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Reaction of 2,6-Xylyl Isoselenocyanate with Organolithium Compounds

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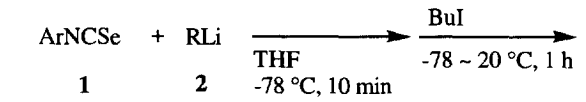
Abstract: Reaction of 2,6-xylyl isoselenocyanate (**1**) with organolithium compounds was examined focussing on the siteselectivities. Phenyllithium attacked selenium exclusively whereas some benzylic organolithiums reacted at the central carbon of **1** to afford the corresponding lithium selenocarboximidates. Phenylethynyllithium and ^{t}BuLi gave mixtures of the carbophilic and selenophilic products. The lithium enolate of isobutyrophenone reacted with **1** at both its C- and O-nucleophilic centers attacking the central carbon of **1**. By the alkylation of lithium selenocarboximidates formed from **1** and benzylic organolithiums, several selenoimidates were synthesized. Copyright © 1996 Elsevier Science Ltd

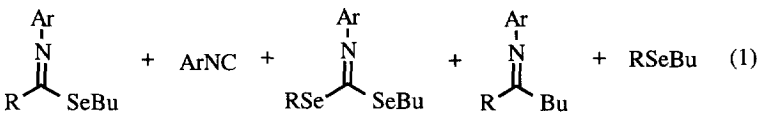
Siteselectivities of thio- and selenocarbonyl compounds toward nucleophiles are not only interesting topics in heteroatom chemistry but also important subjects to be controlled in synthetic chemistry.[1] During a few decades, siteselectivities of a variety of thiocarbonyl compounds, such as thioketones,[2] thioaldehydes,[3] thioamides,[2k,4] thioxoesters,[5] dithioesters,[2b,6] trithiocarbonates,[2b,7] thioketenes,[8] isothiocyanates,[9] and CS_2,[10] have been examined in detail using various organolithiums and Grignard reagents. As for selenocarbonyl compounds, however, only limited numbers of studies have been reported mainly due to their instabilities. Selenoketones,[11] selenoaldehydes,[12] and selenoformates[13] react with organolithiums or Grignard reagents at both carbon and selenium atoms, but only examples of the carbophilic attack are known for selenoamides[14] and CSe_2.[15] Here we describe the results of the reaction of an aryl isoselenocyanate with organolithium reagents.[16]

There have been many studies reported on the reaction of isothiocyanates with organolithiums and Grignard reagents.[9] All these reactions gave thioamides resulting from the carbophilic attack. In comparison with sulfur, selenium is the more electropositive element possessing a higher softness character as an electrophilic center. Since these factors facilitate the nucleophilic attack at selenium than at sulfur, we examined the siteselectivity of 2,6-xylyl isoselenocyanate (**1**)[17] toward various organolithium reagents (**2**). The reaction of **1** with **2** was carried out in THF at -78 °C for 10 min and quenched by the addition of BuI. The structures and yields of the products are shown in eq 1 and Table 1, respectively. Selenoimidates (**3**) are formed by carbophilic attack of organolithiums toward **1** followed by trapping with BuI,[18] and compounds (**4-7**) are selenophilic products. Plausible reaction pathways leading to these compounds are shown in Scheme 1 (*vide infra*). The ratios of the carbophilic product (**3**) over selenophilic products (**4** + **6**) are also shown as C/Se in Table 1.



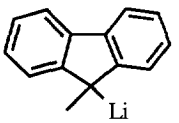
1 **2**

(Ar = 2,6-xylyl)



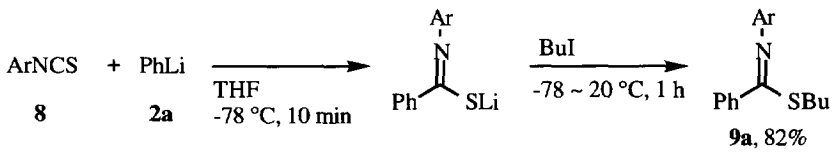
3 **4** **5** **6** **7** (1)

Table 1. Reaction of 2,6-Xylyl Isoselenocyanate with Organolithium Compounds

run	RLi (**2**)		yields (%) of products[a] **3**	**4**	**5**	**6**	**7**	C / Se	p*K*a of R-H
1	PhLi	(**2a**)		100			100	0 / 100	43[b]
2	^{t}BuLi	(**2b**)	33 (18)	4	31 (21)	32 (23)	11	48 / 52	53[c]
3[d]	Ph—≡—Li	(**2c**)	47 (41)	44			(45)	52 / 48	29[e]
4		(**2d**)	88 (85)	12			-[f]	88 / 12	31[e]
5		(**2e**)	100 (100)					100 / 0	22[e]

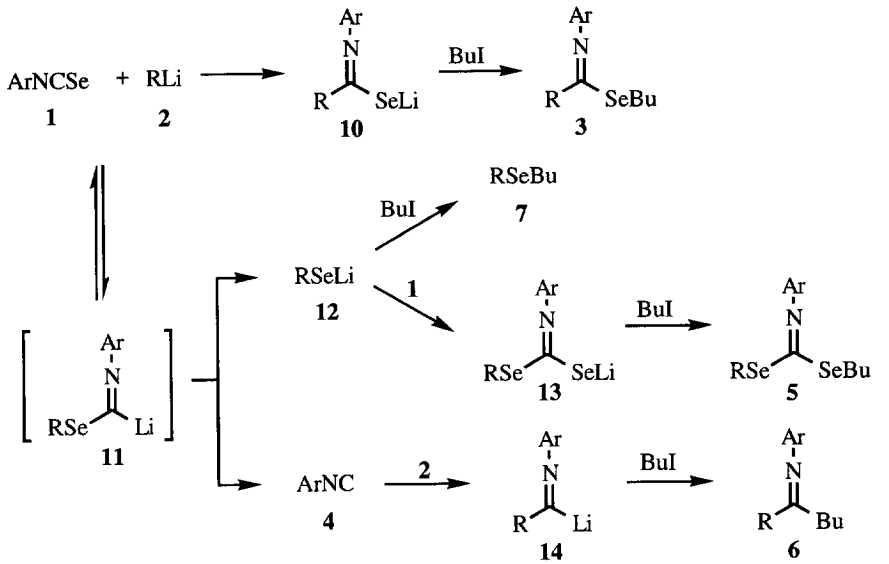
Conditions: **1** (2.0 mmol), **2** (2.2 mmol), THF (25 mL), -78 °C, 10 min; BuI (4.0 mmol), -78 °C, 10 min, ~ 20 °C, 1 h.
a) NMR yields based on **1** (yields in parentheses are isolated yields). b) In cyclohexylamine, see ref. 19. c) Ref. 20. d) ArNCSe was recovered in 9%. e) In DMSO, see ref. 21. f) Not determined.

It is noteworthy that the C/Se ratio varies from 0/100 to 100/0 depending on the nature of organolithium reagents. For example, **1** reacted with phenyllithium (**2a**) in a selenophilic manner to afford 2,6-xylyl isocyanide (**4**) and PhSeBu (**7a**) after trapping with butyl iodide (Table 1, run 1). This is in large contrast to the cases of isothiocyanates which react with organolithium or -magnesium reagents only at their central carbon.[9] In order to compare more clearly the siteselectivities of **1** and its sulfur analogue, we carried out the reaction of 2,6-xylyl isothiocyanate (**8**) with PhLi under identical conditions as in run 1 of Table 1, where only thioimidate (**9a**) was obtained in 82% yield without any thiophilic products (eq 2).



8 **2a** **9a**, 82% (2)

Treatment of **1** with ^{t}BuLi (**2b**) resulted in the formation of a mixture of carbophilic product (**3b**) and selenophilic products (**4**, **5b**, **6b**, and **7b**) (run 2). When phenylethynyllithium (**2c**) was used, **3c** and **4** were obtained in almost equal yields along with PhC≡CSeBu (**7c**) (run 3). The reaction of **1** with 2-phenyl-2-lithio-1,3-dithiane (**2d**) proceeded predominantly in carbophilic manner to afford a selenoimidate (**3d**) in 88% yield (run 4). Furthermore, 9-methylfluorenyllithium (**2e**) gave only **3e** quantitatively without any selenophilic products (run 5).

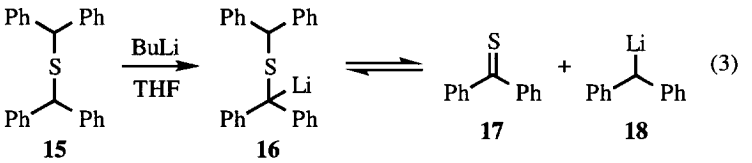


Scheme 1. Possible Pathways for the Formation of the Products

Although reaction mechanisms leading to the selenophilic products are not fully understood, we would like to propose the pathways shown in Scheme 1. The reaction of PhLi (**2a**) gave a simple example, which quantitatively afforded only **4** and **7a**. These products might be formed by the nucleophilic attack of **2a** at the selenium atom of **1** to give **4** and **12a** probably *via* **11a**[22] and subsequent alkylation of **12a** with BuI. Although any products ascribable to the trapping of **11** have not been obtained in the present reactions, the intermediacy of **11** is supported by the following evidence. First, it is reported that selenophilic addition of organolithiums to selenoketones[11c] or selenoformates[13b] affords α-lithio selenides which then eliminate RSeLi to give carbenes. This process is formally just the same as the present one (i.e., **1** + **2** → **4** + **12**). Secondly, oxygen[23] and sulfur[24] analogues of **11** easily undergo fragmentation into isocyanides and alcoholates or thiolates, respectively. If a similar fragmentation of **11** into **4** and **12** is fast, **11** could not necessarily be trapped with BuI.

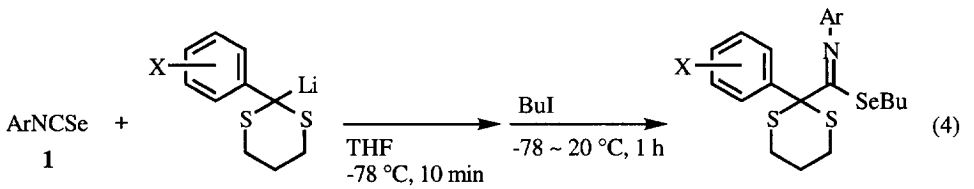
The drastic change of the siteselectivity of **1** depending on the nature of organolithiums can be generalized as follows; i.e. thermodynamically stable carbanions favor the carbophilic attack except the case of ^{t}BuLi.[25] The p*K*a values of the conjugate acids of **2** are listed also in Table 1. A similar tendency was observed in the reaction of thioketones[2k] or selenoketones[11c] with organolithium compounds. These trends can be rationalized by an assumption that the reverse reaction of **11** to **1** and **2** can take place faster than its fragmentation to **4**

and **12** when **2** is thermodynamically stable. A similar situation is evident in the reaction of thiobenzophenone (**17**) where it was confirmed by a control experiment that a thiophilic intermediate (**16**) generated separately from **15** afforded **17** and **18** (eq 3).[2k]



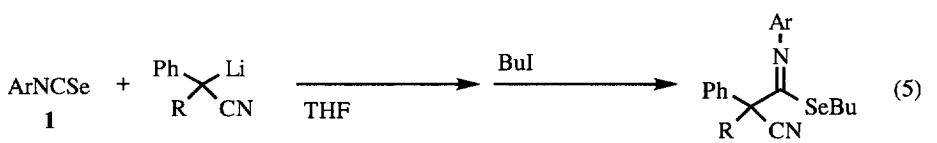
When ^{t}BuLi was used, a somewhat complex mixture of products was formed by the further reaction of the isocyanide (**4**) with ^{t}BuLi giving **6b** through **14b**. The probability of this further reaction observed only in the case of ^{t}BuLi is supported by the facts that ^{t}BuLi readily reacts with isocyanides to give lithio aldimines in high yields whereas PhLi reacts with isocyanides sluggishly and PhC≡CLi does not react with isocyanides.[26] Since the further reaction consumes ^{t}BuLi added in a slightly excess, the remaining isoselenocyanate (**1**) may react with **12b** leading to **5b** *via* **13b**.[27]

Selenoimidates are potentially important compounds in organic chemistry.[28] Hitherto known methods for preparation of selenoimidates are classified into four types of reactions: (i) alkylation of selenoamides with alkyl halides,[29] (ii) reaction of imidoyl chlorides with selenolate anions,[29b,30] (iii) reaction of imidates with selenols,[29b] (iv) reaction of oxime sulfonates with organoaluminum selenolates and the following Beckmann rearrangement.[28a] As the synthetic application of the present reaction, we synthesized selenoimidates (**3f-k**) from **1** and benzyllithiums (**2f-k**) as shown in eqs 4 and 5. Although the yield was moderate when **2f** was used, in other cases the corresponding selenoimidates were obtained in high yields under similar conditions. Since the reaction of **1** with diphenylcyanomethyllithium (**2k**) was slow at -78 °C, the reaction mixture was warmed up to 20 °C before addition of BuI.



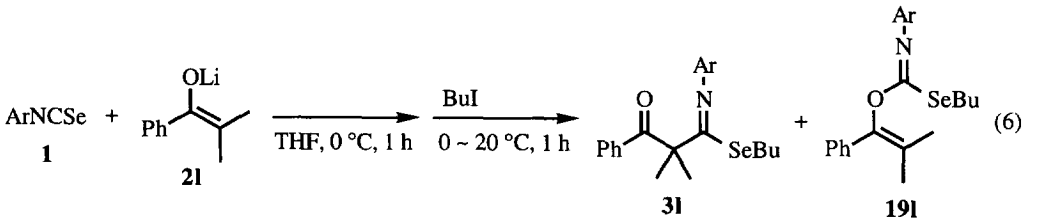
2f: X = *p*-MeO
2g: X = *p*-Me
2h: X = *m*-Cl
2i: X = *p*-Cl

3f, 45%
3g, 67%
3h, 89%
3i, 95%



2j: R = Me	-78 °C, 10 min	-78 ~ 20 °C, 1 h	**3j**, 98%
2k: R = Ph	-78 ~ 20 °C, 1 h	20 °C, 1 h	**3k**, 99%

We then examined the reaction of **1** with a lithium enolate. Although the reaction of **1** with **2l** did not proceed at -78 °C in THF, **1** reacted with **2l** at 0 °C giving a mixture of the carbophilic products (**3l** and **19l**) as shown below.[31] Addition of HMPA improved the yields of both products, but more drastically increased the formation of **19l**.



additive	3l	19l
none	15%	7%
HMPA	28%	46%

In summary, it was revealed that the reaction of 2,6-xylyl isoselenocyanate with organolithium compounds affords carbophilic and/or selenophilic product(s) depending on the nature of organolithium compounds used. Phenyllithium gave only selenophilic products, but thermodynamically more stable carbanions afforded carbophilic products predominantly. The enolate (**2l**) reacted with **1** at both its C- and O- nucleophilic centers giving only carbophilic products. A new supplementary method for the synthesis of selenoimidates was developed by the reaction of **1** with several benzylic organolithium compounds.

EXPERIMENTAL SECTION

General Comments

THF was distilled from sodium benzophenone ketyl. HMPA and hexamethyldisilazane were fractionally distilled and dried over calcium hydride. BuLi, ^{t}BuLi, and PhLi were used as purchased. BuI was distilled from P_2O_5. 2,6-Xylyl isoselenocyanate (**1**)[17] and 2,6-xylyl isothiocyanate (**8**)[32] were prepared according to the literatures, and purified by silica gel column chromatography. Phenylacetylene, 2-phenyl-1,3-dithiane, 2-phenylpropionitrile, diphenylacetonitrile, and isobutyrophenone were obtained from commercial sources and were used after purification by distillation or recrystallization. 9-Methyl-9*H*-fluorene was prepared by methylation of 9*H*-fluorene. 2-Aryl-1,3-dithianes (**2f-i**) were synthesized by the reported procedure.[33]

Melting point was determined on a Yanagimoto Micro Melting Point apparatus. ^{1}H and ^{13}C NMR spectra were recorded on a JEOL JNM-GSX-270 (270 MHz and 68 MHz, respectively) or a JEOL JNM-ALICE-400 (400 MHz and 100 MHz, respectively) spectrometer using Me_4Si as an internal standard. IR spectra were determined on a Perkin Elmer Model 1600 spectrometer. Purification of products was performed on a recycling preparative HPLC (Japan Analytical Industry Co. Ltd., Model LC-908) equipped with JAIGEL-1H and -2H columns (GPC) using $CHCl_3$ as an eluent or by column chromatography using Fuji-Davison silica gel WB-300 (100-250 mesh) or by preparative TLC with Wakogel B-5F silica gel (325 mesh). Mass spectra (EI) were taken on a SHIMADZU GCMC-QP2000 operating in the electron impact mode (70 eV) equipped

with CBP1-M25-025 column. Mass spectra (CI) were obtained on a JEOL JMS-DX303 in the Instrumental Analysis Center of the Faculty of Engineering, Osaka University. Elemental analyses were performed on Perkin Elmer 240C apparatus.

Reaction of 2,6-Xylyl Isoselenocyanate (1) with PhLi (2a)

PhLi (**2a**, 2.2 mmol) was added to a solution of **1** (2.0 mmol) in THF (25 mL) at -78 °C and the mixture was stirred for 10 min. After BuI (4.0 mmol) was added at the same temperature, the stirring was continued for 10 min, and then at 20 °C for another 1 h. Aqueous saturated NH_4Cl solution (50 mL) was added and the product was extracted with ether (50 mL), dried over $MgSO_4$, and concentrated. The yields of **4** (100%) and **7a** (100%) were determined by ^1H NMR measurement of the residue using trioxane ($\delta = 5.15$) as an internal standard.

Reaction of 1 with ^{t}BuLi (2b)

Reaction of **1** with **2b** was carried out as described above. The yields of selenoimidate (**3b**, 33%), ArNC (**4**, 4%), diselenocarbonimidate (**5b**, 31%), ketimine (**6b**, 32%), and ^{t}BuSeBu (**7b**, 11%) were determined by ^1H NMR. The product mixture was subjected to recycling preparative HPLC to afford *Se*-butyl *N*-(2,6-dimethylphenyl)-2,2-dimethylselenopropanimidate (**3b**, 18%), *Se*-butyl *Se'-tert*-butyl *N*-(2,6-dimethylphenyl)diselenocarbonimidate (**5b**, 21%), and *N*-(2,6-dimethylphenyl)-2,2-dimethyl-3-heptanimine (**6b**, 23%). **Data for 3b**. Yellow oil; ^1H NMR (270 MHz, $CDCl_3$) δ 0.72 (t, J = 7.2 Hz, 3 H), 1.09 (sext, J = 7.2 Hz, 2 H), 1.25 (quint, J = 7.2 Hz, 2 H), 1.36 (s, 9 H), 2.14 (s, 6 H), 2.15 (t, J = 7.2 Hz, 2 H), 6.85 (dd, J = 8.5, 6.1 Hz, 1 H), 6.93 (d, J = 6.8 Hz, 2 H); ^{13}C NMR (68 MHz, $CDCl_3$) δ 13.29, 18.17, 22.68, 24.28, 29.28, 32.42, 45.49, 122.77, 125.54, 127.56, 146.41, 168.83; IR (NaCl) 2962, 2871, 1675, 1644, 1592, 1465, 933, 835, 763 cm^{-1}; MS (EI), m/e (%) = 57 (13), 105 (14), 132 (100), 188 (89), 212 (1.5), 268 (0.3), 325 (M^+, 0.2). HRMS Calcd for $C_{17}H_{27}NSe$: 325.1309. Found: 325.1329. **Data for 5b**. Yellow oil; ^1H NMR (270 MHz, $CDCl_3$) δ 0.88 (t, J = 7.4 Hz, 3 H), 1.36 (sext, J = 7.4 Hz, 2 H), 1.68 (quint, J = 7.4 Hz, 2 H), 1.71 (s, 9 H), 2.14 (s, 6 H), 3.00 (t, J = 7.4 Hz, 2 H), 6.91 (dd, J = 8.8, 6.3 Hz, 1 H), 7.00 (d, J = 7.3 Hz, 2 H); ^{13}C NMR (68 MHz, $CDCl_3$) δ 13.51, 18.00, 22.95, 26.98, 31.39, 32.58, 50.27, 123.54, 126.66, 127.91, 149.47, 150.42; IR (NaCl) 2958, 2872, 1598, 1584, 1565, 1464, 1362, 1190, 1153, 851, 764 cm^{-1}; MS (EI), m/e (%) = 57 (58), 105 (10), 212 (100), 268 (74), 292 (0.8), 348 (0.5), 405 (M^+, 0.4). Anal. Calcd for $C_{17}H_{27}NSe_2$: C, 50.63; H, 6.75; N, 3.47. Found: C, 51.06; H, 6.74; N, 3.49. HRMS Calcd for $C_{17}H_{27}NSe_2$: 405.0474. Found: 405.0470. **Data for 6b**. Yellow oil; ^1H NMR (270 MHz, $CDCl_3$) δ 0.68 (t, J = 7.1 Hz, 3 H), 1.10 (sext, J = 7.2 Hz, 2 H), 1.19 (quint, J = 7.2 Hz, 2 H), 1.29 (s, 9 H), 2.00 (s, 6 H), 2.04 (t, J = 7.8 Hz, 2 H), 6.83 (t, J = 7.3 Hz, 1 H), 6.97 (d, J = 7.3 Hz, 2 H); ^{13}C NMR (68 MHz, $CDCl_3$) δ 13.37, 18.02, 23.29, 28.44, 30.10, 40.87, 122.03, 125.05, 127.83, 148.60, 179.81; IR (NaCl) 2960, 2871, 1651, 1468, 761 cm^{-1}; MS (EI), m/e (%) = 57 (2), 105 (11), 132 (13), 146 (2), 188 (100), 245 (M^+, 16). Anal. Calcd for $C_{17}H_{27}N$: C, 83.20; H, 11.09; N, 5.71. Found: C, 83.04; H, 11.10; N, 5.71.

Reaction of 1 with PhC≡CLi (2c)

Into a THF solution (15 mL) of PhC≡CLi (**2c**) prepared from phenylacetylene (2.4 mmol) and BuLi (2.2 mmol) was added **1** (2.0 mmol) in THF (10 mL) at -78 °C and the mixture was stirred for 10 min. After BuI (4.0 mmol) was added at the same temperature, the stirring was continued for 10 min and then the

mixture was warmed to 20 °C in 1 h. Aqueous saturated NH_4Cl solution (50 mL) was added and the product was extracted with ether (50 mL), dried over $MgSO_4$, and concentrated. Yields of selenoimidate (**3c**, 47%) and ArNC (**4**, 44%) were determined by ^1H NMR. Purification by silica gel column chromatography (hexane/ether = 1/0 ~ 1/1) afforded PhC≡CSeBu (**7c**, 45%) and *Se*-butyl *N*-(2,6-dimethylphenyl)-3-phenylselenopropynimidate (**3c**, 41%). **Data for 3c**. Yellow oil obtained as a mixture of stereoisomers (major / minor = 77 / 23); ^1H NMR (270 MHz, $CDCl_3$) δ 0.90 (t, *J* = 7.5 Hz, 3 H, major), 0.95 (t, *J* = 7.5 Hz, 3 H, minor), 1.41 (sext, *J* = 7.5 Hz, 2 H, major), 1.48 (sext, *J* = 7.5 Hz, 2 H, minor), 1.78 (quint, *J* = 7.5 Hz, 2 H, major), 1.85 (quint, *J* = 7.5 Hz, 2 H, minor), 2.11 (s, 6 H, minor), 2.15 (s, 6 H, major), 3.19 (t, *J* = 7.5 Hz, 2 H, major), 3.25 (t, *J* = 7.5 Hz, 2 H, minor), 6.89-7.62 (m, 8 H + 8 H); ^{13}C NMR (68 MHz, $CDCl_3$) δ 13.57 (major), 13.65 (minor), 17.68 (major), 18.03 (minor), 23.00 (major), 23.16 (minor), 26.66 (minor), 28.51 (major), 32.59 (minor), 32.96 (major), 82.74 (minor), 84.47 (major), 95.10 (major), 96.98 (minor), 120.84, 120.87, 121.06, 123.46, 124.44, 126.18, 126.95, 127.68, 128.15, 128.37, 128.64, 129.85, 129.99, 132.29, 146.70, 148.89, 149.15, 150.66; IR (NaCl) 2958, 2929, 2206, 1600 (ν_{CN}, minor), 1575 (ν_{CN}, major), 1464, 1190, 1044, 845, 756, 689 cm^{-1}; MS (CI), m/z (%) = 232 (100), 314 (5), 370 (M^++1, 58). Anal. Calcd for $C_{21}H_{23}NSe$: C, 68.47; H, 6.29; N, 3.80. Found: C, 68.25; H, 6.40; N, 3.79.

***Se*-Butyl *N*-(2,6-dimethylphenyl)-2-phenyl-1,3-dithiane-2-selenocarboximidate (3d)**

Purified by recycling preparative HPLC (85% yield). Yellow oil; ^1H NMR (270 MHz, $CDCl_3$) δ 0.61 (t, *J* = 7.4 Hz, 3 H), 0.94 (sext, *J* = 7.4 Hz, 2 H), 1.04 (quint, *J* = 7.4 Hz, 2 H), 1.92-2.18 (m, 2 H), 2.08 (t, *J* = 7.4 Hz, 2 H), 2.28 (s, 6 H), 2.81 (ddd, *J* = 14.4, 7.6, 3.4 Hz, 1 H), 3.18 (ddd, *J* = 14.1, 8.8, 3.4 Hz, 1 H), 6.91 (dd, *J* = 8.5, 6.1 Hz, 1 H), 6.99 (d, *J* = 6.8 Hz, 2 H), 7.33 (t, *J* = 7.4 Hz, 1 H), 7.41 (t, *J* = 7.4 Hz, 2 H), 7.96 (d, *J* = 7.4 Hz, 2 H); ^{13}C NMR (68 MHz, $CDCl_3$) δ 13.20, 19.25, 22.49, 24.52, 26.24, 28.85, 31.58, 67.35, 123.66, 125.72, 127.98, 128.12, 128.46, 128.63, 139.51, 146.21, 161.89; IR (NaCl) 2956, 2925, 2870, 1643, 1589, 1467, 1444, 1200, 910, 766, 744, 733, 708 cm^{-1}; MS (CI), m/z (%) = 132 (10), 195 (100), 326 (38), 464 (M^++1, 40). HRMS (CI) Calcd for $C_{23}H_{30}NS_2Se$: 464.0985. Found: 464.0998.

***Se*-Butyl *N*-(2,6-dimethylphenyl)-9-methyl-9*H*-fluorene-9-selenocarboximidate (3e)**

Purified by silica gel column chromatography (hexane/ether = 10/1) (100% yield). Yellow oil; ^1H NMR (270 MHz, $CDCl_3$) δ 0.49 (t, *J* = 6.3 Hz, 3 H), 0.62-0.81 (m, 4 H), 1.71 (t, *J* = 7.3 Hz, 2 H), 1.85 (s, 3 H), 2.33 (s, 6 H), 6.87-7.03 (m, 3 H), 7.37 (t, *J* = 7.3 Hz, 2 H), 7.44 (t, *J* = 7.3 Hz, 2 H), 7.58 (d, *J* = 7.3 Hz, 2 H), 7.78 (d, *J* = 7.3 Hz, 2 H); ^{13}C NMR (68 MHz, $CDCl_3$) δ 13.05, 18.69, 22.37, 24.46, 26.14, 31.63, 63.75, 120.28, 123.29, 124.13, 125.51, 127.71, 127.92, 128.12, 141.19, 147.10, 149.22, 163.95; IR (NaCl) 3065, 3040, 3016, 2958, 2926, 2871, 1633, 1590, 1466, 1449, 1436, 955, 762, 748, 733 cm^{-1}; MS (CI), m/z (%) = 179 (32), 310 (100), 448 (M^++1, 27). HRMS (CI) Calcd for $C_{27}H_{30}NSe$: 448.1543. Found: 448.1531.

***Se*-Butyl *N*-(2,6-dimethylphenyl)-2-(*p*-methoxyphenyl)-1,3-dithiane-2-selenocarboximidate (3f)**

Purified by recycling preparative HPLC (45% yield). Yellow oil; ^1H NMR (400 MHz, $CDCl_3$) δ 0.63 (t, *J* = 7.4 Hz, 3 H), 0.97 (sext, *J* = 7.4 Hz, 2 H), 1.07 (quint, *J* = 7.4 Hz, 2 H), 1.93-2.13 (m, 2 H), 2.10 (t, *J* = 7.4 Hz, 2 H), 2.27 (s, 6 H), 2.80 (ddd, *J* = 14.3, 7.2, 3.3 Hz, 2 H), 3.16 (ddd, *J* = 14.2, 8.8, 3.2 Hz, 2 H), 3.82 (s, 3 H), 6.88-6.95 (m, 3 H), 6.99 (d, *J* = 7.3 Hz, 2 H), 7.87 (d, *J* = 9.0 Hz, 2 H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 13.32, 19.31, 22.61, 24.69, 26.25, 28.96, 31.73, 55.26, 66.92, 113.56, 123.38, 125.46, 127.73, 129.81,

131.04, 145.91, 159.03, 161.76; IR (NaCl) 2956, 2929, 1637, 1605, 1590, 1508, 1465, 1253, 1177, 1034, 766, 732 cm^{-1}; MS (EI), m/e (%) = 225 (100), 268 (9), 356 (6), 493 (M^+, 0.3). Anal. Calcd for $C_{24}H_{31}NOS_2Se$: C, 58.52; H, 6.34; N, 2.84. Found: C, 58.51; H, 6.37; N, 2.70.

***Se*-Butyl *N*-(2,6-dimethylphenyl)-2-(*p*-tolyl)-1,3-dithiane-2-selenocarboximidate (3g)**

Purified by recycling preparative HPLC (67% yield). Yellow oil; ^1H NMR (270 MHz, $CDCl_3$) δ 0.62 (t, *J* = 7.1 Hz, 3 H), 0.89-1.12 (m, 4 H), 1.93-2.17 (m, 2 H), 2.10 (t, *J* = 7.3 Hz, 2 H), 2.28 (s, 6 H), 2.36 (s, 3 H), 2.80 (ddd, *J* = 14.3, 7.4, 3.3 Hz, 2 H), 3.18 (ddd, *J* = 14.2, 8.8, 3.4 Hz, 2 H), 6.90 (dd, *J* = 8.8, 5.9 Hz, 1 H), 6.99 (d, *J* = 6.8 Hz, 2 H), 7.21 (d, *J* = 7.8 Hz, 2 H), 7.83 (d, *J* = 8.3 Hz, 2 H); ^{13}C NMR (68 MHz, $CDCl_3$) δ 13.19, 19.27, 21.18, 22.52, 24.57, 26.22, 28.86, 31.63, 67.17, 123.60, 125.72, 127.97, 128.53, 129.19, 136.42, 138.01, 146.24, 162.00; IR (NaCl) 3021, 2956, 2870, 1632, 1589, 1508, 1467, 1440, 1201, 1189, 755, 721, 701 cm^{-1}; MS (CI), m/z (%) = 209 (100), 340 (35), 478 (M^++1, 44). HRMS (CI) Calcd for $C_{24}H_{32}NS_2Se$: 478.1141. Found: 478.1127.

***Se*-Butyl *N*-(2,6-dimethylphenyl)-2-(*m*-chlorophenyl)-1,3-dithiane-2-selenocarboximidate (3h)**

Purified by recycling preparative HPLC (89% yield). Yellow oil; ^1H NMR (270 MHz, $CDCl_3$) δ 0.63 (t, *J* = 7.1 Hz, 3 H), 0.89-1.12 (m, 4 H), 1.93-2.13 (m, 2 H), 2.09 (t, *J* = 7.1 Hz, 2 H), 2.26 (s, 6 H), 2.81 (ddd, *J* = 14.5, 7.7, 3.5 Hz, 2 H), 2.13 (ddd, *J* = 14.5, 8.3, 3.6 Hz, 2 H), 6.92 (dd, *J* = 8.8, 5.9 Hz, 1 H), 7.00 (d, *J* = 6.4 Hz, 2 H), 7.28-7.38 (m, 2 H), 7.86 (dt, *J* = 7.3, 2.0 Hz, 1 H), 7.99 (d, *J* = 2.0 Hz, 1 H); ^{13}C NMR (68 MHz, $CDCl_3$) δ 13.20, 19.16, 22.48, 24.40, 26.27, 28.82, 31.69, 67.23, 123.80, 125.68, 126.90, 128.02, 128.24, 129.07, 129.67, 134.48, 141.90, 145.94, 161.13; IR (NaCl) 2957, 2927, 2871, 1644, 1634, 1589, 1568, 1470, 1422, 1199, 766, 724, 712 cm^{-1}; MS (CI), m/z (%) = 229 (100), 360 (43), 498 (M^++1, 65). HRMS (CI) Calcd for $C_{23}H_{29}ClNS_2Se$: 498.0595. Found: 498.0606.

***Se*-Butyl *N*-(2,6-dimethylphenyl)-2-(*p*-chlorophenyl)-1,3-dithiane-2-selenocarboximidate (3i)**

Purified by recycling preparative HPLC (95% yield). Yellow oil; ^1H NMR (270 MHz, $CDCl_3$) δ 0.63 (t, *J* = 7.1 Hz, 3 H), 0.89-1.12 (m, 4 H), 1.92-2.16 (m, 2 H), 2.08 (t, *J* = 7.3 Hz, 2 H), 2.24 (s, 6 H), 2.79 (ddd, *J* = 14.3, 8.2, 3.5 Hz, 2 H), 3.12 (ddd, *J* = 14.4, 8.1, 3.4 Hz, 2 H), 6.91 (dd, *J* = 8.8, 5.9 Hz, 1 H), 6.99 (d, *J* = 5.9 Hz, 2 H), 7.38 (dt, *J* = 8.8, 2.2 Hz, 2 H), 7.92 (dt, *J* = 8.3, 2.0 Hz, 2 H); ^{13}C NMR (68 MHz, $CDCl_3$) δ 13.19, 19.12, 22.49, 24.46, 26.21, 28.79, 31.65, 67.26, 123.75, 125.63, 127.97, 128.60, 130.34, 134.08, 138.22, 145.89, 161.23; IR (NaCl) 2957, 2928, 2871, 1651, 1644, 1634, 1590, 1488, 1470, 1094, 1014, 758 cm^{-1}; MS (CI), m/z (%) = 132 (17), 229 (100), 360 (10), 498 (M^++1, 35). HRMS (CI) Calcd for $C_{23}H_{29}ClNS_2Se$: 498.0595. Found: 498.0609.

***Se*-Butyl *N*-(2,6-dimethylphenyl)-2-phenylpropionitrile-2-selenocarboximidate (3j)**

Purified by recycling preparative HPLC (98% yield). Yellow oil; ^1H NMR (270 MHz, $CDCl_3$) δ 0.64 (t, *J* = 7.1 Hz, 3 H), 0.93-1.23 (m, 4 H), 2.10 (s, 3 H), 2.10-2.24 (m, 1 H), 2.192 (s, 3 H), 2.198 (s, 3 H), 2.43-2.54 (m, 1 H), 6.92-6.94 (m, 3 H), 7.38-7.48 (m, 3 H), 7.64 (dd, *J* = 7.9, 1.5 Hz, 2 H); ^{13}C NMR (68 MHz, $CDCl_3$) δ 13.13, 17.97, 18.47, 22.42, 26.19, 28.51, 31.46, 54.87, 120.77, 124.13, 125.22, 125.92, 126.49, 128.02, 128.15, 128.63, 129.10, 137.53, 146.15, 159.68; IR (NaCl) 2959, 2873, 1652, 1644, 1634, 1622, 1615, 1591, 1494, 1470, 1446, 1202, 911, 839, 763, 734, 699 cm^{-1}; MS (CI), m/z (%) = 261 (48), 399

(M^++1, 100). HRMS Calcd for $C_{22}H_{26}N_2Se$: 398.1262. Found: 398.1259.

***Se*-Butyl *N*-(2,6-dimethylphenyl)-2,2-diphenylacetonitrile-2-selenocarboximidate (3k)**

Purified by silica gel column chromatography (hexane/ether = 20/1) (99% yield). Yellow oil; ^{1}H NMR (270 MHz, $CDCl_3$) δ 0.65 (t, *J* = 7.4 Hz, 3 H), 1.03 (sext, *J* = 7.4 Hz, 2 H), 1.18 (quint, *J* = 7.4 Hz, 2 H), 2.17 (s, 6 H), 2.42 (t, *J* = 7.4 Hz, 2 H), 6.90 (dd, *J* = 8.8, 5.9 Hz, 1 H), 6.97 (d, *J* = 6.3 Hz, 2 H), 7.34-7.46 (m, 6 H), 7.57 (dd, *J* = 5.3, 1.5 Hz, 4 H); ^{13}C NMR (68 MHz, $CDCl_3$) δ 13.14, 18.40, 22.40, 27.06, 31.16, 64.96, 120.57, 124.03, 125.28, 127.98, 128.63, 128.78, 136.91, 146.32, 159.83; IR (NaCl) 3062, 3026, 2958, 2872, 1624, 1590, 1492, 1466, 1450, 1203, 1091, 1034, 835, 751, 727, 697 cm^{-1}; MS (CI), m/z (%) = 132 (14), 192 (42), 323 (89), 461 (M^++1, 100). HRMS (CI) Calcd for $C_{27}H_{29}N_2Se$: 461.1496. Found: 461.1474.

Reaction of 1 with Lithium Enolate (2l)

Lithium enolate (**2l**) was prepared by adding isobutyrophenone (2.4 mmol) at -78 °C to the solution of LHMDS, generated by the reaction of hexamethyldisilazane (2.4 mmol) and BuLi (2.2 mmol) in THF (25 mL) with HMPA (6.0 mmol). To the solution of **2l** was added **1** (2.0 mmol) at 0 °C, and the mixture was stirred for 1 h. After BuI (4.0 mmol) was added at the same temperature, the mixture was warmed to 20 °C and the stirring was continued for 1 h. Aqueous saturated NH_4Cl solution (50 mL) was added, and the product was extracted with ether (50 mL), dried over $MgSO_4$, and concentrated. The residue was purified by HPLC then by PTLC (hexane/ether = 20/1) to afford *Se*-butyl *N*-(2,6-dimethylphenyl)-2-benzoyl-2-methylselenopropanimidate (**3l**, 28%) and *Se*-butyl *O*-1-phenyl-2-methyl-1-propenyl *N*-(2,6-dimethylphenyl)selenocarbonimidate (**19l**, 46%). **Data for 3l**. Yellow oil; ^{1}H NMR (270 MHz, $CDCl_3$) δ 0.61 (t, *J* = 7.1 Hz, 3 H), 0.93 (sext, *J* = 7.1 Hz, 2 H), 1.01 (quint, *J* = 7.1 Hz, 2 H), 1.74 (s, 6 H), 2.13 (t, *J* = 7.1 Hz, 2 H), 2.17 (s, 6 H), 6.88-6.97 (m, 3 H), 7.43 (t, *J* = 7.3 Hz, 2 H), 7.52 (t, *J* = 7.3 Hz, 1 H), 8.17 (d, *J* = 6.8 Hz, 2 H); ^{13}C NMR (68 MHz, $CDCl_3$) δ 13.17, 18.83, 22.43, 25.47, 26.59, 31.72, 61.20, 123.71, 126.26, 128.12, 128.18, 129.67, 132.40, 136.07, 146.35, 165.48, 199.92; IR (NaCl) 2958, 2931, 1682, 1633, 1590, 1463, 1256, 938, 766, 734, 710 cm^{-1}; MS (CI), m/z (%) = 105 (11), 278 (100), 360 (3), 416 (M^++1, 29). Anal. Calcd for $C_{23}H_{29}NOSe$: C, 66.66; H, 7.05; N, 3.38. Found: C, 66.55; H, 7.26; N, 3.36. **Data for 19l**. White solid; mp 64.0-65.0 °C; ^{1}H NMR (270 MHz, $CDCl_3$) δ 0.92 (t, *J* = 7.4 Hz, 3 H), 1.43 (sext, *J* = 7.4 Hz, 2 H), 1.73 (quint, *J* = 7.4 Hz, 2 H), 1.76 (s, 6 H), 1.89 (s, 3 H), 1.94 (s, 3 H), 3.07 (t, *J* = 7.4 Hz, 2 H), 6.79-6.90 (m, 3 H), 7.24-7.37 (m, 3 H), 7.48 (d, *J* = 6.8 Hz, 2 H); ^{13}C NMR (68 MHz, $CDCl_3$) δ 13.56, 17.52, 18.64, 19.73, 22.94, 25.48, 33.18, 121.31, 123.32, 127.59, 127.82, 127.84, 128.42, 129.29, 135.86, 144.45, 145.04, 152.03; IR (KBr) 2919, 1636, 1591, 901, 760, 706 cm^{-1}; MS (CI), m/z (%) = 91 (4), 105 (2), 131 (100), 148 (11), 268 (27), 416 (M^++1, 23). Anal. Calcd for $C_{23}H_{29}NOSe$: C, 66.66; H, 7.05; N, 3.38. Found: C, 66.51; H, 7.19; N, 3.30.

Reaction of 2,6-Xylyl Isothiocyanate (8) with PhLi (2a)

A mixture of PhLi (**2a**, 2.2 mmol) and **8** (2.0 mmol) in THF (25 mL) was stirred for 10 min at -78 °C. After BuI (4.0 mmol) was added at the same temperature, the stirring was continued at -78 °C for 10 min and then at 20 °C for 1 h. Aqueous saturated NH_4Cl solution (50 mL) was added, and the product was extracted with ether (50 mL), dried over $MgSO_4$, and concentrated. The residue was purified by silica gel column chromatography (hexane/ether = 1/1) to afford *S*-butyl *N*-(2,6-dimethylphenyl)thiobenzimidate (**9a**, 82%).

Yellow oil; ^{1}H NMR (270 MHz, $CDCl_3$, 50 °C) δ 0.81 (t, J = 7.1 Hz, 3 H), 1.31 (sext, J = 7.1 Hz, 2 H), 1.53 (brs, 2 H), 2.09 (s, 6 H), 2.81 (brs, 2 H), 6.84 (t, J = 6.9 Hz, 1 H), 6.95 (d, J = 6.9 Hz, 2 H), 7.31 (brs, 3 H), 7.47 (brs, 2 H); ^{13}C NMR (68 MHz, $CDCl_3$, 50 °C) δ 13.46, 18.06, 21.85, 31.75, 32.04, 123.11, 126.34, 127.51, 127.85, 128.28, 129.81, 137.86, 148.30, 165.55; IR (NaCl) 2959, 2930, 1614, 1590, 1464, 1444, 1221, 950, 765, 705, 695 cm^{-1}; MS (EI), m/e (%) = 77 (7), 105 (9), 208 (100), 297 (M^+, 13). Anal. Calcd for $C_{19}H_{23}NS$: C, 76.72; H, 7.79; N, 4.71. Found: C, 76.65; H, 7.93; N, 4.79.

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