Supporting Information for

Iridium-Catalyzed C3-Selective Asymmetric Allylation of 7-Azaindoles with Secondary Allylic Alcohols

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1. General Methods and Materials

All anaerobic and moisture-sensitive manipulations were carried out with standard Schlenk techniques under predried argon. $^1$H, $^{13}$C, and $^{19}$F NMR spectra were measured on JEOL ECX 500II spectrometers (500 MHz for $^1$H, 126 MHz for $^{13}$C, 471 MHz for $^{19}$F). Chemical shifts are reported in $\delta$ (ppm) referenced to the tetramethylsilane ($\delta$ 0.00) for $^1$H NMR and the residual peaks of CDCl$_3$ ($\delta$ 77.00) for $^{13}$C NMR. The following abbreviations are used; s: singlet, d: doublet, t: triplet, sext: sextet, m: multiplet, br: broad. High-resolution mass spectra were obtained with a JEOL JMS-700 Mstation. IR spectra were measured on a JASCO FT/IR-4100 spectrometer. Chiral High Performance Liquid Chromatography (HPLC) was performed on a Shimadzu system under the conditions given for each measurement. The products were purified by column chromatography on 63-210 mesh silica gel (Kanto Kagaku; Silica Gel 60N). Optical rotations were measured on a JASCO P-2200. Single-crystal X-ray diffraction was collected on a Rigaku RAXIS-RAPID imaging plate diffractometer with a graphite monochromatized Mo Kα ($\lambda = 0.71069 \ \text{Å}$) radiation. All solvents were dried and distilled before use by the usual procedures.

$[\text{Ir(cod)Cl}]_2$, ($R$)-L1 [CAS RN: 1265884-98-7], and ($R$)-L2 [CAS RN: 2093047-92-6] were prepared as described in the literature.1-3 7-Azaindoles 2a [CAS RN: 271-63-6], 2l [CAS RN: 866546-07-8], and 2m [CAS RN: 183208-35-7] were purchased and used as received. 7-Azaindoles 2b [CAS RN: 27257-15-4], 2e [CAS RN: 53277-42-2], 2d [CAS RN: 183208-23-3], 2e [CAS RN: 1260874-86-9], 2f [CAS RN: 183208-22-2], 2g [CAS RN: 74420-05-6], 2h [CAS RN: 934568-25-9], 2i [CAS RN: 1135437-92-1], 2j [CAS RN: 113975-38-5], 2k [CAS RN: 418795-13-8], and allylic alcohols 1a [CAS RN: 4393-06-0], 1b [CAS RN: 51410-44-7], 1c [CAS RN: 58824-48-9], 1d [CAS RN: 39627-62-8], 1e [CAS RN: 1555908-83-2], 1f [CAS RN: 58824-56-9], 1g [CAS RN: 149946-79-2], 1h [CAS RN: 196519-53-6], 1i [CAS RN: 123232-63-3], 1j [CAS RN: 76635-88-6], 1k [CAS RN: 116914-87-5], 1l [CAS RN: 393148-57-7] were prepared according to the reported procedures.4-6

2. General Procedure for the Asymmetric Allylation of 7-Azaindoles 2 with Allylic Alcohols 1 (Schemes 2 and 3)

Representative Procedure for the Reaction of Allylic Alcohol 1a with 7-Azaindole 2b
A mixture of \([\text{Ir(cod)}\text{Cl}_2\) (8.9 mg, 0.132 mmol) and \((R)\text{-L1}\) (26.3 mg, 0.0518 mmol) in THF (2.0 mL) was stirred at room temperature for 15 min. To the mixture was added \(2\text{b}\) (99.3 mg, 0.751 mmol), \(1\text{a}\) (67.6 mg, 0.504 mmol), and TFA (114 mg, 1.00 mmol), and the mixture was stirred under reflux for 15 h. After the solvent was removed on a rotary evaporator, the residue was subjected to column chromatography (silica gel, toluene/EtOAc = 98/2) to give compounds \(3\text{ab}\) (102.1 mg, 0.4111 mmol, 82% yield, 99% ee).

3. Characterization of 3

\((R)-3-(1\text{-Phenylallyl})-1\text{-H-pyrrolo}[2,3-\text{b}]\text{pyridine (3aa)}\)

A mixture of \([\text{Ir(cod)}\text{Cl}_2\) (2.5 mol%) and \((R)\text{-L1}\) (10 mol%) in THF, reflux, 15 h

\(2\text{a}\)

\(3\text{a}\)

\(3\text{aa}\) was prepared according to general procedure using \(1\text{a}\) (68.7 mg, 0.512 mmol) and \(2\text{a}\) (89.3 mg, 0.756 mmol). The crude reaction mixture was purified by column chromatography using toluene/EtOAc (80/20) to afford \(3\text{aa}\) (28.1 mg, 0.1199 mmol, 23% yield, >99.5% ee) as a brown oil. The ee was measured by HPLC (Chiralcel OJ-H column, 1.0 mL/min, hexane/2-propanol = 95/5, 230 nm, \(t_1 = 16.8\) min (minor), \(t_2 = 23.7\) min (major)); \([\alpha]_D^{24} = -20\) (c 0.50, CHCl₃) for >99.5% ee. \(^1\text{H NMR} (500\text{ MHz, CDCl}_3)\) \(\delta\) 11.17 (s, 1H), 8.28 (dd, \(J = 4.6, 1.1\) Hz, 1H), 7.67 (dd, \(J = 8.1, 1.5\) Hz, 1H), 7.35–7.26 (m, 4H), 7.26–7.19 (m, 1H), 7.07 (s, 1H), 6.97 (dd, \(J = 8.0, 4.6\) Hz, 1H), 6.34 (ddd, \(J = 17.2, 10.3, 7.0\) Hz, 1H), 5.25–5.18 (m, 1H), 5.12–5.05 (m, 1H), 4.93 (d, \(J = 6.9\) Hz, 1H); \(^{13}\text{C}{^1\text{H}}\) NMR (126 MHz, CDCl₃) \(\delta\) 149.4, 142.8, 142.3, 140.1, 128.4, 128.35, 128.33, 126.4, 123.3, 119.6, 116.5, 115.7, 115.2, 47.1; IR (neat, cm\(^{-1}\)) 3153, 3084, 3026, 2927, 2887, 2786, 1637,
1602, 1581, 1493, 1451, 1419, 1335, 1294, 1218, 1120, 995, 918, 807, 764, 702, 675, 651, 574, 528, 499; HRMS (FAB) m/z [M+H]^+ calcd for C_{16}H_{15}N_{2} 235.1230; found 235.1233.

(R)-1-Methyl-3-(1-phenylallyl)-1H-pyrrolo[2,3-b]pyridine (3ab)

Compound 3ab was prepared according to general procedure using 1a (67.6 mg, 0.504 mmol) and 2b (99.3 mg, 0.751 mmol). The crude reaction mixture was purified by column chromatography using toluene/EtOAc (99/1) to afford 3ab (102.1 mg, 0.4111 mmol, 82% yield, 99% ee) as a brown oil. The ee was measured by HPLC (Chiralcel OJ-H column, 1.0 mL/min, hexane/2-propanol = 99/1, 230 nm, t₁ = 20.1 min (minor), t₂ = 25.4 min (major)); [α]^{25}_D –6 (c 1.05, CHCl₃) for 99% ee. ^1H NMR (500 MHz, CDCl₃) δ 8.29 (dd, J = 5.2, 1.4 Hz, 1H), 7.62 (dd, J = 7.5, 1.5 Hz, 1H), 7.32–7.20 (m, 5H), 6.93 (dd, J = 8.0, 4.9 Hz, 1H), 6.85 (s, 1H), 6.31 (dd, J = 17.2, 9.7, 7.2 Hz, 1H), 5.24–5.18 (m, 1H), 5.07 (dt, J = 16.6, 1.4 Hz, 1H), 4.91 (d, J = 7.5 Hz, 1H), 3.83 (s, 3H); ^13C{^1H} NMR (126 MHz, CDCl₃) δ 148.3, 142.8, 142.7, 140.1, 128.4, 128.3, 128.0, 127.1, 126.4, 119.5, 115.7, 115.3, 114.9, 47.0, 31.0; IR (neat, cm⁻¹) 3382, 3058, 3029, 2975, 2937, 2862, 1706, 1635, 1598, 1575, 1537, 1491, 1459, 1409, 1347, 1298, 1142, 997, 919, 796, 771, 702; HRMS (FAB) m/z [M+H]^+ calcd for C_{17}H_{17}N_{2} 249.1386; found 249.1382.

(R)-3-(1-(4-Methoxyphenyl)allyl)-1-methyl-1H-pyrrolo[2,3-b]pyridine (3bb)

Compound 3bb was prepared according to general procedure using 1b (83.2 mg, 0.507 mmol) and 2b (92.5 mg, 0.700 mmol). The crude reaction mixture was purified by column chromatography using toluene/EtOAc (9/1) to afford 3bb (120.5 mg, 0.4329 mmol, 85% yield, 96% ee) as a yellow oil. The ee was measured by HPLC (Chiralcel OJ-H
column, 1.0 mL/min, hexane/2-propanol = 99/1, 230 nm, \( t_1 = 11.3 \) min (major), \( t_2 = 16.1 \) min (minor); \([\alpha]_{D}^{25} = -4 \) (c 1.01, CHCl\(_3\)) for 96% ee. \(^1\)H NMR (500 MHz, CDCl\(_3\)) \( \delta \) 8.29 (d, \( J = 4.6 \) Hz, 1H), 7.62 (d, \( J = 8.1 \) Hz, 1H), 7.17 (d, \( J = 8.6 \) Hz, 2H), 6.93 (dd, \( J = 8.0 \), 5.0 Hz, 1H), 6.85 (d, \( J = 8.0 \) Hz, 2H), 6.84 (s, 1H), 6.29 (ddd, \( J = 17.2, 10.3, 7.2 \) Hz, 1H), 5.18 (d, \( J = 10.3 \) Hz, 1H), 5.05 (d, \( J = 17.2 \) Hz, 1H), 4.86 (d, \( J = 6.9 \) Hz, 1H), 3.83 (s, 3H), 3.79 (s, 3H); \(^{13}\)C\({}^{1}\)H\) NMR (126 MHz, CDCl\(_3\)) \( \delta \) 158.2, 148.3, 142.8, 140.4, 134.9, 129.2, 128.0, 127.0, 119.5, 115.6, 115.4, 114.9, 113.8, 55.2, 46.2, 31.0; IR (neat, cm\(^{-1}\)) 3057, 3034, 3004, 2951, 2934, 2910, 1635, 1608, 1599, 1537, 1459, 1409, 1347, 1299, 1177, 1144, 1036, 919, 826, 807, 772, 643, 545; HRMS (FAB) \( m/z \) [M+H\(^+\)] calcd for C\(_{18}\)H\(_{19}\)N\(_2\)O 279.1492; found 279.1489.

(R)-1-Methyl-3-(1-(p-tolyl)allyl)-1H-pyrrolo[2,3-b]pyridine (3cb)

Compound 3cb was prepared according to general procedure using 1c (74.0 mg, 0.499 mmol) and 2b (99.5 mg, 0.753 mmol). The crude reaction mixture was purified by column chromatography using toluene/EtOAc (98/2) to afford 3cb (111.2 mg, 0.4239 mmol, 85% yield, 98% ee) as a brown oil. The ee was measured by HPLC (Chiralcel OD-H column, 1.0 mL/min, hexane/2-propanol = 99/1, 230 nm, \( t_1 = 8.5 \) min (major), \( t_2 = 10.0 \) min (minor)); \([\alpha]_{D}^{25} = +5 \) (c 1.09, CHCl\(_3\)) for 98% ee. \(^1\)H NMR (500 MHz, CDCl\(_3\)) \( \delta \) 8.29 (dd, \( J = 4.6, 1.2 \) Hz, 1H), 7.63 (dd, \( J = 8.1, 1.7 \) Hz, 1H), 7.19–7.08 (m, 4H), 6.93 (dd, \( J = 8.0, 4.9 \) Hz, 1H), 6.84 (s, 1H), 6.30 (ddd, \( J = 17.2, 10.3, 7.2 \) Hz, 1H), 5.21–5.15 (m, 1H), 5.10–5.03 (m, 1H), 4.87 (d, \( J = 6.9 \) Hz, 1H), 3.82 (s, 3H), 2.32 (s, 3H); \(^{13}\)C\({}^{1}\)H\) NMR (126 MHz, CDCl\(_3\)) \( \delta \) 148.3, 142.8, 140.3, 139.8, 136.0, 129.1, 128.1, 128.0, 127.0, 119.6, 115.6, 115.4, 114.9, 113.8, 55.2, 46.7, 31.0, 21.0; IR (neat, cm\(^{-1}\)) 3051, 3007, 2971, 2822, 2854, 1635, 1597, 1571, 1537, 1511, 1490, 1459, 1409, 1347, 1298, 1143, 996, 918, 811, 771, 732, 640, 546, 523; HRMS (FAB) \( m/z \) [M+H\(^+\)] calcd for C\(_{18}\)H\(_{19}\)N\(_2\) 263.1543; found 263.1544.

(R)-1-Methyl-3-(1-(o-tolyl)allyl)-1H-pyrrolo[2,3-b]pyridine (3db)
Compound 3db was prepared according to general procedure using 1d (76.4 mg, 0.516 mmol) and 2b (98.7 mg, 0.747 mmol). The crude reaction mixture was purified by column chromatography using hexane/EtOAc (99/1) to afford 3db (129.8 mg, 0.4947 mmol, 96% yield, >99.5% ee) as a brown oil. The ee was measured by HPLC (Chiralcel OD-H column, 1.0 mL/min, hexane/2-propanol = 99/1, 230 nm, t1 = 7.0 min (major), t2 = 8.9 min (minor)); [α]D27 +23 (c 0.54, CHCl3) for >99.5% ee. 1H NMR (500 MHz, CDCl3) δ 8.29 (dd, J = 5.2, 1.4 Hz, 1H), 7.61 (dd, J = 8.0, 1.4 Hz, 1H), 7.22–7.09 (m, 4H), 6.94 (dd, J = 8.0, 4.6 Hz, 1H), 6.27 (ddd, J = 17.2, 10.3, 6.7 Hz, 1H), 5.21 (dt, J = 9.8, 1.4 Hz, 1H), 5.09 (d, J = 5.8 Hz, 1H), 4.97 (dt, J = 17.2, 1.7 Hz, 1H), 3.82 (s, 3H), 2.33 (s, 3H); 13C{1H} NMR (126 MHz, CDCl3) δ 148.3, 142.8, 140.7, 139.5, 136.0, 130.4, 128.0, 127.8, 127.5, 126.4, 126.0, 119.8, 115.8, 114.9, 114.8, 42.8, 31.0, 19.5; IR (neat, cm−1) 3059, 3014, 2979, 2943, 1598, 1571, 1537, 1488, 1459, 1409, 1347, 1298, 1141, 998, 919, 797, 771, 749, 733, 545; HRMS (FAB) m/z [M+H]+ calcd for C18H19N2 263.1543; found 263.1542.

(R)-3-((2,6-Dimethylphenyl)allyl)-1-methyl-1H-pyrrolo[2,3-b]pyridine (3eb)

Compound 3eb was prepared according to general procedure using 1e (79.9 mg, 0.493 mmol) and 2b (106.6 mg, 0.8066 mmol). The crude reaction mixture was purified by column chromatography using toluene/EtOAc (98/2) to afford 3eb (66.6 mg, 0.2410 mmol, 49% yield, >99.5% ee) as a white solid (mp 125.1-126.1 °C). The ee was measured by HPLC (Chiralcel OJ-H column, 1.0 mL/min, hexane/2-propanol = 99/1, 230 nm, t1 = 5.7 min (major), t2 = 6.5 min (minor)); [α]D25 −76 (c 1.01, CHCl3) for >99.5% ee. 1H NMR (500 MHz, CDCl3) δ 8.26 (dd, J = 4.6, 1.7 Hz, 1H), 7.30–7.24 (m, 1H), 7.09 (t, J = 7.5 Hz, 1H), 7.01 (d, J = 7.4 Hz, 2H), 6.87–6.82 (m, 2H), 6.48 (ddd, J = 16.9, 9.9, 6.7 Hz, 1H), 5.35
(d, J = 6.9 Hz, 1H), 5.24 (d, J = 10.3 Hz, 1H), 5.18–5.10 (m, 1H), 3.84 (s, 3H), 2.23 (s, 6H); 
\(^{13}\)C NMR (126 MHz, CDCl\(_3\)) \(\delta\) 148.2, 142.7, 138.6, 137.9, 137.0, 129.2, 127.9, 126.5, 126.2, 119.7, 116.1, 114.83, 114.76, 42.6, 31.1, 21.3; IR (KBr, cm\(^{-1}\)) 3441, 3055, 3014, 2935, 1536, 1489, 1460, 1407, 1343, 1295, 1215, 1142, 1017, 925, 810, 794, 776; HRMS (FAB) \(m/z\) [M+H]\(^+\) calcd for C\(_{19}\)H\(_{21}\)N\(_2\) 277.1699; found 277.1703.

\((R)-3-(1-(4-Bromophenyl)allyl)-1-methyl-1H-pyrrolo[2,3-b]pyridine (3fb)\)

\[
\text{Br} \\
\text{N} \\
\text{Me} \\
3fb
\]

Compound 3fb was prepared according to general procedure using 1f (107.3 mg, 0.504 mmol) and 2b (98.7 mg, 0.747 mmol). The crude reaction mixture was purified by column chromatography using toluene/EtOAc (98/2) to afford 3fb (103.1 mg, 0.3151 mmol, 63% yield, 99% ee) as a brown oil. The ee was measured by HPLC (Chiralcel OD-H column, 1.0 mL/min, hexane/2-propanol = 99/1, 230 nm, \(t_1 = 9.6\) min (major), \(t_2 = 10.9\) min (minor)); \([\alpha]^{28}_{\text{D}} -10\) (c 0.50, CHCl\(_3\)) for 99% ee. \(^1\)H NMR (500 MHz, CDCl\(_3\)) \(\delta\) 8.30 (dd, \(J = 5.2, 1.4\) Hz, 1H), 7.58 (dd, \(J = 8.0, 1.7\) Hz, 1H), 7.44–7.39 (m, 2H), 7.15–7.10 (m, 2H), 6.94 (dd, \(J = 8.0, 4.6\) Hz, 1H), 6.85 (s, 1H), 6.26 (ddd, \(J = 17.2, 10.3, 7.0\) Hz, 1H), 5.22 (d, \(J = 10.3\) Hz, 1H), 5.06 (dt, \(J = 16.6, 1.4\) Hz, 1H), 4.86 (d, \(J = 6.9\) Hz, 1H), 3.84 (s, 3H); \(^{13}\)C \(^{1}\)H NMR (126 MHz, CDCl\(_3\)) \(\delta\) 148.3, 143.0, 141.8, 139.5, 131.5, 130.1, 127.8, 127.1, 120.3, 119.3, 116.2, 115.0, 114.7, 46.4, 31.1; IR (neat, cm\(^{-1}\)) 3080, 3057, 3007, 2979, 2935, 2858, 1536, 1597, 1572, 1537, 1487, 1459, 1408, 1347, 1298, 1143, 1072, 1011, 921, 802, 771, 546; HRMS (FAB) \(m/z\) [M+H]\(^+\) calcd for C\(_{17}\)H\(_{16}\)BrN\(_2\) 327.0491; found 327.0495.

\((R)-1-Methyl-3-(1-(4-(trifluoromethyl)phenyl)allyl)-1H-pyrrolo[2,3-b]pyridine (3gb)\)

\[
\text{F}_3\text{C} \\
\text{N} \\
\text{Me} \\
3gb
\]
Compound 3gb was prepared according to general procedure using 1g (109.2 mg, 0.540 mmol) and 2b (100.8 mg, 0.7627 mmol). The crude reaction mixture was purified by column chromatography using toluene/EtOAc (98/2) to afford 3gb (68.2 mg, 0.2156 mmol, 40% yield, 99% ee) as a yellow oil. The ee was measured by HPLC (Chiralcel OJ-H column, 1.0 mL/min, hexane/2-propanol = 99/1, 230 nm, t₁ = 9.4 min (minor), t₂ = 10.5 min (major)); [α]$_{25}^{D}$ = -15 (c 0.97, CHCl₃) for 99% ee. $^1$H NMR (500 MHz, CDCl₃) δ 8.31 (dd, $J$ = 4.6, 1.7 Hz, 1H), 7.59 (dd, $J$ = 8.1, 1.7 Hz, 1H), 7.56 (d, $J$ = 8.1 Hz, 1H), 7.38 (d, $J$ = 8.1 Hz, 2H), 6.95 (dd, $J$ = 8.0, 4.6 Hz, 1H), 6.88 (s, 1H), 6.29 (ddd, $J$ = 17.2, 9.8, 7.2 Hz, 1H), 5.28–5.23 (m, 1H), 5.13–5.05 (m, 1H), 4.97 (d, $J$ = 7.5 Hz, 1H), 3.85 (s, 3H); $^{13}$C{^1}H NMR (126 MHz, CDCl₃) δ 148.3, 146.9, 143.1, 139.2, 128.8 (q, $J_{C-F}$ = 32.2 Hz), 128.7, 127.8, 127.2, 125.4 (q, $J_{C-F}$ = 3.6 Hz), 124.2 (q, $J_{C-F}$ = 270.7 Hz), 119.3, 116.5, 115.1, 114.4, 46.8, 31.1; $^{19}$F NMR (471 MHz, CDCl₃) δ -62.2; IR (neat, cm$^{-1}$) 3059, 3010, 2979, 2937, 2862, 1721, 1636, 1617, 1598, 1537, 1491, 1460, 1411, 1326, 1299, 1164, 1123, 1067, 1017, 924, 832, 805, 772, 602; HRMS (FAB) m/z [M+H]$^+$ calcd for C₁₈H₁₆F₃N₂ 317.1260; found 317.1261.

Methyl (R)-4-(1-(1-methyl-1H-pyrrolo[2,3-b]pyridin-3-yl)allyl)benzoate (3hb)

Compound 3hb was prepared according to general procedure using 1h (95.9 mg, 0.499 mmol) and 2b (104.0 mg, 0.7869 mmol). The crude reaction mixture was purified by column chromatography using hexane/EtOAc (3/1) to afford 3hb (82.6 mg, 0.2696 mmol, 54% yield, 99% ee) as a yellow oil. The ee was measured by HPLC (Chiralcel OJ-3 column, 1.0 mL/min, hexane/2-propanol = 96/4, 230 nm, t₁ = 24.9 min (minor), t₂ = 28.2 min (major)); [α]$_{25}^{D}$ = -16 (c 0.99, CHCl₃) for 99% ee. $^1$H NMR (500 MHz, CDCl₃) δ 8.30 (dd, $J$ = 4.6, 1.7 Hz, 1H), 8.01–7.96 (m, 2H), 7.57 (dd, $J$ = 8.0, 1.7 Hz, 1H), 7.36–7.32 (m, 2H), 6.94 (dd, $J$ = 8.1, 4.9 Hz, 1H), 6.87 (s, 1H), 6.30 (ddd, $J$ = 17.2, 9.7, 7.2 Hz, 1H), 5.27–5.22 (m, 1H), 5.08 (dt, $J$ = 17.2, 1.3 Hz, 1H), 4.96 (d, $J$ = 6.9 Hz, 1H), 3.90 (s, 3H), 3.85 (s, 3H); $^{13}$C{^1}H NMR (126 MHz, CDCl₃) δ 167.0, 148.3, 148.1, 143.0, 139.2, 129.8, 128.5, 128.4, 127.8, 127.2, 119.3, 116.4, 115.1, 114.5, 52.0, 47.0, 31.1; IR (neat, cm$^{-1}$) 3423, 3057, 3010, 2979, 2937, 2862, 1721, 1636, 1617, 1598, 1537, 1491, 1460, 1411, 1326, 1299, 1164, 1123, 1067, 1017, 924, 832, 805, 772, 602; HRMS (FAB) m/z [M+H]$^+$ calcd for C₁₈H₁₆F₃N₂ 317.1260; found 317.1261.
3006, 2951, 2857, 1721, 1608, 1572, 1491, 1460, 1436, 1410, 1347, 1280, 1179, 1112, 1019, 922, 805, 767, 727, 710, 602, 579, 545; HRMS (FAB) \textit{m/z} [M+H]^+ \text{calcd for } C_{19}H_{19}N_2O_2 307.1441; \text{found 307.1443.}

\textbf{\textit{(R)}-1-Methyl-3-(1-(4-nitrophenyl)allyl)-1H-pyrrolo[2,3-b]pyridine (3ib)}

\begin{center}
\includegraphics[width=0.2\textwidth]{3ib}
\end{center}

Compound 3ib was prepared according to general procedure using 1i (90.1 mg, 0.503 mmol) and 2b (99.4 mg, 0.752 mmol). The crude reaction mixture was purified by column chromatography using hexane/EtOAc (3/1) to afford 3ib (38.6 mg, 0.132 mmol, 26\% yield, >99.5\% ee) as a yellow oil. The ee was measured by HPLC (Chiralpak AD-3 column, 1.0 mL/min, hexane/2-propanol = 95/5, 230 nm, \(t_1 = 20.4\) min (major), \(t_2 = 21.5\) min (minor)); \([\alpha]^{24}_{D} = 24\) (c 0.17, CHCl_3) for >99.5\% ee. \(^1\text{H NMR (500 MHz, CDCl}_3\) \(\delta 8.32\) (dd, \(J = 4.6, 1.7\) Hz, 1H), 8.19–8.13 (m, 2H), 7.58–7.53 (m, 1H), 7.42 (d, \(J = 8.6\) Hz, 2H), 6.96 (dd, \(J = 8.1, 4.6\) Hz, 1H), 6.92 (s, 1H), 6.30 (ddd, \(J = 17.2, 10.3, 6.9\) Hz, 1H), 5.29 (d, \(J = 9.8\) Hz, 1H), 5.10 (d, \(J = 17.2\) Hz, 1H), 5.03 (d, \(J = 6.9\) Hz, 1H), 3.87 (s, 3H); \(^{13}\text{C}\{^1\text{H}\} NMR (126 MHz, CDCl}_3\) \(\delta 150.4, 148.3, 146.7, 143.3, 138.6, 129.2, 127.6, 127.2, 119.1, 117.1, 115.3, 113.7, 46.8, 31.1;\) IR (neat, cm\(^{-1}\)) 3105, 3077, 3058, 2926, 2855, 1720, 1657, 1637, 1598, 1519, 1491, 1460, 1409, 1345, 1299, 1142, 1123, 1109, 925, 853, 841, 805, 772, 753, 723, 705, 545; HRMS (FAB) \textit{m/z} [M+H]^+ \text{calcd for } C_{17}H_{16}N_2O_2 294.1237; \text{found 294.1237.}

\textbf{\textit{(R)}-1-Methyl-3-(1-(naphthalen-2-yl)allyl)-1H-pyrrolo[2,3-b]pyridine (3jb)}

\begin{center}
\includegraphics[width=0.2\textwidth]{3jb}
\end{center}

Compound 3jb was prepared according to general procedure using 1j (93.7 mg, 0.507 mmol) and 2b (99.4 mg, 0.752 mmol). The crude reaction mixture was purified by column chromatography using hexane/EtOAc (3/1) to afford 3jb (47.6 mg, 0.155 mmol, 31\% yield, >99.5\% ee) as a yellow oil. The ee was measured by HPLC (Chiralpak AD-3 column, 1.0 mL/min, hexane/2-propanol = 95/5, 230 nm, \(t_1 = 20.4\) min (major), \(t_2 = 21.5\) min (minor)); \([\alpha]^{24}_{D} = 24\) (c 0.17, CHCl_3) for >99.5\% ee. \(^1\text{H NMR (500 MHz, CDCl}_3\) \(\delta 8.32\) (dd, \(J = 4.6, 1.7\) Hz, 1H), 8.19–8.13 (m, 2H), 7.58–7.53 (m, 1H), 7.42 (d, \(J = 8.6\) Hz, 2H), 6.96 (dd, \(J = 8.1, 4.6\) Hz, 1H), 6.92 (s, 1H), 6.30 (ddd, \(J = 17.2, 10.3, 6.9\) Hz, 1H), 5.29 (d, \(J = 9.8\) Hz, 1H), 5.10 (d, \(J = 17.2\) Hz, 1H), 5.03 (d, \(J = 6.9\) Hz, 1H), 3.87 (s, 3H); \(^{13}\text{C}\{^1\text{H}\} NMR (126 MHz, CDCl}_3\) \(\delta 150.4, 148.3, 146.7, 143.3, 138.6, 129.2, 127.6, 127.2, 119.1, 117.1, 115.3, 113.7, 46.8, 31.1;\) IR (neat, cm\(^{-1}\)) 3105, 3077, 3058, 2926, 2855, 1720, 1657, 1637, 1598, 1519, 1491, 1460, 1409, 1345, 1299, 1142, 1123, 1109, 925, 853, 841, 805, 772, 753, 723, 705, 545; HRMS (FAB) \textit{m/z} [M+H]^+ \text{calcd for } C_{18}H_{16}N_2O_2 294.1237; \text{found 294.1237.}
0.509 mmol) and 2b (98.0 mg, 0.741 mmol). The crude reaction mixture was purified by column chromatography using hexane/EtOAc (99/1) to afford 3jb (143.1 mg, 0.4796 mmol, 94% yield, 99% ee) as a brown oil. The ee was measured by HPLC (Chiralcel OD-H column, 1.0 mL/min, hexane/2-propanol = 99/1, 230 nm, t1 = 11.2 min (major), t2 = 14.6 min (minor); [α]D27 +3 (c 0.59, CHCl3) for 99% ee. 1H NMR (500 MHz, CDCl3) δ 8.29 (dd, J = 4.6, 1.7 Hz, 1H), 7.84–7.75 (m, 3H), 7.71 (s, 1H), 7.63 (dd, J = 8.0, 1.4 Hz, 1H), 7.48–7.41 (m, 2H), 7.39 (dd, J = 8.0, 1.7 Hz, 1H), 6.91 (dd, J = 7.5, 4.9 Hz, 1H), 6.88 (s, 1H), 6.40 (ddd, J = 17.2, 9.8, 7.2 Hz, 1H), 5.29–5.23 (m, 1H), 5.16–5.05 (m, 2H), 3.84 (s, 3H); 13C{1H} NMR (126 MHz, CDCl3) δ 148.3, 142.9, 140.3, 139.9, 133.5, 132.3, 128.0, 127.8, 127.6, 127.3, 127.1, 126.5, 126.0, 125.5, 119.6, 116.1, 115.2, 115.0, 47.1, 31.1; IR (neat, cm⁻¹) 3055, 3007, 2971, 2938, 1632, 1598, 1571, 1537, 1490, 1459, 1409, 1347, 1299, 1143, 996, 919, 858, 755, 478; HRMS (FAB) m/z [M+H]+ calcd for C21H19N2 299.1543; found 299.1546.

(S)-3-(1-(Furan-2-yl)allyl)-1-methyl-1H-pyrrolo[2,3-b]pyridine (3kb)

Compound 3kb was prepared according to general procedure using 1k (65.0 mg, 0.524 mmol) and 2b (104.0 mg, 0.7869 mmol). The crude reaction mixture was purified by column chromatography using toluene/EtOAc (98/2) to afford 3kb (83.0 mg, 0.348 mmol, 66% yield, 83% ee) as a brown oil. The ee was measured by HPLC (Chiralcel OD-H column, 1.0 mL/min, hexane/2-propanol = 99/1, 230 nm, t1 = 8.9 min (minor), t2 = 9.8 min (major); [α]D21 +4 (c 1.00, CHCl3) for 83% ee. 1H NMR (500 MHz, CDCl3) δ 8.31 (dd, J = 4.6, 1.1 Hz, 1H), 7.74 (dd, J = 8.0, 1.7 Hz, 1H), 7.37 (s, 1H), 7.03–6.96 (m, 2H), 6.32 (dd, J = 3.5, 2.0 Hz, 1H), 6.26 (dd, J = 17.2, 9.7, 7.0 Hz, 1H), 6.09 (d, J = 2.9 Hz, 1H), 5.21 (d, J = 9.7 Hz, 1H), 5.17–5.10 (m, 1H), 4.97 (d, J = 6.9 Hz, 1H), 3.85 (s, 3H); 13C{1H} NMR (126 MHz, CDCl3) δ 155.8, 148.1, 142.9, 141.6, 137.4, 127.8, 126.9, 119.3, 116.1, 115.1, 112.5, 110.2, 106.2, 40.8, 31.1; IR (neat, cm⁻¹) 3116, 3058, 3009, 2975, 2941, 2862, 1723, 1639, 1598, 1538, 1460, 1409, 1348, 1299, 1146, 1010, 921, 799, 770, 599, 546; HRMS (FAB) m/z [M+H]+ calcd for C15H13N2O 239.1179; found 239.1180.

(S)-1-Methyl-3-(1-(thiophen-2-yl)allyl)-1H-pyrrolo[2,3-b]pyridine (3lb)
Compound 3lb was prepared according to general procedure using 1l (71.3 mg, 0.509 mmol) and 2b (101.2 mg, 0.765 mmol). The crude reaction mixture was purified by column chromatography using toluene/EtOAc (98/2) to afford 3lb (107.5 mg, 0.4226 mmol, 83% yield, 90% ee) as a brown oil. The ee was measured by HPLC (Chiralcel OJ-H column, 1.0 mL/min, hexane/2-propanol = 99/1, 230 nm, t1 = 26.6 min (major), t2 = 33.1 min (minor)); [α]28D –17 (c 0.53, CHCl3) for 90% ee. 1H NMR (500 MHz, CDCl3) δ 8.31 (dd, J = 4.6, 1.1 Hz, 1H), 7.72 (dd, J = 8.0, 1.4 Hz, 1H), 7.18 (dd, J = 5.2, 1.1 Hz, 1H), 7.01–6.93 (m, 3H), 6.87 (d, J = 3.5 Hz, 1H), 6.33 (ddd, J = 16.6, 10.0, 7.2 Hz, 1H), 5.24–5.13 (m, 3H), 3.85 (s, 3H); 13C{1H} NMR (126 MHz, CDCl3) δ 148.2, 146.9, 143.0, 139.6, 127.9, 126.9, 124.7, 124.7, 124.7, 124.0, 119.2, 115.7, 115.1, 115.0, 42.2, 31.1; IR (neat, cm⁻¹) 3059, 3007, 2975, 2933, 2858, 1636, 1598, 1571, 1537, 1490, 1459, 1436, 1408, 1347, 1299, 1227, 1141, 1037, 992, 922, 797, 771, 699, 545; HRMS (FAB) m/z [M+H]⁺ calcd for C15H15N2S 255.0951; found 255.0951.

(R)-5-Methoxy-1-methyl-3-(1-phenylallyl)-1H-pyrrolo[2,3-b]pyridine (3ad)

Compound 3ad was prepared according to general procedure using 1a (67.3 mg, 0.502 mmol) and 2d (123.5 mg, 0.7614 mmol). The crude reaction mixture was purified by column chromatography using toluene/EtOAc (98/2) to afford 3ad (113.4 mg, 0.4074 mmol, 81% yield, 83% ee) as a brown oil. The ee was measured by HPLC (Chiralpak AD-3 column, 1.0 mL/min, hexane/2-propanol = 99/1, 230 nm, t1 = 15.7 min (minor), t2 = 16.5 min (major)); [α]26D +11 (c 0.53, CHCl3) for 83% ee. 1H NMR (500 MHz, CDCl3) δ 8.07 (d, J = 2.9 Hz, 1H), 7.34-7.20 (m, 5H), 7.09 (d, J = 2.5 Hz, 1H), 6.82 (s, 1H), 6.30 (ddd, J = 17.2, 9.7, 7.2 Hz), 5.21 (d, J = 10.3 Hz, 1H), 5.08 (d, J = 17.2 Hz, 1H), 4.86 (d, J = 7.5
Hz, 1H), 3.80 (s, 3H), 3.76 (s, 3H); $^{13}$C{$^1$H} NMR (126 MHz, CDCl$_3$) $\delta$ 150.6, 144.0, 142.7, 140.0, 133.2, 128.4, 128.3, 128.0, 126.5, 119.2, 115.7, 114.5, 111.0, 56.4, 47.1, 31.2; IR (neat, cm$^{-1}$) 3080, 3060, 3026, 2937, 2834, 1636, 1601, 1535, 1492, 1452, 1407, 1359, 1291, 1261, 1216, 1174, 1140, 1036, 917, 702; HRMS (FAB) $m/z$ [M+H]$^+$ calcd for C$_{18}$H$_{19}$N$_2$O 279.1492; found 279.1494.

**(R)-5-chloro-1-methyl-3-(1-phenylallyl)-1H-pyrrolo[2,3-b]pyridine (3ae)**

![3ae](image)

Compound 3ae was prepared according to general procedure using 1a (67.1 mg, 0.500 mmol) and 2e (125.4 mg, 0.7527 mmol). The crude reaction mixture was purified by column chromatography using toluene/EtOAc (98/2) to afford 3ae (123.7 mg, 0.4375 mmol, 87% yield, 94% ee) as a yellow oil. The ee was measured by HPLC (Chiralcel OZ-H column, 1.0 mL/min, hexane/2-propanol = 99/1, 254 nm, $t_1 = 4.9$ min (major), $t_2 = 5.6$ min (minor)); $[\alpha]_D^{23} = -3$ (c 0.97, CHCl$_3$) for 94% ee. $^1$H NMR (500 MHz, CDCl$_3$) $\delta$ 8.22 (d, $J = 2.3$ Hz, 1H), 7.59 (d, $J = 2.3$ Hz, 1H), 7.35–7.29 (m, 2H), 7.27–7.22 (m, 3H), 6.87 (s, 1H), 6.28 (ddd, $J = 17.5, 10.2, 7.2$ Hz, 1H), 5.22 (d, $J = 9.8$ Hz, 1H), 5.07 (dt, $J = 17.2, 1.4$ Hz, 1H), 4.85 (d, $J = 6.9$ Hz, 1H), 3.80 (s, 3H); $^{13}$C{$^1$H} NMR (126 MHz, CDCl$_3$) $\delta$ 146.6, 142.3, 141.4, 139.7, 128.8, 128.5, 128.2, 127.1, 126.7, 123.0, 120.1, 116.1, 115.0, 46.9, 31.2; IR (neat, cm$^{-1}$) 3081, 3060, 3027, 2976, 2936, 2872, 1636, 1599, 1559, 1532, 1481, 1407, 1348, 1279, 1254, 1222, 1143, 1092, 921, 885, 763, 750, 723, 701, 607, 578; HRMS (FAB) $m/z$ [M+H]$^+$ calcd for C$_{17}$H$_{16}$ClN$_2$ 283.0997; found 283.0997.

**(R)-5-Bromo-1-methyl-3-(1-phenylallyl)-1H-pyrrolo[2,3-b]pyridine (3af)**

![3af](image)

Compound 3af was prepared according to general procedure using 1a (68.1 mg, 0.508 mmol) and 2f (158.4 mg, 0.7505 mmol). The crude reaction mixture was purified
by column chromatography using toluene/EtOAc (99/1) to afford 3af (125.6 mg, 0.3838 mmol, 76% yield, 97% ee) as a brown oil. The ee was measured by HPLC (Chiraleel OZ-H column, 1.0 mL/min, hexane/2-propanol = 99/1, 230 nm, \( t_1 = 5.3 \) min (major), \( t_2 = 6.0 \) min (minor)); \([\alpha]\)\(^{25}\)D\(_{+18}\) (c 0.50, CHCl\(_3\)) for 97% ee. \(^1\)H NMR (500 MHz, CDCl\(_3\)) \( \delta \) 8.30 (d, \( J = 1.7 \) Hz, 1H), 7.74 (d, \( J = 2.0 \) Hz, 1H), 7.32 (t, \( J = 7.5 \) Hz, 2H), 7.27–7.22 (m, 3H), 6.84 (s, 1H), 6.28 (ddd, \( J = 17.2, 10.3, 7.0 \) Hz, 1H), 5.22 (d, \( J = 9.8 \) Hz, 1H), 5.06 (d, \( J = 17.2 \) Hz, 1H), 4.85 (d, \( J = 6.9 \) Hz, 1H), 3.80 (s, 3H); \(^{13}\)C\({\{^1}\}H\) NMR (126 MHz, CDCl\(_3\)) \( \delta \) 146.6, 143.3, 142.3, 139.7, 130.0, 128.6, 128.5, 128.2, 126.7, 121.0, 116.1, 115.0, 111.0, 46.8, 31.2; IR (neat, cm\(^{-1}\)) 3076, 3060, 3027, 3004, 2979, 2938, 2872, 1636, 1598, 1557, 1531, 1481, 1451, 1408, 1349, 1278, 1255, 1222, 1142, 1079, 995, 920, 882, 815, 762, 701; HRMS (FAB) \( m/z \) [M+H]\(^+\) calcd for C\(_{17}\)H\(_{16}\)BrN\(_2\): 327.0491; found 327.0488.

(R)-4-Chloro-1-methyl-3-(1-phenylallyl)-1H-pyrrolo[2,3-b]pyridine (3ag)

![3ag](image)

Compound 3ag was prepared according to general procedure using 1a (68.5 mg, 0.511 mmol) and 2g (121.2 mg, 0.7275 mmol). The crude reaction mixture was purified by column chromatography using hexane/EtOAc (9/1) to afford 3ag (71.4 mg, 0.253 mmol, 49% yield, 97% ee) as a white solid (mp 69.0–69.3 °C). The ee was measured by HPLC (Chiralpak AD-3 column, 1.0 mL/min, hexane/2-propanol = 99/1, 230 nm, \( t_1 = 7.7 \) min (minor), \( t_2 = 9.1 \) min (major)); \([\alpha]\)\(^{25}\)D\(_{-6}\) (c 0.99, CHCl\(_3\)) for 97% ee. \(^1\)H NMR (500 MHz, CDCl\(_3\)) \( \delta \) 8.15 (d, \( J = 5.2 \) Hz, 1H), 7.33–7.27 (m, 2H), 7.26–7.19 (m, 3H), 6.98 (d, \( J = 5.2 \) Hz, 1H), 6.87 (s, 1H), 6.33 (ddd, \( J = 17.2, 10.3, 6.4 \) Hz, 1H), 5.46 (d, \( J = 6.3 \) Hz, 1H), 5.21 (d, \( J = 10.3 \) Hz, 1H), 4.88 (d, \( J = 17.2 \) Hz, 1H), 3.83 (s, 3H); \(^{13}\)C\({\{^1}\}H\) NMR (126 MHz, CDCl\(_3\)) \( \delta \) 149.1, 143.0, 140.9, 136.2, 128.7, 128.2, 126.3, 117.1, 116.4, 115.9, 115.6, 46.0, 31.5; IR (KBr, cm\(^{-1}\)) 3444, 3085, 3029, 2905, 2941, 2896, 1637, 1590, 1551, 1523, 1487, 1453, 1408, 1348, 1312, 1295, 1150, 1005, 991, 914, 878, 819, 765, 704, 662, 631, 604, 594, 551; HRMS (FAB) \( m/z \) [M+H]\(^+\) calcd for C\(_{17}\)H\(_{16}\)ClN\(_2\): 283.0997; found 283.1001.

(R)-6-Chloro-1-methyl-3-(1-phenylallyl)-1H-pyrrolo[2,3-b]pyridine (3ah)
Compound 3ah was prepared according to general procedure using 1a (67.0 mg, 0.499 mmol) and 2h (126.1 mg, 0.7569 mmol). The crude reaction mixture was purified by column chromatography using toluene/EtOAc (98/2) to afford 3ah (116.3 mg, 0.4113 mmol, 82% yield, 80% ee) as a brown oil. The ee was measured by HPLC (Chiralcel OD-H column, 1.0 mL/min, hexane/2-propanol = 99/1, 230 nm, t1 = 12.3 min (major), t2 = 13.0 min (minor)); [α]26D = −3 (c 1.06, CHCl3) for 80% ee. 1H NMR (500 MHz, CDCl3) δ 7.51 (d, J = 8.0 Hz, 1H), 7.34–7.28 (m, 2H), 7.27–7.21 (m, 3H), 6.93 (d, J = 8.1 Hz, 1H), 6.82 (s, 1H), 6.28 (ddd, J = 17.2, 9.8, 7.2 Hz, 1H), 5.21 (dt, J = 10.3, 1.3 Hz, 1H), 5.06 (dt, J = 16.6, 1.4 Hz, 1H), 4.86 (d, J = 6.9 Hz, 1H), 3.80 (s, 3H); 13C{1H} NMR (126 MHz, CDCl3) δ 147.3, 144.5, 142.4, 139.8, 130.3, 128.5, 128.2, 127.3, 126.6, 118.0, 115.94, 115.87, 115.0, 47.0, 31.2; IR (neat, cm−1) 3081, 3059, 3026, 2978, 2939, 2872, 1636, 1599, 1563, 1533, 1490, 1438, 1410, 1347, 1306, 1119, 998, 918, 876, 812, 759, 732, 701, 640, 589; HRMS (FAB) m/z [M+H]+ calcd for C17H16ClN2 283.0997; found 283.0997.

(R)-1-Methyl-5-nitro-3-(1-phenylallyl)-1H-pyrrolo[2,3-b]pyridine (3ai)

Compound 3ai was prepared according to general procedure using 1a (70.7 mg, 0.527 mmol) and 2i (132.8 mg, 0.7496 mmol). The crude reaction mixture was purified by column chromatography using hexane/EtOAc (95/5) to afford 3ai (19.7 mg, 0.0672 mmol, 13% yield, 80% ee) as a yellow oil. The ee was measured by HPLC (Chiralpak AS-3 column, 1.0 mL/min, hexane/2-propanol = 95/5, 230 nm, t1 = 8.9 min (major), t2 = 10.0 min (minor)); [α]25D = +31 (c 0.60, CHCl3) for 80% ee. 1H NMR (500 MHz, CDCl3) δ 9.18 (d, J = 2.3 Hz, 1H), 8.47 (d, J = 2.3 Hz, 1H), 7.34 (t, J = 7.5 Hz, 2H), 7.27 (t, J = 7.2 Hz, 3H), 7.00 (s, 1H), 6.31 (ddd, J = 16.6, 10.0, 7.0 Hz, 1H), 5.27 (d, J = 10.9 Hz, 1H), 5.10 (d, J = 16.6 Hz, 1H), 4.94 (d, J = 6.9 Hz, 1H), 3.89 (s, 3H); 13C{1H} NMR (126 MHz, CDCl3)
δ 149.9, 141.7, 139.6, 139.2, 138.5, 130.6, 128.7, 128.2, 127.0, 124.3, 118.5, 118.4, 116.6, 46.7, 31.6; IR (neat, cm⁻¹) 3079, 3023, 2978, 2938, 2855, 1855, 1712, 1637, 1560, 1575, 1538, 1511, 1492, 1447, 1414, 1332, 1298, 1214, 1151, 1105, 992, 920, 822, 778, 749, 703, 609; HRMS (FAB) m/z [M+H]⁺ calcd for C₁₇H₁₆N₃O₂ 294.1237; found 294.1237.

(R)-1,2-Dimethyl-3-(1-phenylallyl)-1H-pyrrolo[2,3-b]pyridine (3aj)

Compound 3aj was prepared according to general procedure using 1a (61.0 mg, 0.455 mmol) and 2j (107.2 mg, 0.733 mmol). The crude reaction mixture was purified by column chromatography using toluene/EtOAc (8/2) to afford 3aj (90.7 mg, 0.346 mmol, 76% yield, 96% ee) as a yellow oil. The ee was measured by HPLC (Chiralcel OD-H column, 1.0 mL/min, hexane/2-propanol = 99/1, 230 nm, t₁ = 9.0 min (major), t₂ = 11.0 min (minor)); [α]²⁵D –3 (c 0.91, CHCl₃) for 96% ee. ¹H NMR (500 MHz, CDCl₃) δ 8.19 (dd, J = 4.6, 1.7 Hz, 1H), 7.54 (dd, J = 7.5, 1.4 Hz, 1H), 7.27 (d, J = 4.6 Hz, 4H), 7.19 (sextet, J = 4.2 Hz, 1H), 6.87 (dd, J = 7.5, 4.6 Hz, 1H), 6.42 (ddd, J = 17.2, 10.3, 6.9 Hz, 1H), 5.21 (dt, J = 10.3, 1.6 Hz, 1H), 5.04 (dt, J = 17.2, 1.7 Hz, 1H), 4.98 (d, J = 6.9 Hz, 1H), 3.79 (s, 3H), 2.38 (s, 3H); ¹³C{¹H} NMR (126 MHz, CDCl₃) δ 148.0, 142.9, 141.3, 139.8, 134.1, 128.2, 128.1, 127.0, 126.1, 119.6, 115.7, 115.0, 110.3, 45.8, 28.0, 10.7; IR (neat, cm⁻¹) 3079, 3058, 3026, 2974, 2935, 2859, 1718, 1659, 1635, 1597, 1573, 1548, 1490, 1459, 1416, 1337, 1307, 1173, 1127, 995, 917, 794, 771, 722, 701, 569; HRMS (FAB) m/z [M+H]⁺ calcd for C₁₈H₁₉N₂ 263.1543; found 263.1543.

(R)-1-(4-Methoxybenzyl)-3-(1-phenylallyl)-1H-pyrrolo[2,3-b]pyridine (3ak)

Compound 3ak was prepared according to general procedure using 1a (67.8 mg,
0.505 mmol) and 2k (178.8 mg, 0.7503 mmol). The crude reaction mixture was purified by column chromatography using toluene/EtOAc (98/2) to afford 3ak (129.2 mg, 0.3645 mmol, 72% yield, 98% ee) as a brown oil. The ee was measured by HPLC (Chiralcel OZ-H column, 1.0 mL/min, hexane/2-propanol = 99/1, 230 nm, \( t_1 = 20.3 \) min (major), \( t_2 = 22.5 \) min (minor)); [\( \alpha \)\(_{D} \)]\(^{26} \) = -14 (c 0.55, CHCl\(_3\) ) for 97% ee. \(^1\)H NMR (500 MHz, CDCl\(_3\)) \( \delta \) 8.30 (dd, \( J = 4.6, 1.7 \) Hz, 1H), 7.59 (dd, \( J = 8.1, 1.2 \) Hz, 1H), 7.31-7.26 (m, 2H), 7.25-7.12 (m, 5H), 6.94 (dd, \( J = 7.5, 4.9 \) Hz, 1H), 6.90 (s, 1H), 6.83 (d, \( J = 9.2 \) Hz, 2H), 6.33-6.23 (m, 1H), 5.41 (d, \( J = 14.9 \) Hz, 1H), 5.35 (d, \( J = 15.5 \) Hz, 1H), 5.20-5.15 (m, 1H), 5.08-5.00 (m, 1H), 4.89 (d, \( J = 6.9 \) Hz, 1H), 3.77 (s, 3H); \(^{13}\)C\(\{\text{H}\}\) NMR (126 MHz, CDCl\(_3\)) \( \delta \) 159.0, 148.2, 143.0, 142.7, 140.1, 130.0, 128.7, 128.4, 128.3, 128.1, 126.4, 125.8, 119.5, 115.9, 115.7, 115.2, 114.0, 55.2, 47.2, 47.1; IR (neat, cm\(^{-1}\)) 3059, 3027, 3000, 2956, 2932, 2836, 1725, 1636, 1581, 1549, 1513, 1487, 1451, 1358, 1303, 1249, 1175, 1035, 919, 819, 756, 702; HRMS (FAB) \( m/z \) [M+H]\(^+\) calcld for C\(_{23}\)H\(_{23}\)N\(_2\)O 355.1805; found 355.1805.

\[(R)-3-(1-(o-Toly)allyl)-1H-pyrrolo[2,3-b]pyridine (3da)\]

![Chemical structure of 3da](image)

Compound 3da was prepared according to general procedure using 1d (72.4 mg, 0.489 mmol) and 2a (87.7 mg, 0.742 mmol). The crude reaction mixture was purified by column chromatography using toluene/EtOAc (2/1) to afford 3da (58.0 mg, 0.234 mmol, 48% yield, >99.5% ee) as a pale yellow solid (mp 127.1-127.7 \(^\circ\)C). The ee was measured by HPLC (Chiralcel OJ-H column, 1.0 mL/min, hexane/2-propanol = 95/5, 230 nm, \( t_1 = 14.3 \) min (minor), \( t_2 = 15.9 \) min (major)); [\( \alpha \)\(_{D} \)]\(^{25} \) = +21 (c 1.05, CHCl\(_3\) ) for >99.5% ee. \(^1\)H NMR (500 MHz, CDCl\(_3\)) \( \delta \) 10.74 (s, 1H), 8.27 (dd, \( J = 4.6, 1.5 \) Hz, 1H), 7.69-7.62 (m, 1H), 7.22-7.10 (m, 4H), 7.01-6.94 (m, 2H), 6.30 (ddd, \( J = 16.6, 10.0, 6.6 \) Hz, 1H), 5.23 (d, \( J = 10.3 \) Hz, 1H), 5.11 (d, \( J = 6.3 \) Hz, 1H), 4.98 (d, \( J = 17.2 \) Hz, 1H), 2.34 (s, 3H); \(^{13}\)C\(\{\text{H}\}\) NMR (126 MHz, CDCl\(_3\)) \( \delta \) 149.3, 142.5, 140.6, 139.4, 136.1, 130.4, 128.13, 128.10, 126.4, 126.0, 123.5, 119.7, 116.1, 116.0, 115.3, 42.9, 19.5; IR (KBr, cm\(^{-1}\)) 3083, 2891, 1636, 1606, 1581, 1488, 1458, 1418, 1335, 1294, 1256, 1120, 997, 918, 897, 795, 767, 753, 726, 647, 505; HRMS (FAB) \( m/z \) [M+H]\(^+\) calcld for C\(_{17}\)H\(_{17}\)N\(_2\) 249.1386; found 249.1387.

\[(R)-5-Chloro-3-(1-phenylallyl)-1H-pyrrolo[2,3-b]pyridine (3al)\]

S16
Compound 3al was prepared according to general procedure using 1a (67.4 mg, 0.502 mmol) and 2l (114.0 mg, 0.747 mmol). The crude reaction mixture was purified by column chromatography using toluene/EtOAc (9/1) followed by hexane/acetone (7/3) to afford 3al (43.9 mg, 0.163 mmol, 33% yield, 99% ee) as a yellow oil. The ee was measured by HPLC (Chiralcel OJ-3 column, 1.0 mL/min, hexane/2-propanol = 95/5, 230 nm, t1 = 10.9 min (minor), t2 = 13.4 min (major)); [α]26D +23 (c 0.41, CHCl3) for 99% ee.

\[ \text{HNMR (500 MHz, CDCl}_3 \delta 10.65 (s, 1H), 8.22 (d, J = 2.3 Hz, 1H), 7.64 (d, J = 2.3 Hz, 1H), 7.35-7.29 (m, 2H), 7.29-7.22 (m, 3H), 7.07 (d, J = 1.2 Hz, 1H), 6.31 (ddd, J = 17.2, 10.3, 7.0 Hz, 1H), 5.27-5.21 (m, 1H), 5.12-5.04 (m, 1H), 4.88 (d, J = 7.5 Hz, 1H); } \]

\[ \text{^{13}C\{^1H\}NMR (126 MHz, CDCl}_3 \delta 147.5, 142.2, 141.2, 139.6, 128.6, 128.3, 127.6, 126.7, 124.9, 123.3, 120.3, 116.6, 116.2, 46.9; IR (neat, cm\(^{-1}\)) 3154, 3029, 2915, 2874, 1719, 1636, 1601, 1573, 1477, 1452, 1406, 1289, 1251, 1107, 995, 914, 884, 767, 753, 702, 670, 661, 631; } \]

\[ \text{HRMS (FAB) m/z [M+H]^+ calcd for C}_{16}H_{14}ClN_2 269.0840; } \]

\[ \text{found 269.0841.} \]

**(R)-5-Bromo-3-(1-(o-tolyl)allyl)-1H-pyrrolo[2,3-b]pyridine (3dm)**

Compound 3dm was prepared according to general procedure using 1d (74.3 mg, 0.501 mmol) and 2m (147.8 mg, 0.7501 mmol). The crude reaction mixture was purified by column chromatography using hexane/EtOAc (7/3) followed by toluene/EtOAc (9/1) to afford 3dm (76.9 mg, 0.235 mmol, 47% yield, 99% ee) as a pale yellow solid (m.p. 131.9°C-132.3°C). The ee was measured by HPLC (Chiralcel OZ-H column, 1.0 mL/min, hexane/2-propanol = 98/2, 230 nm, t1 = 6.0 min (major), t2 = 7.6 min (minor)); [α]24D +53 (c 1.03, CHCl3) for 99% ee.

\[ \text{HNMR (500 MHz, CDCl}_3 \delta 10.64 (s, 1H), 8.31 (d, J = 1.7 Hz, 1H), 7.79 (d, J = 1.7 Hz, 1H), 7.24-7.10 (m, 4H), 6.94 (s, 1H), 6.27 (ddd, J = 16.6, 10.6, 6.4 Hz, 1H), 5.25 (d, J = 9.8 Hz, 1H), 5.05 (d, J = 6.3 Hz, 1H), 4.96 (d, J = 17.2 Hz,} \]

S17
1H), 2.32 (s, 3H); $^{13}$C{$^1$H} NMR (126 MHz, CDCl$_3$) δ 147.6, 143.1, 140.1, 139.0, 136.1, 130.6, 130.3, 127.9, 126.7, 126.1, 125.2, 121.4, 116.3, 115.9, 111.1, 42.6, 19.5; IR (KBr, cm$^{-1}$) 3147, 2847, 1636, 1603, 1568, 1481, 1461, 1404, 1287, 1251, 1209, 1107, 1083, 997, 921, 906, 879, 749, 724, 694, 634, 612, 549, 452; HRMS (FAB) m/z [M+H]$^+$ calcd for C$_{17}$H$_{16}$BrN$_2$ 327.0491; found 327.0495.

4. Procedure for the Protonation of 7-Azaindoles 2b with Trifluoroacetic Acid

![Diagram of the reaction](image)

To a solution of 2b (194.9 mg, 1.475 mmol) in THF (3 mL) was added trifluoroacetic acid (227.4 mg, 1.995 mmol) at r.t. After the mixture was stirred at the same temperature for 23 h, it was concentrated on a rotary evaporator to give 2n (329.4 mg, 1.338 mmol, 91% yield) as an orange-pink solid (m.p. 55.1 °C-55.3 °C).

Compound 2n: $^1$H NMR (500 MHz, CDCl$_3$) δ 8.56 (dd, $J = 5.8$, 1.2 Hz, 1H), 8.34 (dd, $J = 8.1$, 1.1 Hz, 1H), 7.38 (dd, $J = 8.0$, 5.8 Hz, 1H), 7.33 (d, $J = 3.4$ Hz, 1H), 6.72 (d, $J = 3.5$ Hz, 1H), 4.09 (s, 3H); $^{13}$C{$^1$H} NMR (126 MHz, CDCl$_3$) δ 161.6 (q, $J_{C-F} = 37.4$ Hz), 140.7, 135.8, 135.6, 132.3, 125.2, 116.0 (q, $J_{C-F} = 287.7$ Hz), 115.3, 102.2, 33.6; $^{19}$F NMR (471 MHz, CDCl$_3$) δ -75.6; IR (KBr, cm$^{-1}$) 3104, 2954, 2822, 2378, 1789, 1685, 1646, 1624, 1527, 1418, 1341, 1271, 1207, 1195, 1134, 884, 834, 804, 734, 723, 709, 526. After recrystallization of 2n from hexane/CHCl$_3$, a crystal structure was obtained (Figure S1, Tables S1-S3).

5. Procedure for the Asymmetric Allylation of 7-Azaindole 2n with Allylic Alcohol 1a (Scheme 6)
A mixture of [Ir(cod)Cl]$_2$ (8.9 mg, 0.132 mmol) and (R)-L1 (26.3 mg, 0.0518 mmol) in THF (2.0 mL) was stirred at room temperature for 15 min. To the mixture was added 2n (185.0 mg, 0.7515 mmol), 1a (68.9 mg, 0.513 mmol), and TFA (29.2 mg, 0.256 mmol), and the mixture was stirred under reflux for 15 h. After the solvent was removed on a rotary evaporator, the residue was subjected to column chromatography (silica gel, toluene/EtOAc = 98/2) to give compounds 3ab (102.6 mg, 0.4132 mmol, 81% yield, 99% ee).

6. Procedure for the Deprotection of 7-Azaindoles 3ak (Scheme 6)

To a solution of 3ak (129.7 mg, 0.3659 mmol, 98% ee) in DCM (2.0 mL) was added BCl$_3$ (1.0 M solution in THF, 2.2 mL, 2.2 mmol) at -78 °C. After the mixture was stirred at the same temperature for 30 min, it was warmed to -20 °C, and then stirred for 1 h before warming to room temperature. After the mixture was stirred for 20 h, MeOH was added. The solution was concentrated on a rotary evaporator. The residue was subjected to column chromatography (silica gel, CHCl$_3$/MeOH = 9/1 followed by hexane/acetone = 2/1) to give compound 3aa (70.0 mg, 0.299 mmol, 82% yield, 99% ee) as a brown oil.

7. Procedure for the Metathesis Reaction of 7-Azaindoles 3ab with Methyl Acrylate
To a solution of Hoveyda-Grubbs 2nd-generation catalyst (19.1 mg, 0.0307 mmol) in toluene (1.0 mL) was added the solution of 3ab (73.1 mg, 0.294 mmol, 99% ee) and methyl acrylate (76.3 mg, 0.886 mmol) in toluene (3.0 mL) at room temperature. After the mixture was stirred at 80 °C for 20 h, it was concentrated on a rotary evaporator. The residue was subjected to column chromatography (silica gel, hexane/EtOAc = 7/3) to give compound 4 (64.1 mg, 0.209 mmol, 71% yield, 99% ee) as a brown oil.

Compound 4: The ee was measured by HPLC (Chiralcel OD-H column, 1.0 mL/min, hexane/2-propanol = 95/5, 230 nm, t₁ = 11.9 min (minor), t₂ = 16.5 min (major)); [α]²⁶_D = -4 (c 0.99, CHCl₃) for 99% ee. ¹H NMR (500 MHz, CDCl₃) δ 8.31 (dd, J = 4.6, 1.7 Hz, 1H), 7.58 (dd, J = 8.0, 1.7 Hz, 1H), 7.43 (dd, J = 15.5, 7.2 Hz, 1H), 7.33 (t, J = 7.5 Hz, 2H), 7.30–7.22 (m, 3H), 6.96 (dd, J = 7.5, 4.9 Hz, 1H), 6.87 (s, 1H), 5.81 (dd, J = 15.5, 1.7 Hz, 1H), 5.06 (d, J = 7.5 Hz, 1H), 3.84 (s, 3H), 3.73 (s, 3H); ¹³C(¹H) NMR (126 MHz, CDCl₃) δ 167.0, 149.6, 148.2, 143.1, 140.8, 128.7, 128.4, 127.7, 127.3, 127.1, 121.9, 119.2, 115.3, 113.5, 51.6, 45.5, 31.1; IR (neat, cm⁻¹) 3059, 3027, 2949, 1721, 1653, 1599, 1538, 1492, 1459, 1436, 1409, 1349, 1298, 1272, 1230, 1194, 1169, 1143, 1038, 985, 801, 756, 731, 702; HRMS (FAB) m/z [M+H]⁺ calcd for C₁₉H₁₉N₂O₃ 307.1441; found 307.1442.

8. Procedure for the Hydroboration of 7-Azaindoles 3ab Followed by Oxidation (Scheme 6)
To a solution of 3ab (74.8 mg, 0.301 mmol, 99% ee) in THF (1.0 mL) was added 9-BBN (1.25 mL, 0.5 M solution in THF, 0.625 mmol) at -78 °C. After the mixture was warmed to room temperature, it was stirred for 20 h. EtOH (0.49 mL), 3 M NaOH aq. (0.25 mL, 2.2 mmol) were added to the mixture at 0 °C. The mixture was extracted with 1M NaOH and Et₂O, and then sat. NH₄Cl and Et₂O. The combined organic extracts were dried over MgSO₄, and concentrated on a rotary evaporator. The residue was subjected to column chromatography (silica gel, hexane/EtOAc = 1/2) to give compound 5 (70.3 mg, 0.264 mmol, 88% yield, 99% ee) as a brown oil.

Compound 5: The ee was measured by HPLC (Chiralpak AD-3 column, 1.0 mL/min, hexane/2-propanol = 90/10, 230 nm, \( t_1 = 35.7 \text{ min (major)}, t_2 = 38.8 \text{ min (minor)} \); \([\alpha]_D^{24} = -21 (c 0.49, \text{ CHCl}_3)\) for 99% ee. \(^1\)H NMR (500 MHz, CDCl₃) \( \delta \) 8.25 (dd, \( J = 4.6, 1.4 \text{ Hz, 1H} \)), 7.67 (dd, \( J = 8.0, 1.4 \text{ Hz, 1H} \)), 7.33–7.23 (m, 4H), 7.21–7.15 (m, 1H), 7.01 (s, 1H), 6.93–6.88 (m, 1H), 4.36 (t, \( J = 7.7 \text{ Hz, 1H} \)), 3.83 (s, 3H), 3.72–3.58 (m, 2H), 2.50–2.38 (m, 1H), 2.31–2.20 (m, 1H), 1.92 (br, 1H); \(^{13}\)C\(^{\text{1}}\)H NMR (126 MHz, CDCl₃) \( \delta \) 148.1, 144.3, 142.8, 128.5, 127.8, 127.7, 126.3, 125.8, 119.7, 116.7, 114.9, 60.9, 39.1, 38.4, 31.1; IR (neat, cm\(^{-1}\)) 3338, 3060, 3026, 2932, 2880, 1600, 1575, 1538, 1492, 1461, 1410, 1348, 1295, 1143, 1038, 1011, 798, 759, 705, 664, 646, 585, 548; HRMS (FAB) \( m/z \) [M+H]\(^+\) calcd for C₁₇H₁₉N₂O 267.1492; found 267.1491.

9. Procedure for the Hydrogenation of 7-Azaindole 3ab (Scheme 6)

To Pd/C (15.0 mg, 10%, 0.014 mmol) was added the solution of 3ab (86.9 g, 0.35
mmol, 99% ee) in MeOH (2.0 mL) at rt. After the mixture was stirred under a hydrogen atmosphere at rt for 16 h, Pd/C was filtered off by celite, and the filtrate was concentrated on a rotary evaporator. The residue was subjected to column chromatography (silica gel, toluene/EtOAc = 98/2) to give compound 6 (77.8 mg, 0.311 mmol, 89% yield, 96% ee) as a colorless oil.

**Compound 6:** The ee was measured by HPLC (OJ-3 column, 1.0 mL/min, hexane/2-propanol = 99/1, 230 nm, t₁ = 13.3 min (minor), t₂ = 20.2 min (major)); [α]²⁴D −36 (c 0.55, CHCl₃) for 96% ee. ¹H NMR (500 MHz, CDCl₃) δ 8.26 (dd, J = 4.6, 1.7 Hz, 1H), 7.65 (dd, J = 8.1, 1.7 Hz, 1H), 7.30–7.23 (m, 4H), 7.21–7.14 (m, 1H), 7.00 (s, 1H), 6.91 (dd, J = 8.1, 4.6 Hz, 1H), 4.00 (t, J = 7.4 Hz, 1H), 3.84 (s, 3H), 2.26–2.14 (m, 1H), 2.08–1.96 (m, 1H), 0.94 (t, J = 7.2, 3H); ¹³C {¹H} NMR (126 MHz, CDCl₃) δ 148.1, 144.9, 142.7, 128.3, 127.9, 127.6, 126.1, 125.7, 119.8, 117.3, 114.8, 44.8, 31.0, 28.8, 12.7; IR (neat, cm⁻¹) 3058, 3026, 2962, 2929, 2871, 1599, 1571, 1537, 1491, 1459, 1409, 1348, 1297, 1146, 798, 771, 704, 581, 545; HRMS (FAB) m/z [M+H]⁺ calcd for C₁₇H₁₉N₂ 251.1543; found 251.1545.
10. The data for X-ray crystal structure of compound [CF₃COO][HC₈N₂H₉][CF₃COOH]

Colorless crystals of [CF₃COO][HC₈N₂H₉][CF₃COOH] suitable for X-ray crystallographic analysis were obtained by recrystallization from hexane/CHCl₃. The ORTEP drawing of [CF₃COO][HC₈N₂H₉][CF₃COOH] is shown in Figure S1. The crystal structure has been deposited at the Cambridge Crystallographic Centre (deposition number: CCDC 2080098). The data can be obtained free of charge via www.ccdc.cam.ac.uk/data_request/cif.

Figure S1. ORTEP illustration of [CF₃COO][HC₈N₂H₉][CF₃COOH] with thermal ellipsoids drawn at the 50% probability level.

Table S1. Crystal data of [CF₃COO][HC₈N₂H₉][CF₃COOH].

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\[ \text{D}_{\text{calc}} = 1.604 \text{ g/cm}^3 \]
\[ F_{000} = 364.00 \]
\[ \mu(\text{MoK}\alpha) = 1.667 \text{ cm}^{-1} \]

**Table S2. Intensity Measurements.**

- **Diffractometer**: R-AXIS RAPID
- **Radiation**: MoK\textit{\alpha} (\( \lambda = 0.71075 \text{ Å} \)) graphite monochromated
- **Voltage, Current**: 50 kV, 90 mA
- **Temperature**: 23.0 °C
- **Detector Aperture**: 460.0 x 256.0 mm
- **Data Images**: 44 exposures
- **\( \omega \) oscillation Range (\( \chi = 45.0, \phi = 0.0 \))**: 130.0 – 190.0 °
- **Exposure Rate**: 30.0 sec./°
- **\( \omega \) oscillation Range (\( \chi = 45.0, \phi = 180.0 \))**: 0.0 – 160.0 °
- **Exposure Rate**: 30.0 sec. /°
- **Detector Position**: 127.40 mm
- **Pixel Size**: 0.100 mm
- **2\( \theta \)_{\text{max}}**: 54.9 °
- **No. of Reflections Measured**: Total: 7411
  Unique: 3387 (\( R_{\text{int}} = 0.0308 \))
- **Corrections**: Lorentz-polarization
  Absorption
  (trans. factors: 0.936 – 0.967)

**Table S3. Structure Solution and Refinement.**

- **Structure Solution**: Direct Methods (SHELXT Version 2018/2)
- **Refinement**: Full-matrix least-squares on \( F^2 \) (SHELXL Version 2018/3)
Function Minimized \[ \Sigma w (F_0^2 - F_c^2)^2 \]
Least Squares Weights \[ w = \frac{1}{\sigma^2(F_0^2) + (0.1017 \cdot P)^2 + 0.0000 \cdot P} \]
where \( P = \frac{(\text{Max}(F_0^2,0) + 2F_c^2)}{3} \)

20 max cutoff \( 54.9^\circ \)
Anomalous Dispersion All non-hydrogen atoms
No. Observations (All reflections) 3387
No. Variables 261
Reflection/Parameter Ratio 12.98
Residuals: R1 (I>2.00\(\sigma(I)\)) 0.0632
Residuals: R (All reflections) 0.1315
Residuals: wR2 (All reflections) 0.2014
Goodness of Fit Indicator 1.037
Max Shift/Error in Final Cycle 0.000
Maximum peak in Final Diff. Map 0.24 e/Å³
Minimum peak in Final Diff. Map –0.20 e/Å³

11. The data for X-ray crystal structure of compound C₁₇H₁₅BrN₂

Yellow crystals of C₁₇H₁₅BrN₂ suitable for X-ray crystallographic analysis were obtained by recrystallization from hexane/EtOAc. The ORTEP drawing of C₁₇H₁₅BrN₂ is shown in Figure S2. The unit cell of C₁₇H₁₅BrN₂ consists of two type crystallographically distinct molecules which form dimer by hydrogen bonding of the hydrogen of N-H and the nitrogen of 7-azaindol. Nineteen hydrogen atoms, H2A, H3A, H4A, H5A, H6A, H8A, H8B, H8C, H10A, H10B, H18, H21, H22, H25A, H25B, H25C, H26, H27A, and H27B, were placed at calculated positions and refined using a riding model. The crystal structure has been deposited at the Cambridge Crystallographic Centre (deposition number: CCDC 2080099). The data can be obtained free of charge via www.ccdc.cam.ac.uk/data_request/cif.
Figure S2. ORTEP illustration of C$_{17}$H$_{15}$BrN$_2$ (two crystallographically independent molecules) with thermal ellipsoids drawn at the 50% probability level.

Table S4. Crystal data of C$_{17}$H$_{15}$BrN$_2$.

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Table S5. Intensity Measurements.

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<td>Diffractometer</td>
<td>R-AXIS RAPID</td>
</tr>
<tr>
<td>Radiation</td>
<td>MoKα ($\lambda = 0.71075$ Å)</td>
</tr>
</tbody>
</table>
Table S6. Structure Solution and Refinement.

Structure Solution
Direct Methods (SHELXT Version 2018/2)

Refinement
Full-matrix least-squares on $F^2$ (SHELXL Version 2018/3)

Function Minimized
$\sum w (F_0^2 - F_c^2)^2$

Least Squares Weights
$w = 1/[\sigma^2(F_0^2) + (0.00611\cdot P)^2 + 0.0000\cdot P]$ where $P = (\text{Max}(F_0^2,0) + 2F_c^2)/3$

20max cutoff
54.9°

Anomalous Dispersion
All non-hydrogen atoms

No. Observations (All reflections)
7098

No. Variables
406

Reflection/Parameter Ratio
17.48

Residuals: R1 (I>2.00$\sigma$(I))
0.0513

Residuals: R (All reflections)
0.0920

Residuals: wR2 (All reflections)
0.1400

No. Observations (All reflections)
7098

No. Variables
406

Reflection/Parameter Ratio
17.48

Residuals: R1 (I>2.00$\sigma$(I))
0.0513

Residuals: R (All reflections)
0.0920

Residuals: wR2 (All reflections)
0.1400
Goodness of Fit Indicator   0.931
Flack parameter   $-0.004(11)$  (Parsons' quotients = 1347)
Max Shift/Error in Final Cycle   0.001
Maximum peak in Final Diff. Map   $0.41 \text{ e}^{-}/\text{Å}^3$
Minimum peak in Final Diff. Map   $-0.37 \text{ e}^{-}/\text{Å}^3$
12. References


13. $^1$H, $^{13}$C, and $^{19}$F NMR Spectra, and Chiral HPLC Charts

--- PROCESSING PARAMETERS ---

--- NMR Spec ---

Filedate  : 02:45:20 19:45:44
Author    : a. name
Sample_id : 02:45:20 19:45:44
Sample    : a. name

--- Chiral HPLC ---

Filedate  : 02:45:20 19:45:44
Author    : a. name
Sample_id : 02:45:20 19:45:44
Sample    : a. name

--- Spectrometer ---

Filedate  : 02:45:20 19:45:44
Author    : a. name
Sample_id : 02:45:20 19:45:44
Sample    : a. name

--- References ---

Filedate  : 02:45:20 19:45:44
Author    : a. name
Sample_id : 02:45:20 19:45:44
Sample    : a. name

--- X : parts per Million : Proton ---

--- Processing Parameters ---

--- NMR Spec ---

Filedate  : 02:45:20 19:45:44
Author    : a. name
Sample_id : 02:45:20 19:45:44
Sample    : a. name

--- Chiral HPLC ---

Filedate  : 02:45:20 19:45:44
Author    : a. name
Sample_id : 02:45:20 19:45:44
Sample    : a. name

--- Spectrometer ---

Filedate  : 02:45:20 19:45:44
Author    : a. name
Sample_id : 02:45:20 19:45:44
Sample    : a. name

--- References ---

Filedate  : 02:45:20 19:45:44
Author    : a. name
Sample_id : 02:45:20 19:45:44
Sample    : a. name

--- X : parts per Million : Proton ---
<table>
<thead>
<tr>
<th>Peak#</th>
<th>Ret. Time</th>
<th>Area%</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>20.12</td>
<td>0.689</td>
</tr>
<tr>
<td>2</td>
<td>25.43</td>
<td>99.311</td>
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<tr>
<td>Total</td>
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<td>100.000</td>
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</tbody>
</table>

<table>
<thead>
<tr>
<th>Peak#</th>
<th>Ret. Time</th>
<th>Area%</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>19.59</td>
<td>50.490</td>
</tr>
<tr>
<td>2</td>
<td>25.43</td>
<td>49.510</td>
</tr>
<tr>
<td>Total</td>
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</tr>
</tbody>
</table>
### Peak Data

#### Graph 1

<table>
<thead>
<tr>
<th>Peak#</th>
<th>Ret. Time</th>
<th>Area%</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>7.03</td>
<td>99.925</td>
</tr>
<tr>
<td>2</td>
<td>8.91</td>
<td>0.075</td>
</tr>
<tr>
<td><strong>Total</strong></td>
<td></td>
<td><strong>100.000</strong></td>
</tr>
</tbody>
</table>

#### Graph 2

<table>
<thead>
<tr>
<th>Peak#</th>
<th>Ret. Time</th>
<th>Area%</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>7.10</td>
<td>49.915</td>
</tr>
<tr>
<td>2</td>
<td>9.00</td>
<td>50.085</td>
</tr>
<tr>
<td><strong>Total</strong></td>
<td></td>
<td><strong>100.000</strong></td>
</tr>
</tbody>
</table>
Peak#  Ret. Time  Area%
1      24.94     0.444
2      28.16     99.556
Total  100.000

Peak#  Ret. Time  Area%
1      24.59     50.153
2      28.29     49.847
Total  100.000
<table>
<thead>
<tr>
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<th>Ret. Time</th>
<th>Area%</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>11.18</td>
<td>99.288</td>
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<tr>
<td>2</td>
<td>14.56</td>
<td>0.712</td>
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<tr>
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</tbody>
</table>

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<table>
<thead>
<tr>
<th>Peak#</th>
<th>Ret. Time</th>
<th>Area%</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>11.24</td>
<td>49.385</td>
</tr>
<tr>
<td>2</td>
<td>14.51</td>
<td>50.615</td>
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<td>100.000</td>
</tr>
<tr>
<td></td>
<td>3ad</td>
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</tr>
<tr>
<td>---</td>
<td>-----</td>
<td>---</td>
</tr>
<tr>
<td><strong>Chemical Structure</strong></td>
<td><img src="image" alt="Chemical Structure Image" /></td>
<td></td>
</tr>
<tr>
<td><strong>Processing Parameters</strong></td>
<td><img src="table" alt="Processing Parameters Table" /></td>
<td></td>
</tr>
</tbody>
</table>

**S57**
Peak# | Ret. Time | Area%  
--- | --- | --- 
1 | 4.93 | 96.830 
2 | 5.56 | 3.170 
Total | | 100.000 

Peak# | Ret. Time | Area%  
--- | --- | --- 
1 | 4.93 | 50.100 
2 | 5.57 | 49.900 
Total | | 100.000
### Peak Analysis

<table>
<thead>
<tr>
<th>Peak#</th>
<th>Ret. Time</th>
<th>Area%</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>7.70</td>
<td>1.449</td>
</tr>
<tr>
<td>2</td>
<td>9.14</td>
<td>98.551</td>
</tr>
<tr>
<td>Total</td>
<td></td>
<td>100.000</td>
</tr>
</tbody>
</table>

### Peak Analysis

<table>
<thead>
<tr>
<th>Peak#</th>
<th>Ret. Time</th>
<th>Area%</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>7.66</td>
<td>50.697</td>
</tr>
<tr>
<td>2</td>
<td>9.12</td>
<td>49.303</td>
</tr>
<tr>
<td>Total</td>
<td></td>
<td>100.000</td>
</tr>
</tbody>
</table>
Hydroxylamine Oxidation of 3a:

**Initial Conditions:**
- **Temperature:** 80°C
- **Time:** 60 minutes
- **Flow Rate:** 1.0 mL/min

**Chromatographic Analysis:**

![Chromatogram](image)

<table>
<thead>
<tr>
<th>Peak#</th>
<th>Ret. Time</th>
<th>Area%</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>12.32</td>
<td>90.043</td>
</tr>
<tr>
<td>2</td>
<td>13.02</td>
<td>9.957</td>
</tr>
<tr>
<td>Total</td>
<td></td>
<td>100.000</td>
</tr>
</tbody>
</table>

**Next Experiment:**

Hydroxylamine Oxidation of 3b:

![Chromatogram](image)

<table>
<thead>
<tr>
<th>Peak#</th>
<th>Ret. Time</th>
<th>Area%</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>12.35</td>
<td>49.958</td>
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<tr>
<td>2</td>
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<td>50.042</td>
</tr>
<tr>
<td>Total</td>
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<td>100.000</td>
</tr>
</tbody>
</table>

S66
### Table 1

<table>
<thead>
<tr>
<th>Peak#</th>
<th>Ret. Time</th>
<th>Area%</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>8.92</td>
<td>89.919</td>
</tr>
<tr>
<td>2</td>
<td>9.96</td>
<td>10.081</td>
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<tr>
<td>Total</td>
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<td>100.000</td>
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</tbody>
</table>

### Table 2

<table>
<thead>
<tr>
<th>Peak#</th>
<th>Ret. Time</th>
<th>Area%</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>8.93</td>
<td>49.926</td>
</tr>
<tr>
<td>2</td>
<td>9.97</td>
<td>50.074</td>
</tr>
<tr>
<td>Total</td>
<td></td>
<td>100.000</td>
</tr>
<tr>
<td>Peak#</td>
<td>Ret. Time</td>
<td>Area%</td>
</tr>
<tr>
<td>-------</td>
<td>-----------</td>
<td>--------</td>
</tr>
<tr>
<td>1</td>
<td>5.98</td>
<td>99.647</td>
</tr>
<tr>
<td>2</td>
<td>7.63</td>
<td>0.353</td>
</tr>
<tr>
<td>Total</td>
<td></td>
<td>100.000</td>
</tr>
</tbody>
</table>

**UV**

<table>
<thead>
<tr>
<th>Peak#</th>
<th>Ret. Time</th>
<th>Area%</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>6.43</td>
<td>50.098</td>
</tr>
<tr>
<td>2</td>
<td>7.61</td>
<td>49.902</td>
</tr>
<tr>
<td>Total</td>
<td></td>
<td>100.000</td>
</tr>
</tbody>
</table>

S78
X: parts per Million: Fluorine19
S83
<table>
<thead>
<tr>
<th>Peak#</th>
<th>Ret. Time</th>
<th>Area%</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>35.66</td>
<td>99.682</td>
</tr>
<tr>
<td>2</td>
<td>38.77</td>
<td>0.318</td>
</tr>
<tr>
<td>Total</td>
<td></td>
<td>100.000</td>
</tr>
</tbody>
</table>

**Diagram:**

- **Graph 1:**
  - mV on the y-axis.
  - Retention time on the x-axis from 33 to 42 minutes.
  - Two peaks with retention times 35.66 and 38.77 minutes.

- **Graph 2:**
  - mV on the y-axis.
  - Retention time on the x-axis from 33 to 42 minutes.
  - Two peaks with retention times 35.66 and 38.77 minutes.
--- S85 ---

--- PROCESSING PARAMETERS ---

--- S85 ---
<table>
<thead>
<tr>
<th>Peak#</th>
<th>Ret. Time</th>
<th>Area%</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>13.26</td>
<td>2.159</td>
</tr>
<tr>
<td>2</td>
<td>20.21</td>
<td>97.841</td>
</tr>
<tr>
<td>Total</td>
<td></td>
<td>100.000</td>
</tr>
</tbody>
</table>

**Diagram 1:**

- Peak at 13.26 min with area 2.159
- Peak at 20.21 min with area 97.841
- Total area 100.000

**Diagram 2:**

- Peak at 13.20 min with area 50.019
- Peak at 20.30 min with area 49.981
- Total area 100.000