

Reactions of 1-benzoselenopyrylium salts with nucleophiles: formation of functionalised selenochromenes^{1†}

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Reactions of the stable 1-benzoselenopyrylium salts **1** with several nucleophiles (methoxide ion, isopropoxide ion, *tert*-butoxide ion, diethylamine and *n*-butylamine) and also LiAlH₄ reduction are described; comparison of the behaviour of 1-benzotelluropyrylium salts is made.

Introduction

The chemistry of the chalcogenopyrylium salts,² six-membered heteroaromatic cations containing a sulfur, selenium or tellurium element, has been extensively studied in recent years because of their aromaticity when compared with that of the pyrylium salts³ and also of the traditional heteroaromatic compounds such as pyridine. However when compared to the chemistry of the thiopyrylium salts **I**, **IV**, **VII**, those of seleno-**II**, **V**, **VIII** and telluro- analogs **III**, **VI**, **IX** have not yet been sufficiently investigated. In particular, the monocyclic thiopyrylium cation **I**^{2,4} has been the subject of numerous studies, and the physical properties of its derivatives, including theoretical calculations and X-ray structures, and their chemistry are well established.

The seleno- **II**^{2,4} and telluro-pyrylium salts **III**^{2,5} have been also synthesized, and their chemistry has been covered in recent reviews.

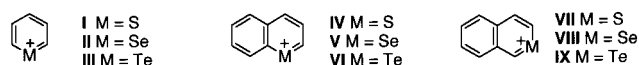


Fig. 1

During the course of our studies on tellurium- and selenium-containing heterocycles,^{6,7} we have reported the isolation of the stable novel 2-benzotelluropyrylium salts **IX**⁸ and 2-benzoselenopyrylium salts **VIII**.⁹ More recently, we have also succeeded in the preparation of their structural isomers, the 1-benzotelluropyrylium salts **VI**,¹⁰ and examined their reactions with nucleophiles. In our previous paper¹ we have reported the preparation of the 1-benzoselenopyrylium salts **V** and we examined their stability. However, their reactivity towards nucleophiles has received little attention¹¹ until now. In this paper the reactions of the isolated stable 1-benzoselenopyrylium salts **V** with nucleophiles are reported and compared with those of the corresponding telluropyrylium salts **VI**.

Results and discussion

Some reactions of the 1-benzoselenopyrylium salts **1**¹ with nucleophiles were examined as shown in Scheme 1, and their results are summarized in Table 1. LiAlH₄ reduction of the salts **1a** in Et₂O or THF at 0 °C afforded a mixture of 4*H*-selenochromene **2Aa** and 2*H*-selenochromene **2Ba**, which could be separated by silica gel chromatography; the latter chromene is the major product. A similar reduction of the 2-*tert*-butylpyrylium salt **1b** gave predominantly the 4*H*-chromene **2Ab** in 81% yield together with the 2*H*-derivative

2Bb in 16% yield. In addition, the 2-phenylpyrylium salt **1c** was reduced by LiAlH₄ to produce 4*H*-selenochromene **2Ac** in 91% yield as the sole product.

Table 1 Reactions of the 1-benzoselenopyrylium salts **4** with nucleophiles

| Nu | R | A: Yield/% appearance | B: Yield/% appearance |
|-----------------------------------|-----------------|---|---|
| 2 Nu = H | H | 24 Pale yellow oil | 58 Pale yellow oil |
| | Bu ^t | 81 Pale yellow oil | 16 Pale yellow oil |
| | Ph | 91 Yellow prisms ^a m.p. 77–78 °C | – |
| 3 Nu = OMe | H | – | 93 Yellow oil |
| | Bu ^t | 21 Colourless prisms ^a m.p. 52–55 °C | 75 Colourless prisms ^a m.p. 76–77 °C |
| | Ph | 93 Yellow oil | – |
| 4 Nu = OPr ⁱ | H | – | 92 Yellow oil |
| | Bu ^t | 91 Yellow oil | – |
| 5 Nu = OBU ^t | Ph | 12 Yellow oil | – |
| | H | – | 80 Yellow oil |
| 6 Nu = NEt ₂ | H | – | 74 Yellow oil |
| | Bu ^t | 93 Yellow prisms ^b m.p. 38–41 °C | – |
| 7 N = NHBu ⁿ | Ph | 96 Yellow oil | – |
| | Bu ^t | 91 | – |

^aRecrystallized from acetone – *n*-hexane. ^bRecrystallized from *n*-hexane.

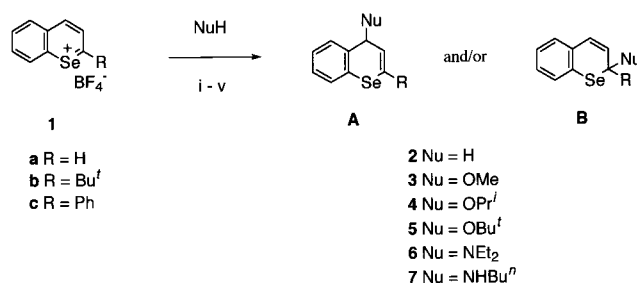
Renson and co-workers^{11a} reported that the NaBH₄ reduction of the parent selenopyrylium salt **V**, in which the counter anion was perchlorate, produced 2*H*-selenochromene as the sole product. On the other hand, it has been found that the reaction of the telluropyrylium salts,¹⁰ with NaBH₄ in MeOH resulted in the nucleophilic addition of methoxide to give the 4-methoxy-4*H*-tellurochromenes as the only products.¹⁰

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† This is a Short Paper, there is therefore no corresponding material in *J. Chem. Research (M)*.

These facts prompted us to examine the reaction of the obtained benzoselenopyrylium salts **1** with NaBH₄ in MeOH.

Upon treatment of the salts **1** with NaBH₄ in absolute MeOH, **1** readily decomposed to yield the 4-methoxy-4*H*-seleno- **3A** and/or the 2-methoxy-2*H*-selenochromenes **3B**, and no reduced products. Thus, MeOH behaved as a nucleophile towards the 1-benzoselenopyrylium salts **1** also. The addition of NaOMe in this reaction increased the yields of the products, as in the case of the telluropirylium salts.¹⁰ Although the telluropirylium salts did not react with a secondary or tertiary alkoxide in the corresponding alcohol to give any characterizable products,¹⁰ the selenopyrylium salts **1a** and **1b** reacted with NaOPr^{*i*} in Pr^{*i*}OH to afford 2-isopropoxy-2*H*- **4Ba** and 4-isopropoxy-4*H*-selenochromene **4Ab** in 92 and 91% yields, respectively. When the 2-phenylpyrylium salt **1c** was treated under the same conditions, it gave the corresponding product **4Ab** in only 12% yield. Treatment of the 2-unsubstituted salt **1a** with KOBu^{*t*} in Bu^{*t*}OH resulted in the nucleophilic attack of Bu^{*t*}O⁻ onto the C-2 position to produce the 2-*tert*-butoxy-2*H*-chromene **5Ba** in 80% yield. Salts **1b** and **1c** having a *tert*-butyl or phenyl group at the C-2 position failed to afford any selenochromenes even in high concentration of butoxide ion, owing to their steric hindrance.



Scheme 1 Reagents and conditions: i, LiAlH₄, THF, 0°C, 30 min (for **2**); ii, NaOMe, MeOH, room temp., 30 min (for **3**); NaOP^{*r*}, Pr^{*i*}OH, room temp, 30 min (for **4**); iv, NaOBu^{*t*}, Bu^{*t*}OH, room temp, 30 min (for **5**); v, HNEt₂, benzene, room temp, 30 min (for **6**); H₂NBu^{*n*}, benzene, room temp, 30 min (for **7**).

These results suggested that the selenopyrylium salts **1** may have high reactivities towards other nucleophiles. The reaction of **1** with diethylamine in benzene at room temperature proceeded as expected. When a *tert*-butyl or phenyl group is located at the C-2 position of **1**, the corresponding 4*H*-selenochromenes **6Ab** and **6Ac** were formed in high yields. However, the 2-unsubstituted salt **1a** underwent the nucleophilic addition at the C-2 position to give **6Ba** in 74% yield. The reaction of **1** with a primary amine, such as *n*-butylamine, produced no characterizable products in the case of **1a**, while the chromenes **7Ab** and **7Ac** having a *tert*-butyl or phenyl group at the C-2 position could be obtained from the corresponding salts in excellent yields. All products **3**, **4**, **5**, **6** and **7** were isolated in a nearly pure state but decomposed during silica gel chromatography. The separation of **3Ab** and **3Bb** was achieved by the fractional recrystallization from acetone *n*-hexane.

The most reactive site of the 1-benzotelluropirylium cations **9b** and **9c** having a *tert*-butyl or phenyl group at the C-2 position was the C-4 position.¹⁰ Thus, only the 4-substituted tellurochromenes were obtained. On the contrary, nucleophilic attack of an alkoxide or amine on the 1-benzoselenopyrylium salts **1** occurred both at the C-2 and C-4 positions. For instance, the parent 1-benzoselenopyrylium salt **1a** having no substituent reacted reasonably with most of the nucleophiles at the C-2 position. However, surprisingly, treatment of the 2-*tert*-butylpyrylium salt **1b** with NaOMe in MeOH gave 2-*tert*-butyl-2-methoxy-2*H*-selenochromene **3Bb** in 75% yield as the

major product together with 2-*tert*-butyl-4-methoxy-4*H*-selenochromene **3Ab** in 21% yield in spite of the severe steric hindrance of a *tert*-butyl group at the C-2 position.

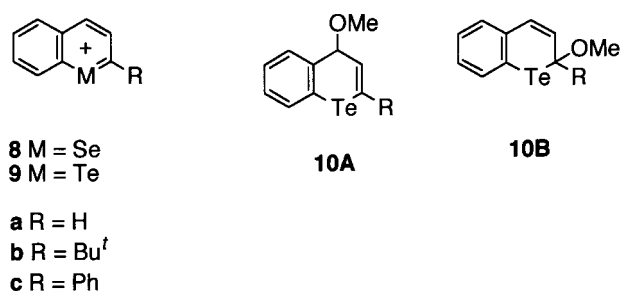


Fig. 2

In order to explain the influence of the cationic heteroatom in the pyrylium rings at the 1 position with respect to the site of reactivity, we have now calculated the net charges on the C-4 and C-2 positions for the 1-benzoseleno- **8** and 1-benzotelluropirylium cations **9** and also the heats of formation (*H_f*) for their nucleophile adducts, 4-methoxy-4*H*- **3Ab** and 2-methoxy-2*H*- selenochromenes **3Bb** and their corresponding tellurium analogs **10A** and **10B**, using the semiempirical PM3 method.¹² The charge data for the cations **8** and **9** are listed in Table 2.

Table 2 PM3 Calculated net charges for the 1-benzoseleno- **8** and 1-benzotelluro-pyrylium cations **9**

| | 8: M = Se | | 9: M = Te | |
|-------------------------------------|------------------|-------|------------------|-------|
| | C-4 | C-2 | C-4 | C-2 |
| a R = H | 0.17 | -0.09 | 0.25 | -0.12 |
| b R = Bu ^{<i>t</i>} | 0.17 | -0.04 | 0.25 | -0.08 |
| c R = Ph | 0.16 | 0.05 | 0.23 | 0.00 |

Regarding the two cations **8b** and **9b**, the charge on the C-4 position is much more positive than that on the C-2 position, also **9b** has a larger difference between the charges compared to **8b**. Comparing the *H_f* for the two possible regioisomers of their methoxylated adducts, 2-methoxy-2*H*-selenochromene **3Bb** is 4.2 kcal/mol more stable than the 4-methoxy derivative **3Ab**; in contrast, 2-methoxy-2*H*-tellurochromene **10B** is more stable than the 4-methoxy derivative **10A** by only 1.8 kcal/mol. For the related monocyclic thiopyrylium cation **1**, Doddi and co-workers^{2,13} suggested that its regioselectivity towards nucleophilic reactions is under kinetic and thermodynamic control; the kinetic regioselectivity is controlled by the relative electron density at the carbon under attack while the thermodynamic regioselectivity depends on the relative stability of the adducts. Thus, the present calculated results support the concept that the 2*H*-adduct **3Bb** is the principal product of the thermodynamic control in the case of the selenopyrylium cation **8b**, whereas the 4*H*-adduct **10A** is the principal product of kinetic control in the case of the telluropirylium cation **9b**. The enhanced stability of **3Bb** may be due to the anomeric effect between the methoxyl group and the ring selenium atom. As shown in Table 1, the distinction of **2Aa** from **2Ab** and **2Ac** in yield also may be ascribed to the thermodynamic and kinetic control in LiAlH₄ reduction of the selenopyrylium salts **1**. 4*H*-Selenochromene **2Aa** is 1.9 kcal/mol less stable than 2*H*-selenochromene **2Ba**, resulting in the formation of **2Aa** as minor product together with the major product, **2Ba**, possibly under thermodynamic control. On the contrary,

2-*tert*-butyl-4*H*-chromene **2Ab** is only 0.3 kcal/mol less stable than the 2*H* derivative **2Bb**. In this case, **2Ab** seems to be the principal product of kinetic control based on the charge difference between the C-4 and C-2 positions in cation **8b**. Finally, 2-phenyl-4*H*-chromene **2Ac** is 0.8 kcal/mol more stable than the 2*H* derivative **2Bc**. Although this difference in the two regioisomers and also the charge difference in cation **8c** are somewhat small, both the differences in regioselectivity are similarly consistent with the hypothesis that **2Ac** is the principal product under both thermodynamic and kinetic control.

Experimental

Melting points were measured on a Yanagimoto micro melting point hot stage apparatus and are uncorrected. IR spectra were determined with a Hitachi 270-30 spectrometer. Mass spectra (MS) and HR-MS were recorded on a JEOL JMS-DX300 instrument. ¹H NMR spectra were determined with a JEOL PMX-60SI (60 MHz), JEOL EX-90A (90 MHz) or JEOL JNM-GSX 400 (400 MHz) spectrometer in CDCl₃ or CD₃CN using tetramethylsilane as internal standard and *J* values are given in Hz. ¹³C NMR spectra and NOE spectra were measured on JEOL JNM-GSX 400 spectrometer. ⁷⁷Se NMR spectra were recorded on a JEOL EX-400 spectrometer at 76.2 MHz, and samples were referenced to Me₂Se as an external standard.

LiAlH₄ reduction of selenopyrylium salts 1: LiAlH₄ (16 mg, 0.33 mmol) was added in small portions to a suspended mixture of **1** (0.3 mmol) in anhydrous THF (6 ml) at 0 °C under an argon atmosphere. The reaction mixture was stirred at room temperature for 30 min, and then quenched by the addition of saturated aqueous Na₂CO₃ solution (5 drops). The resulting solution was dried (MgSO₄) and evaporated *in vacuo*. The resulting residue was chromatographed on silica gel eluted with *n*-hexane to give the 4*H*-selenochromene **2A** and 2*H*-selenochromene **2B**. The 4*H*-selenochromenes **2A** were identical with authentic samples.¹

4*H*-Selenochromene **2Aa**: δ_H (90 MHz, CDCl₃) 3.24 (2H, d, *J* 5, 4-H), 6.36 (1H, dt, *J* 5 and 8, 3-H), 6.90 (1H, d, *J* 8, 2-H), 7.1–7.6 (4H, m, Ph-H) (HRMS: *m/z* Calc. for C₉H₈⁸⁰Se: 195.9791. Found: 195.9789).

2*H*-Selenochromene **2Ba**: δ_H (90 MHz, CDCl₃) 3.40 (2H, d, *J* 5, 2-H), 5.77 (1H, dt, *J* 5 and 10, 3-H), 6.40 (1H, d, *J* 10, 4-H), 7.0–7.5 (4H, m, Ph-H) (HRMS: *m/z* Calc. for C₉H₈⁸⁰Se: 195.9791. Found: 195.9790).

2-*tert*-Butyl-2*H*-selenochromene **2Bb**: δ_H (90 MHz, CDCl₃) 1.00 (9H, s, Bu^t), 3.57 (1H, d, *J* 6, 2-H), 5.76 (1H, dd, *J* 6 and 11, 3-H), 6.50 (1H, d, *J* 11, 4-H), 6.9–7.4 (4H, m, Ph-H) (HRMS: *m/z* Calc. for C₁₃H₁₆⁸⁰Se: 252.0418. Found: 252.0417).

Treatment of selenopyrylium salts 1 with NaOMe in MeOH: NaOMe (28% solution in MeOH, 1 ml) was added to a solution of the selenopyrylium salt **1** (0.5 mmol) in MeOH (10 ml) under an argon atmosphere. The resulting solution was stirred for 30 min and extracted with CH₂Cl₂ (20 × 3). The organic layers were washed with brine (30 ml × 2), dried (MgSO₄), and evaporated *in vacuo* to give **3**. Products were obtained in a nearly pure form, and decomposed during the attempted purification by silica gel chromatography.

2-Methoxy-2*H*-selenochromene **3Ba**: δ_H (90 MHz, CDCl₃) 3.02 (3H, s, OMe), 5.53 (1H, d, *J* 6 Hz, 2-H), 5.87 (1H, dd, *J* 6, 10, 3-H), 6.78 (1H, d, *J* 10, 4-H), 7.0–7.7 (4H, m, Ph-H) (HRMS: *m/z* Calc. for C₁₀H₁₀O⁸⁰Se: 225.9897. Found: 225.9896).

2-*tert*-Butyl-4-methoxy-4*H*-selenochromene **3Ab**: *m/z* 282 (M⁺); δ_H (90 MHz, CDCl₃) 1.23 (9H, s, Bu^t), 3.65 (3H, s, OMe), 4.49 (1H, d, *J* 4, 4-H), 6.15 (1H, d, *J* 4, 3-H), 7.0–7.7 (4H, m, Ph-H) (Anal. Calc. For C₁₄H₁₈OSe: C, 59.79; H, 6.45. Found: C, 59.78; H, 6.55%).

2-*tert*-Butyl-2-methoxy-2*H*-selenochromene **3Bb**: *m/z* 282 (M⁺); δ_H (90 MHz, CDCl₃) 1.12 (9H, s, Bu^t), 3.08 (3H, s, OMe), 5.40 (1H, d, *J* 12, 3-H), 6.78 (1H, d, *J* 12 Hz, 4-H), 7.0–7.7 (4H, m, Ph-H) (Anal. Calc. For C₁₄H₁₈OSe: C, 59.79; H, 6.45. Found: C, 59.74; H, 6.47%).

4-Methoxy-2-phenyl-4*H*-selenochromene **3Ac**: δ_H (90 MHz, CDCl₃) δ 3.47 (3H, s, OMe), 4.80 (1H, d, *J* 5, 4-H), 6.57 (1H, d, *J* 5, 3-H), 7.1–7.8 (9H, m, Ph-H) (HRMS: *m/z* Calc. for C₁₆H₁₄O⁸⁰Se: 302.0210. Found: 302.0212).

Treatment of selenopyrylium salts 1 with NaOPrⁱ in PrⁱOH: NaOPrⁱ (30% solution in PrⁱOH, prepared from Na and PrⁱOH, 1 ml) was added to a solution of the selenopyrylium salt **1** (0.5 mmol) in PrⁱOH (10 ml) under an argon atmosphere. The resulting reaction mixture was worked up as described for the preparation of **3** to give **4**.

2-Isopropoxy-2*H*-selenochromene **4Ba**: δ_H (90 MHz, CDCl₃) 1.13 and 1.18 (each 3H, d, *J* 6, OCHMe₂), 3.95 (1H, dq, *J* 6, 6, OCHMe₂), 5.64 (1H, d, *J* 6, 2-H), 5.95 (1H, dd, *J* 6, 10, 3-H), 6.86 (1H, d, *J* 10,

4-H), 6.9–7.6 (4H, m, Ph-H) (HRMS: *m/z* Calc. for C₁₂H₁₄O⁸⁰Se: 254.0210. Found: 254.0218).

2-*tert*-Butyl-4-isopropoxy-4*H*-selenochromene **4Ab**: δ_H (90 MHz, CDCl₃) 1.21 (9H, s, Bu^t), 1.30 (6H, d, *J* 6, OCHMe₂), 3.92 (1H, dq, *J* 6, 6, OCHMe₂), 4.42 (1H, d, *J* 3, 4-H), 6.07 (1H, d, *J* 3, 3-H), 7.1–7.8 (4H, m, Ph-H) (HRMS: *m/z* Calc. for C₁₆H₂₂O⁸⁰Se: 310.0836. Found: 310.0834).

2-Phenyl-4-isopropoxy-4*H*-selenochromene **4Ac**: δ_H (90 MHz, CDCl₃) 1.19 and 1.33 (each 3H, d, *J* 6, OCHMe₂), 3.95 (1H, m, OCHMe₂), 4.73 (1H, d, *J* 4, 4-H), 6.45 (1H, d, *J* 4, 3-H), 7.1–7.8 (9H, m, Ph-H) (HRMS: *m/z* Calc. for C₁₈H₁₈O⁸⁰Se: 330.0524. Found: 330.0515).

Treatment of selenopyrylium salts 1 with KOBu^t in Bu^tOH; formation of 2-*tert*-butoxy-2*H*-selenochromene **5Ba**: KOBu^t (200 mg) was added to a solution of the selenopyrylium salt **1a** (0.5 mmol) in Bu^tOH (10 ml) under an argon atmosphere. The resulting reaction mixture was worked up as described for the preparation of **3** to give **5Ba**, δ_H (90 MHz, CDCl₃) 1.33 (9H, s, OBu^t), 5.75 (1H, d, *J* 6, 2-H), 5.93 (1H, dd, *J* 6, 10, 3-H), 6.72 (1H, d, *J* 10, 4-H), 7.0–7.4 (4H, m, Ph-H) (HRMS: *m/z* Calc. for C₁₃H₁₆O⁸⁰Se: 268.0367. Found: 268.0366).

Treatment of selenopyrylium salts 1 with HNEt₂: HNEt₂ (0.6 ml) was added slowly to a suspended mixture of the selenopyrylium salt **1** (0.3 mmol) in benzene (10 ml) at room temperature under an argon atmosphere. The reaction mixture was stirred at room temperature for 30 min, and then diluted with benzene (50 ml). The benzene layer was washed with 5 % H₂SO₄ (30 ml × 2) and brine (30 ml × 2), dried (MgSO₄), and evaporated *in vacuo* to give **6**. These products were also obtained in nearly pure states, and decomposed during the attempted purification by silica gel chromatography.

2-Diethylamino-2*H*-selenochromene **6Ba**: δ_H (90 MHz, CDCl₃) 1.05 (6H, t, *J* 7, N(CH₂CH₃)₂), 2.63 (each 2H, q, *J* 7, N(CH₂CH₃)₂), 5.10 (1H, d, *J* 7, 2-H), 5.82 (1H, dd, *J* 7, 10, 3-H), 6.38 (1H, d, *J* 10, 4-H), 7.0–7.8 (4H, m, Ph-H) (HRMS: *m/z* Calc. for C₁₃H₁₇N⁸⁰Se: 267.0527. Found: 267.0518).

2-*tert*-Butyl-4-diethylamino-4*H*-selenochromene **6Ab**: δ_H (90 MHz, CDCl₃) 1.12 (6H, t, *J* 7, N(CH₂CH₃)₂), 1.24 (9H, s, Bu^t), 2.70 (4H, q, *J* 7, N(CH₂CH₃)₂), 4.17 (1H, d, *J* 4, 4-H), 6.13 (1H, d, *J* 4, 3-H), 7.0–7.7 (4H, m, Ph-H) (HRMS: *m/z* Calc. for C₁₇H₂₅N⁸⁰Se: 323.1153. Found: 323.1144).

4-Diethylamino-2-phenyl-4*H*-selenochromene **6Ac**: δ_H (90 MHz, CDCl₃) 1.13 (6H, t, *J* 7, N(CH₂CH₃)₂), 2.73 (4H, q, *J* 7, N(CH₂CH₃)₂), 4.47 (1H, d, *J* 4, 4-H), 6.61 (1H, d, *J* 4, 3-H), 7.1–7.8 (9H, m, Ph-H) (HRMS: *m/z* Calc. for C₁₉H₂₁N⁸⁰Se: 343.0840. Found: 343.0836).

Treatment of selenopyrylium salts 1 with BuⁿNH₂: BuⁿNH₂ (0.6 ml) was added slowly to a suspended mixture of the selenopyrylium salt **1** (0.3 mmol) in benzene (10 ml) at room temperature under an argon atmosphere. The reaction mixture was worked up as described for the preparation of **6** to give **7**.

4-*n*-Butylamino-2-*tert*-butyl-4*H*-selenochromene **7Ab**: δ_H (90 MHz, CDCl₃) 0.88 (3H, t, *J* 7, NCH₂CH₂CH₂CH₃), 1.2–1.8 (4H, m, NCH₂CH₂CH₂CH₃), 2.0 (1H, br, NH), 2.60 (2H, t, *J* 7, NCH₂CH₂CH₂CH₃), 4.07 (1H, d, *J* 6, 4-H), 6.17 (1H, d, *J* 6, 3-H), 7.1–7.7 (9H, m, Ph-H) (HRMS: *m/z* Calc. for C₁₇H₂₅N⁸⁰Se: 323.1152. Found: 323.1158).

4-*n*-Butylamino-2-phenyl-4*H*-selenochromene **7Ac**: δ_H (90 MHz, CDCl₃) 0.87 (3H, t, *J* 7, NCH₂CH₂CH₂CH₃), 1.2–1.8 (4H, m, NCH₂CH₂CH₂CH₃), 2.0 (1H, br, NH), 2.63 (2H, t, *J* 7, NCH₂CH₂CH₂CH₃), 4.30 (1H, d, *J* 6, 4-H), 6.57 (1H, d, *J* 6, 3-H), 7.0–7.8 (9H, m, Ph-H) (HRMS: *m/z* Calc. for C₁₉H₂₁N⁸⁰Se: 343.0840. Found: 343.0857).

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