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Fe powder catalyzed highly efficient synthesis of alkenyl halides via direct coupling of alcohols and alkynes with aqueous HX as exogenous halide sources

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ABSTRACT

A simple and efficient catalytic method for the synthesis of alkenyl halides via direct coupling of alcohols and alkynes using aqueous HX (X=Cl, Br) as halide sources has been developed under mild conditions in the presence of Fe powder (1 mol %). In comparison with the high loading of FeX_3 in previously reported protocols, the present approach provides a remarkable attractive methodology to a diverse range of alkenyl halides due to the advantages of simple operation and low-level metal contamination.

1. Introduction

Alkenyl halides are very important building blocks and extensively applied for the construction of various natural products and pharmaceuticals.[1] Furthermore, they have attracted increasingly synthetic pursuit of chemists owing to their wide applications in transition metals catalyzed cross-coupling transformations such as the Suzuki,[2] Sonogashira[3] and Negishi reactions.[4] Generally, alkenyl halides are prepared from ketones or aldehydes using halogenating reagents, such as phosphorus penthalides,[5] acetyl halides[6] and POX_3.[7] Alternative procedures have also been developed, including the addition of hydrohalides or alkyl halides to alkynes prompted by alumina[8] or $ZnCl_2$,[9] coupling reactions of alkynes and aldehydes mediated by Lewis acids such as iron(III) halides,[10] boron trihalides,[11] or gallium(III) halides,[12] ring opening of bis-activated cyclopropenes promoted by stoichiometric magnesium halides,[13] and the direct reaction of alcohols and vinylboron dihalides in the presence of *n*-BuLi.[14] However, most of these methods suffer from several drawbacks such as drastic reaction conditions, the need of extra steps to prepare active starting materials, low yields, or the use of stoichiometric amounts of expensive and/or toxic reagents. Therefore, there is still a great demand for the development of a mild, convenient and efficient methodology to access alkenyl halides.

Recently, Liu et al.[15] reported an $FeCl_3 \cdot 6H_2O$ (5 mol %) catalyzed method for the formation of alkenyl halides via addition of benzyl halides to aryl alkynes. Jana and Wang et al.[16] developed a new synthetic strategy for preparing alkenyl halides via FeX_3 promoted coupling reaction of alcohols and alkynes, in which FeX_3 ($\geq$33.3 mol %, X=Cl, Br) were used not only as promoters but also as halide sources (Scheme 1). In 2012, Bao et al.[17] reported FeX_3 (1 equiv, X=Cl, Br) mediated reaction for the construction of alkenyl halides from diphenylmethanes and ethynylbenzenes in the presence of stoichiometric DDQ. Yeh et al.[18] described an $FeCl_3$ (1.2 equiv) promoted method for the synthesis of alkenyl chlorides with azaspirocyclic ring skeleton via intramolecular reaction of alcohols with alkynes. Our research group also developed an Fe (1 equiv)/I_2 (1 equiv)/NaI (2 equiv) mediated system to deliver alkenyl iodide compounds through coupling of alcohols and alkynes.[19] More recently, Jiang et al.[20] reported a Pd(II)-catalyzed haloallylation approach to prepare 1,4-dienes in ionic liquids. Herein, we disclose a convenient and efficient method for the synthesis of alkenyl halides via direct coupling of various alcohols and alkynes using aqueous HX (X=Cl, Br) as halide sources in the presence of Fe powder (1 mol %) (Scheme 1). In comparison with the high loading of FeX_3 in previously reported protocols (Fig. 1, **B**), the present approach provides a remarkable attractive

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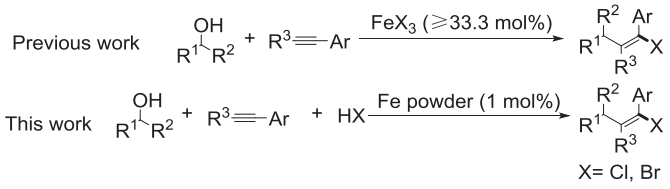
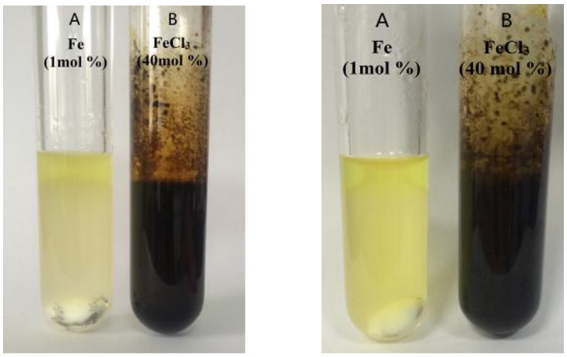
0040-4020/

methodology towards various alkenyl halides due to the advantages of simple operation and low-level metal contamination (Fig. 1, **A**).



Scheme 1. Approaches for the synthesis of alkenyl halides.



(I): 0 h (II): 3 h

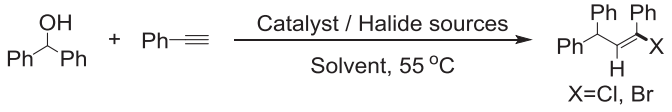
Fig. 1. Comparation experiments between the present reaction system (**A**) and previous reaction system (**B**). (**A**): Diphenylmethanol **1a** (5.43 mmol), phenylacetylene **2a** (1.2 equiv), Fe powder (1 mol %), and 36% aqueous HCl (1.2 equiv), $CHCl_3$ (3 mL). (**B**): Diphenylmethanol **1a** (5.43 mmol), phenylacetylene **2a** (1.2 equiv), $FeCl_3$ (0.4 equiv), CH_2Cl_2 (3 mL).

2. Results and discussion

In an initial experiment, considering the high loading of FeX_3 in the previously reported reaction system of alcohols and alkynes, halide sources such as aqueous NaCl, aqueous LiCl and tetrabutylammonium chloride were investigated to lower the FeX_3 loading. Only a trace amount of desired product **3a** was detected when the model reaction of diphenylmethanol **1a** and phenylacetylene **2a** was catalyzed by $FeCl_3$ (1 mol %) in the presence of above mentioned halide sources (Table 1, entries 1–3). To our delight, when aqueous HCl was used as a chloride source in this reaction, the desired product **3a** was obtained in 86% isolated yield (Table 1, entry 4). Subsequently, the catalytic activity of other iron catalysts was investigated in the presence of aqueous HCl (Table 1, entries 5–7). Notably, cheap and easily available iron powder gave the desired product in good yield (87%) (Table 1, entry 7). No desired product was observed in the absence of catalyst (Table 1, entry 8). After an extensive screening of the reaction parameters such as solvent, temperature and the amount of aqueous HCl (Table 1, entries 9–18), the best yield (87%) was obtained by employing 1 mol % iron powder and aqueous HCl (2.4 mmol) in $CHCl_3$ at 55 °C (Table 1, entry 7). In addition, when aqueous HBr was used as a bromide source, the corresponding alkenyl bromide **3b** was also generated in 84% yield under the optimal reaction conditions (Table 1, entry 19).

Having identified the catalytic system, the scope and generality were investigated by using various combinations of alkynes and alcohols in the presence of aqueous HX (X=Cl, Br). As shown in Table 2, a series of alkenyl halides were obtained in moderate to good yields. In general, the *E* isomers were given as the main products. Various secondary benzylic alcohols were compatible with the reaction, and the corresponding coupling products were obtained in high yields (Table 2, **3a**–**k**). Moreover, allylic alcohols

Table 1
Screening of the reaction conditions[a]



1a **2a** **3a/3b**

Entry	Catalyst	Solvent	Halide sources (mmol)	Yield[b] (%)
1	$FeCl_3$	$CHCl_3$	NaCl (2.4)	Trace
2	$FeCl_3$	$CHCl_3$	LiCl (2.4)	Trace
3	$FeCl_3$	$CHCl_3$	$(C_4H_9)_4NCl$ (2.4)	Trace
4	$FeCl_3$	$CHCl_3$	HCl (2.4)	86
5	$FeCl_2$	$CHCl_3$	HCl (2.4)	86
6	$Fe(acac)_2$	$CHCl_3$	HCl (2.4)	82
7	*Fe*	*$CHCl_3$*	*HCl (2.4)*	*87*
8	None	$CHCl_3$	HCl (2.4)	n.d.
9	Fe	$CHCl_3$	HCl (2.0)	80
10	Fe	$CHCl_3$	HCl (3.0)	86
11	Fe	$CHCl_3$	HCl (2.4)	Trace[c]
12	Fe	$CHCl_3$	HCl (2.4)	71[d]
13	Fe	CH_2Cl_2	HCl (2.4)	74
14	Fe	DCE	HCl (2.4)	60
15	Fe	DBE	HCl (2.4)	80
16	Fe	DMSO	HCl (2.4)	n.d.
17	Fe	CH_3CN	HCl (2.4)	n.d.
18	Fe	THF	HCl (2.4)	n.d.
19	Fe	$CHCl_3$	HBr (2.4)	84

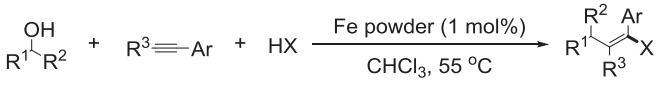
[a] Reaction conditions: diphenylmethanol **1a** (2.0 mmol), phenylacetylene **2a** (2.4 mmol), catalyst (1 mol %), halide sources (saturated aqueous solution of NaCl, saturated aqueous solution of LiCl, 36% aqueous HCl or 47% aqueous HBr was used), solvent (1 mL), 55 °C, overnight.
[b] Isolated yields based on alcohol **1a**.
[c] Reaction performed at 25 °C.
[d] Reaction performed at 40 °C.

such as cyclohex-2-enol and (*E*)-1, 3-diphenylprop-2-en-1-ol were tolerated in this transformation, providing 1-halide-1,4-diene derivatives in moderate to good yields (Table 2, **3l**–**n**). With respect to alkynes, aromatic terminal alkynes containing either electron-rich or electron-deficient groups were all suitable substrates for this protocol, furnishing the corresponding alkenyl halides in excellent yields (Table 2, **3o**–**v**). In addition, heteroarylalkyne such as 3-ethynylthiophene could be used in our case to give the desired product in moderate yield (Table 2, **3w**). Internal aromatic alkynes such as 1-phenyl-1-propyne and 1-phenyl-1-butyne also reacted smoothly, affording the corresponding products in good yields (Table 2, **3x**–**z**). When aliphatic alkynes such as 1-hexyne and 1-octyne were used in the present reaction system, the corresponding products were obtained in 26% and 24% yields, respectively (Table 2, **3a′**–**3b′**).

The feasibility of gram-scale reaction was investigated with the reaction of dibenzosuberol, phenylacetylene, and aqueous HX (X=Cl, Br) in the presence of 1 mol % iron powder (99.998% and 97% purity), which could give the corresponding products **3f** and **3g** in high yields without any significant loss of its reaction efficiency (Scheme 2, Eqs. 1 and 2). Thus, this protocol could be employed as a practical method to construct alkenyl halides.

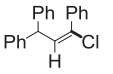
Further investigations have been conducted to gain insights into the reaction mechanism (Scheme 3). It is well known that FeX_2 was produced when Fe reacted with HX (X=Cl, Br). Nevertheless, the control experiments indicated that neither FeX_2 (50 mol %) nor HX (1.2 equiv) could promote independently the coupling reaction of alcohols and alkynes to deliver the desired products (Scheme 3, Eqs. 1 and 2). Previous reports showed that FeX_3 could promote the coupling reaction of alcohols and alkynes,[16] so it is supposed that FeX_3 might catalyze the present reaction because Fe(II) could be easily oxidized to Fe(III) in the presence of HX (X=Cl, Br) under air.[21] Further study supported this assumption and the desired product **3a** was obtained in high yield (86%) when the present reaction was conducted with the combination of 1.2 equiv HCl and 1 mol % $FeCl_3$

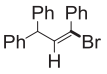
Table 2
Results for reactions of alcohols with alkynes in the presence of Fe (1 mol %)/HX[a,b]

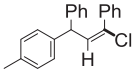


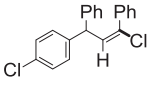
1 **2** **3**

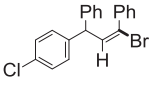
X=Cl, Br

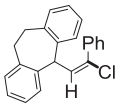

3a (87%), *E:Z* (86:14)

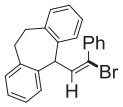

3b (84%), *E:Z* (86:14)

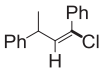

3c (86%), *E:Z* (85:15)

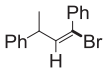

3d (93%), *E:Z* (80:20)

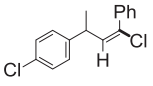

3e (84%), *E:Z* (78:22)

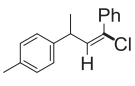

3f (83%), *E:Z* (91:9)

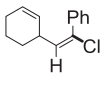

3g (78%), *E:Z* (85:15)

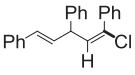

3h (90%), *E:Z* (85:15)

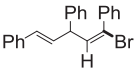

3i (76%), *E:Z* (86:14)

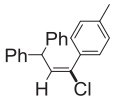

3j (81%), *E:Z* (83:17)

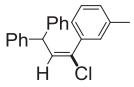

3k (86%), *E:Z* (84:16)

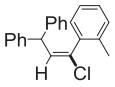

3l (54%), *E:Z* (81:19)

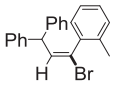

3m (75%), *E:Z* (77:23)

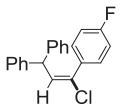

3n (70%), *E:Z* (72:28)


3o (83%), *E:Z* (79:21)


3p (92%), *E:Z* (83:17)


3q (92%), *E:Z* (86:14)


3r (81%), *E:Z* (87:13)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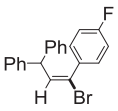
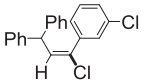
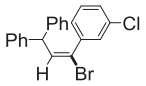
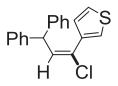
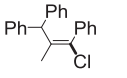
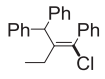

3t (85%), *E:Z* (83:17)

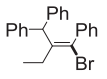

3u (86%), *E:Z* (88:12)

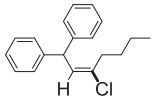

3v (75%), *E:Z* (86:14)

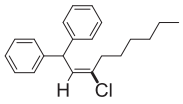

3w (54%), *E:Z* (84:16)


3x (81%), *E:Z* (79:21)


3y (81%), *E:Z* (57:43)[c]


3z (82%), *E:Z* (77:23)

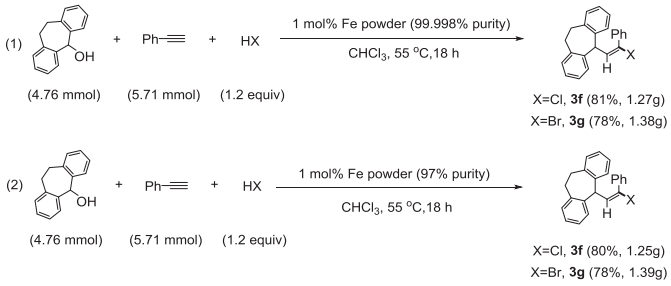

3a' (26%), *E:Z* (69:31)


3b' (24%), *E:Z* (66:34)

[a] Reaction conditions: alcohols **1** (2.0 mmol), alkynes **2** (2.4 mmol), 36% aqueous HCl or 47% aqueous HBr (2.4 mmol), Fe powder (1 mol%), chloroform (1 mL), 55 °C, overnight.

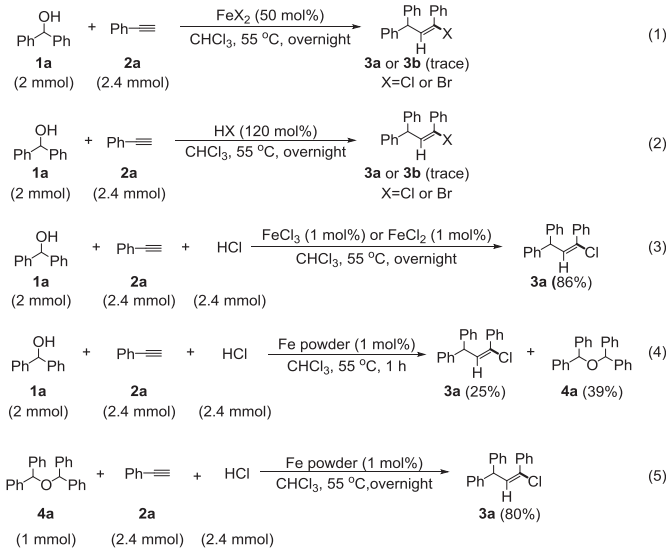
[b] Isolated yields of the *E:Z* mixtures; the *E:Z* ratio was determined by ^{1}H NMR spectroscopy.

[c] *E* isomer was confirmed by X-ray analysis, see supporting information.



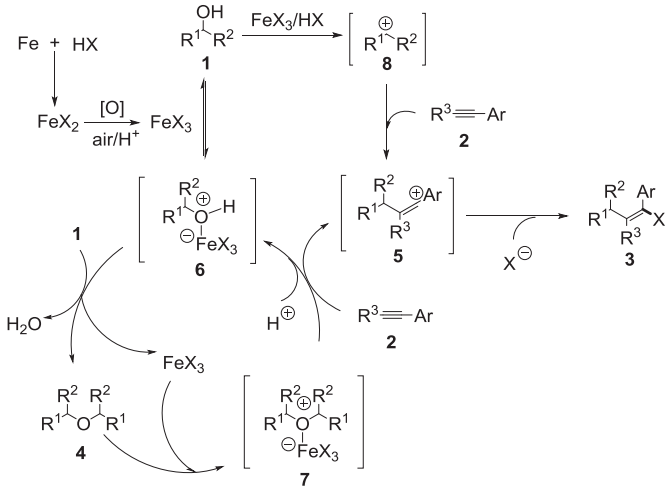
Scheme 2. Gram-scale reactions.

or 1 mol % $FeCl_2$ (Scheme 3, Eq. 3). Moreover, dimeric ether **4a** was detected in the model reaction of **1a** and **2a**, and the isolated **4a** reacted with **2a** leading to the target product **3a** in 80% yield under the standard conditions (Scheme 3, Eqs. 4 and 5). The above results suggested that FeX_3 should be performed as the actual catalyst and dimeric ether might be a key intermediate in the present reaction for the synthesis of alkenyl halides.



Scheme 3. Control experiments.

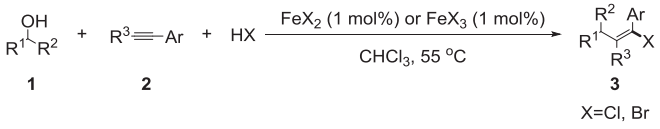
Based on the experimental observations[22] and previous studies,[16,19,23,24] the possible reaction pathways were proposed as shown in Scheme 4. Initially, Fe transformed to FeX_3 in the presence of HX under air.[21] Subsequently, alcohol **1** was activated by FeX_3 and attacked by another alcohol **1** to generate dimeric ether **4**. Next, FeX_3 coordinated with **4** to provide complex **7**, then alkylation of **2** with **7** would give vinyl cation **5** and release intermediate **6**, the latter could participate in the catalytic cycle again. Finally, the nucleophilic attack of halide ion on **5** produced the desired product **3**. Moreover, the pathway for direct haloalkylation of alkynes with alcohols and aqueous HX to form alkenyl halides **3** might also be involved in this transformation.

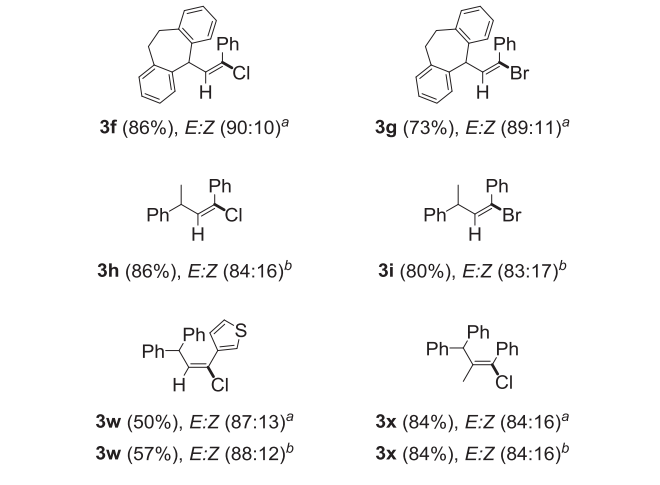


Scheme 4. Possible reaction pathways.

Furthermore, as shown in Table 3, a series of alkenyl halides could also be obtained in moderate to good yields when the reactions of various alcohols with alkynes were separately performed in the presence of FeX_2 (1 mol %)/HX and FeX_3 (1 mol %)/HX (X=Cl, Br) system. The above results supported the proposed reaction mechanism.

Table 3
Results for reactions of alcohols with alkynes in the presence of FeX_2 (1 mol %)/HX[a,c] or FeX_3 (1 mol %)/HX[b,c]





[a] Reaction conditions: alcohols **1** (2.0 mmol), alkynes **2** (2.4 mmol), 36% aqueous HCl or 47% aqueous HBr (2.4 mmol), FeX_2 (1 mol%), chloroform (1 mL), 55 °C, overnight.

[b] Reaction conditions: alcohols **1** (2.0 mmol), alkynes **2** (2.4 mmol), 36% aqueous HCl or 47% aqueous HBr (2.4 mmol), FeX_3 (1 mol%), chloroform (1 mL), 55 °C, overnight.

[c] Isolated yields of the *E:Z* mixtures; the *E:Z* ratio was determined by ^1H NMR spectroscopy.

3. Conclusions

In summary, we have developed a convenient and efficient catalytic method for the synthesis of alkenyl halides from various alcohols and alkynes using aqueous HX (X=Cl, Br) as halide sources with low loading of Fe powder (1 mol %). The present protocol, which utilizes simple and cheap iron powder and readily available starting materials, provides an attractive approach to a diverse range of alkenyl halides in good to excellent yields. Further studies on the detailed reaction mechanism and the synthetic application are ongoing.

4. Experimental section

4.1. General information

All chemicals and solvents were purchased from Aldrich, Acros and Alfa Aesar Chemical Company as reagent grade and used without further purification unless otherwise stated. Iron powder (99.998% purity) was purchased from Alfa Aesar Chemical Company. Iron powder (97% purity) was purchased from Sigma Aldrich Chemical Company. ^{1}H NMR and ^{13}C NMR spectra were recorded in $CDCl_3$ on a Bruker Avance 600 (600 MHz ^{1}H, 150 MHz ^{13}C) or 400 (400 MHz ^{1}H, 100 MHz ^{13}C) spectrometer with TMS as internal standard at room temperature, and the chemical shifts (δ) were expressed in parts per million (ppm) and J values were given in hertz (Hz). Abbreviations for NMR data: s=singlet; d=doublet; t=triplet; dd=doublet of doublets; dt=doublet of triplets; m=multiplet. Mass analyses and HRMS were obtained on an Agilent 5973N MSD mass spectrometer and a Waters Micromass GCT Premier mass spectrometer by the EI method, respectively. X-ray crystallographic analysis was performed with Rigaku-RAXIS-RAPID single-crystal diffractometer. Column chromatography was performed on silica gel (100–200 mesh).

4.2. General experimental procedure

To a stirred mixture of alcohol (2.0 mmol), alkyne (2.4 mmol), and Fe powder (1 mol %) in chloroform (1 mL) was added hydrohalide (2.4 mmol). The reaction mixture was stirred vigorously at 55 °C overnight. Upon completion of the reaction, the mixture was extracted with dichloromethane, dried and concentrated in vacuo to provide raw product. Then the residue was purified by silica-gel (100–200 mesh) column chromatography using petroleum ether as the eluent to obtain a mixture of *E* and *Z* isomers of desired product.

4.3. The procedure of gram-scale reaction for the synthesis of 3f

To a stirred mixture of dibenzosuberol (1 g, 4.76 mmol) and phenylacetylene (5.71 mmol, 1.2 equiv) and Fe powder (1 mol %) in chloroform (3 mL) was added 36% aqueous HCl (5.71 mmol, 1.2 equiv). The reaction mixture was stirred vigorously at 55 °C for 18 h. Upon completion of the reaction, the mixture was extracted with dichloromethane, dried and concentrated in vacuo to provide raw product. Then the residue was purified by silica-gel (100–200 mesh) column chromatography using petroleum ether as the eluent to obtain a mixture of *E* and *Z* isomers of desired product **3f** in 81% yield (iron powder, 99.998% purity) or 80% yield (iron powder, 97% purity) as a colourless oil.

4.4. The procedure of gram-scale reaction for the synthesis of 3g

To a stirred mixture of dibenzosuberol (1 g, 4.76 mmol) and phenylacetylene (5.71 mmol, 1.2 equiv) and Fe powder (1 mol %) in chloroform (3 mL) was added 47% aqueous HBr (5.71 mmol, 1.2 equiv). The reaction mixture was stirred vigorously at 55 °C for 18 h. Upon completion of the reaction, the mixture was extracted with dichloromethane, dried and concentrated in vacuo to provide raw product. Then the residue was purified by silica-gel (100–200 mesh) column chromatography using petroleum ether as the eluent to obtain a mixture of *E* and *Z* isomers of desired product **3g** in 78% yield (iron powder, 99.998% purity) or 78% yield (iron powder, 97% purity) as a colourless oil.

4.5. Characterization data for reactions of alcohols with alkynes in the presence of Fe (1 mol %)/HX

*4.5.1. (3-Chloroprop-2-ene-1,1,3-triyl)tribenzene (**3a**).* ^{1}H NMR (600 MHz, $CDCl_3$, ppm): (*E*)-**3a**: δ=7.69–7.18 (m, 15H, aromatic), 6.53 (d, J=11.0 Hz, 1H, CH), 4.86 (d, J=11.0 Hz, 1H, CH); (*Z*)-**3a**: δ=7.69–7.18 (m, 15H, aromatic), 6.68 (d, J=9.4 Hz, 1H, CH), 5.50 (d, J=9.5 Hz, 1H, CH); ^{13}C NMR ($CDCl_3$, 150 MHz, ppm): δ=143.4, 143.1, 137.0, 131.6, 131.5, 129.7, 129.0, 128.8, 128.7, 128.5, 128.4, 128.2, 126.7, 50.9, 50.8; MS (EI): m/z=304; HRMS (EI) calcd for $C_{21}H_{17}Cl$ 304.1019; found 304.1018.

*4.5.2. (3-Bromoprop-2-ene-1,1,3-triyl)tribenzene (**3b**).* ^{1}H NMR (600 MHz, $CDCl_3$, ppm): (*E*)-**3b**: δ=7.63–7.15 (m, 15H, aromatic), 6.73 (d, J=10.9 Hz, 1H, CH), 4.76 (d, J=10.9 Hz, 1H, CH); (*Z*)-**3b**: δ=7.63–7.15 (m, 15H, aromatic), 6.72 (d, J=9.2 Hz, 1H, CH), 5.42 (d, J=9.4 Hz, 1H, CH); ^{13}C NMR ($CDCl_3$, 150 MHz, ppm): δ=143.0, 142.8, 138.4, 135.6, 133.3, 128.8, 128.7, 128.4, 128.3, 128.2, 127.8, 126.7, 121.3, 53.7, 51.7; MS (EI): m/z=348; HRMS (EI) calcd for $C_{21}H_{17}Br$ 348.0514; found 348.0516.

*4.5.3. (1-Chloro-3-(p-tolyl)prop-1-ene-1,3-diyl)dibenzene (**3c**).* ^{1}H NMR (600 MHz, $CDCl_3$, ppm): (*E*)-**3c**: δ=7.64–7.03 (m, 14H, aromatic), 6.46 (d, J=11.0 Hz, 1H, CH), 4.77 (d, J=11.0 Hz, 1H, CH), 2.35 (s, 3H); (*Z*)-**3c**: δ=7.64–7.03 (m, 14H, aromatic), 6.62 (d, J=9.5 Hz, 1H, CH), 5.41 (d, J=9.4 Hz, 1H, CH), 2.35 (s, 3H); ^{13}C NMR ($CDCl_3$, 150 MHz, ppm): δ=143.6, 140.4, 137.0, 136.3, 131.6, 131.3, 129.4, 129.3, 128.8, 128.7, 128.7, 128.6, 128.4, 128.3, 128.3, 128.2, 128.1, 128.0, 126.7, 126.6, 50.5, 50.4, 21.0; MS (EI): m/z=318; HRMS (EI) calcd for $C_{22}H_{19}Cl$ 318.1175; found 318.1178.

*4.5.4. (1-Chloro-3-(4-chlorophenyl)prop-1-ene-1,3-diyl)dibenzene (**3d**).* ^{1}H NMR (600 MHz, $CDCl_3$, ppm): (*E*)-**3d**: δ=7.63–7.05 (m, 14H, aromatic), 6.40 (d, J=10.9 Hz, 1H, CH), 4.76 (d, J=10.9 Hz, 1H, CH); (*Z*)-**3d**: δ=7.63–7.05 (m, 14H, aromatic), 6.56 (d, J=9.2 Hz, 1H, CH), 5.40 (d, J=9.4 Hz, 1H, CH); ^{13}C NMR ($CDCl_3$, 150 MHz, ppm): δ=142.8, 141.9, 136.8, 132.5, 132.0, 130.9, 129.7, 129.5, 129.0, 128.8, 128.8, 128.6, 128.5, 128.4, 128.3, 128.1, 126.9, 126.7, 50.2, 50.1; MS (EI): m/z=338; HRMS (EI) calcd for $C_{21}H_{16}Cl_2$ 338.0629; found 338.0627.

*4.5.5. (1-Bromo-3-(4-chlorophenyl)prop-1-ene-1,3-diyl)dibenzene (**3e**).* ^{1}H NMR (600 MHz, $CDCl_3$, ppm): (*E*)-**3e**: δ=7.58–7.04 (m, 14H, aromatic), 6.63 (d, J=10.8 Hz, 1H, CH), 4.69 (d, J=10.8 Hz, 1H, CH); (*Z*)-**3e**: δ=7.58–7.04 (m, 14H, aromatic), 6.63 (d, J=9.2 Hz, 1H, CH), 5.34 (d, J=9.3 Hz, 1H, CH); ^{13}C NMR ($CDCl_3$, 150 MHz, ppm): δ=142.5, 141.6, 138.2, 135.0, 132.7, 132.5, 129.7, 129.5, 128.9, 128.8, 128.8, 128.7, 128.5, 128.3, 128.3, 128.1, 127.8, 126.9, 121.8, 53.1, 51.1; MS (EI): m/z=382; HRMS (EI) calcd for $C_{21}H_{16}BrCl$ 382.0124; found 382.0119.

*4.5.6. 5-(2-Chloro-2-phenylvinyl)-10,11-dihydro-5H-dibenzo[a,d][7]annulene (**3f**).* ^{1}H NMR (600 MHz, $CDCl_3$, ppm): (*E*)-**3f**: δ=7.58–7.05 (m, 13H, aromatic), 6.87 (d, J=10.6 Hz, 1H, CH), 4.99 (d, J=10.6 Hz, 1H, CH), 3.31–3.25 (m, 2H, CH_2), 3.12–3.06 (m, 2H, CH_2); (*Z*)-**3f**: δ=7.58–7.05 (m, 13H, aromatic), 6.89 (d, J=8.2 Hz, 1H, CH), 5.45 (d, J=9.0 Hz, 1H, CH), 3.46–3.40 (m, 2H, CH_2), 3.12–3.06 (m, 2H, CH_2); ^{13}C NMR ($CDCl_3$, 150 MHz, ppm): δ=140.4, 140.1, 139.3, 139.0, 138.1, 137.3, 131.2, 131.0, 130.4, 130.2, 129.7, 128.9, 128.8, 128.6, 128.5, 128.4, 128.3, 127.1, 127.0, 126.7, 126.3, 52.6, 49.8, 33.4, 33.0; MS (EI): m/z=330; HRMS (EI) calcd for $C_{23}H_{19}Cl$ 330.1175; found 330.1176.

*4.5.7. 5-(2-Bromo-2-phenylvinyl)-10,11-dihydro-5H-dibenzo[a,d][7]annulene (**3g**).* ^{1}H NMR (600 MHz, $CDCl_3$, ppm): (*E*)-**3g**: δ=7.53–6.95 (m, 14H), 4.88 (d, J=10.4 Hz, 1H, CH), 3.34–3.28 (m, 2H, CH_2), 3.09–3.02 (m, 2H, CH_2); (*Z*)-**3g**: δ=7.53–6.95 (m, 14H),

5.42 (d, J=9.1 Hz, 1H, CH), 3.44–3.38 (m, 2H, CH_2), 3.13–3.07 (m, 2H, CH_2); ^{13}C NMR ($CDCl_3$, 150 MHz, ppm): δ=140.0, 139.8, 139.3, 139.1, 138.8, 135.4, 133.2, 130.4, 130.2, 128.9, 128.8, 128.6, 128.5, 128.2, 127.9, 127.1, 127.0, 126.3, 120.8, 55.1, 51.6, 33.4, 33.0; MS (EI): m/z=374; HRMS (EI) calcd for $C_{23}H_{19}Br$ 374.0670; found 374.0669.

*4.5.8. (1-Chlorobut-1-ene-1,3-diyl)dibenzene (**3h**).* ^1H NMR (600 MHz, $CDCl_3$, ppm): (*E*)-**3h**: δ=7.60–7.19 (m, 10H, aromatic), 6.15 (d, J=10.8 Hz, 1H, CH), 3.63–3.57 (m, 1H, CH), 1.38 (d, J=7.0 Hz, 3H, CH_3); (*Z*)-**3h**: δ=7.60–7.19 (m, 10H, aromatic), 6.27 (d, J=9.2 Hz, 1H, CH), 4.23–4.17 (m, 1H, CH), 1.50 (d, J=7.0 Hz, 3H, CH_3); ^{13}C NMR ($CDCl_3$, 150 MHz, ppm): δ=145.0, 137.3, 134.3, 132.4, 130.2, 128.7, 128.6, 128.4, 128.3, 128.3, 127.1, 126.8, 126.6, 126.4, 39.8, 39.7, 22.4, 20.8; MS (EI): m/z=242; HRMS (EI) calcd for $C_{16}H_{15}Cl$ 242.0862; found 242.0866.

*4.5.9. (1-Bromobut-1-ene-1,3-diyl)dibenzene (**3i**).* ^1H NMR (600 MHz, $CDCl_3$, ppm): (*E*)-**3i**: δ=7.55–7.16 (m, 10H, aromatic), 6.37 (d, J=10.7 Hz, 1H, CH), 3.53 (m, 1H, CH), 1.36 (d, J=7.0 Hz, 3H, CH_3); (*Z*)-**3i**: δ=7.55–7.16 (m, 10H, aromatic), 6.32 (d, J=9.1 Hz, 1H, CH), 4.16–4.10 (m, 1H, CH), 1.49 (d, J=7.0 Hz, 3H, CH_3); ^{13}C NMR ($CDCl_3$, 150 MHz, ppm): δ=144.6, 138.8, 138.5, 136.1, 128.8, 128.7, 128.6, 128.6, 128.5, 128.3, 128.2, 127.7, 127.1, 126.8, 126.4, 119.8, 42.6, 40.8, 22.0, 20.6; MS (EI): m/z=286; HRMS (EI) calcd for $C_{16}H_{15}Br$ 286.0357; found 286.0356.

*4.5.10. 1-Chloro-4-(4-chloro-4-phenylbut-3-en-2-yl)benzene (**3j**).* ^1H NMR (600 MHz, $CDCl_3$, ppm): (*E*)-**3j**: δ=7.58–7.09 (m, 9H, aromatic), 6.08 (d, J=10.7 Hz, 1H, CH), 3.56 (m, 1H, CH), 1.35 (d, J=7.0 Hz, 3H, CH_3); (*Z*)-**3j**: δ=7.58–7.09 (m, 9H, aromatic), 6.19 (d, J=9.1 Hz, 1H, CH), 4.16 (m, 1H, CH), 1.46 (d, J=7.0 Hz, 3H, CH_3); ^{13}C NMR ($CDCl_3$, 150 MHz, ppm): δ=143.5, 143.3, 137.9, 137.2, 133.7, 132.1, 131.8, 130.7, 128.8, 128.7, 128.6, 128.4, 128.3, 128.1, 126.5, 39.2, 39.1, 22.3, 20.8; MS (EI): m/z=276; HRMS (EI) calcd for $C_{16}H_{14}Cl_2$ 276.0473; found 276.0470.

*4.5.11. 1-(4-Chloro-4-phenylbut-3-en-2-yl)-4-methylbenzene (**3k**).* ^1H NMR (600 MHz, $CDCl_3$, ppm): (*E*)-**3k**: δ=7.59–7.08 (m, 9H, aromatic), 6.13 (d, J=10.8 Hz, 1H, CH), 3.57 (m, 1H, CH), 2.35 (s, 3H, CH_3), 1.36 (d, J=6.9 Hz, 3H, CH_3); (*Z*)-**3k**: δ=7.59–7.08 (m, 9H, aromatic), 6.25 (d, J=9.1 Hz, 1H, CH), 4.19–4.13 (m, 1H, CH), 2.35 (s, 3H, CH_3), 1.48 (d, J=7.0 Hz, 3H, CH_3); ^{13}C NMR ($CDCl_3$, 150 MHz, ppm): δ=142.0, 137.4, 136.0, 134.5, 129.9, 129.4, 129.3, 128.7, 128.6, 128.3, 128.3, 126.9, 126.6, 126.5, 39.3, 39.3, 22.5, 21.0, 20.9; MS (EI): m/z=256; HRMS (EI) calcd for $C_{17}H_{17}Cl$ 256.1019; found 256.1023.

*4.5.12. (1-Chloro-2-(cyclohex-2-en-1-yl)vinyl)benzene (**3l**).* ^1H NMR (600 MHz, $CDCl_3$, ppm): (*E*)-**3l**: δ=7.59–7.28 (m, 5H, aromatic), 5.83 (d, J=10.9 Hz, 1H, CH), 5.76 (m, 1H, CH), 5.49 (d, J=9.8 Hz, 1H, CH), 2.93 (m, 1H, CH), 2.05–1.94 (m, 2H, CH_2), 1.78–1.72 (m, 2H, CH_2), 1.51–1.42 (m, 2H, CH_2); (*Z*)-**3l**: δ=7.59–7.28 (m, 5H, aromatic), 6.03 (d, J=8.9 Hz, 1H, CH), 5.85–5.79 (m, 1H, CH), 5.62 (d, J=10.1 Hz, 1H, CH), 3.48 (m, 1H, CH), 2.05–1.94 (m, 2H, CH_2), 1.78–1.72 (m, 2H, CH_2), 1.51–1.42 (m, 2H, CH_2); ^{13}C NMR ($CDCl_3$, 150 MHz, ppm): δ=137.4, 133.9, 131.5, 130.4, 128.7, 128.7, 128.5, 128.4, 128.3, 128.2, 126.4, 36.4, 36.3, 29.3, 28.2, 24.8, 24.7, 20.9, 20.7; MS (EI): m/z=218; HRMS (EI) calcd for $C_{14}H_{15}Cl$ 218.0862; found 218.0863.

*4.5.13. ((4E)-1-chloropenta-1,4-diene-1,3,5-triyl)tribenzene (**3m**).* ^1H NMR (600 MHz, $CDCl_3$, ppm): (*E*)-**3m**: δ=7.66–7.21 (m, 15H, aromatic), 6.61–6.25 (m, 3H, 3CH), 4.36 (dd, J=10.5, 6.4 Hz, 1H, CH); (*Z*)-**3m**: δ=7.66–7.21 (m, 15H, aromatic), 6.61–6.25 (m, 3H, 3CH), 5.00–4.97 (m, 1H, CH); ^{13}C NMR ($CDCl_3$, 150 MHz, ppm): δ=142.3, 142.3, 138.0, 137.2, 137.1, 137.0, 133.5, 131.6, 131.3, 131.0, 130.8, 130.4, 130.4, 128.9, 128.8, 128.8, 128.7, 128.7, 128.6, 128.6, 128.4, 128.4, 128.3, 127.9, 127.7, 127.6, 127.5, 126.9, 126.9, 126.7, 126.4, 48.5, 48.5; MS (EI): m/z=330; HRMS (EI) calcd for $C_{23}H_{19}Cl$ 330.1175; found 330.1171.

*4.5.14. ((4E)-1-Bromopenta-1,4-diene-1,3,5-triyl)tribenzene (**3n**).* ^1H NMR (600 MHz, $CDCl_3$, ppm): (*E*)-**3n**: δ=7.61–7.21 (m, 15H, aromatic), 6.62–6.32 (m, 3H, 3CH), 4.28 (dd, J=10.2, 6.7 Hz, 1H, CH); (*Z*)-**3n**: δ=7.61–7.21 (m, 15H, aromatic), 6.62–6.32 (m, 3H, 3CH), 4.92 (t, J=7.8 Hz, 1H, CH); ^{13}C NMR ($CDCl_3$, 150 MHz, ppm): δ=142.0, 142.0, 139.8, 138.5, 137.2, 137.0, 134.6, 132.2, 131.0, 131.0, 130.9, 130.1, 128.8, 128.8, 128.7, 128.6, 128.6, 128.4, 128.3, 127.9, 127.8, 127.7, 127.6, 127.5, 126.9, 126.4, 126.1, 121.3, 51.4, 49.5; MS (EI): m/z=374; HRMS (EI) calcd for $C_{23}H_{19}Br$ 374.0670; found 374.0667.

*4.5.15. (3-Chloro-3-(p-tolyl)prop-2-ene-1,1-diyl)dibenzene (**3o**).* ^1H NMR (600 MHz, $CDCl_3$, ppm): (*E*)-**3o**: δ=7.54–7.14 (m, 14H, aromatic), 6.44 (d, J=11.0 Hz, 1H, CH), 4.81 (d, J=11.0 Hz, 1H, CH), 2.39 (s, 3H, CH_3); (*Z*)-**3o**: δ=7.54–7.14 (m, 14H, aromatic), 6.58 (d, J=9.5 Hz, 1H, CH), 5.43 (d, J=9.4 Hz, 1H, CH), 2.37 (s, 3H, CH_3); ^{13}C NMR ($CDCl_3$, 150 MHz, ppm): δ=143.5, 138.9, 134.1, 131.7, 131.0, 129.1, 129.0, 128.7, 128.6, 128.6, 128.4, 128.2, 126.6, 50.8, 21.3; MS (EI): m/z=318; HRMS (EI) calcd for $C_{22}H_{19}Cl$ 318.1175; found 318.1173.

*4.5.16. (3-Chloro-3-(m-tolyl)prop-2-ene-1,1-diyl)dibenzene (**3p**).* ^1H NMR (600 MHz, $CDCl_3$, ppm): (*E*)-**3p**: δ=7.48–7.17 (m, 14H, aromatic), 6.50 (d, J=11.0 Hz, 1H, CH), 4.84 (d, J=11.0 Hz, 1H, CH), 2.38 (s, 3H, CH_3); (*Z*)-**3p**: δ=7.48–7.17 (m, 14H, aromatic), 6.64 (d, J=9.5 Hz, 1H, CH), 5.48 (d, J=9.4 Hz, 1H, CH), 2.41 (s, 3H, CH_3); ^{13}C NMR ($CDCl_3$, 150 MHz, ppm): δ=143.5, 143.2, 138.2, 138.1, 138.0, 136.9, 133.7, 131.8, 131.4, 129.8, 129.6, 129.5, 129.4, 128.8, 128.7, 128.4, 128.3, 128.3, 127.4, 126.7, 125.8, 124.0, 50.9, 50.8, 21.5, 21.4; MS (EI): m/z=318; HRMS (EI) calcd for $C_{22}H_{19}Cl$ 318.1175; found 318.1178.

*4.5.17. (3-Chloro-3-(o-tolyl)prop-2-ene-1,1-diyl)dibenzene (**3q**).* ^1H NMR (600 MHz, $CDCl_3$, ppm): (*E*)-**3q**: δ=7.36–7.06 (m, 14H, aromatic), 6.52 (d, J=10.9 Hz, 1H, CH), 4.47 (d, J=10.9 Hz, 1H, CH), 2.26 (s, 3H, CH_3); (*Z*)-**3q**: δ=7.36–7.06 (m, 14H, aromatic), 6.23 (d, J=9.5 Hz, 1H, CH), 5.43 (d, J=9.5 Hz, 1H, CH), 2.36 (s, 3H, CH_3); ^{13}C NMR ($CDCl_3$, 150 MHz, ppm): δ=143.3, 143.1, 136.9, 136.4, 132.5, 132.4, 131.4, 130.5, 130.4, 129.5, 129.1, 129.1, 128.8, 128.7, 128.6, 128.3, 128.2, 126.6, 125.9, 125.8, 50.7, 50.5, 19.9, 19.4; MS (EI): m/z=318; HRMS (EI) calcd for $C_{22}H_{19}Cl$ 318.1175; found 318.1179.

*4.5.18. (3-Bromo-3-(o-tolyl) prop-2-ene-1,1-diyl)dibenzene (**3r**).* ^1H NMR (600 MHz, $CDCl_3$, ppm): (*E*)-**3r**: δ=7.41–7.11 (m, 14H, aromatic), 6.80 (d, J=10.8 Hz, 1H, CH), 4.49 (d, J=10.8 Hz, 1H, CH), 2.29 (s, 3H, CH_3); (*Z*)-**3r**: δ=7.41–7.11 (m, 14H, aromatic), 6.40 (d, J=9.4 Hz, 1H, CH), 5.43 (d, J=9.4 Hz, 1H, CH), 2.38 (s, 3H, CH_3); ^{13}C NMR ($CDCl_3$, 150 MHz, ppm): δ=143.0, 142.8, 142.7, 137.7, 136.6, 136.4, 135.2, 130.5, 130.3, 129.4, 129.0, 128.9, 128.7, 128.6, 128.6, 128.3, 128.1, 126.6, 126.6, 125.9, 125.7, 120.9, 53.2, 51.7, 19.8, 19.4; MS (EI): m/z=362; HRMS (EI) calcd for $C_{22}H_{19}Br$ 362.0670; found 362.0666.

*4.5.19. (3-Chloro-3-(4-fluorophenyl)prop-2-ene-1,1-diyl)dibenzene (**3s**).* ^1H NMR (600 MHz, $CDCl_3$, ppm): (*E*)-**3s**: δ=7.61–7.02 (m, 14H, aromatic), 6.47 (d, J=10.9 Hz, 1H, CH), 4.74 (d, J=10.9 Hz, 1H, CH); (*Z*)-**3s**: δ=7.61–7.02 (m, 14H, aromatic), 6.55 (d, J=9.5 Hz, 1H, CH), 5.41 (d, J=9.3 Hz, 1H, CH); ^{13}C NMR ($CDCl_3$, 150 MHz, ppm): δ=163.6, 162.0, 143.2, 132.9, 131.8, 130.6, 130.6, 130.5, 128.7, 128.7, 128.3, 128.1, 126.7, 126.7, 115.5, 115.4, 115.3, 115.2, 50.9, 50.8; MS (EI): m/z=322; HRMS (EI) calcd for $C_{21}H_{16}ClF$ 322.0925; found 322.0924.

*4.5.20. (3-Bromo-3-(4-fluorophenyl)prop-2-ene-1,1-diyl)dibenzene (**3t**).* ^1H NMR (600 MHz, $CDCl_3$, ppm): (*E*)-**3t**: δ=7.57–7.01 (m, 14H,

aromatic), 6.70 (d, *J*=10.9 Hz, 1H, CH), 4.68 (d, *J*=10.9 Hz, 1H, CH); (*Z*)-**3t**: δ=7.57–7.01 (m, 14H, aromatic), 6.63 (d, *J*=9.4 Hz, 1H, CH), 5.35 (d, *J*=9.3 Hz, 1H, CH); ^{13}C NMR ($CDCl_3$, 150 MHz, ppm): δ=163.5, 161.9, 142.9, 142.7, 136.0, 134.4, 133.4, 130.8, 130.7, 129.6, 129.6, 128.8, 128.7, 128.3, 128.1, 126.8, 124.9, 120.1, 115.5, 115.4, 115.3, 115.1, 53.7, 51.8; MS (EI): *m*/*z*=366; HRMS (EI) calcd for $C_{21}H_{16}BrF$ 366.0419; found 366.0420.

*4.5.21. (3-Chloro-3-(3-chlorophenyl)prop-2-ene-1,1-diyl)dibenzene (**3u**).* ^{1}H NMR (600 MHz, $CDCl_3$, ppm): (*E*)-**3u**: δ=7.62–7.13 (m, 14H, aromatic), 6.51 (d, *J*=11.0 Hz, 1H, CH), 4.76 (d, *J*=11.0 Hz, 1H, CH); (*Z*)-**3u**: δ=7.62–7.13 (m, 14H, aromatic), 6.65 (d, *J*=9.5 Hz, 1H, CH), 5.42 (d, *J*=9.5 Hz, 1H, CH); ^{13}C NMR ($CDCl_3$, 150 MHz, ppm): δ=143.0, 138.5, 134.4, 132.5, 129.9, 129.7, 129.1, 128.9, 128.8, 128.7, 128.3, 128.1, 126.8, 50.8; MS (EI): *m*/*z*=338; HRMS (EI) calcd for $C_{21}H_{16}Cl_2$ 338.0629; found 338.0630.

*4.5.22. (3-Bromo-3-(3-chlorophenyl)prop-2-ene-1,1-diyl)dibenzene (**3v**).* ^{1}H NMR (600 MHz, $CDCl_3$, ppm): (*E*)-**3v**: δ=7.58–7.12 (m, 14H, aromatic), 6.74 (d, *J*=10.9 Hz, 1H, CH), 4.69 (d, *J*=10.9 Hz, 1H, CH); (*Z*)-**3v**: δ=7.58–7.12 (m, 14H, aromatic), 6.73–6.70 (m, 1H, CH), 5.36 (d, *J*=9.4 Hz, 1H, CH); ^{13}C NMR ($CDCl_3$, 150 MHz, ppm): δ=142.7, 142.4, 140.0, 136.6, 134.5, 134.3, 129.6, 129.5, 129.0, 128.8, 128.7, 128.3, 128.1, 127.8, 127.0, 126.8, 126.0, 119.3, 53.7, 51.7; MS (EI): *m*/*z*=382; HRMS (EI) calcd for $C_{21}H_{16}BrCl$ 382.0124; found 382.0121.

*4.5.23. 3-(1-Chloro-3,3-diphenylprop-1-en-1-yl)thiophene (**3w**).* ^{1}H NMR (600 MHz, $CDCl_3$, ppm): (*E*)-**3w**: δ=7.52–7.16 (m, 13H, aromatic), 6.41 (d, *J*=10.7 Hz, 1H, CH), 4.97 (d, *J*=10.7 Hz, 1H, CH); (*Z*)-**3w**: δ=7.52–7.16 (m, 13H, aromatic), 6.60 (d, *J*=9.5 Hz, 1H, CH), 5.41 (d, *J*=9.4 Hz, 1H, CH); ^{13}C NMR ($CDCl_3$, 150 MHz, ppm): δ=143.4, 137.2, 131.6, 128.8, 128.6, 128.4, 128.2, 128.0, 126.7, 126.7, 125.7, 125.3, 51.0, 50.4; MS (EI): *m*/*z*=310; HRMS (EI) calcd for $C_{19}H_{15}ClS$ 310.0583; found 310.0585.

*4.5.24. (3-chloro-2-methylprop-2-ene-1,1,3-triyl)tribenzene (**3x**).* ^{1}H NMR (600 MHz, $CDCl_3$, ppm): (*E*)-**3x**: δ=7.51–7.08 (m, 15H, aromatic), 5.18 (s, 1H, CH), 1.93 (s, 3H, CH_3); (*Z*)-**3x**: δ=7.51–7.08 (m, 15H, aromatic), 4.47 (s, 1H, CH), 1.94 (s, 3H, CH_3); ^{13}C NMR ($CDCl_3$, 150 MHz, ppm): δ=142.0, 139.2, 135.3, 135.0, 129.5, 129.3, 129.2, 129.1, 128.8, 128.5, 128.3, 127.2, 126.8, 126.7, 126.5, 124.7, 123.9, 119.5, 59.7, 54.0, 17.8, 13.4; MS (EI): *m*/*z*=318; HRMS (EI) calcd for $C_{22}H_{19}Cl$ 318.1175; found 318.1171.

*4.5.25. (3-Chloro-2-ethylprop-2-ene-1,1,3-triyl)tribenzene (**3y**).* ^{1}H NMR (600 MHz, $CDCl_3$, ppm): (*E*)-**3y**: δ=7.54–7.12 (m, 15H, aromatic), 5.20 (s, 1H, CH), 2.50 (q, *J*=7.4 Hz, 2H, CH_2), 0.58 (t, *J*=7.3 Hz, 3H, CH_3); (*Z*)-**3y**: δ=7.54–7.12 (m, 15H, aromatic), 4.66 (s, 1H, CH), 2.61–2.54, 2.14–2.07 (m, 2H, CH_2), 1.08 (t, *J*=7.5 Hz, 3H, CH_3); ^{13}C NMR ($CDCl_3$, 150 MHz, ppm): δ=142.1, 140.4, 139.3, 129.6, 129.3, 128.8, 128.4, 128.3, 126.5, 54.0, 25.4, 12.3; MS (EI): *m*/*z*=332; HRMS (EI) calcd for $C_{23}H_{21}Cl$ 332.1332; found 332.1330.

*4.5.26. (3-Bromo-2-ethylprop-2-ene-1,1,3-triyl)tribenzene (**3z**).* ^{1}H NMR (600 MHz, $CDCl_3$, ppm): (*E*)-**3z**: δ=7.51–7.08 (m, 15H, aromatic), 5.17 (s, 1H, CH), 2.48 (q, *J*=7.3 Hz, 2H, CH_2), 0.54 (t, *J*=7.3 Hz, 3H, CH_3); (*Z*)-**3z**: δ=7.51–7.08 (m, 15H, aromatic), 4.63 (s, 1H, CH), 2.58–2.51, 2.15–2.11 (m, 2H, CH_2), 1.05 (t, *J*=7.5 Hz, 3H, CH_3); ^{13}C NMR ($CDCl_3$, 150 MHz, ppm): δ=143.0, 141.9, 141.0, 129.4, 129.3, 129.2, 128.7, 128.4, 128.2, 128.1, 126.5, 121.1, 54.1, 27.9, 12.3; MS (EI): *m*/*z*=376; HRMS (EI) calcd for $C_{23}H_{21}Br$ 376.0827; found 376.0829.

*4.5.27. (3-Chlorohept-2-ene-1,1-diyl)dibenzene (**3a′**).* ^{1}H NMR (600 MHz, $CDCl_3$, ppm): (*E*)-**3b′**: δ=7.33–7.17 (m, 10H, aromatic), 5.98 (d, *J*=9.4 Hz, 1H, CH), 5.24 (d, *J*=9.4 Hz, 1H, CH), 2.41 (t, *J*=7.4 Hz, 2H, CH_2), 1.63–1.54 (m, 2H, CH_2), 1.38–1.30 (m, 2H, CH_2), 0.95–0.88 (m, 3H, CH_3); (*Z*)-**3b′**: δ=7.33–7.17 (m, 10H, aromatic), 6.11 (d, *J*=10.1 Hz, 1H, CH), 4.88 (d, *J*=10.1 Hz, 1H, CH), 2.46 (t, *J*=7.4 Hz, 2H, CH_2), 1.63–1.54 (m, 2H, CH_2), 1.38–1.30 (m, 2H, CH_2), 0.95–0.88 (m, 3H, CH_3); ^{13}C NMR ($CDCl_3$, 150 MHz, ppm): δ=143.5, 143.4, 135.8, 135.6, 130.0, 128.6, 128.5, 128.3, 128.2, 127.4, 126.6, 126.4, 50.0, 49.9, 39.3, 33.8, 29.6, 29.5, 22.0, 21.8, 13.9, 13.8; MS (EI): *m*/*z*=284; HRMS (EI) calcd for $C_{19}H_{21}Cl$ 284.1332; found 284.1334.

*4.5.28. (3-Chloronon-2-ene-1,1-diyl)dibenzene (**3b′**).* ^{1}H NMR (600 MHz, $CDCl_3$, ppm): (*E*)-**3c′**: δ=7.33–7.17 (m, 10H, aromatic), 5.97 (d, *J*=9.4 Hz, 1H, CH), 5.24 (d, *J*=9.4 Hz, 1H, CH), 2.40 (t, *J*=7.3 Hz, 2H, CH_2), 1.62–1.54 (m, 2H, CH_2), 1.32–1.25 (m, 6H, $3CH_2$), 0.90–0.85 (m, 3H, CH_3); (*Z*)-**3c′**: δ=7.33–7.17 (m, 10H, aromatic), 6.11 (d, *J*=10.1 Hz, 1H, CH), 4.88 (d, *J*=10.2 Hz, 1H, CH), 2.46 (t, *J*=7.3 Hz, 2H, CH_2), 1.62–1.54 (m, 2H, CH_2), 1.32–1.25 (m, 6H, $3CH_2$), 0.90–0.85 (m, 3H, CH_3); ^{13}C NMR ($CDCl_3$, 150 MHz, ppm): δ=143.5, 143.4, 135.8, 135.6, 130.0, 128.6, 128.5, 128.3, 128.2, 127.5, 126.6, 126.4, 50.0, 49.9, 39.6, 34.0, 31.6, 31.5, 28.5, 28.3, 27.4, 27.2, 22.6, 22.5, 14.0; MS (EI): *m*/*z*=312; HRMS (EI) calcd for $C_{21}H_{25}Cl$ 312.1645; found 312.1645.

*4.5.29. Oxybis(methanetriyl)tetrabenzene (**4a**).* ^{1}H NMR ($CDCl_3$, 600 MHz, ppm): δ=7.38 (d, *J*=7.3 Hz, 8H), 7.33 (t, *J*=7.5 Hz, 8H), 7.26 (t, *J*=7.3 Hz, 4H), 5.41 (s, 2H); ^{13}C NMR ($CDCl_3$, 150 MHz, ppm): δ=142.2, 128.4, 127.4, 127.3, 80.0; HRMS (ESI) calcd for $C_{26}H_{22}NaO$ 373.1563; found: 373.1554.

4.6. Characterization data for reactions of alcohols with alkynes in the presence of FeX_2 (1 mol %)/HX

*4.6.1. 5-(2-Chloro-2-phenylvinyl)-10,11-dihydro-5H-dibenzo[a,d][7]annulene (**3f**).* ^{1}H NMR (400 MHz, $CDCl_3$, ppm): (*E*)-**3f**: δ=7.66–7.15 (m, 13H, aromatic), 6.97 (d, *J*=10.7 Hz, 1H, CH), 5.10 (d, *J*=10.5 Hz, 1H, CH), 3.40–3.31 (m, 2H, CH_2), 3.20–3.13 (m, 2H, CH_2); (*Z*)-**3f**: δ=7.66–7.15 (m, 13H, aromatic), 6.97 (d, *J*=10.6 Hz, 1H, CH), 5.54 (d, *J*=8.9 Hz, 1H, CH), 3.53–3.48 (m, 2H, CH_2), 3.20–3.13 (m, 2H, CH_2); ^{13}C NMR ($CDCl_3$, 100 MHz, ppm): δ=140.4, 140.1, 139.4, 139.1, 138.1, 137.3, 131.2, 131.1, 130.5, 130.5, 130.4, 129.8, 129.0, 128.9, 128.7, 128.6, 128.5, 128.3, 127.2, 127.1, 126.8, 126.4, 52.7, 49.8, 33.4, 33.0; MS (EI): *m*/*z*=330; HRMS (EI) calcd for $C_{23}H_{19}Cl$ 330.1175; found 330.1173.

*4.6.2. 5-(2-Bromo-2-phenylvinyl)-10,11-dihydro-5H-dibenzo[a,d][7]annulene (**3g**).* ^{1}H NMR (400 MHz, $CDCl_3$, ppm): (*E*)-**3g**: δ=7.62–7.10 (m, 14H), 4.99 (d, *J*=10.4 Hz, 1H, CH), 3.43–3.34 (m, 2H, CH_2), 3.18–3.09 (m, 2H, CH_2); (*Z*)-**3g**: δ=7.62–7.10 (m, 14H), 5.52 (d, *J*=9.0 Hz, 1H, CH), 3.54–3.47 (m, 2H, CH_2), 3.18–3.09 (m, 2H, CH_2); ^{13}C NMR ($CDCl_3$, 100 MHz, ppm): δ=140.0, 139.9, 139.9, 139.4, 139.2, 138.8, 135.4, 133.3, 130.5, 130.3, 129.0, 128.9, 128.9, 128.6, 128.3, 127.9, 127.2, 127.1, 126.4, 120.9, 55.2, 51.7, 33.5, 33.1; MS (EI): *m*/*z*=374; HRMS (EI) calcd for $C_{23}H_{19}Br$ 374.0670; found 374.0671.

*4.6.3. 3-(1-Chloro-3,3-diphenylprop-1-en-1-yl)thiophene (**3w**).* ^{1}H NMR (400 MHz, $CDCl_3$, ppm): (*E*)-**3w**: δ=7.57–7.22 (m, 13H, aromatic), 6.47 (d, *J*=10.6 Hz, 1H, CH), 5.04 (d, *J*=10.7 Hz, 1H, CH); (*Z*)-**3w**: δ=7.57–7.22 (m, 13H, aromatic), 6.66 (d, *J*=9.5 Hz, 1H, CH), 5.47 (d, *J*=9.5 Hz, 1H, CH); ^{13}C NMR ($CDCl_3$, 100 MHz, ppm): δ=143.5, 137.2, 131.6, 128.8, 128.7, 128.4, 128.3, 128.0, 126.8, 126.8, 125.8, 125.3, 51.1, 50.4; MS (EI): *m*/*z*=310; HRMS (EI) calcd for $C_{19}H_{15}ClS$ 310.0583; found 310.0584.

*4.6.4. (3-chloro-2-methylprop-2-ene-1,1,3-triyl)tribenzene (**3x**).* ^{1}H NMR (400 MHz, $CDCl_3$, ppm): (*E*)-**3x**: δ=7.46–7.04 (m, 15H, aromatic), 5.16 (s, 1H, CH), 1.90 (s, 3H, CH_3); (*Z*)-**3x**: δ=7.46–7.04 (m, 15H, aromatic), 4.43 (s, 1H, CH), 1.90 (s, 3H, CH_3); ^{13}C NMR ($CDCl_3$, 100 MHz, ppm): δ=142.1, 139.2, 135.3, 135.0, 129.6, 129.3, 129.2, 128.9, 128.6, 128.5, 128.4, 127.3, 126.9, 126.8, 126.6, 124.8, 124.0,

119.5, 59.7, 54.1, 17.9, 13.6; MS (EI): m/z=318; HRMS (EI) calcd for $C_{22}H_{19}Cl$ 318.1175; found 318.1173.

4.7. Characterization data for reactions of alcohols with alkynes in the presence of FeX_3 (1 mol %)/HX

*4.7.1. (1-Chlorobut-1-ene-1,3-diyl)dibenzene (**3h**).* ^1H NMR (400 MHz, $CDCl_3$, ppm): (*E*)-**3h**: δ=7.67–7.25 (m, 10H, aromatic), 6.22 (d, J=10.8 Hz, 1H, CH), 3.71–3.62 (m, 1H, CH), 1.44 (d, J=7.0 Hz, 3H, CH_3); (*Z*)-**3h**: δ=7.67–7.25 (m, 10H, aromatic), 6.33 (d, J=9.2 Hz, 1H, CH), 4.31–4.22 (m, 1H, CH), 1.55 (d, J=7.0 Hz, 3H, CH_3); ^{13}C NMR ($CDCl_3$, 100 MHz, ppm): δ=145.0, 137.3, 134.4, 132.5, 130.2, 128.8, 128.7, 128.7, 128.5, 128.4, 128.3, 127.1, 126.8, 126.6, 126.5, 39.8, 39.7, 22.5, 20.9; MS (EI): m/z=242; HRMS (EI) calcd for $C_{16}H_{15}Cl$ 242.0862; found 242.0864.

*4.7.2. (1-Bromobut-1-ene-1,3-diyl)dibenzene (**3i**).* ^1H NMR (400 MHz, $CDCl_3$, ppm): (*E*)-**3i**: δ=7.65–7.19 (m, 10H, aromatic), 6.39 (d, J=10.7 Hz, 1H, CH), 3.60–3.52 (m, 1H, CH), 1.39 (d, J=6.9 Hz, 3H, CH_3); (*Z*)-**3i**: δ=7.65–7.19 (m, 10H, aromatic), 6.35 (d, J=9.1 Hz, 1H, CH), 4.18–4.14 (m, 1H, CH), 1.52 (d, J=7.0 Hz, 3H, CH_3); ^{13}C NMR ($CDCl_3$, 100 MHz, ppm): δ=144.6, 138.7, 138.6, 128.8, 128.7, 128.6, 128.4, 128.4, 128.3, 127.7, 127.1, 126.8, 126.8, 126.5, 119.8, 42.6, 40.8, 22.1; MS (EI): m/z=286; HRMS (EI) calcd for $C_{16}H_{15}Br$ 286.0357; found 286.0359.

*4.7.3. 3-(1-Chloro-3,3-diphenylprop-1-en-1-yl)thiophene (**3w**).* ^1H NMR (400 MHz, $CDCl_3$, ppm): (*E*)-**3w**: δ=7.57–7.22 (m, 13H, aromatic), 6.47 (d, J=10.6 Hz, 1H, CH), 5.03 (d, J=10.6 Hz, 1H, CH); (*Z*)-**3w**: δ=7.57–7.22 (m, 13H, aromatic), 6.66 (d, J=9.5 Hz, 1H, CH), 5.47 (d, J=9.5 Hz, 1H, CH); ^{13}C NMR ($CDCl_3$, 100 MHz, ppm): δ=143.5, 137.2, 131.6, 128.8, 128.7, 128.4, 128.3, 128.0, 126.8, 126.8, 128.7, 125.8, 125.3, 51.1, 50.4; MS (EI): m/z=310; HRMS (EI) calcd for $C_{19}H_{15}ClS$ 310.0583; found 310.0583.

*4.7.4. (3-chloro-2-methylprop-2-ene-1,1,3-triyl)tribenzene (**3x**).* ^1H NMR (400 MHz, $CDCl_3$, ppm): (*E*)-**3x**: δ=7.46–7.04 (m, 15H, aromatic), 5.16 (s, 1H, CH), 1.90 (s, 3H, CH_3); (*Z*)-**3x**: δ=7.46–7.04 (m, 15H, aromatic), 4.43 (s, 1H, CH), 1.90 (s, 3H, CH_3); ^{13}C NMR ($CDCl_3$, 100 MHz, ppm): δ=142.1, 139.2, 135.0, 129.6, 129.5, 129.3, 129.2, 128.9, 128.6, 128.5, 128.5, 127.4, 127.0, 126.8, 126.7, 124.9, 124.0, 119.6, 59.7, 54.1, 18.0, 13.6; MS (EI): m/z=318; HRMS (EI) calcd for $C_{22}H_{19}Cl$ 318.1175; found 318.1174.

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Supplementary data

Supplementary data associated with this article can be found in the online version, at http://dx.doi.org/10.1016/j.tet.2015.04.065.

References and notes

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