Gold-catalysed allylic alkylation of aromatic and heteroaromatic compounds with allylic alcohols†

Weidong Rao and Philip Wai Hong Chan*

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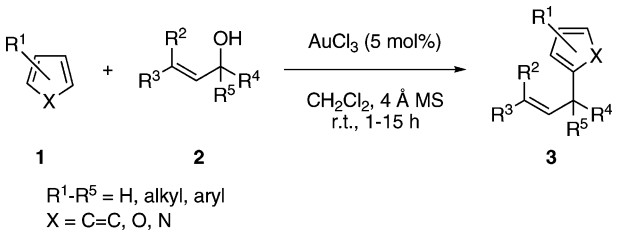
Friedel–Crafts allylic alkylation of a wide variety of aromatic and heteroaromatic compounds with allylic alcohols catalysed by $AuCl_3$ (5 mol%) under mild conditions at room temperature was accomplished in good to excellent yields (up to 99%) and regioselectivity.

Introduction

The Friedel–Crafts allylic alkylation of aromatic and heteroaromatic compounds is one of the most efficient and powerful carbon–carbon bond forming tools in organic synthesis.[1] Among the myriad of works devoted to this reaction, those on developing new methods that make use of inexpensive and readily available electrophiles, mild reaction conditions, simple manipulation, atom-economy[2] and environmentally-friendly catalysts have become very topical.[3–15] One such approach is the replacing of classical Friedel–Crafts allylating reagents such as allylic acetates, carbonates, and halides with allylic alcohols in the presence of a variety of transition metal and Brønsted acid catalysts.[4] Although shown to be efficient, producing H_2O as the only side product, a drawback of these methods is the use of strong acidic conditions and a large excess of the arene or heteroarene substrate to achieve moderate to good product regioselectivities. In the case of metal catalysts, there is also the need for high reaction-temperatures or introduction of a co-catalyst or additive. It therefore remains a challenge to develop a new catalytic system for this useful carbon–carbon bond forming reaction that exhibits outstanding activity in combination with high selectivity under mild conditions. In this context, we envisioned that gold salts would hold promise as a catalyst for developing a new approach for Friedel–Crafts allylic alkylations of aromatic and heteroaromatic compounds with allylic alcohols. A commercially available and robust reagent, this emerging class of Lewis acid catalysts have been shown to be versatile in mediating a wide variety of stereoselective C–X (X = C, N, O, S) bond formations in excellent yields under mild conditions.[16–20] Recently, Campagne and co-workers descibed an efficient gold-catalysed propargylation of allyl silanes with propargylic alcohols could be accomplished in good to excellent yields and selectivity.[17] Following this seminal work, the groups of Dyker[18] and Beller[19] reported similar gold-catalysed approaches for the propargylation and benzylation of aromatic and heteroaromatic compounds with propargylic and benzylic alcohols, respectively. To our knowledge, however, the analogous gold-catalysed allylic alkylation reactions of aromatic and heteroaromatic compounds with allylic alcohols are not known. As part of an ongoing program examining the utility of alcohols as building blocks in organic synthesis,[15] we report herein the allylic alkylation of a wide variety of aromatic and heteroaromatic compounds with allylic alcohols catalysed by gold(III) chloride (Scheme 1). The reactions were found to proceed in products yields up to 99% and with high regioselectivity under mild conditions at room temperature.



Scheme 1 Gold(III) chloride-catalysed allylic alkylation of aromatic and heteroaromatic compounds with allylic alcohols.

Results and discussion

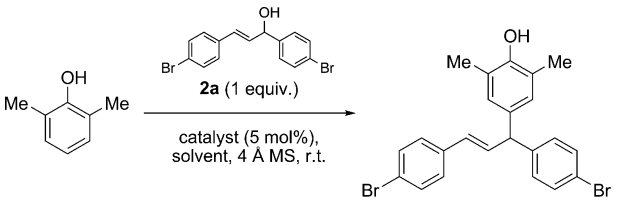
Initially, we chose to focus our attentions on the allylic alkylation of 2,6-dimethylphenol **1a** with (*E*)-1,3-bis(4-bromophenyl)prop-2-en-1-ol **2a** by a variety of Lewis and Brønsted acid catalysts to establish the reaction conditions (Table 1). This revealed a CH_2Cl_2 solution of **1a** (4 equiv.) and **2a** (1 equiv.) at room temperature treated with either 5 mol% of $AuCl_3$, $BF_3.Et_2O$, $InCl_3$, $NaAlCl_4$, $Cu(OTf)_2$, *p*-TsOH.H_2O, or TfOH as catalyst for 15 h gave the best result.[20] In each of these reactions, 4-{(*E*)-1,3-bis(4-bromophenyl)allyl}-2,6-dimethylphenol **3a** was furnished in 95–99% yield and as a single regioisomer based on ^{1}H NMR analysis (entries 1, 5–8 and 15–16). However, only $AuCl_3$ was found to maintain its catalytic activity for all the allylic alcohols studied in this work (see later). Reactions with other Lewis and Brønsted acid catalysts such as AuCl, $CuBr_2$, $ZnCl_2$, and HCl were found to proceed in slightly lower product yields of 81–90% (entries 2, 9–10, and 14). In contrast, markedly lower product yields of 5–48% were obtained when the reaction was repeated with either PPh_3AuCl, PPh_3AuOTf, AgOTf, $AgSbF_6$ or $Yb(OTf)_3$ as catalyst (entries 3–4 and 11–13). As anticipated, no reaction was observed in the absence of a catalyst and both starting materials were recovered in quantitative yields (entry 17).

Inspection of entries 18–21 in Table 1, a comparable product yield of 95% was found when the loading of **1a** was lowered from

Division of Chemistry and Biological Chemistry, School of Physical and Mathematical Sciences, Nanyang Technological University, Singapore, 637371, Singapore. E-mail: waihong@ntu.edu.sg

† Electronic supplementary information (ESI) available: Table S1, ^{1}H and ^{13}C NMR spectra for all compounds. See DOI: 10.1039/b805067h

Table 1 Optimisation of reaction conditions[a]



1a 3a

Entry	Catalyst	**1a** (equiv.)	Solvent	Yield (%)[b]
1	$AuCl_3$	4	CH_2Cl_2	99
2	AuCl	4	CH_2Cl_2	81
3	PPh_3AuCl	4	CH_2Cl_2	5
4	PPh_3AuOTf[c]	4	CH_2Cl_2	21
5	$BF_3.Et_2O$	4	CH_2Cl_2	95
6	$InCl_3$	4	CH_2Cl_2	95
7	$NaAlCl_4$	4	CH_2Cl_2	98
8	$Cu(OTf)_2$	4	CH_2Cl_2	99
9	$CuBr_2$	4	CH_2Cl_2	85
10	$ZnCl_2$	4	CH_2Cl_2	90
11	AgOTf	4	CH_2Cl_2	48
12	$AgSbF_6$	4	CH_2Cl_2	10
13	$Yb(OTf)_3$	4	CH_2Cl_2	23
14	HCl	4	CH_2Cl_2	85
15	TfOH	4	CH_2Cl_2	99
16	*p*-TsOH.H_2O	4	CH_2Cl_2	97
17	—[d]	4	CH_2Cl_2	—[e]
18	$AuCl_3$	2	CH_2Cl_2	95
19	$AuCl_3$	1.5	CH_2Cl_2	83
20	$AuCl_3$	1.2	CH_2Cl_2	72
21	$AuCl_3$	1	CH_2Cl_2	70
22	$AuCl_3$	2	C_6H_6	82
23	$AuCl_3$	2	THF	67
24	$AuCl_3$	2	CH_3CN	10

[a] All reactions were performed at r.t. for 15 h and 4 Å MS with a catalyst: **2a** ratio = 1 : 20. [b] Isolated yields. [c] Prepared *in situ* from reaction of PPh_3AuCl with AgOTf. [d] Reaction conducted in the absence of catalyst. [e] No reaction.

4 to 2 equiv. under the optimized $AuCl_3$-catalyzed conditions. On the other hand, a corresponding decrease in product yield was observed on gradually decreasing the loading of **1a** from 2 to 1 equiv. An examination of solvent effects also revealed a similar outcome with lower product yields of 67–82% afforded on changing the solvent from CH_2Cl_2 to either C_6H_6 or THF (entries 22–23). In contrast, repetition of the reaction with MeCN as solvent gave **3a** in a markedly low product yield of 10% (entry 24).

To define the scope of the $AuCl_3$-catalyzed allylic alkylation reactions, we applied this process to a series of substituted electron-rich aromatic and heteroaomatic compounds **1a–i** and allylic alcohols **2a–l**. The results are summarized in Tables 2–4.

As shown in Table 2, we first focused our attentions to examining the allylic alkylation of substituted aromatic compounds **1a–f** with allylic alcohols **2a–c** bearing electron-withdrawing and electron-donating groups. Under our optimised $AuCl_3$-catalysed conditions, we found the reactions of phenols **1a–b** with allylic alcohols **2a–c** to proceed in excellent yields of 91–97% (entries 1–4). The present procedure was also shown to work well for the allylic alkylations of aryl alkyl ethers **1c–e** with **2a**, which gave the corresponding allylated adducts **3f–h** in good to excellent yields (entries 5–7). On the other hand, steric effects of the aromatic compound may play a role since an *ortho*-substituted bulky group, such as a methyl group, provided **3i** in moderate yield (entry 8).

To further investigate the substrate scope of the present $AuCl_3$-catalyzed procedure, the allylic alkylation of **1a** and **1b** with allylic alcohols containing pendant H, alkyl and aryl combinations as in **2d–l** were examined (Table 3). In the presence of 5 mol% $AuCl_3$, allylated adducts **3j–l** were obtained in near quantitative yields from the respective allylic alkylations of **1a** and **1b** with **2d–f** (entries 1–3). When the less reactive 1° allylic alcohols **2g** and **2h** were employed as the allylating source, the respective allylated adducts **3m** and **3n** were afforded in 51 and 63% yield (entries 4–5). Although requiring a slightly higher temperature of 40 °C and longer reaction time of 15 h, the product yields obtained in these reactions are comparable to those previously reported.[21] We found the reaction of **1a** with terminal allylic alcohols **2i** and **2j** to also proceed smoothly and give **3o** and **3p** in yields of 80 and 96%, respectively (entries 6–7). Likewise, conformationally restricted allylic alcohols **2k** and **2l**, which contains an additional electrophilic carbonyl group, were shown to be good allylating reagents, affording **3q** and **3r** in 77 and 98% yield, respectively (entries 8–9). More notably, in the latter case, we found the combined use of **2l** with other Lewis and Brønsted acid catalysts to be less effective (see Table S1 in the ESI†). Lower product yields of 40–88% were obtained for the allylic alkylation of **1a** with **2l** in the presence of 5 mol% of $BF_3{\cdot}Et_2O$, *p*-TsOH, or TfOH as catalyst.[20] In all cases, no improvement in product yields was observed on increasing the catalyst loading to 15 mol%. In contrast, attempting the allylation with $Cu(OTf)_2$, $InCl_3$, $NaAlCl_4$, or $ZnCl_2$ as catalyst gave no reaction and recovery of both starting materials in near quantitative yields. These results differ significantly from our earlier findings for the allylic alkylation of **1a** with **2a** in the presence of the same Lewis and Brønsted acid catalysts, which gave product yields comparable to those catalysed by $AuCl_3$.

In this work, we have also examined the $AuCl_3$-catalysed allylic alkylations of heteroaromatic compounds (Table 4). By applying our optimized conditions, treatment of **1g** with **2a–c** in the presence of 5 mol% of $AuCl_3$ gave **3s–u** in excellent yields (entries 1–3). Under similar conditions, allylic alkylation of the *N*-methyl protected indole **1i** with **2a** was found to proceed well and furnish **3w** in 95% yield (entry 5). The reaction of **1h** was the only example where the use of 1 equiv. of the heteroarene substrate gave a low product yield of 30% and an excess (1 mL) was required to achieve **3v** in 67% yield (entry 4). The ability to access the allylated heteroaromatic adducts efficiently is noteworthy as this class of compounds are commonly used in organic synthesis as building blocks and a prevalent structural unit found in a myriad of bioactive natural and pharmaceutical compounds.[22]

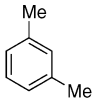
At this juncture, we would like to highlight the regioselective nature of the present reaction. Without exception, all the allylic alkylations described in Tables 2–4 were found to proceed with complete regioselectivity and give the allylated products as single isomers. Under our experimental conditions, allylic substitution of **1** with **2** was found to proceed solely at the *para*-position of the aromatic substrate. The *ortho*-allylated product was only afforded when the *para*-position of the arene substrate was substituted as in **1j** (Scheme 2). The present protocol was also shown to be regioselective for the allylation of hetereoaromatic substrates **1h–j** with carbon–carbon bond formation only occurring at the C-2 center of **1h–i** and at the C-3 center of **1j**.

Table 2 Gold(III) chloride-catalysed allylic alkylation of aromatic compounds **1a–f** with allylic alcohols **2a–c**[a]

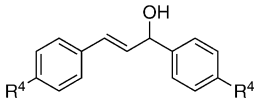
1b

1c, R = $CH_2CH{=}CH_2$
1d, R^1 = Me

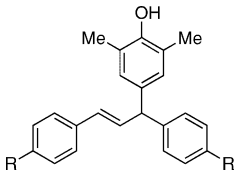
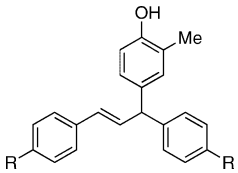
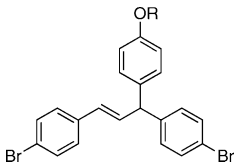
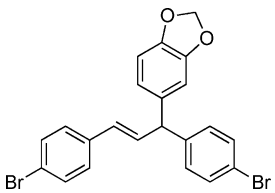
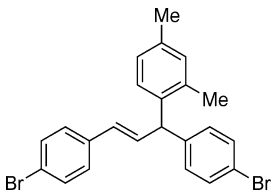
1e



1f



2a, R^4 = Br
2b, R^4 = Me
2c, R^4 = H

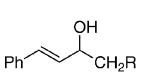
Entry	Substrates	Time/h	Product		Yield (%)[b]
1	**1a** + **2b**	1.5		**3b**, R = Me	91
2	**1a** + **2c**	1		**3c**, R = H	91
3	**1b** + **2a**	1		**3d**, R = Br	97
4	**1b** + **2b**	2		**3e**, R = Me	94
5	**1c** + **2a**	3		**3f**, R = $CH_2CH{=}CH_2$	91
6	**1d** + **2a**	1.5		**3g**, R = Me	93
7	**1e** + **2a**	2		**3h**	74
8	**1f** + **2a**	3		**3i**	50

[a] All reactions were performed in CH_2Cl_2 at r.t. with $AuCl_3$: **1**: **2** ratio = 1 : 80 : 20. [b] Isolated yields.

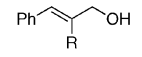
Moreover, the highly regioselective nature of the present procedure is further exemplified by carbon–carbon bond formation only occurring at the less sterically-hindered carbon centre of the allylic moiety in reactions with allylic alcohols containing two different substitutents as in **2d–l**. This is noteworthy as the use of such allylating reagents had been anticipated to lead to a mixture of regioisomeric products. In addition, our findings compare favourably with previous works, which reported that the analogous allylic alkylations with allylic alcohols using other Lewis and Brønsted acid catalysts gave moderate to good product regioselectivities.[21]

Although the above experimental results do not provide a clear perspective on the mechanism of the present procedure, we tentatively propose the reaction to proceed in a manner similar to that put forward by Campagne.[17] This could involve the hydroxyl group becoming a better leaving group through activation of the allylic alcohol by the gold catalyst. The regioselectivities obtained in these reactions may be due to subsequent attack at the

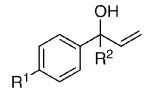
Table 3 Gold(III) chloride-catalysed allylic alkylation of aromatic compounds **1a–b** with allylic alcohols **2d–l**[a]



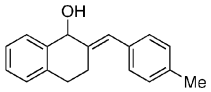
2d, R = H
2e, R = Bn
2f, R = CH=CH$_2$



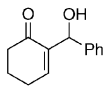
2g, R = H
2h, R = (CH$_2$)$_5$CH$_3$



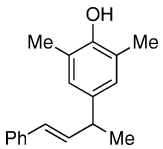
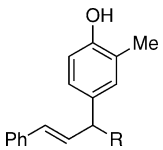
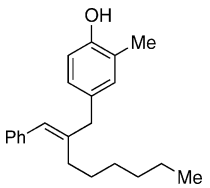
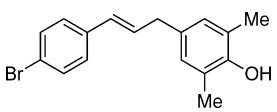
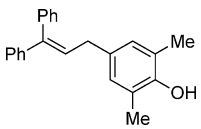
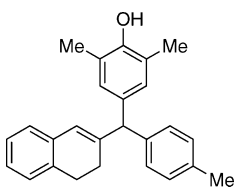
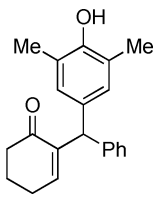
2i, R^1 = Br, R^2 = H
2j, R^1 = H, R^2 = Ph



2k

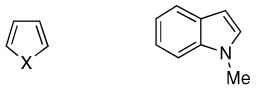


2l

Entry	Substrates	Time/h	Product		Yield (%)[b]
1	**1a** + **2d**	2		**3j**	97
2	**1b** + **2e**	2		**3k**, R = CH$_2$Bn	99
3	**1b** + **2f**	2		**3l**, R = CH$_2$CH=CH$_2$	98
4[c]	**1b** + **2g**	15		**3m**, R = H	51
5[c]	**1b** + **2h**	15		**3n**	63
6	**1a** + **2i**	1		**3o**	80
7	**1a** + **2j**	2		**3p**	96
8	**1a** + **2k**	1		**3q**	77
9	**1a** + **2l**	1.5		**3r**	98

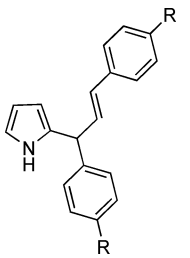
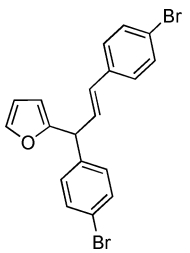
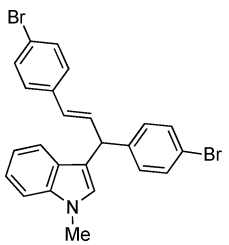
[a] All reactions were performed in CH$_2$Cl$_2$ at r.t. with AuCl$_3$: **1**: **2** ratio = 1 : 80 : 20. [b] Isolated yields. [c] Reaction conducted at 40 °C.

Table 4 Gold(III) chloride-catalysed allylation of heteroaromatic compounds **1g–i** with allylic alcohols **2a–c**[a]

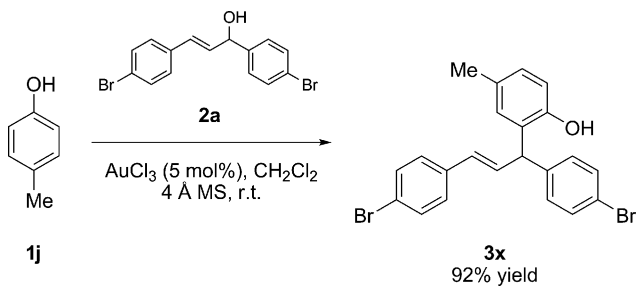


1g, X = NH
1h, X = O

1i

Entry	Substrates	Time/h	Product		Yield (%)[b]
1	**1g** + **2a**	2		**3s**, R = Br	97
2	**1g** + **2b**	1		**3t**, R = Me	93
3	**1g** + **2c**	1.5		**3u**, R = H	95
4[c]	**1h** + **2a**	4		**3v**	67
5	**1i** + **2a**	4		**3w**	95

[a] All reactions were performed in CH_2Cl_2 at r.t. with $AuCl_3$: **1**: **2** ratio = 1 : 80 : 20. [b] Isolated yields. [c] Reaction conducted with 1 mL of furan **1h**.



Scheme 2 Gold(III) chloride-catalysed allylic alkylation of **1j** with **2a**.

sterically less hindered carbon centre of this presumed activated intermediate.

Conclusions

In summary, we have demonstrated an efficient and regioselective gold-catalysed method for the allylic alkylation of aromatic and heteroaromatic compounds that proceeded in good to excellent yields at room temperature. The present protocol is applicable to a variety of electron-rich arenes and heteroarenes and allylic alcohols containing electron-withdrawing and electron-donating, and sterically demanding substrate combinations. While TfOH was found to exhibit comparable catalytic activity in mediating the allylation process, the milder conditions of gold catalysis provides an attractive alternative synthetic approach for this useful carbon–carbon bond forming reaction.

Experimental

General details

All reactions were performed under a nitrogen atmosphere at ambient temperature. Unless specified, all reagents and starting materials were purchased from commercial sources and used as received. Solvents were purified following standard literature procedures; CH_2Cl_2 was purified prior to use by passing through a PURESOLV(tm) Solvent Purification System. Analytical thin

layer chromatography (TLC) was performed using Merck 60 F254 pre-coated silica gel plate. Visualization was achieved by UV light (254 nm). Flash chromatography was performed using Merck silica gel 60 using a gradient solvent system (EtOAc–*n*-hexane as eluant). Unless otherwise stated, ^{1}H and ^{13}C NMR spectra were measured on Bruker Avance 400 MHz spectrometer. Chemical shifts (ppm) were recorded in $CDCl_3$ solution with tetramethylsilane (TMS) as the internal reference standard. Infrared spectra were recorded on Shimadzu IR Prestige-21 FTIR Spectrometer. Solid samples were examined as a thin film between NaCl salt plates. Low resolution mass spectra were determined on a Finnigan LCQ XP MAX mass spectrometer. High resolution mass spectra (HRMS) were obtained using a Finnigan MAT95XP LC/HRMS mass spectrometer.

General procedure for optimising the Lewis and Brønsted acid-catalysed allylic alkylation of 1a with 2a

To a round bottom flask containing **1a** (1–4 equiv.), **2a** (0.3 mmol) and 4 Å molecular sieves (50 mg) in 2 mL of solvent, was added 5 mol% of Lewis or Brønsted acid catalyst (please refer to Table 1) under a N_2 atmosphere. The mixture was stirred at room temperature and monitored by TLC analysis. On completion, the reaction mixture was filtered through Celite® and washed with CH_2Cl_2 (20 mL). The solvent was removed under reduced pressure and the residue was subjected to purification by flash column chromatography to give **3a** with the yields reported in Table 1.

General procedure for gold(III) chloride-catalysed allylic alkylation of aromatic and heteroaromatic compounds 1a–j

To a solution of CH_2Cl_2 (2 mL) containing **1** (1.2 mmol), **2** (0.3 mmol) and 4 Å molecular sieves (50 mg) under an N_2 atmosphere, was added $AuCl_3$ (5 mol%). The mixture was stirred at room temperature and monitored by TLC analysis. On completion, the reaction mixture was filtered through Celite® and washed with CH_2Cl_2 (20 mL). The solvent was removed under reduced pressure and the residue was subjected to purification by flash column chromatography to give the title compound **3**.

(*E*)-4-(1,3-Bis(4-bromophenyl)allyl)-2,6-dimethylphenol (3a). Yellow oil; yield: 99%; ^{1}H NMR δ 2.20 (s, 6H), 4.59 (s, 1H), 4.69 (d, 1H, J = 7.3 Hz), 6.22 (d, 1H, J = 15.8 Hz), 6.56 (dd, 1H, J = 15.8, 7.4 Hz), 6.78 (s, 2H), 7.07 (d, 2H, J = 8.3 Hz), 7.21 (d, 2H, J = 8.4 Hz), 7.39–7.42 (m, 4H); ^{13}C NMR δ 16.1, 52.9, 120.3, 121.1, 123.3, 127.9, 128.6, 130.2, 130.3, 131.6, 131.6, 133.3, 134.2, 136.1, 142.8, 151.0; IR (film, cm^{-1}) 3462, 1485, 1196, 1070, 1009; HRMS (EI) calcd. for $C_{23}H_{19}O^{79}Br_1^{81}Br_1$: 470.9777, found: 470.9795.

(*E*)-4-(1,3-Di-*p*-tolylallyl)-2,6-dimethylphenol (3b). Red–yellow oil; yield: 91%; ^{1}H NMR δ 2.24 (s, 6H), 2.36 (s, 6H), 4.56 (s, 1H), 4.75 (d, 1H, J = 7.5 Hz), 6.33 (d, 1H, J = 15.8 Hz), 6.62 (dd, 1H, J = 15.8, 7.6 Hz), 6.88 (s, 2H), 7.12–7.32 (m, 8H); ^{13}C NMR δ 16.0, 21.1, 21.2, 53.1, 123.0, 126.2, 128.5, 128.7, 129.1, 129.2, 130.6, 132.3, 134.7, 135.5, 135.8, 136.9, 141.2, 150.7; IR (film, cm^{-1}) 3429, 2918, 1589, 1510, 1488, 1198, 804; HRMS (EI) calcd. for $C_{24}H_{23}O$ (M^+ –CH_3): 327.1749, found: 327.1745.

(*E*)-4-(1,3-Diphenylallyl)-2,6-dimethylphenol (3c). Red–yellow oil; yield: 91%; ^{1}H NMR δ 2.20 (s, 6H), 4.53 (s, 1H), 4.76 (d, 1H, J = 7.5 Hz), 6.32 (d, 1H, J = 15.8 Hz), 6.64 (dd, 1H, J = 15.8, 7.6 Hz), 6.84 (s, 2H), 7.17–7.38 (m, 10H); ^{13}C NMR δ 16.1, 53.5, 123.0, 126.3, 126.4, 127.3, 128.5, 128.5, 128.6, 128.8, 131.0, 133.1, 135.2, 137.4, 144.1, 150.8; IR (film, cm^{-1}) 3464, 3026, 2918, 1580, 1481, 1198, 746, 700; HRMS (EI) calcd. for $C_{23}H_{22}O$: 314.1671, found: 314.1663.

(*E*)-4-(1,3-Bis(4-bromophenyl)allyl)-2-methylphenol (3d). Yellow oil; yield: 99%; ^{1}H NMR δ 2.20 (s, 3H), 4.72 (d, 1H, J = 7.3 Hz), 4.88 (s, 1H), 6.22 (d, 1H, J = 15.8 Hz), 6.56 (dd, 1H, J = 15.8, 7.4 Hz), 6.70 (d, 1H, J = 8.2 Hz), 6.87 (d, 1H, J = 8.2 Hz), 6.92 (s, 1H), 7.06–7.42 (m, 8H); ^{13}C NMR δ 15.9, 52.8, 115.1, 120.4, 121.2, 124.1, 127.1, 127.9, 130.4, 131.1, 131.6, 131.7, 133.2, 134.8, 136.1, 142.7, 152.6; IR (film, cm^{-1}) 3394, 2918, 1587, 1485, 1263, 1070, 1009, 818; HRMS (EI) calcd. for $C_{22}H_{18}OBr_2$: 455.9719, found: 455.9710.

(*E*)-4-(1,3-Di-*p*-tolylallyl)-2-methylphenol (3e). Red–yellow oil; yield: 94%; ^{1}H NMR δ 2.26 (s, 3H), 2.37 (s, 6H), 4.80 (d, 1H, J = 7.3 Hz), 4.81(s, 1H), 6.34 (d, 1H, J = 15.8 Hz), 6.63 (dd, 1H, J = 15.8, 7.5 Hz), 6.73 (d, 1H, J = 8.2 Hz), 6.96–7.33 (m, 10H); ^{13}C NMR δ 15.9, 21.1, 21.2, 53.1, 114.9, 123.8, 126.3, 127.2, 128.5, 129.2, 129.2, 130.8, 131.2, 132.3, 134.7, 135.9, 136.1, 137.0, 141.1, 152.3; IR (film, cm^{-1}) 3437, 2932, 1582, 1513, 1199, 801; HRMS (EI) calcd. for $C_{24}H_{24}O$: 328.1827, found: 328.1819.

(*E*)-4,4′-(3-(4-(Allyloxy)phenyl)prop-1-ene-1,3-diyl)bis(bromobenzene) (3f). Colorless oil; yield: 91%; ^{1}H NMR δ 4.51 (d, 2H, J = 5.2 Hz), 4.77 (d, 1H, J = 7.3 Hz), 5.28 (d, 1H, J = 10.5 Hz), 5.40 (d, 1H, J = 16.4 Hz), 6.00–6.09 (m, 1H), 6.22 (d, 1H, J = 15.8 Hz), 6.57 (dd, 1H, J = 15.8, 7.3 Hz), 6.87 (d, 2H, J = 8.6 Hz), 7.06–7.43 (m, 10H); ^{13}C NMR δ 52.7, 68.9, 114.9, 117.8, 120.4, 121.2, 127.9, 129.5, 130.4, 130.5, 131.6, 131.7, 133.1, 133.3, 134.8, 136.0, 142.5, 157.4; IR (film, cm^{-1}) 3026, 1587, 1506, 1485, 1400, 1242, 1177, 1070, 1008; HRMS (EI) calcd. for $C_{24}H_{20}OBr_2$: 481.9881, found: 481.9857.

(*E*)-4,4′-(3-(4-Methoxyphenyl)prop-1-ene-1,3-diyl)bis(bromobenzene) (3g). Yellow oil; yield: 93%; ^{1}H NMR ($CDCl_3$, 400 MHz) δ 3.80 (s, 3H), 4.80 (d, 2H, J = 7.2 Hz), 6.24 (d, 1H, J = 15.8 Hz), 6.59 (dd, 1H, J = 15.8, 7.3 Hz), 6.87 (d, 2H, J = 8.4 Hz), 7.08–7.13 (m, 4H), 7.23 (d, 2H, J = 8.1 Hz), 7.41–7.45 (m, 4H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 52.7, 55.3, 114.1, 120.4, 121.2, 127.9, 129.5, 130.4, 130.5, 131.6, 131.7, 133.1, 134.7, 136.0, 142.6, 158.4; IR (film, cm^{-1}) 1510, 1487, 1265, 1072, 1011, 743 cm^{-1}; HRMS (ESI) calcd. for $C_{22}H_{18}O^{79}Br_1^{81}Br_1Na$: 480.9602, found: 480.9923.

(*E*)-5-(1,3-Bis(4-bromophenyl)allyl)benzo[*d*][1,3]dioxole (3h). Colorless oil; yield: 74%; ^{1}H NMR δ 4.75 (d, 1H, J = 7.2 Hz), 5.94 (s, 2H), 6.25 (d, 1H, J = 15.8 Hz), 6.56 (dd, 1H, J = 15.8, 7.3 Hz), 6.67 (d, 2H, J = 6.1 Hz), 6.77 (d, 1H, J = 5.9 Hz), 7.08–7.45 (m, 8H); ^{13}C NMR δ 53.2, 101.1, 108.3, 109.0, 120.5, 121.3, 121.6, 127.9, 130.3, 130.6, 131.6, 131.7, 132.7, 135.9, 136.5, 142.3, 146.4, 147.9; IR (film, cm^{-1}) 2915, 1587, 1485, 1233, 1040, 1009; HRMS (EI) calcd. for $C_{22}H_{16}O_2Br_2$: 469.9517, found: 469.9518.

(*E*)-1-(1,3-Bis(4-bromophenyl)allyl)-2,4-dimethylbenzene (3i). Colorless oil; yield: 50%; ^{1}H NMR δ 2.21 (s, 3H), 2.31 (s, 3H), 4.96 (d, 1H, J = 6.6 Hz), 6.11 (d, 1H, J = 15.8 Hz), 6.59 (dd, 1H, J = 15.9, 6.7 Hz), 6.99–7.44 (m, 11H); ^{13}C NMR δ 19.6, 20.9, 49.5, 120.3, 121.1, 126.8, 127.8, 128.3, 130.4, 130.6, 131.5, 131.6, 133.0, 136.1, 136.4, 137.6, 141.7; IR (film, cm^{-1}) 1484, 1400, 1070,

1009, 820, 719; HRMS (EI) calcd. for $C_{23}H_{20}Br_2$: 453.9926, found: 453.9891.

(*E*)-2,6-Dimethyl-4-(4-phenylbut-3-en-2-yl)phenol (3j). Pale-yellow oil; yield: 97%; ^{1}H NMR δ 1.41 (d, 3H, J = 7.0 Hz), 2.23 (s, 6H), 3.48–3.54 (m, 1H), 4.49 (s, 1H), 6.32–6.41 (m, 2H), 6.87 (s, 2H), 7.16–7.36 (m, 5H); ^{13}C NMR δ 16.0, 21.4, 41.8, 123.0, 126.2, 127.0, 127.4, 128.0, 128.5, 135.8, 137.3, 137.7, 150.6; IR (film, cm^{-1}) 3425, 3029, 1487, 1000, 695; HRMS (EI) calcd. for $C_{18}H_{20}O$: 252.1514, found: 252.1515.

(*E*)-4-(1,5-Diphenylpent-1-en-3-yl)-2-methylphenol (3k). Red–yellow oil; yield: 99%; ^{1}H NMR δ 2.05–2.13 (m, 2H), 2.14 (s, 3H), 2.54–2.58 (m, 2H), 3.35 (m, 1H), 4.54 (s, 1H), 6.28–6.40 (m, 2H), 6.73 (d, 1H, J = 8.1 Hz), 6.95–6.99 (m, 2H), 7.16–7.35 (m, 10H); ^{13}C NMR δ 15.9, 33.8, 37.5, 47.8, 115.0, 123.8, 125.8, 126.2, 126.2, 127.1, 128.4, 128.5, 129.3, 130.3, 134.5, 136.4, 137.6, 142.3, 152.3; IR (film, cm^{-1}) 3395, 3026, 1510, 1449, 1263, 1115, 752, 698; HRMS (EI) calcd. for $C_{24}H_{24}O$: 328.1827, found: 328.1821.

(*E*)-2-Methyl-4-(1-phenylhexa-1,5-dien-3-yl)phenol (3l). Pale-yellow oil; yield: 98%; ^{1}H NMR δ 2.24 (s, 3H), 2.54 (t, 2H, J = 7.3 Hz), 3.39–3.46 (m, 1H), 4.58 (s, 1H), 4.97–5.07 (m, 2H), 5.69–5.94 (m, 1H), 6.32–6.35 (m, 2H), 6.72 (d, 1H, J = 8.1 Hz), 6.94–6.99 (m, 2H), 7.18–7.35 (m, 5H); ^{13}C NMR δ 15.9, 40.3, 48.1, 114.9, 116.2, 123.7, 126.2, 127.1, 128.5, 129.4, 130.3, 133.9, 136.1, 136.7, 152.2; IR (film, cm^{-1}) 3429, 2918, 1513, 1449, 1263, 1115, 965, 752; HRMS (EI) calcd. for $C_{19}H_{20}O$: 264.1514, found: 264.1508.

4-Cinnamyl-2-methylphenol (3m). Colorless oil; yield: 51%; ^{1}H NMR δ 2.23 (s, 3H), 3.45 (d, 2H, J = 6.6 Hz), 4.55 (s, 1H), 6.29–6.36 (m, 1H), 6.43 (d, 1H, J = 15.8 Hz), 6.71 (d, 1H, J = 8.1 Hz), 6.94–7.36 (m, 7H); ^{13}C NMR δ 15.8, 38.5, 114.9, 123.7, 126.1, 127.0, 127.2, 128.5, 129.8, 130.6, 131.3, 132.3, 137.6, 152.2; IR (film, cm^{-1}) 3368, 2967, 1597, 1495, 1263, 1206, 1111, 966; HRMS (EI) calcd. for $C_{16}H_{16}O$: 224.1201, found: 224.1198.

(*E*)-4-(2-Benzylideneoctyl)-2-methylphenol (3n). Colorless oil; yield: 63%; ^{1}H NMR δ 0.86 (t, 3H, J = 6.5 Hz), 1.20–1.29 (m, 6H), 1.43–1.49 (m, 2H), 2.15 (t, 2H, J = 8.1 Hz), 2.24 (s, 3H), 3.38 (s, 2H), 4.61 (s, 1H), 6.28 (s, 1H), 6.70 (d, 1H, J = 8.1 Hz), 6.94–7.32 (m, 7H); ^{13}C NMR δ 14.1, 15.8, 22.6, 28.2, 29.4, 30.2, 31.6, 43.1, 114.8, 123.5, 126.0, 126.7, 127.6, 128.1, 128.7, 131.7, 132.1, 138.5, 143.3, 152.1; IR (film, cm^{-1}) 3401, 2926, 2857, 1597, 1496, 1464, 1377, 1261, 1111, 698; HRMS (EI) calcd. for $C_{22}H_{28}O$: 308.2140, found: 308.2142.

(*E*)-4-(3-(4-Bromophenyl)allyl)-2,6-dimethylphenol (3o). Yellow oil; yield: 80%; ^{1}H NMR δ 2.22 (s, 6H), 3.39 (d, 2H, J = 5.3 Hz), 4.51 (s, 1H), 6.12–6.37 (m, 2H), 6.83 (s, 2H), 7.20–7.40 (m, 4H); ^{13}C NMR δ 15.9, 38.6, 120.7, 123.1, 127.7, 128.8, 129.3, 130.9, 131.3, 131.6, 136.5, 150.6; IR (film, cm^{-1}) 3433, 2918, 1485, 1263, 1196, 1146; HRMS (EI) calcd. for $C_{17}H_{17}OBr$: 316.0463, found: 316.0450.

4-(3,3-Diphenylallyl)-2,6-dimethylphenol (3p). Yellow oil; yield: 96%; ^{1}H NMR ($CDCl_3$, 300 MHz) δ 2.21(s, 6H), 3.33(d, 2H, J = 7.6 Hz), 4.50 (s, 1H), 6.23 (t, 3H, J = 7.6 Hz), 6.79 (s, 2H), 7.17–7.41 (m, 10H); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 16.0, 35.1, 123.1, 127.0, 127.1, 127.4, 128.0, 128.1, 128.3, 128.5, 130.0, 132.5, 140.0, 141.9, 142.6, 150.5; IR (film, cm^{-1}) 3443, 2912, 1488, 1257, 1183 cm^{-1}; HRMS (ESI) calcd. for $C_{23}H_{22}ONa$: 337.1568, found: 337.1594.

4-{(3,4-Dihydronaphthalen-2-yl)(*p*-tolyl)methyl}-2,6-dimethylphenol (3q). Yellow oil; yield: 77%; ^{1}H NMR δ 2.22 (s, 6H), 2.27 (t, 2H, J = 8.1 Hz), 2.36 (s, 3H), 2.82 (t, 2H, J = 8.2 Hz), 4.54 (s, 1H), 4.74 (s, 1H), 5.97 (d, 1H, J = 0.7 Hz), 6.85 (s, 2H), 6.94 (d, 1H, J = 6.1 Hz), 7.10–7.15 (m, 7H); ^{13}C NMR δ 16.1, 21.1, 28.0, 28.5, 57.5, 122.7, 125.2, 126.0, 126.4, 126.5, 127.2, 129.0, 129.2, 129.4, 133.8, 134.7, 134.8, 135.8, 139.6, 144.5, 150.7; IR (film, cm^{-1}) 3464, 2918, 1511, 1480, 1325, 1195, 752; HRMS (EI) calcd. for $C_{26}H_{26}O$: 354.1984, found: 354.1982.

2-({4-Hydroxy-3,5-dimethylphenyl}(phenyl)methyl)cyclohex-2-enone (3r). White solid; yield: 98%; m.p. 174–176 °C; ^{1}H NMR ($CDCl_3$, 400 MHz) δ 1.98–2.04 (m, 2H), 2.17 (s, 6H), 2.37–2.47 (m, 4H), 4.60 (s, 1H), 5.36 (s, 1H), 6.41 (t, 1H, J = 4.0 Hz), 6.68 (s, 2H), 7.07–7.27 (m, 5H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 16.1, 22.9, 26.2, 38.7, 48.6, 122.8, 126.1, 128.2, 129.0, 129.1, 133.8, 142.8, 143.1, 147.8, 150.7, 198.2; IR (film, cm^{-1}) 1670, 1489, 1263, 908, 738 cm^{-1}; HRMS (ESI) calcd. for $C_{21}H_{22}O_2Na$: 329.1517, found: 329.1977.

(*E*)-2-(1,3-Bis(4-bromophenyl)allyl)-1*H*-pyrrole (3s). Colorless oil; yield: 97%; ^{1}H NMR δ 4.80 (d, 1H, J = 7.4 Hz), 5.94 (s, 1H), 6.16 (dd, 1H, J = 5.4, 2.6 Hz), 6.31 (d, 1H, J = 15.8 Hz), 6.51 (dd, 1H, J = 15.8, 7.5 Hz), 6.71 (s, 1H), 7.10–7.46 (m, 8H), 7.83 (bs, 1H); ^{13}C NMR δ 47.5, 107.1, 108.6, 117.7, 120.9, 121.4, 128.0, 130.2, 130.5, 131.3, 131.7, 131.9, 132.1, 135.8, 140.9; IR (film, cm^{-1}) 3442, 1484, 1400, 1070, 1009, 820, 719; HRMS (EI) calcd. for $C_{19}H_{15}NBr_2$: 414.9571, found: 414.9555.

(*E*)-2-(1,3-Di-*p*-tolylallyl)-1*H*-pyrrole (3t). Colorless oil; yield: 93%; ^{1}H NMR δ 2.37 (s, 3H), 2.39 (s, 3H), 4.85 (d, 1H, J = 7.5 Hz), 6.00 (s, 1H), 6.21 (dd, 1H, J = 5.6, 2.7 Hz), 6.43 (d, 1H, J = 15.8 Hz), 6.57 (dd, 1H, J = 15.7, 7.5 Hz), 6.73 (d, 1H, J = 1.4 Hz), 7.14–7.32 (m, 8H), 7.87 (bs, 1H); ^{13}C NMR δ 21.1, 21.2, 47.8, 106.6, 108.4, 117.1, 126.3, 128.4, 129.3, 129.4, 130.4, 131.0, 133.5, 134.4, 136.5, 137.2, 139.3; IR (film, cm^{-1}) 3429, 3395, 3026, 2918, 1510, 1028, 966, 718; HRMS (EI) calcd. for $C_{21}H_{21}N$: 287.1674, found: 287.1675.

(*E*)-2-(1,3-Diphenylallyl)-1*H*-pyrrole (3u). Colorless oil; yield: 95%; ^{1}H NMR δ 4.86 (d, 1H, J = 7.6 Hz), 5.97 (s, 1H), 6.17 (dd, 1H, J = 5.7, 2.8 Hz), 6.42 (d, 1H, J = 15.8 Hz), 6.59 (dd, 1H, J = 15.8, 7.6 Hz), 6.70 (d, 1H, J = 1.4 Hz), 7.19–7.37 (m, 10H), 7.85 (bs, 1H); ^{13}C NMR δ 48.2, 106.8, 108.5, 117.3, 126.4, 127.0, 127.5, 128.5, 128.6, 128.8, 131.1, 131.3, 133.1, 137.1, 142.2; IR (film, cm^{-1}) 3429, 3026, 1487, 1449, 966, 698; HRMS (EI) calcd. for $C_{19}H_{17}N$: 259.1361, found: 259.1355.

(*E*)-2-(1,3-Bis(4-bromophenyl)allyl)furan (3v). Colorless oil; yield: 67%; ^{1}H NMR δ 4.84 (d, 1H, J = 7.2 Hz), 6.08 (d, 1H, J = 0.6 Hz), 6.29–6.34 (m, 2H), 6.51 (dd, 1H, J = 15.8, 7.2 Hz), 7.11–7.47 (m, 9H); ^{13}C NMR δ 47.7, 107.1, 110.3, 121.0, 121,4, 127.9, 129.9, 130.0, 130.9, 131.7, 131.8, 135.7, 139.8, 142.1, 1, 155.1; IR (film, cm^{-1}) 1583, 1481, 1400, 1075, 1005, 735; HRMS (EI) calcd. for $C_{19}H_{14}OBr_2$: 415.9411, found: 415.9411.

(*E*)-3-(1,3-Bis(4-bromophenyl)allyl)-1-methyl-1*H*-indole (3w). Yellow oil; yield: 95%; ^{1}H NMR δ 3.74 (s, 3H), 5.05 (d, 2H, J = 7.2 Hz), 6.33 (d, 1H, J = 15.8 Hz), 6.65 (dd, 1H, J = 15.6, 7.2 Hz), 6.73 (s, 1H), 7.00–7.43 (m, 12H); ^{13}CNMR δ 32.8, 45.6, 109.4, 116.2, 119.1, 119.7, 120.3, 121.0, 121.9, 126.9, 127.4, 127.9, 129.7, 130.3, 131.5, 131.6, 132.9, 136.2, 137.4, 142.3; IR (film, cm^{-1})

1587, 1485, 1009; HRMS (EI) calcd. for $C_{24}H_{19}NBr_2$: 478.9884, found: 478.9872.

(*E*)-2-(1,3-Bis(4-bromophenyl)allyl)-4-methylphenol (3x). Colorless oil; yield: 92%; ^{1}H NMR δ 2.22 (s, 3H), 4.69 (s, 1H), 4.73 (d, 1H, J = 7.2 Hz), 6.23 (d, 1H, J = 15.8 Hz), 6.57 (dd, 1H, J = 15.8, 7.2 Hz), 6.72 (d, 1H, J = 7.2 Hz), 6.89 (d, 1H, J = 7.3 Hz), 6.93 (s, 1H), 7.08 (d, 2H, J = 8.2 Hz), 7.21–7.43 (m, 6H); ^{13}C NMR δ 20.7, 47.6, 115.1, 116.0, 120.6, 121.3, 127.9, 128.6, 128.7, 130.1, 130.4, 130.8, 131.6, 131.7, 131.9, 135.9, 141.3, 150.9; IR (film, cm^{-1}) 3366, 3024, 1494, 1487, 1008; HRMS (EI) calcd. for $C_{22}H_{18}O^{79}Br_1{}^{81}Br_1$: 457.9698, found: 457.9696.

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