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PAPER
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The role of atropisomers on the photo-reactivity and fatigue of diarylethene-based metal–organic frameworks

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ARTICLE

Synthesis of alkynyltellurides mediated by K_3PO_4 and DMSO

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In the present work, a simple method for the synthesis of alkynyltellurides is described by the reactions of terminal alkynes with diorganyl ditellurides in the presence of catalytic amount of K_3PO_4. In both substrates, it was possible to vary the aryl and alkyl groups, obtaining the products of interest in short reaction time and in yields ranging from 30 to 93%. This methodology, differently from those already reported in literature, has the advantage of the use of catalytic amount of a weak base and no use of metallic catalysis.

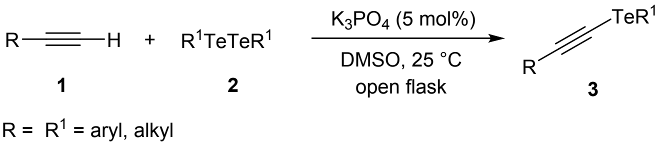
Introduction

Several methodologies have been developed for the synthesis of organic compounds containing the tellurium atom, since they are present in construction of new carbon-carbon bonds,[1] in the synthesis of natural products,[2] and more recently their biological potential.[3] Among these compounds, alkynyltellurides are of great importance in organic synthesis, which can be used in [3 + 2] cycloaddition reactions.[4] Thus, the synthesis of alkynyltellurides have great significance and their biological potential range from antioxidant[5] to antidepressive-like[6] and anxiolytic-like activities.[7]

The preparation of alkynyltellurides generally requires terminal alkynes or haloalkynes as precursors in the presence of different tellurium reagents.[1a-c] The most conventional methodologies for the synthesis of this class of compounds involve the deprotonation of terminal alkynes with strong base and subsequent capture of the generated anion with electrophilic tellurium species or even elemental tellurium.[1a-c, 8]

Alternatively, alkynyltellurides can be synthesized by methodologies using transition metals as catalysts.[9] Although the use of metal represents some limitations about sustainability and green chemistry, copper salts are the most studied until then, appearing in several publications in the literature.[10] Moreover, only a few synthesis methodologies have been described in the literature that do not use metallic catalysis, but rather a strong base in catalytic amounts.[11]

In view of the importance of the synthesis of organic tellurium compounds and considering that the methodologies described for the synthesis of alkynyltellurides use transition metals as catalysts, the present study describes a new synthetic methodology to obtain this class of compounds from terminal alkynes **1** and diorganoyl ditellurides **2**, promoted by a weak base (Scheme 1).



Scheme 1. General scheme of the reaction.

Recently, our research group published the synthesis of selanylalkynes through the reaction between diorganoyl diselenides and terminal alkynes in the presence of silver nitrate as a catalyst, using dichloromethane as solvent (Scheme 2, Eq. (1)).[12] Therefore, the initial proposal for the present work would be extend this methodology for the synthesis of alkynyltellurides. Thus, phenylacetylene **1a** (0.5 mmol), diphenyl ditelluride **2a** (0.25 mmol) and $AgNO_3$ (10 mol%) were added in CH_2Cl_2 (1.5 mL) and the reaction mixture was stirred at 25 °C in open flask. Under these reaction conditions, product **3a** was not obtained, even after 24 h (Scheme 2, Eq. (2)). Similarly, by changing the silver catalyst to AgOTf, Ag_2SO_4 and Ag_2CO_3, no product **3a** was obtained.

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Electronic Supplementary Information (ESI) available: General experimental procedures, characterization details, and ^1H and ^{13}C NMR spectra of compounds. See DOI: 10.1039/x0xx00000x

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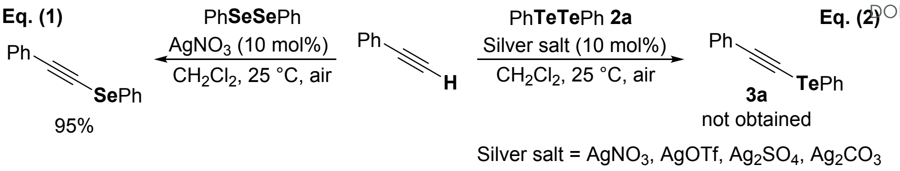


Scheme 2. Silver-catalysed direct chalcogenylation of terminal alkynes with diorganyl dichalcogenides

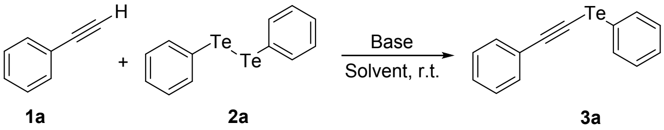
Results and discussion

After an analysis of the literature, we found that most of the transition metal-based synthesis of alkynyl tellurides requires the use of a base, such as Cs$_2$CO$_3$, K$_2$CO$_3$, K$_3$PO$_4$, CsOH, and DMSO as a solvent in the reaction media.[9,10,13] Thus, a mixture of substrates **1a** (0.5 mmol) and **2a** (0.25 mmol) in DMSO (1.5 mL) was stirred at 25 °C in the presence of 10 mol% of AgNO$_3$ and K$_2$CO$_3$ (1 equiv), providing the telluride **3a** in 95% yield after 5 h (Table 1, entry 1). To our delight, the yield of telluride **3a** remains the same when the reaction was performed without silver catalyst (Table 1, entry 2).

After checking that it was not necessary the use silver catalyst for the formation of telluride **3a**, the reaction was carried out in the absence of K$_2$CO$_3$ and after 24 h of reaction, no product **3a** was obtained (Table 1, entry 3). Consequently, in view of these results, we decide to perform an optimization reaction for this base promoted reaction.

Firstly, we evaluated the amount of base required and reactions were carried out with catalytic amounts (20, 10, 5 and 3 mol%) of K$_2$CO$_3$ (Table 1, entries 4-7). In all of these performed reactions, the desired product **3a** was obtained in good yields and it was observed that when 5 mol% of K$_2$CO$_3$ was used an excellent yield of product **3a** was obtained after 5 h of reaction (Table 1, entry 6). Subsequently, some solvents were evaluated, such as CH$_2$Cl$_2$, EtOH, EtOAc, toluene, acetone, 1,4-dioxane and DMF (Table 1, entries 8-14). According our results, none of these tested solvents proved efficient for this reaction. However, only DMF proved adequate for the reaction, even if the yield was not so good and the reaction time was longer compared with that using DMSO (Table 1, entry 6 *vs* 14). The reaction was then screened using different bases (Table 1, entries 15-20). Analyzing the variety of tested inorganic and organic bases, we observed that excellent results were obtained using 5 mol% of K$_2$CO$_3$, Cs$_2$CO$_3$ and K$_3$PO$_4$ (Table 1, entries 6, 16 and 18). Therefore, K$_3$PO$_4$ was chosen for further studies in view of its lower price and/or readily available compared to the K$_2$CO$_3$ and Cs$_2$CO$_3$. Interestingly, when the reaction is carried out under N$_2$ atmosphere, only 55% of the product **3a** is formed, evidencing the necessity of an oxidizing medium in the reaction (Table 1, entry 21).

Table 1. Reaction conditions optimization using phenylacetylene **1a** and diphenyl ditelluride **2a**.[a)]



Entry	Base	Solvent	Time (h)	Yield **3a** (%)[b)]
1[c]	K$_2$CO$_3$ (1 equiv)	DMSO	5	95
2	K$_2$CO$_3$ (1 equiv)	DMSO	5	95
3	-	DMSO	24	-
4	K$_2$CO$_3$ (20 mol%)	DMSO	5	94
5	K$_2$CO$_3$ (10 mol%)	DMSO	5	93
6	K$_2$CO$_3$ (5 mol%)	DMSO	5	93
7	K$_2$CO$_3$ (3 mol%)	DMSO	5	79
8	K$_2$CO$_3$ (5 mol%)	CH$_2$Cl$_2$	24	-
9	K$_2$CO$_3$ (5 mol%)	EtOH	24	10
10	K$_2$CO$_3$ (5 mol%)	EtOAc	24	-
11	K$_2$CO$_3$ (5 mol%)	toluene	24	-
12	K$_2$CO$_3$ (5 mol%)	acetone	24	-
13	K$_2$CO$_3$ (5 mol%)	1,4-dioxane	24	-
14	K$_2$CO$_3$ (5 mol%)	DMF	24	90
15	Na$_2$CO$_3$ (5 mol%)	DMSO	24	88
16	Cs$_2$CO$_3$ (5 mol%)	DMSO	3	94
17	Et$_3$N (5 mol%)	DMSO	24	45
18	**K$_3$PO$_4$ (5 mol%)**	**DMSO**	**3**	**93**
19	NaOAc (5 mol%)	DMSO	24	33
20	NaOH (5 mol%)	DMSO	3	89
21[d]	K$_3$PO$_4$ (5 mol%)	DMSO	3	55

a) Reactions were performed using phenylacetylene **1a** (0.5 mmol) and diphenyl ditelluride **2a** (0.25 mmol), using 1.5 mL of solvent in an open flask and were monitored by TLC until total disappearance of starting materials. [b] Yields are given for isolated products. [c] The reaction was performed in the presence of AgNO$_3$ (10 mol%). [d] Reaction was performed under N$_2$ atmosphere.

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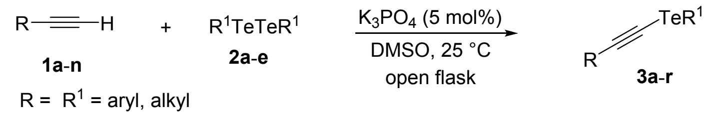
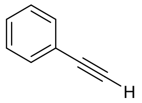
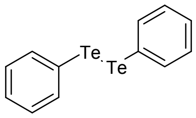
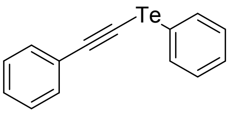
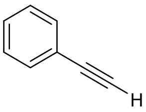
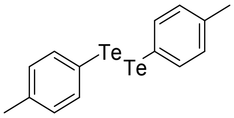
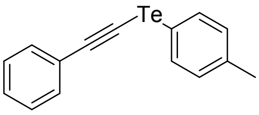
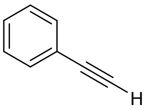
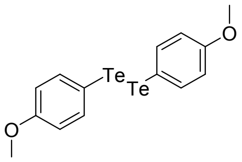
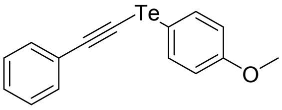
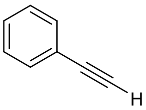
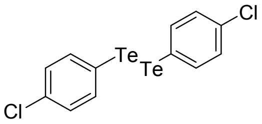
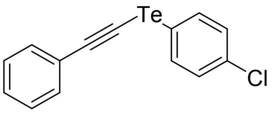
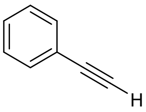
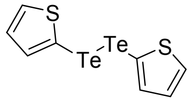
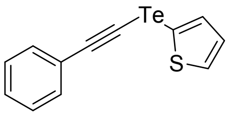
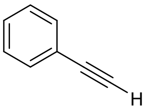
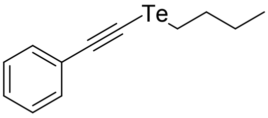
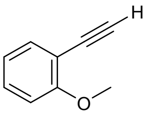
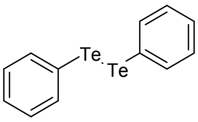
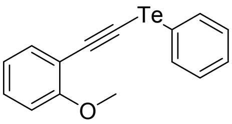
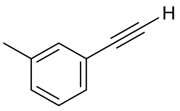
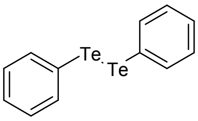
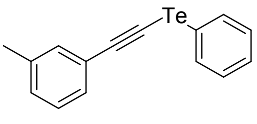
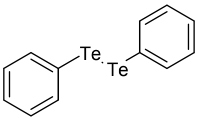
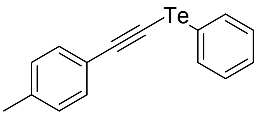
Table 2. Variability in the synthesis of alkynyltellurides **3a-s**.[a)]



Entry	Terminal Alkyne **1**	Ditelluride **2**	Time (h)	Product **3** (Yield) [b)]
1	 **1a**	 **2a**	3	 **3a** (93%)
2	 **1a**	 **2b**	6	 **3b** (93%)
3	 **1a**	 **2c**	8	 **3c** (86%)
4	 **1a**	 **2d**	4	 **3d** (89%)
5	 **1a**	 **2e**	22	 **3e** (62%)
6[c]	 **1a**	 **2f**	24	 **3f** (40%)
7	 **1b**	 **2a**	22	 **3g** (89%)
8	 **1c**	 **2a**	21	 **3h** (81%)
9			8	

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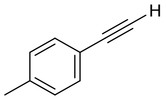
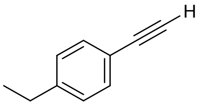
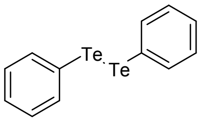
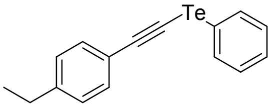
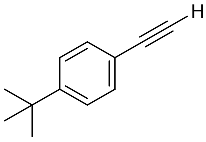
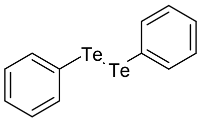
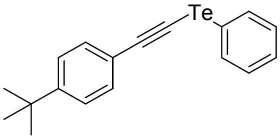
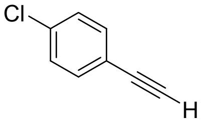
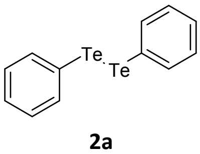
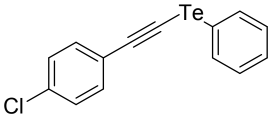
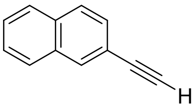
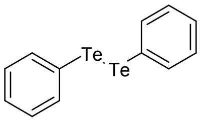
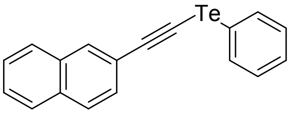
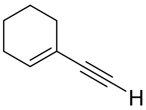
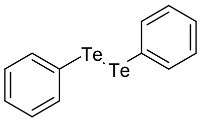
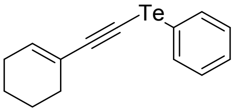
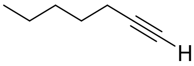
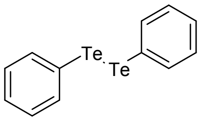
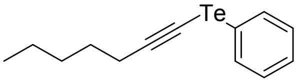
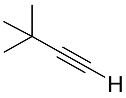
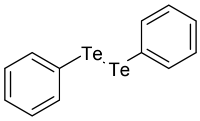
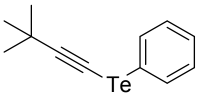
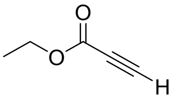
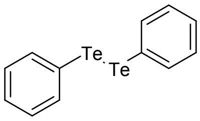
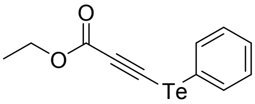
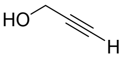
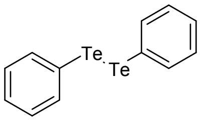
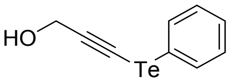
	 **1d**	**2a**		**3i** (90%)
10	 **1e**	 **2a**	6	 **3j** (86%)
11	 **1f**	 **2a**	6	 **3k** (73%)
12	 **1g**	 **2a**	6	 **3l** (86%)
13	 **1h**	 **2a**	8	 **3m** (89%)
14	 **1i**	 **2a**	24	 **3n** (63%)
15	 **1j**	 **2a**	24	 **3o** (71%)
16	 **1k**	 **2a**	24	 **3p** (30%)
17	 **1l**	 **2a**	10	 **3q** (80%)
18	 **1m**	 **2a**	7	 **3r** (64%)

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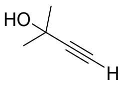
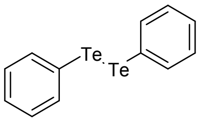
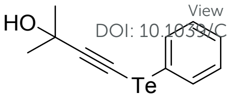
19	 **1n**	 **2a**	10	 **3s** (54%)

a) Reactions are performed using alkynes **1** (0.5 mmol), diorganoyl ditelluride **2** (0.25 mmol), K_3PO_4 (5 mol%) in DMSO (1.5 mL) at 25 °C in an open flask for the time indicated above. [b)] Yields are given for isolated products. [c)] The reaction was performed under N_2 atmosphere.

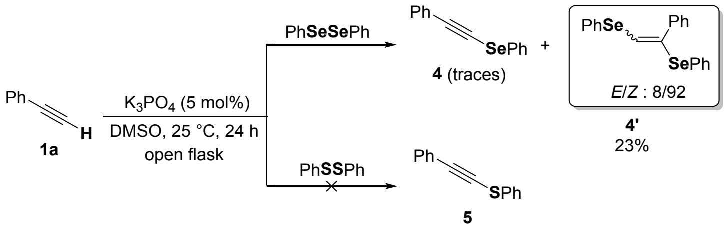
The substrate scope of this reaction was then investigated under the optimized reaction conditions (Table 2). Initially, we evaluated the reactivity of phenylacetylene **1a** in reactions with different functionalized diorganyl ditellurides **2a-f** (Table 2, entries 1-6). Substituted diaryl ditellurides **2b-d** were efficiently reacted with phenylacetylene **1a** and the reactions are not sensitive to the electronic effect of the aromatic ring in the aryltellanyl moiety. Reactions with diaryl ditellurides **2b** and **2c** containing electron-donating groups (EDG) at the aromatic ring gave almost the same yield than reaction with diaryl ditelluride **2d** containing electron-withdrawing group (EWG) (Table 2, entries 2-3 *vs* 4). 1,2-Di(thiophen-2-yl) ditelluride **2e** reacted efficiently with phenylacetylene **1a** giving the product **3e** in 62% yield (Table 2, entry 5). In addition, dibutyl ditelluride **2f** was reacted with phenylacetylene **1a** yielding the desired product in 40% after 24 h (Table 2, entry 6). It is important to note that this reaction was performed under N_2 atmosphere to prevent decomposition of the product.[14]

Under the same optimized reaction conditions, we next evaluated the reactivity of diphenyl ditelluride **2a** using different functionalized terminal alkynes **1b-n** (Table 2, entries 7-19). When the reaction of diphenyl ditelluride **2a** was carried out with a range of terminal aryl alkynes **1b-g** bearing both electron-donating groups (EDG) and electron-withdrawing groups (EWG), the desired alkynyltellurides **3g-l** were obtained in moderate to good yields (Table 2, entries 7-12). Interestingly, EDG and EWG present in the aryl group of the terminal alkynes did not influence the reactivity, with good yields of products being obtained in all cases. When we used 2-ethynylnaphthalene **1h** as a substrate, the desired product **3m** was obtained in 89% yield after 8 h (Table 2, entry 13). We extended the scope of reaction checking the reactivity of non-arylic alkynes, such as 1-ethynylcyclohexene **1i**, 1-heptyne **1j** and 3,3-dimethylbut-1-yne **1k**. After 24 h of reaction, we obtained the desired products **3n-p** in 63, 71 and 30%, respectively (Table 2, entries 14-16). A good result was also achieved when ethyl propiolate **1l** was used as a starting material (Table 2, entry 17).

Interesting results were obtained using propargylic alcohol **1m** and mebynol **1n**, and the desired alkynyltellurides **3r-s** were obtained in moderated yields (64 and 54% yield, respectively) (Table 2, entries 18-19).

Because of the mild reaction conditions, the use of a weak and cheap base/catalyst, and a great substrate scope, our methodology represents an advance with respect to the methodology using CsOH as a catalyst.[11b]

In addition, under the optimized reaction conditions, the possibility of performing the reaction with other diphenyl dichalcogenides, such as diphenyl diselenide and diphenyl disulfide was also investigated (Scheme 3). However, when the phenylacetylene **1a** (0.5 mmol) reacted with diphenyl diselenide (0.25 mmol), the expected product **4** was not obtained and only the product **4'** was obtained in 23% yield as a mixture of (*E*)- and (*Z*)-isomers (*E*/*Z* ratio = 8:92). Unfortunately, the reaction performed with diphenyl disulfide (0.25 mmol) did not provide the formation of desired alkynylsulfide **5** and the starting materials were recovered.



Scheme 3. Reactions with other dichalcogenides.

Since that, our mechanistic studies of this base-mediated synthesis alkynyltellurides in DMSO are not complete, we suggest in Figure 1 a plausible mechanism for the product **3** formation from terminal alkynes **1** and diorganyl ditellurides **2**.

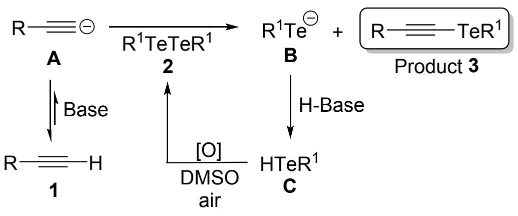


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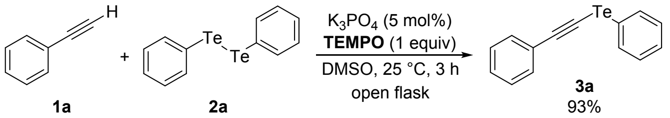
Figure 1. A plausible mechanism of the reaction.

Reversible deprotonation of the terminal alkyne **1** generates an acetylide **A**,[15] which acts as a nucleophile to attack the tellurium atom of the diorganyl ditelluride **2**, furnishing the desired product **3** and tellurolate **B**. Tellurolate **B** reacts with protonated base (H-Base) generating tellurol **C** and the base. Finally, tellurol **C** can be easily oxidized under the air atmosphere and DMSO,[16] regenerating diorganyl ditelluride **2** in the catalytic cycle, that is supported by the influence of an inert atmosphere. The proposed mechanism indicates that this process is able to use both groups on diorganyl ditelluride.

In order to verify if the mechanism really proceeds through an anionic pathway, we employed our optimized reaction conditions to prepare alkynyltelluride **3a** in the presence of 1 equiv of 2,2,6,6-tetramethylpiperidine 1-oxyl (TEMPO) as a radical inhibitor (Scheme 4). Thus, reaction performed with TEMPO provided the alkynyltelluride **3a** in the same yield as that obtained for the reaction in the absence of the radical inhibitor. This result corroborates with the anionic pathway suggested as a plausible mechanism of the reaction.



Scheme 4. Reaction with a radical inhibitor.

Conclusions

In summary, a simple, efficient and transition metal-free methodology for the synthesis of alkynyltellurides was described. The reactions proceed under mild conditions, reacting a range of terminal alkynes with different diorganyl ditellurides using K_3PO_4 as a catalyst, DMSO as a solvent under air atmosphere at 25 °C. The proposed base-mediated methodology was performed with terminal alkynes and ditellurides bearing electron-withdrawing and electron-donating groups affording the corresponding alkynyltellurides in moderated to excellent yields. Due to the mild reaction conditions and to the use of a weak and cheap base/catalyst, this new methodology represents an advance with respect to reported methodologies to access alkynyltellurides.

Experimental

General Information: The reactions were monitored by TLC carried out on Merck silica gel (60 F254) by using UV light as visualizing agent and 5% vanillin in 10% H_2SO_4 and heat as developing agents. Baker silica gel (particle size 0.040–0.063mm) was used for flash chromatography. Hydrogen nuclear magnetic resonance spectra (^1H NMR) were obtained at 400 MHz on Bruker Avance III HD spectrometer. Spectra were recorded in $CDCl_3$ solutions. Chemical shifts are reported in ppm, referenced to tetramethylsilane (TMS) as the external reference. Coupling constants (*J*) are reported in Hertz. Abbreviations to denote the multiplicity of a particular signal are s (singlet), d (doublet), t (triplet), q (quartet), quin (quintet), sex (sextet) and m (multiplet). Carbon-13 nuclear magnetic resonance spectra (^{13}C NMR) were obtained at 100 MHz on Bruker Avance HD III spectrometer. Chemical shifts are reported in ppm, referenced to the solvent peak of $CDCl_3$. Low-resolution mass spectra were obtained with a Shimadzu GCMS-QP 2010 Plus mass spectrometer. High-resolution mass spectra (HRMS) were recorded on a Bruker Micro TOF-QII spectrometer 10416.

General procedure for the synthesis of alkynyltellurides 3a-r: To a 5 mL Schlenk tube equipped with a small magnetic stirring bar containing a solution of an appropriated terminal alkyne (**1a**-**n**, 0.5 mmol) in DMSO (1.5 mL), K_3PO_4 (5 mol%) and the corresponding diorganyl ditelluride (**2a**-**e**, 0.25 mmol) were added. The mixture was stirred at 25 °C for the time indicated in Table 2. The mixture was then extracted using ethyl acetate (10 mL) and washed with water (3 × 10 mL). The organic layer was dried over anhydrous $MgSO_4$ and concentrated under vacuum to yield the crude product, which was purified by flash chromatography on silica gel using a hexane or a mixture of hexane/ethyl acetate as the eluent. Spectral data for the products prepared are listed below.

Phenyl(phenylethynyl)tellane (3a): Yield: 0.143 g (93%); yellow oil. ^1H NMR ($CDCl_3$, 400 MHz) δ (ppm) = 7.73-7.68 (m, 2H); 7.45-7.43 (m, 2H); 7.31-7.21 (m, 6H). ^{13}C NMR ($CDCl_3$, 100 MHz) δ (ppm) = 135.0 (2C), 131.8 (2C), 129.6 (2C), 128.5, 128.2 (2C), 127.8, 123.2, 114.1, 113.1, 47.6. MS (relative intensity) *m/z*: 308 (M^+, 6), 178 (100), 101 (14), 77 (15), 44 (18). HRMS calculated for $C_{14}H_{10}Te$ $[M + H]^+$: 308.9923. Found: 308.9915.

(Phenylethynyl)(*p*-tolyl)tellane (3b): Yield: 0.150 g (93%); yellow solid; mp 61 - 64 °C. ^1H NMR ($CDCl_3$, 400 MHz) δ (ppm) = 7.63 (d, *J* = 8.2 Hz, 2H); 7.44-7.42 (m, 2H); 7.32-7.26 (m, 3H); 7.08-7.06 (m, 2H); 2.33 (s, 3H). ^{13}C NMR ($CDCl_3$, 100 MHz) δ (ppm) = 138.1, 135.7 (2C), 131.8 (2C), 130.6 (2C), 128.4, 128.2 (2C), 123.4, 113.6, 108.6, 47.6, 21.1. MS (relative intensity) *m/z*: 322 (M^+, 13), 192 (100), 189 (12), 101 (13), 65 (10). HRMS calculated for $C_{15}H_{12}Te$ $[M]^+$: 322.0001. Found: 322.0016.

(4-Methoxyphenyl)(phenylethynyl)tellane (3c): Yield: 0.146 g (86%); yellow solid; mp 67 - 68 °C. ^1H NMR ($CDCl_3$, 400 MHz) δ (ppm) = 7.70 (d, *J* = 8.8 Hz, 2H); 7.43-7.40 (m, 2H); 7.30-7.26 (m, 3H); 6.82 (d, *J* = 8.8 Hz, 2H); 3.77 (s, 3H). ^{13}C NMR ($CDCl_3$, 100 MHz) δ (ppm) = 160.0, 138.2 (2C), 131.8 (2C), 128.4, 128.1 (2C), 123.4, 115.6 (2C), 113.0, 101.3, 55.1, 47.9. MS (relative intensity) *m/z*: 338 (M^+, 9), 208 (100), 193 (37), 165 (24), 101 (10), 75 (6). HRMS calculated for $C_{15}H_{13}OTe$ $[M + H]^+$: 339.0029. Found: 339.0011.

(4-Chlorophenyl)(phenylethynyl)tellane (3d): Yield: 0.152 g (89%); white solid; mp 108 - 110 °C. ^1H NMR ($CDCl_3$, 400 MHz) δ (ppm) = 7.63 (d, *J* = 8.1 Hz, 2H); 7.46-7.21 (m, 7H). ^{13}C NMR ($CDCl_3$, 100 MHz) δ (ppm) = 136.3 (2C), 134.4, 131.9 (2C), 129.9 (2C), 128.7, 128.2 (2C), 123.1, 114.6, 110.7, 47.1. MS (relative intensity) *m/z*: 342 (M^+, 12), 212 (100), 176 (20), 151 (6), 101

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(22), 75 (19). HRMS calculated for $C_{14}H_9ClTe$ [M]$^+$: 341.9533. Found: 341.9461.

2-((Phenylethynyl)tellanyl)thiophene (3e): Yield: 0.089 g (62%); yellow solid; mp 54 - 56 °C. ^{1}H NMR (CDCl$_3$, 400 MHz) δ (ppm) = 7.52 – 7.50 (m, 2H), 7.41 –7.38 (m, 2H), 7.28 – 7.26 (m, 3H), 7.0 – 6.98 (m, 1H). ^{13}C NMR (CDCl$_3$, 100 MHz) δ (ppm) = 140.9, 134.8, 131.9 (2C), 128.9, 128.6, 128.1 (2C), 123.1, 111.9, 98.2, 47.9. MS (relative intensity) *m/z*: 314 (M$^+$, 9), 185 (14), 184 (100), 152 (11), 139 (13), 101 (16). HRMS calculated for $C_{12}H_9STe$ [M + H]$^+$: 314.9487. Found: 314.9490.

Butyl(phenylethynyl)tellane (3f): Yield: 0.058 g (40%); orange oil. ^{1}H NMR (CDCl$_3$, 400 MHz) δ (ppm) = 7.42-7.39 (m, 2H); 7.31-7.26 (m, 3H); 2.88 (t, J = 7.4 Hz, 2H); 1.91 (quint. J = 7.4 Hz, 2H); 1.45 (sex. J = 7.4 Hz, 2H); 0.95 (t, J = 7.4 Hz, 3H). ^{13}C NMR (CDCl$_3$, 100 MHz) δ (ppm) = 131.6 (2C), 128.1 (3C), 123.7, 111.3, 44.5, 33.6, 24.6, 13.3, 9.9. MS (relative intensity) *m/z*: 288 (M$^+$, 22), 286 (21), 232 (20), 143 (9), 129 (11), 102 (100), 75 (19), 57 (26), 41 (31). HRMS calculated for $C_{12}H_{14}Te$ [M]$^+$: 288.0158. Found: 288.0175.

[(2-Methoxyphenyl)ethynyl](phenyl)tellane (3g): Yield: 0.150 g (89%); yellow oil. ^{1}H NMR (CDCl$_3$, 400 MHz) δ (ppm) = 7.76-7.71 (m, 2H); 7.42-7.39 (m, 1H); 7.25-7.21 (m, 4H); 6.88 (td, J = 7.5 Hz, 1H); 6.86-6.81 (m, 1H); 3.84 (s, 3H). ^{13}C NMR (CDCl$_3$, 100 MHz) δ (ppm) = 160.2, 134.5 (2C), 133.5, 129.9, 129.5 (2C), 127.5, 120.2, 113.6, 112.4, 110.6, 110.4, 55.6, 51.2. MS (relative intensity) *m/z*: 338 (M$^+$, 19), 208 (100), 178 (11), 165 (27), 131 (51), 88 (15), 77 (37), 44 (22). HRMS calculated for $C_{15}H_{13}OTe$ [M+H]$^+$: 339.0029. Found: 339.0018.

Phenyl(m-tolylethynyl)tellane (3h): Yield: 0.130 g (81%); yellow oil. ^{1}H NMR (CDCl$_3$, 400 MHz) δ (ppm) = 7.82-7.79 (m, 2H); 7.37-7.32 (m, 5H); 7.30-7.26 (m, 1H); 7.20-7.17 (m, 1H); 2.38 (s, 3H). ^{13}C NMR (CDCl$_3$, 100 MHz) δ (ppm) = 137.9, 135.0 (2C), 132.4, 129.7 (2C), 129.5, 128.9, 128.1, 127.8, 123.1, 114.4, 113.2, 46.9, 21.2. MS (relative intensity) *m/z*: 322 (M$^+$, 12), 192 (100), 165 (8), 115 (20), 77 (10), 51 (11). HRMS calculated for $C_{15}H_{13}Te$ [M+H]$^+$: 323.0079. Found: 323.0065.

Phenyl(*p*-tolylethynyl)tellane (3i): Yield: 0.145 g (90%); yellow solid; mp 60 - 62 °C. ^{1}H NMR (CDCl$_3$, 400 MHz) δ (ppm) = 7.72-7.69 (m, 2H); 7.35 (d, J = 7.9 Hz, 2H); 7.24-7.22 (m, 3H); 7.10 (d, J = 7.9 Hz, 2H); 2.33 (s, 3H). ^{13}C NMR (CDCl$_3$, 100 MHz) δ (ppm) = 138.8, 134.9 (2C), 131.8 (2C), 129.6 (2C), 128.9 (2C), 127.7, 120.3, 114.3, 113.3, 46.3, 21.4. MS (relative intensity) *m/z*: 322 (M$^+$, 11), 207 (178), 192 (100), 115 (26), 77(13), 44 (22). HRMS calculated for $C_{15}H_{13}Te$ [M + H]$^+$: 323.0079. Found: 323.0079.

[(4-Ethylphenyl)ethynyl](phenyl)tellane (3j): Yield: 0.144 g (86%); yellow solid; mp 46 - 48 °C. ^{1}H NMR (CDCl$_3$, 400 MHz) δ (ppm) = 7.72-7.69 (m, 2H); 7.40-7.37 (m, 2H); 7.25-7.21 (m, 3H); 7.14-7.11 (m, 2H); 2.62 (q, J = 7.6 Hz, 2H); 1.20 (t, J = 7.6 Hz, 3H). ^{13}C NMR (CDCl$_3$, 100 MHz) δ (ppm) = 145.1, 134.8 (2C), 131.9 (2C), 129.6 (2C), 127.7 (2C), 127.7, 120.5, 114.4, 113.3, 46.3, 28.7, 15.3. MS (relative intensity) *m/z*: 336 (M$^+$, 16), 206 (90), 191 (100), 114 (11), 77 (11), 51 (10). HRMS calculated for $C_{16}H_{15}Te$ [M + H]$^+$: 337.0236, Found: 337.0229.

[(4-*tert*-Butyl)phenyl)ethynyl](phenyl)tellane (3k): Yield: 0.133 g (73%); yellow solid; mp 67 - 69 °C. ^{1}H NMR (CDCl$_3$, 400 MHz) δ (ppm) = 7.72-7.69 (m, 2H); 7.42-7.39 (m, 2H); 7.35-7.32 (m, 2H); 7.26-7.22 (m, 3H); 1.29 (s, 9H). ^{13}C NMR (CDCl$_3$, 100 MHz) δ (ppm) = 151.9, 134.8 (2C), 131.7 (2C), 129.7 (2C), 127.7, 125.2 (2C), 120.3, 114.4, 113.3, 46.3, 34.7, 31.1 (3C). MS (relative intensity) *m/z*: 364 (M$^+$, 14), 291 (13), 234 (34), 219 (100), 141 (9), 77 (9). HRMS calculated for $C_{18}H_{18}Te$ [M]$^+$: 364.0471, Found: 364.0464.

[(4-Chlorophenyl)ethynyl](phenyl)tellane (3l): Yield: 0.147 g (86%); yellow solid. mp 94 – 96 °C. ^{1}H NMR (CDCl$_3$, 400 MHz) δ (ppm) = 7.73 (d, J = 7.0 Hz, 2H), 7.44 – 7.11 (m, 7H). ^{13}C NMR (CDCl$_3$, 100 MHz) δ (ppm) = 135.3 (2C), 134.6, 133.0 (2C), 129.8 (2C), 128.5 (2C), 128.0, 121.8, 112.9, 112.8, 49.0. MS (relative intensity) *m/z*: 342 (M$^+$, 11), 212 (100), 176 (21), 100 (8), 77 (12), 51 (17). HRMS calculated for $C_{14}H_9ClTe$ [M]$^+$: 341.9455. Found: 341.9450.

(Naphthalen-2-ylethynyl)(phenyl)tellane (3m): Yield: 0.159 g (89%); yellow solid; mp 60 - 62 °C. ^{1}H NMR (CDCl$_3$, 400 MHz) δ (ppm) = 7.95 (s, 1H); 7.77-7.73 (m, 5H); 7.50-7.41 (m, 3H); 7.27-7.23 (m, 3H). ^{13}C NMR (CDCl$_3$, 100 MHz) δ (ppm) = 135.1 (2C), 132.8, 132.7, 131.8, 129.7 (2C), 128.4, 127.8, 127.6, 126.8, 126.5, 120.5, 114.6, 113.1, 48.0. MS (relative intensity) *m/z*: 358 (M$^+$, 6), 228 (100), 151 (22), 77 (21), 51 (15). HRMS calculated for $C_{18}H_{13}Te$ [M + H]$^+$: 359.0079, Found: 359.0065.

(Cyclohex-1-en-1-ylethynyl)(phenyl)tellane (3n): Yield: 0.098 g (63%); yellow oil. ^{1}H NMR (CDCl$_3$, 400 MHz) δ (ppm) = 7.75-7.68 (m, 2H); 7.30-7.27 (m, 3H); 6.20 (m, 1H); 2.23-2.18 (m, 4H); 1.72-1.59 (m, 4H). ^{13}C NMR (CDCl$_3$, 100 MHz) δ (ppm) = 136.3, 134.6 (2C), 129.6 (2C), 127.6, 121.1, 116.5, 113.5, 43.4, 29.2, 25.5, 22.2, 21.3. MS (relative intensity) *m/z*: 312 (M$^+$, 35), 308 (19), 165 (86), 153 (49), 103 (21), 77 (100), 51 (51). HRMS calculated for $C_{14}H_{14}Te$ [M]$^+$: 312.0158. Found: 312.0154.

Hept-1-yn-1-yl(phenyl)tellane (3o): Yield: 0.107 g (71%); orange oil. ^{1}H NMR (CDCl$_3$, 400 MHz) δ (ppm) = 7.69-7.64 (m, 2H); 7.25-7.22 (m, 3H); 2.56 (t, J = 7.1 Hz, 2H); 1.57 (quint. J = 6.9 Hz, 2H); 1.43-1.28 (m, 4H); 0.90 (t, J = 7.1 Hz, 3H). ^{13}C NMR (CDCl$_3$, 100 MHz) δ (ppm) = 134.6 (2C), 129.5 (2C), 127.5, 116.1, 113.2, 34.7, 31.0, 28.6, 22.1, 21.0, 13.9. MS (relative intensity) *m/z*: 302 (M$^+$, 23), 143 (42), 129 (23), 115 (100), 95 (30), 77 (41), 55 (19), 41 (17). HRMS calculated for $C_{13}H_{16}Te$ [M]$^+$: 302.0314, Found: 302.0314.

(3,3-Dimethylbut-1-yn-1-yl)(phenyl)tellane (3p): Yield: 0.043 g (30%); yellow oil. ^{1}H NMR (CDCl$_3$, 400 MHz) δ (ppm) = 7.70-7.64 (m, 2H); 7.31-7.23 (m, 3H); 1.34 (s, 9H). ^{13}C NMR (CDCl$_3$, 100 MHz) δ (ppm) = 134.0 (2C), 129.5 (2C), 127.4, 124.4, 113.5, 33.5, 31.1 (3C), 29.7. MS (relative intensity) *m/z*: 288 (M$^+$, 19), 207 (13), 143 (100), 128 (30), 77 (28), 53 (11), 41 (19). HRMS calculated for $C_{12}H_{14}Te$ [M]$^+$: 288.0158. Found: 288.0173.

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Ethyl 3-(phenyltellanyl)propiolate (3q): Yield: 0.122 g (80%); orange oil. ^{1}H NMR (CDCl$_3$, 400 MHz) δ (ppm) = 7.77-7.74 (m, 2H); 7.38-7.28 (m, 3H); 4.25 (q, J = 7.1 Hz, 2H); 1.32 (t, J = 7.2 Hz, 3H). ^{13}C NMR (CDCl$_3$, 100 MHz) δ (ppm) = 152.0, 136.3 (2C), 129.9 (2C), 128.7, 110.8, 107.2, 61.8, 55.4, 13.9. MS (relative intensity) *m/z*: 304 (M$^+$, 21), 232 (12) 129 (91), 102 (100), 77 (62), 51 (74), 44 (8). HRMS calculated for $C_{11}H_{11}O_2Te$ [M + H]$^+$: 304.9821. Found: 304.9811.

3-(Phenyltellanyl)prop-2-yn-1-ol (3r): Yield: 0.084 g (64%); yellow oil. ^{1}H NMR (CDCl$_3$, 400 MHz) δ (ppm) = 7.71-7.67 (m, 2H); 7.29-7.21 (m, 3H); 4.48 (s, 2H); 2.74 (s, 1H). ^{13}C NMR (CDCl$_3$, 100 MHz) δ (ppm) = 135.4 (2C), 129.6 (2C), 128.0, 113.2, 112.3, 52.0, 44.5. MS (relative intensity) *m/z*: 262 (M$^+$, 11), 115 (72), 77 (86), 55 (23), 44 (100). HRMS calculated for C_9H_8OTe [M]$^+$: 261.9637. Found: 261.9633.

2-Methyl-4-(phenyltellanyl)but-3-yn-2-ol (3s): Yield: 0.078 g (54%); yellow oil. ^{1}H NMR (CDCl$_3$, 400 MHz) δ (ppm) = 7.67-7.64 (m, 2H); 7.28-7.22 (m, 3H); 2.34 (s, 1H); 1.57 (s, 6H). ^{13}C NMR (CDCl$_3$, 100 MHz) δ (ppm) = 134.8 (2C), 129.7 (2C), 127.8, 119.7, 112.7, 66.3, 40.0, 31.4. MS (relative intensity) m/z: 290 (10), 272 (11), 141 (100), 102 (26). HRMS calcd. for $C_{11}H_{12}OTe$ [M]$^+$: 289.9945. Found: 289.9945.

Conflicts of interest

There are no conflicts to declare.

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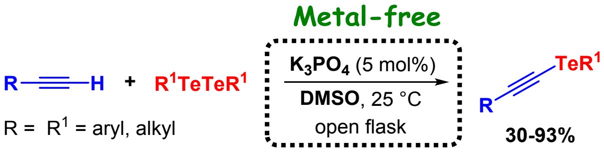

The reaction of diorganyl ditellurides with terminal alkynes is described using K_3PO_4 as a catalyst.