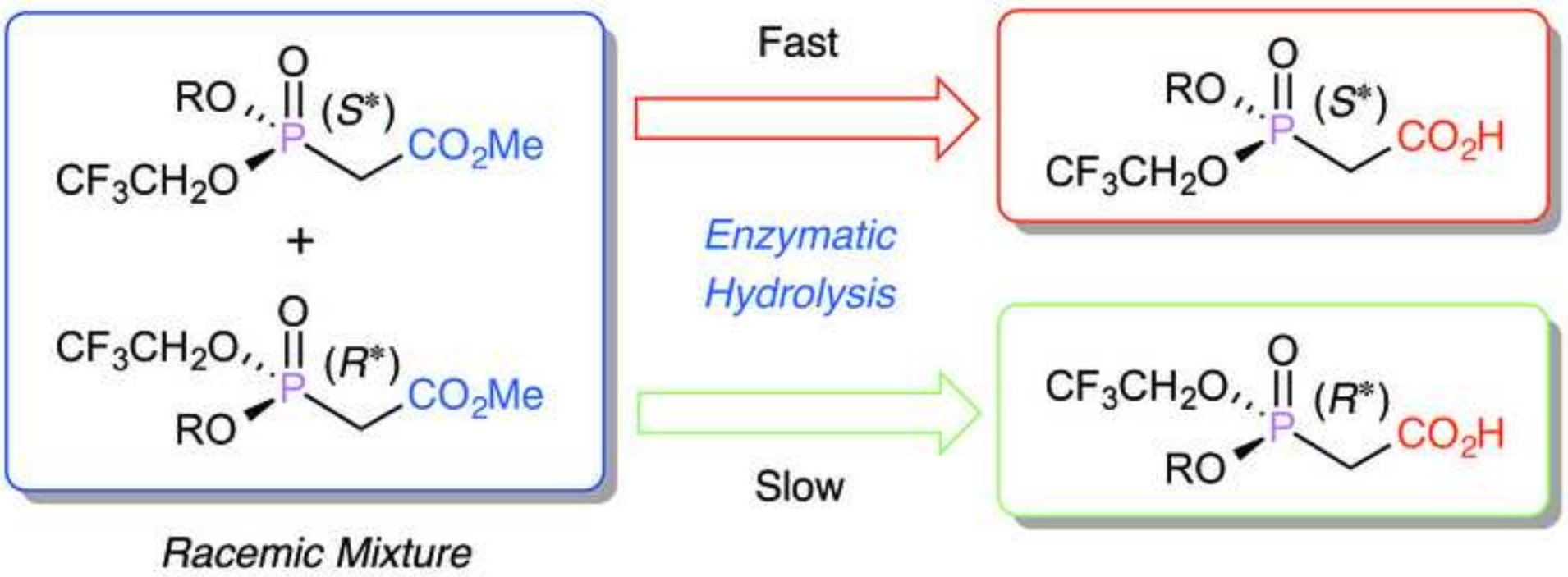
Graphical Abstract

The published version is available via https://doi.org/10.1016/j.cdc.2016.09.001.



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Title: Enzymatic Synthesis of Chiral *P*-Stereogenic Phosphonoacetates

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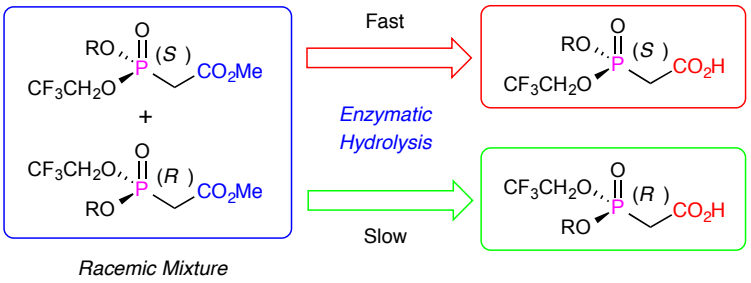
Abstract

In this data article, we describe the enzymatic kinetic resolution of a series of racemic mixed phosphonoacetates, which were successfully prepared from methyl bis(2,2,2-trifluoroethyl)phosphonoacetate (Still-Gennari reagent) by alcoholysis with σ-symmetrical secondary alcohols in the presence of 1,8-diazabicyclo[5.4.0]undec-7-ene (DBU). Porcine liver esterase (PLE)-catalyzed kinetic resolution of some of these racemic mixed phosphonoacetates proceeded in a highly stereoselective manner to furnish the chiral *P*-stereogenic phosphonoacetates (up to >99% ee).

Graphical abstract



Keywords Stereogenic phosphorus atom, Methyl bis(2,2,2-trifluoroethyl)phosphonoacetate, Horner-Wadsworth-Emmons reagent, Kinetic resolution, Enzymatic hydrolysis

Specifications Table

Subject area	*Organic Chemistry*
Compounds	*Methyl 2-[alkoxy(2,2,2-trifluoroethoxy)phosphoryl]acetate, 2-[alkoxy(2,2,2-trifluoroethoxy)phosphoryl]acetic acid*
Data category	*Spectral, synthesized*
Data acquisition format	*NMR, IR, Mass spectra, Elemental analysis, Specific rotation.*
Data type	*Analyzed*
Procedure	*Organic and enzymatic transformation*
Data accessibility	*Within this article*

1. Rationale

Chiral Horner-Wadsworth-Emmons (HWE) reagents are extremely useful for asymmetric olefination of prochiral aldehydes or ketones [1–4]. However, most of these chiral HWE reagents are restricted to the compounds with non-stereogenic phosphorus atom, which are more easily available than *P*-stereogenic HWE reagents. We have already reported the facile synthesis of two kinds of chiral *P*-stereogenic phosphonoacetates (>99% ee) by porcine liver esterase (PLE)-catalyzed kinetic resolution of the corresponding racemic mixed phosphonoacetates [5]. To verify the generality of this synthetic method, a series of racemic mixed phosphonoacetates were synthesized and subjected to enzymatic hydrolysis in the presence of PLE, which has been widely used as a practical biocatalyst in organic synthesis. Nucleophilic substitution of symmetrical secondary alcohols **2a–j** at the phosphorus center of methyl bis(2,2,2-trifluoroethyl)phosphonoacetate (Still-Gennari reagent, **1**) [6,7] furnished racemic mixed phosphonoacetates *rac*-**3a–j** in 66–81% yields [5,8,9]. Enzymatic hydrolysis of *rac*-**3a–j** using PLE gave the corresponding carboxylic acids **4a–j** and allowed recovery of unreacted esters **3a–j**. As a result, racemic mixed phosphonoacetates *rac*-**3a** and *rac*-**3d** afforded the optically enriched *P*-stereogenic phosphonoacetates **3a** (99% ee, 39% yield) and **3d** (>99% ee, 44% yield), respectively.

2. Procedure

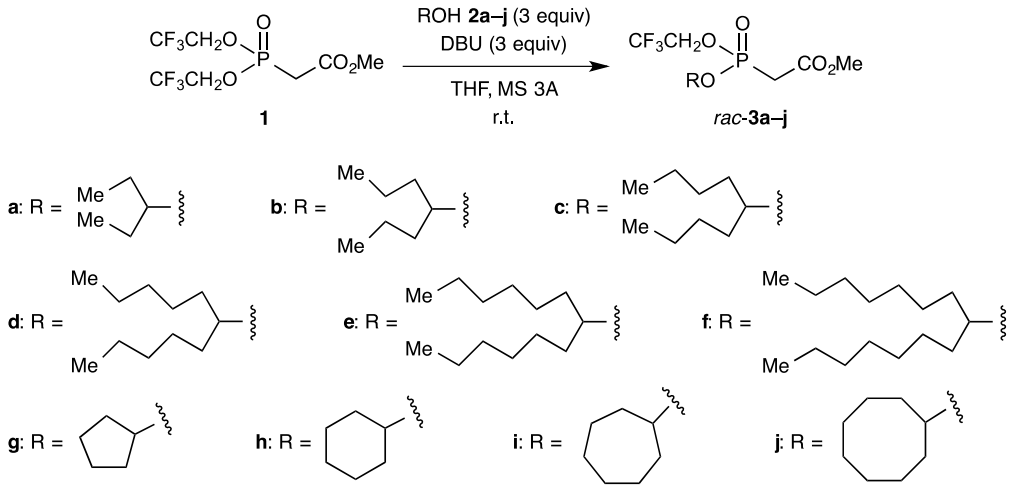
2.1 Materials and methods

All melting points were determined on a Yanagimoto micro melting point apparatus and uncorrected. IR spectra were obtained using a JASCO FT/IR-420 IR Fourier transform spectrometer. ^{1}H-NMR (400 MHz) and ^{13}C-NMR (75 MHz) spectra were recorded on JEOL JNM-AL400, Bruker AV400N, and JEOL JNM-AL300 spectrometers, respectively. Chemical shifts are given in δ values (parts per million) using tetramethylsilane (TMS) as an internal standard. ESI-MS were recorded on a Waters LCT Premier spectrometer. Elemental analyses were performed using a Yanaco CHN CORDER MT-5. Optical rotations were recorded on JASCO digital polarimeter DIP-370. All reactions were monitored by TLC employing 0.25 mm silica gel plates (Merck 5715; 60 F_{254}). Column chromatography was carried out on silica gel (Kanto Chemical 60N; 63–210 µm or Nacalai Tesque 75SL-II-PREP; 75 µm). Chiral-stationary-phase HPLC analyses were performed using a JASCO PU-980 apparatus equipped with a JASCO UV/VIS detector. The absolute configurations of **3a–j** and **4a–j** were not determined. All reagents were used as purchased.

2.2 General procedure for the synthesis of racemic phosphonoacetates *rac*-**3a–j**

DBU (2.24 mL, 15.00 mmol) was added to a solution of methyl bis(2,2,2-trifluoroethyl)phosphonoacetate (**1**) (1.06 mL, 5.00 mmol) and 3-pentanol (**2a**) (1.62 mL, 15.00 mmol) in anhydrous THF (25 mL) containing molecular sieves 3A (powder, 1.59 g) at room temperature under argon. After being stirred at room temperature for 15 h, the reaction mixture was treated with 5% HCl (20 mL) and extracted with AcOEt (100 mL x 3). The extract was washed with brine (30 mL) and dried over anhydrous $MgSO_4$. The organic layer was evaporated *in vacuo* to afford an oily residue, which was

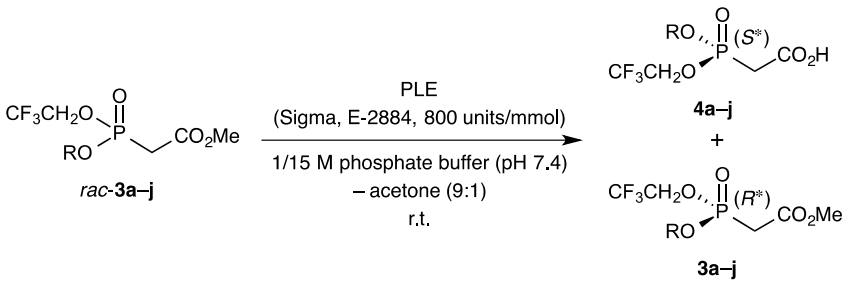
purified by chromatography on silica gel (Kanto Chemical 60N) column [*n*-hexane–AcOEt (3:1)] to give *rac*-**3a** (1.24 g, 81%) as a colorless oil.



Scheme 1. Synthesis of racemic phosphonoacetates *rac*-**3a–j**.

2.3 General procedure for the PLE-catalyzed kinetic resolution of racemic phosphonoacetates *rac*-**3a–j**

PLE (Sigma; E-2884, 240 units, 800 units/mmol) was added to a stirred solution of methyl 2-[(pentan-3-yloxy)(2,2,2-trifluoroethoxy)phosphoryl]acetate (*rac*-**3a**) (91.9 mg, 0.30 mmol) in 1/15 M phosphate buffer (pH 7.4, 9 mL) and acetone (1 mL) at room temperature. After being stirred at room temperature for 1.5 h, the reaction mixture was treated with 5% HCl (5 mL) and then extracted with AcOEt (40 mL x 5). The extract was washed with brine (20 mL) and dried over anhydrous $MgSO_4$. The organic layer was evaporated *in vacuo* to afford an oily residue, which was purified by chromatography on silica gel (Nacalai Tesque 75SL-II-PREP) column [$CHCl_3$–MeOH (50:1)] to give (*S**)-**4a** (53.3 mg, 61%) as a white powder and (*R**)-**3a** (35.5 mg, 39%, 99% ee) as a colorless oil. To the solution of (*S**)-**4a** in MeOH (1 mL) and benzene (3.5 mL) was added an excess amount of $TMSCHN_2$ (2.0 M solution in *n*-hexane, *ca.* 0.3 mL, *ca.* 0.6 mmol). After being stirred at room temperature for 30 min, the reaction mixture was evaporated *in vacuo* to afford a crude product, which was purified by chromatography on a silica gel (Kanto Chemical 60N) column [*n*-hexane–AcOEt (1:1)], giving (*S**)-**3a** (54.3 mg, 97%, 64% ee) as a colorless oil.



Scheme 2. PLE-catalyzed kinetic resolution of racemic phosphonoacetates *rac*-**3a–j**.

2.4 Analytical and spectral data obtained for compounds **3a–j**

Methyl 2-[(Pentan-3-yloxy)(2,2,2-trifluoroethoxy)phosphoryl]acetate (3a)

Colorless oil.

99% ee; $[\alpha]_D^{18}$ +10.0 (*c* 1.00, MeOH).

IR (neat): 2974, 1745, 1263, 1173, 1093, 1001 cm^{-1}

^1H NMR (400 MHz, $CDCl_3$): δ 0.93 (3H, t, $^3J_{H,H}$ = 7.3 Hz), 0.95 (3H, t, $^3J_{H,H}$ = 7.3 Hz), 1.60–1.75 (4H, m), 3.05 (2H, d, $^2J_{H,P}$ = 21.7 Hz), 3.75 (3H, s), 4.35–4.55 (3H, m).

^{13}C NMR (75 MHz, $CDCl_3$): δ 9.2 (s), 9.3 (s), 27.6 (d, $^3J_{C,P}$ = 3.7 Hz), 27.8 (d, $^3J_{C,P}$ = 4.4 Hz), 34.5 (d, $^1J_{C,P}$ = 140.8 Hz), 52.7 (s), 63.1 (qd, $^2J_{C,F}$ = 37.4 Hz, $^2J_{C,P}$ = 5.0 Hz), 82.4 (d, $^2J_{C,P}$ = 7.5 Hz), 123.2 (qd, $^1J_{C,F}$ = 277.4 Hz, $^3J_{C,P}$ = 8.7 Hz), 166.2 (d, $^2J_{C,P}$ = 5.0 Hz).

HRMS (ESI): *m*/*z* $[M + H]^+$ calcd for $C_{10}H_{19}F_3O_5P$: 307.0922; found: 307.0930.

Anal. calcd for $C_{10}H_{18}F_3O_5P$: C, 39.22; H, 5.92. Found: C, 39.05; H, 5.97%.

Methyl 2-[(Heptan-4-yloxy)(2,2,2-trifluoroethoxy)phosphoryl]acetate (3b)

Colorless oil.

IR (neat): 2962, 1745, 1265, 1171, 1093, 1007 cm^{-1}.

^1H NMR (400 MHz, $CDCl_3$): δ 0.92 (3H, t, $^3J_{H,H}$ = 7.3 Hz), 0.93 (3H, t, $^3J_{H,H}$ = 7.3 Hz), 1.28–1.50 (4H, m), 1.52–1.71 (4H, m), 3.03 (2H, d, $^2J_{H,P}$ = 21.5 Hz), 3.75 (3H, s), 4.34–4.61 (3H, m).

^{13}C NMR (75 MHz, $CDCl_3$): δ 13.89 (s), 13.92 (s), 18.2 (s), 18.3 (s), 34.5 (d, $^1J_{C,P}$ = 141.4 Hz), 37.3 (d, $^3J_{C,P}$ = 3.7 Hz), 37.4 (d, $^3J_{C,P}$ = 4.4 Hz), 52.7 (s), 63.1 (qd, $^2J_{C,F}$ = 37.4 Hz, $^2J_{C,P}$ = 4.7 Hz), 79.8 (d, $^2J_{C,P}$ = 7.5 Hz), 123.0 (qd, $^1J_{C,F}$ = 277.6 Hz, $^3J_{C,P}$ = 8.7 Hz), 166.0 (d, $^2J_{C,P}$ = 5.6 Hz).

HRMS (ESI): *m*/*z* $[M + H]^+$ calcd for $C_{12}H_{23}F_3O_5P$: 335.1235; found: 335.1219.

Anal. calcd for $C_{12}H_{22}F_3O_5P$: C, 43.12; H, 6.63. Found: C, 42.89; H, 6.54%.

Methyl 2-[(Nonan-5-yloxy)(2,2,2-trifluoroethoxy)phosphoryl]acetate (3c)

Colorless oil.

IR (neat): 2958, 1745, 1265, 1173, 1093, 1009 cm^{-1}.

^1H NMR (400 MHz, $CDCl_3$): δ 0.83–0.96 (6H, m), 1.22–1.43 (8H, m), 1.54–1.72 (4H, m), 3.04 (2H, d, $^2J_{H,P}$ = 21.5 Hz), 3.75 (3H, s), 4.35–4.60 (3H, m).

^{13}C NMR (75 MHz, $CDCl_3$): δ 13.96 (s), 14.02 (s), 22.6 (s), 27.1 (s), 27.2 (s), 34.5 (d, $^1J_{C,P}$ = 141.4 Hz), 34.9 (d, $^3J_{C,P}$ = 3.7 Hz), 35.0 (d, $^3J_{C,P}$ = 4.4 Hz), 52.7 (s), 63.1 (qd, $^2J_{C,F}$ = 37.4 Hz, $^2J_{C,P}$ = 4.4 Hz), 80.3 (d, $^2J_{C,P}$ = 8.1 Hz), 123.1 (qd, $^1J_{C,F}$ = 277.6 Hz, $^3J_{C,P}$ = 8.7 Hz), 166.0 (d, $^2J_{C,P}$ = 5.0 Hz).

HRMS (ESI): *m*/*z* $[M + H]^+$ calcd for $C_{14}H_{27}F_3O_5P$: 363.1548; found: 363.1556.

Anal. calcd for $C_{14}H_{26}F_3O_5P$: C, 46.41; H, 7.23. Found: C, 46.13; H, 7.17%.

Methyl 2-[(2,2,2-Trifluoroethoxy)(undecan-6-yloxy)phosphoryl]acetate (3d)

Colorless oil.

>99% ee; $[\alpha]_D^{15}$ +7.5 (*c* 0.75, MeOH).

IR (neat): 2956, 2935, 1747, 1265, 1173, 1122, 1093 cm^{-1}.

^{1}H NMR (400 MHz, $CDCl_3$): δ 0.89 (6H, t, $^{3}J_{H,H}$ = 6.7 Hz), 1.16–1.46 (12H, m), 1.52–1.72 (4H, m), 3.03 (2H, d, $^{2}J_{H,P}$ = 21.5 Hz), 3.75 (3H, s), 4.35–4.59 (3H, m).
^{13}C NMR (75 MHz, $CDCl_3$): δ 13.96 (s), 14.02 (s), 22.5 (s), 24.55 (s), 24.60 (s), 31.6 (s), 34.5 (d, $^{1}J_{C,P}$ = 140.8 Hz), 35.1 (d, $^{3}J_{C,P}$ = 3.7 Hz), 35.2 (d, $^{3}J_{C,P}$ = 4.4 Hz), 63.0 (qd, $^{2}J_{C,F}$ = 37.4 Hz, $^{2}J_{C,P}$ = 4.7 Hz), 80.3 (d, $^{2}J_{C,P}$ = 7.5 Hz), 122.9 (qd, $^{1}J_{C,F}$ = 277.6 Hz, $^{3}J_{C,P}$ = 8.7 Hz), 165.9 (d, $^{2}J_{C,P}$ = 5.0 Hz).
HRMS (ESI): *m/z* [M + H]$^{+}$ calcd for $C_{16}H_{31}F_3O_5P$: 391.1861; found: 391.1865.
Anal. calcd for $C_{16}H_{30}F_3O_5P$: C, 49.23; H, 7.75. Found: C, 49.03; H, 7.63%.

Methyl 2-[(Tridecan-7-yloxy)(2,2,2-trifluoroethoxy)phosphoryl]acetate (3e)
Colorless oil.
IR (neat): 2931, 1747, 1267, 1171, 1093, 1003 cm^{-1}.
^{1}H NMR (400 MHz, $CDCl_3$): δ 0.88 (6H, t, $^{3}J_{H,H}$ = 6.5 Hz), 1.17–1.47 (16H, m), 1.52–1.71 (4H, m), 3.03 (2H, d, $^{2}J_{H,P}$ = 21.5 Hz), 3.75 (3H, s), 4.35–4.59 (3H, m).
^{13}C NMR (75 MHz, $CDCl_3$): δ 14.1 (s), 22.69 (s), 22.73 (s), 24.98 (s), 25.03 (s), 29.3 (s), 31.8 (s), 31.9 (s), 34.5 (d, $^{1}J_{C,P}$ = 140.8 Hz), 35.3 (d, $^{3}J_{C,P}$ = 3.7 Hz), 35.4 (d, $^{3}J_{C,P}$ = 4.4 Hz), 52.7 (s), 63.1 (qd, $^{2}J_{C,F}$ = 37.6 Hz, $^{2}J_{C,P}$ = 4.7 Hz), 80.3 (d, $^{2}J_{C,P}$ = 7.5 Hz), 123.1 (qd, $^{1}J_{C,F}$ = 277.4 Hz, $^{3}J_{C,P}$ = 8.7 Hz), 166.0 (d, $^{2}J_{C,P}$ = 5.0 Hz).
HRMS (ESI): *m/z* [M + H]$^{+}$ calcd for $C_{18}H_{35}F_3O_5P$: 419.2174; found: 419.2173.
Anal. calcd for $C_{18}H_{34}F_3O_5P$: C, 51.67; H, 8.19. Found: C, 51.51; H, 8.07%.

Methyl 2-[(Pentadecan-8-yloxy)(2,2,2-trifluoroethoxy)phosphoryl]acetate (3f)
Colorless oil.
IR (neat): 2929, 1747, 1267, 1171, 1093, 1005 cm^{-1}.
^{1}H NMR (400 MHz, $CDCl_3$): δ 0.88 (6H, t, $^{3}J_{H,H}$ = 6.6 Hz), 1.18–1.44 (20H, m), 1.51–1.71 (4H, m), 3.03 (2H, d, $^{2}J_{H,P}$ = 21.5 Hz), 3.75 (3H, s), 4.34–4.59 (3H, m).
^{13}C NMR (75 MHz, $CDCl_3$): δ 14.1 (s), 22.7 (s), 24.96 (s), 25.02 (s), 29.2 (s), 29.3 (s), 29.5 (s), 31.8 (s), 31.9 (s), 34.5 (d, $^{1}J_{C,P}$ = 140.8 Hz), 35.2 (d, $^{3}J_{C,P}$ = 3.7 Hz), 35.5 (d, $^{3}J_{C,P}$ = 4.4 Hz), 52.7 (s), 63.1 (qd, $^{2}J_{C,F}$ = 37.4 Hz, $^{2}J_{C,P}$ = 5.0 Hz), 80.3 (d, $^{2}J_{C,P}$ = 8.1 Hz), 123.0 (qd, $^{1}J_{C,F}$ = 277.6 Hz, $^{3}J_{C,P}$ = 8.7 Hz), 166.0 (d, $^{2}J_{C,P}$ = 5.6 Hz).
HRMS (ESI): *m/z* [M + H]$^{+}$ calcd for $C_{20}H_{39}F_3O_5P$: 447.2487; found: 447.2488.
Anal. calcd for $C_{20}H_{38}F_3O_5P$: C, 53.80; H, 8.58. Found: C, 53.71; H, 8.83%.

Methyl 2-[(Cyclopentyloxy)(2,2,2-trifluoroethoxy)phosphoryl]acetate (3g)
Colorless oil.
IR (neat): 2964, 1745, 1265, 1173, 1093, 1011 cm^{-1}.
^{1}H NMR (400 MHz, $CDCl_3$): δ 1.50–1.69 (3H, m), 1.69–1.95 (5H, m), 3.03 (2H, d, $^{2}J_{H,P}$ = 21.5 Hz), 3.75 (3H, s), 4.40 (1H, doublet of quintets, $^{2}J_{H,H}$ = 12.2 Hz, $^{3}J_{H,F}$ = $^{3}J_{H,P}$ = 8.3 Hz), 4.47 (1H, doublet of quintets, $^{2}J_{H,H}$ = 12.2 Hz, $^{3}J_{H,F}$ = $^{3}J_{H,P}$ = 8.3 Hz), 4.99–5.11 (1H, m).
^{13}C NMR (75 MHz, $CDCl_3$): δ 22.96 (s), 22.99 (s), 34.06 (d, $^{3}J_{C,P}$ = 4.4 Hz), 34.15 (d, $^{3}J_{C,P}$ = 5.0 Hz), 34.4 (d, $^{1}J_{C,P}$ = 140.1 Hz), 52.7 (s), 62.8 (qd, $^{2}J_{C,F}$ = 37.7 Hz, $^{2}J_{C,P}$ = 5.0 Hz), 81.3 (d, $^{2}J_{C,P}$ = 7.5 Hz), 122.8 (qd, $^{1}J_{C,F}$ = 277.8 Hz, $^{3}J_{C,P}$ = 8.5 Hz), 165.9 (d, $^{2}J_{C,P}$ = 5.6 Hz).
HRMS (ESI): *m/z* [M + H]$^{+}$ calcd for $C_{10}H_{17}F_3O_5P$: 305.0766; found: 305.0777.
Anal. calcd for $C_{10}H_{16}F_3O_5P$: C, 39.48; H, 5.30. Found: C, 39.25; H, 5.11%.

Methyl 2-[(Cyclohexyloxy)(2,2,2-trifluoroethoxy)phosphoryl]acetate (3h)

Colorless oil.

IR (neat): 2941, 1745, 1267, 1173, 1093, 1012 cm^{-1}.

^1H NMR (400 MHz, $CDCl_3$): δ 1.19–1.43 (3H, m), 1.45–1.65 (3H, m), 1.68–1.82 (2H, m), 1.84–2.01 (2H, m), 3.05 (2H, d, $^2J_{H,P}$ = 21.5 Hz), 3.75 (3H, s), 4.32–4.64 (3H, m).

^{13}C NMR (75 MHz, $CDCl_3$): δ 23.4 (s), 25.0 (s), 33.45 (d, $^3J_{C,P}$ = 5.0 Hz), 33.46 (d, $^3J_{C,P}$ = 3.7 Hz), 34.5 (d, $^1J_{C,P}$ = 140.1 Hz), 52.7 (s), 62.7 (qd, $^2J_{C,F}$ = 37.6 Hz, $^2J_{C,P}$ = 5.0 Hz), 77.6 (d, $^2J_{C,P}$ = 1.3 Hz), 122.9 (qd, $^1J_{C,F}$ = 277.6 Hz, $^3J_{C,P}$ = 8.4 Hz), 165.9 (d, $^2J_{C,P}$ = 5.0 Hz).

HRMS (ESI): *m/z* $[M + H]^+$ calcd for $C_{11}H_{19}F_3O_5P$: 319.0922; found: 319.0923.

Anal. calcd for $C_{11}H_{18}F_3O_5P$: C, 41.52; H, 5.70. Found: C, 41.52; H, 5.72%.

Methyl 2-[(Cycloheptyloxy)(2,2,2-trifluoroethoxy)phosphoryl]acetate (3i)

Colorless oil.

IR (neat): 2935, 1745, 1263, 1171, 1093, 991 cm^{-1}.

^1H NMR (400 MHz, $CDCl_3$): δ 1.35–1.49 (2H, m), 1.51–1.74 (6H, m), 1.74–1.88 (2H, m), 1.92–2.05 (2H, m), 3.03 (2H, d, $^2J_{H,P}$ = 21.5 Hz), 3.75 (3H, s), 4.40 (1H, doublet of quintet, $^2J_{H,H}$ = 12.1 Hz, $^3J_{H,F}$ = $^3J_{H,P}$ = 8.2 Hz), 4.46 (1H, doublet of quintet, $^2J_{H,H}$ = 12.1 Hz, $^3J_{H,F}$ = $^3J_{H,P}$ = 8.3 Hz), 4.68–4.80 (1H, m).

^{13}C NMR (75 MHz, $CDCl_3$): δ 22.18 (s), 22.22 (s), 28.06 (s), 28.08 (s), 34.5 (d, $^1J_{C,P}$ = 140.1 Hz), 35.7 (d, $^3J_{C,P}$ = 3.1 Hz), 35.8 (d, $^3J_{C,P}$ = 5.0 Hz), 52.7 (s), 62.8 (qd, $^2J_{C,F}$ = 37.4 Hz, $^2J_{C,P}$ = 5.0 Hz), 80.1 (d, $^2J_{C,P}$ = 6.9 Hz), 123.1 (qd, $^1J_{C,F}$ = 277.5 Hz, $^3J_{C,P}$ = 8.4 Hz), 166.0 (d, $^2J_{C,P}$ = 5.0 Hz).

HRMS (ESI): *m/z* $[M + H]^+$ calcd for $C_{12}H_{21}F_3O_5P$: 333.1079; found: 333.1077.

Anal. calcd for $C_{12}H_{20}F_3O_5P$: C, 43.38; H, 6.07. Found: C, 43.58; H, 6.24%.

Methyl 2-[(Cyclooctyloxy)(2,2,2-trifluoroethoxy)phosphoryl]acetate (3j)

Colorless oil.

IR (neat): 2927, 1745, 1265, 1171, 1093, 1002 cm^{-1}.

^1H NMR (400 MHz, $CDCl_3$): δ 1.40–1.80 (10H, m), 1.80–2.01 (4H, m), 3.03 (2H, d, $^2J_{H,P}$ = 21.5 Hz), 3.75 (3H, s), 4.40 (1H, doublet of quintet, $^2J_{H,H}$ = 12.2 Hz, $^3J_{H,F}$ = $^3J_{H,P}$ = 8.2 Hz), 4.47 (1H, doublet of quintet, $^2J_{H,H}$ = 12.2 Hz, $^3J_{H,F}$ = $^3J_{H,P}$ = 8.3 Hz), 4.67–4.81 (1H, m).

^{13}C NMR (75 MHz, $CDCl_3$): δ 22.15 (s), 22.16 (s), 25.0 (s), 27.22 (s), 27.24 (s), 32.7 (d, $^3J_{C,P}$ = 3.1 Hz), 32.8 (d, $^3J_{C,P}$ = 4.4 Hz), 34.5 (d, $^1J_{C,P}$ = 140.1 Hz), 52.7 (s), 62.8 (qd, $^2J_{C,F}$ = 37.6 Hz, $^2J_{C,P}$ = 5.0 Hz), 80.2 (d, $^2J_{C,P}$ = 7.5 Hz), 123.0 (qd, $^1J_{C,F}$ = 277.6 Hz, $^3J_{C,P}$ = 8.7 Hz), 166.0 (d, $^2J_{C,P}$ = 5.0 Hz).

HRMS (ESI): *m/z* $[M + H]^+$ calcd for $C_{13}H_{23}F_3O_5P$: 347.1235; found: 347.1231.

Anal. calcd for $C_{13}H_{22}F_3O_5P$: C, 45.09; H, 6.40. Found: C, 45.10; H, 6.27%.

2.5 Analytical and spectral data obtained for compounds **4a–j**

2-[(Pentan-3-yloxy)(2,2,2-trifluoroethoxy)phosphoryl]acetic Acid (4a)

Colorless plates; mp 46.0–47.0 °C (Et_2O–*n*-hexane).

IR (KBr): 2978, 1716, 1290, 1182, 1095, 1009 cm^{-1}

^1H NMR (400 MHz, $CDCl_3$): δ 0.93 (3H, t, $^3J_{H,H}$ = 7.3 Hz), 0.94 (3H, t, $^3J_{H,H}$ = 7.4 Hz), 1.59–1.77 (4H, m), 2.99–3.17 (2H, m), 4.36–4.74 (3H, m), 8.53 (1H, br s).

^{13}C NMR (75 MHz, $CDCl_3$): δ 9.1 (s), 9.2 (s), 27.5 (d, $^3J_{C,P}$ = 3.7 Hz), 27.6 (d, $^3J_{C,P}$ = 4.4 Hz), 34.3 (d, $^1J_{C,P}$ = 142.0 Hz), 63.6 (qd, $^2J_{C,F}$ = 37.6 Hz, $^2J_{C,P}$ = 5.0 Hz), 83.1 (d, $^2J_{C,P}$ = 8.1 Hz), 123.0 (qd, $^1J_{C,F}$ = 277.4 Hz, $^3J_{C,P}$ = 8.7 Hz), 167.6 (d, $^2J_{C,P}$ = 4.4 Hz).
HRMS (ESI): *m/z* $[M + H]^+$ calcd for $C_9H_{17}F_3O_5P$: 293.0766; found: 293.0745.
Anal. calcd for $C_9H_{16}F_3O_5P$: C, 37.00; H, 5.52. Found: C, 36.96; H, 5.29%.

2-[(Heptan-4-yloxy)(2,2,2-trifluoroethoxy)phosphoryl]acetic Acid (4b)
Colorless oil.
IR (neat): 2964, 2877, 1734, 1292, 1232, 1174, 1095, 1012 cm^{-1}.
^{1}H NMR (400 MHz, $CDCl_3$): δ 0.919 (3H, t, $^3J_{H,H}$ = 7.2 Hz), 0.922 (3H, t, $^3J_{H,H}$ = 7.3 Hz), 1.28–1.50 (4H, m), 1.51–1.73 (4H, m), 3.06 (2H, d, $^2J_{H,P}$ = 21.5 Hz), 4.38–4.70 (3H, m), 10.16 (1H, br s).
^{13}C NMR (75 MHz, $CDCl_3$): δ 13.9 (s), 18.2 (s), 18.3 (s), 34.4 (d, $^1J_{C,P}$ = 142.0 Hz), 37.3 (d, $^3J_{C,P}$ = 3.7 Hz), 37.4 (d, $^3J_{C,P}$ = 4.4 Hz), 63.7 (qd, $^2J_{C,F}$ = 37.5 Hz, $^2J_{C,P}$ = 4.7 Hz), 80.6 (d, $^2J_{C,P}$ = 8.1 Hz), 123.0 (qd, $^1J_{C,F}$ = 277.4 Hz, $^3J_{C,P}$ = 8.7 Hz), 167.6 (d, $^2J_{C,P}$ = 4.4 Hz).
HRMS (ESI): *m/z* $[M + H]^+$ calcd for $C_{11}H_{21}F_3O_5P$: 321.1079; found: 321.1080.
Anal. calcd for $C_{11}H_{20}F_3O_5P$: C, 41.26; H, 6.29. Found: C, 40.96; H, 6.00%.

2-[(Nonan-5-yloxy)(2,2,2-trifluoroethoxy)phosphoryl]acetic Acid (4c)
Colorless oil.
IR (neat): 2960, 2873, 1734, 1292, 1232, 1174, 1095, 1014 cm^{-1}.
^{1}H NMR (400 MHz, $CDCl_3$): δ 0.90 (6H, t, $^3J_{H,H}$ = 6.6 Hz), 1.23–1.44 (8H, m), 1.55–1.73 (4H, m), 3.06 (2H, d, $^2J_{H,P}$ = 20.3 Hz), 4.38–4.72 (3H, m), 10.00 (1H, br s).
^{13}C NMR (75 MHz, $CDCl_3$): δ 13.90 (s), 13.92 (s), 22.51 (s), 22.52 (s), 27.0 (s), 34.5 (d, $^1J_{C,P}$ = 141.4 Hz), 34.76 (d, $^3J_{C,P}$ = 4.4 Hz), 34.83 (d, $^3J_{C,P}$ = 4.4 Hz), 63.6 (qd, $^2J_{C,F}$ = 37.6 Hz, $^2J_{C,P}$ = 4.4 Hz), 80.9 (d, $^2J_{C,P}$ = 8.1 Hz), 122.9 (qd, $^1J_{C,F}$ = 277.4 Hz, $^3J_{C,P}$ = 8.7 Hz), 167.5 (d, $^2J_{C,P}$ = 3.7 Hz).
HRMS (ESI): *m/z* $[M + H]^+$ calcd for $C_{13}H_{25}F_3O_5P$: 349.1392; found: 349.1408.
Anal. calcd for $C_{13}H_{24}F_3O_5P$: C, 44.83; H, 6.95. Found: C, 44.89; H, 6.79%.

2-[(2,2,2-Trifluoroethoxy)(undecan-6-yloxy)phosphoryl]acetic Acid (4d)
Colorless oil.
IR (neat): 2935, 2864, 1734, 1292, 1234, 1174, 1095, 1012 cm^{-1}.
^{1}H NMR (400 MHz, $CDCl_3$): δ 0.89 (6H, t, $^3J_{H,H}$ = 6.7 Hz), 1.20–1.44 (12H, m), 1.54–1.71 (4H, m), 3.03 (1H, dd, $^2J_{H,P}$ = 22.6 Hz, $^2J_{H,H}$ = 15.0 Hz), 3.06 (1H, dd, $^2J_{H,P}$ = 20.7 Hz, $^2J_{H,H}$ = 15.0 Hz), 4.38–4.68 (3H, m), 5.93 (1H, br s).
^{13}C NMR (75 MHz, $CDCl_3$): δ 13.97 (s), 14.01 (s), 22.5 (s), 24.6 (s), 31.65 (s), 31.68 (s), 34.4 (d, $^1J_{C,P}$ = 142.0 Hz), 35.06 (d, $^3J_{C,P}$ = 3.7 Hz), 35.15 (d, $^3J_{C,P}$ = 4.4 Hz), 63.7 (qd, $^2J_{C,F}$ = 37.6 Hz, $^2J_{C,P}$ = 4.4 Hz), 81.0 (d, $^2J_{C,P}$ = 7.5 Hz), 122.9 (qd, $^1J_{C,F}$ = 277.4 Hz, $^3J_{C,P}$ = 8.7 Hz), 167.6 (d, $^2J_{C,P}$ = 4.4 Hz).
HRMS (ESI): *m/z* $[M + H]^+$ calcd for $C_{15}H_{29}F_3O_5P$: 377.1705; found: 377.1718.
Anal. calcd for $C_{15}H_{28}F_3O_5P$: C, 47.87; H, 7.50. Found: C, 47.70; H, 7.48%.

2-[(Tridecan-7-yloxy)(2,2,2-trifluoroethoxy)phosphoryl]acetic Acid (4e)
Colorless oil.

IR (neat): 2931, 2860, 1734, 1292, 1234, 1174, 1095, 1009 cm^{-1}.
^1H NMR (400 MHz, $CDCl_3$): δ 0.88 (6H, t, $^3J_{H,H}$ = 6.5 Hz), 1.19–1.49 (16H, m), 1.54–1.74 (4H, m), 3.05 (2H, d, $^2J_{H,P}$ = 21.7 Hz), 4.38–4.70 (3H, m), 8.50 (1H, br s).
^{13}C NMR (75 MHz, $CDCl_3$): δ 14.1 (s), 22.61 (s), 22.63 (s), 24.9 (s), 29.2 (s), 31.7 (s), 34.4 (d, $^1J_{C,P}$ = 142.0 Hz), 35.1 (d, $^3J_{C,P}$ = 3.7 Hz), 35.2 (d, $^3J_{C,P}$ = 4.4 Hz), 63.6 (qd, $^2J_{C,F}$ = 37.6 Hz, $^2J_{C,P}$ = 4.4 Hz), 80.9 (d, $^2J_{C,P}$ = 8.1 Hz), 122.9 (qd, $^1J_{C,F}$ = 277.6 Hz, $^3J_{C,P}$ = 8.7 Hz), 167.6 (d, $^2J_{C,P}$ = 4.4 Hz).
HRMS (ESI): *m*/*z* $[M + H]^+$ calcd for $C_{17}H_{33}F_3O_5P$: 405.2018; found: 405.1994.
Anal. calcd for $C_{17}H_{32}F_3O_5P$: C, 50.49; H, 7.98. Found: C, 50.57; H, 7.93%.

2-[(Pentadecan-8-yloxy)(2,2,2-trifluoroethoxy)phosphoryl]acetic Acid (4f)
Colorless oil.
IR (neat): 2929, 2858, 1734, 1292, 1232, 1174, 1095, 1009 cm^{-1}.
^1H NMR (400 MHz, $CDCl_3$): δ 0.88 (6H, t, $^3J_{H,H}$ = 6.7 Hz), 1.18–1.45 (20H, m), 1.53–1.73 (4H, m), 3.05 (2H, d, $^2J_{H,P}$ = 21.7 Hz), 4.39–4.69 (3H, m), 8.16 (1H, br s).
^{13}C NMR (75 MHz, $CDCl_3$): δ 14.1 (s), 22.7 (s), 24.9 (s), 29.2 (s), 29.4 (s), 31.78 (s), 31.82 (s), 34.5 (d, $^1J_{C,P}$ = 141.4 Hz), 35.0 (d, $^3J_{C,P}$ = 3.7 Hz), 35.1 (d, $^3J_{C,P}$ = 4.4 Hz), 63.6 (qd, $^2J_{C,F}$ = 37.5 Hz, $^2J_{C,P}$ = 4.7 Hz), 81.0 (d, $^2J_{C,P}$ = 7.5 Hz), 122.9 (qd, $^1J_{C,F}$ = 277.6 Hz, $^3J_{C,P}$ = 8.7 Hz), 167.5 (d, $^2J_{C,P}$ = 3.7 Hz).
HRMS (ESI): *m*/*z* $[M + H]^+$ calcd for $C_{19}H_{37}F_3O_5P$: 433.2331; found: 433.2349.
Anal. calcd for $C_{19}H_{36}F_3O_5P$: C, 52.77; H, 8.39. Found: C, 52.63; H, 8.38%.

2-[(Cyclopentyloxy)(2,2,2-trifluoroethoxy)phosphoryl]acetic Acid (4g)
Colorless plates; mp 39.5–40.5 °C (Et_2O–*n*-hexane).
IR (KBr): 2974, 1718, 1292, 1230, 1176, 1095, 1012 cm^{-1}.
^1H NMR (400 MHz, $CDCl_3$): δ 1.54–1.96 (8H, m), 3.05 (2H, d, $^2J_{H,P}$ = 21.7 Hz), 4.44 (1H, doublet of quintets, $^2J_{H,H}$ = 12.4 Hz, $^3J_{H,F}$ = $^3J_{H,P}$ = 8.2 Hz), 4.60 (1H, doublet of quintets, $^2J_{H,H}$ = 12.4 Hz, $^3J_{H,F}$ = $^3J_{H,P}$ = 8.4 Hz), 5.04–5.13 (1H, m), 9.34 (1H, br s).
^{13}C NMR (75 MHz, $CDCl_3$): δ 22.96 (s), 22.99 (s), 34.0 (d, $^3J_{C,P}$ = 4.4 Hz), 34.1 (d, $^3J_{C,P}$ = 5.6 Hz), 34.3 (d, $^1J_{C,P}$ = 140.1 Hz), 63.3 (qd, $^2J_{C,F}$ = 37.6 Hz, $^2J_{C,P}$ = 5.0 Hz), 82.0 (d, $^2J_{C,P}$ = 7.5 Hz), 122.9 (qd, $^1J_{C,F}$ = 277.5 Hz, $^3J_{C,P}$ = 8.4 Hz), 167.5 (d, $^2J_{C,P}$ = 4.4 Hz).
HRMS (ESI): *m*/*z* $[M + H]^+$ calcd for $C_9H_{15}F_3O_5P$: 291.0609; found: 291.0605.
Anal. calcd for $C_9H_{14}F_3O_5P$: C, 37.25; H, 4.86. Found: C, 37.17; H, 4.83%.

2-[(Cyclohexyloxy)(2,2,2-trifluoroethoxy)phosphoryl]acetic Acid (4h)
Colorless plates; mp 49.5–50.5 °C (Et_2O–*n*-hexane).
IR (KBr): 2945, 2868, 2576, 1730, 1308, 1219, 1180, 1093, 1014 cm^{-1}.
^1H NMR (400 MHz, $CDCl_3$): δ 1.20–1.42 (3H, m), 1.46–1.64 (3H, m), 1.69–1.81 (2H, m), 1.86–2.00 (2H, m), 3.07 (2H, d, $^2J_{H,P}$ = 21.7 Hz), 4.44 (1H, doublet of quintets, $^2J_{H,H}$ = 12.5 Hz, $^3J_{H,F}$ = $^3J_{H,P}$ = 8.1 Hz), 4.51–4.66 (2H, m), 10.08 (1H, br s).
^{13}C NMR (75 MHz, $CDCl_3$): δ 23.4 (s), 25.0 (s), 33.37 (d, $^3J_{C,P}$ = 2.5 Hz), 33.39 (d, $^3J_{C,P}$ = 5.0 Hz), 34.4 (d, $^1J_{C,P}$ = 140.8 Hz), 63.2 (qd, $^2J_{C,F}$ = 37.6 Hz, $^2J_{C,P}$ = 5.0 Hz), 78.2 (d, $^2J_{C,P}$ = 7.5 Hz), 122.9 (qd, $^1J_{C,F}$ = 277.4 Hz, $^3J_{C,P}$ = 8.7 Hz), 167.6 (d, $^2J_{C,P}$ = 4.4 Hz).
HRMS (ESI): *m*/*z* $[M + H]^+$ calcd for $C_{10}H_{17}F_3O_5P$: 305.0766; found: 305.0762.

Anal. calcd for $C_{10}H_{16}F_3O_5P$: C, 39.48; H, 5.30. Found: C, 39.44; H, 5.27%.

2-[(Cycloheptyloxy)(2,2,2-trifluoroethoxy)phosphoryl]acetic Acid (4i)

Colorless oil.

IR (neat): 2935, 2864, 1732, 1290, 1234, 1174, 1095 cm^{-1}.

^1H NMR (400 MHz, $CDCl_3$): δ 1.34–1.49 (2H, m), 1.49–1.61 (4H, m), 1.61–1.73 (2H, m), 1.74–1.88 (2H, m), 1.93–2.06 (2H, m), 3.06 (2H, d, $^2J_{H,P}$ = 22.0 Hz), 4.43 (1H, doublet of quintets, $^2J_{H,H}$ = 12.3 Hz, $^3J_{H,F}$ = $^3J_{H,P}$ = 8.2 Hz), 4.59 (1H, doublet of quintets, $^2J_{H,H}$ = 12.3 Hz, $^3J_{H,F}$ = $^3J_{H,P}$ = 8.2 Hz), 4.71–4.82 (1H, m), 10.56 (1H, br s).

^{13}C NMR (75 MHz, $CDCl_3$): δ 22.07 (s), 22.10 (s), 28.00 (s), 28.02 (s), 34.4 (d, $^1J_{C,P}$ = 141.4 Hz), 35.58 (d, $^3J_{C,P}$ = 3.1 Hz), 35.63 (d, $^3J_{C,P}$ = 4.4 Hz), 63.3 (qd, $^2J_{C,F}$ = 37.7 Hz, $^2J_{C,P}$ = 4.7 Hz), 80.8 (d, $^2J_{C,P}$ = 7.5 Hz), 122.9 (qd, $^1J_{C,F}$ = 277.5 Hz, $^3J_{C,P}$ = 8.7 Hz), 167.6 (d, $^2J_{C,P}$ = 4.4 Hz).

HRMS (ESI): *m*/*z* $[M + H]^+$ calcd for $C_{11}H_{19}F_3O_5P$: 319.0922; found: 319.0909.

Anal. calcd for $C_{11}H_{18}F_3O_5P$: C, 41.52; H, 5.70. Found: C, 41.75; H, 5.53%.

2-[(Cyclooctyloxy)(2,2,2-trifluoroethoxy)phosphoryl]acetic Acid (4j)

Colorless oil.

IR (neat): 2927, 1732, 1290, 1230, 1173, 1095, 1012 cm^{-1}.

^1H NMR (400 MHz, $CDCl_3$): δ 1.41–1.62 (8H, m), 1.64–1.76 (2H, m), 1.99–2.00 (4H, m), 3.05 (2H, d, $^2J_{H,P}$ = 21.5 Hz), 4.43 (1H, doublet of quintets, $^2J_{H,H}$ = 12.2 Hz, $^3J_{H,F}$ = $^3J_{H,P}$ = 8.1 Hz), 4.60 (1H, doublet of quintets, $^2J_{H,H}$ = 12.2 Hz, $^3J_{H,F}$ = $^3J_{H,P}$ = 8.4 Hz), 4.72–4.82 (1H, m), 9.30 (1H, br s).

^{13}C NMR (75 MHz, $CDCl_3$): δ 22.1 (s), 25.0 (s), 27.2 (s), 32.6 (d, $^3J_{C,P}$ = 3.1 Hz), 32.7 (d, $^3J_{C,P}$ = 4.4 Hz), 34.4 (d, $^1J_{C,P}$ = 140.8 Hz), 63.3 (qd, $^2J_{C,F}$ = 37.7 Hz, $^2J_{C,P}$ = 5.0 Hz), 80.9 (d, $^2J_{C,P}$ = 7.5 Hz), 122.9 (qd, $^1J_{C,F}$ = 277.5 Hz, $^3J_{C,P}$ = 8.7 Hz), 167.6 (d, $^2J_{C,P}$ = 3.1 Hz).

HRMS (ESI): *m*/*z* $[M + H]^+$ calcd for $C_{12}H_{21}F_3O_5P$: 333.1079; found: 333.1082.

Anal. calcd for $C_{12}H_{20}F_3O_5P$: C, 43.38; H, 6.07. Found: C, 43.28; H, 5.91%.

3 Data, value and validation

The result of the reaction of methyl bis(2,2,2-trifluoroethyl)phosphonoacetate (**1**) with σ-symmetrical secondary alcohols **2a–j** and PLE-catalyzed kinetic resolution of the resultant racemic mixed phosphonoacetates *rac*-**3a–j** are summarized in Table 1 and Table 2, respectively. The biochemical stereoselectivity factor E was calculated according to E = ln[(1 − c)(1 − ee)] / ln[(1 − c)(1 + ee)], where c = ee / (ee + ee'), ee = enantiomeric excess of unreacted resolution substrates, and ee' = enantiomeric excess of resolution products [10–12].

Table 1.

Synthesis of racemic phosphonoacetates *rac*-**3a–j**.

Entry	ROH	Time (h)	Yield (%)	Entry	ROH	Time (h)	Yield (%)
1	**2a**	15	81 (*rac*-**3a**) [a]	6	**2f**	16	69 (*rac*-**3f**) [a]

2	**2b**	15	74 (*rac*-**3b**) [a]	7	**2g**	2	75 (*rac*-**3g**)
3	**2c**	16	71 (*rac*-**3c**) [a]	8	**2h**	3	80 (*rac*-**3h**)
4	**2d**	15	79 (*rac*-**3d**) [a]	9	**2i**	3.5	71 (*rac*-**3i**)
5	**2e**	15	66 (*rac*-**3e**) [a]	10	**2j**	3.5	72 (*rac*-**3j**)

[a] Molecular Sieves (Type 3A) were used.

Table 2.

PLE-catalyzed kinetic resolution of phosphonoacetates *rac*-**3a–j**.

Entry	*rac*-**3a–j**	Time	**4a–j**		**3a–j**		E [e]
			Yield (%)	Ee (%) [a,b]	Yield (%)	Ee (%) [b]	
1	**3a**	1.5 h	61	64	39	99	22
2	**3b**	50 min	37	72	59	28	8
3	**3c**	3 h	28	76	72	22	9
4	**3d**	48 h	56	76	44	>99	>37
5	**3e**	54 h	48	82 [c]	49	82 [c]	26
6	**3f**	13 d	42	54	56	40	5
7	**3g**	45 min	80	17 [d]	20	68 [d]	3
8	**3h**	1.5 h	84	11 [d]	14	42 [d]	2
9	**3i**	55 min	55	40 [d]	45	51 [d]	4
10	**3j**	40 min	32	70 [d]	67	32 [d]	8

[a] HPLC analysis after methylation with $TMSCHN_2$.

[b] HPLC analysis (CHIRALPAK AD-H, *n*-hexane/2-propanol = 50/1, 1.0 mL/min, 220 nm).

[c] HPLC analysis (CHIRALPAK IA, *n*-hexane/2-propanol = 100/1, 1.0 mL/min, 220 nm).

[d] HPLC analysis (CHIRALPAK AS-H, *n*-hexane/2-propanol = 30/1, 1.0 mL/min, 220 nm).

[e] Biochemical stereoselectivity factor [10–12].

Acknowledgment

This work was supported in part by a JSPS KAKENHI Grant (Number 17590007).

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