Tetrahedron 69 (2013) 942–956

Contents lists available at SciVerse ScienceDirect

Tetrahedron

journal homepage: www.elsevier.com/locate/tet

Multimetallic Ir–Sn_3-catalyzed substitution reaction of π-activated alcohols with carbon and heteroatom nucleophiles

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ARTICLE INFO

Article history:
Received 27 August 2012
Received in revised form 3 October 2012
Accepted 3 October 2012
Available online 8 November 2012

ABSTRACT

An atom economic and catalytic substitution reaction of π-activated alcohols by a multimetallic Ir–Sn_3 complex has been demonstrated. The multimetallic Ir–Sn_3 complex can be easily synthesized from the reaction between $[Cp^*IrCl_2]_2$ and $SnCl_2$. In presence of as little as 1 mol % of the catalyst three different types of π-activated alcohols, namely benzyl, allyl, and propargyl alcohols, have been successfully transformed into alkylated products using carbon (arenes, heteroarenes, allyltrimethylsilane, and 1,3-dicarbonyls), nitrogen (sulfonamides), oxygen (alcohols), and sulfur (thiols) nucleophiles in very high yields. An electrophilic mechanism is proposed from the Hammett correlation study.

1. Introduction

Design, synthesis, and application of the multimetallic complexes have attracted more interest in homogeneous catalysis recently as they have been found to be more advantageous than their individual partners in terms of reactivity and selectivity.[1] The phenomenon can be achieved through a suitable combination of compatible metal centers as well as their ligand frameworks. Several examples have been reported in the literature over the above concepts.[2] In this particular field, considerable effort has been expended from our group to synthesize better catalytic systems within multimetallic regime for electrophilic activations.[3] A heterobimetallic complex, $[(COD)Ir(SnCl_3)Cl(\mu\text{-}Cl)]_2$ **1**, was prepared via an oxidative addition of $SnCl_4$ across $[(COD)IrCl]_2$ and it was anticipated that the bimetallic 'Ir–$SnCl_3$' motif may be the key responsive core for the substrate activation.[3a] It was indeed observed that catalytic activities of **1** were much better than the conventional Lewis or Brønsted acid catalysts toward Friedel–Crafts-type alkylation reactions. To extend the idea, a new class of catalysts can be envisaged where multiple centers coordinate to bring a stronger activation of the substrate and offer superior activity. Such multisite interaction between adjacent metal centers was observed in cluster catalysis where a metal–metal bond is viewed as the edge of the cluster, while three metal centers can comprise a face. Thus a multimetallic complex, $[Cp^*Ir(SnCl_3)_2\{SnCl_2(H_2O)_2\}]$ **2**, bearing 'Ir–Sn_3' motif has been synthesized where, unlike **1**, two $SnCl_3^-$ ligands are attached to the central iridium atom.[4] Complex **2** was found to be an excellent catalyst for α-amidoalkylation reaction of γ-hydroxylactams.

In nucleophilic substitution reactions there has been growing interest in using alcohols (water being the only by-product) instead of halides as the alkylating agents. However the designing of such a catalyst is challenging because (i) alcohols are less activated as an alkylating agent than halides due to bad leaving group ability of hydroxyl moiety, (ii) deactivation of Lewis acidic catalyst takes place by water, which is also a side-product of the reaction. Partial solution to this problem can be achieved by using π-activated alcohols as the alkylating agents along with unusual Lewis acid like lanthanide metal complexes or different Brønsted acidic like chiral phosphoric acid catalysts. The π-activated alcohols are those organic compounds, which have π-electronic systems adjacent to the OH group. In the catalytic nucleophilic substitution reactions catalysts activate the C–OH bond and the adjacent π-systems help in stabilizing the emerging carbocationic species. Benzyl, allyl, and propargyl alcohols are most easily available π-activated alcohols, which contain C=C, C≡C, aromatic ring, or a combination of these three as the stabilizing hands (Scheme 1).[5]

Triflate and halide derivatives of rare earth as well as post-transition metals are most widely used catalytic systems for efficient benzylation, allylation, or propargylation with varieties of nucleophiles. Some transition metal complexes were also reported for efficient alkylation reactions.[6–9] Among them, a very recent example of $Ga(OTf)_3$-catalyzed direct displacement of alcohols with sulfur nucleophiles is interesting.[6c] In 2005 Beller and co-workers

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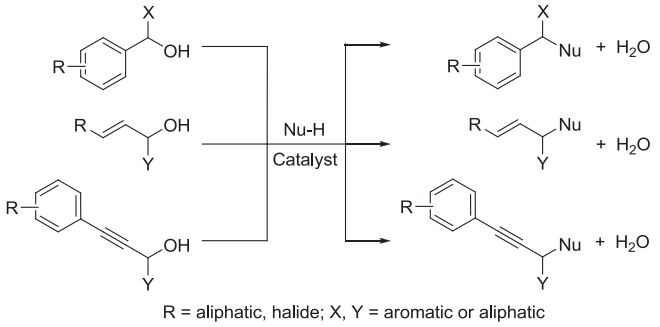
http://dx.doi.org/10.1016/j.tet.2012.10.086



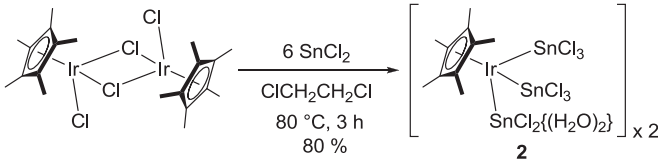
Scheme 1. Catalytic nucleophilic substitution reactions of π-activated alcohols.

documented the utility of 10 mol % $FeCl_3$ in Friedel–Crafts benzylation of different arenes and heteroarenes with good to excellent yields.[6f] Later many research groups employed $FeCl_3$ for catalytic allylation and propargylation reaction with carbon- and heteroatom-centered nucleophiles.[7n,8e] Baba group has successfully reported $InCl_3$ (5 mol %)-catalyzed benzylation and allylation by different types of silyl and 1,3-dicarbonyl nucleophilies.[6e,6g] First bimetallic catalyst for substitution of π-activated alcohols was accounted in 2000 by Nishibayashi group as a series of thiolate-bridged diruthenium complexes such as [Cp*RuCl(μ_2-SR_2)RuCp*Cl] (R=Me, Et, ^{n}Pr or ^{i}Pr) for propargylation of terminal propargyl alcohols with a variety of nucleophiles.[2b] Later they observed that the cationic versions of the diruthenium complexes are also potent for the catalytic allylation reactions of aromatic compounds.[2j] Subsequently, another set of heterobimetallic Group IV(Ti, Zr, Hf)–Ru complexes was also synthesized recently by the same team for the propargylation reactions.[2k]

2. Results and discussions

In continuation to our exploration on multimetallic catalysis, we report here the multimetallic piano-stool Ir–Sn_3 complex **2**-catalyzed benzylation, allylation, and propargylation reactions with various types of carbon (arenes, heteroarenes, 1,3-dicarbonyls, and allyl-TMS), nitrogen (sulfonamides), oxygen (alcohols), and sulfur (thiols) nucleophiles.

The multimetallic Ir–Sn_3 complex **2** was synthesized via insertion reaction of $SnCl_2$ across the iridium-chlorine bonds of [Cp*$IrCl_2$]$_2$ in dichloroethane at 80 °C (Scheme 2).[4] After the reaction was completed (ca. 3 h) the greenish yellow solution was taken out and upon slow diffusion of *n*-hexane to this solution the product **2** crystallized out as greenish yellow blocks in good yield.



Scheme 2. Synthesis of multimetallic Ir–Sn_3 complex **2**.

As depicted in Fig. 1A, **2** adopts a near perfect three-legged piano-stool geometry, as is common to the Cp*Ir(III) complexes. We believe that the piano-stool geometry having three Ir–Sn bonds may hold the key to superior catalytic activity of **2** toward the substitution reactions since the three tin centers can provide an interactive face to bind the alkylating agent R–OH (Fig. 1B).

Initially, the benzylation of toluene **3b** with *para*-methylbenzyl alcohol **10a** was selected as the model reaction and it was observed that 1 mol % of complex **2** can promote the benzylation reaction quantitatively affording 99% of ditolylmethane **13a** (*o*/*p*=32:68) just after 5 min at 80 °C (Table 1, entry 1). It was observed that,

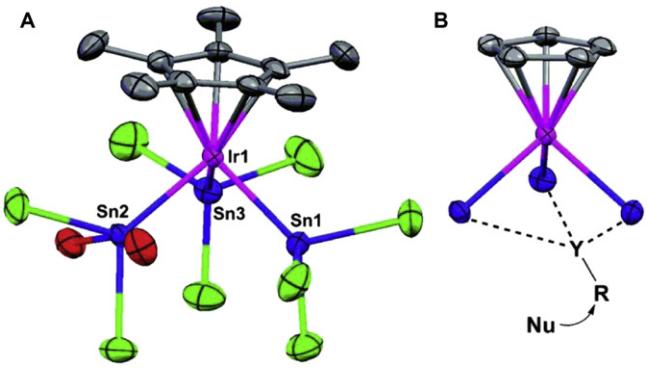
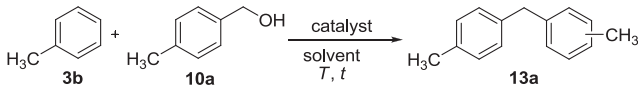


Fig. 1. (A) Solid state structure of **2**. H-atoms are not shown for clarity. (B) Proposed electrophilic activation model involving **2**. R-Y=alkylating agent, Nu=nucleophile.

complex **2** remained catalytically active for a wide range of temperature from 50 °C to 80 °C (entries 2–4). Variation of catalyst concentration showed that, a minimum of 0.5 mol % catalyst loading was required for successful benzylation (entry 5). Similarly, a wide variety of solvents were tested and except tetrahydrofuran, solvents like dichloromethane, acetonitrile, nitromethane, and toluene were found to be equally effective (entries 1–9). The catalytic activity of **2** was uninterrupted even after 15 consecutive cycles without any loss of TOF. Most important feature is that, the catalyst can be easily separated and recycled, as it crystallizes out from the reaction solution after the completion of the reaction. It may be noted that, complex **2** is air and moisture stable and the reaction can be carried out using undried and undistilled solvents in air, without any loss of activity. The heterobimetallic catalyst **1** was tested for its catalytic activity toward the benzylation reaction,

Table 1
Screening of catalysts and optimization of reaction conditions for benzylation reaction[a]



#	Catalyst	Loading (mol %)	Solvent	T (°C)	t, (min)	Yield[b] (%)	TOF (h^{-1})
1	**2**	1	$C_2H_4Cl_2$	80	5	99	1188
2	**2**	1	$C_2H_4Cl_2$	70	15	99	396
3	**2**	1	$C_2H_4Cl_2$	60	45	99	132
4	**2**	1	$C_2H_4Cl_2$	50	180	99	33
5	**2**	0.5	$C_2H_4Cl_2$	70	30	99	198
6	**2**	1	MeCN	70	15	96	384
7	**2**	1	$MeNO_2$	70	15	88	352
8	**2**	1	PhMe	70	15	99	396
9	**2**	1	THF	60	360	5	0.8
10[c]	**1**	1	PhMe	90	15	10	40
11	**1**	1	PhMe	90	360	45	7.5
12[d]	[Ir(COD)Cl]$_2$+4$SnCl_4$	1	PhMe	90	15	95	380
13	[Ir(COD)Cl]$_2$+4$SnCl_4$	1	PhMe	70	360	10	1.7
14	[Ir(COD)Cl]$_2$+4$SnCl_4$	1	PhMe	50	360	2	0.3
15	[Cp*$IrCl_2$]$_2$	5	$C_2H_4Cl_2$	70	360	0	0
16	$SnCl_2$	5	$C_2H_4Cl_2$	70	360	0	0
17	$SnCl_4$	5	$C_2H_4Cl_2$	70	360	25	4.2
18	$InCl_3$	5	$C_2H_4Cl_2$	70	360	40	6.7
19	$FeCl_3$	5	$C_2H_4Cl_2$	70	360	40	6.7
20	$Sc(OTf)_3$	5	$C_2H_4Cl_2$	70	360	15	2.5
21	$La(OTf)_3$	5	$C_2H_4Cl_2$	70	360	35	5.8
22	$Yb(OTf)_3$	5	$C_2H_4Cl_2$	70	360	30	5.0
23	$Cu(OTf)_2$	5	$C_2H_4Cl_2$	70	360	25	4.2
24	No catalyst	—	$C_2H_4Cl_2$	70	360	0	0

[a] Reaction conditions: **3b** (1.0 mmol), **10a** (0.5 mmol), catalyst (0.005 mmol for 1 mol % loading), solvent (2 mL).
[b] Determined by GC.
[c] Prepared according to Ref. 3a.
[d] Generated in situ according to Ref. 3a.

however, it was found that, 1 mol% of complex **1** can afford the product **13a** (*o*/*p*=19:81) only in 45% yield after 6 h (entry 10). Interestingly, a 1:4 mixture of $[Ir(COD)Cl]_2$ and $SnCl_4$ was found to be more effective and yielded the product in 95% yield in 15 min at 90 °C. At lower temperature, however, the conversions were found to be very poor (entries 12–14). Under this similar condition, varieties of Lewis acidic metal (Sc, Yb, La, Cu) triflates and metal (In, Fe, Sn) halides were tested for the catalytic activity, but none of them were found to be as effective as **2** (entries 15–23).

Encouraged by these observations, a number of nucleophiles were tested toward the alkylation with benzyl, allyl, and propargyl alcohols (Charts 1 and 2). Next, the scope of benzylation of different primary, secondary, and tertiary benzyl alcohols was evaluated with an array of carbon nucleophiles like arenes, heteroarenes, 1,3-dicarbonyls, 4-hydroxycoumarine, etc.

obtained as a mixture of two regioisomers in 69:31 ratio. The 1,3-dicarbonyl derivatives **5b–d** may also act as potential nucleophiles in benzylation reactions but they also serve as bidentate ligands to decrease the Lewis acidity of the metal catalyst. However, the $Ir-Sn_3$ complex **2** was found to be effective when dicarbonyl compounds were used as nucleophiles and various 2° benzyl alcohols were efficiently converted to the benzylated products **13l–n** in excellent yields (entries 12–14). It is very important to note that 2° benzyl alcohols **10e** and **10g** with methyl substituent underwent the substitution reaction in the presence of catalyst **2** with no elimination products. Not only that, *p*-bromobenzyl alcohol also quantitatively converted to coumarine derivative **13o** when reacted with 4-hydroxycoumarine in optimal conditions (entry 15). In addition to carbon nucleophiles, various heteroatom nucleophiles were tested. Sulfonamides (**8a** and **8b**) were alkylated

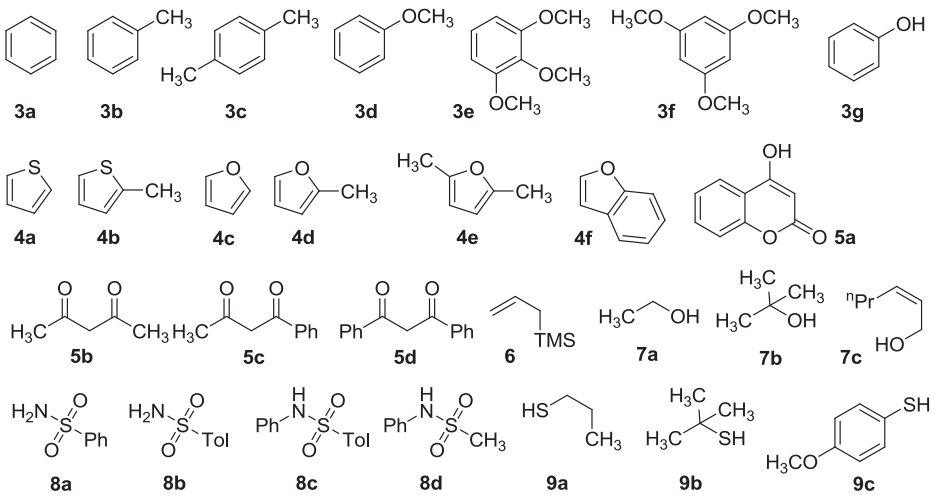
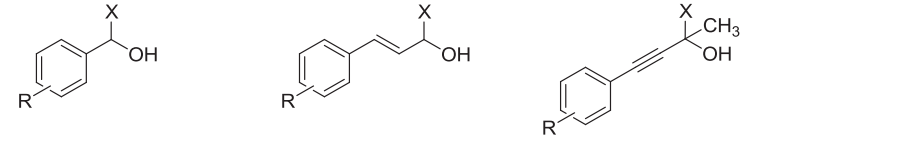


Chart 1. List of active nucleophiles used in this work.



10a: R = *p*-Me, X = H
10b: R = H, X = H
10c: R = *p*-Cl, X = H
10d: R = *p*-Br, X = H
10e: R = *p*-Me, X = Me
10f: R = H, X = Ph
10g: R = H, X = Me

11a: R = *p*-Me, X = H
11b: R = H, X = H
11c: R = *p*-Cl, X = H
11d: R = *p*-Br, X = H
11e: R = *p*-Br, X = Me
11f: R = H, X = Me
11g: H_3C OH
11h: ^nPr OH

12a: R = *p*-Me, X = Me
12b: R = H, X = Me
12c: R = *p*-Cl, X = Me
12d: R = *p*-Br, X = Me
12e: R = *p*-Me, X = H
12f: R = H, X = H
12g: R = *o*-Me_2, X = Me
12h: R = H, X = Et
12i: R = *p*—C≡C–C(Me_2)—OH, X = Me

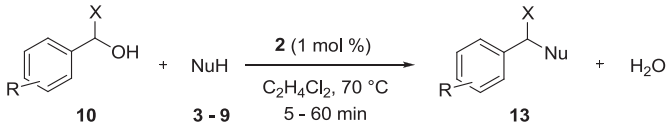
Chart 2. List of π-activated alcohols used in this work.

The reaction of benzyl alcohol **10b**, and *para*-substituted benzyl alcohols **10a** (*p*-Me), **10c** (*p*-Cl), and **10d** (*p*-Br) with *p*-xylene **3c** was found to afford the corresponding diarylmethanes **13b–e** in 92–96% yields (Table 2, entries 2–5). Anisole **3d** could produce the *ortho* and *para* mixture of diarylmethane derivative **13f** quantitatively within just 10 min at 70 °C (entry 6). Benzene **3a** was found to be equally effective and afforded benzylarene **13g** in excellent yield (entry 7). We further probed the efficacy of **2** in the present alkylation reaction for heteroarenes like thiophene **4a**, 2-methylthiophene **4b**, or 2,5-dimethylfuran **4e** and here also the corresponding products **13i–k** were obtained in excellent yields (entries 9–11). In case of thiophene, coupled product **17i** was

using 2° benzyl alcohols to obtain sulfonamide derivatives **13p** and **13q** in good yields (entries 16 and 17). It was also found that ether **13r** and thioethers (**13s** and **13t**) were formed in excellent yield when alcohols and thiols were used as nucleophiles (entries 18–20). Here it is noteworthy to mention that unlike 1° benzyl alcohols for 2° and 3° benzyl alcohols catalytic activation by **2** can be done even at room temperature and products were isolated in excellent yields.

Encouraged by the results obtained with benzyl alcohols, we thought to explore catalytic allylation reaction. Optimization of the reaction conditions and screening of different Lewis acidic catalyst was carried out taking cinnamyl alcohol **11b** and anisole **3d** as the

Table 2
Scope of benzylation reaction catalyzed by **2**[a]



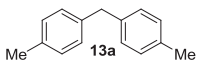
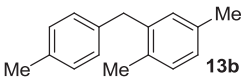
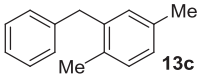
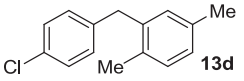
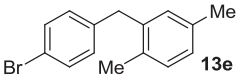
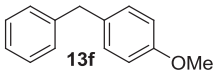
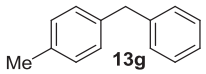
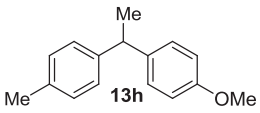
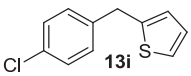
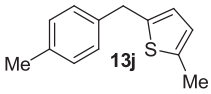
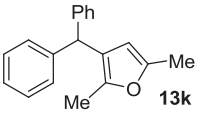
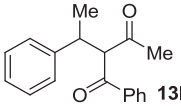
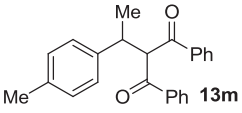
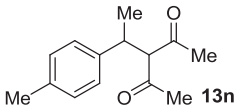
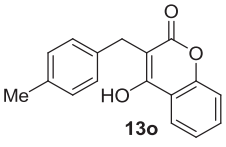
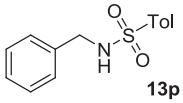
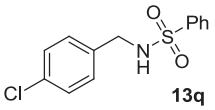
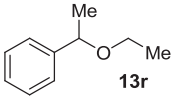
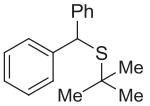
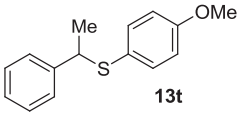
#	Substrates	Major product	Yield[b] (%)
1[c]	**10a**+**3b**	 **13a**	96
2	**10a**+**3c**	 **13b**	96
3	**10b**+**3c**	 **13c**	95
4	**10c**+**3c**	 **13d**	95
5[b]	**10d**+**3c**	 **13e**	92
6[d]	**10b**+**3d**	 **13f**	96
7	**10a**+**3a**	 **13g**	94
8[e]	**10e**+**3d**	 **13h**	94
9[f]	**10c**+**4a**	 **13i**	96
10	**10a**+**4b**	 **13j**	94
11[e]	**10f**+**4e**	 **13k**	96
12[e]	**10g**+**5c**	 **13l**	90
13[e]	**10e**+**5d**	 **13m**	88
14[e]	**10e**+**5b**	 **13n**	88
15	**10a**+**5a**	 **13o**	86

Table 2 (*continued*)

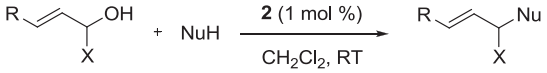
#	Substrates	Major product	Yield[b] (%)
16	**10b**+**8b**	 **13p**	86
17	**10c**+**8a**	 **13q**	85
18[e]	**10g**+**7a**	 **13r**	90
19[e]	**10f**+**9b**	 **13s**	95
20[e]	**10g**+**9c**	 **13t**	94

[a] Reaction conditions: **3**–**9** (1.0 mmol), **10** (0.5 mmol), **2** (0.005 mmol), $C_2H_4Cl_2$ (2 mL).
[b] Isolated yield after column chromatography.
[c] Regioisomers: *ortho*/*para*=32:68.
[d] Regioisomers: *ortho*/*para*=36:64.
[e] Reaction was carried out at RT.
[f] Ratio of the regioisomers of **13i**=69:31.

substrates. The results again showed the superiority of catalyst **2**, and allylation reaction proceeded under mild condition at room temperature with almost quantitative yield of the allylation product. This encouraged us to extend the scope of **2**-catalyzed allylation reactions with different carbon and heteroatom nucleophiles. Initially, the allylic substitution of various allyl alcohols was examined with different carbon-centered nucleophiles (arenes, heteroarenes, and 1,3-dicarbonyl compounds) in dichloromethane at room temperature in the presence of 1 mol % catalyst **2** (Table 3, entries 1–11 and 19–22). For convenience, the alcohol/nucleophile ratio was kept at 1:2, and the corresponding allylation products were isolated in good to excellent yields.

Allyl alcohols bearing aryl substituent **11a**–**d** smoothly underwent the coupling reaction with arenes like anisole **3d** with very high regioselectivity and the alkylated products **14a**–**d** were obtained in excellent yields (entries 1–4). Heteroarenes like thiophene produced allylation products **14e** as a mixture of regioisomers and 2-methylfuran also gave the product **14f** with very high yield (entries 5 and 6). Next, the reactions of allyl alcohols with 1,3-dicarbonyl compounds were explored. High yields of the products **14g**–**j** were obtained from the reaction with cinnamyl alcohol **11b** or 2° allyl alcohol **11e** and 1,3-dicarbonyls like **5b**–**d** (entries 7–\10). Special type of 1,3-dicarbonyl compound like 4-hydroxycoumarin **5a** was also found to be an active nucleophile and produced the allylated coumarine derivative **14k** with good yield (entry 11). To explore the generality of the reaction further, the reaction of allyl alcohols with heteroatom nucleophiles was tested. With 1 mol % loading of **2**, desired ethers **14l** and **14m** were obtained in high yields from the reactions of allyl alcohols with ethanol and *t*-butyl alcohol as oxygen nucleophile (entries 12 and 13). For representative nitrogen-nucleophiles, the reactions between sulfonamides **8b**–**d** and cinnamyl alcohol **11b** were selected and the allylated sulfonamide

Table 3
Scope of allylation reaction catalyzed by **2**[a]



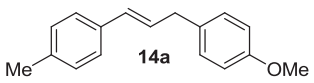
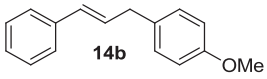
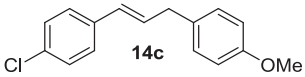
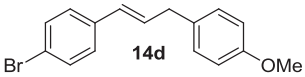
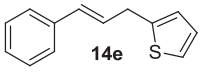
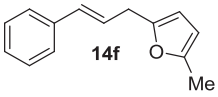
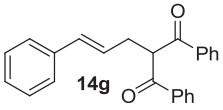
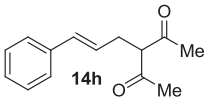
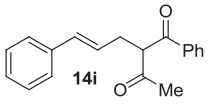
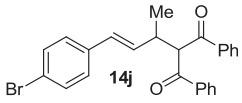
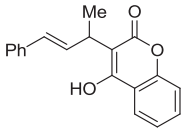
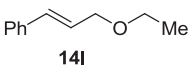
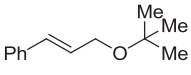
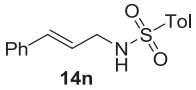
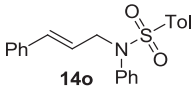
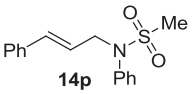
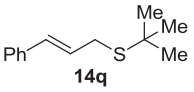
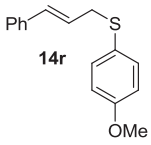
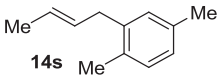
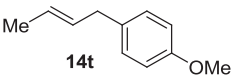
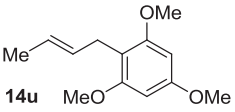
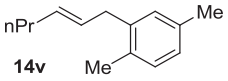
#	Substrates	Major product	Yield[b] (%)
1	**11a**+**3d**	 **14a**	96
2	**11b**+**3d**	 **14b**	92
3	**11c**+**3d**	 **14c**	90
4	**11d**+**3d**	 **14d**	90
5[c]	**11b**+**4a**	 **14e**	94
6	**11b**+**4d**	 **14f**	95
7	**11b**+**5d**	 **14g**	93
8	**11b**+**5b**	 **14h**	92
9	**11b**+**5c**	 **14i**	93
10	**11e**+**5d**	 **14j**	88
11	**11f**+**5a**		83
12	**11b**+**7a**	 **14l**	83
13	**11b**+**7b**	 **14m**	92
14	**11b**+**8b**	 **14n**	92
15	**11b**+**8c**	 **14o**	87

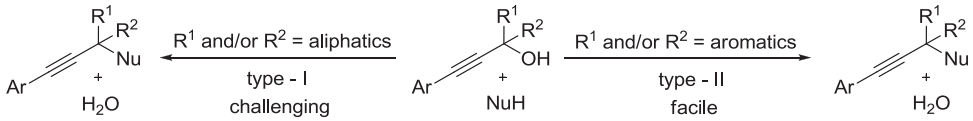
Table 3 (*continued*)

#	Substrates	Major product	Yield[b] (%)
16	**11b**+**8d**	 **14p**	80
17	**11b**+**9b**	 **14q**	96
18	**11b**+**9c**	 **14r**	96
19	**11g**+**3c**	 **14s**	83
20	**11g**+**3d**	 **14t**	82
21	**11g**+**3f**	 **14u**	88
22	**11h**+**3c**	 **14v**	85

[a] Reaction conditions: **3**–**9** (1.0 mmol), **11** (0.5 mmol), **2** (0.005 mmol), CH_2Cl_2 (2 mL).
[b] Isolated yield after column chromatography.
[c] Ratio of the regioisomers in **14e**=72:28.

products **14n**–**p** were obtained in good to excellent yields (entries 14–16). Similarly, carbon–sulfur bonds were successfully made using sulfur nucleophiles like *t*-butyl thiol **9b** or *p*-methoxy thiophenol **9c** (entries 17 and 18). No Friedel–Crafts-type arylated product was observed in case of *p*-methoxy thiophenol, the exclusive product was thioether **14r**. In addition to aryl substituted allyl alcohols, alkyl substituted allyl alcohols like crotyl alcohol **11g** were also subjected to alkylation reaction with *p*-xylene, anisole, or 1,3,5-trimethoxy benzene and the allylated products **14s**–**u** were isolated in good yield (entries 19–21). Similarly, hex-2-en-1-ol **11h** on reaction with *p*-xylene produced the corresponding allylated product **14v** in good yield (entry 22).

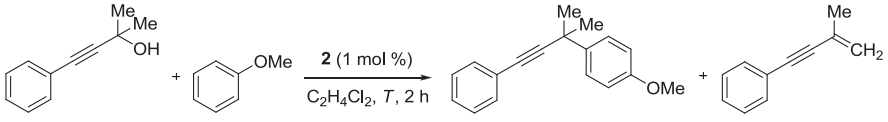
As an obvious extension of benzylation and allylation reaction, it was thought worthwhile to study **2**-catalyzed '*true propargylation*' reactions. Here the word '*true propargylation*' is referred to the kind of propargylic activation (Scheme 3, type-I) where the propargylic carbocationic species are not stabilized by adjacent aromatic ring. It may be noted that, such propargylic substitution reactions are more challenging because of two reasons: (i) emerging cationic species after catalytic activation of C–OH bond is stabilized by only propargylic π-systems, (ii) high possibility of β-H elimination to form enyne compounds. In this context, our goal was to optimize the conditions for propargylation reaction catalyzed by **2** so that the yield the propargylated products in the true propargylation reactions could be maximized. Keeping this in view, the model



Scheme 3. Concept of true propargylation reaction.

reaction between 2-methyl-4-phenyl-but-3-yn-2-ol **12b** (having β-H) as representative alcohol and anisole **3d** as the arene was selected in presence of 1 mol % of multimetallic catalyst **2** and in dichloroethane as solvent. The results are briefly summarized in Scheme 4. From the optimization results it was found that the chance of elimination reaction to produce enyne product could be minimized by increasing the nucleophile to alcohol ratio and by decreasing reaction temperature to 60 °C from 80 °C. Under this particular circumstance the obtained yield of the propargylated product **15b** was found to be 85%.

Finally, when sterically bulkier nucleophile like 1,3,5-trimethoxy benzene **3f** was employed for alkylation with 3° propargylic alcohol then normal propargylic product was not obtained, instead a substituted indene (**17a** and **17b**) was exclusively formed (Scheme 5). The fact that, the key factor behind this unusual transformation is purely steric was proved by the following results: (a) 1,2,3-trimethoxy benzene **3e** gave usual propargylic substituted product **15f** with 3° propargyl alcohol; while (b) 1,3,5-trimethoxy benzene **3f** provided usual propargylated product **15g** with 2° propargylic alcohol. The indene formation can be explained by



Entry	12b:3d	T, °C	Yield of 15b, %	Yield of 16, %
1	1:3	80	75	15
2	1:3	60	85	<5
3	1:1	80	60	30
4	1:1	60	50	25

[a]Reaction conditions: **12b** (0.5 mmol), **2** (0.005 mmol), $C_2H_4Cl_2$ (2 mL).

Scheme 4. Optimization of reaction conditions for propargylation reaction.[a]

After establishing optimal conditions for '*true propargylation*', the generality of this reaction was tested using various arenes and heteroarenes and different propargylic alcohols under the optimized condition and the results are given in Table 4. Anisole was alkylated by four *para*-substituted 3° propargylic alcohols **12a**–**d** in good yield (entries 1–4). Unlike 3° alcohols, activation of 2° propargylic alcohol **12e** and **12f** by **2** was slow and using different nucleophiles like anisole, 1,3,5-trimethoxy benzene, or allyltrimethylsilane the alkylated products **15e**, **15g**, and **15m** were isolated in 65–73% yield after 6 h along with ~20% unreacted starting material (entries 5, 7, and 13). Notably, when phenol was used as a nucleophile for 2° propargylation with **12f** the sole product was **15h**, no ether type product by an attack from phenolic oxygen atom was observed (entry 8). Heteroaromatics like thiophenes, 2-methylthiophene, furan, and benzo[*b*]furan also gave propargylated products **15i**–**l** in good yields (entries 9–12).

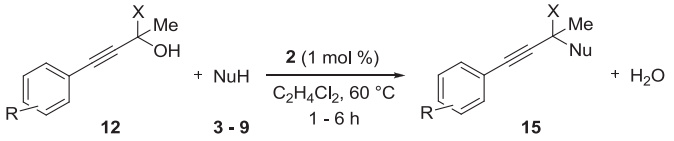
In all the cases mentioned above it was found that the propargylation took place only at the most electron rich center of the aromatic or heteroaromatic compounds. After getting satisfactory results with aromatic compounds, it was thought to use 1,3-dicarbonyl compounds as nucleophiles. However, the results were found to be disappointing. For example, when acetylacetone **5b** was used as the nucleophile only 45% of the coupled product **15n** was obtained along with elimination product (entry 14). In comparison, heteroatom center nucleophiles like aliphatic thiols, alcohols, and tosylamine were also successfully tested as potential nucleophiles and good yields of propargylated products were isolated (entries 15–20). Compound having two activated propargylic alcohol centers like **12i** was successfully activated in presence of just 1 mol % **2** and bis-thioether **15t** was isolated as the major product (entry 20). However, in case of *p*-methoxy thiophenol no Friedel–Craft type product was obtained.

assuming prior nucleophilic attack at acetylinic center of propargylic alcohol due to steric reason followed by intramolecular arylation and subsequent aromatization (Scheme 6).[3g]

To test the likelihood of an electrophilic mechanism in benzylation, allylation as well as propargylation reaction, kinetic study was performed for all three types of alkylation reactions using gas chromatographic technique. From the kinetic study, the relative rate constant values k_R/k_H were evaluated. The studies were conducted with four different *para*-substituted benzyl, allyl, and propargyl alcohols. The rate kinetic study and related Hammett plot for benzylation, allylation, and propargylation reaction are discussed hereafter. Rate studies for benzylation was carried out at 70 °C taking *p*-xylene and four different *para*-substituted benzyl alcohols *p*-R-$C_6H_4CH_2OH$ (R=Me, H, Cl, and Br) and from the graph the corresponding rates for four different benzylation reactions were calculated (Scheme 7). The kinetic study for allylation was done at 30 °C taking anisole and four different *para*-substituted allyl alcohols *p*-R-$C_6H_4CH{=}CHCH_2OH$ (R=Me, H, Cl, and Br). From the graph, the corresponding rates for four different allylation reactions were obtained (Scheme 8). Finally propargylation reactions were carried out at 60 °C for the reaction of anisole with *para*-substituted propargyl alcohols *p*-R-$C_6H_4C{\equiv}C(Me)_2OH$ (R=Me, H, Cl, and Br) and from the graph the corresponding rates for four different propargylation reactions were obtained (Scheme 9).

After obtaining all the rate constant values (k_R) for three different alkylation reactions then the logarithm of (k_R/k_H) value against Hammett substituent constants σ_R was plotted. The linear correlation obtained from these plots resulted in the Hammett reaction constant ρ-values (Fig. 2). The reaction constant values for all three alkylation reactions are moderately negative (between −2 and −4). Specifically the values are −3.3, −2.7 and −2.1 corresponding to benzylation, allylation, and propargylation, respectively. The

Table 4
Scope of propargylation reaction catalyzed by **2**[a]



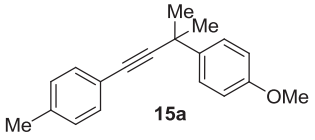
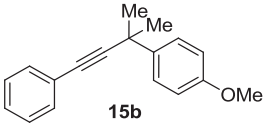
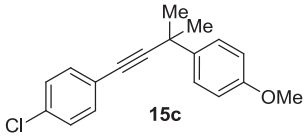
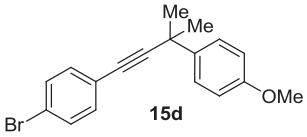
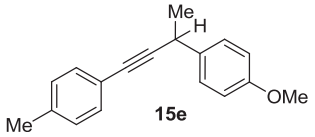
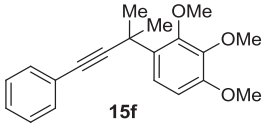
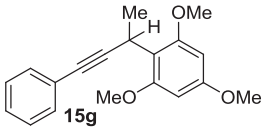
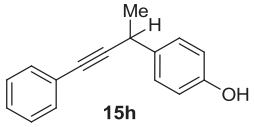
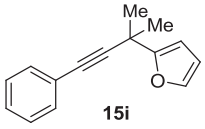
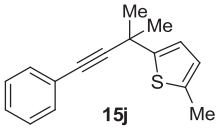
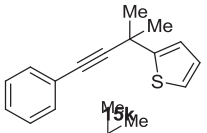
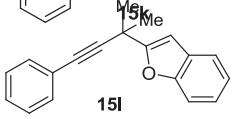
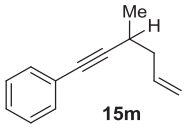
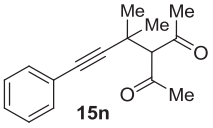
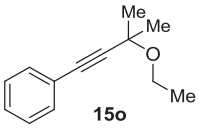
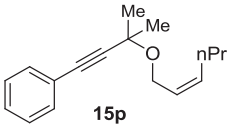
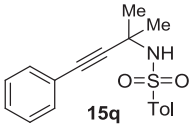
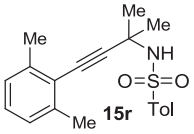
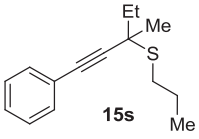
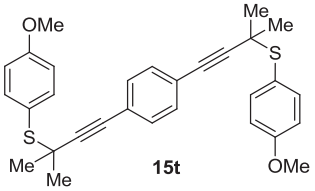
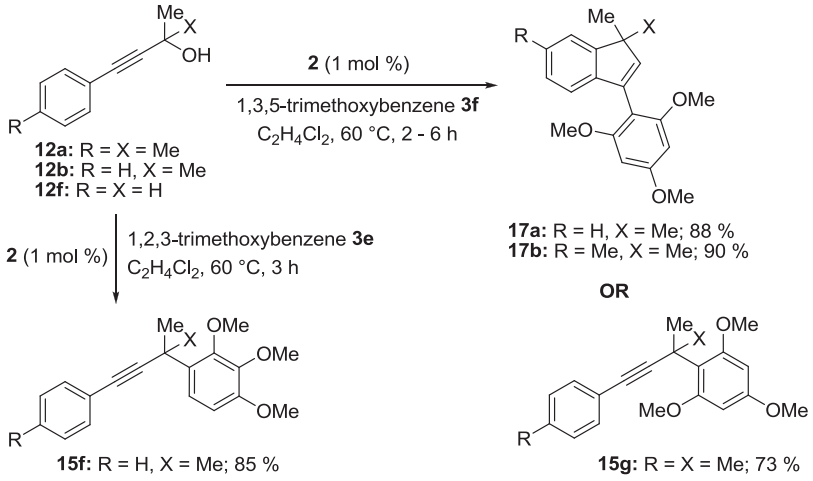
#	Substrates	Major product	Yield[b] (%)
1	**12a**+**3d**	 **15a**	85
2	**12b**+**3d**	 **15b**	85
3	**12c**+**3d**	 **15c**	77
4	**12d**+**3d**	 **15d**	80
5[c,d]	**12e**+**3d**	 **15e**	65
6	**12b**+**3e**	 **15f**	85
7[c]	**12f**+**3f**	 **15g**	73
8[c]	**12f**+**3g**	 **15h**	67
9[e]	**12b**+**4c**	 **15i**	79

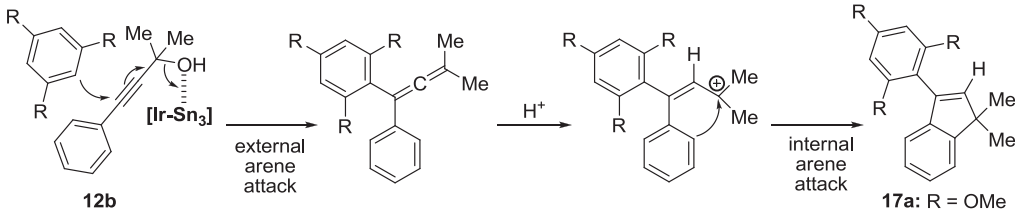
Table 4 (*continued*)

#	Substrates	Major product	Yield[b] (%)
10	**12b**+**4b**	 **15j**	86
11	**12b**+**4a**	 **15k**	74
12	**12b**+**4f**	 **15l**	80
13[c]	**12f**+**6**	 **15m**	67
14[f]	**12b**+**5b**	 **15n**	45
15	**12b**+**7a**	 **15o**	78
16	**12b**+**7c**	 **15p**	83
17	**12b**+**8b**	 **15q**	76
18	**12g**+**8b**	 **15r**	78
19	**12h**+**9a**	 **15s**	86
20	**12i**+**9c**	 **15t**	88

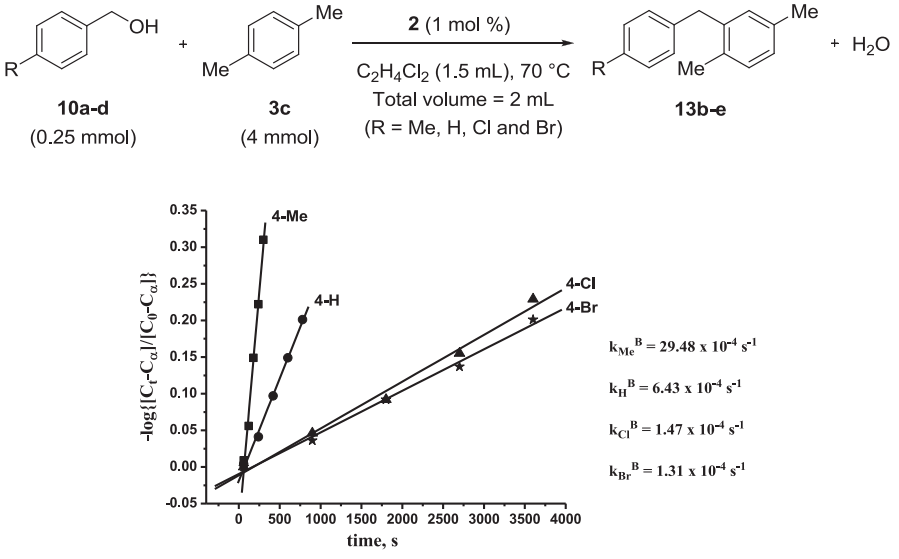
[a] Reaction conditions: **3**–**9** (1.5 mmol), **12** (0.5 mmol), **2** (0.005 mmol), $C_2H_4Cl_2$ (3 mL).
[b] Isolated yield after column chromatography.
[c] Starting material was recovered up to 15%.
[d] Product was isolated as a mixture of *ortho* and *para* isomers.
[e] Furan was used 20 equiv to alcohol.
[f] Enyne product was isolated.



Scheme 5. Indene formation versus propargylation reaction: steric factor.



Scheme 6. Plausible reaction mechanism for indene formation.

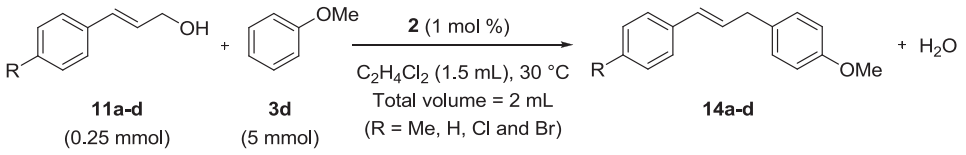


Scheme 7. Rate constants k_R^B for the reactions of *p*-xylene with *p*-substituted benzyl alcohols.

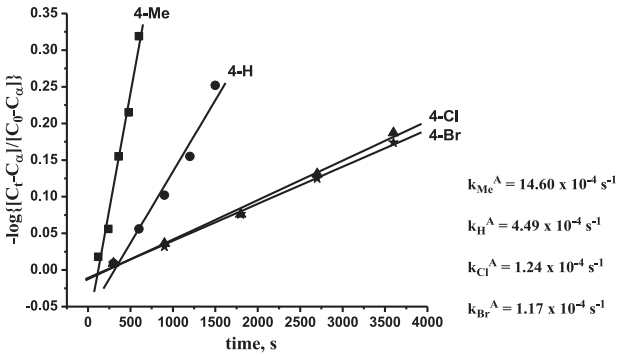
moderately negative values suggest the possibility of generation of weak positive charge ($\delta+$) at the reactive carbon center of the alcohol due to the coordination of alcoholic –OH group to the [Ir–Sn_3] motif of the catalyst.

3. Conclusions

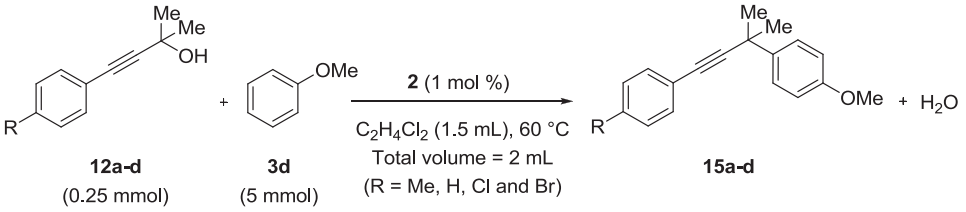
In summary, the present study demonstrated the superior efficiency of the multimetallic catalyst $Cp^*Ir(SnCl_3)_2\{SnCl_2(H_2O)_2\}$ **2** toward nucleophilic substitution reaction of three different π-activated alcohols. The screening of other Lewis acidic catalytic systems for benzylation reaction and subsequent optimization studies showed that **2** is better in terms of selectivity, product yield, TOF, and catalyst loading. It was also observed that **2** is superior to our previously designed heterobimetallic catalyst **1a**. Keeping this in mind, the nucleophilic substitution reactions of benzyl, allyl, and propargyl alcohols with different types of carbon nucleophiles (arenes, heteroarenes, allyltrimethylsilane, 1,3-dicarbonyls etc.), nitrogen-nucleophiles (sulfonamides), oxygen nucleophiles (alcohols), sulfur nucleophiles (thiols) were carried out in presence of



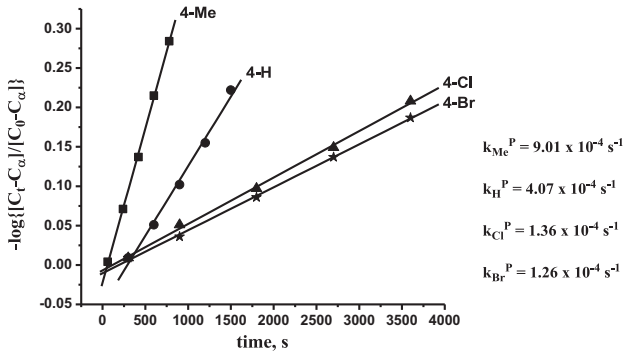
11a-d (0.25 mmol) **3d** (5 mmol) **14a-d**



Scheme 8. Rate constants k_R^A for the reactions of anisole with *p*-substituted allyl alcohols.



12a-d (0.25 mmol) **3d** (5 mmol) **15a-d**



Scheme 9. Rate constants k_R^P for the reactions of anisole with *p*-substituted propargyl alcohols.

1 mol % of catalyst **2** and eventually the substitution products were isolated in good to excellent yields. As a special mention, product bearing an indene moiety was obtained exclusively when 3° propargyl alcohols were reacted with bulky arenes like 1,3,5-trimethoxy benzene. Finally, the likelihood of electrophilic activation of three π-activated alcohols was confirmed using Hammett correlation study; the Hammett reaction constant ρ-values were obtained as moderate negative values for all three alcohols.

4. Experimental

4.1. General remarks

All preparations and manipulations have been performed under an inert atmosphere of argon using standard vacuum lines and Schlenk techniques. All solvents used for the synthesis have been dried and distilled by standard methods and previously deoxygenated in the vacuum line. Pre-coated silica gel $60F_{254}$ (Merck) was used for thin layer chromatography (TLC) and silica gel 60–120 and 100–200 mesh (SRL) was used for column chromatography.

NMR spectra were recorded on Bruker-AC 200 MHz and Bruker-Avance II 400 MHz spectrometer at 300 K. ^{1}H NMR spectra were recorded at 200 MHz and 400 MHz, chemical shifts are reported in parts per million (ppm) from tetramethylsilane with the solvent resonance as the internal standard ($CDCl_3$: δ 7.26 ppm, $(CD_3)_2CO$: δ 2.05 ppm, $(CD_3)_2SO$: δ 2.50 ppm). Data are reported as follows: chemical shifts, multiplicity (s=singlet, d=doublet, t=triplet, q=quartet, br=broad, m=multiplet), integration, coupling constant (Hz). ^{13}C NMR spectra were recorded at 54.6 MHz and 100 MHz with proton decoupling. Chemical shifts are reported in parts per million from tetramethylsilane with the solvent resonance as the internal standard ($CDCl_3$: δ 77.0 ppm, $(CD_3)_2CO$: δ 29.9 and 206.7 ppm, $(CD_3)_2SO$: δ 39.5 ppm). ^{119}Sn NMR spectra were recorded at 149 MHz and chemical shifts are reported in parts per million with respect to $Sn(CH_3)_4$. FTIR (4000–500 cm^{-1}; using KBr pellet) spectra were obtained using a Perkin–Elmer FTIR Spectrometer (Spectrum RX I). UV–visible spectra were recorded at 298 K on Shimadzu UV-1601 UV–VIS Spectrometer using spectrophotometric grade solvent. Elemental analyses were performed on Perkin–Elmer Instruments 2400 Series II CHNS/O Analyzer and Vario EL, Elementar. Melting

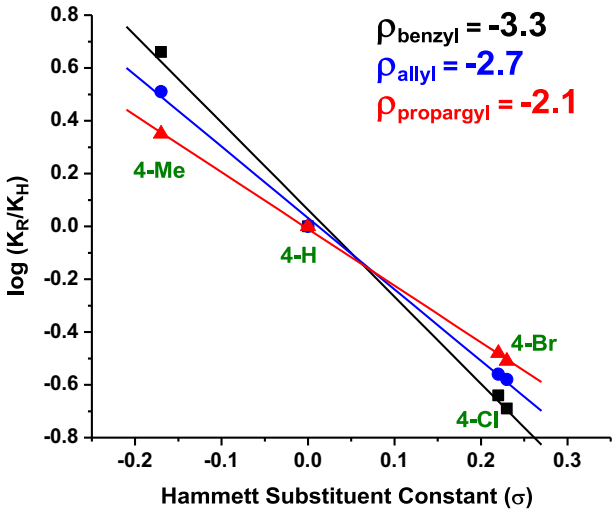


Fig. 2. Hammett correlation plot with respect to alcohols.

points were determined on an Electrothermal 9100 melting point apparatus and are uncorrected. Single crystal X-ray crystallographic data were collected on Bruker Smart APEX system that uses graphite monochromated Mo Kα radiation (λ=0.71073 Å). The structure was solved by direct method and refined by least square method on F^2 employing WinGX package and the relevant programs (SHELX-97 and ORTEP-3) implemented therein. Non-hydrogen atoms were refined anisotropically and hydrogen atoms on carbon atoms were fixed at calculated positions and refined using a riding model.

4.2. Synthesis of starting materials

4.2.1. Synthesis of organometallic complexes. $[(COD)Ir(\mu\text{-}Cl)_2]_2$,[10] $[Cp^*IrCl_2]_2$,[11] $[(COD)Ir(SnCl_3)Cl(\mu\text{-}Cl)]_2$,[3a] and $[Cp^*Ir(SnCl_3)_2\{SnCl_2(H_2O)_2\}]$,[4] were prepared according to the literature procedures.

4.2.2. General procedure for the synthesis of benzyl alcohols.[12] In a 250 mL two-necked round-bottom flask, equipped with a stirrer and a dropping funnel, was placed a solution of aldehyde or ketone (0.1 mol) in 100 mL of methanol. A solution of $NaBH_4$ (1.4 g, 0.037 mol) in 20 mL of 0.2 M NaOH was added at a rate of 0.5 mL/min with occasional cooling to keep the temperature at 18–25 °C. Upon completion, the solution was treated cautiously with dilute H_2SO_4 until the evolution of hydrogen gas ceased. The methanol was removed in a rotatory evaporator, water (50 mL) was added, and the organic product was extracted twice with ether (2×50 mL), washed with brine, and dried over anhydrous Na_2SO_4. Solvent was removed to obtain the product as white/yellow solid in 82–92% yields.

Spectral data of compounds **10a**,[13] **10c**,[13] **10d**,[14] **10e**,[15] **10f**,[15] and **10g**[15] were in excellent agreement with those in the literature.

4.2.3. General procedure for the synthesis of allyl alcohols. Procedure 1:[16] 4-Substituted cinnamic acid (10 mmol) and potassium carbonate (1.38 g, 10 mmol) were suspended in dimethylformamide (10 mL). Methyl iodide (2.13 g, 0.93 mL, 15 mmol) was added in one portion and the mixture was stirred for 2 d or until complete conversion was observed by TLC. After addition of aqueous saturated ammonium chloride (ca. 10 mL), the mixture was stirred for 30 min, then it was extracted with diethyl ether twice (2×25 mL). The combined organic phases were washed twice with brine, then dried over Na_2SO_4. After removing the solvent under reduced pressure, the ester was obtained as an off-white solid, which was used in the next step without further purification.

To a solution of the ester in dichloromethane (20 mL) at −78 °C was added DIBAL (1 M in dichloromethane, 25 mL, 25 mmol) in one portion. After 30 min stirring at −78 °C, the solution was slowly warmed to 0 °C and stirred for 1 h, then cooled to −78 °C. The reaction was quenched by dropwise addition of 1 N aqueous HCl. After warming to RT, additional 6 N HCl and dichloromethane were added carefully until complete dissolution of the precipitate. The aqueous phase was extracted twice with dichloromethane and combined organic phases were dried over Na_2SO_4. Subsequent solvent removal under reduced pressure gave the title alcohol as an off-white solid (78–82% yield), which did not require further purification.

Spectral data of compounds **11a**,[17] **11c**,[17] and **11d**[17] were in excellent agreement with those in the literature.

Procedure 2:[18] The aldehyde (43.2 mmol) was added gradually to a solution of NaOH (2.2 g) in H_2O (20 mL) and ketone (43.3 mmol) in ethanol (12 mL) at 0 °C. The reaction mass was stirred at RT for 4 h. After 4 h, saturated ammonium chloride solution was added to the flask, followed by extraction with ether. The combined organic layers were dried over Na_2SO_4 and concentrated to give a solid, which was purified by column chromatography to give pure enone, which was used in the next step.

Reduction of enone (0.014 mol) was carried out with sodium borohydride (0.56 g, 0.015 mol) in methanol (5 mL) for 2 h at 0–10 °C. After completion of the reaction, the reaction mass was neutralized with dilute HCl (5%) and extracted with ethyl acetate. The organic layer was dried over Na_2SO_4 and evaporated under vacuum. Pure alcohol was obtained in 85–88% yield after column chromatography using petroleum ether/ethyl acetate (90:10) as eluent.

Spectral data of compounds **11e**[15] and **11f**[15] were in excellent agreement with those in the literature.

4.2.4. General procedure for the synthesis of propargyl alcohols. Procedure 1:[15] To a solution of aryl iodide (25 mmol) in dry THF (33 mL) was added Et_3N (7.29 mL), $PdCl_2(PPh_3)_2$ (351 mg, 0.5 mmol), and CuI (327 mg, 1.71 mmol) at room temperature. The mixture was stirred for 30 min and then terminal propargyl alcohol (25 mmol) in THF (10 mL) was added dropwise. The resulting mixture was stirred under an argon atmosphere for 6 h after which the suspension containing the precipitated ammonium salt was passed through a short 100–200 silica gel column eluting with ether. The solvents were concentrated, washed with brine, and dried over anhydrous Na_2SO_4. The crude product was purified by column chromatography and 82–90% yield of the title alcohol was isolated.

Spectral data of compounds **12a**,[15] **12b**,[15] **12c**,[15] **12d**,[19] **12e**,[20] **12f**,[15] and **12g**[21] were in excellent agreement with those in the literature.

Procedure 2:[15] To a light yellow solution of phenylacetylene (40 mmol) in Et_2O (50 mL) was added 1 equiv of *n*-butyllithium (hexane solution, 1.6 M) at −78 °C. After being stirred for a few minutes, the dark yellow solution was allowed to warm to 0 °C using an ice bath. After 15 min, a solution of 1.1 equiv of butanone in Et_2O (40 mL) was slowly added at 0 °C using a dropping funnel. The solution immediately turned red. After being stirred for 2 h, the thus-formed yellow solution was quenched with a saturated ammonium chloride solution. The organic layer was separated from the water layer. The water layer was extracted twice with diethyl ether. The combined organic fractions were then dried on anhydrous Na_2SO_4. After filtration, the solvent was evaporated. The product was purified by column chromatography and product was isolated in 75% yield.

Spectral data of compound **12h**[15] was in excellent agreement with that in the literature.

Procedure 3:[15] A dry Schlenk flask was charged with Pd/C (0.512 g, 0.5 mmol Pd), CuI (0.192 g, 1 mmol), and PPh_3 (0.262 g, 1 mmol), followed by DMA (9.5 mL) and water (0.5 mL). After the addition of *p*-dibromobenzene (2.36 g, 10 mmol), diisopropylamine (2.1 mL), and 2-methyl-3-butyn-2-ol (2.4 mL, 25 mmol), the reaction mixture was purged with argon, sealed, and placed in an 80 °C oil bath for 24 h. After the mixture was cooled to ambient temperature, the charcoal was filtered off and water was added to the solution. The aqueous

phase was extracted with diethyl ether, and the combined organic phases were dried over anhydrous Na_2SO_4. After removal of the solvent in a vacuum, the crude product was purified by column chromatography and propargyl alcohol was isolated in 68% yield.

Spectral data of compound **12i**[15] was in excellent agreement with that in the literature.

4.3. General procedure for the screening of various catalysts and optimization of benzylation reaction

A 10 mL Schlenk flask equipped with a magnetic bar was charged with catalyst (0.005 mmol for 1 mol % loading), toluene (105 μL, 1.0 mmol), *n*-nonane (as internal standard for GC), and solvent (2 mL). The flask was degassed with argon and placed into a constant temperature bath. After the mixture was stirred vigorously for 5 min, *para*-methylbenzyl alcohol (61 mg, 0.5 mmol) was added to it, and the reaction was allowed to continue at that specified temperature for 6 h. Known volume of aliquots was withdrawn from the reaction flask, filtered through a short pad of Celite, diluted with toluene, and the organic layer was analyzed with GC against *n*-nonane as internal standard.

4.4. General procedure for the alkylation reaction with π-activated alcohols catalyzed by 2

To a solution of π-activated alcohol (0.5 mmol) in 3 mL of dichloroethane or dichloromethane were added under an argon atmosphere **2** (5 mg, 0.005 mmol) and nucleophile (1.0 mmol). The reaction mixture was stirred at a specific temperature oil bath. When the reaction was over (monitored by TLC using ethyl acetate/petroleum ether 60–80 °C 1:3 v/v), a saturated aqueous solution of sodium hydrogen carbonate was added. The aqueous layer was then extracted two times with dichloromethane (2×5 mL). The combined organic layers were dried over sodium sulfate; the solvent was removed under reduced pressure. The resulting product was purified by column chromatography on silica gel to obtain the expected coupled products **13**, **14**, and **15**.

*4.4.1. Di-p-tolylmethane (**13a**).*[22] ^{1}H NMR (200 MHz, $CDCl_3$) δ (*ortho* isomer) 2.26 (s, 3H), 2.32 (s, 3H), 3.96 (s, 2H), 7.04–7.17 (m, 8H); (*para* isomer) 2.32 (s, 6H), 3.91 (s, 2H), 7.04–7.17 (m, 8H). ^{13}C NMR (54.6 MHz, $CDCl_3$) δ (*ortho* and *para* isomers) 19.8, 21.1, 39.1, 41.2, 126.1, 126.5, 127.7, 128.8, 128.9, 129.2, 129.4, 130.0, 135.5, 136.7, 137.4, 138.5, 139.3.

*4.4.2. 1,4-Dimethyl-2-(4-methylbenzyl)benzene (**13b**).*[23] ^{1}H NMR (200 MHz, $CDCl_3$) δ 2.15 (s, 3H), 2.25 (s, 6H), 3.83 (s, 2H), 6.80–7.00 (m, 7H).

*4.4.3. 2-Benzyl-1,4-dimethylbenzene (**13c**).*[23] ^{1}H NMR (200 MHz, $CDCl_3$) δ 2.22 (s, 3H), 2.31 (s, 3H), 3.97 (s, 2H), 6.96–7.30 (m, 8H). ^{13}C NMR (54.6 MHz, $CDCl_3$) 19.1, 20.9, 39.4, 125.8, 127.0, 128.3, 128.6, 130.2, 130.7, 133.4, 135.3, 138.6, 140.5.

*4.4.4. 2-(4-Chlorobenzyl)-1,4-dimethylbenzene (**13d**).*[24] ^{1}H NMR (200 MHz, $CDCl_3$) δ 2.20 (s, 3H), 2.32 (s, 3H), 3.95 (s, 2H), 6.95–7.32 (m, 7H).

*4.4.5. 2-(4-Bromobenzyl)-1,4-dimethylbenzene (**13e**).*[25] ^{1}H NMR (200 MHz, $CDCl_3$) δ 2.18 (s, 3H), 2.34 (s, 3H), 3.99 (s, 2H), 6.88–7.32 (m, 7H).

*4.4.6. 1-Benzyl-4-methoxybenzene (**13f**).*[26] *ortho* Isomer: ^{1}H NMR (200 MHz, $CDCl_3$) δ 3.87 (s, 3H), 4.03 (s, 2H), 6.90–7.36 (m, 9H). ^{13}C NMR (54.6 MHz, $CDCl_3$) δ 35.9, 55.4, 110.5, 120.5, 125.8, 127.5, 128.3, 129.0, 129.7, 130.4, 141.1, 157.4; *para* isomer: ^{1}H NMR: (200 MHz, $CDCl_3$) δ 3.81 (s, 3H), 4.07 (s, 2H), 6.86 (d, *J*=8.2 Hz, 2H), 7.14 (d, *J*=8.2 Hz), 7.16–7.39 (m, 5H). ^{13}C NMR (54.6 MHz, $CDCl_3$) δ 41.1, 55.3, 113.9, 125.7, 128.4, 128.8, 129.9, 133.3, 141.6, 158.0.

*4.4.7. 1-Benzyl-4-methylbenzene (**13g**).*[27] ^{1}H NMR (200 MHz, $CDCl_3$) δ 2.35 (s, 3H), 3.97 (s, 2H), 7.12–7.32 (m, 9H). ^{13}C NMR (54.6 MHz, $CDCl_3$) δ 20.9, 41.4, 125.9, 128.3, 128.7, 128.8, 129.0, 135.4, 138.0, 141.3.

*4.4.8. 1-Methoxy-4-(1-p-tolylethyl)benzene (**13h**).*[28] ^{1}H NMR (200 MHz, $CDCl_3$) δ 1.51 (d, *J*=7.2 Hz, 3H), 2.22 (s, 3H), 3.67 (s, 3H), 3.98 (q, *J*=7.2 Hz, 1H), 6.71–6.74 (m, 2H), 6.97–7.06 (m, 6H). ^{13}C NMR (54.6 MHz, $CDCl_3$) δ 21.2, 22.2, 43.6, 55.3, 113.8, 127.4, 128.5, 129.1, 135.4, 138.8, 143.9, 157.8.

*4.4.9. 2-(4-Chlorobenzyl)thiophene (**13i**).*[22] ^{1}H NMR (200 MHz, $CDCl_3$) δ (mixture of isomers) 3.98 (s, 2H), 4.16 (s, 2H), 6.84–6.99 (m, 4H), 7.16–7.33 (m, 10H). ^{13}C NMR (54.6 MHz, $CDCl_3$) δ (mixture of isomers) 35.3, 35.8, 121.4, 124.1, 125.3, 125.8, 126.8, 128.2, 128.5, 128.6, 128.9, 129.9, 130.0, 131.9, 132.2, 138.8, 139.0, 140.8, 143.3.

*4.4.10. 2-Methyl-5-(4-methylbenzyl)thiophene (**13j**).*[29] ^{1}H NMR (200 MHz, $CDCl_3$) δ 2.23 (s, 3H), 2.42 (s, 3H), 3.84 (s, 2H), 6.58 (d, *J*=3.2 Hz, 1H), 6.82 (d, *J*=3.2 Hz, 1H), 7.02 (d, *J*=7.8 Hz, 2H), 7.16 (d, *J*=7.8 Hz, 2H).

*4.4.11. 3-Benzhydryl-2,5-dimethylfuran (**13k**).*[3c] ^{1}H NMR (200 MHz, $CDCl_3$) δ 2.10 (s, 3H), 2.19 (s, 3H), 5.21 (s, 1H), 5.66 (s, 1H), 7.15–7.30 (m, 10H). ^{13}C NMR (54.6 MHz, $CDCl_3$) δ 11.7, 13.5, 47.5, 107.7, 121.8, 126.1, 128.2, 128.8, 144.1, 145.8, 149.2.

*4.4.12. 1-Phenyl-2-(1-phenylethyl)butane-1,3-dione (**13l**).*[3h] ^{1}H NMR (200 MHz, $CDCl_3$) δ (mixtures of diastereomers) 1.21 (d, *J*=6.8 Hz, 3H), 1.29 (d, *J*=7.0 Hz, 3H), 1.90 (s, 3H), 2.24 (s, 3H), 3.72–3.94 (m, 1H), 3.72–3.94 (m, 1H), 4.81 (d, *J*=11.2 Hz, 1H), 4.90 (d, *J*=11.0 Hz, 1H), 7.06–7.64 (m, 8H), 7.06–7.64 (m, 8H), 7.78 (d, *J*=7.2 Hz, 1H), 7.78 (d, *J*=7.2 Hz, 1H), 8.08 (d, *J*=7.2 Hz, 1H), 8.08 (d, *J*=7.2 Hz, 1H). ^{13}C NMR (54.6 MHz, $CDCl_3$): δ (mixtures of diastereomers) 20.3, 21.6, 27.6, 27.9, 40.4, 40.9, 70.8, 71.5, 126.6, 127.0, 127.4, 127.5, 128.5, 128.6, 128.9, 133.5, 133.9, 137.1, 137.2, 143.2, 143.5, 195.2 (2C), 203.2, 203.7.

*4.4.13. 1,3-Diphenyl-2-(1-p-tolylethyl)propane-1,3-dione (**13m**).*[3h] ^{1}H NMR (200 MHz, $CDCl_3$) δ 1.32 (d, *J*=7.0 Hz, 3H), 2.21 (s, 3H), 4.04 (dq, *J*=7.0 and 10.2 Hz, 1H), 5.59 (d, *J*=10.2 Hz, 1H), 6.98 (d, *J*=7.8 Hz, 2H), 7.14 (d, *J*=8.2 Hz, 2H), 7.24–7.46 (m, 2H), 7.48–7.60 (m, 4H), 7.74 (d, *J*=7.8 Hz, 2H), 8.03 (d, *J*=8.0 Hz, 2H). ^{13}C NMR (54.6 MHz, $CDCl_3$) δ 20.4, 20.9, 40.8, 65.1, 127.6, 128.5, 128.6, 128.8, 129.1, 133.0, 133.5, 136.1, 137.0, 137.2, 140.9, 194.7, 195.2.

*4.4.14. 3-(1-p-Tolylethyl)pentane-2,4-dione (**13n**).*[3h] ^{1}H NMR (200 MHz, $CDCl_3$) δ 1.18 (d, *J*=7.0 Hz, 3H), 1.84 (s, 3H), 2.26 (s, 3H), 2.29 (s, 3H), 3.55 (dq, *J*=7.0 and 11.4 Hz, 1H), 4.01 (d, *J*=11.4 Hz, 1H), 7.04–7.12 (m, 4H). ^{13}C NMR (54.6 MHz, $CDCl_3$) δ 20.9, 29.7, 40.1, 76.5, 127.1, 129.4, 136.4, 140.0, 203.6.

*4.4.15. 4-Hydroxy-3-(4-methylbenzyl)-2H-chromen-2-one (**13o**).*[30] ^{1}H NMR (200 MHz, $CDCl_3$) δ 2.37 (s, 3H), 4.15 (s, 2H), 6.05 (s, 1H), 7.11–7.41 (m, 6H), 7.47–7.55 (m, 1H), 7.64 (d, *J*=8.0 Hz, 1H). ^{13}C NMR (54.6 MHz, $CDCl_3$) δ 21.1, 40.4, 110.2, 116.2, 116.4, 123.0, 123.9, 127.3, 130.3, 131.8, 137.4, 138.6, 152.5, 160.1, 163.7.

*4.4.16. N-Benzyl-4-methylbenzenesulfonamide (**13p**).*[31] ^{1}H NMR (200 MHz, $CDCl_3$) δ 2.33 (s, 3H), 4.10 (d, *J*=6.2 Hz, 2H), 5.24 (m, 1H), 7.19–7.33 (m, 7H), 7.81 (d, *J*=8.0 Hz, 2H). ^{13}C NMR (54.6 MHz, $CDCl_3$) δ 21.4, 46.9, 127.1, 127.8, 127.9, 128.5, 129.5, 136.3, 137.1, 143.3.

*4.4.17. N-(4-Chlorobenzyl)benzenesulfonamide (**13q**).*[32] ^{1}H NMR (200 MHz, $CDCl_3$) δ 4.05 (d, *J*=6.3 Hz, 2H), 5.42 (m, 1H), 7.19–7.29 (m,

4H), 7.42–7.58 (m, 3H), 7.81 (d, *J*=7.8 Hz, 2H). ^{13}C NMR (54.6 MHz, $CDCl_3$) δ 46.2, 126.8, 128.7, 129.1, 129.4, 132.1, 133.5, 134.2, 139.9.

*4.4.18. (1-Ethoxyethyl)benzene (**13r**).*[33] ^{1}H NMR (200 MHz, $CDCl_3$) δ 1.23 (t, *J*=7.2 Hz, 3H), 1.46 (d, *J*=6.6 Hz, 3H), 3.40 (q, *J*=7.2 Hz, 2H), 4.45 (q, *J*=6.6 Hz, 1H), 7.26–7.41 (m, 5H). ^{13}C NMR (54.6 MHz, $CDCl_3$) δ 15.2, 23.1, 63.0, 77.9, 126.2, 127.2, 128.4, 128.6, 144.2.

*4.4.19. Benzhydryl(tert-butyl)sulfane (**13s**).*[34] ^{1}H NMR (200 MHz, $CDCl_3$) δ 1.26 (s, 9H), 5.21 (s, 1H), 7.15–7.46 (m, 10H). ^{13}C NMR (54.6 MHz, $CDCl_3$) δ 31.3, 52.2, 126.7, 128.3, 128.4, 143.2.

*4.4.20. (4-Methoxyphenyl)(1-phenylethyl)sulfane (**13t**).*[35] ^{1}H NMR (200 MHz, $CDCl_3$) δ 1.62 (d, *J*=7.0 Hz, 3H), 3.79 (s, 3H), 4.20 (q, *J*=7.0 Hz, 1H), 6.78 (d, *J*=8.6 Hz, 2H), 7.22–7.26 (m, 7H). ^{13}C NMR (54.6 MHz, $CDCl_3$) δ 21.8, 49.1, 55.2, 114.2, 125.1, 127.0, 127.3, 128.3, 136.0, 143.4, 159.6.

*4.4.21. (E)-1-Methoxy-4-(3-p-tolylallyl)benzene (**14a**).*[36] ^{1}H NMR (400 MHz, $CDCl_3$) δ 2.34 (s, 3H), 3.50 (d, *J*=6.6 Hz, 2H), 3.80 (s, 3H), 6.22–6.29 (m, 1H), 6.40 (d, *J*=15.6 Hz, 1H), 6.86 (d, *J*=8.6 Hz, 2H), 7.10–7.20 (m, 4H), 7.29 (d, *J*=8.2 Hz, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 21.1, 38.4, 55.2, 113.8, 125.9, 128.6, 129.1, 129.5, 130.5, 132.1, 134.5, 136.9, 158.7.

*4.4.22. 1-Cinnamyl-4-methoxybenzene (**14b**).*[36] ^{1}H NMR (200 MHz, $CDCl_3$): δ 3.49 (d, *J*=5.8 Hz, 2H), 3.79 (s, 3H), 6.34–6.41 (m, 2H), 6.86 (d, *J*=8.6 Hz, 2H), 7.15–7.39 (m, 7H). ^{13}C NMR (54.6 MHz, $CDCl_3$) δ 38.5, 55.3, 113.9, 126.1, 127.1, 128.5, 129.6, 129.7, 130.7, 132.2, 137.6, 158.6.

*4.4.23. (E)-1-Chloro-4-(3-(4-methoxyphenyl)prop-1-enyl)benzene (**14c**).*[36] ^{1}H NMR (400 MHz, $CDCl_3$) δ 3.48 (d, *J*=6.0 Hz, 2H), 3.79 (s, 3H), 6.28–6.39 (m, 1H), 6.43 (d, *J*=15.6 Hz, 1H), 6.90 (d, *J*=8.6 Hz, 2H), 7.20 (d, *J*=8.6 Hz, 2H), 7.24–7.40 (m, 4H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 38.3, 55.2, 113.8, 127.3, 128.7, 129.2, 129.7, 130.2, 131.8, 132.4, 136.0, 158.2.

*4.4.24. (E)-1-Bromo-4-(3-(4-methoxyphenyl)prop-1-enyl)benzene (**14d**).*[36] ^{1}H NMR (400 MHz, $CDCl_3$) δ 3.49 (d, *J*=4.9 Hz, 2H), 3.81 (s, 3H), 6.30–6.37 (m, 2H), 6.87 (d, *J*=8.8 Hz, 2H), 7.15 (d, *J*=8.8 Hz, 2H), 7.28 (d, *J*=8.6 Hz, 2H), 7.46 (d, *J*=8.6 Hz, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 38.4, 55.2, 113.9, 120.7, 127.4, 129.4, 130.5, 131.3, 131.8, 136.5, 157.9.

*4.4.25. 2-Cinnamylthiophene (**14e**).*[3i] ^{1}H NMR (200 MHz, $CDCl_3$) δ (2-cinnamylthiophene) 3.74 (d, *J*=6.4 Hz, 2H), 6.29–6.56 (m, 2H), 6.86–6.88 (m, 1H), 6.93–6.97 (m, 1H), 7.15–7.39 (m, 5H). (3-Cinnamylthiophene) 3.56 (d, *J*=5.8 Hz, 2H), 6.29–6.56 (m, 2H), 6.97–7.02 (m, 2H), 7.15–7.39 (m, 5H). ^{13}C NMR (54.6 MHz, $CDCl_3$): δ (2- and 3-cinnamylthiophene) 33.4, 33.8, 120.8, 123.7, 124.7, 125.6, 126.1, 126.2, 126.9, 127.1, 127.3, 128.2, 128.3, 128.5, 131.1, 131.4, 137.2, 140.5, 143.1.

*4.4.26. 2-Cinnamyl-5-methylfuran (**14f**).*[3i] ^{1}H NMR (200 MHz, $CDCl_3$) δ 2.29 (s, 3H), 3.53 (d, *J*=6.4 Hz, 2H), 5.91–597 (m, 2H), 6.23–6.39 (m, 1H), 6.52 (d, *J*=15.8 Hz, 1H), 7.19–7.42 (m, 5H). ^{13}C NMR (54.6 MHz, $CDCl_3$) δ 13.5, 31.9, 106.1, 106.3, 126.1, 126.2, 127.2, 128.5, 131.7, 137.4, 150.9, 152.0.

*4.4.27. 2-Cinnamyl-1,3-diphenylpropane-1,3-dione (**14g**).*[37] ^{1}H NMR (400 MHz, $CDCl_3$) δ 3.09 (t, *J*=6.6 Hz, 2H), 5.50 (t, *J*=6.6 Hz, 1H), 6.22–6.35 (m, 1H), 6.52 (d, *J*=15.8 Hz, 1H), 7.22–7.36 (m, 5H), 7.43–7.55 (m, 4H), 7.60–7.68 (m, 2H), 8.03 (d, *J*=7.8 Hz, 4H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 32.6, 56.8, 125.8, 126.4, 127.1, 128.2, 128.5, 128.7, 132.3, 133.4, 135.7, 136.9, 195.6.

*4.4.28. 3-Cinnamylpentane-2,4-dione (**14h**).*[37] ^{1}H NMR (400 MHz, $CDCl_3$) δ 2.13 (s, 3H), 2.22 (s, 3H), 2.74 (t, *J*=7.2 Hz, 1H), 3.16 (d, *J*=4.8 Hz, 1H), 6.00–6.50 (m, 2H), 7.21–7.38 (m, 5H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 23.1, 29.3, 30.4, 31.6, 68.3, 107.3, 125.4, 126.0, 126.1, 127.0, 127.4, 127.6, 128.4, 130.0, 132.6, 136.7, 136.9, 191.7, 203.8.

*4.4.29. 2-Cinnamyl-1-phenylbutane-1,3-dione (**14i**).*[37] ^{1}H NMR (400 MHz, $CDCl_3$) δ 2.15 (s, 3H), 2.80–2.90 (m, 2H), 4.60 (t, *J*=7.2 Hz, 1H), 6.11–6.21 (m, 1H), 6.50–6.55 (m, 1H), 7.20–7.30 (m, 5H), 7.45–7.50 (m, 2H), 7.55–7.65 (m, 1H), 8.01–8.05 (m, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 28.1, 32.2, 62.9, 125.5, 126.0, 126.2, 127.3, 128.4, 128.7, 128.8, 132.2, 133.5, 136.1, 136.9, 195.5, 203.3.

*4.4.30. (E)-2-(4-(4-Bromophenyl)but-3-en-2-yl)-1,3-diphenylpropane-1,3-dione (**14j**).*[3i] ^{1}H NMR (200 MHz, $CDCl_3$) δ 1.23 (d, *J*=6.8 Hz, 3H), 3.51–3.70 (m, 1H), 5.35 (d, *J*=8.0 Hz, 1H), 6.06–6.17 (dd, *J*=8.0 and 16.0 Hz, 1H), 6.31 (d, *J*=16.0 Hz, 1H), 6.98 (d, *J*=8.4 Hz, 2H), 7.29–7.59 (m, 8H), 7.93–8.03 (m, 4H). ^{13}C NMR (54.6 MHz, $CDCl_3$) δ 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.

*4.4.31. (E)-4-Hydroxy-3-(4-phenylbut-3-en-2-yl)-2H-chromen-2-one (**14k**).*[3i] ^{1}H NMR (200 MHz, $CDCl_3$) δ 1.51 (d, *J*=7.0 Hz, 3H), 4.17–4.22 (m, 1H), 6.61–6.71 (m, 1H), 6.78 (d, *J*=16.0 Hz, 1H), 7.19–7.55 (m, 8H), 7.77 (d, *J*=7.8 Hz, 1H). ^{13}C NMR (54.6 MHz, $CDCl_3$) δ 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.

*4.4.32. (E)-(3-Ethoxyprop-1-enyl)benzene (**14l**).*[38] ^{1}H NMR (200 MHz, $CDCl_3$) δ 1.33 (t, *J*=7.0 Hz, 3H), 3.59 (q, *J*=7.0 Hz, 2H), 4.15 (d, *J*=6.0 Hz, 2H), 6.33 (dt, *J*=6.0 and 15.9 Hz, 1H), 6.60 (d, *J*=15.9 Hz, 1H), 7.15–7.50 (m, 5H).

*4.4.33. (E)-(3-tert-Butoxyprop-1-enyl)benzene (**14m**).*[38] ^{1}H NMR (200 MHz, $CDCl_3$) δ 1.22 (s, 9H), 4.05 (d, *J*=5.3 Hz, 2H), 6.20 (dt, *J*=5.3 and 15.8 Hz, 1H), 6.60 (d, *J*=15.8 Hz, 1H), 7.15–7.40 (m, 5H).

*4.4.34. N-Cinnamyl-4-methylbenzenesulfonamide (**14n**).*[3i] ^{1}H NMR ($CDCl_3$, 400 MHz) δ 2.41 (s, 3H), 3.75 (t, *J*=6.4 Hz, 2H), 4.63–4.64 (m, 1H), 5.97–6.04 (m, 1H), 6.43 (d, *J*=16.0 Hz, 1H), 7.23–7.31 (m, 7H), 7.78 (d, *J*=8.0 Hz, 2H). ^{13}C NMR ($CDCl_3$, 100 MHz) δ 21.4, 45.4, 124.0, 126.4, 127.1, 127.8, 128.5, 129.7, 133.0, 136.0, 137.1, 143.5.

*4.4.35. N-Cinnamyl-4-methyl-N-phenylbenzenesulfonamide (**14o**).*[3i] ^{1}H NMR (200 MHz, $CDCl_3$) δ 2.45 (s, 3H), 4.36 (d, *J*=6.4 Hz, 2H), 6.05–6.19 (m, 1H), 6.40 (d, *J*=16.0 Hz, 1H), 7.08–7.36 (m, 12H), 7.55 (d, *J*=8.4 Hz, 2H). ^{13}C NMR (54.6 MHz, $CDCl_3$) δ 21.5, 53.3, 124.1, 126.4, 127.8, 128.5, 128.9, 129.4, 133.7, 135.7, 136.3, 139.3, 143.4.

*4.4.36. N-Cinnamyl-N-phenylmethanesulfonamide (**14p**).*[3i] ^{1}H NMR (200 MHz, $CDCl_3$) δ 2.96 (s, 3H), 4.46 (d, *J*=6.6 Hz, 2H), 6.15–6.29 (dd, *J*=6.6 and 15.8 Hz, 1H), 6.49 (d, *J*=15.8 Hz, 1H), 7.24–7.40 (m, 10H). ^{13}C NMR (54.6 MHz, $CDCl_3$): δ 38.3, 53.4, 123.9, 126.4, 127.9, 128.0, 128.5, 129.4, 134.1, 136.1, 139.3.

*4.4.37. tert-Butyl(cinnamyl)sulfane (**14q**).*[7q] ^{1}H NMR (200 MHz, $CDCl_3$) δ 1.22 (s, 9H), 3.67 (d, *J*=5.1 Hz, 2H), 6.48 (dt, *J*=5.2 and 15.9 Hz, 1H), 6.66 (d, *J*=15.9 Hz, 1H), 7.15–7.44 (m, 5H).

*4.4.38. Cinnamyl(4-methoxyphenyl)sulfane (**14r**).*[7q] ^{1}H NMR (200 MHz, $CDCl_3$) δ 3.58 (d, *J*=6.0 Hz, 2H), 3.78 (s, 3H), 6.21–6.25 (m, 2H), 6.82 (d, *J*=8.6 Hz, 2H), 7.21–7.30 (m, 5H), 7.37 (d, *J*=8.6 Hz, 2H). ^{13}C NMR (54.6 MHz, $CDCl_3$) δ 39.3, 55.3, 114.5, 125.6, 125.7, 126.3, 127.5, 128.5, 132.5, 134.4, 136.9, 159.3.

*4.4.39. 2-(But-2-enyl)-1,4-dimethylbenzene (**14s**).*[3q] (Mixture of *E* and *Z* isomers) ^{1}H NMR (200 MHz, $CDCl_3$) δ 1.67–1.71 (m, 3H), 2.26 (s, 3H), 2.31 (s, 3H), 3.27 (d, *J*=5.5 Hz, 2H), 5.47–5.54 (m, 2H), 6.96–7.06 (m, 3H). ^{13}C NMR (54.6 MHz, $CDCl_3$) δ 12.8, 17.8, 18.8, 18.9,

20.9, 29.7, 31.0. 36.5, 124.5, 125.2, 126.0, 126.7, 128.6, 129.3, 129.4, 129.7, 130.0, 133.0, 135.3, 138.9.

*4.4.40. (E)-1-(But-2-enyl)-4-methoxybenzene (**14t**).*[39] ^{1}H NMR (200 MHz, $CDCl_3$) δ 1.68 (d, J=6.0 Hz, 3H), 3.26 (d, J=6.0 Hz, 2H), 3.79 (s, 3H), 5.44–5.64 (m, 2H), 6.83 (d, J=8.8 Hz, 2H), 7.10 (d, J=8.8 Hz, 2H). ^{13}C NMR (54.6 MHz, $CDCl_3$) δ 17.8, 38.1, 55.2, 113.7, 125.9, 129.3, 130.4, 133.1, 157.8.

*4.4.41. 2-(But-2-enyl)-1,3,5-trimethoxy benzene (**14u**).*[40] ^{1}H NMR (400 MHz, $CDCl_3$) δ (*E* isomer) 1.65 (d, J=6.4 Hz, 3H), 3.29 (d, J=6.0 Hz, 2H), 3.83 (s, 9H), 5.40–5.52 (m, 1H), 5.55–6.62 (m, 1H), 6.18 (s, 2H). (*Z* isomer) 1.80 (d, J=5.5 Hz, 3H), 3.39 (d, J=5.5 Hz, 2H), 3.82 (s, 9H), 5.40–5.51 (m, 1H), 5.56–5.63 (m, 1H), 6.18 (s, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ (*E* and *Z* isomers) 12.6, 17.7, 20.6, 25.6, 55.2, 55.6, 55.8, 90.6, 109.9, 110.2, 123.0, 124.1, 129.4, 129.6, 158.5, 159.2.

*4.4.42. 2-(Hex-2-enyl)-1,4-dimethylbenzene (**14v**).*[3a] (Mixture of *E* and *Z* isomers) ^{1}H NMR (200 MHz, $CDCl_3$) δ 0.90 (t, J=7.0 Hz, 3H), 1.28–1.48 (m, 2H), 1.95–2.05 (m, 2H), 2.25 (s, 3H), 2.31 (s, 3H), 3.28 (d, J=5.3 Hz, 2H), 5.46–5.53 (m, 2H), 6.92–7.06 (m, 3H). ^{13}C NMR (54.6 MHz, $CDCl_3$) δ 13.4, 18.5, 20.6, 22.3, 34.3, 36.3, 126.4, 127.8, 129.4, 129.6, 131.2, 132.7, 135.0, 138.6.

*4.4.43. 1-Methoxy-4-(2-methyl-4-p-tolylbut-3-yn-2-yl)benzene (**15a**).*[3g] ^{1}H NMR (200 MHz, $CDCl_3$) δ 1.65 (s, 6H), 2.34 (s, 3H), 3.81 (s, 3H), 6.87 (dd, J=2.2 and 8.8 Hz, 2H), 7.10 (d, J=7.8 Hz, 2H), 7.34 (d, J=7.8 Hz, 2H), 7.53 (dd, J=2.2 and 8.8 Hz, 2H). ^{13}C NMR (54.6 MHz, $CDCl_3$) δ 21.4, 31.9, 35.7, 55.2, 81.8, 96.0, 113.5, 120.8, 126.6, 128.9, 131.4, 137.5, 139.4, 158.1.

*4.4.44. 1-Methoxy-4-(2-methyl-4-phenylbut-3-yn-2-yl)benzene (**15b**).*[3g] ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.66 (s, 6H), 3.81 (s, 3H), 6.88 (dd, J=2.0 and 8.8 Hz, 2H), 7.29–7.33 (m, 3H), 7.45 (d, J=7.2 Hz, 2H), 7.54 (dd, J=2.0 and 8.8 Hz, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 31.8, 35.7, 55.2, 81.8, 96.7, 113.5, 123.8, 126.6, 127.6, 128.1, 131.5, 139.2, 158.0.

*4.4.45. 1-Chloro-4-(3-(4-methoxyphenyl)-3-methylbut-1-ynyl)benzene (**15c**).*[3g] ^{1}H NMR (200 MHz, $CDCl_3$) δ 1.68 (s, 6H), 3.85 (s, 3H), 6.92 (dd, J=2.2 and 9.0 Hz, 2H), 7.27–7.33 (m, 2H), 7.37–7.42 (m, 2H), 7.56 (dd, J=2.2 and 9.0 Hz, 2H). ^{13}C NMR (54.6 MHz, $CDCl_3$) δ 31.7, 35.7, 55.3, 80.7, 97.9, 113.6, 122.4, 126.6, 128.5, 132.8, 133.6, 138.9, 158.1.

*4.4.46. 1-Bromo-4-(3-(4-methoxyphenyl)-3-methylbut-1-ynyl)benzene (**15d**).*[41] ^{1}H NMR (200 MHz, $CDCl_3$) δ 1.62 (s, 6H), 3.82 (s, 3H), 6.96 (dd, J=2.2 and 9.0 Hz, 2H), 7.26–7.36 (m, 2H), 7.39–7.44 (m, 2H), 7.52 (dd, J=2.2 and 9.0 Hz, 2H). ^{13}C NMR (54.6 MHz, $CDCl_3$) δ 31.4, 35.8, 55.2, 80.4, 97.8, 113.5, 122.9, 126.7, 128.8, 132.9, 133.5, 138.5, 158.2.

*4.4.47. 1-Methoxy-4-(4-p-tolylbut-3-yn-2-yl)benzene (**15e**).*[3g] (*para* Isomer) ^{1}H NMR (200 MHz, $CDCl_3$) δ 1.55 (d, J=7.0 Hz, 3H), 2.34 (s, 3H), 3.80 (s, 3H), 3.93 (q, J=7.0 Hz, 1H), 6.88 (d, J=8.0 Hz, 2H), 7.10 (d, J=8.0 Hz, 2H), 7.31–7.39 (m, 4H); ^{13}C NMR (54.6 MHz, $CDCl_3$) δ 21.4, 24.6, 31.6, 55.3, 82.2, 92.1, 113.9, 120.7, 127.9, 128.9, 131.5, 135.6, 137.7, 158.3; (*ortho* isomer) ^{1}H NMR (200 MHz, $CDCl_3$) δ 1.49 (d, J=7.0 Hz, 3H), 2.33 (s, 3H), 3.85 (s, 3H), 4.38 (q, J=7.0 Hz, 1H), 6.84–7.67 (m, 8H); ^{13}C NMR (54.6 MHz, $CDCl_3$) δ 21.4, 23.0, 26.1, 55.4, 81.7, 92.3, 110.4, 120.7, 120.9, 127.7, 127.9, 128.9, 131.5, 131.8, 137.5, 156.0. Anal. Calcd for $C_{18}H_{18}O$ (250.14): C, 86.36; H, 7.25. Found: C, 86.69; H, 7.46.

*4.4.48. 1,2,3-Trimethoxy-4-(2-methyl-4-phenylbut-3-yn-2-yl)benzene (**15f**).*[3g] ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.73 (s, 6H), 3.86 (s, 3H), 3.87 (s, 3H), 3.98 (s, 3H), 6.61 (d, J=8.8 Hz, 1H), 7.25–7.29 (m, 4H), 7.41–7.44 (m, 2H). ^{13}C NMR (54.6 MHz, $CDCl_3$) δ 30.1, 34.9, 55.9, 60.4, 60.6, 80.6, 98.1, 106.0, 120.9, 124.2, 127.4, 128.1, 131.4, 131.7, 142.8, 152.7, 152.8.

*4.4.49. 1,3,5-Trimethoxy-2-(4-phenylbut-3-yn-2-yl)benzene (**15g**).*[3g] ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.51 (d, J=7.2 Hz, 3H), 3.81 (s, 3H), 3.84 (s, 6H), 4.54 (q, J=7.2 Hz, 1H), 6.16 (s, 2H), 7.21–7.24 (m, 3H), 7.36–7.38 (m, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 20.3, 21.0, 55.3, 55.9, 78.1, 91.3, 94.4, 112.1, 124.7, 126.9, 128.0, 131.5, 158.6, 159.8.

*4.4.50. 4-(4-Phenylbut-3-yn-2-yl)phenol (**15h**).*[42] ^{1}H NMR (200 MHz, $CDCl_3$) δ 1.46 (d, J=7.2 Hz, 3H), 3.98 (q, J=7.2 Hz, 1H), 6.88 (d, J=8.0 Hz, 2H), 7.14 (d, J=8.0 Hz, 2H), 7.20–7.42 (m, 5H). ^{13}C NMR (54.6 MHz, $CDCl_3$) δ 22.5, 27.6, 82.1, 91.9, 115.5, 122.2, 128.3, 128.5, 129.1, 132.2, 153.4.

*4.4.51. 2-(2-Methyl-4-phenylbut-3-yn-2-yl)furan (**15i**).*[3g] ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.66 (s, 6H), 6.23 (d, J=3.2 Hz, 1H), 6.31 (dd, J=2.0 and 3.2 Hz, 1H), 7.27–7.28 (m, 3H), 7.36 (d, J=2.0 Hz, 2H), 7.40–7.44 (m, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 29.0, 32.6, 80.7, 94.1, 103.7, 109.9, 123.4, 127.7, 128.1, 131.6, 141.4, 158.9.

*4.4.52. 2-Methyl-5-(2-methyl-4-phenylbut-3-yn-2-yl)thiophene (**15j**).*[43] ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.70 (s, 6H), 2.44 (s, 3H), 6.58 (d, J=3.2 Hz, 1H), 6.81 (d, J=3.2 Hz, 1H), 7.26–7.48 (m, 5H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 15.3, 32.6, 34.3, 81.2, 95.8, 122.2, 123.7, 124.4, 127.7, 128.1, 131.5, 137.8, 150.3.

*4.4.53. 2-(2-Methyl-4-phenylbut-3-yn-2-yl)thiophene (**15k**).* ^{1}H NMR (200 MHz, $CDCl_3$) δ 1.75 (s, 6H), 6.92–6.97 (m, 1H), 7.06–7.08 (m, 1H), 7.16–7.19 (m, 1H), 7.22–7.36 (m, 3H), 7.42–7.47 (m, 2H); ^{13}C NMR (54.6 MHz, $CDCl_3$) δ 32.8, 81.3, 95.7, 122.7, 123.4, 123.5, 126.5, 127.8, 128.2, 131.6, 152.8. Anal. Calcd for $C_{15}H_{14}S$ (226.08): C, 79.60; H, 6.23. Found: C, 79.76; H, 6.51.

*4.4.54. 2-(2-Methyl-4-phenylbut-3-yn-2-yl)benzofuran (**15l**).*[3g] ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.76 (s, 6H), 6.66 (s, 1H), 7.18–7.30 (m, 6H), 7.43–7.51 (m, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 28.8, 33.0, 81.2, 93.4, 100.8, 111.0, 120.6, 122.5, 123.2, 123.5, 127.8, 128.1, 128.5, 131.6, 154.8, 162.0.

*4.4.55. (3-Methylhex-5-en-1-ynyl)benzene (**15m**).*[42] ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.31 (d, J=7.2 Hz, 3H), 2.27–2.44 (m, 2H), 2.72–2.84 (m, 1H), 5.11–5.20 (m, 2H), 5.92–6.06 (m, 1H), 7.26–7.46 (m, 5H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 20.5, 26.4, 41.1, 82.1, 94.0, 116.1, 124.1, 127.5, 128.1, 131.6, 136.0.

*4.4.56. 3-(2-Methyl-4-phenylbut-3-yn-2-yl)pentane-2,4-dione (**15n**).*[44] ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.59 (s, 6H), 2.18 (s, 6H), 4.22 (s, 1H), 7.23–7.43 (m, 5H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 28.6, 30.1, 31.1, 35.2, 42.2, 83.7, 91.6, 122.8, 128.1, 128.2, 131.6, 203.6.

*4.4.57. (3-Ethoxy-3-methylbut-1-ynyl)benzene (**15o**).*[3g] ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.24 (t, J=7.2 Hz, 3H), 1.55 (s, 6H), 3.68 (q, J=7.2 Hz, 2H), 7.29–7.30 (m, 3H), 7.41–7.43 (m, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 15.8, 29.3, 59.4, 70.2, 83.7, 91.6, 122.9, 128.0, 128.1, 131.6.

*4.4.58. (3-(Hex-2-enyloxy)-3-methylbut-1-ynyl)benzene (**15p**).*[3g] ^{1}H NMR (400 MHz, $CDCl_3$) δ 0.89 (t, J=7.6 Hz, 3H), 1.37–1.42 (m, 2H), 1.57 (s, 6H), 2.04–2.11 (m, 2H), 4.23 (d, J=5.6 Hz, 2H), 5.55–5.61 (m, 2H), 7.29–7.31 (m, 3H), 7.41–7.44 (m, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) 13.6, 22.6, 28.9, 60.1, 65.6, 70.5, 84.1, 91.4, 122.8, 126.7, 128.1, 128.2, 131.6, 133.1.

*4.4.59. 4-Methyl-N-(2-methyl-4-phenylbut-3-yn-2-yl)benzenesulfonamide (**15q**).*[3g] ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.65 (s, 6H), 2.26 (s,

3H), 4.68 (s, 1H), 7.05 (d, *J*=8.0 Hz, 2H), 7.11 (d, *J*=8.0 Hz, 2H), 7.20–7.28 (m, 3H), 7.78 (d, *J*=8.0 Hz, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 21.3, 30.9, 50.5, 83.2, 90.4, 122.3, 127.5, 127.8, 128.1, 129.3, 131.5, 138.4, 143.1.

*4.4.60. N-(4-(2,6-Dimethylphenyl)-2-methylbut-3-yn-2-yl)-4-methylbenzenesulfonamide (**15r**).* ^{1}H NMR (200 MHz, $CDCl_3$) δ 1.66 (s, 6H), 2.13 (s, 3H), 2.18 (s, 6H), 5.27 (br, 1H), 6.93–7.09 (m, 5H), 7.75 (d, *J*=8.2 Hz, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 20.6, 21.1, 31.0, 50.8, 80.9, 98.9, 122.1, 126.3, 127.3, 127.6, 129.0, 138.5, 140.1, 142.9. Anal. Calcd for $C_{20}H_{23}NO_2S$ (341.14): C, 70.35; H, 6.79; N, 4.10. Found: C, 70.48, H, 7.05, N, 4.41.

*4.4.61. (3-Methyl-1-phenylpent-1-yn-3-yl)(propyl)sulfane (**15s**).*[3g] ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.02 (t, *J*=7.4 Hz, 3H), 1.13 (t, *J*=7.2 Hz, 3H), 1.59 (s, 3H), 1.64–1.72 (m, 2H), 1.74–1.81 (m, 1H), 1.83–1.91 (m, 1H), 2.76 (t, *J*=7.2 Hz, 2H), 7.28–7.30 (m, 3H), 7.39–7.42 (m, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 9.8, 13.8, 22.9, 28.2, 32.2, 35.6, 43.7, 83.4, 92.5, 123.3, 127.8, 128.2, 131.6.

*4.4.62. 1,4-Bis(3-(4-methoxyphenylthio)-3-methylbut-1-ynyl)benzene (**15t**).* ^{1}H NMR (200 MHz, $CDCl_3$) δ 1.63 (s, 12H), 3.86 (s, 6H), 6.92 (d, *J*=8.8 Hz, 4H), 7.28–7.30 (m, 4H), 7.62 (d, *J*=8.8 Hz, 4H). ^{13}C NMR (54.6 MHz, $CDCl_3$) δ 30.3, 42.7, 55.5, 82.2, 95.9, 114.1, 123.0, 123.4, 131.4, 138.9, 160.9. Anal. Calcd for $C_{30}H_{30}O_2S_2$ (486.17): C, 74.04; H, 6.21. Found: C, 73.79; H, 6.59.

*4.4.63. (3-Methylbut-3-en-1-ynyl)benzene (**16**).*[3g] ^{1}H NMR (200 MHz, $CDCl_3$) δ 1.99 (s, 3H), 5.30 (d, *J*=3.2 Hz, 1H), 5.40 (d, *J*=3.2 Hz, 1H), 7.29–7.32 (m, 3H), 7.42–7.47 (m, 2H). ^{13}C NMR (54.6 MHz, $CDCl_3$) δ 23.5, 88.4, 90.5, 121.9, 123.2, 126.8, 128.1, 128.2, 131.5.

*4.4.64. 1,1-Dimethyl-3-(2,4,6-trimethoxyphenyl)-1H-indene (**17a**).*[3g] ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.47 (s, 6H), 3.69 (s, 6H), 3.86 (s, 3H), 6.22 (s, 2H), 6.29 (s, 1H), 6.93 (d, *J*=4.4 Hz, 1H), 7.16 (d, *J*=4.8 Hz, 2H), 7.34 (d, *J*=4.4 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 24.7, 48.6, 55.2, 55.9, 91.1, 106.2, 120.7, 120.8, 124.3, 125.9, 132.4, 143.9, 146.6, 153.1, 159.1, 160.6.

*4.4.65. 1,1,5-Trimethyl-3-(2,4,6-trimethoxyphenyl)-1H-indene (**17b**).*[3g] ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.40 (s, 6H), 2.39 (s, 3H), 3.69 (s, 6H), 3.86 (s, 3H), 6.22 (s, 3H), 6.82 (d, *J*=7.6 Hz, 1H), 6.98 (d, *J*=7.6 Hz, 1H), 7.17 (s, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 21.5, 24.9, 48.5, 55.3, 55.9, 91.2, 106.5, 120.5, 121.8, 126.7, 132.3, 134.1, 141.4, 145.8, 153.4, 159.2, 160.6.

4.5. General procedure for the Hammett correlation study

A 10-mL Schlenk flask equipped with a magnetic bar, was charged with catalyst **2** (2.6 mg, 0.0025 mmol), arene (4–5 mmol), DCE (1.5 mL), and internal standard for GC. The flask was degassed with argon and placed into a constant temperature bath. After the mixture was stirred vigorously for 5 min, the corresponding alcohol (0.25 mmol) was added to it, and the reaction was allowed to continue at the specific temperature. Known volume of aliquot was withdrawn periodically, filtered through a short pad of Celite, diluted with dichloroethane, and the organic layer was analyzed with GC against *n*-nonane/*n*-decane as internal standard.

4.5.1. General note on gas chromatography analysis. Benzylation kinetics. GC analysis was performed using a flame ionization detector using 6 ft×1/8 inch×2 mm SS 10% Silicone OV-1 packed column (from Chrompack). *n*-Nonane was used as internal standard. The analytical conditions are as follows: injector temperature: 130 °C; detector temperature: 240 °C; career gas (N_2) flow: 1.9 bar; oven temperature program: 80 °C—1 min—5 °C/min—100 °C—20 °C/min—160 °C—20 min.

Allylation kinetics. GC analysis was performed using a flame ionization detector using 30 m×0.25 mm×0.25 μm SS 100% dimethyl polysiloxane capillary column. *n*-Decane was used as internal standard. The analytical conditions are as follows: injector temperature: 200 °C; detector temperature: 280 °C; career gas (N_2) flow: 1.75 bar; oven temperature program: 55 °C—7 min—5 °C/min—170 °C—1 min—30 °C/min—275 °C—15 min.

Propargylation kinetics. GC analysis was performed using a flame ionization detector using 30 m×0.25 mm×0.25 μm SS 100% dimethyl polysiloxane capillary column. *n*-Nonane was used as internal standard. The analytical conditions are as follows: injector temperature: 200 °C; detector temperature: 280 °C; career gas (N_2) flow: 1.75 bar; oven temperature program: 60 °C—6 min—5 °C/min—170 °C—1 min—30 °C/min—275 °C—7 min.

Acknowledgements

We thank DST (financial support to S.R.), UGC (fellowship to A.K.M.) and CSIR (fellowship to P.N.C.). S.R. thanks Prof. Manish Bhattacharjee for helpful discussions, support, and encouragement.

Supplementary data

Supplementary data associated with this article can be found in the online version, at http://dx.doi.org/10.1016/j.tet.2012.10.086.

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