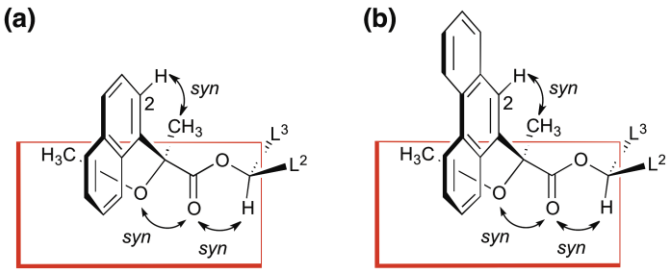
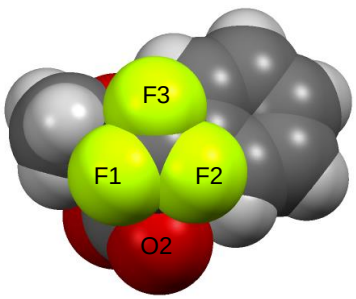
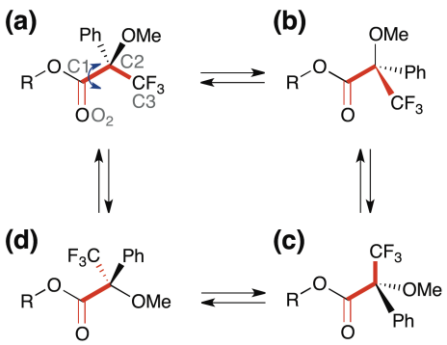


Supplementary Fig. S1 Major conformations of (a) (*S*)-MαNP ester and (b) (*S*)-M9PP ester.



Supplementary Fig. S2 X-ray crystal structure of (*R*)-MTPA anion in salt **3** represented by a space-filling model.

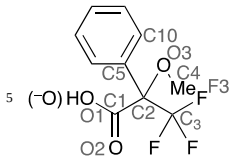


Supplementary Scheme S1 Selected rotamers of the crystalline (R_{acid})-MTPA esters concerning C1–C2 bond. θ is the dihedral angle O2–C1–C2–C3. (a) $\theta = 0°$, (b) $\theta = -60°$, (c) $\theta = 180°$, (d) $\theta = 120°$.

Supplementary Table S1 Dihedral angles in crystalline MTPA salts and MTPA acid

Comp-ound	Species	Space group	Year	Reference[a]	CCDC	Chirality (MTPA)	Amine	O2–C1–C2–C3[b]	C1–C2–C3–F3[c]	O3–C2–C5–C10[d]	C1–C2–O3–C4	O1–C1–C2–O3
1	salt	$P2_12_12_1$	2009	*Helv. Chim. Acta*, 2009, **92**, 14.	694216	*S*	tertiary amine	13.8(3)	173.5(2)	-18.8(3)	-48.2(3)	-46.3(3)
2	salt	$P2_1$	2002	*J. Chem. Soc., Perkin Trans. 2*, 2002, 2093.	190457	*S*	tertiary amine	58.2(4)	175.7(3)	51.6(4)	165.3(3)	-6.9(4)
3	salt	$P2_1$	2002	*J. Chem. Soc., Perkin Trans. 2*, 2002, 2093.	190458	*S*	tertiary amine	33.8(3)	164.7(2)	-34.0(3)	-65.0(3)	-24.4(3)
4	salt	$P2_1$	2000	*J. Chem. Soc., Perkin Trans. 2*, 2000, 111.	140014	*S*	primary amine	22.1(3)	170.2(2)	-24.8(3)	-63.7(3)	-38.3(3)
5	acid	$P2_12_12_1$	2010	*Synthesis*, 2010, 3934.	775752	*R*	(an imidazoline and chloroform)	-9.7(5)	-172.9(3)	12.9(5)	50.7(4)	50.3(4)

[a] We regret the omission of the authors' names. [b] The carboxylate oxygen atom that provided a smaller absolute value was defined as O2. [c] The fluorine atom *anti* to C1 was defined as F3. [d] The *ortho*-carbon atom that provided a smaller absolute value was defined as C10.



Supplementary Table S2 Dihedral angles in crystalline MTPA esters

Comp-ound[a]	MTPA moiety[a]	Space group	Year	Reference[b]	CCDC	Chirality[c] (MTPA)	Alcohol	O2–C1–C2–C3	C1–C2–C3–F3[d]	C1'–O1–C1–O2	H1'–C1'–O1–C1[e]	O3–C2–C5–C10	C1–C2–O3–C4
1	1	*R*3	2011	*J. Am. Chem .Soc.*, 2011, **133**, 17494.	839176	*S*	acetal	23.4(3)	171.8(2)	3.9(3)	51.6(2)	-33.0(3)	-58.1(3)
2	2	$P2_12_12_1$	2011	*Tetrahedron Lett.*, 2011, **52**, 1086.	791283	*S*	phenol	28.5(3)	172.0(2)	-7.3(3)	–	-14.8(3)	-54.8(3)
3[f]	3	$P2_12_12_1$	2010	*Tetrahedron*, 2010, **66**, 4144.	751242	*S*	secondary alcohol	26.5(4)	174.4(3)	-1.3(4)	8.1(4)	-10.7(4)	-54.2(4)
4	4	*C*2	2010	*J. Med. Chem.*, 2010, **53**, 7140.	779154	*R*	phenol	-42.7(1)	-172.55(9)	-0.9(2)	–	45.0(1)	-79.6(1)
5	5	$P2_1$	2010	*Heterocycles*, 2010, **82**, 491.	764823	*R*	secondary alcohol	-53(2)	-172(1)	-12(2)	18(1)	38(2)	-73(1)
6	6	*P*1	2009	*Eur. J. Org. Chem.*, 2009, 5525.	734060	*S*	secondary alcohol	-127.7(4)	169.6(3)	6.0(5)	-2.4(4)	57.7(4)	160.5(3)
6	7	*P*1	2009	*Eur. J. Org. Chem.*, 2009, 5525.	734060	*S*	secondary alcohol	31.2(5)	173.7(3)	15.0(5)	-19.6(4)	-23.2(4)	-58.5(4)
6	8	*P*1	2009	*Eur. J. Org. Chem.*, 2009, 5525.	734060	*S*	secondary alcohol	4.7(5)	179.4(3)	0.5(5)	9.2(4)	-19.8(5)	68.4(4)
6	9	*P*1	2009	*Eur. J. Org. Chem.*, 2009, 5525.	734060	*S*	secondary alcohol	-113.4(4)	174.5(3)	6.6(5)	-9.1(4)	52.7(4)	164.1(3)
6	10	*P*1	2009	*Eur. J. Org. Chem.*, 2009, 5525.	734060	*S*	secondary alcohol	49.6(5)	171.1(4)	0.9(5)	-35.4(4)	-33.2(5)	77.2(4)
6	11	*P*1	2009	*Eur. J. Org. Chem.*, 2009, 5525.	734060	*S*	secondary alcohol	28.0(6)	169.7(4)	4.5(6)	12.1(4)	-19.2(5)	-55.1(5)
7	12	$P2_12_12_1$	2009	*Helv. Chim. Acta*, 2009, **92**, 14.	694216	*S*	primary alcohol	-150.5(2)	164.8(2)	1.8(3)	(-174.1(2))	-12.8(3)	-59.8(2)
7	13	$P2_12_12_1$	2009	*Helv. Chim. Acta*, 2009, **92**, 14.	694216	*S*	secondary alcohol	9.5(3)	173.4(2)	-2.6(3)	-40.0(3)	-15.0(3)	-51.8(3)
8	14	$P2_12_12_1$	2009	*J. Nat. Prod.*, 2009, **72**, 912.	721204	*S*	acetal	59.1(4)	168.0(3)	2.3(5)	-31.8(4)	-55.8(4)	81.0(3)
9	15	$P2_1$	2009	*Org. Biomol. Chem.*, 2009, **7**, 3748.	723548	*S*	secondary alcohol	-163.0(1)	168.1(1)	3.1(2)	-5.2(2)	-25.4(2)	-54.6(2)
10	16	$P2_12_12_1$	2008	*Org. Lett.*, 2008, **10**, 3195.	682032	*R*	secondary alcohol	24.6(3)	176.2(2)	7.2(3)	-5.8(2)	14.5(3)	19.9(3)

11	17	*P*1	2008	*Tetrahedron: Asymmetry*, 2008, **19**, 1274.	683188	*R*	phenol	-15(2)	-174(1)	4(2)	–	40(1)	56(1)
11	18	*P*1	2008	*Tetrahedron: Asymmetry*, 2008, **19**, 1274.	683188	*R*	phenol	-16(2)	-172(1)	3(2)	–	41(1)	56(1)
11	19	*P*1	2008	*Tetrahedron: Asymmetry*, 2008, **19**, 1274.	683188	*R*	phenol	-13(2)	-170(1)	-3(2)	–	42(1)	55(1)
11	20	*P*1	2008	*Tetrahedron: Asymmetry*, 2008, **19**, 1274.	683188	*R*	phenol	-9(2)	-172(1)	-5(2)	–	41(1)	56(1)
12	21	$P2_1$	2007	*J. Org. Chem.*, 2007, **72**, 123.	638387	*S*	secondary alcohol	17.5(2)	172.0(1)	-4.4(2)	24.7(2)	-14.2(2)	-54.9(2)
13	22	*P*1	2006	*J. Nat. Prod.*, 2006, **69**, 636.	284777	*S*	secondary alcohol	17.2(4)	171.9(3)	7.9(4)	-26.8(3)	-32.2(4)	-53.5(3)
13	23	*P*1	2006	*J. Nat. Prod.*, 2006, **69**, 636.	284777	*S*	enol	-173.2(3)	173.7(3)	-5.9(4)	–	-23.8(4)	-53.4(3)
14	24	$P2_1$	2006	*Tetrahedron: Asymmetry*, 2006, **17**, 1275.	282786	*S*	phenol	-165(1)	172(1)	2(2)	–	-26(1)	-52(1)
14	25	$P2_1$	2006	*Tetrahedron: Asymmetry*, 2006, **17**, 1275.	282786	*S*	phenol	25(1)	167.4(9)	-5(1)	–	-22(1)	-48(1)
15	26	$P2_1$	2006	*Bull. Chem. Soc. Jpn.*, 2006, **79**, 914.	292039	*S*	tertiary alcohol	28(1)	166(1)	2(1)	(-175.1(7))	-42(1)	-55(1)
15	27	$P2_1$	2006	*Bull. Chem. Soc. Jpn.*, 2006, **79**, 914.	292039	*S*	secondary alcohol	70(2)	163(2)	-9(2)	58(1)	73(1)	156(1)
16	28	$P2_12_12_1$	2006	*J. Med. Chem.*, 2006, **49**, 4055.	649355	*S*	tertiary alcohol	13.6(3)	174.6(2)	4.3(3)	(-165.9(2))	-25.0(3)	-55.8(2)
17	29	$P2_1$	2006	*Org. Lett.*, 2006, **8**, 2957.	619468	*R*	secondary alcohol	-64.9(4)	-168.0(3)	-1.7(5)	-34.6(4)	49.5(4)	-77.9(3)
18	30	$P2_12_12_1$	2005	*Chirality*, 2005, **17**, 149. *Chem. Commun.*, 2001, 1590.	166488	*R*	secondary alcohol	-5.8(4)	-177.4(2)	-7.8(4)	39.5(3)	34.4(3)	-74.5(3)
19	31	$P2_12_12_1$	2005	*Chirality*, 2005, **17**, 149.	239906	*R*	secondary alcohol	-0.3(6)	-179.0(4)	3.8(6)	20(2)	29.1(5)	-66.7(5)
20	32	$P2_12_12_1$	2005	*J. Org. Chem.*, 2005, **70**, 5618.	279359	*S*	secondary alcohol	14(1)	171.5(8)	2(1)	-42.5(8)	-7.2(9)	-51.1(9)
20	33	$P2_12_12_1$	2005	*J. Org. Chem.*, 2005, **70**, 5618.	279359	*S*	secondary alcohol	18(1)	176.7(6)	-11(1)	-27.9(8)	4.6(7)	-51.2(8)
20	34	$P2_12_12_1$	2005	*J. Org. Chem.*, 2005, **70**, 5618.	279359	*S*	secondary alcohol	-144.6(8)	168.6(7)	-3(1)	-27.6(9)	-34.9(8)	73.9(8)
21	35	$P2_1$	2005	*Heterocycles*, 2005, **66**, 405.	282327	*R*	secondary alcohol	31(1)	173.7(7)	-4(1)	22(1)	2(1)	-42(1)
22	36	*P*1	2005	*Tetrahedron*, 2005, **61**, 6015.	267697	*S*	tertiary alcohol	21(2)	171(1)	2(2)	(-170(1))	-25(1)	-52(1)
22	37	*P*1	2005	*Tetrahedron*, 2005, **61**, 6015.	267697	*S*	tertiary alcohol	24(1)	172(1)	2(2)	(-167(1))	-27(1)	-54(1)
23	38	$P2_1$	2004	*Chem.–Eur. J.*, 2004, **10**, 1141.	220664	*R*	1-(1-pyrrolyl)-alcohol	0(1)	179.0(6)	1(1)	-38.2(9)	11(1)	46(1)
23	39	$P2_1$	2004	*Chem.–Eur. J.*, 2004, **10**, 1141.	220664	*R*	1-(1-pyrrolyl)-alcohol	-20(1)	-175.6(7)	-7(1)	-14(1)	7(1)	45(1)
24	40	$P2_1$	2004	*Chem.–Eur. J.*, 2004, **10**, 1141.	220663	*S*	1-(1-pyrrolyl)-alcohol	-131.9(5)	166.6(5)	4.9(7)	-49.0(6)	-41.4(7)	74.0(6)
25	41	*P*1	2004	*Tetrahedron*, 2004, **60**, 1229.	220660	*S*	phenol	-121.8(5)	160.5(4)	0.7(7)	–	-69.0(6)	73.9(5)
25	42	*P*1	2004	*Tetrahedron*, 2004, **60**, 1229.	220660	*S*	phenol	7.2(8)	176.5(5)	2.8(8)	–	-30.9(8)	62(1)
26	43	$P2_12_12_1$	2003	*J. Org. Chem.*, 2003, **68**, 2728.	173882	*R*	secondary alcohol	-21.7(3)	-171.6(2)	-4.8(3)	-13.3(3)	10.8(3)	53.0(2)
27	44	$P2_1$	2003	*Tetrahedron*, 2003, **59**, 3237.	187136	*S*	secondary alcohol	19.6(5)	175.7(3)	4.7(5)	34.4(4)	-1.4(4)	-45.9(4)

28	45	$P2_12_12_1$	2003	*Tetrahedron*, 2003, **59**, 3237.	187135	*S*	secondary alcohol	25.3(3)	170.6(2)	10.4(3)	-37.5(2)	-11.3(3)	-59.7(3)
29	46	$P2_12_12_1$	2003	*Tetrahedron*, 2003, **59**, 3237.	187131	*S*	secondary alcohol	12.7(4)	173.8(2)	-1.4(4)	-49.0(3)	-19.5(3)	-51.1(3)
30	47	$P2_12_12_1$	2003	*Tetrahedron*, 2003, **59**, 3237.	187130	*S*	secondary alcohol	6.7(4)	174.4(3)	0.3(4)	-48.8(4)	-18.7(4)	-48.7(3)
31	48	$P2_12_12_1$	2003	*Bioorg. Med. Chem.*, 2003, **11**, 3215.	200053	*S*	secondary alcohol	25(2)	169(1)	-8(2)	-35(2)	-36(2)	-60(2)
31	49	$P2_12_12_1$	2003	*Bioorg. Med. Chem.*, 2003, **11**, 3215.	200053	*S*	secondary alcohol	10(2)	174(1)	4(2)	-15(2)	-25(2)	-52(1)
32	50	$P2_12_12_1$	2003	*Org. Lett.*, 2003, **5**, 2559.	217795	*R*	secondary alcohol	-18.2(5)	-172.2(3)	2.0(5)	-41.2(5)	20.0(5)	58.1(4)
33	51	$P2_1$	2001	*J. Am. Chem. Soc.*, 2001, **123**, 3143.	162198	*R*	tertiary silanol	-16.3(5)	-172.3(3)	-8.0(4)	(-178.2(2))	16.1(5)	53.7(5)
34	52	$P2_1$	2001	*Org. Lett.*, 2001, **3**, 3293.	174955	*S*	primary alcohol	11.0(3)	177.5(2)	-5.5(4)	(151.4(2))	-19.6(3)	-44.5(3)
35	53	$P2_12_12_1$	2000	*J. Chem. Soc., Perkin Trans.1*, 2000, 3397.	152120	*R*	secondary alcohol	-8(1)	-176.1(7)	8(1)	25.7(9)	34(1)	-72.7(9)
36	54	*C*2	2000	*J. Org. Chem.*, 2000, **65**, 375.	141822	*S*	secondary alcohol	9.6(6)	176.4(4)	7.2(5)	-32.2(5)	-28.9(5)	-52.2(5)
37	55	$P2_12_12_1$	2000	*J. Am. Chem. Soc.*, 2000, **122**, 10781.	159557	*R*	primary alcohol	153.0(7)	-170.0(6)	1(1)	(166.4(5))	11.2(9)	55.0(8)

[a] The 37 crystalline MTPA esters yielded 55 independent MTPA ester moieties because of the presence of *bis*- and *tris*-MTPA esters, and the multiple conformers in a lattice. [b] We regret the omission of the authors' names. [c] The conformations of (R_{acid})-MTPA esters were discussed in this paper; therefore, (S_{acid})-MTPA esters were then substituted by their mirror images. The assignments of the absolute configurations were not confirmed (see the caution in the experimental section). [d] The fluorine atom *anti* to C1 was defined as F3. [e] The dihedral angles L^1–C1'–O1–C1 were noted in parentheses for the MTPA esters prepared from primary alcohols, tertiary alcohols, or tertiary silanol. L^1 is the carbon atom *anti* to C1. [f] The gray rows show the 20 Mosher-type MTPA esters prepared from secondary alcohols, in which the dihedral angles O2–C1–C2–C3 (= θ) were ranged from –30° to 0° (i.e., –30° < $\theta \leq$ 0°) as (R_{acid})-MTPA esters (Fig. 8).