1-ALLYLATION OF 2-BENZOTELLUROPYRYLIUM SALTS AND
2-BENZOSELENOPYRYLIUM SALTS BY MEANS OF ALLYLTIN
REAGENTS

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Abstract – 3-\textit{tert}-Butyl-2-benzotelluropyrylium salt (1) reacts with an equal
amount of allyltributyltin to afford 1-allyl-3-\textit{tert}-butyl-1\textit{H}-isotellurochromene
(8a) in 93 % yield. Similarly, 1-allyl-1\textit{H}-isotellurochromenes (9) and
isoselenochromenes (10, 11) were prepared from the corresponding pyrylium
salts (2-4) in moderate to good yields.

The chemistry (syntheses, structure, physical properties and reactions) of telluropyrylium\textsuperscript{2-5} and
selenopyrylium compounds,\textsuperscript{2-4} six-membered aromatic heterocycles containing a tellurium or selenium
cation, has attracted considerable attention. The monocyclic pyrylium salts and 1-benzo derivatives
containing these atoms have been covered in recent reviews.\textsuperscript{2-5} Among them, no 2-benzotelluropyrylium
salts, a possible theoretical structural isomer of the latter, have been known until we have recently
prepared; only the unsubstituted 2-benzoselenopyrylium salt was synthesized by Renson and Pirson\textsuperscript{6}
more than 35 years ago. Previously, we clarified that the reactions of the 2-benzotelluropyrylium salts (1, 2)\textsuperscript{7} and 2-benzoselenopyrylium salts (3, 4)\textsuperscript{7} with various nucleophiles including the alkoxide ion, amines
and an active methyl compound (acetone) proceeded with the introduction of the substituent at the
1-position of the cationic ring to exclusively give heteroatom substituted isochromenes (5).\textsuperscript{8} In addition,
the ring transformation of the 2-benzoselenopyrylium salts (3) into the 5\textit{H}-2,3-benzodiazepines (6)\textsuperscript{9} using
hydrazine as a nucleophile was also reported.

We have also provided the preparation of the 1\textit{H}-isoselenochromenes having a carbon functional group,
such as an alkyl, phenyl, vinyl and ethynyl group, at the hetero ring by the reactions of the 2-benzoselene-
pyrylium salts with Grignard reagents. The 2-benzotelluropyrylium salts react with Grignard reagents except for benzylmagnesium bromide to afford the dimeric-type products without normal coupling products. Only the 1-alkyl- and 1-phenyl-1H-isotellurochromenes were obtained by the reaction of the 2-benzotelluropyrylium salts with organocopper reagents. However, no 1H-isotellurochromenes having a carbon functional group, such as a vinyl, allyl or ethynyl group at the C-1 position, have been prepared until now.

The introduction of functional carbon substituents into the heterocycles has been one of the most important issues for the organic synthetic and heterocyclic chemistries. Yamaguchi et al. described that the activated nitrogen heteroaromatics regioselectively reacted with allyltin reagents to produce allylated dihydro-N-heterocycles. We now wish to report the reactions of the 2-benzotelluropyrylium salts and 2-benzoselenopyrylium salts with allylstannane.

At first, we optimized the reagents and conditions for allylation of the 2-benzotelluropyrylium salts using the 3-tert-butyl derivative. The treatment of the pyrylium salt (1) with 1.05 eq. of allyltributyltin (7a) in CH₂Cl₂ at room temperature resulted in the introduction of an allyl group into the heterocation ring to give the desire 1-allyl-3-tert-butyl-1H-isotellurochromene (8a) in 93 % yield without any other products (Table, entry 1). The reaction was completed within only 5 min. The use of Et₂O as a solvent required a longer reaction time. The allylation of the pyrylium salt (1) in THF, 1,2-dichloroethane, chloroform or acetonitrile produced a product in a lower yield. A protic solvent such as an alcohol is not suitable for the reaction of the pyrylium salts due to its instantaneous decomposition upon contact. Other allylation reagents, such as allyltrimethyltin and allyltriphenyltin, afforded a almost similar result; the highest yield was obtained when allyltributyltin was used. The reactions of the salts (1-4) with allyltributyltin (7a) and methallyltributyltin (7b) easily produced the corresponding 1-substituted isochromenes (8b, 9a, 9b, 10a, 10b, 11a, 11b) in 44-95 % yields (entries 2, 5, 6, 9, 10, 13, 14). We next examined the reaction of the pyrylium salts with the allylic tin reagents having methyl group at the 3-position to determine how the reactivity is changed. It was observed that the salts (1) treated with 2-butenyltributyltin (7c) and
## Table. Reaction of 2-Benzotelluropyrylium Salts (1, 2) and 2-Benzoselenopyrylium Salts (3, 4) with Allyltributyltin (7a-d)

![Reaction Scheme](image)

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<sup>a</sup> Isolated yield
<sup>b</sup> Mixture of diastereomers (2: 1) determined by <sup>1</sup>H NMR spectrometry
<sup>c</sup> Mixture of diastereomers (1: 1) determined by <sup>1</sup>H NMR spectrometry

3-methyl-2-butenyltributyltin (7d) produced the 1-(1-methyl-2-propenyl)-1<sup>H</sup>-isotellurochromene (8c) and 1-(1,1-dimethyl-2-propenyl)-1<sup>H</sup>-isotellurochromene (8d) in 86 and 73 % yields as shown in Scheme 2,
respectively (entries 3, 4). The former was obtained as an inseparable mixture of diastereomers (2:1), which were determined by \( ^1\text{H}-\text{NMR} \) spectrum. The MS spectrum of 8d showed a molecular formula of \( \text{C}_{18}\text{H}_{24}\text{Te} \) with a molecular ion at \( m/z = 370 \). The \( ^1\text{H}-\text{NMR} \) spectrum had two singlet signals (each 3H, Me x 2) at \( \delta 1.01 \) and \( \delta 1.02 \) and a singlet signal (1H, 1-H) at \( \delta 3.84 \). Three protons were also observed in the olefinic field. The \( ^{13}\text{C}-\text{NMR} \) spectrum showed one singlet sp\(^3\) carbon at \( \delta 39.19 \) except for tert-butyl group (\( \delta 42.85, \text{s} \)). These spectral data clearly indicate that the structure of this compound is 8d; the \( ^{13}\text{C}-\text{NMR} \) spectrum of 12 should have a triplet sp\(^3\) and a singlet sp\(^2\) carbon. No structural isomer 12, which should formed by the reaction of Grignard and organocopper reagents, were obtained (Scheme 2). Similarly, treatment of the unsubstituted 2-benzotelluropyrylium salts (2) and 2-benzoselenopyrylium salts (3, 4) with 7c and 7d easily proceed to afford the corresponding 1-allyl-1\(^{1}H\)-isotellurochromenes (9c, 9d) and 1-allyl-1\(^{1}H\)-isoselenochromenes (10c, 10d, 11c, 11d) in moderate to good yields, respectively. The results of the allylation reaction are summarized in Table. The vinyl and homoallyltin reagents reacted with the pyrylium salts (1-4) to afford the complex mixture without any products.

![Scheme 2](image)

In this way, the introduction of allyl group into the 2-benzotelluropyrylium salts and 2-benzoselenopyrylium salts was achieved using the allyltin reagents. The obtained novel 1-allyl-1\(^{1}H\)-isochromenes may be able to be useful synthetic intermediates for the ring transformation of the heterocycles containing a tellurium or selenium.
EXPERIMENTAL

Melting points were measured on a Yanagimoto micro melting point hot stage apparatus and are uncorrected. IR spectra were recorded on a Horiba FT-720 spectrophotometer. MS and HRMS spectra were recorded on a JEOL JMS-DX300 instrument. $^1$H NMR spectra were recorded on a PMX-60SI (60 MHz), JEOL EX-90A (90 MHz) or JEOL JNM-GSX 400 (400 MHz) spectrometer in CDCl$_3$ using TMS as internal standard and J values are given in Hz.

Reaction of 2-Benzotelluropyrylium Salt (1, 2) with Allyltin Reagents (7): Formation of 1-Allyl-1$^H$-isotellurochromenes (8, 9)

Allyltributyltin (0.315 mmol) was slowly added to a suspended mixture of the telluropyrylium tetrafluoroborate (1 or 2, 0.3 mmol) in anhydrous CH$_2$Cl$_2$ (5 mL) at rt under an argon atmosphere. The mixture was stirred under the conditions for 5 min, and diluted with CH$_2$Cl$_2$ (20 mL). The organic layer was washed with brine (30 mL x 2) and dried (MgSO$_4$) and evaporated. The resulting residue was chromatographed on silica gel eluted with n-hexane - CH$_2$Cl$_2$ (10:1 to 5:1) to give 8 or 9.

1-Allyl-3-$^t$-tert-butyl-1$^H$-isotellurochromene (8a)

Pale yellow oil. $^1$H NMR (90 MHz) 1.27 (9H, s, $^t$-Bu), 2.68 (2H, br dd, $J = 7, 8$ Hz, CH$_2$CH=CH$_2$), 3.81 (1H, br d, $J = 16$ Hz, trans-CH$_2$CH=CH$_2$), 5.02 (1H, br d, $J = 11$ Hz, cis-CH$_2$CH=CH$_2$), 5.72 (1H, ddt, $J = 7, 11, 16$ Hz, CH$_2$C=CH$_2$), 6.68 (1H, s, 4-H), 7.2-7.3 (4H, m, Ph-H). EI-MS m/z (relative intensity): 342 (M$^+$, 19), 301 (100), 156 (30). EI-HRMS m/z M$^+$ Calcd for C$_{16}$H$_{20}$Te: 342.0628. Found: 342.0627.

3-$^t$-tert-Butyl-1-(2-methyl-2-propenyl)-1$^H$-isotellurochromene (8b)

Pale yellow oil. $^1$H NMR (90 MHz) 1.27 (9H, s, $^t$-Bu), 1.65 (3H, br s, Me), 2.58 (2H, br d, $J = 8$ Hz, CHC$_2$H$_2$), 3.91 (1H, t, $J = 8$ Hz, 1-H), 4.49 and 4.69 (each 1H, br s, C=CH$_2$), 6.59 (1H, s, 4-H), 6.9-7.2 (4H, m, Ph-H). EI-MS m/z (relative intensity): 356 (M$^+$, 15), 301 (100), 269 (23), 156 (19). EI-HRMS m/z M$^+$ Calcd for C$_{17}$H$_{22}$Te: 356.0785. Found: 356.0786.

3-$^t$-tert-Butyl-1-(1-methyl-2-propenyl)-1$^H$-isotellurochromene (8c)

This compound was an inseparable mixture of diastereomers in the ratio 1:2; yellow oil. $^1$H NMR (90 MHz) 0.79 (3H, d, $J = 7$ Hz, Me, major isomer), 1.14 (3H, d, $J = 7$ Hz, Me, minor isomer), 1.26 (9H, s, $^t$-Bu), 2.2-2.8 (1H, m, CHMeCH=CH$_2$), 3.54 (1H, d, $J = 9$ Hz, 1-H, major isomer), 3.64 (1H, d, $J = 9$ Hz, 1-H, minor isomer), 4.64 (1H, br d, $J = 17$ Hz, trans-CHMeCH=CH$_2$, minor isomer), 4.72 (1H, br d, $J = 10$ Hz, cis-CHMeCH=CH$_2$, minor isomer), 4.86 (1H, br d, $J = 17$ Hz, trans-CHMeCH=CH$_2$, major isomer), 4.96 (1H, br d, $J = 10$ Hz, cis-CHMeCH=CH$_2$, major isomer), 5.2-6.1 (1H, m, CHMeCH=CH$_2$), 6.62 (1H, s, 4-H), 6.9-7.2 (4H, m, Ph-H). EI-MS m/z (relative intensity): 356 (M$^+$, 8), 301 (100), 156 (22). EI-HRMS m/z M$^+$ Calcd for C$_{17}$H$_{22}$Te: 356.0785. Found: 356.0788.

3-$^t$-Butyl-1-(1,1-dimethyl-2-propenyl)-1$^H$-isotellurochromene (8d)
Yellow oil. $^1$H NMR (400 MHz) 1.01 and 1.02 (each 3H, s, Me x 2), 1.27 (9H, s, t-Bu), 3.84 (1H, s, 1-H), 4.83 (1H, dd, $J = 1.3$, 17.4 Hz, trans-CH=CH$_2$), 4.87 (1H, dd, $J = 1.3$, 10.8 Hz, cis-CH=CH$_2$), 5.78 (1H, dd, $J = 10.8$, 17.4 Hz, CH=CH$_2$), 6.63 (1H, s, 4-H), 7.10-7.21 (4H, m, Ph-H). $^{13}$C NMR (100 MHz) 25.17 (q), 25.37 (q), 30.50 (q), 37.69 (d), 39.19 (s), 42.85 (s), 111.70 (t), 126.64 (d), 126.86 (d), 127.05 (d), 129.61 (d), 129.90 (d), 130.28 (d), 134.84 (s), 139.70 (s), 145.81 (d). EI-MS $m/z$ (relative intensity): 370 (M$^+$, 5), 301 (100), 156 (17). EI-HRMS $m/z$ M$^+$ Calcd for C$_{18}$H$_{24}$Te: 370.0941. Found: 370.0942

1-allyl-1H-isotellurochromene (9a)

Yellow oil. $^1$H NMR (90 MHz) 2.75 (2H, br dd, $J = 7$, 8 Hz, CH$_2$CH=CH$_2$), 3.84 (1H, br t, $J = 8$ Hz, 1-H), 4.96 (1H, br d, $J = 16$ Hz, trans-CH$_2$CH=CH$_2$), 5.02 (1H, br d, $J = 11$ Hz, cis-CH$_2$CH=CH$_2$), 5.72 (1H, ddt, $J = 7$, 11, 16 Hz, CH$_2$C=CH$_2$), 7.0-7.3 (6H, m, 3-, 4-, Ph-H). EI-MS $m/z$ (relative intensity): 286 (M$^+$, 25), 245 (100), 115 (91). EI-HRMS $m/z$ M$^+$ Calcd for C$_{12}$H$_{12}$Te: 286.0002. Found: 285.9995.

1-(2-Methyl-2-propenyl)-1H-isotellurochromene (9b)

Yellow oil. $^1$H NMR (90 MHz) 1.64 (3H, br s, Me), 2.67 (2H, br d, $J = 8$ Hz, CHC=CH$_2$), 3.96 (1H, br t, $J = 8$ Hz, 1-H), 4.49 and 4.71 (each 1H, br s, C=CH$_2$), 6.8-7.3 (6H, m, 3-, 4-, Ph-H). EI-MS $m/z$ (relative intensity): 300 (M$^+$, 21), 245 (100), 115 (72). EI-HRMS $m/z$ M$^+$ Calcd for C$_{13}$H$_{14}$Te: 300.0158. Found: 300.0159.

1-(1-Methyl-2-propenyl)-1H-isotellurochromene (9c)

This compound was an inseparable mixture of diastereomers in the ratio 1:1; yellow oil. $^1$H NMR (90 MHz) 0.80 (3H, d, $J = 7$ Hz, Me), 1.14 (3H, d, $J = 7$ Hz, Me), 2.2-2.9 (1H, m, CHMeCH=CH$_2$), 3.61 (1H, br d, $J = 8$ Hz, 1-H), 3.69 (1H, br d, $J = 8$ Hz, 1-H), 4.67 (1H, br d, $J = 16$ Hz, trans-CHMeCH=CH$_2$), 4.73 (1H, br d, $J = 10$ Hz, cis-CHMeCH=CH$_2$), 4.89 (1H, br d, $J = 16$ Hz, trans-CHMeCH=CH$_2$), 4.99 (1H, br d, $J = 10$ Hz, cis-CHMeCH=CH$_2$), 5.2-6.1 (1H, m, CHMeCH=CH$_2$), 7.0-7.3 (6H, m, 3-, 4-, Ph-H). EI-MS $m/z$ (relative intensity): 300 (M$^+$, 8), 244 (100), 115 (47). EI-HRMS $m/z$ M$^+$ Calcd for C$_{13}$H$_{14}$Te: 300.0158. Found: 300.0156.

1-(1,1-Dimethyl-2-propenyl)-1H-isotellurochromene (9d)

Pale yellow oil. $^1$H NMR (90 MHz) 1.02 (6H, s, Me x 2), 3.79 (1H, d, $J = 2$ Hz, 1-H), 4.78 (1H, dd, $J = 2$, 18 Hz, trans-CH=CH$_2$), 4.86 (1H, dd, $J = 2$, 10 Hz, cis-CH=CH$_2$), 5.78 (1H, dd, $J = 10$, 18 Hz, CH=CH$_2$), 6.9-7.2 (6H, m, 3-, 4-, Ph-H). EI-MS $m/z$ (relative intensity): 314 (M$^+$, 9), 245 (100), 115 (68). EI-HRMS $m/z$ M$^+$ Calcd for C$_{14}$H$_{16}$Te: 314.0315. Found: 314.0308.

Reaction of 2-Benzoselenopyryl ium Salts (3, 4) with Allyltin Reagents (7): Formation of 1-allyl-1H-isoselenochromenes (10, 11)

The selenopyrylium salt (3 or 4) was treated with allyltin reagent and worked up as described for the preparation of 8 or 9 to give 10 or 11.
1-Allyl-3-tert-butyl-1H-isoselenochromene (10a)

Colorless oil. \(^1\)H NMR (90 MHz) 1.28 (9H, s, \(t\)-Bu), 2.53 (2H, br dd, \(J = 7, 8\) Hz, \(CH_2CH=CH_2\)), 3.82 (1H, t, \(J = 8\) Hz, 1-H), 4.96 (1H, br d, \(J = 16\) Hz, \(trans\)-CH\(_2\)CH=CH\(_2\)), 5.03 (1H, br d, \(J = 11\) Hz, \(cis\)-CH\(_2\)CH=CH\(_2\)), 5.75 (1H, ddt, \(J = 7, 11, 16\) Hz, CH\(_2\)CH=CH\(_2\)), 6.73 (1H, s, 4-H), 7.0-7.3 (4H, m, Ph-H). EI-MS m/z (relative intensity): 292 (M\(^+\), 10), 251 (100), 155 (14). EI-HRMS m/z M\(^+\) Calcd for C\(_{16}\)H\(_{20}\)Se: 292.0731. Found: 292.0732.

3-tert-Butyl-1-(2-methyl-2-propenyl)-1H-isoselenochromene (10b)

Pale yellow oil. \(^1\)H NMR (90 MHz) 1.26 (9H, s, \(t\)-Bu), 1.67 (3H, br s, Me), 2.46 (2H, br d, \(J = 8\) Hz, CHC\(_2\)H\(_2\)), 3.92 (1H, t, \(J = 8\) Hz, 1-H), 4.53 and 4.72 (each 1H, br s, C=C\(_2\)H\(_2\)), 6.66 (1H, s, 4-H), 6.9-7.2 (4H, m, Ph-H). EI-MS m/z (relative intensity): 306 (M\(^+\), 7), 251 (100), 155 (10). EI-HRMS m/z M\(^+\) Calcd for C\(_{17}\)H\(_{22}\)Se: 306.0887. Found: 306.0883.

3-tert-Butyl-1-(1-methyl-2-propenyl)-1H-isoselenochromene (10c)

This compound was an inseparable mixture of diastereomers in the ratio 1:2; pale yellow oil. \(^1\)H NMR (90 MHz) 0.77 (3H, d, \(J = 7\) Hz, Me, major isomer), 1.13 (3H, d, \(J = 7\) Hz, Me, minor isomer), 1.27 (9H, s, \(t\)-Bu), 2.2-2.9 (1H, m, CHMeCH=CH\(_2\)), 3.53 (1H, d, \(J = 9\) Hz, 1-H, major isomer), 3.59 (1H, d, \(J = 9\) Hz, 1-H, minor isomer), 4.65 (1H, br d, \(J = 18\) Hz, \(trans\)-CHMeCH=CH\(_2\), minor isomer), 4.74 (1H, br d, \(J = 10\) Hz, \(cis\)-CHMeCH=CH\(_2\), minor isomer), 4.88 (1H, br d, \(J = 18\) Hz, \(trans\)-CHMeCH=CH\(_2\), major isomer), 4.98 (1H, br d, \(J = 10\) Hz, \(cis\)-CHMeCH=CH\(_2\), major isomer), 5.3-6.2 (1H, m, CHMeCH=CH\(_2\)), 6.74 (1H, s, 4-H), 6.9-7.2 (4H, m, Ph-H). EI-MS m/z (relative intensity): 306 (M\(^+\), 3), 251 (100), 155 (13). EI-HRMS m/z M\(^+\) Calcd for C\(_{17}\)H\(_{22}\)Se: 306.0887. Found: 306.0882.

3-tert-Butyl-1-(1,1-dimethyl-2-propenyl)-1H-isoselenochromene (10d)

Yellow oil. \(^1\)H NMR (400 MHz) 1.00 and 1.02 (each 3H, s, Me x 2), 1.29 (9H, s, \(t\)-Bu), 3.81 (1H, s, 1-H), 4.84 (1H, dd, \(J = 1.3, 17.4\) Hz, \(trans\)-CH=CH\(_2\)), 4.89 (1H, dd, \(J = 1.3, 10.7\) Hz, \(cis\)-CH=CH\(_2\)), 5.80 (1H, dd, \(J = 10.7, 17.4\) Hz, CH=CH\(_2\)), 6.60 (1H, s, 4-H), 7.05-7.20 (4H, m, Ph-H). \(^{13}\)C NMR (100 MHz) 24.31 (q), 24.44 (q), 29.82 (q), 38.20 (s), 43.79 (s), 49.62 (d), 111.89 (t), 120.97 (d), 126.38 (d), 127.85 (s), 128.84 (d), 130.05 (d), 136.35 (s), 145.51 (d), 146.52 (s). EI-MS m/z (relative intensity): 320 (M\(^+\), 3), 251 (100), 155 (14). EI-HRMS m/z M\(^+\) Calcd for C\(_{18}\)H\(_{24}\)Se: 320.1044. Found: 320.1046.

1-Allyl-1H-isoselenochromene (11a)

Pale yellow oil. \(^1\)H NMR (90 MHz) 2.57 (2H, br dd, \(J = 7, 8\) Hz, CH\(_2\)CH=CH\(_2\)), 3.77 (1H, dt, \(J = 2, 8\) Hz, 1-H), 4.86 (1H, br d, \(J = 16\) Hz, \(trans\)-CH\(_2\)CH=CH\(_2\)), 4.93 (1H, br d, \(J = 11\) Hz, \(cis\)-CH\(_2\)CH=CH\(_2\)), 5.67 (1H, ddt, \(J = 7, 11, 16\) Hz, CH\(_2\)CH=CH\(_2\)), 6.58 (1H, dd, \(J = 2, 10\) Hz, 3-H), 6.87 (1H, d, \(J = 10\) Hz, 4-H), 6.9-7.3 (4H, m, Ph-H). EI-MS m/z (relative intensity): 236 (M\(^+\), 18), 195 (100), 115 (71). EI-HRMS m/z M\(^+\) Calcd for C\(_{12}\)H\(_{12}\)Se: 236.0105. Found: 236.0110.

1-(2-Methyl-2-propenyl)-1H-isoselenochromene (11b)
Pale yellow oil. $^1$H NMR (90 MHz), 1.62 (3H, br s, Me), 2.48 (2H, br d, $J = 8$ Hz, CHCH$_2$), 3.84 (1H, br t, $J = 8$ Hz, 1-H), 4.45 and 4.64 (each 1H, br s, C=CH$_2$), 3.84 (1H, br t, $J = 8$ Hz, 1-H), 6.50 (1H, br d, $J = 10$ Hz, 3-H), 6.79 (1H, d, $J = 10$ Hz, 4-H), 6.8-7.2 (4H, m, Ph-H). EI-MS m/z (relative intensity): 250 (M$^+$, 13), 195 (100), 115 (65). EI-HRMS m/z M$^+$ Calcd for C$_{13}$H$_{14}$Se: 250.0261. Found: 250.0263.

1-(1-Methyl-2-propenyl)-1H-isoselenochromene (11c)

This compound was an inseparable mixture of diastereomers in the ratio 1:2, pale yellow oil. $^1$H NMR (90 MHz), 0.81 (3H, d, $J = 7$ Hz, Me, major isomer), 1.14 (3H, d, $J = 7$ Hz, Me, minor isomer), 2.3-2.8 (1H, m, CHMeCH=CH$_2$), 3.60 (1H, dd, $J = 2$, 8 Hz, 1-H, major isomer), 3.67 (1H, dd, $J = 2$, 8 Hz, 1-H, minor isomer), 4.70 (1H, br d, $J = 17$ Hz, trans-CHMeCH=CH$_2$, minor isomer), 4.78 (1H, br d, $J = 10$ Hz, cis-CHMeCH=CH$_2$, minor isomer), 4.91 (1H, br d, $J = 17$ Hz, trans-CHMeCH=CH$_2$, major isomer), 5.00 (1H, br d, $J = 10$ Hz, cis-CHMeCH=CH$_2$, major isomer), 5.3-6.2 (1H, CHMeCH=CH$_2$), 6.64 (1H, dd, $J = 2$, 10 Hz, 3-H), 6.92 (1H, d, $J = 10$ Hz, 4-H), 6.9-7.4 (4H, m, Ph-H). EI-MS m/z (relative intensity): 250 (M$^+$, 5), 195 (100), 115 (55). EI-HRMS m/z M$^+$ Calcd for C$_{13}$H$_{14}$Se: 250.0261. Found: 250.0263.

1-(1,1-Dimethyl-2-propenyl)-1H-isoselenochromene (11d)

Pale yellow oil. $^1$H NMR (90 MHz), 1.02 (6H, s, Me x 2), 3.73 (1H, d, $J = 2$ Hz, 1-H), 4.78 (1H, dd, $J = 2$, 18 Hz, trans-CH=CH$_2$), 4.84 (1H, dd, $J = 2$, 10 Hz, cis-CH=CH$_2$), 5.78 (1H, dd, $J = 10$, 18 Hz, CH=CH$_2$), 6.57 (1H, dd, $J = 2$, 10 Hz, 3-H), 6.77 (1H, d, $J = 10$ Hz, 4-H), 6.9-7.2 (4H, m, Ph-H). EI-MS m/z (relative intensity): 264 (M$^+$, 3), 195 (100), 115 (43). EI-HRMS m/z M$^+$ Calcd for C$_{14}$H$_{16}$Se: 264.0418. Found: 264.0419.

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REFERENCES


