Electronic Supplementary Information for

_N-Sulfonyl α-Imino Ester-Derived Chiral Oxaziridines: Catalytic Asymmetric Synthesis and Application as a Modular Chiral Organic Oxidant_

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**General Information:** Infrared spectra were recorded on a SHIMADZU IRAffinity-1 spectrometer. ¹H NMR spectra were recorded on a JEOL JNM-ECS400 (400 MHz) spectrometer or JEOL JNM-ECA600 (600 MHz). Chemical shifts are reported in ppm from tetramethylsilane (0.00 ppm) resonance as the internal standard. Data are reported as follows: chemical shift, integration, multiplicity (s = singlet, d = doublet, t = triplet, q = quartet, quin = quintet, m = multiplet, br = broad), and coupling constants (Hz). ¹³C NMR spectra were recorded on a JEOL JNM-ECS400 (101 MHz) spectrometer or JEOL JNM-ECA600 (151 MHz) spectrometer with complete proton decoupling. Chemical shifts are reported in ppm from the solvent resonance (CDCl₃: 77.16 ppm). ¹⁹F NMR spectra were recorded on a JEOL JNM-ECS400 (376 MHz) spectrometer. Chemical shifts are reported in ppm from benzotrifluoride (–64.0 ppm) resonance as the external standard. ³¹P NMR spectra were recorded on a JEOL JNM-ECS400 (162 MHz) spectrometer with complete proton decoupling. Chemical shifts are reported in ppm from H₃PO₄ (0.0 ppm) resonance as the external standard. Optical rotations were measured on a HORIBA SEPA-500 polarimeter. The high resolution mass spectra were conducted on Thermo Fisher Scientific Exactive (ESI). Analytical thin layer chromatography (TLC) was performed on Merck precoated TLC plates (silica gel 60 GF₂₅₄, 0.25 mm). Flash column chromatography was performed on PSQ60AB (spherical, av. 55 μm; Fuji Silysia Chemical Ltd.) or silica gel 60 (spherical, 40-50 μm; Kanto Chemical Co., Inc.). Enantiomeric excesses were determined by HPLC analysis using chiral columns [ϕ 4.6 mm x 250 mm, DAICEL CHIRALCEL OD-3 (OD-3), CHIRALPAK AD-3 (AD-3), CHIRALPAK AY-3 (AY-3), CHIRALCEL OX-3 (OX-3), and CHIRALPAK IA (IA) with hexane (H), 2-propanol (IPA), and ethanol (EtOH) as eluent]. Diethyl ether (Et₂O), toluene, dichloroethane ((CH₂Cl)₂), and dichloromethane (CH₂Cl₂) were supplied from Kanto Chemical Co., Inc. as “Dehydrated” and further purified by passing through neutral alumina under nitrogen atmosphere. Aminophosphonium chlorides 1·HCl¹ and iminophosphoranes 1² were prepared by following the literature procedure. Other simple chemicals were purchased and used as such.

Experimental Section:

Characterization of Catalysts:

Tetraaminophosphonium Chloride 1e·HCl (Ar = 3-FC₆H₄): The synthesis was performed by following the literature procedure.¹ ¹H NMR (600 MHz, CDCl₃) δ 7.95 (2H, d, JᵢP-H = 15.0 Hz), 7.90 (2H, br), 7.45-7.36 (6H, m), 7.31 (2H, d, JᵢF-H = 10.2 Hz), 7.07 (2H, br) 7.03 (2H, t, JᵢF-H = 8.4 Hz, JᵢH-H = 8.4 Hz), 6.94 (2H, t, JᵢF-H = 8.4 Hz, JᵢH-H = 8.4 Hz), 3.76 (2H, dd, JᵢP-H = 21.0 Hz, JᵢH-H = 4.8 Hz), 1.94-1.86 (2H, m), 1.89 (6H, d, JᵢP-H = 10.2 Hz), 1.84-1.76 (2H, m), 0.97-0.86 (2H, m), 0.86 (6H, t, JᵢP-H = 10.2 Hz), 0.63 (6H, d, JᵢP-H = 6.6 Hz); ¹³C NMR (151 MHz, CDCl₃) δ 163.2 (d, JᵢF-C = 248.7 Hz), 162.6 (d, JᵢF-C = 245.7 Hz), 150.2 (d, JᵢF-C = 5.9 Hz), 141.0 (d, JᵢF-C = 7.2 Hz), 130.8 (d, JᵢF-C = 8.8 Hz), 130.5 (d, JᵢF-C = 8.8 Hz), 123.5, 122.5, 115.4 (d, JᵢF-C = 23.1 Hz), 115.2 (d, JᵢF-C = 5.7 Hz), 115.1 (d, JᵢF-C = 7.2 Hz), 114.3 (d, JᵢF-C = 24.6 Hz), 73.9 (d, JᵢF-C = 11.5 Hz), 70.7 (d, JᵢF-C = 10.1 Hz), 36.2, 32.4 (d, JᵢF-C = 5.7 Hz), 25.2, 19.0, 12.1; ¹⁹F NMR (376 MHz, CDCl₃) δ –100.9, –110.6; ³¹P NMR (162 MHz, CDCl₃) δ 38.7; IR (film) 3055, 2967, 2716, 1612, 1589, 1489, 1437, 1339, 1238, 1186, 1022, 1001, 966 cm⁻¹; HRMS (ESI) Calcd for C₃₈H₄₄N₄F₄P⁺ ([M–Cl]+) 663.3234. Found 663.3211.; [α]D²⁴ –212.1 (c = 1.18, CHCl₃).

Triaminooiminophosphorane 1e (Ar = 3-FC₆H₄): The synthesis was performed by following the literature procedure.¹ ¹H NMR (600 MHz, CDCl₃) δ 7.43-7.14 (12H, m), 6.94-6.82 (4H, m), 3.73 (2H, dd, JᵢP-H = 18.6 Hz, JᵢH-H = 2.7 Hz), 1.90 (2H, quin-dd, JᵢH-H = 7.2, 6.6, 2.7 Hz), 1.85 (6H, d, JᵢP-H = 9.0 Hz), 1.34 (2H, br), 0.92 (2H, d-quin, JᵢP-H = 16.8, 7.2 Hz), 0.75 (6H, d, JᵢP-H = 7.2 Hz), 0.68 (6H, t, JᵢP-H = 7.2 Hz); ¹³C NMR (151 MHz, CDCl₃) δ 163.0 (d, JᵢF-C = 244.3 Hz), 162.7 (d, JᵢF-C = 245.8 Hz), 154.5, 147.4, 129.4 (d, JᵢF-C = 7.2 Hz), 129.3 (d, JᵢF-C = 7.2 Hz), 123.6, 122.3, 115.1 (d, JᵢF-C = 23.1 Hz), 114.3 (d, JᵢF-C = 21.7 Hz), 113.5, (d, JᵢF-C = 18.9 Hz), 73.8, 71.1, 37.6, 32.3 (d, JᵢP-H = 4.2 Hz), 24.7, 19.5, 12.4, one carbon atom was not found probably due to overlapping; ¹⁹F NMR (376 MHz, CDCl₃) δ –113.1; ³¹P NMR (162 MHz, CDCl₃) δ 45.0; IR (film) 3451, 3405, 3067, 2965, 2876, 1611, 1587, 1485, 1439, 1327, 1230, 1194, 1136, 1107, 1001, 956 cm⁻¹; HRMS (ESI) Calcd for C₃₈H₄₄N₄F₄P⁺ ([M+H]+) 663.3234. Found 663.3210.; [α]D²⁴ –251.4 (c = 1.00, CHCl₃).

Representative Procedure for Synthesis of N-Sulfonyl α-Imino Esters:

N-Sulfonyl α-imino esters were prepared by following the literature procedure with slight modification.² A solution of methyl benzoyl formate (1.28 g, 7.8 mmol), p-toluenesulfonylamide (1.60 g, 9.4 mmol), and triethylamine (2.17 mL, 15.6 mmol) in CH₂Cl₂ (40 mL) was cooled to 0 °C. To the solution was added TiCl₄ (0.86 mL, 7.8 mmol) dropwise under Ar atmosphere. The solution was allowed to warm to ambient temperature and stirred until the complete consumption of methyl benzoyl formate. The reaction mixture was diluted with a mixed solvent of H/ethyl acetate (EA) (4:1, 10 mL) and filtered through a short plug of silica gel (H/EA = 4:1 as eluent). After removal of solvent under reduced pressure, the crude material was purified by silica gel column chromatography (H/EA = 20:1 → 4:1) and subsequent trituration with H/Et₂O.

(10:1) afforded N-sulfonyl α-imino ester 2a as a white solid (1.78 g, 5.6 mmol, 72%). 2a: white solid; 1H NMR (400 MHz, CDCl₃) δ 7.93 (2H, d, J = 7.5 Hz), 7.83 (2H, d, J = 7.5 Hz), 7.60 (1H, t, J = 7.5 Hz), 7.44 (2H, t, J = 7.5 Hz), 7.35 (2H, d, J = 7.5 Hz), 4.09 (3H, s), 2.44 (3H, s); 13C NMR (101 MHz, CDCl₃) δ 167.1, 165.4, 145.0, 135.6, 135.0, 131.4, 130.0, 129.9, 129.2, 128.3, 53.6, 21.8; IR (film) 3065, 2955, 1742, 1605, 1589, 1449, 1329, 1298, 1215, 1159, 1088, 1007 cm⁻¹; HRMS (ESI) Calcd for C₁₆H₁₆O₄NS⁺ ([M+H]⁺) 318.0800. Found 318.0794.

2b: colorless sticky oil; 1H NMR (600 MHz, CDCl₃) δ 7.92 (2H, d, J = 8.2 Hz), 7.72 (2H, d, J = 8.2 Hz), 7.34 (2H, d, J = 8.2 Hz), 7.24 (2H, d, J = 8.2 Hz), 4.08 (3H, s), 2.43 (3H, s), 2.41 (3H, s); 13C NMR (151 MHz, CDCl₃) δ 167.1, 165.6, 146.6, 144.8, 135.9, 130.2, 130.0, 129.9, 128.8, 128.2, 53.5, 22.0, 21.8; IR (film) 2955, 1744, 1587, 1557, 1435, 1323, 1304, 1221, 1159, 1088, 1009 cm⁻¹; HRMS (ESI) Calcd for C₁₇H₁₇O₄NNaS⁺ ([M+Na]⁺) 354.0776. Found 354.0772.

2c: colorless sticky oil; 1H NMR (600 MHz, CDCl₃) δ 7.92 (2H, d, J = 8.4 Hz), 7.86 (2H, d, J = 8.4 Hz), 7.34 (2H, d, J = 8.4 Hz), 7.24 (2H, d, J = 8.4 Hz), 4.09 (3H, s), 2.44 (3H, s); 13C NMR (151 MHz, CDCl₃) δ 166.9 (d, J_F-C = 258.8 Hz), 165.7, 165.2, 145.1, 135.5, 132.7 (d, J_F-C = 10.1 Hz), 129.9, 128.3, 127.7 (d, J_F-C = 2.9 Hz), 116.7 (d, J_F-C = 23.3 Hz), 53.7, 21.8; 19F NMR (376 MHz, CDCl₃) δ −100.9; IR (film) 2957, 1742, 1595, 1574, 1508, 1449, 1327, 1306, 1215, 1155, 1088, 1008 cm⁻¹; HRMS (ESI) Calcd for C₁₆H₁₅O₄NFS⁺ ([M+H]⁺) 336.0706. Found 336.0700.

2d: white solid; 1H NMR (400 MHz, CDCl₃) δ 7.92 (2H, d, J = 8.2 Hz), 7.77 (2H, d, J = 8.2 Hz), 7.42 (2H, d, J = 9.2, 2.2 Hz), 7.35 (2H, d, J = 8.2 Hz), 4.09 (3H, s), 2.44 (3H, s); 13C NMR (101 MHz, CDCl₃) δ 165.9, 165.1, 145.2, 141.7, 135.4, 131.2, 130.0, 129.8, 129.6, 128.4, 53.8, 21.9; IR (film) 2955, 1742, 1605, 1584, 1557, 1435, 1404, 1331, 1306, 1215, 1161, 1088, 1005 cm⁻¹; HRMS (ESI) Calcd for C₁₆H₁₅O₄N₃S₅Cl⁻ ([M+H]⁺) 352.0410. Found 352.0406.

2e: white solid; 1H NMR (400 MHz, CDCl₃) δ 7.92 (2H, d, J = 8.2 Hz), 7.68 (2H, d, J = 8.2 Hz), 4.09 (3H, s), 2.44 (3H, s); 13C NMR (101 MHz, CDCl₃) δ 166.1, 165.0, 145.2, 135.3, 132.6, 131.2, 130.6, 130.3, 128.3, 53.8, 21.8; IR (film) 2955, 1742, 1605, 1578, 1553, 1435, 1398, 1331, 1312, 1298, 1217, 1161, 1088, 1072, 1003 cm⁻¹; HRMS (ESI) Calcd for C₁₆H₁₅O₄N₇S₉Br⁺ ([M+H]⁺) 395.9905. Found 395.9897.

2f: white solid; 1H NMR (600 MHz, CDCl₃) δ 7.93 (2H, d, J = 8.4 Hz), 7.66 (1H, s), 7.61 (1H, d, J = 7.6 Hz), 7.41 (1H, d, J = 7.6 Hz), 7.35 (2H, d, J = 8.4 Hz), 7.33 (1H, t, J = 7.6 Hz), 4.09 (3H, s), 2.44 (3H, s), 2.37 (3H, s); 13C NMR (151 MHz, CDCl₃) δ 167.4, 165.5, 145.0, 139.2, 135.9, 135.7, 131.3, 130.3, 129.9, 129.1, 128.3, 127.5, 53.6, 21.8, 21.4; IR (film) 2955, 1742, 1572, 1433, 1329, 1304, 1238, 1161, 1088, 1041 cm⁻¹; HRMS (ESI) Calcd for C₁₇H₁₈O₄NS⁺ ([M+H]⁺) 332.0951. Found 332.0946.

2g: orange oil; ¹H NMR (400 MHz, CDCl₃) δ 7.93 (2H, d, J = 7.9 Hz), 7.40 (1H, t, J = 1.4 Hz), 7.38-7.31 (4H, m), 7.17-7.10 (1H, m), 4.08 (3H, s), 3.81 (3H, s), 2.44 (3H, s); ¹³C NMR (101 MHz, CDCl₃) δ 167.2, 165.4, 160.1, 145.1, 135.6, 132.7, 130.1, 129.9, 128.3, 123.2, 121.7, 113.6, 55.7, 53.6, 21.8; IR (film) 2955, 2837, 1742, 1605, 1570, 1487, 1450, 1431, 1327, 1250, 1202, 1159, 1088, 1016 cm⁻¹; HRMS (ESI) Calcd for C₁₇H₁₈O₃NS⁺ ([M+H⁺]⁺) 348.0906. Found 348.0897.

2h: white solid; ¹H NMR (400 MHz, CDCl₃) δ 7.92 (2H, d, J = 8.2 Hz), 7.58 (1H, dd, J = 8.0, 2.3 Hz), 7.57 (1H, dd, J = 8.0, 1.5 Hz), 7.43 (1H, td, Jₘ-H = 8.0 Hz, Jₚ-H = 5.2 Hz), 7.36 (2H, d, J = 8.2 Hz), 7.30 (1H, ddd, Jₘ-H = 8.0 Hz, Jₚ-H = 8.0, 2.3, 1.5 Hz), 4.10 (3H, s), 2.45 (3H, s); ¹³C NMR (151 MHz, CDCl₃) δ 165.8, 164.9, 162.8 (d, Jₘ-C = 250.1 Hz), 145.2, 135.3, 133.5 (d, Jₚ-C = 7.3 Hz), 130.8 (d, Jₘ-C = 7.3 Hz), 129.9, 128.3, 126.0, 122.0 (d, Jₚ-C = 21.7 Hz), 116.2 (d, Jₘ-C = 23.1 Hz), 53.7, 21.8; ¹⁹F NMR (376 MHz, CDCl₃) δ −110.5; IR (film) 3073, 2957, 1742, 1616, 1597, 1580, 1485, 1445, 1333, 1308, 1242, 1161, 1090, 1018, 953 cm⁻¹; HRMS (ESI) Calcd for C₁₈H₁₅O₃NF⁺ ([M+H⁺]⁺) 336.0700. Found 336.0703.

2i: white solid; ¹H NMR (600 MHz, CDCl₃) δ 7.92 (2H, d, J = 8.4 Hz), 7.84 (1H, s), 7.67 (1H, d, J = 7.8 Hz), 7.56 (1H, d, J = 7.8 Hz), 7.40 (1H, t, J = 7.8 Hz), 7.36 (2H, d, J = 8.4 Hz), 4.10 (3H, s), 2.45 (3H, s); ¹³C NMR (151 MHz, CDCl₃) δ 165.7, 164.9, 145.3, 135.6, 135.3, 134.8, 133.1, 130.4, 130.0, 129.5, 128.4, 128.2, 53.8, 21.9; IR (film) 2955, 1744, 1607, 1562, 1427, 1333, 1302, 1211, 1161, 1090, 1018 cm⁻¹; HRMS (ESI) Calcd for C₁₉H₁₂O₃Cl⁺ ([M+H⁺]⁺) 352.0410. Found 352.0409.

2j: colorless oil; ¹H NMR (600 MHz, CDCl₃) δ 8.10 (1H, s), 7.98 (1H, d, J = 7.9 Hz), 7.94 (2H, d, J = 8.4 Hz), 7.85 (1H, d, J = 7.9 Hz), 7.60 (1H, t, J = 7.9 Hz), 7.37 (2H, d, J = 8.4 Hz), 4.11 (3H, s), 2.45 (3H, s); ¹³C NMR (151 MHz, CDCl₃) δ 165.6, 164.8, 145.5, 135.1, 133.1, 132.3, 132.0 (q, Jₘ-C = 33.2 Hz), 131.1, 130.1, 129.9, 128.5, 126.4, 123.3 (q, Jₚ-C = 274.9 Hz), 53.9, 21.9; ¹⁹F NMR (376 MHz, CDCl₃) δ −62.9; IR (film) 2957, 1744, 1595, 1435, 1333, 1285, 1209, 1163, 1130, 1090, 1018 cm⁻¹; HRMS (ESI) Calcd for C₁₇H₁₅O₃NF⁺ ([M+H⁺]⁺) 386.0674. Found 386.0667.

2k: white solid; ¹H NMR (600 MHz, CDCl₃) δ 7.92 (2H, d, J = 8.4 Hz), 7.73 (2H, d, J = 8.4 Hz), 7.35 (2H, dd, Jₘ-H = 7.8 Hz, Jₚ-H = 1.8 Hz), 7.04 (1H, tt, Jₘ-H = 7.8 Hz, Jₚ-H = 1.8 Hz), 4.10 (3H, s), 2.46 (3H, s); ¹³C NMR (151 MHz, CDCl₃) δ 164.6, 164.4, 163.1 (dd, Jₘ-C = 252.3, 12.2 Hz), 145.5, 135.0, 134.5 (t, Jₘ-C = 8.5 Hz), 130.1, 128.5, 112.8 (dd, Jₚ-C = 21.7, 5.8 Hz), 110.1 (t, Jₚ-C = 25.3 Hz), 54.0, 21.9; ¹⁹F NMR (376 MHz, CDCl₃) δ −107.0; IR (film) 3086, 2957, 1742, 1624, 1589, 1437, 1335, 1269, 1163, 1126, 1090, 993 cm⁻¹; HRMS (ESI) Calcd for C₁₆H₁₄O₃NF₂⁺ ([M+H⁺]⁺) 354.0612. Found 354.0604.

2l: colorless oil; ¹H NMR (600 MHz, CDCl₃) δ 7.92 (2H, d, J = 8.4 Hz), 7.52 (1H, d, J = 7.8 Hz), 7.41 (1H, t, J = 7.8 Hz), 7.35 (2H, d, J = 8.4 Hz), 7.26 (1H, t, J = 7.8 Hz), 7.25 (1H, d, J = 7.8 Hz), 4.05 (3H, s), 2.45 (3H, s), 2.44 (3H, s); ¹³C NMR (151 MHz, CDCl₃) δ 168.5, 164.4, 144.9, 141.1, 136.1, 133.2, 132.8, 131.4, 130.5, 129.9, 129.7, 128.2, 126.4, 53.6, 22.3, 21.8; IR (film) 2955, 1742, 1597, 1562, 1456, 1329, 1308, 1211, 1159, 1088, 1005 cm⁻¹; HRMS (ESI) Calcd for C₁₉H₁₄O₃N⁺ ([M+Na⁺]⁺) 354.0776. Found 354.0765.
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**2m**: colorless sticky oil; $^1$H NMR (600 MHz, CDCl$_3$) $\delta$ 7.92 (2H, d, $J = 8.4$ Hz), 7.78 (2H, d, $J = 8.4$ Hz), 7.42 (2H, d, $J = 8.4$ Hz), 7.35 (2H, d, $J = 8.4$ Hz), 4.57 (2H, q, $J = 7.2$ Hz), 2.44 (3H, s), 1.48 (3H, t, $J = 7.2$ Hz); $^{13}$C NMR (151 MHz, CDCl$_3$) $\delta$ 166.1, 164.6, 145.1, 141.6, 135.6, 131.2, 130.0, 129.9, 129.6, 128.3, 63.5, 21.8, 14.1; IR (film) 2984, 1740, 1609, 1584, 1558, 1404, 1333, 1298, 1211, 1163, 1088, 1011 cm$^{-1}$; HRMS (ESI) Calcd for C$_{17}$H$_{17}$O$_4$N$_3$S$^+$ ([M+H]$^+$) 366.0567. Found 366.0560.

**2n**: colorless sticky oil; $^1$H NMR (600 MHz, CDCl$_3$) $\delta$ 7.92 (2H, d, $J = 8.4$ Hz), 7.78 (2H, d, $J = 8.4$ Hz), 7.42 (2H, d, $J = 8.4$ Hz), 7.35 (2H, d, $J = 8.4$ Hz), 5.47 (1H, septet, $J = 6.2$ Hz), 2.44 (3H, s), 1.48 (6H, d, $J = 6.2$ Hz); $^{13}$C NMR (151 MHz, CDCl$_3$) $\delta$ 166.2, 164.1, 145.0, 141.5, 135.7, 131.2, 130.2, 129.9, 129.6, 128.3, 72.1, 21.8, one carbon atom was not found probably due to overlapping; IR (film) 2984, 1734, 1609, 1584, 1557, 1489, 1404, 1331, 1294, 1215, 1161, 1088, 997 cm$^{-1}$; HRMS (ESI) Calcd for C$_{18}$H$_{19}$O$_4$N$_3$S$^+$ ([M+H]$^+$) 380.0723. Found 380.0713.

**2o**: white solid; $^1$H NMR (600 MHz, CDCl$_3$) $\delta$ 7.93 (2H, d, $J = 8.1$ Hz), 7.80 (2H, d, $J = 8.7$ Hz), 7.41 (2H, d, $J = 8.7$ Hz), 7.34 (2H, d, $J = 8.1$ Hz), 2.44 (3H, s), 1.70 (9H, s); $^{13}$C NMR (151 MHz, CDCl$_3$) $\delta$ 166.0, 163.3, 144.9, 141.2, 135.9, 131.2, 130.6, 129.9, 129.5, 128.3, 86.7, 28.2, 21.8; IR (film) 2982, 1734, 1607, 1584, 1558, 1456, 1404, 1371, 1333, 1227, 1161, 1090, 995 cm$^{-1}$; HRMS (ESI) Calcd for C$_{19}$H$_{21}$O$_4$N$_3$S$^+$ ([M+H]$^+$) 394.0880. Found 394.0875.

**Representative Procedure for the Catalytic Asymmetric Oxidation of N-Sulfonyl α-Imino Esters:**

To a solution of α-imino ester $^2$a (63.5 mg, 0.2 mmol) and iminophosphorane $^1$e (6.81 mg, 0.01 mmol) in toluene (4.0 mL) was added a 35% aqueous solution of hydrogen peroxide (34.4 µL, 0.4 mmol) dropwise and the reaction mixture was stirred for 12 h at 0 ºC under Ar atmosphere. The resulting solution was diluted with a saturated aqueous solution of Na$_2$SO$_3$ and extracted with EA twice. The combined organic layers were washed with brine, dried over Na$_2$SO$_4$, and filtered. All volatiles were removed under reduced pressure and the crude residue thus obtained was purified by column chromatography on silica gel (H/EA = 20:1 → 10:1 → 4:1) to afford oxaziridine $^3$a as a white solid (54.7 mg, 0.16 mmol, 82%). The enantiomeric excess of $^3$a was determined to be 97% ee by HPLC analysis.

$^4$The $^1$H NMR analysis showed that oxaziridine $^3$ existed as a mixture of diastereomers with respect to the “stereogenic” nitrogen atom (dr = 10:1 to 7:1), but the diastereomers were supposed to be under equilibrium at room temperature.
Calcd for C_{16}H_{15}O_{5}NNaS^{+} ([M+Na]^{+}) 356.0569. Found 356.0562.; [α]_{D}^{26} +77.0 (c = 4.13, CHCl_{3}) for 97% ee; HPLC AY-3, H/IPA = 4:1, flow rate = 1.0 mL/min, λ = 230 nm, 16.9 min (minor enantiomer), 28.3 min (major enantiomer).

3b: colorless oil; \(^1\)H NMR (600 MHz, CDCl_{3}) δ 7.96 (2H, d, J = 8.4 Hz), 7.40 (2H, d, J = 8.4 Hz), 7.38 (2H, d, J = 8.4 Hz), 7.19 (2H, d, J = 8.4 Hz), 4.01 (3H s), 2.48 (3H, s), 2.35 (3H, s); \(^13\)C NMR (151 MHz, CDCl_{3}) δ 164.2, 146.7, 141.8, 132.8, 130.2, 129.6, 127.4, 84.4, 53.6, 22.0, 21.5, two carbon atoms were not found probably due to overlapping; IR (film) 2955, 1749, 1684, 1603, 1347, 1358, 1279, 1204, 1171, 1088, 1007 cm\(^{-1}\); HRMS (ESI) Calcd for C_{17}H_{17}O_{5}NNaS^{+} ([M+Na]^{+}) 370.0725. Found 370.0713.; [α]_{D}^{26} +55.0 (c = 1.87, CHCl_{3}) for 98% ee; HPLC AY-3, H/IPA = 4:1, flow rate = 1.0 mL/min, λ = 230 nm, 21.5 min (minor enantiomer), 27.9 min (major enantiomer).

3c: white solid; \(^1\)H NMR (600 MHz, CDCl_{3}) δ 7.95 (2H, d, J = 8.4 Hz), 7.50 (2H, dd, J_{H-H} = 8.4 Hz, J_{F-H} = 4.8 Hz), 7.42 (2H, d, J = 8.4 Hz), 7.08 (2H, dd, J_{H-H} = 8.4 Hz, J_{F-H} = 8.4 Hz), 4.02 (3H, s), 2.49 (3H, s); 13C NMR (151 MHz, CDCl_{3}) δ 164.6 (d, J_{F-C} = 253.1 Hz), 163.9, 146.9, 132.5, 130.2, 129.7 (d, J_{F-C} = 8.6 Hz), 129.6, 126.3 (d, J_{F-C} = 4.2 Hz), 116.1 (d, J_{F-C} = 23.1 Hz), 83.7, 53.8, 22.0; 19F NMR (376 MHz, CDCl_{3}) δ -100.9; IR (film) 2959, 1755, 1597, 1439, 1360, 1281, 1238, 1204, 1173, 1157, 1090, 1007 cm\(^{-1}\); HRMS (ESI) Calcd for C_{16}H_{14}O_{5}NFNaS^{+} ([M+Na]^{+}) 374.0469. Found 374.0463.; [α]_{D}^{23} +58.5 (c = 1.35, CHCl_{3}) for 95% ee; HPLC OD-3, H/IPA = 10:1, flow rate = 1.0 mL/min, λ = 230 nm, 7.9 min (major enantiomer), 8.9 min (minor enantiomer).

3d: white solid; \(^1\)H NMR (600 MHz, CDCl_{3}) δ 7.95 (2H, d, J = 8.0 Hz), 7.44 (2H, d, J = 8.8 Hz), 7.42 (2H, d, J = 8.0 Hz), 7.37 (2H, d, J = 8.8 Hz), 4.02 (3H, s), 2.49 (3H, s); 13C NMR (101 MHz, CDCl_{3}) δ 163.8, 146.9, 137.8, 132.5, 130.2, 129.6, 129.0, 128.9, 83.6, 53.9, 22.0; IR (film) 2957, 1755, 1595, 1493, 1439, 1408, 1360, 1275, 1204, 1173, 1090, 1005 cm\(^{-1}\); HRMS (ESI) Calcd for C_{16}H_{14}O_{5}N_{35}ClNaS^{+} ([M+Na]^{+}) 390.0179. Found 390.0169.; [α]_{D}^{24} +48.0 (c = 1.69, CHCl_{3}) for 96% ee; HPLC OD-3, H/IPA = 19:1, flow rate = 1.0 mL/min, λ = 230 nm, 10.0 min (major enantiomer), 11.7 min (minor enantiomer).

3e: white solid; \(^1\)H NMR (400 MHz, CDCl_{3}) δ 7.95 (2H, d, J = 8.0 Hz), 7.53 (2H, dd, J_{H-H} = 8.4 Hz, J_{F-H} = 4.8 Hz), 7.42 (2H, d, J = 8.0 Hz), 7.37 (2H, d, J = 8.8 Hz), 4.02 (3H, s), 2.49 (3H, s); 13C NMR (101 MHz, CDCl_{3}) δ 163.7, 146.9, 132.4, 132.2, 130.2, 129.6, 129.5, 129.0, 128.9, 83.7, 53.9, 22.0; IR (film) 2957, 1751, 1593, 1489, 1437, 1402, 1358, 1279, 1202, 1171, 1088, 1003 cm\(^{-1}\); HRMS (ESI) Calcd for C_{16}H_{14}O_{5}N_{79}BrNaS^{+} ([M+Na]^{+}) 433.9674. Found 433.9669.; [α]_{D}^{24} +48.1 (c = 1.75, CHCl_{3}) for 97% ee; HPLC OD-3, H/IPA = 49:1, flow rate = 1.0 mL/min, λ = 230 nm, 16.7 min (major enantiomer), 19.6 min (minor enantiomer).

3f: colorless oil; \(^1\)H NMR (600 MHz, CDCl_{3}) δ 7.96 (2H, d, J = 8.0 Hz), 7.41 (2H, d, J = 8.0 Hz), 7.33-7.24 (4H, m), 4.01 (s, 3H), 2.48 (s, 3H), 2.34 (s, 3H); \(^13\)C NMR (151 MHz, CDCl_{3}) δ 164.2, 146.7, 138.9, 132.7, 132.1, 130.2, 130.1s, 129.6, 128.8, 127.7, 124.5, 84.4, 53.7, 22.0, 21.5; IR (film) 2955, 1761, 1595, 1437, 1358, 1333, 1288, 1219, 1171, 1090, 1038 cm\(^{-1}\); HRMS (ESI) Calcd for C_{16}H_{17}O_{5}NNaS^{+} ([M+Na]^{+}) 370.0720. Found 370.0722.; [α]_{D}^{26} +69.8 (c = 0.82, CHCl_{3}) for 96% ee; HPLC AY-3, H/IPA = 4:1, flow rate = 1.0 mL/min, λ = 230 nm, 15.1 min (minor enantiomer), 27.1 min (major enantiomer).
3g: colorless oil; $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 7.95 (2H, d, $J = 8.2$ Hz), 7.40 (2H, d, $J = 8.2$ Hz), 7.29 (1H, t, $J = 7.6$ Hz), 7.11 (1H, d, $J = 7.6$ Hz), 7.01 (1H, t, $J = 2.3$ Hz), 6.97 (1H, dd, $J = 7.6$, 2.3 Hz), 4.00 (3H, s), 3.78 (3H, s), 2.48 (3H, s); $^{13}$C NMR (101 MHz, CDCl$_3$) $\delta$ 164.0, 160.0, 146.8, 132.7, 131.7, 130.2, 130.0, 129.6, 119.7, 117.4, 112.4, 84.2, 55.6, 53.7, 22.0; IR (film) 2957, 1755, 1597, 1489, 1433, 1358, 1290, 1233, 1169, 1088, 1043, 1015 cm$^{-1}$; HRMS (ESI) Calcd for C$_{17}$H$_{14}$O$_5$NF$_3$NaS$^+$ ([M+Na]$^+$) 386.0674. Found 386.0668; $[\alpha]_D^{25}$ +71.6 ($c = 1.72$, CHCl$_3$) for 97% ee; HPLC OD-3, H/IPA = 10:1, flow rate = 1.0 mL/min, $\lambda = 230$ nm, 9.5 min (major enantiomer), 12.6 min (minor enantiomer).

3h: colorless oil; $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 7.94 (2H, d, $J = 8.4$ Hz), 7.43 (2H, d, $J = 8.4$ Hz), 7.37 (1H, td, $J_{F-H} = 8.0$ Hz, $J_{F-H} = 5.6$ Hz), 7.32 (1H, dt, $J = 8.0$, 1.4 Hz), 7.21 (1H, ddd, $J_{F-H} = 8.0$ Hz, $J_{H-H} = 2.2$, 1.4 Hz), 7.15 (1H, dddd, $J_{F-H} = 8.0$ Hz, $J_{H-H} = 8.0$, 2.2, 1.4 Hz), 4.03 (3H, s), 2.49 (3H, s); $^{13}$C NMR (101 MHz, CDCl$_3$) $\delta$ 163.6, 161.5 (d, $J_{F-C} = 249.7$ Hz), 146.9, 132.7 (d, $J_{F-C} = 7.8$ Hz), 132.4, 130.6 (d, $J_{F-C} = 7.8$ Hz), 130.2, 129.6, 123.1 (d, $J_{F-C} = 2.9$ Hz), 118.5 (d, $J_{F-C} = 21.3$ Hz), 114.6 (d, $J_{F-C} = 24.2$ Hz), 83.3, 53.8, 21.9; $^{19}$F NMR (376 MHz, CDCl$_3$) $\delta$ −110.9; IR (film) 2957, 1763, 1593, 1360, 1335, 1288, 1221, 1171, 1088, 1018 cm$^{-1}$; HRMS (ESI) Calcd for C$_{18}$H$_{14}$O$_5$NF$_3$NaS$^+$ ([M+Na]$^+$) 374.0474. Found 374.0466; $[\alpha]_D^{24}$ +73.8 ($c = 0.84$, CHCl$_3$) for 95% ee; HPLC OD-3, H/IPA = 10:1, flow rate = 1.0 mL/min, $\lambda = 230$ nm, 7.6 min (major enantiomer), 10.1 min (minor enantiomer).

3i: colorless oil; $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 7.95 (2H, d, $J = 8.4$ Hz), 7.49 (1H, t, $J = 1.8$ Hz), 7.44-7.39 (4H, m), 7.33 (1H, t, $J = 8.0$ Hz), 4.02 (3H, s), 2.49 (3H, s); $^{13}$C NMR (151 MHz, CDCl$_3$) $\delta$ 163.6, 147.0, 135.1, 132.3, 132.3, 131.6, 130.3, 130.2, 129.6, 127.5, 125.6, 83.4, 53.9, 22.0; IR (film) 2955, 1755, 1595, 1427, 1360, 1331, 1287, 1204, 1173, 1088, 1018 cm$^{-1}$; HRMS (ESI) Calcd for C$_{15}$H$_{14}$O$_5$NF$_3$ClNaS$^+$ ([M+Na]$^+$) 390.0179. Found 390.0174; $[\alpha]_D^{27}$ +65.5 ($c = 1.29$, CHCl$_3$) for 95% ee; HPLC AY-3, H/IPA = 4:1, flow rate = 1.0 mL/min, $\lambda = 210$ nm, 12.5 min (minor enantiomer), 22.7 min (major enantiomer).

3j: colorless oil; $^1$H NMR (600 MHz, CDCl$_3$) $\delta$ 7.96 (2H, d, $J = 8.2$ Hz), 7.74 (1H, s), 7.73 (1H, d, $J = 7.8$ Hz), 7.72 (1H, d, $J = 7.8$ Hz), 7.54 (1H, t, $J = 7.8$ Hz), 7.43 (2H, d, $J = 8.2$ Hz), 4.04 (3H, s), 2.49 (3H, s); $^{13}$C NMR (151 MHz, CDCl$_3$) $\delta$ 163.6, 147.1, 132.3, 131.7, 131.6 (q, $J_{F-C} = 33.2$ Hz), 130.9, 130.3, 129.6, 129.5, 128.2 (q, $J_{F-C} = 2.9$ Hz), 124.3 (q, $J_{F-C} = 4.3$ Hz), 123.5 (q, $J_{F-C} = 27.1$ Hz), 83.3, 54.0, 22.0; $^{19}$F NMR (376 MHz, CDCl$_3$) $\delta$ −62.8; IR (film) 2957, 1757, 1595, 1437, 1362, 1333, 1263, 1171, 1130, 1018 cm$^{-1}$; HRMS (ESI) Calcd for C$_{17}$H$_{14}$O$_5$NF$_3$NaS$^+$ ([M+Na]$^+$) 424.0442. Found 424.0432; $[\alpha]_D^{24}$ +52.5 ($c = 0.82$, CHCl$_3$) for 85% ee; HPLC AY-3, H/IPA = 4:1, flow rate = 1.0 mL/min, $\lambda = 230$ nm, 7.5 min (minor enantiomer), 14.5 min (major enantiomer).

3k: colorless oil; $^1$H NMR (600 MHz, CDCl$_3$) $\delta$ 7.94 (2H, d, $J = 8.2$ Hz), 7.43 (2H, d, $J = 8.2$ Hz), 7.07 (2H, dt, $J_{F-H} = 7.8$ Hz, $J_{H-H} = 2.2$ Hz), 6.91 (1H, tt, $J_{F-H} = 8.4$ Hz, $J_{H-H} = 2.2$ Hz), 4.04 (3H, s), 2.49 (3H, s); $^{13}$C NMR (151 MHz, CDCl$_3$) $\delta$ 163.3, 163.1 (dd, $J_{F-C} = 250.9$, 12.3 Hz), 147.1, 134.1 (t, $J_{F-C} = 8.8$ Hz), 132.2, 130.3, 129.6, 110.9 (dd, $J_{F-C} = 22.5$, 6.5 Hz), 107.0 (t, $J_{F-C} = 23.5$ Hz), 82.8, 54.1, 22.0; $^{19}$F NMR (376 MHz, CDCl$_3$) $\delta$ −107.0; IR (film) 2959, 1755, 1601, 1437, 1362, 1339, 1244, 1173, 1126, 1090, 993 cm$^{-1}$; HRMS
Representative Procedure for Asymmetric Rubottom Oxidation of Silyl Enol Ether:
Oxaziridine 3o (60.6 mg, 0.15 mmol) was dissolved in CH₂Cl₂ (1.2 mL) and the solution was cooled to 0 ºC. Silyl enol ether 4⁵ (30.8 mg, 0.12 mmol) was added to the solution slowly and the reaction mixture was stirred for 12 h at 0 ºC. The reaction was quenched by addition of dimethyl sulfide (20.0 µL) and the stirring was continued for 1 h. Then, a 1.0 M solution of TBAF in THF (150 µL, 0.15 mmol) was added and the resulting mixture was further stirred for 30 min at 0 ºC. The resulting solution was diluted with H₂O and extracted with EA twice. The combined organic extracts were washed with brine, dried over Na₂SO₄, and filtered. The solvent was removed under reduced pressure and the crude residue was purified by column chromatography on silica gel (H/EA = 20:1 → 10:1 → 4:1) to afford α-hydroxy ketone 5 as a colorless oil (22.1 mg, 0.11 mmol, 90%). The enantiomeric excess of 5 was determined to be 92% ee by HPLC analysis. 5⁶: ¹H NMR (600 MHz, CDCl₃) δ 8.49 (1H, d, J = 7.8 Hz), 8.05 (1H, d, J = 7.8 Hz), 7.91 (1H, d, J = 7.8 Hz), 7.79 (1H, d, J = 7.8 Hz), 7.63 (1H, dt, J = 7.8, 1.4 Hz), 7.58 (1H, t, J = 7.8 Hz), 7.53 (1H, t, J = 7.8 Hz), 5.24 (1H, dq, J = 7.2, 5.4 Hz), 3.94 (1H, d, J = 5.4 Hz), 1.36 (3H, d, J = 7.2 Hz); [α]D²⁷ +150.3 (c = 1.68, CHCl₃) for 92% ee; HPLC OD-3, H/IPA = 10:1, flow rate = 1.0 mL/min, λ = 210 nm, 9.0 min (minor enantiomer), 9.8 min (major enantiomer).

Representative Procedure for Dual Catalytic Asymmetric Rubottom Oxidation of Silyl Enol Ether:

Silyl enol ether 4 (25.6 mg, 0.10 mmol), iminophosphorane 1e (6.81 mg, 0.01 mmol), and α-imino ester 2o (9.85 mg, 0.025 mmol) were dissolved into toluene (200 µL) at 0 ºC. A 35% aqueous solution of hydrogen peroxide (17.2 µL, 0.2 mmol) was added to the solution dropwise and the reaction mixture was stirred for 72 h at 0 ºC. The reaction was quenched by addition of dimethyl sulfide (20.0 µL). After 30 min of stirring, a saturated aqueous solution of Na₂SO₃ was added to the solution and the whole mixture was extracted with EA three times. The combined organic extracts were washed with brine, dried over Na₂SO₄, and filtered. All volatiles were removed by evaporation and the residue was dissolved into CH₂Cl₂ (1.0 mL). To the solution was added a 1 M solution of TBAF in THF (120 µL, 0.12 mmol) and the mixture was stirred for 30 min at 0 ºC. The resulting solution was diluted with H₂O and extracted with EA twice. The combined organic layers were washed with brine, dried over Na₂SO₄, and filtered. The solvent was removed under reduced pressure and the crude material thus obtained was purified by column chromatography on silica gel (H/EA = 20:1 → 10:1 → 4:1) to afford the product 5 as a colorless oil (18.2 mg, 0.091 mmol, 91%). The enantiomeric excess of the product was determined to be 92% ee by HPLC analysis.

Preparation of Allylic Sulfonamides:

Allylic and homoallylic sulfonamides 8 were prepared from the corresponding allylic or homoallylic bromides and aryl sulfonamide according to the literature procedure.⁷

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**Representative Procedure for Asymmetric Epoxidation of Allylic Sulfonamides:**

To a solution of allylic sulfonamide 8a (24.0 mg, 0.1 mmol) in (CH₂Cl)₂ (300 µL) was added oxaziridine 3o (48.8 mg, 0.12 mmol) at 0 °C. After being stirred for 72 h, the reaction mixture was quenched by addition of dimethyl sulfide (20.0 µL) and was further stirred for 30 min at 0 °C. The solvent was removed under reduced pressure and the crude mixture was purified by column chromatography on silica gel (pure CH₂Cl₂ then H/EA = 4:1 → 2:1) to afford 9a as a white solid (20.9 mg, 0.082 mmol, 82%). The enantiomeric excess of 9a was determined to be 88% ee by HPLC analysis.

9a: white solid; ¹H NMR (600 MHz, CDCl₃) δ 7.76 (2H, d, J = 8.4 Hz), 7.32 (2H, d, J = 8.4 Hz), 4.70 (1H, br), 3.28 (1H, ddd, J = 13.6, 6.6, 5.0 Hz), 2.84 (1H, dd, J = 6.6, 5.0 Hz), 2.43 (3H, s), 1.26 (3H, s), 1.21 (3H, s); [α]D²⁷ +37.0 (c = 1.52, CHCl₃) for 88% ee; HPLC IA, H/IPA = 10:1, flow rate = 1.0 mL/min, λ = 210 nm, 26.3 min, (minor enantiomer), 37.5 min (major enantiomer).

8a: white solid; ¹H NMR (400 MHz, CDCl₃) δ 7.75 (2H, d, J = 8.0 Hz), 7.31 (2H, d, J = 8.0 Hz), 5.06 (1H, t, J = 6.4 Hz), 4.17 (1H, br), 3.54 (2H, t, J = 6.4 Hz), 2.43 (3H, s), 1.64 (3H, s), 1.54 (3H, s).

8b: white solid; ¹H NMR (600 MHz, CDCl₃) δ 8.31 (2H, s), 8.07 (1H, s), 5.00 (1H, t, J = 6.6 Hz), 4.57 (1H, br), 3.69 (2H, t, J = 6.6 Hz), 1.62 (3H, s), 1.58 (3H, s); ¹³C NMR (151 MHz, CDCl₃) δ 143.8, 138.9, 133.0 (q, J₁₃C-F = 34.6 Hz), 127.5, 126.2, 122.6 (q, J₁₃C-F = 273.3 Hz), 118.4, 41.5, 25.6, 17.9; ¹⁹F NMR (376 MHz, CDCl₃) δ -62.9; IR (film) 3285, 2980, 1423, 1361, 1341, 1281, 1159, 1136, 1040, 903 cm⁻¹; HRMS (ESI) Calcd for C₁₃H₁₂O₂NF₆S⁻ ([M–H]⁻) 360.0493. Found 360.0490.

8c: colorless oil; ¹H NMR (600 MHz, CDCl₃) δ 8.30 (2H, s), 8.06 (1H, s), 5.39 (1H, q, J = 6.6 Hz), 4.79 (1H, br), 3.60 (2H, t, J = 6.6 Hz), 1.50 (3H, d, J = 6.6 Hz), 1.49 (3H, s); ¹³C NMR (151 MHz, CDCl₃) δ 143.7, 132.9 (q, J₁₃C-F = 34.7 Hz), 130.1, 127.5, 126.2 (q, J₁₃C-F = 3.6 Hz), 124.6, 122.6 (q, J₁₃C-F = 273.2 Hz), 51.5, 13.8, 13.3; ¹⁹F NMR (376 MHz, CDCl₃) δ -62.9; IR (film) 3296, 3088, 2934, 2864, 1418, 1362, 1275, 1165, 1130, 1051, 905 cm⁻¹; HRMS (ESI) Calcd for C₁₃H₁₂O₂NF₆S⁻ ([M–H]⁻) 360.0493. Found 360.0489.

8d: white solid; ¹H NMR (600 MHz, CDCl₃) δ 8.31 (2H, s), 8.07 (1H, s), 4.93 (1H, t, J = 6.9 Hz), 4.56 (1H, br), 3.06 (2H, q, J = 6.9 Hz), 2.20 (2H, q, J = 6.9 Hz), 1.68 (3H, s), 1.58 (3H, s); ¹³C NMR (151 MHz, CDCl₃) δ 143.3, 136.6, 133.1 (q, J₁₃C-F = 33.2 Hz), 127.4, 126.2, 122.5 (q, J₁₃C-F = 273.3 Hz), 119.1, 43.2, 28.3, 25.8, 17.9; ¹⁹F NMR (376 MHz, CDCl₃) δ -62.9; IR (film) 3287, 2986, 1626, 1427, 1360, 1281, 1161, 1136, 1069, 902 cm⁻¹; HRMS (ESI) Calcd for C₁₄H₁₄O₂NF₆S⁻ ([M–H]⁻) 374.0649. Found 374.0645.

**9b:** white solid; $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 8.33 (2H, s), 8.09 (1H, s), 5.06 (1H, br), 3.46 (1H, ddd, $J = 13.6, 8.0, 4.4$ Hz), 3.03 (1H, ddd, $J = 13.6, 8.0, 4.4$ Hz), 2.88 (1H, dd, $J = 8.0, 4.4$ Hz), 1.30 (3H, s), 1.26 (3H, s); $^{13}$C NMR (151 MHz, CDCl$_3$) $\delta$ 143.3, 133.2 ($q$, $J_{F-C} = 34.7$ Hz), 127.5, 126.5, 122.6 ($q$, $J_{F-C} = 273.2$ Hz), 61.8, 59.7, 43.2, 24.5, 18.9; $^{19}$F NMR (376 MHz, CDCl$_3$) $\delta$ −62.9; IR (film) 3262, 3084, 1447, 1354, 1288, 1165, 1134, 1070, 903 cm$^{-1}$; HRMS (ESI) Calcd for C$_{13}$H$_{13}$O$_3$NF$_6$NaS$^+$ ([M+Na]$^+$) 400.0418. Found 400.0409.; $[\alpha]_D^{27} +34.5$ ($c = 1.14$, CHCl$_3$) for 92% ee; HPLC OX-3, H/IPA = 49:1, flow rate = 0.5 mL/min, $\lambda = 210$ nm, 28.7 min (major enantiomer), 32.7 min (minor enantiomer).

**9c:** white solid; $^1$H NMR (600 MHz, CDCl$_3$) $\delta$ 8.29 (2H, s), 8.08 (1H, s), 5.08 (1H, br), 3.22 (1H, dd, $J = 13.2, 5.1$ Hz), 3.15 (1H, dd, $J = 13.2, 7.5$ Hz), 3.08 (1H, $q$, $J = 5.4$ Hz), 1.30 (3H, d, $J = 5.4$ Hz), 1.29 (3H, s); $^{13}$C NMR (151 MHz, CDCl$_3$) $\delta$ 143.2, 133.1 ($q$, $J_{F-C} = 34.7$ Hz), 127.4, 126.4 ($q$, $J_{F-C} = 2.9$ Hz), 122.6 ($q$, $J_{F-C} = 274.8$ Hz), 59.4, 56.9, 48.5, 15.0, 13.6; $^{19}$F NMR (376 MHz, CDCl$_3$) $\delta$ −62.9; IR (film) 3237, 3088, 1626, 1423, 1354, 1285, 1165, 1132, 905 cm$^{-1}$; HRMS (ESI) Calcd for C$_{13}$H$_{13}$O$_3$NF$_6$NaS$^+$ ([M+Na]$^+$) 400.0418. Found 400.0417.; $[\alpha]_D^{25} +9.3$ ($c = 2.42$, CHCl$_3$) for 87% ee; HPLC OX-3, H/IPA = 19:1, flow rate = 0.5 mL/min, $\lambda = 210$ nm, 12.3 min (minor enantiomer), 13.5 min (major enantiomer).

**9d:** white solid; $^1$H NMR (600 MHz, CDCl$_3$) $\delta$ 8.33 (2H, s), 8.07 (1H, s), 5.44 (1H, br), 3.32 (1H, dq, $J = 12.6, 5.4$ Hz), 3.19 (1H, ddt, $J = 12.6, 9.0, 5.4$ Hz), 2.73 (1H, dd, $J = 9.0, 5.4$ Hz), 1.96 (1H, dq, $J = 14.1, 5.4$ Hz), 1.56 (1H, ddd, $J = 14.1, 9.0, 5.4$ Hz), 1.29 (3H, s), 1.24 (3H, s); $^{13}$C NMR (151 MHz, CDCl$_3$) $\delta$ 143.2, 133.1 ($q$, $J_{F-C} = 33.8$ Hz), 127.5, 126.3 ($q$, $J_{F-C} = 2.9$ Hz), 122.6 ($q$, $J_{F-C} = 274.8$ Hz), 62.4, 58.7, 41.8, 28.4, 24.6, 18.9; $^{19}$F NMR (376 MHz, CDCl$_3$) $\delta$ −62.9; IR (film) 3289, 2974, 2930, 1626, 1435, 1360, 1279, 1161, 1136, 1113, 905 cm$^{-1}$; HRMS (ESI) Calcd for C$_{14}$H$_{15}$O$_3$NF$_6$NaS$^+$ ([M+Na]$^+$) 414.0575. Found 414.0558.; $[\alpha]_D^{25} +16.7$ ($c = 2.75$, CHCl$_3$) for 90% ee; HPLC AY-3, H/IPA = 19:1, flow rate = 1.0 mL/min, $\lambda = 210$ nm, 14.0 min (minor enantiomer), 18.1 min (major enantiomer).
Copies of $^1$H and $^{13}$C NMR Spectra:
HPLC traces

3a

3b

3c

3d