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Synthesis of Unsymmetrical Diorganyl Chalcogenides under Greener Conditions: Use of an Iodine/DMSO System, Solvent- and Metal-Free Approach

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Abstract: Herein, we report a greener iodine-catalyzed protocol to access different types of unsymmetrical diorganyl chalcogenides. This new approach works in the absence of solvent and metal. The desired products were obtained in good to excellent yields using one equivalent of arylboronic acids, half an equivalent of various diorganyl dichalcogenides, iodine (10 mol%) as a catalyst and 2 equivalents of dimethyl sulfoxide (DMSO; as oxidant), with a reaction time of 10 min under microwave irradiation.

Keywords: boronic acids; iodine; metal-free conditions; microwave irradiation; selenides; sulfides; tellurides

Introduction

Unsymmetrical organochalcogenides (S, Se, and Te) have become an attractive synthetic target in the past few decades and they have been extensively reported in various research articles,[1] reviews[2] and books.[3] In recent years these compounds have been employed in certain reactions[4] as catalysts,[5a,b] ligands,[5c] ionic liquids[6] and synthetic intermediates in total synthesis[2,3,7] besides being applied in asymmetric catalysis.[4a] Moreover, synthetic organochalcogen compounds have been found to function as antioxidant, anticancer, antihypertensive and antiviral agents.[2d,e,3,8] They also have important applications in materials science.[9]

Similarly, organoboronic acids and their derivatives are easily accessible, stable and are compatible with several functional groups. Due to these properties they have been used as coupling partners in different organic transformations.[10]

Considering the importance of unsymmetrical organochalcogenides, several methods have been developed for their synthesis.[11] Among them, metal-catalyzed aryl-chalcogen bond formation is one of the most commonly used protocols,[2a–c,11] which generally involves the presence of a ligand. Several metal sources, such as Pd,[12] Ni,[13] Cu,[14] Zn,[15] Fe[16] and In,[17] have been used. However, these types of transformations have their own particular drawbacks, such as the use of environmentally unfriendly solvents, expensive ligands and catalysts, precious and rare metals, reducing agents, stoichiometric or greater amounts of reagents, long reaction times, harsh reaction conditions and oxygen-free techniques. Also, there are only a few general methods available which are applicable to the synthesis of S-, Se- and Te-based unsymmetrical diaryl chalcogenides as well as alkyl aryl chalcogenides.[18]

Similarly, different methods have been developed for the synthesis of unsymmetrical chalcogenides using direct C–H functionalization/activation.[19] This strategy is important, since it eliminates an unnecessary step, directly accessing the desired product. However, in most cases the use of a solvent, a transition metal catalyst and additives is required.

In the last few years, the I_2/DMSO system has been applied in various greener organic transformations.[20] However, to date, to the best of our knowledge, there have been no reports involving the application of this catalytic oxidant system to the preparation of organotellurim compounds. In addition, the preparation of organochalcogen compounds through the reaction of organoboronic acids and diorganodichalcogenides using this system has not been explored. Recently, we successfully explored the selenylation and thiolation of indoles catalyzed by the iodine/DMSO system, avoiding the use of solvents and metals, in an open atmosphere.[21]

In this context, it would be advantageous and highly desirable to develop a ligand-free and metal-

Scheme 1. Iodine-catalyzed synthesis of unsymmetrical organochalcogenides under ligand-, metal- and solvent-free conditions.

free protocol involving a solvent-free system which works in shorter reaction times for the preparation of unsymmetrical diorganochalcogenides. As part of our wider research program aimed at designing and developing eco-friendly processes,[21,22] herein we report, for the first time, the use of the I_2/DMSO system in the synthesis of unsymmetrical organochalcogenides, applicable to Te, Se and S, under microwave irradiation. This novel approach worked smoothly with half an equivalent of different dichalcogenides without the need for a ligand, metal or solvent, in a very short reaction time (Scheme 1).

Results and Discussion

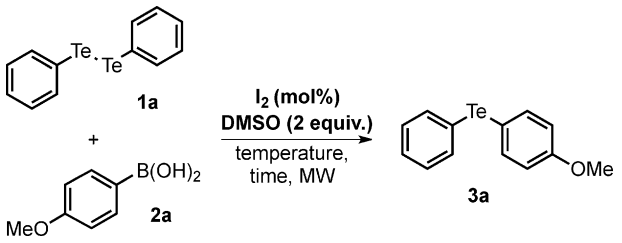
To identify the best reaction conditions, diphenyl ditelluride **1a** and 4-methoxyphenylboronic acid **2a** were used as standard substrates, a stoichiometric amount of oxidant was employed and I_2 was used as a catalyst under microwave irradiation (Table 1 and Table 2). Firstly, the reaction time and microwave parameters were evaluated for this coupling reaction (Table 1). We commenced our studies by varying the reaction time (entries 1–5). On performing the reaction for 1 min we observed the formation of the desired product **3a** in only 49% yield (entry 1). Incremental increases in the reaction time resulted in a significant improvement in the yield of **3a**.

The best result was achieved after 10 min at 100 °C with 100 W of power, where the product **3a** was accessed in 94% yield (entry 4). No substantial change in the yield was observed on applying a 15 min reaction time (entry 5).

In the next step, the temperature was screened and the ideal conditions were observed at 100 °C; lower temperatures afforded lower yields of **3a** (entry 6 *vs.* 4) and higher temperature did not show a strong influence (entry 7 *vs.* 4). The reaction was also carried out under different levels of MW irradiation power. Both lower power (80 W; entry 8) and higher power (entry 9) had a negative effect on the isolated yield of **3a**.

In order to compare and evaluate the influence of the conventional heating methodology, the reaction was also performed in an oil bath heating system (entry 10). A longer reaction time (18 h) gave **3a** in a lower yield, highlighting the superiority of the MW method.

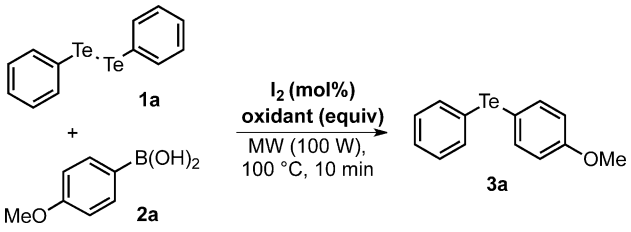
Table 1. Optimization of the microwave parameters.[a]



Entry	MW [W]	T [°C]	t [min]	Yield [%][b]
1	100	100	1	49
2	100	100	3	77
3	100	100	5	84
4	100	100	10	94
5	100	100	15	96
6	100	80	10	84
7	100	120	10	95
8	80	100	10	80
9	120	100	10	85
10[c]		100	18 h	69

[a] *Reaction conditions:* **1a** (0.125 mmol), **2a** (2 equiv.), I_2 (5 mol%), DMSO (2 equiv.) under MW irradiation.
[b] Isolated yield.
[c] Conventional heating in sealed tube.

Table 2. Optimization of the reaction conditions.[a]



Entry	I_2 [mol%]	Oxidant [equiv.]	Yield [%][b]
1	–	DMSO (2)	traces
2	1	DMSO (2)	48
3	5	DMSO (2)	86
4	10	DMSO (2)	94
5	15	DMSO (2)	96
6[c]	–	DMSO (2)	60
7[d]	–	DMSO (2)	84
8	10	–	20
9	10	DMSO (1)	69
10	10	DMSO (3)	95
11	10	TBHP (2)	47
12	10	H_2O_2 (2)	70

[a] *Reaction conditions:* **1a** (0.125 mmol), **2a** (2 equiv.) in the presence of catalyst (10 mol%) and oxidant (2 equiv.) for 10 min at 100 °C and 100 W of MW irradiation.
[b] Isolated yields.
[c] Reaction performed using 10 mol% of NaI.
[d] Reaction performed using 10 mol% of HI.

In the next step, the effects of the catalyst loading and the stoichiometric oxidant on the reaction system were screened (Table 2). In the absence of iodine, the reaction afforded only trace amounts of **3a** (entry 1). With the use of 1 mol% of iodine (entry 2) **3a** was obtained in 48% yield. Increasing the catalyst loading to 5 mol% caused the yield to increase to 86% (entry 3), which was further improved to 94% when 10 mol% of I_2 was used (entry 4). Further increases in the catalyst loading did not appear to have any effect on the isolated yield (entry 5). Subsequently, using NaI (entry 6) instead of I_2 resulted in **3a** with 60% yield while using HI (entry 7) afforded coupled products with 84% yield, indicating that HI is probably one of the intermediates of this transformation.

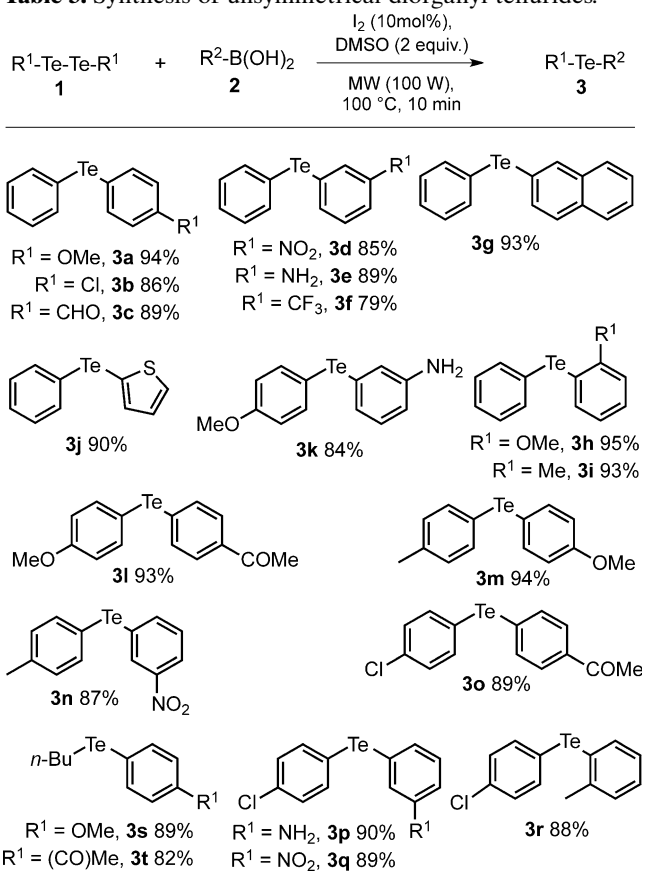
After ascertaining the best options for the catalyst and its loading, the effects of the quantity and type of oxidant used were evaluated. **3a** was obtained in poor yield when the reaction was performed in the absence of DMSO (entry 8), while 1 equiv. of DMSO afforded the desired product in 69% yield (entry 9). It should be noted that increasing the stoichiometric amount of DMSO to 3 equiv. did not affect the yield of **3a** (entry 10 *vs.* 4). Other oxidants were also screened, but they failed to provide a more favorable outcome (entries 11 and 12).

After determining the best reaction parameters, we explored the efficiency and generality of our methodology by applying it to various diorganyl ditellurides **1** and arylboronic acids **2** under the optimized conditions (Table 3).

The reaction worked well for structurally different organic moieties containing both electron-withdrawing (R^1, R^2 = Cl, CF_3, NO_2, COR, etc.) and electron-donating (R^1, R^2 = Me, OMe, NH_2, etc.) groups as well as bulky groups. Firstly, we used different arylboronic acids **2** while keeping diphenyl ditelluride **1a** constant, resulting in **3a–j** in good to excellent yields. In general, substrates **2** with electron-donating groups at the aryl ring afforded good results. The steric hindrance of *ortho*-substituted aryl substrates did not appear to influence the yields of **3h–i**. Similarly, the presence of a bulky substrate (R = 2-naphthyl) resulted in the desired product **3g** in 93% yield. We were also delighted to find that a heteroarylboronic acid afforded the desired product **3j** with 90% yield.

Subsequently, we successfully used electron-donating and electron-withdrawing substituents in the *para*-position of the aryl ring of **1** and checked the electronic as well as the steric effects of **2**. The desired products **3k–r** were obtained in good to excellent yields, the substituents showing no significant negative influence. Aliphatic dichalcogenides are generally considered to be less reactive, giving low yields, due to the β-chalcogen oxide elimination.[17b] Gratifyingly, under our optimized conditions, dibutyl ditelluride

Table 3. Synthesis of unsymmetrical diorganyl tellurides.[a,b]



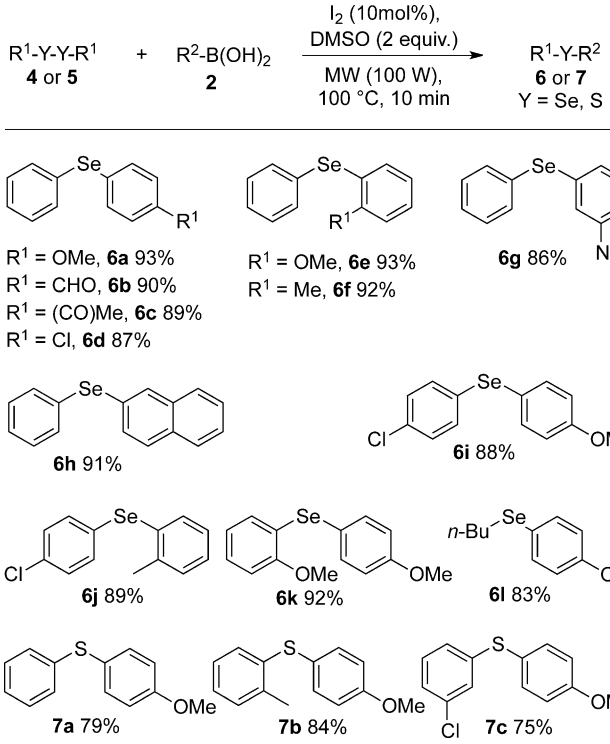
[a] *Reaction conditions:* **1** (0.25 mmol), **2** (0.5 mmol) in the presence of I_2 (10 mol%) and DMSO (2 equiv.) for 10 min at 100 °C and 100 W MW irradiation.

[b] Isolated yields.

furnished the corresponding products **3s–t** in very good yields.

The success in the iodine-catalyzed synthesis of unsymmetrical diorganyl tellurides **3** by intermolecular C–Te bond formation using diorganyl ditellurides **1** and arylboronic acids **2**, prompted us to expand this methodology to diorganyl diselenide **4** as a way to access unsymmetrical diorganyl selenides **6** (Table 4). In order to evaluate the electronic and steric effects, initially, we varied the substituents at the aryl ring of boronic acid **2**, furnishing the corresponding selenides **6a–h**, as shown in Table 4. Electronic effects due to the *para* and *meta* substituents on **2** exerted a limited influence, affording the corresponding product **6a–d** and **6g** in 86–93% yields The reaction seems not to be sensitive to steric effects at the *ortho* position (R = Me, OMe) or bulky groups (R = naphthyl) on the aryl ring of **2**, furnishing the desired products **6e**, 6**f** and **6h** in 91–93% yields. Similarly, substrates **4** with substituents at the aryl ring of the diselenide afforded the corresponding products **6i–k** in 88–92% yields, showing no significant influence of the electronic or steric effects on the diselenides **4**. Subsequently, we success-

Table 4. Synthesis of unsymmetrical diorganyl selenides and sulfides.[a,b]



[a] *Reaction conditions:* **4** or **5** (0.25 mmol), **2** (0.5 mmol) in the presence of I_2 (10 mol%) and DMSO (2 equiv.) for 10 min at 100 °C and 100 W MW irradiation.

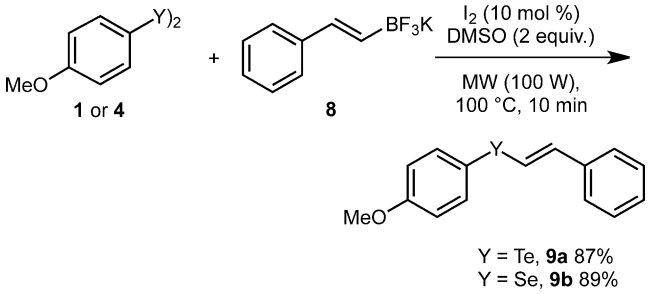
[b] Isolated yields.

fully carried out the reaction between aliphatic diselenide and **2a**, affording *n*-butyl (4-methoxyphenyl) selenide **6l** with 83% yield.

The scope of the reaction regarding the preparation of unsymmetrical diorganyl sulfides was then explored by using different disulfides **5a–c** under the optimal reaction conditions (Table 2, entry 4). Interestingly, the reaction of different diaryl disulfides **5a–c** with 4-methoxyphenylboronic acid **2a** proceeded smoothly and afforded the corresponding products **7a–c** in 75–84% isolated yields (Table 4). The small decrease in the yields can probably be explained by the stronger S–S bond of the diaryl disulfides compared to the respective ditellurides **1** or diselendies **4**.

In order to further investigate the scope of this new coupling methodology, we extended our study to potassium vinyltrifluoroborate **8** as an alternative to boronic acid in these tellurylation and selenylation reactions (Scheme 2), applying the optimal reaction conditions (Table 2, entry 4). Interestingly, the reaction of ditelluride and diselenide with **8** proceeded smoothly and afforded the corresponding coupled product **9a** and **9b** in 87% and 89% isolated yields (Scheme 2).

To demonstrate the synthetic utility of this new coupling protocol, a series of reactions was carried out on different scales (Figure 1; up to 10 mmol). Di-



Scheme 2. Iodine-catalyzed reactions of the potassium salt of vinyltrifluoroborate **8** with diorganyl dichalcogenide.

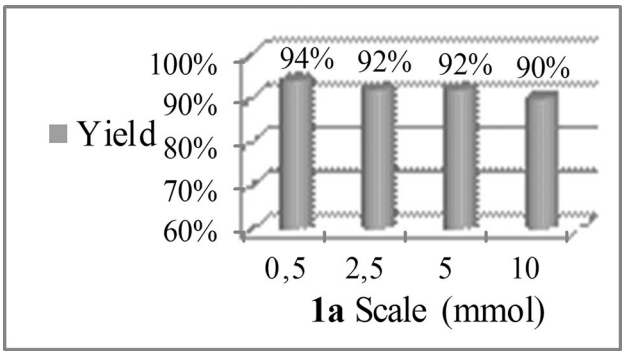
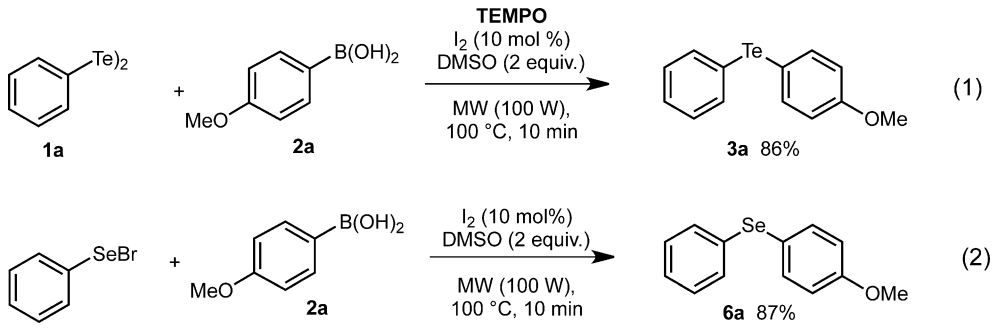


Figure 1. Results for the reaction at different scales.

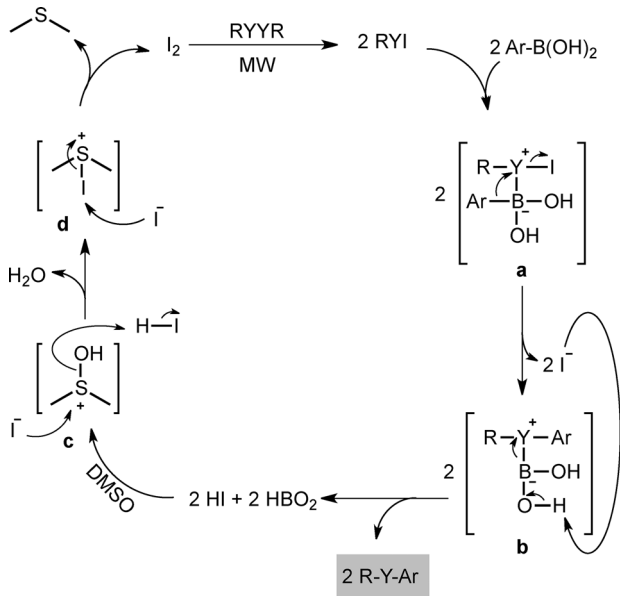
telluride **1a** and boronic acid **2a** were selected as the test materials, affording **3a** with a slight decrease in the yield. Therefore, this method could be used as a practical way to synthesize unsymmetrical diorganyl chalcogenides on a larger scale.

Considering that little is known about the coupling reaction of diorganyl chalcogenides and organoboronic acids under metal-free conditions, control experiments were conducted in order to elucidate the mechanism. Firstly, the addition of a radical inhibitor (TEMPO) under the standard reaction conditions did not hamper the reaction and **3a** was obtained in 86% yield [Scheme 3, Eq. (1)], which excluded the possibility of a radical pathway. This result indicates that, most probably, a radical mechanism is not operating and the PhY radical species is not involved. Secondly, when boronic acid **2a** was treated with PhSeBr instead of diphenyl diselenide **4a**, the product **6a** was isolated with 87% yield [Scheme 3, Eq. (2)], demonstrating that the reaction passes through a phenylselenium cation species.

Based on the above experiments and on previous reports,[23,24] a plausible reaction pathway for the synthesis of the unsymmetrical diorganyl chalcogenides under metal-free conditions is proposed in Scheme 4. Firstly, RYI (Y = Te, Se, S) would be generated through the reaction of diorganyl dichalcogenide RYYR with the catalyst (I_2). Subsequently, the reactive RYI intermediate on reaction with organoboronic acid would generate species **a** which on migration of the aryl moiety from boron to chalcogen and elimina-



Scheme 3. Investigation of the mechanism.



Scheme 4. Plausible reaction pathway.

tion of iodide could result in species **b**. The deboronation of species **b** would furnish the desired product RYAr with the simultaneous formation of HI. In the next step of the mechanism, two equivalents of HI on reaction with DMSO would then regenerate iodine,[24] through the protonated sulfur species **c**. This species would be rapidly converted to the iodine-dimethyl sulfide adduct **d** with the elimination of water. Finally, the cycle would be completed by the conversion of the iododimethylsulfonium iodide species **d** to dimethyl sulfide with the regeneration of the catalyst in the reaction medium.

Conclusions

In conclusion, we have developed a greener iodine-catalyzed, metal-free and solvent-free method for the synthesis of a variety of unsymmetrical diorganyl chalcogenides under microwave irradiation. The desired products were obtained in good to excellent yields in the presence of 10 mol% of iodine, one equiv. of arylboronic acids, half an equiv. of various diorganyl dichalcogenides and 2 equiv. of DMSO (as an oxidant). Also, the reaction was performed without the exclusion of air and moisture at 100 °C for 10 min under microwave irradiation. Various substituents with different electronic and steric effects were tolerated in the optimized reaction conditions. The reaction was shown to be robust and could easily be scaled-up without any significant loss of yield.

The chemistry described herein represents an alternative and eco-friendly synthetic approach for the preparation of unsymmetrical diorganyl chalcogenides.

Experimental Section

General Procedure for the Iodine-Catalyzed Synthesis of Unsymmetrical Organochalcogenides

A mixture of the appropriate arylboronic acid (0.5 mmol), diorganyl dichalcogenide (0.25 mmol), iodine (10 mol%, 12 mg) and 2 equiv. of DMSO (1 mmol, 78 mg) were placed in a microwave glass tube, which was sealed and placed in a CEM Discover microwave device. A maximum irradiation power of 100 W and a temperature of 100 °C were applied for 10 min. When the reaction was completed, the reaction mixture was dissolved in ethyl acetate (15 mL) and washed with 2×10 mL of an aqueous solution of 10% $Na_2S_2O_4$. The organic phase was separated, dried over $MgSO_4$ and concentrated under vacuum. The crude product was purified by flash chromatography on silica gel using hexane or a mixture of hexane/ethyl acetate (99:1) as the eluent.

3-(Phenyltellanyl)aniline (3e): Yield: 0.132 g (89%); yellow oil; ^{1}H NMR (200 MHz, $CDCl_3$): $\delta=7.57$ (d, $J=$ 8.2 Hz, 2H), 7.25–6.92 (m, 6H), 6.60–6.55 (m, 1H), 3.61 (s, 2H); ^{13}C NMR (50 MHz, $CDCl_3$): $\delta=147.3$, 139.1, 134.2, 130.3, 129.7, 128.2, 124.4, 115.0, 112.5; IR (KBr): $\nu=3300$, 3250, 3032, 2926, 1629, 1725, 1501, 1460,1097, 1013, 919, 821, 728 cm^{-1}; HR-MS: $m/z=300.0027$, calcd. for $C_{12}H_{12}NTe$ $[M+H]^+$: 300.0027.

Phenyl[3-(trifluoromethyl)phenyl]tellane (3f): Yield: 0.138 g (79%); yellow oil; ^{1}H NMR (200 MHz, $CDCl_3$): $\delta=$ 7.99–7.68 (m, 4H), 7.57–7.47 (m, 1H), 7.37–7.18 (m, 4H); ^{13}C NMR (50 MHz, $CDCl_3$): $\delta=140.5$ (q, $J_{C,F}=1.5$ Hz),

138.9, 138.1, 133.7 (q, $J_{C,F}=4$ Hz), 131.6 (q, $J_{C,F}=32$ Hz), 129.9, 129.6, 128.6, 124.5 (q, $J_{C,F}=4$), 123.7 (q, $J_{C,F}=271$), 115.9, 113.8; IR (KBr); $\nu=3065$, 3012, 2993, 2923, 1572, 1474, 1417, 1270, 1081, 1017, 997, 793, 695 cm^{-1}; HR-MS: $m/z=351.9716$, calcd. for $C_{13}H_9F_3Te$ $[M]^+$: 351.9714.

2-(Phenyltellanyl)thiophene (3j): Yield: 0.129 g (90%); yellow solid; mp 36–38 °C; ^1H NMR (200 MHz, $CDCl_3$): $\delta=$ 7.58–7.48 (m, 4H), 7.25–7.14 (m, 3H), 7.01–6.97 (m, 1H); ^{13}C NMR (50 MHz, $CDCl_3$): $\delta=142.2$, 138.1, 135.7, 135.2, 129.5, 129.3, 127.6, 116.6; IR (KBr): $\nu=3112$, 3069, 2996, 2926, 1876, 1796, 1658, 1564,1462, 1333, 1214, 1070, 1023, 921, 836, 719, 708 cm^{-1}; HR-MS: $m/z=289.9403$, calcd. for $C_{10}H_8STe$ $[M]^+$: 289.9401.

3-[(4-Methoxyphenyl)tellanyl]aniline (3k): Yield: 0.137 g (84%); brown solid; mp 97–99 °C; ^1H NMR (200 MHz, $CDCl_3$): $\delta=7.72$ (d, $J=8.8$ Hz, 2H), 6.94 (d, $J=4.8$ Hz, 2H), 6.90–6.85 (m, 1H) 6.79 (d, $J=8.8$ Hz, 2H), 6.57–6.47 (m, 1H), 3.79 (s, 3H), 3.56 (s, 2H); ^{13}C NMR (50 MHz, $CDCl_3$): $\delta=160.0$, 147.2, 141.2, 130.0, 126.5, 122.7, 116.7, 115.6, 114.3, 103.3, 55.2; IR (KBr): $\nu=3472$, 3379, 3030, 2962, 2839, 1563, 1487, 1326, 1248, 1099, 987, 815, 774 cm^{-1}; HR-MS: $m/z=$ 329.0051, calcd. for $C_{13}H_{13}NOTe$ $[M]^+$: 329.0054.

1-{4-[(4-Methoxyphenyl)tellanyl]phenyl}ethan-1-one (3l): Yield: 0.164 g (93%); yellow liquid; ^1H NMR (200 MHz, $CDCl_3$): $\delta=7.79$ (d, $J=8.8$ Hz, 2H), 7.69 (d, $J=8.5$ Hz, 2H), 7.49 (d, $J=8.5$ Hz, 2H), 6.84 (d, $J=8.8$ Hz, 2H), 3.83 (s, 3H), 2.53 (s, 3H); ^{13}C NMR (50 MHz, $CDCl_3$): $\delta=197.7$, 160.6, 142.4, 135.7, 134.6, 128.7, 125.6, 115.9, 102.2, 55.3, 26.5 cm^{-1}; IR (KBr): $\nu=3002$, 2959, 2926, 2837, 1682, 1635, 1582, 1488, 1388, 1246, 1176, 1025, 954, 815, 742 cm^{-1}; HR-MS: $m/z=356.0057$, calcd. for $C_{15}H_{14}O_2Te$ $[M]^+$: 356.0051.

(3-Nitrophenyl)(*para*-tolyl]tellane (3n): Yield: 0.148 g (87%); yellow oil; ^1H NMR (200 MHz, $CDCl_3$): $\delta=8.36$ (s, 1H), 8.02 (dd, $J=8.7$, 1.7 Hz, 1H), 7.81–7.68 (m, 3H), 7.29 (t, $J=7.9$ Hz, 1H), 7.11 (d, $J=8.1$ Hz, 2H), 2.37 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): $\delta=148.4$, 141.7, 140.0, 139.4, 131.0, 130.4, 129.8, 122.2, 117.6, 109.0, 21.4; IR (KBr): $\nu=$ 3072, 2964, 2918, 2855, 1529, 1486, 1419, 1342, 1207,1103, 1011, 860, 801, 724 cm^{-1}; HR-MS: $m/z=342.9849$, calcd. for $C_{13}H_{11}NO_2Te$ $[M]^+$: 342.9847.

1-{4-[(4-Chlorophenyl)tellanyl]phenyl}ethanone (3o): Yield: 0.159 g (89%); yellow soild; mp 67–70 °C;^1H NMR (200 MHz, $CDCl_3$): $\delta=7.77$–7.68 (m, 4H), 7.61 (d, $J=$ 8.5 Hz, 2H), 7.24 (d, $J=8.5$ Hz, 2H), 2.56 (m, 3H); ^{13}C NMR (50 MHz, $CDCl_3$): $\delta=197.6$, 140.9, 136.2, 136.1, 135.4, 130.2, 129.0, 123.5, 111.0, 26.6; IR (KBr): $\nu=3063$, 3045, 3006, 1892, 1668, 1578, 1468, 1388, 1354, 1266, 956, 848, 742, 599 cm^{-1}; HR-MS: $m/z=360.9621$, calcd. for $C_{14}H_{12}ClOTe$ $[M+H]^+$: 360.9623.

3-[(4-Chlorophenyl)tellanyl]aniline (3p): Yield: 0.149 g (90%); brown solid; mp: 58–60 °C; ^1H NMR (200 MHz, $CDCl_3$): $\delta=7.57$ (d, $J=8.2$ Hz, 2H), 7.18–6.93 (m, 5H), 6.60–6.55 (m, 1H), 3.61(s, 2H); ^{13}C NMR (50 MHz, $CDCl_3$): $\delta=147.3$, 139.1, 134.2, 130.3, 129.7, 128.2, 124.4, 115.0, 112.5; IR (KBr): $\nu=3457$, 3369, 3069, 3043, 2926, 2851, 1807, 1631, 1599, 1568, 1442, 1391, 1272, 1099, 1013, 993, 826, 791, 673 cm^{-1}; HR-MS: $m/z=332.9551$, calcd. for $C_{12}H_{10}ClNTe$ $[M]^+$: 332.9548.

(4-Chlorophenyl)(3-nitrophenyl)tellane (3q): Yield: 0.160 g (89%); yellow solid; mp 90–92 °C; ^1H NMR (200 MHz, $CDCl_3$): $\delta=8.44$ (s, 1H), 8.09 (dd, $J=8.2$, 1.6 Hz, 1H), 7.86 (d, $J=7.6$ Hz, 1H), 7.72 (d, $J=8.2$ Hz, 2H), 7.40-7.22 (m, 3H); ^{13}C NMR (50 MHz, $CDCl_3$): $\delta=148.6$, 142.5, 140.8, 135.7, 131.3, 130.4, 130.1, 122.8,116.5, 110.8; IR (KBr): $\nu=3096$, 2924, 2849, 1597, 1562, 1468, 1415, 1342, 1268, 1056, 966, 874, 832, 726, 662 cm^{-1}; HR-MS: $m/z=$ 362.92899, calcd. for $C_{12}H_8ClNO_2Te$ $[M]^+$: 362.92900.

[4-Chlorophenyl)(*ortho*-tolyl)tellane (3r): Yield: 0.145 g (88%); white oil; ^1H NMR (200 MHz, $CDCl_3$): $\delta=7.56$ (d, $J=8.4$ Hz, 2H), 7.48 (d, $J=7.5$ Hz, 1H),7.24–7.20 (m, 2H), 7.16 (d, $J=8.4$ Hz, 2H), 6.99–6.91(m, 1H), 2.39(s, 3H); ^{13}C NMR (50 MHz, $CDCl_3$): $\delta=142.1$, 139.8, 137.8, 134.6, 129.9, 129.6, 128.5, 127.0, 118.9, 111.8, 26.2; IR (KBr): $\nu=$ 3055, 3002, 2967, 2922, 1652, 1558, 1470, 1458, 1378, 1089, 1007, 809, 744, 668 cm^{-1}; HR-MS: $m/z=331.9593$, calcd. for $C_{13}H_{11}ClTe[M]^+$: 331.9596.

(4-Chlorophenyl)(*ortho*-tolyl)selane (6j): Yield: 0.125 g (89%); white oil; ^1H NMR (200 MHz, $CDCl_3$): $\delta=7.35$–7.01 (m, 8H), 2.37(s, 3H); ^{13}C NMR (50 MHz, $CDCl_3$): $\delta=$ 140.1,134.1, 133.8, 133.3, 131.2, 130.5, 129.6, 129.3, 128.2, 126.9, 22.5; IR (KBr): $\nu=3059$, 3008, 2969, 1652, 1558, 1472, 1386, 1274, 1089, 1009, 811, 746, 668 cm^{-1}; HR-MS: $m/z=$ 281.9707, calcd. for $C_{13}H_{11}ClSe$ $[M]^+$: 281.9707.

(2-Methoxyphenyl)(4-methoxyphenyl)selane (6k): Yield: 0.134 g (92%); white oil; ^1H NMR (400 MHz, $CDCl_3$): $\delta=$ 7.57 (d, $J=8.7$ Hz, 2H), 7.15–7.10 (m, 1H), 6.90 (d, $J=$ 8.7 Hz, 2H), 6.83–6.70 (m, 3H), 3.89 (s, 3H), 3.82 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): $\delta=160.2$, 155.9, 138.5, 129.0, 126.9, 123.6, 121.6, 117.3, 115.3, 110.1, 55.8, 55.3; IR (KBr): $\nu=3064$, 2961, 2935, 1843, 1792, 1699, 1652, 1558, 1456, 1397, 1240, 1027, 824, 748, 668 cm^{-1}; ^{77}Se NMR ($CDCl_3$): $\delta=$ 349.09; HR-MS: $m/z=294.0150$, calcd. for $C_{14}H_{14}O_2Se$ $[M]^+$: 294.0154.

(3-Chlorophenyl)(4-methoxyphenyl)sulfane (7c): Yield: 94 mg (75%); white solid; mp 59–61 °C; ^1H NMR (400 MHz, $CDCl_3$): $\delta=7.43$ (d, $J=8.9$ Hz, 2H), 7.14–7.04 (m, 3H), 7.00–6.98 (m, 1H), 6.92 (d, $J=8.9$ Hz, 2H), 3.82 (s, 3H); ^{13}C NMR (50 MHz, $CDCl_3$): $\delta=160.4$, 141.4, 136.2, 134.9, 129.9, 127.1, 125.7, 125.6, 122.8, 115.3, 55.5; IR (KBr): $\nu=$ 3083, 3016, 2963, 2937, 2894, 2837, 2045, 1945, 1902, 1876, 1739, 1672, 1493, 1437, 1027, 872, 799, 642 cm^{-1}; HR-MS: $m/z=250.0213$, calcd. for $C_{13}H_{11}ClOS$ $[M]^+$: 250.0214.

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