Supporting Information
for
Copper-catalyzed asymmetric methylation of fluoroalkylated pyruvates with dimethylzinc

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Experimental details and characterization data of new compounds with copies of $^1$H, $^{13}$C and $^{19}$F NMR spectra

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General information:

$^1$H, $^{13}$C, and $^{19}$F NMR spectra were measured on a Bruker AV300M (300 MHz) spectrometer. Chemical shifts of $^1$H NMR were expressed in parts per million relative to the singlet ($\delta = 7.26$) for CHCl$_3$ as internal standard in CDCl$_3$. Chemical shifts of $^{13}$C NMR were expressed in parts per million relative to the central line of the triplet ($\delta = 77.0$) for CDCl$_3$. Chemical shifts of $^{19}$F NMR were expressed in parts per million relative to the singlet ($\delta = -63.24$) for BTF (benzotrifluoride) as an internal standard. Optical rotations were measured on JASCO P-1020. Mass spectra were measured on a JEOL JMS-T100CS (Accu-TOF) spectrometer. IR spectra were measured on a JASCO FT/IR-4200 spectrometer. High performance liquid chromatography (HPLC) was conducted on JASCO PU-980, LG-980-02, DG-980-50, MD-2010, and CO-966 instrument equipped with model UV-975 spectrometers as an ultra violet light. Peak areas were calculated by JASCO chrom NAV (Windows 7) as an automatic integrator. All experiments were carried out under argon atmosphere unless otherwise noted.

Copper(I) thiophene-2-carboxylate (CuTC), Me$_2$Zn (1 M in heptane solution), and tert-butyl methyl ether (dehydrate) were purchased from Aldrich. (R)-BTFM-Galphos was purchased from Strem Chemicals, Inc.

Substrates:

Ethyl trifluoropyruvate 1a and was provided from Central Glass Co., Ltd. Methyl trifluoropyruvate 1b was purchased from TCI. Ethyl difluoropyruvate 1g [1], ethyl bromodifluoropyruvate 1h [2], and ethyl perfluoroalkylpyruvates 1i–k [3] were synthesized according to published procedure.
Typical procedure I: synthesis of dialkyl oxalate

\[
\begin{array}{c}
\text{Cl} \quad \text{Cl} \\
\text{O} \quad \text{O} \\
\text{Cl} \quad \text{Cl} \\
\text{O} \quad \text{O}
\end{array}
\begin{array}{c}
\text{+ ROH} \\
\text{pyridine (2.0 eq.)} \\
\text{DMAP (5.0 mol%)} \\
\text{THF, rt, 13 h}
\end{array}
\begin{array}{c}
\text{OR} \\
\text{OR}
\end{array}
\]

To an oven-dried 200-mL two-neck round-bottomed flask equipped with magnetic stir bar were added \(N,N'\)-dimethylaminopyridine (183 mg, 1.5 mmol), pyridine (4.84 mL, 60 mmol), ROH (60 mmol), and THF (200 mL). Oxalyl chloride (3.3 mL, 30 mmol) was added dropwise to the solution. After stirring at room temperature for 13 h, the reaction mixture was diluted with \(H_2O\) (100 mL) and extracted with \(Et_2O\) (3 × 50 mL). The combined organic layers were washed with saturated aq. \(NaHCO_3\) (100 mL), water (100 mL), brine (100 mL), and dried over \(MgSO_4\), and then filtered and concentrated under reduced pressure. The residue was purified by silica gel column chromatography to give the corresponding dialkyl oxalate.

Diisopropyl oxalate [4]

\[
\begin{array}{c}
\text{O} \\
\text{O} \\
\text{O} \\
\text{O}
\end{array}
\]

The compound was purified by silica gel column chromatography (EtOAc/hexane 1:20) as a colorless liquid (76% yield). The product is known compound, the following data are identical to those given in corresponding literature [5].

\(^1\)H NMR (300 MHz, CDCl\(_3\)) \(\delta\) 5.10 (sept, 2H, \(J = 6.3\) Hz), 1.30 (d, 12H, \(J = 6.3\) Hz); \(^{13}\)C NMR (75 MHz, CDCl\(_3\)) \(\delta\) 157.9, 71.3, 21.5.

Dicyclopentyl oxalate

\[
\begin{array}{c}
\text{O} \\
\text{O} \\
\text{O} \\
\text{O}
\end{array}
\]

The compound was purified by silica-gel column chromatography (EtOAc/hexane 1:20) as a colorless liquid (91% yield).

\(^1\)H NMR (300 MHz, CDCl\(_3\)) \(\delta\) 5.25-5.19 (m, 2H), 1.92-1.80 (m, 4H), 1.78-1.66 (m, 8H), 1.62-1.49 (m, 4H); \(^{13}\)C NMR (75 MHz, CDCl\(_3\)) \(\delta\) 158.1, 80.1, 32.4, 23.6; HRMS (ESI-TOF) calcd for \(C_{12}H_{16}NaO_4\) [M+Na\(^+\): 249.1103, found: 249.1106; FT-IR (neat, cm\(^{-1}\)) 762, 852, 942, 1017, 1122, 1172, 1310, 1363, 1465, 1747, 1763, 2875, 2943, 2974.
Dicyclohexyl oxalate

![Dicyclohexyl oxalate](image)

The compound was purified by silica-gel column chromatography (EtOAc/hexane 1:20) as white solid (92% yield).

$^1$H NMR (300 MHz, CDCl$_3$) $\delta$ 4.94-4.85 (m, 2H), 1.93-1.88 (m, 4H), 1.81-1.74 (m, 4H), 1.60-1.48 (m, 6H), 1.44-1.20 (m, 6H); $^{13}$C NMR (75 MHz, CDCl$_3$) $\delta$ 157.9, 76.0, 31.3, 25.3, 23.7; HRMS (ESI-TOF) calcd for C$_{14}$H$_{22}$NaO$_4$ [M+Na]$^+$: 277.1416, found: 277.1429; FT-IR (KBr, cm$^{-1}$) 758, 807, 920, 1007, 1037, 1089, 1146, 1179, 1247, 1262, 1314, 1360, 1442, 1739, 2060, 2104, 2153, 2228, 2251, 2293, 2495, 2654, 2864, 2951, 3473.

Typical procedure II: synthesis of trifluoropyruvate derivatives [6]

$$
\text{ROCOOR} + \text{TMSCF}_3 \overset{\text{1.0 eq.}}{\longrightarrow} \overset{\text{CsF (10 mol%)}}{\text{THF, rt, 24 h}} \overset{\text{4N HCl then in vacuo}}{\longrightarrow} \overset{\text{HOHO}}{\text{F}_3\text{C-CO}_2\text{R}} (1)
$$

$$
\overset{\text{EtOH (20 eq.)}}{\text{HOHO}} \overset{\text{P}_2\text{O}_5 (22-60 wt%)}{\text{distillation}} \overset{\text{then in vacuo}}{\longrightarrow} \overset{\text{F}_3\text{C-CO}_2\text{R}}{\text{1c-e}} (2)
$$

To an oven-dried 200-mL two-neck round-bottomed flask equipped with magnetic stir bar were added dialkyl oxalate (10 mmol), cesium fluoride (151.9 mg, 1 mmol), TMSCF$_3$ (1.48 mL, 10 mmol), and THF (60 mL). After the reaction mixture was stirred for 24 h at room temperature, 4 N HCl (30 mL) was added and concentrated in vacuo to give the corresponding trifluoropyruvate hydrate (reaction 1). Then, a solution of trifluoropyruvate hydrate in ethanol was stirred at 70 °C for 4 h, and evaporated. The hemiacetal pyruvate was purified by distillation with P$_2$O$_5$ to provide the corresponding trifluoropyruvate (1c,d) (reaction 2).

Isopropyl 3,3,3-trifluoro-2-oxopropanoate (1c)

The compound was purified by distillation with P$_2$O$_5$ (55 wt %, 263 Torr, 35 °C) as a colorless liquid (25% yield).

$^1$H NMR (300 MHz, CDCl$_3$) $\delta$ 5.23 (sept, 1H, $J = 6.3$ Hz), 1.36 (d, 6H, $J = 6.3$ Hz); $^{13}$C NMR (75 MHz, CDCl$_3$) $\delta$ 174.4 (q, $J_{\text{C-F}} = 38.3$ Hz), 156.3, 115.2 (q, $J_{\text{C-F}} = 288.4$ Hz), 73.2, 21.4; $^{19}$F NMR (282 MHz, CDCl$_3$) $\delta$ -75.7 (s, 3F); HRMS (APCI-TOF) calcd for C$_6$H$_7$F$_3$O$_3$ [M]$^+$: 184.0347, found: 184.0345; FT-IR (neat, cm$^{-1}$) 729, 810, 840, 904, 985, 1085, 1157, 1199, 1253, 1378, 1454, 1637, 1740, 2943, 2985, 3439.
Cyclopentyl 3,3,3-trifluoro-2-oxopropanoate (1d)

![Cyclopentyl 3,3,3-trifluoro-2-oxopropanoate](image)

The compound was purified by distillation with P$_2$O$_5$ (60 wt%, 229 Torr, 29 °C) as a colorless liquid (25% yield).

$^1$H NMR (300 MHz, Acetone-$_d_6$) δ 5.44-5.38 (m, 1H), 2.01-1.92 (m, 2H), 1.86-1.77 (m, 2H), 1.77-1.60 (m, 4H); $^{13}$C NMR (75 MHz, Acetone-$_d_6$) δ 174.0 (q, $J_{C-F} = 36.4$ Hz), 156.6, 116.3 (q, $J_{C-F} = 288.2$ Hz), 82.0, 33.0, 24.2; $^{19}$F NMR (282 MHz, Acetone-$_d_6$) δ 75.7 (s, 3F); HRMS (APCI-TOF) calcd for C$_8$H$_9$F$_3$O$_3$ [M]$: 210.0538$, found: 210.0530; FT-IR (neat, cm$^{-1}$) 728, 850, 950, 991, 1024, 1094, 1150, 1202, 1247, 1291, 1747, 1850, 2877, 2966, 3433.

Cyclohexyl 3,3,3-trifluoro-2-oxopropanoate (1e)

![Cyclohexyl 3,3,3-trifluoro-2-oxopropanoate](image)

The compound was purified by distillation with P$_2$O$_5$ (42 wt%, 41 Torr, 52~53 °C) (containing small amount of cyclohexene) as a colorless liquid (42% yield).

$^1$H NMR (300 MHz, CDCl$_3$) δ 5.09-5.01 (m, 1H), 1.98-1.88 (m, 3H), 1.82-1.75 (m, 2H), 1.69-1.50 (m, 3H), 1.49-1.28 (m, 2H); $^{13}$C NMR (75 MHz, CDCl$_3$) δ 174.6 (q, $J_{C-F} = 38.5$ Hz), 156.2, 115.2 (q, $J_{C-F} = 288.4$ Hz), 77.7, 31.1, 25.1, 23.4; $^{19}$F NMR (282 MHz, CDCl$_3$) δ 75.7 (s, 3F); HRMS (APCI-TOF) calcd for C$_9$H$_{11}$F$_3$O$_3$ [M]$^+$: 224.0660, found: 224.0650; FT-IR (neat, cm$^{-1}$) 733, 828, 898, 1008, 1088, 1161, 1195, 1253, 1450, 1744, 1780, 2867, 2935, 3454.

2,4-Dimethylpentan-3-yl ethyl oxalate

To an oven-dried 200-mL two-neck round-bottomed flask equipped with magnetic stir bar were added N,N'-dimethylaminopyridine (366 mg, 3.0 mmol), pyridine (5.3 mL, 66 mmol), 2,4-dimethylpentan-3-ol (8.4 mL, 60 mmol), and THF (200 mL). Ethyl chloroglyoxylate (3.3 mL, 60 mmol) was added dropwise to the solution. After stirring at room temperature for 13 h, the reaction mixture was diluted with H$_2$O (100 mL) and extracted with Et$_2$O (3 × 50 mL). The combined organic layers were washed with saturated aq. NaHCO$_3$ (100 mL), water (100 mL), brine (100 mL), and dried over MgSO$_4$, filtered and concentrated under reduced pressure. Resulting crude product was purified by silica-gel column chromatography (hexane:EtOAc 20:1) to give 2,4-dimethylpentan-3-yl ethyl oxalate as a clear liquid (6.4 g, >99%).
\(^1\)H NMR (300 MHz, CDCl\(_3\)) \(\delta\) 4.73 (t, 1H, \(J = 6.2\) Hz), 4.34 (q, 2H, \(J = 6.9\) Hz), 2.00 (m, 2H), 1.37 (t, 3H, \(J = 7.0\) Hz), 0.92 (d, 6H, \(J = 6.9\) Hz), 0.90 (d, 6H, \(J = 6.6\) Hz); \(^13\)C NMR (75 MHz, CDCl\(_3\)) \(\delta\) 158.6, 86.7, 63.0, 29.5, 19.5, 17.2, 14.1; HRMS (ESI-TOF) calcd for C\(_{11}\)H\(_{20}\)NaO\(_4\) [M+Na\(^+\)]: 239.1259, found: 239.1270; FT-IR (neat, cm\(^{-1}\)) 760, 859, 894, 935, 1011, 1099, 1130, 1187, 1306, 1370, 1389, 1458, 1748, 1767, 2882, 2935, 2970.

2,4-Dimethylpentan-3-yl 3,3,3-trifluoro-2-oxopropanoate (1f)

To a oven-dried 200-mL two-neck round-bottomed flask equipped with magnetic stir bar were added 2,4-dimethylpentan-3-yl ethyl oxalate (2.16 g, 10 mmol), cesium fluoride (151.9 mg, 1 mmol), TMSCF\(_3\) (1.48 mL, 10 mmol), and THF (60 mL). After the reaction mixture was stirred for 24 h at room temperature, 4 N HCl (60 mL) was added and extracted with Et\(_2\)O (3 \(\times\) 50 mL). The combined organic layers were washed with brine (100 mL), and dried over Na\(_2\)SO\(_4\), filtered and concentrated under reduced pressure to afford the corresponding trifluoropyruvate hydrate as a yellow liquid (2.55 g, 99%) (reaction 1).

\(^1\)H NMR (300 MHz, CDCl\(_3\)) \(\delta\) 4.76 (t, 1H, \(J = 6.1\) Hz), 2.08-1.97 (m, 2H), 0.92 (d, 6H, \(J = 6.9\) Hz), 0.91 (d, 6H, \(J = 6.6\) Hz); \(^13\)C NMR (75 MHz, CDCl\(_3\)) \(\delta\) 174.0 (q, \(J_{C-F} = 36.4\) Hz), 156.7, 116.3 (q, \(J_{C-F} = 288.2\) Hz), 82.0, 33.0, 24.2; \(^19\)F NMR (282 MHz, CDCl\(_3\)) \(\delta\) 82.7 (s, 3F); HRMS (APCI-TOF) calcd for C\(_{10}\)H\(_{18}\)F\(_3\)O\(_4\) [M-H]: 243.0997, found: 243.0985; FT-IR (neat, cm\(^{-1}\)) 596, 657, 722, 878, 928, 985, 1085, 1165, 1191, 1253, 1366, 1386, 1466, 1366, 1386, 1466, 1740, 2878, 2943, 2974, 3454.

Then, a solution of trifluoropyruvate hydrate in ethanol was stirred at 70 °C for 4 h, and evaporated. The hemiacetal pyruvate was purified by distillation with P\(_2\)O\(_5\) (40 wt%, 36 Torr, 52 °C) to provide the corresponding trifluoropyruvate (1f) as a colorless liquid (83% yield) (reaction 2).

\(^1\)H NMR (300 MHz, CDCl\(_3\)) \(\delta\) 4.83 (t, 1H, \(J = 6.1\) Hz), 2.12-1.97 (m, 2H), 0.93 (d, 6H, \(J = 6.9\) Hz), 0.92 (d, 6H, \(J = 6.6\) Hz); \(^13\)C NMR (75 MHz, CDCl\(_3\)) \(\delta\) 174.7 (q, \(J_{C-F} = 38.9\) Hz), 157.0 (s), 115.0 (q, \(J_{C-F} = 288.4\) Hz), 88.5, 29.3, 19.2, 16.8; \(^19\)F NMR (282 MHz, CDCl\(_3\)) \(\delta\) 75.8 (s, 3F); HRMS (APCI-TOF) calcd for C\(_{10}\)H\(_{15}\)F\(_3\)O\(_3\) [M]: 240.0973, found: 240.0973; FT-IR (neat, cm\(^{-1}\)) 720, 886, 931, 1010, 1089, 1172, 1191, 1254, 1304, 1371, 1393, 1469, 1743, 1777, 2879, 2943, 2977, 3459.
**Typical procedure III: Cu-catalyzed asymmetric methylation of fluoroalkylated pyruvate**

![Chemical structure]

To a mixture of CuTC (1.0 mg, 0.005 mmol) and (R)-BTFM-Garphos (5.7 mg, 0.0048 mmol) was added CH$_2$Cl$_2$ (1.0 mL) at room temperature under argon atmosphere, and the solution was stirred for 12 h. The solvent was removed under reduced pressure, and the prepared catalyst was dissolved in TBME (0.5 mL) under argon atmosphere. After the solution was cooled to −90 °C, Me$_2$Zn (1.0 M in heptane, 0.4 mL, 0.4 mmol) followed by fluoroalkylated pyruvate 1 (0.2 mmol) in TBME (0.5 mL) were added in 30 min. The reaction mixture was stirred at the same temperature for 1 h. The reaction mixture was quenched with saturated aq. NH$_4$Cl. The organic layer was separated and the aqueous layer was extracted with Et$_2$O twice. The combined organic layer was dried over anhydrous Na$_2$SO$_4$ and evaporated under controlled pressure (350 mmHg). The concentrated solution was used without purification for the next protection reaction. The yield of alcohol product 2 was determined by $^{19}$F NMR analysis using benzotrifluoride (BTF) as an internal standard.

To a solution of DMAP (2.4 mg, 0.02 mmol) and the crude alcohol in CH$_2$Cl$_2$ (2.0 mL) was added NEt$_3$ (56 μL, 0.4 mmol) at room temperature under argon atmosphere. After the reaction mixture was cooled to 0 °C, p-nitrobenzoyl chloride (56 mg, 0.3 mmol) was added. Then the mixture was warmed to room temperature and stirred for 1 h. After 1 N HCl (5.0 mL) was added to the reaction mixture, the organic layer was separated and the aqueous layer was extracted with Et$_2$O twice. The combined organic layer was washed with saturated aq. NaHCO$_3$, water, and brine, and then dried over anhydrous MgSO$_4$ and evaporated under reduced pressure. The residue was purified by silica gel column chromatography to give p-nitrobenzoylated alcohol 2'. Enantiomeric excess was determined by chiral HPLC analysis.

**(S)-3-Ethoxy-1,1,1-trifluoro-2-methyl-3-oxopropan-2-yl 4-nitrobenzoate (2a')**

![Chemical structure]

The yield of alcohol 2a (86%) was determined by $^{19}$F NMR analysis. p-Nitrobenzoylated alcohol 2a' was purified by silica gel column chromatography (EtOAc/hexane 1:40) as a colorless liquid (53% yield for 2 steps, 89% ee).

$^1$H NMR (300 MHz, CDCl$_3$) δ 8.34-8.31 (m, 2H), 8.24-8.20 (m, 2H), 4.33 (q, 4H, J = 6.9 Hz), 1.97 (d, 3H, J = 0.9 Hz), 1.28 (t, 3H, J = 7.0 Hz); $^{13}$C NMR (75 MHz, CDCl$_3$) δ 164.3, 162.3, 151.1, 134.0, 131.2, 123.7, 122.7 (q, J$_{C-F}$ = 282.9 Hz), 80.7 (q, J$_{C-F}$ = 30.4 Hz), 63.2, 16.6, 13.8; $^{19}$F NMR (282 MHz, CDCl$_3$) δ -78.4 (s, 3F); HRMS (APCI-TOF) calcd for C$_{13}$H$_{12}$F$_3$NO$_6$ [M]$: 335.0617, found: 335.0623; FT-IR (neat, cm$^{-1}$) 784, 813, 849, 876, 927, 1011, 1109, 1149, 1273, 1342, 1387, 1452,
1525, 1602, 1740, 2857, 2920, 2952, 2996, 3087, 3116; [α]$_D$$^{22}$ -28.94 (c 0.20, CHCl$_3$), 89% ee; HPLC (column, CHIRALCEL OJ-3, Hexane/2-Propanol = 91/9, flow rate 0.6 mL/min, 20 °C detection UV 254 nm) $t_R$ of major isomer 13.1 min, $t_R$ of minor isomer 23.8 min.

\[
\begin{array}{|c|c|c|c|c|}
\hline
\text{#} & \text{Time [min]} & \text{Area [µV·sec]} & \text{Area%} & \text{Height [µV]} & \text{Height%} \\
\hline
1 & 14.0 & 1997861 & 50.35 & 86782 & 71.58 \\
2 & 26.1 & 1970061 & 49.65 & 34456 & 28.42 \\
\hline
\end{array}
\]

(S)-1-Ethoxy-3,3-difluoro-2-methyl-1-oxopropan-2-yl benzoate (2g’)

\[
\begin{array}{c}
\begin{array}{c}
\text{O} \\
\text{Me} \\
\text{CF}_2\text{H} \\
\text{CO}_2\text{Et}
\end{array}
\end{array}
\]

Reaction temperature was −78 °C. The yield of alcohol 2g (89%) was determined by $^{19}$F NMR analysis. In the protection of alcohol, benzoyl chloride was used instead of p-nitrobenzoyl chloride. Benzyolated alcohol 2g’ was purified by silica gel column chromatography (EtOAc/hexane = 1/40) as a colorless liquid (41% yield for 2 steps, 89% ee).

$^1$H NMR (300 MHz, CDCl$_3$) δ 8.05 (dd, $J = 8.3$, 1.3 Hz, 2H). 7.61 (tt, $J = 6.7$, 1.3 Hz, 1H), 7.44-7.49 (m, 2H), 6.30 (dd, $J_{HH} = 56.8$, 54.8 Hz, 1H), 4.29 (q, $J = 7.1$ Hz, 2H) 1.77 (t, $J_{HF} = 1.6$ Hz, 3H), 1.27 (t, $J = 7.1$ Hz, 3H); $^{13}$C NMR (75 MHz, CDCl$_3$) δ 167.6, 164.8, 133.7, 130.0, 128.8, 128.5, 122.9 (dd, $J_{CF} = 250.0$, 245.0 Hz), 79.7 (dd, $J_{CF} = 27.5$, 21.9 Hz), 62.3, 14.6 (t, $J_{CF} = 3.2$ Hz) 13.9; $^{19}$F NMR (282 MHz, CDCl$_3$) δ -128.40 (dd, $J = 290.2$ Hz, $J_{FH} =54.7$ Hz, 1F), -132.76 (dd, $J = 289.90$ Hz, $J_{FH} =56.4$ Hz, 1F); HRMS (APCI-TOF) calcd for C$_{13}$H$_{14}$F$_2$NaO$_4$ [M+Na]$^+$: 295.0758, found: 295.0761; FT-IR (neat, cm$^{-1}$) 1026, 1093, 1114, 1216, 1279, 1388, 1452, 1602, 1730, 1747, 2938, 2985, 3021; [α]$^D$$^{25}$ -7.47 (c 1.01, CHCl$_3$), 89% ee; HPLC (column, CHIRALCEL OJ-3, Hexane/2-Propanol = 99/1, flow rate 0.6 mL/min, 20 °C detection UV 220 nm) $t_R$ of major isomer 21.2 min, $t_R$ of minor isomer 22.6 min.
(S)-1-Bromo-3-ethoxy-1,1-difluoro-2-methyl-3-oxopropan-2-yl 4-nitrobenzoate (2h')

Reaction temperature was −78 °C. The yield of alcohol 2h (53%) was determined by $^{19}$F NMR analysis. $p$-Nitrobenzoylated alcohol 2h' was purified by silica gel column chromatography (EtOAc/hexane 1:50) as a white solid (32% yield for 2 steps, 82% ee).

$^1$H NMR (300 MHz, CDCl$_3$) δ 8.34-8.31 (m, 2H), 8.25-8.21 (m, 2H), 4.32 (q, 2H, $J = 7.2$ Hz), 2.02 (s, 3H), 1.29 (t, 3H, $J = 7.0$ Hz); $^{13}$C NMR (75 MHz, CDCl$_3$) δ 164.3, 162.4, 151.2, 134.3, 131.3, 123.9, 121.0 (t, $J_{CF} = 311.6$ Hz), 84.8 (dd, $J_{CF} = 25.6$, 23.4 Hz), 63.4, 18.4, 14.0; $^{19}$F NMR (282 MHz, CDCl$_3$) δ -56.9 (d, 1F, $J = 168.6$ Hz), -58.9 (d, 1F, $J = 165.3$ Hz); HRMS (APCI-TOF) calcd for C$_{13}$H$_{12}$BrF$_2$NO$_6$ [M]$: 394.9816$, found: 394.9835; FT-IR (KBr pellet, cm$^{-1}$) 716, 843, 876, 961, 1020, 1106, 1146, 1280, 1347, 1446, 1528, 1610, 1751, 2866, 2936, 2988; $[\alpha]_D^{22}$ -11.99 (c 1.55, CHCl$_3$), 82% ee; HPLC (column, CHIRALCEL OD-3, Hexane/2-Propanol = 91/9, flow rate 0.6 mL/min, 20 °C detection UV 254 nm) $t_R$ of major isomer 18.2 min, $t_R$ of minor isomer 12.5 min.
(S)-1-Ethoxy-3,3,4,4,4-pentafluoro-2-methyl-1-oxobutan-2-yl p-nitrobenzoate (2i')

The yield of alcohol 2i (87%) was determined by $^{19}$F NMR analysis. p-Nitrobenzoylated alcohol 2i' was purified by silica gel column chromatography (EtOAc/hexane 1:40) as a white solid (48% yield for 2 steps, 86% ee).

$^{1}$H NMR (300 MHz, CDCl$_3$) δ 8.30-8.35 (m, 2H), 8.16-8.21 (m, 2H), 4.27-4.37 (m, 2H), 2.04 (q, $J_{H-F} = 0.6$ Hz, 3H), 1.28 (t, $J = 7.1$ Hz, 3H); $^{13}$C NMR (75 MHz, CDCl$_3$) δ 164.2, 162.2, (d, $J_{C-F} = 2.0$ Hz), 151.0, 134.1, 131.0, 123.8, 118.6 (qt, $J_{C-F} = 286.1$, 35.6 Hz), 112.0 (tq, $J_{C-F} = 263.0$, 36.8 Hz), 81.3 (t, $J_{C-F} = 25.4$ Hz), 63.3, 16.6, 13.7; $^{19}$F NMR (282 MHz, CDCl$_3$) δ -79.19 (s, 3F), -121.42 (d, $J = 280.9$ Hz, 1F), -122.98 (d, $J = 279.7$ Hz, 1F); HRMS (APCI-TOF) calcld for C$_{14}$H$_{12}$F$_{5}$NO$_6$ [M$^-$]: 385.0585, found: 385.0582; FT-IR (KBr pellet, cm$^{-1}$) 1014, 1142, 1208, 1222, 1281, 1350, 1385, 1533, 1747, 2942, 2987, 3059; [α]$_D^{25}$ -27.75 (c 1.02, CHCl$_3$), 86% ee; HPLC (column, CHIRALCEL OJ-3, Hexane/2-Propanol = 99/1, flow rate 0.6 mL/min, 20 °C detection UV 220 nm) $t_R$ of major isomer 16.2 min, $t_R$ of minor isomer 31.4 min.
(S)-1-Ethoxy-3,3,4,5,5,6,6,7,7,8,8,9,9,10,10,10-heptadecafluoro-2-methyl-1-oxodecan-2-yl p-nitrobenzoate (2j’)

The yield of alcohol 2j (98%) was determined by $^{19}$F NMR analysis. p-Nitrobenzoylated alcohol 2j’ was purified by silica-gel column chromatography (EtOAc/hexane 1:50) as a colorless oil (48% yield for 2 steps, 78% ee).

$^1$H NMR (300 MHz, CDCl$_3$) δ 8.31-8.35 (m, 2H) 8.16-8.21 (m, 2H), 4.29-4.36 (m, 2H), 2.07 (q, $J_{H-F}$ = 1.3 Hz, 3H), 1.28 (t, $J$ = 7.1 Hz, 3H); $^{13}$C NMR (75 MHz, CDCl$_3$) δ 164.2 162.2, 151.0, 134.1, 131.0, 123.8, 117.6 (qt, $J_{C-F}$ = 286.9, 33.9 Hz), 113.6 (tt, $J_{C-F}$ = 263.9, 30.9 Hz), 122.9 (tq, $J_{C-F}$ = 266.9, 37.4 Hz), 82.2 (t, $J_{C-F}$ = 25.7 Hz), 63.4, 16.8, 13.7; $^{19}$F NMR (282 MHz, CDCl$_3$) δ -80.6--80.70 (m, 3F), -117.75 (d, $J = 288.5$ Hz, 1F), -119.60 (d, $J = 288.2$ Hz, 1F), -123.882 (s, 2F).

HRMS (APCI-TOF) calcd for C$_{15}$H$_{12}$F$_7$NO$_6$ [M]$: 435.0553$, found: 435.0547; FT-IR (neat, cm$^{-1}$) 1090, 1140, 1200, 1233, 1349, 1387, 1534, 1609, 1744, 1761, 2942, 2988, 3059; [α]$_D$-25 -22.60 (c 0.94, CHCl$_3$), 78% ee; HPLC (column, CHIRALCEL OJ-3, Hexane/2-Propanol = 99/1, flow rate 0.6 mL/min, 20 °C detection UV 220 nm) $t_R$ of major isomer 12.2 min, $t_R$ of minor isomer 15.5 min.

(S)-1-Ethoxy-3,3,4,5,5,6,6,7,7,8,8,9,9,10,10,10-heptadecafluoro-2-methyl-1-oxodecan-2-yl p-nitrobenzoate (2k’)

The yield of alcohol 2k (92%) was determined by $^{19}$F NMR analysis. p-Nitrobenzoylated alcohol 2k’ was purified by silica-gel column chromatography (EtOAc/hexane 1:50) as a white solid (85% yield
for 2 steps, 73% ee).

$^1$H NMR (300 MHz, CDCl$_3$) $\delta$ 8.36-8.31 (m, 2H), 8.20-8.16 (m, 2H), 4.36-4.29 (m, 2H), 2.08 (s, 3H), 1.28 (t, 3H, $J = 7.3$ Hz); $^{13}$C NMR (75 MHz, CDCl$_3$) $\delta$ 164.3 162.4 151.2 134.3 131.2 123.9 118.4-104.7 (m) 117.3 (qt, $J_{C-F} = 288.4$, 33.2 Hz), 82.8 (t, $J_{C-F} = 25.4$ Hz), 63.5, 17.1,13.8; $^{19}$F NMR (282 MHz, CDCl$_3$) $\delta$ -80.6--80.8 (m, 3F), -116.4--126.0 (m, 14F); HRMS (APCI-TOF) calcd for C$_{20}$H$_{12}$F$_{17}$NO$_6$ [M]: 685.0393, found: 685.0362; FT-IR (KBr pellet cm$^{-1}$) 847, 969, 1009, 1142, 1214, 1246, 1297, 1472, 1530, 1613, 1732, 2339, 2360, 2860, 2922, 2997, 3112, 3454, 3493; $[\alpha]_D^{22}$ -11.93 (c 0.48, CHCl$_3$), 73% ee; HPLC (column, CHIRALPAK AD-3 and AD-H, Hexane/2-Propanol = 99.5/0.5, flow rate 0.6 mL/min, 20 °C detection UV 254 nm) $t_R$ of major isomer 16.8 min, $t_R$ of minor isomer 24.4 min.
Typical procedure IV: Cu-catalyzed asymmetric methylation of trifluoropyruvate derivatives

To a mixture of CuTC (1.0 mg, 0.005 mmol) and (R)-BTMF-Garphos (5.7 mg, 0.0048 mmol) was added CH$_2$Cl$_2$ (1.0 mL) at room temperature under argon atmosphere, and the solution was stirred for 12 h. The solvent was removed under reduced pressure, and the prepared catalyst was dissolved in TBME (0.5 mL). After the solution was cooled to $-90$ °C, Me$_2$Zn (1.0 M in heptane, 0.4 mL, 0.4 mmol), followed by trifluoropyruvate derivative 1 (0.2 mmol) in TBME (0.5 mL) were added in 30 min. The reaction mixture was stirred at the same temperature for 1 h. After the reaction mixture was quenched with saturated aq. NH$_4$Cl, the organic layer was separated and the aqueous layer was extracted with Et$_2$O twice. The combined organic layer was dried over anhydrous Na$_2$SO$_4$ and evaporated under controlled pressure (350 mmHg). The yields (2c: 59%, 2d: 60%, 2e: 64%, 2f: 71%) were determined by $^{19}$F NMR analysis using BTF as an internal standard. The concentrated solution was used without purification for the next reduction with LiAlH$_4$.

To an oven-dried 30-mL two-neck round-bottomed flask equipped with magnetic stir bar was added LiAlH$_4$ (23 mg, 0.6 mmol) in THF (10 mL). After the solution was cooled to $-78$ °C, the crude alcohol in THF (1 mL) was added dropwise. Then the mixture was warmed to room temperature and stirred for 3 h. The reaction mixture was quenched with water (23 μL), 15% NaOH aq. (23 μL), and water (69 μL). After filtration, the solvent was evaporated under reduced pressure. The concentrated solution was used without purification for the next protection reaction.

To a solution of DMAP (2.4 mg, 0.02 mmol) and the crude diol in CH$_2$Cl$_2$ (2.0 mL) was added NEt$_3$ (112 μL, 0.8 mmol) at room temperature. After the reaction mixture was cooled to 0 °C, $p$-nitrobenzoyl chloride (112 mg, 0.6 mmol) was added. The mixture was warmed to room temperature and stirred for 1 h and 1 N HCl (5.0 mL) was added to the reaction mixture. The organic layer was separated and the aqueous layer was extracted with Et$_2$O twice. The combined organic layers were washed with saturated aq. NaHCO$_3$, water, brine, and dried over anhydrous MgSO$_4$ and evaporated under reduced pressure. The residue was purified by silica-gel column chromatography (EtOAc/hexane 1:20) to give the corresponding di-$p$-nitrobenzoylated product 2$p$ as a white solid (14% yield for 3 steps, 94% ee). Enantiomeric excess was determined by chiral HPLC analysis.

$^1$H NMR (300 MHz, CDCl$_3$) δ 8.31 (d, 2H, $J = 9.0$ Hz), 8.25 (d, 2H, $J = 8.7$ Hz), 8.18 (d, 2H, $J = 9.0$ Hz), 8.12 (d, 2H, $J = 8.7$ Hz), 5.25 (dd, 1H, $J = 12.6, 0.9$ Hz), 4.88 (d, 1H, $J = 12.9$ Hz), 1.95 (s, 3H); $^{13}$C NMR (75 MHz, CDCl$_3$) δ 163.7, 162.5, 151.2, 151.0, 134.8, 134.5, 131.1, 130.9, 124.1 (q, $J_{C\text{-}F}$ =
282.5 Hz), 123.9, 123.8, 81.4 (q, \( J_{C-F} = 29.1 \) Hz), 123.9, 123.8, 81.4 (q, \( J_{C-F} = 1.3 \) Hz); \(^{19}\)F NMR (282 MHz, CDCl\(_3\)) \( \delta \) 79.7 (s, 3F); HRMS (APCI-TOF) calcd for C\(_{18}\)H\(_{13}\)F\(_3\)N\(_2\)O\(_8\) [M]: 442.0624, found: 442.0603; \(^{13}\)C NMR (282 MHz, CDCl\(_3\)) \( \delta \) 63.0, 16.4 (q, \( J_{C-F} = 1.3 \) Hz);

\[ (\text{R})-\text{DTB-MeO-BIPHEP} \text{ (55.7 mg, 0.054 mmol) was added to a mixture of CuTC (9.5 mg, 0.05 mmol), and the solution was stirred for 12 h. The solvent was removed under reduced pressure, and the prepared catalyst was dissolved in TBME (5.0 mL) under an argon atmosphere. After the solution was cooled to \(-78^\circ\text{C}\), Me\(_2\)Zn (1.0 M in heptane, 4.0 mL, 4.0 mmol) was added. The reaction mixture was stirred at the same temperature for 1 h. The reaction mixture was quenched with saturated aq. NH\(_4\)Cl. The organic layer was separated and the aqueous layer was extracted with Et\(_2\)O twice. The combined organic layer was dried over anhydrous Na\(_2\)SO\(_4\) and evaporated under controlled pressure (350 mmHg), and the residue was purified by a distillation (70 kPa, 20 \(^\circ\text{C}\)) to give 2b in 8% yield. The product 2b exhibited the same \(^1\)H and \(^{19}\)F NMR spectra as reported before [7]. \(^1\)H NMR (300 MHz, CDCl\(_3\)) \( \delta \) 1.59 (s, 3H), 3.77 (s, 1H), 3.91 (s, 3H); \(^{19}\)F NMR (282 MHz, CDCl\(_3\)) \( \delta \) -80.04 (s, 3F); \([\alpha]_D^{23} = +23.80 \) (c 0.06, CHCl\(_3\)), 94% ee; HPLC (column, CHIRALCEL OD-3, Hexane/2-Propanol = 91/9, flow rate 0.6 mL/min, 20 \(^\circ\text{C}\) detection UV 254 nm) \( t_R \) of major isomer 47.8 min, \( t_R \) of minor isomer 40.7 min.

**Determination of the absolute configuration (Table 1, entry 17)**

To a mixture of CuTC (9.5 mg, 0.05 mmol) and (R)-DTB-MeO-BIPHEP (55.7 mg, 0.054 mmol) was added CH\(_2\)Cl\(_2\) (5.0 mL) at room temperature under argon atmosphere, and the solution was stirred for 12 h. The solvent was removed under reduced pressure, and the prepared catalyst was dissolved in TBME (5.0 mL) under an argon atmosphere. After the solution was cooled to \(-78^\circ\text{C}\), Me\(_2\)Zn (1.0 M in heptane, 4.0 mL, 4.0 mmol) followed by methyl trifluoropyruvate 1b (244 \( \mu \)L, 2.0 mmol) in TBME (5.0 mL) were added. The reaction mixture was stirred at the same temperature for 1 h. The reaction mixture was quenched with saturated aq. NH\(_4\)Cl. The organic layer was separated and the aqueous layer was extracted with Et\(_2\)O twice. The combined organic layer was dried over anhydrous Na\(_2\)SO\(_4\) and evaporated under controlled pressure (350 mmHg), and the residue was purified by a distillation (70 kPa, 20 \(^\circ\text{C}\)) to give 2b in 8% yield. The product 2b exhibited the same \(^1\)H and \(^{19}\)F NMR spectra as reported before [7]. \(^1\)H NMR (300 MHz, CDCl\(_3\)) \( \delta \) 1.59 (s, 3H), 3.77 (s, 1H), 3.91 (s, 3H); \(^{19}\)F NMR (282 MHz, CDCl\(_3\)) \( \delta \) -80.04 (s, 3F); \([\alpha]_D^{23} = -2.12 \) (c 2.20, CHCl\(_3\)). The absolute configuration was determined to be S in comparison with the optical rotation of reported data [Ref 7: (S)-2b >95% ee, \([\alpha]_D^{20} = -14.4 \) (c 3.65, CHCl\(_3\))] . The absolute configurations of other alcohol products 2a and 2c–k were tentatively assigned by analogy to 2b. Enantiomeric excess of
benzoylated alcohol 2b' prepared by **Typical Procedure III** was determined by chiral HPLC analysis. Compound 2b' was purified by silica-gel column chromatography (EtOAc/hexane 1:40) as a colorless oil (60% yield for 2 steps, 59% ee).

**1H NMR** (300 MHz, CDCl₃) δ 1.94 (q, Jₖ₋₋₆ = 1.0 Hz, 3H), 3.84 (s, 3H), 7.45-7.50 (m, 2H), 7.63 (tt, J = 7.4, 1.9 Hz, 1H), 8.03-8.07 (m, 2H); **13C NMR** (75 MHz, CDCl₃) δ 16.7 (d, Jₖ₋₋₆ = 1.2 Hz), 53.6, 79.8 (q, Jₖ₋₋₆ = 30.2 Hz), 122.9 (q, Jₖ₋₋₆ = 282.8 Hz), 128.6, 129.7, 130.1, 134.0, 164.2, 165.6; **19F NMR** (282 MHz, CDCl₃) δ -78.45 (s, 3F); HRMS (APCI-TOF) calcd for C₁₂H₁₁F₃NaO₄ [M+Na]⁺: 299.0507, found: 299.0493; **FT-IR** (neat, cm⁻¹) 1069, 1110, 1137, 1188, 1216, 1271, 1289, 1304, 1384, 1452, 1602, 1734, 1759, 2928, 2958, 3022; [α]D²⁵ +21.07 (c 0.80, CHCl₃).

**Synthesis of simple perfluoroalkylated ketone (3a)** [8]

![Chemical reaction diagram]

To an oven-dried 200-mL two-neck round-bottomed flask equipped with magnetic stir bar were added ethyl trifluoroacetate (60 mmol), C₈F₁₇-I (66 mmol), and Et₂O (200 mL) under argon atmosphere. After the solution was cooled to -78 °C, MeLi (60 mmol) was added dropwise in 20 min. After stirring at -78 °C for 30 min, the reaction mixture was diluted with 1N HCl (100 mL) and extracted with Et₂O (3 × 50 mL). The combined organic extracts were washed with saturated aq. NaHCO₃ (100 mL), brine (100 mL), dried over Na₂SO₄, filtered and concentrated under reduced pressure. The hydrate product is known compound, the following data are identical to those given in corresponding literature [8] and used for next step without further purification. The yield was determined by **19F NMR** analysis using BTF as an internal standard (reaction 1).

Pink liquid (96% yield). **19F NMR** (282 MHz, CDCl₃) δ -81.2 (brs, 3F), -81.6 (brs, 3F) -120.4 (brs, 2F), -121.5--122.0 (m, 8F), -122.8 (brs, 2F), -126.2 (brs, 2F).

A solution of hydrate (10 mmol) in ethanol (200 mmol) was stirred at 70 °C for 4 h, and evaporated under reduced pressure. The ethyl acetal was purified by distillation with P₂O₅ (760 Torr, 36 °C) to provide the corresponding perfluoroalkylated ketone 3a.

Colorless liquid (39% yield); **13C NMR** (75 MHz, Acetone-δ₆) δ 176.0, 173.5, 114.3 (q, Jₖ₋₋₆ = 287.9 Hz), 114.3 (q, Jₖ₋₋₆ = 287.9 Hz), 114.2-104.5 (m); **19F NMR** (282 MHz, Acetone-δ₆) δ -75.2 (s, 3F), -81.8--81.9 (m, 3F), -118.9 (brs, 2F), -122.0--122.5 (m, 8F), -123.2 (brs, 2F), -126.9 (brs, 2F); HRMS (APCI-TOF) calcd for C₁₀F₂₀O [M⁺]: 515.9630, found: 515.9628; **FT-IR** (neat, cm⁻¹) 527, 558, 655, 724, 787, 818, 852, 910, 1004, 1062, 1146, 1208, 1793.
Catalytic asymmetric methylation of perfluoroalkylated ketone

\[
\begin{align*}
3a & \quad \text{Me}_2Zn (2.0 \text{ eq.}) \\
& \quad (R)-\text{DTB-MeO-BIPHEP} (5 \text{ mol%}) \\
& \quad \text{TBME, -78 °C, 3 h} \\
\rightarrow \\
4a & \quad \text{HO-CF}_3 \\
& \quad \text{Me-CF}_3 \\
& \quad \text{CF}_3 \\
4'a & \quad \text{O}_2N \\
& \quad \text{Me} \\
& \quad \text{CF}_3 \\
& \quad \text{CF}_3 \\
& \quad \text{CF}_3 \\
\end{align*}
\]

To a solution of (R)-DTB-MeO-BIPHEP (5.6 mg, 0.005 mmol) and 3a (30 μL, 0.1 mmol) in TBME (1.0 mL) was added Me₂Zn (1.0 M in heptane, 0.2 mL, 0.2 mmol) dropwise at -78 °C under argon atmosphere, and then the solution was stirred for 3 h. The reaction mixture was quenched with saturated aq. NH₄Cl. The organic layer was separated and the aqueous layer was extracted with Et₂O twice. The combined organic layer was dried over anhydrous Na₂SO₄ and evaporated under controlled pressure (200 mmHg). The concentrated solution was used without purification for the next protection reaction. The yield of alcohol product 4a (87%) was determined by $^{19}$F NMR analysis using benzotrifluoride (BTF) as an internal standard.

$^1$H NMR (300 MHz, CDCl₃) δ 2.90 (s, 1H), 1.67 (s, 3H); $^{19}$F NMR (282 MHz, CDCl₃) δ -78.1 (s, 3F), -82.0--81.0 (m, 3F), -117.8--120.3 (m, 4F), -121.6--122.0 (m, 6F), -122.9 (s, 2F), -126.3 (br s).

To a solution of DMAP (1.2 mg, 0.01 mmol) and the crude product in CH₂Cl₂ (2.0 mL) was added NEt₃ (56 μL, 0.4 mmol) at room temperature under argon atmosphere. After the reaction mixture was cooled to 0 °C, 3,5-dinitrobenzoyl chloride (69 mg, 0.3 mmol) was added. Then the mixture was warmed to room temperature and stirred for 1 h. After 1 N HCl (5.0 mL) was added to the reaction mixture. The organic layer was separated and the aqueous layer was extracted with Et₂O twice. The combined organic layer was washed with saturated aq. NaHCO₃, water, brine, and dried over anhydrous MgSO₄, and evaporated under reduced pressure. The residue was purified by silica-gel column chromatography (EtOAc/hexane 1:60) to give 3,5-dinitrobenzoylated alcohol 4’a as a white solid (45% yield for 2 steps, 24% ee). Enantiomeric excess was determined by chiral HPLC analysis. The absolute configuration was not determined.

$^1$H NMR (300 MHz, CDCl₃) δ 9.30 (t, 1H, $J = 2.1$ Hz), 9.11 (d, 2H, $J = 2.1$ Hz), 2.28 (s, 3H); $^{13}$C NMR (75 MHz, CDCl₃) δ 158.6, 148.9, 132.3, 129.7, 123.4, 121.7 (q, $J_{C-F} = 286.5$ Hz), 120.5-104.3 (m), 117.1 (q, $J_{C-F} = 286.8$, 32.1 Hz), 84.9-83.9 (m); $^{19}$F NMR (282 MHz, CDCl₃) δ -73.5 (m, 3F), -80.8 (m, 3F), -116.4 (brs, 2F), -119.2 (brs, 2F), -121.4--121.9 (m, 6F), -122.7 (brs, 2F), -126.1 (brs, 2F); HRMS (ESI-TOF) calcd for C₁₃H₁₃F₃NaO₄[M⁺]: 725.9907, found: 725.9934; FT-IR (KBr pellet, cm⁻¹) 653, 732, 928, 969, 1100, 1149, 1217, 1254, 1341, 1458, 1544, 1634, 1763, 2861, 2925, 2954, 3105; $[\alpha]_D^{22}$ -1.76 (c 0.61, CHCl₃), 24% ee; HPLC (column, CHIRALCEL OD-3, Hexane/2-Propanol = 96/4, flow rate 0.8 mL/min, 20 °C detection UV 254 nm) $t_R$ of major isomer 19.1 min, $t_R$ of minor isomer 22.4 min.
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