Electronic Supplementary Material (ESI) for RSC Advances.

Methionine epimerization in cyclic peptides

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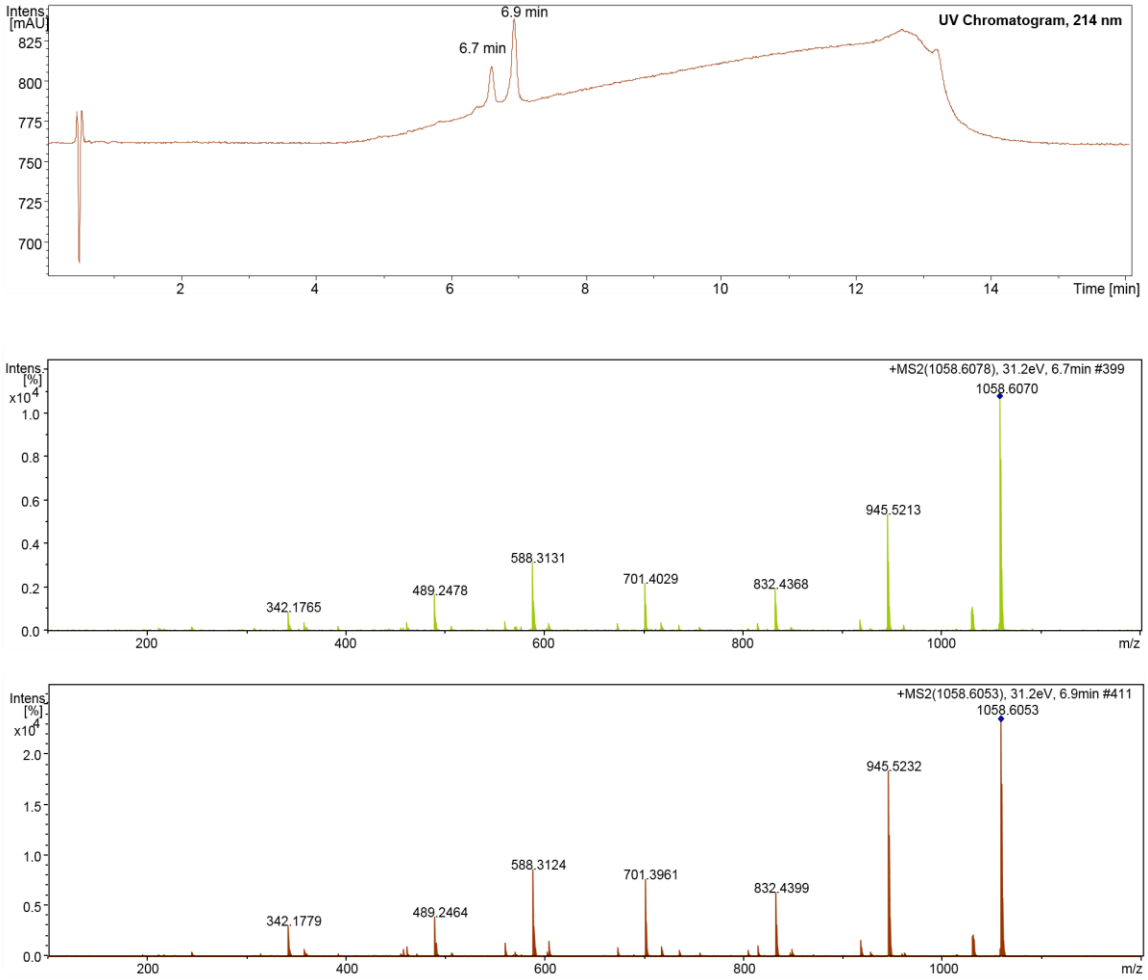

Fig. S1: UV chromatogram of KOH treated LO **2**, MS/MS chromatogram of peak 1 (6.7 min) and peak 2 (6.9 min).

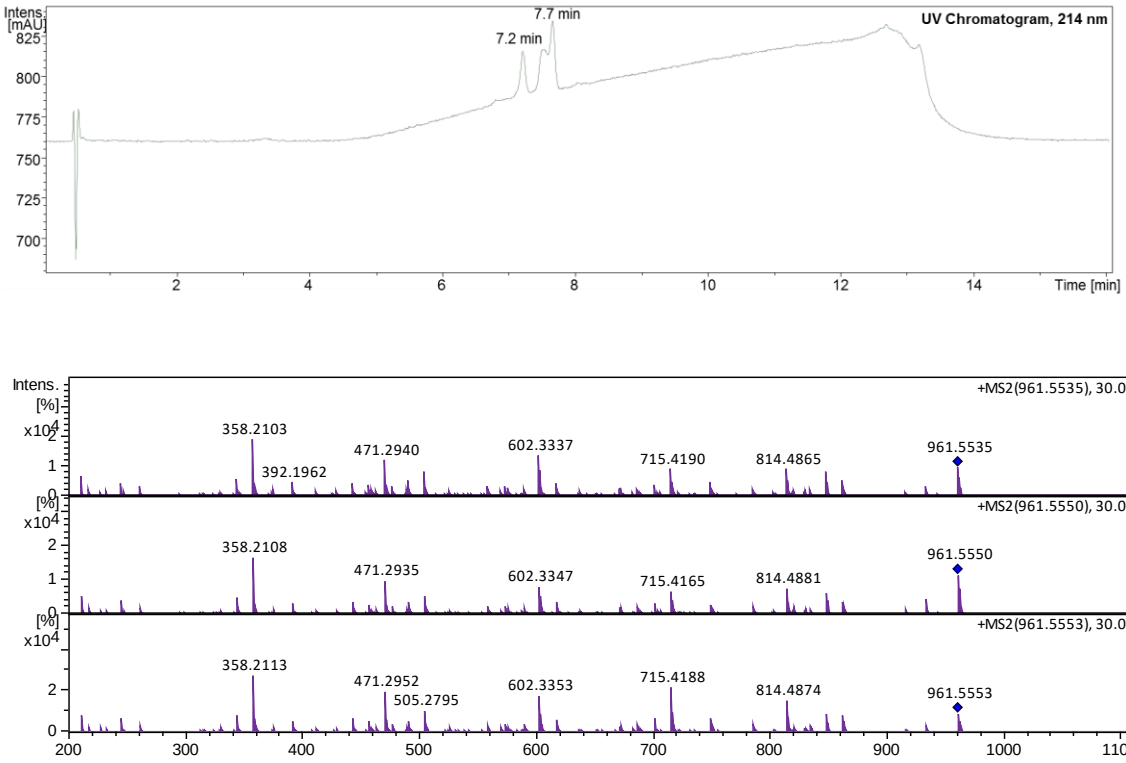

Fig. S2: UV chromatogram of KOH treated LO **5**, MS/MS chromatogram of peak 1 (7.2 min), peak 2 (7.5 min) and peak 3 (7.7 min).

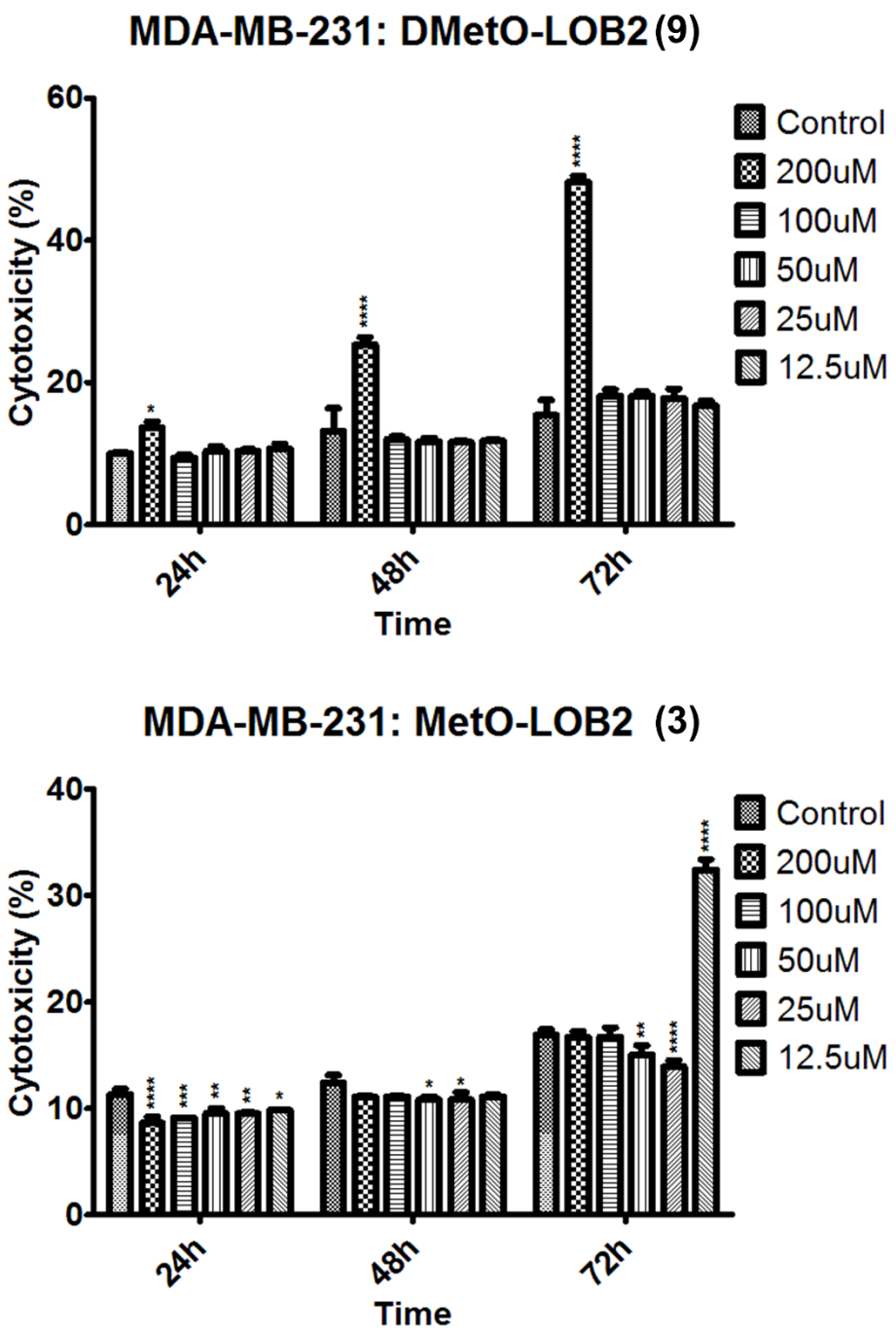

Fig. S3 % cytotoxicity of D-MetO-LOB2 (**9**) and L-MetO-LOB2 (**3**) against the MDA-MB-231 cells.

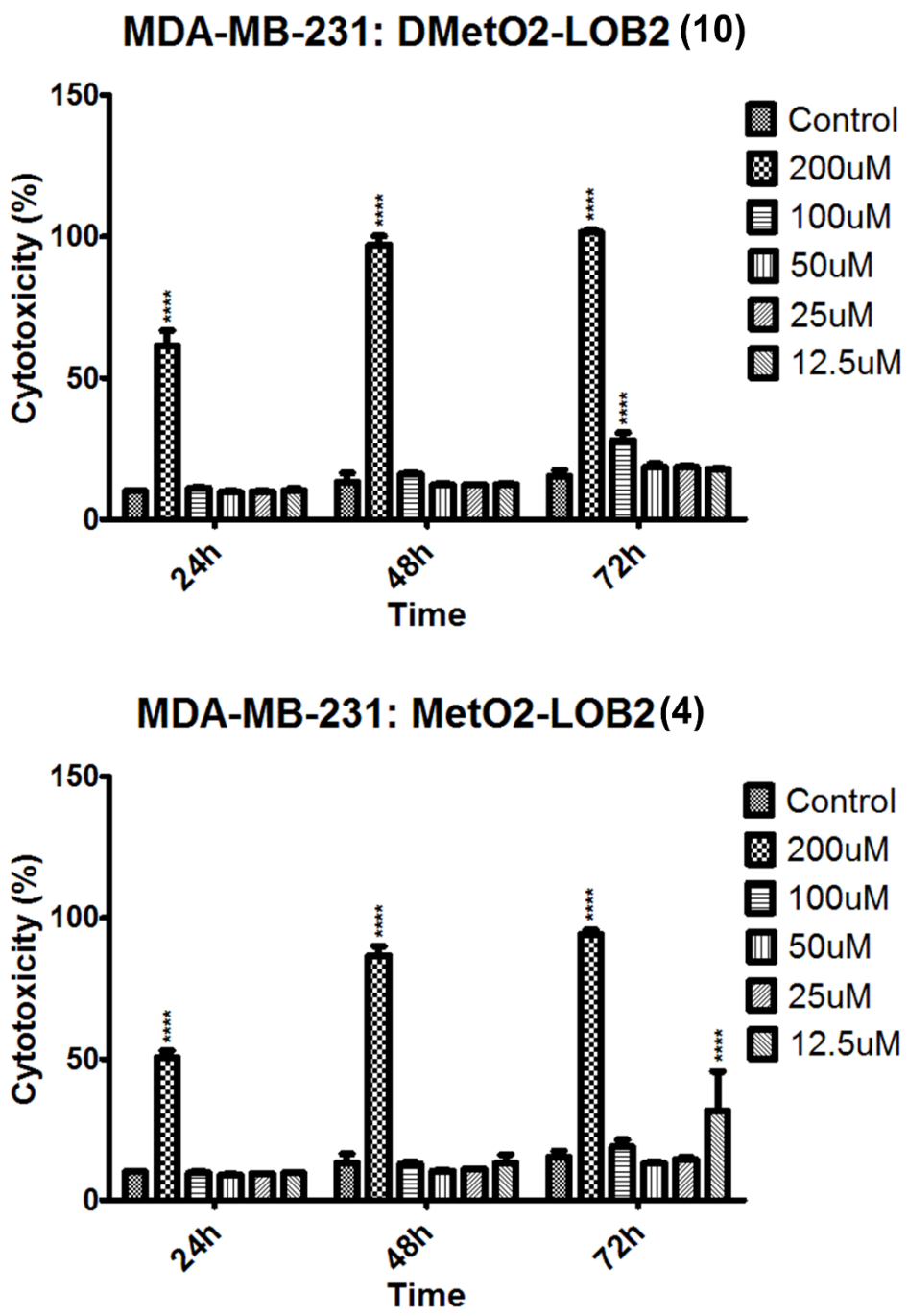

Fig. S4. % cytotoxicity of D-MetO_2-LOB2 (**10**) and L-MetO_2-LOB2 (**4**) against the MDA-MB-231 cells.

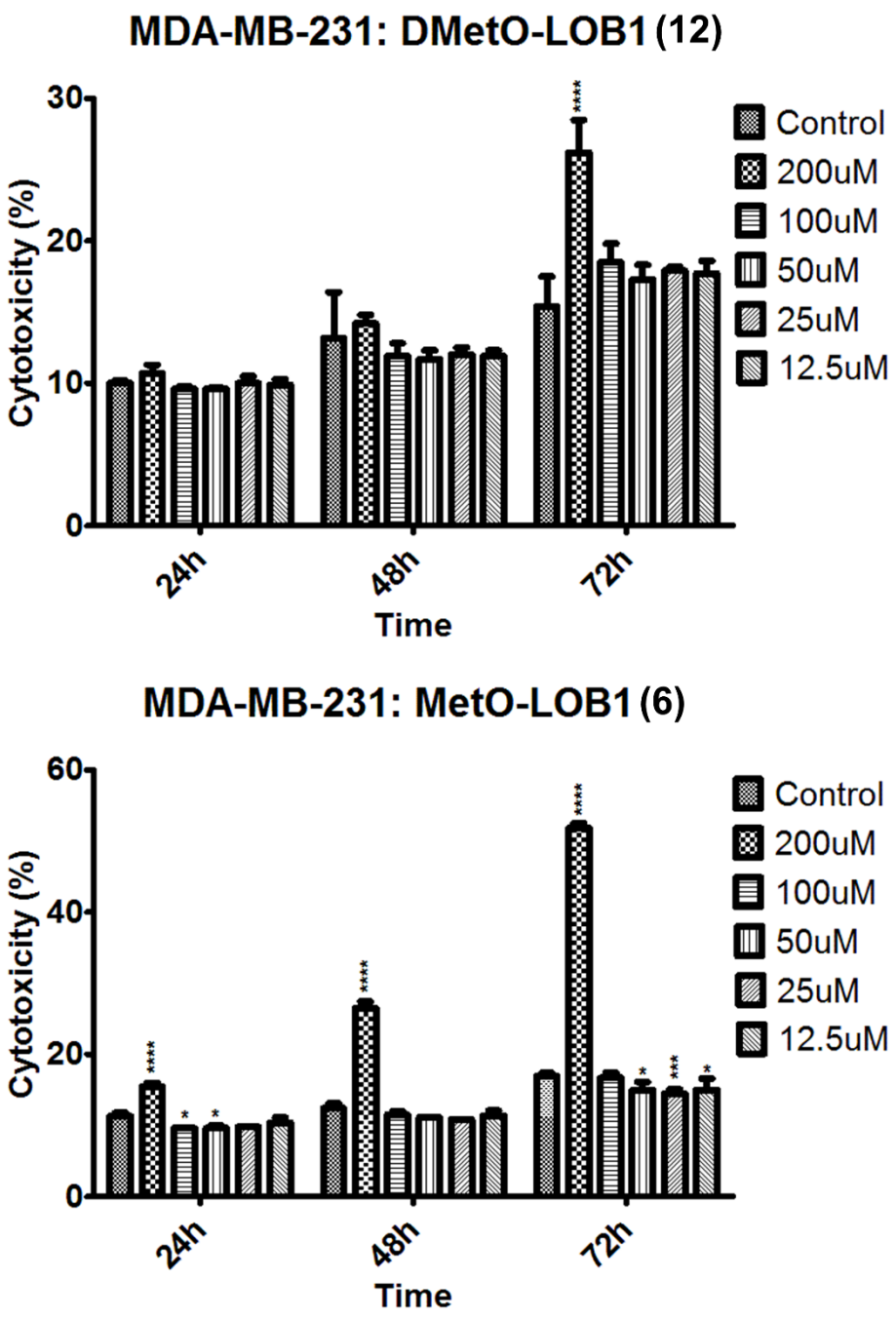

Fig. S5. % cytotoxicity of D-MetO-LOB1 (**12**) and L-MetO-LOB1 (**6**) against the MDA-MB-231 cells.

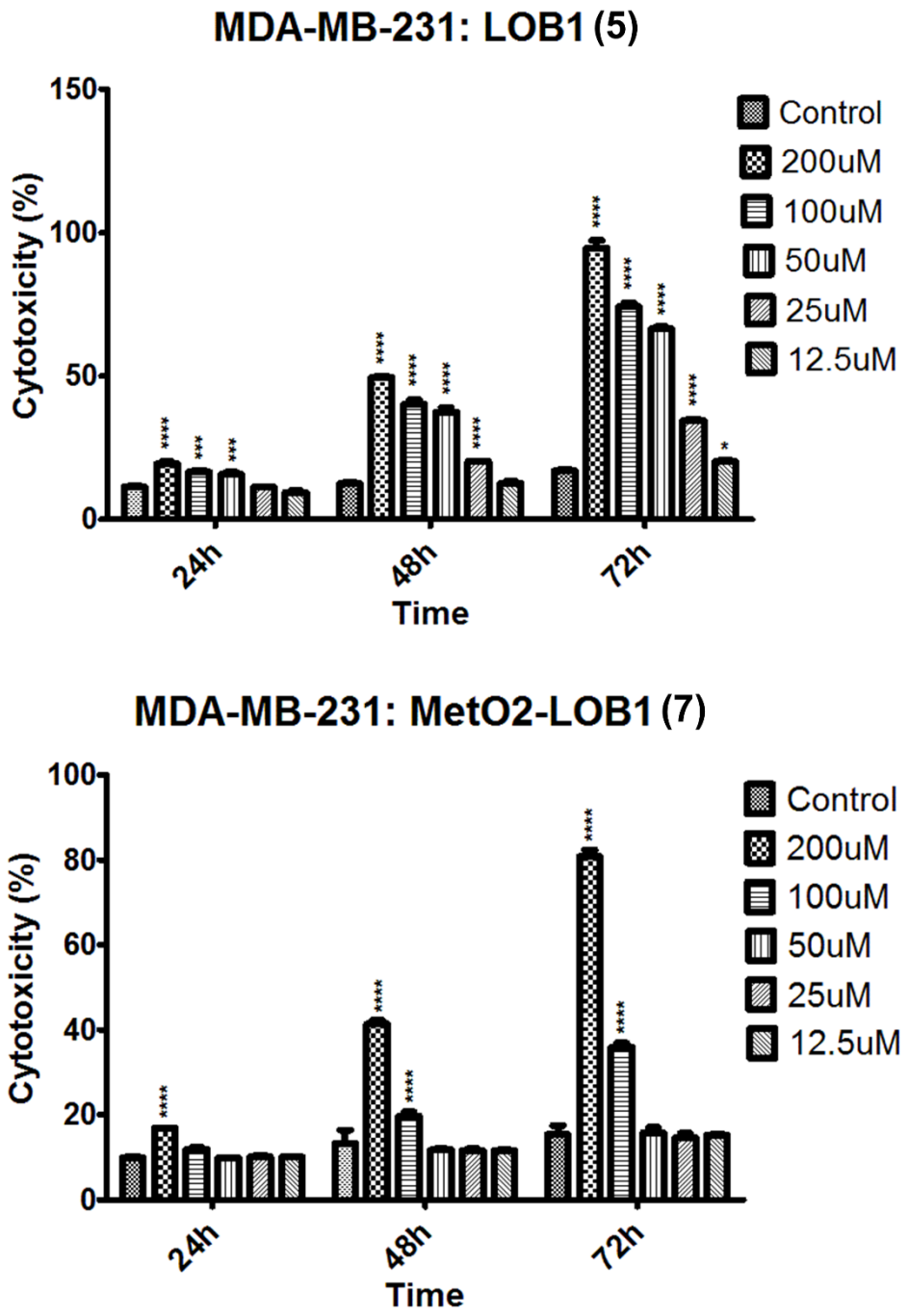

Fig. S6. % cytotoxicity of LOB1 (**5**) and L-MetO_2-LOB1 (**7**) against the MDA-MB-231 cells.

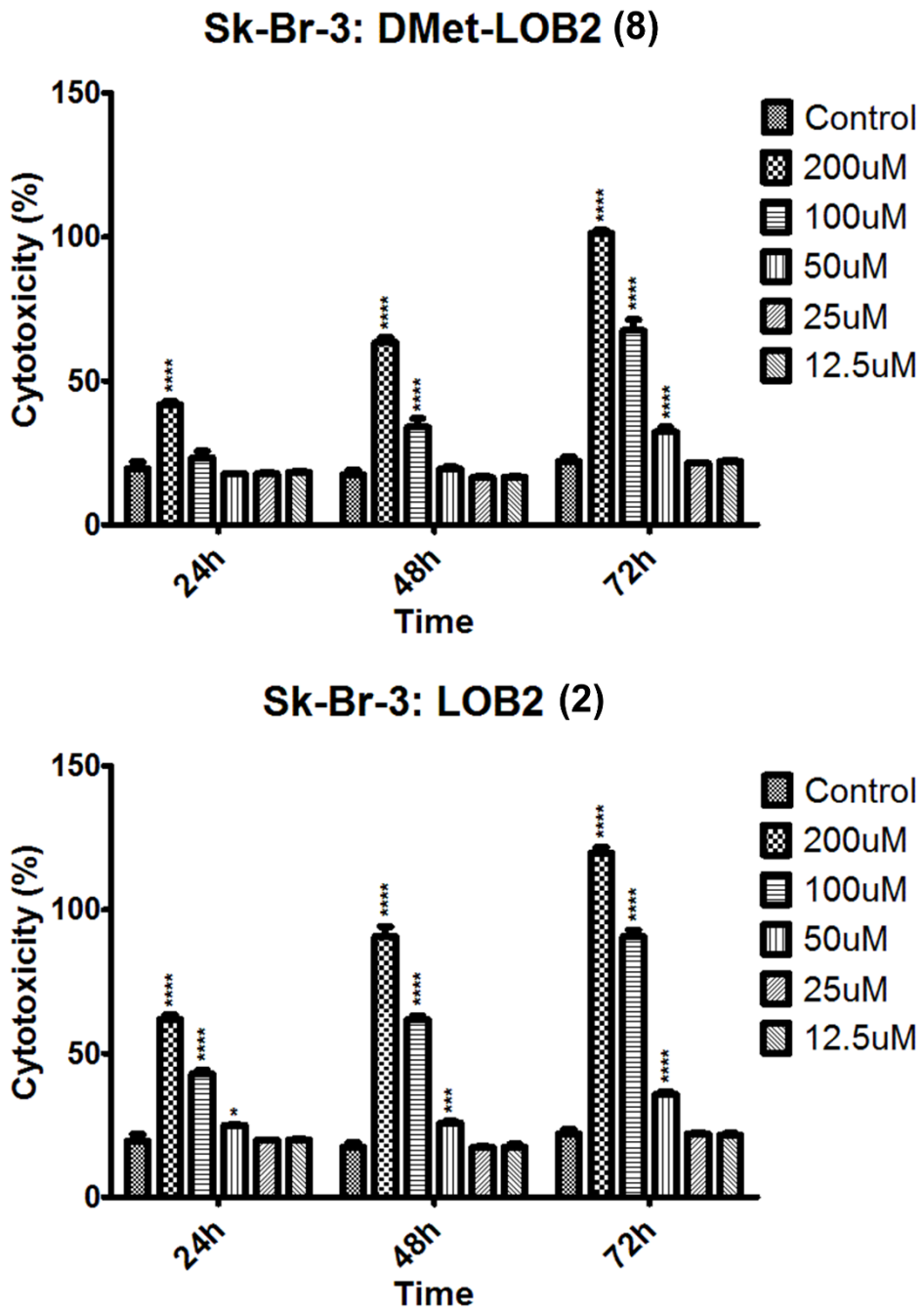

Fig. S7. % cytotoxicity of D-Met-LOB2 (**8**) and LOB2 (**2**) against the Sk-Br-3 cells.

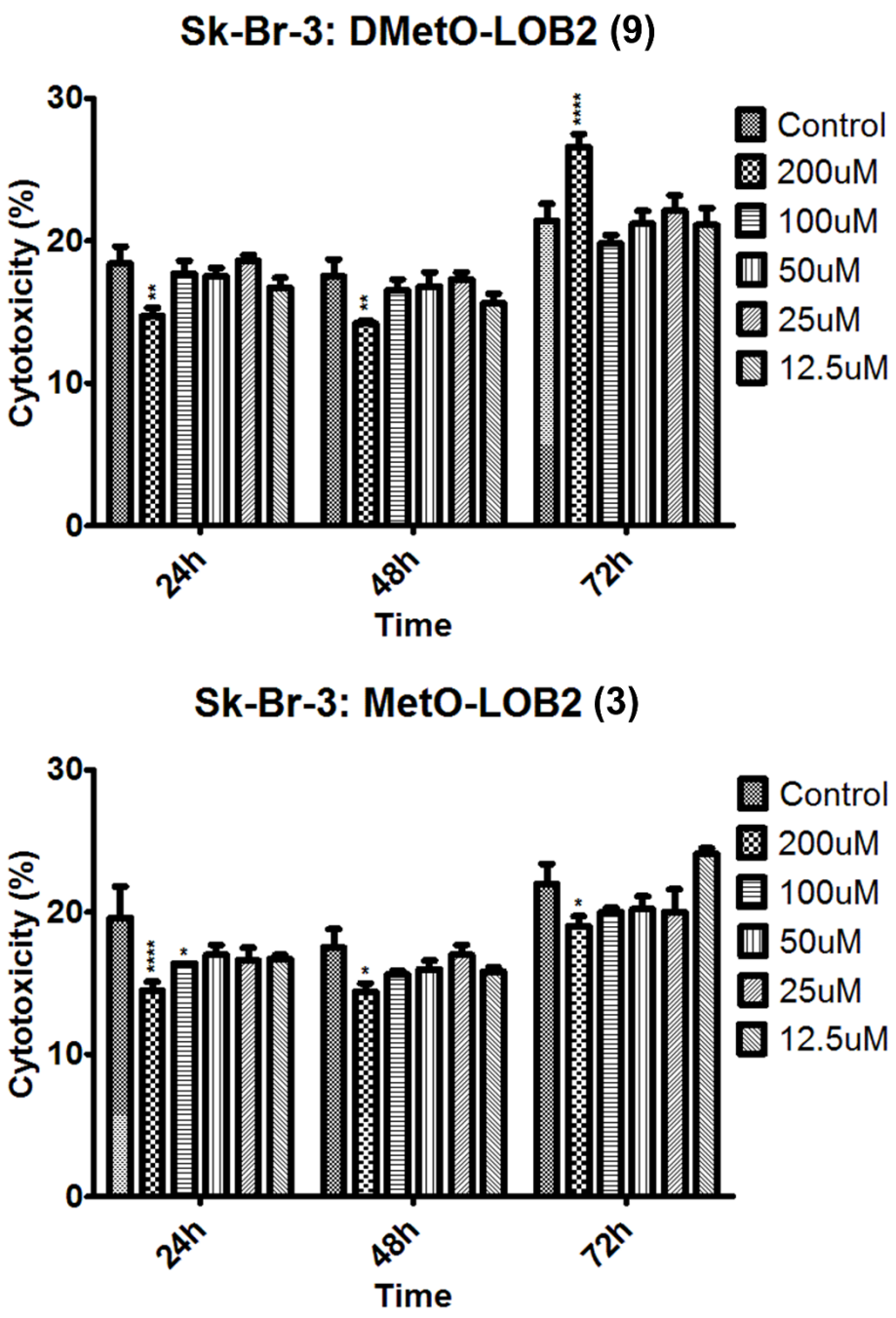

Fig. S8. % cytotoxicity of D-MetO-LOB2 (**9**) and L-MetO-LOB2 (**3**) against the Sk-Br-3 cells.

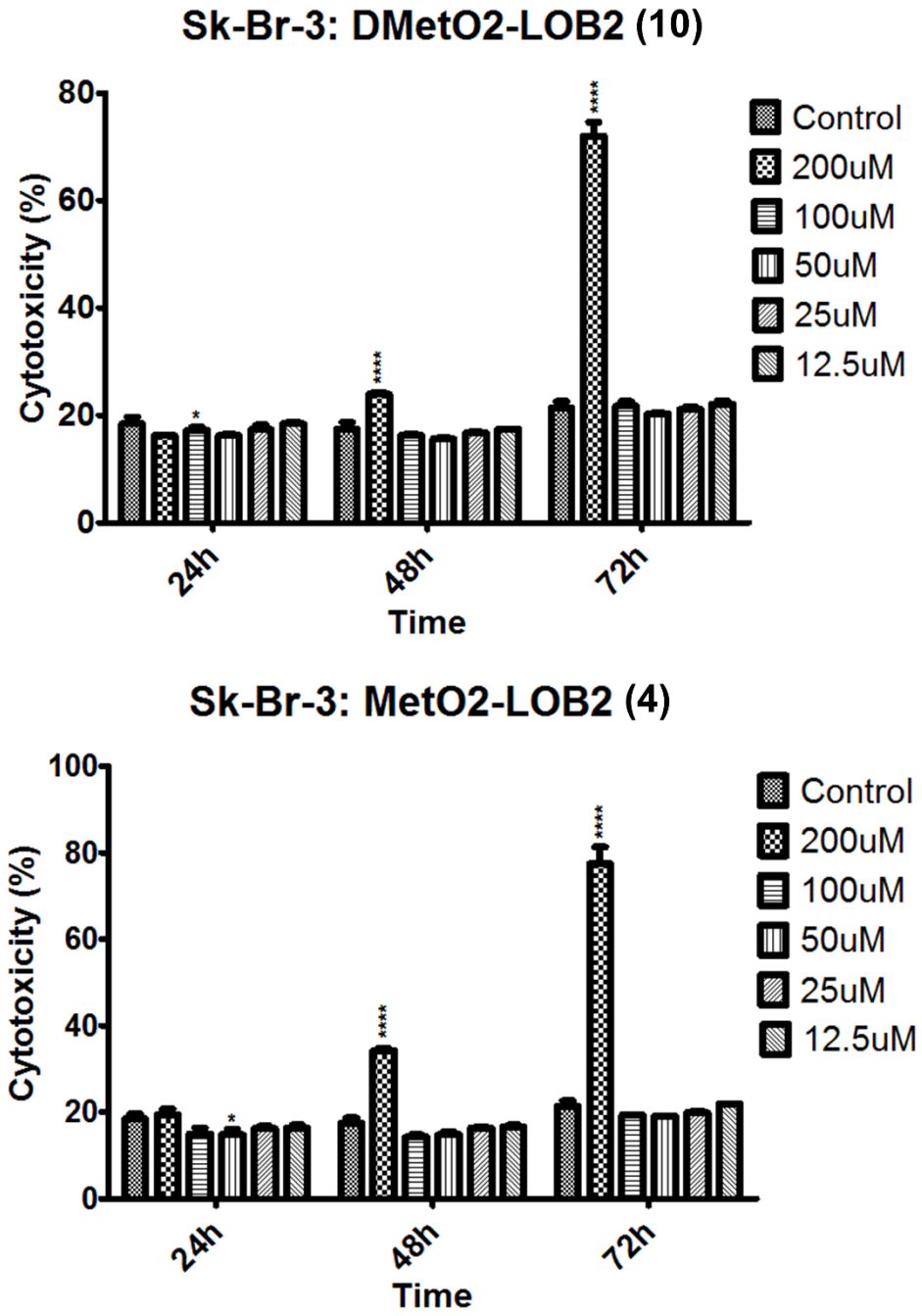

Fig. S9. % cytotoxicity of D-MetO_2-LOB2 (**10**) and L-MetO_2-LOB2 (**4**) against the Sk-Br-3 cells.

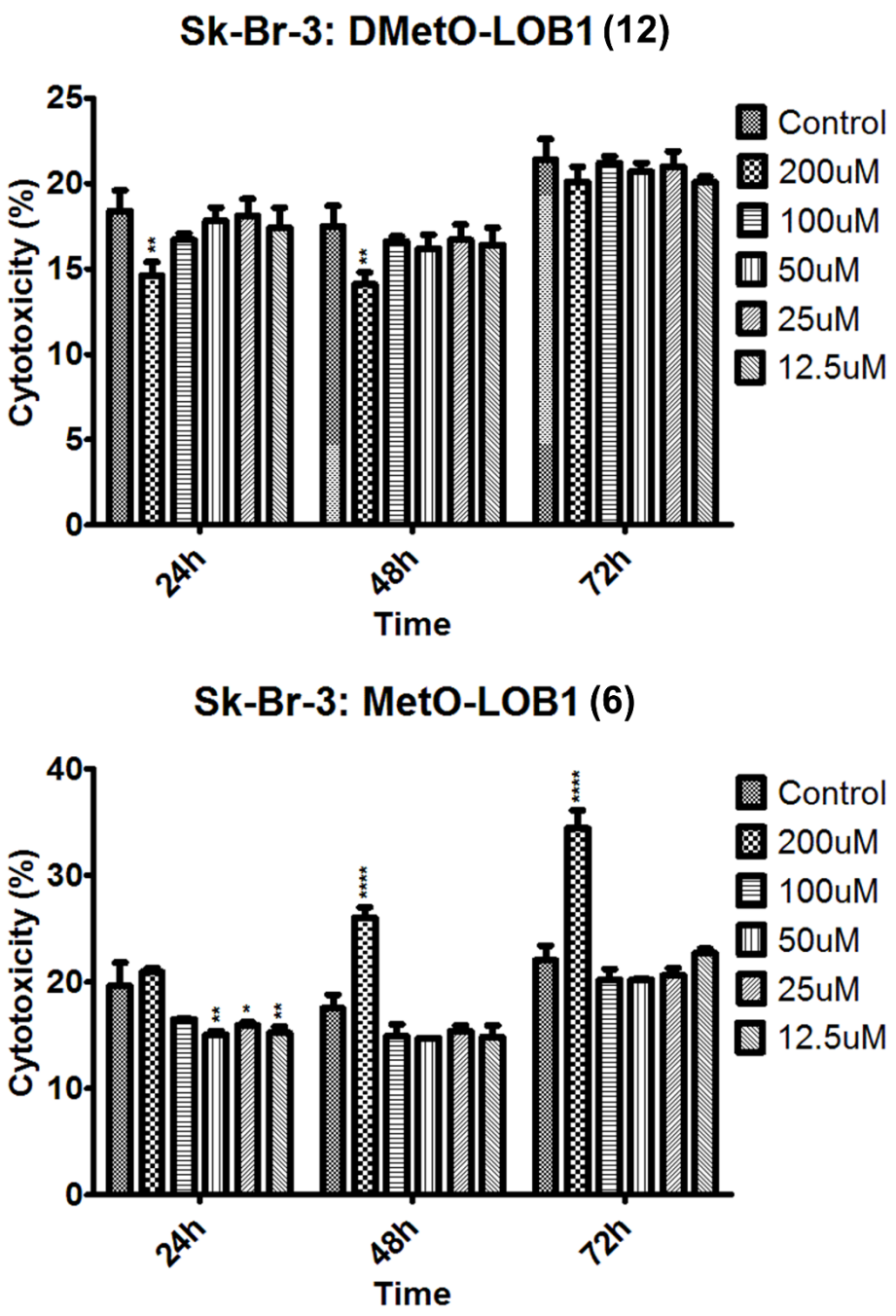

Fig. S10. % cytotoxicity of D-MetO-LOB1 (**12**) and L-MetO-LOB1 (**6**) against the Sk-Br-3 cells.

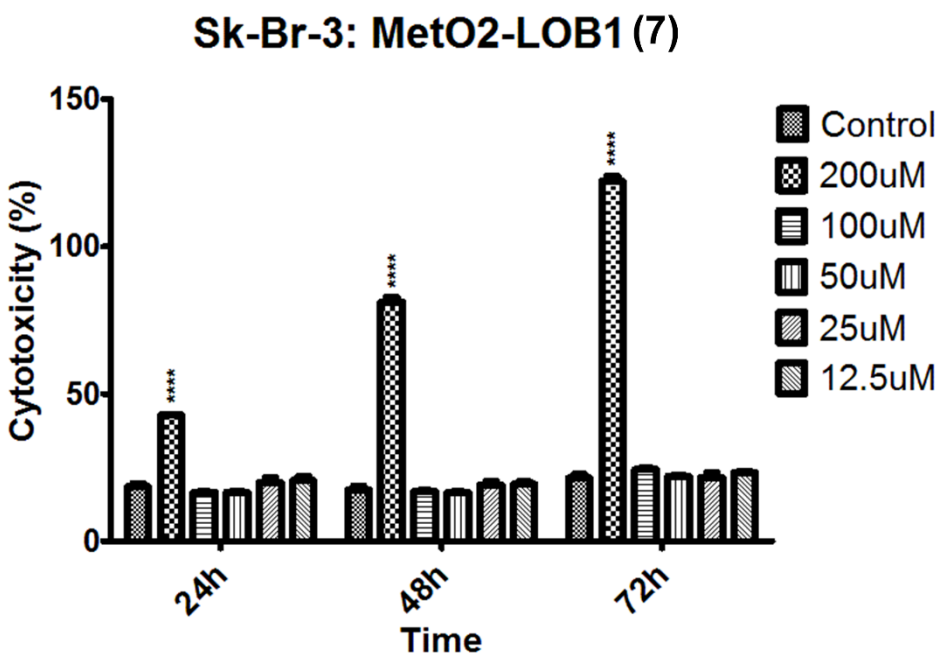

Fig. S11. % cytotoxicity of L-MetO_2-LOB1 (**7**) against the Sk-Br-3 cells.

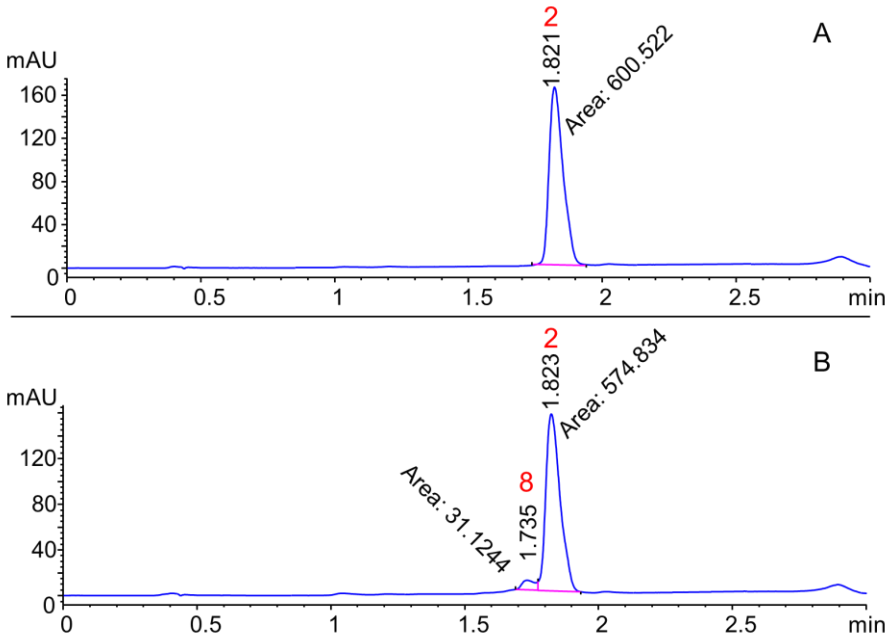

Fig. S12. HPLC chromatogram of (A) LO **2**; (B) KOH treated LO **2**.

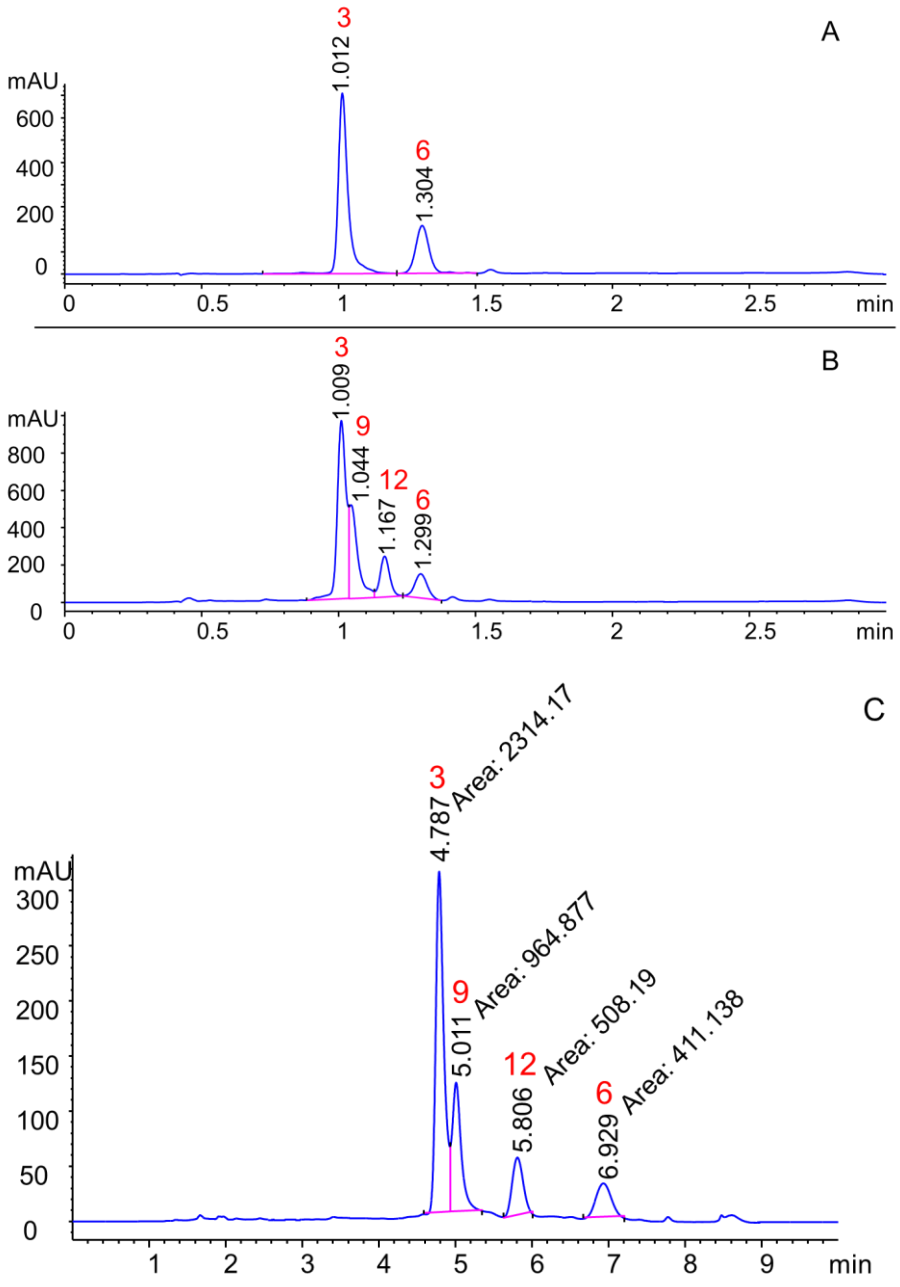

Fig. S13. HPLC chromatogram of (A) LOs **3** and **6**; (B) KOH treated LOs **3** and **6**; (C) KOH treated LOs **3** and **6** (preparative).

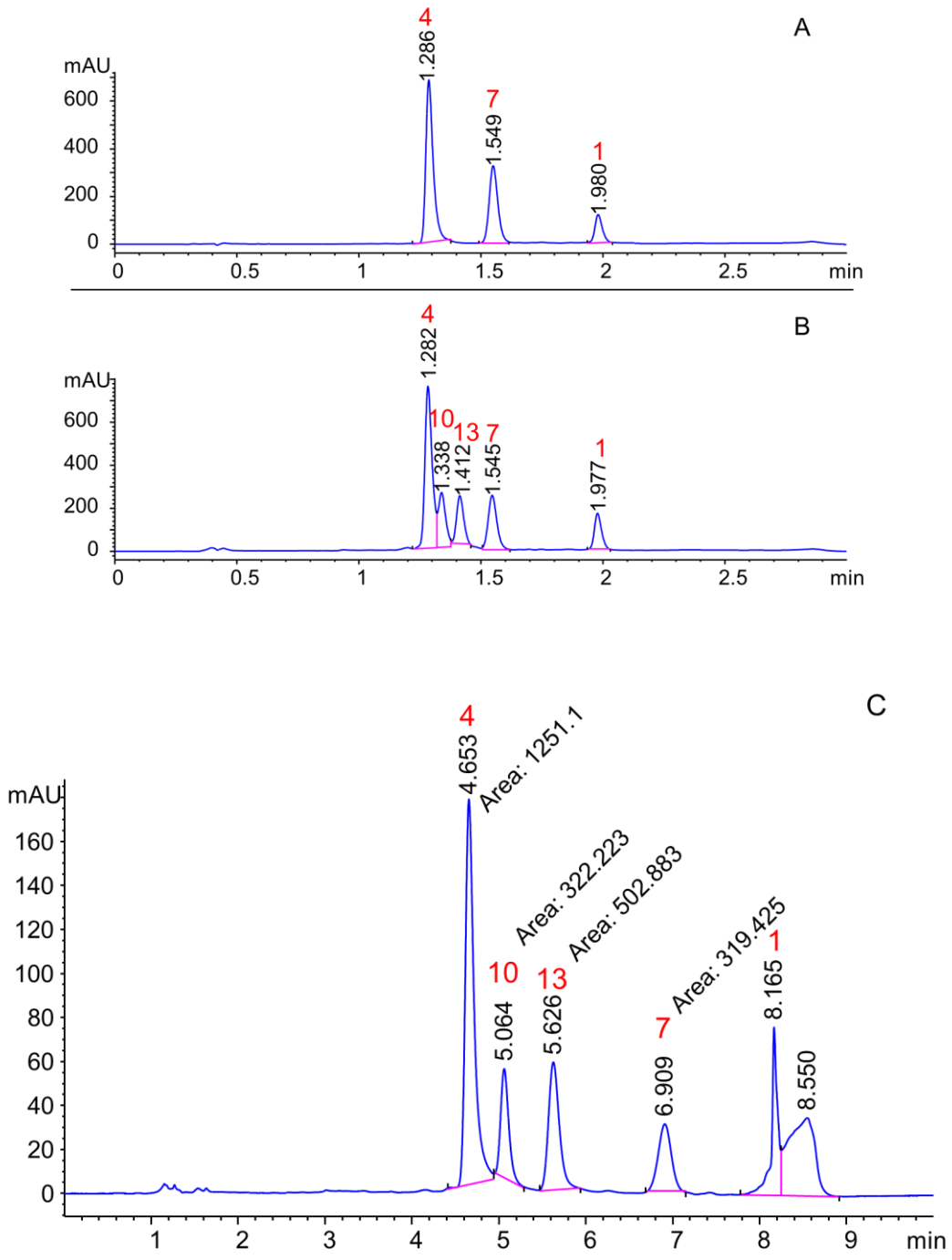

Fig. S14. HPLC chromatogram of (A) LOs **1**, **4** and **7**; (B) KOH treated LOs **1**, **4** and **7**; (C) KOH treated LOs **1**, **4** and **7** (preparative).

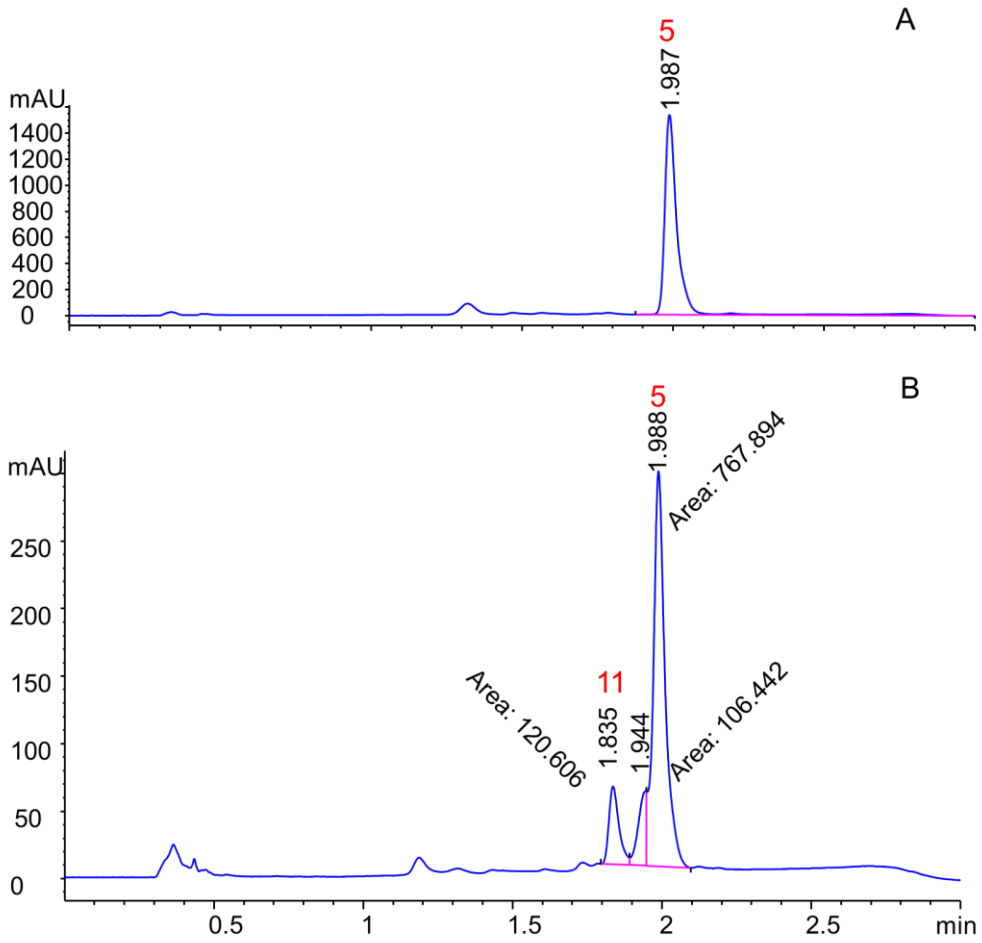

Fig. S15. HPLC chromatogram of (A) LO **5;** (B) KOH treated LO **5**.

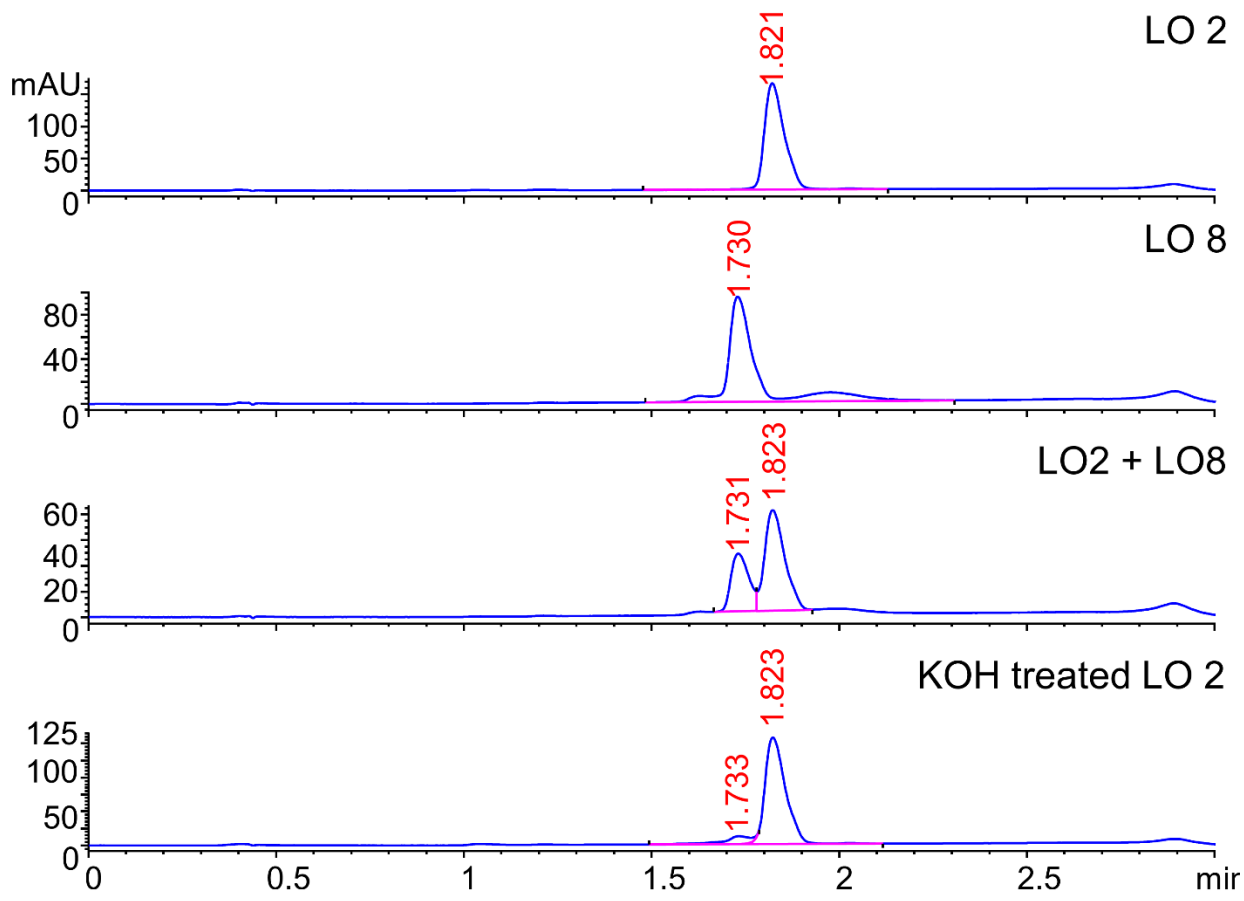

Fig. S16. HPLC chromatogram of LO **2**, LO **8**, LO **2** + LO **8** and KOH treated LO **2**.

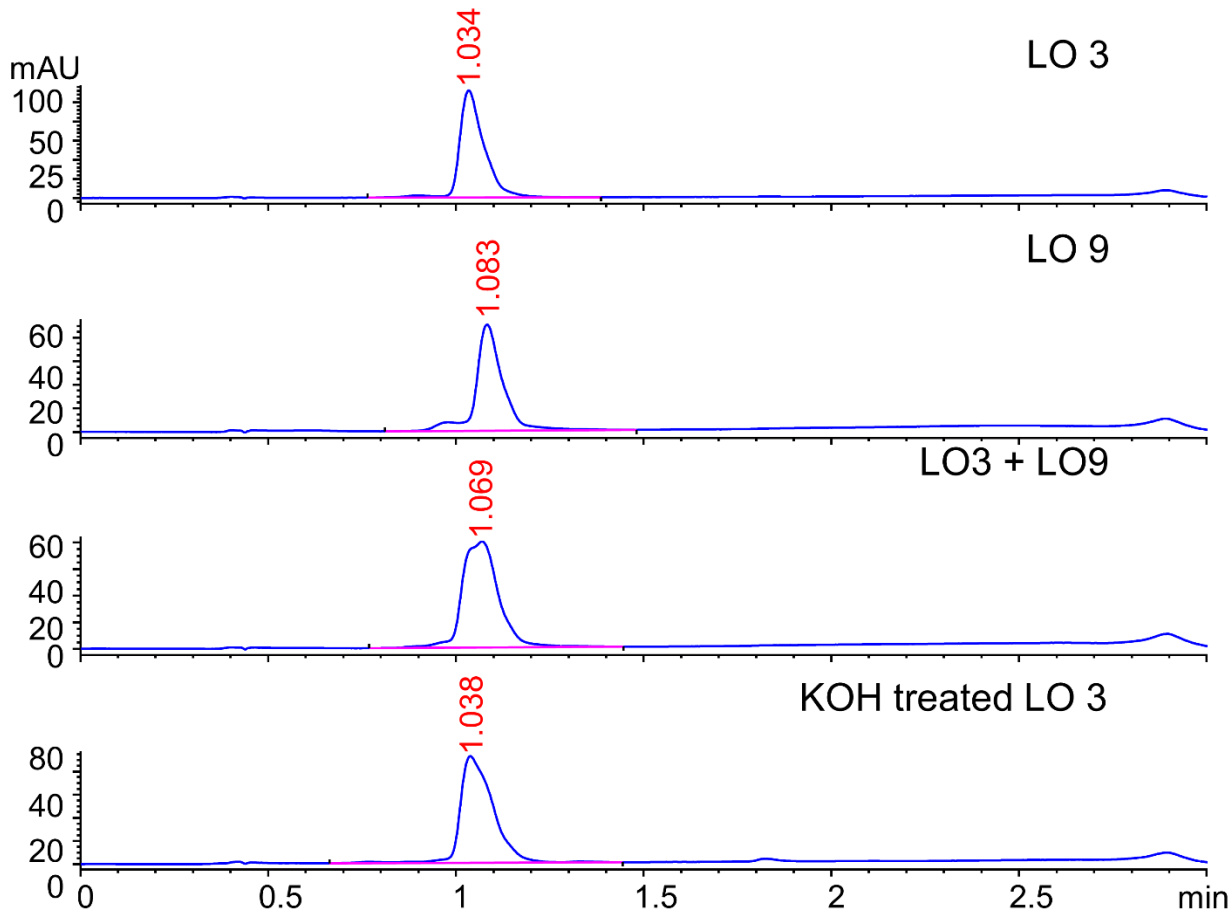

Fig. S17. HPLC chromatogram of LO **3**, LO **9**, LO **3** + LO **9** and KOH treated LO **3**.

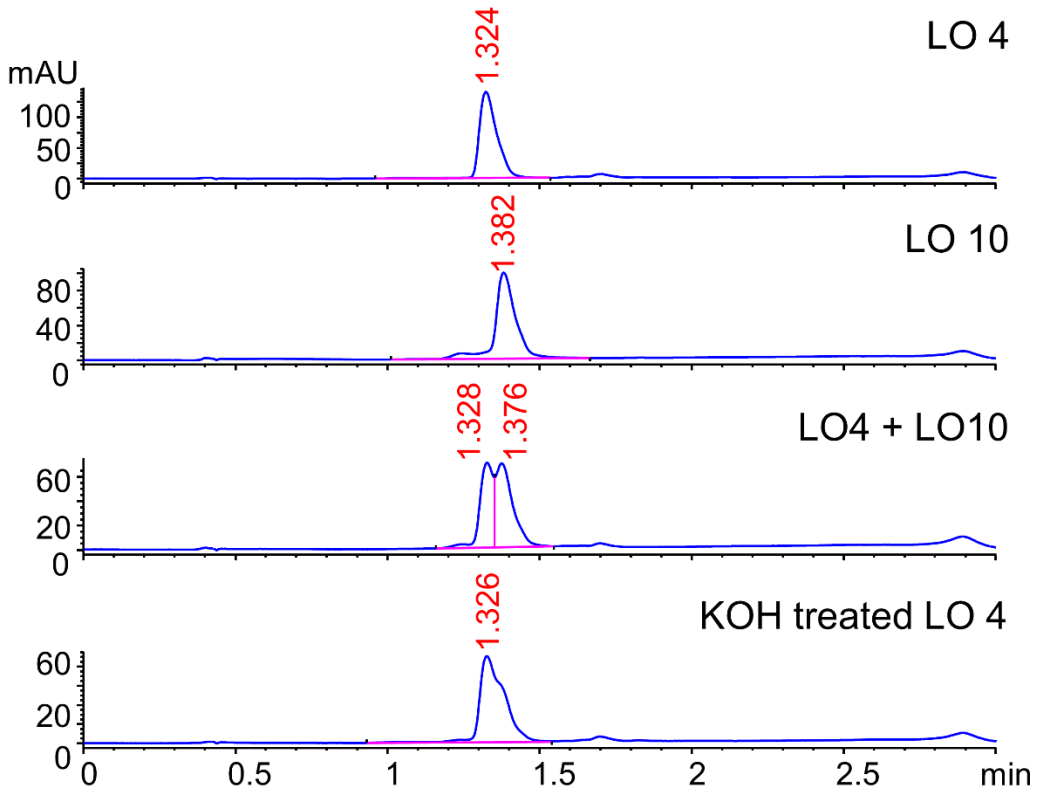

Fig. S18. HPLC chromatogram of LO **4**, LO **10**, LO **4** + LO **10** and KOH treated LO **4**.

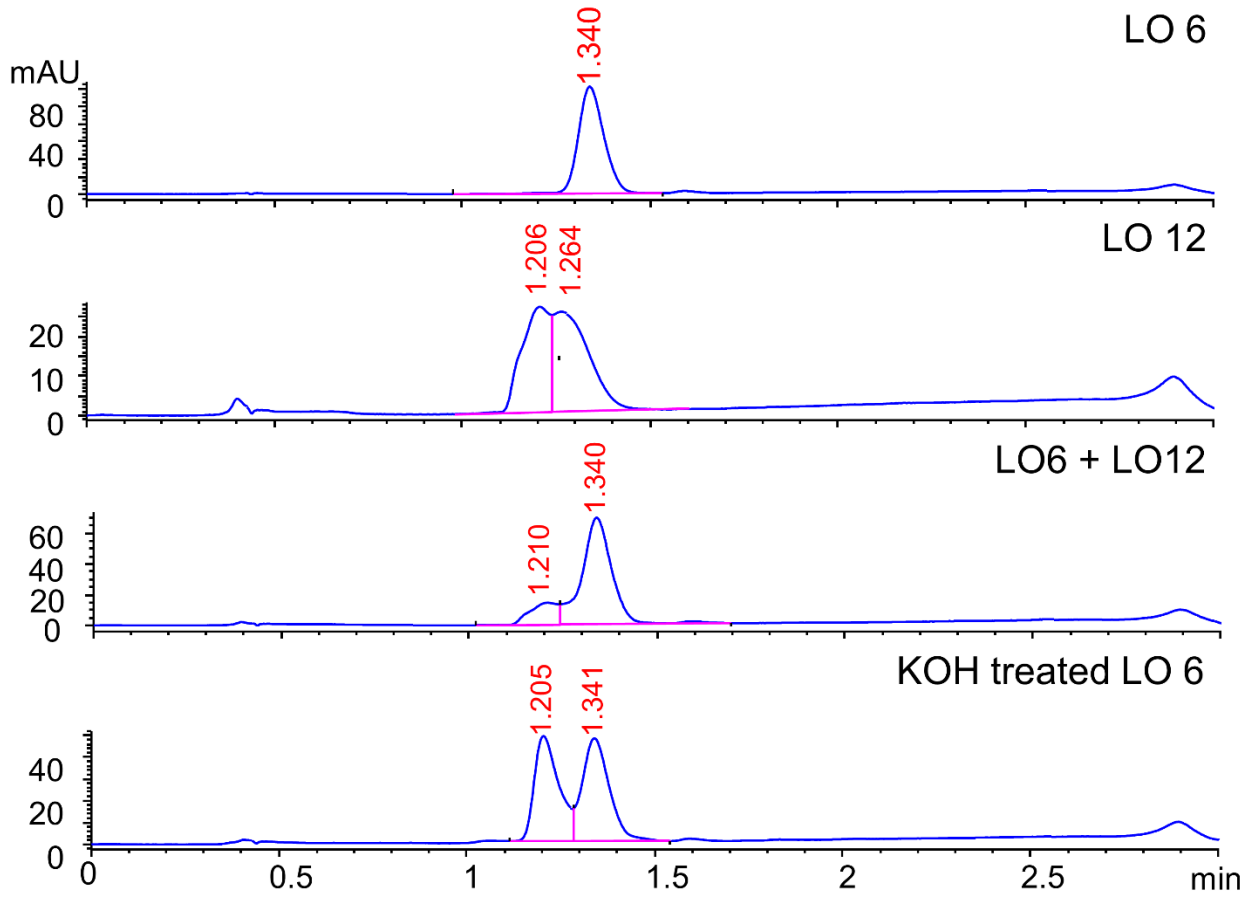

Fig. S19. HPLC chromatogram of LO **6**, LO **12**, LO **6** + LO **12** and KOH treated LO **6**.

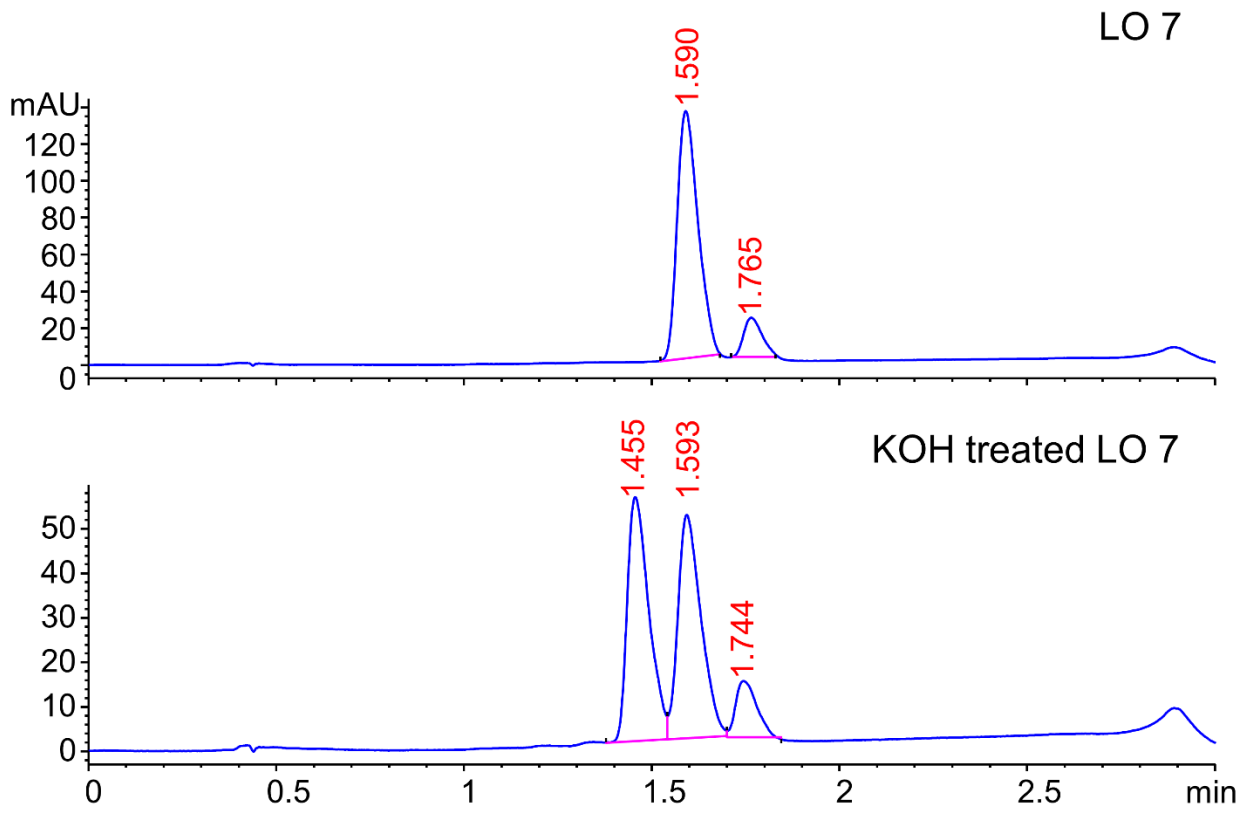

Fig. S20. HPLC chromatogram of LO **7** and KOH treated LO **7**.

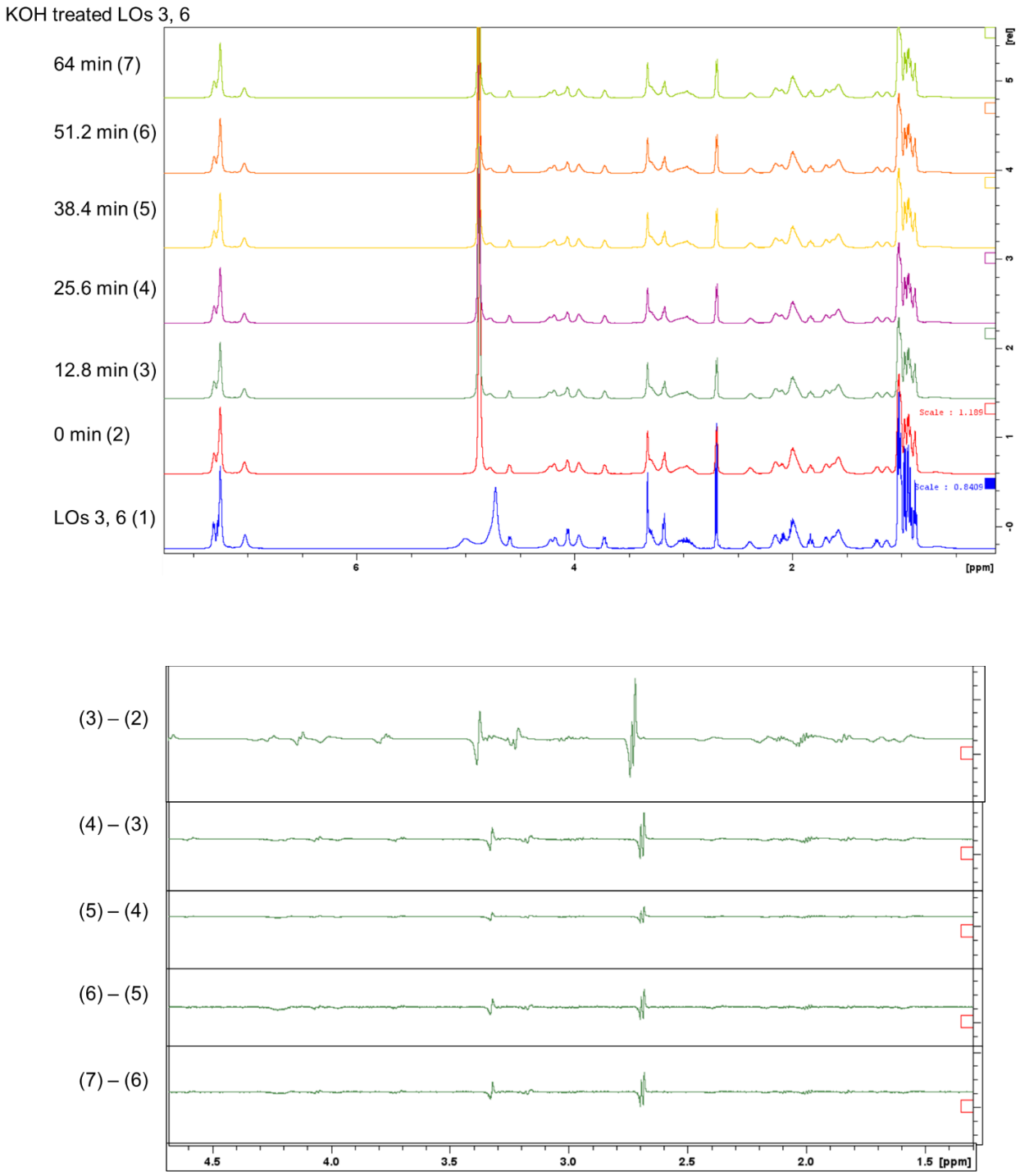

Fig. S21. (A) NMR spectra of LOs **3** and **6** mixture and KOH treated at different time intervals. (B) NMR difference spectra of KOH treated LOs **3** and **6**.

Table S1 Amino acid sequences and masses of LOs **1-13**

LO[a] **(code)**	**amino acid sequence (NαC-)**	**chemical formula**	**MW (Da)**
[1−9-NαC]-linusorb B3 (**1**)	Ile-Leu-Val-Pro-Pro-Phe-Phe-Leu-Ile	$C_{57}H_{85}N_9O_9$	1040.34
[1−9-NαC]-linusorb B2 (**2**)	Met-Leu-Ile-Pro-Pro-Phe-Phe-Val-Ile	$C_{56}H_{83}N_9O_9S$	1058.38
[1−9-NαC],[1-(*R*s,*S*s)-MetO]-linusorb B2 (**3**)	[(*R*s,*S*s)-MetO]-Leu-Ile-Pro-Pro-Phe-Phe-Val-Ile	$C_{56}H_{83}N_9O_{10}S$	1074.38
[1−9-NαC],[1-MetO_2]-linusorb B2 (**4**)	MetO_2-Leu-Ile-Pro-Pro-Phe-Phe-Val-Ile	$C_{56}H_{83}N_9O_{11}S$	1090.38
[1−8-NαC]-linusorb B1 (**5**)	Met-Leu-Val-Phe-Pro-Leu-Phe-Ile	$C_{51}H_{76}N_8O_8S$	961.26
[1−8-NαC],[1-(*R*s,*S*s)-MetO]-linusorb B1 (**6**)	[(*R*s,*S*s)-MetO]-Leu-Val-Phe-Pro-Leu-Phe-Ile	$C_{51}H_{76}N_8O_9S$	977.26
[1−8-NαC],[1-MetO_2]-linusorb B1 (**7**)	MetO_2-Leu-Val-Phe-Pro-Leu-Phe-Ile	$C_{51}H_{76}N_8O_{10}S$	993.26
[1−9-NαC], DMet-linusorb B2 (**8**)	DMet-Leu-Ile-Pro-Pro-Phe-Phe-Val-Ile	$C_{56}H_{83}N_9O_9S$	1058.38
[1−9-NαC],[1-(*R*s,*S*s)-DMetO]-linusorb B2 (**9**)	[(*R*s,*S*s)-DMetO]-Leu-Ile-Pro-Pro-Phe-Phe-Val-Ile	$C_{56}H_{83}N_9O_{10}S$	1074.38
[1−9-NαC],[1-DMetO_2]-linusorb B2 (**10**)	DMetO_2-Leu-Ile-Pro-Pro-Phe-Phe-Val-Ile	$C_{56}H_{83}N_9O_{11}S$	1090.38
[1−8-NαC], DMet-linusorb B1(**11**)	DMet-Leu-Val-Phe-Pro-Leu-Phe-Ile	$C_{51}H_{76}N_8O_8S$	961.26
[1−8-NαC],[1-(*R*s,*S*s)-DMetO]-linusorb B1 (**12**)	[(*R*s,*S*s)-DMetO]-Leu-Val-Phe-Pro-Leu-Phe-Ile	$C_{51}H_{76}N_8O_9S$	977.26
[1−8-NαC],[1-DMetO_2]-linusorb B1 (**13**)	DMetO_2-Leu-Val-Phe-Pro-Leu-Phe-Ile	$C_{51}H_{76}N_8O_{10}S$	993.26