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

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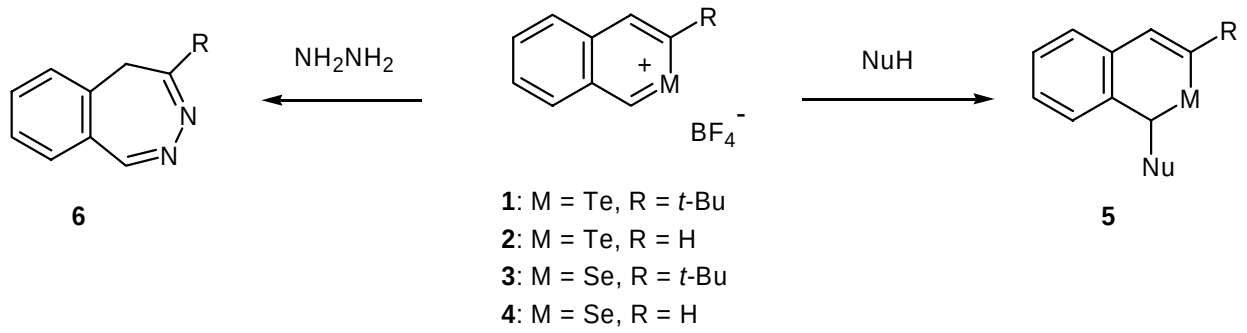
Abstract – 3-*tert*-Butyl-2-benzotelluropyrylium salt (**1**) reacts with an equal amount of allyltributyltin to afford 1-allyl-3-*tert*-butyl-1*H*-isotellurochromene (**8a**) in 93 % yield. Similarly, 1-allyl-1*H*-isotellurochromenes (**9**) and isoselenochromenes (**10, 11**) were prepared from the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

The chemistry (syntheses, structure, physical properties and reactions) of telluropyrylium[2-5] and selenopyrylium compounds,[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.[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[6] more than 35 years ago. Previously, we clarified that the reactions of the 2-benzotelluropyrylium salts (**1, 2**)[7] and 2-benzoselenopyrylium salts (**3, 4**)[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**).[8] In addition, the ring transformation of the 2-benzoselenopyrylium salts (**3**) into the 5*H*-2,3-benzodiazepines (**6**)[9] using hydrazine as a nucleophile was also reported.

We have also provided the preparation of the 1*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-benzoseleno-



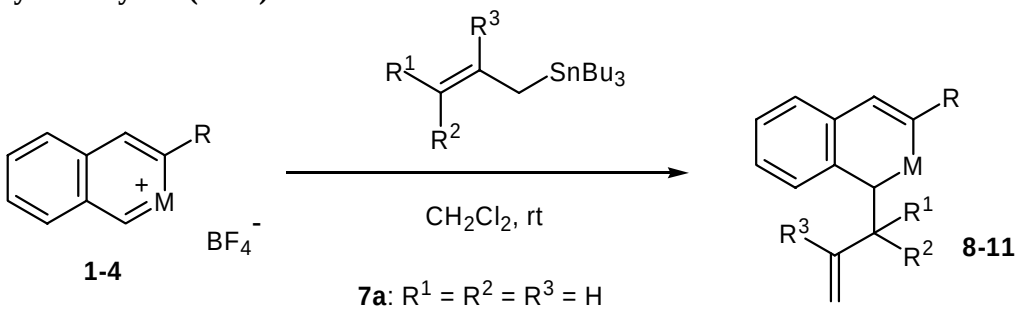
Scheme 1

pyrylium salts with Grignard reagents.[8] The 2-benzotelluropyrylium salts react with Grignard reagents except for benzylmagnesium bromide to afford the dimeric-type products without normal coupling products.[8] Only the 1-alkyl- and 1-phenyl-1*H*-isotellurochromenes were obtained by the reaction of the 2-benzotelluropyrylium salts with organocopper reagents.[10] However, no 1*H*-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*.[11] 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 CH_2Cl_2 at room temperature resulted in the introduction of an allyl group into the heterocation ring to give the desire 1-allyl-3-*tert*-butyl-1*H*-isotellurochromene (**8a**) in 93 % yield without any other products (Table, entry 1). The reaction was completed within only 5 min. The use of Et_2O 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 an 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)



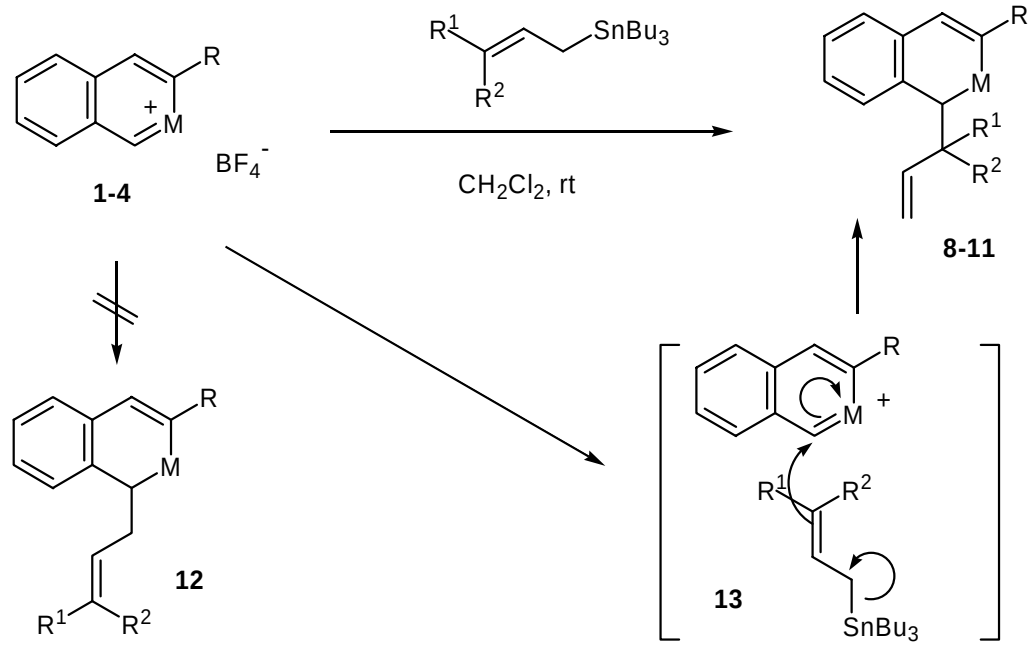
7a: $R^1 = R^2 = R^3 = H$
7b: $R^1 = R^2 = H$, $R^3 = Me$
7c: $R^1 = Me$, $R^2 = R^3 = H$
7d: $R^1 = R^2 = Me$, $R^3 = H$

entry	M	R	R^1	R^2	R^3	product	yield (%)[a]
1	Te	*t*-Bu	H	H	H	**8a**	93
2	Te	*t*-Bu	H	H	Me	**8b**	95
3	Te	*t*-Bu	Me	H	H	**8c**	86[b]
4	Te	*t*-Bu	Me	Me	H	**8d**	73
5	Te	H	H	H	H	**9a**	44
6	Te	H	H	H	Me	**9b**	44
7	Te	H	Me	H	H	**9c**	30[c]
8	Te	H	Me	Me	H	**9d**	34
9	Se	*t*-Bu	H	H	H	**10a**	91
10	Se	*t*-Bu	H	H	Me	**10b**	94
11	Se	*t*-Bu	Me	H	H	**10c**	83[b]
12	Se	*t*-Bu	Me	Me	H	**10d**	61
13	Se	H	H	H	H	**11a**	48
14	Se	H	H	H	Me	**11b**	49
15	Se	H	Me	H	H	**11c**	50[b]
16	Se	H	Me	Me	H	**11d**	51

[a] Isolated yield
[b] Mixture of diastereomers (2: 1) determined by ^{1}H NMR spectrometry
[c] Mixture of diastereomers (1: 1) determined by ^{1}H NMR spectrometry

3-methyl-2-butenyltributyltin (**7d**) produced the 1-(1-methyl-2-propenyl)-1*H*-isotellurochromene (**8c**) and 1-(1,1-dimethyl-2-propenyl)-1*H*-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}H-NMR spectrum. The MS spectrum of **8d** showed a molecular formula of $C_{18}H_{24}Te$ with a molecular ion at *m/z* = 370. The ^{1}H-NMR spectrum had two singlet signals (each 3H, Me x 2) at δ1.01 and δ 1.02 and a singlet signal (1H, 1-H) at δ 3.84. Three protons were also observed in the olefinic field. The ^{13}C-NMR spectrum showed one singlet sp^3 carbon at δ 39.19 except for *tert*-butyl group (δ 42.85, s). These spectral data clearly indicate that the structure of this compound is **8d**; the ^{13}C-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*H*-isotellurochromenes (**9c, 9d**) and 1-allyl-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

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*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_2Cl_2 (5 mL) at rt under an argon atmosphere. The mixture was stirred under the conditions for 5 min, and diluted with CH_2Cl_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_2Cl_2 (10:1 to 5:1) to give **8** or **9**.

1-Allyl-3-*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, C*H*$_2$CH=CH$_2$), 3.81 (1H, t, *J* = 8 Hz, 1-H), 4.95 (1H, br d, *J* = 16 Hz, *trans*-CH$_2$CH=C*H*$_2$), 5.02 (1H, br d, *J* = 11 Hz, *cis*-CH$_2$CH=C*H*$_2$), 5.72 (1H, ddt, *J* = 7, 11, 16 Hz, CH$_2$C*H*=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-*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*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-*tert*-Butyl-1-(1-methyl-2-propenyl)-1*H*-isotellurochromene (8c)

This compound was an inseparable mixuture 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, C*H*MeCH=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=C*H*$_2$, minor isomer), 4.72 (1H, br d, *J* = 10 Hz, *cis*-CHMeCH=C*H*$_2$, minor isomer), 4.86 (1H, br d, *J* = 17 Hz, *trans*-CHMeCH=C*H*$_2$, major isomer), 4.96 (1H, br d, *J* = 10 Hz, *cis*- CHMeCH=C*H*$_2$, major isomer), 5.2-6.1 (1H, m, CHMeC*H*=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-*tert*-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=C*H*$_2$), 4.87 (1H, dd, *J* = 1.3, 10.8 Hz, *cis*-CH=C*H*$_2$), 5.78 (1H, dd, *J* = 10.8, 17.4 Hz, C*H*=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 (s), 130.28 (d), 138.44 (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-1*H*-isotellurochromene (9a)

Yellow oil. ^{1}H NMR (90 MHz) 2.75 (2H, br dd, *J* = 7, 8 Hz, C*H*$_2$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=C*H*$_2$), 5.02 (1H, br d, *J* = 11 Hz, *cis*-CH$_2$CH=C*H*$_2$), 5.72 (1H, ddt, *J* = 7, 11, 16 Hz, CH$_2$C*H*=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)-1*H*-isotellurochromene (9b)

Yellow oil. ^{1}H NMR (90 MHz) 1.64 (3H, br s, Me), 2.67 (2H, br d, *J* = 8 Hz, CHC*H*$_2$), 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)-1*H*-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, C*H*MeCH=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=C*H*$_2$), 4.73 (1H, br d, *J* = 10 Hz, *cis*-CHMeCH=C*H*$_2$), 4.89 (1H, br d, *J* = 16 Hz, *trans*-CHMeCH=C*H*$_2$), 4.99 (1H, br d, *J* = 10 Hz, *cis*-CHMeCH=C*H*$_2$), 5.2-6.1 (1H, m, CHMeC*H*=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)-1*H*-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=C*H*$_2$), 4.86 (1H, dd, *J* = 2, 10 Hz, *cis*-CH=C*H*$_2$), 5.78 (1H, dd, *J* = 10, 18 Hz, C*H*=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-Benzoselenopyrylium Salts (3, 4) with Allyltin Reagents (7): Formation of 1-Allyl-1*H*-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-1*H*-isoselenochromene (10a)

Colorless oil. ^{1}H NMR (90 MHz) 1.28 (9H, s, *t*-Bu), 2.53 (2H, br dd, *J* = 7, 8 Hz, C*H*$_2$CH=CH$_2$), 3.82 (1H, t, *J* = 8 Hz, 1-H), 4.96 (1H, br d, *J* = 16 Hz, *trans*-CH$_2$CH=C*H*$_2$), 5.03 (1H, br d, *J* = 11 Hz, *cis*-CH$_2$CH=C*H*$_2$), 5.75 (1H, ddt, *J* = 7, 11, 16 Hz, CH$_2$C*H*=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)-1*H*-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*H*$_2$), 3.92 (1H, t, *J* = 8 Hz, 1-H), 4.53 and 4.72 (each 1H, br s, C=C*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)-1*H*-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, C*H*MeCH=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=C*H*$_2$, minor isomer), 4.74 (1H, br d, *J* = 10 Hz, *cis*-CHMeCH=C*H*$_2$, minor isomer), 4.88 (1H, br d, *J* = 18 Hz, *trans*-CHMeCH=C*H*$_2$, major isomer), 4.98 (1H, br d, *J* = 10 Hz, *cis*-CHMeCH=C*H*$_2$, major isomer), 5.3-6.2 (1H, m, CHMeC*H*=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)-1*H*-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=C*H*$_2$), 4.89 (1H, dd, *J* = 1.3, 10.7 Hz, *cis*-CH=C*H*$_2$), 5.80 (1H, dd, *J* = 10.7, 17.4 Hz, C*H*=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), 127.07 (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-1*H*-isoselenochromene (11a)

Pale yellow oil. ^{1}H NMR (90 MHz), 2.57 (2H, br dd, *J* = 7, 8 Hz, C*H*$_2$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=C*H*$_2$), 4.93 (1H, br d, *J* = 11 Hz, *cis*-CH$_2$CH=C*H*$_2$), 5.67 (1H, ddt, *J* = 7, 11, 16 Hz, CH$_2$C*H*=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)-1*H*-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), 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)-1*H*-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, C*H*MeCH=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, m, CHMeC*H*=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)-1*H*-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, C*H*=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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