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PAPER

Electrophilic chemistry of propargylic alcohols in imidazolium ionic liquids: Propargylation of arenes and synthesis of propargylic ethers catalyzed by metallic triflates [$Bi(OTf)_3$, $Sc(OTf)_3$, $Yb(OTf)_3$], TfOH, or $B(C_6F_5)_3$†

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Metallic triflates $M(OTf)_3$ (M = Bi, Sc, Yb), immobilized in imidazolium ionic liquids [BMIM][BF_4], [BMIM][PF_6] and [BMIM][OTf] are efficient systems for one-pot reactions of propargylic alcohols 1,3-diphenyl-2-propyn-1-ol **Ia**, 1-methyl-3-phenyl-2-propyn-1-ol **Ib**, and 2-pentyn-1-ol **Ic**, with a wide range of arenes bearing activating substituents, under mild conditions. The [BMIM][PF_6]/$B(C_6F_5)_3$ and [BMIM][PF_6]/TfOH systems were superior in propargylation with **Ib** and **Ic**, while reaction of 3-phenyl-2-propyn-1-ol **Id** with activated aromatics resulted in the formation of diaryl-propanones instead. Propargylation of anisole with **Ib** under $M(OTf)_3$ catalysis is highly *para* selective, but with TfOH or $B(C_6F_5)_3$ as catalyst the *ortho* isomer was also formed. Steric influence of the propargylic moiety on substrate selectivity is reflected in the lack of *ortho* propargylation for phenol and ethylbenzene by using propargylic alcohol **Ia**, and notable formation of the *ortho* isomer employing alcohol **Ib**. In the later case *para* selectivity could be increased by running the reaction at r. t. for 10 h. The $Bi(OTf)_3$-catalyzed reaction of 1,3-dimethoxybenzene with **Ia** led to minor formation of dipropargylated derivative, along with the monopropargyl product. Propargylation of the less reactive arenes (mesitylene, ethylbenzene, toluene), using $Sc(OTf)_3$ as catalyst, led increasingly to the formation of dipropargylic ethers and propargyl ketones, with no ring propargylation product with toluene. Concomitant formation of dipropargylic ether was also observed in $Yb(OTf)_3$-catalyzed propargylation of β-naphthol, whereas propargylation of 2-nitro and 4-nitro-aniline led to *N*-propargylation. The recycling/reuse of the IL was demonstrated in representative cases with no appreciable decrease in the conversions over 3 cycles. It was also shown that recycled IL could be used to propargylate a different aromatic compound. The efficacy of IL/$M(OTf)_3$ and IL/TfOH systems for cross-breeding two propargylic alcohols or a propargylic alcohol with a non-propargylic alcohol and/or self-coupling, to form a wide variety of functionalized ethers is also demonstrated.

Introduction

Direct introduction of the propargyl group into aromatic and heteroaromatic compounds under mild conditions with high efficiency and regioselectivity represents a highly desirable approach for the synthesis of functional alkynes. Previous approaches in pursuit of this goal emphasized organometallic catalysts and focused mainly on 1,3-diphenyl-2-propyn-1-ol **Ia**. For example, Uemura, Nishibayashi and co-workers[1] used a cationic diruthenium complex for propargylation of representative aromatic and heteroaromatic compounds in dichloroethane as solvent. Nishibayashi *et al.* used phosphido- and thiolato-bridged diruthenium complexes for propargylation[2] and also developed an enantioselective propargylation method for indoles.[3] Bustelo and Dixneuf[4] used *in situ* generated mononuclear arene ruthenium complexes for propargylation of furan and 2-methylfuran and for the synthesis of propargylic ethers by cross coupling in relatively modest yields. A rhenium oxo-complex was employed by Toste *et al.*[5] to introduce the propargyl group into reactive arenes/heterocycles. Zhan *et al.*[6] reported a $FeCl_3$-catalyzed reaction using MeCN as solvent. Dyker and associates[7] studied that $AuCl_3$/MeCN system for propargylation of representative electron rich arenes with **Ia**. Other propargylation reagents such as O-propargyl trichloroacetimidates, with BF_3. Et_2O as catalyst,[8] and *N*-tosylpropargyl amine, using $AuCl_3$ as catalyst,[9] have also been employed. Zhu and associates[10] utilized $MoO_2(acac)_2/NH_4PF_6$ as catalyst to achieve direct substitution of propargylic alcohols with oxygen, nitrogen and carbon nucleophiles in modest to good yields.

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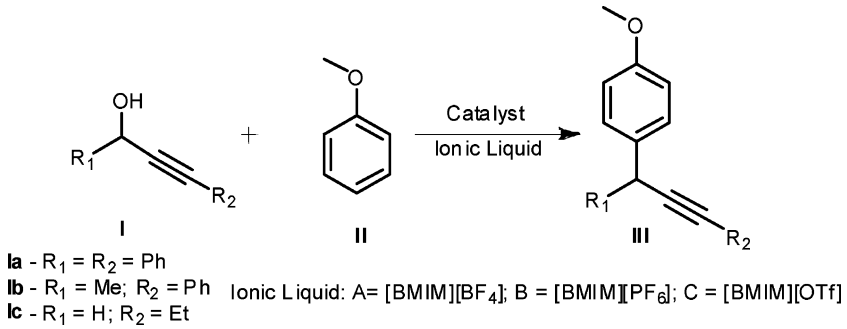


Scheme 1 Model study of propargylation of anisole in ionic liquids.

A number of recent studies have dealt with propargylation of 1,3-dicarbonyl compounds with propargylic alcohols, employing a variety of acidic catalysts such as *p*-toluenesulfonic acid monohydrate in MeCN solvent,[11] heteropoly acids,[12] $Yb(OTf)_3$,[13] and $InCl_3$.[14] A propargylation method utilizing [EMIM][OTf] ionic liquid (IL) in combination with the Brønsted acidic imidazolium IL [BIM-$(CH_2)_3$–SO_3H][OTf] as catalyst at 100 °C has also been reported.[15] Several other studies dealing with propargylic substitution reactions of aryl propargyl methanols with thiols, using methanethiolate-bridged diruthenium complex,[16] with C- and O-nucleophiles using iodine,[17] and with C, O, S, and N-nucleophiles employing $FeCl_3$[18] have also appeared. A number of examples have also been reported for propargylic group transfer using propargylic esters/$TiCl_4$,[19] 3-sulfanyl- and 3-selanylpropargyl alcohols/$Sc(OTf)_3$,[20a] and with allenyltributylstannanes/$Yb(OTf)_3$.[20b]

Interest in the synthesis of target propargyl derivatives stems from their biological and pharmacological importance. Their biopotency is mainly due to their ability to penetrate biological membranes because of their lipophilic, rigid and linear structures. The O, N and aryl-propargylated systems have found application in crop protection field[21a] and as GnRHR antagonists,[21b] inhibitors of HIV-1 reverse-transcriptase[21c] and in the treatment of Alzheimer's disease.[21d] Apart from their biological significance, O-propargylated systems have found application in the synthesis of functional polymers[21e] and propargyl ethers have been used for the synthesis of planar chiral cobalt metallocenes[21f] as potential catalyst for a range of synthetic applications.

In continuation of our work on electrophilic chemistry in room temperature ionic liquids (RT-IL),[22–32] and in connection to a recent ion-molecule study of gaseous propargylic carbocations,[33] we report here a synthetic study in imidazolium ILs, focusing on propargyl group introduction into aromatics and heteroaromatics, and cross coupling of propargylic alcohols to prepare a host of functionalized ethers, under mild conditions, in simple one-pot procedures by using metallic triflates, TfOH, or $B(C_6F_5)_3$ as catalysts, with recycling and reuse of the ILs.

Results and discussion

Propargylation of arenes and heteroarenes

At the onset a survey of propargylation study was performed with propargylic alcohols 1,3-diphenyl-2-propyn-1-ol **Ia**, 1-methyl-3-phenyl-2-propyn-1-ol **Ib**, and 2-pentyn-1-ol **Ic** using anisole as model nucleophile under mild conditions (Scheme 1). Metallic triflates $M(OTf)_3$ (M = Bi, Sc, Yb) immobilized in imidazolium ILs [BMIM][BF_4], [BMIM][PF_6] or [BMIM][OTf] were employed as catalysts. The results are summarized in Table 1.

For alcohol **Ia**, the catalytic activity order $Sc(OTf)_3 > Yb(OTf)_3 > Bi(OTf)_3$ was established in [BMIM][PF_6] based on isolated product yields, and by using ROH : ArH : $M(OTf)_3$ ratio of 1 : 2 : 0.15. The reactions were highly *para* selective (no *ortho* isomer was detected by GC–MS). As a representative case, the $Sc(OTf)_3$-catalyzed reaction in [BMIM][BF_4] was selected for a recycling–reuse study at 50 °C (see Table 1), whereby only a slight decrease in the isolated yields were observed over 3 consecutive cycles. Metallic triflates proved less effective in propargylation with **Ib** at 45 °C. Whereas [BMIM] [PF_6]/TfOH system exhibited comparable results, $B(C_6F_5)_3$ proved superior. Interestingly, with TfOH or $B(C_6F_5)_3$ as promoter, both *ortho* and *para* products were formed. Moreover, with $B(C_6F_5)_3$ traces of the corresponding dipropargylic ether (reaction of propargylic cation with the alcohol) was also detected. Relatively modest isolated yields were obtained in propargylation with **Ic**, employing $Sc(OTf)_3$ or $Bi(OTf)_3$ in [BMIM][OTf] ionic liquid, whereas [BMIM][PF_6]/TfOH system proved more effective (see Table 1).

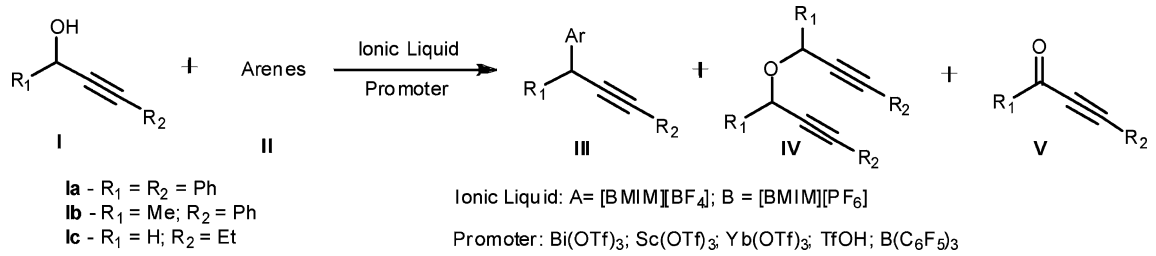
Having identified the most effective catalytic systems for arene propargylation in ILs, the study focused on the synthetic scope of propargylation of reactive and moderately reactive arenes and representative heterocycles with propargyl alcohols **Ia–Ic** (Schemes 2–3 and Tables 2–3). Isolated yields obtained in the present study are comparable, and some cases exceed, those from previously reported studies using cationic diruthenium complex,[1] $AuCl_3$ and $BF_3.Et_2O$.[7]

Steric influence on regioselectivity is manifested in propargylation of anisole and phenol with **Ia**, showing no detectable *ortho* isomer, and with **Ib**, where formation of the *ortho* isomer was competitive. Propargylation of anisole with **Ic** was only successful in TfOH (–5 °C to r.t.). Under these mild conditions, regioselectivity was high (only *para*) but conversion was modest. With reactive arenes, formation of dipropargylic ethers was minimal, but it became competitive in the case of ethylbenzene. With toluene, ring substitution was no longer competing and ether formation was the dominant process. For propargylation of phenol, the $B(C_6F_5)_3$/IL systems proved highly suitable. For mesitylene, [BMIM][BF_4]/$Sc(OTf)_3$ and [BMIM][BF_4]/TfOH systems proved effective with propargylic alcohols **Ia** and **Ib** respectively. The use of TfOH as promoter resulted in competing formation of

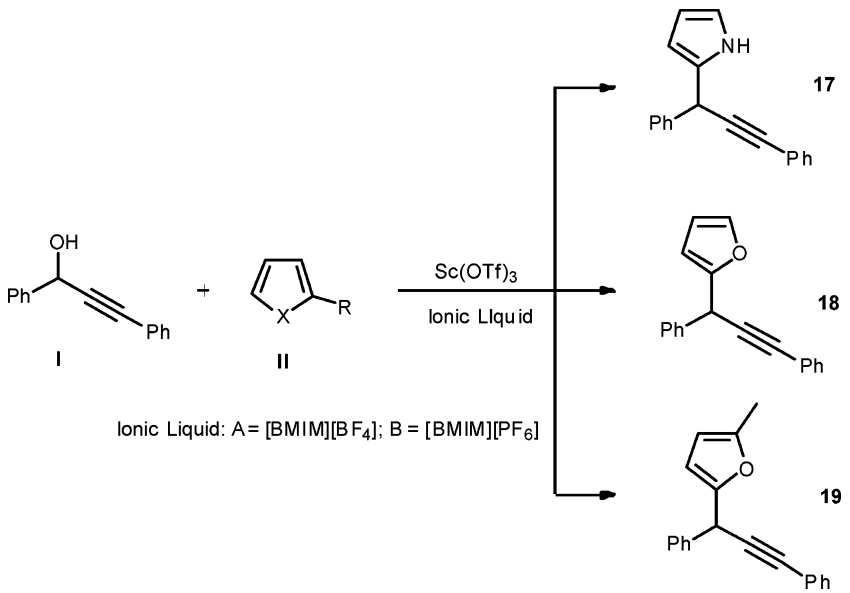
Table 1 A model study of propargylation of anisole with different catalysts in three different imidazolium ILs

I	Catalyst	Ionic Liquid	Molar ratio I : II : Catalyst	Temp. °C	Time (h)	Conversion based on alcohol (%)[a]	Selectivity (%)[a] *ortho*	Selectivity (%)[a] *para*	Isolated yield
Ia	$Bi(OTf)_3$	B	1 : 2 : 0.20	r.t.	12	48	—	47	41
	$Bi(OTf)_3$	B[b]	1 : 2 : 0.20	60	8	89	—	85	80
	$Yb(OTf)_3$	B	1 : 2 : 0.20	60	8	100	—	94	86
	$Sc(OTf)_3$	B	1 : 2 : 0.20	45	6	100	—	97	91
	$Sc(OTf)_3$	A	1 : 2 : 0.15	50	5	100	—	100	94 (1st run)
	$Sc(OTf)_3$	A	1 : 2 : 0.15	50	5	98	—	99	92 (2nd run)[c]
	$Sc(OTf)_3$	A	1 : 2 : 0.15	50	5	93	—	95	88 (3rd run)[c]
Ib	$Sc(OTf)_3$	A	1 : 3 : 0.20	45	14	60	—	50	45
	$Yb(OTf)_3$	B	1 : 3 : 0.20	45	20	45	—	41	25
	TfOH	B	1 : 4 : 0.20	−5 to r.t.	10	80	28	50	59 (*ortho* & *para* together)
	$B(C_6F_5)_3$	B	1 : 2 : 0.15	40	4	94 + 6[d]	26	74	21% -*ortho*[e] & 66% -*para*
Ic	$Bi(OTf)_3$	C	1 : 3 : 0.20	r.t. to 40	18	65	—	50	25
	$Sc(OTf)_3$	C	1 : 3 : 0.20	r.t. to 40	14	70	—	60	36
	TfOH	B	1 : 2.5 : 0.15	−5 to r.t.	4	100	—	100	42

[a] Based on GC assay. [b] Recycled ionic liquid. [c] No catalyst was added. [d] Homo ether (6%). [e] When the reaction was carried out at r.t. (10 h), the *ortho* isomer decreased significantly.



Scheme 2 Propargylation of arenes in ionic liquids catalyzed by Lewis acids.



Scheme 3 Propargylation of heteroarenes in ionic liquids catalyzed by $Sc(OTf)_3$.

the dipropargylic ether. Whereas propargyl introduction into β-naphthol with **Ia** in $[BMIM][BF_4]/Sc(OTf)_3$ proceeded in high yield and high chemoselectivity, lower conversion and concomitant formation of dipropargylic ether were observed with **Ib** in $[BMIM][PF_6]/Yb(OTf)_3$ system. Products **1–16** synthesized in this study are shown in Fig. 1.

In propargylation of representative heterocycles (Table 3), $Sc(OTf)_3$ immobilized in $[BMIM][BF_4]$ or $[BMIM][PF_6]$ proved effective with **Ia**, but under the mild conditions employed no reaction occurred with alcohol **Ib**. Reaction of alcohol **Ia** with isomeric nitroanilines (Scheme 4, Table 4) in $[BMIM][BF_4]/Sc(OTf)_3$ resulted in *N*-propargylation (compounds **20** and **21**).

Table 2 Propargylation of arenes with different catalysts in imidazolium ILs

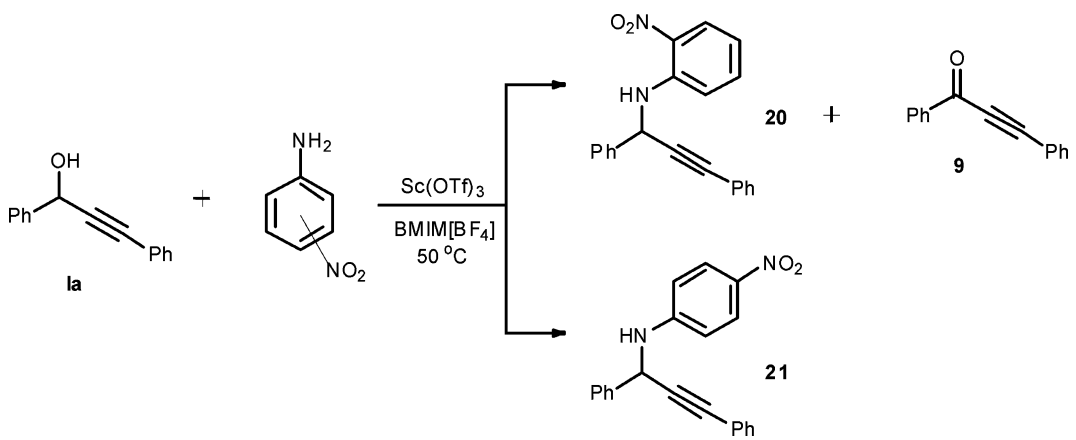
						Selectivity (%)[a]			Isolated yield (%)			
I	II	IL	Catalyst	Temp. °C	Time (h)	III [*ortho*/*para*]	IV	V	III [*ortho*/*para*]	IV	V	Product No.
Ia	Anisole	A	$Sc(OTf)_3$	50	5	98 [–/100]	—	trace	94	—	—	**1**
Ib	Anisole	B	$B(C_6F_5)_3$	40	4	94 [26/74]	6	—	21[b]/66[c]	—	—	**2/3**
Ic	Anisole	B	TfOH	–5 to r.t.	4	100 [–/100]	—	—	42	—	—	**4**
Ia	1,3-Dimethoxybenzene	A	$Sc(OTf)_3$	60	5	94	—	trace	91[d]	—	—	**5**
Ib	1,3-Dimethoxybenzene	B	$Yb(OTf)_3$	50	7.5	93	7	—	81	—	—	**7**
Ia	1,3,5-Trimethoxybenzene	A	$Yb(OTf)_3$	50	5	100	—	—	92	—	—	**8**
Ia	Toluene	A	$Sc(OTf)_3$	50	3.5	—	71	29	—	67	21	**9**
Ia	Ethylbenzene	A	$Sc(OTf)_3$	50	6.5	35 [–/100]	51	14	28	47	11	**10**
Ia	Mesitylene	A	$Sc(OTf)_3$	50	8	87	—	13	80	10	—	**11**
Ib	Mesitylene	B	TfOH	–5 to 50	3.5	67	33	—	62	29	—	**12**
Ia	Phenol	A	$B(C_6F_5)_3$	60	6	98 [–/100]	—	trace	92	—	—	**13**
Ib	Phenol	B	$B(C_6F_5)_3$	50	7.5	88 [52/48]	12	—	61[e]	—	—	**14**
Ia	2-Naphthol	A	$Sc(OTf)_3$	60	6	100	—	—	85	—	—	**15**
Ib	2-Naphthol	B	$Yb(OTf)_3$	40	8	67	33	—	61	27	—	**16**

In all cases, quantitative conversion of the limiting reagent was noted by GC.[a] Based on GC assay. [b] When the reaction was carried out at r.t. for about 10 h, the *ortho* isomer decreased significantly. [c] Product is a mixture of **3** and homo ether of **31** (*i.e.*, **Ib** + **Ib**) by NMR. [d] When $Bi(OTf)_3$ was used (at 60 °C for about 8 h), 21% of disubstitution product (**6**) along with monosubstitution (67%) and the ketone **9** (8%) were obtained. [e] Product obtained as an inseparable mixture of *ortho* and *para* isomers.

Table 3 Propargylation of heteroarenes with $Sc(OTf)_3$ in imidazolium ILs

					Selectivity (%)[a]	Isolated yield (%)	
I	II	IL	Temp. °C	Time (h)	III	III	Product No.
Ia	Pyrrole	A or B	r.t.	1.5	100	74	**17**
Ia	Furan	A or B	45	1.5	100	89	**18**
Ia	2-Methylfuran	A or B	30	1	100	86	**19**

In all the cases, quantitative conversion of the limiting reagent was noticed by GC.[a] Based on GC assay.



Scheme 4 Propargylation of aniline derivatives in $[BMIM][BF_4]$ catalyzed by $Sc(OTf)_3$.

Whereas 3-phenyl-2-propyn-1-ol (**Id**) did not react well under $M(OTf)_3$ catalysis with anisole, 1,3-dimethoxybenzene, or with phenol, it could be activated in TfOH/IL. However, under these conditions, the propargylic derivative was not isolated; instead, the corresponding propanone derivatives (compounds **22–24**) were obtained in satisfactory yields (Scheme 5 and Table 5). These products arise from nucleophilic attack by ArH on the *in situ* formed αβ-unsaturated ketone formed *via* a Meyer–Schuster type rearrangement.[34]

The recycling and reuse of the IL in arene propargylation was demonstrated in $[BMIM][BF_4]/Sc(OTf)_3$ system using propargylic alcohol **Ia** (Fig. 2) in which mesitylene, β-naphthol and pyrrole were sequentially propargylated to obtain products **11**, **15**, and **17** in the same IL and without adding fresh catalyst, with no

Table 4 Propargylation of anilines with $Sc(OTf)_3$

Aniline	IL	Temp. °C	Time (h)	Selectivity[a]	Isolated yield (%)	Product No.
2-Nitroaniline	[BMIM][BF_4]	50	1.5	100	90[b]	**20**
4-Nitroaniilne	[BMIM][BF_4]	50	4	100	91	**21**

In both cases, quantitative conversion of the limiting reagent was noted by GC.[a] Based on GC assay. [b] Product obtained as an inseparable mixture of **20**/**9** (1 : 0.88).

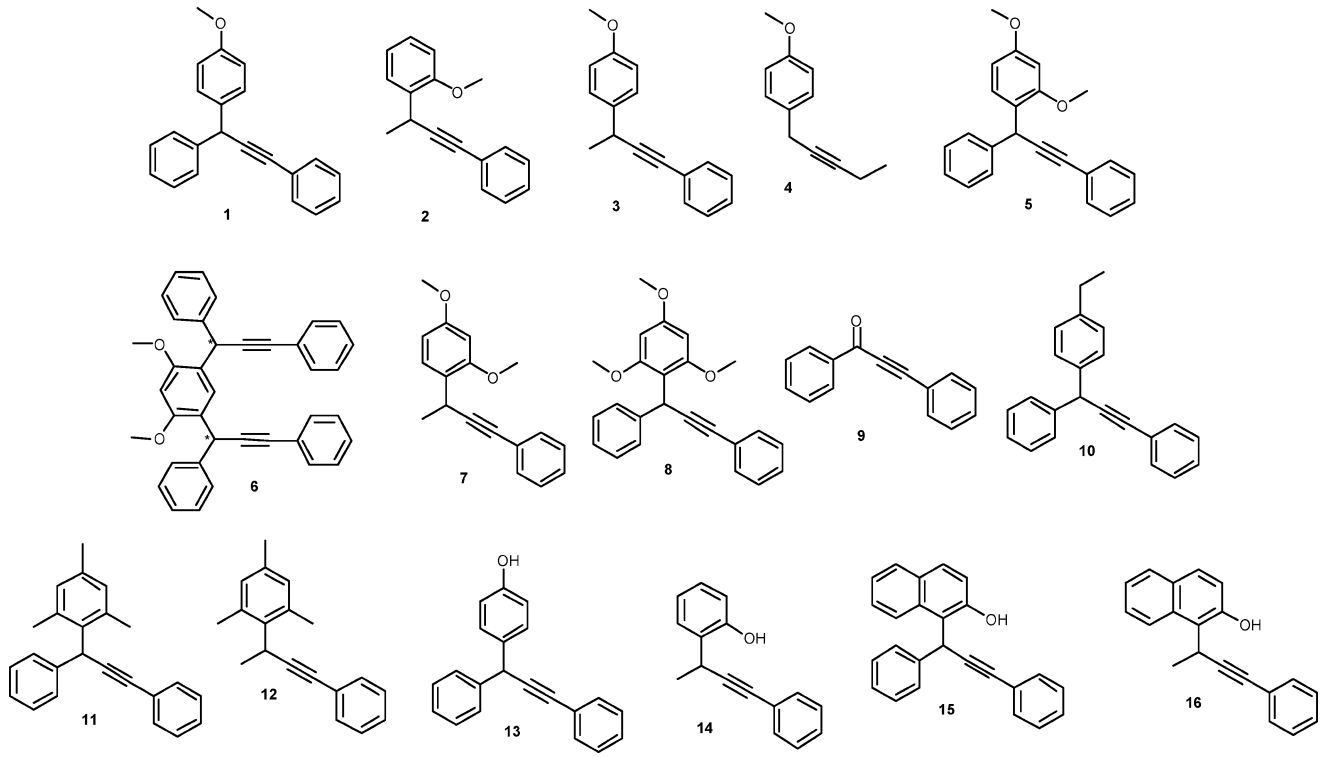
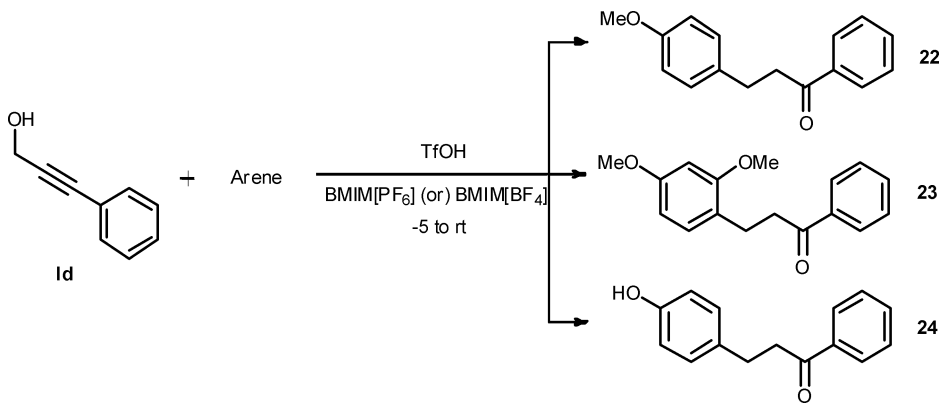


Fig. 1 Structure of aryl propargylated products.



Scheme 5 TfOH-catalyzed propargylation of **Id** in ionic liquids.

noticeable decrease in the conversions. Similarly each ionic liquid was re-used for more than six times with different substrates by systematic handling and drying of the ionic liquid after use.

Synthesis of propargylic ethers

Development of simple one-pot protocols for high yield synthesis of the mono- and bis-propargylic ethers is a desirable goal, because it allows direct access to functional alkynes. In this context, bearing in mind that minor amounts of bis-propargylic ethers these by-products were observed in some cases in reactions with arenes (compound type **IV** in Scheme 2 and Table 2), the focus of the study was shifted to condensation of propargylic alcohol **Ia–Id** with aliphatic and benzylic alcohols, as well as self-condensation of propargyl alcohols and cross coupling of two propargylic alcohols (Scheme 6). The results are summarized in Table 6.

Table 5 Synthesis of aryl bearing propanone derivatives with TfOH in imidazolium ILs

Arene	IL	Catalyst[a]	Temp. °C	Time (h)	Conversion based on alcohol (%)[b]	Selectivity[b]	Isolated yield (%)	Product No.
Anisole	A or B	TfOH	−5 to r.t.	6	100	88	74	**22**
1,3-Dimethoxy benzene	A or B	TfOH	−5 to r.t.	7	100	87	71	**23**
Phenol	A or B	TfOH	−5 to r.t.	6	100	92	86	**24**

[a] The same product was obtained by using $M(OTf)_3$ or $B(C_6F_5)_3$ but in lower yields. However, the expected direct substitution product was not obtained in any of the Lewis acid catalysts employed. Furan and 2-methylfuran did not react even by changing the catalyst. [b] Based on GC assay.

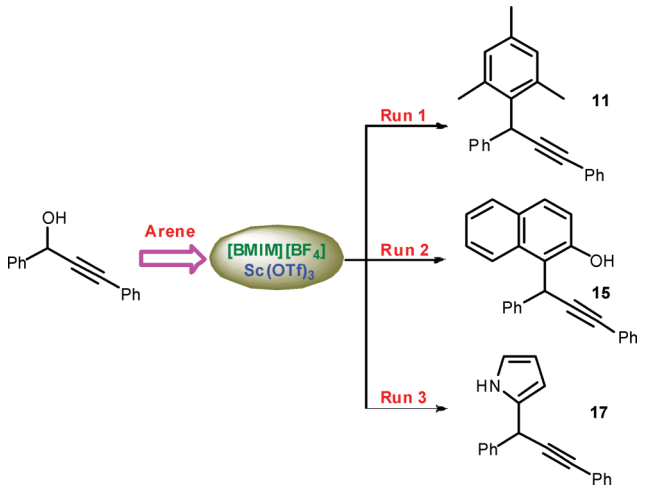


Fig. 2 Recycling–reuse of IL and promoter.

Whereas in crossed condensation reaction of 1,3-diphenyl-2-propyn-1-ol with benzylic and aliphatic alcohols the IL/$Sc(OTf)_3$ system proved quite effective, for other propargylic alcohols the IL/TfOH (at lower temperatures) became the system of choice. The cross-coupling of two different propargylic alcohols to prepare bis-propargylic ethers could be performed in IL/$Sc(OTf)_3$ or in IL/TfOH systems in good to moderate isolated yields. Structure of the ethers **25–36** are shown in Fig. 3.

In summary the utility of IL/$M(OTf)_3$ and IL/TfOH systems for propargyl group introduction into a wide variety of arenes and heteroarenes under mild conditions with recycling and re-use of the IL and the catalysts has been demonstrated in simple one-pot reactions. The same catalytic systems can promote self- or crossed-condensation of propargylic alcohols to synthesize a variety of bis-propargylic ethers. Condensation of propargylic ethers with a variety of benzylic and aliphatic alcohols has also been shown.

Experimental

General. The reagents and the ionic liquids employed in this study were high purity commercial samples, which were used without further purification. Triflic acid (ACROS) was stored in Nalgene bottles flushed with nitrogen in a freezer. The reactions were carried out in small Schlenk tubes under nitrogen. Dry diethyl ether was used for extraction. Column chromatography was performed on silica gel (200–400 mesh) and in some cases, prep-TLC was performed. Melting points were recorded with a MEL-TEMP apparatus and are uncorrected. NMR spectra were recorded in $CDCl_3$ (^1H at 500 MHz; ^{13}C at 125 MHz) on a Varian 500 NMR instrument with chemical shift (δ values in ppm; * indicates interchangeable assignments); IR spectra (solution, cm^{-1}) were obtained on SHIMADZU FT-IR spectrophotometer. Only selected/diagnostic IR and mass data are reported.

GC and GC–MS analysis. A 2 μL sample of each compound was analyzed in duplicate runs on a Hewlett–Packard (HP) gas chromatograph model 5890 series II equipped with a split/splitless injector and a capillary RTX-5 column. The injection port and detector were kept at 250 and 300 °C, respectively. The oven temperature was initially held at 50 °C for 2 min and programmed at 7 °C min^{-1} to 220 °C and held for 10 min isothermally which was then finally ramped to 290 °C (held for 5 min) at 10 °C min^{-1}. The same program was used for GC–MS with 2 μL sample injection. GC–MS analyses were performed on an HP model 5890 series II GC attached to an HP model 5972 series mass selective detector instrument. The split ratio was 10 : 1 with 2 μL of sample injected. Mass spectra in the electron ionization mode (MS-EI) were obtained at 70 eV with ion source temperature at 230 °C. After a 2 min solvent delay, mass spectra were obtained over the m/z range 50–600. The total ion chromatogram (TIC) acquired by GC–MS was used for peak area integration.

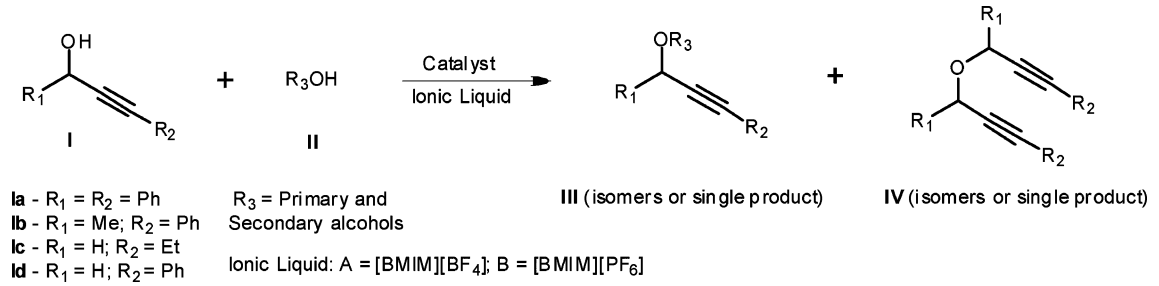
General procedure for propargyl introduction into aromatics. The respective catalyst (15–20 mol%) was added to Schlenk tube containing the desired ionic liquid (4.5 mmol) under N_2 atmosphere and was immobilized by sonication for about 15–20 min. The arene was introduced into the Schlenk tube (kept in an ice bath) under a nitrogen atmosphere followed by the desired propargylic alcohol. The contents were magnetically stirred initially at r. t. for about 15 min followed by stirring in a pre-heated oil bath either at 50 or 60 °C (as applicable; refer to Tables 1–5) until completion (monitored by TLC). Once the reaction was over, the contents were cooled to r. t. and extracted with dry diethyl ether (until the final extraction did not indicate any spot corresponding to the arene or the product). The combined organic layer was washed with bicarbonate solution, dried with $MgSO_4$ and concentrated to give the crude direct substitution product. Purification through column chromatography furnished the desired products.

General procedure for the synthesis of propargylic ethers. $Sc(OTf)_3$ (15–20 mol%) was added to Schlenk tube containing the desired ionic liquid (4.5 mmol) under N_2 atmosphere and was immobilized by sonication for about 15–20 min. The desired

Table 6 Synthesis of propargyl ethers catalyzed by $Sc(OTf)_3$ or TfOH in imidazolium ILs

						Composition of reaction mixture				
I	II	IL	Catalyst	Temp. °C	Time (h)	Selectivity (III,%)[a]	Homo ether (IV,%)[a]	Product ratio (III + IV)[b]	Isolated yield (%)	Product No.
Ia	Benzyl alcohol	A	$Sc(OTf)_3$	50	3	100	—	—	90	**25**
Ib	Benzyl alcohol	B	TfOH	−5 to 30	7	—	—	1 : 0.16[c]	79[d]	**26**
Id	Benzyl alcohol	B	TfOH	−5 to 30	4	89	—	—	62	**27**
Ia	2-Propanol	A	$Sc(OTf)_3$	50	4	100	—	—	82	**28**
Ia	2-Butanol	A	$Sc(OTf)_3$	50	3	100	—	—	91[e]	**29**
Ia	Ia	A	$Sc(OTf)_3$	50	2.5	100	—	—	92[f]	**30**
Ib	Ib	A	TfOH	−5 to 30	4.5	100	70/30	—	63/25	**31**[g]
Id	Id	A	TfOH	−5 to 30	6	100	—	—	61	**32**
Ib	Id	A	TfOH	−5 to 30	3.5	—	—	1 : 0.04[c]	78[d]	**33**
Ib	Ic	A	$Sc(OTf)_3$	60	7.5	—	—	1 : 0.31[c]	54[d]	**34**
Id	Ic	A	$Sc(OTf)_3$	50	7.5	—	—	1 : 0.97	52[d]	**35**
Ib	Cyclohexanol	A	TfOH	−5 to r.t.	3.5	—	—	1 : 0.44	81[d]	**36**

In all cases, quantitative conversion of the limiting reagent was noted by GC; Isomer ratio of the isolated products were calculated by NMR.[a] Based on GC assay. [b] Product ratio was determined by NMR. [c] Homo ether (**Ib** + **Ib** *i.e.*, **31**) itself exists as isomers. [d] Isolated product was a mixture of desired ether and the homo ether of alcohol **Ib** (**31**) due to their very close rf values in TLC. [e] Exists as inseparable isomers (1 : 0.81). [f] Exists as inseparable isomers (1 : 0.67). [g] Obtained as two separable isomers (**31a** & **31b**).



Scheme 6 Synthesis of propargylic ethers in ionic liquids.

alcohol was introduced into the Schlenk tube (kept in an ice bath) under a nitrogen atmosphere followed by the propargylic alcohol. The contents were magnetically stirred initially at r. t. for about 15 min followed by stirring in a pre-heated oil bath either at 50 or 60 °C (as applicable; refer to Table 6) until completion (monitored by TLC). In TfOH-catalyzed reactions the ionic liquid was charged into a Schlenk tube, and following the addition of the desired alcohol and the propargylic alcohol, TfOH was added under N_2 atmosphere at −5°C. Once the reaction was over, the contents were cooled to r. t. and extracted with dry diethyl ether (until the final extraction did not show any spots corresponding to either alcohol). The combined organic layer was washed with bicarbonate solution, dried with $MgSO_4$ and concentrated to give the crude product. Purification through column chromatography furnished the desired products.

Re-use and recycling of IL. After ether extraction, the ionic liquid was dried under high vacuum at 60–70 °C overnight.

4-Methoxy-1-(1,3-diphenylprop-2-ynyl)-benzene (1):[35]**.** Alcohol **Ia** (1 mmol), anisole (2 mmol) and catalyst (15 mol%): Yield 94% (colorless oil). **^{1}H NMR**: 3.79 (s, 3H), 5.19 (s, 1H), 6.88 (d, 2H, J = 9.0 Hz), 7.23–7.51 (m, 12H); **^{13}C NMR**: 42.93, 55.28, 84.72, 90.49, 113.99, 123.55, 126.83, 127.83, 128.0, 128.23, 128.61, 128.92, 131.69, 133.96, 142.08, 158.51; **IR**: 3059, 2924, 1597, 1508, 1491, 1252, 1173, 1029; **Mass (m/z)**: 298 (M^+, 100%); 283, 265, 205, 189, 179, 165, 126, 115.

2-Methoxy-1-(4-phenylbut-3-yn-2-yl)benzene (2). Alcohol **Ib** (1 mmol), anisole (2 mmol) and catalyst (15 mol%); Yield 21% (colorless oil). This was obtained as a separable minor isomer along with its *para* counterpart (**3**). **^{1}H NMR**: 1.53 (d, 3H, J = 7.0 Hz); 3.87 (s, 3H), 4.41 (q, 1H, J = 7.0 Hz), 6.88 (d, 1H, J = 10.0 Hz), 6.99 (t, 1H, J = 7.2 Hz), 7.23–7.48 (m, 6H), 7.67 (dd, 1H, J = 7.5 Hz, J = 1.5 Hz); **^{13}C NMR**: 22.95, 26.15, 55.40, 81.71, 93.19, 110.41, 120.75, 123.99, 127.60, 127.75, 127.90, 128.17, 131.65, 156.06; **IR**: 2972, 2930, 1678, 1609, 1597, 1512, 1248, 1177; **MS** (m/z): 236 (M^+), 221 (100%), 202, 178, 115.

4-Methoxy-1-(4-phenylbut-3-yn-2-yl)-benzene (3). Alcohol **Ib** (1 mmol), anisole (2 mmol) and catalyst (15 mol%); Yield 66% [colorless oil; obtained as a 1 : 0.1 mixture (by NMR) of **3** and isomeric **31** (consisting of **31a** and **31b** in 1 : 0.13 ratio-by NMR) see below]. NMR data for **3** is out of mixture. **^{1}H NMR**: 1.57 (d, 3H, J = 7.5 Hz), 3.81 (s, 3H), 3.95 (q, 1H, J = 7.0 Hz), 6.89 (d, 2H, J = 8.5 Hz), 7.29–7.33 (m, 3H), 7.38 (d, 2H, J = 9.0 Hz), 7.44–7.47 (m, 2H); **^{13}C NMR**: 24.59, 31.64, 55.30, 82.23, 92.96, 113.92, 123.79, 127.70, 127.89, 128.19, 131.61, 135.49, 158.34; **IR**: 2926, 2853, 1599, 1587, 1489, 1456, 1240, 1115, 1076, 1051, 1029; **Mass (m/z)**: 236 (M^+); 221 (100%), 178, 128, 77.

4-Methoxy-1-(pent-2-ynyl)benzene (4). Alcohol **Ic** (1 mmol), anisole (2.5 mmol) and catalyst (20 mol%); Yield 42% (pale red semi-solid). **^{1}H NMR**: 1.16 (t, 3H, J = 7.7 Hz); 2.23 (qt, 2H, J = 7.5 Hz, J = 2.4 Hz), 3.51 (t, 2H, J = 2.3 Hz), 3.79 (s, 3H), 6.85

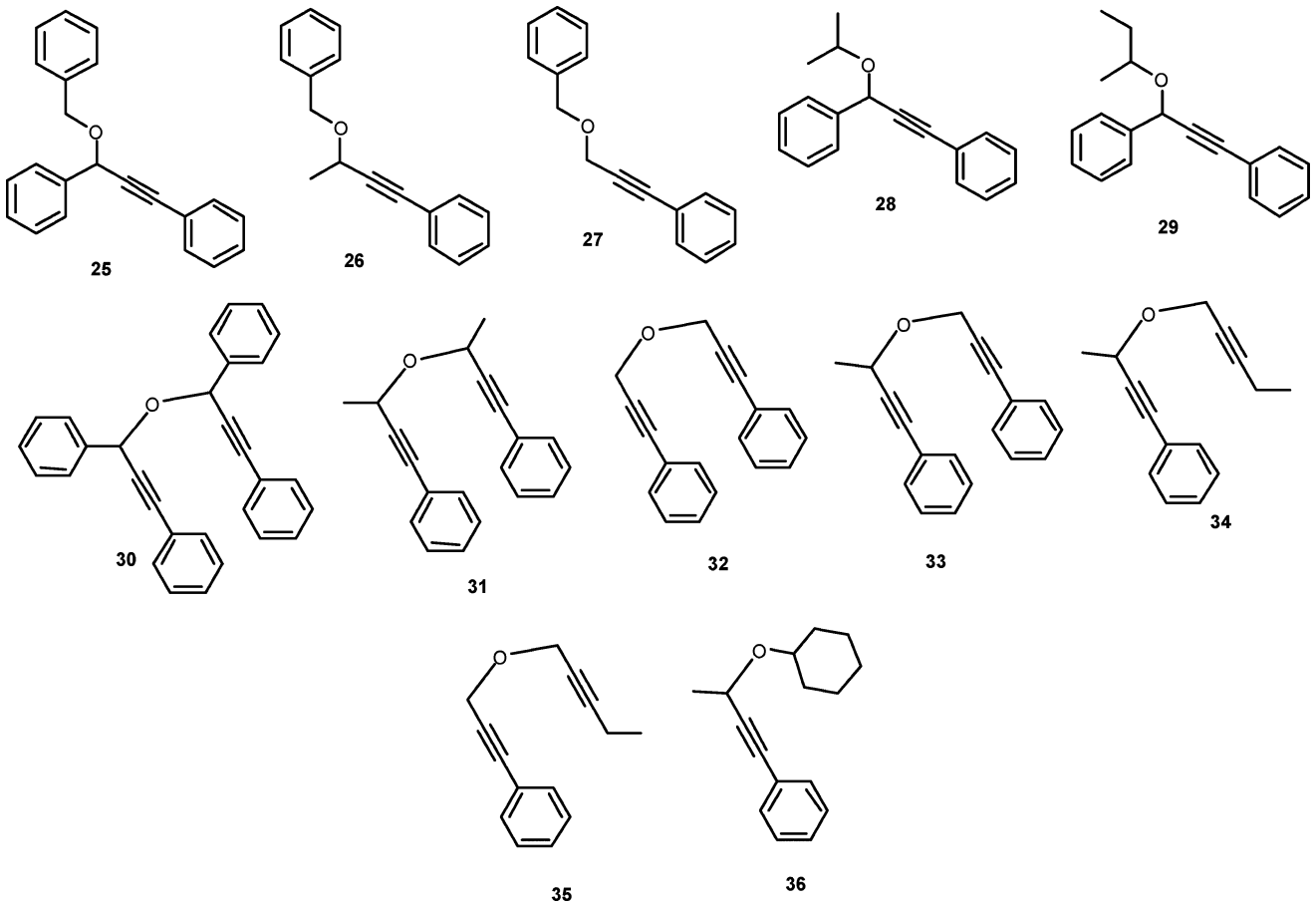


Fig. 3 Propargylic ethers synthesized.

(d, 2H, J = 8.5 Hz), 7.25–7.26 (m, 2H); **^{13}C NMR**: 12.51, 14.25, 24.22, 55.29, 77.33, 83.72, 113.82, 128.78, 134.14, 158.19; **IR**: 2930, 1601, 1512, 1464, 1412, 1246; **MS** (m/z): 174 (M^+,100%), 159, 145, 128, 115, 102, 91, 77, 63, 51, 39.

2,4-Dimethoxy-1-(1,3-diphenylprop-2-ynyl)benzene (5):[35]. Alcohol **Ia** (1 mmol), 1,3-dimethoxybenzene (2 mmol) and catalyst (15 mol%); Yield 91% (white solid; m.p.: 105–106 °C). **^{1}H NMR**: 3.82 (s, 3H), 3.84 (s, 3H), 5.65 (s, 1H), 6.49 (d, 1H, J = 2.5 Hz), 6.54 (dd, 1H, J = 8.8 Hz, J = 2.3 Hz), 7.21–7.34 (m, 6H), 7.49–7.52 (m, 4H), 7.54 (d, 1H, J = 8.5 Hz); **^{13}C NMR**: 36.14, 55.38, 55.57, 83.48, 91.22, 98.65, 104.60, 122.90, 123.83, 126.49, 127.79, 127.83, 128.23, 128.35, 129.53, 131.73, 142.18, 157.11, 159.94; **IR**: 2835, 1609, 1589, 1505, 1489, 1289, 1207, 1113, 1032; **MS** (m/z): 328 (M^+,100%), 313, 252, 189, 115, 77.

1,5-Dimethoxy-2,4-bis-(1,3-diphenylprop-2-ynyl)benzene (6):[7]. Alcohol **Ia** (1 mmol), 1,3-dimethoxybenzene (2 mmol) and $Bi(OTf)_3$ (20 mol%); Obtained as an off white solid (m.p. 154–156 °C). Yield: 21% (mixture of *racemic* and *meso* compounds). Specific NMR assignments for each isomer (out of the isomeric mixture):[7] **^{1}H NMR-*rac***: 3.82* (s, 6H), 5.58 (s, 2H), 6.42 (s, 1H), 7.10–7.13 (m, 2H), 7.25–7.30 (m, 10H), 7.36–7.37 (m, 4H), 7.48–7.50 (m, 4H), 7.95 (s, 1H); **^{13}C NMR-*rac***: 36.31, 55.78, 83.41, 91.04, 95.28, 122.47, 123.70, 126.39, 127.65, 127.76, 128.05, 128.26, 129.50, 131.72, 142.11, 155.98; **^{1}H NMR-*meso***: 3.83* (s, 6H), 5.62 (s, 2H), 6.42 (s, 1H), 7.10–7.13 (m, 2H), 7.17–7.25 (m, 10H), 7.36–7.37 (m, 4H), 7.41–7.43 (m, 4H), 8.05 (s, 1H); **^{13}C NMR-*meso***: 36.41, 55.81, 83.62, 91.15, 95.28, 122.10, 123.66, 126.37, 127.65, 127.82, 128.05, 128.31, 129.21, 131.69, 142.22, 156.09. **IR** (isomeric mixture): 2928, 1611, 1589, 1489, 1302, 1204, 1032; **MS** (m/z): 518 (M^+ not detected), 504, 460, 415, 284, 179, 135.

2,4-Dimethoxy-1-(4-phenylbut-3-yn-2-yl)benzene (7):[36]. Alcohol **Ib** (1 mmol), 1,3-dimethoxybenzene (2.5 mmol) and catalyst (15 mol%); Yield 81% (pale-red oil). **^{1}H NMR**: 1.51 (d, 3H, J = 7.0 Hz), 3.81 (s, 6H), 4.33 (q, 1H, J = 7.0 Hz), 6.49 (d, 1H, J = 2.5 Hz), 6.54 (dd, 1H, J = 8.0 Hz, J = 2.5 Hz), 7.28–7.32 (m, 3H), 7.46–7.48 (m, 2H), 7.56 (d, 1H, J = 8.5 Hz); **^{13}C NMR**: 23.14, 25.67, 55.37, 55.41, 81.55, 93.49, 98.53, 104.20, 124.05, 124.17, 127.57, 128.18, 128.26, 131.63, 157.00, 159.64; **IR**: 2962, 2835, 1593, 1493, 1458, 1410, 1265, 1207, 1149; **Mass** (m/z): 266 (M^+); 251 (100%), 165, 152, 77.

2,4,6-Trimethoxy-1-(1,3-diphenylprop-2-ynyl)benzene (8):[7,37]. Alcohol **Ia** (1 mmol), 1,3,5-trimethoxybenzene (2 mmol) and catalyst (15 mol%); Yield: 92% (off white solid m.p. 125 °C). **^{1}H NMR** 3.84 (s, 6H), 3.89 (s, 3H), 5.82 (s, 1H), 6.17 (s, 2H), 7.14–7.33 (m, 6H), 7.45–7.54 (m, 4H); **^{13}C NMR** 31.50, 55.38, 56.06, 81.27, 90.96, 91.61, 111.48, 124.60, 125.60, 127.31, 127.44, 127.83, 128.15, 131.78, 141.73, 158.70, 160.44; **MS** (m/z): 358 (M^+,100%), 343, 327, 239, 115.

1,3-Diphenylprop-2-yn-1-one (9):[38]. Alcohol **Ia** (1 mmol), either toluene or ethyl benzene (3 mmol) and catalyst (15 mol%); Yield: 21% (using toluene) and 11% (using ethyl benzene); Obtained as colorless viscous oil. **^{1}H NMR**: 7.42–7.45 (m, 2H), 7.48–7.55 (m, 3H), 7.62–7.71 (m, 3H), 8.24 (dd, 2H, J = 8.3 Hz, J = 1.3 Hz); **^{13}C NMR**: 86.89, 93.13, 120.14, 128.64, 128.70, 129.59, 130.81, 133.09, 134.14. 136.88, 178.06; **IR**: 3055, 2199, 1640, 1265. **MS** (m/z): 206 (M^+), 178 (100%), 129, 75, 51.

4-Ethyl-1-(1,3-diphenylprop-2-ynyl)benzene (10). Alcohol **Ia** (1 mmol), ethylbenzene (3 mmol) and catalyst (15 mol%); Yield: 28% (pale-red semi solid). **^{1}H NMR**: 1.22 (t, 3H, J = 7.8 Hz), 2.63 (q, 2H, J = 7.5 Hz), 5.19 (s, 1H), 7.16 (d, 2H, J = 8.5 Hz), 7.29–7.34 (m, 6H), 7.35 (d, 2H, J = 8.0 Hz), 7.44–7.49 (m, 4H); **^{13}C NMR**: 15.54, 28.46, 43.43, 82.85, 86.62, 123.00, 127.35, 127.83, 127.90, 128.14, 128.24, 128.28, 128.61, 128.77, 131.84, 138.00, 141.98; **IR**: 3059, 2928, 1694, 1597, 1489, 1451, 1265; **MS** (m/z): 296 (M^+), 281, 267 (100%), 202, 189, 165, 77.

2,4,6-Trimethyl-1-(1,3-diphenylprop-2-ynyl)benzene (11). Alcohol **Ia** (1 mmol), mesitylene (2 mmol) and catalyst (15 mol%); Yield: 80% (colorless oil). **^{1}H NMR**: 2.32 (s, 3H), 2.33 (s, 3H), 2.34 (s, 3H), 5.76 (s, 1H), 6.92 (s, 2H), 7.31–7.35 (m, 5H), 7.41–7.42 (m, 3H), 7.50–7.52; (m, 2H); **^{13}C NMR**: 20.81, 20.89, 36.92, 84.15, 89.17, 123.82, 126.30, 126.96, 127.18, 127.83, 128.24, 128.32, 128.72, 131.66, 134.78, 136.60, 140.24; **IR**: 3024, 2916, 2198, 1605, 1489, 1451, 1026; **MS** (m/z): 310 (M^+, 100%), 295, 219, 202, 189, 77.

2,4,6-Trimethyl-1-(4-phenylbut-3-yn-2-yl)benzene (12). Alcohol **Ib** (1 mmol), mesitylene (2.5 mmol) and catalyst (20 mol%); Yield: 62% (colorless oil). **^{1}H NMR**: 1.55 (d, 3H, J = 7.3 Hz), 2.26 (s, 3H), 2.50 (s, 6H), 4.43 (q, 1H, J = 7.3 Hz), 6.86 (s, 2H), 7.26–7.27 (m, 3H), 7.38–7.40 (m, 2H); **^{3}C NMR**: 20.41, 20.68, 20.70, 22.70, 26.77, 81.25, 93.05, 124.06, 127.49, 128.15, 130.00, 131.41, 135.80, 135.90 (two coinciding carbon resonances); **IR**: 2957, 2924, 2855, 1491, 1456, 1377, 1262; **MS** (m/z): 248 (M^+), 233 (100%), 218, 202.

4-Hydroxy-1-(1,3-diphenylprop-2-ynyl)benzene (13):[35]. Alcohol **Ia** (1 mmol), phenol (2 mmol) and catalyst (15 mol%); Yield: 92% (pale yellow solid; m.p. 85–87 °C). **^{1}H NMR**: 5.21 (s, 1H), 5.69 (bs, 1H), 6.83 (d, 2H, J = 8.5 Hz), 7.28–7.31 (m, 1H), 7.34–7.39 (m, 7H), 7.48–7.55 (m, 4H); **^{13}C NMR**: 42.91, 84.73, 90.47, 115.46, 123.50, 126.84, 127.83, 127.98, 128.24, 128.61, 129.12, 131.68, 134.03, 142.05, 154.50; **IR**: 3312, 2974, 2924, 2853, 1597, 1512, 1489, 1443, 1233, 1171; **MS** (m/z): 284 (M^+, 100%), 207, 189, 152, 77.

2-Hydroxy-1-(4-phenylbut-3-yn-2-yl)benzene (14):[39]. Alcohol **Ib** (1 mmol), phenol (2 mmol) and catalyst (15 mol%); Yield: 61% (dark-brown viscous oil; mixture of *ortho* (major) and *para* isomers by NMR). NMR data for the *ortho* isomer: **^{1}H NMR** (1.62 (d, 3H, J = 7.5 Hz), 4.21 (q, 1H, J = 7.2 Hz), 5.85 (s, 1H), 6.87 (dd, 1H, J = 8.0 Hz, J = 1.0 Hz), 6.95 (td, 1H, J = 7.5 Hz, J = 1.5 Hz), 7.18 (td, 1H, J = 7.8 Hz, J = 1.6 Hz); 7.31 (m, 3H), 7.39 (dd, 1H, J = 7.5 Hz, J = 1.5 Hz), 7.47–7.48 (m, 2H); **^{13}C NMR**: 22.35, 28.0, 83.43, 91.37, 116.53, 121.12, 122.98, 128.18, 128.19, 128.32, 128.36, 131.65, 131.71, 153.35; **IR** (isomeric mixture): 3454, 2974, 2928, 1597, 1489, 1454; **MS** (m/z): 222 (M^+), 207 (100%), 178, 77.

1-(1,3-Diphenylprop-2-ynyl)naphthalen-2-ol (15):[35]. Alcohol **Ia** (1 mmol), 2-naphthol (1.7 mmol) and catalyst (15 mol%); Yield: 85% (pale-red oil). **^{1}H NMR**: 6.32 (s, 1H), 6.48 (bs, 1H), 7.19 (d, 1H, J = 8.5 Hz), 7.25–7.27 (m, 1H), 7.30–7.38 (m, 6H), 7.45–7.52 (m, 5H), 7.78 (d, 1H, J = 9.0 Hz), 7.82 (d, 1H, J = 8.0 Hz), 8.06 (d, 1H, J = 8.5 Hz); **^{13}C NMR**: 33.61, 86.02, 88.37, 117.64, 118.54, 122.61, 122.74, 123.39, 126.48, 126.74, 127.38, 127.70, 127.77, 128.0, 128.13, 128.97, 129.32, 131.29, 132.39, 139.56, 152.34; **IR**: 3224, 2924, 2853, 1628, 1597, 1516, 1491, 1437; **MS** (m/z): 334 (M^+, 100%), 257, 228, 77.

1-(4-Phenylbut-3-yn-2-yl)naphthalen-2-ol (16). Alcohol **Ib** (1 mmol), 2-naphthol (1.7 mmol) and catalyst (15 mol%); Yield: 61% (dark-brown viscous oil). **^{1}H NMR**: 1.68 (d, 3H, J = 7.0 Hz), 4.94 (q, 1H, J = 7.2 Hz), 7.17 (d, 1H, J = 9.0 Hz), 7.31–7.38 (m, 4H), 7.46–7.54 (m, 3H), 7.71 (d, 1H, J = 9.0 Hz), 7.80 (un resolved dd, 1H, J = 7.5 Hz), 8.00 (d, 1H, J = 8.5 Hz), OH (not observed); **^{13}C NMR**: 23.93, 29.71, 84.72, 90.52, 118.49, 119.64, 121.75, 122.21, 123.16, 126.75, 128.40, 128.58, 128.97, 129.07, 129.52, 131.40, 131.73, 152.38; **IR**: 3433, 3055, 2932, 1620, 1600, 1265; **MS** (m/z): 272 (M^+), 257 (100%), 195, 128, 77.

2-(1,3-Diphenylprop-2-ynyl)-1*H*-pyrrole (17):[18]. Alcohol **Ia** (1 mmol), pyrrole (3 mmol) and catalyst (15 mol%); Yield: 74% (brown solid; m.p. 70–72 °C). **^{1}H NMR**: 5.34 (s, 1H), 6.10–6.12 (m, 1H), 6.22 (dd, 1H, J = 6.2 Hz, J = 2.75 Hz), 6.74–6.76 (m, 1H), 7.31–7.42 (m, 6H), 7.49–7.54 (m, 4H), 8.21 (brs, 1H); **^{13}C NMR**: 37.23, 84.12, 88.56, 106.50, 108.66, 117.43, 123.12, 127.28, 127.77, 128.22, 128.30, 128.74, 130.64, 131.76, 140.17; **IR**: 3433, 2924, 2853, 1597, 1489, 1452, 1090, 1026; **MS** (m/z): 257 (M^+, 100%), 180, 152, 127, 77.

2-(1,3-Diphenylprop-2-ynyl)furan (18):[35]. Alcohol **Ia** (1 mmol), furan (1.5 mmol) and catalyst (15 mol%); Yield: 89% (pale-yellow oil). **^{1}H NMR**: 5.30 (s, 1H), 6.31–6.32 (m, 1H), 6.35–6.36 (m, 1H), 7.33–7.41 (m, 7H), 7.50–7.53 (m, 4H); **^{13}C NMR**: 37.89, 83.95, 87.43, 106.64, 110.35, 123.17, 127.41, 127.88, 128.19, 128.27, 128.68, 131.79, 138.89, 142.29, 153.80; **IR**: 2924, 2853, 1597, 1489, 1452, 1443, 1070; **MS** (m/z): 258 (M^+, 100%), 229, 215, 181, 152, 126, 77.

5-Methyl-2-(1,3-diphenylprop-2-ynyl)furan (19):[1]. Alcohol **Ia** (1 mmol), 2-methylfuran (1.5 mmol) and catalyst (15 mol%); Yield: 86% (pale-yellow oil). **^{1}H NMR**: 2.28 (s, 3H), 5.24 (s, 1H), 5.92 (dd, 1H, J = 3.0 Hz, J = 1.0 Hz), 6.17 (d, 1H, J = 5.0 Hz) 7.29–7.40 (m, 6H), 7.50–7.53 (m, 4H); **^{13}C NMR**: 13.67, 37.91, 83.73, 87.81, 106.22, 107.33, 123.32, 127.04, 127.47, 127.72, 128.03, 128.44, 131.78, 139.19, 151.87, 151.93; **IR**: 2922, 2853, 1597, 1559, 1489, 1452, 1443; **MS** (m/z): 272 (M^+), 257, 229 (100%), 195, 165, 77.

***N*-(2-Nitrophenyl)-1,3-diphenyl-2-propynylamine (20):[10].** Alcohol **Ia** (1 mmol), 2-nitroaniline (1.5 mmol) and catalyst (15 mol%); Yield: 90% (orange color semi solid). Compound **20** could not be separated from 1,3-diphenylprop-2-yn-1-one **9** obtained as byproduct (in 1 : 0.88 ratio respectively). **^{1}H NMR**: 5.70 [d, 1H (CH), J = 6.50 Hz], 6.74–6.77 (m, 1H), 7.13 (d, 1H, J = 8.8 Hz), 7.31–7.34 (m, 3H), 7.43–7.49 (m, 6H), 7.65–7.68 (m, 2H), 8.04–8.06 (m, 1H), 8.45 [d, 1H (NH), J = 6.0 Hz; assignment confirmed by D_2O exchange which also confirmed coupling between NH and CH at 5.70 ppm]. **^{13}C NMR**: 49.73, 85.90, 86.69, 114.99, 116.53, 122.25, 126.82, 127.18, 128.35, 128.48, 128.54, 129.17, 131.83,

132.82, 136.07, 143.52, 144.86; **IR**: 3379, 3061, 2926, 1574, 1501, 1451; **MS** (*m*/*z*): 328 (M^+,100%), 313, 252, 189, 115, 77.

***N*-(4-Nitrophenyl)-1,3-diphenyl-2-propynylamine (21):[10].** Alcohol **Ia** (1 mmol), 4-nitroaniline (1.5 mmol) and catalyst (15 mol%); Yield: 91% (yellow semi solid). **^{1}H NMR**: 4.95 (bs, 1H), 5.60 (s, 1H), 6.75 (d, 2H, *J* = 9.0 Hz), 7.29–7.46 (m, 8H), 7.63–7.65 (m, 2H), 8.13 (d, 2H, *J* = 9.0 Hz); **^{13}C NMR**: 50.07, 85.96, 86.40, 112.42, 122.08, 126.17, 127.27, 128.38, 128.75, 128.78, 129.13, 131.78, 138.03, 139.08, 151.42; **IR**: 3375, 2924, 1597, 1505, 1304; **MS** (*m*/*z*): 326 $(M-2)^+$, 280 (100%), 203, 189, 176, 76.

3-(4-Methoxyphenyl)-1-phenylpropan-1-one (22):[40,41]. Alcohol **Id** (1 mmol), anisole (2 mmol) and catalyst (20 mol%); Yield: 74% (colorless semi-solid). **^{1}H NMR**: 3.01 (t, 2H, *J* = 7.8 Hz), 3.27 (t, 2H, *J* = 7.8 Hz), 3.79 (s, 3H), 6.84 (d, 2H, *J* = 8.5 Hz), 7.17 (d, 2H, *J* = 8.5 Hz), 7.45 (t, 2H, *J* = 7.8 Hz), 7.56 (t, 1H, *J* = 7.2 Hz), 7.95–7.97 (m, 2H); **^{13}C NMR**: 29.28, 40.71 55.27, 113.93, 128.04, 128.05, 128.59, 129.34, 133.02, 136.90, 157.99, 199.40; **IR**: 3053, 2253, 2835, 1512, 1265; **Mass** (*m*/*z*): 240 (M^+), 135, 121 (100%), 105, 77.

3-(2,4-Dimethoxyphenyl)-1-phenylpropan-1-one (23). Alcohol **Id** (1 mmol), 1,3-dimethoxybenzene (2 mmol) and catalyst (20 mol%); Yield: 71% (pale red semi-solid). **^{1}H NMR**: 2.99 (t, 2H, *J* = 7.7 Hz), 3.24 (t, 2H, *J* = 7.8 Hz), 3.80 (s, 3H), 3.81 (s, 3H), 6.43 (dd, 1H, *J* = 8.0 Hz, *J* = 2.5 Hz), 6.47 (unresolved t, 1H, *J* = 2.5 Hz), 7.11 (d, 1H, *J* = 8.5 Hz), 7.45 (t, 2H, *J* = 7.8 Hz), 7.53–7.56 (m, 1H, *J* = 7.3 Hz), 7.97–7.99 (m, 2H); **^{13}C NMR**: 25.14, 39.21, 55.22, 55.37, 98.56, 103.86, 121.88, 128.11, 128.51, 130.34, 132.85, 137.02, 158.38, 159.49, 200.15; **IR**: 3053, 2959, 2936, 1684, 1614, 1587, 1505; **Mass** (*m*/*z*): 270 (M^+), 165, 151 (100%), 121, 105, 77.

3-(4-Hydroxyphenyl)-1-phenylpropan-1-one (24):[42]. Alcohol **Id** (1 mmol), phenol (2 mmol) and catalyst (20 mol%); Yield: 86% (pale red solid; m.p. 105–106). **^{1}H NMR**: 3.0 (t, 2H, *J* = 7.50 Hz), 3.27 (t, 2H, *J* = 7.8 Hz), 5.05 (bs, 1H), 6.77 (d, 2H, *J* = 8.5 Hz), 7.11 (d, 2H, *J* = 9.0 Hz), 7.44 (m, 2H), 7.56 (t, 1H, *J* = 7.5 Hz), 7.95–7.97 (m, 2H); **^{13}C NMR**: 29.31, 40.71, 115.34, 128.07, 128.62, 129.54, 133.12, 133.29, 136.81, 153.94, 199.72; **IR**: 3381, 1674, 1597, 1516, 1449; **MS** (*m*/*z*): 226 (M^+), 105 (100%), 77, 51.

Benzyl-(1,3-diphenyl-prop-2-ynyl)-ether (25):[19]. Alcohol **Ia** (1 mmol), benzyl alcohol (2 mmol) and catalyst (15 mol%); Yield: 90% (pale red oil). **^{1}H NMR**: 4.79 (d, H, *J* = 11.5 Hz), 4.85 (d, 1H, *J* = 11.5 Hz), 5.51 (s, 1H), 7.37–7.49 (m, 11H), 7.55–7.56 (m, 2H), 7.66–7.68 (m, 2H); **^{13}C NMR**: 70.11, 71.01, 86.94, 87.91, 122.62, 127.66, 127.86, 128.24, 128.37, 128.50, 128.54, 128.59, 128.63, 131.89, 137.82, 138.70; **IR**: 3034, 2199, 1689, 1603; **MS** (*m*/*z*): (M^+ not detected), 207 (M-$PhCH_2$), 191 (100%), 105, 77.

Benzyl-(4-phenyl-but-3-yn-2-yl)-ether (26). Alcohol **Ib** (1 mmol), benzyl alcohol (2 mmol) and catalyst (15 mol%); Yield: 79% [colorless oil; obtained as a 1 : 0.16 mixture (by NMR) of **26** and isomeric **31** (consisting of **31a** and **31b** in 1 : 0.83 ratio by NMR) see below]. NMR data for **26** is out of mixture. **^{1}H NMR**: 1.57 (d, 3H, *J* = 6.5 Hz), 4.46 (q, 1H, *J* = 6.5 Hz), 4.59 (d, 1H, *J* = 11.6 Hz), 4.87 (d, 1H, *J* = 11.5 Hz), 7.32–7.38 (m, 7H), 7.41–7.44 (m, 3H); **^{13}C NMR**: 22.21, 64.93, 70.59, 85.24, 89.05, 122.77, 127.70, 128.07, 128.29, 128.33, 128.41, 131.75, 138.03; **IR**: 3053, 1489, 1421, 1265; **MS** (*m*/*z*): 236 (M^+), 193, 129 (100%), 115, 91.

Benzyl-(3-phenyl-prop-2-ynyl)-ether (27):[43]. Alcohol **Id** (1 mmol), benzyl alcohol (2.5 mmol) and catalyst (20 mol%); Yield: 62% (colorless oil). **^{1}H NMR**: 4.42 (s, 1H), 4.58 (s, 2H), 4.70 (s, 1H), 7.28–7.34 (m, 4H), 7.36–7.42 (m, 5H), 7.47–7.49 (m, 1H); **^{13}C NMR**: 57.92, 72.12, 85.06, 86.49, 122.66, 127.65, 127.81, 128.32, 128.42, 128.48, 131.80, 138.28; **IR**: 2974, 2857, 1954, 1659, 1599, 1491, 1454, 1381; **MS** (*m*/*z*): 223 [$(M+1)^+$, 100%], 221, 105.

***i*Propyl-(1,3-diphenyl-prop-2-ynyl)-ether (28):[19].** Alcohol **Ia** (1 mmol), 2-propanol (2 mmol) and catalyst (15 mol%); Yield: 82% (colorless oil): **^{1}H NMR**: 1.26 (d, 3H, *J* = 6.0 Hz), 1.29 (d, 3H, *J* = 6.0 Hz), 4.06 (q, 1H), 5.44 (s, 1H), 7.30–7.41 (m, 6H), 7.46–7.48 (m, 2H), 7.57–7.59 (m, 2H); **^{13}C NMR**: 21.75, 22.90, 69.39, 69.79, 88.60, 88.02, 122.77, 127.39, 128.18, 128.23, 128.37, 128.50, 131.76, 139.55; **IR**: 2976, 2866, 1962, 1491, 1383, 1121; **MS** (*m*/*z*): 250 (M^+), 207, 191 (100%), 179, 129, 105, 77.

***sec*Butyl-(1,3-diphenyl-prop-2-ynyl)-ether (29).** Alcohol **Ia** (1 mmol), 2-butanol (2 mmol) and catalyst (15 mol%); Yield: 91%; (pale yellow shiny solid; m.p.: 79–80 °C): Mixture of geometrical isomers (1 : 0.81 ratio). **^{1}H NMR**: *Isomer I* (*aliphatic signals*): 0.94 (t, 3H, *J* = 7.3 Hz), 1.25 (d, 3H, *J* = 6.0 Hz), 1.51–1.61 (m, 2H), 3.81 (q, 1H, *J* = 6.2 Hz), 5.45 (s, 1H); *Isomer II* (*aliphatic signals*): 1.02 (t, 3H, *J* = 7.5 Hz), 1.29 (d, 3H, *J* = 6.5 Hz), 1.63–1.71 (m, 2H), 3.90 (q, 1H, *J* = 6.3 Hz), 5.44 (s, 1H); *aromatics resonances for both isomers*: 7.31–7.35 (m, 8H), 7.38–7.41 (m, 4H), 7.46–7.49 (m, 4H), 7.59–7.61 (m, 4H); **^{13}C NMR**: *Isomer I* (aliphatic signals): 9.73, 19.14, 28.87, 69.56, 74.93, 86.55, 88.18: *Isomer II* (aliphatic signals): 10.18, 20.07, 29.87, 70.10, 75.35, 86.56, 88.35: *aromatic resonances for both isomers*: 122.83, 122.85, 127.40, 127.48, 128.17, 128.20, 128.24, 128.26, 128.34, 128.36, 128.47, 128.48, 131.71, 131,75, 139.59, 139.69; **IR** (mixture) 2969, 2932, 2876, 2245, 2201, 1599, 1489; **MS** (*m*/*z*): 264 (M^+), 207, 191 (100%), 179, 129, 105, 77.

Bis-(1,3-diphenyl-prop-2-ynyl)-ether (30). Alcohol **Ia** (2 mmol) and catalyst (15 mol%); Yield: 92% (colorless oil): NMR shows the presence of two geometrical isomers in 1 : 0.67 ratio with no appreciable change up to 60 °C (VT-NMR). **^{1}H NMR**: 5.58 (s, 2H), 5.97 (s, 2H), 7.31–7.32 (m, 2H), 7.34–7.36 (m, 5H), 7.38–7.42 (m, 5H), 7.47–7.49 (m, 2H), 7.53–7.55 (m, 2H), 7.63–7.64 (m, 2H), 7.67–7.69 (m, 2H); **^{13}C NMR**: 69.72, 70.18, 86.66, 87.04, 87.82, 80.09, 122.52, 122.56, 127.78, 128.0, 128.24, 128.34, 128.42, 128.48, 128.54, 128.64, 128.65, 128.69, 131.88, 131.92, 138.29, 138.50; **IR**: 3055, 2929, 2359, 2332, 1599, 1489, 1456, 1443; **MS** (*m*/*z*): (M^+ is not noticed), 206 (1,3-diphenyl-prop-2-yn-O. radical), 178 (100%), 129, 51.

Bis-(4-phenyl-but-3-yn-2-yl)-ether (31). Alcohol **Ib** (2 mmol) and catalyst (20 mol%); Two isomers were obtained that could be separated by prep-TLC. *Isomer I*: **^{1}H NMR** (**31a**): Yield: 63% (colorless oil): 1.58 (d, 6H, *J* = 7.0 Hz), 4.84 (q, 2H, *J* = 6.5 Hz), 7.30–7.33 (m, 6H), 7.45–7.47 (m, 4H); **^{13}C NMR**: 22.35, 63.56, 85.02, 88.90, 122.72, 128.26, 128.33, 131.80; **IR**: 2986, 2934, 2866, 1597, 1489, 1443, 1329; **MS** (*m*/*z*): 274 (M^+), 259 (100%), 231, 215. *Isomer II* (**31b**): Yield: 25% (colorless oil): **^{1}H NMR**: 1.58 (d, 6H, *J* = 6.5 Hz), 4.72 (q, 2H, *J* = 6.5 Hz), 7.24–7.29 (m, 6H), 7.41–7.43 (m, 4H); **^{13}C NMR**: 22.03, 63.91, 84.99, 89.30, 122.79, 128.15, 128.23, 131.78; **IR**: 3055, 2988, 2928, 1489, 1265; **MS** (*m*/*z*): 274 (M^+), 259 (100%), 231, 215.

Bis-(3-phenyl-prop-2-ynyl)-ether (32):[44]. Alcohol **Id** (2 mmol) and catalyst (20 mol%); Yield. 61% (colorless oil). **^{1}H NMR**: 4.55 (s, 4H), 7.30–7.34 (m, 6H), 7.45–7.48 (m, 4H); **^{13}C NMR**: 57.44, 84.34, 86.80, 122.48, 128.30, 128.55, 131.82; **IR**: 3053, 1655, 1491, 1265; **MS** (*m*/*z*): 246 (M^+, 100%), 217, 202, 139.

(3-Phenyl-prop-2-ynyl)-(4-phenyl-but-3-yn-2-yl)-ether (33):[21f]. Alcohol **Id** (1 mmol), alcohol **Ib** (1.5 mmol) and catalyst (20 mol%). Yield 78% (pale reddish oil) obtained as a 1 : 0.04 mixture (by NMR) of **33** and **31** (consisting of **31a** and **31b** in 1 : 0.81 ratio). NMR data for **33** is out of the mixture: **^{1}H NMR**: 1.60 (d, 3H, *J* = 6.0 Hz), 4.56 (d, 1H, *J* = 15.5 Hz), 4.64 (d, 1H, *J* = 15.5 Hz), 4.71 (q, 1H, *J* = 6.8 Hz), 7.31–7.33 (m, 6H), 7.46–7.48 (m, 4H); **^{13}C NMR**: 22.14, 56.65, 64.69, 84.96, 85.64, 86.25, 88.22, 122.57, 122.64, 128.27, 128.30, 128.45, 128.47, 131.80, 131.86; **IR** (mixture): 3055, 2986, 2253, 1489, 1265; **MS** (*m*/*z*): 260 (M^+, 100%), 246, 202.

(1-Pent-2-ynyl)-(4-phenyl-but-3-yn-2-yl)-ether (34). Alcohol **Ic** (1 mmol), alcohol **Ib** (1.5 mmol) and catalyst (20 mol%); Yield. 54% (colorless oil) obtained as a 1 : 0.31 mixture (by NMR) of **34** and **31** (consisting of **31a** and **31b** in 1 : 0.81 ratio by NMR). NMR data for **34** is out of the mixture: **^{1}H NMR**: 1.16 (t, 3H, *J* = 7.5 Hz), 1.55 (d, 3H, *J* = 7.0 Hz), 2.25 (qt, 2H, *J* = 7.5 Hz, *J* = 2.1 Hz), 4.25 (dt, 1H, *J* = 15.5 Hz, *J* = 2.3 Hz), 4.39 (dt, 1H, *J* = 15.0 Hz, *J* = 2.1 Hz), 4.59 (q, 1H, *J* = 6.7 Hz), 7.30–7.32 (m, 3H), 7.43–7.45 (m, 2H); **^{13}C NMR**: 12.52, 13.76, 22.08, 56.46, 64.39, 75.01, 85.35, 88.37, 88.42, 122.64, 128.25, 128.35, 131.75; **IR** (mixture): 2986, 2936, 1674, 1599, 1489, 1443; **MS** (*m*/*z*): 212 (M^+, 100%), 197, 169, 153, 141.

(1-Pent-2-ynyl)-(3-phenyl-prop-2-ynyl)-ether (35). Alcohol **Ic** (1 mmol), alcohol **Id** (1.5 mmol) and catalyst (20 mol%); Yield. 52% (colorless oil) obtained as 1 : 0.97 mixture (by NMR) of **35** and **32**. NMR data for **35** out of the mixture: **^{1}H NMR**: 1.16 (t, 3H, *J* = 7.5 Hz), 2.25 (qt, 2H, *J* = 7.7 Hz, *J* = 2.1 Hz), 4.29 (t, 2H, *J* = 2.0 Hz), 4.47 (s, 2H), 7.31–7.34 (m, 3H), 7.43–7.45 (m, 2H); **^{13}C NMR**: 12.48, 13.77, 57.15, 57.28, 74.50, 84.52, 86.80, 89.04, 122.55, 128.28, 128.48, 131.78,; **IR** (mixture): 2974, 2928, 2853, 2239, 1657, 1491; **MS** (*m*/*z*): 198 (M^+, 100%), 141, 115.

Cyclohexyl-(4-phenyl-but-3-yn-2-yl)-ether (36). Alcohol **Ib** (1 mmol), cyclohexanol (1.5 mmol) and catalyst (20 mol%); Yield. 81% (colorless oil) obtained as a 1 : 0.44 (by NMR) mixture of **36** and **31a**. NMR data for **36** is out of the mixture: **^{1}H NMR**: 1.17–1.43 (m, 5H), 1.51 (d, 3H, *J* = 6.6 Hz), 1.53–1.56 (m, 1H), 1.70–1.79 (m, 2H), 1.95–2.0 (m, 2H), 3.65 (septet, 1H, *J* = 4.7 Hz), 4.53 (q, 1H, *J* = 6.6 Hz), 7.29–7.30 (m, 3H), 7.42–7.44 (m, 2H); **^{13}C NMR**: 22.79, 24.21, 24.42, 25.80, 31.59, 33.43, 62.45, 75.61, 83.94, 90.25, 123.01, 128.13, 128.23, 131.69; **IR** (mixture): 2986, 2932, 2857, 2203, 1694, 1489, 1327; **MS** (*m*/*z*): 227 [$(M-1)^+$], 213 ($M-CH_3$), 129 (100%), 109.

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