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Heteropolyacid-Catalyzed Direct Deoxygenation of Propargyl and Allyl Alcohols

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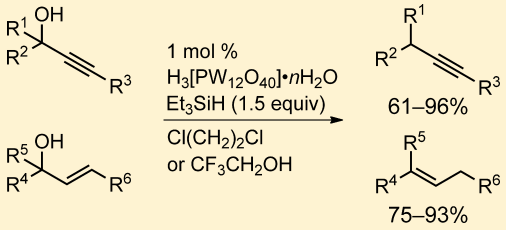
Supporting Information

ABSTRACT: The combination of $H_3[PW_{12}O_{40}]\cdot nH_2O$ (1 mol %) and Et_3SiH led to the direct catalytic deoxygenation of propargyl alcohols, in which proper solvent selection $Cl(CH_2)_2Cl$ vs CF_3CH_2OH was the key to obtaining better product yields. Under similar conditions, the deoxygenation of allyl alcohols proceeded to give thermodynamically stable alkenes with migration of the double bonds in good yields.



The heteropolyacids and their corresponding salts have received increasing attention as clean and safe catalysts due to their nontoxicity, high stability, and ease of handling.[1] Among them, the most popular are the Keggin-type heteropolyacids with the general formula $H_n[XM_{12}O_{40}]$, where X represents the central heteroatom and M represents the addenda atoms, and their catalytic activity is easily tunable by the arrangement of each component. They possess strong acidity and redox properties that have been applied to several types of organic reactions. One of their most effective uses is for catalytic oxidation reactions, and some of them have been performed on an industrial scale.[2] In contrast, the reactivity of heteropolyacids in combination with reducing reagents is relatively unknown; examples are limited to the deoxygenation of carbonyl compounds in a hydrogen atmosphere[3] and the 1,2-reduction of enones using $NaBH_4$.[4] In this communication, we present a new combination of $H_3[PW_{12}O_{40}]\cdot nH_2O$ (1 mol %) with Et_3SiH that produces the deoxygenation of propargyl and allyl alcohols under mild conditions (rt to 50 °C, <6 h).

As a part of our ongoing program directed toward the development of new catalytic transformations of propargyl and allyl alcohols,[5] we recently reported that heteropolycompounds alone promoted the stereoselective Meyer–Schuster rearrangement of propargyl alcohols to give *Z*- and *E*-α,β-unsaturated carbonyl compounds in good yields (see Scheme 1 for a typical example).[6]

During this study, we observed the formation of the dimeric derivative **3a** from **1a**, which was hypothesized as obtained via the propargyl cation species. Therefore, we undertook the development of novel reactions using these generated reactive propargyl cations. While intensively studying the combination of heteropolyacids with various nucleophiles, we found that the combination of a catalytic amount (1 mol %) of $Na_3[PMo_{12}O_{40}]\cdot nH_2O$ and Et_3SiH (1.5 equiv) achieved the deoxygenation of **1a** within 0.5 h to give the alkyne **4a** in 64% yield (Table 1, entry 1). It was intriguing that heteropolyacids, which mainly served as oxidizing agents, were compatible with the active hydride source, Et_3SiH. Furthermore, although the heteropolyacids have very low pK_a values, similar to that of sulfuric acid,[7] the reaction of **1a** using sulfuric acid (1 mol %) instead of $Na_3[PMo_{12}O_{40}]\cdot nH_2O$ afforded the dimeric ether **3a** in 68% yield without the formation of **4a** (entry 7). To optimize the reaction conditions, the validity of various commercially available heteropolycompounds for the reaction of **1a** was screened in $Cl(CH_2)_2Cl$. The protonated forms of the heteropolycompounds generally provided better yields of **4a** in shorter times than the corresponding sodium salts

Scheme 1. Heteropolyacid-Catalyzed Rearrangement of Propargyl Alcohols

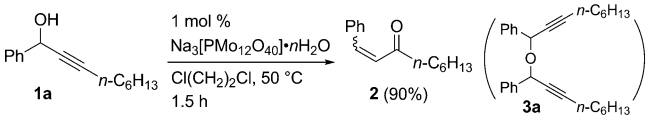
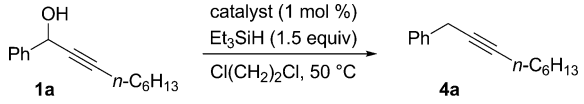


Table 1. Preliminary Survey for the Deoxygenation of 1a into 4a



entry	catalyst	time (h)	yield (%)
1	$Na_3[PMo_{12}O_{40}]\cdot nH_2O$	0.5	64
2	$H_3[PMo_{12}O_{40}]\cdot nH_2O$	5 min	62
3	$Na_4[SiMo_{12}O_{40}]\cdot nH_2O$	3	35
4	$H_4[SiMo_{12}O_{40}]\cdot nH_2O$	0.5	63
5	$Na_3[PW_{12}O_{40}]\cdot nH_2O$	7.5	37
6	$H_3[PW_{12}O_{40}]\cdot nH_2O$	0.75	84
7	H_2SO_4	7.5	0
8	none	7	<1

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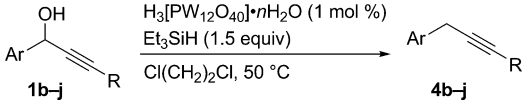
(entries 1 vs 2, 3 vs 4, and 5 vs 6). In particular, $H_3[PW_{12}O_{40}]\cdot nH_2O$ proved to be highly active, affording **4a** in 84% yield (entry 6). Among various silicon-based reductants, such as Et_3SiH, Me_2PhSiH, $(EtO)_3SiH$, and polymethylhydrosiloxane, Et_3SiH was found to be the most effective. It is worth noting that neither the 1,3-rearrangement of the hydroxyl group nor the isomerization into the allene occurred under these conditions.

Next, the reactivity of diverse secondary propargyl alcohols **1b–j** was tested using $H_3[PW_{12}O_{40}]\cdot nH_2O$ (1 mol %) and Et_3SiH (1.5 equiv) in $Cl(CH_2)_2Cl$; these results are shown in Table 2. Under standard conditions, the reactions reached

Table 2. $H_3[PW_{12}O_{40}]\cdot nH_2O$-Catalyzed Deoxygenation of Secondary Propargyl Alcohols 1b–j



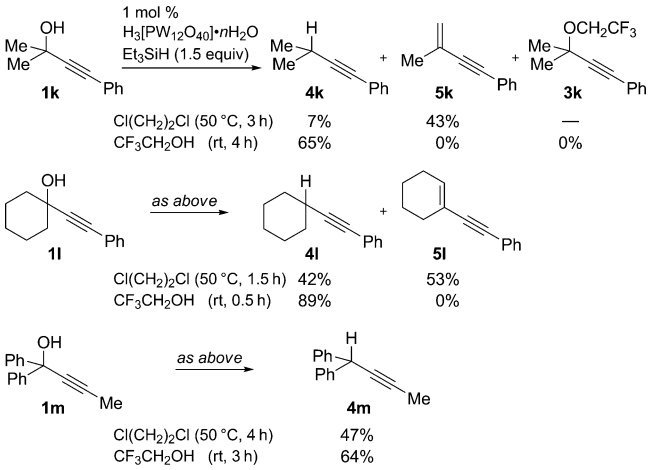
entry		Ar	R	time (h)		yield (%)
1	**1b**	*p*-$MeOC_6H_4$	*n*-C_6H_{13}	5 min	**4b**	91
2	**1c**	*p*-MeC_6H_4	*n*-C_6H_{13}	0.25	**4c**	96
3	**1d**	*p*-ClC_6H_4	*n*-C_6H_{13}	2	**4d**	88
4[a]	**1e**	*m*-ClC_6H_4	*n*-C_6H_{13}	1.75	**4e**	61 (79)[b]
5	**1f**	Ph	Ph	1	**4f**	77
6	**1g**	*p*-ClC_6H_4	Ph	0.75	**4g**	73
7	**1h**	1-naphthyl	Ph	0.50	**4h**	88
8	**1i**	Ph	*t*-Bu	0.75	**4i**	73
9	**1j**	Ph	$Si(i\text{-}Pr)_3$	6	**4j**	93

[a]The reaction was conducted at 70 °C. [b]NMR yield obtained using 1,4-dimethoxybenzene as an internal standard.

completion typically within 2 h to give the desired compounds **4b–j** in good yields. This demonstrated the excellent applicability of the reaction to **1** with various substituents, such as alkyl, aryl, and silyl groups, at the acetylene terminus. In contrast, the electronic nature of the propargylic benzene rings influenced the reaction rate. Thus, the substrates with electron-rich aromatic groups reacted in shorter times (entries 1 and 2). In the case of the less activated **1e** with an electron-withdrawing chloro substituent at the *meta*-position of the phenyl ring, the reaction required a higher temperature (70 °C) and gave **4e** in good yield (entry 4). The substrates with aliphatic substituents were less reactive under deoxygenation conditions. For example, when 1-cyclohexyl-3-phenyl-2-propyn-1-ol was used, 72% of the substrate was recovered, and some unidentified products were obtained.[8] Therefore, the reduction probably proceeded via the propargyl cation intermediates generated by $H_3[PW_{12}O_{40}]\cdot nH_2O$.

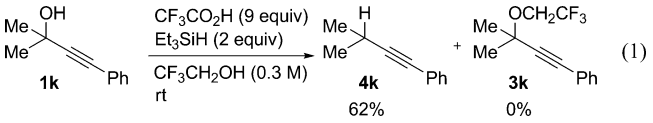
While the developed catalytic deoxygenation was effective for the secondary propargyl alcohols **1a–j**, a similar reaction of the tertiary propargyl alcohol **1k** mainly afforded the dehydration product **5k** along with a trace amount of the desired compound **4k** (Scheme 2). After reexamination of the reaction conditions, the solvent was changed to CF_3CH_2OH, which is known to stabilize cations.[9] This change enhanced the deoxygenation as well as the reaction rate to give **4k** in 65% yield without the formation of **5k** and **3k** at room temperature. The reduction of the other tertiary propargyl alcohols, **1l** and **1m**, was also more effectively conducted in CF_3CH_2OH than in $Cl(CH_2)_2Cl$. Additionally, the reaction of the secondary alcohol **1a** in

Scheme 2. Comparison of Solvent Effects between $Cl(CH_2)_2Cl$ and CF_3CH_2OH for the Deoxygenation of the Tertiary Propargyl Alcohols 1k–m



CF_3CH_2OH gave **4a** in 83% yield, comparable to the result obtained in $Cl(CH_2)_2Cl$.

The reaction of carbonyl compounds with metal alkynylides followed by direct deoxygenation of the propargyl alcohols obtained was one of the most reliable methods to install an alkyl moiety onto terminal alkynes in high overall yields.[10–12] In such cases, the deoxygenation was usually conducted using reducing reagents, such as Et_3SiH[11] and $NaBH_4$,[12] in the presence of trifluoroacetic acid in larger than stoichiometric amounts.[13] In this study, the use of 1 mol % of $H_3[PW_{12}O_{40}]\cdot nH_2O$ was more effective for the Et_3SiH-mediated deoxygenation of propargyl alcohols, and this produced results similar to those obtained using excess amounts of trifluoroacetic acid (eq 1).[14]



(1)

In addition to this, Nishibayashi and co-workers reported the first example of the catalytic and direct deoxygenation of propargyl alcohols with Et_3SiH using a catalytic amount (5 mol %) of a thiolate-bridged diruthenium complex.[13b] Our method allows for similar reactions using a smaller amount of the catalyst in a shorter reaction time.[15]

Next, we applied the newly developed direct deoxygenation protocol to allyl alcohols **6**.[16] The reactions proceeded smoothly, even at room temperature, to afford high yields of the alkenes **7a–e** with migration of the double bonds. In these reactions, the formation of the regioisomers **8a–e** was not observed (Table 3). For some substrates, the use of CF_3CH_2OH dramatically increased the yields of **7** (entries 3 and 4). A similar $H_3[PW_{12}O_{40}]\cdot nH_2O$-catalyzed deoxygenation of **6e** produced **7e** in 75% yield (entry 5), while the reaction using trifluoroacetic acid (9 equiv) and Et_3SiH (2 equiv) in $Cl(CH_2)_2Cl$ resulted in 73% of phenylcyclohexane with a trace amount of **7e**.

We have considered that these reactions proceed through allyl cation intermediates generated by $H_3[PW_{12}O_{40}]\cdot nH_2O$, followed by the regioselective addition of a hydride, because a similar deoxygenation of **9a** also afforded **7a** in 85% yield (Scheme 3). This mechanism is supported by the fact that the

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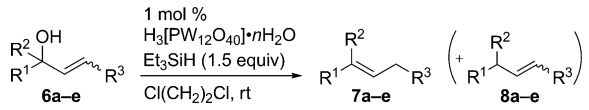
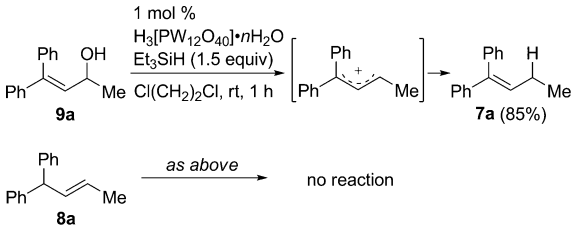
Table 3. $H_3[PW_{12}O_{40}]\cdot nH_2O$-Catalyzed Deoxygenation of Allyl Alcohols 6a−e



entry		R^1	R^2	R^3	time (h)		yield (%)
1	**6a**[a]	Ph	Ph	Me	3	**7a**	89
2	**6b**[b]	*c*-C_6H_{11}	*c*-C_6H_{11}	$(CH_2)_2Ph$	1.5	**7b**	93
3	**6c**[b]	Bn	Bn	Me	3 (0.5)[c]	**7c**	23 (92)[c]
4	**6d**[b]	$Ph(CH_2)_2$	$Ph(CH_2)_2$	Et	1 (0.5)[c]	**7d**	54 (78)[c]
5	**6e**	Ph	$-(CH_2)_3-$		3	**7e**	75

[a]Using **6a** with a 59:41 mixture of *E*/*Z* isomers. [b]Using the *E*-isomer of **6**. [c]Run in CF_3CH_2OH.

Scheme 3. Reactions of 9a and 8a with $H_3[PW_{12}O_{40}]$−Et_3SiH



formation of **8a**, or a mixture of **8a** and **7a**, followed by olefin isomerization to **7a** is precluded since the transformation of **8a**[17] to **7a** was not observed under similar conditions.

In conclusion, we demonstrated that the heteropolyacid $H_3[PW_{12}O_{40}]\cdot nH_2O$, which was mainly used as a catalyst for oxidation reactions, is compatible with Et_3SiH. This combination achieved the direct deoxygenation of propargyl alcohols **1** and allyl alcohols **6** under mild conditions to give alkynes **4** and alkenes **7**, respectively, in high yields. In addition, the use of CF_3CH_2OH as a solvent significantly enhanced the selective deoxygenation of some tertiary propargyl and allyl alcohols.

EXPERIMENTAL SECTION

2-Methyl-4-phenyl-3-butyn-2-ol (**1k**) was purchased from Wako Pure Chemical Industries. 1-Phenyl-2-nonyn-1-ol (**1a**), 1-(*p*-methylphenyl)-2-nonyn-1-ol (**1c**), 1-(*p*-chlorophenyl)-2-nonyn-1-ol (**1d**), 1,3-diphenyl-2-propyn-1-ol (**1f**), and 4,4-dimethyl-1-phenyl-2-pentyn-1-ol (**1i**) were prepared according to the method described in our previous paper.[6]

General Procedure for the Preparation of Other Propargyl Alcohols 1. To a solution of the alkyne (1.2 equiv) in Et_2O (1.0 M) was added dropwise *n*-butyllithium (1.6 M in hexanes; 1.2 equiv) at 0 °C. After the mixture was stirred for 60 min at this temperature, the appropriate carbonyl compound (1.0 equiv) was added. The reaction mixture was allowed to get to room temperature over 30 min. Upon completed consumption of the carbonyl compound, the reaction was quenched with saturated aqueous NH_4Cl. The organic materials were extracted with Et_2O, and the combined organic extracts were washed with brine, dried over $MgSO_4$, and evaporated in vacuo. The residue was purified by column chromatography (silica gel, hexanes/EtOAc) to give the propargyl alcohol **1**.

*1-(p-Methoxyphenyl)-2-nonyn-1-ol (**1b**).* 46% yield: Prepared from anisaldehyde (0.92 mL, 7.6 mmol), 1-octyne (1.00 g, 9.1 mmol) and *n*-butyllithium (1.65 M in hexanes; 5.5 mL, 9.1 mmol).

A pale yellow oil: ^1H NMR (500 MHz, $CDCl_3$) δ 7.47 (d, J = 9.0 Hz, 2H), 6.90 (d, J = 9.0 Hz, 2H), 5.43−5.38 (m, 1H), 3.81 (s, 3H), 2.27 (td, J = 7.0, 2.5 Hz, 2H), 2.02 (d, J = 6.0 Hz, 1H), 1.58−1.51 (m, 2H), 1.44−1.24 (m, 6H), 0.89 (t, J = 7.0 Hz, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 159.5, 133.6, 128.0, 113.8, 87.5, 80.0, 64.4, 55.3, 31.3, 28.6, 22.5, 18.8, 14.0; IR ($CHCl_3$) ν 3441, 2222 cm^{-1}. HRMS (ESI-TOF) m/z calcd for $C_{16}H_{22}O_2Na$ $[M + Na]^+$: 269.1517. Found: 269.1500.

*1-(m-Chlorophenyl)-2-nonyn-1-ol (**1e**).* 81% yield: Prepared from 3-chlorobenzaldehyde (500 mg, 3.6 mmol), 1-octyne (470 mg, 4.3 mmol) and *n*-butyllithium (1.65 M in hexane; 2.7 mL, 4.3 mmol).

A pale yellow oil: ^1H NMR (500 MHz, $CDCl_3$) δ 7.52 (s, 1H), 7.41−7.35 (m, 1H), 7.32−7.16 (m, 2H), 5.39 (d, J = 5.0 Hz, 1H), 2.29 (d, J = 5.0 Hz, 1H), 2.24 (t, J = 7.0 Hz, 2H), 1.51 (quint, J = 7.5 Hz, 2H), 1.41−1.21 (m, 6H), 0.86 (t, J = 7.0 Hz, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 143.1, 134.3, 129.7, 128.2, 126.8, 124.7, 88.3, 79.3, 64.1, 31.3, 28.5, 28.4, 22.5, 18.7, 14.0; IR ($CHCl_3$) ν 3593, 2931, 1597 cm^{-1}. HRMS (ESI-TOF) m/z calcd for $C_{15}H_{19}ClONa$ $[M + Na]^+$: 273.1017. Found: 273.1014.

*1-(p-Chlorophenyl)-3-phenyl-2-propyn-1-ol (**1g**).*[18] 60% yield: Prepared from *p*-chlorobenzaldehyde (1.00 g, 7.1 mmol), phenylacetylene (870 mg, 8.5 mmol) and *n*-butyllithium (1.67 M in hexanes; 5.1 mL, 8.5 mmol).

An off-white solid: mp 49−52 °C (lit.[18] mp 42−44 °C); ^1H NMR (500 MHz, $CDCl_3$) δ 7.56 (d, J = 8.5 Hz, 2H), 7.47 (dd, J = 8.0, 2.0 Hz, 2H), 7.39−7.30 (m, 5H), 5.67 (d, J = 6.0 Hz, 1H), 2.37 (d, J = 6.0 Hz, 1H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 139.0, 134.2, 131.7, 128.8, 128.3, 128.1, 122.1, 88.2, 86.9, 64.4; IR ($CHCl_3$) ν 3441, 2230 cm^{-1}.

*1-Naphthalen-1-yl-3-phenyl-2-propyn-1-ol (**1h**).*[19] Quantitative yield: Prepared from 1-naphthaldehyde (1.3 mL, 9.6 mmol), phenylacetylene (1.20 g, 12 mmol) and *n*-butyllithium (1.67 M in hexanes; 6.9 mL, 12 mmol).

An off-white solid: mp 77−80 °C; ^1H NMR (500 MHz, $CDCl_3$) δ 8.39 (d, J = 8.5 Hz, 1H), 7.94 (d, J = 7.5 Hz, 1H), 7.91 (d, J = 8.0 Hz, 1H), 7.87 (d, J = 8.0 Hz, 1H), 7.62−7.47 (m, 5H), 7.35−7.30 (m, 3H), 6.37 (d, J = 6.5 Hz, 1H), 2.41 (d, J = 6.5 Hz, 1H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 135.6, 134.0, 131.7, 130.5, 129.4, 128.7, 128.6, 128.3, 126.4, 125.9, 125.2, 124.7, 123.9, 122.4, 88.5, 87.3, 63.3; IR ($CHCl_3$) ν 3428, 2230 cm^{-1}.

*1-Phenyl-3-triisopropylsilyl-2-propyn-1-ol (**1j**).*[20] 94% yield: Prepared from benzaldehyde (0.72 mL, 7.1 mmol), (triisopropylsilyl)-acetylene (1.55 g, 8.5 mmol) and *n*-butyllithium (1.67 M in hexanes; 5.2 mL, 8.5 mmol).

A colorless oil: ^1H NMR (500 MHz, $CDCl_3$) δ 7.61−7.57 (m, 2H), 7.41−7.31 (m, 3H), 5.49 (d, J = 7.0 Hz, 1H), 2.13 (d, J = 7.0 Hz, 1H), 1.09 (s, 21H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 140.5, 128.5, 128.3, 126.8, 106.8, 88.0, 65.1, 18.6, 11.1; IR ($CHCl_3$) ν 3420, 2172 cm^{-1}.

*1-(2-Phenylethynyl)cyclohexanol (**1l**).*[21] 55% yield: Prepared from cyclohexanone (0.21 mL, 2.0 mmol), phenylacetylene (250 mg, 2.4 mmol) and *n*-butyllithium (1.62 M in hexanes; 1.5 mL, 2.4 mmol).

An off-white solid: mp 54−56 °C (lit.[21] mp 57−59 °C); ^1H NMR (500 MHz, $CDCl_3$) δ 7.47−7.41 (m, 2H), 7.33−7.29 (m, 2H), 7.28−7.25 (m, 1H), 2.06−1.96 (m, 3H), 1.80−1.51 (m, 7H), 1.34−1.24 (m, 1H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 131.6, 128.22, 128.18, 122.8, 92.7, 84.3, 69.1, 40.0, 25.2, 23.4; IR ($CHCl_3$) ν 3545, 2224 cm^{-1}.

*1,1-Diphenyl-2-butyn-1-ol (**1m**).*[22] 87% yield: Prepared from benzophenone (501 mg, 2.8 mmol) and 1-propynylmagnesium bromide (0.5 M in THF; 10 mL, 5.0 mmol).

An off-white solid: mp 28−30 °C; ^1H NMR (500 MHz, $CDCl_3$) δ 7.61−7.58 (m, 4H) 7.34−7.30 (m, 4H), 7.27−7.23 (m, 2H), 2.70 (s,

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1H), 1.98 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 145.4, 128.1, 127.5, 126.0, 83.7, 82.1, 74.4, 3.8; IR ($CHCl_3$) ν 3588, 2236 cm^{-1}.

General Procedure for the Deoxygenation of Propargyl Alcohols 1. To a solution of the propargyl alcohol **1** (0.25 mmol) in $Cl(CH_2)_2Cl$ or CF_3CH_2OH (0.80 mL, 0.30 M) were added $H_3[PW_{12}O_{40}]\cdot nH_2O$ (5.4 mg, 0.0025 mmol) and Et_3SiH (0.060 mL, 0.38 mmol). The reaction mixture was stirred at 50 °C or room temperature until complete consumption of **1** and then quenched with saturated aqueous $NaHCO_3$. The organic materials were extracted with EtOAc, and the combined organic extracts were washed with brine, dried over $MgSO_4$, and evaporated in vacuo. The residue was purified by column chromatography (silica gel, usually hexanes/EtOAc) to give the alkyne **4**.

*1-Phenyl-2-nonyne (**4a**).* 44.9 mg, 84%. A colorless oil: ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.37−7.20 (m, 5H), 3.59 (br s, 2H), 2.22 (tt, J = 7.0, 2.5 Hz, 2H), 1.58−1.49 (m, 2H), 1.44−1.36 (m, 2H), 1.34−1.24 (m, 4H), 0.89 (t, J = 7.0 Hz, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 137.6, 128.4, 127.8, 126.3, 82.7, 77.4, 31.4, 29.0, 28.6, 25.1, 22.6, 18.8, 14.1; IR ($CHCl_3$) ν 2932, 2203, 1599 cm^{-1}. HRMS (ESI-TOF) m/z calcd for $C_{15}H_{21}$ [M + H]$^+$: 201.1638. Found: 201.1633.

*1-(p-Methoxyphenyl)-2-nonyne (**4b**).*[13a] 47.6 mg, 91%. A yellow oil: ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.25 (d, J = 8.5 Hz, 2H), 6.85 (d, J = 8.5 Hz, 2H), 3.79 (s, 3H), 3.52 (br s, 2H), 2.21 (tt, J = 7.0, 2.5 Hz, 2H), 1.55−1.48 (m, 2H), 1.43−1.36 (m, 2H), 1.35−1.24 (m, 4H), 0.89 (t, J = 7.0 Hz, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 158.1, 129.7, 128.7, 113.8, 82.4, 77.9, 55.3, 31.3, 29.0, 28.6, 24.2, 22.6, 18.8, 14.1; IR ($CHCl_3$) ν 2932, 2201, 1512 cm^{-1}.

*1-(p-Methylphenyl)-2-nonyne (**4c**).* 48.4 mg, 96%. A yellow oil: ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.23 (d, J = 8.0 Hz, 2H), 7.12 (d, J = 8.0 Hz, 2H), 3.54 (br s, 2H), 2.33 (s, 3H), 2.21 (tt, J = 7.0, 2.5 Hz, 2H), 1.56−1.48 (m, 2H), 1.44−1.24 (m, 6H), 0.89 (t, J = 7.0 Hz, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 135.8, 134.6, 129.0, 127.7, 82.5, 77.7, 31.4, 29.0, 28.6, 24.7, 22.6, 21.0, 18.8, 14.1; IR ($CHCl_3$) ν 2930, 2201, 1514 cm^{-1}. HRMS (ESI-TOF) m/z calcd for $C_{16}H_{26}N$ [M + NH_4]$^+$: 232.2060. Found: 232.2040.

*1-(p-Chlorophenyl)-2-nonyne (**4d**).*[13a] 45.2 mg, 88%. A yellow oil: ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.29−7.22 (m, 4H), 3.53 (t, J = 2.5 Hz, 2H) 2.20 (tt, J = 7.0, 2.5 Hz, 2H), 1.55−1.47 (m, 2H), 1.42−1.23 (m, 6H), 0.88 (t, J = 7.0 Hz, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 136.1, 132.1, 129.2, 128.4, 83.2, 76.9, 31.3, 28.9, 28.6, 24.6, 22.6, 18.8, 14.1; IR ($CHCl_3$) ν 2931, 2307, 1491 cm^{-1}.

*1-(m-Chlorophenyl)-2-nonyne (**4e**).* 22.1 mg, 61%. A colorless oil: ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.36 (s, 1H), 7.26−7.18 (m, 3H), 3.56 (s, 2H), 2.25−2.19 (m, 2H), 1.53 (quint, J = 7.0 Hz, 2H), 1.45−1.37 (m, 2H), 1.36−1.24 (m, 4H), 0.89 (t, J = 7.0 Hz, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 139.6, 134.2, 129.5, 128.0, 126.6, 126.0, 83.4, 76.6, 31.4, 28.9, 28.6, 24.8, 22.6, 18.8, 14.1; IR ($CHCl_3$) ν 2932, 2311, 1597 cm^{-1}. HRMS (ESI-TOF) m/z calcd for $C_{15}H_{23}ClN$ [M + NH_4]$^+$: 252.1514. Found: 252.1514.

*1,3-Diphenyl-1-propyne (**4f**).*[23] 36.8 mg, 77%. A colorless oil: ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.47−7.41 (m, 4H), 7.37−7.24 (m, 6H), 3.85 (s, 2H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 136.7, 131.6, 128.5, 128.2, 127.9, 127.8, 126.6, 123.6, 87.5, 82.6, 25.7; IR ($CHCl_3$) ν 2891, 2315, 1599 cm^{-1}.

*3-(p-Chlorophenyl)-1-phenyl-1-propyne (**4g**).*[23] 35.1 mg, 73%. A light yellow oil: ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.46−7.42 (m, 2H), 7.35 (d, J = 8.5 Hz, 2H), 7.33−7.28 (m, 5H), 3.80 (s, 2H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 135.2, 132.4, 131.6, 129.3, 128.6, 128.2, 128.0, 123.4, 86.8, 83.0, 25.2; IR ($CHCl_3$) ν 3011, 2299, 1599 cm^{-1}.

*1-(3-Phenyl-2-propynyl)naphthalene (**4h**).*[24] 53.6 mg, 88%. An orange solid: mp 58−62 °C; ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.11 (d, J = 8.0 Hz, 1H), 7.90 (d, J = 8.0 Hz, 1H), 7.80 (d, J = 8.0 Hz, 1H), 7.72 (d, J = 7.0 Hz, 1H), 7.58 (td, J = 7.0, 2.0 Hz, 1H), 7.53 (td, J = 7.0, 2.0 Hz, 1H), 7.50−7.44 (m, 3H), 7.34−7.28 (m, 3H), 4.25 (s, 2H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 133.7, 132.5, 131.6, 131.4, 128.7, 128.2, 127.8, 127.6, 126.2, 125.73, 125.71, 125.6, 123.6, 123.4, 87.2, 83.5, 23.7; IR ($CHCl_3$) ν 3021, 2313, 1599 cm^{-1}.

*4,4-Dimethyl-1-phenyl-2-pentyne (**4i**).*[25] 37.1 mg, 73%. A light yellow oil: ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.37−7.29 (m, 4H), 7.24−7.20 (m, 1H), 3.59 (s, 2H), 1.25 (s, 9H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 137.6, 128.3, 127.7, 126.3, 91.4, 75.8, 31.3, 27.5, 24.9; IR ($CHCl_3$) ν 2970, 2253, 1605 cm^{-1}.

*3-Phenyl-1-triisopropylsilyl-1-propyne (**4j**).* 47.8 mg, 93%. A colorless oil: ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.38 (dd, J = 7.5, 1.0 Hz, 2H), 7.32 (t, J = 7.5 Hz, 2H), 7.23 (t, J = 7.5 Hz, 1H), 3.71 (s, 2H), 1.10−1.08 (m, 21H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 136.7, 128.4, 127.8, 126.4, 105.6, 82.9, 26.2, 18.6, 11.3; IR ($CHCl_3$) ν 2943, 2173, 1605 cm^{-1}. HRMS (ESI-TOF) m/z calcd for $C_{18}H_{29}Si$ [M + H]$^+$: 273.2033. Found: 273.2009.

*3-Methyl-1-phenyl-1-butyne (**4k**).*[26] 30.6 mg, 65%. A colorless oil: ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.41−7.37 (m, 2H), 7.30−7.24 (m, 3H), 2.82−2.73 (m, 1H), 1.26 (d, J = 7.0 Hz, 6H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 131.5, 128.1, 127.4, 123.9, 95.7, 80.0, 23.0, 21.1; IR ($CHCl_3$) ν 2972, 2230, 1599 cm^{-1}.

*1-Cyclohexyl-2-phenylethyne (**4l**).*[26] 40.1 mg, 89%. A pale yellow oil: ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.41−7.38 (m, 2H), 7.30−7.24 (m, 3H), 2.62−2.55 (m, 1H), 1.92−1.85 (m, 2H), 1.81−1.71 (m, 2H), 1.59−1.48 (m, 3H), 1.40−1.31 (m, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 131.5, 128.1, 127.4, 124.1, 94.4, 80.4, 32.7, 29.6, 25.9, 24.9; IR ($CHCl_3$) ν 2932, 2230 cm^{-1}.

*1,1-Diphenyl-2-butyne (**4m**).*[27] 29.4 mg, 64%. A yellow oil: ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.37 (d, J = 7.5 Hz, 4H), 7.30 (t, J = 7.5 Hz, 4H), 7.21 (t, J = 7.5 Hz, 2H), 4.95 (s, 1H), 1.92 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 142.3, 128.5, 127.8, 126.7, 80.4, 79.6, 43.2, 3.8; IR ($CHCl_3$) ν 3009, 2309, 1599 cm^{-1}.

*3-Methyl-1-phenyl-3-(2,2,2-trifluoroethoxy)-1-butyne (**3k**).* To a solution of the propargyl alcohol **1k** (32.9 mg, 0.21 mmol) in CF_3CH_2OH (0.70 mL, 0.30 M) were added trifluoroacetic acid (1.6 μL, 0.021 mmol) and Et_3SiH (0.050 mL, 0.31 mmol). The reaction mixture was stirred at room temperature for 5 h and then quenched with saturated aqueous $NaHCO_3$. The organic materials were extracted with EtOAc, and the combined organic extracts were washed with brine, dried over Na_2SO_4, and evaporated in vacuo. The residue was purified by column chromatography (silica gel, hexanes/EtOAc = 30:1) to give the alkyne **4k** (4.1 mg, 14%) and **3k** (37.2 mg, 75%).

A colorless oil: ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.44−7.40 (m, 2H), 7.46−7.30 (m, 3H), 4.02 (q, J = 8.5 Hz, 2H), 1.59 (s, 6H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 131.7, 128.6, 128.3, 124.1 (q, J = 277.1 Hz), 122.1, 89.3, 85.4, 72.4, 62.5 (q, J = 34.8 Hz), 28.5; ^{19}F NMR (470 MHz, $CDCl_3$) δ −77.4; IR ($CHCl_3$) ν 2990, 2222, 1599 cm^{-1}. HRMS (ESI-TOF) m/z calcd for $C_{13}H_{13}F_3NaO$ [M + Na]$^+$: 265.0811. Found: 265.0819.

The spectral data for the enyne compounds **5k** and **5l** were consistent with the reported ones.[28,29]

Preparation of Allyl Alcohols 6. 1-Phenyl-2-cyclohexen-1-ol (**6e**) was prepared according to the method described in our previous paper.[5c]

*1,1-Diphenyl-2-buten-1-ol (**6a**).* To a solution of benzophenone (1.00 g, 5.5 mmol) in THF (11 mL) was added 1-propenylmagnesium bromide (0.5 M in THF; 14 mL, 7.2 mmol) at 0 °C. After stirring at room temperature for 4.5 h, the reaction was quenched with saturated aq NH_4Cl. The mixture was extracted with Et_2O. The organic layer was washed with brine, dried over $MgSO_4$, and evaporated in vacuo. The residue was purified by column chromatography (silica gel, hexanes/EtOAc = 10:1) to give the alkene **6a** (1.23 g, quant.) as a 59:41 mixture of E/Z isomers.

Data: ^{1}H NMR (500 MHz, $CDCl_3$) ***E* isomer** δ 7.40−7.20 (m, 10H), 6.13 (dd, J = 15.5, 2.0 Hz, 1H), 5.63 (dq, J = 15.5, 6.5 Hz, 1H), 2.26 (s, 1H), 1.79 (dd, J = 6.5, 2.0 Hz, 3H); ***Z* isomer** δ 7.47−7.20 (m, 10H), 6.15 (d, J = 11.5, 2.0 Hz, 1H), 5.81 (dq, J = 11.5, 7.0 Hz, 1H), 2.36 (s, 1H), 1.56 (dd, J = 7.0, 2.0 Hz, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 147.5, 146.4, 136.9, 129.2, 128.1, 128.0, 127.0, 126.8, 126.3, 125.9, 79.0, 78.9, 17.8, 14.8; IR ($CHCl_3$) ν 3595, 3011, 1599 cm^{-1}. HRMS (ESI-TOF) m/z calcd for $C_{16}H_{17}O$ [M + H]$^+$: 225.1274. Found: 225.1246.

*(E)-1,1-Dicyclohexyl-5-phenyl-2-penten-1-ol (**6b**).* To a solution of 4-phenyl-1-butyne (1.01 g, 7.8 mmol) in THF (15.5 mL) was added *n*-butyllithium (1.65 M in hexanes; 5.6 mL, 9.2 mmol) at −78 °C, and the reaction mixture was stirred for 1 h at the same temperature. Dicyclohexyl ketone (2.4 mL, 12 mmol) was added to the mixture,

which was allowed to get to room temperature. After 3.5 h of an additional stirring, the reaction quenched with saturated aq NH_4Cl. The mixture was extracted with Et_2O. The organic layer was washed with brine, dried over $MgSO_4$, and evaporated in vacuo. The residue was purified by column chromatography (silica gel, hexanes/EtOAc = 20:1) to give 1,1-dicyclohexyl-5-phenyl-2-pentyn-1-ol (2.51 g, quant.).

The obtained propargyl alcohol was added to a solution of Red-Al (65% in toluene; 5.0 mL, 17 mmol) in THF (28 mL) at room temperature. The reaction was heated at 50 °C for 24 h. After cooling down, the mixture was quenched with a saturated solution of Rochelle's salt. The mixture was extracted with Et_2O. The organic layer was washed with brine, dried over $MgSO_4$, and evaporated in vacuo. The residue was purified by column chromatography (silica gel, hexanes/EtOAc = 20:1) to give **6b** (1.52 g, 60%).

A colorless oil: ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.27 (t, J = 8.0 Hz, 2H), 7.20−7.14 (m, 3H), 5.56−5.46 (m, 1H), 5.25 (d, J = 15.5 Hz, 1H), 2.72 (t, J = 7.5 Hz, 2H), 2.42 (dt, J = 7.5, 7.0 Hz, 2H), 1.80−1.50 (m, 10H), 1.43 (tt, J = 12.0, 3.0 Hz, 2H), 1.25−1.00 (m, 7H), 0.97−0.78 (m, 4H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 141.8, 134.1, 128.5, 128.2, 127.9, 125.7, 78.6, 43.0, 35.9, 34.1, 27.2, 26.8, 26.60, 26.57, 26.0; IR ($CHCl_3$) ν 3607, 2932, 1603 cm^{-1}. HRMS (ESI-TOF) m/z calcd for $C_{23}H_{34}ONa$ $[M + Na]^+$: 349.2502. Found: 349.2512.

*(E)-2-Benzyl-1-phenyl-3-penten-2-ol (**6c**).* 60% yield: Prepared from 1,3-diphenyl-2-propanone (2.00 g, 9.5 mmol), 1-propynylmagnesium bromide (0.50 M in THF; 29 mL, 14 mmol) and Red-Al (65% in toluene; 5.7 mL, 19 mmol), according to the method for the synthesis of **6b**.

A colorless oil: ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.30−7.15 (m, 10H), 5.54 (dd, J = 15.5, 2.0 Hz, 1H), 5.29 (dq, J = 15.5, 6.5 Hz, 1H), 2.89 and 2.85 (ABq, J = 13.5 Hz, 4H), 1.61 (dd, J = 6.5, 2.0 Hz, 3H), 1.59 (s, 1H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 136.9, 135.9, 130.8, 127.8, 126.3, 124.2, 74.8, 47.6, 17.5; IR ($CHCl_3$) ν 3566, 3011, 1603 cm^{-1}. HRMS (ESI-TOF) m/z calcd for $C_{18}H_{20}ONa$ $[M + Na]^+$: 275.1406. Found: 275.1385.

*(E)-3-Phenethyl-1-phenyl-4-hepten-3-ol (**6d**).* To a solution of (2-bromoethyl)benzene (2.4 mL, 17 mmol) in Et_2O (20 mL) was dropwise added *t*-butyllithium (1.76 M in pentane; 20 mL, 35 mmol) at −78 °C, and the mixture was allowed to get to room temperature over 2 h. The reaction was again cooled at −78 °C, to which was added a solution of phenyl 2-pentenoate (1.30 g, 7.4 mmol) in Et_2O (5 + 5 + 5 mL). After stirring at room temperature for 3.5 h, the reaction was quenched with saturated aq NH_4Cl at 0 °C. The mixture was extracted with Et_2O. The organic layer was washed with brine, dried over $MgSO_4$, and evaporated in vacuo. The residue was purified by column chromatography (silica gel, hexanes/EtOAc = 20:1) to give the alkene **6d** (938 mg, 43%).

A pale yellow oil: ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.30−7.16 (m, 10H), 5.76 (dt, J = 15.5, 6.5 Hz, 1H), 5.52 (d, J = 15.5 Hz, 1H), 2.72−2.62 (m, 4H), 2.17−2.10 (m, 2H), 1.96−1.80 (m, 4H), 1.46 (s, 1H), 1.04 (t, J = 7.5 Hz, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 142.4, 133.9, 131.0, 128.30, 128.28, 125.6, 74.7, 43.1, 30.0, 25.3, 13.9; IR ($CHCl_3$) ν 3599, 3017, 1603 cm^{-1}. HRMS (ESI-TOF) m/z calcd for $C_{21}H_{26}ONa$ $[M + Na]^+$: 317.1876. Found: 317.1897.

General Procedure for the Deoxygenation of Allyl Alcohols 6. To a solution of the allyl alcohol **6** (0.25 mmol) in $Cl(CH_2)_2Cl$ or CF_3CH_2OH (0.80 mL, 0.30 M) were added $H_3[PW_{12}O_{40}]\cdot nH_2O$ (5.4 mg, 0.0025 mmol) and Et_3SiH (0.060 mL, 0.38 mmol). The reaction mixture was stirred at room temperature until complete consumption of **6**. The remainder of the procedure is the same as described in the General Procedure for the Deoxygenation of Propargyl Alcohols **1** section. The residue was purified by column chromatography (silica gel, usually hexanes/EtOAc) to give the alkene **7**.

*1,1-Diphenyl-1-butene (**7a**).*[30] 49.6 mg, 89%. A colorless oil: ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.40−7.17 (m, 10H), 6.08 (t, J = 7.5 Hz, 1H), 2.16−2.09 (m, 2H), 1.04 (t, J = 7.5 Hz, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 142.8, 140.9, 140.2, 131.7, 129.9, 128.1, 128.0, 127.2, 126.8, 126.7, 23.2, 14.5; IR ($CHCl_3$) ν 3030, 1597 cm^{-1}.

*1,1-Dicyclohexyl-5-phenyl-1-pentene (**7b**).* 40.4 mg, 93%. A colorless oil: ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.30−7.25 (m, 2H), 7.20−7.15 (m, 3H), 5.10 (t, J = 7.5 Hz, 1H), 2.61 (t, J = 8.0 Hz, 2H), 2.34 (tt, J = 11.5, 3.5 Hz, 1H), 2.08 (td, J = 7.5, 7.0 Hz, 2H), 1.84 (tt, J = 11.5, 3.5 Hz, 1H), 1.76−1.57 (m, 10H), 1.48−1.41 (m, 2H), 1.37−1.08 (m, 10H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 150.6, 142.8, 128.4, 128.2, 125.6, 121.7, 40.7, 40.3, 35.4, 35.1, 32.2, 31.1, 27.2, 26.7, 26.4, 26.2; IR ($CHCl_3$) ν 2928, 2853, 1603 cm^{-1}. HRMS (ESI-TOF) m/z calcd for $C_{23}H_{35}$ $[M + H]^+$: 311.2733. Found: 311.2742.

*2-Benzyl-1-phenyl-2-pentene (**7c**).* 47.9 mg, 92%. A colorless oil: ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.31−7.25 (m, 4H), 7.22−7.18 (m, 2H), 7.14 (t, J = 7.0 Hz, 4H), 5.41 (t, J = 7.5 Hz, 1H), 3.29 (s, 2H), 3.19 (s, 2H), 2.23−2.16 (m, 2H), 1.04 (t, J = 7.5 Hz, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 140.2, 140.0, 136.5, 130.4, 129.0, 128.6, 128.3, 128.2, 125.9, 125.8, 42.9, 35.1, 21.5, 14.6; IR ($CHCl_3$) ν 2965, 1601 cm^{-1}. HRMS (ESI-TOF) m/z calcd for $C_{18}H_{21}$ $[M + H]^+$: 237.1638. Found: 237.1631.

*3-Phenethyl-1-phenyl-3-heptene (**7d**).* 37.2 mg, 78%. A colorless oil: ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.31−7.14 (m, 10H), 5.18 (t, J = 7.0 Hz, 1H), 2.76−2.65 (m, 4H), 2.39−2.29 (m, 4H), 1.96−1.90 (m, 2H), 1.33−1.24 (m, 2H), 0.85 (t, J = 7.0 Hz, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 142.5, 142.4, 137.8, 128.4, 128.34, 128.28, 128.2, 126.1, 125.8, 125.7, 38.8, 34.95, 34.93, 32.5, 29.8, 23.0, 13.9; IR ($CHCl_3$) ν 2960, 1603 cm^{-1}. HRMS (ESI-TOF) m/z calcd for $C_{21}H_{27}$ $[M + H]^+$: 279.2107. Found: 279.2135.

*1-Phenylcyclohexene (**7e**).*[31] 38.2 mg, 75%. A colorless oil: ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.39 (d, J = 7.0 Hz, 2H), 7.31 (t, J = 7.0 Hz, 2H), 7.25−7.19 (m, 1H), 6.13 (t, J = 3.5 Hz, 1H), 2.45−2.39 (m, 2H), 2.25−2.19 (m, 2H), 1.83−1.77 (m, 2H), 1.70−1.64 (m, 2H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 142.7, 136.5, 128.2, 126.5, 124.9, 124.8, 27.4, 25.8, 23.0, 22.1; IR ($CHCl_3$) ν 2934, 1597 cm^{-1}.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

NMR data for substrates and products. This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes

The authors declare no competing financial interest.

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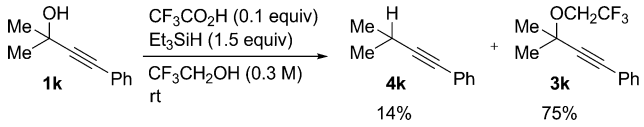

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