Enantioselective Friedel–Crafts Alkylations Catalyzed by Bis(oxazolinyl)pyridine–Scandium Triflate Complexes

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Supporting Information

General Information. All reactions were carried out under an atmosphere of nitrogen in flame-dried glassware with magnetic stirring. Purification of reaction products was carried out by flash column chromatography using EM Reagent silica gel 60 (230-400 mesh). Analytical thin layer chromatography was performed on EM Reagent 0.25 mm silica gel 60-F plates. Visualization was accomplished with UV light and aqueous ceric ammonium molybdate solution or anisaldehyde followed by heating.

Melting points were measured with a Büchi SMP-20 melting point apparatus equipped with an Omega Model 450 AET thermocouple and are uncorrected. Optical rotations were measured on a Jasco DIP-0181 digital polarimeter with a sodium lamp and are reported as follows: $[\alpha]_D^{25}$ (c = g/100 mL, solvent). Infrared spectra were recorded on a Perkin Elmer 1600 series FT-IR spectrometer.

^1H NMR spectra were recorded on Varian Unity Inova500 (500 MHz) or Varian Mercury400 (400 MHz) spectrometers and are reported in ppm using solvent as the internal standard (CDCl_3 at 7.26 ppm). Data are reported as: (b = broad, s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet; coupling constant(s) in Hz, integration). ^{13}C NMR spectra were recorded on a Varian Mercury400 (100 MHz) spectrometer. Chemical shifts are reported in ppm from tetramethylsilane, with the solvent resonance employed as the internal standard (deuteriochloroform at 77.0 ppm). High-resolution mass spectra were obtained on Jeol AX-505 or SX-102 spectrometers in the Harvard University Mass Spectrometry Laboratory. Exact mass measurements were obtained by internal calibration with an appropriate lock mass compound. Analytical high performance liquid chromatography (HPLC) was performed on a Hewlett-Packard 1050 Series HPLC, equipped with a variable wavelength detector, using a Chiralcel AD, OD-H, or OJ-H column (0.46 cm x 25 cm) from Daicel. X-Ray crystallographic data was collected using a Siemens SMART CCD (charge coupled device) based diffractometer equipped with an LT-2 low-temperature apparatus operating at 213 K.

Materials. Solvents were purified by filtration through a column of activated alumina under an argon atmosphere.¹ Scandium(III) triflate ($\text{Sc}(\text{OTf})_3$) was purchased from the Strem Chemical company, stored in an inert atmosphere dry box, and used without further purification. *N*-Methylindole and 4 and 5-substituted-indoles are commercially available and were used without purification. Indole, MagtrieveTM, sulfur trioxide•pyridine complex, dimethyl-3-methoxy-aniline, sodium hydride, potassium *t*-butoxide, and morpholine were purchased from Aldrich and used without further purification. The acid chlorides, trimethyl phosphite, and dimethyl phosphite are commercially available and were distilled before use.

General Arbuzov Procedure for the Preparation of the Acyl Phosphonates 2a-2c. The procedure outlined by Breuer and Evans² for the addition reaction was followed. To a round-bottom flask under nitrogen was added 1.0 equiv of the corresponding acid chloride. An addition funnel was attached to the flask and charged with 0.9

(1) Pangborn, A. B.; Giardello, M. A.; Grubbs, R. H.; Rosen, R. K.; Timmers, F. J. *Organometallics* **1996**, *15*, 1518-1520.

(2) (a) Karaman, R.; Goldblum, A.; Breuer, E.; Leader, H. *J. Chem. Soc., Perkin Trans. 1* **1989**, 765-74 and references cited therein. (b) Evans, D. A.; Johnson, J. S. *J. Am. Chem. Soc.* **1998**, *120*, 4895-4896.

equiv of trimethylphosphite. The reaction was cooled to 0 °C for 20 min before the trimethylphosphite was added slowly (3-4 drops/minute) to the acid chloride solution. The reaction was stirred at 0 °C for 1 h before the ice bath was removed. The reaction was stirred for an additional 3-5 h at rt, which included 1 h after bubbling of the methyl chloride gas had subsided. The acyl phosphonates were then distilled before use.

(2E-But-2-enoyl)-phosphonic Acid Dimethyl Ester (2a). According to the General Procedure outlined above, 14.2 mL (14.9 g, 120 mmol) of trimethylphosphite was added to 13.0 mL (12.1 g, 133 mmol) of crotonyl chloride. After 1 h at 0 °C, the reaction was stirred at rt for 5 h. The solution was distilled to afford 4.91 g (27.6 mmol, 21%, >95% purity based on ¹H NMR) of the known acyl phosphonate **2a** as a yellow liquid: bp 85-87 °C (600 mtorr) (lit.²; 71-83 °C (500 mtorr)).

(2E-Pent-2-enoyl)-phosphonic Acid Dimethyl Ester (2b). According to the General Procedure outlined above, 4.88 mL (5.14 g, 41.4 mmol) of trimethylphosphite was added to 5.46 g (41.4 mmol) of *E*-pent-2-enoyl chloride. After 1 h at 0 °C, the reaction was stirred at rt for 5 h. The solution was distilled to afford 2.15 g (11.2 mmol, 27%, >95% purity based on ¹H NMR) of the acyl phosphonate **2b** as a yellow liquid: bp 95-100 °C (580 mtorr). ¹H NMR (500 MHz, CDCl₃) 7.56(d, *J* = 16.1, 6.3 Hz, 1H), 6.40(tt, *J* = 16.1 and 1.5 Hz, 1H), 3.85(d, *J* = 10.7 Hz, 6H), 2.40-2.32(m, 2H), 1.12(t, *J* = 7.8 Hz, 3H); ¹³C NMR (100 MHz, CDCl₃) 157.6, 129.3, 128.7, 54.0, 53.9; ³¹P NMR (201 MHz, CDCl₃) 1.37 IR (film): 3522.0 (br), 3259.3, 2961.1, 1669.1, 1634.7, 1607.9, 1456.7, 1259.0, 1183.5, 1028.3 (br), 834.8 cm⁻¹; HRMS (CI): Exact mass calcd for C₇H₁₃O₄P [M+H]⁺ 193.0629. Found: 193.0631.

(2E-4-Methyl-pent-2-enoyl)-phosphonic Acid Dimethyl Ester (2c). According to the General Procedure outlined above, 11.4 mL (12.0 g, 96.3 mmol) of trimethylphosphite was added to 14.2 g (107 mmol) of *E*-4-methyl-pent-2-enoyl chloride. After 1 h at 0 °C, the reaction was stirred at rt for 4 h. The solution was distilled to afford 5.12 g (25.0 mmol, 26%, >95% purity based on ¹H NMR) of the known acyl phosphonate **2b** as a yellow liquid: bp 85-88 °C (350 mtorr) (lit.²; 82-84 °C (250 mtorr)).

(2E-4-(tert-Butyl-diphenyl-silanyloxy)-1-hydroxyl-but-2-enyl)-phosphonic Acid Dimethyl Ester. The procedure of Baraldi³ for the Pudovik reaction was followed. To a vacuum flame-dried 10-mL round-bottom flask was added 1.17 mL (1.41 g, 12.8 mmol) of dimethyl phosphite and 1.02 mL (0.74 g, 7.3 mmol) of triethylamine. To the resulting solution was added 4.31 g (13.3 mmol) of the known^{3b} 4-(tert-butyl-diphenyl-silanyloxy)-but-2-enal in 100 mg portions (1 portion/ 5 min). The reaction was stirred at 70 °C for 1 h. The reaction was cooled to rt, diluted with 40 mL of Et₂O, and washed with 40 mL of H₂O and then 40 mL of brine. The organic layer was dried with Na₂SO₄ and concentrated to a thick oil *in vacuo* to afford 4.85 g (11.1 mmol, 83%, >98% purity based on ¹H NMR) of the title compound after flash silica chromatography (EtOAc, R_f = 0.30). mp = 86-89 °C; ¹H NMR (500 MHz, CDCl₃) 7.69-7.65 (m, 4H), 7.44-7.35 (m, 6H), 6.02-5.96 (m, 2H), 4.62-4.54 (m 1H), 4.27-4.24 (m, 2H), 3.80 (dd, *J* = 10.3, 2.6 Hz, 6H), 1.06 (s, 9H); ¹³C NMR (100 MHz, CDCl₃) 135.5, 133.5 (d, *J* = 2.2 Hz), 132.4 (d, *J* = 12.4 Hz), 129.7, 127.7, 123.8 (d, *J* = 162 Hz), 63.6, 53.6 (dd, *J* = 22.0, 7.3 Hz); ³¹P (202 MHz, CDCl₃) 25.04 (s); IR (film): 3285.9 (br), 3070.2, 2954.1, 2855.6, 1471.6, 1427.7, 1389.9, 1237.3, 1187.2, 1111.8, 1032.3 cm⁻¹; HRMS (CI): Exact mass calcd for C₂₂H₃₁O₅PSi [M+H]⁺: 435.1756. Found: 435.1756.

(2E-4-(tert-Butyl-diphenyl-silanyloxy)-but-2-enoyl)-phosphonic Acid Dimethyl Ester (2d). The procedure of Baraldi for the Parikh-Doering oxidation³ was followed. To a 250-mL round-bottom flask under nitrogen was added 4.32 g (9.95 mmol) of (2E-4-(tert-butyl-diphenyl-silanyloxy)-1-hydroxyl-but-2-enyl)-phosphonic acid dimethyl ester, 100 mL of dichloromethane, 5.12 mL (3.85 g, 29.8 mmol) of Hunig's base, and 19.8 mL (21.8 g, 279 mmol) of DMSO. The reaction vessel was cooled to -10 °C before 4.67 g (29.9 mmol) of sulfur trioxide•pyridine complex was added. The reaction was allowed to slowly warm to rt with stirring over a 45-min period. The reaction was diluted with 150 mL of Et₂O, washed with 100 mL of water, 100 mL of 5% aq. NaHCO₃, 100 mL of sat. CuSO₄, and then 100 mL of brine. The organic phase was dried with Na₂SO₄ and concentrated *in vacuo*. The title compound was isolated by flash silica chromatography (60% EtOAc/Hexanes, R_f = 0.2) to afford 2.72 g (6.29 mmol, 63.2%, >95% purity based on ¹H NMR) of **2d**. ¹H NMR (500 MHz, CDCl₃) 7.69-7.64 (m, 4H), 7.56 (dt, *J* = 15.7, 3.3 Hz, 1H), 7.47-7.37 (m, 6H), 6.90-6.81 (m, 1H), 4.46 (m, 2H), 3.86 (d, *J* = 11.0 Hz, 6H), 1.09 (s, 9H); ¹³C NMR (100 MHz, CDCl₃) 153.8, 135.4, 132.6, 130.0, 127.9, 127.8, 127.1, 63.0, 54.0 (d, *J* = 6.6 Hz), 26.7, 19.2; ³¹P (202 MHz, CDCl₃) 1.05 (s); IR (film): 3061.2, 2956.9, 2932.1, 2857.5, 1717.9, 1642.0, 1471.9, 1428.0, 1262.4, 1186.1, 1113.5, 1034.6 cm⁻¹; HRMS (CI): Exact mass calcd for C₂₂H₂₉O₅PSi [M+H]⁺: 433.1600. Found: 433.1608.

(3) (A) Baraldi, P. G.; Guarneri, M.; Moroder, F.; Pollini, G. P.; Simoni, D. *Synthesis* **1982**, 653-655. (B) Mori, Y.; Kawade, J.; Furukawa, H. *Tetrahedron* **1995**, 51, 5315-5330.

(2E-3-Phenyl-prop-2-en-1-yl)-phosphonic Acid Dimethyl Ester (2e). Following the oxidation outlined by Spilling,⁴ 1.0 g (4.1 mmol) of the known^{2b} (2E-3-phenyl-1-hydroxyl-prop-2-enyl)-phosphonic acid dimethyl ester was added to 18 mL of acetonitrile in a 50-mL round-bottom flask under nitrogen. To the resulting solution was added 7.0 g (83 mmol) of Magtrieve™ (CrO₂). The reaction was refluxed until the disappearance of the hydroxyl phosphonate by TLC, 2.5 h. The reaction was filtered through a short silica plug (EtOAc) and concentrated to a thick liquid *in vacuo*. The resulting material was diluted with 50 mL dichloromethane and washed with 50 mL sat. Na₂CO₃ and concentrated *in vacuo*. The procedure provided 0.70 g (2.9 mmol, 71%, >95% purity based on ¹H NMR) of the known compound **2e**.^{2b}

General Procedures for the Preparation of Substituted *N*-Benzyl- and *N*-Allyl-indoles 5b-5h.

Method A: Following the procedure outlined by Guida,⁵ 1.0 equiv of indole was added to a solution of 1.2 equiv of potassium *tert*-butoxide and 0.1 equiv of 18-crown-6 in Et₂O (0.05 M relative to indole). The reaction was stirred vigorously for 15 min before being cooled to 0 °C. A 2.0 M solution of benzyl bromide or allyl bromide in Et₂O (1.2 equiv) was added, and the reaction was subsequently allowed to warm to rt. The reaction was stirred for an additional 2-3 h at rt. The title compound was purified by either Kugelrohr distillation or flash silica chromatography.

Method B: The procedure by Ottoni⁶ for the alkylation was followed. To a 0.13 M solution of the parent indole (1.0 equiv) in ethanol was added 1.25 equiv of potassium hydroxide. The solution was stirred until homogeneous (5-25 min). The ethanol was removed *in vacuo* to afford a white solid. The resulting deprotonated indole was diluted to 0.13 M with acetone before 1.0 equiv of benzyl bromide was added. The reaction was stirred for 5-25 min at rt. The potassium bromide precipitate was removed by pipet filtration and the resulting mother liquid reduced to a solid *in vacuo*. The title compound was purified by flash silica chromatography.

1-Benzyl-1H-indole (5c) and 1-Allyl-1H-indole (5b): The title compounds are known and were prepared by the method of Guida.⁵

1-Benzyl-5-chloro-1H-indole (5e). Following Method B, to a solution of 300 mg (1.97 mmol) of 5-chloro-1H-indole in 15 mL of ethanol was added 137 mg (2.45 mmol) of potassium hydroxide. The reaction was stirred at rt for 5 min. After concentration, 15 mL of acetone was added followed by 0.235 mL (1.97 mmol) of benzyl bromide. The reaction was stirred at rt for 5 min before filtration. The reaction afforded 390 mg (1.61 mmol, 82%, >98% purity based on ¹H NMR) of the title compound after chromatography (5% EtOAc/hexanes, R_f = 0.37). Analytical data for **5e**: mp = 58-60 °C; ¹H NMR (500 MHz, CDCl₃) 7.63 (m, 1H), 7.34-7.28 (m, 5H),

(4) Liao, Y.; Shabany H.; Spilling C. D.; *Tetrahedron Letters* **1998**, 39, 8389-8392.

(5) Guida, W. C.; Mathre, D. J. *J. Org. Chem.* **1980**, 45, 3172-3176.

(6) Ottoni, O.; Cruz, R.; Alves, R. *Tetrahedron* **1998**, 54, 13915-13928.

7.19-7.10 (m, 3H), 6.51 (m, 1H), 5.33 (s, 2H); ^{13}C NMR (100 MHz, CDCl_3) 137.0, 134.6, 129.7, 129.6, 128.8, 127.7, 126.6, 125.3, 122.0, 120.3, 110.7, 101.3, 50.3; IR (film): 3028, 2926, 1604, 1508, 1471, 1436, 1184 cm^{-1} ; HRMS (EI): Exact mass calcd for $\text{C}_{15}\text{H}_{12}\text{NCl} [\text{M}]^+$: 241.0658. Found: 241.0651.

1-Benzyl-5-bromo-1H-indole (5d). Following Method B, to a solution of 386 mg (1.97 mmol) of 5-bromo-1H-indole in 15 mL of ethanol was added 137 mg (2.45 mmol) of potassium hydroxide. The reaction was stirred at rt for 5 min. After concentration, 15 mL of acetone was added followed by 0.235 mL (1.97 mmol) of benzyl bromide. The reaction was stirred at rt for 5 min before filtration. The reaction afforded 392 mg (1.37 mmol, 70%, >97% purity based on ^1H NMR) of the title compound after chromatography (5% EtOAc/hexanes, R_f = 0.29). Analytical data for **5d**: mp = 85-86 $^{\circ}\text{C}$; ^1H NMR (500 MHz, CDCl_3) 7.79 (m, 1H), 7.34-7.25 (m, 5H), 7.17-7.08 (m, 3H), 6.51 (m, 1H), 5.32 (s, 2H); ^{13}C NMR (100 MHz, CDCl_3) 137.0, 134.9, 130.4, 129.5, 128.8, 127.8, 126.6, 124.5, 123.4, 112.9, 111.2, 101.2, 50.3; IR (film): 3084, 3023, 2910, 1603, 1503, 1469, 1182, 1048 cm^{-1} ; HRMS (EI): Exact mass calcd for $\text{C}_{15}\text{H}_{12}\text{BrN} [\text{M}]^+$: 285.0153. Found: 285.0153.

1-Benzyl-5-methoxy-1H-indole (5g). Following Method B, to a solution of 500 mg (3.40 mmol) of 5-methoxy-1H-indole in 25 mL of ethanol was added 238 mg (4.24 mmol) of potassium hydroxide. The reaction was stirred at rt for 5 min. After concentration, 25 mL of acetone was added followed by 0.405 mL (3.40 mmol) of benzyl bromide. The reaction was stirred at rt for 5 min before filtration. The reaction afforded 581 mg (2.45 mmol, 72%, >95% purity based on ^1H NMR) of the title compound after chromatography (5% EtOAc/hexanes, R_f = 0.43). Analytical data for **5g**: mp = 66-68 $^{\circ}\text{C}$; ^1H NMR (500 MHz, CDCl_3) 7.31-7.25 (m, 3H), 7.15 (m, 1H), 7.12-7.09 (m, 4H), 6.82 (m, 1H), 6.47 (m, 1H), 5.30 (s, 2H), 3.85 (s, 3H); ^{13}C NMR (100 MHz, CDCl_3) 154.1, 137.6, 129.0, 128.8, 128.7, 127.6, 126.7, 112.0, 110.4, 102.5, 101.1, 55.8, 50.3; IR (film): 3101, 3028, 3000, 2934, 2828, 1618, 1577, 1487, 1448, 1357, 1303, 1189, 1131 cm^{-1} ; HRMS (EI): Exact mass calcd for $\text{C}_{16}\text{H}_{15}\text{ON} [\text{M}]^+$: 237.1154. Found: 237.1154.

1-Benzyl-1H-indole-5-carboxylic Acid Methyl Ester (5f). Following the method reported by Dillard,⁷ 30.0 mg (0.17 mmol) of 1H-indole-5-carboxylic acid methyl ester was added to 0.5 mL of *N,N*-dimethylformamide in a vacuum flame-dried 10-mL round-bottom flask under an atmosphere of nitrogen. Then, 4.1 mg (0.17 mmol) of sodium hydride was added in a single portion. The reaction was stirred at rt for 1 h. Benzyl bromide (29.3 mg, 0.17 mmol) was added to the reaction and the resulting solution stirred at rt for 3.5 h. The reaction

(7) Dillard, R. D.; Bach, N. J.; Draheim, S. E.; Berry, D. R.; Carlson, D. G.; Chirgadze, N. Y.; Clawrence, D. K.; Hartley, L. W.; Johnson, L. M.; Jones, N. D.; McKinney, E. R.; Mihelich, E. D.; Olkowski, J. L.; Schevitz, R. W.; Smith, A. C.; Snyder, D. W.; Sommers, C. D.; Wery, J. *J. Med. Chem.* **1996**, 39, 5119-5136.

was quenched with 10 mL of water and extracted 2 x 15 mL with EtOAc. The combined organic extracts were washed with brine and dried with Na₂SO₄. The resulting mother liquid was concentrated to a solid *in vacuo*. The title compound was purified by flash silica chromatography (10% EtOAc /hexanes, R_f = 0.23) to afford 15.6 mg (0.059 mmol, 34%, >99% purity based on ¹H NMR) of **5f**. Analytical data for **5f**: mp = 68-70 °C; ¹H NMR (400 MHz, CDCl₃) 8.44-8.43 (m, 1H), 7.90-7.88 (m, 1H), 7.33-7.27 (m, 4H), 7.18 (d, *J* = 3.3 Hz, 1H), 7.11-7.09 (m, 2H), 6.65 (d, *J* = 3.3 Hz, 1H), 5.34 (s, 2H), 3.93 (s, 3H); ¹³C NMR (100 MHz, CDCl₃) 168.1, 138.7, 136.8, 129.6, 128.8, 128.2, 127.8, 126.7, 124.0, 123.1, 121.6, 109.3, 103.3, 51.8, 50.2; IR (film): 3029.9, 2948.5, 2856.6, 1710.8, 1612.6, 1513.8, 1496.0, 1449.6, 1434.3, 1347.0, 1310.7, 1267.9, 1194.7, 1136.7, 1096.6 cm⁻¹; HRMS (CI): Exact mass calcd for C₁₇H₁₅O₂N [M+H]⁺: 266.1181. Found: 266.1175.

1-Benzyl-4-chloro-1H-indole (5h). Following the method reported by Dillard,⁷ 400 mg (2.64 mmol) of 4-chloro-1H-indole was added to 7.0 mL of *N,N*-dimethylformamide in a 25-ml round-bottom flask under an atmosphere of nitrogen. Sodium hydride (120 mg, 2.64 mmol) was added to the reaction in a single portion, and the solution was stirred at rt for 1 h. To the resulting solution was added 0.314 mL (451 mg, 2.64 mmol) of benzyl bromide. After 20 h of moderate stirring, the reaction was quenched with 50 mL of water and extracted 2 x 25 mL with EtOAc. The combined organic extracts were washed with brine and dried with Na₂SO₄. The resulting mother liquid was concentrated to a solid *in vacuo*. The title compound was purified by flash silica chromatography (10% EtOAc /hexanes, R_f = 0.34) to afford 622 mg (2.57 mmol, 97%, >90% purity based on ¹H NMR) of **5h**. Analytical data for **5h**: mp = 57-58 °C; ¹H NMR (500 MHz, CDCl₃) 7.35-7.28 (m, 3H), 7.21-7.10 (m, 6H), 6.70 (m, 1H), 5.32 (s, 2H); ¹³C NMR (100 MHz, CDCl₃) 137.00, 136.98; 128.83, 128.80, 127.75, 127.44, 126.7, 126.2, 122.3, 119.3, 108.4, 100.34, 50.5; IR (film): 3094, 3062, 3030, 2925, 1606, 1565, 1508, 1481, 1453, 1434, 1338, 1253, 1209 cm⁻¹; HRMS (CI): Exact mass calcd for C₁₅H₁₂ClN [M+H]⁺: 242.0736. Found: 242.0727.

Dependence of Enantioselectivity on Ligand Substitution

A previous communication from the Evans laboratory demonstrated that C₂-symmetric bis(oxazolinyl)pyridine-scandium(III) complexes (**1**, **1a-1c**) are effective Lewis acid catalysts for the addition of allenylsilanes to ethyl glyoxylate.⁸ We sought to utilize this highly organized scandium(III) Lewis acid for asymmetric Friedel-Crafts alkylations. The enantioselectivity and facial selectivity of the Friedel-Crafts reaction was highly dependent upon ligand substitution (Table 1). Catalysts **1a-1c** all provided the product with complete conversion but with moderate enantioselectivity (69-72% ee). Increasing the steric requirements along the plane of the pybox ligand-Sc(III) complex with Sc((*S,S*)-IndaPybox) (**1**) afforded an increase in selectivity to 98% ee with almost complete conversion (98%). It should be noted that the catalyst derived from (*S*)-phenylglycine (Sc((*S,S*)-PhPybox), **1c**) provided the product **4a** with the opposite sense of stereo-induction as

(7) Dillard, R. D.; Bach, N. J.; Draheim, S. E.; Berry, D. R.; Carlson, D. G.; Chirgadze, N. Y.; Clawrence, D. K.; Hartley, L. W.; Johnson, L. M.; Jones, N. D.; McKinney, E. R.; Mihelich, E. D.; Olkowski, J. L.; Schevitz, R. W.; Smith, A. C.; Snyder, D. W.; Sommers, C. D.; Wery, J. *J. Med. Chem.* **1996**, 39, 5119-5136.

(8) Evans, D. A.; Sweeney, Z. K.; Rovis, T.; Tedrow, J. S.; *J. Am. Chem. Soc.* **2001**, 123, 12095-12096.

the structurally similar Sc((*S,S*)-IndaPybox) (**1**).⁹ Studies on the nature of the reversal of selectivity are in progress.

Table 1. Dependence on Enantioselectivity and Facial Selectivity on Ligand Substitution^a

entry	catalyst	conversion (%)	% ee ^b	conf. ^d
1	1a	99	72	(<i>S</i>)
2	1b	99	69	(<i>S</i>)
3	1c	99	72	(<i>R</i>)
4	1	98 ^c	98	(<i>S</i>)

^aAll reactions were carried out in CH_2Cl_2 for 3 h at -78°C at a concentration of 0.2 M. ^bEnantiomeric excess determined by chiral HPLC using a Chiracel OD-H column. ^cIsolated yield of 92%. ^dAbsolute configuration determined by X-ray analysis of crystalline derivative.

[3a*S*]-[2(3'*aR,8'*aS**),3a α ,8a α]-2,2'-(2,6-Pyridinediyl)bis-[3a,8a-dihydro-8*H*-indeno[1,2-*d*]oxazole (**1**), 2,6-Bis-(4*S*-phenyl-4,5-dihydro-oxazol-2-yl)-pyridine (**1c**), 2,6-Bis-(4*S*-benzyl-4,5-dihydro-oxazol-2-yl)-pyridine (**1b**), 2,6-Bis-(4*S*-iso-propyl-4,5-dihydro-oxazol-2-yl)-pyridine (**1a**):** These compounds were prepared in two steps from the corresponding amino alcohols by the method of Davies.¹⁰

General Procedure for the Preparation of Scandium(III) Triflate Complexes (1**, **1a-1c**).** A 2-dram oven-dried vial was charged with a stirbar, $\text{Sc}(\text{OTf})_3$ (16.2 mg, 0.033 mmol, 0.1 equiv), and the corresponding pybox ligand (0.040 mmol, 0.12 equiv) in a dry box. The vial was capped with a septum and removed from the dry box. Dichloromethane (1.0 mL) was added to the vial under an atmosphere of dry N_2 . The resulting mixture was stirred vigorously at rt for 2 h until the reaction became homogeneous.

General Catalytic Procedure: The resulting catalyst solution was cooled to the desired temperature, and the acyl phosphonate (1.0 equiv, 0.33 mmol) was added. After 1 min, a 1.0 M solution of the nucleophile (1.2

- (9) For a discussion of ligand induced reversal of stereoinduction observed in other reactions catalyzed by metal bis(oxazoline) complexes see: Johnson, J. S.; Evans, D. A.; *Acc. Chem. Res.* **2000**, 33, 325-335
 (10) Davies, I. W.; Gerena, L.; Lu, N.; Larsen, R. D.; Reider, P. J. *J. Org. Chem.* **1996**, 61, 9629-9630.

equiv, 0.40 mL, 0.40 mmol) was added slowly to the reaction along the side of the vial. The reaction was stirred at a constant temperature until consumption of the acyl phosphonate as monitored by thin layer chromatography. Methanol (0.50 mL), followed by DBU (0.10 mL), were added directly to the reaction mixture. The cold bath was removed and the reaction was allowed to stir for 30 min at rt. The reaction was diluted with EtOAc (20 mL), then washed with sat. NH_4Cl and brine. The organic layer was dried over anhydrous Na_2SO_4 , filtered, and concentrated *in vacuo*. The remaining material was purified by flash column chromatography (SiO_2) using a mixture of EtOAc and hexanes as eluent to afford α -indolyl carbonyl compounds.

Variation of *N*-Protecting Group

(*S*)-3-(1*H*-Indol-3-yl)-butyric Acid Methyl Ester (6a). To a $-78\text{ }^\circ\text{C}$ solution of the catalyst complex prepared as described above was added 50 μL (0.33 mmol) of **2a**, followed by a slow addition of 400 μL (0.40 mmol) of a 1 M solution of indole in dichloromethane. After 3 h of moderate stirring, the reaction was quenched as described above. The title compound was purified by flash chromatography (SiO_2 , 15% EtOAc/hexanes) to afford 58 mg (0.27 mmol, 83%, >98% purity based on ^1H NMR) of **6a**. Analytical data for **6a**: $[\alpha]_{\text{D}}^{25} = +2.7^\circ$ (*c* 1.10, CH_2Cl_2); ^1H NMR (500 MHz, CDCl_3) 7.94 (s, 1H), 7.67 (d, $J = 8.1$ Hz, 1H), 7.34 (m, 1H), 7.22 (m, 1H), 7.13 (m, 1H), 6.98 (s, 1H), 3.67 (s, 3H), 3.63 (m, 1H), 2.85 (dd, $J = 15.1, 6.2$ Hz, 1H), 2.60 (dd, $J = 15.0, 8.8$ Hz, 1H), 1.43 (d, $J = 7.0$ Hz, 3H); ^{13}C NMR (100 MHz, CDCl_3) 173.3, 136.4, 126.3, 122.0, 120.7, 120.0, 119.2, 119.1, 111.2, 51.5, 42.2, 27.9, 21.0; IR (film): 3413, 3059, 2962, 1725, 1449, 1340, 1282, 1171, 1099 cm^{-1} ; HRMS (EI): Exact mass calcd for $\text{C}_{13}\text{H}_{15}\text{O}_2\text{N}$ $[\text{M}]^+$: 217.1103. Found: 217.1107. Product ratios were determined by HPLC analysis (Chiralcel OD-H, 15% *i*PrOH/hexanes, 0.7 mL/min, 254 nm); *S* isomer (major) $t_{\text{r}} = 19.0$ min and *R* isomer (minor) $t_{\text{r}} = 12.9$ min.

(*S*)-3-(1-Methyl-1*H*-indol-3-yl)-butyric Acid Methyl Ester (4a). To a $-78\text{ }^\circ\text{C}$ solution of the catalyst complex prepared as described above was added 50 μL (0.33 mmol) of **2a**, followed by a slow addition of 400 μL (0.40 mmol) of a 1 M solution of *N*-methylindole in dichloromethane. After 4 h of moderate stirring, the reaction was quenched as described above. The title compound was purified by flash chromatography (SiO_2 , 10% EtOAc/hexanes) to afford 57 mg (0.25 mmol, 75%, >99% purity based on ^1H NMR) of **4a**. Analytical data for **4a**: $[\alpha]_{\text{D}}^{25} = +8.1^\circ$ (*c* 2.0, CH_2Cl_2); ^1H NMR (500 MHz, CDCl_3) 7.63 (m, 1H), 7.30-7.20 (m, 2H), 7.12-7.09 (m, 1H), 6.85 (s, 1H), 3.74 (s, 3H), 3.65 (s, 3H), 3.60 (m, 1H), 2.81 (dd, $J = 15.1, 5.9$ Hz, 1H), 2.56 (dd, $J = 14.7, 8.3$ Hz, 1H), 1.40 (d, $J = 7.3$ Hz, 3H); ^{13}C NMR (100 MHz, CDCl_3) 173.3, 137.1, 126.7, 124.8, 121.5, 119.3, 119.2, 118.6, 109.3, 51.5, 42.4, 32.6, 27.9, 21.2; IR (film): 3053, 2953, 2825, 1732, 1483, 1134, 1012 cm^{-1} ; HRMS (ES): Exact mass calcd for $\text{C}_{14}\text{H}_{18}\text{O}_2\text{N}$ $[\text{M}+\text{H}]^+$: 232.1337. Found: 232.1328. Product ratios were determined by HPLC analysis (Chiralcel OD-H, 3% *i*PrOH/2% EtOH/hexanes, 0.8 mL/min, 254 nm); *R* isomer (minor) $t_{\text{r}} = 12.9$ min and *S* isomer (major) $t_{\text{r}} = 16.3$ min.

(*S*)-3-(1-Allyl-1*H*-indol-3-yl)-butyric Acid Methyl Ester (6b). To a $-78\text{ }^\circ\text{C}$ solution of the catalyst complex prepared as described above was added 50 μL (0.33 mmol) of **2a**, followed by a slow addition of 400 μL (0.40 mmol) of a 1 M solution of *N*-allylindole in

dichloromethane. After 5 h of moderate stirring, the reaction was quenched as described above. The title compound was purified by flash chromatography (SiO₂, 5% EtOAc/hexanes) to afford 66 mg (0.25 mmol, 76%, >98% purity based on ¹H NMR) of **6b**. Analytical data for **6b**: [α]_D²⁵ = + 8.8° (*c* 1.35, CH₂Cl₂); ¹H NMR (500 MHz, CDCl₃) 7.65-7.64 (m, 1H), 7.29-7.26 (m, 1H), 7.21-7.18 (m, 1H), 7.12-7.10 (m, 1H), 6.89 (s, 1H), 6.02-5.94 (m, 1H), 5.12 (m, 1H), 5.10-5.05 (m, 1H), 4.68 (m, 1H), 3.65 (s, 3H), 3.63 (m, 1H), 2.82 (dd, *J* = 14.6, 6.4 Hz, 1H), 2.56 (dd, *J* = 15.1, 8.8 Hz, 1H), 1.41 (d, *J* = 6.8 Hz, 3H); ¹³C NMR (100 MHz, CDCl₃) 173.3, 136.5, 133.6, 126.9, 123.8, 123.8, 121.6, 119.7, 119.3, 118.8, 117.1, 109.6, 51.5, 48.6, 42.4, 27.9, 21.1; IR (film): 3054, 2953, 1736, 1644, 1613, 1551, 1467, 1435, 1373, 1191, 1169, 1012 cm⁻¹; HRMS (CI): Exact mass calcd for C₁₆H₁₉O₂N [M+H]⁺: 258.1494. Found: 258.1490. Product ratios were determined by HPLC analysis (Chiralcel OD-H, 3% *i*PrOH/2% EtOH/hexanes, 0.6 mL/min, 254 nm); *S* isomer (major) *t*_r = 16.0 min and *R* isomer (minor) *t*_r = 14.9 min.

(S)-3-(1-Benzyl-1H-indol-3-yl)-butyric Acid Methyl Ester (6c). To a -78 °C solution of the catalyst complex prepared as described above was added 50 μL (0.33 mmol) of **2a**, followed by a slow addition of 400 μL (0.40 mmol) of a 1 M solution of *N*-benzylindole in dichloromethane. After 20 h of moderate stirring, the reaction was quenched as described above. The title compound was purified by flash chromatography (SiO₂, 10% EtOAc/hexanes) to afford 87 mg (0.28 mmol, 85%, >95% purity based on ¹H NMR) of **6c**. Analytical data for **6c**: [α]_D²⁵ = +8.2° (*c* 1.39, CH₂Cl₂); ¹H NMR (500 MHz, CDCl₃) 7.70-7.68 (m, 1H), 7.33-7.27 (m, 4H), 7.21-7.18 (m, 1H), 7.15-7.11 (m, 3H), 6.95 (s, 1H), 3.66 (s, 3H), 5.30 (s, 2H), 3.67-3.62 (m, 1H), 2.85 (dd, *J* = 15.1, 6.4 Hz, 1H), 2.60 (dd, *J* = 14.7, 8.3 Hz, 1H), 1.44 (d, *J* = 6.8 Hz, 3H); ¹³C NMR (100 MHz, CDCl₃) 173.2, 137.6, 136.8, 128.7, 127.5, 127.0, 126.7, 124.2, 121.7, 120.0, 119.3, 118.9, 109.7, 51.4, 49.8, 42.3, 28.0, 21.1; IR (film): 3029, 2953, 1734, 1631, 1551, 14481, 1453, 1357, 1248, 1171, 1029, 1013 cm⁻¹; HRMS (ES): Exact mass calcd for C₂₀H₂₂O₂N [M+H]⁺: 308.1650. Found: 308.1645. Product ratios were determined by HPLC analysis (Chiralcel OD-H, 3% *i*PrOH/2% EtOH/hexanes, 0.8 mL/min, 254 nm); *S* isomer (major) *t*_r = 16.2 min and *R* isomer (minor) *t*_r = 14.8 min.

Variation of Phosphonate Structure

(R)-3-(1-Methyl-1H-indol-3-yl)-4-methyl-pentanoic acid methyl ester (4c). To a -78 °C solution of the catalyst complex prepared as described above was added 62 μL (0.33 mmol) of **2c**, followed by a slow addition of 400 μL (0.40 mmol) of a 1 M solution of *N*-methylindole in dichloromethane. After 20 h of moderate stirring, the reaction was quenched as described above. The title compound was purified by flash chromatography (SiO₂, 10% EtOAc/hexanes) to afford 91 mg (0.27 mmol, 82%, >95% purity based on ¹H NMR) of **4c**. Analytical data for **4c**: [α]_D²⁵ = +3.9° (*c* 1.07, CH₂Cl₂); ¹H NMR (500 MHz, CDCl₃) 7.62 (d, *J* = 7.8 Hz, 1H), 7.21 (m, 1H), 7.19 (m, 1H), 7.09 (m, 1H), 6.83 (s, 1H), 3.74 (s, 3H), 3.52 (s, 3H), 3.34 (m, 1H), 2.80 (dd, *J* = 15.1, 5.4 Hz, 1H), 2.67 (dd, *J* = 14.6, 9.3 Hz, 1H), 2.05 (m, 1H), 0.91 (d, *J* = 6.3 Hz, 3H), 0.87 (d, *J* = 6.8 Hz, 3H); ¹³C NMR (100 MHz, CDCl₃) 173.6, 136.9, 127.8, 126.3, 121.2, 119.6, 118.5, 116.0, 109.0, 51.4, 39.6, 37.7, 32.6, 32.4, 20.4, 20.1; IR (film): 3053, 2956, 2873, 1738, 1470, 1328, 1268, 1165 cm⁻¹; HRMS (ES): Exact mass calcd for C₁₆H₂₂O₂N [M+H]⁺: 260.1650. Found: 260.1642. Product ratios were determined by HPLC analysis (Chiralcel OD-H, 5% *i*PrOH/hexanes, 0.7 mL/min, 254 nm); *R* isomer (major) *t*_r = 12.6 min and *S* isomer (minor) *t*_r = 9.5 min.

(S)-3-(1-Methyl-1H-indol-3-yl)-pentanoic Acid Methyl Ester (4b). To a $-78\text{ }^{\circ}\text{C}$ solution of the catalyst complex prepared as described above was added $56\text{ }\mu\text{L}$ (0.33 mmol) of **2b**, followed by a slow addition of $400\text{ }\mu\text{L}$ (0.40 mmol) of a 1 M solution of *N*-methyllindole in dichloromethane. After 17 h of moderate stirring, the reaction was quenched as described above. The title compound was purified by flash chromatography (SiO_2 , 10% EtOAc/hexanes) to afford 52 mg (0.21 mmol , 65% , $>97\%$ purity based on ^1H NMR) of **4b**. Analytical data for **4b**: $[\alpha]_{\text{D}}^{25} = +11.0^{\circ}$ ($c\text{ }0.93$, CH_2Cl_2); ^1H NMR (500 MHz , CDCl_3) $7.63\text{--}7.61\text{ (m, 1H)}$, $7.28\text{--}7.24\text{ (m, 1H)}$, $7.21\text{--}7.18\text{ (m, 1H)}$, $7.09\text{--}7.06\text{ (m, 1H)}$, 6.84 (s, 1H) , 3.73 (s, 3H) , 3.58 (s, 3H) , $3.39\text{--}3.33\text{ (m, 1H)}$, $2.70\text{ (d, } J = 7.8\text{ Hz, 1H)}$, $1.80\text{--}1.74\text{ (m, 2H)}$, $0.85\text{ (t, } J = 7.3\text{ Hz, 3H)}$; ^{13}C NMR (100 MHz , CDCl_3) 173.4 , 137.1 , 127.1 , 125.8 , 121.4 , 119.4 , 118.5 , 117.1 , 109.2 , 51.4 , 40.7 , 35.0 , 32.6 , 28.4 , 12.0 ; IR (film): 3051 , 2958 , 2930 , 2874 , 1739 , 1614 , 1549 , 1468 , 1375 , 1253 , 1168 cm^{-1} ; HRMS (ES): Exact mass calcd for $\text{C}_{15}\text{H}_{20}\text{O}_2\text{N}$ $[\text{M}+\text{H}]^+$: 246.1495 . Found: 246.1491 . Product ratios were determined by HPLC analysis (Chiralcel OD-H, 3% $i\text{PrOH}/2\%$ EtOH/hexanes, 0.8 mL/min , 254 nm); *S* isomer (major) $t_{\text{r}} = 16.7\text{ min}$ and *R* isomer (minor) $t_{\text{r}} = 12.4\text{ min}$.

(S)-3-(1-Methyl-1H-indol-3-yl)-1-morpholin-4-(tert-butyl-diphenyl-silanyloxy)-butan-1-one. To a $-78\text{ }^{\circ}\text{C}$ solution of the catalyst complex prepared as described above was added $129\text{ }\mu\text{L}$ (0.33 mmol) of **2d**, followed by a slow addition of $400\text{ }\mu\text{L}$ (0.40 mmol) of a 1 M solution of *N*-methyllindole in dichloromethane. After 17 h of moderate stirring, $432\text{ }\mu\text{L}$ (4.95 mmol , 15 equiv) of morpholine was added to the vial. The vial was subsequently removed from the $-78\text{ }^{\circ}\text{C}$ bath and stirred at rt for 17 h . The reaction was diluted with 20 mL of ethyl acetate, washed with sat. NH_4Cl , and brine. The organic layer was dried with Na_2SO_4 . The reaction was concentrated to give a thick liquid *in vacuo*. The title compound was purified by flash chromatography (SiO_2 , $40\text{--}60\%$ EtOAc/hexanes) to afford 131 mg (0.24 mmol , 73% , $>98\%$ purity based on ^1H NMR) of product. Analytical data for the title compound: $[\alpha]_{\text{D}}^{25} = +24.6^{\circ}$ ($c\text{ }0.66$, CH_2Cl_2); ^1H NMR (500 MHz , CDCl_3) $7.66\text{--}7.61\text{ (m, 4H)}$, $7.47\text{--}7.34\text{ (m, 7H)}$, $7.29\text{--}7.27\text{ (m, 1H)}$, $7.22\text{--}7.19\text{ (m, 1H)}$, $7.06\text{--}7.03\text{ (m, 1H)}$, 7.00 (s, 1H) , $4.04\text{ (dd, } J = 10.3, 4.9\text{ Hz, 1H)}$, $3.91\text{ (dd, } J = 9.8, 7.8\text{ Hz, 1H)}$, $3.76\text{--}3.73\text{ (m, 1H)}$, 3.73 (s, 3H) , $3.72\text{--}3.55\text{ (m, 2H)}$, $3.48\text{--}3.33\text{ (m, 5H)}$, $3.17\text{--}3.12\text{ (m, 2H)}$, $2.75\text{ (dd, } J = 14.6, 8.8\text{ Hz, 1H)}$, 1.10 (s, 9H) ; ^{13}C NMR (100 MHz , CDCl_3) 170.9 , 136.8 , $135.6\text{ (d, } J = 2.2\text{ Hz)}$, $133.5\text{ (d, } J = 2.2\text{ Hz)}$, $129.6\text{ (d, } J = 6.6\text{ Hz)}$, $127.6\text{ (d, } J = 3.7\text{ Hz)}$, 127.2 , 126.6 , 121.5 , 119.1 , 118.7 , 114.4 , 109.2 , 67.2 , 66.7 , 66.3 , 46.3 , 41.8 , 36.5 , 35.2 , 32.6 , 26.9 , 19.3 ; IR (film): 3047.8 , 2929.8 , 2856.0 , 1643.5 , 1460.7 , 1427.2 , 1327.7 , 1299.9 , 1240.3 , 1113.0 cm^{-1} ; HRMS (CI): Exact mass calcd for $\text{C}_{33}\text{H}_{40}\text{O}_3\text{N}_2\text{Si}$ $[\text{M}+\text{H}]^+$: 541.2886 . Found: 541.2883 . Product ratios were determined by HPLC analysis (Chiralcel OD-H, 30% $i\text{PrOH}/\text{hexanes}$, 0.75 mL/min , 254 nm); *S* isomer (major) $t_{\text{r}} = 7.4\text{ min}$ and *R* isomer (minor) $t_{\text{r}} = 18.0\text{ min}$.

(S)-3-(1-Methyl-1H-indol-3-yl)-4-(tert-butyl-diphenyl-silanyloxy)-Butyric Acid Methyl Ester (4d). To a $-78\text{ }^{\circ}\text{C}$ solution of the catalyst complex prepared as described above was added $129\text{ }\mu\text{L}$ (0.33 mmol) of **2d**, followed by a slow addition of $400\text{ }\mu\text{L}$ (0.40 mmol) of a 1 M solution of *N*-methyllindole in dichloromethane. After 17 h of moderate stirring, the reaction was quenched as described above. The title compound was purified by flash chromatography (SiO_2 , $10\text{--}15\%$ EtOAc/hexanes) to afford 92 mg (0.19 mmol , 57% , $>98\%$

purity based on ^1H NMR) of **4d**. Analytical data for **4d**: $[\alpha]_{\text{D}}^{25} = +16.2^\circ$ (c 1.0, CH_2Cl_2); ^1H NMR (500 MHz, CDCl_3) 7.65-7.63 (m, 2H), 7.57-7.55 (m, 2H), 7.43-7.29 (m, 7H), 7.25-7.23 (m, 1H), 7.19-7.15 (m, 1H), 7.02-6.99 (m, 1H), 6.87 (s, 1H), 3.94-3.90 (m, 1H), 3.75-3.72 (m, 2H), 3.69 (s, 3H), 3.58 (s, 3H), 3.19-3.15 (m, 1H), 2.76-2.71 (m, 1H), 1.05 (s, 9H); ^{13}C NMR (100 MHz, CDCl_3) 173.5, 136.8, 135.6 (d, $J = 10.2$ Hz), 133.6, 129.5 (d, $J = 11.0$ Hz), 127.6 (d, $J = 7.3$ Hz), 127.2, 126.2, 121.5, 119.1, 118.7, 114.3, 109.1, 67.2, 51.5, 37.1, 15.9, 32.6, 26.9, 19.3; IR (film): 3049.9, 2930.6, 1857.1, 1737.6, 1472.3, 1427.7, 1361.4, 1328.8, 1243.3, 1166.7, 1111.7, 1061.8, 1006.9 cm^{-1} ; HRMS (CI): Exact mass calcd for $\text{C}_{30}\text{H}_{35}\text{O}_3\text{NSi}$ $[\text{M}+\text{H}]^+$: 486.2464. Found: 486.2457. Product ratios were determined by HPLC analysis (Chiralcel OD-H, 2% i PrOH/ 1% EtOH/hexanes, 0.8 mL/min, 254 nm); *S* isomer (major) $t_{\text{r}} = 16.3$ min and *R* isomer (minor) $t_{\text{r}} = 13.2$ min.

(R)-3-(1-Methyl-1H-indol-3-yl)-3-phenyl-propionic Acid Methyl Ester (4e). To an oven-dried 2-dram vial in a dry box was added 19.5 mg (0.040 mmol, 0.2 equiv) of scandium (III) triflate and 18.7 mg (0.048 mmol, 0.24 equiv) of (*S,S*)-IndaPybox. The vial was subsequently capped with a septum and charged with 1.0 mL of dichloromethane. The catalyst was allowed to age under nitrogen with moderate stirring for 2 h at rt. The homogeneous catalyst solution was cooled to -78°C for 20 min. To the -78°C solution of the catalyst complex was added 70 μL (0.33 mmol) of **2e**, followed by a slow addition of 400 μL (0.40 mmol) of a 1 M solution of *N*-methylindole in dichloromethane. After 48 h of moderate stirring, the reaction was quenched as described above. The title compound was purified by flash chromatography (SiO_2 , 10% EtOAc/hexanes) to afford 82 mg (0.28 mmol, 85%, >99% purity based on ^1H NMR) of **4e**. Analytical data for **4e**: $[\alpha]_{\text{D}}^{25} = -21.1^\circ$ (c 0.88, CH_2Cl_2); ^1H NMR (500 MHz, CDCl_3) 7.45-7.43 (m, 1H), 7.35-7.28 (m, 5H), 7.22-7.18 (m, 2H), 7.05-7.01 (m, 1H), 6.89 (s, 1H), 4.81 (dd, $J = 8.1, 7.7$ Hz, 1H), 3.75 (s, 3H), 3.61 (s, 3H), 3.17 (dd, $J = 15.1, 7.7$ Hz, 1H), 3.04 (dd, $J = 15.0, 8.1$ Hz, 1H); ^{13}C NMR (100 MHz, CDCl_3) 172.5, 143.8, 137.2, 128.4, 127.6, 126.9, 126.4, 125.9, 121.7, 119.5, 118.8, 117.2, 109.1, 51.6, 41.3, 39.1, 32.7; IR (film): 3057, 3027, 2950, 1738, 1484, 1435, 1328, 1264, 1156, 1014 cm^{-1} ; HRMS (ES): Exact mass calcd for $\text{C}_{19}\text{H}_{20}\text{O}_2\text{N}$ $[\text{M}+\text{H}]^+$ 294.1494. Found: 294.1500. Product ratios were determined by HPLC analysis (Chiralcel AD, 8% i PrOH/hexanes, 0.6 mL/min, 254 nm); *R* isomer (major) $t_{\text{r}} = 11.3$ min and *S* isomer (minor) $t_{\text{r}} = 12.5$ min.

Variation of Indole Structure

(S)-3-(1-Benzyl-5-chloro-1H-indol-3-yl)-butyric Acid Methyl Ester (6e). To a -78°C solution of the catalyst complex prepared as described above was added 50 μL (0.33 mmol) of **2a**, followed by a slow addition of 400 μL (0.40 mmol) of a 1 M solution of 1-benzyl-5-chloro-1H-indole (**5e**) in dichloromethane. After 19 h of moderate stirring, the reaction was quenched as described above. The title compound was purified by flash chromatography (SiO_2 , 10% EtOAc/hexanes) to afford 74 mg (0.22 mmol, 66%, >95% based on ^1H NMR) of **6e**. Analytical data for **6e**: $[\alpha]_{\text{D}}^{25} = +1.3^\circ$ (c 1.25, CH_2Cl_2); ^1H NMR (500 MHz, CDCl_3) 7.64 (m, 1H), 7.34-7.28 (m, 3H), 7.17-7.11 (m, 2H), 7.08 (m, 2H), 6.97 (m, 1H), 5.27 (s, 2H), 3.66 (s, 3H), 3.58-3.56 (m, 1H), 2.80 (dd, $J = 15.1, 6.3$ Hz, 1H), 2.58 (dd, $J = 15.1, 8.3$ Hz, 1H), 1.41 (d, $J = 6.8$ Hz, 1H); ^{13}C NMR (100 MHz, CDCl_3) 173.0, 137.2, 135.1, 128.8, 128.0, 127.7, 126.6, 125.7, 124.8, 122.0, 119.6, 118.8, 110.8, 51.5, 50.1, 42.3, 27.8, 21.1; IR (film): 2951, 1734, 1605, 1496, 1472, 1354, 1286, 1168, 1068 cm^{-1} ; HRMS (ES): Exact mass calcd for $\text{C}_{20}\text{H}_{21}\text{O}_2\text{NCl}$ $[\text{M}+\text{H}]^+$: 342.1261. Found: 342.1252. Product ratios were determined by HPLC

analysis (Chiralcel OD-H, 5% *i*PrOH/hexanes, 0.8 mL/min, 254 nm); *S* isomer (major) t_r = 17.9 min and *R* isomer (minor) t_r = 16.6 min.

(S)-3-(1-Benzyl-5-bromo-1*H*-indol-3-yl)-butyric Acid Methyl Ester (6d). To a $-78\text{ }^{\circ}\text{C}$ solution of the catalyst complex prepared as described above was added 50 μL (0.33 mmol) of **2a**, followed by a slow addition of 400 μL (0.40 mmol) of a 1 M solution of 1-benzyl-5-bromo-1*H*-indole (**5d**) in dichloromethane. After 19 h of moderate stirring, the reaction was quenched as described above. The title compound was purified by flash chromatography (SiO_2 , 10% EtOAc/hexanes) to afford 82 mg (0.21 mmol, 64%, >98% based on ^1H NMR) of **6d**. Analytical data for **6d**: $[\alpha]_{\text{D}}^{25} = +3.8^{\circ}$ (c 1.93, benzene); ^1H NMR (500 MHz, CDCl_3) 7.76 (m, 1H), 7.31-7.26 (m, 3H), 7.24-7.22 (m, 1H), 7.10 (m, 1H), 7.06-7.04 (m, 2H), 6.93 (s, 1H), 5.24 (s, 2H), 3.63 (s, 3H), 3.56-3.47 (m, 1H), 2.76 (dd, J = 14.6, 6.3 Hz, 1H), 2.56 (dd, J = 15.1, 8.3 Hz, 1H), 1.39 (d, J = 7.3 Hz, 3H); ^{13}C NMR (100 MHz, CDCl_3) 172.9, 137.1, 135.4, 128.8, 128., 127.7, 126.6, 125.5, 124.6, 121.9, 119.6, 112.4, 111.3, 51.5, 50.1, 42.3, 27.8, 21.1; IR (film): 2953, 1734, 1606, 1560, 1470, 1437, 1354, 1286, 1248, 1168 cm^{-1} ; HRMS (CI): Exact mass calcd for $\text{C}_{20}\text{H}_{20}\text{O}_2\text{BrN}$ $[\text{M}+\text{H}]^+$: 386.0755. Found: 386.0757. Product ratios were determined by HPLC analysis (Chiralcel OD-H, 5% *i*PrOH/hexanes, 0.8 mL/min, 254 nm); *S* isomer (major) t_r = 19.3 min and *R* isomer (minor) t_r = 17.5 min.

(S)-3-(1-Benzyl-5-methoxy-1*H*-indol-3-yl)-butyric Acid Methyl Ester (6g). To a $-78\text{ }^{\circ}\text{C}$ solution of the catalyst complex prepared as described above was added 50 μL (0.33 mmol) of **2a**, followed by a slow addition of 400 μL (0.40 mmol) of a 1 M solution of 1-benzyl-5-methoxy-1*H*-indole (**5g**) in dichloromethane. After 19 h of moderate stirring, the reaction was quenched as described above. The title compound was purified by flash chromatography (SiO_2 , 10% EtOAc/hexanes) to afford 74 mg (0.22 mmol, 67%, > 95% based on ^1H NMR) of **6g**. Analytical data for **6g**: $[\alpha]_{\text{D}}^{25} = +1.9^{\circ}$ (c 1.57, CH_2Cl_2); ^1H NMR (500 MHz, CDCl_3) 7.33-7.27 (m, 3H), 7.15-7.09 (m, 4H), 6.93 (s, 1H), 6.86 (m, 1H), 5.26 (s, 2H), 3.89 (s, 3H), 3.66 (s, 3H), 3.60-3.55 (m, 1H), 2.83 (dd, J = 15.1, 5.9 Hz, 1H), 2.58 (dd, J = 15.1, 8.8 Hz, 1H), 1.42 (d, J = 6.8 Hz, 3H); ^1H NMR (100 MHz, CDCl_3) 173.3, 153.6, 137.7, 132.0, 128.7, 127.5, 127.3, 126.6, 124.8, 119.4, 111.8, 110.5, 101.2, 55.9, 51.4, 50.0, 42.2, 27.9, 21.0; IR (film): 2951, 1733, 1619, 1576, 1487, 1452, 1355, 1278, 1221, 1166, 1030 cm^{-1} ; HRMS (ES): Exact mass calcd for $\text{C}_{21}\text{H}_{24}\text{O}_3\text{N}$ $[\text{M}+\text{H}]^+$: 338.1756. Found: 338.1761. Product ratios were determined by HPLC analysis (Chiralcel OD-H, 5% *i*PrOH/hexanes, 0.8 mL/min, 254 nm); *S* isomer (major) t_r = 22.5 min and *R* isomer (minor) t_r = 20.7 min.

(S)-3-(1-Benzyl-5-carbomethoxy-1*H*-indol-3-yl)-butyric Acid Methyl Ester (6f). To a $-78\text{ }^{\circ}\text{C}$ solution of the catalyst complex prepared as described above was added 50 μL (0.33 mmol) of **2a**, followed by a slow addition of 400 μL (0.40 mmol) of a 1 M solution of 1-benzyl-1*H*-indole-5-carboxylic acid methyl ester (**5f**) in dichloromethane. After 16 h of moderate stirring, the reaction was quenched as described above. The title compound was purified by flash chromatography (SiO_2 , 15% EtOAc/hexanes) to afford 82 mg (0.22 mmol, 68%, >97% purity based on ^1H NMR) of **6f**. Analytical data for **6f**: $[\alpha]_{\text{D}}^{25} = -3.7^{\circ}$ (c 1.69, CH_2Cl_2); ^1H NMR (500 MHz, CDCl_3) 8.42 (m, 1H), 7.88-7.86 (m, 1H), 7.32-7.24 (m, 4H), 7.08 (m, 2H), 6.98 (s, 1H), 5.29 (s, 2H), 3.93 (s, 3H), 3.67 (m, 1H), 3.63 (s, 3H), 2.82 (dd, J = 15.1, 6.4 Hz, 1H), 2.60 (dd, J = 15.1, 8.3 Hz, 1H), 1.42 (d, J = 6.8 Hz, 1H); ^{13}C NMR (100 MHz, CDCl_3)

172.9, 168.1, 139.2, 137.0, 128.8, 127.7, 126.7, 126.6, 125.6, 123.2, 122.3, 121.7, 121.1, 109.3, 51.8, 51.5, 50.0, 42.3, 27.8, 21.3; IR (film): 2951, 1710, 1613, 1495, 1452, 1435, 1307, 1285, 1246, 1173, 1129, 1089 cm^{-1} ; HRMS (CI): Exact mass calcd for $\text{C}_{22}\text{H}_{23}\text{O}_4\text{N}$ $[\text{M}+\text{H}]^+$: 366.1705. Found: 366.1708. Product ratios were determined by HPLC analysis (Chiralcel OD-H, 20% *i*PrOH/hexanes, 0.7 mL/min, 254 nm); *S* isomer (major) t_r = 25.8 min and *R* isomer (minor) t_r = 20.5 min.

(S)-3-(1-Benzyl-4-chloro-1H-indol-3-yl)-butyric Acid Methyl Ester (6h). To an oven dried 2-dram vial in a dry-box was added 19.5 mg (0.040 mmol, 0.2 equiv) of scandium (III) triflate and 18.7 mg (0.048 mmol, 0.24 equiv) of (*S,S*)-IndaPybox. The vial was subsequently capped with a septum and charged with 1.0 mL of dichloromethane. The catalyst was allowed to age with moderate stirring for 2 h at rt. The catalyst solution was cooled to $-78\text{ }^{\circ}\text{C}$ for 20 min. To the $-78\text{ }^{\circ}\text{C}$ solution of the catalyst complex was added 30 μL (0.20 mmol) of **2a**, followed by a slow addition of 240 μL (0.24 mmol) of a 1 M solution of 1-benzyl-4-chloro-1H-indole (**5h**) in dichloromethane. After 48 h of moderate stirring, the reaction was quenched as described above. The title compound was purified by flash chromatography (SiO_2 , 10-15% EtOAc/hexanes) to afford 34 mg (0.10 mmol, 51%, >98% purity based on ^1H NMR) of **6h**. Analytical data for **6h**: $[\alpha]_{\text{D}}^{25} = -7.3^{\circ}$ (*c* 0.35, CH_2Cl_2); ^1H NMR (500 MHz, CDCl_3) 7.32-7.28 (m, 3H), 7.14-7.10 (m, 1H), 7.08-7.00 (m, 4H), 6.98 (s, 1H), 5.26 (s, 2H), 4.17 (m, 1H), 3.64 (s, 3H), 2.93 (dd, $J = 15.0, 5.5$ Hz, 1H), 2.48 (dd, $J = 15.0, 9.2$ Hz, 1H), 1.40 (d, $J = 7.0$ Hz, 3H); ^{13}C NMR (100 MHz, CDCl_3) 173.1, 138.1, 137.1, 132.1, 128.8, 127.7, 126.6, 126.4, 125.4, 122.2, 120.8, 120.4, 51.4, 50.1, 43.1, 27.6, 21.7; IR (film): 3053, 3022, 2951, 1736, 1478, 1434, 1332, 1167, 1008 cm^{-1} ; HRMS (ES): Exact mass calcd for $\text{C}_{20}\text{H}_{21}\text{O}_2\text{NCl}$ $[\text{M}+\text{H}]^+$: 342.1261. Found: 342.1265. Product ratios were determined by HPLC analysis (Chiralcel OJ-H, 20% *i*PrOH/hexanes, 0.8 mL/min, 254 nm); *S* isomer (major) t_r = 24.3 min and *R* isomer (minor) t_r = 27.8 min.

(S)-3-(4-Dimethylamino-2-methoxy-phenyl)-butyric Acid Methyl Ester (9). To an oven dried 2-dram vial in a dry box was added 12.8 mg (0.026 mmol, 0.08 equiv) of scandium(III) triflate and 12.9 mg (0.033 mmol, 0.10 equiv) of (*S,S*)-IndaPybox. The vial was subsequently capped with a septum and charged with 1.0 mL of dichloromethane. The catalyst was allowed to age with moderate stirring for 2 h at rt. The homogeneous catalyst solution was cooled to $-78\text{ }^{\circ}\text{C}$ for 20 min. To the $-78\text{ }^{\circ}\text{C}$ solution of the catalyst complex was added 50 μL (0.33 mmol) of **2a**, followed by a slow addition of 200 μL (1.2 mmol, 4.8 equiv) *N,N*-dimethyl-3-methoxy-aniline (**8**). The vial was immediately placed in a $-40\text{ }^{\circ}\text{C}$ bath. After 48 h of moderate stirring, the reaction was quenched as described above. The title compound was purified by flash chromatography (SiO_2 , 10-15% EtOAc/hexanes) to afford 65 mg (0.26 mmol, 78%, >98% purity based on ^1H NMR) of **9**. Analytical data for **9**: $[\alpha]_{\text{D}}^{25} = +0.3^{\circ}$ (*c* 0.43, CH_2Cl_2); ^1H NMR (500 MHz, CDCl_3) 7.05 (m, 1H), 6.35-6.20 (m, 2H), 3.86 (s, 3H), 3.67 (s, 3H), 3.56 (m, 1H), 2.96 (s, 3H), 2.68 (dd, $J = 14.7, 5.4$ Hz, 1H), 2.50 (dd, $J = 15.1, 9.3$ Hz, 1H), 1.26 (d, $J = 7.3$ Hz, 3H); ^{13}C NMR (100 MHz, CDCl_3) 173.5, 157.6, 150.4, 127.2, 122.0, 104.7, 96.5, 55.2, 51.3, 41.4, 40.8, 29.5, 20.1; IR (film): 2952, 2836, 2801, 1737, 1616, 1517, 1439, 1238 cm^{-1} ; HRMS (EI): Exact mass calcd for $\text{C}_{14}\text{H}_{21}\text{O}_3\text{N}$ $[\text{M}]^+$: 251.1521. Found: 251.1531. Product ratios were determined by HPLC analysis (Chiralcel OD-H, 2% *i*PrOH/hexanes, 0.5 mL/min, 254 nm); *R* isomer (minor) t_r = 15.7 min and *S* isomer (major) t_r = 17.2 min.

(S)-3-(1-Methyl-1H-indol-3-yl)-1-morpholin-4-yl-butan-1-one (7). To a $-78\text{ }^{\circ}\text{C}$ solution of the catalyst complex prepared as described above was added $50\text{ }\mu\text{L}$ (0.33 mmol) of **2a**, followed by a slow addition of $400\text{ }\mu\text{L}$ (0.40 mmol) of a 1 M solution of *N*-methylindole (**3**) in dichloromethane. After 16 h of moderate stirring, $432\text{ }\mu\text{L}$ (4.95 mmol , 15 equiv) of morpholine was added to the vial. The vial was immediately removed from the $-78\text{ }^{\circ}\text{C}$ bath and stirred vigorously at rt for 3 h . The reaction was diluted with 20 mL of ethyl acetate and washed with sat. NH_4Cl and brine. The organic layer was dried with Na_2SO_4 , filtered, and concentrated to a dark thick liquid *in vacuo*. The title compound was purified by flash chromatography (SiO_2 , EtOAc) to afford 83 mg (0.29 mmol , 88% , $>97\%$ purity based on ^1H NMR) of **7**. Analytical data for **7**: $[\alpha]_{\text{D}}^{25} = -1.5^{\circ}$ ($c\text{ }1.38$, CH_2Cl_2); ^1H NMR (500 MHz , CDCl_3) δ 7.64 (m, 1H), 7.32-7.19 (m, 2H), 7.12-7.08 (m, 1H), 6.89 (s, 1H), 3.74 (s, 3H), 3.67-3.54 (m, 3H), 3.41-3.32 (m, 3H), 3.28 (m, 1H), 3.20 (m, 1H), 3.08 (m, 1H), 2.80 (dd, $J = 14.2, 6.3\text{ Hz}$, 1H), 2.55 (dd, $J = 14.7, 7.8\text{ Hz}$, 1H), 1.47 (d, $J = 6.8\text{ Hz}$, 3H); ^{13}C NMR (100 MHz , CDCl_3) δ 170.9, 137.1, 126.7, 125.1, 121.6, 119.4, 119.3, 118.7, 109.3, 66.7, 66.2, 46.2, 41.8, 41.0, 32.6, 28.5, 21.2; IR (film): 3056, 2961, 2856, 1638, 1460, 1426, 1371, 1328, 1239, 1028, cm^{-1} ; HRMS (CI): Exact mass calcd for $\text{C}_{17}\text{H}_{22}\text{O}_2\text{N}_2$ $[\text{M}+\text{H}]^+$: 287.1759. Found: 287.1762. Product ratios were determined by HPLC analysis (Chiralcel OD-H, 25% $i\text{PrOH}$ /hexanes, 0.8 mL/min , 254 nm); *R* isomer (minor) $t_{\text{r}} = 11.0\text{ min}$ and *S* isomer (major) $t_{\text{r}} = 18.1\text{ min}$.

Determination of absolute stereochemistry:

An X-ray crystal structure was obtained of the (*R*)- -methyl-benzyl amide derivative of ester **4**. The absolute stereochemistry of all other products were assigned by analogy.

***N*-((1*R*)-1-Phenylethyl)-(3*S*)-3-(1-methylindol-3-yl)-butanamide (12).** To a solution of **4** (30 mg , 0.13 mmol) in THF (2.0 mL) and dioxane (1.0 mL) was added LiOH (0.60 mL , 1.0 M aqueous solution). After 15 h , the reaction was acidified to pH 1 with 1 N HCl, then extracted with dichloromethane ($3\times$). The organic layer was then concentrated *in vacuo* to afford the corresponding acid (30 mg) which was used directly in the subsequent amide formation reaction: ^1H NMR (500 MHz , CDCl_3) δ 11.20 (brs, 1H), 7.62 (m, 1H), 7.33-7.24 (m, 2H), 7.16-7.12 (m, 1H), 6.90 (s, 1H), 3.77 (s, 3H), 3.65 (m, 1H), 2.90 (dd, $J = 15.1, 5.9\text{ Hz}$, 1H), 2.63 (dd, $J = 15.1, 8.3\text{ Hz}$, 1H), 1.46 (d, $J = 5.4\text{ Hz}$, 3H); ^{13}C NMR (100 MHz , CDCl_3) δ 178.8, 137.1, 126.6, 124.9, 121.6, 119.1, 119.0, 118.7, 109.3, 42.2, 32.6, 27.7, 21.2; IR (film): 3200-2680 (br), 3052, 2963, 1704, 1484, 1292 cm^{-1} . HRMS (ES): Exact mass calcd for $\text{C}_{13}\text{H}_{16}\text{O}_5\text{N}$ $[\text{M}+\text{H}]^+$: 218.1181. Found: 218.1180.

To the solution of unpurified carboxylic acid (30 mg , 0.13 mmol) in dichloromethane (1.5 mL) was added DMAP (30 mg) and (*R*)- -methyl benzyl amine (0.100 mL , 0.76 mmol) followed by EDC (80 mg , 0.42 mmol). After 8 h , the reaction was diluted with EtOAc and washed with 1 N HCl, sat. aq. NaHCO_3 ($2\times$), 1 N HCl and then brine. The organic layer was dried (Na_2SO_4) then concentrated *in vacuo*. The resulting solid was recrystallized from dichloromethane to afford crystals of pure amide **12** (30 mg , 72%) which were suitable for X-ray diffraction. Analytic data for **12**: mp = $137\text{--}139\text{ }^{\circ}\text{C}$; $[\alpha]_{\text{D}}^{25} = +31.0^{\circ}$ ($c\text{ }0.03$, CH_2Cl_2); ^1H NMR (500

MHz, CDCl₃) 7.65 (m, 1H), 7.32-7.00 (m, 8H), 6.81 (s, 1H), 5.40 (dd, $J = 7.7$ Hz, 1H), 4.98 (dq, $J = 7.0$, 7.0 Hz, 1H), 3.70 (s, 3H), 3.57 (m, 1H), 2.65 (dd, $J = 13.9$, 8.0 Hz, 1H), 2.50 (dd, $J = 13.9$, 6.7 Hz, 1H), 1.41 (d, $J = 7.0$ Hz, 3H), 1.13 (d, $J = 7.0$ Hz, 3H); ¹³C NMR (100 MHz, CDCl₃) 171.1, 143.2, 137.2, 138.5, 127.1, 126.6, 126.0, 125.5, 121.7, 119.3, 118.9, 118.8, 109.4, 48.5, 45.2, 32.6, 28.9, 21.4, 21.3. IR (film): 3304, 3074, 2926, 1642, 1547, 1208 cm⁻¹; HRMS (ES): Exact mass calcd for C₂₁H₂₄O₂N [M+H]⁺: 321.1967. Found: 321.1692.

Table 1. Crystal data and structure refinement for **12**.

Identification code	cwd91t	
Empirical formula	C ₂₁ H ₂₃ N ₂ O	
Formula weight	319.41	
Temperature	213(2) K	
Wavelength	0.71073 Å	
Crystal system	Monoclinic	
Space group	P2(1)	
Unit cell dimensions	a = 4.879(5) Å	= 90°.
	b = 13.132(8) Å	= 91.94(4)°.
	c = 14.211(10) Å	= 90°.
Volume	909.9(12) Å ³	
Z	2	
Density (calculated)	1.166 Mg/m ³	
Absorption coefficient	0.072 mm ⁻¹	
F(000)	342	
Crystal size	0.5 x 0.5 x 8.6 mm ³	
Theta range for data collection	1.43 to 24.83°.	
Index ranges	-5<=h<=5, -11<=k<=15, -15<=l<=16	
Reflections collected	4857	
Independent reflections	2845 [R(int) = 0.1452]	
Completeness to theta = 24.83°	99.5 %	
Absorption correction	None	
Refinement method	Full-matrix least-squares on F ²	
Data / restraints / parameters	2845 / 1 / 217	
Goodness-of-fit on F ²	1.035	
Final R indices [I>2sigma(I)]	R1 = 0.1026, wR2 = 0.2367	
R indices (all data)	R1 = 0.1472, wR2 = 0.2617	
Absolute structure parameter	-7(5)	
Largest diff. peak and hole	0.403 and -0.305 e.Å ⁻³	

Table 2. Atomic coordinates ($\times 10^4$) and equivalent isotropic displacement parameters ($\text{\AA}^2 \times 10^3$) for **12**. $U(\text{eq})$ is defined as one third of the trace of the orthogonalized U^{ij} tensor.

	x	y	z	U(eq)
N(2)	-2512(9)	-6079(4)	-9656(3)	37(1)
C(10)	-3809(13)	-4980(5)	-7440(4)	36(2)
C(8)	-2736(11)	-5081(5)	-6417(4)	33(2)
C(16)	-2671(13)	-5080(6)	-11149(4)	38(2)
O(1)	-6766(8)	-5856(4)	-9123(3)	48(1)
C(12)	-2993(11)	-5927(5)	-7990(4)	33(2)
N(1)	-290(11)	-4888(4)	-5074(3)	41(1)
C(13)	-4295(11)	-5950(5)	-8986(4)	28(1)
C(7)	-3612(11)	-5830(5)	-5763(4)	32(2)
C(14)	-3322(13)	-6080(6)	-10661(4)	40(2)
C(9)	-787(13)	-4543(5)	-5981(4)	35(2)
C(2)	-1985(12)	-5673(5)	-4926(4)	38(2)
C(20)	-3494(19)	-3929(7)	-12438(5)	72(3)
C(21)	-4119(17)	-4812(7)	-11958(5)	63(2)
C(4)	-4177(19)	-7028(7)	-4179(5)	62(2)
C(11)	-2700(20)	-4034(6)	-7907(5)	60(2)
C(15)	-1930(20)	-6961(6)	-11123(5)	59(2)
C(17)	-721(17)	-4417(6)	-10809(5)	60(2)
C(6)	-5612(14)	-6586(6)	-5778(5)	45(2)
C(1)	1725(14)	-4460(6)	-4406(5)	51(2)
C(19)	-1573(17)	-3278(6)	-12080(6)	62(2)
C(3)	-2285(16)	-6300(6)	-4134(5)	50(2)
C(18)	-100(19)	-3556(7)	-11286(7)	75(3)
C(5)	-5905(18)	-7200(6)	-4990(6)	59(2)

Table 3. Bond lengths [$\text{\AA}$] and angles [$^\circ$] for **12**.

N(2)-C(13)	1.323(7)
N(2)-C(14)	1.469(7)
C(10)-C(11)	1.517(10)
C(10)-C(12)	1.529(9)
C(10)-C(8)	1.534(8)
C(8)-C(9)	1.322(9)
C(8)-C(7)	1.429(9)
C(16)-C(17)	1.366(10)
C(16)-C(21)	1.374(10)
C(16)-C(14)	1.523(10)
O(1)-C(13)	1.221(6)
C(12)-C(13)	1.532(8)
N(1)-C(2)	1.343(8)
N(1)-C(9)	1.380(8)
N(1)-C(1)	1.456(8)
C(7)-C(6)	1.392(9)
C(7)-C(2)	1.422(9)
C(14)-C(15)	1.504(11)
C(2)-C(3)	1.407(10)

C(20)-C(19)	1.355(12)
C(20)-C(21)	1.385(12)
C(4)-C(3)	1.328(11)
C(4)-C(5)	1.423(12)
C(17)-C(18)	1.359(12)
C(6)-C(5)	1.391(11)
C(19)-C(18)	1.367(11)

C(13)-N(2)-C(14)	122.6(5)
C(11)-C(10)-C(12)	109.9(5)
C(11)-C(10)-C(8)	111.8(6)
C(12)-C(10)-C(8)	109.1(5)
C(9)-C(8)-C(7)	106.8(5)
C(9)-C(8)-C(10)	127.9(6)
C(7)-C(8)-C(10)	125.2(5)
C(17)-C(16)-C(21)	117.7(7)
C(17)-C(16)-C(14)	122.8(6)
C(21)-C(16)-C(14)	119.5(6)
C(10)-C(12)-C(13)	112.4(5)
C(2)-N(1)-C(9)	107.9(5)
C(2)-N(1)-C(1)	126.9(6)
C(9)-N(1)-C(1)	125.2(6)
O(1)-C(13)-N(2)	124.6(5)
O(1)-C(13)-C(12)	121.5(5)
N(2)-C(13)-C(12)	113.9(5)
C(6)-C(7)-C(2)	119.2(6)
C(6)-C(7)-C(8)	134.9(6)
C(2)-C(7)-C(8)	105.8(5)
N(2)-C(14)-C(15)	108.3(6)
N(2)-C(14)-C(16)	112.9(5)
C(15)-C(14)-C(16)	111.1(5)
C(8)-C(9)-N(1)	111.3(5)
N(1)-C(2)-C(3)	131.0(6)
N(1)-C(2)-C(7)	108.1(6)
C(3)-C(2)-C(7)	120.9(6)
C(19)-C(20)-C(21)	120.3(7)
C(16)-C(21)-C(20)	120.8(7)
C(3)-C(4)-C(5)	123.1(7)
C(18)-C(17)-C(16)	121.2(7)
C(5)-C(6)-C(7)	119.5(7)
C(20)-C(19)-C(18)	118.6(8)
C(4)-C(3)-C(2)	118.3(7)
C(17)-C(18)-C(19)	121.0(8)
C(6)-C(5)-C(4)	119.0(7)

Symmetry transformations used to generate equivalent atoms:

Table 4. Anisotropic displacement parameters ($\text{\AA}^2 \times 10^3$) for **12**. The anisotropic displacement factor exponent takes the form: $-2^2 [h^2 a^{*2} U^{11} + \dots + 2 h k a^* b^* U^{12}]$

	U^{11}	U^{22}	U^{33}	U^{23}	U^{13}	U^{12}
N(2)	27(2)	59(4)	24(3)	2(3)	-5(2)	-2(2)

C(10)	51(4)	48(4)	8(3)	2(3)	-1(3)	8(3)
C(8)	36(3)	40(4)	21(3)	2(3)	0(2)	-4(3)
C(16)	46(4)	48(4)	20(3)	-9(3)	-6(3)	4(3)
O(1)	30(2)	83(4)	31(3)	5(3)	-1(2)	2(3)
C(12)	38(3)	46(4)	16(3)	9(3)	-3(2)	9(3)
N(1)	53(3)	48(4)	22(3)	-8(3)	-7(2)	-5(3)
C(13)	31(3)	28(4)	26(3)	6(3)	3(2)	-2(3)
C(7)	34(3)	36(4)	25(3)	-15(3)	3(2)	3(3)
C(14)	47(3)	63(5)	9(3)	-5(3)	-6(3)	-16(3)
C(9)	47(4)	30(4)	27(3)	-5(3)	10(3)	-6(3)
C(2)	40(3)	53(5)	20(3)	-8(3)	1(3)	2(3)
C(20)	94(6)	80(7)	38(4)	22(5)	-40(5)	-29(5)
C(21)	86(6)	70(6)	31(4)	-1(4)	-26(4)	-26(5)
C(4)	96(7)	59(6)	31(5)	16(4)	18(4)	7(5)
C(11)	119(7)	37(5)	24(4)	0(3)	-3(4)	12(4)
C(15)	110(7)	49(5)	18(4)	-9(3)	-15(4)	-18(5)
C(17)	90(6)	49(5)	40(4)	11(4)	-35(4)	-20(4)
C(6)	51(4)	56(5)	27(4)	-11(3)	9(3)	-4(3)
C(1)	47(4)	71(5)	35(4)	-25(4)	-12(3)	-6(4)
C(19)	84(6)	45(5)	53(5)	15(4)	-24(5)	-6(4)
C(3)	61(5)	68(6)	21(4)	-7(3)	2(3)	3(4)
C(18)	96(7)	50(6)	75(6)	3(5)	-39(5)	-25(5)
C(5)	75(6)	51(5)	52(5)	-8(4)	20(4)	-11(4)

Table 5. Hydrogen coordinates ($\times 10^4$) and isotropic displacement parameters ($\text{\AA}^2 \times 10^{-3}$) for **12**.

	x	y	z	U(eq)
H(2A)	-792	-6168	-9495	44
H(10A)	-5835	-4936	-7445	43
H(12A)	-3559	-6536	-7648	40
H(12B)	-992	-5946	-8030	40
H(14A)	-5328	-6191	-10718	48
H(9A)	140	-3996	-6253	41
H(20A)	-4408	-3780	-13015	86
H(21A)	-5549	-5233	-12188	76
H(4A)	-4383	-7448	-3651	74
H(11A)	-3423	-3993	-8550	90
H(11B)	-713	-4069	-7908	90
H(11C)	-3250	-3435	-7562	90
H(15A)	-2365	-7586	-10797	89
H(15B)	39	-6855	-11095	89
H(15C)	-2566	-7009	-11776	89
H(17A)	208	-4560	-10233	72
H(6A)	-6755	-6682	-6316	53
H(1A)	1640	-4819	-3811	77
H(1B)	1332	-3744	-4310	77
H(1C)	3545	-4533	-4652	77
H(19A)	-1259	-2648	-12372	74
H(3A)	-1177	-6207	-3587	60

H(18A)	1365	-3145	-11067	89
H(5A)	-7226	-7722	-4993	71

Table 6. Torsion angles [°] for **12**.

C(11)-C(10)-C(8)-C(9)	-9.8(9)
C(12)-C(10)-C(8)-C(9)	111.9(8)
C(11)-C(10)-C(8)-C(7)	173.4(6)
C(12)-C(10)-C(8)-C(7)	-64.9(7)
C(11)-C(10)-C(12)-C(13)	-64.4(7)
C(8)-C(10)-C(12)-C(13)	172.7(5)
C(14)-N(2)-C(13)-O(1)	2.7(10)
C(14)-N(2)-C(13)-C(12)	-177.4(6)
C(10)-C(12)-C(13)-O(1)	-53.2(8)
C(10)-C(12)-C(13)-N(2)	126.9(6)
C(9)-C(8)-C(7)-C(6)	177.4(7)
C(10)-C(8)-C(7)-C(6)	-5.2(11)
C(9)-C(8)-C(7)-C(2)	-0.4(7)
C(10)-C(8)-C(7)-C(2)	177.0(5)
C(13)-N(2)-C(14)-C(15)	-134.6(6)
C(13)-N(2)-C(14)-C(16)	101.9(7)
C(17)-C(16)-C(14)-N(2)	22.3(9)
C(21)-C(16)-C(14)-N(2)	-156.5(6)
C(17)-C(16)-C(14)-C(15)	-99.6(8)
C(21)-C(16)-C(14)-C(15)	81.6(8)
C(7)-C(8)-C(9)-N(1)	0.3(7)
C(10)-C(8)-C(9)-N(1)	-177.0(6)
C(2)-N(1)-C(9)-C(8)	-0.1(7)
C(1)-N(1)-C(9)-C(8)	-179.9(6)
C(9)-N(1)-C(2)-C(3)	178.9(7)
C(1)-N(1)-C(2)-C(3)	-1.3(11)
C(9)-N(1)-C(2)-C(7)	-0.1(7)
C(1)-N(1)-C(2)-C(7)	179.7(6)
C(6)-C(7)-C(2)-N(1)	-177.9(6)
C(8)-C(7)-C(2)-N(1)	0.3(7)
C(6)-C(7)-C(2)-C(3)	3.0(9)
C(8)-C(7)-C(2)-C(3)	-178.8(6)
C(17)-C(16)-C(21)-C(20)	3.8(12)
C(14)-C(16)-C(21)-C(20)	-177.3(8)
C(19)-C(20)-C(21)-C(16)	-4.7(14)
C(21)-C(16)-C(17)-C(18)	-4.4(13)
C(14)-C(16)-C(17)-C(18)	176.7(8)
C(2)-C(7)-C(6)-C(5)	-2.6(9)
C(8)-C(7)-C(6)-C(5)	179.8(7)
C(21)-C(20)-C(19)-C(18)	5.9(15)
C(5)-C(4)-C(3)-C(2)	0.0(12)
N(1)-C(2)-C(3)-C(4)	179.4(7)
C(7)-C(2)-C(3)-C(4)	-1.7(10)
C(16)-C(17)-C(18)-C(19)	5.9(15)
C(20)-C(19)-C(18)-C(17)	-6.5(15)
C(7)-C(6)-C(5)-C(4)	1.1(11)
C(3)-C(4)-C(5)-C(6)	0.3(12)

X-ray Crystal Structure of Sc((S,S)-Inda-pybox)(OTf)₃•H₂O **Table 7.** Crystal data and structure refinement for Sc((S,S)-Inda-pybox)(OTf)₃•H₂O

Identification code	jwu12t	
Empirical formula	C ₂₈ H ₁₉ F ₉ N ₃ O ₁₄ S ₃ Sc	
Formula weight	933.60	
Temperature	213(2) K	
Wavelength	0.71073 Å	
Crystal system	Monoclinic	
Space group	C2	
Unit cell dimensions	a = 32.314(7) Å	a = 90°.
	b = 11.193(2) Å	b = 108.345(6)°.
	c = 11.312(2) Å	g = 90°.
Volume	3883.4(14) Å ³	
Z	4	
Density (calculated)	1.597 Mg/m ³	
Absorption coefficient	0.460 mm ⁻¹	
F(000)	1880	
Crystal size	1 x 0.4 x 0.4 mm ³	
Theta range for data collection	1.33 to 28.30°.	

Index ranges	-43<=h<=42, -8<=k<=14, -15<=l<=15
Reflections collected	13072
Independent reflections	6965 [R(int) = 0.0854]
Completeness to theta = 28.30°	97.7 %
Refinement method	Full-matrix least-squares on F ²
Data / restraints / parameters	6965 / 1 / 503
Goodness-of-fit on F ²	1.096
Final R indices [I>2sigma(I)]	R1 = 0.0756, wR2 = 0.2040
R indices (all data)	R1 = 0.0779, wR2 = 0.2117
Absolute structure parameter	0.02(5)
Largest diff. peak and hole	2.547 and -0.670 e.Å ⁻³

Table 8. Atomic coordinates ($\times 10^4$) and equivalent isotropic displacement parameters ($\text{\AA}^2 \times 10^3$) for $\text{Sc}((\text{S,S})\text{-Inda-pybox})(\text{OTf})_3 \cdot \text{H}_2\text{O}$. $U(\text{eq})$ is defined as one third of the trace of the orthogonalized U^{ij} tensor.

	x	y	z	$U(\text{eq})$
Sc(1)	1260(1)	3828(1)	10157(1)	24(1)
C(1)	1119(2)	6544(5)	9138(4)	34(1)
C(2)	1096(2)	7565(5)	8399(5)	44(1)
C(3)	1248(2)	7435(6)	7391(6)	50(1)
C(4)	1419(2)	6351(6)	7162(6)	45(1)
C(5)	1415(2)	5400(5)	7929(5)	37(1)
C(6)	982(2)	6496(5)	10269(5)	35(1)
C(7)	918(1)	5920(5)	12060(4)	32(1)
C(8)	1324(2)	6231(5)	13166(4)	34(1)
C(9)	1664(2)	5500(6)	13766(5)	45(1)
C(10)	2011(2)	5959(8)	14722(5)	52(2)
C(11)	2003(2)	7161(8)	15068(6)	57(2)
C(12)	1658(2)	7892(6)	14461(5)	49(1)
C(13)	1309(2)	7407(5)	13504(5)	39(1)
C(14)	893(2)	8044(6)	12734(6)	48(1)
C(15)	693(2)	7142(5)	11688(5)	40(1)
C(16)	1569(2)	4180(5)	7802(4)	36(1)
C(17)	1670(2)	2243(5)	8014(4)	35(1)
C(18)	1309(2)	1532(5)	7103(5)	40(1)
C(19)	952(2)	989(6)	7301(5)	45(1)
C(20)	651(2)	410(8)	6307(7)	63(2)
C(21)	723(3)	361(9)	5157(8)	75(2)
C(22)	1079(3)	893(8)	4972(6)	69(2)
C(23)	1377(2)	1469(6)	5945(5)	51(2)
C(24)	1787(3)	2049(7)	5938(6)	59(2)
C(25)	1938(2)	2752(6)	7195(5)	47(1)
O(1)	810(1)	7475(3)	10582(4)	40(1)
O(2)	1778(1)	3995(4)	6987(4)	46(1)
N(1)	1267(1)	5494(4)	8905(4)	32(1)
N(2)	1043(1)	5578(4)	10937(3)	30(1)
N(3)	1508(1)	3326(4)	8466(3)	31(1)

S(1)	2307(1)	4783(2)	11674(2)	47(1)
S(2)	1415(1)	821(1)	11045(1)	32(1)
S(3)	189(1)	4091(1)	8379(1)	33(1)
C(26)	2644(2)	3955(8)	10977(8)	61(2)
C(27)	1958(3)	794(8)	12187(8)	68(2)
C(28)	124(3)	3890(15)	6775(6)	104(5)
O(3)	1886(1)	4144(4)	11227(3)	36(1)
O(4)	2286(2)	5949(6)	11193(11)	114(3)
O(5)	2521(2)	4577(9)	12952(5)	96(3)
O(6)	1429(1)	1949(3)	10385(3)	32(1)
O(7)	1135(2)	898(4)	11804(4)	52(1)
O(8)	1377(2)	-226(4)	10320(5)	56(1)
O(9)	619(1)	3544(4)	8996(3)	35(1)
O(10)	-155(1)	3442(6)	8567(5)	66(2)
O(11)	167(2)	5332(6)	8562(7)	76(2)
F(1)	2478(2)	3990(14)	9755(7)	167(6)
F(2)	3037(1)	4407(5)	11254(5)	72(1)
F(3)	2673(2)	2840(6)	11295(11)	135(4)
F(4)	2008(2)	1700(7)	12942(5)	109(2)
F(5)	2258(2)	787(7)	11607(8)	110(3)
F(6)	2001(2)	-226(7)	12845(8)	126(3)
F(7)	147(3)	2848(12)	6414(7)	186(7)
F(8)	460(2)	4462(14)	6521(6)	170(6)
F(9)	-250(2)	4339(10)	6085(4)	144(4)
O(12)	1012(1)	3259(3)	11666(3)	33(1)
O(13)	104(1)	9781(5)	8872(4)	51(1)
O(15)	9923(2)	7536(8)	3672(7)	87(2)

Table 9. Bond lengths [Å] and angles [°] for Sc((*S,S*)-Inda-pybox)(OTf)₃•H₂O.

Sc(1)-O(3)	2.035(3)
Sc(1)-O(9)	2.097(3)
Sc(1)-O(6)	2.168(4)
Sc(1)-O(12)	2.195(4)
Sc(1)-N(2)	2.343(4)
Sc(1)-N(1)	2.346(4)
Sc(1)-N(3)	2.363(4)
C(1)-N(1)	1.327(7)
C(1)-C(2)	1.403(7)
C(1)-C(6)	1.480(7)
C(2)-C(3)	1.385(8)
C(3)-C(4)	1.391(9)
C(4)-C(5)	1.376(7)
C(5)-N(1)	1.337(6)
C(5)-C(16)	1.475(8)
C(6)-N(2)	1.253(7)
C(6)-O(1)	1.327(6)
C(7)-N(2)	1.500(6)
C(7)-C(8)	1.541(7)
C(7)-C(15)	1.545(8)
C(8)-C(9)	1.365(8)
C(8)-C(13)	1.376(8)
C(9)-C(10)	1.389(8)
C(10)-C(11)	1.404(12)
C(11)-C(12)	1.379(11)
C(12)-C(13)	1.404(8)
C(13)-C(14)	1.528(9)
C(14)-C(15)	1.535(8)
C(15)-O(1)	1.464(7)
C(16)-N(3)	1.268(7)
C(16)-O(2)	1.321(5)
C(17)-N(3)	1.474(6)
C(17)-C(18)	1.518(8)
C(17)-C(25)	1.560(7)

C(18)-C(19)	1.381(9)
C(18)-C(23)	1.396(7)
C(19)-C(20)	1.393(8)
C(20)-C(21)	1.392(12)
C(21)-C(22)	1.368(15)
C(22)-C(23)	1.374(11)
C(23)-C(24)	1.477(11)
C(24)-C(25)	1.563(10)
C(25)-O(2)	1.477(7)
S(1)-O(4)	1.407(7)
S(1)-O(5)	1.411(6)
S(1)-O(3)	1.479(4)
S(1)-C(26)	1.792(8)
S(2)-O(8)	1.414(5)
S(2)-O(7)	1.434(4)
S(2)-O(6)	1.475(4)
S(2)-C(27)	1.821(7)
S(3)-O(10)	1.398(5)
S(3)-O(11)	1.409(7)
S(3)-O(9)	1.479(3)
S(3)-C(28)	1.774(7)
C(26)-F(3)	1.294(12)
C(26)-F(2)	1.311(7)
C(26)-F(1)	1.316(11)
C(27)-F(4)	1.303(12)
C(27)-F(5)	1.333(12)
C(27)-F(6)	1.346(9)
C(28)-F(7)	1.246(18)
C(28)-F(9)	1.315(9)
C(28)-F(8)	1.368(17)

O(3)-Sc(1)-O(9)	177.71(15)
O(3)-Sc(1)-O(6)	86.08(15)
O(9)-Sc(1)-O(6)	95.12(15)
O(3)-Sc(1)-O(12)	97.16(13)
O(9)-Sc(1)-O(12)	85.03(13)

O(6)-Sc(1)-O(12)	76.43(13)
O(3)-Sc(1)-N(2)	89.38(15)
O(9)-Sc(1)-N(2)	90.57(14)
O(6)-Sc(1)-N(2)	149.28(13)
O(12)-Sc(1)-N(2)	74.03(14)
O(3)-Sc(1)-N(1)	91.37(15)
O(9)-Sc(1)-N(1)	86.49(15)
O(6)-Sc(1)-N(1)	142.47(14)
O(12)-Sc(1)-N(1)	140.86(14)
N(2)-Sc(1)-N(1)	67.92(14)
O(3)-Sc(1)-N(3)	89.76(14)
O(9)-Sc(1)-N(3)	88.69(14)
O(6)-Sc(1)-N(3)	74.27(13)
O(12)-Sc(1)-N(3)	149.32(15)
N(2)-Sc(1)-N(3)	136.15(14)
N(1)-Sc(1)-N(3)	68.27(15)
N(1)-C(1)-C(2)	123.9(5)
N(1)-C(1)-C(6)	111.3(4)
C(2)-C(1)-C(6)	124.7(5)
C(3)-C(2)-C(1)	116.0(5)
C(2)-C(3)-C(4)	120.6(5)
C(5)-C(4)-C(3)	118.4(5)
N(1)-C(5)-C(4)	122.4(5)
N(1)-C(5)-C(16)	111.8(4)
C(4)-C(5)-C(16)	125.8(5)
N(2)-C(6)-O(1)	121.1(4)
N(2)-C(6)-C(1)	121.2(5)
O(1)-C(6)-C(1)	117.7(5)
N(2)-C(7)-C(8)	110.9(4)
N(2)-C(7)-C(15)	103.0(4)
C(8)-C(7)-C(15)	103.2(4)
C(9)-C(8)-C(13)	121.9(5)
C(9)-C(8)-C(7)	127.9(5)
C(13)-C(8)-C(7)	110.2(5)
C(8)-C(9)-C(10)	119.4(6)
C(9)-C(10)-C(11)	119.4(6)

C(12)-C(11)-C(10)	120.8(6)
C(11)-C(12)-C(13)	118.9(6)
C(8)-C(13)-C(12)	119.6(6)
C(8)-C(13)-C(14)	112.9(5)
C(12)-C(13)-C(14)	127.5(6)
C(13)-C(14)-C(15)	102.4(5)
O(1)-C(15)-C(14)	109.4(5)
O(1)-C(15)-C(7)	103.5(4)
C(14)-C(15)-C(7)	108.9(5)
N(3)-C(16)-O(2)	120.3(5)
N(3)-C(16)-C(5)	121.3(4)
O(2)-C(16)-C(5)	118.4(5)
N(3)-C(17)-C(18)	112.6(4)
N(3)-C(17)-C(25)	103.3(4)
C(18)-C(17)-C(25)	103.9(4)
C(19)-C(18)-C(23)	121.1(6)
C(19)-C(18)-C(17)	128.6(5)
C(23)-C(18)-C(17)	110.4(5)
C(18)-C(19)-C(20)	118.7(6)
C(19)-C(20)-C(21)	119.5(8)
C(22)-C(21)-C(20)	121.4(7)
C(21)-C(22)-C(23)	119.4(7)
C(22)-C(23)-C(18)	119.8(7)
C(22)-C(23)-C(24)	127.2(6)
C(18)-C(23)-C(24)	112.9(6)
C(23)-C(24)-C(25)	103.9(5)
O(2)-C(25)-C(17)	102.0(4)
O(2)-C(25)-C(24)	109.6(5)
C(17)-C(25)-C(24)	106.5(6)
C(6)-O(1)-C(15)	105.1(4)
C(16)-O(2)-C(25)	105.4(4)
C(1)-N(1)-C(5)	118.6(4)
C(1)-N(1)-Sc(1)	120.7(3)
C(5)-N(1)-Sc(1)	120.6(4)
C(6)-N(2)-C(7)	105.6(4)
C(6)-N(2)-Sc(1)	117.8(3)

C(7)-N(2)-Sc(1)	136.4(3)
C(16)-N(3)-C(17)	106.0(4)
C(16)-N(3)-Sc(1)	117.1(3)
C(17)-N(3)-Sc(1)	136.4(3)
O(4)-S(1)-O(5)	119.7(6)
O(4)-S(1)-O(3)	112.9(4)
O(5)-S(1)-O(3)	111.9(4)
O(4)-S(1)-C(26)	105.8(5)
O(5)-S(1)-C(26)	101.3(4)
O(3)-S(1)-C(26)	102.8(3)
O(8)-S(2)-O(7)	116.2(3)
O(8)-S(2)-O(6)	115.3(2)
O(7)-S(2)-O(6)	112.1(2)
O(8)-S(2)-C(27)	106.6(4)
O(7)-S(2)-C(27)	103.0(4)
O(6)-S(2)-C(27)	101.5(3)
O(10)-S(3)-O(11)	114.3(4)
O(10)-S(3)-O(9)	112.8(3)
O(11)-S(3)-O(9)	114.9(3)
O(10)-S(3)-C(28)	104.3(6)
O(11)-S(3)-C(28)	106.3(6)
O(9)-S(3)-C(28)	102.8(3)
F(3)-C(26)-F(2)	109.1(7)
F(3)-C(26)-F(1)	106.9(10)
F(2)-C(26)-F(1)	106.4(7)
F(3)-C(26)-S(1)	112.1(6)
F(2)-C(26)-S(1)	111.9(6)
F(1)-C(26)-S(1)	110.1(7)
F(4)-C(27)-F(5)	111.6(8)
F(4)-C(27)-F(6)	109.2(8)
F(5)-C(27)-F(6)	107.6(8)
F(4)-C(27)-S(2)	110.2(6)
F(5)-C(27)-S(2)	109.8(6)
F(6)-C(27)-S(2)	108.4(6)
F(7)-C(28)-F(9)	107.6(10)
F(7)-C(28)-F(8)	103.6(11)

F(9)-C(28)-F(8)	109.9(12)
F(7)-C(28)-S(3)	117.0(11)
F(9)-C(28)-S(3)	110.4(6)
F(8)-C(28)-S(3)	108.0(8)
S(1)-O(3)-Sc(1)	157.4(3)
S(2)-O(6)-Sc(1)	147.7(2)
S(3)-O(9)-Sc(1)	146.0(3)

Table 10. Anisotropic displacement parameters ($\text{\AA}^2 \times 10^3$) for $\text{Sc}((\text{S,S})\text{-Inda-pybox})(\text{OTf})_3 \cdot \text{H}_2\text{O}$. The anisotropic displacement factor exponent takes the form: $-2 \text{ }^2[\text{h}^2 \text{a}^*2\text{U}^{11} + \dots + 2 \text{h k a}^* \text{b}^* \text{U}^{12}]$

	U^{11}	U^{22}	U^{33}	U^{23}	U^{13}	U^{12}
Sc(1)	22(1)	22(1)	28(1)	2(1)	9(1)	1(1)
C(1)	37(2)	25(2)	39(2)	0(2)	11(2)	-5(2)
C(2)	67(3)	25(2)	45(2)	-3(2)	25(2)	-4(2)
C(3)	76(4)	34(3)	46(3)	11(2)	28(3)	1(3)
C(4)	63(3)	33(3)	49(3)	11(2)	31(2)	1(3)
C(5)	40(2)	30(2)	45(2)	5(2)	21(2)	0(2)
C(6)	36(2)	27(2)	43(2)	-5(2)	15(2)	-3(2)
C(7)	30(2)	27(2)	43(2)	-5(2)	19(2)	-6(2)
C(8)	40(2)	32(2)	33(2)	-3(2)	17(2)	-5(2)
C(9)	53(3)	48(3)	35(2)	5(2)	15(2)	4(3)
C(10)	42(3)	74(5)	39(2)	-1(3)	9(2)	4(3)
C(11)	48(3)	80(5)	43(3)	-4(3)	14(2)	-17(3)
C(12)	67(4)	39(3)	45(3)	-9(2)	22(2)	-12(3)
C(13)	48(3)	36(3)	37(2)	-6(2)	21(2)	-10(2)
C(14)	63(3)	29(3)	58(3)	-11(2)	27(3)	-1(2)
C(15)	41(2)	29(3)	52(3)	-5(2)	20(2)	1(2)
C(16)	40(2)	39(3)	36(2)	4(2)	22(2)	9(2)
C(17)	46(2)	33(2)	32(2)	5(2)	19(2)	15(2)
C(18)	50(3)	34(3)	40(2)	2(2)	20(2)	15(2)
C(19)	46(3)	43(3)	45(2)	-11(2)	11(2)	3(2)
C(20)	61(4)	64(5)	60(4)	-25(3)	14(3)	-4(4)
C(21)	91(6)	68(5)	57(4)	-27(4)	11(4)	8(5)

C(22)	102(6)	62(5)	42(3)	-12(3)	20(3)	30(5)
C(23)	71(4)	47(3)	40(2)	5(2)	25(2)	25(3)
C(24)	88(5)	58(4)	49(3)	7(3)	46(3)	30(4)
C(25)	63(3)	44(3)	49(3)	14(2)	37(2)	25(3)
O(1)	50(2)	22(2)	49(2)	-2(1)	19(2)	4(2)
O(2)	62(2)	38(2)	53(2)	15(2)	39(2)	14(2)
N(1)	35(2)	26(2)	39(2)	4(2)	17(2)	0(2)
N(2)	33(2)	26(2)	34(2)	-3(1)	16(1)	0(2)
N(3)	35(2)	27(2)	33(2)	2(2)	15(1)	8(2)
S(1)	30(1)	40(1)	71(1)	-13(1)	15(1)	-8(1)
S(2)	39(1)	23(1)	37(1)	2(1)	16(1)	-1(1)
S(3)	25(1)	41(1)	33(1)	1(1)	7(1)	4(1)
C(26)	43(3)	59(4)	86(4)	-15(4)	29(3)	-19(3)
C(27)	61(4)	58(5)	69(4)	25(4)	-4(3)	-2(4)
C(28)	86(5)	188(14)	29(2)	-4(5)	6(3)	66(8)
O(4)	63(3)	37(3)	250(11)	23(5)	61(5)	-3(3)
O(5)	41(2)	164(8)	66(3)	-30(4)	-6(2)	-4(4)
O(6)	40(2)	25(2)	37(1)	4(1)	21(1)	3(1)
O(7)	70(3)	35(2)	71(3)	9(2)	52(2)	3(2)
O(8)	81(3)	28(2)	69(3)	-9(2)	40(2)	-8(2)
O(9)	27(1)	37(2)	39(2)	1(1)	7(1)	2(1)
O(10)	32(2)	88(4)	80(3)	28(3)	17(2)	3(2)
O(11)	51(3)	48(3)	112(5)	4(3)	1(3)	10(2)
F(1)	73(3)	345(17)	102(4)	-90(8)	55(3)	-57(6)
F(2)	37(2)	75(3)	110(3)	0(3)	32(2)	-8(2)
F(3)	84(4)	55(3)	303(12)	-29(5)	113(6)	-7(3)
F(4)	107(4)	109(6)	71(3)	-4(3)	-26(3)	-33(4)
F(5)	41(2)	91(5)	195(7)	39(5)	34(3)	6(3)
F(6)	98(4)	100(5)	144(6)	88(5)	-14(4)	-3(4)
F(7)	169(8)	240(13)	88(4)	-94(7)	-46(5)	121(9)
F(8)	99(4)	362(18)	64(3)	67(6)	46(3)	23(7)
F(9)	103(4)	269(13)	40(2)	15(4)	-5(2)	81(6)

Table 11. Hydrogen coordinates ($\times 10^4$) and isotropic displacement parameters ($\text{\AA}^2 \times 10^{-3}$) for $\text{Sc}((\text{S,S})\text{-Inda-pybox})(\text{OTf})_3 \cdot \text{H}_2\text{O}$.

	x	y	z	U(eq)
H(2)	983	8293	8578	53
H(3)	1236	8086	6856	60
H(4)	1534	6270	6500	54
H(7)	728	5322	12275	38
H(9)	1662	4693	13533	54
H(10)	2249	5469	15133	63
H(11)	2236	7472	15722	68
H(12)	1657	8701	14684	59
H(14A)	960	8802	12401	58
H(14B)	698	8195	13229	58
H(15)	373	7082	11502	47
H(17)	1851	1742	8706	42
H(19)	914	1010	8090	54
H(20)	401	56	6411	75
H(21)	523	-46	4494	90
H(22)	1119	864	4185	83
H(24A)	1736	2592	5227	71
H(24B)	2004	1453	5902	71
H(25)	2256	2703	7611	56

Table 12. Torsion angles [°] for Sc((S,S)-Inda-pybox)(OTf)₃•H₂O.

N(1)-C(1)-C(2)-C(3)	-1.3(9)
C(6)-C(1)-C(2)-C(3)	178.7(5)
C(1)-C(2)-C(3)-C(4)	-1.0(10)
C(2)-C(3)-C(4)-C(5)	2.8(10)
C(3)-C(4)-C(5)-N(1)	-2.3(9)
C(3)-C(4)-C(5)-C(16)	178.0(6)
N(1)-C(1)-C(6)-N(2)	5.6(7)
C(2)-C(1)-C(6)-N(2)	-174.4(5)
N(1)-C(1)-C(6)-O(1)	-177.3(4)
C(2)-C(1)-C(6)-O(1)	2.7(7)
N(2)-C(7)-C(8)-C(9)	-62.6(7)
C(15)-C(7)-C(8)-C(9)	-172.2(5)
N(2)-C(7)-C(8)-C(13)	117.1(5)
C(15)-C(7)-C(8)-C(13)	7.4(5)
C(13)-C(8)-C(9)-C(10)	-1.9(8)
C(7)-C(8)-C(9)-C(10)	177.7(5)
C(8)-C(9)-C(10)-C(11)	1.1(9)
C(9)-C(10)-C(11)-C(12)	-0.8(9)
C(10)-C(11)-C(12)-C(13)	1.3(9)
C(9)-C(8)-C(13)-C(12)	2.5(8)
C(7)-C(8)-C(13)-C(12)	-177.2(5)
C(9)-C(8)-C(13)-C(14)	-178.2(5)
C(7)-C(8)-C(13)-C(14)	2.1(6)
C(11)-C(12)-C(13)-C(8)	-2.1(8)
C(11)-C(12)-C(13)-C(14)	178.7(5)
C(8)-C(13)-C(14)-C(15)	-10.7(6)
C(12)-C(13)-C(14)-C(15)	168.5(5)
C(13)-C(14)-C(15)-O(1)	-97.4(5)
C(13)-C(14)-C(15)-C(7)	15.1(6)
N(2)-C(7)-C(15)-O(1)	-13.3(5)
C(8)-C(7)-C(15)-O(1)	102.2(4)
N(2)-C(7)-C(15)-C(14)	-129.6(4)
C(8)-C(7)-C(15)-C(14)	-14.1(5)
N(1)-C(5)-C(16)-N(3)	8.3(7)

C(4)-C(5)-C(16)-N(3)	-172.0(6)
N(1)-C(5)-C(16)-O(2)	-170.8(5)
C(4)-C(5)-C(16)-O(2)	8.9(8)
N(3)-C(17)-C(18)-C(19)	-61.9(7)
C(25)-C(17)-C(18)-C(19)	-172.9(6)
N(3)-C(17)-C(18)-C(23)	118.3(5)
C(25)-C(17)-C(18)-C(23)	7.3(6)
C(23)-C(18)-C(19)-C(20)	-2.3(9)
C(17)-C(18)-C(19)-C(20)	177.9(6)
C(18)-C(19)-C(20)-C(21)	2.0(11)
C(19)-C(20)-C(21)-C(22)	-1.5(14)
C(20)-C(21)-C(22)-C(23)	1.3(14)
C(21)-C(22)-C(23)-C(18)	-1.6(11)
C(21)-C(22)-C(23)-C(24)	177.4(8)
C(19)-C(18)-C(23)-C(22)	2.1(9)
C(17)-C(18)-C(23)-C(22)	-178.1(6)
C(19)-C(18)-C(23)-C(24)	-177.0(6)
C(17)-C(18)-C(23)-C(24)	2.8(7)
C(22)-C(23)-C(24)-C(25)	169.4(7)
C(18)-C(23)-C(24)-C(25)	-11.6(7)
N(3)-C(17)-C(25)-O(2)	-16.8(5)
C(18)-C(17)-C(25)-O(2)	101.0(5)
N(3)-C(17)-C(25)-C(24)	-131.7(5)
C(18)-C(17)-C(25)-C(24)	-14.0(6)
C(23)-C(24)-C(25)-O(2)	-94.2(6)
C(23)-C(24)-C(25)-C(17)	15.5(6)
N(2)-C(6)-O(1)-C(15)	-5.1(6)
C(1)-C(6)-O(1)-C(15)	177.8(4)
C(14)-C(15)-O(1)-C(6)	127.3(5)
C(7)-C(15)-O(1)-C(6)	11.3(5)
N(3)-C(16)-O(2)-C(25)	-6.3(7)
C(5)-C(16)-O(2)-C(25)	172.8(5)
C(17)-C(25)-O(2)-C(16)	14.1(6)
C(24)-C(25)-O(2)-C(16)	126.7(5)
C(2)-C(1)-N(1)-C(5)	1.8(8)
C(6)-C(1)-N(1)-C(5)	-178.2(4)

C(2)-C(1)-N(1)-Sc(1)	-177.1(4)
C(6)-C(1)-N(1)-Sc(1)	2.8(5)
C(4)-C(5)-N(1)-C(1)	0.1(8)
C(16)-C(5)-N(1)-C(1)	179.8(4)
C(4)-C(5)-N(1)-Sc(1)	179.0(4)
C(16)-C(5)-N(1)-Sc(1)	-1.2(6)
O(3)-Sc(1)-N(1)-C(1)	-94.6(4)
O(9)-Sc(1)-N(1)-C(1)	86.2(4)
O(6)-Sc(1)-N(1)-C(1)	-180.0(3)
O(12)-Sc(1)-N(1)-C(1)	8.5(5)
N(2)-Sc(1)-N(1)-C(1)	-5.9(3)
N(3)-Sc(1)-N(1)-C(1)	176.2(4)
O(3)-Sc(1)-N(1)-C(5)	86.4(4)
O(9)-Sc(1)-N(1)-C(5)	-92.7(4)
O(6)-Sc(1)-N(1)-C(5)	1.1(5)
O(12)-Sc(1)-N(1)-C(5)	-170.4(3)
N(2)-Sc(1)-N(1)-C(5)	175.2(4)
N(3)-Sc(1)-N(1)-C(5)	-2.7(4)
O(1)-C(6)-N(2)-C(7)	-4.2(6)
C(1)-C(6)-N(2)-C(7)	172.8(4)
O(1)-C(6)-N(2)-Sc(1)	171.8(3)
C(1)-C(6)-N(2)-Sc(1)	-11.2(6)
C(8)-C(7)-N(2)-C(6)	-99.0(5)
C(15)-C(7)-N(2)-C(6)	10.8(5)
C(8)-C(7)-N(2)-Sc(1)	86.1(5)
C(15)-C(7)-N(2)-Sc(1)	-164.0(3)
O(3)-Sc(1)-N(2)-C(6)	100.5(4)
O(9)-Sc(1)-N(2)-C(6)	-77.2(4)
O(6)-Sc(1)-N(2)-C(6)	-178.3(3)
O(12)-Sc(1)-N(2)-C(6)	-161.9(4)
N(1)-Sc(1)-N(2)-C(6)	8.7(3)
N(3)-Sc(1)-N(2)-C(6)	11.5(4)
O(3)-Sc(1)-N(2)-C(7)	-85.2(4)
O(9)-Sc(1)-N(2)-C(7)	97.1(4)
O(6)-Sc(1)-N(2)-C(7)	-3.9(6)
O(12)-Sc(1)-N(2)-C(7)	12.5(4)

N(1)-Sc(1)-N(2)-C(7)	-176.9(4)
N(3)-Sc(1)-N(2)-C(7)	-174.2(4)
O(2)-C(16)-N(3)-C(17)	-5.5(6)
C(5)-C(16)-N(3)-C(17)	175.5(5)
O(2)-C(16)-N(3)-Sc(1)	168.0(4)
C(5)-C(16)-N(3)-Sc(1)	-11.1(6)
C(18)-C(17)-N(3)-C(16)	-97.5(5)
C(25)-C(17)-N(3)-C(16)	13.9(5)
C(18)-C(17)-N(3)-Sc(1)	91.0(5)
C(25)-C(17)-N(3)-Sc(1)	-157.6(4)
O(3)-Sc(1)-N(3)-C(16)	-84.4(4)
O(9)-Sc(1)-N(3)-C(16)	93.9(4)
O(6)-Sc(1)-N(3)-C(16)	-170.4(4)
O(12)-Sc(1)-N(3)-C(16)	171.9(3)
N(2)-Sc(1)-N(3)-C(16)	4.4(4)
N(1)-Sc(1)-N(3)-C(16)	7.2(3)
O(3)-Sc(1)-N(3)-C(17)	86.4(5)
O(9)-Sc(1)-N(3)-C(17)	-95.3(5)
O(6)-Sc(1)-N(3)-C(17)	0.4(4)
O(12)-Sc(1)-N(3)-C(17)	-17.3(6)
N(2)-Sc(1)-N(3)-C(17)	175.3(4)
N(1)-Sc(1)-N(3)-C(17)	178.0(5)
O(4)-S(1)-C(26)-F(3)	-176.7(8)
O(5)-S(1)-C(26)-F(3)	57.8(8)
O(3)-S(1)-C(26)-F(3)	-58.1(7)
O(4)-S(1)-C(26)-F(2)	60.3(8)
O(5)-S(1)-C(26)-F(2)	-65.2(7)
O(3)-S(1)-C(26)-F(2)	178.9(6)
O(4)-S(1)-C(26)-F(1)	-57.8(8)
O(5)-S(1)-C(26)-F(1)	176.6(8)
O(3)-S(1)-C(26)-F(1)	60.8(8)
O(8)-S(2)-C(27)-F(4)	-176.2(6)
O(7)-S(2)-C(27)-F(4)	-53.4(7)
O(6)-S(2)-C(27)-F(4)	62.8(7)
O(8)-S(2)-C(27)-F(5)	60.5(7)
O(7)-S(2)-C(27)-F(5)	-176.7(6)

O(6)-S(2)-C(27)-F(5)	-60.6(7)
O(8)-S(2)-C(27)-F(6)	-56.8(8)
O(7)-S(2)-C(27)-F(6)	66.0(8)
O(6)-S(2)-C(27)-F(6)	-177.9(7)
O(10)-S(3)-C(28)-F(7)	-61.2(10)
O(11)-S(3)-C(28)-F(7)	177.6(10)
O(9)-S(3)-C(28)-F(7)	56.6(11)
O(10)-S(3)-C(28)-F(9)	62.3(13)
O(11)-S(3)-C(28)-F(9)	-58.9(13)
O(9)-S(3)-C(28)-F(9)	-179.9(11)
O(10)-S(3)-C(28)-F(8)	-177.6(9)
O(11)-S(3)-C(28)-F(8)	61.3(10)
O(9)-S(3)-C(28)-F(8)	-59.7(10)
O(4)-S(1)-O(3)-Sc(1)	12.3(9)
O(5)-S(1)-O(3)-Sc(1)	151.0(7)
C(26)-S(1)-O(3)-Sc(1)	-101.1(7)
O(9)-Sc(1)-O(3)-S(1)	25(4)
O(6)-Sc(1)-O(3)-S(1)	146.9(6)
O(12)-Sc(1)-O(3)-S(1)	-137.4(6)
N(2)-Sc(1)-O(3)-S(1)	-63.5(6)
N(1)-Sc(1)-O(3)-S(1)	4.4(6)
N(3)-Sc(1)-O(3)-S(1)	72.6(6)
O(8)-S(2)-O(6)-Sc(1)	146.1(4)
O(7)-S(2)-O(6)-Sc(1)	10.2(5)
C(27)-S(2)-O(6)-Sc(1)	-99.1(5)
O(3)-Sc(1)-O(6)-S(2)	99.3(4)
O(9)-Sc(1)-O(6)-S(2)	-82.6(4)
O(12)-Sc(1)-O(6)-S(2)	1.0(4)
N(2)-Sc(1)-O(6)-S(2)	17.2(6)
N(1)-Sc(1)-O(6)-S(2)	-173.5(3)
N(3)-Sc(1)-O(6)-S(2)	-169.8(4)
O(10)-S(3)-O(9)-Sc(1)	-130.9(5)
O(11)-S(3)-O(9)-Sc(1)	2.5(6)
C(28)-S(3)-O(9)-Sc(1)	117.5(7)
O(3)-Sc(1)-O(9)-S(3)	-69(4)
O(6)-Sc(1)-O(9)-S(3)	170.0(4)

O(12)-Sc(1)-O(9)-S(3)	94.2(4)
N(2)-Sc(1)-O(9)-S(3)	20.3(4)
N(1)-Sc(1)-O(9)-S(3)	-47.6(4)
N(3)-Sc(1)-O(9)-S(3)	-115.9(4)