# Iron-Catalyzed Formation of C–Se and C–Te Bonds through Cross Coupling of Aryl Halides with Se(0) and Te(0)/Nano-Fe<sub>3</sub>O<sub>4</sub>@GO

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**Abstract:** The formation of C–Se and C–Te bonds is of synthetic and biological importance. Graphene oxide based nano-Fe<sub>3</sub>O<sub>4</sub> (nano-Fe<sub>3</sub>O<sub>4</sub>@GO) is used as a reusable catalyst for the efficient synthesis of diselenides and ditellurides, through cross coupling of Se(0) or Te(0) with aryl iodides. The magnetic heterogeneous catalyst could be easily recovered and reused many times without significant loss of catalytic activity. In addition the superiority of nano-Fe<sub>3</sub>O<sub>4</sub>@GO over pristine nano-Fe<sub>3</sub>O<sub>4</sub> is established.

**Key words:** graphene oxide, cross coupling, recyclability, nano-Fe<sub>3</sub>O<sub>4</sub> catalyst, diselenide, ditelluride

Graphene (G) has a monolayer arrangement of carbon atoms in a honeycomb network; graphene has attracted enormous scientific activity due to its excellent electrical, thermal, and mechanical properties. <sup>1–5</sup> Graphene-based composites are emerging as a new class of materials; they have created the opportunity for the novel use of twodimensional carbon as a superior platform for metal nanoparticles (platinum, palladium, gold, copper) and metal oxides (titanium dioxide, clay, silica, cobalt oxide, zinc oxide).<sup>6-12</sup> One of the most important derivatives of graphene is graphene oxide (GO), which is a layered compound with oxygen functional groups that can be used as anchoring sites for metal nanoparticles to produce graphene nanoparticle hybrids.13 In particular, the combination of graphene and functional nanoparticles may lead to nanocomposites of graphene bearing with metals or inorganic metal oxides or sulfides with interesting properties for many potential applications including chemical sensors, energy storages, catalyses, hydrogen storages, supercapacitors, lithium ion batteries, etc.<sup>14-16</sup> Fabrication of these functional nanocomposites via a controllable, costeffective, and fast approach has likewise aroused interest among researchers.<sup>17</sup> In recent years, composite systems containing magnetic nanoparticles have become the subject of intensive research, because of their potential integration in a broad range of technological applications such as magnetic fluids,<sup>18</sup> data storage,<sup>19</sup> biotechnology/bio-medicine,<sup>20</sup> catalysis,<sup>21</sup> magnetic resonance imaging,<sup>22</sup> environmental remediation,<sup>23</sup> etc. Nanocomposites of magnetite  $Fe_3O_4$  nanoparticles (NPs), due to the presence of iron ions in two valence states Fe<sup>2+</sup> and Fe<sup>3+</sup>, have in-

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teresting properties.<sup>24</sup> Layering magnetite nanoparticles on the surface of graphene oxide results in nanocomposites that can be tailored with different desirable functional properties such as biocompatibility, electrical conductivity, or chemical and physical stability that are necessary for particular applications.<sup>25</sup>

Over the last few decades, organodichalcogens, the selenium or tellurium counterparts of organic peroxides, have played an important role in organic chemistry as intermediates because of their stability, ease of handling, and reactivity.<sup>26,27</sup> Traditional methods for the formation of diselenides include oxidation of selenols,<sup>28</sup> reaction of sodium or lithium diselenides with alkyl halides,<sup>29</sup> reaction of selenourea with alkyl halides,<sup>30</sup> reduction of selenocyanates.<sup>31</sup> Aluminum-induced, copper-catalyzed coupling of aryl iodides with selenium afforded the corresponding diaryl selenides.<sup>32,33</sup> Correspondingly, Kumar et al. reported a copper-catalyzed/mediated Se-N coupling reaction for the synthesis of isoselenazolones.<sup>34</sup> In addition, various metal-based catalysts in combination with different ligands are generally employed for synthesis of selenides by cross coupling of their halides, but most of these synthetic approaches involve specially designed ligands or well-defined catalyst/reagent(s); this may increase the cost and limit the scope of their applications.35

Novel catalytic procedures, especially in the absence of a ligand, are required for the efficient synthesis of diselenides. Heterogeneous nanocatalysts offer higher surface area and low-coordinated sites that are responsible for the higher catalytic activity.<sup>36</sup> Organic reactions catalyzed by metallic nanoparticles are currently an area of intensive research because they afford a more effective process and allow improvement in relation to traditional methodologies. Recently, Braga et al. reported a one-pot synthesis of symmetrical diselenides and ditellurides from halides with CuO NPs/Se(0) as well as Te(0)/KOH, but they did not survey the recovery and reusability of this catalyst.<sup>37</sup>

Iron has been investigated as a catalyst in the formation of carbon–carbon and carbon–heteroatom bonds due to its low cost, nontoxicity, and ease of application. Iron–cata-lyzed cross-coupling reactions of aryl halides with nitrogen, oxygen, and sulfur nucleophiles resulted in the formation of C–N, C–O, and C–S bonds, respectively.<sup>38–42</sup> Finally, as part of our ongoing research on the synthesis and applications of graphene nanocomposites,<sup>43</sup> herein we disclose an efficient method for the preparation of symmetrical diaryl diselenides and ditellurides over graphene oxide supported nano-Fe<sub>3</sub>O<sub>4</sub> catalyst (nano-Fe<sub>3</sub>O<sub>4</sub>@GO). To the best of our knowledge, this is the first report of C–Se and C–Te bond formation via iron–catalyzed cross–coupling of Se(0) or Te(0) with aryl iodides to give symmetrical diorgano dichalcoganides. Also, the catalytic activity of nano-Fe<sub>3</sub>O<sub>4</sub>@GO is compared and contrasted to that of pristine Fe<sub>3</sub>O<sub>4</sub> MPs demonstrating the significance of catalyst design. While both catalysts enjoy rather easier workups, nano-Fe<sub>3</sub>O<sub>4</sub>@GO affords higher yields with shorter reaction times (Figure 1).



Figure 1

We find a conspicuous superiority of nano-Fe<sub>3</sub>O<sub>4</sub>@GO over pristine Fe<sub>3</sub>O<sub>4</sub> nanoparticles through their catalytic synthesis of diselenides and ditellurides; higher yields and considerably shorter reaction times were encountered using nano-Fe<sub>3</sub>O<sub>4</sub>@GO (Figure 1, Table 1). Such catalytic activities appear to be related to the microstructures, dispersity, morphology, and magnetic properties of pristine and graphene oxide supported Fe<sub>3</sub>O<sub>4</sub> nanoparticles, as indicated by FT-IR, X-ray diffraction (XRD), transmission electron spectroscopy (TEM), and vibrating sample magnetometer (VSM) analyses.

The infra red spectra of the synthesized graphene oxide, nano-Fe<sub>3</sub>O<sub>4</sub>, and nano-Fe<sub>3</sub>O<sub>4</sub>@GO appear consistent with their structures (see the Supporting Information, Figure S1). In the graphene oxide spectrum, the peak at 1731 cm<sup>-1</sup> corresponds to the stretching band of C=O in carboxylic acid or carbonyl moieties. The intense bands at 3432 and 1253 cm<sup>-1</sup> are attributed to stretching and bending, respectively, of O-H. The peak at 1620 cm<sup>-1</sup> (aromatic C=C) could be assigned to the skeletal vibrations of unoxidized graphitic domains of graphene oxide.44 In the infrared spectrum of pristine nano-Fe<sub>3</sub>O<sub>4</sub>, we encountered a peak at 584 cm<sup>-1</sup> for the Fe–O vibration, while the absorption at 3440 cm<sup>-1</sup> is attributed to the O–H stretching vibrations of the adsorbed moisture on the surface of nano-Fe<sub>3</sub>O<sub>4</sub>.<sup>45</sup> The FT-IR spectrum of nano-Fe<sub>3</sub>O<sub>4</sub>@GO shows both the Fe–O (around 578 cm<sup>-1</sup>) and graphene absorptions, confirming the existence of Fe<sub>3</sub>O<sub>4</sub> in this nanohybrid, yet this spectrum differs from those of graphene oxide and pristine nano-Fe<sub>3</sub>O<sub>4</sub> by the anticipated broadening and weakening of the composite absorptions, indicating that nano-Fe<sub>3</sub>O<sub>4</sub> is coordinated to graphene oxide.<sup>46</sup> XRD of the synthesized nano-Fe<sub>3</sub>O<sub>4</sub>@GO is comparable to that of pristine nano-Fe<sub>3</sub>O<sub>4</sub> indexing to (220), (311), (400), (422), (511), and (440) planes of a cubic unit cell of magnetite, and appearing at 30.07°, 35.53°, 43.41°, 53.51°, 57.19°, and 62.73°, respectively (Supporting Information, Figure S2). The structural properties of nano- $Fe_3O_4$ , even after their loading on the surface of graphene oxide, are not changed and the nanocomposite retains its crystallinity. TEM of pristine nano-Fe<sub>3</sub>O<sub>4</sub> shows agglomeration of nanoparticles induced by their inherent magnetism. These magnetic forces are overcome by grafting the nanoparticles onto the surface of graphene oxide, making the TEM of our hybrid sample show nearly spherical nano-Fe<sub>3</sub>O<sub>4</sub> that are homogeneously distributed over the graphene oxide sheets (Figure 2). Hence, better dispersion of nano-Fe<sub>3</sub>O<sub>4</sub> on graphene oxide improves the catalytic activity of nano-Fe<sub>3</sub>O<sub>4</sub>@GO.



Figure 2 TEM images of (a) nano-Fe $_3O_4$  and (b) nano-Fe $_3O_4@GO$  hybrid nanoparticles.

More specifically, the magnetization value of nano-Fe<sub>3</sub>O<sub>4</sub> and nano-Fe<sub>3</sub>O<sub>4</sub>@GO are 60.0 and 21.0 emu/g at 25 °C, respectively (Figure 3). Evidently, the smaller magnetization of our nanohybrid catalyst than pristine Fe<sub>3</sub>O<sub>4</sub> nanoparticles is due to the dispersion of the Fe<sub>3</sub>O<sub>4</sub> nanoparticles on the surface of graphene oxide.



Figure 3 Magnetization curves for pristine nano-Fe $_3O_4$  and nano-Fe $_3O_4$ @GO hybrid

In the first set of experiments, the activity of our synthesized nanocatalysts was compared and contrasted under the same reaction conditions, employing iodobenzene (1a) as a representative halide, elemental selenium (2.0 equiv), and KOH (2.0 equiv) in dimethyl sulfoxide (2.0 mL), monitoring formation of the corresponding diphenyl diselenide (2a) (Table 1). Our results indicate that nano-Fe<sub>3</sub>O<sub>4</sub>@GO (7 mol%) gives diphenyl diselenide in 50% yield after two hours, and the reaction is complete after four hours (98%), and extending the reaction time to 24 hours has no influence on the product yield. In contrast, pristine nano-Fe<sub>3</sub>O<sub>4</sub> (10 mol%) gives no product after four hours, but after eight hours diphenyl diselenide (2a) is produced in 40%, and a maximum yield of 63% is obtained after 24 hours. Similar results are obtained with replacing Se with Te, where nano-Fe<sub>3</sub>O<sub>4</sub>@GO (7 mol%) gives diphenyl ditelluride in 96% yield after four hours, but in the presence of pristine nano-Fe<sub>3</sub>O<sub>4</sub> (10 mol%), diphenyl ditelluride is obtained in a maximum yield of 60% after 24 hours.

 
 Table 1
 Optimization of Time and Comparison between Catalytic
 Activities of Prepared Nanocatalysts

Ph–I + Se <sup>0</sup>	DMSO, KOH	DMSO, KOH, 90 °C				
1a		2a				
Entry	Time (h)	Yield <sup>a</sup> (%)				
		Nano-Fe <sub>3</sub> O <sub>4</sub> @GO (7 mol%)	Nano-Fe <sub>3</sub> O <sub>4</sub> (10 mol%)			
1	1	-	_			
2	2	50	-			
3	3	84	_			
4	4	98	-			
5	8	98	40			
6	24	98	63			

<sup>a</sup> Isolated vield.

Table 2 Optimization of Solvent and Catalyst Amount

Ph–I + Se <sup>0</sup> –	KOH, 4 h, 90 °C	Ph-Se-Se-Ph	
1a		2a	
Entry	Solvent	Nano-Fe <sub>3</sub> O <sub>4</sub> @GO (mol%)	Yield <sup>a</sup> (%)
1	DMSO	0.0	_
2	DMSO	1.5	75
3	DMSO	3.5	92
4	DMSO	7	98
5	DMSO	15	98
6	DMF	7	87
7	MeCN	7	81
8	toluene	7	-
9	THF	7	_

<sup>a</sup> Isolated yield.

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In addition, we have shown the impact of the amount of catalyst (nano-Fe<sub>3</sub>O<sub>4</sub>@GO) (Table 2, entries 1–5) and different solvents (entries 6-9) on the product yield. No product is observed in the absence of the catalyst (entry 1). When the amount of nano-Fe<sub>3</sub>O<sub>4</sub>(a)GO is increased from 1.5 to 7 mol%, the yield of diphenyl diselenide (2a) rises from 75% to 98% (entries 2-4). Increasing the amount of catalyst to 15 mol% does not show a significant influence, affording the desired product with the same yield (98%, entry 5). The desired product is not obtained in toluene or tetrahydrofuran (entries 8 and 9). However, the reaction is highly facilitated by polar aprotic solvents among them, dimethyl sulfoxide is the most efficient solvent for this reaction affording the best yield for preparation of diphenyl diselenide (2a) (entry 4). These results are consistent with a previous report<sup>34</sup> and suggest that the success of the reaction depends on the polarity of the solvent.

In order to explore the scope and limitations of this methodology, a series of aryl and heteroaryl halides 1 were examined in the synthesis of symmetrical diselenides 2a-i and ditellurides **3a–h**, under standard conditions (Table 3).

Table 3 Synthesis of Diselenides and Ditellurides via a One-Pot Counling Reaction Procedure

couping	Siteaet					
R–X + 1	R–X + E <sup>0</sup> — 1		DMSO, KOH, 4 h, 90 °C		R–E–E–R 2 E = Se 3 E = Te	
Entry	R		Х	Е	Product	Yield <sup>a</sup> (%)
1	Ph		IBrCl	Se	2a 2a 2a	98 73 60
2	4-N	∕leC <sub>6</sub> H₄	Ι	Se	2b	95
3	4-N	AeOC <sub>6</sub> H <sub>4</sub>	Ι	Se	2c	98
4	3-N	AeOC <sub>6</sub> H <sub>4</sub>	Ι	Se	2d	85
5	4-0	D <sub>2</sub> NC <sub>6</sub> H <sub>4</sub>	Ι	Se	2e	96
6	4-0	ClC <sub>6</sub> H <sub>4</sub>	Ι	Se	2f	78
7	4-E	BrC <sub>6</sub> H <sub>4</sub>	Ι	Se	2g	84
8	4-H	$\mathrm{IOCC}_{6}\mathrm{H}_{4}$	Ι	Se	2h	93
9	2-tl	nienyl	Ι	Se	2i	90
10	Ph		Ι	Te	<b>3</b> a	96
11	4-N	AeC <sub>6</sub> H <sub>4</sub>	Ι	Te	3b	96
12	4-N	AeOC <sub>6</sub> H <sub>4</sub>	Ι	Te	3c	98
13	4-0	D <sub>2</sub> NC <sub>6</sub> H <sub>4</sub>	Ι	Te	3d	95
14	4-0	ClC <sub>6</sub> H <sub>4</sub>	Ι	Te	3e	75
15	4-E	BrC <sub>6</sub> H <sub>4</sub>	Ι	Te	3f	78
16	4 <b>-</b> F	$IOCC_6H_4$	Ι	Те	3g	95
17	2-tl	nienvl	I	Те	3h	87

<sup>a</sup> Isolated yield.

As anticipated, iodides are more reactive than bromides and chlorides. In addition, both electron-rich and electrondeficient aryl iodides are effective in the synthesis of the corresponding products in good to excellent yields. An improvement associated with this methodology is that a wide range of functional groups are tolerated in this process, including: methyl, methoxy, aldehyde, nitro, bromo, and heteroaryl moieties. These results allow for the exploration of the regioselectivity of the reaction, with the preparation of selective bromo and chloro dichalcogenides (Table 3, entries 6, 7, 15, and 16).

Finally, the catalytic activity and the ability to recycle and reuse our nano-Fe<sub>3</sub>O<sub>4</sub>@GO were studied. The catalyst was separated by an external magnet and it was reused in subsequent experiments under similar reaction conditions. Yields of the product decreased only slightly after four trials (Table 4).

 Table 4
 Reusability of Nano-Fe<sub>3</sub>O<sub>4</sub>@GO Catalyst

Run	Yield (%)	Recovery of nano-Fe <sub>3</sub> O <sub>4</sub> @GO
1	98	99
2	98	99
3	95	99
4	91	99

In conclusion, an interesting methodology has been developed for synthesis of synthetically and biologically important dichalcogenides in a recyclable, catalytic protocol. For the first time, pristine nano-Fe<sub>3</sub>O<sub>4</sub>, and graphene oxide based nano-Fe<sub>3</sub>O<sub>4</sub> (nano-Fe<sub>3</sub>O<sub>4</sub>@GO) are employed as magnetic heterogeneous catalysts, in syntheses of diselenides and ditellurides, using elemental Se(0) or Te(0) and aryl iodides. Although diaryl monoselenides and monotellurides are often formed in such coupling reactions in the presence of a copper catalyst,<sup>32,33,36</sup> surprisingly our catalyst synthesized diaryl diselenides and ditellurides as the sole product of this reaction. While both catalysts enjoy rather easier workups, nano-Fe<sub>3</sub>O<sub>4</sub>@GO affords higher yields with shorter reaction times.

Natural flake graphite was provided by Qingdao Dingding Graphite Products Factory. FeCl<sub>3</sub>·6 H<sub>2</sub>O, and FeCl<sub>2</sub>·4 H<sub>2</sub>O (Aldrich, 98%), deionized H<sub>2</sub>O, and NH<sub>4</sub>OH (Merck, 25%) were employed to produce Fe<sub>3</sub>O<sub>4</sub> nanoparticles (NPs). KMnO<sub>4</sub>, H<sub>2</sub>SO<sub>4</sub> (98%), and H<sub>2</sub>O<sub>2</sub> (30%) were purchased from Aldrich Co. Other reagents and solvents used in this work were obtained from Fluka or Merck and they were used without further purification.

FT-IR spectra were recorded using KBr pellets with a Thermo Spectrometer. Samples were characterized by X-ray diffraction (XRD; Philips Xpert MPD, Cu K $\alpha$  irradiation,  $\lambda = 1.5418$  Å). In addition, transmission electron microscopy (TEM; Philips, EM208S, Netherlands, at 100 kV of acceleration voltage) was employed to observe the morphology of nano-Fe<sub>3</sub>O<sub>4</sub>@GO hybrids and Fe<sub>3</sub>O<sub>4</sub> NPs. The magnetic properties of nano-Fe<sub>3</sub>O<sub>4</sub>@GO nanocomposite and magnetite nanoparticles were compared as a function of the applied magnetic field H using a LDJ 9600 Vibrating Sample Magne-

tometer (VSM) with a maximum applied magnetic field of 6 kOe. The hysteresis of the magnetization was obtained by varying H between +8000 and -8000 Oe at 300 K. The <sup>1</sup>H and <sup>13</sup>C spectra were measured at 500.1, and 125.7 MHz, respectively, on a Bruker DRX 500-Avance FT-NMR instrument with CDCl<sub>3</sub> as the solvent. Mass spectra were recorded on Agilent Model: Agilent 5975 instrument. Elemental analyses were performed using Perkin Elmer 2400 Series Elemental Analyzer.

#### Nano-Fe<sub>3</sub>O<sub>4</sub>@GO

Nano-Fe<sub>3</sub>O<sub>4</sub>@GO was synthesized via a previously reported twostep method.<sup>43</sup> Graphene oxide (GO) was prepared from purified natural graphite using modified Hummer's method where graphite was treated with H<sub>2</sub>SO<sub>4</sub> and KMnO<sub>4</sub>.<sup>47</sup> Then uniform coatings of Fe<sub>3</sub>O<sub>4</sub> NPs on GO were obtained by co-precipitation of FeCl<sub>3</sub>·6 H<sub>2</sub>O and FeCl<sub>2</sub>·4 H<sub>2</sub>O (2:1 molar ratio), in the presence of GO, giving nano-Fe<sub>3</sub>O<sub>4</sub>@GO. Specifically, GO (40 mg) in H<sub>2</sub>O (40 mL) was sonicated for 30 min, to which a soln of FeCl<sub>3</sub> (800 mg) and FeCl<sub>2</sub> (300 mg) in deionized H<sub>2</sub>O (50 mL) was added at r.t. The soln temperature was raised to 85 °C. At this point, the pH was increased to 10 by addition of 30% NH<sub>3</sub> soln. After stirring rapidly for 45 min, the resulting black precipitate was centrifuged at 4000 rpm for 15 min and washed with deionized H<sub>2</sub>O (3 ×) and finally dried at 60 °C, where a uniform thin leaf formed over the watch glass. For comparison, unsupported Fe<sub>3</sub>O<sub>4</sub> NPs were prepared using the same procedure in the absence of GO.

#### **Diselenides 2 and Ditellurides 3; General Procedure**

Se(0) (1.0 mmol) in anhyd DMSO (2.0 mL) and KOH (2.0 equiv) was added to a stirred soln of aryl halide (1.0 mmol) and nano- $Fe_3O_4$ @GO (or  $Fe_3O_4$  NPs), at 90 °C (TLC monitoring). When the reaction was complete, the contents of the flask were allowed to cool, and EtOAc–H<sub>2</sub>O (1:1) were added and the organic layer was washed and separated. The aqueous layer was further washed with a further portion of EtOAc (10 mL), and the combined organic extracts were dried (anhyd MgSO<sub>4</sub>). The solvent and volatiles were completely removed under vacuum to give the crude product, which was subjected to column chromatography rendering diaryl diselenides. <sup>1</sup>H and <sup>13</sup>C NMR spectra of different diselenides appeared are given that are consistent with those of the authentic samples. Ditellurides were synthesized analogously starting from Te(0).

#### **Diphenyl Diselenide** (2a)<sup>37</sup>

Orange solid; yield: 154 mg (98%); mp 58-60 °C.

IR (KBr): 3049, 1562, 1448, 723 cm<sup>-1</sup>.

<sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>):  $\delta$  = 7.29–7.21 (m, 3 H), 7.60–7.56 (m, 2 H).

<sup>13</sup>C NMR (125 MHz, CDCl<sub>3</sub>): δ = 127.7, 129.3, 131.6, 133.0.

#### Di-p-tolyl Diselenide (2b)37

Pale yellow oil; yield: 162 mg (95%).

IR (KBr): 2923, 1624, 1391, 792 cm<sup>-1</sup>.

<sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>):  $\delta$  = 2.34 (s, 3 H), 7.09 (d, *J* = 8.4 Hz, 2 H), 7.50 (d, *J* = 8.4 Hz, 2 H).

<sup>13</sup>C NMR (125 MHz, CDCl<sub>3</sub>): δ = 22.7, 127.7, 130.9, 133.4, 138.0.

**Bis(4-methoxyphenyl)** Diselenide (2c)<sup>37</sup>

Yellow solid; yield: 183 mg (98%); mp 135–137 °C.

IR (KBr): 2930, 1586, 1289, 818 cm<sup>-1</sup>.

<sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>):  $\delta$  = 3.82 (s, 3 H), 6.76 (d, *J* = 8.7 Hz, 2 H), 7.53 (d, *J* = 8.7 Hz, 2 H).

<sup>13</sup>C NMR (125 MHz, CDCl<sub>3</sub>):  $\delta$  = 55.3, 114.9, 122.3, 136.1, 160.3.

**Bis(3-methoxyphenyl) Diselenide (2d)**<sup>37</sup> Pale yellow oil; yield: 159 mg (85%).

IR (KBr): 2927, 1581, 1280, 912 cm<sup>-1</sup>.

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<sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>):  $\delta$  = 3.78 (s, 3 H), 6.79–6.76 (m, 1 H), 7.26–7.16 (m, 3 H). <sup>13</sup>C NMR (125 MHz, CDCl<sub>3</sub>):  $\delta$  = 55.3, 113.9, 116.7, 123.5, 129.8, 130.9, 159.9.

**Bis(4-nitrophenyl) Diselenide (2e)**<sup>37</sup> Brownish-orange solid; yield: 194 mg (96%); mp 124–126 °C. IR (KBr): 3079, 1503, 1334, 837 cm<sup>-1</sup>. <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>):  $\delta$  = 7.64 (d, *J* = 8.6 Hz, 2 H), 8.19 (d,

J = 8.6 Hz, 2 H). <sup>13</sup>C NMR (125 MHz, CDCl<sub>3</sub>):  $\delta = 124.3, 130.5, 138.9, 147.6$ .

**Bis(4-chlorophenyl)** Diselenide (2f)<sup>37</sup> Orange oil; yield: 149 mg (78%).

IR (KBr): 3070, 1451, 1013, 821 cm<sup>-1</sup>. <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>):  $\delta$  = 7.25 (d, *J* = 8.4 Hz, 2 H), 7.50 (d, *J* = 8.4 Hz, 2 H). <sup>13</sup>C NMR (125 MHz, CDCl<sub>3</sub>):  $\delta$  = 128.8, 129.4, 133.3, 134.3.

#### Bis(4-bromophenyl) Diselenide (2g)<sup>37</sup>

Dark orange oil; yield: 197 mg (84%).

IR (KBr): 3037, 1473, 1004, 817 cm<sup>-1</sup>. <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>):  $\delta$  = 7.59–7.40 (m, 4 H). <sup>13</sup>C NMR (125 MHz, CDCl<sub>3</sub>):  $\delta$  = 122.4, 132.3, 133.4, 134.6.

#### **4,4'-Diselanediyldibenzaldehyde (2h)**<sup>37</sup> Brown oil; yield: 172 mg (93%).

IR (KBr): 3479, 1656, 1134, 837 cm<sup>-1</sup>.

<sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>):  $\delta$  = 7.33 (d, *J* = 8.4 Hz, 2 H), 7.54 (d, *J* = 8.4 Hz, 2 H), 9.75 (s, 1 H). <sup>13</sup>C NMR (125 MHz, CDCl<sub>3</sub>):  $\delta$  = 124.4, 126.5, 132.0, 136.7, 191.1.

#### Dithiophen-2-yl Diselenide (2i)

Dark orange oil; yield: 147 mg (90%).

IR (KBr): 3479, 1533, 1104, 771 cm<sup>-1</sup>.

<sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>):  $\delta$  = 6.87 (m, 1 H), 7.09 (m, 1 H), 7.31 (m, 1 H).

<sup>13</sup>C NMR (125 MHz, CDCl<sub>3</sub>):  $\delta$  = 128.0, 131.4, 134.7, 135.3.

MS: *m/z* (%) = 57 (20), 69 (29), 82 (30), 91 (100), 165 (23), 211 (9), 245 (30), 279 (7), 326 (M<sup>+</sup>, 18).

Anal. Calcd for  $C_8H_6S_2Se_2$ : C, 29.64; H, 1.87. Found: C, 29.93; H, 1.91.

#### **Diphenyl Ditelluride (3a)**<sup>37</sup>

Yellow oil; yield: 199 mg (96%).

IR (KBr): 3055, 1569, 1467, 732 cm<sup>-1</sup>.

<sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>):  $\delta$  = 7.24–7.20 (m, 3 H), 7.75–7.69 (m, 2 H).

<sup>13</sup>C NMR (125 MHz, CDCl<sub>3</sub>): δ = 114.0, 127.8, 129.6, 138.0.

#### **Di-***p***-tolyl Ditelluride (3b)**<sup>37</sup>

Yellow oil; yield: 212 mg (96%).

IR (KBr): 2971, 1824, 1459, 792 cm<sup>-1</sup>.

<sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>):  $\delta$  = 2.37 (s, 3 H), 7.03 (d, *J* = 7.8 Hz, 2 H), 7.59 (d, *J* = 7.8 Hz, 2 H).

<sup>13</sup>C NMR (125 MHz, CDCl<sub>3</sub>):  $\delta$  = 21.3, 110.7, 130.5, 138.1, 141.0.

#### Bis(4-methoxyphenyl) Ditelluride (3c)<sup>37</sup>

Orange oil; yield: 232 mg (98%). IR (KBr): 3027, 1456, 1283, 808 cm<sup>-1</sup>. <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>):  $\delta$  = 3.72 (s, 3 H), 6.80 (d, *J* = 8.8 Hz, 2 H), 7.71 (d, *J* = 8.8 Hz, 2 H). <sup>13</sup>C NMR (125 MHz, CDCl<sub>3</sub>):  $\delta$  = 55.2, 111.4, 127.4, 135.2, 161.3.

**Bis(4-nitrophenyl)** Ditelluride (3d)<sup>37</sup>

Brownish-orange oil; yield: 240 mg (95%).

IR (KBr): 3023, 1511, 1321, 817 cm<sup>-1</sup>.

<sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>):  $\delta$  = 8.41 (d, *J* = 8.7 Hz, 2 H), 8.85 (d, *J* = 8.7 Hz, 2 H). <sup>13</sup>C NMR (125 MHz, CDCl<sub>3</sub>):  $\delta$  = 114.8, 124.6, 131.8, 153.3.

## **Bis(4-chlorophenyl) Ditelluride (3e)**<sup>37</sup> Dark orange oil; yield: 180 mg (75%).

IR (KBr): 3075, 1466, 1008, 721 cm<sup>-1</sup>. <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>):  $\delta$  = 7.17 (d, *J* = 8.4 Hz, 2 H), 7.60 (d, *J* = 8.4 Hz, 2 H). <sup>13</sup>C NMR (125 MHz, CDCl<sub>3</sub>):  $\delta$  = 112.1, 129.9, 134.7, 139.4.

#### **Bis(4-bromophenyl) Ditelluride (3f)**<sup>37</sup>

Dark orange oil; yield: 222 mg (78%).

IR (KBr): 3043, 1464, 1020, 791 cm<sup>-1</sup>. <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>):  $\delta$  = 7.53 (d, *J* = 8.3 Hz, 2 H), 7.53 (d, *J* = 8.3 Hz, 2 H). <sup>13</sup>C NMR (125 MHz, CDCl<sub>3</sub>):  $\delta$  = 112.7, 122.9, 132.8, 139.6.

### **4,4'-Ditellanediyldibenzaldehyde (3g)**<sup>37</sup> Dark brown oil; yield: 223 mg (95%).

IR (KBr): 3454, 1663, 1113, 816 cm<sup>-1</sup>.

<sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>):  $\delta$  = 7.61 (d, *J* = 8.4 Hz, 2 H), 7.84 (d, *J* = 8.4 Hz, 2 H), 9.81 (s, 1 H). <sup>13</sup>C NMR (125 MHz, CDCl<sub>3</sub>):  $\delta$  = 119.4, 129.8, 131.1, 138.2.

#### Dithiophen-2-yl Ditelluride (3h)

Dark orange oil; yield: 185 mg (87%).

IR (KBr): 3423, 1503, 1085, 737 cm<sup>-1</sup>.

<sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>):  $\delta$  = 6.94 (m, 1 H), 7.46–7.42 (m, 2 H). <sup>13</sup>C NMR (125 MHz, CDCl<sub>3</sub>):  $\delta$  = 114.4, 128.8, 130.9, 133.9.

MS: *m/z* (%) = 57 (60), 82 (100), 119 (51), 149 (62), 166 (98), 197 (32), 245 (97), 408 (29), 426 (M<sup>+</sup>, 2).

Anal. Calcd for  $C_8H_6S_2Te_2$ : C, 22.80; H, 1.43. Found: C, 22.96; H, 1.52.

**Supporting Information** for this article is available online at http://www.thieme-connect.com/ejournals/toc/synthesis.

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