Supporting Information for

Synthesis of 6-Thiocyanatophenanthridines by Visible Light and Air Promoted Radical Thiocyanation of 2-Isocynobiphenyls

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(L.D.S. Yadav)

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I. **General Information:** All commercially available reagents were obtained from commercial suppliers and used without further purification. Solvents were purified by the usual methods and stored over molecular sieves. All reactions were performed using oven-dried glass ware under an air atmosphere. Organic solutions were concentrated using a Buchi rotary evaporator. Column chromatography was carried out over silica gel (Merck 100–200 mesh) and TLC was performed using silica gel GF254 (Merck) plates. Melting points were determined by open glass capillary method and are uncorrected. Luxeon Rebel high power green LEDs [2.50 W, $\lambda = 535$ nm] were used for irradiation. $^1$H NMR (400 MHz) and $^{13}$C NMR (100 MHz) spectra were recorded on a Bruker AVII spectrometer in CDCl$_3$ using TMS as internal reference with chemical shift values being reported in $\delta$ (ppm). All coupling constants ($J$) are reported in Hertz (Hz). MS (EI) spectra were recorded on double focusing mass spectrometer.

II. **Stern–Volmer analysis of excited eosin Y (EY*)**

We conducted fluorescence quenching experiments (Stern–Volmer analysis) to ascertain whether the excited eosin Y (EY*) is quenched by NH$_4$SCN. It was observed that in the presence of NH$_4$SCN the emission intensity of EY* was dramatically diminished, whereas there was no such effect on addition of 2-isocyanobiphenyl.

![Graph of fluorescence intensity of eosin Y versus concentration](image)

**Figure 1** Graph of fluorescence intensity of eosin Y versus concentration
III. General Procedure for the Synthesis of 6-Thiocyanatophenanthridines 2

A mixture of isocyanobiphenyl 1 (1 mmol), NH₄SCN 2 (1.0 mmol), eosin Y (2 mol%), and CH₃CN (3 mL) was taken in a flask open to air and stirred at rt for 8-16 h under irradiation with green LEDs [2.50 W, λ = 535 nm] (Table 2). After completion of the reaction (monitored by TLC), water (5 mL) was added and the mixture was extracted with ethyl acetate (3 × 5 mL). The combined organic phase was dried over anhydrous Na₂SO₄, filtered, and evaporated under reduced pressure. The resulting crude product was purified by silica gel chromatography using a mixture of hexane/ethyl acetate (4:1) as eluent to afford an analytically pure sample of product 2.

Characterization data of compounds 2 are given below:

I. Spectral data of synthesized compounds 2

**Compound (2a).** Yellowish solid (198 mg, 84% yield), mp 152–154 °C. ¹H NMR (400 MHz, CDCl₃) δ: 8.90 (d, J = 8.4 Hz, 1H), 8.63 (d, J = 8.4 Hz, 1H), 8.51 (d, J = 8.0 Hz, 1H), 8.22 (d, J = 7.6 Hz, 1H), 7.81 (m, 1H), 7.75–7.66 (m, 3H). ¹³C NMR (100 MHz, CDCl₃): δ 158.7, 140.8, 134.8, 131.1, 130.6, 129.2, 129.0, 128.3, 126.6, 125.0, 122.7, 121.7, 120.6, 98.4; HRMS (EI) calcd for C₁₄H₈N₂S: 236.0408, found 236.0405.

**Compound (2b).** Yellow solid (235 mg, 94% yield), mp 145–147 °C. ¹H NMR (400 MHz, CDCl₃) δ 8.89 (d, J = 8.4 Hz, 1H), 8.54 (d, J = 8.0 Hz, 1H), 8.21 (s, 1H), 8.06 (d, J = 8.4 Hz, 1H), 7.75–7.71 (m, 1H), 7.65–7.61 (m, 1H), 7.50 (d, J = 8.4 Hz, 1H), 2.54 (s, 3H). ¹³C NMR(100
MHz, CDCl₃) δ 156.9, 139.2, 139.0, 134.4, 130.8, 130.7, 130.4, 128.1, 126.4, 124.6, 122.7, 121.4, 120.6, 98.6, 22.1. HRMS (EI) calcd for C₁₅H₁₀N₂S 250.0565, found 250.0569.

**Compound (2c).** Yellow solid (232 mg, 88% yield), mp 162-164 °C. ¹H NMR (400 MHz, CDCl₃): δ 8.65 (d, J = 8.6 Hz, 1H), 8.35 (t, J = 4.1 Hz, 1H), 8.20 (s, 1H), 7.87–7.83 (m, 1H), 7.77–7.73 (m, 1H), 7.48 (s, 1H), 2.86 (s, 3H), 2.61 (s, 3H). ¹³C NMR (100 MHz, CDCl₃): δ 154.9, 139.0, 138.8, 133.8, 131.6, 130.7, 127.5, 125.6, 124.8, 122.7, 122.1, 121.5, 120.4, 119.2, 22.1, 17.7. HRMS (EI) calcd for C₁₆H₁₂N₂S 264.0721, found 264.0718.

**Compound (2d).** Yellowish solid (259 mg, 89% yield), mp 124–125 °C. ¹H NMR (400 MHz, CDCl₃) δ 8.95 (d, J = 2.0 Hz, 1H), 8.57(d, J = 8.8 Hz, 1H), 8.52–8.49 (m, 1H), 8.26–8.23 (m, 1H), 7.92 (dd, J = 8.8, 2.0 Hz, 1H), 7.76–7.72 (m, 2H), 1.46 (s, 9H). ¹³C NMR (100 MHz, CDCl₃) δ 152.8, 149.6, 140.5, 132.6, 131.2, 129.0, 128.9, 128.7, 127.0, 126.1, 125.0, 124.4, 122.5, 121.4, 120.5, 98.7, 35.4, 31.2. HRMS (EI) calcd for C₁₈H₁₆N₂S 292.1034, found 292.1030.
**Compound (2e).** Yellow solid (228 mg, 86% yield), mp 140-141 °C. $^1$H NMR (400 MHz, CDCl$_3$): $\delta$ 8.57 (d, $J= 8.4$ Hz, 1H), 8.45 (d, $J= 9.0$ Hz, 1H), 8.35 (d, $J= 8.4$ Hz, 1H), 7.86 (t, $J= 7.7$Hz, 1H), 7.76–7.72 (m, 2H), 7.41 (dd, $J= 9.0$, 2.7Hz, 1H), 4.01 (s, 3H). $^{13}$C NMR (100 MHz, CDCl$_3$): $\delta$ 160.3, 146.8, 143.3, 134.2, 131.3, 127.0, 125.8, 123.1, 122.0, 121.8, 120.8, 120.6, 119.2, 110.3, 55.6. HRMS (EI) calcd for C$_{15}$H$_{10}$N$_2$OS 266.0514, found 266.0517.

![Compound 2e](image)

**Compound (2f).** Yellow solid (231 mg, 87% yield), mp 145–147 °C. $^1$H NMR (400 MHz, CDCl$_3$): $\delta$ 8.58 (d, $J= 9.2$ Hz, 1H), 8.47–8.44 (m, 1H), 8.30 (d, $J= 2.4$ Hz, 1H), 8.26-8.24 (m, 1H) 7.74-7.71 (m, 2H), 7.51 (dd, $J= 9.2$, 2.4 Hz, 1H) 4.02 (s, 3H). $^{13}$C NMR (100 MHz, CDCl$_3$): $\delta$ 157.6, 151.7, 140.0, 131.1, 129.4, 129.1, 128.2, 125.2, 124.2, 122.0, 121.5, 121.3, 109.0, 98.6, 55.5; HRMS (EI) calcd for C$_{15}$H$_{10}$N$_2$OS: 266.0514, found 266.0510.

![Compound 2f](image)

**Compound (2g).** Yellow solid (141 mg, 53% yield), mp 138-140 °C. $^1$H NMR (400 MHz, CDCl$_3$): $\delta$ 9.62–9.58 (m, 1H), 8.34–8.31 (m, 1H), 8.08–8.05 (m, 1H), 7.84–7.72 (m, 3H), 7.42 (d, $J= 8.0$ Hz, 1H), 4.02 (s, 3H). $^{13}$C NMR (100 MHz, CDCl$_3$): $\delta$ 158.2, 146.0, 142.2, 130.8, 129.0, 128.5, 128.1, 128.0, 125.0, 124.5, 123.7, 122.0, 118.0, 112.1, 55.8. HRMS (EI) calcd for C$_{15}$H$_{10}$N$_2$OS: 266.0514, found 266.0512.

![Compound 2g](image)
Compound (2h). Yellowish solid (216 mg, 80% yield), mp 150–153 °C. $^1$H NMR (400 MHz, CDCl$_3$) δ 8.90 (d, $J = 2.0$ Hz, 1H), 8.56 (d, $J = 8.8$ Hz, 1H), 8.45 (m, 1H), 8.23 (dd, $J = 8.0$, 1.6 Hz, 1H), 8.82–8.78 (m, 3H). $^{13}$C NMR(100 MHz, CDCl$_3$) δ 151.6, 140.5, 133.1, 132.8, 131.4, 131.3, 129.6, 129.4, 127.5, 124.4, 124.1, 121.6, 121.4, 97.0. HRMS (EI) calcd for C$_{14}$H$_7$ClN$_2$S 270.0018, found 270.0019.

![Image of Compound 2h](image)

Compound (2i). Yellowish solid (193 mg, 76% yield) mp 137-139 °C. $^1$H NMR (400 MHz, CDCl$_3$): δ 8.50 (d, $J = 8.4$ Hz, 1H), 8.44–8.41 (m, 1H), 8.30 (dd, $J = 9.2$, 5.6Hz, 1H), 8.20 (dd, $J = 9.9$, 2.7Hz, 1H), 7.95 (td, $J = 7.2$, 1.1Hz, 1H), 7.87–7.82 (m, 1H), 7.59–7.53 (m, 1H). $^{13}$C NMR (100 MHz, CDCl$_3$): δ 162.6 (d, $J = 249.2$ Hz) 145.8, 138.5, 133.5, 133.4, 131.3, 128.6, 126.7, 126.0, 122.6, 121.8, 121.7, 118.4, 107.1 HRMS (EI) calcd for C$_{14}$H$_7$FN$_2$S 254.0314, found 254.0317

![Image of Compound 2i](image)

Compound (2j). Yellowish solid (224 mg, 73% yield), mp 149–1151 °C. $^1$H NMR (400 MHz, CDCl$_3$) δ 8.95 (d, $J = 8.8$ Hz, 1H), 8.62 (d, $J = 8.0$ Hz, 1H), 8.56 (d, $J = 8.4$ Hz, 1H), 8.52 (s, 1H), 7.92–7.87 (m, 2H), 7.82–7.78 (m, 1H). $^{13}$C NMR (100 MHz, CDCl$_3$) δ 154.1, 140.0, 134.1, 131.2, 131.1, 128.6, 128.5, 127.8, 127.1, 124.7, 123.8 (q, $J = 270.8$ Hz) 123.1, 123.0, 121.2, 97.8. HRMS (EI) calcd for C$_{15}$H$_7$F$_3$N$_2$S 308.0282, found 308.0279.

![Image of Compound 2j](image)
Compound (2k). Yellowish solid (193 mg, 71% yield), mp 163-167 °C. \(^1\)H NMR (400 MHz, CDCl\(_3\)): \(\delta 8.52 (d, J = 8.4\) Hz, 1H), 8.46–8.42 (m, 1H), 8.03–7.99 (m, 2H), 7.91–7.87 (m, 1H), 7.38–7.34 (m, 1H). \(^13\)C NMR (100 MHz, CDCl\(_3\)): \(\delta 162.0 (d, J = 252.1\) Hz) 159.7 (d, \(J = 262.1\) Hz) 146.0, 132.7, 131.8, 129.3, 128.7, 127.7, 126.1, 123.0, 122.1, 121.5, 105.0, 103.0. HRMS (EI) calcd for C\(_{14}\)H\(_6\)F\(_2\)N\(_2\)S 272.0220, found 272.0216.

Compound (2l). Brown solid (193 mg, 69% yield), mp 175-178 °C. \(^1\)H NMR (400 MHz, CDCl\(_3\)): \(\delta 9.16 (d, J = 2.3\) Hz, 1H), 8.79–8.76 (m, 2H), 8.56 (dd, \(J = 9.2, 2.4\) Hz, 1H), 8.45 (t, \(J = 4.2\) Hz, 1H), 8.14–8.10 (m, 1H), 7.99–7.95 (m, 1H). \(^13\)C NMR (100 MHz, CDCl\(_3\)): \(\delta 149.0, 147.7, 141.1, 132.8, 132.4, 130.1, 129.4, 126.7, 126.4, 123.6, 123.3, 122.7, 122.5, 121.3. HRMS (EI) calcd for C\(_{14}\)H\(_7\)N\(_3\)O\(_2\)S 281.0259, found 281.0262.

Compound (2m). Orange solid (185 mg, 71% yield), mp 186–189 °C. \(^1\)H NMR (400 MHz, CDCl\(_3\)) \(\delta 9.25 (s, 1H), 8.74 (d, J = 8.8\) Hz, 1H), 8.52 (d, \(J = 8.0\) Hz, 1H), 8.26 (d, \(J = 8.4\) Hz, 1H), 8.01 (d, \(J = 8.4\) Hz, 1H), 7.93–7.78 (m, 2H). \(^13\)C NMR(100 MHz, CDCl\(_3\)) \(\delta 152.0, 141.4, 137.1, 133.4, 131.7, 131.5, 131.1, 130.0, 124.0, 123.6, 122.3, 120.1, 118.2, 110.4, 97.4. HRMS (EI) calcd for C\(_{15}\)H\(_7\)N\(_3\)S 261.0361, found 261.0357.
**Compound (2n).** Yellow solid (220 mg, 75% yield), mp 161–162 °C. $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 9.65 (s, 1H), 8.71 (d, $J = 8.8$ Hz, 1H), 8.56 (d, $J = 8.0$ Hz, 1H), 8.45 (d, $J = 8.4$ Hz, 1H), 8.27 (d, $J = 8.0$ Hz, 1H), 8.86–8.72 (m, 2H), 4.05 (s, 3H). $^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ 166.1, 153.1, 141.3, 137.6, 131.2, 130.5, 130.3, 130.0, 129.4, 128.0, 124.1, 123.0, 122.3, 120.1, 98.0, 52.6. HRMS (EI) caleld for C$_{16}$H$_{10}$N$_2$O$_2$S 294.0463, found 294.0467.

![Image of compound 2n](image)

**Compound (2o).** Yellowish solid (220 mg, 74% yield), mp 184–186 °C. $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 8.70 (s, 1H), 8.67 (s, 1H), 8.21 (d, $J = 8.8$ Hz, 1H), 7.74–7.40 (dd, $J = 8.8$, 2.0 Hz, 1H), 7.56 (s, 1H), 3.06 (s, 3H), 2.60 (s, 3H). $^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ 153.0, 139.8, 137.0, 136.5, 135.5, 134.0, 132.6, 131.4, 128.4, 127.1, 126.4, 125.6, 122.2, 98.6, 26.7, 21.7. HRMS (EI) caleld for C$_{16}$H$_{11}$ClN$_2$S 298.0331, found 298.0328.

![Image of compound 2o](image)

**Compound (2p and 2p').** Yellow solid (188 mg, 71 % yield), $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 8.85 (d, $J = 9.6$ Hz, 1H), 8.45 (d, $J = 8.0$ Hz, 1.6H), 8.22–8.18 (m, 2.2H), 7.95 (s, 1H), 7.78–7.67 (m, 3.8H), 7.31 (d, $J = 9.6$ Hz, 1H), 7.14 (d, $J = 7.6$ Hz, 0.6H), 4.05 (s, 3H), 4.02 (s, 1.8H). $^{13}$C
NMR (100 MHz, CDCl₃) δ 161.0, 156.5, 152.7, 152.5, 141.1, 140.5, 137.4, 137.1, 131.5, 131.2, 130.5, 130.2, 129.2, 128.7, 128.5, 124.7, 124.3, 122.3, 121.8, 116.8, 115.3, 114.6, 113.7, 109.5, 103.5, 98.5, 55.6, 54.8. HRMS (ESI) calcd for C₁₅H₁₀N₂OS 266.0514, found 266.0518.

II. Copies of $^1$H and $^{13}$C NMR spectra of the synthesized compounds