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# A bifunctional ligand enables efficient gold-catalyzed hydroarylation of terminal unactivated propargylic alcohols with heteroareneboronic acids

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ABSTRACT

Terminal allylic alcohols are important motifs in natural products, and also key intermediates/precursors in numerous novel reaction transformations. In this study, enabled by a bifunctional ligand featuring a basic amino group, a gold-catalyzed hydroarylation of terminal unactivated propargylic alcohols with heteroareneboronic acids has been first established, and efficiently affords various terminal aryl-substituted allylic alcohols with moderate to high yields under mild conditions.



## 1. Introduction

Since the pioneering work by Hayashi [1] and Shirakawa [2] in 2001, the transition metal-catalyzed hydroarylation of internal alkyne with arylboron reagent has been extensively studied. However, probably due to the easily undergoing self-dimerization under these metal catalysts [3], only a few scattered protocols have been focused on this reaction by using terminal unactivated alkynes as the substrates (Scheme 1). For example, in an earlier study, the hydroarylation of terminal alkynes with arylboronic acids catalyzed by $Pd(PPh_3)_4$/AcOH afforded branched Markovnikov terminal alkenes [4] (Scheme 1A). Similar results were also found in a $PdCl_2(PPh_3)_2$-catalyzed reaction of terminal alkynes with $NaBPh_4$ under acid (AcOH) conditions [5] (Scheme 1B). In two recent studies by employing $Ni(acac)_2$ [3] (Scheme 1C) or $Pd(PPh_3)_4$[6] (Scheme 1D) as catalyst, the reactions of terminal alkynols with arylboronic acids afforded linear anti-Markovnikov products. It is noted that in the latter two examples, the hydroxyl group in the alkynol substrate displayed directing effect in realizing the regioselectivity of the reaction.

On the other hand, some direct hydroarylations of activated terminal alkynes with electron-rich arenes catalyzed by gold complex/salts have been also reported [7]. Although these strategies can avoid self-dimerization of the terminal alkynes, the reaction of alkynes with electron-poor arenes is either unsuccessful or inefficient.

In one of our previous study enabled by a bifunctional ligand **L1** (Scheme 2), we have first developed a gold(I)-catalyzed hydroalkenylation of terminal propargylic alcohols with alkenyltrifluoroborate under mild conditions [8] (Scheme 1E). Ligand **L1**,

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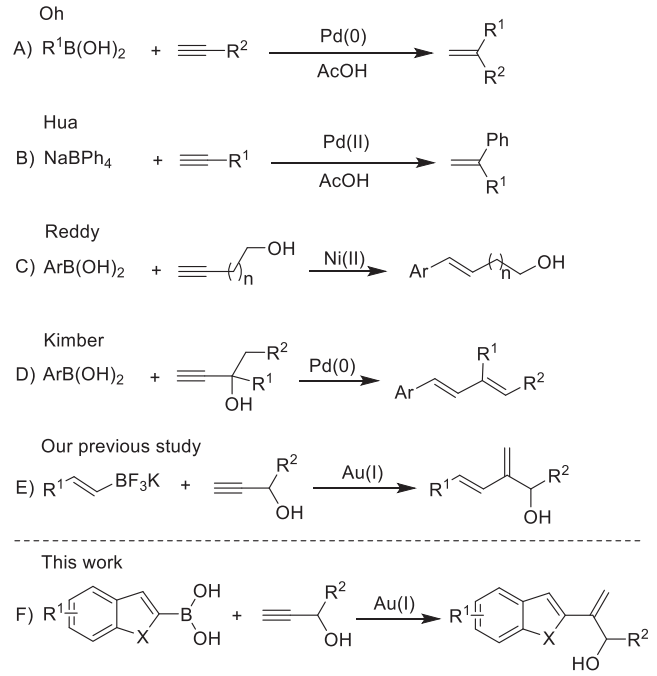
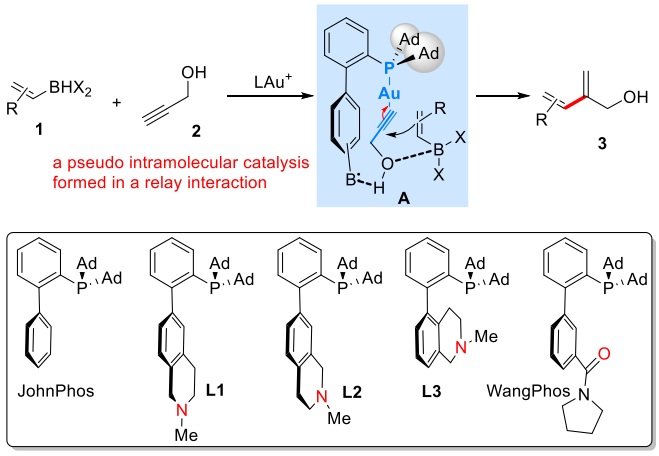



**Scheme 1.** Hydroarylation or Hydroalkenylation of alkynes using metal catalysts.




**Scheme 2.** Our previous design for hydroalkenylation by employing bifunctional ligands and gold metal.

together with its three analogues **L2**, **L3**, and WangPhos, as shown in Scheme 2, was designed by Zhang [9] and contains a JohnPhos framework featuring a unique basic amino or amide group at the lower half of the pendant benzene ring. The mechanistic study disclosed that in this chemistry, the remote basic group could promote a cooperation interaction, in a "relay" fashion, between itself, the hydroxyl group, and the alkenylboron moiety, to achieve a pseudo intramolecular catalysis and subsequently increase the nucleophilicity of alkenyl moiety attacking at the C–C triple bond (Scheme 2, structure A), thus resulting in high reaction efficiency. Very recently, another gold-catalyzed reaction of terminal alkynes with 2-naphthols enabled by WangPhos has also witnessed this similar interaction [10].

It should be noted that in the Pd, Rh, or Ni-catalyzed hydroarylation, the hydroxyl group in the substrate has always played as a directing group by coordinating to the metal center to induce the regioselectivity of the reaction. Nevertheless, in our previous study, the hydroxyl group in the propargylic alcohol worked as an intermediary by connecting the bifunctional ligand with the substrate, to efficiently accelerate the reaction.

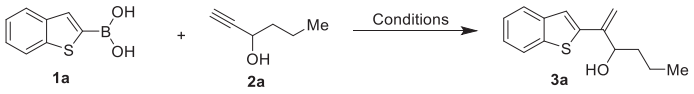
To the best of our knowledge, gold-catalyzed hydroarylation of alkynes with arylboronic acid to incorporate aryl-substituted alkenes have not been studied to date. We envisioned that whether our above gold catalysts could be employed to realize the hydroarylation of terminal propargylic alcohols with arylboronic acid and subsequently generate useful terminal allylic alcohol products, which are often presence in many natural product [11] and key intermediates/precursors in various novel reaction transformations [12]. Although organometallic addition [12b,12d,13], or C–C cross coupling [12f,14] can be frequently used to prepare this kind of alkenols, harsh reaction conditions (such as very low or high temperature, inert atmosphere, and/or anhydrous solvent) dramatically limit their widespread application. Therefore, a more operationally simple technique with mild reaction condition is still needed. Herein we report our recent efforts on the development of a gold(I)-catalyzed hydroarylation of terminal unactivated propargylic alcohols with heteroareneboronic acids, as a further example for making use of these synthetic valuable terminal alkynes.

## 2. Results and discussion

At the outset, by selecting 1-hexyn-3-ol as the substrate, various arylboronic acids were investigated and benzo[*b*]thiophen-2-boronic acid was found to be the suitable nucleophilic aryl source, affording the product **3a** in 81% yield using our previous reaction conditions (entry 1, Table 1). Under the same reaction conditions, replacing ligand **L1** with its analogue **L2** (entry 2), **L3** (entry 3), or WangPhos (entry 4), the reaction led to decreased efficiency, whereas commonly employed ligands, such as $PPh_3$ (entry 5) or JohnPhos (entry 6) showed no or weak ability, even with the presence of exogenous base (entry 7), which indicates the significantly enabling role of the remote amino moiety of these bifunctional ligands for the relay catalysis. A broad screening of the reaction conditions such as chloride abstractors (entries 8–10), solvent systems (entries 11–14), mole ratios of the substrates (entry 15) or catalyst (entry 16) revealed the optimal conditions as a molar ratio of **1a**:**2a** = 3:1, **L1**AuCl (2.5 mol%)/NaBARF(2.5 mol%), DCE/$H_2O$ (v/v = 2:1, 0.24 M), ambient temperature, 24 h, and open flask (entry 16). Of note that 2.5 mol% of **L1**AuCl/NaBARF was chosen in the reaction as the yield is nearly identical to that of using twice amount of the catalyst (entry 16 vs entry 12). It should be mentioned that the reaction could give moderate yield in $H_2O$ (entry 14), while no product in dry DCE (entry 13). Of particular note is that it could proceed in open flask at room temperature using water-containing solvent, thus simplifying the operational procedure in comparison with the transition metal-catalyzed hydroarylation.

With the optimal conditions in hand, the scope of this reaction was examined. As shown in Table 2, in regard to the substituents in the alkynol, the steric cyclohexyl (**3b**), the hydroxyl-containing alkyl group (**3c**), and the sulfonamide-functionalized alkyl group (**3d**) are all allowed in this reaction, resulting in good yields (67–74%). The internal C–C triple bond (**3e**) and double bond (**3f**) are also tolerated under the gold catalysis. When the benzene ring is functionalized with various substituents, such as H (**3g**), monosubstituted 4-F (**3h**), 2-Cl (**3i**), 3-Br (**3j**); di-substituted 2,4-$F_2$ (**3k**), 2,3-$Cl_2$ (**3l**), tri-substituted electron donating group 3,4,5-$(OMe)_3$ (**3m**), and electron withdrawing group $CF_3$ (**3n**), the reactions proceeded smoothly in moderate to excellent yields (47–90%). In the case of **3i**, the reaction exhibits a slight low

**Table 1**
Optimization of the reaction conditions[a].




| Entry | 1a:2a | Catalyst (mol%) | Solvent (v/v) | Yield (%)[b] |
|---|---|---|---|---|
| 1 | 3:1 | **L1**AuCl/$AgNTf_2$ (5/5) | DCM/$H_2O$ (4/1) | 81 |
| 2 | 3:1 | **L2**AuCl/$AgNTf_2$ (5/5) | DCM/$H_2O$ (4/1) | 70 |
| 3 | 3:1 | **L3**AuCl/$AgNTf_2$ (5/5) | DCM/$H_2O$ (4/1) | 18 |
| 4 | 3:1 | WangPhosAuCl/$AgNTf_2$ (5/5) | DCM/$H_2O$ (4/1) | 52 |
| 5 | 3:1 | $PPh_3$AuCl/$AgNTf_2$ (5/5) | DCM/$H_2O$ (4/1) | 0 |
| 6 | 3:1 | JohnPhosAuCl/$AgNTf_2$ (5/5) | DCM/$H_2O$ (4/1) | 6 |
| 7 | 3:1 | JohnPhosAuCl/$AgNTf_2$/$Et_3N$ (5/5/5) | DCM/$H_2O$ (4/1) | 5 |
| 8 | 3:1 | **L1**AuCl/AgOTf (5/5) | DCM/$H_2O$ (4/1) | 60 |
| 9 | 3:1 | **L1**AuCl/$AgSbF_6$ (5/5) | DCM/$H_2O$ (4/1) | 49 |
| 10 | 3:1 | **L1**AuCl/NaBARF[c] (5/5) | DCM/$H_2O$ (4/1) | 88 |
| 11 | 3:1 | **L1**AuCl/NaBARF (5/5) | PhMe/$H_2O$ (4:1) | 58 |
| 12 | 3:1 | **L1**AuCl/NaBARF (5/5) | DCE/$H_2O$ (2/1, 0.24 M) | 90 (81) |
| 13 | 3:1 | **L1**AuCl/NaBARF (5/5) | dry DCE | 0 |
| 14 | 3:1 | **L1**AuCl/NaBARF (5/5) | $H_2O$ | 40 |
| 15 | 2:1 | **L1**AuCl/NaBARF (2.5/2.5) | DCE/$H_2O$ (2/1, 0.24 M) | 58 |
| **16** | **3:1** | **L1AuCl/NaBARF (2.5/2.5)** | **DCE/$H_2O$ (2/1, 0.24 M)** | **88 (79)** |

[a] 0.05 mmol of alkynols was used at an initial concentration of 0.16 M. The reaction was stirred at room temperature for 24 h.
[b] NMR yield obtained by using 1,3,5-trimethoxylbenzene as an internal standard, and isolated yield indicated in the parentheses.
[c] NaBARF represents Sodium tetrakis[3,5-bis(trifluoromethyl)phenyl]borate.

efficiency perhaps owning to the steric hindrance of 2-substituted chloride. Substituents on the benzo[*b*]thiophenyl scaffold were also examined (Table 3). Halides (**3o**-**p**), methyl group (**3q**-r), and $CF_3$ (**3s**) are all suitable, delivering the products in moderate to good yields (57–79%). The methyl group substituted at 3-position (**3r**) of the benzo[*b*]thiophenyl skeleton poses steric hindrance but still permits the reaction in moderate yield (67%). The hydroarylation at 3-position (**3t**) of the benzo[*b*]thiophenyl skeleton also proceeded well in moderate yield (51%). Replacement of the benzo[*b*]thiophenyl scaffold with the benzo[*b*]furan (**3u-v**) or thiophenyl (**3w**) is also feasible to this reaction. However, the low yield of **3w** might be resulted from the easy protodeboronation of thiophenyl-2-boronic acid, and the generated thiophene might be continually reacted with alkyne under gold catalysis, resulting in the formation of complicated unknown side products.

The hydroarylation of the internal propargylic alcohols containing alkyl or aryl end with benzo[*b*]thiophenyl-2-boronic acid is unsuccessful under this gold catalysis. However, the reaction of halo (Br and I)-terminal alkynols could give the corresponding products **3x**-**y** by using 8.0 mol% equivalents catalyst under the heat (40 °C) condition (Scheme 3A and 3B). Notably, the C–Br or C–I bond is often a liability in Pd, Rh, or Ni catalysis while tolerates in this reaction. Surprisingly, the $CO_2$Me-terminal alkynol could proceed well under the standard conditions and afford the product **3z** in moderate yield (Scheme 3C). Obviously, the electron-withdrawing effect is beneficial to the hydroarylation of internal propargylic alcohols. The stereoselectivities for these isomers at the C–C double bond were confirmed by NOESY spectroscopy analysis (see supporting information).

To establish the synthetic utility of this chemistry (Scheme 4), **3a** was reacted with N-phenylmaleimide at 80 °C in toluene, and the Diels-Alder syn-cycloaddition product **4a** was obtained in 65% yield, whereas the dehydration and double bond rearrangement lead to the product with no exo or endo isomer. The *trans*-configuration of the C–C double bond and the relative stereostructure of two hydrogen atoms on the succinimide moiety were confirmed by NOESY/COSY spectroscopy analysis (please see supporting information). Furthermore, the reaction of the cholesterol-derived **I** with benzo[*b*]thiophenyl-2-boronic acid by employing this methodology readily afforded the diastereoisomers **4b-1** and **4b-2** in almost equal yields (total 84%). Finally, a modification on the ibuprofen precursor **II** has been also carried out and smoothly furnished the product **4c** in good yield (74%), however, its diastereoisomer could not be monitored by $^1H$ or $^{13}C$ NMR analysis and isolated by using silica gel column.

The proposed mechanism of this chemistry might be similar to that of the gold catalysis in our previous article: under the relayed interactions, the attacking of the C–C double bond in the benzo[*b*]thiophenyl-2-boronic acid to the triple bond of the alkyne, which is activated by the gold metal (**A**), promotes the formation of gold carbenoid and cyclopropane (**B**), and followed with the deboronation of the benzo[*b*]thiophenyl moiety and cleavage of the cyclopropane (**C**), the target compound **2a** forms after the protodeauration and the hydrolysis of boric acid (Scheme 5).

## 3. Conclusion

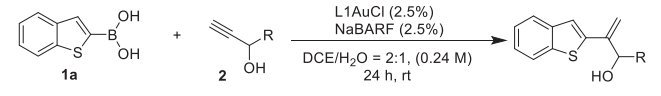
In conclusion, a gold(I)-catalyzed hydroarylation of unactivated terminal or activated internal propargylic alcohols with heteroareneboronic acids has been developed with a wide range of substrate scope. Low loading of the catalyst leads to this synthetic methodology more affordable. Running in open flask at room temperature by using water-containing solvent makes this procedure operationally simple. This method is highlighted by the synthetic utilities in both organic synthesis and bioactive molecular modification. This chemistry can be compensation to traditional transition metal-catalyzed hydroarylation and would also broaden the field of gold catalysis.

## 4. Experimental section

### 4.1. General information

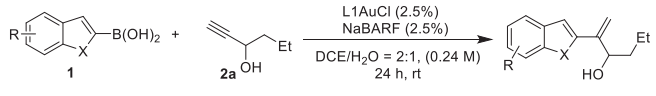
Solvents such as DMF and THF were obtained from commercial suppliers and kept with 4 Å MS (stored under $N_2$ atmosphere). Toluene, DCM, and DCE were dried under $CaH_2$ and distilled. Unless

**Table 2**
The scope study of alkynols[a].

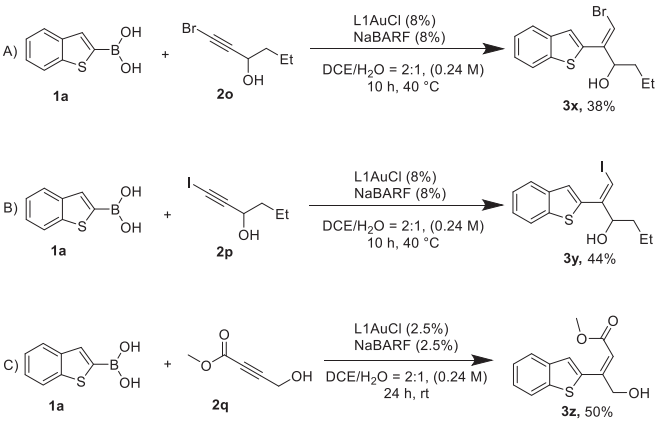



| Entry | Substrate **2** | Product | Yield (%) |
|---|---|---|---|
| 1 | **2b** | **3b** | 70 |
| 2 | **2c** | **3c** | 74 |
| 3 | **2d** | **3d** | 67 |
| 4 | **2e** | **3e** | 66 |
| 5 | **2f** | **3f** | 59 |
| 6 | **2g** | **3g** | 90 |
| 7 | **2h** | **3h** | 79 |
| 8 | **2i** | **3i** | 47 |
| 9 | **2j** | **3j** | 85 |
| 10 | **2k** | **3k** | 75 |
| 11 | **2l** | **3l** | 65 |
| 12 | **2m** | **3m** | 70 |
| 13 | **2n** | **3n** | 90 |

**Table 3**
The scope study of heteroareneboronic acids[a].

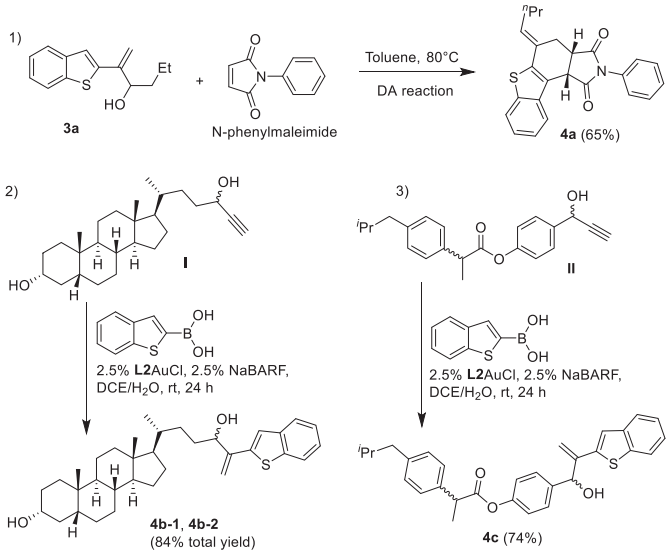



| Entry | Substrate **1** | Product | Yield (%) |
|---|---|---|---|
| 1 | **1b** | **3o** | 57 |
| 2 | **1c** | **3p** | 79 |
| 3 | **1d** | **3q** | 79 |
| 4 | **1e** | **3r** | 67 |
| 5 | **1f** | **3s** | 74 |
| 6 | **1g** | **3t** | 51 |
| 7 | **1h** | **3u** | 61 |
| 8 | **1i** | **3v** | 48 |
| 9 | **1j** | **3w** | 17 |

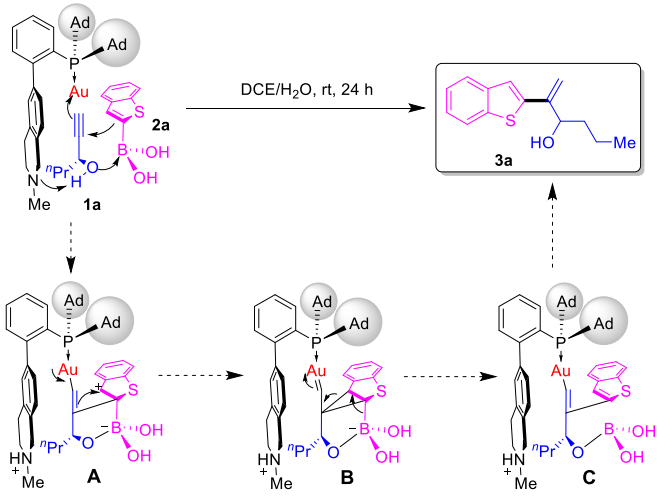



**Scheme 3.** Hydroarylation of electron-withdrawing propargylic alcohols.

otherwise noted, other chemicals obtained from commercial suppliers were used without further purification. Analytical thin layer chromatography was performed on Polygram SIL HSGF254 plates. Visualization was accomplished with short wave UV light or $KMnO_4$ staining. Melting points (m.p.) were determined by using a SRSOptiMelt automated melting point instrument without correction. Flash column chromatography was performed using silica gel (200–300 mesh). Mass spectrometry data were collected with a Bruker maXis/Q-TOF instrument for high-resolution or a Bruker amaZon SL instrument for low-resolution with both by using ESI ionization. The NMR spectra were recorded on Bruker AC 500 or 700 NMR spectrometer with TMS as an internal standard. The residual solvent peaks were used for the chemical shifts as an internal references (ppm): $^1H$ ($CDCl_3$: $\delta = 7.26$, DMSO-$d_6$: $\delta = 2.50$, MeOD: $\delta = 3.31$), $^{13}C$ ($CDCl_3$: $\delta = 77.0$, DMSO-$d_6$: $\delta = 39.5$, MeOD: $\delta = 49.0$). The data are reported as follows: chemical shift, multiplicity (s = singlet, d = doublet, t = triplet, q = quartet, and m = multiplet), integration, and coupling constant in Hz. The substrates of heteroareneboronic acids **1a**-d, **1f**-**j** and propargylic alcohols **2a**-**b**, **2g**-**k**, **2q** are commercial available. Compounds **2c** [15], **2e**-**f** [16], **2l**-**n** [16,17], **2o**-**p** [18] are known and were synthesized via the addition of ethynylmagnesium chloride to the corresponding aldehyde by following the last procedure for the synthesis of compound **2d**.




**Scheme 4.** Applications of this synthetic methodology.




**Scheme 5.** Proposed mechanism of the reaction.

## 4.2. Synthesis of substrate

### 4.2.1. Synthesis of compound **1e**

3-Methylbenzo[*b*]thiophene (1.0 equiv., 10 mmol, 1.5 g) was dissolved in anhydrous THF (15 mL) and stirred at −78 °C for about 10 min, and $^{n}$BuLi (1.2 equiv., 12 mmol, 5.0 mL) was added dropwise to the above solution. After 30 min, B($O^{i}$Pr)$_3$ (1.5 equiv., 15 mmol, 3.5 mL) was added dropwise and the reaction was slowly warmed up to room temperature. After continually stirred for about 3 h at this temperature, the reaction was quenched with saturated $NH_4Cl$ aqueous and further stirred for another 1 h. THF was removed and the residue was dissolved in AcOEt, and washed with $H_2O$. The organic layer was dried with $MgSO_4$ and removed. The crude product was recrystallized by using AcOEt/PE (1:1) to afford compound **1**e as white solid. M.p.: 136–138 °C. Yield: 68%. $^1$H NMR (700 MHz, MeOD) $\delta$ 7.83 (d, $J$ = 7.5 Hz, 1H), 7.76 (d, $J$ = 7.4 Hz, 1H), 7.35 (dtd, $J$ = 16.0, 7.2, 1.1 Hz, 2H), 2.52 (s, 3H). $^{13}$C NMR (176 MHz, MeOD) $\delta$ 143.59, 142.30, 140.13, 125.73, 124.74, 123.18, 123.14, 14.37. HRMS result was not available.

### 4.2.2. Synthesis of compound ***2d***

9-Bromononan-1-ol (1.0 equiv., 10 mmol, 2.22 g) and N-methylmethanesulfonamide (2.0 equiv., 20 mmol, 2.18 g) dissolved in DMF (15 mL) were heated with $K_2CO_3$ (2.0 equiv. 20 mmol, 2.76 g) at 60 °C till the completion of the reaction. DMF was removed under the reduced pressure, and the residue was dissolved in AcOEt and washed with water. The organic layer was dried with $MgSO_4$ and removed. The crude product was used directly in next step. The above crude product was dissolved in dichloromethane ($CH_2Cl_2$), and PCC (2.0 equiv. 20 mmol, 4.3 g) was added in portions at 0 °C. The reaction was then stirred at room temperature for about 4 h. After completion, $CH_2Cl_2$ was added and the reaction was washed with water. The organic layer was dried with $MgSO_4$ and removed. The residue was purified with silica gel column chromatography to afford the corresponding aldehyde as colorless oil. Yield: 54%, $^1$H NMR (700 MHz, $CDCl_3$) $\delta$ 9.75 (t, $J$ = 1.8 Hz, 1H), 3.11–3.09 (m, 2H), 2.82 (s, 3H), 2.77 (s, 3H), 2.41 (td, $J$ = 7.4, 1.8 Hz, 2H), 1.64–1.59 (m, 2H), 1.59–1.54 (m, 2H), 1.31 (s, 8H). $^{13}$C NMR (176 MHz, $CDCl_3$) $\delta$ 202.93, 49.90, 43.81, 35.24, 34.42, 29.16, 28.97, 28.90, 27.71, 26.28, 21.93. LRMS(ESI) (*m/z*): 250.1 $[M+H]^+$.

The aldehyde product was dissolved in anhydrous THF and stirred at −20 °C for about 10 min. Ethynylmagnesium chloride was added dropwise, and the reaction was stirred at this temperature for about 3 h. After completion, saturated $NH_4Cl$ aqueous was added, and the solvent was removed under the reduced pressure. The residue was dissolved in AcOEt and washed with water. The organic layer was dried with $MgSO_4$ and removed. The crude product was purified with silica gel column chromatograph to afford **2d** as a **s**light yellow solid, M.p.: 60–63 °C. Yield: 90%. $^1$H NMR (700 MHz, $CDCl_3$) $\delta$ 4.36 (t, $J$ = 6.5 Hz, 1H), 3.13–3.07 (m, 2H), 2.82 (s, 3H), 2.77 (s, 3H), 2.45 (d, $J$ = 2.1 Hz, 1H), 1.91 (s, 1H), 1.76–1.64 (m, 2H), 1.60–1.53 (m, 2H), 1.48–1.40 (m, 2H), 1.31 (s, 8H). $^{13}$C NMR (176 MHz, $CDCl_3$) $\delta$ 84.98, 72.76, 62.19, 49.92, 37.52, 35.27, 34.41, 29.25, 29.01, 28.96, 27.70, 26.32, 24.85. LRMS(ESI) (*m/z*): 276.2 $[M+H]^+$.

### 4.2.3. The syntheses of intermediates ***I*** *from cholic aldehyde [19] and* ***II*** *from ibuprofen aldehyde precursor [19] are similar to the last step of compound* ***2d***

Compound **I**: white solid, M.p.: 119–121 °C. Yield: 37%. $^1$H NMR (700 MHz, $CDCl_3$) $\delta$ 4.34–4.31 (m, 1H), 3.67–3.58 (m, 1H), 2.46 (d, $J$ = 2.1 Hz, 1H), 1.98–1.96 (m, 1H), 1.88–1.81 (m, 2H), 1.81–1.73 (m, 3H), 1.68–1.63 (m, 2H), 1.62–1.60 (m, 1H), 1.60–1.54 (m, 3H), 1.52–1.48 (m, 1H), 1.46–1.35 (m, 6H), 1.32 (dd, $J$ = 11.8, 2.4 Hz, 1H), 1.24–1.20 (m, 3H), 1.16–1.08 (m, 3H), 1.07–1.01 (m, 2H), 0.99–0.94 (m, 1H), 0.93 (d, $J$ = 1.0 Hz, 3H), 0.91 (s, 3H), 0.64 (s, 3H). $^{13}$C NMR (176 MHz, $CDCl_3$) $\delta$ 85.14 (85.02), 72.88 (72.72), 71.88, 62.82 (62.68), 56.48, 55.98, 42.68, 42.07, 40.41, 40.14, 36.42, 35.83, 35.37 (35.35), 35.32, 34.55, 34.30 (34.22), 31.08 (30.96), 30.52, 28.21, 27.17, 26.40, 24.19, 23.36, 20.80, 18.63 (18.59), 12.02. LRMS(ESI) (*m/z*): 387.3 $[M+H]^+$.

Compound **II**: colorless oil. Yield: 74%. $^1$H NMR (700 MHz, $CDCl_3$) $\delta$ 7.54–7.51 (m, 2H), 7.29 (d, $J$ = 8.1 Hz, 2H), 7.14 (d, $J$ = 8.1 Hz, 2H), 7.03–7.00 (m, 2H), 5.45 (d, $J$ = 1.9 Hz, 1H), 3.93 (q, $J$ = 7.1 Hz, 1H), 2.66 (d, $J$ = 2.2 Hz, 1H), 2.47 (d, $J$ = 7.2 Hz, 2H), 1.87 (dp, $J$ = 13.6, 6.8 Hz, 1H), 1.60 (d, $J$ = 7.2 Hz, 3H), 0.91 (s, 3H), 0.90 (s, 3H). $^{13}$C NMR (176 MHz, $CDCl_3$) $\delta$ 173.14, 150.94, 140.87, 137.44, 137.10, 129.52, 127.71, 127.18, 121.62, 83.19, 75.01, 63.87, 45.24, 45.03, 30.18, 22.38, 18.50. LRMS(ESI) (*m/z*): 337.2 $[M+H]^+$.

## 4.3. General procedure for the hydroarylation of propargylic alcohols with heteroareneboronic acids

In a 4 mL vial, heteroareneboronic acids (3.equiv., 0.9 mmol), propargylic alcohols (1.0 equiv., 0.3 mmol), and **L1**AuCl (0.025

equiv., 5.7 mg) were dissolved in DCE (0.84 mL), and NaBARF (0.025 equiv., 6.6 mg) and $H_2O$ (0.42 mL) were then added successively. The reaction was stirred at room temperature for 24 h. After completion, AcOEt (30 mL) was added and the reaction mixture was washed with water (10 mL × 3). The organic layer was dried with $MgSO_4$, removed, and the residue was purified with silica gel column chromatograph to afford the corresponding allylic alcohols.

The procedure for the synthesis compounds **3x**-**y** is mostly similar to the general procedure except that the reaction was heated at 40 °C for 10 h by using 8% **L1**AuCl (18.2 mg)/NaBARF (21.1 mg).

#### 4.3.1. 2-(benzo[b]thiophen-2-yl)hex-1-en-3-ol (*3a*)

Following the general procedure, compound **3a** was obtained as a slight yellow solid: M.p.: 54–56 °C. Yield: 79%. $^1$H NMR (700 MHz, $CDCl_3$) $\delta$ 7.78 (d, $J$ = 7.8 Hz, 1H), 7.72 (dd, $J$ = 7.1, 1.4 Hz, 1H), 7.36 (s, 1H), 7.34–7.28 (m, 2H), 5.59 (s, 1H), 5.43 (s, 1H), 4.76–4.55 (m, 1H), 1.86 (s, 1H), 1.81–1.74 (m, 1H), 1.73–1.64 (m, 1H), 1.56–1.49 (m, 1H), 1.47–1.38 (m, 1H), 0.94 (t, $J$ = 7.4 Hz, 3H). $^{13}$C NMR (176 MHz, $CDCl_3$) $\delta$ 145.36, 142.29, 140.13, 138.81, 124.63, 124.36, 123.61, 121.98, 120.75, 113.58, 73.69, 38.51, 19.08, 13.91. HRMS (ESI) $m/z$: $[M+Na]^+$ Calcd for $C_{14}H_{16}NaOS$ 255.0814; Found: 255.0819.

#### 4.3.2. 2-(benzo[b]thiophen-2-yl)-1-cyclohexylprop-2-en-1-ol (*3b*)

Following the general procedure, compound **3b** was obtained as a slight yellow solid. M.p.: 70–72 °C. Yield: 70%. $^1$H NMR (700 MHz, $CDCl_3$) $\delta$ 7.78 (d, $J$ = 7.8 Hz, 1H), 7.75–7.68 (m, 1H), 7.39 (s, 1H), 7.32 (dtd, $J$ = 16.3, 7.2, 1.3 Hz, 2H), 5.62 (s, 1H), 5.36 (s, 1H), 4.38 (d, $J$ = 6.6 Hz, 1H), 2.05–1.94 (m, 1H), 1.90 (s, 1H), 1.84–1.74 (m, 1H), 1.73–1.65 (m, 3H), 1.24–0.99 (m, 6H). $^{13}$C NMR (176 MHz, $CDCl_3$) $\delta$ 144.06, 142.39, 140.13, 138.87, 124.56, 124.32, 123.60, 121.96, 121.05, 115.07, 79.19, 41.78, 30.01, 27.97, 26.33, 26.14, 25.91. HRMS (ESI) $m/z$: $[M+Na]^+$ Calcd for $C_{17}H_{20}NaOS$ 295.1127; Found: 295.1123.

#### 4.3.3. The synthesis of 6-(benzo[b]thiophen-2-yl)hept-6-ene-1,5-diol (*3c*)

Following the general procedure, compound **3c** was obtained as a slight yellow solid. M.p.: 106–108 °C. Yield: 74%. $^1$H NMR (700 MHz, MeOD) $\delta$ 7.75 (d, $J$ = 7.4 Hz, 1H), 7.71 (d, $J$ = 7.7 Hz, 1H), 7.38 (s, 1H), 7.31–7.24 (m, 2H), 5.54 (s, 1H), 5.41 (s, 1H), 4.62 (dd, $J$ = 7.5, 4.9 Hz, 1H), 3.51 (t, $J$ = 6.3 Hz, 2H), 1.76 (dtt, $J$ = 14.4, 9.6, 5.0 Hz, 1H), 1.63 (ddd, $J$ = 13.8, 9.8, 7.8, 4.3 Hz, 1H), 1.57–1.48 (m, 3H), 1.48–1.39 (m, 1H). $^{13}$C NMR (176 MHz, MeOD) $\delta$ 147.31, 143.86, 141.69, 140.11, 125.71, 125.43, 124.66, 122.85, 121.82, 113.72, 74.17, 62.88, 37.49, 33.49, 23.32. HRMS (ESI) $m/z$: $[M+Na]^+$ Calcd for $C_{15}H_{18}NaO_2S$ 285.0920; Found: 285.0926.

#### 4.3.4. The synthesis of N-(10-(benzo[b]thiophen-2-yl)-9-hydroxyundec-10-en-1-yl)-N-methylmethanesulfonamide (*3d*)

Following the general procedure, compound **3d** was obtained as colorless oil. Yield: 67%. $^1$H NMR (700 MHz, $CDCl_3$) $\delta$ 7.77 (d, $J$ = 7.7 Hz, 1H), 7.71 (d, $J$ = 7.2 Hz, 1H), 7.35 (s, 1H), 7.33–7.27 (m, 2H), 5.57 (s, 1H), 5.42 (s, 1H), 4.66 (dd, $J$ = 7.6, 4.9 Hz, 1H), 3.08 (t, $J$ = 7.0, 2H), 2.81 (s, 3H), 2.76 (s, 3H), 1.98 (s, 1H), 1.78 (dtd, $J$ = 15.7, 10.5, 5.3 Hz, 1H), 1.72–1.60 (m, 1H), 1.54 (dd, $J$ = 13.8, 6.8 Hz, 2H), 1.48 (dtd, $J$ = 15.4, 10.6, 5.1 Hz, 1H), 1.42–1.35 (m, 1H), 1.28 (s, 8H). $^{13}$C NMR (176 MHz, $CDCl_3$) $\delta$ 145.31, 142.28, 140.11, 138.77, 124.60, 124.34, 123.58, 121.94, 120.72, 113.59, 73.83, 49.91, 36.29, 35.26, 34.38, 29.30, 29.23, 28.97, 27.68, 26.31, 25.69. HRMS (ESI) $m/z$: $[M+Na]^+$ Calcd for $C_{21}H_{31}NNaO_3S_2$ 432.1638; Found: 432.1641.

#### 4.3.5. The synthesis of 2-(benzo[b]thiophen-2-yl)-7-phenylhept-1-en-4-yn-3-ol (*3e*)

Following the general procedure, compound **3e** was obtained as a slight yellow solid. M.p.: 63–68 °C. Yield: 66%. $^1$H NMR (700 MHz, $CDCl_3$) $\delta$ 7.80–7.76 (m, 1H), 7.74–7.70 (m, 1H), 7.47 (s, 1H), 7.35–7.29 (m, 2H), 7.28–7.24 (m, 2H), 7.20 (t, $J$ = 6.5 Hz, 3H), 5.64 (s, 1H), 5.63 (s, 1H), 5.36 (d, $J$ = 4.7 Hz, 1H), 2.84 (t, $J$ = 7.5 Hz, 2H), 2.57 (td, $J$ = 7.5, 2.0 Hz, 2H), 2.16 (s, 1H). $^{13}$C NMR (176 MHz, $CDCl_3$) $\delta$ 141.47, 141.10, 140.35, 140.16, 138.87, 128.43, 128.36, 126.32, 124.80, 124.37, 123.84, 121.96, 121.81, 115.24, 87.15, 79.63, 64.36, 34.68, 20.93. HRMS (ESI) $m/z$: $[M+Na]^+$ Calcd for $C_{21}H_{18}NaOS$ 341.0971; Found: 341.0965.

#### 4.3.6. The synthesis of (E)-4-(benzo[b]thiophen-2-yl)-1-phenylpenta-1,4-dien-3-ol (*3f*)

Following the general procedure, compound **3f** was obtained as a slight yellow solid. M.p.: 53–55 °C. Yield: 59%. $^1$H NMR (700 MHz, $CDCl_3$) $\delta$ 7.78–7.75 (m, 1H), 7.71 (dd, $J$ = 6.4, 2.4 Hz, 1H), 7.43 (s, 1H), 7.40 (d, $J$ = 7.4 Hz, 2H), 7.34–7.28 (m, 4H), 7.25 (dd, $J$ = 11.5, 4.2 Hz, 1H), 6.79 (d, $J$ = 15.9 Hz, 1H), 6.42 (dd, $J$ = 15.9, 6.1 Hz, 1H), 5.70 (s, 1H), 5.56 (s, 1H), 5.35 (d, $J$ = 6.1 Hz, 1H), 2.12 (s, 1H). $^{13}$C NMR (176 MHz, $CDCl_3$) $\delta$ 143.60, 141.90, 140.12, 138.86, 136.35, 132.04, 129.66, 128.58, 127.93, 126.65, 124.76, 124.38, 123.76, 121.98, 121.46, 114.71, 74.17. HRMS (ESI) $m/z$: $[M+Na]^+$ Calcd for $C_{19}H_{16}NaOS$ 315.0814; Found: 315.0809.

#### 4.3.7. 2-(benzo[b]thiophen-2-yl)-1-phenylprop-2-en-1-ol (*3g*)

Following the general procedure, compound **3g** was obtained as a slight red solid. M.p.: 79–82 °C. Yield: 90%. $^1$H NMR (700 MHz, $CDCl_3$) $\delta$ 7.72–7.68 (m, 1H), 7.62–7.57 (m, 1H), 7.49–7.46 (m, 2H), 7.36–7.31 (m, 2H), 7.29–7.26 (m, 1H), 7.26–7.22 (m, 2H), 7.14 (s, 1H), 5.77 (s, 1H), 5.73 (s, 1H), 5.58 (d, $J$ = 1.1 Hz, 1H), 2.30 (s, 1H). $^{13}$C NMR (176 MHz, $CDCl_3$) $\delta$ 143.66, 141.94, 141.31, 140.03, 138.70, 128.65, 128.13, 126.98, 124.67, 124.28, 123.68, 121.91, 121.56, 115.15, 75.51. HRMS (ESI) $m/z$: $[M+Na]^+$ Calcd for $C_{17}H_{14}NaOS$ 289.0658; Found: 289.0660.

#### 4.3.8. 2-(benzo[b]thiophen-2-yl)-1-(4-fluorophenyl)prop-2-en-1-ol (*3h*)

Following the general procedure, compound **3h** was obtained as a slight yellow solid. M.p.: 86–88 °C. Yield: 79%. $^1$H NMR (700 MHz, $CDCl_3$) $\delta$ 7.76–7.69 (m, 1H), 7.67–7.59 (m, 1H), 7.50–7.44 (m, 2H), 7.30–7.27 (m, 2H), 7.14 (s, 1H), 7.08–7.01 (m, 2H), 5.79 (s, 1H), 5.75 (d, $J$ = 3.5 Hz, 1H), 5.60 (d, $J$ = 1.1 Hz, 1H), 2.25 (d, $J$ = 4.0 Hz, 1H). $^{13}$C NMR (176 MHz, $CDCl_3$) $\delta$ 162.49 (d, $J_{C\text{-}F}$ = 246.5 Hz), 143.67, 141.65, 139.95, 138.70, 137.04, 128.74 (d, $J_{C\text{-}F}$ = 8.1 Hz), 124.78, 124.37, 123.69, 121.93, 121.61, 115.51 (d, $J_{C\text{-}F}$ = 21.5 Hz), 115.19, 74.89. HRMS (ESI) $m/z$: $[M+Na]^+$ Calcd for $C_{17}H_{13}FNaOS$ 307.0563; Found: 307.0558.

#### 4.3.9. 2-(benzo[b]thiophen-2-yl)-1-(2-chlorophenyl)prop-2-en-1-ol (*3i*)

Following the general procedure, compound **3i** was obtained as colorless oil. Yield: 47%. $^1$H NMR (700 MHz, $CDCl_3$) $\delta$ 7.77–7.72 (m, 1H), 7.69–7.63 (m, 1H), 7.59–7.53 (m, 1H), 7.43–7.38 (m, 1H), 7.28 (dt, $J$ = 5.2, 3.3 Hz, 2H), 7.27–7.24 (m, 2H), 7.21 (s, 1H), 6.22 (s, 1H), 5.82 (s, 1H), 5.50 (d, $J$ = 1.1 Hz, 1H). $^{13}$C NMR (176 MHz, $CDCl_3$) $\delta$ 142.49, 142.26, 140.09, 138.70, 138.67, 133.52, 129.69, 129.45, 128.36, 127.26, 124.77, 124.35, 123.76, 121.94, 121.01, 115.45, 71.13. HRMS (ESI) $m/z$: $[M+Na]^+$ Calcd for $C_{17}H_{13}ClNaOS$ 323.0268; Found: 323.0263.

#### 4.3.10. 2-(benzo[b]thiophen-2-yl)-1-(3-bromophenyl)prop-2-en-1-ol (*3j*)

Following the general procedure, compound **3j** was obtained as a slight yellow solid. M.p.: 49–52 °C. Yield: 85%. $^1$H NMR (700 MHz, $CDCl_3$) $\delta$ 7.76–7.71 (m, 1H), 7.67 (t, $J$ = 1.6 Hz, 1H), 7.66–7.63 (m, 1H), 7.42 (td, $J$ = 6.9, 3.2 Hz, 2H), 7.31–7.27 (m, 2H), 7.22 (t, $J$ = 7.8 Hz,

1H), 7.18 (s, 1H), 5.80 (s, 1H), 5.72 (s, 1H), 5.57 (d, $J = 0.9$ Hz, 1H), 2.30 (s, 1H). $^{13}$C NMR (176 MHz, $CDCl_3$) $\delta$ 143.54, 143.24, 141.38, 139.95, 138.73, 131.15, 130.15, 129.93, 125.53, 124.83, 124.39, 123.76, 122.75, 121.94, 121.74, 115.80, 74.99. HRMS (ESI) *m/z*: $[M+Na]^+$ Calcd for $C_{17}H_{13}BrNaOS$ 366.9763; Found: 366.9748, 366.9753.

#### 4.3.11. 2-(benzo[b]thiophen-2-yl)-1-(2,4-difluorophenyl)prop-2-en-1-ol (**3k**)

Following the general procedure, compound **3k** was obtained as a slight red solid. M.p.: 80–82 °C. Yield: 75%. $^1$H NMR (700 MHz, $CDCl_3$) $\delta$ 7.76–7.72 (m, 1H), 7.68–7.64 (m, 1H), 7.49–7.44 (m, 1H), 7.31–7.27 (m, 2H), 7.19 (s, 1H), 6.88–6.80 (m, 2H), 6.08 (s, 1H), 5.81 (s, 1H), 5.60 (d, $J$ = 1.1 Hz, 1H), 2.43 (s, 1H). $^{13}$C NMR (176 MHz, $CDCl_3$) $\delta$ 162.33 (dd, $J_{C\text{-}F}$ = 392.8, 12.0 Hz), 160.92 (dd, $J_{C\text{-}F}$ = 392.1, 12.0 Hz), 142.60, 141.66, 140.00, 138.68, 129.42 (dd, $J_{C\text{-}F}$ = 9.4, 5.1 Hz), 124.86, 124.42, 123.76, 121.95, 120.99, 115.04, 111.65 (dd, $J_{C\text{-}F}$ = 21.2, 2.6 Hz), 103.93 (d, $J_{C\text{-}F}$ = 51.3 Hz), 103.92, 67.75 (d, $J_{C\text{-}F}$ = 2.0 Hz). HRMS (ESI) *m/z*: $[M+Na]^+$ Calcd for $C_{17}H_{12}F_2NaOS$ 325.0469; Found: 325.0463.

#### 4.3.12. 2-(benzo[b]thiophen-2-yl)-1-(2,3-dichlorophenyl)prop-2-en-1-ol (**3l**)

Following the general procedure, compound **3l** was obtained as colorless oil. Yield: 65%. $^1$H NMR (700 MHz, $CDCl_3$) $\delta$ 7.77–7.72 (m, 1H), 7.70–7.65 (m, 1H), 7.51 (dd, $J$ = 7.8, 1.5 Hz, 1H), 7.43 (dd, $J$ = 8.0, 1.5 Hz, 1H), 7.32–7.27 (m, 2H), 7.23–7.18 (m, 2H), 6.22 (s, 1H), 5.81 (s, 1H), 5.44 (d, $J$ = 1.1 Hz, 1H), 2.39 (s, 1H). $^{13}$C NMR (176 MHz, $CDCl_3$) $\delta$ 142.27, 142.07, 141.03, 140.02, 138.74, 133.31, 131.73, 130.15, 127.59, 126.49, 124.88, 124.44, 123.80, 121.97, 121.04, 115.77, 71.71. HRMS (ESI) *m/z*: $[M+Na]^+$ Calcd for $C_{17}H_{12}Cl_2NaOS$ 356.9878; Found: 356.9870.

#### 4.3.13. 2-(benzo[b]thiophen-2-yl)-1-(3,4,5-trimethoxyphenyl)prop-2-en-1-ol (**3m**)

Following the general procedure, compound **3m** was obtained as colorless oil. Yield: 70%. $^1$H NMR (700 MHz, $CDCl_3$) $\delta$ 7.74 (dd, $J$ = 5.1, 4.0 Hz, 1H), 7.66–7.61 (m, 1H), 7.31–7.26 (m, 2H), 7.18 (s, 1H), 6.72 (s, 2H), 5.79 (s, 1H), 5.68 (s, 1H), 5.59 (s, 1H), 3.84 (s, 6H), 3.83 (s, 3H). $^{13}$C NMR (176 MHz, $CDCl_3$) $\delta$ 153.36, 143.58, 141.85, 140.01, 138.74, 137.70, 136.85, 124.75, 124.37, 123.70, 121.94, 121.58, 115.40, 104.01, 75.64, 60.82, 56.11. HRMS (ESI) *m/z*: $[M+Na]^+$ Calcd for $C_{20}H_{20}NaO_4S$ 379.0975; Found: 379.0984.

#### 4.3.14. 2-(benzo[b]thiophen-2-yl)-1-(4-(trifluoromethyl)phenyl) prop-2-en-1-ol (**3n**)

Following the general procedure, compound **3n** was obtained as a slight yellow solid. M.p.: 125–129 °C. Yield: 90%. $^1$H NMR (700 MHz, $CDCl_3$) $\delta$ 7.75–7.72 (m, 1H), 7.66–7.59 (m, 5H), 7.31–7.27 (m, 2H), 7.19 (s, 1H), 5.81 (d, $J$ = 4.8 Hz, 2H), 5.56 (s, 1H), 2.34 (d, $J$ = 4.0 Hz, 1H). $^{13}$C NMR (176 MHz, $CDCl_3$) $\delta$ 145.11, 143.38, 141.22, 139.91, 138.74, 130.13 (q, $J_{C\text{-}F}$ = 32.4 Hz) 127.10, 125.53 (d, $J_{C\text{-}F}$ = 2.9 Hz), 124.93, 124.45, 124.04 (q, $J_{C\text{-}F}$ = 272.2 Hz), 123.78, 121.91 (d, $J_{C\text{-}F}$ = 15.9 Hz), 116.00, 75.21. HRMS (ESI) *m/z*: $[M+Na]^+$ Calcd for $C_{18}H_{13}F_3NaOS$ 357.0531; Found: 357.0526.

#### 4.3.15. 2-(5-fluorobenzo[b]thiophen-2-yl)hex-1-en-3-ol (**3o**)

Following the general procedure, compound **3o** was obtained as colorless oil. Yield: 57%. $^1$H NMR (700 MHz, $CDCl_3$) $\delta$ 7.68 (dd, $J$ = 8.7, 4.8 Hz, 1H), 7.37 (dd, $J$ = 9.4, 2.3 Hz, 1H), 7.31 (s, 1H), 7.06 (td, $J$ = 8.8, 2.4 Hz, 1H), 5.59 (s, 1H), 5.44 (s, 1H), 4.65 (dd, $J$ = 7.6, 5.0 Hz, 1H), 1.89 (s, 1H), 1.76 (dd, $J$ = 15.1, 10.6, 5.5 Hz, 1H), 1.72–1.63 (m, 1H), 1.57–1.46 (m, 1H), 1.47–1.36 (m, 1H), 0.94 (t, $J$ = 7.4 Hz, 3H). $^{13}$C NMR (176 MHz, $CDCl_3$) $\delta$ 160.86 (d, $J_{C\text{-}F}$ = 241.4 Hz), 145.17, 144.79, 141.06 (d, $J_{C\text{-}F}$ = 9.3 Hz), 134.21, 123.08 (d, $J_{C\text{-}F}$ = 9.2 Hz), 120.48 (d, $J_{C\text{-}F}$ = 3.8 Hz), 114.21, 113.36 (d, $J_{C\text{-}F}$ = 25.2 Hz), 109.01 (d, $J_{C\text{-}F}$ = 22.9 Hz), 73.74, 38.44, 19.06, 13.88. HRMS (ESI) *m/z*: $[M+Na]^+$ Calcd for $C_{14}H_{15}FNaOS$ 273.0720; Found: 273.0718.

#### 4.3.16. 2-(4-chlorobenzo[b]thiophen-2-yl)hex-1-en-3-ol (**3p**)

Following the general procedure, compound **3p** was obtained as colorless oil. Yield: 79%.$^1$H NMR (700 MHz, $CDCl_3$) $\delta$ 7.65 (d, $J$ = 8.0 Hz, 1H), 7.50 (s, 1H), 7.32 (d, $J$ = 7.6 Hz, 1H), 7.22 (t, $J$ = 7.8 Hz, 1H), 5.61 (s, 1H), 5.47 (s, 1H), 4.69 (s, 1H), 1.87 (s, 1H), 1.81–1.73 (m, 1H), 1.73–1.66 (m, 1H), 1.57–1.48 (m, 1H), 1.48–1.38 (m, 1H), 0.95 (t, $J$ = 7.4 Hz, 3H). $^{13}$C NMR (176 MHz, $CDCl_3$) $\delta$ 145.10, 143.34, 140.00, 138.30, 128.52, 125.20, 124.35, 120.47, 118.85, 114.45, 73.52, 38.45, 19.00, 13.88. HRMS (ESI) *m/z*: $[M+Na]^+$ Calcd for $C_{14}H_{15}ClNaOS$ 289.0424; Found: 289.0427.

#### 4.3.17. 2-(5-methylbenzo[b]thiophen-2-yl)hex-1-en-3-ol (**3q**)

Following the general procedure, compound **3q** was obtained as a slight yellow solid. M.p.: 72–74 °C. Yield: 79%. $^1$H NMR (700 MHz, $CDCl_3$) $\delta$ 7.66 (d, $J$ = 8.2 Hz, 1H), 7.52 (s, 1H), 7.29 (s, 1H), 7.15 (dd, $J$ = 8.1, 0.7 Hz, 1H), 5.58 (s, 1H), 5.42 (s, 1H), 4.68 (dd, $J$ = 7.2, 5.1 Hz, 1H), 2.46 (s, 3H), 1.86 (s, 1H), 1.78 (dd, $J$ = 14.9, 10.5, 5.7 Hz, 1H), 1.73–1.63 (m, 1H), 1.57–1.50 (m, 1H), 1.47–1.39 (m, 1H), 0.95 (t, $J$ = 7.4 Hz, 3H). $^{13}$C NMR (176 MHz, $CDCl_3$) $\delta$ 145.49, 142.41, 140.45, 135.96, 134.08, 126.38, 123.57, 121.61, 120.45, 113.26, 73.64, 38.53, 21.35, 19.08, 13.90. HRMS (ESI) *m/z*: $[M+Na]^+$ Calcd for $C_{15}H_{18}NaOS$ 269.0971; Found: 269.0972.

#### 4.3.18. 2-(3-methylbenzo[b]thiophen-2-yl)hex-1-en-3-ol (**3r**)

Following the general procedure, compound **3r** was obtained as colorless oil. Yield: 67%. $^1$H NMR (700 MHz, $CDCl_3$) $\delta$ 7.79 (d, $J$ = 7.9 Hz, 1H), 7.69 (d, $J$ = 8.0 Hz, 1H), 7.41–7.35 (m, 1H), 7.36–7.30 (m, 1H), 5.67 (t, $J$ = 1.3 Hz, 1H), 5.31 (d, $J$ = 1.1 Hz, 1H), 4.50 (dd, $J$ = 7.5, 4.8 Hz, 1H), 2.41 (s, 3H), 1.62–1.55 (m, 1H), 1.54–1.43 (m, 2H), 1.42–1.32 (m, 1H), 0.89 (t, $J$ = 7.3 Hz, 3H). $^{13}$C NMR (176 MHz, $CDCl_3$) $\delta$ 145.51, 140.43, 138.79, 135.79, 128.92, 124.34, 124.03, 122.08, 122.04, 117.23, 75.19, 37.88, 18.84, 13.85, 12.84. HRMS (ESI) *m/z*: $[M+Na]^+$ Calcd for $C_{15}H_{18}NaOS$ 269.0971; Found: 269.0983.

#### 4.3.19. 2-(6-(trifluoromethyl)benzo[b]thiophen-2-yl)hex-1-en-3-ol (**3s**)

Following the general procedure, compound **3s** was obtained as a slight yellow solid. M.p.: 85–87 °C. Yield: 74%. $^1$H NMR (700 MHz, $CDCl_3$) $\delta$ 8.05 (s, 1H), 7.80 (d, $J$ = 8.3 Hz, 1H), 7.55 (d, $J$ = 8.3 Hz, 1H), 7.43 (s, 1H), 5.64 (s, 1H), 5.49 (s, 1H), 4.71–4.64 (m, 1H), 1.84 (d, $J$ = 2.8 Hz, 1H), 1.76 (dd, $J$ = 15.5, 10.6, 5.5 Hz, 1H), 1.71–1.63 (m, 1H), 1.55–1.48 (m, 1H), 1.47–1.37 (m, 1H), 0.95 (t, $J$ = 7.4 Hz, 3H). $^{13}$C NMR (176 MHz, $CDCl_3$) $\delta$ 145.68, 144.92, 142.44, 138.55, 126.61 (q, $J_{C\text{-}F}$ = 32.4 Hz), 124.45 (d, $J_{C\text{-}F}$ = 272.0 Hz), 123.86, 121.12 (d, $J_{C\text{-}F}$ = 2.5 Hz), 120.44, 119.40 (d, $J_{C\text{-}F}$ = 3.9 Hz), 115.11, 73.82, 38.39, 19.05, 13.87. HRMS (ESI) *m/z*: $[M+Na]^+$ Calcd for $C_{15}H_{15}F_3NaOS$ 323.0688; Found: 323.0683.

#### 4.3.20. 2-(benzo[b]thiophen-3-yl)hex-1-en-3-ol (**3t**)

Following the general procedure, compound **3t** was obtained as colorless oil. Yield: 51%。 $^1$H NMR (700 MHz, $CDCl_3$) $\delta$ 7.88 (dd, $J$ = 8.1, 1.0 Hz, 2H), 7.41–7.34 (m, 3H), 5.63 (t, $J$ = 1.1 Hz, 1H), 5.36 (d, $J$ = 0.9 Hz, 1H), 4.57 (dd, $J$ = 7.4, 4.9 Hz, 1H), 1.60–1.51 (m, 1H), 1.51–1.42 (m, 2H), 1.39–1.30 (m, 1H), 0.86 (t, $J$ = 7.3 Hz, 3H). $^{13}$C NMR (176 MHz, $CDCl_3$) $\delta$ 146.25, 140.20, 138.60, 135.48, 124.35, 124.21, 123.05, 122.72, 114.91, 75.27, 38.05, 18.93, 13.87. HRMS (ESI) *m/z*: $[M+Na]^+$ Calcd for $C_{14}H_{16}NaOS$ 255.0814; Found: 255.0812.

#### 4.3.21. 2-(Benzofuran-2-yl)hex-1-en-3-ol (**3u**)

Following the general procedure, compound **3u** was obtained as colorless oil. Yield: 61%. $^1$H NMR (700 MHz, $CDCl_3$) $\delta$ 7.55 (d, $J$ = 7.7 Hz, 1H), 7.47 (dd, $J$ = 8.2, 0.6 Hz, 1H), 7.32–7.24 (m, 1H),

7.25–7.14 (m, 1H), 6.79 (s, 1H), 5.92 (s, 1H), 5.49 (s, 1H), 4.64 (dd, $J$ = 7.6, 5.1 Hz, 1H), 1.92 (s, 1H), 1.84–1.77 (m, 1H), 1.76–1.70 (m, 1H), 1.59–1.49 (m, 1H), 1.48–1.39 (m, 1H), 0.97 (t, $J$ = 7.4 Hz, 3H). $^{13}$C NMR (176 MHz, $CDCl_3$) $\delta$ 154.37, 154.24, 141.15, 128.69, 124.64, 122.80, 121.05, 112.35, 110.95, 103.31, 72.23, 38.89, 19.08, 13.89. HRMS (ESI) $m/z$: $[M+Na]^+$ Calcd for $C_{14}H_{16}NaO_2$ 239.1043; Found: 239.1041.

#### 4.3.22. 2-(5-Bromobenzofuran-2-yl)hex-1-en-3-ol (**3v**)

Following the general procedure, compound **3v** was obtained as a white solid. M.p.: 61–63 °C. Yield: 48%. $^1$H NMR (700 MHz, $CDCl_3$) $\delta$ 7.66 (d, $J$ = 1.9 Hz, 1H), 7.36 (dd, $J$ = 8.6, 1.9 Hz, 1H), 7.32 (d, $J$ = 8.6 Hz, 1H), 6.73 (s, 1H), 5.91 (s, 1H), 5.52 (s, 1H), 4.61 (dd, $J$ = 7.6, 5.1 Hz, 1H), 1.75 (d, $J$ = 5.4 Hz, 2H), 1.55–1.49 (m, 1H), 1.46–1.38 (m, 1H), 0.96 (t, $J$ = 7.4 Hz, 3H). $^{13}$C NMR (176 MHz, $CDCl_3$) $\delta$ 155.49, 153.13, 140.81, 130.73, 127.49, 123.65, 115.81, 113.40, 112.42, 102.76, 72.24, 38.85, 19.09, 13.90. HRMS (ESI) $m/z$: $[M+Na]^+$ Calcd for $C_{14}H_{15}BrNaO_2$ 317.0148; Found: 317.0146, 319.0147.

#### 4.3.23. 2-(Thiophen-2-yl)hex-1-en-3-ol (**3w**)

Following the general procedure, compound **3w** was obtained as colorless oil. Yield: 17%. $^1$H NMR (700 MHz, $CDCl_3$) $\delta$ 7.21 (d, $J$ = 5.1 Hz, 1H), 7.13 (d, $J$ = 3.6 Hz, 1H), 6.99 (dd, $J$ = 5.1, 3.7 Hz, 1H), 5.45 (s, 1H), 5.27 (s, 1H), 4.58 (dd, $J$ = 7.7, 4.8 Hz, 1H), 1.80 (s, 1H), 1.74–1.68 (m, 1H), 1.65–1.59 (m, 1H), 1.53–1.45 (m, 1H), 1.44–1.35 (m, 1H), 0.93 (t, $J$ = 7.4 Hz, 3H). $^{13}$C NMR (176 MHz, $CDCl_3$) $\delta$ 145.13, 142.21, 127.27, 124.52, 123.99, 111.25, 73.97, 38.43, 19.05, 13.89. HRMS (ESI) $m/z$: $[M+H]^+$ Calcd for $C_{10}H_{15}OS$ 183.0838; Found: 183.0839.

#### 4.3.24. (Z)-2-(benzo[b]thiophen-2-yl)-1-bromohex-1-en-3-ol (**3x**)

Following the revised general procedure, compound **3x** was obtained as colorless oil. Yield: 38%. $^1$H NMR (700 MHz, $CDCl_3$) $\delta$ 7.84 (d, $J$ = 7.7 Hz, 1H), 7.81 (d, $J$ = 7.1 Hz, 1H), 7.46 (s, 1H), 7.39–7.33 (m, 2H), 6.75 (d, $J$ = 0.8 Hz, 1H), 4.56–4.52 (m, 1H), 1.91 (s, 1H), 1.65–1.54 (m, 3H), 1.51–1.42 (m, 1H), 1.41–1.33 (m, 1H), 0.90 (t, $J$ = 7.4 Hz, 3H). $^{13}$C NMR (176 MHz, $CDCl_3$) $\delta$ 141.97, 140.05, 139.17, 137.01, 124.82, 124.67, 124.38, 123.79, 122.06, 108.16, 76.24, 37.88, 18.83, 13.76. HRMS (ESI) $m/z$: $[M+Na]^+$ Calcd for $C_{14}H_{15}BrNaOS$ 332.9919; Found: 332.9913, 334.9891.

#### 4.3.25. (Z)-2-(benzo[b]thiophen-2-yl)-1-iodohex-1-en-3-ol (**3y**)

Following the revised general procedure, compound **3y** was obtained as colorless oil. Yield: 44%. $^1$H NMR (700 MHz, $CDCl_3$) $\delta$ 7.84 (d, $J$ = 7.9 Hz, 1H), 7.82 (dd, $J$ = 7.1, 1.2 Hz, 1H), 7.41–7.33 (m, 3H), 6.93 (d, $J$ = 0.7 Hz, 1H), 4.53 (dd, $J$ = 7.1, 5.5 Hz, 1H), 1.64–1.50 (m, 2H), 1.49–1.41 (m, 1H), 1.40–1.32 (m, 1H), 0.90 (t, $J$ = 7.4 Hz, 3H). $^{13}$C NMR (176 MHz, $CDCl_3$) $\delta$ 148.71, 140.08, 139.78, 139.26, 124.61, 124.49, 124.39, 123.80, 122.16, 82.32, 77.05, 37.84, 18.75, 13.76. HRMS (ESI) $m/z$: $[M+Na]^+$ Calcd for $C_{14}H_{15}INaOS$ 380.9781; Found: 380.9779.

#### 4.3.26. Methyl (Z)-3-(benzo[b]thiophen-2-yl)-4-hydroxybut-2-enoate (**3z**)

Following the general procedure, compound **3z** was obtained as colorless oil. Yield: 50%. $^1$H NMR (700 MHz, $CDCl_3$) $\delta$ 7.82–7.79 (m, 1H), 7.78 (dd, $J$ = 6.6, 2.3 Hz, 1H), 7.45 (s, 1H), 7.37–7.32 (m, 2H), 6.33 (s, 1H), 4.52 (d, $J$ = 1.7 Hz, 2H), 3.70 (s, 3H). $^{13}$C NMR (176 MHz, $CDCl_3$) $\delta$ 166.33, 147.82, 140.19, 139.24, 136.67, 125.00, 124.77, 124.48, 124.05, 122.10, 117.50, 66.62, 51.64. HRMS (ESI) $m/z$: $[M+H]^+$ Calcd for $C_{13}H_{13}O_3S$ 249.0580; Found: 249.0581.

### 4.4. Diels-Alder reaction for the synthesis of (3aS,10cS,E)-5-butylidene-2-phenyl-3a,4,5,10c-tetrahydro-1H-benzo[4,5]thieno[3,2-e]isoindole-1,3(2H)-dione (**4a**)

In a 4 mL vial, compound **3a** (1.0 equiv., 0.13 mmol, 30 mg) and N-phenylmaleimide (2.0 equiv., 0.26 mmol, 45 mg) was heated at 80 °C in toluene for about 4 h. After completion, toluene was removed, and the residue was dissolved in AcOEt and washed with $H_2O$. The organic layer was dried with $MgSO_4$ and removed. The crude product was purified with silica gel column chromatograph to afford **4a** as a white solid. M.p.: 123–126 °C, yield: 65%. $^1$H NMR (700 MHz, $CDCl_3$) $\delta$ 8.22 (d, $J$ = 8.0 Hz, 1H), 7.74 (d, $J$ = 8.0 Hz, 1H), 7.39 (dt, $J$ = 7.0, 4.2 Hz, 3H), 7.35–7.31 (m, 2H), 7.23 (dd, $J$ = 8.5, 1.1 Hz, 2H), 6.02 (t, $J$ = 7.4 Hz, 1H), 4.59 (d, $J$ = 8.2 Hz, 1H), 3.66 (dd, $J$ = 8.1, 6.2, 4.6 Hz, 1H), 3.37 (dd, $J$ = 14.6, 4.5 Hz, 1H), 2.65 (dd, $J$ = 14.6, 5.4 Hz, 1H), 2.37–2.22 (m, 2H), 1.51 (dt, $J$ = 21.3, 6.8 Hz, 3H), 0.98 (t, $J$ = 7.4 Hz, 3H). $^{13}$C NMR (176 MHz, $CDCl_3$) $\delta$ 177.08, 174.28, 140.93, 138.94, 137.94, 131.70, 131.07, 128.98, 128.46, 126.25, 125.03, 124.51, 123.65, 122.22, 122.04, 41.65, 40.43, 30.14, 24.68, 22.64, 13.91. HRMS (ESI) $m/z$: $[M+H]^+$ Calcd for $C_{24}H_{22}NO_2S$ 388.1366; Found: 388.1368.

### 4.5. The synthesis of (3R,5R,8R,9S,10S,13R,14S,17R)-17-((2R)-6-(benzo[b]thiophen-2-yl)-5-hydroxyhept-6-en-2-yl)-10,13-dimethylhexadecahydro-1H-cyclopenta[a]phenanthren-3-ol (**4b**)

Following the general procedure, two diastereoisomers **4b-1** and **4b-2** with equal amount were obtained, total yield 84%.

Compound **4b-1**, M.p.: 80–82 °C. $^1$H NMR (700 MHz, $CDCl_3$) $\delta$ 7.77 (d, $J$ = 7.6 Hz, 1H), 7.72 (d, $J$ = 7.4 Hz, 1H), 7.36 (s, 1H), 7.34–7.29 (m, 2H), 5.58 (s, 1H), 5.41 (s, 1H), 4.63–4.57 (m, 1H), 3.64–3.57 (m, 1H), 1.92 (d, $J$ = 12.5 Hz, 1H), 1.89–1.80 (m, 2H), 1.77 (dd, $J$ = 14.4, 3.0 Hz, 2H), 1.75–1.70 (m, 1H), 1.65–1.59 (m, 2H), 1.59–1.53 (m, 1H), 1.53–1.47 (m, 2H), 1.41–1.33 (m, 6H), 1.29 (dd, $J$ = 18.8, 7.6 Hz, 1H), 1.26–1.16 (m, 4H), 1.08 (tdd, $J$ = 19.6, 13.0, 6.7 Hz, 4H), 1.04–0.97 (m, 2H), 0.95 (td, $J$ = 14.2, 3.3 Hz, 1H), 0.90 (s, 3H), 0.87 (d, $J$ = 6.6 Hz, 3H), 0.61 (s, 3H). $^{13}$C NMR (176 MHz, $CDCl_3$) $\delta$ 145.30, 142.28, 140.14, 138.85, 124.60, 124.34, 123.61, 121.98, 120.82, 113.84, 74.66, 71.88, 56.41, 55.99, 42.65, 42.07, 40.39, 40.11, 36.42, 35.81, 35.60, 35.31, 34.53, 32.84, 31.97, 30.52, 28.20, 27.17, 26.38, 24.17, 23.35, 20.78, 18.66, 12.00. HRMS (ESI) $m/z$: $[M+Na]^+$ Calcd for $C_{34}H_{48}NaO_2S$ 543.3267; Found: 543.3254.

Compound **4b-2**, M.p.: 84–86 °C. $^1$H NMR (700 MHz, $CDCl_3$) $\delta$ 7.79–7.76 (m, 1H), 7.73–7.70 (m, 1H), 7.34 (s, 1H), 7.31 (ddt, $J$ = 8.5, 7.2, 3.6 Hz, 2H), 5.58 (s, 1H), 5.42 (s, 1H), 4.62 (dd, $J$ = 7.6, 4.8 Hz, 1H), 3.66–3.56 (m, 1H), 1.93 (dt, $J$ = 12.6, 3.1 Hz, 1H), 1.87–1.79 (m, 2H), 1.79–1.71 (m, 4H), 1.70–1.64 (m, 2H), 1.56–1.53 (m, 1H), 1.50 (ddt, $J$ = 11.2, 5.4, 2.9 Hz, 2H), 1.42–1.33 (m, 6H), 1.31 (dd, $J$ = 11.8, 2.4 Hz, 1H), 1.29–1.17 (m, 5H), 1.09 (dd, $J$ = 14.5, 10.4, 6.3 Hz, 2H), 1.04–0.99 (m, 2H), 0.95 (td, $J$ = 14.2, 3.4 Hz, 1H), 0.90 (s, 3H), 0.88 (d, $J$ = 6.6 Hz, 3H), 0.62 (s, 3H). $^{13}$C NMR (176 MHz, $CDCl_3$) $\delta$ 145.48, 142.38, 140.12, 138.84, 124.59, 124.33, 123.60, 121.98, 120.69, 113.58, 74.24, 71.88, 56.44, 56.05, 42.66, 42.07, 40.39, 40.12, 36.42, 35.81, 35.53, 35.31, 34.54, 32.98, 31.96, 30.52, 28.28, 27.17, 26.40, 24.19, 23.35, 20.78, 18.61, 12.02. HRMS (ESI) $m/z$: $[M+Na]^+$ Calcd for $C_{34}H_{48}NaO_2S$ 543.3267; Found: 543.3258.

### 4.6. The synthesis of 4-(2-(benzo[b]thiophen-2-yl)-1-hydroxyallyl) phenyl 2-(4-isobutylphenyl)propanoate (**4c**)

Following the general procedure, compound **4c** was obtained as colorless oil. Yield: 74%。 $^1$H NMR (700 MHz, $CDCl_3$) $\delta$ 7.73–7.67 (m, 1H), 7.61–7.57 (m, 1H), 7.45 (d, $J$ = 8.6 Hz, 2H), 7.29–7.21 (m, 4H), 7.12 (d, $J$ = 8.0 Hz, 3H), 6.98 (d, $J$ = 8.6 Hz, 2H), 5.75 (s, 1H), 5.71 (s, 1H), 5.55 (s, 1H), 3.91 (q, $J$ = 7.1 Hz, 1H), 2.45 (d, $J$ = 7.2 Hz, 2H),

1.90–1.80 (m, 1H), 1.58 (d, $J = 7.2$ Hz, 3H), 0.90 (s, 3H), 0.89 (s, 3H). $^{13}$C NMR (176 MHz, $CDCl_3$) $\delta$ 173.14, 150.55, 143.54, 141.70, 140.82, 139.97, 138.78, 138.67, 137.10, 129.48, 127.98, 127.16, 124.71, 124.30, 123.72, 121.88, 121.62, 121.52, 115.32, 74.94, 45.22, 45.00, 30.15, 22.36, 18.43. HRMS (ESI) $m/z$: $[M+Na]^+$ Calcd for $C_{30}H_{30}NaO_3S$ 493.1808; Found: 493.1810.

## Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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## Appendix A. Supplementary data

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