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Highly selective formation of propargyl- and allenyltrichlorosilanes and their regiospecific addition to various types of aldehydes: preparation of both allenic and homopropargylic alcohols

Uwe Schneider, Masaharu Sugiura and Shū Kobayashi*

Graduate School of Pharmaceutical Sciences, The University of Tokyo, The HFRE Division, ERATO, Japan Science and Technology Agency (JST), Hongo, Bunkyo-ku, Tokyo 113-0033, Japan

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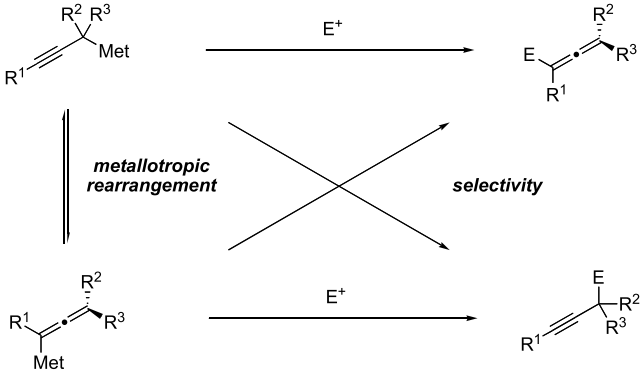
Abstract—The highly selective preparation of propargyl- and allenyltrichlorosilanes via metal-catalyzed silylation of propargyl chloride has been developed. These trichlorosilyl nucleophiles were then shown to add to various types of aldehydes to afford the corresponding allenic and homopropargylic alcohols, respectively, in high yields with complete regiospecificity. Remarkably, these carbon–carbon bond-forming reactions simply proceeded in *N*,*N*-dimethylformamide (DMF) without using any metal catalysts.

1. Introduction

Functionalized allenes and alkynes such as allenic and homopropargylic alcohols have proved to be extremely versatile, key intermediates in modern organic synthesis,[1] for example, in coupling reactions,[2] ene–yne metathesis[3] and formation of heterocycles.[4] Carbon–carbon bond-forming reactions such as the regiospecific addition of propargyl and allenyl nucleophiles to aldehydes provide very attractive routes to these types of compounds.[1] However, drawbacks concerning the use of propargyl and allenyl metal derivatives are potential metallotropic rearrangement[5] between these species and non-regiospecific addition to electrophiles resulting in formation of product mixtures (Scheme 1).[6] Moreover, accessibility to these propargyl and allenyl nucleophiles is highly substrate-dependent.[5,6,7]

Additionally, because of recent demands for safe and environmentally benign organic synthesis, the use of organometallic nucleophiles or metal catalysts is sometimes undesirable, especially for large-scale synthesis. In this context,[8] we recently reported that neutral (non-ionic)



Scheme 1. Potential metallotropic rearrangement and selectivity problem.

Lewis bases such as *N*,*N*-dimethylformamide (DMF), sulfoxides or phosphine oxides promote the nucleophilic addition of allyl- and crotyltrichlorosilanes to aldehydes,[9] imines[10] and *N*-acylhydrazones (Scheme 2).[11]

Remarkably, all these reactions proceeded without using any metal catalysts since these non-ionic Lewis bases, which are defined as neutral coordinate-organocatalysts (*NCO*s),[12] are able to activate the trichlorosilyl nucleophiles by coordination to the silicon atom resulting in the formation of highly reactive hypervalent silicon species. Previously, we also reported selective preparation of both propargyl- and allenyltrichlorosilanes starting from the same corresponding propargyl halides.[13a] Their

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* Corresponding author. Tel.: +81 3 5841 4790; fax: +81 3 5684 0634; e-mail: skobayas@mol.f.u-tokyo.ac.jp

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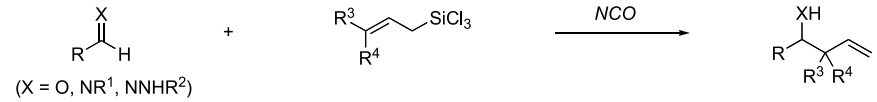


Scheme 2. *NCO*-mediated additions of allyl- and crotyltrichlorosilanes to aldehydes,[9] imines,[10] and *N*-acylhydrazones.[11]

nucleophilic addition to several aldehydes in order to form the corresponding allenic and homopropargylic alcohols, respectively, was also described. However, selectivities, yields and substrate scope still remained to be improved. Herein, we report a more practical and greatly improved protocol for the silylation of propargyl chloride resulting in significantly enhanced selectivities. Moreover, the nucleophilic, regiospecific addition of both propargyl- and allenyltrichlorosilanes to various types of aldehydes afforded the corresponding allenic or homopropargylic alcohols exclusively.

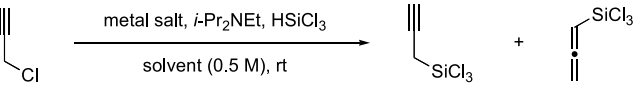
2. Results and discussion

The preparation of propargyl and allenyl organometallics from the corresponding propargyl halides typically requires stoichiometric amounts of metals.[5–7] In contrast, our procedure needs only a catalytic amount of a metal salt together with an amine base and trichlorosilane. In the literature, it has been reported that propargyl chloride reacts with trichlorosilane in the presence of triethylamine and copper(I) chloride under thermal conditions (THF, 60 °C, 12 h) to give a mixture of propargyltrichlorosilane (**2**) and allenyltrichlorosilane (**3**; ratio **2**:**3**=86:14).[14] It is also known that the distillation of a mixture of compounds **2** and **3** provokes (further) isomerization towards product **3** (ratio **2**:**3**=33:67).[13a] We wanted to reinvestigate the silylation procedure of propargyl chloride based on our previous work in order to develop a more practical protocol and improve selectivities for trichlorosilanes **2** and **3** (Table 1).

The initial solvent screening revealed that the silylation proceeded efficiently only in non-polar solvents such as diethyl ether (EE) or *t*-butyl methyl ether (TBME). On the other hand, in acetonitrile or propionitrile the reaction was sluggish, whereas in dichloromethane (DCM), tetrahydrofuran (THF) or *N*,*N*-dimethylformamide (DMF) the silylation scarcely proceeded. In our previous work, a slight excess of the amine base with respect to trichlorosilane in a solvent mixture by using a copper(I) catalyst was necessary to obtain a high selectivity in favor of product **2** (Table 1, entry 1). We found that under similar conditions in EE as a sole solvent the reaction was faster, but less selective (entry 2). We, therefore, reinvestigated the silylation conditions and after extensive optimization, it was found that a slight excess of trichlorosilane with respect to Hünig's base in EE afforded propargyltrichlorosilane (**2**) exclusively (entry 3). Even more significantly, only 1 mol% CuCl was sufficient to catalyze the transformation while maintaining exceptional selectivity (entry 4). Previously, we found that the Ni(II)-catalyzed formation of allenyltrichlorosilane (**3**) as the major product (moderate to good selectivities) was highly solvent- and temperature-dependent (entries 5 and 6). However, with our newly optimized protocol just by switching from Cu(I) to Ni(II), the exclusive formation of trichlorosilane **3** was observed (entry 7). Here again, it is noted that only 1 mol% of the Ni(II) catalyst was sufficient to promote this highly selective silylation (entry 8).

Next, we turned our attention towards the use of in situ prepared trichlorosilyl nucleophiles **2** and **3** in the reaction with aldehydes in DMF for the synthesis of both allenic and homopropargylic alcohols. We have previously demonstrated that allyltrichlorosilane regiospecifically reacts with various aldehydes in DMF without metal catalysis to afford the corresponding homoallylic alcohols in high yields.[9] In these reactions, DMF might coordinate to the silicon atom

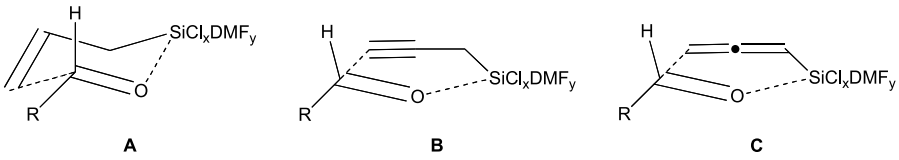
Table 1. Optimization of the selective silylation of propargyl chloride (**1**)



1 **2** **3**

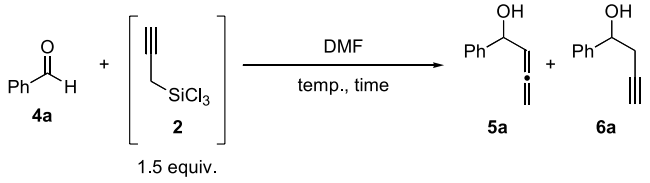
Entry	Metal salt (mol%)	*i*-Pr_2NEt (equiv)	$HSiCl_3$ (equiv)	Solvent[a]	Time (h)	Conversion (%)[b]	Ratio **2**:**3**[b]
1[c]	CuCl (3)	1.0	1.1	EE/EtCN	12	nd	94:6
2	CuCl (5)	2.0	1.5	EE	6–8	>95	85:15
3	CuCl (5)	2.0	2.2	EE	6	>99	>99:1
4	CuCl (1)	2.0	2.2	EE	12	>99	>99:1
5[c]	NiL_2 (3)[d]	1.1	1.0	THF[e]	12	nd	3:>97
6[c]	$Ni(acac)_2$ (3)	1.1	1.0	EE	n.d	nd	9:91
7	$Ni(acac)_2$ (5)	2.0	2.2	EE	6	>99	1:>99
8	$Ni(acac)_2$ (1)	2.0	2.2	EE	12	>99	1:>99

[a] EE=diethyl ether.
[b] Determined by ^1H NMR analysis by aliquot dilution in $CDCl_3$.
[c] Ref. 13a.
[d] L=PhC(O)CH=C(O)Ph.
[e] The reaction was carried out under reflux.



Scheme 3. Assumed transition states of the reactions between various trichlorosilanes and aldehydes.[9,13a]

Table 2. DMF-mediated allenylation of benzaldehyde (**4a**) with in situ prepared propargyltrichlorosilane (**2**)



Entry	DMF (M)	Temperature (°C)	Time (h)	Yield (%)	Ratio **5a**:**6a**[a]
1[b]	0.25	0	12	60	91:9
2	0.5	10	12–48	55–63	>99:1
3	0.4	10	24	72	>99:1
4	0.2	10	24	80–84	>99:1
5	0.1	10	24	83–89	>99:1
6	0.1	0	24	92	>99:1
7[c]	0.1	0	24	80	>99:1

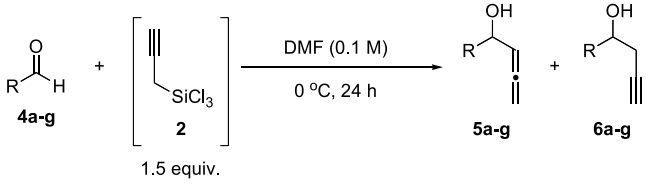
[a] Determined by ^{1}H NMR analysis of the isolated material.
[b] Best previously data published by our group: 1.2 equiv of **2** were used (see Ref. 13a).
[c] Three equivalents of in situ prepared propargyltrichlorosilane (**2**) were used.

of the allyltrichlorosilane resulting in the formation of a highly reactive hypervalent silicon species, which in turn smoothly adds to aldehydes via a supposed cyclic transition state **A** (Scheme 3). We assumed that the same kind of intermediates could be formed with trichlorosilyl nucleophiles **2** and **3** and these transition states **B** and **C** are represented in Scheme 3.[†,13a]

We first examined the conditions for the reaction between in situ prepared propargyltrichlorosilane (**2**) and benzaldehyde (**4a**) as a model substrate, the results are shown in Table 2.

The allenylation proceeded smoothly in DMF at 10 °C with moderate yields (entry 2), which are in the same range as our previous result (entry 1). Whilst the selectivity was lower previously (entry 1), now exclusive formation of allenic alcohol **5a** was observed (entry 2). Further optimization revealed the importance of the amount of DMF; with gradually increasing amounts of DMF, which is considered to be both solvent and an *NCO*, the yields were significantly improved to 89% (entries 3–5). This improvement might be attributed to both a more homogenous reaction mixture and more efficient activation of nucleophile **2** by DMF.[‡] Finally, conducting the reaction at 0 °C provided the highest yield (92%, entry 6), whereas the use of 3 equiv of nucleophile **2** (instead of 1.5 equiv) was less efficient, probably a solubility issue (entry 7). It is, however, remarkable that in all cases allenic alcohol **5a** was the single product; no trace of homopropargylic alcohol **6a** could be detected.[§]

Table 3. DMF-mediated allenylation of various aldehydes **4** with in situ prepared propargyltrichlorosilane (**2**)



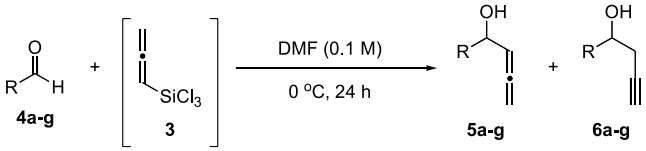
Entry	Substrate **4**: R	Yield (%)	Ratio **5**:**6**[a]
1	**4a**: Ph	92	>99:1
2	**4b**: 4-MeOC$_6$H$_4$	88	>99:1
3	**4c**: 3-Furyl	55	>99:1
4	**4d**: *n*-Octyl	80	>99:1
5	**4e**: *c*-Hexyl	61	>99:1
6	**4f**: PhCH$_2$CH$_2$	90	>99:1
7	**4g**: (*E*)-*n*-PrCH=CH	79	>99:1

[a] Determined by ^{1}H NMR analysis of the isolated material.

Next, we extended the optimized allenylation conditions to various aldehydes, the results are represented in Table 3.

[†] In these supposed S_E2' type additions, propargyltrichlorosilane (**2**) and allenyltrichlorosilane (**3**) would convert aldehydes into the corresponding allenic and homopropargylic alcohols, respectively.
[‡] It should be pointed out that the same reaction carried out in a non-coordinating solvent such as EE or DCM (instead of DMF), under otherwise identical conditions, proceeded only scarcely (yields <5%), thereby underlining the crucial role of DMF.
[§] In this context, it is important to mention that we carried out a control experiment with benzaldehyde (**4a**) by using a solution of **2** obtained after vacuum transfer at low temperature (instead of the supernatant from in situ preparation of **2**, that might contain a trace of Cu(I)). Since we observed that the reaction proceeded smoothly (even though the yield was slightly lower) while maintaining the exclusive regiospecificity, it can be considered that a trace amount of the metal salt (potentially present) does not affect the reaction outcome.

Table 4. DMF-mediated propargylation of various aldehydes **4** with in situ prepared allenyltrichlorosilane (**3**)



Entry	Substrate **4**: R	Yield (%)	Ratio **5**:**6**[a]
1	**4a**: Ph	90	1:>99
2	**4b**: 4-MeO–C_6H_4	78	1:>99
3	**4c**: 3-Furyl	65	1:>99
4	**4d**: *n*-Octyl	79	1:>99
5	**4e**: *c*-Hexyl	56	1:>99
6	**4f**: $PhCH_2CH_2$	72	1:>99
7	**4g**: (*E*)-*n*-propyl–CH=CH	70	1:>99

[a] Determined by ^{1}H NMR analysis of the isolated material.

We were delighted to find that a wide range of substrates tolerated the optimized reaction conditions. Aromatic aldehydes **4a**,**b** and aliphatic aldehyde **4f**, containing an aromatic moiety, were excellent substrates (88–92% yield, entries 1,2 and 6). On the other hand, heteroaromatic aldehyde **4c** and the branched sterically demanding aliphatic aldehyde **4e** gave lower yields (entries 3 and 5). Finally, aliphatic aldehyde **4d** and α,β-unsaturated substrate **4g** proved to be very reactive under the conditions employed providing high yields of the desired products (79–80% yields, entries 4 and 7). It is notable that in all cases the allenylation reactions proceeded with complete regiospecificity; allenic alcohols **5a**–**g** were found to be the single products and no traces of the corresponding homopropargylic alcohols **6a**–**g** could be observed.

We then examined the substrate generality concerning the propargylation of several aldehydes. We employed the optimized allenylation conditions, and simply used in situ prepared allenyltrichlorosilane (**3**) instead of nucleophile **2** (Table 4).

As was the case in the previous allenylation study, several aldehydes were reactive towards propargylation with trichlorosilyl nucleophile **3**. Benzaldehyde (**4a**) proved to be the best substrate providing the corresponding homopropargylic alcohol **6a** exclusively in 90% yield (entry 1). Although the sterically hindered compound **4e** gave a little lower yield (entry 5), all other aldehydes were found to give the corresponding homopropargylic alcohols **6** in good yields (entries 2–4, 6, and 7). In all cases, the reactions proceeded with complete regiospecificity.[¶] This remarkable regiospecificity in both the allenylation and the propargylation of various aldehydes with trichlorosilyl nucleophiles **2** and **3** might be explained by the approach of the silanes and aldehydes shown in Scheme 3.

[¶] As in the earlier study, a control experiment with benzaldehyde (**4a**) by using a solution of **3** obtained after vacuum transfer at low temperature (instead of the supernatant from in situ preparation of **3**, that might contain a trace of Ni(II)), revealed comparable reactivity along with the same exceptional regiospecificity. This confirms that a trace amount of Ni(II), potentially present, does not influence the course of the reaction.

3. Conclusion

In summary, the highly selective preparation of both propargyl- and allenyltrichlorosilanes via metal-catalyzed silylation of propargyl chloride has been developed. These trichlorosilyl nucleophiles proved to add regiospecifically to various types of aldehydes to afford the corresponding allenic and homopropargylic alcohols, respectively, in high yields. Remarkably, these organocatalytic carbon–carbon bond-forming reactions simply proceeded in *N*,*N*-dimethylformamide (DMF) without using any metal catalysts.

4. Experimental

4.1. General information

^{1}H and ^{13}C NMR spectra were recorded on JEOL JNM-LA300 or JNM-LA400 spectrometers in $CDCl_3$ unless otherwise noted. Tetramethylsilane (TMS; $\delta=0$ ppm) and $CDCl_3$ ($\delta=77.0$ ppm) served as internal standards for ^{1}H NMR and for ^{13}C NMR, respectively. 1,2,4,5-Tetrachlorobenzene was used as internal standard for monitoring, with time, by ^{1}H NMR analysis the in situ preparation of trichlorosilanes **2** and **3**. IR spectra were measured with a JASCO FT/IR-610 infrared spectrometer. High-resolution electrospray ionization mass spectroscopy analysis HRMS (ESI) was carried out using a Bruker Daltonics BioTOF II mass spectrometer. Column chromatography was conducted on Silica gel 60 (Merck), and preparative thin layer chromatography (PTLC) was carried out using Wakogel B-5F. All reactions were conducted under an argon atmosphere in dried glassware. Dry diethylether (EE) was purchased from Wako Co. Ltd and was used without distillation; dry *N*,*N*-dimethylformamide (DMF) was purchased from Wako Co. Ltd and was used after distillation from barium(II) oxide. 3-Chloroprop-1-yne (**1**) and *N*,*N*-diisopropylethylamine were purchased from Tokyo Kasei Kogyo Co. Ltd and were used after distillation. Trichlorosilane was purchased from Tokyo Kasei Kogyo Co. Ltd and was used without distillation. Copper(I) chloride and bis(2,4-pentanedionato)nickel(II) were dried at 50 °C under vacuum for 12 h before transfer into a glovebox. All other solvents and reagents were purified and dried according to standard procedures.

4.2. Procedure for the selective in situ preparation of trichlorosilanes 2 and 3

To a stirred suspension of dry copper(I) chloride (10.0 mg, 100 μmol, 5 mol%) or dry bis(2,4-pentanedionato)nickel(II) (25.7 mg, 100 μmol, 5 mol%) in dry EE (4 mL, 0.5 M) at room temperature were added dropwise *N*,*N*-diisopropylethylamine (680 μL, 4.0 mmol, 2.0 equiv), 3-chloroprop-1-yne (**1**; 143 μL, 2.0 mmol, 1.0 equiv) and trichlorosilane (445 μL, 4.4 mmol, 2.2 equiv), successively. The mixture was stirred at room temperature for 6 h and the product ratios **2**:**3** were determined by ^{1}H NMR analysis of an aliquot diluted with $CDCl_3$. Under the indicated optimized conditions, compound **1** was completely consumed (>99% conversion) and exclusive formation of propargyltrichlorosilane (**2**; by using CuCl) or allenyltrichlorosilane (**3**; by

using $Ni(acac)_2$) was observed (~75% NMR yield, >99:1 ratios for each isomer).

4.3. Procedure for the selective synthesis of allenic alcohols 5 or homopropargylic alcohols 6

The supernatant solution of in situ prepared trichlorosilanes **2** or **3** (1.5 equiv) in EE was added dropwise via a syringe to stirred solutions of the corresponding aldehydes **4a–g** (1.0 equiv) in DMF (0.1 M with respect to aldehydes **4a–g**) at 0 °C. The mixtures were stirred at 0 °C for 24 h, and quenched by dropwise addition of aq HCl (1 M, 1 mL per 0.5 mmoL of used nucleophile **2** or **3**). After stirring at 0 °C for an additional 30 min, the mixtures were warmed to room temperature and extracted with EE (three times, after addition of H_2O). The combined organic layers were washed (brine), dried (Na_2SO_4), filtered and concentrated in vacuo. The residues were purified by preparative thin-layer chromatography (PTLC; eluant: *n*-hexane/ethyl acetate 5:1–15:1) to afford the corresponding allenic alcohols **5a–g** (by using nucleophile **2**) or the corresponding homopropargylic alcohols **6a–g** (by using nucleophile **3**) exclusively.

4.4. Analytical data for the synthesized compounds

4.4.1. Trichloro(prop-2-ynyl)silane (2).[13a,d] ^1H NMR ($CDCl_3$) δ 2.10 (t, $J=3.3$ Hz, 1H), 2.44 (d, $J=3.3$ Hz, 2H).

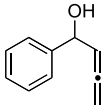
2

4.4.2. Trichloro(propa-1,2-dienyl)silane (3).[13a,d] ^1H NMR ($CDCl_3$) δ 4.91 (d, $J=6.9$ Hz, 2H), 5.35 (t, $J=6.9$ Hz, 1H).

3

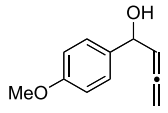
4.5. Allenic alcohols 5a–g

4.5.1. 1-Phenylbuta-2,3-dien-1-ol (5a).[13a,d,16] Colorless oil; ^1H NMR ($CDCl_3$) δ 2.09 (br s, 1H), 4.86 (ddd, $J=1.0$, 2.5, 6.4 Hz, 2H), 5.21 (dt, $J=2.5$, 6.4 Hz, 1H), 5.38 (dt, $J=6.4$, 6.8 Hz, 1H), 7.20–7.49 (m, 5H); ^{13}C NMR ($CDCl_3$) δ 71.9, 78.2, 95.2, 126.1, 127.8, 128.5, 142.8, 207.1; IR (neat) 3399, 3030, 1955, 1677, 1494, 1451, 1360, 1264, 1187, 1025, 852, 700 cm^{-1}; HRMS (ESI) calcd for $C_{10}H_{10}O$ $[M+H]^+$: *m/z* 147.0810, found: *m/z* 147.0814.



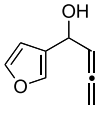
5a

4.5.2. 1-(4-Methoxyphenyl)buta-2,3-dien-1-ol (5b).[16] Pale yellow oil; ^1H NMR ($CDCl_3$) δ 2.12 (br s, 1H), 3.80 (s, 3H), 4.87–4.92 (m, 2H), 5.18 (s, 1H), 5.40 (dt, $J=6.5$, 6.8 Hz, 1H), 6.85 (d, $J=8.7$ Hz, 2H), 7.29 (d, $J=8.7$ Hz, 2H); ^{13}C NMR ($CDCl_3$) δ 55.4, 71.8, 78.1, 95.3, 113.9, 127.2, 135.0, 159.1, 206.9; IR (neat) 3402, 2837, 1955, 1610, 1589, 1514, 1247, 1174, 1033 cm^{-1}; HRMS (ESI) calcd for $C_{11}H_{12}O_2$ $[M+H]^+$: *m/z* 177.0916, found: *m/z* 177.0915.



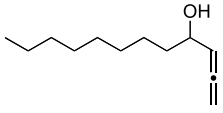
5b

4.5.3. 1-(Furan-3-yl)buta-2,3-dien-1-ol (5c). Pale yellow oil; ^1H NMR ($CDCl_3$) δ 1.98 (br s, 1H), 4.84–4.90 (m, 2H), 5.19 (s, 1H), 5.38 (q, $J=6.5$ Hz, 1H), 6.40 (d, $J=1.0$ Hz, 1H), 7.37 (s, 1H), 7.45 (s, 1H); ^{13}C NMR ($CDCl_3$) δ 67.9, 78.0, 95.1, 107.8, 128.1, 139.0, 143.1, 206.5; IR (neat) 3380, 2907, 1957, 1497, 1451, 1000, 867 cm^{-1}; HRMS (ESI) calcd for $C_8H_8O_2$ $[M+H]^+$: *m/z* 137.0603, found: *m/z* 137.0602.



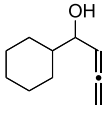
5c

4.5.4. Dodeca-1,2-dien-4-ol (5d).[13a] Colorless oil; ^1H NMR ($CDCl_3$) δ 0.81 (t, $J=6.6$ Hz, 3H), 1.23–1.85 (m, 15H), 4.07–4.15 (m, 1H), 4.78 (dd, $J=2.3$, 6.4 Hz, 2H), 5.17 (q, $J=6.4$ Hz, 1H); ^{13}C NMR ($CDCl_3$) δ 14.1, 22.8, 25.5, 29.2, 29.5, 29.9, 32.0, 37.6, 70.0, 77.6, 95.0, 206.7; IR (neat) 3334, 2929, 1956, 1464, 1005, 841 cm^{-1}; HRMS (ESI) calcd for $C_{12}H_{22}O$ $[M+H]^+$: *m/z* 183.1749, found: *m/z* 183.1748.



5d

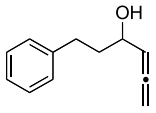
4.5.5. 1-Cyclohexylbuta-2,3-dien-1-ol (5e).[13d] Colorless oil; ^1H NMR ($CDCl_3$) δ 0.87–1.26 (m, 10H), 1.30–1.47 (m, 1H), 1.67 (s, 1H), 3.87 (ddd, $J=2.1$, 6.4, 6.8 Hz, 1H), 4.74 (dd, $J=2.1$, 6.8 Hz, 2H), 5.14 (dt, $J=6.4$, 6.8 Hz, 1H); ^{13}C NMR ($CDCl_3$) δ 26.0, 26.6, 28.7, 44.0, 74.1, 77.5, 93.4, 207.2; IR (neat) 3360, 2924, 1955, 1453, 1015, 836, 700 cm^{-1}; HRMS (ESI) calcd for $C_{10}H_{16}O$ $[M+H]^+$: *m/z* 153.1279, found: *m/z* 153.1279.



5e

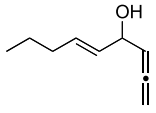
4.5.6. 1-Phenylhexa-4,5-dien-3-ol (5f).[13a,d] Colorless oil; ^1H NMR ($CDCl_3$) δ 1.69 (br s, 1H), 1.82 (dt, $J=6.9$, 7.8 Hz,

2H), 2.67 (dt, J=4.4, 7.8 Hz, 2H), 4.08–4.15 (m, 1H), 4.80 (dd, J=2.5, 6.8 Hz, 2H), 5.20 (dt, J=6.4, 6.8 Hz, 1H), 7.11–7.27 (m, 5H); ^{13}C NMR ($CDCl_3$) δ 31.7, 39.0, 68.9, 77.8, 94.7, 125.9, 128.4, 128.5, 141.8, 207.1; IR (neat) 3384, 2928, 1955, 1716, 1454, 849, 700 cm^{-1}; HRMS (ESI) calcd for $C_{12}H_{14}O$ $[M+H]^+$: m/z 175.1123, found: m/z 175.1125.



5f

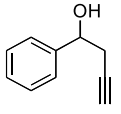
4.5.7. (*E*)-Nona-1,2,5-trien-4-ol (5g). Pale yellow oil; ^{1}H NMR ($CDCl_3$) δ 0.83 (t, J=7.0 Hz, 3H), 1.36 (q, J=7.0 Hz, 2H), 1.89–2.05 (m, 3H), 4.83 (dd, J=2.5, 6.0 Hz, 2H), 5.28 (dt, J=2.5, 6.0 Hz, 1H), 5.59 (dd, J=6.3, 15.7 Hz, 1H), 5.70–5.78 (m, 1H), 5.99 (dt, J=6.6, 15.7 Hz, 1H); ^{13}C NMR ($CDCl_3$) δ 13.5, 21.2, 35.3, 71.6, 78.2, 95.3, 129.0, 135.4, 207.0; IR (neat) 3365, 3011, 2891, 1952, 1498, 1453, 1003, 844, 703 cm^{-1}; HRMS (ESI) calcd for $C_9H_{14}O$ $[M+H]^+$: m/z 139.1123, found: m/z 139.1120.



5g

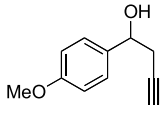
4.6. Homopropargylic alcohols 6a–g

4.6.1. 1-Phenylbut-3-yn-1-ol (6a).[13a,15] Colorless oil; ^{1}H NMR ($CDCl_3$) δ 2.01 (t, J=2.7 Hz, 1H), 2.25 (br s, 1H), 2.58 (dd, J=2.7, 6.3 Hz, 2H), 4.81 (t, J=6.3 Hz, 1H), 7.20–7.37 (m, 5H); ^{13}C NMR ($CDCl_3$) δ 29.5, 71.0, 72.3, 80.6, 125.7, 128.0, 128.5, 142.4; IR (neat) 3294, 3032, 2913, 2118, 1668, 1625, 1494, 1453, 1048, 756, 700 cm^{-1}; HRMS (ESI) calcd for $C_{10}H_{10}O$ $[M+H]^+$: m/z 147.0810, found: m/z 147.0815.



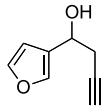
6a

4.6.2. 1-(4-Methoxyphenyl)but-3-yn-1-ol (6b).[15] Pale yellow oil; ^{1}H NMR ($CDCl_3$) δ 1.96 (t, J=2.5 Hz, 1H), 2.48–2.64 (m, 3H), 3.71 (s, 3H), 4.74 (t, J=6.4 Hz, 1H), 6.79 (d, J=8.9 Hz, 2H), 7.24 (d, J=8.9 Hz, 2H); ^{13}C NMR ($CDCl_3$) δ 29.5, 55.7, 71.2, 72.4, 80.4, 113.8, 126.9, 135.2, 159.4; IR (neat) 3443, 3290, 2959, 2919, 2832, 2110, 1603, 1245, 1026, 800 cm^{-1}; HRMS (ESI) calcd for $C_{11}H_{12}O_2$ $[M+H]^+$: m/z 177.0916, found: m/z 177.0918.



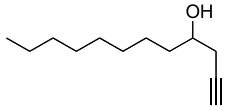
6b

4.6.3. 1-(Furan-3-yl)but-3-yn-1-ol (6c). Pale yellow oil; ^{1}H NMR ($CDCl_3$) δ 1.90 (br s, 1H), 2.02 (d, J=2.3 Hz, 1H), 2.58–2.60 (m, 2H), 4.78 (t, J=6.2 Hz, 1H), 6.38 (d, J=1.0 Hz, 1H), 7.33 (s, 1H), 7.40 (s, 1H); ^{13}C NMR ($CDCl_3$) 28.3, 65.3, 71.2, 80.3, 108.4, 127.3, 139.4, 143.4; IR (neat) 3400, 3308, 2111, 1450, 750, 695 cm^{-1}; HRMS (ESI) calcd for $C_8H_8O_2$ $[M+H]^+$: m/z 137.0603, found: m/z 137.0612.



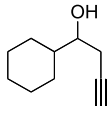
6c

4.6.4. Dodec-1-yn-4-ol (6d).[13a] Colorless oil; ^{1}H NMR ($CDCl_3$) δ 0.81 (t, J=6.4 Hz, 3H), 1.19–1.70 (m, 14H), 1.98 (t, J=2.5 Hz, 1H), 2.15–2.41 (m, 3H), 3.70 (tt, J=5.7, 6.3 Hz, 1H); ^{13}C NMR ($CDCl_3$) δ 14.1, 22.5, 25.6, 27.2, 28.8, 29.2, 29.8, 31.8, 36.0, 69.7, 70.5, 81.0; IR (neat) 3330, 2940, 2108, 1455, 828, 700 cm^{-1}; HRMS (ESI) calcd for $C_{12}H_{22}O$ $[M+H]^+$: m/z 183.1749, found: m/z 183.1750.



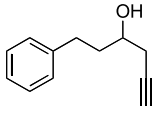
6d

4.6.5. 1-Cyclohexylbut-3-yn-1-ol (6e). Colorless oil; ^{1}H NMR ($CDCl_3$) δ 0.95–1.82 (m, 12H), 1.98 (t, J=2.3 Hz, 1H), 2.32 (dd, J=2.3, 6.0 Hz, 2H), 4.77–4.89 (m, 1H); ^{13}C NMR ($CDCl_3$) δ 26.0, 26.6, 28.6, 29.2, 45.4, 70.8, 72.9, 81.6; IR (neat) 3365, 2919, 2109, 1450, 1022, 839, 715 cm^{-1}; HRMS (ESI) calcd for $C_{10}H_{16}O$ $[M+H]^+$: m/z 153.1279, found: m/z 153.1277.



6e

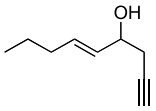
4.6.6. 1-Phenylhex-5-yn-3-ol (6f).[13a] Pale yellow oil; ^{1}H NMR ($CDCl_3$) δ 1.78–1.89 (m, 2H), 1.99 (br s, 1H), 2.05 (t, J=2.5 Hz, 1H), 2.27–2.45 (m, 2H), 2.61–2.83 (m, 2H), 3.78 (tt, J=5.7, 12.0 Hz, 1H), 7.11–7.25 (m, 5H); ^{13}C NMR ($CDCl_3$) δ 28.1, 31.9, 37.5, 69.0, 71.2, 80.5, 126.0, 128.2, 128.4, 141.5; IR (neat) 3385, 2920, 2115, 1710, 1451, 833, 699 cm^{-1}; HRMS (ESI) calcd for $C_{12}H_{14}O$ $[M+H]^+$: m/z 175.1123, found: m/z 175.1124.



6f

4.6.7. (*E*)-Non-5-en-1-yn-4-ol (6g). Pale yellow oil; ^{1}H NMR ($CDCl_3$) δ 0.82 (t, J=7.2 Hz, 3H), 1.33 (q, J=7.2 Hz, 2H), 1.87–2.10 (m, 3H), 1.98 (t, J=2.7 Hz, 1H), 2.37 (dd,

J=2.7, 6.0 Hz, 2H), 4.18 (dt, J=6.0, 6.4 Hz, 1H), 5.47 (dd, J=6.4, 15.4 Hz, 1H), 5.64 (dt, J=6.4, 15.4 Hz, 1H); ^{13}C NMR ($CDCl_3$) δ 13.6, 21.1, 29.4, 35.2, 71.1, 72.5, 80.6, 129.1, 133.7; IR (neat) 3370, 3011, 2889, 2107, 1498, 1456, 1004, 840, 709 cm^{-1}; HRMS (ESI) calcd for $C_9H_{14}O$ [M+H]$^+$: m/z 139.1123, found: m/z 139.1123.



6g

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