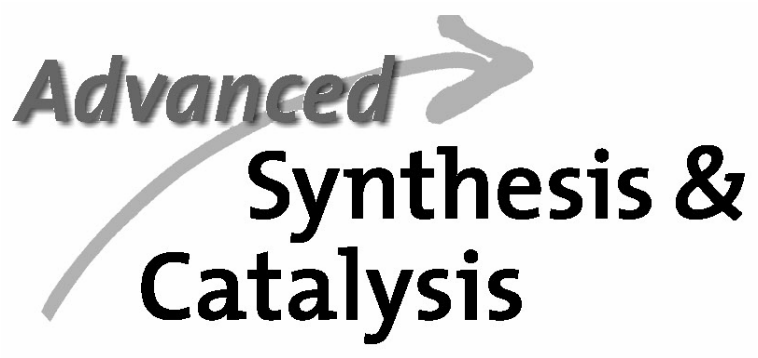

Supporting Information

Supporting Information

Dynamic Kinetic Resolution of Primary Alcohols with an Unfunctionalized Stereogenic Center in the ß-Position

*Dirk Strübing, Patrik Krumlinde, Julio Piera and Jan-E. Bäckvall**

General

Unless otherwise noted, all reagents were used as received from commercial suppliers. Furthermore, all manipulations were performed under argon. Flash chromatography was carried out with 60 Å (35-70 µm) silica gel. ^{1}H and ^{13}C NMR spectra were recorded at 400 and at 100, respectively. Chemical shifts (d) are reported in ppm, using the residual solvent peak in $CDCl_3$ (d(H)= 7.26 and d(C)= 77.00 ppm) as internal standard, and coupling constants (*J*) are given in Hz. The studied lipase from *Burkholderia cepacia* (PS-D I) was purchased from Aldrich.

The enantiomeric excesses (ee) for all compounds were determined via different procedures listed in the table below using racemic compounds as references. Since the determination of the respective ee-values for compounds **8b-i** was not successfully accomplished via chiral HPLC- or GC-analysis, those products were hydrolyzed with a 1 M methanolic solution of NaOH to the corresponding alcohols **2b-i**.

compound	method	retention-times [min]
4a	**A**	24.6/26.1
2b	**B**	11.6/11.9
2c	**C**	23.6/27.1
2d	**D**	9.1/9.3
2e	**D**	9.9/10.0
2f	**D**	33.5/36.6
2g	**E**	41.3/44.3
2h	**F**	29.8/33.1
2i	**D**	6.6/6.7

A: chiral HPLC-analysis (Chiracel OD-H), hexane:2-propanol = 99.2:0.8, flow = 0.5 mL/min.

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B: chiral GC-analysis: (CP-Chirasil-DEX CB, 25 X mm), Injector 250°C, 1.8 mL/min (constant flow), carrier: H_2Program:

T [°C]	Rate [c/min]	Hold [min]	Total [min]
110	0	0	0
135	2	0	12.5
200	80	6	19.31

C: chiral HPLC-analysis (Chiracel OJ), hexane:2-propanol = 95:5, flow = 0.5 mL/min.

D: chiral GC-analysis: (CP-Chirasil-DEX CB, 25 X mm), Injector 250°C, 1.8 mL/min (constant flow), carrier: H_2
Program:

T [°C]	Rate [c/min]	Hold [min]	Total [min]
110	0	0	0
180	5	0	14
200	80	6	20.25

E: chiral HPLC-analysis (Chiracel AS), hexane:2-propanol = 95:5, flow = 0.5 mL/min.

F: chiral HPLC-analysis (Chiracel OB), hexane:2-propanol = 98:2, flow = 0.5 mL/min.

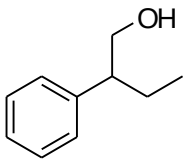
G: chiral HPLC-analysis (Chiracel AS), hexane:2-propanol = 98:2, flow = 0.5 mL/min.

Experimental data:

Part I (primary alcohols):

Except of **2a** which is commercially available, all racemic alcohols were synthesized by literature-known procedures.[1] Analytical data were in accordance with the references, provided in the respective literature.

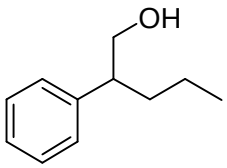
2-Phenylbutan-1-ol (2b):



^{1}H NMR (400 MHz, $CDCl_3$) δ= 7.38-7.20 (m, 5H), 3.76 (dd, *J* = 10.8 Hz, 5.9 Hz, 1H), 3.71 (dd, *J* = 10.8 Hz, 7.7 Hz, 1H), 2.7 (m, 1H), 1.78 (m, 1H), 1.70 (s, 1H), 1.60 (m, 1H),

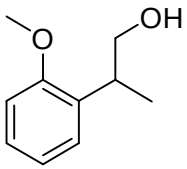
0.86 (t, *J* = 7.4 Hz, 3H) ppm **$^{13}C\{^{1}H\}$ NMR** (100 MHz, $CDCl_3$) δ= 142.3, 128.5, 128.0, 126.6, 67.2, 50.4, 24.9, 11.9 ppm.

2-Phenylpentan-1-ol (2c):



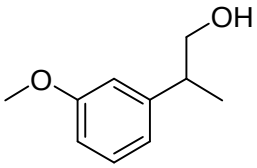
^{1}H NMR (400 MHz, $CDCl_3$) δ= 7.36-7.30 (m, 2H), 7.27-7.19 (m, 3H), 3.80-3.66 (m, 2H), 2.80 (m, 1H), 1.73-1.51 (m, 2H), 1.34 (s, 1H), 1.23 (m, 2H), 0.88 (t, *J* = 7.3 Hz, 3H) ppm. **$^{13}C\{^{1}H\}$ NMR** (100 MHz, $CDCl_3$) δ= 142.5, 128.6, 128.0, 126.7, 67.6, 48.4, 34.2, 20.5, 14.1 ppm.

2-(2-Methoxyphenyl)propan-1-ol (2d):



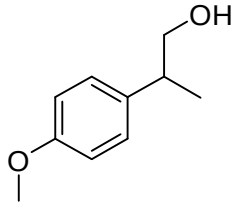
^{1}H NMR (400 MHz, $CDCl_3$) δ= 7.25-7.19 (m, 2H), 6.97-6.93 (m, 1H), 6.89-6.87 (m, 1H), 3.83 (s, 3H), 3.76-3.66 (m, 2H), 3.44 (m, 1H), 1.53 (brs, 1H), 1.26 (d, *J* = 7.2 Hz, 3H) ppm. **$^{13}C\{^{1}H\}$ NMR** (100 MHz, $CDCl_3$) δ= 157.5, 132.0, 127.6, 127.5, 121.0, 110.8, 68.0, 55.6, 35.4, 16.7 ppm

2-(3-Methoxyphenyl)propan-1-ol (2e):



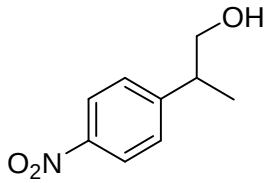
^{1}H NMR (400 MHz, $CDCl_3$) δ= 7.27-7.23 (m, 1H), 6.84-6.76 (m, 3H), 3.80 (s, 3H), 3.68 (d, *J* = 7.2 Hz, 2H), 2.92 (m, 1H), 1.45 (brs, 1H), 1.26 (d, *J* = 6.8 Hz, 3H) ppm. **$^{13}C\{^{1}H\}$ NMR** (100 MHz, $CDCl_3$) δ= 160.0, 145.6, 129.8, 120.0, 113.7, 111.9, 68.8, 55.3, 42.7, 17.7 ppm.

2-(4-Methoxyphenyl)propan-1-ol (2f):



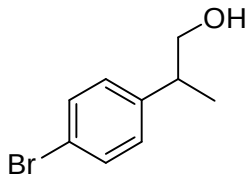
^{1}H NMR (400 MHz, $CDCl_3$) δ= 7.15 (d, *J* = 8.8 Hz, 2H), 6.87 (d, *J* = 8.8 Hz, 2H), 3.78 (s, 3H), 3.65 (d, *J* = 6.8 Hz, 2H), 2.88 (m, 1H), 1.72 (brs, 1H), 1.24 (d, *J* = 6.8 Hz, 3H); **^{13}C{^{1}H} NMR** (100 MHz, $CDCl_3$) δ= 158.5, 135.9, 128.6, 114.2, 68.9, 55.4, 41.7, 17.9 ppm.

2-(4-Nitrophenyl)propan-1-ol (2g):



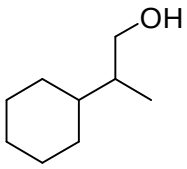
^{1}H NMR (400 MHz, $CDCl_3$) δ= 8.17 (d, *J* = 8.6 Hz, 2H), 7.40 (d, *J* = 8.6 Hz, 2H), 3.77 (dd, *J* = 8.6 Hz, 4.1 Hz, 1H), 3.73 (dd, *J* = 8.6 Hz, 4.8 Hz, 1H), 3.07 (m, 1H), 1.62 (s, 1H), 1.31 (d, *J* = 7.0 Hz, 3H) ppm. **^{13}C{^{1}H} NMR** (100 MHz, $CDCl_3$) δ= 151.9, 146.7, 128.3, 123.7, 68.0, 42.3, 17.3 ppm.

2-(4-Bromophenyl)propan-1-ol (2h):



^{1}H NMR (400 MHz, $CDCl_3$) δ= 7.44 (d, *J* = 8.4 Hz, 2H), 7.11 (d, *J* = 8.4 Hz, 2H), 3.64 (d, *J* = 6.9 Hz, 2H), 2.89 (dq, *J* = 6.9 Hz, 6.9 Hz, 1H), 1.75 (s, 1H), 1.24 (d, *J* = 6.9 Hz, 3H) ppm. **^{13}C{^{1}H} NMR** (100 MHz, $CDCl_3$) δ= 142.8, 131.5, 129.2, 120.2, 68.3, 41.8, 17.4 ppm.

2-Cyclohexylpropan-1-ol (2i)

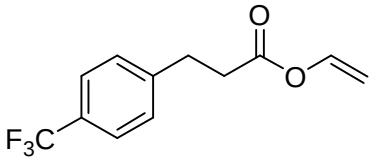


^{1}H NMR (400 MHz, $CDCl_3$) δ= 3.59 (dd, *J* = 10.5 Hz, 5.7 Hz, 1H), 3.43 (dd, *J* = 10.5 Hz, 6.9 Hz, 1H), 1.75-1.68 (m, 2H), 1.66 (s, 1H), 1.65-1.58 (m, 3H), 1.47 (m, 1H), 1.36-0.91 (m, 6H), 0.87 (d, *J* = 6.9 Hz, 3H) ppm. **^{13}C{^{1}H} NMR** (100 MHz, $CDCl_3$) δ= 66.2, 40.9, 39.3, 30.9, 28.7, 26.8, 26.7, 26.6, 13.3 ppm.

Part 2 (acyl donors)

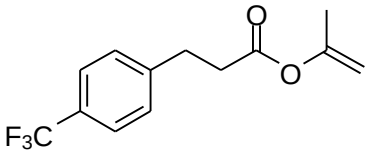
Vinyl 3-(4-(trifluoromethyl)phenyl)propanoate (3):

Acyl donor (**3**) was prepared according to a procedure reported in the literature.[2]



^{1}H NMR (400 MHz, $CDCl_3$) δ= 7.56 (d, *J* = 8.0 Hz, 2H), 7.33 (d, *J* = 8.0 Hz, 2H), 7.27 (dd, *J* = 14.0 Hz, 6.3 Hz, 1H), 4.88 (dd, *J* = 14.0 Hz, 1.7 Hz, 1H), 4.59 (dd, *J* = 6.3 Hz, 1.7 Hz, 1H), 3.05 (t, *J* = 7.6 Hz, 2H), 2.74 (t, *J* = 7.6 Hz, 2H) ppm. **^{13}C{^{1}H} NMR** (100 MHz, $CDCl_3$) δ= 169.5, 144.1, 141.0, 128.7, 125.5 (q, $^{3}J_{CF}$ = 3.7 Hz), 98.0, 35.0, 30.3 ppm. **HR–MS** (ESI): calc. for $C_{12}H_{11}F_3O_2Na$: 267.0608; found. 267.0603 $[M+Na]^+$.

Prop-1-en-2-yl 3-(4-(trifluoromethyl)phenyl)propanoate (4) :

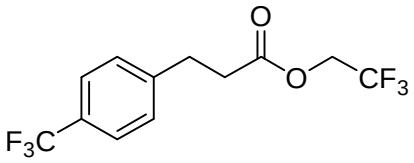


Procedure: A flame-dried schlenk-tube was charged under Ar with 3-(4-(Trifluoromethyl)phenyl)propanoic acid (10 mmol), $RuCl_2$(*p*-cumene)$_2$ (1 mol%),

Na_2CO_3 (4 mol%), $P(Ph)_3$ (2 mol%) and toluene (30 mL) and than flushed with propyne. Afterwards, the reaction was stirred at 60°C for 24h. After cooling, all volatile compounds were removed under reduced pressure. Silica gel flash chromatography (*n*-pentane/EtOAc) afforded **(4)** as a colorless oil in 15% yield.

^{1}H NMR (400 MHz, $CDCl_3$) δ= 7.55 (d, *J* = 8.0 Hz, 2H), 7.34 (d, *J* = 8.0 Hz, 2H), 4.70 (m, 1H), 4.63 (m, 1H), 3.04 (t, *J* = 7.6 Hz, 2H), 2.73 (t, *J* = 7.6 Hz, 2H), 1.87 (m, 3H) ppm. **^{13}C{^{1}H} NMR** (100 MHz, $CDCl_3$) δ= 170.5, 152.9, 144.3, 128.8 (q, $^2J_{CF}$ = 29.9 Hz), 128.7, 125.5 (q, $^3J_{CF}$ = 3.7 Hz), 124.2 (q, $^1J_{CF}$ = 273.7 Hz), 102.1, 35.4, 30.6, 19.5 ppm. **HR–MS** (ESI): calc. for $C_{13}H_{13}F_3O_2Na$: 281.0765; found. 281.0760 $[M+Na]^+$.

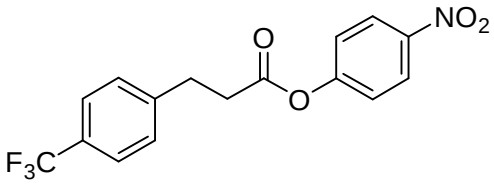
2,2,2-Trifluoroethyl 3-(4-(trifluoromethyl)phenyl)propanoate (5):



Procedure: A 2-necked round bottomed flask was charged with 3-(4-(Trifluoromethyl)phenyl)propanoic acid (3 mmol), 2,2,2-Trifluoroethanol (5 mL) and one drop of DMF. Under ice-cooling, $SOCl_2$ (9 mmol) was added dropwise. Afterwards, the reaction mixture was allowed to reflux for 3h. After cooling, the reaction was quenched with 2M aqueous $NaHCO_3$-solution (20 mL) and then extracted with CH_2Cl_2 (3·20 mL). The combined organic phases were dried over Na_2SO_4 and concentrated under reduced pressure. Silica gel flash chromatography (*n*-^{3}pentane/EtOAc) afforded **(5)** as a colorless oil in 61% yield.

^{1}H NMR (400 MHz, $CDCl_3$) δ= 7.56 (d, *J* = 8.0 Hz, 2H), 7.32 (d, *J* = 8.0 Hz, 2H), 4.46 (q, *J* = 8.4 Hz, 2H), 3.04 (t, *J* = 7.6 Hz, 2H), 2.77 (t, *J* = 7.6 Hz, 2H) **^{13}C{^{1}H} NMR** (100 MHz, $CDCl_3$) δ= 170.8, 143.8, 129.0 (q, $^2J_{CF}$ = 32.4 Hz), 128.6, 125.5 (q, $^3J_{CF}$ = 3.8 Hz), 60.4 (q, $^2J_{CF}$ = 36.7 Hz), 34.7, 30.3 ppm **HR–MS** (ESI): calc. for $C_{12}H_{10}F_6O_2Na$: 323.0482; found. 323.0477 $[M+Na]^+$.

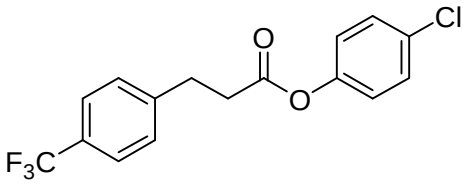
4-Nitrophenyl 3-(4-(trifluoromethyl)phenyl)propanoate (6):



Procedure: A 2-necked round bottomed flask was charged with 3-(4-(Trifluoromethyl)phenyl)propanoic acid (4 mmol), $N(Et)_3$ (4.4 mmol), 4-DMAP (10 mol%) (5 mL) and CH_2Cl_2 (15 mL). Under ice-cooling, 4-Nitrophenyl chloroformate (4 mmol in 10 mL CH_2Cl_2) was added dropwise to the reaction mixture. Afterwards, the reaction mixture was allowed to stir at 0°C for 30 min. Then, the mixture was diluted with CH_2Cl_2 (50 mL) and washed with sat. $NaHCO_3$-solution (20 mL), 0.1 M HCl (20 mL) and brine (20 mL), respectively. The organic phase was dried over Na_2SO_4 and concentrated under reduced pressure. Silica gel flash chromatography (*n*-pentane/EtOAc) afforded **(6)** as a white solid in 53% yield.

^{1}H NMR (400 MHz, $CDCl_3$) δ= 8.26 (d, *J* = 9.1 Hz, 2H), 7.59 (d, *J* = 8.1 Hz, 2H), 7.39 (d, *J* = 8.1 Hz, 2H), 7.20 (d, *J* = 9.1 Hz, 2H), 3.14 (t, *J* = 7.5 Hz, 2H), 2.96 (t, *J* = 7.5 Hz, 2H) ppm. **^{13}C{^{1}H} NMR** (100 MHz, $CDCl_3$) δ= 170.0, 155.2, 145.4, 143.7, 128.9, 125.6 (q, $^3J_{CF}$ = 3.6 Hz), 125.2, 122.3, 35.4, 30.4 ppm. **HR–MS** (ESI): calc. for $C_{20}H_{21}F_3O_2Na$: 362.0616; found. 362.611 $[M+Na]^+$.

4-Chlorophenyl 3-(4-(trifluoromethyl)phenyl)propanoate (7):



Procedure: A 2-necked round bottomed flask was charged with 3-(4-(Trifluoromethyl)phenyl)propanoic acid (4 mmol), $N(Et)_3$ (4.4 mmol), 4-DMAP (10 mol%) (5 mL) and CH_2Cl_2 (15 mL). Under ice-cooling, 4-Chlorophenyl chloroformate (4 mmol in 10 mL CH_2Cl_2) was added dropwise to the reaction mixture. Afterwards, the reaction mixture was allowed to stir at 0°C for 30 min. Then, the mixture was diluted with CH_2Cl_2 (50 mL) and washed with sat. $NaHCO_3$-solution (20 mL), 0.1 M HCl (20 mL) and brine (20 mL), respectively. The organic phase was dried over Na_2SO_4 and concentrated under reduced pressure. Silica gel flash chromatography (*n*-pentane/EtOAc) afforded **(7)** as a white solid in 48% yield.

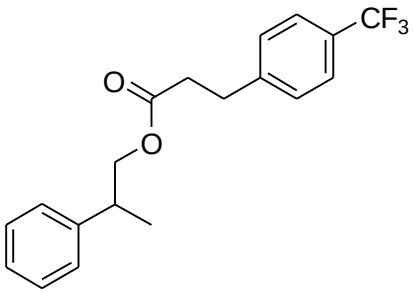
^{1}H NMR (400 MHz, $CDCl_3$) δ= 7.58 (d, *J* = 8.0 Hz, 2H), 7.38 (d, *J* = 8.0 Hz, 2H), 7.33 (d, *J* = 8.9 Hz, 2H), 6.96 (d, *J* = 8.9 Hz, 2H), 3.12 (t, *J* = 7.5 Hz, 2H), 2.91 (t, *J* = 7.5 Hz, 2H) ppm. **^{13}C{^{1}H} NMR** (100 MHz, $CDCl_3$) δ= 170.7, 149.0, 144.0, 131.3, 129.5, 128.8, 125.6 (q, $^3J_{CF}$ = 3.7 Hz), 122.8, 35.4, 30.5 ppm **HR–MS** (ESI): calc. for $C_{16}H_{12}ClF_2O_2Na$: 351.0375; found. 351.0361 $[M+Na]^+$.

Part 3 (DKR-products)

General procedure for the DKR of primary alcohols:

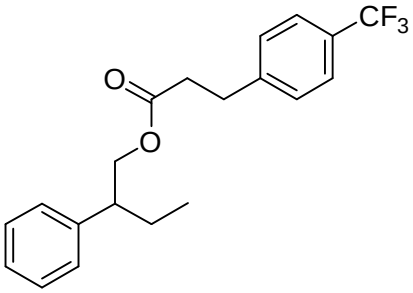
A flame-dried schlenk-tube was charged under Ar with 0.5 mmol of the respective alcohol, 0.6 mmol 4-Nitrophenyl 3-(4-(trifluoromethyl)phenyl)propanoate (**6**), 5 mol% Shvo-catalyst (**1**), 15 mg PS-D "Amano" I and toluene (5mL). The mixture was stirred for 24h at 80°C. Afterwards 5mg of fresh PS-D "Amano" I were added and the reaction was allowed to continue for additional 12h at 80°C. After cooling, all volatile compounds were removed under reduced pressure. Silica gel flash chromatography (*n*-pentane/EtOAc) afforded the corresponding products.

2-Phenylpropyl 3-(4-(trifluoromethyl)phenyl)propanoate (8a):



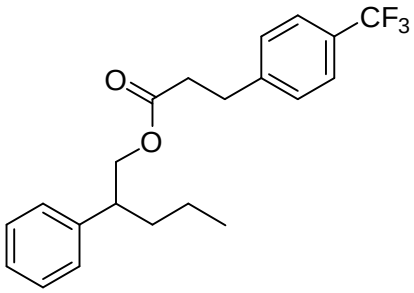
Yield : 87 %. **ee:** 93%. **^{1}H NMR** (400 MHz, $CDCl_3$) δ= 7.51 (d, *J* = 8.1 Hz, 2H), 7.33-7.17 (m, 7H), 4.20 (dd, *J* = 10.8 Hz, 7.1 Hz, 1H), 4.13 (dd, *J* = 10.8 Hz, 7.0 Hz, 1H), 3.06 (m, 1H), 2.94 (t, *J* = 7.6 Hz, 2H), 2.60 (t, *J* = 7.6 Hz, 2H), 1.26 (d, *J* = 7.0 Hz) ppm. **^{13}C{^{1}H} NMR** (100 MHz, $CDCl_3$) δ= 172.3, 144.5, 143.0, 128.6, 128.5, 127.2, 126.7, 125.4 (q, $^3J_{CF}$ = 3.7 Hz), 69.5, 38.9, 35.3, 30.6, 18.0 ppm. **HR–MS** (ESI): calc. for $C_{19}H_{19}F_3O_2Na$: 359.1234; found. 359.1229 $[M+Na]^+$.

2-Phenylbutyl 3-(4-(trifluoromethyl)phenyl)propanoate (8b):



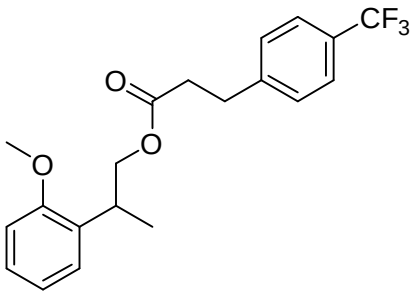
Yield: 80 %. **ee:** 78%. **^{1}H NMR** (400 MHz, $CDCl_3$) δ= 7.53 (d, *J* = 8.1 Hz, 2H), 7.32 (m, 2H), 7.24 (m, 3H), 7.17 (m, 2H), 4.24 (m, 2H), 2.94 (t, *J* = 7.6 Hz, 2H), 2.81 (m, 1H), 2.60 (t, *J* = 7.6 Hz, 2H), 1.73 (m, 1H), 1.6 (m, 1H), 0.83 (t, *J* = 7.4 Hz, 3H) ppm. **^{13}C{^{1}H} NMR** (100 MHz, $CDCl_3$) δ= 172.3, 144.5, 141.6, 128.6, 128.6 (q, $^{2}J_{CF}$ = 32.3 Hz), 128.4, 127.8, 126.7, 125.3 (q, $^{3}J_{CF}$ = 3.7 Hz), 124.2 (q, $^{1}J_{CF}$ = 271.8 Hz), 68.3, 46.6, 35.3, 30.5, 25.3, 11.7 ppm. **HR–MS** (ESI): calc. for $C_{20}H_{21}F_3O_2Na$: 377.1391; found. 377.1386 $[M+Na]^+$.

2-Phenylpentyl 3-(4-(trifluoromethyl)phenyl)propanoate (8c):



Yield: 70 %. **ee:** 86%. **^{1}H NMR** (400 MHz, $CDCl_3$) δ= 7.51 (d, *J* = 8.0 Hz, 2H), 7.32-7.20 (m, 5H), 7.15 (d, *J* = 8.0 Hz, 2H), 4.21 (dd, ^{1}J = 6.8, ^{2}J = 1.2 Hz, 2H), 2.91 (t, *J* = 7.4 Hz, 2H), 2.90 (m, 1H), 2.58 (t, *J* = 7.4 Hz, 2H), 1.66-1.53 (m, 2H), 1.25-1.15 (m, 2H), 0.86 (t, *J* = 7.4 Hz, 3H) ppm. **^{13}C{^{1}H} NMR** (100 MHz, $CDCl_3$) δ= 172.5, 144.7, 142.1, 128.9 (q, $^{2}J_{CF}$ = 31.9 Hz), 128.8, 128.6, 128.0, 126.8, 125.6 (q, $^{3}J_{CF}$ = 3.8 Hz), 124.4 (q, $^{1}J_{CF}$ = 270.1 Hz), 68.8, 44.8, 35.5, 34.7, 30.9, 30.7, 20.5, 14.2 ppm. **HR–MS** (ESI): calc. for $C_{21}H_{23}F_3O_2Na$: 387.1548; found. 387.1540 $[M+Na]^+$.

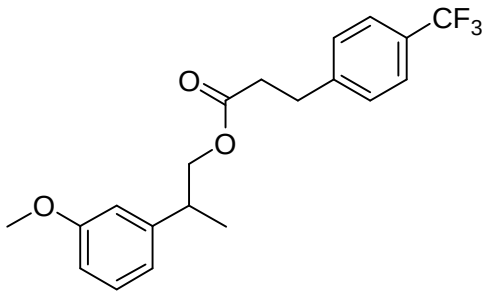
2-(2-Methoxyphenyl)propyl 3-(4-(trifluoromethyl)phenyl)propanoate (8d)



Yield: 72 %. **ee:** >99%. **^{1}H NMR** (400 MHz, $CDCl_3$) δ= 7.54 (d, *J* = 8.0 Hz, 2H), 7.27 (d, *J* = 8.0 Hz, 2H), 7.23 (td, *J* = 8.2 Hz, 1.7 Hz, 1 H), 7.17 (dd, *J* = 7.6 Hz, 1.7 Hz, 1H), 6.94 (td, *J* = 7.6 Hz, 1.0 Hz, 1H), 6.88 (dd, *J* = 8.2 Hz, 1.0 Hz, 1H), 4.26 (dd, *J* = 10.6 Hz, 6.2 Hz, 1H), 4.18 (dd, *J* = 10.6 Hz, 7.3 Hz, 1H), 3.83 (s, 3H), 3.53 (m, 1H), 2.97 (t, *J* =

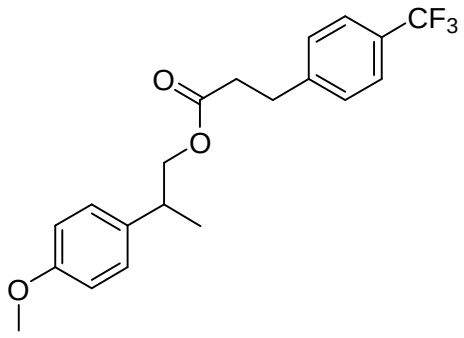
7.6 Hz, 2H) 2.63 (t, *J* = 7.6 Hz, 2H), 1.26 (d, *J* = 7.0 Hz, 3H) ppm. **$^{13}C\{^{1}H\}$ NMR** (100 MHz, $CDCl_3$) δ= 172.4, 157.1, 144.6, 131.0, 128.6, 128.5 (q, $^{2}J_{CF}$ = 32.3 Hz) 127.5, 127.3, 125.3 (q, $^{3}J_{CF}$ = 3.8 Hz), 124.2 (q, $^{1}J_{CF}$ = 271.8 Hz) 120.5, 110.4, 68.5, 55.2, 35.3, 32.1, 30.6, 16.8 ppm. **HR–MS** (ESI): calc. for $C_{20}H_{21}F_3O_2Na$: 389.1341; found. 389.1335 $[M+Na]^+$.

2-(3-Methoxyphenyl)propyl 3-(4-(trifluoromethyl)phenyl)propanoate (8e):



Yield: 85 %. **ee:** 83%. **^{1}H NMR** (400 MHz, $CDCl_3$) δ= 7.53 (d, *J* = 8.0 Hz, 2H), 7.26 (d, *J* = 8.0 Hz, 2H), 7.23 (d, *J* = 7.8 Hz, 1H), 6.82-6.78 (m, 3H), 4.22 (dd, *J* = 10.8 Hz, 7.1 Hz, 1H), 4.15 (dd, *J* = 10.8 Hz, 7.1 Hz, 1H), 3.81 (s, 3H), 3.06 (m, 1H), 2.97 (t, *J* = 7.6 Hz, 2H), 2.63 (t, *J* = 7.6 Hz, 2H), 1.27 (d, *J* = 7.0 Hz, 3H) ppm. **$^{13}C\{^{1}H\}$ NMR** (100 MHz, $CDCl_3$) δ= 172.3, 159.7, 144.7, 144.5, 129.4, 128.6, 128.6 (q, $^{2}J_{CF}$ = 32.4 Hz), 125.3 (q, $^{3}J_{CF}$ = 3.7 Hz), 124.2 (q, $^{1}J_{CF}$ = 271.9 Hz) 119.6, 113.3, 111.6, 69.4, 55.1, 38.9, 35.3, 30.6, 17.9 ppm. **HR–MS** (ESI): calc. for $C_{20}H_{21}F_3O_2Na$: 389.1341; found. 389.1335 $[M+Na]^+$.

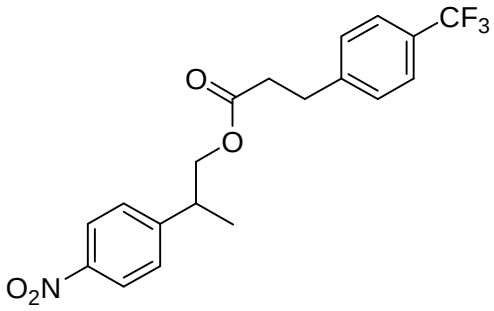
2-(4-Methoxyphenyl)propyl 3-(4-(trifluoromethyl)phenyl)propanoate (8f):



Yield: 70 %. **ee:** 71%. **^{1}H NMR** (400 MHz, $CDCl_3$) δ= 7.54 (d, *J* =8.0 Hz, 2H), 7.27 (d, *J* = 8.0 Hz, 2H), 7.13 (d, *J* = 8.7 Hz, 2H), 6.87 (d, *J* = 8.7 Hz, 2H), 4.18 (dd, *J* = 10.8 Hz, 7.1 Hz, 1H), 4.12 (dd, *J* = 10.8 Hz, 7.1 Hz, 1H), 3.80 (s, 3H), 3.04 (m, 1H), 2.97 (t, *J* =

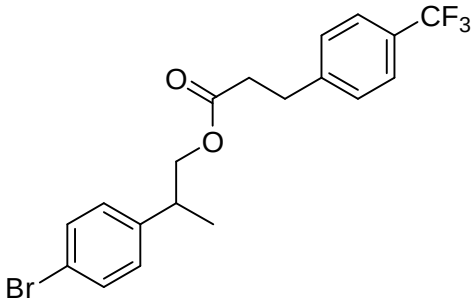
7.6 Hz, 2H), 2.63 (t, *J* = 7.6 Hz, 2H), 1.25 (d, *J* = 7.0 Hz, 3H) **^{13}C{^{1}H} NMR** (100 MHz, $CDCl_3$) δ= 172.3, 158.3, 144.6, 135.0, 128.6, 128.6 (q, $^{2}J_{CF}$ = 32.3 Hz), 128.1, 125.3 (q, $^{3}J_{CF}$ = 3.8 Hz), 124.2 (q, $^{1}J_{CF}$ = 271.7 Hz), 113.8, 69.7, 55.1, 38.0, 35.2, 30.6, 18.0 ppm**. HR–MS** (ESI): calc. for $C_{20}H_{21}F_3O_2Na$: 389.1341; found. 389.1335 $[M+Na]^+$.

2-(4-Nitrophenyl)propyl 3-(4-(trifluoromethyl)phenyl)propanoate (8g):



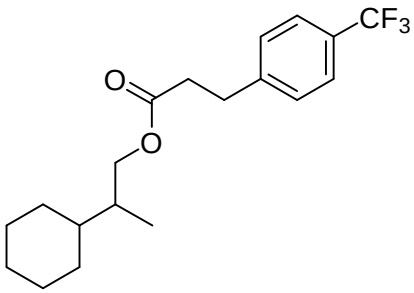
Yield: 85 %. **ee:** 67%. **^{1}H NMR** (400 MHz, $CDCl_3$) δ= 8.15 (d, *J* = 8.8 Hz, 2H), 7.52 (d, *J* = 8.0 Hz, 2H), 7.34 (d, *J* = 8.8 Hz, 2H), 7.26 (d, *J* = 8.0 Hz, 2H), 4.19 (d, *J* = 7.0 Hz, 2H), 3.18 (qt, *J* = 7.0 Hz, 7.0 Hz, 1H), 2.94 (t, *J* = 7.6 Hz, 2H), 2.60 (t, *J* = 7.6 Hz, 2H), 1.28 (d, *J* = 7.0 Hz, 3H) ppm. **^{13}C{^{1}H} NMR** (100 MHz, $CDCl_3$) δ= 172.1, 150.7, 146.9, 144.3, 128.7 (q, $^{2}J_{CF}$ = 32.4 Hz), 128.6, 128.1, 125.4 (q, $^{3}J_{CF}$ = 3.8 Hz), 124.2 (q, $^{1}J_{CF}$ = 271.7 Hz), 123.7, 68.5, 38.9, 35.1, 30.5, 17.7 ppm. **HR–MS** (ESI): calc. for $C_{19}H_{18}F_3NO_4Na$: 404.1086; found. 404.1080 $[M+Na]^+$.

2-(4-Bromophenyl)propyl 3-(4-(trifluoromethyl)phenyl)propanoate (8h):



Yield: 81 %. **ee:** 70%. **^{1}H NMR** (400 MHz, $CDCl_3$) δ= 7.53 (d, *J* = 8.1 Hz, 2H), 7.42 (d, *J* = 8.4 Hz, 2H), 7.26 (d, *J* = 8.1 Hz, 2H), 7.06 (d, *J* = 8.4 Hz, 2H), 4.14 (m, 2H), 3.03 (m, 1H), 2.95 (t, *J* = 7.6 Hz, 2H), 2.60 (t, *J* = 7.6 Hz, 2H), 1.23 (d, *J* = 7.0 Hz, 3H) ppm. **^{13}C{^{1}H} NMR** (100 MHz, $CDCl_3$) δ= 172.2, 144.4, 142.0, 131.5, 129.0, 128.6, 128.6 (q, $^{2}J_{CF}$ = 33.3 Hz), 125.4 (q, $^{3}J_{CF}$ = 3.8 Hz), 124.2 (q, $^{1}J_{CF}$ = 271.9 Hz), 120.4, 69.1, 38.4, 35.2, 30.5, 17.8 ppm. **HR–MS** (ESI): calc. for $C_{19}H_{18}BrF_3O_2Na$: 437.0340; found. 437.0326 $[M+Na]^+$.

2-Cyclohexylpropyl 3-(4-(trifluoromethyl)phenyl)propanoate (8i):



Yield: 84 %. **ee:** 84%. **^{1}H NMR** (400 MHz, $CDCl_3$) δ= 7.54 (d, *J* = 8.0 Hz, 2H), 7.32 (d, *J* = 8.0 Hz, 2H), 4.05 (dd, *J* = 10.8 Hz, 5.7 Hz, 1H), 3.88 (dd, *J* = 10.8 Hz, 7.3 Hz, 1H), 3.01 (t, *J* = 7.6 Hz, 2H), 2.66 (t, *J* = 7.6 Hz, 2H), 1.75-1.55 (m, 6H), 1.29-0.90 (m, 6H), 0.84 (d, *J* = 7.0 Hz, 3H)ppm. **^{13}C{^{1}H} NMR** (100 MHz, $CDCl_3$) δ= 172.6, 144.6, 128.6, 128.6 (q, $^{2}J_{CF}$ = 32.4 Hz) 125.4 (q, $^{3}J_{CF}$ = 3.7 Hz), 124.2 (q, $^{1}J_{CF}$ = 267.4 Hz), 70.0, 39.8, 37.5, 35.4, 30.7, 30.6, 28.9, 26.6, 26.6, 26.5, 13.7 ppm. **HR–MS** (ESI): calc. for $C_{19}H_{25}F_3O_2Na$: 365.1704; found. 365.1699 $[M+Na]^+$.

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[1] For instance, see for a general procedure: W. Adam, S. G. Bosio, N. J. Turro, B. T. Wolff, *J. Org. Chem.* **2004**, *69*, 1704-1715.

[2] M. Kawasaki, M. Goto, S. Kawabata, T. Kometani, *Tetrahedron: Asymmetry* **2001**, *12*, 585-596.