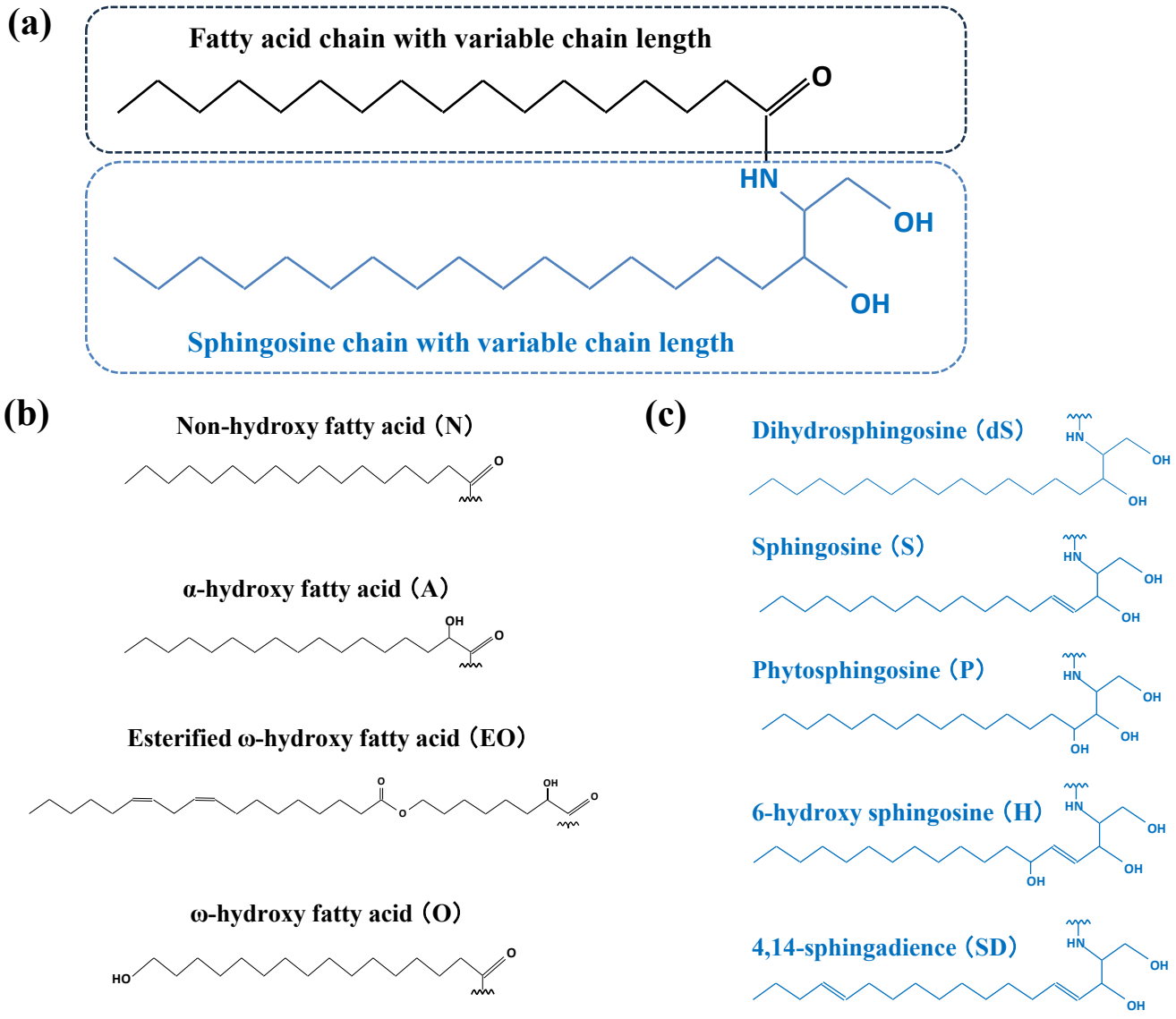

Fig. S1 Basic structure of CER, fatty acid and sphingosine chains in SC CERs.
(a) Basic Structure of CERs, (b) Structure of fatty acid chains in SC CERs and
(c) Structure of the sphingosine chains in SC CER

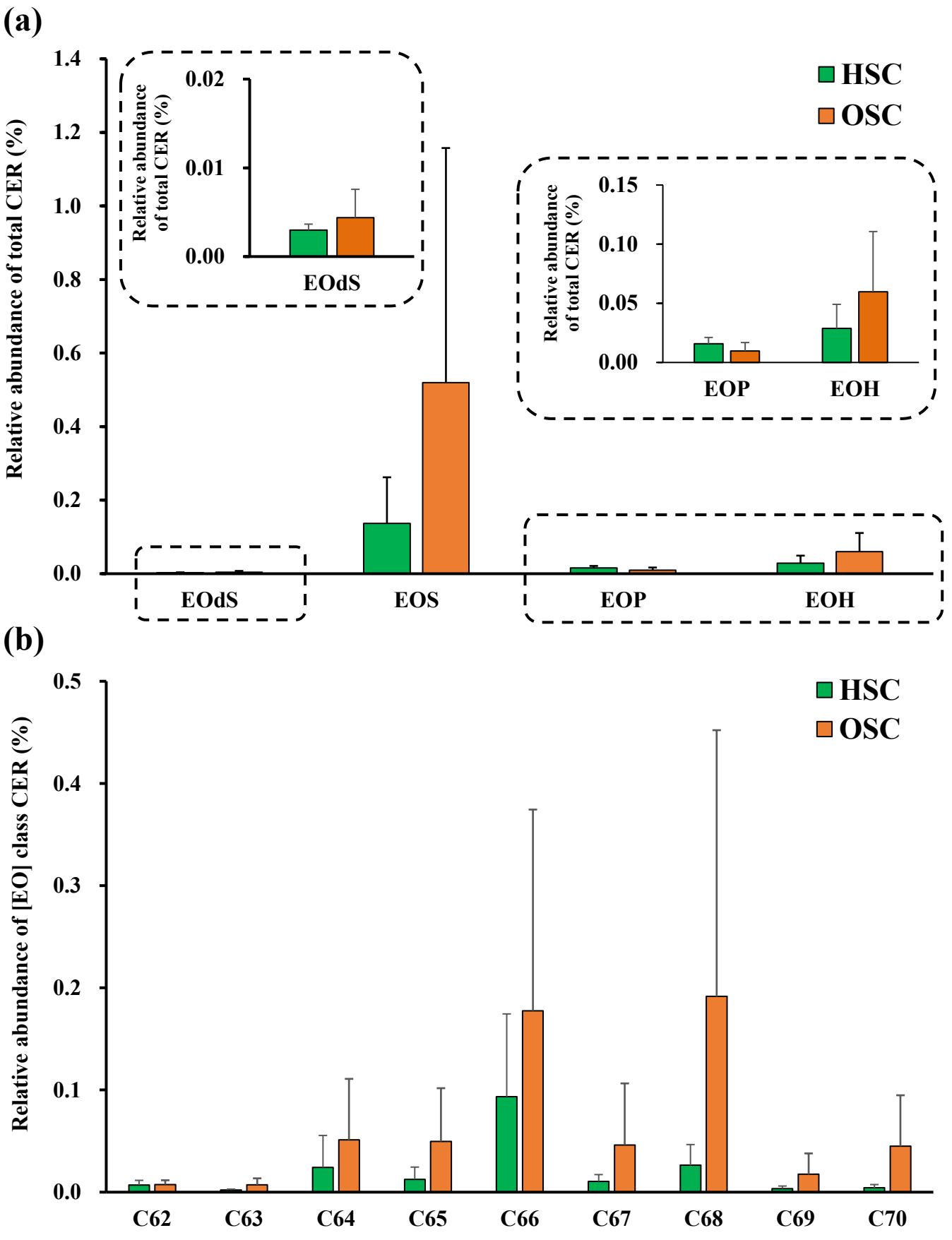

Fig. S2 Comparison of relative abundance of (a) subclasses and (b) carbon chain lengths of [EO] CERs in HSC and OSC.

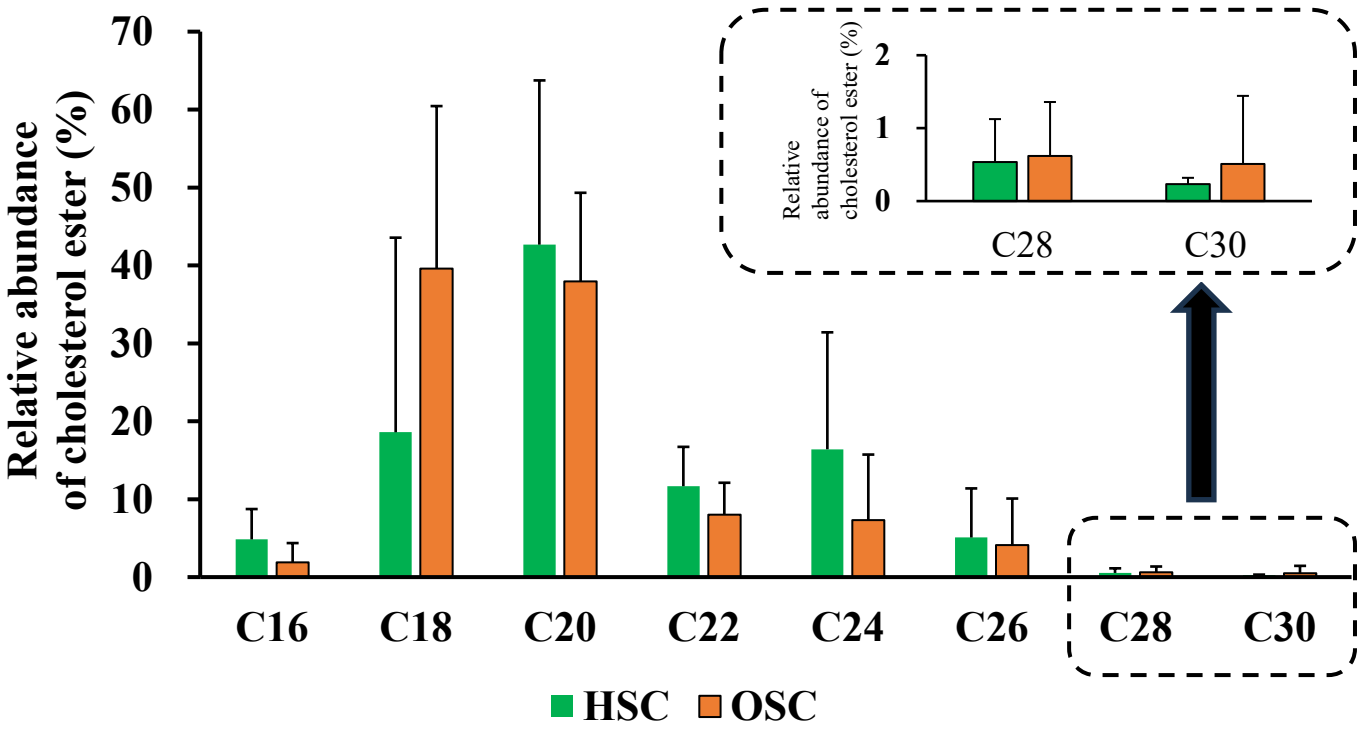

Fig. S3 Comparison of relative abundance of cholesterol ester ratios in HSC and OSC.

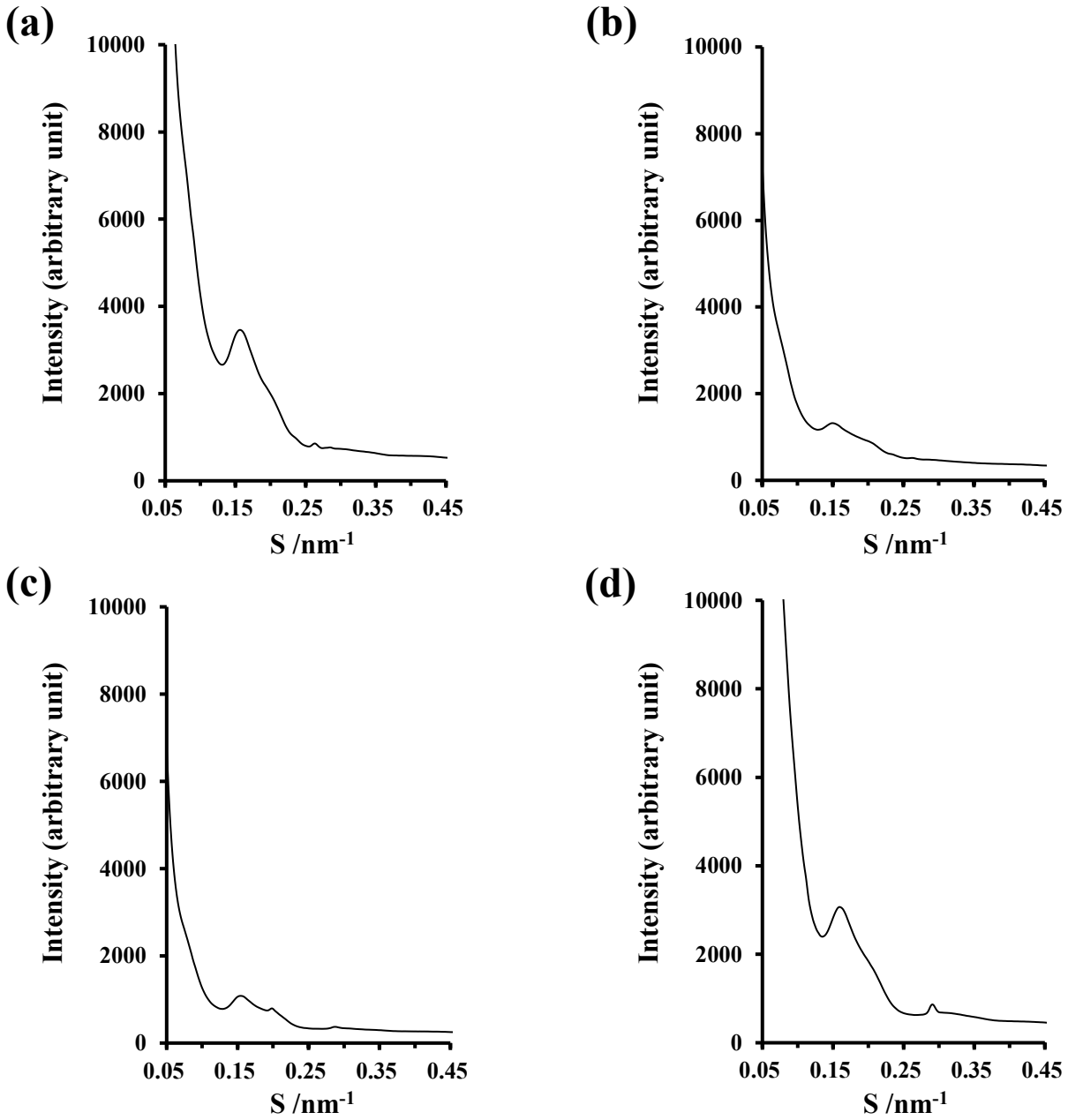

Fig. S4 SAXD profiles at HSC.
(a) HSC-02, (b) HSC-03, (c) HSC-04 and (d) HSC-05

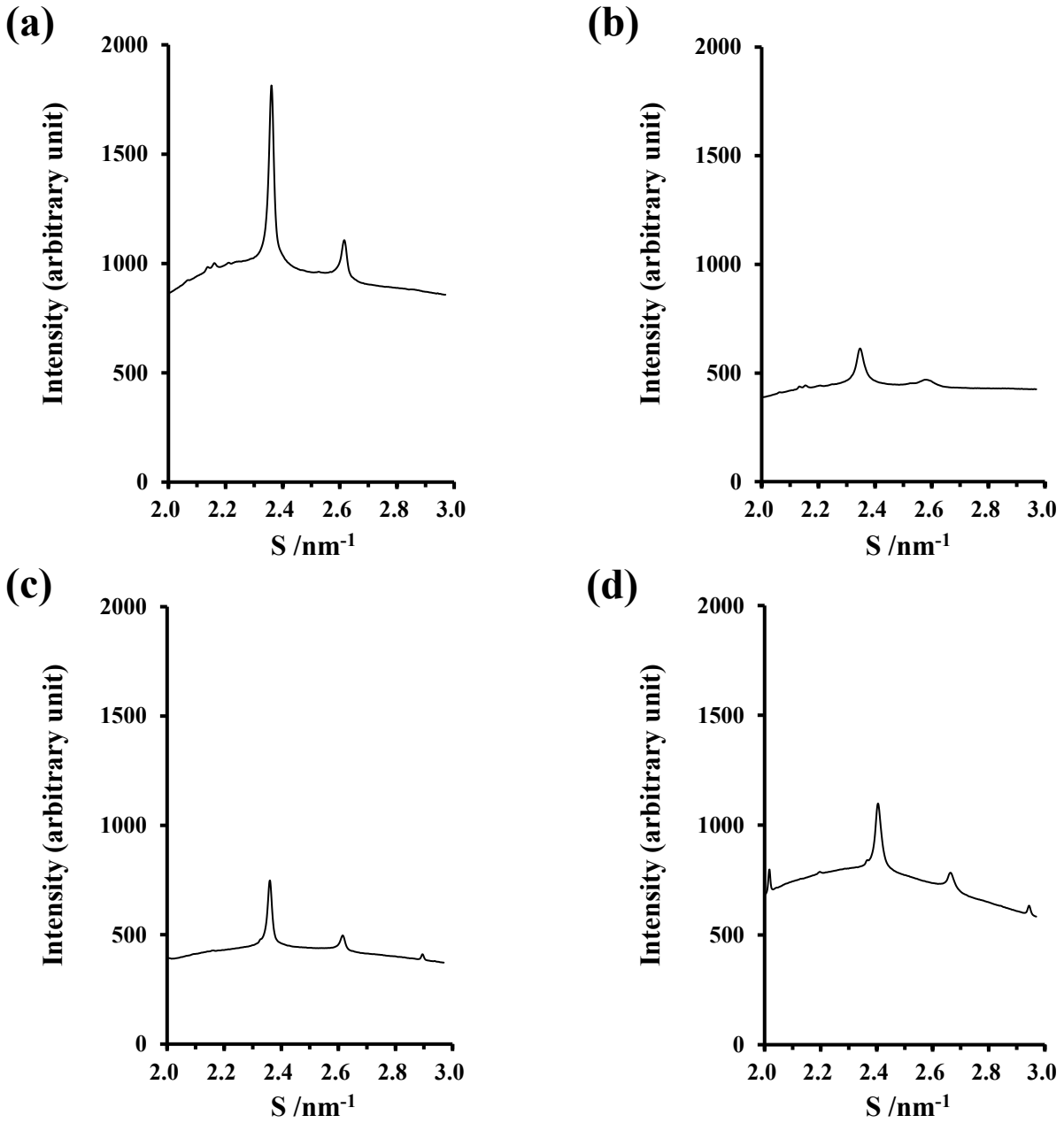

Fig. S5 WAXD profiles at HSC.
(a) HSC-02, (b) HSC-03, (c) HSC-04 and (d) HSC-05

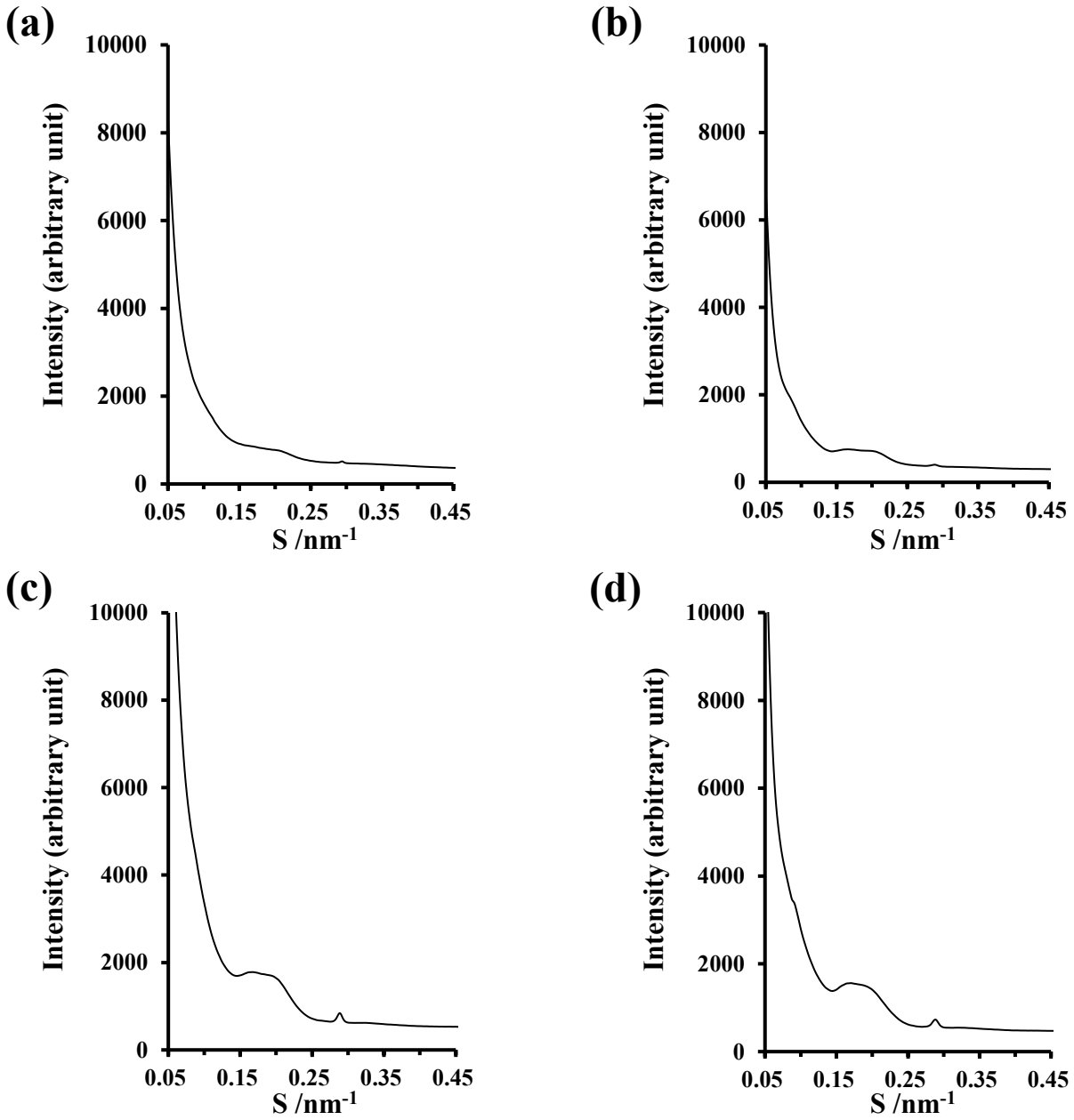

Fig. S6 SAXD profiles at OSCs.
(a) OSC-21,(b) OSC-35, (c) OSC-44, (d) OSC-46

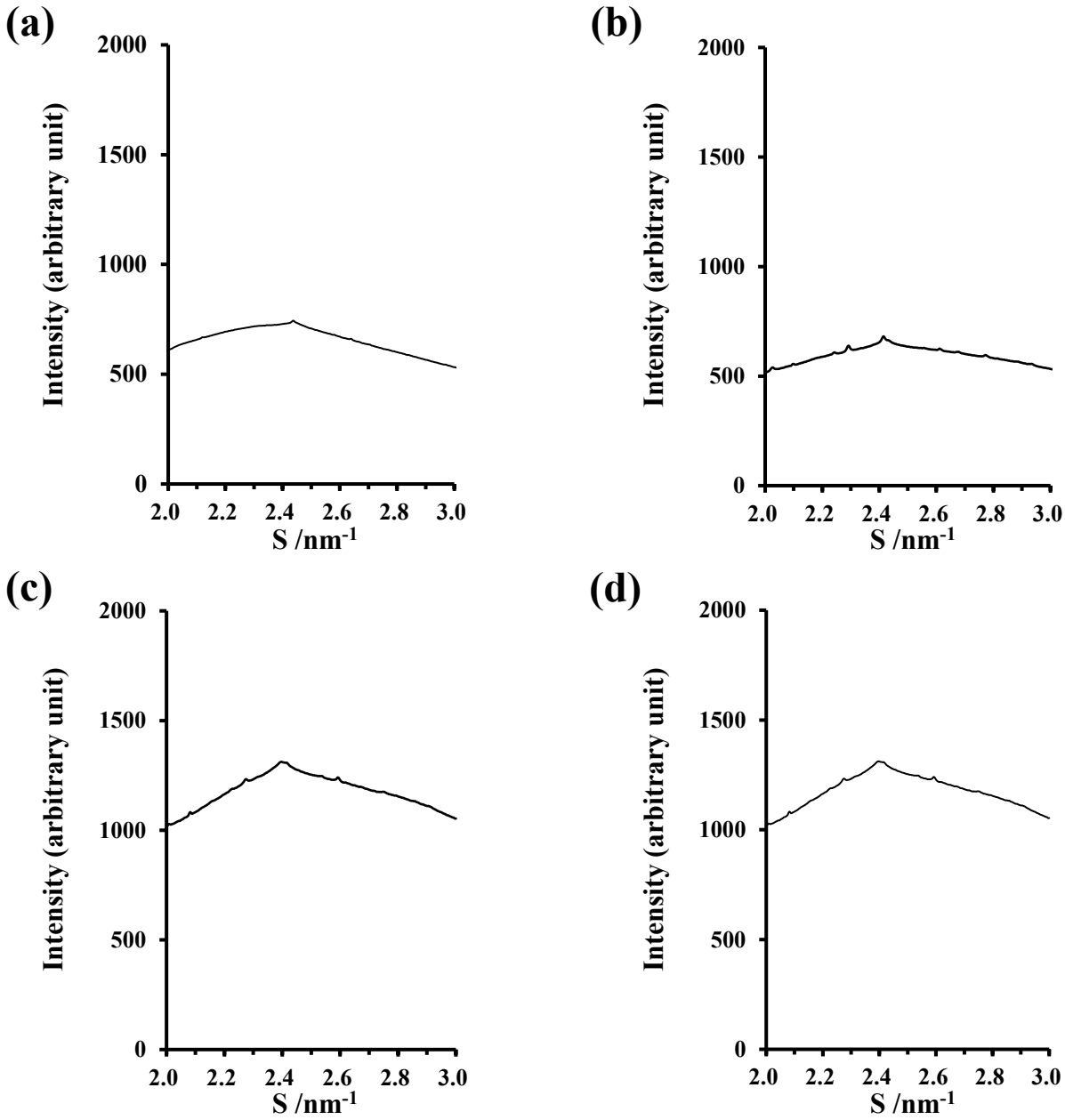

Fig. S7 WAXD profiles at OSCs.
(a) OSC-21, (b) OSC-35, (c) OSC-44 and (d) OSC-47

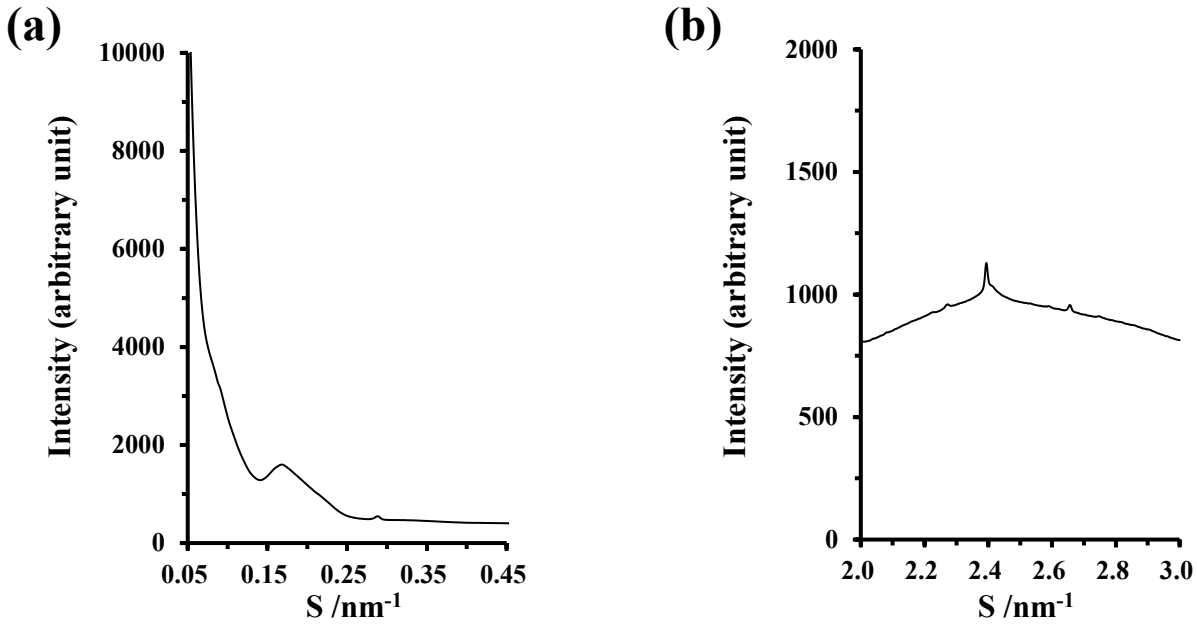

Fig. S8 SAXD (a) and WAXD (b) profiles at OSC-39.

Table S1 The sample back ground of HSCs

Number	Age	Gender	Sample site
HSC-01	29	Female	Abdomen
HSC-02	66	Female	Mammary
HSC-03	51	Female	Mammary
HSC-04	54	Female	Abdomen
HSC-05	68	Female	Abdomen

Table S2 The sample back ground of OSCs

Sample code	Age	Gender	Height (cm)	Weight (kg)	BSA (m^2)	PS	Ccr (mL/min)	CT－CAE grade of HFS	Onset date of HFS after starting OSM
OSC-13	77	Female	149.7	42.8	1.34	0	67.7	2	35
OSC-21	75	Male	157	54.9	1.54	0	49.6	2	41
OSC-34	78	Male	162.3	72.8	1.78	0	68.9	2	70
OSC-35	53	Female	155.3	44.9	1.40	0	128.1	2	40
OSC-39	76	Male	153.2	57.5	1.54	0	62.3	2	51
OSC-44	71	Male	167.1	69.6	1.78	0	88.9	2	44
OSC-47	67	Male	168.2	84.1	1.94	0	116.8	2	60

BSA：Body surface area（DuBois）
PS：Performance status
Ccr：Creatinine clearance
CTCAE: Common Terminology Criteria for Adverse Events version 5.0

Table S3 Chromatographic parameters used for qualitative analysis of CERs.

Column	ACQUITY UPLC® BEH C18 (2.1×100 mm, 1.7 μm) (Waters, Milford, MA, USA)
Column temperature	80°C
Flow rate	0.5 mL/min
Injection volume	10 μL
Mobile phase A	80% (v/v) MeOH with 0.1% HCOOH
Mobile phase B	MeOH/IPA/HCOOH (90/10/0.1、v/v/v)
Gradient	**Time (min)** / **Mobile phase ratio (A : B, %)** 0.0 / 100 : 0 50.0 / 0 : 100 60.0 / 0 : 100 60.1 / 100 : 0 80.1 / 100 : 0
System	ACQUITY UPLC® I-Class PLUS (Waters)
Sample solvent	MeOH/$CHCl_3$ (95/5、v/v)
Sample tray temperature	10°C

Table S4 MS/MS Method

Scan type	Multiple Reaction Monitoring (MRM), Selected Ion Recording (SIR)
Polarity	Positive, Negative
Ion Source	Electrospray ionization
Capillary voltage (kV)	3.10
Desolvation temperature (°C)	500
Source temperature (°C)	150
Desolvation gas flows (L/h)	1000
Cone gas flows (L/h)	150
System	Xevo TQ-XS (Waters)

Table S5 Compound information and ionization condition of CER and Internal standard in MRM method.

Compound	Precursor Ion (m/z)	Fragment Ion (m/z)	Dwell (s)	Cone Voltage (V)	Collision Energy (eV)
N14dS18	512.51	266.19	0.025	14	36
N15dS18	526.52	266.19	0.025	14	36
N16dS18	540.54	266.19	0.025	14	36
N17dS18	554.55	266.19	0.025	14	36
N18dS18	568.57	266.19	0.025	14	36
N19dS18	582.58	266.19	0.025	14	36
N20dS18	596.60	266.19	0.025	14	36
N21dS18	610.62	266.19	0.025	14	36
N22dS18	624.63	266.19	0.025	14	36
N23dS18	638.65	266.19	0.025	14	36
N24dS18	652.66	266.19	0.025	14	36
N25dS18	666.68	266.19	0.025	14	36
N26dS18	680.69	266.19	0.025	14	36
N27dS18	694.71	266.19	0.025	14	36
N28dS18	708.73	266.19	0.025	14	36
N29dS18	722.74	266.19	0.025	14	36
N30dS18	736.76	266.19	0.025	14	36
N31dS18	750.77	266.19	0.025	14	36
N32dS18	764.79	266.19	0.025	14	36
N14S18	510.49	264.23	0.025	6	36
N15S18	524.51	264.23	0.025	6	36
N16S18	538.52	264.23	0.025	6	36
N17S18	552.54	264.23	0.025	6	36
N18S18	566.55	264.23	0.025	6	36
N19S18	580.57	264.23	0.025	6	36
N20S18	594.58	264.23	0.025	6	36
N21S18	608.60	264.23	0.025	6	36
N22S18	622.62	264.23	0.025	6	36
N23S18	636.63	264.23	0.025	6	36
N24S18	650.65	264.23	0.025	6	36
N25S18	664.66	264.23	0.025	6	36
N26S18	678.68	264.23	0.025	6	36
N27S18	692.69	264.23	0.025	6	36
N28S18	706.71	264.23	0.025	6	36
N29S18	720.73	264.23	0.025	6	36
N30S18	734.74	264.23	0.025	6	36
N31S18	748.76	264.23	0.025	6	36
N32S18	762.77	264.23	0.025	6	36

Table S5 Compound information and ionization condition of CER and Internal standard in MRM method *(Continued)*.

Compound	Precursor Ion (m/z)	Fragment Ion (m/z)	Dwell (s)	Cone Voltage (V)	Collision Energy (eV)
N14P18	528.50	300.27	0.025	14	24
N15P18	542.52	300.27	0.025	14	24
N16P18	556.53	300.27	0.025	14	24
N17P18	570.55	300.27	0.025	14	24
N18P18	584.56	300.27	0.025	14	24
N19P18	598.58	300.27	0.025	14	24
N20P18	612.60	300.27	0.025	14	24
N21P18	626.61	300.27	0.025	14	24
N22P18	640.63	300.27	0.025	14	24
N23P18	654.64	300.27	0.025	14	24
N24P18	668.66	300.27	0.025	14	24
N25P18	682.67	300.27	0.025	14	24
N26P18	696.69	300.27	0.025	14	24
N27P18	710.70	300.27	0.025	14	24
N28P18	724.72	300.27	0.025	14	24
N29P18	738.74	300.27	0.025	14	24
N30P18	752.75	300.27	0.025	14	24
N31P18	766.77	300.27	0.025	14	24
N32P18	780.78	300.27	0.025	14	24
N14H18	526.49	280.24	0.025	14	36
N15H18	540.50	280.24	0.025	14	36
N16H18	554.52	280.24	0.025	14	36
N17H18	568.53	280.24	0.025	14	36
N18H18	582.55	280.24	0.025	14	36
N19H18	596.56	280.24	0.025	14	36
N20H18	610.58	280.24	0.025	14	36
N21H18	624.60	280.24	0.025	14	36
N22H18	638.61	280.24	0.025	14	36
N23H18	652.63	280.24	0.025	14	36
N24H18	666.64	280.24	0.025	14	36
N25H18	680.66	280.24	0.025	14	36
N26H18	694.67	280.24	0.025	14	36
N27H18	708.69	280.24	0.025	14	36
N28H18	722.70	280.24	0.025	14	36
N29H18	736.72	280.24	0.025	14	36
N30H18	750.74	280.24	0.025	14	36
N31H18	764.75	280.24	0.025	14	36
N32H18	778.77	280.24	0.025	14	36

Table S5 Compound information and ionization condition of CER and Internal standard in MRM method *(Continued)*.

Compound	Precursor Ion (m/z)	Fragment Ion (m/z)	Dwell (s)	Cone Voltage (V)	Collision Energy (eV)
A14dS18	528.50	266.25	0.025	20	28
A15dS18	542.52	266.25	0.025	20	28
A16dS18	556.53	266.25	0.025	20	28
A17dS18	570.55	266.25	0.025	20	28
A18dS18	584.56	266.25	0.025	20	28
A19dS18	598.58	266.25	0.025	20	28
A20dS18	612.60	266.25	0.025	20	28
A21dS18	626.61	266.25	0.025	20	28
A22dS18	640.63	266.25	0.025	20	28
A23dS18	654.64	266.25	0.025	20	28
A24dS18	668.66	266.25	0.025	20	28
A25dS18	682.67	266.25	0.025	20	28
A26dS18	696.69	266.25	0.025	20	28
A27dS18	710.70	266.25	0.025	20	28
A28dS18	724.72	266.25	0.025	20	28
A29dS18	738.74	266.25	0.025	20	28
A30dS18	752.75	266.25	0.025	20	28
A31dS18	766.77	266.25	0.025	20	28
A32dS18	780.78	266.25	0.025	20	28
A14S18	526.49	264.24	0.025	8	34
A15S18	540.50	264.24	0.025	8	34
A16S18	554.52	264.24	0.025	8	34
A17S18	568.53	264.24	0.025	8	34
A18S18	582.55	264.24	0.025	8	34
A19S18	596.56	264.24	0.025	8	34
A20S18	610.58	264.24	0.025	8	34
A21S18	624.60	264.24	0.025	8	34
A22S18	638.61	264.24	0.025	8	34
A23S18	652.63	264.24	0.025	8	34
A24S18	666.64	264.24	0.025	8	34
A25S18	680.66	264.24	0.025	8	34
A26S18	694.67	264.24	0.025	8	34
A27S18	708.69	264.24	0.025	8	34
A28S18	722.70	264.24	0.025	8	34
A29S18	736.72	264.24	0.025	8	34
A30S18	750.74	264.24	0.025	8	34
A31S18	764.75	264.24	0.025	8	34
A32S18	778.77	264.24	0.025	8	34

Table S5 Compound information and ionization condition of CER and Internal standard in MRM method *(Continued)*.

Compound	Precursor Ion (m/z)	Fragment Ion (m/z)	Dwell (s)	Cone Voltage (V)	Collision Energy (eV)
A14P18	544.50	300.27	0.025	10	28
A15P18	558.51	300.27	0.025	10	28
A16P18	572.53	300.27	0.025	10	28
A17P18	586.54	300.27	0.025	10	28
A18P18	600.56	300.27	0.025	10	28
A19P18	614.57	300.27	0.025	10	28
A20P18	628.59	300.27	0.025	10	28
A21P18	642.61	300.27	0.025	10	28
A22P18	656.62	300.27	0.025	10	28
A23P18	670.64	300.27	0.025	10	28
A24P18	684.65	300.27	0.025	10	28
A25P18	698.67	300.27	0.025	10	28
A26P18	712.68	300.27	0.025	10	28
A27P18	726.70	300.27	0.025	10	28
A28P18	740.72	300.27	0.025	10	28
A29P18	754.73	300.27	0.025	10	28
A30P18	768.75	300.27	0.025	10	28
A31P18	782.76	300.27	0.025	10	28
A32P18	796.78	300.27	0.025	10	28
A15H18	556.50	280.24	0.025	8	34
A16H18	570.51	280.24	0.025	8	34
A17H18	584.53	280.24	0.025	8	34
A18H18	598.54	280.24	0.025	8	34
A19H18	612.56	280.24	0.025	8	34
A20H18	626.57	280.24	0.025	8	34
A21H18	640.59	280.24	0.025	8	34
A22H18	654.61	280.24	0.025	8	34
A23H18	668.62	280.24	0.025	8	34
A24H18	682.64	280.24	0.025	8	34
A25H18	696.65	280.24	0.025	8	34
A26H18	710.67	280.24	0.025	8	34
A27H18	724.68	280.24	0.025	8	34
A28H18	738.70	280.24	0.025	8	34
A29H18	752.72	280.24	0.025	8	34
A30H18	766.73	280.24	0.025	8	34
A31H18	780.75	280.24	0.025	8	34
A32H18	794.76	280.24	0.025	8	34

Table S5 Compound information and ionization condition of CER and Internal standard in MRM method *(Continued)*.

Compound	Precursor Ion (m/z)	Fragment Ion (m/z)	Dwell (s)	Cone Voltage (V)	Collision Energy (eV)
E18O26dS18	958.92	266.20	0.025	10	48
E18O27dS18	972.93	266.20	0.025	10	48
E18O28dS18	986.95	266.20	0.025	10	48
E18O29dS18	1000.97	266.20	0.025	10	48
E18O30dS18	1014.98	266.20	0.025	10	48
E18O31dS18	1029.00	266.20	0.025	10	48
E18O32dS18	1043.01	266.20	0.025	10	48
E18O33dS18	1057.03	266.20	0.025	10	48
E18O34dS18	1071.04	266.20	0.025	10	48
E18O26S18	956.90	264.23	0.025	46	40
E18O27S18	970.92	264.23	0.025	46	40
E18O28S18	984.93	264.23	0.025	46	40
E18O29S18	998.95	264.23	0.025	46	40
E18O30S18	1012.97	264.23	0.025	46	40
E18O31S18	1026.98	264.23	0.025	46	40
E18O32S18	1041.00	264.23	0.025	46	40
E18O33S18	1055.01	264.23	0.025	46	40
E18O34S18	1069.03	264.23	0.025	46	40
E18O26P18	974.91	300.26	0.025	20	52
E18O27P18	988.93	300.26	0.025	20	52
E18O28P18	1002.95	300.26	0.025	20	52
E18O29P18	1016.96	300.26	0.025	20	52
E18O30P18	1030.98	300.26	0.025	20	52
E18O31P18	1044.99	300.26	0.025	20	52
E18O32P18	1059.01	300.26	0.025	20	52
E18O33P18	1073.02	300.26	0.025	20	52
E18O34P18	1087.04	300.26	0.025	20	52
E18O26H18	972.90	280.24	0.025	10	48
E18O27H18	986.91	280.24	0.025	10	48
E18O28H18	1000.93	280.24	0.025	10	48
E18O29H18	1014.95	280.24	0.025	10	48
E18O30H18	1028.96	280.24	0.025	10	48
E18O31H18	1042.98	280.24	0.025	10	48
E18O32H18	1056.99	280.24	0.025	10	48
E18O33H18	1071.01	280.24	0.025	10	48
E18O34H18	1085.02	280.24	0.025	10	48
NdS-D	571.52	266.20	0.025	8	28

Table S6 Compound information and ionization condition of FFA and Internal standard in SIR method.

Compound	Precursor Ion (m/z)	Dwell (s)	Cone Voltage (V)
Saturated FFA			
C16:0	255.20	0.003	10
C17:0	269.26	0.003	10
C18:0	283.26	0.003	10
C19:0	297.29	0.003	10
C20:0	311.30	0.003	10
C21:0	325.32	0.003	10
C22:0	339.33	0.003	10
C23:0	353.35	0.003	10
C24:0	367.36	0.003	10
C25:0	381.38	0.003	10
C26:0	395.39	0.003	10
C27:0	409.41	0.003	10
C28:0	423.42	0.003	10
C29:0	437.44	0.003	10
C30:0	451.45	0.003	10
α-hydroxy FFA			
C16:0	271.27	0.003	40
C17:0	285.25	0.003	40
C18:0	299.23	0.003	12
C19:0	313.28	0.003	40
C20:0	327.30	0.003	40
C21:0	341.31	0.003	40
C22:0	355.33	0.003	40
C23:0	369.34	0.003	40
C24:0	383.36	0.003	40
C25:0	397.38	0.003	40
C26:0	411.39	0.003	40
C27:0	425.41	0.003	40
C28:0	439.42	0.003	40
C29:0	453.44	0.003	40
C30:0	467.45	0.003	40
Unsaturated FFA			
C16:1	253.21	0.003	10
C18:1	281.24	0.003	10
C18:2	279.23	0.003	10
NdS-D	615.52	0.003	60

Table S7 Compound information and ionization condition of Cho ester and Internal standard in MRM method

Compound	Precursor Ion (m/z)	Fragment Ion (m/z)	Dwell (s)	Cone Voltage (V)	Collision Energy (eV)
Cholesteryl palmitate	625.55	369.2	0.003	72	36
Cholesteryl stearate	653.52	369.2	0.003	72	36
Cholesteryl arachidate	681.65	369.2	0.003	72	36
Cholesteryl behenate	709.68	369.2	0.003	72	36
Cholesteryl lignocerate	737.71	369.2	0.003	72	36
Cholesteryl hexacosanoate	765.74	369.2	0.003	72	36
Cholesteryl octacosanoate	793.77	369.2	0.003	72	36
Cholesteryl triacontanoate	822.40	369.2	0.003	72	36
Cholesterol-d	394.41	377.4	0.003	72	36