Electronic Supplementary Material (ESI) for Green Chemistry.

Supporting data

Bioresourced Surfactant From Glycerol and Dodecanol Through Direct Etherification

Zhaoyu Fan,[a,b] Yan Zhao,[b] Florentina Preda,[b] Jean-Marc Clacens,[b] Hui Shi,[b] Limin Wang,[a*] Xiaoshuang Feng,[b*] and Floryan De Campo[b]

[a] Key Laboratory of Advanced Materials and Institute of Fine Chemicals, East China University of Science and Technology, 130 Mei Long Rd., Shanghai 200237, PR China.

[b] Eco-Efficient Products and Processes Laboratory (E2P2L), Solvay/CNRS UMI 3464, 3966 Jin Du Rd., Xin Zhuang Industrial Zone, Shanghai 201108, PR China.

Experimental

Materials

Sodium 4-vinylbenzenesulfonate (90%), and Divinylbenzene (DVB, 80%) were purchased from Aldrich, 2,2,6,6-Tetramethyl-piperidin-1-yl)oxyl (TEMPO, 98%) was from Acros, (Chloromethyl)phenylethyl trimethoxysilane (CPMS) is from Meryer, fumed silica (Aerosil 200) was from Evonik, styrene (Sinopharm) and DVB passed through a basic alumina column to remove the inhibitor. Toluene (Sinopharm) was dried over CaH_2 and distilled. All other chemicals were purchased with analytical grade from Sinopharm and used without further purification.

Dodecyl polyethoxylate ether (AEO7, 97%) with seven ethoxylate units as average was received from Solvay and monododecylpolyglyceryl ether (MAGE4, 97%) was bought from Daicel Japan with four glycerol units as average. They were selected as benchmarks for the physicochemical properties and laundry performance evaluation.

Methods

Nuclear magnetic resonance (NMR) spectra were registered on a Bruker Avance III at 300 MHz. Size exclusion chromatography (SEC) for polystyrene was performed in THF on a Pl Gel mixed B 10 µm (2*30 cm), 100 Å 10 µm (1*30 cm) columns calibrated by linear PSt standards. SEC for PSSNa was estimated on Waters equipped with four Ultrahydrogel columns with elution rate 1 mL min^{-1}, the eluent was 0.2 M $NaNO_3$ and 0.01 M Na_2HPO_4 in a mixture of acetonitrile/water (v/v = 2:8), and the molar masses were calibrated by PSSNa standards (Polysciences). The acid-base titration was performed in water/acetone (v/v = 1:1) with 848 Titrino plus from Metrohm equipped with electrode for solvent with model of 6.0229.100 (LiCl set in Ethanol). Thermo gravimetric analysis (TGA) was done on a TA Instruments SDT Q600 machine, with equilibrium at 30 °C and a ramp of 10 °C min^{-1} up to 900 °C under air atmosphere. The particle size distribution (PSD) of the parent and modified silica particles were measured using a Malvern Nano ZS using light scattering cells of 10 mm. BET analysis was performed on a TriStar II 3020 prosimeter from Micromeritics. Gas chromatography (GC) was performed on an Agilent Technologies 7890A System equipped with both Hydrogen Flame Ion Detector (FID) and Electron Ionization Mass Detector (MS) connecting with column: HP5-MS (30 m × 0.25 mm × 0.25 µm). High performance liquid chromatography (HPLC) was recorded with Agilent 1290 Infinity LC equipped with Refraction Index (RI) detector and column: Shiseido Capcell Pac C18 UG80 4.6 mm × 250 mm × 5 µm. Supercritical Fluid Chromatography Mass Spectrometry (SFC/MS) was recorded with Waters Acquity UPC^2 system coupled with a Xevo G2-S QTOF Masspectrometer (Electrospray) equipped with column: UPC^2 BEH 3.0 × 100 mm × 1.7 µm.

The glycerol/dodecanol (G/D) interfacial tensions, i.e. γG/D, were measured on a Sigma 700 tensiometer from BiolinScientific AB equipped with a Du Noüy ring set at 3 mm min^{-1} for low interfacial tensions. The droplet size was measured using an Olympus IX-51 light transmission microscope equipped with a × 10 ocular, × 4, × 10, × 40, and × 100 objectives, and DP2-BSM software. Software Visilog was used to analyze the droplet size.

Surface tension and critical micelle concentration of surfactants were measured on a Sigma 700 tensiometer from BiolinScientific AB equipped with a Wilhelmy plate and a Du Noüy ring. Foam height was tested with standard Ross mile method. Cloud point was obtained with stand method following Chinese standards ASTM D2024-2009. Laundry performance was measured with Laundrometer SDLATLAS M228 Rotawash from SDL Atlas, Ltd with hard water (250 ppm) at 30 °C for 1 hour following standard AATCC method. The stains removal rate was calculated based on Lab value measurement from spectrophotometer ColorQuest XE from Hunter Lab.

Procedure for preparation of random sulfonated polystyrene

Styrene (50 mL, 0.435 mmol) and 4-(bromomethyl) benzoic acid (243 mg, 1.13 mmol) were introduced in a 100 mL of Schlenk fitted magnetic bar. Copper (I) bromide (163 mg, 1.13 mmol) and 2, 2' bipyridine (354 mg, 2.26 mmol) were mixed to give a black powder and then added to the mixture. The mixture was degassed through three cycles of frozen-vacuum-thawed and then polymerized at 110 °C with stirring for 24 h. After terminated by exposure to air and diluted with THF (50 mL), the solution passed a neutral alumina column to remove the copper salts. The obtained solution was concentrated by rotary evaporator and precipitated in large excess of methanol. After precipitated for another time, polystyrene was dried in the oven at 40 °C in vacuo overnight. 22.5 g of polystyrene were recovered. M_n(NMR) = 22.0 Kg mol^{-1}, M_n(GPC) = 26.6 Kg mol^{-1} (PDI = 1.20).

In a round-bottomed flask with a solution of above polystyrene (2.0 g, M_n (NMR) = 22.0 Kg mol^{-1}) in 1,2-dichloroethane (30 mL), acetic anhydride and sulfuric acid 98% (molar/molar = 2:1), were successively added drop wise under stirring according to the desired sulfonation degree. The homogeneous mixture was stirred at 25 °C between 11 h and 52 h until the desired sulfonation degree was reached (monitored by ^{1}H NMR in acetone-d^6). After all the volatiles were removed through rotary evaporator, the residue was dissolved in acetone and precipitated in excess of diethyl ether. The sulfonated polystyrene was recovered with centrifuge at 10000 rpm for 5 min. After two times precipitation and centrifugation, the obtained yellow sulfonated polymer was lastly lyophilized from dispersed water solution. Related data were listed in Table 2.

Procedure for preparation of block sulfonated polystyrene

To a two neck of 250 mL round flask fitted with magnetic bar, sodium 4-vinylbenzenesulfonate (5.0 g, 24.2 mmol), TEMPO (0.378 g, 2.42 mmol) were dispersed in mixed solvents of ethylene glycol and deionized water (20 g, v/v = 4:1). Nitrogen was bubbled for 30 min to remove oxygen at 60 °C. $K_2S_2O_8$ (0.327 g, 1.21 mmol) and $Na_2S_2O_5$ (0.154 g, 0.807 mmol) predegassed respectively in 3 mL and 1 mL of deionized water were added and stirred at 60 °C for another 30 min. The temperature was then raised to 125 °C and kept stirring for 4.5 h. The mixture was precipitated in methanol (100 mL). After centrifugation (10000 rpm for 5 min), the polymer was washed with methanol and dried under vacuum at 50 °C overnight. 4.86 g of polymer (PSSNa) was yielded. M_n (GPC) = 6500 Kg mol^{-1} (PDI = 1.27).

The solution of prepared PSSNa (2.0 g) in ethylene glycol and deionized water (10 mL, v/v = 9:1) was degassed for 30 min with nitrogen, following by the addition of styrene (3.4 mL, 30 mmol) and predegassed $K_2S_2O_8$ (56 mg, 0.21 mmol in 1.5 mL of water) and $Na_2S_2O_5$ (36 mg, 0.19 mmol). After the mixture was stirred at 35 °C for 30 min, the temperature was raised to 120 °C and kept for 4 h. The mixture was precipitated in large excess of a mixed solvent of diethyl ether and MeOH (v/v = 6:4). After centrifugation (10000 rpm for 5 min), the obtained polymer was further washed with THF and then dried under vacuum at 50 °C overnight.

The obtained PSSNa-b-PSt (2.5 g) was further acidified with a hydrogen exchange resin (4.2 eq. g^{-1}) in water and THF (v/v = 1:1) for 6 h. As the proton exchange occurred, the solution became white. After resin was removed by filtration, THF in the solution was evaporated; the remained aqueous solution was lyophilized. White copolymer PSSA(Na)-b-PSt was obtained and its acidity data was listed in Table 2.

Procedure for preparation of sulfonated polystyrene grafted silica nanoparticles

To a 500 mL of three necked round bottle fitted with condensed column, the activated silica particles (10 g) were charged and dried under vacuum overnight at 50 °C. Under nitrogen atmosphere, 200 mL of dried toluene were added to generate the dispersion. The dispersion was heated until refluxed. CPMS (18.7 g, 68 mmol) was introduced. After the mixture was refluxed for 16 h, toluene was evaporated. The particles were purified by dispersing in acetone and then centrifuged (10000 rpm, 20 min) for several cycles. The CPMS-grafted particles were dried in vacuum at 50 °C overnight. 6.2 g of CMPS@SiO_2 were obtained, yield: 62%. TGA: 5.7% of weight loss (see Fig. S1), FTIR (cm^{-1}, KBr): 667, 1383, 1634, 2928, 3435.

To a 250 mL of Schlenk flask, 3 g of above prepared CPMS grafted silica (0.5 mmol ATRP sites), styrene (1.0 mmol, 120 mL), $CuCl_2$ (26.2 mg, 0.2mmol), CuCl (195 mg, 2.0 mmol) and 2, 2'-bipyridine (673 mg, 4.3 mmol) were charged. After three frozen, vacuum and thawed cycles, the flask was put into an oil bath at 90 °C and kept under stirring for 24 h. The grafted particles were precipitated in MeOH (100 mL). After removal of the organic solvents, the solid particles were dispersed in dichloromethane (100 mL) and washed several times with an EDTA aqueous solution (100 mL, 6 g L^{-1}). The organic phase was concentrated and precipitated in methanol (100 mL). The polymer was filtered and dried at 50°C in vacuum overnight. 5.4 g of PSt@SiO_2 were recovered. TGA weight loss is 46.2% (Fig. S1).

The obtained PSt@SiO_2 was sulfonated using the method as described for polystyrene. Lastly, PSt-co-PSSA@SiO_2 particles were yielded from lyophilization from their water dispersion. Related characterization data were listed in Table 3.

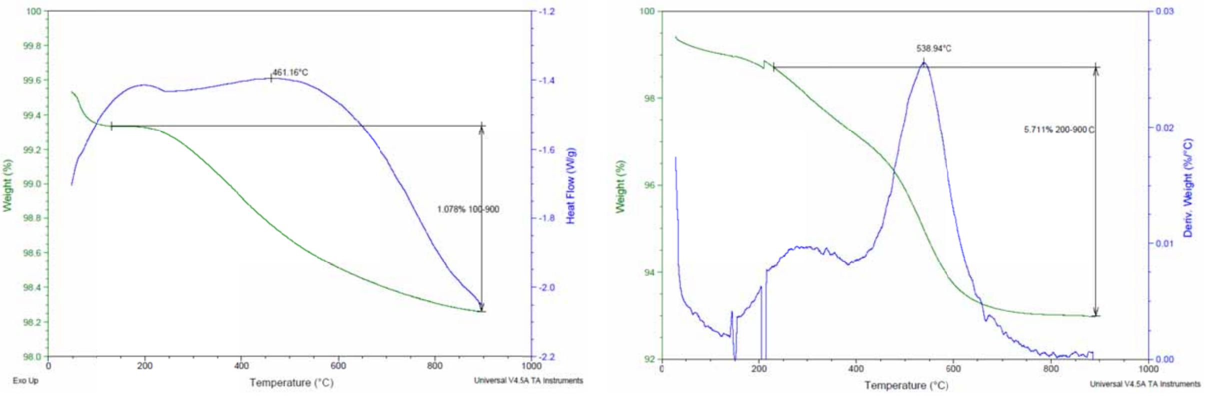
Procedure for interfacial tension and emulsion preparation

The samples were dispersed in dodecanol (30 mL) in an ultrasound bath for 30 min, glycerol (30 mL) was then introduced slowly, and the system was stabilized at 35 °C for 24 h. The system was sent for interfacial tensions measurement with a Du Noüy ring. The moving rate of ring was set at 1 mm min^{-1} for low interfacial tensions.

Before the emulsification tests, both glycerol and dodecanol were placed in a thermostated bath (Julabo) at 35 °C for at least 30 min. A first series of G/D emulsification tests were carried out using a series of polystyrenes and its grafted silica particles. The G/D emulsions were prepared in 10 mL glass tubes at 35 °C under vigorous shearing (13000 rpm, ultra-turax Fluko FA25) at a G/D volume ratio of 1:1 (w/w = 6:4) and a catalyst concentration of 1 wt% adapted from our previous work.[43 43 43] After the preparation, the temperature was raised to 70 °C to survey the emulsion stability and droplet size with microscope.

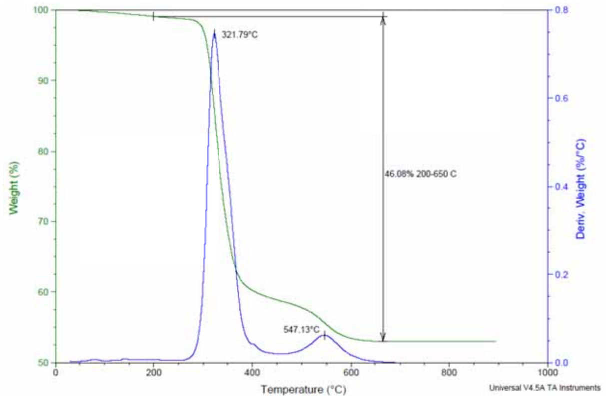
Procedure for etherification process

Glycerol (3.68 g, 0.04 mol), dodecanol (1.86 g, 0.01 mol) and catalysts, were added into a 20 mL tube. The mixture was homogenized at 35 °C under vigorous shearing (13000 rpm, ultra-turax Fluko FA25), sealed with a cap. The reactions were performed in an oil bath at 150 °C under vigorous stirring at nitrogen atmosphere or in static vacuum for 24 h. After the reaction, the conversion of reaction was first measured by GC. Regarding to the purification procedure, pyridine was added to neutralize the catalysts, and then mixture was precipitated in large excess of THF/diethyl ether (v/v = 1:1), the bottom layer was removed after few hours storage. The obtained solution was concentrated by rotary evaporator. After most of dodecanol were removed through distillation under high vacuum, the residue was dissolved in methanol/H_2O (50 mL, v/v = 10:1), further washed with heptane (50 mL). The remaining solution (bottom layer) was concentrated by rotary evaporator and further dried in vacuum oven at 50 °C overnight. The obtained product was characterized by ^{1}H NMR, GC, HPLC and SFC/MS. The NMR spectrum was shown in Fig. S4.



TGA/DSC curve of SiO_2

TGA/DSC curve of SiO_2-CMPS



TGA/DSC curve of SiO_2-PSt

Fig. S1 TGA profile of parent silica (SiO_2), Silica grafted with CMPS (SiO_2-CPMS) and Silica grafted with polystyrene (SiO_2-PSt).

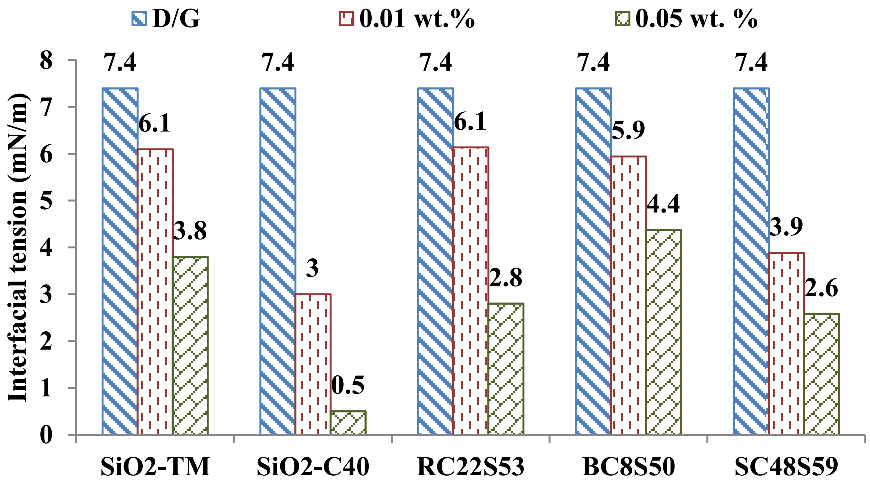


Fig. S2 Interfacial reduction of the G/D interface with selected polystyrene and its grafted silica particles at concentration of 0.01 wt% and 0.05 wt%.

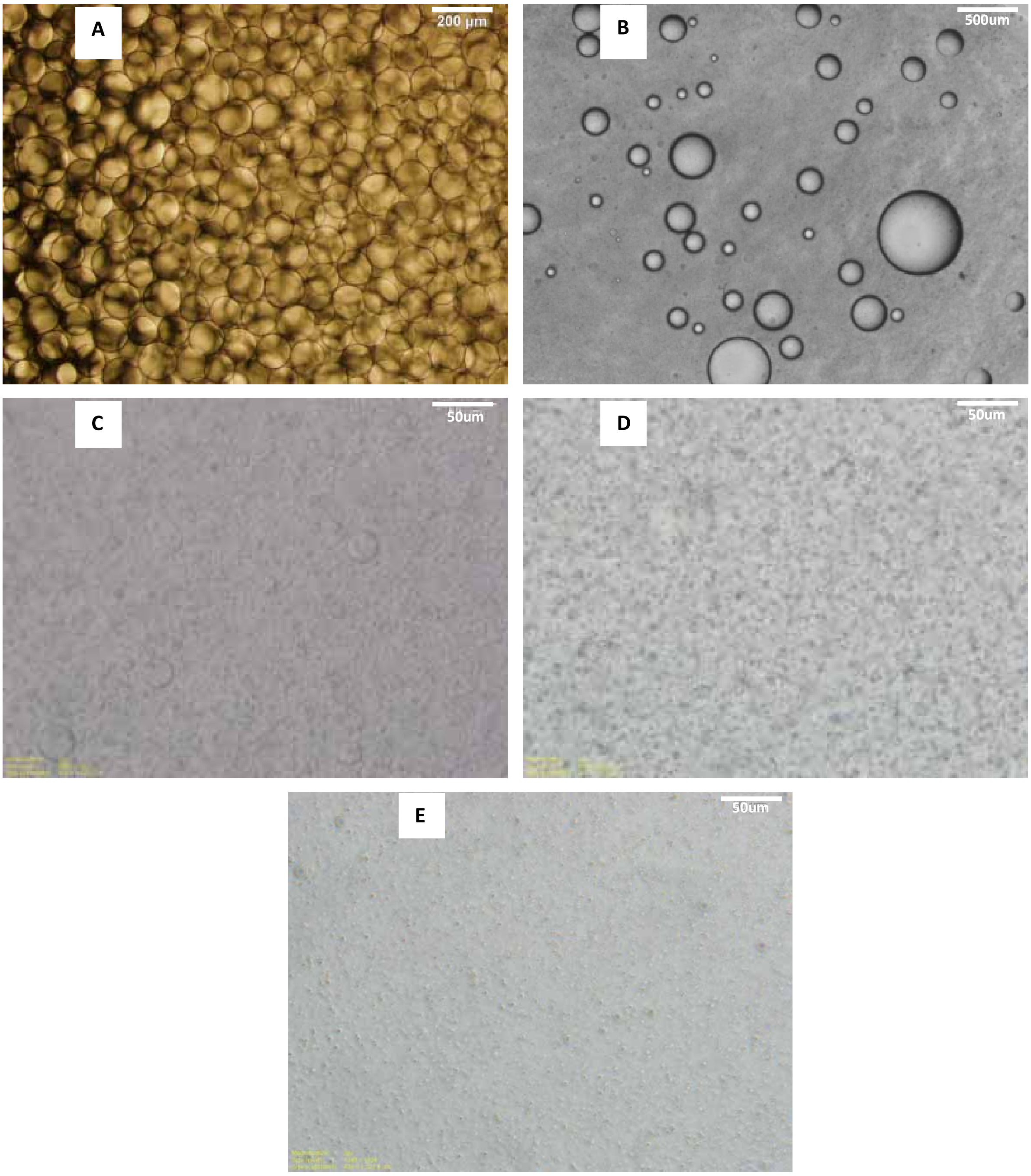


Fig. S3 Microscopic pictures of the emulsion at 30 min after shearing A) SiO_2-TM at 30 min with concentration at 1 wt%, droplets of glycerol in dodecanol; B) SiO_2-C40 at 30 min with concentration at 1 wt%, droplets of glycerol in dodecanol; C) $RC_{22}S_{53}$ at 30 min with concentration 0.1wt%, droplets of glycerol in dodecanol; D) BC_8S_{50} at 30 min with concentration 0.1 wt%, droplets of dodecanol in glycerol; E) $SC_{48}S_{59}$ at 30 min with concentration 0.1 wt%, droplets of dodecanol in glycerol.

Table S1 Summarized PIC etherification results obtained with different amphiphilic bifunctional catalysts

Entry	Catalyst	Catalyst quantity (Acidity/Dodecanol, eq.)	Conv. of D (%)	Yield of Surface active products (%)	Selectivity to Surface active products (%)	Yield of DE (%)	Selectivity to DE (%)
1	$RC_{211}S_{56}$	0.10	19	18	95	1	5
2	$RC_{211}S_{56}$	0.08	20	19	96	1	4
3	$RC_{211}S_{56}$	0.05	17	16	97	1	3
4	$RC_{211}S_{56}$	0.03	13	13	97	0	2
5	$RC_{211}S_{56}$	0.01	10	10	99	0	1
6	$BC_{46}S_{50}$	0.08	18	16	93	1	7
7	$BC_{46}S_{50}$	0.05	17	16	95	1	5
8	$BC_{46}S_{50}$	0.03	12	11	95	1	5
9	$BC_{46}S_{50}$	0.01	3	3	93	0	7
10	$SC_{46}S_{90}$-WR	0.05	63	52	83	11	17
11	$SC_{46}S_{59}$-WR	0.04	51	44	86	7	14
12	$SC_{46}S_{59}$-WR	0.02	22	18	80	4	20

Reaction conditions: 150 °C for 24 h under vigorous stirring at nitrogen atmosphere.

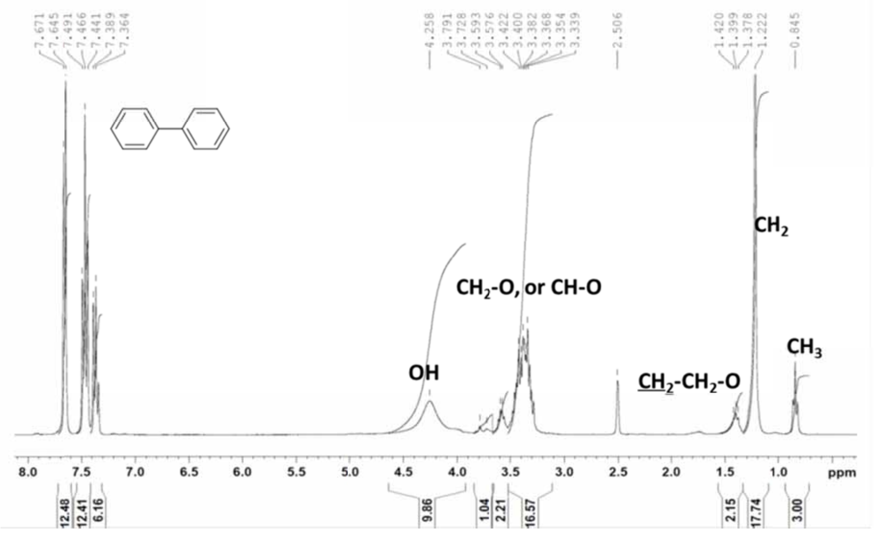


Fig. S4 Typical ^{1}H NMR spectrum of reaction mixture after etherification.

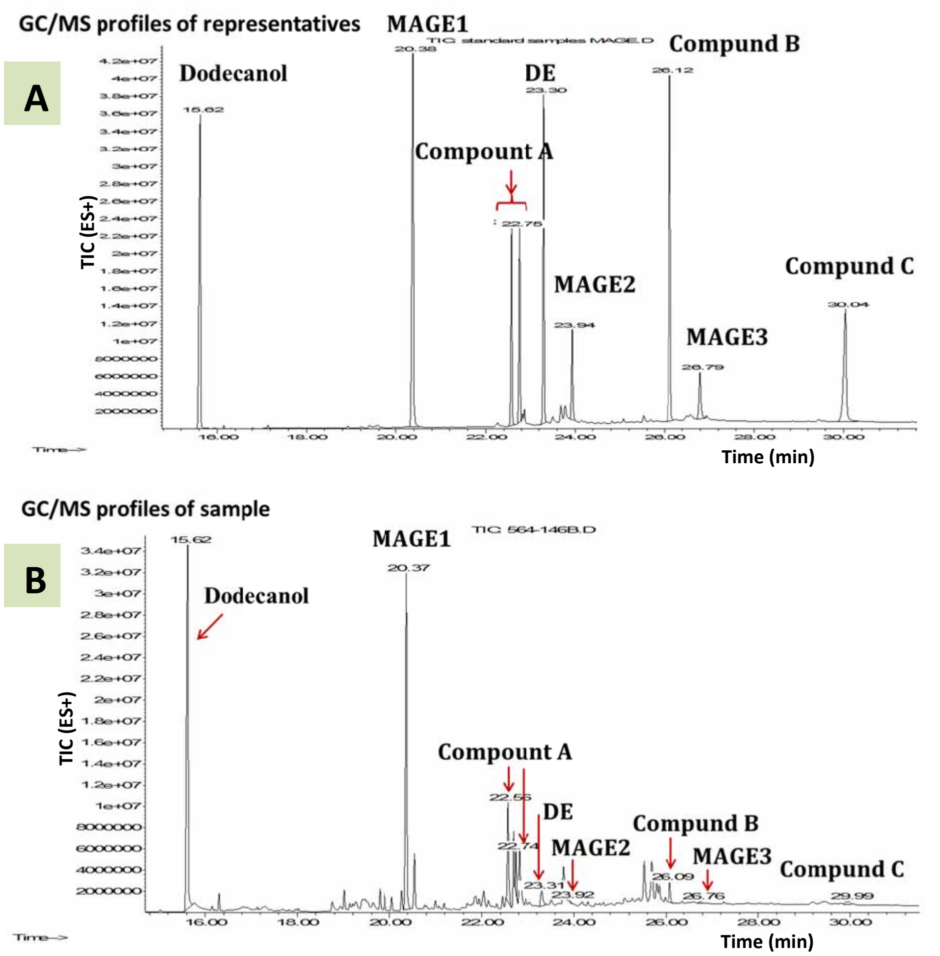


Fig. S5 Typical GC/MS chromatogram of standard representatives (A) and MAGE sample (B).

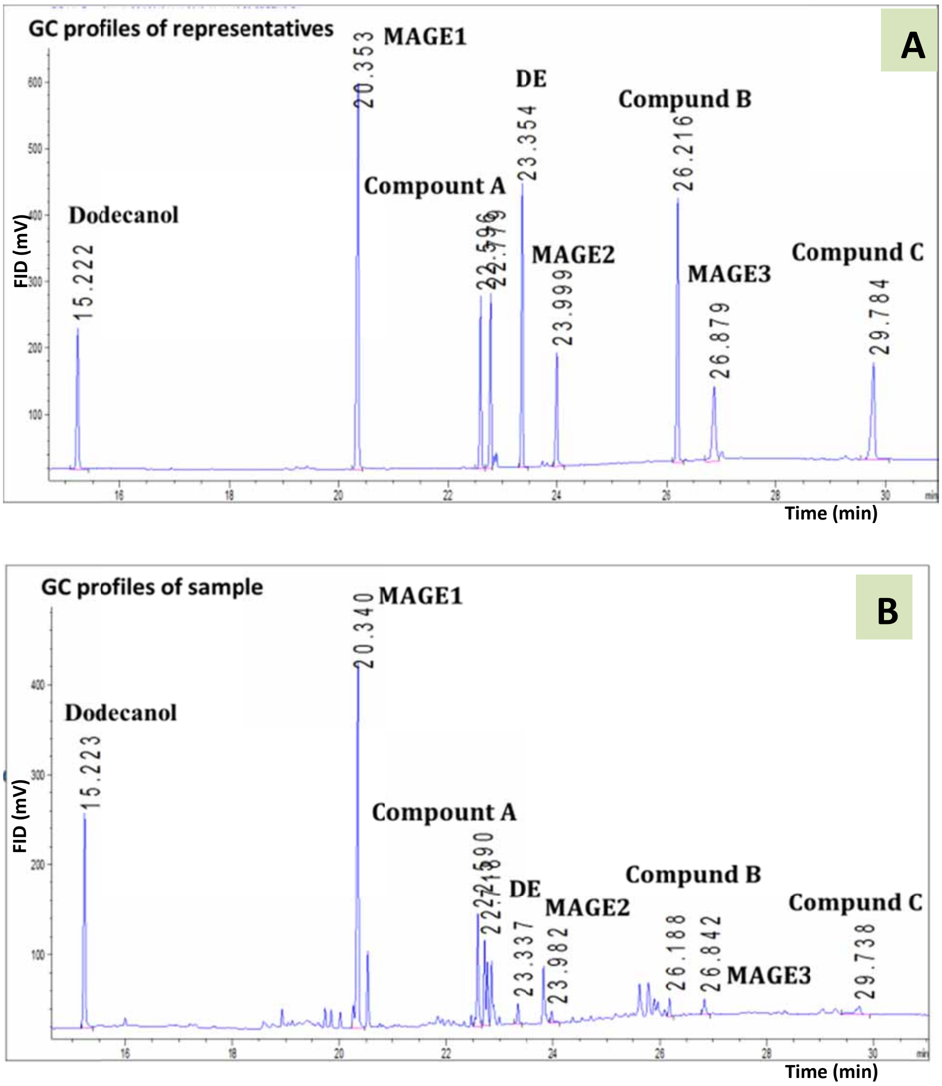
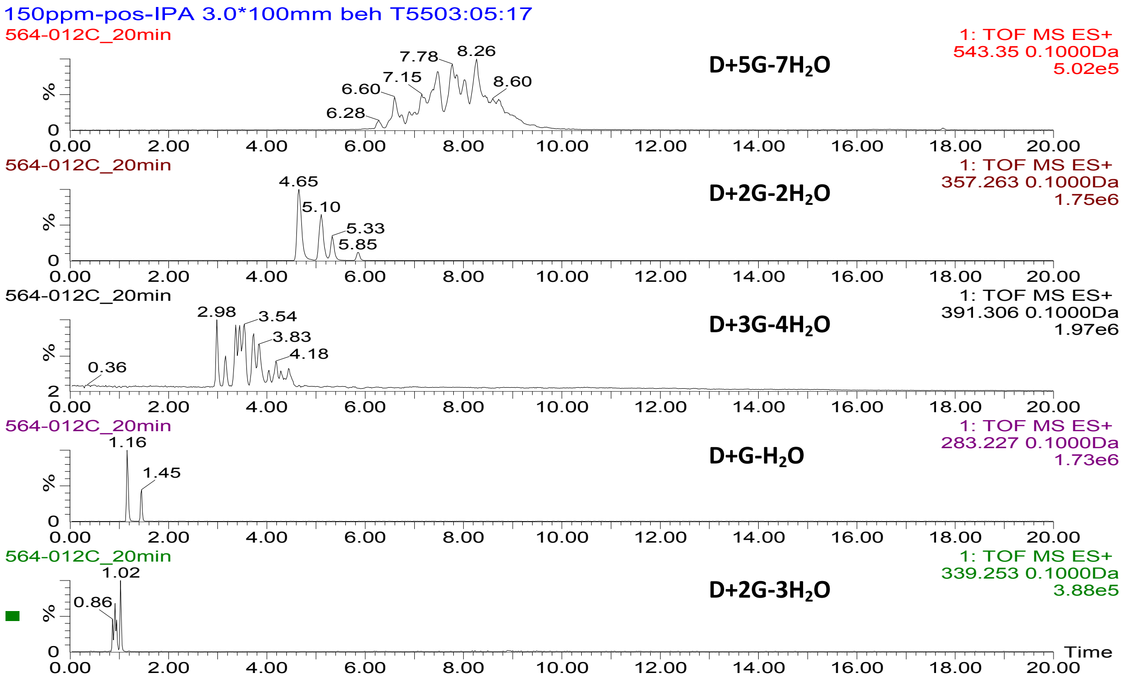
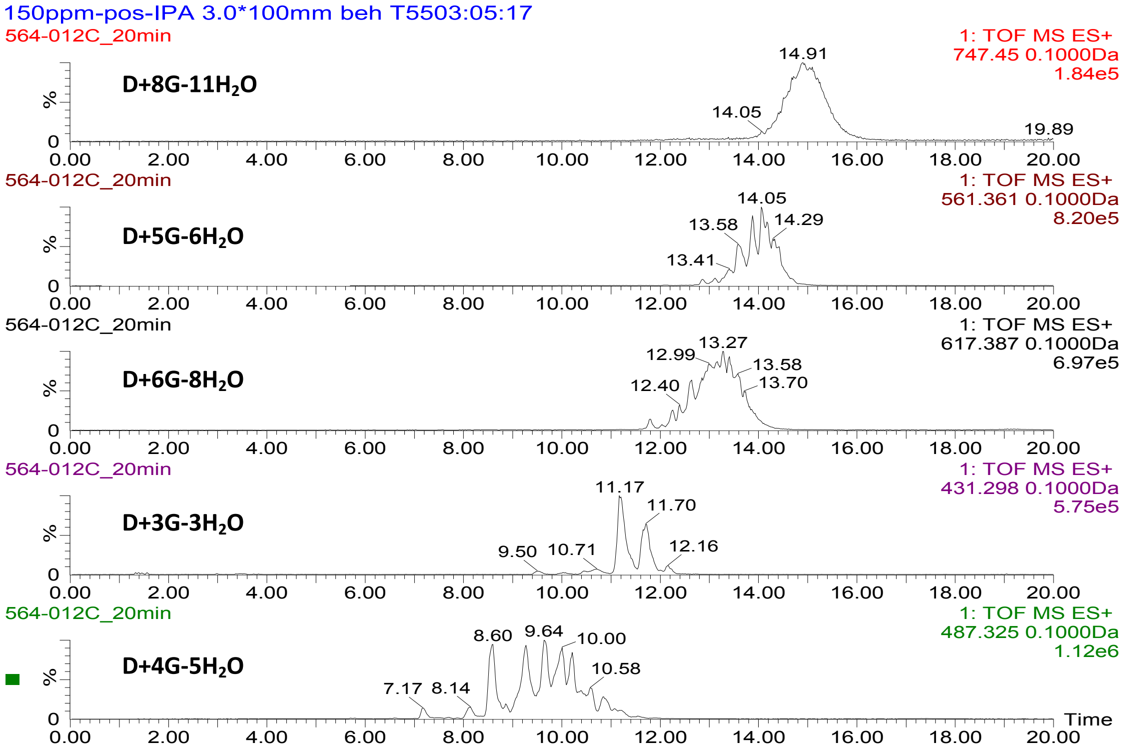
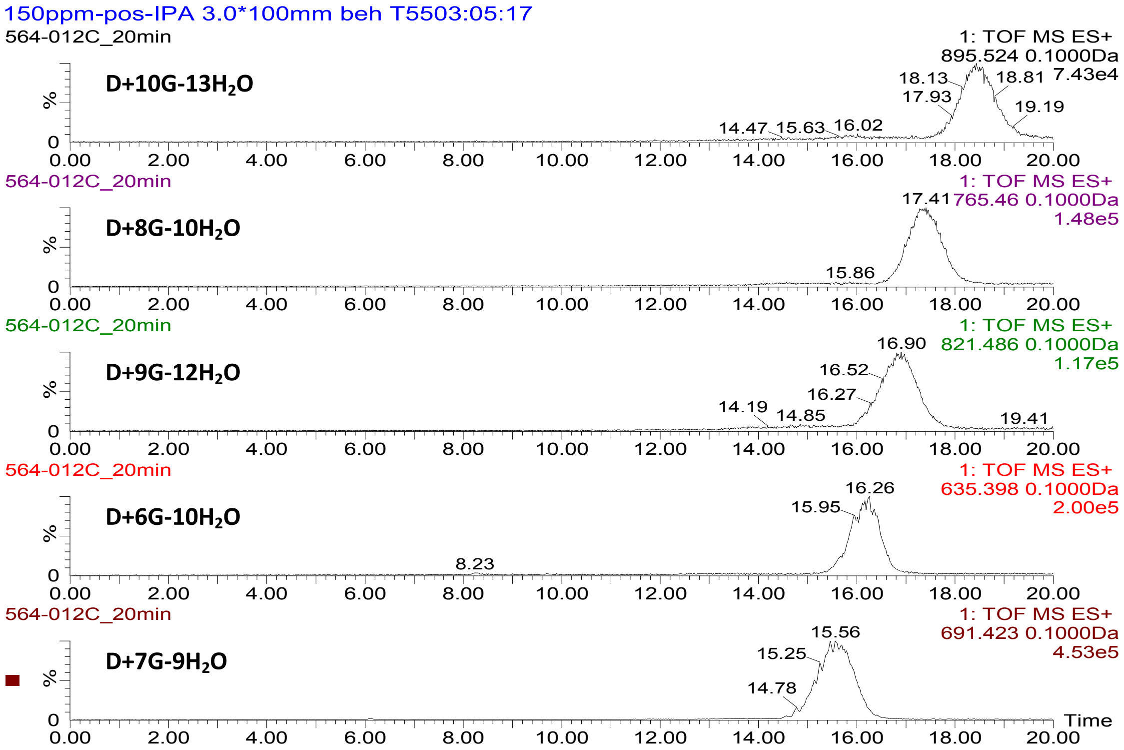
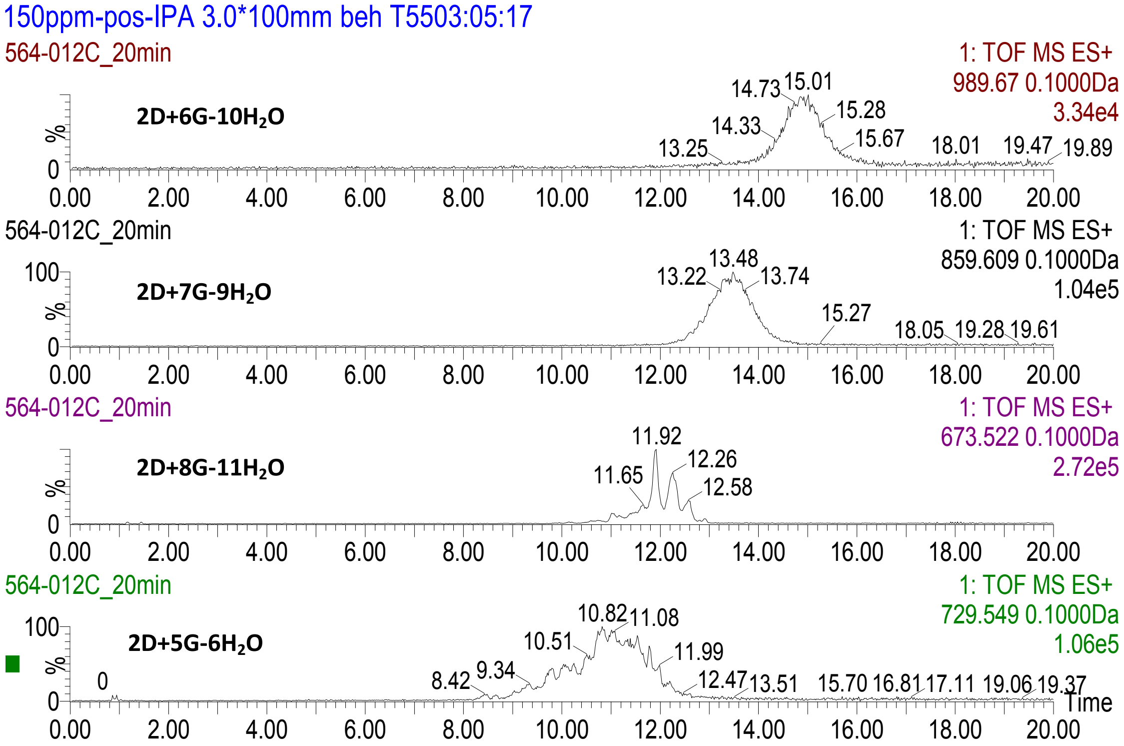


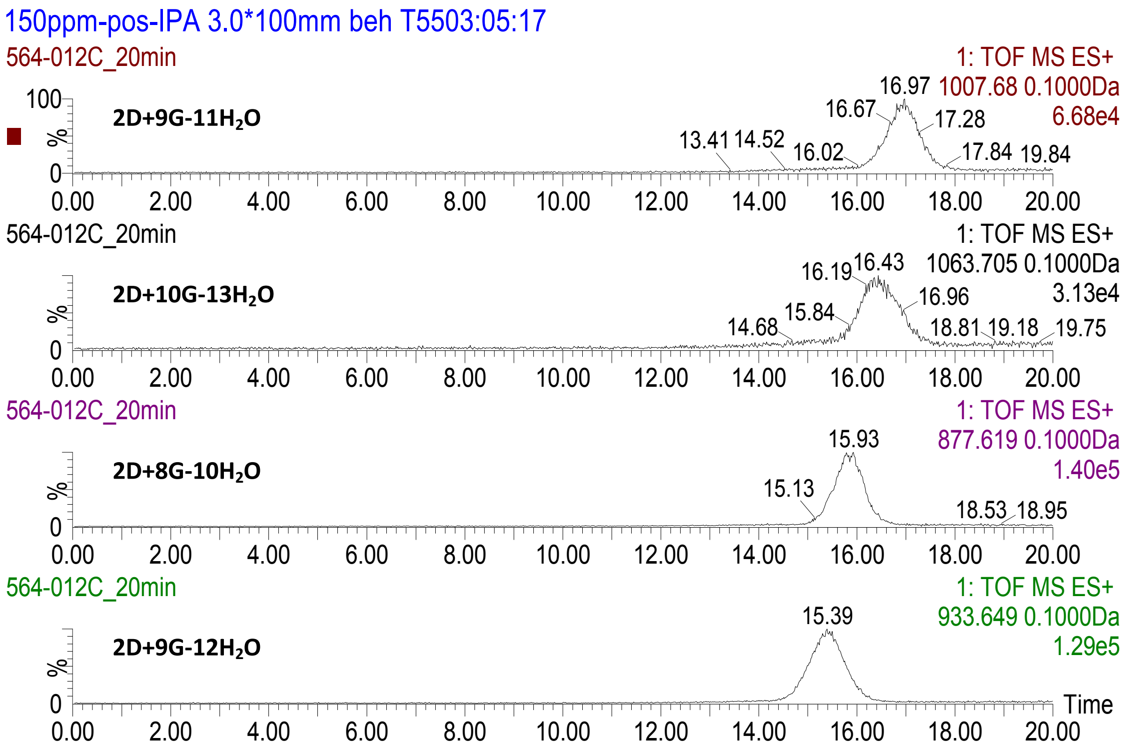
Fig. S6 Typical GC profiles of representative standards (A) and sample (B). Please refer to scheme 4 for the structure.

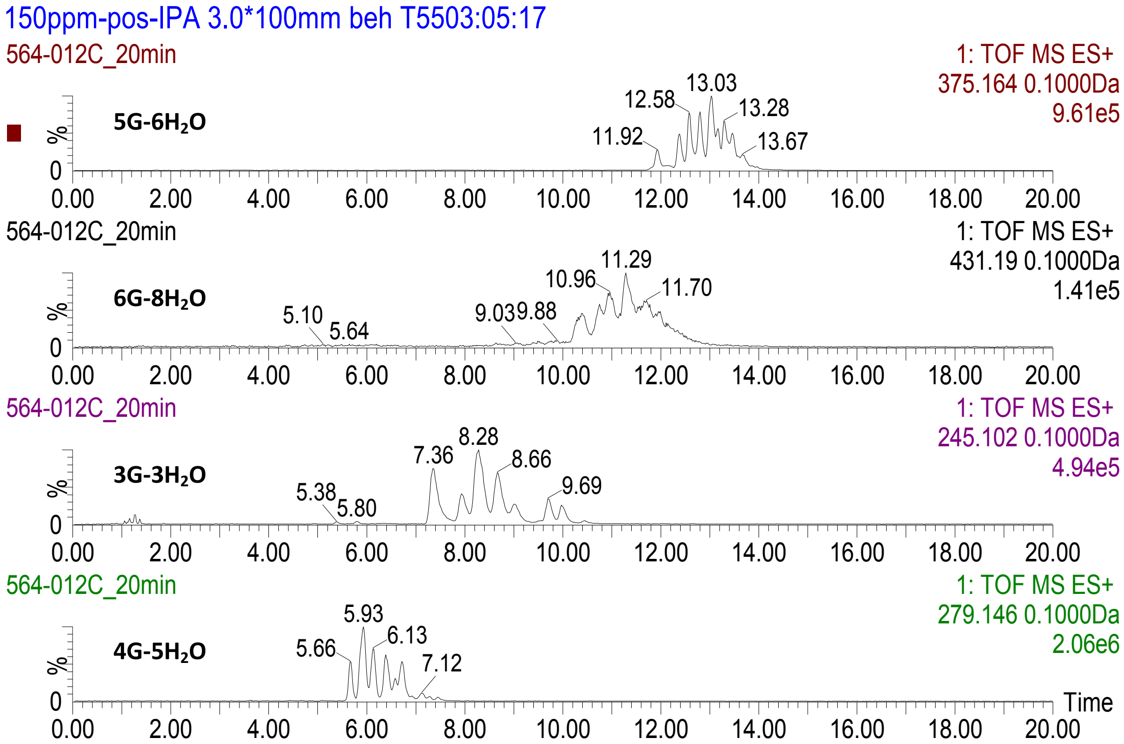

150ppm-pos-IPA 3.0*100mm beh T5503:05:17
564-012C_20min
1: TOF MS ES+
543.35 0.1000Da
5.02e5
D+5G-7H$_2$O
6.28
6.60
7.15
7.78
8.26
8.60
564-012C_20min
1: TOF MS ES+
357.263 0.1000Da
1.75e6
D+2G-2H$_2$O
4.65
5.10
5.33
5.85
564-012C_20min
1: TOF MS ES+
391.306 0.1000Da
1.97e6
D+3G-4H$_2$O
0.36
2.98
3.54
3.83
4.18
564-012C_20min
1: TOF MS ES+
283.227 0.1000Da
1.73e6
D+G-H$_2$O
1.16
1.45
564-012C_20min
1: TOF MS ES+
339.253 0.1000Da
3.88e5
D+2G-3H$_2$O
0.86
1.02
%
0
2
Time
0.00
2.00
4.00
6.00
8.00
10.00
12.00
14.00
16.00
18.00
20.00


150ppm-pos-IPA 3.0*100mm beh T5503:05:17
564-012C_20min
1: TOF MS ES+
747.45 0.1000Da
1.84e5
D+8G-11H$_2$O
14.05
14.91
19.89
564-012C_20min
1: TOF MS ES+
561.361 0.1000Da
8.20e5
D+5G-6H$_2$O
13.41
13.58
14.05
14.29
564-012C_20min
1: TOF MS ES+
617.387 0.1000Da
6.97e5
D+6G-8H$_2$O
12.40
12.99
13.27
13.58
13.70
564-012C_20min
1: TOF MS ES+
431.298 0.1000Da
5.75e5
D+3G-3H$_2$O
9.50
10.71
11.17
11.70
12.16
564-012C_20min
1: TOF MS ES+
487.325 0.1000Da
1.12e6
D+4G-5H$_2$O
7.17
8.14
8.60
9.64
10.00
10.58
%
0
Time
0.00
2.00
4.00
6.00
8.00
10.00
12.00
14.00
16.00
18.00
20.00


150ppm-pos-IPA 3.0*100mm beh T5503:05:17
564-012C_20min
1: TOF MS ES+
895.524 0.1000Da
7.43e4
D+10G-13H2O
18.13
17.93
18.81
19.19
14.47
15.63
16.02
%
0
564-012C_20min
1: TOF MS ES+
765.46 0.1000Da
1.48e5
17.41
D+8G-10H2O
15.86
564-012C_20min
1: TOF MS ES+
821.486 0.1000Da
1.17e5
16.90
16.52
16.27
14.19
14.85
19.41
D+9G-12H2O
564-012C_20min
1: TOF MS ES+
635.398 0.1000Da
2.00e5
16.26
15.95
8.23
D+6G-10H2O
564-012C_20min
1: TOF MS ES+
691.423 0.1000Da
4.53e5
15.56
15.25
14.78
D+7G-9H2O
Time
0.00
2.00
4.00
6.00
8.00
10.00
12.00
14.00
16.00
18.00
20.00


150ppm-pos-IPA 3.0*100mm beh T5503:05:17
564-012C_20min
1: TOF MS ES+
989.67 0.1000Da
3.34e4
2D+6G-10H2O
14.73
15.01
15.28
14.33
13.25
15.67
18.01
19.47
19.89
564-012C_20min
1: TOF MS ES+
859.609 0.1000Da
1.04e5
2D+7G-9H2O
100
13.48
13.22
13.74
15.27
18.05
19.28
19.61
564-012C_20min
1: TOF MS ES+
673.522 0.1000Da
2.72e5
2D+8G-11H2O
11.92
11.65
12.26
12.58
564-012C_20min
1: TOF MS ES+
729.549 0.1000Da
1.06e5
2D+5G-6H2O
100
10.82
11.08
10.51
11.99
8.42
9.34
12.47
13.51
15.70
16.81
17.11
19.06
19.37
0
Time
%
0.00
2.00
4.00
6.00
8.00
10.00
12.00
14.00
16.00
18.00
20.00


150ppm-pos-IPA 3.0*100mm beh T5503:05:17
564-012C_20min
1: TOF MS ES+
1007.68 0.1000Da
6.68e4
2D+9G-11H2O
100
%
0
13.41 14.52 16.02 16.67 16.97 17.28 17.84 19.84
564-012C_20min
1: TOF MS ES+
1063.705 0.1000Da
3.13e4
2D+10G-13H2O
14.68 15.84 16.19 16.43 16.96 18.81 19.18 19.75
564-012C_20min
1: TOF MS ES+
877.619 0.1000Da
1.40e5
2D+8G-10H2O
15.13 15.93 18.53 18.95
564-012C_20min
1: TOF MS ES+
933.649 0.1000Da
1.29e5
2D+9G-12H2O
15.39
Time
0.00 2.00 4.00 6.00 8.00 10.00 12.00 14.00 16.00 18.00 20.00


150ppm-pos-IPA 3.0*100mm beh T5503:05:17
564-012C_20min
1: TOF MS ES+
375.164 0.1000Da
9.61e5
5G-6H2O
%
0
11.92 12.58 13.03 13.28 13.67
564-012C_20min
1: TOF MS ES+
431.19 0.1000Da
1.41e5
6G-8H2O
5.10 5.64 9.03 9.88 10.96 11.29 11.70
564-012C_20min
1: TOF MS ES+
245.102 0.1000Da
4.94e5
3G-3H2O
5.38 5.80 7.36 8.28 8.66 9.69
564-012C_20min
1: TOF MS ES+
279.146 0.1000Da
2.06e6
4G-5H2O
5.66 5.93 6.13 7.12
Time
0.00 2.00 4.00 6.00 8.00 10.00 12.00 14.00 16.00 18.00 20.00

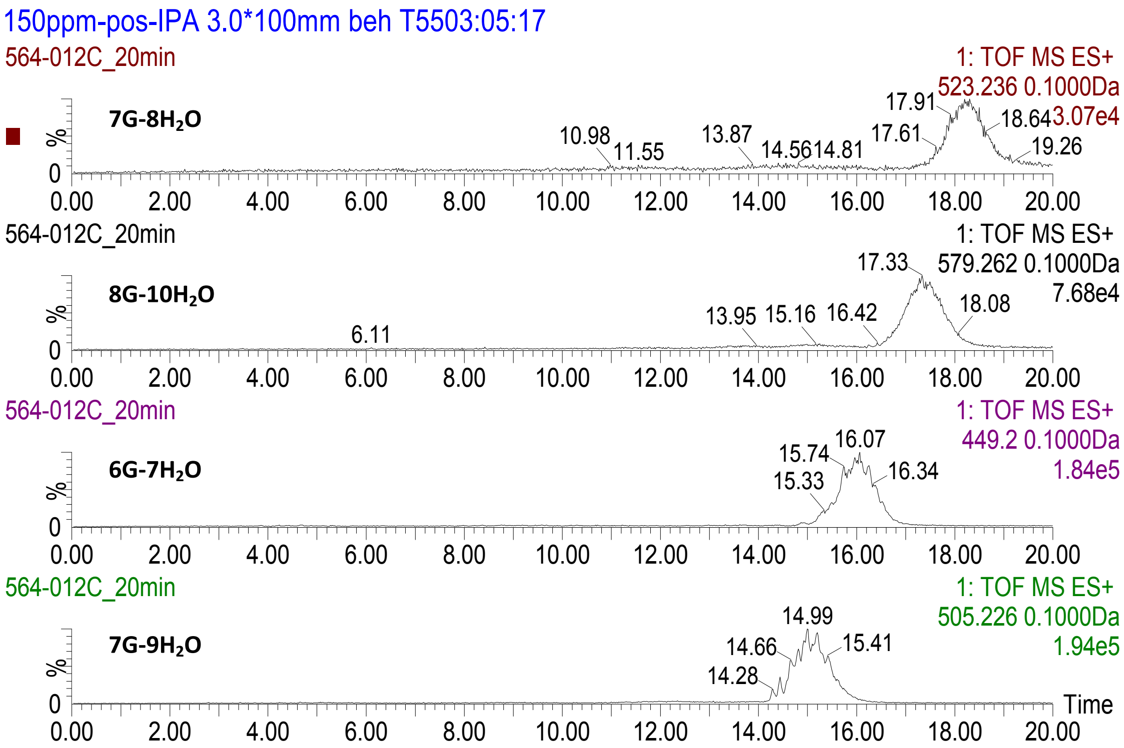


Fig. S7 SFC/HRMS results. Unit for X-axis is minute and unit for Y-axis is ion strength percentage (ES+).

Table S2 Laundry performance results of cotton, polyester&cotton and polyester

Entry	Stains	AEO7	MAGE4	AGEM1	AGEM2	AGEM3
1	JB01	19	18	19	16	15
2	JB02	6	7	8	8	6
3	JB03	15	16	14	11	8
4	CS61	27	26	27	26	37
5	EMPA	11	10	12	12	10
6	**Sum on cotton**	**78**	**77**	**80**	**73**	**77**
7	20C	5	3	2	1	0
8	20D	14	10	10	11	6
9	20PF	11	8	6	6	2
10	**Sum on Polyester&Cotton**	**30**	**22**	**18**	**17**	**8**
11	30C	20	19	16	19	3
12	30D	18	14	10	4	1
13	30PF	10	7	6	5	1
14	**Sum on polyester**	**48**	**40**	**32**	**28**	**5**
15	**Total SUM**	**155**	**138**	**130**	**118**	**90**

JB01: carbon black with oil on cotton; JB02: egg protein on cotton; JB03: sebum on cotton; CS61: Beef lard on cotton; EMPA: lipstick on cotton; 20C: pigment, lanolin on polyester/cotton 65/35; 20D: pigment, sebum on polyester/cotton 65/35; 20PF: pigment, vegetable fat on polyester/cotton 65/35; 30C: pigment, lanolin on polyester; 30D: pigment, sebum on polyester; 30PF: pigment, vegetable fat on polyester.