Supporting Information

Widely Useful DMAP-Catalyzed Esterification under Auxiliary Base- and Solvent-Free Conditions

*Akira Sakakura, Kimio Kawajiri, Takuro Ohkubo, Yuji Kosugi and Kazuaki Ishihara**

Graduate School of Engineering, Nagoya University, Chikusa, Nagoya, 464-8603 Japan

General Method. IR spectra were recorded on a JASCO FT/IR-460 plus spectrometer. ^{1}H spectra were measured on a Varian Gemini-2000 spectrometer (300 MHz) at ambient temperature. Data were recorded as follows: chemical shift in ppm from internal tetramethysilane on the δ scale, multiplicity (s = singlet; d = doublet; t = triplet; m = multiplet), coupling constant (Hz), and integration. ^{13}C NMR spectra were measured on a Varian Gemini-2000 spectrometer (75 MHz) at ambient temperature. Chemical shifts were recorded in ppm from the solvent resonance employed as the internal standard ($CDCl_3$ at 77.0 ppm). All experiments were carried out under an atmosphere of dry nitrogen. For TLC analysis, Merck precoated TLC plates (silica gel 60 F_{254} 0.25 mm) were used. For purification of products, Fuji Silysia silica gel NH (100–200 mesh) was used. Chemical materials were obtained from commercial supplies and used without further purification. Polystyrene-supported DMAP was purchased from Aldrich. All products in the present work except 2,3,5,6-*O*-tetraisobutyl-L-ascorbic acid (Table 1, entry 12) are known compounds. Acetyl tributyl citrate (Table 1, entry 13) and glyceryl trioleate (Table 2) are commercially available (Aldrich, TCI, Wako, and so on).

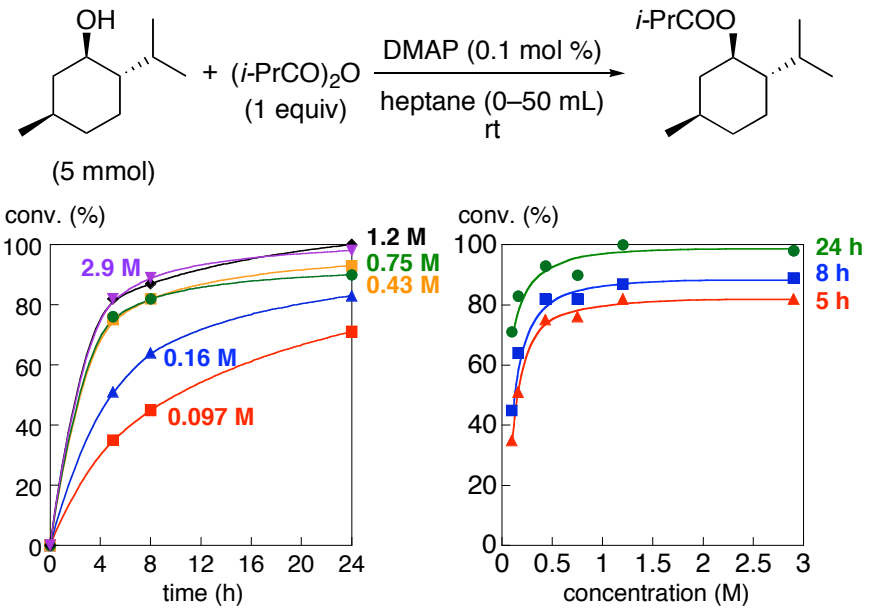
Estimation of Concentrations of *l*-Menthol in the DMAP-Catalyzed Isobutyrylation (Figure 2)

Concentrations of *l*-menthol in the reaction mixtures were estimated as follows.

- *l*-menthol (FW 156.27, d 0.89); 5 mmol = 0.88 mL [A]
- isobutyric anhydride (FW 158.19, d 0.954); 5 mmol = 0.83 mL [B]
- *i*-Pr_2NEt (FW 129.24, d 0.742); 5 mmol = 0.87 mL

entry	solvent (mL) [C]	*i*-Pr_2NEt (mL) [D]	total volume of the reaction mixture (mL) [A+B+C+D]	concentration of *l*-menthol (M) [5/(A+B+C+D)]
1	0	0	1.71	2.9
2	5	0	6.71	0.75
3	0	0.87	2.58	1.9
4	5	0.87	7.58	0.66

Effect of Concentration in the DMAP-catalyzed Isobutyrylation of *l*-Menthol in Heptane under Base-free Conditions. The reaction of *l*-menthol (5 mmol) was conducted with $(i\text{-PrCO})_2O$ (5 mmol) in the presence of DMAP (0.1 mol%) in heptane (0–50 mL).



The DMAP-catalyzed isobutyrylation in heptane showed similar reactivities at concentrations ranging from 0.5 to 2.9 M, and the reactivity decreased at concentrations below 0.5 M.

Concentrations of *l*-menthol in the reaction mixtures were estimated as follows.

entry	heptane (mL)	total volume of the reaction mixture (mL)	concentration of *l*-menthol (M)
1	0 (solvent-free)	1.71	2.9
2	2.5	4.21	1.2
3	5	6.71	0.75
4	10	11.71	0.43
5	30	31.71	0.16
6	50	51.71	0.097

Estimation of Concentrations of *l*-Menthol in the DMAP-Catalyzed Acylations under Base-Free Conditions (Figure 3)

Concentrations of *l*-menthol in the reaction mixtures were estimated as follows.

- *l*-menthol (FW 156.27, d 0.89); 5 mmol = 0.88 mL [A]
- acetic anhydride (FW 102.09, d 1.08); 5.5 mmol = 0.52 mL [B1]
- isobutyric anhydride (FW 158.19, d 0.954); 5.5 mmol = 0.92 mL [B2]
- pivalic anhydride (FW 186.25, d 0.918); 5.5 mmol = 1.12 mL [B3]
- *i*-Pr_2NEt (FW 129.24, d 0.742); 5.5 mmol = 0.96 mL
- heptane 5.0 mL [D]

Acetylation

solvent-free (graph C)				in heptane (graph D)			
entry	*i*-Pr_2NEt (mL) [C]	total volume of the reaction mixture (mL) [A+B1+C]	concentration of *l*-menthol (M) [5/(A+B1+C)]	entry	*i*-Pr_2NEt (mL) [C]	total volume of the reaction mixture (mL) [A+B1+C+D]	concentration of *l*-menthol (M) [5/(A+B1+C+D)]
1	0	1.40	3.6	3	0	5.40	0.93
2	0.96	2.36	2.1	4	0.96	7.36	0.68

Isobutyrylation

solvent-free (graph E)				in heptane (graph F)			
entry	*i*-Pr_2NEt (mL) [C]	total volume of the reaction mixture (mL) [A+B1+C]	concentration of *l*-menthol (M) [5/(A+B1+C)]	entry	*i*-Pr_2NEt (mL) [C]	total volume of the reaction mixture (mL) [A+B1+C+D]	concentration of *l*-menthol (M) [5/(A+B1+C+D)]
5	0	1.80	2.8	7	0	6.80	0.74
6	0.96	2.76	1.8	8	0.96	7.76	0.64

Pivaloylation

solvent-free (graph G)				in heptane (graph H)			
entry	*i*-Pr_2NEt (mL) [C]	total volume of the reaction mixture (mL) [A+B1+C]	concentration of *l*-menthol (M) [5/(A+B1+C)]	entry	*i*-Pr_2NEt (mL) [C]	total volume of the reaction mixture (mL) [A+B1+C+D]	concentration of *l*-menthol (M) [5/(A+B1+C+D)]
9	0	2.00	2.5	11	0	7.00	0.71
10	0.96	2.96	1.7	12	0.96	7.96	0.63

Typical Procedure for Acylation of Alcohols with Acid Anhydrides (Table 1). To a mixture of *l*-menthol (7.81 g, 50 mmol) and DMAP (31 mg, 0.25 mmol) was added isobutyric anhydride (9.12 mL, 55 mmol) at ambient temperature. After being stirred at ambient temperature for 9 h, water (90 μL, 5.0 mmol) was added and then the mixture was stirred for 1 h. Purification by distillation under reduced pressure [bp. 98 °C at 0.0006 Torr (ULVAC VPC-050)] gave (1*R*,2*S*,5*R*)-5-methyl-2-(1-methylethyl)-cyclohexyl 2-methylpropanoate (11.1 g, 98% yield).

3-Phenylpropyl acetate (entry 1):[1,2] ^{1}H NMR (300 MHz, $CDCl_3$) δ 1.90–2.01 (m, 2H), 2.05 (s, 3H), 2.69 (t, *J* = 7.4 Hz, 2H), 4.09 (t, *J* = 6.5 Hz, 2H), 7.11–7.33 (m, 5H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 21.0, 30.1, 32.1, 63.8, 126.0, 128.4, 128.4, 141.2, 171.2.

3-Phenylpropyl 2-methylpropanoate (entry 2):[1,3] ^{1}H NMR (300 MHz, $CDCl_3$) δ 1.18 (d, *J* = 7.0 Hz, 6H), 1.90–2.02 (m, 2H), 2.55 (septet, *J* = 7.0 Hz, 1H), 2.69 (t, *J* = 7.8 Hz, 2H), 4.09 (t, J = 6.5 Hz, 2H), 7.11–7.34 (m, 5H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 19.0, 30.2, 32.1, 34.5, 63.5, 126.0, 128.4, 128.4, 141.2, 177.2.

3-Phenylpropyl 2,2-dimethylpropanoate (entry 3):[1,3] ^{1}H NMR (300 MHz, $CDCl_3$) δ 1.26 (s, 9H), 1.97–2.03 (m, 2H), 2.74 (t, *J* = 7.6 Hz, 2H), 4.12 (t, J = 6.3 Hz, 2H), 7.21–7.34 (m, 5H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 27.2, 30.3, 32.1, 38.7, 63.5, 126.0, 128.4, 128.4, 141.2, 178.5.

(1*R*,2*S*,5*R*)-5-Methyl-2-(1-methylethyl)cyclohexyl acetate (entry 4):[1,7] ^{1}H NMR (300 MHz, $CDCl_3$) δ 0.76 (d, *J* = 7.0 Hz, 3H), 0.89 (d, *J* = 7.0 Hz, 3H), 0.90 (d, *J* = 6.6 Hz, 3H), 0.84–1.14 (m, 3H),

1.30–1.60 (m, 2H), 1.79–1.93 (m, 2H), 1.93–2.04 (m, 2H), 2.03 (s, 3H), 4.67 (dt, J = 4.4, 10.8 Hz, 1H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 16.3, 20.7, 21.3, 22.0, 23.4, 26.3, 31.3, 34.2, 40.9, 47.0, 74.1, 170.7.

(1*R*,2*S*,5*R*)-5-Methyl-2-(1-methylethyl)cyclohexyl 2-methylpropanoate (entries 5, 6):[1,8] ^{1}H NMR (300 MHz, $CDCl_3$) δ 0.75 (d, J = 6.9 Hz, 3H), 0.89 (d, J = 7.1 Hz, 3H), 0.90 (d, J = 6.4 Hz, 3H), 0.81–1.10 (m, 3H), 1.15 (d, J = 6.9 Hz, 3H), 1.16 (d, J = 6.9 Hz, 3H), 1.32–1.59 (m, 2H), 1.62–1.74 (m, 2H), 1.82–2.02 (m, 2H), 2.51 (septet, J = 6.9 Hz, 1H), 4.65 (dt, J = 4.4, 10.9 Hz, 1H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 16.1, 19.0, 20.8, 22.0, 23.3, 26.1, 31.3, 34.2, 40.4, 47.0, 73.7, 176.7.

(1*R*,2*S*,5*R*)-5-Methyl-2-(1-methylethyl)cyclohexyl 2,2-dimethylpropanoate (entry 7):[1,9] ^{1}H NMR (300 MHz, $CDCl_3$) δ 0.75 (d, J = 7.0 Hz, 3H), 0.80–1.11 (m, 3H), 0.89 (d, J = 6.8 Hz, 3H), 0.90 (d, J = 6.8 Hz, 3H), 1.19 (s, 9H), 1.30–1.44 (m, 1H), 1.44–1.56 (m, 1H), 1.62–1.72 (m, 2H), 1.82–2.00 (m, 2H), 4.62 (dt, J = 4.4, 10.8 Hz, 1H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 16.0, 20.8, 22.0, 23.2, 26.1, 27.1, 31.3, 34.3, 38.7, 40.7, 47.0, 73.7, 178.0.

Glyceryl triacetate (entry 8):[10] ^{1}H NMR (300 MHz, $CDCl_3$) δ 2.09 (s, 6H), 2.10 (s, 3H), 4.16 (dd, J = 5.8, 12.1 Hz, 2H), 4.30 (dd, J = 4.6, 12.1 Hz, 2H), 5.25 (tt, J = 4.6, 5.8 Hz, 1H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 169.7, 169.4, 68.5, 61.6, 20.1, 19.9.

Glyceryl triisobutyrate (entry 9):[11] ^{1}H NMR (300 MHz, $CDCl_3$) δ 1.17 (d, J = 7.2 Hz, 3H), 1.17 (d, J = 7.2 Hz, 6H), 2.57 (sept, J = 7.2 Hz, 3H), 4.16 (dd, J = 6.0, 12.0 Hz, 2H), 4.32 (dd, J = 4.2, 12.0 Hz, 2H), 5.29 (tt, J = 4.2, 6.0 Hz, 1H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 18.4, 18.4, 33.4, 33.5, 61.6, 68.5, 175.5, 175.8.

Methyl 2,3,4,6-*O*-tetraacetyl-α-D-glucopyranoside (entry 10):[12] ^{1}H NMR (300 MHz, $CDCl_3$) δ 2.02 (s, 3H), 2.03 (s, 3H), 2.09 (s, 3H), 2.11 (s, 3H), 3.42 (s, 3H), 3.99 (ddd, *J* = 2.4, 4.8, 9.9 Hz, 1H), 4.11 (dd, *J* = 2.4, 12.3 Hz, 1H), 4.27 (dd, *J* = 4.8, 12.3 Hz, 1H), 4.91 (dd, *J* = 3.6, 9.9 Hz, 1H), 4.96 (d, *J* = 3.6 Hz, 1H), 5.08 (dd, *J* = 9.6, 9.9 Hz, 1H), 5.49 (dd, *J* = 9.6, 9.9 Hz, 1H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 20.4, 20.4, 20.5, 55.2, 61.6, 66.9, 68.2, 69.8, 70.5, 96.5, 169.4, 169.8, 169.9, 170.4.

Methyl 2,3,4,6-*O*-tetraisobutyl-α-D-glucopyranoside (entry 11):[13] ^{1}H NMR (300 MHz, $CDCl_3$) δ 1.06–1.30 (m, 24H), 2.39–2.71 (m, 4H), 3.41 (s, 3H), 4.01 (ddd, *J* = 2.1, 5.1, 10.2 Hz, 1H), 4.13 (dd, *J* = 2.1, 12.3 Hz, 1H), 4.20 (dd, *J* = 5.1, 12.6 Hz, 1H), 4.89 (dd, *J* = 3.6, 10.2 Hz, 1H), 4.95 (d, *J* = 3.6 Hz, 1H), 5.11 (dd, *J* = 9.9, 10.2 Hz, 1H), 5.54 (dd, *J* = 9.9, 10.2 Hz, 1H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 18.6, 18.7, 18.7, 18.8, 33.6, 33.7, 33.8, 55.3, 61.6, 67.3, 67.8, 69.4, 70.6, 96.7, 175.3, 175.7, 176.1, 176.6.

2,3,5,6-*O*-Tetraisobutyl-L-ascorbic acid (entry 12): $[\alpha]^{23.5}_{D}$ –40.8 (c 1.05, $CHCl_3$); IR (neat) 1794, 1745, 1697, 1470, 1388, 1338, 1205, 1187, 1145, 1085; ^{1}H NMR (300 MHz, $CDCl_3$) δ 1.10 (d, *J* = 7.2 Hz, 3H), 1.12 (d, *J* = 7.2 Hz, 3H), 1.17 (d, *J* = 7.2 Hz, 6H), 1.24 (d, *J* = 7.2 Hz, 3H), 1.24 (d, *J* = 7.2 Hz, 9H), 2.54 (sept, *J* = 7.2 Hz, 1H), 2.56 (sept, *J* = 7.2 Hz, 1H), 2.75 (sept, *J* = 7.2 Hz, 1H), 2.77 (sept, *J* = 7.2 Hz, 1H), 4.30 (dd, *J* = 7.8, 11.7 Hz, 1H), 4.43 (dd, *J* = 5.4, 11.7 Hz, 1H), 5.31 (d, *J* = 1.8 Hz, 1H), 5.50 (ddd, *J* = 1.8, 5.4, 7.8 Hz, 1H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 18.3, 18.3, 18.4, 18.5, 18.6, 18.6, 18.6, 33.3, 33.5, 33.6, 61.9, 65.8, 74.8, 121.7, 149.0, 165.3, 170.4, 172.0, 175.5, 176.1; HRMS (FAB) calcd for $C_{22}H_{33}O_{10}$ ($M+H^+$) 457.2074, found 457.2079.

Acetyl tributyl citrate (entry 13): ^{1}H NMR (300 MHz, $CDCl_3$) δ 0.93 (t, *J* = 7.5 Hz, 9H), 1.33–1.43 (m, 6H), 1.58–1.65 (m, 6H), 2.07 (s, 3H), 3.20 (d, *J* = 15.5 Hz, 2H), 3.30 (d, *J* = 15.5 Hz, 2H), 4.09 (t, *J* = 6.6 Hz, 4H), 4.61 (t, *J* = 6.6 Hz, 2H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 13.5, 18.9, 20.8, 30.1, 30.4, 38.4, 64.5, 65.7, 77.9, 168.8, 169.3.

α,α-Dimethylbenzyl acetate (entry 15):[1,14] ^{1}H NMR (300 MHz, $CDCl_3$) δ 1.77 (s, 6H), 2.04 (s, 3H), 7.20–7.40 (m, 5H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 22.3, 28.6, 81.4, 124.2, 126.9, 128.2, 145.8, 169.7.

α,α-Dimethylbenzyl 2-methylpropanoate (entry 16):[15] ^{1}H NMR (300 MHz, $CDCl_3$) δ 1.15 (d, *J* = 6.9 Hz, 6H), 1.76 (s, 6H), 2.53 (septet, *J* = 6.9 Hz, 1H), 7.20–7.38 (m, 5H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 18.9, 28.5, 34.7, 80.9, 124.1, 126.8, 128.2, 146.0, 175.6.

2,4,6-Trimethylphenyl acetate (entry 17):[16] ^{1}H NMR (300 MHz, $CDCl_3$) δ 2.15 (s, 6H), 2.30 (s, 3H), 2.36 (s, 3H), 6.91 (s, 2H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 16.7, 21.0, 21.3, 129.7, 130.1, 135.8, 146.4, 169.6.

2,4,6-Trimethylphenyl 2-methylpropanoate (entry 18):[17] ^{1}H NMR (300 MHz, $CDCl_3$) δ 1.35 (d, *J* = 6.9 Hz, 6H), 2.09 (s, 6H), 2.26 (s, 3H), 2.86 (septet, *J* = 6.9 Hz, 1H), 6.86 (s, 2H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 16.1, 19.1, 20.7, 34.2, 129.1, 129.6, 135.0, 145.7, 174.8.

***p*-Nitrophenyl 2-methylpropanoate** (entry 19):[18] ^{1}H NMR (300 MHz, $CDCl_3$) δ 1.34 (d, *J* = 6.9 Hz, 6H), 2.85 (septet, *J* = 6.9 Hz, 1H), 7.27 (d, *J* = 9.0 Hz, 2H), 8.27 (d, *J* = 9.0 Hz, 2H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 18.5, 34.0, 122.2, 124.9, 144.9, 155.5, 174.4.

Octyl 3,3-dimethylacrylate (entry 19):[19] ^{1}H NMR (300 MHz, $CDCl_3$) δ 0.88 (t, *J* = 6.6 Hz, 3H), 1.20–1.42 (m, 10H), 1.63 (m, 2H), 1.89 (d, *J* = 1.2 Hz, 3H), 2.17 (d, *J* = 1.5 Hz, 3H), 4.08 (t, *J* = 6.6 Hz, 2H), 5.68 (qq, *J* = 1.2, 1.5 Hz, 1H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 14.0, 20.0, 22.6, 26.0, 27.3, 28.7, 29.2, 29.2, 31.7, 63.6, 116.1, 156.2, 166.7.

***p*-Methoxyphenyl 3,3-dimethylacrylate** (entry 20):[20] ^{1}H NMR (300 MHz, $CDCl_3$) δ 1.98 (d, *J* = 1.5 Hz, 3H), 2.22 (d, *J* = 1.2 Hz, 3H), 3.80 (s, 3H), 5.90 (qq, *J* = 1.2, 1.5 Hz, 1H), 6.89 (d, *J* = 9.0 Hz, 2H), 7.01 (d, *J* = 9.0 Hz, 2H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 20.4, 27.6, 55.5, 114.3, 115.1, 122.5, 144.1, 157.0, 159.7, 165.3.

Typical Procedure for Esterification between Alcohols and Carboxylic Acids (Table 2). To a mixture of α-tocopherol (2.15 g, 5.0 mmol), linoleic acid (1.71 mL, 5.5 mmol) and DMAP (3.1 mg, 0.025 mmol) was added pivalic anhydride (1.07 mL, 5.5 mmol) at ambient temperature. After being stirred at 50 °C for 27 h, water (9 μL, 0.5 mmol) was added and the mixture was stirred at 50 °C for 1 h. The resultant mixture was concentrated under reduced pressure [ca. 0.0006 Torr (ULVAC VPC-050)] at 90 °C (bath temp.) to recover the generated pivalic acid. The residue was passed through a short silica gel pad (10 g) using a mixture of hexane and ethyl acetate (100:1, 60 mL), to give α-tocopherol linoleate (3.05 g, 88% yield).

(1*R*,2*S*,5*R*)-5-Methyl-2-(1-methylethyl)cyclohexyl 3-phenylpropionate:[21] ^{1}H NMR (300 MHz, $CDCl_3$) δ 0.62 (d, *J* = 6.9 Hz, 3H), 0.68–1.75 (m, 14H), 1.78–1.93 (m, 1H), 2.53 (t, *J* = 7.8 Hz, 2H), 2.87 (t, *J* = 7.8 Hz, 2H), 4.59 (dt, *J* = 4.6, 10.9 Hz, 1H), 7.05–7.26 (m, 5H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 16.2, 20.7, 22.0, 23.3, 26.0, 31.0, 31.3, 34.1, 36.1, 40.8, 46.9, 74.1, 126.1, 128.2, 128.3, 140.4, 172.4.

(1*R*,2*S*,5*R*)-5-Methyl-2-(1-methylethyl)cyclohexyl cyclohexanecarboxylate:[22] ^{1}H NMR (300 MHz, $CDCl_3$) δ 0.74 (d, *J* = 7.0 Hz, 3H), 0.80–2.00 (m, 19H), 0.89 (d, *J* = 7.0 Hz, 3H), 0.90 (d, *J* = 6.4 Hz, 3H), 2.26 (tt, *J* = 3.7, 11.0 Hz, 1H), 4.65 (tt, *J* = 4.2, 10.8 Hz, 1H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 16.1, 22.0, 23.3, 24.2, 25.4, 25.5, 25.8, 26.1, 29.0, 29.1, 31.3, 34.3, 40.9, 43.5, 47.1, 73.5, 175.7.

(1*R*,2*S*,5*R*)-5-Methyl-2-(1-methylethyl)cyclohexyl cinnamoate:[23] ^{1}H NMR (300 MHz, $CDCl_3$) δ 0.79 (d, *J* = 7.0 Hz, 3H), 0.91 (d, *J* = 6.9 Hz, 3H), 0.92 (d, *J* = 6.3 Hz, 3H), 1.10 (m, 1H), 1.40–1.58 (m, 2H), 1.70 (m, 2H), 1.93 (m, 1H), 2.07 (m, 1H), 4.83 (dt, *J* = 4.5, 10.8 Hz, 1H), 6.44 (d, *J* = 15.9 Hz,

1H), 7.34–7.42 (m, 3H), 7.49–7.58 (m, 2H), 7.67 (d, J = 15.9 Hz, 1H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 16.3, 20.6, 21.9, 23.4, 26.2, 31.3, 34.1, 40.9, 47.0, 74.0, 118.5, 127.9, 128.7, 130.0, 134.4, 144.2, 166.4.

Boc-L-Phe-O-*n*-C_8H_{17}:[24] ^{1}H NMR (300 MHz, $CDCl_3$) δ 0.89 (t, J = 6.9 Hz, 3H), 1.18–1.46 (m, 10H), 1.42 (s, 9H), 1.51–1.65 (m, 2H), 3.01–3.16 (m, 2H), 4.08 (t, J = 6.9 Hz, 2H), 4.57 (q, J = 8.4 Hz, 1H), 4.98 (br d, , J = 8.7 Hz, 1H), 7.10–7.33 (m, 5H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 14.0, 22.6, 25.8, 27.0, 28.2, 28.4, 29.1, 31.7, 38.4, 54.4, 65.5, 79.8, 126.9, 128.4, 129.3, 136.0, 155.0, 171.2.

α-Tocopherol linoleate:[25] ^{1}H NMR (300 MHz, $CDCl_3$) δ 0.78–0.94 (m, 15H), 0.98–1.62 (m, 36H), 1.23 (s, 3H), 1.79 (m, 4H), 1.92–2.16 (m, 4H), 1.96 (s, 3H), 2.01 (s, 3H), 2.09 (s, 3H), 2.58 (t, J = 7.2 Hz, 4H), 2.78 (t, J = 5.7 Hz, 2H), 5.28–5.45 (m, 4H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 11.8, 12.1, 12.9, 14.1, 19.5, 19.6, 19.7, 20.5, 21.0, 22.5, 22.6, 22.7, 24.4, 24.8, 25.1, 25.6, 27.1, 27.2, 27.9, 29.1, 29.2, 29.3, 29.3, 31.5, 31.6, 32.6, 32.7, 34.1, 37.2, 37.3, 37.4, 37.5, 39.3, 74.9, 117.2, 122.9, 124.8, 126.6, 127.8, 128.0, 129.9, 130.1, 140.4, 149.2, 172.3.

Glycerol trioleate: ^{1}H NMR (300 MHz, $CDCl_3$) δ 0.88 (t, J = 6.6 Hz, 9H), 1.08–1.42 (m, 60H), 1.61 (br t, J = 6.3 Hz, 6H), 1.92–2.10 (m, 12H), 2.31 (t, J = 6.9 Hz, 4H), 2.32 (t, J = 7.5 Hz, 2H), 4.14 (dd, J = 6.0, 11.7 Hz, 2H), 4.30 (dd, J = 4.5, 11.7 Hz, 2H), 5.27 (m, 1H), 5.23–5.45 (m, 6H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 14.1, 22.6, 24.8, 27.1, 27.2, 29.0, 29.1, 29.1, 29.3, 29.5, 29.6, 29.7, 31.9, 34.0, 34.1, 68.8, 62.0, 129.6, 129.9, 172.8, 173.2.

Methyl 2,3,4,6-*O*-tetraoleoyl-α-D-glucopyranoside:[26] ^{1}H NMR (300 MHz, $CDCl_3$) δ 0.88 (t, J = 6.9 Hz, 12H), 1.00–1.44 (m, 80H), 1.44–1.68 (m, 8H), 1.88–2.12 (m, 16H), 2.14–2.42 (m, 8H), 3.40 (s,

3H), 3.98 (ddd, J = 2.4, 4.8, 9.9 Hz, 1H), 4.12 (dd, J = 2.4, 12.3 Hz, 1H), 4.21 (dd, J = 4.8, 12.3 Hz, 1H), 4.88 (dd, J = 3.6, 10.2 Hz, 1H), 4.95 (d, J = 3.6 Hz, 1H), 5.08 (dd, J = 9.9, 9.9 Hz, 1H), 5.26–5.42 (m, 8H), 5.50 (t, J = 9.9, 10.2 Hz, 6H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 14.1, 22.7, 24.7, 24.8, 24.9, 27.1, 27.2, 29.0, 29.1, 29.1, 29.3, 29.4, 29.7, 29.7, 31.9, 33.9, 34.1, 55.3, 61.7, 67.2, 68.1, 69.6, 70.7, 96.7, 129.6, 129.6, 129.7, 129.9, 130.0, 172.2, 172.6, 172.9, 173.4.

Isobutyrylation of Alcohols Using Polystyrene-Supported DMAP as a Recyclable Catalyst. The reaction of an alcohol (5 mmol) and acid anhydride (5.5 mmol) was conducted with polystyrene-supported DMAP **5** (5–10 mol %) at rt for 12–48 h. After the reaction was completed, the reaction mixture was purified by distillation to give a pure corresponding ester and a residual salt of **5** with isobutyric acid (isobutyrylation of *l*-menthol). Alternatively, the salt of **5** was recovered from the reaction mixture by decantation, and the supernatant was purified by a short SiO_2 pad (isobutyrylation of 3-phenylpropanol and 2,4,6-trimethylphenol).

Direct Ester Condensation of Carboxylic Acids with Alcohols Using Polystyrene-Supported DMAP as a Recyclable Catalyst. The reaction of cyclohexanecarboxylic acid (5.5 mmol) with *l*-menthol (5 mmol) and pivalic anhydride (5.5 mmol) was conducted with polystyrene-supported DMAP **5** (10 mol %) at 50 °C for 24 h. After the reaction was completed, a salt of **5** with a carboxylic acid was recovered by decantation. The supernatant was purified by a short SiO_2 pad to give the corresponding ester.

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