Ultrasound-Assisted Synthesis of Functionalized 1,3-Enynes by Palladium-Catalyzed Cross-Coupling Reaction of α-Styrylbutyltelluride with Alkynyltrifluoroborate Salts

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Abstract: An ultrasound-assisted synthesis of functionalized 1,3-enyne scaffolds is described and illustrated by palladium-catalyzed cross-coupling of potassium alkynyltrifluoroborate salts and α-styrylbutyltellurides. This procedure offers easy access to 1,3-enyne architecture that contains aliphatic and aromatic groups in good to excellent yields.

Key words: cross-coupling reaction, 1,3-enyne, α-styrylbutyltelluride, potassium alkynyltrifluroborate salts

Functionalized enyne scaffolds play an important role in the biosynthesis of several polyacetylenic compounds in the plants that belongs to *Apiaceae*, *Araliaceae* and *Asteraceae* family.[1,2] These polyacetylenic systems are common structural features found in many biologically important synthetic and natural products.[3–5] Molecules embedded with these scaffolds are known to exhibit diverse pharmacological activities such as antibiotic[6] and anticancer.[7] Naturally occurring acetylenes have attracted wide interest during the past two decades. Even though these scaffolds have been studied by many research groups for more than a century, but the most exciting results were obtained after 1980, through the discovery of a new antibiotic family, the so called enediyne antibiotics.[8–12] In addition, these scaffolds are fascinating and challenging research objects in order to explore their intrinsic photophysical and photochemical properties.

Numerous synthetic methodologies are available for the synthesis of enyne[13] units which involves the chemoselective triple-bond reduction of conjugated unsymmetrical diacetylene systems by using sodium borohydride,[14] flash vacuum pyrolysis of *N*-propargyloxadiazolinone through a quartz tube,[15] by the reaction of 2-furyllithium with β-bromostyrene in the presence of palladium catalyst,[16] and palladium-catalyzed cross-coupling reaction of haloalkenes and haloalkynes with 1-alkenyldisiamylboranes or 1-alkenyl-1,3,2-benzodioxaboroles in the presence of bases such as sodium alkoxides.[17] In last decade Montevecchi and his research group reported the synthesis of enynes by DDQ-prompted oxidation of phenylalkylacetylenes.[18] In last few decades, some research groups have paid their attention on the synthesis of enyne scaffolds by palladium- or rhodium-catalyzed dimerization of terminal alkynes but these approaches were associated with the mixture of isomers.[19] Recently, Santelli and his research group has reported the tetraphosphine–palladium-catalyzed synthesis of enynes using vinyl bromides with terminal alkynes as coupling moieties.[20]

Most of the available methodologies for the synthesis of enyne systems suffered by low yield, harsh reaction conditions, and formation of some undesired side products.[17,18] Thus, there is a need to develop an expedient route for the synthesis of these systems that could offer an economical route with the flexibility of introducing the electron-donor or -acceptor groups into their molecular architecture.

Recently, Molander and his group introduced potassium organotrifluoroborate salts as a nucleophilic partner in the Suzuki–Miyaura reaction instead of unstable organoboron reagents.[21] These reagents are readily prepared by addition of KHF_2 salt to an organoboron intermediates,[22] and they were monomeric, crystalline compounds that were easily handled and indefinitely stable to moisture and air.

Organotellurium compounds have successfully been used in several metal-assisted cross-coupling reactions as alternative of halogens.[23,24] Recently, we reported the synthesis of biaryls, stereodefined stilbenes and 1,3-dienes, using organotellurium compounds as alternative of halogens in cross-coupling reactions.[25] Tellurium compounds containing halides moiety in their structures exhibited high chemoselectivity. Reaction occurred exclusively at the telluride moiety, and none at the halide.[25a,b]

Our recent efforts[25b,26] indicated that the metal-assisted cross-coupling reaction of potassium organotrifluoroborate salts and organotellurium compounds can be successfully achieved in few minutes by using ultrasonic waves as a source of energy.

The ultrasound effects are attributed to a physical process called cavitation.[27]

Herein, we report an alternative approach for the synthesis of 1,3-enyne systems in high yields by the Suzuki–Miyaura reaction of potassium alkynyltrifluoroborate salts and α-styrylbutyltelluride. The strength of the procedure lies in the formation of C–C bond and introduction of aliphatic and aromatic functionalities into their molecular architecture.

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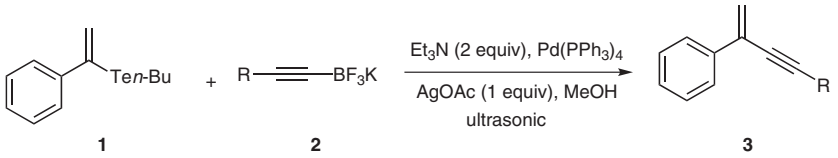
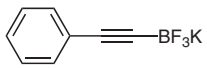
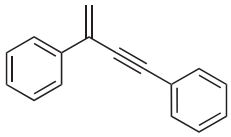
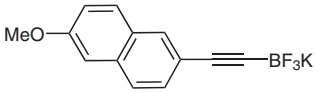
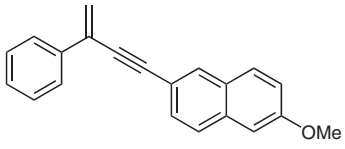
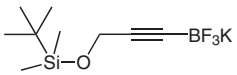
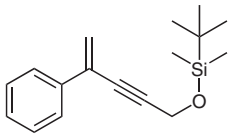
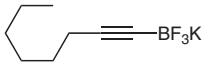
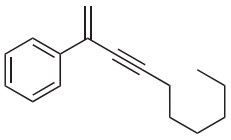
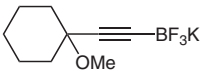
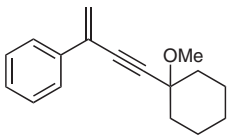
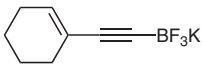
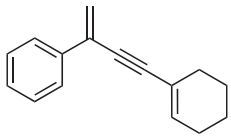
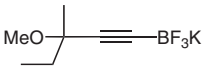
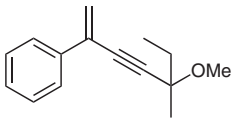
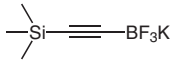
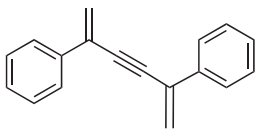
Table 1 Suzuki–Miyaura Reaction of α-*n*-Butyltelluro Styrene and Potassium Alkynyltrifluoroborate Salts

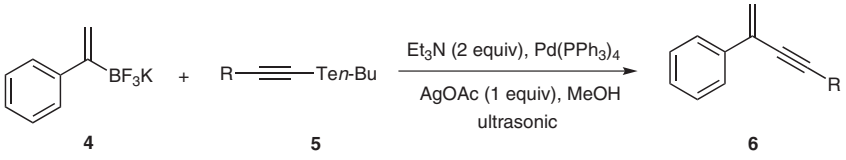


1 **2** **3**

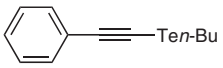
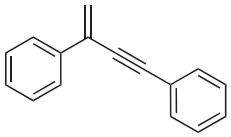
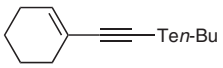
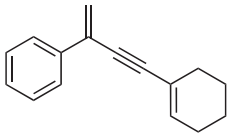
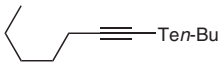
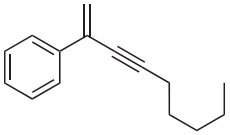
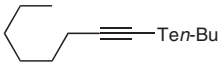
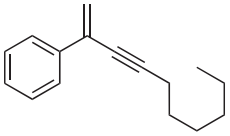
Entry	Alkynyltrifluoroborate salts **2**	Products **3**	Reaction time (min)	Yield (%)
1	 **2a**	 **3a**	20	79
2	 **2b**	 3b	20	85
3	 **2c**	 **3c**	20	70
4	 **2d**	 **3d**	20	73
5	 **2e**	 **3e**	20	74
6	 **2f**	 **3f**	20	79
7	 **2g**	 **3g**	20	74
8	 **2h**	 **3h**	20	77

Our approach to prepare functionalized 1,3-enyne derivatives **3a**–**h** was based on metal-assisted cross-coupling reaction of α-styrylbutyltelluride (**1**) with potassium alkynyltrifluoroborate salts **2a**–**h**. The parent precursor α-styrylbutyltelluride (**1**) was conveniently prepared in high yields by Grignard reaction of α-bromostyrene followed by addition of tellurium and butylation by *n*-bromobutane,[25a] while the precursors potassium alkynyltrifluoroborate salts **2a**–**h** were prepared by the lithiation of

Table 2 Suzuki–Miyaura Reaction of Potassium α-Styryltrifluoroborate Salt and Alkynylbutyltellurides



4 5 6

Entry	Alkynyltellurides **5**	Products **6**	Reaction time (min)	Yield (%)
1	 **5a**	 **6a**	20	73
2	 **5b**	 **6b**	20	74
3	 **5c**	 **6c**	20	68
4	 **5d**	 **6d**	20	71

alkynes followed by the addition of trimethyl borate and KHF_2 salt, respectively.[28]

Initially, we paid our attention on the determination of the optimal conditions for the Suzuki–Miyaura reaction of α-styrylbutyltelluride (**1**) and potassium alkynyltrifluoroborate salts **2a**–**h**. Toward this end, α-styrylbutyltelluride (**1**) and potassium phenylethynyltrifluoroborate salt (**2a**) were chosen as model substrates and a variety of conditions were screened. The reactions were monitored by TLC or GC.

First of all, to determine the appropriate palladium catalyst, we performed two reactions with two different palladium catalysts $Pd(Acac)_2$ and $Pd(PPh_3)_4$ in which Ag_2O was used as additive, K_2CO_3 as base, and methanol as solvent, but no reaction was observed with $Pd(Acac)_2$ while with $Pd(PPh_3)_4$ the desired compound **3a** (1,3-enyne derivative) was isolated in 64% yield.

The next step was the determination of the best base and the necessity of an additive in the reaction. Initially was used inorganic base as potassium carbonate in the presence of Ag_2O and the desired compound was isolated in 64% yield. When the same reaction was performed with an organic base, triethylamine, the desired compound was achieved in 72% yield. Further to check the effect of base we performed the same reaction without base, but no reaction was observed.

Further, to investigate the effect of additive, the same reaction was performed with two different additives CuI and AgOAc, but no reaction was observed with CuI while the desired product **3a** was isolate in 78% yield with AgOAc. Further, to establish the stoichiometry of the reaction, we performed this reaction with two equivalents of AgOAc but the reaction leads to the formation of side products. Interestingly, no reaction was observed in the absence of additive.

The role of silver acetate can be attributed to the removal of phosphine ligands of the catalyst or from one of the catalytic intermediates formed in the course of the reaction.[25a] The catalyst loadings were analyzed and the best result was afforded with 10 mol% of $Pd(PPh_3)_4$ (79% yield).

During the optimization studies for 1,3-enyne derivative **3a**, it was observed that the reaction mixture of 1.0 equivalent of α-styrylbutyltelluride (**1**), 1.0 equivalent of potassium phenylethynyltrifluoroborate salt (**2a**), 1.0 equivalent of AgOAc, 2 equivalents of triethylamine, and 10 mol% of $Pd(PPh_3)_4$ in methanol irradiated under ultrasonic waves for 20 minutes, was found the best conditions for the synthesis of enyne derivative **3a**. After achieving the best conditions for the synthesis of desired compound **3a**, there was synthesized a series of these functionalized 1,3-enynes **3a**–**g** using the optimized conditions in 70–

85% yields (see Table 1). After completion the reaction mixture was poured into water and neutralized with ammonium chloride solution followed by the extraction with ethyl acetate. The crude product thus obtained was purified by flash column chromatography using hexane as eluent. The reaction was monitored by TLC and GC.

Further, when the same reaction was performed with potassium trimethylsilylacetylenetrifluoborate salt (**2h**), surprisingly, we did not get the desired product trimethyl(3-phenylbut-3-en-1-ynyl)silane. No signal appeared due to the three methyl groups attached with Si atom in ^{1}H NMR spectrum. The spectroscopic data of isolated compound **3h** matched with 2,5-diphenylhexa-1,5-dien-3-yne. The ^{1}H NMR spectrum of this compound showed two singlets at δ = 5.76 and 5.98 ppm, respectively, due to four hydrogen atoms of the terminal alkene groups and two multiplets appeared due to the aromatic ring. The molecular ion peak (*m/z*) in GC-MS at 230 and the presence of one signal at δ = 89.70 ppm (^{13}C NMR) due to both acetylenic carbon atoms confirmed the structure of isolated compound **3h** as 2,5-diphenylhexa-1,5-dien-3-yne. The formation of this compound can be explained because the trimethylsilyl group could be a viable donor in palladium-catalyzed cross-coupling reactions.[29] All the synthesized compounds were characterized by spectroscopic analyses.[30]

Further, in order to generalize this approach, *n*-butyltellurides of functionalized alkynes[25c] **5a–d** were prepared and the reactions with potassium α-styryltrifluroborate salt[25a] (**4**) were attempted. These reactions yielded, under similar conditions, functionalized 1,3-enynes **6a–d** in 68–74% yields (see Table 2).

In summary, we have demonstrated the ultrasound-assisted synthesis of functionalized 1,3-enyne systems by Suzuki–Miyaura reaction of easily accessible α-styrylbutyltellurides with potassium alkynyltrifluoroborate salts instead of unstable organoboronic acids. Further applications of our methodology for the synthesis of functionalized 1,3-enynes are currently in progress.

Acknowledgment

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(30) **General Procedure for the Synthesis of 3a–h**

A suspension of α-styrylbutyltelluride (**1**, 0.143 g, 0.5 mmol), potassium alkynyltrifluoroborate salt(**2**) (0.103 g, 0.50 mmol), $Pd(PPh_3)_4$ (0.055 g, 0.05 mmol), Et_3N (0.101g, 1 mmol) and AgOAc (0.083 g, 0.5 mmol) in MeOH (3 mL) was irradiated in a water bath of an ultrasonic cleaner for 20 min. Then, the reaction was diluted with EtOAc (30 mL). The organic layer was washed with sat. solution of NH_4Cl (2 × 10 mL) and H_2O (2 × 10 mL), dried over $MgSO_4$, and concentrated under vacuum. The crude product was purified by flash column chromatography (SiO_2) using hexane as eluent and characterized as follows:

But-3-en-1-yne-1,3-diyldibenzene (**3a**): yellow oil. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 5.80 (s, 1 H, CH), 6.03 (s, 1 H, CH), 7.32–7.48 (m, 5 H, ArH), 7.54–7.61 (m, 3 H, ArH), 7.74–7.81 (m, 2 H, ArH). ^{13}C NMR (75.5 MHz, $CDCl_3$): δ = 88.56, 90.78, 120.67, 123.11, 126.12, 128.36, 128.42, 129.21, 130.63, 131.68, 132.51, 137.28. IR (neat): 755.84, 782.57, 1111.48, 1225.69 cm^{-1}. GC-MS: *m*/*z* (relative intensity, %) = 204 (100), 203 (81), 202 (92), 101 (45).

2-Methoxy-6-(3-phenylbut-3-em-1ynyl)naphthalene (**3b**): colorless oil. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 3.94 (s, 3 H, OMe), 5.80 (s, 1 H, CH), 6.00 (s, 1 H, CH), 7.11–7.20 (m, 2 H, ArH), 7.27 (s, 1 H, ArH), 7.33–7.46 (m, 3 H, ArH), 7.55 (d, *J* = 8.6 Hz, 1 H, ArH), 7.68–7.81 (m, 3 H, ArH), 7.99 (s, 1 H, ArH). ^{13}C NMR (75.5 MHz, $CDCl_3$): δ = 55.38, 88.26, 91.42, 105.83, 117.99, 119.48, 120.49, 126.87, 128.10, 128.37, 128.45, 128.50, 129.04, 129.38, 130.76, 131.42, 134.23, 137.40. IR (neat): 747.75, 776.73, 1123.46, 1232.64 cm^{-1}. GC-MS: *m*/*z* (relative intensity, %) = 284 (100), 269 (10), 241 (45), 120 (45).

tert-Butyldimethyl(4-phenylpent-4-en-2-ynyloxy)silane (**3c**): colorless oil. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 0.17 (s, 6 H, 2 Me), 0.93 (s, 9 H, 3 Me), 4.55 (s, 2 H, CH_2), 5.66 (s, 1 H, CH), 5.92 (s, 1 H, CH), 7.27–7.39 (m, 3 H, ArH), 7.63–7.69 (m, 2 H, ArH). ^{13}C NMR (75.5 MHz, $CDCl_3$): δ = –5.08, 18.32, 25.82, 52.20, 83.92, 89.35, 120.70, 125.57, 126.03, 128.30, 130.27, 137.09. IR (neat): 761.12, 789.67, 1104.28, 1218.70 cm^{-1}. GC-MS: *m*/*z* (relative intensity, %) = 272 (100), 257 (18), 242 (28), 167 (48).

Dec-1-en-3-yn-2-ylbenzene (**3d**): colorless oil. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 0.90 (t, *J* = 6.6 Hz, 3 H, Me), 1.28–1.67 (m, 8 H, 4 CH_2), 2.40 (t, *J* = 6.6 Hz, 2 H, CH_2), 5.57 (s, 1 H, CH), 5.83 (s, 1 H, CH), 7.27–7.51 (m, 3 H, ArH), 7.62–7.69 (m, 2 H, ArH). ^{13}C NMR (75.5 MHz, $CDCl_3$): δ = 14.05, 19.42, 22.58, 28.65, 28.72, 31.36, 79.76, 92.10, 119.30, 126.07, 128.08, 128.25, 131.00, 137.83. IR (neat): 750.00, 773.47, 1134.53, 1227.52 cm^{-1}. GC-MS: *m*/*z* (relative intensity, %) = 212 (43), 197 (40), 183 (32), 169 (52), 155 (82), 141 (100), 129 (67).

[4-(1-Methoxycyclohexyl)but-1-en-3-yn-2-yl]benzene (**3e**): colorless oil. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 1.23–1.36 (m, 2 H, CH_2), 1.59–1.70 (m, 6 H, 3 CH_2), 1.96–2.04 (m, 2 H, CH_2), 3.53 (s, 3 H, OMe), 5.66 (s, 1 H, CH), 5.91 (s, 1 H, CH), 7.23–7.40 (m, 3 H, ArH), 7.62–7.68 (m, 2 H, ArH). ^{13}C NMR (75.5 MHz, $CDCl_3$): δ = 22.92, 25.50, 36.83, 50.91, 74.41, 85.22, 91.91, 120.58, 126.00, 128.28, 128.38, 130.29, 137.33. IR (neat): 745.94, 769.78, 1127.56, 1240.67 cm^{-1}. GC-MS: *m*/*z* (relative intensity, %) = 240 (19), 225 (51), 197 (100), 137 (100).

(4-Cyclohexenylbut-1-em-3yn-2yl)benzene (**3f**): colorless oil. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 1.61–1.69 (m, 4 H, 2 CH_2), 2.11–2.24 (m, 4 H, 2 CH_2), 5.61 (s, 1 H, CH), 5.87 (s, 1 H, CH), 6.21 (s, 1 H, CH), 7.29–7.36 (m, 3 H, ArH), 7.62–7.68 (m, 2 H, ArH). ^{13}C NMR (75.5 MHz, $CDCl_3$): δ = 21.30, 22.11, 25.55, 29.00, 85.78, 92.60, 119.41, 120.46, 125.85, 127.97, 128.08, 130.62, 135.22, 137.34. IR (neat): 754.41, 780.07, 1121.48 cm^{-1}. GC-MS: *m*/*z* (relative intensity, %) = 208 (100), 178 (64), 165 (55), 115 (26).

(5-Methoxy-5-methylhept-1-em-3-yn-2yl)benzene (**3g**): colorless oil. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 1.03 (t, *J* = 7.4 Hz, 3 H, Me), 1.46 (s, 3 H, Me), 1.69–1.88 (m, 2 H, CH_2), 3.40 (s, 3 H, OMe), 5.64 (s, 1 H, CH), 5.90 (s, 1 H, CH), 7.22–7.50 (m, 3 H, ArH), 7.59–7.66 (m, 2 H, ArH). ^{13}C NMR (75.5 MHz, $CDCl_3$): δ = 8.52, 24.87, 33.81, 51.38, 74.32, 84.25, 91.64, 120.39, 125.74, 128.05, 128.13, 129.99, 137.06. IR (neat): 759.83, 788.50, 1105.48, 1236.67 cm^{-1}. GC-MS: *m*/*z* (relative intensity, %) = 214 (4), 199 (8), 185 (100).

Hexa-1,5-dien-3yne-2,5-diyldibenzene (**3h**): colorless oil. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 5.76 (s, 2 H, 2 CH), 5.98 (s, 2 H, 2 CH), 7.22–7.50 (m, 6 H, ArH), 7.59–7.66 (m, 4 H, ArH). ^{13}C NMR (75.5 MHz, $CDCl_3$): δ = 89.70, 120.84, 125.89, 128.15, 128.22, 130.36, 137.00. IR (neat): 743.60, 778.43, 1134.56, 1234.54 cm^{-1}. GC-MS: *m*/*z* (relative intensity, %) = 230 (100), 215 (40), 202 (17), 115 (49).