

**Table S1.** Nontargeted analysis of non-volatile compounds during endogenous enzyme reaction stage.

$t_R$ (min)	$m/z$ (-MS)	MS <sup>n</sup> (-MS)	VIP		Identification
			Enzymatic reaction	Nonenzymatic reaction	
6.476	883.137	169.01,289.07,441.08	1.98744	/	ECG/CG derivatives*
5.961	731.126	407.08,289.07,125.02	1.95325	2.07496	Oolongtheanin*
9.836	293.213	275.2,293.21,171.1	1.91885	/	(2'E,4'Z,8E)-Colneleic acid*
5.811	937.146	169.01,309.04,125.02	1.87739	1.79077	Punicafolin*
5.81	916.168	169.01,305.07,125.02	1.87588	/	ECG/CG derivatives*
8.157	713.117	125.02,169.01,321.08	1.8335	/	ECG/CG derivatives*
4.894	441.042	305.07,137.02,125.02	1.82424	/	ECG/CG
4.895	305.067	125.02,167.03,179.03	1.82369	1.97517	EGC
2.074	169.014	169.01,125.02	1.82061	/	GA
8.129	867.143	169.01,125.02,389.07	1.80216	1.86159	Theaflavin-3, 3'-gallate
7.926	563.120	241.05,125.02,269.05	/	2.49988	Theaflavin
8.08	715.132	125.02,169.01,321.076,281.045	/	2.10356	Theaflavin-3-gallate
4.894	441.04	305.06,125.02,327.05	/	2.00858	EGC derivatives*
5.81	916.168	169.014,305.07	/	1.77857	EGCG derivatives*
0.958	191.051	93.03,85.03,59.01	/	1.64008	Quinic acid*

\*: Represents compounds that have not been validated by standard.