The [3 + 2] cycloaddition reaction of thiazole carbene-derived C-C-Se 1,3-dipoles: a concise and highly efficient strategy for the construction of multifunctional dihydroselenophenes and selenopheno[2,3-*b*]pyrazines†

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The first study on the reaction of C^+-C-Se^- 1,3-dipoles with electron-deficient alkenes and alkyne is reported. 2-Arylselenocarbamoylthiazolium inner salts, the unique thiazole carbene-derived C^+-C-Se^- 1,3-dipoles, reacted efficiently with methoxycarbonylallenes or dimethyl acetylenedicarboxylate to produce dihydroselenophenes or selenopheno[2,3-*b*]pyrazines, respectively, in high yields. Both reactions probably proceeded *via* a [3 + 2] cycloaddition of C^+-C-Se^- 1,3-dipoles with alkenes or alkyne followed by different transformations of the thiazole-spiro-selenophene intermediates. This work provides a concise and efficient strategy for the construction of multifunctional dihydroselenophenes and selenopheno[2,3-*b*]pyrazines, which are not easy accessible by other methods.

Introduction

Selenophene[1] and fused selenophene derivatives have attracted continued interest owing to their rich chemical and biological activities, and important physical properties. 2,5-Bis(selenophen-2-yl)-*N*-methylpyrrole, for example, is a antineoplastic agent with a broad spectrum of antitumoral activity against several human cancer cells,[2] while a series of 2-(selenophen-2-yl)pyrroles, 2-(selenophen-2-yl)thiophenes, 2-(selenophen-2-yl)selenophenes and 2,5-bis(selenophen-2-yl)thiophenes strongly inhibit liver cancer cells.[3] 2,5-Diphenylselenophene and other organoselenium compounds have been reported to induce phase II enzyme activities,[4] and selenophenyl ketones or thioketones could be used in the treatment of diseases related to protein aging.[5] Some benzoselenophene derivatives exhibit antibacterial and antifungal activity.[6] In addition to the potential applications in pharmaceuticals, selenophene derivatives can also be utilized in the area of functional materials due to their important optical and electronic properties. Aromatic ring-fused selenophenes,[7,8] or polymers of selenophenes[9] and fused selenophenes,[10] for instance, are good organic semiconductors for various optoelectronic devices such as organic field-effect transistors and light-emitting diodes. Because of the wide applications, the interest in the synthesis of selenophene and fused selenophene derivatives remains undiminished. The known methods for the construction of selenophenes are mainly based on the ring-closure reactions of acetylenes, olefins, β-diketo compounds and α,β-unsaturated acetonitriles with selenium reagents, including selenium chloride, sodium selenide, elemental selenium, or dimethyl diselenide (MeSeSeMe).[6,11] Preparation of aromatic ring fused selenophenes generally starts from intramolecular cyclization of selenium substituted aromatic compounds.[7,12] Although numerous syntheses of selenophene derivatives have been reported, further development of concise and efficient strategy for the construction of selenophenes and fused selenophenes is of great importance.

Nucleophilic *N*-heterocyclic carbenes are known to react with aryl isocyanates[13] or isothiocyanates[14–19] to form stable zwitterionic inner salts. In 2006, we reported for the first time that the 2-thiocarbamoylbenzimidazolium or -imidazolinium salts prepared from the reaction of benzimidazole or imidazoline carbenes with aryl isothiocyanates are unique ambident C^+-C-S^- and C^+-C-N^- bis-dipolar compounds.[16] Since then, we have developed ambident 1,3-dipoles derived from *N*-heterocyclic carbenes and isothiocyanates into versatile synthons in the construction of novel spiro- and fused thiophene and pyrrole derivatives.[16–19] Although *N*-heterocyclic carbene-derived C^+-C-S^- dipoles have been intensively investigated, their selenium analogues, the C^+-C-Se^- dipoles are still not explored. We envisioned that the reaction of *N*-heterocyclic carbenes with isoselenocyanates would form 2-selenocarbamoyl *N*-heterocyclic inner salts that might act as C^+-C-Se^- dipoles for the construction of selenophene derivatives. Therefore, we undertook the current study on the reaction of 2-selenocarbamoyl thiazolium salts with dimethyl acetylenedicarboxylate and methoxycarbonylallenes.

Results and discussion

Bis(1,3-diphenyl-2-imidazolidinylidene), which was regarded as an equivalent or a precursor of 1,3-diphenyl imidazoline carbene, is known to react with aryl isoselenocyanates to form 1 + 2 adducts, spiro[imidazolidine-2,4′-imidazolidine]-2′,5′-diselenones (1,3,6,9-tetraazaspiro[4.4]nonane-2,4-diselones).[14] However, the stable 1,3-dipolar adducts of *N*-heterocyclic carbenes with isoselenocyanates have not been reported before. According to our experiences in the preparation of 1,3-dipolar adducts from the reaction of *N*-heterocyclic carbenes with aryl isothiocyanates,[16–19] we attempted the preparation of stable C^+-C-Se^- dipoles, namely

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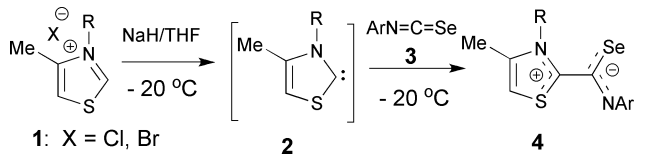
† Electronic supplementary information (ESI) available: Experimental procedure for the preparation of 2-arylselenocarbamoyl thiazolium salts **4** and full characterization for compounds **4**. CCDC reference numbers 721793 (**6a**) and 721794 (**8j**). For ESI and crystallographic data in CIF or other electronic format see DOI: 10.1039/b904575a

Table 1 Preparation of 2-selenocarbamoylthiazolium inner salts **4**[a]

Entry	**1**: R	**3**: Ar	Yield of **4**[b]
1	**1a**: Bn	**3a**: Ph	**4a**: 65
2	**1a**: Bn	**3b**: 4-ClPh	**4b**: 69
3	**1a**: Bn	**3c**: 3,4-Cl_2Ph	**4c**: 73
4	**1a**: Bn	**3d**: 4-CF_3Ph	**4d**: 76
5	**1b**: 4-MeBn	**3b**: 4-ClPh	**4e**: 61
6	**1b**: 4-MeBn	**3d**: 4-CF_3Ph	**4f**: 65
7	**1c**: 4-MeOBn	**3a**: Ph	**4g**: 55
8	**1c**: 4-MeOBn	**3b**: 4-ClPh	**4h**: 80
9	**1c**: 4-MeOBn	**3d**: 4-CF_3Ph	**4i**: 88
10	**1d**: 4-ClBn	**3a**: Ph	**4j**: 65
11	**1d**: 4-ClBn	**3b**: 4-ClPh	**4k**: 55
12	**1d**: 4-ClBn	**3d**: 4-CF_3Ph	**4l**: 71
13	**1e**: 4-BrBn	**3a**: Ph	**4m**: 66
14	**1e**: 4-BrBn	**3b**: 4-ClPh	**4n**: 68
15	**1e**: 4-BrBn	**3c**: 3,4-Cl_2Ph	**4o**: 61
16	**1f**: Et	**3c**: 3,4-Cl_2Ph	**4p**: 81

[a] Reaction conditions: THF, –20 °C, 2.5–3.5 h. [b] Isolated yield.

2-selenocarbamoyl thiazolium inner salts, from the reaction of thiazole carbenes with aryl isoselenocyanates at low temperature. Thus, thiazole carbenes **2**, which were generated in situ from the thiazolium salts **1** with sodium hydride, reacted with aryl isoselenocyanates **3** in dry THF at –20 °C to produce the desired 2-selenocarbamoylthiazolium inner salts **4** in 55–88% yields (Scheme 1 and Table 1). It should be pointed out that the reaction between thiazole carbene **2** and an electron-rich aryl substituted isoselenocyanate **3**, such as 4-tolyl or 4-anisyl isoselenocyanates, did not give stable dipolar adducts. It is most probably due to the anion centers of dipoles **4** not being efficiently stabilized by the electron-rich aryl rings.



Scheme 1 The reaction of thiazolium salts **1** with aryl isoselenocyanates **3** in the presence of sodium hydride.

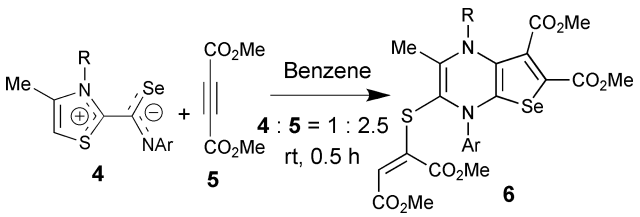
We then studied the reaction between 2-selenocarbamoyl thiazolium salts **4** and dimethyl acetylenedicarboxylate (DMAD), a strong dipolarophile that gave spiro-thiophenes[16,17] or fused thiophenes[19] in the reactions with *N*-heterocyclic carbene-derived C^+-C-S^- dipoles. Firstly, the reaction of *N*-benzyl 2-(4-methoxyphenyl)selenocarbamoylthiazolium salt **4g** with DMAD was optimized by varying the ratio of starting materials and solvents at ambident temperature (Table 2). It was found that the reaction of **4g** with DMAD proceeded very rapidly and efficiently. No matter whether in a polar or non-polar solvent, such as benzene, THF, dichloromethane, acetone and acetonitrile, the reaction finished in half a hour at room temperature to give product selenopheno[2,3-*b*]pyrazine **6g** in good to excellent yields. Although thiazolium salt **4g** was only slightly soluble in benzene, the reaction took place immediately when DMAD was added, and the highest yield (90%) of **6g** was obtained from the reaction of **4g** with 2.5 equivalent of DMAD in benzene at room temperature.

The scope of the reaction was then examined under optimized conditions by using thiazolium salts **4** bearing different substituents. It was found that the 1,3-dipoles **4** with either an electron-rich or an electron-deficient benzyl and phenyl groups on the thiazole ring and on the selenocarbamoyl moiety, respectively, reacted with DMAD efficiently to afford selenopheno[2,3-*b*]pyrazines **6** in 80–93% yields (Scheme 2 and Table 3). The reaction of 3-ethyl and 3-butyl thiazolium salts **4** with DMAD gave high yields of products, though these products were not fully characterized due to their instability.

Table 2 The reaction of 3-benzyl-2-(4-methoxphenyl)selenocarbamoyl-4-methylthiazolium salt **4g** with DMAD **5** under different conditions[a]

Entry	**4g**:**5**	Solvent	Yield of **6g** (%)[b]
1	1:1	benzene	57
2	1.1.5	benzene	68
3	1.2.0	benzene	78
4	1.2.5	benzene	90
5	1.2.5	CH_2Cl_2	86
6	1.2.5	THF	84
7	1.2.5	CH_3COCH_3	88
8	1.2.5	CH_3CN	77

[a] At room temp. for 0.5 h. [b] Isolated yield.



Scheme 2 The reaction of 2-arylselenocarbamoylthiazolium salts **4** with DMAD.

To further extend the applications of the *N*-heterocyclic carbene-derived C-C-Se 1,3-dipoles, we investigated the reaction between 2-arylselenocarbamoylthiazolium salts **4** and methoxycarbonylallenes **7**. Under similar conditions as for the reaction with DMAD, the reaction of **4** with methoxycarbonylallenes **7** proceeded very slowly. To promote the reaction, the non-polar solvent benzene was replaced by THF to increase the solubility of thiazolium salts **4**, and the reaction temperature was elevated to the boiling point of THF. Under these conditions, the reaction of thiazolium salts **4** with allenes **7** proceeded smoothly to produce products **8** in 61–78% yields in about 3 h (Scheme 3 and Table 4).

Table 3 The reaction of 2-arylselenocarbamoylthiazolium salts **4** with DMAD under optimized conditions

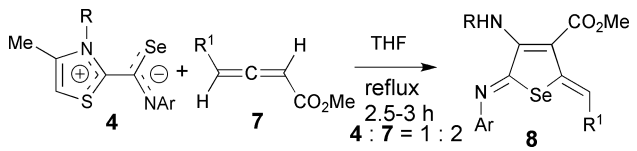
Entry	**4**	R	Ar	**6**	Yield (%)[a]
1	**4a**	Bn	Ph	**6a**	82
2	**4b**	Bn	4-ClPh	**6b**	89
3	**4d**	Bn	4-CF_3Ph	**6d**	87
4	**4e**	4-MeBn	4-ClPh	**6e**	84
5	**4f**	4-MeBn	4-CF_3Ph	**6f**	87
6	**4g**	4-MeOBn	Ph	**6g**	90
7	**4h**	4-MeOBn	4-ClPh	**6h**	90
8	**4i**	4-MeOBn	4-CF_3Ph	**6i**	90
9	**4j**	4-ClBn	Ph	**6j**	93
10	**4k**	4-ClBn	4-ClPh	**6k**	89
11	**4l**	4-ClBn	4-CF_3Ph	**6l**	80

[a] Isolated yield.

Table 4 The reaction of 2-arylselenocarbamoylthiazolium salts **4** with methoxycarbonylallenes **7**[a]

Entry	4	R	Ar	7	R^1	8	Yield (%)[b]
1	**4c**	Bn	3,4-Cl_2Ph	**7a**	Et	**8a**	67
2	**4o**	4-BrBn	3,4-Cl_2Ph	**7a**	Et	**8b**	78
3	**4a**	Bn	Ph	**7b**	*i*-Pr	**8c**	72
4	**4i**	4-MeOBn	4-CF_3Ph	**7b**	*i*-Pr	**8d**	61
5	**4m**	4-BrBn	Ph	**7b**	*i*-Pr	**8e**	73
6	**4n**	4-BrBn	4-ClPh	**7b**	*i*-Pr	**8f**	76
7	**4o**	4-BrBn	3,4-Cl_2Ph	**7b**	*i*-Pr	**8g**	71
8	**4p**	Et	3,4-Cl_2Ph	**7b**	*i*-Pr	**8h**	71
9	**4n**	4-BrBn	4-ClPh	**7c**	Bn	**8i**	68
10	**4o**	4-BrBn	3,4-Cl_2Ph	**7c**	Bn	**8j**	72

[a] Reaction conditions: **4**:**7** = 1:2, THF, reflux, 2.5–3 h. [b] Isolated yield.



Scheme 3 The reaction of 2-arylselenocarbamoylthiazolium salts **4** with methoxycarbonylallenes **7**.

In sharp contrast to the reaction with DMAD that afforded fused selenophenes **6**, dipoles **4** reacted with allenes to give monocyclic compounds, the dihydroselenophene derivatives **8**.

The structures of all products were fully characterized by spectroscopic data and microanalysis. The ^{1}H NMR, MS and microanalysis data indicated that products **6** were the 1 + 2 adducts of dipoles **4** with DMAD, while compounds **8** were derived from 1 + 1 addition of two reactants with the loss of a $CH_3C{=}CHS$ moiety. Although spectroscopic data did not allow full verification of the structures of products, X-ray diffraction analysis determined unambiguously that compound **6a** was (*E*)-dimethyl 1-benzyl-3-(1,2-dimethoxycarbonylvinylthio)-2-methyl-4-phenyl-1,4-dihydroselenopheno[2,3-*b*]pyrazine-6,7-dicarboxylate, while **8j** was (2*Z*,5*Z*)-methyl 4-(4-bromobenzylamino)-5-(3,4-dichlorophenylimino)-2-(2-phenylethylidene)-2,5-dihydroselenophene-3-carboxylate (Fig. 1).[20] It is worth noting that both the exocyclic C=C and C=N bonds of dihydroselenophene **8** adopt the *Z*-configurations to avoid the steric repulsion among the substituents of selenophene ring.

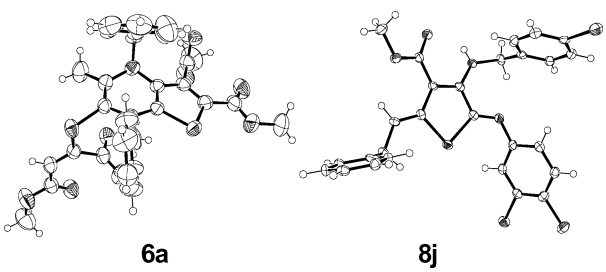
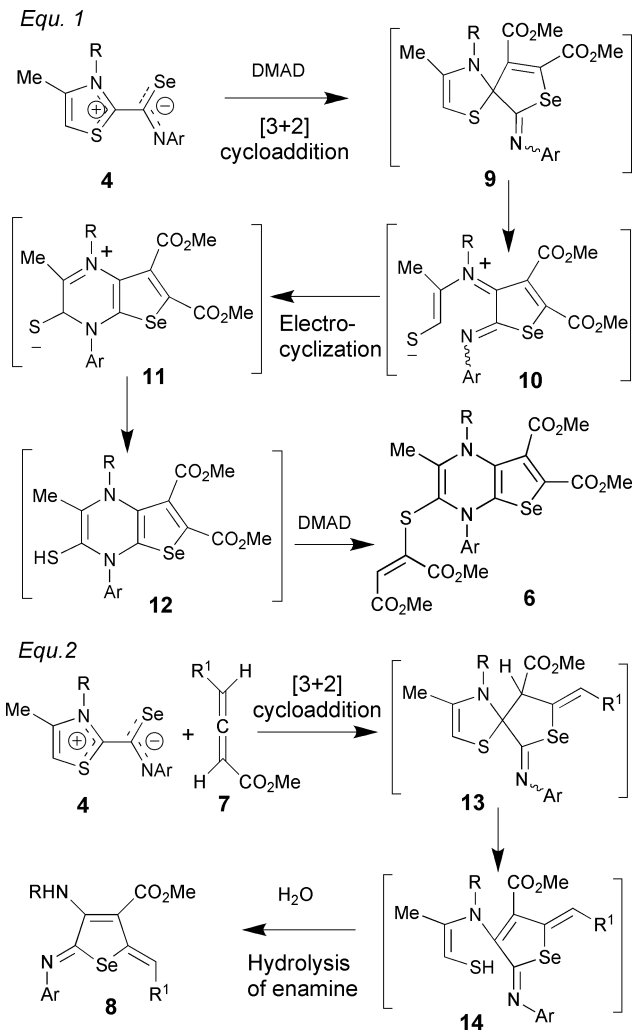


Fig. 1 Ortep drawings of X-ray structures of **6a** and **8j** (50% probability was chosen for the ellipsoids).

Both the formation of selenopheno[2,3-*b*]pyrazines **6** and dihydroselenophenes **8** can be best explained by the [3 + 2] cycloaddition between the C-C-Se dipolar specie of **4** and DMAD or methoxycarbonylallene **7** followed by different ring transformations. In the former case, the thiazoline-spiro-dihydroselenophene intermediate **9** derived from cycloaddition of C-C-Se dipole **4** with DMAD probably underwent cleavage of the S–C bond of the thiazole ring to give a zwitterion **10**. Electrocyclization of **10** followed by isomerization formed the selenopheno[2,3-*b*]pyrazine intermediate **12**. *S*-Nucleophilic addition of **12** to DMAD affords product **6** (Scheme 4, equ. 1). In the latter case, [3 + 2] cycloaddition of dipole **4** with methoxycarbonylallenes **7** formed a thiazoline-spiro-tetrahydroselenophene intermediate **13**. Deprotonation of tetrahydroselenophene and cleavage of S–C bond of thiazoline of **13** gave rise to the formation of an enamine substituted dihydroselenophene **14**. Hydrolysis of enamine **14** with a trace amount of water in solvent and/or in the eluent of column chromatography produced products **8** (Scheme 4, equ. 2). Apparently, the aromatization of dihydroselenophenes **9** to selenophenes **11** or the conversion of tetrahydroselenophenes **13** to highly conjugated dihydroselenophenes **14** was, respectively, the driving force in the transformation of spiro intermediates **9** or **13** that lead to the formation of fused selenophenes or mono dihydroselenophenes.



Scheme 4 The proposed mechanisms for the formation of selenopheno[2,3-*b*]pyrazines **6** and dihydroselenophenes **8**.

Conclusions

In conclusion, we have demonstrated that the 2-arylselenocarbamoylthiazolium salts derived from thiazole carbenes and aryl isoselenocyanates are unique C^+-C-Se^- 1,3-dipoles being able to react efficiently with DMAD or methoxycarbonylallenes to produce selenopheno[2,3-*b*]pyrazine or dihydroselenophene derivatives respectively in good to excellent yields. Both reactions were proposed to proceed *via* a [3 + 2] cycloaddition of C^+-C-Se^- 1,3-dipoles with the alkyne or alkenes followed by different transformation of the thiazole-spiro-selenophene intermediates. The easy availability and high reactivity render the 2-arylselenocarbamoylthiazolium salts powerful 1,3-dipoles in the synthesis of novel multifunctional dihydroselenophene and selenopheno[2,3-*b*]pyrazine derivatives, which are not ready accessible by other methods.

Experimental

Melting points are uncorrected. ^{1}H NMR (500 or 400 MHz) and ^{13}C NMR (125 or 100 MHz) spectra were recorded in the indicated solvents. *J* values are reported in Hz. IR spectra were recorded using an AVATAR 360 FT-IR spectrometer. Mass spectra were recorded on a Trace MS (EI) or Surveyor MSQ Plus (ESI) instrument and elemental analyses were performed on a GMBH Vario EL instrument. Column chromatography was performed using 200–300 mesh silica gel or neutral Al_2O_3. Thiazolium salts **1** were prepared according to literature.[21] For the experimental procedure for the preparation of 2-arylselenocarbamoyl thiazolium salts **4** see Electronic Supplementary Information.†

1. General procedure for the reaction of 2-arylselenocarbamoylthiazolium salts 4 with DMAD

Under nitrogen atmosphere and at room temperature, DMAD (2.5 mmol) was added dropwise to the suspension of 2-arylselenocarbamoylthiazolium salts **4** (1 mmol) in benzene (40 mL). The mixture was then stirred at room temperature for 0.5 hour. After removal of the solvent under vacuum at a temperature below 35 °C, the residue was chromatographed on a neutral Al_2O_3 column eluting with a mixture of petroleum ether (30–60 °C) and ethyl acetate (from 5:1 to 3:1). The eluent was evaporated under vacuum below 35 °C, and the products **6** were isolated in 80–93% yields.

(*E*)-Dimethyl 1-benzyl-3-(1,2-dimethoxycarbonylvinylthio)-2-methyl-4-phenyl-1,4-dihydroselenopheno[2,3-*b*]pyrazine-6,7-dicarboxylate (6a). 82%, red crystals, mp 108–109 °C; ν_{max}/cm^{-1} 1742, 1728, 1687; δ_H (500 MHz, CD_3COCD_3) 7.37–7.42 (m, 3H, Ar-H), 7.32 (t, *J* 7.8, 2H, Ar-H), 7.25–7.28 (m, 3H, Ar-H), 6.69 (d, *J* 7.6, 2H, Ar-H), 5.80 (s, 1H, CH=C), 4.40 (s, 2H, CH_2Ph), 3.94 (s, 3H, OCH_3), 3.77 (s, 3H, OCH_3), 3.69 (s, 3H, OCH_3), 3.68 (s, 3H, OCH_3), 2.12 (s, 3H, pyrazinyl-CH_3); δ_C (100 MHz, CD_3COCD_3) 166.7, 165.2, 164.3, 162.7, 154.2, 148.6, 144.0, 143.9, 137.4, 137.0, 130.3, 130.1, 129.9, 129.4, 128.9, 128.3, 126.5, 120.8, 120.0, 116.2, 57.0, 53.3, 53.2, 52.6, 52.2, 18.2. MS (ESI) *m/z*: 657 (M + 1), 679 (M + Na^+). Anal. Calcd for $C_{30}H_{28}N_2O_8SSe$: C 54.96, H 4.30, N 4.27; Found: C 55.03, H 4.70, N 4.19.

(*E*)-Dimethyl 1-benzyl-4-(4-chlorophenyl)-3-(1,2-dimethoxycarbonylvinylthio)-2-methyl-1,4-dihydroselenopheno[2,3-*b*]pyrazine-6,7-dicarboxylate (6b). 89%, red crystals, mp 175–176 °C; ν_{max}/cm^{-1} 1741, 1718, 1701; δ_H (400 MHz, CD_3COCD_3) 7.21–7.26 (m, 3H, Ar-H), 7.19 (d, *J* 8.8, 2H, Ar-H), 7.09 (dd, *J* 7.6 and 1.5, 2H, Ar-H), 6.54 (d, *J* 8.8, 2H, Ar-H), 5.66 (s, 1H, CH=C), 4.27 (s, 2H, CH_2Ph), 3.80 (s, 3H, OCH_3), 3.64 (s, 3H, OCH_3), 3.54 (s, 3H, OCH_3), 3.53 (s, 3H, OCH_3), 1.99 (s, 3H, pyrazinyl-CH_3); δ_C (125 MHz, CD_3COCD_3) 165.7, 164.3, 163.3, 161.7, 152.1, 147.4, 144.1, 142.1, 136.4, 135.9, 131.9, 130.0, 129.4, 129.1, 128.6, 128.1, 126.9, 121.2, 118.4, 115.6, 55.8, 52.4, 52.3, 51.8, 51.3, 17.3; MS (ESI) *m/z*: 690 (M), 713 (M + Na^+). Anal. Calcd for $C_{30}H_{27}ClN_2O_8SSe$: C 52.22, H 3.94, N 4.06; Found: C 52.60, H 3.88, N 3.85.

(*E*)-Dimethyl 1-benzyl-3-(1,2-dimethoxycarbonylvinylthio)-2-methyl-4-(4-trifluoromethylphenyl)-1,4-dihydroselenopheno[2,3-*b*]-pyrazine-6,7-dicarboxylate (6d). 87%, yellow crystals, mp 149–150 °C; ν_{max}/cm^{-1} 1740, 1721, 1702, 1613; δ_H (400 MHz, CD_3COCD_3) 7.49 (d, *J* 8.4, 2H, Ar-H), 7.05–7.11 (m, 3H, Ar-H), 7.01 (dd, *J* 7.6 and 1.2, 2H, Ar-H), 6.86 (d, *J* 8.4, 2H, Ar-H), 5.69 (s, 1H, CH=C), 4.38 (s, 2H, CH_2Ph), 3.81 (s, 3H, OCH_3), 3.68 (s, 3H, OCH_3), 3.51 (s, 3H, OCH_3), 3.50 (s, 3H, OCH_3), 2.05 (s, 3H, pyrazinyl-CH_3); δ_C (100 MHz, CD_3COCD_3) 166.5, 165.3, 164.2, 162.6, 149.4, 149.0, 148.6, 148.3, 137.4, 135.6, 134.7, 129.4, 129.3, 128.8, 127.3, 127.27, 127.23, 127.19, 127.0, 126.7, 125.5, 123.9, 123.1, 116.6, 115.9, 55.4, 53.4, 53.2, 52.9, 52.1, 17.9; MS (ESI) *m/z*: 725 (M + 1), 747 (M + Na^+). Anal. Calcd for $C_{31}H_{27}F_3N_2O_8SSe$: C 51.46, H 3.76, N 3.87; Found: C 51.48, H 3.79, N 3.51.

(*E*)-Dimethyl 4-(4-chlorophenyl)-3-(1,2-dimethoxycarbonylvinylthio)-2-methyl-1-(4-methylbenzyl)-1,4-dihydroselenopheno-[2,3-*b*]pyrazine-6,7-dicarboxylate (6e). 84%, red crystals, mp 109–110 °C; ν_{max}/cm^{-1} 1736, 1714, 1602; δ_H (400 MHz, CD_3COCD_3) 7.17 (d, *J* 8.8, 2H, Ar-H), 7.03 (d, *J* 7.8, 2H, Ar-H), 6.94 (d, *J* 8.0, 2H, Ar-H), 6.52 (d, *J* 8.8, 2H, Ar-H), 5.65 (s, 1H, CH=C), 4.22 (s, 2H, CH_2Ph), 3.79 (s, 3H, OCH_3), 3.64 (s, 3H, OCH_3), 3.53 (s, 3H, OCH_3), 3.52 (s, 3H, OCH_3), 2.22 (s, 3H, CH_3Ph), 1.97 (s, 3H, pyrazinyl-CH_3); δ_C (100 MHz, CD_3COCD_3) 166.6, 165.2, 164.2, 162.6, 153.0, 148.2, 145.2, 143.0, 138.6, 136.9, 134.1, 132.7, 131.2, 130.2, 129.99, 129.98, 127.6, 122.2, 119.4, 116.6, 56.5, 53.3, 53.2, 52.6, 52.2, 21.2, 18.2; HRMS (TOF-EI): 704.0504, Anal. Calcd for $C_{31}H_{29}ClN_2O_8SSe$: 704.0498.

(*E*)-Dimethyl 3-(1,2-dimethoxycarbonylvinylthio)-2-methyl-1-(4-methylbenzyl)-4-(4-trifluoromethylphenyl)-1,4-dihydroselenopheno[2,3-*b*]pyrazine-6,7-dicarboxylate (6f). 87%, yellow crystals, mp 122–123 °C; ν_{max}/cm^{-1} 1737, 1716, 1611; δ_H (500 MHz, CD_3COCD_3) 7.62 (d, *J* 8.3, 2H, Ar-H), 7.02 (s, 4H, Ar-H), 6.99 (d, *J* 8.4, 2H, Ar-H), 5.84 (s, 1H, CH=C), 4.47 (s, 2H, CH_2Ph), 3.96 (s, 3H, OCH_3), 3.84 (s, 3H, OCH_3), 3.66 (s, 3H, OCH_3), 3.64 (s, 3H, OCH_3), 2.25 (s, 3H, CH_3Ph), 2.20 (s, 3H, pyrazinyl-CH_3); δ_C (125 MHz, CD_3COCD_3) 165.6, 164.4, 163.3, 161.7, 148.9, 148.3, 147.7, 147.3, 137.5, 134.8, 134.1, 133.4, 129.0, 128.4, 126.23, 126.21, 125.9, 125.6, 125.5, 124.7, 123.3, 122.0, 115.7, 115.3, 54.4, 52.5, 52.3, 52.0, 51.3, 20.1, 17.0; MS (ESI) *m/z*: 738 (M), 761 (M + Na^+). Anal. Calcd for $C_{32}H_{29}F_3N_2O_8SSe$: C 52.11, H 3.96, N 3.80; Found: C 52.30, H 3.95, N 3.64.

(*E*)-Dimethyl 1-(4-methoxybenzyl)-3-(1,2-dimethoxycarbonylvinylthio)-2-methyl-4-phenyl-1,4-dihydroselenopheno[2,3-*b*]pyrazine-6,7-dicarboxylate (6g). 90%, red crystals, mp 118–119 °C; ν_{max}/cm^{-1} 1737, 1714; δ_H (500 MHz, C_6D_6) 7.17 (d, *J* 8.0, 2H, Ar-H), 7.09 (t, *J* 7.4, 2H, Ar-H), 6.97 (t, *J* 7.1, 1H, Ar-H), 6.87 (d, *J* 7.7, 2H, Ar-H), 6.80 (d, *J* 8.0, 2H, Ar-H), 5.83 (s, 1H, CH=C), 4.46 (s, 2H, CH_2Ph), 3.82 (s, 3H, OCH_3), 3.64 (s, 3H, OCH_3), 3.40 (s, 3H, OCH_3), 3.395 (s, 3H, OCH_3), 3.31 (s, 3H, OCH_3), 2.02 (s, 3H, pyrazinyl-CH_3); δ_C (125 MHz, C_6D_6) 166.5, 164.6, 163.5, 162.1, 159.9, 154.2, 148.3, 143.5, 142.9, 137.0, 130.7, 129.3, 129.2, 128.7, 127.3, 126.3, 120.5, 120.0, 115.5, 114.0; MS (EI) *m*/*z*: 508 (100), 686 (M$^+$, 2%). Anal. Calcd for $C_{31}H_{30}N_2O_9SSe$: C 54.31, H 4.41, N 4.09; Found: C 54.37, H 4.60, N 3.88.

(*E*)-Dimethyl 4-(4-chlorophenyl)-1-(4-methoxybenzyl)-3-(1,2-dimethoxycarbonylvinylthio)-2-methyl-1,4-dihydroselenopheno-[2,3-*b*]pyrazine-6,7-dicarboxylate (6h). 90%, red crystals, mp 108–109 °C; ν_{max}/cm^{-1} 1736, 1709; δ_H (400 MHz, CD_3COCD_3) 7.16 (d, *J* 8.8, 2H, Ar-H), 6.99 (d, *J* 8.7, 2H, Ar-H), 6.76 (d, *J* 8.6, 2H, Ar-H), 6.58 (d, *J* 8.8, 2H, Ar-H), 5.65 (s, 1H, CH=C), 4.20 (s, 2H, CH_2Ph), 3.80 (s, 3H, OCH_3), 3.68 (s, 3H, OCH_3), 3.64 (s, 3H, OCH_3), 3.53 (s, 3H, OCH_3), 3.52 (s, 3H, OCH_3), 1.97 (s, 3H, pyrazinyl-CH_3); δ_C (100 MHz, CD_3COCD_3) 166.6, 165.2, 164.2, 162.6, 160.7, 153.0, 148.2, 145.4, 143.1, 136.8, 132.6, 131.3, 131.2, 130.2, 129.3, 127.6, 122.3, 119.4, 116.5, 114.7, 56.1, 55.6, 53.3, 53.2, 52.7, 52.2, 18.2; MS (ESI) *m*/*z*: 720 (M), 743 (M + Na$^+$). Anal. Calcd for $C_{31}H_{29}ClN_2O_9SSe$: C 51.71, H 4.06, N 3.89; Found: C 51.77, H 3.95, N 3.46.

(*E*)-Dimethyl 1-(4-methoxybenzyl)-3-(1,2-dimethoxycarbonylvinylthio)-2-methyl-4-(4-trifluoromethylphenyl)-1,4-dihydroselenopheno[2,3-*b*]pyrazine-6,7-dicarboxylate (6i). 93%, yellow crystals, mp 117–118 °C; ν_{max}/cm^{-1} 1734, 1707; δ_H (500 MHz, CD_3COCD_3) 7.61 (d, *J* 8.2, 2H, Ar-H), 7.05 (d, *J* 7.8, 2H, Ar-H), 7.00 (d, *J* 8.2, 2H, Ar-H), 6.74 (d, *J* 7.7, 2H, Ar-H), 5.83 (s, 1H, CH=C), 4.44 (s, 2H, CH_2Ph), 3.96 (s, 3H, OCH_3), 3.83 (s, 3H, OCH_3), 3.71 (s, 3H, OCH_3), 3.65 (s, 3H, OCH_3), 3.64 (s, 3H, OCH_3), 2.19 (s, 3H, pyrazinyl-CH_3); δ_C (125 MHz, CD_3COCD_3) 165.7, 164.5, 163.4, 161.8, 159.6, 148.9, 148.5, 147.8, 147.3, 134.9, 134.1, 129.7, 128.5, 126.23, 126.21, 125.9, 125.6, 125.4, 124.6, 123.3, 122.1, 115.6, 115.4, 113.7, 54.5, 54.1, 52.6, 52.3, 52.1, 51.3, 17.1; MS (ESI) *m*/*z*: 754 (M), 777 (M + Na$^+$). Anal. Calcd for $C_{32}H_{29}F_3N_2O_9SSe$: C 51.00, H 3.88, N 3.72; Found: C 51.17, H 3.62, N 3.61.

(*E*)-Dimethyl 1-(4-chlorobenzyl)-3-(1,2-dimethoxycarbonylvinylthio)-2-methyl-4-phenyl-1,4-dihydroselenopheno[2,3-*b*]pyrazine-6,7-dicarboxylate (6j). 93%, red crystals, mp 131–132 °C; ν_{max}/cm^{-1} 1739, 1729, 1697; δ_H (500 MHz, CD_3COCD_3) 7.42 (d, *J* 8.3, 2H, Ar-H), 7.36 (t, *J* 7.9, 2H, Ar-H), 7.30 (t, *J* 7.2, 1H, Ar-H), 7.24 (d, *J* 8.3, 2H, Ar-H), 6.71 (d, *J* 7.7, 2H, Ar-H), 5.79 (s, 1H, CH=C), 4.40 (s, 2H, CH_2Ph), 3.94 (s, 3H, OCH_3), 3.77 (s, 3H, OCH_3), 3.69 (s, 3H, OCH_3), 3.68 (s, 3H, OCH_3), 2.12 (s, 3H, pyrazinyl-CH_3); δ_C (125 MHz, CD_3COCD_3) 165.8, 164.3, 163.3, 161.8, 153.4, 147.5, 143.0, 142.7, 136.1, 135.1, 133.6, 130.9, 129.5, 128.6, 127.4, 125.3, 120.1, 119.7, 115.5, 55.4, 52.4, 52.3, 51.7, 51.3, 17.4; MS (ESI) *m*/*z*: 691 (M + 1), 713 (M + Na$^+$). Anal. Calcd for $C_{30}H_{27}ClN_2O_8SSe$: C 52.22, H 3.94, N 4.06; Found: C 52.44, H 3.55, N 3.94.

(*E*)-Dimethyl 1-(4-chlorobenzyl)-4-(4-chlorophenyl)-3-(1,2-dimethoxycarbonylvinylthio)-2-methyl-1,4-dihydroselenopheno[2,3-*b*]pyrazine-6,7-dicarboxylate (6k). 89%, red crystals, mp 159–160 °C; ν_{max}/cm^{-1} 1739, 1711, 1695; δ_H (500 MHz, CD_3COCD_3) 7.40 (d, *J* 8.1, 2H, Ar-H), 7.36 (d, *J* 8.5, 2H, Ar-H), 7.23 (d, *J* 8.2, 2H, Ar-H), 6.74 (d, *J* 8.5, 2H, Ar-H), 5.81 (s, 1H, CH=C), 4.42 (s, 2H, CH_2Ph), 3.95 (s, 3H, OCH_3), 3.79 (s, 3H, OCH_3), 3.68 (s, 3H, OCH_3), 3.67 (s, 3H, OCH_3), 2.14 (s, 3H, pyrazinyl-CH_3); δ_C (125 MHz, CD_3COCD_3) 165.7, 164.3, 163.3, 161.7, 152.2, 147.3, 144.1, 142.0, 135.8, 135.0, 133.6, 131.8, 130.8, 129.8, 129.5, 128.6, 126.4, 121.5, 118.9, 115.8, 55.1, 52.5, 52.3, 51.8, 51.3, 17.3; MS (ESI) *m*/*z*: 724 (M), 747 (M + Na$^+$). Anal. Calcd for $C_{30}H_{26}ClN_2O_8SSe$: C 49.74, H 3.62, N 3.87; Found: C 49.97, H 3.63, N 3.66.

(*E*)-Dimethyl 1-(4-chlorobenzyl)-3-(1,2-dimethoxycarbonylvinylthio)-2-methyl-4-(4-trifluoromethylphenyl)-1,4-dihydroselenopheno[2,3-*b*]pyrazine-6,7-dicarboxylate (6l). 80%, yellow crystals, mp 129–130 °C; ν_{max}/cm^{-1} 1743, 1733, 1716, 1706, 1605; δ_H (500 MHz, CD_3COCD_3) 7.66 (d, *J* 8.5, 2H, Ar-H), 7.23 (d, *J* 8.3, 2H, Ar-H), 7.16 (d, *J* 8.3, 2H, Ar-H), 7.03 (d, *J* 8.4, 2H, Ar-H), 5.85 (s, 1H, CH=C), 4.52 (s, 2H, CH_2Ph), 3.97 (s, 3H, OCH_3), 3.84 (s, 3H, OCH_3), 3.66 (s, 3H, OCH_3), 3.64 (s, 3H, OCH_3), 2.21 (s, 3H, pyrazinyl-CH_3); δ_C (125 MHz, CD_3COCD_3) 165.6, 164.4, 163.3, 161.7, 148.6, 147.6, 147.1, 135.1, 134.8, 133.6, 133.4, 130.2, 128.5, 126.4, 126.3, 126.0, 125.8, 125.4, 124.8, 123.3, 121.8, 116.0, 115.9, 53.9, 52.6, 52.3, 52.0, 51.3, 17.0; MS (–c ESI) *m*/*z*: 757 (M – 1). Anal. Calcd for $C_{34}H_{30}N_4O_2S$: C 49.12, H 3.46, N 3.70; Found: C 49.30, H 3.31, N 3.49.

2. General procedure for the reaction of 2-arylselenocarbamoylthiazolium salts 4 with methoxycarbonylallenes 7

Under nitrogen atmosphere, 2-arylselenocarbamoylthiazolium salts **4** (1 mmol) were mixed with methoxycarbonylallenes **7** (2 mmol) in dry THF (50 mL). The mixture was then stirred in refluxing THF for 2.5–3 h. After removal of the solvent under vacuum, the residue was chromatographed on a silicon gel column to give products **8** in 61–78% yields (petroleum ether (30–60 °C) : ethyl acetate = 9:1).

(2*Z*,5*Z*)-Methyl 4-(benzylamino)-5-(3,4-dichlorophenylimino)-2-propylidene-2,5-dihydroselenophene-3-carboxylate (8a). 67%, yellow crystals, mp 64–65 °C; ν_{max}/cm^{-1} 3288, 1649, 1605, 1579; δ_H (400 MHz, $CDCl_3$) 8.24 (brs, 1H, NH), 7.36 (d, *J* 8.5, 1H, Ar-H), 7.20–7.29 (m, 5H, Ar-H), 6.97 (d, *J* 2.4, 1H, Ar-H), 6.72 (dd, *J* 8.5 and 2.4, 1H, Ar-H), 6.43 (t, *J* 7.4, 1H, HC=C), 4.87 (s, 2H, CH_2Ph), 3.77 (s, 3H, OCH_3), 2.04–2.12 (m, 2H, C*H*$_2$CH$_3$), 0.99 (t, *J* 7.4, 3H, CH_2CH_3); δ_C (100 MHz, $CDCl_3$) 166.4, 163.6, 154.4, 150.7, 138.3, 132.2, 130.2, 127.9, 127.7, 127.6, 126.4, 126.3, 126.2, 120.3, 117.8, 107.5, 50.5, 48.3, 27.1, 13.0; MS (ESI) *m*/*z*: 495 (M + 1). Anal. Calcd for $C_{22}H_{20}Cl_2N_2O_2Se$: C 53.46, H 4.08, N 5.67; Found: C 53.18, H 4.55, N 5.18.

(2*Z*,5*Z*)-Methyl 4-(4-bromobenzylamino)-5-(3,4-dichlorophenylimino)-2-propylidene-2,5-dihydroselenophene-3-carboxylate (8b). 78%, yellow crystals, mp 105–106 °C; ν_{max}/cm^{-1} 3288, 1648, 1606, 1582; δ_H (400 MHz, $CDCl_3$) 8.43 (brs, 1H, NH), 7.46 (d, *J* 8.4, 2H, Ar-H), 7.44 (d, *J* 8.5, 1H, Ar-H), 7.18 (d, *J* 8.4, 2H, Ar-H), 7.04 (d, *J* 2.4, 1H, Ar-H), 6.77 (dd, *J* 8.5 and 2.4, 1H, Ar-H), 6.54 (t, *J* 7.4, 1H, HC=C), 4.93 (d, *J* 4.6, 2H, CH_2Ph), 3.86 (s, 3H, OCH_3),

2.12–2.19 (m, 2H, CH_2CH$_3$), 1.06 (t, *J* 7.5, 3H, CH$_2$CH_3); δ_C (100 MHz, $CDCl_3$) 167.5, 164.6, 155.5, 151.6, 138.5, 133.3, 131.7, 131.2, 129.0, 128.82, 128.75, 127.7, 121.2, 121.1, 118.8, 108.8, 51.5, 48.5, 28.1, 14.0; MS (ESI) *m*/*z*: 573 (M + 1). Anal. Calcd for $C_{22}H_{19}BrCl_2N_2O_2Se$: C 46.10, H 3.34, N 4.89; Found: C 46.46, H 3.68, N 4.75.

(2*Z*,5*Z*)-Methyl 4-(benzylamino)-2-(2-methylpropylidene)-5-(phenylimino)-2,5-dihydroselenophene-3-carboxylate (8c). 72%, yellow crystals, mp 92–93 °C; ν_{max}/cm^{-1} 3291, 1651, 1612, 1584; δ_H (400 MHz, $CDCl_3$) 8.27 (brs, 1H, NH), 7.31 (t, *J* 7.6, 2H, Ar-H), 7.24–7.27 (m, 5H, Ar-H), 7.10 (t, *J* 7.4, 1H, Ar-H), 6.88 (d, *J* 7.6, 2H, Ar-H), 6.24 (d, *J* 9.2, 1H, HC=C), 4.92 (s, 2H, CH_2Ph), 3.77 (s, 3H, OCH_3), 2.11–2.20 (m, 1H, CH(CH$_3$)$_2$), 0.97 (d, *J* 6.6, 6H, CH(CH_3)$_2$); δ_C (100 MHz, $CDCl_3$) 167.6, 162.6, 155.8, 152.6, 139.5, 131.7, 129.4, 128.6, 127.5, 127.4, 127.2, 125.4, 119.1, 107.8, 51.4, 49.3, 35.1, 22.9; MS (EI) *m*/*z*: 91 (100), 440 (M$^+$, 10%). Anal. Calcd for $C_{23}H_{24}N_2O_2Se$: C 62.87, H 5.51, N 6.38; Found: C 63.11, H 5.31, N 6.28.

(2*Z*,5*Z*)-Methyl 4-(4-methoxybenzylamino)-2-(2-methylpropylidene)-5-(4-trifluoromethylphenylimino)-2,5-dihydroselenophene-3-carboxylate (8d). 61%, yellow crystals, mp 89–90 °C; ν_{max}/cm^{-1} 3289, 1653, 1618, 1593; δ_H (400 MHz, $CDCl_3$) 8.12 (brs, 1H, NH), 7.57 (d, *J* 8.3, 2H, Ar-H), 7.17 (d, *J* 8.8, 2H, Ar-H), 6.96 (d, *J* 8.2, 2H, Ar-H), 6.81 (d, *J* 8.7, 2H, Ar-H), 6.26 (d, *J* 9.2, 1H, HC=C), 4.80 (s, 2H, CH_2Ph), 3.78 (s, 3H, OCH_3), 3.74 (s, 3H, OCH_3), 2.09–2.18 (m, 1H, CH(CH$_3$)$_2$), 0.97 (d, *J* 6.6, 6H, CH(CH_3)$_2$); δ_C (100 MHz, $CDCl_3$) 167.3, 164.6, 159.0, 155.5, 155.3, 132.4, 131.3, 128.9, 127.4, 127.2, 127.0, 126.82, 126.78, 126.75, 126.71, 125.5, 122.8, 119.4, 114.1, 108.3, 55.3, 51.4, 48.9, 35.3, 22.9; MS (–c ESI) *m*/*z*: 537 (M – 1). Anal. Calcd for $C_{25}H_{25}F_3N_2O_3Se$: C 55.87, H 4.69, N 5.21; Found: C 55.89, H 4.86, N 5.17.

(2*Z*,5*Z*)-Methyl 4-(4-bromobenzylamino)-2-(2-methylpropylidene)-5-(phenylimino)-2,5-dihydroselenophene-3-carboxylate (8e). 73%, yellow crystals, mp 99–100 °C; ν_{max}/cm^{-1} 3285, 1647, 1605, 1585, 1574; δ_H (400 MHz, $CDCl_3$) 8.44 (brs, 1H, NH), 7.38 (d, *J* 8.4, 2H, Ar-H), 7.31 (t, *J* 7.6, 2H, Ar-H), 7.12 (d, *J* 8.5, 2H, Ar-H), 7.09–9.13 (m, 1H, Ar-H), 6.85 (dd, *J* 7.4 and 1.2 Hz, 2H, Ar-H), 6.26 (d, *J* 9.2, 1H, HC=C), 4.90 (s, 2H, CH_2Ph), 3.77 (s, 3H, OCH_3), 2.11–2.20 (m, 1H, CH(CH$_3$)$_2$), 0.96 (d, *J* 6.6, 6H, CH(CH_3)$_2$); δ_C (100 MHz, $CDCl_3$) 167.7, 162.6, 156.0, 152.6, 138.8, 132.1, 131.6, 129.5, 129.2, 127.2, 125.5, 121.0, 119.1, 108.1, 51.4, 48.5, 35.2, 22.9; MS (EI) *m*/*z*: 77 (95), 104 (85), 169 (100), 171 (95), 518 (M$^+$, 10%). Anal. Calcd for $C_{23}H_{23}BrN_2O_2Se$: C 53.30, H 4.47, N 5.40; Found: C 53.54, H 4.88, N 5.20.

(2*Z*,5*Z*)-Methyl 4-(4-bromobenzylamino)-5-(4-chlorophenylimino)-2-(2-methylpropylidene)-2,5-dihydroselenophene-3-carboxylate (8f). 76%, yellow crystals, mp 125–126 °C; ν_{max}/cm^{-1} 3284, 1649, 1607, 1585; δ_H (400 MHz, $CDCl_3$) 8.40 (brs, 1H, NH), 7.38 (d, *J* 8.4, 2H, Ar-H), 7.27 (d, *J* 8.7, 2H, Ar-H), 7.10 (d, *J* 8.5, 2H, Ar-H), 6.79 (d, *J* 8.7, 2H, Ar-H), 6.28 (d, *J* 9.3, 1H, HC=C), 4.87 (s, 2H, CH_2Ph), 3.77 (s, 3H, OCH_3), 2.11–2.19 (m, 1H, CH(CH$_3$)$_2$), 0.97 (d, *J* 6.6, 6H, CH(CH_3)$_2$); δ_C (100 MHz, $CDCl_3$) 167.6, 163.4, 155.8, 150.9, 138.7, 132.5, 131.7, 130.8, 129.6, 129.1, 127.1, 121.0, 120.6, 108.3, 51.5, 48.5, 35.3, 22.9; MS (EI) *m*/*z*: 169 (100), 171 (85), 552 (M$^+$, 2%). Anal. Calcd for $C_{23}H_{22}BrClN_2O_2Se$: C 49.98, H 4.01, N 5.07; Found: C 49.87, H 3.93, N 5.05.

(2*Z*,5*Z*)-Methyl 4-(4-bromobenzylamino)-5-(3,4-dichlorophenylimino)-2-(2-methylpropylidene)-2,5-dihydroselenophene-3-carboxylate (8g). 71%, yellow crystals, mp 139–140 °C; ν_{max}/cm^{-1} 3286, 1648, 1597, 1583, 1574; δ_H (400 MHz, $CDCl_3$) 8.36 (brs, 1H, NH), 7.39 (d, *J* 8.5, 2H, Ar-H), 7.36 (d, *J* 8.5, 1H, Ar-H), 7.09 (d, *J* 8.4, 2H, Ar-H), 6.96 (d, *J* 2.4, 1H, Ar-H), 6.69 (dd, *J* 8.5 and 2.4, 1H, Ar-H), 6.30 (d, *J* 9.3, 1H, HC=C), 4.85 (s, 2H, CH_2Ph), 3.78 (s, 3H, OCH_3), 2.11–2.20 (m, 1H, CH(CH$_3$)$_2$), 0.98 (d, *J* 6.6, 6H, CH(CH_3)$_2$); δ_C (100 MHz, $CDCl_3$) 167.4, 164.7, 155.6, 151.7, 138.6, 133.3, 133.1, 131.7, 131.2, 129.0, 128.8, 127.0, 121.2, 121.1, 118.8, 108.7, 51.5, 48.5, 35.3, 22.9; MS (ESI) *m*/*z*: 587 (M + 1). Anal. Calcd for $C_{23}H_{21}BrCl_2N_2O_2Se$: C 47.05, H 3.60, N 4.77; Found: C 47.30, H 3.89, N 4.79.

(2*Z*,5*Z*)-Methyl 5-(3,4-dichlorophenylimino)-4-(ethylamino)-2-(2-methylpropylidene)-2,5-dihydroselenophene-3-carboxylate (8h). 71%, yellow crystals, mp 126–127 °C; ν_{max}/cm^{-1} 3250, 1647, 1610, 1586; δ_H (400 MHz, $CDCl_3$) 7.44 (d, *J* 8.5, 1H, Ar-H), 7.12 (d, *J* 2.4, 1H, Ar-H), 6.87 (dd, *J* 8.5 and 2.4, 1H, Ar-H), 6.27 (d, *J* 9.3, 1H, HC=C), 3.86 (s, 3H, OCH_3), 3.68 (q, *J* 7.2, 2H, CH_2CH$_3$), 2.16–2.25 (m, 1H, CH(CH$_3$)$_2$), 1.24 (t, *J* 7.2, 3H, CH$_2$CH_3), 1.03 (d, *J* 6.6, 6H, CH(CH_3)$_2$); δ_C (100 MHz, $CDCl_3$) 167.4, 165.0, 155.4, 151.9, 133.2, 131.9, 131.2, 128.7, 127.2, 121.4, 118.9, 107.4, 51.4, 40.4, 35.2, 23.0, 16.0; MS (–c ESI) *m*/*z*: 446 (M – 1). Anal. Calcd for $C_{18}H_{20}Cl_2N_2O_2Se$: C 48.45, H 4.52, N 6.28; Found: C 48.81, H 4.75, N 6.34.

(2*Z*,5*Z*)-Methyl 4-(4-bromobenzylamino)-5-(4-chlorophenylimino)-2-(2-phenylethylidene)-2,5-dihydroselenophene-3-carboxylate (8i). 68%, yellow crystals, mp 101–102 °C; ν_{max}/cm^{-1} 3439, 1655, 1589, 1564; δ_H (400 MHz, $CDCl_3$) 8.66 (brs, 1H, NH), 7.47 (d, *J* 8.4, 2H, Ar-H), 7.36 (d, *J* 8.7, 2H, Ar-H), 7.29 (t, *J* 7.0, 2H, Ar-H), 7.18–7.23 (m, 5H, Ar-H), 6.88 (d, *J* 8.7, 2H, Ar-H), 6.71 (t, *J* 7.6, 1H, HC=C), 4.99 (s, 2H, NHCH_2Ph), 3.81 (s, 3H, OCH_3), 3.48 (d, *J* 7.6, 2H, C=CHCH_2Ph); δ_C (100 MHz, $CDCl_3$) 167.6, 163.0, 156.4, 150.7, 139.6, 138.6, 131.7, 131.0, 130.4, 129.7, 129.1, 128.6, 128.4, 126.4, 123.6, 121.1, 120.5, 108.2, 51.6, 48.5, 40.8; MS (ESI) *m*/*z*: 601 (M + 1). Anal. Calcd for $C_{27}H_{22}BrClN_2O_2Se$: C 53.98, H 3.69, N 4.66; Found: C 53.66, H 3.69, N 4.36.

(2*Z*,5*Z*)-Methyl 4-(4-bromobenzylamino)-5-(3,4-dichlorophenylimino)-2-(2-phenylethylidene)-2,5-dihydroselenophene-3-carboxylate (8j). 72%, yellow crystals, mp 121–122 °C; ν_{max}/cm^{-1} 3204, 1662, 1584; δ_H (400 MHz, $CDCl_3$) 8.51 (brs, 1H, NH), 7.39 (d, *J* 8.3, 2H, Ar-H), 7.36 (d, *J* 8.5, 1H, Ar-H), 7.19–7.23 (m, 2H, Ar-H), 7.08–7.15 (m, 5H, Ar-H), 6.97 (d, *J* 2.4, 1H, Ar-H), 6.71 (dd, *J* 8.5 and 2.4, 1H, Ar-H), 6.66 (t, *J* 7.6, 1H, HC=C), 4.89 (s, 2H, NHCH_2Ph), 3.74 (s, 3H, OCH_3), 3.41 (d, *J* 7.6, 2H, C=CHCH_2Ph); δ_C (100 MHz, $CDCl_3$) 167.5, 164.4, 156.1, 151.5, 139.4, 138.5, 133.3, 131.7, 131.3, 130.3, 129.04, 129.0, 128.6, 128.4, 126.4, 124.2, 121.2, 121.1, 118.7, 108.6, 51.6, 48.5, 40.8; MS (EI) *m*/*z*: 44 (100), 169 (40), 171 (52), 634 (M$^+$, 6%). Anal. Calcd for $C_{27}H_{21}BrCl_2N_2O_2Se$: C 51.05, H 3.33, N 4.41; Found: C 51.12, H 3.39, N 4.31.

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