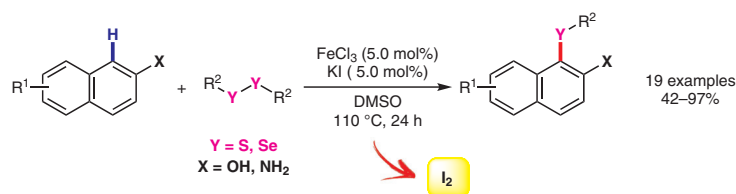



# Chalcogenylation of Naphthalene Derivatives Catalyzed by Iron(III) Chloride and Potassium Iodide

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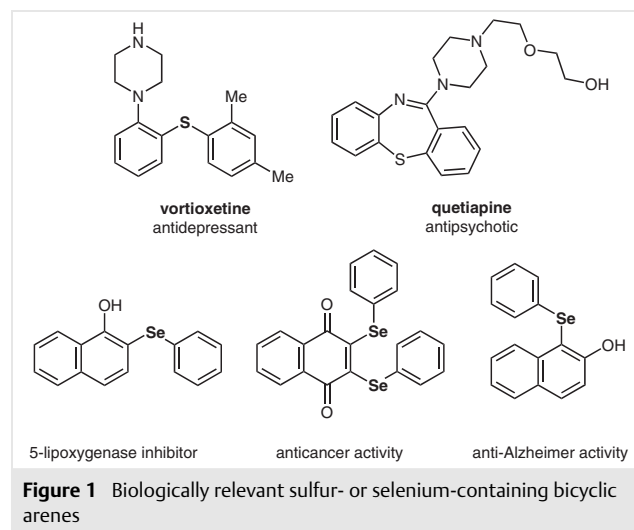
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**Abstract** We have developed an efficient chalcogenylation of electron-rich naphthalene derivatives catalyzed by  $\text{FeCl}_3$  and KI. The methodology provides access to several nonsymmetrical diorganoyl chalcogenides (S, Se) by selective C1 chalcogenylation of 2-naphthols or 2-naphthylamines using simple and cheap catalysts. Several control experiments supported the hypothesis that a redox reaction between Fe(III) and KI produces  $\text{I}_2$ , which catalyzed the chalcogenylation.

**Key words** iron catalysis, potassium iodide catalysis, sulfanylation, selenylation, naphthylamines, naphthols

Substituted naphthalene derivatives are a recognized class of compounds that form the main structural scaffolds of several relevant natural products.<sup>1</sup> These derivatives also have found outstanding applications in materials science,<sup>2</sup> and numerous commercially available drugs have such moieties in their core structures.<sup>3</sup> As a result, many efforts have been directed toward the development of new methods for the regioselective synthesis of substituted naphthalene compounds.<sup>4</sup> In particular, the efficient and selective conversion of a  $\text{C}(\text{sp}^2)\text{-H}$  bond into a  $\text{C-chalcogen}$  (S, Se, Te) bond in naphthalene derivatives has received considerable attention<sup>5,6</sup> because of the potential therapeutic applications of the organochalcogen compounds,<sup>7</sup> as well their exceptional properties as organic optoelectronic materials.<sup>8</sup> As examples of the importance of organochalcogenides, the nonsymmetrical organosulfide vortioxetine is an antidepressant used to treat adults with major depressive disorder,<sup>7i,j</sup> and quetiapine is an atypical antipsychotic that is indicated for the treatment of schizophrenia and bipolar disorders, including bipolar depression (Figure 1).<sup>7k,l</sup> Moreover, a number of selenium-containing bicyclic arenes have been also reported to have a range of attractive biological properties, including 5-lipoxygenase inhibition,<sup>7m</sup> anticancer,<sup>7n</sup> anti-inflammatory,<sup>7o</sup> and anti-Alzheimer activities,<sup>9q</sup> among others.<sup>7p-r</sup>

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**Figure 1** Biologically relevant sulfur- or selenium-containing bicyclic arenes

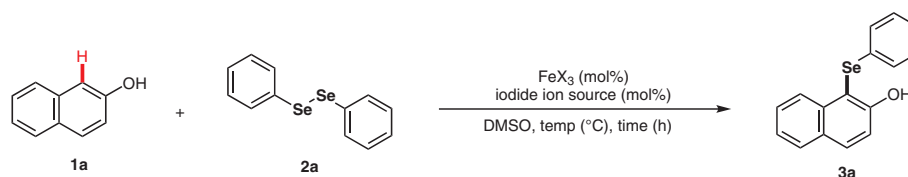
Given the prominent status of the naphthalenes functionalized with organochalcogen groups, the development of cheap and efficient methods for preparing these compounds is highly desirable. Generally, the chalcogenylation

of bicyclic arenes and hetarenes is performed by using various electrophilic organochalcogen reagents, which are often formed in situ, in combination with electron-rich aromatic compounds.<sup>5a-j,5l,m,6a-c,9a-o</sup> Among electron-rich naphthalenes, the regioselective chalcogenylation of naphthols remains challenging, and only recently have some feasible methods been described. In this respect, the transition-metal-free sulfanylation of naphthols has received attention. However, many of the existing methods require handling of difficult reagents that require multistep preparation.<sup>5a-i</sup> Additionally, the base-promoted chalcogenylation of naphthols seems to be an efficient and cheap method, although the presence of a hydroxy group is a prerequi-

site.<sup>5l,6c-e</sup> Moreover, an electrochemical selenylation of several activated arenes at Pt electrodes in an undivided electrochemical cell has also been described.<sup>6a</sup>

Transition-metal-catalyzed direct chalcogenylations of 1- or 2-naphthols have also been developed but, until now, were limited to sulfanylations exclusively and required the use of Pd,<sup>5j</sup> Cu,<sup>5k</sup> Ag,<sup>5l</sup> or V<sup>5m</sup> catalysts. Cobalt catalysis permits a chelation-assisted direct sulfanylation of naphthols and phenols,<sup>5n</sup> a difficult task under metal-free conditions. Driven by the increasing interest in chemical utilization of abundant and nontoxic transition metals, iron catalysis has attracted considerable attention in the field of organic synthesis because of the high natural abundance, environmentally benign character, low cost, and low toxicity of this

**Table 1** Optimization of the Reaction Conditions<sup>a</sup>



Entry <sup>a</sup>	Catalyst (mol%)	Additive (mol%)	Time (h)	Temp (°C)	Yield <sup>b</sup> (%)
1	FeCl <sub>3</sub> (2.5)	KI (2.5)	24	110	87
2	FeCl <sub>3</sub> (5.0)	KI (5.0)	24	110	>99 (97) <sup>c</sup>
3	FeCl <sub>3</sub> (10)	KI (10)	24	110	69
4	FeCl <sub>3</sub> (15)	KI (15)	24	110	35
5	FeCl <sub>3</sub> (20)	KI (20)	24	110	9
6	FeCl <sub>3</sub> (30)	KI (30)	24	110	6
7	FeCl <sub>3</sub> (5.0)	–	24	110	38
8	–	KI (5.0)	24	110	–
9	FeCl <sub>3</sub> (5.0)	KI (5.0)	24	90	53
10	FeCl <sub>3</sub> (5.0)	KI (5.0)	24	70	17
11	FeCl <sub>3</sub> (5.0)	KI (5.0)	24	120	–
12	FeCl <sub>3</sub> (5.0)	KI (5.0)	12	110	38
13	FeCl <sub>3</sub> (5.0)	KI (5.0)	18	110	48
14	FeCl <sub>3</sub> (5.0)	KF (5.0)	24	110	11
15	FeCl <sub>3</sub> (5.0)	KCl (5.0)	24	110	6
16	FeCl <sub>3</sub> (5.0)	KBr (5.0)	24	110	12
17	FeBr <sub>3</sub> (5.0)	KI (5.0)	24	110	20
18	FeCl <sub>3</sub> ·6H <sub>2</sub> O (5.0)	KI (5.0)	24	110	3
19	Fe(NO <sub>3</sub> ) <sub>3</sub> ·9H <sub>2</sub> O (5.0)	KI (5.0)	24	110	16
20	Fe <sub>2</sub> O <sub>3</sub> (5.0)	KI (5.0)	24	110	2
21	Fe <sub>2</sub> (CO <sub>3</sub> ) <sub>3</sub> (5.0)	KI (5.0)	24	110	8
22	PhFeO <sub>7</sub>	KI (5.0)	24	110	18
23	Cu <sub>2</sub> O (5.0)	KI (5.0)	24	110	9

<sup>a</sup> Reaction conditions: **1a** (0.50 mmol), **2a** (0.25 mmol), FeX<sub>3</sub> (mol%), additive (mol%), anhyd DMSO (2.0 mL), air atmosphere.

<sup>b</sup> Determined by GC/MS with anthracene as a standard.

<sup>c</sup> Isolated yield.

metal.<sup>10,11</sup> Despite the several advantages of iron, its use in direct chalcogenylations remains underdeveloped. Fe(III)-catalyzed C3 sulfanylations of indoles by diorganoyl disulfides<sup>11a</sup> or thiols<sup>11b</sup> have been reported. More recently, our group reported a mild and efficient Fe(III)-catalyzed direct C3 chalcogenylation of indoles, and we assessed the mechanistic effects of iodide ions in the system.<sup>11c</sup> As part of our continuing interest in organochalcogen chemistry<sup>6d,11c,12,13</sup> and in the design of environmentally friendly chalcogenylation reactions, we report a regioselective C1 chalcogenylation of electron-rich naphthalene derivatives by using a cheap system involving FeCl<sub>3</sub> and iodide ions under air atmosphere.

Our study began by evaluating the reaction of 2-naphthol (**1a**) with diphenyl diselenide (**2a**) as model substrates. From our seminal mechanistic studies,<sup>11c</sup> we chose a combination of iron (III) chloride (FeCl<sub>3</sub>) and potassium iodide (KI) in dimethyl sulfoxide (DMSO), known to give molecular iodine (I<sub>2</sub>), which we hoped would catalyze the chalcogenylation. Therefore, in our first experiment we employed 2.5 mol% of FeCl<sub>3</sub> and 2.5 mol% of KI as an additive in DMSO, which gave an 87% yield of 1-(phenylselenanyl)-2-naphthol (**3a**) after 24 hours at 110 °C under an air atmosphere (Table 1, entry 1). This success prompted us to improve the yield and to evaluate the role of each reagent in the transformation. Fortunately, the yield was improved to 99% on running the reaction with 5.0 mol% of FeCl<sub>3</sub> and 5.0 mol% of KI (entry 2), whereas further increases in the catalyst and additive loadings to 10, 15, 20, or 30 mol% did not improve the yield of **3a** (entries 3–6). Carrying out the reaction with FeCl<sub>3</sub> (5.0 mol%) and without KI provided compound **3a** in 38% yield (entry 7), demonstrating the important role of iodide ions in this system. Furthermore, the desired product was not detected in the absence of FeCl<sub>3</sub> (entry 8). In the next step, we screened the effects of temperature and time on the reaction system (entries 9–13). Decreasing the temperature from 110 °C to 90 °C or 70 °C furnished lower yields of **3a** (entries 9 and 10), and no product was detected when the reaction was performed at 120 °C (entry 11). Shorter reaction times considerably reduced the yield of the expected product (entries 12 and 13). Because the oxidation of iodine ion by Fe(III) rapidly produces I<sub>2</sub>,<sup>14</sup> the involvement of this redox reaction in our system was evaluated by using alternative additives. We obtained a lower yield of **3a** when KF, KCl, or KBr was used (entries 14–16), suggesting a particular role for the combination of Fe(III) and iodide ions in this reaction. In the next step, several other Fe(III) sources were evaluated (entries 17–22); however, **3a** was obtained in low yields in these cases. We have to point out a detrimental effect of water on the yield, as observed with FeCl<sub>3</sub>·6H<sub>2</sub>O (entry 18).

Considering the hygroscopic nature of FeCl<sub>3</sub>, one would expect a reduction of the yield as a result of contamination of the catalyst with water, but the high yield of **3a** under the optimized conditions ruled out any related issue. Finally, to

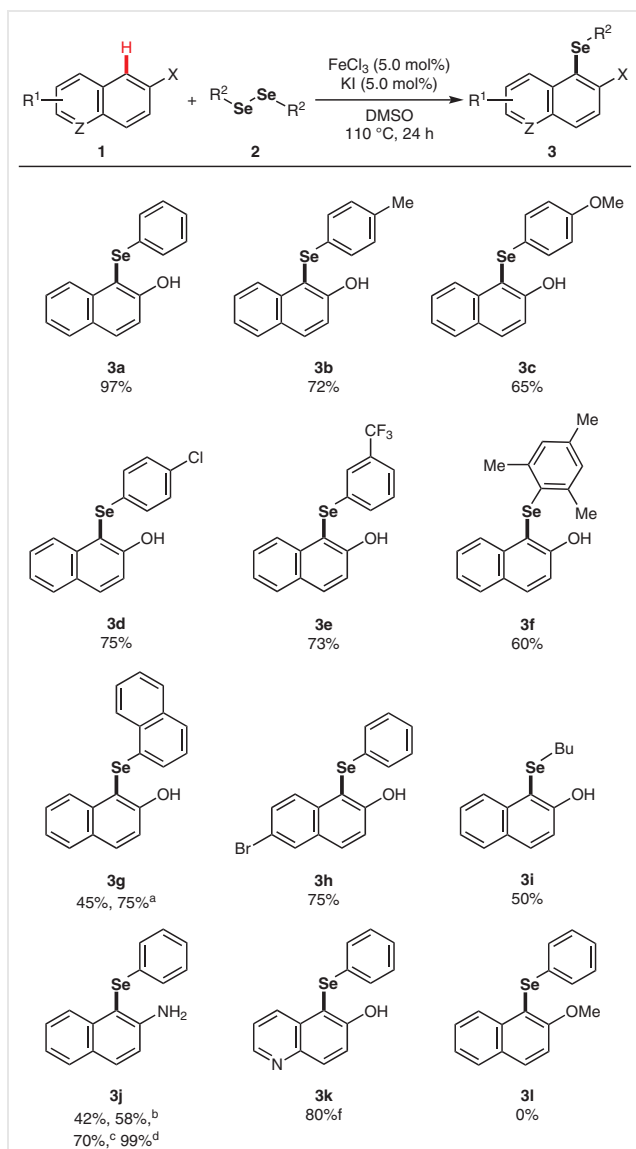
verify that the reaction was not catalyzed by trace amounts of copper impurities,<sup>15</sup> an experiment was carried out with Cu<sub>2</sub>O (Table 1, entry 23), and only a 9% yield of the expected product was obtained. This result confirmed the key role of Fe(III) in this method.

A variety of solvents were also evaluated under the reaction conditions. On running the reaction in DMF, NMP, THF, or xylene, a low yield was observed (9, 13, 8 and 3%, respectively), and only trace amounts of **3a** were detected in MeCN or CH<sub>2</sub>Cl<sub>2</sub>. An exceptional reaction yield was observed only in DMSO, (Table 1, entry 2), which suggests a specific solvent effect on this reaction. This is probably related to regeneration of the I<sub>2</sub> generated in situ.<sup>6b,9m–o,11c,16–18</sup>

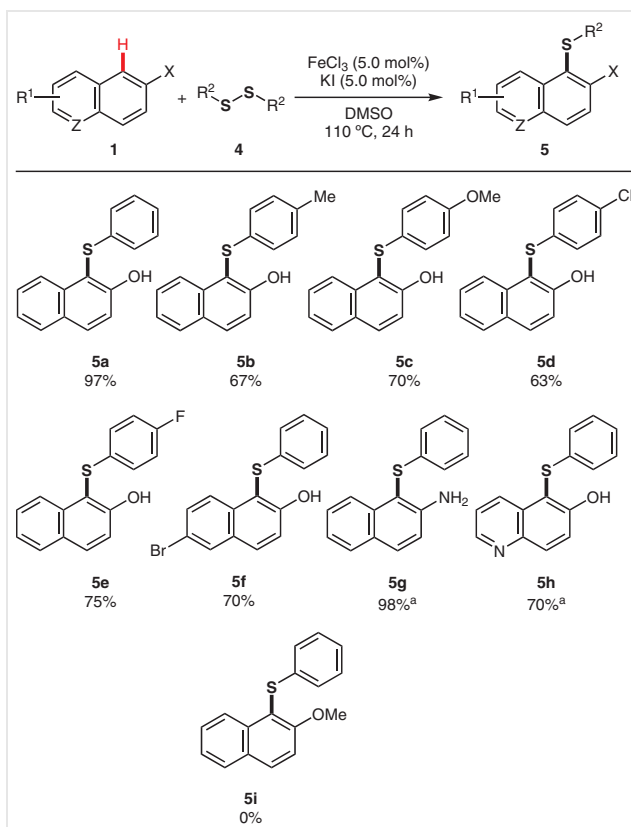
Having optimized the reaction conditions (Table 1, entry 2), we evaluated the scope of this method with regard to the electron-rich naphthalene derivative and the diorganoyl dichalcogenide partner (Schemes 1 and 2). In general, moderate to good yields were observed with diaryl diselenides bearing electron-donating or electron-withdrawing groups (**3b–e**). However, bulky diaryl diselenides gave products **3f** and **3g** in moderate yields, suggesting that steric effects on the diselenides influenced the yield of this reaction. We observed that a longer reaction time of 32 hours improved the yield of **3g** to 75%. Further, 6-bromo-2-naphthol gave a good yield of **3h** (75%), and the reaction was also effective for dialkyl diselenides (**3i**). The amounts of FeCl<sub>3</sub> and KI required to give good selenylation yields from 2-naphthylamine and 6-hydroxyquinoline were evaluated. The best results were obtained by using 30 mol% of FeCl<sub>3</sub> and 30 mol% of KI, which provided a 99% yield of **3j** and an 80% yield of **3k**. Because the well-known acid–base reaction of Fe(III) and *n* electrons in the nitrogen atoms of anilines or pyridines can deactivate the catalyst and the electron-rich naphthalene derivative, the use of higher catalyst amounts is plausible. Additionally, no selenylation of 2-methoxynaphthalene was observed and only the starting materials were detected on a detailed inspection of the GC/MS trace.

The method was successfully extended to diorganoyl disulfides **4** (Scheme 2), which reacted with electron-rich naphthalenes to give products **5a–h** in moderate to excellent yields. Again, moderate to good yields were obtained with diaryl disulfides bearing electron-donating or electron-withdrawing groups (**5b–e**) and with a functionalized 2-naphthol (**5f**). The sulfanylation of 2-naphthylamine and 6-hydroxyquinoline required higher catalyst and additive loadings to obtain good to excellent yields (**5g** and **5h**). The product **5i** was not obtained from the reaction of 2-methoxynaphthalene with diphenyl disulfide.

To gain some insight into the mechanism of this reaction, we conducted a series of control experiments (Scheme 3). Under the optimized reaction conditions, the addition of 2.0 equivalents of the radical scavenger TEMPO or hydroquinone (HQ) (Scheme 3a) decreased the yield of product



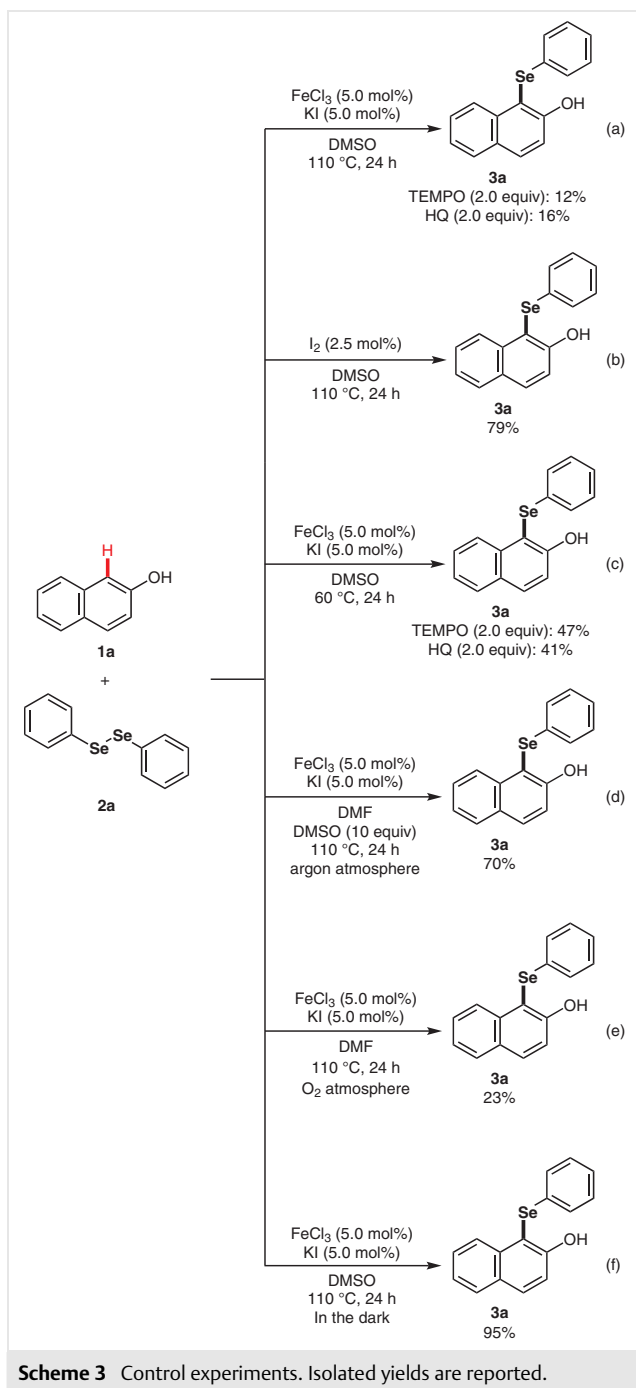
**3a**, which at first glance might suggest a radical pathway. However, when the reaction was developed with 2.5 mol% of I<sub>2</sub>, the theoretically maximum amount produced from FeCl<sub>3</sub> (5.0 mol%) and KI (5.0 mol%) under the standard conditions, product **3a** was obtained in 79% yield (Scheme 3b), which would suggest an ionic pathway. Our previous electron paramagnetic resonance experiments on the chalcogenylation of indoles catalyzed by FeCl<sub>3</sub> and KI ruled out a radical mechanism.<sup>11c</sup> The harsher conditions (110 °C) employed in the chalcogenylation of the naphthalene deriva-



**Scheme 2** Sulfanylations of naphthalene derivatives catalyzed by FeCl<sub>3</sub> and KI. *Reagents and conditions:* **1** (0.5 mmol), **4** (0.25 mmol), FeCl<sub>3</sub> (5.0 mol%), KI (5.0 mol%), anhyd DMSO (2.0 mL), air atmosphere, 110 °C, for 24 h. Isolated yields are reported. <sup>a</sup> FeCl<sub>3</sub> (30 mol%), KI (30 mol%).

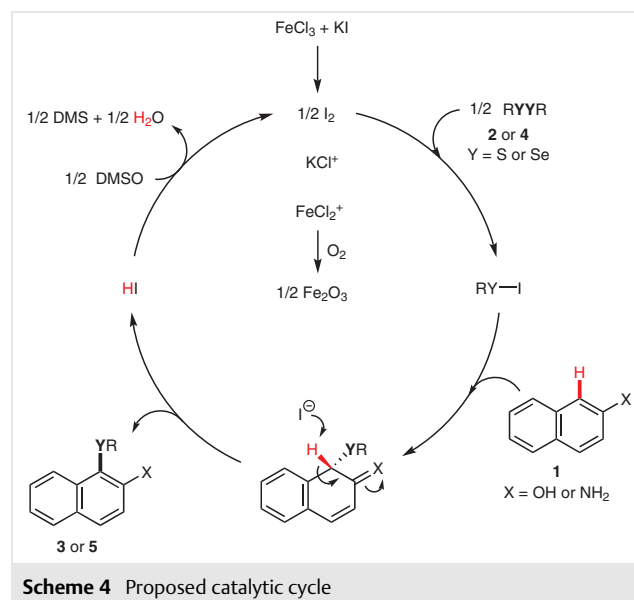
tives probably permit the recognized side reactions between Fe(III) and TEMPO<sup>19a–d</sup> or HQ,<sup>20</sup> poisoning the Fe(III) that is required for the oxidation of iodide ions.

This was supported by performing the reactions in the presence of TEMPO or HQ at 60 °C for longer reaction times (Scheme 3c), whereupon the yield of **3a** increased to 47% and 41%, respectively. Importantly, the essential contribution of iodide ions to the high reaction yield is also compelling evidence that corroborates an ionic mechanism involving the formation of I<sub>2</sub> in situ (Table 1, entries 2 and 14–16). The crucial effect of solvent on this system was also assessed (Scheme 3d). An experiment performed under an inert atmosphere (argon) and in strictly anhydrous conditions using a polar aprotic solvent (DMF) and ten equivalents of DMSO gave a 70% yield of **3a**, indicating that this solvent plays a role in the regeneration of the I<sub>2</sub> formed in situ from HI.<sup>6b,9m–o,11c,16,17</sup> Also, when the reaction was performed in DMF under an O<sub>2</sub> atmosphere the yield was 23%, which further supports the role of DMSO in the oxidation of HI (Scheme 3e). Finally, when the standard reaction was performed in darkness, the yield was 95% (Scheme 3f), which ruled out any photochemical pathway.



On the basis of these results and previous reports,<sup>6b,9m-o,11c,16,17</sup> a plausible catalytic cycle was proposed (Scheme 4). Initially, a rapid redox reaction between Fe(III) and KI produces I<sub>2</sub> in the reaction medium,<sup>14</sup> in accordance with previous studies.<sup>11c</sup> Subsequently, the oxidation of the diorganoyl dichalcogenide (**2** or **4**) by I<sub>2</sub> produces an electrophilic

chalcogen species (RY-I) that undergoes an electrophilic aromatic substitution at the C1 position of the electron-rich bicyclic arene catalyzed by Fe(III), which is still in the system, affording the corresponding product (**3** or **5**) and HI. The molecular iodine catalyst is restored by the reaction of HI with DMSO, completing the catalytic cycle.<sup>6b,9m-o,11c,16,17</sup>



In summary, a chalcogenylation of electron-rich naphthalene derivatives catalyzed by FeCl<sub>3</sub> and KI has been developed.<sup>21</sup> The method features simple and cheap catalysts and gives nonsymmetrical diorganoyl chalcogenides (S, Se) by selective C1 chalcogenylation of 2-naphthols or 2-naphthylamines. Control experiments supported the hypothesis that iodide ions are oxidized by Fe(III) to produce molecular iodine, which is the actual catalyst for the reaction in this system.

## Conflict of Interest

The authors declare no conflict of interest.

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## Supporting Information

Supporting information for this article is available online at <https://doi.org/10.1055/s-0040-1706748>.

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- (21) **Chalcogenylation of Naphthalene Derivatives Catalyzed by FeCl<sub>3</sub> and KI: General Procedure**  
An oven-dried 10 mL glass tube was charged with the appropriate naphthalene derivative **1** (0.5 mmol, 1.0 equiv), diorganoyl dichalcogenide **2** or **4** (0.25 mmol), and KI (5.0 mol%, 4.1 mg). FeCl<sub>3</sub> (5.0 mol%, 4.0 mg) was then weighed quickly, dissolved in DMSO (2.0 mL), and added to the glass tube. The mixture was stirred at 110 °C for 24 h then cooled to r.t. and added to sat. aq Na<sub>2</sub>S<sub>2</sub>O<sub>3</sub> (5.0 mL). The resulting mixture was extracted with EtOAc (3 × 5.0 mL), and the organic extracts were separated, dried (MgSO<sub>4</sub>), and concentrated under vacuum. The residue was purified by flash chromatography (silica gel, hexane–EtOAc)
- 1-(Phenylselanyl)-2-naphthol (3a)<sup>6d</sup>**  
Flash chromatography [silica gel, hexane–EtOAc (90:10)] gave a white solid; yield: 145.1 mg (97%); mp 77–78 °C. <sup>1</sup>H NMR (400 MHz, DMSO-*d*<sub>6</sub>): δ = 10.21 (s, 1H), 8.26 (dd, *J* = 8.5, 1.1 Hz, 1H), 7.94 (d, *J* = 8.9 Hz, 1H), 7.84 (dd, *J* = 8.1 and 1.3 Hz, 1H), 7.46 (ddd, *J* = 8.4, 6.8, 1.4 Hz, 1H), 7.36 (d, *J* = 8.9 Hz, 1H), 7.32 (ddd, *J* = 8.0, 6.8, 1.2 Hz, 1H), 7.16–7.09 (m, 5H). <sup>13</sup>C NMR (100 MHz, DMSO-*d*<sub>6</sub>): δ = 158.1, 146.1, 136.5, 133.3, 132.5, 129.6, 129.1, 128.9, 128.0, 126.9, 126.0, 123.6, 118.6, 108.1. MS (EI): *m/z* (%) = 300 (32.2) [M<sup>+</sup>], 298 (16.1), 220 (100.0), 194 (29.9), 115 (80.8), 102 (13.1), 77 (18.9), 51 (30.8).