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3,3-Disubstituted Allyl Alcohols from Palladium-Catalyzed Coupling of Hydroaluminated Propargyl Alcohols with Aryl Iodides

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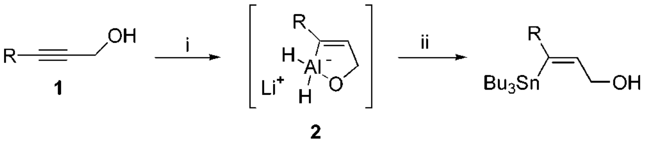
3,3-Disubstituted prop-2-en-1-ols **4** were synthesized with a high degree of stereoselectivity from 3-substituted prop-2-yn-1-ols **1** via hydroalumination and subsequent Pd-catalyzed coupling with aryl iodides **3**.

Trisubstituted alkenes are common motifs in nature, and their preparation remains a challenging problem in synthetic organic chemistry.[1−3] Substituted allyl alcohols are useful intermediates in synthesis[3−7] and can, for example, be hydrogenated[6] or isomerized to aldehydes[7] enantioselectively. Preparation of substituted allyl alcohols is usually based on Reformatsky reaction of the corresponding ketone[8] or Horner−Wadsworth−Emmons reaction but often gives a mixture of isomers.[7,9,10]

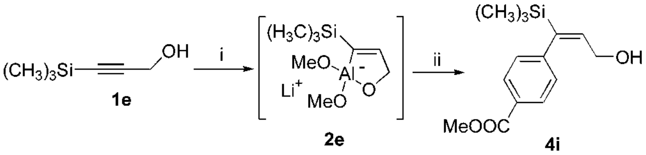
Palladium-catalyzed coupling of 3-tributylstannyl allyl alcohols with aryl or alkenyl halides can also be used for this purpose.[11] The preparation of 3-tributylstannyl allyl alcohols is usually accomplished by regio- and stereospecific hydroalumination of 2-propyn-1-ols **1** and subsequent transmetalation from aluminum to tin[12] (Scheme 1). The stereo- and regioselectivity of this reaction are believed to result from the formation of cyclic intermediate **2**. Since a handful of reports on the transition metal catalyzed coupling reactions using organoalanes have been reported,[13] it is somewhat surprising that hydroaluminated intermediates such as **2** have not yet been used for this type of reaction. Herein, we report our results on the direct Pd-catalyzed coupling of cyclic organoalanes **2** with aromatic halides in which 3,3-disubstituted allyl alcohols are formed.

Scheme 1[a]



[a] Reagents: (i) $LiAlH_4$; (ii) (1) AcOEt, (2) Bu_3SnOMe.

Scheme 2[a]



[a] Reagents: (i) (1) $LiAlH_4$, (2) $(MeO)_2CO$; (ii) $PdCl_2(PPh_3)_2$, methyl-4-iodobenzoate (**3a**).

Hydroaluminated 3-trimethylsilylprop-2-en-1-ol **2e** was used to optimize the coupling reaction. Starting 3-trimethylsilylprop-2-en-1-ol **1e** was hydroaluminated with $LiAlH_4$ in the presence of NaOMe, which suppresses isomerization.[12b] Excess hydride was then quenched by addition of dimethyl carbonate, and the resulting aluminate was subjected to the reaction with methyl 4-iodobenzoate **3a** in the presence of $PdCl_2(PPh_3)_2$ (Scheme 2). However, only a low yield (Table 1, entry 1) of the desired coupled product **4i** was obtained. Addition of $ZnCl_2$[13b] increased the yield considerably. The optimal amount of $ZnCl_2$ was found to be 60 mol % (Table 1, entry 4). Among the catalysts screened, $PdCl_2(PPh_3)_2$ gave the best results in this case. $NiCl_2(PPh_3)_2$ was also an active catalyst; however, the yield was lower than that achieved with $PdCl_2(PPh_3)_2$ (Table 1, entry 7). Methyl 4-bromo-

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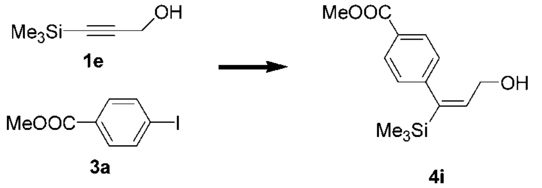
10.1021/jo0162235 CCC: $22.00

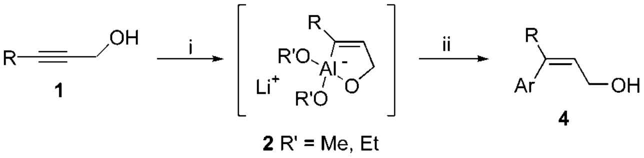
Table 1. Influence of the Catalytic System on the Yield of Coupling Reactions



entry	amount of $ZnCl_2$ (mol %)	catalyst	yield (%)
1	0	$PdCl_2(PPh_3)_2$	11
2	5	$PdCl_2(PPh_3)_2$	44
3	20	$PdCl_2(PPh_3)_2$	51
4	60	$PdCl_2(PPh_3)_2$	90[a]
5	100	$PdCl_2(PPh_3)_2$	71
6	60	Pd_2dba_3, $AsPh_3$ (PdL_2)	82[a]
7	60	$NiCl_2(PPh_3)_2$	56
8[b]	60	Pd_2dba_3, $AsPh_3$ (PdL_2)	23

[a] Starting iodide was not detected in the reaction mixture. [b] Methyl-4-bromobenzoate was used instead of methyl-4-iodobenzoate.

Scheme 3[a]



[a] Reagents: (i) (1) $LiAlH_4$, (2) EtOAc or $(MeO)_2CO$; (ii) Pd-catalysis, $ZnCl_2$, ArI (**3**).

benzoate was less reactive compared to iodide **3a** giving only 23% of the coupled product **4i** (Table 1, entry 8).

The scope of the reaction was examined using a variety of propargyl alcohols and aryl iodides (Table 2, Scheme 3). The reaction tolerates an array of functionalities on both substrates, although aryl iodides with electron-withdrawing groups usually gave higher yields than those substituted with donors. Vinyl iodides can also be subjected to the coupling reaction with **2**. As for the catalyst, $Pd(PPh_3)_2Cl_2$ is generally the most effective, but $Pd_2dba_3/AsPh_3$ or $Pd(PPh_3)_4$ gave better results with some substrates (Table 2). The stereochemistry of the reaction is determined by the hydroalumination step.[14] A single isomer is formed with high selectivity when 3-alkyl-substituted propargyl alcohols are used, while trimethylsilyl- and arylpropargyl alcohols gave products with 90−95% isomeric purity.

In some cases, unreacted aryl iodide remains in the reaction mixture and addition of more catalyst does not increase the yield. In these reactions, the larger excess of aluminate (ca. 2 equiv) increased the yield (Table 2, entries 2, 13, and 14). In most cases, it is convenient to use ethyl acetate for quenching of the remaining hydride.[15] However, if the starting aryl iodide contains a methyl ester group, it is necessary to use dimethyl carbonate to avoid transesterification by ethoxide formed in the reduction of ethyl acetate. Excess ethyl acetate (or dimethyl carbonate) in the reaction mixture can also acylate the substituted allyl alcohol. This problem was overcome by addition of methanol to the reaction mixture before workup.

Substitution at the 1-position of the starting propargyl alcohol decreases the yield of disubstituted allyl alcohol considerably. Thus, reaction of 4-(2-thienyl)but-3-yn-2-ol (**1g**) and 4-methoxyiodobenzene (**3i**) afforded the desired product **4o** in 27% yield (Table 2, entry 15), while with 1,1-disubstituted propargyl alcohol 2-methyl-4-(2-thienyl)but-3-yn-2-ol an inseparable mixture of products was obtained. Propargyl alcohol itself gave, after hydroalumination and reaction with 4-iodoanisole (**3i**), only a low yield (27%) of the desired 4-methoxycinnamyl alcohol (**4n**) as an approximately 1:1 mixture of *E* and *Z* isomers accompanied with 3-(4-methoxyphenyl)prop-2-yn-1-ol (Table 2, entry 14). The reaction of vinyl iodide *(E)*-1-iodohept-1-yn (**3j**) and but-2-yn-1-ol (**1a**) afforded the desired coupled product **4p** in 45% yield (Table 2, entry 16).

In conclusion, a new convenient and highly stereoselective one-pot synthesis of 3,3-disubstituted allyl alcohols starting from substituted propargyl alcohols and aryl iodides was developed. The procedure eliminates preparation, purification, and use of toxic stannanes necessary for the commonly used Stille reaction[16] and tolerates amide, ester, ether, and nitro groups, giving moderate to high yields of allyl alcohols with good regio- and stereoselectivity.

Experimental Section

All reactions were performed under a dry argon atmosphere. THF was distilled from benzophenone ketyl under an Ar atmosphere prior to use. Petroleum ether refers to the fraction boiling at 40−60 °C. 4-Methylpent-2-yn-1-ol (**1b**),[17] 5-methoxypent-2-yn-1-ol (**1c**),[12b] 3-phenylprop-2-yn-1-ol (**1d**),[18] *N*,*N*-dimethyl-4-iodobenzamide (**3g**),[19] 4-iodoacetanilide (**3h**),[20] and 1-iodohept-1-yne (**3j**)[22] were prepared according to the reported procedures. Methyl esters of corresponding iodobenzoic acids were prepared by esterification of commercially available acids in refluxing methanol with H_2SO_4 as a catalyst. NMR spectra were measured on either a Varian Gemini 300 (^1H, 300.07 MHz), Bruker AMX3 400 (^1H, 400.13 MHz; ^{13}C, 100.6 MHz), or Bruker DRX 500 Avance (^1H, 500.13 MHz; ^{13}C, 125.77 MHz) spectrometer at 298 K. HPLC analysis (LiChrosfer 100 RP-18, methanol/water 85:15) with 2-methyl naphthalene as an internal standard was used for the optimization of the coupling reactions.

General Procedure. Sodium methoxide (5 mg, 0.09 mmol) was added to a 1 M solution of $LiAlH_4$ in THF (1−1.5 mL, 1−1.5 mmol). The mixture was cooled to 0 °C, and a solution of the appropriate alkynol **1** (1−1.5 mmol) in THF (1 mL) was slowly added. The temperature and reaction time of hydroalumination step for individual compounds are listed separately below. After hydroalumination was completed, the reaction mixture was cooled to 0 °C; ethyl acetate (0.25 mL, 2.5 mmol) was added, and the mixture was stirred for 10 min without cooling. Dimethyl carbonate (0.15 mL, 1.7 mmol) was used instead of ethyl acetate when the starting aryl iodide

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[14] This was confirmed by a coupled ^{13}C NMR spectrum of the product **4a**, in which the $^{3}J(CH_3, H)$ of the methyl group and the hydrogen of the double bond is 6.9 Hz. This coupling constant value corresponds to a cis relationship.

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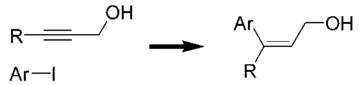
Table 2. Coupling Reaction of Hydroaluminated Propargyl Alcohols 1 with Iododerivatives (Scheme 3)



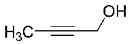
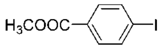
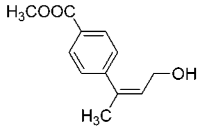
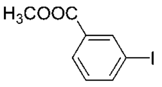
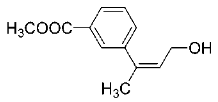
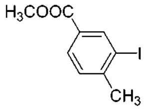
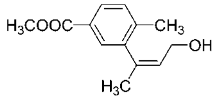
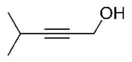
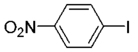
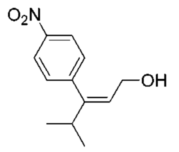
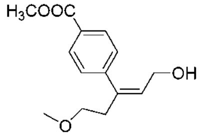
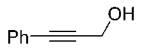
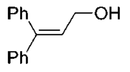
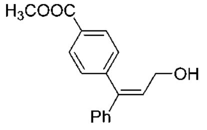
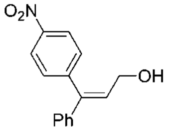
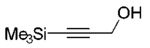
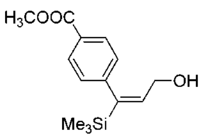
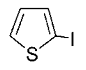
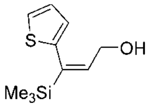
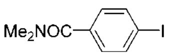
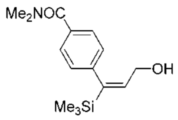
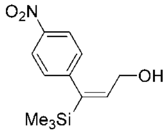
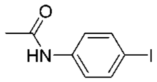
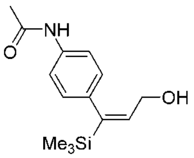
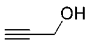
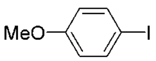
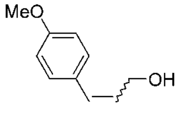
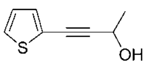
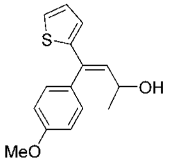
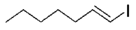
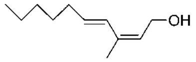
Entry	Propargyl Alcohol	Iododerivative	Propargyl Alcohol : ArI	Catalyst	Product *E/Z*[b]	Yield[a] (%)
1	 **1a**	 **3a**	1.4:1	Pd_2dba_3, $AsPh_3$	 **4a** 0/100	78
2	**1a**	 **3b**	2.1:1	$PdCl_2(PPh_3)_2$	 **4b** 0/100	70
3a	**1a**	 **3c**	1.5:1	$Pd(PPh_3)_4$	 **4c** 0/100	46
3b				Pd_2dba_3, $AsPh_3$		55
4	 **1b**	 **3d**	1.5:1	Pd_2dba_3, $AsPh_3$	 **4d** 0/100	72
5	 **1c**	**3a**	1.5:1	$PdCl_2(PPh_3)_2$	 **4e** 0/100	40
6	 **1d**	Ph—I **3e**	1:1.5	$PdCl_2(PPh_3)_2$	 **4f**	38
7	**1d**	**3a**	1.2:1	Pd_2dba_3, $AsPh_3$	 **4g** <5/95	50
8	**1d**	**3d**	1.5:1	$PdCl_2(PPh_3)_2$	 **4h** 10/90	72
9	 **1e**	**3a**	1.2:1	$PdCl_2(PPh_3)_2$	 **4i** 90/10	73

Table 2 (Continued)

Entry	Propargyl Alcohol	Ioododerivative	Propargyl Alcohol : ArI	Catalyst	Product *E/Z* [b]	Yield[a] (%)
10	**1e**	 **3f**	1.2:1	$PdCl_2(PPh_3)_2$	 **4j** 95/5	53
11	**1e**	 **3g**	1:1	$Pd(PPh_3)_4$	 **4k** 90/10	74
12	**1e**	**3d**	1.2:1	$PdCl_2(PPh_3)_2$	 **4l** 90/10	56
13a	**1e**	 **3h**	1.2:1	Pd_2dba_3, $AsPh_3$	 **4m** 90/10	46
13b			2.1:1			
14	 **1f**	 **3i**	2:1	Pd_2dba_3, $AsPh_3$	 **4n** ~1/1	27
15	 **1g**	**3i**	1:1	$PdCl_2(PPh_3)_2$	 **4o** 100/0	27
16	**1a**	 **3j**	1.5:1	Pd_2dba_3, $AsPh_3$	 **4p** 0/100	45

[a] Isolated yield. [b] Determined by ^1H NMR spectroscopy.

contained a methyl ester group. (Alcoholate transesterifies the product in the reaction mixture.) Aryl iodide (1 mmol), palladium catalyst (Table 1, 5 mol %), and zinc(II) chloride (82 mg, 60 mol %) were then added to the reaction mixture under an argon atmosphere. When $PdCl_2(PPh_3)_2$ is used as a catalyst, it should be added to the reaction mixture before quenching of hydrides with ethyl acetate. Reaction time and temperature for each coupling reaction are listed individually below. Methanol (1 mL) was then added, and after 2 h at room temperature, the reaction mixture was poured into brine/water (1:1), acidified with 5% hydrochloric acid to become slightly acidic (pH = 5−6), and extracted with ether (three times). The combined ethereal extracts were dried over $MgSO_4$; the solvent was evaporated under vacuum, and the crude product was purified by chromatography on silica gel. In some cases, the product contained a small amount of colored impurities, which were not separable by chromatography or detectable by NMR or elemental analysis. It was possible to remove them by boiling a methanolic solution of the product with charcoal and filtering.

(Z)-3-(4-Methoxycarbonylphenyl)but-2-en-1-ol (4a). Sodium methoxide (40 mg, 0.75 mmol), but-2-yn-1-ol (**1a**) (0.75 mL, 10 mmol), $LiAlH_4$ (10 mmol), dimethyl carbonate (1 mL, 11 mmol), methyl 4-iodobenzoate (**3a**) (1.834 g, 7 mmol),

$Pd_2dba_3{\cdot}CHCl_3$ (0.169 g, 2.5 mol %), $AsPh_3$ (0.214 g, 10 mol %), and $ZnCl_2$ (0.574 g, 60 mol %) were used in the procedure. Hydroalumination was performed by stirring the mixture at room temperature for 4 h, and the coupling reaction was run at room temperature for 3 h followed by heating at 50 °C for 1.5 h. Chromatography on silica gel (petroleum ether/ether/acetone 8:1:1) gave 1.121 g (78%) of isomerically pure product. Analytical data correspond to those previously reported.[11] Coupled ^{13}C NMR (100.6 MHz, $CDCl_3$) δ 167.6 (s, C=O), 146.3 s, 139.9 s, 129.4s (2ArC + Ar$C(CH_3)=$), 60.8 (t, $J = 142.7$ Hz, CH_2OH), 52.8 (q, $J = 147$ Hz, OCH_3), 25.7 (dq, $^1J(CH) = 127.3$, $^3J(CH_3,H) = 6.9$ Hz).

(*Z*)-3-(3-Methoxycarbonylphenyl)but-2-en-1-ol (4b). Sodium methoxide (5 mg, 0.09 mmol), but-2-yn-1-ol (**1a**) (0.192 g, 1.5 mmol), $LiAlH_4$ (1.6 mmol), $PdCl_2(PPh_3)_2$ (25 mg, 5 mol %), dimethyl carbonate (0.15 mL, 1.7 mmol), methyl 3-iodobenzoate (**3b**) (0.183 g, 0.7 mmol), and $ZnCl_2$ (57 mg, 60 mol %) were used in the procedure. Hydroalumination was performed by stirring the mixture at room temperature for 4 h and the coupling at room temperature overnight. Chromatography on silica gel (petroleum ether/acetone 4:1) gave 0.101 g (70%) of oily, isomerically pure product: ^1H NMR (300 MHz, $CDCl_3$) δ 7.82−8.00 (m, 2H, ArH), 7.34−7.47 (m, 2H, ArH), 5.77 (dt, $J_t = 6.9$ Hz, $J_d = 1.1$ Hz, 1H, $=CHCH_2OH$), 4.05 (t, $J = 6.0$ Hz, 2H, CH_2OH), 3.92 (s, 3H, OCH_3), 2.10 (d, $J = 1.1$ Hz, 3H, $=CCH_3$), 1.31 (t, $J = 5.5$ Hz, 1H, OH); IR ($CHCl_3$) ν 3612, 3473, 3018, 1954, 1720, 1440, 1286, 1121, 1087, 988 cm^{-1}; HRMS calcd for $C_{12}H_{13}O_2$ $[M - OH]^+$ 189.0915, found 189.0995.

(*Z*)-3-(5-Methoxycarbonyl-2-methylphenyl)but-2-en-1-ol (4c). Sodium methoxide (5 mg, 0.09 mmol), but-2-yn-1-ol (**1a**) (0.192 g, 1.5 mmol), $LiAlH_4$ (1.6 mmol), dimethyl carbonate (0.15 mL, 1.7 mmol), methyl 3-iodo-4-methylbenzoate (**3c**) (0.276 g, 1 mmol), $Pd(PPh_3)_4$ (56 mg, 5 mol %), and $ZnCl_2$ (82 mg, 60 mol %) were used in the procedure. Hydroalumination was performed by stirring the reaction mixture at room temperature for 4 h, and the coupling reaction was run for 2 h at room temperature followed by heating at 60 °C for 2 h. Chromatography on silica gel (petroleum ether/acetone 4:1) gave 0.102 g (46%) of oily, isomerically pure product: ^1H NMR (300 MHz, $CDCl_3$) δ 7.84 (dd, $J = 7.7$, 1.7 Hz, 1H, ArH), 7.69 (d, $J = 2.1$ Hz, 1H, ArH), 7.27 (d, $J = 8.2$ Hz, 1H, ArH), 5.78 (dt, $J = 6.9$, 1.6 Hz, 1H, $=CHCH_2OH$), 3.90 (s, 3H, CO_2CH_3), 3.80 (t, $J = 5.5$ Hz, 2H, CH_2OH), 2.27 (s, 3H, $ArCH_3$), 1.99 (d, $J = 1.1$ Hz, 3H, $=CCH_3$), 1.13 (t, $J = 5.5$ Hz, 1H, −OH); ^{13}C NMR-APT (125.7 MHz, $CDCl_3$) CH, CH_3 δ 19.4, 24.9, 52.0, 127.1, 128.2, 129.0, 130.1; C, CH_2 δ 60.25, 127.8, 138.8, 140.5, 141.0, 167.1; IR ($CHCl_3$) ν 3620, 3019, 2973, 2953, 1717, 1609, 1438, 1294, 1262, 1119, 996 cm^{-1}. Anal. Calcd for $C_{13}H_{16}O_3$: C, 70.89; H, 7.32. Found: C, 70.83; H, 7.64.

(*Z*)-3-(4-Nitrophenyl)-4-methylpent-2-en-1-ol (4d). Sodium methoxide (5 mg, 0.09 mmol), 4-methylpent-2-yn-1-ol (**1b**) (0.147 g, 1.5 mmol), $LiAlH_4$ (1.6 mmol), dimethyl carbonate (0.15 mL, 1.7 mmol), 4-iodonitrobenzene (**3d**) (0.249 g, 1 mmol), $Pd_2dba_3{\cdot}CHCl_3$ (24 mg, 2.5 mol %), $AsPh_3$ (30 mg, 10 mol %), and $ZnCl_2$ (82 mg, 60 mol %) were used in the procedure. Hydroalumination was performed by stirring the mixture at room temperature overnight and the coupling by heating at 65 °C for 5 min. Chromatography on silica gel (petroleum ether/ether/acetone 8:1:1) gave 0.160 g (72%) of the isomerically pure product: ^1H NMR (300 MHz, $CDCl_3$) δ 8.21 (d, $J = 8.8$ Hz, 2H, ArH), 7.28 (d, $J = 8.8$ Hz, 2H, ArH), 5.75 (t, $J = 6.9$ Hz, 1H, $=CHCH_2OH$), 3.94 (d, $J = 7.1$ Hz, 2H, CH_2OH), 2.61 (septet, $J = 6.7$ Hz, 1H, $CH(CH_3)_2$), 1.04 (d, $J = 6.6$ Hz, 6H, $CH(CH_3)_2$); ^{13}C NMR-APT (125.7 MHz, $CDCl_3$) CH, CH_3 δ 21.4, 35.4, 123.3, 124.7, 129.4; C, CH_2 δ 60.0, 146.9, 147.4, 148.6; IR ($CHCl_3$) ν 3613, 3446, 3014, 2967, 2875, 1598, 1521, 1350, 1109, 1026, 1014, 979, 859 cm^{-1}. Anal. Calcd for $C_{12}H_{15}O_3N$: C, 65.14; H, 6.83; N, 6.33. Found: C, 64.95; H, 7.02; N, 6.08.

(*Z*)-3-(4-Methoxycarbonylphenyl)-5-methoxypent-2-en-1ol (4e). Sodium methoxide (5 mg, 0.09 mmol), 5-methoxypent-3-yn-1-ol (**1c**) (0.171 g, 1.5 mmol), $LiAlH_4$ (1.6 mmol), dimethyl carbonate (0.15 mL, 1.7 mmol), methyl 4-iodobenzoate (**3a**) (0.131 g, 1 mmol), $Pd_2dba_3{\cdot}CHCl_3$ (24 mg, 2.5 mol %), $AsPh_3$ (30 mg, 10 mol %), and $ZnCl_2$ (82 mg, 60 mol %) were used in the procedure. Hydroalumination was performed by stirring the mixture at room temperature overnight, and the coupling reaction was run for 2 h at room temperature followed by heating at 60 °C for 3 h. Chromatography on silica gel (petroleum ether/ether/acetone 8:1:1) gave 0.100 g (40%) of isomerically pure product: ^1H NMR (300 MHz, $CDCl_3$) δ 7.98−8.04 (m, 2H, ArH), 7.20−7.26 (m, 2H, ArH), 5.81 (t, $J = 6.9$ Hz, 1H, $=CHCH_2OH$), 4.03 (d, $J = 6.6$ Hz, 2H, CH_2OH), 3.92 (s, 3H, CO_2CH_3), 3.34 (t, $J = 6.6$ Hz, 2H, $H_3COCH_2CH_2-$), 3.26 (s, 3H, $H_3COCH_2CH_2-$), 2.67 (t, $J = 6.6$ Hz, 2H, $H_3COCH_2CH_2-$); IR ($CHCl_3$) ν 3020, 2954, 1722, 1438, 1407, 1284, 1194, 1116 cm^{-1}; HRMS calcd for $C_{14}H_{17}O_3$ $[M - OH]^+$ 233.1330, found 233.1240.

3,3-Diphenylprop-2-en-1-ol (4f). Sodium methoxide (5 mg, 0.09 mmol), 3-phenylprop-2-yn-1-ol (**1d**) (0.133 g, 1.0 mmol), $LiAlH_4$ (1.0 mmol), $PdCl_2(PPh_3)_4$ (36 mg, 5 mol %), ethyl acetate (0.35 mL, 3.5 mmol), iodobenzene (**3e**) (0.307 g, 1.5 mmol), and $ZnCl_2$ (82 mg, 60 mol %) were used in the procedure. Hydroalumination was performed by stirring the mixture at 0 °C for 1 h and the coupling by heating of the mixture at 60 °C overnight. Chromatography on silica gel (petroleum ether/ether/acetone 8:1:1) gave 0.079 g (38%) of the pure product. The compound was described previously:[22] ^1H NMR (300 MHz, $CDCl_3$) δ 7.15−7.41 (m, 10H, ArH), 6.25 (t, $J = 6.9$ Hz, 1H, $=CHCH_2OH$), 4.20−4.36 (m, 2H, CH_2OH), 1.38 (s, 1H, OH).

(*Z*)-3-(4-Methoxycarbonylphenyl)-3-phenylprop-2-en-1-ol (4 g). Sodium methoxide (10 mg, 0.18 mmol), 3-phenylprop-2-yn-1-ol (**1d**) (0.316 g, 2.4 mmol), $LiAlH_4$ (2.4 mmol), $PdCl_2(PPh_3)_4$ (72 mg, 5 mol %), dimethyl carbonate (0.2 mL, 2.3 mmol), methyl 4-iodobenzoate (**3a**) (0.524 g, 2 mmol), and $ZnCl_2$ (0.164 g, 60 mol %) were used in the procedure. Hydroalumination was performed by stirring the mixture at 0 °C for 1 h and the coupling reaction by heating of the mixture at 60 °C overnight. Chromatography on silica gel (petroleum ether/acetone 4:1) gave 0.270 g (50%) of the product containing a trace amount of (*Z*)-isomer. Analytical data correspond to those previously reported.[11]

(*Z*)-3-(4-Nitrophenyl)-3-phenylprop-2-en-1-ol (4h). Sodium methoxide (5 mg, 0.09 mmol), 3-phenylprop-2-yn-1-ol (**1d**) (0.198 g, 1.5 mmol), $LiAlH_4$ (1.6 mmol), $PdCl_2(PPh_3)_4$ (36 mg, 5 mol %), dimethyl carbonate (0.15 mL, 1.7 mmol), 4-iodonitrobenzene (**3d**) (0.249 g, 1 mmol), and $ZnCl_2$ (82 mg, 60 mol %) were used in the procedure. Hydroalumination was performed by stirring the mixture at 0 °C for 1 h and the coupling by stirring the mixture for 3 h at room temperature followed by heating at 50 °C for 3 h. Chromatography on silica gel (petroleum ether/ether/acetone 8:1:1) gave 0.183 g (72%) of the product containing 10% of the (*Z*)-isomer. Crystals formed from the oily product are the compound with a higher isomerical purity: ^1H NMR (300 MHz, $CDCl_3$) δ 8.24−8.29 (m, 2H, ArH), 7.13−7.44 (m, 7H, ArH), 6.35 (t, $J = 6.9$ Hz, 1H, $=CHCH_2OH$), 4.20 (d, $J = 6.6$ Hz, 2H, CH_2OH), 1.48 (s, 1H, OH); peaks of the (*Z*)-isomer 8.15, 6.39, 4.27; ^{13}C NMR-APT (125.7 MHz, $CDCl_3$) CH, CH_3 δ 123.4, 127.4, 128.1, 128.4, 129.3, 130.6; C, CH_2 δ 60.1, 140.5, 142.1, 146.0, 147.1; IR ($CHCl_3$) ν 3612, 3443, 3014, 1599, 1520, 1347, 1015, 850. Anal. Calcd for $C_{15}H_{13}NO_3$: C, 70.58; H, 5.13; N, 5.49. Found: C, 70.45; H, 5.42; N, 5.26.

(*E*)-3-(4-Methoxycarbonylphenyl)-3-trimethylsilylprop-2-en-1-ol (4i). Sodium methoxide (5 mg, 0.09 mmol), 3-(trimethylsilyl)prop-2-yn-1-ol (**1e**) (0.176 mL, 1.2 mmol), $LiAlH_4$ (1.2 mmol), $PdCl_2(PPh_3)_2$ (36 mg, 5 mol %), dimethyl carbonate (0.15 mL, 1.7 mmol), $ZnCl_2$ (82 mg, 60 mol %), and methyl 4-iodobenzoate (**3a**) (0.262 g, 1 mmol) were used in the procedure. Hydroalumination was performed by stirring the mixture at room temperature for 2 h, and the coupling reaction was run for 70 min at 65 °C. Chromatography on silica gel (petroleum ether/ether/acetone 8:1:1) gave 0.193 g (73%) of oily material. The product contained 10% of the (*Z*)-isomer. Analytical data correspond to those previously reported:[11] ^1H NMR (300 MHz, $CDCl_3$) δ 7.97 (d, $J = 8.2$ Hz, 2H, ArH), 7.00 (d, $J = 8.2$ Hz, 2H, ArH), 6.15 (t, $J = 6.0$ Hz, 1H, $=CHCH_2OH$), 3.99 (d, $J = 6.0$ Hz, 2H, CH_2OH), 3.91 (s, 3H, CO_2CH_3), 0.07 (s, 9H, Si(CH_3)$_3$); peaks of (Z)-isomer 7.09 d, 6.25 t, 4.36 d, 0.15 s.

(*E*)-3-(2-Thienyl)-3-trimethylsilylprop-2-en-1-ol (4j). Sodium methoxide (5 mg, 0.09 mmol), 3-(trimethylsilyl)prop-2-yn-1-ol (**1e**) (0.176 mL, 1.2 mmol), $LiAlH_4$ (1.4 mmol), $PdCl_2(PPh_3)_2$ (36 mg, 5 mol %), ethyl acetate (0.4 mL, 4 mmol), $ZnCl_2$ (82 mg, 60 mol %), and 2-iodothiophene (**3f**) (0.210 g, 1 mmol) were used in the procedure. Hydroalumination was performed by stirring the mixture at room temperature for 2 h and the coupling reaction by heating at 65 °C overnight. Chromatography on silica gel (petroleum ether/acetone 4:1) gave 0.115 g (53%) of oily product. The compound contained 5% of the (*Z*)-isomer: ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.22 (dd, *J* = 5.0, 1.1 Hz, 1H, ArH), 6.99 (dd, *J* = 5.0, 3.3 Hz, 1H, ArH), 6.65 (dd, *J* = 1.1, 3.3 Hz, 1H, ArH), 6.22 (t, *J* = 5.8 Hz, 1H, =C*H*CH$_2$OH), 4.06 (t, *J* = 5.8 Hz, 2H, CH$_2$OH), 1.42 (t, *J* = 5.8 Hz, 2H, OH), 0.13 (s, 9H, Si(CH_3)$_3$); peaks of the (*Z*)-isomer 6.52 t, 4.36 t, 0.23 s; IR ($CHCl_3$) ν 3614, 3458, 3019, 2959, 2898, 1721, 1666, 1435, 1408, 1250, 1037, 1018, 888, 841 cm^{-1}. Anal. Calcd for $C_{10}H_{16}OSSi$: C, 56.55; H, 7.59; S, 15.10. Found: C, 56.24; H, 7.40; S, 15.08.

(*E*)-3-(4-*N*,*N*-Dimethylaminocarbonylphenyl)-3-trimethylsilylprop-2-en-1-ol (4k). Sodium methoxide (50 mg, 0.9 mmol), 3-(trimethylsilyl)prop-2-yn-1-ol (**1e**) (1.46 mL, 10 mmol), $LiAlH_4$ (10 mmol), ethyl acetate (2.5 mL, 25 mmol), $Pd(PPh_3)_4$ (575 mg, 5 mol %), $ZnCl_2$ (0.84 g, 60 mol %), and *N*,*N*-dimethyl-4-iodobenzamide (**3g**) (2.75 g, 10 mmol) were used in the procedure. Hydroalumination was performed by stirring the mixture at room temperature for 2 h, and the coupling reaction was run at 65 °C overnight. Chromatography on silica gel (heptane/ethyl acetate/ethanol 40:55:5) gave 2.062 g (74%) of oily product. The compound contained 10% of the (*Z*)-isomer. Crystallization from petroleum ether/toluene afforded isomerically pure product: mp 78 °C; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.38 (d, *J* = 8.2 Hz, 2H, ArH), 6.95 (d, *J* = 8.2 Hz, 2H, ArH), 6.15 (t, *J* = 6 Hz, 1H, =C*H*CH$_2$OH), 4.01 (t, *J* = 5.22 Hz, 2H, C*H*$_2$OH), 3.11 (s, 3H, N(C*H*$_3$)$_2$), 3.01 (s, 3H, N(C*H*$_3$)$_2$), 1.27−1.35 (m, 1H, OH), 0.08 (s, 9H, Si(CH_3)$_3$); peaks of the (*Z*)-isomer 7.04 d, 6.22 t, 4.35 d, 0.14 s; ^{13}C NMR-APT (125.7 MHz, $CDCl_3$) CH, CH_3 δ −1.8, 35.4, 39.7, 127.1, 127.2, 140.2; C, CH_2 δ 60.5, 133.4, 143.3, 145.9, 171.7; IR ($CHCl_3$) ν 3615, 3009, 2957, 1823, 1488, 1401, 1250, 1083, 1018, 910, 841 cm^{-1}. Anal. Calcd for $C_{15}H_{23}NO_2Si$: C, 64.94; H, 8.36; N, 5.05. Found: C, 64.89; H, 8.36; N, 5.01.

(*E*)-3-(4-Nitrophenyl)-3-trimethylsilylprop-2-en-1-ol (4l). Sodium methoxide (5 mg, 0.09 mmol), 3-(trimethylsilyl)prop-2-yn-1-ol (**1e**) (0.176 mL, 1.2 mmol), $LiAlH_4$ (1.2 mmol), $PdCl_2(PPh_3)_2$ (36 mg, 5 mol %), ethyl acetate (0.25 mL, 2.5 mmol), $ZnCl_2$ (82 mg, 60 mol %), 4-iodonitobenzene (**3d**) (0.249 g, 1 mmol) were used in the procedure. Hydroalumination was performed by stirring the mixture at room temperature for 2 h and the coupling reaction by heating at 65 °C overnight. Chromatography on silica gel (petroleum ether/ether/acetone 8:1:1) gave 0.140 g (56%) of oily product. The compound contained 10% of the (*Z*)-isomer: ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.18 (d, *J* = 8.2 Hz, 2H, ArH), 7.09 (d, *J* = 8.2 Hz, 2H, ArH), 6.20 (t, *J* = 6.0 Hz, 1H, =C*H*CH$_2$OH), 3.99 (d, *J* = 6.0 Hz, 2H, C*H*$_2$OH), 0.10 (s, 9H, Si(CH_3)$_3$); peaks of the (*Z*)-isomer 7.17 d, 6.27 t, 4.49 d, 0.17 s; ^{13}C NMR-APT (125.7 MHz, $CDCl_3$) CH, CH_3 δ −1.9, 123.6, 128.1, 140.3; C, CH_2 δ 60.6, 145.7, 146.2, 149.5; IR ($CHCl_3$) ν 3614, 3014, 2959, 1594, 1518, 1345, 1251, 1110, 1014, 913, 858, 841, 828 cm^{-1}. Anal. Calcd for $C_{12}H_{17}NO_3Si$: C, 57.36; H, 6.82; N, 5.57. Found: C, 57.37; H, 6.83; N, 5.32.

(*E*)-3-(4-Acetamidophenyl)-3-trimethylsilylprop-2-en-1-ol (4m). Sodium methoxide (5 mg, 0.09 mmol), 3-(trimethylsilyl)prop-2-yn-1-ol (**1e**) (0.192 mL, 1.5 mmol), $LiAlH_4$ (1.6 mmol), dimethyl carbonate (0.15 mL, 1.7 mmol), 4-iodoacetanilide (**3h**) (0.183 g, 0.7 mmol), $Pd_2dba_3{\cdot}CHCl_3$ (17 mg, 2.5 mol %), triphenyl arsine (21 mg, 10 mol %), and $ZnCl_2$ (57 mg, 60 mol %) were used in the procedure. Hydroalumination was performed by stirring the mixture at room temperature for 2 h and the coupling reaction by heating at 65 °C overnight. Chromatography on silica gel (petroleum ether/ether/acetone/methanol 50:30:17:3) gave 0.085 g (46%) of the crystalline material, containing 10% of the (*Z*)-isomer: mp 114 °C; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.43 (d, *J* = 8.2 Hz, 2H, ArH), 7.14 (s, 1H, NH), 6.89 (d, *J* = 8.8 Hz, 2H, ArH), 6.13 (t, *J* = 6.0 Hz, 1H, =C*H*CH$_2$OH), 4.03 (t, *J* = 5.8 Hz, 1H, C*H*$_2$OH), 2.18 (s, 3H, C*H*$_3$CONH), 1.29 (t, *J* = 5.8, 1H, OH), 0.07 (s, 9H, Si(CH_3)$_3$); peaks of the (*Z*)-isomer 6.99 d, 6.22 t, 4.35 t, 0.15 s. ^{13}C NMR-APT (125.7 MHz, $CDCl_3$) CH, CH_3 δ −1.8, 24.5, 119.8, 127.8, 139.6; C, CH_2 δ 60.7, 135.9, 137.5, 146.6, 168.6; IR ($CHCl_3$) ν 3437, 3019, 1957, 1719, 1685, 1585, 1512, 1399, 1310, 1286, 1250, 1014, 909, 842 cm^{-1}. Anal. Calcd for $C_{14}H_{21}NO_2Si$: C, 63.84; H, 8.04; N, 5.32. Found: C, 63.80; H, 8.07; N, 4.89.

3-(4-Methoxyphenyl)prop-2-en-1-ol (4n). Sodium methoxide (10 mg, 0.18 mmol), propargyl alcohol (**1f**) (0.112 g, 2 mmol), $LiAlH_4$ (2 mmol), dimethyl carbonate (0.15 mL, 1.7 mmol), 4-iodoanisole (**3i**) (0.234 g, 1 mmol), $Pd_2dba_3{\cdot}CHCl_3$ (24 mg, 2.5 mol %), $AsPh_3$ (30 mg, 10 mol %), and $ZnCl_2$ (82 mg, 60 mol %) were used in the procedure. Hydroalumination was performed by mixing the components at −78 °C followed by stirring at room temperature overnight. The coupling reaction was run at 60 °C overnight. Chromatography on silica gel (dichloromethane) gave 0.044 g (27%) of the product as a mixture of both geometric isomers (∼1:1) and 0.045 g (27%) of the 3-(4-methoxyphenyl)prop-2-yn-1-ol. Compounds were described previously.[23] (*E*)/(*Z*) 3-(4-Methoxyphenyl)prop-2-en-1-ol: ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.33 (d, *J* = 8.8 Hz, 2H, ArH), 7.17 (d, *J* = 8.8 Hz, 2H, ArH), 6.88 (d, *J* = 8.8 Hz, 2H, ArH), 6.86 (d, *J* = 8.8 Hz, 2H, ArH), 6.56 (d, *J* = 16.5 Hz, 1H, ArCH=), 6.51 (d, *J* = 12.1 Hz, 1H, ArCH=), 6.24 (td, J_t = 6.1 Hz, J_d = 15.9 Hz, 1H, ArCH=C*H*), 5.78 (td, J_t = 6.6 Hz, J_d = 11.5 Hz, 1H, ArCH=C*H*), 4.44 (bs, 2H, C*H*$_2$OH), 4.30 (bs, 2H, C*H*$_2$OH), 3.82 (s, 3H, OCH_3), 3.81 (s, 3H, OCH_3). 3-(4-Methoxyphenyl)prop-2-yn-1-ol: ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.38 (d, *J* = 8.8 Hz, 2H, ArH), 6.83 (d, *J* = 8.8 Hz, 2H, ArH), 4.79 (s, 2H, C*H*$_2$OH), 3.81 (s, 3H), 1.67 (s, 1H, OH).

(*E*)-4-(4-Methoxyphenyl)-4-(thiophen-2-yl)but-3-en-2-ol (4o). Sodium methoxide (5 mg, 0.09 mmol), 4-(thiophen-2-yl)but-4-yn-2-ol (**1g**) (0.152 g, 1.0 mmol), $LiAlH_4$ (1.1 mmol), $PdCl_2(PPh_3)_4$ (36 mg, 5 mol %), ethyl acetate (0.35 mL, 3.5 mmol), 4-iodoanisole (**3i**) (0.234 g, 1 mmol), and $ZnCl_2$ (82 mg, 60 mol %) were used in the procedure. Hydroalumination was performed by stirring the mixture at 0 °C for 4h and the coupling reaction by heating at 45 °C for 2 days. Chromatography on silica gel (petroleum ether/ether/acetone 8:1:1) gave 0.070 g (27%) of the pure product: ^{1}H NMR (300 MHz, $CDCl_3$) δ 7,15−7.23 (m, 3H, ArH), 6.88−6.97 (m, 3H, ArH), 6.68 (dd, *J* = 3.3, 1.1 Hz, 1H, ArH), 6.09 (d, *J* = 9.3 Hz, 1H, =C*H*CH$_2$OH), 4.32 (dq, J_d = 9.3 Hz, J_q= 6.2 Hz, 1H, C*H*(OH)CH_3), 3.85 (s, 3H, OCH_3), 1.46 (s, 1H, OH), 1.31 (d, *J* = 6.1 Hz, 3H, CH(OH)C*H*$_3$); IR ($CHCl_3$) ν 3805, 3011, 2974, 2992, 2838, 1608, 1510, 1462, 1376, 1289, 1247, 1176, 1035 cm^{-1}. Anal. Calcd for $C_{15}H_{16}O_2S$: C, 69.20; H, 6.19; S, 12.31. Found: C, 69.11; H, 6.24; S, 12.14.

(2*Z*,4*E*)-3-Methyldeca-2,4-dien-1-ol (4p). Sodium methoxide (5 mg, 0.09 mmol), but-2-yn-1-ol (**1a**) (0.192 g, 1.5 mmol), $LiAlH_4$ (1.6 mmol), ethyl acetate (0.35 mL, 3.5 mmol), 1-iodohept-1-ene (**3j**) (0.224 g, 1 mmol), $Pd_2dba_3{\cdot}CHCl_3$ (24 mg, 2.5 mol %), triphenyl arsine (30 mg, 10 mol %), and $ZnCl_2$ (82 mg, 60 mol %) were used in the procedure. Hydroalumination was performed by stirring the mixture at room temperature for 4 h and the coupling reaction by heating at 50 °C overnight and then at 60 °C for 4 h. Chromatography on silica gel (petroleum ether/ether/acetone 8:1:1) gave 0.075 g (45%) of product: ^{1}H NMR (500 MHz, $CDCl_3$) δ 6.44 (d, *J* = 15.5 Hz, 1H), 5.81 (dt, J_d = 15.5 Hz, J_t = 7.2 Hz, 1H), 5.50 (t, *J* = 7.1 Hz, 1H), 4.30 (d, *J* = 7.2 Hz, 2H), 2.16 (q, *J* = 7.2 Hz, 2H), 1.88 (s, 3H), 1.44 (quintet, *J* = 7.2 Hz, 2H), 1.27−1.40 (m, 4H), 1.23 (bs, 1H), 0.92 (t, *J* = 6.9 Hz, 3H); IR ($CHCl_3$) ν 3609, 3016, 2959, 2930, 2859, 1083, 1456, 1379, 990, 986. Anal. Calcd for $C_{11}H_{20}O$: C, 78.51; H, 11.98. Found: C, 78.26; H, 11.57.

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[23] Salih, R. G.; Shandala, M. Y. *Collect. Czech. Chem. Commun.* **1976**, *41*, 262.