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Supporting Information

iso-Fatty Acid Metabolism in *Caenorhabditis elegans'* Ceramide Biosynthesis

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Figure S1: ESI-(+)-HR-MS^e ceramide (**18**) profiling using the characteristic d17:1*iso* sphingosine-derived marker ion at *m/z* 250.2529 $[C_{17}H_{32}N]^+$ shows (a) enrichment of ceramides (**18**) in the *C. elegans* N2 lipidome along with (b) their release into the exometabolome. ●: *N*-*iso*-acyl (R’ = CH_3)

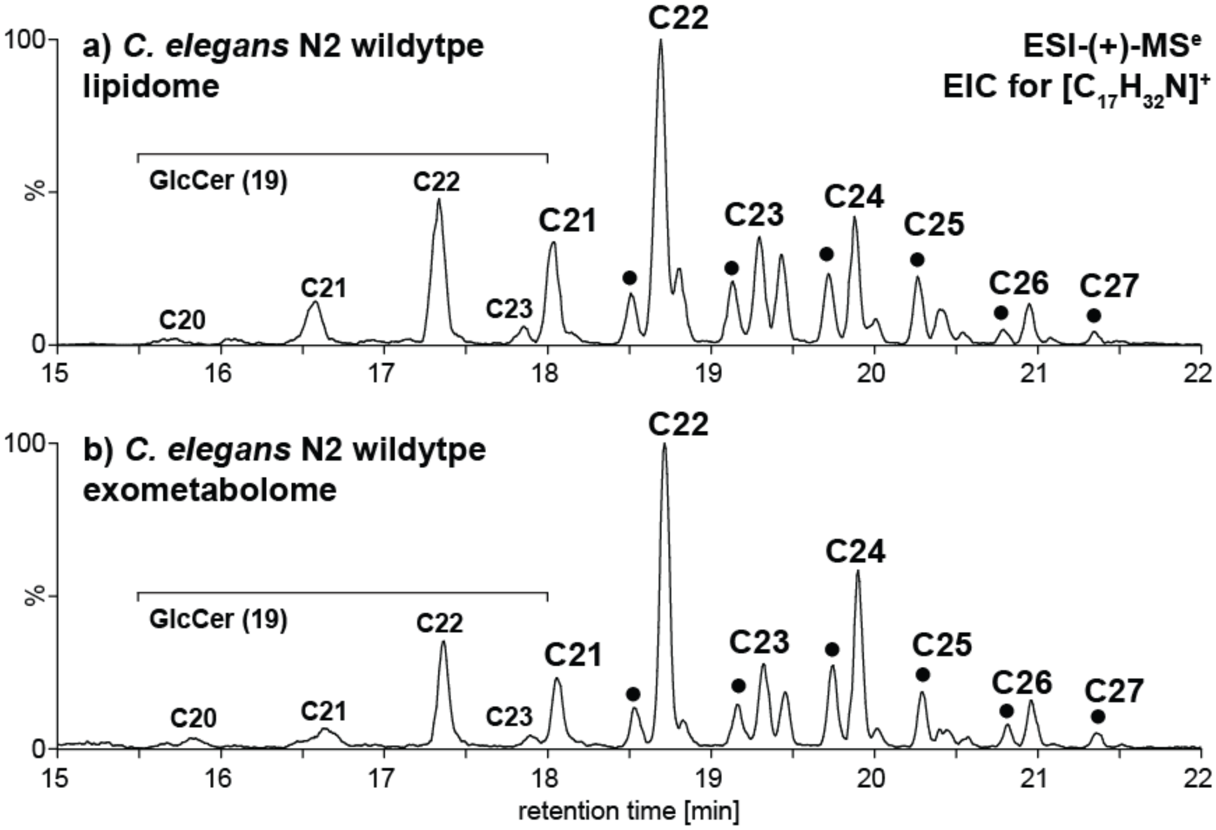

Figure S2a: ESI-(+)-HR-MS^e ceramide (**18**) profiling of nematode lipidomes using the characteristic d17:1*iso* sphingosine-derived marker ion at *m/z* 250.2529 [$C_{17}H_{32}N$]$^+$. ●: *N*-*iso*-acyl (R' = CH_3)

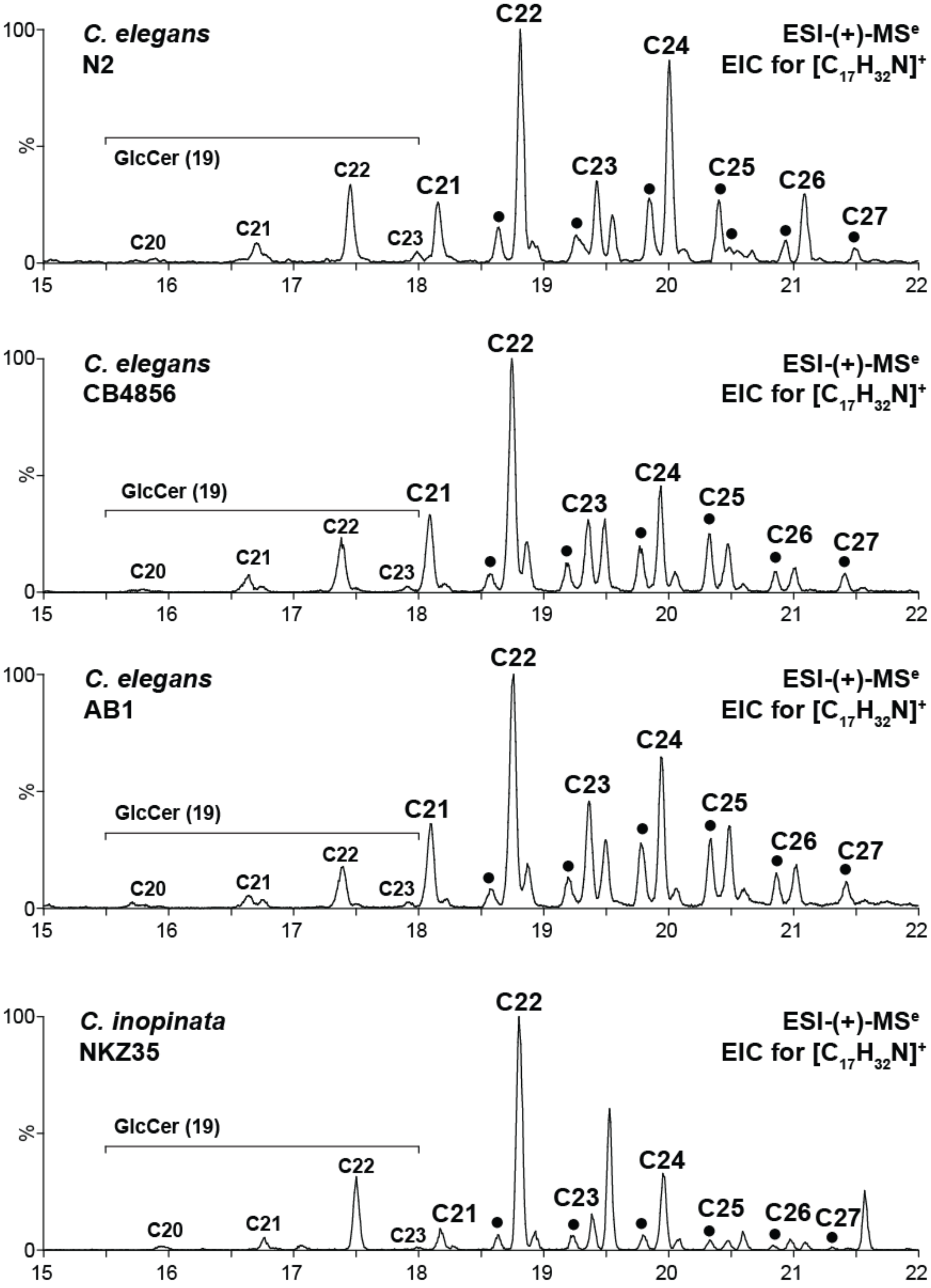

Figure S2b: ESI-(+)-HR-MS^{e} ceramide (**18**) profiling of nematode lipidomes using the characteristic d17:1*iso* sphingosine-derived marker ion at *m/z* 250.2529 [$C_{17}H_{32}N$]$^{+}$. ●: *N*-*iso*-acyl (R' = CH_3)

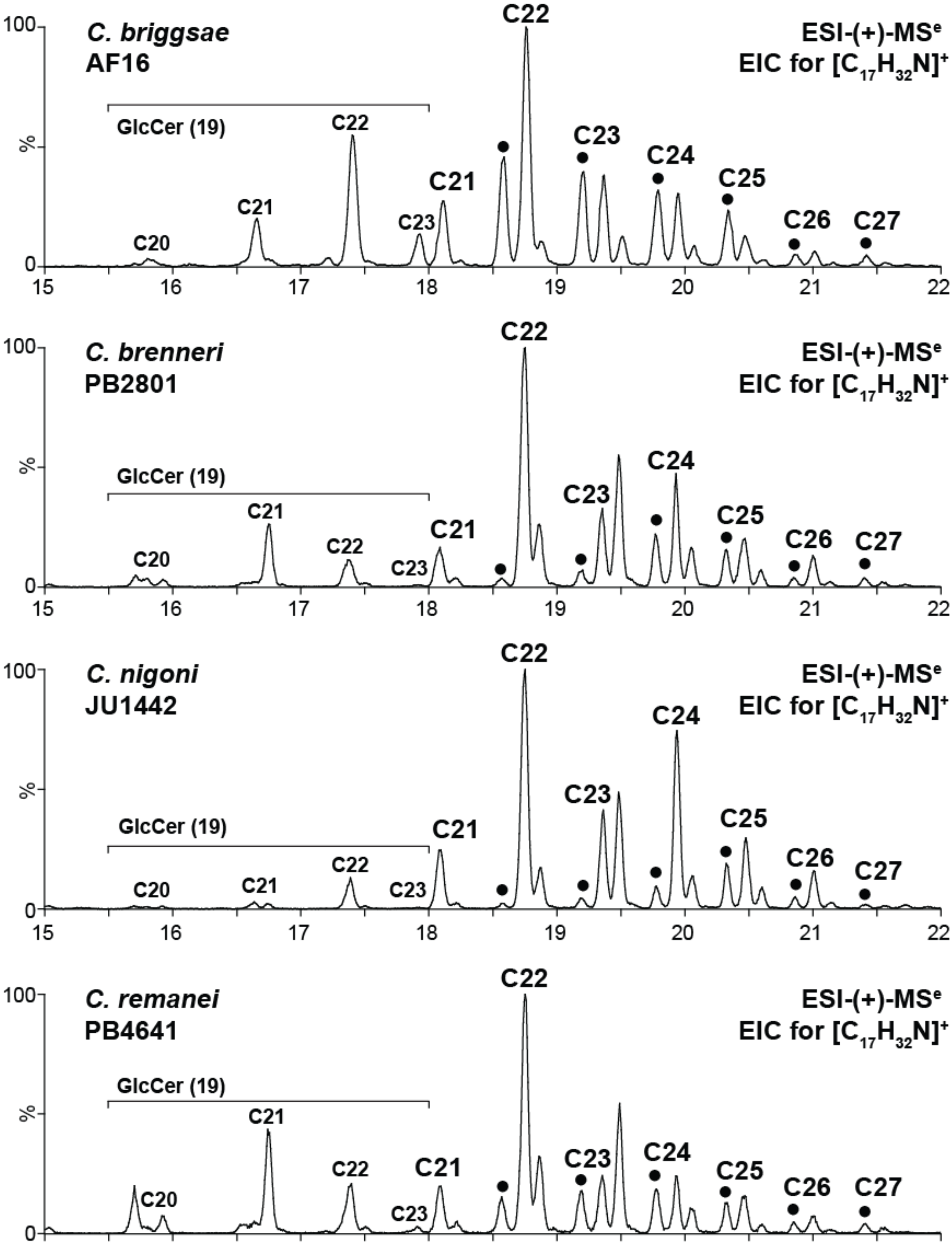

Figure S2c: ESI-(+)-HR-MS^e ceramide (**18**) profiling of nematode lipidomes using the characteristic d17:1*iso* sphingosine-derived marker ion at *m/z* 250.2529 [$C_{17}H_{32}N$]$^+$. ●: *N*-*iso*-acyl (R' = CH_3)

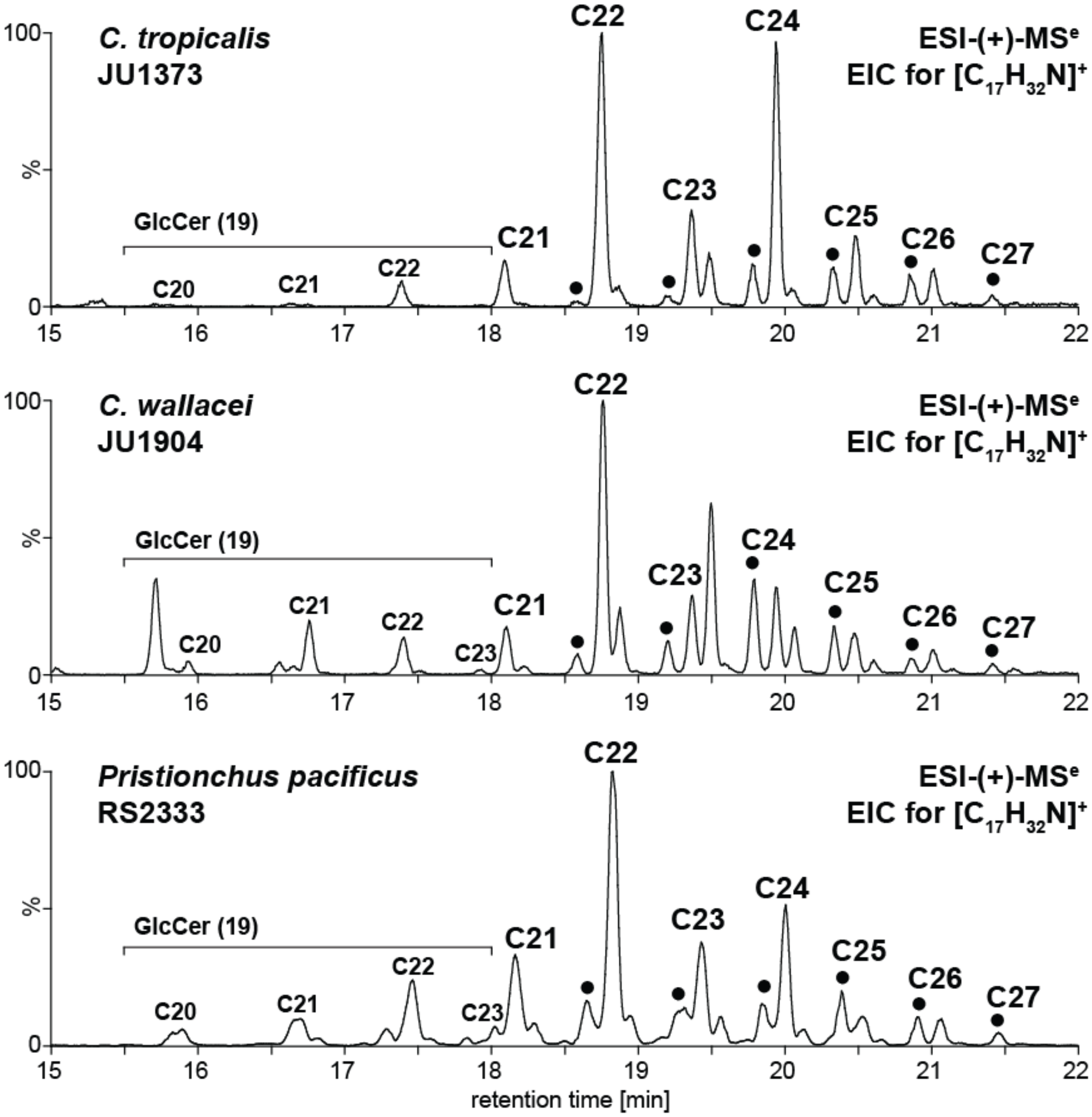

Figure S2d: ESI-(+)-HR-MS^e ceramide (**18**) profiling of nematode lipidomes using the characteristic d17:1*iso* sphingosine-derived marker ion at *m/z* 250.2529 [$C_{17}H_{32}N$]$^+$. ●: *N*-*iso*-acyl (R' = CH_3)

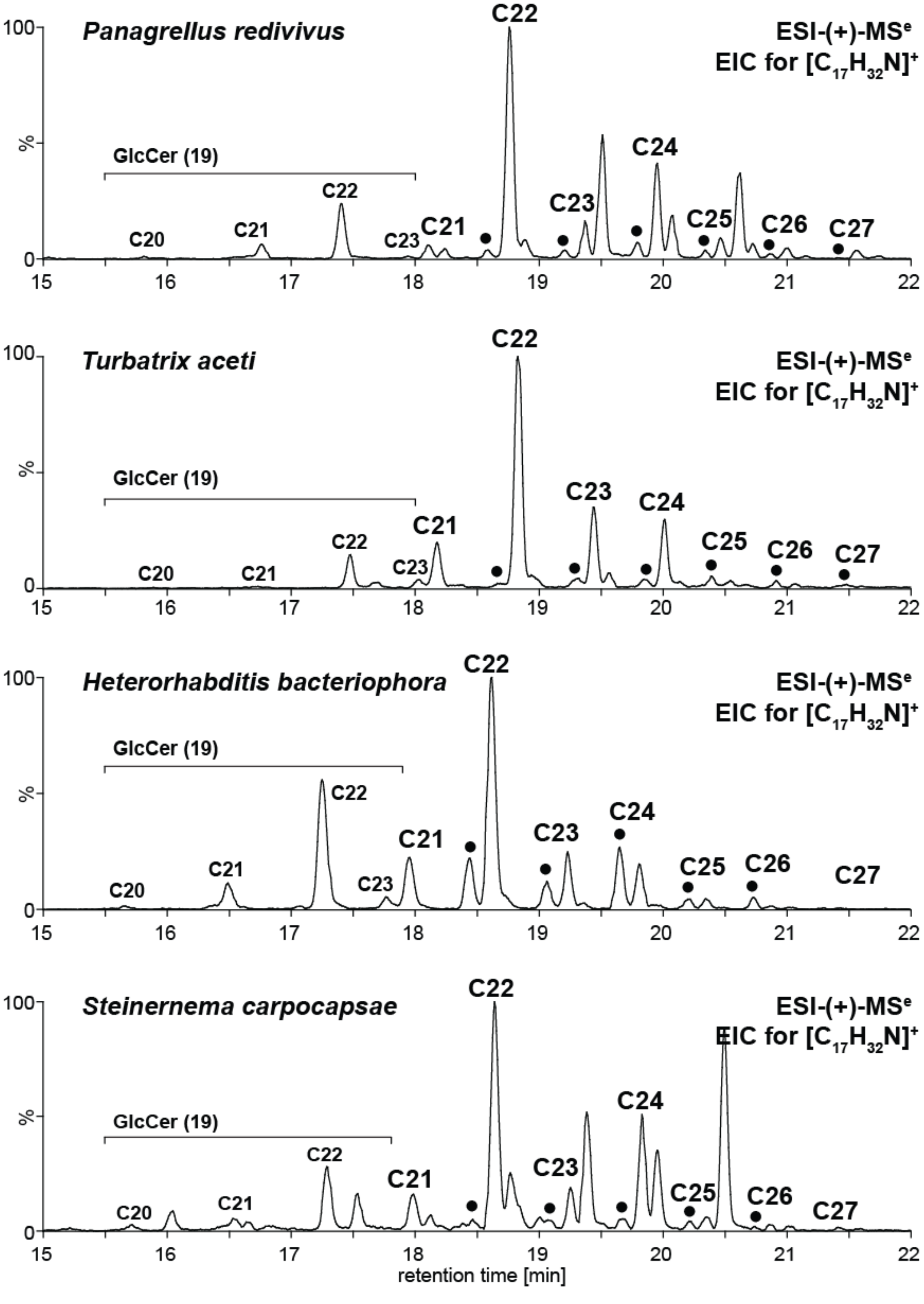

Figure S3a: ESI-(+)-HR-MS^e ceramide (**18**) profiling using the characteristic d17:1*iso* sphingosine-derived marker ion at *m/z* 250.2529 $[C_{17}H_{32}N]^+$ for the *C. elegans* N2 wildtype and peroxisomal trafficking machinery (*prx*) mutants. ●: *N*-*iso*-acyl (R' = CH_3)

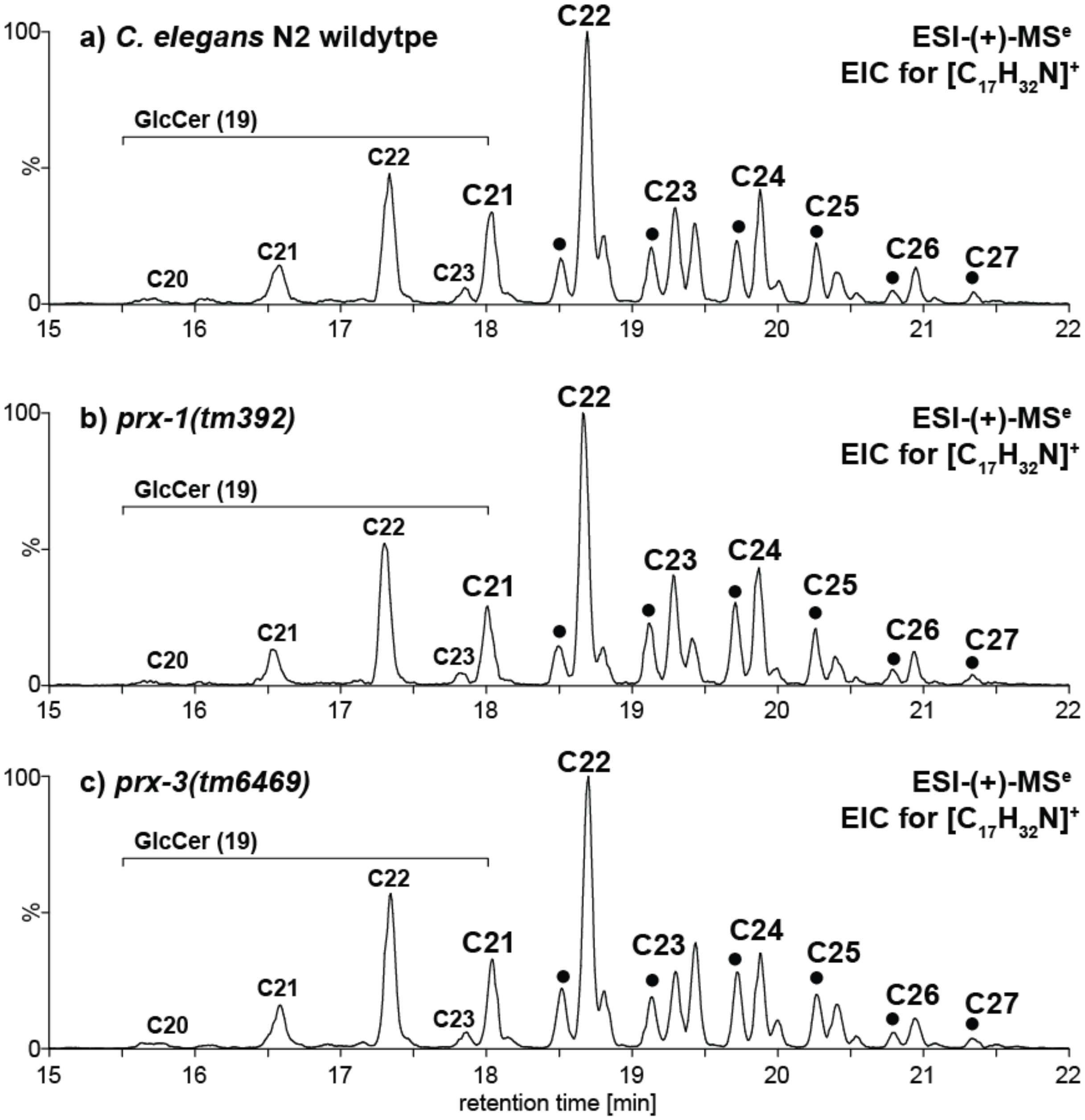

Figure S3b: ESI-(+)-HR-MS^{e} ceramide (**18**) profiling using the characteristic d17:1*iso* sphingosine-derived marker ion at *m/z* 250.2529 $[C_{17}H_{32}N]^+$ for the *C. elegans* N2 wildtype and peroxisomal trafficking machinery (*prx*) mutants. ●: *N*-*iso*-acyl (R' = CH_3)

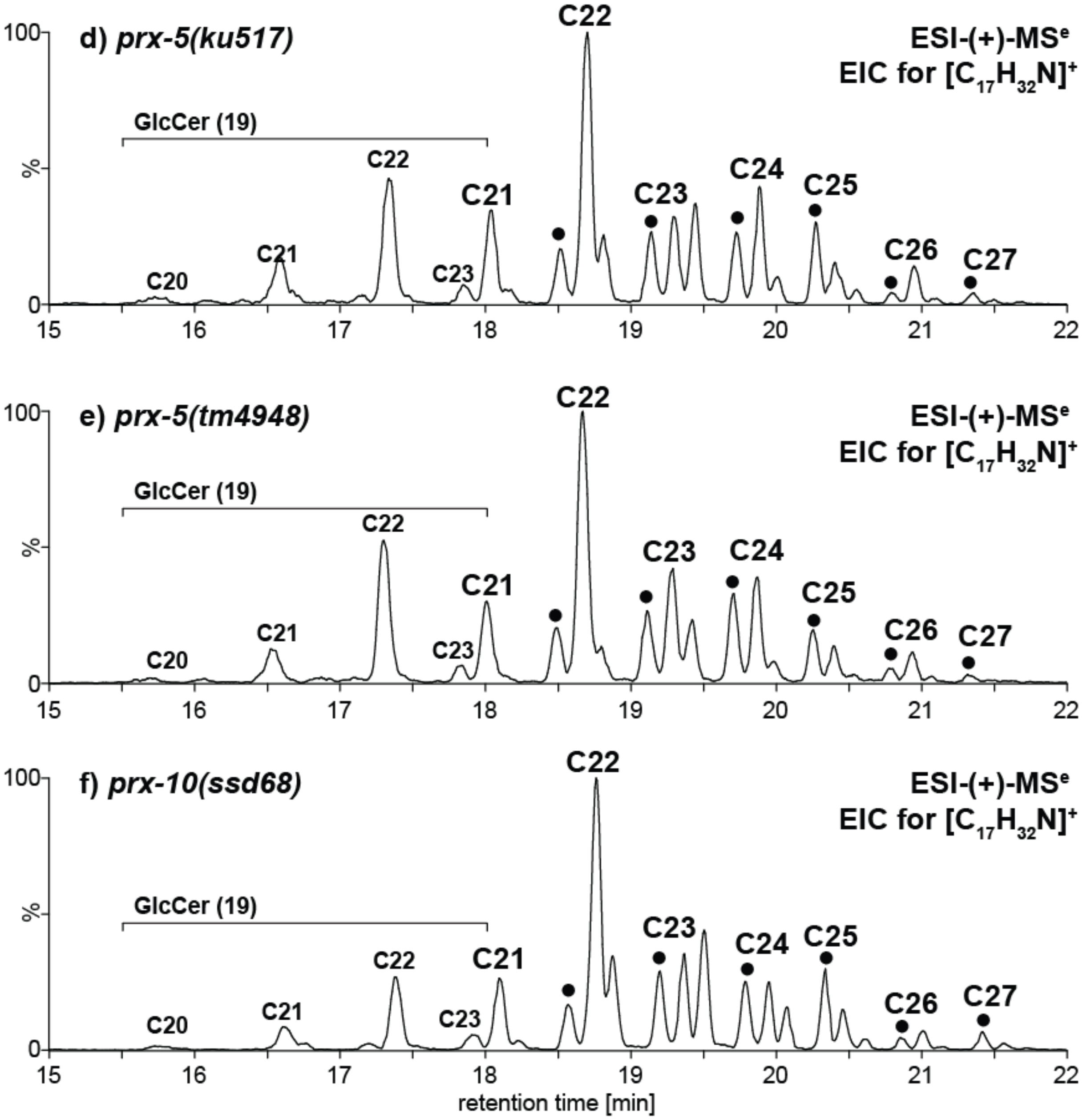

Figure S4a: ESI-(+)-HR-MS^e ceramide profiling using characteristic marker ions at *m/z* 250.2529 $[C_{17}H_{32}N]^+$ and *m/z* 236.2373 $[C_{16}H_{30}N]^+$ shows low abundance of ceramides (**18**) with the usual d17:1*iso* sphingosine (**17**) backbone along with high abundance of ceramides (**6b**) with the unusual d16:1 sphingosine (**9b**) backbone in *elo-5(gk208)* fed with *E. coli* and supplemented with C17*iso* (**15b**). ●: *N*-*iso*-acyl (R' = CH_3)

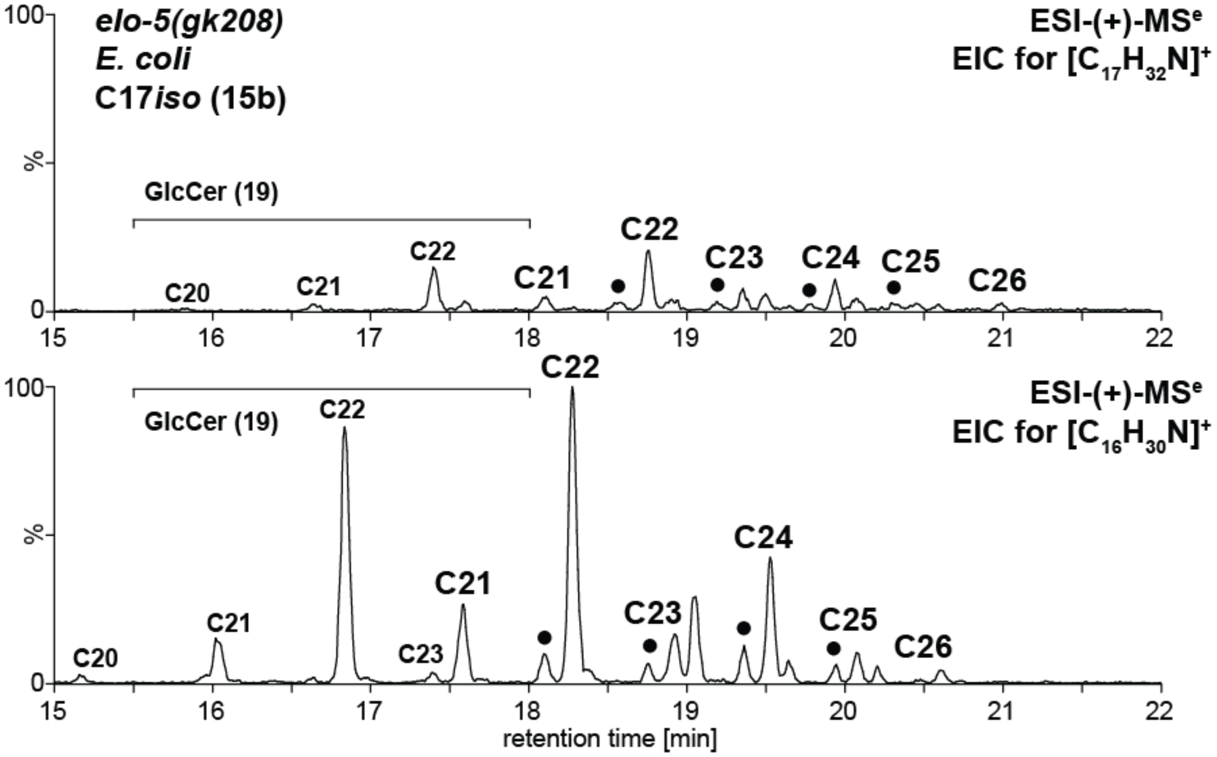

Figure S4b: ESI-(+)-HR-MS^e ceramide profiling using characteristic marker ions at *m/z* 250.2529 $[C_{17}H_{32}N]^+$ and *m/z* 236.2373 $[C_{16}H_{30}N]^+$ shows complete rescue of ceramides (**18**) with the usual d17:1*iso* sphingosine (**17**) backbone along with the disappearance of ceramides (**6b**) with the unusual d16:1 sphingosine (**9b**) backbone in *elo-5(gk208)* fed with BCFA-rich *Bacillus subtilis*. ●: *N*-*iso*-acyl (R' = CH_3)

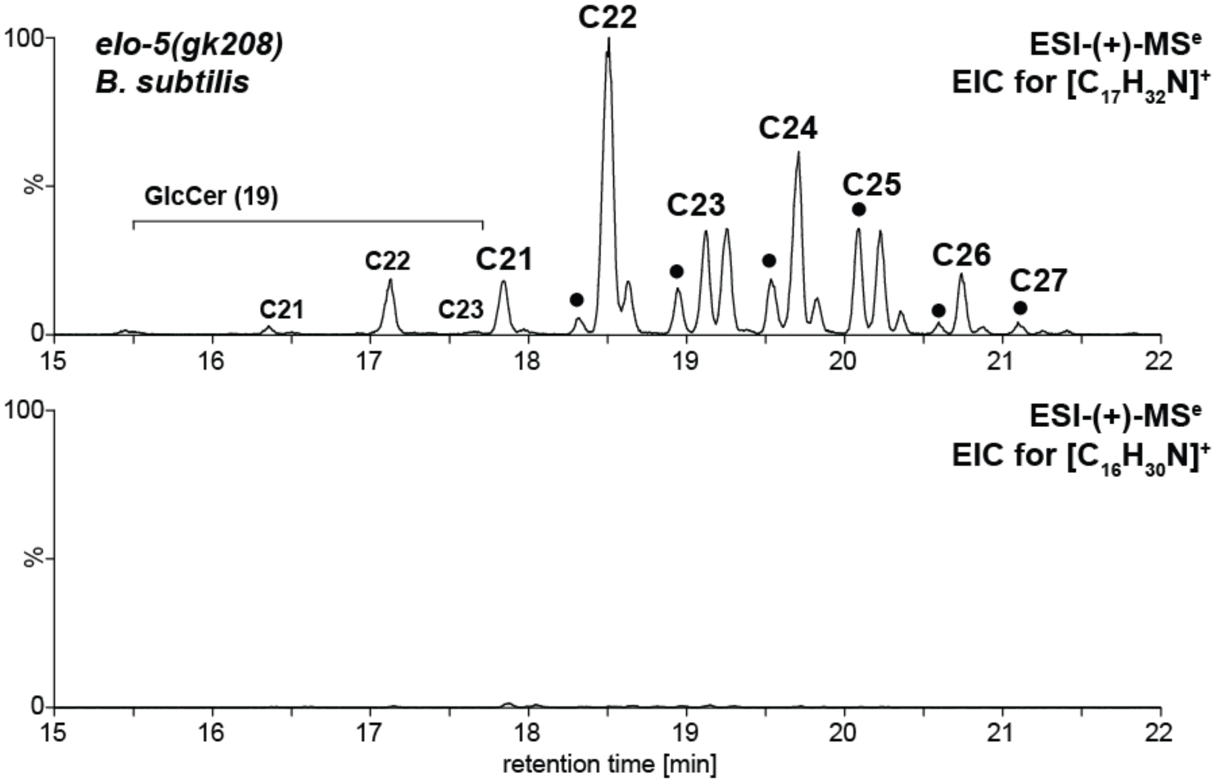

Figure S4c: ESI-(+)-HR-MS ceramide profiling using extracted ion chromatograms for $[M+H]^+$ molecular ion adducts and their $[^{13}C_5]$-isotopomers in the lipidome of the *elo-5(gk208);daf-22(ok693)* double mutant fed with a L-$[U\text{-}^{13}C_6]$-leucine enriched *B. subtilis ilvB2 leuA169* mutant, which represents a rich source of L-$[U\text{-}^{13}C_6]$-leucine ($[^{13}C_6]$-**10**) enriched proteins and $[^{13}C_5]$-C15*iso* ($[^{13}C_5]$-**14b**) and $[^{13}C_5]$-C17*iso* ($[^{13}C_5]$-**15b**) enriched lipids, shows that the early eluting ceramide isomers with *N*-(2-hydroxy)-*iso*-acyl moieties carry a $[^{13}C_5]$-label within their *N-iso*-acyl moieties (compare Figure S4d). For representative ESI-(-)-HR-MS spectra showing the $[^{13}C]$-isotopomer distribution of the molecular ions adducts see Figure 3d. ●: *N-iso*-acyl (R' = CH_3)

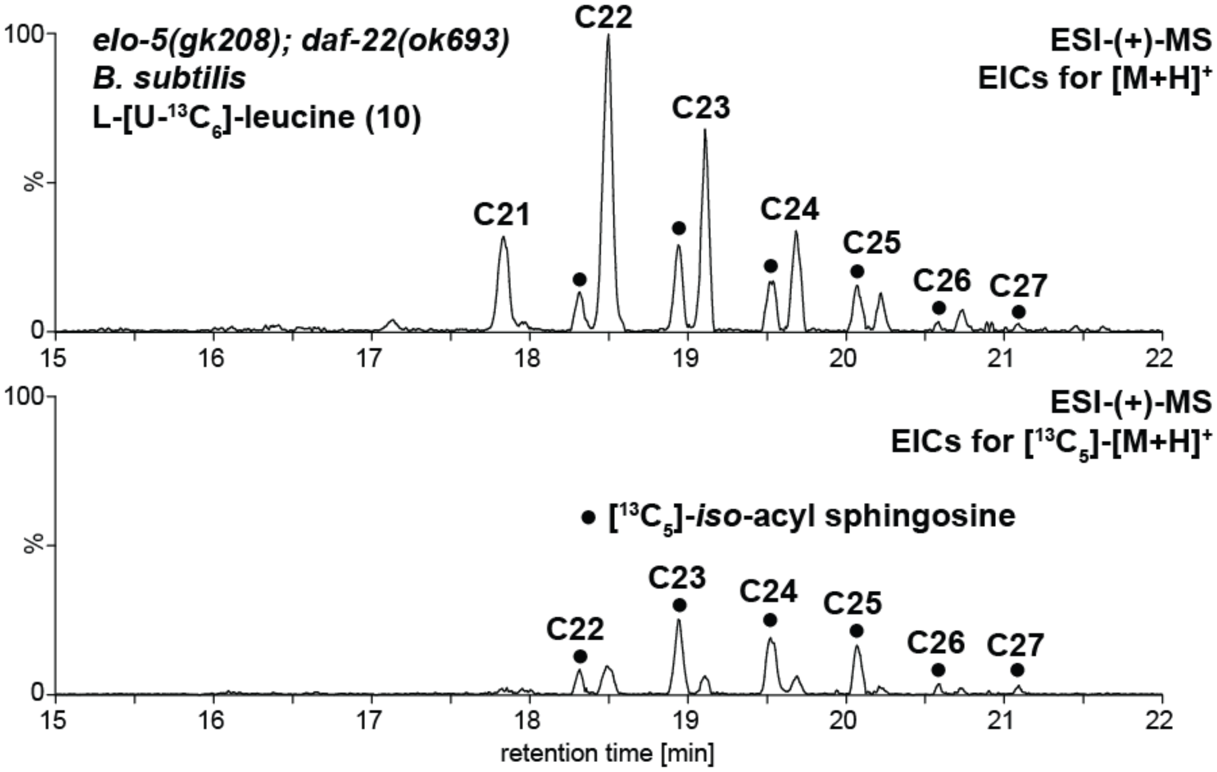

Figure S4d: ESI-(+)-HR-MS^e ceramide profiling using the marker ions at *m/z* 250.2529 $[C_{17}H_{32}N]^+$ and *m/z* 255.2697 $[^{12}C_{12}{}^{13}C_5H_{32}N]^+$ shows the absence of $[^{13}C_5]$-label in the d17:1*iso* sphingosine (**17**) unit of ceramides from the *elo-5(gk208);daf-22(ok693)* double mutant fed with L-$[U\text{-}^{13}C_6]$-leucine enriched *B. subtilis ilvB2 leuA169*, which represents a rich source of L-$[U\text{-}^{13}C_6]$-leucine ($[^{13}C_6]$-**10**) enriched proteins and $[^{13}C_5]$-C15*iso* ($[^{13}C_5]$-**14b**) and $[^{13}C_5]$-C17*iso* ($[^{13}C_5]$-**15b**) enriched lipids, demonstrating that incorporation of L-leucine (**10**) and BCFAs (**14b**, **15b**) into d17:1*iso* sphingosine (**17**) depends on *daf-22*. ●: *N*-*iso*-acyl (R' = CH_3)

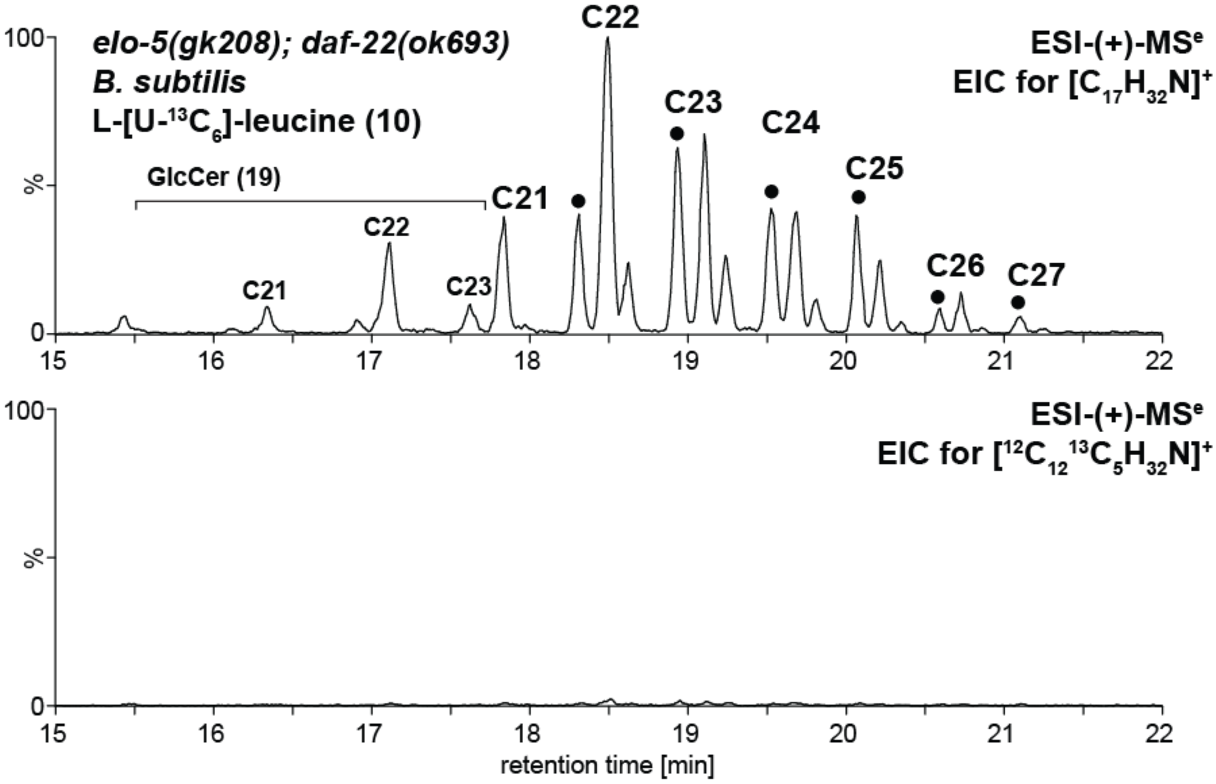

Figure S5. ESI-(+)-HR-MS spectra show [D_6]-enrichment of Cer d17:1*iso*/22:0(2OH) (**18**, n = 3, X = OH, R' = H) upon incorporation of [D_6]-C17*iso* (**15b**) in *C. elegans elo-5(gk208)*, which is suppressed in the *elo-5(gk208); daf-22(ok693)* double mutant.

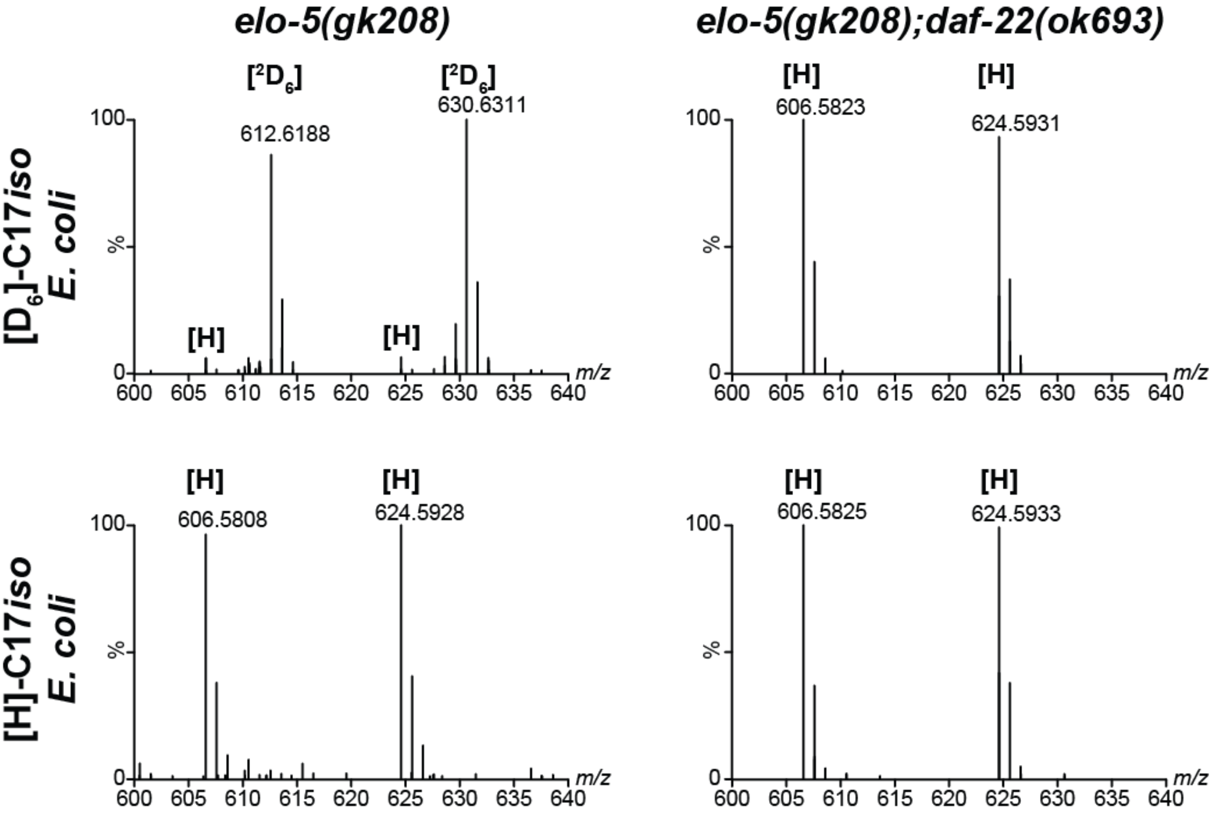

Figure S6. ESI-(-)-HR-MS analysis of the *C. elegans* N2 lipidome using extracted ion chromatograms for [M-H]$^-$ molecular ions shows an alternating series of *iso*-fatty acids from C15*iso* till C27*iso*.

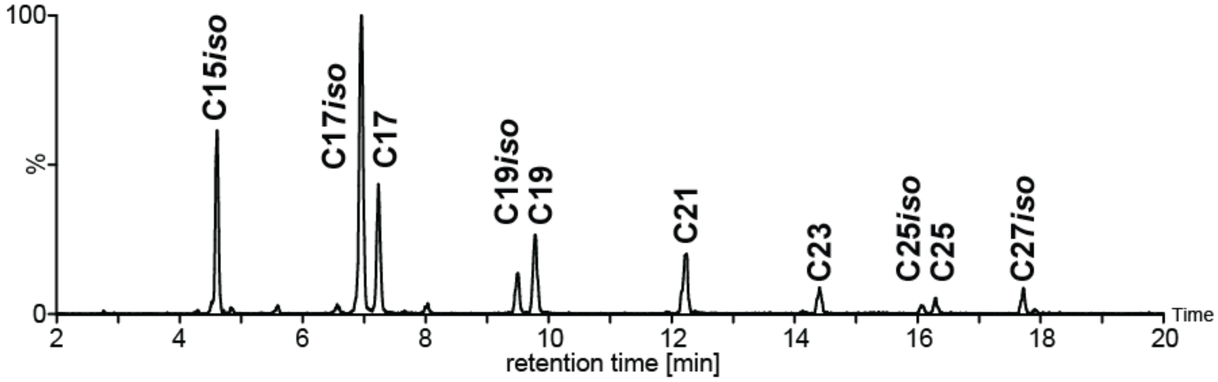

Figure S7. ESI-(+)-HR-MS spectra of the $[M+H]^+$ molecular ion adducts of 3-keto sphinganine (**33**) at *m/z* 286.2741 $[C_{17}H_{36}NO_2]^+$ and sphinganine (**34**) at *m/z* 288.2897 $[C_{17}H_{38}NO_2]^+$ showing $[^{13}C_5]$-enrichment upon incorporation of the L-$[U-^{13}C_6]$-leucine enriched *E. coli BL21(DE3) ΔilvD ΔleuB ΔavtA ΔilvE* mutant by the N2 wildtype as well as the *daf-22(ok693)* mutant.

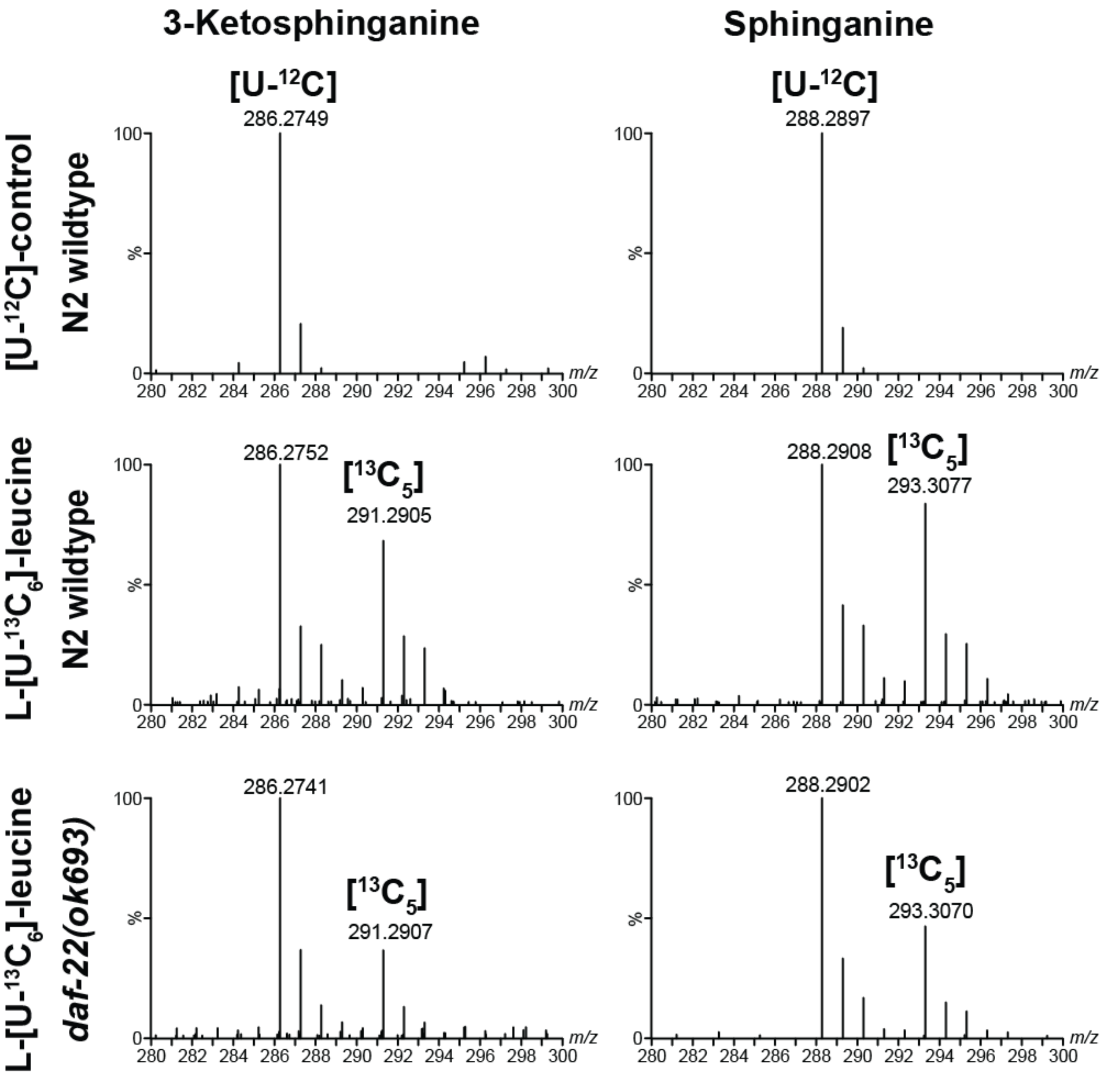

Table S1: ESI-HR-MS data of C*. elegans'* ceramides (**18**) carrying *N*-acyl residues (X = H); SP: 17:1*iso* sphingosine (**17**) unit, *N*: *N*-acyl moiety;

a: L-[U-$^{13}C_6$]-enriched *E. coli* BL21(DE3) *ΔilvD ΔleuB ΔavtA ΔilvE*, b: L-[U-$^{13}C_6$]-enriched *B. subtilis ilvB2 leuA169.*

#	***N*-acyl**	**RT**	**ESI-(+)**						**ESI-(-)**			***WT or elo-5***		***daf-22 OR elo-5/daf-22***		
		[min]	**Calc. *m/z***	**Obs. *m/z***	**$[M + H]^+$**	**Calc. *m/z***	**Obs. *m/z***	**$[M - OH]^+$**	**Calc. *m/z***	**Obs. *m/z***	**$[M + FA]^-$**	$[^{13}C_6]$ Leu [a]	$[D_6]$ BCFA	$[^{13}C_6]$ Leu [a]	$[D_6]$ BCFA	$[^{13}C_6]$ Leu [b]
1	C16*iso*	14.81	524.5037	524.5022	$C_{33}H_{66}NO_3$	506.4932	506.5921	$C_{33}H_{64}NO_2$	568.4946	568.4934	$C_{34}H_{66}NO_5$	?	?	?	?	?
2	C16	15.04	524.5037	524.5046	$C_{33}H_{66}NO_3$	506.4932	506.5935	$C_{33}H_{64}NO_2$	568.4946	568.4942	$C_{34}H_{66}NO_5$	?	?	?	?	?
3	C17*iso*	15.71	538.5194	538.5205	$C_{34}H_{68}NO_3$	520.5088	520.5091	$C_{34}H_{66}NO_2$	582.5103	582.5104	$C_{35}H_{68}NO_5$	?	?	?	?	?
4	C17	15.93	538.5194	538.5198	$C_{34}H_{68}NO_3$	520.5088	520.5092	$C_{34}H_{66}NO_2$	582.5103	582.5115	$C_{35}H_{68}NO_5$	?	?	?	?	?
5	C18*iso*	16.57	552.5350	552.5351	$C_{35}H_{70}NO_3$	534.5245	534.5237	$C_{35}H_{68}NO_2$	596.5259	596.5257	$C_{36}H_{70}NO_5$	?	?	?	?	?
6	C18	16.78	552.5350	552.5349	$C_{35}H_{70}NO_3$	534.5245	534.5240	$C_{35}H_{68}NO_2$	596.5259	596.5253	$C_{36}H_{70}NO_5$	?	?	?	?	?
7	C19*iso*	17.35	566.5507	566.5510	$C_{36}H_{72}NO_3$	548.5401	548.5400	$C_{36}H_{70}NO_2$	610.5416	610.5413	$C_{37}H_{72}NO_5$	?	?	?	?	?
8	C19	17.55	566.5507	566.5515	$C_{36}H_{72}NO_3$	548.5401	548.5401	$C_{36}H_{70}NO_2$	610.5416	610.5415	$C_{37}H_{72}NO_5$	?	?	?	?	?
9	C20*iso*	18.05	580.5663	580.5651	$C_{37}H_{74}NO_3$	562.5558	562.5551	$C_{37}H_{72}NO_2$	624.5572	624.5560	$C_{38}H_{74}NO_5$	*N*&SP	SP	*N*	-	*N*
10	C20	18.26	580.5663	580.5666	$C_{37}H_{74}NO_3$	562.5558	562.5557	$C_{37}H_{72}NO_2$	624.5572	624.5568	$C_{38}H_{74}NO_5$	SP	SP	-	-	-
11	C21*iso*	18.74	594.5820	594.5829	$C_{38}H_{76}NO_3$	576.5714	576.5695	$C_{38}H_{74}NO_2$	624.5572	638.5731	$C_{39}H_{76}NO_5$	*N*&SP	SP	*N*	-	*N*
12	C21	18.88	594.5820	594.5822	$C_{38}H_{76}NO_3$	576.5714	576.5707	$C_{38}H_{74}NO_2$	624.5572	638.5739	$C_{39}H_{76}NO_5$	SP	SP	-	-	-
13	C22*iso*	19.35	608.5976	608.5975	$C_{39}H_{78}NO_3$	590.5871	590.5860	$C_{39}H_{76}NO_2$	652.5885	652.5886	$C_{40}H_{78}NO_5$	*N*&SP	SP	*N*	-	*N*
14	C22	19.50	608.5976	608.5978	$C_{39}H_{78}NO_3$	590.5871	590.5866	$C_{39}H_{76}NO_2$	652.5885	652.5881	$C_{40}H_{78}NO_5$	SP	SP	-	-	-
15	C23*iso*	19.92	622.6133	622.6133	$C_{40}H_{80}NO_3$	604.6027	604.6018	$C_{40}H_{78}NO_2$	666.6042	666.6039	$C_{41}H_{80}NO_5$	*N*&SP	SP	*N*	-	*N*
16	C23	20.08	622.6133	622.6146	$C_{40}H_{80}NO_3$	604.6027	604.6031	$C_{40}H_{78}NO_2$	666.6042	666.6023	$C_{41}H_{80}NO_5$	SP	SP	-	-	-
17	C24*iso*	20.47	636.6289	636.6294	$C_{41}H_{82}NO_3$	618.6184	618.6179	$C_{41}H_{80}NO_2$	680.6198	680.6190	$C_{42}H_{82}NO_5$	*N*&SP	SP	*N*	-	*N*
18	C24	20.62	636.6289	636.6292	$C_{41}H_{82}NO_3$	618.6184	618.6179	$C_{41}H_{80}NO_2$	680.6198	680.6187	$C_{42}H_{82}NO_5$	SP	SP	-	-	-
19	C25*iso*	21.01	650.6446	650.6440	$C_{42}H_{84}NO_3$	632.6340	632.6329	$C_{42}H_{82}NO_2$	694.6355	694.6343	$C_{43}H_{84}NO_5$	*N*&SP	SP	*N*	-	*N*
20	C25	21.15	650.6446	650.6428	$C_{42}H_{84}NO_3$	632.6340	632.6334	$C_{42}H_{82}NO_2$	694.6355	694.6328	$C_{43}H_{84}NO_5$	SP	SP	-	-	-
21	C26*iso*	21.55	664.6602	664.6605	$C_{43}H_{86}NO_3$	646.6497	646.6493	$C_{43}H_{84}NO_2$	708.6511	708.6490	$C_{44}H_{86}NO_5$	*N*&SP	SP	*N*	-	*N*
22	C26	21.73	664.6602	664.6599	$C_{43}H_{86}NO_3$	646.6497	646.6510	$C_{43}H_{84}NO_2$	708.6511	708.6483	$C_{44}H_{86}NO_5$	SP	SP	-	-	-
23	C27*iso*	22.17	678.6759	678.6762	$C_{44}H_{88}NO_3$	660.6653	660.6650	$C_{44}H_{86}NO_2$	722.6668	722.6645	$C_{45}H_{88}NO_5$	*N*&SP	SP	*N*	-	*N*
24	C27	?	678.6759	?	$C_{44}H_{88}NO_3$	660.6653	?	$C_{44}H_{86}NO_2$	722.6668	?	$C_{45}H_{88}NO_5$	?	?	?	?	?
										Observed label		**$[^{13}C_5]$**	**$[D_6]$**	**$[^{13}C_5]$**	**-**	**$[^{13}C_5]$**

Table S2: ESI-HR-MS data of C. *elegans'* ceramides (**18**) carrying *N*-(2-hydroxy)-acyl residues (X = OH); SP: 17:1*iso* sphingosine (**17**) unit, *N*: *N*-acyl moiety; a: L-[U-$^{13}C_6$]-enriched *E. coli* BL21(DE3) *ΔilvD ΔleuB ΔavtA ΔilvE*, b: L-[U-$^{13}C_6$]-enriched *B. subtilis ilvB2 leuA169.*

#	***N*-acyl**	**RT**	**ESI-(+)**						**ESI-(-)**			***WT or elo-5***		***daf-22 OR elo-5/daf-22***		
		[min]	**Calc. *m/z***	**Obs. *m/z***	**$[M + H]^+$**	**Calc. *m/z***	**Obs. *m/z***	**$[M - OH]^+$**	**Calc. *m/z***	**Obs. *m/z***	**$[M + FA]^-$**	$[^{13}C_6]$ Leu [a]	$[D_6]$ BCFA	$[^{13}C_6]$ Leu [a]	$[D_6]$ BCFA	$[^{13}C_6]$ Leu [b]
1	C16*iso*	?	540.4986	?	$C_{33}H_{66}NO_4$	522.4881	?	$C_{33}H_{64}NO_3$	584.4896	?	$C_{34}H_{66}NO_6$	?	?	?	?	?
2	C16	13.94	540.4986	540.4985	$C_{33}H_{66}NO_4$	522.4881	522.4888	$C_{33}H_{64}NO_3$	584.4896	584.4894	$C_{34}H_{66}NO_6$	?	?	?	?	?
3	C17*iso*	14.70	554.5143	554.5142	$C_{34}H_{68}NO_4$	536.5037	536.5035	$C_{34}H_{66}NO_3$	598.5052	598.5045	$C_{35}H_{68}NO_6$	?	?	?	?	?
4	C17	14.91	554.5143	554.5147	$C_{34}H_{68}NO_4$	536.5037	536.5037	$C_{34}H_{66}NO_3$	598.5052	598.5046	$C_{35}H_{68}NO_6$	?	?	?	?	?
5	C18*iso*	15.59	568.5299	568.5286	$C_{35}H_{70}NO_4$	550.5194	550.5192	$C_{35}H_{68}NO_3$	612.5209	612.5203	$C_{36}H_{70}NO_6$	?	?	?	?	?
6	C18	15.82	568.5299	568.5303	$C_{35}H_{70}NO_4$	550.5194	550.5196	$C_{35}H_{68}NO_3$	612.5209	612.5211	$C_{36}H_{70}NO_6$	?	?	?	?	?
7	C19*iso*	16.43	582.5456	582.5452	$C_{36}H_{72}NO_4$	564.5350	564.5344	$C_{36}H_{70}NO_3$	626.5365	626.5359	$C_{37}H_{72}NO_6$	?	?	?	?	?
8	C19	16.64	582.5456	582.5457	$C_{36}H_{72}NO_4$	564.5350	564.5352	$C_{36}H_{70}NO_3$	626.5365	626.5360	$C_{37}H_{72}NO_6$	?	?	?	?	?
9	C20*iso*	?	596.5612	?	$C_{37}H_{74}NO_4$	578.5507	?	$C_{37}H_{72}NO_3$	640.5522	?	$C_{38}H_{74}NO_6$	*N*&SP	SP	*N*	-	*N*
10	C20	17.41	596.5612	596.5616	$C_{37}H_{74}NO_4$	578.5507	578.5508	$C_{37}H_{72}NO_3$	640.5522	640.5519	$C_{38}H_{74}NO_6$	SP	SP	-	-	-
11	C21*iso*	17.95	610.5769	610.5774	$C_{38}H_{76}NO_4$	592.5663	592.5668	$C_{38}H_{74}NO_3$	654.5687	654.5701	$C_{39}H_{76}NO_6$	*N*&SP	SP	*N*	-	*N*
12	C21	18.13	610.5769	610.5767	$C_{38}H_{76}NO_4$	592.5663	592.5658	$C_{38}H_{74}NO_3$	654.5687	654.5687	$C_{39}H_{76}NO_6$	SP	SP	-	-	-
13	C22*iso*	18.57	624.5925	624.5922	$C_{39}H_{78}NO_4$	606.5820	606.5808	$C_{39}H_{76}NO_3$	668.5835	668.5834	$C_{40}H_{78}NO_6$	*N*&SP	SP	*N*	-	*N*
14	C22	18.77	624.5925	624.5928	$C_{39}H_{78}NO_4$	606.5820	606.5813	$C_{39}H_{76}NO_3$	668.5835	668.5831	$C_{40}H_{78}NO_6$	SP	SP	-	-	-
15	C23*iso*	19.21	638.6082	638.6077	$C_{40}H_{80}NO_4$	620.5976	620.5964	$C_{40}H_{78}NO_3$	682.5991	682.6000	$C_{41}H_{80}NO_6$	*N*&SP	SP	*N*	-	*N*
16	C23	19.36	638.6082	638.6074	$C_{40}H_{80}NO_4$	620.5976	620.5971	$C_{40}H_{78}NO_3$	682.5991	682.5997	$C_{41}H_{80}NO_6$	SP	SP	-	-	-
17	C24*iso*	19.80	652.6238	652.6248	$C_{41}H_{82}NO_4$	634.6133	634.6138	$C_{41}H_{80}NO_3$	696.6148	696.6142	$C_{42}H_{82}NO_6$	*N*&SP	SP	*N*	-	*N*
18	C24	19.95	652.6238	652.6234	$C_{41}H_{82}NO_4$	634.6133	634.6125	$C_{41}H_{80}NO_3$	696.6148	696.6137	$C_{42}H_{82}NO_6$	SP	SP	-	-	-
19	C25*iso*	20.33	666.6395	666.6394	$C_{42}H_{84}NO_4$	648.6289	648.6274	$C_{42}H_{82}NO_3$	710.6304	710.6292	$C_{43}H_{84}NO_6$	*N*&SP	SP	*N*	-	*N*
20	C25	20.49	666.6395	666.6382	$C_{42}H_{84}NO_4$	648.6289	648.6277	$C_{42}H_{82}NO_3$	710.6304	710.6287	$C_{43}H_{84}NO_6$	SP	SP	-	-	-
21	C26*iso*	20.86	680.6551	680.6558	$C_{43}H_{86}NO_4$	662.6446	662.6442	$C_{43}H_{84}NO_3$	724.6461	724.6453	$C_{44}H_{86}NO_6$	*N*&SP	SP	*N*	-	*N*
22	C26	21.01	680.6551	680.6545	$C_{43}H_{86}NO_4$	662.6446	662.6431	$C_{43}H_{84}NO_3$	724.6461	724.6447	$C_{44}H_{86}NO_6$	SP	SP	-	-	-
23	C27*iso*	21.41	694.6708	694.6708	$C_{44}H_{88}NO_4$	676.6602	676.6595	$C_{44}H_{86}NO_3$	738.6617	738.6602	$C_{45}H_{88}NO_6$	*N*&SP	SP	*N*	-	*N*
24	C27	21.58	694.6708	694.6703	$C_{44}H_{88}NO_4$	676.6602	676.6601	$C_{44}H_{86}NO_3$	738.6617	738.6598	$C_{45}H_{88}NO_6$	?	?	?	?	?
										Observed label		**$[^{13}C_5]$**	**$[D_6]$**	**$[^{13}C_5]$**	**-**	**$[^{13}C_5]$**

Table S3: ESI-HR-MS data of C. *elegans'* 1-O-glucosyl ceramides (**19**) carrying *N*-(2-hydroxy)-acyl residues (X = OH).

#	***N*-acyl**	**RT**	**ESI-(+)**			**ESI-(-)**		
			Calc. *m/z*	**Obs. *m/z***	**[M + H]$^+$**	**Calc. *m/z***	**Obs. *m/z***	**[M + FA]$^-$**
1	C16*iso*	?	702.5515	?	$C_{39}H_{76}NO_9$	746.5424	?	$C_{40}H_{76}NO_{11}$
2	C16	11.91	702.5515	702.5504	$C_{39}H_{76}NO_9$	746.5424	746.5443	$C_{40}H_{76}NO_{11}$
3	C17*iso*	12.72	716.5671	716.5676	$C_{40}H_{78}NO_9$	760.5580	760.5569	$C_{41}H_{78}NO_{11}$
4	C17	12.99	716.5671	716.5665	$C_{40}H_{78}NO_9$	760.5580	?	$C_{41}H_{78}NO_{11}$
5	C18*iso*	?	730.5828	?	$C_{41}H_{80}NO_9$	774.5737	?	$C_{42}H_{80}NO_{11}$
6	C18	?	730.5828	?	$C_{41}H_{80}NO_9$	774.5737	?	$C_{42}H_{80}NO_{11}$
7	C19*iso*	13.74	744.5984	744.5975	$C_{42}H_{82}NO_9$	788.5893	?	$C_{43}H_{82}NO_{11}$
8	C19	14.03	744.5984	744.5972	$C_{42}H_{82}NO_9$	788.5893	?	$C_{43}H_{82}NO_{11}$
9	C20*iso*	?	758.6141	?	$C_{43}H_{84}NO_9$	802.6050	802.6055	$C_{44}H_{84}NO_{11}$
10	C20	15.85	758.6141	768.5536	$C_{43}H_{84}NO_9$	802.6050	?	$C_{44}H_{84}NO_{11}$
11	C21*iso*	16.45	772.6297	772.6303	$C_{44}H_{86}NO_9$	816.6206	816.6240	$C_{45}H_{86}NO_{11}$
12	C21	16.66	772.6297	772.6308	$C_{44}H_{86}NO_9$	816.6206	816.6204	$C_{45}H_{86}NO_{11}$
13	C22*iso*	17.24	786.6454	786.6450	$C_{45}H_{88}NO_9$	830.6363	830.6341	$C_{46}H_{88}NO_{11}$
14	C22	17.43	786.6454	786.6448	$C_{45}H_{88}NO_9$	830.6363	830.6356	$C_{46}H_{88}NO_{11}$
15	C23*iso*	17.95	800.6610	800.6604	$C_{46}H_{90}NO_9$	844.6519	844.6533	$C_{47}H_{90}NO_{11}$
16	C23	18.14	800.6610	800.6591	$C_{46}H_{90}NO_9$	844.6519	844.6532	$C_{47}H_{90}NO_{11}$
17	C24*iso*	18.61	814.6767	814.6757	$C_{47}H_{92}NO_9$	858.6676	858.6674	$C_{48}H_{92}NO_{11}$
18	C24	18.79	814.6767	814.6753	$C_{47}H_{92}NO_9$	858.6676	858.6685	$C_{48}H_{92}NO_{11}$
19	C25*iso*	19.21	828.6923	828.6898	$C_{48}H_{94}NO_9$	872.6832	872.6835	$C_{49}H_{94}NO_{11}$
20	C25	19.37	828.6923	828.6873	$C_{48}H_{94}NO_9$	872.6832	872.6821	$C_{49}H_{94}NO_{11}$
21	C26*iso*	19.79	842.7080	842.7084	$C_{49}H_{96}NO_9$	886.6989	886.6987	$C_{50}H_{96}NO_{11}$
22	C26	19.95	842.7080	842.7060	$C_{49}H_{96}NO_9$	886.6989	886.6964	$C_{50}H_{96}NO_{11}$
23	C27*iso*	20.32	856.7236	856.7206	$C_{50}H_{98}NO_9$	900.7145	900.7138	$C_{51}H_{98}NO_{11}$
24	C27	?	856.7236	?	$C_{50}H_{98}NO_9$	900.7145	?	$C_{51}H_{98}NO_{11}$

Experimental Procedures

Synthesis of *iso*-fatty acids

Synthesis of 15-methylhexadecane-1,15-diol (24)

Under nitrogen a solution of 5.0 g pentadecanolide (**23**, 20.8 mmol) in 40 mL dry tetrahydrofuran at 0 °C was treated with 20.8 mL of 3 M methylmagnesium iodide solution in diethyl ether (62.4 mmol). After stirring at RT for 16 h the reaction was cooled to 0 °C and quenched with acetic acid until the formed solids were dissolved. The mixture was treated with 100 mL of water and the product was extracted with 2 x 50 mL dichloromethane, washed with brine, dried over $MgSO_4$, and concentrated under reduced pressure. Column chromatography on silica gel using a mixture of hexane and ethyl acetate (9:1, *v/v*) as eluent furnished 5.4 g (19.8 mmol, 95% yield) of **24** as a white solid. ^{1}H-NMR (600 MHz, $CDCl_3$): 3.64 (*t*, *J* = 6.7, 2 H); 1.60 – 1.54 (*m*, 2 H); 1.48 – 1.44 (*m*, 2 H); 1.42 – 1.25 (*m*, 23 H); 1.21 (s, 6 H). ^{13}C-NMR (151 MHz, $CDCl_3$): 71.2 (C); 63.2 (CH_2); 44.1 (CH_2); 32.9 (CH_2); 30.3 (CH_2); 29.8 (7 CH_2); 29.6 (CH_2); 29.4 (2 CH_3); 25.9 (CH_2); 24.5 (CH_2).

Synthesis of [D_6]-15-methylhexadecane-1,15-diol ([D_6]-24)

A solution of 2.4 g pentadecanolide (**23**, 10 mmol) was treated with 30 mL 1 M [D_3]-methylmagnesium iodide solution in diethyl ether as described for **23** with natural abundance methylmagnesium iodide to furnish 2.6 g (9.3 mmol, 93% yield) of [D_6]-**24** as a white solid. ^{1}H-NMR (600 MHz, $CDCl_3$): 3.64 (*t*, *J* = 6.6, 2 H); 1.60 – 1.54 (*m*, 2 H); 1.47 – 1.43 (*m*, 2 H); 1.38 – 1.23 (*m*, 23 H). ^{13}C-NMR (151 MHz, $CDCl_3$): 71.0 (C); 63.2 (CH_2); 44.0 (CH_2); 32.9 (CH_2); 30.3 (CH_2); 29.8 (6 CH_2); 29.7 (CH_2); 29.6 (CH_2); 25.9 (CH_2); 24.5 (CH_2).

Synthesis of 15-methylhexadecan-1-ol (25)

Under nitrogen a solution of 5.4 g 15-methylhexadecane-1,15-diol (**24**, 19.8 mmol) in dry 50 mL dichloromethane at 0 °C was treated with 4.4 mL boron trifluoride etherate (39.6 mmol) and 6.3 mL triethyl silane (39.6 mmol). The reaction was stirred for 1 h at room temperature, quenched with 120 mL ice-water, and the product extracted with 2 x 50 mL dichloromethane, washed with saturated $NaHCO_3$ solution, dried over $MgSO_4$, and concentrated under reduced pressure. Column chromatography on silica gel using a mixture of hexane and ethyl acetate (9:1, *v/v*) as eluent furnished 4.7 g (18.4 mmol, 93% yield) of **25** as a white solid. ^{1}H-NMR (600 MHz, $CDCl_3$): 3.64 (*t*, *J* = 6.6, 2 H); 1.61 – 1.48 (*m*, 4 H); 1.48 – 1.23 (*m*, 21 H); 1.15 (*m*, 1 H); 0.86 (*d*, *J* = 6.6, 6 H). ^{13}C-NMR (151 MHz, $CDCl_3$): 63.2 (CH_2); 39.2 (CH_2); 32.9 (CH_2); 30.1 (CH_2); 29.9 (CH_2); 29.8 (8 CH_2); 29.5 (CH); 25.9 (CH_2); 22.8 (2 CH_2).

Synthesis of [D_6]-15-methylhexadecan-1-ol ([D_6]-25)

A solution of 2.6 g [D_6]-15-methylhexadecan-1-ol ([D_6]-**24**, 9.3 mmol) was treated as described for **24** to furnish 2.3 g (8.8 mmol, 95% yield) of [D_6]-**25** as a white solid. ^{1}H-NMR (600 MHz, $CDCl_3$): 3.64 (*t*, *J* = 6.7, 2 H); 1.60 – 1.54 (*m*, 2 H); 1.48 (*m*, 1 H); 1.38 – 1.22 (*m*, 23 H); 1.17 – 1.12 (*m*, 2 H). ^{13}C-NMR (151 MHz, $CDCl_3$): 63.2 (CH_2); 39.1 (CH_2); 33.0 (CH_2); 30.1 (CH_2); 29.9 (2 CH_2); 29.8 (5 CH_2); 29.6 (CH); 27.5 (2 CH_2); 25.9 (CH_2).

Synthesis of 15-methylhexadecanoic acid (C17*iso*, 15b)

A solution of 1.8 g 15-methylhexadecane-1-ol (**25**, 7.0 mmol) in 80 mL dichloromethane was treated with 1.2 g tetrabutylammonium bromide (3.8 mmol), 3.4 g $KMnO_4$ (21.8 mmol), 10.7 ml acetic acid and 28 mL of water and refluxed at 60 °C for 16 h. The reaction was quenched with Na_2SO_3 solution and the product extracted with 2 x 50 mL dichloromethane, dried over $MgSO_4$, and concentrated under reduced pressure. Column chromatography on silica gel using a mixture of hexane and ethyl acetate (3:2, *v/v*) as eluent furnished 1.7 g (6.32 mmol, 90% yield) of **15b** as a white solid. ^{1}H-NMR (600 MHz, $CDCl_3$): 2.35 (*t*, *J* = 7.5, 2 H); 1.63 (*m*, 2 H); 1.52 (*m*, 1 H); 1.25 (*m*, 20 H); 1.14 (*m*, 2 H); 0.86 (*d*, *J* = 6.7, 6 H). ^{13}C-NMR (151 MHz, $CDCl_3$): 180.3 (C); 39.2

(CH_2); 34.2 (CH_2); 30.1 (CH_2); 29.9 (CH_2); 29.8 (4 CH_2); 29.6 (CH_2); 29.4 (CH_2); 29.2 (CH_2); 28.1 (CH); 27.6 (CH_2); 24.8 (CH_2); 22.8 (2 CH_3). EI-MS (70 eV): 270.2 ([M]$^{+\bullet}$, $C_{17}H_{34}O_2$; calc. 270.3). ESI-(-)-HR-MS: 269.4493 ([M-H]$^-$, $C_{17}H_{33}O_2$; calc. 269.4495).

Synthesis of [D_6]-15-methylhexadecanoic acid ([D_6]-C17*iso*, [D_6]-15b)

A solution of 1.8 g [D_6]-15-methylhexadecane-1-ol ([D_6]-**25**, 6.9 mmol) was treated as described for **25** to furnish 1.7 g (6.1 mmol, 89% yield) of [D_6]-**15b** as a white solid. ^{1}H-NMR (600 MHz, $CDCl_3$): 2.35 (*t*, *J* = 7.5, 2 H); 1.63 (*m*, 2 H); 1.48 (*m*, 1 H); 1.25 (*m*, 21 H); 1.13 (*m*, 2 H). ^{13}C-NMR (151 MHz, $CDCl_3$): 180.1 (C); 39.1 (CH_2); 34.2 (CH_2); 30.1 (CH_2); 29.9 (CH_2); 29.8 (4 CH_2); 29.6 (CH_2); 29.4 (CH_2); 29.2 (CH); 27.6 (2 CH_2); 24.8 (CH_2). EI-MS (70 eV): 276.2 ([M]$^{+\bullet}$, $C_{17}H_{28}D_6O_2$; calc. 276.3). ESI-(-)-HR-MS: 275.4870 ([M-H]$^-$, $C_{17}H_{27}D_6O_2$; calc. 275.4862).

Synthesis of 2-methyldodec-11-en-2-ol (27)

Under nitrogen atmosphere a solution of 6.6 g methyl 10-undecenoate (**26**, 33.3 mmol) in 50 mL dry tetrahydrofuran at 0 °C was treated with 33.3 mL (100.0 mmol) of 3 M methylmagnesium iodide solution in diethyl ether. After stirring at RT for 16 h the reaction was cooled to 0 °C and quenched with acetic acid until the formed solids were dissolved. The mixture was treated with 100 mL of water and the product was extracted with 2 x 50 mL dichloromethane, washed with brine, dried over $MgSO_4$, and concentrated under reduced pressure. Column chromatography on silica gel using a gradient of hexane and diethyl ether as eluent furnished 6.1 g (30.7 mmol, 92% yield) of **27** as a yellowish oil. ^{1}H-NMR (600 MHz, $CDCl_3$): 5.80 (*ddt*, *J* = 16.9, 10.2, 6.7, 1 H); 5.01 (*ddt*, *J* = 17.0, 2.0, 1.7, 1 H); 4.95 (*ddt*, *J* = 10.2, 2.2, 1.3, 1 H); 2.10 – 2.03 (*m*, 2 H); 1.51 – 1.45 (*m*, 2 H); 1.44 – 1.26 (*m*, 12 H); 1.21 (*m*, 6 H). ^{13}C-NMR (151 MHz, $CDCl_3$): 139.4 (CH); 114.2 (CH_2); 71.2 (C); 44.1 (CH_2); 33.9 (CH_2); 30.3 (CH_2); 29.7 (2 CH_3); 29.6 (CH_2); 29.4 (CH_2); 29.3 (CH_2); 29.1 (CH_2); 24.5 (CH_2).

Synthesis of [D_6]-2-methyldodec-11-en-2-ol ([D_6]-27)

A solution of 6.6 g methyl 10-undecenoate (**26**, 33.3 mmol) was treated with 100 mL (100 mmol) 1 M [D_3]-methylmagnesium iodide solution in diethyl ether as described for **26** with natural abundance methylmagnesium iodide to furnish 5.5 g (26.9 mmol, 81% yield) of [D_6]-**27** as a yellowish oil. ^{1}H-NMR (600 MHz, $CDCl_3$): 5.83 (*ddt*, *J* = 16.9, 10.2, 6.7, 1 H); 5.01 (*ddt*, *J* = 16.9, 1.9, 1.7, 1 H); 4.95 (*ddt*, *J* = 10.2, 2.3, 1.2, 1 H); 2.10 – 2.02 (*m*, 2 H); 1.45 (*m*, 2 H); 1.29 (*m*, 12 H). ^{13}C-NMR (151 MHz, $CDCl_3$): 139.4 (CH); 114.2 (CH_2); 70.9 (C); 44.0 (CH_2); 33.4 (CH_2); 30.3 (CH_2); 29.7 (CH_2); 29.6 (CH_2); 29.3 (CH_2); 29.1 (CH_2); 24.4 (CH_2).

Synthesis of 11-methyldodec-1-ene (28)

Under nitrogen atmosphere a solution of 6.1 g 2-methyldodec-11-en-2-ol (**27**, 30.7 mmol) in 60 mL dry dichloromethane at 0 °C was treated with 6.8 mL boron trifluoride etherate (61.4 mmol) and 9.7 mL triethyl silane (61.4 mmol). The mixture was stirred for 1 h at room temperature, quenched with 100 mL ice-water, and the product was extracted with 2 x 50 mL dichloromethane. The organic phase was washed with saturated $NaHCO_3$ solution, dried over $MgSO_4$, and concentrated under reduced pressure. Column chromatography on silica gel using hexane as eluent furnished 4.7 g (26.0 mmol, 85% yield) of **28** as a colorless oil. ^{1}H-NMR (600 MHz, $CDCl_3$): 5.84 (*ddt*, *J* = 16.9, 10.2, 6.7, 1 H); 5.00 (*ddt*, *J* = 16.8, 2.0, 1.6, 1 H); 4.95 (*ddt*, *J* = 10.3, 2.2, 1.3, 1 H); 2.10 – 2.03 (*m*, 2 H); 1.54 (*m*, 1 H); 1.45 – 1.36 (*m*, 2 H); 1.36 – 1.23 (*m*, 11 H); 1.21 – 1.14 (*m*, 2 H); 0.87 (*d*, *J* = 6.7, 6 H). ^{13}C-NMR (151 MHz, $CDCl_3$): 139.4 (CH); 114.2 (CH_2); 39.2 (CH_2); 34.0 (CH_2); 30.1 (CH_2); 29.8 (CH_2); 29.7 (2 CH_2); 29.3 (CH_2); 28.1 (CH_2); 27.6 (CH_2); 22.8 (2 CH_3).

Synthesis of [D_6]-11-methyldodec-1-ene ([D_6]-28)

A solution of 5.1 g [D_6]-2-methyldodec-11-en-2-ol ([D_6]-**27**, 33.3 mmol) was treated as described for **27** to furnish 3.2 g (16.99 mmol, 68% yield) of [D_6]-**28** as a colorless oil. ^{1}H-NMR (600 MHz, $CDCl_3$): 5.82 (*ddt*, *J* = 16.9, 10.2, 6.7, 1 H); 5.00 (*ddt*, *J* = 16.5, 3.7, 1.7, 1 H); 4.93 (*ddt*, *J* = 10.3, 2.4, 1.3, 2 H); 2.08 – 2.01 (*m*, 2 H); 1.38 (*p*, *J* = 7.2, 2 H); 1.34 – 1.21 (*m*, 11 H); 1.15 (q, *J* = 7.0, 2 H). ^{13}C-NMR (151 MHz, $CDCl_3$): 139.4 (CH); 114.2 (CH_2); 39.1 (CH_2); 34.0 (CH_2); 30.1 (CH_2); 29.8 (CH_2); 29.7 (CH_2); 29.3 (CH_2); 29.1 (CH_2); 27.6 (2 CH_3).

Synthesis of 11-methyldodecan-1-ol (29)

Under nitrogen a solution of 2.0 g 11-methyldodec-1-ene (**28**, 11 mmol) in 20 mL dry tetrahydrofuran at 0 °C was treated with 13.2 mL of 1 M borane in tetrahydrofuran (13.2 mmol). After 2 h, 0.5 mL water was added and the solution was stirred for 20 minutes until gas evolution ceased. Subsequently, the mixture was cooled to 0° C and equal portions of 30% hydrogen peroxide solution and 3 M NaOH were carefully added. The mixture was stirred for 30 minutes, diluted by addition of 100 ml water and the product was extracted with 2 x 50 mL diethyl ether. The organic phase was dried over Na_2SO_4 and concentrated under reduced pressure. Column chromatography on silica gel using a gradient of hexane and diethyl ether as eluent furnished 1.8 g (8.92 mmol, 81%) of **29** as a light-yellow oil ^{1}H-NMR (600 MHz, $CDCl_3$): 3.63 (*t*, *J* = 6.7, 2 H); 1.59 – 1.45 (*m*, 5 H); 1.36 – 1.20 (*m*, 16 H); 1.17 – 1.11 (*m*, 2 H); 0.86 (*d*, *J* = 6.6, 6 H). ^{13}C-NMR (151 MHz, $CDCl_3$): 63.2 (CH_2); 39.1 (CH); 33.0 (CH_2); 30.1 (CH_2); 29.8 (3 CH_2); 29.6 (CH_2); 28.1 (CH_2); 27.6 (CH_2); 25.9 (CH_2); 22.8 (2 CH_3).

Synthesis of [D$_6$]-11-methyldodecan-1-ol ([D$_6$]-29)

A solution of 1.9 g [D$_6$]-11-methyldodec-1-ene ([D$_6$]-**28**, 10.1 mmol) was treated as described for **28** to furnish 1.9 g (9.2 mmol, 91% yield) of [D$_6$]-**29** as a yellowish oil. ^{1}H-NMR (600 MHz, $CDCl_3$): 3.66 (*t*, *J* = 6.7, 2 H); 1.61 – 1.54 (*m*, 2 H); 1.52 – 1.47 (*m*, 1 H); 1.40 – 1.22 (*m*, 14 H); 1.18 – 1. 11 (*m*, 2 H). ^{13}C-NMR (151 MHz, $CDCl_3$): 63.2 (CH_2); 39.1 (CH_2); 33.0 (CH_2); 30.1 (CH_2); 29.9 (CH_2); 29.8 (2 CH_2); 29.6 (CH_2); 27.6 (2 CH_2); 25.9 (CH_2).

Synthesis of 11-methyldodecanoic acid (C13*iso*, 13b)

A solution of 260 mg 11-methyldodecan-1-ol (**29**, 1.30 mmol) in 20 ml dichloromethane was treated with 420 mg tetrabutylammonium bromide (1.30 mmol), 820 mg of $KMnO_4$ (5.20 mmol), 2.5 mL acetic acid, and 6 mL water. The mixture was refluxed at 60 °C for 16 h. The reaction was quenched by addition of Na_2SO_3 until the brown solids disappeared. The product was extracted with 2 x 50 mL dichloromethane, dried over $MgSO_4$, and concentrated under reduced pressure. Column chromatography on silica gel using a mixture of hexane and ethyl acetate (6:4, *v/v*) as eluent furnished 250 mg (1.17 mmol, 90% yield) of **13b** as a white solid. ^{1}H-NMR (600 MHz, $CDCl_3$): 2.35 (*t*, *J* = 7.5, 2 H); 1.63 (*m*, 2 H); 1.51 (*m*, 1 H); 1.38 – 1.19 (*m*, 12 H); 1.18 – 1. 11 (*m*, 2 H); 0.86 (*d*, *J* = 6.8, 6 H). ^{13}C-NMR (151 MHz, $CDCl_3$): 180.4 (C); 39.2 (CH_2); 34.2 (CH_2); 30.0 (CH_2); 29.8 (CH_2); 29.6 (CH_2); 29.4 (CH_2); 29.2 (CH_2); 28.1 (CH); 27.6 (CH_2); 24.8 (CH_2); 22.8 (2 CH_3). EI-MS (70 eV): 214.2 ([M]$^{+\bullet}$, $C_{13}H_{26}O_2$; calc. 214.2). ESI-(-)-HR-MS: 213.3417 ([M-H]$^-$, $C_{13}H_{25}O_2$; calc. 213.3415).

Synthesis of [D$_6$]-11-methyldodecanoic acid ([D$_6$]-C13*iso*, [D$_6$]-13b)

A solution of 0.7 g [D$_6$]-11-methyldodecan-1-ol ([D$_6$]-**29**, 3.4 mmol) was treated as described for **29** to furnish 650 mg (2.9 mmol, 86% yield) of [D$_6$]-**13b** as a white solid. ^{1}H-NMR (600 MHz, $CDCl_3$): 2.37 (*t*, *J* = 7.5, 2 H); 1.65 (*m*, 2 H); 1.50 (*m*, 1 H); 1.42 – 1.21 (*m*, 12 H); 1.19 – 1.12 (*m*, 2 H). ^{13}C-NMR (151 MHz, $CDCl_3$): 180.3 (CH); 39.2 (CH_2); 34.1 (CH_2); 29.9 (CH_2); 29.8 (CH_2); 29.7 (CH_2); 29.6 (CH_2); 29.4 (CH_2); 29.2 (CH_2); 27.6 (CH); 24.8 (CH_2). EI-MS (70 eV): 220.2 ([M]$^{+\bullet}$, $C_{13}H_{20}D_6O_2$; calc. 220.2). ESI-(-)-HR-MS: 219.3790 ([M-H]$^-$, $C_{13}H_{19}D_6O_2$; calc. 219.3782).

Synthesis of 1-bromo-11-methyldodecane (30)

A solution of 2.2 g 11-methyldodecan-1-ol (**29**, 11 mmol) in 20 mL dry dichloromethane at 0 °C was treated with 5.8 g triphenyl phosphine (22 mmol) and 1.1 mL of elemental bromine (22 mmol) was added dropwise. After 2 h, the reaction was quenched and washed with 50 mL saturated $Na_2S_2O_3$ solution. The product was extracted with 2 x 25 ml dichloromethane, dried over $MgSO_4$, and concentrated under reduced pressure. Column chromatography on silica gel using a mixture of hexane and ethyl acetate (9:1, *v/v*) as eluent furnished 1.8 g (6.84 mmol, 62% yield) of **30** as a colorless oil. ^{1}H-NMR (600 MHz, $CDCl_3$): 3.41 (*t*, *J* = 6.9, 2 H); 1.90 – 1.82 (*m*, 2 H); 1.55 – 1.47 (*m*, 1 H); 1.46 – 1.38 (*m*, 2 H); 1.36 – 1.21 (*m*, 12 H); 1.18 – 1. 12 (*m*, 2 H); 0.87 (*d*, *J* = 6.6, 6 H). ^{13}C-NMR (151 MHz, $CDCl_3$): 39.2 (CH_2); 34.2 (CH_2); 33.0 (CH_2); 30.1 (CH_2); 29.8 (CH_2); 29.7 (CH_2); 29.6 (CH_2); 28.9 (CH_2); 28.3 (CH_2); 28.1 (CH); 27.6 (CH_2); 22.8 (2 CH_3).

Synthesis of [D$_6$]-1-bromo-11-methyldodecane ([D$_6$]-30)

A solution of 1.2 g [D$_6$]-11-methyldodecan-1-ol ([D$_6$]-**29**, 5.81 mmol) was treated as described for **29** to furnish 0.97 g (3.60 mmol, 62% yield) of [D$_6$]-**30** as a colorless oil. ^{1}H-NMR (600 MHz, CDCl$_3$): 3.41 (*t*, *J* = 6.9, 2 H); 1.86 (*tt*, *J* = 14.6, 7.0, 2 H); 1.48 (*m*, 1 H); 1.46 – 1.38 (*m*, 2 H); 1.32 – 1.23 (*m*, 12 H); 1.18 – 1. 11 (*m*, 2 H). ^{13}C-NMR (151 MHz, CDCl$_3$): 39.1 (CH$_2$); 34.2 (CH$_2$); 33.0 (CH$_2$); 30.1 (CH$_2$); 29.8 (CH$_2$); 29.7 (CH$_2$); 29.6 (CH$_2$); 28.9 (CH$_2$); 28.3 (CH$_2$); 28.3 (CH); 27.5 (CH$_2$).

Synthesis of 13-methyltetradec-1-ene (31)

Under nitrogen a solution of 700 mg 1-bromo-11-methyldodecane (**30**, 2.66 mmol) in 10 mL dry tetrahydrofuran was treated with 8 mL of 1 M vinylmagnesium bromide solution in tetrahydrofuran (8.0 mmol). The mixture was cooled to 0 °C and 5.3 mL of 0.1 M dilithium tetrachlorocuprate (II) solution in tetrahydrofuran (0.53 mmol) was added dropwise. After 16 h at RT the reaction was quenched with 50 mL saturated NH$_4$Cl solution. The product was extracted with 2 x 50 mL hexane, dried over MgSO$_4$, and concentrated under reduced pressure. Column chromatography on silica gel using hexane as eluent furnished 400 mg (1.90 mmol, 71% yield) of **31** as a colorless oil. ^{1}H-NMR (600 MHz, CDCl$_3$): 5.82 (*ddt*, *J* = 16.9, 10.3, 6.7, 1 H); 4.99 (*ddt*, *J* = 16.5, 3.7, 1.6, 1 H); 4.93 (*ddt*, *J* = 10.2, 2.3, 1.3, 1 H); 2.08 – 2.01 (*m*, 2 H); 1.56 – 1.47 (*m*, 1 H); 1.26 (*m*, 16 H); 1.18 – 1.12 (*m*, 2 H); 0.86 (*d*, *J* = 6.6, 6 H). ^{13}C-NMR (151 MHz, CDCl$_3$): 139.4 (CH); 114.2 (CH$_2$); 39.2 (CH$_2$); 34.0 (CH$_2$); 30.1 (CH$_2$); 29.9 (2 CH$_2$); 29.8 (2 CH$_2$); 29.5 (CH$_2$); 29.1 (CH$_2$); 28.1 (CH); 27.6 (CH$_2$); 22.8 (2 CH$_3$).

Synthesis of [D$_6$]-13-methyltetradec-1-ene ([D$_6$]-31)

A solution of 815 mg of [D$_6$]-1-bromo-11-methyldodecane (3.03 mmol) ([D$_6$]-**30**, 3.0 mmol) was treated as described for **30** to furnish 440 mg (2.0 mmol, 67% yield) of [D$_6$]-**31** as a colorless oil. ^{1}H-NMR (600 MHz, CDCl$_3$): 5.82 (*ddt*, *J* = 16.9, 10.2, 6.6, 1 H); 5.00 (*ddt*, *J* = 16.7, 2.0, 1.5, 1 H); 4.93 (*ddt*, *J* = 10.2, 2.4, 1.3, 1 H); 2.08 – 2.01 (*m*, 2 H); 1.48 (*m*, 1 H); 1.42 – 1.34 (*m*, 2 H); 1.33 – 1.20 (*m*, 14 H); 1.16 – 1.12 (*m*, 2 H). ^{13}C-NMR (151 MHz, CDCl$_3$): 139.4 (CH); 114.2 (CH$_2$); 39.1 (CH$_2$); 34.0 (CH$_2$); 30.1 (CH$_2$); 29.8 (2 CH$_2$); 29.7 (CH$_2$); 29.3 (CH$_2$); 29.0 (CH$_2$); 28.1 (CH); 27.5 (2 CH$_3$).

Synthesis of 13-Methyltetradecan-1-ol (32)

Under nitrogen a solution of 400 mg 11-methyltetradec-1-ene (**31**, 1.9 mmol) in 5 mL dry tetrahydrofuran at 0 °C was treated with 2.3 mL of 1 M borane in tetrahydrofuran (2.3 mmol). After 2 h, 0.1 mL water was added and the solution was stirred for 20 minutes until gas evolution ceased. Subsequently, the mixture was cooled to 0° C and equal portions of 30% hydrogen peroxide solution and 3 M NaOH were carefully added. The mixture was stirred for 30 minutes, diluted by addition of 20 ml water and the product was extracted with 2 x 10 mL diethyl ether. The organic phase was dried over Na$_2$SO$_4$ and concentrated under reduced pressure. Column chromatography on silica gel using a gradient of hexane and diethyl ether as eluent furnished 275 mg (1.2 mmol, 64%) of **32** as a colorless oil. ^{1}H-NMR (600 MHz, CDCl$_3$): 3.66 (*t*, *J* = 6.7, 2 H); 1.60 – 1.47 (*m*, 5 H); 1.26 (*m*, 16 H); 1.16 – 1.11 (*m*, 2 H); 0.86 (*d*, *J* = 6.7, 6 H). ^{13}C-NMR (151 MHz, CDCl$_3$): 63.4 (CH$_2$); 39.2 (CH$_2$); 32.9 (CH$_2$); 30.5 (CH$_2$); 30.1 (CH$_2$); 29.9 (CH$_2$); 29.8 (3 CH$_2$); 29.6 (CH$_2$); 28.1 (CH); 27.6 (CH$_2$); 25.9 (CH$_2$); 22.8 (2 CH$_3$).

Synthesis of [D$_6$]-13-methyltetradecan-1-ol ([D$_6$]-32)

A solution of 435 mg [D$_6$]-11-methyltetradec-1-ene ([D$_6$]-**31**, 2.0 mmol) was treated as described for **31** to furnish 283 mg (1.2 mmol, 60% yield) of [D$_6$]-**32** as a colorless oil. ^{1}H-NMR (600 MHz, CDCl$_3$): 3.64 (*t*, *J* = 6.7, 2 H); 1.58 – 1.51 (*m*, 2 H); 1.50 – 1.44 (*m*, 2 H); 1.25 (*m*, 17 H); 1.16 – 1.12 (*m*, 2 H). ^{13}C-NMR (151 MHz, CDCl$_3$): 63.2 (CH$_2$); 39.1 (CH$_2$); 33.0 (CH$_2$); 30.1 (CH$_2$); 29.9 (2 CH$_2$); 29.8 (CH$_2$); 29.6 (CH$_2$); 29.3 (CH$_2$); 27.6 (CH); 25.9 (CH$_2$).

Synthesis of 13-methyltetradecanoic acid (C15*iso*, 14b)

A solution of 276 mg 13-methyltetradecan-1-ol (**32**, 1.21 mmol) in 20 mL dichloromethane was treated with 386 mg of tetra-butylammonium bromide (1.21 mmol), 764 mg of KMnO$_4$ (4.84 mmol), 2 mL acetic acid, and 6.8 mL of water. The mixture was refluxed at 60 °C for 16 h. The reaction was quenched by addition of Na_2SO_3 until the brown solids disappeared. The product was extracted with 2 x 10 mL dichloromethane, dried over $MgSO_4$, and concentrated under reduced pressure. Column chromatography on silica gel using a mixture of hexane and ethyl acetate (6:4, *v/v*) as eluent furnished 221 mg (0.91 mmol, 75% yield) of **14b** as a white solid. ^{1}H-NMR (600 MHz, $CDCl_3$): 2.35 (*t*, *J* = 7.5, 2 H); 1.63 (*m*, 1 H); 1.51 (*m*, 1 H); 1.26 (*m*, 17 H); 1.18 – 1.12 (*m*, 2 H); 0.86 (*d*, *J* = 6.7, 6 H). ^{13}C-NMR (151 MHz, $CDCl_3$): 179.8 (C); 39.2 (CH_2); 34.1 (CH_2); 30.1 (CH_2); 29.9 (CH_2); 29.8 (2 CH_2); 29.6 (2 CH_2); 29.2 (CH_2); 28.1 (CH_2); 27.6 (CH_2); 24.8 (CH_2); 22.8 (2 CH_3). EI-MS (70 eV): 242.2 ($[M]^{+\bullet}$, $C_{15}H_{30}O_2$; calc. 242.2). ESI-(-)-HR-MS: 241.3961 ($[M\text{-}H]^-$, $C_{15}H_{29}O_2$; calc. 241.3955).

Synthesis of [D_6]-13-methyltetradecanoic acid ([D_6]-C15*iso*, [D_6]-14b)

A solution of 535 mg of [D_6]-13-methyltetradecan-1-ol ([D_6]-**32**, 2.29 mmol) was treated as described for **32** to furnish 420 mg (1.67 mmol, 73% yield) of [D_6]-**14b** as a white solid. ^{1}H-NMR (600 MHz, $CDCl_3$): 2.37 (*t*, *J* = 7.5, 2 H); 1.65 (*tt*, *J* = 14.8, 7.4, 2 H); 1.50 (*m*, 1 H); 1.40 – 1.22 (*m*, 16 H); 1.20 – 1. 12 (*m*, 2 H). ^{13}C-NMR (151 MHz, $CDCl_3$): 180.1 (C); 39.1 (CH_2); 34.2 (CH_2); 30.2 (CH_2); 29.9 (CH_2); 29.8 (2 CH_2); 29.6 (CH_2); 29.4 (CH_2); 29.2 (CH); 27.6 (2 CH_3); 24.8 (CH_2). EI-MS (70 eV): 248.2 ($[M]^{+\bullet}$, $C_{15}H_{24}D_6O_2$; calc. 248.3). ESI-(-)-HR-MS: 247.4328 ($[M\text{-}H]^-$, $C_{15}H_{23}D_6O_2$; calc. 247.4322).

NMR spectroscopy

NMR spectra were recorded in $CDCl_3$ at 600 MHz for ^{1}H and 151 MHz for ^{13}C using a Bruker Avance Neo Ascend 600 MHz. Residual solvent signals at 7.26 ppm for ^{1}H and at 77.16 ppm for ^{13}C were used as internal references. Chemical shifts (δ) are expressed in parts per million (ppm) and coupling constants (J) in hertz (Hz). Processing and analyses were performed using the Mnova NMR software package (v.14.2.0, MestReLab Research S.L., Spain).