

Electronic Supplementary Material (ESI) for New Journal of Chemistry.
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Supporting Information

Phototransformation-Pattern of Antiplatelet Drug Tirofiban in Aqueous

Solution, Relevant to Drug Delivery and Storage.

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Table S1. Relative retention times (rRTs), accurate masses with errors, elemental compositions, H/D exchange and MSⁿ product ions of the photoproducts.

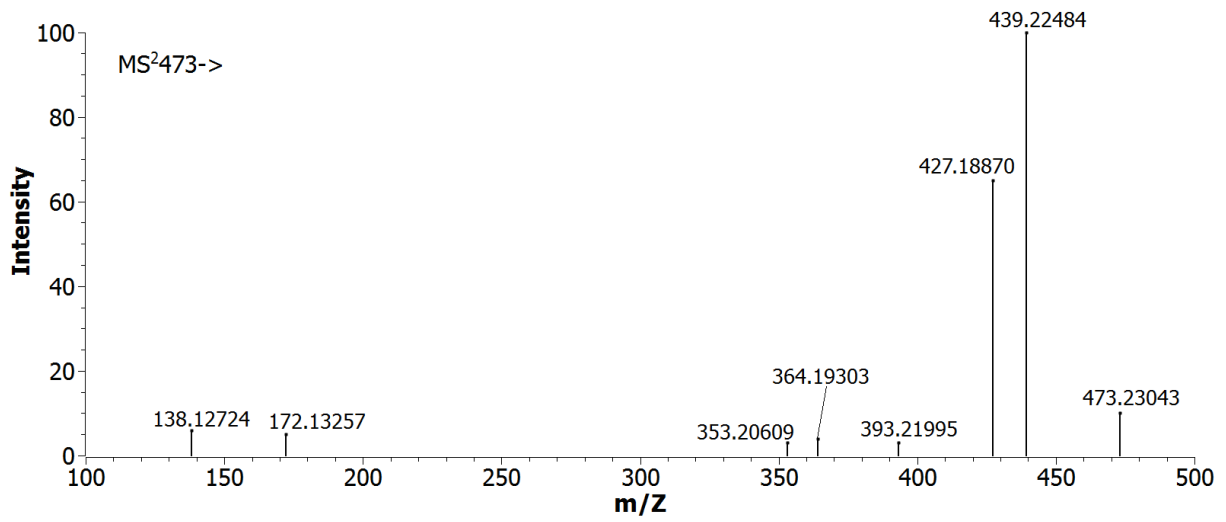
Precursor ion (number of labile hydrogens using H/D exchange)	MS ⁿ mode	Best possible elemental formulae	Theoretical mass m/z	Measured Accurate mass m/z	Relative error (ppm)	Relative retention time (Tirofiban's retention time : 8.5 min)
PD-1 (6)	Precursor ion	C ₂₂ H ₃₇ N ₂ O ₇ S ⁺	473.23160	473.23043	-2.4724	0.4
	MS ² (473->)	C ₂₂ H ₃₅ N ₂ O ₅ S ⁺	439.22612	439.22484	-2.9142	
	MS ² (473->)	C ₂₀ H ₃₁ N ₂ O ₆ S ⁺	427.18973	427.18870	-2.4111	
	MS ² (473->)	C ₂₁ H ₃₃ N ₂ O ₃ S ⁺	393.22064	393.21995	-1.7547	
	MS ² (473->)	C ₁₈ H ₂₉ N ₂ O ₅ ⁺	353.20710	353.20609	-2.8595	
	MS ² (473->)	C ₂₀ H ₃₀ NO ₃ S ⁺	364.19409	364.19303	-2.9105	
	MS ² (473->)	C ₉ H ₁₈ NO ₂ ⁺	172.13321	172.13257	-3.7181	
	MS ² (473->)	C ₉ H ₁₆ N ⁺	138.12773	138.12724	-3.5474	
PD-2 (5)	Precursor ion	C ₂₂ H ₃₇ N ₂ O ₆ S ⁺	457.23668	457.23549	-2.6026	0.48
	MS ² (457->)	C ₂₁ H ₃₃ N ₂ O ₃ S ⁺	393.22064	393.22013	-1.2970	
	MS ² (457->)	C ₂₀ H ₃₀ NO ₃ S ⁺	364.19409	364.1931	-2.7183	
	MS ² (457->)	C ₁₈ H ₂₉ N ₂ O ₄ ⁺	337.21218	337.21179	-1.1565	
	MS ² (457->)	C ₁₇ H ₂₆ NO ₃ ⁺	292.19072	292.18995	-2.6353	
	MS ² (457->)	C ₁₇ H ₂₄ NO ₂ ⁺	274.18016	274.17983	-1.2036	
	MS ² (457->)	C ₉ H ₁₈ NO ⁺	156.13829	156.13796	-2.1135	

	MS ² (457->)	C ₉ H ₁₆ N ⁺	138.12773	138.12711	-4.4886	
	MS ² (457->)	C ₈ H ₁₃ ⁺	109.10118	109.10065	-4.8579	
PD-3 (5)	Precursor ion	C ₂₂ H ₃₅ N ₂ O ₆ S ⁺	455.22103	455.21974	-2.8338	0.51
	MS ² (455->)	C ₂₂ H ₃₃ N ₂ O ₅ S ⁺	437.21047	437.20997	-1.1436	
	MS ² (455->)	C ₂₁ H ₃₃ N ₂ O ₄ S ⁺	409.21555	409.21429	-3.0791	
	MS ² (455->)	C ₁₈ H ₂₇ N ₂ O ₄ ⁺	335.19653	335.19602	-1.5215	
	MS ² (455->)	C ₁₈ H ₂₅ N ₂ O ₃ ⁺	317.18597	317.18556	-1.2926	
	MS ² (455->)	C ₁₇ H ₂₄ NO ₃ ⁺	290.17507	290.17471	-1.2406	
	MS ² (455->)	C ₉ H ₁₆ NO ⁺	154.12264	154.12214	-3.2442	
	MS ² (455->)	C ₉ H ₁₄ N ⁺	136.11208	136.11188	-1.4694	
PD-4 (6)	Precursor ion	C ₂₂ H ₃₇ N ₂ O ₇ S ⁺	473.23160	473.23056	-2.1977	0.53
	MS ² (473->)	C ₂₂ H ₃₅ N ₂ O ₆ S ⁺	455.22103	455.21989	-2.5043	
	MS ² (473->)	C ₂₂ H ₃₃ N ₂ O ₅ S ⁺	437.21047	437.20913	-3.0649	
	MS ² (473->)	C ₂₁ H ₃₅ N ₂ O ₅ S ⁺	427.22612	427.22496	-2.7152	
	MS ² (473->)	C ₂₁ H ₃₃ N ₂ O ₄ S ⁺	409.21755	409.21652	-2.5170	
	MS ² (473->)	C ₂₁ H ₃₃ N ₂ O ₃ S ⁺	393.22064	393.21985	-2.0091	
	MS ² (473->)	C ₁₈ H ₂₉ N ₂ O ₅ ⁺	353.20710	353.20593	-3.3125	
	MS ² (473->)	C ₁₇ H ₂₇ NO ₃ ⁺	307.20162	307.20128	-1.1068	
	MS ² (473->)	C ₁₇ H ₂₅ N ₂ O ₂ ⁺	289.19105	289.19033	-2.4897	
	MS ³ (473->289->)	C ₁₆ H ₂₂ NO ₂ ⁺	260.16451	260.16409	-1.6144	
	MS ³ (473->289->)	C ₁₄ H ₂₀ NO ₂ ⁺	234.14886	234.14826	-2.5625	
	MS ³ (473->289->)	C ₉ H ₁₈ NO ⁺	156.13829	156.13756	-4.6753	
	MS ³ (473->289->)	C ₈ H ₁₀ NO ⁺	152.07060	152.06989	-4.6689	
	MS ³ (473->289->)	C ₉ H ₁₆ N ⁺	138.12773	138.12731	-3.0407	
PD-5 (5)	Precursor ion	C ₂₂ H ₃₇ N ₂ O ₆ S ⁺	457.23668	457.23510	-3.4555	0.56
	MS ² (457->)	C ₂₂ H ₃₅ N ₂ O ₅ S ⁺	439.22612	439.22489	-2.8004	
	MS ² (457->)	C ₂₁ H ₃₅ N ₂ O ₃ S ⁺	395.23629	395.23517	-2.8337	
	MS ² (457->)	C ₂₁ H ₃₂ NO ₃ S ⁺	378.20974	378.20863	-2.9349	
	MS ² (457->)	C ₁₈ H ₂₉ N ₂ O ₄ ⁺	337.21218	337.21133	-2.5207	
	MS ² (457->)	C ₁₇ H ₂₆ NO ₃ ⁺	292.19072	292.19021	-1.7454	
	MS ² (457->)	C ₉ H ₁₈ N ⁺	140.14338	140.14291	-3.3537	
PD-6 (5)	Precursor ion	C ₂₁ H ₃₇ N ₂ O ₅ S ⁺	429.24177	429.24093	-1.9569	0.59
	MS ² (429->)	C ₂₁ H ₃₅ N ₂ O ₃ S ⁺	395.23629	395.23552	-1.9482	
	MS ² (429->)	C ₁₇ H ₂₆ NO ₃ ⁺	292.19072	292.18985	-2.9775	
	MS ² (429->)	C ₁₆ H ₂₄ NO ₂ ⁺	262.18016	262.17933	-3.1658	
	MS ² (429->)	C ₉ H ₁₈ N ⁺	140.14338	140.14278	-4.2813	

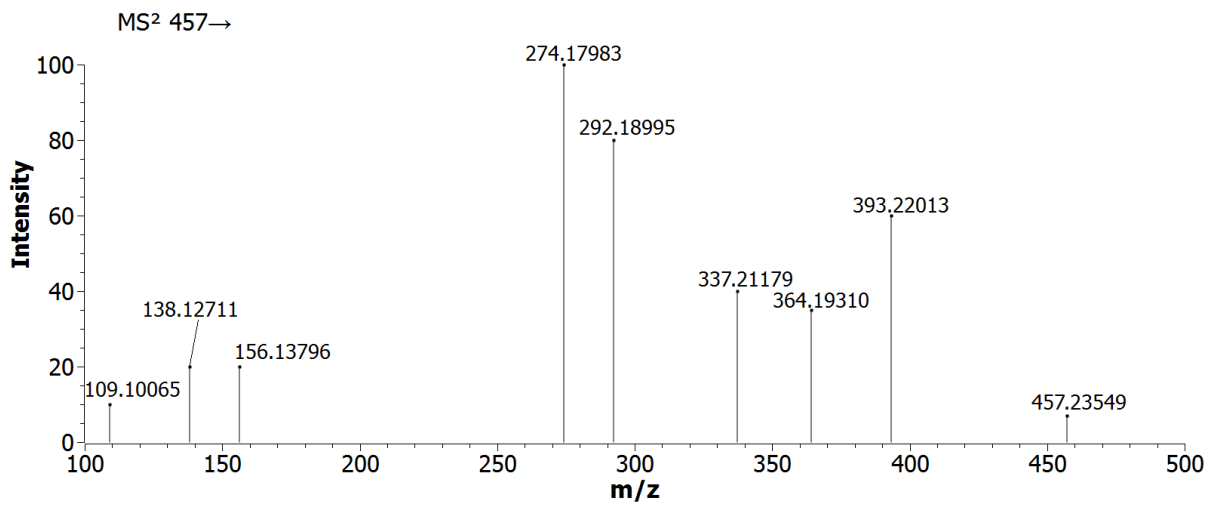
PD-7 (6)	Precursor ion	$C_{22}H_{37}N_2O_7S^+$	473.23160	473.23054	-2.2399	0.72
	MS^2 (473->)	$C_{22}H_{35}N_2O_5S^+$	439.22612	439.22490	-2.7776	
	MS^2 (473->)	$C_{21}H_{35}N_2O_5S^+$	427.22612	427.22481	-3.0663	
	MS^2 (473->)	$C_{21}H_{35}N_2O_3S^+$	395.23629	395.23513	-2.9350	
	MS^2 (473->)	$C_{18}H_{29}N_2O_5S^+$	353.20710	353.20634	-2.1517	
	MS^2 (473->)	$C_{16}H_{24}NO_2^+$	262.18016	262.17942	-2.8225	
	MS^2 (473->)	$C_9H_{18}N^+$	140.14338	140.14287	-3.6391	
PD-8 (4)	Precursor ion	$C_{22}H_{35}N_2O_6S^+$	455.22103	455.22002	-2.2187	0.74
	MS^2 (455->)	$C_{22}H_{33}N_2O_5S^+$	437.21047	437.20987	-1.3723	
	MS^2 (455->)	$C_{21}H_{33}N_2O_3S^+$	393.22064	393.21954	-2.7974	
	MS^2 (455->)	$C_{22}H_{33}N_2O_3^+$	373.24857	373.24753	-2.7863	
	MS^2 (455->)	$C_{21}H_{33}N_2O^+$	329.25874	329.25773	-3.0675	
	MS^2 (455->)	$C_{18}H_{29}N_2O_3^+$	321.21727	321.21630	-3.0198	
	MS^2 (455->)	$C_{17}H_{26}NO_2^+$	276.19581	276.19491	-3.2586	
	MS^2 (455->)	$C_{17}H_{27}N_2O^+$	275.21179	275.21097	-2.9795	
	MS^2 (455->)	$C_{17}H_{25}NO^+$	260.20089	260.19995	-3.6126	
	MS^2 (455->)	$C_9H_{18}N^+$	140.14338	140.14289	-3.4536	
PD-9 (5)	Precursor ion	$C_{22}H_{37}N_2O_6S^+$	457.23668	457.23534	-2.9306	0.89
	MS^2 (457->)	$C_{21}H_{33}N_2O_3S^+$	393.22064	393.22011	-1.3478	
	MS^2 (457->)	$C_{18}H_{28}NO_3S^+$	338.17844	338.17803	-1.2124	
	MS^2 (457->)	$C_{18}H_{29}N_2O_4^+$	337.21218	337.21163	-1.6310	
	MS^2 (457->)	$C_{17}H_{26}NO_3^+$	292.19072	292.18997	-2.5668	
	MS^2 (457->)	$C_{17}H_{24}NO_2^+$	274.18016	274.17970	-1.6777	
	MS^2 (457->)	$C_9H_{18}NO^+$	156.13829	156.13795	-2.1776	
	MS^2 (457->)	$C_9H_{16}N^+$	138.12773	138.12713	-4.3438	
PD-10 (5)	Precursor ion	$C_{22}H_{37}N_2O_6S^+$	457.23668	457.23504	-3.5868	0.9
	MS^2 (457->)	$C_{22}H_{35}N_2O_5S^+$	439.22612	439.22491	-2.7548	
	MS^2 (457->)	$C_{21}H_{35}N_2O_4S^+$	411.23120	411.23012	-2.6263	
	MS^2 (457->)	$C_{21}H_{32}NO_4S^+$	394.20466	394.20385	-2.0548	
	MS^2 (457->)	$C_{21}H_{32}NO_2^+$	330.20466	330.20418	-1.4536	
	MS^2 (457->)	$C_{18}H_{29}N_2O_3^+$	321.21727	321.21658	-2.1481	
	MS^2 (457->)	$C_{17}H_{26}NO_2^+$	276.19581	276.19506	-2.7155	
	MS^2 (457->)	$C_{17}H_{27}N_2O^+$	275.21179	275.21132	-1.7078	
	MS^2 (457->)	$C_{17}H_{25}NO^+$	260.20089	260.20021	-2.6134	
	MS^2 (457->)	$C_9H_{18}N^+$	140.14338	140.14270	-4.8522	
PD-11 (4)	Precursor ion	$C_{21}H_{37}N_2O_4S^+$	413.24685	413.24575	-2.6618	0.95

	MS ² (413->)	C ₂₁ H ₃₅ N ₂ O ₃ S ⁺	395.23629	395.23521	-2.7325	
	MS ² (413->)	C ₁₇ H ₂₆ NO ₂ ⁺	276.19581	276.19517	-2.3172	
	MS ² (413->)	C ₉ H ₁₈ N ⁺	140.14338	140.14287	-3.6391	
PD-12 (6)	Precursor ion	C ₂₂ H ₃₇ N ₂ O ₇ S ⁺	473.23160	473.23081	-1.6694	0.97
	MS ² (473->)	C ₂₂ H ₃₅ N ₂ O ₆ S ⁺	455.22103	455.22041	-1.3620	
	MS ² (473->)	C ₂₂ H ₃₃ N ₂ O ₃ ⁺	437.21047	437.20925	-2.7904	
	MS ² (473->)	C ₂₁ H ₃₃ N ₂ O ₃ S ⁺	393.22064	393.21983	-2.0599	
	MS ² (473->)	C ₂₂ H ₃₃ N ₂ O ₃ ⁺	373.24857	373.24793	-1.7147	
	MS ² (473->)	C ₂₁ H ₃₃ N ₂ O ⁺	329.25874	329.25790	-2.5512	
	MS ² (473->)	C ₁₈ H ₂₉ N ₂ O ₃ ⁺	321.21727	321.21654	-2.2726	
	MS ² (473->)	C ₁₇ H ₂₆ NO ₂ ⁺	276.19581	276.19532	-1.7741	
	MS ² (473->)	C ₁₇ H ₂₇ N ₂ O ⁺	275.21179	275.21093	-3.1249	
	MS ² (473->)	C ₁₇ H ₂₅ NO ⁺	260.20089	260.19973	-4.4581	
	MS ² (473->)	C ₉ H ₁₈ N ⁺	140.14338	140.14270	-4.8522	

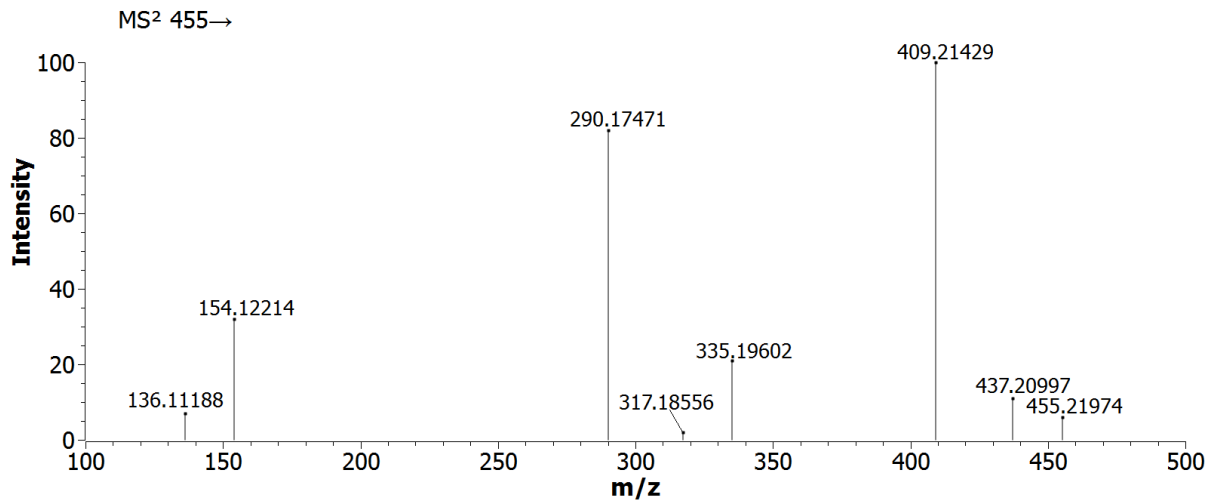
PD-1



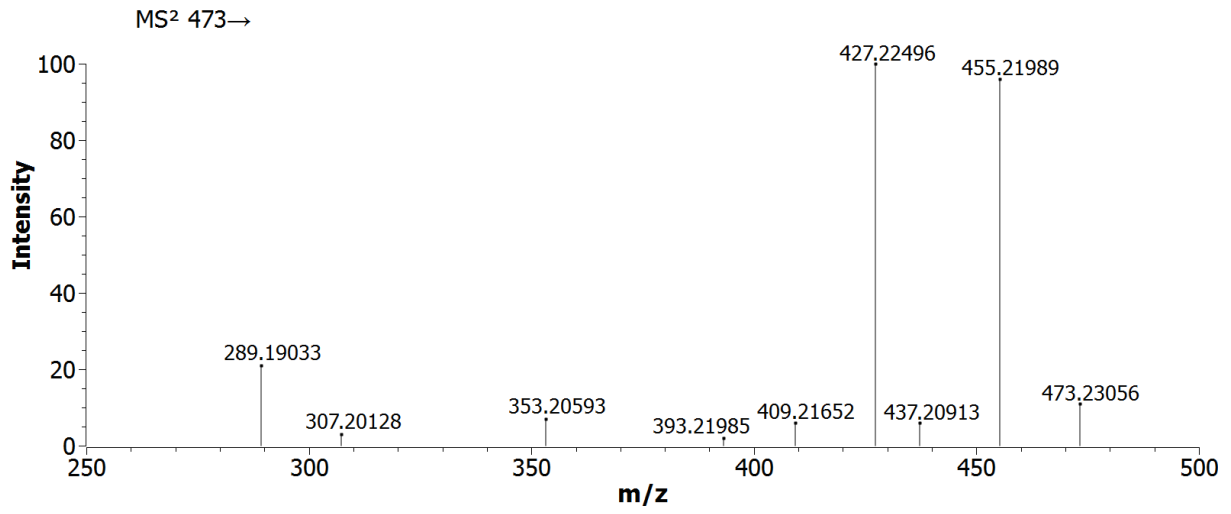
PD-2



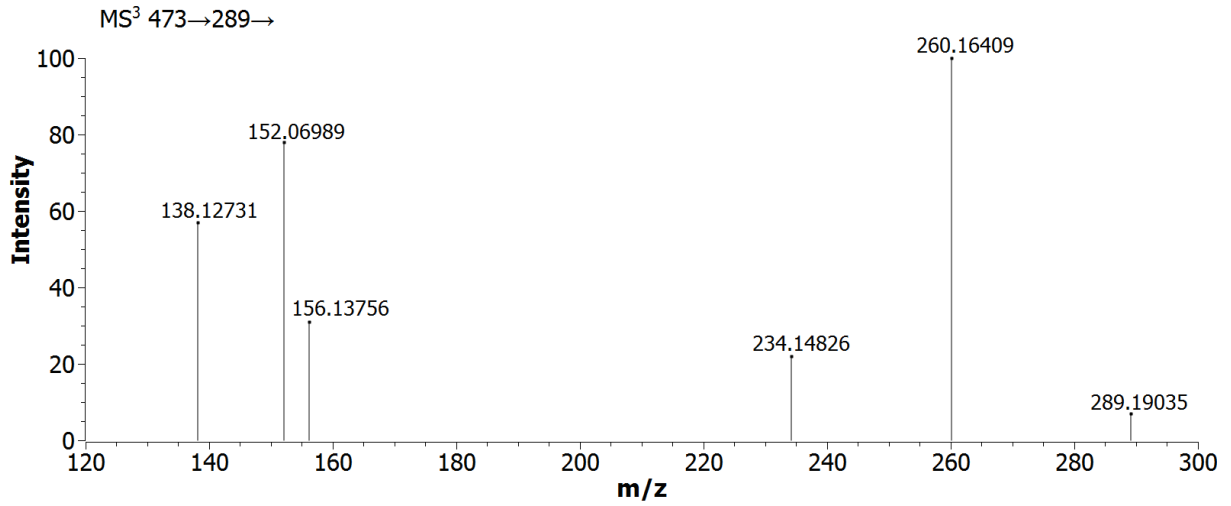
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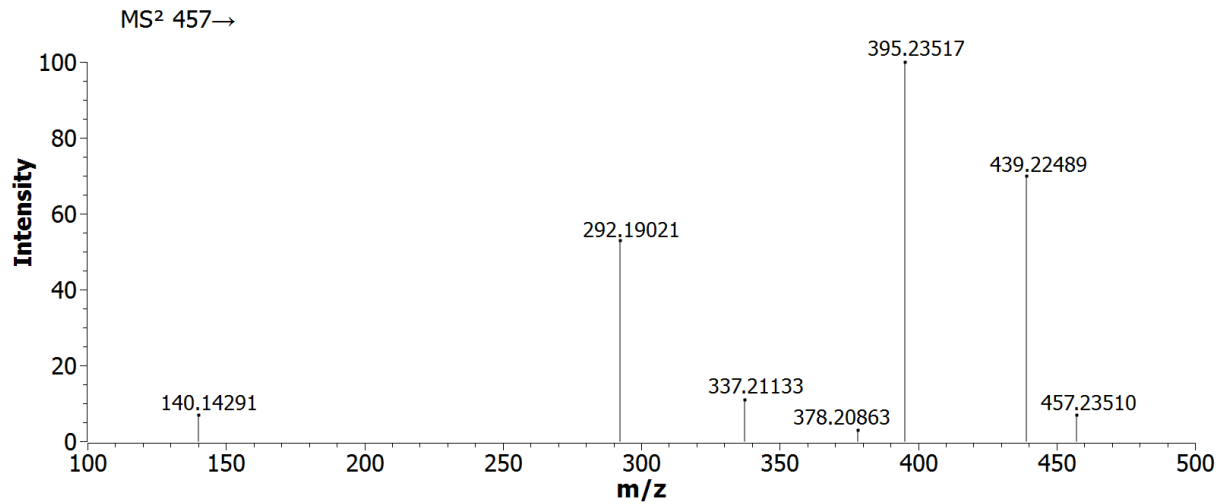
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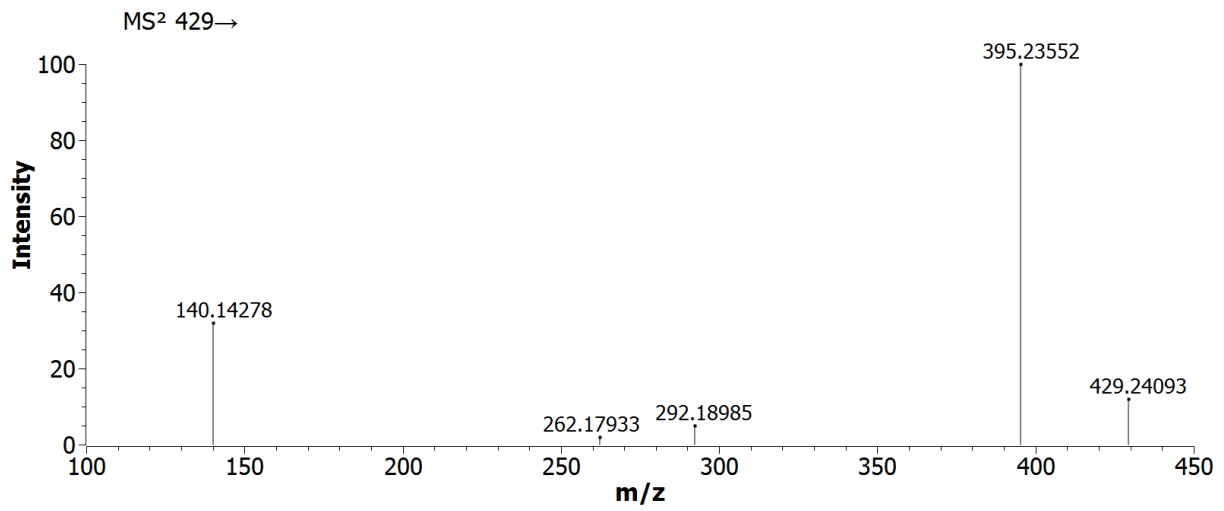
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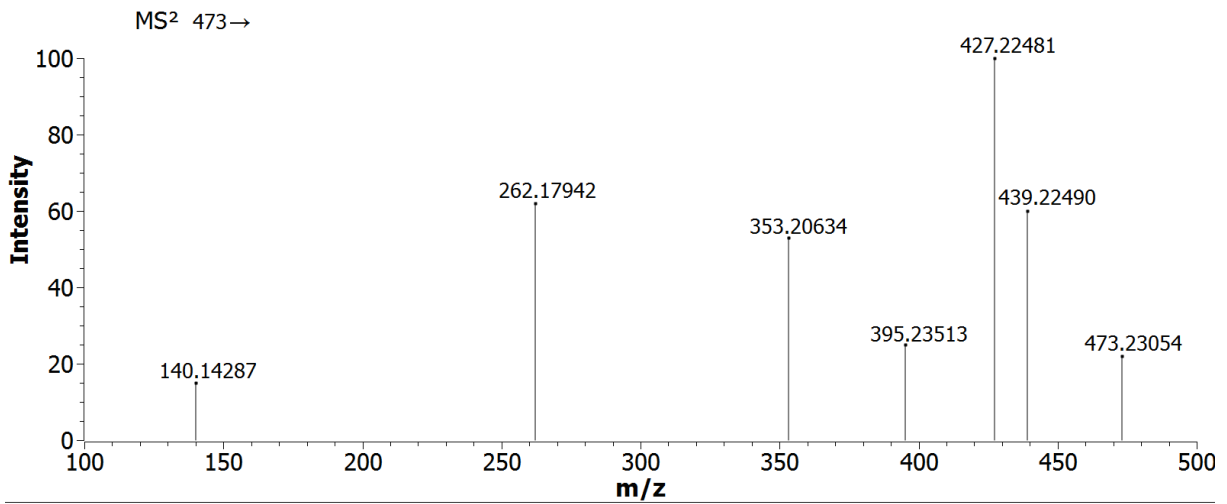
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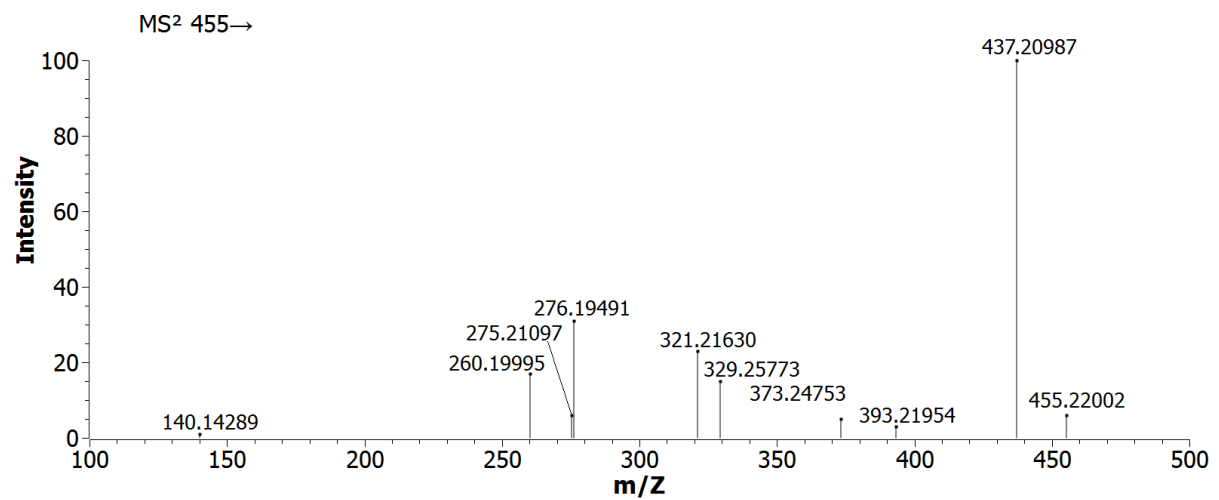
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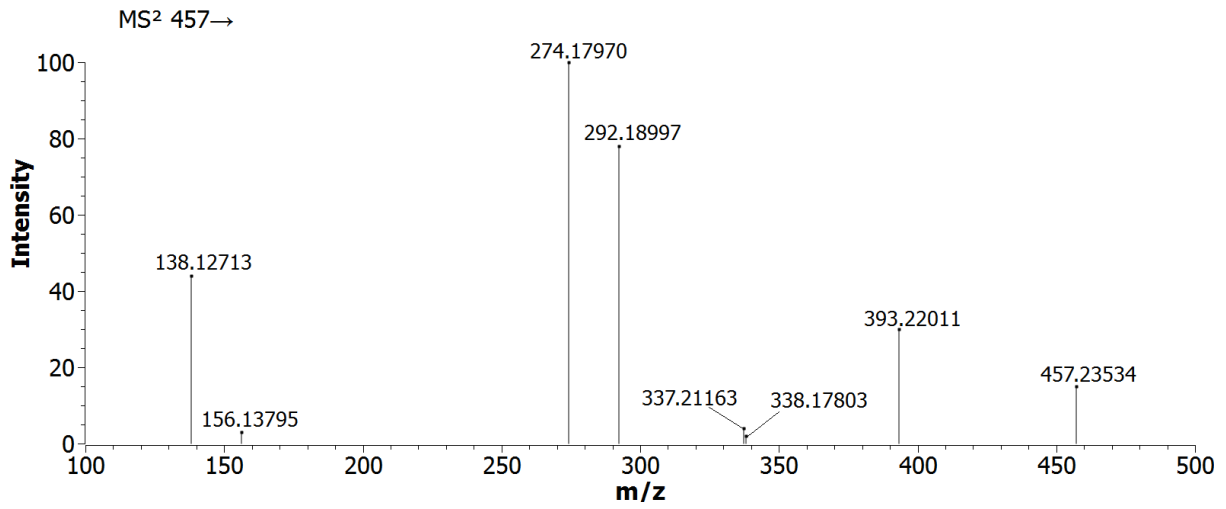
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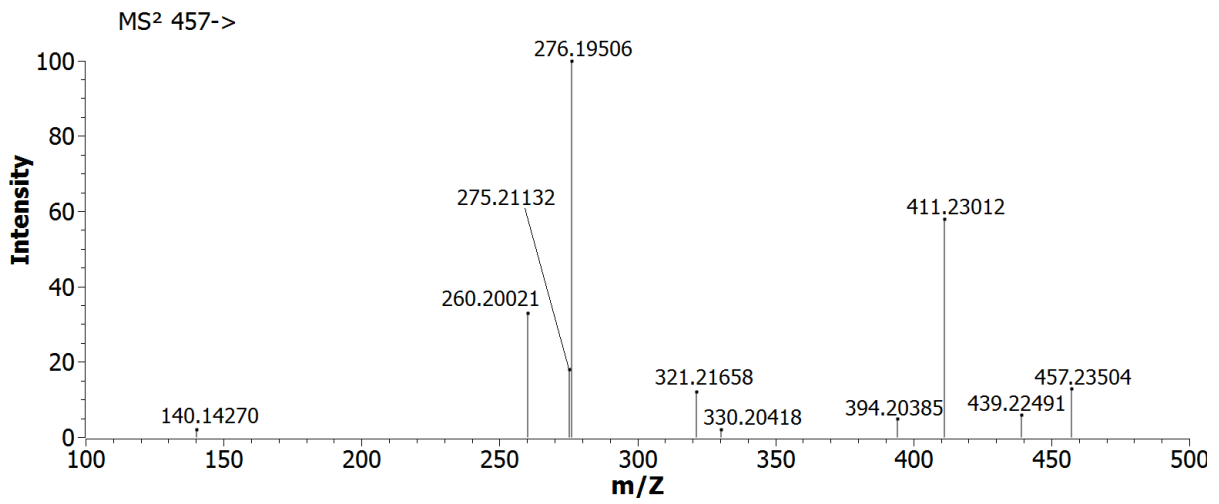
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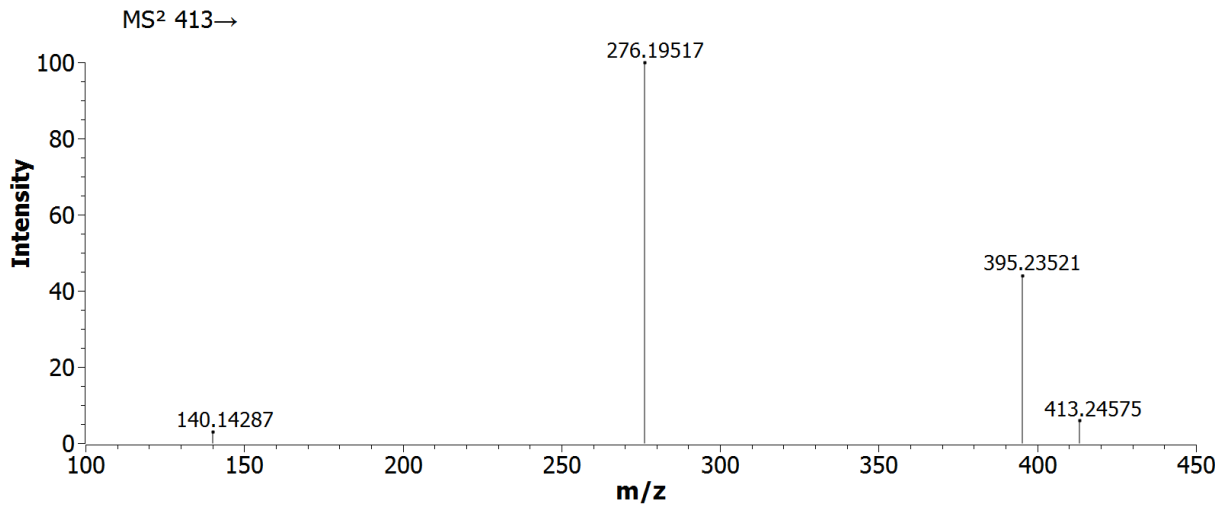
PD-9



PD-10



PD-11



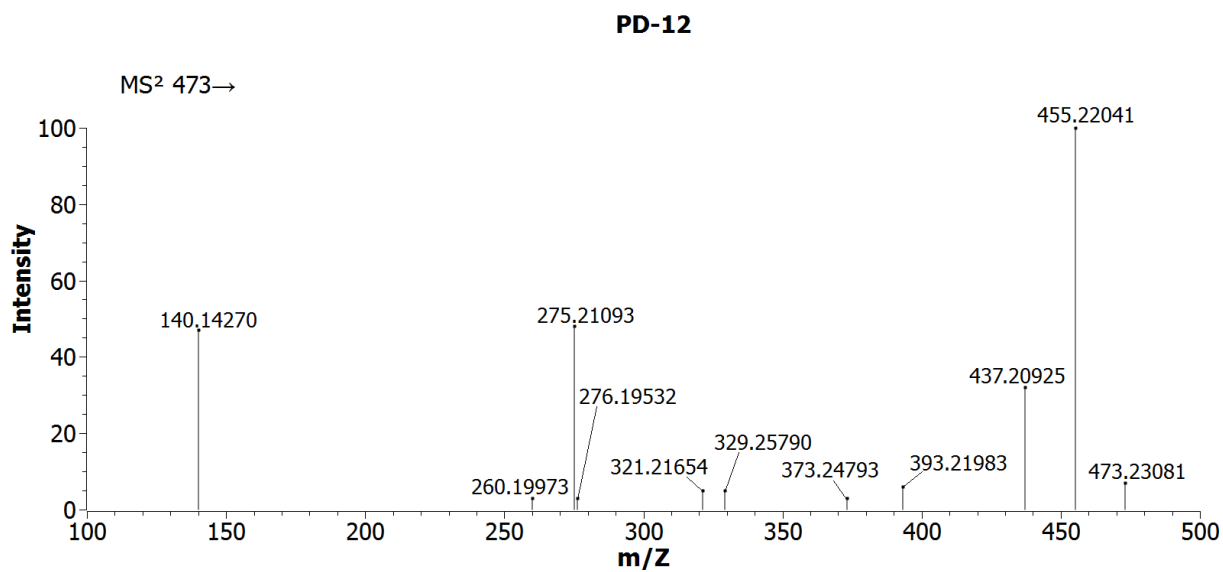


Figure S2. Representative LC-ESI/MS² spectra of photoproducts (PD-1 – PD-12) and representative LC-ESI/MS³ spectrum of PD-4.