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## New insights into the seleniranium ion promoted cyclization of prenyl and propenylbenzene aryl ethers

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### ABSTRACT

The chromane core is widely represented in nature being part of a wide array of secondary metabolites of plant, fungal, and bacterial origin. In this paper an improved method for the chemical synthesis of differently substituted chromanes is described. Substituted 2*H*-1-benzopyrans have been synthesized in good to excellent yields (52 % - 81 %) by treatment of 3,3-dimethylallyl and propenylbenzene ethers of differently substituted phenols with phenylselenenyl chloride.

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### 1. Introduction

Chromane (benzopyran) nucleus is nowadays well recognized to be among the most important pharmacophores with proven and promising therapeutic applications. This core is widely represented in nature being present in the backbone of several classes of secondary metabolites like tocopherols, flavonoids, and anthocyanins.<sup>1</sup> Many chromane derivatives exert valuable pharmacological activities as antitumor, antiplatelet aggregation,<sup>2</sup> antimicrobial,<sup>3</sup> antioxidant,<sup>4</sup> TNF- $\alpha$  inhibitory,<sup>5</sup> antifungal,<sup>6</sup> antispasmodic, estrogenic,<sup>7</sup> antiviral,<sup>8</sup> anti-helminthic, anticancer,<sup>9</sup> anti-HIV,<sup>10</sup> antitubercular,<sup>11</sup> anti-inflammatory,<sup>12</sup> herbicidal, analgesic, and anticonvulsant<sup>13</sup> agents. The group of vitamins E (tocopherols and tocotrienols) is an explicative example to this concern.<sup>14</sup> Thus chromane derivatives can be regarded as novel hits with great potentialities for further research about new pharmacophores. Moreover chromanes have been also used as synthons in the production of fluorescent pigments and dyes, and electrophotographic and electroluminescent devices.<sup>15</sup>

The chromane core has been mainly built by multicomponent condensation reactions of suitably substituted phenols and aromatic aldehydes, as exhaustively reviewed in the recent literature.<sup>1,16</sup> However some of the already described methodologies are featured by some disadvantages, like severe conditions, low yields, long reaction times, poor regioselectivity, undesired side reactions, employment of hazardous organic bases (piperidine, pyridine, ammonia, and others) or toxic heavy metals as catalysts. Another synthetic approach reported in the literature consists in the direct condensation of *O*-allyl aryl ethers

promoted by homogeneous or heterogeneous catalysts and/or microwaves.<sup>17</sup> Mo(CO)<sub>6</sub>,<sup>18</sup> Ph<sub>3</sub>PAuNTf<sub>2</sub>,<sup>19</sup> Bi(OTf)<sub>3</sub>,<sup>20</sup> zeolites<sup>21</sup> and similar heterogeneous catalysts<sup>22</sup> have been used to this purpose. However also these processes suffer from lack of regioselectivity and the cyclization to give chromanes is in most cases accompanied by cleavage of the allyl moiety to a large extent and by its Claisen rearrangement providing *C*-allyl derivatives, thus decreasing the yields of desired adducts. Much attention had to be paid to firmly set the reaction conditions (e.g. temperature, catalyst upload, etc.) to avoid the occurrence of such side reactions.

During the last three decades, organoselenium compounds have been the subject of huge and renovated interest and have been discovered as extremely versatile reagents and substrates for organic synthesis. In particular it has been stated how selenium can be easily introduced into a carbon skeleton via an electrophilic, radical, or nucleophilic mechanism, and can be just as conveniently removed by a plethora of easy to handle processes providing a wide array of functionalities (e.g. carbon-carbon double bonds, alcohols, ethers, amides, amines, carboxylic acids, esters, heterocycles, and several others). Very recently explicative overall views of organoselenium compounds chemistry and applications have been published.<sup>23, 24</sup> In this context several cyclization reactions deriving from an intramolecular trapping of a seleniranium ion intermediate have been reported in the recent literature.<sup>25</sup> However only few examples of the intramolecular addition of carbon nucleophiles to seleniranium ions have been described. To the best of our knowledge only four examples of such process have been cited in the literature.<sup>26, 27</sup> In 1998 Déziel and coworkers performed the

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