Electronic Supplementary Material for Chemical Communications

Significant enhancement on selectivity in silica supported sulfonic acids catalyzed reactions

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Supporting Information

Chemicals : all functionnalized carboxylic acids, glycerol and dicyclopentadiene were purchased to Sigma-Aldrich and used as received without any purification. Silica precursors, tetraethoxysilane (TEOS) and mercaptopropyltrimethoxysilane (MPTMS), were provided by Acros.

Apparatus : ^{1}H and ^{13}C NMR spectra were recorded on a Bruker Avance 300 DPX 300. Chemical shift are expressed in ppm relative to Me_4Si. IR spectra were recorded on a FT-IR Perkin Elmer (spectrum one) using ATR technology. Elemental analyses were measured on a NA 2100 Instrument. Specific area were determined on a TRISTAR 3000. Pore diameters were determined from the adsorption branch of the N_2 isotherm using the BJH method.

Chromatographic analyses

The reaction progress was monitored on a Varian 3300 GPC equipped with a BPX5 column (12m x 0.22 mm; phase thickness: 0.25 µm) supplied by SGE, a Flame Detector Ionization and an injector on-column. Prior analysis, products were silylated according to the Sahasrabuhde method (*J. Am. Oil. Chem. Soc*., 1957, **44**, 376). Yields and reaction progress were determined by internal calibration with dodecane. Table 1 summarizes the different response coefficients.

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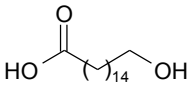
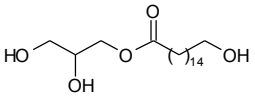
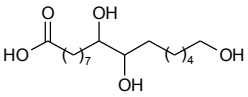
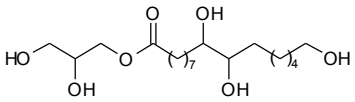
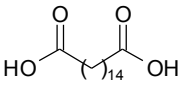
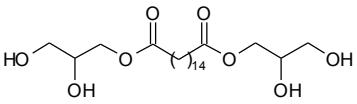
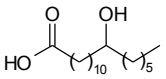
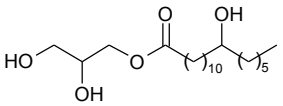
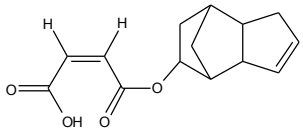
Table 1 : response coefficients of studied derivatives relative to dodecane

Derivative	Response coefficient
	0.749
	0.826
	0.661
	1.031
	0.816
	0.805
	0.669
	0.748
	1.864

Preparation of HMS materials was inspired from the procedure described by Shanks et *al*. (see ref 11 in the manuscript) except than *n*-dodecylamine was replaced by *n*-hexadecylamine as structure directing agent.

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Synthesis of HMS_1-SO_3H:

Typically, 3.2g (0.013mol) of *n*-hexadecylamine was dissolved at room temperature in aqueous ethanol (ethanol/water: 21/27). Then 8.3 g of tetraethoxysilane (TEOS, 0.039mol) and 1.97g of 3-mercaptopropyltrimethoxysilane (MPTMS, 0.01 mol) was simultaneously but separately added to the template mixture. The resulting solution was stirred for 20 h at room temperature and the white solid was recovered by filtration. Removal of the *n*-hexadecylamine was carried out by soxhlet extraction over boiling ethanol for 18h affording the hybrid organic-inorganic HMS_1-SH. Thiol groups were oxidized with 35% aqueous H_2O_2 (2g/g of solid) in a methanol/water mixture. The suspension was stirred for 24 hours at room temperature and then washed with ethanol and water. Finally, the resulting solid was suspended in 0.1M H_2SO_4 (1g of solid per 100mL of solution) and stirred for an additional 4h before filtration and extensive washing with H_2O. The recovered HMS_1-SO_3H was dried in an oven at 50°C (10^{-1} mmHg) for 18h.

Synthesis of HMS_2-SO_3H:

HMS_2-SO_3H was synthesized as described above except that the initial molar ratio tetraethoxysilane/3-mercaptopropylsilane was increase from 4 to 10 (TEOS : 0.05 mol and MPTMS : 0.005)

Synthesis of SBA-15-SO_3H

Pluronic (4g) was dissolved in 125g of aqueous HCl (1.9M) and stirred at room temperature. The solution was then heated at 40°C before addition of 7.7 g (0.0369 mol) of TEOS. After stirring for 45mn, MPTMS (0.8 g, 0.0041 mol) and 0.0369 mol of 35% H_2O_2 was added. The solution was then stirred for 24h at 40°C and aged into a teflon autoclave for an additional 24h at 100°C. The resulting solid was finally collected by filtration and thoroughly washed with water. The recovered SBA-15-SO_3H was dried in an oven at 50°C (10^{-1} mmHg) for 18h.

Titration of solid

0.2 g of acid solid was suspended in 20mL of aqueous solution of KCl (0.1M) and stirred for 30 mn. Titration of the resulting solution was then carried out with a solution of KOH 0.02M and the pH evolution was monitored by a Metrohm pH meter.

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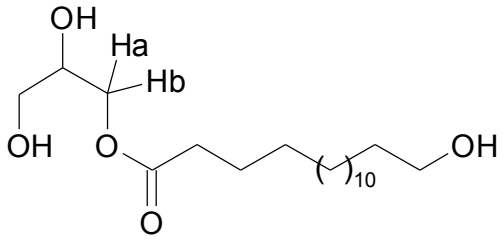
General procedure for the esterification of functional carboxylic acids with glycerol

Functional carboxylic acids (1mmol), glycerol (6mmol) and 2.5 mol% of supported sulfonic groups were mixed in an opening conic tube and stirred at the desired temperature (see table 1 in the manuscript) under air. At the end of the reaction, reaction products were directly extracted from the crude with ethyl acetate (2 x 3mL). The organic phase was evaporated and the ester derivatives were finally purified by flash silica gel chromatography (Silica Gel 60□m) using a mixture ethyl acetate-heptane (7/3) as eluent for esters from juniperic, aleuritic and thapsic acids and 1/1 from ester produced from 12-hydroxystearic acid. All the different targeted esters were obtained as a white solid.

2,3-dihydroxypropyl 16-hydroxyhexadecanoate (from juniperic acid)



^{1}H RMN (300 MHz, C_5D_5N) δ (ppm) 1.26 (m, 20H, CH_2), 1.52 (m, 2H, CH_2), 1.65 (m, 2H, CH_2), 1.76 (m, 2H, CH_2), 2.36 (t, 2H, CH_2, $^{3}J_{HH}$ = 7.4 Hz), 3.89 (t, 2H, CH_2OH, $^{3}J_{HH}$ = 6.5 Hz), 4.13 (d, 2H, CH_2OH, $^{3}J_{HH}$ = 5.4Hz), 4.46 (m, 1H, CHOH), 4.67 (dd, 1H, CHa, $^{2}J_{HH}$ = 11.1 Hz, $^{3}J_{HH}$ = 6.3 Hz), 4.74 (dd, 1H, CHb, $^{2}J_{HH}$ = 11.1 Hz, $^{3}J_{HH}$ = 4.8 Hz), 5.88 (s, 1H, OH), 6.51 (s, 1H, OH), 6.86 (s, 1H, OH).

^{13}C RMN (75 MHz, C_5D_5N) δ (ppm) 26.2 (CH_2), 27.4 (CH_2), 30.2-30.9 (CH_2), 34.7 (CH_2), 35.2 (CH_2), 62.9 (CH_2O), 65,2 (CH_2O), 67.6 (CH_2O), 71.8 (CHOH), 174.6 (C=O).

IR (neat) ν 1172, 1192, 1391, 1462, 1733 (C=O), 2848 (C-H), 2915 (C-H), 3310 (O-H) cm^{-1}

Elemental analysis: Calculated for $C_{19}H_{38}O_4$: %C 65.86, %H 11.05. Measured: %C 65.79; %H 11.03

mp= 74-75°C

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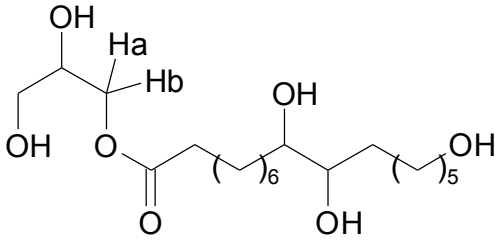
2,3-dihydroxypropyl-9,10,16-trihydroxyhexadecanoate



^{1}H RMN (300 MHz, C_5D_5N) δ (ppm) 2.72 (m, 8H, CH_2), 3.06 (m, 6H, CH_2), 3.27 (m, 8H, CH_2), 3.79 (t, 2H, CH_2, $^{3}J_{HH}$ = 7.5 Hz), 5.30 (m, 2H, 2 x CHOH), 5.34 (t, 2H, CH_2OH, $^{3}J_{HH}$ = 6.4 Hz), 5.6 (d, 2H, CH_2OH, $^{3}J_{HH}$ = 5.4 Hz), 5.94 (m, 1H, CHOH), 6.14 (dd, 1H, CHa, $^{2}J_{HH}$ = 11.1 Hz, $^{3}J_{HH}$ = 6.3 Hz), 6.20 (dd, 1H, CHb, $^{2}J_{HH}$ = 11.1 Hz, $^{3}J_{HH}$ = 4.5 Hz), 6.5 (broad peak, 2H, 2 x OH), 7.25 (broad peak, 2H, 2 x OH), 7.41 (broad peak, 1H, OH)

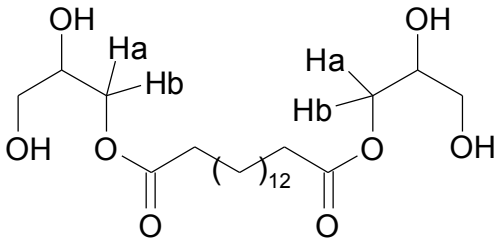
^{13}C RMN (75 MHz, CDCl3) δ (ppm) 23.9 (CH_2), 24.4 (CH_2), 24.7 (CH_2), 24.8 (CH_2), 27.8-28.4 (CH_2), 31.7 (CH_2), 32.6 (CH_2), 33.3 (CH_2), 62.1 (CH_2OH), 62.5 (CH_2OH), 64.3 (CH_2OH), 69.4 (CHOH), 73.6 (CHOH), 76.4 (CHOH), 173.5 (C=O).

IR (neat) ν 1047, 1172, 1413, 14642, 1736 (C=O), 2849 (C-H), 2927 (C-H), 3338 (O-H) cm^{-1}

Elemental analysis: Calculated for $C_{19}H_{38}O_7$: %C 60.29; %H 10.12. Measured: %C 60.49; %H 9.80.

mp=54-55°C

Bis(2,3-dihydroxypropyl) 16-hydroxy hexadecanoate (from thapsic acid)



^{1}H RMN (300 MHz, C_5D_5N) δ (ppm) 1.21 (m, 20H, CH_2), 1.67 (m, 4H, CH_2), 2.37 (t, 4H, CH_2, $^{3}J_{HH}$ = 7.5 Hz), 4.13 (d, 2H, CH_2OH, $^{3}J_{HH}$ = 5.5 Hz), 4.46 (m, 2H, CHOH), 4.66 (dd, 1H, CHa,

$^{2}J_{HH}$ = 11.1 Hz, $^{3}J_{HH}$ = 6.3 Hz), 4.74 (dd, 1H, CHb, $^{2}J_{HH}$ = 11.1 Hz, $^{3}J_{HH}$ = 4.8 Hz), 5.03 (br s, 2H, OH), 6.79 (br s, 2H, OH).

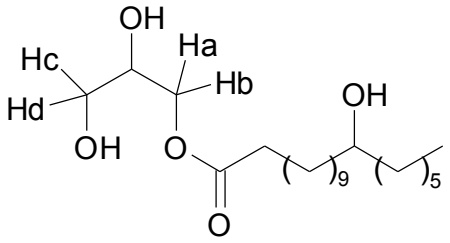
^{13}C RMN (75 MHz, C_5D_5N) δ (ppm) 24.4 (CH_2), 28.5-29.0 (CH_2), 33.8 (CH_2), 63.4 (CH_2O), 65.9 (CH_2O), 70.1 (CHOH), 172.9 (C=O).

IR (neat) ν 1167, 1195, 1242, 1286, 1387, 17323 (C=O), 2848 (C-H), 2915 (C-H), 3239 (O-H) cm^{-1}

Elemental analysis: Calculated for $C_{22}H_{42}O_8$: %C 60.81; %H 9.74. Measured: %C 60.95; %H 9.71

mp=85-86°C

2,3-dihydroxypropyl-12-hydroxyoctadecanoate (from 12-hydroxystearic)



^{1}H RMN (300 MHz, $CDCl_3$) δ (ppm) 0.82 (t, 3H, CH_3, $^{3}J_{HH}$ = 6.5 Hz), 1.20 (m, 24H, CH_2), 1.36 (m, 2H, 2 CH_2), 1.56 (m, 2H, CH_2, $^{3}J_{HH}$ = 7.1 Hz), 2.28 (t, 2H, CH_2, $^{3}J_{HH}$ = 7.5 Hz), 3.53 (dd, 2H, CHc, $^{2}J_{HH}$ = 11.4 Hz, $^{3}J_{HH}$ = 6.0 Hz), 3.53 (dd, 2H, CHd, $^{2}J_{HH}$ = 11.4 Hz, $^{3}J_{HH}$ = 4.0 Hz), 3.86 (m, 1H, CHOH), 4.08 (m, 3H, CHaHb, CHOH), one OH group was not seen.

^{13}C RMN (75 MHz, $CDCl_3$) δ (ppm) 14.5 (CH_3), 23.0 (CH_2), 25.9 (CH_2), 26.0 (CH_2), 29.4-30.0 (CH_2), 32.1 (CH_2), 34.5 (CH_2), 37.8 (CH_2), 63.7 (CH_2O), 65.5 (CH_2O), 70.6 (CHOH), 72.4 (CHOH), 174,7 (C=O).

IR (neat) ν 1059, 1175, 1464, 1729 (C=O), 2850 (C-H), 2926 (C-H), 3338 (O-H) cm^{-1}

Elemental analysis: Calculated for $C_{21}H_{42}O_5.H_2O$ %C 64.25, %H 11.30. Measured: %C 64.66, %H 11.48.

mp=72-73°C

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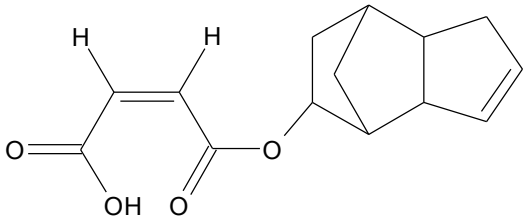
Selective esterification of maleic with dicyclopentadiene.

Maleic acid (1mmol), dicyclopentadiene (3mmol) and 2.5 mol% of supported sulfonic groups were mixed in an opening conic tube and stirred at 105°C. Ater total consumption of the maleic acid, the crude was diluted in 3mL of ethyl acetate and purified by flash silica gel chromatography (Silica Gel 60μm) using ethyl acetate/heptane (3/7) as eluent affording the monester derivative as a yellow pale viscous oil.

(2Z)-4-(3a,4,5,6,7,7a-hexahydro-1H-4,7-methanoinden-5-yloxy)-4-oxobut-2-enoic acid (from maleic acid and dicyclopentadiene)



^{1}H RMN (300 MHz, $CDCl_3$) δ (ppm) 1.27 (m, 2H, CH_2); 1.45 (m, 2H, CH_2), 1,80 (m, 2H, CH_2); 1,82 (m, 1H, CH); 2.01 (m, 1H, CH); 2.08 (m, 1H, CH); 2.53 (m, 1H, CH); 4.76 (m, 1H, CHO); 5.36 (m, 1H, CH); 5.64 (m, 1H, CH) ; 6.24 (d, 1H, CH, $^{3}J_{HH}$ = 12.6 Hz); 6.34 (d, 1H, CH, $^{3}J_{HH}$ = 12.6 Hz), CO_2H not seen.

^{13}C RMN (75 MHz, $CDCl_3$) δ (ppm) 29.9 (CH_2), 39.2 (CH_2), 39.8 (CH_2), 42.8 (CH), 43.8 (CH), 46.8 (CH), 52.0 (CH), 81.1 (CH), 130.8 (CH), 131.4 (CH), 134.2 (CH), 137.2 (CH), 165.7 (C=O), 168.5 (C=O).

IR (neat) ν 990, 1053, 1167, 1412, 1634 (COOH), 1720 (C=O), 2845 (C-H), 2957 (C-H), 3343 (O-H) cm^{-1}

Elemental analysis: Calculated for $C_{14}H_{16}O_4$: %C 67.73, %H 6.50. Measured: %C 67.85 %H 6.82