Synthesis of a Novel C₂-Symmetric Thiourea and Its Application in the Pd-Catalyzed Cross-Coupling Reactions with Arenediazonium Salts under Aerobic Conditions *

Mingji Dai,[†] Bo Liang,[†] Cuihua Wang,[†] Jiahua Chen^{*,†} and Zhen Yang^{*,†,‡}

Key Laboratory of Bioorganic Chemistry and Molecular Engineering of Ministry of Education, Department of Chemical Biology, College of Chemistry, Peking University, Beijing, 100871 China, and VivoQuest, Inc. 711 Executive Blvd. Valley Cottage, NY, 10989

Supporting information

General Methods

All reagents were used as received. All solvents were distilled prior to use. The boiling point of petroleum ether is between 60-90 °C. For chromatography, 200-300 mesh silica gel (Qingdao, China) was employed. ¹H-NMR and ¹³C-NMR were recorded at 300 MHz and 75 MHz with Varian Mercury 300 spectrometer or at 400 MHz and 100.6 MHz with Bruker ARX400 spectrometer. Abbreviations for ¹H NMR: s = singlet, d = doublet, t = triplet, q = quartlet, m = multiplet, or br = broad. Chemical shifts are reported in ppm using tetramethylsilane as internal standard. Mass spectra were obtained on a VG ZAB-HS mass spectrometer. IR spectra were recorded with a Nicolet 5MX-S infrared spectrometer.

Ligand preparation:

Synthesis of chiral intermediate 2: Palladium acetate (11.2 mg, 0.05 mmol), BINAP (62.2mg, 0.10mmol), (1R, 2R)-(-)-1,2-diaminocyclohexane **1** (Aldrich) (114.2 mg, 1.0 mmol) and 2-bromotoluene (359.2 mg, 2.1 mmol) were added to Shlenk flask with anhydrous toluene (30 ml) and degassed under nitrogen for 20min. Then sodium *t*-butoxide (288.3 mg, 3.0 mmol) was added and the reaction mixture was heated to 100 °C for 20 hours. The mixture was cooled to room temperature, and diluted with

hexanes (50 ml), and then filtered through a plug of silica. The compound absorbed on the silica gel was washed with methylene chloride, and the elude was concentrated under vacuum. The residue was purified by flash chromatography (PE/EA = 8/1) to give a white solid (264.6 mg, 90%). mp: 83-84 °C; $[\alpha]_{\text{D}(589\text{nm})}^{20} = -25.8^\circ$ (C = 3.8 mg/mL, CHCl₃); ¹H NMR (300 MHz, CDCl₃): δ 1.25-1.48 (m, 4H), 1.80 (m, 2H), 2.02 (s, 6H), 2.34-2.37 (m, 2H), 3.36 (m, 2H), 6.67-6.78 (m, 4H), 7.04 (d, 2H), 7.11-7.16 (m, 2H); ¹³C NMR (75 MHz, CDCl₃): δ 17.57, 24.71, 32.78, 57.61, 110.26, 117.02, 122.76, 126.99, 130.34, 145.79; IR (thin film, cm⁻¹): 3480, 3397, 3033, 2947, 2850, 1605, 1504, 1445, 1314, 1255, 1140, 1043, 981, 744; MS m/z (EI) 294 (M⁺), 262, 215, 183, 170, 152, 139, 107, 77.

Synthesis of ligand 3: Diamine **2** (294 mg, 1.0mmol) was added to a mixed solvent (60mL of 1% NaHCO₃ water solution and 60mL of dioxane). To this solution was added thiophosgene (230mg, 2.0mmol) and the mixture was stirred at room temperature for 24 hours. The reaction mixture was extracted with ethyl acetate for three times (3 x 50mL), and the combined organic phase was washed with water, and dried over Na₂SO₄. The solvent was removed under vacuum and the residue was purified by chromatography (PE/EA = 4/1) to give the ligand **3** 319.2 mg as white solids in a 95% yield; mp: 120 °C (decompose); $[\alpha]_{\text{D}(589\text{nm})}^{20} = -2.6^\circ$ (C = 4.2 mg/mL, CHCl₃); ¹H NMR (400MHz, CDCl₃): δ 1.33-1.52 (m, 4H), 1.82-1.85 (m, 4H), 2.40 (s, 6H), 3.65-3.67 (m, 2H), 7.16 (d, 2H), 7.18-7.33 (m, 6H); ¹³C NMR (100MHz, CDCl₃): δ 18.39, 24.24, 28.27, 68.98, 125.82, 127.02, 127.96, 130.97, 137.83, 138.83, 186.49; IR (thin film, cm⁻¹): 3033, 2936, 2866, 1639, 1497, 1453, 1393, 1287, 1146, 721; M/z (EI) 336(M⁺), 321, 307, 293, 275, 255, 241, 118, 91.

Preparation of arenediazonium tetrafluoroborate salts

General Procedure

To 1.06g of boron trifluoride etherate (7.5mmol) contained in a three-neck round-bottom flask fitted with two addition funnels and a reflux condenser connected to a gas buret was added 5.0mmol of the aromatic amine in a minimal volume of the anhydrous solvent, usually 10mL. Prior to addition of the amine, the boron trifluoride etherate was cooled at -15 °C in an ice-acetone bath. If a solid amine-BF₃ complex had formed, additional solvent or ethyl ether was added to produce a homogeneous solution. *tert*-butyl nitrite (0.618 g, 6.0 mmol) in 5mL of the same solvent was added dropwise to the rapidly stirred reaction solution over a 10-min period. Following complete addition, the temperature of the reaction solution was maintained at -15 °C for

10min and then allowed to warm to 5 °C in an ice-water bath over a 20-min period. A crystalline precipitation usually formed during the addition of *tert*-butyl nitrite, and following the 20-min period at 5 °C precipitation was complete. Pentane (40 mL) was then added to the reaction solution, and the solid was suction filtered, washed with cold ether, air-dried and weighed.

Synthesis of compound 5-14

General Procedure

Pd(OAc)₂ (0.005 mmol), lignad **3** (0.005 mmol), olefins or arylboronic acid (0.6mmol) and arenediazonium tetrafluoroborate (0.5mmol) were mixed in methanol (5 mL), and the reaction mixture was stirred at room temperature for 4 hours under aerobic conditions. The reaction was worked up by removing the solvent under vacuum and the residue was purified by silica gel chromatography.

Compound 4a: ¹H NMR (300MHz, CDCl₃): δ 2.36 (s, 3H), 7.07 (s, 2H), 7.16 (dd, *J* = 7.8 Hz, 2H), 7.21-7.26 (m, 1H), 7.35 (t, 2H), 7.41 (dd, *J* = 7.8 Hz, 2H), 7.50 (d, *J* = 7.2 Hz, 2H); ¹³C NMR (75 MHz, CDCl₃): δ 21.21, 126.35, 126.39, 127.35, 127.65, 128.57, 128.61, 129.35, 134.49, 137.45; MS *m/z* (EI) 194 (M⁺), 179, 165, 152, 115, 96, 83, 69, 57.

Compound 5a: ¹H NMR (300MHz, CDCl₃): δ 7.12 (s, 2H), 7.26-7.30 (m, 2H), 7.35-7.40 (m, 4H), 7.52-7.55 (m, 4H); ¹³C NMR (75MHz, CDCl₃): δ 126.50, 127.61, 128.67, 137.31; MS *m/z* (EI) 180 (M⁺), 165, 152, 115, 102, 89, 77, 76, 63, 51, 39.

Compound 6a: ¹H NMR (400 MHz, CDCl₃): δ 2.37 (s, 3H), 7.06-7.08 (m, 3H), 7.23-7.26 (m, 2H), 7.31-7.37 (m, 4H), 7.49-7.52 (m, 2H); ¹³C NMR (100 MHz, CDCl₃): δ 21.45, 123.71, 126.48, 127.21, 127.54, 128.46, 128.47, 128.57, 128.67, 128.79, 137.26, 137.42, 138.22; MS *m/z* (EI) 194 (M⁺), 179, 165, 152, 115, 91, 89.

Compound 7a: ¹H NMR (300 MHz, CDCl₃): δ 7.04 (s, 2H), 7.26-7.42 (m, 7H), 7.48 (d, *J* = 7.5 Hz, 2H); ¹³C NMR (75 MHz, CDCl₃): δ 126.52, 127.32, 127.63, 127.84, 128.70,

128.80, 129.28, 133.13, 135.81, 136.94; MS m/z (EI) 214(M⁺), 178, 152, 115, 89, 76, 74, 51, 39, 27.

Compound 8a: ¹H NMR (300 MHz, CDCl₃): δ7.04 (d, *J* = 16.2 Hz, 1H), 7.12-7.28 (m, 3H), 7.34 (t, 3H), 7.47-7.53 (m, 3H), 7.62-7.65 (m, 1H); ¹³C NMR (75 MHz, CDCl₃): δ124.68, 126.41, 126.78, 126.85, 128.00, 128.46, 128.67, 129.76, 131.20, 133.39, 135.36, 137.00; MS m/z (EI) 214(M⁺), 179, 152, 139, 136, 123, 109, 102, 89, 76, 69, 57, 51, 27.

Compound 9a: ¹H NMR (300 MHz, CDCl₃): δ7.13 (d, *J* = 13.5 Hz, 1H), 7.24 (s, 1H), 7.30-7.43 (m, 3H), 7.54-7.57 (m, 2H), 7.61-7.64 (m, 2H), 8.20-8.23 (m, 2H); ¹³C NMR (75 MHz, CDCl₃): δ124.08, 126.20, 126.80, 126.97, 128.80, 128.84, 133.25, 136.11, 143.79, 146.69; MS m/z (EI) 225(M⁺), 208, 195, 178, 165, 152, 131, 115, 102, 89, 77, 63, 51, 39, 27.

Compound 10a: ¹H NMR (300 MHz, CDCl₃): δ7.04 (d, *J* = 16.2 Hz, 1H), 7.28-7.38 (m, 4H), 7.49-7.59 (m, 4H), 7.70-7.73 (m, 1H), 7.89-7.92 (m, 1H); ¹³C NMR (75 MHz, CDCl₃): δ123.35, 124.62, 126.97, 127.84, 128.03, 128.50, 128.69, 132.86, 132.98, 133.73, 136.37, 147.87; MS m/z (EI) 225 (M⁺), 208, 196, 178, 165, 152, 139, 134, 119, 105, 92, 77, 65, 64, 51, 39, 27.

Compound 11a: ¹H NMR (300 MHz, CDCl₃): δ7.05 (d, *J* = 16.5 Hz, 1H), 7.17 (d, *J* = 16.5 Hz, 1H), 7.26-7.39 (m, 3H), 7.42-7.51 (m, 3H), 7.72 (d, *J* = 8.4 Hz, 1H), 8.02-8.05 (m, 1H), 8.28-8.29 (m, 1H); ¹³C NMR (75 MHz, CDCl₃): δ120.71, 121.83, 125.89, 126.71, 128.39, 128.71, 129.39, 131.56, 132.09, 136.11, 138.97, 148.54; MS m/z (EI) 225(M⁺), 178, 165, 152, 139, 121, 115, 102, 89, 76, 63, 43, 39, 27.

Compound 4b: ¹H NMR (300 MHz, CDCl₃): δ2.37 (s, 3H), 3.79 (s, 3H), 6.39 (d, *J* = 15.9 Hz, 1H), 7.18 (d, *J* = 8.4 Hz, 2H), 7.42 (d, *J* = 8.1 Hz, 2H), 7.68 (d, *J* = 15.9 Hz,

1H); ^{13}C NMR (75 MHz, CDCl_3): δ 21.40, 51.57, 116.66, 128.03, 129.57, 131.62, 140.68, 144.84, 167.59; MS m/z (EI) 176(M^+), 161, 145, 131, 115, 102, 91, 65, 57, 51, 39.

Compound 5b: ^1H NMR (300 MHz, CDCl_3): δ 3.78(s, 3H), 6.43 (d, J = 15.9 Hz, 1H), 7.34-7.36 (m, 3H), 7.47-7.50 (m, 2H), 7.68 (d, J = 16.5Hz, 1H); ^{13}C NMR (75 MHz, CDCl_3): δ 51.46, 117.63, 127.90, 128.71, 130.11, 134.21, 144.68, 167.20; MS m/z (EI) 162 (M^+), 131, 103, 91, 77, 63, 51, 39.

Compound 6b: ^1H NMR (300MHz, CDCl_3): δ 2.34 (s, 3H), 3.78 (s, 3H), 6.41 (d, J = 15.9 Hz, 1H), 7.15-7.29 (m, 4H), 7.65 (d, J = 15.9 Hz, 1H); ^{13}C NMR: δ 21.10, 51.43, 117.37, 125.10, 128.57, 128.60, 130.96, 134.17, 138.33, 144.87, 167.29; MS m/z (EI) 176 (M^+), 161, 145, 131, 115, 102, 91, 77, 65, 58, 51, 39, 27.

Compound 7b: ^1H NMR (300 MHz, CDCl_3): δ 3.81(s, 3H), 6.40 (d, J = 16.2 Hz, 1H), 7.36 (d, J = 8.7Hz, 2H), 7.44(d, J = 8.4 Hz, 2H), 7.64 (d, J = 16.2 Hz, 1H); ^{13}C NMR: δ 51.72, 118.32, 129.11, 129.17, 132.81, 136.14, 143.35, 167.10; MS m/z (EI) 196 (M^+), 165, 151, 137, 123, 109, 101, 95, 75, 69, 57, 41, 27.

Compound 8b: ^1H NMR (300 MHz, CDCl_3): δ 3.81 (s, 3H), 6.42 (d, J = 16.2 Hz, 1H), 7.24-7.30 (m, 2H), 7.37-7.40 (m, 1H), 7.57-7.60 (m, 1H), 8.08 (d, J = 15.9 Hz, 1H); ^{13}C NMR (300 MHz, 75.46): δ 51.64, 120.27, 126.93, 127.44, 129.99, 130.91, 132.45, 134.75, 140.39, 166.70; MS m/z (EI) 196 (M^+), 161, 146, 137, 118, 101, 75, 63, 51, 43.

Compound 9b: ^1H NMR (300 MHz, CDCl_3): δ 3.85 (s, 3H), 6.58 (d, J = 15.9 Hz, 1H), 7.68-7.76 (m, 3H), 8.26 (d, J = 8.7 Hz, 2H); ^{13}C NMR: δ 52.01, 122.03, 124.12, 128.60, 140.42, 141.84, 148.46, 166.40; MS m/z (EI) 207 (M^+), 190, 176, 161, 160, 130, 118, 102, 90, 76, 63, 51, 39.

Compound 10b: ^1H NMR (300 MHz, CDCl_3): δ 3.84 (s, 3H), 6.38 (d, J = 15.9 Hz, 1H), 7.57-7.68 (m, 3H), 8.04-8.07 (m, 1H), 8.12 (d, J = 15.9 Hz, 1H); ^{13}C NMR (75 MHz, CDCl_3): δ 51.93, 122.78, 124.84, 129.06, 130.27, 130.46, 133.48, 140.08, 148.24, 166.14; MS m/z (EI) 207 (M^+), 176, 161, 148, 130, 120, 102, 92, 77, 62, 51, 39, 29.

Compound 11b: ^1H NMR (300MHz, CDCl_3): δ 3.85 (s, 3H), 6.58 (d, J = 15.9 Hz, 1H), 7.61 (t, 1H), 7.74 (d, J = 15.9 Hz, 1H), 7.85 (d, J = 8.4 Hz, 1H), 8.22-8.26 (m, 1H), 8.38-8.39 (m, 1H); ^{13}C NMR: (75 MHz, CDCl_3): δ 51.91, 120.87, 122.33, 124.44, 129.89, 133.54, 136.01, 141.86, 148.58, 166.46; MS m/z (EI) 207 (M^+), 190, 176, 162, 160, 149, 129, 118, 116, 102, 90, 76, 71, 57, 50, 39.

Compound 12b: ^1H NMR (300 MHz, CDCl_3): δ 3.82 (s, 3H), 6.31 (d, J = 15.9 Hz, 1H), 7.01-7.06 (m, 1H), 7.34 (t, 1H), 7.53-7.55 (m, 1H), 7.87-7.92 (m, 2H); ^{13}C NMR (75 MHz, CDCl_3): δ 51.76, 101.08, 120.68, 127.25, 128.46, 131.14, 137.62, 139.89, 147.76, 166.55; MS m/z (EI) 288 (M^+), 161, 146, 130, 118, 102, 90, 75, 74, 51, 39.

Compound 13b: ^1H NMR (300 MHz, CDCl_3): δ 3.81 (s, 3H), 6.43 (d, J = 15.6 Hz, 1H), 7.38 (d, J = 8.4 Hz, 2H), 7.52 (d, J = 8.4 Hz, 2H), 7.63 (d, J = 16.2 Hz, 1H); ^{13}C NMR (75 MHz, CDCl_3): δ 51.75, 118.41, 124.49, 129.38, 132.07, 133.21, 143.41, 167.09; MS m/z (EI) 240 (M^+), 211, 209, 183, 181, 102, 89, 75, 74, 63, 51, 41, 27.

Compound 14b: ^1H NMR (300 MHz, CDCl_3): δ 3.82 (s, 3H), 6.38 (d, J = 15.9 Hz, 1H), 7.21-7.32 (m, 2H), 7.57-7.61 (m, 2H), 8.05 (d, J = 15.9 Hz, 1H); ^{13}C NMR (75 MHz, CDCl_3): δ 51.71, 120.32, 120.51, 125.19, 126.96, 127.48, 127.59, 127.62, 130.03, 130.93, 131.10, 133.29, 134.29, 140.44, 142.99, 166.64; MS m/z (EI) 240 (M^+), 211, 209, 183, 181, 161, 146, 130, 118, 102, 75, 74, 63, 51, 28.

Compound 15b: ^1H NMR (300 MHz, CDCl_3): δ 3.74 (s, 3H), 3.79 (s, 3H), 6.31 (d, J = 15.9 Hz, 1H), 6.90 (d, J = 8.7 Hz, 2H), 7.48 (d, J = 9.0 Hz, 2H), 7.66 (d, J = 15.9 Hz, 1H); ^{13}C NMR (75 MHz, CDCl_3): δ 51.53, 55.33, 114.29, 115.23, 127.08, 129.68, 144.50, 161.36, 167.75; MS m/z (EI) 192(M^+), 161, 149, 134, 133, 118, 103, 90, 89, 77, 63, 51, 39.

Compound 16b: ^1H NMR (300 MHz, CDCl_3): δ 2.41(s, 3H), 3.79 (s, 3H), 6.34 (d, J = 15.9 Hz, 1H), 7.16-7.25 (m, 3H), 7.52 (d, J = 7.2 Hz, 1H), 7.98 (d, J = 15.6 Hz, 1H); ^{13}C NMR (75 MHz, CDCl_3): δ 19.60, 51.49, 118.66, 126.20, 126.24, 129.88, 130.64, 133.19, 137.48, 142.37, 167.29; MS m/z (EI) 176(M^+), 161, 159, 145, 127, 116, 115, 102, 91, 89, 77, 65, 58, 51, 39.

Compound 17b: ^1H NMR (300 MHz, CDCl_3): δ 3.82 (s, 6H), 6.48 (d, J = 15.9 Hz, 2H), 7.54 (s, 4H), 7.68 (d, J = 16.2 Hz, 2H); ^{13}C NMR (75 MHz, CDCl_3): δ 51.74, 118.84, 128.46, 136.06, 143.61, 167.10; MS m/z (EI) 246 (M^+), 231, 215, 183, 173, 171, 155, 127, 115, 102, 92, 78, 71, 64, 51.

Compound 4C: ^1H NMR (300 MHz, CDCl_3): δ 2.37(s, 6H); 7.20-7.23 (m, 4H), 7.45-7.48 (m, 4H); ^{13}C NMR (75 MHz, CDCl_3): δ 21.06, 126.77, 129.41, 136.66, 138.23.

Compound 4D: ^1H NMR (300MHz, CDCl_3): δ 2.39 (s, 3H), 3.80 (s, 3H), 6.95-7.04 (m, 2H), 7.20-7.23 (m, 2H), 7.28-7.32 (m, 2H), 7.41-7.44 (m, 2H); ^{13}C NMR (75 MHz, CDCl_3): δ 21.20, 55.48, 111.08, 120.74, 128.34, 128.72, 129.37, 130.62, 130.76, 135.53, 136.58, 156.43.

Compound 5C: ^1H NMR (300 MHz, CDCl_3): δ 3.80 (s, 3H), 6.98(d, J = 8.7 Hz, 2H), 7.27-7.32 (m, 1H), 7.38-7.43 (m, 2H), 7.51-7.60 (m, 4H); ^{13}C NMR (75 MHz, CDCl_3): δ 55.31, 114.16, 126.63, 126.71, 128.12, 128.69, 133.75, 140.80, 159.11; MS m/z (EI) 184(M^+), 169, 152, 141, 115, 89, 76, 71, 57, 43, 39

Compound 6C: ^1H NMR (300 MHz, CDCl_3): δ 2.39 (s, 3H), 3.79 (s, 3H), 6.94-7.14 (m, 2H), 7.14(m, 1H), 7.27-7.32 (m, 5H); ^{13}C NMR (75 MHz, CDCl_3): δ 21.52, 55.48, 111.06, 120.71, 126.63, 127.68, 127.82, 128.46, 130.19, 130.85, 137.46, 138.42, 156.40.

Compound 7C: ^1H NMR (300 MHz, CDCl_3): δ 3.84 (s, 3H), 6.95-6.98 (m, 2H), 7.35-7.38 (m, 2H), 7.46-7.49 (m, 4H); ^{13}C NMR (75 MHz, CDCl_3): δ 55.33, 114.27, 127.90, 127.98, 128.81, 132.44, 132.63, 139.22, 159.31.

Compound 9C: ^1H NMR (300 MHz, CDCl_3): δ 2.17 (s, 3H), 7.20-7.31 (m, 4H), 7.49 (d, J = 8.4 Hz, 2H), 8.28(d, J = 8.7 Hz, 2H); ^{13}C NMR (75 MHz, CDCl_3): δ 20.28, 123.37, 126.08, 128.42, 129.36, 130.06, 130.68, 135.01, 139.57, 146.81, 148.78; MS m/z (EI) 213(M^+), 196, 183, 165, 152, 139, 128, 115, 91, 83, 75, 63, 57, 51, 39.

Compound 9D: ^1H NMR (300 MHz, CDCl_3): δ 7.46 (d, J = 8.4 Hz, 2H), 7.56 (d, J = 8.7 Hz, 2H), 7.70 (d, J = 8.7 Hz, 2H), 8.28 (d, J = 8.4 Hz, 2H); ^{13}C NMR (75 MHz, CDCl_3): δ 124.09, 127.55, 128.53, 129.26, 135.13, 137.04, 146.16, 147.10; MS m/z (EI) 233 (M^+), 205, 203, 187, 175, 167, 152, 139, 126, 101, 76, 74, 63, 51.

Compound 9E: ^1H NMR (300 MHz, CDCl_3): δ 7.45-7.48 (m, 3H), 7.59 (m, 2H), 7.70 (d, J = 9.0 Hz, 2H), 8.24 (d, J = 9.0 Hz, 2H); ^{13}C NMR (75 MHz, CDCl_3): δ 123.95, 127.24, 127.63, 128.82, 129.04, 138.58, 146.93, 147.45; MS m/z (EI) 199 (M^+), 169, 152, 141, 127, 115, 97, 95, 76, 69, 57, 43, 41, 27.

Compound 9F: ^1H NMR (300 MHz, CDCl_3): δ 3.82 (s, 3H), 7.01-7.09 (m, 2H), 7.31-7.33 (m, 1H), 7.37-7.43 (m, 1H), 7.69 (d, J = 11.4 Hz, 2H), 8.23 (d, J = 11.4 Hz, 2H); ^{13}C NMR (75 MHz, CDCl_3): δ 55.43, 111.32, 120.98, 123.08, 128.07, 130.11, 130.22, 130.54, 145.36, 146.48, 156.28; MS m/z (EI) 229 (M^+), 214, 199, 184, 168, 152, 139, 128.

Compound 10C: ^1H NMR (300 MHz, CDCl_3): δ 7.32-7.36 (m, 2H), 7.41-7.51 (m, 5H), 7.59-7.62 (m, 1H), 7.84-7.88 (m, 1H); ^{13}C NMR (75 MHz, CDCl_3): δ 123.96, 127.79, 128.09, 128.13, 128.59, 131.86, 132.22, 136.20, 137.30, 149.19; MS m/z (EI) 199 (M^+), 182, 171, 152, 143, 141, 127, 116, 115, 102, 87, 76, 63, 51, 39.

Compound 11C: ^1H NMR (300 MHz, CDCl_3): δ 7.41-7.50 (m, 3H), 7.55-7.62 (m, 3H), 7.87-7.91 (m, 1H), 8.15-8.19 (m, 1H), 8.42 (m, 1H); ^{13}C NMR (75 MHz, CDCl_3): δ 121.81, 121.92, 127.04, 128.46, 129.07, 129.62, 132.94, 138.54, 142.75, 148.62; MS m/z (EI) 199 (M^+), 152, 141, 127, 115, 102, 76, 74, 63, 51, 39.

Compound 12C: ^1H NMR (300 MHz, CDCl_3): δ 6.98-7.04 (m, 1H), 7.27-7.44 (m, 7H), 7.94 (d, J = 7.2 Hz, 1H); ^{13}C NMR (75 MHz, CDCl_3): δ 127.12, 127.58, 127.90, 128.07, 128.72, 129.22, 130.03, 139.43, 144.14, 146.57; MS m/z (EI) 280 (M^+), 152, 140, 126, 102, 92, 76, 63, 51, 39, 27.

Compound 13C: ^1H NMR (300 MHz, CDCl_3): δ 3.84 (s, 3H), 6.95-6.98 (m, 2H), 7.25-7.39 (m, 2H), 7.42-7.54 (m, 4H); ^{13}C NMR (75 MHz, CDCl_3): δ 55.33, 114.28, 120.75, 127.96, 128.26, 131.75, 132.44, 139.68, 159.35.

X-ray structure ligand 3:

Table 1. Crystal data and structure refinement for SX505.

Identification code	sx505
Empirical formula	C ₂₁ H ₂₄ N ₂ S
Formula weight	336.48
Temperature	293(2) K
Wavelength	0.71073 Å
Crystal system, space group	MONOCLINIC, P2(1)/n
Unit cell dimensions	a = 11.9354(5) Å alpha = 90 deg. b = 12.8695(5) Å beta = 104.464(2) deg. c = 12.7849(5) Å gamma = 90 deg.
Volume	1901.55(13) Å ³
Z, Calculated density	4, 1.175 Mg/m ³
Absorption coefficient	0.174 mm ⁻¹
F(000)	720
Crystal size	0.81 x 0.59 x 0.35 mm
Theta range for data collection	2.28 to 27.48 deg.
Limiting indices	-15 ≤ h ≤ 15, -15 ≤ k ≤ 16, -16 ≤ l ≤ 16
Reflections collected / unique	7603 / 4331 [R(int) = 0.0172]
Completeness to theta = 27.48	99.3 %
Absorption correction	EMPIRICAL
Max. and min. transmission	0.9417 and 0.8711
Refinement method	Full-matrix least-squares on F ²
Data / restraints / parameters	4331 / 0 / 217

Goodness-of-fit on F^2	0.838
Final R indices [$I > 2\sigma(I)$]	$R_1 = 0.0382$, $wR_2 = 0.0998$
R indices (all data)	$R_1 = 0.0664$, $wR_2 = 0.1043$
Largest diff. peak and hole	0.244 and -0.219 e. $\text{\AA}^{-3}$

Table 2. Atomic coordinates ($\times 10^4$) and equivalent isotropic displacement parameters ($\text{\AA}^2 \times 10^3$) for SX505.
 $U(\text{eq})$ is defined as one third of the trace of the orthogonalized U_{ij} tensor.

	x	y	z	$U(\text{eq})$
S(1)	7897(1)	114(1)	6852(1)	55(1)
N(1)	8041(1)	-1250(1)	8508(1)	44(1)
N(2)	9620(1)	-1140(1)	7901(1)	48(1)
C(1)	8524(1)	-758(1)	7764(1)	43(1)
C(2)	8760(1)	-2174(1)	8914(1)	44(1)
C(3)	8777(1)	-2635(1)	10008(1)	54(1)
C(4)	9658(2)	-3522(1)	10188(1)	61(1)
C(5)	10839(2)	-3179(2)	10065(2)	67(1)
C(6)	10792(1)	-2640(1)	8986(1)	62(1)
C(7)	9930(1)	-1760(1)	8893(1)	47(1)
C(8)	10471(1)	-653(1)	7448(1)	49(1)
C(9)	10589(2)	-965(2)	6447(2)	69(1)
C(10)	11432(2)	-463(2)	6053(2)	102(1)
C(11)	12138(2)	279(2)	6644(3)	112(1)
C(12)	12024(2)	564(2)	7639(3)	96(1)
C(13)	11180(2)	96(1)	8043(2)	67(1)
C(14)	9825(2)	-1794(2)	5812(2)	110(1)
C(15)	6827(1)	-1232(1)	8442(1)	44(1)
C(16)	6315(1)	-338(1)	8741(1)	53(1)
C(17)	5133(2)	-385(2)	8658(2)	70(1)
C(18)	4494(2)	-1266(2)	8343(2)	74(1)
C(19)	5022(2)	-2142(2)	8092(1)	68(1)
C(20)	6187(1)	-2128(1)	8134(1)	53(1)
C(21)	6977(2)	632(1)	9139(2)	72(1)

Table 3. Bond lengths [Å] and angles [deg] for SX505.

S(1)-C(1)	1.6570(15)
N(1)-C(1)	1.3819(17)
N(1)-C(15)	1.4302(17)
N(1)-C(2)	1.4816(18)
N(2)-C(1)	1.3667(18)
N(2)-C(8)	1.4338(18)
N(2)-C(7)	1.4651(19)
C(2)-C(7)	1.501(2)
C(2)-C(3)	1.515(2)
C(2)-H(2A)	0.9800
C(3)-C(4)	1.531(2)
C(3)-H(3A)	0.9700
C(3)-H(3B)	0.9700
C(4)-C(5)	1.522(2)
C(4)-H(4A)	0.9700
C(4)-H(4B)	0.9700
C(5)-C(6)	1.532(2)
C(5)-H(5A)	0.9700
C(5)-H(5B)	0.9700
C(6)-C(7)	1.514(2)
C(6)-H(6A)	0.9700
C(6)-H(6B)	0.9700
C(7)-H(7A)	0.9800
C(8)-C(13)	1.378(2)
C(8)-C(9)	1.381(2)
C(9)-C(10)	1.393(3)
C(9)-C(14)	1.503(3)
C(10)-C(11)	1.369(4)
C(10)-H(10A)	0.9300
C(11)-C(12)	1.363(4)
C(11)-H(11A)	0.9300
C(12)-C(13)	1.380(3)
C(12)-H(12A)	0.9300
C(13)-H(13A)	0.9300
C(14)-H(14A)	0.9600
C(14)-H(14B)	0.9600
C(14)-H(14C)	0.9600
C(15)-C(20)	1.384(2)
C(15)-C(16)	1.401(2)
C(16)-C(17)	1.390(2)

C(16)-C(21)	1.497(2)
C(17)-C(18)	1.369(3)
C(17)-H(17A)	0.9300
C(18)-C(19)	1.368(3)
C(18)-H(18A)	0.9300
C(19)-C(20)	1.379(2)
C(19)-H(19A)	0.9300
C(20)-H(20A)	0.9300
C(21)-H(21A)	0.9600
C(21)-H(21B)	0.9600
C(21)-H(21C)	0.9600

C(1)-N(1)-C(15)	122.88(12)
C(1)-N(1)-C(2)	107.67(11)
C(15)-N(1)-C(2)	121.52(11)
C(1)-N(2)-C(8)	122.89(12)
C(1)-N(2)-C(7)	109.44(11)
C(8)-N(2)-C(7)	122.44(12)
N(2)-C(1)-N(1)	107.34(12)
N(2)-C(1)-S(1)	125.70(11)
N(1)-C(1)-S(1)	126.95(11)
N(1)-C(2)-C(7)	99.74(11)
N(1)-C(2)-C(3)	120.72(12)
C(7)-C(2)-C(3)	110.93(13)
N(1)-C(2)-H(2A)	108.2
C(7)-C(2)-H(2A)	108.2
C(3)-C(2)-H(2A)	108.2
C(2)-C(3)-C(4)	106.34(12)
C(2)-C(3)-H(3A)	110.5
C(4)-C(3)-H(3A)	110.5
C(2)-C(3)-H(3B)	110.5
C(4)-C(3)-H(3B)	110.5
H(3A)-C(3)-H(3B)	108.7
C(5)-C(4)-C(3)	112.78(14)
C(5)-C(4)-H(4A)	109.0
C(3)-C(4)-H(4A)	109.0
C(5)-C(4)-H(4B)	109.0
C(3)-C(4)-H(4B)	109.0
H(4A)-C(4)-H(4B)	107.8
C(4)-C(5)-C(6)	113.43(14)
C(4)-C(5)-H(5A)	108.9
C(6)-C(5)-H(5A)	108.9
C(4)-C(5)-H(5B)	108.9
C(6)-C(5)-H(5B)	108.9

H(5A)-C(5)-H(5B)	107.7
C(7)-C(6)-C(5)	106.35(13)
C(7)-C(6)-H(6A)	110.5
C(5)-C(6)-H(6A)	110.5
C(7)-C(6)-H(6B)	110.5
C(5)-C(6)-H(6B)	110.5
H(6A)-C(6)-H(6B)	108.7
N(2)-C(7)-C(2)	99.98(11)
N(2)-C(7)-C(6)	119.66(13)
C(2)-C(7)-C(6)	110.50(13)
N(2)-C(7)-H(7A)	108.7
C(2)-C(7)-H(7A)	108.7
C(6)-C(7)-H(7A)	108.7
C(13)-C(8)-C(9)	121.60(16)
C(13)-C(8)-N(2)	118.85(15)
C(9)-C(8)-N(2)	119.51(16)
C(8)-C(9)-C(10)	116.8(2)
C(8)-C(9)-C(14)	121.27(16)
C(10)-C(9)-C(14)	122.0(2)
C(11)-C(10)-C(9)	121.6(2)
C(11)-C(10)-H(10A)	119.2
C(9)-C(10)-H(10A)	119.2
C(12)-C(11)-C(10)	120.8(2)
C(12)-C(11)-H(11A)	119.6
C(10)-C(11)-H(11A)	119.6
C(11)-C(12)-C(13)	119.0(2)
C(11)-C(12)-H(12A)	120.5
C(13)-C(12)-H(12A)	120.5
C(8)-C(13)-C(12)	120.2(2)
C(8)-C(13)-H(13A)	119.9
C(12)-C(13)-H(13A)	119.9
C(9)-C(14)-H(14A)	109.5
C(9)-C(14)-H(14B)	109.5
H(14A)-C(14)-H(14B)	109.5
C(9)-C(14)-H(14C)	109.5
H(14A)-C(14)-H(14C)	109.5
H(14B)-C(14)-H(14C)	109.5
C(20)-C(15)-C(16)	120.97(14)
C(20)-C(15)-N(1)	118.81(13)
C(16)-C(15)-N(1)	120.12(14)
C(17)-C(16)-C(15)	116.56(17)
C(17)-C(16)-C(21)	120.17(16)
C(15)-C(16)-C(21)	123.27(15)
C(18)-C(17)-C(16)	122.59(18)

C(18)-C(17)-H(17A)	118.7
C(16)-C(17)-H(17A)	118.7
C(19)-C(18)-C(17)	119.77(18)
C(19)-C(18)-H(18A)	120.1
C(17)-C(18)-H(18A)	120.1
C(18)-C(19)-C(20)	119.91(19)
C(18)-C(19)-H(19A)	120.0
C(20)-C(19)-H(19A)	120.0
C(19)-C(20)-C(15)	120.12(17)
C(19)-C(20)-H(20A)	119.9
C(15)-C(20)-H(20A)	119.9
C(16)-C(21)-H(21A)	109.5
C(16)-C(21)-H(21B)	109.5
H(21A)-C(21)-H(21B)	109.5
C(16)-C(21)-H(21C)	109.5
H(21A)-C(21)-H(21C)	109.5
H(21B)-C(21)-H(21C)	109.5

Symmetry transformations used to generate equivalent atoms:

Table 4. Anisotropic displacement parameters ($\text{\AA}^2 \times 10^3$) for SX505.

The anisotropic displacement factor exponent takes the form:

$$-2 \pi^2 [h^2 a^{*2} U_{11} + \dots + 2 h k a^* b^* U_{12}]$$

	U11	U22	U33	U23	U13	U12
S(1)	58(1)	45(1)	59(1)	14(1)	7(1)	3(1)
N(1)	44(1)	37(1)	53(1)	9(1)	14(1)	7(1)
N(2)	45(1)	47(1)	53(1)	12(1)	14(1)	7(1)
C(1)	46(1)	35(1)	46(1)	1(1)	10(1)	1(1)
C(2)	49(1)	35(1)	48(1)	4(1)	13(1)	7(1)
C(3)	65(1)	47(1)	52(1)	9(1)	18(1)	5(1)
C(4)	78(1)	47(1)	54(1)	15(1)	9(1)	12(1)
C(5)	65(1)	59(1)	72(1)	16(1)	7(1)	20(1)
C(6)	55(1)	60(1)	71(1)	13(1)	17(1)	22(1)
C(7)	49(1)	42(1)	48(1)	6(1)	12(1)	7(1)
C(8)	46(1)	43(1)	62(1)	10(1)	19(1)	6(1)
C(9)	80(1)	66(1)	68(1)	11(1)	35(1)	9(1)
C(10)	115(2)	104(2)	114(2)	37(2)	77(2)	28(2)
C(11)	70(2)	97(2)	186(3)	64(2)	65(2)	13(1)
C(12)	52(1)	66(2)	166(3)	26(2)	18(1)	-5(1)
C(13)	53(1)	53(1)	92(1)	4(1)	12(1)	1(1)
C(14)	163(2)	100(2)	72(2)	-23(1)	41(2)	-10(2)
C(15)	44(1)	45(1)	43(1)	5(1)	11(1)	4(1)
C(16)	51(1)	51(1)	54(1)	-2(1)	11(1)	10(1)
C(17)	60(1)	77(2)	75(1)	2(1)	22(1)	21(1)
C(18)	50(1)	99(2)	75(1)	9(1)	19(1)	3(1)
C(19)	61(1)	75(1)	65(1)	10(1)	13(1)	-18(1)
C(20)	58(1)	48(1)	54(1)	1(1)	17(1)	-4(1)
C(21)	80(1)	55(1)	79(1)	-16(1)	15(1)	12(1)

Table 5. Hydrogen coordinates ($\times 10^4$) and isotropic displacement parameters ($\text{\AA}^2 \times 10^3$) for SX505.

	x	y	z	U(eq)
H(2A)	8555	-2725	8371	53
H(3A)	8016	-2895	10017	65
H(3B)	9004	-2114	10569	65
H(4A)	9743	-3804	10907	73
H(4B)	9366	-4073	9673	73
H(5A)	11338	-3783	10130	80
H(5B)	11180	-2708	10649	80
H(6A)	11548	-2372	8975	74
H(6B)	10544	-3123	8392	74
H(7A)	10195	-1290	9508	56
H(10A)	11518	-635	5371	123
H(11A)	12703	591	6364	134
H(12A)	12506	1066	8039	116
H(13A)	11089	286	8719	80
H(14A)	9296	-2037	6213	164
H(14B)	10294	-2363	5683	164
H(14C)	9398	-1513	5134	164
H(17A)	4761	204	8823	84
H(18A)	3705	-1269	8299	89
H(19A)	4595	-2747	7893	81
H(20A)	6544	-2721	7955	64
H(21A)	6461	1146	9299	108
H(21B)	7327	893	8592	108
H(21C)	7570	480	9781	108

Table 6. Torsion angles [deg] for SX505.

C(8)-N(2)-C(1)-N(1)	-165.46(14)
C(7)-N(2)-C(1)-N(1)	-10.53(16)
C(8)-N(2)-C(1)-S(1)	15.8(2)
C(7)-N(2)-C(1)-S(1)	170.71(12)
C(15)-N(1)-C(1)-N(2)	-164.99(13)
C(2)-N(1)-C(1)-N(2)	-15.75(16)
C(15)-N(1)-C(1)-S(1)	13.8(2)
C(2)-N(1)-C(1)-S(1)	162.99(11)
C(1)-N(1)-C(2)-C(7)	34.28(15)
C(15)-N(1)-C(2)-C(7)	-175.97(12)
C(1)-N(1)-C(2)-C(3)	155.86(14)
C(15)-N(1)-C(2)-C(3)	-54.39(19)
N(1)-C(2)-C(3)-C(4)	-176.54(13)
C(7)-C(2)-C(3)-C(4)	-60.56(16)
C(2)-C(3)-C(4)-C(5)	54.11(18)
C(3)-C(4)-C(5)-C(6)	-54.0(2)
C(4)-C(5)-C(6)-C(7)	54.2(2)
C(1)-N(2)-C(7)-C(2)	31.40(15)
C(8)-N(2)-C(7)-C(2)	-173.54(13)
C(1)-N(2)-C(7)-C(6)	152.03(14)
C(8)-N(2)-C(7)-C(6)	-52.9(2)
N(1)-C(2)-C(7)-N(2)	-37.70(14)
C(3)-C(2)-C(7)-N(2)	-166.05(12)
N(1)-C(2)-C(7)-C(6)	-164.72(12)
C(3)-C(2)-C(7)-C(6)	66.92(16)
C(5)-C(6)-C(7)-N(2)	-175.16(14)
C(5)-C(6)-C(7)-C(2)	-59.95(18)
C(1)-N(2)-C(8)-C(13)	89.4(2)
C(7)-N(2)-C(8)-C(13)	-62.3(2)
C(1)-N(2)-C(8)-C(9)	-92.68(19)
C(7)-N(2)-C(8)-C(9)	115.59(18)
C(13)-C(8)-C(9)-C(10)	-2.1(3)
N(2)-C(8)-C(9)-C(10)	-179.88(16)
C(13)-C(8)-C(9)-C(14)	178.96(19)
N(2)-C(8)-C(9)-C(14)	1.1(3)
C(8)-C(9)-C(10)-C(11)	2.2(3)
C(14)-C(9)-C(10)-C(11)	-178.8(2)
C(9)-C(10)-C(11)-C(12)	-1.1(4)
C(10)-C(11)-C(12)-C(13)	-0.2(4)
C(9)-C(8)-C(13)-C(12)	0.8(3)
N(2)-C(8)-C(13)-C(12)	178.66(15)

C(11)-C(12)-C(13)-C(8)	0.3(3)
C(1)-N(1)-C(15)-C(20)	107.34(16)
C(2)-N(1)-C(15)-C(20)	-37.80(19)
C(1)-N(1)-C(15)-C(16)	-76.06(18)
C(2)-N(1)-C(15)-C(16)	138.80(15)
C(20)-C(15)-C(16)-C(17)	-3.2(2)
N(1)-C(15)-C(16)-C(17)	-179.73(14)
C(20)-C(15)-C(16)-C(21)	176.55(16)
N(1)-C(15)-C(16)-C(21)	0.0(2)
C(15)-C(16)-C(17)-C(18)	2.5(3)
C(21)-C(16)-C(17)-C(18)	-177.23(17)
C(16)-C(17)-C(18)-C(19)	-0.2(3)
C(17)-C(18)-C(19)-C(20)	-1.5(3)
C(18)-C(19)-C(20)-C(15)	0.8(3)
C(16)-C(15)-C(20)-C(19)	1.7(2)
N(1)-C(15)-C(20)-C(19)	178.23(13)

Symmetry transformations used to generate equivalent atoms:

Table 7. Hydrogen bonds for SX505 [A and deg.].

D-H...A	d(D-H)	d(H...A)	d(D...A)	<(DHA)
---------	--------	----------	----------	--------