Supporting Information

In Situ Electrophilic Activation of Hydrogen Peroxide for Catalytic Asymmetric α-Hydroxylation of 3-Substituted Oxindoles

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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. Chemical shifts are reported in ppm from the tetramethylsilane (0.0 ppm) resonance as the internal standard (CDCl3). Data are reported as follows: chemical shift, integration, multiplicity (s = singlet, d = doublet, t = triplet, q = quartet, sept =septet, m = multiplet, and br = broad) and coupling constants (Hz). 13C NMR spectra were recorded on a JEOL JNM-ECS400 (101 MHz) spectrometer with complete proton decoupling. Chemical shifts are reported in ppm from the solvent resonance as the internal standard (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. Optical rotations were measured on a HORIBA SEPA-500 polarimeter. The high resolution mass spectra were conducted on Thermo Fisher Scientific Exactive. 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.) and Silica gel 60 (Merck 1.09385.9929, 230-400 mesh). Enantiomeric excesses were determined by HPLC analysis using chiral columns [ϕ 4.6 mm x 250 mm, DAICEL CHIRALCEL OD-3 (OD3), CHIRALCEL OZ-3 (OZ3), CHIRALPAK AS-H (ASH) and CHIRALPAK ID-3 (ID3) with hexane (Hex), isopropyl alcohol (IPA) and ethanol (EtOH) as eluent.

All air- and moisture-sensitive reactions were performed under an atmosphere of argon (Ar) in dried glassware. Dichloromethane (CH2Cl2), diethyl ether (Et2O), and tetrahydrofuran (THF) were supplied from Kanto Chemical Co., Inc. as “Dehydrated” and further purified by passing through neutral alumina under nitrogen atmosphere. Ethyl acetate (EtOAc) was purchased from Wako Pure Chemical Industries, Ltd. as “Dehydrated”. 1,2,3-Triazolium salts 1-X were synthesized by following the literature methods.1 Other simple chemicals were purchased and used as such.
Experimental Section:

Characterization of 1,2,3-Triazolium Salt 1·Br

1a·Br: 1H NMR (400 MHz, CDCl₃) δ 10.2 (1H, brs), 8.65 (1H, brs), 8.20 (2H, d, J = 6.9 Hz), 7.87-7.82 (3H, m), 7.64 (1H, t, J = 7.6 Hz), 7.45-7.29 (8H, m), 7.27-7.22 (2H, m), 7.20-7.14 (4H, m), 7.03-6.97 (4H, m), 6.91-6.84 (4H, m), 6.55 (2H, d, J = 7.8 Hz), 4.85 (2H, s), 1.63 (3H, d, J = 7.3 Hz); 13C NMR (101 MHz, CDCl₃) δ 167.4, 142.9, 140.3, 139.9, 138.5, 135.3, 133.7, 132.9, 132.4, 132.0, 131.9, 131.1, 130.2, 129.9, 129.4, 129.2, 129.0, 128.9, 128.8, 128.5, 128.4, 128.3, 128.2, 127.8, 127.6, 127.2, 120.3, 69.4, 65.9, 55.2, 15.8, two peaks for aromatic carbons were not found probably due to overlapping; IR 3221, 2934, 1672, 1520, 1275, 1148, 746, 702 cm⁻¹; HRMS (ESI) Calcd for C₄₅H₃₂N₄O⁺ ([M⁺]) 625.2962. Found 625.2969.; [α]D²⁰ = −44.3 (c = 1.0, MeOH).

1b·Br: 1H NMR (400 MHz, CDCl₃) δ 10.2 (1H, brs), 9.07 (1H, brs), 8.29 (2H, brd), 8.20-7.98 (3H, m), 7.61 (1H, t, J = 7.6 Hz), 7.47-7.43 (6H, m), 7.37 (1H, t, J = 7.3 Hz), 7.31 (2H, t, J = 7.4 Hz), 7.28 (2H, t, J = 7.8 Hz), 7.22 (2H, t, J = 7.6 Hz), 7.18-7.06 (7H, m), 7.06-6.96 (5H, m), 6.96-6.92 (2H, m), 6.42 (2H, d, J = 7.3 Hz), 4.76 (2H, brs), 3.55 (1H, brd, J = 14.6 Hz), 3.03 (1H, dd, J = 14.6, 11.2 Hz); 13C NMR (101 MHz, CDCl₃) δ 167.6, 142.4, 140.3, 139.9, 138.2, 135.4, 134.6, 133.5, 132.9, 132.4, 132.0, 131.8, 130.8, 130.3, 129.6, 129.3, 129.1, 129.0, 128.9, 128.8, 128.6, 128.5, 128.4, 128.3, 127.8, 127.7, 127.1, 127.1, 119.8, 70.4, 69.1, 55.1, 35.4, four peaks for aromatic carbons were not found probably due to overlapping; IR 3219, 3029, 2193, 1967, 1674, 1486, 1290 cm⁻¹; HRMS (ESI) Calcd for C₃₅H₂₈N₄O⁺ ([M⁺]) 701.3275. Found 701.3267.; [α]D²⁷ = −39.0 (c = 1.0, MeOH).

1c·Br: 1H NMR (400 MHz, CDCl₃) δ 10.25 (1H, brs), 8.71 (1H, brs), 8.25 (2H, brs), 7.83 (2H, brs), 7.67 (2H, m), 7.52-7.36 (8H, m), 7.29-7.05 (12H, m), 6.89 (2H, brs), 6.64 (2H, d, J = 7.3 Hz), 5.04 (2H, brs), 1.86 (2H, brm), 1.07 (3H, d, J = 6.4 Hz), 0.91 (1H, m), 0.63 (3H, d, J = 6.9 Hz); 13C NMR (101 MHz, CDCl₃) δ 167.9, 142.7, 140.4, 138.5, 133.5, 132.3, 132.1, 131.8, 130.8, 130.5, 129.7, 129.3, 129.0, 128.9, 128.7, 128.6, 128.5, 128.4, 128.3, 128.1, 127.7, 127.1, 69.1, 68.7, 55.6, 38.4, 25.5, 23.2, 22.0, five peaks for aromatic carbons were not found probably due to overlapping; IR 3030, 2957, 1674, 1519, 1485, 1287, 1146 cm⁻¹; HRMS (ESI) Calcd for C₄₅H₃₂N₄O₂⁺ ([M⁺⁺]⁺) 667.3431. Found 667.3429.; [α]D¹⁹ = +35.4 (c = 1.0, CHCl₃).

1d·Br: 1H NMR (400 MHz, CDCl₃) δ 9.94 (1H, brs), 8.51 (1H, brs), 8.20 (2H, d, J = 6.2 Hz), 7.79 (2H, brs), 7.66 (2H, td, J = 7.7, 1.2 Hz), 7.51-7.35 (9H, m), 7.30-7.15 (9H, m), 7.07 (2H, t, J = 7.6 Hz), 6.85 (2H, d, J = 7.1 Hz), 6.64 (2H, d, J = 7.5 Hz), 5.07 (2H, brs), 2.13-2.07 (1H, m), 1.90-1.81 (1H, m), 1.33-1.25 (1H, m), 0.84-0.75 (4H, m); 13C NMR (101 MHz, CDCl₃) δ 167.9, 142.8, 140.6, 138.6, 133.7, 133.1, 132.4, 132.2, 131.9, 130.8, 130.6, 129.8, 129.3, 129.2, 129.0, 128.8, 128.7, 128.6, 128.6, 128.4, 128.3, 128.3, 127.8, 127.7, 127.4, 120.3, 70.4, 69.1, 55.8, 31.9, 19.3, 13.7, three peaks for aromatic carbons were not found.
probably due to overlapping; IR 3235, 2932, 1674, 1485, 1285, 1146, 748, 704 cm⁻¹; HRMS (ESI) Calcd for C₄₅H₄₃N₃O⁺ ([M⁺]) 653.3275. Found 653.3270.; [α]D²² = -27.7 (c = 1.0, MeOH).

Preparation of 3-Substituted Oxindole:

N-Boc oxindoles were synthesized by following the literature methods. Substrates 2a-f and 2h-2r are known compounds, and their characterization date were in agreement with those reported in the literature. Unknown compound 2g was characterized.

![2g](image)

2g: ¹H NMR (400 MHz, CDCl₃) δ 8.35 (1H, brs), 8.00 (1H, d, J = 8.7 Hz), 7.89 (1H, d, J = 8.2 Hz), 7.82 (1H, d, J = 8.2 Hz), 7.53 (2H, brm), 7.38 (2H, t, J = 8.0 Hz), 7.11 (3H, brm), 5.64 (1H, brs), 1.64 (9H, s); ¹³C NMR (101 MHz, CDCl₃) δ 173.8, 149.6, 140.6, 134.4, 129.0, 128.7, 128.2, 126.8, 126.1, 125.7, 125.5, 124.8, 124.0, 115.3, 84.5, 53.5, 28.2, four peaks for aromatic carbons were not found probably due to overlapping; IR 3456, 3001, 2978, 1778, 28.2, 17.5, 128.1. HRMS (ESI) Calcd for C₂₃H₂₁NO₃Na⁺ ([M+Na]⁺) 382.1414. Found 382.1414.

General Procedure for 1c-Br-Catalyzed Asymmetric α-Hydroxylation of Oxindole 2:

A solution of 1c-Br (3.76 mg, 0.005 mmol), oxindole 2a (30.9 mg, 0.10 mmol) and K₂CO₃ (13.8 mg, 0.10 mmol) in Et₂O (1.0 mL) was degassed by alternating vacuum evacuation/Ar backfill. Then the resulting mixture was cooled to −10 °C. To this solution was added 30% H₂O₂ aq. (50 µL, 0.50 mmol) and CCl₃CN (10 µL, 0.10 mmol), then the mixture was stirred for 24 h. The reaction mixture was diluted with a saturated aqueous solution of NH₄Cl and the extractive work-up was performed with EtOAc. After drying over Na₂SO₄, filtration, and removal of solvent, the resulting crude residue was purified by column chromatography using CHROMATOREX DIOL MB100-40/75 (Hex/CHCl₃ = 3:1 as eluent) to afford 3a (28.6 mg, 0.088 mmol, 88% yield) as a white solid. 3a: ¹H NMR (400 MHz, CDCl₃) δ 7.94 (1H, d, J = 8.2 Hz), 7.40 (1H, dt, J = 8.0, 1.2 Hz), 7.36-7.29 (6H, m), 7.20 (1H, t, J = 7.8 Hz), 3.42 (1H, s), 1.63 (9H, s); ¹³C NMR (101 MHz, CDCl₃) δ 176.0, 149.2, 139.9, 139.8, 130.3, 128.8, 128.7, 125.7, 125.4, 125.2, 115.6, 85.0, 77.8, 28.2, one peak for aromatic carbon was not found probably due to overlapping; IR 3456, 3001, 2978, 1788, 1609, 1479, 1342, 1285, 1146, 908, 719 cm⁻¹; HRMS (ESI) Calcd for C₁₉H₁₈NO₃Na⁺ ([M+Na]⁺) 348.1206. Found 348.1206.; HPLC ID3, Hex/IPA = 10:1, flow rate = 0.5 mL/min, λ = 210 nm, 15.8 min (major isomer), 17.5 min (minor isomer). [α]D²³ = +45.6 (c = 3.0, CHCl₃).
Characterization of Hydroxylation Products 3:

3b: $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 7.93 (1H, d, $J = 8.4$ Hz), 7.39 (1H, t, $J = 8.1$ Hz), 7.31 (1H, d, $J = 7.6$ Hz), 7.23 (2H, d, $J = 8.4$ Hz), 7.19 (1H, t, $J = 7.7$ Hz), 7.13 (2H, d, $J = 8.4$ Hz), 3.33 (1H, s), 2.31 (3H, s), 1.62 (9H, s); $^{13}$C NMR (101 MHz, CDCl$_3$) $\delta$ 176.0, 149.2, 139.8, 138.6, 137.0, 130.3, 130.2, 129.5, 125.6, 125.4, 125.2, 115.5, 84.9, 77.7, 28.2, 21.2; IR 3482, 2984, 2932, 1730, 1609, 1468, 1369, 1285, 1146, 999, 732 cm$^{-1}$; HRMS (ESI) Calcd for C$_{20}$H$_{23}$NO$_4$Na$^+$ ([M+Na]$^+$) 362.1363. Found 362.1364.; HPLC OD3, Hex/IPA = 10:1, flow rate = 1.0 mL/min, $\lambda = 210$ nm, 6.5 min (minor isomer), 7.2 min (major isomer). $[\alpha]_D^{24} = +37.6$ (c = 2.6, CHCl$_3$).

3c: $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 7.93 (1H, d, $J = 8.4$ Hz), 7.40 (1H, dt, $J = 8.1$, 1.6 Hz), 7.33 (1H, dd, $J = 7.6$, 0.7 Hz), 7.28 (2H, d, $J = 9.2$ Hz), 7.21 (1H, dt, $J = 7.7$, 0.9 Hz), 6.85 (2H, d, $J = 9.2$ Hz), 3.78 (3H, s), 3.30 (1H, s), 1.62 (9H, s); $^{13}$C NMR (101 MHz, CDCl$_3$) $\delta$ 176.1, 159.9, 149.2, 139.7, 131.9, 130.3, 130.2, 127.2, 125.4, 125.2, 115.5, 114.2, 84.9, 55.4, 28.2, one peak for aliphatic carbon was not found probably due to overlapping; IR 3445, 2974, 2932, 1730, 1607, 1464, 1342, 1248, 1146, 999, 729 cm$^{-1}$; HRMS (ESI) Calcd for C$_{20}$H$_{23}$NO$_4$Na$^+$ ([M+Na]$^+$) 378.1312. Found 378.1311.; HPLC ID3, Hex/IPA = 10:1, flow rate = 1.0 mL/min, $\lambda = 210$ nm, 12.5 min (major isomer), 15.0 min (minor isomer). $[\alpha]_D^{24} = +22.5$ (c = 2.2, CHCl$_3$).

3d: $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 7.93 (1H, d, $J = 8.4$ Hz), 7.41 (1H, dt, $J = 7.8$, 1.6 Hz), 7.35-7.28 (3H, m), 7.21 (1H, dt, $J = 7.8$, 0.9 Hz), 7.01 (2H, t, $J = 8.9$ Hz), 3.41 (1H, s), 1.62 (9H, s); $^{13}$C NMR (101 MHz, CDCl$_3$) $\delta$ 175.7, 163.0 (d, $J_{\text{C}-\text{C}} = 254.3$ Hz), 149.1, 139.7, 135.6 (d, $J_{\text{C}-\text{C}} = 2.9$ Hz), 130.5, 130.0, 127.8 (d, $J_{\text{C}-\text{C}} = 8.7$ Hz), 125.5, 125.1, 115.7 (d, $J_{\text{C}-\text{C}} = 22.2$ Hz), 115.6, 85.2, 77.3, 28.2; $^{19}$F NMR (376 MHz, CDCl$_3$) $\delta$ −131.3; IR 3443, 2980, 2972, 1768, 1605, 1504, 1369, 1285, 1111, 908, 771 cm$^{-1}$; HRMS (ESI) Calcd for C$_{19}$H$_{18}$NO$_4$FNa$^+$ ([M+Na]$^+$) 366.1112. Found 366.1116.; HPLC OZ3, Hex/IPA = 10:1, flow rate = 1.0 mL/min, $\lambda = 210$ nm, 5.6 min (major isomer), 7.7 min (minor isomer). $[\alpha]_D^{24} = +20.5$ (c = 2.1, CHCl$_3$).

3e: $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 7.93 (1H, d, $J = 8.4$ Hz), 7.39 (1H, dt, $J = 8.0$, 1.5 Hz), 7.30 (1H, dd, $J = 7.6$, 0.9 Hz), 7.21 (1H, t, $J = 7.3$ Hz), 7.19-7.17 (2H, m), 7.12-7.10 (2H, m), 3.32 (1H, brs), 2.31 (3H, s), 1.63 (9H, s); $^{13}$C NMR (101 MHz, CDCl$_3$) $\delta$ 176.0, 149.2, 139.8, 138.6, 130.4, 130.3, 129.5, 128.7, 126.2, 125.4, 125.2, 122.7, 115.5, 85.0, 77.8, 28.2, 21.7, one peak for aromatic carbon was not found probably due to overlapping; IR 3444, 2972, 2932, 1730, 1605, 1479, 1337, 1248, 1142, 908, 729 cm$^{-1}$; HRMS (ESI) Calcd for C$_{20}$H$_{22}$NO$_4$Na$^+$ ([M+Na]$^+$) 362.1363. Found 362.1364.; HPLC OD3, Hex/IPA = 10:1, flow rate = 1.0 mL/min, $\lambda = 210$ nm, 5.2 min (major isomer), 5.8 min (minor isomer). $[\alpha]_D^{24} = +42.3$ (c = 2.6, CHCl$_3$).

3f: $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 7.92 (1H, d, $J = 8.4$ Hz), 7.39 (1H, dt, $J = 8.0$, 1.6 Hz), 7.30 (1H, dd, $J = 7.6$, 1.1 Hz), 7.23 (1H, t, $J = 8.0$ Hz), 7.19 (1H, dt, $J = 7.6$, 1.1 Hz), 6.98 (1H, t, $J = 2.1$ Hz), 6.86-6.82 (2H, m), 3.78 (3H, s), 3.40 (1H, s), 1.62 (9H, s); $^{13}$C NMR (101 MHz, CDCl$_3$) $\delta$ 175.8, 159.9, 149.1, 141.5, 139.8, 130.3, 130.3, 129.8, 125.4, 125.1, 117.9, 115.6, 114.0, 111.7, 85.0, 77.8, 55.4, 28.2; IR 3462, 2980, 2938, 1730, 1599, 1454, 1393, 1285, 1144.
910, 752 cm\(^{-1}\); HRMS (ESI) Calcd for C\(_{20}\)H\(_{21}\)NO\(_3\)Na\(^+\) ([M+Na\(^+\)]) 378.1312. Found 378.1311.; HPLC ID3, Hex/IPA = 10:1, flow rate = 1.0 mL/min, λ = 210 nm, 11.7 min (minor isomer), 13.6 min (major isomer). \([\alpha]_D^{24} = +47.1\) (c = 2.9, CHCl\(_3\)).

3g: \(^1\)H NMR (400 MHz, CDCl\(_3\)) \(\delta\) 8.03 (1H, d, \(J = 8.2\) Hz), 7.89 (1H, d, \(J = 7.3\) Hz), 7.84 (2H, d, \(J = 8.0\) Hz), 7.70 (1H, brd, \(J = 7.8\) Hz), 7.48 (1H, t, \(J = 7.8\) Hz), 7.41 (1H, dt, \(J = 6.9, 1.2\) Hz), 7.40 (1H, d, \(J = 7.2\) Hz), 7.35 (1H, dt, \(J = 8.3, 1.4\) Hz), 7.17 (1H, dd, \(J = 7.6, 1.2\) Hz), 7.08 (1H, dt, \(J = 7.6, 0.9\) Hz), 3.32 (1H, s), 1.65 (9H, s); \(^{13}\)C NMR (101 MHz, CDCl\(_3\)) \(\delta\) 175.5, 149.4, 139.8, 134.7, 134.5, 130.6, 130.5, 130.1, 130.3, 129.3, 126.7, 125.8, 125.4, 125.1, 125.0, 125.0, 124.3, 115.9, 85.1, 78.5, 28.2; IR 3514, 3009, 2916, 1788, 1607, 1454, 1369, 1250, 1145, 976, 734 cm\(^{-1}\); HRMS (ESI) Calcd for C\(_{23}\)H\(_{25}\)NO\(_4\)Na\(^+\) ([M+Na\(^+\)]) 398.1363. Found 398.1354.; HPLC ID3, Hex/IPA = 10:1, flow rate = 1.0 mL/min, λ = 210 nm, 10.5 min (minor isomer), 11.4 min (major isomer). \([\alpha]_D^{25} = +102.7\) (c = 2.2, CHCl\(_3\)).

3h: \(^1\)H NMR (400 MHz, CDCl\(_3\)) \(\delta\) 7.98 (1H, d, \(J = 8.4\) Hz), 7.84-7.79 (3H, m), 7.78 (1H, s), 7.49-7.4.0 (4H, m), 7.33 (1H, dt, \(J = 7.8, 0.9\) Hz), 7.20 (1H, dt, \(J = 7.8, 0.9\) Hz), 3.45 (1H, br), 1.63 (9H, s); \(^{13}\)C NMR (101 MHz, CDCl\(_3\)) \(\delta\) 175.9, 149.2, 139.9, 137.2, 133.3, 133.1, 130.5, 130.2, 128.9, 128.5, 127.7, 126.7, 126.6, 125.5, 125.3, 124.9, 123.3, 115.7, 85.1, 78.0, 28.2; IR 3453, 3022, 2980, 1730, 1607, 1479, 1337, 1248, 1146, 1009, 750 cm\(^{-1}\); HRMS (ESI) Calcd for C\(_{23}\)H\(_{25}\)NO\(_4\)Na\(^+\) ([M+Na\(^+\)]) 398.1363. Found 398.1359.; HPLC OZ3, Hex/IPA = 10:1, flow rate = 1.0 mL/min, λ = 210 nm, 7.9 min (major isomer), 11.1 min (minor isomer). \([\alpha]_D^{24} = +63.9\) (c = 1.9, CHCl\(_3\)).

3i: \(^1\)H NMR (400 MHz, CDCl\(_3\)) \(\delta\) 7.85 (1H, d, \(J = 8.2\) Hz), 7.39 (1H, dt, \(J = 8.4, 0.7\) Hz), 7.36 (1H, dd, \(J = 8.2, 1.4\) Hz), 7.22 (1H, dt, \(J = 7.8, 1.4\) Hz), 2.70 (1H, s), 2.00 (2H, q, \(J = 7.8\) Hz), 1.64 (9H, s), 0.79 (3H, t, \(J = 7.8\) Hz); \(^{13}\)C NMR (101 MHz, CDCl\(_3\)) \(\delta\) 177.2, 149.1, 139.7, 130.0, 128.8, 125.0, 124.0, 115.4, 84.8, 77.0, 32.7, 28.2, 7.7; IR 3489, 2976, 2931, 1788, 1611, 1454, 1346, 1287, 1144, 928, 750 cm\(^{-1}\); HRMS (ESI) Calcd for C\(_{13}\)H\(_{13}\)NO\(_4\)Na\(^+\) ([M+Na\(^+\)]) 300.1206. Found 300.1207.; HPLC OZ3, Hex/IPA = 10:1, flow rate = 1.0 mL/min, λ = 210 nm, 5.3 min (major isomer), 9.9 min (minor isomer). \([\alpha]_D^{25} = +42.1\) (c = 1.2, CHCl\(_3\)).

3j: \(^1\)H NMR (400 MHz, CDCl\(_3\)) \(\delta\) 7.85 (1H, d, \(J = 8.2\) Hz), 7.39 (1H, t, \(J = 8.2\) Hz), 7.36 (1H, d, \(J = 8.2\) Hz), 7.21 (1H, t, \(J = 7.8\) Hz), 2.72 (1H, brs), 2.02-1.91 (2H, m), 1.64 (9H, s), 1.30-1.21 (2H, m), 1.19-1.12 (1H, m), 1.08-0.99 (1H, m), 0.82 (3H, t, \(J = 7.3\) Hz); \(^{13}\)C NMR (101 MHz, CDCl\(_3\)) \(\delta\) 177.3, 149.1, 139.6, 130.0, 129.0, 125.0, 124.0, 115.4, 84.8, 76.5, 39.4, 28.2, 25.2, 22.8, 13.9; IR 3446, 2934, 2872, 1728, 1612, 1454, 1337, 1287, 1140, 978, 750 cm\(^{-1}\); HRMS (ESI) Calcd for C\(_{17}\)H\(_{22}\)NO\(_3\)Na\(^+\) ([M+Na\(^+\)]) 328.1519. Found 328.1518.; HPLC OZ3, Hex/IPA = 10:1, flow rate = 1.0 mL/min, λ = 210 nm, 5.0 min (major isomer), 8.4 min (minor isomer). \([\alpha]_D^{24} = +41.5\) (c = 1.7, CHCl\(_3\)).
3k: $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 7.85 (1H, d, $J = 8.4$ Hz), 7.38 (1H, dd, $J = 7.6$, 0.9 Hz), 7.37 (1H, dt, $J = 8.0$, 1.6 Hz), 7.21 (1H, dt, $J = 7.6$, 0.9 Hz), 2.67 (1H, s), 1.92 (2H, d, $J = 6.0$ Hz), 1.64 (9H, s), 1.61-1.43 (5H, m), 1.21-1.04 (4H, m), 0.97-0.80 (2H, m); $^{13}$C NMR (101 MHz, CDCl$_3$) $\delta$ 177.3, 149.1, 139.6, 130.0, 129.1, 125.0, 124.3, 115.4, 84.7, 76.2, 46.6, 34.4, 34.2, 33.3, 28.2, 26.1; IR 3462, 2978, 2920, 1730, 1610, 1488, 1344, 1287, 1150, 1001, 750 cm$^{-1}$; HRMS (ESI) Calcd for C$_{20}$H$_{27}$NO$_2$Na$^+$ ([M+Na$^+$]) 368.1832. Found 368.1810.; HPLC OZ3, Hex/IPA = 10:1, flow rate = 1.0 mL/min, $\lambda = 210$ nm, 5.4 min (major isomer), 9.3 min (minor isomer). $[\alpha]_D^{25} = +45.5$ (c = 2.5, CHCl$_3$).

3l: $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 7.84 (1H, d, $J = 8.4$ Hz), 7.40 (1H, dd, $J = 7.6$, 1.4 Hz), 7.36 (1H, dt, $J = 8.0$, 1.4 Hz), 7.21 (1H, t, $J = 7.6$ Hz), 5.72-5.61 (1H, m), 5.16 (1H, brs), 5.13 (1H, brd, $J = 6.4$ Hz), 2.82 (1H, s), 2.72 (1H, dd, $J = 13.8$, 6.4 Hz), 2.62 (1H, dd, $J = 13.8$, 8.5 Hz), 1.64 (9H, s); $^{13}$C NMR (101 MHz, CDCl$_3$) $\delta$ 176.5, 149.0, 139.4, 130.1, 130.0, 128.7, 125.0, 124.2, 121.3, 115.4, 84.8, 75.6, 43.9, 28.2; IR 3458, 2920, 2849, 1728, 1610, 1479, 1344, 1287, 1150, 984, 750 cm$^{-1}$; HRMS (ESI) Calcd for C$_{16}$H$_{19}$NO$_2$Na$^+$ ([M+Na$^+$]) 312.1206. Found 312.1207.; HPLC OZ3, Hex/IPA = 10:1, flow rate = 1.0 mL/min, $\lambda = 210$ nm, 5.4 min (major isomer), 9.7 min (minor isomer). $[\alpha]_D^{24} = +32.6$ (c = 0.9, CHCl$_3$).

3m: $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 7.63 (1H, d, $J = 8.2$ Hz), 7.28 (1H, dt, $J = 8.2$, 1.4 Hz), 7.19-7.10 (5H, m), 6.91 (2H, d, $J = 6.2$ Hz), 3.27 (1H, d, $J = 12.8$ Hz), 3.15 (1H, d, $J = 12.8$ Hz), 3.00 (1H, s), 1.57 (9H, s); $^{13}$C NMR (101 MHz, CDCl$_3$) $\delta$ 177.0, 148.6, 139.3, 133.4, 130.4, 130.0, 128.2, 128.0, 127.2, 124.7, 124.4, 115.1, 84.5, 46.1, 28.1; one peak for aliphatic carbon was not found probably due to overlapping; IR 3429, 2980, 2961, 1776, 1604, 1468, 1341, 1287, 1149, 912, 785 cm$^{-1}$; HRMS (ESI) Calcd for C$_{20}$H$_{27}$NO$_2$Na$^+$ ([M+Na$^+$]) 362.1363. Found 362.1367.; HPLC ID3, Hex/IPA = 10:1, flow rate = 1.0 mL/min, $\lambda = 210$ nm, 8.2 min (major isomer), 9.3 min (minor isomer). $[\alpha]_D^{24} = +65.3$ (c = 2.1, CHCl$_3$).

3n: $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 7.65 (1H, d, $J = 8.5$ Hz), 7.29 (1H, dt, $J = 8.5$, 1.8 Hz), 7.19 (1H, dd, $J = 7.6$, 1.8 Hz), 7.15 (1H, t, $J = 7.6$ Hz), 6.84 (2H, d, $J = 8.7$ Hz), 6.67 (2H, d, $J = 8.7$ Hz), 3.75 (3H, s), 3.21 (1H, d, $J = 13.6$ Hz), 3.09 (1H, d, $J = 13.6$ Hz), 2.88 (1H, brs), 1.58 (9H, s); $^{13}$C NMR (101 MHz, CDCl$_3$) $\delta$ 177.1, 158.9, 148.7, 139.4, 131.5, 130.0, 128.3, 125.4, 124.7, 124.4, 115.2, 113.5, 84.6, 55.3, 45.3, 28.2, one peak for aliphatic carbon was not found probably due to overlapping; IR 3429, 2980, 2913, 1776, 1612, 1468, 1369, 1250, 1150, 912, 746 cm$^{-1}$; HRMS (ESI) Calcd for C$_{21}$H$_{29}$NO$_3$Na$^+$ ([M+Na$^+$]) 392.1468. Found 392.1455.; HPLC ASH, Hex/IPA = 10:1, flow rate = 1.0 mL/min, $\lambda = 210$ nm, 10.0 min (major isomer), 17.9 min (minor isomer). $[\alpha]_D^{24} = +56.9$ (c = 2.0, CHCl$_3$).

3o: $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 7.62 (1H, d, $J = 8.3$ Hz), 7.29 (1H, dt, $J = 8.3$, 1.9 Hz), 7.19 (1H, dd, $J = 7.6$, 1.9 Hz), 7.15 (1H, dt, $J = 7.6$, 0.9 Hz), 6.89-6.78 (4H, m), 3.24 (1H, d, $J = 13.4$ Hz), 3.16 (1H, brs), 3.13 (1H, d, $J = 13.4$ Hz), 1.57 (9H, s); $^{13}$C NMR (101 MHz, CDCl$_3$) $\delta$ 177.0, 162.2 (d, $J_{FC} = 251.4$ Hz), 148.5, 139.3, 131.9 (d, $J_{FC} = 7.7$ Hz),
130.1, 129.2, 128.0, 124.8, 124.3, 115.1, 114.9 (d, $J_{F,H} = 22.2$ Hz), 84.7, 45.2, 28.1, one peak for aliphatic carbon was not found probably due to overlapping; $^{19}$F NMR (376 MHz, CDCl$_3$) $\delta$ –115.4; IR 3478, 2982, 2922, 1788, 1603, 1468, 1344, 1250, 1148, 837, 754 cm$^{-1}$; HRMS (ESI) Calcd for C$_{20}$H$_{20}$NO$_4$FNa$^+$ ([M+Na]$^+$) 380.1269. Found 380.1269.; HPLC ASH, Hex/IPA = 10:1, flow rate = 0.5 mL/min, $\lambda$ = 210 nm, 15.8 min (major isomer), 23.3 min (minor isomer). $[\alpha]_D^{24}$ = +58.1 (c = 2.5, CHCl$_3$).

3p: $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 7.80 (1H, d, $J = 8.2$ Hz), 7.37-7.30 (5H, m), 7.18 (1H, dd, $J = 8.2, 1.4$ Hz), 7.10 (1H, d, $J = 1.4$ Hz), 3.37 (1H, s), 2.31 (3H, s), 1.62 (9H, s); $^{13}$C NMR (101 MHz, CDCl$_3$) $\delta$ 176.1, 149.2, 140.1, 137.4, 135.2, 130.8, 130.2, 128.8, 128.6, 125.6, 115.3, 84.8, 77.9, 28.2, 21.1, one peak for aromatic carbons was not found probably due to overlapping; IR 3469, 2980, 2930, 1726, 1599, 1485, 1332, 1277, 1105, 906, 731 cm$^{-1}$; HRMS (ESI) Calcd for C$_{20}$H$_{20}$NO$_4$Na$^+$ ([M+Na]$^+$) 362.1363. Found 362.1364.; HPLC ID3, Hex/IPA = 10:1, flow rate = 1.0 mL/min, $\lambda$ = 210 nm, 8.6 min (major isomer), 9.4 min (minor isomer). $[\alpha]_D^{24}$ = +25.5 (c = 2.6, CHCl$_3$).

3q: $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 7.85 (1H, d, $J = 9.0$ Hz), 7.36-7.30 (5H, m), 6.91 (1H, dd, $J = 9.0, 2.8$ Hz), 6.84 (1H, d, $J = 2.8$ Hz), 3.75 (3H, s), 3.53 (1H, s), 1.61 (9H, s); $^{13}$C NMR (101 MHz, CDCl$_3$) $\delta$ 176.1, 157.5, 149.2, 139.9, 133.0, 131.5, 128.8, 128.7, 125.6, 116.7, 115.8, 110.5, 84.8, 78.1, 55.8, 28.2; IR 3435, 2978, 2934, 1726, 1599, 1412, 1333, 1246, 1144, 1003, 772 cm$^{-1}$; HRMS (ESI) Calcd for C$_{20}$H$_{20}$NO$_4$Na$^+$ ([M+Na]$^+$) 378.1312. Found 378.1311.; HPLC ID3, Hex/IPA = 10:1, flow rate = 1.0 mL/min, $\lambda$ = 210 nm, 11.1 min (major isomer), 13.5 min (minor isomer). $[\alpha]_D^{25}$ = –13.5 (c = 2.8, MeOH).

3r: $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 7.92 (1H, dd, $J = 9.0, J_{F,H} = 4.6$ Hz), 7.36-7.32 (5H, m), 7.08 (1H, dt, $J = 9.0, 2.7$ Hz), 7.01 (1H, dd, $J = 2.7, J_{F,H} = 7.3$ Hz), 3.57 (1H, s), 1.61 (9H, s); $^{13}$C NMR (101 MHz, CDCl$_3$) $\delta$ 175.7, 160.4 (d, $J_{F,C} = 248.7$ Hz), 149.1, 139.4, 135.6 (d, $J_{F,C} = 19.3$ Hz), 132.1 (d, $J_{F,C} = 8.7$ Hz), 128.9, 125.5, 117.1 (d, $J_{F,C} = 8.7$ Hz), 116.9 (d, $J_{F,C} = 24.2$ Hz), 112.6 (d, $J_{F,C} = 24.2$ Hz), 85.3, 77.8, 28.2, one peak for aromatic carbon was not found probably due to overlapping; $^{19}$F NMR (376 MHz, CDCl$_3$) $\delta$ –116.3; IR 3464, 2984, 2934, 1726, 1611, 1479, 1342, 1261, 1144, 1009, 760 cm$^{-1}$; HRMS (ESI) Calcd for C$_{18}$H$_{18}$NO$_4$FNa$^+$ ([M+Na]$^+$) 366.1112. Found 366.1114.; HPLC ID3, Hex/IPA = 10:1, flow rate = 1.0 mL/min, $\lambda$ = 210 nm, 6.0 min (major isomer), 6.9 min (minor isomer). $[\alpha]_D^{24}$ = +54.2 (c = 2.3, CHCl$_3$).
Determination of the absolute configuration of hydroxylation product:
The absolute configuration of the hydroxylation products 3a and 3l were established to be R by comparing their optical rotations with that of known enantiomers after removing the N-Boc group. The absolute configuration of 3b-3k and 3m-3r were assumed by analogy.

\[
\begin{align*}
3a & \quad \text{R} \quad \text{OH} \\
& \quad \text{Boc} \\
\text{3l} & \quad R = \text{CH}_2\text{CH}=\text{CH}_2 \\
& \quad \text{OH} \\
& \quad \text{Boc} \\
\end{align*}
\]

\[
\begin{align*}
4a & \quad \text{R} \quad \text{OH} \\
& \quad \text{Boc} \\
\text{4l} & \quad R = \text{CH}_2\text{CH}=\text{CH}_2 \\
& \quad \text{OH} \\
& \quad \text{Boc} \\
\end{align*}
\]

To a solution of 3a (27.7 mg, 0.085 mmol, 93% ee) in dichloromethane (1.0 mL) was added trifluoroacetic acid (TFA) (38 μL) and the resulting solution was stirred for 17 h at room temperature. The mixture was then diluted with a saturated aqueous solution of NaHCO₃ at 0 °C and the extractive workup was performed with EtOAc. After drying over Na₂SO₄, filtration, and removal of solvent, the resulting crude powder was washed with hexane to afford 4a (14.2 mg, 0.063 mmol, 74% yield, 93%ee)

Reference:
$^{19}$F NMR Spectral Data:

$^3d$

$X$ : parts per Million : $^{19}$F

$^3o$

$X$ : parts per Million : $^{19}$F
HPLC Spectral Data:

3a

3b

3c

3d