Supporting Information

Catalytic enantioselective synthesis of β-trifluoromethyl pyrrolines

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Experimental Section

General Methods:

All reactions were performed in oven-dried glassware under a positive pressure of nitrogen. Solvents were transferred via syringe and were introduced into the reaction vessels through a rubber septum. All reactions were monitored by thin-layer chromatography (TLC) carried out on 0.25 mm Merck silica-gel (60-F254). The TLC plates were visualized with UV light and 7% phosphomolybdic acid or KMnO₄ in water/heat. Column chromatography was carried out on a column packed with silica-gel 60N spherical neutral size 63-210 μm. The ¹H-NMR (300 MHz), ¹⁹F-NMR (282 MHz), ¹³C-NMR (150.9 MHz) spectra for solution in CDCl₃ were recorded on a Bruker Avance 600 and a Varian Mercury 300. Chemical shifts (δ) are expressed in ppm downfield from internal TMS or CHCl₃. HPLC analyses were performed on a JASCO U-2080 Plus using 4.6 x 250 mm CHIRALPAK AD-3 or CHIRALCEL OJ-H or CHIRALPAK IB column. Mass spectra were recorded on a SHIMADZU LCMS-2010EV. Optical rotations were measured on a HORIBA SEPA-300. Infrared spectra were recorded on a JASCO FT/IR-200 spectrometer. The β-trifluoromethylated enones 3 were prepared according to literature.¹

General procedure for the asymmetric conjugated addition of nitromethane to β-trifluoromethylated enones 3:
To a stirred solution of β-trifluoromethylated enone 3 (0.20 mmol), catalyst 7 (2.3 mg, 0.004 mmol, 2 mol%) in toluene (1.0 mL) was added nitromethane (58.8 μL, 1.00 mmol, 5.0 equiv) at ambient temperature under nitrogen atmosphere. After completion of reaction checked by TLC, the reaction mixture was concentrated under reduced pressure. The residue was purified by column chromatography on silica gel (n-hexane/ethyl acetate = 90/10) to give (S)-4.

(S)-4,4,4-Trifluoro-3-(nitromethyl)-1-phenylbutan-1-one (4a)

Reaction of 3a (20.0 mg, 0.10 mmol), catalyst 7 (1.1 mg, 0.002 mmol, 2 mol%), nitromethane (26.9 μL, 0.50 mmol, 5.0 equiv) in toluene (0.5 mL) at ambient temperature for 20 h gave (S)-4a (26.1 mg, 99%, 97% ee) as a white solid.

1H NMR (CDCl3, 300 MHz) δ 3.35 (dd, J = 9.0, 18.6 Hz, 1H), 3.47 (dd, J = 3.9, 18.3 Hz, 1H), 3.88-3.99 (m, 1H), 4.63 (dd, J = 4.8, 13.8 Hz, 1H), 4.72 (dd, J = 6.8, 13.8 Hz, 1H), 7.51 (t, J = 7.5 Hz, 2H), 7.64 (t, J = 7.4 Hz, 1H), 7.97 (d, J = 7.5 Hz, 2H); 13C NMR (CDCl3, 150.9 MHz) δ 34.2 (m), 37.9 (q, J = 28.2 Hz), 72.3 (m), 126.1 (q, J = 280.0 Hz), 128.1, 128.9, 134.2, 135.5, 194.7; 19F NMR (CDCl3, 282 MHz) δ -71.3 (d, J = 9.0 Hz, 3F) ; IR (KBr) 3068, 2962, 1691, 1558, 1451, 1396, 1172, 1102, 959, 930, 897, 799, 758, 724, 690, 653, 552, 510 cm⁻¹; mp = 48.0-49.0 ºC (CHCl3); MS (ESI, m/z) 300 [(M+Na) +], HRMS (ESI) calcd. for C11H10F3NNaO3 [(M+Na) +]: 284.0510 Found: 284.0506; The ee of the product was determined by HPLC using an IB column (n-hexane/i-PrOH = 90/10, flow rate 1.0 mL/min, λ = 254 nm, τmaj = 16.1 min, τmin = 12.3 min); [α]D25 = -7.4 (c = 0.64, CHCl3), 97% ee.

(S)-4,4,4-Trifluoro-3-(nitromethyl)-1-m-tolylbutan-1-one (4b)

Reaction of 3b (42.8 mg, 0.20 mmol), catalyst 7 (2.3 mg, 0.004 mmol, 2 mol%), nitromethane (58.8 μL, 1.00 mmol, 5.0 equiv) in toluene (1.0 mL) at ambient temperature for 70 h gave (S)-4b (52.4 mg, 95%, 98% ee) as a white solid.

1H NMR (CDCl3, 300 MHz) δ 2.43 (s, 3H), 3.32 (dd, J = 9.3, 18.3 Hz, 1H), 3.45 (dd, J = 4.1, 18.5 Hz, 1H), 3.87-3.98 (m, 1H), 4.62 (dd, J = 4.5, 14.1 Hz, 1H), 4.70 (dd, J = 6.5, 14.1 Hz, 1H), 7.36-7.46 (m, 2H), 7.74-7.77 (m, 2H); 13C NMR (CDCl3, 150.9 MHz) δ 21.3, 34.2 (m), 37.9 (q, J =
28.7 Hz), 72.4 (m), 125.2, 126.1 (q, J = 280.0 Hz), 128.6, 128.8, 134.9, 135.6, 138.8, 194.8; 19F NMR (CDCl3, 282 MHz) δ -71.3 (d, J = 7.9 Hz, 3F); IR (KBr) 3018, 2928, 1681, 1562, 1430, 1385, 1300, 1251, 1173, 972, 798, 724, 686, 630, 597, 549, 505, 464 cm⁻¹; mp = 49.0-50.0 °C (CHCl₃); MS (ESI, m/z) 298 [(M+K)⁺], HRMS (ESI) calcd. for C₁₂H₁₂F₃NNaO₃ [(M+Na)⁺]: 298.0667 Found: 298.0670; The ee of the product was determined by HPLC using an IB column (n-hexane/i-PrOH = 70/30, flow rate 1.0 mL/min, λ = 254 nm, τmaj = 14.5 min, τmin = 15.9 min); [α]D²⁵ = +0.3 (c = 1.19, CHCl₃), 98% ee.

(S)-4,4,4-Trifluoro-3-(nitromethyl)-1-ρ-tolylbutan-1-one (4c)

Reaction of 3c (42.8 mg, 0.20 mmol), catalyst 7 (2.3 mg, 0.004 mmol, 2 mol%), nitromethane (58.8 μL, 1.00 mmol, 5.0 equiv) in toluene (1.0 mL) at ambient temperature for 48 h gave (S)-4c (53.1 mg, 96%, 96% ee) as a white solid.

1H NMR (CDCl₃, 300 MHz) δ 2.43 (s, 3H), 3.30 (dd, J = 9.3, 18.3 Hz, 1H), 3.43 (dd, J = 3.9, 18.3 Hz, 1H), 3.86-3.97 (m, 1H), 4.62 (dd, J = 4.5, 14.1 Hz, 1H), 4.69 (dd, J = 6.9, 13.7 Hz, 1H), 7.30 (d, J = 14.4 Hz, 2H), 7.86 (d, J = 8.1 Hz, 2H); 13C NMR (CDCl₃, 150.9 MHz) δ 21.7, 34.0 (m), 37.9 (q, J = 28.7 Hz), 72.4 (m), 126.1 (q, J = 280.0 Hz), 128.2, 129.6, 133.1, 145.2, 194.2; 19F NMR (CDCl₃, 282 MHz) δ -71.4 (d, J = 9.0 Hz, 3F); IR (KBr) 3022, 2922, 1683, 1556, 1345, 1119, 972, 919, 846, 808, 764, 730, 651, 590, 567, 506, 459 cm⁻¹; mp = 43.0-44.5 °C (CHCl₃); MS (ESI, m/z) 298 [(M+K)⁺], HRMS (ESI) calcd. for C₁₂H₁₂F₃NNaO₃ [(M+Na)⁺]: 298.0667 Found: 298.0670; The ee of the product was determined by HPLC using an OJ-H column (n-hexane/i-PrOH = 70/30, flow rate 1.0 mL/min, λ = 254 nm, τmaj = 18.2 min, τmin = 14.9 min); [α]D²⁵ = -8.5 (c = 0.80, CHCl₃), 96% ee.

(S)-4,4,4-Trifluoro-1-(4-methoxyphenyl)-3-(nitromethyl)butan-1-one (4d)

Reaction of 3d (46.0 mg, 0.20 mmol), catalyst 7 (2.3 mg, 0.004 mmol, 2 mol%), nitromethane (58.8 μL, 1.00 mmol, 5.0 equiv) in toluene (1.0 mL) at ambient temperature for 48 h gave (S)-4d (56.1 mg, 96%, 97% ee) as a white solid.

1H NMR (CDCl₃, 300 MHz) δ 3.27 (dd, J = 9.2, 18.5 Hz, 1H), 3.40 (dd, J = 4.1, 18.2 Hz, 1H), 3.83-3.97 (m, 1H), 3.89 (s, 3H), 4.63 (dd, J = 5.0, 14.3 Hz, 1H), 4.69 (dd, J = 6.8, 14.0 Hz, 1H),
6.94-6.99 (m, 2H), 7.91-7.96 (m, 2H); $^{13}$C NMR (CDCl$_3$, 150.9 MHz) δ 33.7 (m), 37.9 (q, $J$ = 28.2 Hz), 55.5, 72.4 (m), 114.0, 126.2 (q, $J$ = 280.0 Hz), 128.6, 130.4, 164.3, 193.0; $^{19}$F NMR (CDCl$_3$, 282 MHz) δ -71.3 (d, $J$ = 7.9 Hz, 3F); IR (KBr) 2965, 2844, 1667, 1550, 1255, 1120, 1030, 968, 919, 842, 818, 733, 652, 569, 499, 419 cm$^{-1}$; mp = 90.0-92.0 ºC (CHCl$_3$); MS (ESI, $m/z$) 314 [(M+Na$^+$)]; HRMS (ESI) calcd. for C$_{12}$H$_{12}$F$_3$NNaO$_4$ [(M+Na$^+$)]: 314.0616 Found: 314.0626; The ee of the product was determined by HPLC using an OJ-H column (n-hexane/i-PrOH = 70/30, flow rate 1.0 mL/min, $\lambda$ = 254 nm, $\tau_{maj}$ = 41.2 min, $\tau_{min}$ = 31.6 min); [$\alpha$]$_D$ = -10.8 (c = 1.43, CHCl$_3$), 97% ee.

(S)-4,4,4-Trifluoro-1-(4-fluorophenyl)-3-(nitromethyl)butan-1-one (4e)

![Chemical structure of 4e](image)

Reaction of 3e (43.6 mg, 0.20 mmol), catalyst 7 (2.3 mg, 0.004 mmol, 2 mol%), nitromethane (58.8 μL, 1.00 mmol, 5.0 equiv) in toluene (1.0 mL) at ambient temperature for 70 h gave (S)-4e (49.1 mg, 88%, 97% ee) as a colorless oil.

$^1$H NMR (CDCl$_3$, 300 MHz) δ 3.33 (dd, $J$ = 9.0, 18.3 Hz, 1H), 3.44 (dd, $J$ = 4.1, 18.5 Hz, 1H), 3.85-3.97 (m, 1H), 4.63 (dd, $J$ = 4.8, 13.8 Hz, 1H), 4.72 (dd, $J$ = 6.8, 14.0 Hz, 1H), 7.18 (t, $J$ = 8.6 Hz, 2H), 8.01 (dd, $J$ = 5.3, 8.9 Hz, 2H); $^{13}$C NMR (CDCl$_3$, 150.9 MHz) δ 34.1 (m), 37.9 (q, $J$ = 28.2 Hz), 72.3 (m), 116.1 (d, $J$ = 22.6 Hz), 126.0 (q, $J$ = 280.0 Hz), 130.9 (d, $J$ = 9.1 Hz), 132.0 (d, $J$ = 3.0 Hz), 166.3 (d, $J$ = 256.5 Hz), 193.1; $^{19}$F NMR (CDCl$_3$, 282 MHz) δ -103.5 (m, 1F), -71.3 (d, $J$ = 7.9 Hz, 3F); IR (neat) 2928, 1688, 1599, 1562, 1508, 1380, 1342, 1301, 1228, 1176, 1124, 1003, 973, 911, 837, 735, 651, 587, 548, 474 cm$^{-1}$; MS (ESI, $m/z$) 302 [(M+Na$^+$)]; HRMS (ESI) calcd. for C$_{11}$H$_9$F$_4$NNaO$_3$ [(M+Na$^+$)]: 302.0416 Found: 302.0414; The ee of the product was determined by HPLC using an OJ-H column (n-hexane/i-PrOH = 70/30, flow rate 1.0 mL/min, $\lambda$ = 254 nm, $\tau_{maj}$ = 18.4 min, $\tau_{min}$ = 15.1 min); [$\alpha$]$_D$ = -6.6 (c = 1.20, CHCl$_3$), 97% ee.

(S)-1-(4-Chlorophenyl)-4,4,4-trifluoro-3-(nitromethyl)butan-1-one (4f)

![Chemical structure of 4f](image)

Reaction of 3f (46.9 mg, 0.20 mmol), catalyst 7 (2.3 mg, 0.004 mmol, 2 mol%), nitromethane (58.8 μL, 1.00 mmol, 5.0 equiv) in toluene (1.0 mL) at ambient temperature for 71 h gave (S)-4f (59.1 mg, 99%, 97% ee) as a white solid.

$^1$H NMR (CDCl$_3$, 300 MHz) δ 3.32 (dd, $J$ = 9.2, 18.5 Hz, 1H), 3.43 (dd, $J$ = 4.5, 18.3 Hz, 1H),...
(S)-1-(4-Bromophenyl)-4,4,4-trifluoro-3-(nitromethyl)butan-1-one (4g)

Reaction of 3g (55.8 mg, 0.20 mmol), catalyst 7 (2.3 mg, 0.004 mmol, 2 mol%), nitromethane (58.8 μL, 1.00 mmol, 5.0 equiv) in toluene (1.0 mL) at ambient temperature for 72 h gave (S)-4g (62.8 mg, 92%, 98% ee) as a white solid.

1H NMR (CDCl₃, 300 MHz) δ 3.32 (dd, J = 8.9, 18.5 Hz, 1H), 3.43 (dd, J = 4.4, 18.2 Hz, 1H), 3.85-3.96 (m, 1H), 4.63 (dd, J = 4.8, 13.8 Hz, 1H), 4.72 (dd, J = 6.6, 13.8 Hz, 1H), 7.49 (d, J = 8.4 Hz, 2H), 7.91 (d, J = 8.4 Hz, 2H); 13C NMR (CDCl₃, 150.9 MHz) δ 34.2 (m), 37.8 (q, J = 28.2 Hz), 72.2 (m), 126.0 (q, J = 280.0 Hz), 129.5, 132.2, 134.2, 193.7; 19F NMR (CDCl₃, 282 MHz) δ -71.3 (d, J = 7.9 Hz, 3F); IR (KBr) 3032, 2974, 1928, 1676, 1558, 1487, 1344, 1172, 973, 895, 817, 784, 737, 704, 637, 564, 509, 472 cm⁻¹; mp = 40.0-41.0 °C (CHCl₃); MS (ESI, m/z) 362 [(M+Na)+], HRMS (ESI) calcd. for C₁₁H₉BrF₃NNaO₃ [(M+Na)+]: 361.9616 Found: 361.9615; The ee of the product was determined by HPLC using an IB column (n-hexane/i-PrOH = 90/10, flow rate 1.0 mL/min, λ = 254 nm, τmaj = 12.7 min, τmin = 13.8 min); [α]D²⁵ = -8.9 (c = 1.37, CHCl₃), 98% ee.

(S)-4,4,4-Trifluoro-3-(nitromethyl)-1-(4-nitrophenyl)butan-1-one (4h)

Reaction of 3h (49.0 mg, 0.20 mmol), catalyst 7 (2.3 mg, 0.004 mmol, 2 mol%), nitromethane (58.8 μL, 1.00 mmol, 5.0 equiv) in toluene (1.0 mL) at ambient temperature for 90 h gave (S)-4h (57.3 mg, 94%, 97% ee) as a white solid.
1H NMR (CDCl3, 300 MHz) δ 3.44 (dd, J = 8.4, 18.6 Hz, 1H), 3.53 (dd, J = 4.5, 18.6 Hz, 1H), 3.88-3.98 (m, 1H), 4.66 (dd, J = 6.5, 14.0 Hz, 1H), 8.15 (d, J = 8.4 Hz, 2H), 8.36 (d, J = 8.4 Hz, 2H); 13C NMR (CDCl3, 150.9 MHz) δ 34.9 (m), 37.8 (q, J = 28.7 Hz), 72.1 (m), 124.1, 125.8 (q, J = 280.0 Hz), 129.2, 139.8, 150.8, 193.4; 19F NMR (CDCl3, 282 MHz) δ -71.2 (d, J = 8.7 Hz, 3F); IR (KBr) 3113, 2931, 1687, 1563, 1525, 1345, 1254, 1217, 1125, 1059, 1006, 851, 788, 748, 723, 687, 489 cm\(^{-1}\); mp = 80.0-81.0 ºC (CHCl3); MS (ESI, m/z) 329 [(M+Na)+], HRMS (ESI) calcd. for C11H9F3N2NaO5 [(M+Na)+]: 329.0361 Found: 329.0368.; The ee of the product was determined by HPLC using an OJ-H column (n-hexane/i-PrOH = 70/30, flow rate 1.0 mL/min, λ = 254 nm, τ\(_{maj}\) = 47.5 min, τ\(_{min}\) = 64.5 min); [α]\(_D\)\(^{25}\) = -8.2 (c = 1.53, CHCl3), 97% ee.

**Table: Chemical Constants**

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<th>Property</th>
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<td>mp</td>
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<td>MS (ESI, m/z)</td>
<td>329 [(M+Na)+]</td>
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**Reaction of 3i (50.0 mg, 0.20 mmol), catalyst 7 (2.3 mg, 0.004 mmol, 2 mol%), nitromethane (58.8 µL, 1.00 mmol, 5.0 equiv) in toluene (1.0 mL) at ambient temperature for 72 h gave (S)-4i (60.3 mg, 97%, 97% ee) as a white solid.**

1H NMR (CDCl3, 300 MHz) δ 3.46 (dd, J = 9.2, 18.2 Hz, 1H), 3.58 (dd, J = 4.1, 18.5 Hz, 1H), 3.96-4.01 (m, 1H), 4.66 (dd, J = 4.7, 14.0 Hz, 1H), 4.74 (dd, J = 6.5, 14.0 Hz, 1H), 7.55-7.66 (m, 2H), 7.87-7.92 (m, 2H), 7.95-8.00 (m, 2H), 8.46 (s, 1H); 13C NMR (CDCl3, 150.9 MHz) δ 34.2 (m), 38.0 (q, J = 28.2 Hz), 72.4 (m), 123.3, 126.1 (q, J = 281 Hz), 127.2, 127.8, 128.9, 129.1, 129.6, 130.1, 132.3, 132.8, 135.9, 194.5; 19F NMR (CDCl3, 282 MHz) δ -71.2 (d, J = 8.7 Hz, 3F); IR (KBr) 3035, 2931, 1675, 1569, 1469, 1430, 1384, 1254, 1168, 1117, 974, 941, 857, 823, 748, 625, 592, 549, 474 cm\(^{-1}\); mp = 74.5-76.5 ºC (CHCl3); MS (ESI, m/z) 334 [(M+Na)+], HRMS (ESI) calcd. for C15H12F3NNaO3 [(M+Na)+]: 334.0667 Found: 334.0669; The ee of the product was determined by HPLC using an IB column (n-hexane/i-PrOH = 90/10, flow rate 1.0 mL/min, λ = 254 nm, τ\(_{maj}\) = 17.1 min, τ\(_{min}\) = 14.9 min); [α]\(_D\)\(^{25}\) = -24.3 (c = 1.65, CHCl3), 97% ee.

**Reaction of 3j (38.0 mg, 0.20 mmol), catalyst 7 (2.3 mg, 0.004 mmol, 2 mol%), nitromethane (58.8 µL, 1.00 mmol, 5.0 equiv) in toluene (1.0 mL) at ambient temperature for 72 h gave (S)-4j (47.6 mg, 95%, 98% ee) as a yellow oil.**

1H NMR (CDCl3, 300 MHz) δ 3.20 (dd, J = 9.0, 18.0 Hz, 1H), 3.35 (dd, J = 4.4, 18.2 Hz, 1H),
3.83-3.94 (m, 1H), 4.64 (dd, J = 5.1, 13.8 Hz, 1H), 4.71 (dd, J = 6.5, 14.0 Hz, 1H), 6.61 (dd, J = 1.7, 3.8 Hz, 1H), 7.29 (dd, J = 0.8, 4.1 Hz, 1H), 7.64-7.65 (m, 1H); 13C NMR (CDCl3, 150.9 MHz) δ 33.8 (m), 37.5 (q, J = 28.7 Hz), 72.3 (m), 112.8, 118.2, 125.9 (q, J = 280.0 Hz), 147.2, 151.6, 183.6; 19F NMR (CDCl3, 282 MHz) δ -71.4 (d, J = 9.0 Hz, 3F); IR (neat) 3142, 2929, 1681, 1567, 1469, 1386, 1254, 1176, 1126, 1037, 974, 838, 767, 735, 639, 594 cm⁻¹; MS (ESI, m/z) 274 [(M+Na)+], HRMS (ESI) calcd. for C9H8F3NNaO4 [(M+Na)+]: 274.0303 Found: 274.0304; The ee of the product was determined by HPLC using an IB column (n-hexane/i-PrOH = 95/5, flow rate 1.0 mL/min, λ = 254 nm, τmaj = 23.3 min, τmin = 20.0 min); [α]D²⁵ = -8.7 (c = 1.12, CHCl3), 98% ee.

**General procedure for the enantioselective one-pot synthesis of β-trifluoromethyl pyrrolines 2:**

To a stirred solution of β-trifluoromethylated enone 3 (0.10 mmol), catalyst 7 (1.1 mg, 0.002 mmol, 2 mol%) in toluene (0.5 mL) was added nitromethane (26.9 μL, 0.50 mmol, 5.0 equiv) at ambient temperature under nitrogen atmosphere. After completion of reaction checked by TLC, the reaction mixture was concentrated under reduced pressure. To a stirred solution of crude 4 in THF/MeOH (2/1, 1.5 mL) was added acetic acid (90.0 μL, 16.0 equiv), Fe (251 mg, 45.0 equiv) successively at the ambient temperature, and the resulting mixture was heated at 65 ºC for 10 h under nitrogen atmosphere. After cooling down to room temperature, the reaction mixture was filtrated through Celite, rinsed with AcOEt. The whole mixture was washed with sat. NaHCO₃ aq., brine, dried over Na₂SO₄ and concentrated under reduced pressure. The residue was purified by column chromatography on silica gel (CHCl₃) to give β-trifluoromethyl pyrrole (S)-2.

**(S)-5-Phenyl-3-(trifluoromethyl)-3,4-dihydro-2H-pyrrole (2a)**

Reaction of 3a (20.0 mg, 0.10 mmol), catalyst 7 (1.1 mg, 0.002 mmol, 2 mol%), nitromethane (26.9 μL, 0.50 mmol, 5.0 equiv) in toluene (0.5 mL) at ambient temperature for 50 h gave the crude product of 4a. Reduction-cyclization-dehydration reaction of crude 4a, acetic acid (90.0 μL, 16.0 equiv), Fe (251 mg, 45.0 equiv) in THF/MeOH (2/1, 1.5 mL) at 65 ºC for 10 h gave (S)-2a (19.0 mg, 89%, 98% ee) as a white solid.

1H NMR (CDCl3, 300 MHz) δ 3.12-3.32 (m, 3H), 4.20-4.37 (m, 2H), 7.40-7.50 (m, 3H), 7.78-7.84 (m, 2H); 13C NMR (CDCl3, 150.9 MHz) δ 35.9 (m), 40.9 (q, J = 28.2 Hz), 61.2 (m), 127.5 (q, J = 277.2 Hz), 127.6, 128.6, 131.0, 133.4, 170.9; 19F NMR (CDCl3, 282 MHz) δ -72.2 (d, J = 8.7 Hz, 3F); IR (KBr) 3032, 2944, 1628, 1578, 1496, 1439, 1385, 1351, 1276, 1108, 1024, 928, 797, 764, 694, 553, 520.7, 458 cm⁻¹; mp = 61.0-62.0 ºC (CHCl3); MS (ESI, m/z) 214 [M+H]+, HRMS (ESI) calcd. for C11H11F3N [M+H]+: 214.0844 Found: 214.0835; The ee of the product was determined by
HPLC using an OJ-H column (n-hexane/i-PrOH = 95/5, flow rate 0.5 mL/min, λ = 254 nm, τ_{maj} = 14.9 min, τ_{min} = 19.6 min); [α]_{D}^{25} = -42.4 (c = 0.32, CHCl₃), 98% ee.

(S)-5-p-Tolyl-3-(trifluoromethyl)-3,4-dihydro-2H-pyrrole (2c)

Reaction of 3c (21.4 mg, 0.10 mmol), catalyst 7 (1.1 mg, 0.002 mmol, 2 mol%), nitromethane (26.9 μL, 0.50 mmol, 5.0 equiv) in toluene (0.5 mL) at ambient temperature for 50 h gave the crude product of 4c. Reduction-cyclization-dehydration reaction of crude 3c, acetic acid (90.0 μL, 16.0 equiv), Fe (251 mg, 45.0 equiv) in THF/MeOH (2/1, 1.5 mL) at 65 ºC for 10 h gave (S)-2c (20.9 mg, 92%, 98% ee) as a white solid.

1H NMR (CDCl₃, 300 MHz) δ 2.39 (s, 3H), 3.10-3.26 (m, 3H), 4.18-4.35 (m, 2H), 7.23 (d, J = 7.8 Hz, 2H), 7.71 (d, J = 8.1 Hz, 2H); 13C NMR (CDCl₃, 150.9 MHz) δ 21.5, 35.9 (m), 40.8 (q, J = 28.2 Hz), 61.1 (m), 127.57 (q, J = 277.2 Hz), 127.57, 129.3, 130.7, 141.3, 170.8; 19F NMR (CDCl₃, 282 MHz) δ -72.2 (d, J = 8.7 Hz, 3F); IR (KBr) 2950, 2879, 1924, 1622, 1569, 1514, 1459, 1387, 1343, 1320, 1109, 960, 821, 714, 609, 517, 468 cm⁻¹; mp = 62.0-64.5 ºC (CHCl₃); MS (ESI, m/z) 228 [M+H]⁺, HRMS (ESI) calcd. for C₁₂H₁₃F₃N [M+H]⁺: 228.1000 Found: 228.1007; The ee of the product was determined by HPLC using an OJ-H column (n-hexane/i-PrOH = 95/5, flow rate 0.5 mL/min, λ = 254 nm, τ_{maj} = 15.9 min, τ_{min} = 23.2 min); [α]_{D}^{25} = -43.5 (c = 0.36, CHCl₃), 98% ee.

(S)-5-(4-Methoxyphenyl)-3-(trifluoromethyl)-3,4-dihydro-2H-pyrrole (2d)

Reaction of 3d (23.0 mg, 0.10 mmol), catalyst 7 (1.1 mg, 0.002 mmol, 2 mol%), nitromethane (26.9 μL, 0.50 mmol, 5.0 equiv) in toluene (0.5 mL) at ambient temperature for 50 h gave the crude product of 4d. Reduction-cyclization-dehydration reaction of crude 3d, acetic acid (90.0 μL, 16.0 equiv), Fe (251 mg, 45.0 equiv) in THF/MeOH (2/1, 1.5 mL) at 65 ºC for 10 h gave (S)-2d (23.6 mg, 97%, 98% ee) as a white solid.

1H NMR (CDCl₃, 300 MHz) δ 3.10-3.24 (m, 3H), 3.85 (s, 3H), 4.16-4.32 (m, 2H), 6.93 (d, J = 8.7 Hz, 2H), 7.77 (d, J = 8.7 Hz, 2H); 13C NMR (CDCl₃, 150.9 MHz) δ 35.8 (m), 40.9 (q, J = 28.2 Hz), 55.3, 61.0 (m), 113.9, 126.2, 127.6 (q, J = 276.7 Hz), 129.3, 161.8, 170.2; 19F NMR (CDCl₃, 282 MHz) δ -72.2 (d, J = 8.7 Hz, 3F); IR (KBr) 2962, 2841, 1623, 1575, 1516, 1462, 1385, 1345, 1319,
1158, 1111, 1037, 845, 821, 556 cm⁻¹; mp = 79.5-81.0 °C (CHCl₃); MS (ESI, m/z) 244 [M+H]⁺, HRMS (ESI) calcd. for C₁₂H₁₅F₃NO [M+H]⁺: 244.0949 Found: 244.0948; The ee of the product was determined by HPLC using an AD-3 column (n-hexane/i-PrOH = 95/5, flow rate 0.5 mL/min, λ = 254 nm, τₘₐₐₐ = 26.9 min, τₘᵢₙ = 25.7 min); [α]D²⁵ = -42.7 (c = 0.53, CHCl₃), 98% ee.

(S)-5-(4-Chlorophenyl)-3-(trifluoromethyl)-3,4-dihydro-2H-pyrrole (2f)

Reaction of 3f (23.5 mg, 0.10 mmol), catalyst 7 (1.1 mg, 0.002 mmol, 2 mol%), nitromethane (26.9 μL, 0.50 mmol, 5.0 equiv) in toluene (0.5 mL) at ambient temperature for 72 h gave the crude product of 4f. Reduction-cyclization-dehydration reaction of crude 4f, acetic acid (90.0 μL, 16.0 equiv), Fe (251 mg, 45.0 equiv) in THF/MeOH (2/1, 1.5 mL) at 65 °C for 10 h gave (S)-2f (23.3 mg, 94%, 98% ee) as a white solid.

¹H NMR (CDCl₃, 300 MHz) δ 3.12-3.25 (m, 3H), 4.19-4.37 (m, 2H), 7.40 (d, J = 8.4 Hz, 2H), 7.75 (d, J = 8.7 Hz, 2H); ¹³C NMR (CDCl₃, 150.9 MHz) δ 35.9 (m), 40.9 (q, J = 28.2 Hz), 61.3 (m), 127.4 (q, J = 277.2 Hz), 128.86, 128.91, 131.8, 137.1, 169.8; ¹⁹F NMR (CDCl₃, 282 MHz) δ -72.3 (d, J = 8.7 Hz, 3F); IR (KBr) 2955, 2880, 1625, 1492, 1439, 1387, 1321, 1274, 1116, 1034, 1014, 957, 828, 714, 553, 528, 455 cm⁻¹; mp = 67.0-68.0 °C (CHCl₃); MS (ESI, m/z) 248 [M+H]⁺, HRMS (ESI) calcd. for C₁₁H₁₀ClF₃N [M+H]⁺: 248.0454 Found: 248.0459; The ee of the product was determined by HPLC using an OJ-H column (n-hexane/i-PrOH = 95/5, flow rate 0.5 mL/min, λ = 254 nm, τₘₐₐₐ = 14.6 min, τₘᵢₙ = 22.6 min); [α]D²⁵ = -38.2 (c = 0.45, CHCl₃), 98% ee.

(S)-5-(4-Bromophenyl)-3-(trifluoromethyl)-3,4-dihydro-2H-pyrrole (2g)

Reaction of 3g (27.9 mg, 0.10 mmol), catalyst 7 (1.1 mg, 0.002 mmol, 2 mol%), nitromethane (26.9 μL, 0.50 mmol, 5.0 equiv) in toluene (0.5 mL) at ambient temperature for 72 h gave the crude product of 4g. Reduction-cyclization-dehydration reaction of crude 4g, acetic acid (90.0 μL, 16.0 equiv), Fe (251 mg, 45.0 equiv) in THF/MeOH (2/1, 1.5 mL) at 65 °C for 10 h gave (S)-2g (26.7 mg, 91%, 98% ee) as a white solid.

¹H NMR (CDCl₃, 300 MHz) δ 3.12-3.24 (m, 3H), 4.18-4.36 (m, 2H), 7.56 (d, J = 8.4 Hz, 2H), 7.69 (d, J = 8.4 Hz, 2H); ¹³C NMR (CDCl₃, 150.9 MHz) δ 35.9 (m), 40.9 (q, J = 28.7 Hz), 61.3 (m),
125.6, 127.4 (q, J = 277.2 Hz), 129.1, 131.8, 132.2, 169.9; 19F NMR (CDCl3, 282 MHz) δ -72.3 (d, J = 7.9 Hz, 3F); IR (KBr) 2956, 2877, 1624, 1590, 1564, 1488, 1438, 1385, 1343, 1321, 1272, 1114, 1072, 1033, 709, 551, 456 cm⁻¹; mp = 78.0-79.0 °C (CHCl3); MS (ESI, m/z) 292 [M+H]+, HRMS (ESI) calcd. for C11H10BrF3N [M+H]+: 291.9949 Found: 291.9942; The ee of the product was determined by HPLC using an OJ-H column (n-hexane/i-PrOH = 95/5, flow rate 0.5 mL/min, λ = 254 nm, τmaj = 16.0 min, τmin = 28.2 min); [α]D²⁵ = -33.3 (c = 0.61, CHCl3), 98% ee.

(S)-4-(3-(Trifluoromethyl)-3,4-dihydro-2H-pyrrol-5-yl)aniline (2h)

Reaction of 3h (24.5 mg, 0.10 mmol), catalyst 7 (1.1 mg, 0.002 mmol, 2 mol%), nitromethane (26.9 μL, 0.50 mmol, 5.0 equiv) in toluene (0.5 mL) at ambient temperature for 90 h gave the crude product of 4h. Reduction-cyclization-dehydration reaction of crude 4h, acetic acid (90.0 μL, 16.0 equiv), Fe (251 mg, 45.0 equiv) in THF/MeOH (2/1, 1.5 mL) at 65 °C for 10 h gave (S)-2h (19.5 mg, 85%, 98% ee) as a white solid.

1H NMR (CDCl3, 300 MHz) δ 3.08-3.21 (m, 3H), 4.06-4.30 (m, 5H), 6.67 (d, J = 8.7 Hz, 2H), 7.62 (d, J = 8.4 Hz, 2H); 13C NMR (CDCl3, 150.9 MHz) δ 35.7 (m), 40.8 (q, J = 27.7 Hz), 60.8 (m), 114.4, 123.7, 127.6 (q, J = 277.2 Hz), 129.3, 149.1, 170.4; 19F NMR (CDCl3, 282 MHz) δ -72.1 (d, J = 7.9 Hz, 3F); IR (KBr) 3329, 3215, 2873, 1601, 1520, 1437, 1378, 1350, 1264, 1220, 1177, 1144, 1102, 1027, 984, 831, 550, 465 cm⁻¹; mp = 128.0-131.0 °C (CHCl3); MS (ESI, m/z) 229 [M+H]+, HRMS (ESI) calcd. for C11H12F3N2 [M+H]+: 229.0953 Found: 229.0952; The ee of the product was determined by HPLC using an OJ-H column (n-hexane/i-PrOH = 70/30, flow rate 1.0 mL/min, λ = 254 nm, τmaj = 10.6 min, τmin = 16.0 min); [α]D²⁵ = -47.8 (c = 0.50, CHCl3), 98% ee.

(S)-5-(Naphthen-2-yl)-3-(trifluoromethyl)-3,4-dihydro-2H-pyrrole (2i)

Reaction of 3i (25.0 mg, 0.10 mmol), catalyst 7 (1.1 mg, 0.002 mmol, 2 mol%), nitromethane (26.9 μL, 0.50 mmol, 5.0 equiv) in toluene (0.5 mL) at ambient temperature for 72 h gave the crude product of 4i. Reduction-cyclization-dehydration reaction of crude 4i, acetic acid (90.0 μL, 16.0 equiv), Fe (251 mg, 45.0 equiv) in THF/MeOH (2/1, 1.5 mL) at 65 °C for 10 h gave (S)-2i (25.0 mg, 95%, 97% ee) as a white solid.

1H NMR (CDCl3, 300 MHz) δ 3.17-3.43 (m, 3H), 4.25-4.43 (m, 2H), 7.50-7.57 (m, 2H), 7.84-7.91
(m, 3H), 8.06 (d, J = 8.7 Hz, 1H), 8.13 (s, 1H); $^{13}$C NMR (CDCl$_3$, 150.9 MHz) $\delta$ 36.0 (m), 40.9 (q, J = 28.2 Hz), 61.3 (m), 124.2, 126.6, 127.4, 127.6 (q, J = 277.2 Hz), 127.8, 128.41, 128.44, 128.7, 130.9, 132.8, 134.5, 170.9; $^{19}$F NMR (CDCl$_3$, 282 MHz) $\delta$ -72.1 (d, J = 9.9 Hz, 3F); IR (KBr) 3071, 2934, 1620, 1436, 1379, 1320, 1270, 1204, 1155, 1106, 1022, 960, 897, 869, 826, 754, 623, 576, 480 cm$^{-1}$; mp = 91.0-92.0 °C (CHCl$_3$); MS (ESI, m/z) 264 [M+H]$^+$, HRMS (ESI) calcd. for C$_{15}$H$_{13}$F$_3$N [M+H]$^+$: 264.1000 Found: 264.0997; The ee of the product was determined by HPLC using an AD-3 column (n-hexane/i-PrOH = 95/5, flow rate 0.5 mL/min, $\lambda = 254$ nm, $\tau_{maj} = 23.9$ min, $\tau_{min} = 33.6$ min); [$\alpha$]$_D^{25}$ = -34.7 (c = 0.14, CHCl$_3$), 97% ee.
(S)-4a

HPLC using an IB

\((n\text{-hexane/i-PrOH} = 90/10, \text{flow rate} 1.0 \text{ mL/min,} \lambda = 254 \text{ nm})\)

<table>
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<tr>
<th>No.</th>
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<th>High (%)</th>
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<tr>
<td>1</td>
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<td>49.945</td>
<td>56.471</td>
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<tr>
<td>2</td>
<td>15.967</td>
<td>50.055</td>
<td>43.529</td>
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</table>

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<tr>
<th>No.</th>
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<th>Area (%)</th>
<th>High (%)</th>
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<tr>
<td>1</td>
<td>12.258</td>
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<td>1.977</td>
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<td>2</td>
<td>16.133</td>
<td>98.565</td>
<td>98.023</td>
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</table>

(S)-4b

HPLC using an IB

\((n\text{-hexane/i-PrOH} = 70/30, \text{flow rate} 1.0 \text{ mL/min,} \lambda = 254 \text{ nm})\)

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<td>2</td>
<td>15.875</td>
<td>0.914</td>
<td>0.848</td>
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</table>
**ESI13**

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### (S)-4c

HPLC using an OJ-H

\( (n\text{-hexane/i-PrOH} = 70/30, \text{flow rate} 1.0 \text{mL/min}, \lambda = 254 \text{nm}) \)

<table>
<thead>
<tr>
<th>No.</th>
<th>tR (min)</th>
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<tbody>
<tr>
<td>1</td>
<td>15.458</td>
<td>50.115</td>
<td>54.325</td>
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<td>2</td>
<td>18.908</td>
<td>49.885</td>
<td>45.675</td>
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</table>

### (S)-4d

HPLC using an OJ-H

\( (n\text{-hexane/i-PrOH} = 70/30, \text{flow rate} 1.0 \text{mL/min}, \lambda = 254 \text{nm}) \)

<table>
<thead>
<tr>
<th>No.</th>
<th>tR (min)</th>
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<tbody>
<tr>
<td>1</td>
<td>32.375</td>
<td>50.139</td>
<td>55.278</td>
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<tr>
<td>2</td>
<td>42.792</td>
<td>49.861</td>
<td>44.722</td>
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</table>

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(S)-4e

HPLC using an OJ-H

(n-hexane/PrOH = 70/30, flow rate 1.0 mL/min, λ = 254 nm)

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<th>Area (%)</th>
<th>High (%)</th>
<th>No.</th>
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<td>15.592</td>
<td>50.010</td>
<td>55.793</td>
<td>1</td>
<td>15.117</td>
<td>1.730</td>
<td>2.261</td>
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<td>2</td>
<td>19.325</td>
<td>49.990</td>
<td>44.207</td>
<td>2</td>
<td>18.383</td>
<td>98.270</td>
<td>97.739</td>
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(S)-4f

HPLC using an IB

(n-hexane/PrOH = 95/5, flow rate 1.0 mL/min, λ = 254 nm)

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<th>Area (%)</th>
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<th>No.</th>
<th>tR (min)</th>
<th>Area (%)</th>
<th>High (%)</th>
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</thead>
<tbody>
<tr>
<td>1</td>
<td>17.183</td>
<td>49.544</td>
<td>51.351</td>
<td>1</td>
<td>17.717</td>
<td>98.716</td>
<td>98.729</td>
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<td>2</td>
<td>18.533</td>
<td>50.456</td>
<td>48.649</td>
<td>2</td>
<td>19.667</td>
<td>1.284</td>
<td>1.271</td>
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(S)-4g
HPLC using an IB
(n-hexane/i-PrOH = 90/10, flow rate 1.0 mL/min, λ = 254 nm)

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<td>1</td>
<td>13.758</td>
<td>49.816</td>
<td>51.528</td>
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<td>2</td>
<td>15.158</td>
<td>50.184</td>
<td>48.472</td>
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</tbody>
</table>

(S)-4h
HPLC using an OJ-H
(n-hexane/i-PrOH = 70/30, flow rate 1.0 mL/min, λ = 254 nm)

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<th>No.</th>
<th>tR (min)</th>
<th>Area (%)</th>
<th>High (%)</th>
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<tbody>
<tr>
<td>1</td>
<td>12.650</td>
<td>99.056</td>
<td>98.999</td>
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<td>2</td>
<td>13.808</td>
<td>0.944</td>
<td>1.001</td>
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<tr>
<td>1</td>
<td>49.617</td>
<td>50.160</td>
<td>56.908</td>
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<td>2</td>
<td>65.683</td>
<td>49.840</td>
<td>43.092</td>
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<th>Area (%)</th>
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<tr>
<td>1</td>
<td>47.492</td>
<td>98.559</td>
<td>98.761</td>
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<td>2</td>
<td>64.533</td>
<td>1.441</td>
<td>1.239</td>
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</table>
HPLC using an IB

\((n\text{-hexane/i}-\text{PrOH} = 90/10, \text{flow rate } 1.0 \text{ mL/min}, \lambda = 254 \text{ nm})\)

\[
\begin{array}{cccc}
\text{No.} & tR (\text{min}) & \text{Area} (%) & \text{High} (%) \\
1 & 15.617 & 49.914 & 52.896 \\
2 & 18.133 & 50.086 & 47.104 \\
\end{array}
\]

\[
\begin{array}{cccc}
\text{No.} & tR (\text{min}) & \text{Area} (%) & \text{High} (%) \\
1 & 14.925 & 1.502 & 2.124 \\
2 & 17.117 & 98.498 & 97.876 \\
\end{array}
\]

HPLC using an IB

\((n\text{-hexane/i}-\text{PrOH} = 95/5, \text{flow rate } 1.0 \text{ mL/min}, \lambda = 254 \text{ nm})\)

\[
\begin{array}{cccc}
\text{No.} & tR (\text{min}) & \text{Area} (%) & \text{High} (%) \\
1 & 20.008 & 49.968 & 53.812 \\
2 & 23.783 & 50.032 & 46.188 \\
\end{array}
\]

\[
\begin{array}{cccc}
\text{No.} & tR (\text{min}) & \text{Area} (%) & \text{High} (%) \\
1 & 19.983 & 1.078 & 1.324 \\
2 & 23.333 & 98.922 & 98.676 \\
\end{array}
\]
ESI17

**[(S)-2a](#)**

HPLC using an OJ-H

\((n\text{-hexane/i-PrOH} = 95/5, \text{flow rate } 0.5 \text{ mL/min, } \lambda = 254 \text{ nm})\)

<table>
<thead>
<tr>
<th>No.</th>
<th>tR (min)</th>
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<tbody>
<tr>
<td>1</td>
<td>14.875</td>
<td>49.943</td>
<td>53.414</td>
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<td>2</td>
<td>19.542</td>
<td>50.057</td>
<td>46.586</td>
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**[(S)-2c](#)**

HPLC using an OJ-H

\((n\text{-hexane/i-PrOH} = 95/5, \text{flow rate } 0.5 \text{ mL/min, } \lambda = 254 \text{ nm})\)

<table>
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<th>No.</th>
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<tbody>
<tr>
<td>1</td>
<td>15.917</td>
<td>50.198</td>
<td>55.503</td>
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<td>23.233</td>
<td>49.802</td>
<td>44.497</td>
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### (S)-2d

HPLC using an AD-3

(*n*-hexane/*i*-PrOH = 95/5, flow rate 0.5 mL/min, $\lambda = 254$ nm)

<table>
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<th>High (%)</th>
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<tr>
<td>1</td>
<td>26.133</td>
<td>49.801</td>
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<td>2</td>
<td>27.300</td>
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<td>48.916</td>
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</table>

### (S)-2f

HPLC using an OJ-H

(*n*-hexane/*i*-PrOH = 95/5, flow rate 0.5 mL/min, $\lambda = 254$ nm)

<table>
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<th>No.</th>
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<td>14.558</td>
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<td>56.176</td>
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<td>2</td>
<td>22.583</td>
<td>49.956</td>
<td>43.824</td>
</tr>
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</table>

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\[
(\text{S})-2g
\]
HPLC using an OJ-H
\((n\text{-hexane}/i\text{-PrOH} = 95/5, \text{ flow rate 0.5 mL/min, } \lambda = 254 \text{ nm})\)

<table>
<thead>
<tr>
<th>No.</th>
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<th>High (%)</th>
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<tr>
<td>1</td>
<td>16.042</td>
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<td>37.600</td>
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\[
(\text{S})-2h
\]
HPLC using an OJ-H
\((n\text{-hexane}/i\text{-PrOH} = 70/30, \text{ flow rate 1.0 mL/min, } \lambda = 254 \text{ nm})\)

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<th>No.</th>
<th>tR (min)</th>
<th>Area (%)</th>
<th>High (%)</th>
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<tr>
<td>1</td>
<td>10.650</td>
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<td>10.567</td>
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<td>99.234</td>
</tr>
<tr>
<td>2</td>
<td>16.033</td>
<td>0.955</td>
<td>0.766</td>
</tr>
</tbody>
</table>
(S)-2i
HPLC using an AD-3

($n$-hexane/$i$-PrOH = 95/5, flow rate 0.5 mL/min, $\lambda = 254$ nm)

<table>
<thead>
<tr>
<th>No.</th>
<th>tR (min)</th>
<th>Area (%)</th>
<th>High (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>23.758</td>
<td>49.751</td>
<td>56.554</td>
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<tr>
<td>2</td>
<td>33.408</td>
<td>50.249</td>
<td>43.446</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>No.</th>
<th>tR (min)</th>
<th>Area (%)</th>
<th>High (%)</th>
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</thead>
<tbody>
<tr>
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<td>98.875</td>
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<td>2</td>
<td>33.575</td>
<td>1.352</td>
<td>1.125</td>
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</tbody>
</table>
4a

$^{19}$F NMR
Electronic Supplementary Material (ESI) for Chemical Communications
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$	ext{Me} \quad \begin{array}{c}
\text{O} \\
\text{CH}_2\text{NO}_2 \\
\text{CF}_3
\end{array}$

$^19\text{F} \text{NMR}$
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$^{19}$F NMR

$4c$

![Chemical structure diagram]
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$^{13}$C NMR

ESI29
$^{19}$F NMR

4d

MeO

O

CH$_2$NO$_2$

CF$_3$

1.0

0.0

-0.2

-0.4

ESI31
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Electronic Supplementary Material (ESI) for Chemical Communications

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Current Data Parameters
NAME  KT-408
EXPO  10
PROCNO  1

F2 - Acquisition Parameters
Date_  20121001
Time  12.44
INSTRUM  drx600
FREQUNIT  mm BBO BB=1H
FPROG  capp10
TD  131073
SOLVENT  CDCl3
NS  831
DS  6
SWH  45454.547 Hz
FIDRES  0.346791 Hz
AQ  1.4418930 sec
RG  1625.5
DW  11000 usec
DE  6000 usec
TE  296.3 K
E1  0.6000000000 sec
d11  0.0300000000 sec
DELTA  0.0000000000 sec
TDD  1

===== CHANNEL f1 =====
WBC1  13C
P1  8.00 usec
FL1  3.70 dB
SF01  150.922366 MHz

===== CHANNEL f2 =====
CPDPRG2  waltz16
RWC2  1H
RCPD2  80.00 usec
TL2  -5.30 dB
FL2  9.34 dB
FL3  9.50 dB
SF02  600.1324009 MHz

F2 - Processing parameters
SI  131073
SF  150.9028136 MHz
NHM  EN
SSR  0
LH  1.00 Hz
DB  0
FC  1.40
Electronic Supplementary Material (ESI) for Chemical Communications
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13C NMR

13C NMR

Current Data Parameters
NAME  KT-415
EXPNO  10
PROCNO  1

F2 - Acquisition Parameters
Data_  20110530
Time  22.51
INSTROM  drx600
F0 = 100.61 MHz
POLPROG  sqp30
TD  131072
SOLVENT  CDCl3
NS  4096
DS  4
SWH  45454.547 Hz
FIDRES  0.346791 Hz
AQ  1.4418530 sec
RG  1824.4
DM  11.0000 usec
DE  6.0000 usec
TD  296.6 K
D1  0.60000002 sec
d1l  0.03000000 sec
DELTAS  0.50000000 sec
TDO  1

********** CHANNEL F1 **********
M Pul  13C
P1  8.00 usec
PL1  3.70 dm
SQF1  156.9223664 MHz

********** CHANNEL F2 **********
CPDPBG2  wait16
M Pul  15H
PCD02  80.00 usec
PL2  -5.00 dm
PL12  9.54 dm
PUL3  9.50 dm
SQF2  600.1324005 MHz

F2 - Processing parameters
SI  131072
SF  150.9028159 MHz
WM  EM
SB  0
LB  1.00 Hz
DC  1.40
ESI46
$^{13}$C NMR
$^{1}H$ NMR
$^{19}$F NMR
$^{19}$F NMR
ESI62

Electronic Supplementary Material (ESI) for Chemical Communications
This journal is © The Royal Society of Chemistry 2012
$^{19}$F NMR

$2g$

Electronic Supplementary Material (ESI) for Chemical Communications

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ESI66

Electronic Supplementary Material (ESI) for Chemical Communications
This journal is © The Royal Society of Chemistry 2012
ESI67
$^{1}H$ NMR
$^{19}$F NMR

2i
13C NMR

Current Data Parameters
NAME  EX-2476
EXPNO  10
PROCNO  1

F2 - Acquisition Parameters
Data-  21110601
Time  14.13
INSTNUM  daz600
PROBD  5 mm BBO BB-1H
PULPROG  zgppq30
TD  131072
SOLVENT  CDCl3
NS  1632
DS  4
SWH  45454.547 Hz
FIDRES  0.346791 Hz
AQ  1.4418530 sec
RG  1149.4
DW  11.000 usec
DE  6.00 usec
TE  295.9 K
D1  0.60000002 sec
d11  0.03000000 sec
d11A  0.50000000 sec
TOD  1

======== CHANNEL f1 ========
NUC1  13C
P1  8.00 usec
PL1  3.70 dB
SPFO1  150.9223664 MHz

======== CHANNEL f2 ========
CPDPPG2  waltz16
NUC2  1H
PCEP2  80.00 usec
PL2  5.00 dB
PL12  9.54 dB
PL13  9.50 dB
SPFO2  600.1324005 MHz

F2 - Processing parameters
ST  131072
SF  150.9028138 MHz
WDM  EM
SSB  0
LB  1.00 Hz
GB  0
PC  1.40
X-ray crystallographic structure of (S)-4i

Figure S1
X-ray crystallographic structure of racemic 2g

Figure S2