An instrumentation perspective on reaction monitoring by ambient mass spectrometry

Trends in Analytical Chemistry, Vol. 35, 2012

Depanjan Sarkar
CY12D055

Introduction

Better understanding of the reaction sequence and reaction steps would enable chemists to control chemical reactions more efficiently and to find the optimal reaction conditions.

Electron-spin resonance (ESR) spectroscopy, ultraviolet/ visible (UV/Vis) spectroscopy, chemically-induced dynamic nuclear polarization (CIDNP), IR spectroscopy etc. have been used for the direct detection of radical intermediates.

However, in general, these reaction-monitoring methods cannot simultaneously detect substrates, intermediates, and reaction products from reaction solutions

For example, to use UV/Vis spectroscopy for the monitoring of one species, a chromophore needs to be present in it in order to be detected. ESR can be used to detect directly only species with unpaired electrons (e.g., transition metals and free radicals)

MS is a more universal technique, since it directly measures the molecular weight of species of interest, and, by choosing appropriate ionization methods, most chemical compounds and free radicals can be ionized

Here different instrumental techniques for online and offline reaction monitoring has been discussed.

Cold spray ionization (CSI)

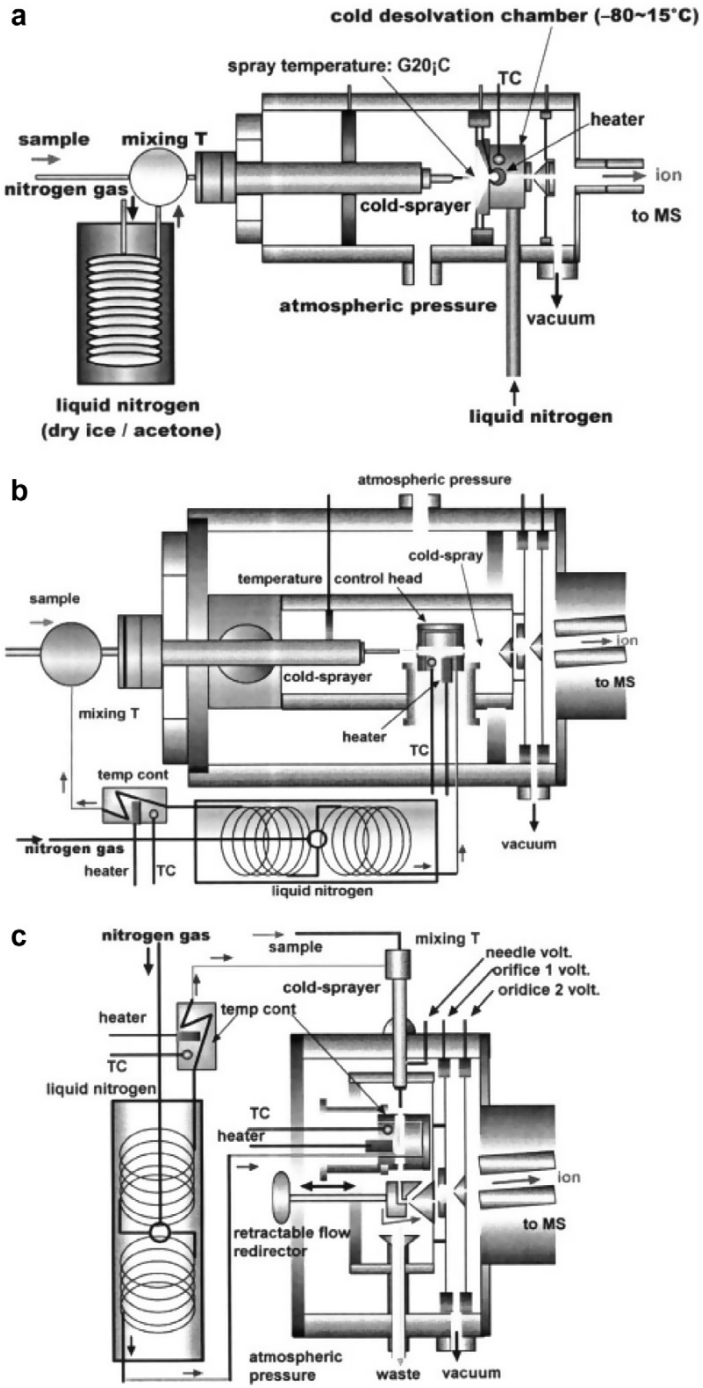
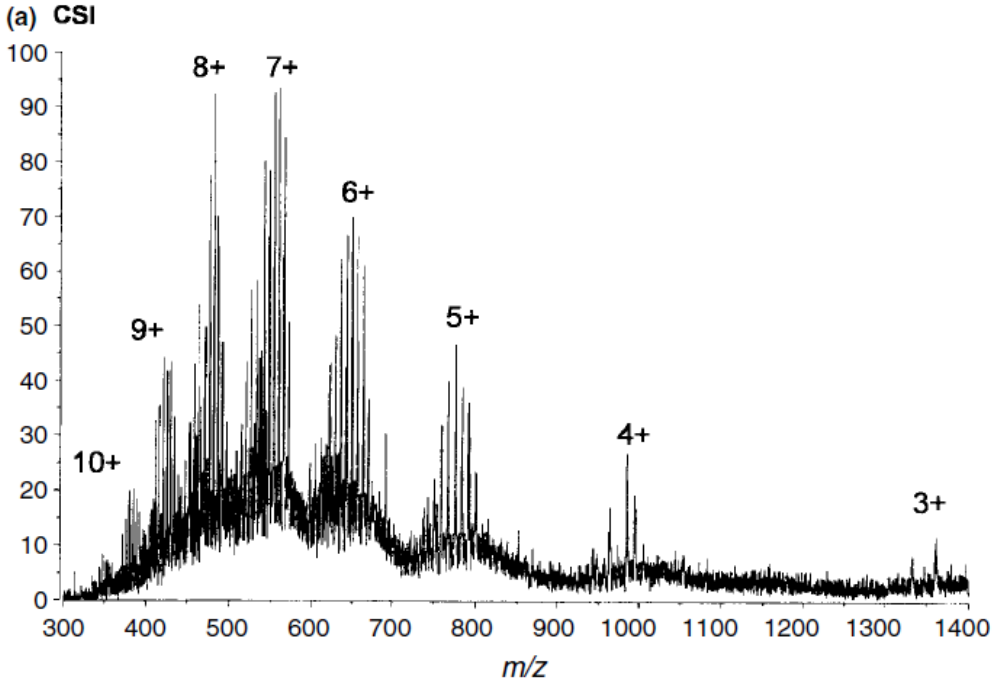
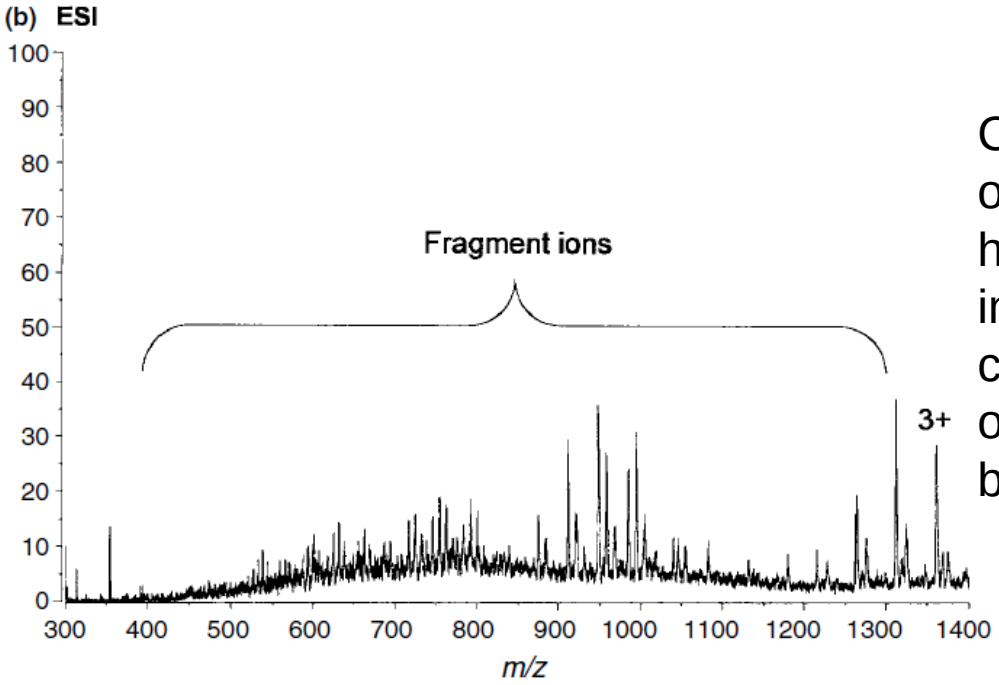
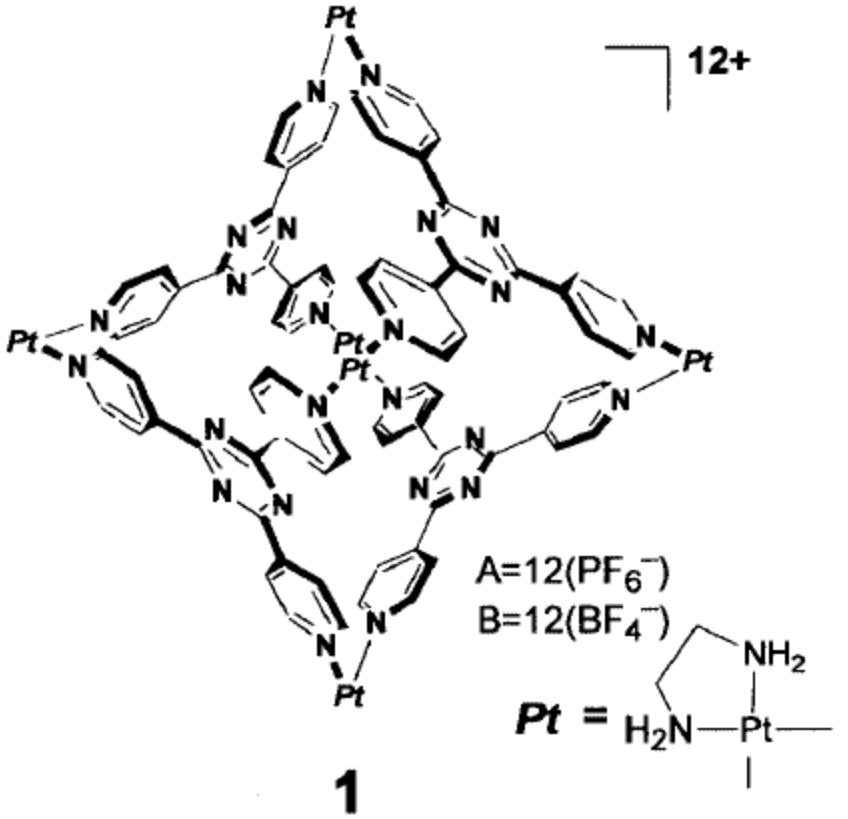


Figure 1(a) shows a prototype of the CSI apparatus, (b) (axial spray) and (c) (orthogonal spray).





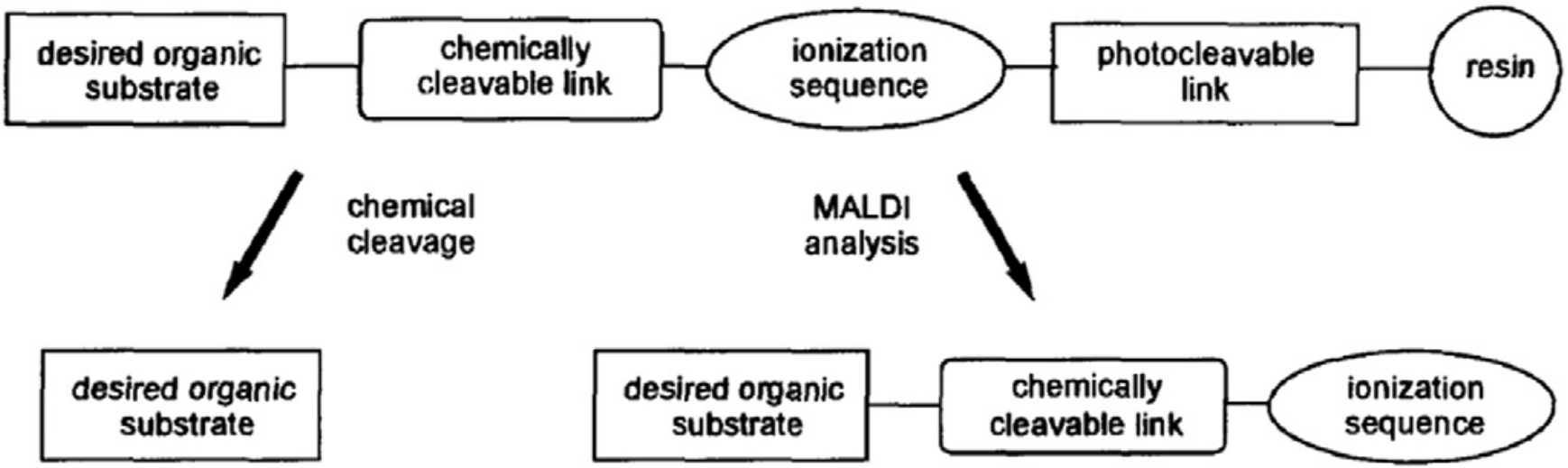


1

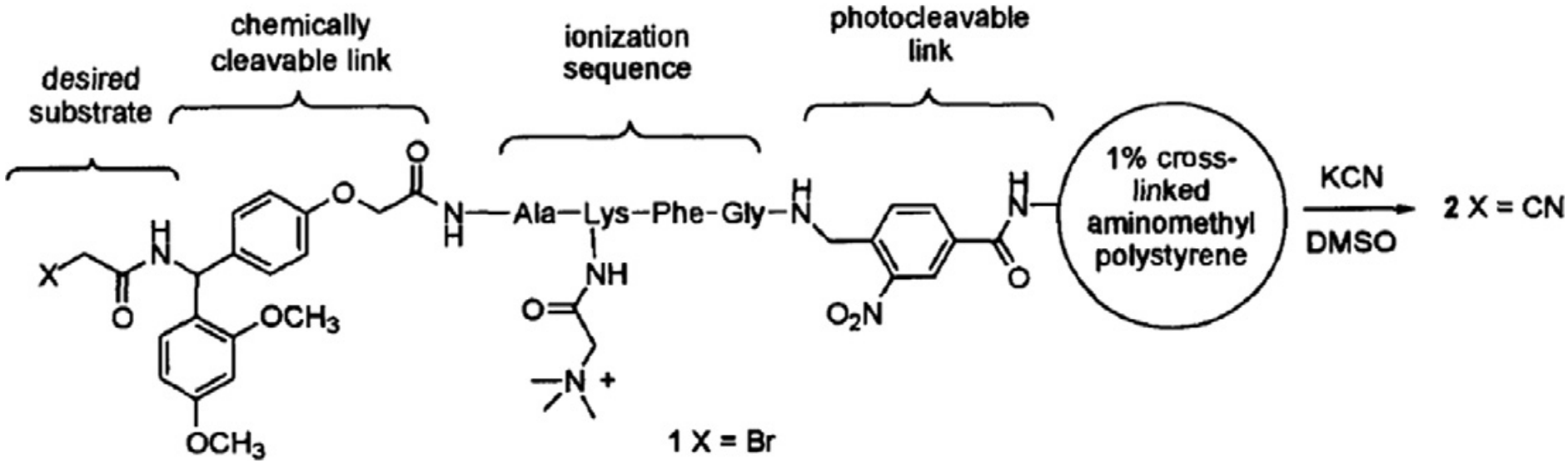
CSI has been used to study labile organometallic compounds, including host guest complexes, the multiple-link interlocking complex, the box-type complex, Grignard reagents and other organometallic compounds, and biomolecules (e.g., proline aggregation)

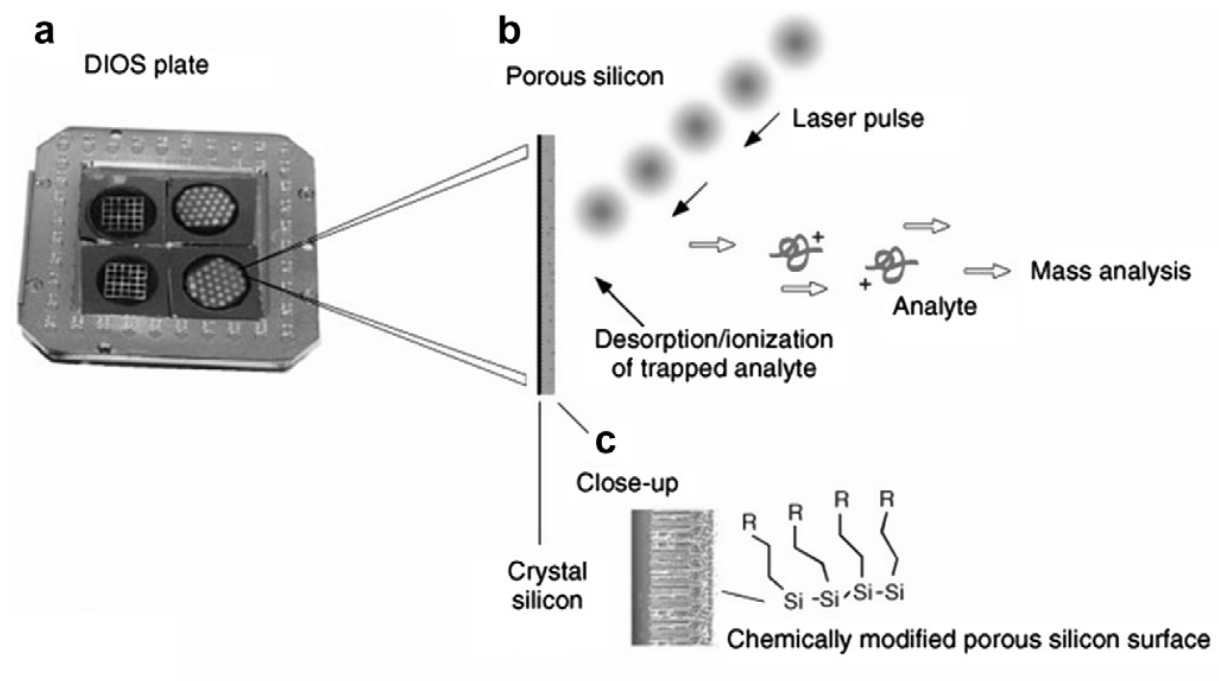
MALDI

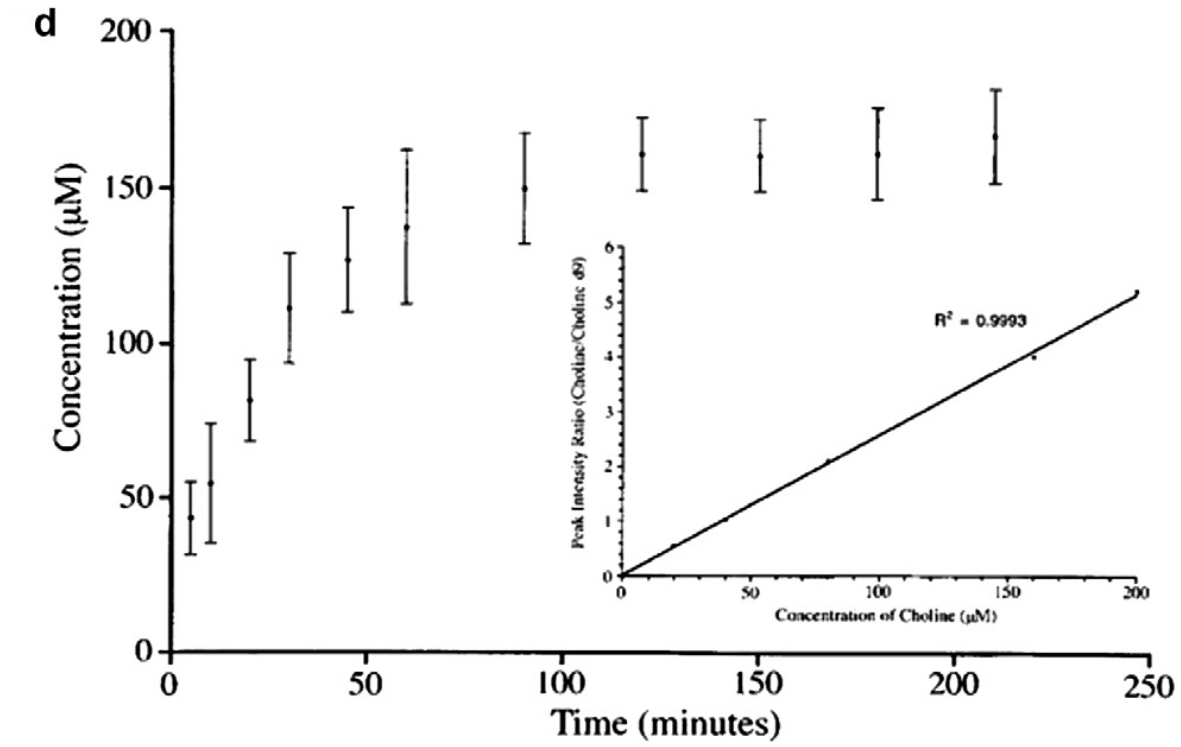
Schematic representation



Real scheme

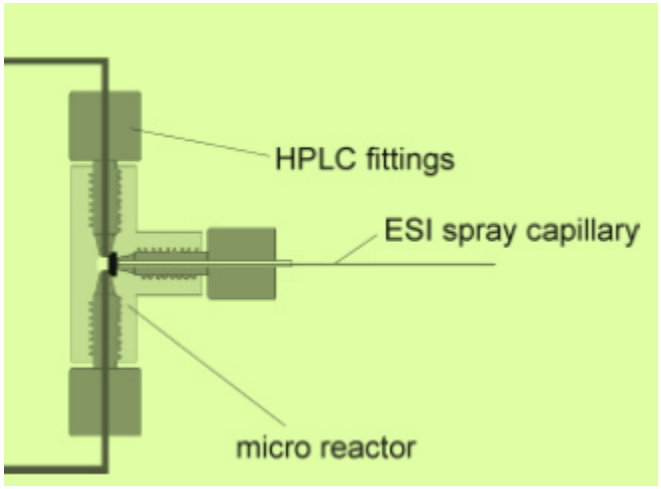


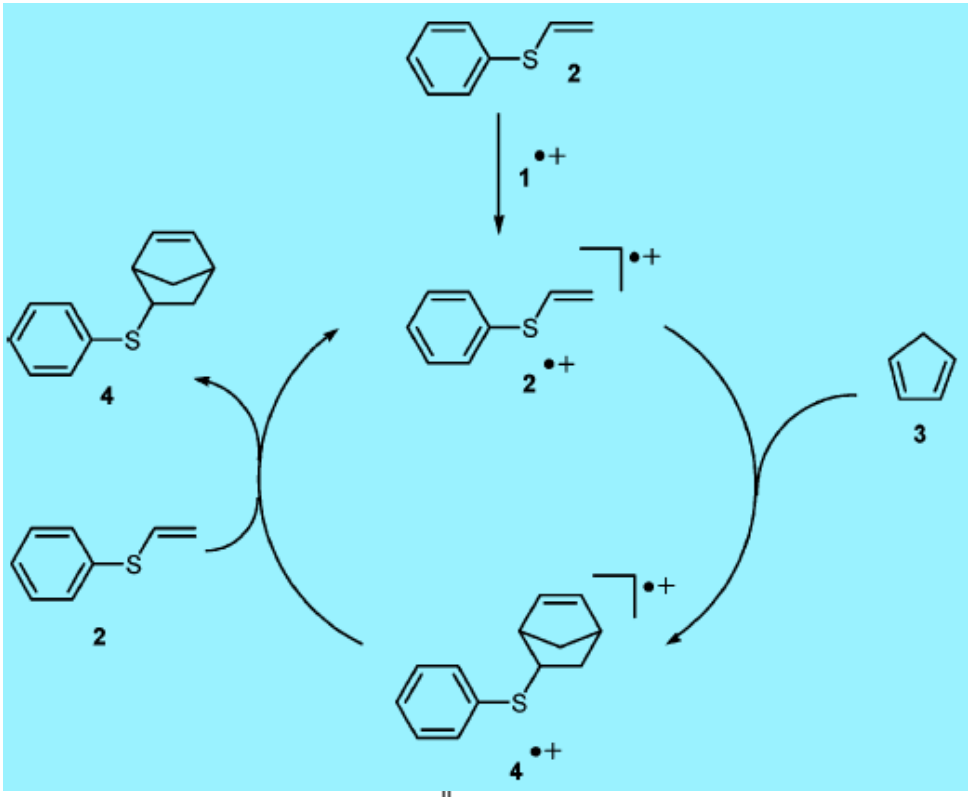


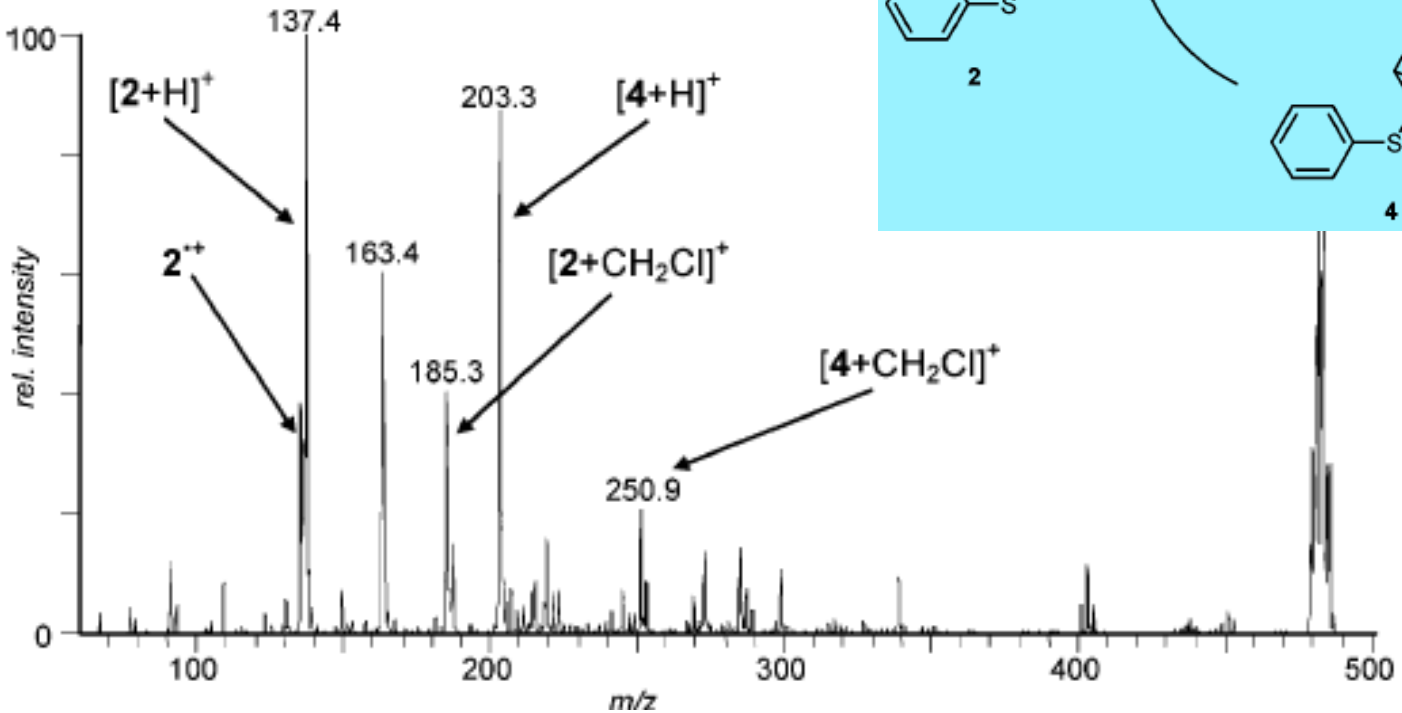


Configuration of the desorption/ionization on porous silicon (DIOS) chip: (a) on a matrix-assisted laser desorption/ionization (MALDI) plate, four porous silicon plates are place. (b) silicon-based laser desorption/ionization (c) cross-section of the porous silicon and the surface functionalities after hydrosilylation (d) plot of the conversion of acetylcholine (ACh) to choline at 25C at an initial concentration of 200 mM substrate and a concentration of 40 pM enzyme

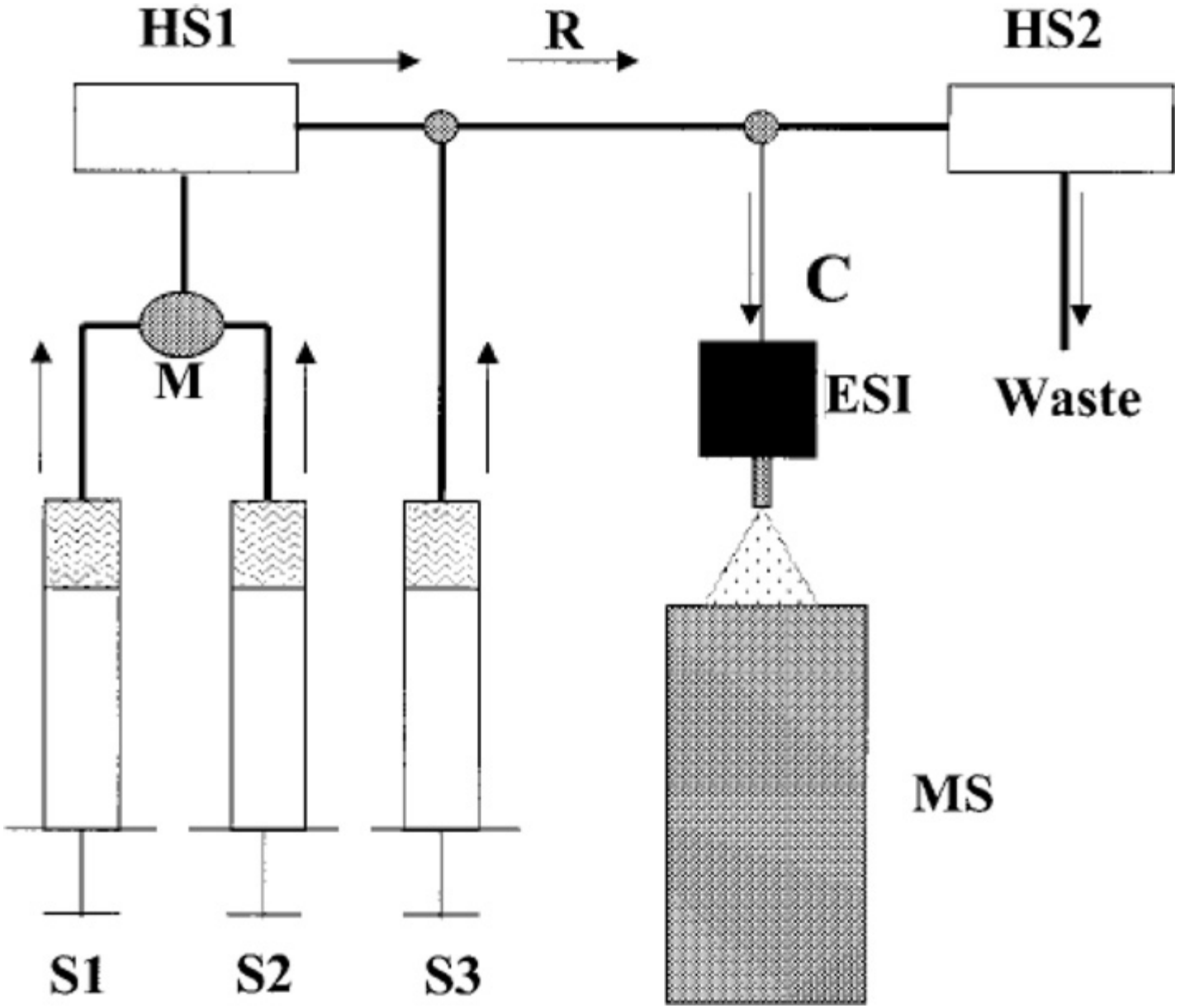
Online ESI

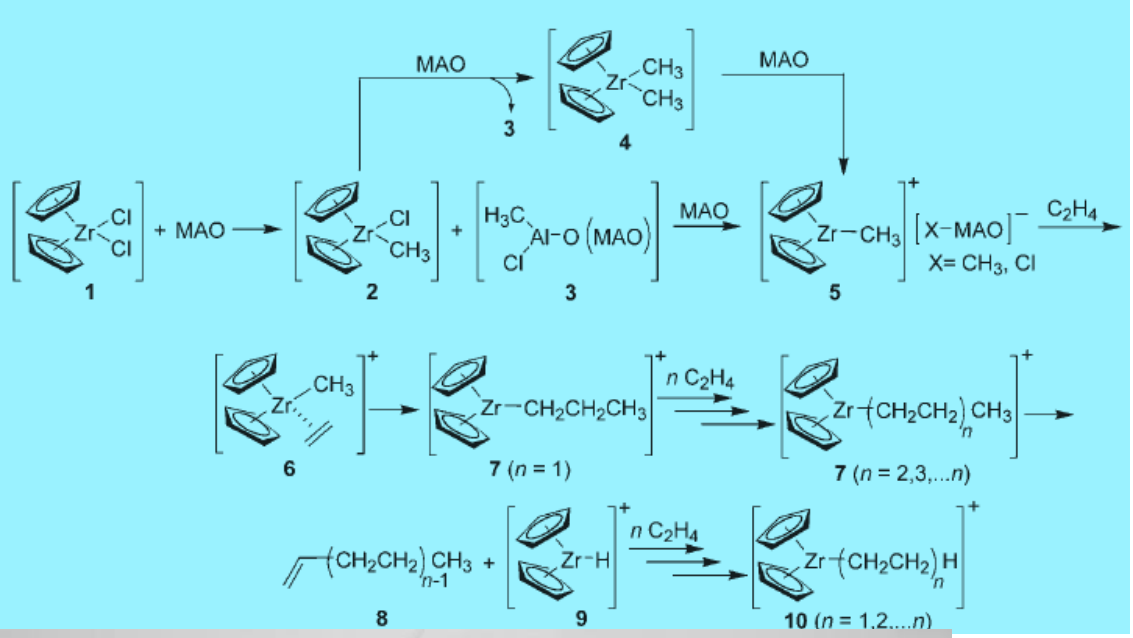

HPLC fittings
ESI spray capillary
micro reactor


2
1 •+
4
2 •+
3
2
4 •+

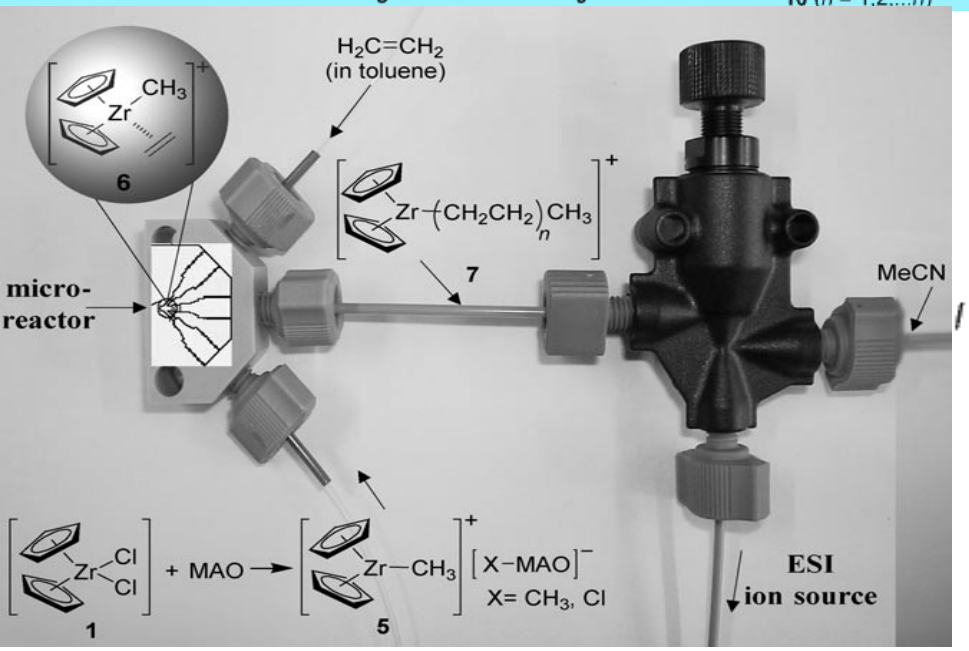

100
0
rel. intensity
137.4
[2+H]+
203.3
[4+H]+
2•+
163.4
[2+CH2Cl]+
185.3
[4+CH2Cl]+
250.9
100
200
300
400
500
m/z

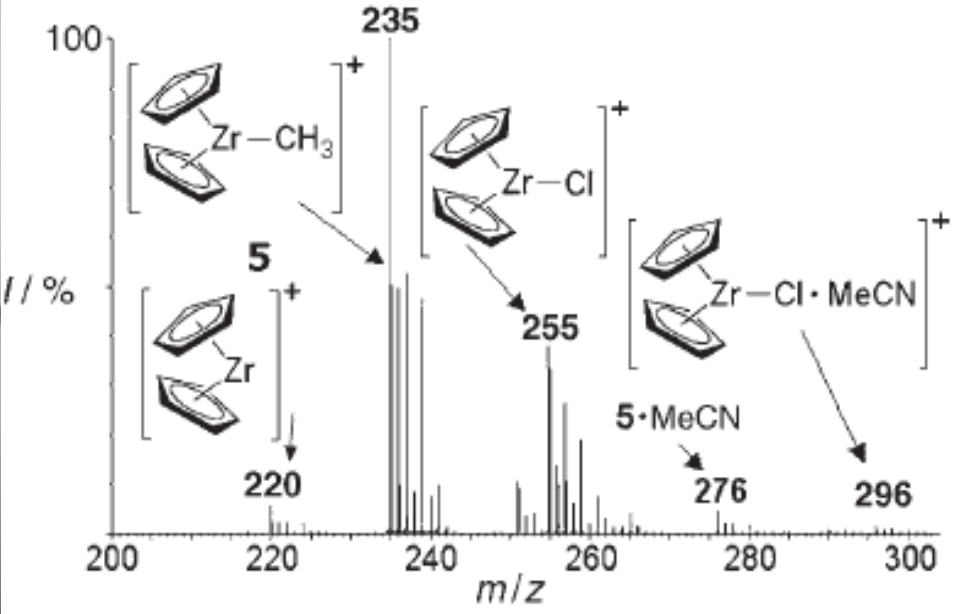
Stopped-flow electrospray ionization mass spectrometry



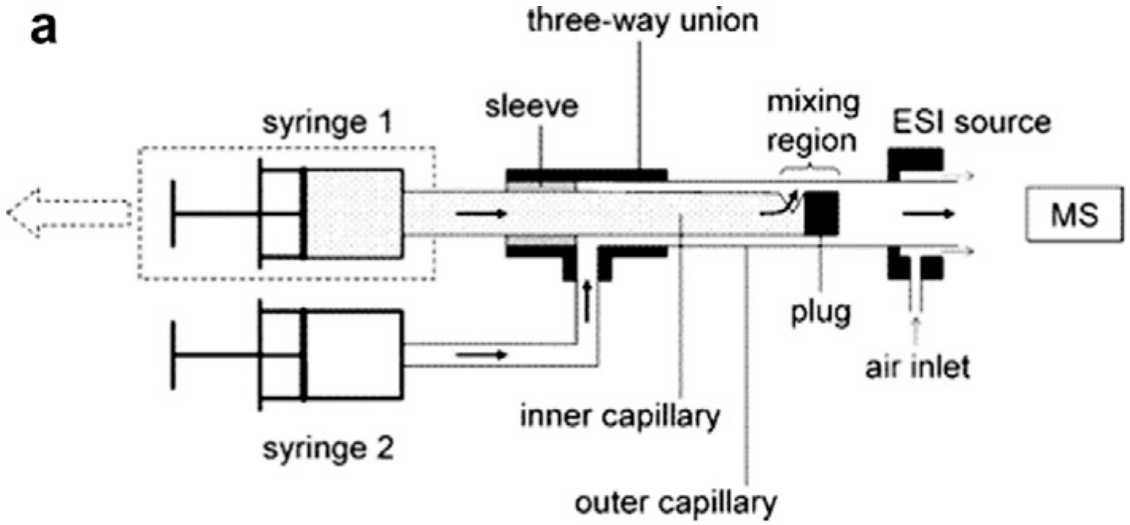


Application of stopped flow ESI MS

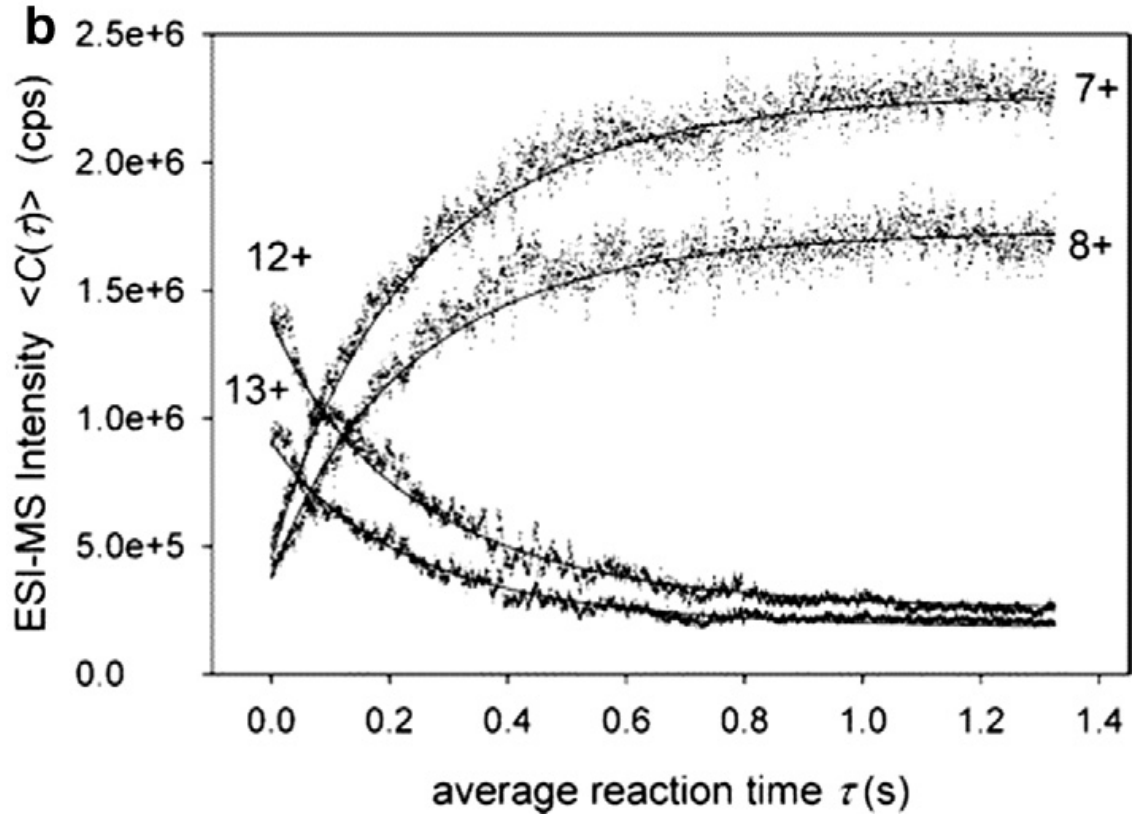




Proposed mechanism of the Ziegler–Natta polymerization of C_2H_4 with the homogeneous catalyst [Cp_2ZrCl_2]/ oligomeric methyl aluminoxane (MAO).

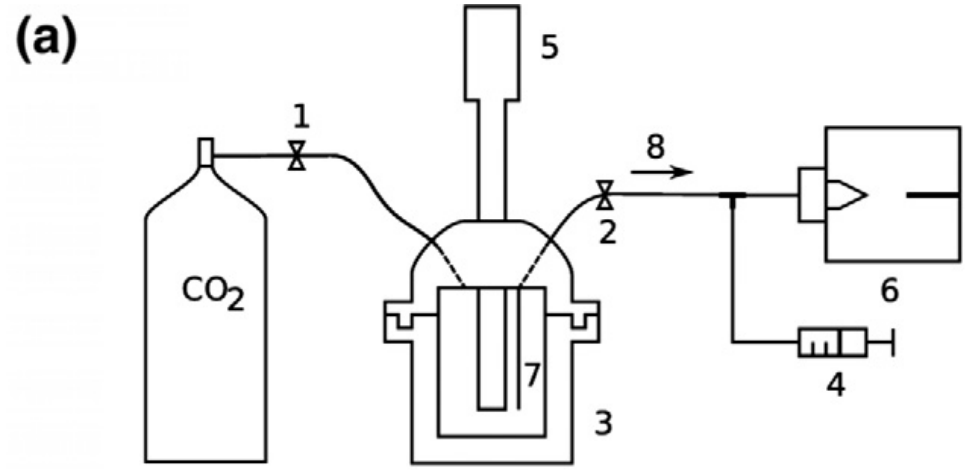


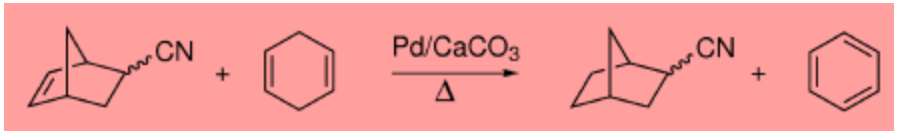
Adjustable reaction chamber
Time scale is 0-1.4 sec

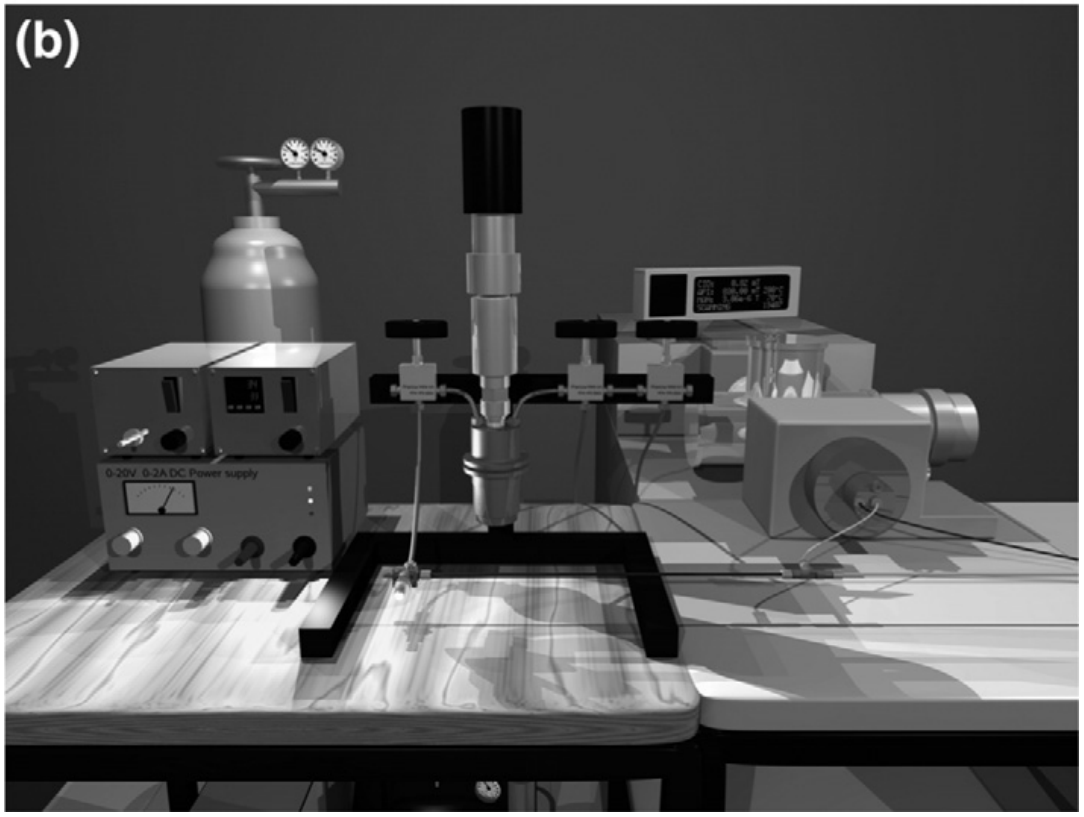


Kinetic study of ubiquitin refolding using this reaction-monitoring device by monitoring its protonated molecules in four different charge states

High pressure ESI MS

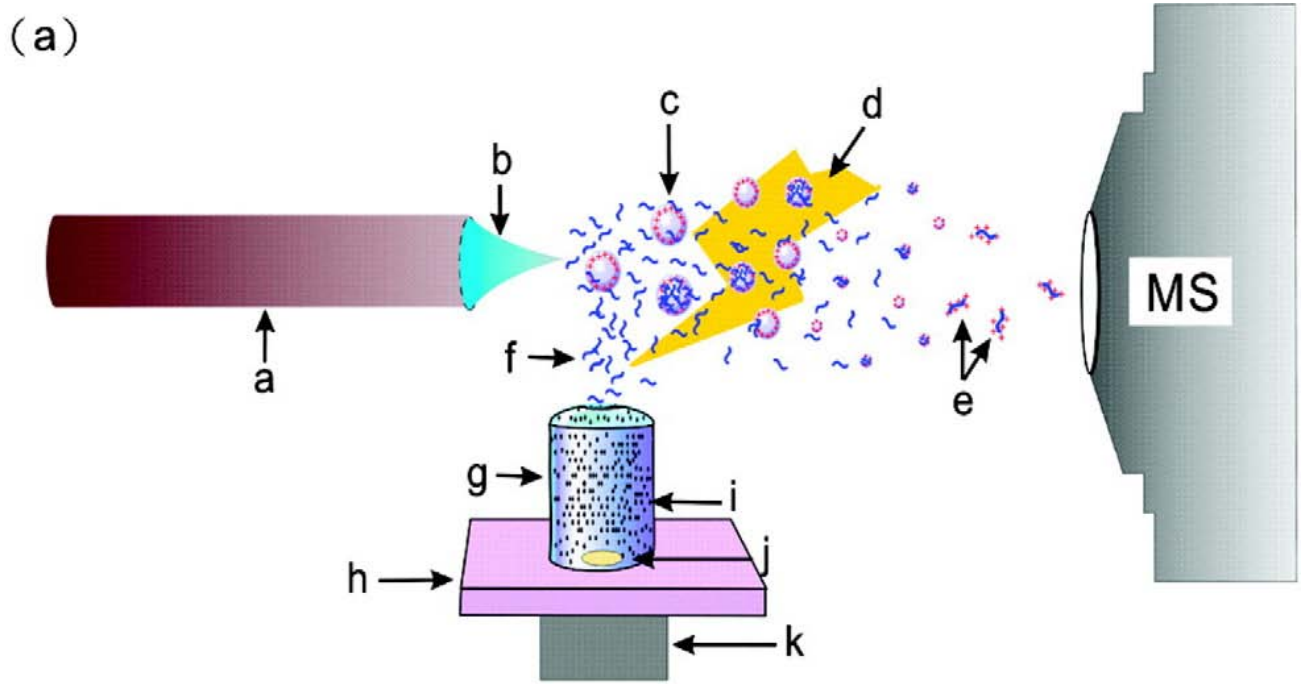


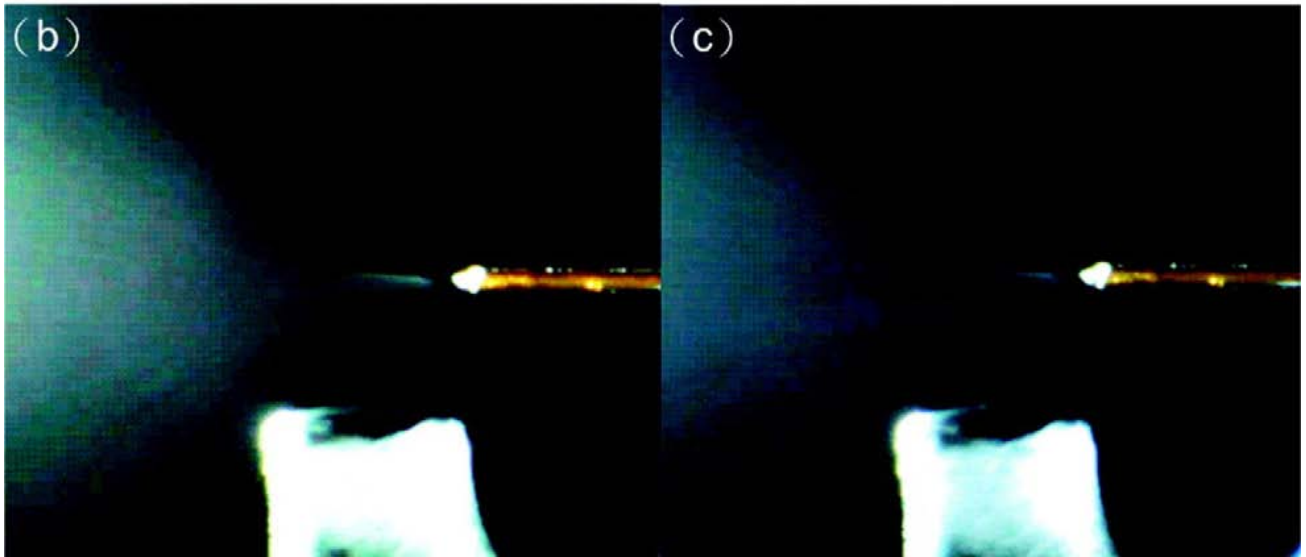


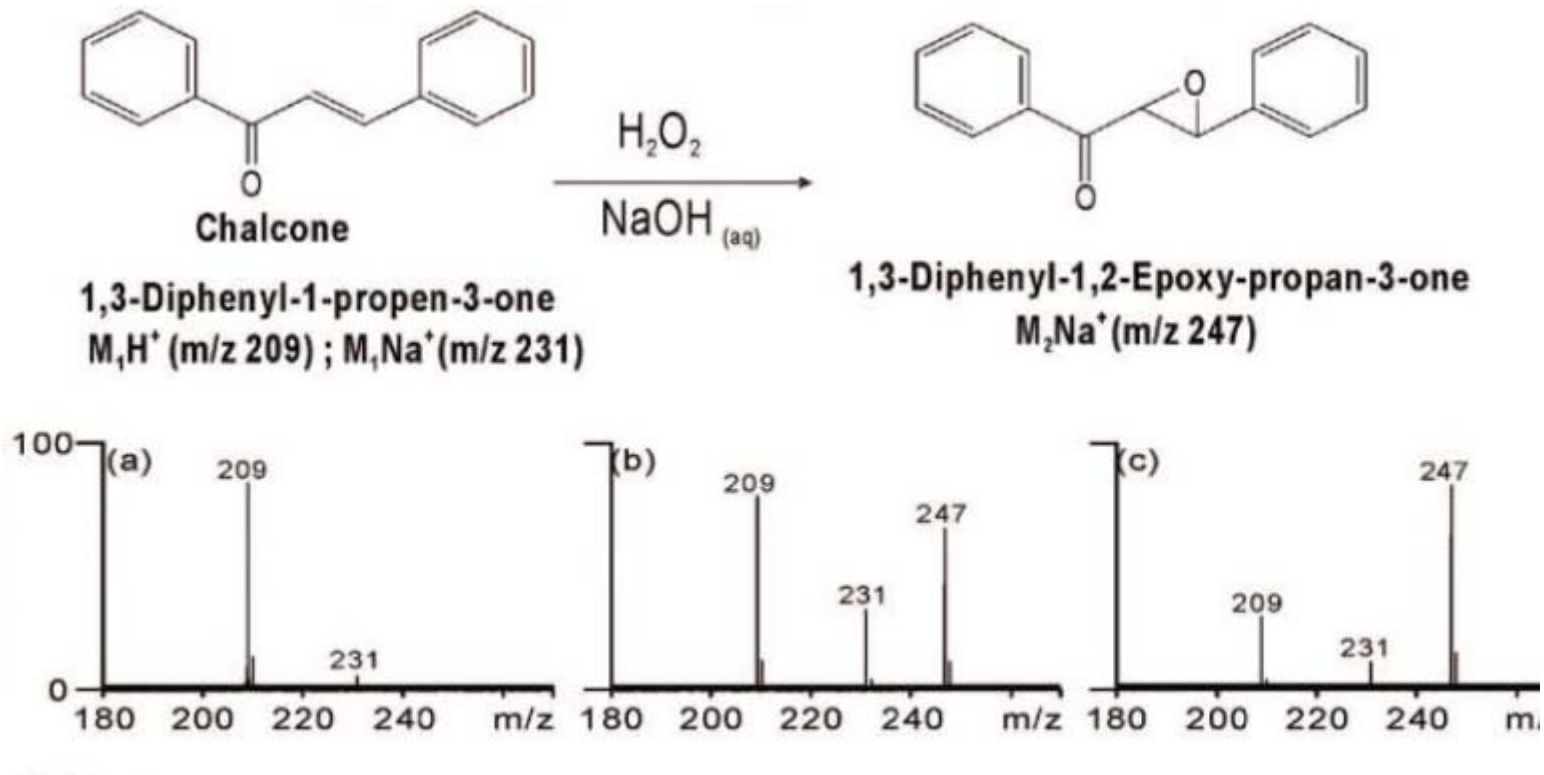


(a) Design for on-line electrospray ionization (ESI) analysis of reaction under high pressures. 1: high-pressure valve; 2: high-pressure split valve; 3: reactor assembly with fishing tube and sonotrode; 4: syringe for electrospray solvent; 5: ultrasonic chamber 6: mass spectrometer ion source; 7: fishing tube; 8, sample path and direction. (b) Reactor and MS assembly.

Liquid electrospray-assisted laser desorption/ionization (ELDI)

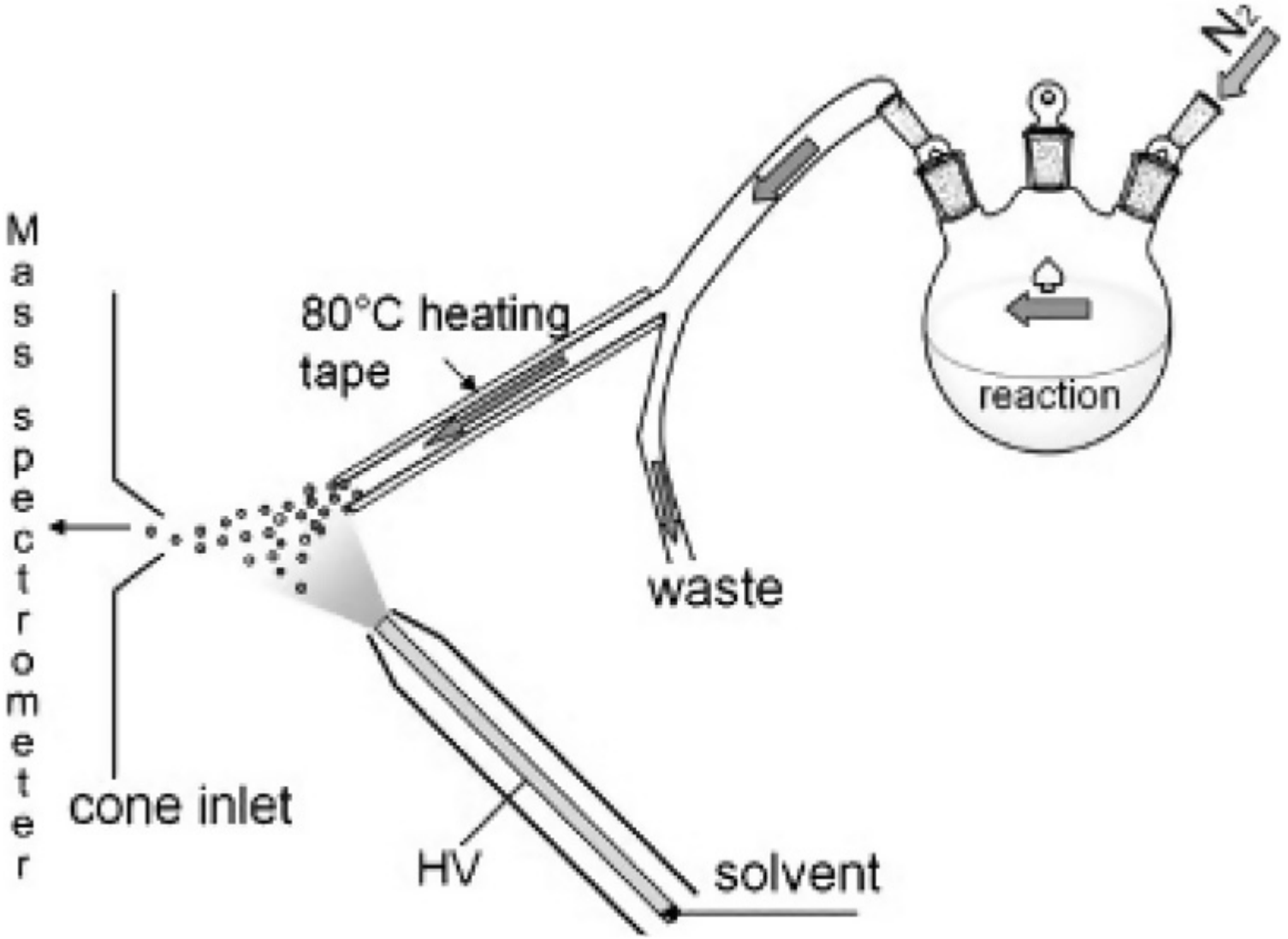




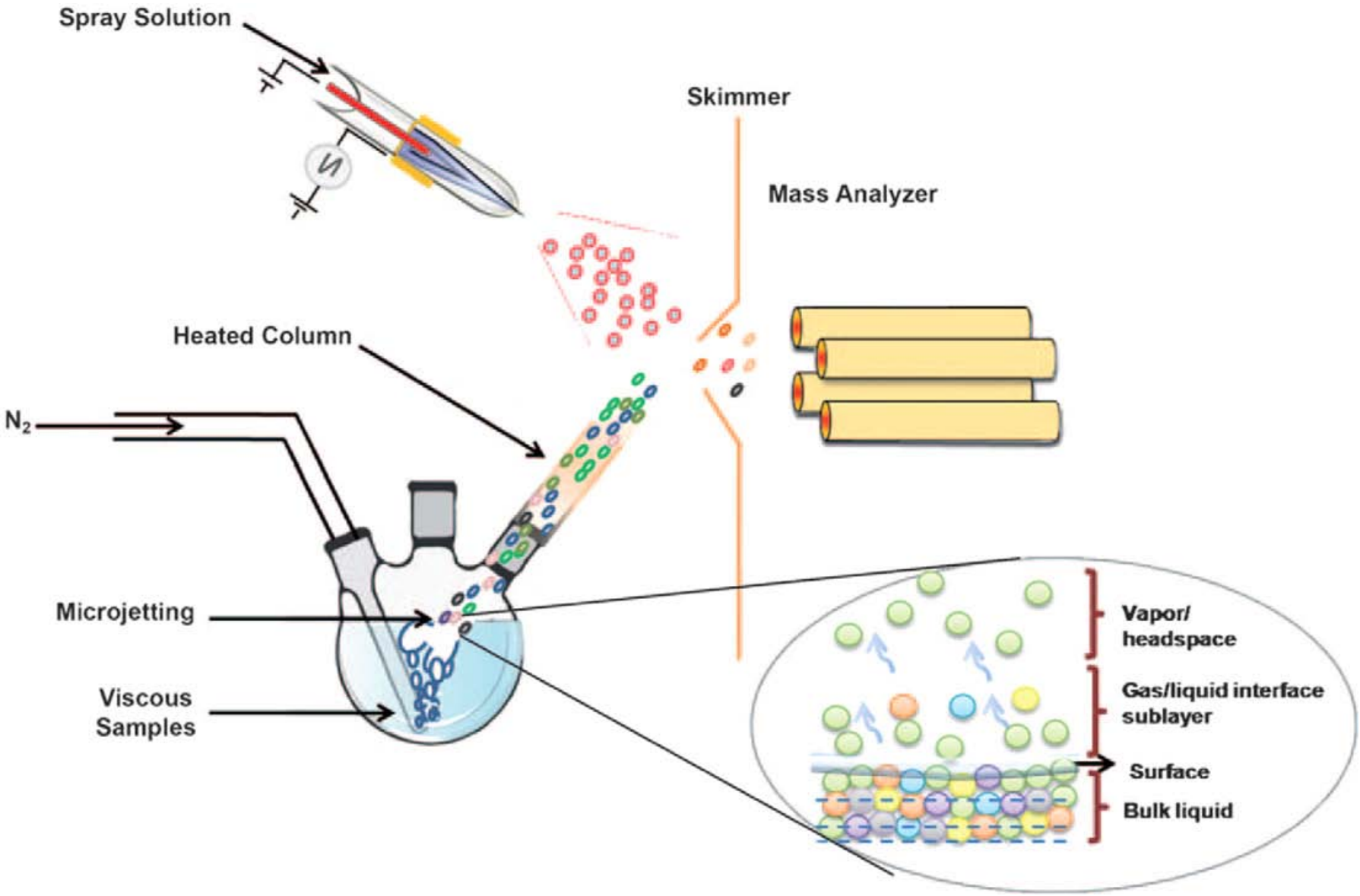


Using liquid ELDI to continuously monitor the state of the epoxidation of chalcone in ethanol. Positive-ion liquid ELDI mass spectra were recorded at three different stages: (a) immediately after H_2O_2 had been added into the sample solution and (b) immediately and (c) 1 min after the sample solution had been changed to basic through the addition of 1 M NaOH.

Extractive electrospray ionization (EESI)

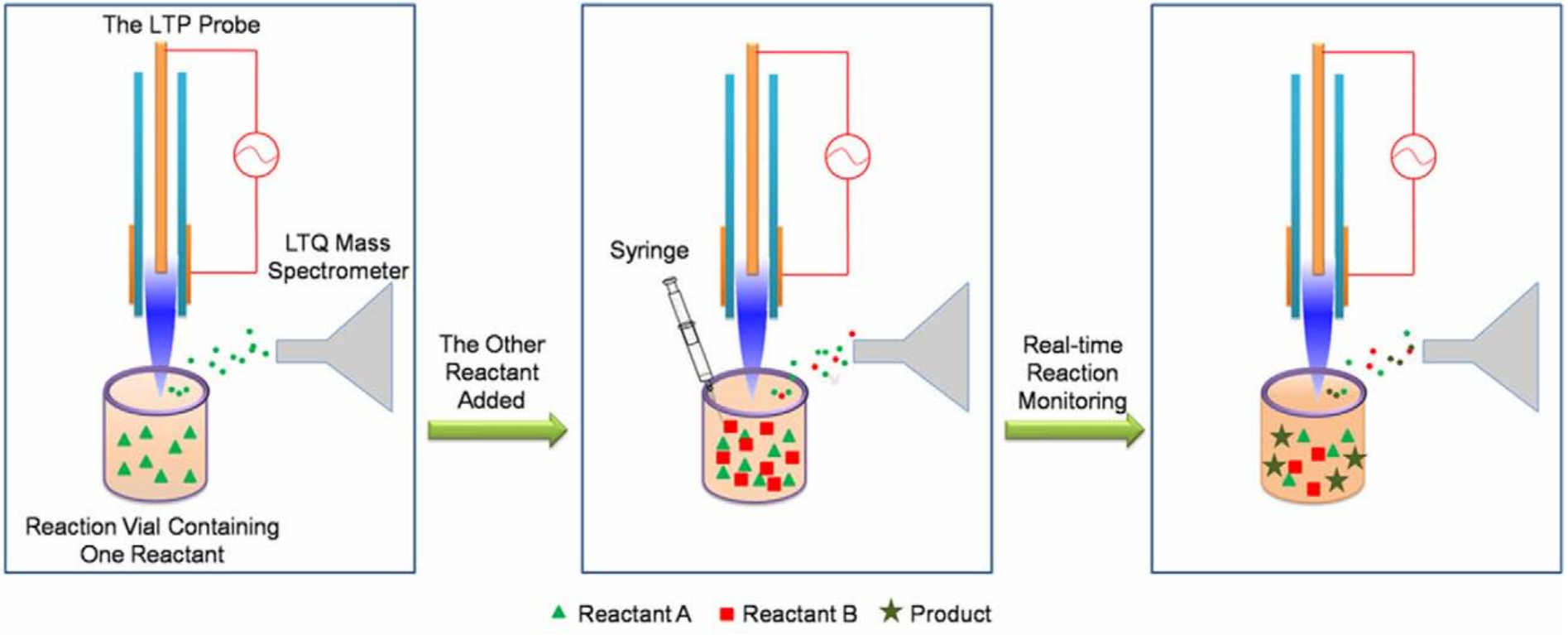


Extractive electrospray ionization (EESI)

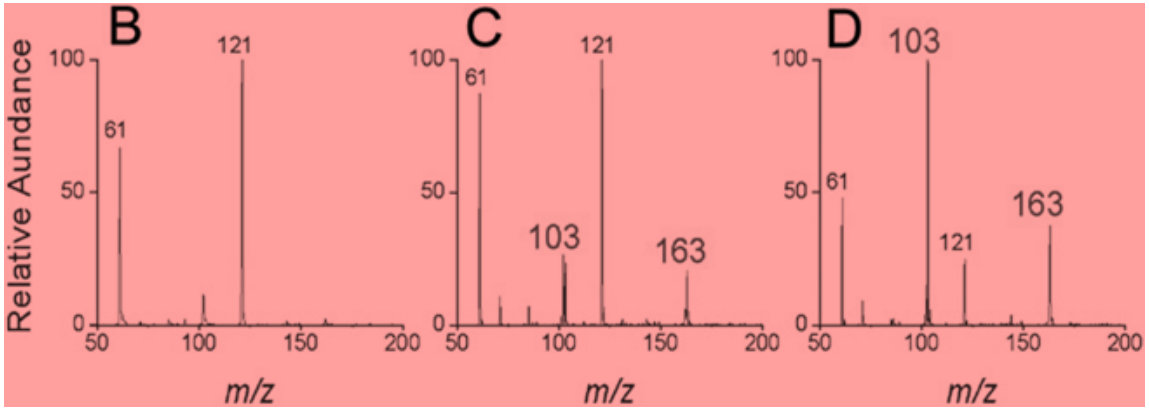


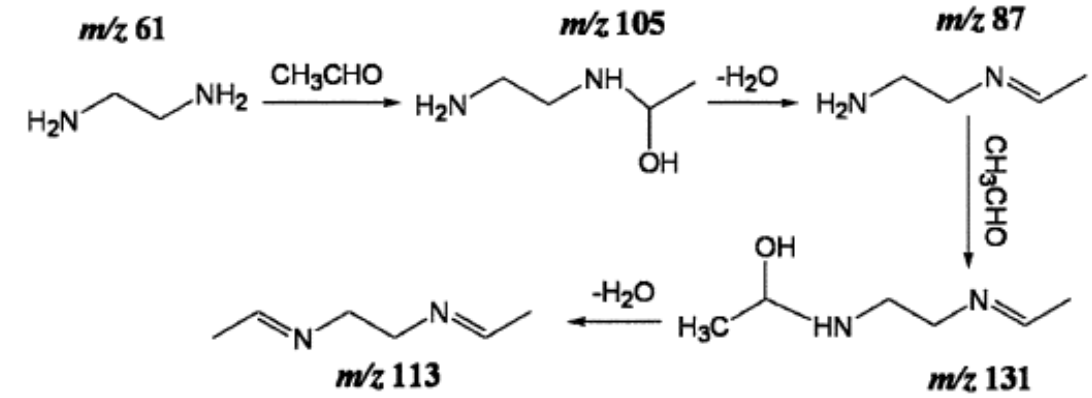
conversion of fructose to 5-hydroxymethylfurfural at 80^{o}C in 1-ethyl-3 methylimidazolium chloride was monitored. Time scale 0-0.2 sec

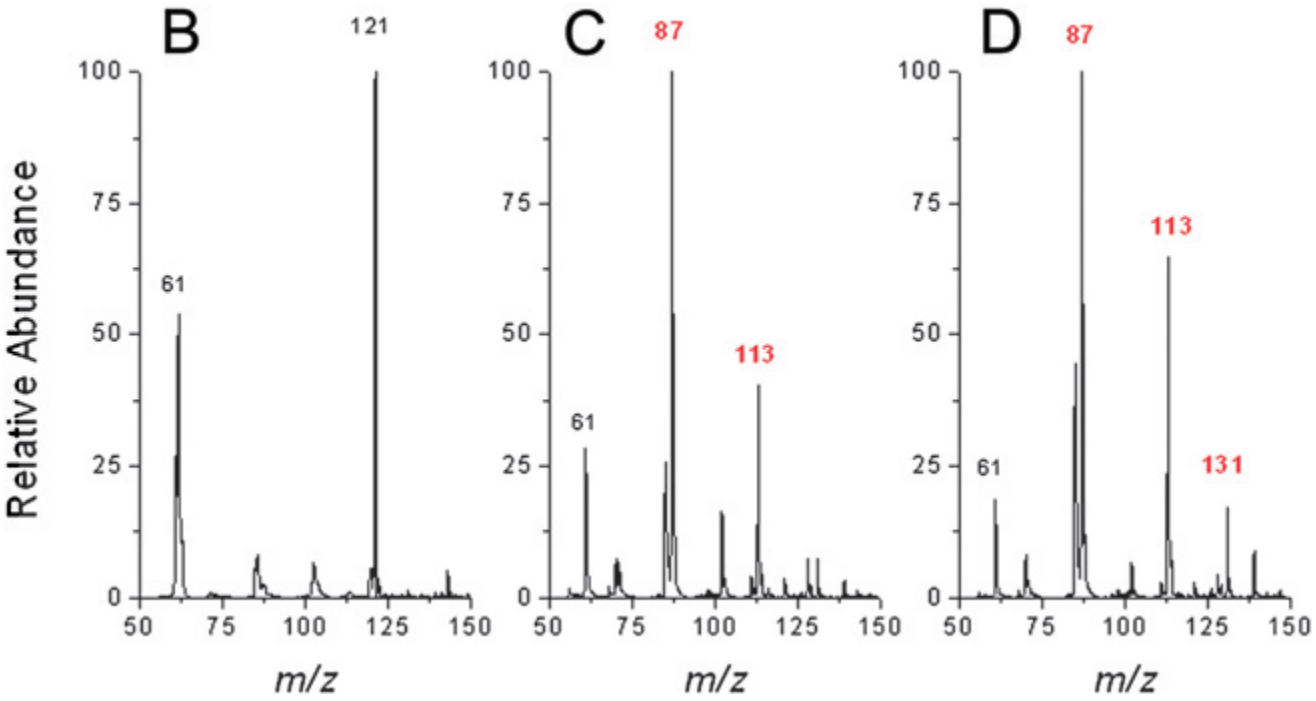
Low-temperature plasma (LTP)



$$H_2NCH_2CH_2NH_2 + (CH_3CO)_2O \longrightarrow H_2NCH_2CH_2NHCOCH_3 + CH_3COOH$$




m/z 61
m/z 105
m/z 87
CH3CHO
-H2O
CH3CHO
-H2O
m/z 113
m/z 131


B
C
D
Relative Abundance
m/z
121
87
113
131
61

Thank you