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Synthesis of α-Hydroxyallenes by Copper-Catalyzed S_N2' Substitution of Propargylic Dioxolanones

Xiaoping Tang,[a] Simon Woodward,*[a] and Norbert Krause*[b]

Keywords: Allenes / Copper / Homogeneous catalysis / Nucleophilic substitution / Grignard reaction

A new catalytic method for the synthesis of α-hydroxyallenes is described. Efficient S_N2' substitution of propargylic dioxolanones has been achieved with a copper(I)/$P(OBu)_3$ catalyst using Grignard reagents as the nucleophiles. The reaction tolerates a wide variety of propargylic dioxolanones, the corresponding primary and secondary α-hydroxyallenes are obtained in good to excellent yields and excellent diastereoselectivity.

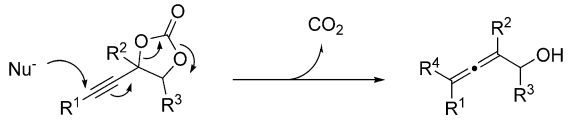
Introduction

Allenes are highly valuable synthetic precursors in organic chemistry. Their unique structure is an essential prerequisite for the synthesis of many structurally interesting and biologically active compounds.[1] Over the past 30 years, the use of organometallic reagents for the synthesis of allenes has been highly developed.[2] In particular, the metal-mediated S_N2' nucleophilic substitution of propargylic electrophiles proved to be one of the most general methods for the preparation of various allenes. The electrophilic propargylic moiety can bear an epoxide,[3] an ether,[4] a halide,[5] an acetate,[6] an acetal,[7] or a sulfonate,[8,9] as the leaving group, the complimentary organometallic nucleophile can either be an organocopper,[10] a Grignard reagent,[11] an organozinc[12] or an organoboronate[13] derivative (Scheme 1).

Scheme 1. S_N2' nucleophile substitution of propargylic electrophiles.

A large number of methods have been developed for the synthesis of allenes. α-Hydroxyallenes are typically obtained from the corresponding propargylic epoxide,[3,12,14] but few other complimentary approaches have been reported.[15] α-Hydroxyallenes are valuable synthetic intermediates in organic synthesis, which readily undergo further transformations often with good to complete transfer of the allenic chirality.[16] Recently, gold-catalyzed cycloisomerization of α-hydroxyallenes and α-allenic ketones has been developed.[17] In connection with this chemistry it is beneficial to develop new and versatile methods for the synthesis of α-hydroxyallenes.

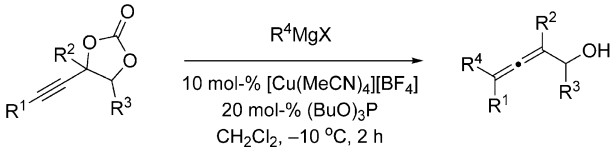
Propargylic dioxolanones are very promising alternatives to propargylic epoxides in the synthesis of α-hydroxyallene for three reasons: i) under a S_N2' pathways, the release of CO_2 is expected to facilitate the formation of the α-hydroxyallene (Scheme 2); ii) dioxolanones can be easily prepared from an enyne via a dihydroxylation and lactonization sequence; iii) asymmetric dihydroxylation[18] can be used to prepare the diol precursor, which can provide a route for the synthesis of enantiomerically enriched α-hydroxyallenes.



Scheme 2. Formation of α-hydroxyallenes from propargylic dioxolanones.

Herein, we report an efficient copper-catalyzed S_N2' substitution of propargylic dioxolanones for the synthesis of α-hydroxyallenes (Scheme 3). The inexpensive and readily available copper salt $[Cu(MeCN)_4][BF_4]$[19] together with tributyl phosphite are used as the catalyst, while a Grignard reagent acts as the nucleophile. A range of primary and secondary α-hydroxyallenes has been synthesized in good to excellent yields and excellent diastereoselectivity.

[a] School of Chemistry, The University of Nottingham, University Park, Nottingham, NG7 2RD, UK
Fax: +44-115-951-3564
E-mail: simon.woodward@nottingham.ac.uk
[b] Organic Chemistry, Dortmund University of Technology, Otto-Hahn-Straβe 6, 44227 Dortmund, Germany
Fax: +49-231-755-3884
E-mail: norbert.krause@tu-dortmund.de
Supporting information for this article is available on the WWW under http://www.eurjoc.org/ or from the author.

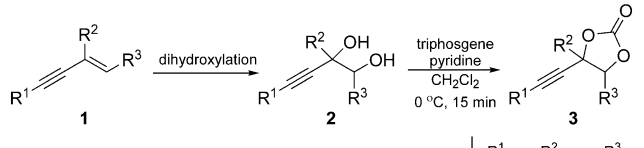


Scheme 3. Copper-catalyzed S_N2' substitution of propargylic dioxolanones.

Results and Discussion

Synthesis of Propargylic Dioxolanones

Propargylic dioxolanones **3** were easily prepared from enynes **1** in two steps. The latter are either commercially available or easily obtained by Sonogashira coupling between a terminal alkyne and a vinyl halide or other methods.[20] The diol intermediates **2** were prepared in good yields by subsequent dihydroxylation of enynes **1**. Several conditions are compatible in this step. The Sharpless asymmetric dihydroxylation[21] was applied for the synthesis of enantiomerically enriched diols, or quinuclidine can be used as ligand for osmium in racemic approaches. Ruthenium-catalyzed dihydroxylation also provided efficient access to diols when aromatic enynes are involved.[22] The diols **2** when treated with triphosgene in the presence of pyridine allow convenient installation of the carbonyl group. These reactions all proceeded efficiently and gave the propargylic dioxolanones in good yields (Scheme 4).

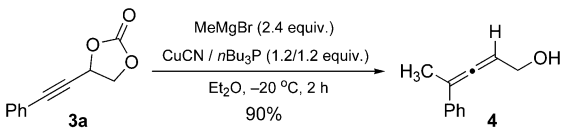


	R1	R2	R3
1a/2a/3a	Ph	H	H
1b/2b/3b	Ph	H	Me
1c/2c/3c	Me	-(CH2)4-	
1d/2d/3d	Et	Me	H
1e/2e/3e	H	Me	H

Scheme 4. Synthesis of propargylic dioxolanones.

Studies on the S_N2' Substitution of Propargylic Dioxolanones

To show the viability of propargylic dioxolanones **3** for the formation of α-hydroxyallenes the S_N2' reaction was first carried out following a literature procedure,[1c] using a *stoichiometric* amount of cuprate (Scheme 5). Satisfyingly, the corresponding allene **4** was isolated in 90% yield.



Scheme 5. S_N2' substitution of **3a** with stoichiometric cuprate.

Initial studies towards developing an efficient copper-catalyzed S_N2' substitution of **3** showed that several possible byproducts can be formed in the catalytic reaction (Figure 1). The S_N2 product was observed together with the desired S_N2' adduct. Diol **2** was also obtained as a byproduct, formed by nucleophilic attack at the carbonyl group. Moreover, a small amount of enyne **1** was observed as well due to an electron transfer reaction.

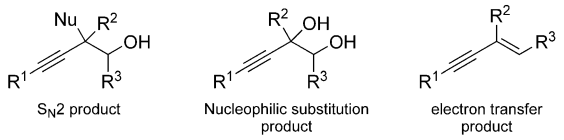
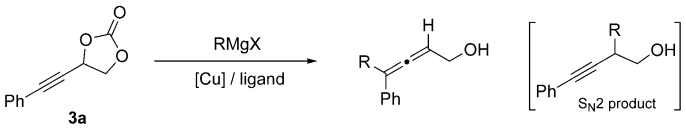


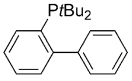
Figure 1. Byproducts of the S_N2' substitution of propargylic dioxolanones.

Fortunately, all of these back-ground reactions were suppressed after optimizing the reaction conditions. Selected results are shown in Table 1. Propargylic dioxolanone **3a** was chosen as a model substrate for system optimization while RMgX (R = Me, Et, *i*Pr) were used as the nucleophiles.

A number of copper salts were tested (9 examples), of which a selection is shown (Entries 1–6). The reactivity of the catalyst varied with the copper source. Both $CuBr{\cdot}SMe_2$ (Entry 4) and $Cu(OTf)_2$ (Entry 5) gave very low conversion. Surprisingly, CuCN (Entry 1), which was used in the stoichiometric trial reaction (Scheme 5), showed only moderate activity. Among all the copper salts tested, $[Cu(MeCN)_4][BF_4]$ showed superior reactivity and provided >99% conversion in only 2 h. The salt $[Cu(MeCN)_4][BF_4]$ is attractive as it is readily available, easy to handle and air stable.[19] Further studies also revealed that the reaction is ligand accelerated, the reactivity of the catalyst decreased significantly in the absence of a P-ligand (Entry 2 vs. Entry 3). Therefore, a range of phosphorus ligands were tested in the reaction (17 examples). The results showed that the ligand choice has a dramatic influence on the chemoselectivity of the reaction (Entries 6–11). When JohnPhos [2-(di-*tert*-butylphosphanyl)biphenyl] was used as ligand (Entry 9), only 12% of the desired S_N2' product was obtained, but 61% of the enyne byproduct formed by electron transfer. The initially used ligand $P(n\text{Bu})_3$ gave the desired substitution product together with 27% of diol byproduct (Entry 6). The other phosphane ligand PCy_3 (Entry 8) showed similar chemoselectivity as $P(n\text{Bu})_3$. However, phosphite ligands (Entries 10–11) gave excellent chemoselectivity, only the S_N2'/S_N2 products were observed. Moreover, $P(OBu)_3$ (Entry 11) gave the best regioselectivity between S_N2' and S_N2 adduct, and was used as ligand in the following studies. The investigation of the solvent effect in the reaction was then carried out. The catalyst showed no reactivity in the presence of THF (Entry 12), which might be due to the strong coordinating properties of the THF. Another interesting observation was the success of CH_2Cl_2 when used as solvent (Entries 13, 16, 17), which is in agreement with the results obtained with copper catalyzed conjugate addition.[23] In

Table 1. Optimization of the S_N2' substitution of propargylic dioxolanone **3a**.



Entry	Cu salt[a]	R	Ligand	Solvent	% Conversion[b]	S_N2'/S_N2; diol/enyne[c]
1	CuCN	Me	$P(nBu)_3$	Et_2O	46	n.d.[d]
2	CuSCN	Me	$P(nBu)_3$	Et_2O	61	n.d.
3	CuSCN	Me	–	Et_2O	20	n.d.
4	$CuBr{\cdot}SMe_2$	Me	$P(nBu)_3$	Et_2O	27	n.d.
5	$Cu(OTf)_2$	Me	$P(nBu)_3$	Et_2O	8	n.d.
6	$[Cu(MeCN)_4][BF_4]$	Me	$P(nBu)_3$	Et_2O	100	30:43; 27/–
7	$[Cu(MeCN)_4][BF_4]$	Me	$O{=}PBu_3$	Et_2O	100	20:49; 18/13
8	$[Cu(MeCN)_4][BF_4]$	Me	PCy_3	Et_2O	100	28:37; 14/11
9	$[Cu(MeCN)_4][BF_4]$	Me		Et_2O	100	12:27; –/61
10	$[Cu(MeCN)_4][BF_4]$	Me	$P(OEt)_3$	Et_2O	100	45:55; –/–
11	$[Cu(MeCN)_4][BF_4]$	Me	$P(OBu)_3$	Et_2O	100	50:50; –/–
12	$[Cu(MeCN)_4][BF_4]$	Me	$P(OBu)_3$	THF	< 10	n.d.
13	$[Cu(MeCN)_4][BF_4]$	Me	$P(OBu)_3$	CH_2Cl_2	100	59:41; –/–
14	$[Cu(MeCN)_4][BF_4]$	Et	$P(OBu)_3$	Et_2O	80[e]	80:20; –/–
15	$[Cu(MeCN)_4][BF_4]$	Et	$P(OBu)_3$	toluene	52[e]	86:14; –/–
16	$[Cu(MeCN)_4][BF_4]$	Et	$P(OBu)_3$	CH_2Cl_2	80[e]	90:10; –/–
17	$[Cu(MeCN)_4][BF_4]$	*i*Pr	$P(OBu)_3$	CH_2Cl_2	82[e]	100:0; –/–

[a] Ratio of **3a**/RMgX/[Cu]/ligand = 1:2:0.1:0.2, solvent (3 mL), –10 °C, 2 h. [b] Conversion of **3a** is based on ^1H NMR analysis of the crude product. [c] Ratio between the S_N2', S_N2, diol and enyne product is based on ^1H NMR analysis of the crude product. [d] n.d.: not determined. [e] Isolated yield of allene.

comparison to use of Et_2O, CH_2Cl_2 gave better regioselectivity between S_N2' and S_N2 substitution while identical reactivity was maintained (Entries 11 vs. 13, 14 vs. 16). Most importantly however, the studies of Table 1 showed that the regioselectivity between S_N2' and S_N2 mainly depends on the steric properties of the nucleophile (Entries 13–17). When the least sterically demanding nucleophile MeMgBr was used, a mixture of S_N2' and S_N2 products was obtained in a 59:41 ratio (Entry 13). When the relatively larger nucleophile EtMgBr was employed in the reaction (Entry 16), good regioselectivity was observed, with a 90:10 ratio in favor of the desired S_N2' products. When the steric demand of the nucleophile was increased further to *i*PrMgCl (Entry 17), only the desired S_N2' product was obtained.

Through the above study of the reaction conditions, a highly efficient copper catalyst for the S_N2' substitution of propargylic dioxolanone with Grignard reagent was found. The desired α-hydroxyallene was obtained in excellent yield leaving only for the reaction to be generalized.

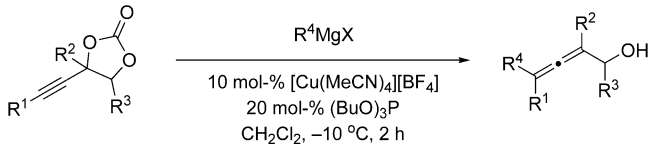
The optimized reaction conditions were then applied to a small library of propargylic dioxolanones with a collection of Grignard reagents (Table 2). Both aromatic (R^1 = Ph) and aliphatic [R^1 = Me, Et, -$(CH_2)_4$-] propargylic dioxolanones showed similar reactivity and gave the corresponding α-hydroxyallene in good to excellent yields (allenes **5**–**20**). The terminal propargylic dioxolanone **3e** (R^1 = H) gave the α-hydroxyallenes **21**–**23** in relatively lower yields, due to a competing deprotonation of terminal alkyne in the presence of the Grignard reagent. Regarding to the Grignard reagent, both aliphatic (Et, *i*Pr, *t*Bu) and aromatic (Ph) nucleophiles were successfully utilized in the reaction. Functionalized Grignard reagents,[24] generated by halogen–metal exchange between *i*PrMgCl and aromatic iodides, also gave very promising results. The corresponding α-hydroxyallenes **13**–**14**, **18**–**20** and **23**, bearing functionalized aryl groups, were isolated in moderate to good yields.

A series of secondary α-hydroxyallenes **8**–**14** were also synthesized in excellent diastereoselectivity, where only one diastereoisomer was observed. Indeed, in most of the copper-mediated S_N2' substitution of propargylic electrophiles, the corresponding allenes are formed by an overall *anti*-substitution.[25] In order to determine if our results are in agreement with the literature observation, we carried out a gold-catalyzed cycloisomerization on allene **9** to form the dihydrofuran **24** (Scheme 6).[17] NOE experiments of the dihydrofuran **24** revealed a *cis* configuration between H and *t*Bu group, therefore confirming the *anti*-selectivity of the S_N2' substitution.

Pleasingly, the new copper-catalyzed S_N2' substitution of propargylic dioxolanones showed a great versatility for the synthesis of α-hydroxyallenes. A range of primary and secondary α-hydroxyallenes bearing various functional groups were synthesized in good to excellent yields regard to this protocol.

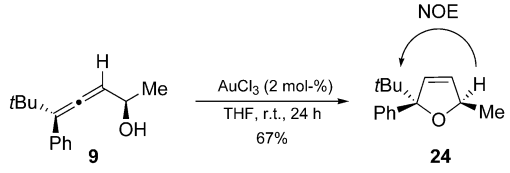
In addition, we studied the potential of applying this method to the synthesis of enantiomerically enriched allenes. The enantiomerically enriched propargylic dioxolanone (*S*)-**3a** was synthesized by the Sharpless asymmetric

Table 2. Scope of the copper-catalyzed S_N2' substitution of propargylic dioxolanones.



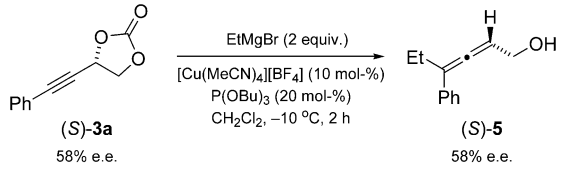
Allene	Substrate	Grignard	R^1	R^2	R^3	R^4	% Yield[a]
5	**3a**	EtMgBr	Ph	H	H	Et	80[b]
6	**3a**	*i*PrMgCl	Ph	H	H	*i*Pr	82
7	**3a**	*t*BuMgCl	Ph	H	H	*t*Bu	78
8	**3b**	*i*PrMgCl	Ph	H	Me	*i*Pr	89
9	**3b**	*i*BuMgCl	Ph	H	Me	*t*Bu	92
10	**3c**	*i*PrMgCl	Me	–$(CH_2)_4$–		*i*Pr	78
11	**3c**	*i*BuMgCl	Me	–$(CH_2)_4$–		*t*Bu	81
12	**3c**	PhMgCl	Me	–$(CH_2)_4$–		Ph	83
13	**3c**	2-FC_6H_4MgCl	Me	–$(CH_2)_4$–		2-FC_6H_4	76
14	**3c**	4-$MeO_2CC_6H_4MgCl$	Me	–$(CH_2)_4$–		4-$MeO_2CC_6H_4$	62
15	**3d**	*i*PrMgCl	Et	Me	H	*i*Pr	90
16	**3d**	*i*BuMgCl	Et	Me	H	*t*Bu	90
17	**3d**	PhMgCl	Et	Me	H	Ph	88
18	**3d**	2-FC_6H_4MgCl	Et	Me	H	2-FC_6H_4	85
19	**3d**	3-$MeOC_6H_4MgCl$	Et	Me	H	3-$MeOC_6H_4$	57
20	**3d**	4-$MeO_2CC_6H_4MgCl$	Et	Me	H	4-$MeO_2CC_6H_4$	61
21	**3e**	*t*BuMgCl	H	Me	H	*t*Bu	62
22	**3e**	PhMgCl	H	Me	H	Ph	58
23	**3e**	2-FC_6H_4MgCl	H	Me	H	2-FC_6H_4	39

[a] Isolated yield. [b] S_N2'/S_N2: 90:10, based on ^1H NMR of the purified product.



Scheme 6. Gold-catalyzed cycloisomerization of allene **9**.

dihydroxylation. The copper-catalyzed S_N2' substitution was then performed, and the desired enantiomerically enriched allene (*S*)-**5** was isolated with complete chirality transfer (Scheme 7). However, the propargylic dioxolanone (*S*)-**3a** only had 58% enantiomeric excess due to unfortunately low enantioselectivity in the dihydroxylation step.



Scheme 7. Synthesis of enantiomerically enriched allene (*S*)-**5**.

Conclusions

A new copper-catalyzed S_N2' substitution of propargylic dioxolanones has been developed. This protocol provides an efficient and versatile access to α-hydroxyallenes. It also shows potential in the synthesis of enantiomerically enriched allenes. A variety of primary and secondary α-hydroxyallenes were obtained with good to excellent yields via a highly *anti*-selective pathway. The application of this method to the synthesis of natural products is currently under progress.

Experimental Section

General: Infrared spectra were recorded using Perkin–Elmer 983 G infrared, Perkin–Elmer 882 infrared spectrophotometers or a Bruker IFS 66 spectrometer. Proton and ^{13}C NMR spectra were recorded with Bruker (AM400, AV400 or DRX 400) spectrometers using $CHCl_3$ (δ = 7.27 ppm) tetramethylsilane (δ = 0.00 ppm) as standard; *J* values are given in Hz. All spectra were recorded at ambient temperature unless otherwise noted. Mass spectra were obtained with a Finnigan-MAT 1020 or Autospec VG (electron impact ionisation, EI), Finnigan-QMS (electrospray ionisation, ESI), VG-ZAB, or Finnigan MAT 8200 (EI, 70 eV). All reactions involving air sensitive materials were carried out under argon using standard Schlenk techniques. Reaction solvents were distilled under argon from appropriate agent immediately prior to use. Data of known compound is in agreement with the literature report.

(But-3-en-1-ynyl)benzene (1a):[26] A mixture of $Pd(PPh_3)_4$ (55 mg, 0.048 mmol, 0.32 mol-%) and CuI (57 mg, 0.3 mmol, 2 mol-%) were dissolved in Et_2NH (7.5 mL) under argon. After cooling to –10 °C, phenylacetylene (1.6 mL, 15 mmol) and vinyl bromide (20 mL, 1.0 M in THF, 20 mmol) were added. The reaction mixture was kept stirring at room temp. for 20 h. The reaction mixture was poured on H_2O, and extracted into Et_2O. The organic phase was washed with HCl (1 M), dried with $MgSO_4$ and concentrated to give crude compound. The crude was purified by column chromatography (light petroleum) over silica gel to give pure product **1a** as colorless oil (1.72 g, 89%). ^1H NMR (400 MHz, $CDCl_3$, 25 °C, TMS): δ = 7.49–7.45 (m, 2 H), 7.36–7.32 (m, 3 H), 6.09–6.01 (dd, *J* = 11.2 and 17.6 Hz, 1 H), 5.79 (d, *J* = 17.6 Hz, 1 H),

5.59 (d, J = 11.2 Hz, 1 H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$, 25 °C, TMS): δ = 131.6, 128.3, 126.9, 123.1, 117.2, 89.9, 88.1 ppm. IR ($CHCl_3$ solution): $\tilde{\nu}$ = 2925, 2875, 2223, 1756, 1600 cm^{-1}.

(*Z*)-(Pent-3-en-1-ynyl)benzene (1b):[27] $Pd(PPh_3)_4$ (55 mg, 0.048 mmol, 0.32 mol-%), CuI (57 mg, 0.3 mmol, 2 mol-%), phenylacetylene (1.6 mL, 15 mmol) and 1-bromoprop-1-ene (1.7 mL, 20 mmol, *E*/*Z* mixture) were treated the same procedure as **1a**. After purification, pure product **1b** was obtained as yellow oil (1.93 g, 91%, *Z*/*E*: 77:23). ^{1}H NMR (400 MHz, $CDCl_3$, 25 °C, TMS): δ = 7.46–7.40 (m, 2 H), 7.31–7.28 (m, 3 H), 6.09–5.99 (m, 1 H), 5.70 (d, J = 10.8 Hz, 1 H), 1.96 (d, J = 6.8 Hz, 3 H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$, 25 °C, TMS): δ = 139.6, 131.2, 128.1, 127.9, 123.5, 109.9, 93.8, 86.1, 16.0 ppm. IR (KBr): $\tilde{\nu}$ = 3468, 3027, 2912, 1714, 1489, 1384, 755 cm^{-1}.

1-(Prop-1-ynyl)cyclohexene (1c):[28] 1-Ethynylcyclohexene (1.18 mL, 10 mmol) was dissolved in THF (10 mL) under argon. The solution was cooled to – 78 °C. *n*BuLi (8 mL, 2.5 M in hexane, 20 mmol) was added, the mixture was stirred for 2 h while allowing the temperature to raise. MeI (1.24 mL, 20 mmol) was then added. The reaction mixture was kept stirring overnight while warm to room temp. The reaction mixture was quenched with NH_4Cl (saturated solution), and extracted with Et_2O. The organic phase was washed with brine, dried with $MgSO_4$ and concentrated to give crude compound. The crude was purified by column chromatography (cyclohexane) over silica gel to give pure product **1c** as yellow oil (0.98 g, 82%). ^{1}H NMR (400 MHz, $CDCl_3$, 25 °C, TMS): δ = 5.99 (br. s, 1 H), 2.12–2.02 (m, 4 H), 1.93 (s, 3 H), 1.65–1.52 (m, 4 H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$, 25 °C, TMS): δ = 133.1, 120.8, 82.6, 81.4, 29.4, 25.4, 22.3, 21.5, 4.0 ppm. IR (KBr): $\tilde{\nu}$ = 2928, 2857, 2360, 2341, 1436, 1384 cm^{-1}.

4-Phenylbut-3-yne-1,2-diol (2a): To a flask was added $NaIO_4$ (1.28 g, 6 mmol), H_2O (3 mL) and H_2SO_4 (0.8 mL, 0.8 mmol, 1 M). After all the solids were dissolved the solution was cooled to 0 °C. $RuCl_3$ (0.2 mL, 0.02 mmol, 0.1 M in H_2O) was added and the mixture was stirred until the color turned bright yellow. Ethyl acetate (12 mL) was added, followed by acetonitrile (12 mL) after 5 min. After further 5 min, compound **1a** (4 mmol, 512 mg) was added in one portion and the resulting slurry was stirred until all starting material was consumed. The mixture was poured onto $NaHCO_3$ (15 mL, satd.) and $Na_2S_2O_3$ (20 mL, satd.) solution. The mixture was extracted with EtOAc, the combined organic phase was dried with $MgSO_4$ and concentrated to give crude compound. The crude was purified by flash column chromatography (Et_2O/light petroleum: 9:1) over silica gel to give pure product **2a** (528 mg, 81% yield) as yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$, 25 °C, TMS): δ = 7.44 (m, 2 H), 7.36–7.29 (m, 3 H), 4.73 (dd, J = 6.6 and 3.8 Hz, 1 H), 3.88–3.79 (m, 2 H), 3.07 (br., 1 H, OH), 2.74 (br., 1 H, OH) ppm. ^{13}C NMR (100 MHz, $CDCl_3$, 25 °C, TMS): δ = 131.8, 128.4, 128.3, 122.1, 86.5, 86.2, 66.6, 63.8 ppm. IR ($CHCl_3$ solution): $\tilde{\nu}$ = 3606, 2932, 2223, 1600, 1490, 1373, 1069, 991, 916, 863 cm^{-1}. HRMS: $[M]^+$ $C_{10}H_{10}O_2$, theoretical mass 162.0681; found 162.0684.

5-Phenylpent-4-yne-2,3-diol (2b):[29] Compound **1b** (1.42 g, 10 mmol), $NaIO_4$ (3.2 g, 15 mmol), $RuCl_3$ (0.5 mL, 0.1 M in H_2O), H_2SO_4 (2 mL, 1 M) and NaOAc/MeCN/H_2O (30 mL:30 mL/7.5 mL) were treated the same procedure as **2a**. After purification, compound **2b** (1.12 g, 64% yield, *dr* = 77:23) was obtained as yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$, 25 °C, TMS): δ = 7.47–7.44 (m, 2 H), 7.35–7.31 (m, 3 H), 4.54 (d, J = 3.6 Hz, 1 H), 4.01–3.95 (m, 1 H), 1.35 (d, J = 6.4 Hz, 3 H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$, 25 °C, TMS): δ = 131.7, 128.6, 128.2, 122.0, 86.8, 86.0, 70.2, 67.5, 18.3 ppm. IR (KBr): $\tilde{\nu}$ = 3317, 1490, 1384, 1083, 755, 690 cm^{-1}. HRMS: $[M]^+$ $C_{11}H_{12}O_2$, theoretical mass 176.0832; found 176.0824.

1-(Prop-1-ynyl)cyclohexane-1,2-diol (2c):[30] Compound **1c** (1.20 g, 10 mmol) and $K_3Fe(CN)_6$ (9.8 g), K_2CO_3 (4.1 g), quinuclidine (178 mg), $K_2OsO_2(OH)_4$ (180 mg), methanesulfonamide (928 mg) were suspended in *t*BuOH/H_2O (50 mL each) and stirred at room temp. for 2 d. Na_2SO_3 (15 g) was added, the mixture was extracted with EtOAc, the combined organic layers were dried with $MgSO_4$ and concentrated under reduced pressure. The crude was purified by flash column chromatography (Et_2O/light petroleum: 9:1) over silica gel afforded pure compound **2c** (0.61 g, 40% yield) as yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$, 25 °C, TMS): δ = 3.65–3.63 (m, 1 H), 2.42–2.33 (m, 1 H), 2.33–2.25 (m, 1 H), 2.11–1.91 (m, 2 H), 1.83 (s, 3 H), 1.78–1.69 (m, 1 H), 1.68–1.50 (m, 5 H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$, 25 °C, TMS): δ = 81.6, 80.6, 74.2, 70.1, 35.6, 28.3, 21.9, 21.0, 3.5 ppm. IR (KBr): $\tilde{\nu}$ = 3398, 2936, 2359, 1445, 1064, 998 cm^{-1}.

2-Methylhex-3-yne-1,2-diol (2d): 2-Methyl-1-hexen-3-yne (1.24 mL, 10 mmol) and $K_3Fe(CN)_6$ (9.8 g), K_2CO_3 (4.1 g), quinuclidine (178 mg), $K_2OsO_2(OH)_4$ (180 mg) and methanesulfonamide (928 mg) were treated the same procedure as **2c**. After purification **2d** (900 mg, 70%) was obtained as colourless oil. ^{1}H NMR (400 MHz, $CDCl_3$, 25 °C, TMS): δ = 3.64 (d, J = 11.2 Hz, 1 H), 3.49 (d, J = 11.2 Hz, 1 H), 2.72 (br., 1 H, OH), 2.25 (br., 1 H, OH), 2.26–2.20 (q, J = 7.6 Hz, 2 H), 1.45 (s, 3 H), 1.17 (t, J = 7.6 Hz, 3 H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$, 25 °C, TMS): δ = 86.6, 80.9, 70.9, 68.6, 25.6, 13.8, 12.3 ppm. IR ($CHCl_3$ solution): $\tilde{\nu}$ = 3585, 2981, 2927, 2878, 2360, 1456, 1378, 1319, 1049, 975 cm^{-1}. HRMS: $[M - CH_2OH]^+$ C_6H_9O, theoretical mass 97.0648; found 97.0651.

2-Methylbut-3-yne-1,2-diol (2e): 2-Methylbut-1-en-3-yne (0.93 mL, 10 mmol) and $K_3Fe(CN)_6$ (9.8 g), K_2CO_3 (4.1 g), quinuclidine (178 mg), $K_2OsO_2(OH)_4$ (180 mg) and methyanesulfonamide (928 mg) were treated the same procedure as **2c**. After purification **2e** (650 mg, 65%) was obtained as yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$, 25 °C, TMS): δ = 3.69 (d, J = 8.4 Hz, 1 H), 3.55 (d, J = 8.4 Hz, 1 H), 2.70 (br., 1 H, OH), 2.50 (s, 1 H), 2.15–2.09 (br., 1 H, OH), 1.51 (s, 3 H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$, 25 °C, TMS): δ = 85.5, 72.5, 70.6, 68.4, 25.1 ppm. IR ($CHCl_3$ solution): $\tilde{\nu}$ = 3586, 3304, 2986, 2935, 2876, 2112, 1602, 1455, 1380, 1352, 1321, 1082, 1049, 976, 948, 886, 643 cm^{-1}.

General Procedure for the Formation of Dioxolanones: To diol (4.81 mmol) in CH_2Cl_2 (14 mL) in an argon flashed flask in an ice bath was added pyridine (24 mmol). Solution of triphosgene (5.29 mmol) in CH_2Cl_2 was added and the reaction was allowed to stir for 10 min when determined complete by TLC. The reaction was diluted with Et_2O. The crude mixture, including salts, was washed vigorously with a $CuSO_4$ (satd.) solution until all salts dissolved. The layers were then separated and the organic layer was washed with brine. After separation, the organic layer was dried with $MgSO_4$ and concentrated. The crude mixture was then purified by flash column chromatography over silica gel to give pure product.

4-(Phenylethynyl)-1,3-dioxolan-2-one (3a): Compound **2a** (890 mg, 5.5 mmol), triphosgene (2 g, 6.6 mmol) and pyridine (2.23 mL, 27 mmol) were treated according to the general procedure. After purification, compound **3a** (940 mg, 91% yield) was obtained as yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$, 25 °C, TMS): δ = 7.46–7.44 (m, 2 H), 7.40–7.31 (m, 3 H), 5.53 (dd, J = 8.2 and 6.9 Hz, 1 H), 4.69 (t, J = 8.2 Hz, 1 H), 4.48 (dd, J = 8.2 and 6.9 Hz, 1 H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$, 25 °C, TMS): δ = 153.9, 131.9, 129.7, 128.5, 120.6, 89.8, 81.7, 69.7, 66.6 ppm. IR ($CHCl_3$ solution): $\tilde{\nu}$ = 2922, 2238, 1818, 1599, 1490, 1386, 1297, 1149, 1070,

997 cm^{-1}. HRMS: [M + Na^+] $C_{11}H_8NaO_3$, theoretical mass 211.0371; found 211.0368.

4-(But-1-ynyl)-4-methyl-1,3-dioxolan-2-one (3b): Compound **2b** (1.05 g, 6 mmol), triphosgene (2.0 g, 6.6 mmol) and pyridine (2.4 mL, 30 mmol) were treated according to the general procedure. After purification, compound **3b** (803 mg, 66% yield, only one diastereomer) was obtained as yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$, 25 °C, TMS): δ = 7.48–7.46 (m, 3 H), 7.40–7.33 (m, 2 H), 5.04 (d, J = 7.1 Hz, 1 H), 4.83–4.76 (m, 1 H), 1.59 (d, J = 6.3 Hz, 3 H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$, 25 °C, TMS): δ = 153.4, 131.9, 129.6, 128.4, 120.6, 89.9, 81.0, 79.2, 72.8, 18.5 ppm. IR (KBr): $\tilde{\nu}$ = 3441, 2233, 1802, 1384, 1354, 1179, 1065, 1022, 758 cm^{-1}. HRMS: $[M]^+$ $C_{12}H_{10}O_3$, theoretical mass 202.0624; found 202.0615.

3a-(Prop-1-ynyl)hexahydrobenzo[*d*][1,3]dioxol-2-one (3c): Compound **2c** (1.6 g, 10 mmol), triphosgene (3.3 g, 11 mmol) and pyridine (4.0 mL, 50 mmol) were treated according to the general procedure. After purification, compound **3c** (1.31 g, 72% yield) was obtained as yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$, 25 °C, TMS): δ = 4.57 (t, J = 3.8 Hz, 1 H), 2.21–2.02 (m, 2 H), 1.88 (s, 3 H), 1.87–1.74 (m, 2 H), 1.73–1.32 (m, 4 H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$, 25 °C, TMS): δ = 154.0, 85.5, 80.3, 78.1, 74.9, 34.3, 25.3, 20.1, 18.7, 3.7 ppm. IR (KBr): $\tilde{\nu}$ = 2945, 2866, 2253, 1806, 1297, 1228, 1196, 1015 cm^{-1}. HRMS: $[M]^+$ $C_{10}H_{12}O_3$, theoretical mass 180.0781; found 180.0784.

4-(But-1-ynyl)-4-methyl-1,3-dioxolan-2-one (3d): Compound **2d** (730 mg, 5.7 mmol), triphosgene (1.90 g, 6.3 mmol) and pyridine (2.3 mL, 28.5 mmol) were treated according to the general procedure. After purification, compound **3d** (812 mg, 92% yield) was obtained as yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$, 25 °C, TMS): δ = 4.44 (d, J = 8.2 Hz, 1 H), 4.18 (d, J = 8.2 Hz, 1 H), 2.22 (q, J = 7.5 Hz, 2 H), 1.70 (s, 3 H), 1.12 (t, J = 7.5 Hz, 3 H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$, 25 °C, TMS): δ = 153.8, 90.7, 76.5, 76.0, 75.6, 26.9, 13.1, 12.2 ppm. IR (KBr): $\tilde{\nu}$ = 2983, 2253, 1809, 1385, 1237, 1060 cm^{-1}. HRMS: $[M]^+$ $C_8H_{10}O_3$, theoretical mass 154.0624; found 154.0617.

Ethynyl-4-methyl-1,3-dioxolan-2-one (3e): Compound **2e** (440 mg, 4.4 mmol), triphosgene (1.47 g, 4.8 mmol) and pyridine (1.82 mL, 22 mmol) were treated according to the general procedure. After purification, compound **3e** (490 mg, 88% yield) was obtained as yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$, 25 °C, TMS): δ = 4.53 (d, J = 8.4 Hz, 1 H), 4.25 (d, J = 8.4 Hz, 1 H), 2.76 (s, 1 H), 1.78 (s, 3 H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$, 25 °C, TMS): δ = 153.3, 125.7, 80.3, 76.3, 75.1, 26.3 ppm. IR (KBr): $\tilde{\nu}$ = 3289, 1802, 1387, 1236, 1099, 1061 cm^{-1}. HRMS: $[M]^+$ $C_6H_6O_3$, theoretical mass 126.0317; found 126.0324.

Preparation of [Cu(MeCN)$_4$][BF$_4$]: A mixture of Cu_2O (1 g), MeCN (25 mL) and HBF_4 (5 mL, 47% solution) were added to a flask fitted with a reflux condenser, and heated to 50–60 °C until all the solids dissolve. The hot solution was filtered and the filtrate was left to cool to room temperature then 4 °C. A large crop of colorless crystal was formed, filtrate the crystal and wash with dry Et_2O gave $[Cu(MeCN)_4][BF_4]$ salt, which can be stored under air for months. The decomposition can be simple detected by color change from colorless to blue.

General Procedure A of S_N2' Substitution. Using Commercial Available Grignard Reagent: To a dry argon flashed Schlenk was added $[Cu(MeCN)_4][BF_4]$ (0.1 mmol, 10 mol-%), $(BuO)_3P$ (0.2 mmol, 20 mol-%) and CH_2Cl_2 (2 mL), the mixture was stirred at room temp. for 1 h. After cooling the reaction to – 10 °C, the Grignard reagent (2 mmol) was added, the reaction was stirred for 30 min at –10 °C, a solution of the dioxolanone (1 mmol) in CH_2Cl_2 (1 mL) was then added, and the reaction was kept at –10 °C for 2 h. The reaction mixture was quenched with NH_4Cl saturated solution and the crude mixture was extracted with Et_2O. The combined organic phase was washed with H_2O_2 (3%) and brine, dried with $MgSO_4$ and concentrated. The crude was purified by flash column chromatography over silica gel to give pure product.

General Procedure B of S_N2' Substitution. Using Functionalized Grignard Reagent: The iodobenzene (2.5 mmol) was dissolved in THF (1 mL) in a dry argon-flashed Schlenk flask and cooled to –40 °C, *i*PrMgCl (2.5 mmol) was then added. After 1 h at –40 °C, the Grignard reagent was added to the freshly prepared solution of $[Cu(MeCN)_4][BF_4]$ (0.1 mmol, 10 mol-%) and $(BuO)_3P$ (0.2 mmol, 20 mol-%) in CH_2Cl_2 (2 mL) at –10 °C. After stirring for 30 min at –10 °C, a solution of the dioxolanone (1 mmol) in CH_2Cl_2 (1 mL) was added, and the reaction was kept at –10 °C for 2 h. The reaction mixture was quenched with NH_4Cl saturated solution and the crude mixture was extracted with Et_2O. The combined organic phase was washed with H_2O_2 (3%) and brine, dried with $MgSO_4$ and concentrated. The crude was purified by flash column chromatography over silica gel to give pure product.

4-Phenylhexa-2,3-dien-1-ol (5): Compound **3a** (188 mg, 1 mmol), $[Cu(MeCN)_4][BF_4]$ (31.4 mg, 0.1 mmol, 10 mol-%), $(BuO)_3P$ (54 μL, 0.2 mmol, 20 mol-%) and EtMgBr (3.0 M in Et_2O, 0.67 mL, 2 mmol) were treated according to the general procedure A. After purification, compound **5** (140 mg, 80% yield) was obtained as yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$, 25 °C, TMS): δ = 7.43 (d, J = 7.4 Hz, 2 H), 7.35 (t, J = 7.4 Hz, 2 H), 7.24 (t, J = 7.4 Hz, 1 H), 5.82–5.78 (m, 1 H), 4.27 (t, J = 5.1 Hz, 2 H), 2.52–2.48 (m, 2 H), 1.18 (t, J = 7.3 Hz, 3 H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$, 25 °C, TMS): δ = 202.5, 136.4, 128.4, 126.9, 126.0, 110.7, 95.9, 60.7, 22.9, 12.6 ppm. IR ($CHCl_3$ solution): $\tilde{\nu}$ = 3610, 2970, 2932, 2876, 1946, 1741, 1598, 1493, 1456, 1379, 1141, 1078, 994, 912 cm^{-1}. HRMS: $[M]^+$ $C_{12}H_{14}O$, theoretical mass 174.1045; found 174.1040. HPLC: Daicel Chiralpak OJ-H, *i*PrOH/hexanes, 90:10, UV: 254 nm, flow rate: 1.0 mL min^{-1}. T_S = 21.4 min, T_R = 25.7 min.

5-Methyl-4-phenylhexa-2,3-dien-1-ol (6): Compound **3a** (188 mg, 1 mmol), $[Cu(MeCN)_4][BF_4]$ (31.4 mg, 0.1 mmol, 10 mol-%), $(BuO)_3P$ (54 μL, 0.2 mmol, 20 mol-%) and *i*PrMgCl (1.0 M in Et_2O, 2 mL, 2 mmol) were treated according to the general procedure A. After purification, compound **6** (154 mg, 82% yield) was obtained as yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$, 25 °C, TMS): δ = 7.39 (d, J = 7.3 Hz, 2 H), 7.32 (t, J = 7.3 Hz, 2 H), 7.22 (t, J = 7.3 Hz, 1 H), 5.76 (dt, J = 5.6 and 2.3 Hz, 1 H), 4.23 (t, J = 5.6 Hz, 2 H), 2.90–2.82 (m, 1 H), 1.14 (t, J = 6.9 Hz, 6 H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$, 25 °C, TMS): δ = 201.8, 136.3, 128.4, 126.9, 126.6, 116.3, 96.2, 60.9, 28.1, 22.6, 22.1 ppm. IR (KBr): $\tilde{\nu}$ = 3335, 2963, 2870, 2360, 1384, 1011, 760, 694 cm^{-1}. HRMS: $[M]^+$ $C_{13}H_{16}O$, theoretical mass 188.1201; found 188.1200.

5,5-Dimethyl-4-phenylhexa-2,3-dien-1-ol (7): Compound **3a** (188 mg, 1 mmol), $[Cu(MeCN)_4][BF_4]$ (31.4 mg, 0.1 mmol, 10 mol-%), $(BuO)_3P$ (54 μL, 0.2 mmol, 20 mol-%) and *t*BuMgCl (2.0 M in Et_2O, 1 mL, 2 mmol) were treated according to the general procedure A. After purification, compound **7** (158 mg, 78% yield) was obtained as yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$, 25 °C, TMS): δ = 7.31–7.24 (m, 3 H), 7.23–7.19 (m, 2 H), 5.41 (t, J = 5.8 Hz, 1 H), 4.11 (d, J = 5.8 Hz, 2 H), 1.12 (s, 9 H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$, 25 °C, TMS): δ = 200.4, 137.2, 129.2, 127.7, 126.7, 118.7, 92.3, 61.1, 34.2, 29.7 ppm. IR (KBr): $\tilde{\nu}$ = 3344, 2963, 2866, 1441, 1381, 1012, 758, 700 cm^{-1}. HRMS: $[M]^+$ $C_{14}H_{18}O$, theoretical mass 202.1352; found 202.1342.

6-Methyl-5-phenylhepta-3,4-dien-2-ol (8): Compound **3b** (202 mg, 1 mmol), $[Cu(MeCN)_4][BF_4]$ (31.4 mg, 0.1 mmol, 10 mol-%),

$(BuO)_3P$ (54 μL, 0.2 mmol, 20 mol-%) and *i*PrMgCl (2.0 M in Et_2O, 1 mL, 2 mmol) were treated according to the general procedure A. After purification, compound **8** (192 mg, 89% yield) was obtained as yellow oil. ^1H NMR (400 MHz, $CDCl_3$, 25 °C, TMS): δ = 7.40 (d, J = 7.9 Hz, 2 H), 7.32 (t, J = 7.7 Hz, 2 H), 7.22 (t, J = 7.3 Hz, 1 H), 5.72–5.71 (m, 1 H), 4.45 (br. s, 1 H), 2.90–2.82 (m, 1 H), 1.37 (d, J = 6.7 Hz, 3 H), 1.16 (d, J = 6.7 Hz, 3 H), 1.14 (d, J = 6.7 Hz, 3 H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$, 25 °C, TMS): δ = 200.4, 136.3, 128.4, 126.8, 126.4, 116.6, 101.3, 66.2, 28.0, 23.6, 22.6, 22.1 ppm. IR (KBr): $\tilde{\nu}$ = 3436, 2966, 2928, 1713, 1384, 1365, 1121, 1077, 761, 694 cm^{-1}. HRMS: $[M]^+$ $C_{14}H_{18}O$, theoretical mass 202.1352; found 202.1345.

6,6-Dimethyl-5-phenylhepta-3,4-dien-2-ol (9): Compound **3b** (202 mg, 1 mmol), $[Cu(MeCN)_4][BF_4]$ (31.4 mg, 0.1 mmol, 10 mol-%), $(BuO)_3P$ (54 μL, 0.2 mmol, 20 mol-%) and *t*BuMgBr (2.0 M in Et_2O, 1 mL, 2 mmol) were treated according to the general procedure A. After purification, compound **9** (199 mg, 92% yield) was obtained as white solid; m.p. 42 °C. ^1H NMR (400 MHz, $CDCl_3$, 25 °C, TMS): δ = 7.33–7.27 (m, 3 H), 7.25–7.22 (m, 2 H), 5.40 (d, J = 5.2 Hz, 1 H), 4.39–4.30 (m, 1 H), 1.32 (d, J = 6.3 Hz, 3 H), 1.14 (s, 9 H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$, 25 °C, TMS): δ = 199.0, 137.2, 129.2, 127.7, 126.7, 119.1, 97.3, 65.9, 34.3, 29.7, 23.1 ppm. IR (KBr): $\tilde{\nu}$ = 3348, 2966, 1442, 1361, 1075, 701 cm^{-1}. HRMS: $[M]^+$ $C_{15}H_{20}O$, theoretical mass 216.1509; found 216.1505.

2-(2,3-Dimethylbut-1-enylidene)cyclohexanol (10):[31] Compound **3c** (180 mg, 1 mmol), $[Cu(MeCN)_4][BF_4]$ (31.4 mg, 0.1 mmol, 10 mol-%), $(BuO)_3P$ (54 μL, 0.2 mmol, 20 mol-%) and *i*PrMgBr (2.0 M in Et_2O, 1 mL, 2 mmol) were treated according to the general procedure A. After purification, compound **10** (140 mg, 78% yield) was obtained as white solid; m.p. 36 °C. ^1H NMR (400 MHz, $CDCl_3$, 25 °C, TMS): δ = 3.96–3.90 (m, 1 H), 2.35–2.29 (m, 1 H), 2.14–2.07 (m, 1 H), 2.07–1.89 (m, 2 H), 1.85–1.75 (m, 2 H), 1.72 (s, 3 H), 1.69–1.61 (m, 1 H), 1.43–1.27 (m, 3 H), 0.98 (dd, J = 6.7 and 1.5 Hz, 6 H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$, 25 °C, TMS): δ = 190.2, 111.3, 108.0, 68.9, 36.2, 32.5, 30.1, 26.9, 23.7, 21.7, 18.2 ppm. IR (KBr): $\tilde{\nu}$ = 3418, 2931, 2856, 2360, 1446, 1384, 1075, 999 cm^{-1}. HRMS: $[M]^+$ $C_{12}H_{20}O$, theoretical mass 180.1509; found 180.1509.

2-(2,3,3-Trimethylbut-1-enylidene)cyclohexanol (11):[31] Compound **3c** (180 mg, 1 mmol), $[Cu(MeCN)_4][BF_4]$ (31.4 mg, 0.1 mmol, 10 mol-%), $(BuO)_3P$ (54 μL, 0.2 mmol, 20 mol-%) and *t*BuMgCl (2.0 M in Et_2O, 1 mL, 2 mmol) were treated according to the general procedure A. After purification, compound **11** (158 mg, 81% yield) was obtained as white solid; m.p. 83 °C. ^1H NMR (400 MHz, $CDCl_3$, 25 °C, TMS): δ = 3.97–3.90 (m, 1 H), 2.35–2.29 (m, 1 H), 2.05–1.90 (m, 2 H), 1.83–1.74 (m, 2 H), 1.71 (s, 3 H), 1.68–1.60 (m, 1 H), 1.39–1.27 (m, 3 H), 1.01 (s, 9 H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$, 25 °C, TMS): δ = 190.5, 113.8, 107.0, 68.9, 36.0, 34.1, 29.9, 29.2, 26.8, 23.6, 15.7 ppm. IR (KBr): $\tilde{\nu}$ = 3232, 2930, 2360, 1433, 1385, 1358, 1114, 993, 973 cm^{-1}. HRMS: $[M]^+$ $C_{13}H_{22}O$, theoretical mass 194.1665; found 194.1669.

2-(2-Phenylprop-1-enylidene)cyclohexanol (12):[31] Compound **3c** (180 mg, 1 mmol), $[Cu(MeCN)_4][BF_4]$ (31.4 mg, 0.1 mmol, 10 mol-%), $(BuO)_3P$ (54 μL, 0.2 mmol, 20 mol-%) and PhMgCl (1.8 M in THF, 1.1 mL, 2 mmol) were treated according to the general procedure A. After purification, compound **12** (177 mg, 83% yield) was obtained as white solid; m.p. 101 °C. ^1H NMR (400 MHz, $CDCl_3$, 25 °C, TMS): δ = 7.38 (d, J = 7.5 Hz, 2 H), 7.31 (t, J = 7.6 Hz, 2 H), 7.20 (d, J = 7.3 Hz, 1 H), 4.20–4.10 (m, 1 H), 2.50–2.43 (m, 1 H), 2.14 (s, 3 H), 2.13–2.05 (m, 2 H), 1.90–1.70 (m, 3 H), 1.51–1.40 (m, 3 H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$, 25 °C, TMS): δ = 194.9, 137.5, 128.2, 126.6, 125.6, 109.7, 104.4, 69.3, 36.1, 29.6, 26.9, 23.5, 17.9 ppm. IR (KBr): $\tilde{\nu}$ = 3217, 2938, 1445, 1075, 995, 970, 761, 694 cm^{-1}. HRMS: $[M]^+$ $C_{15}H_{18}O$, theoretical mass 214.1352; found 214.1350.

2-[2-(2-Fluorophenyl)prop-1-enylidene]cyclohexanol (13): Compound **3c** (180 mg, 1 mmol), $[Cu(MeCN)_4][BF_4]$ (31.4 mg, 0.1 mmol, 10 mol-%), $(BuO)_3P$ (54 μL, 0.2 mmol, 20 mol-%) and *i*PrMgBr (2.0 M in Et_2O, 1.25 mL, 2.5 mmol) and 1-fluoro-2-iodobenzene (0.29 mL, 2.5 mmol) were treated according to the general procedure B. After purification, compound **13** (176 mg, 76% yield) was obtained as white solid; m.p. 76 °C. ^1H NMR (400 MHz, $CDCl_3$, 25 °C, TMS): δ = 7.27 (dt, J = 7.7 and 1.7 Hz, 1 H), 7.19–7.13 (m, 1 H), 7.07 (dt, J = 7.7 and 1.2 Hz, 1 H), 7.02–6.96 (m, 1 H), 4.11–4.06 (m, 1 H), 2.46–2.41 (m, 1 H), 2.12 (d, J = 1.4 Hz, 3 H), 2.09–2.04 (m, 2 H), 1.86–1.65 (m, 3 H), 1.46–1.37 (m, 3 H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$, 25 °C, TMS): δ = 196.8, 161.2, 158.8, 128.7, 128.0, 123.8, 115.7, 107.4, 99.0, 69.2, 35.5, 29.6, 26.6, 23.5, 19.9 ppm. IR (KBr): $\tilde{\nu}$ = 3397, 2933, 1490, 1446, 1213, 997, 756 cm^{-1}. HRMS: $[M]^+$ $C_{15}H_{17}OF$, theoretical mass 232.1258; found 232.1258.

Methyl 4-[1-(2-Hydroxycyclohexylidene)prop-1-en-2-yl]benzoate (14): Compound **3c** (180 mg, 1 mmol), $[Cu(MeCN)_4][BF_4]$ (31.4 mg, 0.1 mmol, 10 mol-%), $(BuO)_3P$ (54 μL, 0.2 mmol, 20 mol-%) and *i*PrMgBr (2.0 M in Et_2O, 1.25 mL, 2.5 mmol) and methyl 4-iodobenzoate (654 mg, 2.5 mmol) were treated according to the general procedure B. After purification, compound **14** (168 mg, 62% yield) was obtained as white solid; m.p. 86 °C. ^1H NMR (400 MHz, $CDCl_3$, 25 °C, TMS): δ = 7.94 (d, J = 8.5 Hz, 2 H), 7.41 (d, J = 8.5 Hz, 2 H), 4.20–4.13 (m, 1 H), 3.88 (s, 3 H), 2.51–2.43 (m, 1 H), 2.13 (s, 3 H), 2.13–2.05 (m, 2 H), 1.89–1.82 (m, 1 H), 1.81–1.72 (m, 2 H), 1.53–1.43 (m, 3 H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$, 25 °C, TMS): δ = 196.4, 166.9, 142.5, 129.5, 128.0, 125.4, 110.1, 103.7, 69.3, 51.9, 36.1, 29.4, 26.8, 23.4, 17.7 ppm. IR (KBr): $\tilde{\nu}$ = 3435, 2934, 1720, 1606, 1436, 1279, 1113, 773 cm^{-1}. HRMS: $[M]^+$ $C_{17}H_{20}O_3$, theoretical mass 272.1407; found 272.1406.

4-Ethyl-2,5-dimethylhexa-2,3-dien-1-ol (15): Compound **3d** (154 mg, 1 mmol), $[Cu(MeCN)_4][BF_4]$ (31.4 mg, 0.1 mmol, 10 mol-%), $(BuO)_3P$ (54 μL, 0.2 mmol, 20 mol-%) and *i*PrMgCl (2.0 M in Et_2O, 1 mL, 2 mmol) were treated according to the general procedure A. After purification, compound **15** (138 mg, 90% yield) was obtained as yellow oil. ^1H NMR (400 MHz, $CDCl_3$, 25 °C, TMS): δ = 3.93 (s, 2 H), 2.16–2.06 (m, 1 H), 1.98 (q, J = 7.3 Hz, 2 H), 1.68 (s, 3 H), 0.98 (d, J = 6.7 Hz, 6 H), 0.94 (t, J = 7.3 Hz, 3 H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$, 25 °C, TMS): δ = 193.7, 117.9, 103.5, 63.7, 31.5, 24.0, 22.1, 21.9, 15.9, 12.5 ppm. IR (KBr): $\tilde{\nu}$ = 3436, 2962, 2931, 2870, 1713, 1461, 1384, 1013 cm^{-1}. HRMS: $[M]^+$ $C_{10}H_8O$, theoretical mass 154.1352; found 154.1350.

4-Ethyl-2,5,5-trimethylhexa-2,3-dien-1-ol (16): Compound **3d** (154 mg, 1 mmol), $[Cu(MeCN)_4][BF_4]$ (31.4 mg, 0.1 mmol, 10 mol-%), $(BuO)_3P$ (54 μL, 0.2 mmol, 20 mol-%) and *t*BuMgCl (2.0 M in Et_2O, 1 mL, 2 mmol) were treated according to the general procedure A. After purification, compound **16** (152 mg, 90% yield) was obtained as yellow oil. ^1H NMR (400 MHz, $CDCl_3$, 25 °C, TMS): δ = 3.96 (d, J = 5.6 Hz, 2 H), 2.00 (q, J = 7.3 Hz, 2 H), 1.70 (s, 3 H), 1.04 (s, 9 H), 0.94 (t, J = 7.3 Hz, 3 H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$, 25 °C, TMS): δ = 193.9, 120.6, 103.1, 63.7, 34.1, 29.4, 20.3, 15.9, 12.8 ppm. IR (KBr): $\tilde{\nu}$ = 3342, 2963, 2360, 2341, 1456, 1384, 1009 cm^{-1}. HRMS: $[M]^+$ $C_{11}H_{20}O$, theoretical mass 168.1509; found 168.1511.

2-Methyl-4-phenylhexa-2,3-dien-1-ol (17): Compound **3d** (154 mg, 1 mmol), $[Cu(MeCN)_4][BF_4]$ (31.4 mg, 0.1 mmol, 10 mol-%), $(BuO)_3P$ (54 μL, 0.2 mmol, 20 mol-%) and PhMgCl (1.8 M in THF, 1.1 mL, 2 mmol) were treated according to the general procedure

A. After purification, compound **17** (165 mg, 88% yield) was obtained as yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$, 25 °C, TMS): δ = 7.39 (d, J = 7.8 Hz, 2 H), 7.32 (t, J = 7.6 Hz, 2 H), 7.21 (t, J = 7.3 Hz, 1 H), 4.17–4.10 (d, 2 H), 2.47 (q, J = 7.3 Hz, 2 H), 1.85 (s, 3 H), 1.13 (t, J = 7.3 Hz, 3 H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$, 25 °C, TMS): δ = 199.3, 137.7, 128.7, 127.1, 126.4, 111.3, 105.2, 64.5, 23.7, 16.0, 13.1 ppm. IR (KBr): $\tilde{\nu}$ = 3436, 2964, 2930, 1714, 1384, 1222, 1012, 755, 694 cm^{-1}. HRMS: $[M]^+$ $C_{13}H_{16}O$, theoretical mass 188.1196; found 188.1197.

4-(2-Fluorophenyl)-2-methylhexa-2,3-dien-1-ol (18): Compound **3d** (154 mg, 1 mmol), $[Cu(MeCN)_4][BF_4]$ (31.4 mg, 0.1 mmol, 10 mol-%), $(BuO)_3P$ (54 μL, 0.2 mmol, 20 mol-%), *i*PrMgCl (2.0 M in Et_2O, 1.25 mL, 2.5 mmol) and 1-fluoro-2-iodobenzene (0.29 mL, 2.5 mmol) were treated according to the general procedure B. After purification, compound **18** (175 mg, 85% yield) was obtained as yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$, 25 °C, TMS): δ = 7.28 (m, 1 H), 7.23–7.16 (m, 1 H), 7.09 (m, 1 H), 7.05–6.99 (m, 1 H), 4.09 (s, 2 H), 2.49–2.38 (m, 2 H), 1.79 (s, 3 H), 1.08 (t, J = 7.3 Hz, 3 H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$, 25 °C, TMS): δ = 199.7, 161.1, 158.6, 129.0, 128.1, 123.8, 115.7, 105.2, 102.5, 63.9, 25.3, 15.5, 12.6 ppm. IR (KBr): $\tilde{\nu}$ = 3408, 2966, 1711, 1445, 1384, 1011, 754 cm^{-1}. HRMS: $[M]^+$ $C_{13}H_{15}OF$, theoretical mass 206.1101; found 206.1092. $C_{13}H_{15}OF$ (206.110): calcd. C 75.7, H 7.3; found C 75.7, H 7.5.

4-(3-Methoxyphenyl)-2-methylhexa-2,3-dien-1-ol (19): Compound **3d** (154 mg, 1 mmol), $[Cu(MeCN)_4][BF_4]$ (31.4 mg, 0.1 mmol, 10 mol-%), $(BuO)_3P$ (54 μL, 0.2 mmol, 20 mol-%), *i*PrMgCl (2.0 M in Et_2O, 1.25 mL, 2.5 mmol) and 3-iodoanisole (0.3 mL, 2.5 mmol) were treated according to the general procedure B. After purification, compound **19** (125 mg, 57% yield) was obtained as yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$, 25 °C, TMS): δ = 7.21 (t, J = 7.8 Hz, 1 H), 6.97 (d, J = 7.8 Hz, 1 H), 6.91 (s, 1 H), 6.74 (m, 1 H), 4.12–4.09 (m, 2 H), 3.79 (s, 3 H), 2.43 (q, J = 7.3 Hz, 2 H), 1.82 (s, 3 H), 1.09 (t, J = 7.3 Hz, 3 H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$, 25 °C, TMS): δ = 198.7, 159.5, 138.8, 129.1, 118.5, 112.0, 111.5, 110.6, 104.8, 63.9, 55.1, 23.2, 15.5, 12.6 ppm. IR (KBr): $\tilde{\nu}$ = 3365, 2963, 2931, 2359, 1603, 1455, 1285, 1042, 777, 693 cm^{-1}. HRMS: $[M]^+$ $C_{14}H_{18}O_2$, theoretical mass 218.1301; found 218.1302.

Methyl 4-(6-Hydroxy-5-methylhexa-3,4-dien-3-yl)benzoate (20): Compound **3d** (154 mg, 1 mmol), $[Cu(MeCN)_4][BF_4]$ (31.4 mg, 0.1 mmol, 10 mol-%), $(BuO)_3P$ (54 μL, 0.2 mmol, 20 mol-%), *i*PrMgCl (2.0 M in Et_2O, 1.25 mL, 2.5 mmol) and methyl 4-iodobenzoate (654 mg, 2.5 mmol) were treated according to the general procedure B. After purification, compound **20** (150 mg, 61% yield) was obtained as white solid; m.p. 89 °C. ^{1}H NMR (400 MHz, $CDCl_3$, 25 °C, TMS): δ = 7.94 (d, J = 8.5 Hz, 2 H), 7.41 (d, J = 8.5 Hz, 2 H), 4.18–4.10 (m, 2 H), 3.88 (s, 3 H), 2.45 (q, J = 7.3 Hz, 2 H), 1.84 (s, 3 H), 1.10 (t, J = 7.3 Hz, 3 H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$, 25 °C, TMS): δ = 199.9, 166.9, 142.2, 129.5, 128.1, 125.7, 110.0, 105.3, 63.9, 51.9, 23.0, 15.4, 12.5 ppm. IR (KBr): $\tilde{\nu}$ = 3427, 2967, 2359, 1715, 1605, 1435, 1384, 1279, 1112, 1016 cm^{-1}. HRMS: $[M]^+$ $C_{15}H_{18}O_3$, theoretical mass 246.1250; found 246.1257.

2,5,5-Trimethylhexa-2,3-dien-1-ol (21): Compound **3e** (126 mg, 1 mmol), $[Cu(MeCN)_4][BF_4]$ (31.4 mg, 0.1 mmol, 10 mol-%), $(BuO)_3P$ (54 μL, 0.2 mmol, 20 mol-%) and *t*BuMgCl (2.0 M in Et_2O, 1 mL, 2 mmol) were treated according to the general procedure A. After purification, compound **21** (87 mg, 62% yield) was obtained as yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$, 25 °C, TMS): δ = 5.29–5.25 (m, 1 H), 3.99–3.94 (m, 2 H), 1.69 (d, J = 2.8 Hz, 3 H), 1.01 (s, 9 H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$, 25 °C, TMS): δ = 195.9, 106.6, 102.3, 63.7, 32.1, 30.1, 15.7 ppm. IR (KBr): $\tilde{\nu}$ = 3338, 2959, 1384, 1020, 970 cm^{-1}. HRMS: $[M]^+$ $C_9H_{16}O$, theoretical mass 140.1196; found 140.1195.

2-Methyl-4-phenylbuta-2,3-dien-1-ol (22): Compound **3e** (126 mg, 1 mmol), $[Cu(MeCN)_4][BF_4]$ (31.4 mg, 0.1 mmol, 10 mol-%), $(BuO)_3P$ (54 μL, 0.2 mmol, 20 mol-%) and PhMgBr (1.8 M in THF, 1.1 mL, 2 mmol) were treated according to the general procedure A. After purification, compound **22** (93 mg, 58% yield) was obtained as yellow solid; m.p. 68 °C. ^{1}H NMR (400 MHz, $CDCl_3$, 25 °C, TMS): δ = 7.33–7.27 (m, 4 H), 7.23–7.18 (m, 1 H), 6.30–6.26 (m, 1 H), 4.20–4.11 (m, 2 H), 1.86 (d, J = 2.8 Hz, 3 H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$, 25 °C, TMS): δ = 200.6, 134.6, 128.5, 126.9, 126.6, 104.7, 97.1, 63.7, 15.3 ppm. IR (KBr): $\tilde{\nu}$ = 3401, 2359, 1712, 1439, 1384, 1012, 693 cm^{-1}. HRMS: $[M]^+$ $C_{11}H_{12}O$, theoretical mass 160.0888; found 160.0891.

4-(2-Fluorophenyl)-2-methylbuta-2,3-dien-1-ol (23): Compound **3e** (126 mg, 1 mmol), $[Cu(MeCN)_4][BF_4]$ (31.4 mg, 0.1 mmol, 10 mol-%), $(BuO)_3P$ (54 μL, 0.2 mmol, 20 mol-%), *i*PrMgCl (2.0 M in Et_2O, 1.25 mL, 2.5 mmol) and 1-fluoro-2-iodobenzene (0.29 mL, 2.5 mmol) were treated according to the general procedure B. After purification, compound **23** (70 mg, 39% yield) was obtained as yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$, 25 °C, TMS): δ = 7.34–7.30 (m, 1 H), 7.17–7.11 (m, 1 H), 7.07–6.97 (m, 2 H), 6.46–6.43 (m, 1 H), 4.18–4.09 (m, 2 H), 1.83 (d, J = 2.9 Hz, 3 H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$, 25 °C, TMS): δ = 201.7, 160.8, 158.4, 128.2, 123.9, 115.6, 115.4, 104.4, 89.3, 63.7, 15.2 ppm. IR (KBr): $\tilde{\nu}$ = 3349, 2923, 2360, 1494, 1456, 1384, 1233, 1092, 1031, 753 cm^{-1}. HRMS: $[M]^+$ $C_{11}H_{11}OF$, theoretical mass 178.0788; found 178.0781.

2-*tert*-Butyl-5-methyl-2-phenyl-2,5-dihydrofuran (24): Compound **9** (108 mg, 0.5 mmol) was dissolved in THF (5 mL) under argon. $AuCl_3$ (3 mg, 0.01 mmol, 2 mol-%) was added. The mixture was kept stirring under argon for 24 h. The solvent was removed under reduced pressure. The crude was purified by flash column chromatography (Et_2O/cyclohexane: 1:9) over silica gel to give pure product **24** (72 mg, 67%) as white solid; m.p. 62 °C. ^{1}H NMR (400 MHz, $CDCl_3$, 25 °C, TMS): δ = 7.34 (d, J = 7.2 Hz, 2 H), 7.25 (t, J = 7.2 Hz, 2 H), 7.19 (d, J = 7.2 Hz, 1 H), 6.28 (dd, J = 6.0 and 2.5 Hz, 1 H), 5.71 (dd, J = 6.0 and 1.2 Hz, 1 H), 4.72–4.65 (m, 1 H), 1.31 (d, J = 6.5 Hz, 3 H), 0.89 (s, 9 H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$, 25 °C, TMS): δ = 143.6, 131.3, 130.5, 127.2, 126.8, 126.0, 97.4, 79.7, 36.7, 26.0, 20.4 ppm. IR (KBr): $\tilde{\nu}$ = 2976, 1443, 1384, 1095, 1048, 909, 700 cm^{-1}. HRMS: $[M]^+$ $C_{15}H_{20}O$, theoretical mass 216.1509; found 216.1504.

Supporting Information (see also the footnote on the first page of this article): ^{1}H and ^{13}C NMR spectra of all the propargylic dioxolanones and allenes.

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