Copper-Promoted Carbon-Nitrogen Bond Formation with 2-Iodo-Selenophene and Amides

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SUPPORTING INFORMATION

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Materials and Methods

Proton nuclear magnetic resonance spectra (^1H NMR) were obtained at 400 MHz. Spectra were recorded in CDCl_3 solutions. Chemical shifts are reported in ppm, referenced to the solvent peak of CDCl_3 or tetramethylsilane (TMS) as the external reference. Data are reported as follows: chemical shift (δ), multiplicity, coupling constant (J) in Hertz and integrated intensity. Carbon-13 nuclear magnetic resonance spectra (^{13}C NMR) were obtained at 100 MHz. Chemical shifts are reported in ppm, referenced to the solvent peak of CDCl_3 . Abbreviations to denote the multiplicity of a particular signal are s (singlet), d (doublet), t (triplet), q (quartet), quint (quintet), sex (sextet) and m (multiplet). High resolution mass spectra were recorded on a double focusing magnetic sector mass spectrometer using EI at 70 eV. Column chromatography was performed using silica gel (230-400 mesh) following the methods described by Still.¹ Thin layer chromatography (TLC) was performed using silica gel GF₂₅₄, 0.25 mm thickness. For visualization, TLC plates were either placed under ultraviolet light, or stained with iodine vapor, or acidic vanillin. The following solvents were dried and purified by distillation from the reagents indicated: tetrahydrofuran from sodium with a benzophenone ketyl indicator. All other solvents were ACS or HPLC grade unless otherwise noted. Air- and moisture-sensitive reactions were conducted in flame-dried or oven dried glassware equipped with tightly fitted rubber septa and under a positive atmosphere of dry nitrogen or argon. Reagents and solvents were handled using standard syringe techniques. Temperatures above room temperature were maintained by use of a mineral oil bath with an electrically heated coil connected to a controller.

General Procedure for the Preparation of the Carbon-Nitrogen bond formation:

To a stirred solution of benzamide **3b** (0.073 g, 0.6 mmol) and 2-iodo-selenophene **2** (0.128 g, 0.5 mmol) in 1,4-dioxane (3mL) under argon atmosphere were added CuI (0.01 g, 10 mol%), and ethylenediamine (0.0067 g, 20 mmol %) followed by K_3PO_4 (0.127 g, 0.6 mmol) and stirred at reflux for 24 h. The reaction mixture was filtered and the filtrate was concentrated in vacuo. The crude product was separated on SiO_2 column chromatography using hexane and EtOAc (3:1) as eluents to afford the coupled products

¹ Still, W.C.; Kahn, M.; Mitra, A. *J. Org. Chem.* **1978**, *43*, 2923-2925

as white needles. **N-(selenophen-2-yl)benzamide (4b)**: Yield: 0.096 g (77%) ^1H NMR: (CDCl_3 , 400 MHz) δ : 9.31(s, 1H); 7.89 (d, $J = 7.4$ Hz, 2H), 7.6(d, $J = 6.16$ Hz, 1H), 7.55-7.16 (m, 1H), 7.46-7.42 (m, 2H), 7.16-7.13 (m, 1H), 6.9(d, $J = 3.39$ Hz, 1H). ^{13}C NMR: (CDCl_3 , 100 MHz) δ : 163.6, 141.6, 132.9, 132.2, 128.9, 127.1, 126.0, 123.7, 112.6. MS m/z (relative intensity): 251(39), 105(100), 95(8.7), 77(69), 51(35). HRMS calcd. for $\text{C}_{11}\text{H}_9\text{NOSe}$: 250.9849. Found: 250.9855.

N-(selenophen-2-yl)acetamide (4a): Yield: 0.47 g (48%). ^1H NMR: (CDCl_3 , 400 MHz) δ : 8.94(d, $J = 6.0$ Hz, 1H), 7.55(d, $J = 4.7$ Hz, 1H), 7.09-7.07(m, 1H), 6.96(s, 1H), 2.21(s, 3H). ^{13}C NMR: (CDCl_3 , 100 MHz) δ : 166.5, 141.4, 125.8, 123.2, 111.8, 23.15. MS m/z (relative intensity): 189(4.7), 147(3.8), 44(100), 40(66). HRMS calcd. for $\text{C}_6\text{H}_7\text{NOSe}$: 188.9692. Found: 188.9701.

N-phenyl-N-(selenophen-2-yl)benzamide (4c): Yield: 0.12 g (70%). ^1H NMR: (CDCl_3 , 400 MHz) δ : 7.71(dd, $J = 0.92$ Hz and $J = 6.0$ Hz, 1H), 7.39-7.16 (m, 10H), 7.05(dd, $J = 6.16$ Hz and $J = 4.16$ Hz, 1H), 6.3(dd, $J = 0.92$ Hz and $J = 4.16$ Hz, 1H). ^{13}C NMR: (CDCl_3 , 100 MHz) δ : 167.7, 146.8, 141.4, 135.2, 129.7, 129.6, 129.4, 128.5, 128.4, 127.8, 127.7, 125.7, 125.4. MS m/z (relative intensity): 327(8.3), 105(100), 95(12.5), 77(41.6), 51(16). HRMS calcd. for $\text{C}_{17}\text{H}_{13}\text{NOSe}$: 327.0162. Found: 327.0169.

4-amino-N-(selenophen-2-yl)benzamide (4d): Yield: 0.06 g (45%). ^1H NMR: ($\text{DMSO}-d_6$, 400 MHz) δ : 11.27(s, 1H), 7.76 (d, $J = 8.77$ Hz, 2H), 7.49 (d, $J = 6.2$ Hz, 1H), 7.09(dd, $J = 0.8$ Hz and $J = 4.09$ Hz, 1H), 6.96 (dd, $J = 0.8$ Hz and $J = 4.09$ Hz, 1H), 6.62(d, $J = 8.77$ Hz, 2H), 5.81(s, 2H). ^{13}C NMR: ($\text{DMSO}-d_6$, 100 MHz) δ : 163.32, 152.9, 143.5, 129.8, 126.6, 122.4, 119.4, 113.1, 111.9. MS m/z (relative intensity): 265(0.88), 207(9), 105(85), 77(47), 40(100). HRMS: calcd. for $\text{C}_{11}\text{H}_{10}\text{N}_2\text{OSe}$: 265.9958. Found: 265.9964.

1-(selenophen-2-yl)pyrrolidin-2-one (4e): Yield: 0.08 g (77%). ^1H NMR: (CDCl_3 , 400 MHz) δ : 7.61(d, $J = 5.85$ Hz, 1H), 7.04(dd, $J = 4.06$ Hz and $J = 6.06$ Hz, 1H), 6.50(d, $J = 3.9$ Hz, 1H), 3.83(t, $J = 7.2$ Hz, 2H), 2.56(t, $J = 8.16$ Hz, 2H), 2.16(quint, $J = 7.55$ Hz, 2H). ^{13}C NMR: (CDCl_3 , 100 MHz) δ : 171.9, 142.06, 126.73, 123.10, 111.14, 48.55, 31.08, 17.44. MS m/z (relative intensity): 215(100), 160(62), 106(45.8). HRMS calcd. for $\text{C}_8\text{H}_9\text{NOSe}$: 214.9849. Found: 214.9855.

1-(selenophen-2-yl)piperidin-2-one (4f): Yield: 0.026 g (23%). ^1H NMR: (CDCl_3 , 400 MHz) δ : 7.6(d, $J = 6.10$ Hz, 1H), 7.14(dd, $J = 4.03$ Hz and $J = 6.07$ Hz, 1H), 6.67(d, $J = 3.76$ Hz, 1H), 3.86(t, $J = 6.24$ Hz, 2H), 2.65(t, $J = 6.62$ Hz, 2H), 1.89-1.78(m, 4H). ^{13}C

NMR: (CDCl₃, 100 MHz) δ : 171.93, 145.7, 125.8, 123.1, 111.3, 49.8, 37.1, 29.8, 23.3. MS m/z (relative intensity): 229(100), 200(23), 173(23), 160(19), 120(69), 93(19). HRMS calcd for C₉H₁₁NOSe: 229.0006. Found: 229.0012

1-(selenophen-2-yl)azepan-2-one (4g): Yield: 0.025 g (21%). ¹H NMR: (CDCl₃, 400 MHz) δ : 7.51(d, J = 1.02 Hz and J = 6.10 Hz, 1H), 7.14(dd, J = 4.26 Hz and J = 6.17 Hz, 1H), 6.65(dd, J = 0.82 Hz and J = 4.19 Hz, 1H), 3.97-3.92(m, 2H), 2.75-2.70(m, 2H), 1.73(s, broad, 6H). ¹³C NMR: (CDCl₃, 100 MHz) δ : 172.9, 145.7, 125.4, 124.8, 111.3, 49.9, 37.1, 29.2, 27.0, 23.3. MS m/z (relative intensity): 243(3.25), 207(12), 147(23), 96(47), 44(83), 41(84), 40(100). HRMS cald. for: C₁₀H₁₃NOSe: 243.0162. Found: 243.0169.

3-(selenophen-2-yl)oxazolidin-2-one (4h): Yield: 0.092 g (90%) ¹H NMR: (CDCl₃, 400 MHz) δ : 7.56(d, J = 5.8 Hz, 1H), 7.07(dd, J = 4.02 Hz and J = 6.13 Hz, 1H), 6.42(d, J = 3.8 Hz, 1H), 4.49(t, J = 7.89 Hz, 2H), 4.02(t, J = 8.18 Hz, 2H) ¹³C NMR: (CDCl₃, 100 MHz) δ : 155.1, 142.1, 126.7, 123.1, 111.1, 62.3, 45.7. MS m/z (relative intensity): 216(100), 158(58), 93(24). HRMS cald. for C₉H₁₀OSe: C₇H₇NO₂Se: 216.9641. Found: 216.9649.

(S)-4-benzyl-3-(selenophen-2-yl)oxazolidin-2-one (4i): Yield: 0.15 g (95%) ¹H NMR: (CDCl₃, 400 MHz) δ : 7.65(d, J = 0.8 Hz and J = 5.36 Hz, 1H), 7.36-7.27(m, 4H), 7.20-7.16(m, 2H), 6.74(d, J = 4.09 Hz, 1H), 4.61-4.58(m, 1H), 4.31(t, J = 8.20 Hz, 1H), 4.28(dd, J = 2.9 Hz and J = 6.6 Hz, 1H), 3.27(dd, J = 2.9 Hz and J = 14.0 Hz, 1H), 2.96(dd, J = 8.14 Hz and J = 14 Hz, 1H). ¹³C NMR: (CDCl₃, 100 MHz) δ : 154.8, 142.4, 134.9, 129.4, 129.0, 127.5, 126.9, 123.7, 112.2, 66.5, 58.0, 36.1. MS m/z (relative intensity): 307(23), 216(45), 207(32), 172(56), 91(89), 80(60), 44(100). HRMS calcd. for C₁₄H₁₄NO₂Se: 307.0111. Found: 307.0119. [α]_D²⁰ = +23°, CH₂Cl₂ (c = 1.14)

(S)-4-isopropyl-3-(selenophen-2-yl)oxazolidin-2-one (4j): Yield: 0.10 g (78%) ¹H NMR: (CDCl₃, 400 MHz) δ : 7.55 (dd, J = 0.80 Hz and J = 6.17 Hz, 1H), 7.02 (dd, J = 4.08 Hz and J = 6.13 Hz, 1H), 6.49 (dd, J = 0.80 Hz and J = 4.2 Hz, 1H), 4.44-4.31(m, 3H), 2.47(sept, J = 6.72 Hz, 1H), 0.91(d, J = 7.06 Hz, 3H), 0.79(d, J = 6.72 Hz, 3H). ¹³C NMR: (CDCl₃, 100 MHz) δ : 155.2, 142.4, 126.7, 123.7, 112.7, 63.6, 61.8, 26.5, 17.5, 14.1. MS m/z (relative intensity): 259(100), 216(65), 172(91), 145(23), 80(50). HRMS calcd. for C₁₀H₁₄NO₂Se: 259.0112. Found: 259.0118. [α]_D²⁰ = +35°, CH₂Cl₂ (c = 0.9).

4-(S)-sec-butyl-3-(selenophen-2-yl)oxazolidin-2-one (4k): Yield: 0.088 g (65%) ^1H NMR: (CDCl_3 , 400 MHz) δ : 7.62(dd, $J = 0.9$ Hz and $J = 6.0$ Hz, 1H), 7.11(dd, $J = 4.09$ Hz and $J = 6.13$ Hz, 1H), 6.82(dd, $J = 0.8$ Hz and $J = 3.08$ Hz, 1H), 4.48-4.45(m, 1H), 4.41(t, $J = 8.47$ Hz, 1H), 4.32(dd, $J = 2.63$ Hz and $J = 8.08$ Hz, 1H), 2.31(sept, $J = 2.98$ Hz, 1H), 1.30(quint, $J = 7.30$ Hz, 2H), 1.01(t, $J = 7.30$ Hz, 3H), 0.86(d, $J = 7.01$ Hz, 3H) ^{13}C NMR: (CDCl_3 , 100 MHz) δ : 155.3, 142.6, 126.7, 123.7, 112.5, 60.1, 63.6, 33.2, 25.3, 11.9, 11.6. MS m/z (relative intensity): 273(30), 216(41.0), 172(74.5), 145(29), 80(67), 55(86), 41(100). HRMS calcd. for: $\text{C}_{11}\text{H}_{16}\text{O}_2\text{NSe}$: 273.0267. Found: 273.0274. $[\alpha]_{\text{D}}^{20} = +47^0$, CH_2Cl_2 ($c = 0.9$).

1-(selenophen-2-yl)-1H-pyrrole (4l): Yield: 0.049 g (50%). ^1H NMR: (CDCl_3 , 400 MHz) δ : 7.68(dd, $J = 1.02$ Hz and $J = 5.88$ Hz, 1H); 7.20-7.15(m, 1H), 7.00-6.97(m, 3H); 6.31-6.28(m, 2H). ^{13}C NMR: (CDCl_3 , 100 MHz) δ : 136.5, 128.3, 124.7, 121.6, 117.3, 110.6. MS m/z (relative intensity): 197(100), 169(19.5), 117(91), 90(23). HRMS calcd. for: $\text{C}_8\text{H}_7\text{NSe}$: 196.9744. Found: 196.9751

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