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Stereoselective synthesis of functionalized (1*E*,5*E*)-1,5-dien-3-ynes containing ester or sulfonyl groups by palladium-catalyzed addition and cross-coupling reactions

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Trimethylsilylacetylene undergoes clean *cis*-addition to alkynyl sulfones or esters **1** in the presence of catalytic palladium acetate and tri(2,6-dimethoxyphenyl)phosphine to give (*E*)-1-sulfonyl (or ethoxycarbonyl)-4-trimethylsilyl-substituted 1,3-enyne **2** in excellent yields. The cross-coupling reaction of (*E*)-1-sulfonyl (or ethoxycarbonyl)-4-trimethylsilyl-substituted 1,3-enyne **2** with (*E*)-alkenyl iodides **3** in the presence of $Pd(PPh_3)_4$ and tris(diethylamino)sulfonium trimethyldifluorosilicate (TASF) affords stereoselectively (1*E*,5*E*)-1-sulfonyl (or ethoxycarbonyl)-substituted 1,5-dien-3-ynes **4** in good yields.

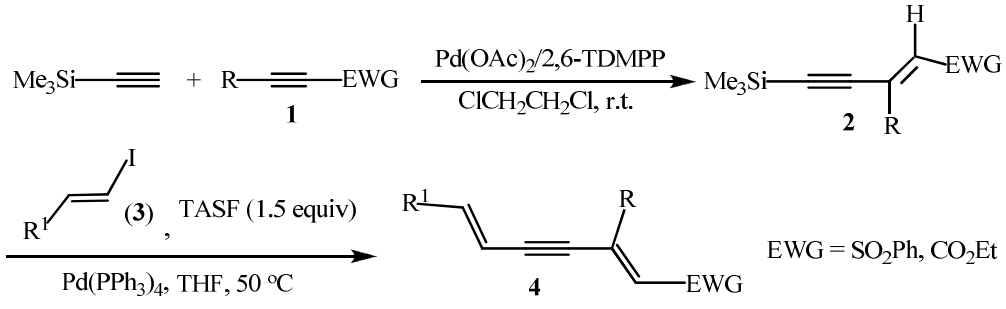
Introduction

Construction of conjugated compounds, such as enynes, enediynes, and dienynes, is of great significance since they are found in diverse fields ranging from natural products[1] and pharmaceuticals[2] to functional materials.[3] Furthermore, conjugated molecules are versatile building blocks for many naturally occurring biologically active compounds and π-conjugated polymers.[4] In particular, the high π-electron delocalization behavior in these π-conjugated molecules allows their wide application in advanced organic materials, such as molecular wires, nonlinear optics, organic conductors, electroluminescence, etc.[4g,5] For the formation of $sp–sp^2$ carbon–carbon bond, transition metal-catalyzed cross-coupling reaction is the key step.[6] Suzuki

reaction,[7] Sonogashira reaction,[8] Stille reaction[9] and Negishi reaction[10] are used complementarily in such construction. A number of stereoselective methods for obtaining conjugated dienynes have been described,[11] generally, the key steps were two sequential palladium-catalyzed cross-couplings between an acetylenic derivative and two alkenyl units. Hiyama and co-workers reported that trimethylsilyl(trimethyl-stannyl)ethyne could couple sequentially with two different alkenyl iodides in the presence of the same palladium catalyst to afford stereo-defined 1,5-dien-3-ynes in one-pot.[11a] Rossi and co-workers converted trimethylsilylethynylzinc chloride into alka-1,5-dien-3-yne upon the stepwise procedure, coupling with alkenyl halide, desilylation, and coupling with another alkenyl halide.[11c] Tellier and co-workers reported that butenynylzinc bromides derived from 1,1-difluoroethene underwent the Negishi coupling with alkenyl iodides to give terminal 1,5-dien-3-ynes.[11b] Hoshi and co-workers reported that alka-1,5-dien-3-ynes could be synthesized stereoselectively via a sequential Suzuki-type and Sonogashira reaction of alkenyldisiamylborane with trimethylsilylethynyl bromide and alkenyl iodides in a one-pot manner.[11d]

The synthesis of dienynes containing metal or heteroatom functional groups has also attracted considerable interest in organic synthesis because many useful functional group transformations can be achieved by introduction and removal of metal or heteroatom functions. Alami *et al.* reported the regioselective synthesis of stannylated dienynes by the palladium-catalyzed hydrostannylation of enediynes.[12] Liu and coworkers reported that 2,5-di(trimethylsilyl)-substituted (1*E*,5*E*)-1,5-dien-3-ynes could be obtained with high stereoselectivity via the Brønsted acid catalyzed

dehydration of cumulenols.[13] Functionalized 1,5-dien-3-ynes could also be prepared by transition metal-catalyzed bond reorganization of 1,3-diynes.[14] Very recently, Jiang and co-workers reported the synthesis of various dihalo-, haloacyl-, and diacyl-substituted 1,5-dien-3-ynes by palladium-catalyzed bond reorganization of 1,3-diynes bearing propargylic alcohol moieties.[15] Despite the significant progress that has been achieved in the synthesis of functionalized 1,5-dien-3-ynes,[12-15] further advances are still desirable, particularly with regard to the controlled incorporation of different functional groups by a simple and convenient protocol. To the best of our knowledge, no well-established method is used to prepare stereoselectively (1*E*,5*E*)-1-sulfonyl (or ethoxycarbonyl)-substituted 1,5-dien-3-ynes. Herein, we wish to report that (1*E*,5*E*)-1-sulfonyl (or ethoxycarbonyl)-substituted 1,5-dien-3-ynes could be conveniently synthesized via the *cis*-addition of trimethylsilylacetylene to alkynyl sulfones or esters in the presence of catalytic palladium acetate and tri(2,6-dimethoxyphenyl)phosphine (2,6-TDMPP), followed by the cross-coupling reaction with (*E*)-alkenyl iodides in the presence of $Pd(PPh_3)_4$ and tris(diethylamino)sulfonium trimethyldifluorosilicate (TASF) (Scheme 1).



Scheme 1. Synthesis of functionalized 1,5-dien-3-ynes containing ester or sulfonyl groups

Results and Discussion

One general method for the synthesis of 1-sulfonyl-substituted 1,3-enynes involves the condensation of methyl phenyl sulfone with α,β-acetylenic aldehydes or ketones in the presence of a base and the subsequent dehydration of the condensation products using methylsulfonyl chloride and triethylamine as dehydrating agents, but low yields and poor stereoselectivity are usually obtained.[16] Trost *et al.* reported that terminal alkynes could undergo clean *cis*-1,2-addition to alkynyl esters in the presence of catalytic $Pd(OAc)_2$ and tri(2,6-dimethoxyphenyl)phosphine to produce 2-en-4-ynoates in excellent yields.[17] We also found that the *cis*-addition reaction of trimethylsilyl-acetylene to alkynyl sulfones or esters **1** could proceed smoothly in the presence of 2 mol% of $Pd(OAc)_2$ and 2 mol% of tri(2,6-dimethoxyphenyl)phosphine (2,6-TDMPP) in 1,2-dichloroethane at room temperature to afford highly regio- and stereo-selectively (*E*)-1-sulfonyl (or ethoxycarbonyl)-4-trimethylsilyl-substituted 1,3-enynes **2** in excellent yields after 6 h (Scheme 1). The typical results are summarized in Table 1. As shown in Table 1, a variety of alkynyl sulfones and alkynyl esters could be used as the substrates and the isolation of products only involved direct flash chromato-graphy to give the desired (*E*)-1-sulfonyl (or ethoxycarbonyl)-4-trimethylsilyl-substituted 1,3-enynes **2**.

Investigations of the crude products **2** by ^{1}H NMR spectroscopy (400 MHz) showed their isomeric purities of more than 99%. One olefinic proton signal of compounds **2a-2g** appears as a singlet at δ = 5.87-6.71, which indicates that the

addition reaction of trimethylsilylacetylene to alkynyl sulfones or alkynyl esters **1** had taken place with strong preference for the addition of the hydrogen atom at the carbon adjacent to the phenylsulfonyl or ester groups. The (1*E*)-configuration of the compound **2b** was confirmed by the NOESY in the ^{1}H NMR spectrum. The correlation between the allylic protons (δ = 2.49) and aromatic protons was observed. There was no correlation between the vinylic proton (δ = 6.36) and the allylic protons (δ = 2.49). The NOE results indicate that the compound **2b** has the expected *E*-configuration and that trimethylsilylacetylene undergoes clean *cis*-1,2-addition to an internal alkynyl sulfone or alkynyl ester in the presence of catalytic $Pd(OAc)_2$ and 2,6-TDMPP in 1,2-dichloroethane.

Table 1 Synthesis of (*E*)-1-sulfonyl (or ethoxycarbonyl)-4-trimethylsilyl-substituted 1,3-enynes **2**[a]

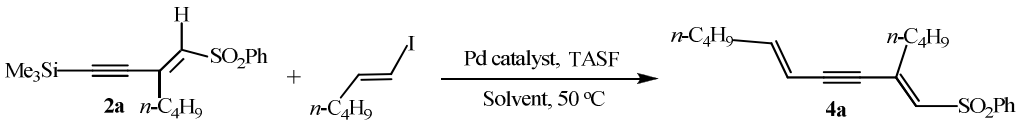
Entry	EWG	R	Product	Yield[b] (%)
1	SO_2Ph	*n*-C_4H_9	**2a**	89
2	SO_2Ph	*n*-C_6H_{13}	**2b**	90
3	SO_2Ph	Ph	**2c**	91
4	SO_2Ph	$CH_3OCH_2CH_2$	**2d**	86
5	CO_2Et	*n*-C_4H_9	**2e**	90
6	CO_2Et	Ph	**2f**	91
7	CO_2Et	Cyclopropyl	**2g**	88

[a] Reaction conditions: trimethylsilylacetylene (1.1 mmol), alkynyl sulfone or ester (1 mmol), $Pd(OAc)_2$ (0.02 mmol), 2,6-TDMPP (0.02 mmol), 1,2-dichloroethane (2 mL), room temperature, 6 h. [b] Isolated yields.

The cross-coupling of organosilicon reagents with organic halides has evolved to be comparable in scope to other palladium-catalyzed coupling methods.[18] Alkynylsilanes, which are easily prepared by addition of alkynyllithium or alkynylmagnesium reagents to chlorosilanes, are competent reagents for the palladium-catalyzed cross-coupling reaction.[19] Hiyama *et al.* reported that the palladium-catalyzed cross-coupling reaction of alkynylsilanes with alkenyl halides could proceed smoothly in the presence of tris(diethylamino)sulfonium trimethyldifluorosilicate (TASF) to afford the desired 1,3-enynes in good yields.[11a,19a] To prepare highly stereoselectively (1*E*,5*E*)-1-sulfonyl (or ethoxycarbonyl)-substituted 1,5-dien-3-ynes, we investigated the palladium-catalyzed cross-coupling reaction of (*E*)-1-sulfonyl (or ethoxycarbonyl) -4-trimethylsilyl-substituted 1,3-enynes **2** with (*E*)-alkenyl iodides **3** (Scheme 1). Our initial efforts were devoted to the selection of an efficient catalyst and a suitable solvent for efficient cross-coupling reaction of (*E*)-1-sulfonyl (or ethoxycarbonyl)-4-trimethylsilyl-substituted 1,3-enynes **2** with (*E*)-alkenyl iodides **3**. Thus, (*E*)-1-phenylsulfonyl-2-butyl-4-trimethylsilyl-1-buten-3-yne **2a** (1.2 mmol) and (*E*)-1-iodo -1-hexene (1.0 mmol) were treated in different solvents (5 mL), at 50 °C, with Pd(0) and Pd(II) catalysts in the presence of TASF (1.5 mmol) (Table 2). As shown in Table 2, among the palladium catalysts tested [$PdCl_2(MeCN)_2$, $Pd(PPh_3)_4$, $PdCl_2(PPh_3)_2$, and $PdCl_2(dppf)$], $Pd(PPh_3)_4$ proved to be the most efficient. For the solvents evaluated [DMF, THF, dioxane, and HMPA], THF was the best choice. A lower yield was observed and a longer reaction time was required when the amount of $Pd(PPh_3)_4$ was decreased (entries 8 and 9). Taken together, good result was obtained when the cross-

coupling reaction was carried out with 5 mol% $Pd(PPh_3)_4$ in THF in presence of TASF (1.5 equiv) at 50 °C for 2 h under Ar atmosphere (entry 2).

Table 2 Influences of the catalysts and solvents in the cross-coupling reaction[a]



Entry	Catalyst (mol%)	Solvent	Time (h)	Isolated yield **4a** (%)
1	$PdCl_2(MeCN)_2$ (5)	THF	4	54
2	$Pd(PPh_3)_4$ (5)	THF	2	84
3	$PdCl_2(PPh_3)_2$ (5)	THF	4	60
4	$PdCl_2$(dppf) (5)	THF	4	62
5	$Pd(PPh_3)_4$ (5)	DMF	4	69
6	$Pd(PPh_3)_4$ (5)	dioxane	4	59
7	$Pd(PPh_3)_4$ (5)	HMPA	4	73
8	$Pd(PPh_3)_4$ (2.5)	THF	6	80
9	$Pd(PPh_3)_4$ (1)	THF	24	75

[a] Reaction was performed with **2a** (1.2 mmol), (*E*)-1-iodo-1-hexene (1.0 mmol), TASF (1.5 mmol), solvent (5 mL) at 50 °C under Ar.

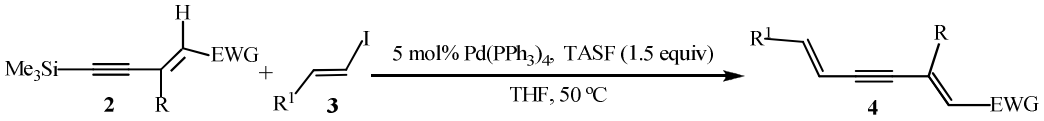
To examine the scope for this cross-coupling reaction, the coupling reactions of a variety of (*E*)-1-sulfonyl (or ethoxycarbonyl)-4-trimethylsilyl-substituted 1,3-enynes **2** with various (*E*)-alkenyl iodides **3** were investigated under the optimum conditions and the experimental results are listed in Table 3. As shown in Table 3, the palladium-catalyzed cross-coupling reactions of a variety of (*E*)-1-sulfonyl-4-trimethylsilyl-substituted 1,3-enynes **2** with (*E*)-alkenyl iodides **3** proceeded smoothly in the

presence of 5 mol% $Pd(PPh_3)_4$ and TASF (1.5 equiv) in THF at 50 °C to afford highly stereoselectively the corresponding (1*E*,5*E*)-1-sulfonyl-substituted 1,5-dien-3-ynes **4a-g** in good yields (Table 3, entries 1-7). Similarly, stereo-defined (1*E*,5*E*)-1-ethoxycarbonyl-substituted 1,5-dien-3-ynes **4h-n** could also be conveniently obtained in good yields by the palladium-catalyzed cross-coupling reactions of (*E*)-1-ethoxy-carbonyl-4-trimethylsilyl-substituted 1,3-enynes **2** with (*E*)-alkenyl iodides **3** under the same reaction conditions (Table 3, entries 8-14). In all cases, a single geometric isomer was formed according to Scheme 1. The (5*E*)-configuration of the compounds **4a-4n** has been proved by their ^{1}H NMR spectra which showed a doublet at δ = 5.46-6.32 with a coupling constant of 16.0-16.4 Hz, and this is also the evidence of the retention of the *E*-configuration of the starting compounds **3**.

We also attempted a one-pot bis-functionalization of trimethylsilylacetylene. After the addition reaction of trimethylsilylacetylene (1.1 equiv) with 1-phenylsulfonyl-1-hexyne using 2 mol% $Pd(OAc)_2$ and 2 mol% tri(2,6-dimethoxyphenyl)phosphine (2,6-TDMPP) in 1,2-dichloroethane at room temperature for 6 h, (*E*)-1-iodo-1-hexene (1.0 equiv) and TASF (1.5 equiv) were added and the mixture was stirred at 80 °C for 24 h, unfortunately, the desired coupling product **4a** was not obtained. Even if the reaction temperature was reduced to 60 or 50 °C, no desired **4a** was observed. We then examined the effect of the solvents on the secondary transformation. It was found that, after the addition reaction of trimethylsilylacetylene (1.1 equiv) with 1-phenyl- sulfonyl-1-hexyne using 2 mol% $Pd(OAc)_2$ and 2 mol% tri(2,6-dimethoxyphenyl)- phosphine (2,6-TDMPP) in 1,2-dichloroethane at room

temperature for 6 h, solvent removal under reduced pressure and stirring of the residue with THF, (*E*)-1-iodo- 1-hexene (1.0 equiv) and TASF (1.5 equiv) at 50 °C for 24 h, only trace of desired **4a** was detected. The other solvents such as dioxane, DMF, and HMPA were also found to be ineffective.

Table 3 Synthesis of (1*E*,5*E*)-1-sulfonyl (or ethoxycarbonyl)-substituted 1,5-dien-3-ynes **4** [a]



Entry	EWG	R	R^1	Product	Yield[b] (%)
1	SO_2Ph	*n*-C_4H_9	*n*-C_4H_9	**4a**	84
2	SO_2Ph	*n*-C_4H_9	Ph	**4b**	79
3	SO_2Ph	Ph	Ph	**4c**	80
4	SO_2Ph	*n*-C_6H_{13}	Ph	**4d**	83
5	SO_2Ph	*n*-C_6H_{13}	*n*-C_4H_9	**4e**	76
6	SO_2Ph	*n*-C_6H_{13}	$CH_3OCH_2CH_2$	**4f**	74
7	SO_2Ph	Ph	$CH_3OCH_2CH_2$	**4g**	78
8	CO_2Et	*n*-C_4H_9	Ph	**4h**	86
9	CO_2Et	*n*-C_4H_9	*n*-C_6H_{13}	**4i**	81
10	CO_2Et	Ph	Ph	**4j**	83
11	CO_2Et	Ph	*n*-C_6H_{13}	**4k**	80
12	CO_2Et	cyclopropyl	Ph	**4l**	77
13	CO_2Et	cyclopropyl	*n*-C_4H_9	**4m**	75
14	CO_2Et	*n*-C_4H_9	$CH_3OCH_2CH_2$	**4n**	82

[a] Reaction was performed with **2** (1.2 mmol), **3** (1 mmol), $Pd(PPh_3)_4$ (0.05 mmol), TASF (1.5 mmol), THF (5 mL) at 50 °C under Ar for 2 h. [b] Isolated yields.

Conclusion

In summary, we have developed a highly efficient approach for the stereoselective synthesis of functionalized (1*E*,5*E*)-1,5-dien-3-ynes containing ester and sulfonyl groups by the *cis*-addition of trimethylsilylacetylene to alkynyl sulfones or esters in the presence of catalytic palladium acetate and tri(2,6-dimethoxyphenyl)phosphine (2,6-TDMPP), followed by the palladium-catalyzed cross-coupling reaction with (*E*)-alkenyl iodides in the presence of TASF. The present method has some attractive advantages of readily available starting materials, straightforward and simple procedures, mild reaction conditions, high stereoselectivity and good yields.

Experimental

General comments

All chemicals were reagent grade and used as purchased. All solvents were dried and distilled before use. The products were purified by flash chromatography on silica gel. A mixture of light petroleum ether (30-60 °C) and diethyl ether was generally used as eluent. All products were characterized by comparison of their spectra and physical data with authentic samples. IR spectra were determined on a Perkin-Elmer 683 instrument. ^{1}H NMR spectra were recorded on a Bruker Avance 400 (400 MHz) spectrometer with TMS as an internal standard in $CDCl_3$ as solvent. ^{13}C NMR spectra were recorded on a Bruker Avance 400 (100 MHz) spectrometer in $CDCl_3$ as solvent. Mass spectra were obtained on a Finnigan 8239 mass spectrometer. Microanalyses were measured by using a Yanaco MT-3 CHN microelemental analyzer. Alkynyl

sulfones[20] and alkynyl esters[21] were prepared according to literature procedures.

General procedure for the palladium-catalyzed addition reaction of trimethylsilylacetylene to alkynyl sulfones or esters

To a solution of alkynyl sulfone or alkynyl ester (1.0 mmol) and trimethylsilylacetylene (1.1 mmol) in 1,2-dichloroethane (2.0 mL) was added $Pd(OAc)_2$ (0.02 mmol) and 2,6-TDMPP (0.02 mmol) at room temperature under an argon atmosphere. The reaction mixture was stirred at room temperature for 6 h and concentrated under reduced pressure and the residue was purified by column chromatography (light petroleum ether/diethyl ether, 3:1 or 10:1) on silica gel.

(*E*)-1-Phenylsulfonyl-2-butyl-4-trimethylsilyl-1-buten-3-yne 2a [Table 1, entry 1]. Oil. IR (neat): ν_{max}/cm^{-1} 3066, 2960, 2932, 2873, 2145, 1576, 1447, 1307, 1251, 1150, 1085, 844, 724, 605. ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm): 7.73 (d, J = 7.2 Hz, 2H), 7.45-7.35 (m, 3H), 6.36 (s, 1H), 2.49 (t, J = 7.2 Hz, 2H), 1.33-1.30 (m, 2H), 1.19-1.13 (m, 2H), 0.72 (t, J = 7.2 Hz, 3H), 0.00 (s, 9H). ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm): 141.8, 140.4, 134.4, 133.3, 129.2, 127.4, 103.1, 102.9, 31.1, 30.2, 22.2, 13.7, -0.52. Anal. Calcd. for $C_{17}H_{24}O_2SiS$: C, 63.72; H, 7.55. Found: C, 63.46; H, 7.31.

(*E*)-1-Phenylsulfonyl-2-hexyl-4-trimethylsilyl-1-buten-3-yne 2b [Table 1, entry 2]. Oil. IR (neat): ν_{max}/cm^{-1} 2931, 2860, 2147, 1576, 1447, 1308, 1252, 1151, 1086, 845, 723, 605. ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm): 7.74-7.72 (m, 2H), 7.45-7.35 (m, 3H), 6.36 (s, 1H), 2.49 (t, J = 7.6 Hz, 2H), 1.35-1.30 (m, 2H), 1.18-1.04 (m, 6H), 0.70 (t, J = 7.2 Hz, 3H), 0.00 (s, 9H). ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm): 142.2, 141.1,

134.8, 133.9, 129.7, 127.9, 103.4, 103.3, 32.0, 31.8, 29.2, 28.5, 22.9, 14.5, 0.0. Anal. Calcd. for $C_{19}H_{28}O_2SiS$: C, 65.48; H, 8.10. Found: C, 65.21; H, 7.82.

(*E*)-1-Phenylsulfonyl-2-phenyl-4-trimethylsilyl-1-buten-3-yne 2c [Table 1, entry 3]. Oil. IR (neat): ν_{max}/cm^{-1} 3060, 2926, 2215, 1562, 1447, 1307, 1251, 1151, 1085, 843, 722. ^1H NMR (400 MHz, $CDCl_3$) δ (ppm): 7.45 (d, J = 7.6 Hz, 2H), 7.35 (t, J = 7.4 Hz, 1H), 7.23-7.12 (m, 7H), 6.71 (s, 1H), 0.00 (s, 9H). ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm): 141.3, 137.9, 136.7, 134.4, 133.8, 130.3, 129.6, 129.4, 128.4, 128.3, 104.6, 103.4, 0.0. Anal. Calcd. for $C_{19}H_{20}O_2SiS$: C, 67.03; H, 5.92. Found: C, 66.77; H, 5.69.

(*E*)-1-Phenylsulfonyl-2-(2-methoxyethyl)-4-trimethylsilyl-1-buten-3-yne 2d [Table 1, entry 4]. Oil. IR (neat): ν_{max}/cm^{-1} 2961, 2890, 2345, 1586, 1449, 1304, 1251, 1149, 1119, 1087, 849, 607. ^1H NMR (400 MHz, $CDCl_3$) δ (ppm): 7.76 (d, J = 7.2 Hz, 2H), 7.45-7.35 (m, 3H), 6.40 (s, 1H), 3.43 (t, J = 6.4 Hz, 2H), 3.15 (s, 3H), 2.84 (t, J = 6.4 Hz, 2H), 0.00 (s, 9H). ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm): 141.2, 136.7, 136.0, 133.6, 129.3, 127.6, 103.6, 102.1, 70.1, 58.7, 31.3, -0.45. Anal. Calcd. for $C_{16}H_{22}O_3SiS$: C, 59.61; H, 6.88. Found: C, 59.38; H, 7.02.

(*E*)-1-(Ethoxycarbonyl)-2-butyl-4-trimethylsilyl-1-buten-3-yne 2e [Table 1, entry 5]. Oil. IR (neat): ν_{max}/cm^{-1} 2960, 2933, 2874, 2145, 1717, 1610, 1466, 1368, 1252, 1193, 1146, 1037, 844, 760. ^1H NMR (400 MHz, $CDCl_3$) δ (ppm): 5.87 (s, 1H), 3.95 (q, J = 7.2 Hz, 2H), 2.52 (t, J = 7.6 Hz, 2H), 1.40-1.29 (m, 2H), 1.21-1.09 (m, 2H), 1.07 (t, J = 7.2 Hz, 3H), 0.72 (t, J = 7.4 Hz, 3H), 0.00 (s, 9H). ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm): 165.8, 142.8, 124.7, 105.6, 99.9, 60.0, 31.7, 30.5, 22.3, 14.2, 13.9,

-0.3. Anal. Calcd. for $C_{14}H_{24}O_2Si$: C, 66.64; H, 9.59. Found: C, 66.37; H, 9.33.

(*E*)-1-(Ethoxycarbonyl)-2-phenyl-4-trimethylsilyl-1-buten-3-yne 2f [Table 1, entry 6]. Oil. IR (neat): ν_{max}/cm^{-1} 2961, 2901, 2139, 1726, 1597, 1445, 1369, 1251, 1160, 1085, 1034, 845, 761. ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm): 7.24-7.21 (m, 2H), 7.14-7.12 (m, 3H), 6.13 (s, 1H), 3.86 (q, J = 7.2 Hz, 2H), 0.92 (t, J = 7.2 Hz, 3H), 0.00 (s, 9H). ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm): 165.3, 137.7, 136.2, 128.9, 128.6, 127.8, 125.6, 105.1, 101.0, 60.4, 13.9, -0.3. Anal. Calcd. for $C_{16}H_{20}O_2Si$: C, 70.57; H, 7.40. Found: C, 70.71; H, 7.56.

(*E*)-1-(Ethoxycarbonyl)-2-cyclopropyl-4-trimethylsilyl-1-buten-3-yne 2g [Table 1, entry 7]. Oil. IR (neat): ν_{max}/cm^{-1} 2961, 2902, 2150, 1712, 1598, 1395, 1384, 1252, 1155, 1042, 920, 857, 734. ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm): 6.09 (s, 1H), 4.18 (q, J = 7.2 Hz, 2H), 3.16-3.12 (m, 1H), 1.28 (t, J = 7.2 Hz, 3H), 0.93-0.86 (m, 4H), 0.19 (s, 9H). ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm): 166.4, 145.8, 123.2, 101.1, 99.8, 59.8, 14.2, 12.0, 8.4, -0.4. Anal. Calcd. for $C_{13}H_{20}O_2Si$: C, 66.08; H, 8.53. Found: C, 65.86; H, 8.72.

General procedure for palladium-catalyzed cross-coupling of (*E*)-1-sulfonyl (or ethoxycarbonyl)-4-trimethylsilyl-substituted 1,3-enynes 2 with (*E*)-alkenyl iodides 3

A THF solution of TASF (1.0 M, 1.5 mL, 1.5 mmol) was added to (*E*)-1-sulfonyl (or ethoxycarbonyl)-4-trimethylsilyl-substituted 1,3-enyne **2** (1.2 mmol) and $Pd(PPh_3)_4$ (0.05 mmol) dissolved in THF (3.5 mL) at –78 °C under an argon atmosphere. (*E*)-Alkenyl iodide **3** (1.0 mmol) was injected to the resulting solution, and the

mixture was slowly warmed to ambient temperature, allowed to react for 2 h at 50 °C. After being cooled to room temperature, the mixture was quenched with aq sodium bicarbonate (5 mL) and diluted with diethyl ether (20 mL). The ether solution was dried over $MgSO_4$ and concentrated under reduced pressure. The residue was purified by flash column chromatography on silica gel (light petroleum ether/diethyl ether, 3:1 or 10:1).

(1*E*,5*E*)-1-Phenylsulfonyl-2-butyl-1,5-decadien-3-yne 4a [Table 3, entry 1]. Oil. IR (neat): ν_{max}/cm^{-1} 2958, 2930, 2187, 1570, 1447, 1317, 1149, 1085, 958, 821, 752. ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm): 7.91 (d, J = 7.2 Hz, 2H), 7.62-7.52 (m, 3H), 6.48 (s, 1H), 6.25 (dt, J = 16.0, 7.6 Hz, 1H), 5.58 (d, J = 16.0 Hz, 1H), 2.68 (t, J = 7.6 Hz, 2H), 2.18-2.11 (m, 2H), 1.51-1.25 (m, 8H), 0.92-0.87 (m, 6H). ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm): 148.6, 142.1, 141.4, 133.3, 132.7, 129.2, 127.3, 108.6, 95.9, 86.7, 33.0, 31.5, 30.6, 30.4, 22.4, 22.1, 13.9, 13.8. MS (EI, 70 eV): *m/z* (%) = 330 (13) $[M]^+$, 288 (25), 205 (70), 163 (64), 91 (83), 77 (100), 57 (65). Anal. Calcd. for $C_{20}H_{26}O_2S$: C, 72.69; H, 7.93. Found: C, 72.78; H, 7.70.

(1*E*,5*E*)-1-Phenylsulfonyl-2-butyl-6-phenyl-1,5-hexadien-3-yne 4b [Table 3, entry 2]. Oil. IR (neat): ν_{max}/cm^{-1} 3031, 2930, 2180, 1561, 1447, 1314, 1147, 1085, 954, 819, 749. ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm): 7.93 (d, J = 7.2 Hz, 2H), 7.63-7.53 (m, 3H), 7.41-7.31 (m, 5H), 7.01 (d, J = 16.0 Hz, 1H), 6.55 (s, 1H), 6.26 (d, J = 16.0 Hz, 1H), 2.73 (t, J = 7.6 Hz, 2H), 1.56-1.51 (m, 2H), 1.39-1.33 (m, 2H), 0.92 (t, J = 7.2 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm): 144.2, 141.9, 141.0, 135.6, 133.4, 133.1, 129.4, 129.3, 128.9, 127.4, 126.6, 106.7, 96.2, 90.2, 31.4, 30.5, 22.4, 13.9. MS

(EI, 70 eV): *m/z* (%) = 350 (66) $[M]^+$, 219 (96), 209 (72), 165 (100), 152 (74), 115 (65), 77 (46). Anal. Calcd. for $C_{22}H_{22}O_2S$: C, 75.41; H, 6.33. Found: C, 75.17; H, 6.56.

(1*E*,5*E*)-1-Phenylsulfonyl-2,6-diphenyl-1,5-hexadien-3-yne 4c [Table 3, entry 3]. Oil. IR (neat): ν_{max}/cm^{-1} 3060, 2926, 2180, 1557, 1447, 1307, 1147, 1084, 956, 819, 751. ^1H NMR (400 MHz, $CDCl_3$) δ (ppm): 7.63 (d, J = 7.2 Hz, 2H), 7.52 (t, J = 7.4 Hz, 1H), 7.43-7.30 (m, 12H), 7.02 (d, J = 16.4 Hz, 1H), 6.90 (s, 1H), 6.26 (d, J = 16.4 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm): 144.5, 140.9, 137.6, 135.5, 134.9, 134.2, 133.2, 129.6, 129.5, 129.0, 128.9, 128.8, 128.0, 127.7, 126.7, 106.6, 97.5, 90.5. MS (EI, 70 eV): *m/z* (%) = 370 (8.3) $[M]^+$, 305 (25), 229 (100), 215 (40), 77 (54). Anal. Calcd. for $C_{24}H_{18}O_2S$: C, 77.81; H, 4.90. Found: C, 77.54; H, 4.62.

(1*E*,5*E*)-1-Phenylsulfonyl-2-hexyl-6-phenyl-1,5-hexadien-3-yne 4d [Table 3, entry 4]. Oil. IR (neat): ν_{max}/cm^{-1} 3032, 2929, 2858, 2181, 1567, 1447, 1314, 1148, 1085, 954, 819, 749. ^1H NMR (400 MHz, $CDCl_3$) δ (ppm): 7.93 (d, J = 7.6 Hz, 2H), 7.63-7.53 (m, 3H), 7.40-7.33 (m, 5H), 7.01 (d, J = 16.0 Hz, 1H), 6.55 (s, 1H), 6.26 (d, J = 16.0 Hz, 1H), 2.72 (t, J = 7.6 Hz, 2H), 1.58-1.50 (m, 2H), 1.30-1.21 (m, 6H), 0.89 (t, J = 7.0 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm): 144.2, 142.0, 141.1, 135.6, 133.4, 133.1, 129.4, 129.3, 128.9, 127.4, 126.6, 106.7, 96.2, 90.2, 31.6, 31.5, 28.9, 28.3, 22.5, 14.1. MS (EI, 70 eV): *m/z* (%) = 378 (26) $[M]^+$, 308 (36), 247 (78), 165 (65), 77 (100), 57 (45). Anal. Calcd. for $C_{24}H_{26}O_2S$: C, 76.15; H, 6.92. Found: C, 75.87; H, 6.70.

(1*E*,5*E*)-1-Phenylsulfonyl-2-hexyl-1,5-decadien-3-yne 4e [Table 3, entry 5]. Oil. IR

(neat): ν_{max}/cm^{-1} 2959, 2929, 2188, 1574, 1447, 1317, 1149, 1085, 958, 821, 753. ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm): 7.91 (d, J = 7.6 Hz, 2H), 7.64-7.52 (m, 3H), 6.48 (s, 1H), 6.25 (dt, J = 16.0, 7.6 Hz, 1H), 5.59 (d, J = 16.0 Hz, 1H), 2.67 (t, J = 7.6 Hz, 2H), 2.18-2.11 (m, 2H), 1.52-1.26 (m, 12H), 0.91-0.86 (m, 6H). ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm): 148.7, 142.0, 141.5, 133.3, 132.6, 129.2, 127.3, 108.6, 96.0, 86.6, 33.0, 31.7, 31.6, 30.6, 28.9, 28.2, 22.5, 22.1, 14.1, 13.8. MS (EI, 70 eV): *m/z* (%) = 358 (3.3) $[M]^+$, 205 (15), 149 (100), 77 (63), 57 (56). Anal. Calcd. for $C_{22}H_{30}O_2S$: C, 73.70; H, 8.43. Found: C, 73.83; H, 8.19.

(1*E*,5*E*)-1-Phenylsulfonyl-2-hexyl-8-methoxy-1,5-octadien-3-yne 4f [Table 3, entry 6]. Oil. IR (neat): ν_{max}/cm^{-1} 2929, 2859, 2189, 1571, 1447, 1316, 1149, 1085, 912, 821, 733. ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm): 7.91 (d, J = 7.6 Hz, 2H), 7.64-7.53 (m, 3H), 6.48 (s, 1H), 6.24 (dt, J = 16.0, 7.6 Hz, 1H), 5.68 (d, J = 16.0 Hz, 1H), 3.44 (t, J = 6.8 Hz, 2H), 3.33 (s, 3H), 2.67 (t, J = 7.6 Hz, 2H), 2.44-2.39 (m, 2H), 1.51-1.45 (m, 2H), 1.28-1.24 (m, 6H), 0.88 (t, J = 7.2 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm): 144.6, 142.0, 141.3, 133.3, 132.9, 129.3, 127.3, 110.5, 95.4, 87.1, 71.1, 58.7, 33.6, 31.6, 31.5, 28.9, 28.2, 22.5, 14.1. MS (EI, 70 eV): *m/z* (%) = 360 (2.3) $[M]^+$, 277 (15), 125 (38), 77 (87), 57 (100). Anal. Calcd. for $C_{21}H_{28}O_3S$: C, 69.96; H, 7.83. Found: C, 70.13; H, 7.59.

(1*E*,5*E*)-1-Phenylsulfonyl-2-phenyl-8-methoxy-1,5-octadien-3-yne 4g [Table 3, entry 7]. Oil. IR (neat): ν_{max}/cm^{-1} 2928, 2189, 1557, 1447, 1306, 1149, 1084, 909, 824, 733. ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm): 7.61-7.59 (m, 2H), 7.52-7.48 (m, 1H), 7.39-7.28 (m, 7H), 6.83 (s, 1H), 6.26 (dt, J = 16.0, 7.6 Hz, 1H), 5.68 (d, J = 16.0 Hz,

1H), 3.42 (t, J = 6.8 Hz, 2H), 3.32 (s, 3H), 2.43-2.38 (m, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm): 145.1, 141.0, 137.7, 134.8, 134.2, 133.2, 129.5, 128.9, 128.8, 127.9, 127.7, 110.5, 96.7, 87.5, 71.1, 58.7, 33.6. MS (EI, 70 eV): *m/z* (%) = 352 (1.8) $[M]^+$, 277 (54), 178 (61), 105 (66), 84 (100), 77 (69). Anal. Calcd. for $C_{21}H_{20}O_3S$: C, 71.56; H, 5.72. Found: C, 71.29; H, 5.54.

(1*E*,5*E*)-1-(Ethoxycarbonyl)-2-butyl-6-phenyl-1,5-hexadien-3-yne 4h [Table 3, entry 8]. Oil. IR (neat): ν_{max}/cm^{-1} 2959, 2931, 2180, 1709, 1595, 1448, 1159, 909, 733. ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm): 7.43-7.31 (m, 5H), 7.02 (d, J = 16.0 Hz, 1H), 6.32 (d, J = 16.0 Hz, 1H), 6.08 (s, 1H), 4.19 (q, J = 7.2 Hz, 2H), 2.80 (t, J = 7.6 Hz, 2H), 1.63-1.57 (m, 2H), 1.43-1.38 (m, 2H), 1.29 (t, J = 7.2 Hz, 3H), 0.95 (t, J = 7.2 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm): 165.9, 143.2, 143.0, 136.0, 129.1, 128.8, 126.5, 123.7, 107.5, 93.8, 92.8, 60.0, 32.1, 30.8, 22.5, 14.3, 14.0. MS (EI, 70 eV): *m/z* (%) = 282 (45) $[M]^+$, 253 (85), 211 (100), 165 (78), 115 (57). Anal. Calcd. for $C_{19}H_{22}O_2$: C, 80.81; H, 7.85. Found: C, 80.53; H, 7.62.

(1*E*,5*E*)-1-(Ethoxycarbonyl)-2-butyl-1,5-dodecadien-3-yne 4i [Table 3, entry 9]. Oil. IR (neat): ν_{max}/cm^{-1} 2959, 2930, 2188, 1714, 1601, 1466, 1159, 909, 735. ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm): 6.24 (dt, J = 16.0, 7.2 Hz, 1H), 6.01 (s, 1H), 5.63 (d, J = 16.0 Hz, 1H), 4.16 (q, J = 7.2 Hz, 2H), 2.75 (t, J = 7.6 Hz, 2H), 2.18-2.11 (m, 2H), 1.58-1.25 (m, 15H), 0.95-0.91 (m, 6H). ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm): 166.0, 147.2, 143.5, 123.1, 109.2, 93.5, 89.1, 59.9, 33.3, 32.1, 31.6, 30.7, 28.8, 28.6, 22.6, 22.4, 14.2, 14.1, 13.9. MS (EI, 70 eV): *m/z* (%) = 290 (17) $[M]^+$, 261 (48), 233 (47), 179 (52), 163 (100), 91 (73), 57 (59). Anal. Calcd. for $C_{19}H_{30}O_2$: C, 78.57; H,

10.41. Found: C, 78.71; H, 10.29.

(1*E*,5*E*)-1-(Ethoxycarbonyl)-2,6-diphenyl-1,5-hexadien-3-yne 4j [Table 3, entry 10]. Oil. IR (neat): ν_{max}/cm^{-1} 3059, 3030, 2981, 2928, 2181, 1717, 1589, 1447, 1163, 909, 733. ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm): 7.46-7.28 (m, 10H), 7.03 (d, J = 16.0 Hz, 1H), 6.34-6.30 (m, 2H), 4.09 (q, J = 7.2 Hz, 2H), 1.14 (t, J = 7.2 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm): 165.4, 143.7, 143.4, 138.5, 136.7, 135.9, 129.2, 128.8, 128.4, 127.9, 126.6, 124.4, 107.4, 95.2, 92.4, 60.4, 14.0. MS (EI, 70 eV): *m/z* (%) = 302 (14) $[M]^+$, 273 (55), 115 (37), 105 (100), 77 (59), 71 (76), 57 (96). Anal. Calcd. for $C_{21}H_{18}O_2$: C, 83.42; H, 6.00. Found: C, 83.19; H, 5.78.

(1*E*,5*E*)-1-(Ethoxycarbonyl)-2-phenyl-1,5-dodecadien-3-yne 4k [Table 3, entry 11]. Oil. IR (neat): ν_{max}/cm^{-1} 2958, 2928, 2188, 1717, 1592, 1445, 1257, 1162, 910, 733. ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm): 7.42-7.40 (m, 2H), 7.36-7.33 (m, 3H), 6.29-6.22 (m, 2H), 5.64 (d, J = 16.0 Hz, 1H), 4.06 (q, J = 7.2 Hz, 2H), 2.16-2.11 (m, 2H), 1.42-1.24 (m, 8H), 1.13 (t, J = 7.2 Hz, 3H), 0.88 (t, J = 6.6 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm): 165.4, 147.8, 138.8, 136.8, 128.7, 128.4, 127.8, 124.0, 109.1, 94.9, 88.9, 60.3, 33.4, 31.6, 28.8, 28.5, 22.6, 14.1, 14.0. MS (EI, 70 eV): *m/z* (%) = 310 (26) $[M]^+$, 265 (39), 211 (51), 185 (52), 165 (100), 57 (52). Anal. Calcd. for $C_{21}H_{26}O_2$: C, 81.25; H, 8.44. Found: C, 81.03; H, 8.19.

(1*E*,5*E*)-1-(Ethoxycarbonyl)-2-cyclopropyl-6-phenyl-1,5-hexadien-3-yne 4l [Table 3, entry 12]. Oil. IR (neat): ν_{max}/cm^{-1} 2982, 2935, 2183, 1705, 1587, 1448, 1159, 1038, 911, 734. ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm): 7.42-7.29 (m, 5H), 6.97 (d, J = 16.0 Hz, 1H), 6.25 (d, J = 16.0 Hz, 1H), 6.10 (s, 1H), 4.20 (q, J = 7.2 Hz, 2H), 3.25-3.22

(m, 1H), 1.30 (t, J = 7.2 Hz, 3H), 0.98-0.93 (m, 4H). ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm): 166.6, 146.4, 143.3, 135.8, 129.1, 128.8, 126.6, 122.4, 107.1, 93.6, 88.2, 59.9, 14.3, 12.5, 8.6. MS (EI, 70 eV): *m/z* (%) = 266 (27) $[M]^+$, 237 (100), 191 (46), 165 (61), 105 (81), 77 (83). Anal. Calcd. for $C_{18}H_{18}O_2$: C, 81.17; H, 6.81. Found: C, 80.89; H, 6.65.

(1*E*,5*E*)-1-(Ethoxycarbonyl)-2-cyclopropyl-1,5-decadien-3-yne 4m [Table 3, entry 13]. Oil. IR (neat): ν_{max}/cm^{-1} 2959, 2931, 2190, 1709, 1591, 1266, 1158, 1038, 922, 858. ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm): 6.10 (dt, J = 16.0, 7.6 Hz, 1H), 5.93 (s, 1H), 5.46 (d, J = 16.0 Hz, 1H), 4.07 (q, J = 7.2 Hz, 2H), 3.13-3.05 (m, 1H), 2.07-2.00 (m, 2H), 1.32-1.14 (m, 7H), 0.83-0.76 (m, 7H). ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm): 166.7, 147.5, 146.7, 121.9, 108.8, 93.3, 84.4, 59.8, 32.9, 30.6, 22.1, 14.3, 13.8, 12.4, 8.5. MS (EI, 70 eV): *m/z* (%) = 246 (14) $[M]^+$, 217 (55), 147 (54), 128 (97), 91 (100). Anal. Calcd. for $C_{16}H_{22}O_2$: C, 78.01; H, 9.00. Found: C, 77.76; H, 9.15.

(1*E*,5*E*)-1-(Ethoxycarbonyl)-2-butyl-8-methoxy-1,5-octadien-3-yne 4n [Table 3, entry 14]. Oil. IR (neat): ν_{max}/cm^{-1} 2959, 2930, 2189, 1713, 1602, 1465, 1159, 1120, 911, 733. ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm): 6.24 (dt, J = 16.0, 7.2 Hz, 1H), 6.01 (s, 1H), 5.72 (d, J = 16.0 Hz, 1H), 4.16 (q, J = 7.2 Hz, 2H), 3.46 (t, J = 6.6 Hz, 2H), 3.35 (s, 3H), 2.75 (t, J = 7.6 Hz, 2H), 2.46-2.41 (m, 2H), 1.58-1.51 (m, 2H), 1.41-1.33 (m, 2H), 1.28 (t, J = 7.2 Hz, 3H), 0.92 (t, J = 7.2 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm): 165.9, 143.3, 143.1, 123.4, 111.1, 93.0, 89.6, 71.3, 59.9, 58.7, 33.6, 32.1, 30.7, 22.4, 14.3, 13.9. MS (EI, 70 eV): *m/z* (%) = 264 (27) $[M]^+$, 235 (100), 219 (93), 161 (70), 91 (48). Anal. Calcd. for $C_{16}H_{24}O_3$: C, 72.69; H, 9.15. Found: C, 72.83;

H, 8.96.

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Graphical Abstract

Stereoselective synthesis of functionalized (1*E*,5*E*)-1,5-dien-3-ynes containing ester or sulfonyl groups by palladium-catalyzed addition and cross-coupling reactions

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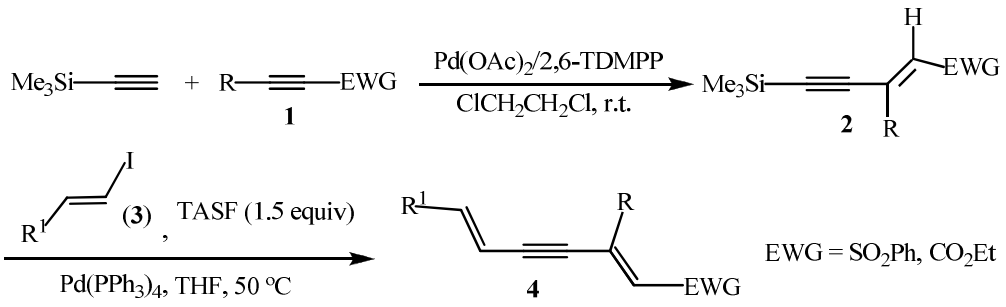

(1*E*,5*E*)-1-sulfonyl (or ethoxycarbonyl)-substituted 1,5-dien-3-ynes could be easily synthesized via the *cis*-addition of trimethylsilylacetylene to alkynyl sulfones or esters in the presence of catalytic palladium acetate and tri(2,6-dimethoxyphenyl)phosphine, followed by the cross-coupling reaction with (*E*)-alkenyl iodides in the presence of $Pd(PPh_3)_4$ and tris(diethylamino)sulfonium trimethyldifluorosilicate.