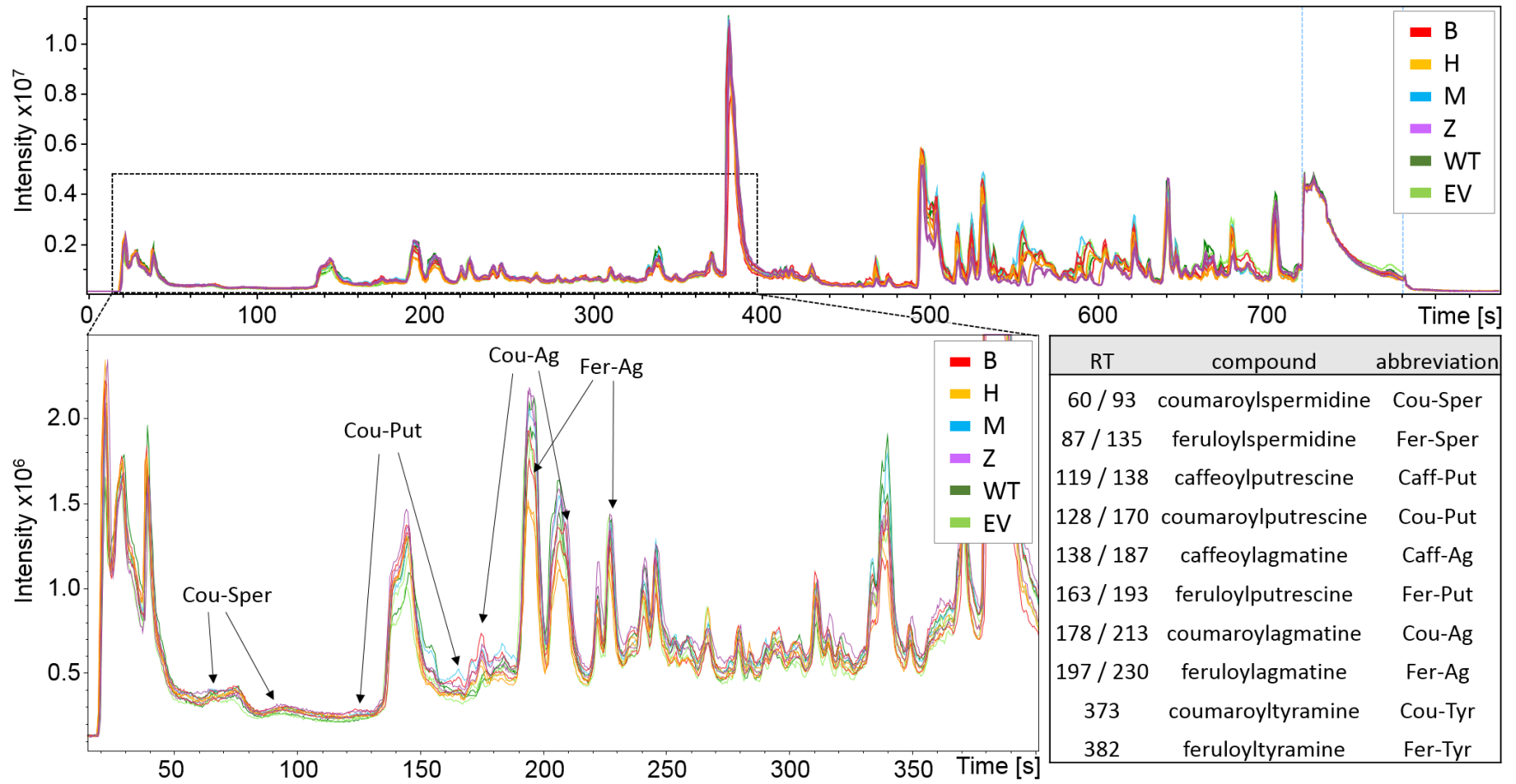


**Supplemental Figure 1.** Purification of Recombinant ACT.

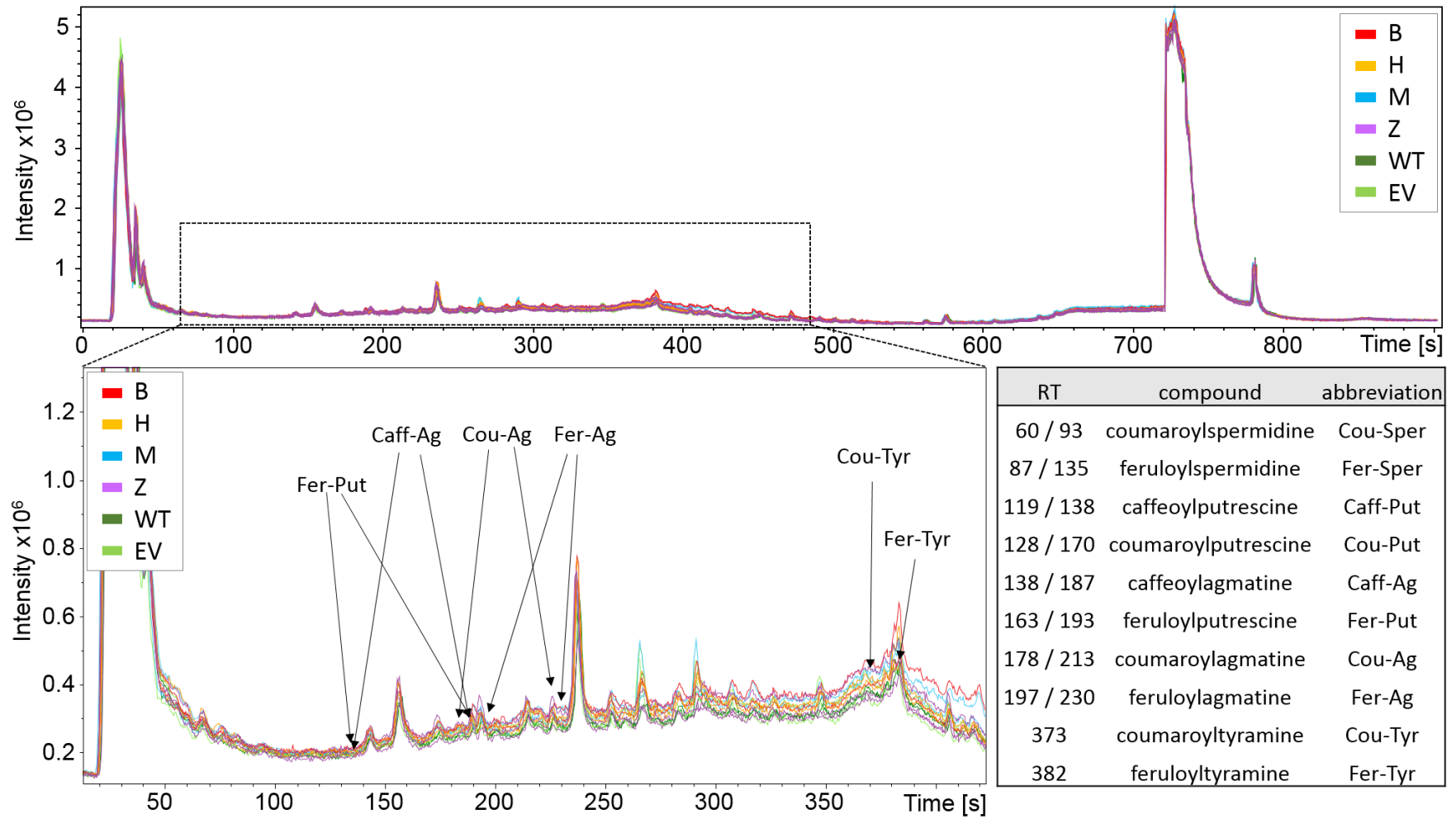
Polyacrylamide gel of cell lysate (lane 1), and elution fractions with increasing imidazole concentrations (lanes 2-4) and size marker (M).

The arrow marks the position of the purified ACT protein of ~51 kD.

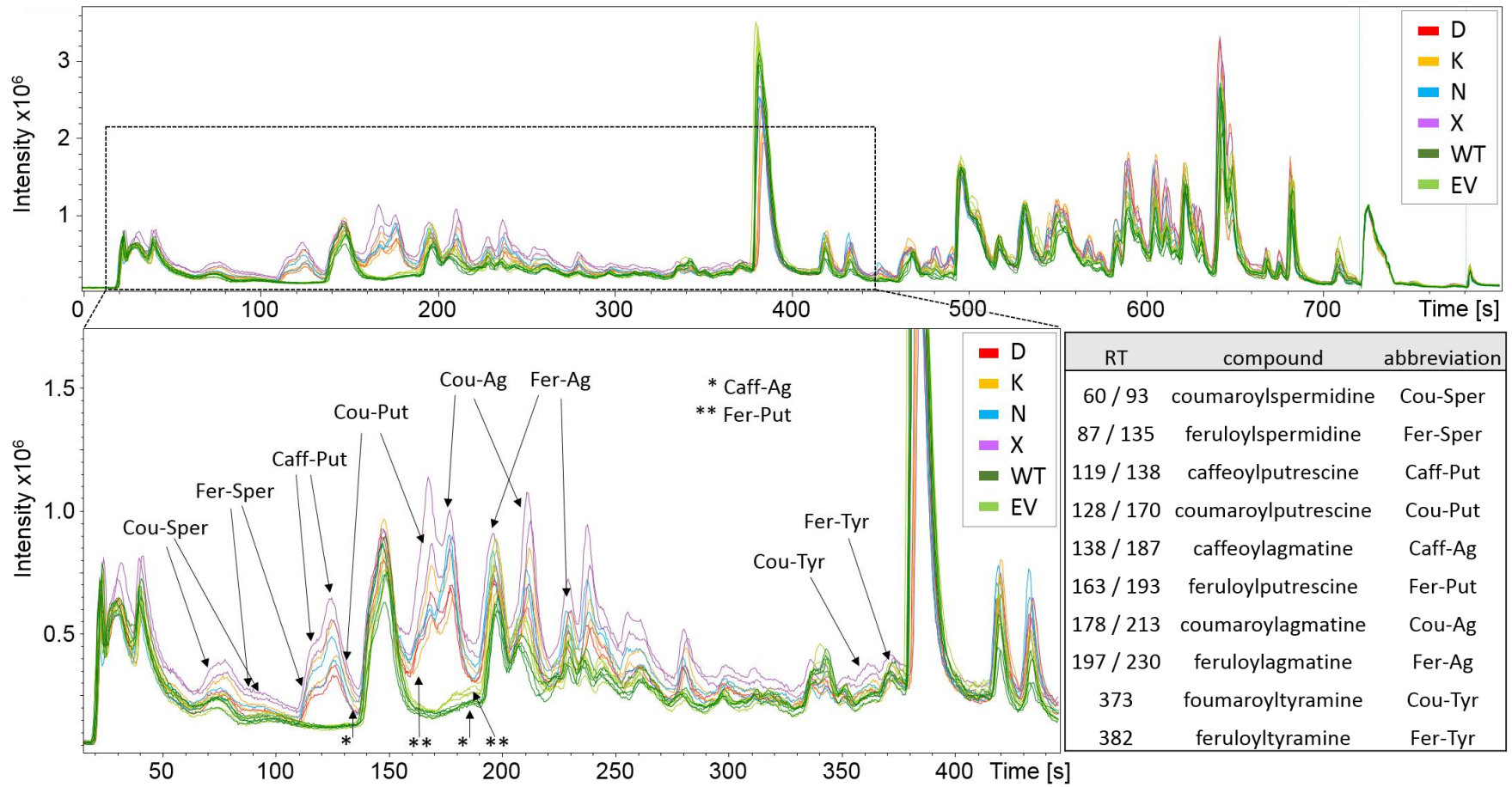
A



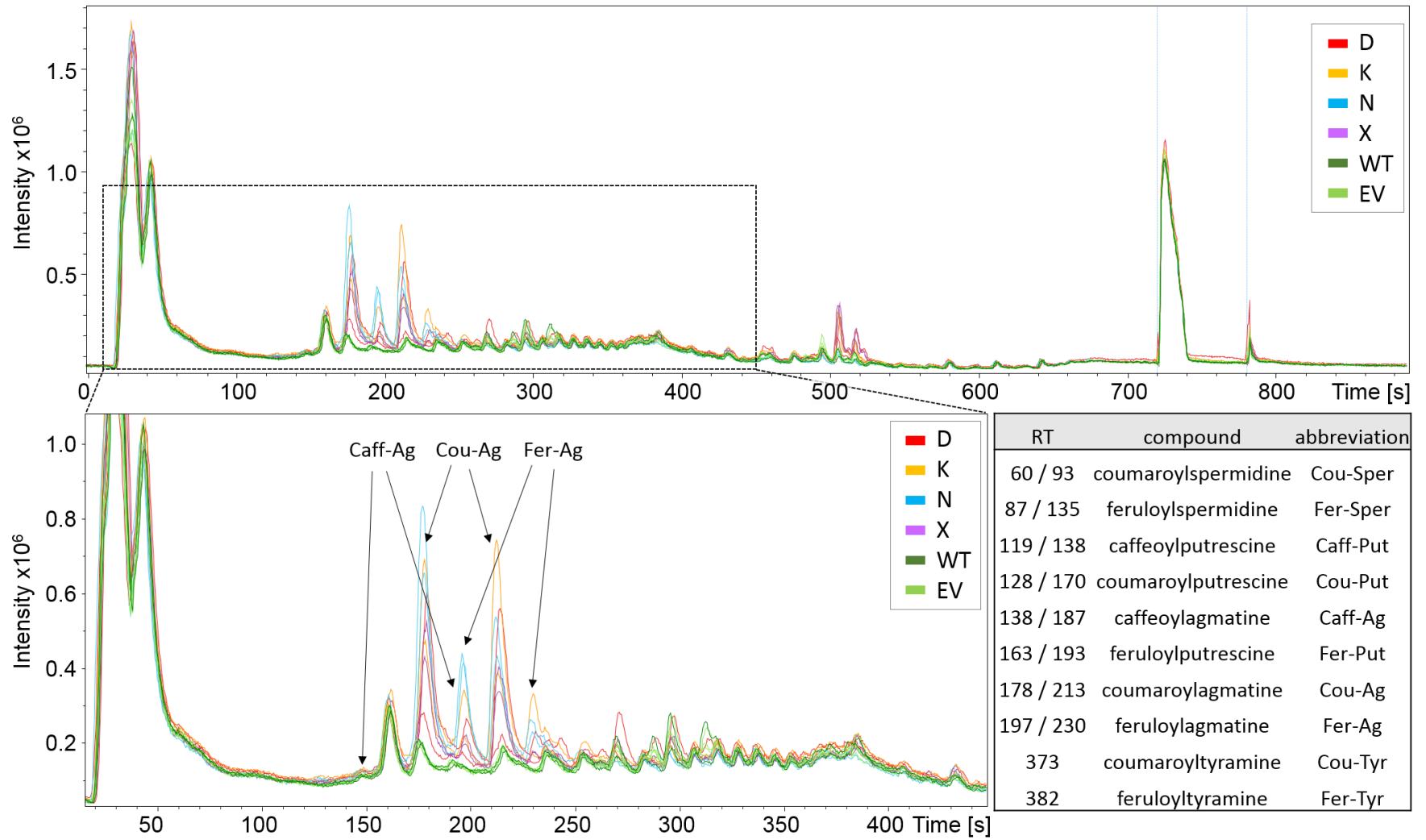
**B**



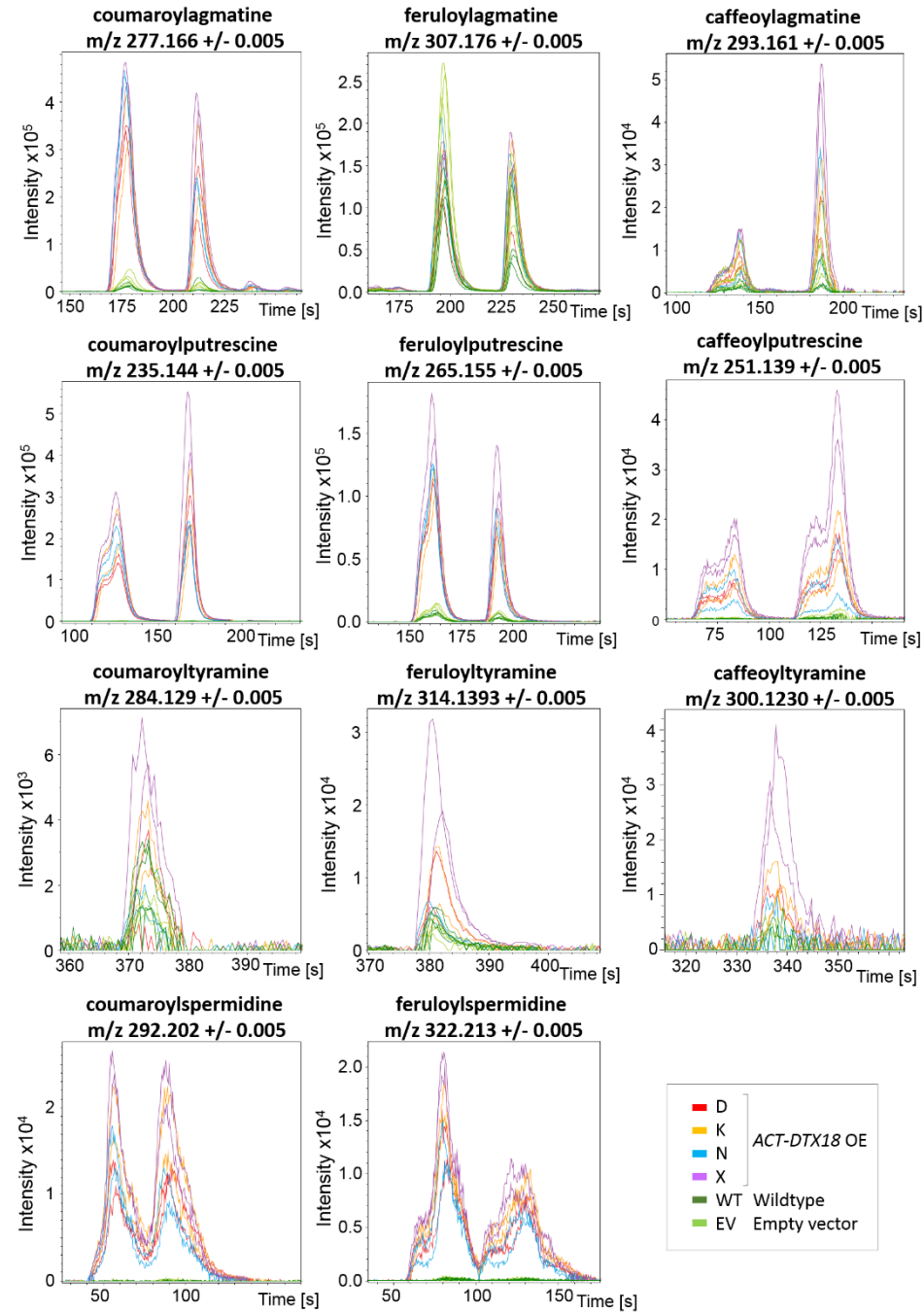
C



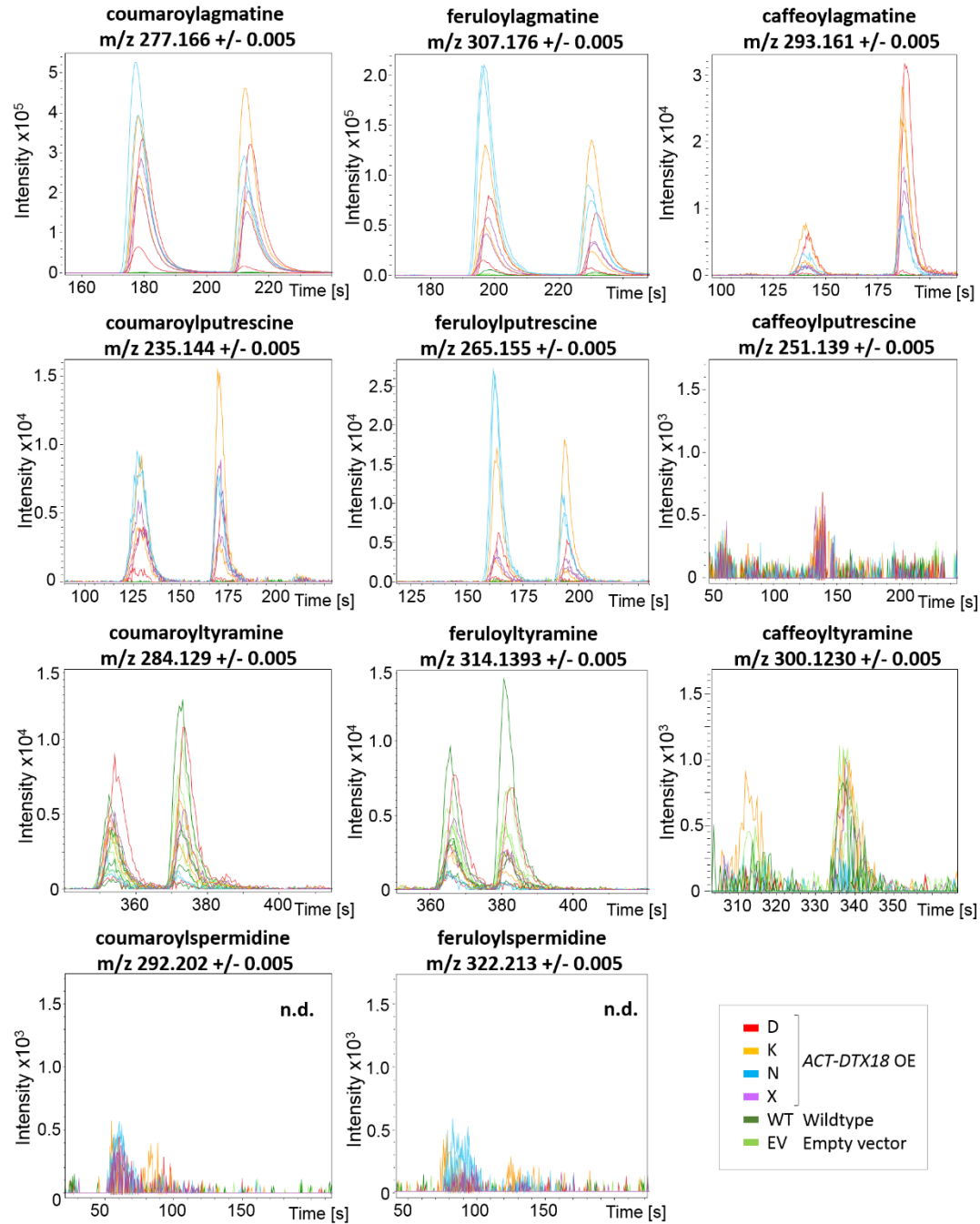
D



**E**



F



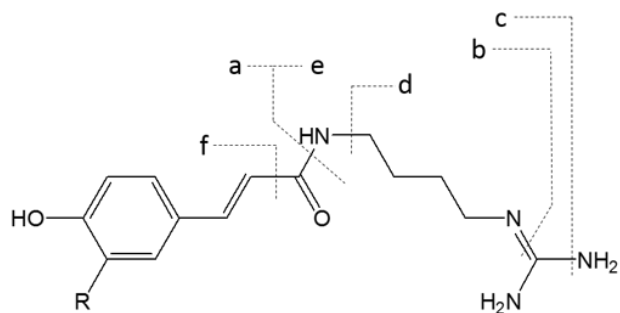
**Supplemental Figure 2** HPLC Chromatograms of Leaves and Droplets of Control and *ACT* and *ACT-DTX18*-Expressing Potato Plants.

**A,B,C,D:** Representative HPLC-MS total ion chromatograms of plant extracts of leaf disks or inoculum from control (wild-type and empty vector) and transgenic plants one day after infection by *P. infestans*. **A:** leaf disks of control and *ACT*-expressing potato plants (lines B, H, M, Z) **B:** inoculum of control and *ACT*-expressing potato plants (lines B, H, M, Z), **C:** leaf disks of control and *ACT-DTX18*-expressing plants (lines D, K, N, X), **D:** inoculum of control and *ACT-DTX18*-expressing plants (lines D, K, N, X). **E,F:** HPLC-MS extracted ion chromatograms of leaf disks (**E**) or inoculum (**F**) from *Phytophthora infestans*-infected *ACT-DTX18*-expressing potato plants, wild-type plants and empty vector controls. Two representative EICs are shown for each plant line.

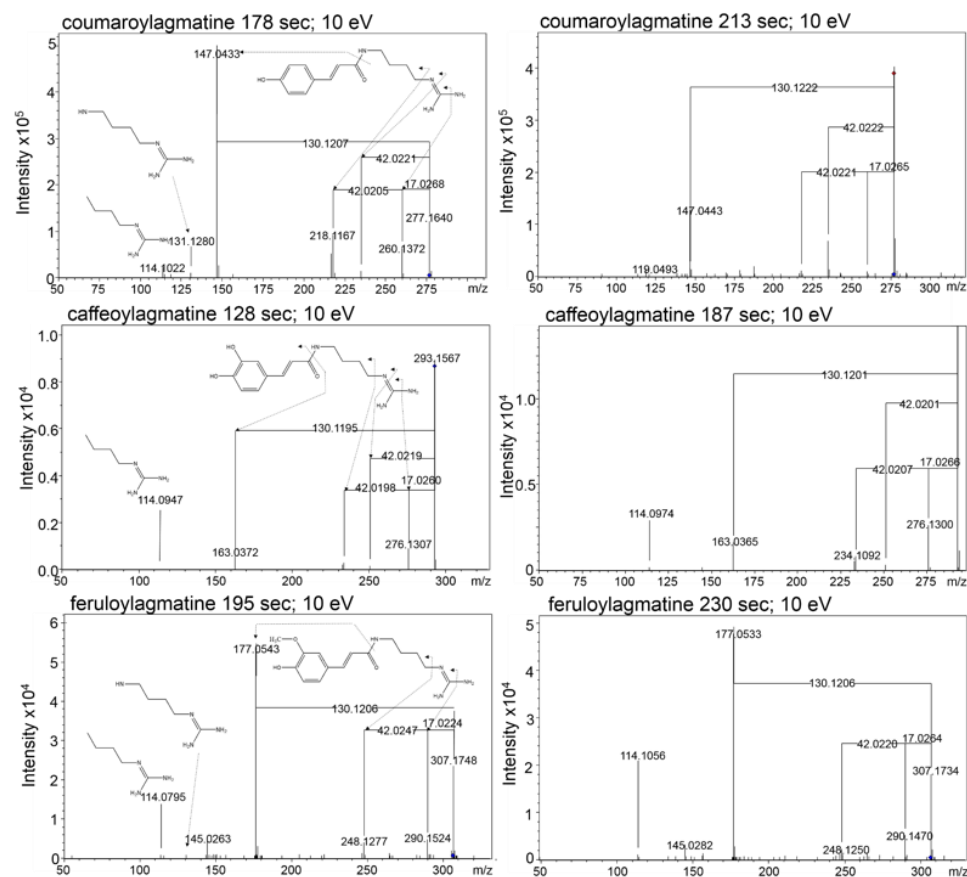
A

RT	compound	formula	m/z calc	m/z observed in MS	ppm mismatch	Collision energy [eV]	R	m/z fragments
178	coumaroylagmatine	C <sub>14</sub> H <sub>20</sub> N <sub>4</sub> O <sub>2</sub>	277.1659	277.1664	1.80	10; 20	H	147.043 (a); 218.118 (b); 260.137 (c); 114.103 (d); 131.128 (e); 119.0453 (f); 235.144
213	coumaroylagmatine	C <sub>14</sub> H <sub>20</sub> N <sub>4</sub> O <sub>2</sub>	277.1659	277.1664	1.80	10; 20	H	147.044 (a); 218.117 (b); 260.137(c); 114.102 (d); 119.0453 (f); 131.128 (e); 235.142
138	caffeoylagmatine	C <sub>14</sub> H <sub>20</sub> N <sub>4</sub> O <sub>3</sub>	293.1608	293.1609	0.28	10 ; 20	OH	163.0372 (a); 234.111 (b); 276.131 (c); 114.1022 (d); 131.127 (e) 135.0408 (f); 251.145
187	caffeoylagmatine	C <sub>14</sub> H <sub>20</sub> N <sub>4</sub> O <sub>3</sub>	293.1608	293.161	0.62	10 ; 20	OH	163.037 (a); 234.109 (b); 276.130 (c); 114.1022 (d); 131.129 (e)135.0408 (f); 251.145
197	feruloylagmatine	C <sub>15</sub> H <sub>22</sub> N <sub>4</sub> O <sub>3</sub>	307.1765	307.1769	1.41	10; 20	O-CH <sub>3</sub>	177.053 (a); 248.125 (b); 290.147 (c); 114.080 (d); 131.128 (e); 149.0572 (f)
230	feruloylagmatine	C <sub>15</sub> H <sub>22</sub> N <sub>4</sub> O <sub>3</sub>	307.1765	307.1767	0.76	10; 20	O-CH <sub>3</sub>	177.054 (a); 248.0245 (b); 290.152 (c); 114.1056 (d); 131.127 (e); 149.0573 (f)

- (a) coumaroyl- / caffeoyl- / feruloyl- core, neutral loss of agmatine  
 (b) neutral loss of agmatine head group  
 (c) neutral loss of NH<sub>3</sub>  
 (d) agmatine fragment  
 (e) agmatine  
 (f) coumaroyl- / caffeoyl- / feruloyl- core fragment



- 1) coumaroylagmatine: R = -H  
 2) caffeoylagmatine: R = -OH  
 3) feruloylagmatine: R = -O-CH<sub>3</sub>

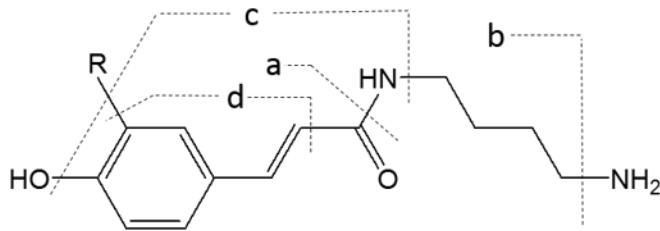




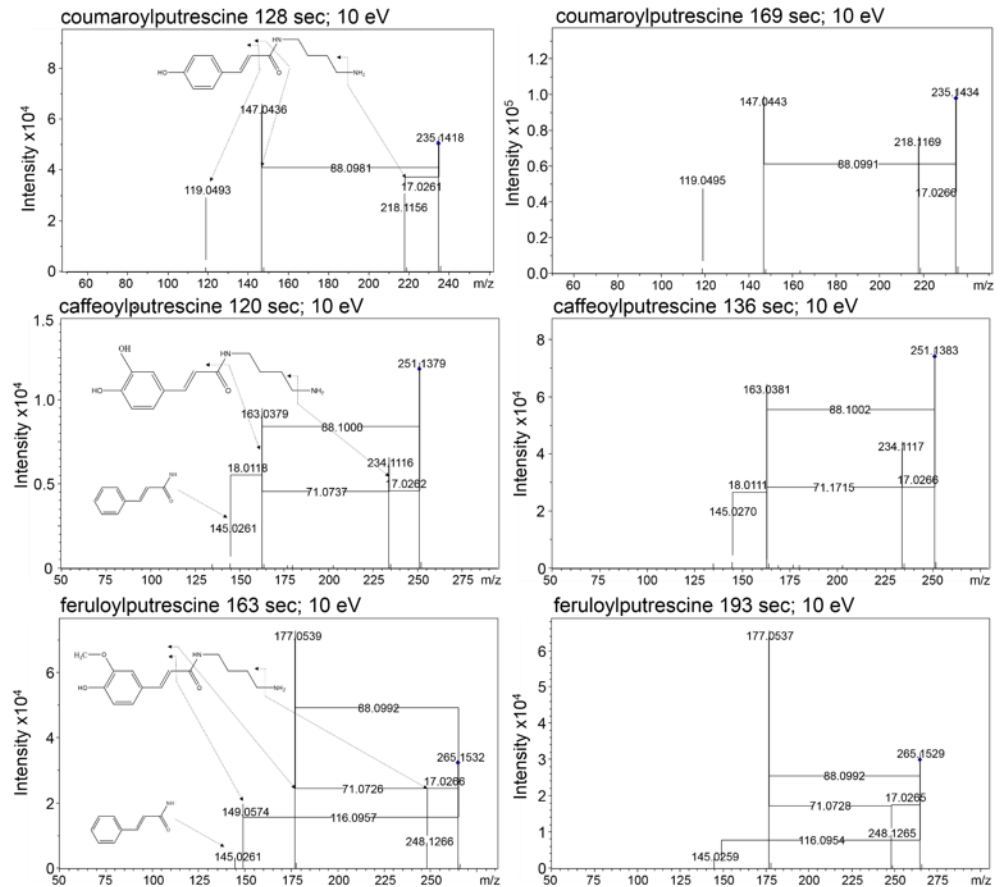
**B**

RT	compound	formula	m/z calc	m/z observed in MS	ppm mismatch	Collision energy [eV]	R	m/z fragments
128	coumaroylputrescine	C <sub>13</sub> H <sub>18</sub> N <sub>2</sub> O <sub>2</sub>	235.1441	235.1444	1.26	10 ; 20	H	147.044 (a); 218.118 (b); 119.049 (d)
170	coumaroylputrescine	C <sub>13</sub> H <sub>18</sub> N <sub>2</sub> O <sub>2</sub>	235.1441	235.1444	1.26	10 ; 20	H	147.044 (a); 218.118 (b); 119.049 (d)
119	caffeoylputrescine	C <sub>13</sub> H <sub>18</sub> N <sub>2</sub> O <sub>3</sub>	251.1391	251.1393	1.12	10 ; 20	OH	163.038 (a); 234.112 (b); 145.027 (c)
138	caffeoylputrescine	C <sub>13</sub> H <sub>18</sub> N <sub>2</sub> O <sub>3</sub>	251.1391	251.1392	0.72	10 ; 20	OH	163.038 (a); 234.116 (b); 145.026 (c)
163	feruloylputrescine	C <sub>14</sub> H <sub>20</sub> N <sub>2</sub> O <sub>3</sub>	265.1547	265.155	1.25	10 ; 20	O-CH <sub>3</sub>	177.054 (a); 248.127 (b); 149.057 (d); 145.026 (c)
193	feruloylputrescine	C <sub>14</sub> H <sub>20</sub> N <sub>2</sub> O <sub>3</sub>	265.1547	265.155	1.25	10 ; 20	O-CH <sub>3</sub>	177.054 (a); 248.127 (b); 149.058 (d); 145.026 (c)

- a) coumaroyl- / caffeoyl- / feruloyl- core, neutral loss of putrescine  
 (b) neutral loss of NH<sub>3</sub>  
 (c) neutral loss of H<sub>2</sub>O from coumaroyl-core  
 (d) neutral loss of carboxyl group from HCA core



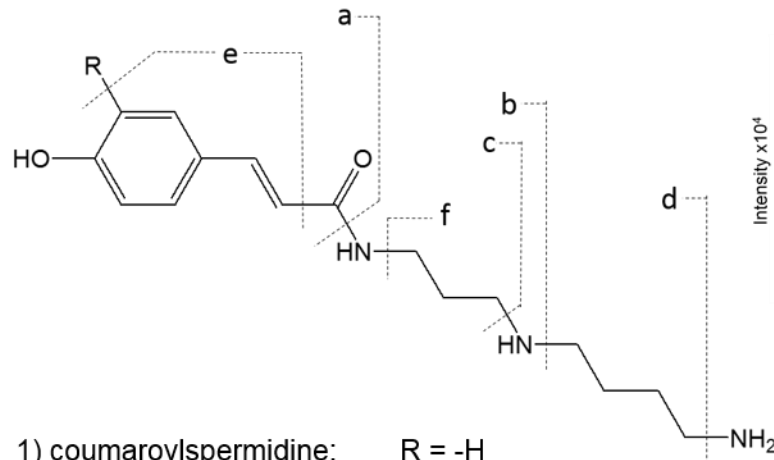
- 1) coumaroylputrescine: R = -H  
 2) caffeoylputrescine: R = -OH  
 3) feruloylputrescine: R = -O-CH<sub>3</sub>



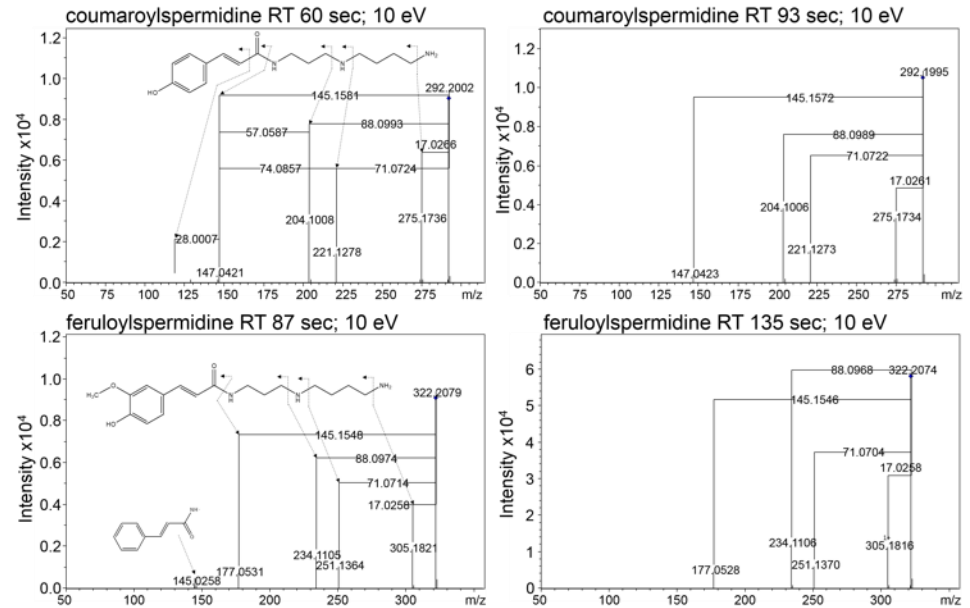
C

RT	compound	formula	m/z calc	m/z observed in MS	ppm mismatch	Collision energy [eV]	R	m/z fragments
60	coumaroylspermidine	C <sub>16</sub> H <sub>25</sub> N <sub>3</sub> O <sub>2</sub>	292.2020	292.2024	1.53	10 ; 20	H	147.042 (a); 204.101 (b); 221.127 (c); 275.173 (d); 119.042 (e); 129.136 (f)
93	coumaroylspermidine	C <sub>16</sub> H <sub>25</sub> N <sub>3</sub> O <sub>2</sub>	292.2020	292.2025	1.87	10 ; 20	H	147.042 (a); 204.101 (b); 221.127 (c); 275.173 (d); 129.136 (f)
87	feruloylspermidine	C <sub>17</sub> H <sub>27</sub> N <sub>3</sub> O <sub>3</sub>	322.2125	322.2131	1.81	10 ; 20	O-CH <sub>3</sub>	177.053 (a); 234.111 (b); 251.136 (c); 305.182 (d); 129.137 (f)
135	feruloylspermidine	C <sub>17</sub> H <sub>27</sub> N <sub>3</sub> O <sub>3</sub>	322.2125	322.2130	1.50	10 ; 20	O-CH <sub>3</sub>	177.053 (a); 234.111 (b); 251.137 (c); 305.182 (d) 129.137 (f)

- (a) coumaroyl- / feruloyl- core, neutral loss of spermidine
- (b) neutral loss of putrescine
- (c) neutral loss of putrescine (-NH)
- (d) neutral loss of NH<sub>3</sub>
- (e) neutral loss of carboxy from HCA core
- (f) spermidine fragment

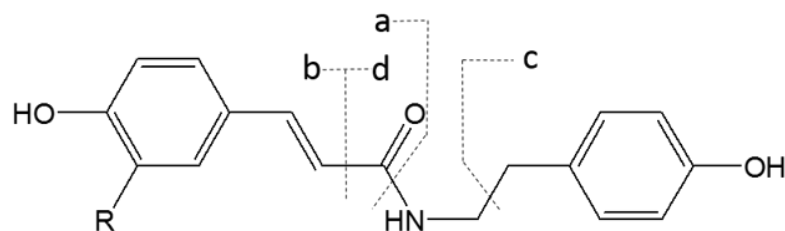


- 1) coumaroylspermidine: R = -H
- 2) feruloylspermidine: R = -O-CH<sub>3</sub>



RT	compound	formula	m/z calc	m/z observed in MS	ppm mismatch	Collision energy [eV]	R	m/z fragments
373	coumaroyltyramine	C <sub>17</sub> H <sub>17</sub> NO <sub>3</sub>	284.1281	284.1285	1.34	10 ; 20	H	147.042 (a); 119.045 (b); 121.062 (c); 164.073 (d)
338	caffeoyltyramine	C <sub>17</sub> H <sub>17</sub> NO <sub>4</sub>	300.1230	300.1232	0.67	10 ; 20	OH	163.041 (a); 147.044 (a-R);
382	feruloyltyramine	C <sub>18</sub> H <sub>19</sub> NO <sub>4</sub>	314.1387	314.1391	1.32	10 ; 20	O-CH <sub>3</sub>	177.053 (a); 149.060 (b); 121.060 (c)

(a) coumaroyl- / feruloyl- core, neutral loss of tyramine  
 (b) decarboxylated coumaroyl- / feruloyl- core  
 (c) tyramine fragment; (d) tyramine + carboxyl group



- 1) coumaroyltyramine: R = -H  
 2) caffeoyltyramine: R = -OH  
 3) feruloyltyramine: R = -O-CH<sub>3</sub>

**Supplemental Figure 3.** MSMS of Hydroxyl Cinnamic Acid Derivatives. Candidate precursor ions of HCAAs (**A**: agmatine, **B**: putrescine, **C**: spermidine, **D**: tyramine conjugates) were selected based on their accurate m/z obtained in LC-MS metabolite profiling measurements. MSMS was performed on plant extracts from *ACT-DTX18*-expressing lines. Precursor ions were isolated at the respective retention times and fragmented by CID with nitrogen as collision gas and 10 and 20 eV collision energy. Neutral losses and fragment ions were annotated to structures of HCAAs as indicated in the MSMS.

