The Preparation and Utility of Bis(sulfinyl)imidoamidine Ligands for the Copper-Catalyzed Diels–Alder Reaction

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General Methods. Acrolein, piperylene, cyclopentadiene, cyclohexadiene, isoprene, and 2,3-dimethylbutadiene were distilled immediately prior to use. Diels–Alder substrates **10a–d** were prepared according to the procedure of Mathre. *(R)*-*N*-*tert*-Butanesulfinamide **7** was prepared by the literature method and was the enantiomer used in all experiments except where noted.² *(S)*-*p*-Toluenesulfinamide **9** was prepared according to the literature procedure.³ Unless otherwise noted, all other materials were obtained from commercial suppliers and used without further purification. Tetrahydrofuran (THF) was distilled under N₂ from sodium/benzophenone ketyl. Methylene chloride (CH₂Cl₂) was distilled from CaH₂. HPLC grade reagent alcohol refers to a blend of 90.7% ethanol, 4.5% methanol, and 4.8% isopropanol and was purchased from Fisher. Extracts were dried over Na₂SO₄ and solvents were removed by rotary evaporation at aspirator pressure. Chromatography was carried out using Merck 60 230–240 mesh silica gel. All reactions were performed under an inert nitrogen atmosphere unless otherwise noted. Melting points were determined in open pyrex capillaries and are reported uncorrected. IR spectra were recorded using KBr pellets, NaCl plates, or as solutions in CH₂Cl₂ and only partial data is reported. Unless otherwise noted, NMR chemical shifts were measured in CDCl₃ and are reported in ppm downfield from an internal solvent peak. Elemental analyses were performed by M-H-W Laboratories, Phoenix, AZ or at the University of California, Berkeley Microanalytical Facility.

(*R,R*)-Bis-*tert*-butanesulfinyl aldimine **8a.** To a slurry of 640 mg (4.00 mmol, 4.0 equiv) of CuSO₄ in 5 mL of CH₂Cl₂ was added 135 mg (1.00 mmol) of 2,6-pyridinedicarboxaldehyde followed by 240 mg (2.00 mmol, 2.0 equiv) of *(R)*-*tert*-butanesulfinamide **7**. The mixture was stirred at rt for 4 h and then filtered through a plug of celite and the filter cake washed with CH₂Cl₂. The solvent was removed and the crude solid chromatographed (4:1 hexanes:EtOAc) to afford 254 mg (74%) of product as a colorless solid. X-ray quality crystals were grown from Et₂O by slow evaporation (see below for X-ray structural data). [α]_D²³ –447° (*c* 1.0, CHCl₃); IR 1605, 1092 cm^{–1}. mp 152–153 °C. ¹H NMR (300 MHz) δ 1.30 (s, 18H), 7.94 (t, *J* = 7.8, 1H), 8.14 (d, *J* = 7.8, 2H), 8.77 (s, 2H). ¹³C NMR (101 MHz) δ 23.0, 58.6, 125.0, 137.9, 153.2, 163.6. Anal. Calcd for C₁₅H₂₃N₃S₂O₂: C, 52.78; H, 6.79; N, 12.31. Found: C, 53.00; H, 6.60; N, 12.28.

(*R,R*)-Bis-*tert*-butanesulfinyl ketimine **8b.** Sulfinamide **7** (145 mg, 1.20 mmol) and 2,6-diacetylpyridine (82 mg, 0.50 mmol) were dissolved in 5 mL of THF. Ti(OEt)₄ (20% by weight titanium, 0.50 mL, 2.0 mmol) was added and the mixture was heated to 75 °C for 4 h. The slurry was diluted with 20 mL of CH₂Cl₂ and 2.0 mL of water was slowly added to the vigorously stirred mixture. The resulting suspension was filtered through a pad of celite, the filter cake was washed with CH₂Cl₂, and the solvent was removed under reduced pressure. The crude mixture was chromatographed with 4:1 hexanes:EtOAc to afford 105 mg (58%) of the title compound as a yellow solid. The compound was crystallized by slow evaporation of ether to afford X-ray quality crystals (see below for X-ray structural data). [α]_D²³ –121° (*c* 1.0, CHCl₃); IR 2976, 1695, 1357, 1070 cm^{–1}. ¹H NMR (300 MHz) δ 1.34 (s, 18H), 2.91 (s, 6H), 7.84 (t, *J* = 7.8, 1H),

8.22 (d, $J = 7.8$, 2H). ^{13}C NMR (75 MHz) δ 18.5, 22.5, 57.7, 123.7, 137.1, 154.3, 177.1. Anal. Calcd for $\text{C}_{17}\text{H}_{18}\text{N}_3\text{S}_2\text{O}_2$: C, 55.25; H, 7.36; N, 11.37. Found: C, 55.01; H, 7.36; N, 11.36.

(*R*)-tert-Butanesulfinyl aldimine 8c. Sulfinamide **7** (121 mg, 1.00 mmol) and 2-pyridinecarboxaldehyde (107 mg, 1.00 mmol) were dissolved in 2.0 mL of CH_2Cl_2 and CuSO_4 (320 mg, 2.00 mmol) was added. The mixture was stirred for 1 h at rt, filtered through a pad of celite, and the filter cake was washed with CH_2Cl_2 . After the solvent was removed under reduced pressure, chromatography (3:1 hexanes:EtOAc) afforded 203 mg (95%) of the title compound as a colorless oil. $[\alpha]_{\text{D}}^{23} -172^\circ$ (c 1.0, CHCl_3); IR 1607, 1088 cm^{-1} . ^1H NMR (300 MHz) δ 1.29 (s, 9H), 7.42 (m, 1H), 7.82 (m, 1H), 8.01 (d, $J = 7.8$, 1H), 8.71 (s, 1H), 8.75 (d, $J = 5.0$, 1H). ^{13}C NMR (101 MHz) δ 22.9, 58.3, 123.3, 126.2, 137.1, 150.1, 152.7, 164.0. Anal. Calcd for $\text{C}_{10}\text{H}_{14}\text{N}_2\text{OS}$: C, 57.12; H, 6.71; N, 13.32. Found: C, 56.96; H, 6.65; N, 13.30.

(*R,R*)-Bis-tert-butanesulfinyl imine 8d. Sulfinamide **7** (390 mg, 3.10 mmol) and isophthalaldehyde (200 mg, 1.50 mmol) were dissolved in CH_2Cl_2 . CuSO_4 was added and the mixture stirred for 18 h at rt. The crude mixture was filtered through celite and the filter cake was washed with CH_2Cl_2 . After removing solvent, chromatography (4:1 to 1:1 hexanes:EtOAc) afforded 497 mg (98%) of the title compound as a colorless foam. $[\alpha]_{\text{D}}^{23} -107^\circ$ (c 1.0, CHCl_3); IR 1601, 1572, 1079 cm^{-1} . ^1H NMR (500 MHz) δ 1.25 (s, 18H), 7.57 (t, $J = 7.5$, 1H), 7.97 (d, $J = 7.5$, 2H), 8.28 (s, 1H), 8.62 (s, 2H). ^{13}C NMR (125 MHz) δ 22.6, 58.0, 129.6, 130.0, 132.6, 134.7, 161.8. Anal. Calcd for $\text{C}_{16}\text{H}_{24}\text{N}_2\text{S}_2\text{O}_2$: C, 56.43; H, 7.11; N, 8.23. Found: C, 56.45; H, 6.98; N, 7.98.

(*R,R*)-Bis-tert-butanesulfinyl imine 8e. To a solution of 575 mg (5.75 mmol) of dimethylmalonaldehyde⁴ in 15 mL of toluene was added **7** (1.16 g, 9.60 mmol) followed by $\text{Ti}(\text{OEt})_4$ (20% by weight Ti, 5.24 g, 23.0 mmol). The solution was brought to reflux and stirred for 3 h. Brine (5 mL) was added and the mixture was filtered through a plug of celite and washed with 200 mL of EtOAc. After removal of solvent, the crude yellow oil was chromatographed (2:1 hexanes:EtOAc) to afford 600 mg (34%) of a white crystalline solid ($R_f = 0.30$). mp 85-87 $^\circ\text{C}$. $[\alpha]_{\text{D}}^{23} -379^\circ$ (c 1.0, CHCl_3); IR 1612, 1088 cm^{-1} . ^1H NMR (300 MHz) δ 1.18 (s, 18H), 1.41 (s, 6H), 8.10 (s, 2H). ^{13}C NMR (101 MHz) δ 22.6, 23.0, 47.9, 57.2, 171.0. Anal. Calcd for $\text{C}_{13}\text{H}_{26}\text{N}_2\text{S}_2\text{O}_2$: C, 50.94; H, 8.55; N, 9.14. Found: C, 51.06; H, 8.70; N, 9.03.

(*R*)-tert-Butanesulfinyl aldimine 8f. To a mixture of freshly distilled furfural (192 mg, 2.00 mmol) and **7** (242 mg, 2.00 mmol) was added $\text{Ti}(\text{OEt})_4$ (20% by weight Ti, 1.0 mL, 4.0 mmol). The mixture was stirred at rt for 4 h before diluting with CH_2Cl_2 and adding 2.0 mL of brine. The resulting suspension was filtered through celite, the filter cake washed with CH_2Cl_2 , and the solvent removed under reduced pressure. Chromatography (Et_2O) afforded 326 mg (82%) of the title compound as a colorless oil. $[\alpha]_{\text{D}}^{23} -168^\circ$ (c 1.0, CHCl_3); IR 1613, 1081 cm^{-1} . ^1H NMR (300 MHz) δ 1.26 (s, 9H), 6.57 (dd, $J = 1.8, 3.5$, 1H), 7.01 (dd, $J = 0.7, 3.5$, 1H), 7.65 (m, 1H), 8.40 (s, 1H). ^{13}C NMR (75 MHz) δ 22.8, 58.1, 112.8, 119.0, 147.1, 150.1, 151.1. Anal. Calcd for $\text{C}_9\text{H}_{13}\text{NO}_2\text{S}$: C, 54.24; H, 6.57; N, 7.03. Found: C, 54.49; H, 6.30; N, 6.82.

(*R*)-tert-Butanesulfinyl aldimine 8g. To a slurry of CuSO_4 (640 mg, 4.00 mmol) in 10 mL of CH_2Cl_2 was added **7** (242 mg, 2.00 mmol) and 2-quinolinecarboxaldehyde (314 mg, 2.00 mmol). After stirring 3 h, the mixture was filtered over celite and the filter cake washed with CH_2Cl_2 . The solvent was removed to afford a tan solid weighing 508 mg (98%). $[\alpha]_{\text{D}}^{23} -309^\circ$ (c 1.0, CHCl_3); IR 1591, 1504, 1363, 1082 cm^{-1} . ^1H NMR (300 MHz) δ 1.32 (s, 9H), 7.66 (m, 1H), 7.81 (m, 1H), 7.89 (m, 1H), 8.17 (d, $J = 8.6$, 1H), 8.20 (m, 2H), 8.94 (s, 1H). ^{13}C NMR (75 MHz) δ 23.0, 58.5, 119.2, 128.0, 128.7, 129.3, 130.5, 130.6, 137.2, 148.4, 152.8, 164.6. Anal. Calcd for $\text{C}_{14}\text{H}_{16}\text{N}_2\text{SO}$: C, 64.58; H, 6.20; N, 10.76. Found: C, 64.80; H, 6.12; N, 10.77.

(*R,R*)-Bis-*tert*-butanesulfinyl imine 8h. To a slurry of CuSO₄ (750 mg, 4.72 mmol) in 10 mL of CH₂Cl₂ was added **7** (314 mg, 2.59 mmol) and dibenzofuran-4,6-dicarboxaldehyde⁵ (266 mg, 1.18 mmol). The mixture was stirred for 36 h before filtering over celite. The crude mixture was chromatographed (1:1 hexanes:Et₂O) to obtain 348 mg (69%) of the title compound as a colorless solid. $[\alpha]_D^{23}$ -119° (*c* 1.0, CHCl₃); IR 1592, 1401, 1169, 1085 cm⁻¹. ¹H NMR (300 MHz) δ 1.35 (s, 18H), 7.51 (dd, *J* = 6.6, 7.8, 2H), 8.04 (d, *J* = 6.6, 2H), 8.14 (d, *J* = 7.8, 2H), 9.12 (s, 2H). ¹³C NMR (75 MHz) δ 22.7, 58.1, 119.5, 123.6, 124.5, 124.7, 128.0, 155.0, 157.4. Anal. Calcd for C₂₂H₂₆N₂S₂O₂: C, 61.37; H, 6.09; N, 6.51. Found: C, 61.19; H, 6.33; N, 6.40.

(*S,S*)-Bis-*p*-toluenesulfinyl imine 8i. To a round-bottomed flask charged with CuSO₄ (480 mg, 3.00 mmol), *p*-toluenesulfinamide (232 mg, 1.50 mmol) and 7.5 mL of CH₂Cl₂ was added 2,6-pyridinedicarboxaldehyde (101 mg, 0.750 mmol) and the mixture was stirred for 1 h at rt. The mixture was worked up in the same way as ligand **8a** and chromatographed (4:1 hexanes:EtOAc, *R_f* = 0.40) to obtain the title compound as a colorless solid weighing 210 mg (68%). ¹H NMR (300 MHz) δ 2.40 (s, 6H), 7.32 (d, *J* = 8.1, 4H), 7.65 (d, *J* = 8.1, 4H), 7.86 (t, *J* = 7.8, 1H), 8.09 (d, *J* = 7.8, 2H), 8.90 (s, 2H). Anal. Calcd for C₂₁H₁₉N₃O₂S₂: C, 61.59; H, 4.68; N, 10.29. Found: C, 61.62; H, 4.88; N, 10.12.

General method for Diels–Alder reactions of 10a and cyclopentadiene using ligands 8. A 10 mL round-bottomed flask was charged with Cu(OTf)₂ (18 mg, 0.1 mmol) and 1.1 equiv of the respective ligand. CH₂Cl₂ (2.5 mL) was added and the mixtures was stirred for 1 h. The reaction mixture was cooled to -78 °C and **10a** (71 mg, 0.5 mmol) was added, followed by 208 μL (2.50 mmol) of freshly distilled cyclopentadiene. The reaction mixture was stirred at -78 °C for 6 h and then filtered over a 1" plug of silica and eluted with 100 mL of a 50:50 hexanes:EtOAc solution. Crude NMR was used to determine the diastereomeric ratio by integration of the olefinic protons of the *exo* diastereomer [δ 6.16 (m, 2H)]. Enantioselectivities for **11a** were obtained using chiral HPLC (Chiralcel OD, 1.0 mL/min; 90:10 hexanes:iPrOH; *exo* diastereomers *t_R* = 18.6 min and 19.4 min; *endo* isomer (2-*S*) *t_R* = 20.5 min; *endo* isomer (2-*R*) *t_R* = 22.9 min). Yields are based on isolated products which had been purified by chromatography (neat CH₂Cl₂). Absolute stereochemistry was assigned according to elution order on HPLC and confirmed by comparison to literature optical rotation values.⁶

(*R*)-*O*-Methyl-*N*-*tert*-butanesulfinyl imidate 13. To a 100 mL round-bottomed flask charged with 6.05 g of **7** (50.0 mmol) was added 50 mL of trimethyl orthoformate and 5 mg of *p*-toluenesulfonic acid. The mixture was brought to reflux and the resulting solution was stirred for 3 h at which time the reaction was determined to be complete by TLC (neat EtOAc). The volatile material was removed under reduced pressure and 25 mL of ether was added. The mixture was filtered and concentrated to afford 8.1 g (98%) of a colorless oil which was of sufficient purity to continue on to the next step. Alternatively, the crude oil can be purified by chromatography (9:1 hexanes:EtOAc) (92%). $[\alpha]_D^{23}$ -177.4° (*c* 1.0, CHCl₃); IR 1611, 1245, 1082 cm⁻¹. ¹H NMR (300 MHz) δ 1.18 (s, 9H), 3.78 (s, 3H), 7.80 (s, 1H). ¹³C NMR (75 MHz) 22.2, 55.0, 56.5, 160.6. Anal. Calcd for C₆H₁₃NO₂S: C, 44.15; H, 8.03; N, 8.58. Found: C, 43.96; H, 7.89; N, 8.57.

(*R*)-*tert*-Butanesulfinyl imidoamidine 14. To a slurry of KH (35 % by weight in mineral oil, 125 mg, 1.2 mmol) in 2.0 mL of THF was added a 2.0 mL solution of 2-methylaminopyridine (108 mg, 1.00 mmol). After gas evolution had ceased (ca. 15 min), a 2.0 mL solution of imidate **13** was added. The mixture was stirred for 1 h and quenched with 5.0 mL of 1M NaHSO₄. 100 mL of EtOAc was added and the layers were separated. The organic layer was washed consecutively with saturated NaHCO₃ and brine, dried over Na₂SO₄, filtered, and concentrated. Chromatography (3:2 hexanes: EtOAc) afforded 122 mg (51%) of the title compound as a

colorless oil. $[\alpha]_D^{23} -404^\circ$ (c 1.0, CHCl_3); IR 2956, 1582, 1476, 1437, 1304, 1138, 1069 cm^{-1} . ^1H NMR (300 MHz) δ 1.20 (s, 9H), 3.50 (s, 3H), 7.0-7.05 (m, 2H), 7.65-7.71 (m, 1H), 8.35 (d, $J=1.8\text{Hz}$, 1H), 8.95 (s, 1H). ^{13}C NMR (125 MHz, d_6 -DMSO, 100 $^\circ\text{C}$) δ 22.1, 31.7, 56.0, 111.2, 119.7, 139.3, 148.4, 152.5, 154.5. HRMS(FAB): Mass Calcd for $\text{C}_{11}\text{H}_{17}\text{N}_3\text{OS}$ ($M+1$): 240.117059, found 240.117060.

(*R*)-*N*-Methyl-*N'*-*tert*-butanesulfinyl amidine 15a. To a 50 mL round-bottomed flask charged with 2.07 g (12.7 mmol) of **13** was added 11 mL of 2.0 M MeNH_2 (22 mmol) in THF. The solution was stirred at rt for 12 h and the solvent was removed under reduced pressure to afford a crystalline solid weighing 2.06 g (99%). mp 65-67 $^\circ\text{C}$. $[\alpha]_D^{23} -172.0^\circ$ (c 1.0, CHCl_3); ^1H NMR (300 MHz) δ 1.14 (s, 9H), 2.93 (d, $J=4.8$, 3H), 5.14 (br s, 1H), 7.81 (d, $J=3.9$, 1H). ^{13}C (101 MHz) δ 21.8, 27.8, 55.5, 155.2. Anal. Calcd for $\text{C}_6\text{H}_{13}\text{N}_2\text{SO}$: C, 44.41; H, 8.70; N, 17.27. Found: C, 44.53; H, 8.83; N, 19.96.

(*R,R*)-*N*-Methyl-bis-(*tert*-butanesulfinyl)imidoamidine 16a. To a slurry of 5 g of KH (35 % dispersion in mineral oil, 5.0 mmol) in 10 mL of THF at 0 $^\circ\text{C}$ was added 815 mg (5.00 mmol) of amidine **15a** in 10 mL of THF. During the course of addition a thick white mixture was obtained. The slurry was stirred at 0 $^\circ\text{C}$ for 15 min and then 900 mg (5.00 mmol) of imidate **13** was added to obtain a thick gray suspension. After 30 min, the reaction was quenched with 10 mL of 1 N NaHSO_4 . EtOAc (200 mL) was added and the layers separated. The organic phase was washed with 20 mL of saturated NaHCO_3 , water, and brine. The extracts were dried over Na_2SO_4 , filtered, and the solvent removed under reduced pressure to obtain a white solid. Purification by chromatography (2:1 hexanes: EtOAc) and crystallization from Et_2O afforded white crystals weighing 945 mg (63%). $[\alpha]_D^{23} -764^\circ$ (c 1.0, CHCl_3). IR 1582, 1077 cm^{-1} . mp 180-181 $^\circ\text{C}$. ^1H NMR (300 MHz) δ 1.19 (s, 18H), 3.35 (s, 3H), 8.15 (br s, 2H); ^{13}C in $(\text{CD}_3)_2\text{SO}$ at 80 $^\circ\text{C}$ (101 MHz) δ 22.4; 30.7, 56.9, 155.4. Anal. Calcd for $\text{C}_{11}\text{H}_{23}\text{N}_3\text{O}_2\text{S}_2$: C, 45.02; H, 7.90; N, 14.32; found C, 45.23; H, 7.61; N, 14.58.

***N*-Isobutyl-*N'*-*tert*-butanesulfinyl amidine 15b.** To a solution of **13** (163 mg, 1.00 mmol) in 5 mL of THF was added isobutylamine (730 mg, 0.990 mL, 10.0 mmol) and the solution stirred at rt for 1 h. EtOAc (100 mL) was added and the solution washed consecutively with 1 M NaHSO_4 , saturated NaHCO_3 , and water. The organic layer was dried, filtered, and the solvent was removed to afford 165 mg (81%) of the title compound as a white solid. The amidine exists as an inseparable mixture of two rotational isomers in an ~85:15 ratio. $[\alpha]_D^{23} -104^\circ$ (c 1.0, CHCl_3); ^1H NMR (500 Mz) Major isomer δ 0.83 (m, 6H), 1.03 (s, 9H), 1.82 (m, 1H), 3.03-3.10 (m, 2H), 6.66 (br s, 1H), 7.76 (d, $J=4.5$, 1H). Minor isomer δ 0.85 (d, $J=6.7\text{ Hz}$, 6H), 1.03 (s, 9H), 1.68 (m, 1H), 2.96 (m, 1H), 6.52 (br s, 1H), 7.61 (br s, 1H).

***N*-Benzyl-*N'*-*tert*-butanesulfinyl amidine 15c.** To a solution of **13** (163 mg, 1.00 mmol) in 5 mL of THF was added benzylamine (1.07 g, 1.09 mL, 1.00 mmol). The solution was stirred for 1 h at rt and then worked up with the same method employed for **15b**. The crude material was chromatographed with 1:1 hexanes: EtOAc to afford 216 mg (91%) of the title compound as a colorless oil. The compound exists as an inseparable ~92:8 mixture of rotational isomers. $[\alpha]_D^{23} -105^\circ$ (c 0.5, CHCl_3); ^1H NMR (500 MHz) Major isomer δ 1.03 (s, 9H), 4.98 (d, $J=5.8$, 2H), 6.80 (br s, 1H), 7.20-7.30 (m, 5H), 7.78 (d, $J=4.2$, 1H). Minor isomer δ 1.08 (s, 9H), 4.45 (d, $J=4.2$, 1H), 6.53 (br s, 1H), 7.20-7.30 (m, 5H), 8.17 (br s, 1H). Anal. Calcd for $\text{C}_{12}\text{H}_{18}\text{N}_2\text{OS}$: C, 60.47; H, 7.61; N, 11.75. Found: C, 60.65; H, 7.89; N, 11.49.

(*R*)-*N*-Trifluoroethyl-*N'*-*tert*-butanesulfinyl amidine 15d. A sealed tube was charged with sulfinyl imidate (1.54 g, 9.45 mmol) and trifluoroethylamine (1.50 g, 150 mmol). The tube was sealed and heated to 60 $^\circ\text{C}$ for 2 h. The flask was cooled to rt and the volatile material removed

under reduced pressure. The crude material was dissolved in a 25:1 mixture of hexanes:Et₂O and crystallized upon cooling to yield 1.82 g (84%) of the title compound. $[\alpha]_D^{23} -168^\circ$ (*c* 1.0, CHCl₃); IR 3240, 3055, 1614, 1260, 1141, 1030 cm⁻¹. ¹H NMR (300 MHz) δ 1.11 (s, 9H), 3.85 (m, 1H), 4.12 (m, 1H), 6.78 (br s, 1H), 7.88 (d, *J* = 3.9, 1H). Anal. Calcd for C₇H₁₃F₃N₂OS: C, 36.51; H, 5.69; N, 12.17. Found: C, 36.83; H, 5.89; N, 11.87.

(*R,R*)-*N*-Isobutyl-bis-(*tert*-butanesulfinyl)imidoamidine 16b. To a solution of **15b** (165 mg, 0.800 mmol) in 5 mL of THF at -78 °C was slowly added BuLi (2.5 M in hexanes, 380 μ L, 0.96 mmol). After stirring for 15 min, a solution of **13** (130 mg, 0.800 mmol) in 1.5 mL of THF was slowly added. The solution was stirred for 15 min and then warmed to rt. After 1 h, TLC analysis (1:1 hexanes:EtOAc) revealed that **13** had been completely consumed. The reaction was quenched with 3 mL of 1 M NaHSO₄ and worked up in an identical fashion to that used for preparation of **16a**. Chromatography (2:1 hexanes:EtOAc) afforded 155 mg (58%) of the title compound as a white solid. $[\alpha]_D^{23} -648^\circ$ (*c* 1.0, CHCl₃); ¹H NMR (300 MHz) δ 0.84 (m, 6H), 1.10 (s, 18H), 2.15 (m, 1H), 3.57 (m, 1H), 3.68 (dd, *J* = 7.5, 12.9, 1H), 8.07 (s, 2H). ¹³C NMR (75 MHz) δ 20.3, 20.7, 22.3, 26.5, 57.1, 153.5. Anal. Calcd for C₁₄H₂₉N₃O₂S₂: C, 50.11; H, 8.71; N, 12.52. Found: C, 49.92; H, 8.60; N, 12.30.

(*R,R*)-*N*-Benzyl-bis-(*tert*-butanesulfinyl)imidoamidine 16c. Compound **16c** was prepared in a fashion identical to that of **16b**. Deprotonation of **15c** (217 mg, 0.920 mmol) with BuLi (2.5 M in hexanes, 0.440 μ L, 1.1 mmol) at -78 °C was followed by addition of **2.13** (150 mg, 0.920 mmol). Chromatography (2:1 hexanes:EtOAc) afforded 275 mg (81%) of the title compound as a white solid. $[\alpha]_D^{23} -416^\circ$ (*c* 1.0, CHCl₃); ¹H NMR (300 MHz) δ 1.06 (s, 18H), 4.90 (d, *J* = 14.4, 1H), 5.29 (d, *J* = 14.4, 1H), 7.27 (m, 5H), 8.20 (s, 2H). Anal. Calcd for C₁₇H₂₇N₃O₂S₂: C, 55.25; H, 7.36; N, 11.37. Found: C, 55.30; H, 7.23; N, 11.43.

***N*-Trifluoroethyl-bis(*tert*-butanesulfinyl)imidoamidine 16d.** A round-bottomed flask was charged with amidine **15d** (550 mg, 2.40 mmol), methyl imidate **13** (407 mg, 3.00 mmol) and K₂CO₃ (360 mg, 2.60 mmol) and the resulting mixture stirred at reflux for 24 h. The mixture was cooled to rt, filtered, and purified by column chromatography (2:1 hexanes:EtOAc) to afford 260 mg (30%) of the title compound. $[\alpha]_D^{23} -692^\circ$ (*c* 0.25, CHCl₃); IR 1582, 1260, 1131, 1069 cm⁻¹. mp 147-150 °C. ¹H NMR (300 MHz) δ 1.18 (s, 9H), 4.55 (m, 1H), 4.70 (m, 1H), 8.20 (br s, 2H). Anal. Calcd for C₁₂H₂₂N₃F₃O₂S₂: C, 39.88; H, 6.13; N, 11.63. Found: C, 40.11; H, 6.31; N, 11.35.

(*R*)-*N*-*tert*-Butanesulfinyl formamidine 18. To a 50 mL round-bottomed flask charged with imidate **13** (960 mg, 5.9 mmol) was added 20 mL of 2.0 M NH₃ in EtOH (40 mmol) and the reaction stirred at rt for 30 min. The solvents were removed and the residue triturated with hexanes to afford 800 mg (91%) of the title compound as a colorless solid. $[\alpha]_D^{23} -229^\circ$ (*c* 1.0, CHCl₃); ¹H NMR (500 MHz) δ 1.14 (s, 9H), 5.45 (br s, 2H), 7.80 (t, *J* = 9.0, 1H). ¹³C NMR (125 MHz) δ 22.2, 56.0, 157.0. Anal. Calcd for C₅H₁₂N₂SO: C, 40.51; H, 8.16; N, 18.90. Found: C, 40.34; H, 8.45; N, 19.12.

(*R*)-*O*-Methyl-*N*-*tert*-butanesulfinyl acetimidate 19. To a 25 mL round-bottomed flask charged with **7** (1.55 g, 12.8 mmol) were added 12.0 mL of trimethyl orthoacetate (94.0 mmol) and 10.0 mg (0.0526 mmol) of *p*-toluenesulfonic acid. A reflux condenser was affixed to the reaction vessel and the reaction mixture was stirred at reflux for 3 h. The volatile material was removed in vacuo and the crude oil was purified by chromatography (4:1 hexanes:EtOAc) to afford 1.90 g (89%) of the title compound as a colorless oil. $[\alpha]_D^{23} -122^\circ$ (*c* 1.0, CHCl₃). IR 1620, 1281, 1081 cm⁻¹. ¹H NMR (300 MHz) δ 1.21 (s, 9H), 2.29 (s, 3H), 3.76 (s, 3H). ¹³C NMR

(75 MHz) δ 19.0, 22.0, 54.2, 56.0, 174.4. Anal. Calcd for $C_7H_{15}NSO_2$: C, 47.42; H, 8.53; N, 7.90. Found: C, 47.46; H, 8.68; N, 7.98.

(*R,R*)-Bis(*tert*-butanesulfinyl)imidoamidine 20. A solution of sulfinyl amidine **18** (400 mg, 2.70 mmol) in 10 mL of THF was slowly added to a slurry of KH (35 % in mineral oil, 120 mg, 3.0 mmol). After gas evolution ceased (ca. 15 min), the mixture was cooled to -78°C and a 5 mL solution of *O*-methyl-*N-tert*-butanesulfinyl acetimidate **19** (420 mg, 2.40 mmol) was slowly added. The reaction was slowly warmed to rt over 1 h and then quenched with 1 M NaHSO_4 . 200 mL of EtOAc was added, the layers were separated, and the organic phase was washed with saturated NaHCO_3 and brine. After drying with Na_2SO_4 , the mixture was filtered, and the solvent removed. Column chromatography (50:50 CH_2Cl_2 :EtOAc) afforded 550 mg (78%) of the title compound as a white solid. ^1H NMR shows a mixture of two rotamers in a ~70:30 ratio. Major ^1H NMR (300 MHz) δ 1.17 (s, 9H), 1.27 (s, 9H), 2.33 (s, 3H), 2.46 (s, 1H), 7.98 (d, $J = 11.1$, 1H). HRMS (FAB) calcd for Anal. Calcd for $\text{C}_{11}\text{H}_{23}\text{N}_3\text{O}_2\text{S}_2$ ($M+1$): 294.1312 Found: 294.1310.

(*R,R*)-Bis(*tert*-butanesulfinyl)imidoamidine 17. A pressure tube was charged with KH (35 % in mineral oil, 105 mg, ~1.0 mmol). Imidoamidine **20** (235 mg, 0.800 mmol) was dissolved in 5 mL of hot THF, cooled to rt and added in portions to the pressure tube under a flow of N_2 . After gas evolution had ceased (ca. 15 min) a yellow solution was obtained. MeI (500 μL , 1.20 g, 9.00 mmol) was added and the tube was closed. After stirring for 12 h at rt, TLC (95:05 hexanes:EtOAc) revealed that no starting material remained. Saturated NaHCO_3 (15 mL) was added followed by 100 mL of EtOAc. The layers were separated and the organic phase was washed with brine. The organic layer was dried with saturated NaCl, and the solvent was removed under reduced pressure. Flash purification (96:04 CH_2Cl_2 :*i*PrOH) afforded a white solid weighing 117 mg (48%). $[\alpha]_D^{23} -404^\circ$ (c 1.0, CHCl_3); IR 1645, 1573, 1285, 1054 cm^{-1} . ^1H NMR (300 MHz) δ 1.15 (s, 9H), 1.20 (s, 9H), 2.58 (s, 3H), 3.33 (s, 3H), 8.45 (s, 1). ^{13}C NMR (125 MHz) 17.6, 22.0, 22.0, 56.3, 56.7, 150.3, 165.7. Anal. Calcd for $\text{C}_{12}\text{H}_{25}\text{N}_3\text{O}_2\text{S}_2$: C, 46.87; H, 8.20; N, 13.67. Found: C, 46.88; H, 8.53; N, 13.31.

(*S*)-*O*-Methyl-(*N*)-*p*-toluenesulfinyl imidate 22. To a round bottomed flask charged with (*S*)-*N-p*-toluenesulfinamide **9** (465 mg, 3.00 mmol) was added 3.0 mL of trimethyl orthoformate (30 mmol) and 15 mL of THF. To this solution was added *p*-toluenesulfonic acid monohydrate (3.0 mg, 0.16 mmol) and the mixture was stirred for 3 h at rt. 10 mL of Et_2O was added and then the mixture was filtered. The crude material was concentrated in vacuo and chromatographed (4:1 hexanes:EtOAc, $R_f = 0.20$) to afford the title compound as a colorless oil weighing 452 mg (76%). $[\alpha]_D^{23} +165^\circ$ (c 0.5, CHCl_3); IR 1602, 1243, 1093, 1085 cm^{-1} . ^1H NMR (300 MHz) δ 2.38 (s, 3H), 2.79 (s, 3H), 7.28 (d, 2H, $J = 8.1$ Hz), 7.56 (d, 2H, $J = 8.1$ Hz), 8.00 (s, 1H). ^{13}C NMR (75 MHz) 21.7, 55.2, 124.8, 130.0, 142.0, 143.9, 159.8. Anal. Calcd for $\text{C}_9\text{H}_{11}\text{NO}_2\text{S}$: C, 54.80; H, 5.62; N, 7.10. Found: C, 54.53; H, 5.66; N, 7.01. The imidate was checked for enantiopurity by chiral HPLC (Chiralcel OD, 9/1 hexanes/*i*PrOH, 1.0 mL/min) (*S*)-*p*-toluenesulfinyl imidate $t_R = 9.5$ min; (*R*)-*p*-toluenesulfinyl imidate $t_R = 10.3$ min. A small amount of racemic methyl-*p*-toluenesulfinate ($R_f = 0.28$) was also produced during the course of the reaction and isolated. The NMR spectra for this material matched that reported in the literature.⁷

(*S*)-*N*-Methyl-*N'*-*p*-toluenesulfinyl amidine 23. To a 10 mL flask charged with (*S*)-*O*-methyl-*N-p*-toluenesulfinyl imidate **22** (210 mg, 1.06 mmol) was added 3.0 mL of MeNH_2 in MeOH (2.0 M, 6.0 mmol). The mixture was stirred for 20 min and the solvent was removed under reduced pressure to afford the title compound as a colorless solid weighing 210 mg (99%). The enantiopurity was checked by HPLC and found to be greater than 98%. HPLC conditions:

(Chiralpak AD, 9:1 hexanes:iPrOH, 1.0 mL/min) (*R*)-*p*-toluenesulfinyl amidine t_R = 21.2 min; (*S*)-*p*-toluenesulfinyl amidine t_R = 27.2 min. $[\alpha]_D^{23} +141^\circ$ (c 0.5, CHCl_3); IR 3255(br), 3052, 1606, 1329, 1048 cm^{-1} . ^1H NMR (300 MHz) δ 2.36 (s, 3H), 2.79 (s, 3H), 7.08 (br s, 1H), 7.24 (2H, J = 8.1 Hz), 7.51 (d, 2H, J = 8.1 Hz), 8.01 (s, 1H). ^{13}C NMR (75 MHz) 21.7, 28.2, 125.1, 129.9, 141.5, 145.6, 157.2. Anal. Calcd for $\text{C}_9\text{H}_{12}\text{N}_2\text{OS}$: C, 55.08; H, 6.16; N, 14.17. Found: C, 54.95, H, 6.16; N, 13.95.

(*S,S*)-*N*-Methyl-bis(*p*-toluenesulfinyl)imidoamidine 21. A 25 mL round-bottomed flask was charged with (*S*)-*p*-toluenesulfinyl amidine **23** (181 mg, 0.928 mmol) and (*S*)-*p*-toluenesulfinyl imidate **22** (181 mg, 0.923 mmol) was added K_2CO_3 (146 mg, 1.10 mmol) and the mixture was stirred at 60 $^\circ\text{C}$ for 14 h. The mixture was added to a separatory funnel with 100 mL EtOAc and 10 mL of water. The layers were separated and the organic phase was dried with Na_2SO_4 , filtered, and concentrated. Chromatography (2:1 hexanes:EtOAc) afforded 139 mg (44%) of the title compound as a colorless solid. $[\alpha]_D^{23} +864^\circ$ (c 0.5, CHCl_3); IR 1562, 1280, 1061 cm^{-1} . ^1H NMR (300 MHz) 2.38 (s, 6H), 3.42 (s, 3H), 7.26 (t, J = 5.7, 4H), 7.54 (t, J = 5.7, 4H), 8.34 (br s, 2H). Anal. Calcd for $\text{C}_{16}\text{H}_{17}\text{N}_3\text{O}_2\text{S}_2$: C, 55.31; H, 4.93; N, 11.76. Found: C, 55.27; H, 5.27; N, 11.76.

General Method for catalyst preparation and Diels–Alder reactions using siam ligands. Catalyst preparation for ligand **16a** is given as a representative example. A 10 mL round-bottomed flask wrapped in aluminum foil was charged with CuCl_2 (6.7 mg, 0.050 mmol), AgSbF_6 (34.3 mg, 0.100 mmol), ligand **16a** (16.1 mg, 0.055 mmol), and 50 mg of activated 3 Å molecular sieves. Freshly distilled CH_2Cl_2 was then added (2.5 mL) and the mixture was stirred at rt for 1 h. The dienophile (0.500 mmol) was added and the reaction mixture was immediately cooled to the desired temperature. Freshly distilled diene (2.50 mmol) was then added to the vessel. The reactions were monitored by TLC (neat CH_2Cl_2) for disappearance of dienophile and upon complete consumption of the dienophile, or after the given length of time, the reactions were filtered over a 1" plug of silica with 100mL of a 50:50 hexanes:EtOAc solution. The crude mixtures were analyzed by ^1H NMR and chiral HPLC (see individual compounds for analysis). Unless otherwise noted, authentic racemic compounds were prepared using 1.0 equiv of Et_2AlCl in CH_2Cl_2 and used for comparison to catalytic asymmetric reactions. Yields are based on chromatographically purified samples. All catalysts using ligands **14**, **16a-d**, **17**, **21**, and **29** were prepared using the same general method.

Diels–Alder adducts of cyclopentadiene and imides 10 (Table 5).

Cycloadduct 11a. The general procedure was used to generate the catalyst mixtures. After 1 h, imide **10a** (70.5 g, 0.500 mmol) was added, the mixture cooled to -78°C , and freshly distilled cyclopentadiene (208 μL , 2.50 mmol) was added. Within 10 min, TLC analysis (neat CH_2Cl_2) revealed that no imide remained and the reaction mixture was filtered over silica. An aliquot was used for ^1H NMR and HPLC analysis (see above). The remainder was chromatographed using neat CH_2Cl_2 to obtain the 98 mg (96%) of the cycloadduct as a colorless crystalline solid. Spectral data corresponded exactly to that previously reported in the literature.⁶

Cycloadduct 11b. The general procedure was used to generate the catalyst mixture. After 1 h, **10b** (77.5 g, 0.500 mmol) was added, the mixture was cooled to -40°C and freshly distilled cyclopentadiene (208 μL , 2.50 mmol) was added. After 8 h the reaction was worked up by the general procedure. HPLC analysis (Chiralcel OD, 96:4 hexanes:Reagent Alcohols, 1.0 mL/min) *exo* isomers t_R = 16.5 min, *endo*_{major} t_R = 18.0 min, *endo*_{minor} t_R = 19.5 min. Spectral data corresponded exactly to that previously reported in the literature.⁸ The *endo/exo* ratio was

determined by ^1H NMR integration of the *exo* olefinic protons [δ 5.65 (m, 2H)]. Chromatography with neat CH_2Cl_2 afforded 83 mg (76%) of the product as a colorless solid.

Cycloadduct 11c. The catalyst was prepared from ligand **16a** (0.050 mmol) using the general method. Imide **10c** (97.0 mg, 0.452 mmol) was added and the mixture was cooled to 0 °C. Cyclopentadiene (420 μL , 5.00 mmol) was added and the mixture was stirred for 16 h at 0 °C followed by the normal workup. The *endo/exo* selectivity of the crude mixture was determined by integration of one of the *exo* olefinic protons [δ 6.03 (m, 1H)]. Chromatography (neat CH_2Cl_2) afforded the product as colorless oil weighing 75 mg (58%). Spectral data corresponded exactly to that previously reported in the literature.⁸ A small amount of the pure *endo* diastereomer was isolated by HPLC using a Rainin Microsorb (Si) column (9:1 hexanes:iPrOH, 1.0 mL/min) *exo* isomers t_{R} = 10.3 min, *endo* isomer t_{R} = 11.3 min. The purified *endo* product was then analyzed by HPLC to determine the ee (94%). HPLC analysis (Chiralpak AS, 9:1 hexanes:iPrOH, 1.0 mL/min) *endo*_{minor} t_{R} = 15.3 min, *endo*_{major} t_{R} = 16.7 min.

Cycloadduct 11d. The catalyst was prepared according to the general method. Imide **10d** (100 mg, 0.470 mmol) was added and the mixture was cooled -78 °C. Cyclopentadiene (200 μL , 2.40 mmol) was added and the reaction was worked up after 2 h by the general method. An aliquot of the unpurified mixture was analyzed by ^1H NMR. Integration of the *exo* olefinic protons [δ 6.13 (m, 2H)] was used to determine the *endo/exo* ratio. The remainder was purified with neat CH_2Cl_2 to afford 109 mg (85%) of the cycloadduct as a colorless oil. Spectral data corresponded exactly to that previously reported in the literature.⁹

The purified product was converted to the iodolactone by the literature protocol and analyzed using chiraldex GC G-TA column (180 °C, flow = 10 psi) *endo*_{minor} t_{R} = 35.5 min, *endo*_{major} t_{R} = 37.5 min (96% ee).⁹

Diels–Alder adduct 11e. The catalyst mixture (10 mol%) was prepared according to the general method and cyclohexadiene (286 μL , 240 mg, 3.00 mmol) and **10a** (84.6, 0.600 mmol) were added and stirred for 16 h at 0 °C. After normal workup an aliquot was analyzed by chiral HPLC (Chiralpak AD, 95:05 hexanes: iPrOH, 1.0 mL/min) *exo* isomers t_{R} = 18.0 min, *endo*_{minor} t_{R} = 20.1 min, *endo*_{major} isomer t_{R} = 22.5 min. (90% ee). Spectral data corresponded exactly to that previously reported in the literature.⁹

(1*R*,2*S*,4*R*)-2-methylbicyclo[2.2.1] hept-5-ene-carboxaldehyde (24). The general procedure was followed using acrolein (42.0 mg, 50.0 μL , 0.749 mmol) and cyclopentadiene (313 μL , 3.50 mmol). The reaction mixture was stirred at -78 °C for 2 h before filtering over silica with neat CH_2Cl_2 to afford the crude product as a colorless oil with 58 mg (65%). Spectral data corresponded exactly to that previously reported in the literature.¹⁰

The cycloadduct was reacted with 2,4-(*S,S*)-pentanediol according to the literature procedure and the corresponding acetal analyzed by GC (J&W GB-1; init. temp 90 °C, final temp. 120 °C at 1.0 °C/min, flow = 10.0 psi) major diastereomer t_{R} = 34.4 min, minor diastereomer t_{R} = 36.5 min.¹⁰

Diels–Alder adduct 25a. The catalyst was prepared with **16a** according to the general procedure. Imide **10a** (70.6 mg, 0.500 mmol) was added followed by 0.300 mL (3.55 mmol) of freshly distilled isoprene to afford 67 mg (83%) of the product as a colorless solid after chromatography with neat CH_2Cl_2 . Stereochemical assignment is based upon comparison of the optical rotation to the literature value. $[\alpha]_{\text{D}}^{23}$ -36.9° (c 1.96, CHCl_3). (Lit $[\alpha]_{\text{D}}^{23}$ -24.2° (c 1.96, CHCl_3) for 60 % ee).⁹

Enantiomeric excess was determined by derivatization by the literature protocol to afford two diastereomers of the (*R*)- α -methylbenzylamide. The diastereomers were separated on Si-OH

HPLC. (Rainin Microsorb, 97/03 hexanes/iPrOH, 1.0 mL/min) major diastereomer t_R = 17.4 min, minor diastereomer t_R = 21.2 min. (92% ee).

Diels–Alder cycloadduct 25b. The catalyst (0.035 mmol) was prepared by the general procedure. Imide **10a** (49.3 mg, 0.354 mmol) was added and the mixture was cooled to 0 °C before adding 0.300 mL (3.10 mmol) of 2,3-dimethyl-butadiene. After stirring for 16 h at 0 °C, the mixture was chromatographed directly to afford 67 mg (92%) of the product as a white solid. For comparison, authentic racemic material was prepared using 1.0 equiv of Et_2AlCl as a catalyst. The purified product was separated on HPLC (Chiralpak AS, 1.0 mL/min, 97:03 hexanes:iPrOH) major enantiomer t_R = 23.1 min, minor enantiomer t_R = 25.6 min. (92% ee). $[\alpha]_D^{23}$ –55.7° (c 1.96, CHCl_3). [Lit 60% ee $[\alpha]_D^{23}$ –35.7° (c 1.96, CHCl_3)].⁹

Diels–Alder product 25c. The general method was used to prepare the catalyst. Imide **10a** (70.6 mg, 0.500 mmol) was added followed by 1,3-pentadiene (0.400 mL, 273 mg, 4.02 mmol). The mixture was stirred at room temperature for 16 h and then the crude reaction mixture was chromatographed directly with neat CH_2Cl_2 to afford 19 mg of the title compound as an inseparable mixture of diastereomers and regioisomers. The ^1H NMR spectra of the major isomer was consistent with the spectra previously reported.⁹ The ratio of the diastereomers (2.0:1.0:0.4) was determined by integration of the protons of the 2-methyl groups [major *endo* δ 0.87 (d, J = 7.1, 3H); isomer 2 δ 0.96 (d, J = 7.1, 3H); isomer 3 δ 1.00 (d, J = 7.1, 3H)]. The enantiomeric excess was determined by chiral HPLC analysis. (Chiralcel OD, 1.0 mL/min, 90/10 hexanes/EtOH) minor *endo* t_R = 15.1 min, major *endo* t_R = 18.9 min, other isomers 10.2 min, 12.3 min, 13.9 min, 18.0 min.

Diels–Alder product 25d. The general method was used to prepare the catalyst mixture. The flask was cooled to 0 °C before adding **10a** (28.0 mg, 0.200 mmol) and 2-phenyl butadiene (130 mg, 1.00 mmol). After 2 h the reaction mixture was chromatographed with neat CH_2Cl_2 to afford 43 mg (83%) of the product as a colorless oil. The product was derivatized to the corresponding (*R*)-(+)- α -methyl-benzylamide by the procedure of Evans to determine the ee (45%).⁹ $[\alpha]_D^{23}$ –16.0° (c 0.5, CHCl_3) IR ^1H NMR (300 MHz) δ 1.79–1.88 (m, 1H), 2.13–2.18 (m, 1H), 2.46–2.60 (m, 4H), 3.73–3.85 (m, 1H), 4.05 (t, J = 8.1, 2H), 4.42 (t, J = 8.1, 2H), 6.11 (s, 1), 7.20–7.39 (m, 5H). ^{13}C NMR (75 MHz) δ 26.4, 27.3, 28.2, 38.3, 43.2, 62.3, 122.8, 125.4, 127.2, 128.6, 136.6, 142.1, 153.6, 176.7. Anal. Calcd for $\text{C}_{16}\text{H}_{17}\text{NO}_3$: C, 70.83; H, 6.32; N, 5.22. Found: C, 70.49; H, 6.44; N, 5.22.

The product was derivatized with (*R*)-(+)- α -methylbenzylamine to afford the diastereomeric amides which were separated on Si HPLC Rainin Microsorb (1.0 mL/min; hexanes/isopropanol 95/05) major t_R = 10.8 min, minor t_R = 11.7 min. ^1H NMR (300 MHz) 1.50 (d, J = 9.9, 3H), 2.01–2.11 (m, 1H), 2.38–2.55 (m, 5H), 5.10–5.18 (m, 1H), 5.62–5.70 (m, 1H), 6.10 (br s, 1H), 7.28–7.35 (m, 5H).

Preparation of TBDPS substituted diene.

1-(*tert*)-Butyl-diphenyl-silanyloxy)-but-3-en-2-one. A round bottomed flask equipped with a reflux condenser was charged with Mg (146 mg, 6.00 mmol) in 5 mL of THF. To this was slowly added a 1.0 M solution of vinyl bromide in THF (6.0 mL, 6.0 mmol) with gentle heating to initiate Grignard formation. After the Mg was consumed the mixture was cooled to –78 °C and the Weinreb amide¹¹ (1.78 g, 5.00 mmol) was added as a solution in 5.0 mL THF. The reaction was warmed to 0 °C and stirred for 2 h then cooled to –78 °C once again before quenching with 5

mL of 1.0 M HCl. Et₂O was added and the layers were separated. After washing with sat NaHCO₃ and brine, the organic phase was dried with Na₂SO₄, filtered, and the solvent was removed under reduced pressure. Chromatography afforded 615 mg of the title compound (38%). ¹NMR (300 MHz) δ 1.17 (s, 9H), 4.44 (s, 2H), 5.28 (dd, *J*=1.6, 11.6, 1H), 6.35 (dd, *J*=1.6, 17.6, 1H), 6.73 (dd, *J*=10.6, 17.6), 7.40-7.50 (m, 6H), 7.72-7.75 (m, 4 H). ¹³C NMR (75 MHz) δ 19.7, 27.1, 69.3, 128.3, 129.3, 130.3, 132.1, 133.1, 135.9, 198.3.

tert-Butyl-(2-methylene-but-3-enyloxy)-diphenyl-silane. (Table 6, entry 5). A 50 mL round-bottomed flask was charged with methyltriphenylphosphonium bromide (1.78 g, 5.00 mmol) and 10 mL of THF and cooled to -78 °C. BuLi (2.5 M in hexanes, 2.0 mL, 5.0 mmol) was slowly added to obtain an orange mixture. The reaction mixture was warmed to 0 °C, stirred for 15 min, and cooled again to -78 °C. The ketone (615 mg, 1.89 mmol) was added in 5 mL of THF, the mixture was warmed to 0 °C, and stirred an additional 15 min. The reaction mixture was cooled to -78 °C and quenched with 15 mL of 1M HCl. After extractive workup and purification by column chromatography (neat hexanes *R_f*= 0.20) the title compound was isolated as a colorless oil weighing 330 mg (55%). IR 2956, 2929, 2856, 1428, 1114 cm⁻¹. ¹NMR (300 MHz) δ 1.14 (s, 9H), 4.44 (s, 2H), 5.02 (d, *J*=11.1, 1H), 5.09 (d, *J*=18.0, 1H), 5.25 (s, 1H), 5.57 (s, 1H), 6.42 (dd, *J*=11.1, 18.0, 1H), 7.40-7.50 (m, 6H), 7.67-7.70 (m, 4 H). ¹³C NMR (75 MHz) δ 19.7, 27.2, 63.4, 113.5, 115.2, 128.1, 130.1, 133.9, 135.9, 136.9, 144.9. Anal. Calcd for C₂₁H₂₆OSi; C, 78.21; H, 8.13. Found: C, 78.25. H, 7.96.

Diels-Alder Product 25e. The catalyst (10 mol %) was prepared as in the general method. Imide **10a** (38.3 mg, 0.271 mmol) and the diene (300 mg, 0.934 mmol) were added. The mixture was stirred at rt for 16 h. Chromatography (neat CH₂Cl₂) afforded 41 mg (33%) of the product as a colorless oil. The enantiomeric excess (62%) was determined by derivitization to the corresponding (*R*)-(+)-α-methyl-benzylamide. IR 2965, 2929, 2856, 1778, 1691, 1386, 1114 cm⁻¹. ¹H NMR (300 MHz) δ 1.06 (s, 9H), 1.63-1.74 (m, 1H), 1.95-2.12 (m, 3H), 2.26-2.36 (m, 2H), 3.65-3.75 (m, 1H), 4.02-4.06 (m, 2H), 4.05 (s, 2H), 4.39-4.44 (m, 2H), 5.70 (s, 1H), 7.36-7.45 (m, 6H), 7.66-7.69 (m, 4H). Mass Calcd for C₂₄H₃₄NO₄Si (MLi⁺) 470.2347, found 470.2339.

The purified product was derivatized with (*R*)-(+)-α-methyl-benzylamine by the general method of Evans.⁹ The diastereomers were separated by Si-OH HPLC (Rainin Microsorb, 99:01 hexanes:iPrOH, 1.0 mL/min) major diastereomer *t_R* = 33.0 min; minor diastereomer *t_R* = 36.3 min. (62% ee). Authentic racemic material was prepared using 1.0 eq of ZnI₂ as catalyst in CH₂Cl₂ at rt and derivatized by the above method. HRMS (FAB): Mass Calcd for C₃₂H₃₉NO₂Si (MLi⁺) 504.2910, found 504.2912.

Diels-Alder adduct 26. The catalyst mixture (0.055 mmol) was prepared by the general procedure using **16c** (22.0 mg, 0.061 mmol). After 1 h, imide **10d** (102 mg, 0.0515 mmol) was added followed by 2,3-dimethylbutadiene (300 μL, 5.50 mmol) was added. After 16 h, the mixture was chromatographed directly (neat CH₂Cl₂, *R_f*= 0.30) to afford the product as a colorless oil weighing 124 mg (80%). Authentic racemic material was prepared using Et₂AlCl and the resulting enantiomers were separated by chiral HPLC. HPLC Analysis (Chiralcel AD, 1.0 ml/min, 9/1 hexanes/reagent alcohols) major *t_R* = 10.2 min, minor *t_R* = 11.9 min. 81% ee. [α]_D²³ -106° (*c* 0.5, CHCl₃). ¹NMR (300 MHz) δ 1.23 (t, *J*=7.2, 3H), 1.61 (s, 3H), 1.63 (s, 3H), 1.94-2.20 (m, 2H), 2.29-2.40 (m, 2H), 2.93-3.01 (m, 1H), 3.97-4.13 (m, 5H), 4.38-4.44 (m, 2H). ¹³C (75 MHz) 14.0, 18.5, 18.6, 34.1, 34.2, 40.5, 42.0, 42.7, 60.5, 62.0, 123.8, 123.9, 153.2, 175.0, 176.1. HRMS (FAB): Mass Calcd for C₁₅H₂₁N₁O₅ (MLi⁺) 302.1579, found 302.1580.

***N*-tert-Butanesulfinyl imidate 33.** To a 100 mL round-bottom flask was added 4.67 g of trimethyl-4-bromobutylorthoester (20.7 mmol) followed by 1.00 g of (*R*)-*tert*-butanesulfinamide **7** (8.26 mmol) and 21 mL of THF (0.4 M). Following this, 2.20 g of anhydrous MgSO₄ (18.3 mmol) was added in one portion, and the reaction mixture heated to reflux in an oil bath. After stirring for roughly 72 h, the mixture was cooled to rt and filtered from the spent MgSO₄ and the solvent evaporated to afford a nearly 1:1 mixture of the resultant sulfinylimidate product **31** and 4-bromo-methylbutyrate **32** by ¹H NMR. A portion of this material (1.46 g) was dissolved in 13 mL of DMF and 77.0 mg of NaI (0.514 mmol) was added followed by NaN₃ 402 mg (6.18 mmol) and the mixture allowed to stir at rt. After stirring overnight, the reaction mixture was diluted with 40 mL of a 3:1 hexanes/CH₂Cl₂ solution and washed with H₂O (3x15 mL). The organic layer was then dried, filtered, and the solvents evaporated. The residue was then loaded on a plug of silica gel and eluted with 30-55% EtOAc in hexanes to afford 754 mg of the title compound as a clear oil in 59% yield from **7**. [α]_D²³ -129° (*c* 0.48, CHCl₃); IR 2096, 1633, 2174, 1074 cm⁻¹. ¹H NMR (500 MHz) δ 1.25 (s, 9H), 1.91-1.99 (m, 2H), 2.72-2.82 (m, 2H), 3.33-3.36 (m, 2H), 3.73 (s, 3H); ¹³C NMR (125 MHz) 21.8, 25.6, 29.8, 50.7, 54.2, 55.9, 63.28, 175.2. Anal. Calcd for C₉H₁₈N₄O₂S: C, 43.88; H, 7.37; N, 22.74. Found: C, 43.69; H, 7.49; N, 22.66.

Sulfinyl amidine 34. To a 25 mL rb flask was added 258 mg of sulfinyl imidate **33** (1.05 mmol) and 5.24 mL of THF (0.2 M) was added. Following this, 385 mg of triphenylphosphine (1.47 mmol) and 0.375 mL of H₂O (20.8 mmol) were added and the reaction mixture was heated to reflux. After stirring overnight, the reaction solution was cooled to rt, and the solvents remove in vacuo. The residue was loaded on a plug of silica gel and eluted with 2% MeOH in CH₂Cl₂ with 0.1% Et₃N to afford 153 mg (78%) of the title product as an inseparable mixture of 2 rotational isomers in a 55:45 ratio. mp 116-118 °C. [α]_D²³ -581° (*c* 1.0, CHCl₃). IR 1602, 1313, 1023 cm⁻¹. ¹H NMR (500 MHz) δ 1.03 (s, 9H), 1.84-1.94 (m, 2H), 2.45-2.75 (m, 2H), 3.31 (m, 2H), 7.52 (br s, 0.45 H), 8.35 (br s, 0.55 H). HRMS (FAB) calcd for C₈H₁₆N₂OS (M+1): 189.1062. Found: 189.1063.

Bis(*tert*-butanesulfinyl)imidoamidine 29. To a 5 mL rb flask was added 38.0 mg (0.233 mmol) of sulfinyl imidate **13**, 0.71 mL of THF (0.3 M), and 32.0 mg of oven-dried K₂CO₃ (0.233 mmol). To this mixture was added 40.0 mg of sulfinyl amidine **34** (0.213 mmol), and the allowed to stir at rt for 24h. After this time, the reaction mixture was diluted with 20 mL of EtOAc and washed with H₂O (2x), dried, filtered, and the solvents evaporated. Chromatography with 30-60% EtOAc in hexanes to afford 43 mg of the desired product as white powder in 63% yield. [α]_D²³ -516° (*c* 1.0, CHCl₃). IR 1585, 1399, 1078 cm⁻¹. ¹H NMR (500 MHz) δ 1.15 (s, 9H), 1.20 (s, 9H), 2.14-2.19 (m, 2H), 2.94-3.00 (m, 1H), 3.22-3.29 (m, 1H), 3.67-3.72 (m, 1H), 3.82-3.88 (m, 1H), 8.70 (s, 1H); ¹³C NMR (125 MHz) 19.5, 21.9, 22.0, 30.3, 45.9, 56.3, 56.7, 147.2, 169.4. Anal. Calcd for C₁₃H₂₅N₃O₂S₂: C, 48.87; H, 7.89; N, 13.15. Found: C, 48.78; H, 7.92; N, 13.19.

Nonlinearity Study. The Diels-Alder reactions employing imide **10a** were performed according to the standard protocol with mixtures of (*R,R*)-**16a** and (*S,S*)-**16a**, which was prepared in an identical fashion from (*S*)-*tert*-butanesulfinamide **7**. The ee's of the ligand mixtures were determined by chiral HPLC of a CH₂Cl₂ solution (Chiralcel OD, 1.0 mL/min, 9/1 Hexanes/*i*PrOH) (*S,S*)-**16a** (*t*_R = 7.7 min, and (*R,R*)-**16a** *t*_R = 15.1 min. The subsequently generated products **11a** were analyzed by HPLC as described above.

Mass Spectral Study of Catalyst. The Cu(II)**16a** catalyst mixture was prepared using the general method. After 1 h the reaction mixture was filtered through a 0.45 μm PTFE membrane, diluted with MeCN, and analyzed by electrospray MS (+ ion). The full ion trace along with expanded sections showing the expected isotope distributions for Cu(**16a**)₂, Cu(**16a**)₃, Cu₂(**16a**)₂(SbF₆), Cu₂(**16a**)₃(SbF₆) are shown below.

Full Ion Trace.

Zn-sulfinylimidoamidine complex 2.26. A 10 mL round-bottomed flask was charged with ZnI_2 (18.0 mg, 0.056 mmol) and **siam 2.16a** (16.5 mg, 0.056 mmol). CH_2Cl_2 (2.5 mL) was added and the mixture stirred in the dark for 36 h. The mixture was filtered and Et_2O was allowed to diffuse in slowly affording colorless needles from which a sample was suitable for X-ray analysis (data below). IR 1576, 1289, 995, 977 cm^{-1} . ^1H NMR (300 MHz) δ 1.27 (s, 18H), 3.33 (s, 3H), 8.67 (s, 2H). The complex crystallized along with at least 3 molecules of CH_2Cl_2 which are omitted from the structure and tables for clarity and brevity (see below).

X-ray Crystal Structure ORTEP Plots and Data.

Figure S-1. Two ORTEP views of 2,6-bis-*tert*-butanesulfinylaldimine (**8a**).

Experimental Methods (8a).

Identification Code	8a
Empirical Formula	C ₁₅ H ₂₃ N ₃ O ₂ S ₂
Formula Weight	341.49
Crystal Color, Habit	Colorless, needles
Crystal Dimensions	0.51 x 0.10 x 0.10 mm
Crystal System	orthorhombic
Lattice Type	Primitive
Lattice Parameters	$a = 14.0252(3) \text{ \AA}$ $b = 21.1869(2) \text{ \AA}$ $c = 6.222(1) \text{ \AA}$
Volume	1848.93(4) $\text{\AA}^3$
Space Group	P2 ₁ 2 ₁ 2 ₁ (#18)
Z value	2
D _{calc}	1.284 g/cm ³
F ₀₀₀	728.00
$\mu(\text{MoK}\alpha)$	2.97 cm ⁻¹
Diffractionmeter	SMART CCD
Radiation	MoK α ($\lambda = 0.71069 \text{ \AA}$) Graphite monochromated
Detector Position	60.00 mm
Exposure Time	10.0 seconds per frame
Scan type	ω (0.3 degrees per frame)
2 θ_{max}	52.1°
No. of Reflections Measured	Total: 8999
Corrections	Unique: 2002 ($R_{\text{int}} = 0.055$) Lorentz-polarization Absorption ($T_{\text{max}} = 0.99$ $T_{\text{min}} = 0.76$)
Structure Solution	Direct Methods
Refinement	Full-matrix least-squares
Function Minimized	$\Sigma w(F_o - F_c)^2$
Least Squares Weights	$w = 1/\sigma^2(F_o) = [\sigma_c^2(F_o) + (p^2/4)F_o^2]^{-1}$
p-factor	0.0300
Anomalous Dispersion	All non-hydrogen atoms
No. Observations ($I > 2.00\sigma(I)$)	2631
No. Variables	199
Reflection/Parameter Ratio	13.22
Residuals: R; Rw; Rall	0.037; 0.039; 0.054
Goodness of Fit Indicator	1.38
Max Shift/Error in Final Cycle	0.00
Maximum peak in Final Diff. Map	0.25 e ⁻ / $\text{\AA}^3$
Minimum peak in Final Diff. Map	-0.28 e ⁻ / $\text{\AA}^3$

Table S-1.1. Atomic coordinates and B(eq) values for **(8a)**.

atom	x	y	z	B(eq)
S(1)	-0.48389(6)	-0.13007(4)	0.2837(1)	2.50(2)
S(2)	-0.37238(6)	-0.57250(4)	0.3616(1)	2.30(2)
O(1)	-0.4926(2)	-0.1555(1)	0.5045(3)	3.36(6)
O(2)	-0.3386(2)	-0.54228(9)	0.5633(3)	3.09(6)
N(1)	-0.4046(2)	-0.3515(1)	0.1815(4)	1.90(5)
N(2)	-0.4647(2)	-0.1905(1)	0.1061(4)	2.12(6)
N(3)	-0.3828(2)	-0.5180(1)	0.1614(4)	2.15(6)
C(1)	-0.4279(2)	-0.3007(1)	0.0635(5)	1.84(7)
C(2)	-0.4446(2)	-0.3032(1)	-0.1567(5)	2.10(7)
C(3)	-0.4376(2)	-0.3609(1)	-0.2586(5)	2.32(7)
C(4)	-0.4154(2)	-0.4139(1)	-0.1414(5)	2.00(6)
C(5)	-0.3990(2)	-0.4074(1)	0.0790(5)	1.84(7)
C(6)	-0.4419(2)	-0.2429(1)	0.1918(5)	2.02(6)
C(7)	-0.6057(2)	-0.1120(1)	0.1872(5)	2.32(7)
C(8)	-0.5991(3)	-0.0906(2)	-0.0434(6)	3.97(9)
C(9)	-0.6680(2)	-0.1695(2)	0.2167(7)	3.89(9)
C(10)	-0.6384(2)	-0.0581(1)	0.3330(6)	3.42(8)
C(11)	-0.3795(2)	-0.4604(1)	0.2230(5)	2.18(6)
C(12)	-0.2715(2)	-0.6169(1)	0.2458(5)	1.94(6)
C(13)	-0.1867(2)	-0.5735(1)	0.2174(5)	2.72(7)
C(14)	-0.3052(3)	-0.6456(1)	0.0345(5)	3.01(8)
C(15)	-0.2514(2)	-0.6679(1)	0.4132(5)	2.80(8)
H(1)	-0.4603	-0.2661	-0.2349	2.5243
H(2)	-0.4481	-0.3639	-0.409	2.7781
H(3)	-0.4113	-0.4541	-0.2088	2.3992
H(4)	-0.4336	-0.2448	0.3432	2.4212
H(5)	-0.5759	-0.1243	-0.1298	4.7705
H(6)	-0.6604	-0.0782	-0.0926	4.7705
H(7)	-0.5566	-0.0558	-0.0531	4.7705
H(8)	-0.7323	-0.1588	0.186	4.6694
H(9)	-0.6632	-0.1839	0.3609	4.6694
H(10)	-0.6476	-0.2019	0.1219	4.6694
H(11)	-0.6395	-0.0721	0.478	4.1002
H(12)	-0.7006	-0.045	0.2918	4.1002
H(13)	-0.5955	-0.0236	0.3198	4.1002
H(14)	-0.3637	-0.4517	0.3685	2.6161
H(15)	-0.1794	-0.5481	0.3421	3.2659
H(16)	-0.1967	-0.5472	0.0958	3.2659
H(17)	-0.1307	-0.598	0.1965	3.2659
H(18)	-0.3166	-0.6129	-0.0668	3.6078
H(19)	-0.2575	-0.6732	-0.0196	3.6078
H(20)	-0.3624	-0.6686	0.0581	3.6078
H(21)	-0.2332	-0.6487	0.5448	3.3629
H(22)	-0.3073	-0.6924	0.435	3.3629
H(23)	-0.2013	-0.6944	0.3638	3.3629

Table S-1.2. Anisotropic displacement parameters (**8a**).

atom	U11	U22	U33	U12	U13	U23
S(1)	0.0322(4)	0.0251(4)	0.0376(5)	0.0016(3)	-0.006(4)	-0.0092(4)
S(2)	0.0315(4)	0.0237(4)	0.0323(5)	0.0014(4)	0.0055(4)	0.0034(4)
O(1)	0.056(2)	0.046(1)	0.026(1)	0.015(1)	-0.007(1)	-0.012(1)
O(2)	0.064(2)	0.030(1)	0.023(1)	0.008(1)	0.006(1)	-0.001(1)
N(1)	0.029(1)	0.025(1)	0.018(1)	0.001(1)	0.003(1)	0.000(1)
N(2)	0.030(1)	0.022(1)	0.029(2)	0.002(1)	0.001(1)	-0.001(1)
N(3)	0.027(1)	0.022(1)	0.033(2)	0.003(1)	0.002(1)	0.000(1)
C(1)	0.023(2)	0.023(2)	0.023(2)	0.000(1)	0.004(1)	0.000(1)
C(2)	0.029(2)	0.028(2)	0.023(2)	0.004(1)	0.004(1)	0.004(1)
C(3)	0.033(2)	0.033(2)	0.023(2)	0.003(1)	-0.001(1)	-0.004(2)
C(4)	0.029(2)	0.024(2)	0.023(2)	0.000(1)	0.001(1)	-0.005(1)
C(5)	0.024(2)	0.021(2)	0.025(2)	0.001(1)	0.004(1)	-0.001(1)
C(6)	0.031(2)	0.028(2)	0.017(2)	0.002(1)	0.001(1)	-0.004(1)
C(7)	0.035(2)	0.024(2)	0.029(2)	0.007(1)	0.001(1)	0.001(1)
C(8)	0.065(3)	0.050(2)	0.036(2)	0.025(2)	0.001(2)	0.004(2)
C(9)	0.032(2)	0.036(2)	0.080(3)	0.002(2)	-0.003(2)	0.001(2)
C(10)	0.048(2)	0.038(2)	0.044(2)	0.014(2)	0.002(2)	-0.005(2)
C(11)	0.028(2)	0.031(2)	0.023(2)	0.003(1)	0.005(1)	-0.001(1)
C(12)	0.026(2)	0.019(1)	0.029(2)	0.003(1)	-0.001(1)	-0.001(1)
C(13)	0.027(2)	0.033(2)	0.044(2)	0.001(1)	0.004(2)	-0.002(2)
C(14)	0.051(2)	0.030(2)	0.034(2)	0.006(2)	-0.004(2)	-0.006(2)
C(15)	0.041(2)	0.026(2)	0.039(2)	0.006(2)	-0.001(2)	0.000(2)

Table S-1.3. Bond angles (**8a**).

atom	atom	atom	angle	atom	atom	atom	angle
O(1)	S(1)	N(2)	109.8(1)	N(1)	C(5)	C(11)	113.3(2)
O(1)	S(1)	C(7)	107.5(1)	C(4)	C(5)	C(11)	123.8(3)
N(2)	S(1)	C(7)	95.2(1)	N(2)	C(6)	C(1)	122.1(3)
O(2)	S(2)	N(3)	110.6(1)	S(1)	C(7)	C(8)	108.3(2)
O(2)	S(2)	C(12)	107.7(1)	S(1)	C(7)	C(9)	109.1(2)
N(3)	S(2)	C(12)	97.2(1)	S(1)	C(7)	C(10)	103.8(2)
C(1)	N(1)	C(5)	117.4(2)	C(8)	C(7)	C(9)	113.3(3)
S(1)	N(2)	C(6)	114.9(2)	C(8)	C(7)	C(10)	111.0(3)
S(2)	N(3)	C(11)	115.1(2)	C(9)	C(7)	C(10)	110.9(3)
N(1)	C(1)	C(2)	123.3(3)	N(3)	C(11)	C(5)	122.8(3)
N(1)	C(1)	C(6)	113.7(3)	S(2)	C(12)	C(13)	109.8(2)
C(2)	C(1)	C(6)	122.8(3)	S(2)	C(12)	C(14)	107.6(2)
C(1)	C(2)	C(3)	118.3(3)	S(2)	C(12)	C(15)	103.6(2)
C(2)	C(3)	C(4)	119.8(3)	C(13)	C(12)	C(14)	112.7(3)
C(3)	C(4)	C(5)	118.4(3)	C(13)	C(12)	C(15)	111.4(2)
N(1)	C(5)	C(4)	122.8(3)	C(14)	C(12)	C(15)	111.2(2)

Table S-1.4. Selected bond distances (**8a**).

atom	atom	distance	atom	atom	distance
S(1)	O(1)	1.482(2)	C(1)	C(6)	1.475(4)
S(1)	N(2)	1.713(2)	C(2)	C(3)	1.380(4)
S(1)	C(7)	1.851(3)	C(3)	C(4)	1.376(4)
S(2)	O(2)	1.486(2)	C(4)	C(5)	1.398(4)

S(2)	N(3)	1.705(2)	C(5)	C(11)	1.463(4)
S(2)	C(12)	1.846(3)	C(7)	C(8)	1.508(4)
N(1)	C(1)	1.343(4)	C(7)	C(9)	1.509(4)
N(1)	C(5)	1.348(3)	C(7)	C(10)	1.530(4)
N(2)	C(6)	1.272(3)	C(12)	C(13)	1.513(4)
N(3)	C(11)	1.279(3)	C(12)	C(14)	1.525(4)
C(1)	C(2)	1.391(4)	C(12)	C(15)	1.527(4)

Table S-1.5. Torsion angles (**8a**).

atom	atom	atom	atom	angle
S(1)	N(2)	C(6)	C(1)	176.6(2)
S(2)	N(3)	C(11)	C(5)	-172.1(2)
O(1)	S(1)	N(2)	C(6)	-13.7(3)
O(1)	S(1)	C(7)	C(8)	-175.9(2)
O(1)	S(1)	C(7)	C(9)	-52.1(3)
O(1)	S(1)	C(7)	C(10)	66.2(2)
O(2)	S(2)	N(3)	C(11)	-13.5(3)
O(2)	S(2)	C(12)	C(13)	-54.8(2)
O(2)	S(2)	C(12)	C(14)	-177.8(2)
O(2)	S(2)	C(12)	C(15)	64.4(2)
N(1)	C(1)	C(2)	C(3)	0.5(4)
N(1)	C(1)	C(6)	N(2)	-179.6(3)
N(1)	C(5)	C(4)	C(3)	0.4(4)
N(1)	C(5)	C(11)	N(3)	171.5(3)
N(2)	S(1)	C(7)	C(8)	-63.2(2)
N(2)	S(1)	C(7)	C(9)	60.5(2)
N(2)	S(1)	C(7)	C(10)	178.8(2)
N(2)	C(6)	C(1)	C(2)	-4.4(5)
N(3)	S(2)	C(12)	C(13)	59.6(2)
N(3)	S(2)	C(12)	C(14)	-63.4(2)
N(3)	S(2)	C(12)	C(15)	178.8(2)
N(3)	C(11)	C(5)	C(4)	-5.3(5)
C(1)	N(1)	C(5)	C(4)	0.6(4)
C(1)	N(1)	C(5)	C(11)	-176.2(2)
C(1)	C(2)	C(3)	C(4)	0.5(4)
C(2)	C(1)	N(1)	C(5)	-1.1(4)
C(2)	C(3)	C(4)	C(5)	-1.0(4)
C(3)	C(2)	C(1)	C(6)	-174.3(3)
C(3)	C(4)	C(5)	C(11)	176.9(3)
C(5)	N(1)	C(1)	C(6)	174.1(2)
C(6)	N(2)	S(1)	C(7)	-124.4(2)
C(11)	N(3)	S(2)	C(12)	-125.5(2)

Figure S-2. ORTEP views of bis-*tert*-butanesulfinyl ketimine (**8b**).

Experimental Methods (8b).

Identification Code	8b
Empirical Formula	C ₁₇ H ₂₇ N ₃ O ₂ S ₂
Formula Weight	369.54
Crystal Color, Habit	yellow, plates
Crystal Dimensions	0.43 x 0.18 x 0.02 mm
Crystal System	Monoclinic
Lattice Type	C-centered
Lattice Parameters	$a = 9.0744(14) \text{ \AA}$ $b = 7.2109(11) \text{ \AA}$ $c = 14.700(2) \text{ \AA}$ $\beta = 96.463(3)^\circ$
Volume	955.8(2) $\text{\AA}^3$
Space Group	C2 (#5)
Z value	2
D _{calc}	1.284 g/cm ³
F ₀₀₀	396.00
$\mu(\text{MoK}\alpha)$	2.93 cm ⁻¹
Diffractometer	SMART CCD
Radiation	MoK α ($\lambda = 0.71069 \text{ \AA}$) Graphite monochromated
Detector Position	60.00 mm
Exposure Time	10.0 seconds per frame
Scan type	ω (0.3 degrees per frame)
2 θ_{max}	49.4°
No. of Reflections Measured	Total: 4528
Corrections	Unique: 1748 ($R_{\text{int}} = 0.056$) Lorentz-polarization Absorption ($T_{\text{max}} = 0.96$ $T_{\text{min}} = 0.70$)
Structure Solution	Direct Methods (SIR92)
Refinement	Full-matrix least squares
Function Minimized	$\Sigma w(F_o - F_c)^2$
Least Squares Weights	$w = 1/\sigma^2(F_o) = [\sigma_c^2(F_o) + (p^2/4)F_o^2]^{-1}$
p-factor	0.0300
Anomalous Dispersion	All non-hydrogen atoms
No. Observations	601
($I > 2.00 \sigma(I)$)	
No. Variables	109
Reflection/Parameter Ratio	6.35
Residuals: R; Rw; Rall	0.045; 0.045; 0.068
Goodness of Fit Indicator	1.66
Max Shift/Error in Final Cycle	0.00
Maximum peak in Final Diff. Map	0.35 e ⁻ / $\text{\AA}^3$
Minimum peak in Final Diff. Map	-0.29 e ⁻ / $\text{\AA}^3$

Table S-2.1. Atomic coordinates and B(eq) values (8b).

atom	x	y	z	B(eq)
S(1)	0.1798(2)	0.6478	0.25998(14)	2.39(4)

O(1)	0.2339(6)	0.8275(7)	0.3021(4)	3.18(14)
N(1)	0.5000	0.6401(15)	0.0000	1.69(17)
N(2)	0.2841(6)	0.5634(9)	0.1825(4)	1.89(13)
C(1)	0.5000	0.2568(14)	0.0000	2.70(3)
C(2)	0.4316(9)	0.3519(11)	0.0645(5)	2.15(18)
C(3)	0.4327(8)	0.5481(10)	0.0625(5)	1.87(17)
C(4)	0.3568(7)	0.6533(15)	0.1286(4)	1.70(14)
C(5)	0.3710(8)	0.8645(10)	0.1243(5)	2.40(2)
C(6)	0.2332(9)	0.4704(11)	0.3499(5)	2.12(18)
C(7)	0.1346(9)	0.5136(12)	0.4236(5)	3.40(2)
C(8)	0.3953(8)	0.4877(12)	0.3824(5)	3.40(2)
C(9)	0.1937(8)	0.2770(10)	0.3091(5)	2.60(2)
H(1)	0.5000	0.1250	0.0000	3.3222
H(2)	0.3848	0.2867	0.1097	2.5814
H(3)	0.3176	0.9194	0.1692	2.9474
H(4)	0.4726	0.8984	0.1355	2.9474
H(5)	0.3318	0.9069	0.0652	2.9474
H(6)	0.1491	0.4225	0.4704	4.1170
H(7)	0.1588	0.6323	0.4486	4.1170
H(8)	0.0338	0.5122	0.3976	4.1170
H(9)	0.4206	0.4006	0.4300	4.0213
H(10)	0.4152	0.6095	0.4047	4.0213
H(11)	0.4510	0.4633	0.3329	4.0213
H(12)	0.2086	0.1863	0.3560	3.1152
H(13)	0.0930	0.2761	0.2834	3.1152
H(14)	0.2556	0.2503	0.2627	3.1152

Table S-2.2. Anisotropic displacement parameters (**8b**).

atom	U11	U22	U33	U12	U13	U23
S(1)	0.0346(10)	0.0156(9)	0.0429(11)	0.0006(14)	0.0147(8)	0.0029(14)
O(1)	0.063(4)	0.011(3)	0.050(4)	-0.007(3)	0.020(3)	-0.008(3)
N(1)	0.027(4)	0.013(4)	0.025(4)	0.000	0.005(4)	0.000
N(2)	0.029(3)	0.012(3)	0.031(4)	-0.009(3)	0.001(3)	0.001(3)
C(1)	0.057(8)	0.005(6)	0.044(8)	0.000	0.017(7)	0.000
C(2)	0.041(5)	0.014(4)	0.029(4)	-0.002(4)	0.012(4)	0.004(4)
C(3)	0.028(4)	0.011(4)	0.031(4)	-0.006(4)	0.000(4)	-0.005(4)
C(4)	0.026(4)	0.017(4)	0.020(4)	-0.002(6)	-0.001(3)	-0.003(5)
C(5)	0.036(5)	0.010(4)	0.049(5)	-0.003(4)	0.016(4)	0.000(4)
C(6)	0.041(5)	0.010(4)	0.029(5)	-0.002(4)	0.001(4)	-0.003(4)
C(7)	0.060(6)	0.022(5)	0.053(6)	0.008(4)	0.027(5)	0.007(5)
C(8)	0.042(5)	0.033(5)	0.051(6)	-0.004(4)	-0.001(4)	0.007(4)
C(9)	0.043(6)	0.016(5)	0.040(5)	-0.006(4)	0.006(4)	0.011(4)

Table S-2.3. Bond angles (8b).

atom	atom	atom	angle	atom	atom	atom	angle
O(1)	S(1)	N(2)	114.3(3)	N(2)	C(4)	C(3)	117.9(8)
O(1)	S(1)	C(6)	104.7(3)	N(2)	C(4)	C(5)	126.0(7)
N(2)	S(1)	C(6)	96.4(3)	C(3)	C(4)	C(5)	116.1(6)
C(3)	N(1)	C(3)	120(1)	S(1)	C(6)	C(7)	103.8(5)
S(1)	N(2)	C(4)	127.9(6)	S(1)	C(6)	C(8)	109.7(5)
C(2)	C(1)	C(2)	120(1)	S(1)	C(6)	C(9)	108.3(5)
C(1)	C(2)	C(3)	118.7(7)	C(7)	C(6)	C(8)	113.1(7)
N(1)	C(3)	C(2)	121.1(8)	C(7)	C(6)	C(9)	109.5(7)
N(1)	C(3)	C(4)	119.0(7)	C(8)	C(6)	C(9)	112.1(7)
C(2)	C(3)	C(4)	119.9(7)				

Table S-2.4. Bond distances (8b).

atom	atom	distance	atom	atom	distance
S(1)	O(1)	1.495(5)	C(1)	C(2)	1.374(9)
S(1)	N(2)	1.675(6)	C(2)	C(3)	1.42(1)
S(1)	C(6)	1.864(8)	C(3)	C(4)	1.465(9)
N(1)	C(3)	1.335(8)	C(4)	C(5)	1.53(1)
N(1)	C(3)	1.335(8)	C(6)	C(7)	1.51(1)
N(2)	C(4)	1.266(8)	C(6)	C(8)	1.50(1)
C(1)	C(2)	1.374(9)	C(6)	C(9)	1.54(1)

Table S-2.5. Torsion angles (2.8b).

atom	atom	atom	atom	angle
S(1)	N(2)	C(4)	C(3)	-176.2(5)
S(1)	N(2)	C(4)	C(5)	2(1)
O(1)	S(1)	N(2)	C(4)	-32.3(7)
O(1)	S(1)	C(6)	C(7)	68.6(5)
O(1)	S(1)	C(6)	C(8)	-52.5(6)
O(1)	S(1)	C(6)	C(9)	-175.0(5)
N(1)	C(3)	C(2)	C(1)	-1(1)
N(1)	C(3)	C(4)	N(2)	174.6(5)
N(1)	C(3)	C(4)	C(5)	-4.2(9)
N(1)	C(3)	C(2)	C(1)	-1(1)
N(1)	C(3)	C(4)	N(2)	174.6(5)
N(1)	C(3)	C(4)	C(5)	-4.2(9)
N(2)	S(1)	C(6)	C(7)	-174.1(5)
N(2)	S(1)	C(6)	C(8)	64.8(6)
N(2)	S(1)	C(6)	C(9)	-57.8(5)
N(2)	C(4)	C(3)	C(2)	-4(1)
C(1)	C(2)	C(3)	C(4)	178.1(5)
C(1)	C(2)	C(3)	C(4)	178.1(5)
C(2)	C(1)	C(2)	C(3)	0.4(5)
C(2)	C(3)	N(1)	C(3)	0.4(5)
C(2)	C(3)	C(4)	C(5)	176.9(7)
C(3)	N(1)	C(3)	C(4)	-178.5(7)
C(4)	N(2)	S(1)	C(6)	-141.6(6)

Figure S-3. ORTEP view of bis(sulfinyl)imidoamidine (16a).

Figure S-4. ORTEP view of both molecules (**16a**) in the crystal lattice.

Experimental Methods (16a).

Identification Code	16a
Empirical Formula	C ₁₁ H ₂₃ N ₃ O ₂ S ₂
Formula Weight	293.44
Crystal Color, Habit	Colorless, tablet
Crystal Dimensions	0.33 x 0.18 x 0.13 mm
Crystal System	trigonal
Lattice Type	Primitive
Lattice Parameters	$a = 12.5140(7) \text{ \AA}$ $c = 35.701(2) \text{ \AA}$
Volume	4841.8(5) $\text{\AA}^3$
Space Group	P3 ₂ 21 (#154)
Z value	12
D _{calc}	1.208 g/cm ³
F ₀₀₀	1896.00
$\mu(\text{MoK}\alpha)$	3.29 cm ⁻¹
Diffractometer	SMART CCD
Radiation	MoK α ($\lambda = 0.71069 \text{ \AA}$) Graphite monochromated
Detector Position	60.00 mm
Exposure Time	10.0 seconds per frame
Scan type	ω (0.3 degrees per frame)
$2\theta_{\text{max}}$	49.4°
No. of Reflections Measured	Total: 10549
Corrections	Unique: 5473 ($R_{\text{int}} = 0.069$) Lorentz-polarization Absorption ($T_{\text{max}} = 0.97$ $T_{\text{min}} = 0.70$)
Structure Solution	Direct Methods (SIR92)
Refinement	Full-matrix least-squares
Function Minimized	$\Sigma w(F_o - F_c)^2$
Least Squares Weights	$w = 1/\sigma^2(F_o) = [\sigma_c^2(F_o) + (p^2/4)F_o^2]^{-1}$
p-factor	0.0300
Anomalous Dispersion	All non-hydrogen atoms
No. Observations ($I > 2.00\sigma(I)$)	2987
No. Variables	325
Reflection/Parameter Ratio	9.19
Residuals: R; Rw; Rall	0.031; 0.029; 0.079
Goodness of Fit Indicator	0.96
Max Shift/Error in Final Cycle	0.00
Maximum peak in Final Diff. Map	0.22 e ⁻ / $\text{\AA}^3$
Minimum peak in Final Diff. Map	-0.15 e ⁻ / $\text{\AA}^3$

Table S-3.1 Atomic coordinates and B(eq) values (**16a**):

atom	x	y	z	B(eq)
S(1)	0.77387(9)	0.24679(9)	0.04646(3)	2.53(3)
S(2)	0.74138(10)	-0.27955(10)	-0.05769(3)	2.93(3)
S(3)	0.55522(10)	0.23560(10)	-0.11396(3)	2.82(3)
S(4)	0.2549(1)	0.0575(1)	0.07183(3)	2.89(3)
O(1)	0.9072(2)	0.2855(2)	0.04317(7)	3.24(7)
O(2)	0.8740(2)	-0.1826(2)	-0.06137(7)	3.29(7)
O(3)	0.4514(2)	0.1089(2)	-0.12048(7)	3.25(7)
O(4)	0.1699(2)	-0.0508(2)	0.04822(7)	3.57(7)
N(1)	0.6839(3)	0.1046(3)	0.02928(8)	2.43(8)
N(2)	0.6688(3)	-0.0575(3)	-0.00501(8)	2.08(8)
N(3)	0.6608(3)	-0.2216(3)	-0.03709(8)	2.51(8)
N(4)	0.5538(3)	0.2828(3)	-0.06989(9)	2.55(8)
N(5)	0.4601(3)	0.2338(3)	-0.01193(9)	2.36(8)
N(6)	0.3595(3)	0.1721(3)	0.04492(9)	2.52(8)
C(1)	0.7368(3)	0.0546(3)	0.0115(1)	2.2(1)
C(2)	0.7245(3)	-0.1131(4)	-0.0230(1)	2.2(1)
C(3)	0.5347(4)	-0.1199(4)	-0.0027(1)	3.6(1)
C(4)	0.7319(3)	0.2092(3)	0.0959(1)	2.26(10)
C(5)	0.5930(4)	0.1523(4)	0.0993(1)	4.1(1)
C(6)	0.7780(4)	0.1268(4)	0.1100(1)	4.2(1)
C(7)	0.7976(4)	0.3345(4)	0.1156(1)	3.3(1)
C(8)	0.6713(4)	-0.3014(4)	-0.1043(1)	2.9(1)
C(9)	0.5390(4)	-0.4046(4)	-0.1012(1)	4.3(1)
C(10)	0.6787(4)	-0.1839(4)	-0.1186(1)	4.0(1)
C(11)	0.7448(4)	-0.3397(5)	-0.1291(1)	5.9(2)
C(12)	0.4727(4)	0.2048(3)	-0.0479(1)	2.4(1)
C(13)	0.3729(3)	0.1457(4)	0.0113(1)	2.6(1)
C(14)	0.5380(4)	0.3574(3)	0.0025(1)	3.5(1)
C(15)	0.6948(3)	0.2196(4)	-0.1085(1)	2.8(1)
C(16)	0.7065(4)	0.1698(4)	-0.1461(1)	3.9(1)
C(17)	0.6749(4)	0.1315(4)	-0.0775(1)	3.5(1)
C(18)	0.8032(4)	0.3473(4)	-0.1018(1)	4.3(1)
C(19)	0.1668(4)	0.1335(3)	0.0865(1)	2.4(1)
C(20)	0.1034(4)	0.1489(4)	0.0525(1)	2.8(1)
C(21)	0.2556(4)	0.2548(4)	0.1047(1)	3.6(1)
C(22)	0.0755(4)	0.0453(4)	0.1145(1)	4.1(1)

Table S-3.2. Anisotropic displacement parameters (**16a**).^a

atom	U11	U22	U33	U12	U13	U23
S(1)	0.0300(7)	0.0254(6)	0.0376(6)	0.0117(6)	0.0001(5)	-0.0009(5)
S(2)	0.0427(8)	0.0334(7)	0.0363(7)	0.0198(6)	-0.0059(6)	-0.0072(6)
S(3)	0.0320(7)	0.0372(7)	0.0387(6)	0.0179(6)	-0.0001(6)	0.0041(6)
S(4)	0.0438(7)	0.0340(7)	0.0367(6)	0.0231(6)	0.0002(6)	0.0042(6)
O(1)	0.025(2)	0.030(2)	0.056(2)	0.004(1)	0.006(1)	-0.012(1)
O(2)	0.033(2)	0.047(2)	0.049(2)	0.022(2)	-0.004(1)	-0.011(2)
O(3)	0.027(2)	0.039(2)	0.047(2)	0.009(1)	-0.006(1)	-0.005(1)
O(4)	0.054(2)	0.028(2)	0.048(2)	0.017(2)	0.006(2)	-0.004(1)
N(1)	0.028(2)	0.029(2)	0.031(2)	0.012(2)	-0.004(2)	-0.009(2)
N(2)	0.018(2)	0.021(2)	0.033(2)	0.005(2)	-0.003(2)	-0.010(2)
N(3)	0.032(2)	0.027(2)	0.030(2)	0.011(2)	-0.001(2)	-0.008(2)
N(4)	0.026(2)	0.033(2)	0.039(2)	0.016(2)	0.006(2)	0.004(2)
N(5)	0.019(2)	0.029(2)	0.038(2)	0.009(2)	0.002(2)	-0.001(2)
N(6)	0.027(2)	0.033(2)	0.035(2)	0.015(2)	-0.004(2)	-0.002(2)
C(1)	0.025(3)	0.027(3)	0.023(2)	0.008(2)	-0.002(2)	0.003(2)
C(2)	0.031(3)	0.033(3)	0.024(2)	0.018(2)	0.000(2)	0.001(2)
C(3)	0.024(3)	0.044(3)	0.056(3)	0.007(2)	-0.001(2)	-0.012(2)
C(4)	0.025(2)	0.026(3)	0.039(3)	0.015(2)	-0.007(2)	-0.006(2)
C(5)	0.041(3)	0.053(3)	0.048(3)	0.013(3)	0.008(2)	-0.008(3)
C(6)	0.073(4)	0.059(3)	0.040(3)	0.042(3)	-0.007(3)	-0.002(2)
C(7)	0.039(3)	0.046(3)	0.039(3)	0.019(2)	-0.009(2)	-0.009(2)
C(8)	0.038(3)	0.037(3)	0.033(3)	0.017(2)	0.000(2)	-0.004(2)
C(9)	0.052(3)	0.043(3)	0.052(3)	0.011(3)	-0.020(3)	-0.008(2)
C(10)	0.040(3)	0.059(3)	0.039(3)	0.015(3)	-0.005(2)	0.003(2)
C(11)	0.081(4)	0.115(5)	0.049(3)	0.066(4)	-0.011(3)	-0.031(3)
C(12)	0.029(3)	0.031(3)	0.037(3)	0.018(2)	-0.007(2)	-0.003(2)
C(13)	0.030(3)	0.031(3)	0.040(3)	0.018(2)	-0.004(2)	-0.002(2)
C(14)	0.036(3)	0.034(3)	0.053(3)	0.010(3)	-0.001(2)	-0.009(2)
C(15)	0.021(2)	0.041(3)	0.042(3)	0.014(2)	-0.002(2)	-0.003(2)
C(16)	0.047(3)	0.060(3)	0.049(3)	0.033(3)	0.001(2)	-0.007(2)
C(17)	0.041(3)	0.059(3)	0.045(3)	0.034(3)	-0.003(2)	0.010(2)
C(18)	0.036(3)	0.055(3)	0.068(3)	0.019(3)	-0.003(2)	-0.016(3)
C(19)	0.033(3)	0.028(3)	0.028(2)	0.015(2)	0.006(2)	0.002(2)
C(20)	0.039(3)	0.036(3)	0.037(3)	0.023(2)	0.003(2)	0.002(2)
C(21)	0.049(3)	0.042(3)	0.047(3)	0.023(3)	-0.006(2)	-0.012(2)
C(22)	0.056(3)	0.048(3)	0.049(3)	0.024(3)	0.015(2)	0.009(3)

Table S-3.3. Bond angles (16a).

atom	atom	atom	angle	atom	atom	atom	angle
O1	S1	N1	111.4(2)	S1	C4	C6	109.9(3)
O1	S1	C4	106.8(2)	S1	C4	C7	104.0(2)
N1	S1	C4	97.2(2)	C5	C4	C6	113.2(3)
O2	S2	N3	110.6(1)	C5	C4	C7	110.3(3)
O2	S2	C8	107.2(2)	C6	C4	C7	110.8(3)
N3	S2	C8	96.7(2)	S2	C8	C9	107.4(3)
O3	S3	N4	111.4(2)	S2	C8	C10	111.6(3)
O3	S3	C15	105.6(2)	S2	C8	C11	104.9(3)
N4	S3	C15	96.6(2)	C9	C8	C10	111.3(4)
O4	S4	N6	110.4(2)	C9	C8	C11	110.6(4)
O4	S4	C19	106.7(2)	C10	C8	C11	110.9(4)
N6	S4	C19	97.6(2)	N4	C12	N5	122.1(4)
S1	N1	C1	117.5(3)	N5	C13	N6	120.9(4)
C1	N2	C2	121.0(3)	S3	C15	C16	103.9(3)
C1	N2	C3	119.2(3)	S3	C15	C17	109.7(3)
C2	N2	C3	119.8(3)	S3	C15	C18	107.2(3)
S2	N3	C2	116.0(3)	C16	C15	C17	111.6(3)
S3	N4	C12	116.9(3)	C16	C15	C18	110.8(3)
C12	N5	C13	120.4(3)	C17	C15	C18	113.2(3)
C12	N5	C14	120.8(3)	S4	C19	C20	108.8(2)
C13	N5	C14	118.8(3)	S4	C19	C21	108.0(3)
S4	N6	C13	117.6(3)	S4	C19	C22	103.8(3)
N1	C1	N2	120.5(3)	C20	C19	C21	112.8(3)
N2	C2	N3	121.2(3)	C20	C19	C22	111.8(3)
S1	C4	C5	108.1(3)	C21	C19	C22	111.0(3)

Table S-3.4. Bond distances (16a).

atom	atom	distance	atom	atom	distance
S1	O1	1.491(3)	N4	C12	1.269(4)
S1	N1	1.676(3)	N5	C12	1.365(4)
S1	C4	1.834(4)	N5	C13	1.376(5)
S2	O2	1.494(3)	N5	C14	1.449(5)
S2	N3	1.678(3)	N6	C13	1.277(4)
S2	C8	1.836(4)	C4	C5	1.518(5)
S3	O3	1.482(3)	C4	C6	1.499(5)
S3	N4	1.684(3)	C4	C7	1.529(5)
S3	C15	1.866(4)	C8	C9	1.511(5)
S4	O4	1.496(3)	C8	C10	1.516(6)
S4	N6	1.678(3)	C8	C11	1.517(5)
S4	C19	1.856(4)	C15	C16	1.516(5)
N1	C1	1.283(4)	C15	C17	1.493(5)
N2	C1	1.358(4)	C15	C18	1.511(5)
N2	C2	1.367(4)	C19	C20	1.514(5)
N2	C3	1.457(4)	C19	C21	1.508(5)
N3	C2	1.284(4)	C19	C22	1.504(5)

Table S-3.5. Torsion Angles (16a).

atom	atom	atom	atom	angle	atom	atom	atom	atom	angle
S1	N1	C1	N2	-176.1(3)	N1	S1	C4	C7	-174.4(2)
S2	N3	C2	N2	-178.9(3)	N1	C1	N2	C2	-178.0(3)
S3	N4	C12	N5	-177.8(3)	N1	C1	N2	C3	0.7(5)
S4	N6	C13	N5	-177.5(3)	N3	S2	C8	C9	-69.2(3)
O1	S1	N1	C1	-9.0(3)	N3	S2	C8	C10	53.0(3)
O1	S1	C4	C5	-172.1(3)	N3	S2	C8	C11	173.1(3)
O1	S1	C4	C6	-48.1(3)	N3	C2	N2	C1	176.5(3)
O1	S1	C4	C7	70.6(3)	N3	C2	N2	C3	-2.2(5)
O2	S2	N3	C2	-9.7(3)	N4	S3	C15	C16	177.0(3)
O2	S2	C8	C9	176.7(3)	N4	S3	C15	C17	57.6(3)
O2	S2	C8	C10	-61.0(3)	N4	S3	C15	C18	-65.6(3)
O2	S2	C8	C11	59.1(3)	N4	C12	N5	C13	-178.5(3)
O3	S3	N4	C12	4.4(3)	N4	C12	N5	C14	1.5(5)
O3	S3	C15	C16	62.6(3)	N6	S4	C19	C20	66.4(3)
O3	S3	C15	C17	-56.8(3)	N6	S4	C19	C21	-56.4(3)
O3	S3	C15	C18	180.0(3)	N6	S4	C19	C22	-174.4(3)
O4	S4	N6	C13	-15.6(3)	N6	C13	N5	C12	-179.3(3)
O4	S4	C19	C20	-47.7(3)	N6	C13	N5	C14	0.7(5)
O4	S4	C19	C21	-170.5(2)	C1	N1	S1	C4	-120.3(3)
O4	S4	C19	C22	71.5(3)	C2	N3	S2	C8	-120.9(3)
N1	S1	C4	C5	-57.1(3)	C12	N4	S3	C15	-105.2(3)
N1	S1	C4	C6	66.9(3)	C13	N6	S4	C19	-126.7(3)

Figure S-5. ORTEP view of $\text{Cu}_2(\text{siam})_4\text{Cl}_2(\text{Cu}_2\text{Cl}_6)$ (**27**).

Figure S-6. ORTEP alternate view of (27) (Cu_2Cl_6 counterion omitted for clarity).

Experimental Methods (27).

Identification Code	27
Empirical Formula	$\text{Cu}_4\text{Cl}_{16}\text{C}_{48}\text{H}_{112}\text{N}_{12}\text{O}_8\text{S}_8$
Formula Weight	2063.40
Crystal Color, Habit	orange, prism
Crystal Dimensions	0.25 x 0.23 x 0.12 mm
Crystal System	orthorhombic
Lattice Type	primitive
Lattice Parameters	$a = 17.9275(5) \text{ \AA}$ $b = 18.2786(3) \text{ \AA}$ $c = 27.4798(8) \text{ \AA}$
Volume	8867.5(4) $\text{\AA}^3$
Space Group	$P2_12_12_1$ (#154)
Z value	4
D_{calc}	1.545 g/cm^3
F_{000}	4256.00
$\mu(\text{MoK}\alpha)$	16.66 cm^{-1}
Diffractometer	SMART CCD
Radiation	MoK α ($\lambda = 0.71069 \text{ \AA}$) Graphite monochromated
Detector Position	60.00 mm
Exposure Time	10.0 seconds per frame
Scan type	ω (0.3 degrees per frame)
$2\theta_{\text{max}}$	47.4°
No. of Reflections Measured	Total: 24968
	Unique: 7286 ($R_{\text{int}} = 0.106$)
Corrections	Lorentz-polarization Absorption ($T_{\text{max}} = 0.87$ $T_{\text{min}} = 0.60$)
Structure Solution	Direct Methods (SIR92)
Refinement	Full-matrix least-squares
Function Minimized	$\sum w(F_o - F_c)^2$
Least Squares Weights	$w = 1/\sigma^2(F_o) = [\sigma_c^2(F_o) + (p^2/4)F_o^2]^{-1}$
p-factor	0.0300
Anomalous Dispersion	All non-hydrogen atoms
No. Observations ($I > 2.00\sigma(I)$)	5877
No. Variables	514
Reflection/Parameter Ratio	11.43
Residuals: R; Rw; Rall	0.082; 0.081; 0.177
Goodness of Fit Indicator	2.16
Max Shift/Error in Final Cycle	0.00
Maximum peak in Final Diff. Map	1.25 $e^-/\text{\AA}^3$
Minimum peak in Final Diff. Map	-0.87 $e^-/\text{\AA}^3$

Table S.4.1 Atomic coordinates and B(eq) values (27).

atom	x	y	z	B(eq)
Cu(1)	0.7144(1)	-0.0916(1)	-0.02615(9)	2.11(7)
Cu(2)	0.5465(1)	0.0866(1)	0.13454(9)	1.82(6)
Cu(3)	0.4164(2)	0.1490(2)	0.2608(1)	6.5(1)
Cu(4)	0.2436(2)	0.0992(2)	0.2637(1)	7.5(1)
Cl(1)	0.7784(4)	-0.1602(4)	-0.0864(2)	5.8(2)
Cl(2)	0.6252(3)	0.0034(3)	0.0589(2)	1.9(1)
Cl(3)	0.4780(4)	0.1752(3)	0.1938(2)	4.7(2)
Cl(4)	0.5132(5)	0.1494(5)	0.3118(3)	9.2(3)
Cl(5)	0.3074(4)	0.2027(4)	0.2406(3)	7.8(3)
Cl(6)	0.3515(4)	0.0603(4)	0.3005(3)	8.8(3)
Cl(7)	0.1368(4)	0.1452(7)	0.2808(3)	12.5(4)
Cl(8)	0.2090(6)	-0.0020(5)	0.2291(3)	12.3(4)
S(1)	0.5701(3)	-0.1718(3)	-0.0576(2)	2.0(2)
S(2)	0.4631(3)	-0.0428(3)	0.1828(2)	2.0(2)
S(3)	0.6886(3)	0.0261(3)	-0.1054(2)	2.3(2)
S(4)	0.4054(3)	0.1227(3)	0.0735(2)	1.8(1)
S(5)	0.8658(3)	-0.0184(3)	-0.0040(2)	2.4(2)
S(6)	0.6091(3)	0.2384(3)	0.1085(2)	2.2(2)
S(7)	0.7503(3)	-0.2192(3)	0.0432(2)	1.9(1)
S(8)	0.6662(3)	0.0704(3)	0.2148(2)	1.9(1)
O(1)	0.6090(6)	-0.0976(6)	-0.0498(4)	1.6(3)
O(2)	0.5363(7)	-0.0063(6)	0.1692(5)	1.8(3)
O(3)	0.7199(7)	0.0089(6)	-0.0562(5)	2.1(3)
O(4)	0.4548(6)	0.0647(6)	0.0967(4)	1.4(3)
O(5)	0.7998(7)	-0.0621(6)	0.0156(5)	2.3(3)
O(6)	0.5659(6)	0.1740(6)	0.0932(5)	1.8(3)
O(7)	0.6903(6)	-0.1714(6)	0.0215(4)	1.4(3)
O(8)	0.6453(6)	0.0992(6)	0.1643(5)	1.8(3)
N(1)	0.5095(8)	-0.1845(7)	-0.0128(6)	1.1(3)
N(2)	0.4678(8)	-0.1493(8)	0.0659(6)	1.4(3)
N(3)	0.4401(8)	-0.1030(8)	0.1386(6)	2.0(4)
N(4)	0.6097(8)	0.0737(8)	-0.0985(6)	2.1(4)
N(5)	0.5161(8)	0.1050(8)	-0.0432(6)	1.7(4)
N(6)	0.4283(8)	0.1314(7)	0.0155(5)	1.4(3)
N(7)	0.8585(10)	0.0673(9)	0.0172(7)	3.3(4)
N(8)	0.7845(9)	0.1565(8)	0.0507(6)	1.9(4)
N(9)	0.6961(9)	0.2331(8)	0.0841(6)	2.1(4)
N(10)	0.7687(8)	-0.1902(8)	0.1002(6)	1.6(4)
N(11)	0.7508(8)	-0.1007(8)	0.1570(6)	1.6(3)
N(12)	0.7159(9)	-0.0057(8)	0.2080(6)	2.8(4)
C(1)	0.514(1)	-0.145(1)	0.0257(8)	1.9(5)
C(2)	0.479(1)	-0.1056(10)	0.1027(8)	1.5(4)
C(3)	0.411(1)	-0.204(1)	0.0675(9)	4.0(6)
C(4)	0.507(1)	-0.152(1)	-0.1081(8)	2.0(5)
C(5)	0.555(1)	-0.140(1)	-0.1532(9)	4.6(6)
C(6)	0.458(1)	-0.087(1)	-0.0958(8)	3.5(5)
atom	x	y	z	B(eq)
C(7)	0.457(1)	-0.223(1)	-0.1172(9)	4.4(6)
C(8)	0.4917(10)	-0.1070(9)	0.2312(7)	1.3(4)
C(9)	0.516(1)	-0.060(1)	0.2714(9)	3.8(6)
C(10)	0.421(1)	-0.149(1)	0.2455(8)	3.4(5)
C(11)	0.553(1)	-0.156(1)	0.2146(8)	3.1(5)
C(12)	0.580(1)	0.0734(10)	-0.0557(8)	1.8(4)

C(13)	0.4878(10)	0.0975(9)	0.0027(7)	1.0(4)
C(14)	0.480(1)	0.149(1)	-0.0855(9)	4.6(6)
C(15)	0.745(1)	0.099(1)	-0.1296(7)	2.1(4)
C(16)	0.821(1)	0.067(1)	-0.1349(9)	4.1(6)
C(17)	0.712(1)	0.125(1)	-0.1766(9)	4.0(6)
C(18)	0.752(1)	0.161(1)	-0.0919(8)	3.6(5)
C(19)	0.318(1)	0.078(1)	0.0667(8)	3.5(6)
C(20)	0.324(1)	0.003(1)	0.0411(8)	3.3(5)
C(21)	0.265(1)	0.129(1)	0.0396(9)	4.0(6)
C(22)	0.290(1)	0.067(1)	0.1191(9)	4.4(6)
C(23)	0.798(1)	0.087(1)	0.0363(7)	2.1(4)
C(24)	0.715(1)	0.1698(10)	0.0683(7)	1.4(4)
C(25)	0.841(1)	0.210(1)	0.0495(9)	3.6(6)
C(26)	0.945(1)	-0.051(1)	0.0332(8)	2.7(5)
C(27)	0.960(1)	-0.128(1)	0.0168(8)	3.0(5)
C(28)	0.933(1)	-0.043(1)	0.0851(9)	4.1(6)
C(29)	1.010(1)	-0.004(1)	0.0190(8)	3.2(5)
C(30)	0.576(1)	0.315(1)	0.0723(9)	4.3(6)
C(31)	0.577(1)	0.294(1)	0.0167(8)	3.1(5)
C(32)	0.493(1)	0.322(1)	0.0895(8)	3.4(6)
C(33)	0.617(1)	0.381(1)	0.0865(9)	4.0(6)
C(34)	0.7396(9)	-0.1314(9)	0.1138(7)	1.0(4)
C(35)	0.716(1)	-0.0374(10)	0.1662(7)	1.3(4)
C(36)	0.796(1)	-0.137(1)	0.1929(8)	3.2(5)
C(37)	0.702(1)	-0.304(1)	0.0601(8)	2.5(5)
C(38)	0.757(1)	-0.354(1)	0.0848(8)	3.5(5)
C(39)	0.633(1)	-0.290(1)	0.0891(9)	3.8(6)
C(40)	0.679(1)	-0.333(1)	0.0066(9)	4.1(6)
C(41)	0.739(1)	0.135(1)	0.2363(8)	2.8(5)
C(42)	0.801(1)	0.138(1)	0.2002(9)	3.8(6)
C(43)	0.763(1)	0.107(1)	0.2838(8)	3.9(6)
C(44)	0.696(1)	0.207(1)	0.2419(8)	2.6(5)

Table S-4.2 Anisotropic displacement parameters (27).

atom	U11	U22	U33	U12	U13	U23
Cu(2)	0.031(2)	0.020(1)	0.018(2)	0.000(1)	0.001(2)	0.003(1)
Cu(3)	0.090(3)	0.054(2)	0.103(3)	-0.004(2)	0.039(3)	-0.008(2)
Cu(4)	0.077(3)	0.127(3)	0.082(3)	-0.030(3)	0.015(2)	-0.040(3)
Cl(1)	0.096(6)	0.095(5)	0.029(5)	0.064(5)	0.023(4)	0.008(4)
Cl(2)	0.026(4)	0.022(3)	0.023(4)	-0.007(3)	-0.003(3)	0.001(3)
Cl(3)	0.058(5)	0.064(5)	0.056(5)	-0.017(4)	0.027(4)	-0.019(4)
Cl(4)	0.099(7)	0.137(8)	0.113(8)	0.014(6)	-0.005(6)	0.006(7)
Cl(5)	0.068(6)	0.062(5)	0.167(9)	-0.005(4)	-0.014(6)	-0.019(5)
Cl(6)	0.110(7)	0.074(6)	0.152(9)	0.005(5)	0.057(7)	0.044(6)
Cl(7)	0.038(5)	0.35(1)	0.085(8)	0.006(7)	0.006(5)	-0.063(9)
Cl(8)	0.24(1)	0.135(8)	0.090(8)	-0.117(8)	-0.012(9)	-0.002(6)
S(1)	0.024(4)	0.032(4)	0.020(4)	-0.001(3)	0.002(3)	-0.003(3)
S(2)	0.030(4)	0.032(3)	0.016(4)	-0.001(3)	0.009(3)	0.005(3)
S(3)	0.030(4)	0.037(4)	0.021(4)	0.000(3)	0.005(4)	0.002(3)
S(4)	0.024(4)	0.025(3)	0.021(4)	0.004(3)	0.001(3)	0.003(3)
S(5)	0.028(4)	0.033(4)	0.030(4)	-0.003(3)	0.001(4)	0.010(3)
S(6)	0.043(5)	0.017(3)	0.023(4)	-0.004(3)	-0.007(4)	0.001(3)
S(7)	0.033(4)	0.019(3)	0.022(4)	0.002(3)	0.001(3)	-0.005(3)
S(8)	0.033(4)	0.025(3)	0.015(4)	-0.001(3)	0.004(3)	0.001(3)

Table S-4.3. Relevant bond angles (27).

atom	atom	atom	angle	atom	atom	atom	angle
C16	C15	C18	106(2)	S7	C37	C40	100(1)
O4	Cu2	O8	171.1(5)	N1	S1	C4	100.7(8)
O1	Cu1	O5	158.4(5)	S6	C30	C32	102(2)
Cl1	Cu1	O3	99.9(4)	O1	S1	C4	102.2(8)
C9	C8	C10	110(2)	S8	C41	C44	103(1)
C20	C19	C22	109(2)	S5	C26	C29	105(1)
C5	C4	C7	108(2)	S5	C26	C27	106(1)
S1	C4	C7	108(1)	S8	C41	C43	106(1)
C20	C19	C21	111(2)	S1	C4	C5	107(1)
Cu1	O5	S5	122.5(8)	C28	C26	C29	108(2)
S2	C8	C10	106(1)	C32	C30	C33	108(2)
N5	C13	N6	121(2)	O1	S1	N1	108.6(7)
S3	C15	C18	110(1)	O2	S2	N3	108.6(8)
S2	C8	C9	104(1)	S7	C37	C38	109(1)
C9	C8	C11	111(2)	C27	C26	C29	109(2)
C10	C8	C11	113(2)	S6	C30	C33	109(2)
S4	C19	C21	109(1)	C31	C30	C32	109(2)
Cu2	O6	S6	124.8(8)	C39	C37	C40	109(2)
S2	C8	C11	111(1)	S1	C4	C6	110(1)
S4	C19	C22	105(2)	S6	C30	C31	110(2)
N8	C24	N9	122(2)	S8	C41	C42	110(2)
C16	C15	C17	114(2)	C43	C41	C44	111(2)
S4	C19	C20	114(2)	S7	C37	C39	112(1)
C21	C19	C22	109(2)	C38	C37	C40	112(2)
O5	S5	C26	103.3(8)	C42	C41	C43	112(2)
C5	C4	C6	114(2)	C12	N5	C14	113(2)
O6	Cu2	O8	89.2(5)	S5	C26	C28	113(2)
C17	C15	C18	112(2)	C38	C37	C39	114(2)
N7	C23	N8	123(2)	C42	C41	C44	114(2)
O6	S6	N9	109.0(8)	S4	N6	C13	115(1)
N10	S7	C37	97.1(9)	S6	N9	C24	115(1)
C6	C4	C7	110(2)	C27	C26	C28	115(2)
N9	S6	C30	97(1)	C23	N8	C24	116(2)
N6	S4	C19	99.3(9)	S3	N4	C12	117(1)
N4	C12	N5	126(2)	C31	C30	C33	117(2)
O4	S4	C19	103.6(9)	S2	N3	C2	118(1)
O8	S8	N12	108.5(8)	S7	N10	C34	118(1)
Cu2	O2	S2	125.5(7)	S8	N12	C35	118(1)
O6	S6	C30	106.7(9)	S5	N7	C23	118(2)
O8	S8	C41	104.0(9)	C34	N11	C35	118(2)
O3	S3	N4	108.9(8)	S1	N1	C1	119(1)
O3	S3	C15	106.3(8)	C1	N2	C2	119(2)
N4	S3	C15	97.5(8)	C1	N2	C3	120(2)
N12	S8	C41	101.1(9)	C34	N11	C36	120(2)
O4	S4	N6	109.0(7)	C2	N2	C3	121(2)
O5	S5	N7	107.9(8)	C12	N5	C13	121(2)
O7	S7	N10	108.9(7)	C23	N8	C25	121(2)
O2	S2	C8	102.4(8)	Cu1	O7	S7	121.7(7)
Cu1	O1	S1	121.4(7)	C35	N11	C36	122(2)
O7	S7	C37	104.8(8)	C24	N8	C25	123(2)
N3	S2	C8	99.9(8)	Cu2	O8	S8	123.9(7)

Cu2	O4	S4	124.1(6)	N2	C2	N3	124(2)
S3	C15	C16	105(1)	N10	C34	N11	124(2)
S3	C15	C17	110(1)	N11	C35	N12	124(2)
N7	S5	C26	100.0(9)	C13	N5	C14	126(2)
Cu1	O3	S3	123.0(8)	N1	C1	N2	126(2)
O1	Cu1	O7	88.2(5)	Cl3	Cu2	O8	95.3(4)
Cl1	Cu1	O5	100.0(4)	Cl3	Cu2	O2	101.0(4)
Cl1	Cu1	O7	100.1(4)	Cl3	Cu2	O6	86.6(4)
Cl3	Cu2	O4	93.6(4)	O5	Cu1	O7	89.2(5)
O2	Cu2	O4	90.1(5)	Cl3	Cu1	O1	101.5(4)
O2	Cu2	O8	89.1(5)	O3	Cu1	O7	160.0(5)
O2	Cu2	O6	172.3(5)	O3	Cu1	O5	87.3(5)
O4	Cu2	O6	90.4(5)	O1	Cu1	O3	87.9(5)

Table S-4.4. Relevant bond distances (27).

atom	atom	distance	atom	atom	distance
Cu1	Cl1	2.371(6)	S1	O1	1.54(1)
Cu1	O1	2.00(1)	S1	N1	1.66(2)
Cu1	O3	2.02(1)	S1	C4	1.83(2)
Cu1	O5	1.99(1)	S2	O2	1.52(1)
Cu1	O7	2.01(1)	S2	N3	1.69(2)
Cu2	Cl3	2.604(7)	S2	C8	1.85(2)
Cu2	O2	1.96(1)	S3	O3	1.50(1)
Cu2	O4	1.99(1)	S3	N4	1.67(2)
Cu2	O6	1.99(1)	S3	C15	1.80(2)
Cu2	O8	1.96(1)	S4	O4	1.52(1)
S6	C30	1.81(2)	S4	N6	1.65(2)
S7	O7	1.51(1)	S4	C19	1.77(2)
S7	N10	1.69(2)	S5	O5	1.52(1)
S7	C37	1.84(2)	S5	N7	1.68(2)
S8	O8	1.53(1)	S5	C26	1.85(2)
S8	N12	1.66(2)	S6	O6	1.47(1)
S8	C41	1.85(2)	S6	N9	1.70(2)
N1	C1	1.28(2)	N12	C35	1.29(2)
N2	C1	1.38(2)	C4	C5	1.52(3)
N2	C2	1.30(2)	C4	C6	1.52(3)
N2	C3	1.43(2)	C4	C7	1.59(3)
N3	C2	1.21(2)	C8	C9	1.47(3)
N4	C12	1.29(2)	C8	C10	1.53(2)
N5	C12	1.33(2)	C8	C11	1.48(2)
N5	C13	1.37(2)	C15	C16	1.49(2)
N5	C14	1.56(3)	C15	C17	1.50(3)
N6	C13	1.28(2)	C15	C18	1.54(3)
N7	C23	1.25(2)	C19	C20	1.54(3)
N8	C23	1.36(2)	C19	C21	1.53(3)
N8	C24	1.36(2)	C19	C22	1.54(3)
N8	C25	1.41(2)	C26	C27	1.50(2)
N9	C24	1.28(2)	C26	C28	1.45(3)
N10	C34	1.25(2)	C26	C29	1.50(3)
N11	C34	1.33(2)	C30	C31	1.58(3)
N11	C35	1.34(2)	C30	C32	1.56(3)
N11	C36	1.44(2)	C30	C33	1.46(3)

C37	C38	1.51(3)	C41	C42	1.50(3)
C37	C39	1.49(3)	C41	C43	1.47(3)
C37	C40	1.62(3)	C41	C44	1.53(2)

Table S-4.5. Relevant torsion angles (27).

atom	atom	atom	atom	angle	atom	atom	atom	atom	angle
Cu1	O1	S1	N1	105.8(9)	Cl1	Cu1	O1	S1	57.7(8)
Cu1	O1	S1	C4	-148.4(9)	Cl1	Cu1	O3	S3	58.5(9)
Cu1	O3	S3	N4	105.3(9)	Cl1	Cu1	O5	S5	58.3(8)
Cu1	O3	S3	C15	-150.6(9)	Cl1	Cu1	O7	S7	56.1(8)
Cu1	O5	S5	N7	107(1)	Cl3	Cu2	O2	S2	60.0(9)
Cu1	O5	S5	C26	-148.2(9)	Cl3	Cu2	O4	S4	54.4(8)
Cu1	O7	S7	N10	101.8(9)	Cl3	Cu2	O6	S6	61.2(8)
Cu1	O7	S7	C37	-155.1(9)	Cl3	Cu2	O8	S8	69.5(8)
Cu2	O2	S2	N3	94(1)	S5	O5	Cu1	O3	-41.3(8)
Cu2	O2	S2	C8	-161.1(9)	S5	O5	Cu1	O7	158.4(8)
Cu2	O4	S4	N6	97.1(9)	S5	N7	C23	N8	-174(1)
Cu2	O4	S4	C19	-158(1)	S6	O6	Cu2	O2	-111(4)
Cu2	O6	S6	N9	101(1)	S6	O6	Cu2	O4	154.8(9)
Cu2	O6	S6	C30	-154(1)	S6	O6	Cu2	O8	-34.1(9)
Cu2	O8	S8	N12	101.9(9)	S6	N9	C24	N8	-176(1)
Cu2	O8	S8	C41	-151.1(9)	S7	O7	Cu1	O1	157.6(8)
S1	O1	Cu1	O3	157.4(9)	S7	O7	Cu1	O3	-124(1)
S1	O1	Cu1	O5	-126(1)	S7	O7	Cu1	O5	-43.9(8)
S1	O1	Cu1	O7	-42.2(8)	S7	N10	C34	N11	-178(1)
S1	N1	C1	N2	-180(1)	S8	O8	Cu2	O2	-31.4(9)
S2	O2	Cu2	O4	-33.7(9)	S8	O8	Cu2	O4	-116(3)
S2	O2	Cu2	O6	-128(4)	S8	O8	Cu2	O6	156.1(9)
S2	O2	Cu2	O8	155.2(9)	S8	N12	C35	N11	-177(1)
S2	N3	C2	N2	-180(1)	O1	S1	N1	C1	-16(2)
S3	O3	Cu1	O1	-42.8(9)	O1	S1	C4	C5	69(1)
S3	O3	Cu1	O5	158.2(9)	O1	S1	C4	C6	-55(1)
S3	O3	Cu1	O7	-122(1)	O1	S1	C4	C7	-175(1)
S3	N4	C12	N5	-177(1)	O2	S2	N3	C2	-5(2)
S4	O4	Cu2	O2	155.4(9)	O2	S2	C8	C9	66(1)
S4	O4	Cu2	O6	-32.2(9)	O2	S2	C8	C10	-177(1)
S4	O4	Cu2	O8	-120(3)	O2	S2	C8	C11	-54(1)
S4	N6	C13	N5	-175(1)	O3	S3	N4	C12	-15(2)
S5	O5	Cu1	O1	-118(1)	O3	S3	C15	C16	64(2)
O3	S3	C15	C18	-50(2)	O3	S3	C15	C17	-174(1)
O4	S4	N6	C13	-9(1)	N3	S2	C8	C9	178(1)
O4	S4	C19	C20	-51(2)	N3	S2	C8	C10	-66(1)
O4	S4	C19	C21	-175(1)	N3	S2	C8	C11	57(1)
O4	S4	C19	C22	68(2)	N3	C2	N2	C1	177(2)
O5	S5	N7	C23	-13(2)	N3	C2	N2	C3	-6(3)
O5	S5	C26	C27	71(2)	N4	S3	C15	C16	176(1)
O5	S5	C26	C28	-56(2)	N4	S3	C15	C17	-61(2)
O5	S5	C26	C29	-174(1)	N4	S3	C15	C18	62(2)
O6	S6	N9	C24	-17(2)	N4	C12	N5	C13	176(2)
O6	S6	C30	C31	-51(2)	N4	C12	N5	C14	-4(3)
O6	S6	C30	C32	64(2)	N6	S4	C19	C20	61(2)
O6	S6	C30	C33	179(2)	N6	S4	C19	C21	-63(2)
O7	S7	N10	C34	-9(2)	N6	S4	C19	C22	-180(1)

O7	S7	C37	C38	-177(1)	N6	C13	N5	C12	176(2)
O7	S7	C37	C39	-50(2)	N6	C13	N5	C14	-4(3)
O7	S7	C37	C40	65(1)	N7	S5	C26	C27	-178(1)
O8	S8	N12	C35	-15(2)	N7	S5	C26	C28	55(2)
O8	S8	C41	C42	-56(2)	N7	S5	C26	C29	-63(2)
O8	S8	C41	C43	-177(1)	N7	C23	N8	C24	176(2)
O8	S8	C41	C44	66(1)	N7	C23	N8	C25	-7(3)
N1	S1	C4	C5	-179(1)	N9	S6	C30	C31	62(2)
N1	S1	C4	C6	57(1)	N9	S6	C30	C32	177(1)
N1	S1	C4	C7	-63(1)	N9	S6	C30	C33	-68(2)
N1	C1	N2	C2	180(2)	N9	C24	N8	C23	178(2)
N1	C1	N2	C3	2(3)	N9	C24	N8	C25	2(3)
N10	S7	C37	C39	62(2)	N10	S7	C37	C38	-65(2)
N10	S7	C37	C40	177(1)	C1	N1	S1	C4	-123(2)
N10	C34	N11	C35	180(2)	C2	N3	S2	C8	-112(2)
N10	C34	N11	C36	-4(3)	C12	N4	S3	C15	-125(2)
N12	S8	C41	C42	57(2)	C13	N6	S4	C19	-117(1)
N12	S8	C41	C43	-65(2)	C23	N7	S5	C26	-120(2)
N12	S8	C41	C44	179(1)	C24	N9	S6	C30	-127(2)
N12	C35	N11	C34	173(2)	C34	N10	S7	C37	-117(2)
N12	C35	N11	C36	-4(3)	C35	N12	S8	C41	-124(2)

Figure S-7. ORTEP view of $\text{Zn}_2(\text{16a})_2\text{I}_2$ (**28**).