Supplementary Information for

Photochemical Intramolecular Cyclization of o-Alkynylaryl Isocyanides with Organic Dichalcogenides Leading to 2,4-Bischalcogenated Quinoline Derivatives

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General Remarks.

$^1$H NMR spectra were recorded on a spectrometer (300 MHz or 400 MHz) using CDCl$_3$ as the solvent with tetramethylsilane (TMS) as the internal standard. $^{13}$C NMR spectra were obtained on a spectrometer (75 MHz or 100 MHz) using CDCl$_3$ as the solvent. Chemical shifts in $^{13}$C NMR were measured relative to CDCl$_3$ by using $\delta$ 77.0 ppm. Infrared spectra were determined on a FT-IR spectrometer. Melting points were determined on a micro melting point apparatus. Conventional mass spectra were recorded with a gas chromatograph mass spectrometer. High resolution mass spectra were obtained on a mass spectrometer. Terminal acetylenes (4-methylphenylacetylene,$^S_1$ 4-methoxyphenylacetylene,$^S_1$ 4-chlorophenylacetylene,$^S_1$ 4-nitrophenylacetylene,$^S_2$ and 4-cyanophenylacetylene$^S_2$), organic dichalcogenides (diphenyl diselenide (4a),$^S_3$ bis(4-methylphenyl) diselenide (4b),$^S_3$ bis(4-methoxyphenyl) diselenide (4c),$^S_3$ bis(4-fluorophenyl) diselenide (4e),$^S_3$ diphenyl ditelluride (6a),$^S_4$ bis(4-methoxyphenyl) ditelluride (6b),$^S_5$ bis(4-fluorophenyl) ditelluride (6c),$^S_6$ and dibutyl ditelluride (6d),$^S_7$), and o-alkynylaryl isocyanides$^S_8$ were prepared according to the literature. The formation of o-alkynylaryl isocyanides was determined by $^1$H NMR with 1,3,5-trioxane as the internal standard because of their instability. Other reagents could be purchased commercially and used without further purification.
Table S1. Photochemical Reaction of Several Isocyanides 1 with Cyclohexanethiol

\[
\begin{align*}
\text{entry} & \quad 1 & \quad R^1 & \quad 8 & \quad \text{yield (%)}^b \\
1 & \text{1a} & \text{C}_6\text{H}_5 & \text{8a} & 82 \\
2 & \text{1b} & 4\text{-Me-}C_6\text{H}_4 & \text{8b} & 66 \\
3 & \text{1d} & 4\text{-Cl-C}_6\text{H}_4 & \text{8d} & 67 \\
4 & \text{1e} & 4\text{-F-}C_6\text{H}_4 & \text{8e} & 75 \\
5 & \text{1f} & n\text{-Bu} & \text{8f} & 72 \\
6 & \text{1g} & 1\text{-cyclohexenyl} & \text{8g} & 64 \\
\end{align*}
\]

\(^a\) Reaction conditions: isocyanide (1, 0.10 mmol), thiol (0.20 mmol), CDCl\(_3\) (0.50 mL), room temperature, \(h\nu (> 300 \text{ nm: irradiation with a high pressure Hg lamp through Pyrex})\). \(^b\) Isolated yield.

Table S2. Optimization of the Synthesis of 2-Sulfanylquinoline 9a

\[
\begin{align*}
\text{entry} & \quad \text{solvent} & \quad \text{additive} & \quad \text{yield of 9a (%)}^b \\
1 & \text{CHCl}_3 & \_ & 29 \\
2 & \text{CHCl}_3 & \text{Et}_3\text{N} & 70 \\
3 & \text{THF} & \text{Et}_3\text{N} & 85 (78) \\
4 & \text{CHCl}_3 & \text{K}_2\text{CO}_3 & 11 \\
\end{align*}
\]

\(^a\) Reaction conditions: isocyanide (1a, 0.05 mmol), benzenethiol, solvent (0.5 mL), room temperature, 4 h. \(^b\) Determined by \(^1\text{H} \text{NMR}\). A value in parenthesis is isolated yield.
Table S3. Scope and Limitation of Several Isocyanides 1

![Diagram](image)

<table>
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<tr>
<th>entry</th>
<th>R¹</th>
<th>1 product</th>
<th>9 yield (%)</th>
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<td>1a</td>
<td>9a</td>
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<tr>
<td>2</td>
<td>4-Me-C₆H₄-</td>
<td>1b</td>
<td>9b</td>
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<td>3</td>
<td>4-Cl-C₆H₄-</td>
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</tr>
<tr>
<td>5</td>
<td>CH₃(CH₂)₃-</td>
<td>1f</td>
<td>9f</td>
</tr>
</tbody>
</table>

* Reaction conditions: isocyanide (1, 0.05 mmol), benzenethiol (0.075 mmol), THF (0.5 mL), Et₃N (0.5 mL), room temperature, 4 h.  
  b Isolated yield.
UV-Vis Spectra of o-Alkynylaryl Iso cyanides 1a and 1f

**Figure S1.** UV-Vis Spectrum of o-Alkynylaryl Iso cyanide 1a (1.2 x 10^{-5} M in CHCl₃).

**Figure S2.** UV-Vis Spectrum of o-Alkynylaryl Iso cyanide 1f (4.7 x 10^{-6} M in CHCl₃).
Characterization Data.

3-(4-Methylphenyl)quinoline (8b): Quinoline 8b (14.5 mg, 0.066 mmol, 66%) 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 (CHCl₃). Slightly yellow oil; ¹H NMR (300 MHz, CDCl₃, ppm) δ 2.44 (s, 3H), 7.34 (d, J = 7.5 Hz, 2H), 7.57–7.64 (m, 3H), 7.71 (d, J = 1.5, 6.9, 8.4 Hz, 1H), 7.87 (d, J = 8.4 Hz, 1H), 8.13 (d, J = 8.4 Hz, 1H), 8.28 (d, J = 2.1 Hz, 1H), 9.18 (d, J = 2.1 Hz, 1H); ¹³C NMR (75 MHz, CDCl₃, ppm) δ 21.2, 126.9, 127.2, 127.9, 128.1, 129.2, 129.7, 129.9, 132.8, 133.8, 135.0, 138.0, 147.2, 149.9; IR (NaCl, cm⁻¹) 3026, 2957, 2922, 2866, 1516, 1493, 1462, 1362, 1340, 1188, 1124, 1040, 1020, 908, 816, 785, 750, 718; MS (FAB) m/z 220 ([M+H]⁺, 100).

3-(4-Chlorophenyl)quinoline (8d): Quinoline 8d (16.1 mg, 0.067 mmol, 67%) 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 (CHCl₃). White solid; mp 130–132 °C (crystallized from acetone); ¹H NMR (400MHz, CDCl₃, ppm) δ 7.50 (d, J = 8.6 Hz, 2H), 7.60 (ddd, J = 1.4, 6.9, 7.8 Hz, 1H), 7.65 (d, J = 8.6 Hz, 2H), 7.75 (ddd, J = 1.4, 6.9, 8.2 Hz, 1H), 7.89 (d, J = 7.8 Hz, 1H), 8.16 (d, J = 8.2 Hz, 1H), 8.30 (d, J = 1.8 Hz, 1H), 9.14 (s, 1H); ¹³C NMR (100 MHz, CDCl₃, ppm) δ 127.2, 128.0, 128.6, 129.1, 129.4, 129.7, 132.6, 133.3, 134.4, 136.2, 139.9, 147.1, 149.2; MS (EI) m/z 239 (M⁺, 100).

3-(4-Fluorophenyl)quinoline (8e): Quinoline 8e (16.7 mg, 0.075 mmol, 75%) 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 (CHCl₃). White solid; mp 100–102 °C (crystallized from acetone); ¹H NMR (300 MHz, CDCl₃, ppm) δ 7.22 (t, J = 8.6 Hz, 2H), 7.59 (dt, J = 1.0, 7.5 Hz, 1H), 7.65–7.78 (m, 3H), 7.88 (d, J = 7.9 Hz, 1H), 8.14 (d, J = 8.4 Hz, 1H), 8.27 (s, 1H), 9.14 (s, 1H); ¹³C NMR (100 MHz, CDCl₃, ppm) δ 116.2 (d, JCF = 21.0 Hz), 127.2, 127.9, 129.0, 129.0 (d, JCF = 7.6 Hz), 129.6, 132.9, 133.3, 133.8 (d, JCF = 3.8 Hz), 146.9, 149.3, 162.9 (d, JCF = 245.8 Hz); IR (NaCl, cm⁻¹) 3076, 3052, 1508, 1497, 1231, 953, 905, 831, 785, 746; MS (EI) m/z 223 (M⁺, 100).

3-n-Butylquinoline (8f): Quinoline 8f (13.4 mg, 0.072 mmol, 72%) 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 (CHCl₃). Colorless oil; ¹H NMR (300 MHz, CDCl₃, ppm) δ 0.96 (t, J = 7.1 Hz, 3H), 1.33–1.50 (m, 2H), 1.61–1.82 (m, 2H), 2.81 (hep, J = 7.8 Hz, 2H), 7.52 (t, J = 8.4 Hz, 1H), 7.65 (t, J = 8.4 Hz, 1H), 7.77 (d, J = 8.4 Hz, 1H), 7.91 (s, 1H), 8.07 (d, J = 8.4 Hz, 1H), 8.79 (s, 1H); ¹³C NMR (75 MHz, CDCl₃, ppm) δ 13.9, 22.3, 32.9, 33.3, 126.5, 127.3, 128.2, 128.4, 129.1, 134.1, 135.3, 146.7, 152.1; HRMS (FAB) calcd for C₁₃H₁₆N [M+H]⁺ 186.1283, found 186.1279.

3-(1-Cyclohexenyl)quinoline (8g): Quinoline 8g (13.3 mg, 0.064 mmol, 64%) 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 (CHCl₃). Pale yellow oil; ¹H NMR
General Procedures for the Synthesis of 2-Sulfanylquinolines.

To a solution of 2-(phenylethynyl)phenyl isocyanide (1a, 0.05 mmol), benzenethiol (0.075 mmol), and THF (0.5 mL) was added triethylamine (0.5 mL), and the mixture was stirred at room temperature for 4 h. After the reaction was complete, the resulting mixture was concentrated in vacuo, and purified by PTLC on silica gel (Hex: AcOEt = 9:1) and recycle GPC (CHCl₃) to give 3-phenyl-2-phenylsulfanylquinoline (9a): 12.2 mg, 0.039 mmol, 78%) as a colorless oil. Further purification was carried out by recycle GPC (CHCl₃) for all 2-sulfanylquinolines 9.

3-Phenyl-2-phenylsulfanylquinoline (9a): Colorless oil; ¹H NMR (300 MHz, CDCl₃, ppm) δ 7.33–7.62 (m, 12H), 7.69–7.78 (m, 2H), 7.86 (s, 1H); ¹³C NMR (75 MHz, CDCl₃, ppm) δ 125.8, 126.3, 127.4, 128.3, 128.4, 128.7, 128.9, 129.4, 129.6, 130.2, 131.1, 134.9, 135.7, 138.0, 147.3, 158.3; IR (NaCl, cm⁻¹) 3057, 2934, 2858, 1497, 1331, 1188, 1128, 957, 903, 787, 752; MS (EI) m/z 328.1160, found 328.1168.

3-(4-Methylphenyl)-2-phenylsulfanylquinoline (9b): Quinoline 9b (9.3 mg, 0.029 mmol, 57%) 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 (CHCl₃). Slightly yellow oil; ¹H NMR (300 MHz, CDCl₃, ppm) δ 2.45 (s, 3H), 7.31 (d, J = 7.7 Hz, 2H), 7.36–7.44 (m, 4H), 7.47 (d, J = 8.1 Hz, 2H), 7.52–7.60 (m, 3H), 7.70–7.76 (m, 2H), 7.84 (s, 1H); ¹³C NMR (100 MHz, CDCl₃, ppm) δ 121.4, 125.7, 126.3, 127.3, 128.3, 128.7, 128.9, 129.1, 129.2, 129.4, 131.1, 132.4, 134.6, 135.0, 135.6, 138.2, 147.2, 158.4; IR (NaCl, cm⁻¹) 3062, 3024, 2920, 2873, 1616, 1591, 1577, 1508, 1475, 1439, 1387, 1362, 1339, 1132, 1082, 1024, 968, 818, 748, 689; HRMS (FAB) calcd for C₂₁H₁₈NS [M+H]+ 314.1003, found 314.0995.

3-(4-Chlorophenyl)-2-phenylsulfanylquinoline (9d): Quinoline 9d (12.7 mg, 0.037 mmol, 73%) 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 (CHCl₃). Colorless oil; ¹H NMR (400 MHz, CDCl₃, ppm) δ 7.37–7.4 (m, 3H), 7.42–7.49 (m, 4H), 7.50–7.55 (m, 2H), 7.59 (ddd, J = 1.4, 6.8, 8.3 Hz, 1H), 7.71–7.78 (m, 2H), 7.84 (s, 1H); ¹³C NMR (100 MHz, CDCl₃, ppm) δ 126.0, 126.2, 127.4, 128.3, 128.4, 128.6, 128.8, 129.7, 130.8, 130.9, 133.5, 134.4, 134.8, 136.0, 136.3, 147.2, 158.0; IR (NaCl, cm⁻¹) 3057, 1616, 1583, 1558, 1491, 1475, 1387, 1360, 1339, 1134, 1096, 1082, 1016, 968, 829, 748, 689; HRMS (FAB) calcd for C₂₁H₁₄ClNS [M]+ 347.0535, found 347.0542.

3-(4-Fluorophenyl)-2-phenylsulfanylquinoline (9e): Quinoline 9e (13.1 mg, 0.040 mmol, 80%) was obtained from 1e (0.10 mmol) according to the general procedure. The crude mixture was

(300 MHz, CDCl₃, ppm) δ 1.63–1.78 (m, 2H), 1.80–1.93 (m, 2H), 2.24–2.35 (m, 2H), 2.46–2.58 (m, 2H), 6.32–6.42 (m, 1H), 7.51 (t, J = 8.4 Hz, 1H), 7.65 (t, J = 8.4 Hz, 1H), 7.79 (d, J = 8.4 Hz, 1H), 8.01 (s, 1H), 8.07 (d, J = 8.4 Hz, 1H), 9.04 (s, 1H); ¹³C NMR (75 MHz, CDCl₃, ppm) δ 22.0, 22.9, 26.0, 27.1, 126.6, 127.2, 127.9, 128.7, 129.2, 129.9, 130.4, 133.6, 136.6, 146.5, 152.1; IR (NaCl, cm⁻¹) 3058, 2934, 2858, 1497, 1331, 1188, 1128, 957, 903, 787, 752; MS (EI) m/z 209 (M⁺, 73).
purified by PTLC on silica gel (Hex:AcOEt = 9:1) and recycle GPC (CHCl₃). White solid; mp 103–104 °C (crystallized from acetone); ¹H NMR (400 MHz, CDCl₃, ppm) δ 7.17 (t, J = 8.7 Hz, 2H), 7.36–7.40 (m, 3H), 7.44 (ddd, J = 1.4, 6.9, 7.3 Hz, 1H), 7.49–7.55 (m, 4H), 7.58 (ddd, J = 1.4, 6.9, 7.3 Hz, 1H), 7.71–7.77 (m, 2H), 7.84 (s, 1H); ¹³C NMR (100 MHz, CDCl₃, ppm) δ 115.4 (d, JCF = 21.0 Hz), 125.9, 126.2, 127.3, 128.3, 128.7, 129.5, 130.8, 131.3 (d, JCF = 7.6 Hz), 131.9, 133.6, 133.8, 134.8, 134.9, 147.2, 158.1, 162.7 (d, JCF = 247.7 Hz); IR (NaCl, cm⁻¹) 3057, 1593, 1558, 1505, 1475, 1387, 1362, 1339, 1223, 1159, 1134, 1082, 1067, 1016, 968, 835, 748, 689; HRMS (FAB) calcd for C₂₁H₁₅FNS [M+H]⁺ 332.0909, found 332.0905.

3-n-Butyl-2-phenylsulfanylquinoline (9f): Quinoline 9f (9.3 mg, 0.032 mmol, 64%) 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 (CHCl₃). Colorless oil; ¹H NMR (300 MHz, CDCl₃, ppm) δ 1.00 (t, J = 7.5 Hz, 3H), 1.48 (sex, J = 7.5 Hz, 2H), 1.77 (hep, J = 7.5 Hz, 2H), 2.86 (t, J = 7.5 Hz, 2H), 3.33–3.45 (m, 4H), 7.51 (ddd, J = 1.4, 6.8, 8.4 Hz, 1H), 7.57–7.63 (m, 2H), 7.64–7.74 (m, 2H), 7.78 (s, 1H); ¹³C NMR (75 MHz, CDCl₃, ppm) δ 13.9, 22.6, 31.5, 32.1, 125.5, 126.8, 128.2, 128.3, 128.5, 128.8, 131.1, 134.1, 134.2, 134.5, 146.7, 158.8; IR (NaCl, cm⁻¹) 3059, 2957, 2930, 2858, 1614, 1595, 1556, 1487, 1477, 1439, 1396, 1331, 1175, 1134, 1042, 1024, 953, 897, 858, 779, 748, 706, 687; HRMS (FAB) calcd for C₁₉H₁₉NS [M⁺] 293.1238, found 293.1230.
References and Notes for Supplementary Information


Supplementary Material (ESI) for Organic & Biomolecular Chemistry
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