Supporting Information for

A practical and efficient synthesis of methyl levulinate from cellulosic biomass catalyzed by an aluminum-based mixed acid catalyst system

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1. Methyl levulinate (MeLev) synthesis from cedar powder

1.1 General information

All reagents were of research grade and used without further purification. $Al(OH)_3$ was purchased from Sigma-Aldrich. p-toluenesulfonic acid (PTSA) and methanol were purchased from Kishida Chemical. Cedar powder (α-cellulose = 43.6 wt%) was supplied by Nippon Paper Industries and was cutter-milled and sieved to decrease the particle size from 100 to 425 μm.

HPLC analysis was carried out on a JASCO LC-2000Plus system equipped with a Scherzo SS-C18 column (250 × 4.0 mm I.D., Imtakt Corp.). The quantitative analysis of MeLev was performed using a 20 vol% aqueous solution of methanol containing 10 mM formic acid as the mobile phase and 2-methyl tetrahydrofuran as the internal standard.

NMR analysis was carried out on a JEOL JNM-ECX400 system at room temperature. For ^{1}H NMR, tetramethylsilane (TMS) ($\delta = 0$) in $CDCl_3$ served as an internal standard.

1.2 Catalytic reaction and separation

To a 200 mL stainless steel autoclave equipped with a magnetic stirring bar, cedar powder (5.0 g), $Al(OH)_3$ (0.20 mmol), p-toluenesulfonic acid (2.0 mmol), and methanol (50 mL) were added and the apparatus was purged with N_2 (0.5 MPa). Then, the apparatus was heated to 180 °C and maintained at this temperature for 5 h with stirring. After the apparatus was cooled to room temperature and depressurized, the reaction solution was recovered. According to the HPLC analysis, the yield of MeLev was 72% based on the α-cellulose in the cedar powder. The formed MeLev was separated using a Kugelrohr distillation apparatus. The isolation yield of MeLev was 1.11g (63% based on the α-cellulose in the cedar powder).

1.3 ^{1}H NMR analysis of MeLev isolated

The ^{1}H NMR spectrum of MeLev isolated was shown in Fig. S1. Methyl levulinate (methyl 4-oxopentanoate): ^{1}H NMR (400 MHz, $CDCl_3$): δ 2.197 (s, 3H), 2.584 (t, J = 6.4 Hz, 2H), 2.761 (t, J = 6.4 Hz, 2H), 3.681 (s, 3H).

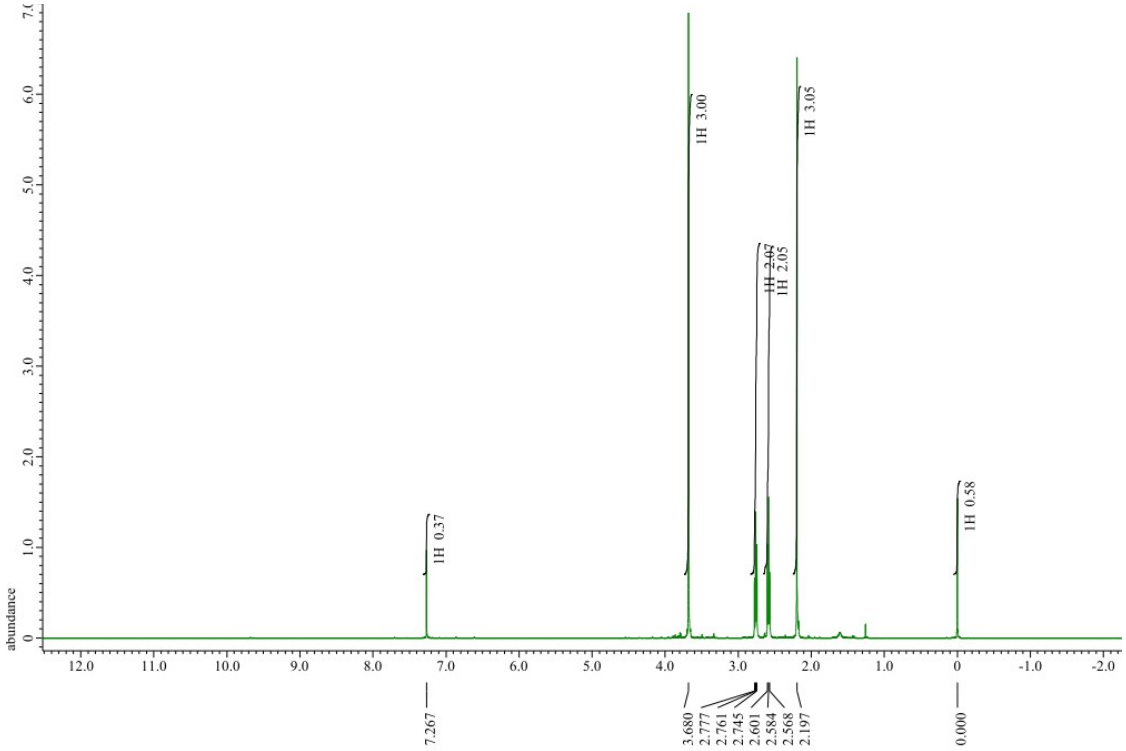

Fig. S1 ^{1}H NMR spectrum of MeLev isolated

2. Identification of metal species observed in ESI-MS analyses

The metal species detected with ESI-MS analyses (Fig. 5) are in good agreement with their calculated isotope distribution spectra.

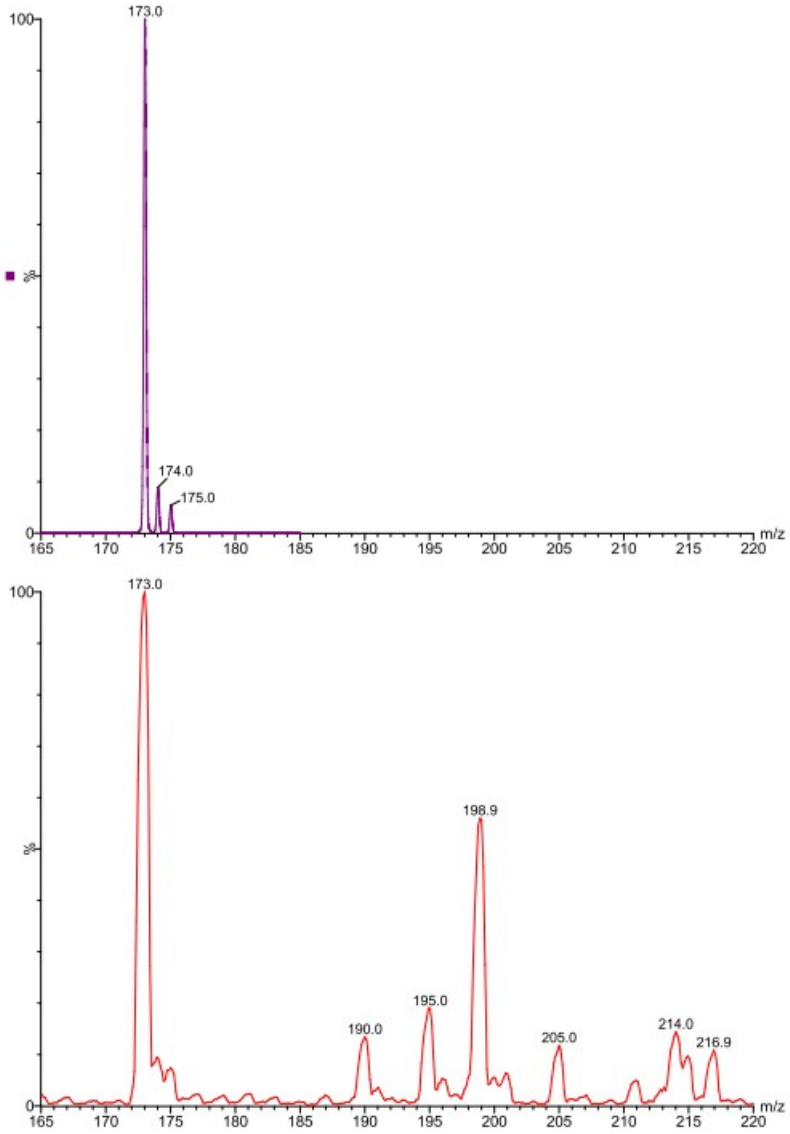

Fig. S2 The isotope distribution spectrum of (a) $[TsOH_2]^+$ (top) and the observed ESI-MS peaks in Fig. 5 (bottom).

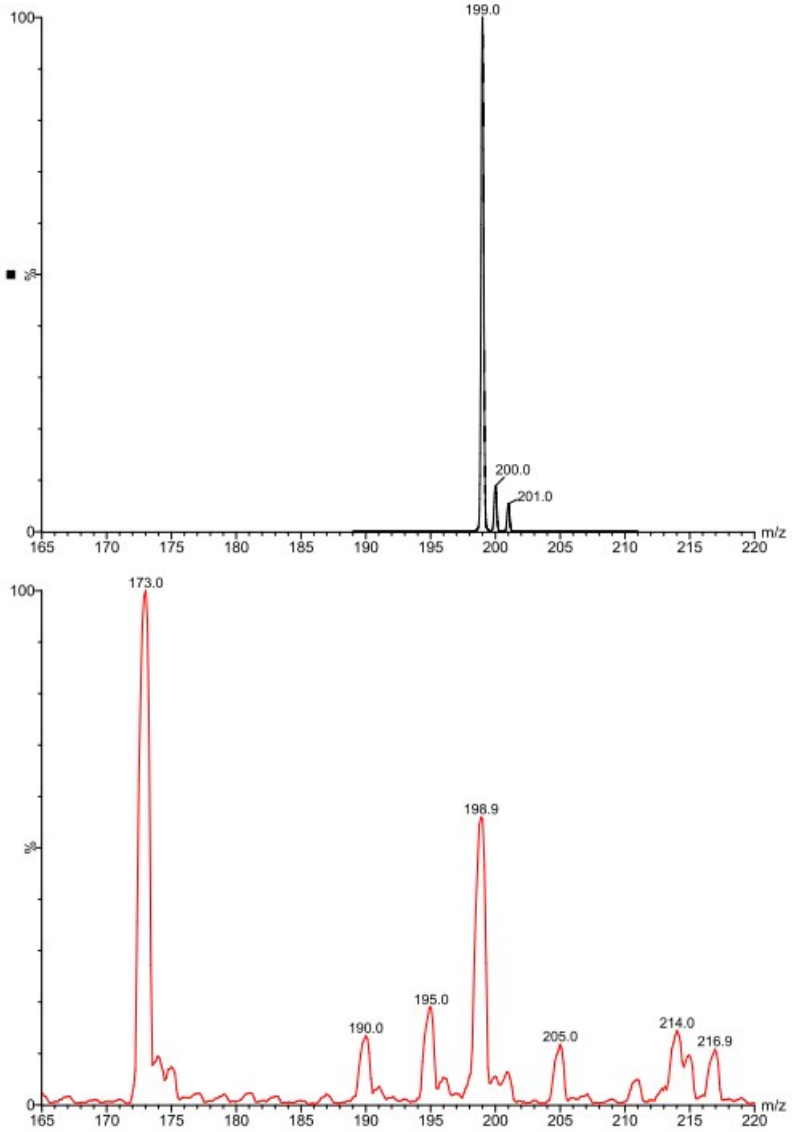

Fig. S3 The isotope distribution spectrum of (b) $[Al(OTs)H]^+$ (top) and the observed ESI-MS peaks in Fig. 5 (bottom).

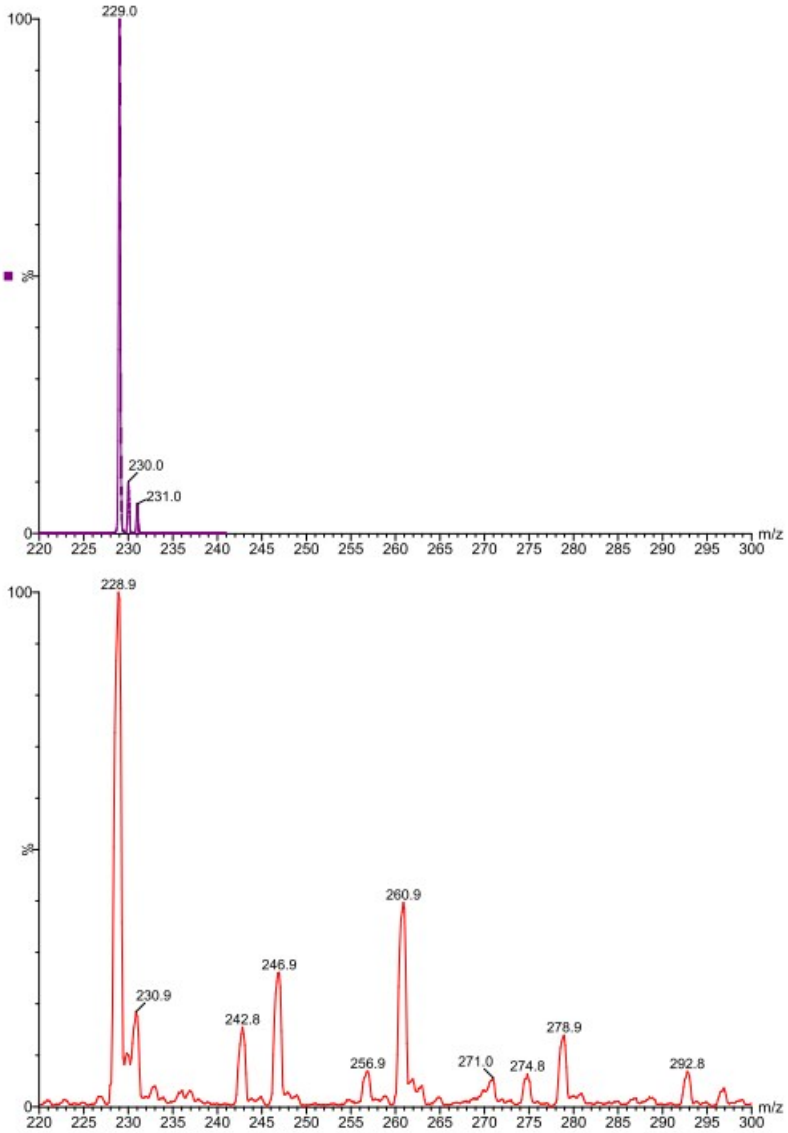

Fig. S4 The isotope distribution spectrum of (c) $[Al(OTs)(OMe)]^+$ (top) and the observed ESI-MS peaks in Fig. 5 (bottom).

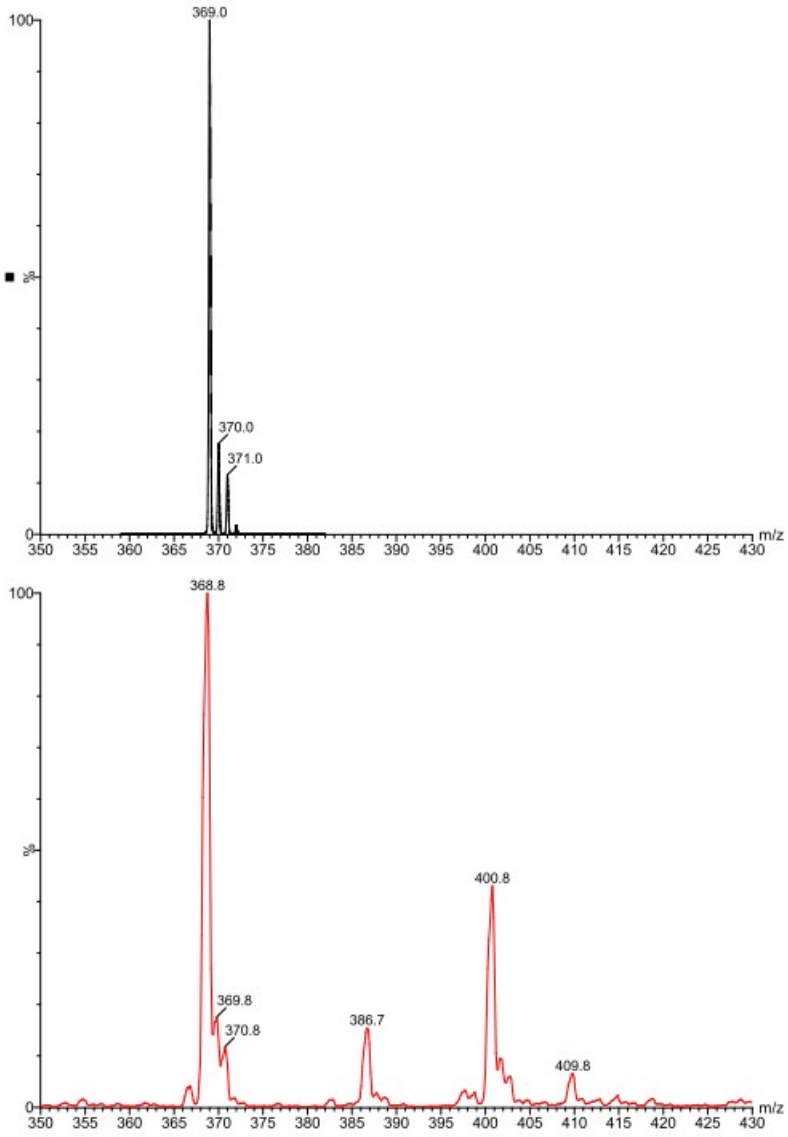

Fig. S5 The isotope distribution spectrum of (d) $[Al(OTs)_2]^+$ (top) and the observed ESI-MS peaks in Fig. 5 (bottom).

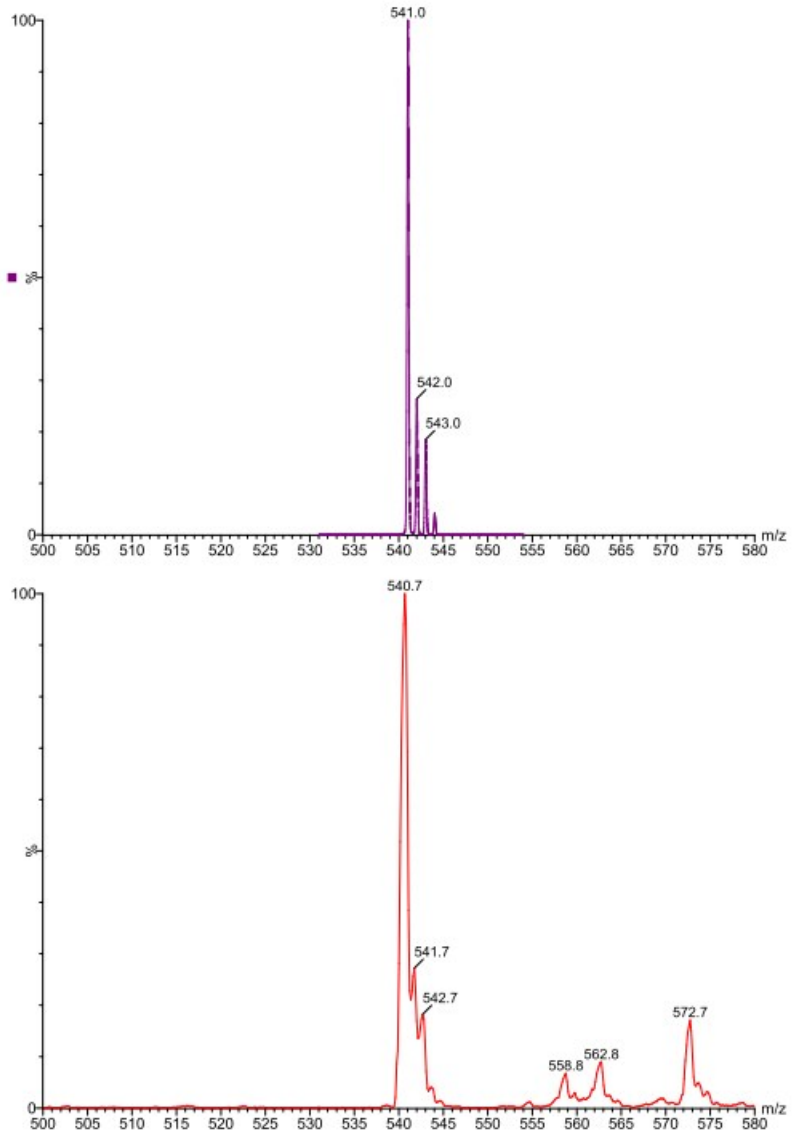

Fig. S6 The isotope distribution spectrum of (e) $[Al(OTs)_3H]^+$ (top) and the observed ESI-MS peaks in Fig. 5 (bottom).

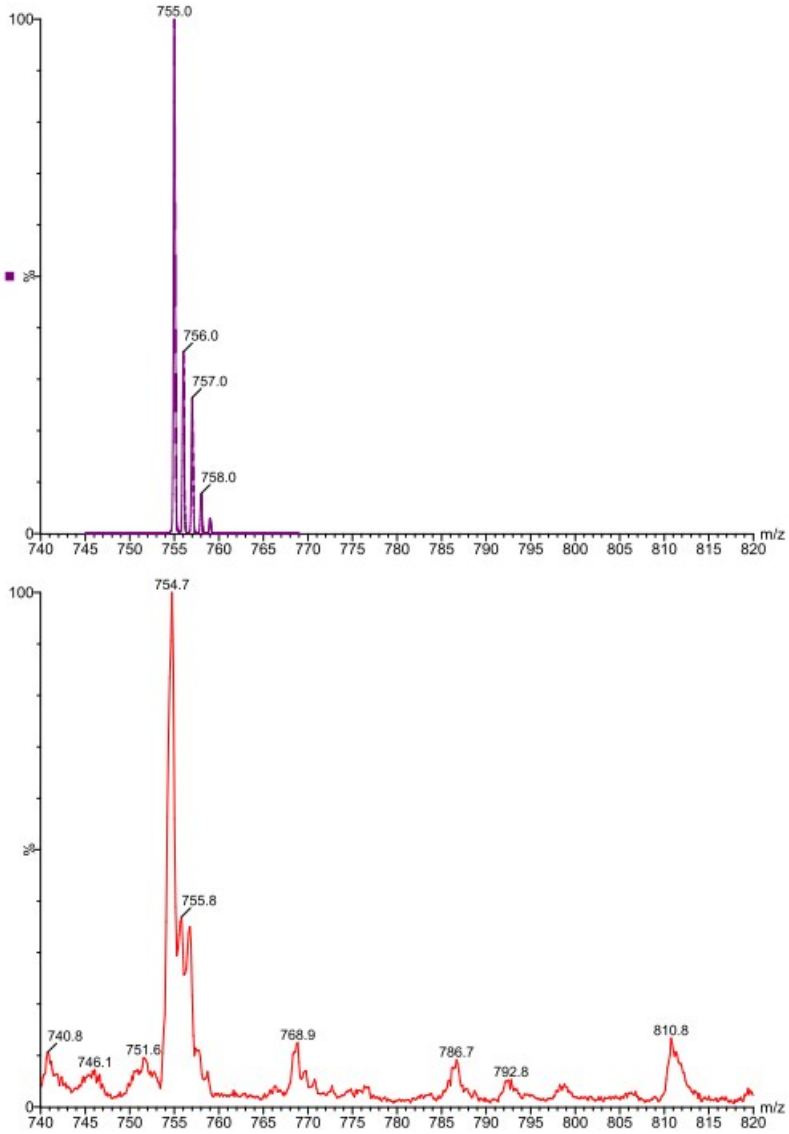

Fig. S7 The isotope distribution spectrum of (f) $[Al_2(OTs)_4OH]^+$ (top) and the observed ESI-MS peaks in Fig. 5 (bottom).

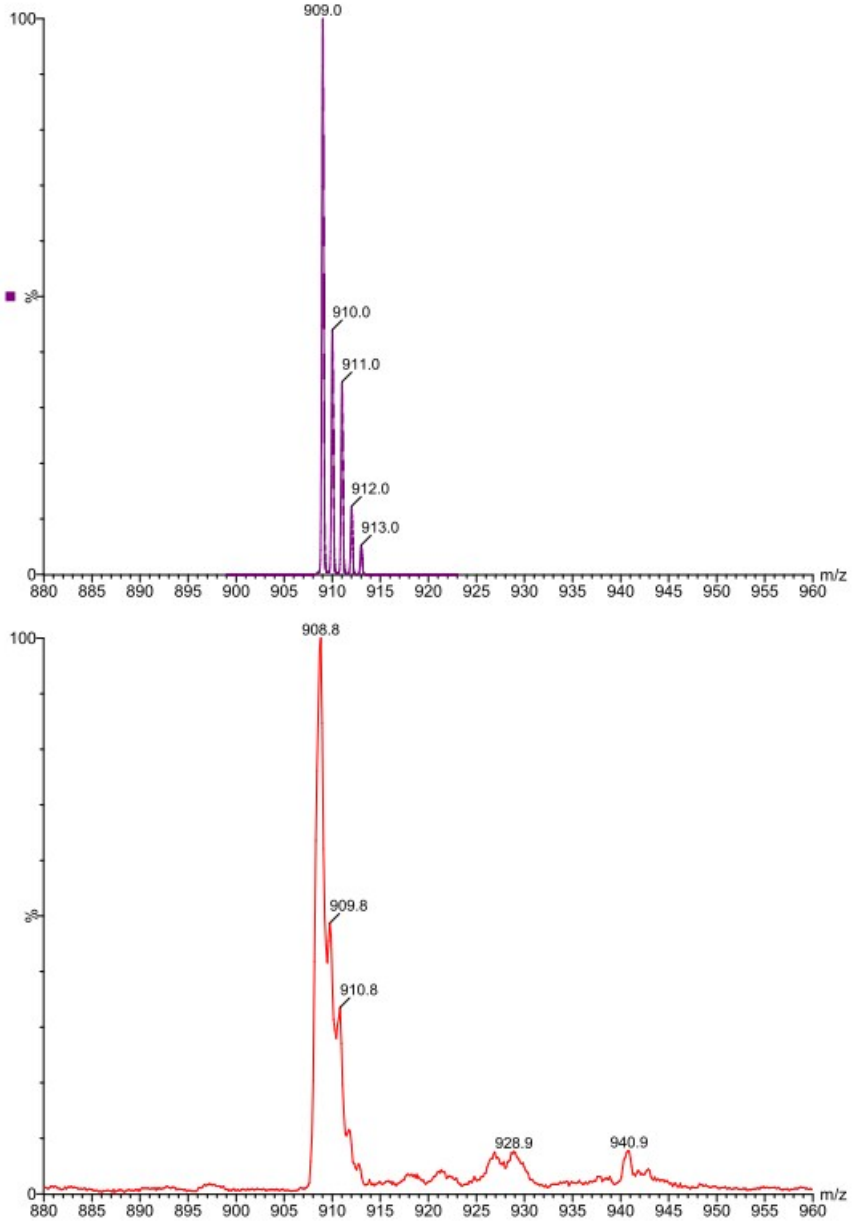

Fig. S8 The isotope distribution spectrum of (g) $[Al_2(OTs)_5]^+$ (top) and the observed ESI-MS peaks in Fig. 5 (bottom).