2$, can activate allylic alcohols toward (i) direct nucleophilic substitution with various carbon and heteroatom-centered nucleophiles, as well as (ii) the disproportionation of allylic alcohols (Fig. 1).

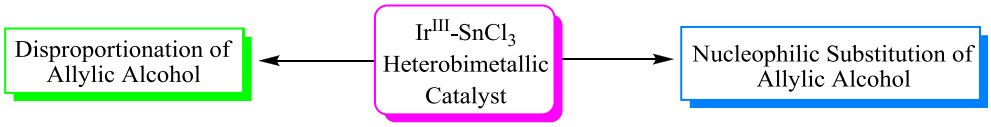


Fig. 1. Dual role of Ir–Sn heterobimettalic catalyst.

2. Results and discussion

First, we envisaged the allylation of *m*-xylene with cinnamyl alcohol **1a** and its derivatives (acetate, ether, formate, halide etc.) catalyzed by the Ir^{III}–$SnCl_3$ complex in 1,2-dichloroethane (DCE) at 80 °C for 1 h (Table 1). The corresponding allylated product **2a** was formed in almost quantitatively for cinnamyl alcohol **1a**, acetate **1b**, and formate **1c** (Table 1, entries 1–3). Unlikely, cinnamyl bromide **1d** gave only 33% of the desired product **2a** in 1 h with full consumption of the starting bromide (entry 4). But cinnamyl methyl ether **1e** was found to be less reactive than other allylating agents (alcohol, acetate, formate) yielding only 40% of the allylated product **2a** (entry 5). A longer reaction time improved the yield to 80%, consuming cinnamyl methyl ether completely (entry 6).

It is very much clear from the above experimental observation that Ir^{III}–$SnCl_3$ heterobimetallic catalyst can efficiently activate varieties of functional groups (–OAc, –OC(O)OEt, –OMe) toward allylation of arenes. Furthermore, these starting materials have to be prepared in an extra step from the corresponding allylic alcohols. Thus, ideal substrates would be the allylic alcohols themselves, with water being the only by-product in this case.

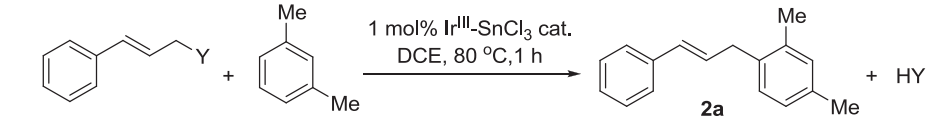
For model studies on allylation we had chosen cinnamyl alcohol **1a** as representative alcohol and *m*-xylene as the arene in the presence of 1 mol % of Ir^{III}–$SnCl_3$ bimetallic catalyst and in DCE (Scheme 1). Each reaction was monitored for a 5 h period. When the reaction was conducted at room temperature, much of the alcohol remained un-reacted. Also the targeted allylation product **2a** and dicinnamyl ether **3a** were obtained in ca. 4% and 25% GC yields. Reaction at 50 °C led to the formation of **2a** along with **3a** in ca. 36% and 45% yields. Gratifyingly, a 100% conversion of alcohol to **2a** was observed at 80 °C, and the GC yield was 95% within 1 h. A similar outcome was found after 3 h when alcohol and nucleophile was taken in ratio of 1:1.5. Individually, the dicinnamyl ether **3a** provided the desired allylation product **2a** (82% isolated yield) with *m*-xylene in presence of the 3 mol % catalyst at 80 °C using DCE as solvent after 2 h.

Initial catalyst screening included a number of heterobimetallic catalysts and Lewis acid catalysts (Table 2). Unsurpassed catalytic efficiency was observed in the case of [Ir(μ-Cl)(COD)Cl($SnCl_3$)]$_2$, which afforded the desired allylated product **2a** after 1 h in 95% yield (Table 2, entry 10). Other heterobimetallic catalysts bearing Ir–Sn and Rh–Sn motif also promoted the reaction but at varying efficiencies (entries 1–5). Note that individually [Ir(COD)(μ-Cl)]$_2$ was inactive, while $SnCl_4$ was poorly active (entries 6, 7). Even $IrCl_3$ and cationic Ir(I) species [Ir(COD)($MeCN$)$_2$]PF_6 were also less effective (entries 8, 9). The above observations emphasize the indispensability of high-valent Ir^{III}–$SnCl_3$ motif; although we are yet to fully comprehend the exact nature of synergism in such a motif. In contrast, lower product yields were found when the reaction was repeated on changing the solvent from DCE to DCM, C_6H_6, MeCN, or THF (entries 11–14). A similar outcome was found in presence of $MeNO_2$ as solvent (entry 15). Both allylic alcohol and arene remained silent in absence of Ir^{III}–$SnCl_3$ bimetallic catalyst under the same conditions (entry 16).

Next we examined the allylic substitution of various allylic alcohols by employing different carbon-centered nucleophiles (arenes, heteroarenes, allyltrimethylsilane, and 1,3-dicarbonyl compounds) in DCE at 80 °C in presence of 1 mol % Ir^{III}–$SnCl_3$ catalyst (Table 3). For convenience, the alcohol/nucleophile ratio was kept at 1:3, and the corresponding allylation products were isolated in moderate to good yields.

Allylic alcohols bearing both alkyl and aryl substituent smoothly underwent the coupling reaction with arenes and

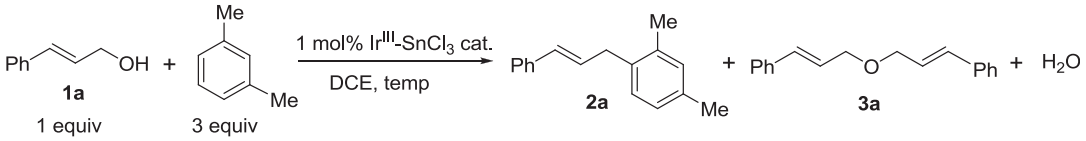
Table 1
Allylation of *m*-xylene with different cinnamyl derivatives **1** catalyzed by Ir^{III}–$SnCl_3$ complex[a]



1a, Y = OH; **1b**, Y = OC(O)Me
1c, Y = OC(O)OEt; **1d**, Y = Br
1e, Y = OMe

#	Substrate **1**	Yield of **2a**[b] (%)
1	**1a**	95
2	**1b**	>99
3	**1c**	>99
4	**1d**	33
5	**1e**	40
6	**1e**	80[c]

[a] Unless otherwise mentioned, reaction conditions: cinnamyl derivative (0.5 mmol), *m*-xylene (1.5 mmol), Ir^{III}–$SnCl_3$ cat. (0.005 mmol), solvent DCE (2 mL), 80 °C.
[b] GC yield.
[c] For 4 h.



Scheme 1. Control studies on allylation with cinnamyl alcohol **1a** and *m*-xylene: effect of temperature.

Table 2
Allylation of *m*-xylene with cinnamyl alcohol **1a**: effect of catalyst and solvent[a]

#	Catalyst (1 mol %)	Solvent	Yield of **2a**[b] (%)	Yield of **3a**[b] (%)
1	$[Ir(\mu\text{-}Br)(COD)Br(SnBr_3)]_2$	DCE	70	—
2	$[Rh(\mu\text{-}Cl)(COD)Cl(SnCl_3)]_2$	DCE	62	10
3	$[Rh(\mu\text{-}Br)(COD)Br(SnBr_3)]_2$	DCE	57	7
4	$IrCl(CO)(PPh_3)_2SnCl_4$	DCE	12	—
5	$[Ir(COD)_2(SnCl_3)]$	DCE	5	—
6	$[Ir(COD)(\mu\text{-}Cl)]_2$	DCE	—	—
7	$SnCl_4$	DCE	25	<5
8	$IrCl_3$	DCE	15	<5
9	$[Ir(COD)(MeCN)_2]PF_6$	DCE	10	—
10	**$[Ir(\mu\text{-}Cl)(COD)Cl(SnCl_3)]_2$**	**DCE**	**95**	—
11	$[Ir(\mu\text{-}Cl)(COD)Cl(SnCl_3)]_2$	DCM	40[c]	<5
12	$[Ir(\mu\text{-}Cl)(COD)Cl(SnCl_3)]_2$	C_6H_6	60	10
13	$[Ir(\mu\text{-}Cl)(COD)Cl(SnCl_3)]_2$	MeCN	45	—
14	$[Ir(\mu\text{-}Cl)(COD)Cl(SnCl_3)]_2$	THF	32[d]	—
15	$[Ir(\mu\text{-}Cl)(COD)Cl(SnCl_3)]_2$	$MeNO_2$	90	—
16	No catalyst	DCE	—	—

Bold entry indicates the efficiency of the catalyst.
[a] Unless otherwise mentioned, reaction conditions: cinnamyl alcohol (0.5 mmol), *m*-xylene (1.5 mmol), catalyst (0.005 mmol), solvent (2 mL), 80 °C.
[b] GC yield.
[c] Temp=40 °C.
[d] Temp=60 °C.

heteroarenes (Table 3, entries 1–12) with complete regioselectivity. Friedel–Crafts arylated products were isolated in excellent yields during the reaction of 1-methynaphthalene and anisole with alcohol **1a** (entries 1, 2). Allylic alcohol **1f** and **1g**, bearing electron-donating and electron-withdrawing substituents at the *para* position of the phenyl ring, afforded the respective allylated product **2d** and **2e** in good yields (entries 3, 4) with 1,3,5-trimethoxybenzene. It is noteworthy that both isomeric alcohols **1a** and **1h** reacted with anisole to give same product **2c** (entries 2 and 5). Additionally, allylic alcohol **1i** and **1j**, with alkyl substituent reacted very sluggishly with 1,3,5-trimethoxybenzene, affording mixture of products **2f**, **2f′** and **2f″** in poor yields (entries 6, 7). The reaction of alcohol **1a** with 3,5-dimethylphenol afforded **2g** in 62% yield (entry 8). Allylation occurred smartly in case of heteroarenes, *e.g.*, thiophene, 2-methylfuran, benzo[*b*]furan, and indole in moderate to excellent yield (entries 9–12). The reaction of **1a** with thiophene afforded the allylated thiophene derivatives **2h** and **2h′** as a mixture of regioisomers at 2- and 3- positions, respectively, (entry 9). Alcohol **1k** reacted smoothly with indole giving almost 90% of the desired 3-allylated indole **2k** with only 5% of the easily separable bis-allylation product **2k′**, when alcohol/indole ratio was kept as 1:1 (entry 12).

Table 3
Reaction of allylic alcohols with C-nucleophiles catalyzed by Ir^{III}–$SnCl_3$ complex[a]

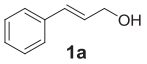
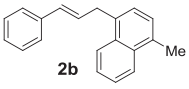
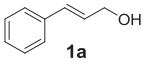
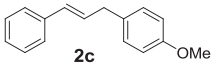
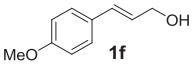
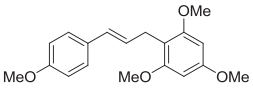
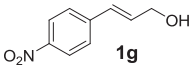
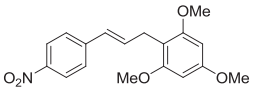
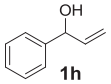
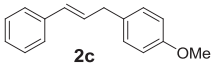
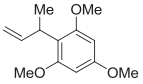
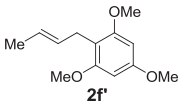
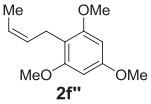
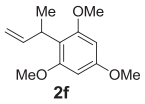
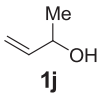
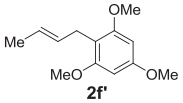
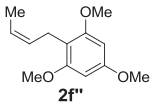
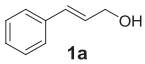
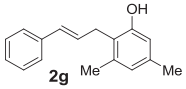
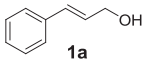
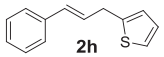
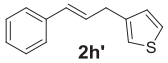
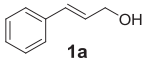
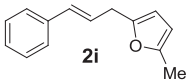
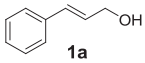
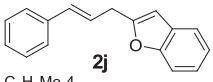
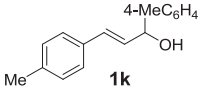
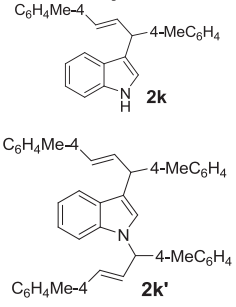
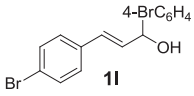
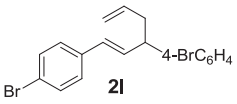
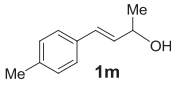
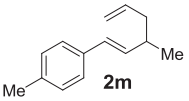
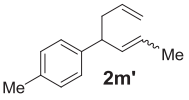
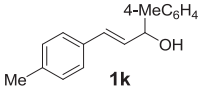
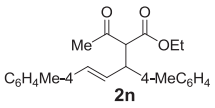
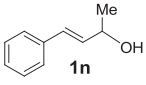
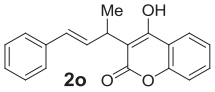
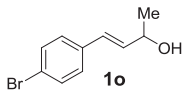
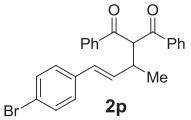
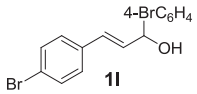
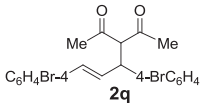
#	Electrophile	Nucleophile	Product	Time (min)	Yield[b] (%)
1	 **1a**	1-Methylnaphthalene	 **2b**	60	84
2	 **1a**	Anisole	 **2c**	45	95
3	 **1f**	1,3,5-Trimethoxybenzene	 **2d**	30	88
4	 **1g**	1,3,5-Trimethoxybenzene	 **2e**	120	79
5	 **1h**	Anisole	 **2c**	30	90
			 **2f**		
6	 **1i**	1,3,5-Trimethoxybenzene	 **2f'**	300	42[c]
			 **2f''**		

Table 3 (*continued*)

#	Electrophile	Nucleophile	Product	Time (min)	Yield[b] (%)
			 **2f**		
7	 **1j**	1,3,5-Trimethoxybenzene	 **2f'**	300	45[d]
			 **2f''**		
8	 **1a**	3,5-Dimethylphenol	 **2g**	60	62
9	 **1a**	Thiophene	 **2h**	45	75[e]
			 **2h'**		
10	 **1a**	2-Methylfuran	 **2i**	45	78
11	 **1a**	Benzo[*b*]furan	 **2j**	45	85
12	 **1k**	Indole	 **2k** **2k'**	30	93[f,g]
13	 **1l**	Allyltrimethylsilane	 **2l**	30	89
14	 **1m**	Allyltrimethylsilane	 **2m**	45	77[h]
			 **2m'**		
15	 **1k**	Ethylacetoacetate	 **2n**	30	82
16	 **1n**	4-Hydroxycoumarin	 **2o**	60	80

(*continued on next page*)

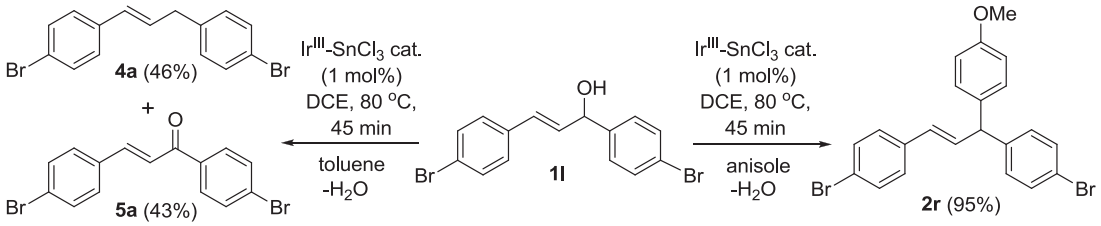
Table 3 (*continued*)

#	Electrophile	Nucleophile	Product	Time (min)	Yield[b] (%)
17	 **1o**	Dibenzoylmethane	 **2p**	45	82
18	 **1l**	Acetylacetone	 **2q**	30	90

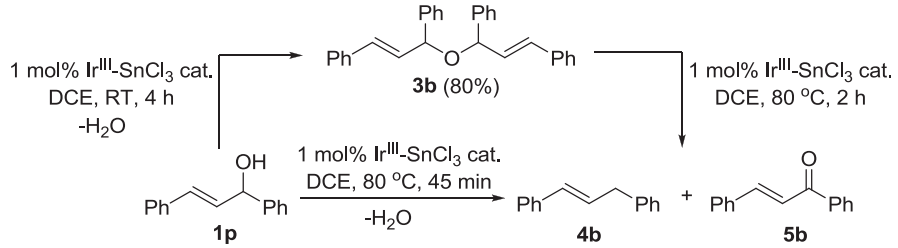
[a] Unless otherwise mentioned, reaction conditions: alcohol (0.5 mmol), nucleophile (1.5 mmol), Ir^{III}–$SnCl_3$ cat. (0.005 mmol), DCE (2 mL), 80 °C.
[b] Isolated yield.
[c] Ratio of **2f**, **2f′**, and **2f″**=1:5.7:1.3.
[d] Ratio of **2f**, **2f′**, and **2f″**=2:7.8:1.
[e] Ratio of **2h** and **2h′**=4:1.
[f] Ratio of **2k** and **2k′**=9:1.
[g] Ratio of alcohol and indole=1:1.
[h] Ratio of **2m** and **2m′**=2:1.

With the bimetallic Ir^{III}–$SnCl_3$ catalyst we next explored the coupling reactions of allylic alcohols with other carbon nucleophiles, *e.g.*, organosilicon nucleophile (allyltrimethylsilane) and 1,3-dicarbonyl compounds (Table 3, entries 13–18). We were pleased to find that in the similar reaction conditions the substituted 1,5-diene **2l** was obtained from symmetrical alcohol **1l** and allyltrimethylsilane in excellent yield (entry 13). A mixture of regioisomers was isolated when an unsymmetrical alcohol **1m** coupled with allytrimethylsilane (entry 14). Moreover, yields over 80% were obtained when the reactions were conducted with alcohols (**1k**,**l**, and **1n**,**o**) and nucleophiles like ethylacetoacetate, 4-hydroxycoumarin, dibenzoylmethane, and acetylacetone (entries 15–18). In 4-hydroxycoumarin, the allylation took place at the 3-position (entry 16). It may be mentioned that substituted coumarin analogs are of importance as they constitute valuable building blocks for potential new pharmaceuticals, especially anticoagulants.[18]

While extending the scope of the allylation reaction, we came across the disproportionation behavior of diaryl-substituted allylic alcohol in certain cases when the normal allylation was completely inhibited due to the poor philicity of the nucleophilic partner. For example, the allylic alcohol **1l** gave desired allylated product **2r** with anisole, whereas it underwent disproportionation, with elimination of water molecule, in attempted reaction with toluene as the nucleophile yielding alkene **4a** and unsaturated ketone **5a**, instead of the desired coupling product (Scheme 2). Furthermore, the diallylic ether **3b** was isolated on treatment of **1p** with Ir^{III}–$SnCl_3$ catalyst in DCE at room temperature after 4 h in absence of any nucleophile, while disproportionation took place smoothly when the reaction was carried out at 80 °C, providing 1,3-diphenyl-1-propene **4b** and chalcone **5b** with excellent yields (Scheme 3). In a separate experiment, when **3b** was treated with Ir^{III}–$SnCl_3$ catalyst in DCE at 80 °C, it disproportionated to **4b** and **5b**. So we can propose that the disproportionation reaction likely goes via ether intermediacy.[7] We were pleased to find that the disproportionation reaction also proceeds smoothly with electron-withdrawing and electron-donating substituents in the phenyl ring (Table 4, entries 1, 3 and 4). For unsymmetric diaryl-substituted allylic alcohols, two reduction isomers **4** and **4′** involving double bond isomerization were obtained along with mixture of isomeric chalcones **5** and **5′** (entries 5–7). However, monoaryl-substituted allylic alcohol, cinnamyl alcohol **1a** resulted in complex reaction mixtures, whereas 4-phenylbut-3-en-2-ol **1n** produced only 30% of di(1-phenyl-1-buten-3-yl) ether **3c** (vide GC) along with other unidentified compounds.

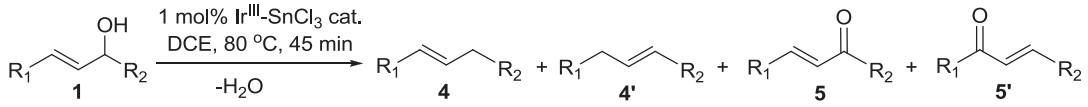


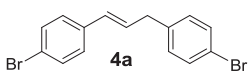
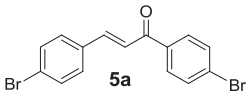
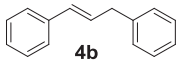
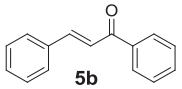
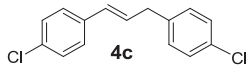
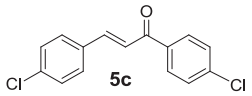
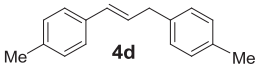
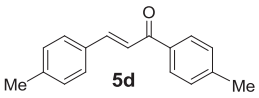
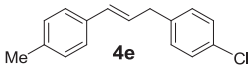
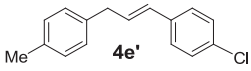
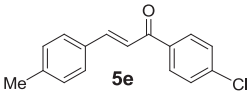
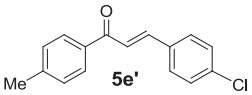
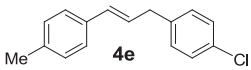
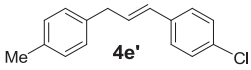
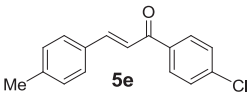
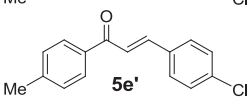
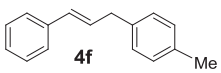
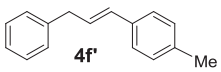
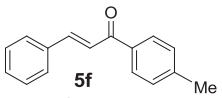
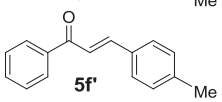
Scheme 2.



Scheme 3.

Table 4
Ir^{III}–$SnCl_3$ catalyzed disproportionation of allylic alcohols[a]

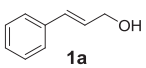
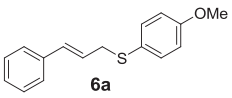
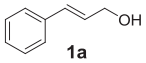
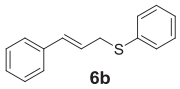
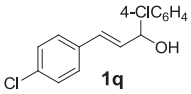
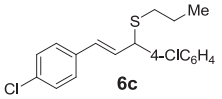
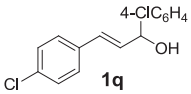
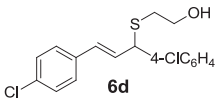
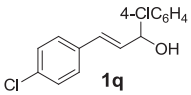
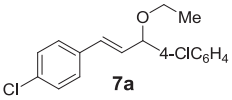
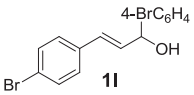
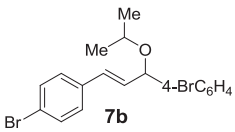
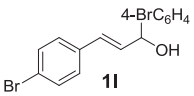
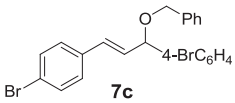
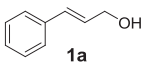
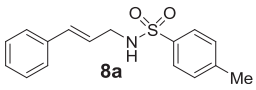
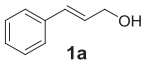
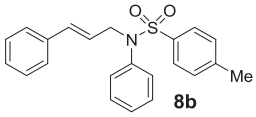
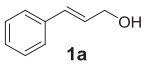
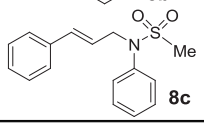


#	**1**, R_1; R_2	Product **4**	Yield[b] (%)	Product **5**	Yield[b] (%)
1	**1l**, 4-BrC_6H_4; 4-BrC_6H_4		46		41
2	**1p**, Ph; Ph		48		44
3	**1q**, 4-ClC_6H_4; 4-ClC_6H_4		43		39
4	**1k**, 4-MeC_6H_4; 4-MeC_6H_4		51		43
5	**1r**, 4-MeC_6H_4; 4-ClC_6H_4	 	47[c]	 	45[d]
6	**1s**, 4-ClC_6H_4; 4-MeC_6H_4	 	46[c]	 	43[e]
7	**1t**, 4-MeC_6H_4; Ph	 	49[c]	 	45[f]
8	**1a**, Ph; H	—	—	—	—
9	**1n**, Ph; Me	—	—	—	—

[a] Unless otherwise mentioned, reaction conditions: alcohol (0.5 mmol), Ir^{III}–$SnCl_3$ cat. (0.005 mmol), DCE (2 mL), 80 °C.
[b] Isolated yield.
[c] Ratio of the isomers could not be determined by NMR.
[d] Ratio of **5e** and **5e′**=1:1.2.
[e] Ratio of **5e** and **5e′**=1:2.
[f] Ratio of **5f** and **5f′**=1.4:1.

To explore the generality of the reaction further, we briefly examined the reaction of allylic alcohols with representative sulfur, oxygen, and nitrogen nucleophiles (Table 5). Usually, sulfur-containing compounds can act as catalyst poisons due to their strong coordinating properties.[19,20] However, we could successfully construct C(sp^3)–S bond by the nucleophilic substitution of allylic alcohol with sulfur nucleophiles, using 1 mol % of Ir^{III}–$SnCl_3$ catalyst. No Friedel–Crafts arylated product was obtained while using 4-methoxythiophenol and thiophenol as nucleophiles, and the allylic sulfide **6a** and **6b** was the only product (entries 1 and 2). Facile reaction of alcohol **1r** with 1-propanethiol resulted in the formation of desired product **6c** (entry 3). Similar reactions of allylic alcohols with ethanol, 2-propanol, and benzyl alcohol as *O*-nucleophile were examined, and the desired ethers **7a**–**c** were obtained in remarkable yields (entries 5–7). The allylic benzylic ether **7c** reduced to **4a** almost quantitatively at 80 °C after 1 h. However, for allylic alkyl ethers, *e.g.*, **7a** and **7b**, no reduction products were observed in the same reaction conditions. Notably, allylation of tethered dinucleophile 2-marcaptoethanol was 100% *S*-selective over competitive O-alkylation (entry 4). The reaction of allylic alcohols with *N*-nucleophiles, such as aniline, *N*,*N*-dimethylaniline, acetamide, piperidine led to the formation of complex mixtures. However, less nucleophilic substrates, such as sulfonamides were amenable for the transformation. Thus, the reactions of alcohol **1a** with various sulfonamide derivatives afforded the corresponding allylated products **8a**–**c** in excellent yields (entries

Table 5
Reaction of allylic alcohols **1** with S-, O-, and N-nucleophiles catalyzed by Ir^{III}–$SnCl_3$ complex[a]

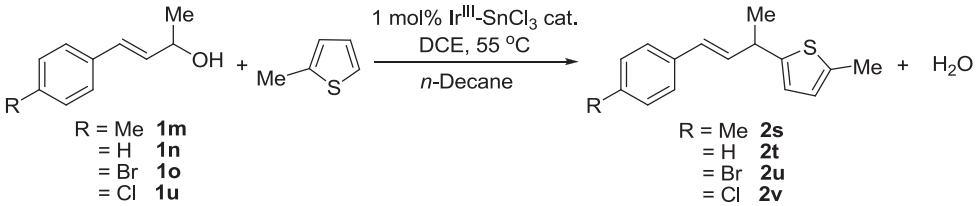
#	Alcohol	Nu-H	Product	Time (min)	Yield[b] (%)
1	 **1a**	4-Methoxythiophenol	 **6a**	40	89
2	 **1a**	Thiophenol	 **6b**	60	80
3	 **1q**	Propanethiol	 **6c**	20	82
4	 **1q**	2-Mercaptoethanol	 **6d**	45	83
5	 **1q**	Ethanol	 **7a**	30	75
6	 **1l**	2-Propanol	 **7b**	30	80
7	 **1l**	Benzyl alcohol	 **7c**	20	82[c]
8	 **1a**	*p*-Toluenesulfonamide	 **8a**	60	75
9	 **1a**	*N*-Tosylaniline	 **8b**	45	84
10	 **1a**	*N*-Mesylaniline	 **8c**	45	81

[a] Unless otherwise mentioned, reaction conditions: alcohol (0.5 mmol), nucleophile (1.5 mmol), Ir^{III}–$SnCl_3$ cat. (0.005 mmol), DCE (2 mL), 80 °C.
[b] Isolated yield.
[c] Temp=50 °C.

8–10). It is worth to be mentioned that, product **8b**,**c** are the intermediates of 3-substituted tetrahydroquinoline derivatives syntheses by halonium ion induced intramolecular cyclization.[21]

Finally, to test the likelihood of electrophilic allylation mechanism, we subjected the reaction to Hammett analysis to determine the reaction constant (ρ value). This was attempted by the kinetic analysis (details in the Supplementary data) using GC for the reaction of 2-methylthiophene with four different *para*-substituted allylic alcohols *p*-R–C_6H_4–CH=CH–CH(Me)OH (R=Me, H, Br, Cl) at 55 °C (Scheme 4). From the plot, Hammett reaction constant ρ was found to be moderately negative (−2.00) (Fig. 2). It indicates the possibility of generation of weak positive charge ($\delta+$) at the allylic carbon of the alcohol due to the coordination of alcoholic OH group to the hard tin center of Ir^{III}–$SnCl_3$ catalyst.[6d]

While further studies are required to arrive at the mechanistic details of the present allylation reaction, a preliminary outline for



Scheme 4. Allylation of 2-methylthiophene with various *para*-substituted allylic alcohols **1**.

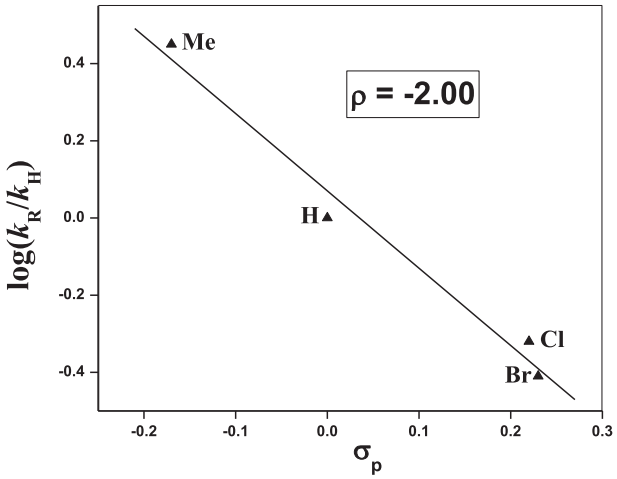
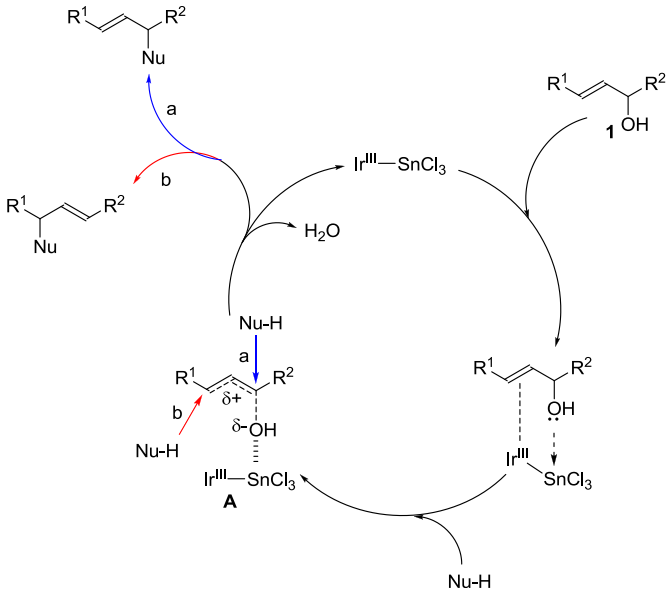


Fig. 2. Hammett plot of log (k_R/k_H) versus σ_p^+ for allylation of 2-methylthiophene with allylic alcohols *p*-R–C_6H_4–CH=CH–CH(Me)OH (R=Me, H, Br, Cl).

the nucleophilic substitution of allylic alcohol using Ir^{III}–$SnCl_3$ bimetallic catalyst is shown in Scheme 5, which is derived mainly from the results of substrate scope, Hammett correlation study and our previous experience with the present catalyst. The proposal invokes prior activation of allylic alcohol **1** via coordination at the hard Lewis acidic tin center of the catalyst, which can act as an ambient electrophile as in intermediate **A**. Attack of a nucleophile on **A** will give rise to the corresponding product with the elimination of water molecule.



Scheme 5. Plausible mechanism of the nucleophilic substitution of allylic alcohol **1**.

3. Conclusions

In summary, we have shown that allylic alcohols can easily be activated by our in-house made heterobimetallic [Ir(μ-Cl)(COD)Cl($SnCl_3$)]$_2$ catalyst, and nucleophilic substitution of allylic alcohols can be achieved with various carbon (arene, heteroarene, allytrimethylsilane, 1,3-dicarbonyl compounds), sulfur (thiol), oxygen (alcohol), nitrogen (sulfonamide), leading to normal allylic substitution products with high regioselectivity. In parallel, the bimetallic catalyst can accelerate the disproportionation of di-aryl substituted allylic alcohols in the absence of any nucleophile. By virtue of their generality, selectivity, and efficiency, the strategies presented here could be a meaningful addition to the existing methods of allylic functionalization.

4. Experimental

4.1. General remarks

^{1}H NMR spectra were recorded at 400 MHz and 200 MHz on Bruker Spectrometers. Chemical shifts are reported in parts per million from tetramethylsilane with the solvent resonance as the internal standard (chloroform-*d*: δ 7.26 ppm). ^{13}C NMR spectra were recorded at 100 MHz and 54.6 MHz with complete proton decoupling. Chemical shifts are reported in ppm from tetramethylsilane with the solvent resonance as the internal standard (chloroform-*d*: δ 77.0 ppm). Elemental analyses were carried out using a CHNS/O Analyzer Perkin–Elmer 2400 Series II instrument.

All reactions were carried out under an argon atmosphere in flame-dried glassware using Schlenk techniques. Chromatographic purifications were done using either 60–120 or 100–200 mesh silica gel. For reaction monitoring, pre-coated silica gel 60 F_{254} TLC sheets were used. Petroleum ether refers to the fraction boiling in the range 60–80 °C. 1,2-Dichloroethane (DCE) was dried and distilled prior to use. $IrCl_3 \cdot xH_2O$, 1,5-cyclooctadiene, and tin tetrachloride were commercially available. [Ir(COD)(μ-Cl)]$_2$ was prepared according to the literature procedure[22] and the heterobimetallic catalysts [Ir(COD)($SnCl_3$)Cl(μ-Cl)]$_2$,[23] [Ir(μ-Br)(COD)Br($SnBr_3$)]$_2$,[23] [Rh(μ-Cl)(COD)Cl($SnCl_3$)]$_2$,[23] [Rh(μ-Br)(COD)Br($SnBr_3$)]$_2$,[23] [IrCl(CO)(PPh_3)$_2$($SnCl_4$)],[24] [Ir(COD)$_2$($SnCl_3$)][25] were prepared according to literature procedure. Allylic alcohols **1a**, **1h–j** were commercially available. Allylic alcohols (**1f**,**g**, **1k–u**), cinnamyl alcohol derivatives (**1c–e**), *N*-tosylaniline and *N*-mesylaniline were also prepared according to literature[26] (see Supplementary data).

4.2. Representative procedure for the allylation of anisole with cinnamyl alcohol 1a catalyzed by [Ir(μ-Cl)(COD)Cl($SnCl_3$)]$_2$

A 10 mL Schlenk flask equipped with a magnetic bar was charged with [Ir(μ-Cl)(COD)Cl($SnCl_3$)]$_2$ (0.005 mmol), anisole (1.5 mmol), cinnamyl alcohol **1a** (0.5 mmol), and 1,2-dichloroethane (2 mL). The flask was degassed, flushed with argon and placed in a constant temperature bath at 80 °C. The reaction was allowed to continue at 80 °C, and monitored by TLC. After completion, solvent was removed under reduced pressure and the mixture was subjected to column chromatography over silica gel (eluent: gradient mixture of EtOAc/pet. ether) to afford the allylic product **2a** in 95% isolated yield.

4.3. Representative procedure for the disproportionation of allylic alcohol 1p catalyzed by [Ir(μ-Cl)(COD)Cl($SnCl_3$)]$_2$

A 10 mL Schlenk flask equipped with a magnetic bar was charged with [Ir(μ-Cl)(COD)Cl($SnCl_3$)]$_2$ (0.005 mmol), allylic alcohol **1p** (0.5 mmol), and 1,2-dichloroethane (2 mL). The flask was degassed, flushed with argon and placed in a constant temperature bath at 80 °C. The reaction was allowed to continue at 80 °C, and monitored by TLC. After completion, solvent was removed under reduced pressure and the mixture was subjected to column chromatography over silica gel (eluent: gradient mixture of EtOAc/pet. ether) to afford the alkene **4b** and chalcone **5b** in 48% and 44% isolated yield, respectively.

4.4. Spectral and analytical data of products

The spectral data of the compounds **2a**,[27] **2c**,[28] **2f**,[29] **2f′**,[29] **2g**,[30] **2h**,[9b] **2h′**,[9b] **2i**,[9b] **2j**,[16i] **2n**,[31] **2r**,[15c] **3a**,[6e] **3b**,[32] **3c**,[33] **4a**,[34] **4b**,[7] **4c**,[7]

4d,[7] **4e**,[7] **4e′**,[7] **4f**,[7] **4f′**,[7] **6a**,[9d] **6b**,[9d] **8a**,[35] **8b**,[21a] **8c**[21a] were in excellent agreement with those in the literature. The spectral data for the products **2b**, **2d**,**e**, **2k**, **2k′**, **2l**, **2m**, **2m′**, **2o**–**q**, **2s**–**v**, **6c**,**d**, **7a**–**c** are shown below.

*4.4.1. 1-Cinnamyl-4-methylnaphthalene (**2b**).* ^{1}H NMR ($CDCl_3$, 200 MHz): δ ppm 2.62 (s, 3H), 3.89 (d, 2H, *J*=4.4 Hz), 6.40–6.43 (m, 2H), 7.09–7.23 (m, 7H), 7.43–7.48 (m, 2H), 7.94–8.05 (m, 2H). ^{13}C NMR ($CDCl_3$, 54.6 MHz): δ ppm 19.5, 36.5, 124.6, 124.8, 125.5, 125.6, 126.2, 126.4, 127.1, 128.5, 129.2, 131.2, 132.1, 133.0, 133.1, 134.4, 137.6. CHN: Anal. Calcd. for ($C_{20}H_{18}$), C: 92.98, H: 7.02; found, C: 93.12, H: 6.91.

*4.4.2. (E)-1,3,5-Trimethoxy-2-(3-(4-methoxyphenyl)allyl)benzene (**2d**).* ^{1}H NMR ($CDCl_3$, 200 MHz): δ ppm 3.44 (d, 2H, *J*=5.8 Hz), 3.77 (s, 3H), 3.81 (s, 9H), 6.05–6.21 (m, 3H), 6.29 (d, 1H, *J*=16.0 Hz), 6.78 (d, 2H, *J*=8.4 Hz), 7.29 (d, 2H, *J*=8.4 Hz). ^{13}C NMR ($CDCl_3$, 54.6 MHz): δ ppm 26.1, 55.2, 55.3, 55.8, 90.8, 109.3, 113.7, 127.1, 127.3, 128.5, 131.1, 158.4, 158.8, 159.5. CHN: Anal. Calcd. for ($C_{19}H_{22}O_4$), C: 72.59, H: 7.05; found, C: 72.75, H: 7.18.

*4.4.3. (E)-1,3,5-Trimethoxy-2-(3-(4-nitrophenyl)allyl)benzene (**2e**).* ^{1}H NMR ($CDCl_3$, 200 MHz): δ ppm 3.52 (d, 2H, *J*=6.0 Hz), 3.82 (s, 9H), 6.17 (s, 2H), 6.33–6.60 (m, 2H), 7.41 (d, 2H, *J*=8.8 Hz), 8.09 (d, 2H, *J*=8.8 Hz). ^{13}C NMR ($CDCl_3$, 54.6 MHz): δ ppm 26.3, 55.4, 55.8, 90.7, 107.8, 123.8, 126.4, 127.5, 135.2, 144.9, 146.2, 158.8, 159.9. CHN: Anal. Calcd. for ($C_{18}H_{19}NO_5$), C: 65.64, H: 5.81, N: 4.25; found, C: 65.11, H: 6.15, N: 4.55.

*4.4.4. (E)-3-1,3-Di(p-tolyl)allyl-1H-indole (**2k**).* ^{1}H NMR ($CDCl_3$, 200 MHz): δ ppm 2.39 (s, 3H), 2.41 (s, 3H), 5.14 (d, 1H, *J*=7.0 Hz), 6.48 (d, 1H, *J*=15.8 Hz), 6.69–6.80 (dd, 1H, *J*=7.2, 15.8 Hz), 6.90 (s, 1H), 7.06–7.39 (m, 1H), 7.52 (d, 1H, *J*=8.0 Hz), 7.88 (b, 1H). ^{13}C NMR ($CDCl_3$, 54.6 MHz): δ ppm 21.3, 21.4, 46.1, 111.4, 119.2, 119.6, 120.2, 122.3, 122.8, 126.5, 127.1, 128.6, 129.4, 129.5, 130.5, 132.1, 135.1, 136.1, 136.9, 137.1, 140.8. CHN: Anal. Calcd. for ($C_{25}H_{23}N$), C: 88.98, H: 6.87, N: 4.15; found, C: 89.09, H: 6.51, N: 4.40.

*4.4.5. 1,3-Bis((E)-1,3-di(p-tolyl)allyl)-1H-indole (**2k′**).* ^{1}H NMR ($CDCl_3$, 200 MHz): δ ppm 2.31 (s, 6H), 2.33 (s, 3H), 5.08 (d, 1H, *J*=7.4 Hz), 6.19 (d, 1H, *J*=6.6 Hz), 6.39 (d, 2H, *J*=15.8 Hz), 6.58–6.72 (m, 2H), 6.95–7.02 (m, 3H), 7.07–7.11 (m, 9H), 7.19–7.28 (m, 8H), 7.43 (d, 1H, *J*=7.8 Hz). ^{13}C NMR ($CDCl_3$, 54.6 MHz): δ ppm 21.1, 21.2, 46.0, 61.7, 110.3, 117.7, 119.2, 120.2, 121.6, 124.6, 126.3, 126.6, 126.8, 127.6, 128.3, 129.0, 129.1, 129.3, 129.4, 130.1, 131.9, 133.4, 134.8, 135.6, 136.9, 137.5, 137.9, 140.7. CHN: Anal. Calcd. for ($C_{42}H_{39}N$), C: 90.44, H: 7.05, N: 2.51; found, C: 90.23, H: 6.93, N: 2.84.

*4.4.6. (E)-4,4′-(Hexa-1,5-diene-1,3-diyl)bis(bromobenzene) (**2l**).* ^{1}H NMR ($CDCl_3$, 200 MHz): δ ppm 2.47–2.55 (m, 2H), 3.39–3.50 (m, 1H), 4.95–5.05 (m, 2H), 5.58–5.78 (m, 1H), 7.08 (d, 2H, *J*=8.4 Hz), 7.15 (d, 2H, *J*=8.2 Hz), 7.37 (d, 2H, *J*=8.2 Hz), 7.41 (d, 2H, *J*=8.0 Hz). ^{13}C NMR ($CDCl_3$, 54.6 MHz): δ ppm 39.9, 48.3, 116.9, 120.3, 121.1, 127.8, 129.1, 129.6, 131.7, 133.7, 135.9, 136.2, 142.5. CHN: Anal. Calcd. for ($C_{18}H_{16}Br_2$), C: 55.13, H: 4.11; found, C: 55.49, H: 4.06.

*4.4.7. (E)-1-Methyl-4-(3-methylhexa-1,5-dienyl)benzene(**2m**) and 1-(hepta-1,5-dien-4-yl)-4-methylbenzene (**2m′**).* ^{1}H NMR ($CDCl_3$, 400 MHz): δ ppm 1.13 (d, 3H, *J*=6.8 Hz), 1.69 (d, 3H, *J*=6.4 Hz), 2.12–2.27 (m, 2H), 2.36 (s, 3H), 2.36 (s, 3H), 2.39–2.49 (m, 1H), 2.39–2.49 (m, 2H), 3.27–3.33 (m, 1H), 4.97–5.09 (m, 2H), 4.97–5.09 (m, 2H), 5.44–5.51 (m, 1H), 5.59–5.64 (m, 1H), 5.71–5.90 (m, 1H), 5.71–5.90 (m, 1H), 6.11–6.16 (m, 2H, *J*=7.6, 16.0 Hz), 6.37 (d, 2H, *J*=16.0 Hz), 7.11–7.15 (m, 2H), 7.11–7.15 (m, 4H), 7.29 (d, 2H, *J*=8.0 Hz). ^{13}C NMR ($CDCl_3$, 54.6 MHz): δ ppm 17.9, 20.0, 21.0, 21.1, 36.9, 40.4, 41.5, 48.4, 115.8, 115.9, 124.8, 125.9, 127.5, 128.1, 129.1, 129.2, 134.8, 135.1, 135.5, 136.6, 137.1, 141.7. CHN: Anal. Calcd. for ($C_{14}H_{18}$), C: 90.26, H: 9.74; found, C: 90.81, H: 9.32.

*4.4.8. (E)-4-Hydroxy-3-(4-phenylbut-3-en-2-yl)-2H-chromen-2-one (**2o**).* ^{1}H NMR ($CDCl_3$, 200 MHz): δ ppm 1.51 (d, 3H, *J*=7.0 Hz), 4.17–4.22 (m, 1H), 6.61–6.71 (m, 1H), 6.78 (d, 1H, *J*=16.0 Hz), 7.19–7.55 (m, 8H), 7.77 (d, 1H, *J*=7.8 Hz). ^{13}C NMR ($CDCl_3$, 54.6 MHz): δ ppm 16.5, 32.7, 107.7, 116.0, 116.4, 122.9, 123.9, 126.4, 128.1, 128.7, 131.6, 131.7, 131.9, 135.9, 152.5, 160.7, 163.3. CHN: Anal. Calcd. for ($C_{19}H_{16}O_3$), C: 78.06, H: 5.52; found, C: 77.91, H: 5.63.

*4.4.9. (E)-2-(4-(4-Bromophenyl)but-3-en-2-yl)-1,3-diphenylpropane-1,3-dione (**2p**).* ^{1}H NMR ($CDCl_3$, 200 MHz): δ ppm 1.23 (d, 3H, *J*=6.8 Hz), 3.51–3.70 (m, 1H), 5.35 (d, 1H, *J*=8.0 Hz), 6.06–6.17 (dd, 1H, *J*=8.0, 16.0 Hz), 6.31 (d, 1H, *J*=16.0 Hz), 6.98 (d, 2H, *J*=8.4 Hz), 7.29–7.59 (m, 8H), 7.93–8.03 (m, 4H). ^{13}C NMR ($CDCl_3$, 54.6 MHz): δ ppm 18.9, 38.6, 62.9, 120.9, 127.7, 128.7, 128.9, 129.4, 131.4, 133.2, 133.4, 133.6, 136.1, 136.9, 194.8, 195.1. CHN: Anal. Calcd. for ($C_{25}H_{21}BrO_2$), C: 69.29, H: 4.88; found, C: 69.41, H: 5.10.

*4.4.10. (E)-3-(1,3-Bis(4-bromophenyl)allyl)pentane-2,4-dione (**2q**).* ^{1}H NMR ($CDCl_3$, 200 MHz): δ ppm 1.96 (s, 3H), 2.24 (s, 3H), 4.29 (m, 2H), 6.07–6.18 (m, 1H), 6.34 (d, 1H, *J*=15.8 Hz), 7.10–7.16 (m, 4H), 7.37–7.48 (m, 4H). ^{13}C NMR ($CDCl_3$, 54.6 MHz): δ ppm 29.7, 30.0, 48.3, 74.2, 121.3, 121.7, 127.9, 129.4, 129.7, 131.0, 131.7, 132.2, 135.3, 138.9, 202.1, 202.3. CHN: Anal. Calcd. for ($C_{20}H_{18}Br_2O_2$), C: 53.36, H: 4.03; found, C: 53.71, H: 4.23.

*4.4.11. (E)-2-Methyl-5-(4-p-tolylbut-3-en-2-yl)thiophene (**2s**).* ^{1}H NMR ($CDCl_3$, 200 MHz): δ ppm 1.54 (d, 3H, *J*=6.8 Hz), 2.38 (s, 3H), 2.49 (s, 3H), 3.77–3.91 (m, 1H), 6.25–6.37 (dd, 1H, *J*=7.2, 15.8 Hz), 6.48 (d, 1H, *J*=15.8 Hz), 6.59–6.69 (m, 2H), 7.15 (d, 2H, *J*=8.0 Hz), 7.32 (d, 2H, *J*=8.0 Hz). ^{13}C NMR ($CDCl_3$, 54.6 MHz): δ ppm 15.5, 21.4, 22.4, 38.7, 122.9, 124.9, 126.4, 128.9, 129.4, 133.8, 134.8, 137.1, 137.9, 147.8. CHN: Anal. Calcd. for ($C_{16}H_{18}S$), C: 79.29, H: 7.49; found, C: 79.10, H: 7.62.

*4.4.12. (E)-2-Methyl-5-(4-phenylbut-3-en-2-yl)thiophene (**2t**).* ^{1}H NMR ($CDCl_3$, 200 MHz): δ ppm 1.55 (d, 3H, *J*=7.0 Hz), 2.49 (s, 3H), 3.79–3.93 (m, 1H), 6.31–6.42 (dd, 1H, *J*=6.8, 15.8 Hz), 6.52 (d, 1H, *J*=15.8 Hz), 6.57–6.70 (m, 2H), 7.22–7.45 (m, 5H). ^{13}C NMR ($CDCl_3$, 54.6 MHz): δ ppm 15.4, 22.1, 38.5, 122.8, 124.7, 126.3, 127.3, 128.5, 128.9, 134.7, 137.4, 137.8, 147.4. CHN: Anal. Calcd. for ($C_{15}H_{16}S$), C: 78.90, H: 7.06; found, C: 79.06, H: 7.11.

*4.4.13. (E)-2-(4-(4-Bromophenyl)but-3-en-2-yl)-5-methylthiophene (**2u**).* ^{1}H NMR ($CDCl_3$, 200 MHz): δ ppm 1.52 (d, 3H, *J*=6.8 Hz), 2.47 (s, 3H), 3.76–3.89 (m, 1H), 6.27–6.38 (dd, 1H, *J*=6.2, 15.8 Hz), 6.42 (d, 1H, *J*=15.8 Hz), 6.63–6.67 (m, 2H), 7.25 (d, 2H, *J*=8.4 Hz), 7.44 (d, 2H, *J*=8.4 Hz). ^{13}C NMR ($CDCl_3$, 54.6 MHz): δ ppm 15.4, 22.1, 38.5, 121.0, 122.9, 124.8, 127.8, 127.9, 131.7, 135.6, 136.4, 138.0, 147.1. CHN: Anal. Calcd. for ($C_{15}H_{15}BrS$), C: 58.64, H: 4.92; found, C: 58.77, H: 5.10.

*4.4.14. (E)-2-(4-(4-Chlorophenyl)but-3-en-2-yl)-5-methylthiophene (**2v**).* ^{1}H NMR ($CDCl_3$, 200 MHz): δ ppm 1.53 (d, 3H, *J*=7.0 Hz), 2.47 (s, 3H), 3.76–3.89 (m, 1H), 6.26–6.37 (dd, 1H, *J*=6.6, 15.8 Hz), 6.44 (d, 1H, *J*=15.8 Hz), 6.61–6.67 (m, 2H), 7.19–7.30 (m, 4H). ^{13}C NMR ($CDCl_3$, 54.6 MHz): δ ppm 15.4, 22.0, 38.4, 122.9, 124.8, 127.5, 127.7, 128.7, 132.8, 135.4, 135.9, 137.9, 147.1. CHN: Anal. Calcd. for ($C_{15}H_{15}ClS$), C: 68.55, H: 5.75; found, C: 68.69, H: 5.86.

*4.4.15. (E)-(1,3-Bis(4-chlorophenyl)allyl)(propyl)sulfane(**6c**).* ^{1}H NMR ($CDCl_3$, 200 MHz): δ ppm 0.98 (t, 3H, *J*=7.2 Hz), 1.53–1.71 (m, 2H), 2.45 (t, 2H, *J*=7.8 Hz), 4.57 (d, 1H, *J*=7.6 Hz), 6.26–6.37 (dd, 1H, *J*=7.6, 15.8 Hz), 6.44 (d, 1H, *J*=15.8 Hz), 7.19–7.39 (m, 8H). ^{13}C NMR ($CDCl_3$, 54.6 MHz): δ ppm 13.6, 22.7, 33.8, 51.5, 127.7, 128.8, 128.9,

129.2, 129.9, 130.1, 133.1, 133.4, 135.0, 139.2. DEPT 135: δ ppm 13.6, 22.7, 33.8, 51.5, 127.7, 128.8, 128.9, 129.2, 129.9, 130.1. CHN: Anal. Calcd. for ($C_{18}H_{18}Cl_2S$), C: 64.09, H: 5.38; found, C: 64.53, H: 5.11.

*4.4.16. (E)-2-(1,3-Bis(4-chlorophenyl)allylthio)ethanol (**6d**).* ^{1}H NMR ($CDCl_3$, 200 MHz): δ ppm 2.32 (s, 1H), 2.58–2.76 (m, 2H), 3.72 (t, 2H, J=6.0 Hz), 4.63 (d, 1H, J=8.0 Hz), 6.24–6.35 (dd, 1H, J=8.0, 15.8 Hz), 6.44 (d, 1H, J=15.8 Hz), 7.23–7.38 (m, 8H). ^{13}C NMR ($CDCl_3$, 54.6 MHz): δ ppm 34.7, 51.3, 60.9, 127.8, 128.8, 129.0, 129.2, 129.5, 130.5, 133.4, 133.6, 134.7, 138.7. DEPT 135: δ ppm 34.7, 51.3, 60.9, 127.8, 128.8, 129.0, 129.2, 129.5, 130.5. CHN: Anal. Calcd. for ($C_{17}H_{16}Cl_2OS$), C: 60.18, H: 4.75; found, C: 60.02, H: 4.86.

*4.4.17. (E)-4,4′-(3-Ethoxyprop-1-ene-1,3-diyl)bis(chlorobenzene) (**7a**).* ^{1}H NMR ($CDCl_3$, 200 MHz): δ ppm 1.27 (t, 3H, J=7.2 Hz), 3.52 (q, 2H, J=7.2 Hz), 4.89 (d, 1H, J=6.8 Hz), 6.18–6.29 (dd, 1H, J=6.8, 15.8 Hz), 6.56 (d, 1H, J=15.8 Hz), 7.12–7.45 (m, 8H). ^{13}C NMR ($CDCl_3$, 54.6 MHz): δ ppm 15.4, 64.2, 81.7, 127.8, 128.2, 128.7, 130.2, 130.9, 133.5, 135.0, 139.9. DEPT 135: δ ppm 15.4, 64.2, 81.7, 127.8, 128.2, 128.7, 130.2, 130.9. CHN: Anal. Calcd. for ($C_{17}H_{16}Cl_2O$), C: 66.46, H: 5.25; found, C: 66.59, H: 5.38.

*4.4.18. (E)-4,4′-(3-Isopropoxyprop-1-ene-1,3-diyl)bis(-bromobenzene) (**7b**).* ^{1}H NMR ($CDCl_3$, 200 MHz): δ ppm 1.15 (d, 3H, J=6.2 Hz), 1.20 (d, 3H, J=6.2 Hz), 3.60–3.72 (m, 1H), 4.96 (d, 1H, J=6.6 Hz), 6.15–6.26 (dd, 1H, J=6.6, 15.8 Hz), 6.47 (d, 1H, J=15.8 Hz), 7.19 (d, 2H, J=8.6 Hz), 7.24 (d, 2H, J=8.2 Hz), 7.38 (d, 2H, J=8.6 Hz), 7.46 (d, 2H, J=8.2 Hz). ^{13}C NMR ($CDCl_3$, 54.6 MHz): δ ppm 22.2, 22.5, 69.1, 78.7, 121.4, 121.5, 128.1, 128.6, 129.8, 131.6, 135.5, 140.8. CHN: Anal. Calcd. for ($C_{18}H_{18}Br_2O$), C: 52.17, H: 4.42; found, C: 52.85, H: 4.20.

*4.4.19. (E)-4,4′-(3-(Benzyloxy)prop-1-ene-1,3-diyl)bis(-bromobenzene) (**7c**).* ^{1}H NMR ($CDCl_3$, 200 MHz): δ ppm 4.58 (s, 2H), 4.98 (d, 1H, J=6.6 Hz), 6.24–6.35 (dd, 1H, J=6.6, 15.8 Hz), 6.58 (d, 1H, J=15.8 Hz), 7.23–7.56 (m, 13H). ^{13}C NMR ($CDCl_3$, 54.6 MHz): δ ppm 70.4, 80.8, 121.8, 127.8, 128.2, 128.5, 128.7, 130.6, 131.8, 135.4, 138.1, 139.9. DEPT 135: δ ppm 70.4, 80.8, 127.8, 128.2, 128.5, 128.7, 130.6, 131.8. CHN: Anal. Calcd. for ($C_{22}H_{18}Br_2O$), C: 57.67, H: 3.96; found, C: 57.41, H: 4.02.

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Supplementary data

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References and notes

1. Süss-Fink, G.; Meister, G. *Adv. Organomet. Chem.* **1993**, *35*, 41; In *Metal Clusters in Catalysis*; Gates, B. C., Guzci, L., Knözinger, V. H., Eds.; Elsevier: Amsterdam, 1993–.
2. Rowlands, G. J. *Tetrahedron* **2001**, *57*, 1865.
3. Ma, J.-A.; Cahard, D. *Angew. Chem., Int. Ed.* **2004**, *43*, 4566.
4. (a) Sinha, P.; Roy, S. *Organometallics* **2004**, *23*, 67; (b) Banerjee, M.; Roy, S. *Org. Lett.* **2004**, *6*, 2137; (c) Banerjee, M.; Roy, S. *J. Mol. Catal. A: Chem.* **2006**, *246*, 231.
5. (a) Shibasaki, M. In *Stimulating Concepts in Chemistry*; Vögtle, F., Stoddart, J. F., Shibasaki, M., Eds.; Wiley-VCH: Weinheim, Germany, 2000; pp 105–121; (b) Shibasaki, M.; Yoshikawa, N. *Chem. Rev.* **2002**, *102*, 2187; (c) van den Beuken, E. K.; Feringa, B. L. *Tetrahedron* **1998**, *54*, 12985; (d) Yamagiwa, N.; Matsunaga, S.; Shibasaki, M. *J. Am. Chem. Soc.* **2003**, *125*, 16178; (e) Sammis, G. M.; Danjo, H.; Jacobsen, E. N. *J. Am. Chem. Soc.* **2004**, *126*, 9928.
6. (a) Choudhury, J.; Podder, S.; Roy, S. *J. Am. Chem. Soc.* **2005**, *127*, 6162; (b) Choudhury, J.; Roy, S. *J. Mol. Catal. A: Chem.* **2008**, *279*, 37; (c) Podder, S.; Choudhury, J.; Roy, S. *J. Org. Chem.* **2007**, *72*, 3129; (d) Chatterjee, P. N.; Roy, S. *J. Org. Chem.* **2010**, *75*, 4413; (e) Podder, S.; Roy, S. *Tetrahedron* **2007**, *63*, 9146; (f) Podder, S.; Choudhury, J.; Roy, S. *J. Org. Chem.* **2007**, *72*, 3100; (g) Roy, U. K.; Roy, S. *Chem. Rev.* **2010**, *110*, 2472 and references therein.
7. Wang, J.; Huang, W.; Zhang, Z.; Xiang, X.; Liu, R.; Zhou, X. *J. Org. Chem.* **2009**, *74*, 3299.
8. Fitzpatrick, P. F.; Flory, D. R., Jr.; Villafranca, J. J. *Biochemistry* **1985**, *24*, 2108.
9. (a) Nishibayashi, Y.; Yamanashi, M.; Takagi, Y.; Hidai, M. *Chem. Commun.* **1997**, 859; (b) Onodera, G.; Imajima, H.; Yamanashi, M.; Nishibayashi, Y.; Hidai, M.; Uemura, S. *Organometallics* **2004**, *23*, 5841; (c) Hubert, C.; Renaud, J.; Demerseman, B.; Fischmeister, C.; Bruneau, C. *J. Mol. Catal. A: Chem.* **2005**, *237*, 161; (d) Zaitsev, A. B.; Caldwell, H. F.; Pregosin, P. S.; Veiros, L. F. *Chem.—Eur. J.* **2009**, *15*, 6468.
10. (a) Polet, D.; Rathgeb, X.; Faiciola, C. A.; Langlois, J.; Hajjajji, S. E.; Alexakis, A. *Chem.—Eur. J.* **2009**, *15*, 1205; (b) Xu, Q.; Liu, W.; Dai, L.; You, S. *J. Org. Chem.* **2010**, *75*, 4615 and the references therein.
11. Yatsumonji, Y.; Ishida, Y.; Tsubouchi, A.; Takeda, T. *Org. Lett.* **2007**, *9*, 4603.
12. Yang, H.; Fang, L.; Zhang, M.; Zhhu, C. *Eur. J. Org. Chem.* **2009**, 666.
13. (a) Ozawa, F.; Okamoto, H.; Kawagishi, S.; Yamamoto, S.; Minami, T.; Yoshifuji, M. *J. Am. Chem. Soc.* **2002**, *124*, 10968; (b) Manabe, K.; Kobayashi, S. *Org. Lett.* **2003**, *5*, 3241; (c) Kayaki, Y.; Koda, T.; Ikariya, T. *J. Org. Chem.* **2004**, *69*, 2595; (d) Tsukamoto, H.; Sato, M.; Kondo, Y. *Chem. Commun.* **2004**, 1200; (e) Kimura, M.; Futamata, M.; Mukai, R.; Tamaru, Y. *J. Am. Chem. Soc.* **2005**, *127*, 4592; (f) Yang, S.-C.; Hsu, Y.-C.; Gan, K.-H. *Tetrahedron* **2006**, *62*, 3949; (g) Usui, I.; Schmidt, S.; Keller, M.; Breit, B. *Org. Lett.* **2008**, *10*, 1207; (h) Gan, K.-H.; Jhong, C.-J.; Yang, S.-C. *Tetrahedron* **2008**, *64*, 1204; (i) Usui, I.; Schmidt, S.; Breit, B. *Org. Lett.* **2009**, *11*, 1453.
14. Yadav, J. S.; Reddy, B. V. S.; Rao, T. S.; Rao, K. V. R. *Tetrahedron Lett.* **2008**, *49*, 614.
15. A few selected recent references: Ag-catalyst: (a) Bandini, M.; Eichholzer, A.; Kotrusz, P.; Tragni, M.; Troisi, S.; Umani-Ronchi, A. *Adv. Synth. Catal.* **2009**, *351*, 319 Au-catalyzed; (b) Guo, S.; Song, F.; Liu, Y. *Synlett* **2007**, 964; (c) Rao, W.; Chan, P. W. H. *Org. Biomol. Chem.* **2008**, *6*, 2426 In-catalyzed; (d) Yasuda, M.; Somyo, T.; Baba, A. *Angew. Chem., Int. Ed.* **2006**, *45*, 793; (e) Krishna, P. R.; Sekhar, E. R.; Prapurna, Y. L. *Tetrahedron Lett.* **2007**, *48*, 9048; (f) Yadav, J. S.; Reddy, B. V. S.; Aravind, S.; Kumar, G. G. K. S. N.; Reddy, A. S. *Tetrahedron Lett.* **2007**, *48*, 6117 Fe-catalyzed; (g) Jana, U.; Maiti, S.; Biswas, S. *Tetrahedron Lett.* **2007**, *48*, 7160; (h) Jana, U.; Maiti, S.; Biswas, S. *Tetrahedron Lett.* **2007**, *48*, 4065 $Sc(OTf)_3$-catalyzed; (i) Tsuchimoto, T.; Tobita, K.; Hiyama, T.; Fukuzawa, S. *J. Org. Chem.* **1997**, *62*, 6997 $Yb(OTf)_3$-catalyzed; (j) Huang, W.; Wang, J.; Shen, Q.; Zhou, X. *Tetrahedron Lett.* **2007**, *48*, 3969; (k) Huang, W.; Wang, J.; Shen, Q.; Zhou, X. *Tetrahedron* **2007**, *63*, 11636 $Bi(OTf)_3$-catalyzed; (l) Qin, H.; Yamagiwa, N.; Matsunaga, S.; Shibasaki, M. *Angew. Chem., Int. Ed.* **2007**, *46*, 409; (m) Rueping, M.; Nachtsheim, B. J.; Kuenkel, A. *Org. Lett.* **2007**, *9*, 825 Other metal triflates-catalyzed; (n) Noji, M.; Konno, Y.; Ishii, K. *J. Org. Chem.* **2007**, *72*, 5161.
16. A few selected recent references: Brønsted acid-catalyzed: (a) Espeel, P. H.; Janssens, B.; Jacobs, P. A. *J. Org. Chem.* **1993**, *58*, 7688; (b) Smith, K.; Pollaud, G. M. *J. Chem. Soc., Perkin Trans. 1* **1994**, 3519; (c) Smith, K.; Pollaud, G. M.; Matthews, I. *Green Chem.* **1999**, 75; (d) Kaur, G.; Kaushik, M.; Trehan, S. *Tetrahedron Lett.* **1997**, *38*, 2521; (e) Motokura, K.; Fujita, N.; Mori, K.; Mizugaki, T.; Ebitani, K.; Kaneda, K. *Angew. Chem., Int. Ed.* **2006**, *45*, 2605; (f) Liu, P. N.; Zhou, Z. Y.; Lau, C. P. *Chem.—Eur. J.* **2007**, *13*, 8610; (g) Shirakawa, S.; Kobayashi, S. *Org. Lett.* **2007**, *9*, 311; (h) Motokura, K.; Nakagiri, N.; Mizugaki, T.; Ebitani, K.; Kaneda, K. *J. Org. Chem.* **2007**, *72*, 6006; (i) Bras, J. L.; Muzart, J. *Tetrahedron* **2007**, *63*, 7942; (j) Wang, G.; Shen, Y.; Wu, X. *Eur. J. Org. Chem.* **2008**, 4367; (k) Reddy, C. R.; Srikanth, B.; Rao, N. N.; Shin, D. *Tetrahedron* **2008**, *64*, 11666; (l) Yadav, J. S.; Reddy, B. V. S.; Pandurangam, T.; Rao, K. V. R.; Praneeth, K.; Kumar, G. G. K. S. N.; Madavi, C.; Kunwar, A. C. *Tetrahedron Lett.* **2008**, *49*, 4296 A recent review on Brønsted or Lewis acids catalyzed direct substitution of allylic, benzylic and propargylic alcohol; (m) Emer, E.; Sinisi, R.; Capdevila, M. G.; Petruzziello, D.; Vincentiis, F. D.; Cozzi, P. G. *Eur. J. Org. Chem.* **2011**, 647.
17. A few selected recent references: molecular iodine-catalyzed: (a) Yadav, J. S.; Reddy, B. V. S.; Rao, K. V.; Raj, K. S.; Rao, P. P.; Prasad, A. R.; Gunasekar, D. *Tetrahedron Lett.* **2004**, *45*, 6505; (b) Liu, Z.; Liu, L.; Shafiq, Z.; Wu, Y.; Wang, D.; Chen, Y. *Tetrahedron Lett.* **2007**, *48*, 3963; (c) Rao, W.; Tay, A. H. L.; Goh, P. J.; Choy, J. M. L.; Ke, J. K.; Chan, P. W. H. *Tetrahedron Lett.* **2008**, *49*, 122; (d) Lin, X.; Dai, X.; Mao, Z.; Wang, Y. *Tetrahedron* **2009**, *65*, 9233.
18. Staunton, J. In *Comprehensive Organic Chemistry*; Sammes, P. G., Ed.; Pergamon: Oxford, 1979; Vol. 4.
19. Inada, Y.; Nishibayashi, Y.; Hidai, M.; Uemura, S. *J. Am. Chem. Soc.* **2002**, *124*, 15172.
20. Hegedus, L. L.; McCabe, R. W. *Catalyst Poisoning*; Marcel Dekker: New York, NY, 1984.
21. 3-halo-tetrahydroquinoline synthesis via halonium ion intermediate: A few recent references: (a) Barluenga, J.; Tricado, M.; Rubio, E.; González, J. M. *J. Am. Chem. Soc.* **2004**, *126*, 3416; (b) Hajra, S.; Maji, B.; Karmakar, A. *Tetrahedron Lett.* **2005**, *46*, 8599 and the references therein.
22. Walter, R.; Kirchner, S.; Franz, R. U.S. Patent 6,399,804, 2002.
23. Choudhury, J.; Krishna Kumar, D.; Roy, S. *J. Organomet. Chem.* **2007**, *692*, 5614.
24. Dammanna, C. B.; Hughey, J. L., IV; Jicha, D. C.; Meyer, T. J.; Rakita, P. E.; Weaver, T. R. *Inorg. Chem.* **1973**, *12*, 2206.
25. Young, J. F.; Gillard, R. D.; Wilkinson, G. *J. Chem. Soc.* **1964**, 5176.
26. Kamal, A.; Reddy, J. S.; Bharathi, E. V.; Dastagiri, D. *Tetrahedron Lett.* **2008**, *49*, 348.
27. Yamaguchi, J.; Takagi, Y.; Nakayama, A.; Fujiwara, T.; Takeda, T. *Chem. Lett.* **1991**, *20*, 133.
28. Yamamoto, Y.; Itonaga, K. *Chem.—Eur. J.* **2008**, *14*, 10705.
29. Butsugan, Y.; Nagai, K.; Nagaya, F.; Tabuchi, H.; Yamada, K.; Araki, S. *Bull. Chem. Soc. Jpn.* **1988**, *61*, 1707.
30. Borgulya, J.; Hansen, H. J.; Barner, R.; Schmid, H. *Helv. Chim. Acta* **1963**, *46*, 2444.
31. Kothandaraman, P.; Rao, W.; Zhang, X.; Chan, P. W. H. *Tetrahedron* **2009**, *65*, 1833.
32. Evans, P.; Johnson, P.; Taylor, R. J. K. *Eur. J. Org. Chem.* **2006**, 1740.
33. Malkov, A. V.; Spoor, P.; Vinader, V.; Kočovský, P. *J. Org. Chem.* **1999**, *64*, 5308.
34. Mo, H.; Bao, W. *J. Org. Chem.* **2010**, *75*, 4856.
35. Ghorai, M. K.; Kumar, A.; Tiwari, D. P. *J. Org. Chem.* **2010**, *75*, 137.