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# Copper-catalyzed direct C–H arylselenation of 4-nitro-pyrazoles and other heterocycles with selenium powder and aryl iodides. Access to unsymmetrical heteroaryl selenides†

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A one-pot, Cu-catalyzed direct C–H arylselenation protocol using elemental Se and aryl iodides was developed for nitro-substituted, *N*-alkylated pyrazoles, imidazoles and other heterocycles including 4*H*-chromen-4-one. This general and concise method allows one to obtain a large number of unsymmetrical heteroaryl selenides bearing a variety of substituents. The presence of the nitro group was confirmed to be essential for the C–H activation and can also be used for further functionalisation and manipulation. Several examples of heteroannulated benzoselenazines were also synthesized using the developed synthetic protocol.

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## Introduction

Organoselenium compounds have been known for many years to have biological activity that can be useful in medicine.<sup>1</sup> Their therapeutic properties include antitumor,<sup>2</sup> antioxidant,<sup>3,4</sup> anti-inflammatory, antiviral, antimicrobial and neuroprotective action.<sup>5</sup> Among these, the antioxidant effect seems to be the most important mode of action recognized for organoselenium therapeutics as the oxidative stress is a symptom and often the cause of many diseases. Mammalian organisms are equipped with glutathione peroxidases (GPx)<sup>6,7</sup> – a family of antioxidant enzymes that naturally contain selenium in their active site in the form of a selenocysteine<sup>8</sup> (Sec) residue. One of the most thoroughly studied synthetic drugs that demonstrates the so called GPx-like activity<sup>9</sup> – ebselen, is often considered a comparative standard when investigating other organoselenium drug candidates.<sup>10–12</sup>

Diorganyl selenides receive much attention, both due to their biological activity<sup>13–17</sup> and their value in synthetic chemistry.<sup>18–24</sup> Non-cyclic diorganyl selenides can be grouped, according to the structure of the organyl substituents, as symmetrical and unsymmetrical compounds. This nominal

division, present in the literature comes from the varying difficulty and complexity of the synthetic methodology. In a historical context, sodium or potassium selenides (Na<sub>2</sub>Se, K<sub>2</sub>Se) or polyselenides (Na<sub>2</sub>Se<sub>x</sub> or K<sub>2</sub>Se<sub>x</sub>) can be reacted with bromides to yield symmetrical dialkyl selenides<sup>25–27</sup> or with arenediazonium salts to prepare symmetrical diaryl selenides.<sup>28–34</sup> In a more modern context, TM-catalyzed cross-coupling reactions are one of the most common methods for the preparation of aryl chalcogenides.<sup>35</sup> Particularly, copper-catalyzed methods utilizing: elemental selenium with aryl halides,<sup>36–38</sup> potassium selenocyanates with aryl halides,<sup>39,40</sup> triarylbismuthanes with elemental selenium<sup>41</sup> or boronic acids with diaryl diselenides,<sup>42</sup> elemental selenium<sup>43</sup> or selenourea<sup>44</sup> – can be applied. Some of these methods yield also diselenides as by- or main-products, depending on the reaction conditions. Unsymmetrical diaryl selenides can be obtained by similar methods from elemental selenium,<sup>36,38</sup> diselenides<sup>45–48</sup> and selenols<sup>49,50</sup> as a selenium source. Additionally, two other methods have been developed. Nucleophilic substitution of bromine in PhSeBr by mild nucleophiles (arylbionic acids, arylsiloxanes, and arylstannanes) catalyzed by alumina-supported copper catalyst<sup>51</sup> and a transition metal-free, base promoted reaction of arylhydrazines with diaryl diselenides.<sup>52</sup>

Unsymmetrical aryl-Se-heteroaryl compounds represent yet another advanced challenge as synthetic targets. Structures bearing pyridine and thiophen moieties at selenium are available by previously mentioned methods from diselenides.<sup>53–55</sup> Special attention should be paid to those reagents in the context of unsymmetrical heteroaryl selenides' synthesis. In a recent review, Arsenyan summarizes the progress in this matter, listing

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all the possible synthetic pathways to obtain aryl-Se-heteroaryl compounds (bearing a variety of pharmacophores) from diaryl diselenides.<sup>56</sup> These transformations include nucleophilic and electrophilic reactions (synthons  $RSe^+$  and  $RSe^-$ ), reactions involving radicals ( $RSe^\cdot$ ), copper catalysis, single electron transfer (SET) reactions (photochemical reactions) and direct heteroaryl selenation of activated  $C(sp^2)$ -H bond.

The C-H bond is the most widespread structural fragment in organic chemistry, and its functionalization has been the subject of intensive studies.<sup>67-71</sup> In recent years, TM-catalyzed C-H activation reactions emerged as one of the most important methodologies in modern organic chemistry. This applies also to selenation. The TM-catalyzed direct arylselenation of C-H bonds is one of the most efficient methods for the synthesis of unsymmetrical diaryl selenides. The to-date developed protocols involve the use of diselenides (palladium,<sup>63</sup> rhodium,<sup>72</sup> ruthenium<sup>64,73</sup> iron oxide,<sup>74</sup> silver,<sup>75,76</sup> and copper<sup>65,66,77</sup> catalyzed) or  $ArSeCl$  (ruthenium<sup>78</sup> catalyzed) as selenium source. There are also a few very recent examples of copper-catalyzed one-pot three-component procedures involving Se powder, which can be considered an obvious step in methodology development, since diselenides are easily obtained from aryl iodides and selenium powder in similar catalytic conditions.<sup>37</sup>

Wu *et al.* obtained a library of (phenylseleno)-1H-indoles selecting CuO as the best catalyst.<sup>61</sup> Their protocol is also suitable for the formation of an intramolecular C-Se-C bond. The authors pointed out that the free NH group of the indol was critical as the *N*-substituted starting materials did not undergo arylselenation in selected conditions. However, Guo *et al.* showed that also *N*-substituted indoles can undergo C-H arylselenation in specific conditions.<sup>59</sup> In the same paper, the authors revisit the selenation of imidazo[1,2-*a*]pyridines, previously submitted to reaction with 4-coumarinyl triflates.<sup>60</sup> 2-(2-Bromophenyl)imidazo[1,2-*a*]pyridines were also explored as starting materials in an intramolecular variant of the reaction by Wang *et al.*<sup>58</sup> In another paper, Wu *et al.* proposed conditions for C-H arylselenation of 2-phenyl- and 2-aryl-1,3,4-oxadiazoles,<sup>62</sup> a scaffold found in many drugs.<sup>79</sup> Slightly different conditions for the same starting materials were also selected by Braga *et al.*<sup>57</sup>

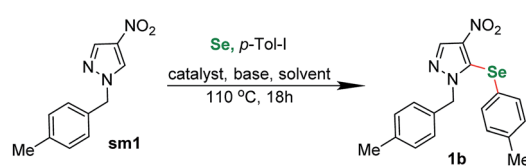
Since we have our long-standing interest in TM-catalyzed C-H activation, we were curious if a general, practical and concise approach could be realized for the arylselenation of other heterocycles – widening the scope of the starting materials. The regioselectivity of C-H activation reactions of more complex functionalized substrates containing two or more

reactive C-H bonds is an important topic of current research.<sup>67-71,80-90</sup> The regioselectivity of such reactions is controlled by the presence of functional groups in the substrate. This includes directing substituents (carbonyl, cyano, *etc.*),<sup>80-83,85,88-90</sup> halogen substituents (mostly fluorine or chlorine),<sup>80-83,85,88-93</sup> and ring heteroatoms (namely – sulfur, nitrogen, and oxygen). The use of the nitro group as a regio-directing substituent in C-H activations has been investigated previously<sup>94,95</sup> also by our group in the context of arylation of nitro-pyrazoles,<sup>96</sup> nitro-imidazoles<sup>97</sup> and other nitro-heteroarenes.<sup>98</sup> Herein we describe a one-pot method to obtain unsymmetrical diorganyl selenides from C-H activated heterocycles (including nitro-substituted), aryl iodides and elemental selenium powder.

## Results and discussion

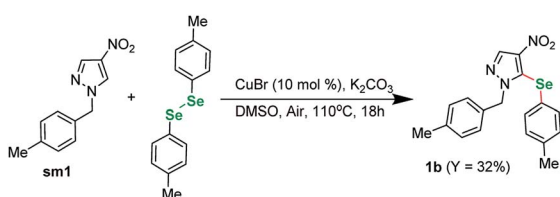
In order to confirm the validity of the literature protocols we started our investigations by performing a test reaction

Table 1 Optimization of the reaction conditions<sup>a</sup>



Entry	Catalyst	Base	Solvent	Yield%	Ref.
1	CuBr	K <sub>2</sub> CO <sub>3</sub>	DMSO	38	
2	CuI	KHCO <sub>3</sub>	DMSO	23	57
3	CuI	None	DMF	NR	58
4	Cu(OAc) <sub>2</sub>	KOH	DMF	30 <sup>b</sup>	59
5	CuO	None	DMF	NR	60
6	CuO	Na <sub>3</sub> PO <sub>4</sub> · 12H <sub>2</sub> O	DMSO	46 <sup>c</sup>	61
7	CuCl <sub>2</sub>	Na <sub>2</sub> CO <sub>3</sub>	DMF	39 <sup>c</sup>	62
8	CuI	K <sub>2</sub> CO <sub>3</sub>	DMSO	14 <sup>c</sup>	37
9	Pd(OAc) <sub>2</sub>	K <sub>2</sub> CO <sub>3</sub>	DMSO	51 <sup>c</sup>	63
10	PdCl <sub>2</sub> (PPh <sub>3</sub> ) <sub>2</sub>	K <sub>2</sub> CO <sub>3</sub>	DMSO	55 <sup>c</sup>	
11	[Ru( <i>p</i> -cymene)Cl <sub>2</sub> ] <sub>2</sub>	K <sub>2</sub> CO <sub>3</sub>	DCE	27	64
12	CuI	None	DMSO	NR	65
13	CuO	K <sub>2</sub> CO <sub>3</sub>	DMF	43 <sup>c</sup>	66
14	CuBr <sub>2</sub>	K <sub>2</sub> CO <sub>3</sub>	DMF	45 <sup>c</sup>	66
15	CuBr <sub>2</sub>	K <sub>2</sub> CO <sub>3</sub>	DMA	40 <sup>c</sup>	
16	CuBr <sub>2</sub>	K <sub>2</sub> CO <sub>3</sub>	Toluene	9 <sup>c</sup>	
17	CuBr <sub>2</sub>	K <sub>2</sub> CO <sub>3</sub>	DMSO	74 <sup>c</sup>	
18	<b>CuBr<sub>2</sub></b>	<b>K<sub>2</sub>CO<sub>3</sub></b>	<b>DMSO</b>	<b>83</b>	
19	CuCl <sub>2</sub>	K <sub>2</sub> CO <sub>3</sub>	DMSO	63	
20	CuBr <sub>2</sub>	KOH	DMSO	70	
21	NiCl <sub>2</sub> (PPh <sub>3</sub> ) <sub>2</sub>	K <sub>2</sub> CO <sub>3</sub>	DMSO	Trace <sup>c</sup>	
22	ReOCl <sub>3</sub> (PPh <sub>3</sub> ) <sub>2</sub>	K <sub>2</sub> CO <sub>3</sub>	DMSO	15 <sup>c</sup>	
23	Co(OAc) <sub>2</sub>	K <sub>2</sub> CO <sub>3</sub>	DMSO	10 <sup>c</sup>	
24	FeCl <sub>2</sub>	K <sub>2</sub> CO <sub>3</sub>	DMSO	9 <sup>c</sup>	
25	AgOAc	K <sub>2</sub> CO <sub>3</sub>	DMSO	12 <sup>c</sup>	
26	PtCl <sub>2</sub> (bpy)	K <sub>2</sub> CO <sub>3</sub>	DMSO	29 <sup>c</sup>	

<sup>a</sup> Reaction conditions unless specified otherwise: 1 equiv. **sm1**, 2 equiv. aryl iodide, 3 equiv. selenium powder (100 mesh), 4 equiv. base, catalyst (10 mol%), 1 mL dry solvent. Performed in a Teflon screw cap-sealed pressure tube. <sup>b</sup> Ligand added – Phen (10 mol%). <sup>c</sup> Reaction loaded in glovebox under argon.



Scheme 1 Test reaction for 4-nitro-1H-pyrazole derivative.



Table 2 Scope of the pyrazole substrates vs. aryl iodides<sup>a</sup>

Entry	Structure	R=	Number	Time/h	Temp./°C	Yield/%
1		<i>m</i> -Me	<b>1a</b>	24	115	77
2		<i>p</i> -Me	<b>1b</b>	25	115	83
3		<i>p</i> -Et	<b>1c</b>	24	115	85
4		<i>m</i> -CF <sub>3</sub>	<b>1d</b>	26	115	80
5		<i>p</i> -CF <sub>3</sub>	<b>1e</b>	25	115	70
6		<i>o</i> -F	<b>1f</b>	25	115	77
7		<i>m</i> -F	<b>1g</b>	25	115	79
8		<i>p</i> -F	<b>1h</b>	35	115	81
9		<i>p</i> -Br	<b>1i</b>	25	115	64
10		<i>m</i> -CF <sub>3</sub>	<b>2a</b>	30	115	83
11		<i>o</i> -F	<b>2b</b>	30	115	71
12		<i>m</i> -F	<b>2c</b>	25	115	82
13		<i>p</i> -Cl	<b>2d</b>	25	115	79
14		<i>p</i> -MeO	<b>2e</b>	25	115	72
15		2-(3-Br-py)	<b>2f</b>	25	115	56
16		<i>o</i> -F	<b>3a</b>	26	115	75
17		<i>m</i> -F	<b>3b</b>	26	115	80
18		<i>p</i> -F	<b>3c</b>	26	115	86
19		<i>o</i> -Me	<b>4a</b>	24	115	69
20		<i>o</i> -F	<b>4b</b>	24	115	74
21		<i>m</i> -F	<b>4c</b>	24	115	81
22		<i>p</i> -F	<b>4d</b>	30	115	79
23		<i>m</i> -Me	<b>5a</b>	24	110	79
24		<i>p</i> -Me	<b>5b</b>	24	110	89
25		<i>p</i> -Et	<b>5c</b>	24	110	83
26		<i>m</i> -CF <sub>3</sub>	<b>5d</b>	24	110	76
27		<i>p</i> -CF <sub>3</sub>	<b>5e</b>	17	110	85
28		<i>o</i> -F	<b>5f</b>	18	110	80
29		<i>m</i> -F	<b>5g</b>	19	110	79
30		<i>p</i> -F	<b>5h</b>	17	110	74
31		<i>o</i> -Br	<b>5i</b>	22	110	66
32		<i>p</i> -Cl	<b>5j</b>	24	110	71
33		<i>m</i> -NO <sub>2</sub>	<b>5k</b>	24	110	80
34		<i>p</i> -MeO	<b>5l</b>	24	110	75
35		<i>o</i> -CH <sub>3</sub> OOC	<b>5m</b>	20	110	65

<sup>a</sup> Reaction conditions unless specified otherwise: 1 equiv. **sm1–sm5**, 2 equiv. aryl iodide, 3 equiv. selenium powder (100 mesh), 4 equiv. K<sub>2</sub>CO<sub>3</sub>, CuBr<sub>2</sub> (10 mol%), 1 mL dry DMSO. Performed in a Teflon screw cap-sealed pressure tube, loaded in air.

between a *N*-substituted nitro-heterocycle and diphenyl diselenide (Scheme 1). Basing on our previous research on TM-catalyzed C–H functionalization of nitro-substituted (hetero)arenes we selected pyrazole **sm1** as a model compound for this experiment. The conditions were selected following the literature on reactions involving diaryl diselenides and our experience. The reaction between **sm1** (1 equiv.) and 1,2-di-*p*-tolylidiselane (1 equiv.) catalyzed by CuBr (0, 1 equiv.) under basic conditions (3 equiv. K<sub>2</sub>CO<sub>3</sub>) in DMSO under air gave the expected product in 32% yield after 18 h in 110 °C. The selenation occurred exclusively at the C(5) position of the pyrazole ring.

With this encouraging result in hand we moved to a three-component reaction. The above conditions applied to the same starting material **sm1** in reaction with 4-iodotoluene and selenium powder gave the expected product in 38% yield (Table

1, entry 1). With this result we began the optimization of the conditions.

At start we applied the conditions matching those known in the literature to work for selenation of heteroaryls with elemental selenium. Braga *et al.*<sup>57</sup> tested many variants involving CuI and a handful of other copper salts for the selenation of 1,3,4-oxadiazoles, for most of which he obtained quite satisfactory results. In our case however, the combination of CuI and KHCO<sub>3</sub> gave only 23% yield (Table 1, entry 2). Following the procedure optimized by Wang *et al.*<sup>58</sup> we skipped the base and switched to DMF, this combination also was not optimal (Table 1, entry 3). This is not however surprising, since the authors of the mentioned work assumed a radical pathway in their reaction involving a derivative of imidazo[1,2-*a*]pyridine.

The same substrates were investigated by Guo *et al.* twice, in combination with aryl iodides and coumarinyl triflates.



Application of similar conditions did not raise the yield significantly (Table 1, entries 4 and 5). Another set of conditions, following the work of Wu and Wu *et al.*<sup>64</sup> pointed at CuO in the combination with strong base in DMSO under argon (46% yield, Table 1, entry 6). This prompted us to apply Cu(II) salt again (Table 1, entry 7). A few other combinations were tried (entries 8, 12, 13, 19) with moderate success, but only after switching to CuBr<sub>2</sub> the yields raised to higher levels (entries 14–18 and 20). Finally, the optimal conditions were found (entry 18). Beside the copper salt, the choice of the base seems to be less important than the choice of the solvent and aerobic conditions. This indicates that an oxidant might be consumed during the course of the reaction, since both – DMSO and O<sub>2</sub> in air can act as oxidizing agents. A handful of other conditions were tested, including catalysts based on more expensive transition metals, known to work in C–H activation protocols. Among those, only the use of Pd(II) salts yielded more than 50% of the target product.

Having acquired the optimal conditions for our starting material, we moved on to the scope assessment. 4-Nitropyrzazole **sm1** was submitted to reaction with a number of substituted iodobenzene derivatives (Table 2, entries 1–9). The results were mostly satisfactory, although in some cases the duration and temperature of the reaction had to be slightly extended. In order to test the influence of the alkyl substituent at N(1) position we submitted derivatives with phenethyl-(**sm2**), phenylpropyl-(**sm3**) and butyl-(**sm4**) substituents to the reaction. It is of note, for the 4-nitropyrzoles in question the reactions with *o*-fluoroiodobenzene all gave similar results (yield = 71–77%, Table 2, entries 6, 11, 16, 20). In the case of *m*-fluoroiodobenzene the yields are slightly lower and range from 67 to 76% (Table 2, entries 7, 12, 17, 21), what can be attributed to a different inductive EWG effect.

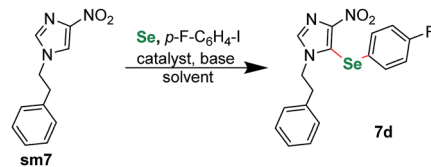
It is worth to mention that the removal or exchange of the pyrazole C(4)-nitro substituent makes the starting materials unreactive in our protocol. The unsubstituted 1-phenethyl-1*H*-pyrazole as well as the ethyl 1-phenethyl-1*H*-pyrazole-4-carboxylate derivatives gave only faint traces of the products or no reaction at all when submitted to the reaction with a variety of phenyl iodides. This result shows the impact of the directing effect of the nitro group. The same situation is true for 4-nitro *N*-phenyl pyrazoles. Derivatives with *p*-tolyl- and 4-fluorophenyl-substituents both gave negative results what indicates that electron-withdrawing substituents at the N(1) position can also render the starting material unreactive at the C(5) position. Therefore, as a next step we submitted an electron rich 3-methyl-1-phenyl-1*H*-pyrazole-5-amine (**sm5**) that has only the C(4)–H bond available for transformation. As expected, this starting material underwent the C–H activation under the optimized conditions much easier. This allowed for a broader scope of aryl iodides to be tested, however all the attempts gave very satisfactory results. Lower yields were recorded only for *o*-Br and *o*-CH<sub>3</sub>OOC substituted aryl iodides, what could be caused by the volume of those substituents (Table 2, entries 31 and 35 respectively).

Following our previous work, we were eager to test also 4-nitro imidazole derivatives within our protocol. The first

attempts however were disappointing in terms of the yield. We conducted a short optimization again (Table 3), for starting material **sm7**. The prolongation of the reaction course and raising the temperature had only limited influence on the reaction yield. CuBr<sub>2</sub> remained the best catalyst. Finally, switching to Cs<sub>2</sub>CO<sub>3</sub> as base and DMA as solvent raised the yield to about 68% (Table 3, entry 8). Similarly as for pyrazoles, the selenation occurred exclusively at the C(5) position of the imidazole ring. We also conducted several experiments regarding *N*-substitution of 4-nitroimidazoles. Similarly as for pyrazoles, starting material with *p*-tolyl- substituent at the N(1) position gave only trace product. We also submitted to the protocol two *N*-methyl derivatives. 1-Methyl-4-nitro-1*H*-imidazole did not react at all, whereas 1,2-dimethyl-4-nitro-1*H*-imidazole gave only trace product.

To the best of our knowledge there are only a few reports of compounds structurally similar to ours that contain the pyrazole or imidazole structural moiety, all of them were obtained from diselenides as selenium source. Perin and Schumacher *et al.* developed an oxidant promoted mild protocol using potassium peroxymonosulfate (Oxone) to conduct direct selenation of *N*-unsubstituted pyrazoles.<sup>99</sup> Yan *et al.* successfully selenated a series of *N*-phenyl substituted pyrazoles *via* I<sub>2</sub> mediated protocol.<sup>100</sup> Zhang and Zhong *et al.* used a FeBr<sub>3</sub>/I<sub>2</sub> complex to introduce phenyl- and benzyl-selanyl groups into a series of *N*-phenyl aminopyrazoles.<sup>101</sup> Schiesser *et al.* performed a lithium/selenium exchange on a N-SEM protected (2-(trimethylsilyl)ethoxymethyl-) imidazole ring as a step in the synthesis of selenofonsartan analogues.<sup>102</sup> We tested also

Table 3 Optimization of reaction conditions for imidazole derivatives<sup>b</sup>



Entry	Catalyst	Base	Solvent	Temp./°C	Time/h	Yield/%
1	CuBr <sub>2</sub>	K <sub>2</sub> CO <sub>3</sub>	DMSO	110	18	10
2	CuBr <sub>2</sub>	K <sub>2</sub> CO <sub>3</sub>	DMSO	125	96	18
3	CuBr <sub>2</sub>	K <sub>2</sub> CO <sub>3</sub>	DMSO	130	40	14
4	CuBr <sub>2</sub>	K <sub>2</sub> CO <sub>3</sub>	Toluene	130	40	NR
5	CuBr <sub>2</sub>	K <sub>2</sub> CO <sub>3</sub>	DMF	130	40	22
6	CuBr <sub>2</sub>	K <sub>2</sub> CO <sub>3</sub>	DMA	130	40	34
7	CuBr <sub>2</sub>	Cs <sub>2</sub> CO <sub>3</sub>	DMSO	115	24	49
8	<b>CuBr<sub>2</sub></b>	<b>Cs<sub>2</sub>CO<sub>3</sub></b>	<b>DMA</b>	<b>115</b>	<b>24</b>	<b>68</b>
9	CuBr <sub>2</sub>	Li <sub>2</sub> CO <sub>3</sub>	DMSO	115	40	NR
10	CuI	K <sub>2</sub> CO <sub>3</sub>	DMSO	115	40	NR
11	Cu(OAc) <sub>2</sub>	K <sub>2</sub> CO <sub>3</sub>	DMSO	115	40	Trace
12	NiCl <sub>2</sub> ·6H <sub>2</sub> O	K <sub>2</sub> CO <sub>3</sub>	DMSO	115	40	NR
13	AgOAc	K <sub>2</sub> CO <sub>3</sub>	DMSO	115	40	Trace
14	PdCl <sub>2</sub> (PPh <sub>3</sub> ) <sub>2</sub>	K <sub>2</sub> CO <sub>3</sub>	DMSO	115	40	Trace <sup>a</sup>

<sup>a</sup> Reaction conditions unless specified otherwise: 1 equiv. **sm7**, 2 equiv. aryl iodide, 3 equiv. selenium powder (100 mesh), 4 equiv. base, catalyst (10 mol%), 1 mL dry solvent. Performed in a Teflon screw cap-sealed pressure tube. <sup>b</sup> Loaded in glovebox under argon.



benzimidazole derivative **sm10** as an example of fused imidazole derivative. The outcome was quite satisfying (Table 4, entry 9–72% yield, entry 10–77% yield). A triazole derivative **sm11** was also tested as an example of this family of five-membered heterocycles.

Chromones and their derivatives are common motifs abundant in biologically active compounds, numerous natural products, and pharmaceuticals.<sup>103–105</sup> Following our interest in those scaffolds<sup>106,107</sup> we submitted 4*H*-chromen-4-one (**sm12**) to aryloselenation to our optimized reaction conditions. The two attempts we undertook gave satisfactory results (Table 4, entries 12 and 13). To the best of our knowledge there are only a few literature reports of selenated chromones (either by direct C–H activation<sup>108,109</sup> or *via de novo* cyclization<sup>110,111</sup>) none of them obtained with the use of elemental selenium. With respect to the latter methodology we also submitted an enaminone to our protocol however, the reaction of (*E*)-3-(dimethylamino)-1-(2-hydroxyphenyl)prop-2-en-1-one was unsuccessful. A few other heteroaryl starting materials were tested within the

current protocol giving negative results. Among them were: 3-methyl-5-nitro-1-phenyl-1*H*-pyrazolo[3,4-*b*]pyridine, 1,3-dimethyl-6-aminouracil, 3,4,5-trimethoxyaniline and 3-nitropyridine.

Following other seminal works in the field we were curious to see if our protocol can be used to perform an intramolecular cyclization introducing selenium. We procured a series of heterocycles bearing 2-iodobenzyl- substituent at the N(1) ring atom: 1-(2-iodobenzyl)-1*H*-pyrazole, 1-(2-iodobenzyl)-4-nitro-1*H*-pyrazole, ethyl 1-(2-iodobenzyl)-1*H*-pyrazole-4-carboxylate, 1-(2-iodobenzyl)-1*H*-imidazole, 1-(2-iodobenzyl)-4-nitro-1*H*-imidazole, ethyl 1-(2-iodobenzyl)-1*H*-imidazole-4-carboxylate and 1-(2-iodobenzyl)-1*H*-benzo[*d*]imidazole. Similarly, to the parent starting materials tested in the intermolecular attempts, only the nitro-derivatives and benzimidazole successfully reacted giving benzoselenazines **13a**, **13b** and **13c** in 79%, 62% and 70% yield respectively (Fig. 2).

Basing on the literature reports, our observations and the outcome of the optimizations (Tables 1 and 3) we propose the

Table 4 Scope of the imidazoles and other heteroaryl substrates vs. aryl iodides<sup>b</sup>

Entry	Structure	R=	Number	Time/h	Temp./°C	Yield/%
1			<b>6</b>	24	115	65 <sup>a</sup>
2		<i>p</i> -Me	<b>7a</b>	24	115	86 <sup>a</sup>
3		<i>o</i> -F	<b>7b</b>	30	115	55 <sup>a</sup>
4		<i>m</i> -F	<b>7c</b>	24	120	73 <sup>a</sup>
5		<i>p</i> -F	<b>7d</b>	30	115	68 <sup>a</sup>
6			<b>8</b>	24	120	60 <sup>a</sup>
7		<i>o</i> -F	<b>9a</b>	25	120	57 <sup>a</sup>
8		<i>p</i> -F	<b>9b</b>	30	120	73 <sup>a</sup>
9		3,5-diCF <sub>3</sub>	<b>10a</b>	24	115	72
10		<i>m</i> -OCF <sub>3</sub>	<b>10b</b>	24	115	77
11			<b>11</b>	24	115	67
12		<i>p</i> -Et	<b>12a</b>	30	120	46
13		<i>p</i> -F	<b>12b</b>	30	120	48

<sup>a</sup> Reaction conditions unless specified otherwise: 1 equiv. **sm6**–**sm12**, 2 equiv. aryl iodide, 3 equiv. selenium powder (100 mesh), 4 equiv. K<sub>2</sub>CO<sub>3</sub>, CuBr<sub>2</sub> (10 mol%), 1 mL dry DMSO. Performed in a Teflon screw cap-sealed Pressure Tube, loaded in air. <sup>b</sup> Base – Cs<sub>2</sub>CO<sub>3</sub> and solvent – DMA.



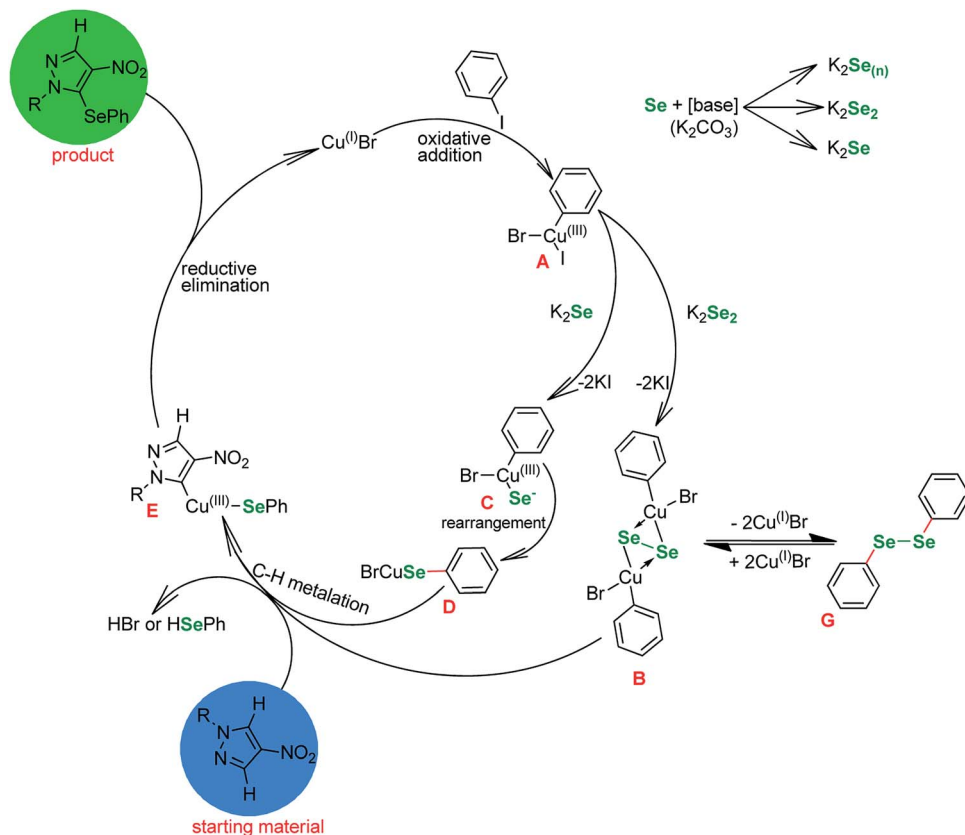


Fig. 1 Proposed mechanism of the reaction.

following mechanism (Fig. 1). Since the reaction is not proceeding without base (Table 1, entries 3, 5 and 12) it is safe to assume that the selenium enters the catalytic cycle in a form of a selenide anion ( $\text{Se}^{2-}$ )<sup>61,62</sup> or diselenide anion ( $\text{Se}_2^{2-}$ ).<sup>57</sup> The reduction of elemental selenium with base is a well known process. The first step in the catalytic cycle involving copper is oxidative addition of  $\text{Cu}^{\text{I}}$  halide into the I-C<sub>Ar</sub> bond of the phenyl iodide, forming  $\text{Cu}^{\text{III}}$  intermediate **A**.

These species react with the reduced selenium to produce a copper–selenium complex. At this point it is unpractical to distinguish between mono, di and polyselenide anions and whether the Se–Se bond is retained or not. Many authors formally agree on the existence of a square-planar species **B**, which is a common point with similar to our copper-catalyzed selenations utilizing diselenides, since it can undergo a reversible transformation to diphenyl diselenide **G**.<sup>59</sup> However, at this point it is necessary to depict the transfer of the Se atom (C to D) and the formation of Se–C bond. Next, the selenium–copper complex enters reaction with the heterocyclic starting material in a metalation step, with the formal extraction of HBr or HSePh species. The intermediate **E** undergoes reductive elimination to give the desired product and regenerate the catalyst.

We have also detected an unusual byproduct in the crude mixtures from reactions **1a–1i**. Diselenide **1by** (Fig. 3) was isolated during the chromatographic purification of products



Fig. 2 Cyclic benzoselenazine derivatives.



Fig. 3 Byproduct **1by**: (1,2-bis(1-(4-methylbenzyl)-4-nitro-1H-pyrazole-5-yl)diselane).

**1e** and **1g** from the crude mixtures in 10% and 8% yield. The presence of this diselenide can be explained as follows (Fig. 4). The starting material is oxidized by  $\text{Cu}^{\text{III}}$  species forming a copper complex that reacts with  $\text{K}_2\text{Se}_2$  to give an analogous to **B** square-planar species **B'**, that can also undergo a reversible transformation yielding byproduct **G'**.

Finally, compounds **1c**, **2f**, **5b**, **5d**, **5f**, **5i**, **5k** and **5m** were obtained as single crystals suitable for X-ray diffraction analysis. X-ray crystallographic analyses of the title structures helped us to corroborate the structural constitution of the



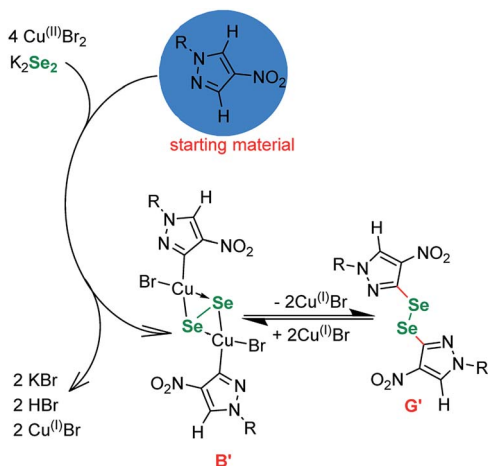


Fig. 4 Mechanistic explanation for the presence of byproduct 1b.

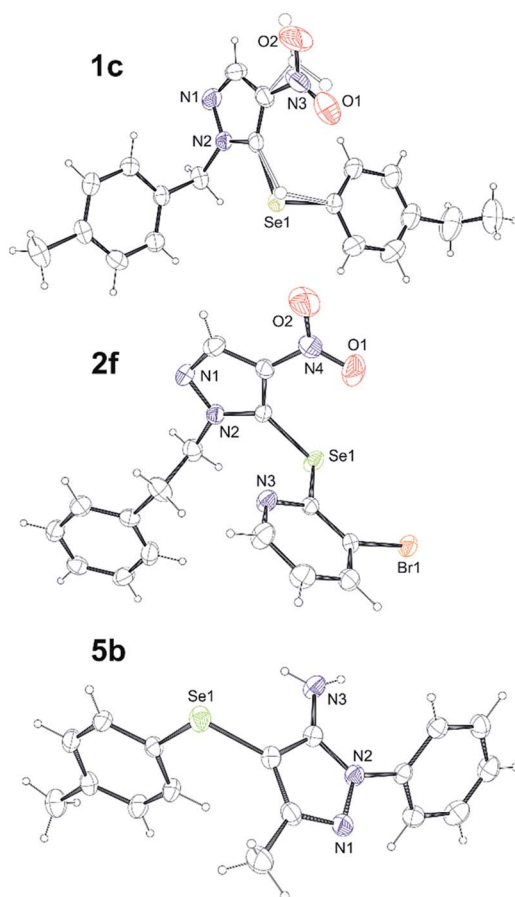


Fig. 5 Ortep drawings of molecules 1c, 2f and 5b found in crystals. The thermal ellipsoids are drawn with 30% probability. Only the labels for atoms heavier than carbon atom are given. In 1c minor components of disordered groups are depicted with spheres of arbitrary radius.

samples and determined the position of Se–Ar substituent (See Fig. 1 in ESI†). The representative structures of compounds 1c, 2f and 5b are depicted in the Fig. 5.

## Conclusions

We have proposed a general method to obtain unsymmetrical heteroaryl-aryl selenides containing 4-nitropyrazole, 4-nitroimidazole and a few other scaffolds by copper-catalyzed direct C–H selenation of *N*-substituted heteroaryls with iodobenzenes and elemental selenium. The scope and limitations of our methodology has been assessed in respect to both organic starting materials. A plausible mechanism has been proposed in relation to the previous research. The established reaction conditions work very well for 4-nitropyrazole derivatives and acceptably good for 4-nitroimidazoles. A total of 48 compounds have been prepared, majority of them bearing easily transformable nitro group and a few of them substituted with a similarly useful groups in the benzene ring. The protocol is also useful for closing a benzoselenazine ring from appropriate starting materials.

## Conflicts of interest

Authors declare no conflict of interest.

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