Electronic Supplementary Information

Enhanced activity and remarkable improved stability of a Burkholderia cepacia lipase by the coating with a triazolium alkylPEG sulfate ionic liquid

T. Nishihara,[a] A. Shiomi,[a] S. Kadotani,[a] T. Nokami,[a, b] T. Itoh[a, b*]

[a]*Department of Chemistry and Biotechnology, Graduate School of Engineering, Tottori University*
4-101 Koyamacho-minami, Tottori City, 680-8552 Tottori, Japan
[b]*Center for Research on Green Sustainable Chemistry, Graduate School of Engineering, Tottori University*
4-101 Koyamacho-minami, Tottori City, 680-8552 Tottori, Japan
E-mmail: titoh@chem.tottori-u.ac.jp

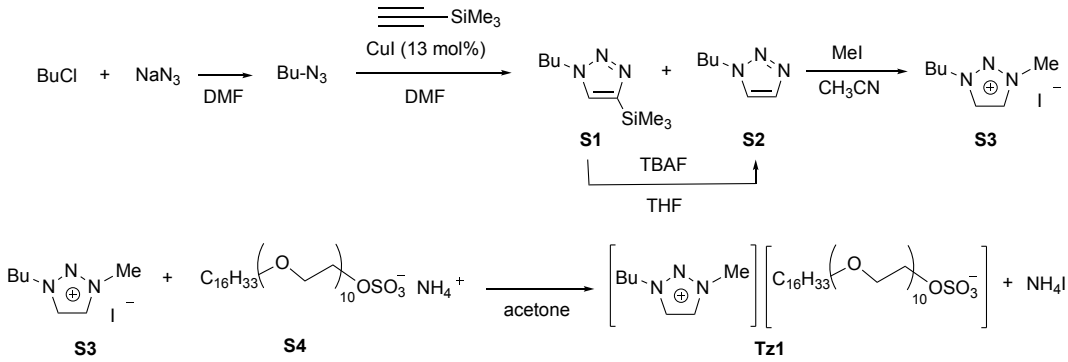
Contents

General Procedures

Regents and solvents were purchased from common commercial sources and were used as received or purified by distillation over appropriate drying agents. Reactions requiring anhydrous conditions were carried out under argon with dry, freshly distilled solvents, and magnetic stirring. Reactions except the preparation of the ionic liquids were monitored by thin layer chromatography using silica gel plate and GC. Thin layer chromatography was performed with the indicated solvents and Wako gel B-5F. The ^{1}H-NMR spectra and ^{13}C-NMR spectra were recorded by a Bruker Avance III spectrometer. Chemical shifts are expressed in ppm downfield from tetramethylsilane (TMS) in $CDCl_3$ as an internal reference. IR spectra were obtained on SHIMADZU FT-IR 8000 spectrometers. High resolution mass spectra were recorded on a Thermo Fisher Scientific EXACTIVE mass spectrometer. Optical rotation was measured with a JASCO DIP-370 digital polarimeter. The rate was determined by gas chromatography analysis (Quadrex bonded fused silica methyl silicone, ϕ 0.25 mm × 25 m, N_2). The optical purity was determined by HPLC analysis using Daicel OD, OD-H, OB, AD, or OJ-H and capillary gas chromatography (Chiraldex G-TA, ϕ 0.25 mm × 20 m, 100 ºC, He).

1. Synthesis of ionic liquids Tz1, Tz2, and Tz3

1-1. Synthesis of Tz1.



A mixture of NaN_3 (2.39 g, 35.9 mmol) and 1-chlorobutane (1.33 g, 14.4 mmol) in DMF (18.5ml) was stirred at 80°C for 21 h. To this mixture was added copper iodide (0.35 g, 1.84 mmol) and trimethylsilylethyne (1.74 g, 18.3 mmol), then the mixture was stirred for 72 h at the same temperature. After being cooled to rt, the precipitate was removed by filtration through a glass sintered filter, then the filtrate was dryness by evaporation. Silicagel flash column chromatography gave 1-butyl-4-(trimethylsilyl)-1,2-3-triazole **S1**[1] (1.18 g, 6.01 mmol) and 1-butyl-1,2-3-triazole **S2**[1] (0.29 g, 2.32 mmol) in 42% and 16% yield, respectively. To a THF (6.0 ml) solution of **S1** was added tributylammonium fluoride (TBAF, 9.01 mmol) and the moixture was stirred for 24 h, then evaporated to dryness to give **S2** (0.69g, 15.5 mmol) in 92% yield. **S2** (0.69g, 5.51 mmol) was dissolved in 2 ml of acetonitrile (CH_3CN), then iodomethane (3.89 g, 27.6 mmol) was added at 0°C under dark conditions. The mixture was stirred at rt for one week, then washed with ether 3 times, then lyophilized to dryness to afford 3-butyl-1-methyl-1*H*-1,2,3-triazol-3-ium iodide (**S3**)[2] (1.41 g, 5.27 mmol) in 96% yield. A mixture of **S3**[2] (0.52 g, 1.87 mmol) and $[NH_4][C_{16}H_{33}(OCH_2CH_2)_{10}OSO_3]$[3](1.47 g, 1.87 mmol) in 2.0 ml of acetone was stirred at rt for 24 h, then filtrated through a membrane filter to remove the precipitate (NH_4I) formed. To the filtrate was diluted with dry acetone (10 ml) and active charcoal (2.12 g) and the mixture was stireed at 50°C for 2 h, then remove the active charcoal by filtration through a glass sintered filter with a Celite pad. The filtrate was dried by evapolation and subsequent lyophilization to afford **Tz1** (0.497 g, 0.55 mmol) in 30% yield.

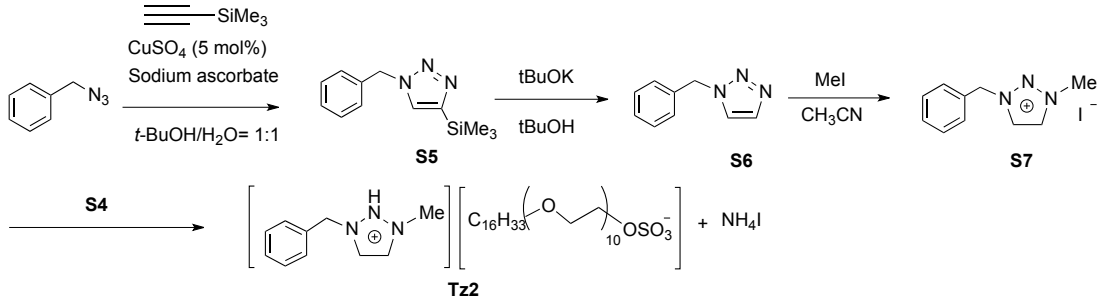
Tz1: mp 28.3°C; ^{1}H NMR (600 MHz, $CDCl_3$, *J*=Hz) δ 0.88 (3H, t, *J*=7.2), 1.00 (3H, t, *J*=7.2), 1.25 (30H, m), 1.46 (2H, sextet, *J*=7.2), 1.60 (2H, m), 1.61 (2H, m), 3.4 (2H, t, *J*=6.6), 3.58 (2H, d, *J*=5.4), 3.65-3.63 (34H, m), 3.72 (2H, m), 4.25 (3H, s), 4.73 (2H, t, *J*=7.8), 9.22 (1H, s), 9.44(1H, s); ^{13}C NMR(150 MHz, $CDCl_3$, *J*=Hz) δ 13.36, 14.09, 22.64, 25.76, 26.04, 29.31, 29.45, 29.49, 29.52, 29.57, 29.60, 29.64, 31.41, 31.87, 41.12, 54.08, 61.49, 61.67, 61.70, 62.79, 69.98, 70.10, 70.13, 70.25, 70.42, 71.50, 71.71, 72.50, 72.66, 131.41, 132.29; IR(neat, cm^{-1}) 3421, 2916, 2850, 1538, 1466, 1345, 1280, 1242, 1109, 964, 842; ESI-MS (Cation): calcd for $C_7H_{14}N_3^+$ 140.1182 , found 140.1180.

S1: ^{1}H NMR(600 MHz, $CDCl_3$, *J*=Hz) δ 0.33 (9H, s), 0.96 (3H, t, *J*=7.4), 1.37 (2H, m, *J*=7.4), 1.89 (2H, m), 4.38 (2H, t, *J*=7.4), 7.48 (1H, s); ^{13}C NMR (150 MHz, $CDCl_3$, *J*=Hz) δ -0.9, 13.7, 20.0, 32.7, 49.7, 128.9, 146.7; IR(neat, cm^{-1}) 3116, 2956, 2860, 2932, 1677, 14), 1466, 1382, 1248, 1382, 1092, 1048, 1001, 839, 756, 655, 631.

S2 [1]**:** ^{1}H NMR (600 MHz, $CDCl_3$, *J*=Hz) δ 0.96 (3H, t, *J*=7.2), 1.36 (m, 2H, *J*=7.2), 1.90 (2H, m), 4.40 (2H, t, *J*=7.2), 7.55 (1H, s), 7.70 (1H, s);^{13}C NMR (150 MHz, $CDCl_3$, *J*=Hz) δ 13.7, 19.9, 32.5, 50.1, 123.3, 134.0; IR (neat, cm^{-1})3447, 3123, 2960, 2935, 2875, 1642, 1482, 1466, 1381, 1268, 1216, 1115, 1072, 1028, 952, 787, 753, 703, 639.

S3 [2]: ^{1}H NMR (600 MHz, $CDCl_3$, *J*=Hz) δ 1.00 (3H, t, *J*=7.8), 1.44 (2H, m, *J*=7.2), 2.05(2H, m), 4.54 (3H, s), 4.76 (2H, t, *J*=7.2), 9.38 (1H, s), 9.49 (1H, s); ^{13}C NMR (150 MHz, $CDCl_3$, *J*=Hz) δ 13.4, 19.3, 31.4, 41.3, 54.1, 131.3, 132.1; IR(neat, cm^{-1}) 3461, 3134, 3077, 2956, 2936, 2874, 1528, 1463, 1346, 1311, 1212, 1192, 1126, 1086, 807, 748, 732, 687, 651.

1-2. Synthesis of Tz2.



A mixture of NaN_3 (1.62 g, 25.0 mmol) and benzylbromide (1.82 g, 10.7 mmol) in CH_3CN (25 ml) was stirred at 65°C for 24 h. After allowed to cool to rt, the mixture was diluted with ethyl acetate (20 ml) and washed with water. The organic layer was dried with anhydrous $MgSO_4$ and evaporated to dryness. To the resulting residue were added *t*-BuOH/H_2O=1/1 (18 ml), $CuSO_4$ (74.0 mg, 0.46 mmol), sodium ascorbate (185.9 mg, 0.94 mmol), and trimethylsilylacetylene (933 mg, 9.50 mmol), then the mixture was stirred at rt for 17 h. The reaction was quenched by addition of saturated NH_4Cl aqueous solution, then extracted with ethyl axcetate. The organic layer was washed with water 3 times, then evaporated to dryness. SiO_2 flash column chromatography gave 1-benzyl-4-(trimethylsilyl)-1,2,3-triazole **S5** (1.620 g, 7.01 mmol) in 66% yield (2 steps) as a white solid.

To a *t*-BuOH (2.0 ml) solution of **S5** (223.3 mg, 0.97 mmol) was added *t*-BuOK (168 mg, 1.5 mmol) and the mixture was stirred at 40°C for 14 h, then the mixture was diluted water (2.0 ml) and extracted with ether 3 times. The organic layer was dried with $MgSO_4$ and evaporated to dryness, then subsequent SiO_2 flash column chromatography afforded 1-benzyl-1,2,3-triazole **S6**[4] (121.6 mg, 0.76 mmol) in 78% yield as a white solid.

To a **S6** (101.7 mg, 0.63 mmol) solution of 0.1 ml of acetonitrile (CH_3CN) was added iodomethane (178.3 mg, 1.26 mmol) at 0°C. The mixture was stirred at rt for 2 days under dark conditions and washed with ether 3 times, then the organic layer was evaporated to dryness and subsequent lyophilization to afford 3-benzyl-1-methyl-1*H*-1,2,3-triazol-3-ium iodide (**S7**) (112 mg, 0.37 mmol) in 59% yield. A mixture of **S7** (99.7 m g, 1.87 mmol) and $[NH_4][C_{16}H_{33}(OCH_2CH_2)_{10}OSO_3]$ [3] (261.3 mg, 0.33 mmol) in 2.0 ml of acetone was stirred at rt for 24 h, then precipitate (NH_4I) produced

was removed through a membrane filter and the filtrate was dried by evapolation and subsequent lyophilization to give **Tz2** (283.7 mg, 0.55 mmol) in 91% yield.

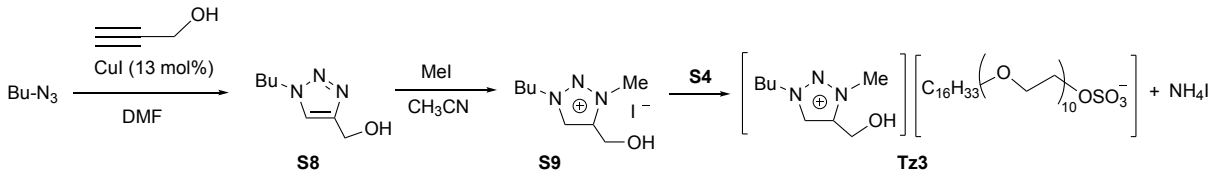
Tz2: mp: 29.0 ℃; ^{1}H NMR(600 MHz, $CDCl_3$, *J*=Hz) δ 9.24(s, 1H), 9.21(s, 1H), 7.59-7.57(m, 2H), 7.41(t, 3H, *J*=3.6), 5.95(s, 2H), 4.48(s, 3H), 3.74-3.57(m, 36H), 3.43(t, 2H, *J*=6.6), 1.57(t, 2H, *J*=7.2), 1.31(m, 26H), 0.88(t, 3H, *J*=7.2);^{13}C NMR(150 MHz, $CDCl_3$, *J*=Hz) δ 132.50, 131.32, 131.16, 130.03, 129.54, 129.51, 72.52, 71.56, 70.61, 70.54, 70.51, 70.46, 70.26, 70.18, 70.04, 69.87, 68.86, 66.34, 61.57, 57.52, 41.00, 31.92, 29.70, 29.65, 29.63, 29.51, 29.36, 26.10, 22.69, 14.12; IR(neat, cm^{-1}) 3922.48, 3149.64, 3075.42, 3044.15, 2991.81, 2917.26, 281.04, 1774.84, 1529.57, 1494.27, 1455.32, 1385.77, 1345.32, 1301.16, 1282.12, 1215.74, 1173.44, 1114.49, 1090.39, 1029.65, 950.03, 913.82, 827.69, 791.18, 720.39, 693.46, 577.66; ESI-MS: calcd for $C_{10}H_{12}N_3^+$174.1026, found 174.1024

S5: ^{1}H NMR(600MHz, MeOD, *J*=Hz): δ 7.88(s, 1H), 7.27-7.21(m, 5H), 5.2(s, 2H), 0.20(s, 1H); ^{13}C NMR(150 MHz, $CDCl_3$, *J*=Hz): δ 148.21, 136.10, 130.16, 129.86, 129.69, 129.18, 54.65, -0.04; IR(neat, cm^{-1}) 3106.29, 3026.32, 2957.55, 2901.92, 1884.20, 149.42, 1484.22, 1458.54, 1448.95, 1415.97, 1354.82, 1322.12, 1246.28, 1193.17, 1153.38, 1099.55, 1075.69, 1053.47, 1028.95, 1001.12, 947.49, 840.35, 763.62, 722.69, 695.82, 651.57, 635.43, 584.50, 473.52, 406.40.

S6[4]: ^{1}H NMR (600 MHz, $CDCl_3$, *J*=Hz) δ 8.00 (s, 1H), 7.76 (s, 1H), 7.41-7.34 (m, 5H), 4.94 (s, 2H); ^{13}C NMR (150 MHz, $CDCl_3$, *J*=Hz) δ 134.71, 134.26, 129.13, 128.75, 123.02, 123.26, 53.99; IR (neat, cm^{-1}) 3136.70, 3107.65, 3064.95, 3026.49, 2974.70, 2942.66, 2703.01, 2418.95, 2304.10, 2112.10, 1957.13, 1869.75, 1810.34, 1754.79, 1686.44, 1606.93, 1496.27, 1464.41, 1454.53, 1438.61, 1371.11, 1337.73, 1307.90, 1285.70, 1216.55, 1160.43, 1113.82, 1085.03, 1075.20, 1030.94, 967.42, 951.23, 898.40, 812.36, 773.80, 724.44, 693.01, 573.82, 457.01

S7: ^{1}H NMR(600 MHz, $CDCl_3$, *J*=Hz) δ 9.40(s, 1H), 9.32(s, 1H), 7.60-7.59(m, 2H), 7.43(t, 3H, *J*=3.0), 5.97(s, 2H), 4.51(s, 3H); ^{13}C NMR(150 MHz, $CDCl_3$, *J*=Hz) δ 132.41, 131.16, 131.05, 130.13, 129.59, 129.54, 57.50, 41.19; IR(neat, cm^{-1}) 3922.41, 3149.07, 3075.56, 3044.16, 2992.05, 2966.63, 2938.61, 2876.43, 2124.81, 1949.31, 1774.32, 1529.26, 1494.18, 1455.04, 1385.67, 1319.13, 1301.15, 1282.61, 1215.34, 1173.41, 1152.63, 1089.47, 1029.40, 791.30, 719.94, 693.30, 577.54.

1-3. synthesis of Tz3.



A mixture of NaN_3 (2.40 g, 36.9 mol) and 1-bromobutane (2.03 g, 14.8 mmol) in DMF (18 ml) was stirred at 80°C for 16 h, then allowed to cool to rt. To the mixture was addee CuI (359.2 mg, 1.89 mmol) and propargyl alcohol (1.115 g, 19.9 mmol), and the mixture was stirred at 80°C for 18 h. After allowed to cool to rt, the precipitate formed was removed by filtration through glass sintered

filter and the filtrate was evaporated and subsequent SiO_2 column chromatography to give (1-butyl-1,2,3-triazol-4-yl)methanol (**S8**) (1.024 g, 6.77 mmol) in 46% yield.

Reaction of **S8** (780.1 mg, 5.03 mmol) with iodomethane (1.464 g, 10.3 mmol) for 3 days under dark conditions gave **S9** (1.394 g, 4.72 mmol) in 94% yiled.

A mixture of $[NH_4][C_{16}H_{33}(OCH_2CH_2)_{10}OSO_3]$ [3] (779.7 mg, 1.00 mmol) and 1-butyl-4-(hydroxymethyl)-3-methyl-1*H*-1,2,3-triazolium iodide (**S9**)(296.7 mg, 1.00 mmol) in acetone (5.0 ml) was stirered at rt for 24 h, then NH_4I precipitated was remnoved by filtration through a membrane filter. The filtrate was evaporated to dryness and subsequent lyophilization to afford **Tz3** (923.6 mg) in 99% yield.

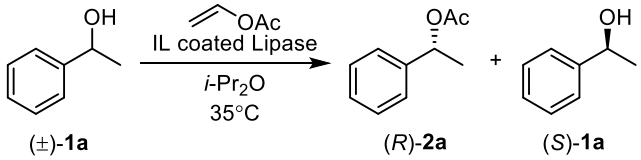
Tz3: mp 25.0°C; ^{1}H NMR(600 MHz, $CDCl_3$, *J*=Hz) δ 8.80(s, 1H), 4.99(s, 2H), 4.58(t, 2H, *J*=7.2), 4.37(s, 3H), 3.75-3.58(m, 38H), 3.44(t, 2H, *J*=6.6), 2.03(m, 2H), 1.58-1.56(m, 2H), 1.47-1.25(m, 26H), 1.00(t, 3H, *J*=7.2), 0.88(t, 3H, *J*=7.2); ^{13}C NMR(150 MHz, $CDCl_3$, *J*=Hz) δ 143.95, 129.95, 72.3, 71.57, 70.37, 70.10, 70.01, 61.42, 53.99, 52.71, 39.10, 31.94, 31.22, 29.71, 29.68, 29.64, 29.52, 29.38, 26.10, 22.71, 19.48, 14.16; IR(neat, cm^{-1}) 3236.72, 2923.16, 2854.40, 2114.50, 1465.96, 1349.20, 1301.97, 1251.88, 1115.11, 952.20; ESI-MS: calcd for $C_8H_{16}N_3O^+$170.1288, found 170.1287.

S8: ^{1}H NMR(600 MHz, $CDCl_3$, *J*=Hz) δ 7.56(s, 1H), 4.78(s, 2H), 4.34(t, 2H, *J*=7.2), 1.90-1.85(m, 2H), 1.38-1.26(m, 2H), 0.95(t, 3H, *J*=7.2); ^{13}C NMR(150 MHz, $CDCl_3$, *J*=Hz) δ 147.83, 121.64, 56.15, 50.07, 32.20, 19.66, 13.41; IR(neat, cm^{-1}) 3332.02, 3139.57, 2959.70, 2934.83, 2874.04, 1463.15, 1437.93, 1380.94, 1336.93, 1221.28, 1144.61, 1050.36, 1013.79, 772.45, 655.51.

S9: ^{1}H NMR(600 MHz, $CDCl_3$, *J*=Hz) δ 9.02(s, 1H), 5.03(s, 2H), 4.87(s, 1H), 4.65(t, 2H, *J*=7.2), 4.39(s, 3H), 2.05-2.00(m, 2H), 1.47-1.41(m, 2H), 0.99(t, 3H, *J*=7.2); ^{13}C NMR(150 MHz, $CDCl_3$, *J*=Hz) δ 143.56, 129.75, 54.04, 52.63, 39.76, 31.22, 19.39, 13.39; IR(neat, cm^{-1}) 3288.44, 3076.94, 2958.96, 2935.38, 2872.89, 1583.84, 1459.12, 1381.21, 1317.49, 1236.78, 1160.85, 1124.86, 1078.67, 1040.50, 809.14, 637.21, 531.80; ESI-MS: calcd for $C_8H_{16}N_3O^+$170.1288, found 170.1276.

2. Enzymatic reaction

2-1. Kinetic resolution of (±)- 1-phenylethanol (1a).



2-1-1. Results of Triazolium IL-catalyzed reactions.

Tz1-PS catalyzed reaction:

A mixture of (±)-**1a** (50.3 mg, 0.41 mmol), vinyl acetate (54.5 mg, 0.63 mmol), and **Tz1-PS** (5.3 mg) in *i*-Pr_2O (2.0 ml) was stirred at 35℃ for 40 min. The reaction was quenched by addition of 1.0 ml of ethyl acetate and removed the enzyme by filtration through a glass sintered filter with a Celite pad, then silica gel thin layer chromatography (TLC) (hexane/ ethyl acetate= 4:1) gave (*R*)-**2a** and (*S*)-**1a**.

The reaction rate of the lipase-catalyzed reaction was determined by capillary GC-analysis (Quadrex bonded fused silica methyl silicone, ϕ 0.25 mm × 25 m, He) in the presence of an internal reference. The enantioselectivity was determined by HPLC analysis using a chiral column (Chiralcel OB, hexane: 2-propanol = 8 : 1, 200 : 1).

(*R*)-**2a**: 21.9 mg, 0.133 mmol, Y= 32.6 %, >99 % *ee*, $[\alpha]^{24}_{D}$ +119.1 (c 1.08, $CHCl_3$)

(*S*)-**1a**: 24.3 mg, 0.199 mmol, Y= 48.5 %, 71.0 % *ee*, $[\alpha]^{19}_{D}$ -19.6 (c 1.02, $CHCl_3$)

Conv. 41.5%, *E* value >200 (4271), Rate: 595.6 mM h^{-1} mg $enzyme^{-1}$

Tz2-PS catalyzed reaction:

(*R*)-**2a**: 10.8 mg, 0.0658 mmol, Y= 16.0 %, >99 % *ee*, $[\alpha]^{24}_{D}$ +113.8 (c 1.13, $CHCl_3$)

(*S*)-**1a**: 19.3 mg, 0.158 mmol, Y= 38.5 %, 75.6 % *ee*, $[\alpha]^{24}_{D}$ -159.1 (c 0.93, $CHCl_3$)

Conv. 43.1%, *E* value >200 (4582), Rate: 630.7 mM h^{-1} mg $enzyme^{-1}$

Tz3-PS catalyzed reaction:

(*R*)-**2a**: 23.8 mg, 0.145 mmol, Y= 35.3 %, >99 % *ee*, $[\alpha]^{27}_{D}$ +86.9 (c 0.99, $CHCl_3$)

(*S*)-**1a**: 22.9 mg, 0.188 mmol, Y= 45.7 %, 83.4 % *ee*, $[\alpha]^{28}_{D}$ -12.6 (c 1.08, $CHCl_3$)

Conv. 45.5%, *E* value >200 (5280), Rate: 501.7 mM h^{-1} mg $enzyme^{-1}$

2.1-2. Results of the control experiments.

Commercial Lipase-PS catalyzed reaction:

To a solution of (±)-**1a** (50.0 mg, 0.41 mmol), vinyl acetate (53.0 mg, 0.62 mmol) in *i*-Pr_2O (2.0 mL) was added Lipase PS (25 mg, Enzyme content: 0.25 mg) and the mixture was stirred at 35 ºC for 8 h. The reaction rate of the lipase-catalyzed reaction was determined by capillary GC-analysis. (*R*)-**2a** and (*S*)-**3a** were obtained by preparative silica gel thin layer chromatography (TLC).

(*R*)-**2a**: 30.9 mg, 0.19 mmol, Y= 46.0 %, >99 % *ee*

(*S*)-**1a**: 18.0 mg, 0.15 mmol, Y= 36 %, 88 % *ee*

Conv. 47.0%, *E* value >200 (584), Rate: 90 mM h^{-1} mg $enzyme^{-1}$

Celite free Lipase PS catalyzed reaction:

Commercial lipase PS (1.00 g, enzyme protein 10 mg; 3.1 x 10^{-4} mmol) was dissolved in 10 ml of 0.1 M phosphate buffer (pH 7.2) and the mixture was centrifuged twice at 3,500 rpm for 5 min, then the resulting supernatant was lyophilized to afford the Celite-free lipase PS (224 mg). The estimated amount of the lipase protein in this Celite-free lipase PS powder was 4.5 % (w/w).

To a solution of (±)-**1a** (50.2 mg, 0.41 mmol), vinyl acetate (52.9 mg, 0.62 mmol) in *i*-Pr_2O (2.0 mL) was added the Celite free Lipase PS (4.5 mg, enzyme content: 0.20 mg) and the mixture was stirred at 35 ºC for 8 h. The reaction rate of the lipase-catalyzed reaction was determined by capillary GC-analysis. (*R*)-**2a** and (*S*)-**3a** were obtained by preparative silica gel thin layer chromatography (TLC).

(*R*)-**2a**: 26.9 mg, 0.16 mmol, Y= 40.0 %, >99 % *ee*

(*S*)-**1a**: 19.5 mg, 0.16 mmol, Y= 39 %, 86 % *ee*

Conv. 46.0%, *E* value >200 (556), Rate: 84 mM h^{-1} mg $enzyme^{-1}$

IL1-PS catalyzed reaction:

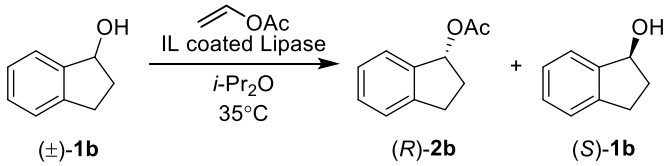
To a solution of (±)-**1a** (50.1 mg, 0.41 mmol) and vinyl acetate (52.9 mg, 0.62 mmol) in *i*-Pr_2O (2.0 mL) was added **IL1-PS** (7.0 mg, the enzyme content: 0.20 mg) and the mixture was stirred at 35ºC for 30 min. (*R*)-**2a** and (*S*)-**3a** were obtained by preparative silica gel thin layer chromatography (TLC).

(*R*)-**2a**: 18.1 mg, 0.11 mmol, Y= 27.0 %, >99 % *ee*

(*S*)-**1a**: 20.0 mg, 0.16 mmol, Y= 39 %, 77 % *ee*

Conv. 43.0%, *E* value >200 (E 466), Rate: 884 mM h^{-1} mg $enzyme^{-1}$

2-2. Kinetic resolution of (±)- 1-indanole(1b).



Tz1-PS catalyzed acetylation:

A mixture of (±)-**1b** (53.6 mg, 0.40 mmol), vinyl acetate (52.2 mg, 0.61 mmol), and **Tz1-PS** (5.4 mg) in *i*-Pr_2O (2.0 ml) was stirred at 35℃ for 40 min. The reaction was quenched by addition of 1.0 ml of ethyl acetate and the enzyme was removed by filtration through a glass sintered filter with a Celite pad, then silica gel TLC (hexane/ ethyl acetate= 4:1) gave (*R*)-**2b** and (*S*)-**1b**.

(*R*)-**2b**: 21.6 mg, 0.123 mmol, Y= 30.7 %, >99 % *ee*, $[\alpha]^{28}_D$ +9.16 (c 0.62, $CHCl_3$)

(*S*)-**1b**: 14.6 mg, 0.109 mmol, Y= 27.2 %, >99 % *ee*, $[\alpha]^{27}_D$ +4.62 (c 0.91, $CHCl_3$)

Conv. 50.0%, *E* value >200 (15198), Rate: 577.0 mM h^{-1} mg $enzyme^{-1}$

Tz2-PS catalyzed acetylation:

(*R*)-**2b**: 32.7 mg, 0.1856 mmol, Y= 46.4 %, >99 % *ee*, $[\alpha]^{28}_D$ +67.5 (c 1.04, $CHCl_3$)

(*S*)-**1b**: 24.7 mg, 0.1841 mmol, Y= 46.0 %, 44.9 % *ee*, $[\alpha]^{28}_D$ +26.8 (c 1.11, $CHCl_3$)

Conv. 44.9%, *E* value >200(5082), Rate: 828.3 mM h^{-1} mg $enzyme^{-1}$

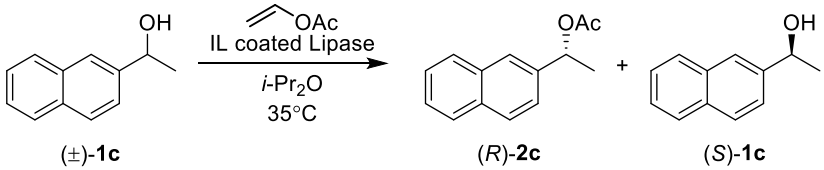
Tz3-PS catalyzed acetylation:

(*R*)-**2b**: 35.3 mg, 0.200 mmol, Y= 50.1 %, >99 % *ee*, $[\alpha]^{25}_D$ +88.8 (c 1.55, $CHCl_3$)

(*S*)-**1b**: 26.3 mg, 0.196 mmol, Y= 49.0 %, >99 % *ee*, $[\alpha]^{25}_D$ +24.5 (c 1.15, $CHCl_3$)

Conv. 50.0%, *E* value >200(15198), Rate: 984.4 mM h^{-1} mg $enzyme^{-1}$

2-3. Kinetic resolution of (±)-1-(naphthalen-2-yl)ethan-1-ol (1c).



Tz1-PS catalyzed acetylation:

A mixture of (±)-**1c** (68.7 mg, 0.40 mmol), vinyl acetate (53.8 mg, 0.62 mmol), and **Tz1-PS** (6.8 mg) in *i*-Pr_2O (2.0 ml) was stirred at 35℃ for 40 min. The reaction was quenched by addition of 1.0 ml

of ethyl acetate and the enzyme was removed by filtration through a glass sintered filter with a Celite pad, then silica gel TLC (hexane/ ethyl acetate= 7:1) gave (*R*)-**2c** and (*S*)-**1c**.

(*R*)-**2c**: 39.9 mg, 0.186 mmol, Y= 46.6%, >99% *ee*, $[\alpha]^{28}_{D}$ +8.49 (c 1.20, $CHCl_3$)

(*S*)-**1c**: 28.6 mg, 0.166 mmol, Y= 41.5%, 91.7% *ee*, $[\alpha]^{29}_{D}$ -15.4 (c 1.04, $CHCl_3$)

Conv. 47.9%, *E* value >200 (6560), Rate: 365.5 mM h^{-1} mg $enzyme^{-1}$

Tz2-PS catalyzed acetylation:

(*R*)-**2c**: 21.2 mg, 0.0989 mmol, Y= 24.7%, >99% *ee*, $[\alpha]^{24}_{D}$ +89.6 (c 1.86, $CHCl_3$)

(*S*)-**1c**: 54.0 mg, 0.314 mmol, Y= 78.4%, 28.6% *ee*, $[\alpha]^{25}_{D}$ -15.7 (c 1.54, $CHCl_3$)

Conv. 22.3%, *E* value >200(660), Rate: 338.3 mM h^{-1} mg $enzyme^{-1}$

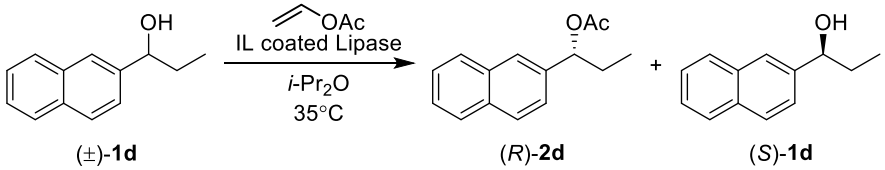
Tz3-PS catalyzed acetylation:

(*R*)-**2c**: 15.1 mg, 0.0705 mmol, Y= 17.6%, >99% *ee*, $[\alpha]^{27}_{D}$ +110.3 (c 1.42, $CHCl_3$)

(*S*)-**1c**: 52.5 mg, 0.305 mmol, Y= 76.2%, 22.6% *ee*, $[\alpha]^{19}_{D}$ -16.8 (c 1.31, $CHCl_3$)

Conv. 18.5%, *E* value >200 (498), Rate: 300.1 mM h^{-1} mg $enzyme^{-1}$

2-4. Kinetic resolution of (±)-1-(naphthalen-2-yl)propan-1-ol (1d).



Tz1-PS catalyzed acetylation:

A mixture of (±)-**1d** (74.6 mg, 0.40 mmol), vinyl acetate (57.3 mg, 0.62 mmol), and **Tz1-PS** (7.8 mg) in *i*-Pr_2O (2.0 ml) was stirred at 35℃ for 40 min. The reaction was quenched by addition of 1.0 ml of ethyl acetate and the enzyme was removed by filtration through a glass sintered filter with a Celite pad, then silica gel TLC (hexane/ ethyl acetate= 7:1) gave (*R*)-**2d** and (*S*)-**1d**.

(*R*)-**2d**: 39.9 mg, 0.0898 mmol, Y= 22.4%, >99% *ee*, $[\alpha]^{29}_{D}$ +6.85 (c 1.49, $CHCl_3$)

(*S*)-**1d**: 53.4 mg, 0.234 mmol, Y= 58.5%, 64.2% *ee*, $[\alpha]^{29}_{D}$ -2.54 (c 4.25, $CHCl_3$)

Conv. 39.1%, *E* value >200 (3898), Rate: 37.2 mM h^{-1} mg $enzyme^{-1}$

Tz2-PS catalyzed acetylation:

(*R*)-**2d**: 23.7 mg, 0.104 mmol, Y= 26.0%, >99% *ee*, $[\alpha]^{27}_{D}$ +72.8 (c 0.81, $CHCl_3$)

(*S*)-**1d:** 51.4 mg, 0.276 mmol, Y= 69.0%, 32.7% *ee*, $[\alpha]^{27}_{D}$ -1.41 (c 1.11, $CHCl_3$)

Conv. 24.7%, *E* value >200 (2754), Rate: 32.6 mM h^{-1} mg $enzyme^{-1}$

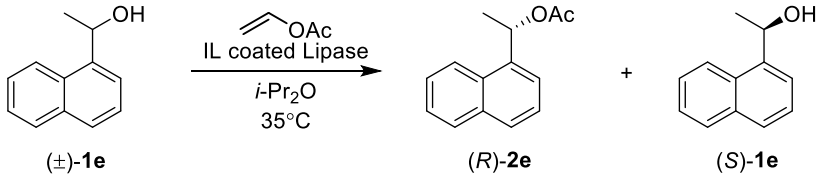
Tz3-PS catalyzed acetylation:

(*R*)-**2d**: 17.8 mg, 0.0780 mmol, Y= 19.5%, >99% *ee*, $[\alpha]^{26}_{D}$ +84.5 (c 1.70, $CHCl_3$)

(*S*)-**1d**: 56.1 mg, 0.301 mmol, Y= 75.3%, 21.7% *ee*, $[\alpha]^{26}_{D}$ -19.5 (c 1.13, $CHCl_3$)

Conv. 47.9%, *E* value >200 (6560), Rate: 365.5 mM h^{-1} mg $enzyme^{-1}$

2-5. Kinetic resolution of (±)-1-(naphthalen-1-yl)ethan-1-ol (1e).



(±)-**1e** (*R*)-**2e** (*S*)-**1e**

Tz1-PS catalyzed acetylation:

A mixture of (±)-**1e** (68.9 mg, 0.40 mmol), vinyl acetate (56.7 mg, 0.66 mmol), and **Tz1-PS** (6.9 mg) in *i*-Pr_2O (2.0 ml) was stirred at 35℃ for 40 min. The reaction was quenched by addition of 1.0 ml of ethyl acetate and the enzyme was removed by filtration through a glass sintered filter with a Celite pad, then silica gel TLC (hexane/ ethyl acetate= 4:1) gave (*R*)-**2e** and (*S*)-**1e**.

(*R*)-**2e**: 4.3 mg, 0.0201 mmol, Y= 5.0%, >99% *ee*, $[\alpha]^{26}_D$ +4.00 (c 0.35, $CHCl_3$)

(*S*)-**1e**: 59.6 mg, 0.346 mmol, Y= 86.5%, 3.5% *ee*, $[\alpha]^{26}_D$ -1.31 (c 1.07, $CHCl_3$)

Conv. 3.4%, *E* value >200 (2070), Rate: 2.2 mM h^{-1} mg $enzyme^{-1}$

Tz2-PS catalyzed acetylation:

(*R*)-**2e**: 7.7 mg, 0.0359 mmol, Y= 9.0%, >99% *ee*, $[\alpha]^{25}_D$ +45.07 (c 0.75, $CHCl_3$)

(*S*)-**1e**: 65.0 mg, 0.377 mmol, Y= 94.4%, 7.6% *ee*, $[\alpha]^{25}_D$ -6.67 (c 1.29, $CHCl_3$)

Conv. 7.1%, *E* value >200 (2155), Rate: 8.8 mM h^{-1} mg $enzyme^{-1}$

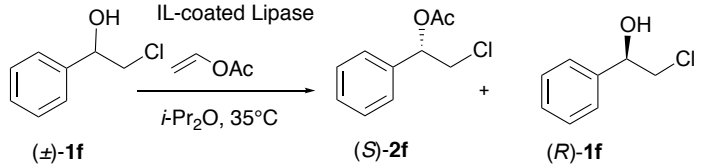
Tz3-PS catalyzed acetylation:

(*R*)-**2e**: 18.1 mg, 0.0845 mmol, Y= 21.1%, 97.6% *ee*, $[\alpha]^{26}_D$ +49.5 (c 1.48, $CHCl_3$)

(*S*)-**1e**: 49.3 mg, 0.286 mmol, Y= 71.6%, 24.5% *ee*, $[\alpha]^{26}_D$ -16.5 (c 1.33, $CHCl_3$)

Conv. 20.1%, *E* value 105, Rate: 13.0 mM h^{-1} mg $enzyme^{-1}$

2-6. Kinetic resolution of (±)-2-chloro-1-phenylethan-1-ol (1f).



(±)-**1f** (*S*)-**2f** (*R*)-**1f**

Lipase PS-catalyzed reaction:

A mixture of (±)-**1f** (62.2 mg, 0.40 mmol), vinyl acetate (54.4 mg, 0.63 mmol), and **lipase PS** (33.0 mg) in *i*-Pr_2O (2.0 ml) was stirred at 35℃ for 40 min. The reaction was quenched by addition of 1.0 ml of ethyl acetate and the enzyme was removed by filtration through a glass sintered filter with a Celite pad, then silica gel TLC (hexane/ ethyl acetate= 4:1) gave (*S*)-**2f** and (*R*)-**1f**. The produced acetate **2f** was assigned to be as (*S*)-form and the unreacted alcohol **1f** was to be (*R*)-form by the Cahn-Ingold-Prelog priority rule. However, the stereoselectivity of the enzyme was the same as other compounds.

(*S*)-**2f**: 7.5 mg, 0.0378 mmol, Y= 9.4%, >99% *ee*, $[\alpha]^{24}_D$ +11.733 (c 0.75, $CHCl_3$)

(*R*)-**1f**: 44.5 mg, 0.284 mmol, Y= 71.0%, 11.4% *ee*, $[\alpha]^{24}_D$ -6.38 (c 1.63, $CHCl_3$)

Conv. 10.2%, *E* value >200 (2237), Rate: 2.5 mM h^{-1} mg $enzyme^{-1}$

IL1-PS-catalyzed reaction:

A mixture of (±)-**1f** (62.4 mg, 0.40 mmol), vinyl acetate (53.9 mg, 0.63 mmol), and **IL1-PS** (6.0 mg) in *i*-Pr_2O (2.0 ml) was stirred at 35℃ for 40 min. The reaction was quenched by addition of 1.0 ml of ethyl acetate and the enzyme was removed by filtration through a glass sintered filter with a Celite pad, then silica gel TLC (hexane/ ethyl acetate= 4:1) gave (*S*)-**2f** and (*R*)-**1f**.
(*S*)-**2f**: 22.1 mg, 0.111 mmol, Y= 27.8%, 97.9% *ee*, $[\alpha]^{24}_D$ +45.9 (c 0.88, $CHCl_3$)
(*R*)-**1f**: 36.3 mg, 0.232 mmol, Y= 58.0%, 44.9% *ee*, $[\alpha]^{22}_D$ -23.9 (c 1.08, $CHCl_3$)
Conv. 31.4%, *E* value 147, Rate: 68.1 mM h^{-1} mg $enzyme^{-1}$

Tz1-PS catalyzed acetylation:

A mixture of (±)-**1f** (62.6 mg, 0.40 mmol), vinyl acetate (52.8 mg, 0.60 mmol), and **Tz1-PS** (6.3 mg) in *i*-Pr_2O (2.0 ml) was stirred at 35℃ for 40 min. The reaction was quenched by addition of 1.0 ml of ethyl acetate and the enzyme was removed by filtration through a glass sintered filter with a Celite pad, then silica gel TLC (hexane/ ethyl acetate= 4:1) gave (*S*)-**2f** and (*R*)-**1f**.
(*S*)-**2f**: 22.0 mg, 0.11.7 mmol, Y= 27.7%, 96.5% *ee*, $[\alpha]^{23}_D$ +73.4 (c 1.54, $CHCl_3$)
(*R*)-**1f**: 32.0 mg, 0.2043 mmol, Y= 51.1%, 48.0% *ee*, $[\alpha]^{24}_D$ -12.0 (c 1.22, $CHCl_3$)
Conv. 33.2%, *E* value 90, Rate: 66.8 mM h^{-1} mg $enzyme^{-1}$

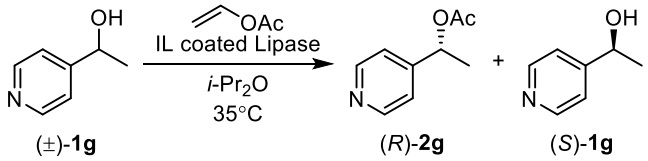
Tz2-PS catalyzed acetylation:

(*S*)-**2f**: 17.3 mg, 0.0871 mmol, Y= 21.7%, 97.2% *ee*, $[\alpha]^{22}_D$ +66.8 (c 1.00, $CHCl_3$)
(*R*)-**1f**: 41.4 mg, 0.2644 mmol, Y= 66.1%, 40.2% *ee*, $[\alpha]^{23}_D$ -21.3 (c 1.25, $CHCl_3$)
Conv. 29.3%, *E* value 1.5, Rate: 59.9 mM h^{-1} mg $enzyme^{-1}$

Tz3-PS catalyzed acetylation:

(*S*)-**2f**: 19.8 mg, 0.0997 mmol, Y= 24.9%, 97.4% *ee*, $[\alpha]^{21}_D$ +65.1 (c 1.13, $CHCl_3$)
(*R*)-**1f**: 35.1 mg, 0.224 mmol, Y= 56.0%, 42.5% *ee*, $[\alpha]^{22}_D$ -24.9 (c 1.11, $CHCl_3$)
Conv. 30.4%, *E* value 115, Rate: 63.2 mM h^{-1} mg $enzyme^{-1}$

2-7. Kinetic resolution of (±)-1-(pyridin-4-yl)ethan-1-ol (1g).



Tz1-PS catalyzed acetylation:

A mixture of (±)-**1g** (49.3 mg, 0.40 mmol), vinyl acetate (58.0 mg, 0.61 mmol), and **Tz1**-PS (6.9 mg) in *i*-Pr_2O (2.0 ml) was stirred at 35℃ for 40 min. The reaction was quenched by addition of 1.0 ml of ethyl acetate and the enzyme was removed by filtration through a glass sintered filter with a Celite pad, then silica gel TLC (ethyl acetate only) gave (*R*)-**2g** and (*S*)-**1g**.
(*R*)-**2g**: 18.8 mg, 0.115 mmol, Y= 28.6%, >99% *ee*, $[\alpha]^{27}_D$ -0.0087 (c 2.51, $CHCl_3$)
(*S*)-**1g**: 29.0 mg, 0.236 mmol, Y= 58.9%, 49.8% *ee*, $[\alpha]^{28}_D$ -1.159 (c 0.69, $CHCl_3$)
Conv. 33.3%, *E* value >200 (3287), Rate: 1016.3 mM h^{-1} mg $enzyme^{-1}$

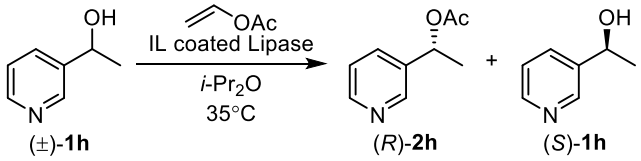
Tz2-PS catalyzed acetylation:

(*R*)-**2g**: 23.6 mg, 0.143 mmol, Y= 35.7%, 99.8% *ee*, $[\alpha]^{25}_{D}$ +95.1 (c 2.00, $CHCl_3$)
(*S*)-**1g**: 28.8 mg, 0.234 mmol, Y= 58.5%, 58.0% *ee*, $[\alpha]^{26}_{D}$ -46.9 (c 2.26, $CHCl_3$)
Conv. 36.8%, *E* value >200 (1803), Rate: 592.2 mM h^{-1} mg $enzyme^{-1}$

Tz3-PS catalyzed acetylation:

(*R*)-**2g**: 25.9 mg, 0.157 mmol, 39.2 %, >99 % *ee*, $[\alpha]^{25}_{D}$ +74.0 (c 2.53, $CHCl_3$)
(*S*)-**1g**: 29.3 mg, 0.238 mmol, 59.5 %, 55.7 % *ee*, $[\alpha]^{26}_{D}$ -21.5 (c 1.17, $CHCl_3$)
Conv. 35.9%, *E* value >200 (701), Rate: 605.7 mM h^{-1} mg $enzyme^{-1}$

2-8. Kinetic resolution of (±)-1-(pyridin-3-yl)ethan-1-ol (1h).



(±)-**1h** (*R*)-**2h** (*S*)-**1h**

Tz1-PS catalyzed acetylation:

A mixture of (±)-**1h** (49.6 mg, 0.40 mmol), vinyl acetate (54.1 mg, 0.63 mmol), and **Tz1**-PS (5.2 mg) in *i*-Pr_2O (2.0 ml) was stirred at 35℃ for 40 min. The reaction was quenched by addition of 1.0 ml of ethyl acetate and the enzyme was removed by filtration through a glass sintered filter with a Celite pad, then silica gel TLC (ethyl acetate only) gave (*R*)-**2h** and (*S*)-**1h**.

(*R*)-**2h**: 24.5 mg, 0.149 mmol, Y= 37.3%, >99% *ee*, $[\alpha]^{27}_{D}$ +2.37 (c 2.11, $CHCl_3$)
(*S*)-**1h**: 36.0 mg, 0.292 mmol, Y= 73.1%, 56.5% *ee*, $[\alpha]^{27}_{D}$ -1.19 (c 3.19, $CHCl_3$)
Conv. 36.2%, *E* value >200 (589), Rate: 723.9 mM h^{-1} mg $enzyme^{-1}$

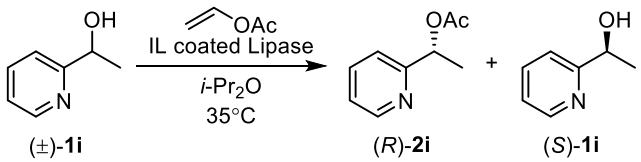
Tz2-PS catalyzed acetylation:

(*R*)-**2h**: 18.3 mg, 0.115 mmol, Y= 28.8%, >99% *ee*, $[\alpha]^{27}_{D}$ +82.9 (c 0.81, $CHCl_3$)
(*S*)-**1h**: 38.3 mg, 0.311 mmol, 77.8%, Y= 47.9% *ee*, $[\alpha]^{26}_{D}$ -15.6 (c 1.10, $CHCl_3$)
Conv. 32.4%, *E* value >200 (3220), Rate: 310.3 mM h^{-1} mg $enzyme^{-1}$

Tz3-PS catalyzed acetylation:

(*R*)-**2h**: 18.6 mg, 0.151 mmol, Y= 37.8%, >99% *ee*, $[\alpha]^{23}_{D}$ +84.5 (c 2.51, $CHCl_3$)
(*S*)-**1h**: 18.2 mg, 0.1102 mmol, Y= 27.6%, 40.9% *ee*, $[\alpha]^{23}_{D}$ -20.8 (c 1.71, $CHCl_3$)
Conv. 29.2%, *E* value >200 (373), Rate: 342.4 mM h^{-1} mg $enzyme^{-1}$

2-9. Kinetic resolution of (±)-1-(pyridin-2-yl)ethan-1-ol (1i)



(±)-**1i** (*R*)-**2i** (*S*)-**1i**

Tz1-PS catalyzed acetylation:

A mixture of (±)-**1i** (49.5 mg, 0.40 mmol), vinyl acetate (55.2 mg, 0.64 mmol), and **Tz1**-PS (5.1 mg) in *i*-Pr_2O (2.0 ml) was stirred at 35℃ for 40 min. The reaction was quenched by addition of 1.0 ml

of ethyl acetate and the enzyme was removed by filtration through a glass sintered filter with a Celite pad, then silica gel TLC (ethyl acetate only) gave (*R*)-**2i** and (*S*)-**1i**.

(*R*)-**2i**: 16.3 mg, 0.132 mmol, Y= 33.0 %, >99% *ee*, $[\alpha]^{27}_{D}$ +1.16 (c 0.69, $CHCl_3$)

(*S*)-**1i**: 23.7 mg, 0.192 mmol, Y= 48.1%, 42.2% *ee*, $[\alpha]^{28}_{D}$ -2.37 (c 2.11, $CHCl_3$)

Conv. 36.2%, *E* value >200(589), Rate: 604.8 mM h^{-1} mg $enzyme^{-1}$

Tz2-PS catalyzed acetylation:

(*R*)-**2i**: 11.2 mg, 0.0678 mmol, Y= 17.0%, >99% *ee*, $[\alpha]^{25}_{D}$ +23.6 (c 0.95, $CHCl_3$)

(*S*)-**1i**: 19.5 mg, 0.158 mmol, Y= 39.6%, 24.0% *ee*, $[\alpha]^{25}_{D}$ -3.8 (c 1.07, $CHCl_3$)

Conv. 19.4%, *E* value >200 (2528), Rate: 65.3 mM h^{-1} mg $enzyme^{-1}$

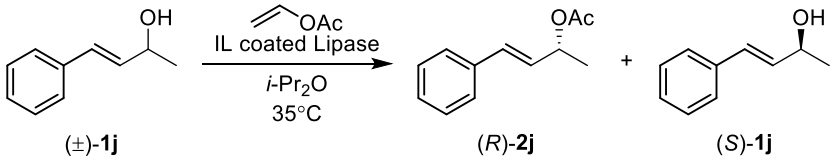
Tz3-PS catalyzed acetylation:

(*R*)-**2i**: 17.2 mg, 0.104 mmol, Y= 26.0%, >99% *ee*, $[\alpha]^{26}_{D}$ +68.1 (c 0.96, $CHCl_3$)

(*S*)-**1i**: 17.6 mg, 0.145 mmol, Y= 36.1%, 62.9% *ee*, $[\alpha]^{26}_{D}$ -7.78 (c 0.72, $CHCl_3$)

Conv. 38.7%, *E* value >200 (764), Rate: 145.2 mM h^{-1} mg $enzyme^{-1}$

2-10. Kinetic resolution of (±)-1-(E)-4-phenylbut-3-en-2-ol (1j)



Tz1-PS catalyzed acetylation:

A mixture of (±)-**1j** (59.2 mg, 0.40 mmol), vinyl acetate (56.2 mg, 0.64 mmol), and **Tz1**-PS (6.2 mg) in *i*-Pr_2O (2.0 ml) was stirred at 35℃ for 40 min. The reaction was quenched by addition of 1.0 ml of ethyl acetate and the enzyme was removed by filtration through a glass sintered filter with a Celite pad, then silica gel TLC (hexane/ ethyl acetate = 6:1) gave (*R*)-**2j** and (*S*)-**1j**.

(*R*)-**2j**: 33.3 mg, 0.175 mmol, Y= 43.8%, >99% *ee*, $[\alpha]^{27}_{D}$ +28.0 (c 0.35, $CHCl_3$)

(*S*)-**1j**: 29.2 mg, 0.197 mmol, Y= 49.3%, 77.7% *ee*, $[\alpha]^{27}_{D}$ -2.42 (c 1.32, $CHCl_3$)

Conv. 43.8%, *E* value >200(4744), Rate: 549.7 mM h^{-1} mg $enzyme^{-1}$

Tz2-PS catalyzed acetylation:

(*R*)-**2j**: 17.8 mg, 0.0937 mmol, Y= 23.4%, >99% *ee*, $[\alpha]^{23}_{D}$ +135.2 (c 1.25, $CHCl_3$)

(*S*)-**1j**: 29.2 mg, 0.258 mmol, Y= 64.5%, 36.1% *ee*, $[\alpha]^{23}_{D}$ -12.7 (c 1.18, $CHCl_3$)

Conv. 26.5%, *E* value >200 (2849), Rate: 471.9 mM h^{-1} mg $enzyme^{-1}$

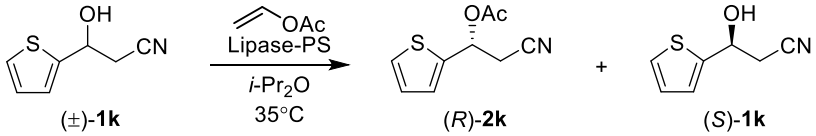
Tz3-PS catalyzed acetylation:

(*R*)-**2j**: 14.9 mg, 0.0784 mmol, Y= 19.6%, >99% *ee*, $[\alpha]^{26}_{D}$ +116.7 (c 1.16, $CHCl_3$)

(*S*)-**1j**: 42.7 mg, 0.288 mmol, Y= 72.1%, 27.0% *ee*, $[\alpha]^{26}_{D}$ -8.79 (c 1.41, $CHCl_3$)

Conv. 21.3%, *E* value >200 (2603), Rate: 397.6 mM h^{-1} mg $enzyme^{-1}$

2-11. Kinetic resolution of (±)-1-3-hydroxy-3-(thiophen-2-yl)propanenitrile (1k)



(±)-**1k** (*R*)-**2k** (*S*)-**1k**

A mixture of (±)-**1k** (60.9 mg, 0.40 mmol), vinyl acetate (55.7 mg, 0.64 mmol), and lipase PS (30.5 mg) in *i*-Pr_2O (2.0 ml) was stirred at 35℃ for 12 h. The reaction was quenched by addition of 1.0 ml of ethyl acetate and the enzyme was removed by filtration through a glass sintered filter with a Celite pad, then silica gel TLC (hexane/ ethyl acetate = 1:1) gave (*R*)-**2k** and (*S*)-**1k**.

(*R*)-**2k**: 8.2 mg, 0.0420 mmol, Y= 10.2%, 98.8% *ee*, $[\alpha]^{27}_D$ +83.0 (c 0.66, $CHCl_3$)

(*S*)-**1k**: 52.9 mg, 0.3969 mmol, Y= 86.8%, 13.5% *ee*, $[\alpha]^{26}_D$ -68.9 (c 1.22, $CHCl_3$)

Conv. 12.0%, *E* value 189, Rate: 6.6 mM h^{-1} mg $enzyme^{-1}$

IL1-PS catalyzed acetylation:

A mixture of (±)-**1k** (61.5 mg, 0.40 mmol), vinyl acetate (53.1 mg, 0.62 mmol), and **IL1**-PS (6.0 mg) in *i*-Pr_2O (2.0 ml) was stirred at 35℃ for 1 h. The reaction was quenched by addition of 1.0 ml of ethyl acetate and the enzyme was removed by filtration through a glass sintered filter with a Celite pad, then silica gel TLC (hexane/ ethyl acetate = 1:1) gave (*R*)-**2k** and (*S*)-**1k**.

(*R*)-**2k**: 26.0 mg, 0.133 mmol, Y= 33.3%, 92.3% *ee*, $[\alpha]^{27}_D$ -14.2 (c 1.07, $CHCl_3$)

(*S*)-**1k**: 34.5 mg, 0.2252 mmol, Y= 56.3%, 47.6% *ee*, $[\alpha]^{28}_D$ +80.2 (c 0.91, $CHCl_3$)

Conv. 34.0%, *E* value 40, Rate: 294.9 mM h^{-1} mg $enzyme^{-1}$

Tz1-PS catalyzed acetylation:

A mixture of (±)-**1k** (61.2 mg, 0.40 mmol), vinyl acetate (53.8 mg, 0.62 mmol), and **Tz1**-PS (6.2 mg) in *i*-Pr_2O (2.0 ml) was stirred at 35℃ for 1 h. The reaction was quenched by addition of 1.0 ml of ethyl acetate and the enzyme was removed by filtration through a glass sintered filter with a Celite pad, then silica gel TLC (hexane/ ethyl acetate = 1:1) gave (*R*)-**2k** and (*S*)-**1k**.

(*R*)-**2k**: 24.9 mg, 0.128 mmol, Y= 31.1%, 97.2% *ee*, $[\alpha]^{24}_D$ +77.0 (c 1.06, $CHCl_3$)

(*S*)-**1k**: 41.7 mg, 0.272 mmol, Y= 66.4%, 43.3% *ee*, $[\alpha]^{24}_D$ -14.5 (c 1.02, $CHCl_3$)

Conv. 30.8%, *E* value 108, Rate: 167.9 mM h^{-1} mg $enzyme^{-1}$

Tz2-PS catalyzed acetylation:

(*R*)-**2k**: 16.2 mg, 0.0831 mmol, Y= 20.8%, 96.4% *ee*, $[\alpha]^{28}_D$ -88.3 (c 1.20, $CHCl_3$)

(*S*)-**1k**: 44.5 mg, 0.291 mmol, Y= 72.6%, 24.1% *ee*, $[\alpha]^{27}_D$ +80.4 (c 1.66, $CHCl_3$)

Conv. 20.0%, *E* value 75, Rate: 160.2 mM h^{-1} mg $enzyme^{-1}$

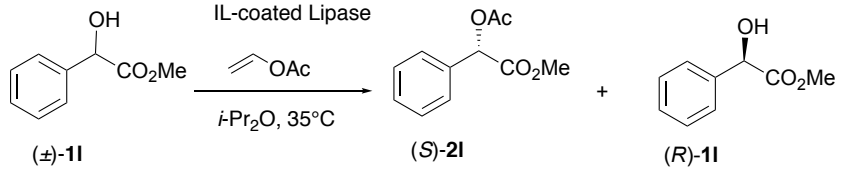
Tz3-PS catalyzed acetylation:

(*R*)-**2k**: 20.2 mg, 0.106 mmol, Y= 26.6%, 95.9% *ee*, $[\alpha]^{24}_D$ +89.7 (c 1.69, $CHCl_3$)

(*S*)-**1k**: 45.5 mg, 0.2970 mmol, Y= 74.2%, 32.0% *ee*, $[\alpha]^{25}_D$ -9.73 (c 1.11, $CHCl_3$)

Conv. 25.0%, *E* value 65, Rate: 218.9 mM h^{-1} mg $enzyme^{-1}$

2-12. Kinetic resolution of (±)-methyl 2-hydroxy-2-phenylacetate (1l)



Tz1-PS catalyzed acetylation:

A mixture of (±)-**1l** (66.5 mg, 0.40 mmol), vinyl acetate (55.2 mg, 0.64 mmol), and **Tz1**-PS (6.7 mg) in *i*-Pr_2O (2.0 ml) was stirred at 35℃ for 1 h. The reaction was quenched by addition of 1.0 ml of ethyl acetate and the enzyme was removed by filtration through a glass sintered filter with a Celite pad, then silica gel TLC (hexane/ ethyl acetate = 4:1) gave (*S*)-**2l** and (*R*)-**1l**. The acetate **2l** produced was assigned to be as (*S*)-form and the alcohol **1l** unreacted was to be (*R*)-form by the Cahn-Ingold-Prelog priority rule. However, the stereoselectivity of the enzyme was the same as other compounds.

(*S*)-**2l**: 25.2 mg, 0.121 mmol, Y= 30.3%, 90.6% *ee*, $[\alpha]^{21}_D$ +115.8 (c 2.03, $CHCl_3$)

(*R*)-**1l**: 25.4 mg, 0.1528 mmol, Y= 38.2%, >99% *ee*, $[\alpha]^{22}_D$ -150.3 (c 2.02, $CHCl_3$)

Conv. 52.4%, *E* value 151, Rate: 17.5 mM h^{-1} mg $enzyme^{-1}$

Tz2-PS catalyzed acetylation:

(*S*)-**2l**: 32.3 mg, 0.155 mmol, Y= 38.8%, 96.5% *ee*, $[\alpha]^{22}_D$ +100.0 (c 1.13, $CHCl_3$)

(*R*)-**1l**: 32.6 mg, 0.2023 mmol, Y= 50.6%, 81.4% *ee*, $[\alpha]^{23}_D$ -78.9 (c 1.26, $CHCl_3$)

Conv. 45.8%, *E* value 142, Rate: 16.0 mM h^{-1} mg $enzyme^{-1}$

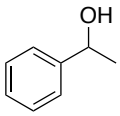
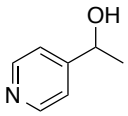
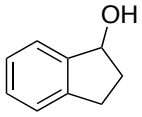
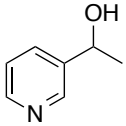
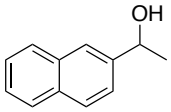
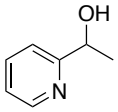
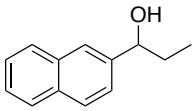
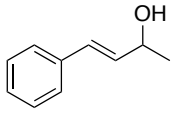
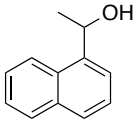
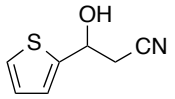
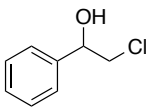
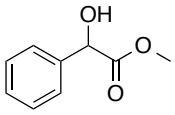
Tz3-PS catalyzed acetylation:

(*S*)-**2l**: 35.0 mg, 0.168 mmol, Y= 42.0%, 95.1% *ee*, $[\alpha]^{24}_D$ +128.4 (c 1.00, $CHCl_3$)

(*R*)-**1l**: 35.3 mg, 0.2124 mmol, Y= 53.1%, 93.6% *ee*, $[\alpha]^{25}_D$ -141.9 (c 1.04, $CHCl_3$)

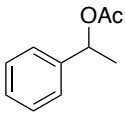
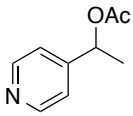
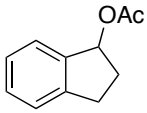
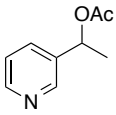
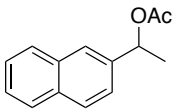
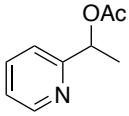
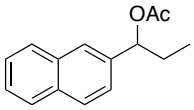
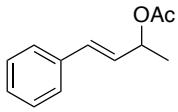
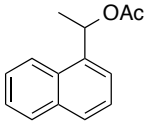
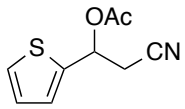
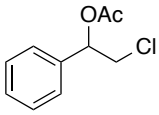
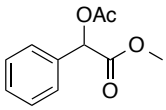
Conv. 49.6%, *E* value 140, Rate: 17.5 mM h^{-1} mg $enzyme^{-1}$

Table S1. List of retention time (tR) of alcohols in the HPLC analysis reported in Table 1.

Compound	Separation conditions: flow speed (solvent ratio), column temp	tR(min.)	Compound	Separation conditions: flow speed (solvent ratio), column temp	tR(min.)
 **1a**	OB-H 1.0 ml/min 5.0% 35℃	S: 8.494 R: 12.756	 **1g**	OD-H 1.0ml/min 7.0% 35℃	S: 16.164 R: 18.096
 **1b**	OD-H 1.0ml/min 2.0% 35℃	S: 16.945 R: 19.046	 **1h**	OB-H 1.0ml/min 11.1% 35℃	S: 6.912 R: 10.911
 **1c**	OB-H 1.0ml/min 1.0% 35℃	S: 35.269 R: 40.379	 **1i**	OD-H 1.0ml/min 1.0% 35℃	S: 23.885 R: 21.317
 **1d**	OD-H 1.0ml/min 11% 35℃	S: 8.104 R: 8.989	 **1j**	OJ-H 1.0ml/min 1.0% 35℃	S: 39.065 R: 41.715
 **1e**	OB-H 1.0ml/min 2.5% 35℃	S: 17.048 R: 26.603	 **1k**	OJ-H 1.0ml/min 15% 25℃	S: 38.558 R: 43.239
 **1f**	OB-H 1.0ml/min 1.0% 35℃	R[a)] : 21.883 S[a)]: 26.773	 **1l**	OB-H 1.0ml/min 5.0% 35℃	R[a)]: 16.143 S[a)]: 17.255

[a)]The assignment was made by the Cahn-Ingold-Prelog priority rule.

Table S2. List of retention time (tR) of acetates in the HPLC analysis reported in Table 1.

Compound	Separation conditions: flow speed (solvent ratio), column temp	tR(min.)	Compound	Separation conditions: flow speed (solvent ratio), column temp	tR(min.)
 **2a**	OB-H 1.0ml/min 0.5% 35℃	S: 19.825 R: 17.606	 **2f**	OB-H 1.0ml/min 5.0% 35℃	S: 7.644 R: 6.962
 **2b**	OD-H 0.5ml/min 0.1% 40℃	S: 16.297 R: 10.122	 **2g**	OD-H 1.0ml/min 4.8% 35℃	S: 13.005 R: 11.175
 **2c**	OD-H 1.0ml/min 1.5% 35℃	S: 15.558 R: 13.642	 **2h**	OB-H 1.0ml/min 2.5% 35℃	S: 16.048 R: 17.484
 **2d**	OB-H 1.0ml/min 0.5% 35℃	S: 19.863 R: 17.437	 **2j**	OB-H 1.0ml/min 5.0% 35℃	S: 7.932 R: 9.319
 **2e**	OJ-H 1.0ml/min 0.5% 35℃	S: 15.348 R: 14.376	 **2k**	OJ-H 0.5ml/min 0.1% 25℃	S: 58.997 R: 65.606
 **2k**	OJ-H 1.0ml/min 1.0% 35℃	R[a)]: 11.616 S[a)]: 9.511	 **2l**	OB-H 1.0ml/min 1.0% 35℃	R[a)]: 21.621 S[a)]: 19.006

[a)] The assignment was made by the Cahn-Ingold-Prelog priority rule.

3. Determination of the Kinetic Parameters

The reaction rates were determined by the experiments as follows: the reaction mixture was sampled at appropriate reaction interval (10 min, 15 min, and 20 mim) and determined % conversion by capillary GC analysis (Quadrex bonded fused silica methyl silicone, ϕ 0.25 mm × 25 m, He) in the presence of an internal reference.

3-1. (*R*)-1h as a model substrate.

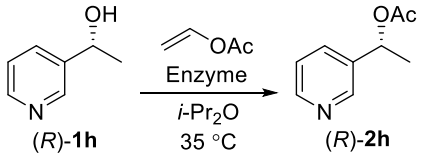


Table S3. Results of IL1-PS in *i*-Pr_2O for (*R*)-1h.

[S] (M)	V (M min^{-1} mg^{-1})[a)]	1 /[S] (M^{-1})	1 /V (M^{-1} min mg)[a)]
0.35	2.86	0.104	9.58
0.3	3.33	0.064	15.6
0.25	4.00	0.103	9.71
0.2	5.00	0.066	15.1
0.15	6.67	0.053	19.0
0.1	10.0	0.033	30.1

[a)]"mg" corresponds to the lipase protein

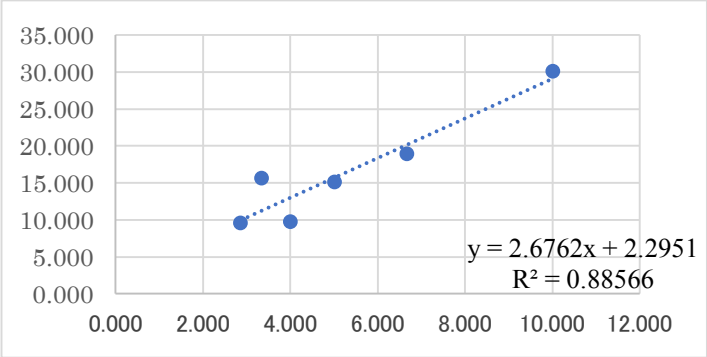


Figure S1. Lineweaver-Burk plots of **IL1**-PS-catalyzed reaction of (*R*)-**1h** in *i*-Pr_2O. Here "y" means 1/[V], "x" means 1/[S]. Using the results, kinetic date were determined as follows: V_{max}= 0.436 (M min^{-1} mg^{-1}), K_m=1.166 (M), K_{cat}=2.33 (min^{-1}), K_{cat}/K_m=2.00 (M^{-1} min^{-1}).

Table S4. Results of Tz1-PS in *i*-Pr_2O for (*R*)-1h.

[S] (M)	V (M min^{-1} mg^{-1})[a)]	1 /[S] (M^{-1})	1 /V (M^{-1} min mg)[a)]
0.35	2.86	0.078	12.8
0.3	3.33	0.076	13.2
0.25	4.00	0.071	14.1
0.2	5.00	0.068	14.6

0.15	6.67	0.062	16.0
0.1	10.0	0.049	20.4

[a)]"mg" corresponds to the lipase protein

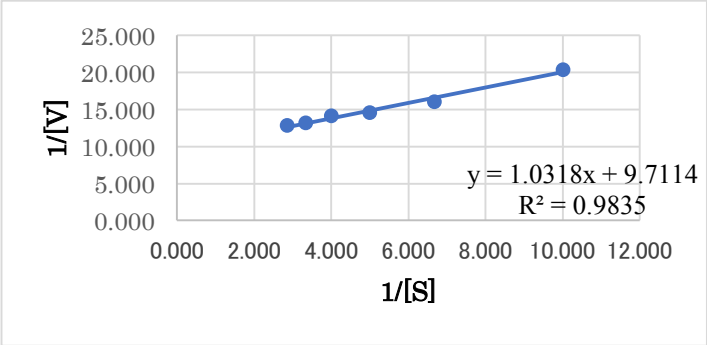


Figure S2. Lineweaver-Burk plots of **Tz1**-PS-catalyzed reaction of (*R*)-**1h** in *i*-Pr_2O. Here "y" means 1/[V], "x" means 1/[S]. Using the results, kinetic date were determined as follows: V_{max}= 0.103 (M min^{-1} mg^{-1}), K_m=0.106 (M), K_{cat}=0.566 (min^{-1}), K_{cat}/K_m=5.32 (M^{-1} min^{-1}).

Table S5. Results of Tz2-PS in *i*-Pr_2O for (*R*)-1h.

[S] (M)	V (M min^{-1} mg^{-1})[a)]	1 /[S] (M^{-1})	1 /V (M^{-1} min mg)[a)]
0.35	2.86	0.044	22.6
0.3	3.33	0.061	16.4
0.25	4.00	0.036	28.1
0.2	5.00	0.038	26.3
0.15	6.67	0.027	37.1
0.1	10.0	0.017	57.9

[a)]"mg" corresponds to the lipase protein

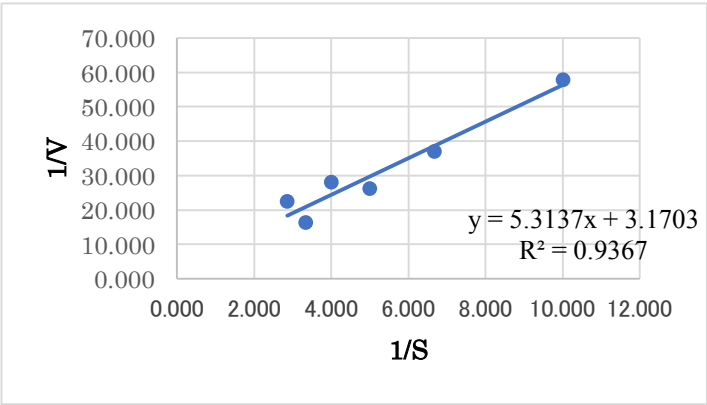


Figure S3. Lineweaver-Burk plots of **Tz2**-PS-catalyzed reaction of (*R*)-**1h** in *i*-Pr_2O. Here "y" means 1/[V], "x" means 1/[S]. Using the results, kinetic date were determined as follows: V_{max}= 0.315 (M min^{-1} mg^{-1}), K_m=1.68 (M), K_{cat}=1.57 (min^{-1}), K_{cat}/K_m=0.937 (M^{-1} min^{-1}).

Table S6. Results of Tz3-PS in *i*-Pr_2O for (*R*)-1h.

[S] (M)	V (M min^{-1} mg^{-1})[a)]	1 /[S] (M^{-1})	1 /V (M^{-1} min mg)[a)]
0.35	2.86	0.044	22.9
0.3	3.33	0.036	27.7
0.25	4.00	0.039	25.9
0.2	5.00	0.024	41.5
0.15	6.67	0.020	50.9
0.1	10.0	0.016	64.3

[a)]"mg" corresponds to the lipase protein

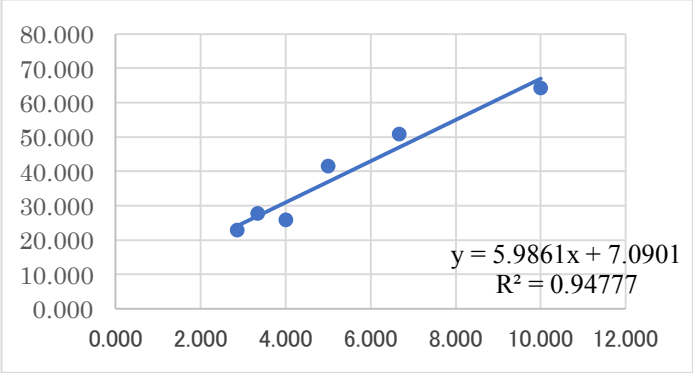


Figure S4. Lineweaver-Burk plots of **Tz3**-PS-catalyzed reaction of (*R*)-**1h** in *i*-Pr_2O. Here "y" means 1/[V], "x" means 1/[S]. Using the results, kinetic date were determined as follows: V_{max}= 0.141 (M min^{-1} mg^{-1}), K_m=0.844 (M), K_{cat}=0.778 (min^{-1}), K_{cat}/K_m=0.922 (M^{-1} min^{-1}).

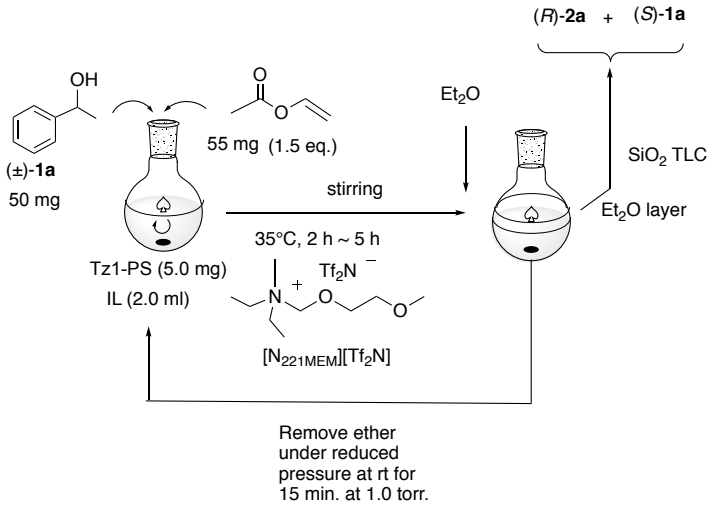


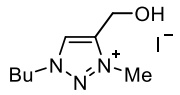
Figure S5. Recycle procedure of **Tz1**-PS.

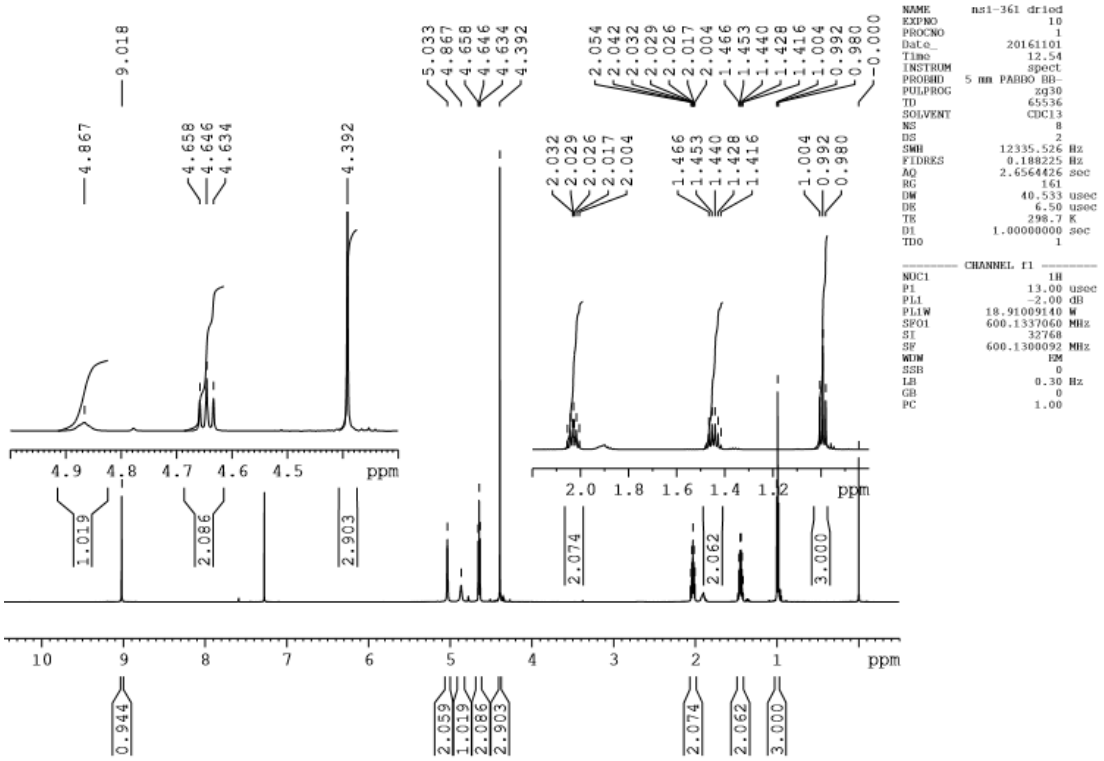
Table S7. Results of recyclable use experimentof Tz1-PS in $[N_{221MEM}][Tf_2N]$.

Run	Substrate Amount: mg	Reaction time	product	Isolated acetate and alcohol Amount: mg	mmol	%Yield	% ee	Conv. and E value
1st	50.5	1 h	(*R*)-**2a**:	28.6	0.176	43.7%	>99% *ee*	Conv. 48.0%,
			(*S*)-**1a**:	17.2	0.758	35.2%	92.4% *ee*	*E* >200
2nd	49.5	1 h	(*R*)-**2a**:	28.9	0.176	42.9%	>99% *ee*	Conv. 49.2%,
			(*S*)-**1a**:	20.0	0.164	40.0%	96.9% *ee*	*E* >200
3rd	49.8	1.5 h	(*R*)-**2a**:	28.5	0.175	42.1%	>99% *ee*	Conv. 50.0%,
			(*S*)-**1a**:	11.7	0.0958	23.4%	>99% *ee*	*E* >200
4th	50.5	2.5 h	(*R*)-**2a**:	29.3	0.202	44.6%	>99% *ee*	Conv. 50.0%,
			(*S*)-**1a**:	9.6	0.0786	28.8%	>99% *ee*	*E* >200
5th	50.7	2 h	(*R*)-**2a**:	28.8	0.176	44.0%	>99% *ee*	Conv. 50.0%,
			(*S*)-**1a**:	11.0	0.0900	22.5%	>99% *ee*	*E* >200
6th	51.8	2 h	(*R*)-**2a**:	31.3	0.191	47.7%	>99% *ee*	Conv. 50.0%,
			(*S*)-**1a**:	25.5	0.209	52.3%	>99% *ee*	*E* >200
7th	50.8	1.5 h	(*R*)-**2a**:	24.3	0.146	36.5%	99.2% *ee*	Conv. 48.7%,
			(*S*)-**1a**:	19.1	0.156	39.1%	94.0% *ee*	*E* >200
8th	59.1	1.5 h	(*R*)-**2a**:	23.9	0.146	36.4%	>99% *ee*	Conv. 46.4%,
			(*S*)-**1a**:	13.7	0.112	28.0%	86.6% *ee*	*E* >200
9th	54.4	1.5 h	(*R*)-**2a**:	28.1	0.171	42.8%	>99% *ee*	Conv. 47.6%,
			(*S*)-**1a**:	26.9	0.220	55.1%	90.8% *ee*	*E* >200
10th	51.0	2 h	(*R*)-**2a**:	20.9	0.127	31.8%	>99% *ee*	Conv. 48.8%,
			(*S*)-**1a**:	20.1	0.165	41.1%	95.2% *ee*	*E* >200
a month[a)]	50.0	2 h	(*R*)-**2a**:	31.1	0.191	47.7%	>99% *ee*	Conv. 50.0%,
			(*S*)-**1a**:	27.0	0.225	50.3%	>99% *ee*	*E* >200
6 months[b)]	50.0	2 h	(*R*)-**2a**:	27.5	0.169	41.8%	>99% *ee*	Conv. 48.8%,
			(*S*)-**1a**:	20.1	0.165	41.1%	95.2% *ee*	*E* >200
12 months [b)]	49.0	2 h	(*R*)-**2a**:	27.8	0.1693	42.3%	>99% *ee*	Conv. 50.0%,
			(*S*)-**1a**:	19.9	0.1629	40.7%	>99% *ee*	*E* >200
18 months [b)]	51.3	5 h	(*R*)-**2a**:	24.2	0.149	36.1%	>99% *ee*	Conv. 44.2%,
			(*S*)-**1a**:	22.0	0.180	44.0%	79.1% *ee*	*E* >200
2 years [b)]	51.2	5 h	(*R*)-**2a**:	30.2	0.184	44.9%	98.5% *ee*	Conv. 50.2%,
			(*S*)-**1a**:	20.6	0.1686	41.1%	99.3% *ee*	*E* >200

[a)]Stored at rt (ca. 25°C). [b)] Stored at 4°C in a refrigerator

^{1}H NMR of **S9**

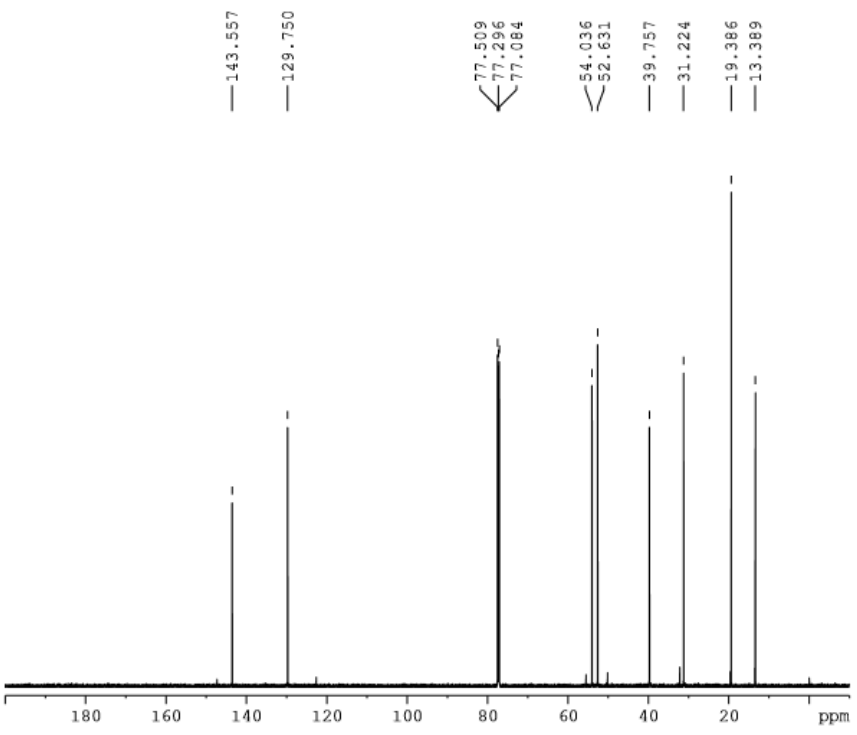





```
NAME          ns1-361 dried
EXPNO                    10
PROCNO                    1
Date_              20161101
Time                  12.54
INSTRUM               spect
PROBHD   5 mm PABBO BB-
PULPROG               zg30
TD                   65536
SOLVENT              CDCl3
NS                       8
DS                       2
SWH               12335.526 Hz
FIDRES            0.188225 Hz
AQ                2.6564426 sec
RG                     161
DW                40.533 usec
DE                 6.50 usec
TE                 298.7 K
D1                1.00000000 sec
TD0                      1

======== CHANNEL f1 ========
NUC1                   1H
P1                 13.00 usec
PL1                -2.00 dB
PL1W           18.91009140 W
SFO1           600.1337060 MHz
SI                   32768
SF             600.1300092 MHz
WDW                    EM
SSB                     0
LB                 0.30 Hz
GB                      0
PC                   1.00
```

^{13}C NMR of **S9**

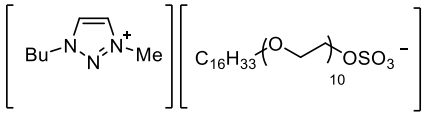


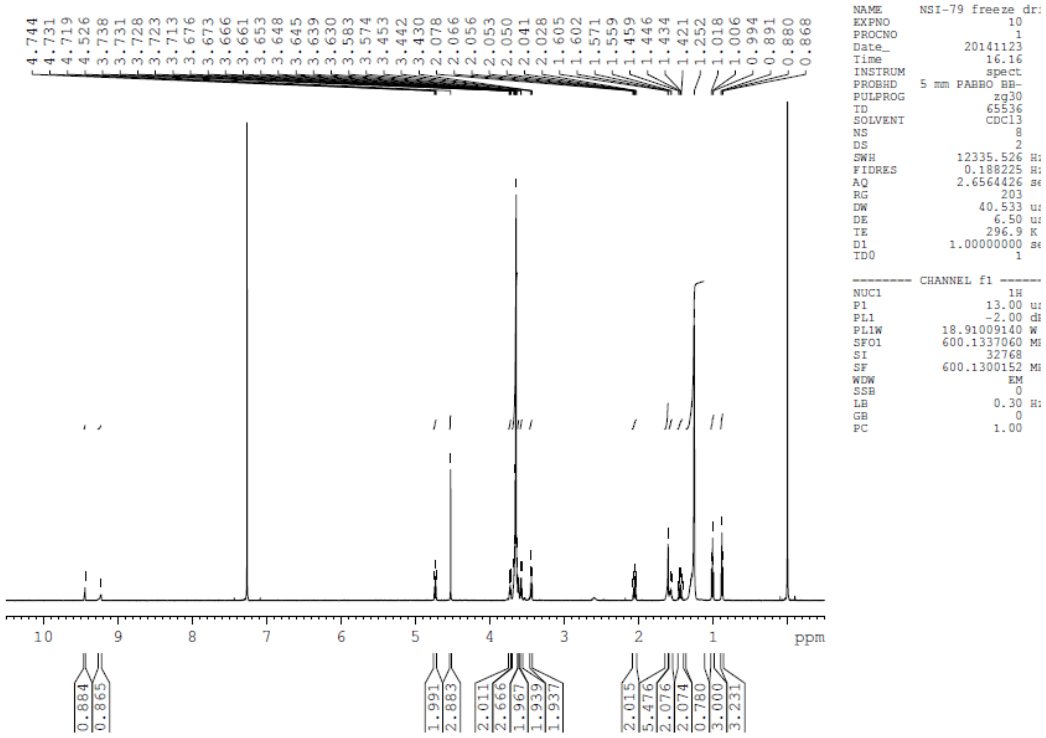

```
NAME             NSI-361 C
EXPNO                   10
PROCNO                   1
Date_             20170221
Time                12.00
INSTRUM             spect
PROBHD   5 mm PABBO BB-
PULPROG             zgpg30
TD                   65536
SOLVENT              CDCl3
NS                     250
DS                       2
SWH              36057.691 Hz
FIDRES           0.550197 Hz
AQ               0.9088159 sec
RG                     203
DW                13.867 usec
DE                 6.50 usec
TE                 294.0 K
D1               2.00000000 sec
D11              0.03000000 sec
TD0                      1

======== CHANNEL f1 ========
NUC1                   13C
P1                 10.00 usec
PL1                -1.00 dB
PL1W          125.22619629 W
SFO1          150.9178988 MHz

======== CHANNEL f2 ========
CPDPRG2             waltz16
NUC2                   1H
PCPD2              80.00 usec
PL2                -2.00 dB
PL12               13.78 dB
PL13               14.00 dB
PL2W          18.91009140 W
PL12W          0.49968192 W
PL13W          0.47499999 W
SFO2          600.1324005 MHz
SI                   32768
SF            150.9028090 MHz
WDW                    EM
SSB                     0
LB                 1.00 Hz
GB                      0
PC                   1.40
```

^{1}H NMR of **Tz1**

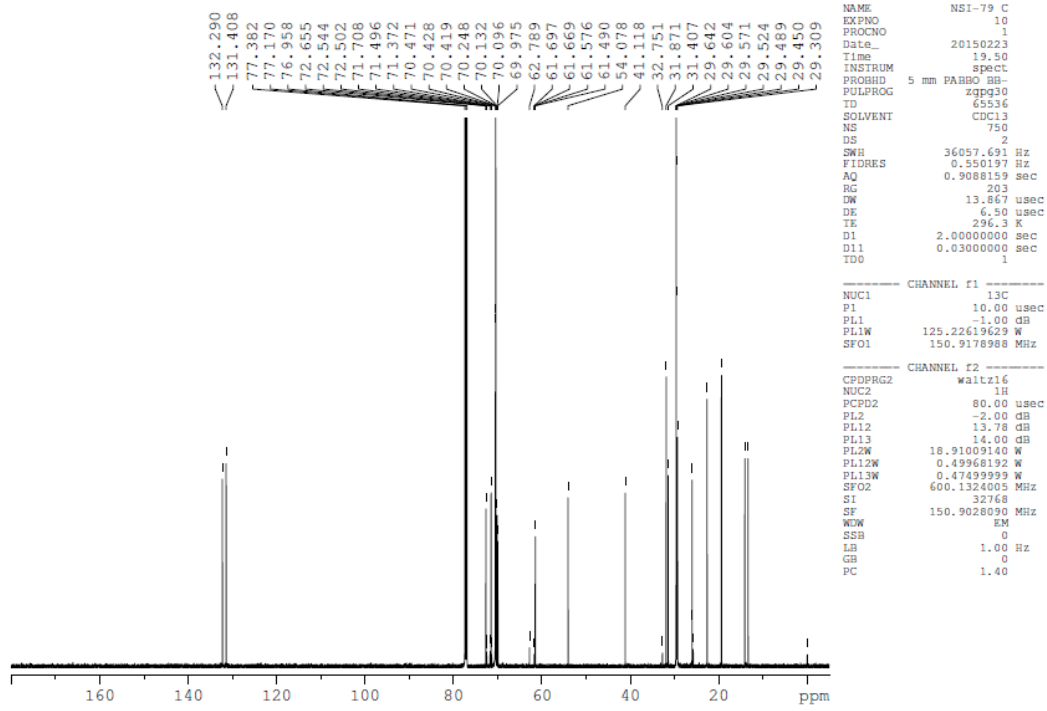





```
NAME          NSI-79 freeze dr
EXPNO                       10
PROCNO                       1
Date_              20141123
Time                    16.16
INSTRUM                 spect
PROBHD   5 mm PABBO BB-
PULPROG                 zg30
TD                      65536
SOLVENT                 CDCl3
NS                          8
DS                          2
SWH                12335.526 H
FIDRES              0.188225 H
AQ                  2.6564426 s
RG                        203
DW                     40.533 u
DE                      6.50 u
TE                     296.9 K
D1                 1.00000000 s
TD0                         1

======== CHANNEL f1 ========
NUC1                       1H
P1                      13.00 u
PL1                     -2.00 d
PL1W               18.91009140 W
SFO1              600.1337060 M
SI                        32768
SF                600.1300152 M
WDW                        EM
SSB                         0
LB                       0.30 H
GB                          0
PC                       1.00
```

^{13}C NMR of **Tz1**

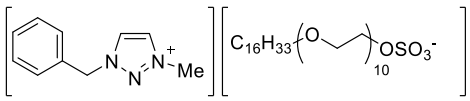


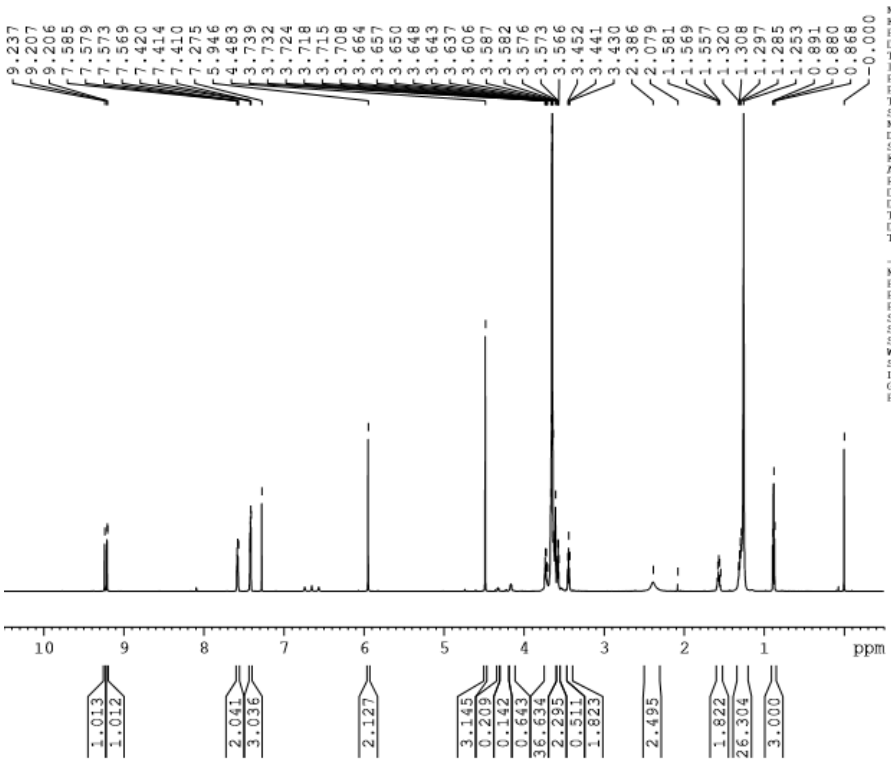

```
NAME                NSI-79 C
EXPNO                     10
PROCNO                     1
Date_            20150223
Time                  19.50
INSTRUM               spect
PROBHD   5 mm PABBO BB-
PULPROG             zgpg30
TD                    65536
SOLVENT               CDCl3
NS                      750
DS                        2
SWH              36057.691 Hz
FIDRES            0.550197 Hz
AQ                0.9088159 sec
RG                      203
DW                   13.867 usec
DE                    6.50 usec
TE                   296.3 K
D1               2.00000000 sec
D11              0.03000000 sec
TD0                       1

======== CHANNEL f1 ========
NUC1                     13C
P1                    10.00 usec
PL1                   -1.00 dB
PL1W           125.22619629 W
SFO1            150.9178988 MHz

======== CHANNEL f2 ========
CPDPRG2             waltz16
NUC2                     1H
PCPD2                 80.00 usec
PL2                   -2.00 dB
PL12                  13.78 dB
PL13                  14.00 dB
PL2W           18.91009140 W
PL12W           0.49968192 W
PL13W           0.47499999 W
SFO2            600.1324005 MHz
SI                      32768
SF              150.9028090 MHz
WDW                      EM
SSB                       0
LB                     1.00 Hz
GB                        0
PC                     1.40
```

^{1}H NMR of **Tz2**

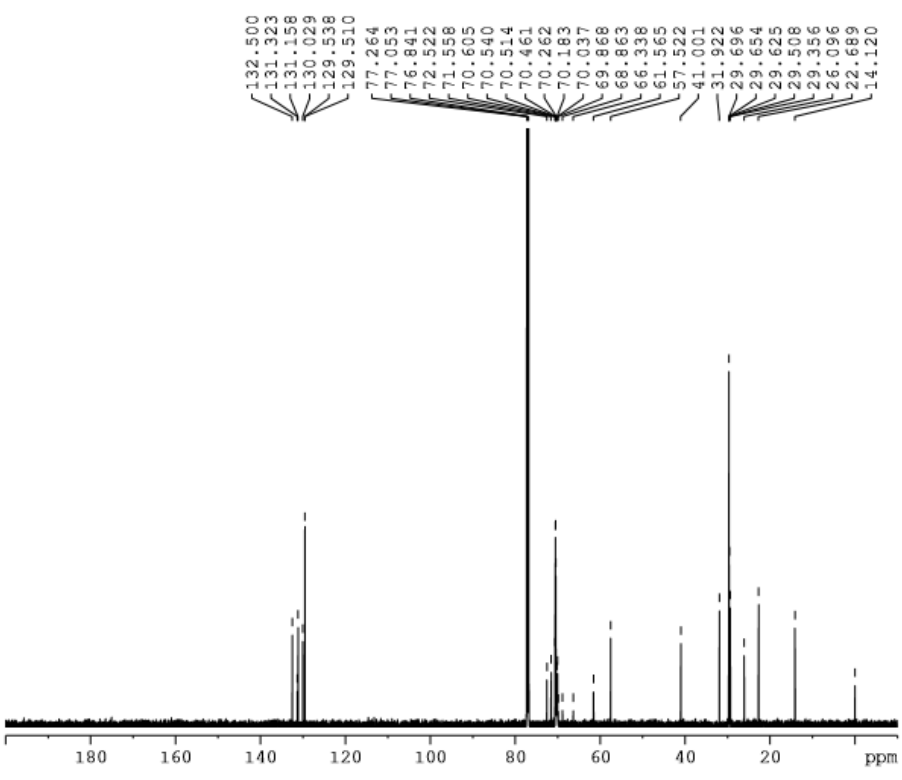




NAME NSI-342 freezed 2
EXPNO 10
PROCNO 1
Date_ 20161001
Time 12.22
INSTRUM spect
PROBHD 5 mm PABBO BB-
PULPROG zg30
TD 65536
SOLVENT CDCl3
NS 16
DS 2
SWH 12335.526 Hz
FIDRES 0.188225 Hz
AQ 2.6564426 sec
RG 90.5
DW 40.533 use
DE 6.50 use
TE 298.2 K
D1 1.00000000 sec
TD0 1

CHANNEL f1
NUC1 1H
P1 13.00 use
PL1 -2.00 dB
PL1W 18.91009140 W
SFO1 600.1337060 MHz
SI 32768
SF 600.1300075 MHz
WDW EM
SSB 0
LB 0.30 Hz
GB 0
PC 1.00

^{13}C NMR of **Tz2**

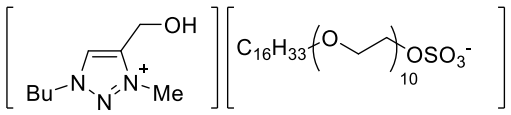


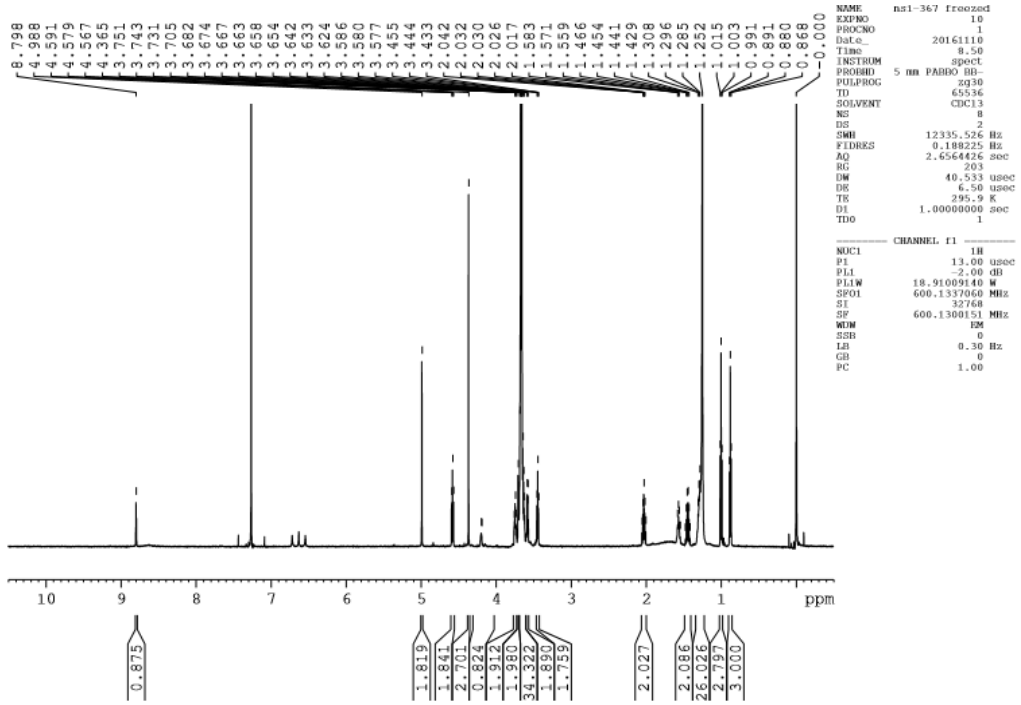
NAME NSI-342 freezed c
EXPNO 10
PROCNO 1
Date_ 20161001
Time 12.58
INSTRUM spect
PROBHD 5 mm PABBO BB-
PULPROG zgpg30
TD 65536
SOLVENT CDCl3
NS 700
DS 2
SWH 36057.691 Hz
FIDRES 0.550197 Hz
AQ 0.9088159 sec
RG 203
DW 13.867 usec
DE 6.50 usec
TE 299.9 K
D1 2.00000000 sec
D11 0.03000000 sec
TD0 1

CHANNEL f1
NUC1 13C
P1 10.00 usec
PL1 -1.00 dB
PL1W 125.22619629 W
SFO1 150.9178988 MHz

CHANNEL f2
CPDPRG2 waltz16
NUC2 1H
PCPD2 80.00 usec
PL2 -2.00 dB
PL12 13.78 dB
PL13 14.00 dB
PL2W 18.91009140 W
PL12W 0.49968192 W
PL13W 0.47499999 W
SFO2 600.1324005 MHz
SI 32768
SF 150.9028080 MHz
WDW EM
SSB 0
LB 1.00 Hz
GB 0
PC 1.40

^{1}H NMR of **Tz3**

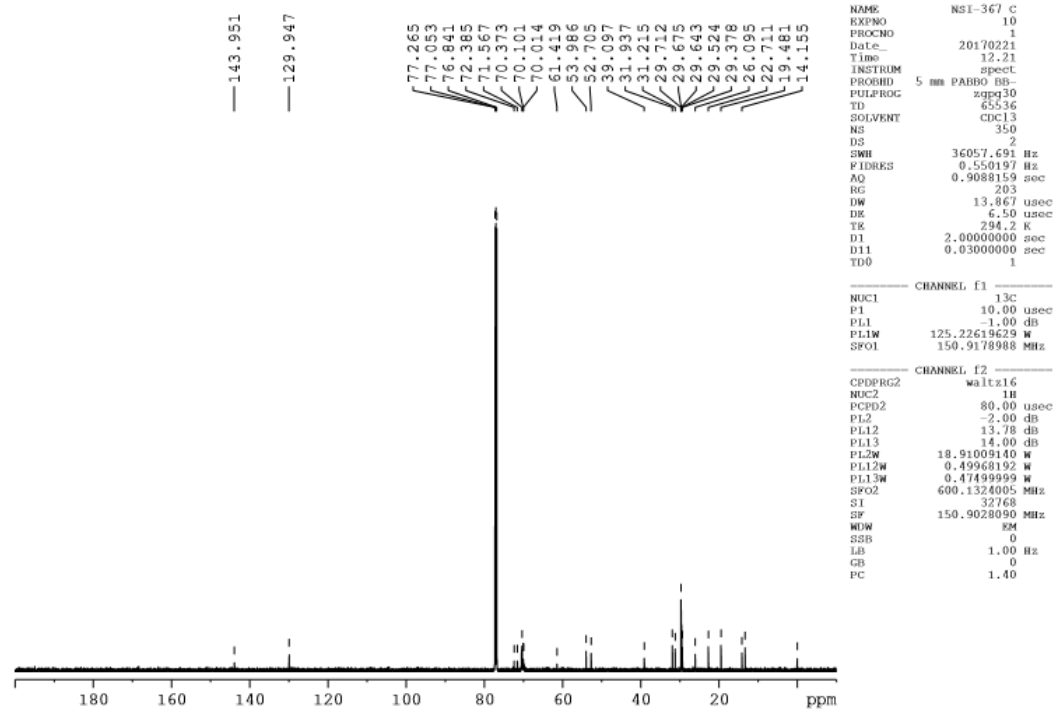




NAME ns1-367 freezed
EXPNO 10
PROCNO 1
Date_ 20161110
Time 8.50
INSTRUM spect
PROBHD 5 mm PABBO BB-
PULPROG zg30
TD 65536
SOLVENT CDCl3
NS 8
DS 2
SWH 12335.526 Hz
FIDRES 0.188225 Hz
AQ 2.6564426 sec
RG 203
DW 40.533 usec
DE 6.50 usec
TE 295.9 K
D1 1.00000000 sec
TD0 1

CHANNEL f1
NUC1 1H
P1 13.00 usec
PL1 -2.00 dB
PL1W 18.91009140 W
SFO1 600.1337060 MHz
SI 32768
SF 600.1300151 MHz
WDW EM
SSB 0
LB 0.30 Hz
GB 0
PC 1.00

^{13}C NMR of **Tz3**



NAME NSI-367 C
EXPNO 10
PROCNO 1
Date_ 20170221
Time 12.21
INSTRUM spect
PROBHD 5 mm PABBO BB-
PULPROG zgpg30
TD 65536
SOLVENT CDCl3
NS 350
DS 2
SWH 36057.691 Hz
FIDRES 0.550197 Hz
AQ 0.9088159 sec
RG 203
DW 13.867 usec
DE 6.50 usec
TE 294.2 K
D1 2.00000000 sec
D11 0.03000000 sec
TD0 1

CHANNEL f1
NUC1 13C
P1 10.00 usec
PL1 -1.00 dB
PL1W 125.22619629 W
SFO1 150.9178988 MHz

CHANNEL f2
CPDPRG2 waltz16
NUC2 1H
PCPD2 80.00 usec
PL2 -2.00 dB
PL12 13.78 dB
PL13 14.00 dB
PL2W 18.91009140 W
PL12W 0.49968192 W
PL13W 0.47499999 W
SFO2 600.1324005 MHz
SI 32768
SF 150.9028090 MHz
WDW EM
SSB 0
LB 1.00 Hz
GB 0
PC 1.40

References

[1] Y. Jeong, J-S. Ryu, *J. Org. Chem*. 2010, **75**, 4183.

[2] N. Srivastava, M. Shukla, S. Saha, *Indian J. Chem*. 2010, **49A**, 757.

[3] T. Itoh, Y. Matsushita, Y. Abe, S-H. Han, S. Wada, S. Hayase, M. Kawatsura, S. Takai, M. Morimoto, Y. Hirose, Y. *Chem. Eur. J.* 2006, **12**, 9228.

[4] R. Romeo, S. V. Giofre, C. Carnovale, A. Campisi, R. Parenti, L. Bandini, M. A. Chiacchio, *Bioorg. Med. Chem*. **2013**, *21*, 7929.