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Propargylic Activation Across a Heterobimetallic Ir−Sn Catalyst: Nucleophilic Substitution and Indene Formation with Propargylic Alcohols

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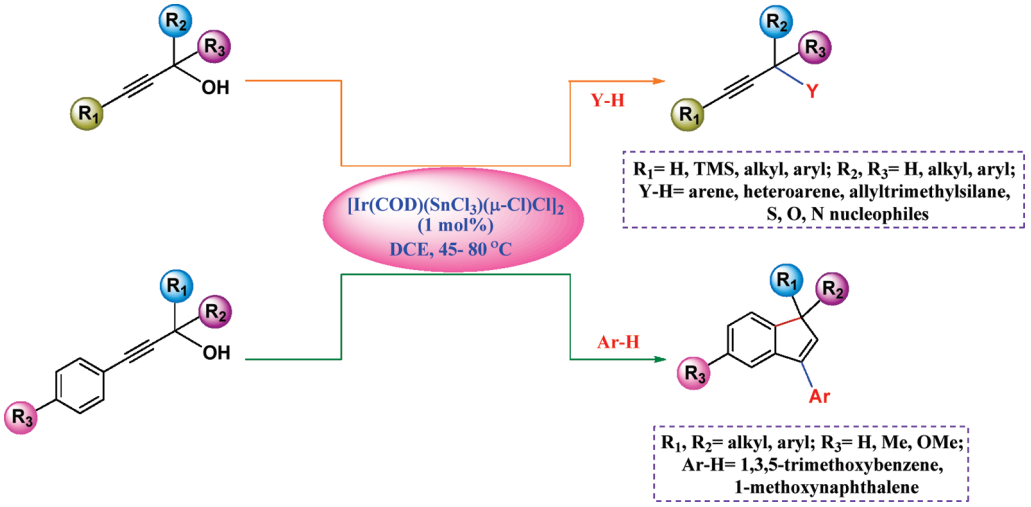

A nucleophilic substitution of propargylic alcohols with carbon (arene, heteroarene, and allyltrimethylsilane), sulfur (thiol), oxygen (alcohol), and nitrogen (sulfonamide) nucleophiles has been demonstrated using a high-valent $[Ir(COD)(SnCl_3)Cl(\mu\text{-}Cl)]_2$ catalyst in 1,2-dichloroethane to afford the corresponding propargylic products in moderate to excellent yields. Alkyl or aryl substituted tertiary propargylic alcohols produce substituted indenes with bulky arenes via allenylic intermediate. An electrophilic mechanism is proposed from Hammett correlation.

Introduction

Heterobimetallic catalysis constitutes an important subarea within the broader domain of multimetallic catalysis. The successful design of homogeneous heterobimetallic catalysts is a topic of ongoing interest.[1−5] This is mainly due to the fact that the incorporation of two metals in a single scaffold often results in selective substrate binding, dual and synergistic activation, and higher efficiency toward coupling.[6,7] Obviously, the success of such bimetallic catalysis truly depends on the stereoelectronic features of and around the two metals, and their ability to communicate during substrate binding and activation. Our continuing success in dual-reagent catalysis involving a transition metal partner and tin as a main group metal partner[8] led us to propose a new heterobimetallic catalysis concept within the Ir−Sn domain for the activation of different electrophiles, for

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example, benzyl alcohols, ethers, and aldehydes.[9] Keeping in view the importance of metal-catalyzed activation of propargylic substrates (see later) and our own enthusiasm,[10] we became interested to test whether the heterobimetallic motif is amenable toward propargylic activation. The success of our endeavor is presented in this article, which demonstrates the profound reactivity of the Ir−Sn catalyst $[Ir(COD)(SnCl_3)Cl(\mu\text{-}Cl)]_2$ for the activation of propargylic alcohols as electrophiles, bearing both terminal and internal alkyne moieties, and their nucleophilic substitution with various carbon (arene, heteroarene and allyltrimethylsilane), sulfur (thiol), oxygen (alcohol), and nitrogen (sulfonamide) nucleophiles in a regioselective manner with high turnover frequency (TOF). Additionally, the Ir−Sn catalyst is also capable of steering a ring-closure with the formation of 1,3-substituted indenes from alkyl- and aryl-substituted tertiary phenyl propargylic alcohols and bulky arenes like 1,3,5-trimethoxybenzene or 1-methoxynaphthalene, where the steric factor possibly plays a pivotal role. Motifs bearing indenes as core structures constitute an integral part of a number of natural products and bioactive pharmaceutical compounds.[11] They are also well-exploited as building blocks for functional materials[12] and as ligands in metallocene-based olefin polymerization catalysts.[13]

Transition-metal-catalyzed nucleophilic substitution reactions involving propargylic alcohol and its surrogates remain one of the demanding transformations because of the ease of transposing the flexible alkyne moiety to a variety of functional groups. Often the products of the propargylic substitution reactions are also interesting building blocks for different complex natural product syntheses, for example, *O*-methyldetrol, mimosifoliol, and β-apopicropodophyllin.[14,15] In this context, one may note that there are few successful reports of catalytic propargylic substitution reaction of propargylic alcohols and their derivatives with carbon and heteroatom-centered nucleophiles. A variety of transition metals, such as Ru, Re, Rh, Ir, Ni, Pd, Pt, and Cu, form organometallic species as intermediates, and several Lewis acids and Brønsted acids are also applicable as catalysts in these reactions.[16] Likewise, many synthetic methods have demonstrated the formation of indene skeletons from propargylic derivatives.[17] Notably, it may be emphasized here that, to the best of our knowledge, only four recent reports are available where indenes are produced directly from propargylic alcohols in the presence of Lewis acid catalysts.[18]

Results and Discussions

For model studies we had chosen 2-methyl-4-phenyl-but-3-yn-2-ol **1a** (having β-H) as representative alcohol and anisole **2a** as the arene in the presence of 1 mol % of $Ir^{III}-Sn^{IV}$ bimetallic catalyst and in 1,2-dichloroethane (DCE) as solvent. Initial catalyst screening included both heterobimetallic and monometallic catalysts (Table 1).

The catalytic efficiency of the Ir−Sn heterobimetallic catalyst $[Ir(COD)(SnCl_3)Cl(\mu\text{-}Cl)]_2$ was highest and the desired propargylic product **3aa** was obtained in 75% yield after 3 h (Table 1, entry 1). Other heterobimetallic catalysts

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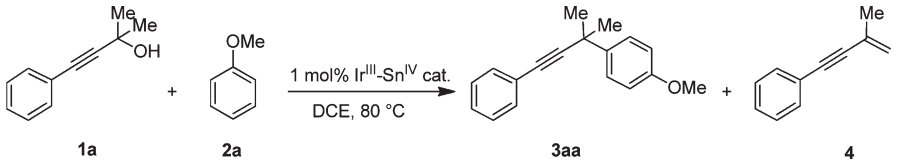
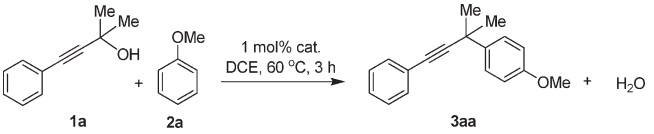
SCHEME 1. Propargylation Reaction: Model Study with Alcohol 1a and Arene 2a



bearing the Ir−Sn and Rh−Sn motif also promoted the reaction but at varying efficiencies (entries 2−5). In contrast, individually $[Ir(COD)(\mu\text{-Cl})]_2$ was inactive, while $SnCl_4$ was poorly active. Even $IrCl_3$ and cationic Ir(I) species $[Ir(COD)(sol)]PF_6$ showed very low efficiency (entries 6−9). Both iron and bismuth chlorides also promoted the reaction (entries 10 and 11).

TABLE 1. Propargylation of Anisole 2a with Propargyl Alcohol 1a: Effect of Catalyst[a]



entry	catalyst	yield of **3aa** (%)	TOF (h^{-1})
1	$[Ir(\mu\text{-Cl})(COD)Cl(SnCl_3)]_2$	75	25.0
2	$[Ir(\mu\text{-Br})(COD)Br(SnBr_3)]_2$	60	20.0
3	$[Rh(\mu\text{-Cl})(COD)Cl(SnCl_3)]_2$	49	16.3
4	$[Rh(\mu\text{-Br})(COD)Br(SnBr_3)]_2$	41	13.7
5	$IrCl(CO)(PPh_3)_2(SnCl_4)$	7	2.3
6	$[Ir(COD)(\mu\text{-Cl})]_2$	0	0
7	$[Ir(COD)(sol)]PF_6$	15	5.0[b]
8	$IrCl_3$	5	1.6
9	$SnCl_4$	10	3.3
10	$FeCl_3$	59	19.7
11	$BiCl_3$	42	14.0[c]

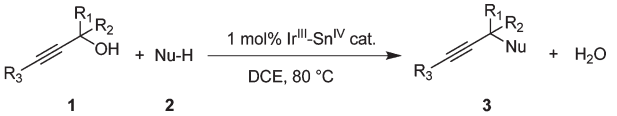
[a]Unless otherwise mentioned, reaction conditions are the following: alcohol **1a** (0.25 mmol), anisole **2a** (0.75 mmol), catalyst (0.0025 mmol), solvent DCE (1 mL), 60 °C for 3 h. [b]sol = MeCN. [c]1 mol % $BiCl_3$ was used from a stock solution of $BiCl_3$ in MeCN.

A reaction conducted at 80 °C using $[Ir(COD)(SnCl_3)Cl(\mu\text{-Cl})]_2$ as the catalyst and alcohol/arene ratio as 1:3 resulted in 78% of **3aa** along with about 10% of the eliminated product **4** after 75 min (Scheme 1). Under similar conditions, but with an alcohol/arene ratio of 1:1.5, the yields of **3aa** and **4** were 62 and 29%, respectively, after 2 h.

Next we examined the propargylic substitution using various propargylic alcohols and arenes, heteroarenes, allyltrimethylsilane, and heteroatom-centered nucleophiles in DCE at 80 °C in the presence of 1 mol % of catalyst. For convenience, the alcohol/nucleophile molar ratio was kept at 1:3, and the corresponding propargylic products were isolated in moderate to good yields (Table 2).

Propargylic alcohols bearing internal as well as terminal alkyne groups smoothly underwent the coupling reaction with electron-rich arenes and heteroarenes (Table 2, entries 1−15) with complete regioselectivity. Friedel-Crafts arylated products were isolated in excellent yields during the reaction of anisole, 1,2-dimethoxybenzene, 1,3,5-trimethoxybenzene, and 1-methoxynaphthalene with alcohols **1b** and **1c** (Table 2, entries 1−4). Propargylic alcohol bearing a terminal alkyne group gave lower yields with 1,3-dimethoxybenzene and 1-methoxynaphthalene (Table 2, entries 5 and 6). Propargylation occurred with complete regioselectivity in the case of

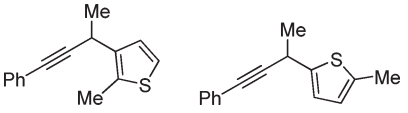
TABLE 2. Reactions of Various Propargylic Alcohols 1 with Nucleophiles 2[a]



Nu-H= C-, S-, O- and N- nucleophiles

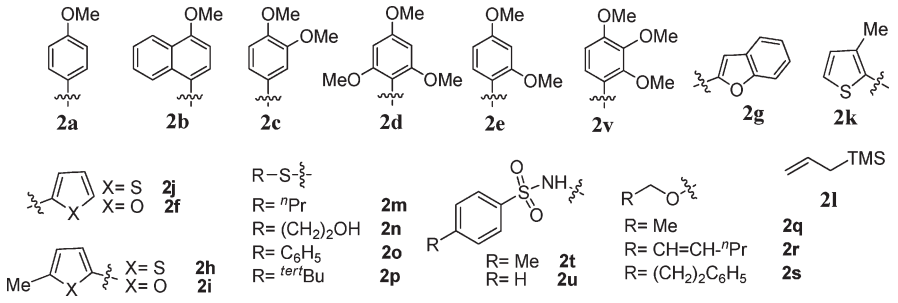
entry	**1**, R_1; R_2; R_3	Nu-H	time (min)	yield of **3** (%)
	Carbon Nucleophiles			
1	**1b**, H; 4-MeC_6H_4; Ph	**2b**	30	**3bb**, 92
2	**1b**	**2c**	30	**3bc**, 85
3	**1c**, H; 4-ClC_6H_4; Ph	**2a**	40	**3ca**, 81
4	**1c**	**2d**	15	**3cd**, 96
5	**1d**, H; 4-MeC_6H_4; H	**2b**	60	**3db**, 75
6	**1d**	**2e**	60	**3de**, 77
7	**1a**, Me; Me; Ph	**2f**	720	**3af**, 75[b]
8	**1a**	**2g**	75	**3ag**, 72
9	**1e**, H; Me; Ph	**2h**	360	**3eh**, 52[c]
10	**1f**, Me; Et; Ph	**2i**	60	**3fi**, 78
11	**1b**	**2i**	30	**3bi**, 85
12	**1b**	**2j**	30	**3bj**, 83
13	**1b**	**2k**	30	**3bk**, 90
14	**1d**	**2f**	1200	**3df**, 70[b]
15	**1c**	**2k**	40	**3ck**, 87
16	**1b**	**2l**	30	**3bl**, 95
17	**1c**	**2l**	30	**3cl**, 91
18	**1g**, Me; 4-MeC_6H_4; Ph	**2l**	30	**3gl**, 85
19	**1d**	**2l**	80	**3dl**, 75
20	**1h**, H; 4-MeC_6H_4; n-Bu	**2l**	45	**3hl**, 89
21	**1i**, H; 4-ClC_6H_4; TMS	**2l**	60	**3il**, 80
	Sulfur Nucleophiles			
22	**1f**	**2m**	45	**3fm**, 82
23	**1j**, H; Ph; Ph	**2n**	30	**3jn**, 75
24	**1d**	**2o**	75	**3do**, 79
25	**1g**	**2p**	30	**3gp**, 90
	Oxygen Nucleophiles			
26	**1a**	**2q**	600	**3aq**, 60
27	**1a**	**2r**	240	**3ar**, 75
28	**1j**	**2s**	180	**3js**, 70
	Nitrogen Nucleophiles			
29	**1a**	**2t**	90	**3at**, 80
30	**1b**	**2u**	50	**3bu**, 95
31	**1j**	**2t**	50	**3jt**, 90

[a]Unless otherwise mentioned, reaction conditions were as follows: alcohol (0.25 mmol), nucleophile (0.75 mmol), Ir−Sn cat. (0.0025 mmol), solvent DCE (1 mL), 80 °C. [b]Alcohol (0.25 mmol), furan (5.0 mmol), Ir−Sn cat. (0.0025 mmol), solvent DCE (1 mL), room temperature. [c]Ratio of the isomers of **3eh** is 3:1 [particular isomers could not be identified from NMR]:



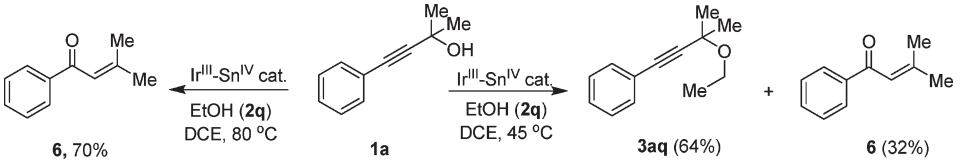
heteroarenes, for example, thiophene, furan, benzo[*b*]furan, 2-methylfuran, 2-methylthiophene, and 3-methylthiophene

CHART 1. Active Nucleophiles for Propargylation Reaction[a]



[a]The position of substitution is indicated by the truncated bond.

SCHEME 2. Meyer−Schuster-Type Rearrangement vs Etherification of Tertiary Propargylic Alcohol 1a in the Presence of Ethanol: Dependence of Temperature



in moderate to excellent yield (Table 2, entries 7, 8, and 10−15). Secondary aliphatic substrate **1e** reacted sluggishly to give only 52% of the desired product **3eh** and as a mixture of regioisomers (Table 2, entry 9). Because of the lower boiling point of furan, we used furan **2f** (Chart 1) in excess (20 equiv with respect to alcohol) and the reaction was conducted at room temperature. In case of tertiary aliphatic alcohols **1a** and **1f**, desired propargylic products were obtained in moderate yields along with a small amount of eliminated product (β-H elimination; Table 2, entries 7, 8, and 10). In all the cases, propargylation took place at the electron-rich center of the aromatic compounds. It may be mentioned that our attempts to activate alkyl-substituted aromatics using the bimetallic catalyst failed.

With the bimetallic $Ir^{III}-Sn^{IV}$ catalyst we next explored the coupling reactions of various propargylic alcohols with allyltrimethylsilane **2l** as a nucleophile. We were pleased to find that only 1 mol % of the catalyst in DCE at 80 °C successfully produced the substituted 1,5-enynes in excellent yields and no α,β-unsaturated ketones via the Meyer−Schuster-type rearrangement were detected.[19] The bimetallic complex efficiently catalyzed the substitution reaction of various aryl- and alkyl-substituted propargylic alcohols with excellent yields (Table 2, entries 16−21). We also noted that the reaction can tolerate moisture or air without comprising product yield. Substituents in the alkyne moiety, such as aryl, alkyl, or trimethylsilane (**1b−d**, **1g−i**) did not affect the course of the reaction. Propargylic alcohol **1d** bearing a terminal alkyne moiety was also allylated successfully (Table 2, entry 19) without any polymerization. The primary propargylic alcohol 3-phenylprop-2-yn-1-ol ($R_1 = R_2 = H$, $R_3 = Ph$) did not offer any coupling reaction with aromatic compounds as well as allytrimethylsilane in presence of the catalyst.

To explore the generality of the reaction further, we briefly examined the reaction of alcohols **1a**, **1b**, **1d**, **1f**, **1g**, and **1j** with representative sulfur, oxygen, and nitrogen nucleophiles (Table 2, entries 22−31). Generally sulfur-containing compounds are potential catalyst poisons due to their strong coordinating properties.[20,21] However, we could successfully construct a $C(sp^3)-S$ bond by the nucleophilic substitution of propargylic alcohols with varieties of thiols using 1 mol % of $Ir^{III}-Sn^{IV}$ catalyst. No Friedel−Crafts arylated product was obtained while using thiophenol **2o** as a nucleophile, and the propargylic sulfide **3do** was the only product (Table 2, entry 24). Facile reaction of **1f** and **1g** with 1-propanethiol **2m** and *tert*-butanethiol **2p** resulted in the formation of desired product **3fm** and **3gp**, respectively, with excellent yield. Propargylation of mercaptoethanol **2n** was 100% *S*-selective over competitive *O*-alkylation (Table 2, entry 23). Similar reactions of propargylic alcohols with *O*-nucleophiles were briefly examined and the desired ethers were obtained in moderate yields (Table 2, entry 26−28). Both aryl- and alkyl-substituted propargylic alcohols **1a** and **1j** underwent propargylic etherification to afford propargylic ethers in moderate yields with ethanol, hex-2-en-1-ol, and 3-phenylpropan-1-ol (**2q−2s**). Notably, in the presence of ethanol as nucleophile, rearranged enone **6** was isolated from **1a** as the sole product at 80 °C.[19,22] Upon reducing the temperature to 45 °C, the desired ether **3aq** along with α,β-unsaturated ketone **6** were obtained in a 2:1 ratio (Scheme 2). The formation of **6** could not be stopped even on further lowering of temperature to 25 °C. The reaction of

(19) Several catalysts have been employed to carry out the conversion of propargyl alcohols to enones (Meyer−Schuster rearrangement), see (a) Narasaka, K.; Kusama, H.; Hayashi, Y. *Tetrahedron* **1992**, *48*, 2059. (b) Yoshimatsu, M.; Naito, M.; Kawahigashi, M.; Shimizu, H.; Kataoka, T. *J. Org. Chem.* **1995**, *60*, 4798. (c) Lorber, C. Y.; Osborn, J. A. *Tetrahedron Lett.* **1996**, *37*, 853. (d) Fukuda, Y.; Utimoto, K. *Bull. Chem. Soc. Jpn.* **1991**, *64*, 2013.

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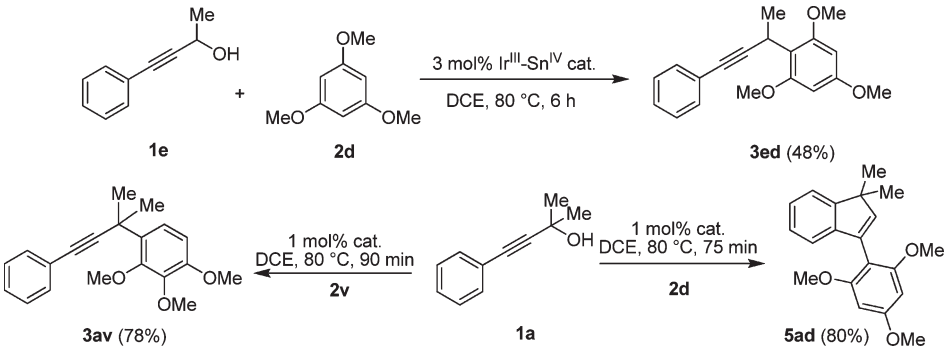
(22) Georgy, M.; Boucard, V.; Campagne, J. M. *J. Am. Chem. Soc.* **2005**, *127*, 14180.

SCHEME 3. Propargylation vs Indene Formation: Dependence of Both Propargylic Alcohol and Arene



propargylic alcohols with *N*-nucleophiles such as aniline, *N*,*N*-dimethylaniline, acetamide, and piperidine led to the formation of complex mixtures. Lesser nucleophilic substrates such as sulfonamides were amenable for the transformation. Thus, the reactions of alcohols **1a**, **1b**, and **1j** with *p*-toluenesulfonamide **2t** and benzene sulfonamide **2u** afforded the corresponding propargylated products in excellent yields (Table 2, entries 29−31).

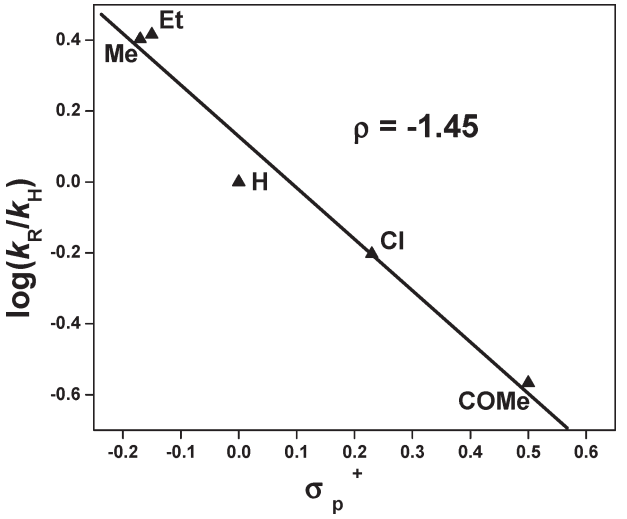


FIGURE 1. Hammett plot of $\log(k_R/k_H)$ vs σ_p^+ for propargylation of anisole with propargylic alcohols *p*-R-C_6H_4−C≡C−$C(Me)_2OH$ (R = Et, Me, H, Cl, COMe).

To test the likelihood of an electrophilic propargylation mechanism, we subjected the reaction to Hammett analysis and evaluated the reaction constant (ρ value). This was attempted by kinetic analysis using GC for the reaction of anisole **2a** with five different *para*-substituted propargylic alcohols *p*-R-C_6H_4−C≡C−$C(Me)_2OH$ (R = Et, Me, H, Cl, COMe) at 70 °C (details in the Supporting Information). The Hammett plot (Figure 1) resulted in a moderately negative ρ-value (−1.45). It indicates the possibility of the generation of a weak positive charge ($\delta+$) at the propargylic carbon due to the interaction of the alcohol with the bimetallic catalyst.

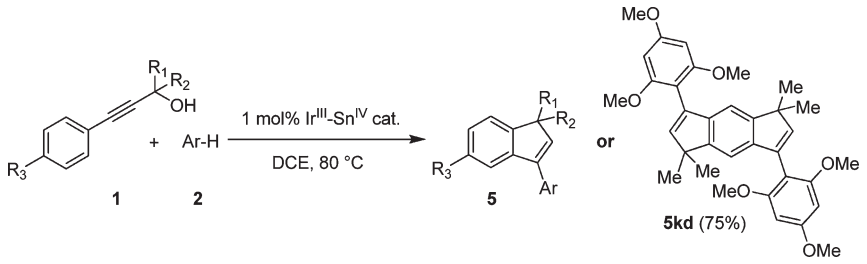
To gain preliminary insight into the initial activation of the propargylic alcohol across the [Ir−Sn] heterobimetallic catalyst, we undertook in situ 1D and 2D ^{1}H NMR studies using a representative alcohol PhC≡CCH(Ph)OH (**1j**). The spectrum of **2n** was recorded in C_6D_6 solvent in the absence of any reagent, as well as in the presence of (ii) heterobimetallic [Ir−Sn] catalyst $[Ir(\mu\text{-}Cl)(COD)Cl(SnCl_3)]_2$, (iii) $PhSnCl_3$ as a representative Sn(IV) species, and (iv) $[IrCp^*Cl_2]_2$ as a representative Ir(III) species. The results are briefly highlighted: (1) In the absence of any reagent, both the −C*H* and −O*H* protons of **1j** appeared as a doublet at 5.45 and 1.64 ppm, respectively, with a coupling constant of 6.0 Hz. The coupling between −C*H* and −O*H* protons was also supported by the COSY spectrum (see Supporting Information). (2) Upon the addition of the [Ir−Sn] catalyst, the initial doublet of the −C*H* proton of **1j** was converted to a singlet at 5.45 ppm, while the −O*H* proton became a broad singlet. The COSY spectrum clearly indicated the absence of coupling between the −C*H* and the −O*H* proton. (3) In presence of $PhSnCl_3$, the initial doublet of the −C*H* proton of **1j** was converted to a singlet at 5.44 ppm. The COSY spectrum also indicated the absence of coupling between the −C*H* and the −O*H* proton. (4) In the presence of $[IrCp^*Cl_2]_2$, the features of −C*H* and −O*H* protons of **1j** did not show any change from the original spectra.

From the above studies we conclude that the preactivation of the propargylic alcohol across the [Ir−Sn] catalyst involves initial coordination of the alcoholic −OH group at the hard Sn-center. Because Ir(III) alone does not influence either the propargylation reaction or the NMR features of **1j**, we therefore suggest that the enhanced efficiency of the [Ir−Sn] catalyst in our case could be due to the higher Lewis acidity of the Ir^{III}−Sn^{IV} bond compared to Sn(IV) alone. We are yet to understand the exact nature of the electronic perturbation in the metal−metal bond that causes the enhancement in Lewis acidity.

While extending the scope of the propargylation reaction, we had yet another interesting observation (Scheme 3). Secondary propargylic alcohol **1e** reacted with a sterically bulky arene such as 1,3,5-trimethoxybenzene **2d**, providing the desired propargylic product **3ed** in low yield (48%). In contrast, tertiary propargylic alcohol **1a** reacted with **2d**, resulting in the exclusive formation of 1,3-substituted indene **5ad** (80%), which may go via an allene intermediate.[18d] The influence of the steric effect in guiding the reaction became evident from the reaction of **1a** with isomeric arene 1,2,3-trimethoxybenzene **2v**, which afforded the desired propargylic product **3av** (78%).

The generality of the indene formation reaction was explored using aryl- and alkyl-substituted tertiary phenyl propargylic alcohols **1a**, **1f**, **1g**, **1k**, **1l**, **1m**, **1n**, and **1o** with bulky arenes such as **2b** and **2d** (Table 3, entries 1−8). The structures of **5ad** and **5kd** were established by X-ray

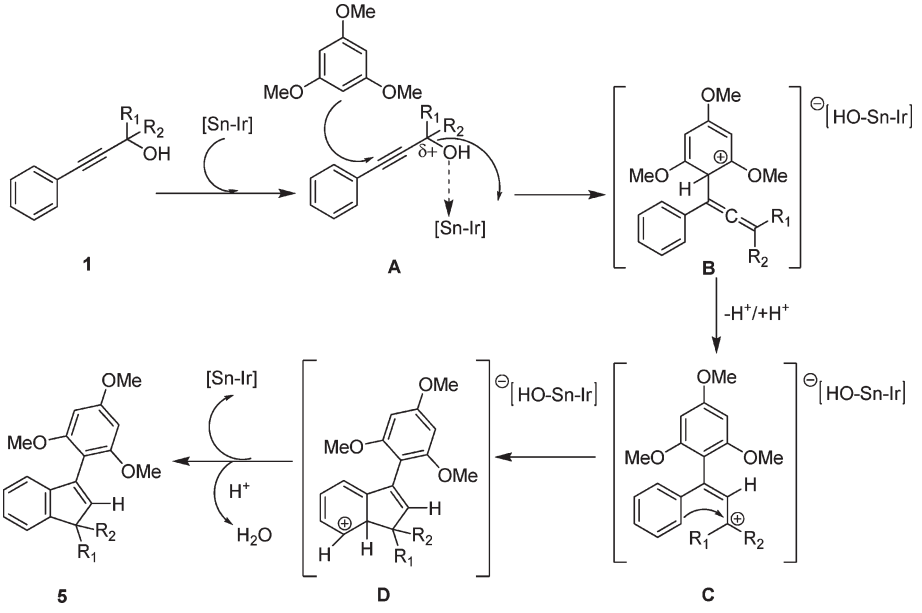
TABLE 3. Reaction of Tertiary Propargylic Alcohol 1 with Bulky Arenes 2[a]



entry	**1**, R_1; R_2; R_3	Ar−H	time (min)	yield of **5** (%)
1	**1a**, Me; Me; H	**2d**	75	**5ad**, 80
2	**1f**, Me; Et; H	**2b**	75	**5fb**, 82
3	**1g**, Me; 4-MeC_6H_4; H	**2d**	45	**5gd**, 91
4	**1k**, Me; Me; C≡C−$C(Me)_2$OH	**2d**	60	**5kd**, 75
5	**1l**, Me; *iso*-Bu; H	**2b**	50	**5lb**, 80
6	**1m**, Ph; 4-MeC_6H_4; H	**2d**	30	**5md**, 92
7	**1n**, Me; Me; Me	**2d**	45	**5nd**, 85
8	**1o**, Me; Me; OMe	**2b**	45	**5ob**, 87
9	**1q**, Me; Me; Cl	**2d**	75	[b]

[a]Unless otherwise mentioned, reaction conditions were as follows: alcohol (0.25 mmol), nucleophile (0.75 mmol), Ir−Sn cat. (0.0025 mmol), solvent DCE (1 mL), 80 °C. [b]Resulted in a complex mixture; the desired indene was not obtained.

SCHEME 4. Plausible Mechanism of Indene Formation Reaction



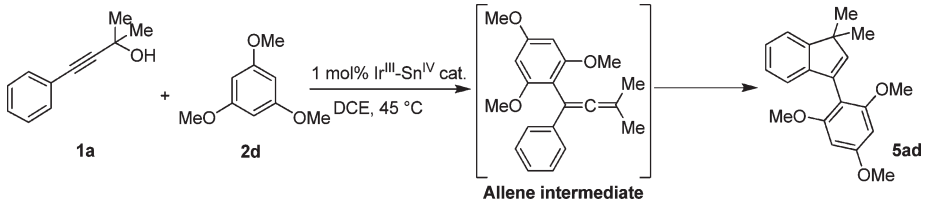
crystallographic analysis (Supporting Information). However, reaction of an aryl-substituted propargylic alcohol **1q** bearing an electron withdrawing halide substituent at the arene ring with **2d** led to an undefined complex mixture (entry 9).

A preliminary proposal for the formation of indene via the intermediacy of an allenyl species is shown in Scheme 4. The proposal invokes prior activation of propargylic alcohol via coordination at the hard Lewis acidic Sn(IV) center of the catalyst, resulting in intermediate **A**, which can act as an ambient electrophile. Due to steric reasons, a bulkier arene would attack at the less crowded acetylenic center[23] rather than the more crowded tertiary propargylic center, leading to the intermediate **B**. Indene **5** would result via subsequent intramolecular hydroarylation of species **C** and rearomatization of species **D**. Thus, the unfavorable steric interactions between the substituents of the electrophiles and the incoming nucleophiles govern the observed regioselection in the product.

To gain support on the proposed pathway, we monitored the reaction of propargylic alcohol **1a** with arene **2d** in the presence of 1 mol % of the catalyst in DCE at 45 °C for 3.5 h by ^{1}H NMR spectroscopy (Scheme 5). The signals due to the

(23) For similar regioselectivties observed in other reactions with propargylic cations, see (a) Yoshimatsu, M.; Yamamoto, T.; Sawa, A.; Kato, T.; Tanabe, G.; Muraoka, O. *Org. Lett.* **2009**, *11*, 2952. (b) Huang, W.; Shen, Q. S.; Wang, J. L.; Zhou, X. G. *J. Org. Chem.* **2008**, *73*, 1586. (c) Sanz, R.; Miguel, D.; Martínez, A.; Gutiérrez, J. M. Á.; Rodríguez, F. *Org. Lett.* **2007**, *9*, 727. (d) Ishikawa, T.; Aikawa, T.; Mori, Y.; Saito, S. *Org. Lett.* **2003**, *5*, 51. (e) Ishikawa, T.; Okano, M.; Aikawa, T.; Saito, S. *J. Org. Chem.* **2001**, *66*, 4635.

SCHEME 5. Reaction of Tertiary Propargylic Alcohol 1a with Bulky Arene 2d for an In Situ ^{1}H NMR Study



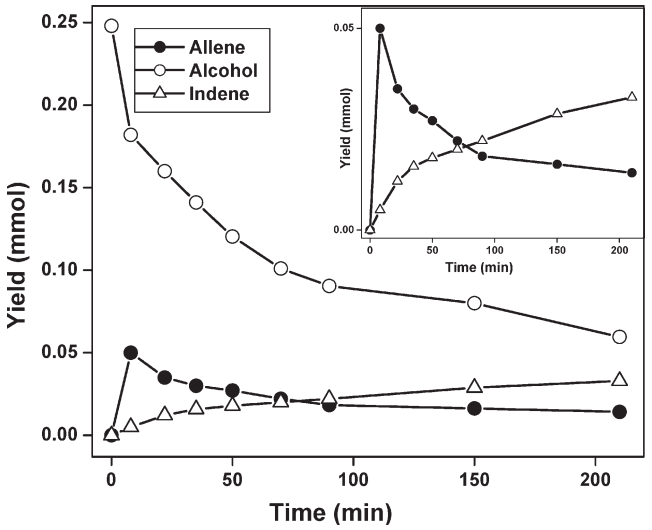
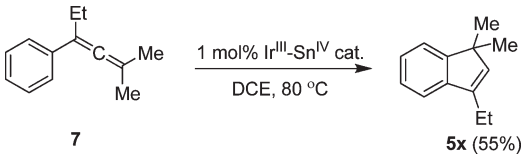


FIGURE 2. Time evolution of allene and indene **5ad** in the reaction of alcohol **1a** (0.25 mmol) with arene **2d** (0.75 mmol) catalyzed by the $Ir^{III}-Sn^{IV}$ complex at 45 °C. Inset shows the zoomed portion of the main plot highlighting the allene and indene formation.

SCHEME 6. Cyclization of Tetra-Substituted Allene to Indene by $Ir^{III}-Sn^{IV}$ Catalyst



methyl protons ($-CH_3$) of alcohol **1a** (δ 1.6 ppm), allenyl intermediate (δ 1.8 ppm),[24] and indene **5ad** (δ 1.4 ppm) were chosen for the study, which was monitored against triphenylmethane as the internal standard. From the data, the time evolution of the reactant and product was plotted (Figure 2). It was found that, in the first part of the reaction, allene was formed more rapidly than the product **5ad** and reached a maximum at 8 min. Thereafter, the yield of allene decreased, while the yield of product **5ad** increased.

To further test our proposal on the plausible interplay of the allenyl intermediate, we reacted the tetra-substituted allene $Ph(Et)C{=}C{=}C(Me)_2$ **7** in the presence of 1 mol % catalyst in DCE at 80 °C. Gratifyingly, this led to the corresponding indene **5x** in 55% yield within 1 h (Scheme 6).

Conclusions

In summary, we have shown that propargylic alcohols can be activated in a facile manner by the heterobimetallic $[Ir(COD)(SnCl_3)Cl(\mu\text{-}Cl)]_2$ catalyst, and the nucleophilic substitution of both internal and terminal propargylic alcohols can be achieved with various carbon (arene, heteroarene, and allyltrimethylsilane), sulfur (thiol), oxygen (alcohol), and nitrogen (sulfonamide) nucleophiles, leading to a normal propargylic product with high regioselectivity. In parallel, the bimetallic catalyst can steer the reaction between a bulky arene and a substituted tertiary phenyl propargylic alcohol to yield an indene via the intermediacy of allene as an intermediate. By virtue of their generality, selectivity, and efficiency, the catalytic reactions presented in this article could be a meaningful addition to the existing methods of propargylic functionalization as well as for the synthesis of substituted indenes.

Experimental Section

General Methods. ^{1}H NMR spectra were recorded at 400 and 200 MHz. Chemical shifts are reported in ppm from tetramethylsilane, with the solvent resonance as the internal standard (chloroform: δ 7.26 ppm). Data are reported as follows: chemical shifts, multiplicity (s = singlet, d = doublet, t = triplet, q = quartet, br = broad, dd = double doublet, dt = doublet of triplet, td = triplet of doublet, m = multiplet), integration, coupling constant (Hz). ^{13}C NMR spectra were recorded at 100 MHz and 54.6 MHz with proton decoupling. Chemical shifts are reported in ppm from tetramethylsilane with the solvent resonance as the internal standard (chloroform: δ 77.0 ppm). ESI-MS experiments were conducted at +ve ionization mode. Melting points are uncorrected. GC analysis was performed using a flame ionization detector and 30 m $\times$ 0.25 mm $\times$ 0.25 μm SS 100% dimethyl polysiloxane capillary column. *n*-Nonane was used as internal standard. The X-ray diffraction intensity data were collected at 293 K using a CCD diffractometer.

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, precoated 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. $[Ir(COD)(\mu\text{-}Cl)]_2$ and the heterobimetallic catalyst $[Ir(COD)(SnCl_3)Cl(\mu\text{-}Cl)]_2$ were prepared following literature methods.[9a,25] The propargylic alcohols, namely, **1b**, **1c**, **1f**, **1g**, **1h**, **1i**, **1j**, **1l**, and **1m** were prepared according to the literature.[26] Another set of propargylic alcohols, for example, **1a**, **1e**, **1k**, **1n**, **1o**, **1p**, **1q**, and **1r** were also prepared according to a previously reported procedure.[10d]

General Procedure. The following typical procedure has been adopted for the synthesis of all the propargylic as well as indene products.

Typical Procedure for the Propargylation of Anisole 2a with 2-Methyl-4-phenyl-but-3-yn-2-ol 1a Using $[Ir^{III}-Sn^{IV}]$ Catalyst. A 10 mL Schlenk flask equipped with a magnetic bar was

(24) Zhang, H.; Fu, X.; Chen, J.; Wang, E.; Liu, Y.; Li, Y. *J. Org. Chem.* **2009**, *74*, 9351.

(25) Walter, R.; Kirchner, S.; Franz, R. U.S. Patent 6,399,804, 2002.

(26) Spee, M. P. R.; Boersma, J.; Meijer, M. D.; Slagt, M. Q.; Koten, G.; Geus, J. W. *J. Org. Chem.* **2001**, *66*, 1647.

charged with $[Ir(COD)(SnCl_3)Cl(\mu\text{-}Cl)]_2$ (3 mg, 0.0025 mmol), anisole **2a** (82 μL, 0.75 mmol), and 1,2-dichloroethane (1 mL). The flask was degassed with argon and placed into a constant temperature bath at 80 °C. After the mixture was stirred vigorously for 5 min, 2-methyl-4-phenyl-but-3-yn-2-ol **1a** (40 mg, 0.25 mmol) was added to it and the reaction was allowed to continue at 80 °C (TLC monitoring; petroleum ether 60−80 °C/ethylacetate 19:1 v/v). Following completion of the reaction, solvent was removed under reduced pressure, and the mixture was subjected to column chromatography over silica gel (100−200 mesh, eluent: petroleum ether 60−80 °C/ethylacetate 49:1 v/v) to afford a corresponding propargylic product **3aa** as a light yellow oil in 78% isolated yield.

Analytical Data of Products. 1-Methoxy-4-(2-methyl-4-phenylbut-3-yn-2-yl)benzene (3aa). ^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) 1.66 (s, 6H), 3.81 (s, 3H), 6.88 (dd, 2H, J = 8.8 and 2.0 Hz), 7.29−7.33 (m, 3H), 7.45 (d, 2H, J = 7.2 Hz), 7.54 (dd, 2H, J = 8.8 and 2.0 Hz). ^{13}C NMR (100 MHz, $CDCl_3$): 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. DEPT-135: 31.8, 55.2, 113.5, 126.6, 127.6, 128.1, 131.5. HRMS (ESI) Calcd for $C_{18}H_{18}O + H^+$, 251.1436; found, 251.1417.

(3-Methylbut-3-en-1-ynyl)benzene (4)[27]**.** ^{1}H NMR (200 MHz, $CDCl_3$): δ (ppm) 1.99 (s, 3H), 5.30 (d, 1H, J = 3.2 Hz), 5.40 (d, 1H, J = 3.2 Hz), 7.29−7.32 (m, 3H), 7.42−7.47 (m, 2H). ^{13}C NMR (54.6 MHz, $CDCl_3$): 23.5, 88.4, 90.5, 121.9, 123.2, 126.8, 128.1, 128.2, 131.5. DEPT-135: 23.5, 121.9, 128.1, 128.2, 131.5.

1-Methoxy-4-(3-phenyl-1-*p*-tolylprop-2-ynyl)naphthalene (3bb). Pale yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) 2.31 (s, 3H), 4.01 (s, 3H), 5.79 (s, 1H), 6.81 (d, 1H, J = 8.0 Hz), 7.10 (d, 2H, J = 7.6 Hz), 7.27−7.29 (m, 3H), 7.33 (d, 2H, J = 7.6 Hz), 7.43−7.49 (m, 4H), 7.59 (d, 1H, J = 8.0 Hz), 8.06 (d, 1H, J = 7.6 Hz), 8.31 (d, 1H, J = 7.6 Hz). ^{13}C NMR (100 MHz, $CDCl_3$): 21.1, 40.1, 55.4, 84.8, 90.9, 103.2, 122.6, 123.7, 124.1, 124.9, 126.1, 126.6, 126.7, 127.8, 128.2, 128.9, 129.2, 131.6, 131.8, 136.3, 138.4, 155.1. DEPT-135: 21.1, 40.1, 55.4, 103.2, 122.6, 124.1, 124.9, 126.6, 126.7, 127.8, 128.2, 129.2, 131.8. HRMS (ESI) Calcd for $C_{27}H_{22}O + H^+$, 363.1749; found, 363.1740.

1,2-Dimethoxy-4-(3-phenyl-1-*p*-tolylprop-2-ynyl)benzene (3bc). Pale yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) 2.33 (s, 3H), 3.85 (s, 3H), 3.86 (s, 3H), 5.13 (s, 1H), 6.82 (d, 1H, J = 8.8 Hz), 6.97 (d, 2H, J = 6.0 Hz), 7.13 (d, 2H, J = 8.0 Hz), 7.29−7.33 (m, 5H), 7.46−7.48 (m, 2H). ^{13}C NMR (100 MHz, $CDCl_3$): 20.9, 42.8, 55.8 (2), 84.5, 90.5, 111.1, 111.2, 119.8, 123.5, 127.6, 127.8, 128.1, 129.2, 131.6, 134.4, 136.4, 138.9, 147.8, 148.9. DEPT-135: 20.9, 42.8, 55.8 (2), 111.1, 111.2, 119.8, 127.6, 127.8, 128.1, 129.2, 131.5. HRMS (ESI) Calcd for $C_{24}H_{22}O_2 + H^+$, 343.1698; found, 343.1693.

1-Chloro-4-(1-(4-methoxyphenyl)-3-phenylprop-2-ynyl)benzene (3ca). Colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) 3.79 (s, 3H), 5.14 (s, 1H), 6.87 (d, 2H, J = 8.4 Hz), 7.27−7.37 (m, 9H), 7.44−7.48 (m, 2H). ^{13}C NMR (100 MHz, $CDCl_3$): 42.3, 55.2, 85.1, 89.9, 113.9, 123.3, 128.1, 128.3, 128.7, 128.8, 129.2, 131.2, 131.6, 133.4, 140.6, 158.6. DEPT-135: 42.3, 55.2, 113.9, 128.1, 128.3, 128.7, 128.8, 129.2, 131.6. HRMS (ESI) Calcd for $C_{22}H_{17}ClO + H^+$, 333.1046; found, 333.1040.

2-(1-(4-Chlorophenyl)-3-phenylprop-2-ynyl)-1,3,5-trimethoxybenzene (3cd). White solid. Mp 82 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) 3.78 (s, 6H), 3.80 (s, 3H), 5.81 (s, 1H), 6.14 (s, 2H), 7.20 (d, 2H, J = 8.4 Hz), 7.27−7.29 (m, 2H), 7.41−7.45 (m, 5H). ^{13}C NMR (100 MHz, $CDCl_3$): 30.9, 55.2, 55.9, 81.4, 90.2, 91.3, 110.7, 124.2, 127.5, 127.7, 128.1, 128.7, 131.4, 131.6, 140.2, 158.4, 160.5. DEPT-135: 30.9, 55.2, 55.9, 91.3, 127.5, 127.7, 128.1, 128.7, 131.6. HRMS (ESI) Calcd for $C_{24}H_{21}ClO_3 + H^+$, 393.1257; found, 393.1255.

1-Methoxy-4-(1-*p*-tolylprop-2-ynyl)naphthalene (3db). Pale yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) 2.30 (s, 3H), 2.49 (d, 1H, J = 2.8 Hz), 4.01 (s, 3H), 5.59 (d, 1H, J = 2.8 Hz), 6.79 (d, 1H, J = 8.0 Hz), 7.09 (d, 2H, J = 7.6 Hz), 7.27 (d, 2H, J = 8.0 Hz), 7.42−7.47 (m, 2H), 7.54 (d, 1H, J = 7.6 Hz), 7.94−7.97 (m, 1H), 8.28−8.31 (m, 1H). ^{13}C NMR (100 MHz, $CDCl_3$): 20.9, 39.1, 55.4, 72.8, 85.1, 103.1, 122.5, 123.7, 124.8, 126.1, 126.4, 126.5, 127.6, 128.1, 129.1, 131.5, 136.4, 137.7, 155.1. HRMS (ESI) Calcd for $C_{21}H_{18}O + H^+$, 287.1436; found, 287.1426.

2,4-Dimethoxy-1-(1-*p*-tolylprop-2-ynyl)benzene (3de). Colorless oil. ^{1}H NMR (200 MHz, $CDCl_3$): δ (ppm) 2.31 (s, 3H), 2.37 (d, 1H, J = 2.8 Hz), 3.82 (s, 6H), 5.36 (d, 1H, J = 2.8 Hz), 6.43−6.51 (m, 2H), 7.09 (d, 2H, J = 8.0 Hz), 7.28 (d, 2H, J = 8.0 Hz), 7.41 (d, 1H, J = 8.2 Hz). ^{13}C NMR (54.6 MHz, $CDCl_3$): 21.0, 34.9, 55.3, 55.5, 71.1, 85.7, 98.6, 104.5, 122.4, 127.5, 129.0, 129.2, 136.0, 138.5, 157.0, 159.9. DEPT-135: 21.0, 34.9, 55.3, 55.5, 71.1, 98.6, 104.5, 127.5, 129.0, 129.2. HRMS (ESI) Calcd for $C_{18}H_{18}O_2 + H^+$, 267.1385; found, 267.1388.

2-(2-Methyl-4-phenylbut-3-yn-2-yl)furan (3af). Yellow oil. ^{1}H NMR (400 MHz, CDCl3): δ (ppm) 1.66 (s, 6H), 6.23 (d, 1H, J = 3.2 Hz), 6.31 (dd, 1H, J = 3.2 and 2.0 Hz), 7.27−7.28 (m, 3H), 7.36 (d, 2H, J = 2.0 Hz), 7.40−7.44 (m, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) 29.0, 32.6, 80.7, 94.1, 103.7, 109.9, 123.4, 127.7, 128.1, 131.6, 141.4, 158.9. DEPT-135: 29.0, 103.7, 109.9, 127.7, 128.1, 131.6, 141.4. Anal. Calcd ($C_{15}H_{14}O$): C, 85.68; H, 6.71. Found: C, 85.58; H, 6.75.

2-(2-Methyl-4-phenylbut-3-yn-2-yl)benzofuran (3ag). White solid. ^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) 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, $CDCl_3$): 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. DEPT-135: 28.8, 100.8, 111.0, 120.6, 122.5, 123.5, 127.8, 128.1, 131.6. HRMS (ESI) Calcd for $C_{19}H_{16}O + H^+$, 261.1279; found, 261.1278.

Methyl-(4-phenylbut-3-yn-2-yl)thiophene (3eh): Mixture of 2- and 3-Regioisomers. ^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) 1.63 (d, 3H, J = 7.2 Hz), 2.45 (s, 3H), 4.16 (q, 1H, J = 7.2 Hz), 6.58 (d, 1H, J = 3.2 Hz), 6.80 (d, 1H, J = 3.2 Hz), 7.27−7.29 (m, 3H), 7.42−7.45 (m, 2H). Minor isomer: 1.52 (d, 3H, J = 7.2 Hz), 2.47 (s, 3H), 4.01 (q, 1H, J = 7.2 Hz), 7.03 (d, 1H, J = 5.2 Hz), 7.09 (d, 1H, J = 5.2 Hz). ^{13}C NMR (100 MHz, $CDCl_3$; major + minor isomers): 12.8, 15.3, 22.9, 24.3, 25.9, 27.9, 81.1, 81.8, 91.9, 92.6, 117.8, 121.3, 123.3, 123.4, 123.6, 124.5, 125.1, 127.3, 127.6, 127.7, 127.8, 128.1, 128.2, 131.5, 131.6, 138.2, 138.2, 144.5. HRMS (ESI) Calcd for $C_{15}H_{14}S + H^+$, 227.0894; found, 227.0898.

2-Methyl-5-(3-methyl-1-phenylpent-1-yn-3-yl)furan (3fi). Colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) 0.97 (t, 3H, J = 7.2 Hz), 1.59 (s, 3H), 1.79−1.86 (m, 1H), 1.90−1.97 (m, 1H), 2.28 (s, 3H), 5.87 (d, 1H, J = 3.2 Hz), 6.14 (d, 1H, J = 3.2 Hz), 7.27−7.30 (m, 3H), 7.40−7.45 (m, 2H). ^{13}C NMR (100 MHz, $CDCl_3$): 9.7, 13.6, 26.9, 34.4, 37.7, 81.8, 93.2, 105.6, 105.8, 123.7, 127.7, 128.1, 131.6, 150.9, 156.0. DEPT-135: 9.7, 13.6, 26.9, 34.4, 105.6, 105.8, 127.7, 128.1, 131.6. Anal. Calcd ($C_{17}H_{18}O$): C, 85.67; H, 7.61. Found: C, 85.49; H, 7.65.

2-Methyl-5-(3-phenyl-1-*p*-tolylprop-2-ynyl)furan (3bi)[28]**.** ^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) 2.24 (s, 3H), 2.34 (s, 3H), 5.16 (s, 1H), 5.88 (d, 1H, J = 2.8 Hz), 6.11 (d, 1H, J = 2.8 Hz), 7.15 (d, 2H, J = 8.0 Hz), 7.28−7.30 (m, 3H), 7.36 (d, 2H, J = 8.0 Hz), 7.45−7.47 (m, 2H). ^{13}C NMR (100 MHz, $CDCl_3$): 13.6, 21.1, 37.5, 83.5, 88.0, 106.1, 107.1, 123.3, 127.7, 127.9, 128.1, 129.2, 131.7, 136.2, 136.8, 151.8. 152.0. DEPT-135: 13.6, 21.1, 37.5, 106.1, 107.1, 127.7, 127.9, 128.1, 129.2, 131.7. HRMS (ESI) Calcd for $C_{21}H_{18}O + H^+$, 287.1436; found, 287.1442.

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2-(3-Phenyl-1-*p*-tolylprop-2-ynyl)thiophene (3bj). Pale yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) 2.35 (s, 3H), 5.39 (s, 1H), 6.92 (dd, 1H, J = 3.2 and 4.8 Hz), 7.01 (d, 1H, J = 3.2 Hz), 7.16−7.19 (m, 3H), 7.30−7.32 (m, 3H), 7.39 (d, 2H, J = 8.0 Hz), 7.47−7.49 (m, 2H). ^{13}C NMR (100 MHz, $CDCl_3$): 21.1, 38.7, 84.1, 89.6, 123.2, 124.7, 124.9, 126.6, 127.5, 128.1, 128.2, 129.4, 131.6, 136.9, 138.3, 146.1. DEPT-135: 21.1, 38.7, 124.7, 124.9, 126.6, 127.5, 128.1, 128.2, 129.4, 131.6. Anal. Calcd ($C_{20}H_{16}S$): C, 83.29; H, 5.59. Found: C, 82.97; H, 5.48.

3-Methyl-2-(3-phenyl-1-*p*-tolylptop-2-ynyl)thiophene (3bk). Yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) 2.22 (s, 3H), 2.33 (s, 3H), 5.40 (s, 1H), 6.79 (d, 1H, J = 5.2 Hz), 7.09 (d, 1H, J = 5.2 Hz), 7.14 (d, 2H, J = 8.0 Hz), 7.27−7.30 (m, 3H), 7.35 (d, 2H, J = 8.0 Hz), 7.45−7.47 (m, 2H). ^{13}C NMR (100 MHz, $CDCl_3$): 14.1, 21.1, 36.6, 83.7, 89.8, 122.5, 123.3, 127.5, 128.1, 128.2, 129.3, 130.3, 131.7, 133.3, 136.7, 137.7, 138.4. DEPT-135: 14.1, 21.1, 36.6, 122.5, 127.5, 128.1, 128.2, 129.3, 130.3, 131.7. Anal. Calcd ($C_{21}H_{18}S$): C, 83.40; H, 6.00. Found: C, 83.75; H, 5.96.

2-(1-*p*-Tolylprop-2-ynyl)furan (3df). Colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) 2.34 (s, 3H), 2.42 (d, 1H, J = 2.4 Hz), 5.02 (d, 1H, J = 2.4 Hz), 6.21 (d, 1H, J = 3.2 Hz), 6.29−6.34 (m, 1H), 7.12−7.16 (m, 2H), 7.29−7.38 (m, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): 21.1, 36.6, 71.7, 82.1, 106.5, 110.2, 127.5, 129.3, 135.1, 137.1, 142.2, 153.3. HRMS (ESI) Calcd for $C_{14}H_{12}O + H^+$, 197.0966; found, 197.0960.

2-(1-(4-Chlorophenyl)3-phenylprop-2-ynyl)-3-methylthiophene (3ck). Colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) 2.25 (s, 3H), 5.41 (s, 1H), 6.81 (d, 1H, J = 5.2 Hz), 7.11 (d, 1H, J = 5.2 Hz), 7.29−7.47 (m, 9H). ^{13}C NMR (100 MHz, $CDCl_3$): 14.0, 36.3, 84.3, 88.8, 122.9, 123.0, 128.2, 128.3, 128.7, 129.0, 130.4, 131.6, 132.9, 133.6, 137.5, 139.2. DEPT-135: 14.0, 36.3, 122.9, 128.2, 128.3, 128.7, 129.0, 130.4, 131.6. Anal. Calcd ($C_{20}H_{15}ClS$): C, 74.40; H, 4.68. Found: C, 74.81; H, 4.65.

1-Methyl-4-(1-phenylhex-5-en-1-yn-3-yl)benzene (3bl)[29]**.** ^{1}H NMR (200 MHz, $CDCl_3$): δ (ppm) 2.35 (s, 3H), 2.58 (t, 2H, J = 7.0 Hz), 3.89 (t, 1H, J = 7.0 Hz), 5.06−5.15 (m, 2H), 5.83−6.01 (m, 1H), 7.16 (d, 2H, J = 7.8 Hz), 7.27−7.34 (m, 5H), 7.44−7.47 (m, 2H). ^{13}C NMR (54.6 MHz, $CDCl_3$): 21.1, 38.2, 42.8, 83.6, 91.2, 116.9, 123.8, 127.4, 127.7, 128.2, 129.2, 131.6, 135.6, 136.4, 138.4.

1-Chloro-4-(1-phenylhex-5-en-1-yn-3-yl)benzene (3cl)[30]**.** ^{1}H NMR (200 MHz, $CDCl_3$): δ (ppm) 2.57 (t, 2H, J = 7.0 Hz), 3.90 (t, 1H, J = 7.0 Hz), 5.04−5.14 (m, 2H), 5.78−5.95 (m, 1H), 7.27−7.52 (m, 9H). ^{13}C NMR (54.6 MHz, $CDCl_3$): 37.9, 42.6, 84.1, 90.3, 117.5, 123.4, 127.9, 128.3, 128.6, 128.9, 131.7, 132.6, 135.1, 139.8.

1-Methyl-4-(3-methyl-1-phenylhex-5-en-1-yn-3-yl)benzene (3gl). Colorless oil. ^{1}H NMR (200 MHz, $CDCl_3$): δ (ppm) 1.65 (s, 3H), 2.35 (s, 3H), 2.62 (t, 2H, J = 6.8 Hz), 5.03−5.15 (m, 2H), 5.79−5.93 (m, 1H), 7.16 (d, 2H, J = 8.0 Hz), 7.29−7.34 (m, 2H), 7.44−7.50 (m, 5H). ^{13}C NMR (54.6 MHz, $CDCl_3$): 20.9, 29.1, 40.3, 48.6, 83.9, 94.9, 117.6, 123.8, 126.1, 127.7, 128.2, 128.9, 131.6, 134.9, 135.9, 142.3. Anal. Calcd ($C_{20}H_{20}$): C, 92.26; H, 7.74. Found: C, 92.38; H, 7.85.

1-(Hex-5-en-1-yn-3-yl)-4-methylbenzene (3dl). Colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) 2.28 (d, 1H, J = 2.4 Hz), 2.33 (s, 3H), 2.51 (t, 2H, J = 6.8 Hz), 3.67 (dt, 1H, J = 2.4 and 6.8 Hz), 5.05−5.11 (m, 2H), 5.82−5.89 (m, 1H), 7.14 (d, 2H, J = 8.0 Hz), 7.25 (d, 2H, J = 8.0 Hz). ^{13}C NMR (100 MHz, $CDCl_3$): 20.9, 37.2, 42.3, 71.1, 85.5, 116.9, 127.2, 129.1, 135.2, 136.4, 137.7. Anal. Calcd ($C_{13}H_{14}$): C, 91.71; H, 8.29. Found: C, 91.83; H, 8.24.

1-(Dec-1-en-5-yn-4-yl)-4-methylbenzene (3hl)[29]**.** ^{1}H NMR (200 MHz, $CDCl_3$): δ (ppm) 0.97 (t, 3H, J = 6.8 Hz), 1.47−1.59 (m, 4H), 2.28 (td, 2H, J = 6.8 and 2.2 Hz), 2.49 (t, 2H, J = 7.0 Hz), 3.67 (td, 1H, J = 5.0 and 2.2 Hz), 5.05−5.15 (m, 2H), 5.81−6.01 (m, 1H), 7.17 (d, 2H, J = 7.8 Hz), 7.29 (d, 2H, J = 7.8 Hz). ^{13}C NMR (54.6 MHz, $CDCl_3$): 13.6, 18.5, 21.1, 21.9, 31.2, 37.7, 43.1, 81.3, 83.5, 116.5, 127.4, 129.1, 136.0, 136.1, 139.3.

(3-(4-Chlorophenyl)hex-5-en-1-ynyl)trimethylsilane (3il). Colorless oil. ^{1}H NMR (200 MHz, $CDCl_3$): δ (ppm) 0.18 (s, 9H), 2.46 (t, 2H, J = 7.0 Hz), 3.68 (t, 1H, J = 7.0 Hz), 4.98−5.06 (m, 1H), 7.27−7.49 (m, 4H). ^{13}C NMR (54.6 MHz, $CDCl_3$): 0.11, 38.3, 42.6, 88.3, 107.1, 117.3, 128.5, 128.9, 132.5, 134.8, 139.5. HRMS (ESI) Calcd for $C_{15}H_{19}ClSi + H^+$, 263.1023; found, 263.1029.

(3-Methyl-1-phenylpent-1-yn-3-yl)(propyl)sulfane (3fm). Colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) 1.02 (t, 3H, J = 7.4 Hz), 1.13 (t, 3H, J = 7.2 Hz), 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, 2H, J = 7.2 Hz), 7.28−7.30 (m, 3H), 7.39−7.42 (m, 2H). ^{13}C NMR (100 MHz, $CDCl_3$): 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. DEPT-135: 9.8, 13.8, 22.9, 28.2, 32.2, 35.6, 127.8, 128.2, 131.6. HRMS (ESI) Calcd for $C_{15}H_{20}S + H^+$, 233.1364; found, 233.1356.

2-(1,3-Diphenylprop-2-ynylthio)ethanol (3jn)[20]**.** ^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) 2.15 (br, 1H), 2.86 (dt, 1H, J = 13.9 and 6.0 Hz), 3.00 (dt, 1H, J = 13.9 and 6.0 Hz), 3.74−3.81 (m, 2H), 5.06 (s, 1H), 7.33−7.40 (m, 6H), 7.46−7.51 (m, 2H), 7.56−7.60 (m, 2H). ^{13}C NMR (100 MHz, $CDCl_3$): 34.9, 39.2, 60.8, 86.2, 87.0, 122.6, 127.8, 127.9, 128.3, 128.4, 128.7, 131.7, 138.1.

Phenyl(1-*p*-tolyoprop-2-ynyl)sulfane (3do). Colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) 2.34 (s, 3H), 2.56 (d, 1H, J = 2.6 Hz), 4.97 (d, 1H, J = 2.6 Hz), 7.11 (d, 2H, J = 8.0 Hz), 7.22−7.31 (m, 5H), 7.41−7.45 (m, 2H). ^{13}C NMR (100 MHz, $CDCl_3$): 21.1, 42.8, 74.3, 82.1, 127.6, 127.8, 128.2, 128.6, 129.2, 133.5, 134.2, 137.7. HRMS (ESI) Calcd for $C_{16}H_{14}S + H^+$, 239.0894; found, 239.0881.

***tert*-Butyl(4-phenyl-2-*p*-tolylbut-3-yn-2-yl)sulfane (3gp).** Colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) 1.25 (s, 9H), 1.92 (s, 3H), 2.34 (s, 3H), 7.14 (d, 2H, J = 8.0 Hz), 7.33−7.36 (m, 3H), 7.49−7.52 (m, 2H), 7.71 (d, 2H, J = 8.0 Hz). ^{13}C NMR (100 MHz, $CDCl_3$): 20.9, 31.8, 34.1, 46.1, 47.4, 85.7, 93.2, 123.4, 126.7, 128.0, 128.2, 128.6, 131.3, 136.7, 141.4. DEPT-135: 20.9, 31.8, 34.1, 126.7, 128.0, 128.2, 128.6, 131.3. HRMS (ESI) Calcd for $C_{21}H_{24}S + H^+$, 309.1677; found, 309.1686.

(3-Ethoxy-3-methylbut-1-ynyl)benzene (3aq)[31]**.** ^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) 1.24 (t, 3H, J = 7.2 Hz), 1.55 (s, 6H), 3.68 (q, 2H, J = 7.2 Hz), 7.29−7.30 (m, 3H), 7.41−7.43 (m, 2H). ^{13}C NMR (100 MHz, $CDCl_3$): 15.8, 29.3, 59.4, 70.2, 83.7, 91.6, 122.9, 128.0, 128.1, 131.6. DEPT-135: 15.8, 29.3, 59.4, 128.0, 128.1, 131.6. HRMS (ESI) Calcd for $C_{13}H_{16}O + H^+$, 189.1279; found, 189.1272.

(3-(Hex-2-enyloxy)-3-methylbut-1-ynyl)benzene (3ar). Pale yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) 0.89 (t, 3H, J = 7.6 Hz), 1.37−1.42 (m, 2H), 1.57 (s, 6H), 2.04−2.11 (m, 2H), 4.23 (d, 2H, J = 5.6 Hz), 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. DEPT-135: 13.6, 22.6, 28.9, 60.1, 65.6, 126.7, 128.1, 128.2, 131.6, 133.1. HRMS (ESI) Calcd for $C_{17}H_{22}O + H^+$, 243.1749; found, 243.1742.

(3-(3-Phenylpropoxy)prop-1-yne-1,3-diyl)dibenzene (3js). Colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) 1.98 (m, 2H), 2.74 (t, 2H, J = 7.2 Hz), 3.57−3.59 (m, 1H), 3.75−3.79 (m, 1H), 5.39 (s, 1H), 7.16−7.47 (m, 13H), 7.59 (d, 2H, J = 7.2 Hz). ^{13}C NMR (100 MHz, $CDCl_3$): 31.3, 32.3, 67.5, 72.1, 87.2, 87.4, 122.6, 125.7, 127.4, 128.1, 128.2, 128.3, 128.4, 128.5, 128.6,

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131.8, 138.9, 141.9. DEPT-135: 31.3, 32.3, 67.5, 72.1, 125.7, 127.4, 128.1, 128.2, 128.3, 128.4, 128.5, 128.6, 131.8. HRMS (ESI) Calcd for $C_{24}H_{22}O + H^+$, 327.1749; found, 327.1755.

4-Methyl-*N*-(2-methyl-4-phenylbut-3-yn-yl)benzenesulfonamide (3at). White solid. ^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) 1.65 (s, 6H), 2.26 (s, 3H), 4.68 (s, 1H), 7.05 (d, 2H, J = 8.0 Hz), 7.11 (d, 2H, J = 8.0 Hz), 7.20−7.28 (m, 3H), 7.78 (d, 2H, J = 8.0 Hz). ^{13}C NMR (100 MHz, $CDCl_3$): 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. DEPT-135: 21.3, 30.9, 127.5, 127.8, 128.1, 129.3, 131.5. HRMS (ESI) Calcd for $C_{18}H_{19}NO_2S + Na^+$, 336.1034; found, 336.1042.

***N*-(3-Phenyl-1-*p*-tolylprop-2-ynyl)benzenesulfonamide (3bu).** White solid. Mp 120 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) 2.34 (s, 3H), 4.96 (d, 1H, J = 9.0 Hz), 5.55 (d, 1H, J = 9.0 Hz), 7.12−7.16 (m, 4H), 7.22−7.31 (m, 3H), 7.41−7.53 (m, 5H), 7.93 (d, 2H, J = 7.2 Hz). ^{13}C NMR (100 MHz, $CDCl_3$): 21.1, 49.5, 85.6, 86.4, 121.9, 127.2, 127.4, 128.1, 128.6, 128.9, 129.4, 131.6, 132.6, 134.4, 138.3, 140.4. DEPT-135: 21.1, 49.5, 127.2, 127.4, 128.1, 128.6, 128.9, 129.4, 131.6, 132.6. HRMS (ESI) Calcd for $C_{22}H_{19}NO_2S + Na^+$, 384.1034; found, 384.1052.

***N*-(1,3-Diphenylprop-2-ynyl)-4-methylbenzenesulfonamide (3jt)[31].** White solid. Mp = 196 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) 2.32 (s, 3H), 4.84 (d, 1H, J = 9.0 Hz), 5.56 (d, 1H, J = 9.0 Hz), 7.12 (d, 2H, J = 6.4 Hz), 7.27−7.38 (m, 8H), 7.46 (d, 2H, J = 7.2 Hz), 7.82 (d, 2H, J = 8.4 Hz). ^{13}C NMR (100 MHz, $CDCl_3$): 21.4, 49.7, 85.4, 86.7, 121.9, 127.3, 127.5, 128.1, 128.5, 128.6, 128.7, 129.6, 131.5, 137.3, 143.6. HRMS (ESI) Calcd for $C_{22}H_{19}NO_2S + Na^+$, 384.1034; found, 384.1026.

3-Methyl-1-phenylbut-2-en-1-one (6)[32]. ^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) 2.02 (s, 3H), 2.21 (s, 3H), 6.75 (s, 1H), 7.42−7.54 (m, 3H), 7.92 (d, 2H, J = 7.2 Hz). ^{13}C NMR (100 MHz, $CDCl_3$): 21.1, 27.9, 121.1, 128.1, 128.3, 132.1, 156.6, 191.4.

1-Ethyl-4-(3-(4-methoxyphenyl)-3-methylbut-1-ynyl)benzene (3pa). Light yellow oil. ^{1}H NMR (200 MHz, $CDCl_3$): δ (ppm) 1.22 (t, 3H, J = 7.6 Hz), 1.65 (s, 3H), 2.62 (q, 2H, J = 7.6 Hz), 3.81 (s, 3H), 6.88 (dd, 2H, J = 8.0 and 2.4 Hz), 7.14 (d, 2H, J = 8.4 Hz), 7.38 (d, 2H, J = 8.4 Hz), 7.54 (dd, 2H, J = 8.0 and 2.4 Hz). ^{13}C NMR (54.6 MHz, $CDCl_3$): 15.4, 28.8, 31.9, 35.8, 55.3, 81.9, 96.1, 113.6, 121.2, 126.7, 127.7, 131.6, 139.4, 144.0, 158.1. DEPT-135: 15.4, 28.8, 31.9, 55.3, 113.6, 126.7, 127.7, 131.6. HRMS (ESI) Calcd for $C_{20}H_{22}O + H^+$, 279.1749; found, 279.1756.

1-Methoxy-4-(2-methyl-4-*p*-tolylbut-3-yn-2-yl)benzene (3na). Yellow oil. ^{1}H NMR (200 MHz, $CDCl_3$): δ (ppm) 1.65 (s, 6H), 2.34 (s, 3H), 3.81 (s, 3H), 6.87 (dd, 2H, J = 8.8 and 2.2 Hz), 7.10 (d, 2H, J = 7.8 Hz), 7.34 (d, 2H, J = 7.8 Hz), 7.53 (dd, 2H, J = 8.8 and 2.2 Hz). ^{13}C NMR (54.6 MHz, $CDCl_3$): 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. DEPT-135: 21.4, 31.9, 55.2, 113.5, 126.6, 128.9, 131.4. HRMS (ESI) Calcd for $C_{19}H_{20}O + H^+$, 265.1592; found, 265.1595.

1-Chloro-4-(3-(4-methoxyphenyl)-3-methylbut-1-ynyl)benzene (3qa). White solid. ^{1}H NMR (200 MHz, $CDCl_3$): δ (ppm) 1.68 (s, 6H), 3.85 (s, 3H), 6.92 (dd, 2H, J = 9.0 and 2.2 Hz), 7.27−7.33 (m, 2H), 7.37−7.42 (m, 2H), 7.56 (dd, 2H, J = 9.0 and 2.2 Hz). ^{13}C NMR (54.6 MHz, $CDCl_3$): 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. DEPT-135: 31.7, 55.3, 113.6, 126.6, 128.5, 132.8. HRMS (ESI) Calcd for $C_{18}H_{17}ClO + H^+$, 285.1046; found, 285.1053.

1-(4-(3-(4-methoxyphenyl)-3-methylbut-1-ynyl)phenyl)ethanone (3ra). White solid. Mp 71 °C. ^{1}H NMR (200 MHz, $CDCl_3$): δ (ppm) 1.67 (s, 6H), 2.60 (s, 3H), 3.81 (s, 3H), 6.88 (dd, 2H, J = 8.8 and 2.0 Hz), 7.51 (d, 4H, J = 8.2 Hz), 7.89 (dd, 2H, J = 8.8 and 2.0 Hz). ^{13}C NMR (54.6 MHz, $CDCl_3$): 26.6, 31.6, 35.8, 55.3, 81.2, 100.6, 113.7, 126.6, 128.1, 128.9, 131.7, 135.8, 138.7, 158.2, 197.4. DEPT-135: 26.6, 31.6, 55.3, 113.7, 126.6, 128.1, 131.7. HRMS (ESI) Calcd for $C_{20}H_{20}O_2 + H^+$, 293.1542; found, 293.1532.

1,3,5-Trimethoxy-2-(4-phenylbut-3-yn-2-yl)benzene (3ed). Colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) 1.51 (d, 3H, J = 7.2 Hz), 3.81 (s, 3H), 3.84 (s, 6H), 4.54 (q, 1H, J = 7.2 Hz), 6.16 (s, 2H), 7.21−7.24 (m, 3H), 7.36−7.38 (m, 2H). ^{13}C NMR (100 MHz, $CDCl_3$): 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. DEPT-135: 20.3, 21.0, 55.3, 55.9, 91.3, 126.9, 128.0, 131.5. HRMS (ESI) Calcd for $C_{19}H_{20}O_3 + H^+$, 297.1491; found, 297.1472.

1,2,3-Trimethoxy-4-(2-methyl-4-phenylbut-3-yn-2-yl)benzene (3av). Colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) 1.73 (s, 6H), 3.86 (s, 3H), 3.87 (s, 3H), 3.98 (s, 3H), 6.61 (d, 1H, J = 8.8 Hz), 7.25−7.29 (m, 4H), 7.41−7.44 (m, 2H). ^{13}C NMR (54.6 MHz, $CDCl_3$): 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. HRMS (ESI) Calcd for $C_{20}H_{22}O_3 + H^+$, 311.1647; found, 311.1654.

1,1-Dimethyl-3-(2,4,6-trimethoxyphenyl)-1*H*-indene (5ad). White solid. Mp 116 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) 1.47 (s, 6H), 3.69 (s, 6H), 3.86 (s, 3H), 6.22 (s, 2H), 6.29 (s, 1H), 6.93 (d, 1H, J = 4.4 Hz), 7.16 (d, 2H, J = 4.8 Hz), 7.34 (d, 1H, J = 4.4 Hz). ^{13}C NMR (100 MHz, $CDCl_3$): 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. DEPT-135: 24.7, 55.2, 55.9, 91.1, 120.7, 120.8, 124.3, 125.9, 146.6. HRMS (ESI) Calcd for $C_{20}H_{22}O_3 + H^+$, 311.1647; found, 311.1633.

1-(1-Ethyl-1-methyl-1*H*-indene-3-yl)-4-methoxynaphthalene (5fb). Yellow gummy liquid. ^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) 0.69 (t, 3H, J = 7.2 Hz), 1.42 (s, 3H), 1.79−1.88 (m, 1H), 1.94−2.03 (m, 1H), 4.07 (s, 3H), 6.18 (s, 1H), 6.89 (s, 1H), 7.20 (t, 1H, J = 7.6 Hz), 7.34 (t, 1H, J = 7.6 Hz), 7.41−7.51 (m, 5H), 7.64 (d, 1H, J = 8.4 Hz), 8.28 (d, 1H, J = 8.4 Hz). ^{13}C NMR (100 MHz, $CDCl_3$): 9.4, 23.1, 31.2, 53.0, 55.7, 99.3, 122.6, 123.8, 124.1, 124.9, 125.6, 127.1, 128.1, 128.8, 129.1, 129.9, 139.3, 143.1, 152.1, 154.4. DEPT-135: 9.4, 23.1, 31.2, 55.7, 99.5, 122.6, 123.8, 124.1, 125.6, 127.1, 128.1, 128.8, 143.1. HRMS (ESI) Calcd for $C_{23}H_{22}O + H^+$, 315.1749; found, 315.1740.

1-Methyl-1-*p*-tolyl-3-(2,4,6-trimethoxyphenyl)-1*H*-indene (5gd). White solid. Mp 86 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) 1.81 (s, 3H), 2.29 (s, 3H), 3.73 (s, 6H), 3.87 (s, 3H), 6.24 (s, 2H), 6.42 (s, 1H), 6.95 (d, 1H, J = 7.2 Hz), 7.06 (d, 2H, J = 8.0 Hz), 7.10−7.17 (m, 3H), 7.33 (d, 2H, J = 8.0 Hz). ^{13}C NMR (100 MHz, $CDCl_3$): 21.1, 22.5, 55.4, 55.6, 55.9, 91.1, 106.1, 121.1, 122.2, 125.1, 126.1, 126.2, 129.1, 134.2, 135.7, 140.5, 144.1, 146.3, 153.6, 159.3, 160.9. DEPT-135: 21.1, 22.5, 55.4, 55.9, 91.1, 121.1, 122.2, 125.1, 126.1, 126.2, 129.1, 146.3. HRMS (ESI) Calcd for $C_{26}H_{26}O_3 + H^+$, 387.1960; found, 387.1956.

1,1,5,5-Tetramethyl-3,7-bis(2,4,6-trimethoxyphenyl)-1,5-dihydros-indacene (5kd). White solid. ^{1}H NMR (200 MHz, $CDCl_3$): δ (ppm) 1.35 (s, 12H), 3.71 (s, 12H), 3.88 (s, 6H), 6.21 (s, 2H), 6.25 (s, 4H), 6.86 (s, 2H). ^{13}C NMR (100 MHz, $CDCl_3$): 25.1, 48.1, 55.2, 55.7, 90.9, 106.7, 113.6, 132.7, 140.9, 145.8, 151.3, 159.1, 160.4. DEPT-135: 25.1, 55.2, 55.7, 90.9, 113.6, 145.8.

1-(1-*iso*-Butyl-1-methyl-1*H*-indene-3-yl)-4-methoxynaphthalene (5lb). Pale yellow gummy liquid. ^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) 0.62 (d, 3H, J = 6.8 Hz), 0.86 (d, 3H, J = 6.8 Hz), 1.27−1.30 (m, 1H), 1.39 (s, 3H), 1.87−1.91 (m, 2H), 4.08 (s, 3H), 6.26 (s, 1H), 6.91 (s, 1H), 7.21 (t, 1H, J = 7.6 Hz), 7.35 (t, 1H, J = 7.6 Hz), 7.41−7.50 (m, 5H), 7.64 (d, 1H, J = 8.4 Hz), 8.29 (d, 1H, J = 8.4 Hz). ^{13}C NMR (100 MHz, $CDCl_3$): 24.5, 24.9, 25.1, 25.5, 47.5, 52.8, 55.7, 99.5, 122.6, 123.8, 124.1, 124.9, 125.6, 127.1, 128.1, 128.8, 129.1, 129.9, 139.3, 143.1,

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152.1, 154.4. DEPT-135: 24.5, 24.9, 25.1, 25.5, 47.5, 55.7, 99.5, 122.6, 123.8, 124.1, 125.6, 127.1, 128.1, 128.8, 143.1. HRMS (ESI) Calcd for $C_{25}H_{26}O + H^+$, 343.2062; found, 343.2056.

1-Phenyl-1-*p*-tolyl-3-(2,4,6-trimethoxyphenyl)-1*H*-indene (5md). White solid. Mp 118 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) 2.30 (s, 3H), 3.71 (s, 6H), 3.86 (s, 3H), 6.22 (s, 2H), 6.67 (s, 1H), 6.98 (d, 1H, J = 6.8 Hz), 7.05 (d, 2H, J = 8.4 Hz), 7.11−7.40 (m, 10H). ^{13}C NMR (100 MHz, $CDCl_3$): 20.9, 55.3, 55.8, 65.7, 90.9, 105.7, 121.5, 124.7, 124.8, 126.2, 126.3, 127.8, 127.9, 128.1, 128.8, 134.2, 135.8, 141.1, 144.4, 144.5, 144.7, 150.2, 159.2, 160.8. DEPT-135: 20.9, 55.3, 55.8, 90.9, 121.5, 124.7, 124.8, 126.2, 126.3, 127.8, 127.9, 128.1, 128.8, 144.7. HRMS (ESI) Calcd for $C_{31}H_{28}O_3 + H^+$, 449.2117; found, 449.2121.

1,1,5-Trimethyl-3-(2,4,6-trimethoxyphenyl)-1*H*-indene (5nd). White solid. Mp 122 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) 1.40 (s, 6H), 2.39 (s, 3H), 3.69 (s, 6H), 3.86 (s, 3H), 6.22 (s, 3H), 6.82 (d, 1H, J = 7.6 Hz), 6.98 (d, 1H, J = 7.6 Hz), 7.17 (s, 1H). ^{13}C NMR (100 MHz, $CDCl_3$): 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. HRMS (ESI) Calcd for $C_{21}H_{24}O_3 + H^+$, 325.1803; found, 325.1798.

1-Methoxy-4-(5-methoxy-1,1-dimethyl-1*H*-indene-3-yl)naphthalene (5ob). Yellowish solid. Mp 106 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) 1.43 (s, 6H), 3.90 (s, 3H), 4.08 (s, 3H), 6.21 (s, 1H), 6.95 (s, 1H), 6.99 (d, 2H, J = 8.4 Hz), 7.23 (t, 1H, J = 7.6 Hz), 7.35 (t, 1H, J = 7.6 Hz), 7.42 (d, 2H, J = 8.4 Hz), 7.71 (d, 1H, J = 8.4 Hz), 8.28 (d, 1H, J = 8.4 Hz). ^{13}C NMR (54.6 MHz, $CDCl_3$): 24.5, 48.8, 55.4, 55.8, 99.3, 113.6, 122.7, 123.9, 124.1, 125.1, 125.7, 129.1, 129.3, 130.1, 131.5, 142.2, 143.9, 153.1, 154.6, 158.9. HRMS (ESI) Calcd for $C_{23}H_{22}O_2 + H^+$, 331.1698; found, 331.1703.

3-Ethyl-1,1-dimethyl-1*H*-indene (5x)[33]**.** ^{1}H NMR (400 MHz, $CDCl_3$): 1.26 (t, 3H, J = 7.2 Hz), 1.33 (s, 6H), 2.46 (dd, 2H, J = 7.2 and 2.0 Hz), 6.02 (s, 1H), 7.16−7.38 (m, 3H).

(5-Methylhexa-3,4-dien-3-yl)benzene (7). ^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) 1.14 (t, 3H, J = 7.2 Hz), 1.85 (s, 6H), 2.43 (q, 2H, J = 7.2 Hz), 7.18−7.42 (m, 5H). ^{13}C NMR (54.6 MHz, $CDCl_3$): 12.6, 20.5, 23.2, 98.9, 105.3, 125.9, 126.1, 128.2, 138.5, 201.6. DEPT-135: 12.6, 20.5, 23.2, 125.9, 126.1, 128.2.

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Supporting Information Available: Experimental procedures, characterization data, kinetics plot, and ^{1}H and ^{13}C NMR spectra for all compounds and crystallographic data for **5ad** and **5kd**. This material is available free of charge via the Internet at http://pubs.acs.org.

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