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Photoinduced Intramolecular Cyclization of *o*-Ethenylaryl Isocyanides with Organic Disulfides Mediated by Diphenyl Ditelluride

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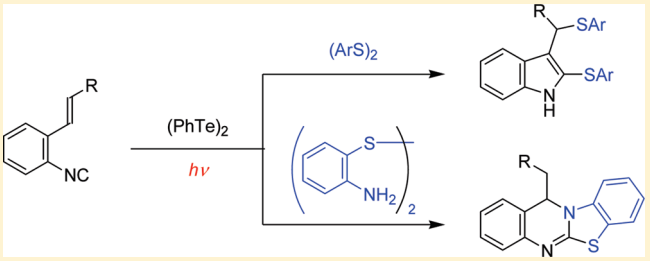
Supporting Information

ABSTRACT: Photoinduced reaction of *o*-ethenylaryl isocyanides with organic disulfides in the presence of diphenyl ditellurides affords the corresponding bisthiolated indole derivatives via a radical cyclization process. The cyclization can proceed at room temperature upon visible-light irradiation and exhibits good tolerance to functional groups. Several organic disulfides also can be employed for this cyclization, and the corresponding bisthiolated indole derivatives are obtained selectively. In addition, the photoinduced reaction of *o*-ethenylaryl isocyanides with bis(2-aminophenyl) disulfide affords tetracyclic compounds in one portion.



INTRODUCTION

Indole derivatives are present in a number of natural products such as alkaloids and many of them indicate valuable bioactivities. Therefore, the indole derivatives have been often designed and synthesized as new pharmaceutical active agents.[1] Therefore, development of new methods for the preparation of various indole derivatives is of great importance in pharmaceutical sciences as well as organic synthesis.[2] Heterocycles having organosulfur groups are also important in the fields of pharmacology, materials sciences, and organic synthesis.[3,4] We and other groups have developed a series of photoinduced addition reactions of organic dichalcogenides to acetylenes,[5] allenes,[6] conjugated dienes,[7] and alkenes.[8] Furthermore, the photoinduced addition to isocyanides has been attained by the combination of organic disulfides and organic diselenides (or ditellurides).[9] Isocyanides are useful parent compounds for the synthesis of *N*-heterocycles. For this purpose, nucleophilic reactions,[10] transition metal-catalyzed reactions,[11] radical reactions,[12] and photochemical reactions[13] have been reported.[14] These results prompted us to examine the synthesis of *N*-heterocycles by the photoinduced reaction of *o*-ethenylaryl isocyanides with organic disulfides, diselenides, and ditellurides.

Herein, we report a highly selective synthesis of bisthiolated indole derivatives **3**[15] by the photoinduced intramolecular cyclization of *o*-ethenylaryl isocyanides **1** with organic disulfides **2** in the presence of diphenyl ditelluride (Scheme 1). We also report a novel one-pot preparation of tetracyclic compounds **4** from *o*-ethenylaryl isocyanides **1** and bis(2-aminophenyl) disulfide. The formed tetracyclic compounds **4** consist of both dihydroquinazoline and benzothiazole units.

RESULTS AND DISCUSSION

On the basis of our previous work on the photoinduced thioselenation and thiotelluration of isocyanides,[9] we first propose a possible reaction pathway for the synthesis of bisthiolated indole derivatives by the photoinduced reaction of *o*-ethenylaryl isocyanide **1** with organic disulfide **2** in the presence of diphenyl ditelluride, as shown in Scheme 2. In the initiation step, the homolytic dissociation of diphenyl ditelluride upon photoirradiation with the light of wavelength over 400 nm generates PhTe$^\bullet$ species selectively, and the sequential S_H2 reaction of PhTe$^\bullet$ with organic disulfide forms the ArS$^\bullet$ species and the thiotelluride. The addition reaction of ArS$^\bullet$ to the isocyano group gives an imidoyl radical intermediate (**A**),[16] and the subsequent 5-*exo* cyclization forms the radical intermediate (**B**).[17] The generated radical species **B** undergoes S_H2 reaction with $(PhTe)_2$,[18] and the following tautomerization forms indole derivative (**C**). The homolytic cleavage takes place to generate radical species **D** due to the instability of the C−Te bond of **C**.[19] Finally, the abstraction of the ArS group from the thiotelluride forms the corresponding bisthiolated indole **3**.

Keeping this proposed pathway in mind, we examined the photoinduced reaction of isocyanide **1a** with diphenyl disulfide (**2a**) in the presence of diphenyl ditelluride under several reaction conditions (Table 1). Upon photoirradiation with a high-pressure Hg lamp through a glass filter, the reaction of isocyanide **1a** (0.4 M) with 1.5 equiv of $(PhS)_2$ and $(PhTe)_2$ afforded the corresponding

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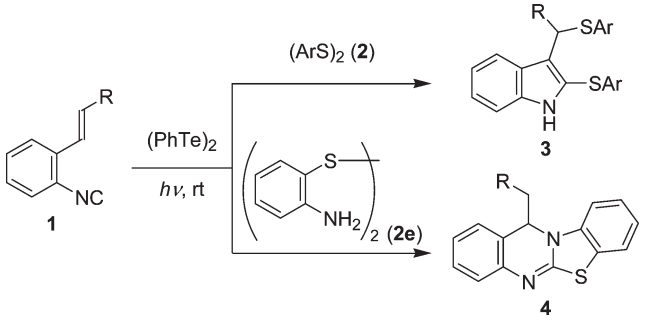
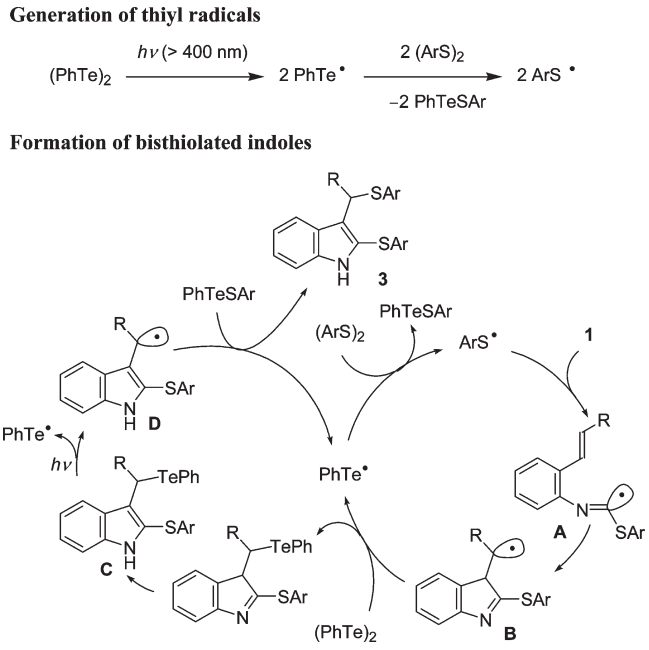
Scheme 1. Preparation of 3 and 4

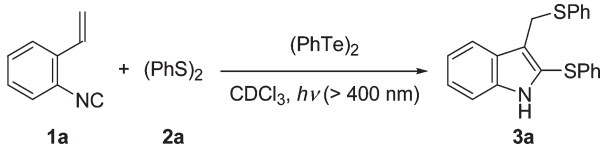


Scheme 2. Possible Reaction Pathways for the Synthesis of Bisthiolated Indoles



bisthiolated indole **3a** in 56% yield (entry 1).[20] When 0.2 M of the isocyanide **1a** was used, the indole **3a** was obtained in 37% yield with the recovery of isocyanide **1a** (33% yield) (entry 2). Under the lower concentration of the substrate (0.05 M), the desired indole derivative was not formed, and instead, 97% yield of isocyanide **1b** was recovered unchanged (entry 3). The result suggests that the addition of the thiyl radical generated in situ to the isocyano group is a key step for this indole synthesis. When the amounts of $(PhS)_2$ and $(PhTe)_2$ were reduced, the yields of the bisthiolated indole **3a** decreased (entries 4 and 5). To clarify the role of diphenyl ditelluride and photoirradiation, we also examined the control reactions, i.e., (i) the photoinduced reaction of methyl 2-(2-isocyanophenyl)acrylate (**1b**) with **2a** in the absence of diphenyl ditelluride and (ii) the reaction of **1b** with **2a** in the presence of diphenyl ditelluride in the dark. In each case, the bisthiolated indole **3b** was not formed. Instead, isocyanide **1b** was recovered unchanged (entries 6 and 7). These results suggest that the photoinduced dissociation of diphenyl ditelluride is important for the photoinduced synthesis of the bisthiolated indoles.

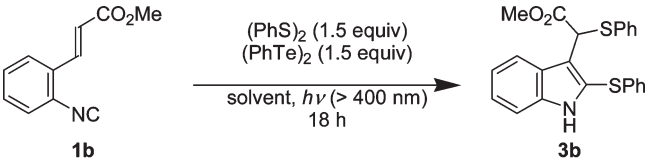
Table 1. Photoinduced Reaction of Isocyanide 1a with $(PhS)_2$ in the Presence of $(PhTe)_2$[a]



entry	$(PhS)_2$ (equiv)	$(PhTe)_2$ (equiv)	concn (M)	time (h)	yield (%)[b] 3a	yield (%)[b] 1a
1	1.5	1.5	0.40	31	56[c]	ND
2	1.5	1.5	0.20	40	37	33
3[d]	1.5	1.5	0.05	24	0[f]	97[g]
4	1.0	1.0	0.20	40	18	33
5	1.0	0.5	0.20	40	28	19
6[d]	1.5	none	0.40	24	0[f]	95[g]
7[d,e]	1.5	1.5	0.40	24	0[f]	95[g]

[a] Reaction condition: isocyanide (**1a**, 0.1 mmol), $(PhS)_2$ (**2a**), $(PhTe)_2$, $CDCl_3$, room temperature, *hν*: irradiation with a high-pressure Hg lamp through a glass filter (>400 nm). [b] Determined by ^1H NMR. [c] Isolated yield. [d] Methyl 2-(2-isocyanophenyl)acrylate (**1b**) was used in place of **1a**. [e] In the dark. [f] Indole **3b** was the desired product. [g] Isocyanide **1b** was recovered unchanged.

Scheme 3. Photoinduced Cyclization of 1b in Several Solvents



solvent =	3b
$CHCl_3$	47%
MeCN	30%
acetone	42%
THF	8%
AcOEt	trace
hexane	trace
benzene	18%
EtOH	8%

We also examined the cyclization reactions in several solvents (Scheme 3). When isocyanide **1b** was treated in $CHCl_3$, MeCN, and acetone, the corresponding indole **3b** was obtained in 47%, 30%, and 42% yields, respectively. The use of THF, AcOEt, hexane, and benzene as a solvent was ineffective for this indole synthesis. In the case of protic solvent such as EtOH, **3b** was obtained in 8% yield. Instead, a fragmentation of **1b** took place.

In addition, the photoinduced reaction of isocyanide **1b** with **2a** was attempted in the presence of $(PhSe)_2$ in place of $(PhTe)_2$. However, a complex mixture including the bisthiolated indole, the selenothiolated indole, and the acyclic thioselenation product was obtained (total 20% yield) (Scheme 4).[9b] Although organic diselenides also have good carbon radical capturing ability as well as organic ditelluride,[18] the generating C−Se bond is more stable than the C−Te bond under photoirradiation condition. Therefore, the selenium intermediates formed in situ survive under the

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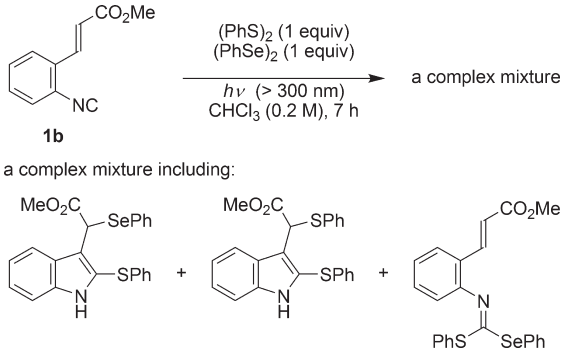
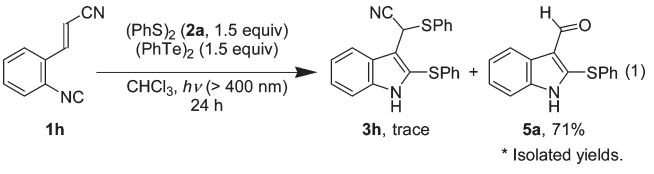
Scheme 4. Photoinduced Reaction of Isocyanide 1b with $(PhS)_2$ and $(PhSe)_2$



photoirradiation condition. This resulted in the formation of a complex mixture. On the other hand, the C−Te bond can reversibly undergo homolytic cleavage under photoirradiation conditions. Hence, the most stable product was obtained selectively. Indeed, organic tellurides-mediated selective polymerization of olefins was achieved in recent years.[21] Thus, $(PhTe)_2$ is not only an effective trapping reagent for carbon radicals but also a useful precursor for carbon radical intermediates under the photoirradiation condition.

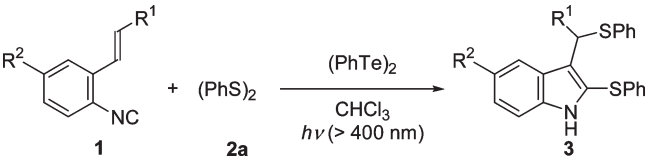
We next examined the scope and limitation of this indole synthesis, and the results are summarized in Table 2. Ester, ketone, and phenyl groups at the terminal position of the vinyl group are tolerant of the photoinduced reaction condition. This reaction afforded the corresponding bisthiolated indoles **3b**, **3c**, and **3d** in moderate to good yields (entries 2−4). Isocyanides, which have substituents on the phenyl group, also underwent the photoinduced cyclization to give indole derivatives. 2-Ethenyl-4-methylphenyl isocyanide (**1e**) gave the bisthiolated indole **3e** in 33% yield (entry 5). On the other hand, the photoinduced reaction of isocyanides **1f** and **1g**, which have fluoro and trifluoromethyl groups, respectively, gave the corresponding bisthiolated indoles **3f** and **3g** in 68% and 48% yields (entries 6 and 7).

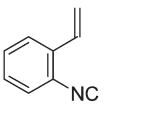
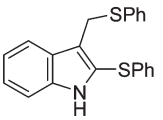
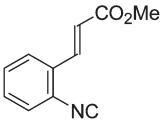
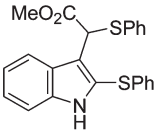
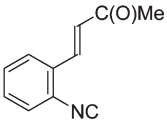
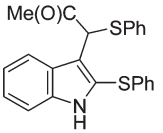
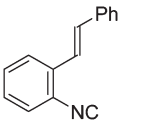
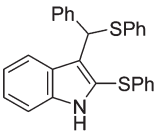
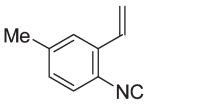
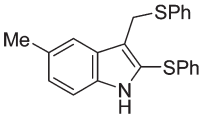
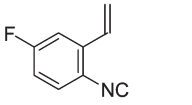
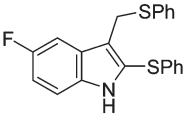
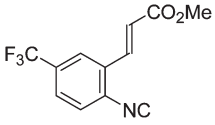
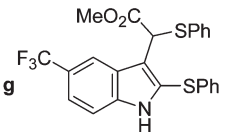
In the case of the isocyanide bearing acrylonitrile group, a trace amount of bisthiolated indole **3h** was formed, and 2-thiylindole-3-carbaldehyde **5a** was obtained as the major product in 71% yield (eq 1). α-Thiylacetonitrile moieties are known to undergo hydrolysis under acidic/basic conditions (or in the presence of hydrolase) to convert to the corresponding aldehyde groups.[22] Therefore, the indole carbaldehyde **5a** was formed via the formation of bisthiolated indole **3h** and the following hydrolysis of **3h**.



We also examined the photoinduced reaction of *o*-ethenylaryl isocyanide **1** with several organic disulfides **2** (Scheme 5). When bis(4-tolyl) disulfide (**2b**) and bis(4-chlorophenyl) disulfide (**2c**) were used for the cyclization, the corresponding bisthiolated indoles **3i** and **3j** were obtained in 67% and 53% yields,

Table 2. Photoinduced Cyclization of Several Isocyanides 1 with $(PhS)_2$ in the Presence of $(PhTe)_2$[a]



entry	isocyanide	1	product		yield (%)[b]
1[c]		1a		3a	56
2		1b		3b	47
3		1c		3c	59
4[d]		1d		3d	63
5[e]		1e		3e	33
6		1f		3f	68
7		1g		3g	48

[a] Reaction conditions: isocyanide (**1**, 0.15 mmol), $(PhS)_2$ (**2a**, 0.225 mmol), $(PhTe)_2$ (0.225 mmol), $CHCl_3$ (0.4 mL), *hν*: irradiation with a high-pressure Hg lamp through a glass filter (>400 nm), room temperature, 24 h. [b] Isolated yield. [c] 31 h. [d] 18 h. [e] 30 h.

respectively. Unfortunately, the reaction with di-*n*-butyl disulfide (**2d**) did not take place. The bond energies of the S−S bond were listed as follows: PhS−SPh = 206 kJ/mol; MeS−SMe = 274 kJ/mol; EtS−SEt = 277 kJ/mol.[23] These values suggest that the homolytic cleavage of dialkyl disulfides is somewhat difficult compared with that of diaryl disulfides.

After the cyclization reactions, a mixture of diphenyl ditelluride, diphenyl disulfide, and diphenyl thiotelluride was recovered concomitantly when the product was purified. When the recovered dichalcogenides were used for the photoinduced cyclization of isocyanide **1b** with $(PhS)_2$, the corresponding indole **3b** was obtained successfully in 51% yield (eq 2).

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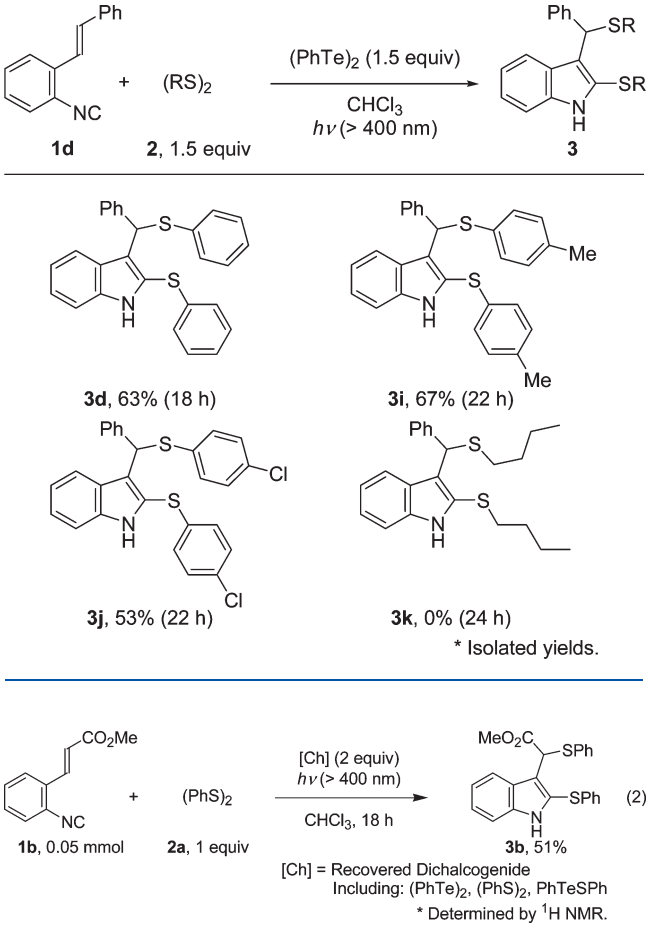
Scheme 5. Photoinduced Cyclization of Isocyanides 1d with Several Organic Disulfides 2

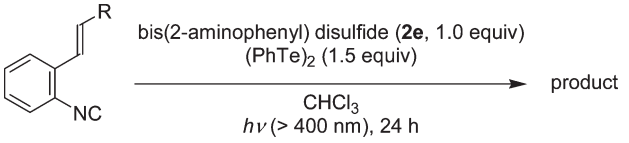


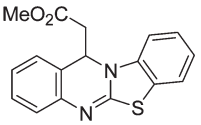
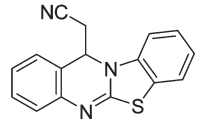
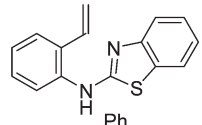
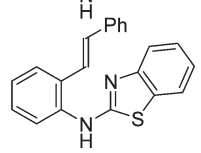
When the photoinduced reaction of isocyanide **1b** with bis(2-aminophenyl) disulfide (**2e**) was examined, the desired bisthiolated indole was not observed. Surprisingly, however, the tetracyclic compound **4a**, which had both dihydroquinazoline and benzothiazole units, was obtained in 71% yield (Table 3, entry 1).[24] Isocyanide **1h** also afforded the similar tetracyclic compound **4b** in 65% yield (entry 2). In contrast, the photoinduced reactions of isocyanides **1a** and **1d** with disulfide **2e** in the presence of $(PhTe)_2$ gave benzothiazole derivatives **6a** and **6b** having unreacted vinyl group in 66% and 58% yields without the generation of tetracyclic derivative (entries 3 and 4).

When the reaction of isocyanide **1b** with disulfide **2e** was examined in the dark, no tetracycle **4a** was obtained. In addition, when the photoirradiated reaction of isocyanide **1b** with disulfide **2e** was conducted in the absence of $(PhTe)_2$, no reaction took place. These results suggest that the formation of the tetracyclic compounds requires the photoirradiation and diphenyl ditelluride.

A plausible reaction pathway for the formation of tetracyclic compounds **4** is shown in Scheme 6. The reaction pathway may involve the following steps: (i) the photoinduced thiotelluration of *o*-ethenylaryl isocyanide **1** gives an intermediate **E**; (ii) the nucleophilic substitution of the phenyltelluro group of **E** by the amino group at the ortho-position leads to the formation of **F**; and (iii) the intramolecular aza-Michael addition reaction provides **4**.

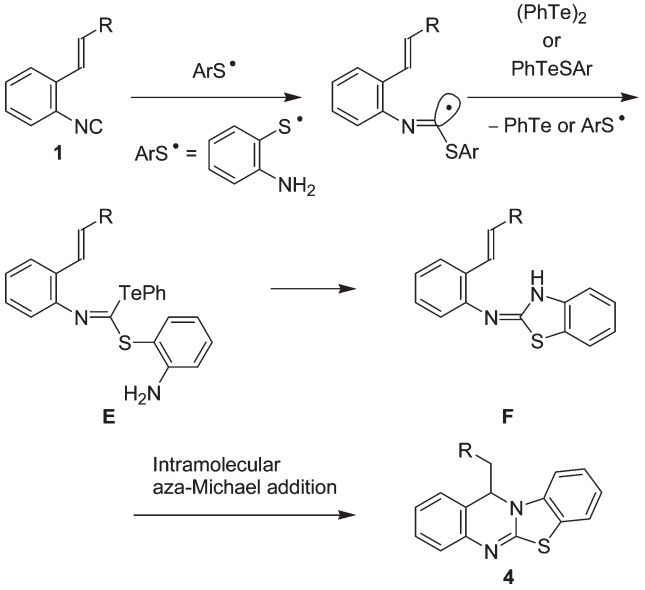
Table 3. Photoinduced Sequential Cyclization with Bis(2-aminophenyl) Disulfide (2e) in the Presence of Diphenyl Ditelluride[a]



entry	R	1	product		yield (%)[b]
1	MeO_2C-	**1b**		**4a**	71
2	NC-	**1h**		**4b**	65
3	H-	**1a**		**6a**	66
4	Ph-	**1d**		**6b**	58

[a] Reaction conditions: isocyanide (**1**, 0.1 mmol), bis(2-aminophenyl) disulfide (**2e**, 0.10 mmol), $(PhTe)_2$ (0.15 mmol), $CHCl_3$ (0.25 mL), *hν*: irradiation with a high-pressure Hg lamp through a glass filter (>400 nm), room temperature, 24 h. [b] Isolated yield.

Scheme 6. A Plausible Reaction Pathway for the Photoinduced Cyclization of Isocyanide 1 with Bis(2-aminophenyl) Disulfide (2e)



We have reported the photoinduced thiotelluration of aryl isocyanides in the presence of $(PhS)_2$ and $(PhTe)_2$.[9b] Thus, the

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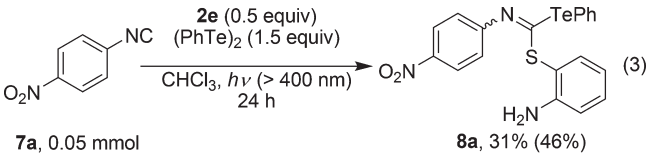
reaction also proceeds via the addition of thiyl radical to the isocyano group at first. Indeed, the photoinduced reaction of 4-nitrophenyl isocyanide (**7a**) with (o-H_2N-C_6H_4S)$_2$ (**2e**) and $(PhTe)_2$ afforded the corresponding thiotellurated imine **8a**, selectively (eq 3).



CONCLUSION

In summary, we have developed the photoinduced intramolecular cyclization of *o*-ethenylaryl isocyanides with organic disulfide in the presence of diphenyl ditelluride. This cyclization reaction affords the bisthiolated indole derivatives under mild reaction condition (at room temperature) upon photoirradiation. In the cases of bis(2-aminophenyl) disulfide, the photoinduced reaction afforded the tetracyclic compounds bearing dihydroquinazoline and benzothiazole units, selectively. Further studies about the syntheses of *N*-heterocycles by the photoinduced intramolecular cyclization of isocyanides having an unsaturated bond are now in progress.

EXPERIMENTAL SECTION

General Comments. ^{1}H NMR spectra were recorded at 300 and 400 MHz with $CDCl_3$ as the solvent and tetramethylsilane (TMS) as the internal standard. ^{13}C NMR spectra were obtained at 75 and 100 MHz with $CDCl_3$ as the solvent. Chemical shifts in ^{13}C NMR were measured relative to $CDCl_3$ by using δ 77.0 ppm. Infrared spectra were recorded with a FT-IR spectrometer. Melting points were determined on a micro melting point apparatus. High-resolution mass spectra were obtained on a mass spectrometer (FAB or EI). Diphenyl ditelluride[25] and 4-nitrophenyl isocyanide (**7a**)[9b,26] were prepared and determined according to the literature. Other reagents such as anilines as the starting materials for *o*-ethenylaryl isocyanides, diphenyl disulfide, bis(4-tolyl) disulfide, bis(4-chlorophenyl) disulfide, di-*n*-butyl disulfide, bis(2-aminophenyl) disulfide, methyl acrylate, methyl vinyl ketone, styrene, acrylonitrile, and tri-*n*-butylvinylstannane were commercially available and used without further purification.

Typical Procedure for the Synthesis of Bisthiolated Indoles via the Photoinduced Intramolecular Cyclization of *o*-Ethenylaryl Isocyanides with Organic Disulfides in the Presence of Diphenyl Ditelluride. A mixture of 2-styrylphenyl isocyanide (**1d**, 31 mg, 0.15 mmol), diphenyl disulfide (**2a**, 49 mg, 0.225 mmol), and diphenyl ditelluride (92 mg, 0.225 mmol) in $CHCl_3$ (0.4 mL) was irradiated with a high-pressure Hg lamp through a glass filter ($h\nu$ > 400 nm) at room temperature for 18 h. After the photoirradiation, $CHCl_3$ was removed in vacuo from the resulting mixture. The crude mixture was purified by PTLC on silica gel (eluent: Hex/AcOEt = 4/1), and 2-phenylsulfanyl-3-(phenyl-phenylsulfanylmethyl)-1*H*-indole (**3d**, 40 mg, 0.095 mmol, 63%) was obtained as a white solid (mp 118−119 °C).

2-Phenylsulfanyl-3-phenylsulfanylmethyl-1*H*-indole (3a): white solid; mp 91−92 °C; ^{1}H NMR (400 MHz, $CDCl_3$, ppm) δ 4.46 (s, 2H), 7.02−7.07 (m, 2H), 7.12−7.30 (m, 9H), 7.33−7.37 (m, 2H), 7.76 (d, J = 7.8 Hz, 1H), 8.03 (s, 1H); ^{13}C NMR (100 MHz, $CDCl_3$, ppm) δ 29.8, 110.9, 118.6, 120.0, 120.1, 123.7, 126.1, 126.3, 127.3, 128.7, 129.1, 129.6, 130.5, 135.1, 136.1, 136.5, 136.9; IR (NaCl, cm^{-1}) 3371, 3229, 3057, 2924, 2853, 1719, 1582, 1477, 1439, 1340, 1290, 1242, 1192, 1069, 1024, 997, 739, 689; HRMS (EI) calcd for $C_{21}H_{17}NS_2$ [M$^+$] 347.0802, found 347.0820.

2-Phenylsulfanyl-3-(methoxycarbonyl-phenylsulfanyl-methyl)-1*H*-indole (3b): slightly yellow oil; ^{1}H NMR (400 MHz, $CDCl_3$, ppm) δ 3.63 (s, 3H), 5.59 (s, 1H), 7.01−7.05 (m, 2H), 7.12−7.28 (m, 9H), 7.31−7.35 (m, 2H), 8.08 (d, J = 7.8 Hz, 1H), 8.11 (s, 1H); ^{13}C NMR (100 MHz, $CDCl_3$, ppm) δ 49.8, 52.7, 110.9, 117.3, 120.4, 121.5, 123.9, 124.8, 125.8, 126.3, 127.7, 127.8, 128.8, 129.0, 133.3, 133.8, 135.6, 137.0, 170.4; IR (NaCl, cm^{-1}) 3360, 3057, 2950, 1732, 1479, 1439, 1151, 743, 690; HRMS (EI) calcd for $C_{23}H_{19}NO_2S_2$ [M]$^+$ 405.0857, found 405.0856.

2-Phenylsulfanyl-3-(acetyl-phenylsulfanylmethyl)-1*H*-indole (3c): colorless oil; ^{1}H NMR (400 MHz, $CDCl_3$, ppm) δ 2.08 (s, 3H), 5.63 (s, 1H), 6.95−7.01 (m, 2H), 7.10−7.31 (m, 11H), 7.85 (d, J = 7.8 Hz, 1H), 8.16 (s, 1H); ^{13}C NMR (100 MHz, $CDCl_3$, ppm) δ 28.2, 58.4, 111.0, 116.8, 120.6, 121.1, 124.0, 125.2, 125.8, 126.5, 127.5, 127.7, 128.7, 129.2, 133.5, 133.9, 135.5, 137.0, 202.7; IR (NaCl, cm^{-1}) 3348, 3055, 3009, 2978, 2916, 1705, 1612, 1582, 1512, 1473, 1443, 1420, 1350, 1296, 1242, 1219, 1150, 1088, 1018, 772, 748, 687; HRMS (FAB) calcd for $C_{23}H_{20}NOS_2$ [M + H]$^+$ 390.0986, found 390.0986.

2-Phenylsulfanyl-3-(phenyl-phenylsulfanylmethyl)-1*H*-indole (3d): white solid; mp 118−119 °C; ^{1}H NMR (300 MHz, $CDCl_3$, ppm) δ 6.15 (s, 1H), 6.89−6.96 (m, 2H), 7.06−7.31 (m, 14H), 7.57 (d, J = 7.7 Hz, 2H), 7.99 (s, 1H), 8.04 (d, J = 8.0 Hz, 1H); ^{13}C NMR (75 MHz, $CDCl_3$, ppm) δ 50.5, 111.0, 120.0, 121.9, 122.3, 123.5, 123.6, 126.1, 126.3, 126.9, 126.9, 127.5, 128.2, 128.3, 128.6, 129.1, 131.9, 135.8, 135.9, 137.2, 140.5; IR (NaCl, cm^{-1}) 3404, 3057, 3014, 1580, 1477, 1439, 1406, 1340, 1242, 1069, 1024, 739, 689; HRMS (FAB) calcd for $C_{27}H_{22}NS_2$ [M + H]$^+$ 424.1194, found 424.1188.

5-Methyl-2-phenysulfanyl-3-phenylsulfanylmethyl-1*H*-indole (3e): colorless oil; ^{1}H NMR (400 MHz, $CDCl_3$, ppm) δ 2.46 (s, 3 H), 4.44 (s, 2H), 7.00−7.24 (m, 10H), 7.33−7.40 (m, 2H), 7.50 (s, 1H), 7.94 (s, 1H); ^{13}C NMR (75 MHz, $CDCl_3$, ppm) δ 21.5, 29.8, 110.7, 118.2, 119.5, 123.6, 125.5, 126.0, 126.3, 127.2, 128.7, 129.1, 129.5, 130.1, 130.5, 135.3, 136.5, 136.7; IR (NaCl, cm^{-1}) 3285, 2974, 2936, 2878, 1720, 1583, 1556, 1514, 1479, 1408, 1371, 1279, 1204, 1177, 1155, 1123, 1026, 995, 741, 691, 662; HRMS (CI) calcd for $C_{22}H_{20}NS_2$ [M + H]$^+$ 362.1037, found 362.1040.

5-Fluoro-2-phenylsulfanyl-3-phenylsulfanylmethyl-1*H*-indole (3f): white solid; mp 106−107 °C; ^{1}H NMR (300 MHz, $CDCl_3$, ppm) δ 4.40 (s, 2H), 6.98 (ddd, J = 2.6, 8.8, 9.2 Hz, 1H), 7.03−7.09 (m, 2H), 7.14−7.25 (m, 7H), 7.32−7.41 (m, 3H), 8.01 (s, 1H); ^{13}C NMR (75 MHz, $CDCl_3$, ppm) δ 29.8, 104.9 (d, J_{C-F} = 23.4 Hz), 111.7 (d, J_{C-F} = 9.9 Hz), 112.3 (d, J_{C-F} = 25.9 Hz), 118.5, 123.3, 125.9, 126.4, 126.6, 127.5, 127.6, 128.8, 129.2, 130.8, 133.4, 136.2, 157.8 (d, J_{C-F} = 234.4 Hz); IR (NaCl, cm^{-1}) 3716, 3713, 3051, 1582, 1479, 1445, 1356, 1296, 1232, 1184, 1070, 1024, 997, 970, 854, 829, 799, 739, 689, 604; HRMS (CI) calcd for $C_{21}H_{17}FNS_2$ [M + H]$^+$ 366.0786, found 366.0779.

5-Trifluoromethyl-2-phenylsulfanyl-(3-methoxycarbonyl-phenylsulfanylmethyl)-1*H*-indole (3g): colorless oil; ^{1}H NMR (400 MHz, $CDCl_3$, ppm) δ 3.66 (s, 3H), 5.57 (s, 1H), 7.01−7.05 (m, 2H), 7.16−7.24 (m, 6H), 7.31−7.36 (m, 3H), 7.47 (dd, J = 1.4, 8.4 Hz, 1H), 8.24 (s, 1H), 8.36 (s, 1H); ^{13}C NMR (100 MHz, $CDCl_3$, ppm) δ 49.5, 52.8, 111.3, 118.0, 119.5 (q, J_{C-F} = 4.4 Hz), 120.5 (q, J_{C-F} = 3.8 Hz), 122.9 (q, J_{C-F} = 33.0 Hz), 125.2, 126.8, 127.4, 128.2, 128.2, 128.9, 129.3, 133.2, 133.6, 134.6, 170.1; IR (NaCl, cm^{-1}) 3333, 3055, 3001, 2955, 2839, 1728, 1628, 1582, 1474, 1435, 1358, 1327, 1281, 1157, 1119, 1049, 1003, 941, 903, 810, 741, 687, 648; HRMS (FAB) calcd for $C_{24}H_{19}F_3NO_2S_2$ [M + H]$^+$ 474.0809, found 474.0796.

2-Tolylsulfanyl-3-(phenyl-tolylsulfanylmethyl)-1*H*-indole (3i): slightly yellow oil; ^{1}H NMR (300 MHz, $CDCl_3$, ppm) δ 2.24

(s, 6H), 6.10 (s, 1H), 6.79−6.86 (m, 2H), 6.87−6.96 (m, 4H), 7.06−7.27 (m, 8H), 7.56 (d, J = 6.8 Hz, 2H), 7.95 (s, 1H), 8.03 (d, J = 7.9 Hz, 1H); ^{13}C NMR (75 MHz, $CDCl_3$, ppm) δ 20.9, 21.1, 50.9, 110.9, 119.8, 121.7, 121.8, 123.3, 124.4, 126.3, 126.8, 128.2, 128.2, 128.2, 129.4, 129.8, 132.1, 132.6, 136.2, 136.9, 137.0, 137.1, 140.8; IR (NaCl, cm^{-1}) 3395, 3263, 3055, 3024, 2970, 2924, 2870, 1697, 1597, 1558, 1489, 1443, 1366, 1342, 1250, 1211, 1180, 1157, 1088, 1018, 964, 802, 748, 694; HRMS (FAB) calcd for $C_{29}H_{26}NS_2$ $[M + H]^+$ 452.1507, found 452.1535.

2-Chlorophenylsulfanyl-3-(phenyl-4-chlorophenylsulfanylmethyl)-1*H*-indole (3j): white solid; mp 110−111 °C; ^{1}H NMR (300 MHz, $CDCl_3$, ppm) δ 6.06 (s, 1H), 6.72−6.81 (m, 2H), 7.02−7.30 (m, 12H), 7.48−7.56 (m, 2H), 8.00−8.09 (m, 2H); ^{13}C NMR (75 MHz, $CDCl_3$, ppm) δ 51.0, 111.1, 120.2, 121.9, 122.1, 122.9, 123.9, 126.1, 127.2, 128.1, 128.4, 128.4, 128.8, 129.2, 132.2, 133.3, 133.7, 134.0, 134.4, 137.2, 140.0; IR (NaCl, cm^{-1}) 3233, 3355, 3024, 2970, 2932, 1697, 1589, 1473, 1446, 1389, 1366, 1342, 1250, 1204, 1180, 1157, 1088, 1011, 818, 748, 694; HRMS (FAB) calcd for $C_{27}H_{20}Cl_2NS_2$ $[M + H]^+$ 492.0414, found 492.0440.

2-Phenylsulfanyl-1*H*-indole-3-carboaldehyde (5a):[27] white solid; mp 182−183 °C; ^{1}H NMR (400 MHz, $CDCl_3$, ppm) δ 7.24−7.30 (m, 3H), 7.33−7.40 (m, 3H), 7.40−7.44 (m, 2H), 8.24−8.28 (m, 1H), 8.63 (s, 1H), 10.25 (s, 1H); ^{13}C NMR (100 MHz, $CDCl_3$, ppm) δ 110.8, 118.5, 121.0, 123.1, 124.4, 125.8, 128.6, 129.9, 131.2, 131.7, 136.2, 140.5, 185.3; MS (EI) m/z 253 (M^+, 100).

Procedure for the Synthesis of Tetracyclic Compounds 4. A mixture of methyl 2-(2-isocyanophenyl)acrylate (**1b**, 19 mg, 0.10 mmol), bis(2-aminophenyl) disulfide (**2e**, 25 mg, 0.10 mmol), and diphenyl ditelluride (61 mg, 0.15 mmol) in $CDCl_3$ (0.25 mL) was irradiated with a high-pressure Hg lamp through a glass filter ($h\nu$ > 400 nm) at room temperature for 24 h. After the photoirradiation, $CDCl_3$ was removed in vacuo from the resulting mixture. The crude product was purified by PTLC on silica gel (eluent: Hex/AcOEt = 9/1), and methyl (12*H*-benzo[4,5]thiazolo[2,3-*b*]quinazolin-12-yl) acetate (**4a**, 22 mg, 0.071 mmol, 71%) was obtained as a slightly yellow oil.

Methyl (12*H*-Benzo[4,5]thiazolo[2,3-*b*]quinazolin-12-yl)-acetate (4a): slightly yellow oil; ^{1}H NMR (400 MHz, $CDCl_3$, ppm) δ 2.80−2.84 (m, 2H), 3.60 (s, 3H), 5.93−6.01 (m, 1H), 7.07 (ddd, J = 1.4, 7.3, 7.3 Hz, 1H), 7.11−7.17 (m, 4H), 7.25−7.35 (m, 2H), 7.43 (d, J = 7.8 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$, ppm) δ 40.4, 52.1, 52.7, 109.5, 120.7, 122.4, 123.3, 123.6, 123.9, 124.6, 125.7, 126.4, 129.4, 137.9, 141.5, 159.6, 170.3; IR (NaCl, cm^{-1}) 3063, 3017, 2947, 2924, 1736, 1582, 1558, 1481, 1458, 1335, 1296, 1273, 1242, 1219, 1180, 1026, 980, 748, 694; HRMS (FAB) calcd for $C_{17}H_{15}N_2O_2S$ $[M + H]^+$ 311.0854, found 311.0870.

(12*H*-Benzo[4,5]thiazolo[2,3-*b*]quinazolin-12-yl)acetonitrile (4b): slightly yellow solid; mp 172−173 °C; ^{1}H NMR (400 MHz, $CDCl_3$, ppm) δ 2.81−2.87 (m, 2H), 5.78−5.83 (m, 1H), 7.08 (d, J = 8.2 Hz, 1H), 7.14−7.23 (m, 3H), 7.30−7.39 (m, 3H), 7.46 (d, J = 7.8 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$, ppm) δ 24.2, 52.4, 109.0, 116.0, 118.1, 122.8, 123.6, 123.8, 124.3, 125.0, 126.3, 126.5, 130.2, 137.2, 141.6, 158.7; IR (NaCl, cm^{-1}) 3071, 3017, 2970, 2932, 2253, 1690, 1589, 1558, 1481, 1458, 1366, 1335, 1304, 1273, 1250, 1204, 1126, 1088, 1018, 980, 935, 918, 872, 849, 756, 687; HRMS (FAB) calcd for $C_{16}H_{12}N_3S$ $[M + H]^+$ 278.0752, found 278.0746.

2-Benzothiazolyl-(2-ethenylphenyl)amine (6a): white solid; mp 172−173 °C; ^{1}H NMR (400 MHz, $CDCl_3$, ppm) δ 5.39 (dd, J = 0.9, 11.0 Hz, 1H), 5.76 (dd, J = 0.9, 17.4 Hz, 1H), 6.96 (dd, J = 11.0, 17.4 Hz, 1H), 7.13 (ddd, J = 0.8, 7.5, 7.6 Hz, 1H), 7.23−7.34 (m, 2H), 7.36 (ddd, J = 1.4, 7.8, 7.8 Hz, 1H), 7.52−7.60 (m, 3H), 7.69 (dd, J = 0.9, 7.8 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$, ppm) δ 117.8, 119.3, 120.8, 120.9, 122.3, 124.0, 126.1, 126.3, 127.1, 129.0, 131.8, 132.2, 136.7, 136.8, 151.5; IR (NaCl, cm^{-1}) 3171, 3125, 3062, 3027, 2929, 2831, 1612, 1558, 1481, 1450, 1312, 1265, 1188, 1157, 1126, 1096, 1018, 988, 918, 849, 748, 725, 694; HRMS (FAB) calcd for $C_{15}H_{13}N_2S$ $[M + H]^+$ 253.0799, found 253.0779.

2-Benzothiazolyl-(2-styrylphenyl)amine (6b): slightly yellow solid; mp 149−150 °C; ^{1}H NMR (400 MHz, $CDCl_3$, ppm) δ 7.05−7.16 (m, 3H), 7.28−7.39 (m, 6H), 7.43−7.48 (m, 2H), 7.54−7.59 (m, 2H), 7.70 (ddd, J = 1.4, 5.5, 7.8 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$, ppm) δ 119.3, 120.8, 122.3, 122.9, 124.1, 126.0, 126.4, 126.7, 127.0, 128.1, 128.6, 128.7, 130.4, 132.1, 132.3, 136.8, 137.0, 144.6, 151.5; IR (NaCl, cm^{-1}) 3371, 3171, 3116, 3063, 3024, 2939, 2862, 1690, 1605, 1535, 1450, 1312, 1265, 1250, 1180, 1126, 1096, 1072, 1018, 964, 918, 872, 849, 756, 694; HRMS (FAB) calcd for $C_{21}H_{17}N_2S$ $[M + H]^+$ 329.1112, found 329.1124.

***N*-(4-Nitrophenyl) 1-(2-Aminophenylsulfanyl-phenyltellanylmethane) Imine (8a):** light yellow oil; ^{1}H NMR (400 MHz, $CDCl_3$, ppm) δ 4.30 (s, 2H), 6.71−6.78 (m, 2H), 6.87 (d, J = 8.7 Hz, 2H), 7.23−7.29 (m, 3H), 7.35 (d, J = 7.8 Hz, 1H), 7.39 (dd, J = 6.9, 7.3 Hz, 1H), 7.87 (d, J = 7.3 Hz, 2H), 8.11 (d, J = 8.7 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$, ppm) δ 109.4, 113.3, 115.7, 118.7, 120.0, 124.9, 129.4, 129.4, 132.5, 136.5, 137.3, 141.5, 144.3, 152.6, 156.7; IR (NaCl, cm^{-1}) 3479, 3371, 3217, 3063, 2924, 1589, 1528, 1504, 1443, 1327, 1312, 1258, 1219, 1173, 1111, 856, 772, 687; HRMS (FAB) calcd for $C_{19}H_{16}N_3O_2STe$ $[M + H]^+$ 480.0026, found 480.0001.

Preparation of *o*-Ethenylaryl Isocyanides 1, e.g., 1a. To a solution of 2-bromoaniline (11 mL, 101 mmol) in toluene (50 mL) was added formic acid (ca. 80% aq) (10 mL), and the mixture was stirred at 110 °C for 4 h. Volatiles were removed from the resulting mixture. The crude solid was recrystallized from toluene to give 2-bromoformanilide (15.3 g, 76.4 mmol, 76%).

To a 50-mL two-necked flask were added 2-bromoformanilide (1.0 g, 5.0 mmol), tributylvinylstannane (1.5 mL, 5.16 mmol), and tetrakis-(triphenylphosphine)palladium (120 mg, 0.10 mmol) in toluene (20 mL) under nitrogen atmosphere, and then the mixture was stirred at 110 °C. After heating for 16 h, volatiles were removed from the resulting mixture under the reduced pressure, and the crude mixture was purified by column chromatography on silica gel (eluent: hexane/AcOEt = 1/1). Then, 2-ethenylformanilide (562 mg, 3.8 mmol, 76%) was obtained.

To a mixture of methyl 2-ethenylformanilide (147 mg, 1 mmol) and diisopropylamine (0.20 mL, 1.4 mmol) in chloroform (3.0 mL) was added phosphoryl chloride (0.13 mL, 1.4 mmol) at 0 °C under nitrogen atmosphere. The mixture was warmed to room temperature, and then stirred for 2 h. Saturated aqueous sodium carbonate was poured into the resulting mixture. The following extraction of the product with diethyl ether, concentration under the reduced pressure, and the purification of the resulting crude product by column chromatography on silica gel (eluent: hexane/AcOEt = 2/1) gave 2-ethenylphenyl isocyanide (**1a**, 95.6 mg, 0.74 mmol, 74%) as a colorless oil.

2-Ethenylphenyl isocyanide (1a):[28] colorless oil; ^{1}H NMR (400 MHz, $CDCl_3$, ppm) δ 5.50 (d, J = 11.4 Hz, 1H), 5.87 (d, J = 17.4 Hz, 1H), 7.04 (dd, J = 11.4, 17.4 Hz, 1H), 7.31−7.41 (m, 4H); ^{13}C NMR (100 MHz, $CDCl_3$, ppm) δ 119.8, 125.6, 125.7, 127.0, 128.4, 129.3, 130.9, 133.8, 168.3; MS (EI) m/z 129 (M^+, 100).

2-Ethenyl-4-methylphenyl Isocyanide (1e): colorless oil; ^{1}H NMR (300 MHz, $CDCl_3$, ppm) δ 2.37 (s, 3H), 5.46 (dd, J = 0.8, 11.2 Hz, 1H), 5.84 (dd, J = 0.8, 17.4 Hz, 1H), 6.94−7.09 (m, 2H), 7.23 (d, J = 8.0 Hz, 1H), 7.39 (s, 1H); ^{13}C NMR (75 MHz, $CDCl_3$, ppm) δ 21.3, 117.7, 126.0, 126.8, 129.1, 131.0, 133.5, 139.5, 166.1; IR (NaCl, cm^{-1}) 3077, 3031, 2953, 2923, 2855, 2118, 1684, 1558, 1508, 1489, 1458, 1338, 1191, 1163, 1103, 1074, 1038, 989, 918, 860, 816, 754, 719; HRMS (FAB) calcd for $C_{10}H_{10}N$ $[M + H]^+$ 144.0813, found 144.0824.

2-Ethenyl-4-fluorophenyl isocyanide (**1f**) was too unstable to isolate and the formation of **1f** was determined by ^{1}H NMR with 1,3,5-trioxane as an internal standard.

Preparation of *o*-Ethenylaryl Isocyanides 1, e.g., 1b. To a 50-mL two-necked flask were added 2-bromoformanilide (320 mg,

1.6 mmol), palladium(II) acetate (5.6 mg, 0.022 mmol), tris(*o*-tolyl)-phosphine (11 mg, 0.035 mmol), methyl acrylate (0.16 mL, 1.8 mmol), and triethylamine (0.28 mL, 2.0 mmol) in acetonitrile (3 mL) under nitrogen atmosphere, and then the reaction was conducted at 100 °C. After heating for 18 h, volatiles were removed from the reaction system under the reduced pressure, and the crude mixture was purified by column chromatography on silica gel (eluent: hexane/AcOEt = 1/1). Then, methyl 3-(2-formamidophenyl)acrylate (230 mg, 1.12 mmol, 72%) was obtained.

To a mixture of methyl 3-(2-formamidophenyl)acrylate (205 mg, 1.0 mmol) and diisopropylamine (0.21 mL, 1.5 mmol) in chloroform (3.0 mL) was added phosphoryl chloride (0.14 mL, 1.5 mmol) at 0 °C under nitrogen atmosphere. The mixture was warmed to room temperature, and then stirred for 2 h. Saturated aqueous sodium carbonate was poured into the resulting mixture. The following extraction of the product with diethyl ether, concentration under the reduced pressure, and the purification of the obtained crude product by column chromatography on silica gel (eluent: hexane/AcOEt = 2/1) gave methyl 3-(2-isocyanophenyl)acrylate (**1b**, 107 mg, 0.57 mmol, 57%) as a white solid (mp 56 °C).[11d]

Methyl 3-(2-Isocyanophenyl)acrylate (1b):[11d] white solid; mp 56 °C; ^{1}H NMR (400 MHz, $CDCl_3$, ppm) δ 3.84 (s, 3H), 6.54 (d, J = 16.5 Hz, 1H), 7.42−7.47 (m, 3H), 7.65−7.69 (m, 1H), 7.98 (d, J = 16.5 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$, ppm) δ 51.9, 121.9, 125.9, 126.8, 127.6, 129.6, 130.6, 130.7, 137.8, 166.3, 168.6; MS (EI) m/z 187 (M^+, 100).

4-(2-Isocyanophenyl)-3-buten-2-one (1c):[11d] pale yellow oil; ^{1}H NMR (400 MHz, $CDCl_3$, ppm) δ 2.45 (s, 3H), 6.76 (d, J = 16.5 Hz, 1H), 7.43−7.48 (m, 3H), 7.68−7.72 (m, 1H), 7.81 (d, J = 16.5 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$, ppm) δ 27.2, 126.2, 126.8, 127.6, 129.7, 130.8, 130.8, 130.9, 136.4, 168.8, 198.0; MS (EI) m/z 129 (M^+, 100).

Methyl 3-(2-Isocyano-5-trifluoromethylphenyl)acrylate (1g): white solid; mp 85−86 °C; ^{1}H NMR (400 MHz, $CDCl_3$, ppm) δ 3.86 (s, 3H), 6.62 (d, J = 16.0 Hz, 1H), 7.58 (d, J = 8.2 Hz, 1H), 7.68 (d, J = 8.2 Hz, 1H), 7.92 (s, 1H), 7.96 (d, J = 16.0 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$, ppm) δ 52.2, 122.8 (q, J_{CF} = 270.5 Hz), 123.8, 124.1 (q, J_{CF} = 3.8 Hz), 127.3 (q, J_{CF} = 3.8 Hz), 128.3, 131.6, 131.7 (q, J_{CF} = 34.3 Hz), 136.3, 165.7, 171.6; IR (NaCl, cm^{-1}) 3078, 3032, 2955, 2847, 2122, 1713, 1489, 1435, 1335, 1288, 1180, 1165, 1103, 1072, 1034, 988, 926, 864, 841, 772, 702; HRMS (FAB) calcd for $C_{12}H_9F_3NO_2$ [M + H]$^+$ 256.0585, found 256.0873.

3-(2-Isocyanophenyl)acrylonitrile (1h):[11d] white solid; mp 81−82 °C; ^{1}H NMR (400 MHz, $CDCl_3$, ppm) δ 6.06 (d, J = 16.5 Hz, 1H), 7.45−7.53 (m, 3H), 7.60−7.65 (m, 1H), 7.73 (d, J = 16.5 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$, ppm) δ 100.6, 117.1, 125.5, 126.1, 127.8, 129.5, 129.8, 131.7, 143.9, 169.6; MS (EI) m/z 129 (M^+, 100).

2-(2-Isocyanophenyl)styrene (**1d**) was too unstable to isolate and the formation of **1d** was determined by ^{1}H NMR with 1,3,5-trioxane as an internal standard.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information. ^{1}H and ^{13}C NMR spectra of **3**, **4**, **5**, **6**, and **8**, and CIF fires of **4b** and **6a**. This material is available free of charge via the Internet at http://pubs.acs.org.

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