Supplementary information

A Rational Design of Phosphonium Salt Type Ionic Liquids for Ionic Liquid Coated-Lipase Catalyzed Reaction

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Preparation of IL1: 1-Butyl-2,3-dimethylimidazolium polyoxyethylene alkyl sulfate (IL1)

(1) 1-Butyl-2,3-dimethylimidazolium chloride

A solution of 1,2-dimethylimidazole (55.4 g, 0.58 mol) and 1-chlorobutane (53.3 g, 0.58 mol) was stirred for 24 h under reflux conditions. After being cooled to room temperature, excess 1-chlorobutane was removed under reduced pressure to give 1-butyl-2,3-dimethylimidazolium chloride ([bdmim][Cl]) as a half melted white solid and it was used to the next reaction without further purification.

(2)Ammonium polyoxyethylene(n) alkyl sulfate

A mixture of Brij56 (polyoxyethylene(10) cetyl ether)(13.7 g, 20.0 mmol) and sulfamic acid (1.94 g, 20.0 mmol) was stirred for 17 h at 110 ºC under argon and dried under reduced pressure at 66.7 Pa at 60 ºC for 3 h to give ammonium Brij56-sulfate as a white solid.

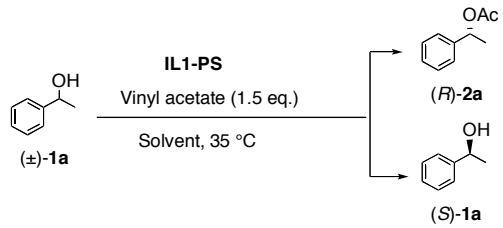
(3) 1-Butyl-2,3-dimethylimidazolium polyoxyethylene alkyl sulfate (IL1)

After the preparation of ammonium polyoxyethylene(10) cetyl sulfate and 1-butyl-2,3-dimethylimidazolium chloride, these two crude products were added to an acetone solution (20 mL) and the mixture was stirred for 24 h at rt. Ammonium chloride which precipitated was removed by filtration through a sintered glass filter with a Celite pad. The filtrate was concentrated under vacuum for a little while, and then activated carbon was added and was stirred for 10 minutes. The activated carbon was removed by filtration through a sintered glass filter with a Celite pad and the filtrate was filtered through Al_2O_3 (neutral type I, activated) short column. The filtrate was evaporated and dried under reduced pressure at 5 Torr for 24 h at 60 ºC to give 1-butyl-2,3-dimethylimidazolium polyoxyethylene(10) cetyl sulfate (13.6 g, 0.015 mol) as a yellowish solid at room temperature in 74% yield: mp 35-37ºC; ^{1}H NMR (500 MHz, ppm, $CDCl_3$, *J*= Hz) δ 0.80 (3H, t, *J*= 7.4), 0.88 (3H, t, *J*= 7.3), 1.10-1.30 (32H, m), 1.29-1.31 (2H, m), 1.47-1.50 (4H, m), 1.70-1.73 (2H, m), 2.61 (3H, s), 3,36 (4H, t, *J*= 5.1), 3.49-3.62 (34H, m), 3.81 (3H, s), 4.00 (2H, t, *J*= 5.1), 4.07 (2H, t, *J*= 7.8), 7.24 (1H, s), 7.38 (1H, s); ^{13}C NMR (125 MHz, ppm, $CDCl_3$) δ 9.48, 13.20, 13.77, 19.23, 22.30, 25.73, 28.98, 29.11, 29.23, 29.31, 31.35, 31.54, 35.06, 48.01, 61.20, 65.78, 69.68, 69.05, 70.19, 71.12, 72.26, 120.17, 122.65, 143.57; IR (neat, cm^{-1}) 2916, 2851, 1468, 1350, 1252, 1115, 951, 845; MALDI-TOF MS (matrix: SA) found 1344 (average MW).

Preparation of IL1-supported lipase PS (IL1-PS) by lyophilization

To a buffer solution (pH 7.2)(10 mL) was added 1.0 g commercial Lipase PS-C (Amano). The mixture was centrifuged at 3000 rpm for 5 minutes. IL1 (29.0 mg, ca. 3.1×10^{-2} mmol) was dissolved into the resulting supernatant, that involves ca. 3.1×10^{-4} mmol of lipase PS protein, and the mixture was lyophilized to give IL1-PS (344 mg) as a white powder.

Lipase-catalyzed transesterification of (±)-1a using IL1-PS.



To a solution of (±)-**1a** (50 mg, 0.41 mmol) and vinyl acetate (55 mg, 0.64 mmol) in *i*-Pr_2O (2.0 mL) was added IL1-PS (5.0 mg) and the mixture was stirred at 35 ºC. The reaction course was monitored by capillary GC-analysis and silica gel TLC. (*R*)-**2a** and (*S*)-**1a** were obtained by preparative silica gel thin layer chromatography (TLC). The enantioselectivity was determined by HPLC analysis on a chiral column (Chiralcel OB, hexane: 2-propanol = 9 : 1).

(*R*)-**2a**: Rf 0.55 (hexane/ethyl acetate = 4/1); ^{1}H NMR (500 MHz, ppm, $CDCl_3$, *J*= Hz) 1.47 (3H, d, *J*= 6.9 Hz), 2.00 (3H, s), 5.81 (1H, q, *J*= 6.9 Hz), 7.19-7.29 (5H, m); ^{13}C NMR (125 MHz, ppm, $CDCl_3$) δ 21.25, 22.12,

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72.22, 126.00, 127.77, 128.40, 141.59, 170.21; IR (neat, cm^{-1}) 2980, 1730, 1495, 1370, 1240, 1030, 940, 760. (*S*)-**1a**: Rf 0.25 (hexane/ethyl acetate = 4:1); ^{1}H NMR (500 MHz, ppm, $CDCl_3$, *J*= Hz) δ 1.43 (3H, d, *J*= 6.4 Hz), 1.75 (1H, s, OH), 4.83 (1H, q, *J*= 6.4 Hz), 7.28-7.30 (5H, m); ^{13}C NMR (125 MHz, ppm, $CDCl_3$) δ 25.01, 70.13, 125.30, 127.26, 128.33, 145.76; IR (neat, cm^{-1}) 3330, 3030, 2970, 2890, 1490, 1450, 1010, 900.

Table S1. Results of IL1-PS-catalyzed transesterification of (±)-**1a** in various solvents

Entry	Enzyme	Solvent	%ee of (R)-2 (% Yield)[b]	%ee of (S)-1[a] (% Yield)[b]	Rate [c] ([M/mg enzyme, hr^{-1}])	Conv.[d]	E value[d]
1	IL1-PS	*i*-Pr_2O	>99(34)	98(53)	3.4	50	>200
2	IL1-PS	[bmim][C_5F_8]	93 (26)	35 (71)	0.73	27	38
3	IL1-PS	[bmim][NTf_2]	96 (18)	22 (75)	0.52	19	60
4	IL1-PS	[N_{221ME}][NTf_2]	99 (30)	99 (25)	1.5	46	>200
5	IL1-PS	[P_{4441}][NTf_2]	99 (30)	85 (40)	2.0	46	>200
6	IL1-PS	[P_{444EM}][NTf_2]	99 (34)	40 (54)	0.25	29	>200
7	IL1-PS	[P_{444ME}][NTf_2]]	>99 (39)	98 (44)	4.2	49	>200
8	IL1-PS	[P_{444MEM}][NTf_2]	>99 (46)	88 (53)	6.2	47	>200
9	IL1-PS	[P_{tdmbm}][NTf_2]	>99 (49)	96 (38)	2.9	49	>200

[a] Determined by HPLC (Chiralcel OB-H, n-hexane:2-PrOH= 20:1). [b]Isolated yield. [c] The rate was determined by GC analysis at 30 min. of reaction. [d] Calculated by %ee of (*R*)-**2a** (ee_p) and %ee of (*S*)-**1a** (ee_s). E= $\ln[(1-c(1+ee_p))/\ln[(1-c(1-ee_p))$, here c means conv. which was calculated by the following formula: $c = ee_s/(ee_p+ee_s)$.