SUPPORTING INFORMATION

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Title: Syntheses and Applications of (Thio)Urea-Containing Chiral Quaternary Ammonium Salt Catalysts
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1. General Information:

$^1$H- and $^{13}$C-NMR spectra were recorded on a Bruker Avance III 300 MHz spectrometer and on a Bruker Avance III 700 MHz spectrometer with TCI cryoprobe. All NMR spectra were referenced on the solvent peak. High resolution mass spectra were obtained using an Agilent 6520 Q-TOF mass spectrometer with an ESI source and an Agilent G1607A coaxial sprayer. All analyses were made in the positive ionization mode. Purine (exact mass for $[M+H]^+ = 121.050873$) and 1,2,3,4,5,6-hexakis(2,2,3,3-tetrafluoropropoxy)-1,3,5,2,4,6-triazatryptophosphinane (exact mass for $[M+H]^+ = 922.009798$) were used for internal mass calibration. IR spectra were recorded on a Shimadzu IR Affinity-1 fourier transform infrared spectrometer. Optical rotations were recorded on a Perkin Elmer Polarimeter Model 241 MC and on a Schmidt + Haensch Polarimeter Model UniPol L 1000. HPLC was performed using a Dionex Summit HPLC system with a Chiralcel OD-H (250 x 4.6 mm), a Chiralcel OD-R (250 x 4.6 mm, 10 µm), or a Chiralpak AD-H (250 x 4.6 mm, 5 µm) chiral stationary phase.

All chemicals were purchased from commercial suppliers and used without further purification unless otherwise stated. All reactions were performed under an Ar-atmosphere. Starting β-ketoesters were either purchased from commercial suppliers or prepared according to literature-known methods.  

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1) a) T. A. Moss, D. R. Fenwick, D. J. Dixon J. Am. Chem. Soc. 2008, 130, 10076-10077; b) D. Y. Kim, E. J. Park, Org. Lett. 2002, 4, 545-547; c) X. Wang, Q. Lan, S. Shirakawa, K. Maruoka, Chem. Commun. 2010, 46, 321-323; d) E.-M. Tanzer, W. B. Schweizer, M.-O. Ebert, R. Gilmour, Chem. Eur. J. 2012, 18, 2006-2013; e) M. Lian, J. Du, Q. Meng, Z. Gao Eur. J. Org. Chem. 2010, 6525-6530.
2. Syntheses of Bifunctional Ammonium Salts:

Syntheses of Cyclohexanediamine-Based Catalysts 1a – 1o:

**General Syntheses of 7 (R¹ ≠ Me): Step 1:** The corresponding benzaldehyde (3 mmol) was added to a solution of 6 (3 mmol) (prepared from (S,S)-cyclohexanediamine-5-dihydrochloride according to literature) in THF:MeOH = 1:1 (12 mL) and the solution was stirred at r.t. for 2 h. After the addition of 1.5 eq NaBH₄ stirring was continued for another 2 h at r.t.. The reaction was quenched by addition of H₂O and extracted with H₂O/Et₂O. The organic phase was washed with brine, dried over Na₂SO₄, and evaporated to dryness to obtain the crude product which could be directly used without any purification. **Step 2:** A mixture of the crude sec-amine (3 mmol) and K₂CO₃ (2 eq.) in 3 ml methyl iodide was stirred at reflux for 3 d. Excess methyl iodide was removed under reduced pressure and the product was purified by column chromatography (silica gel, DCM:MeOH, 40:1 → 10:1) to obtain compounds 7 in the reported yields.

**Compound 7a:** Obtained in 64% (two steps, 3 mmol scale) as an oily residue. [α]₀²² relaxed (c = 7.5, DCM) = -2.0°; ¹H NMR (700 MHz, δ, CDCl₃, 298 K): 1.27-1.36 (m, 1H), 1.44 (s, 9H), 1.52-1.65 (m, 2H), 1.71-1.77 (m, 1H), 1.87-1.94 (m, 1H), 1.95-2.02 (m, 2H), 2.51-2.56 (m, 1H), 2.71 (s, 3H), 2.75 (s, 3H), 4.08-4.15 (m, 1H), 4.89 (s, 1H, J = 12.4 Hz), 4.94 (d, 1H, J = 12.4 Hz), 5.00 (d, 1H, J = 9.3 Hz), 7.40-7.49 (m, 5H) ppm; ¹³C NMR (176 MHz, δ, CDCl₃, 298 K): 24.6, 24.7, 27.5, 28.5, 35.6, 49.2, 50.5, 51.5, 65.8, 76.3, 80.9, 127.2, 129.4, 131.0, 133.4, 155.6 ppm; IR (film): ν = 3435, 3237, 2976, 2936, 2864, 1691, 1510, 1450, 1366, 1321, 1275, 1240, 1157, 1045, 1024, 993, 914, 851, 775 cm⁻¹; HRMS (ESI) m/z calcd for C₂₀H₃₃N₂O₂⁺: 333.2537 [M⁺], found: 333.2539.

2) H.-J. Schanz, M. Linseis, D. Gilheany, Tetrahedron: Asymmetry 2003, 14, 2763-2769.
3) D. W. Lee, H.-J. Ha, W. K. Lee, Synth. Commun. 2007, 37, 737-742.
**Compound 7b:** Obtained in 24% (plus 33% isolated tert. amine intermediate that could be resubmitted again) (two steps, 1 mmol scale) as an oily residue. $[\alpha]_D^{22} (c = 0.33, \text{DCM}) = -2.7^\circ$; $^1$H NMR (300 MHz, $\delta$, CDCl$_3$, 298 K): 1.27-1.42 (m, 1H), 1.48 (s, 9H), 1.56-1.65 (m, 2H), 1.76-1.88 (m, 1H), 1.91-2.10 (m, 3H), 2.57-2.66 (m, 1H), 3.20 (s, 3H), 3.28 (s, 3H), 4.06-4.20 (m, 1H), 4.91-5.04 (m, 1H), 5.10 (d, 1H, $J = 12.4$ Hz), 5.34 (d, 1H, $J = 12.9$ Hz), 5.84 (d, 1H, $J = 10.0$ Hz), 7.73 (t, 1H, $J = 8.0$ Hz), 8.14 (d, 1H, $J = 7.8$ Hz), 8.31-8.40 (m, 2H) ppm; $^{13}$C NMR (75 MHz, $\delta$, CDCl$_3$, 298 K): 24.7, 24.7, 27.5, 28.5, 35.6, 49.2, 50.4, 51.6, 64.5, 77.4, 81.5, 125.9, 127.7, 129.4, 130.9, 139.8, 148.6, 155.7 ppm; IR (film): $\nu = 2976, 2936, 2866, 1697,$ $1533, 1508, 1456, 1352, 1321, 1279, 1242, 1163, 1047, 1024, 768, 731 \text{ cm}^{-1}$; HRMS (ESI) $m/z$ calcd for C$_{20}$H$_{32}$N$_3$O$_4$: 378.2393 [M$^+$], found: 378.2395.

**Compound 7c:** Obtained in 42% (two steps, 1 mmol scale) as an oily residue. $[\alpha]_D^{22} (c = 1.1, \text{DCM}) = -0.2^\circ$; $^1$H NMR (300 MHz, $\delta$, CDCl$_3$, 298 K): 1.23-1.40 (m, 1H), 1.48 (s, 9H), 1.49-1.85 (m, 3H), 1.89-2.08 (m, 3H), 2.50-2.59 (m, 1H), 3.06 (s, 3H), 3.19 (s, 3H), 3.85 (s, 3H), 4.05-4.20 (m, 1H), 4.77 (d, 1H, $J = 12.4$ Hz), 4.90-5.02 (m, 1H), 4.92 (d, 1H, $J = 12.4$ Hz), 5.94 (d, 1H, $J = 10.2$ Hz), 6.96 (d, 2H, $J = 8.6$ Hz), 7.41 (d, 2H, $J = 8.6$ Hz) ppm; $^{13}$C NMR (75 MHz, $\delta$, CDCl$_3$, 298 K): 24.6, 27.3, 28.4, 35.4, 48.6, 49.8, 51.4, 55.5, 65.6, 75.6, 80.8, 114.7, 118.7, 134.6, 155.4, 161.4 ppm; IR (film): $\nu = 3447, 3258, 2976, 2934, 2864, 2839, 1690, 1611, 1514, 1449, 1366, 1321, 1283, 1252, 1159, 1024, 916, 837, 768 \text{ cm}^{-1}$; HRMS (ESI) $m/z$ calcd for C$_{21}$H$_{35}$N$_2$O$_3$: 363.2648 [M$^+$], found: 363.2656.

**Compound 7d:** Obtained in 37% (+ 25% recovered tert.-amine intermediate that could be resubmitted to the methylation again) (two steps, 5 mmol scale) as an oily residue. $[\alpha]_D^{23} (c = 1.0, \text{DCM}) = -5.2^\circ$; $^1$H NMR (300 MHz, $\delta$, CDCl$_3$, 298 K): 1.25-1.38 (m, 1H), 1.45 (s, 9H), 1.58-1.77 (m, 3H), 1.85-2.08 (m, 3H), 2.52-2.64 (m, 1H), 2.99 (s, 3H), 3.14 (s, 3H), 4.14-4.28 (m, 1H), 5.07-5.20 (m, 1H), 5.30 (d, 1H, $J = 13.4$ Hz), 5.47 (d, 1H, $J = 13.4$ Hz), 6.16 (d, 1H, $J = 10.1$ Hz), 7.40-7.53 (m, 2H), 7.54-7.63 (m, 1H), 7.67 (d, 1H, $J = 7.0$ Hz), 7.86 (d, 1H, $J = 8.0$ Hz), 7.94 (d, 1H, $J = 8.3$ Hz), 8.22 (d, 1H, $J = 8.2$ Hz) ppm; $^{13}$C NMR (75 MHz, $\delta$, CDCl$_3$, 298 K): 24.5, 24.6, 27.6, 28.4, 35.6, 48.8, 50.6, 51.6, 62.3, 76.5, 80.7, 123.3, 123.6, 125.0, 126.6, 128.1, 129.3, 132.0, 133.1, 134.0, 134.1, 155.6 ppm; IR (film): $\nu = 3439, 3244, 3005, 2976, 2936,
2864, 1697, 1508, 1456, 1393, 1366, 1273, 1242, 1159, 1047, 1024, 870, 808, 783, 733 cm$^{-1}$; HRMS (ESI) m/z calcld for C$_{24}$H$_{35}$N$_2$O$_2$:$^+$: 383.2699 [M$^+$], found: 383.2693.

**Compound 7e:** Obtained in 61% (two steps, 2 mmol scale) as an oily residue. [$\alpha$]$_D^{23}$ (c = 0.5, DCM) = -4.5$^\circ$; $^1$H NMR (300 MHz, $\delta$, CDCl$_3$, 298 K): 1.24-1.50 (m, 2H), 1.47 (s, 9H), 1.56-1.67 (m, 2H), 1.67-1.79 (m, 1H), 1.86-2.13 (m, 2H), 2.51-2.64 (m, 1H), 3.11 (s, 3H), 3.22 (s, 3H), 4.06-4.23 (m, 1H), 4.82-4.94 (m, 1H), 5.00 (d, 1H, $J$ = 12.6 Hz), 5.11 (d, 1H, $J$ = 12.6 Hz), 6.14 (d, 1H, $J$ = 9.9 Hz), 7.48-7.59 (m, 3H), 7.80-7.88 (m, 3H), 8.02 (s, 1H) ppm; $^{13}$C NMR (75 MHz, $\delta$, CDCl$_3$, 298 K): 24.7, 24.8, 27.5, 28.5, 35.5, 49.3, 50.4, 51.5, 65.9, 76.4, 80.9, 124.5, 127.3, 127.8, 128.0, 128.4, 129.2 (2x), 132.9, 133.9, 134.0, 155.6 ppm; IR (film): $\tilde{\nu}$ = 3237, 2934, 2862, 1701, 1508, 1450, 1391, 1366, 1321, 1277, 1242, 1167, 1020 cm$^{-1}$; HRMS (ESI) m/z calcld for C$_{24}$H$_{35}$N$_2$O$_2$:$^+$: 383.2699 [M$^+$], found: 383.2698.

**Synthesis of 7f:** K$_2$CO$_3$ (319 mg, 2.31 mmol, 2 eq) was added to a solution of mono-Boc-protected diamine 6 (247 mg, 1.16 mmol) in 5 ml AcN. After the addition of 360 $\mu$l (5.78 mmol, 5 eq) methyl iodide the suspension was stirred for 3 d. After evaporation of excess methyl iodide and AcN, the residue was dissolved in DCM and filtered to give 7f as an oily residue in quantitative yield. The product was used without further purification. [$\alpha$]$_D^{22}$ (c = 6.9, DCM) = +8.3$^\circ$; $^1$H NMR (300 MHz, $\delta$, CDCl$_3$, 298 K): 1.20-1.46 (m, 2H), 1.43 (s, 9H) 1.50-1.66 (m, 1H), 1.70-1.80 (m, 1H), 1.85-1.98 (m, 3H), 2.33-2.44 (m, 1H), 3.42 (s, 9H), 3.86-4.01 (m, 1H), 4.65 (m, 1H), 5.76 (d, 1H, NH) ppm; $^{13}$C NMR (75 MHz, $\delta$, CDCl$_3$, 298 K): 24.6, 24.7, 27.2, 28.5, 35.2, 51.4, 75.0, 81.0, 155.5 ppm; IR (film): $\tilde{\nu}$ = 3443, 3244, 3005, 2974, 2940, 2862, 1690, 1506, 1449, 1390, 1365, 1321, 1277, 1248, 1159, 1107, 1045, 1022, 960, 932, 868, 847 cm$^{-1}$; HRMS (ESI) m/z calcld for C$_{14}$H$_{29}$N$_2$O$_2$:$^+$: 257.2224 [M$^+$], found: 257.2226.

**General Syntheses of Catalysts 1a – 1o:**

**Step 1:** A solution of the quaternary ammonium salt 7 and trifluoroacetic acid (10 eq.) in DCM (10 mL / mmol) was stirred at r.t. for at least 2 h. After evaporation to dryness, the crude amine was directly subjected to the final coupling step (the reaction can also be carried out using aqueous HI). **Step 2:** A mixture of the amine, R$_2$NCX (1.5 eq.), and K$_2$CO$_3$ (3 eq.) in DCM (10 mL / mmol) was stirred at r.t. for 8-18 h. After filtration and evaporation to dryness, the crude product was purified by column chromatography (DCM:MeOH, 50:1 $\rightarrow$ 10:1) to obtain catalysts 1 in the reported yields.
**Compound 1a.** Obtained in 71% (2 steps, 0.5 mmol scale) as a colourless oil. $[\alpha]_D^{23}$ (c = 0.9, DCM) = -30.9°; $^1$H NMR (300 MHz, δ, CDCl$_3$, 298 K): 1.15-1.32 (m, 1H), 1.36-1.53 (m, 2H), 1.59-1.75 (m, 2H), 1.79-1.90 (m, 1H), 1.94-2.05 (m, 1H), 2.28-2.38 (m, 1H), 2.86 (s, 3H), 3.00 (s, 3H), 3.84-3.95 (m, 1H), 4.15-4.29 (m, 1H), 4.67-4.78 (m, 2H), 6.90 (t, 1H, $J_1 = 7.6$ Hz), 7.17 (dd, 2H, $J_1 = 7.6$ Hz, $J_2 = 7.6$ Hz), 7.26-7.40 (m, 5H), 7.47 (d, 2H, $J = 7.9$ Hz), 7.84 (d, 1H, $J = 9.8$ Hz), 9.06 (s, 1H) ppm; $^{13}$C NMR (75 MHz, δ, CDCl$_3$, 298 K): 24.6, 25.2, 27.2, 35.7, 48.8, 50.4, 50.9, 66.5, 77.4, 119.1, 122.5, 127.1, 129.0, 129.6, 131.1, 133.3, 139.9, 155.6 ppm; IR (film): $\tilde{\nu}$ = 3262, 3190, 3038, 2941, 2865, 1670, 1597, 1549, 1499, 1443, 1321, 1258, 1202, 1130, 800, 733 cm$^{-1}$; HRMS (ESI): $m/z$ calcd for C$_{22}$H$_{30}$N$_3$O$^+$: 352.2383 [M$^+$]; found: 352.2392.

**Compound 1b.** Obtained in 50% (2 steps, 0.1 mmol scale) as a yellowish oil. $[\alpha]_D^{23}$ (c = 0.3, DCM) = -19.4°; $^1$H NMR (300 MHz, δ, CDCl$_3$, 298 K): 1.28-1.45 (m, 1H), 1.50-1.69 (m, 2H), 1.73-1.87 (m, 2H), 1.91-2.10 (m, 1H), 2.14-2.25 (m, 1H), 2.46-2.60 (m, 1H), 3.08 (s, 3H), 3.20 (s, 3H), 4.35-4.47 (m, 1H), 4.69 (d, 1H, $J = 12.6$ Hz), 5.10 (d, 1H, $J = 12.6$ Hz), 5.20-5.35 (m, 1H), 7.15 (t, 1H, $J = 7.4$ Hz), 7.31 (dd, 2H, $J_1 = 7.7$ Hz, $J_2 = 7.4$ Hz), 7.37-7.51 (m, 5H), 7.60 (d, 2H, $J = 7.7$ Hz), 8.81 (d, 1H, $J = 9.6$ Hz), 9.24 (s, 1H) ppm; $^{13}$C NMR (75 MHz, δ, CDCl$_3$, 298 K): 24.3, 24.9, 27.3, 35.0, 50.0, 51.1, 54.0, 65.9, 77.7, 124.4, 125.8, 126.9, 128.8, 129.5, 131.1, 133.3, 138.6, 180.2 ppm; IR (film): $\tilde{\nu}$ = 3206, 3032, 2936, 2860, 1599, 1533, 14497, 1449, 1348, 1321, 1265, 1215, 1155, 1134, 1028, 982 cm$^{-1}$; HRMS (ESI): $m/z$ calcd for C$_{22}$H$_{30}$N$_3$S$^+$: 368.2155 [M$^+$]; found: 368.2152.

**Compound 1c.** Obtained in 70% (2 steps, 2 mmol scale) as a yellowish oil. $[\alpha]_D^{23}$ (c = 0.5, DCM) = -47.9°; $^1$H NMR (300 MHz, δ, CDCl$_3$, 298 K): 1.25-1.44 (m, 1H), 1.51-1.71 (m, 2H), 1.73-1.88 (m, 2H), 1.91-2.05 (m, 1H), 2.08-2.19 (m, 1H), 2.49-2.60 (m, 1H), 3.05 (s, 3H), 3.22 (s, 3H), 4.25-4.50 (m, 2H), 4.94 (d, 1H, $J = 12.7$ Hz), 5.00 (d, 1H, $J = 12.7$ Hz), 7.32-7.54 (m, 7H), 7.72 (dd, 1H, $J_1 = 8.0$, $J_2 = 1.3$ Hz), 7.83 (dd, 1H, $J_1 = 8.1$, $J_2 = 2.0$ Hz), 8.74 (t, 1H, $J_2 = 2.1$ Hz), 9.21 (s, 1H) ppm; $^{13}$C NMR (75 MHz, δ, CDCl$_3$, 298 K): 24.4, 24.9, 27.2, 35.8, 48.7, 50.4, 50.7, 66.8, 77.2, 113.1, 117.1, 124.3, 126.8, 129.4, 129.5, 131.0, 133.2, 140.6, 148.6, 154.9 ppm; IR (film): $\tilde{\nu}$ = 3252, 3190, 3061, 3034, 2936, 2860, 1686, 1597, 1543, 1522, 1481, 1449, 1342, 1321, 1258, 1204, 1080, 100 cm$^{-1}$; HRMS (ESI): $m/z$ calcd for C$_{22}$H$_{29}$NaO$_3$$^+$: 397.2240 [M$^+$]; found: 397.2242.
**Compound 1d.** Obtained in 48% (2 steps, 0.15 mmol scale) as a slightly yellow residue. $[\alpha]_D^{22} = -35.7^\circ$; $^1$H NMR (700 MHz, $\delta$, CDCl$_3$, 298 K): 1.35-1.47 (m, 1H), 1.62-1.70 (m, 2H), 1.83-1.92 (m, 2H), 2.01-2.08 (m, 1H), 2.24-2.29 (m, 1H), 2.51-2.57 (m, 1H), 3.11 (s, 3H), 3.23 (s, 3H), 4.31-4.38 (m, 1H), 4.65 (d, 1H, $J = 12.6$ Hz), 5.09 (d, 1H, $J = 12.6$ Hz), 5.27-5.33 (m, 1H), 7.39-7.55 (m, 6H), 7.86 (d, 1H, $J = 8.1$ Hz), 7.98 (d, 1H, $J = 8.0$ Hz), 8.93 (s, 1H), 9.37 (d, 1H, $J = 9.9$ Hz), 9.80 (s, 1H) ppm; $^{13}$C NMR (176 MHz, $\delta$, CDCl$_3$, 298 K): 24.2, 24.9, 27.1, 34.9, 50.1, 51.3, 53.6, 66.2, 78.0, 118.4, 119.7, 126.5, 129.2, 129.3, 129.7, 131.4, 133.2, 140.2, 148.1, 179.9 ppm; IR (film): $\nu$ = 3200, 3030, 2943, 2864, 1526, 1474, 1348, 1265, 1217, 985, 735 cm$^{-1}$; HRMS (ESI): $m/z$ calcd for C$_{22}$H$_{29}$N$_4$O$_2$S$^+$: 413.2011 [M$^+$]; found: 413.2014.

**Compound 1e.** Obtained in 47% (2 steps, 0.2 mmol scale) as a yellowish oil. $[\alpha]_D^{23} = -16.6^\circ$; $^1$H NMR (300 MHz, $\delta$, CDCl$_3$, 298 K): 1.31-1.45 (m, 1H), 1.50-1.65 (m, 2H), 1.72-1.93 (m, 2H), 1.95-2.05 (m, 1H), 2.10-2.22 (m, 1H), 2.50-2.61 (m, 1H), 3.04 (s, 3H), 3.23 (s, 3H), 4.25-4.45 (m, 2H), 4.95 (d, 1H, $J = 12.7$ Hz), 5.07 (d, 1H, $J = 12.7$ Hz), 7.25-7.45 (m, 7H), 7.56 (d, 1H, $J = 9.5$ Hz), 7.64 (d, 1H, $J = 8.1$ Hz), 8.10 (s, 1H), 8.88 (s, 1H) ppm; $^{13}$C NMR (75 MHz, $\delta$, CDCl$_3$, 298 K): 24.5, 24.9, 27.3, 35.8, 48.6, 50.5, 50.7, 66.9, 77.3, 115.2, 119.0, 126.8, 129.2, 129.4, 130.9, 133.2, 139.8, 155.0 ppm; IR (film): $\bar{\nu} = 3264, 3208, 3088, 3063, 3034, 2943, 2864, 1684, 1558, 1541, 1447, 1339, 1319, 1260, 1215, 1165, 1123, 1069, 791$ cm$^{-1}$; HRMS (ESI): $m/z$ calcd for C$_{23}$H$_{29}$F$_3$N$_3$O$_3$+: 420.2263 [M$^+$]; found: 420.2269.

**Compound 1f.** Obtained in 62% (2 steps, 0.2 mmol scale) as a yellow oil. $[\alpha]_D^{23} = -24.9^\circ$; $^1$H NMR (300 MHz, $\delta$, CDCl$_3$, 298 K): 1.22-1.33 (m, 1H), 1.36 (t, 3H, $J = 7.2$ Hz), 1.52-1.69 (m, 2H), 1.70-1.89 (m, 2H), 1.90-1.97 (m, 1H), 2.06-2.18 (m, 1H), 2.50-2.61 (m, 1H), 3.05 (s, 3H), 3.23 (s, 3H), 4.15-4.30 (m, 1H), 4.36 (q, 2H, $J = 7.2$ Hz), 4.38-4.52 (m, 1H), 4.95 (d, 1H, $J = 12.3$ Hz), 5.07 (d, 1H, $J = 12.3$ Hz), 7.26-7.55 (m, 7H), 7.64-7.74 (m, 2H), 8.39 (t, 1H, $J = 1.7$ Hz), 8.73 (s, 1H) ppm; $^{13}$C NMR (75 MHz, $\delta$, CDCl$_3$, 298 K): 14.4, 24.4, 25.0, 27.2, 35.9, 48.8, 50.4, 50.9, 60.9, 66.6, 77.1, 119.6, 123.3, 137.7, 127.0, 128.7, 129.3, 130.8, 131.0, 133.2, 139.4, 155.0, 166.7 ppm; IR (film): $\bar{\nu} = 3456, 3256, 3192, 3065, 2936, 2862, 1686, 1593, 1549, 1481, 1439, 1366, 1321, 1287, 1204, 1103, 1022, 851, 756, 727$ cm$^{-1}$; HRMS (ESI): $m/z$ calcd for C$_{25}$H$_{34}$N$_3$O$_3$$: 424.2600$ [M$^+$]; found: 424.2604.
**Compound 1g.** Obtained in 43% (2 steps, 0.1 mmol scale) as a yellowish oil. \([\alpha]_D^{23} (c = 0.9, DCM) = +8.0^\circ; \) 
\(^1\)H NMR (300 MHz, \(\delta\), CDCl\(\text{3}\), 298 K): 1.20-1.60 (m, 3H), 1.64-1.80 (m, 2H), 1.86-1.97 (m, 1H), 2.00-2.11 (m, 1H), 2.28-2.41 (m, 1H), 3.34 (s, 9H), 3.89 (td, 1H, \(J_1 = 11.0\) Hz, \(J_2 = 3.2\) Hz), 4.10-4.25 (m, 1H), 6.95-7.02 (m, 2H), 7.25 (m, 2H), 7.52 (d, 2H, \(J = 7.9\) Hz), 8.38 (s, 1H) ppm; \(^{13}\)C NMR (75 MHz, \(\delta\), CDCl\(\text{3}\), 298 K): 24.5, 24.8, 27.2, 35.7, 50.3, 54.4, 76.4, 119.1, 122.9, 129.0, 139.2, 155.0 ppm; IR (film): \(\tilde{\nu} = 3258, 3188, 3130, 3032, 2938, 2861, 1682, 1595, 1541, 1497, 1441, 1319, 1256, 1223, 1204, 959, 843\) cm\(^{-1}\); HRMS (ESI): \(m/z\) calcd for C\(_{16}\)H\(_{26}\)N\(_3\)O\(^+\): 276.2070 [M\(^+\)]; found: 276.2065.

**Compound 1h.** Obtained in 70% (2 steps, 0.15 mmol scale) as a yellowish oil. \([\alpha]_D^{23} (c = 0.3, DCM) = -46.6^\circ; \) 
\(^1\)H NMR (300 MHz, \(\delta\), CD\(_3\)CN, 298 K): 1.38-1.52 (m, 2H), 1.65-1.85 (m, 3H), 2.00-2.16 (m, 2H), 2.20-2.38 (m, 1H), 3.06 (s, 3H), 3.09 (s, 3H), 3.70-3.81 (m, 1H), 4.32-4.48 (m, 1H), 4.81 (d, 1H, \(J = 12.8\) Hz), 4.97 (d, 1H, \(J = 12.8\) Hz), 6.95 (d, 1H, \(J = 8.7\) Hz), 7.50 (t, 1H, \(J = 8.0\) Hz), 7.42-7.55 (m, 3H), 8.01 (d, 1H, \(J = 7.7\) Hz), 8.32-8.45 (m, 2H), 8.65 (s, 1H). 9.14 (s, 1H) ppm; \(^{13}\)C NMR (75 MHz, \(\delta\), CD\(_3\)CN, 298 K): 23.4, 24.1, 25.7, 34.8, 49.2, 49.5, 50.6, 63.6, 76.8, 116.2, 122.2, 123.4, 124.9, 127.6, 129.2, 129.4, 129.6, 130.2, 139.1, 140.8, 148.2, 148.3, 154.4 ppm; IR (film): \(\tilde{\nu} = 3252, 3188, 3130, 3032, 2938, 2861, 1682, 1595, 1541, 1497, 1441, 1319, 1256, 1223, 1204, 959, 843\) cm\(^{-1}\); HRMS (ESI): \(m/z\) calcd for C\(_{22}\)H\(_{28}\)N\(_5\)O\(_5\)\(^+\): 442.2090 [M\(^+\)]; found: 442.2094.

**Compound 1i.** Obtained in 31% (2 steps, 0.2 mmol scale) as a yellowish oil. \([\alpha]_D^{23} (c = 0.5, DCM) = -35.1^\circ; \) 
\(^1\)H NMR (300 MHz, \(\delta\), CDCl\(\text{3}\), 298 K): 1.30-1.50 (m, 1H), 1.55-1.68 (m, 2H), 1.75-2.06 (m, 3H), 2.10-2.25 (m, 1H), 2.48-2.58 (m, 1H), 3.03 (s, 3H), 3.18 (s, 3H), 3.81 (s, 3H), 4.10-4.24 (m, 1H), 4.32-4.49 (m, 1H), 4.88 (d, 1H, \(J = 12.2\) Hz), 4.94 (d, 1H, \(J = 12.2\) Hz), 6.87 (d, 2H, \(J = 8.8\) Hz), 7.33 (d, 2H, \(J = 8.8\) Hz), 7.42 (t, 1H, \(J = 8.7\) Hz), 7.63 (d, 1H, \(J = 9.5\) Hz), 7.73 (dd, 1H, \(J_1 = 8.1\) Hz, \(J_2 = 2.1\) Hz), 7.87 (dd, 1H, \(J_1 = 8.2\) Hz, \(J_2 = 2.1\) Hz), 8.80 (d, 1H, \(J = 2.1\) Hz), 9.16 (s, 1H) ppm; \(^{13}\)C NMR (75 MHz, \(\delta\), CDCl\(\text{3}\), 298 K): 24.4, 24.9, 27.2, 35.5, 48.4, 50.4, 53.4, 55.4, 66.8, 77.2, 113.1, 114.8, 117.2, 118.3, 124.3, 134.5, 140.5, 148.7, 154.9, 161.5 ppm; IR (film): \(\tilde{\nu} = 3252, 3028, 2934, 2862, 2837, 1886, 1611, 1524, 1516, 1476, 1341, 1254, 1204, 1180, 1028, 831, 735\) cm\(^{-1}\); HRMS (ESI): \(m/z\) calcd for C\(_{23}\)H\(_{31}\)N\(_4\)O\(_4\)\(^+\): 427.2345 [M\(^+\)]; found: 427.2335.
**Compound 1j.** Obtained in 53% (2 steps, 0.15 mmol scale) as an oily residue. $[\alpha]_D^{23}$ (c = 0.45, DCM) = $-45.5^\circ$; $^1$H NMR (700 MHz, $\delta$, CDCl$_3$, 298 K): 1.31-1.44 (m, 1H), 1.62-1.77 (m, 3H), 1.90-2.03 (m, 2H), 2.15-2.21 (m, 1H), 2.60-2.66 (m, 1H), 2.88 (s, 3H), 3.13 (s, 3H), 4.52-4.60 (m, 2H), 5.40 (d, 1H, $J$ = 13.4 Hz), 5.65 (d, 1H, $J$ = 13.4 Hz), 7.10-7.18 (m, 2H), 7.22-7.28 (m, 1H), 7.38-7.49 (m, 2H), 7.61-7.72 (m, 3H), 7.81 (dd, 1H, $J_1$ = 8.1 Hz, $J_2$ = 1.6 Hz), 7.89 (dd, 1H, $J_1$ = 8.3 Hz, $J_2$ = 1.8 Hz), 8.07 (d, 1H, $J$ = 8.3 Hz), 8.88 (s, 1H), 9.36 (s, 1H) ppm; $^{13}$C NMR (176 MHz, $\delta$, CDCl$_3$, 298 K): 24.6, 25.1, 27.5, 36.2, 47.9, 50.7, 51.3, 63.8, 113.2, 117.4, 123.0, 123.3, 124.5, 124.8, 126.5, 127.9, 129.2, 129.6, 131.9, 132.9, 133.8, 134.0, 140.8, 148.8, 155.2 ppm; IR (film): $\tilde{\nu}$ = 3250, 3057, 2943, 2860, 1685, 1597, 1545, 1528, 1483, 1352, 1207, 766 cm$^{-1}$; HRMS (ESI): $m/z$ calcd for C$_{26}$H$_{31}$N$_4$O$_3$: 447.2396 [M$^+$]; found: 447.2405.

**Compound 1k.** Obtained in 39% (2 steps, 0.12 mmol scale) as a yellowish oil. $[\alpha]_D^{22}$ (c = 0.45, DCM) = $-55.5^\circ$; $^1$H NMR (700 MHz, $\delta$, CDCl$_3$, 298 K): 1.37 (t, 3H, $J$ = 7.4 Hz), 1.35-1.42 (m, 1H), 1.65-1.74 (m, 2H), 1.76-1.83 (m, 1H), 1.93-2.05 (m, 2H), 2.18-2.24 (m, 1H), 2.58-2.64 (m, 1H), 2.88 (s, 3H), 3.15 (s, 3H), 4.37 (q, 2H, $J$ = 7.4 Hz), 4.42-4.50 (m, 1H), 4.54-4.60 (m, 1H), 5.42 (d, 1H, $J$ = 13.3 Hz), 5.63 (d, 1H, $J$ = 13.3 Hz), 7.15-7.20 (m, 2H), 7.25-7.30 (m, 1H), 7.38 (t, 1H, $J$ = 7.9 Hz), 7.46 (d, 1H, $J$ = 6.6 Hz), 7.67 (d, 1H, $J$ = 7.9 Hz), 7.71 (d, 1H, $J$ = 8.1 Hz), 7.73-7.77 (m, 2H), 7.82 (d, 1H, $J$ = 9.9 Hz), 8.07 (d, 1H, $J$ = 8.4 Hz), 8.48 (s, 1H), 8.84 (s, 1H) ppm; $^{13}$C NMR (176 MHz, $\delta$, CDCl$_3$, 298 K): 14.5, 24.6, 25.1, 27.6, 36.2, 48.0, 50.6, 51.5, 61.1, 63.6, 77.5, 119.7, 123.1, 123.4, 123.5, 124.0, 124.7, 126.5, 128.0, 129.0, 129.1, 131.3, 131.8, 133.0, 133.7, 134.0, 139.7, 155.4, 166.8 ppm; IR (film): $\tilde{\nu}$ = 3254, 3196, 3042, 2934, 2860, 1709, 1686, 1593, 1551, 1481, 1439, 1287, 1260, 1228, 1101, 1022, 806, 783, 758, 735 cm$^{-1}$; HRMS (ESI): $m/z$ calcd for C$_{20}$H$_{36}$N$_3$O$_3$: 474.2757 [M$^+$]; found: 474.2762.
**Compound 1l.** Obtained in 60% (2 steps, 0.2 mmol scale) as a yellowish oil. $[\alpha]_D^{23} (c = 1.0, \text{DCM}) = 36.6^\circ$; $^1$H NMR (300 MHz, $\delta$, CDCl$_3$, 298 K): 1.38 (t, 3H, $J = 7.4$ Hz), 1.55-1.98 (m, 6H), 2.08-2.22 (m, 1H), 2.51-2.61 (m, 1H), 3.03 (s, 3H), 3.23 (s, 3H), 4.20-4.33 (m, 1H), 4.38 (q, 2H, $J = 7.4$ Hz), 4.40-4.55 (m, 1H), 5.11 (d, 1H, $J = 12.9$ Hz), 5.27 (d, 1H, $J = 12.9$ Hz), 7.30-7.50 (m, 4H), 7.52-7.58 (m, 2H), 7.60-7.68 (m, 2H), 7.70-7.77 (m, 2H), 7.89 (s, 1H), 8.48 (s, 1H), 8.88 (s, 1H) ppm; $^{13}$C NMR (75 MHz, $\delta$, CDCl$_3$, 298 K): 14.4, 24.5, 25.0, 27.2, 35.9, 48.3, 50.5, 51.0, 61.0, 67.0, 77.3, 119.6, 123.3, 123.8, 124.1, 127.0, 127.6, 127.8, 128.2, 128.8, 128.9, 131.1, 132.6, 133.6, 133.7, 139.6, 155.1, 166.7 ppm; IR (film): $\tilde{\nu} = 3256, 3196, 3042, 2980, 2934, 2860, 1686, 1593, 1545, 1477, 1439, 1366, 1287, 1227, 1204, 1103, 1020, 914, 864, 820, 754, 727 \text{ cm}^{-1}$; HRMS (ESI): $m$/z calcd for C$_{29}$H$_{36}$N$_3$O$_3$: 474.2757 [M+]; found: 474.2765.

**Compound 1m.** Obtained in 57% (2 steps, 0.1 mmol scale) as a yellowish oil. $[\alpha]_D^{23} (c = 0.4, \text{DCM}) = -28.6^\circ$; $^1$H NMR (700 MHz, $\delta$, CDCl$_3$, 298 K): 1.22-1.57 (m, 5H), 1.71-2.05 (m, 4H), 2.12-2.23 (m, 1H), 2.59-2.65 (m, 1H), 2.84 (s, 3H), 3.12 (s, 3H), 4.36 (q, $J = 7.0$ Hz, 2H), 4.41-4.50 (m, 1H), 4.53-4.63 (m, 1H), 5.42 (d, $J = 13.3$ Hz, 1H), 5.68 (d, $J = 13.3$ Hz, 1H), 7.07-7.19 (m, 2H), 7.36-7.46 (m, 1H), 7.61-7.71 (m, 3H), 7.72-7.83 (m, 3H), 8.00 (d, $J = 8.3$ Hz, 2H), 8.07 (d, $J = 8.5$ Hz, 1H), 9.19 (s, 1H) ppm; $^{13}$C NMR (175 MHz, $\delta$, CDCl$_3$, 298 K): 14.5, 24.65, 25.1, 27.7, 36.1, 47.4, 50.8, 51.0, 60.8, 64.3, 77.2, 117.7, 123.1, 123.4, 124.4, 124.7, 126.5, 128.0, 129.2, 130.9, 131.9, 133.0, 133.8, 134.0, 143.9, 155.1, 166.7 ppm; IR (film): $\tilde{\nu} = 3250, 3198, 3101, 3044, 2980, 2938, 2864, 1697, 1595, 1537, 1410, 1322, 1277, 1258, 1206, 1173, 1105, 1020, 857, 783 \text{ cm}^{-1}$; HRMS (ESI): $m$/z calcd for C$_{29}$H$_{36}$N$_3$O$_3$: 474.2757 [M+]; found: 474.2767.

**Compound 1n.** Obtained in 49% (2 steps, 0.2 mmol scale) as a yellowish oil. $[\alpha]_D^{23} (c = 0.3, \text{DCM}) = -44.0^\circ$; $^1$H NMR (700 MHz, $\delta$, CDCl$_3$, 298 K): 0.98 (t, 3H, $J = 7.4$ Hz, 3H), 1.34-1.52 (m, 4H), 1.67-1.88 (m, 4H), 1.90-2.06 (m, 2H), 2.18-2.25 (m, 1H), 2.57-2.67 (m, 1H), 2.85 (s, 3H), 3.14 (s, 3H), 4.31 (q, $J = 7.4$ Hz, 2H), 4.43-4.51 (m, 1H), 4.53-4.60 (m, 1H), 5.43 (d, $J = 13.1$ Hz, 1H), 5.63 (d, $J = 13.1$ Hz, 1H), 7.12-7.22 (m, 2H), 7.27-7.33 (m, 1H), 7.44 (d, $J = 6.6$ Hz, 1H), 7.66-7.75 (m, 2H), 7.75-7.84 (m, 3H), 8.00 (d, $J = 8.4$ Hz, 2H), 8.08 (d,
\( J = 8.4 \text{ Hz}, \ 1H \), 9.13 (s, 1H) ppm; \(^{13}\text{C NMR (175 MHz,} \delta, \ \text{CDCl}_3, \ 298 \text{ K}): 13.9, 19.4, 24.6, 25.1, 27.7, 31.1, 36.1, 47.6, 50.7, 51.1, 64.2, 64.7, 77.2, 117.7, 123.0, 123.3, 124.4, 124.7, 126.6, 128.1, 129.2, 130.9, 132.0, 133.0, 133.8, 134.0, 143.8, 155.1, 166.7 \text{ ppm}; \text{IR (film): } \tilde{\nu} = 3246, 3198, 3103, 2934, 2866, 1686, 1595, 1533, 1508, 1410, 1321, 1275, 1256, 1204, 1171, 1101, 912, 856, 806, 770, 727 \text{ cm}^{-1}; \text{HRMS (ESI): } m/z \text{ calcd for C}_{31}\text{H}_{40}\text{N}_3\text{O}_3^+: 502.3070 [M^+]; \text{found: 502.3079.}

**Compound 1o.** Obtained in 57% (2 steps, 0.2 mmol scale) as a yellowish oil. \([\alpha]_D^{23} = -49.1^\circ; \ ^1\text{H NMR (300 MHz,} \delta, \ \text{CDCl}_3, \ 298 \text{ K): 1.25-1.48 (m, 2H), 1.62-1.90 (m, 2H), 1.91-2.08 (m, 2H), 2.15-2.28 (m, 1H), 2.58-2.70 (m, 1H), 2.90 (s, 3H), 3.17 (s, 3H), 3.94 (s, 6H), 4.45-4.70 (m, 2H), 5.42 (d, 1H, J = 13.1 Hz), 5.70 (d, 1H, J = 13.1 Hz), 7.15 (t, 2H, J = 7.6 Hz), 7.24 (d, 1H, J = 7.8 Hz), 7.45 (d, 1H, J = 7.1 Hz), 7.66 (t, 2H, J = 8.6 Hz), 7.97 (d, 1H, J = 9.7 Hz), 8.08 (d, 1H, J = 8.6 Hz), 8.42 (t, 1H, J = 1.4 Hz), 8.56 (d, 2H, J = 1.4 Hz), 9.05 (s, 1H) ppm; \ ^{13}\text{C NMR (75 MHz,} \delta, \ \text{CDCl}_3, \ 298 \text{ K): 24.5, 25.0, 27.4, 36.1, 48.0, 50.6, 51.4, 52.4, 63.5, 77.3, 122.9, 123.2, 123.8, 124.6, 125.0, 126.4, 127.8, 129.0, 131.2, 131.7, 132.8, 133.6, 133.9, 139.9, 155.2, 166.3 \text{ ppm}; \text{IR (film): } \tilde{\nu} = 3244, 3028, 2943, 2866, 1717, 1684, 1558, 1541, 1508, 1437, 1346, 1317, 1242, 1123, 1047, 997, 876, 808, 788, 754 \text{ cm}^{-1}; \text{HRMS (ESI): } m/z \text{ calcd for C}_{30}\text{H}_{36}\text{N}_3\text{O}_5^+: 518.2655 [M^+]; \text{found: 518.2662.}
Syntheses of Cyclohexanediamine-Based Catalysts 1p – 1r:

Synthesis of 9: Step 1: A mixture of 8 (prepared according to literature4) (1.817 g, 10.0 mmol) and di-tert-butyl dicarbonate (2.61 g, 12.0 mmol, 1.2 eq) in 50 ml DCM was stirred at r.t. for 20 h and the solvent was removed under reduced pressure. The product was purified by column chromatography (silica gel, DCM:MeOH, 40:1 → 10:1) to give the Boc-protected tert-amine in 72% yield (2.04 g, 7.2 mmol). Step 2: A mixture of tert-amine (378 mg, 1.3 mmol), K₂CO₃ 185 mg (1.3 mmol, 1 eq) and 4 ml methyl iodide was stirred at 40 °C in a Schlenk flask for 3 d. Excess methyl iodide was removed under reduced pressure and the product was purified by column chromatography (silica gel, DCM:MeOH, 60:1 → 10:1) to give 9 in 45% (255 mg, 0.6 mmol). [α]D²³ (c = 1.3, DCM) = -2.4°; ¹H NMR (700 MHz, δ, CDCl₃, 298 K): 1.24-1.33 (m, 1H), 1.35-1.48 (m, 1H), 1.41 (s, 9H), 1.58-1.66 (m, 1H), 1.69-1.79 (m, 3H), 1.81-1.94 (m, 5H), 2.06-2.13 (m, 1H), 2.24-2.34 (m, 2H), 3.18 (s, 3Hg), 3.52-3.57 (m, 1H), 3.64-3.69 (m, 1H), 3.72-3.76 (m, 1H), 3.94-4.00 (m, 1H), 4.07-4.12 (m, 1H), 4.58-4.63 (m, 1H), 6.01 (d, 1H, J = 8.6 Hz) ppm; ¹³C NMR (176 MHz, δ, CDCl₃, 298 K): 20.8, 20.9 (2x), 24.5, 24.7, 26.0, 28.5, 35.0, 45.2, 51.2, 61.4, 62.3, 71.7, 80.8, 155.5 ppm; IR (film): ν = 3237, 2968, 2934, 2862, 1692, 1508, 1450, 1391, 1366, 1321, 1275, 1242, 1155, 1109, 1043, 1020, 999, 957, 930, 885, 866, 856, 816, 783, 731 cm⁻¹; HRMS (ESI) m/z calcd for C₁₇H₃₃N₂O₂⁺: 297.2537 [M⁺], found: 297.2531.

General Syntheses of Catalysts 1p – 1r: Step 1: A solution of the quaternary ammonium salt 9 and trifluoroacetic acid (10 eq.) in DCM (10 mL / mmol) was stirred at r.t. for 2 h. After evaporation to dryness, the crude amine was directly subjected to the final coupling step. Step 2: A mixture of the amine, R²NCX (1.5 eq.), and K₂CO₃ (3 eq.) in DCM (10 mL / mmol) was stirred at r.t. for 8-18 h. After filtration and evaporation to dryness, the crude product was purified by column chromatography (DCM:MeOH, 40:1 → 10:1) to obtain catalysts 1 in the reported yields.

4) Y. Zhu, J. Malerich, V. Rawal, Angew. Chem. Int. Ed. 2010, 49, 153-156.
**Compound 1p.** Obtained in 64% (0.2 mmol scale, 2 steps) as a colourless oil. $\left[\alpha\right]_D^{22} (c = 0.3, \text{DCM}) = +2.9^\circ$; $^1$H NMR (300 MHz, $\delta$, CDCl$_3$, 298 K): 1.22-1.58 (m, 3H), 1.60-1.99 (m, 8H), 2.01-2.11 (m, 2H), 3.14 (s, 3H), 3.16-3.27 (m, 1H), 3.54-3.71 (m, 2H), 3.89 (td, 1H, $J_1 = 10.8$ Hz, $J_2 = 2.9$ Hz), 4.14-4.29 (m, 1H), 4.23-4.33 (m, 1H), 6.97 (t, 1H, $J = 7.4$ Hz), 7.23 (dd, 2H, $J_1 = 7.6$ Hz, $J_2 = 7.4$ Hz), 7.29 (d, 1H, $J = 10.0$ Hz), 7.53 (d, 2H, $J = 7.6$ Hz), 8.49 (s, 1H) ppm; $^{13}$C NMR (75 MHz, $\delta$, CDCl$_3$, 298 K): 20.8, 21.0, 21.2, 24.5, 25.2, 26.0, 35.9, 46.1, 50.2, 62.0, 63.9, 71.4, 119.0, 122.7, 128.9, 139.4, 155.2 ppm; IR (film): $\tilde{\nu} =$ 3254, 3190, 3034, 2938, 2864, 1686, 1597, 1545, 1499, 1441, 1321, 1265, 1221, 1207 cm$^{-1}$; HRMS (ESI): $m/z$ calcld for C$_{19}$H$_{30}$N$_3$O+: 316.2383 [M$^+$]; found: 316.2392.

**Compound 1q.** Obtained in 42% (0.1 mmol scale, 2 steps) as a colourless oil. $\left[\alpha\right]_D^{22} (c = 0.4, \text{DCM}) = +41.8^\circ$; $^1$H NMR (300 MHz, $\delta$, CDCl$_3$, 298 K): 1.23-1.60 (m, 3H), 1.66-2.02 (m, 8H), 2.10-2.22 (m, 1H), 2.23-2.36 (m, 2H), 3.21 (s, 3H), 3.26-3.36 (m, 1H), 3.48-3.59 (m, 1H), 3.59-3.70 (m, 1H), 4.04-4.14 (m, 1H), 4.11-4.21 (m, 1H), 7.53 (d, 2H, $J = 8.5$ Hz), 7.93 (d, 2H, $J = 8.5$ Hz), 9.04 (d, 1H, $J = 10.0$ Hz), 9.89 (s, 1H) ppm; $^{13}$C NMR (75 MHz, $\delta$, CDCl$_3$, 298 K): 20.8, 21.0, 21.3, 24.0, 24.9, 25.7, 34.7, 46.2, 53.6, 61.9, 63.7, 72.8, 122.7, 124.3, 125.7, 126.5, 142.3, 180.0 ppm; IR (film): $\tilde{\nu} =$ 2940, 2864, 1578, 1522, 1451, 1321, 1252, 1163, 1107, 1065, 1016, 843 cm$^{-1}$; HRMS (ESI): $m/z$ calcld for C$_{20}$H$_{29}$F$_3$N$_3$S+: 400.2030 [M$^+$]; found: 400.2032.

**Compound 1r.** Obtained in 46% (0.2 mmol scale, 2 steps) as a colourless oil. $\left[\alpha\right]_D^{22} (c = 1.2, \text{DCM}) = +1.1^\circ$; $^1$H NMR (300 MHz, $\delta$, CDCl$_3$, 298 K): 1.24-1.60 (m, 3H), 1.38 (t, 3H, $J = 6.8$ Hz), 1.69-2.05 (m, 8H), 2.07-2.15 (m, 1H), 2.23-2.40 (m, 2H), 3.20 (s, 3H), 3.218-3.32 (m, 1H), 3.56-3.66 (m, 1H), 3.67-3.78 (m, 1H), 3.90-4.01 (m, 1H), 4.22-4.40 (m, 2H), 4.35 (q, 2H, $J = 6.8$ Hz), 7.32 (t, 1H, $J = 7.7$ Hz), 7.48 (d, 1H, $J = 10.0$ Hz), 7.62-7.71 (m, 2H), 8.30 (s, 1H), 8.64 (s, 1H) ppm; $^{13}$C NMR (75 MHz, $\delta$, CDCl$_3$, 298 K): 14.4, 20.6, 20.9, 21.1, 24.3, 25.0, 25.8, 30.9, 35.7, 46.0, 50.0, 60.9, 62.0, 63.9, 71.2, 119.5, 123.3, 123.7, 128.7, 131.0, 139.4, 154.9, 166.7 ppm; IR (film): $\tilde{\nu} =$ 3254, 3192, 3088, 3035, 2937, 2864, 1684, 1593, 1543, 1437, 1364, 1287, 1204, 1101, 1022, 858, 814, 754 cm$^{-1}$; HRMS (ESI): $m/z$ calcld for C$_{22}$H$_{34}$N$_3$O$_3$+: 388.2595 [M$^+$]; found: 388.2602.
Synthesis of Cyclohexanediamine-Based Catalyst 1s:

**Compound 1s: Step 1:** A mixture of 5 (170 mg, 1.49 mmol) and 10 (490 mg, 1 eq.) in DMSO (3 mL) was stirred at 90 °C for 1 d. DMSO was removed under reduced pressure and the crude 11 was directly submitted to the coupling step. **Step 2:** A mixture of the amine 11 (1.49 mmol), CyNCO (416 mg, 1.5 eq.), and K₂CO₃ (205 mg, 1 eq.) in DCM (3 mL) was stirred at r.t. for 18 h. After filtration and evaporation to dryness, the crude product was purified by column chromatography (DCM:MeOH, 40:1 → 10:1) to obtain 1s in 41% (233 mg, 0.61 mmol). [α]D²³ (c = 0.27, DCM) = -96.3°; ¹H NMR (300 MHz, δ, CD₃OD, 298 K): 0.85-2.30 (m, 18H), 3.01-3.21 (m, 1H), 4.00-4.18 (m, 1H), 4.44-4.69 (m, 1H), 5.71 (d, 1H, J = 7.9 Hz), 8.01 (dd, 2H, J₁ = 7.8 Hz, J₂ = 6.4 Hz), 8.58 (t, 1H, J = 7.8 Hz), 9.07 (d, 2H, J = 6.4 Hz), ppm; ¹³C NMR (75 MHz, δ, CD₃OD, 298 K): 25.4, 25.7, 25.8, 25.9, 26.6, 31.2, 32.6, 33.8, 34.2, 34.5, 54.0, 78.1, 80.8, 128.9, 145.5, 147.2, 158.9 ppm; IR (film): ν = 3294, 3051, 2855, 1630, 1571, 1487, 1450, 1321, 1165, 779 cm⁻¹; HRMS (ESI) m/z calcd for C₁₈H₂₈N₃O⁺: 302.2227 [M⁺], found: 302.2232.

Synthesis of Diphenylethylenediamine-Based Catalyst 2a:

**Compound 2a: Step 1:** A mixture of K₂CO₃ (620 mg, 4.48 mmol, 2 eq), mono-Boc-protected diamine 32 (prepared according to literature⁵) (630 mg, 2.01 mmol), and MeI (1mL, 16 mmol) in 50 ml AcN was stirred at 80 °C for 3 d. After filtration and evaporation to dryness the product was used without further purification for the deprotection and coupling. **Step 2:** A solution of 33 (350 mg, 0.73 mmol) and trifluoroacetic acid (0.56 mL, 10 eq.) in DCM (10

⁵) D. W. Lee, H.-J. Ha, W. K. Lee Synth. Commun. 2007, 37, 737-742.
mL) was stirred at r.t. for 3 h. After evaporation to dryness, the crude amine was directly subjected to the final coupling step. **Step 3:** A mixture of the amine (0.73 mmol), PhNCO (143 mg, 1.5 eq.), and K$_2$CO$_3$ (0.5 g, 3 eq.) in DCM (5 mL) was stirred at r.t. for 19 h. After filtration and evaporation to dryness, the crude product was purified by column chromatography (DCM:MeOH, 40:1 → 10:1) to obtain 2a as an oily residue (0.14 g, 0.28 mmol, 38% over 3 steps). [α]$_D^{23}$ (c = 0.95, DCM) = -127.4°; $^1$H NMR (300 MHz, δ, CDCl$_3$, 298 K): 3.19 (s, 9H), 5.28 (d, 1H, $J = 10.9$ Hz), 5.87 (dd, 1H, $J_1 = 10.9$ Hz, $J_2 = 9.5$ Hz), 6.78-6.98 (m, 4H), 7.00-7.28 (m, 8H), 7.32-7.42 (m, 3H), 8.18 (d, 1H, $J = 9.5$ Hz), 8.97 (s, 1H) ppm; $^{13}$C NMR (75 MHz, δ, CDCl$_3$, 298 K): 54.6, 54.8, 80.6, 119.0, 122.5, 126.9, 127.7, 127.8, 128.7, 128.9, 129.1, 129.5, 130.6, 131.2, 133.9, 139.2, 154.9 ppm; IR (film): $\nu = 3256$, 3198, 3034, 2959, 2920, 2851, 1670, 1597, 1545, 1489, 1443, 1314, 1202, 1128, 949, 833, 800, 756, 731 cm$^{-1}$; HRMS (ESI) $m/z$ calcd for C$_{24}$H$_{28}$N$_3$O$: 347.2227$ [M$^+$], found: 347.2233.

**Synthesis of Anthracene-Based Catalyst 3a:**

**Compound 3a:** **Step 1:** Enantioenriched 13 (prepared according to literature$^6$) (396 mg, 1.68 mmol) was dissolved in a mixture MeOH (3 mL) and H$_2$O (0.5 mL), cooled to 0 °C and HCl in MeOH (1.25 M, 1.8 mL) was added dropwise over 15 min. After further 45 min a solution of Boc$_2$O (376 mg, 2.16 mmol) in MeOH (2 mL) was added dropwise over 30 min and the mixture was stirred for 5 h at ambient temperature. After extraction with DCM and brine, drying of the organic phase over Na$_2$SO$_4$ and evaporation to dryness, the crude product was purified by column chromatography (DCM:MeOH = 10:1) to yield the mono-Boc-protected 13 (167 mg, 30%). $^1$H NMR (300 MHz, δ, CDCl$_3$, 298 K): 1.41 (m, 2H), 2.80 (s, 1H), 3.47-3.45 (m, 1H), 4.13 (d, $J = 2.6$ Hz, 1H), 4.24 (s, 1H), 7.32-7.15 (m, 8H) ppm; $^{13}$C NMR (75 MHz, δ, CDCl$_3$, 298 K): 28.5, 49.4, 52.3, 61.1, 61.2, 79.7, 124.5, 124.6, 125.7, 126.3, 126.5, 126.6, 126.7, 126.8, 138.9, 139.3, 140.8, 142.4, 155.8 ppm. **Step 2:** K$_2$CO$_3$ (345 mg, 2.5 mmol, 5 eq) was added to a solution of mono-Boc-protected diamine (167mg, 0.5 mmol) in 5 ml AcN. After the addition of 310 µl (5 mmol, 10 eq) methyl

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$^6$ M. E. Fox, A. Gerlach, I. C. Lennon, G. Meek, C. Praquin, *Synthesis* **2005**, 19, 3196-3198.
iodide the suspension was stirred for 1 d. After evaporation of excess methyl iodide and AcN, the residue was dissolved in DCM and filtered to give Boc-protected ammonium intermediate as an oily residue in quantitative yield. The product was used without further purification.

**Step 3:** A solution of the Boc-protected quaternary ammonium salt (178 mg, 0.35 mmol) and trifluoroacetic acid (270 µL, 10 eq.) in DCM (2 mL) was stirred at r.t. for 6 h. After evaporation to dryness, a mixture of this crude amine, 3-nitro phenylisocyanate (57 mg, 0.35 mmol), and K₂CO₃ (240 mg, 1.75 mmol) in AcN (2 mL) was stirred at r.t. for 18 h. After filtration and evaporation to dryness, the crude product was purified by column chromatography (DCM:MeOH, 40:1 → 10:1) to obtain catalyst 3a as an oily residue (130 mg, 66%). [α]D²⁰ (c = 3.2, MeOH) = +21.4°; ¹H NMR (300 MHz, δ, CD₃OD, 298 K): 3.08 (s, 9H), 3.68-3.77 (m, 1H), 4.43-5.2 (m, 1H), 4.60 (s, 1H), 5.17 (s, 1H), 7.28-7.59 (m, 8H), 7.61-7.64 (m, 2H), 7.82-7.88 (m, 1H), 8.52 (s, 1H) ppm; ¹³C NMR (75 MHz, δ, CD₃OD, 298 K): 45.6, 51.7 (2x), 53.4, 51.7, 54.1, 114.0, 114.0, 125.2, 125.9, 126.4, 127.0, 127.5, 128.6, 128.8, 128.9, 128.9, 130.9, 138.8, 140.7, 141.3, 142.0, 150.1, 156.0 ppm; IR (film): ν = 3018, 2970, 2934, 1676, 1458, 1420, 1348, 1231, 1155, 951, 932, 880, 764 cm⁻¹; HRMS (ESI) m/z calcd for C₂₆H₂₇N₄O₃⁺: 443.2078 [M⁺], found: 443.2083.

**Synthesis of Tartaric Acid-Based Catalysts 4:**

![Synthesis of Tartaric Acid-Based Catalysts 4](image)

**Syntheses of 16a: Step 1:** A solution of 14 (1.43 g, 8.9 mmol) (prepared according to literature⁷) in DCM (38 mL) was cooled to 0 °C. A solution of allylchloroformate (385 µL, 0.4 eq.) in DCM (10 mL) was added dropwise over 2 h. The mixture was stirred for further 16 h on an ice bath. After extraction with EtOAc/Na₂CO₃ (sat.) the organic layer was washed with brine, dried over Na₂SO₄ and evaporated to dryness to give a 2:1 mixture of 15 and the di-Alloc-protected amine which was used directly for the next step. **Step 2:** A mixture of crude

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⁷ a) T. Shibuguchi, Y. Fukuta, Y. Akachi, A. Sekine, T. Ohshima, M. Shibasaki, Tetrahedron Lett. 2002, 43, 9539-9543; b) T. Ohshima, V. Granadesikan, T. Shibuguchi, Y. Fukuta, T. Nemoto, M. Shibasaki, J. Am. Chem. Soc. 2003, 125, 11206-11207; c) T. Ohshima, T. Shibuguchi, Y. Fukuta, M. Shibasaki, Tetrahedron 2004, 60, 7743-7754.
15, K₂CO₃ (744 mg, 5.4 mmol), and 1.2 ml methyl iodide in AcN (12 mL) was stirred at reflux for 2 d. Excess methyl iodide was removed under reduced pressure and the product was purified by column chromatography (silica gel, DCM:MeOH, 40:1 → 10:1) to obtain compound 16a as an oily residue (840 mg, 23% over 2 steps). [α]ₑ²³ (c = 0.5, DCM) = +9.8°; ¹H NMR (300 MHz, δ, CDCl₃, 298 K): 1.28 (s, 3H), 1.31 (s, 3H), 3.39 (s, 9H), 3.39-3.46 (m, 2H), 3.60-3.73 (m, 1H), 3.77-3.86 (m, 1H), 3.95-4.04 (m, 1H), 4.15-4.26 (m, 1H), 4.42 (d, 2H, J = 5.2 Hz), 5.05-5.11 (m, 1H), 5.14-5.24 (m, 1H), 5.70-5.85 (m, 1H), 5.88 (t, 1H, J = 6.2 Hz) ppm; ¹³C NMR (75 MHz, δ, CDCl₃, 298 K): 27.0, 27.1, 40.8, 55.0, 65.6, 67.7, 72.3, 78.0, 110.9, 117.6, 132.8, 156.9 ppm; IR (film): ν = 3434, 3283, 2986, 2936, 1707, 1526, 1476, 1375, 1248, 1167, 1094, 991, 920, 845 cm⁻¹; HRMS (ESI) m/z calcd for C₁₄H₂₇N₂O₄⁺: 287.1965 [M⁺], found: 287.1972.

**Syntheses of 16b:**

**Step 1:** A solution of 14 (300 mg, 1.87 mmol) (prepared according to literature⁷) in DCM (8 mL) was cooled to 0 °C. A solution of allylchloroformate (80 µL, 0.4 eq.) in DCM (2 mL) was added dropwise over 2 h. The mixture was stirred for further 16 h on an ice bath. After extraction with EtOAc/Na₂CO₃ (sat.) the organic layer was washed with brine, dried over Na₂SO₄ and evaporated to dryness to give a 2:1 mixture of 15 and the di-Alloc-protected amine which was used directly for the next step.

**Step 2:** Benzaldehyde (122 µL, 1.2 mmol) was added to a solution of crude 15 in THF:MeOH = 1:1 (5 mL) and the solution was stirred at r.t. for 2 h. After the addition of NaBH₄ (68 mg) stirring was continued for another 16 h at r.t. The reaction was quenched by addition of H₂O and extracted with H₂O/EtOAc. The organic phase was washed with brine, dried over Na₂SO₄, and evaporated to dryness to obtain the crude product which was directly used without any purification.

**Step 3:** A mixture of the crude sec-amine and K₂CO₃ (138 mg, 1 mmol) in 2 ml methyl iodide was stirred at reflux for 3 d. Excess methyl iodide was removed under reduced pressure and the product was purified by column chromatography (silica gel, DCM:MeOH, 40:1 → 10:1) to obtain compound 16b as an oily residue (101 mg, 11% over 3 steps). [α]ₑ²³ (c = 0.85, DCM) = +2.0°; ¹H NMR (300 MHz, δ, CDCl₃, 298 K): 1.40 (s, 3H), 1.42 (s, 3H), 3.36 (s, 6H), 3.40-3.52 (m, 1H), 3.55-3.68 (m, 2H), 3.81-3.92 (m, 1H), 4.20 (d, 1H, J = 13.5 Hz), 4.39 (t, 1H, J = 9.0 Hz), 4.49 (d, 2H, J = 5.0 Hz), 4.93 (d, 1H, J = 12.5 Hz), 5.08 (d, 1H, J = 12.5 Hz), 5.15 (dd, 1H, J₁ = 10.1 Hz, J₂ = 1.2 Hz), 5.26 (dd, 1H, J₁ = 17.5 Hz, J₂ = 1.2 Hz), 5.78-5.92 (m, 1H), 6.00 (t, 1H, J = 6.4 Hz), 7.40-7.50 (m, 3H), 7.62-7.70 (m, 2H) ppm; ¹³C NMR (75 MHz, δ, CDCl₃, 298 K): 27.1, 40.8, 50.7, 51.9, 64.7, 65.7, 69.1, 72.7, 78.3, 111.0, 117.6, 126.9,
129.3, 130.9, 132.8, 133.4, 157.0 ppm; IR (film): $\tilde{\nu}$ = 3428, 2986, 2938, 1707, 1649, 1528, 1477, 1456, 1385, 1254, 1167, 1094, 993, 922 cm$^{-1}$; HRMS (ESI) $m/z$ calcd for C$_{20}$H$_{31}$N$_2$O$_4$+: 363.2278 [M$^+$], found: 363.2288.

**Syntheses of 16c:** 
**Step 1:** A solution of 14 (210 mg, 1.3 mmol) (prepared according to literature$^7$) in DCM (5 mL) was cooled to 0 °C. A solution of allylchloroformate (55 µL, 0.4 eq.) in DCM (1 mL) was added dropwise over 2 h. The mixture was stirred for further 16 h on an ice bath. After extraction with EtOAc/Na$_2$CO$_3$ (sat.) the organic layer was washed with brine, dried over Na$_2$SO$_4$ and evaporated to dryness to give a 2:1 mixture of 15 and the di-Alloc-protected amine which was used directly for the next step. 
**Step 2:** Benzylbromide (105 µL, 0.88 mmol) was added to a mixture of crude 15 and K$_2$CO$_3$ (63 mg, 0.45 mmol) in AcN (3 mL) and the solution was stirred at reflux for 24 h. After filtration and evaporation to dryness MeI (2 mL) and K$_2$CO$_3$ (63 mg, 0.45 mmol) were added and the mixture was stirred at reflux for 2 d. Excess methyl iodide was removed under reduced pressure and the product was purified by column chromatography (silica gel, DCM:MeOH, 40:1 → 10:1) to obtain compound 16c as an oily residue (146 mg, 22% overall). [$\alpha$]$^\circ_23$ (c = 0.45, DCM) = -23.3°;

$^1$H NMR (300 MHz, $\delta$, CDCl$_3$, 298 K): 1.41 (s, 6H), 3.09 (s, 3H), 3.32-3.60 (m, 3H), 3.81-3.90 (m, 1H), 4.22 (d, 1H, $J = 13.4$ Hz), 4.35-4.41 (m, 2H), 4.42-4.56 (m, 1H), 4.60 (d, 1H, $J = 12.3$ Hz), 4.75 (d, 1H, $J = 12.4$ Hz), 5.05-5.14 (m, 2H), 5.23 (d, 1H, $J = 17.4$ Hz), 5.42 (d, 1H, $J = 12.4$ Hz), 5.72-5.88 (m, 1H), 6.11 (t, 1H, $J = 5.9$ Hz), 7.35-7.50 (m, 6H), 7.55-7.71 (m, 4H) ppm; $^{13}$C NMR (75 MHz, $\delta$, CDCl$_3$, 298 K): 27.1, 27.2, 41.0, 47.7, 61.3, 65.5, 65.6, 66.5, 72.8, 78.4, 111.0, 117.5, 126.7, 126.9, 129.3, 129.4, 130.9, 132.7, 133.4, 133.5, 156.9 ppm; IR (film): $\tilde{\nu}$ = 3275, 3032, 2985, 2935, 1707, 1522, 1508, 1456, 1373, 1236, 1217, 1159, 1086, 991, 926, 785, 754, 725 cm$^{-1}$; HRMS (ESI) $m/z$ calcd for C$_{26}$H$_{35}$N$_2$O$_4$+: 439.2591 [M$^+$], found: 439.2594.

**General Syntheses of Catalysts 4a – 4c:** 
**Step 1:** A solution of the quaternary ammonium salt 16, Pd(PPh$_3$)$_4$ (5 mol%), NaBH$_4$ (3 eq.) in DCM:MeOH = 1:1 was stirred at r.t. for 2 h. After filtration and evaporation to dryness, the crude amine was directly subjected to the final coupling step. 
**Step 2:** A mixture of the amine, R$^2$NCX (1.5 eq.), and K$_2$CO$_3$ (3 eq.) in DCM (20 mL / mmol amine) was stirred at r.t. for 18 h. After filtration and evaporation to dryness, the crude product was purified by column chromatography (DCM:MeOH, 40:1 → 10:1) to obtain catalysts 4 in the reported yields.
**Compound 4a.** Obtained in 51% (2 steps, 1 mmol scale) as a slightly yellow oil. $\left[\alpha\right]_D^{23} (c = 0.8, \text{DCM}) = +15.4^\circ$; $^1$H NMR (300 MHz, $\delta$, CDCl$_3$, 298 K): 1.35 (s, 3H), 1.38 (s, 3H), 3.28 (s, 9H), 3.32-3.48 (m, 2H), 3.68-3.79 (m, 1H), 3.81-3.93 (m, 1H), 4.25-4.35 (m, 1H), 4.45 (d, 1H, $J = 13.9$ Hz), 6.43 (t, 1H, $J = 7.5$ Hz), 6.90 (t, 1H, $J = 7.4$ Hz), 7.17 (t, 2H, $J = 8.1$ Hz), 7.46 (d, 2H, $J = 7.8$ Hz), 8.30 (s, 1H) ppm; $^{13}$C NMR (75 MHz, $\delta$, CDCl$_3$, 298 K): 27.0, 27.1, 41.1, 55.1, 68.7, 74.4, 79.9, 111.5, 118.9, 122.5, 128.8, 139.4, 156.0 ppm; IR (film): $\tilde{\nu}$ = 3414, 2988, 2928, 1674, 1599, 1551, 1499, 1441, 1385, 1314, 1238, 1170, 1105, 1084, 920 cm$^{-1}$; HRMS (ESI): $m/z$ calcd for C$_{17}$H$_{28}$N$_3$O$_3$ $^+$: 322.2131 [M$^+$]; found: 322.2132.

**Compound 4b.** Obtained in 69% (2 steps, 0.3 mmol scale) as a yellowish oil. $\left[\alpha\right]_D^{23} (c = 1.35, \text{DCM}) = +10.7^\circ$; (300 MHz, $\delta$, CDCl$_3$, 298 K): 1.41 (s, 3H), 1.44 (s, 3H), 3.20 (s, 3H), 3.28 (s, 3H), 3.28-3.48 (m, 2H), 3.88-4.02 (m, 2H), 4.45-4.53 (m, 1H), 4.62-4.70 (m, 1H), 4.71 (d, 1H, $J = 12.3$ Hz), 4.94 (d, 1H, $J = 12.3$ Hz), 6.78 (t, 1H, $J = 6.4$ Hz), 7.28-7.43 (m, 3H), 7.44-7.54 (m, 3H), 7.70-7.78 (m, 2H), 8.66 (t, 1H, $J = 1.9$ Hz), 8.93 (s, 1H) ppm; $^{13}$C NMR (75 MHz, $\delta$, CDCl$_3$, 298 K): 27.0, 27.1, 41.3, 50.6, 51.5, 67.1, 69.6, 74.6, 77.5, 111.5, 112.8, 116.8, 124.0, 126.0, 129.3, 129.5, 131.4, 133.0, 140.8, 148.6, 155.5 ppm; IR (film): $\tilde{\nu}$ = 3264, 3065, 2985, 2935, 2874, 1690, 1596, 1526, 1481, 1350, 1223, 1080, 999, 783 cm$^{-1}$; HRMS (ESI): $m/z$ calcd for C$_{23}$H$_{31}$N$_4$O$_5$ $^+$: 443.2289 [M$^+$]; found: 443.2297.

**Compound 4c.** Obtained in 40% (2 steps, 0.5 mmol scale) as a yellowish oil. $\left[\alpha\right]_D^{23} (c = 0.9, \text{DCM}) = -18.8^\circ$; $^1$H NMR (300 MHz, $\delta$, CDCl$_3$, 298 K): 1.35 (s, 3H), 1.43 (s, 3H), 2.93 (s, 3H), 2.97-3.13 (m, 1H), 3.20-3.35 (m, 1H), 3.82-3.97 (m, 2H), 4.03 (d, 1H, $J = 12.4$ Hz), 4.48-4.68 (m, 2H), 4.61 (d, 1H, $J = 12.4$ Hz), 5.08 (d, 1H, $J = 12.4$ Hz), 5.53 (d, 1H, $J = 12.4$ Hz), 6.91 (t, 1H, $J = 6.0$ Hz), 7.20-7.75 (m, 14H), 8.63 (t, 1H, $J = 2.1$ Hz), 8.94 (s, 1H) ppm; $^{13}$C NMR (75 MHz, $\delta$, CDCl$_3$, 298 K): 26.9, 27.1, 41.2, 47.7, 63.6, 65.3, 66.4, 74.3, 77.7, 111.4, 112.8, 116.7, 123.9, 126.2, 128.5, 128.7, 129.2, 129.5, 129.6, 131.3, 132.1, 132.2, 133.2, 140.8, 148.6, 155.4 ppm; IR (film): $\tilde{\nu}$ = 3281, 3065, 2986, 2934, 1697, 1595, 1541, 1526, 1350, 1223, 1166, 1093, 785, 754 cm$^{-1}$; HRMS (ESI): $m/z$ calcd for C$_{29}$H$_{35}$N$_4$O$_5$ $^+$: 519.2602 [M$^+$]; found: 519.2610.
3. Asymmetric α-Fluorination:

**General procedure for the α-fluorination of β-ketoesters:** Reactions were usually carried out using 0.1 – 0.5 mmol of the ketoester. Aqueous K$_3$PO$_4$ (2M, 2 eq.) was added to a mixture of ketoester and catalyst 10 (2 mol%) in m-xylene (20 mL / mmol ketoester) and the mixture was cooled to -10 °C. NFSI was added portion-wise over 2 h and the mixture was heavily stirred for another 10 h at -10 °C (Ar-atmosphere). The reaction was quenched by addition of NH$_4$Cl(sat) and the mixture was extracted with CH$_2$Cl$_2$. After drying over Na$_2$SO$_4$, and evaporation to dryness, the product was purified by silica gel column chromatography (heptanes:EtOAc = 20:1) to give the products in the reported yields.

(R)-19a. Obtained in 95% yield with e.r. = 92 : 8 upon reacting 17a (112 mg, 0.48 mmol) with NFSI (18). Analytical data are in accordance with those reported in literature.$^8$ [α]$_D^{23}$ (c = 0.65, CHCl$_3$) = +3.2°; $^1$H NMR (700 MHz, δ, CDCl$_3$, 298 K): 1.41 (s, 9H), 3.38 (dd, $J$ = 22.8, 17.6 Hz, 1H), 3.71 (dd, $J$ = 17.6, 10.9 Hz, 1H), 7.44 (t, $J$ = 6.8 Hz, 1H), 7.48 (d, $J$ = 7.4 Hz, 1H), 7.67 (t, $J$ = 7.6 Hz, 1H), 7.81 (d, $J$ = 7.7 Hz, 1H) ppm; $^{13}$C NMR (175 MHz, δ, CDCl$_3$, 298 K): 27.9, 38.4 (d, $J$ = 24.1 Hz), 84.2, 94.5 (d, $J$ = 202.4 Hz), 125.5, 126.6, 128.6, 133.7, 136.6, 151.1 (d, $J$ = 3.5 Hz), 166.4 (d, $J$ = 27.9 Hz), 195.9 (d, $J$ = 17.9 Hz) ppm; $^{19}$F NMR (282 MHz, δ, CDCl$_3$, 298 K): -164.0 (dd, $J$ = 22.8, 10.9 Hz) ppm; IR (film): $\tilde{\nu}$ = 3003, 2981, 2936, 1753, 1717, 1607, 1466, 1370, 1296, 1209, 1152, 1074, 924, 835, 746, 723 cm$^{-1}$; HRMS (ESI): $m/z$ calcd for C$_{14}$H$_{15}$FO$_3$: 268.13435 [M+NH$_4$]$^+$; found: 268.13488. The enantioselectivity was determined by HPLC (Chiralpak AD-H, eluent: hexane:i-PrOH = 200:1, 0.75 mL/min, 10°C, retention times: (S)-enantiomer 25.0 min, (R)-enantiomer 32.2 min).

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8) a) D. Y. Kim, E. J. Park, Org. Lett. 2002, 4, 545-547; b) X. Wang, Q. Lan, S. Shirakawa, K. Maruoka, Chem. Commun. 2010, 46, 321-323; c) E.-M. Tanzer, W. B. Schweizer, M.-O. Ebert, R. Gilmour, Chem. Eur. J. 2012, 18, 2006-2013; d) J. Luo, W. Wu, L.-W. Xu, Y. Meng, Y. Lu, Tetrahedron Lett. 2013, 54, 2623-2626.
19b. Obtained in 92% yield with e.r. = 85 : 15 upon reacting 17b (106 mg, 0.56 mmol) with NFSI (18). The product can recrystallized from heptanes/EtOAc to obtain almost enantiopure material (e.r. = 99 : 1). Analytical data are in accordance with those reported in literature.8 [α]D 23 (c = 0.2, CH2Cl2) = -27.0°; 1H NMR (700 MHz, δ, CDCl3, 298 K): 3.44 (dd, J = 23.3, 17.5 Hz, 1H), 3.80 (dd, J = 17.5, 11.7 Hz, 1H), 3.82 (s, 3H), 7.42-7.52 (m, 2H), 7.71 (t, J = 7.7 Hz, 1H), 7.85 (d, J = 7.7 Hz, 1H) ppm; 13C NMR (175 MHz, δ, CDCl3, 298 K): 38.5 (d, J = 23.0 Hz), 53.4, 94.7 (d, J = 201.9 Hz), 125.8, 126.7, 128.8, 133.3, 136.9, 150.9 (d, J = 3.8 Hz), 167.8 (d, J = 27.7 Hz), 195.2 (d, J = 18.2 Hz) ppm; 19F NMR (282 MHz, δ, CDCl3, 298 K): -164.5 (dd, J = 23.3, 11.7 Hz) ppm; IR (film): = 2961, 2918, 2849, 1769, 1721, 1611, 1589, 1477, 1422, 1267, 1198, 1180, 1074, 1051, 924, 812, 752, 716 cm⁻¹; HRMS (ESI): m/z calcd for C11H9FO3: 209.0608 [M+H]+; found: 209.0613. The enantioselectivity was determined by HPLC (Chiralcel OD-H, eluent: hexane:i-PrOH = 95:5, 0.75 mL/min, 10°C, retention times: major 28.8 min, minor 36.5 min).

19c. Obtained in 86% yield with e.r. = 85 : 15 upon reacting 17c (105 mg, 0.4 mmol) with NFSI (18). Analytical data are in accordance with those reported in literature.8 [α]D 23 (c = 1.07, CH2Cl2) = -8.1°; 1H NMR (300 MHz, δ, CDCl3, 298 K): 3.35 (dd, J = 22.6, 17.7 Hz, 1H), 3.69 (dd, J = 17.7, 11.8 Hz, 1H), 5.13 (d, J = 12.2 Hz, 1H), 5.20 (d, J = 12.2 Hz, 1H), 7.10-7.28 (m, 5H), 7.37-7.44 (m, 2H), 7.61 (t, J = 7.3 Hz, 1H), 7.75 (d, J = 7.3 Hz, 1H) ppm; 19F NMR (282 MHz, δ, CDCl3, 298 K): -164.5 (dd, J = 22.6, 11.8 Hz) ppm; IR (film): = 3096, 3064, 3037, 1761, 1720, 1607, 1585, 1450, 1377, 1294, 1263, 1213, 1184, 1078, 926, 800, 739 cm⁻¹; HRMS (ESI): m/z calcd for C17H13FO3: 302.11870 [M+NH4]+; found: 302.11951. The enantioselectivity was determined by HPLC (Chiralpak AD-H, eluent: hexane:i-PrOH = 90:10, 0.75 mL/min, 10°C, retention times: minor 22.7 min, major 24.4 min).

19d. Obtained in 52% yield with e.r. = 89 : 11 upon reacting 17e (21 mg, 0.07 mmol) with NFSI (18). The compound tends to hydrolyse and decarboxylate during column chromatography. [α]D 23 (c = 0.36, CH2Cl2) = +10.8°; 1H NMR (300 MHz, δ, CDCl3, 298 K): 1.79 (s, 3H), 1.80 (s, 3H), 3.45 (dd, J = 22.6, 17.5 Hz, 1H), 3.78 (dd, J = 17.5, 10.3 Hz, 1H), 7.19-7.35 (m, 5H), 7.48-7.55 (m, 2H), 7.72 (t, J = 7.6 Hz, 1H), 7.88 (d, J = 7.5 Hz, 1H) ppm; 13C NMR (75 MHz, δ, CDCl3, 298 K): 28.1, 28.3, 38.2 (d, J = 22.6 Hz), 85.2, 94.6 (d, J = 204.8 Hz), 124.1, 125.6, 126.5 (d, J = 1.3 Hz), 127.4, 128.4, 128.6, 129.5, 136.5, 144.5, 150.8 (d, J = 4.0 Hz), 165.6 (d, J = 26.5 Hz),
195.7 (d, $J = 17.6$ Hz) ppm; $^{19}$F NMR (282 MHz, $\delta$, CDCl$_3$, 298 K): -164.6 (dd, $J = 22.6$, 10.3 Hz) ppm; IR (film): $\tilde{\nu} = 2986, 1763, 1724, 1607, 1449, 1300, 1273, 1196, 1138, 1072, 924, 789, 764$ cm$^{-1}$; HRMS (ESI): $m/z$ calcd for C$_{19}$H$_{17}$FO$_3$: 330.15000 [M+NH$_4$]$^+$; found: 330.15058. The enantioselectivity was determined by HPLC (Chiralpak AD-H, eluent: hexane:i-PrOH = 90:10, 0.75 mL/min, 10°C, retention times: major 14.2 min, minor 15.8 min).

19e. Obtained in 97% yield with e.r. = 93 : 7 upon reacting 17e (99 mg, 0.32 mmol) with NFSI (18). Analytical data are in accordance with those reported in literature. 8 $[\alpha]_D^{23}$ (c = 0.92, CH$_2$Cl$_2$) = -0.8°; $^1$H NMR (300 MHz, $\delta$, CDCl$_3$, 298 K): 1.54 (s, 6H), 1.96 (s, 6H), 2.06 (s, 3H), 3.31 (dd, $J = 22.8, 17.5$ Hz, 1H), 3.65 (dd, $J = 17.5, 10.1$ Hz, 1H), 7.35-7.46 (m, 2H), 7.60 (t, $J = 7.2$ Hz, 1H), 7.75 (d, $J = 7.2$ Hz, 1H) ppm; $^{13}$C NMR (75 MHz, $\delta$, CDCl$_3$, 298 K): 30.6, 35.8, 38.2 (d, $J = 24.0$ Hz), 40.9, 84.0, 94.1 (d, $J = 200.8$ Hz), 125.2, 126.4, 128.2, 133.5, 136.1, 150.8 (d, $J = 4.0$ Hz), 165.6 (d, $J = 27.5$ Hz), 195.6 (d, $J = 18.0$ Hz) ppm; $^{19}$F NMR (282 MHz, $\delta$, CDCl$_3$, 298 K): -164.1 (dd, $J = 22.8$, 10.1 Hz) ppm; IR (film): $\tilde{\nu} = 2910, 2853, 1759, 1724, 1607, 1458, 1287, 1194, 1072, 922, 754$ cm$^{-1}$; HRMS (ESI): $m/z$ calcd for C$_{20}$H$_{21}$FO$_3$: 346.18285 [M+NH$_4$]$^+$; found: 346.18330. The enantioselectivity was determined by HPLC (Chiralcel OD-R, eluent: H$_2$O:AcN = 55:45, 0.8 mL/min, 10 °C, retention times: major 90.6 min, minor 97.0 min).

23a. Obtained in 73% yield with e.r. = 88 : 12 upon reacting 22a (21 mg, 0.07 mmol) with NFSI (18). Analytical data are in full accordance with those reported in literature. 9 $[\alpha]_D^{23}$ (c = 0.28, CH$_2$Cl$_2$) = -27.5°; $^1$H NMR (300 MHz, $\delta$, CDCl$_3$, 298 K): 1.46 (s, 9H), 3.40 (dd, $J = 22.5, 17.4$ Hz, 1H), 3.73 (dd, $J = 17.4$, 11.3 Hz, 1H), 7.58-7.66 (m, 1H), 7.68-7.74 (m, 2H) ppm; $^{13}$C NMR (75 MHz, $\delta$, CDCl$_3$, 298 K): 27.8, 37.9 (d, $J = 24.8$ Hz), 84.5, 94.3 (d, $J = 201.6$ Hz), 126.5, 129.8 (d, $J = 1.1$ Hz), 132.1, 132.2, 132.4 (d, $J = 1.3$ Hz), 152.3 (d, $J = 3.8$ Hz), 165.7 (d, $J = 29.8$ Hz), 194.7 (d, $J = 18.6$ Hz) ppm; $^{19}$F NMR (282 MHz, $\delta$, CDCl$_3$, 298 K): -163.4 (dd, $J = 22.5$, 11.3 Hz) ppm; IR (film): $\tilde{\nu} = 3069, 2972, 2928, 1759, 1724, 1597, 1576, 1368, 1288, 1269, 1213, 1150, 1084, 1057, 932, 912, 845, 835, 799, 785$ cm$^{-1}$; HRMS (ESI): $m/z$ calcd for C$_{14}$H$_{14}$BrFO$_3$: 346.04486 [M+NH$_4$]$^+$; found: 346.04519. The enantioselectivity was determined by HPLC (Chiralcel OD-H, eluent: hexane:i-PrOH = 95:5, 0.75 mL/min, 10°C, retention times: major 14.2 min, minor 15.8 min).

9) Q-H. Deng, H. Wadepohl, L. H. Gade, Chem. Eur. J. 2011, 17, 14922-14928.
23b. Obtained in 85% yield with e.r. = 89 : 11 upon reacting 22b (25 mg, 0.07 mmol) with NFSI (18). [α]D\textsuperscript{23} (c = 0.51, CH\textsubscript{2}Cl\textsubscript{2}) = -38.8°; \textsuperscript{1}H NMR (700 MHz, δ, CDCl\textsubscript{3}, 298 K): 1.62 (s, 6H), 2.04 (s, 6H), 2.15 (s, 3H), 3.37 (dd, J = 22.5, 17.2 Hz, 1H), 3.70 (dd, J = 17.2, 10.7 Hz, 1H), 7.59 (d, J = 8.1 Hz, 1H), 7.67 (s, 1H), 7.68 (d, J = 8.1 Hz, 1H), ppm; \textsuperscript{13}C NMR (175 MHz, δ, CDCl\textsubscript{3}, 298 K): 31.0, 36.0, 38.1 (d, J = 19.0 Hz) ppm; \textsuperscript{19}F NMR (282 MHz, δ, CDCl\textsubscript{3}, 298 K): -163.6 (dd, J = 22.5, 10.7 Hz) ppm; IR (film): \textnu = 2913, 2849, 1757, 1726, 1595, 1415, 1265, 1196, 1078, 1051, 914, 833 cm\textsuperscript{-1}; HRMS (ESI): m/z calcd for C\textsubscript{20}H\textsubscript{20}BrFO\textsubscript{3}: 424.09181 [M+NH\textsubscript{4}]\textsuperscript{+}; found: 424.09321. The enantioselectivity was determined by HPLC (Chiralpak AD-H, eluent: hexane:i-PrOH = 90:10, 0.75 mL/min, 10°C, retention times: minor 16.3 min, major 22.8 min).

25a. Obtained in 75% yield with e.r. = 91 : 9 upon reacting 24a (25 mg, 0.07 mmol) with NFSI (18). Analytical data are in full accordance with those reported in literature.\textsuperscript{8d} [α]D\textsuperscript{23} (c = 0.3, CH\textsubscript{2}Cl\textsubscript{2}) = -1.2°; \textsuperscript{1}H NMR (300 MHz, δ, CDCl\textsubscript{3}, 298 K): 1.46 (s, 9H), 3.41 (dd, J = 22.5, 17.9 Hz, 1H), 3.74 (dd, J = 17.9, 10.7 Hz, 1H), 7.11-7.25 (m, 2H), 7.82-7.92 (m, 1H) ppm; \textsuperscript{13}C NMR (75 MHz, δ, CDCl\textsubscript{3}, 298 K): 27.8, 38.2 (d, J = 24.7 Hz), 84.4, 94.4 (d, J = 202.1 Hz), 113.3 (d, J = 25.9 Hz), 116.9 (d, J = 23.3 Hz), 128.0 (d, J = 11.0 Hz), 130.0, 153.9 (dd, J = 10.4, 4.1 Hz), 165.9 (d, J = 26.4 Hz), 167.8 (d, J = 257.7 Hz), 193.8 (d, J = 17.6 Hz) ppm; \textsuperscript{19}F NMR (282 MHz, δ, CDCl\textsubscript{3}, 298 K): -98.8 (m), -163.2 (dd, J = 22.5, 10.7 Hz) ppm; IR (film): \textnu = 2982, 2938, 1763, 1734, 1616, 1595, 1483, 1371, 1259, 1156, 1078, 943, 839 cm\textsuperscript{-1}; HRMS (ESI): m/z calcd for C\textsubscript{14}H\textsubscript{14}F\textsubscript{2}O\textsubscript{3}: 286.12493 [M+NH\textsubscript{4}]\textsuperscript{+}; found: 286.12564. The enantioselectivity was determined by HPLC (Chiralpak AD-H, eluent: hexane:i-ProOH = 95:5, 0.75 mL/min, 10°C, retention times: minor 16.3 min, major 13.2 min).

25b. Obtained in 86% yield with e.r. = 92 : 8 upon reacting 24b (25 mg, 0.07 mmol) with NFSI (18). [α]D\textsuperscript{23} (c = 0.32, CH\textsubscript{2}Cl\textsubscript{2}) = -0.9°; \textsuperscript{1}H NMR (700 MHz, δ, CDCl\textsubscript{3}, 298 K): 1.62 (s, 6H), 2.05 (s, 6H), 2.15 (s, 3H), 3.38 (dd, J = 22.2, 17.8 Hz, 1H), 3.71 (dd, J = 17.8, 10.6 Hz, 1H), 7.10-7.20 (m, 2H), 7.80-7.88 (m, 1H) ppm; \textsuperscript{13}C NMR (175 MHz, δ, CDCl\textsubscript{3}, 298 K): 31.0, 36.0, 38.4 (d, J =
24.4 Hz), 41.2, 84.6, 94.3 (d, \( J = 204.8 \) Hz), 113.5 (d, \( J = 22.8 \) Hz), 117.0 (d, \( J = 23.8 \) Hz), 128.0 (d, \( J = 10.4 \) Hz), 130.2, 154.0 (dd, \( J = 10.4, 4.0 \) Hz), 165.5 (d, \( J = 27.8 \) Hz), 168.0 (d, \( J = 259.7 \) Hz), 194.0 (d, \( J = 18.3 \) Hz) ppm; \(^{19}\)F NMR (282 MHz, \( \delta \), CDCl\(_3\), 298 K): -98.8 (m), -163.3 (dd, \( J = 22.2, 10.6 \) Hz) ppm; IR (film): \( \tilde{\nu} = 2913, 2855, 1761, 1732, 1616, 1595, 1483, 1458, 1373, 1258, 1198, 1049, 943 \) cm\(^{-1}\); HRMS (ESI): \( m/z \) calcd for C\(_{20}\)H\(_{20}\)F\(_2\)O\(_3\): 364.17188 [M+NH\(_4\)]\(^+\); found: 364.17256. The enantioselectivity was determined by HPLC (Chiralpak AD-H, eluent: hexane:i-PrOH = 90:10, 0.75 mL/min, 10°C, retention times: minor 16.3 min, major 21.2 min).

27a. Obtained in 79% yield with e.r. = 85 : 15 upon reacting 26a (20 mg, 0.07 mmol) with NFSI (18). \([\alpha]_D^{23}\) (c = 0.37, CH\(_2\)Cl\(_2\)) = +9.2\(^\circ\); \(^1\)H NMR (300 MHz, \( \delta \), CDCl\(_3\), 298 K): 1.37 (s, 9H), 1.47 (s, 9H), 3.36 (dd, \( J = 23.0, 17.5 \) Hz, 1H), 3.71 (dd, \( J = 17.5, 11.3 \) Hz, 1H), 7.43 (d, \( J = 7.9 \) Hz, 1H), 7.77 (dd, \( J = 7.9, 1.9 \) Hz, 1H), 7.85 (d, \( J = 1.9 \) Hz, 1H) ppm; \(^{13}\)C NMR (75 MHz, \( \delta \), CDCl\(_3\), 298 K): 27.9, 31.2, 34.9, 38.0 (d, \( J = 3.8 \) Hz), 84.1, 94.7 (d, \( J = 200.1 \) Hz), 121.7, 126.0, 133.4, 148.6 (d, \( J = 3.8 \) Hz), 152.1, 166.5 (d, \( J = 27.5 \) Hz), 196.1 (d, \( J = 16.6 \) Hz) ppm; \(^{19}\)F NMR (282 MHz, \( \delta \), CDCl\(_3\), 298 K): -163.3 (dd, \( J = 22.2, 11.3 \) Hz) ppm; IR (film): \( \tilde{\nu} = 2965, 2938, 2870, 1761, 1719, 1616, 1495, 1369, 1287, 1256, 1213, 1194, 1155, 1074, 957, 839, 760 \) cm\(^{-1}\); HRMS (ESI): \( m/z \) calcd for C\(_{18}\)H\(_{23}\)FO\(_3\): 324.19695 [M+NH\(_4\)]\(^+\); found: 324.19740. The enantioselectivity was determined by HPLC (Chiralpak AD-H, eluent: hexane:i-PrOH = 95:5, 0.75 mL/min, 10°C, retention times: major 7.4 min, minor 7.9 min).

27b. Obtained in 96% yield with e.r. = 86 : 14 upon reacting 26b (27 mg, 0.07 mmol) with NFSI (18). \([\alpha]_D^{23}\) (c = 0.56, CH\(_2\)Cl\(_2\)) = +11.8\(^\circ\); \(^1\)H NMR (700 MHz, \( \delta \), CDCl\(_3\), 298 K): 1.34 (s, 9H), 1.62 (s, 6H), 2.07 (s, 6H), 2.15 (s, 3H), 3.33 (dd, \( J = 22.2, 17.0 \) Hz, 1H), 3.68 (dd, \( J = 17.0, 11.1 \) Hz, 1H), 7.40 (d, \( J = 7.5 \) Hz, 1H), 7.73 (d, \( J = 7.5 \) Hz, 1H), 7.83 (s, 1H) ppm; \(^{13}\)C NMR (175 MHz, \( \delta \), CDCl\(_3\), 298 K): 31.0, 31.3, 35.0, 36.0, 38.1 (d, \( J = 24.0 \) Hz), 41.2, 84.2, 94.8 (d, \( J = 200.9 \) Hz), 121.8, 126.1, 133.6, 134.5, 148.7 (d, \( J = 3.5 \) Hz), 152.2, 166.2 (d, \( J = 27.1 \) Hz), 196.3 (d, \( J = 18.8 \) Hz) ppm; \(^{19}\)F NMR (282 MHz, \( \delta \), CDCl\(_3\), 298 K): -163.3 (dd, \( J = 22.2, 11.1 \) Hz) ppm; IR (film): \( \tilde{\nu} = 2957, 2913, 2855, 1763, 1719, 1541, 1286, 1192, 1074, 1049, 792 \) cm\(^{-1}\); HRMS (ESI): \( m/z \) calcd for C\(_{24}\)H\(_{30}\)FO\(_3\): 402.24390 [M+NH\(_4\)]\(^+\); found: 402.24465. The enantioselectivity was determined by HPLC (Chiralpak AD-H, eluent: hexane:i-PrOH = 90:10, 0.75 mL/min, 10°C, retention times: minor 10.4 min, major 11.4 min).
29. Obtained in 73% yield with e.r. = 87 : 13 upon reacting 28 (97 mg, 0.4 mmol) with NFSI (18). Analytical data are in full accordance with those reported in literature.\(^{8b}\) \([\alpha]_D^{23}\) (c = 1.03, CH\(_2\)Cl\(_2\)) = +6.4\(^\circ\); \(^1\)H NMR (300 MHz, \(\delta\), CDCl\(_3\), 298 K): 1.21 (s, 9H), 2.33-2.50 (m, 1H), 2.52-2.71 (m, 1H), 2.93-3.18 (m, 2H), 7.20 (d, \(J = 7.3\) Hz, 1H), 7.29 (t, \(J = 7.5\) Hz, 1H), 7.42-7.52 (m, 1H), 8.0 (d, \(J = 7.8\) Hz, 1H) ppm; \(^{19}\)F NMR (282 MHz, \(\delta\), CDCl\(_3\), 298 K): -163.3 (dd, \(J = 19.4, 11.0\) Hz) ppm; IR (film): \(\nu = 2999, 2984, 2967, 2940, 2905, 2874, 2845, 1721, 1699, 1601, 1456, 1373, 1310, 1292, 1221, 1028, 1080, 999, 916, 835, 766, 739\ cm\(^{-1}\); HRMS (ESI): \(m/z\) calcld for C\(_{15}\)H\(_{17}\)FO\(_3\): 282.15000 [M+NH\(_4\)]\(^+\); found: 282.14944. The enantioselectivity was determined by HPLC (Chiralcel OD-H, eluent: hexane:i-PrOH = 200:1, 0.8 mL/min, 10\(^\circ\)C, retention times: major 21.0 min, minor 22.9 min).

31. Obtained in 66% yield with e.r. = 89 : 11 upon reacting 30 (26 mg, 0.14 mmol) with NFSI (18). Analytical data are in accordance with those reported in literature.\(^{8b}\) \([\alpha]_D^{24}\) (c = 0.15, CH\(_2\)Cl\(_2\)) = +44.0\(^\circ\); \(^1\)H NMR (300 MHz, \(\delta\), CDCl\(_3\), 298 K): 1.52 (s, 9H), 2.03-2.20 (m, 2H), 2.20-2.39 (m, 1H), 2.43-2.62 (m, 3H) ppm; \(^13\)C NMR (75 MHz, \(\delta\), CDCl\(_3\), 298 K): 18.0 (d, \(J = 4.0\) Hz), 27.9, 33.9 (d, \(J = 21.0\) Hz), 35.7, 84.1, 94.3 (d, \(J = 199.9\) Hz), 166.4 (d, \(J = 27.3\) Hz), 208.1 (d, \(J = 17.4\) Hz) ppm; \(^{19}\)F NMR (282 MHz, \(\delta\), CDCl\(_3\), 298 K): -162.8 (dd, \(J = 22.0, 16.5\) Hz) ppm; IR (film): \(\nu = 2978, 2938, 2903, 1771, 1751, 1541, 1150\ cm\(^{-1}\); HRMS (ESI): \(m/z\) calcld for C\(_{10}\)H\(_{15}\)FO\(_3\): 220.13435 [M+NH\(_4\)]\(^+\); found: 220.13392. The enantioselectivity was determined by HPLC (Chiralpak AD-H, eluent: hexane:i-PrOH = 95:5, 0.75 mL/min, 10\(^\circ\)C, retention times: minor 8.6 min, major 9.9 min).
4. Copies of NMR Spectra of Key-Intermediates and Most Relevant Catalysts:
Nov-413-12

7d (Ar = α-Np-CH₂⁻)

Nov-413-11

7d (Ar = α-Np-CH₂⁻)
Current Data Parameters

NAME         Nov-121-03
EXPNO                21
PROCNO                1

F2 - Acquisition Parameters
Date_          20120629
Time              21.16
INSTRUM           spect
PROBHD   5 mm PABBO BB-
PULPROG          zgpg30
TD                65536
SOLVENT           CDCl3
NS                 2048
DS                    4
SWH           18028.846 Hz
FIDRES         0.275098 Hz
AQ            1.8175317 sec
RG                 2050
DW               27.733 usec
DE                27.73 usec
TE                298.0 K
D1           2.00000000 sec
D11          0.03000000 sec

======== CHANNEL f1 ========
NUC1                13C
P1                 7.75 usec
PLW1        50.00000000 W
SFO1         75.4752949 MHz

======== CHANNEL f2 ========
CPDPRG[2        waltz16
NUC2                 1H
PCPD2             80.00 usec
PLW2        20.00000000 W
PLW12        0.22000000 W
PLW13        0.13613001 W
SFO2        300.1312005 MHz

F2 - Processing parameters
SI                32768
SF           75.4677490 MHz
WDW                  EM
SSB      0
LB                 1.00 Hz
GB       0
PC                 1.40
5. Copies of NMR Spectra of Selected Known and of the New Fluorination Products:
Nov-546-02

\[ \text{H}_3 \text{C} - \text{C} \text{(F) - CO}_2 \text{Bu} \]

27a

Nov-546-02

\[ \text{H}_3 \text{C} - \text{C} \text{(F) - CO}_2 \text{Bu} \]

27a
6. HPLC-Chromatograms (Chiral Stationary Phase):

3 Nov-531

| No. | Ret.Time (min) | Peak Name | Height (mAU) | Area (mAU*min) | Rel.Area (%) | Amount | Type |
|-----|----------------|-----------|--------------|----------------|--------------|--------|------|
| 1   | 25.02          | n.a.      | 245,853      | 129,777        | 7.82         | n.a.   | BMB* |
| 2   | 32.28          | n.a.      | 950,178      | 1529,542       | 92.18        | n.a.   | BMB* |
| Total|                |           | 1196,031     | 1659,319       | 100.00       | 0.000  |      |
### Sample Information

| Sample Name      | Injection Volume | Vial Number | Channel      | Wavelength | Quantif. Method | Control Program         | Temperature/Column | Recording Time | Flow ml/min | Sample Amount |
|------------------|------------------|-------------|--------------|------------|----------------|-------------------------|-------------------|----------------|--------------|--------------|
| Nov-528          | 10,0             | RA3         | UV_VIS_2     | n.a.       | OD_H           | OD_H_90Min_95_5_flow075| 10                | 30.7.2013 18:52 | 0.750        | 1,0000       |

### Chromatogram

![Chromatogram](chart.png)

### Table

| No. | Ret. Time (min) | Peak Name | Height (mAU) | Area (mAU*min) | Ref. Area (%) | Amount | Type   |
|-----|----------------|-----------|--------------|----------------|---------------|--------|--------|
| 1   | 28.83          | n.a.      | 886,701      | 704,635        | 84,87         | n.a.   | BMB*   |
| 2   | 36.48          | n.a.      | 151,402      | 125,598        | 15,13         | n.a.   | BMB*   |
| Total|                |           | 1038,103     | 830,232        | 100,00        | 0,000  |        |

95 n-Hexan : 5 iso-Prop.
### Nov-528-Krist1

| Sample Name          | Nov-528-Krist1              | Injection Volume: | 10,0 |
|----------------------|----------------------------|-------------------|------|
| Vial Number:         | RA6                         | Channel:          | UV_VIS_2 |
| Sample Type:         | unknown                     | Wavelength:       | n.a. |
| Control Program:     | OD_H_90Min_95_5_flow075     | Bandwidth:        | n.a. |
| Quantif. Method:     | OD_H                       | Temperature/Column: | 10  |
| Recording Time:      | 30.7.2013 21:54             | Flow ml/min:      | 0.750 |
| Run Time (min):      | 50.03                       | Sample Amount:    | 1.0000 |

| No. | Ret.Time | Peak Name | Height | Area  | Ref.Area | Amount | Type |
|-----|----------|-----------|--------|-------|----------|--------|------|
| 1   | 28,83    | n.a.      | 162,579| 116,457| 99,11    | n.a.   | BMB* |
| 2   | 36,18    | n.a.      | 1,363  | 1,043 | 0,89     | n.a.   | BMB* |
| Total|          |           | 163,942| 117,500| 100,00 | 0,000 |

95 n-Hexan : 5 iso-Prop.
Nov-533 verdünnt (90/10)

Sample Name: Nov-533 verdünnt (90/10)  Injection Volume: 10,0
Vial Number: RC2  Channel: UV_VIS_1
Sample Type: unknown  Wavelength: n.a.
Control Program: AD_H_30Min_200_1_flow075  Bandwidth: n.a.
Quantif. Method: AD_H  Dilution Factor: 1,0000
Recording Time: 2.8.2013 14:35  Sample Weight: 1,0000
Run Time (min): 30,00  Sample Amount: 1,0000

| No. | Ret.Time (min) | Peak Name | Height (mAU) | Area (mAU*min) | Ref.Area (%) | Amount | Type |
|-----|---------------|-----------|--------------|----------------|--------------|--------|------|
| 1   | 22,73         | n.a.      | 77,796       | 32,222         | 15,13        | n.a.   | BMB* |
| 2   | 24,35         | n.a.      | 369,983      | 180,743        | 84,87        | n.a.   | BMB* |
| Total: |               |           | 447,778      | 212,964        | 100,00       | 0,000  |

WVL: 220 nm
## 2 Nov-552 gesäułt (90:10)

| Sample Name: | Nov-552 gesäułt (90:10) | Injection Volume: | 10.0 |
|--------------|--------------------------|-------------------|------|
| Vial Number: | RC2                      | Channel:          | UV_VIS_2 |
| Sample Type: | unknown                  | Wavelength:       | n.a. |
| Control Program: | AD_H_30Min_200_1_flow075 | Bandwidth:        | n.a. |
| Quantf. Method: | AD_H                    | Dilution Factor:  | 1.0000 |
| Recording Time: | 20.8.2013 16:07         | Sample Weight:    | 1.0000 |
| Run Time (min): | 30.00                   | Sample Amount:    | 1.0000 |

| No. | Ret.Time | Peak Name | Height | Area | Ref.Area | Amount | Type |
|-----|----------|-----------|--------|------|----------|--------|------|
| 1   | 14,25    | n.a.      | 454,405| 125,980| 88,81    | n.a.   | BM * |
| 2   | 15,79    | n.a.      | 53,275 | 15,880| 11,19    | n.a.   | BMB* |

**Total:** 507,679 141,861 100.00 0.000

![Graph](attachment:image.png)

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21.8.2013 8:09 PM
**3 NOV-532-16-26**

Sample Name: NOV-532-16-26  
Injection Volume: 10,0

Vial Number: RA1  
Channel: UV_VIS_2

Sample Type: unknown  
Wavelength: n.a.

Control Program: OD_R_120Min_55_45_flow08  
Temperature/Column: 10

Quantif. Method: OD_R  
Bandwidth: n.a.

Recording Time: 7.8.2013 13:12  
Flow ml/min: 0.800

Run Time (min): 120,00  
Sample Amount: 1,0000

| No. | Ret.Time | Peak Name | Height | Area | Ref.Area | Amount | Type |
|-----|----------|-----------|--------|------|----------|--------|------|
| 1   | 90.58    | n.a.      | 279.976| 725.099| n.a.     | 93.40  | BM * |
| 2   | 97.03    | n.a.      | 19.186 | 51.208 | n.a.     | 6.60   | MB*  |
| Total|          |           | 299.162| 776.307|          | 100.00 | 0.000 |

H2O
1 Nov-545 (95:5)

| No. | Ret. Time(min) | Peak Name | Height(mAU) | Area(mAU*min) | Ref. Area(%) | Amount | Type |
|-----|----------------|-----------|-------------|---------------|-------------|--------|------|
| 1   | 12.33          | n.a.      | 350,358     | 76,125        | 88.30       | n.a.   | BMB* |
| 2   | 14.33          | n.a.      | 25,539      | 10,090        | 11.70       | n.a.   | BMB* |

Total: 375,898 86,215 100.00 0.000

95 n-Hexan : 5 iso-Prop.
**4 Nov-549 (90:10)**

| Sample Name: | Nov-549 (90:10) | Injection Volume: | 10,0 |
|--------------|----------------|-------------------|------|
| Vial Number: | RC4            | Channel:          | UV_VIS_2 |
| Sample Type: | unknown        | Wavelength:       | n.a. |
| Control Program: | AD_H_90Min_200_1_flow075 | Bandwidth:       | n.a. |
| Quantif. Method: | AD_H             | Dilution Factor:  | 1,0000 |
| Recording Time: | 20.8.2013 18:13 | Sample Weight:    | 1,0000 |
| Run Time (min): | 30,17            | Sample Amount:    | 1,0000 |

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**No. Ret.Time Peak Name Height Area Ref.Area Amount Type**

| No. | Ret.Time | Peak Name | Height | Area | Ref.Area | Amount | Type |
|-----|----------|-----------|--------|------|----------|--------|------|
| 1   | 16.33    | n.a.      | 55,840 | 18,569 | 11.37    | n.a.   | BMB  |
| 2   | 22.79    | n.a.      | 293,118| 144,638| 88.63    | n.a.   | BMB  |

**Total:**

| Total |         |         |        |      |         |        |      |
|-------|---------|---------|--------|------|---------|--------|------|
|       | 348,058 | 163,197 | 100.00 | 0.000|         |        |      |

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**WVL:250 nm**

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**default/Integration**

Chromeleon (c) Dionex 1996-2006
Version 6.80 SR12 Build 3578 (207189)
6 Nov-549 Krist1 (90:10)

Sample Name: Nov-549 Krist1 (90:10)  Injection Volume: 10,0
Vial Number: RC5  Channel: UV_VIS_2
Sample Type: unknown  Wavelength: n.a.
Control Program: AD_H_30Min_200_1_flow075  Bandwidth: n.a.
Quantif. Method: AD_H  Dilution Factor: 1,0000
Recording Time: 20.8.2013 19:39  Sample Weight: 1,0000
Run Time (min): 30,00  Sample Amount: 1,0000

| No. | Ret.Time | Peak Name | Height mAU | Area mAU*min | Ref.Area % | Amount | Type   |
|-----|----------|-----------|------------|--------------|------------|--------|--------|
| 1   | 16,28    | n.a.      | 0,809      | 0,269        | 3,18       | n.a.   | BMB*   |
| 2   | 22,77    | n.a.      | 17,095     | 8,204        | 96,82      | n.a.   | BMB*   |
| Total: |          |           | 17,904     | 8,473        | 100,00     | 0,000  |        |

WAS_20130820_NOV_ADH #6 [modified by Admin] UV_VIS_2
WVL:250 nm

after recrystallization

BMB*
1 Nov-547 (95:5)

Sample Name: Nov-547 (95:5)  
Injection Volume: 10.0
Vial Number: RB2  
Channel: UV_VIS_2
Sample Type: unknown  
Wavelength: n.a.
Control Program: AD_H_90Min_200_1_flow075
Bandwidth: n.a.
Quantf. Method: AD_H  
Dilution Factor: 1,0000
Recording Time: 18.8.2013 19:15
Sample Weight: 1,0000
Sample Amount: 1,0000

| No. | Ret.Time (min) | Peak Name | Height (mAU) | Area (mAU*min) | Ref.Area | Amount (mAU*min) | Type   |
|-----|----------------|-----------|--------------|----------------|----------|-----------------|--------|
| 1   | 11,63          | n.a.      | 80,834       | 20,966         | 8,92     | n.a.            | BMB*   |
| 2   | 13,24          | n.a.      | 565,423      | 214,058        | 91,08    | n.a.            | BMB*   |
| Total|                |           | 646,257      | 235,023        | 100.00   | 0,000           |        |

WAS_20130818_NOV_ADH #1 [modified by Admin] UV_VIS_2

25a
### Nov-551 (90:10)

| Sample Name: | Nov-551 (90:10) | Injection Volume: | 10.0 |
|--------------|-----------------|------------------|------|
| Vial Number: | RC3             | Channel:         | UV_VIS_2 |
| Sample Type: | unknown         | Wavelength:      | n.a. |
| Control Program: | AD_H_90Min_200_1_flow075 | Bandwidth:    | n.a. |
| Quantif. Method: | AD_H | Dilution Factor: | 1.0000 |
| Recording Time: | 20.8.2013 17:01 | Sample Weight: | 1.0000 |
| Run Time (min): | 30.02 | Sample Amount: | 1.0000 |

### Chromatogram

![Chromatogram](attachment:image)

**WAS_20130820_NOV_ADH #3 [modified by Admin]**

| No. | Ret.Time min | Peak Name | Height mAU | Area mAU*min | Ref.Area % | Amount | Type |
|-----|--------------|-----------|------------|--------------|------------|--------|------|
| 1   | 16.28        | n.a.      | 73.770     | 24.140       | 7.78       | n.a.   | BMB  |
| 2   | 21.18        | n.a.      | 623.326    | 286.155      | 92.22      | n.a.   | BMB  |

Total: 697.096 310.295 100.00 0.000
## 2 Nov-546 (95:5)

| No. | Ret.Time | Peak Name | Height | Area | Ref.Area | Amount | Type |
|-----|----------|-----------|--------|------|----------|--------|------|
| 1   | 7.44     | n.a.      | 1594,905 | 276,931 | 85,49  | n.a. | BM * |
| 2   | 7.92     | n.a.      | 280,134 | 47,008 | 14,51  | n.a. | M *  |
| Total: | 1875,039 | 323,939 | 100,00 | 0,000 |

Sample Name: Nov-546 (95:5)  
Injection Volume: 10,0  
Vial Number: RB3  
Channel: UV_VIS_2  
Sample Type: unknown  
Wavelength: n.a.  
Control Program: AD_H_90Min_200_1_flow075  
Bandwidth: n.a.  
Quantf. Method: AD_H  
Dilution Factor: 1,0000  
Recording Time: 18.8.2013 19:35  
Sample Weight: 1,0000  
Run Time (min): 12,65  
Sample Amount: 1,0000  

**Diagram:**

- Ret.Time: 7.44 min, Peak Name: n.a., Height: 1594,905 mAU, Area: 276,931 mAU*min, Ref.Area: 85,49 %, Amount: n.a., Type: BM *
- Ret.Time: 7.92 min, Peak Name: n.a., Height: 280,134 mAU, Area: 47,008 mAU*min, Ref.Area: 14,51 %, Amount: n.a., Type: M *

Total: 1875,039 mAU, 323,939 mAU*min, 100,00 %, 0,000 mAU.
7 Nov-550 (90:10)

Sample Name: Nov-550 (90:10)  
Injection Volume: 10.0  
Vial Number: RC6  
Channel: UV_VIS_2  
Sample Type: unknown  
Wavelength: n.a.
Control Program: AD_H_90Min_200_1_flow075  
Bandwidth: n.a.  
Quantif. Method: AD_H  
Dilution Factor: 1,0000  
Recording Time: 20.8.2013 20:10  
Sample Weight: 1,0000  
Sample Amount: 1,0000

**Table: No. Ret.Time Peak Name Height Area Ref.Area Amount Type**
| No. | Ret.Time | Peak Name | Height | Area | Ref.Area | Amount | Type |
|-----|----------|-----------|--------|------|----------|--------|------|
| 1   | 10,41    | n.a.      | 126,352| 25,351| 14,39    | n.a.   | BMb  |
| 2   | 11,38    | n.a.      | 619,120| 150,840| 85,61    | n.a.   | bMB  |
| Total|          |           | 745,472| 176,191| 100,00   | 0,000  |

WVL:250 nm
**Sample Name:** Nov-535-19-22  
**Injection Volume:** 10.0

**Vial Number:** RA1  
**Channel:** UV_VIS_2

**Sample Type:** unknown  
**Wavelength:** n.a.

**Control Program:** OD_H_120Min_200_1_flow08  
**Temperature/Column:** 10

**Recording Time:** 8.8.2013 10:28  
**Flow ml/min:** 0.800

**Run Time (min):** 35.89  
**Sample Amount:** 1.0000

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| No. | Ret.Time (min) | Peak Name | Height (mAU) | Area (mAU*min) | Rel.Area | Amount (mAU) | Type |
|-----|----------------|-----------|--------------|----------------|----------|--------------|------|
| 1   | 21.01          | n.a.      | 107,714      | 654,177        | 86.79    | n.a.         | BM*  |
| 2   | 22.93          | n.a.      | 158,403      | 99,567         | 13.21    | n.a.         | MB*  |

**Total:** 1165,544 753,744 100.00 0.000

200 n-Hexan : 1 iso-Prop.
2 Nov-548 konz (95:5)

Sample Name: Nov-548 konz (95:5)  Injection Volume: 10.0
Vial Number: RB5  Channel: UV_VIS_1
Sample Type: unknown  Wavelength: n.a.
Control Program: AD_H_90Min_200_1_flow075  Bandwidth: n.a.
Quantif. Method: AD_H  Dilution Factor: 1.0000
Recording Time: 19.8.2013 10:24  Sample Weight: 1.0000
Run Time (min): 12.99  Sample Amount: 1.0000

| No. | Ret.Time (min) | Peak Name | Height (mAU) | Area (mAU*min) | Ref.Area (%) | Amount | Type |
|-----|----------------|-----------|--------------|----------------|--------------|--------|------|
| 1   | 8.58           | n.a.      | 13,666       | 2,594          | 10.89        | n.a.   | BM*  |
| 2   | 9.89           | n.a.      | 94,126       | 21,232         | 89.11        | n.a.   | MB*  |
| Total|                |           | 107,792      | 23,826         | 100.00       | 0.000  |      |

WVL: 220 nm

Sample Weight: 1.0000
Sample Amount: 1.0000


default/Integration

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