Accepted Manuscript

Fe(III)-Catalyzed direct C3 chalcogenylation of indole: The effect of iodide ions

Eduardo Q. Luz, Diego Seckler, Janylson Souza Araújo, Leonardo Angst, David B. Lima, Elise Ane Maluf Rios, Ronny R. Ribeiro, Daniel S. Rampon

PII: S0040-4020(19)30064-X

DOI: https://doi.org/10.1016/j.tet.2019.01.037

Reference: TET 30089

To appear in: *Tetrahedron*

Received Date: 5 November 2018

Revised Date: 9 January 2019

Accepted Date: 17 January 2019

Please cite this article as: Luz EQ, Seckler D, Araújo JS, Angst L, Lima DB, Maluf Rios EA, Ribeiro RR, Rampon DS, Fe(III)-Catalyzed direct C3 chalcogenylation of indole: The effect of iodide ions, *Tetrahedron* (2019), doi: https://doi.org/10.1016/j.tet.2019.01.037.

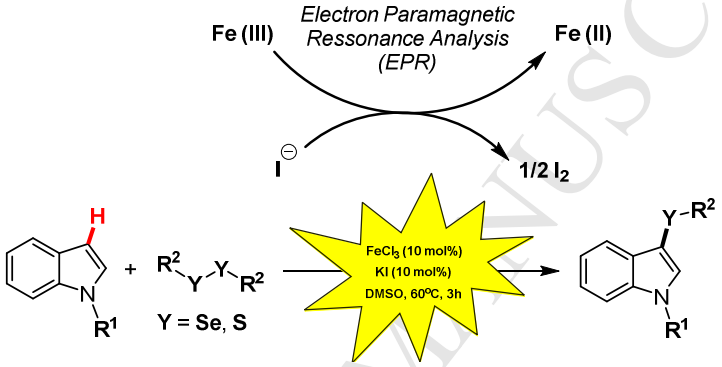
Graphical Abstract

To create your abstract, type over the instructions in the template box below.
Fonts or abstract dimensions should not be changed or altered.

Leave this area blank for abstract info.

Fe(III)-Catalyzed Direct C3 Chalcogenylation of Indole: The Effect of Iodide Ions

Eduardo Q. Luz,[a] Diego Seckler, [a] Janylson Souza Araújo,[a] Leonardo Angst, [a] David B. Lima, [a] Elise Ane Maluf Rios, [a] Ronny R. Ribeiro[b] and Daniel S. Rampon*[a]



ELSEVIER

Tetrahedron
journal homepage: www.elsevier.com

Fe(III)-Catalyzed Direct C3 Chalcogenylation of Indole: The Effect of Iodide Ions

Eduardo Q. Luz,[a] Diego Seckler,[a] Janylson Souza Araújo,[a] Leonardo Angst,[a] David B. Lima,[a] Elise Ane Maluf Rios,[a] Ronny R. Ribeiro,[b] and Daniel S. Rampon[a,*]

[a] *Laboratory of Polymers and Molecular Catalysis (LAPOCA), Department of Chemistry, Federal University of Paraná–UFPR, P. O. Box 19032, Curitiba, PR, 81531-990, Brazil.*
[b] *Department of Chemistry, Federal University of Paraná–UFPR, P. O. Box 19032, Curitiba, PR, 81531-990, Brazil.*

ARTICLE INFO

Article history:
Received
Received in revised form
Accepted
Available online

Keywords:
Direct Chalcogenylation
Indoles
3-selenylindoles
Iron (III)
Iodides

ABSTRACT

A mild and efficient iron (III)-catalyzed C3 chalcogenylation of indoles has been developed and the role of the iodide ions in this transformation was investigated. EPR experiments revealed the reduction of Fe(III) to Fe(II) under the reaction conditions, supporting the formation of molecular iodine in the system, which in effect catalyze the reaction. The scope of the chalcogenylation was broad and the synthesis of more functionalized 3-selenylindoles was explored.

1. Introduction

The functionalization of 1*H*-indole core has received considerable attention[1] since this heterocycle is an important structural unit in many bioactive compounds and organic materials with technological interest.[2,3] Among them, 3-chalcogenylindoles has been an emergent class of synthetic structures due their potential therapeutic value in the treatment of different diseases such HIV,[4] cancer,[5] cardiovascular,[6] allergies,[7] and bacterial diseases.[8] Further, it also has been used as potent inhibitor of tubulin polymerization,[8] as cyclooxygenase-2 (COX-2) inhibitors,[9] and exhibited antinociceptive properties.[10]

On the other hand, organoselenium compounds are well-known for their biological activities[11] and synthetic applicability,[12] making them attractive targets. Furthermore, they are incredibly useful from functional organic materials perspective, employed for architecture of electroconductive polymers, organic semiconductors, and liquid crystals.[13] Thus, undoubtedly there is a great demand for the development of straightforward construction of C-S and C-Se bonds.

The methodologies reported for the preparation of 3-chalcogenylindoles commonly involve the direct chalcogenylation of indole nucleus with various electrophilic organochalcogen reagents.[14] However, these methods are limited by either the instability or inaccessibility of the reagents, and/or incompatibility of the substrates. Besides, the metal free conditions employing safe diorganoyl dichalcogenides also has attracted interest,[15] although the use of stoichiometric amount of activators is often a drawback. The transition metal catalyzed direct chalcogenylation of indoles also have been developed,[16] and these reactions have proven to be efficient for the synthesis of a wide variety of 3-chalcogenylindoles regardless of the expensive and toxic nature of most metal catalysts employed. These approaches also allowed the positional control of C-H chalcogenylation, which is a challenging issue under metal free methodologies.[17]

In contrast, iron is one of the most abundant metals on earth, and consequently one of the most inexpensive and environmentally friendly.[18] Despite the advantages of iron catalysis,[19] its use for synthesis of 3-chalcogenylindoles was little explored.[20] Fang and co-workers reported the selective C3 sulfenylation of indoles with diorganoyl disulfides using iron (III) fluoride combined with a catalytic amount of molecular iodine (I_2) in acetonitrile.[20a] The sulfenylation of indole was also reported with thiols and iron (III) chloride with excellent selectivity and good yields.[20b] Taking into account the synthesis of 3-selenylindoles catalyzed by Fe(III)/I_2, there are no reports about a systematic mechanistic studies in which these attractive methods were carefully investigated. Particularly, the reaction between iron (III) and iodide ions in solution is a well suited way to produce I_2 that could catalyze a number of reactions,[21] including the chalcogenylation of indoles with diorganyl dichalcogenides.[21g] Nonetheless, it is surprising that this cheap and simple system was just evaluated in catalytic reactions for air oxidative coupling of thiols to disulfides without detailed mechanistic studies.[22]

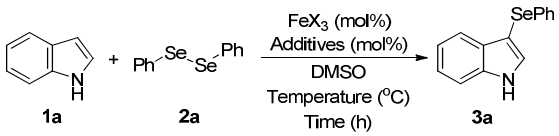
In this perspective, herein we detail a new protocol for synthesis of 3-chalcogenylindoles from diorganoyl dichalcogenides and indoles derivatives using the Fe(III)/KI system. The mechanism of this mild and quick reaction was

investigated, thus providing a comprehensive data about these poorly studied catalysts combination in organic reactions.

2. Results and Discussion

In order to get the optimized reaction conditions, the selenylation of indole **1a** with diphenyl diselenide **2a** was selected as the model reaction using iron (III) chloride ($FeCl_3$) as catalyst and a series of additives in DMSO (Table 1). Initially, the reaction was carried out with 10 mol% of catalyst and 0.5 equivalent of **2a** at 110 °C under an air atmosphere, which gave the desired product **3a** in 75% yield after 24 h (Table 1, entry 1). This reactivity pattern suggests the formation of electrophilic organoselenium species in this reaction conditions since the C-3 selectivity of 1*H*-indole under electrophilic aromatic substitutions is well known.

Table 1. Optimization of the reaction conditions.



#[a]	Catalyst (mol%)	Additive (mol%)	Time [h]	Temp. [°C]	Yield [%][b]
1	$FeCl_3$ (10)	-	24	110	75
2	$FeCl_3$ (10)	-	24	80	51
3	$FeCl_3$ (10)	-	24	130	75
4	$FeCl_3$ (10)	KI (30)	24	110	91
5	$FeCl_3$ (10)	KBr (30)	24	110	75
6	$FeCl_3$ (10)	KCl (30)	24	110	64
7	$FeCl_3$ (10)	KF (30)	24	110	49
8	-	KI (30)	24	110	14
9	$FeCl_3$ (10)	KI (30)	24	60	94
10	$FeCl_3$ (10)	KI (30)	24	40	82
11	$FeCl_3$ (10)	KI (30)	24	25	33
12	$FeCl_3$ (10)	KI (30)	3	60	95
13	$FeCl_3$ (10)	KI (10)	3	60	97
14	$FeCl_3$ (10)	KI (5)	3	60	65
15	$FeCl_3$ (5)	KI (5)	24	60	82
16	Fe_2O_3 (10)	KI (10)	3	60	-
17	$FeBr_3$ (10)	KI (10)	3	60	62
18	$Fe(NO_3)_3 \cdot 9\ H_2O$	KI (10)	3	60	69
19	$FeCl_3 \cdot 6\ H_2O$	KI (10)	3	60	52
20	Cu_2O (10)	KI (10)	3	60	32
21	$FeCl_3$ (10)	NaI (10)	3	60	85
22	$FeCl_3$ (10)	CsI (10)	3	60	95
23	$FeCl_3$ (10)	-	3	60	12

[a]Reaction conditions: **1** (1.0 mmol), **2** (0.5 mmol), FeX_3 (mol %), additive (mol %) and dry DMSO (2 mL) under air atmosphere at 60 °C. [b]Isolated yields.

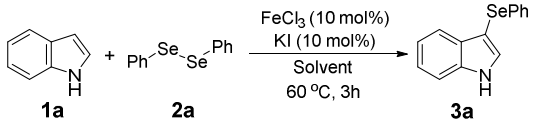
The variation of the reaction temperature showed that heating at 130 °C gave no better result, and lowering the temperature led to a decrease in the product yield (entries 2 and 3). Considering that the nucleophilic cleavage of Y-Y bond (S or Se) by attack of nucleophilic species could be mediated by Lewis acids to produce electrophilic organochalcogen species[23] it was proposed that the presence of iodide ions under similar conditions could improve the yield of **3a**. In this sense, when 30 mol% of KI was added to reaction under similar conditions, the yield of **3a** was enhanced to 91% (entry 4). Although this was a distinct effect of KI in this methodology since the improved product yields were not detected with other halide ions (entries 4-7). In addition, in absence of a Fe(III) catalyst the reaction was ineffective (entry 8).

This prompted us to evaluate the temperature and time of the reaction in the presence of iodide ion as additive. Fortunately, the decreasing of reaction temperature to 60 °C produced no appreciable variation in the product yield (entry 9), but a considerable decreased was observed under lower temperatures (entries 9-11). Based on these data, the reaction was followed by thin layer chromatography (TLC), which indicated that the starting materials were consumed after only 3 h, with the selenylated product being obtained in 95% yield (entry 12). It is worth noting that this could be considered one of the mildest protocols to access 3-selenylindoles through transition metal catalysis with diorganoyl diselenides.[16,17,20a,20c] Additionally, the yield of **3a** remained high when only 10 mol% of KI was employed (entry 13), whereas a further decrease in the amount of this additive gave 65% yield (entry 14).

All of these results described above indicated that there is a proper stoichiometry between Fe(III) and iodide ions in this catalytic system. Furthermore, when the reaction was performed with 5 mol% of $FeCl_3$ and 5 mol% of KI reasonably good yield of **3a** was obtained only after 24 h (entry 15). Several other Fe(III) sources were tested (entries 16-19), however only moderate yields of the product could be achieved and no reaction was detected with Fe_2O_3. The detrimental effect of water in this system was properly observed with $FeCl_3.6\ H_2O$ (entry 19). In this sense, taking into account the hygroscopic nature of $FeCl_3$, it was expected a reduction of yields if the H_2O from catalyst contamination was present, and this were not observed under optimized conditions. Also, since iron is often contaminated with trace amounts of copper,[24] the reaction was carried out with Cu_2O, and only 32% yield of **3a** was found. These findings show the essential role of Fe(III) catalyst in this methodology. Next, the influence of the cation was investigated in this transformation. In this regard, the yield of product **3a** remained high with either NaI or CsI, which supports no cation effects in this reaction (entries 21 and 22). Finally, without KI the reaction afforded only 12% of 3-(phenylselenyl)-1*H*-indole **3a** (entry 23).

With these conditions in hands, some representative solvents were screened to verify that DMSO was the most efficient one for this reaction system (Table 2). Interestingly, acceptable yield of the product **3a** was obtained only in DMF (Table 2, entry 1), and other solvents such as 1,4-dioxane, acetonitrile or ethanol gave unsatisfactory results (entries 2-4). Unfortunately, when the reactions were carried out with toluene or 1,2-dichloroethane the expected product was not obtained.

Table 2.The effect of reaction solvent.



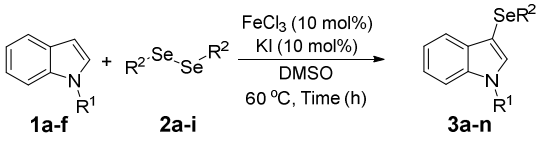
Entry[a]	Solvent	Yield[%][b]
1	DMF	56
2	1,4-Dioxane	32
3	CH_3CN	21
4	EtOH	36
5	DCE	-
6	Toluene	-

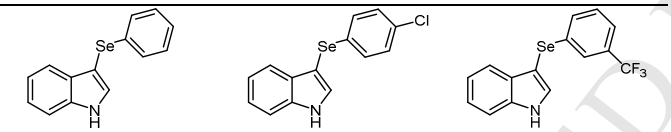
[a]Reaction conditions: **1** (1.0 mmol), **2** (0.5 mmol), $FeCl_3$ (10 mol%), KI (10 mol%) and dry solvent (2 mL) under air atmosphere at 60 °C. [b]Isolated yields.

To explore the scope and limitation of this method, the reaction between a variety of indoles (**1a-e**) and diorganoyl diselenides (**2a-i**) were investigated under the best conditions (Table 3). The progresses of these reactions were also monitored by TLC. In each case, the reaction regioselectively provided the 3-selenylindoles (**3a**-**3l**) in good to excellent yield (61−98%). When the reactions were performed using 1-methylindole or 1-benzylindole the desired products **3j** and **3k** were obtained in 85% and 74% yields, respectively. Furthermore, 2-methylindole can also react with diphenyl diselenide **2a** to produce the compound **3l** in 83% yield. However, indoles with an electron-withdrawing group at the 1-position (**1f**) failed to give the expected product. Surprisingly, and a great particularity of this system, the protocol allowed a direct access to 2-selenylindoles (**3m**) in good yield after 6h when the 3-methyl substituted heterocycle was used. The C-3 selenylation follow by a C-2 migration offers a possible explanation in this regard.[25]

The reaction also worked efficiently for structurally diverse diorganoyl diselenides **2**. In general, the product yield from diaryl diselenides containing electron-withdrawing groups (**3b** and **3c**) were higher than those with electron-donating groups (**3d**, **3e**, **3f** and **3g**), and longer reaction times were required with these latter substrates to reach good to excellent yields. Notably, the reaction was effective for dialkyl diselenides, and the compound **3i** was prepared in high yield.

Table 3. Synthesis of 2- and 3-selenylindoles.[a]

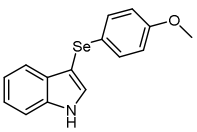




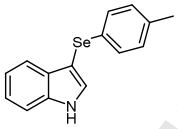
3a, 3h, 97%

3b, 3h, 92%

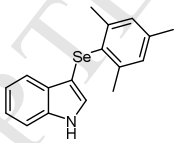
3c, 3h, 98%



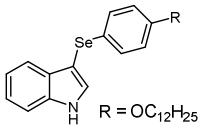
3d, 12h, 76%



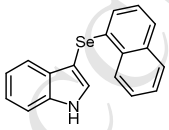
3e, 5h, 78%



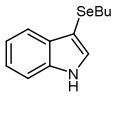
3f, 7h, 95%



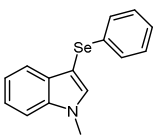
3g, 18h, 92%



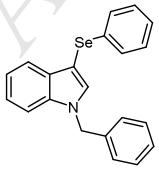
3h, 3h, 61%



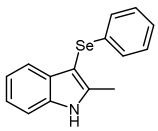
3i, 5h, 93%



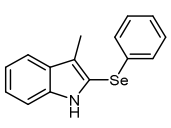
3j, 3h, 85%



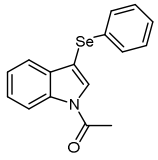
3k, 3h, 74%



3l, 3h, 83%



3m, 3h, 76%

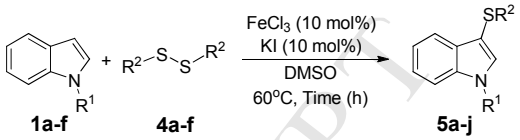


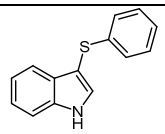
3n, 72h, 0%

[a]Reaction conditions: **1** (1.0 mmol), **2** (0.5 mmol), $FeCl_3$ (10 mol%), KI (10 mol%) and dry DMSO (2 mL) under air atmosphere at 60 ºC, isolated yields.

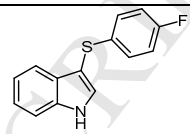
The scope of the reaction regarding the preparation of 2- and 3-sulfenylindoles was explored next (Table 4). Generally, the sulfenylation of indoles showed similar electronic effects to those observed during the selenylation, albeit longer reaction times were required to reach good to excellent yields of the desired products (**5a**-**5h**). Again, when C-3 position of indole ring was attached by a methyl group, the C-2 sulfenylation was the reaction product (**5g**) probably via a process similar to Plancher rearrangement.[25]

Table 4. Synthesis of 2- and 3-thiophenylindoles.[a]

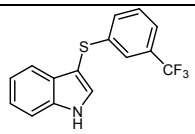




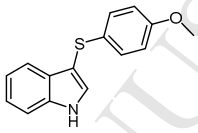
5a, 8h, 96%



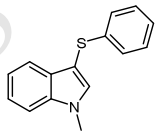
5b, 5h, 86%



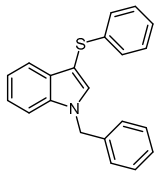
5c, 6h, 84%



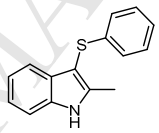
5d, 8h, 75%



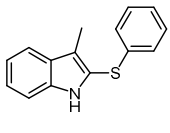
5e, 8h, 82%



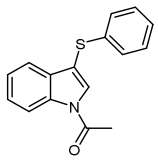
5f, 8h, 72%



5g, 3h, 87%



5h, 6h, 74%



5i, 72h, 0%

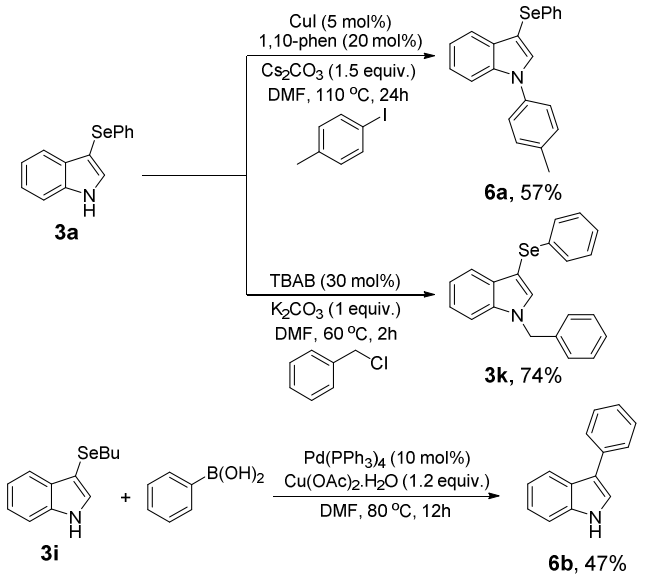
[a]Reaction conditions: **1** (1.0 mmol), **4** (0.5 mmol), $FeCl_3$ (10 mol%), KI (10 mol%) and dry DMSO (2 mL) under air atmosphere at 60 ºC, isolated yields.

Considering the high reactivity of indole ring, the synthesized 3-selenylindoles offers several possibilities to prepare more functionalized compounds, and by the first time this was evaluated (Scheme 1). This privileged structure have considerable relevance in transition metal catalyzed reactions, since catalyst poisoning by organochalcogen species was one of the serious limiting factors in this area.[27] For instance, the compound **3a** underwent a clean Ullmann *N*-arylation[28] on the indole moiety with 1-iodo-4-methylbenzene, affording **6a** in moderate yield. The straightforward *N*-alkylation of 3-selenylindoles constitutes an interesting alternative route to preparing *N*-benzyl-3-selenylindoles. Thus, the reaction of **3a** with benzyl chloride, TBAB and K_2CO_3 gave **3k** in 74% isolated yield.[14u] The presence of $C_{sp}{}^2$-Se bond on the organic substrates also allow potential for further elaboration, particularly in the formation of new C-C bond. For this purpose, under Zeni and co-workers conditions,[29] the Suzuki reaction between **3i** and phenylboronic acid produced the selectively the C-3 arylation product **6b**.

To clarify the reaction mechanism, some control experiments were carried out (Scheme 2). Firstly, the addition of the radical scavenger TEMPO (2,2,6,6-tetramethyl-1-piperidinyloxy, 1.0 equiv.) under optimized reaction conditions did not hamper this transformation and **3a** was obtained in 84% isolated yield (Scheme 2a). This data suggest that a radical pathway is unlikely.

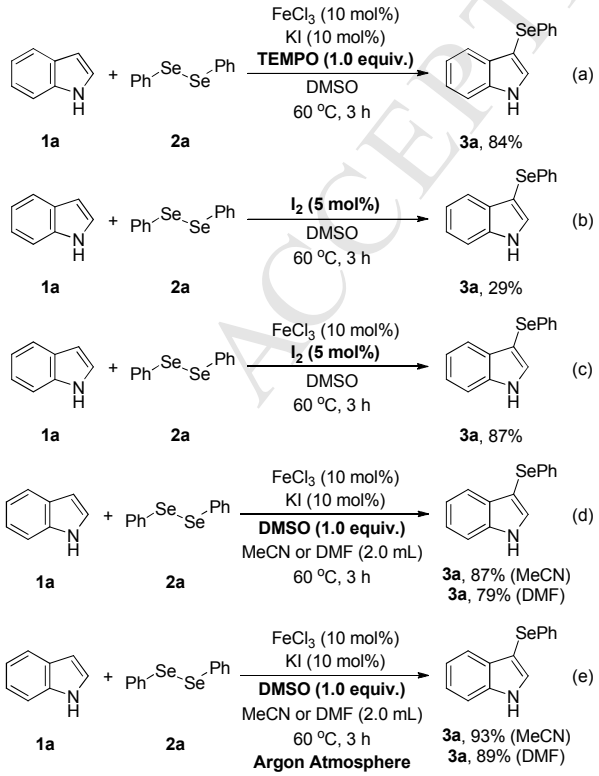
Secondly, considering the plausible formation of molecular iodine in reaction medium through oxidation of iodide anions with Fe(III),[21c] a theoretically maximum amount of I_2 (5 mol%)

produced under this conditions was used as the only catalyst, which afforded **3a** in 29% yield (Scheme 2b). Notably, when 10 mol% of $FeCl_3$ was employed along with 5 mol% of I_2, the product **3a** was obtained in 87% yield (Scheme 2c).



Scheme 1. Applications of 3-selenylindoles in transition metal catalyzed reactions and *N*-alkylations.

These experiments indicated that ArSeI species could be involved in the mechanism[15e,21g] and the crucial role of Fe(III) in this reaction. The essential role of dimethylsulfoxide was also evaluated (Scheme 2d). Under the optimized reaction conditions and with polar aprotic solvents (MeCN or DMF), the yield of **3a** remained high when only 1.0 equivalent of DMSO was used, which corroborates with formation of HI in the system and the recognized role of DMSO for regenerate iodine.[21g] Since this reaction was studied under air conditions, the role of O_2 as terminal oxidant was also evaluated (Scheme 2e). The yields of **3a** remained high when the reaction was developed under inert argon atmosphere and with only 1.0 equivalent of DMSO, which showed the key role of solvent in this method.

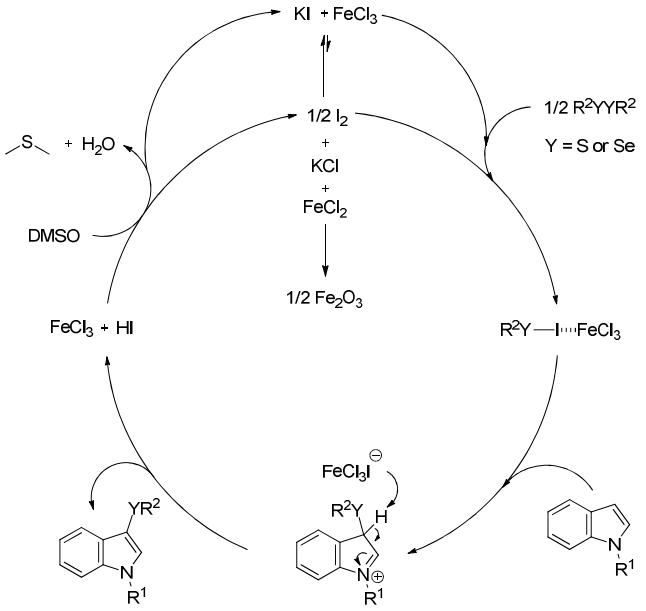


Scheme 2. Preliminary Mechanism Investigation

To gain more insight about this selenylation processes, a series of mechanistic studies by Electron Paramagnetic Resonance (EPR) spectroscopy were performed. The presence of radical species in the medium and the role of iron in this reaction could be elucidated since EPR spectroscopy is sensitive to unpaired electrons, from organic radicals to some transition metals species.[30] Any stable organic radical present in the samples is expected to result in a narrow EPR spectral line with a gyromagnetic factor (g) around 2.0; on the other hand, Fe(III) species manifests spectroscopically as a broader line, around g = 4.3.[31] For a given EPR species, the spectral intensity is proportional to its concentration in the sample.

The progress of the optimized reaction was measured by taking aliquots at several times, and the spectra were recorded at 77 K (Figure 1, Supporting Information). None of the analyzed samples presented any signal of organic radicals. Nevertheless, signals of Fe(III) were present in all samples in DMSO, and their intensity normalized to concentration suggests that after addition of 10 mol% of KI the Fe(III) concentration drops 25%, which indicates the well known equilibrium between Fe(III)/Fe(II) in the system and the formation of I_2. Additionally, after addition of diphenyl diselenide (**2a**) and 1*H*-indole (**1a**) the Fe(III) concentration reduced to 47% from the initial value (after 1 h) due the consumption of I_2 for the selenylation reaction. Considering the aerobic conditions of the system, the Fe(III) concentration rose during the last 2 h of reaction due to the expected formation of Fe(III) oxides. On the other hand, when the reaction was developed with 10 mol% of $FeCl_2$, $FeBr_2$ or FeI_2 under optimized conditions, the product **3a** was not observed, which support the essential role of Fe(III) and I_2 in this system and ruled out specific effects of Fe(II).

Based on the above results, a plausible mechanism would be herein presented (Scheme 3). First, the $FeCl_3$ and KI reaches an equilibrium with the formation of I_2 and Fe(II) in the reaction medium,[21] and this is consistent with the EPR experiments. Subsequently, an electrophilic intermediate of the form RYI (Y = S, Se) is generated, and the reaction at C-3 position of the indole derivative catalyzed by Fe(III) that is still present in the system afford the desired 3-chalcogenylindole, with concomitant formation of HI.[21g] The role of iron in this step accounts the mild reaction conditions observed. Finally, the I_2 could be regenerated through oxidation of hydrogen iodide with DMSO.[32,21g,33] Despite the suggested involvement of RYI (Y = S, Se) species in this mechanism, their formation are faster than ^{77}Se NMR timescale,[34] which avoided the direct observation.



Scheme 3. Proposed reaction mechanism.

3. Conclusion

In conclusion, we have disclosed a mild and efficient direct chalcogenylation of indoles catalyzed by iron (III) chloride and potassium iodide. The mechanism of this reaction was detailed by EPR experiments that supports the reduction of Fe(III) to Fe(II) and the formation of I_2 in this system which effectively catalyzed the reaction. The scope of the chalcogenylation was broad and the synthesis of more functionalized 3-selenylindoles and 3-sulfenylindoles were explored.

4. Experimental Section

4.1 General remarks

The reactions were monitored by TLC carried out on Merk silica gel (60 F_{254}) by using UV light as visualization agent and the mixture between 5% of vanillin in 10% of H_2SO_4 under heating conditions as developing agents. Merck silica gel (particle size 0.040-0.063 mm) was used to flash chromatography. Hydrogen nuclear magnetic resonance spectra (NMR ^{1}H) were obtained at 400 MHz in a Bruker Nuclear Ascend 400 spectrometer and at 200 MHz in Bruker DPX 200 spectrometer. The spectra were recorded in $CDCl_3$ solutions. The chemical shifts are reported in ppm, referenced to tetramethylsilane (TMS) as the internal reference. Coupling constants (*J*) are reported in Hertz. Carbon-13 nuclear magnetic resonance spectra (^{13}C NMR) were obtained at 100 and 50 MHz spectrometers. Selenium-77 nuclear magnetic resonance spectra (^{77}Se NMR) were obtained at 76 MHz spectrometers. The chemical shifts are reported in ppm, referenced to the solvent peak of $CDCl_3$. High-resolution mass spectra (HRMS) were recorded in positive ion mode (ESI) using a Q-TOF spectrometer. Low-resolution mass spectra were obtained with a GCMS-QP2010 Plus Shimadzu mass spectrometer. X-band Electron Paramagnetic Resonance (EPR) spectra were recorded on a Bruker EMX micro spectrometer equipped with a high quality factor TE102 resonant cavity from frozen DMSO solutions at 77 K. The samples were placed in standard 4 mm o.d. EPR quartz tubes and the low temperature spectra were obtained using an insertion quartz finger Dewar. Quantitative analysis were based on a MgO:Cr intensity standard sample.

4.2 General procedure for preparation $FeCl_3$/KI mediated chalcogenylation of indoles derivatives: A mixture of indole **1a-f** (1.0 mmol), dichalcogenide **2a-i** or **4a-f** (0.5 mmol), $FeCl_3$ (10 mol%) and KI (10 mol%) in dry DMSO (2 mL) was stirred at 60 °C for 3 h until complete consumption of the starting material, as monitored by TLC. The initial yellow or brownish solution changes to brown throughout the reaction time. After the reaction was finished, the brown mixture was poured into EtOAc (15 mL) and washed with brine (3 × 10 mL), followed by extraction of the aqueous layer with EtOAc (5 × 3 mL). The combined organic layer was dried over anhydrous Mg_2SO_4 and concentrated under reduced pressure. The crude product was purified by flash column chromatography (hexane–EtOAc) to afford the 3-chalcogenyl indole product.

4.2.1. 3-(Phenylselenyl)-1H-indole **(3a)**:[21g] Yield: 0.265 g (97%); white solid; mp 134-137 ºC. ^{1}H NMR ($CDCl_3$, 400 MHz) δ (ppm) = 8.29 (br s, 1H); 7.63 (d, *J* = 8.0 Hz, 1H); 7.42-7.36 (m, 2H); 7.25-7.20 (m, 3H); 7.17-7.05 (m, 4H). ^{13}C NMR ($CDCl_3$, 100 MHz) δ (ppm) = 136.4, 133.8, 131.2, 130.0, 128.9, 128.7, 125.6, 122.9, 120.8, 120.3, 111.3, 98.2. ^{77}Se NMR (76 MHz, $CDCl_3$) δ (ppm) = 464.5, 212.0. MS (Rel. Int.) *m/z*: 273 (20.4), 193 (100), 116 (6.5), 77 (8.3).

4.2.2. 3-(4-Chlorophenylselenyl)-1H-indole **(3b)**:[21g] Yield: 0.282 g (92%); white solid; mp 117-120 ºC. ^{1}H NMR ($CDCl_3$, 400 MHz) δ (ppm) = 8.37 (br s, 1H); 7.59 (d, *J* = 7.9 Hz, 1H); 7.44-7.40 (m, 2H); 7.25-7.20 (m, 3H); 7.17-7.05 (m, 4H). ^{13}C NMR ($CDCl_3$, 100 MHz) δ (ppm) = 136.4, 132.0, 131.6, 131.2, 130.0, 129.7, 129.0, 123.1, 121.0 120.2 114.4, 98.0. ^{77}Se NMR (76 MHz, $CDCl_3$) δ (ppm) = 464.5, 214.6. MS (Rel. Int.) *m/z*: 307 (16.3), 227 (100), 192 (8.9), 116 (15.5), 77 (10.0).

4.2.3. 3-((3-(Trifluoromethyl)phenyl)selenyl)-1H-indole **(3c)**:[21g] Yield: 0.334 g (98%); yelow solid; mp 75-77 ºC. ^{1}H NMR ($CDCl_3$, 400 MHz) δ (ppm) = 8.46 (br s, 1H); 7.60 (d, *J* = 8.0 Hz, 1H); 7.54 (s, 1H); 7.49 (d, *J* = 2.6 Hz, 1H); 7.44 (d, *J* = 8.0 Hz, 1H); 7.34-7.24 (m, 3H); 7.20-7.16 (m, 2H). ^{13}C NMR ($CDCl_3$, 100 MHz) δ (ppm) = 136.47, 135.25, 131.82, 131.44, 131.2 (q, *J* = 318.0 Hz), 129.7, 129.2, 125.2 (q, *J* = 3.8 Hz), 124.3 (q, *J* = 268.8 Hz), 123.2, 122.4, (q, *J* = 4.3 Hz) 121.1, 120.2, 111.5, 97.4. ^{77}Se NMR (76 MHz, $CDCl_3$) δ (ppm) = 464.5, 224.8. MS (Rel. Int.) *m/z*: 340 (7.6), 261 (100), 116 (15.9), 77 (10.0).

4.2.4. 3-((4-Methoxyphenyl)seleno)-1H-indole **(3d)**:[26a] Yield: 0.230 g (76%); white solid; mp 112-115 ºC. ^{1}H NMR ($CDCl_3$, 400 MHz) δ (ppm) = 8.32 (br s, 1H); 7.65 (d, *J* = 8.8 Hz, 1H); 7.41 (d, *J* = 2.5 Hz, 1H); 7.38 (d, *J* = 8.1 Hz, 1H); 7.29-7.13 (m, 4H); 7.38 (d, *J* = 8.8 Hz, 2H); 3.70 (s, 3H). ^{13}C NMR ($CDCl_3$, 100 MHz) δ (ppm) = 158.4, 136.3, 131.3, 130.5, 129.9, 123.4, 122.8, 120.7, 120.3, 114.8, 111.3, 99.6, 55.2. ^{77}Se NMR (76 MHz, $CDCl_3$) δ (ppm) = 464.5, 202.2. MS (Rel. Int.) *m/z*: 303 (18.7), 223 (100), 117 (9.8), 77 (14.0).

4.2.4. 3-(4-tolylselanyl)-1H-indole **(3e)**:[15b] Yield: 0.223 g (78%); white solid; mp 104-107 ºC. ^{1}H NMR ($CDCl_3$, 400 MHz) δ (ppm) = 8.19 (br s, 1H); 7.55 (d, *J* = 7.8 Hz, 1H); 7.31-7.28 (m, 2H); 7.17-7.13 (m, 1H); 7.10-7.05 (m, 3H); 6.85 (d, *J* = 7.8 Hz, 1H); 2.14 (s, 3H). ^{13}C NMR ($CDCl_3$, 100 MHz) δ (ppm) = 136.4, 135.5, 131.0, 129.9, 129.7, 129.6, 129.1, 122.8, 120.7, 120.3, 111.3, 98.7, 20.8. ^{77}Se NMR (76 MHz, $CDCl_3$) δ (ppm) = 464.5, 205.8. MS (Rel. Int.) *m/z*: 287 (19.8), 207 (100), 169 (2.8), 91 (7.3), 77 (6.1).

4.2.5. 3-(mesitylselanyl)-1H-indole **(3f)**: Yield: 0.300 g (95%); white solid; mp 135-137 ºC. ^{1}H NMR ($CDCl_3$, 400 MHz) δ (ppm) = 8.09 (br s, 1H); 7.53 (d, *J* = 8.1 Hz, 1H); 7.29 (d, *J* = 8.1 Hz, 1H); 7.16 (td, *J* = 8.1 and 1.3 Hz, 1H); 7.11-7.07 (m, 2H); 6.86 (s, 2H); 2.55 (s, 6H); 2.21 (s, 3H). ^{13}C NMR ($CDCl_3$, 100 MHz) δ (ppm) = 142.5, 137.8, 136.2, 129.6, 128.7, 127.9, 122.4, 120.2, 111.1, 101.1, 24.4 , 20.8. ^{77}Se NMR (76 MHz, $CDCl_3$) δ (ppm) = 464.5, 125.2. MS (Rel. Int.) *m/z*: 315 (29.3), 198 (52.9), 119 (13.2), 1/17 (100), 77 (40). HRMS: Calculated mass for $C_{17}H_{17}NSe$ $[M+H]^+$: 316.0604, found: 316.0605.

4.2.6. 3-((4-(dodecyloxy)phenyl)selanyl)-1H-indole **(3g)**: Yield: 0.209 g (92%); white solid; mp 57-58 ºC ^{1}H NMR ($CDCl_3$, 400 MHz) δ (ppm) = 8.27 (br s, 1H), 7.63 (dd, *J* = 7.9, 1H); 7.37 (d, *J* = 2.5 Hz, 1H); 7.34 (d, *J*= 7.9 Hz, 1H); 7.23-7.18 (m, 3H); 7.13 (td, *J* = 7.4 and 1.1 Hz, 1H); 6.67 (d, *J* = 8.7 Hz, 2H); 3.82 (t, *J* = 6.6 Hz, 2H); 1.68 (p, *J* = 6.6 Hz, 2H); 1.32-1.12 (m, 18H); 0.86 (t, *J* = 6.6 Hz, 3H). ^{13}C NMR ($CDCl_3$, 100 MHz) δ(ppm) = 157.9, 136.4, 131.3, 130.5, 129.9, 123.1, 122.8, 120.7, 120.4, 115.4, 111.2, 99.7, 68.1, 31.9, 29.6, 29.6, 29.5, 29.5, 29.3 29.3, 29.2, 26.0, 22.7, 14.1. ^{77}Se NMR (76 MHz, $CDCl_3$) δ (ppm) = 464.5, 202.2. HRMS: Calculated mass for $C_{26}H_{35}NOSe$ $[M+H]^+$: 458.1957, found: 458.1953.

4.2.7. 3-(naphthalen-1-ylselanyl)-1H-indole **(3h)**: Yield: 0.197 g (61%); yellow oil. ^{1}H NMR ($CDCl_3$, 200 MHz) δ (ppm) = 8.37 (s, 1H); 8.29 (d, *J* = 8.3 Hz, 1H); 7.72 (dd, *J* = 7.8 and 1.7 Hz, 1H); 7.64-7.32 (m, 1H); 7.30-6.90 (m, 1H). ^{77}Se NMR (76 MHz, $CDCl_3$) δ (ppm) = 464.5, 175.2. ^{13}C NMR ($CDCl_3$, 100 MHz) δ (ppm) = 136.4, 133.7, 132.5, 131.6, 129.8, 128.4, 126.6, 126.1, 126.0, 125.96, 125.9, 125.5, 122.7, 120.6, 120.1, 111.5, 96.6. HRMS: Calculated mass for $C_{18}H_{13}NSe$ $[M+Na]^+$: 346.0111, found: 346.0112.

4.2.8. 3-(butylselanyl)-1H-indole **(3i)**:[16j] Yield: 0.236 g (93%); collorless oil. ^{1}H NMR ($CDCl_3$, 400 MHz) δ (ppm) = 8.14 (br s, 1H); 7.76-7.72 (m, 1H); 7.38-7.26 (m, 1H); 7.28-7.11 (m, 3H); 2.67 (t, *J* = 7.4 Hz, 2H), 1.58 (p, *J* = 15.2 Hz, 2H), 1.36 (h, *J* = 7.3 Hz, 4H), 0.84 (t, *J* = 7.3 Hz, 3H). ^{13}C NMR ($CDCl_3$, 100 MHz) δ (ppm) = 136.2, 130.3, 122.5, 120.3, 120.2, 111.2, 98.9, 32.6, 28.5, 22.7, 13.5. ^{77}Se NMR (76 MHz, $CDCl_3$) δ (ppm) =

464.5, 94.0.MS (Rel. Int.) *m/z*: 253 (21.3), 196 (17.3), 117 (100), 57 (3.6).

4.2.9. 1-methyl-3-(phenylselanyl)indole **(3j)**:[21g] Yield: 0.244 g (85%); white solid; mp 65-68 °C. ^{1}H NMR ($CDCl_3$, 400 MHz) δ (ppm) = 7.62 (d, *J* = 7.9 Hz, 1H); 7.35 (d, *J* = 7.9 Hz, 1H); 7.29-7.21 (m, 4H); 7.17-7.13 (m, 1H); 7.12-7.04 (m, 3H); 3.80 (s, 3H). ^{13}C NMR ($CDCl_3$, 100 MHz) δ (ppm) = 137.5, 135.6, 134.2, 130.7, 128.9, 128.6, 125.5, 122.4, 120.5, 120.4, 109.5, 96.1, 33.9. ^{77}Se NMR (76 MHz, $CDCl_3$) δ (ppm) = 464.5, 208.8. MS (Rel. Int.) *m/z*: 286 (20.7), 207 (100), 130 (21.3), 91 (1.5), 77 (13.9).

4.2.10. 1-benzyl-3-(phenylselanyl)indole **(3k)**:[26b] Yield: 0.345 g (95%); white solid, mp 77-79 °C. ^{1}H NMR ($CDCl_3$, 400 MHz) δ (ppm) = 7.64 (d, *J* = 7.9 Hz, 1H); 7.34-7.24 (m, 4H); 7.24-7.20 (m, 3H); 7.17-7.10 (m, 6H); 7.39 (s, 1H); 5.35 (s, 2H). ^{13}C NMR ($CDCl_3$, 100 MHz) δ (ppm) = 137.1, 136.7, 135.0, 134.1, 130.9, 128.9, 128.9, 128.6, 127.9, 127.0, 125.5, 122.6, 120.7, 120.6, 110.0, 97.0, 50.4. ^{77}Se NMR (76 MHz, $CDCl_3$) δ (ppm) = 464.5, 210.6. MS (Rel. Int.) *m/z*: 363 (10.7), 283 (42.3), 165 (15.4), 91 (100), 77 (7.5).

4.2.11. 2-methyl-3-(phenylselanyl)-1H-indole **(3l)**:[26c] Yield: 0.246 g (86%); white solid, mp 97-98 ºC. ^{1}H NMR ($CDCl_3$, 400 MHz) δ (ppm) = 8.13 (br s, 1H), 7.55 (d, *J* = 7.8 Hz, 1H), 7.28 (d, *J* = 7.9 Hz, 1H), 7.22 – 7.00 (m, 7H), 2.49 (s, 3H). ^{13}C NMR ($CDCl_3$, 100 MHz) δ (ppm) = 140.8, 135.7, 133.9, 131.2, 128.9, 128.4, 125.3, 122.1, 120.6, 119.7, 110.5, 96.3, 13.1. ^{77}Se NMR (76 MHz, $CDCl_3$) δ (ppm) = 464.5, 285.9. MS (Rel. Int.) *m/z*: 286 (20.9), 206 (100), 130 (54.3), 77 (15.7).

4.2.12. 3-methyl-2-(phenylselanyl)-1H-indole **(3m)**:[26b] Yield: 0.218 g (76%); white solid; mp 136-138 ºC. ^{1}H NMR ($CDCl_3$, 400 MHz) δ (ppm) = 7.97 (br s, 1H); 7.58 (d, *J* = 7.9 Hz, 1H); 7.29-7.20 (m, 1H); 7.20-7.08 (m, 6H), 2.40 (s, 3H). ^{13}C NMR ($CDCl_3$, 100 MHz) δ (ppm) = 137.6, 132.1, 129.3, 128.3, 126.4, 123.1, 119.8, 119.5, 119.3, 118.2, 110.7, 10.3. ^{77}Se NMR (76 MHz, $CDCl_3$) δ (ppm) = 464.5, 285.7. MS (Rel. Int.) *m/z*: 286 (43.2), 206 (100), 130 (66.9), 77 (95.4).

4.2.13. 3-(phenylthio)-1H-indole **(5a)**:[26d] Yield: 0.221 g (98%); white solid; mp 150-151 ºC. ^{1}H NMR ($CDCl_3$, 400 MHz) δ (ppm) = 8.41 (br s, 1H); 7.61 (d, *J* = 8.1 Hz, 1H); 7.49 (d, *J* = 2.6 Hz, 1H); 7.44 (d, *J* = 8.1 Hz, 1H); 7.28-7.26 (m, 2H); 7.18-7.05 (m, 6H). ^{13}C NMR ($CDCl_3$, 100 MHz) δ (ppm) = 139.2, 136.5, 130.6, 129.1, 128.7, 126.1, 125.6, 124.8, 124.1, 121.9, 120.9, 120.7. MS (Rel. Int.) *m/z*: 225 (100), 148 (14.8), 117 (1.8), 77 (23.6).

4.2.14. 3-((4-fluorophenyl)thio)-1H-indole **(5b)**:[26d] Yield: 0.209 g (86%); white solid; mp 133-134 ºC. ^{1}H NMR ($CDCl_3$, 400 MHz) δ (ppm) = 8.30 (br s, 1H); 7.58 (dd, *J* = 8.0 Hz, 1H); 7.47-7.33 (m, 2H); 7.21-7.05 (m, 4H); 6.85 (t, *J* = 8.7 Hz, 1H). ^{13}C NMR ($CDCl_3$, 100 MHz) δ (ppm) = 160.9 (d, *J* = 244.1 Hz); 136.5; 134.0 (d, *J* = 2.4 Hz); 130.4; 127.9 (d, *J* = 7.7 Hz); 122.0; 119.8; 119.5; 115.7 (d, *J* = 22.0 Hz); 111.6; 103.5; 102.6. MS (Rel. Int.) *m/z*: 243 (100), 223 (4.8), 157 (2.8), 117 (6.4).

4.2.15. 3-((3-(trifluoromethyl)phenyl)thio)-1H-indole **(5c)**:[14k] Yield: 0.246 g (84%); white solid, mp 130-132 ºC. ^{1}H NMR ($CDCl_3$, 400 MHz) δ (ppm) = 8.48 (s, 1H); 7.57 (d, *J* = 8.0 Hz, 1H); 7.48 (d, *J* = 2.7 Hz, 1H); 7.43 (d, *J* = 8.0 Hz, 1H); 7.40 (s, 1 H); 7.29-7.15 (m, 6H). ^{13}C NMR ($CDCl_3$, 100 MHz) δ (ppm) = 141.0; 136.6 131.06 (q, *J* = 31.6 Hz); 130.9; 129.0; 128.8 123 (q, *J* = 272.4 Hz); 123.3; 122.4 (d, *J* = 4.2 Hz); 121.5 (d, *J* = 4.0 Hz); 121.2; 119.4; 111.7; 101.6. MS (Rel. Int.) *m/z*: 293 (100), 223 (20.4), 148 (23.9), 116 (3.6), 77 (15.3).

4.2.16. 3-((4-methoxyphenyl)thio)-1H-indole **(5d)**:[20a] Yield: 0.256 g (75%); yellow solid; mp 112-113 °C. ^{1}H NMR ($CDCl_3$, 400 MHz) δ (ppm) = 8.36 (br s, 1H); 7.62 (d, *J* = 7.8 Hz, 1H); 7.39 (d, *J* = 2.6 Hz, 1H); 7.36 (d, *J* = 8.1 Hz, 1H); 7.27-7.17 (m, 1H); 7.16-7.09 (m, 3H); 6.72 (d, *J* = 8.8 Hz, 1H); 3.70 (s, 3H). ^{13}C NMR ($CDCl_3$, 100 MHz) δ (ppm) = 157.8, 136.5, 130.0, 129.5, 129.0, 128.6, 122.8, 120.7, 119.6, 114.5, 111.5, 104.5, 55.30. MS (Rel. Int.) *m/z*: 255 (100), 240 (38.5), 139 (3.9), 117 (2.5), 77 (11.4).

4.2.17. 1-methyl-3-(phenylthio)indole **(5e)**:[20a] Yield: 0.196 g (82%); white solid; mp 85-87 ºC. ^{1}H NMR ($CDCl_3$, 400 MHz) δ (ppm) = 7.60 (d, *J* = 8.0 Hz, 1H); 7.35 (d, *J* = 8.0 Hz, 1H); 7.31-7.22 (m, 2H); 7.18-7.07 (m, 5H); 7.05-6.96 (m, 1H); 3.78 (s, 3H). ^{13}C NMR ($CDCl_3$, 100 MHz) δ (ppm) = 139.7, 137.5, 135.0, 129.8, 128.6, 125.8, 124.6, 122.5, 120.5, 119.7, 109.7, 100.6, 33.0. MS (Rel. Int.) *m/z*: 238 (100), 223 (18.8), 222 (13.5), 196 (3.01), 77 (18.3).

4.2.18. 1-benzyl-3-(phenylthio)indole (**5f**):[26e] Yield: 0.226 g (72%); yellow oil. ^{1}H NMR ($CDCl_3$, 400 MHz) δ (ppm) = 7.53 (d, *J* = 7.4 Hz, 1H); 7.28 (s, 1H); 7.25- 7.16 (m, 4H); 7.15-7.10 (m, 1H); 7.08-6.99 (m, 7H); 6.94 (td, *J* = 6.7 and 1.8 Hz, 1H); 5.21 (s, 2H). ^{13}C NMR ($CDCl_3$, 100 MHz) δ (ppm) = 139.5, 137.2, 136.6, 134.4, 130.0, 129.0, 128.7, 127.9, 128.0, 125.8, 124.7, 122.7, 120.7, 119.9, 110.2, 101.5. MS (Rel. Int.) *m/z*: 315 (86.7), 223 (100), 206 (3.5), 91 (84.6), 77 (14.7).

4.2.19. 2-methyl-3-(phenylthio)-1H-indole **(5g)**:[20a] Yield: 0.207 g (87%); brown solid; mp 110-111 ºC. ^{1}H NMR ($CDCl_3$, 400 MHz) δ (ppm) = 8.10 (s, 1H); 7.53 (d, *J* = 7.8 Hz, 1H); 7.28 (d, *J* = 7.9 Hz, 1H); 7.24-7.07 (m, 4H); 7.07–6.87 (m, 3H); 2.45 (s, 3H).^{13}C NMR ($CDCl_3$, 100 MHz) δ (ppm) = 141.1, 139.3, 135.4, 130.3, 128.7, 125.5, 124.5, 122.1, 120.7, 118.9, 110.6, 99.3, 12.1. MS (Rel. Int.) *m/z*: 239 (18.9), 238 (100), 161 (22,3), 130 (13.7), 118 (20.7), 91 (5.3), 77 (14.5).

4.2.20. 3-methyl-2-(phenylthio)-1H-indole **(5h)**:[26f] Yield: 0.177 g (74%); white solid; mp 76-77 °C. ^{1}H NMR ($CDCl_3$, 400 MHz) δ (ppm) = 7.89 (s, 1H); 7.58 (d, *J* = 8.0 Hz, 1H); 7.31-7.06 (m, 6H); 7.06-6.98 (m, 2H); 2.38 (s, 3H). ^{13}C NMR ($CDCl_3$, 100 MHz) δ (ppm) = 137.1, 136.9, 129.1, 128.5, 126.5, 125.7, 123.5, 121.5, 119.8, 119.6, 119.4, 110.9, 9.4. MS (Rel. Int.) *m/z*: 239 (100), 161 (17.4), 130 (21.7), 91 (5.4), 77 (19.4).

4.3 Procedure for preparation of 1-tolyl-3-(phenylselenyl)-1*H*-indole (6a):[35] An oven-dried resealable Schlenk tube was charged with CuI (9,5 mg, 0.05 mmol, 5 mol%), 1.10-phenanthroline (36 mg, 0.2 mmol, 20 mol%), Cs_2CO_3 (456 mg, 1.4 mmol), 1-iodo-4-metilbenzene (218 mg, 1 mmol), evacuated and backfilled with argon. 3-(Phenylselenyl)-1*H*-indole (3a) (273 mg, 1 mmol) and DMF (1.0 mL) were added under argon. The Schlenk tube was sealed and the reaction mixture was stirred at 110 °C for 24 h. The resulting suspension was cooled to room temperature and filtered through a 0.5×1 cm pad of silica gel eluting with EtOAc. The filtrate was concentrated under vacuum and the crude product was purified by chromatography on silica gel (2× 30 cm; hexane–EtOAc 95:5) affording 203 mg (56% yield) of the compound as a pale brown oil.

4.3.1. 1-tolyl-3-(phenylselenyl)-1H-indole **(6a)**: Yield: 0.203 g (56%); brown oil. ^{1}H NMR ($CDCl_3$, 400 MHz) δ (ppm) = 7.68 (d, *J* = 8.0 Hz, 1H); 7.57 (s, 1H); 7.53 (d, *J* = 8.2 Hz, 1H); 7.39 (d, *J* = 8.3 Hz, 2H); 7.31 (dd, *J* = 8.1, 1.5 Hz, 4H); 7.30-7.05 (m, 6H); 2.43 (s, 3H). ^{13}C NMR ($CDCl_3$, 100 MHz) δ (ppm) = 137.0, 136.9, 136.5, 134.5, 133.6, 131.1, 130.3, 129.0, 128.9, 125.7, 124.4, 123.1, 121.2, 120.7, 110.8, 98.9, 21.0. HRMS: Calculated mass for $C_{21}H_{17}NSe$ $[M+]^+$: 363.0526, found: 363.0532.

4.4 Procedure for preparation of 3-(phenyl)-1*H*-indole (6b):[29] A mixture of 3-(butylselanyl)-1*H*-indole (0.25 mmol), $Pd(PPh_3)_4$ (0.1 equiv) and phenylboronic acid (1.2 equiv) were dissolved in DMF (3 mL). After this, the $Cu(OAc)_2.H_2O$ (1.2 equiv) was added. This mixture was then heated in oil bath for 1 h at 80 °C. After the reaction was cooled to room temperature, diluted with AcOEt (3 mL) and then washed with saturated solution of NH_4Cl (20 mL). The organic phase was separated, dried over $MgSO_4$ and concentrated under vacuum. The crude product was purified by flash chromatography and eluted with hexane.

4.4.1. 3-phenyl-1H-indole **(6b)**:[36] Yield: 0.0226 g (47%); White solid; mp 85-87 °C. ^{1}H NMR ($CDCl_3$, 400 MHz) δ (ppm) = 8.22 (s, 1H), 7.79 (d, *J* = 7.9 Hz, 1H), 7.71 (d, *J* = 7.6 Hz, 2H), 7.50-7.44 (m, 3 H), 7.38 (d, *J* = 0.9 Hz, 1H), 7.31-7.27 (m, 4 H). ^{13}C NMR ($CDCl_3$, 100 MHz) δ (ppm) = 136.7, 135.6 , 128.8, 127.5 ,

126.0, 125.8, 122.4, 121.7, 120.3, 120.0, 118.4, 111.4. MS (Rel. Int.) *m*/z: 193 (100), 165 (24.6), 77 (3.4).

4.5 Procedure for preparation of 1-benzyl-3-(phenylselanyl)indole (3k):[14u] A mixture of **3a** (0,3 mmol; 0,090 g), benzyl chloride (0,4 mmol; 0,050 g mmol), K_2CO_3 (0,3 mmol; 0,041), TBAB (30 mol%; 0,09 mmol; 0,029 g) and DMF (2 ml) was stirred at room temperature for 2 h. At the end of this period, the mixture was poured into cold-water (50 ml) and extracted with EtOAc. The organic layer was separated, washed with a saturated solution of $NaHCO_3$ (10 ml), followed by brine (10 ml) and dried over $MgSO_4$. The solvent was evaporated to give the crude product, and then purified by flash chromatography eluted with hexane, affording 81 mg of desired product (74%); white solid, mp 77-79 °C.).[26b]

Acknowledgements

This study was financed in part by the Coordenação de Aperfeiçoamento de Pessoal de Nível Superior – Brasil (CAPES) – Finance Code 001, CNPq Process: 400400/2016-2, Fundação Araucária and UFPR.

References and Notes

1 (a) Dalpozzo, R. *Chem. Soc. Rev*. **2015**, *44*, 742-778; (b) Karamyan, A. J. K.; Hamann, M. T. *Chem. Rev*. **2010**, *110*, 4489-4489; (c) Bandini, M.; Eichholzer, A. *Angew. Chem. Int. Ed*. **2009**, *48*, 9608-9644; (d) Chelucci, G. *Coord. Chem. Rev*. **2017**, *331*, 37-53; (e) Sandtorv, A. H. *Adv. Synth. Catal*. **2015**, *357*, 2403-2435; (f) Leitch, J. A.; McMullin, C. L.; Mahon, M. F.; Bhonoah, Y.; Frost, C. G. *ACS Catal*. **2017**, *7*, 2616-2623. (g) Humphrey, G. R.; Kuethe, J. T. *Chem. Rev*. **2006**, *106*, 2875-2911; (h) Taber, D. F.; Tirunahari, P. K. *Tetrahedron* **2011**, *67*, 7195-7210; (i) Gribble, G. W. *J. Chem. Soc., Perkin Trans*. 1, **2000**, 1045-107; (j) Bagdi, A. K.; Santa, S.; Monir, K.; Hajra, A. *Chem. Commun.* **2015**, *51*, 1555-1575; (k) Cai, D.; Byth, K. F.; Shapiro, G. I. *Cancer Res.* **2006**, *66*, 435-444; (l) Byth, K. F.; Geh, C.; Forder, C. L.; Oakes, S. E.; Thomas, A. P. *Mol. Cancer Ther*. **2006**, *5*, 655-664.

2 (a) Napper, A. D.; Hixon, J.; McDonagh, T.; Keavey, K.; Pons, J. F.; Barker, J.; Thomas, R. J. *J. Med. Chem*. **2005**, *48*, 8045-8054; (b) Craig, S.; Gao, L.; Lee, I.; Gray, T.; Berdis, A. J. *J. Med. Chem*. **2012**, *55*, 2437-2451; (c) de Sa, A.; Fernando, R.; Barreiro, R. J.; Fraga, M.; Alberto, C. *Mini Rev. Med. Chem*. **2009**, *9*, 782-793; (d) Weng, J. R.; Omar, H. A.; Kulp, S. K.; Chen, C. S. *Mini Rev. Med. Chem*. **2010**, *10*, 398-404; (e) Vitaku, E.; Smith, D. T.; Njardarson, J. T. *J. Med. Chem*. **2014**, *57*, 10257-10274; (f) Kaushik, N. K.; Kaushik, N.; Attri, P.; Kumar, N.; Kim, C. H.; Verma, A. K.; Choi, E. H. *Molecules*. **2013**, *18*, 6620-6662.

3 (a) Lee, C. W.; Lee, J. Y.; *Adv. Mater*. **2013**, *25*, 5450-5454; (b) Wang, Z.; Li, K.; Zhao, D.; Lan, J.; You, J. *Angew. Chem. Int. Ed*. **2011**, *50*, 5365-5369; (c) Verma, C. J.; Pandey, R. K.; Prakash, R. *Mat. Sci. Eng. b*. **2018**, *227*, 80-88; (d) Mishra, R.; Gupta, S.; Kumar, A.; Prakash, R. *Mater. Chem. Phys*. **2017**, *183*, 606-614; (e) Phasuksom, K.; Sirivat, A. *Synthetic Met*. **2016**, *219*, 142-153; (f) Zhou, X.; Chen, Q.; Wang, A.; Xu, J.; Wu, S.; Shen, J. *ACS Appl. Mater. Interfaces*, **2016**, *8*, 3776-3783; (g) Zhou, X.; Wang, A. Q.; Pan, Y. M.; Yu, C. F.; Zou, Y.; Zhou, Y.; Chen, Q.; Wu, S. S. *J. Mater. Chem. A*. **2015**, *3*, 13011-13015.

4 (a) Jiang, H. X.; Zhuang, D. M.; Huang, Y.; Cao, X. X.; Yao, J. H.; Li, J. Y.; Jiang, B. *Org. Biomol. Chem*. **2014**, *12*, 3446-3458; (b) Zhang, M. Z-.; Chen, Q.; Yang, G. F. *Eur. J. Med. Chem*. **2015**, *89*, 421-441; (c) Ashok, P.; Lu, C. L.; Chander, S.; Zheng, Y. T.; Murugesan, S. *Chem. Biol. Drug. Des*. **2015**, *85*, 722-728; (d) La Regina, G.; Coluccia, A.; Brancale, A.; Piscitelli, F.; Gatti, V.; Maga, G.; Novellino, E. *J. Med. Chem*. **2011**, *54*, 1587-1598; (e) Nuth, M.; Guan, H.; Zhukovskaya, N.; Saw, Y. L.; Ricciardi, R. P. *J. Med. Chem*. **2013**, *56*, 3235-3246.

5 (a) Prakash, B.; Amuthavalli, A.; Edison, D.; Sivaramkumar, M. S.; Velmurugan, R. *Med. Chem. Res.* **2018**, *27*, 321-331; (b) Johnson, I. S.; Armstrong, J. G.; Gorman, M.; Burnett, J. P. *Cancer Res*. **1963**, *23*, 1390-1427; (c) Megna, B. W.; Carney, P. R.; Nukaya, M.; Geiger, P.; Kennedy, G. D. *J. Surg. Res*. **2016**, *204*, 47-54; (d) Gehrcke, M.; Giuliani, L. M.; Ferreira, L. M.; Barbieri, A. V.; Sari, M. H. M.; da Silveira, E. F.; Cruz, L. *Mater. Sci. Eng. C*. **2017**, *74*, 279-286; (e) Cai, M.; Hu, J.; Tian, J. L.; Yan, H.; Zheng, C. G.; Hu, W. L. *Chin. Chem. Lett*. **2015**, *26*, 675-680; (f) Youssif, B. G.; Abdelrahman, M. H.; Abdelazeem, A. H.; Ibrahim, H. M.; Salem, O. I.; Mohamed, M. F.; Bukhari, S. N. A. *Eur. J. Med. Chem*. **2018**, *146*, 260-273; (g) Shaw, S.; Bian, Z.; Zhao, B.; Tarr, J. C.; Veerasamy, N.; Jeon, K.; Sensintaffar, J. L. *J. Med. Chem*. **2018**, *61*, 2410-2421; (h) Pelz, N. F.; Bian, Z.; Zhao, B.; Shaw, S.; Tarr, J. C.; Belmar, J.; Sensintaffar, J. L. *J. Med. Chem*. **2016**, *59*, 2054-2066; (i) Suzen, S. *Curr. Org. Chem*. **2017**, *21*, 2068-2076.

6 (a) Funk, C. D. *Nat. Rev. Drug Discovery* **2005**, ***4***, 664-672; (b) Kumar, A.; Agarwal, J. C.; Nath, C.; Gurtu, S.; Sinha, J. N.; Bhargava, K. P.; Shanker, K. *J. Heterocyclic Chem.* **1981**, *18*, 1269-1271.

7 (a) Abraham, R.; Prakash, P.; Mahendran, K.; Ramanathan, M. *Microb. Pathogenesis*, **2018**, *114*, 409-413; (b) Unangst, P. C.; Connor, D. T.; Stabler, S. R.; Weikert, R. J.; Carethers, M. E.; Kennedy, J. A.; Thueson, D. O.; Chestnut, J. C.; Adolphson, R. L.; Conroy, M. C. *J. Med. Chem.* **1989**, *32*, 1360-1366.

8 (a) Zoraghi, R.; S. Campbell, S.; Kim, C.; Dullaghan, E. M.; Blair, L. M.; Gillar, R. M.; Sperry, J. *Bioorg. Med. Chem. Lett*. **2014**, *24*, 5059-5062; (b) Daly, S.; Hayden, K.; Malik, I.; Porch, N.; Tang, H.; Rogelj, S.; Magedov, I. V. *Bioorg. Med. Chem. Lett.* **2011**, *21*, 4720-4723; (c) Nandakumar, A.; Thirumurugan, P.; Perumal, P. T.; Vembu, P.; Ponnuswamy, M. N.; Ramesh, P. *Bioorg. Med. Chem. Lett.* **2010**, *20*, 4252-4258; (d) La Regina, G.; Bai, R.; Rensen, W. M.; Di Cesare, E.; Coluccia, A.; Piscitelli, F.; Famiglini, V.; Regio, A.; Nalli, M.; Pelliccia, S.; Da Pozzo, E.; Costa, B.; Granata, I.; Porta, A.; Maresca, B.; Soriani, A.; Iannitto, M. L.; Santoni, A.; Li, J.; Cona, M. M.; Chen, F.; Ni, Y.; Brancale, A.; Dondio, G.; Vultaggio, S.; Varasi, M.; Mercurio, C.; Martini, C.; Hamel, E.; Lavia, P.; Novellino, E.; Silvestri, R. J. *Med. Chem*. **2013**, *56*, 123-149.

9 (a) Campbell, J. A.; Bordunov, V.; Broka, C. A.; Browner, M. F.; Kress, J. M.; Mirzadegan, T.; Villasenor, A. *Bioorg. Med. Chem. Lett*. **2004**, *14*, 4741-4745; (b) Lamie, P. F.; Ali, W. A.; Bazgier, V.; Rárová, L. *Eur. J. Med. Chem* . **2016**, *123*, 803-813.

10 (a) Chagas, P. M.; Bortolatto, C. F.; Wilhelm, E. A.; Roehrs, J. A.; Nogueira, C. W. *Behav. Pharmacol.* **2013**, *24*, 37-44; (b) Pavin, N. F.; Donato, F.; Cibin, F. W.; Jesse, C. R.; Schneider, P. H.; de Salles, H. D.; Savegnago, L. *Eur. J. Pharm.* **2011**, *668*, 169-176.

11 For some examples, see: (a) Parnham, M. J.; Graf, E. *Prog. Drug. Res.* **1991**, *36*, 9-47; (b) Woods, J. A.; Hadfield, J. A.; McGown, A. T.; Fox, B. W. *Bioorg. Med. Chem*. **1993**, *1*, 333-340; (c) Nogueira, C. W.; Zeni, G.; Rocha, J. B. T. *Chem. Rev.* **2004**, *104*, 6255-6286; (d) Engman, L.; Cotgreave, I.; Angulo, M.; Taylor, C. W.; Paine-Murrieta, G. D.; Powis, G. *Anticancer Res.* **1997**, *17*, 4599-4605; (e) Millois, C.; Diaz, P. *Org. Lett.* **2000**, *2*, 1705-1708; (f) Meotti, F. C.; Silva, D. O.; dos Santos, A. R. S.; Zeni, G.; Rocha, J. B. T.; Nogueira, C. W. *Environ. Toxicol. Pharmacol*. **2003**, *15*, 37-44.

12 (a) M.Freudendahl, D.; Santoro, S.; Shahzad, S. A.; Santi, C.; Wirth, T. *Angew. Chem. Int. Ed.* **2009,** *48*, 8409-8411; *Angew. Chem*. **2009**, *121*, 8559-8562; (b) Godoi, M.; Paixão, M. W.; Braga, A. L. *Dalton Trans.* **2011**, *40*, 11347-11355; (c) Reich, H. J. J. *J. Org. Chem.* **1975**, *40*, 2570-2572; (d) Sharpless, K. B.; Laurer, R. F. *J. Am. Chem. Soc*. **1972**, *94*, 7154-7155; (e) Frizon, T. E. A.; Rafique, J.; Saba, S.; Bechtold, I. V.; Gallardo, H.; Braga, A. L. *Eur. J. Org. Chem.* **2015**, 3470-3476; (f) Ho, P. C. -W.; Rafique, J.; Lee, J.; Lee, M. L. L.; Jenkins, H. A.; Britten, J. F.; Braga, A. L.; Vargas-Baca, I. *Dalton Trans.* **2017**, *46*, 6570-6579.

13 (a) Rampon, D. S.; Rodembusch, F. C.; Schneider, J. M. F. F.; Bechtold, I. H.; Goncalves, P. F. B.; Merlo, A.; Schneider, P. H. J. *Mater. Chem.* **2010**, *20*, 715-722; (b) Patra, A.; Bendikov, M. J. *Mater. Chem.* **2010**, *20*, 422-433; (c) Patra, A.; Wijsboom, Y. H.; Zade, S. S.; Li, M.; Sheynin, Y.; Leitus, G.; Bendikov, M. J. *J. Am. Chem. Soc.* **2008**, *130*, 6734- 6736; (d) Li, M.; Sheynin, Y.; Patra, A.; M. Bendikov, M. *Chem. Mater.* **2009**, *21*, 2482-2488; (e) Hou, J.; Park, M. -H.; Zhang, S.; Yao, Y.; Chen, L.-M.; Li, J. -H.; Yang, Y. *Macromolecules*. **2008**, *41*, 6012-6018; (f) Kim, B.; Yeom, H. R.; Yun, M. H.; Kim, J. Y.; Yang, C. *Macromolecules **2012**, 45*, 8658-8664; (g) Gao, D.; Hollinger, J.; Seferos, D. S. *ACS Nano*. **2012**, *6*, 7114-7121; (h) Palermo, E. F.; McNeil, A. J.; *Macromolecules* **2012**, *45*, 5948-5955; (i) Haid, S.; Mishra, A.; Uhrich, C.; Pfeiffer, M.; Bauerle, P. *Chem. Mater*. **2011**, *23*, 4435-4444; (j) Okamoto, T.; Kudoh, K.; Wakamiya, A.; Yamaguchi, S. *Org. Lett.* **2005**, *7*, 5301-5304; (k) Takimiya, K.; Kunugi, Y.; Konda, Y.; Ebata, H.; Toyotakimia, Y.; Otsubo, T. *J. Am. Chem. Soc.* **2006**, *128*, 3044-3050; (l) Patra, A.; Wijsboom, Y. H.; Leitus, G.; Bendikov, M. *Chem. Mater*. **2011**, *23*, 896-906; (m) Perepichka, I. F.; Perepichka, D. F.; Handbook of Thiophene-based Materials; Wiley-VCH: Weinheim, **2009**; (n) Rampon, D. S.; Rodembusch, F. S.; Schneider, J. M. F. M.;

Bechtold, I. H.; Gonçalves, P. F. B.; A. Merlo, A.; Schneider, P. H. *J. Mater. Chem.* **2010**, *20*, 715-722; (o) Mei, J.; Diao, Y.; Appleton, A. L.; Fang, Z.; Bao, Z. *J. Am. Chem. Soc.* **2013**, *135*, 6724-6746.

14 (a) Anzai, K. *J. Heterocyclic Chem.* **1979**, *3*, 567; (b) Tudge, M.; Tamiya, M.; Savarin, C.; Humphrey, G. R. *Org. Lett.* **2006**, *8*, 565-568; (c) Matsugi, M.; Murata, K.; Gotanda, K.; Nambu, H.; Anilkumar, G.; Matsumoto, K.; Kita, Y. *J. Org. Chem.* **2001**, *66*, 2434-2441; (d) Varun, B. V.; Prabhu, K. R. *J. Org. Chem.* **2014**, *79*, 9655-9668; (e) Xiao, F.; Xie, H.; Liu, S.; Deng, G. J. *Adv. Synth. Catal.* **2014**, *356*, 364-368; (f) Yang, F. L.; Tian, S. K. *Angew. Chem.* **2013**, *125*, 5029-5032; (g) Raghuvanshi, D. S.; Verma, N. *RSC Adv.* **2017**, *7*, 22860-22868; (h) Nookaraju, U.; Begari, E.; Yetra, R. R.; Kumar. P. *Chemistry Select* **2016**, *1*, 81-84; (i) Subbarayappa, A.; Ravi, C.; Ravi, X. A. *Eur. J. Org. Chem.* **2017**, 3646-3651; (j) Silveira, C. C.; Mendes, S. R.; Wolf, L.; Martins, G. M. *Tetrahedron Lett.* **2010**, *51*, 2014-2016; (k) Kumaraswamy, G.; Rajua, R.; Narayanarao, V. *RSC Adv.* **2015**, *5*, 22718-22723; (l) Wang, D.; Guo, S.; Zhang, R.; Lin, S.; Ya, Z. *RSC Adv.* **2016**, *6*, 54377-54381; (m) Yang, F.; Tian, S. *Angew. Chem. Int. Ed.* **2013**, *125*, 5029-5032; (n) Yang, Y.; Zhang, S.; Tang, L.; Hu, Y.; Zha, Z.; Wang, Z. *Green Chem.* **2016**, *18*, 2609-2613; (o) Li, J.; Cai, Z.; Wang, S.; Ji, S.; *Org. Biomol. Chem.* **2016**, *14*, 9384-9387; (p) Wang, F. X.; Zhou, S. D.; Wang, C.; Tian, S. K. *Org. Biomol. Chem.* **2017**, *15*, 5284-5288; (q) He, Y.; Jiang, J.; Bao, W.; Deng, W.; Xiang. J. *Tetrahedron Lett.* **2017**, *58*, 4583-4586; (r) Zimmermann, E. G.; Thurow, S.; Freitas, C. S.; S. R. Mendes, S. R.; G. Perin, G.; Alves, D.; Jacob, R. G.; Lenardão E. J. *Molecules* **2013**, *18*, 4081-4090; (s) Matsugi, M.; Murata, K.; Gotanda, K.; Nambu, H.; Anilkumar, G.; Matsumoto, K.; Kita, Y. *J. Org. Chem.* **2001**, *66*, 2434-2441; (t) Yang, F.-L.; Tian, S. -K. *Angew. Chem. Int. Ed.* **2013**, *52*, 4929-5032; (u) Kumar, P. P.; Reddy, Y. D.; Reddy, V. R.; Devi, D. R.; Dubey, P. K. *J. of Sulfur Chem.* **2014**, *35*, 356-361.

15 (a) Huang, D.; Chen, J.; Dan, W.; Ding, J.; Liu, M.; Wu, H. *Adv. Synth. Catal.* **2012**, *354*, 2123-2128; (b) Silveira, C. C.; Mendes, S. R.; Wolf, L.; Martins, G. M.; von Mühlen, L. *Tetrahedron* **2012**, *68*, 10464-10469; (c) Zou, L. H.; Reball, J.; Mottweiler, J.; Bolm, C. *Chem. Commun*. **2012**, *48*, 11307-11309; (d) Dong, D. Q.; Hao, S. H.; Yang, D. S.; Li, L. X.; Wang, Z. L. *Eur. J. Org. Chem.* **2017**, 6576-6592; (e) We, W.; Wei, Y. *Green Chem.* **2012**, *14*, 2066-2070.

16 (a) Leitch, J. A.; Bhonoah, Y.; Frost, C. G. *ACS Catal.* **2017**, *7*, 5618-5627; (b) Yang, L.; Huang, H. *Chem. Rev.* **2015**, *115*, 3468-3517; (c) Guo, T.; Huang, F.; Yu, L.; Yu, Z. *Tetrahedron Lett.* **2015**, *56*, 296-302; (d) Song, W.; Ackermann, L. *Chem. Commun*. **2013**, *49*, 6638-6640; (e) Wang, H.; Moselage, M.; Gonzalez, M. J.; Ackermann, L. *ACS Catal.* **2016**, *6*, 2705-2709; (f) Ackermann, L.; Lygin, A. V. *Org. Lett.* **2012**, *14*, 764-767; (g) Ackermann, L.; Barfüßer, S.; Potukuchi, H. K. *Adv. Synth. Catal.* **2009**, *351*, 1064-1072; (h) T. -S.; Kou, L.; Ma, S.; Engle, K. M.; Yu, J. -Q. *Synthesis* **2012**, *44*, 1778-1791; (i) Wallis, J. D.; Dunitz, J. D. *Chem. Commun*. **1983**, 910–911; (j) Vieira, B. M.; Thurow, S.; Brito, J. S.; Perin, G.; Alves, D.; Jacob, R. G.; Lenardão, E. J. *Ultrason. Sonochem.* **2015**, *27*, 192-199; (k) Gogoi, P.; Gogoi, S. R.; Kalita, M.; Barman, P. *Synlett*. **2013**, *24*, 873-877.

17 Gandeepan, P.; Koeller, J.; Ackermann, L. *ACS Catal*. **2017**, *7*, 1030-1034.

18 Cotton, F. A.; Wilkinson, G. *Anorg. Chem.* 4th ed.; Verlag Chemie: Weinheim, **1982**, p 767.

19 (a) Shang, R.; Llies, L.; Nakamura, E. *Chem. Rev.* **2017**, *117*, 9086-9139; (b) Fürstner, A. *ACS Cent. Sci.* **2016**, *2*, 778-789; (c) Balamaran, E.; Nandakumar, A.; Jaiswal, G.; Sahoo, M. K. *Catal. Sci. Technol.* **2017**, *7*, 3177-3195; (d) Bauer, I.; Knölker, H. J. *Chem. Rev.* **2015**, *115*, 3170–3387; (e) Bolm, C.; Legros, J.; Le Paih, J.; Zani, L. *Chem. Rev.* **2004**, *104*, 6217−6254; (f) Jia, F.; Li. Z. *Org. Chem. Front.* **2014**, *1*, 194–214. (g)

20 (a) Fang, X. L.; Tang, R. Y.; Zhong, P.; Li, J. H. *Synthesis*, **2009**, 4183-4189; (b) Yadav, J. S.; Reddy, B. V. S.; Reddy, Y. J.; Praneeth, K. *Synthesis*, **2009**, 1520-1524.

21 (a) Vieira, A. A.; Azeredo, J. B.; Godoi, M.; Santi, C.; da Silva Junior, E. N.; Braga, A. L. *J. Org. Chem.* **2015**, *80*, 2120-2127; (b) Wang, X.; Stanbury, D. D. *Inorg. Chem.* **2006**, *45*, 3415-3423; (c) Nikolaychuk, P. A.; Kuvaeva, A. O. *J. Chem. Educ.* **2016**, *93*, 1267-1269; (d) Vrkljan, P. B.; Bauer, J.; Tomisic, V. *J. Chem. Educ*, **2008**, *85*, 1123-1125; (e) Maitlis, P. M.; Haynes, A.; James, B. R.; Catellani, M.; Chiusoli, G. P. *Dalton Trans.* **2004**, *21*, 3409-3419; (f) Yusubov, M. S.; Zhdankin, V. V.; *Resource-Efficient Technologies 1*, **2015**, *1*, 49-67. (g) Azeredo, J. B.; Godoi, M.; Martins, G. M.; Silveira, C. C.; Braga, A. L. *J. Org. Chem.* **2014**, *79*, 4125-4130.

22 Iranpoor, N.; Zeynizadeh, B. *Synthesis*, **1999**, 49-50.

23 (a) Higashi, L.; Lundeen, M.; Hilti, E.; Seff, K. *Inorg. Chem.* **1977**, *16*, 310-313; (b) Vásquez-Céspedes, S.; Ferry, A.; Candish, L.; Glorius, F. *Angew. Chem. Int. Ed.* **2015**, *54*, 5772-5776.

24 Thomé, I.; Nijs, A.; Bolm. C. *Chem. Soc. Rev.* **2012**, *41*, 979-987.

25 For general reviews on Plancher rearrangement: (a) Wang, Z. *Comprehensive Organic Name Reactions and Reagents*, John Wiley & Sons, **2010**; 2248-2250; (b) Mari, M.; Lucarini, S.; Bartoccini, F.; Piersanti, G.; Spadoni, G. *Beilstein J. Org. Chem.* **2014**, *10*, 1991-1998; (c) Jackson, H.; Smith, A. E. *Tetrahedron* **1968**, *24*, 2227-2239; (d) Jackson, A. H.; Naidoo, B.; Smith, P. *Tetrahedron* **1968**, *24*, 6119-6129; (g) Biswas, K. M.; Jackson, A. H. *Tetrahedron* **1969**, *25*, 227-241; (h) Liu, K. G.; Robichaud, A. J.; Lo, J. R.; Mattes, J. F.; Cai, Y. *Org. Lett.* **2006**, *8*, 5769-5771; (i) Hamel, P.; Préville, P. *J. Org. Chem.* **1996**, *61*, 1573-1577.

26 (a) Luo, D.; Wu, G.; Yang, H.; Liu, M.; Gao, W.; Huang, X.; Chen, J.; Wu, H. *J. Org. Chem.* **2016**, *81*, 4485-4493; (b) Zhao, X.; Yu, Z.; Xu, T.; Wu, P.; Yu, H. *Org. Lett.* **2007**, *9*, 5263-5266; (c) Barton, D. H. R.; Lusinchi, X.; Milliet, P. *Tetrahedron Lett.* **1982**, *23*, 4949-4952; (d) Ranjit, S.; Lee, R.; Heryadi, D.; Shen, C.; Wu, J.; Zhang, P.; Huang, K. W.; Liu, X. *J. Org. Chem.* **2011**, *76*, 8999-9007; (e) Li, Z.; Hong, J.; Zhou, X. *Tetrahedron*, **2011**, *67*, 3690-3697; (f) Rahaman, R.; Devi, N.; Sarma, K.; Barman, P. *RSC Adv.* **2016**, *6*, 10873-10879.

27 Beletskaya, I. P.; Ananikov, V. P. *Chem. Rev.* **2011**, *111*, 1596-1636.

28 (a) Sambiagio, C.; Marsden, S. P.; Blacker, A. J.; McGowan, P. C. *Chem. Soc. Rev.* **2014**, *43*, 3525-3550; (b) Wolter, M.; Klapars, A.; Buchwald, S. L. *Org. Lett.* **2001**, *3*, 3803-3805.

29 Stein, A. L.; Bilheri, F. N.; Zeni, G. *Chem. Commun.* **2015**, *51*, 15522-15525.

30 Weil, J. A.; Bolton, J. R. *Electron Paramagnetic Resonance – Elementary Theory and Practical Applications*, 2nd ed., John Wiley & Sons, Inc. Hoboken, New Jersey. **2007**.

31 Castner, T.; Newell, G. S.; Holton, W. C.; Slichter, C. P.; *J. Chem. Phys.* **1960**, *32*, 668–673.

32 (a) Tamres, M.; Bhat, S. N. *J. Am. Chem. Soc.* **1972**, *94*, 2577-2578; (b) Lo, S. J.; Tamres, M.; Can, M. *J. Chem.* **1983**, *61*, 1933-1940.

33 It seems plausible that in absence of DMSO, the $FeCl_3$ catalyst acts only as Lewis acid, and the coordination of selenium atom in diorganoyl diselenide to Fe(III) could produce a stronger electrophile (energy reduction of σ*Se-Se orbital), which facilitates the nucleophilic attack of indole C3 position. In this way, the O_2 could oxidize the Fe(III) aryl(or alkyl) selenolates produced *in situ* in order to regenerate the diorganoyl diselenides and close the catalytic cycle. See references 16j and 16k (and references herein). However, it is clear that this is an inefficient pathway, which requires harsh conditions.

34 (a) Kubiniok, S.; du Mont, W.-W.; Pohl, S.; Saak, W. *Angew. Chem. Int. Ed. Engl*. **1988**, *27*, 431-433; (b) Barnes, N. A.; Godfrey, S. M.; Hughes, J.; Khan, R. Z.; Mushtaq, I.; Ollerenshaw, R. T. A.; Pritchard, R. G.; Sarwar, S. *Dalton Trans*. **2013**, *42*, 2735-2744.

35 Wolter, M.; Klapars, A.; Buchwald, S. L. *Org. Lett.* **2001**, *3*, 3803-3805.

36 Chen, J.; Wu, J. *Angew. Chem. Int. Ed.* **2017**, *56*, 3951-3955.