

# Supporting Information

## **Paraffin-Inert Atmospheric Solid Analysis probe (piASAP): A Fast and Easy Approach to Characterize Extremely Air Sensitive Metallocenes by Mass Spectrometry**

Ahmad Naim,<sup>‡</sup> Mathilde Farenc,<sup>†,§</sup> Marie Hubert-Roux,<sup>‡,§</sup> Thierry Chavagnan,<sup>⊥</sup> Virginie  
Cirriez,<sup>||</sup> Alexandre Welle,<sup>||</sup> Aurelien Vantomme,<sup>||</sup> Evgueni Kirillov,<sup>⊥</sup> Jean-François  
Carpentier,<sup>⊥</sup> Carlos Afonso,<sup>\*,‡,§</sup> and Pierre Giusti<sup>\*,†,§</sup>

<sup>†</sup>Total Research and Technologies Gonfreville BP 27, 76700 Harfleur, France

<sup>‡</sup>Normandy University, INSA Rouen, UMR 6014 University of Rouen, Chimie Organique et  
Bioorganique - Réactivité et Analyse (COBRA), 76821 Mont Saint Aignan, France

<sup>§</sup>International Joint Laboratory - iC2MC: Complex Matrices Molecular Characterization, TRTG, BP 27,  
76700 Harfleur, France

<sup>||</sup>Total Research and Technologies Feluy, Zone Industrielle C B-7181 Feluy, Belgium

<sup>⊥</sup>University of Rennes, CNRS, ISCR (Institut des Sciences Chimiques de Rennes) UMR 6226, 35000  
Rennes, France

\*Corresponding author: Prof. Carlos Afonso, Email: carlos.afonso@univ-rouen.fr

Dr. Pierre Giusti, Email: pierre.giusti@total.com



Figure S1. General graphical representation of piASAP: liquid sample sealed with paraffin before the analysis.

Relative intensity of $[M+H]^+$ (%)		
Complex		
Sampling cone (V)	1	2
40	1.94	0.19
20	0.38	--
10	1.11	20.15

Table S1. Effect of sampling cone voltage on the relative intensity of  $[M+H]^+$  for complexes **1** and **2**.

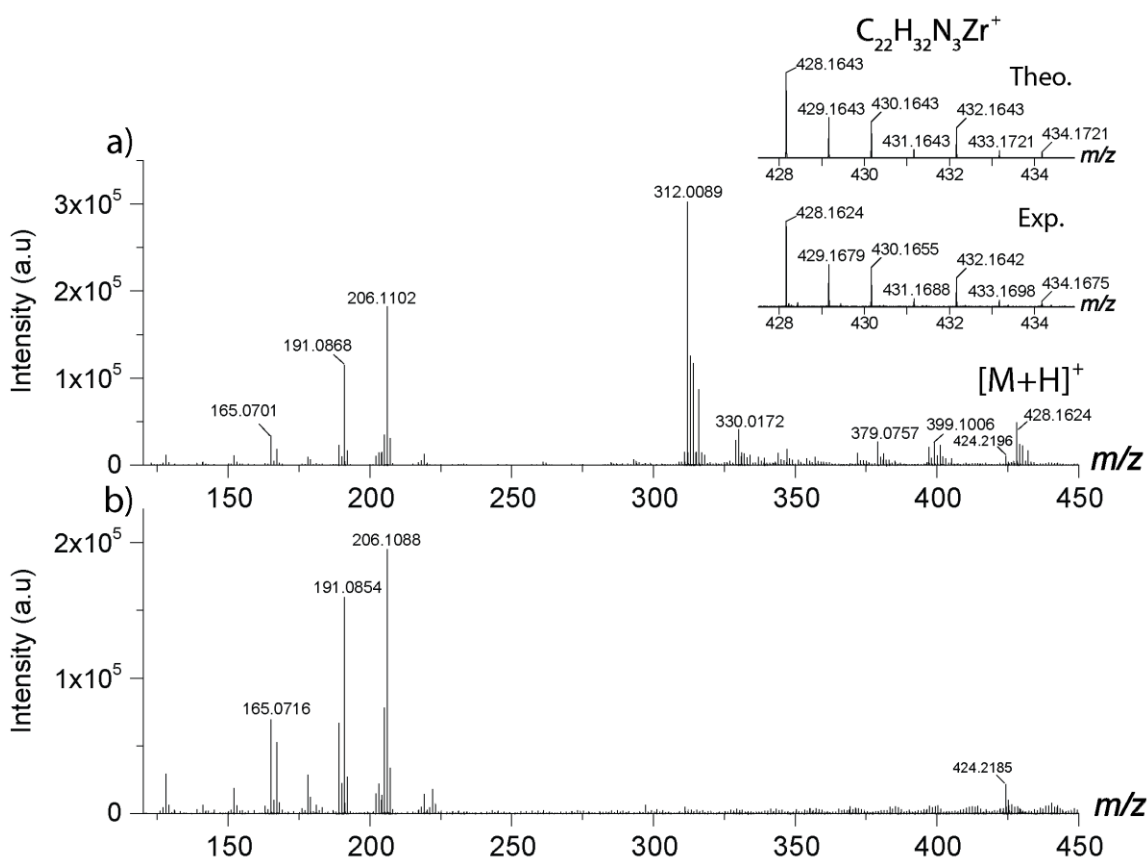


Figure S1. Analysis of air sensitive mononuclear zirconium complex  $\{Ind\}Zr(NMe_2)_3$  (**2**) by piASAP and ASAP techniques. (a) and (b) are mass spectra of piASAP and ASAP prepared under inert and aerobic conditions, respectively. The zoomed areas showcase the theoretical and experimental isotopic patterns of complex **2**. Both spectra were measured at sampling cone 10 V.

<i>m/z</i>	<i>Formula (error, confid.)</i>
879.3193	C <sub>46</sub> H <sub>63</sub> N <sub>6</sub> Zr <sub>2</sub> <sup>+</sup> (-1.7ppm, 100%) [M+H] <sup>+</sup>
834.2620	C <sub>44</sub> H <sub>56</sub> N <sub>5</sub> Zr <sub>2</sub> <sup>+</sup> (-1.2ppm, 99.96%)
833.2536	C <sub>44</sub> H <sub>55</sub> N <sub>5</sub> Zr <sub>2</sub> <sup>+</sup> (-1.9ppm)
805.2090	C <sub>41</sub> H <sub>49</sub> N <sub>6</sub> Zr <sub>2</sub> <sup>+</sup> (-2.9ppm)
790.2115	C <sub>42</sub> H <sub>50</sub> N <sub>4</sub> Zr <sub>2</sub> <sup>+</sup> (-1.9ppm)
789.1997	C <sub>42</sub> H <sub>49</sub> N <sub>4</sub> Zr <sub>2</sub> <sup>+</sup> (-6.8ppm)
788.1953	C <sub>42</sub> H <sub>48</sub> N <sub>4</sub> Zr <sub>2</sub> <sup>+</sup> (-2.5ppm)
761.1478	C <sub>38</sub> H <sub>41</sub> N <sub>6</sub> Zr <sub>2</sub> <sup>+</sup> (-1.2ppm)
763.1581	C <sub>38</sub> H <sub>43</sub> N <sub>6</sub> Zr <sub>2</sub> <sup>+</sup> (-8.1ppm)
745.1531	C <sub>40</sub> H <sub>43</sub> N <sub>3</sub> Zr <sub>2</sub> <sup>+</sup> (-2.7ppm)
718.1033	C <sub>36</sub> H <sub>36</sub> N <sub>5</sub> Zr <sub>2</sub> <sup>+</sup> (-4.5ppm)

Table S2. Ions of *E*-Zr dimer (**1**) detected by piASAP between *m/z* 880-700 at sampling cone 40 V.

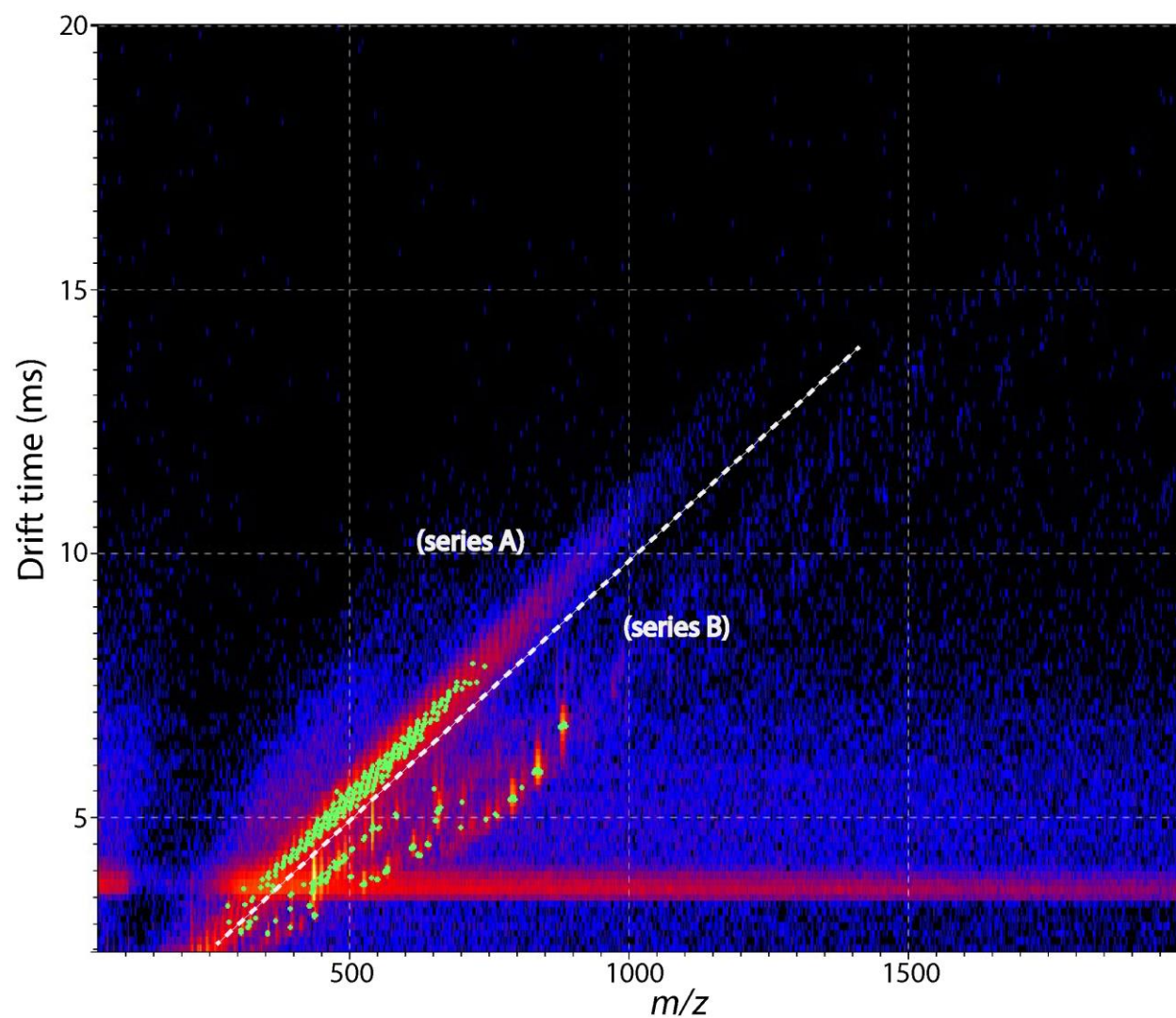


Figure S2. 2-Dimensional plot of Drift time as a function of  $m/z$  of complex **1** measured at cone voltage of 10V. Series A comprises the paraffin ions. Series B represents the analyte ions detected with lower drift time. IMS parameters applied: IMS wave velocity 600 m/s, IMS wave height 40 V and IMS wave delay 450  $\mu$ s and using nitrogen (90 mL/min), as drift gas.

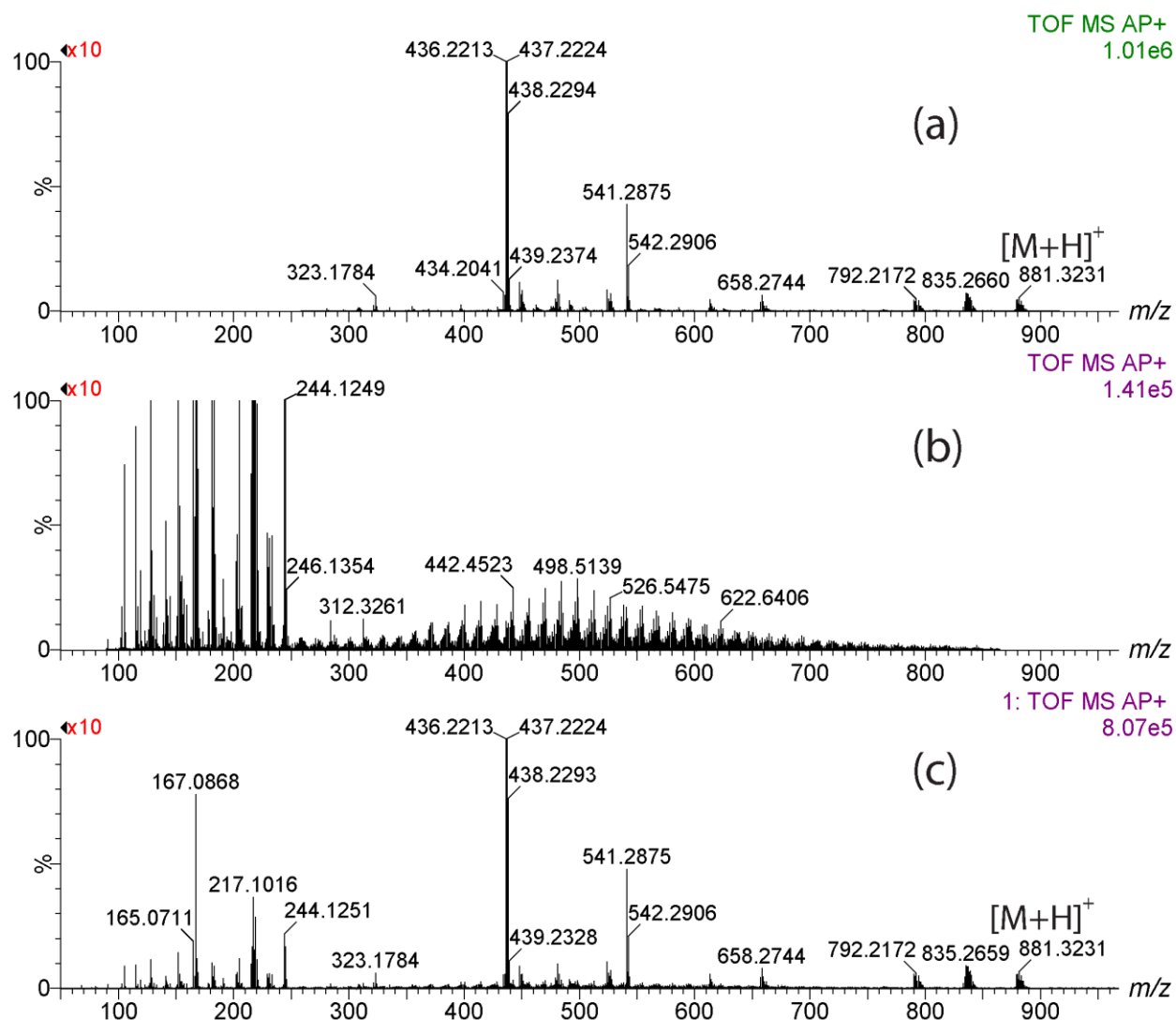


Figure S3. Mass spectra of piASAP analysis of (1) extracted from the IMS-MS data showing (a) analyte ions (lower drift time), (b) paraffin ions (higher drift time), and (c) full data MS data without extraction.

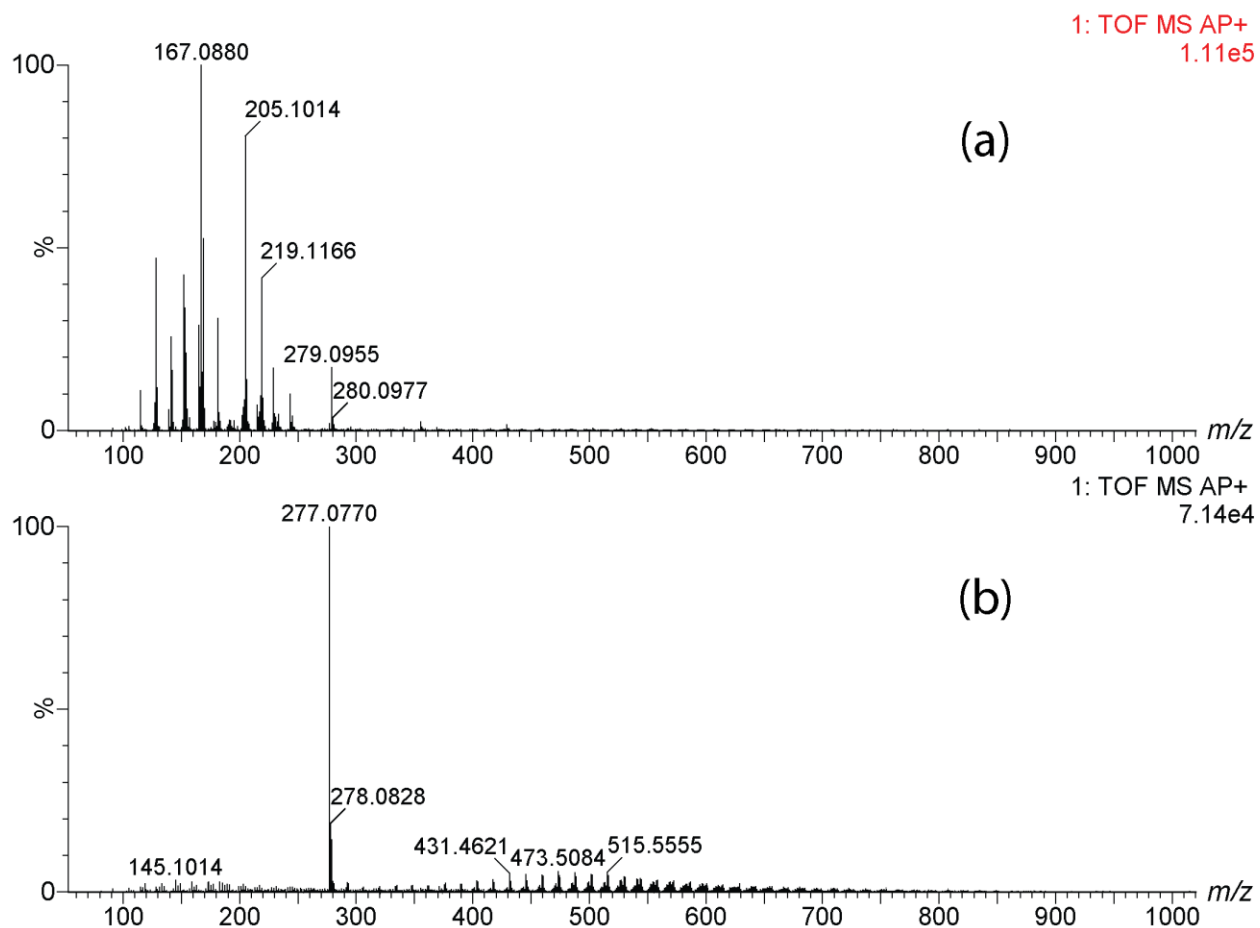


Figure S4. Mass spectra of control piASAP experiments: (a) paraffin and toluene (as a solvent), (b) paraffin only. *n.b.* the toluene contains some impurities below  $m/z$  300.

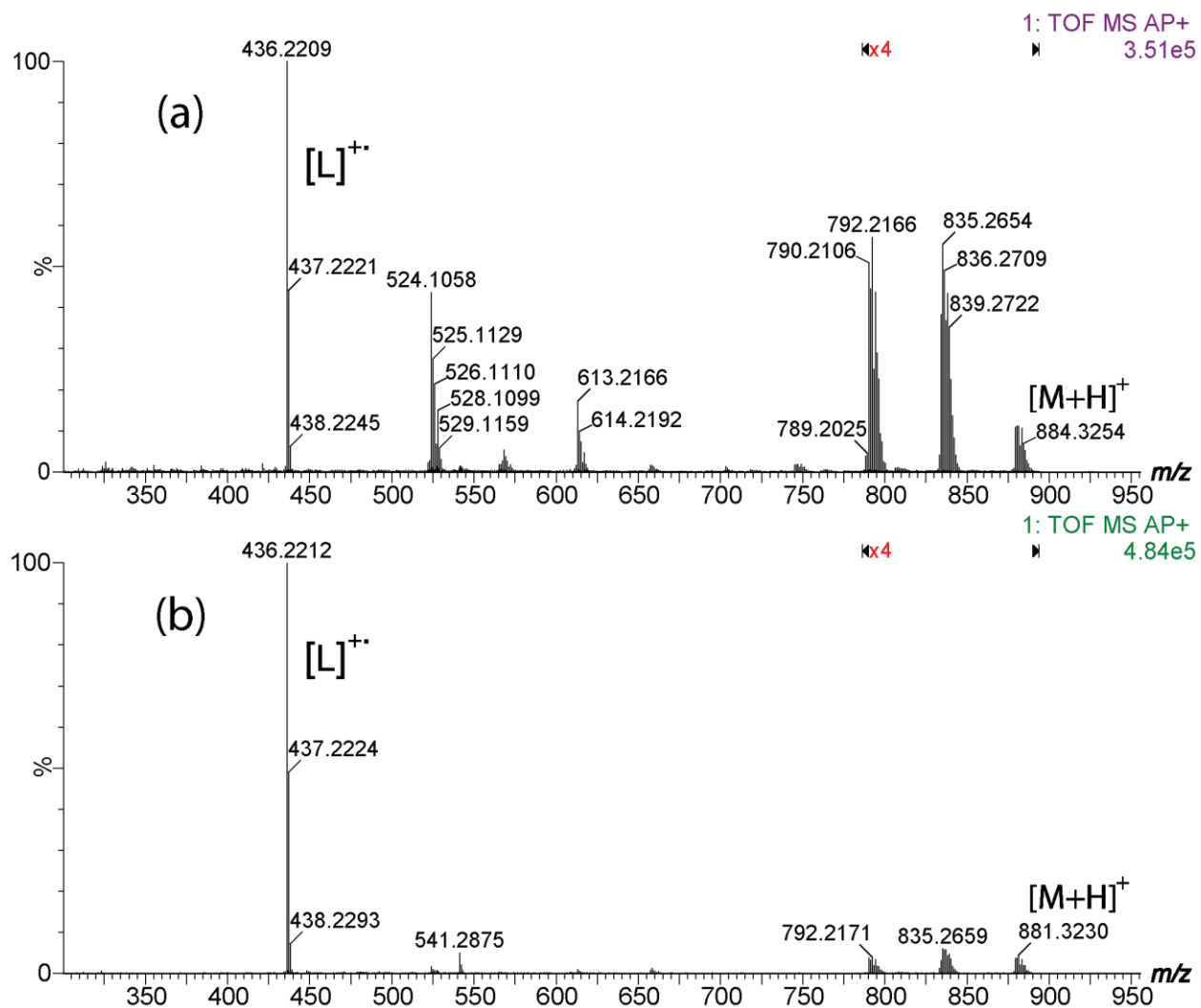


Figure S5. Effect of sampling cone voltages ((a) 40V and (b) 10V) on the intensity of  $[M+H]^+$  and ligand ions of *E*-Zr dimer (**1**) analyzed by piASAP in toluene.



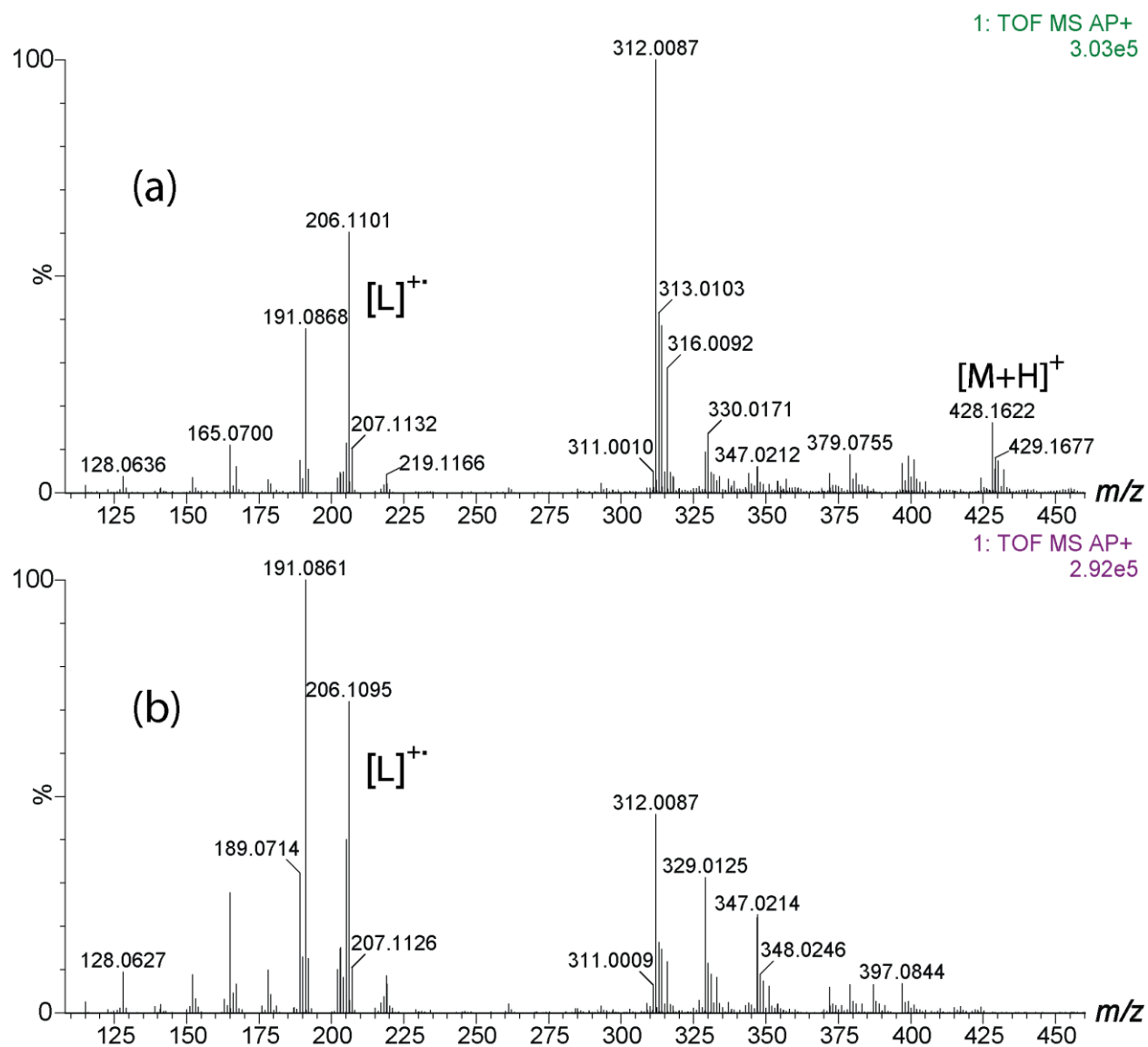


Figure S6. Effect of sampling cone voltages ((a) 10V and (b) 40V) on the intensity of  $[M+H]^+$  and ligand ions of  $\{Ind\}Zr(NMe_2)_3$  (**2**) complex analyzed by piASAP in toluene.

<i>m/z</i>	<i>Formula (error, confid.)</i>
428.1643	C <sub>22</sub> H <sub>32</sub> N <sub>3</sub> Zr <sup>+</sup> (0ppm, 100%) [M+H] <sup>+</sup>
424.2190	C <sub>33</sub> H <sub>28</sub> <sup>+</sup> (-0.2ppm, 99.71%)
401.1177	C <sub>20</sub> H <sub>27</sub> N <sub>2</sub> OZr <sup>+</sup> (1.7ppm)
399.0997	C <sub>20</sub> H <sub>25</sub> N <sub>2</sub> OZr <sup>+</sup> (-4.3ppm)
397.0854	C <sub>20</sub> H <sub>23</sub> N <sub>2</sub> OZr <sup>+</sup> (-0.8ppm)
379.0754	C <sub>20</sub> H <sub>21</sub> N <sub>2</sub> Zr <sup>+</sup> (0.5ppm)
372.0534	C <sub>18</sub> H <sub>20</sub> NO <sub>2</sub> Zr <sup>+</sup> (-1.9 ppm)
330.0189	C <sub>14</sub> H <sub>14</sub> N <sub>3</sub> OZr <sup>+</sup> (1.5 ppm)
312.0096	C <sub>16</sub> H <sub>14</sub> OZr <sup>+</sup> (1.3 ppm, 100%)
206.1094	C <sub>16</sub> H <sub>14</sub> <sup>+</sup> (-1.0 ppm) L <sup>+</sup> •
292.9902	C <sub>16</sub> H <sub>11</sub> Zr <sup>+</sup> (-2.0 ppm)
191.0859	C <sub>15</sub> H <sub>11</sub> <sup>+</sup> (-1.0 ppm)

Table S3. Ions of {Ind}Zr(NMe<sub>2</sub>)<sub>3</sub> (**2**) complex detected by piASAP between *m/z* 440-200 at sampling cone 10 V.

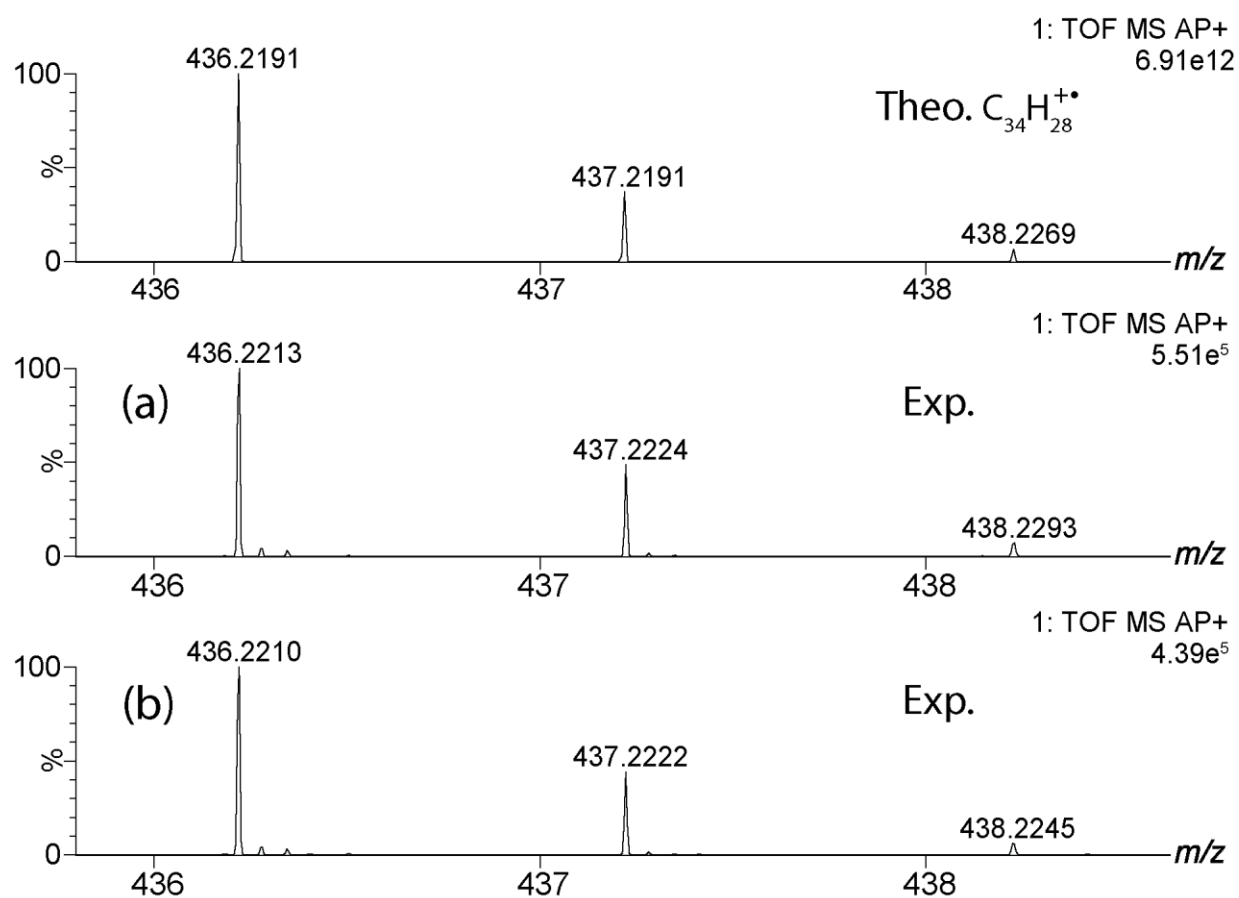


Figure S7. Isotopic pattern of ligand ( $L^+$ ) of  $E$ -Zr dimer (**1**) at 10 V (a) and 40 V (b) and its related theoretical isotopic pattern.

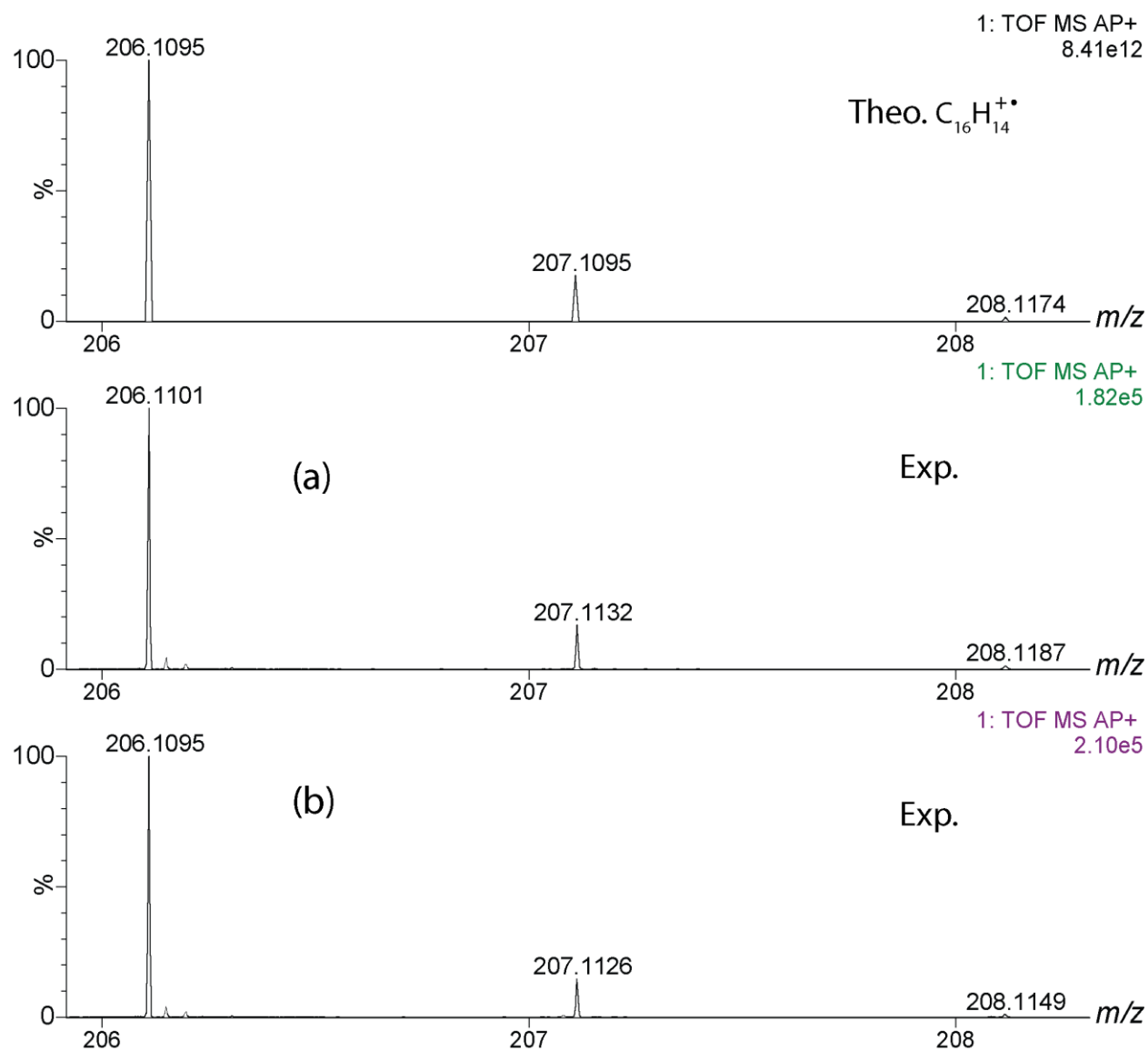


Figure S8. Isotopic pattern of ligand ( $L^{+}$ ) of  $\{Ind\}Zr(NMe_2)_3$  (**2**) at 10 V (a) and 40 V of sampling cone (b) and its corresponding expected isotopic pattern.

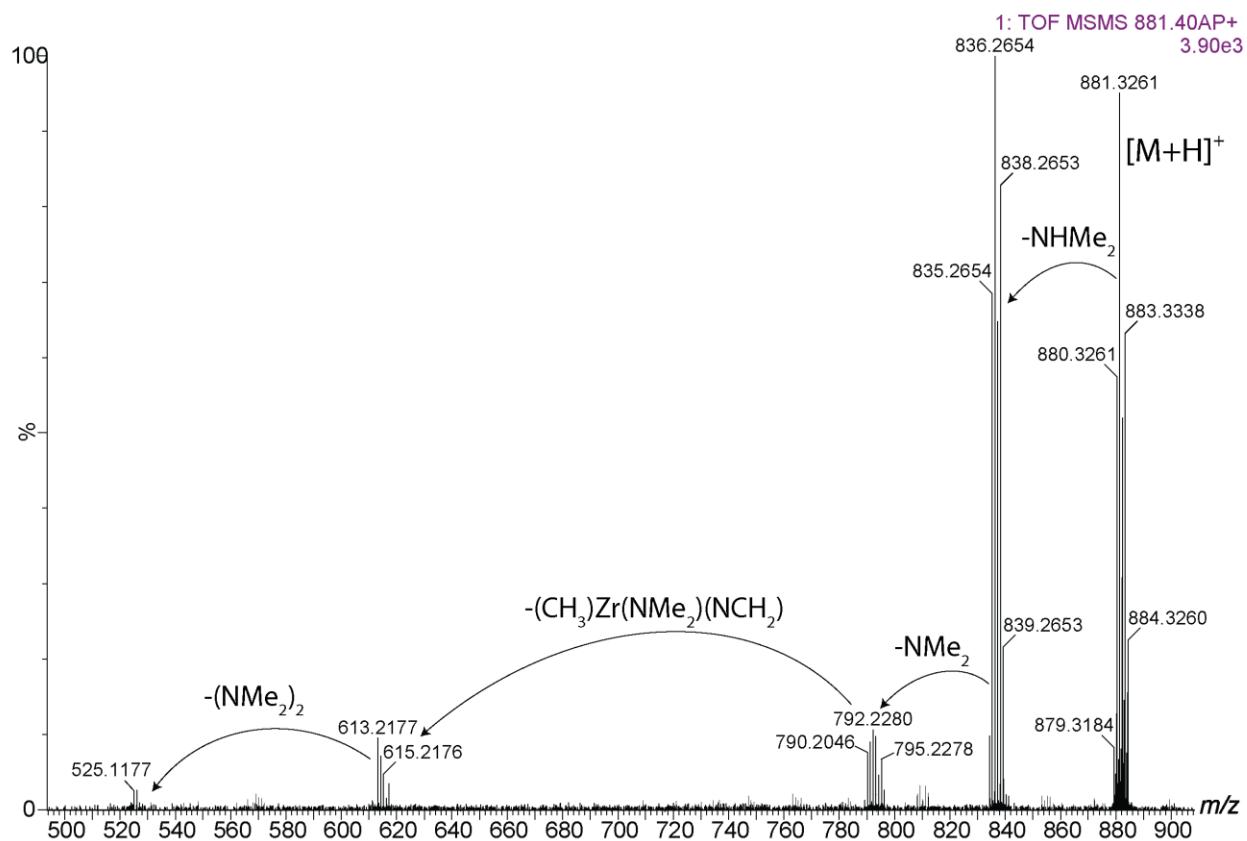


Figure S9. PiASAP MS/MS spectrum of *E*-Zr dimer (**1**). The applied sampling cone and collision energy were used 40 eV and 20 eV, respectively.

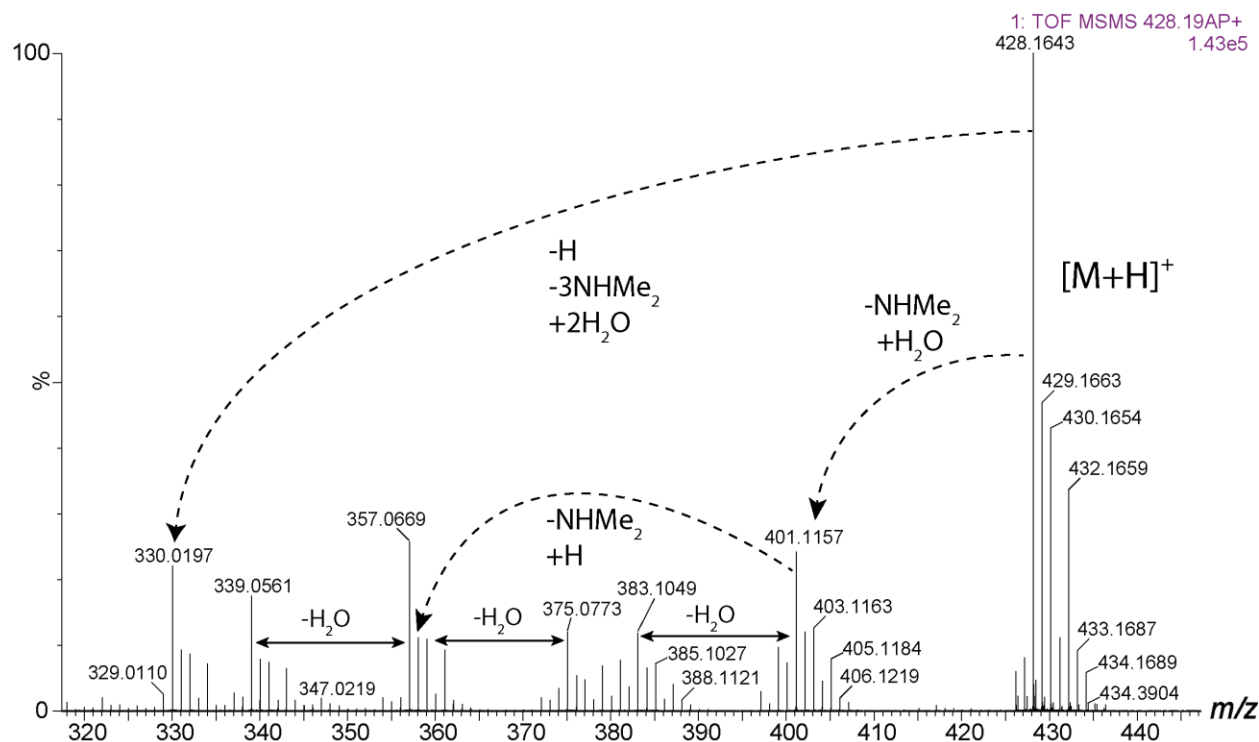


Figure S10. PiASAP MSMS spectrum analysis of  $\{\text{Ind}\}\text{Zr}(\text{NMe}_2)_3$  (**2**). The applied sampling cone and collision energy used were 10V and 5 eV, respectively.

<i>m/z</i>	<i>Formula (error, confid.)</i>
428.1643	$\text{C}_{22}\text{H}_{32}\text{N}_3\text{Zr}^+$ (0ppm, 100%) $[\text{M}+\text{H}]^+$
401.1157	$\text{C}_{20}\text{H}_{27}\text{N}_2\text{OZr}^+$ (-3.2ppm, 100%)
399.1008	$\text{C}_{20}\text{H}_{25}\text{N}_2\text{OZr}^+$ (-1.5ppm)
383.1049	$\text{C}_{20}\text{H}_{25}\text{N}_2\text{Zr}^+$ (-4.2ppm, 99.95%)
375.0773	$\text{C}_{18}\text{H}_{23}\text{NO}_2\text{Zr}^+$ (-0.8ppm)
357.0669	$\text{C}_{18}\text{H}_{21}\text{NOZr}^+$ (-0.3ppm, 100%)
347.0219	$\text{C}_{14}\text{H}_{15}\text{N}_3\text{O}_2\text{Zr}^+$ (2.3ppm)
339.0561	$\text{C}_{18}\text{H}_{19}\text{NZr}^+$ (-1.2ppm)
330.0197	$\text{C}_{16}\text{H}_{16}\text{O}_2\text{Zr}^+$ (0ppm, 96.48%)
312.0093	$\text{C}_{16}\text{H}_{14}\text{OZr}^+$ (0.3ppm, 99.16%)

Table S4. Fragment ions of  $\{\text{Ind}\}\text{Zr}(\text{NMe}_2)_3$  (**2**) complex detected by MSMS piASAP between *m/z* 400-300.