

ESI-MS Studies on the Mechanism of Pd(0)-Catalyzed Three-Component Tandem Double Addition-Cyclization Reaction

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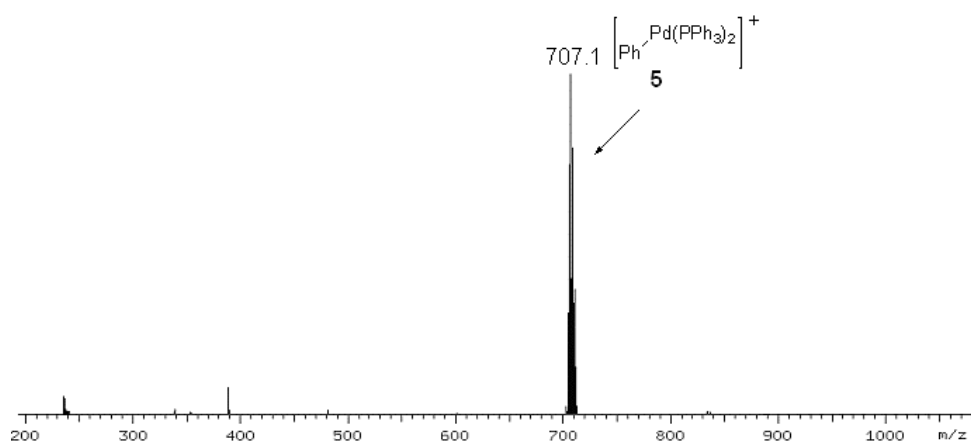


Figure S1. ESI(+)-MS carried out with a CapExit voltage of 52.6 V for the sample taken from the reaction mixture of iodobenzene **2** (0.06 mmol) and Pd(PPh₃)₄ (0.0025 mmol) in THF (6 mL) stirred at rt in a nitrogen atmosphere at the reaction time of 30 min and diluted by the mixed CH₃CN and CH₃OH (v/v=1:1).

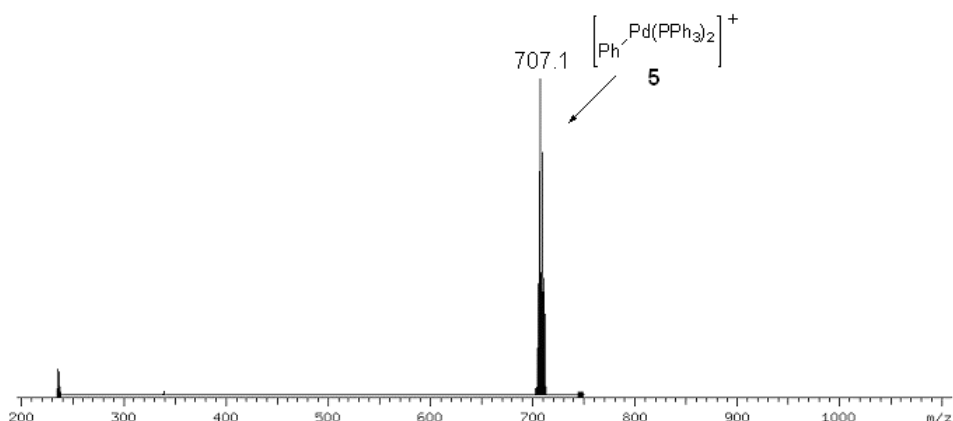


Figure S2. ESI(+)-MS carried out with a CapExit voltage of 52.6 V for the sample taken from the reaction mixture of iodobenzene **2** (0.06 mmol) and $\text{Pd(PPh}_3)_4$ (0.0025 mmol) in THF (6 mL) stirred at 85°C in a nitrogen atmosphere at the reaction time of 30 min and diluted by the mixed CH_3CN and CH_3OH (v/v=1:1).

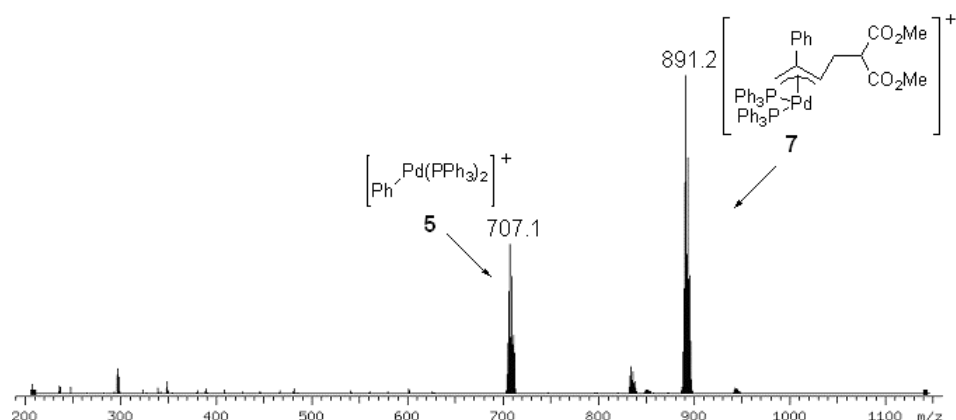


Figure S3. ESI(+)-MS carried out with the standard procedure for MS detection for the sample taken from the reaction mixture of 2-(2, 3-allenyl)malonate **1** (0.05 mmol), iodobenzene **2** (0.06 mmol) and $\text{Pd(PPh}_3)_4$ (0.0025 mmol) in THF (6 mL) stirred at 85°C in a nitrogen atmosphere at the reaction time of 30 min.

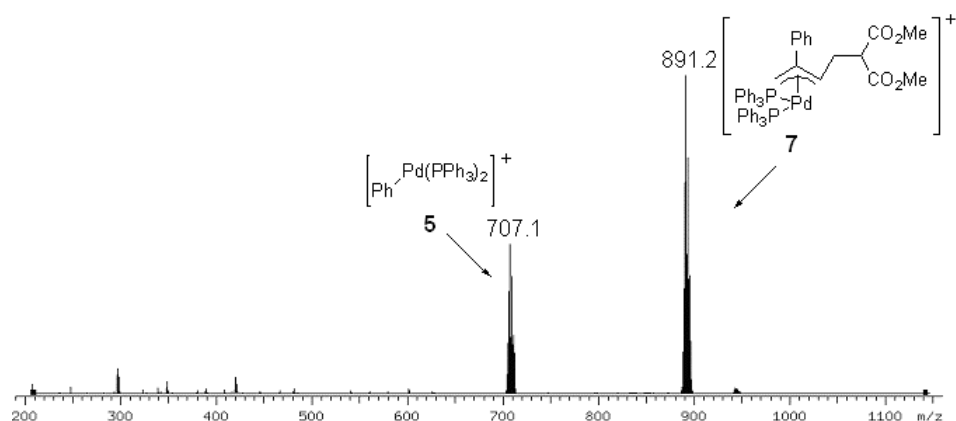
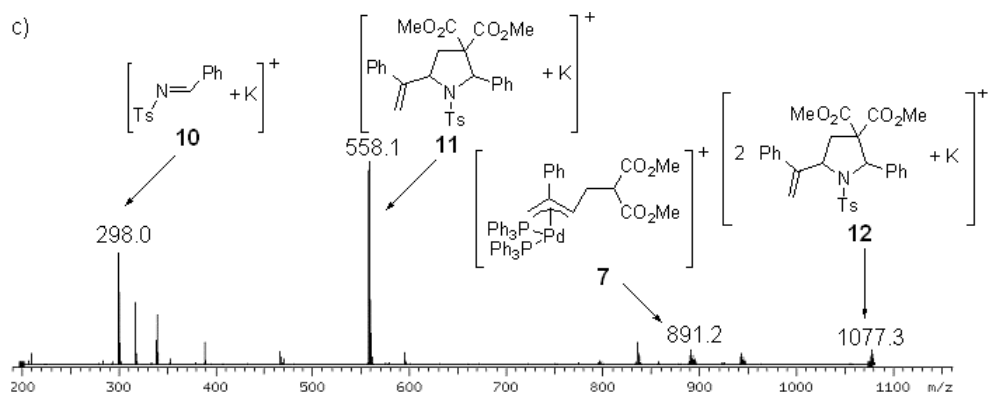
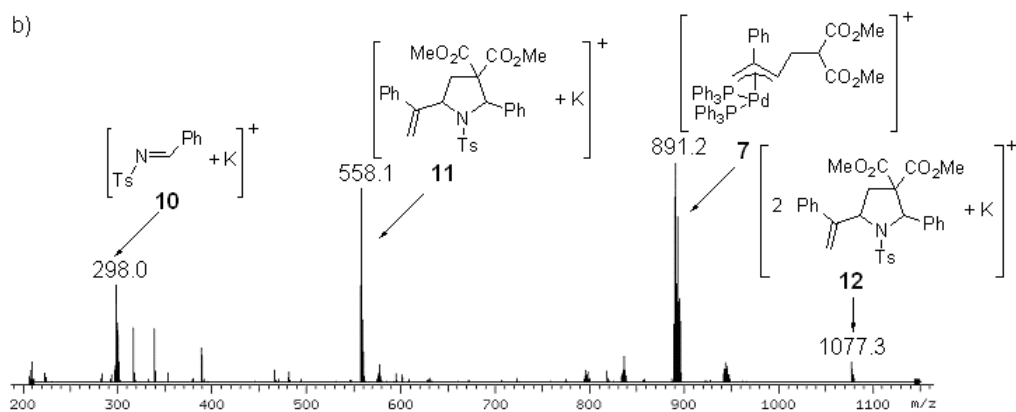
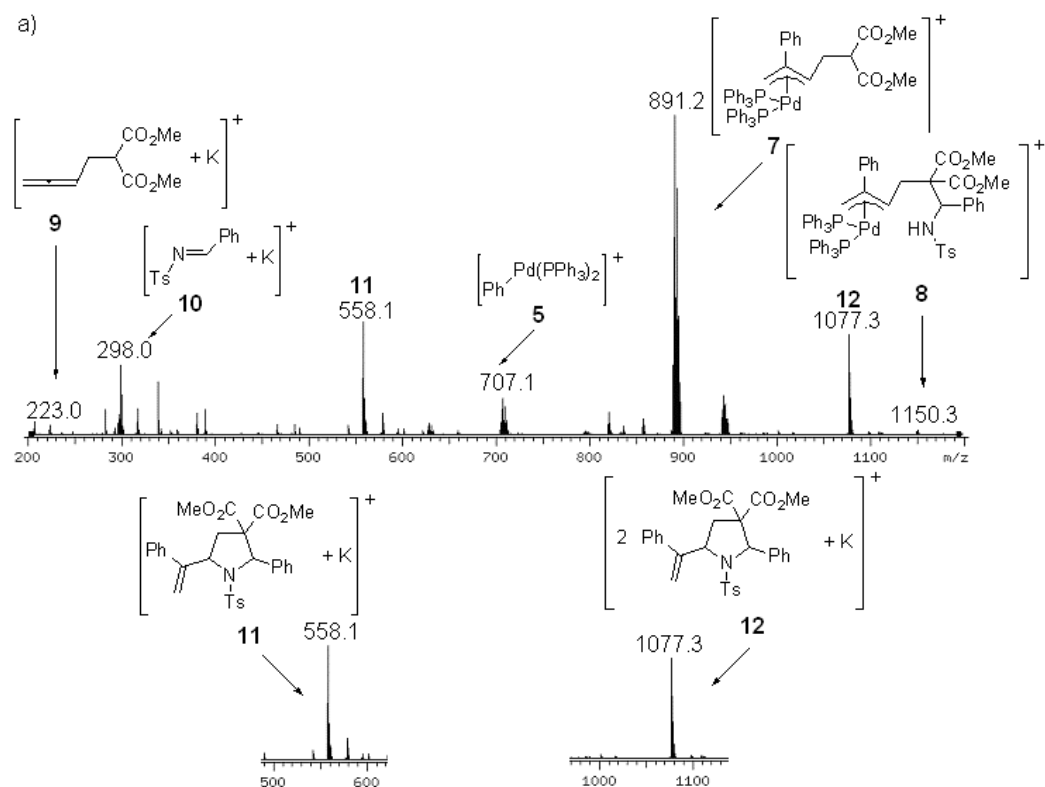


Figure S4. ESI(+)-MS carried out with the standard procedure for MS detection for the sample taken from the reaction mixture of 2-(2, 3-allenyl)malonate **1** (0.05 mmol), iodobenzene **2** (0.06 mmol), imine **3** (0.06 mmol), and $\text{Pd}(\text{PPh}_3)_4$ (0.0025 mmol) in THF (6 mL) stirred at 85°C in a nitrogen atmosphere at the reaction time of 1 h. (The MS results for the samples taken at the reaction time between 30 min to 2 h were similar to this spectra.)



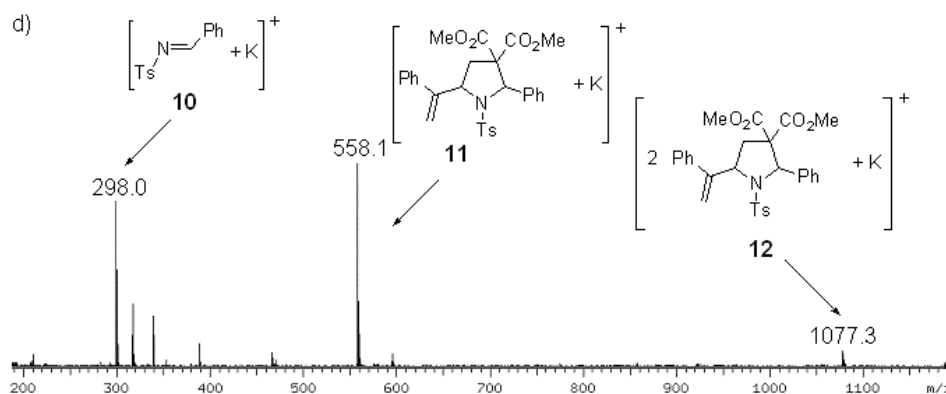


Figure S5. ESI(+)-MS carried out with the standard procedure for MS detection for the sample taken from the reaction mixture of 2-(2, 3-allenyl)malonate **1** (0.05 mmol), iodobenzene **2** (0.06 mmol), imine **3** (0.06 mmol), $\text{Pd}(\text{PPh}_3)_4$ (0.0025 mmol), and K_2CO_3 (0.05 mmol) in THF (6 mL) stirred at 85°C in a nitrogen atmosphere at the reaction time of a) 5 h, b) 15 h, c) 24 h, and d) 36 h.

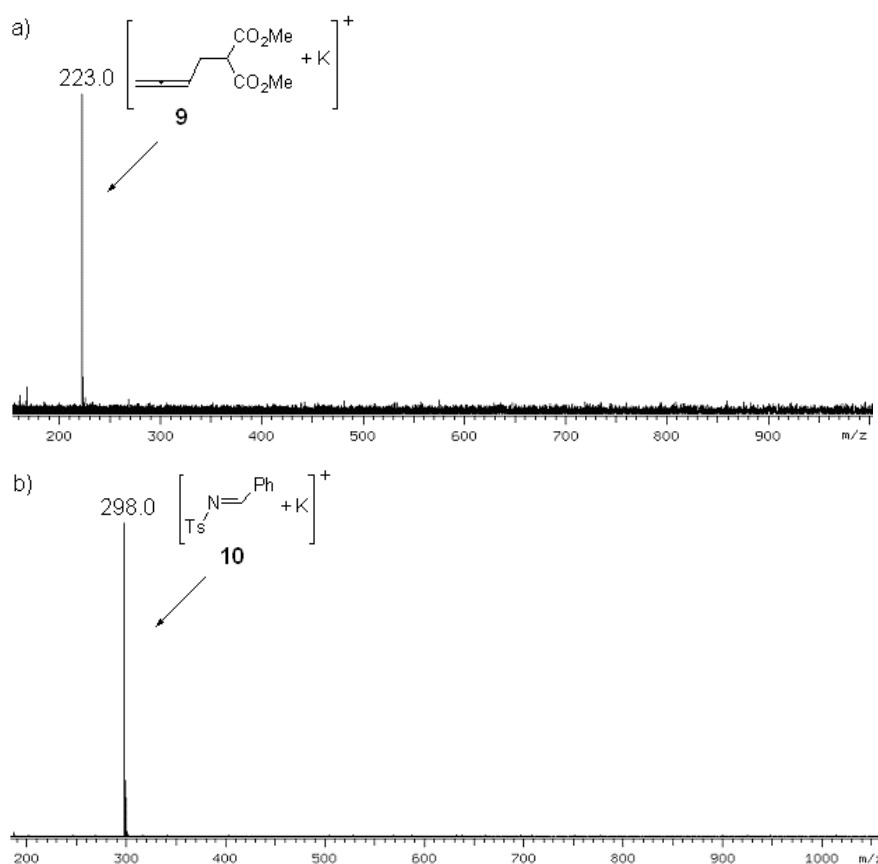
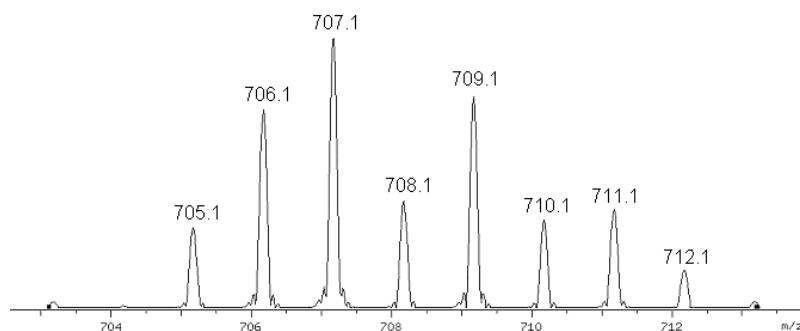


Figure S6. ESI(+)-MS carried out with a CapExit voltage of 52.6 V for a) 2-(2,

3-allenyl)malonate **1** and b) imine **3**, diluted by a solution of CH₃CN saturated with K₂CO₃.

Experimental and theoretical isotopic distribution of the palladium intermediate ions.

a) Experimental isotopic distributions of intermediate **5**.



Theoretical isotopic distributions of intermediate **5**.

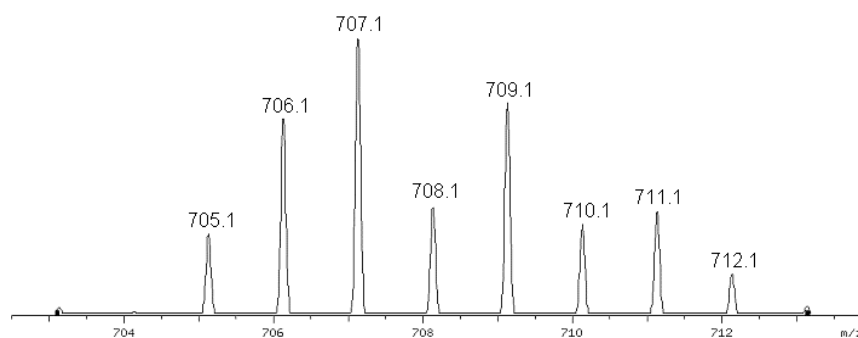
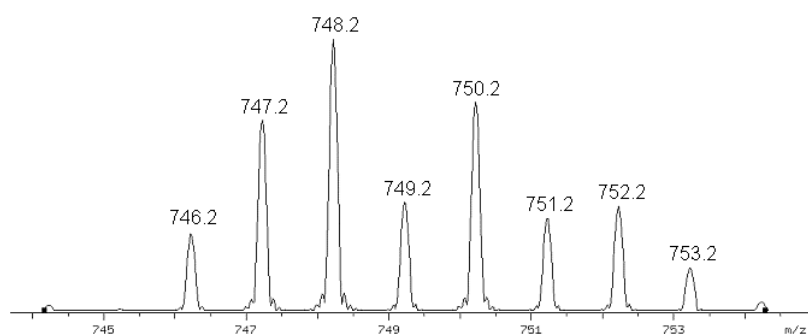


Table 1. Experimental and theoretical isotopic distribution of intermediate **5**.

m/z	Experimental mass	Theoretical mass	Relative error (ppm)
705.1	705.1241	705.1249	-1.1
706.1	706.1264	706.1264	0
707.1	707.1263	707.1259	0.6
708.1	708.1292	708.1286	0.8
709.1	709.1261	709.1255	0.8
710.1	710.1287	710.1284	0.4
711.1	711.1278	711.1271	1.0
712.1	712.1299	712.1298	0.1

b) Experimental isotopic distributions of intermediate **6**.



Theoretical isotopic distributions of intermediate **6**.

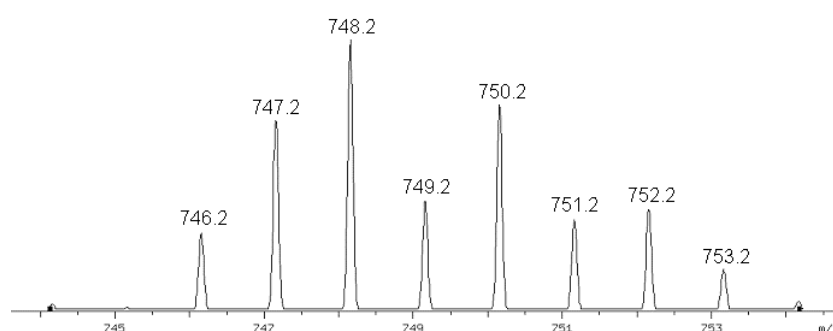
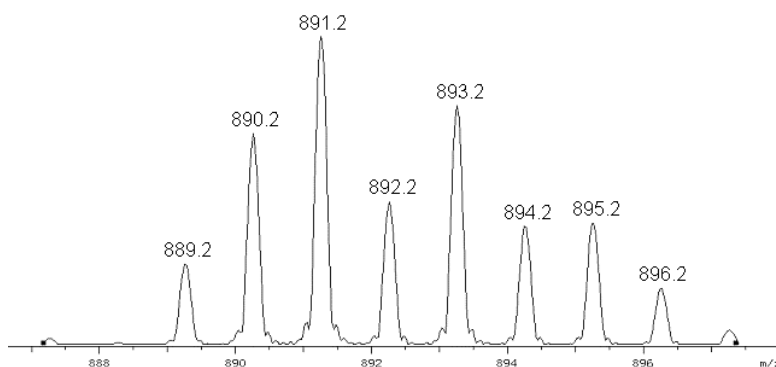


Table 2. Experimental and theoretical isotopic distribution of intermediate **6**.

m/z	Experimental mass	Theoretical mass	Relative error (ppm)
746.2	746.1513	746.1515	-0.3
747.2	747.1529	747.1529	0
748.2	748.1527	748.1525	0.3
749.2	749.1550	749.1551	-0.1
750.2	750.1517	750.1521	-0.5
751.2	751.1549	751.1549	0
752.2	752.1542	752.1537	0.7
753.2	753.1570	753.1563	0.9

c) Experimental isotopic distributions of intermediate **7**.



Theoretical isotopic distributions of intermediate **7**.

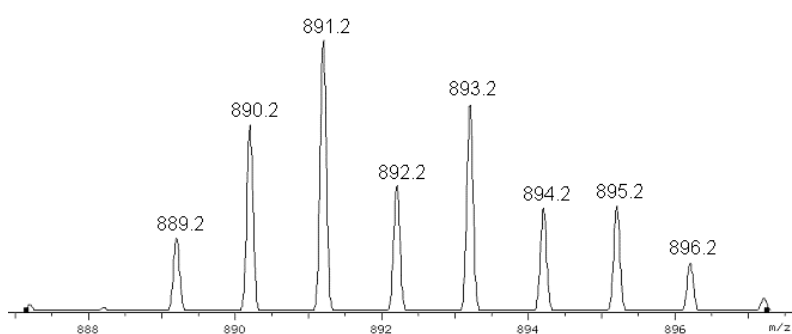
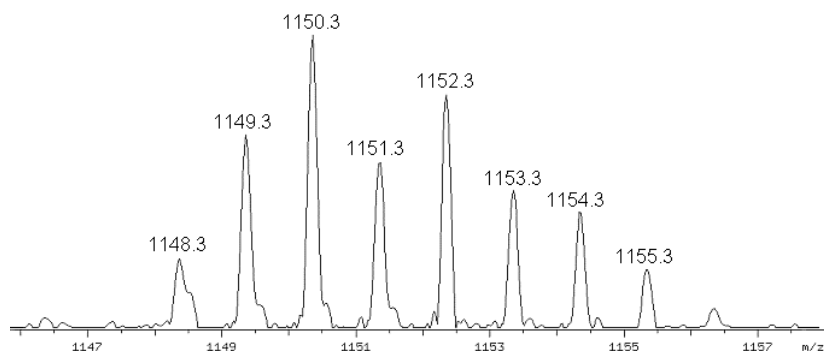


Table 3. Experimental and theoretical isotopic distribution of intermediate **7**.

m/z	Experimental mass	Theoretical mass	Relative error (ppm)
889.2	889.1984	889.1986	-0.2
890.2	890.2006	890.2000	0.7
891.2	891.1999	891.1997	0.2
892.2	892.2024	892.2023	0.1
893.2	893.1992	893.1994	-0.2
894.2	894.2016	894.2021	-0.6
895.2	895.2005	895.2011	-0.7
896.2	896.2029	896.2036	-0.8

d) Experimental isotopic distributions of intermediate **8**.



Theoretical isotopic distributions of intermediate **8**.

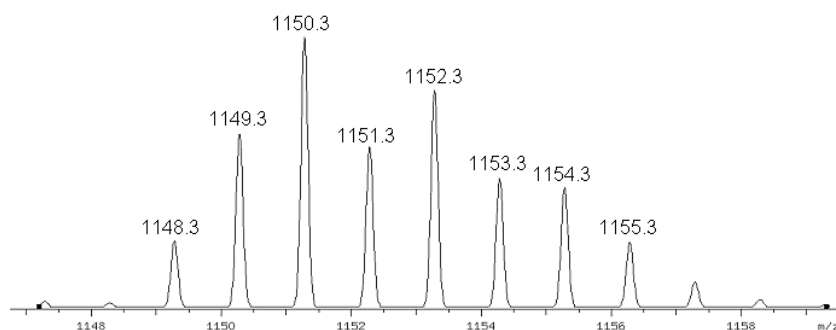


Table 4. Experimental and theoretical isotopic distribution of intermediate **8**.

m/z	Experimental mass	Theoretical mass	Relative error (ppm)
1148.3	1148.2659	1148.2653	0.5
1149.3	1149.2668	1149.2667	0.1
1150.3	1150.2657	1150.2666	-0.8
1151.3	1151.2680	1151.2688	-0.7
1152.3	1152.2660	1152.2665	-0.4
1153.3	1153.2683	1153.2688	-0.4
1154.3	1154.2684	1154.2680	0.3
1155.3	1155.2706	1155.2701	0.4