Electronic Supplementary Material (ESI) for Organic & Biomolecular Chemistry.

Catalytic enantioselective cascade Michael/cyclization reaction of 3-isothiocyanato oxindoles with exocyclic α,β-unsaturated ketones en route to 3,2'-pyrrolidinyl bispirooxindoles

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SUPPORTING INFORMATION: PART A

A. General Information:

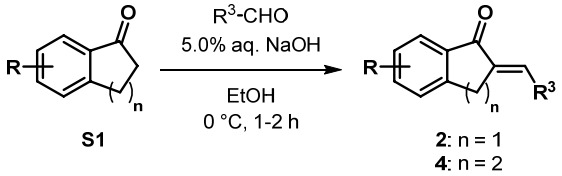
Infrared (FT-IR) spectra were recorded on a Perkin Elmer Spectrum BX spectrophotometer, ν_{max} in cm^{-1} and the bands are characterized as broad (br), strong (s), medium (m), and weak (w). NMR spectra were recorded on Bruker Ultrashield spectrometer at 400 MHz (for ^{1}H-NMR) and 100 MHz (for ^{13}C-NMR). Chemical shifts are reported in ppm from tetramethylsilane with the solvent resonance as internal standard ($CDCl_3$: δ 7.26, CD_3OD: δ 3.31 for ^{1}H-NMR and $CDCl_3$: δ 77.16, CD_3OD: δ 49.00 for ^{13}C-NMR). For ^{1}H-NMR, data are reported as follows: chemical shift, multiplicity (s = singlet, d = doublet, dd = double doublet, t = triplet, q = quartet, br = broad, m = multiplet), coupling constants (Hz) and integration. High resolution mass spectrometry was performed on Micromass Q-TOF Micro instrument. Optical rotations were measured on JASCO P-2000 polarimeter. Melting points were measured using ANALAB μ-Thermocal 10 melting point apparatus. All melting points were measured in open glass capillary and values are uncorrected. Enantiomeric ratios were determined by Shimadzu LC-20AD HPLC instrument and SPD-20A UV/Vis detector using stationary phase chiral columns (25 cm × 0.46 cm) in comparison with authentic racemic compounds.

Unless otherwise noted all reactions have been carried out with distilled and dried solvents under an atmosphere of N_2. Oven (120 °C) dried glassware with standard vacuum line techniques were used. All work up and purification were carried out with reagent grade solvents in air. Thin-layer chromatography was performed using Merck silica-gel 60 F_{254} pre-coated plates (0.25 mm). Column chromatography was performed using silica-gel (230-400 or 100-200 mesh).

B. Preparation of 3-isothiocyanato oxindoles: 3-Isothiocyanato oxindoles **(1a-1e)** were prepared according to the previously reported procedure.[1]

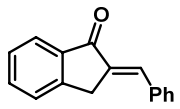
C. Preparation of catalysts: Catalysts **(I-V)** were prepared according to the literature procedure.[2]

D. Synthesis and characterization of exocyclic α,β-unsaturated ketones (2): β-Alkylidene-α-indanones (**2**) and β-alkylidene-α-tetralones (**4**) were prepared by following the reported literature procedure.[3]

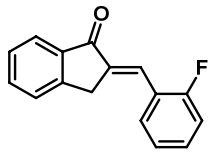


In a round bottom flask fitted with a magnetic stir-bar, compound **S1** (1.0 equiv) and aldehyde (1.0 equiv) were taken in ethanol (0.5 M) and cooled to 0 °C. 5% Aqueous solution of NaOH (0.1 M) was added drop-wise to the mixture at 0 °C and the resulting solution was stirred for 1h at the same temperature. Solid compound precipitated out which was filtered, washed with cold ethanol and dried under reduced pressure to obtain the desired product. The crude product was used for the next step without further purification.

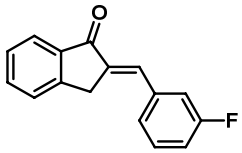
(*E*)-2-Benzylidene-2,3-dihydro-1*H*-inden-1-one (2a): White solid (675 mg, 3.06 mmol, 81% yield); **FT-IR (Thin film):** 3022 (w), 1687 (s), 1615 (s), 1490 (m), 737 (s); **^{1}H-NMR (400 MHz, $CDCl_3$):** δ 7.29 (d, *J* = 7.5 Hz, 1H), 7.69-7.67 (m, 3H), 7.26 (t, *J* = 7.3 Hz, 1H), 7.56 (d, *J* = 7.5 Hz, 1H), 7.48-7.38 (m, 4H), 4.06 (s, 2H); **^{13}C-NMR (100 MHz, $CDCl_3$):** δ 194.5, 149.8, 138.2, 138.2, 135.6, 134.8, 134.7, 134.1, 130.9, 129.8, 129.1, 127.8, 126.3, 124.6, 124.6, 32.6; **HRMS (ESI+):** Calcd for $C_{16}H_{13}O$ ($[M+H]^+$): 221.0966, Found: 221.0963.



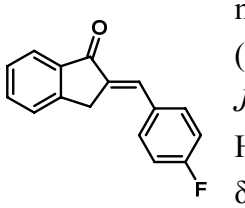
(*E*)-2-(2-Fluorobenzylidene)-2,3-dihydro-1*H*-inden-1-one (2b): White solid (850 mg, 3.56 mmol, 94% yield); **FT-IR (Thin film):** 2932 (w), 1695 (s), 1624 (s), 1454 (m), 730 (s); **^{1}H-NMR (400 MHz, $CDCl_3$):** δ 7.89 (br s, 2H), 7.69 (t, *J* = 7.5 Hz, 1H), 7.60 (t, *J* = 7.4 Hz, 1H), 7.53 (d, *J* = 7.5 Hz, 1H), 7.41 (t, *J* = 7.6 Hz, 1H), 7.36 (t, *J* = 6.9 Hz, 1H), 7.22 (t, *J* = 7.5 Hz, 1H), 7.13 (t, *J* = 9.3 Hz, 1H), 3.98 (s, 2H); **^{13}C-NMR (100 MHz, $CDCl_3$):** δ 193.9, 161.9 (d, *J* = 254.7 Hz), 149.7, 138.0, 136.6 (d, *J* = 1.3 Hz), 134.9, 131.4, 131.3, 130.1 (d, *J* = 2.3 Hz), 127.8, 126.3, 125.6 (d, *J* = 5.5 Hz), 124.6, 124.4 (d, *J* = 3.8 Hz), 123.6, 123.5, 116.2 (d, *J* = 22.2 Hz), 32.3 (d, *J* = 2.1 Hz); **HRMS (ESI+):** Calcd for $C_{16}H_{12}FO$ ($[M+H]^+$): 239.0872, Found: 239.0875.



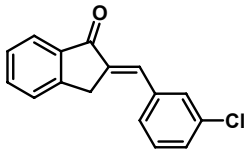
(*E*)-2-(4-Fluorobenzylidene)-2,3-dihydro-1*H*-inden-1-one (2c): White solid (800 mg, 3.35 mmol, 88% yield); **FT-IR (Thin film):** 2939 (w), 1695 (s), 1623 (s), 1579 (m), 731 (s); **^{1}H-NMR (400 MHz, $CDCl_3$):** δ 7.90 (d, *J* = 7.6 Hz, 1H), 7.64-7.61 (m, 2H), 7.55 (d, *J* = 7.5 Hz, 1H), 7.45-7.41 (m, 3H), 7.35 (d, *J* = 9.5 Hz, 1H), 7.12-7.07 (m, 1H), 4.02 (s, 2H); **^{13}C-NMR (100 MHz, $CDCl_3$):** δ 194.2, 163.1 (d, *J* = 246.5 Hz), 149.6, 137.9, 137.7, 137.6, 136.0, 135.0, 132.5 (d, *J* = 2.6 Hz), 130.5 (d, *J* = 8.0 Hz), 127.9, 126.8 (d, *J* = 2.8 Hz), 126.3, 124.6, 116.8 (d, *J* = 15.7 Hz), 116.6 (d, *J* = 15.2 Hz), 32.4; **HRMS (ESI+):** Calcd for $C_{16}H_{12}FO$ ($[M+H]^+$): 239.0872, Found: 239.0872.



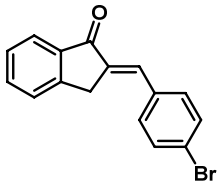
(*E*)-2-(4-Fluorobenzylidene)-2,3-dihydro-1*H*-inden-1-one (2d): White solid (900 mg, 3.77 mmol, 99% yield); **FT-IR (Thin film):** 3022 (w), 1684 (s), 1588 (s), 1500 (m), 1223 (m), 832 (s), 726 (s); **^{1}H-NMR (400 MHz, $CDCl_3$):** δ 7.89 (d, *J* = 7.5 Hz, 1H), 7.67-7.59 (m, 4H), 7.55 (d, *J* = 7.5 Hz, 1H), 7.42 (t, *J* = 7.3 Hz, 1H), 7.14 (t, *J* = 8.5 Hz, 2H), 4.00 (s, 2H); **^{13}C-NMR (100 MHz, $CDCl_3$):** δ 194.3, 163.5 (d, *J* = 252.8 Hz), 149.6, 138.1, 134.8, 134.4, 132.8, 132.7, 131.7 (d, *J* = 3.3 Hz), 127.9, 126.3, 124.6, 116.4, 116.1, 32.4; **HRMS (ESI+):** Calcd for $C_{16}H_{12}FO$ ($[M+H]^+$): 239.0872, Found: 239.0874.



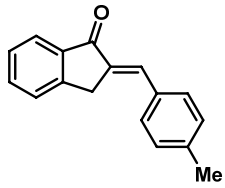
(*E*)-2-(3-Chlorobenzylidene)-2,3-dihydro-1*H*-inden-1-oneone (2e): White solid (850 mg, 3.34 mmol, 88% yield); **FT-IR (Thin film):** 3414 (w), 1694 (s), 1628 (s); **^{1}H-NMR (400 MHz, $CDCl_3$):** δ 7.88 (d, *J* = 7.6 Hz, 1H), 7.61 (t, *J* = 7.1 Hz, 2H), 7.56-7.54 (m, 2H), 7.50 (d, *J* = 6.7 Hz, 1H), 7.41 (t, *J* = 7.4 Hz, 1H), 7.37-7.34 (m, 2H), 4.00 (s, 2H); **^{13}C-NMR (100 MHz, $CDCl_3$):** δ 194.0, 149.6, 137.9, 137.3, 136.1, 135.0, 132.3, 130.2, 130.1, 129.6, 129.0, 127.9, 126.3, 124.6, 32.4; **HRMS (ESI+):** Calcd for $C_{16}H_{12}ClO$ ($[M+Na]^+$): 255.0577, Found: 255.0579.



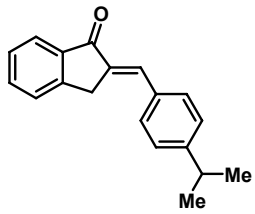
(*E*)-2-(4-Bromobenzylidene)-2,3-dihydro-1*H*-inden-1-one (2f): White solid (900 mg, 3.01 mmol, 79% yield); **FT-IR (Thin film):** 3413 (w), 1691 (s), 1618 (s), 1477 (m), 1269 (m), 1072 (m); **^{1}H-NMR (400 MHz, $CDCl_3$):** δ 7.87 (d, *J* = 7.6 Hz, 1H), 7.60 (t, *J* = 7.4 Hz, 1H), 7.56-7.53 (m, 4H), 7.48 (d, *J* = 7.5 Hz, 2H), 7.40 (t, *J* = 7.4 Hz, 1H), 3.95 (s, 2H); **^{13}C-NMR (100 MHz, $CDCl_3$):** δ 194.1, 149.5, 137.9, 135.4, 134.9, 134.3, 132.5, 132.3, 132.1, 127.9, 126.3, 124.6, 124.1, 32.4; **HRMS (ESI+):** Calcd for $C_{16}H_{11}BrNaO$ ($[M+Na]^+$): 320.9891, Found: 320.9892.



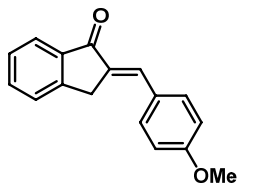
(*E*)-2-(4-Methylbenzylidene)-2,3-dihydro-1*H*-inden-1-one (2g): White solid (840 mg, 3.58 mmol, 95% yield); **FT-IR (Thin film):** 2882 (w), 1682 (s), 1601 (s), 1456 (m), 1090 (m), 735 (s); **^{1}H-NMR (400 MHz, $CDCl_3$):** δ 7.88 (d, *J* = 7.5 Hz, 1H), 7.63 (s, 1H), 7.60-7.51 (m, 4H), 7.39 (t, *J* = 7.4 Hz, 1H), 7.24 (d, *J* = 8.0 Hz, 2H), 3.98 (s, 2H), 2.38 (s, 3H); **^{13}C-NMR (100 MHz, $CDCl_3$):** δ 194.5, 149.7, 140.2, 138.2, 134.6, 134.1, 133.8, 132.7, 130.9, 129.8, 127.7, 126.2, 124.4, 32.6, 21.6; **HRMS (ESI+):** Calcd for $C_{17}H_{14}NaO$ ($[M+Na]^+$): 257.0942, Found: 257.0945.



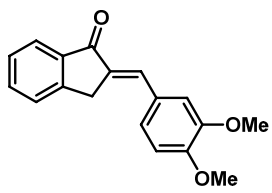
(*E*)-2-(4-Isopropylbenzylidene)-2,3-dihydro-1*H*-inden-1-one (2h): White solid (700 mg, 2.66 mmol, 71% yield); **FT-IR (Thin film):** 3459 (w), 2961 (m), 1695 (s), 1627 (s), 1465 (m); **^{1}H-NMR (400 MHz, $CDCl_3$):** δ 7.91 (d, *J* = 7.5 Hz, 1H), 7.67 (s, 1H), 7.63-7.59 (m, 3H), 7.55 (d, *J* = 7.5 Hz, 1H), 7.41 (t, *J* = 7.3 Hz, 1H), 7.32 (d, *J* = 8.1 Hz, 2H), 4.03 (s, 2H), 2.99-2.92 (m, 1H), 1.29 (s, 3H), 1.28 (s, 3H); **^{13}C-NMR (100 MHz, $CDCl_3$):** δ 194.5, 151.1, 149.7, 138.3, 134.6, 134.1, 134.0, 133.1, 131.0, 127.7, 127.2, 126.3, 124.5, 34.2, 32.6, 23.9; **HRMS (ESI+):** Calcd for $C_{19}H_{18}NaO$ ($[M+Na]^+$): 285.1255, Found: 285.1257.



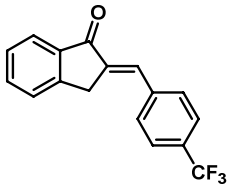
(*E*)-2-(4-Methoxybenzylidene)-2,3-dihydro-1*H*-inden-1-one (2i): White solid (900 mg, 3.59 mmol, 95% yield); **FT-IR (Thin film):** 2193 (w), 1688 (s), 1591 (s), 1504 (m), 1247 (s), 730 (s); **^{1}H-NMR (400 MHz, $CDCl_3$):** δ 7.89 (d, *J* = 7.5 Hz, 1H), 7.64-7.62 (m, 3H), 7.58 (d, *J* = 7.3 Hz, 1H), 7.54 (d, *J* = 7.5 Hz, 1H), 7.41 (t, *J* = 7.3 Hz, 1H), 6.97 (d, *J* = 8.5 Hz, 2H), 3.99 (s, 2H), 3.85 (s, 3H); **^{13}C-NMR (100 MHz, $CDCl_3$):** δ 194.5, 161.0, 149.6, 138.4, 134.4, 133.9, 132.7, 132.5, 128.3, 127.7, 126.2, 124.4, 114.6, 55.5, 32.6; **HRMS (ESI+):** Calcd for $C_{17}H_{14}NaO_2$ ($[M+Na]^+$): 273.0891, Found: 273.0889.



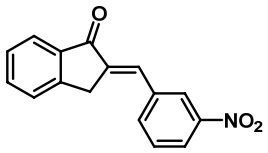
(*E*)-2-(3,4-Dimethoxybenzylidene)-2,3-dihydro-1*H*-inden-1-one (2j): White solid (850 mg, 3.03 mmol, 80% yield); **FT-IR (Thin film):** 3612 (w), 1690 (s), 1513 (s), 1253 (s), 1022 (m); **^{1}H-NMR (400 MHz, $CDCl_3$):** δ 7.84 (d, *J* = 7.5 Hz, 1H), 7.56-7.53 (m, 2H), 7.49 (d, *J* = 7.5 Hz, 1H), 7.36 (t, *J* = 7.3 Hz, 1H), 7.23 (dd, *J* = 8.4 Hz, 1.5 Hz, 1H), 7.10 (d, *J* = 1.4 Hz, 1H), 6.88 (d, *J* = 8.4 Hz, 1H), 3.91 (br s, 5H), 3.88 (s, 3H); **^{13}C-NMR (100 MHz, $CDCl_3$):** δ 194.2, 150.6, 149.4, 149.1, 138.2, 134.4, 134.0, 132.6, 128.4, 127.6, 126.1, 124.6, 124.2, 113.5, 111.3, 56.0, 32.3; **HRMS (ESI+):** Calcd for $C_{18}H_{16}NaO_3$ ($[M+Na]^+$): 303.0997, Found: 303.0994.



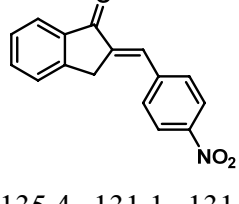
(*E*)-2-(4-(Trifluoromethyl)benzylidene)-2,3-dihydro-1*H*-inden-1-oneone (2k): White solid (900 mg, 3.12 mmol, 82% yield); **FT-IR (Thin film):** 3076 (w), 1692 (s), 1624 (s), 1466 (m), 1316 (s), 1162 (m), 1108 (s), 737 (s); **^{1}H-NMR (400 MHz, $CDCl_3$):** δ 7.91 (d, *J* = 7.6 Hz, 1H), 7.75 (d, *J* = 8.2 Hz, 2H), 7.70 (d, *J* = 8.2 Hz, 2H), 7.66 (br s, 1H), 7.63 (d, *J* = 7.3 Hz, 1H), 7.56 (d, *J* = 7.5 Hz, 1H), 7.44 (t, *J* = 7.3 Hz, 1H), 4.05 (s, 2H); **^{13}C-NMR (100 MHz, $CDCl_3$):** δ 194.0, 149.6, 138.9, 137.8, 137.1, 135.1, 132.0, 130.7, 128.0, 126.4, 125.9 (d, *J* = 3.6 Hz), 125.4, 124.8, 122.6, 32.4; **HRMS (ESI+):** Calcd for $C_{17}H_{12}F_3O$ ($[M+H]^+$): 289.0840, Found: 289.0841.



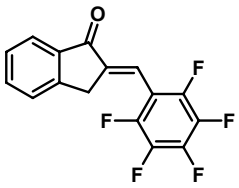
(*E*)-2-(3-Nitrobenzylidene)-2,3-dihydro-1*H*-inden-1-one (2l): White solid (900 mg, 3.39 mmol, 50% yield); **FT-IR (Thin film):** 3174 (w), 1692 (m), 1606 (s), 1527 (s), 1339 (m); **^{1}H-NMR (400 MHz, $CDCl_3$):** δ 8.54 (s, 1H), 8.25 (dd, *J* = 8.2 Hz, 1.3 Hz, 1H), 7.94 (t, *J* = 6.9 Hz, 2H), 7.69-7.60 (m, 4H), 7.46 (t, *J* = 7.4 Hz, 1H), 4.11 (s, 2H); **^{13}C-NMR (100 MHz, $CDCl_3$):** δ 193.8, 149.5, 148.8, 137.7, 137.6, 137.2, 136.6, 135.3, 130.9, 130.1, 128.2, 126.5, 124.8, 124.4, 124.0, 32.4; **HRMS (ESI+):** Calcd for $C_{16}H_{11}NNaO_3$ ($[M+Na]^+$): 288.0637, Found: 288.0638.



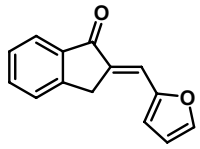
(*E*)-2-(4-Nitrobenzylidene)-2,3-dihydro-1*H*-inden-1-one (2m): White solid (850 mg, 3.20 mmol, 85% yield); **FT-IR (Thin film):** 3412 (w), 1690 (s), 1626 (m), 1510 (s), 1337 (s); **^{1}H-NMR (400 MHz, $CDCl_3$):** δ 8.32 (d, *J* = 8.6 Hz, 2H), 7.94 (d, *J* = 7.6 Hz, 1H), 7.81 (d, *J* = 8.6 Hz, 2H), 7.69 (br s, 1H), 7.65 (d, *J* = 7.3 Hz, 1H), 7.58 (d, *J* = 7.5 Hz, 1H), 7.47 (t, *J* = 7.4 Hz, 1H), 4.10 (s, 2H); **^{13}C-NMR (100 MHz, $CDCl_3$):** δ 193.8, 149.5, 147.9, 141.8, 138.6, 137.7, 135.4, 131.1, 131.0, 128.2, 126.4, 124.9, 124.3, 32.5; **HRMS (ESI+):** Calcd for $C_{16}H_{12}NO_3$ ($[M+H]^+$): 266.0817, Found: 266.0820.



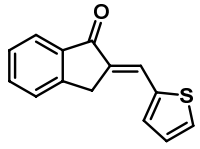
(*E*)-2-(Perfluorophenyl)methylene)-2,3-dihydro-1*H*-inden-1-one (2n): White solid (900 mg, 2.90 mmol, 77% yield); **FT-IR (Thin film):** 1703 (s), 1522 (s), 1492 (s), 978 (s); **^{1}H-NMR (400 MHz, $CDCl_3$):** δ 7.89 (d, *J* = 7.6 Hz, 1H), 7.64 (td, *J* = 7.6 Hz, 1.0 Hz, 1H), 7.51-7.49 (m, 2H), 7.44 (t, *J* = 7.5 Hz, 1H), 3.81 (s, 2H); **^{13}C-NMR (100 MHz, $CDCl_3$):** δ 192.6, 149.5, 145.9, 142.8, 137.6, 135.6, 128.1, 126.4, 124.9, 117.9, 110.9, 110.8, 32.0 (t, *J* = 6.0 Hz); **HRMS (ESI+):** Calcd for $C_{16}H_7F_5NaO$ ($[M+Na]^+$): 333.0315, Found: 333.0313.



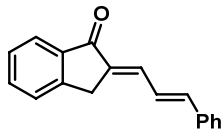
(*E*)-2-(Furan-2-ylmethylene)-2,3-dihydro-1*H*-inden-1-one (2o): White solid (750 mg, 3.31 mmol, 87% yield); **FT-IR (Thin film):** 3107 (w), 2910 (W), 1686 (s), 1618 (s), 1472 (s), 1267 (m); **^{1}H-NMR (400 MHz, $CDCl_3$):** δ 7.86 (d, *J* = 7.6 Hz, 1H), 7.61-7.60 (m, 1H), 7.57 (d, *J* = 7.0 Hz, 1H), 7.53 (d, *J* = 7.5 Hz, 1H), 7.44 (t, *J* = 1.7 Hz, 1H), 7.39 (d, *J* = 7.3 Hz, 1H), 6.75 (d, *J* = 3.4 Hz, 1H), 6.55-6.53 (m, 1H), 4.02 (s, 2H); **^{13}C-NMR (100 MHz, $CDCl_3$):** δ 194.1, 152.4, 149.9, 145.5, 138.6, 134.5, 132.7, 127.6, 126.3, 124.3, 120.1, 116.7, 112.8, 32.4; **HRMS (ESI+):** Calcd for $C_{14}H_{11}O_2$ ($[M+H]^+$): 211.0759, Found: 211.0761.



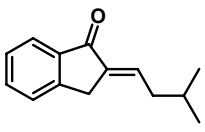
(*E*)-2-(Thiophen-2-ylmethylene)-2,3-dihydro-1*H*-inden-1-one (2p): Yellow solid (625 mg, 2.76 mmol, 73% yield); **FT-IR (Thin film):** 3022 (w), 1687 (s), 1613 (s), 1577 (m), 730 (s), 703 (s); **^{1}H-NMR (400 MHz, $CDCl_3$):** δ 7.88-7.87 (m, 2H), 7.59 (td, *J* = 7.7 Hz, 1.1 Hz, 1H), 7.57-7.54 (m, 2H), 7.42-7.38 (m, 2H), 7.15 (dd, *J* = 5.0 Hz, 3.7 Hz, 1H), 3.90 (s, 2H); **^{13}C-NMR (100 MHz, $CDCl_3$):** δ 193.9, 149.1, 140.0, 138.6, 134.6, 133.2, 132.8, 130.6, 128.3, 127.7, 126.6, 126.3, 124.4, 32.4; **HRMS (ESI+):** Calcd for $C_{14}H_{10}NaOS$ ($[M+Na]^+$): 249.0350, Found: 249.0349.



(*E*)-2-((*E*)-3-Phenylallylidene)-2,3-dihydro-1*H*-inden-1-one (2q): Yellow solid (570 mg, 2.37 mmol, 61% yield); **FT-IR (Thin film):** 3024 (w), 1689 (s), 1615 (s); **^{1}H-NMR (400 MHz, $CDCl_3$):** δ 7.87 (d, *J* = 7.6 Hz, 1H), 7.59 (td, *J* = 7.6 Hz, 0.8 Hz,1H), 7.52 (d, *J* = 7.3 Hz, 3H), 7.44-7.31 (m, 5H), 7.05-7.03 (m, 2H), 3.85 (s, 2H); **^{13}C-NMR (100 MHz, $CDCl_3$):** δ 193.8, 149.0, 142.1, 139.4, 136.5, 136.2, 134.5, 133.4, 129.3, 129.0, 127.7, 127.4, 126.4, 124.5, 124.3, 30.5; **HRMS (ESI+):** Calcd for $C_{18}H_{14}NaO$ ($[M+Na]^+$): 269.0942, Found: 269.0944.



(*E*)-2-(3-Methylbutylidene)-2,3-dihydro-1*H*-inden-1-one (2r): Yellow oil (500 mg, 2.49 mmol, 66% yield); **FT-IR (Thin film):** 2958 (s), 1704 (s), 1651 (s), 1608 (m), 1466 (m), 1324 (m), 1265 (m), 1093 (m), 921 (m); **^{1}H-NMR (400 MHz, $CDCl_3$):** 7.84 (d, *J* = 7.6 Hz, 1H), 7.56 (t, *J* = 7.2 Hz, 1H), 7.47 (d, *J* = 7.6 Hz, 1H), 7.37 (t, *J* = 7.4 Hz, 1H), 6.93-6.88 (m, 1H), 3.64 (s, 2H), 2.19 (t, *J* = 7.3 Hz, 2H), 1.91-1.81 (m, 1H), 0.96 (d, *J* = 6.6 Hz, 6H); **^{13}C-NMR (100 MHz, $CDCl_3$):** δ 193.4, 149.5, 139.0, 137.3, 137.1, 134.5, 127.5, 126.4, 124.4, 39.1, 30.2, 28.4, 22.7; **HRMS (ESI+):** Calcd for $C_{14}H_{16}NaO$ ($[M+Na]^+$): 223.1099, Found: 223.1099.



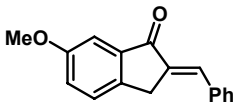
2-Methylene-2,3-dihydro-1*H*-inden-1-one (2s): Compound **2s** was prepared by following the reported literature procedure.[4] Yellow oil (395 mg, 2.74 mmol, 72% yield); **FT-IR (Thin film):** 3396 (w), 1705 (s), 1642 (m), 1609 (m); **^{1}H-NMR (400 MHz, $CDCl_3$):** δ 7.86 (d, *J* = 7.7 Hz, 1H), 7.60 (td, *J* = 7.5 Hz, 1.0 Hz, 1H), 7.48 (dt, *J* = 7.7 Hz, 0.8 Hz, 1H), 7.40 (t, *J* = 7.5 Hz, 1H), 6.31 (td, *J* = 2.3 Hz, 0.7 Hz, 1H), 5.64-5.63 (m, 1H), 3.75 (s, 2H); **^{13}C-NMR (100 MHz, $CDCl_3$):** δ 193.6, 150.0, 143.4, 138.4, 135.0, 127.7, 126.5, 124.8, 119.4, 31.9; **HRMS (ESI+):** Calcd for $C_{10}H_8NaO$ ($[M+Na]^+$): 167.0473, Found: 167.0474.

(*E*)-2-Benzylidene-5-chloro-2,3-dihydro-1*H*-inden-1-one (2t): White solid (500 mg, 1.96 mmol, 65% yield); **FT-IR (Thin film):** 1695 (s), 1625 (s), 1599 (m), 766 (s); **^{1}H-NMR (400 MHz, $CDCl_3$):** δ 7.83 (d, *J* = 8.1 Hz, 1H), 7.67-7.64 (m, 3H), 7.54 (s, 1H), 7.49-7.45 (m, 2H), 7.43-7.39 (m, 2H), 4.02 (s, 2H); **^{13}C-NMR (100 MHz, $CDCl_3$):** δ 193.0, 151.2, 141.0, 136.7, 135.3, 134.7, 134.2, 130.9, 130.0, 129.1, 128.6, 126.5, 125.7, 32.3; **HRMS (ESI+):** Calcd for $C_{16}H_{11}ClNaO$ ($[M+Na]^+$): 277.0396, Found: 277.0393.

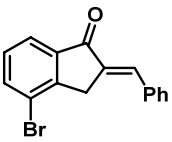
(*E*)-2-Benzylidene-5-bromo-2,3-dihydro-1*H*-inden-1-one (2u): White solid (590 mg, 1.97 mmol, 83% yield); **FT-IR (Thin film):** 3052 (w), 1694 (s), 1623 (s), 1596 (m), 763 (s); **^{1}H-NMR (400 MHz, $CDCl_3$):** δ 7.75 (d, *J* = 8.1 Hz, 1H), 7.72 (br s, 1H), 7.68 (t, *J* = 1.9 Hz, 1H), 7.66-7.64 (m, 2H), 7.56 (dt, *J* = 8.1 Hz, 0.7 Hz, 1H), 7.49-7.40 (m, 3H), 4.02 (s, 2H); **^{13}C-NMR (100 MHz, $CDCl_3$):** δ 193.2, 151.3, 137.0, 135.3, 134.8, 134.1, 131.5, 130.9, 130.1, 129.8, 129.6, 129.1, 125.8, 32.3; **HRMS (ESI+):** Calcd for $C_{16}H_{11}BrNaO$ ($[M+Na]^+$): 320.9891, Found: 320.9889.

(*E*)-2-Benzylidene-5-fluoro-2,3-dihydro-1*H*-inden-1-one (2v): White solid (490 mg, 2.05 mmol, 62% yield); **FT-IR (Thin film):** 1692 (s), 1617 (s), 1239 (s), 770 (s); **^{1}H-NMR (400 MHz, $CDCl_3$):** δ 7.91 (dd, *J* = 8.4 Hz, 5.3 Hz, 1H), 7.66-7.65 (m, 3H), 7.48-7.41 (m, 3H), 7.25-7.21 (m, 1H), 7.13 (td, *J* = 8.9 Hz, 2.1 Hz, 1H), 4.04 (s, 2H); **^{13}C-NMR (100 MHz, $CDCl_3$):** δ 192.7, 167.1 (d, *J* = 257.4 Hz), 152.5 (d, *J* = 10.2 Hz), 135.3, 134.6, 134.4, 134.2, 130.8, 129.9, 129.1, 128.9, 128.8, 126.9, 126.8, 116.1 (d, *J* = 23.5 Hz), 113.1 (d, *J* = 22.5 Hz), 32.5; **HRMS (ESI+):** Calcd for $C_{16}H_{11}FNaO$ ($[M+Na]^+$): 261.0691, Found: 261.0692.

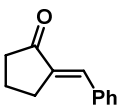
(*E*)-2-Benzylidene-6-methoxy-2,3-dihydro-1*H*-inden-1-one (2w): White solid (630 mg, 2.52 mmol, 65% yield); **FT-IR (Thin film):** 1686 (s), 1620 (s), 1484 (m), 1444 (m), 1276 (m), 770 (s), 684 (m); **^{1}H-NMR (400 MHz, $CDCl_3$):** δ 7.65-7.63 (m, 3H), 7.45-7.38 (m, 4H), 7.32 (d, *J* = 2.4 Hz, 1H), 7.17 (dd, *J* = 8.4 Hz, 2.5 Hz, 1H), 3.93 (s, 2H), 3.84 (s, 3H); **^{13}C-NMR (100 MHz, $CDCl_3$):** δ 194.3, 159.7, 142.5, 139.3, 135.7, 135.5, 133.8, 130.8, 129.7, 129.0, 127.0, 124.0, 105.9, 55.7, 31.9; **HRMS (ESI+):** Calcd for $C_{17}H_{14}NaO_2$ ($[M+Na]^+$): 273.0891, Found: 273.0892.



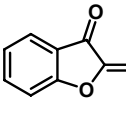
(*E*)-2-Benzylidene-4-bromo-2,3-dihydro-1*H*-inden-1-one (2x): White solid (600 mg, 2.01 mmol, 85% yield); **FT-IR (Thin film):** 2897 (w), 1699 (s), 1624 (m), 1592 (m), 1113 (s), 757 (s); **^{1}H-NMR (400 MHz, $CDCl_3$):** δ 7.85 (d, *J* = 7.5 Hz, 1H), 7.76 (dd, *J* = 7.7 Hz, 0.6 Hz, 1H), 7.70-7.68 (m, 3H), 7.48 (t, *J* = 7.3 Hz, 2H), 7.44-7.40 (m, 1H), 7.32 (t, *J* = 7.7 Hz, 1H), 3.94 (s, 2H); **^{13}C-NMR (100 MHz, $CDCl_3$):** δ 193.6, 149.6, 140.2, 137.4, 135.2, 135.1, 133.8, 131.0, 130.2, 129.6, 129.2, 123.3, 121.8, 33.7; **HRMS (ESI+):** Calcd for $C_{16}H_{11}BrNaO$ ($[M+Na]^+$): 320.9891, Found: 320.9890.



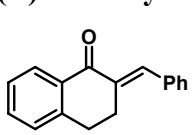
(*E*)-2-Benzylidenecyclopentan-1-one (2y): Yellow solid (880 mg, 5.11 mmol, 86% yield); **FT-IR (Thin film):** 1711 (s), 1623 (s), 1407 (m), 1232 (m), 1174 (m), 927 (m); **^{1}H-NMR (400 MHz, $CDCl_3$):** 7.53 (d, *J* = 7.4 Hz, 2H), 7.42-7.35 (m, 4H), 2.96 (td, *J* = 7.3 Hz, 2.5 Hz, 2H), 2.40 (t, *J* = 7.9 Hz, 2H), 2.06-1.98 (m, 2H); **^{13}C-NMR (100 MHz, $CDCl_3$):** δ 208.1, 136.2, 135.6, 132.3, 130.6, 129.4, 128.8, 37.9, 29.4, 20.3; **HRMS (ESI+):** Calcd for $C_{12}H_{12}OH$ ($[M+Na]^+$): 173.0966, Found: 173.0968.



(*Z*)-2-Benzylidenebenzofuran-3(2*H*)-one (2z): White solid (300 mg, 1.35 mmol, 90% yield); **FT-IR (Thin film):** 3025 (w), 1708 (s), 1654 (s), 1599 (s), 1457 (m), 1300 (m); **^{1}H-NMR (400 MHz, $CDCl_3$):** δ 7.91 (d, *J* = 7.6 Hz, 2H), 7.79 (d, *J* = 7.5 Hz, 1H), 7.64 (t, *J* = 7.7 Hz, 1H), 7.45 (t, *J* = 7.4 Hz, 2H), 7.41-7.38 (m, 1H), 7.32 (d, *J* = 8.3 Hz, 1H), 7.21 (t, *J* = 7.5 Hz, 1H), 6.89 (s, 1H); **^{13}C-NMR (100 MHz, $CDCl_3$):** δ 184.9, 166.3, 147.0, 137.0, 132.4, 131.6, 130.0, 129.0, 124.8, 123.6, 121.7, 113.1, 113.0; **HRMS (ESI+):** Calcd for $C_{15}H_{10}NaO_2$ ($[M+Na]^+$): 245.0578, Found: 245.0577.

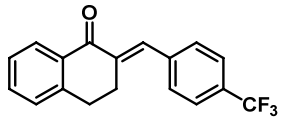


(*E*)-2-Benzylidene-3,4-dihydronaphthalen-1(2*H*)-one (4a): White solid (450 mg, 1.92 mmol, 56% yield); **FT-IR (Thin film):** 3023 (w), 1656 (s), 1591 (s), 1488 (s), 1293 (m), 742 (s), 690 (s); **^{1}H-NMR (400 MHz, $CDCl_3$):** δ 8.14 (dd, *J* = 7.4 Hz, 0.7 Hz, 1H), 7.88 (s, 1H), 7.48 (td, *J* = 7.4 Hz, 1.2 Hz, 1H), 7.47-7.40 (m, 4H), 7.38-7.33 (m, 2H), 7.25-7.24 (m, 1H), 3.14 (td, *J* = 7.6 Hz, 1.5 Hz, 2H), 2.95 (t, *J* = 6.4 Hz, 2H); **^{13}C-NMR (100 MHz, $CDCl_3$):** δ 188.0, 143.4, 136.8, 136.0, 135.6, 133.6, 133.4, 130.0, 128.7,



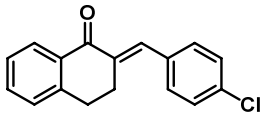
128.6, 128.4, 128.3, 127.2, 29.0, 27.3; **HRMS (ESI+):** Calcd for $C_{17}H_{15}O$ ($[M+H]^+$): 235.1123, Found: 235.1125.

(*E*)-2-(4-(Trifluoromethyl)benzylidene)-3,4-dihydronaphthalen-1(2*H*)-one (4b): White solid



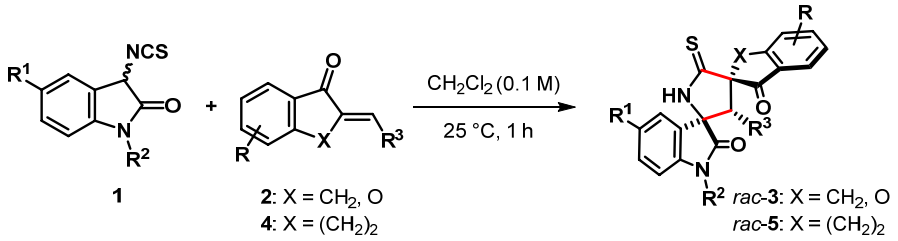
(900 mg, 2.97 mmol, 87% yield); **FT-IR (Thin film):** 3403 (w), 1668 (m), 1598 (m), 1332 (m), 1114 (s); **^{1}H-NMR (400 MHz, $CDCl_3$):** δ 8.14 (d, *J* = 7.7 Hz, 1H), 7.84 (br s, 1H), 7.66 (d, *J* = 8.2 Hz, 2H), 7.53-7.48 (m, 3H), 7.37 (t, *J* = 7.5 Hz, 1H), 7.26 (d, *J* = 7.5 Hz, 1H), 3.09 (t, *J* = 5.8 Hz, 2H), 2.96 (t, *J* = 6.3 Hz, 2H); **^{13}C-NMR (100 M Hz, $CDCl_3$):** δ 187.6, 143.3, 139.6, 137.5, 134.8, 133.7, 133.3, 130.0, 128.4, 128.4, 127.3, 125.5, 125.5, 28.9, 27.3; **HRMS (ESI+):** Calcd for $C_{18}H_{13}F_3NaO$ ($[M+Na]^+$): 325.0816, Found: 325.0814.

(*E*)-2-(4-Chlorobenzylidene)-3,4-dihydronaphthalen-1(2*H*)-one (4c): White solid (850 mg,



3.16 mmol, 92% yield); **FT-IR (Thin film):** 3414 (w), 1666 (s), 1595 (s), 1299 (m), 1091 (m); **^{1}H-NMR (400 MHz, $CDCl_3$):** δ 8.12 (d, *J* = 7.5 Hz, 1H), 7.79 (br s, 1H), 7.48 (td, *J* = 7.4 Hz, 0.9 Hz, 1H), 7.39-7.34 (m, 5H), 7.25 (d, *J* = 7.9 Hz, 1H), 3.08 (t, *J* = 6.4 Hz, 2H), 2.94 (t, *J* = 6.4 Hz, 2H); **^{13}C-NMR (100 MHz, $CDCl_3$):** δ 187.7, 143.2, 136.1, 135.3, 134.6, 134.4, 133.5, 133.5, 131.2, 128.8, 128.4, 128.3, 127.2, 28.9, 27.3; **HRMS (ESI+):** Calcd for $C_{17}H_{13}ClNaO$ ($[M+Na]^+$): 291.0553, Found: 291.0554.

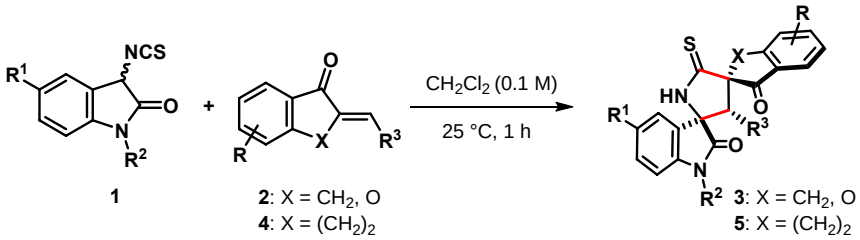
E. General procedure for the preparation of racemic Michael addition-cyclization cascade products (*rac*-3 or *rac*-5):



In an oven and vacuum-dried reaction tube, an exocyclic α,β-unsaturated ketone (0.055 mmol, 1.1 equiv) was taken with 0.2 mL of freshly distilled CH_2Cl_2 under positive argon pressure. After 2 min a solution of 3-isothiocyanato oxindole **1** (0.050 mmol, 1.0 equiv) in CH_2Cl_2 (0.3 mL) was added over 5 min. After 1 h, the reaction mixture was diluted with CH_2Cl_2 (1.0 mL) and sat. aqueous NH_4Cl solution (2.0 mL) at the reaction temperature. Organic layer was separated and the aqueous layer was extracted with CH_2Cl_2 (3 × 4.0 mL). Combined organic layer was dried over anh. Na_2SO_4 and concentrated under reduced pressure. The residue was purified by flash

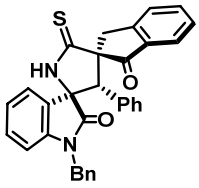
column chromatography on silica-gel (230-400 mesh) using 1:4 EtOAc/CH_2Cl_2 to obtain *rac*-**3** or *rac*-**5**.

F. General procedure for the enantioselective Michael addition/cyclization cascade of 3-isothiocyanato oxindoles with exocyclic α,β-unsaturated ketones:



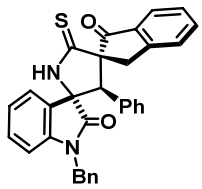
In an oven and vacuum-dried reaction tube, catalyst **IV** (0.01 mmol, 0.1 equiv) and an exocyclic α,β-unsaturated ketone (0.11 mmol, 1.1 equiv) were taken with 0.5 mL of freshly distilled CH_2Cl_2 under positive argon pressure. After 5 min, a solution of 3-isothiocyanato oxindole **1** (0.10 mmol, 1.0 equiv) in CH_2Cl_2 (0.5 mL) was added over 5 min at 25 °C. The resulting reaction mixture was stirred for at the same temperature. The reaction was monitored by TLC. After the completion of the reaction, the reaction mixture was diluted with CH_2Cl_2 (1.0 mL) and sat. aqueous NH_4Cl solution (5.0 mL) at the reaction temperature. Organic layer was separated from the aqueous layer. The aqueous layer was extracted with CH_2Cl_2 (3 × 4.0 mL). Combined organic layer was washed with brine (10 mL), dried over anh. Na_2SO_4 and concentrated under reduced pressure. The residue was purified by flash column chromatography on silica-gel (230-400 mesh) using 1:10 EtOAc/CH_2Cl_2 to obtain **3** or **5**.

Compound 3aa: Purified by silica-gel (230-400 mesh) flash column chromatography (EtOAc/CH_2Cl_2 1:10); White solid (47.0 mg, 0.094 mmol, 94% yield); **m.p.** 180-181 °C (decomposition); **FT-IR (Thin film):** 3334 (w), 1720 (s), 1608 (m), 1488 (m), 1467 (s), 1367 (s); **^{1}H-NMR (400 MHz, $CDCl_3$):** δ 8.48 (br s, 1H), 7.81 (d, *J* = 7.6 Hz, 1H), 7.59 (d, *J* = 7.4 Hz, 1H), 7.54 (t, *J* = 7.9 Hz, 1H), 7.41 (d, *J* = 7.7 Hz, 1H), 7.36-7.23 (m, 3H), 7.11 (dd, *J* = 16.9 Hz, 7.5 Hz, 2H), 6.98 (q, *J* = 7.9 Hz, 4H), 6.75 (d, *J* = 7.5 Hz, 2H), 6.58 (d, *J* = 7.5 Hz, 1H), 6.54 (d, *J* = 7.5 Hz, 2H), 5.31 (d, *J* = 16.2 Hz, 1H), 5.14 (s, 1H), 4.39 (d, *J* = 16.2 Hz, 1H), 3.81 (d, *J* = 16.6 Hz, 1H), 3.58 (d, *J* = 16.6 Hz, 1H); **^{13}C-NMR (100 MHz, $CDCl_3$):** δ 208.8, 201.9, 174.6, 152.8, 142.7, 136.0, 135.5, 134.4, 131.5, 131.0, 130.3, 128.8, 128.7, 128.6, 128.4, 128.0, 127.4, 126.7, 126.4, 125.3, 125.0, 123.5, 110.7, 73.4, 70.2, 59.0, 44.2, 38.3; **HRMS (ESI+):** Calcd for $C_{32}H_{24}N_2NaO_2S$ ($[M+Na]^+$): 523.1456, Found: 523.1459; **Optical rotation:** $[\alpha]_D^{21}$ +36.5 (*c* 1.0, $CHCl_3$) for an enantiomerically enriched sample with 98:2 er. The enantiomeric ratio was determined by HPLC analysis using Daicel Chiralpak AD-H column (50:50

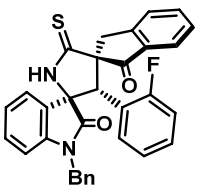


n-Hexane/EtOH, 1.0 mL/min, 20 °C, 254 nm, τ_{major} = 11.7 min, τ_{minor} = 15.2 min). The stereochemistry of the product **3aa** was assigned in analogy with **3ao**. See Supporting Information: Part B for HPLC chromatograms.

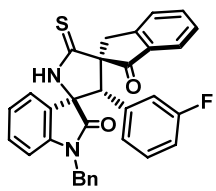
Compound *ent*-3aa: Reaction was performed on a 0.1 mmol scale under identical reaction conditions as for **3aa** using pseudoenantiomeric catalyst **V**. Purified by silica-gel (230-400 mesh) flash column chromatography (EtOAc/CH_2Cl_2 1:10); White solid (48.0 mg, 0.096 mmol, 96% yield). **Optical rotation:** $[\alpha]_D^{21}$ –33.0 (*c* 1.0, $CHCl_3$) for an enantiomerically enriched sample with 95.5:4.5 er. The enantiomeric ratio was determined by HPLC analysis using Daicel Chiralpak AD-H column (50:50 *n*-Hexane/EtOH, 1.0 mL/min, 20 °C, 254 nm, τ_{minor} = 11.7 min, τ_{major} = 15.2 min).



Compound 3ab: Purified by silica-gel (230-400 mesh) flash column chromatography (EtOAc/CH_2Cl_2 1:10); White solid (50.0 mg, 0.096 mmol, 96% yield); **m.p.** 110-111 °C; **FT-IR (Thin film):** 3334 (w), 1718 (s), 1605 (m), 1461 (s), 1361 (m), 750 (s); **^{1}H-NMR (400 MHz, $CDCl_3$):** δ 8.35 (br s, 1H), 7.83 (d, *J* = 7.6 Hz, 1H), 7.57 (d, *J* = 7.3 Hz, 1H), 7.53 (t, *J* = 7.5 Hz, 1H), 7.39-7.37 (m, 1H), 7.34 (d, *J* = 7.5 Hz, 1H), 7.30 (d, *J* = 7.6 Hz, 1H), 7.24-7.22 (m, 1H), 7.14-7.08 (m, 2H), 7.04 (t, *J* = 7.5 Hz, 2H), 6.85 (t, *J* = 9.2 Hz, 1H), 6.66 (d, *J* = 7.2 Hz, 2H), 6.63 (d, *J* = 7.9 Hz, 1H), 6.60 (d, *J* = 7.7 Hz, 1H), 6.54 (t, *J* = 7.4 Hz, 1H), 5.64 (s, 1H), 5.29 (d, *J* = 16.1 Hz, 1H), 4.44 (d, *J* = 16.1 Hz, 1H), 3.84 (d, *J* = 16.6 Hz, 1H), 3.54 (d, *J* = 16.1 Hz, 1H); **^{13}C-NMR (100 MHz, $CDCl_3$):** δ 208.5, 201.2, 174.5, 161.3 (d, *J* = 250.1 Hz), 152.5, 142.7, 135.6, 135.4, 134.6, 131.1, 130.3, 129.9, 129.8, 128.7, 127.9 127.4, 126.5, 126.4, 126.2, 125.3, 125.1, 123.5, 118.9 (d, *J* = 12.3 Hz), 116.0 (d, *J* = 23.8 Hz), 110.7, 73.1, 69.7, 49.3, 44.2, 38.2; **HRMS (ESI+):** Calcd for $C_{32}H_{23}FN_2NaO_2S$ ($[M+Na]^+$): 541.1362, Found: 541.1359; **Optical rotation:** $[\alpha]_D^{21}$ +18.5 (*c* 1.0, $CHCl_3$) for an enantiomerically enriched sample with 97:3 er. The enantiomeric ratio was determined by HPLC analysis using Daicel Chiralpak AD-H column (60:40 *n*-Hexane/*i*-PrOH, 1.0 mL/min, 20 °C, 254 nm, τ_{minor} = 12.5 min, τ_{major} = 14.1 min). The stereochemistry of the product **3ab** was assigned in analogy with **3ao**. See Supporting Information: Part B for HPLC chromatograms.



Compound 3ac: Purified by silica-gel (230-400 mesh) flash column chromatography (EtOAc/CH_2Cl_2 1:10); White solid (50.0 mg, 0.096 mmol, 96% yield); **m.p.** 140-141 °C; **FT-IR (Thin film):** 3417 (w), 1721 (s), 1606 (m), 1473 (s), 1467 (s), 1367 (m); **^{1}H-NMR (400 MHz, $CDCl_3$):** δ 8.47 (br s, 1H), 7.82 (d, *J* = 7.6 Hz, 1H), 7.58-7.54 (m, 2H), 7.42 (d, *J* = 7.6 Hz, 1H), 7.35 (q, *J* = 7.4 Hz,



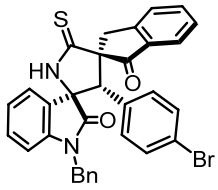
2H), 7.27-7.24 (m, 1H), 7.13 (t, *J* = 7.3 Hz, 1H), 7.04 (t, *J* = 7.5 Hz, 2H), 6.97-6.92 (m, 1H), 6.81 (td, *J* = 8.3 Hz, 2.0 Hz, 1H), 6.66-6.64 (m, 3H), 6.55 (d, *J* = 7.7 Hz, 1H), 6.38 (d, *J* = 10.3 Hz, 1H), 5.27 (d, *J* = 16.1 Hz, 1H), 5.12 (s, 1H), 4.44 (d, *J* = 16.1 Hz, 1H), 3.80 (d, *J* = 16.6 Hz, 1H), 3.50 (d, *J* = 16.6 Hz, 1H); **^{13}C-NMR (100 MHz, $CDCl_3$):** δ 208.3, 201.6, 174.5, 162.4 (d, *J* = 246.8 Hz), 152.7, 142.7, 135.9, 135.7, 134.4, 134.0, 134.0, 131.3, 130.1, 130.1, 128.8, 128.1, 127.6, 126.5 126.4, 126.2, 126.0, 125.2, 125.1, 123.7, 116.8 (d, *J* = 22.6 Hz), 115.4 (d, *J* = 20.6 Hz), 110.9, 73.1, 70.1, 58.2, 44.3, 38.2; **HRMS (ESI+):** Calcd for $C_{32}H_{23}FN_2NaO_2S$ ($[M+Na]^+$): 541.1362, Found: 541.1364; **Optical rotation:** $[\alpha]_D^{21}$ +41.6 (*c* 1.0, $CHCl_3$) for an enantiomerically enriched sample with 98:2 er. The enantiomeric ratio was determined by HPLC analysis using Daicel Chiralpak AD-H column (50:50 *n*-Hexane/EtOH, 1.0 mL/min, 20 °C, 254 nm, τ_{major} = 11.6 min, τ_{minor} = 15.6 min). The stereochemistry of the product **3ac** was assigned in analogy with **3ao**. See Supporting Information: Part B for HPLC chromatograms.

Compound 3ad: Purified by silica-gel (230-400 mesh) flash column chromatography (EtOAc/CH_2Cl_2 1:10); White solid (49.0 mg, 0.094 mmol, 94% yield); **m.p.** 250-251 °C (decomposition); **FT-IR (Thin film):** 3412 (w), 1721 (s), 1607 (m), 1467 (m), 1368 (m); **^{1}H-NMR (400 MHz, $CDCl_3$):** δ 8.26 (br s, 1H), 7.81 (d, *J* = 7.6 Hz, 1H), 7.56 (q, *J* = 7.5 Hz, 2H), 7.41 (d, *J* = 7.7 Hz, 1H), 7.38-7.31 (m, 2H), 7.26-7.23 (m, 1H), 7.14 (t, *J* = 7.3 Hz, 1H), 7.04 (t, *J* = 7.5 Hz, 2H), 6.74-6.64 (m, 4H), 6.61 (d, *J* = 7.7 Hz, 1H), 6.57 (d, *J* = 7.5 Hz, 2H), 5.28 (d, *J* = 16.0 Hz, 1H), 5.12 (s, 1H), 4.38 (d, *J* = 16.1 Hz, 1H), 3.81 (d, *J* = 16.6 Hz, 1H), 3.51 (d, *J* = 16.6 Hz, 1H); **^{13}C-NMR (100 MHz, $CDCl_3$):** δ 208.6, 201.7, 174.6, 162.7 (d, *J* = 249.9 Hz), 152.7, 142.7, 135.9, 135.7, 134.4, 132.0, 131.9, 131.1, 128.7, 128.0, 127.6, 126.4 125.1 (d, *J* = 21.5 Hz), 123.6, 115.5 (d, *J* = 21.1 Hz), 110.8, 73.3, 70.1, 58.2, 44.2, 38.1; **HRMS (ESI+):** Calcd for $C_{32}H_{23}FN_2NaO_2S$ ($[M+Na]^+$): 541.1362, Found: 541.1364; **Optical rotation:** $[\alpha]_D^{21}$ +22.8 (*c* 1.0, $CHCl_3$) for an enantiomerically enriched sample with 98:2 er. The enantiomeric ratio was determined by HPLC analysis using Daicel Chiralpak AD-H column (50:50 *n*-Hexane/EtOH, 1.0 mL/min, 20 °C, 254 nm, τ_{minor} = 10.2 min, τ_{major} = 12.2 min). The stereochemistry of the product **3ad** was assigned in analogy with **3ao**. See Supporting Information: Part B for HPLC chromatograms.

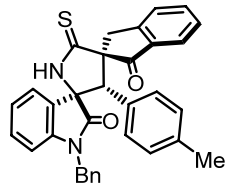
Compound 3ae: Purified by silica-gel (230-400 mesh) flash column chromatography (EtOAc/CH_2Cl_2 1:10); White solid (50.0 mg, 0.093 mmol, 93% yield); **m.p.** 128-129 °C; **FT-IR (Thin film):** 3431 (w), 1721 (s), 1641 (s), 1467 (m), 1367 (m), 1277 (m); **^{1}H-NMR (400 MHz, $CDCl_3$):** δ 8.56 (br s, 1H), 7.82 (d, *J* = 7.6 Hz, 1H), 7.59-7.54 (m, 2H), 7.43 (d, *J* = 7.6 Hz, 1H), 7.35 (q, *J* = 7.3 Hz, 2H), 7.28 (d, *J* = 7.5 Hz, 1H), 7.15-7.08 (m, 2H), 7.05 (t, *J* = 7.5

Hz, 2H), 6.88 (t, *J* = 7.9 Hz, 1H), 6.72 (s, 1H), 6.65-6.61 (m, 4H), 5.28 (d, *J* = 16.0 Hz, 1H), 5.08 (s, 1H), 4.43 (d, *J* = 16.1 Hz, 1H), 3.81 (d, *J* = 16.6 Hz, 1H), 3.48 (d, *J* = 16.6 Hz, 1H); **^{13}C-NMR (100 MHz, $CDCl_3$):** δ 208.4, 201.5, 174.5, 152.6, 142.7, 135.8, 135.7, 134.5, 134.4, 133.6, 131.3, 130.2, 129.8, 128.8, 128.7, 128.3, 128.1, 127.6, 126.4, 126.2, 125.2, 125.1, 123.7, 110.9, 73.1, 70.1, 58.2, 44.3, 38.1; **HRMS (ESI+):** Calcd for $C_{32}H_{23}ClN_2NaO_2S$ ($[M+Na]^+$): 557.1066, Found: 557.1069; **Optical rotation:** $[\alpha]_D^{23}$ +50.7 (*c* 1.0, $CHCl_3$) for an enantiomerically enriched sample with 98:2 er. The enantiomeric ratio was determined by HPLC analysis using Daicel Chiralpak AD-H column (50:50 *n*-Hexane/EtOH, 1.0 mL/min, 20 °C, 254 nm, τ_{major} = 11.6 min, τ_{minor} = 17.8 min). The stereochemistry of the product **3ae** was assigned in analogy with **3ao**. See Supporting Information: Part B for HPLC chromatograms.

Compound 3af: Purified by silica-gel (230-400 mesh) flash column chromatography (EtOAc/CH_2Cl_2 1:10); White solid (53.5 mg, 0.092 mmol, 92% yield); **m.p.** 89-90 °C; **FT-IR (Thin film):** 3274 (w), 1722 (s), 1607 (m), 1465 (w), 1368 (w); **^{1}H-NMR (400 MHz, $CDCl_3$):** δ 8.51 (br s, 1H), 7.80 (d, *J* = 7.6 Hz, 1H), 7.58-7.54 (m, 2H), 7.42 (d, *J* = 7.5 Hz, 1H), 7.38-7.31 (m, 2H), 7.25-7.23 (m, 1H), 7.15 (t, *J* = 7.1 Hz, 1H), 7.11-7.05 (m, 4H), 6.62-6.55 (m, 5H), 5.31 (d, *J* = 16.1 Hz, 1H), 5.05 (s, 1H), 4.38 (d, *J* = 16.1 Hz, 1H), 3.81 (d, *J* = 16.7 Hz, 1H), 3.48 (d, *J* = 16.7 Hz, 1H); **^{13}C-NMR (100 MHz, $CDCl_3$):** δ 208.5, 201.6, 174.5, 152.6, 142.6, 135.8, 135.7, 134.3, 131.8, 131.8, 131.2, 130.4, 128.8, 128.1, 127.6, 126.4, 126.3, 126.2, 125.2, 125.0, 123.7, 123.0, 110.8, 73.2, 70.0, 58.4, 44.2, 38.0; **HRMS (ESI+):** Calcd for $C_{32}H_{23}BrN_2NaO_2S$ ($[M+Na]^+$): 601.0561, Found: 601.0563; **Optical rotation:** $[\alpha]_D^{21}$ +38.6 (*c* 1.0, $CHCl_3$) for an enantiomerically enriched sample with 97:3 er. The enantiomeric ratio was determined by HPLC analysis using Daicel Chiralpak AD-H column (50:50 *n*-Hexane/EtOH, 1.0 mL/min, 20 °C, 254 nm, τ_{minor} = 11.3 min, τ_{major} = 14.5 min). The stereochemistry of the product **3af** was assigned in analogy with **3ao**. See Supporting Information: Part B for HPLC chromatograms.

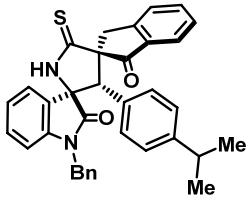


Compound 3ag: Purified by silica-gel (230-400 mesh) flash column chromatography (EtOAc/CH_2Cl_2 1:10); White solid (43.5 mg, 0.085 mmol, 85% yield); **m.p.** 120-121 °C; **FT-IR (Thin film):** 3431 (w), 1721 (s), 1638 (m), 1615 (m), 1471 (m), 1471 (m), 1371 (m); **^{1}H-NMR (400 MHz, $CDCl_3$):** δ 8.45 (br s, 1H), 7.80 (d, *J* = 7.6 Hz, 1H), 7.59 (d, *J* = 7.2 Hz, 1H), 7.54 (t, *J* = 7.4 Hz, 1H), 7.41 (d, *J* = 7.6 Hz, 1H), 7.34 (t, *J* = 7.1 Hz, 1H), 7.29 (d, *J* = 7.5 Hz, 1H), 7.26-7.23 (m, 1H), 7.11 (t, *J* = 7.3 Hz, 1H), 6.98 (d, *J* = 7.5 Hz, 2H), 6.77 (d, *J* = 7.9 Hz, 2H), 6.63 (d, *J* = 8.0 Hz, 2H), 6.55 (t, *J* = 8.4 Hz, 3H), 5.31 (d, *J* = 16.1 Hz, 1H), 5.10 (s, 1H), 4.38 (d, *J* = 16.1 Hz, 1H), 3.80 (d, *J* = 16.6 Hz, 1H), 3.59 (d, *J* = 16.6 Hz, 1H), 2.17 (s, 3H); **^{13}C-NMR (100 MHz, $CDCl_3$):** δ 209.1, 201.9, 174.6, 152.9, 142.7, 138.2, 136.0, 135.5, 134.4,

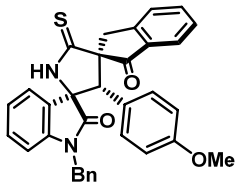


131.0, 130.2, 129.3, 128.6, 128.3, 127.9, 127.4, 126.8, 126.4, 126.4, 125.2, 125.1, 123.4, 110.6, 73.4, 70.2, 58.9, 44.2, 38.3, 21.1; **HRMS (ESI+):** Calcd for $C_{33}H_{26}N_2NaO_2S$ ($[M+Na]^+$): 537.1613, Found: 537.1614; **Optical rotation:** $[\alpha]_D^{21}$ +36.8 (*c* 1.0, $CHCl_3$) for an enantiomerically enriched sample with 97.5:2.5 er. The enantiomeric ratio was determined by HPLC analysis using Daicel Chiralpak AD-H column (50:50 *n*-Hexane/EtOH, 1.0 mL/min, 20 °C, 254 nm, τ_{major} = 12.2 min, τ_{minor} = 16.6 min). The stereochemistry of the product **3ag** was assigned in analogy with **3ao**. See Supporting Information: Part B for HPLC chromatograms.

Compound 3ah: Purified by silica-gel (230-400 mesh) flash column chromatography (EtOAc/CH_2Cl_2 1:10); White solid (51.0 mg, 0.094 mmol, 94% yield); **m.p.** 163-164 °C; **FT-IR (Thin film):** 3416 (w), 1722 (s), 1608 (m), 1467 (s), 1367 (m), 1010 (m); **^{1}H-NMR (400 MHz, $CDCl_3$):** δ 8.46 (br s, 1H), 7.82 (d, *J* = 7.6 Hz, 1H), 7.58 (d, *J* = 7.2 Hz, 1H), 7.54 (d, *J* = 7.4 Hz, 1H), 7.41 (d, *J* = 7.6 Hz, 1H), 7.37-7.30 (m, 2H), 7.23 (d, *J* = 7.4 Hz, 1H), 7.10 (t, *J* = 7.3 Hz, 1H), 7.01 (t, *J* = 7.5 Hz, 2H), 6.81 (d, *J* = 8.2 Hz, 2H), 6.67-6.60 (m, 5H), 5.31 (d, *J* = 16.1 Hz, 1H), 5.15 (s, 1H), 4.42 (d, *J* = 16.1 Hz, 1H), 3.77 (d, *J* = 16.5 Hz, 1H), 3.56 (d, *J* = 16.5 Hz, 1H); **^{13}C-NMR (100 MHz, $CDCl_3$):** δ 208.8, 201.9, 174.7, 152.9, 148.8, 142.7, 136.1, 135.4, 134.5, 130.9, 130.0, 128.7, 128.7, 127.9, 127.4, 126.7, 126.6, 126.5, 126.4, 125.3, 125.0, 123.5, 110.6, 73.3, 70.4, 58.3, 44.3, 38.3, 33.5, 23.8, 23.7; **HRMS (ESI+):** Calcd for $C_{35}H_{30}N_2NaO_2S$ ($[M+Na]^+$): 565.1926, Found: 565.1926; **Optical rotation:** $[\alpha]_D^{21}$ +42.7 (*c* 1.0, $CHCl_3$) for an enantiomerically enriched sample with 96:4 er. The enantiomeric ratio was determined by HPLC analysis using Daicel Chiralpak AD-H column (50:50 *n*-Hexane/EtOH, 1.0 mL/min, 20 °C, 254 nm, τ_{minor} = 6.6 min, τ_{major} = 9.2 min). The stereochemistry of the product **3ah** was assigned in analogy with **3ao**. See Supporting Information: Part B for HPLC chromatograms.

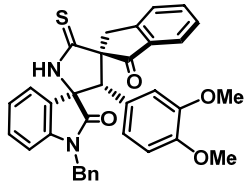


Compound 3ai: Purified by silica-gel (230-400 mesh) flash column chromatography (EtOAc/CH_2Cl_2 1:10); White solid (50.0 mg, 0.094 mmol, 94% yield); **m.p.** 150-151 °C; **FT-IR (Thin film):** 3336 (w), 1721 (s), 1608 (m), 1466 (m), 1366 (m), 1253 (m); **^{1}H-NMR (400 MHz, $CDCl_3$):** δ 8.26 (br s, 1H), 7.80 (d, *J* = 7.6 Hz, 1H), 7.58 (d, *J* = 7.3 Hz, 1H), 7.54 (t, *J* = 7.5 Hz, 1H), 7.41 (d, *J* = 7.6Hz, 1H), 7.37-7.22 (m, 3H), 7.12 (t, *J* = 7.2 Hz, 1H), 7.00 (t, *J* = 7.5 Hz, 2H), 6.66 (d, *J* = 8.6 Hz, 2H), 6.58-6.48 (m, 5H), 5.29 (d, *J* = 16.1 Hz, 1H), 5.08 (s, 1H), 4.36 (d, *J* = 16.2 Hz, 1H), 3.79 (d, *J* = 16.6 Hz, 1H), 3.64 (s, 3H), 3.58 (d, *J* = 16.6 Hz, 1H); **^{13}C-NMR (100 MHz, $CDCl_3$):** δ 209.2, 202.0, 174.6, 159.7, 152.9, 142.7, 136.0, 135.5, 134.4, 131.5, 131.0, 128.7, 128.0, 127.5, 126.7, 126.4, 126.4, 125.2, 125.0, 123.4, 123.2, 114.0, 110.7, 73.5, 70.2, 58.7, 55.2, 44.1, 38.2; **HRMS (ESI+):** Calcd for $C_{33}H_{26}N_2NaO_3S$ ($[M+Na]^+$):

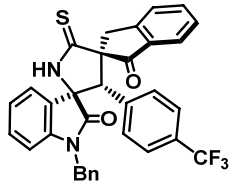


553.1562, Found: 553.1564; **Optical rotation:** $[\alpha]_D^{21}$ +25.1 (*c* 1.0, $CHCl_3$) for an enantiomerically enriched sample with 94.5:5.5 er. The enantiomeric ratio was determined by HPLC analysis using Daicel Chiralpak AD-H column (50:50 *n*-Hexane/EtOH, 1.0 mL/min, 20 °C, 254 nm, τ_{minor} = 9.4 min, τ_{major} = 14.6 min). The stereochemistry of the product **3ai** was assigned in analogy with **3ao**. See Supporting Information: Part B for HPLC chromatograms.

Compound 3aj: Purified by silica-gel (230-400 mesh) flash column chromatography (EtOAc/CH_2Cl_2 1:10); White solid (52.0 mg, 0.093 mmol, 93% yield); **m.p.** 138-139 °C; **FT-IR (Thin film):** 3437 (w), 1721 (s), 1609 (m), 1463 (s), 1368 (m), 1272 (m); **^{1}H-NMR (400 MHz, $CDCl_3$):** δ 8.45 (br s, 1H), 7.81 (d, *J* = 7.6 Hz, 1H), 7.59 (d, *J* = 7.4 Hz, 2H), 7.54 (t, *J* = 7.5 Hz, 1H), 7.41 (d, *J* = 7.6 Hz, 1H), 7.34 (t, *J* = 7.4 Hz, 1H), 7.29 (dt, *J* = 7.7 Hz, 1.2 Hz, 1H), 7.25- 7.23 (m, 1H), 7.11 (t, *J* = 7.4 Hz, 1H), 6.99 (t, *J* = 7.6 Hz, 2H), 6.59 (d, *J* = 7.6 Hz, 1H), 6.56 (d, *J* = 7.5 Hz, 2H), 6.45 (d, *J* = 8.4 Hz, 1H), 6.35 (dd, *J* = 8.4 Hz, 1.9 Hz, 1H), 6.15 (d, *J* = 1.9 Hz, 1H), 5.28 (d, *J* = 16.1 Hz, 1H), 5.06 (s, 1H), 4.38 (d, *J* = 16.1 Hz, 1H), 3.78 (d, *J* = 16.5 Hz, 1H), 3.70 (s, 3H), 3.55 (d, *J* = 16.5 Hz, 1H), 3.27 (s, 3H) ; **^{13}C-NMR (100 MHz, $CDCl_3$):** δ 209.1, 202.1, 174.5, 152.9, 149.1, 148.5, 142.9, 136.0, 135.6, 134.3, 130.9, 128.7, 128.0, 127.6, 127.0, 126.5, 126.4, 125.2, 125.0, 123.7, 123.4, 123.1, 112.7, 110.9, 110.8, 73.3, 70.3, 58.7, 55.7, 55.7, 44.2, 38.4; **HRMS (ESI+):** Calcd for $C_{34}H_{28}N_2NaO_4S$ ($[M+Na]^+$): 583.1667, Found: 583.1668; **Optical rotation:** $[\alpha]_D^{21}$ +32.1 (*c* 1.0, $CHCl_3$) for an enantiomerically enriched sample with 95:5 er. The enantiomeric ratio was determined by HPLC analysis using Daicel Chiralpak AD-H column (50:50 *n*-Hexane/EtOH, 1.0 mL/min, 20 °C, 254 nm, τ_{minor} = 11.7 min, τ_{major} = 13.8 min). The stereochemistry of the product **3aj** was assigned in analogy with **3ao**. See Supporting Information: Part B for HPLC chromatograms.



Compound 3ak: Purified by silica-gel (230-400 mesh) flash column chromatography (EtOAc/CH_2Cl_2 1:10); White solid (50.0 mg, 0.088 mmol, 88% yield); **m.p.** 90-91 °C; **FT-IR (Thin film):** 3242 (w), 1715 (s), 1607 (m), 1463 (s), 1321 (s), 1116 (s), 748 (s); **^{1}H-NMR (400 MHz, $CDCl_3$):** δ 8.33 (br s, 1H), 7.82 (d, *J* = 7.6 Hz, 1H), 7.60-7.55 (m, 2H), 7.41 (d, *J* = 7.8 Hz, 1H), 7.38- 7.34 (m, 2H), 7.28-7.21 (m, 3H), 7.12 (t, 7.3 Hz, 1H), 7.01 (t, *J* = 7.5 Hz, 2H), 6.85 (d, *J* = 8.1 Hz, 2H), 6.66 (d, *J* = 7.8 Hz, 1H), 6.62 (d, *J* = 7.5 Hz, 2H), 5.27 (d, *J* = 15.8 Hz, 1H), 5.20 (s, 1H), 4.40 (d, *J* = 15.8 Hz, 1H), 3.82 (d, *J* = 16.6 Hz, 1H), 3.45 (d, *J* = 16.6 Hz, 1H); **^{13}C-NMR (100 MHz, $CDCl_3$):** δ 208.2, 201.5, 174.4, 152.5, 142.7, 135.8, 134.4, 131.3, 130.8, 130.5, 128.7, 128.2, 127.7, 126.4, 126.2, 125.5, 125.4, 125.3, 125.1, 123.8, 110.9, 73.0, 70.1, 58.2, 44.3, 38.1; **HRMS (ESI+):** Calcd for $C_{33}H_{23}F_3N_2NaO_2S$ ($[M+Na]^+$): 591.1330, Found: 591.1332; **Optical rotation:** $[\alpha]_D^{21}$ +35.1 (*c* 1.0, $CHCl_3$) for an enantiomerically enriched



sample with 99:1 er. The enantiomeric ratio was determined by HPLC analysis using Daicel Chiralpak AD-H column (50:50 *n*-Hexane/EtOH, 1.0 mL/min, 20 °C, 254 nm, τ_{minor} = 6.5 min, τ_{major} = 9.8 min). The stereochemistry of the product **3ak** was assigned in analogy with **3ao**. See Supporting Information: Part B for HPLC chromatograms.

Compound 3al: Purified by silica-gel (230-400 mesh) flash column chromatography (EtOAc/CH_2Cl_2 1:10); White solid (53.0 mg, 0.097 mmol, 97% yield); **m.p.** 127-128 °C; **FT-IR (Thin film):** 3436 (w), 1723 (s), 1606 (m), 1526 (s), 1413 (m), 1334 (s), 1019 (m); **^{1}H-NMR (400 MHz, $CDCl_3$):** δ 8.81 (br s, 1H), 7.94 (dt, *J* = 7.3 Hz, 2.2 Hz, 1H), 7.82 (d, *J* = 7.6 Hz, 1H), 7.64 (dd, *J* = 7.4 Hz, 0.8 Hz, 1H), 7.56 (td, *J* = 7.4 Hz, 1.0 Hz, 1H), 7.46-7.32 (m, 5H), 7.20-7.16 (m, 2H), 7.10 (d, *J* = 7.4 Hz, 1H), 6.99 (t, *J* = 7.5 Hz, 2H), 6.72 (d, *J* = 7.5 Hz, 1H), 6.68 (d, *J* = 7.4 Hz, 2H), 5.22-5.18 (m, 2H), 4.48 (d, *J* = 15.8 Hz, 1H), 3.86 (d, *J* = 16.8 Hz, 1H), 3.41 (d, *J* = 16.8 Hz, 1H); **^{13}C-NMR (100 MHz, $CDCl_3$):** δ 207.8, 201.3, 174.2, 152.4, 147.9, 142.5, 136.8, 135.9, 135.7, 134.5, 133.7, 131.7, 129.7, 128.7, 128.3, 127.8, 126.6, 126.5, 125.6, 125.3, 125.2, 124.1, 124.0, 123.4, 111.0, 72.8, 70.0, 57.7, 44.4, 38.0; **HRMS (ESI+):** Calcd for $C_{32}H_{23}N_3NaO_4S$ ($[M+Na]^+$): 568.1307, Found: 568.1309; **Optical rotation:** $[\alpha]_D^{21}$ +86.7 (*c* 1.0, $CHCl_3$) for an enantiomerically enriched sample with 98.5:1.5 er. The enantiomeric ratio was assigned in HPLC analysis using Daicel Chiralpak AD-H column (50:50 *n*-Hexane/EtOH, 1.0 mL/min, 20 °C, 254 nm, τ_{minor} = 12.8 min, τ_{major} = 18.4 min). The stereochemistry of the product **3al** was assigned in analogy with **3ao**. See Supporting Information: Part B for HPLC chromatograms.

Compound 3am: Purified by silica-gel (230-400 mesh) flash column chromatography (EtOAc/CH_2Cl_2 1:10); White solid (50.0 mg, 0.092 mmol, 92% yield); **m.p.** 198-199 °C; **FT-IR (Thin film):** 3337 (w), 1722 (s), 1605 (m), 1521 (m), 1468 (m), 1349 (s); **^{1}H-NMR (400 MHz, $CDCl_3$):** δ 8.66 (br s, 1H), 7.82 (d, *J* = 7.6 Hz, 1H), 7.75 (d, *J* = 8.6 Hz, 2H), 7.57 (q, *J* = 7.4 Hz, 2H), 7.42-7.36 (m, 3H), 7.29 (t, *J* = 7.5 Hz, 1H), 7.11 (t, *J* = 7.3 Hz, 1H), 6.98 (t, *J* = 7.5 Hz, 2H), 6.85 (d, *J* = 8.6 Hz, 2H), 6.73 (m, 3H), 5.24-5.20 (m, 2H), 4.46 (d, *J* = 15.8 Hz, 1H), 3.85 (d, *J* = 16.7 Hz, 1H), 3.41 (d, *J* = 16.7 Hz, 1H); **^{13}C-NMR (100 MHz, $CDCl_3$):** δ 207.9, 201.3, 174.1, 152.3, 147.8, 142.6, 139.0, 136.0, 135.7, 134.5, 131.6, 130.9, 128.7, 128.3, 127.9, 126.8, 126.4, 125.8, 125.3, 125.2, 123.9, 123.5, 111.0, 72.8, 70.0, 58.1, 44.4, 38.1; **HRMS (ESI+):** Calcd for $C_{32}H_{23}N_3NaO_4S$ ($[M+Na]^+$): 568.1307, Found: 568.1305; **Optical rotation:** $[\alpha]_D^{22}$ +51.5 (*c* 1.0, acetone) for an enantiomerically enriched sample with 98.5:1.5 er. The enantiomeric ratio was determined by HPLC analysis using Daicel Chiralpak AD-H column (50:50 *n*-Hexane/EtOH, 1.0 mL/min, 20 °C, 254 nm, τ_{minor} = 10.7 min, τ_{major} = 23.1 min). The

stereochemistry of the product **3am** was assigned in analogy with **3ao**. See Supporting Information: Part B for HPLC chromatograms.

Compound 3an: Purified by silica-gel (230-400 mesh) flash column chromatography (EtOAc/CH_2Cl_2 1:10); White solid (56.0 mg, 0.095 mmol, 95% yield); **m.p.** 133-134 °C; **FT-IR (Thin film):** 2923 (w), 2852 (m), 1729 (s), 1608 (m), 1496 (m), 1464 (s), 1123 (m); **^{1}H-NMR (400 MHz, $CDCl_3$):** δ 8.50 (br s, 1H), 7.77 (d, *J* = 7.6 Hz, 1H), 7.61 (t, *J* = 7.3 Hz, 1H), 7.46 (d, *J* = 7.6 Hz, 2H), 7.38 (t, *J* = 7.5 Hz, 1H), 7.25-7.23 (m, 3H), 7.19 (d, *J* = 8.1 Hz, 1H), 7.17-7.15 (m, 2H), 6.99 (t, *J* = 7.5 Hz, 1H), 6.67 (d, *J* = 7.8 Hz, 1H), 5.68 (s, 1H), 5.25 (d, *J* = 15.5 Hz, 1H), 4.51 (d, *J* = 15.5 Hz, 1H), 3.96 (d, *J* = 16.9 Hz, 1H), 3.16 (d, *J* = 16.9 Hz, 1H); **^{13}C-NMR (100 MHz, $CDCl_3$):** δ 205.7, 199.4, 175.2, 152.8, 142.5, 135.8, 135.3, 134.4, 131.3, 128.9, 128.1, 128.0, 127.4, 126.2, 126.1, 125.6, 125.2, 123.0, 109.7, 73.2, 70.8, 47.5, 44.7, 39.4 ; **HRMS (ESI+):** Calcd for $C_{32}H_{19}F_5N_2NaO_2S$ ($[M+Na]^+$): 613.0985, Found: 613.0983; **Optical rotation:** $[\alpha]_D^{22}$ +44.8 (*c* 1.0, $CHCl_3$) for an enantiomerically enriched sample with 96:4 er. The enantiomeric ratio was determined by HPLC analysis using Daicel Chiralpak AD-H column (50:50 *n*-Hexane/EtOH, 1.0 mL/min, 20 °C, 254 nm, τ_{major} = 6.5 min, τ_{minor} = 8.4 min). The stereochemistry of the product **3an** was assigned in analogy with **3ao**. See Supporting Information: Part B for HPLC chromatograms.

Compound 3ao: Purified by silica-gel (230-400 mesh) flash column chromatography (EtOAc/CH_2Cl_2 1:10); Yellow solid (46.0 mg, 0.094 mmol, 94% yield); **m.p.** 195-196 °C; **FT-IR (Thin film):** 3402 (w), 1724 (s), 1607 (m), 1468 (m), 1369 (m), 1017 (m); **^{1}H-NMR (400 MHz, $CDCl_3$):** δ 8.44 (br s, 1H), 7.87 (d, *J* = 7.6 Hz, 1H), 7.59 (t, *J* = 7.4 Hz, 1H), 7.45 (t, *J* = 8.4 Hz, 2H), 7.39 (t, *J* = 7.4 Hz, 1H), 7.29 (d, *J* = 7.5 Hz, 1H), 7.20-7.14 (m, 5H), 7.05-7.03 (m, 2H), 6.93-6.92 (m, 1H), 6.71 (d, *J* = 7.7 Hz, 1H), 5.94-5.92 (m, 1H), 5.26 (d, *J* = 15.0 Hz, 1H), 5.22 (s, 1H), 4.61 (d, *J* = 15.9 Hz, 1H), 3.77 (d, *J* = 16.8 Hz, 1H), 3.57 (d, *J* = 16.7 Hz, 1H); **^{13}C-NMR (100 MHz, $CDCl_3$):** δ 207.9, 201.5, 173.9, 152.9, 146.6, 142.9, 142.7, 135.9, 135.6, 134.8, 131.0, 128.9, 128.0, 127.8, 127.1, 126.3, 126.0, 125.6, 125.3, 123.4, 110.4, 109.9, 109.6, 71.7, 69.2, 52.4, 44.5, 39.3; **HRMS (ESI+):** Calcd for $C_{30}H_{22}N_2NaO_3S$ ($[M+Na]^+$): 513.1249, Found: 513.1246; **Optical rotation:** $[\alpha]_D^{21}$ +35.3 (*c* 1.0, $CHCl_3$) for an enantiomerically enriched sample with 90:10 er. The enantiomeric ratio was determined by HPLC analysis using Daicel Chiralpak AD-H column (50:50 *n*-Hexane/EtOH, 1.0 mL/min, 20 °C, 254 nm, τ_{minor} = 10.4 min, τ_{major} = 12.7 min). The stereochemistry of the product **3ao** was assigned in single crystal X-Ray diffraction analysis. See Supporting Information: Part B for HPLC chromatograms.

Compound 3ap: Purified by silica-gel (230-400 mesh) flash column chromatography (EtOAc/CH_2Cl_2 1:10); Yellow solid (43.5 mg, 0.086 mmol, 86% yield); **m.p.** 185-186 °C (decomposition); **FT-IR (Thin film):** 3334 (w), 1720 (s), 1608 (m), 1469 (m), 1368 (m); **^{1}H-NMR (400 MHz, $CDCl_3$):** δ 8.44 (br s, 1H), 7.83 (d, *J* = 7.6 Hz, 1H), 7.57-7.54 (m, 2H), 7.42 (d, *J* = 7.6 Hz, 1H), 7.38-7.33 (m, 2H), 7.24-7.22 (m, 1H), 7.15-7.12 (m, 1H), 7.07 (m, 2H), 6.96 (d, *J* = 5.0 Hz, 1H), 6.71-6.69 (m, 3H), 6.63 (d, *J* = 7.8 Hz, 1H), 6.54 (d, *J* = 3.3 Hz, 1H), 5.47 (s, 1H), 5.30 (d, *J* = 16.0 Hz, 1H), 4.47 (d, *J* = 16.0 Hz, 1H), 3.79 (d, *J* = 16.6 Hz, 1H), 3.65 (d, *J* = 16.6 Hz, 1H); **^{13}C-NMR (100 MHz, $CDCl_3$):** δ 208.4, 201.7, 174.1, 153.0, 143.4, 136.0, 135.6, 134.5, 132.6, 131.5, 129.2, 128.8, 128.0, 127.6, 126.6, 126.5, 126.4, 126.4, 125.7, 125.1, 123.6, 110.7, 72.9, 70.3, 55.1 44.3, 39.1; **HRMS (ESI+):** Calcd for $C_{30}H_{22}N_2NaO_2S$ ($[M+Na]^+$): 529.1020, Found: 529.1019; **Optical rotation:** $[\alpha]_D^{21}$ +27.6 (*c* 1.0, $CHCl_3$) for an enantiomerically enriched sample with 93:7 er. The enantiomeric ratio was determined by HPLC analysis using Daicel Chiralpak AD-H column (50:50 *n*-Hexane/EtOH, 1.0 mL/min, 20 °C, 254 nm, τ_{major} = 12.6 min, τ_{minor} = 14.7 min). The stereochemistry of the product **3ap** was assigned in analogy with **3ao**. See Supporting Information: Part B for HPLC chromatograms.

Compound 3aq: Purified by silica-gel (230-400 mesh) flash column chromatography (EtOAc/CH_2Cl_2 1:10); White solid (51.0 mg, 0.097 mmol, 97% yield); **m.p.** 108-109 °C; **FT-IR (Thin film):** 3028 (w), 2923 (m), 1721 (s), 1608 (m), 1469 (s), 1367 (s); **^{1}H-NMR (400 MHz, $CDCl_3$):** δ 8.66 (br s, 1H), 7.83 (d, *J* = 7.7 Hz, 1H), 7.60-7.56 (m,1H), 7.48 (t, *J* = 7.5 Hz, 2H), 7.36 (d, *J* = 7.4 Hz, 1H), 7.30 (t, *J* = 7.4 Hz, 1H), 7.22-7.20 (m, 1H), 7.15-7.12 (m, 3H), 7.08 (d, *J* = 7.6 Hz, 2H), 7.00 (t, *J* = 7.4 Hz, 1H), 6.92-6.90 (m, 2H), 6.80 (t, *J* = 7.6 Hz, 2H), 6.66 (d, J = 7.7 Hz, 1H), 6.45 (d, *J* = 15.5 Hz, 1H), 5.53 (d, *J* = 15.5 Hz, 9.9 Hz, 1H), 5.37 (d, *J* = 16.1 Hz, 1H), 4.57 (d, *J* = 6.5 Hz, 1H), 4.54 (d, *J* = 12.8 Hz, 1H), 3.79 (d, *J* = 16.8 Hz, 1H), 3.62 (d, *J* = 16.7 Hz, 1H); **^{13}C-NMR (100 MHz, $CDCl_3$):** δ 208.7, 202.1, 174.7, 152.8, 142.4, 137.6, 136.2, 135.7, 134.6, 130.8, 128.7, 128.6, 128.4, 128.1, 127.6, 126.7, 126.7, 126.4, 125.8, 125.1, 124.8, 123.6, 119.0, 110.7, 73.3, 70.1, 56.9, 44.4 38.0; **HRMS (ESI+):** Calcd for $C_{31}H_{26}N_2NaO_3S$ ($[M+Na]^+$): 549.1613, Found: 549.1614; **Optical rotation:** $[\alpha]_D^{22}$ +28.8 (*c* 1.0, $CHCl_3$) for an enantiomerically enriched sample with 95.5:4.5 er. The enantiomeric ratio was determined by HPLC analysis using Daicel Chiralpak AD-H column (60:40 *n*-Hexane/ *i*-PrOH, 1.0 mL/min, 20 °C, 254 nm, τ_{minor} = 21.7 min, τ_{major} = 23.8 min). The stereochemistry of the product **3aq** was assigned in analogy with **3ao**. See Supporting Information: Part B for HPLC chromatograms.

Compound 3ar: Purified by silica-gel (230-400 mesh) flash column chromatography (EtOAc/CH_2Cl_2 1:10); White solid (45.0 mg, 0.094 mmol, 94% yield); **m.p.** 186-187 °C (decomposition); **FT-IR (Thin film):** 3348 (w), 1722 (s), 1608 (m), 1471 (m), 1364 (m), 1019 (m); **^{1}H-NMR (400 MHz, $CDCl_3$):** δ 8.33 (br s, 1H), 7.86 (d, *J* = 7.6 Hz, 1H), 7.64 (d, *J* = 7.3 Hz, 1H), 7.53 (d, *J* = 7.6 Hz, 1H), 7.43 (t, *J* = 7.4 Hz, 1H), 7.36-7.24 (m, 7H), 7.14 (t, *J* = 7.5 Hz, 1H), 6.88 (d, *J* = 7.8 Hz, 1H), 5.17 (d, *J* = 15.4 Hz, 1H), 4.74 (d, *J* = 15.4 Hz, 1H), 3.97 (t, *J* = 7.5 Hz, 1H), 3.63 (d, *J* = 16.9 Hz, 1H), 3.47 (d, *J* = 16.9 Hz, 1H), 0.90-0.76 (m, 2H), 0.71-0.61 (m, 1H), 0.54 (d, *J* = 6.3 Hz, 3H), 0.50 (d, *J* = 6.2 Hz, 3H); **^{13}C-NMR (100 MHz, $CDCl_3$):** δ 208.7, 202.4, 174.6, 152.9, 142.7, 136.1, 135.5, 135.4, 130.6, 128.9, 128.1, 128.1, 127.9, 127.9, 126.4, 125.6, 125.2, 123.4, 110.2, 72.9, 69.2, 49.1, 44.7, 37.5, 36.0, 25.5, 22.8, 22.2; **HRMS (ESI+):** Calcd for $C_{30}H_{28}N_2NaO_2S$ ($[M+Na]^+$): 503.1769, Found: 503.1768; **Optical rotation:** $[\alpha]_D^{21}$ +39.7 (*c* 1.0, $CHCl_3$) for an enantiomerically enriched sample with 83:17 er. The enantiomeric ratio was determined by HPLC analysis using Daicel Chiralpak AD-H column (50:50 *n*-Hexane/EtOH, 1.0 mL/min, 20 °C, 254 nm, τ_{minor} = 6.2 min, τ_{major} = 9.3 min). The stereochemistry of the product **3ar** was assigned in analogy with **3ao**. See Supporting Information: Part B for HPLC chromatograms.

Compound 3as: Purified by silica-gel (230-400 mesh) flash column chromatography (EtOAc/CH_2Cl_2 1:10); White solid (41.5 mg, 0.097 mmol, 97% yield); **m.p.** 139-140 °C; **FT-IR (Thin film):** 3344 (w), 1723 (s), 1609 (m), 1486 (m), 1364 (s); **^{1}H-NMR (400 MHz, $CDCl_3$):** δ 8.54 (br s, 1H), 7.83 (d, *J* = 7.6 Hz, 1H), 7.63 (t, *J* = 7.1 Hz, 1H), 7.49 (d, *J* = 7.6 Hz, 1H), 7.41 (t, *J* = 7.4 Hz, 1H), 7.36 (d, *J* = 7.3 Hz, 1H), 7.32-7.22 (m, 6H), 7.11 (t, *J* = 7.4 Hz, 1H), 6.79 (d, *J* = 7.7 Hz, 1H), 5.06 (d, *J* = 15.7 Hz, 1H), 4.84 (d, *J* = 15.7 Hz, 1H), 4.05 (d, *J* = 16.6 Hz, 1H), 3.52 (d, *J* = 13.2 Hz, 1H), 3.34 (d, *J* = 16.7 Hz, 1H), 2.33 (d, *J* = 13.2 Hz, 1H); **^{13}C-NMR (100 MHz, $CDCl_3$):** δ 207.8, 201.9, 174.6, 152.5, 142.0, 135.8, 135.6, 135.2, 130.5, 129.1, 129.0, 128.1, 127.9, 127.5, 126.3, 125.2, 123.8, 123.8, 110.3, 69.4, 66.6, 45.2, 44.9, 44.6; **HRMS (ESI+):** Calcd for $C_{26}H_{20}N_2NaO_2S$ ($[M+Na]^+$): 447.1143, Found: 447.1147; **Optical rotation:** $[\alpha]_D^{22}$ +43.2 (*c* 1.0, $CHCl_3$) for an enantiomerically enriched sample with 98.5:1.5 er. The enantiomeric ratio was determined by HPLC analysis using Daicel Chiralpak AD-H column (50:50 *n*-Hexane/EtOH, 1.0 mL/min, 20 °C, 254 nm, τ_{minor} = 12.3 min, τ_{major} = 18.6 min). The stereochemistry of the product **3as** was assigned in analogy with **3ao**. See Supporting Information: Part B for HPLC chromatograms.

Compound 3at: Purified by silica-gel (230-400 mesh) flash column chromatography (EtOAc/CH_2Cl_2 1:10); White solid (51.0 mg, 0.095 mmol, 95% yield); **m.p.** 122-123 °C; **FT-IR (Thin film):** 3398 (w), 1724 (s), 1602 (m), 1467 (m), 1370 (m), 1219 (s), 1018 (s); **^{1}H-NMR (400 MHz, $CDCl_3$):** δ 8.76 (br s, 1H), 7.71 (d, *J* = 8.2 Hz, 1H), 7.56 (d, *J* = 7.1 Hz, 1H), 7.39 (s, 1H), 7.33-7.24 (m, 3H), 7.14 (t, *J* = 7.5 Hz, 1H), 7.08 (t, *J* = 7.4 Hz, 1H), 6.97 (t, *J* = 7.6 Hz, 4H), 6.72 (d, *J* = 7.7 Hz, 2H), 6.58 (d, *J* = 7.7 Hz, 1H), 6.55 (d, *J* = 7.6 Hz, 2H), 5.30 (d, *J* = 16.3 Hz, 1H), 5.08 (s, 1H), 4.39 (d, *J* = 16.2 Hz, 1H), 3.78 (d, *J* = 16.9 Hz, 1H), 3.52 (d, *J* = 16.9 Hz, 1H); **^{13}C-NMR (100 MHz, $CDCl_3$):** δ 208.2, 200.5, 174.6, 154.2, 142.7, 142.1, 134.4, 134.3, 131.2, 131.1, 130.2, 128.8, 128.8, 128.7, 128.5, 127.4, 126.6, 126.4, 126.3, 126.0, 125.2, 123.6, 110.8, 73.4, 70.4, 58.8, 44.2, 37.8; **HRMS (ESI+):** Calcd for $C_{32}H_{23}ClN_2NaO_2S$ ($[M+Na]^+$): 557.1066, Found: 557.1068; **Optical rotation:** $[\alpha]_D^{22}$ +74.9 (*c* 1.0, $CHCl_3$) for an enantiomerically enriched sample with 99:1 er. The enantiomeric ratio was determined by HPLC analysis using Daicel Chiralpak AD-H column (40:60 *n*-Hexane/EtOH, 1.0 mL/min, 20 °C, 254 nm, τ_{major} = 11.7 min, τ_{minor} = 35.2 min). The stereochemistry of the product **3at** was assigned in analogy with **3ao**. See Supporting Information: Part B for HPLC chromatograms.

Compound 3au: Purified by silica-gel (230-400 mesh) flash column chromatography (EtOAc/CH_2Cl_2 1:10); White solid (56.0 mg, 0.095 mmol, 95% yield); **m.p.** 115-116 °C; **FT-IR (Thin film):** 3269 (w), 1723 (s), 1596 (m). 1487 (m), 1467 (s), 1370 (s), 1219 (s), 1019 (m); **^{1}H-NMR (400 MHz, $CDCl_3$):** δ 8.80 (br s, 1H), 7.63 (d, *J* = 8.2 Hz, 1H), 7.57-7.56 (m, 2H), 7.45 (d, *J* = 8.2 Hz, 1H), 7.33-7.24 (m, 2H), 7.13 (t, *J* = 7.5 Hz, 1H), 7.08 (d, *J* = 7.5 Hz, 1H), 6.97 (d, *J* = 7.6 Hz, 4H), 6.71 (d, *J* = 7.6 Hz, 2H), 6.57 (d, *J* = 7.5 Hz, 1H), 6.52 (d, *J* = 7.5 Hz, 2H), 5.29 (d, *J* = 16.3 Hz, 1H), 5.08 (s, 1H), 4.38 (d, *J* = 16.3 Hz, 1H), 3.79 (d, *J* = 16.9 Hz, 1H), 3.54 (d, *J* = 16.9 Hz, 1H); **^{13}C-NMR (100 MHz, $CDCl_3$):** δ 208.2, 200.7, 174.6, 154.3, 142.6, 134.8, 134.3, 131.6, 131.2, 131.1, 130.2, 129.7, 128.7, 128.7, 128.6, 127.4, 126.4, 126.3, 126.0, 125.2, 123.6, 110.8, 73.4, 70.3, 58.8, 44.2, 37.7; **HRMS (ESI+):** Calcd for $C_{32}H_{23}BrN_2NaO_2S$ ($[M+Na]^+$): 601.0561, Found: 601.0561; **Optical rotation:** $[\alpha]_D^{22}$ +84.6 (*c* 1.0, $CHCl_3$) for an enantiomerically enriched sample with 98.5:1.5 er. The enantiomeric ratio was determined by HPLC analysis using Daicel Chiralpak AD-H column (40:60 *n*-Hexane/EtOH, 1.0 mL/min, 20 °C, 254 nm, τ_{major} = 12.8 min, τ_{minor} = 31.9 min). The stereochemistry of the product **3au** was assigned in analogy with **3ao**. See Supporting Information: Part B for HPLC chromatograms.

Compound 3av: Purified by silica-gel (230-400 mesh) flash column chromatography (EtOAc/CH_2Cl_2 1:10); White solid (50.0 mg, 0.096 mmol, 96% yield); **m.p.** 127-128 °C; **FT-IR (Thin film):** 3266 (w), 1723 (s), 1613 (m), 1595 (m), 1471 (m), 1369 (m), 1256 (m), 1219 (m); **^{1}H-NMR (400 MHz, $CDCl_3$):** δ 8.73 (br s, 1H), 7.79 (dd, *J* = 8.4 Hz, 5.3 Hz, 1H), 7.57 (d, *J* = 7.2 Hz, 1H), 7.31 (d, *J* = 7.5 Hz, 1H), 7.25-7.24 (m, 1H), 7.15-7.02 (m, 4H), 6.98 (t, *J* = 7.5 Hz, 4H), 6.72 (d, *J* = 7.7 Hz, 2H), 6.58 (d, *J* = 7.6 Hz, 1H), 6.53 (d, *J* = 7.6 Hz, 2H), 5.30 (d, *J* = 16.3 Hz, 1H), 5.08 (s, 1H), 4.39 (d, *J* = 16.2 Hz, 1H), 3.79 (d, *J* = 16.9 Hz, 1H), 3.55 (d, *J* = 16.9 Hz, 1H); **^{13}C-NMR (100 MHz, $CDCl_3$):** δ 208.4, 200.0, 174.6, 167.5 (d, *J* = 258.0), 155.7 (d, *J* = 10.5 Hz), 142.7, 134.3, 132.4, 131.3, 131.1, 130.2, 128.8, 128.7, 128.5, 127.4, 127.3, 127.2, 126.5, 126.3, 125.2, 123.6, 116.5, 116.3, 113.2, 113.0, 110.8, 73.4, 70.5, 58.9, 44.2, 38.0; **HRMS (ESI+):** Calcd for $C_{32}H_{23}FN_2NaO_2S$ ($[M+Na]^+$): 541.1362, Found: 541.1363; **Optical rotation:** $[\alpha]_D^{22}$ +30.3 (*c* 1.0, $CHCl_3$) for an enantiomerically enriched sample with 98.5:1.5 er. The enantiomeric ratio was determined by HPLC analysis using Daicel Chiralpak AD-H column (40:60 *n*-Hexane/EtOH, 1.0 mL/min, 20 °C, 254 nm, τ_{major} = 9.6 min, τ_{minor} = 32.7 min). The stereochemistry of the product **3av** was assigned in analogy with **3ao**. See Supporting Information: Part B for HPLC chromatograms.

Compound 3aw: Purified by silica-gel (230-400 mesh) flash column chromatography (EtOAc/CH_2Cl_2 1:10); White solid (51.0 mg, 0.096 mmol, 96% yield); **m.p.** 150-151 °C; **FT-IR (Thin film):** 3270 (w), 1710 (s), 1607 (m), 1480 (s), 1359 (m), 1275 (m), 745 (s); **^{1}H-NMR (400 MHz, $CDCl_3$):** δ 8.51 (br s, 1H), 7.58 (d, *J* = 7.4 Hz, 1H), 7.32-7.22 (m, 4H), 7.14-7.07 (m, 3H), 6.97 (q, *J* = 8.1 Hz, 4H), 6.73 (d, *J* = 7.5 Hz, 2H), 6.57 (d, *J* = 7.5 Hz, 1H), 6.54 (d, *J* = 7.6 Hz, 2H), 5.30 (d, *J* = 16.2 Hz, 1H), 5.11 (s, 1H), 4.38 (d, *J* = 16.2 Hz, 1H), 3.79 (s, 3H), 3.72 (d, *J* = 16.4 Hz, 1H), 3.51 (d, *J* = 16.4 Hz, 1H); **^{13}C-NMR (100 MHz, $CDCl_3$):** δ 209.0, 201.8, 174.5, 159.8, 145.8, 142.7, 137.2, 134.4, 131.5, 131.0, 130.2, 128.8, 128.6, 128.4, 127.4, 127.0, 126.7, 126.4, 125.3, 123.5, 110.7, 105.9, 73.3, 70.9, 59.0, 55.7, 44.2, 37.6; **HRMS (ESI+):** Calcd for $C_{33}H_{26}N_2NaO_3S$ ($[M+Na]^+$): 553.1562, Found: 553.1562; **Optical rotation:** $[\alpha]_D^{22}$ +13.2 (*c* 1.0, $CHCl_3$) for an enantiomerically enriched sample with 97.5:2.5 er. The enantiomeric ratio was determined by HPLC analysis using Daicel Chiralpak AD-H column (50:50 *n*-Hexane/EtOH, 1.0 mL/min, 20 °C, 254 nm, τ_{major} = 14.5 min, τ_{minor} = 16.9 min). The stereochemistry of the product **3aw** was assigned in analogy with **3ao**. See Supporting Information: Part B for HPLC chromatograms.

Compound 3ax: Purified by silica-gel (230-400 mesh) flash column chromatography (EtOAc/CH_2Cl_2 1:10); White solid (55.0 mg, 0.095 mmol, 95% yield); **m.p.** 110-111 °C; **FT-IR (Thin film):** 3296 (w), 1713 (s), 1602 (m), 1465 (s), 1368 (s), 1252 (m), 1117 (m), 1033 (m), 749 (m); **^{1}H-NMR (400 MHz, $CDCl_3$):** δ 8.71 (br s, 1H), 7.73 (d, *J* = 7.5 Hz, 1H), 7.66 (d, *J* = 7.7 Hz, 1H), 7.62 (d, *J* = 7.0 Hz, 1H), 7.31-7.20 (m, 3H), 7.14 (t, *J* = 7.5 Hz, 1H), 7.09 (t, *J* = 7.3 Hz, 1H), 6.98 (t, *J* = 7.5 Hz, 4H), 6.75 (d, *J* = 7.7 Hz, 2H), 6.58 (d, *J* = 7.4 Hz, 1H), 6.54 (d, *J* = 7.5 Hz, 2H), 5.29 (d, *J* = 16.2 Hz, 1H), 5.11 (s, 1H), 4.41 (d, *J* = 16.2 Hz, 1H), 3.73 (d, *J* = 17.1 Hz, 1H), 3.45 (d, *J* = 17.1 Hz, 1H); **^{13}C-NMR (100 MHz, $CDCl_3$):** δ 207.9, 201.3, 174.5, 152.4, 142.7, 138.2, 137.9, 134.4, 131.2, 131.1, 130.2, 129.7, 128.8, 128.7, 128.6, 127.4, 126.4, 126.3, 125.2, 123.8, 123.7, 121.8, 110.8, 73.4, 70.3, 58.9, 44.2, 39.1; **HRMS (ESI+):** Calcd for $C_{32}H_{23}BrN_2NaO_2S$ ($[M+Na]^+$): 601.0561, Found: 601.0560; **Optical rotation:** $[\alpha]_D^{22}$ +109.7 (*c* 1.0, $CHCl_3$) for an enantiomerically enriched sample with 99:1 er. The enantiomeric ratio was determined by HPLC analysis using Daicel Chiralpak AD-H column (40:60 *n*-Hexane/EtOH, 1.0 mL/min, 20 °C, 254 nm, τ_{minor} = 5.8 min, τ_{major} = 13.2 min). The stereochemistry of the product **3ax** was assigned in analogy with **3ao**. See Supporting Information: Part B for HPLC chromatograms.

Compound 3ay: Purified by silica-gel (230-400 mesh) flash column chromatography (EtOAc/CH_2Cl_2 1:10); Yellow solid (40.0 mg, 0.088 mmol, 88% yield); **m.p.** 113-114 °C; **FT-IR (Thin film):** 3336 (w), 1732 (s), 1610 (m), 1469 (m), 1365 (s); **^{1}H-NMR (400 MHz, $CDCl_3$):** δ 8.32 (br s, 1H), 7.56 (d, *J* = 7.3 Hz, 1H), 7.25-7.16 (m, 3H), 7.11-7.05 (m, 3H), 6.98 (t, *J* = 7.5 Hz, 2H), 6.77 (d, *J* = 7.7 Hz, 2H), 6.52-6.48 (m, 3H), 5.25 (d, *J* = 16.1 Hz, 1H), 4.82 (s, 1H), 4.33 (d, *J* = 16.1 Hz, 1H), 2.79-2.76 (m, 1H), 2.65-2.59 (m, 1H), 2.47-2.42 (m, 1H), 2.35-2.32 (m, 1H), 2.06-2.02 (m 1H), 1.31-1.26 (m, 1H); **^{13}C-NMR (100 MHz, $CDCl_3$):** δ 214.3, 209.1, 174.7, 142.6, 134.4, 131.4, 130.9, 130.6, 128.7, 128.6, 128.6, 127.4, 126.6, 126.3, 125.4, 123.2, 110.6, 73.6, 70.1, 59.5, 44.1, 38.1, 34.4, 19.2; **HRMS (ESI+):** Calcd for $C_{28}H_{24}N_2NaO_2S$ ($[M+Na]^+$): 475.1456, Found: 475.1452; **Optical rotation:** $[\alpha]_D^{21}$ −13.8 (*c* 1.0, $CHCl_3$) for an enantiomerically enriched sample with 79:21 er. The enantiomeric ratio was determined by HPLC analysis using Daicel Chiralpak AD-H column (50:50 *n*-Hexane/EtOH, 1.0 mL/min, 20 °C, 254 nm, τ_{minor} = 7.0 min, τ_{major} = 9.4 min). The stereochemistry of the product **3ay** was assigned in analogy with **3ao**. See Supporting Information: Part B for HPLC chromatograms.

Compound 3az: Purified by silica-gel (230-400 mesh) flash column chromatography (EtOAc/CH_2Cl_2 1:10); White solid (49.0 mg, 0.097 mmol, 97% yield); **m.p.** 117-118 °C; **FT-IR (Thin film):** 3278 (w), 1724 (s), 1610 (s), 1469 (s), 1372 (s), 1011 (m); **^{1}H-NMR (400 MHz, $CDCl_3$):** δ 8.74 (br s, 1H), 8.05-8.02 (m, 1H), 7.61-7.57 (m, 2H), 7.29-7.26 (m, 1H), 7.25-7.19 (m, 2H), 7.16-7.12 (m, 1H), 7.09-7.02 (m, 6H), 6.95 (t, *J* = 7.6 Hz, 2H), 6.65 (t, *J* = 7.4 Hz, 2H), 6.49-6.47 (m, 1H), 5.26 (d, *J* = 16.2 Hz, 1H), 4.74 (s, 1H), 4.45 (d, *J* = 16.2 Hz, 1H); **^{13}C-NMR (100 MHz, $CDCl_3$):** δ 199.8, 196.2, 173.5, 171.8, 142.4, 138.6, 134.3, 130.9, 130.8, 129.0, 128.7, 128.7, 128.3, 127.5, 126.8, 126.5, 125.1, 123.5, 123.0, 121.2, 113.4, 110.2, 95.5, 74.1, 58.8, 44.2; **HRMS (ESI+):** Calcd for $C_{31}H_{22}N_2NaO_3S$ ($[M+Na]^+$): 525.1249, Found: 535.1248; **Optical rotation:** $[\alpha]_D^{22}$ +238.0 (*c* 1.0, $CHCl_3$) for an enantiomerically enriched sample with 97:3 er. The enantiomeric ratio was determined by HPLC analysis using Daicel Chiralpak AD-H column (50:50 *n*-Hexane/EtOH, 1.0 mL/min, 20 °C, 254 nm, τ_{minor} = 5.6 min, τ_{major} = 7.5 min). The stereochemistry of the product **3az** was assigned in analogy with **3ao**. See Supporting Information: Part B for HPLC chromatograms.

Compound 3ba: Purified by silica-gel (230-400 mesh) flash column chromatography (EtOAc/CH_2Cl_2 1:10); White solid (40.0 mg, 0.094 mmol, 94% yield); **m.p.** 250-251 °C (decomposition.); **FT-IR (Thin film):** 3411 (w), 2921 (m), 1721 (s), 1607 (s), 1470 (m), 1121 (m), 1019 (m); **^{1}H-NMR (400 MHz, $CDCl_3$):** δ 8.40 (br s, 1H), 7.80 (d, *J* = 7.6 Hz, 1H), 7.57-7.51 (m, 2H), 7.47 (t, *J* = 7.7 Hz, 1H), 7.37 (d, *J* = 7.6 Hz, 1H), 7.33 (d, *J* = 7.5 Hz, 1H), 7.28 (d, *J* = 7.5 Hz, 1H), 7.02 (t, *J* = 7.3 Hz, 1H), 6.92 (t, *J* = 7.6 Hz, 2H), 6.85 (d, *J* = 7.7Hz, 1H), 6.68 (d, *J* = 7.6 Hz, 2H), 5.08 (s, 1H), 3.75 (d, *J* = 16.5 Hz, 1H), 3.51 (d, *J* = 16.5 Hz, 1H), 3.15 (s, 3H); **^{13}C-NMR (100 MHz, $CDCl_3$):** δ 208.4, 202.1, 174.2, 152.8, 143.7, 136.1, 135.5, 131.8, 131.2, 129.6, 128.5, 128.1, 128.0, 126.5, 126.3, 125.5, 125.0, 123.6, 109.7, 72.9, 70.3, 57.9, 38.4, 27.2; **HRMS (ESI+):** Calcd for $C_{26}H_{20}N_2NaO_2S$ ($[M+Na]^+$): 447.1143, Found: 447.1141; **Optical rotation:** $[\alpha]_D^{21}$ +73.1 (*c* 1.0, $CHCl_3$) for an enantiomerically enriched sample with 98:2 er. The enantiomeric ratio was determined by HPLC analysis using Daicel Chiralpak AD-H column (50:50 *n*-Hexane/EtOH, 1.0 mL/min, 20 °C, 254 nm, τ_{minor} = 7.9 min, τ_{major} = 11.1 min). The stereochemistry of the product **3ab** was assigned in analogy with **3ao**. See Supporting Information: Part B for HPLC chromatograms.

Compound 3ca: Purified by silica-gel (230-400 mesh) flash column chromatography (EtOAc/CH_2Cl_2 1:10); White solid (41.0 mg, 0.091 mmol, 91% yield); **m.p.** 230-231 °C (decomposition); **FT-IR (Thin film):** 3432 (w), 1722 (m), 1605 (s), 1466 (m), 1332 (m), 1019 (m); **^{1}H-NMR (400 MHz, $CDCl_3$):** δ 8.20 (br s, 1H), 7.80 (d, *J* = 7.6 Hz, 1H), 7.54 (q, *J* = 7.8 Hz, 2H), 7.43 (d, *J* = 7.7 Hz, 1H), 7.38 (d, *J* = 7.6 Hz, 1H), 7.34 (t, *J* = 7.4 Hz, 1H), 7.27-7.24 (m, 1H), 7.02 (t, *J* = 7.4 Hz, 1H), 6.92 (t, *J* = 7.6 Hz, 2H), 6.83 (d, *J* = 7.8 Hz, 1H), 6.69 (d, *J* = 7.4 Hz, 2H), 5.07 (s, 1H), 3.83-3.75 (m, 2H), 3.54 (d, *J* = 16.6 Hz, 1H), 3.42-3.34 (m, 1H), 1.45-1.32 (m, 2H), 0.56 (t, *J* = 7.4 Hz, 3H); **^{13}C-NMR (100 MHz, $CDCl_3$):** δ 208.8, 201.9, 174.0, 152.8, 143.3, 136.0, 135.5, 131.6, 131.0, 129.8, 128.4, 128.3, 128.0, 126.7, 126.3, 125.4, 125.1, 123.2, 109.8, 73.0, 70.1, 58.7, 42.2, 38.4, 20.5, 10.8; **HRMS (ESI+):** Calcd for $C_{28}H_{24}N_2NaO_2S$ ($[M+Na]^+$): 475.1456, Found: 475.1458; **Optical rotation:** $[\alpha]_D^{21}$ +103.7 (*c* 1.0, $CHCl_3$) for an enantiomerically enriched sample with 97:3 er. The enantiomeric ratio was determined by HPLC analysis using Daicel Chiralpak AD-H column (50:50 *n*-Hexane/EtOH, 1.0 mL/min, 20 °C, 254 nm, τ_{minor} = 6.3 min, τ_{major} = 8.3 min). The stereochemistry of the product **3ca** was assigned in analogy with **3ao**. See Supporting Information: Part B for HPLC chromatograms.

Compound 3da: Purified by silica-gel (230-400 mesh) flash column chromatography (EtOAc/CH_2Cl_2 1:10); White solid (51.0 mg, 0.096 mmol, 96% yield); **m.p.** 98-99 °C; **FT-IR (Thin film):** 3429 (w), 1721 (m), 1609 (s), 1510 (m), 1470 (m), 1331 (m), 1022 (m); **^{1}H-NMR (400 MHz, $CDCl_3$):** δ 8.72 (br s, 1H), 7.78 (d, *J* = 7.6 Hz, 1H), 7.58 (d, *J* = 7.2 Hz, 1H), 7.51 (td, *J* = 7.4 Hz, 1H), 7.38 (d, *J* = 7.6 Hz, 1H), 7.33-7.28 (m, 2H), 7.25-7.22 (m, 1H), 7.10 (t, *J* = 7.4 Hz, 1H), 6.95 (t, *J* = 7.7 Hz, 2H), 6.72 (d, *J* = 7.5 Hz, 2H), 6.59 (d, *J* = 7.6 Hz, 1H), 6.53-6.47 (m, 4H), 5.21 (d, *J* = 15.8 Hz, 1H), 5.11 (s, 1H), 4.33 (d, *J* = 15.8 Hz, 1H), 3.81 (d, *J* = 16.6 Hz, 1H), 3.69 (s, 3H), 3.56 (d, *J* = 16.7 Hz, 1H); **^{13}C-NMR (100 MHz, $CDCl_3$):** δ 208.7, 201.9, 174.5, 158.7, 152.8, 142.7, 135.9, 135.5, 131.5, 131.0, 130.1, 128.6, 128.3, 127.9, 127.7, 126.6, 126.4, 126.3, 125.2, 125.0, 123.5, 114.1, 110.8, 73.3, 70.2, 58.8, 55.2, 43.7, 38.2; **HRMS (ESI+):** Calcd for $C_{33}H_{26}N_2NaO_3S$ ($[M+Na]^+$): 553.1566, Found: 553.1562; **Optical rotation:** $[\alpha]_D^{21}$ +26.6 (*c* 1.0, $CHCl_3$) for an enantiomerically enriched sample with 97:3 er. The enantiomeric ratio was determined by HPLC analysis using Daicel Chiralpak AD-H column (50:50 *n*-Hexane/EtOH, 1.0 mL/min, 20 °C, 254 nm, τ_{minor} = 11.4 min, τ_{major} = 14.1 min). The stereochemistry of the product **3da** was assigned in analogy with **3ao**. See Supporting Information: Part B for HPLC chromatograms.

Compound 3ea: Purified by silica-gel (230-400 mesh) flash column chromatography (EtOAc/CH_2Cl_2 1:10); White solid (41.5 mg, 0.094 mmol, 94% yield); **m.p.** 145-146 °C; **FT-IR (Thin film):** 3173 (w), 1721 (s), 1601 (s), 1552 (s), 1413 (m), 1334 (m), 1111 (m); **^{1}H-NMR (400 MHz, $CDCl_3$):** δ 8.53 (br s, 1H), 7.79 (d, *J* = 7.6 Hz, 1H), 7.52 (t, *J* = 7.1 Hz, 1H), 7.39 (d, *J* = 7.6 Hz, 1H), 7.35-7.32 (m, 2H), 7.26-7.24 (m, 1H), 7.01 (t, *J* = 7.3 Hz, 1H), 6.94 (t, *J* = 7.5 Hz, 1H), 6.75 (d, *J* = 7.9 Hz, 1H), 6.68 (d, *J* = 7.5 Hz, 2H), 5.07 (s, 1H), 3.75 (d, *J* = 16.6 Hz, 1H), 3.48 (d, *J* = 16.6 Hz, 1H), 3.13 (s, 3H), 2.47 (s, 3H); **^{13}C-NMR (100 MHz, $CDCl_3$):** δ 208.1, 202.1, 174.2, 152.8, 141.4, 136.1, 135.5, 133.2, 132.0, 131.5, 129.5, 128.4, 128.0, 127.9, 126.5, 126.3, 126.0, 125.0, 109.5, 73.0, 70.3, 57.7, 38.3, 27.2, 21.5; **HRMS (ESI+):** Calcd for $C_{27}H_{22}N_2NaO_2S$ ($[M+Na]^+$): 461.1300, Found: 461.1300; **Optical rotation:** $[\alpha]_D^{21}$ +30.5 (*c* 1.0, $CHCl_3$) for an enantiomerically enriched sample with 97:3 er. The enantiomeric ratio was determined by HPLC analysis using Daicel Chiralpak AD-H column (50:50 *n*-Hexane/EtOH, 1.0 mL/min, 20 °C, 254 nm, τ_{minor} = 5.9 min, τ_{major} = 7.9 min). The stereochemistry of the product **3ea** was assigned in analogy with **3ao**. See Supporting Information: Part B for HPLC chromatograms.

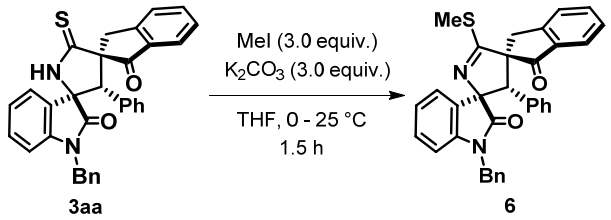
Compound 5aa: Purified by silica-gel (230-400 mesh) flash column chromatography (EtOAc/CH_2Cl_2 1:10); White solid (48.0 mg, 0.093 mmol, 93% yield); **m.p.** 96-97 °C; **FT-IR (Thin film):** 3428 (w), 1642 (m), 1466 (m), 1363 (w); **^{1}H-NMR (400 MHz, $CDCl_3$):** δ 8.50 (br s, 1H), 8.08 (d, *J* = 7.7 Hz, 1H), 7.73 (d, *J* = 7.3 Hz, 1H), 7.44 (t, *J* = 7.4 Hz, 1H), 7.29 (t, *J* = 7.9 Hz, 1H), 7.24 (d, *J* = 7.8 Hz, 1H), 7.19-7.16 (m, 3H), 7.10 (t, *J* = 7.3 Hz, 1H), 7.05-6.98 (m, 4H), 6.89 (d, *J* = 7.7 Hz, 2H), 6.51-6.47 (m, 3H), 5.64 (s, 1H), 5.29 (d, *J* = 16.3 Hz, 1H), 4.32 (d, *J* = 16.3 Hz, 1H), 4.05-3.97 (m, 1H), 2.84-2.77 (m, 2H), 2.37-2.30 (m, 1H); **^{13}C-NMR (100 MHz, $CDCl_3$):** δ 206.5, 204.5, 193.2, 176.0, 144.0, 143.0, 134.4, 133.6, 132.4, 131.7, 131.5, 130.9, 128.8, 128.8, 128.5, 128.3, 127.4, 127.1, 126.8, 126.3, 125.6, 123.0, 110.6, 73.4, 66.7, 59.3, 44.1, 31.9, 25.7; **HRMS (ESI+):** Calcd for $C_{33}H_{26}N_2NaO_2S$ ($[M+Na]^+$): 537.1613, Found: 537.1612; **Optical rotation:** $[\alpha]_D^{21}$ −6.5 (*c* 1.0, $CHCl_3$) for an enantiomerically enriched sample with 96:4 er. The enantiomeric ratio was determined by HPLC analysis using Daicel Chiralpak AD-H column (50:50 *n*-Hexane/EtOH, 1.0 mL/min, 20 °C, 254 nm, τ_{minor} = 7.4 min, τ_{major} = 12.2 min). The stereochemistry of the product **5aa** was assigned in analogy with **3ao**. See Supporting Information: Part B for HPLC chromatograms.

Compound 5ab: Purified by silica-gel (230-400 mesh) flash column chromatography (EtOAc/CH_2Cl_2 1:10); White solid (55.0 mg, 0.094 mmol, 94% yield); **m.p.** 142-143 °C; **FT-IR (Thin film):** 3347 (w), 1729 (s), 1607 (m), 1469 (s), 1369 (m), 1325 (s), 1123 (s); **^{1}H-NMR (400 MHz, $CDCl_3$):** δ 8.64 (br s, 1H), 8.07 (d, *J* = 7.8 Hz, 1H), 7.74 (d, *J* = 7.3 Hz, 1H), 7.45 (t, *J* = 7.3 Hz, 1H), 7.31-7.25 (m, 4H), 7.19 (t, *J* = 7.8 Hz, 2H), 7.11 (t, *J* = 7.2 Hz, 1H), 7.01-6.97 (m, 4H), 6.57-6.54 (m, 3H), 5.70 (s, 1H), 5.28 (d, *J* = 16.1 Hz, 1H), 4.32 (d, *J* = 16.1 Hz, 1H), 4.09-4.03 (m, 1H), 2.82-2.79 (m, 2H), 2.23-2.15 (m, 1H); **^{13}C-NMR (100 MHz, $CDCl_3$):** δ 205.5, 192.7, 176.0, 144.0, 142.9, 135.9, 134.4, 133.8, 132.2, 131.7, 131.2, 128.8, 128.7, 128.6, 127.6, 126.9, 126.5, 126.3, 125.7, 125.1, 125.1, 123.3, 110.8, 73.1, 66.7, 58.4, 44.3, 31.7, 25.7; **HRMS (ESI+):** Calcd for $C_{34}H_{25}F_3N_2NaO_2S$ ($[M+Na]^+$): 605.1487, Found: 605.1487; **Optical rotation:** $[\alpha]_D^{21}$ +9.6 (*c* 1.0, $CHCl_3$) for an enantiomerically enriched sample with 96:4 er. The enantiomeric ratio was determined by HPLC analysis using Daicel Chiralpak AD-H column (50:50 *n*-Hexane/EtOH, 1.0 mL/min, 20 °C, 254 nm, τ_{minor} = 5.1 min, τ_{major} = 12.6 min). The stereochemistry of the product **3ab** was assigned in analogy with **3ao**. See Supporting Information: Part B for HPLC chromatograms.

Compound 5ac: Purified by silica-gel (230-400 mesh) flash column chromatography (EtOAc/CH_2Cl_2 1:10); White solid (50.0 mg, 0.091 mmol, 91% yield); **m.p.** 133-134 °C; **FT-IR (Thin film):** 3344 (w), 2922 (m), 1728 (s), 1603 (m), 1465 (s), 1365 (m), 1013 (m); **^{1}H-NMR (400 MHz, $CDCl_3$):** δ 8.67 (br s, 1H), 8.07 (d, *J* = 7.7 Hz, 1H), 7.72 (d, *J* = 7.4 Hz, 1H), 7.45 (t, *J* = 7.4 Hz, 1H), 7.32-7.27 (m, 2H), 7.18 (t, *J* = 7.4 Hz, 2H), 7.16-7.13 (m, 1H), 7.06 (t, *J* = 7.5 Hz, 2H), 7.01 (d, *J* = 8.4 Hz, 2H), 6.81 (d, *J* = 8.4 Hz, 2H), 6.52 (d, *J* = 7.6 Hz, 3H), 5.60 (s, 1H), 5.31 (d, *J* = 16.2 Hz, 1H), 4.32 (d, *J* = 16.2 Hz, 1H), 4.08-4.00 (m, 1H), 2.84-2.78 (m, 2H), 2.25 (td, *J* = 13.5 Hz, 4.7 Hz, 1H); **^{13}C-NMR (100 MHz, $CDCl_3$):** δ 205.9, 192.9, 176.0, 144.0, 142.9, 134.6, 134.4, 133.7, 132.7, 132.3, 131.0, 130.2, 128.7, 128.7, 128.5, 128.5, 127.6, 126.8, 126.7, 126.2, 125.6, 123.2, 110.7, 73.3, 66.6, 58.4, 44.2, 31.7, 25.7; **HRMS (ESI+):** Calcd for $C_{33}H_{25}ClN_2NaO_2S$ ($[M+Na]^+$): 571.1223, Found: 571.1223; **Optical rotation:** $[\alpha]_D^{21}$ +9.3 (*c* 1.0, $CHCl_3$) for an enantiomerically enriched sample with 94:6 er. The enantiomeric ratio was determined by HPLC analysis using Daicel Chiralpak AD-H column (50:50 *n*-Hexane/EtOH, 1.0 mL/min, 20 °C, 254 nm, τ_{minor} = 7.0 min, τ_{major} = 15.9 min). The stereochemistry of the product **5ac** was assigned in analogy with **3ao**. See Supporting Information: Part B for HPLC chromatograms.

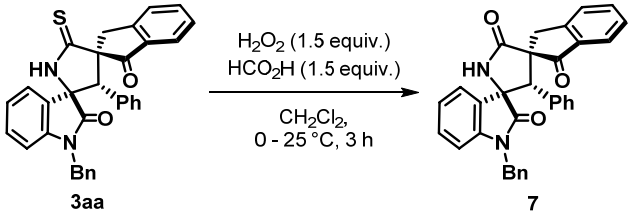
G. Synthetic transformations of the product 3aa:

Conversion of 3aa to 6:



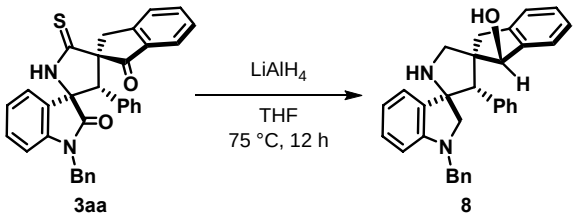
In an oven dried 10 mL round bottom flask, fitted with a magnetic stir-bar, a solution of **3aa** (25.0 mg, 0.049 mmol, 1.0 equiv.; with 98:2 er) in freshly distilled THF (1.5 mL) was taken and K_2CO_3 (20.7 mg, 0.149 mmol, 3.0 equiv.) was added. The solution was cooled to 0 °C and iodomethane (0.1 mL, 0.149 mmol, 3.0 equiv.) was added drop-wise to it. Reaction mixture was warmed slowly to 25 °C over 20 min and allowed to stir at 25 °C. After stirring for 1.5 h at 25 °C, the reaction mixture was diluted with H_2O (5 mL) and EtOAc (10 mL). Organic phase was separated from the aqueous layer. The aqueous layer was extracted with EtOAc (3 × 5 mL). The combined organic layer was washed with brine (5 mL), dried over anh. Na_2SO_4 and concentrated under reduced pressure. The residue was purified by column chromatography on silica-gel (230-400 mesh) using 1:9 EtOAc/ CH_2Cl_2 to afford **6** as white solid (22.0 mg, 0.043 mmol, 85% yield). **m.p.** 199-200 °C; **FT-IR (Thin film):** 1719 (s), 1606 (m), 1464 (m), 1362 (m), 1218 (s), 1021 (m); **^{1}H-NMR (400 MHz, $CDCl_3$):** δ 7.84 (d, *J* = 7.7 Hz, 1H), 7.60 (t, *J* = 7.5 Hz, 1H), 7.45 (d, *J* = 7.6 Hz, 1H), 7.40 (t, *J* = 7.5 Hz, 1H), 7.29 (d, *J* = 7.3 Hz, 1H), 7.22 (t, *J* = 7.6 Hz, 1H), 7.15-7.07 (m, 3H), 7.03 (t, *J* = 7.4 Hz, 2H), 6.97 (t, *J* = 7.5 Hz, 2H), 6.76 (d, *J* = 7.7 Hz, 2H), 6.67 (d, *J* = 7.4 Hz, 2H), 6.56 (d, *J* = 7.7 Hz, 1H), 5.33 (d, *J* = 16.1 Hz, 1H), 5.11 (s, 1H), 4.42 (d, *J* = 16.1 Hz, 1H), 3.60 (s, 2H), 2.43 (s, 3H); **^{13}C-NMR (100 MHz, $CDCl_3$):** δ 201.9, 179.4, 176.6, 152.1, 143.3, 135.8, 135.8, 135.1, 133.2, 130.3, 123.0, 128.7, 128.4, 128.2, 127.8, 127.3, 126.6, 126.5, 125.1, 125.0, 122.6, 110.1, 83.1, 71.7, 60.0, 43.9, 36.3, 13.8; **HRMS (ESI+):** Calcd for $C_{33}H_{26}N_2NaO_2S$ ($[M+Na]^+$): 537.1613, Found: 537.1614; **Optical rotation:** $[\alpha]_D^{22}$ −93.9 (*c* 1.0, $CHCl_3$) for an enantiomerically enriched sample with 98:2 er. The enantiomeric ratio was determined by HPLC analysis using Phenomenex Cellulose-1 column (50:50 *n*-Hexane/EtOH, 1.0 mL/min, 20 °C, 254 nm, τ_{major} = 4.2 min, τ_{minor} = 5.0 min).

Conversion of 3aa to 7:



In a 25 mL round bottom flask, **3aa** (25 mg, 0.049 mmol, 1.0 equiv.; with 98:2 er) was dissolved in 4 mL CH_2Cl_2. The reaction mixture was then cooled to 0 °C, 30% aqueous H_2O_2 (0.2 mL) and 88% aqueous formic acid (0.2 mL) were added successively. The resulting mixture was warmed to 25 °C and stirred vigorously for 3 h. The reaction mixture was quenched with 1 M aqueous K_2CO_3 (5 mL) solution. Organic phase was separated from aqueous phase. The aqueous layer was extracted with CH_2Cl_2 (3 × 5 mL). The combined organic phase was washed with brine (15 mL), dried over anh. Na_2SO_4 and concentrated under reduced pressure. The crude product was purified by column chromatography on silica-gel (230-400 mesh) using 1:1 EtOAc/CH_2Cl_2 to afford **7** as white solid (22.0 mg, 0.045 mmol, 91% yield). **m.p.** 215-216 °C (decomposed); **FT-IR (Thin film):** 3276 (w), 1728 (s), 1694 (m), 1607 (m), 1464 (s), 1364 (s); **^{1}H-NMR (400 MHz, $CDCl_3$):** δ 7.78 (d, *J* = 7.6 Hz, 1H), 7.61-7.59 (m, 1H), 7.53 (td, *J* = 7.4 Hz, 1.1 Hz, 1H), 7.42 (d, *J* = 7.7 Hz, 1H), 7.33 (t, *J* = 7.4 Hz, 1H), 7.30-7.22 (m, 2H), 7.15-7.08 (m, 2H), 6.98 (q, *J* = 7.4 Hz, 4H), 6.76 (d, *J* = 7.6 Hz, 3H), 6.54-6.50 (m, 3H), 5.30 (d, *J* = 16.2 Hz, 1H), 5.07 (s, 1H), 4.35 (d, *J* = 16.2 Hz, 1H), 3.76 (d, *J* = 16.7 Hz, 1H), 3.51 (d, *J* = 16.7 Hz, 1H); **^{13}C-NMR (100 MHz, $CDCl_3$):** δ 201.6, 176.8, 175.5, 152.8, 142.9, 135.7, 135.6, 134.5, 131.9, 130.7, 130.5, 128.8, 128.6, 128.4, 128.2, 128.1, 127.5, 126.4, 126.4, 125.0, 124.8, 123.2, 110.5, 67.3, 61.8, 57.5, 44.2, 35.1; **HRMS (ESI+):** Calcd for $C_{32}H_{24}N_2NaO_3$ ($[M+Na]^+$): 507.1685, Found: 507.1686; **Optical rotation:** $[\alpha]_D^{22}$ −34.6 (*c* 1.0, $CHCl_3$) for an enantiomerically enriched sample with 98:2 er. The enantiomeric ratio was determined by HPLC analysis using Daicel Chiralpak AD-H column (50:50 *n*-Hexane/EtOH, 1.0 mL/min, 20 °C, 254 nm, τ_{minor} = 16.3 min, τ_{major} = 17.8 min).

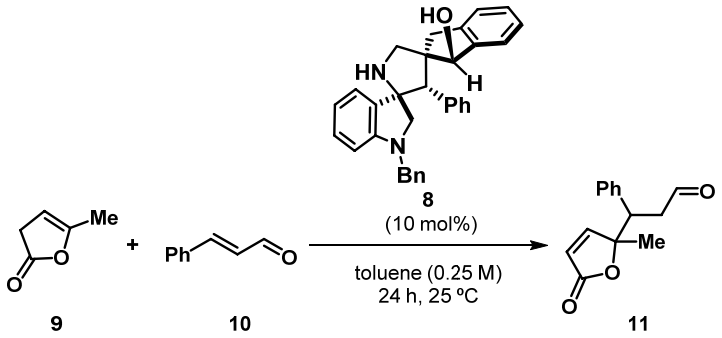
Conversion of 3aa to 8:



In a 25 mL round bottom flask, equipped with a reflux condenser, **3aa** (100.0 mg, 0.199 mmol, 1.0 equiv.; with 98:2 er) was dissolved in freshly distilled THF (4.0 mL) and cooled to 0 °C.

$LiAlH_4$ (46 mg, 1.21 mmol; 6.0 equiv.) was added to it and the resulting mixture was allowed to reflux for 12 h at 75 °C. After complete consumption of the starting material the reaction mixture was cooled to 0 °C and was quenched with EtOAc (5 mL). The reaction mixture was filtered over celite® and concentrated under reduced pressure. The crude product was purified by column chromatography on silica-gel (230-400 mesh) using 1:1 EtOAc/CH_2Cl_2 to afford **8** as yellow oil (50.0 mg, 0.109 mmol, 55% yield). **FT-IR (Thin film):** 3382 (w), 1019 (s); **^{1}H-NMR (400 MHz, $CDCl_3$):** δ 7.35 (t, *J* = 6.8 Hz, 2H), 7.25-7.09 (m, 9H), 7.05-6.99 (m, 5H), 6.70 (t, *J* = 7.4 Hz, 1H), 6.27 (d, *J* = 7.9 Hz, 1H), 5.07 (s, 1H), 4.20 (d, *J* = 15.3 Hz, 1H), 4.03 (d, *J* = 15.3 Hz, 1H), 3.78 (s, 1H), 3.63 (t, *J* = 10.3 Hz, 4H), 3.45 (d, *J* = 9.2 Hz, 1H), 3.38 (d, *J* = 10.5 Hz, 1H), 2.97 (d, *J* = 15.5 Hz, 1H), 2.79 (d, *J* = 15.5 Hz, 1H); **^{13}C-NMR (100 MHz, $CDCl_3$):** δ 152.5, 143.6, 140.1, 138.2, 138.0, 132.9, 131.2, 129.0, 128.6, 127.8, 127.4, 127.1, 126.9, 126.8, 124.6, 124.5, 123.7, 117.5, 107.9, 82.7, 73.7, 68.3, 62.6, 60.3, 53.4, 53.0, 39.7; **HRMS (ESI+):** Calcd for $C_{32}H_{31}N_2O$ ($[M+H]^+$): 459.2436, Found: 459.2437; **Optical rotation:** $[\alpha]_D^{22}$ +31.0 (*c* 1.0, $CHCl_3$) for an enantiomerically enriched sample with 98:2 er. The enantiomeric ratio was determined by HPLC analysis using Daicel Chiralpak AD-H column (50:50 *n*-Hexane/EtOH, 1.0 mL/min, 20 °C, 254 nm, τ_{major} = 5.8 min, τ_{minor} = 25.8 min).

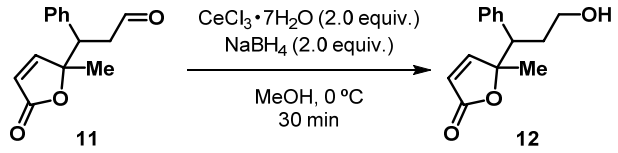
H. Application of compound 8 as catalyst:



In a reaction tube, catalyst **8** (7.0 mg, 0.01 mmol, 0.1 equiv.) and cinnamaldehyde **10** (22 mg, 0.16 mmol, 1.1 equiv.) were taken with 0.4 mL of toluene. After 5 min a solution of α-Angelica lactone **9** (15 mg, 0.15 mmol, 1.0 equiv.) in toluene (0.2 mL) was added over 5 min at 25 °C. The resulting reaction mixture was stirred for 24 h. The reaction was monitored by TLC. After the completion of the reaction, the reaction mixture was diluted with EtOAc (1.0 mL) and sat. aqueous NH_4Cl solution (5.0 mL) at the reaction temperature. Organic layer was separated and the aqueous layer was extracted with EtOAc (3 × 4.0 mL). Combined organic layer was washed with brine (10 mL), dried over anh. Na_2SO_4 and concentrated under reduced pressure. The residue was purified by flash column chromatography on silica-gel (230-400 mesh) using 2:3 EtOAc/petroleum ether to obtain **11** as yellow oil (34.0 mg, 0.15 mmol, 96% yield; with 1:1 dr).

^{1}H-NMR (400 MHz, $CDCl_3$): δ 9.63 (s, 1H), 9.59 (s, 1H), 7.36-7.28 (m, 10H), 7.18-7.16 (m, 2H), 6.07 (d, *J* = 5.6 Hz, 1H), 5.92 (d, *J* = 5.6 Hz, 1H), 3.74 (dd, *J* = 8.6 Hz, 5.5 Hz, 1H), 3.56 (dd, *J* = 8.6 Hz, 5.6 Hz, 1H), 2.95-2.80 (m, 4H), 1.45 (s, 3H), 1.31(s, 3H); **^{13}C-NMR (100 MHz, $CDCl_3$):** δ 199.8, 199.7, 172.3, 171.9, 160.7, 158.7, 138.3, 138.1, 129.4, 128.9, 128.8, 128.6, 127.9, 127.9, 121.5, 120.9, 89.8, 89.7, 46.6, 45.9, 44.6, 44.1, 23.6, 22.2; The spectral data are consistent with those reported in the literature.[5]

The enantiomeric ratios were determined after reduction of **11** to the corresponding alcohol **12** following the procedure as shown below:



In an oven dried 10 mL two-neck round-bottom flask, **11** (35 mg, 0.15 mmol, 1.0 equiv.) and $CeCl_3.7H_2O$ (75 mg, 0.30 mmol, 2.0 equiv.) was taken in 3.0 mL of absolute methanol under argon and the resulting solution was cooled to 0 °C. To this was added $NaBH_4$ (11.5 mg, 0.30 mmol, 2.0 equiv.) at once and the resulting mixture was stirred at 0 °C. After 30 min, the reaction mixture was quenched with 2 mL of sat. NH_4Cl solution and diluted with 5 mL CH_2Cl_2. Organic phase was separated and the aqueous phase was extracted with CH_2Cl_2 (2 × 5 mL). Combined organic phase was dried over anh. Na_2SO_4 and concentrated under reduced pressure. The residue was purified by silica-gel (230-400 mesh) flash column chromatography (1:1 EtOAc/petroleum ether) to obtain **12** as a colorless thick oil (24 mg, 0.103 mmol, 95% yield; with 1:1 dr); **^{1}H-NMR (400 MHz, $CDCl_3$):** δ 7.34-7.29 (m, 3H), 7.27-7.25 (m, 1H), 7.16 (d, *J* = 6.9 Hz, 1H), 5.89 (d, *J* = 5.6 Hz, 1H), 3.57-3.53 (m, 1H), 3.35-3.29 (m, 1H), 3.23 (dd, *J* = 11.8 Hz, 3.3 Hz, 1H), 2.15-2.06 (m, 1H), 1.95-1.87 (m, 1H), 1.44 (s, 3H); **^{13}C-NMR (100 MHz, $CDCl_3$):** δ 172.6, 159.5, 138.5, 128.9, 127.7, 121.1, 90.5, 60.5, 49.5, 31.9, 23.6. The spectral data are consistent with those reported in the literature.[6] The diastereomers could be separated through preparative TLC. The enantiomeric ratio of one diastereomer (er 89:11) was determined by HPLC analysis using Daicel Chiralpak AD-H column (50:50 *n*-Hexane/EtOH, 1.0 mL/min, 20 °C, 210 nm, τ_{major} = 4.6 min, τ_{minor} = 6.0 min). The enantiomeric ratio for the other diastereomer (er 80:20) was determined by HPLC analysis using Daicel Chiralpak AS-H column (90:10 *n*-Hexane/EtOH, 1.0 mL/min, 20 °C, 210 nm, τ_{major} = 22.6 min, τ_{minor} = 24.4 min).

I. Single crystal X-ray diffraction analysis of 3ao:

A single crystal of **3ao** (recrystallized from $CHCl_3$ at 0 °C) was mounted and the diffraction data were collected at 273 K on a Bruker SMART APEX CCD diffractometer using SMART/SAINT software. Intensity data were collected using graphite-monochromatized Mo-Ka

radiation (0.71073 Å). The structures were solved by direct methods using the SHELX-97 and refined by full-matrix least-squares on F^2. Empirical absorption corrections were applied with SADABS. All Non-hydrogen atoms were refined anisotropically and hydrogen atoms were included in geometric positions. Structure was drawn using Olex-2 and ORTEP-3. The crystallographic refinement parameters are given below:

Table 1. Crystal data and structure refinement for 3ao

Identification code	**3ao**	
CCDC Number	CCDC 1492583	
Empirical formula	$C_{31}H_{23}Cl_3N_2O_3S$	
Formula weight	609.92	
Temperature	273(2) K	
Wavelength	71.073 pm	
Crystal system	orthorhombic	
Space group	$P2_12_12_1$	
Unit cell dimensions	a = 801.94(5) pm	α = 90°
	b = 1688.48(11) pm	β = 90°
	c = 2078.55(13) pm	γ = 90°
Volume	2.8145 (3) nm^3	
Z	4	
Density (calculated)	1.439 Mg/m^3	
Absorption coefficient	0.437 mm^{-1}	
F (000)	1256	
Crystal size	0.4 × 0.3× 0.2 mm^3	
Theta range for data collection	6.218 to 49.99°	
Index ranges	$-9 \le h \le 9$, $-20 \le k \le 20$, $-24 \le l \le 24$	
Reflections collected	117951	
Independent reflections	4957 [R_{int} = 0.0690]	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	4957 / 0 / 454	
Goodness-of-fit on F^2	1.083	
Final R indices [I > 2 σ (I)]	R1 = 0.0325, ωR2 = 0.0683	
R indices (all data)	R1 = 0.0386, ωR2 = 0.0705	
Absolute structure parameter	0.02(7)	
Largest diff. peak and hole	0.580 and −0.490 $e.Å^{-3}$	

Table 2. Atomic coordinates ($\times 10^4$) and equivalent isotropic displacement parameters ($pm^2 \times 10^{-1}$) for 3ao. U(eq) is defined as one third of the trace of the orthogonalized U^{ij} tensor.

Atom	*x*	*y*	*z*	U(eq)
C35	4451(5)	3175(3)	180.4(19)	36.1(9)
Cl3	4242(2)	2199.9(8)	440.7(8)	93.0(6)
O4	3426(3)	-968.2(15)	-2315.8(11)	31.6(6)
C1	2775(4)	-1559.6(19)	-1939.2(15)	19.7(7)
C2	2339(5)	-2178(2)	-2300.8(17)	26.3(8)
C3	2718(5)	-1970(2)	-2950.3(17)	30.8(9)
C5	2817(4)	-1377.1(18)	-1234.7(15)	17.2(7)
C6	1741(4)	-1912.9(18)	-795.4(14)	18.4(7)
C7	2347(4)	-525.2(18)	-1039.8(15)	19.0(7)
C8	1889(4)	-629.9(19)	-334.6(15)	21.6(7)
C9	4089(5)	1447(2)	-1614.7(18)	28.7(8)
C10	3257(5)	2037(2)	-1938.8(17)	30.5(9)
C11	1586(5)	1944(2)	-2102.2(17)	29.1(8)
C12	725(5)	1262(2)	-1943.3(16)	25.3(8)
C13	1563(4)	667.3(18)	-1617.4(15)	20.1(7)
C14	3217(4)	760.5(19)	-1453.8(15)	21.3(7)
C15	879(4)	-129(2)	-1407.7(17)	20.4(7)
C16	3841(4)	48(2)	-1124.6(16)	22.7(7)
C19	2706(4)	-2679.5(19)	-622.6(14)	18.6(7)
C20	79(4)	-2230.6(19)	-1024.5(14)	18.2(7)
C21	131(4)	-3054.9(19)	-981.7(15)	20.5(7)
C22	-1214(4)	-3523(2)	-1142.6(17)	26.1(8)
C23	-2645(5)	-3141(2)	-1350.6(17)	30.6(9)
C24	-2728(5)	-2325(2)	-1385.1(17)	28.5(8)
C25	-1361(4)	-1864(2)	-1212.5(16)	22.8(7)
C26	2110(6)	-4131(2)	-598.5(17)	29.2(8)
C27	2153(4)	-4640.0(19)	-1193.1(17)	25.8(8)
C28	3077(5)	-4412(2)	-1725.6(19)	33.1(9)

C29	3154(6)	-4890(3)	-2265(2)	48.1(12)
C30	2310(6)	-5599(3)	-2269(2)	52.7(14)
C31	1371(6)	-5824(3)	-1749(3)	54.3(14)
C32	1308(6)	-5348(2)	-1213(3)	44.0(11)
N1	1588(3)	-1394.4(15)	-235.3(13)	19.4(6)
N2	1688(4)	-3305.3(15)	-738.3(13)	22.2(6)
C4	3353(5)	-1245(3)	-2938.0(17)	34.0(9)
O2	5252(3)	-104.9(15)	-960.8(13)	33.7(6)
O3	4139(3)	-2699.8(13)	-431.7(11)	23.7(5)
S1	1706.1(13)	84.3(5)	205.0(4)	31.9(2)
Cl1	4371.0(17)	3209.0(8)	-658.7(5)	55.6(3)
Cl2	2878.2(12)	3774.0(6)	517.7(5)	41.3(3)

Table 3. Anisotropic displacement parameters ($pm^2 \times 10^{-1}$) for 3ao. The anisotropic displacement factor exponent takes the form: $-2\pi^2[h^2a^{*2}U_{11} + ... + 2hka^*b^*U_{12}]$

Atom	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
C35	33(2)	46(2)	30(2)	-4.3(18)	6.7(18)	-1(2)
Cl3	123.1(14)	55.3(8)	100.5(12)	34.5(8)	69.0(11)	31.4(9)
O4	42.1(15)	30.3(14)	22.3(12)	0.6(11)	9.3(12)	-5.5(12)
C1	17.0(16)	21.3(17)	20.7(16)	2.9(14)	2.1(14)	3.0(14)
C2	27.0(19)	28(2)	23.8(17)	-2.3(16)	0.2(15)	0.3(16)
C3	26.1(19)	46(2)	20.7(18)	-8.4(17)	-0.1(15)	6.5(18)
C5	15.5(16)	17.0(16)	18.9(15)	0.6(13)	-0.1(14)	0.3(14)
C6	20.3(16)	18.3(16)	16.5(15)	-0.9(13)	2.3(13)	-1.2(14)
C7	19.7(16)	17.3(16)	20.0(16)	0.2(13)	-0.3(14)	0.1(14)
C8	21.0(18)	21.3(17)	22.4(17)	0.3(14)	-2.5(14)	4.8(14)
C9	29(2)	24.4(19)	33(2)	0.5(16)	-6.0(17)	-6.9(16)
C10	41(2)	20.6(19)	29.6(19)	4.7(15)	-2.8(18)	-9.9(17)
C11	38(2)	20.8(18)	29.0(19)	5.2(15)	-3.6(17)	3.0(17)
C12	26.7(19)	24.2(19)	25.2(18)	1.9(15)	-4.0(16)	1.4(16)
C13	24.0(17)	18.6(16)	17.7(15)	-1.1(13)	2.3(14)	0.8(15)

C14	24.3(18)	19.3(17)	20.2(16)	-0.8(13)	-2.1(14)	-0.7(15)
C15	20.6(17)	19.9(17)	20.7(17)	-0.9(15)	-0.6(14)	1.0(15)
C16	27.1(19)	19.6(17)	21.4(17)	-1.1(14)	-1.5(14)	-2.4(15)
C19	22.1(17)	21.5(17)	12.2(15)	-0.4(13)	1.1(13)	-0.4(14)
C20	18.9(16)	22.0(17)	13.7(15)	0.7(13)	2.4(13)	-2.9(14)
C21	24.6(18)	20.9(17)	15.9(16)	-0.8(13)	2.3(14)	-2.2(15)
C22	30(2)	25(2)	22.9(18)	-2.4(15)	2.6(15)	-5.2(16)
C23	22.9(19)	42(2)	26.8(19)	-6.5(17)	2.2(15)	-11.2(18)
C24	18.1(17)	40(2)	26.9(19)	0.9(17)	2.8(15)	0.4(17)
C25	19.0(17)	27(2)	22.8(18)	2.6(15)	3.7(14)	0.8(15)
C26	43(2)	18.8(17)	26.0(19)	3.6(15)	-2.2(19)	1.6(17)
C27	25.1(18)	17.3(17)	35(2)	-2.0(15)	-4.1(17)	3.3(14)
C28	30(2)	30(2)	40(2)	-1.9(18)	1.3(18)	-0.2(17)
C29	51(3)	57(3)	36(2)	-5(2)	5(2)	21(3)
C30	52(3)	53(3)	53(3)	-33(3)	-22(3)	25(3)
C31	43(3)	33(2)	87(4)	-30(3)	-10(3)	-1(2)
C32	45(3)	25(2)	62(3)	-8(2)	9(2)	-5.6(19)
N1	22.0(14)	19.4(14)	16.8(13)	-0.4(11)	0.6(12)	-0.3(12)
N2	28.8(15)	15.1(14)	22.7(14)	-0.3(11)	-2.9(13)	1.5(12)
C4	40(2)	44(2)	17.8(17)	2.5(17)	4.9(16)	2(2)
O2	21.7(13)	30.0(14)	49.3(16)	8.3(13)	-10.3(12)	-2.7(11)
O3	23.0(13)	23.8(12)	24.2(12)	3.2(10)	-3.9(10)	3.4(10)
S1	51.4(6)	21.0(4)	23.5(4)	-4.2(4)	-1.1(4)	6.1(4)
Cl1	69.8(8)	67.9(8)	29.2(5)	-12.7(5)	3.2(5)	-0.1(7)
Cl2	32.1(5)	51.0(6)	40.8(5)	-14.6(5)	6.1(4)	-2.4(5)

Table 4. Bond lengths [pm] and angles [°] for 3ao

C35	Cl3	1.742(4)	C12	C13	1.385(5)
C35	Cl1	1.746(4)	C13	C14	1.379(5)
C35	Cl2	1.762(4)	C13	C15	1.516(5)
O4	C1	1.372(4)	C14	C16	1.472(5)

O4	C4	1.376(4)	C16	O2	1.210(4)
C1	C2	1.334(5)	C19	N2	1.357(4)
C1	C5	1.497(4)	C19	O3	1.216(4)
C2	C3	1.428(5)	C20	C21	1.395(5)
C3	C4	1.327(6)	C20	C25	1.367(5)
C5	C6	1.548(4)	C21	C22	1.378(5)
C5	C7	1.541(4)	C21	N2	1.412(4)
C6	C19	1.550(4)	C22	C23	1.386(5)
C6	C20	1.514(4)	C23	C24	1.382(6)
C6	N1	1.462(4)	C24	C25	1.392(5)
C7	C8	1.522(4)	C26	C27	1.505(5)
C7	C15	1.555(4)	C26	N2	1.464(4)
C7	C16	1.550(4)	C27	C28	1.386(5)
C8	N1	1.329(4)	C27	C32	1.374(5)
C8	S1	1.653(3)	C28	C29	1.383(6)
C9	C10	1.376(5)	C29	C30	1.375(7)
C9	C14	1.394(5)	C30	C31	1.371(8)
C10	C11	1.392(6)	C31	C32	1.374(6)
C11	C12	1.382(5)			

Table 5. Bond angles [°] for 3ao

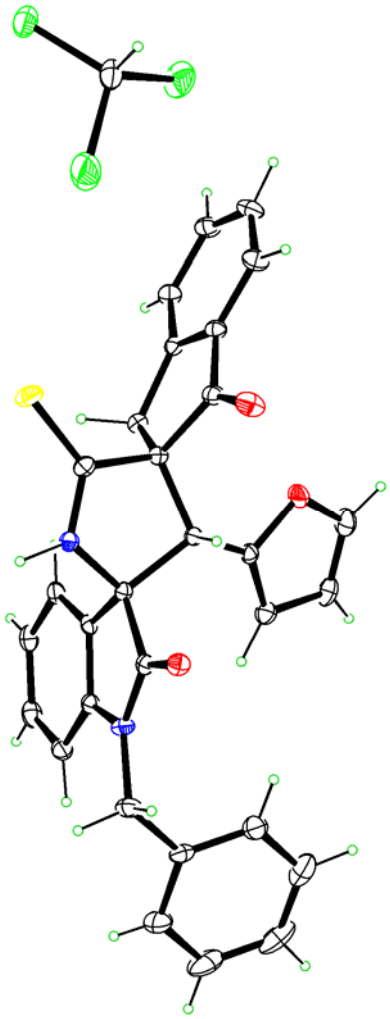
Cl3	C35	Cl1	109.7(2)	C9	C14	C16	128.4(3)
Cl3	C35	Cl2	110.5(2)	C13	C14	C9	121.2(3)
Cl1	C35	Cl2	110.6(2)	C13	C14	C16	110.4(3)
C1	O4	C4	105.8(3)	C13	C15	C7	104.4(3)
O4	C1	C5	113.6(3)	C14	C16	C7	107.5(3)
C2	C1	O4	110.4(3)	O2	C16	C7	123.9(3)
C2	C1	C5	135.9(3)	O2	C16	C14	128.6(3)
C1	C2	C3	106.5(3)	N2	C19	C6	108.0(3)
C4	C3	C2	106.9(3)	O3	C19	C6	124.8(3)
C1	C5	C6	116.4(3)	O3	C19	N2	127.2(3)

C1	C5	C7	116.3(3)	C21	C20	C6	107.9(3)
C7	C5	C6	104.7(2)	C25	C20	C6	132.3(3)
C5	C6	C19	110.3(3)	C25	C20	C21	119.6(3)
C20	C6	C5	120.8(3)	C20	C21	N2	110.4(3)
C20	C6	C19	102.5(2)	C22	C21	C20	122.2(3)
N1	C6	C5	99.6(2)	C22	C21	N2	127.4(3)
N1	C6	C19	111.0(2)	C21	C22	C23	117.2(3)
N1	C6	C20	112.9(3)	C24	C23	C22	121.4(4)
C5	C7	C15	117.2(3)	C23	C24	C25	120.4(4)
C5	C7	C16	111.3(3)	C20	C25	C24	119.1(3)
C8	C7	C5	101.8(2)	N2	C26	C27	112.7(3)
C8	C7	C15	109.9(3)	C28	C27	C26	120.6(3)
C8	C7	C16	111.6(3)	C32	C27	C26	120.6(4)
C16	C7	C15	105.1(3)	C32	C27	C28	118.7(4)
C7	C8	S1	126.2(2)	C29	C28	C27	120.6(4)
N1	C8	C7	107.8(3)	C30	C29	C28	119.4(4)
N1	C8	S1	125.9(3)	C31	C30	C29	120.4(4)
C10	C9	C14	118.5(3)	C30	C31	C32	119.8(5)
C9	C10	C11	120.3(3)	C31	C32	C27	121.0(5)
C12	C11	C10	121.1(4)	C8	N1	C6	116.3(3)
C11	C12	C13	118.6(3)	C19	N2	C21	111.2(3)
C12	C13	C15	127.5(3)	C19	N2	C26	124.6(3)
C14	C13	C12	120.3(3)	C21	N2	C26	124.1(3)
C14	C13	C15	112.2(3)	C3	C4	O4	110.3(3)

Table 6. Hydrogen atom coordinates (Å×10^4) and isotropic displacement parameters (Å^2×10^3) for 3ao

Atom	*x*	*y*	*z*	U(eq)
H13	3250(50)	-4160(20)	-400(17)	28(10)
H7	3780(40)	2510(20)	-2028(16)	19(9)
H12	1860(50)	-2680(20)	-2166(17)	29(10)

H20	620(40)	-428(19)	-1762(16)	15(8)
H19	-130(40)	-50(20)	-1123(16)	20(8)
H9	-380(50)	1180(20)	-2081(16)	23(9)
H17	-3700(50)	-2090(20)	-1541(17)	28(10)
H18	-1430(40)	-1350(20)	-1245(16)	19(9)
H6	5230(50)	1490(20)	-1495(18)	32(10)
H21	1080(50)	-1580(20)	150(20)	40(12)
H8	1000(40)	2360(20)	-2356(17)	25(9)
H15	-1080(40)	-4080(20)	-1114(16)	25(10)
H3	2340(60)	-5930(30)	-2600(20)	59(14)
H16	-3540(50)	-3430(20)	-1486(18)	34(11)
H10	3770(50)	-870(20)	-3240(20)	43(12)
H11	2500(60)	-2260(30)	-3310(20)	53(13)
H5	740(60)	-5470(30)	-900(20)	53(15)
H1	3690(50)	-3920(20)	-1721(18)	33(10)
H14	1340(50)	-4340(30)	-290(20)	50(13)
H4	770(60)	-6310(30)	-1760(20)	56(13)
H2	3830(60)	-4710(30)	-2620(20)	60(15)
H30	5530(50)	3370(20)	300(18)	36(11)
H31	3880(40)	-1457(18)	-1065(15)	10(8)



ORTEP representation of the X-ray structure of enantiopure **3ao** (thermal ellipsoids at 30% probability)

J. References:

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