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# An efficient and general procedure for the synthesis of alkynyl chalcogenides (selenides and tellurides) by alumina-supported Cu(II)-catalyzed reaction of alkynyl bromides and diphenyl dichalcogenides

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ABSTRACT

Alumina ($Al_2O_3$) supported Cu(II) efficiently catalyzes the reaction of alkynyl bromides and diphenyl diselenides and ditellurides in presence of Zn dust or indium(I) bromide to provide the corresponding alkynyl selenides and tellurides. The reactions of a wide variety of substituted alkynyl bromides have been addressed. The zinc dust or InBr is required for the cleavage of diphenyl selenides/tellurides. The mechanism of the reaction is established. The yields of products are high and the catalyst is recycled.

## 1. Introduction

The organochalcogenides, in general, have received considerable attention in recent times because of their potential applications in organic synthesis and as useful materials.[1] The alkynyl chalcogenides, particularly tellurides have been studied less compared to other derivatives although these compounds are of much use as versatile intermediates for a variety of reactions, such as hydrohalogenation,[2] hydroamination,[3] hydroboration,[4] hydrosulfonation,[5] among others.[6–8] They have also been used as important dienophiles in cycloaddition reactions.[9] In addition, they, especially tellurides have attracted recent interest for medical applications.[10] Thus development of efficient methods for these useful compounds is of considerable interest. From literature search we found that only a limited number of methods have been reported for alkynyl chalcogenides[11–16] and interestingly these methods addressed primarily selenides and alkynyl tellurides are rarely exemplified[12–15] despite their immense importance.[10] Thus our aim is to develop a general procedure for selenides as well as tellurides. The classical approach utilized the high acidity of terminal acetylenic C–H bond to form alkynyl metal derivative by treatment with strong organometallic bases and subsequent reaction with elemental chalcogen.[11] However, this method has serious limitations with sensitive functionalities using a strong base and this limits the scope of the reaction. In recent years two protocols received attention. One involves the reaction of terminal alkynes with diphenyl dichalcogenides in presence of a base, CuI and/or Lewis acid.[12,13] The other one includes the reaction of alkynyl bromides with diphenyl dichalcogenides in presence of CuI and ligand.[14,15] The selenodecarboxylation of aryl propiolic acid with diorganodiselenide promoted by iodosobenzene diacetate made a different approach for the synthesis of alkynyl selenides.[16] Most of these methods used costly reagents like CuI, which was not recyclable and focused only on alkynyl selenides. We report here a general procedure for the synthesis of alkynyl selenides as well as tellurides by a simple reaction of alkynyl bromides and diphenyl diselenides/ditellurides catalyzed by alumina-supported Cu(II) (Cu/$Al_2O_3$), a unique reagent recently developed by our group (Scheme 1).[17]

## 2. Results and discussion

To standardize the reaction conditions a series of experiments were performed under varying reaction parameters, such as solvent, time, temperature and additive (Zn/InBr) for a representative reaction of phenyl acetylene bromide and diphenyl diselenide/telluride. The results are summarized in Table 1. It was found that reaction with diphenyl diselenide proceeded efficiently in presence

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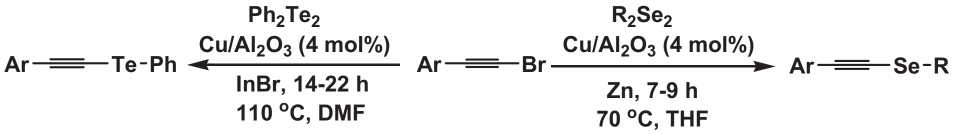
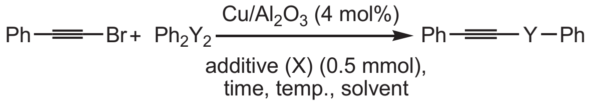


**Scheme 1.** Synthesis of alkynyl selenides and tellurides.

**Table 1**
Standardization of reaction conditions



| Entry | Y | X | Solvent | Time (h) | Temp (°C) | Yield[a] (%) |
|---|---|---|---|---|---|---|
| 1 | Se | Zn | Toluene | 12 | 110 | 14 |
| 2 | Se | Zn | DMF | 16 | 110 | 73 |
| 3 | Se | Zn | DMSO | 12 | 100 | 76 |
| 4[b] | Se | Zn | THF | 12 | 70 | — |
| 5 | Se | Zn | $H_2O$ | 12 | 110 | — |
| **6** | **Se** | **Zn** | **THF** | **8** | **70** | **92** |
| 7 | Se | Zn | THF | 8 | rt | — |
| 8 | Te | Zn | THF | 8 | 70 | — |
| 9 | Te | Zn | DMF | 24 | 110 | 12 |
| 10 | Te | InBr | DMSO | 16 | 110 | 72 |
| 11 | Te | InBr | Toluene | 16 | 110 | 17 |
| 12 | Te | InBr | THF | 16 | 70 | — |
| 13 | Te | InBr | $H_2O$ | 16 | 100 | — |
| **14** | **Te** | **InBr** | **DMF** | **16** | **110** | **81** |
| 15[b] | Te | InBr | DMF | 12 | 70 | 23 |
| 16 | Te | InBr | DMF | 12 | 70 | 36 |
| 17 | Te | InBr | DMF | 12 | rt | — |

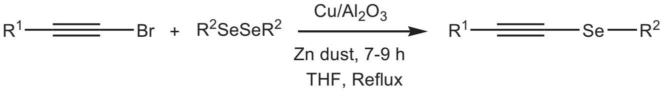
[a] Yields refer to those of pure products characterized by IR, $^1$H NMR and $^{13}$C NMR spectroscopic data.
[b] Reaction carried out without catalyst.

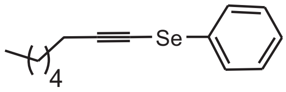
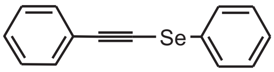
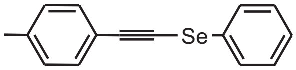
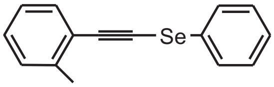
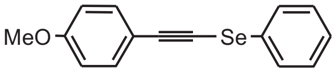
of zinc dust in THF at 70 °C being complete by 8 h (Table 1, entry 6, highlighted in bold as best condition). THF was found to be best among other solvents studied. However the reaction with diphenyl ditelluride did not go well with zinc dust giving only 12% yield of product even after heating for 24 h. Replacement of zinc by InBr,[18] another additive, proved successful. Best result in terms of yield (81%) was obtained when the reaction was carried out in DMF at 110 °C for 16 h (Table 1, entry 14, highlighted in bold as best condition). Interestingly, THF, which was found to be best in selenide reaction, did not work at all in telluride reaction. $H_2O$ was found to be useless in both the reactions. None of these reactions occurred at room temperature. The selenylation in absence of Zn and tellurylation without InBr did not initiate at all. The amount of the catalyst was optimized to 4 mol % for best results.

In a typical experimental procedure, a mixture of alkynyl bromide and diphenyl diselenide was heated at 70 °C in THF in presence of zinc powder and Cu/$Al_2O_3$ for a certain period of time (TLC). Standard work-up and purification by column chromatography provided the product. The same procedure was followed for alkynyl tellurides with replacement of Zn powder by InBr and using DMF in place of THF.

A series of diversely substituted alkyl, aryl and heteroaryl alkynes were subjected to reaction with diaryl diselenides by this procedure to produce the corresponding alkynyl selenides. The results were reported in Table 2. Significantly, alkyl-, aryl- and heteroaryl-substituted alkynes gave uniform results in terms of

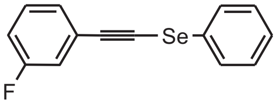
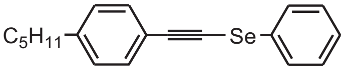
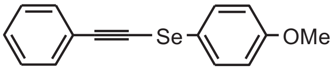
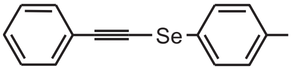
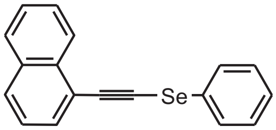
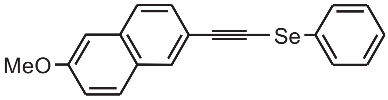
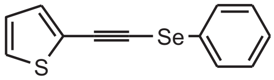
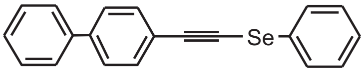
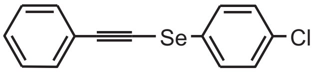
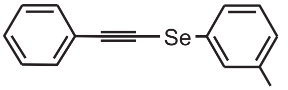
**Table 2**
Synthesis of alkynyl selenides



| Entry | R$^1$ | R$^2$ | Time (h) | Product | Yield[a] (%) |
|---|---|---|---|---|---|
| 1 | *n*-Hexyl | Ph | 8 |  | 83 |
| 2 | Ph | Ph | 8 |  | 92 |
| 3 | *p*-$MeC_6H_4$ | Ph | 8 |  | 88 |
| 4 | *o*-$MeC_6H_4$ | Ph | 9 |  | 83 |
| 5 | *p*-$EtC_6H_4$ | Ph | 8 |  | 90 |
| 6 | *p*-$OMeC_6H_4$ | Ph | 8 |  | 89 |
| 7 | *p*-$BrC_6H_4$ | Ph | 8 |  | 87 |

(*continued on next page*)

**Table 2** (*continued*)

| Entry | $R^1$ | $R^2$ | Time (h) | Product | Yield[a] (%) |
|---|---|---|---|---|---|
| 8 | *m*-$FC_6H_4$ | Ph | 7 |  | 89 |
| 9 | *p*-$ClC_6H_4$ | Ph | 7 |  | 86 |
| 10 | *p*-$^n$Pentyl$C_6H_4$ | Ph | 8 |  | 91 |
| 11 | Ph | *p*-OMe$C_6H_4$ | 8 |  | 85 |
| 12 | Ph | *p*-Me$C_6H_4$ | 8 |  | 83 |
| 13 | 1-Naphthyl | Ph | 8 |  | 86 |
| 14 | 6-Methoxy-2-naphthyl | Ph | 9 |  | 81 |
| 15 | 2-Thienyl | Ph | 7 |  | 91 |
| 16 | Biphenyl | Ph | 8 |  | 89 |
| 17 | Ph | *p*-$ClC_6H_4$ | 8 |  | 86 |
| 18 | Ph | *m*-$FC_6H_4$ | 8 |  | 78 |
| 19 | Ph | Me | 8 |  | 88 |

[a] Yields refer to those of pure products characterized by IR, $^1$H NMR and $^{13}$C NMR spectroscopic data.

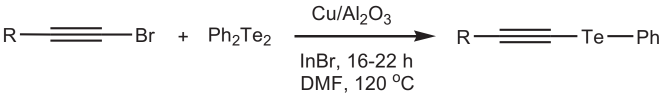
yield and reaction time. The reaction with both electron donating (Table 2, entries 11 and 12) and electron withdrawing (Table 2, entries 17 and 18) groups-substituted diaryl diselenides also provided high yields. The dialkyl (methyl) diselenide too underwent reaction with phenyl acetylene bromide without any difficulty (Table 2, entry 19). The selenylation is highly chemoselective as reaction occurs only at Br on alkynyl chain leaving Br on the aromatic ring unaffected (Table 2, entry 7). Thienyl acetylenic bromide participates in this reaction without any difficulty and the corresponding selenide may be of interest (Table 2, entry 15).

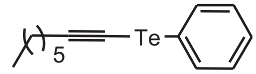
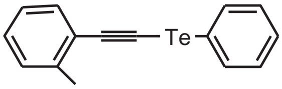
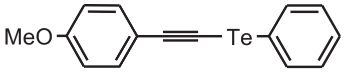
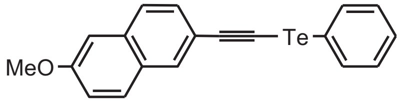
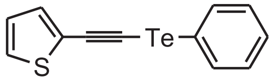
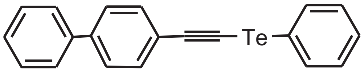
Several alkynyl bromides substituted with hexyl, substituted phenyl, naphthyl and thiophenyl moieties participated in tellurylation reaction by the procedure described earlier, to produce the corresponding alkynyl tellurides. The results were summarized in Table 3. The reaction proceeded uniformly irrespective of the nature of alkynyl bromide.

In general, all selenylation and tellurylation reactions are clean and high yielding. Several functionalities, such as OMe, Cl, Br, F are well accepted in this reaction. The reactions are uniform with *o*-, *m*- and *p*-substituted alkynyl bromides. The tellurylation reactions required longer reaction period than those for selenylation. The Cu/$Al_2O_3$ catalyst was recovered and recycled for six subsequent runs without any appreciable loss in catalytic activity (Fig. 1). Several of the alkynyl selenides and almost all of these tellurides are new and not reported earlier.

To investigate the mechanism of the reaction, a series of experiments were conducted. The XPS (X-ray photo electron spectroscopy) study of the fresh and used catalyst of the selenylation reaction at the Cu-2p level shows the $2p_{3/2}$ lines at 934.536 and 934.585 eV, respectively, with characteristic shake up features (Figs. 2 and 3).[19] This clearly indicates that Cu is in +2 oxidation state before and after the reaction.

**Table 3**
Synthesis of alkynyl tellurides



| Entry | R | Time (h) | Product | Yield[a] (%) |
|---|---|---|---|---|
| 1 | $n$-$C_6H_{13}$ | 22 |  | 75 |
| 2 | Ph | 16 |  | 81 |
| 3 | $o$-$MeC_6H_4$ | 18 |  | 78 |
| 4 | $p$-$EtC_6H_4$ | 18 |  | 81 |
| 5 | $p$-$OMeC_6H_4$ | 16 |  | 83 |
| 6 | $p$-$BrC_6H_4$ | 21 |  | 85 |
| 7 | $p$-$ClC_6H_4$ | 19 |  | 87 |
| 8 | 6-Methoxy-2-naphthyl | 14 |  | 76 |
| 9 | 2-Thienyl | 16 |  | 82 |
| 10 | Biphenyl | 21 |  | 83 |

[a] Yields refer to those of pure products characterized by IR, $^1H$ NMR and $^{13}C$ NMR spectroscopic data.

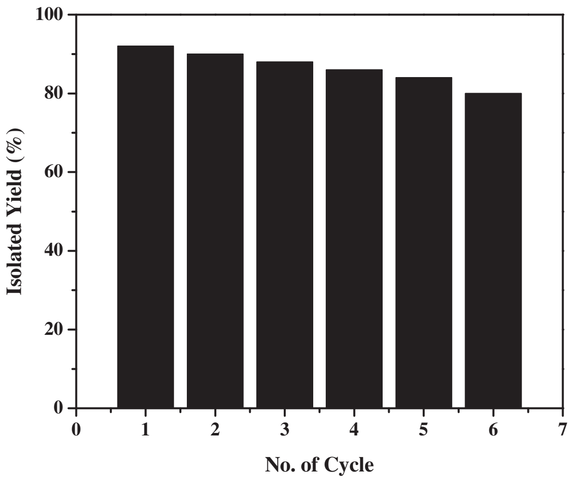


**Fig. 1.** Recyclability of catalyst.

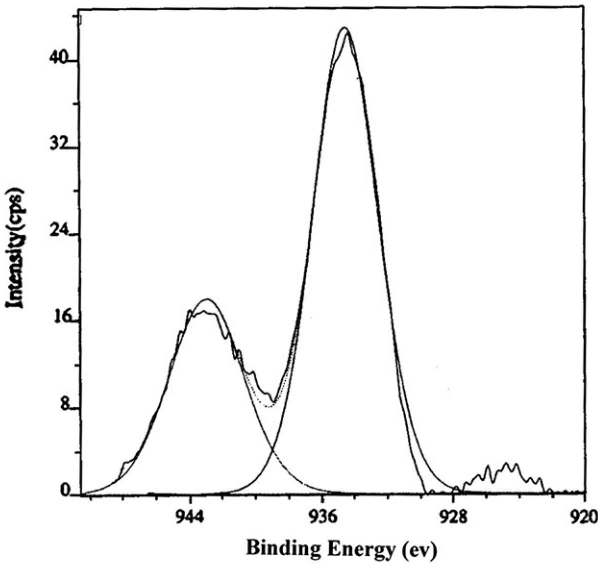


**Fig. 2.** XPS of Cu $2p_{3/2}$ for fresh catalyst.

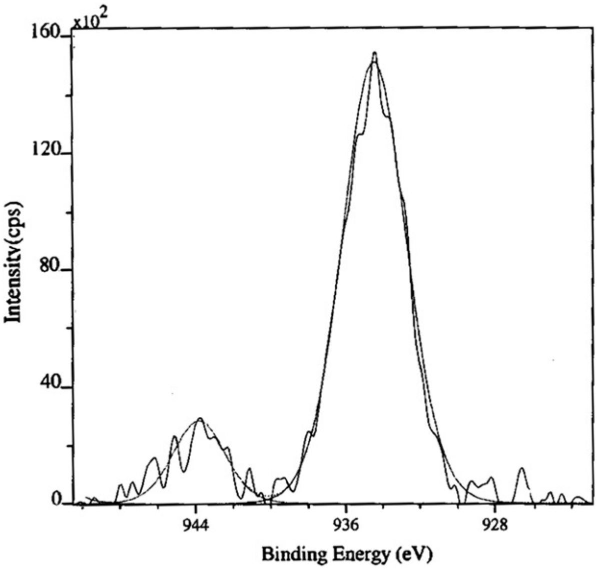
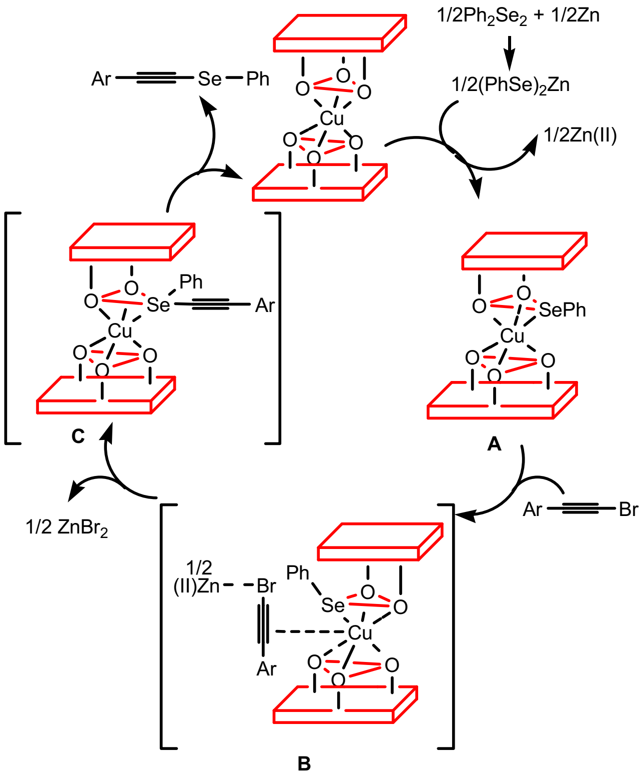


**Fig. 3.** XPS of Cu $2p_{3/2}$ for regenerated $Cu/Al_2O_3$ catalyst.

Thus, we propose that the reaction proceeds through a Cu(II) assisted nucleophilic displacement process. In the first step Zn interacts with $Ph_2Se_2$ to form $(PhSe)_2Zn$, which transfers the PhSe moiety to Cu(II) catalyst to form intermediate **A**. This intermediate then combines with alkynyl bromide to generate a complex **B**, which produces the product, selenide through a transient intermediate **C** with regeneration of Cu(II) catalyst (Scheme 2).



**Scheme 2.** Plausible mechanism for synthesis of alkynyl selenide.

To get further evidence in support of Cu(II)-assisted nucleophilic displacement mechanism, when $Ph_2Se_2$ was stirred with $Cu/Al_2O_3$ in THF in presence of Zn at 70 °C for 12 h a dirty white complex **A** was obtained. The FTIR of this complex shows an additional band at 2800–3200 $cm^{-1}$ corresponding to the aromatic C–H stretching frequencies indicating the addition of PhSe moiety to Cu(II) centre (Fig. 4). The formation of this type of complex is also not unprecedented.[20,21] The XPS study of this complex **A** shows Cu $2p_{3/2}$ and Se 3d lines at 934.448 and 53.277 eV, respectively (Figs. 5 and 6). This also suggests Cu(II)–Se bond formation. The tellurylation reaction also proceeds through the same mechanism as XPS analysis study of the intermediate complex and recovered Cu catalyst showed similar characteristic peaks (Figs. 7 and 8).

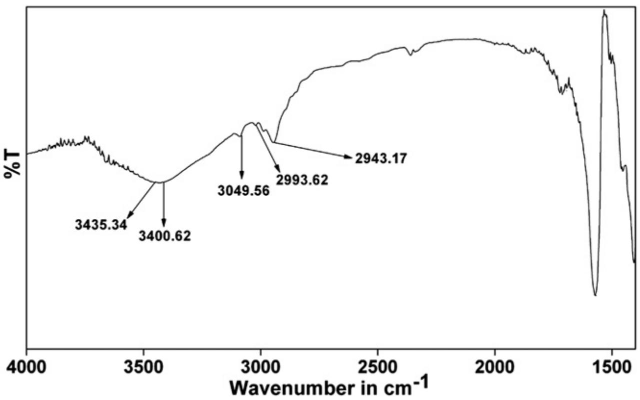


**Fig. 4.** FT-IR spectrum of intermediate **A**.

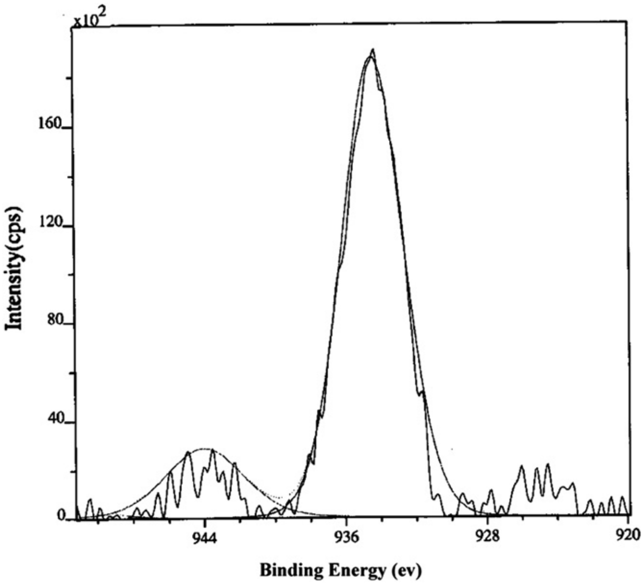


**Fig. 5.** XPS of Cu $2p_{3/2}$ for **A**.

## 3. Conclusion

In conclusion, we have developed a very efficient and general procedure for the synthesis of alkynyl selenides and tellurides by reaction of alkynyl bromides and diphenyl diselenides and ditellurides catalyzed by heterogeneous $Cu(II)/Al_2O_3$ catalyst in presence of zinc and InBr, respectively. The attractive features of this protocol are involvement of hitherto unexplored Cu(II) as catalyst, general applicability to both selenide and tellurides, easy availability and recyclability of the catalyst. Significantly, this procedure provides an easy access to a library of alkynyl selenides and tellurides including alkyl as well as aryl moieties with a scope of functionalization, which was not addressed in the existing methods.[12–15]

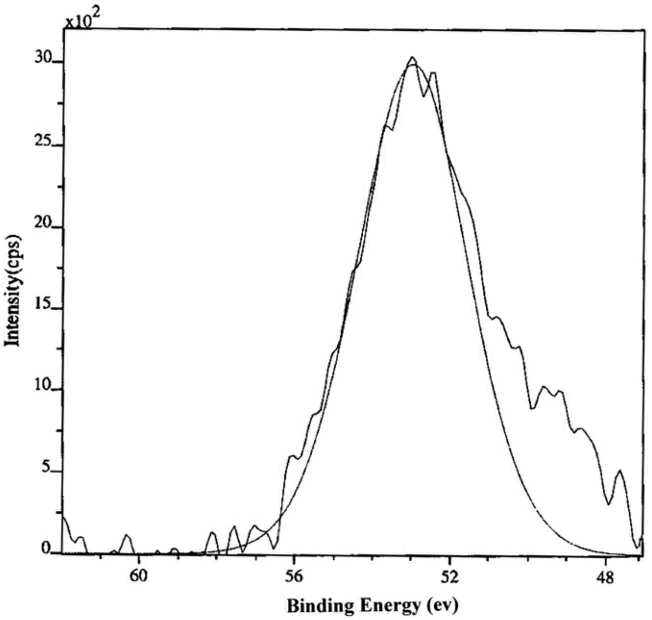


**Fig. 6.** Se 3d peaks of intermediate **A**.

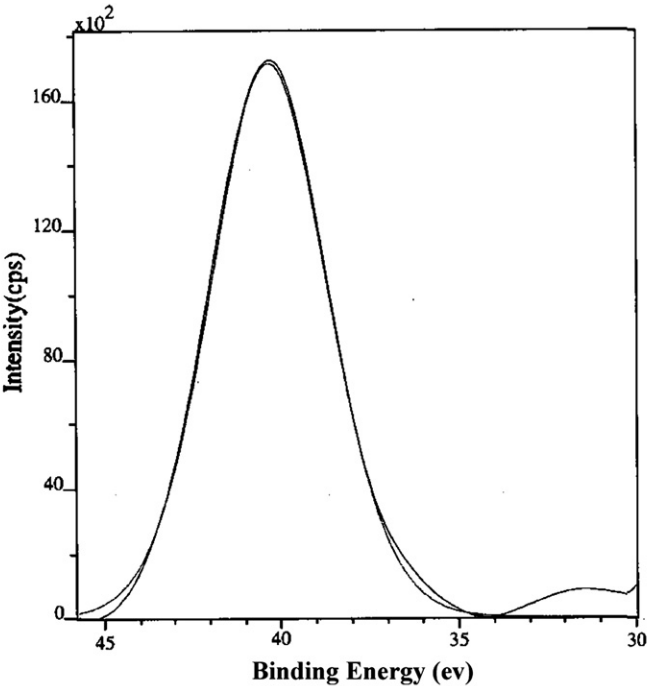


**Fig. 7.** Te 4d peaks of the corresponding tellurium intermediate.

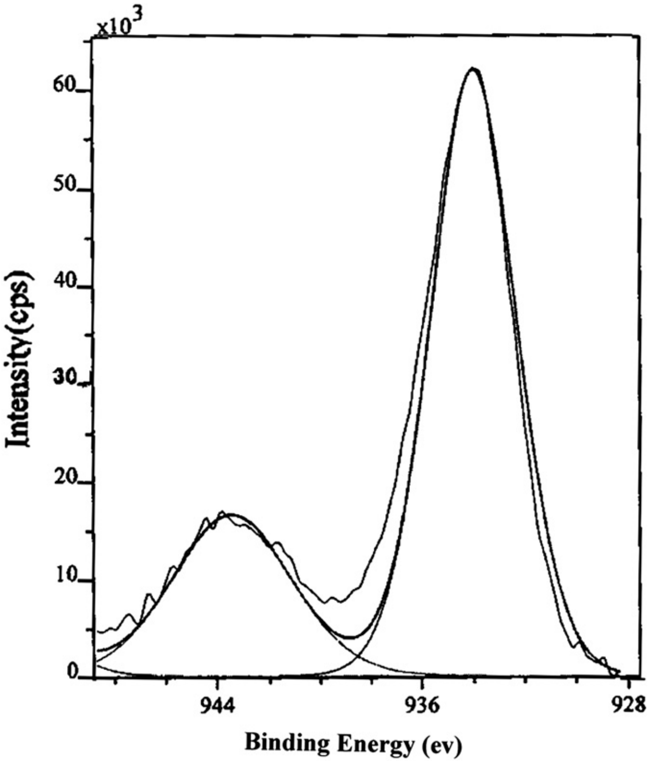


**Fig. 8.** XPS of Cu $2p_{3/2}$ for regenerated $Cu/Al_2O_3$ catalyst for tellurylation.

## 4. Experimental section

### 4.1. General

$^1H$ NMR and $^{13}C$ NMR spectra were recorded on a Bruker instrument at 500 and 125 MHz, respectively. The chemical shifts ($\delta$) are reported in parts per million, using TMS as an internal standard and $CDCl_3$ as the solvent. HRMS were recorded on a Microtek Qtof Micro YA263 spectrometer. IR spectra were recorded on a Shimadzu 8300 FTIR spectrometer. The starting materials, diphenyl diselenide, diphenyl ditelluride and alkynes were purchased from Aldrich and used without further purification. The solvents are purchased from local vendors (Process Chemicals, Kolkata, India) and were dried by us in the laboratory. The bromo alkynes are prepared from commercial alkynes by a reported procedure.[22]

### 4.2. General experimental procedure for the synthesis of alkynyl selenides. Representative procedure for phenyl (phenylethynyl)selane (Table 2, entry 2)

To a solution of 1-(2-bromoethynyl)benzene (181 mg, 1 mmol) and diphenyl diselenide (156 mg, 0.5 mmol) in THF (4 mL), $Cu/Al_2O_3$ (70 mg) and zinc powder (32.5 mg, 0.5 mmol) were added and the mixture was stirred under argon at 70 °C for 8 h (TLC). After being allowed to cool, the THF was evaporated and the reaction mixture was extracted with ethyl acetate (3×10 mL). The extract was washed with water and brine and dried over $Na_2SO_4$. The crude product was purified by column chromatography over silica gel (hexane) to afford pure phenyl (2-phenylethynyl)selane as a yellow liquid (236 mg, 92%), IR (neat): 3016, 2978, 2845, 2158, 1679, 1588, 1512, 1473 $cm^{-1}$; $^1H$ NMR ($CDCl_3$, 500 MHz) $\delta$ 7.26–7.30 (m, 2H), 7.33–7.40 (m, 2H), 7.54–7.57 (m, 2H), 7.64–7.66 (m, 2H); $^{13}C$ NMR ($CDCl_3$, 125 MHz) $\delta$ 69.4, 103.1, 123.3 (2C), 127.2 (2C), 128.7, 129.0, 129.7 (2C), 131.7, 131.9 (2C). These data are in agreement with the reported one.[15]

In control experiments without catalyst or without additive (InBr), the same procedure was followed in absence of the particular component.

This procedure was followed for all the reactions listed in Table 2. A few of these products are known compounds (Table 2, entries 2, 3, 6, 7, 9, 10, 11, 12, 13, 17 and 19) and were identified by comparison of their spectra with those reported earlier.[13,15,16,23–25] The products, which were not reported earlier, were characterized by their spectroscopic data (IR, $^1H$ NMR, $^{13}C$ NMR and HRMS). These data are provided below in order of their entries in Table 2.

*4.2.1. Oct-1-yn-1-yl(phenyl)selane (Table 2, entry 1).* Yield 83%, yellow viscous liquid, IR (neat): 2956, 2929, 2858, 2218, 1577, 1458, 1379 cm$^{-1}$; $^1$H NMR (CDCl$_3$, 500 MHz) $\delta$ 0.847–0.849 (m, 1H), 0.89–0.93 (m, 2H), 1.08–1.10 (m, 2H), 1.17–1.24 (m, 1H), 1.28–1.31 (m, 2H), 1.32–1.38 (m, 1H), 1.42–1.48 (m, 1H), 1.54–1.63 (m, 1H), 2.11 (t, *J*=7.5 Hz, 1H), 2.46 (t, *J*=7.0 Hz, 1H), 7.22–7.26 (m, 1H), 7.29–7.38 (m, 2H), 7.52 (d, *J*=7.5 Hz, 1H), 7.61 (d, *J*=7.0 Hz, 1H); $^{13}$C NMR (CDCl$_3$, 125 MHz) $\delta$ 14.1, 20.7, 22.6, 28.7, 31.5, 37.5, 57.6, 103.3, 126.8, 128.6, 128.7, 129.3, 136.1, 142.2; HRMS calcd for C$_{14}$H$_{18}$Se (M$^+$+H): 267.0652, found: 267.0648.

*4.2.2. Phenyl(o-tolylethynyl)selane (Table 2, entry 4).* Yield 83%, yellow liquid, IR (KBr): 3055, 2918, 2135, 1572, 1475, 1433, 1223 cm$^{-1}$; $^1$H NMR (CDCl$_3$, 500 MHz) $\delta$ 2.54 (s, 3H), 7.20 (t, *J*=7.0 Hz, 1H), 7.27–7.32 (m, 3H), 7.36–7.39 (m, 2H), 7.53 (d, *J*=7.5 Hz, 1H), 7.66 (d, *J*=6 Hz, 2H); $^{13}$C NMR (CDCl$_3$, 125 MHz) $\delta$ 20.8, 72.8, 102.1, 123.1, 125.7, 127.1, 128.6, 129.0, 129.2 (2C), 129.3, 129.6 (2C), 132.1, 140.5; HRMS calcd for C$_{15}$H$_{12}$Se (M$^+$): 272.0104, found: 272.0106.

*4.2.3. ((4-Ethylphenyl)ethynyl)(phenyl)selane (Table 2, entry 5).* Yield 90%, yellow viscous liquid, IR (neat): 3055, 2964, 2872, 2158, 1684, 1577, 1475 cm$^{-1}$; $^1$H NMR (CDCl$_3$, 500 MHz) $\delta$ 1.20 (t, *J*=6.5 Hz, 3H), 2.63 (q, *J*=8.0 Hz, 2H), 6.69–7.16 (m, 2H), 7.21–7.25 (m, 2H), 7.26–7.31 (m, 1H), 7.41 (d, *J*=8.0 Hz, 2H), 7.56–7.59 (m, 2H); $^{13}$C NMR (CDCl$_3$, 125 MHz) $\delta$ 15.5, 29.0, 68.3, 103.4, 120.5, 127.2, 128.1 (2C), 129.1 (2C), 129.3, 129.7 (2C), 132.1 (2C), 145.3; HRMS calcd for C$_{16}$H$_{14}$Se (M$^+$): 286.0261, found: 286.0260.

*4.2.4. ((3-Fluorophenyl)ethynyl)(phenyl)selane (Table 2, entry 8).* Yield 89%, yellow viscous liquid, IR (neat): 3061, 2966, 2885, 2163, 1684, 1568, 1566, 1498 cm$^{-1}$; $^1$H NMR (CDCl$_3$, 500 MHz) $\delta$ 7.03–7.10 (m, 1H), 7.19–7.21 (m, 1H), 7.26–7.37 (m, 5H), 7.60 (d, *J*=8.0 Hz, 2H); $^{13}$C NMR (CDCl$_3$, 125 MHz) $\delta$ 71.2, 101.7 (d, *J*=2.5 Hz), 116.1 (d, *J*=20.0 Hz), 118.5 (d, *J*=22.5 Hz), 125.1 (d, *J*=10 Hz), 127.5 (d, *J*=20 Hz), 128.70, 129.4 (2C), 129.8 (2C), 130.1, 162.50 (d, *J*=243 Hz); Anal. Calcd for C$_{14}$H$_9$FSe: C, 61.11; H, 3.30; found: C, 60.98; H, 3.32%.

*4.2.5. ((6-Methoxynaphthalen-2-yl)ethynyl)(phenyl)selane (Table 2, entry 14).* Yield 81%, pale yellow solid, mp 96 °C, IR (KBr): 3059, 2958, 2931, 2837, 2152, 1624, 1597, 1475, 1228 cm$^{-1}$; $^1$H NMR (CDCl$_3$, 500 MHz) $\delta$ 3.93 (s, 3H), 7.12 (d, *J*=2.5 Hz, 1H), 7.17–7.19 (m, 1H), 7.29 (d, *J*=7.0 Hz, 1H), 7.36 (t, *J*=7.5 Hz, 2H), 7.52–7.54 (m, 1H), 7.64 (d, *J*=8.0 Hz, 2H), 7.70 (t, *J*=8.5 Hz, 2H), 7.97 (s, 1H); $^{13}$C NMR (CDCl$_3$, 125 MHz) $\delta$ 55.4, 68.7, 103.7, 106.0, 118.2, 119.6, 127.0, 128.5, 129.1, 129.2 (2C), 129.3, 129.5, 129.7, 132.0 (2C), 134.5, 158.6; HRMS calcd for C$_{19}$H$_{14}$OSe (M$^+$+H): 339.0288, found: 339.0285.

*4.2.6. 2-((Phenylselanyl)ethynyl)thiophene (Table 2, entry 15).* Yield 91%, yellow viscous liquid, IR (neat): 3105, 3057, 2920, 2850, 2154, 1674, 1575, 1475, 1356 cm$^{-1}$; $^1$H NMR (CDCl$_3$, 500 MHz) $\delta$ 7.15 (t, *J*=5.0 Hz, 1H), 7.23–7.26 (m, 3H), 7.29–7.31 (m, 2H), 7.51 (t, *J*=4.0 Hz, 1H), 7.55–7.60 (m, 1H); $^{13}$C NMR (CDCl$_3$, 125 MHz) $\delta$ 68.9, 97.9, 122.4, 125.4, 127.2, 129.2 (2C), 129.4 (2C), 129.6, 129.9, 133.8; HRMS calcd for C$_{12}$H$_8$SSe (M$^+$+H): 264.9590, found: 264.9609.

*4.2.7. ([1,1′-Biphenyl]-4-ylethynyl)(phenyl)selane (Table 2, entry 16).* Yield 89%, yellow solid, mp 98 °C, IR (KBr): 3325, 3057, 2924, 2158, 1575, 1475, 1437, 1066, 1006 cm$^{-1}$; $^1$H NMR (CDCl$_3$, 500 MHz) $\delta$ 7.26–7.30 (m, 1H), 7.34–7.39 (m, 3H), 7.46 (t, *J*=7.5 Hz, 2H), 7.59–7.63 (m, 8H); $^{13}$C NMR (CDCl$_3$, 125 MHz) $\delta$ 70.1, 103.0, 122.2, 127.1 (2C), 127.3, 127.8 (2C), 129.0 (2C), 129.1, 129.2 (2C), 129.7 (2C), 132.3 (2C), 140.4, 141.4; Anal. Calcd for C$_{20}$H$_{14}$Se: C, 72.07; H, 4.23; found: C, 71.90; H, 4.25%.

*4.2.8. (3-Fluorophenyl)(2-phenylethynyl)selane (Table 2, entry 18).* Yield 78%, yellow liquid, IR (neat): 3061, 3019, 2160, 1589, 1472, 1425, 1263, 1213 cm$^{-1}$; $^1$H NMR (CDCl$_3$, 500 MHz) $\delta$ 6.97 (t, *J*=8.5 Hz, 1H), 7.25–7.36 (m, 6H), 7.51–7.53 (m, 2H); $^{13}$C NMR (CDCl$_3$, 125 MHz) $\delta$ 68.3, 104.2, 114.2 (d, *J*=21.2 Hz, 1C), 115.0, 116.1 (d, *J*=25.0 Hz, 1C), 123.0, 124.3, 128.7 (2C), 128.8 (d, *J*=22.5 Hz, 1C), 130.7, 131.9 (2C), 163.3 (d, *J*=247.5 Hz, 1C); Anal. Calcd for C$_{14}$H$_9$FSe: C, 66.11; H, 3.30; found: C, 66.14; H, 3.28%.

### 4.3. General experimental procedure for the synthesis of alkynyl tellurides. Representative procedure for phenyl (phenylethynyl)tellane (Table 3, entry 2)

To a solution of 1-(2-bromoethynyl)benzene (181 mg, 1 mmol) and diphenyl ditelluride (204 mg, 0.5 mmol) in DMF (4 mL), Cu/Al$_2$O$_3$ (70 mg) and InBr (96.5 mg, 0.5 mmol) were added and the mixture was stirred under argon at 110 °C for 16 h (TLC). After being allowed to cool, and the reaction mixture was extracted with ethyl acetate (3×10 mL). The extract was washed with water and brine and dried over Na$_2$SO$_4$. The crude product was purified by column chromatography over silica gel (hexane) to afford pure phenyl(2-phenylethynyl)tellane as a yellow liquid (247 mg, 81%), IR (neat): 3071, 2926, 2162, 1963, 1577, 1483, 1286 cm$^{-1}$; $^1$H NMR (CDCl$_3$, 500 MHz) $\delta$ 7.26–7.29 (m, 3H), 7.33 (t, *J*=3.5 Hz, 3H), 7.47 (t, *J*=6.5 Hz, 2H), 7.75 (t, *J*=6.5 Hz, 2H); $^{13}$C NMR (CDCl$_3$, 125 MHz) $\delta$ 47.5, 113.3, 114.4, 123.6, 128.1, 128.4 (2C), 128.8, 129.9 (2C), 132.1 (2C), 135.3 (2C).

In control experiments without catalyst or without additive (InBr), the same procedure was followed in absence of the particular component.

This procedure was followed for all the reactions listed in Table 3. Only one of these products is known compound (Table 3, entry 2) and was identified by comparison of its spectra with those reported earlier.[15] The products, which were not reported earlier, were characterized by their spectroscopic data (IR, $^1$H NMR, $^{13}$C NMR and HRMS). These data are provided below in order of their entries in Table 3.

*4.3.1. Oct-1-yn-1-yl(phenyl)tellane (Table 3, entry 1).* Yield 75%, yellow viscous liquid, IR (neat): 3031, 3024, 2918, 2166, 1898, 1546, 1413, 1236 cm$^{-1}$; $^1$H NMR (CDCl$_3$, 500 MHz) $\delta$ 0.91 (t, *J*=7.0 Hz, 3H), 1.29–1.34 (m, 4H), 1.42–1.45 (m, 2H), 1.55–1.60 (m, 2H), 2.58 (t, *J*=7.0 Hz, 2H), 7.25–7.27 (m, 3H), 7.67–7.68 (m, 2H); $^{13}$C NMR (CDCl$_3$, 125 MHz) $\delta$ 14.2, 21.36, 22.7, 28.6, 29.0, 31.4, 34.9, 113.3, 116.3, 127.7, 129.69 (2C), 134.8 (2C); Anal. Calcd for C$_{14}$H$_{18}$Te: C, 53.57; H; 5.78, found: C, 52.98; H, 5.81.

*4.3.2. Phenyl(o-tolylethynyl)tellane (Table 3, entry 3).* Yield 78%, yellow liquid, IR (neat): 3053, 2943, 2918, 2135, 1948, 1574, 1474, 1435, 1377, 1223, 1109 cm$^{-1}$; $^1$H NMR (CDCl$_3$, 500 MHz) $\delta$ 2.48 (s, 3H), 7.15–7.17 (m, 1H), 7.22 (d, *J*=6.5 Hz, 2H), 7.26–7.29 (m, 3H), 7.44 (d, *J*=7.5 Hz, 1H), 7.76 (t, *J*=6.5 Hz, 2H); $^{13}$C NMR (CDCl$_3$, 125 MHz) $\delta$ 20.9, 50.8, 113.6, 125.6, 128.0, 128.7, 129.5, 129.9 (2C), 132.35, 135.1 (2C), 140.8; Anal. Calcd for C$_{15}$H$_{12}$Te: C, 56.33; H, 3.78; found: C, 55.12; H, 4.01.

*4.3.3. ((4-Ethylphenyl)ethynyl)(phenyl)tellane (Table 3, entry 4).* Yield 81%, pale yellow liquid, IR (neat): 3078, 2940, 1739, 1597, 1518, 1344, 1228, 1109, 1028 cm$^{-1}$; $^1$H NMR (CDCl$_3$, 500 MHz) $\delta$ 1.24 (t, *J*=7.5 Hz, 3H), 2.26–2.70 (m, 2H), 7.17 (d, *J*=8.0 Hz, 2H), 7.26–7.30 (m, 3H), 7.41 (d, *J*=8.5 Hz, 2H), 7.74–7.76 (m, 2H); $^{13}$C NMR (CDCl$_3$, 125 MHz) $\delta$ 15.5, 28.9, 46.3, 113.5, 114.7, 120.8, 128.0 (2C), 130.0 (2C), 132.28 (3C), 135.1 (2C), 145.3; Anal. Calcd for C$_{16}$H$_{14}$Te: C, 57.56; H, 4.23; found: C, 58.01; H, 4.31.

*4.3.4. ((4-Methoxyphenyl)ethynyl)(phenyl)tellane (Table 3, entry 5).* Yield 83%, pale yellow liquid, IR (neat): 3285, 3051, 2958, 2835, 2137, 1603, 1572, 1506, 1292, 1249, 1171, 1032 cm$^{-1}$; $^1$H NMR (CDCl$_3$, 500 MHz) $\delta$ 3.71 (s, 3H), 6.73–6.77 (m, 3H), 7.15–7.18 (m, 2H), 7.32–7.35 (m, 2H), 7.63–7.65 (m, 2H); $^{13}$C NMR ($CDCl_3$, 125 MHz) $\delta$ 45.3, 55.4, 113.6, 114.0 (2C), 114.4, 115.7, 127.9, 129.8 (2C), 133.8 (2C), 135.1 (2C), 160.1; HRMS calcd for $C_{15}H_{12}OTe$ ($M^+$+Na): 360.9848, found: 360.9817.

*4.3.5. ((4-Bromophenyl)ethynyl)(phenyl)tellane (Table 3, entry 6).* Yield 85%, yellow viscous liquid, IR (neat): 3070, 3053, 2162, 1576, 1475, 1437, 1390, 1066, 1008, 823 cm$^{-1}$; $^{1}$H NMR ($CDCl_3$, 500 MHz) $\delta$ 7.16–7.25 (m, 5H), 7.38 (d, $J$=8.5 Hz, 2H), 7.66 (t, $J$=6.0 Hz, 2H); $^{13}$C NMR ($CDCl_3$, 125 MHz) $\delta$ 49.2, 113.0, 113.2, 122.5, 123.0, 128.3, 130.0 (2C), 139.7 (2C), 133.4 (2C), 135.6 (2C); Anal. Calcd for $C_{14}H_9BrTe$: C, 43.71; H, 2.36, found: C, 43.24; H, 2.40.

*4.3.6. ((4-Chlorophenyl)ethynyl)(phenyl)tellane (Table 3, entry 7).* Yield 87%, pale yellow viscous liquid, IR (neat): 3049, 2965, 2137, 1572, 1506, 1474, 1435, 1016 cm$^{-1}$; $^{1}$H NMR ($CDCl_3$, 500 MHz) $\delta$ 7.19–7.24 (m, 5H), 7.31 (d, $J$=9.0 Hz, 2H), 7.66–7.68 (m, 2H), $^{13}$C NMR ($CDCl_3$, 125 MHz) $\delta$ 49.0, 113.0, 113.1, 122.0, 128.3, 128.8 (2C), 130.0 (2C), 133.25 (2C), 134.8, 135.5 (2C); HRMS calcd for $C_{14}H_9ClTe$ ($M^+$+H): 342.9533, found: 342.9531.

*4.3.7. ((6-Methoxynaphthalen-2-yl)ethynyl)(phenyl)tellane (Table 3, entry 8).* Yield 76%, pale yellow solid, mp 98 °C IR (KBr): 3085, 3023, 2161, 1584, 1473, 1357, 1218 cm$^{-1}$; $^{1}$H NMR ($CDCl_3$, 500 MHz) $\delta$ 3.80 (s, 3H), 6.99 (s, 1H), 7.05 (d, $J$=8.5 Hz, 1H), 7.18 (d, $J$=4.5 Hz, 3H), 7.38 (d, $J$=8.5 Hz, 1H), 7.55–7.58 (m, 2H), 7.67 (t, $J$=6.5 Hz, 2H), 7.81 (s, 1H); $^{13}$C NMR ($CDCl_3$, 125 MHz) $\delta$ 46.8, 55.4, 65.8, 106.0, 113.4, 115.0, 118.4, 119.5, 127.0, 128.0, 128.4, 129.3, 129.5, 130.0, 132.0, 132.2, 134.5, 135.2, 158.6; Anal. Calcd for $C_{19}H_{14}OTe$: C, 59.13; H, 3.66; found: C, 58.37; H, 3.58.

*4.3.8. 2-((Phenyltellanyl)ethynyl)thiophene (Table 3, entry 9).* Yield 82%, pale yellow liquid, IR (neat): 3103, 3051, 2137, 1572, 1473, 1435, 1354, 1016 cm$^{-1}$; $^{1}$H NMR ($CDCl_3$, 500 MHz) $\delta$ 7.17 (d, $J$=5.0 Hz, 1H), 7.26–7.30 (m, 4H), 7.51 (d, $J$=2.5 Hz, 1H), 7.75–7.76 (m, 2H); $^{13}$C NMR ($CDCl_3$, 125 MHz) $\delta$ 47.1, 109.0, 113.2, 122.7, 125.3, 128.1, 129.9 (2C), 130.1, 130.3, 135.3 (2C); Anal. Calcd for $C_{12}H_8STe$: C, 46.22; H, 2.59, found: C, 45.68; H, 2.12.

*4.3.9. ([1,1′-Biphenyl]-4-ylethynyl)(phenyl)tellane (Table 3, entry 10).* Yield 83%, pale yellow solid, mp 101 °C, IR (KBr): 3286, 3053, 2924, 1599, 1572, 1479, 1433, 1261 cm$^{-1}$; $^{1}$H NMR ($CDCl_3$, 500 MHz) $\delta$ 7.26–7.31 (m, 3H), 7.37 (t, $J$=7.0 Hz, 1H), 7.44–7.48 (m, 2H), 7.54–7.63 (m, 6H), 7.76 (t, $J$=7.5 Hz, 2H); $^{13}$C NMR ($CDCl_3$, 125 MHz) $\delta$ 48.2, 113.3, 114.3, 122.4, 127.2 (2C), 127.3 (2C), 127.8, 128.1, 129.1 (2C), 129.9 (2C), 132.5 (2C), 135.3 (2C), 140.4, 141.5; Anal. Calcd for $C_{20}H_{14}Te$: C, 62.90; H, 3.69, found: C, 61.94; H, 3.21.

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## Supplementary data

Supplementary data ($^{1}$H NMR and $^{13}$C NMR spectra of all products listed in Table 2 and Table 3). Supplementary data related to this article can be found at http://dx.doi.org/10.1016/j.tet.2012.08.046.

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