Imidoylation of Acidic Hydrocarbons with Selenium and Isocyanides: A New Synthetic Method for Preparation of Selenoimidates

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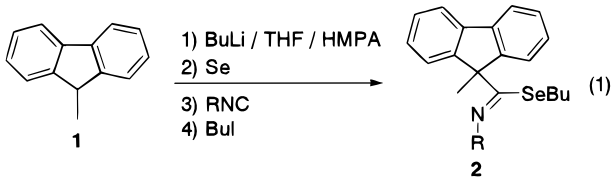
Selenoimidates are potentially useful compounds in synthetic organic chemistry, for example, as precursors of imidoyl radicals[2] and iminoethers.[3] Hitherto known methods for preparation of selenoimidates are (i) alkylation of selenoamides with alkyl halides,[4] (ii) reaction of imidoyl chlorides with selenolate anions,[4b,5] (iii) reaction of imidates with selenols,[4b] (iv) reaction of oxime sulfonates with organoaluminum selenolates,[3] (v) reaction of isoselenocyanates with organolithiums,[6] and (vi) reaction of imidoyl radicals with diaryl diselenides.[7]

We have recently shown that lithiated hydrocarbons derived from fluorene, triphenylmethane, and related compounds can be carbonylated with carbon monoxide and selenium resulting in the formation of lithium selenocarboxylates, which were trapped with methyl iodide to give selenol esters.[8] Our continuing interest in developing new synthetic reactions mediated by selenium led us to apply this principle to the preparation of selenoimidates by using isocyanides, which have an isoelectronic structure with carbon monoxide. Described herein is the synthesis of selenoimidates from hydrocarbons having an acidic hydrogen, selenium, and a variety of isocyanides.

9-Methyl-9*H*-fluorene (**1**) was lithiated with BuLi in THF/HMPA at −78 °C, and then selenium was added at the same temperature. After the mixture was warmed up to 20 °C, BuNC was added, and the mixture was stirred for 1 h. Addition of BuI at 0 °C followed by usual workup and purification using preparative HPLC gave the corresponding selenoimidate **2a** in 76% yield (eq 1, run 1 in Table 1).



A series of isocyanides was tested under similar conditions and the results are summarized in Table 1. Both aliphatic and aromatic isocyanides afforded the corresponding selenoimidates in good yields as shown in runs 2−6. However, benzyl isocyanide (run 7) gave low yield of the product probably because it has acidic benzylic hydrogens. Thus, when $PhMe_2CNC$ was used (run 8), selenoimidate **2h** was obtained in 87% yield. A similar reaction by using sulfur in place of selenium did not afford the corresponding thioimidate at all.

Next, we examined the reaction employing hydrocarbons having different carbon skeletons. As shown in Table 2, 9-cinnamylfluorene (**3**), 1,2,3,4,5-pentamethylcyclopentadiene (**5**), 4-methyl-4*H*-cyclopenta[*def*]phenanthrene (**7**), triphenylmethane (**9**), and 2-phenylpropionitrile (**13**) were selenoimidoylated efficiently at the benzylic or allylic carbons under similar conditions (runs 1−4 and 6). Interestingly, selenoimidoylation of diphenyl-4-pyridylmethane (**11**) occurred at the nitrogen atom to give isoselenourea[9] **12** (run 5). This site selectivity can be explained by the fact that the anion charge of lithio-4-pyridyldiphenylmethane is localized at the nitrogen atom of the pyridyl ring.[10]

All selenoimidates listed in Tables 1 and 2 could easily be isolated and obtained as single stereoisomers. The *Z*-configuration for selenoimidates was determined by NOE experiments for **2a**, **2b**, and **2h**, and confirmed by X-ray analysis for **10**.

To prove the mechanism of this reaction, the following control experiments were carried out. First, reaction of 9-methylfluorenyllithium with selenium afforded the corresponding selenide **15**[8a] in 93% yield after trapping with methyl iodide in the absence of isocyanides (eq 2). Second, when a mixture of 9-methylfluorenyllithium and *t*-BuNC was quenched with BuI, the isocyanide was not incorporated (eq 3).[11] Third, treatment of 9-methylfluorenyllithium with butyl isoselenocyanate gave selenoimidate **2a** in high yield (eq 4).[6]

These results prompted us to propose the reaction pathways as shown in Scheme 1. Reaction of fluorenyllithium **17** with selenium affords selenolate **18**, which then reacts with isocyanide to give lithium selenocar-

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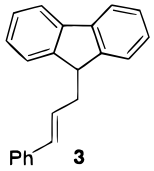
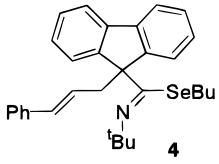
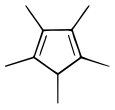
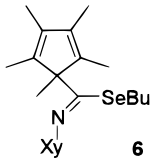
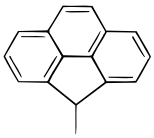
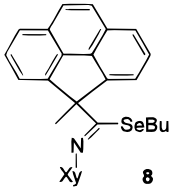
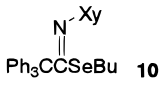
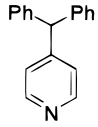
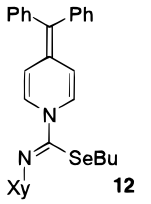
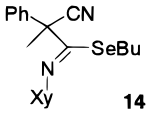
Table 1. Selenoimidoylation of 9-Methyl-9*H*-fluorene[a]

run	RNC	product[b]	isolated yield (%)
1	*n*-BuNC	**2a**	76
2	*c*-C_6H_{11}NC	**2b**	71
3	*t*-BuNC	**2c**	87
4	TMBI[c]	**2d**	76
5	PhNC	**2e**	76
6	XyNC[d]	**2f**	70
7	$PhCH_2NC$	**2g**	29
8	$PhMe_2CNC$	**2h**	87

[a] Conditions: **1** (2.0 mmol), BuLi (2.2 mmol), THF (25 mL), HMPA (6.0 mmol), −78 °C, 30 min; Se (2.4 mmol), −78 (∼ 20) °C, 30 min; RNC (2.2 mmol), 20 °C, 1 h; BuI (4.0 mmol), 0 °C, 30 min. [b] All selenoimidates were obtained as single stereoisomers. [c] TMBI = 1,1,3,3-tetramethylbutyl isocyanide. [d] Xy = 2,6-xylyl.

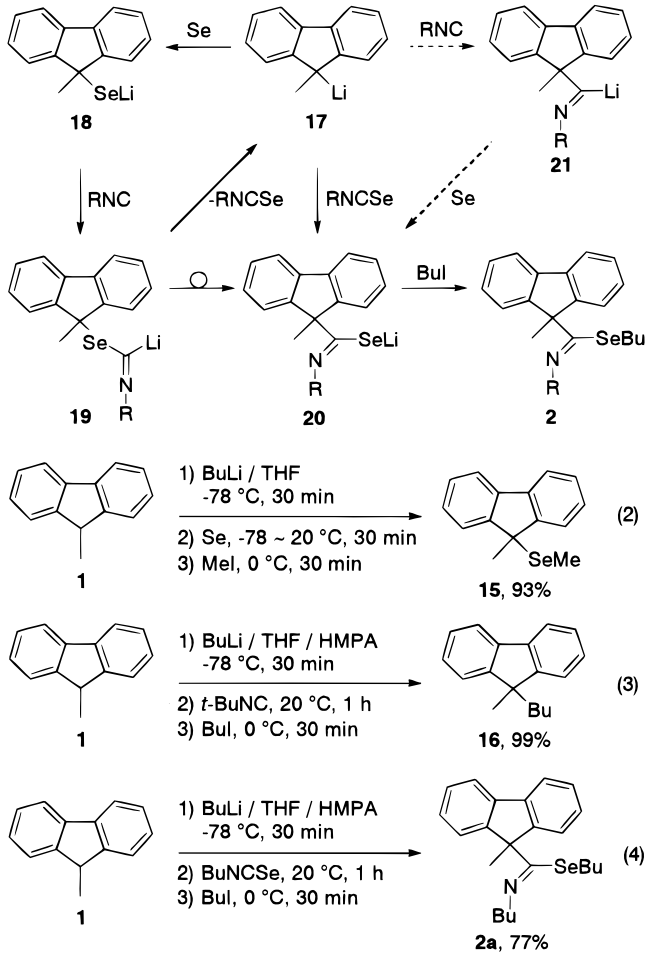
Table 2. Selenoimidoylation of Acidic Hydrocarbons[a]

run	substrate	isocyanide	product[b]	isolated yield (%)
1	 **3**	*t*-BuNC	 **4**	92
2	 **5**	XyNC[c]	 **6**	70
3	 **7**	XyNC[c]	 **8**	68
4	Ph_3CH **9**	XyNC[c]	 **10**	43
5	 **11**	XyNC[c]	 **12**	85
6	 **13**	XyNC[c]	 **14**	83

[a] Conditions: substrate (2.0 mmol), BuLi (2.2 mmol), THF (25 mL), HMPA (6.0 mmol), −78 °C, 30 min; Se (2.4 mmol), −78 (∼ 20) °C, 30 min; isocyanide (2.2 mmol), 20 °C, 1 h; BuI (4.0 mmol), 0 °C, 30 min. [b] All selenoimidates were obtained as single stereoisomers. [c] Xy = 2,6-xylyl.

boximidate **20**, probably via formal rearrangement of **19**.[12,13] It is still a question whether the rearrangement proceeds intramolecularly or intermolecularly with elimination of isoselenocyanate. Trapping of **20** with BuI forms selenoimidate **2**. An alternative pathway via generation of lithio aldimine **21** by the direct reaction of **17** with isocyanide and subsequent trapping with selenium seems unlikely from the control experiment shown in eq 3.[11]

Scheme 1. Plausible Reaction Pathways



When BuLi or PhLi was employed instead of fluorenyllithium under similar conditions, only BuSeBu or PhSeBu was obtained, respectively, without any imidoylated products. This may be because high activation energy is required for the rearrangement process in these cases where Bu and Ph migrate as a carbanion.

Next, we examined hydrolysis of selenoimidates because there has been no example of such to date. Although thioimidates are known to be hydrolyzed giving amides and thiol esters depending on their structure and/or pH value of the buffer,[14] we found that *N*-alkylselenoimidates **2a**−**d,g** underwent hydrolysis easily giving amides **22** in excellent yields by simply passing them through a silica gel column eluted with *n*-hexane−ether

(12) Although it is not yet certain whether **19** can really exist in the reaction media or whether it is more like a transition state than an intermediate, isocyanides were known to insert into an S−Li or O−Li bond intramolecularly. (a) Dondoni, A.; Fantin, G.; Fogagnolo, M.; Medici, A.; Pedrini, P. *Synthesis* **1987**, 693−696. (b) Bortolini, O.; Fantin, G.; Fogagnolo, M.; Medici, A.; Pedrini, P. *Heterocycles* **1990**, *31*, 1213−1216. (c) Fantin, G.; Fogagnolo, M.; Medici, A.; Pedrini, P. *Heterocycles* **1993**, *36*, 473−484.

(13) Intermolecular insertion of isocyanides into an O−Li bond seems to be reversible because isocyanides were formed by hydrogen abstraction from imidates with alkyllithiums. (a) Koga, N.; Koga, G.; Anselme, J.-P. *Tetrahedron Lett.* **1970**, 3309−3312. (b) Pornet, J.; Miginiac, M. L. *Tetrahedron Lett.* **1971**, 967−970.

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Table 3. Hydrolysis of Seleno- and Thioimidates

run	imidate	Z	R	product	isolated yield (%)
1	**2a**	Se	*n*-Bu	**22a**	92
2	**2b**	Se	*c*-C_6H_{11}	**22b**	99
3	**2c**	Se	*t*-Bu	**22c**	95
4	**2d**	Se	TMB[a]	**22d**	92
5	**2g**	Se	$PhCH_2$	**22g**	91
6	**2e**	Se	Ph		0
7	**2f**	Se	Xy[b]		0
8	**23a**	S	*n*-Bu	**22a**	11
9	**23b**	S	Ph		0

[a] TMB = 1,1,3,3-tetramethylbutyl. [b] Xy = 2,6-xylyl.

(eq 5). The yields of the resulting amides are listed in

Table 3. But this method cannot be applied to selenoimidates possessing an aromatic substituent, probably because of the difficulty of protonation in the first stage of hydrolysis (runs 6, 7). Under similar conditions, *N*-alkylthioimidate **23a** was only partially hydrolyzed to amide **22a**, and *N*-arylthioimidate **23b** was recovered unchanged (runs 8, 9).

In summary, thermodynamically stable organolithiums derived from acidic hydrocarbons underwent selenoimidoylation with selenium and isocyanides under mild conditions to yield lithium selenocarboximidates. Trapping of the lithium selenocarboximidates with BuI resulted in the formation of the corresponding selenoimidates. It was also revealed that *N*-alkylselenoimidates could be converted to amides in excellent yields simply by passing them through a silica gel column.

Experimental Section

THF was distilled from sodium benzophenone ketyl. HMPA was fractionally distilled and dried over calcium hydride. BuLi (1.6 M solution in hexane) and Se were used as purchased. MeI and BuI were distilled from P_2O_5. Acidic hydrocarbons were purified by distillation or recrystallization prior to use. 1,2,3,4,5-Pentamethylcyclopentadiene, triphenylmethane, 2-phenylpropionitrile, and diphenyl-4-pyridylmethane were obtained from commercial sources. 9-Methyl-9*H*-fluorene and 4-methyl-4*H*-cyclopenta[*def*]phenanthrene were prepared by alkylation (with MeI) of the corresponding unsubstituted substrates. BuNC, *c*-C_6H_{11}NC, *t*-BuNC, 1,1,3,3-tetramethylbutyl isocyanide (TMBI), and $PhCH_2NC$ were used as purchased. Other isocyanides were synthesized by the reported procedures.[15] PhNCS was used as purchased. BuNCSe was prepared according to the literature[16] and purified by distillation. Hydrolysis of selenoimidates was performed on a column (3.6 × 6 cm) using Fuji-Silysia silica gel WB-300 (100−250 mesh).

Imidoylation of Acidic Hydrocarbons with Selenium and Isocyanides: A Typical Procedure. To a THF (25 mL)/HMPA (1 mL, 6 mmol) solution of 9-methyl-9*H*-fluorene (**1**, 2.0 mmol) was added BuLi (1.66 M in hexane, 1.30 mL, 2.2 mmol) at −78 °C under nitrogen. After 30 min, finely ground selenium powder (2.4 mmol) was added, and the mixture was warmed to 20 °C. A homogeneous dark-red solution was obtained within 30 min. To the flask was added butyl isocyanide (2.2 mmol), and stirring was continued for 1 h. After BuI (4.2 mmol) was added to the solution at 0 °C, the mixture was warmed again to 20 °C. Aqueous saturated NH_4Cl solution (50 mL) was added, and the product was extracted with ether (50 mL), dried over $MgSO_4$, and evaporated to give a yellow residue. Purification by recycling preparative HPLC afforded ***Se*-butyl *N*-butyl-9-methyl-9*H*-fluorene-9-selenocarboximidate** (**2a**) as yellow oil. ^{1}H NMR (270 MHz, $CDCl_3$, δ): 0.63 (t, J = 7.1 Hz, 3 H), 0.86−1.04 (m, 4 H), 1.01 (t, J = 7.2 Hz, 3 H), 1.51 (sext, J = 7.2 Hz, 2 H), 1.66 (s, 3 H), 1.78 (quint, J = 7.2 Hz, 2 H), 2.19 (t, J = 7.3 Hz, 2 H), 3.62 (t, J = 7.2 Hz, 2 H), 7.24−7.44 (m, 6 H), 7.77 (d, J = 7.8 Hz, 2 H). NOE experiment: irradiation at methylene triplet (NCH_2) at δ 3.62 resulted in a 6.0% enhancement of the signal at δ 2.19 ($SeCH_2$). ^{13}C NMR (68 MHz, $CDCl_3$, δ): 13.39, 14.01, 20.66, 22.48, 24.39, 26.59, 32.59, 32.90, 56.93, 63.66, 120.12, 123.80, 127.36, 127.80, 141.57, 149.50, 159.68. Anal. Calcd for $C_{23}H_{29}NSe$: C, 69.33; H, 7.34; N, 3.52. Found: C, 69.31; H, 7.22; N, 3.59.

***Se*-Butyl *N*-*tert*-Butyl-9-cinnamyl-9*H*-fluorene-9-selenocarboximidate (4).** Yellow oil. ^{1}H NMR (270 MHz, $CDCl_3$, δ): 0.54 (t, J = 6.8 Hz, 2 H), 0.81−0.87 (m, 4 H), 1.52 (s, 9 H), 1.67 (t, J = 7.3 Hz, 2 H), 2.98 (d, J = 7.3 Hz, 2 H), 5.75−5.86 (m, 1 H), 5.96 (d, J = 15.6 Hz, 1 H), 7.01−7.45 (m, 11 H), 7.69 (d, J = 7.3 Hz, 2 H). ^{13}C NMR (68 MHz, $CDCl_3$) δ: 13.16, 22.68, 26.82, 29.96, 32.33, 44.92, 58.09, 68.87, 119.89, 125.05, 125.86, 126.56, 127.13, 127.37, 127.68, 128.24, 132.39, 138.01, 141.49, 147.96, 150.23. HRMS (EI) Calcd for $C_{31}H_{36}NSe$: 502.2013. Found: 502.2022.

***Se*-Butyl *N*-(2,6-Dimethylphenyl)-1,2,3,4,5-pentamethylcyclopentadiene-1-selenocarboximidate (6).** Yellow oil. ^{1}H NMR (270 MHz, $CDCl_3$, δ): 0.69 (t, J = 7.3 Hz, 3 H), 1.02 (sext, J = 7.3 Hz, 2 H), 1.11 (quint, J = 7.3 Hz, 2 H), 1.31 (s, 3 H), 1.82 (s, 6 H), 1.89 (s, 6 H), 2.11 (t, J = 7.3 Hz, 2 H), 2.21 (s, 6 H), 6.85 (dd, J = 8.3, 6.4 Hz, 1 H), 6.95 (d, J = 7.3 Hz, 2 H). ^{13}C NMR (68 MHz, $CDCl_3$, δ): 10.71, 11.40, 13.29, 18.78, 20.38, 22.77, 23.23, 32.18, 69.40, 122.90, 125.52, 127.71, 138.01, 139.08, 147.18, 162.73. Anal. Calcd for $C_{23}H_{33}NSe$: C, 68.64; H, 8.26; N, 3.48. Found: C, 68.32; H, 8.24; N, 3.50.

***Se*-Butyl *N*-(2,6-Dimethylphenyl)-4-methyl-4*H*-cyclopenta[*def*]phenanthrene-4-selenocarboximidate (8).** Yellow oil. ^{1}H NMR (270 MHz, $CDCl_3$, δ): 0.36 (t, J = 7.0 Hz, 3 H), 0.54 (sext, J = 7.0 Hz, 2 H), 0.60 (quint, J = 7.0 Hz, 2 H), 1.44 (t, J = 7.3 Hz, 2 H), 2.02 (s, 3 H), 2.35 (s, 6 H), 6.91 (t, J = 7.3 Hz, 1 H), 7.02 (d, J = 7.3 Hz, 2 H), 7.65−7.74 (m, 4 H), 7.85−7.89 (m, 4 H). ^{13}C NMR (68 MHz, $CDCl_3$, δ): 12.89, 18.54, 22.24, 24.40, 25.35, 31.45, 66.72, 120.58, 123.31, 124.00, 125.51, 125.55, 127.88, 127.98, 128.18, 137.09, 147.12, 148.09, 163.25. HRMS (CI) Calcd for $C_{29}H_{30}NSe$: 472.1544. Found: 472.1529.

***Se*-Butyl *N*-(2,6-Dimethylphenyl)triphenylselenoacetimidate (10).** White solid; mp 88 °C. ^{1}H NMR (270 MHz, $CDCl_3$, δ): 0.60 (t, J = 6.8 Hz, 3 H), 0.85−1.02 (m, 4 H), 1.95 (t, J = 6.8 Hz, 2 H), 2.21 (s, 6 H), 6.88 (t, J = 5.9 Hz, 1 H), 6.96 (d, J = 8.4 Hz, 2 H), 7.28−7.33 (m, 9 H), 7.51 (dd, J = 8.4, 1.8 Hz, 6 H). ^{13}C NMR (68 MHz, $CDCl_3$, δ): 13.24, 19.17, 22.50, 26.78, 31.30, 72.09, 123.95, 125.52, 126.51, 127.37, 128.07, 131.25, 143.92, 146.86, 164.88. Anal. Calcd for $C_{32}H_{33}NSe$: C, 75.28; H, 6.51; N, 2.74. Found: C, 75.08; H, 6.52; N, 2.70.

***Se*-Butyl *N*′-(2,6-Dimethylphenyl)-4-diphenylmethylidene-4*H*-azine-*N*-selenocarbamidate (12).** Yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$, δ): 0.85 (t, J = 7.5 Hz, 3 H), 1.28 (sext, J = 7.5 Hz, 2 H), 1.53 (quint, J = 7.5 Hz, 2 H), 2.06 (s, 6 H), 2.72 (t, J = 7.5 Hz, 2 H), 6.16 (d, J = 8.4 Hz, 2 H), 6.91 (t, J = 7.6 Hz, 1 H), 7.00 (d, J = 7.6 Hz, 2 H), 7.15−7.31 (m, 12 H). ^{13}C NMR (100 MHz, $CDCl_3$, δ): 13.39, 18.39, 22.75, 27.57, 32.64, 112.11, 123.40, 124.06, 126.14, 127.28, 127.74, 127.84, 128.02, 128.22, 130.24, 142.56, 146.39, 147.08. HRMS (EI) Calcd for $C_{31}H_{32}N_2Se$: 512.1731. Found: 512.1728.

***Se*-Butyl *N*-(2,6-Dimethylphenyl)-2-phenylpropionitrile-2-selenocarboximidate (14).** Yellow oil. ^{1}H 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), 2.19 (s, 3 H), 2.20 (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. HRMS (EI) Calcd for $C_{22}H_{26}N_2Se$: 398.1262. Found: 398.1259.

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9-Methyl-9-methylseleno-9*H*-fluorene (15).[8a] ^{1}H NMR (270 MHz, $CDCl_3$, δ): 1.28 (s, 3 H), 1.87 (s, 3 H), 7.28−7.41 (m, 4 H), 7.56−7.70 (m, 4 H). ^{13}C NMR (68 MHz, $CDCl_3$, δ): 3.56, 24.85, 49.02, 119.67, 128.83, 127.47, 127.74, 138.93, 150.14.

9-Butyl-9-methyl-9*H*-fluorene (16).[17] ^{1}H NMR (270 MHz, $CDCl_3$, δ): 0.58−0.70 (m, 5 H), 1.08 (q, J = 7.3 Hz, 2 H), 1.46 (s, 3 H), 1.93−2.00 (m, 2 H), 7.25−7.40 (m, 6 H), 7.70 (d, J = 6.8 Hz, 2 H). ^{13}C NMR (68 MHz, $CDCl_3$, δ): 13.75, 22.94, 26.37, 26.66, 40.32, 50.52, 119.44, 122.35, 126.41, 126.70, 139.70, 151.66.

Hydrolysis of Selenoimidates: A Typical Procedure. *Se*-Butyl *N*-butyl-9-methyl-9*H*-fluorene-9-selenocarboximidate (**2a**, 0.48 mmol) was charged on a silica gel column (3.6 × 6 cm) with *n*-hexane−ether (1:1, 300 mL) to give ***N*-butyl-9-methyl-9*H*-fluorene-9-carboxamide** (**22a**) as colorless oil. ^{1}H NMR (270 MHz, $CDCl_3$, δ): 0.77 (t, J = 7.2 Hz, 3 H), 1.07 (sext, J = 7.2 Hz, 2 H), 1.22 (quint, J = 7.2 Hz, 2 H), 1.77 (s, 3 H), 3.02 (q, J = 7.2 Hz, 2 H), 5.05 (brs, 1 H), 7.32−7.44 (m, 4 H), 7.59 (d, J = 6.8 Hz, 2 H), 7.75 (d, J = 6.8 Hz, 2 H). ^{13}C NMR (68 MHz, $CDCl_3$, δ): 13.58, 19.74, 23.20, 31.29, 39.42, 58.22, 120.33, 124.09, 127.97, 128.17, 140.12, 148.11, 172.97. HRMS (EI) Calcd for $C_{19}H_{21}NO$: 279.1623. Found: 279.1625.

Preparation of Thioimidates 23: **A Typical Procedure.** To a THF (25 mL)/HMPA (1 mL, 6 mmol) solution of 9-methyl-9*H*-fluorene (**1**, 2.03 mmol) was added BuLi (1.64 M in hexane, 1.35 mL, 2.21 mmol) at −78 °C under nitrogen. After 30 min, butyl isothiocyanate (2.20 mmol) was added at 20 °C, and the mixture was stirred for 1 h. After BuI (4.74 mmol) was added to the solution at 0 °C, the mixture was warmed again to 20 °C. Aqueous saturated NH_4Cl solution (50 mL) was added, and the product was extracted with ether (50 mL), dried over $MgSO_4$, and evaporated to give a yellow residue. Purification by recycling preparative HPLC afforded ***S*-butyl *N*-butyl-9-methyl-9*H*-fluorene-9-thiocarboximidate** (**23a**) as yellow oil. ^{1}H NMR (270 MHz, $CDCl_3$, δ): 0.58 (t, J = 6.8 Hz, 3 H), 0.83−0.89 (m, 4 H), 1.01 (t, J = 7.2 Hz, 3 H), 1.51 (sext, J = 7.2 Hz, 2 H), 1.65 (s, 3 H), 1.78 (quint, J = 7.2 Hz, 2 H), 2.06 (t, J = 7.3 Hz, 2 H), 3.63 (t, J = 7.2 Hz, 2 H), 7.24−7.42 (m, 6 H), 7.76 (d, J = 7.8 Hz, 2 H). ^{13}C NMR (68 MHz, $CDCl_3$, δ): 13.37, 14.03, 20.69, 21.35, 25.15, 31.74, 32.76, 33.16, 54.12, 62.54, 120.13, 123.72, 127.39, 127.74, 141.32, 149.71, 162.52. HRMS (CI) Calcd for $C_{27}H_{30}NS$: 352.2099. Found: 352.2107.

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Supporting Information Available: Full compound characterization data and copies of ^{1}H and ^{13}C NMR spectra of all new compounds, and an ORTEP diagram and X-ray structure data for selenoimidate **10**. This material is available free of charge via the Internet at http://pubs.acs.org.

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