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PAPER

Photochemical intramolecular cyclization of *o*-alkynylaryl isocyanides with organic dichalcogenides leading to 2,4-bischalcogenated quinolines†

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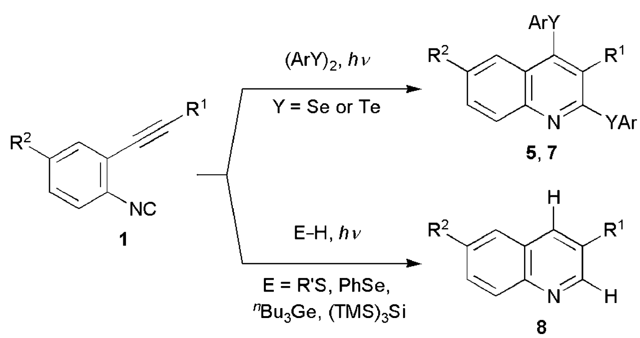
When a mixture of *o*-alkynylaryl isocyanides and organic dichalcogenides such as diselenides or ditellurides was irradiated with light of wavelength over 300 or 400 nm, the intramolecular cyclization of the isocyanides took place to afford the corresponding 2,4-bischalcogenated quinolines selectively. The photochemical cyclization of 2-(phenylethynyl)phenyl isocyanide could also proceed in the presence of hydrogen transfer reagents such as tris(trimethylsilyl)silane, tributylgermyl hydride, alkanethiols, and benzeneselenol, providing the corresponding 3-phenylquinoline as the result of 2,4-dihydrogenation.

Introduction

N-Heterocyclic compounds such as quinoline derivatives are included in numerous natural products and bioactive compounds, and therefore, the development of new methods for the preparation of *N*-heterocycles as a key structure is of great importance in pharmaceutical and medicinal chemistry as well as organic synthesis.[1,2] Intramolecular cyclization involving radical species as a key intermediate is one of the efficient methods for the synthesis of many heterocyclic motifs.[3] Since the first example of the intramolecular radical cyclization reaction of isocyanides bearing an unsaturated bond was reported in 1994, the synthetic applications of the isocyanides to form *N*-heterocycles have been developed not only by radical methods,[4] but also by transition metal-catalyzed methods[5] and nucleophilic cyclization methods[6] in last two decades. In particular, the intramolecular radical cyclization of isocyanides having an unsaturated bond was employed for the preparation of indole or pyrrole derivatives mainly, and examples of quinoline synthesis under radical conditions are still limited.[7]

Heterocycles containing chalcogen atoms have gained roles in the fields of pharmacology, materials science, and organic synthesis, based on the recent clarification of the characteristic features of chalcogen compounds.[8] For example, it has been revealed that organochalcogen compounds show antioxidant, antitumor, antimicrobial, and antiviral properties.[9] In a recent study, a series of radical addition reactions of organic chalcogenides such as disulfides, diselenides, and ditellurides to unsaturated bonds such as acetylenes,[10] allenes,[11] conjugated dienes,[12] alkenes,[13] and isocyanides[14] have been advanced by our and other research groups. Because a lot of these radical addition reactions proceed under photoirradiation conditions, the development of novel photochemical synthetic procedures for chalcogenated *N*-heterocycles can be anticipated.

Herein, we wish to report a novel photochemical intramolecular cyclization of *o*-alkynylaryl isocyanides in the presence of organic dichalcogenides such as diselenides and ditellurides, leading to 2,4-bischalcogenated quinolines selectively (Scheme 1). In addition, the photochemical reaction in the presence of hydrogen sources, *e.g.*, tris(trimethylsilyl)silane, tributylgermyl hydride, alkanethiols, and benzeneselenol, can access the 2,4-dihydrogenated quinolines smoothly.



Scheme 1 Photochemical cyclization of isocyanide **1**.

Results and discussion

We first examined the photochemical reaction of 2-(phenylethynyl)phenyl isocyanide (**1a**) with diphenyl dichalcogenides, such as diphenyl disulfide (**2a**), diphenyl diselenide (**4a**), and diphenyl ditelluride (**6a**) (Table 1). When isocyanide **1a** was treated with diphenyl disulfide (**2a**) with photoirradiation, the desired cyclic product **3a** was not obtained at all (the starting materials were recovered unchanged) (entry 1). In contrast, the

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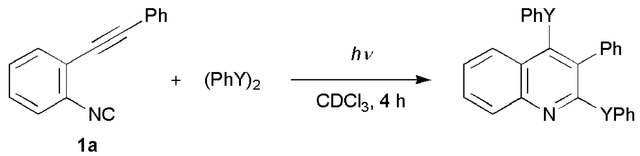
† This paper is dedicated to the memory of the passing Professor Athel Beckwith, prominent free radical chemist.‡

Table 1 Photochemical reaction of isocyanide **1a** with organic dichalcogenides[a]



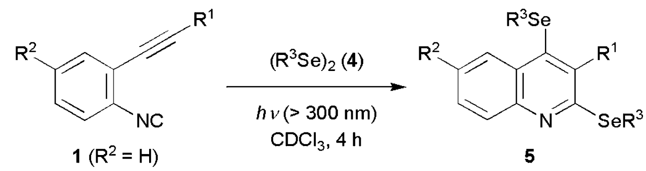
Entry	Y	Product	Yield (%)[b]
1	S (**2a**, 2 equiv.)	**3a**	0
2	Se (**4a**, 1 equiv.)	**5a**	46
3	Se (**4a**, 2 equiv.)	**5a**	65
4	Se (**4a**, 3 equiv.)	**5a**	72
5[c]	Te (**6a**, 1 equiv.)	**7a**	34
6[c]	Te (**6a**, 2 equiv.)	**7a**	48
7[c]	Te (**6a**, 5 equiv.)	**7a**	68
8[c,d]	Te (**6a**, 2 equiv.)	**7a**	(65)

[a] Reaction conditions: isocyanide (**1a**, 0.10 mmol), diphenyl dichalcogenides, $CDCl_3$ (0.5 mL), room temperature, 4 h, *hυ* (>300 nm: irradiation with a high pressure Hg lamp through Pyrex). [b] Isolated yield. [c] *hυ* (>400 nm: irradiation with a high pressure Hg lamp through a glass filter). [d] The reaction time was 14 h. The value in parenthesis was determined by ^{1}H NMR.

photochemical reaction of **1a** with 1 equivalent of diphenyl diselenide (**4a**) afforded the 2,4-bisselenated quinoline **5a** in 46% yield (entry 2). In the reaction mixture, the oligomer of **1a** and a small amount of unreacted **1a** were obtained. The yield of **5a** successfully increased with the amount of $(PhSe)_2$ (entries 3 and 4).[15] Furthermore, diphenyl ditelluride (**6a**) could also be employed for the photochemical cyclization, leading to the corresponding 2,4-bistellurated quinoline **7a** in 34% yield (entry 5).[16] In the case of ditelluride **6a**, increasing the amount of **6a** also provided **7a** in good yields, because the excess amounts of ditelluride might contribute to the efficiency in the abstraction of the telluro group by the carbon radical intermediate (entries 6 and 7). Prolonging the reaction time also increased the yield of **7a** (entry 8). When the reactions of **1a** with **4a** or **6a** were performed in the dark, no cyclization reaction took place. These results indicate that the intramolecular cyclization reactions of *o*-alkynylaryl isocyanides with diselenides and ditellurides require the photoirradiation.

We next examined the scope and limitations of this photochemical cyclization with organic dichalcogenides using several isocyanides **1**. The results of the reaction of **1** with organic diselenides **4** are summarized in Table 2. Isocyanides bearing methyl, methoxy, chloro, and fluoro substituents on the arylethynyl groups underwent the photochemical intramolecular cyclization successfully, affording the corresponding 2,4-bisselenated quinolines **5b**, **5c**, **5d**, and **5e**, respectively, in good yields (entries 2–5). Isocyanide **1f** having 1-hexynyl group could also undergo the photochemical cyclization to give **5f** (entry 6). A 1-cyclohexenyl group being conjugated with ethynyl group was tolerant of these conditions to produce **5g** in high yield (entry 7). However, isocyanide **1h** containing a TMS group gave a low yield of the cyclization product **5h**, probably because of the bulkiness of the TMS group (entry 8). Similar conditions could be employed with several diaryl diselenides **4b**, **4c**, **4d**, and **4e**, leading to the corresponding quinolines **5i**, **5j**, **5k**, and **5l** in good yields (entries 9–12). When dibenzyl diselenide (**4f**) was used for this photochemical reaction, the corresponding quinoline **5m** was obtained in lower yield

Table 2 Photochemical reaction of isocyanides **1** with organic diselenides **4**[a]



Entry	1	R^1	4	R^3	Product	Yield (%)[b]
1	**1a**	C_6H_5	**4a**	C_6H_5	**5a**	65
2	**1b**	4-Me-C_6H_4	**4a**		**5b**	72
3	**1c**	4-MeO-C_6H_4	**4a**		**5c**	70
4	**1d**	4-Cl-C_6H_4	**4a**		**5d**	69
5	**1e**	4-F-C_6H_4	**4a**		**5e**	62
6	**1f**	^{n}Bu	**4a**		**5f**	71
7	**1g**	1-cyclohexenyl	**4a**		**5g**	82
8	**1h**	TMS	**4a**		**5h**	9
9	**1a**		**4b**	4-Me-C_6H_4	**5i**	72
10	**1a**		**4c**	4-MeO-C_6H_4	**5j**	77
11	**1a**		**4d**	4-Cl-C_6H_4	**5k**	65
12	**1a**		**4e**	4-F-C_6H_4	**5l**	69
13	**1a**		**4f**	Bn	**5m**	<10

[a] Reaction conditions: isocyanide (**1**, 0.10 mmol), organic diselenide (**4**, 0.20 mmol), $CDCl_3$ (0.5 mL), room temperature, 4 h, *hυ* (>300 nm: irradiation with a high pressure Hg lamp through Pyrex). [b] Isolated yield.

(entry 13). This is most probably due to the lower carbon radical capturing ability of aliphatic diselenides compared with aromatic ones.

Conclusive determination of the structure of the photochemical cyclization product was unambiguously ascertained through X-ray crystal analysis (Fig. 1). Thus, the formation of the quinoline structure in the photochemical cyclization of isocyanides **1** with organic dichalcogenides was clearly confirmed.

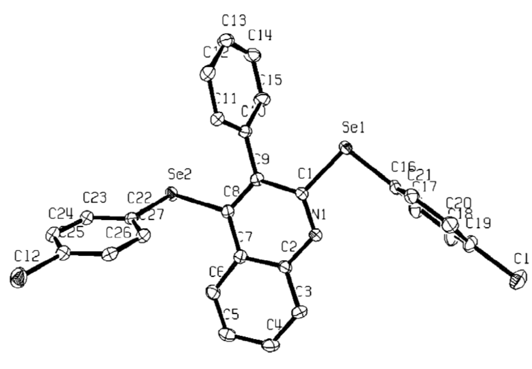
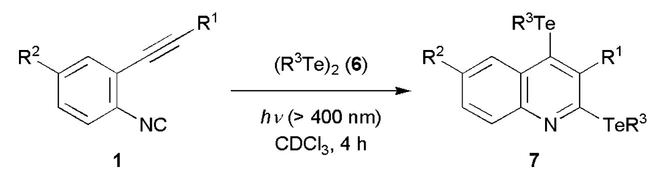


Fig. 1 ORTEP diagram of **5k**. H atoms were omitted.

The photochemical reaction of isocyanides **1** with organic ditelluride **6** was also examined (Table 3).[17] When isocyanides having methyl, methoxy, and chloro substituents at the *p*-position were treated with $(PhTe)_2$ with photoirradiation, the corresponding quinolines **7b**, **7c**, and **7d** were obtained in moderate yields (entries 2–4).[18] The photochemical reactions of **1f** and **1g** containing *n*-butyl and 1-cyclohexenyl groups took place smoothly, forming the corresponding 2,4-bistellurated quinolines **7f** and **7g** in good yields, respectively (entries 5 and 6). Unfortunately, isocyanides **1i** and **1j** having powerful electron-withdrawing groups produced **7i**

Table 3 Photochemical reaction of isocyanides **1** with organic ditellurides **6**[a]



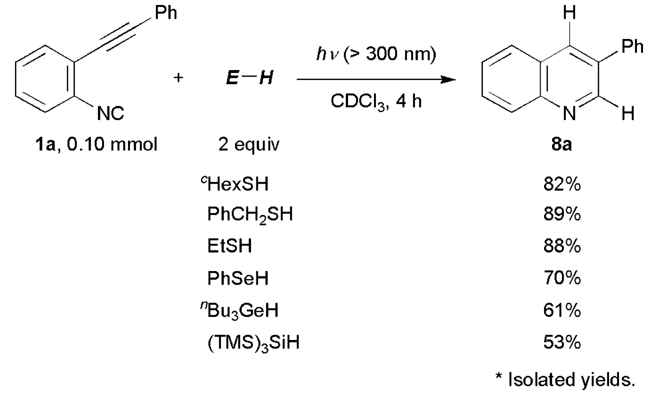
Entry	1	R^1	R^2	6	R^3	7	Yield (%)[b]
1	**1a**	C_6H_5	H	**6a**	C_6H_5	**7a**	48
2	**1b**	4-Me-C_6H_4	H	**6a**		**7b**	40
3	**1c**	4-MeO-C_6H_4	H	**6a**		**7c**	49
4	**1d**	4-Cl-C_6H_4	H	**6a**		**7d**	50
5	**1f**	^{n}Bu	H	**6a**		**7f**	82
6	**1g**	1-cyclohexenyl	H	**6a**		**7g**	68
7	**1i**	4-O_2N-C_6H_4	H	**6a**		**7i**	32
8	**1j**	4-NC-C_6H_4	H	**6a**		**7j**	26
9	**1k**	Bn	H	**6a**		**7k**	42
10	**1l**	C_6H_5	Me	**6a**		**7l**	63
11	**1m**	C_6H_5	F	**6a**		**7m**	61
12	**1a**		H	**6b**	4-MeO-C_6H_4	**7n**	40
13	**1a**		H	**6c**	4-F-C_6H_4	**7o**	66
14	**1a**		H	**6d**	^{n}Bu	**7p**	(23)

[a] Reaction conditions: isocyanide (**1**, 0.10 mmol), organic ditelluride (**6**, 0.20 mmol), $CDCl_3$ (0.5 mL), room temperature, 4 h, $h\nu$ (>400 nm: irradiation with a high pressure Hg lamp through a glass filter). [b] Isolated yield. Value in parenthesis was determined by ^{1}H NMR.

and **7j** in low yields, due to the competing oligomerization of the isocyanides (entries 7 and 8). In the case of **1k** having a benzyl unit, the corresponding quinoline **7k** was obtained in 42% yield (entry 9). At the same time, the formation of an oligomer of **1k** was observed. *p*-Substituted aromatic isocyanides **1l** and **1m** could also afford the corresponding 2,4-bistellurated quinolines **7l** and **7m** in good yields (entries 10 and 11). Similar conditions could be employed with several organic ditellurides **6b** and **6c**, forming **7n** and **7o** (entries 12 and 13). When isocyanide **1a** was treated with dibutyl ditelluride (**6d**) with photoirradiation, the formation of **7p** was observed; however, **7p** could not be isolated because of its instability (entry 14).

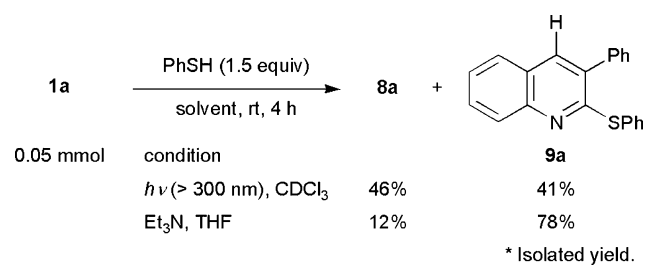
In this photochemical intramolecular cyclization, some reaction pathways are considered. A possible pathway involves the following: (i) the formation of chalcogen-centered radicals upon photoirradiation; (ii) the addition of the generated radicals to isocyano or alkynyl groups; (iii) the intramolecular cyclization and the subsequent trapping with dichalcogenides to give the corresponding quinolines. However, radical cyclization prefers the 5-*exo* cyclization to give indoles not quinolines.[19] Alternatively, a related theoretical study reported that the aza-Bergman cyclization of the (*Z*)-enyne isocyanide system is possible.[20] Therefore, another possible pathway may include the photochemical aza-Bergman cyclization of **1** to form the corresponding biradical species (see, **A** in Scheme 4).

To get insight into the reaction pathway for this cyclization, we examined the photochemical reaction of isocyanide **1a** in the presence of efficient hydrogen transfer reagents (Scheme 2). Upon photoirradiation of isocyanide **1a** in the presence of cyclohexanethiol, intramolecular cyclization *via* hydrogen abstraction took place, affording 3-phenylquinoline (**8a**) in 82% yield.[21] Similarly, photochemical reaction in the presence of phenylmethanethiol,



Scheme 2 Photochemical reactions of isocyanide **1a**. ^{c}HexSH = cyclohexanethiol.

ethanethiol and benzeneselenol gave **8a** with excellent selectivity.[22] The photochemical reaction of isocyanide **1a** with benzenethiol was also carried out; however, the reaction gave 3-phenylquinoline (**8a**) and 2-phenylsulfanyl-3-phenylquinoline (**9a**) in 46% and 41% yields, respectively (Scheme 3). The selective syntheses of 2-substituted quinolines by the reaction of *o*-alkynylaryl isocyanides with nucleophiles were reported in ref. 6a, 6c, 6e and 6f. Thus, the generation of 2-sulfanylquinoline may include the nucleophilic addition of the thiolate anion to the isocyano groups due to the higher acidity of arenethiols compared with alkanethiols. Then, the reaction of **1a** with benzenethiol in the presence of triethylamine in the dark provided the corresponding 2-sulfanylquinoline **9a** in 78% yield (for 2-sulfanylquinoline synthesis by this method, see the ESI‡).[23]

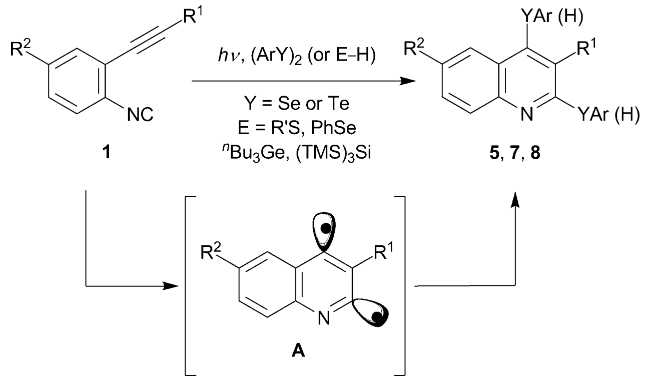


Scheme 3 The reaction of isocyanide **1a** with benzenethiol.

In addition, tributylgermyl hydride and tris(trimethylsilyl)silane could also provide **8a** in 61% and 53% yields, respectively.[24,25]

If the photochemical cyclization using hydrogen transfer reagents involves the radical cyclization process *via* the addition of heteroatom-centered radicals to an unsaturated bond, 2- or 4-heteroatom substituted quinolines should be formed. In addition, the UV-visible spectrum of **1** indicates that its absorption reaches 500 nm (see the ESI‡). Therefore, these results strongly suggest that a photochemical aza-Bergman cyclization takes place to form the corresponding biradical species, which abstract hydrogen from E-H species.

A plausible reaction pathway for the photochemical intramolecular cyclization of isocyanides **1** in the presence of organic dichalcogenides or hydrogen sources is shown in Scheme 4. Upon photoirradiation with light of wavelength over 300 nm (or 400 nm), aza-Bergman cyclization of **1** proceeds, forming 2,4-biradical



Scheme 4 A plausible reaction pathway for the photochemical cyclization of isocyanide **1**.

species **A**. The following abstraction of organic chalcogen groups[26] or hydrogen produces the corresponding quinolines **5**, **7**, and **8**.

Conclusions

In summary, we have described a novel photochemical cyclization of *o*-alkynylaryl isocyanides **1** in the presence of organic dichalcogenides. The reaction can access the corresponding 2,4-dichalcogenated quinolines selectively. This photochemical cyclization can be applied to the synthesis of 3-substituted quinolines by the reaction of isocyanides **1** with hydrogen transfer reagents such as hydrosilane, germyl hydride, thiols, and selenol. Further studies on the synthetic application of this system are now in progress.

Experiment

General procedure for the photochemical intramolecular cyclization of *o*-alkynylaryl isocyanide with organic diselenide

In a NMR tube (ϕ = 5 mm, length = 180 mm) were placed 2-(phenylethynyl)phenyl isocyanide (**1a**, 20 mg, 0.10 mmol) and diphenyl diselenide (**4a**, 62 mg, 0.20 mmol) in $CDCl_3$ (0.5 mL) under ambient atmosphere, and the mixture was irradiated with a high pressure Hg lamp through Pyrex ($h\nu > 300$ nm) for 4 h. After the photoirradiation, the resulting mixture was concentrated *in vacuo*, and the purification by preparative TLC (PTLC) on silica gel (hexane (Hex) : AcOEt = 9 : 1) and recycle GPC ($CHCl_3$) gave 3-phenyl-2,4-bis(phenylselanyl)quinoline (**5a**, 33.4 mg, 0.065 mmol, 65%) as a slightly yellow solid (mp 129–130 °C).

3-Phenyl-2,4-bis(phenylselanyl)quinoline (5a). Slightly yellow solid; mp 129–130 °C (crystalized from acetone); ^{1}H NMR (400 MHz, $CDCl_3$, ppm) δ 6.99–7.12 (m, 5H), 7.22–7.27 (m, 2H), 7.34–7.48 (m, 7H), 7.55 (ddd, J = 1.4, 6.8, 8.4 Hz, 1H), 7.64–7.69 (m, 2H), 7.71 (dd, J = 1.4, 8.4 Hz, 1H), 8.30 (dd, J = 1.4, 8.4 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$, ppm) δ 126.5, 126.5, 128.0, 128.3, 128.3, 128.6, 128.8, 129.0, 129.1, 129.1, 129.5, 129.9, 130.7, 132.2, 136.3, 138.7, 138.8, 141.1, 141.1, 148.3, 158.2; IR (NaCl, cm^{-1}) 3055, 3030, 1576, 1541, 1506, 1489, 1474, 1456, 1437, 1372, 1339, 1313, 1286, 1136, 1092, 1072, 1020, 881, 762, 737, 689; HRMS (FAB) calcd for $C_{27}H_{20}NSe_2$ [M+H]$^+$ 517.9926, found 517.9932.

3-(4-Methylphenyl)-2,4-bis(phenylselanyl)quinoline (5b). Quinoline **5b** (38.1 mg, 0.072 mmol, 72%) was obtained from **1b** (0.10 mmol) according to the general procedure. The crude mixture was purified by PTLC on silica gel (Hex : AcOEt = 9 : 1) and recycle GPC ($CHCl_3$). Pale yellow oil; ^{1}H NMR (300 MHz, $CDCl_3$, ppm) δ 2.44 (s, 3H), 7.00–7.12 (m, 5H), 7.16 (d, J = 8.3 Hz, 2H), 7.24 (d, J = 8.3 Hz, 2H), 7.33–7.42 (m, 4H), 7.54 (m, 1H), 7.64–7.74 (m, 3H), 8.27 (d, J = 8.4 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$, ppm) δ 21.6, 126.4, 126.4, 127.9, 128.3, 128.8, 129.0, 129.0, 129.1, 129.1, 129.4, 129.6, 130.6, 132.3, 135.9, 136.3, 138.5, 138.5, 141.0, 141.3, 148.3, 158.5; IR (NaCl, cm^{-1}) 3057, 3030, 2999, 2833, 1576, 1545, 1508, 1474, 1456, 1437, 1373, 1339, 1313, 1286, 1136, 1090, 1072, 1020, 814, 760, 735, 723, 689; HRMS (FAB) calcd for $C_{28}H_{22}NSe_2$ [M+H]$^+$ 532.0083, found 532.0088.

3-(4-Methoxyphenyl)-2,4-bis(phenylselanyl)quinoline (5c). Quinoline **5c** (38.1 mg, 0.070 mmol, 70%) was obtained from **1c** (0.10 mmol) according to the general procedure. The crude mixture was purified by PTLC on silica gel (Hex : AcOEt = 9 : 1) and recycle GPC ($CHCl_3$). Pale yellow oil; ^{1}H NMR (400 MHz, $CDCl_3$, ppm) δ 3.87 (s, 3H), 6.93 (d, J = 8.7 Hz, 2H), 7.00–7.10 (m, 5H), 7.17 (d, J = 8.7 Hz, 2H), 7.34–7.40 (m, 4H), 7.53 (ddd, J = 1.4, 6.8, 8.7 Hz, 1H), 7.65–7.72 (m, 3H), 8.27 (dd, J = 0.9, 8.7 Hz, 1H); ^{13}C NMR (75 MHz, $CDCl_3$, ppm) δ 55.2, 113.7, 126.4, 126.5, 128.1, 128.3, 128.8, 129.0, 129.0, 129.1, 129.2, 129.4, 130.7, 131.1, 136.3, 139.0, 144.5, 144.7, 147.0, 148.3, 157.1, 159.8; IR (NaCl, cm^{-1}) 3057, 3000, 2958, 2928, 2833, 1608, 1576, 1547, 1508, 1475, 1437, 1375, 1339, 1313, 1285, 1248, 1175, 1136, 1092, 1034, 1022, 999, 885, 829, 760, 737, 689; HRMS (FAB) calcd for $C_{28}H_{22}NOSe_2$ [M+H]$^+$ 548.0032, found 548.0026.

3-(4-Chlorophenyl)-2,4-bis(phenylselanyl)quinoline (5d). Quinoline **5d** (37.8 mg, 0.069 mmol, 69%) was obtained from **1d** (0.10 mmol) according to the general procedure. The crude mixture was purified by PTLC on silica gel (Hex : AcOEt = 9 : 1) and recycle GPC ($CHCl_3$). Slightly yellow oil; ^{1}H NMR (400 MHz, $CDCl_3$, ppm) δ 6.97–7.02 (m, 2H), 7.03–7.16 (m, 5H), 7.31–7.45 (m, 6H), 7.57 (ddd, J = 1.4, 6.8, 8.2 Hz, 1H), 7.62–7.66 (m, 2H), 7.72 (d, J = 8.2 Hz, 1H), 8.33 (d, J = 8.2 Hz, 1H); ^{13}C NMR (75 MHz, $CDCl_3$, ppm) δ 126.6, 126.7, 128.1, 128.4, 128.5, 128.8, 128.9, 129.1, 129.2, 129.8, 131.0, 131.3, 131.9, 134.6, 136.3, 137.1, 139.2, 139.7, 148.4, 157.9; IR (NaCl, cm^{-1}) 3058, 3029, 1541, 1506, 1489, 1474, 1437, 1373, 1338, 1313, 1286, 1136, 1094, 1072, 1016, 883, 826, 760, 735, 689; HRMS (FAB) calcd for $C_{27}H_{19}ClNSe_2$ [M+H]$^+$ 551.9536, found 551.9533.

3-(4-Fluorophenyl)-2,4-bis(phenylselanyl)quinoline (5e). Quinoline **5e** (32.8 mg, 0.062 mmol, 62%) was obtained from **1e** (0.10 mmol) according to the general procedure. The crude mixture was purified by PTLC on silica gel (Hex : AcOEt = 9 : 1) and recycle GPC ($CHCl_3$). Slightly yellow solid; mp 140–141 °C (crystalized from acetone); ^{1}H NMR (300 MHz, $CDCl_3$, ppm) δ 6.97–7.13 (m, 7H), 7.14–7.21 (m, 2H), 7.34–7.45 (m, 4H), 7.57 (ddd, J = 1.4, 7.0, 8.3 Hz, 1H), 7.62–7.68 (m, 2H), 7.72 (dd, J = 1.4, 8.3 Hz, 1H), 8.34 (dd, J = 1.4, 8.3 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$, ppm) δ 115.3 (d, $J_{C\text{-}F}$ = 21.0 Hz), 126.6, 126.7, 128.1, 128.4, 128.8, 128.9, 128.9, 129.1, 129.1, 129.7, 130.9, 131.7 (d, $J_{C\text{-}F}$ = 8.6 Hz), 131.9, 134.6 (d, $J_{C\text{-}F}$ = 3.8 Hz), 136.2, 139.3, 139.9, 148.3, 158.3, 162.8 (d, $J_{C\text{-}F}$ = 246.9 Hz); IR (NaCl, cm^{-1}) 3072, 3030, 1541, 1506, 1489, 1474, 1456, 1437, 1371, 1339, 1313, 1221, 1158, 1136, 1092, 1013, 881, 772, 737, 689; HRMS (FAB) calcd for $C_{27}H_{19}FNSe_2$ [M+H]$^+$ 535.9832, found 535.9838.

3-*n*-Butyl-2,4-bis(phenylselanyl)quinoline (5f). Quinoline **5f** (35.0 mg, 0.071 mmol, 71%) was obtained from **1f** (0.10 mmol) according to the general procedure. The crude mixture was purified by PTLC on silica gel (Hex : AcOEt = 9 : 1) and recycle GPC ($CHCl_3$). Pale yellow oil; ^{1}H NMR (400 MHz, $CDCl_3$, ppm) δ 0.98 (t, J = 7.3 Hz, 3H), 1.51 (sextet, J = 7.3 Hz, 2H), 1.59–1.70 (m, 2H), 3.23 (t, J = 8.2 Hz, 2H), 7.12 (s, 5H), 7.35 (t, J = 7.6 Hz, 1H), 7.38–7.43 (m, 2H), 7.48 (t, J = 7.6 Hz, 1H), 7.65 (d, J = 8.2 Hz, 1H), 7.70–7.76 (m, 2H), 8.26 (d, J = 8.2 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$, ppm) δ 13.8, 23.1, 32.6, 35.8, 126.3, 126.5, 128.4, 128.4, 128.7, 128.8, 128.8, 128.9, 129.3, 129.6, 132.2, 136.2, 137.8, 141.0, 141.0, 147.5, 158.0; IR (NaCl, cm^{-1}) 3057, 3028, 2955, 2928, 2858, 1578, 1543, 1522, 1508, 1476, 1458, 1437, 1373, 1354, 1296, 1275, 1180, 1140, 1067, 1032, 1020, 999, 907, 760, 735, 689; HRMS (FAB) calcd for $C_{25}H_{24}NSe_2$ [M+H]$^+$ 498.0239, found 498.0231.

3-(1-Cyclohexenyl)-2,4-bis(phenylselanyl)quinoline (5g). Quinoline **5g** (42.6 mg, 0.082 mmol, 82%) was obtained from **1g** (0.10 mmol) according to the general procedure. The crude mixture was purified by PTLC on silica gel (Hex : AcOEt = 9 : 1) and recycle GPC ($CHCl_3$). Yellow oil; ^{1}H NMR (300 MHz, $CDCl_3$, ppm) δ 1.71–1.80 (m, 2H), 1.81–1.92 (m, 2H), 2.11–2.24 (m, 2H), 2.42–2.52 (m, 2H), 5.63 (s, 1H), 7.09–7.21 (m, 5H), 7.31 (t, J = 7.5 Hz, 1H), 7.37–7.43 (m, 2H), 7.48 (t, J = 7.5 Hz, 1H), 7.66 (d, J = 7.9 Hz, 1H), 7.71–7.78 (m, 2H), 8.16 (d, J = 8.3 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$, ppm) δ 21.7, 23.0, 25.5, 28.5, 126.1, 126.3, 127.8, 128.2, 128.4, 128.8, 128.9, 129.1, 129.2, 129.5, 130.0, 130.2, 131.6, 133.0, 136.1, 136.6, 142.9, 148.1, 158.0; IR (NaCl, cm^{-1}) 3057, 3028, 2930, 2855, 2829, 1578, 1541, 1521, 1508, 1475, 1437, 1375, 1339, 1304, 1285, 1136, 1070, 1043, 1020, 999, 881, 760, 735, 689; HRMS (FAB) calcd for $C_{27}H_{24}NSe_2$ [M+H]$^+$ 522.0239, found 522.0248.

3-Phenyl-2,4-bis(4-methylphenylselanyl)quinoline (5i). Quinoline **5i** (39.1 mg, 0.072 mmol, 72%) was obtained from **1a** (0.10 mmol) according to the general procedure. The crude mixture was purified by PTLC on silica gel (Hex : AcOEt = 9 : 1) and recycle GPC ($CHCl_3$). Pale yellow solid; mp 124–126 °C (crystalized from acetone); ^{1}H NMR (400 MHz, $CDCl_3$, ppm) δ 2.23 (s, 3H), 2.40 (s, 3H), 6.87 (d, J = 8.2 Hz, 2H), 6.92 (d, J = 8.2 Hz, 2H), 7.18 (d, J = 7.8 Hz, 2H), 7.35–7.46 (m, 5H), 7.51–7.57 (m, 3H), 7.66–7.70 (m, 1H), 7.72 (dd, J = 0.9, 8.7 Hz, 1H), 8.30 (dd, J = 0.9, 8.7 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$, ppm) δ 21.0, 21.4, 125.1, 125.4, 126.3, 128.2, 128.4, 128.5, 129.0, 129.1, 129.3, 129.7, 129.9, 130.9, 131.8, 132.5, 136.2, 138.3, 138.8, 138.9, 140.8, 148.3, 158.4; IR (NaCl, cm^{-1}) 3055, 3020, 2919, 2862, 1541, 1506, 1489, 1474, 1443, 1373, 1339, 1313, 1286, 1136, 1092, 1070, 1015, 800, 756, 721, 698; HRMS (FAB) calcd for $C_{29}H_{24}NSe_2$ [M+H]$^+$ 546.0239, found 546.0236.

3-Phenyl-2,4-bis(4-methoxyphenylselanyl)quinoline (5j). Quinoline **5j** (44.3 mg, 0.077 mmol, 77%) was obtained from **1a** (0.10 mmol) according to the general procedure. The crude mixture was purified by PTLC on silica gel (Hex : AcOEt = 9 : 1) and recycle GPC ($CHCl_3$). Pale yellow oil; ^{1}H NMR (400 MHz, $CDCl_3$, ppm) δ 3.71 (s, 3H), 3.85 (s, 3H), 6.61 (d, J = 8.7 Hz, 2H), 6.91 (d, J = 8.7 Hz, 2H), 6.98 (d, J = 8.7 Hz, 2H), 7.20–7.27 (m, 2H), 7.35–7.46 (m, 4H), 7.50–7.58 (m, 3H), 7.70 (d, J = 7.8 Hz, 1H), 8.36 (d, J = 7.8 Hz, 1H); ^{13}C NMR (75 MHz, $CDCl_3$, ppm) δ 55.2, 55.3, 114.6, 114.9, 119.6, 122.0, 126.2, 128.1, 128.2, 128.5, 128.9, 129.1, 129.3, 130.1, 133.4, 138.0, 138.9, 139.5, 140.4, 148.4, 158.8, 158.9, 160.0; IR (NaCl, cm^{-1}) 3059, 3002, 2930, 2902, 2835, 1589, 1574, 1549, 1489, 1475, 1460, 1441, 1373, 1339, 1286, 1246, 1173, 1136, 1092, 1074, 1030, 1005, 881, 822, 760, 721, 698; HRMS (FAB) calcd for $C_{29}H_{24}NO_2Se_2$ [M+H]$^+$ 578.0137, found 578.0142.

3-Phenyl-2,4-bis(4-chlorophenylselanyl)quinoline (5k). Quinoline **5k** (37.8 mg, 0.065 mmol, 65%) was obtained from **1a** (0.10 mmol) according to the general procedure. The crude mixture was purified by PTLC on silica gel (Hex : AcOEt = 9 : 1) and recycle GPC ($CHCl_3$). Slightly yellow solid; mp 145–146 °C (crystalized from acetone); ^{1}H NMR (400 MHz, $CDCl_3$, ppm) δ 6.92 (d, J = 8.2 Hz, 2H), 7.02 (d, J = 8.2 Hz, 2H), 7.19–7.23 (m, 2H), 7.34 (d, J = 8.7 Hz, 2H), 7.39–7.51 (m, 4H), 7.55–7.62 (m, 3H), 7.74 (d, J = 8.2 Hz, 1H), 8.27 (d, J = 8.2 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$, ppm) δ 126.7, 127.0, 127.8, 128.3, 128.7, 129.0, 129.1, 129.2, 129.3, 129.7, 130.1, 132.1, 132.7, 133.2, 134.7, 137.6, 138.3, 138.5, 140.7, 148.2, 157.8; IR (NaCl, cm^{-1}) 3058, 3029, 1543, 1508, 1489, 1474, 1458, 1387, 1375, 1339, 1313, 1286, 1219, 1136, 1088, 1070, 1030, 1011, 881, 810, 760, 729, 698; HRMS (FAB) calcd for $C_{27}H_{18}Cl_2NSe_2$ [M+H]$^+$ 585.9147, found 585.9137.

3-Phenyl-2,4-bis(4-fluorophenylselanyl)quinoline (5l). Quinoline **5l** (37.8 mg, 0.069 mmol, 69%) was obtained from **1a** (0.10 mmol) according to the general procedure. The crude mixture was purified by PTLC on silica gel (Hex : AcOEt = 9 : 1) and recycle GPC ($CHCl_3$). Pale yellow solid; mp 112–113 °C (crystalized from acetone); ^{1}H NMR (400 MHz, $CDCl_3$, ppm) δ 6.76 (t, J = 8.7 Hz, 2H), 6.99 (dd, J = 5.5, 8.7 Hz, 2H), 7.07 (t, J = 8.7 Hz, 2H), 7.18–7.23 (m, 2H), 7.38–7.48 (m, 4H), 7.54–7.64 (m, 3H), 7.70 (d, J = 8.2 Hz, 1H), 8.32 (d, J = 8.2 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$, ppm) δ 116.1 (d, $J_{C\text{-}F}$ = 21.9 Hz), 116.3 (d, $J_{C\text{-}F}$ = 21.9 Hz), 123.6, 126.2 (d, $J_{C\text{-}F}$ = 3.8 Hz), 126.5, 126.8 (d, $J_{C\text{-}F}$ = 3.8 Hz), 128.3, 128.7, 128.7, 129.1, 129.7, 129.9, 133.3 (d, $J_{C\text{-}F}$ = 8.6 Hz), 138.4 (d, $J_{C\text{-}F}$ = 8.6 Hz), 139.1, 140.2, 140.4, 148.2, 158.1, 161.9 (d, $J_{C\text{-}F}$ = 246.9 Hz), 163.1 (d, $J_{C\text{-}F}$ = 246.9 Hz); IR (NaCl, cm^{-1}) 3058, 3030, 1583, 1549, 1485, 1373, 1339, 1313, 1286, 1227, 1157, 1136, 1090, 1069, 1013, 881, 824, 760, 721, 698; HRMS (FAB) calcd for $C_{27}H_{18}F_2NSe_2$ [M+H]$^+$ 553.9738, found 553.9732.

General procedure for the photochemical intramolecular cyclization of *o*-alkynylaryl isocyanide with organic ditelluride

In a NMR tube (ϕ = 5 mm, length = 180 mm) were placed 2-(phenylethynyl)phenyl isocyanide (**1a**, 20 mg, 0.10 mmol) and diphenyl ditelluride (**6a**, 82 mg, 0.20 mmol) in $CDCl_3$ (0.5 mL) under ambient atmosphere, and the mixture was irradiated with a high pressure Hg lamp through a glass filter ($h\nu$ > 400 nm) for 4 h. After the photoirradiation, the resulting mixture was concentrated *in vacuo*, and the purification by PTLC on silica gel (Hex : AcOEt = 9 : 1) and recycle GPC ($CHCl_3$) gave 3-phenyl-2,4-bis(phenyltellanyl)phenylquinoline (**7a**, 29.3 mg, 0.048 mmol, 48%) as a yellow oil.

3-Phenyl-2,4-bis(phenyltellanyl)quinoline (7a). Yellow oil; ^{1}H NMR (300 MHz, $CDCl_3$, ppm) δ 7.03 (t, J = 7.2 Hz, 2H), 7.13–7.18 (m, 3H), 7.29–7.56 (m, 10 H), 7.70 (d, J = 8.4 Hz, 1H), 7.90 (d, J = 6.6 Hz, 2H), 8.22 (d, J = 8.4 Hz, 1H); ^{13}C NMR (75 MHz,

$CDCl_3$, ppm) δ 116.0, 118.0, 126.6, 127.5, 128.3, 128.5, 129.0, 129.2, 129.4, 129.5, 129.7, 133.4, 134.9, 135.1, 136.7, 139.8, 143.3, 147.2, 148.8, 149.0; IR (NaCl, cm^{-1}) 3053, 1651, 1574, 1537, 1472, 1435, 1367, 1333, 1312, 1279, 1132, 1080, 1063, 1016, 997, 756, 733, 689; HRMS (EI) calcd for $C_{27}H_{19}NTe_2$ $[M]^+$ 616.9642, found 616.9635.

3-(4-Methylphenyl)-2,4-bis(phenyltellanyl)quinoline (7b). Quinoline **7b** (25.2 mg, 0.040 mmol, 40%) was obtained from **1b** (0.10 mmol) according to the general procedure. The crude mixture was purified by PTLC on silica gel (Hex : AcOEt = 9 : 1) and recycle GPC ($CHCl_3$). Yellow oil; ^{1}H NMR (300 MHz, $CDCl_3$, ppm) δ 2.47 (s, 3H), 7.04 (t, *J* = 7.5 Hz, 2H), 7.13–7.25 (m, 4H), 7.31–7.42 (m, 7H), 7.53 (t, *J* = 7.5 Hz, 1H), 7.71 (d, *J* = 8.4 Hz, 1H), 7.91 (d, *J* = 6.6 Hz, 2H), 8.20 (d, *J* = 8.4 Hz, 1H); ^{13}C NMR (75 MHz, $CDCl_3$, ppm) δ 21.6, 116.1, 118.1, 126.5, 127.4, 128.3, 128.8, 129.0, 129.1, 129.3, 129.4, 129.6, 129.8, 133.4, 136.7, 139.1, 139.8, 140.5, 146.9, 148.8, 149.3; IR (NaCl, cm^{-1}) 3051, 3024, 2918, 2853, 1647, 1574, 1535, 1508, 1473, 1433, 1367, 1333, 1313, 1281, 1132, 1080, 1065, 1016, 997, 968, 908, 878, 816, 758, 731, 689; HRMS (FAB) calcd for $C_{28}H_{22}NTe_2$ $[M+H]^+$ 631.9877, found 631.9885.

3-(4-Methoxyphenyl)-2,4-bis(phenyltellanyl)quinoline (7c). Quinoline **7c** (31.4 mg, 0.049 mmol, 49%) was obtained from **1c** (0.10 mmol) according to the general procedure. The crude mixture was purified by PTLC on silica gel (Hex : AcOEt = 9 : 1) and recycle GPC ($CHCl_3$). Yellow oil; ^{1}H NMR (300 MHz, $CDCl_3$, ppm) δ 3.90 (s, 3H), 6.93 (d, *J* = 8.7 Hz, 2H), 7.04 (t, *J* = 7.2 Hz, 2H), 7.01–7.17 (m, 3H), 7.26–7.40 (m, 6H), 7.53 (t, *J* = 6.9 Hz, 1H), 7.70 (d, *J* = 8.4 Hz, 1H), 7.91 (d, *J* = 8.1 Hz, 2H), 8.19 (d, *J* = 7.8 Hz, 1H); ^{13}C NMR (75 MHz, $CDCl_3$, ppm) δ 55.3, 113.9, 116.1, 118.5, 126.5, 127.5, 128.3, 129.0, 129.1, 129.4, 129.8, 131.1, 132.3, 133.3, 135.8, 136.7, 136.9, 139.8, 146.9, 148.7, 149.9, 160.1; IR (NaCl, cm^{-1}) 3055, 2926, 2837, 1645, 1607, 1574, 1510, 1474, 1435, 1331, 1292, 1250, 1177, 1032, 833, 737, 689; HRMS (FAB) calcd for $C_{28}H_{22}NOTe_2$ $[M+H]^+$ 647.9826, found 647.9820.

3-(4-Chlorophenyl)-2,4-bis(phenyltellanyl)quinoline (7d). Quinoline **7d** (32.2 mg, 0.050 mmol, 50%) was obtained from **1d** (0.10 mmol) according to the general procedure. The crude mixture was purified by PTLC on silica gel (Hex : AcOEt = 9 : 1) and recycle GPC ($CHCl_3$). Yellow oil; ^{1}H NMR (300 MHz, $CDCl_3$, ppm) δ 7.03 (t, *J* = 7.8 Hz, 2H), 7.09–7.19 (m, 3H), 7.25–7.41 (m, 8H), 7.55 (t, *J* = 8.4 Hz, 1H), 7.70 (d, *J* = 8.4 Hz, 1H), 7.88 (d, *J* = 8.1 Hz, 2H), 8.25 (d, *J* = 8.4 Hz, 1H); ^{13}C NMR (75 MHz, $CDCl_3$, ppm) δ 115.7, 117.7, 126.8, 127.6, 128.4, 128.7, 129.1, 129.4, 129.5, 129.8, 130.0, 131.2, 133.3, 135.0, 136.9, 139.8, 141.3, 146.0, 148.7, 148.8; IR (NaCl, cm^{-1}) 3055, 1645, 1574, 1531, 1489, 1474, 1435, 1394, 1367, 1333, 1281, 1217, 1092, 1016, 997, 878, 827, 756, 735, 689; HRMS (FAB) calcd for $C_{27}H_{19}ClNTe_2$ $[M+H]^+$ 651.9331, found 651.9338.

3-*n*-Butyl-2,4-bis(phenyltellanyl)quinoline (7f). Quinoline **7f** (48.6 mg, 0.082 mmol, 82%) was obtained from **1f** (0.10 mmol) according to the general procedure. The crude mixture was purified by PTLC on silica gel (Hex : AcOEt = 9 : 1) and recycle GPC ($CHCl_3$). Yellow oil; ^{1}H NMR (300 MHz, $CDCl_3$, ppm) δ 0.99 (t, *J* = 7.5 Hz, 3H), 1.45–1.70 (m, 4H), 3.26 (t, *J* = 8.4 Hz, 2H), 7.07 (t, *J* = 7.5 Hz, 2H), 7.15 (t, *J* = 7.5 Hz, 1H), 7.32–7.42 (m, 6H), 7.48 (t, *J* = 6.9 Hz, 1H), 7.66 (d, *J* = 8.4 Hz, 1H), 7.98 (d, *J* = 6.6 Hz, 2H), 8.29 (d, *J* = 8.4 Hz, 1H); ^{13}C NMR (75 MHz, $CDCl_3$, ppm) δ 13.8, 23.1, 33.6, 43.7, 115.3, 116.0, 126.8, 127.4, 128.4, 128.5, 129.1, 129.3, 129.6, 129.8, 130.5, 133.8, 135.6, 140.0, 145.7, 148.0, 148.3; IR (NaCl, cm^{-1}) 3053, 2955, 2923, 2870, 2855, 1651, 1574, 1529, 1474, 1435, 1366, 1342, 1288, 1271, 1178, 1136, 1076, 1063, 1016, 997, 901, 758, 729, 689; HRMS (FAB) calcd for $C_{25}H_{24}NTe_2$ $[M+H]^+$ 598.0033, found 598.0034.

3-(1-Cyclohexenyl)-2,4-bis(phenyltellanyl)quinoline (7g). Quinoline **7g** (41.9 mg, 0.068 mmol, 68%) was obtained from **1g** (0.10 mmol) according to the general procedure. The crude mixture was purified by PTLC on silica gel (Hex : AcOEt = 9 : 1) and recycle GPC ($CHCl_3$). Yellow oil; ^{1}H NMR (300 MHz, $CDCl_3$, ppm) δ 1.67–2.00 (m, 4H), 2.05–2.35 (m, 2H), 2.48–2.76 (m, 2H), 5.64 (m, 1H), 7.02–7.20 (m, 3H), 7.22–7.53 (m, 7H), 7.67 (d, *J* = 9.0 Hz, 1H), 7.97 (dd, *J* = 3.0, 9.0 Hz, 2H), 8.12 (d, *J* = 9.0 Hz, 1H); ^{13}C NMR (75 MHz, $CDCl_3$, ppm) δ 21.5, 23.1, 25.3, 28.4, 116.2, 117.8, 126.4, 126.7, 127.4, 128.2, 128.8, 129.0, 129.3, 129.4, 129.6, 132.7, 132.9, 136.1, 139.5, 139.6, 142.0, 148.7, 148.9, 148.9; IR (NaCl, cm^{-1}) 3053, 2930, 2855, 1645, 1574, 1531, 1474, 1433, 1369, 1327, 1302, 1281, 1132, 1065, 1042, 1016, 997, 977, 920, 908, 758, 731, 691; HRMS (FAB) calcd for $C_{27}H_{24}NTe_2$ $[M+H]^+$ 622.0033, found 622.0034.

3-(4-Nitorophenyl)-2,4-bis(phenyltellanyl)quinoline (7i). Quinoline **7i** (21.2 mg, 0.032 mmol, 32%) was obtained from **1i** (0.10 mmol) according to the general procedure. The crude mixture was purified by PTLC on silica gel (Hex : AcOEt = 9 : 1) and recycle GPC ($CHCl_3$). Yellow oil; ^{1}H NMR (300 MHz, $CDCl_3$, ppm) δ 7.03 (t, *J* = 7.5 Hz, 2H), 7.18–7.24 (m, 3H), 7.28–7.35 (m, 4H), 7.40 (d, *J* = 7.5 Hz, 1H), 7.48 (t, *J* = 7.8 Hz, 1H), 7.63 (t, *J* = 7.8 Hz, 1H), 7.75 (d, *J* = 8.7 Hz, 1H), 7.85 (d, *J* = 8.1 Hz, 2H), 8.15 (d, *J* = 8.4 Hz, 2H), 8.32 (d, *J* = 8.1 Hz, 1H); ^{13}C NMR (75 MHz, $CDCl_3$, ppm) δ 115.4, 117.2, 123.5, 127.2, 128.0, 128.6, 129.2, 129.5, 129.6, 129.7, 129.9, 130.0, 131.1, 133.2, 137.1, 139.9, 144.9, 145.3, 147.8, 148.8, 149.1; IR (NaCl, cm^{-1}) 3055, 1597, 1520, 1474, 1435, 1345, 1312, 1277, 1080, 1016, 851, 758, 730, 691; HRMS (FAB) calcd for $C_{27}H_{19}N_2O_2Te_2$ $[M+H]^+$ 662.9571, found 662.9579.

3-(4-Cyanophenyl)-2,4-bis(phenyltellanyl)quinoline (7j). Quinoline **7j** (16.8 mg, 0.026 mmol, 26%) was obtained from **1j** (0.10 mmol) according to the general procedure. The crude mixture was purified by PTLC on silica gel (Hex : AcOEt = 9 : 1) and recycle GPC ($CHCl_3$). Yellow oil; ^{1}H NMR (300 MHz, $CDCl_3$, ppm) δ 7.04 (t, *J* = 6.0 Hz, 2H), 7.17–7.24 (m, 4H), 7.30–7.49 (m, 5H), 7.59–7.64 (m, 3H), 7.74 (d, *J* = 7.5 Hz, 1H), 7.85 (d, *J* = 6.6 Hz, 2H), 8.31 (d, *J* = 7.5 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 109.8, 115.5, 117.3, 118.0, 127.2, 127.9, 128.2, 128.6, 129.2, 129.5, 129.6, 130.0, 130.8, 131.7, 132.1, 133.3, 137.1, 139.9, 146.0, 147.3, 149.5, 149.9; IR (NaCl, cm^{-1}) 3053, 2228, 1647, 1474, 1435, 1016, 997, 910, 835, 758, 735, 691; HRMS (FAB) calcd for $C_{28}H_{19}N_2Te_2$ $[M+H]^+$ 642.9673, found 642.9682.

3-Phenylmethyl-2,4-bis(phenyltellanyl)quinoline (7k). Quinoline **7k** (26.2 mg, 0.042 mmol, 42%) was obtained from **1k** (0.10 mmol) according to the general procedure. The crude mixture was purified by PTLC on silica gel (Hex : AcOEt = 9 : 1) and recycle GPC ($CHCl_3$). Yellow oil; ^{1}H NMR (300 MHz, $CDCl_3$, ppm) δ 4.84 (s, 2H), 7.02–7.41 (m, 14H), 7.52 (t, *J* = 8.3 Hz, 1H), 7.70 (d, *J* = 8.1 Hz, 1H), 7.91 (d, *J* = 8.1 Hz, 2H), 8.32 (d, *J* = 8.4 Hz, 1H); ^{13}C NMR (75 MHz, $CDCl_3$, ppm) δ 49.2, 115.1, 116.6, 126.5, 126.9, 127.5, 128.3, 128.6, 128.8, 128.9, 129.0, 129.4, 129.6, 130.4, 132.8, 134.1, 136.1, 138.5, 139.8, 143.3, 148.1, 149.8; IR (NaCl, cm^{-1}) 3053, 3026, 2976, 2878, 2821, 1643, 1574, 1547, 1528, 1493, 1472, 1452, 1433, 1366, 1342, 1286, 1168, 1132, 1123, 1063, 1016, 1008, 987, 943, 908, 876, 760, 729, 689; HRMS (FAB) calcd for $C_{28}H_{22}NTe_2$ $[M+H]^+$ 631.9877, found 631.9881.

6-Methyl-3-phenyl-2,4-bis(phenyltellanyl)quinoline (7l). Quinoline **7l** (39.4 mg, 0.063 mmol, 63%) was obtained from **1l** (0.10 mmol) according to the general procedure. The crude mixture was purified by PTLC on silica gel (Hex : AcOEt = 9 : 1) and recycle GPC ($CHCl_3$). Yellow oil; ^{1}H NMR (300 MHz, $CDCl_3$, ppm) δ 2.35 (s, 3H), 7.01 (t, J = 7.4 Hz, 2H), 7.13 (t, J = 7.5 Hz, 1H), 7.20 (d, J = 6.9 Hz, 2H), 7.25–7.46 (m, 9H), 7.60 (d, J = 8.4 Hz, 1H), 7.88 (d, J = 7.8 Hz, 2H), 7.95 (s, 1H); ^{13}C NMR (75 MHz, $CDCl_3$, ppm) δ 21.6, 116.1, 117.9, 127.4, 128.2, 128.5, 128.6, 128.9, 129.1, 129.3, 129.6, 129.7, 131.3, 132.3, 136.4, 136.9, 139.7, 143.3, 146.9, 147.3, 147.4; IR (NaCl, cm^{-1}) 3053, 3024, 2990, 2918, 2856, 1645, 1574, 1531, 1489, 1474, 1435, 1373, 1340, 1308, 1273, 1177, 1140, 1086, 1028, 1016, 997, 926, 908, 824, 756, 731, 698, 691; HRMS (FAB) calcd for $C_{28}H_{22}NTe_2$ $[M+H]^+$ 631.9877, found 631.9871.

6-Fluoro-3-phenyl-2,4-bis(phenyltellanyl)quinoline (7m). Quinoline **7m** (38.5 mg, 0.061 mmol, 61%) was obtained from **1m** (0.10 mmol) according to the general procedure. The crude mixture was purified by PTLC on silica gel (Hex : AcOEt = 9 : 1) and recycle GPC ($CHCl_3$). Yellow oil; ^{1}H NMR (300 MHz, $CDCl_3$, ppm) δ 7.06 (t, J = 7.5 Hz, 2H), 7.15–7.24 (m, 3H), 7.30–7.51 (m, 9H), 7.70 (dd, J = 5.4, 8.7 Hz, 1H), 7.88 (m, 2H), 7.92 (d, J = 2.4 Hz, 1H); ^{13}C NMR (75 MHz, $CDCl_3$, ppm) δ 117.1 (d, $J_{C\text{-}F}$ = 24.7 Hz), 117.8, 119.1 (d, $J_{C\text{-}F}$ = 25.9 Hz), 127.8, 128.4, 128.6, 128.8 (d, $J_{C\text{-}F}$ = 2.5 Hz), 129.0, 129.1, 129.2, 129.6 (d, $J_{C\text{-}F}$ = 2.5 Hz), 131.1, 131.3, 131.9, 132.0, 136.9, 139.9, 143.2, 145.9, 158.1, 160.5 (d, $J_{C\text{-}F}$ = 244.2 Hz); IR (NaCl, cm^{-1}) 3055, 1622, 1574, 1553, 1533, 1481, 1435, 1342, 1306, 1200, 1169, 1082, 1016, 943, 827, 754, 731, 698, 691; Anal. Calcd. for $C_{27}H_{18}FNTe_2$: C, 51.42; H, 2.88; N, 2.22. Found: C, 51.32; H, 2.89; N, 2.51.

3-Phenyl-2,4-bis(4-methoxyphenyltellanyl)quinoline (7n). Quinoline **7n** (27.1 mg, 0.040 mmol, 40%) was obtained from **1a** (0.10 mmol) according to the general procedure. The crude mixture was purified by PTLC on silica gel (Hex : AcOEt = 9 : 1) and recycle GPC ($CHCl_3$). Pale yellow oil; ^{1}H NMR (300 MHz, $CDCl_3$, ppm) δ 3.72 (s, 3H), 3.84 (s, 3H), 6.60 (d, J = 8.8 Hz, 2H), 6.87 (d, J = 8.8 Hz, 2H), 7.20–7.26 (m, 2H), 7.29 (d, J = 8.8 Hz, 2H), 7.32–7.56 (m, 5H), 7.68 (d, J = 7.2 Hz, 1H), 7.78 (d, J = 8.8 Hz, 2H), 8.25 (d, J = 7.5 Hz, 1H); ^{13}C NMR (75 MHz, $CDCl_3$, ppm) δ 55.1, 55.2, 104.8, 107.7, 115.0, 115.3, 126.4, 128.5, 129.0, 129.1, 129.5, 129.8, 129.9, 133.1, 139.4, 139.7, 141.7, 143.3, 146.7, 148.1, 148.8, 159.6, 160.0; IR (NaCl, cm^{-1}) 3057, 3003, 2959, 2937, 2835, 1645, 1585, 1531, 1489, 1472, 1460, 1441, 1398, 1367, 1333, 1285, 1246, 1177, 1134, 1080, 1065, 1028, 1003, 910, 822, 760, 731, 700; HRMS (FAB) calcd for $C_{29}H_{24}NO_2Te_2$ $[M+H]^+$ 677.9932, found 677.9926.

3-Phenyl-2,4-bis(4-fluorophenyltellanyl)quinoline (7o). Quinoline **7o** (42.9 mg, 0.066 mmol, 66%) was obtained from **1a** (0.10 mmol) according to the general procedure. The crude mixture was purified by PTLC on silica gel (Hex : AcOEt = 9 : 1) and recycle GPC ($CHCl_3$). Pale yellow oil; ^{1}H NMR (300 MHz, $CDCl_3$, ppm) δ 6.74 (t, J = 8.7 Hz, 2H), 7.02 (t, J = 8.7 Hz, 2H), 7.20 (d, J = 6.9 Hz, 2H), 7.29 (dd, J = 5.6, 9.0 Hz, 2H), 7.39–7.50 (m, 4H), 7.56 (t, J = 8.4 Hz, 1H), 7.69 (d, J = 8.4 Hz, 1H), 7.83 (dd, J = 5.7, 8.7 Hz, 2H), 8.21 (d, J = 8.4 Hz, 1H); ^{13}C NMR (75 MHz, $CDCl_3$, ppm) δ 116.4 (d, $J_{C\text{-}F}$ = 21.0 Hz), 116.8 (d, $J_{C\text{-}F}$ = 21.0 Hz), 126.3, 126.7, 128.6, 128.7, 128.8, 128.8, 129.1, 129.4 (d, $J_{C\text{-}F}$ = 3.7 Hz), 129.7, 129.7 (d, $J_{C\text{-}F}$ = 3.7 Hz), 133.1, 139.3 (d, $J_{C\text{-}F}$ = 7.4 Hz), 139.6, 142.1 (d, $J_{C\text{-}F}$ = 7.4 Hz), 142.9, 146.9, 148.8, 148.9, 162.7 (d, $J_{C\text{-}F}$ = 245.5 Hz), 163.2 (d, $J_{C\text{-}F}$ = 246.7 Hz); IR (NaCl, cm^{-1}) 3059, 3026, 1651, 1582, 1537, 1485, 1443, 1389, 1367, 1333, 1312, 1294, 1281, 1227, 1161, 1134, 1086, 1028, 1015, 968, 876, 822, 754, 700, 667, 648; HRMS (FAB) calcd for $C_{27}H_{18}F_2NTe_2$ $[M+H]^+$ 653,9532, found 653.9529.

General procedure for the photochemical intramolecular cyclization of *o*-alkynylaryl isocyanide in the presence of hydrogen source, *e.g.*, cyclohexanethiol

In a NMR tube (ϕ = 5 mm, length = 180 mm) were placed 2-(phenylethynyl)phenyl isocyanide (**1a**, 20 mg, 0.10 mmol) and cyclohexanethiol (23 mg, 0.20 mmol) in $CDCl_3$ (0.5 mL) under nitrogen atmosphere, and the reaction was performed for 4 h upon irradiation with a high-pressure Hg lamp through a Pyrex ($h\nu$ > 300 nm). After the photoirradiation, the resulting mixture was concentrated *in vacuo*, and the purification by PTLC (Hex : AcOEt = 9 : 1) and recycle GPC ($CHCl_3$) gave 3-phenylquinoline (**8a**, 16.8 mg, 0.082 mmol, 82%) as a colorless oil.

3-Phenylquinoline (8a)[17]. Colorless oil; ^{1}H NMR (300 MHz, $CDCl_3$, ppm) δ 7.37–7.62 (m, 4H), 7.65–7.77 (m, 3H), 7.90 (d, J = 8.4 Hz, 1H), 8.15 (d, J = 8.4 Hz, 1H), 8.32 (s, 1H), 9.20 (s, 1H); ^{13}C NMR (75 MHz, $CDCl_3$, ppm) δ 127.0, 127.4, 128.0, 128.1, 128.1, 129.1, 129.2, 129.3, 133.2, 133.8, 137.9, 147.3, 149.9; IR (NaCl, cm^{-1}) 3030, 1653, 1558, 1541, 1493, 1448, 1418, 1362, 1339, 1026, 953, 903, 787, 762, 696; MS (EI) m/z 205 (M^+, 100).

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15 At the initial stage of this research, the photochemical reaction of **1a** with **4a** produced a mixture including bisselenated quinoline **5a** and oligomers of **1a**. By further detailed examination, pure **5a** could be mainly obtained and separated from the resulting mixture.

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19 The rate constants of intramolecular 5-*exo* and 6-*endo* radical cyclization of 5-hexynyl radical were determined: 5-*exo* cyclization, 2.3×10^5 s^{-1}; 6-*endo* cyclization, 4.1×10^3 s^{-1}, see: (*a*) A. L. J. Beckwith, *Tetrahedron*, 1981, **37**, 3073; (*b*) A. L. J. Beckwith and C. H. Schiesser, *Tetrahedron*, 1985, **41**, 3925; (*c*) G. A. Russell and H. Tashtoush, *J. Am. Chem. Soc.*, 1983, **105**, 1398.

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23 The results of the optimization of the reaction conditions and the scope and limitation of several isocyanides are summarized in Table S2 and S3 in the ESI‡.

24 The rate constants for hydrogen abstraction of carbon radicals from tributylhydrogermane and tris(trimethylsilyl)silane were reported: ^{n}Bu$_3$GeH, 5.0×10^5 M^{-1} s^{-1}; (TMS)$_3$SiH, 3.8×10^5 M^{-1} s^{-1}, see: (*a*) C. Chatgilialoglu, *Acc. Chem. Res.*, 1992, **25**, 188; (*b*) C. Chatgilialoglu, M. Ballestri, J. Escudié and I. Pailhous, *Organometallics*, 1999, **18**, 2395 and ref. 19b.

25 We also examined the photochemical reaction of isocyanide **1a** with 2 equivalents of *n*-tributyltin hydride (the rate constant for hydrogen abstraction of carbon radicals of ^{n}Bu$_3$SnH was reported to be 2.4×10^6 M^{-1} s^{-1}, see ref. 19b). The reaction also afforded 3-phenylquinoline **8a** in 76% yield. SeeT. A. Mitamura and A. Ogawa, *J. Org. Chem.*, 2011, **76**, 1163.

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