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Nickel-Catalyzed Intramolecular Decarbonylative Coupling of Aryl Selenol Esters

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Abstract: This report describes a method for Ni-catalyzed intramolecular decarbonylative coupling, which enables the conversion of areneselenol esters to diaryl selenides. The inexpensive and readily available catalyst can be employed under mild reaction conditions for the construction of structurally diverse diaryl selenides, including heterocyclic and natural product derivatives.

Keywords: Nickel catalysis; Decarbonylation; Diaryl selenides; Seleno esters; Extrusion strategy

Selenium is known as a fundamental element in life sciences. Organoselenides, particularly arylselenides, have attracted considerable attention as key reagents in organic synthesis; moreover, they possess unique photoelectric properties and important biological activities (Figure 1).[1–5] Arylselenides also play pivotal roles in catalysis, fluorescence analysis, and synthesis of functional organic materials. This point has motivated the report of different methodologies to synthesize these compounds.

Diarylselenides are most commonly prepared via transition-metal-catalyzed coupling of aryl halides, aryl silanes, or aryl boronic acids with phenylselenyl chloride, diphenyl diselenide, or phenylselenyl tributyltin reagents.[6–19]

Recently, the transition-metal-catalyzed intramolecular decarbonylative coupling of naturally abundant carboxylic acid derivatives has attracted increased attention.[20–33] This process offers several advantages over conventional cross-couplings. First, carboxylic acids and their derivatives are often more readily available and less expensive than their aryl halide counterparts. Second, this process helps reduce the amount of harmful toxic waste (CO as the major side product). Finally, this reaction proceeds in the absence of nucleophiles.

Significant effort has also been devoted to the transition-metal-catalyzed decarbonylative intramolecular couplings of ketones, esters, and other carboxylic acid derivatives to form C–C and C-heteroatom bonds.[34–49] Herein, we report our findings on an alternate synthetic route to diaryl selenides via the nickel-catalyzed intramolecular decarbonylative coupling of selenoesters (Scheme 1).

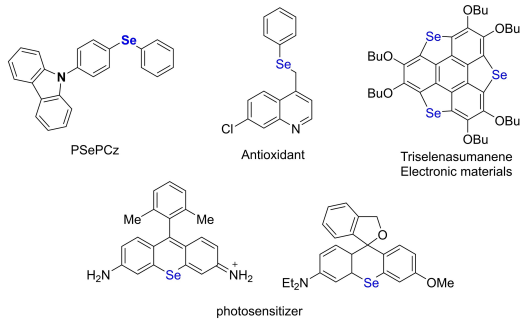
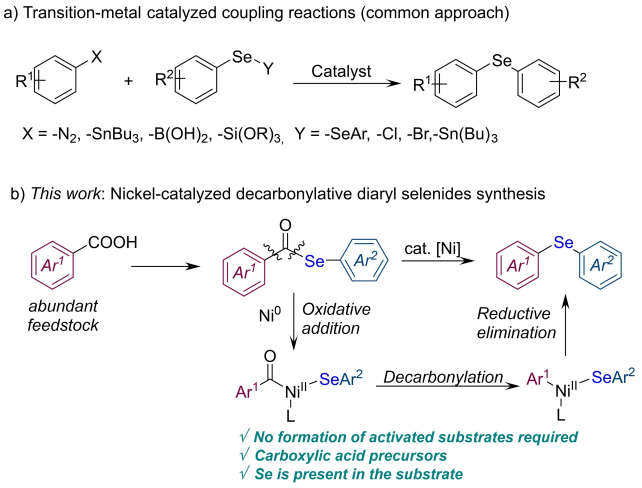


Figure 1. Examples of diarylselenides as core structure for organic electronic material, photosensitizers and biological molecules.

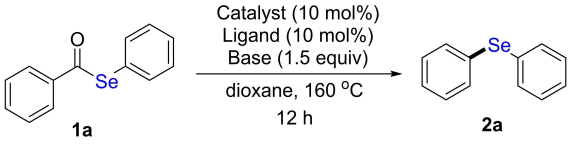


Scheme 1. Ni-Catalyzed decarbonylation of selenoesters.

At the outset of our studies, we noted one literature reports of metal-mediated decarbonylation of arenese-lenol esters.[50] However, the example employed stoi-chiometric quantities of Ni complex with a narrow scope of unfunctionalized substrates. To explore the proposed intramolecular decarbonylative coupling, Se-phenyl benzoselenoate **1a** was chosen as the model substrate. The reaction proceeded smoothly in the presence of catalytic amounts of Ni $(acac)_2$ and dppe to provide the desired product **2a** and the hydrolysis of selenoesters was not detected (Table 1, entry 1). This result encouraged us to attempt further optimization, and we assessed the efficiency of a variety of Ni catalysts. $NiCl_2$ was found to be more effective than NiI_2, $Ni(acac)_2$, $Ni(OAc)_2$ and $NiCl_2$(dppe) (Table 1, entries 1–5). $Ni(cod)_2$ also showed high catalytic activity (Table 1, entry 6). However, from the view-point of practical operation, $NiCl_2$ was the better option. Next, a range of ligands (dppp, dppm, and 1,10-phenanthroline) was tested and found to be less effective than dppe (Table 1, entries 8–10). Bases were also screened, and Na_2CO_3 was found to be the optimal choice (Table 1, entries 11, 12). We also attempted to lower the reaction temperature; unfortunately, the yields decreased sharply at low temperatures (Table 1, entries 14 and 15). Control experiments showed that both the phosphine and Ni-complex played pivotal roles in this reaction (Table 1, entries 16 and 17). Finally, the loading of catalyst was investigated; however, reducing the catalyst loading gave a lower yield (Table1, entry 18).

With the optimized reaction conditions in hand, we next investigated the substrate scope of the nickel-catalyzed intramolecular decarbonylative coupling of selenoesters. Selenoesters bearing electron-donating as well as electron-withdrawing groups reacted smoothly to provide diaryl selenides **2** in good yields. The reaction also showed excellent compatibility with a

Table 1. Opimization of the reaction conditions.[a]



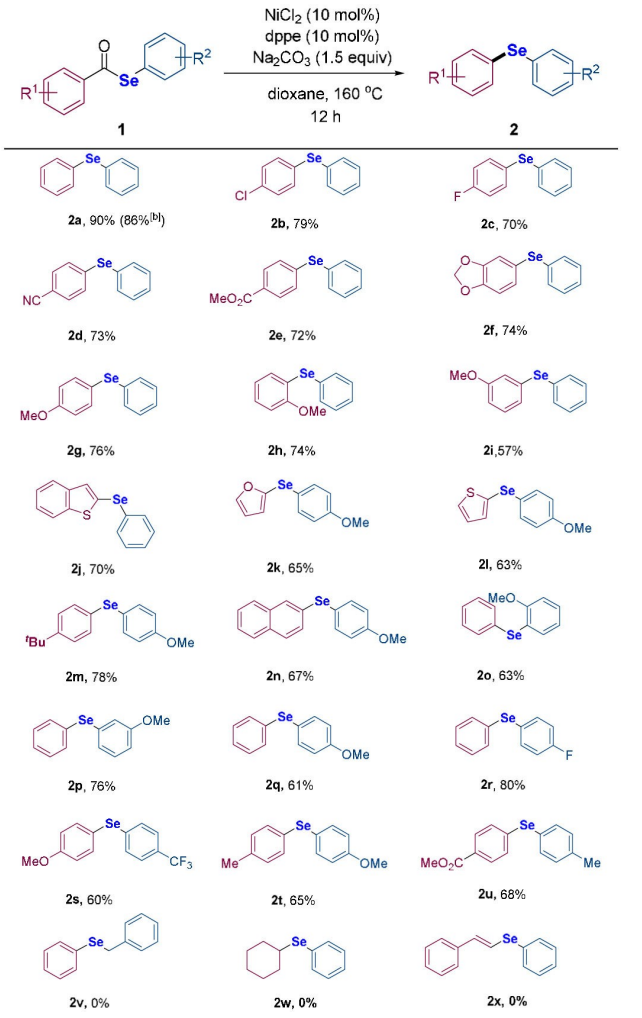
Entry	Catalyst	Ligand	Base	Yield (%)[b]
1	$Ni(acac)_2$	dppe	Na_2CO_3	50
2	NiI_2	dppe	Na_2CO_3	67
3	$NiCl_2$	dppe	Na_2CO_3	90
4	$Ni(OAc)_2$	dppe	Na_2CO_3	78
5	$NiCl_2$(dppe)	–	Na_2CO_3	85
6	$Ni(cod)_2$	dppe	Na_2CO_3	90
7	$Ni(cod)_2$	dppe	–	90
8	$NiCl_2$	dppp	Na_2CO_3	85
9	$NiCl_2$	dppm	Na_2CO_3	30
10	$NiCl_2$	1,10-phenanthroline	Na_2CO_3	27
11	$NiCl_2$	dppe	NaOH	45
12	$NiCl_2$	dppe	Et_3N	15
13	$NiCl_2$	dppe	–	13
14[c]	$NiCl_2$	dppe	Na_2CO_3	trace
15[d]	$NiCl_2$	dppe	Na_2CO_3	40
16	–	dppe	Na_2CO_3	<5
17	$NiCl_2$	–	Na_2CO_3	30
18[e]	$NiCl_2$	dppe	Na_2CO_3	60

[a] Standard conditions: **1a** (0.1 mmol), catalyst (0.01 mmol), ligand (0.01 mmol), base (0.15 mmol), dioxane (0.5 mL), at 160 °C in sealed tube, 12 h.
[b] Isolated yields.
[c] At room temperature.
[d] At 120 °C.
[e] $NiCl_2$ (5 mol%) and dppe (5 mol%) were used.
dppe = 1,2-Bis(diphenylphosphino)ethane;
dppp = 1,3-Bis(diphenylphosphino) propane;
dppm = Bis(diphenylphosphino)methane.

variety of functional groups such as methyl chloride (**2b**), fluoride (**2c**), nitrile (**2d**), ester (**2e**), and ether (**2f–2i**) groups. Substrates with a substituent at the *meta*- and *ortho*-position also worked well to give the corresponding products (**2h**, **2i**). Furthermore, this protocol could be extended to heterocyclic (**2j–2l**) and polyaromatic (**2n**) substrates, providing the desired products in moderate to good yields. Next, the scope of the Se-derived fragment was examined (Table 2). Substrates containing *para*-, *meta*-, and *ortho*-meth-oxyl groups (**2o–2q**) afforded the corresponding selenides in good yields. Electron-withdrawing groups such as fluoro (**2r**) and trifluoromethyl (**2s**) were well tolerated under the catalytic conditions. However, no products were detected when alkyl or alkenyl selenol esters were used under the standard conditions(**2v–2x**).

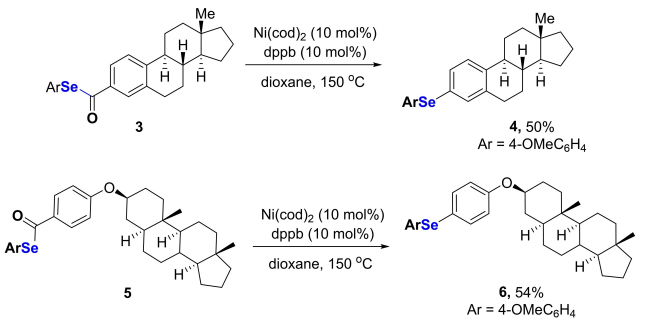
Diversification of natural products or drugs meets the increasing demand in biochemical and pharmaceut-

Table 2. Substrate Scope.[a]



[a] Reaction conditions: **1** (0.1 mmol), $NiCl_2$ (0.01 mmol), dppe (0.01 mmol), Na_2CO_3 (0.15 mmol), dioxane (0.5 mL), at 160 °C in sealed tube. Isolated yields.
[b] 1.0 mmol scale.

ical communities. These modification strategies could provide functionalized analogs with enhanced biological activities or improved therapeutic capabilities compared to their natural counterparts. In order to verify the applicability and universality of this protocol a complex structural system, the diversification of natural product derivatives was implemented. Selenoesters derived from estrone and epiandrosterone were subjected to the optimized reaction conditions. As shown in Scheme 2, this reaction offers a general method for introducing the selenide group into a natural product or its derivative, while the ester moiety acts as a functional handle for further modification. For these substrates, only trace amount of products could be obtained under standard conditions. When



Scheme 2. Diversification of natural product derivatives.

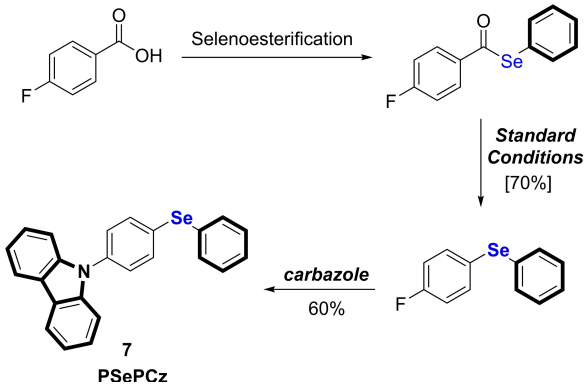
$Ni(cod)_2$ was used instead of $NiCl_2$ in the catalytic system, the yields were much improved.

To further highlight the utility of this novel method, a sequential reaction was designed for the synthesis of the organic functional material **PSePCz**, which could be used to fabricate sensing systems for H_2O_2 and 2,4,6-trinitrotoluene (TNT).[51] As shown in Scheme 3, **PSePCz** was easily accessible from readily available carboxylic acids in three steps.

In summary, we have developed a practical decarbonylative diaryl selenide synthesis from aryl selenoesters via Ni catalysis. As opposed to the traditional diaryl selenide syntheses, this protocol is characterized by high atom efficiency; it can be executed with readily available carboxylic acids as coupling precursors, and only small amounts of harmful toxic wastes are generated. By virtue of its high chemoselectivity, our protocol holds promise for application in the discovery of biological Se-containing lead compounds, preparation of Se-containing medicinal compounds, and synthesis of functional organic materials. Related studies are underway in our laboratory.

Experimental Section

General Procedure for the Synthesis of Selenoether 2. In a glovebox, substrate **1** (0.1 mmol) was added to a solution of



Scheme 3. Synthesis of PSePCz.

$NiCl_2$ (0.01 mmol), dppe (0.01 mmol) and Na_2CO_3 (0.15 mmol) in 1,4-dioxane (0.5 mL). Then the vessel was sealed and removed from glovebox. The contents of the vial were then stirred at 160 °C for 12 h. The reaction was cooled to room temperature, and the crude mixture was filtered through a pad of silica gel. The filtrate was then concentrated *in vacuo* to give a residue, which was purified by flash column chromatography over silica gel to give product **2**.

Acknowledgements

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