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Magnetite (Fe_3O_4) nanoparticles: an efficient and recoverable catalyst for the synthesis of alkynyl chalcogenides (selenides and tellurides) from terminal acetylenes and diorganyl dichalcogenides

Marcelo Godoi, Daiane G. Liz, Eduardo W. Ricardo, Manuela S.T. Rocha, Juliano B. Azeredo, Antonio L. Braga *

Departamento de Química, Universidade Federal de Santa Catarina, Florianópolis, SC 88040-970, Brazil

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ABSTRACT

We present herein a new and efficient methodology for the synthesis of alkynyl chalcogenides from terminal acetylenes and diorganyl dichalcogenides, catalyzed by Fe_3O_4 nanoparticles. This new approach provided the desired products in good to excellent yields. Moreover, the catalyst was easily recoverable using an external magnet and reused for further experiments without loss of catalytic activity.

1. Introduction

Organochalcogenides have gained special attention mainly because of their specific biological activity, e.g., antioxidant, antitumor, antimicrobial, and antiviral.[1] Furthermore, this class of compounds has become an attractive synthetic target in several transformations.[2,3]

Alkynyl chalcogenides have been widely used as powerful intermediates in synthetic organic chemistry.[4] These kinds of compounds have been successfully employed, for example, as precursors in several transformations, such as hydrohalogenation[5] and hydrosulfonation,[6] and for the synthesis of some heterocycles.[7]

In general, alkynyl chalcogenides are prepared using hypervalent species of iodine or through the reaction of alkynyl bromides with nucleophilic species of chalcogen generated from a metal.[8,9] Also, the treatment of acetylene with strong bases or organometallic reagents followed by reaction with a diorganyl dichalcogenide or organochalcogenyl halide has been reported.[10] However, most of these methods have limitations, such as the use of excess amounts of alkynes or strong bases, the low air stability of some organometallic reagents, and the difficulties associated with the manipulation of some organochalcogen compounds.

Alkynyl selenides and tellurides can also be conveniently synthesized through the transition metal-catalyzed reaction of dichalcogenides with either alkynes or bromo alkynes under different conditions.[11] Methodologies involving heterogeneous catalysis have been preferred due to the easy isolation and separation of the catalyst after the completion of the reaction.[12] Nonetheless, the development of new methods to prepare these kinds of organochalcogenides employing non-toxic and easily recovered catalysts is highly desirable.

Magnetic nano catalysts have attracted considerable attention due to their unique properties, such as large surface area and facile separation using external magnets.[13] In this context, magnetically recoverable iron oxides have emerged as powerful catalysts and have been recently applied in organic synthesis.[14]

Although iron nano catalysts have been used for several transformations, they have not yet been employed in the field of organochalcogen chemistry. Thus, in line with our ongoing research in this area[15] a new method for the synthesis of alkynyl chalcogenides using Fe_3O_4 nanopowder as a recyclable catalyst is reported herein (Scheme 1).

* Corresponding author. Tel./fax: +55 48 3721 6427; e-mail addresses: braga.antonio@ufsc.br, albraga1@gmail.com (A.L. Braga).

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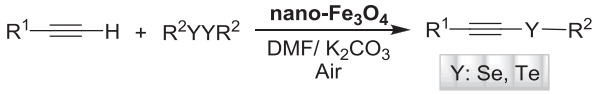
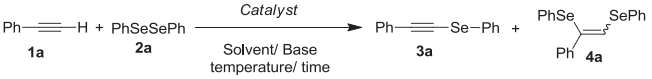


Scheme 1. Synthesis of alkynyl selenides and tellurides.

2. Results and discussion

We began our study by screening the activity of the catalysts, using phenylacetylene and diphenyl diselenide as standard substrates, in the presence of K_2CO_3 and DMF (Table 1). Firstly, we evaluated the amount of Fe_3O_4 nanoparticles required to obtain an efficient reaction. Carrying out the reaction with 2 mol % of catalyst afforded the desired product with only 30% yield (entry 1). On increasing the catalyst amount to 5 mol %, the yield of the reaction was enhanced to 67% (entry 2). Notably, when 10 mol % of nano-Fe_3O_4 was used the product **3a** was achieved in 78% yield (entry 3). However, the yield value was not significantly increased when the catalyst loading was increased to 20 mol % (entry 4).

Table 1
Screening of the catalysts[a]



Entry	Catalyst (mol %)	Yield **3a** (%)[b]	Yield **4a** (%)[b]
1	Nano-Fe_3O_4 (2)	30	12
2	Nano-Fe_3O_4 (5)	67	8
3	Nano-Fe_3O_4 (10)	78	4
4	Nano-Fe_3O_4 (20)	79	4
5	Nano-Fe_3O_4 (10)	60	5
6	Nano-$CuFe_2O_3$(10)	70	10
7	Fe_3O_4 (10)	33	30
8	Fe° (10)	38	38
9	$FeCl_3$(10)	40	30
10	Fe(acac)$_3$(10)	40	30
11	—	Traces	45

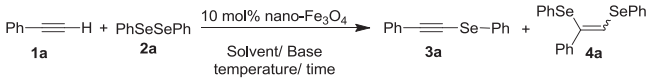
[a] Reaction conditions: phenylacetylene (0.5 mmol), diphenyl diselenide (0.25 mmol), K_2CO_3 (0.5 mmol), catalyst, DMF.
[b] Yields for isolated products.

On the other hand, the catalytic activity of the bulk Fe_3O_4 was very low when compared to its nanoparticle analogue, affording the desired product in only 33% yield (entry 7 vs 3). Similarly, the other bulk iron catalysts employed furnished the product **3a** in lower yields (entries 8–10). Moreover, we also detected the formation of vinylic selenide as a by-product, which was not significant in the presence of 10 mol % of nano-Fe_3O_4, as shown in Table 1.

Having defined the best catalyst we investigated several parameters including time, temperature, base, and solvent (Table 2). First of all, the time was screened and 14 h was the most appropriate choice (entries 1–3). Next, we investigated the effect of raising the reaction temperature from 80 to 120 °C and a slight decreased in the yield was observed (entry 4). In addition, the product **3a** was not obtained when the reaction was performed at room temperature (entry 5).

The influence of the base was also evaluated in detail (entries 6–9). The results showed that using Cs_2CO_3 and KOH as the base afforded the desired alkynyl selenide in 58 and 50% yields, respectively (entries 6 and 7). However, on employing Na_2CO_3 only an insignificant amount of product was obtained, and in the absence of base the formation of compound **3a** was not observed (entries 8 and 9).

Table 2
Optimization of the reaction conditions[a]



Entry	Time (h)	T (°C)	Base	Solvent	Yield **3a** (%)[b]	Yield **4a** (%)[b]
1	10	80	K_2CO_3	DMF	66	4
2	14	80	K_2CO_3	DMF	78	4
3	28	80	K_2CO_3	DMF	69	10
4	14	120	K_2CO_3	DMF	73	6
5	14	25	K_2CO_3	DMF	—	—
6	14	80	Cs_2CO_3	DMF	58	5
7	14	80	KOH	DMF	50	20
8	14	80	Na_2CO_3	DMF	Traces	22
9	14	80	—	DMF	—	6
10	14	80	K_2CO_3	DMSO	65	8
11	14	80	K_2CO_3	CH_3CN	38	23
12	14	80	K_2CO_3	DMF/H_2O	40	14
13	14	80	K_2CO_3	THF	—	6
14	14	80	K_2CO_3	[bmmim]BF_4	16	83

[a] Reaction conditions: phenylacetylene (0.5 mmol), diphenyl diselenide (0.25 mmol), base (0.5 mmol), and Fe_3O_4 nanopowder (0.05 mmol, 10 mol %), solvent.
[b] Yields for isolated products.

Finally, we evaluated the effect of the solvents on the reaction system (entries 9–14). However, no improvement in the chemical yield of **3a** was achieved when we changed the solvent. Interestingly, when the reaction was carried out using an ionic liquid as the solvent, compound **3a** was obtained in poor yield increasing the amount of by-product (entry 14). Thus, focusing exclusively on the synthesis of alkynyl chalcogenides, the best reaction condition found is shown in entry 2.

After obtaining the optimized conditions we investigated the scope and applicability of the present protocol (Table 3). Firstly, we synthesized a series of alkynyl selenides by reacting acetylenes with different diorganyl diselenides (entries 1–9). In terms of electronic effects, the reaction was not sensitive, since the treatment of phenylacetylene with diselenides containing either a withdrawing or a donating electron group afforded the corresponding products in very good yields (entries 2 and 3). In contrast, a diselenide containing a releasing group at the *ortho* position of the aromatic ring provided the respective product in lower yield (entry 4). Furthermore, an aliphatic diselenide, in this case di-butyl diselenide, also reacted well with phenylacetylene, affording the respective product in satisfactory yield (entry 5).

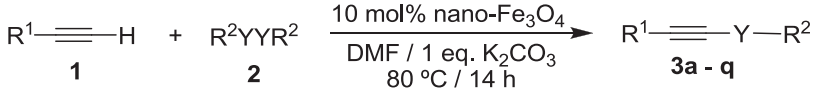
Aryl-substituted alkynes also showed good activity under the optimized conditions allowing the preparation of alkynyl selenides in good yields (entries 6–8). However, with the employment of *n*-octyne the corresponding product was synthesized in moderate yield (entry 9).

Next we explored the generality of the reaction regarding the preparation of alkynyl tellurides (entries 10–17). It was found that the combination of phenylacetylene and diphenyl ditelluride, under standard conditions, furnished the desired product in 91% yield (entry10). However, when we employed a ditelluride with a withdrawing group at the *para* position of the aromatic ring a decrease in the yield was observed (entry 2).

It can be noted that the presence of a methyl group at the same position on the aromatic ring provided the respective alkynyl telluride in 92% yield (entry 12). In addition, the reaction proceeded well when an alkyl ditelluride was employed, affording the product **3m** in reasonable yield (entry 13).

Subsequently, the combination of structurally diverse alkynes with diphenyl ditelluride was also evaluated (entries 14–16). A series of aromatic alkynes with different substituents provided the expected products **3n–p** with 60–70% yield (entries 14–16).

Table 3
Synthesis of several alkynyl chalcogenides[a]



1 2 3a - q

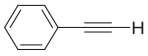
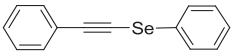
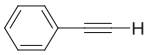
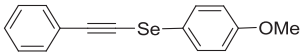
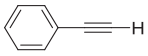
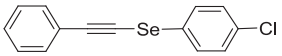
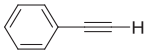
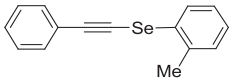
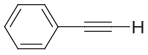
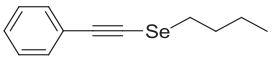
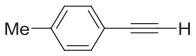
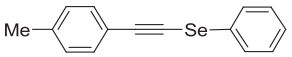
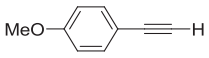
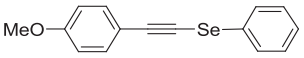
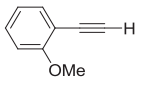
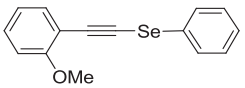
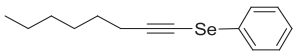
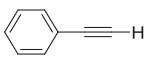
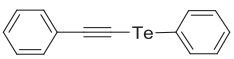
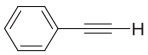
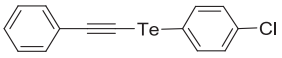
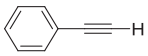
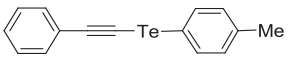
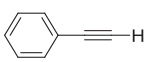
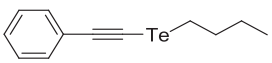
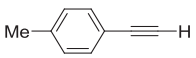
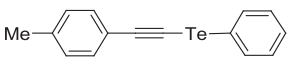
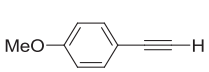
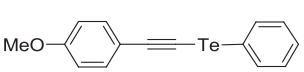
Entry	Alkyne	R^2	Y	Product	Yield[b]
1		Ph	Se	 **3a**	78
2		*p*-MeOPh	Se	 **3b**	76
3		*p*-ClPh	Se	 **3c**	77
4		*o*-MePh	Se	 **3d**	45
5		n-C_4H_9	Se	 **3e**	51
6		Ph	Se	 **3f**	60
7		Ph	Se	 **3g**	65
8		Ph	Se	 **3h**	65
9		Ph	Se	 **3i**	50
10		Ph	Te	 **3j**	91
11		*p*-ClPh	Te	 **3k**	70
12		*p*-MePh	Te	 **3l**	92
13		n-C_4H_9	Te	 **3m**	66
14		Ph	Te	 **3n**	60
15		Ph	Te	 **3o**	65

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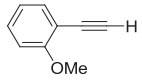
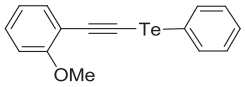
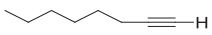
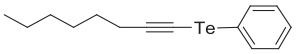
Table 3 (*continued*)

Entry	Alkyne	R^2	Y	Product	Yield[b]
16		Ph	Te	 **3p**	70
17		Ph	Te	 **3q**	52

[a] Reaction conditions: acetylene (0.5 mmol), diorganyl dichalcogenide (0.25 mmol), base (0.5 mmol), and Fe_3O_4 nanopowder (0.05 mmol, 10 mol %), DMF.
[b] Isolated yields.

Moreover, the methodology was also applicable to the preparation of an aliphatic alkynyl telluride, which was obtained in reasonable yield (entry 17).

We also tested the recyclability of the Fe_3O_4 nanoparticles in order to evaluate the sustainability of the present methodology. Therefore, the catalyst was recovered from the reaction medium using an external magnet and reused for further reactions. As a noteworthy result, the catalyst maintained its activity and acceptable efficiency for up to four recycling experiments (Fig. 1).

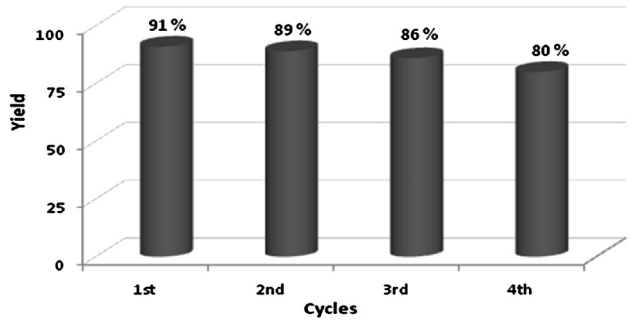
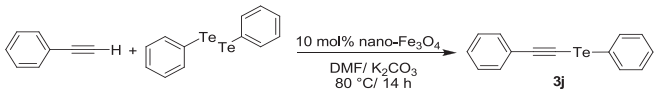


Fig. 1. Recyclability of the catalyst.



Additionally, transmission electron microscopy (TEM) analysis of the Fe_3O_4 nanopowder was performed before use and after an additional four reaction runs (Fig. 2). These results might suggest that the magnetite nanoparticles were present in the reaction even in the fourth run.

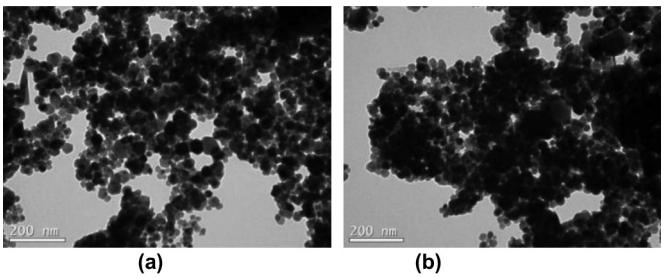
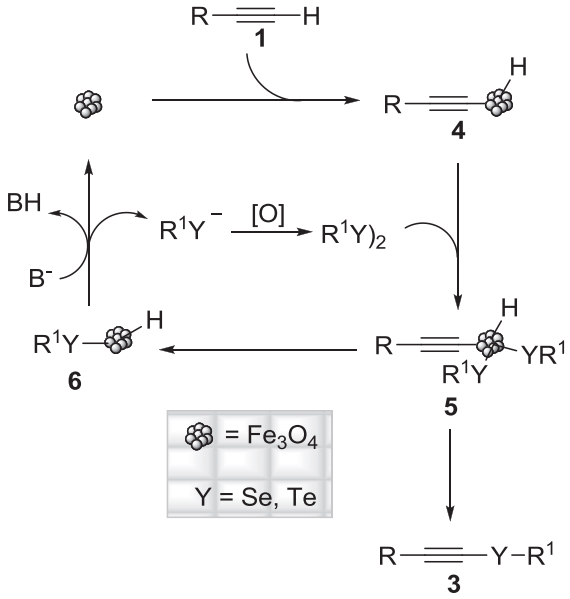


Fig. 2. TEM images of Fe_3O_4 nanoparticles. (a) Fresh Fe_3O_4 nanopowder (b) Fe_3O_4 nanopowder after fourth run.

Based on reports in the literature,[16] we can outline a plausible reaction pathway for the preparation of alkynyl chalcogenides (Scheme 2). It can be postulated that in the first step the [alkenyl-iron] cluster **4** could be formed from the terminal alkyne and the catalyst. Instantly, this cluster could react with diorganyl dichalcogenide leading to **5**. Next, the reductive elimination could take place, giving the desired alkynyl chalcogenides and species **6**. Lastly, in the presence of base, the catalyst would be regenerated, completing the catalytic cycle.



Scheme 2. Plausible reaction pathway.

3. Conclusion

In summary, we have developed a mild and efficient methodology for the synthesis of alkynyl chalcogenides, using Fe_3O_4 nanoparticles as a reusable catalyst. This new protocol generally afforded the corresponding products in good to excellent yields. In addition, the nanocatalyst was easily recovered from the reaction medium by simple magnetic force, avoiding tedious work-up separation, and reused for up to four cycles without significant loss of activity.

4. Experimental section

4.1. General remarks

^1H and ^{13}C NMR spectra were recorded in $CDCl_3$ at 400 MHz and 200 MHz or at 100 MHz and 50 MHz, respectively. Chemical shifts

(δ) are reported (in parts per million) relative to the TMS (^{1}H NMR) and to the solvent (^{13}C NMR). The solvents were used without further purification. Thin layer chromatography (TLC) was performed using Merck Silica Gel GF_{254}, 0.25 mm thickness. For visualization, TLC plates were either placed under ultraviolet light, or stained with iodine vapor, or acidic vanillin. The Fe_3O_4 nanopowder was purchased from Sigma–Aldrich (particle size: 50–100 nm; surface area: 60 m^2/g).

4.2. General procedure for the preparation of alkynyl chalcogenides

The terminal acetylene (0.5 mmol) and Fe_3O_4 nanopowder (0.05 mmol, 10 mol %) were placed into a round-bottom flask, followed by diorganyl dichalcogenide (0.25 mmol) and DMF. The reaction was stirred at 80 °C in an oil bath for 14 h. After this time, the reaction was cooled to room temperature, quenched with water, and the aqueous layer was extracted with ethyl acetate. The organic phase was dried over $MgSO_4$, filtered, and the volatiles were completely removed under vacuum to give the crude residue. Purification by flash chromatography with a mixture of hexane/ethyl acetate (99:1) afforded the desired alkynyl chalcogenide.

4.3. Recyclability of the catalyst

After completion of the experiment, the reaction system was cooled to room temperature and the Fe_3O_4 nanoparticles were collected on an external magnet, washed with a 1:1 mixture of ethyl acetate and water (3 mL), and dried under vacuum. The recovered catalyst was reused directly for the next run.

4.3.1. Phenyl(phenylethynyl)selane[9] (***3a***). ^{1}H NMR (200 MHz, $CDCl_3$): 7.65–7.55 (m, 2H); 7.45–7.54 (m, 2H); 7.32–7.17 (m, 6H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): 131.7; 129.5; 128.9; 128.3; 127.1; 123.1; 102.9; 69.2 ppm.

4.3.2. (4-Methoxyphenyl)(phenylethynyl)selane[12b] (***3b***). ^{1}H NMR (200 MHz, $CDCl_3$): 7.53 (d, 2H, J=8.9 Hz); 7.50–7.41 (m, 2H); 7.34–7.27 (m, 3H); 6.88 (d, 2H, J=8.9 Hz); 3.79 (s, 3H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): 159.4; 131.8; 131.7; 128.4; 128.3; 123.3; 118.3; 115.3; 101.5; 70.4; 55.4 ppm.

4.3.3. (4-Chlorophenyl)(phenylethynyl)selane[9] (***3c***). ^{1}H NMR (200 MHz, $CDCl_3$): 7.85–7.76 (m, 1H); 7.55–7.47 (m, 2H); 7.37–7.30 (m, 3H); 7.23–7.15 (m, 3H); 2.37 (s, 3H) ppm. ^{13}C NMR (50 MHz, $CDCl_3$): 136.5; 131.7; 130.22; 129.5; 129.3; 128.5; 128.3; 127.1; 123.2; 103.0; 69.1; 20.9 ppm.

4.3.4. (Phenylethynyl)(o-tolyl)selane[4c] (***3d***). ^{1}H NMR (200 MHz, $CDCl_3$): 7.65–7.55 (m, 2H); 7.45–7.54 (m, 2H); 7.32–7.17 (m, 6H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): 131.7; 129.5; 128.9; 128.3; 127.1; 123.1; 102.9; 69.2 ppm.

4.3.5. Butyl(phenylethynyl)selane[11c] (***3e***). ^{1}H NMR (200 MHz, $CDCl_3$): 7.44–7.38 (m, 2H); 7.33–7.27 (m, 3H); 2.88 (t, 2H, J=6 Hz); 1.93–1.78 (m, 2H); 1.57–1.43 (m, 2H); 0.96 (t, 3H, J=14.67 Hz) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): 131.4; 128.2; 128.0; 123.7; 99.3; 70.5; 32.2; 29.3; 22.5; 13.5 ppm.

4.3.6. Phenyl(p-tolylethynyl)selane[11b] (***3f***). ^{1}H NMR (200 MHz, $CDCl_3$): 7.64–7.58 (m, 2H); 7.48–7.28 (m, 5H); 7.21–7.14 (m, 2H); 2.40 (s, 3H) ppm. ^{13}C NMR (50 MHz, $CDCl_3$): 138.9; 132.4; 131.8; 129.6; 129.2; 128.9; 127.0; 120.1; 103.2; 68.2; 21.6 ppm.

4.3.7. ((4-Methoxyphenyl)ethynyl)(phenyl)selane[12b] (***3g***). ^{1}H NMR (200 MHz, $CDCl_3$): 7.65–7.59 (m, 2H); 7.44 (dd, 1H, J=7.7 and 1.8 Hz); 7.36–7.19 (m, 4H); 6.95–6.84 (m, 2H); 3.92 (s, 3H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): 160.1; 133.3; 129.9; 129.4; 128.6; 126.8; 120.3; 112.3; 110.5; 99.6; 72.7; 55.7 ppm.

4.3.8. ((2-Methoxyphenyl)ethynyl)(phenyl)selane[7b] (***3h***). ^{1}H NMR (200 MHz, $CDCl_3$): 7.65–7.59 (m, 2H); 7.44 (dd, 1H, J=7.7 and 1.8 Hz); 7.36–7.19 (m, 4H); 6.95–6.84 (m, 2H); 3.92 (s, 3H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): 160.1; 133.3; 129.9; 129.4; 128.6; 126.8; 120.3; 112.3; 110.5; 99.6; 72.7; 55.7 ppm.

4.3.9. But-1-ynyl(phenyl)selane[11c] (***3i***). ^{1}H NMR (400 MHz, $CDCl_3$): 7.53–7.46 (m, 2H); 7.32–7.22 (m, 3H); 2.46 (t, 2H, J=8 Hz); 1.44 (m, 6H); 0.90 (t, 3H, J=8 Hz) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): 133.2; 129.6; 128.7; 126.9; 105.1; 57.6; 31.6; 28.9; 28.8; 22.81; 20.8; 14.3 ppm.

4.3.10. Phenyl(phenylethynyl)tellane[11c] (***3j***). ^{1}H NMR (400 MHz, $CDCl_3$): 7.79–7.77 (m, 2H); 7.52–7.50 (m, 2H); 7.38–7.33 (m, 3H); 7.32–7.29 (m, 3H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): 135.0; 131.8; 129.7; 128.6; 128.2; 127.9; 123.3; 114.2; 113.1; 47.5 ppm.

4.3.11. (4-Chlorophenyl)(phenylethynyl)tellane (***3k***). ^{1}H NMR (200 MHz $CDCl_3$): 7.55–7.49 (m, 4H); 7.38–7.27 (m, 5H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): 133.3; 131.8; 130.3; 129.6; 128.7; 128.4; 127.1; 122.9; 103.3; 68.6 ppm. HRMS (ESI+) m/z: calculated for $C_{14}H_9TeCl$ $[M+CH_3OH]^+$: 372.9623; found, 372.9629.

4.3.12. (Phenylethynyl)(p-tolyl)tellane[10e] (***3l***). ^{1}H NMR (400 MHz, $CDCl_3$): 7.66 (d, 2H, J=8.0 Hz); 7.47–7.42 (m, 2H); 7.33–7.28 (m, 3H); 7.09 (d, 2H, J=8.0 Hz); 2.34 (s, 3H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): 138.1; 135.7; 131.8; 130.6; 128.5; 128.2; 123.5; 113.7; 108.6; 47.5; 21.1 ppm.

4.3.13. Butyl(phenylethynyl)tellane[12b] (***3m***). ^{1}H NMR (200 MHz, $CDCl_3$): 7.44–7.36 (m, 2H); 7.34–7.25 (m, 3H); 2.90 (t, 2H, J=7.5 Hz); 1.99–1.85 (m, 2H); 1.55–1.37 (m, 2H); 0.96 (t, 3H, J=7.3 Hz) ppm. ^{13}C NMR (50 MHz, $CDCl_3$): 131.7; 128.1; 123.7; 111.3; 44.4; 33.6; 24.7; 13.4; 9.94 ppm.

4.3.14. Phenyl(p-tolylethynyl)tellane[10e] (***3n***). ^{1}H NMR (400 MHz, $CDCl_3$): 7.66 (d, 2H, J=8.0 Hz); 7.47–7.42 (m, 2H); 7.33–7.28 (m, 3H); 7.09 (d, 2H, J=8.0 Hz); 2.34 (s, 3H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): 138.1; 135.7; 131.8; 130.6; 128.5; 128.2; 123.5; 113.7; 108.6; 47.5; 21.1 ppm.

4.3.15. ((4-Methoxyphenyl)ethynyl)(phenyl)tellane[12b] (***3o***). ^{1}H NMR (400 MHz, $CDCl_3$): 7.76–7.73 (m, 2H); 7.44 (d, 2H, J=8.5 Hz); 7.29–7.26 (m, 3H); 6.86 (d, 2H, J=8.5 Hz); 3.82 (s, 3H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): 159.9; 134.9; 133.7; 129.7; 127.8; 115.5; 114.2; 113.8; 113.4; 55.3; 45.1 ppm.

4.3.16. ((2-Methoxyphenyl)ethynyl)(phenyl)tellane[7b] (***3p***). ^{1}H NMR (400 MHz, $CDCl_3$): 7.77–7.74 (m, 2H); 7.42 (dd, 1H, J=7.6 and 1.7 Hz); 7.29–7.24 (m, 4H); 6.93–6.87 (m, 2H); 3.88 (s, 3H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): 160.3; 134.6; 133.7; 129.9; 129.6; 127.6; 120.3; 113.7; 112.5; 110.7; 55.7; 51.1 ppm.

4.3.17. But-1-ynyl(phenyl)tellane[10e] (***3q***). ^{1}H NMR (400 MHz, $CDCl_3$): 7.70–7.64 (m, 2H); 7.28–7.19 (m, 3H); 2.57 (t, 2H, J=8 Hz); 1.60–1.52 (m, 2H); 1.45–1.38 (m, 2H); 1.32–1.25 (m, 4H); 0.89 (t, 3H, J=8 Hz) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): 137.9; 134.7; 129.6; 127.6; 116.2; 34.7; 31.3; 28.9; 28.5; 22.6; 21.1; 14.1 ppm.

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