Click-enabled tetrazine ionic liquid as advanced material for chemo-selective gas detection via inverse electron-demand Diels–Alder reaction

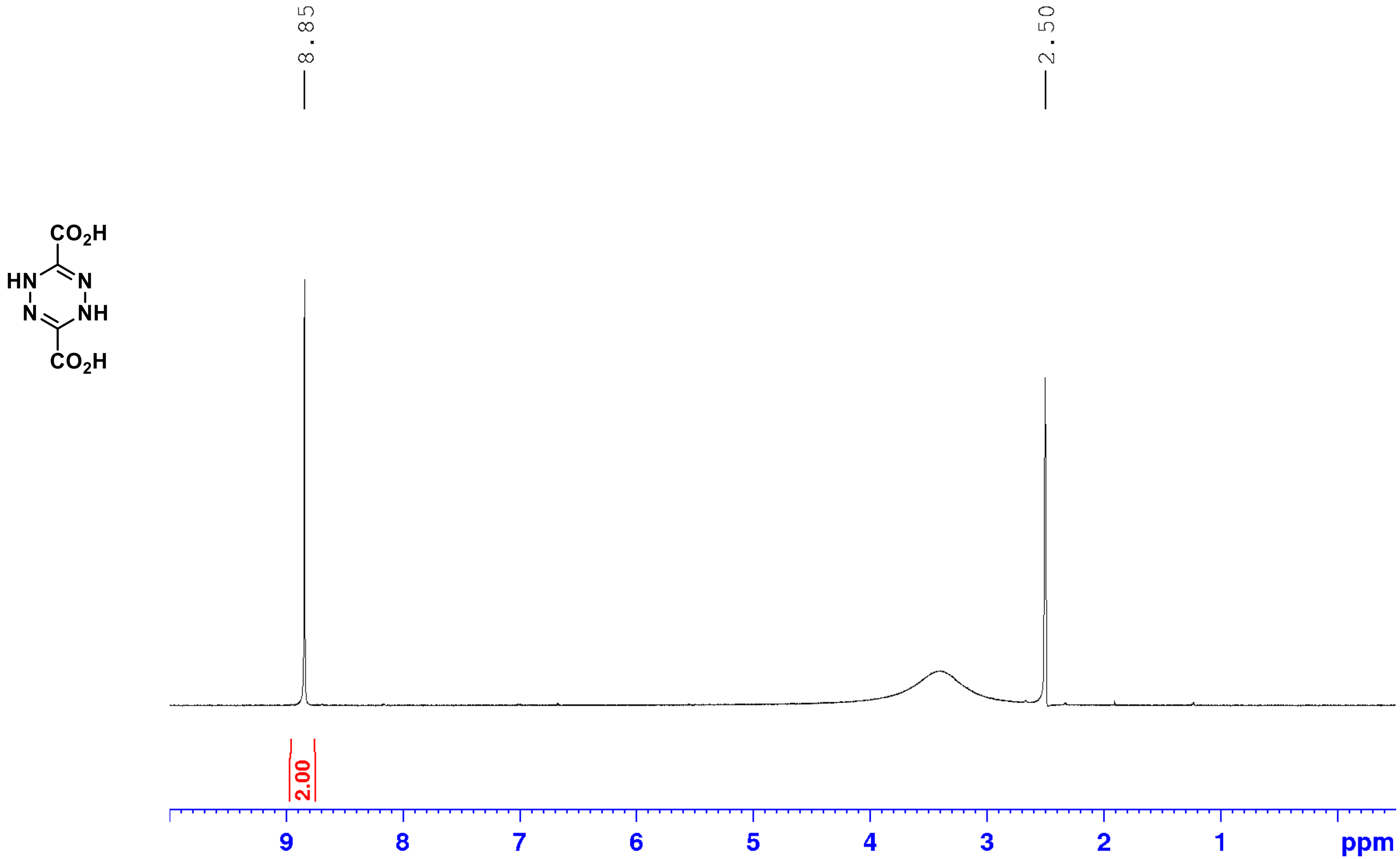
Chien-Yuan Chen, Yu-Hsin Chung, Yu-Qian Qiu, Wen-Chun Su, Wen-Ting Hsiao, and Yen-Ho Chu*

Department of Chemistry and Biochemistry, National Chung Cheng University

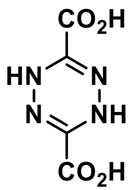
Chiayi 62102, Taiwan, Republic of China

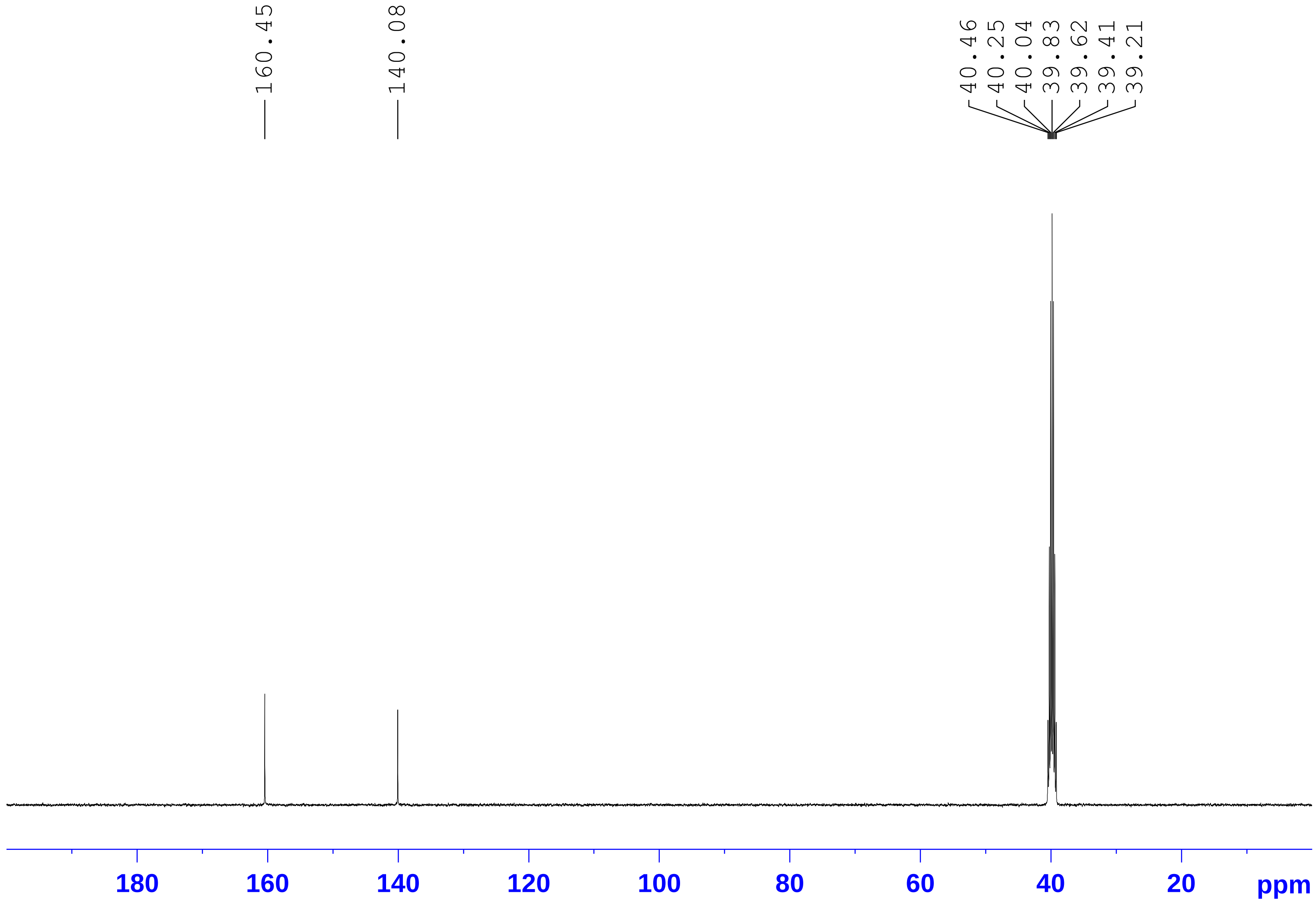
* Corresponding author. Tel: 886 52729139; fax: 886 52721040; e-mail: cheyhc@ccu.edu.tw

[1]H NMR spectrum of 1,4-dihydro-1,2,4,5-tetrazine-3,6-dicarboxylic acid



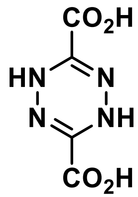
^{13}C NMR spectrum of 1,4-dihydro-1,2,4,5-tetrazine-3,6-dicarboxylic acid





High-resolution mass spectrum of 1,4-dihydro-1,2,4,5-tetrazine-3,6-dicarboxylic acid

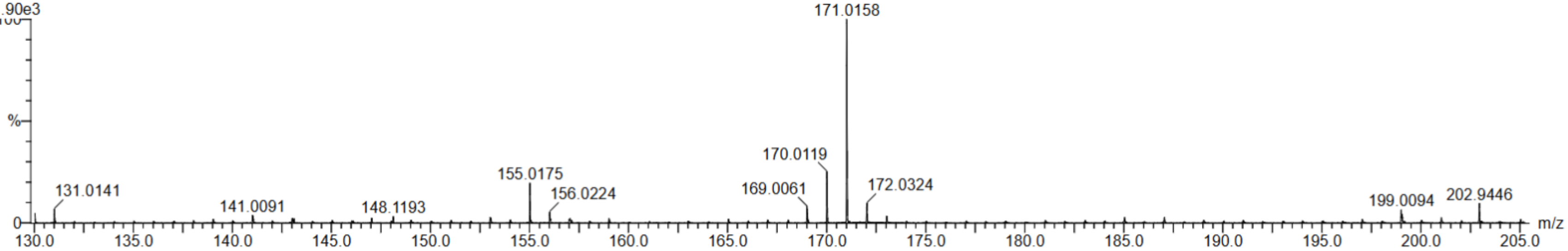
Elemental Composition Report



Single Mass Analysis
Tolerance = 30.0 PPM / DBE: min = -1.5, max = 100.0
Selected filters: None

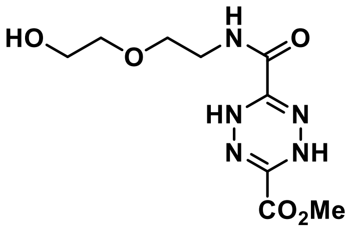
Monoisotopic Mass, Even Electron Ions
2 formula(e) evaluated with 1 results within limits (all results (up to 1000) for each mass)
Elements Used:
C: 0-100 H: 0-400 N: 4-4 O: 4-4

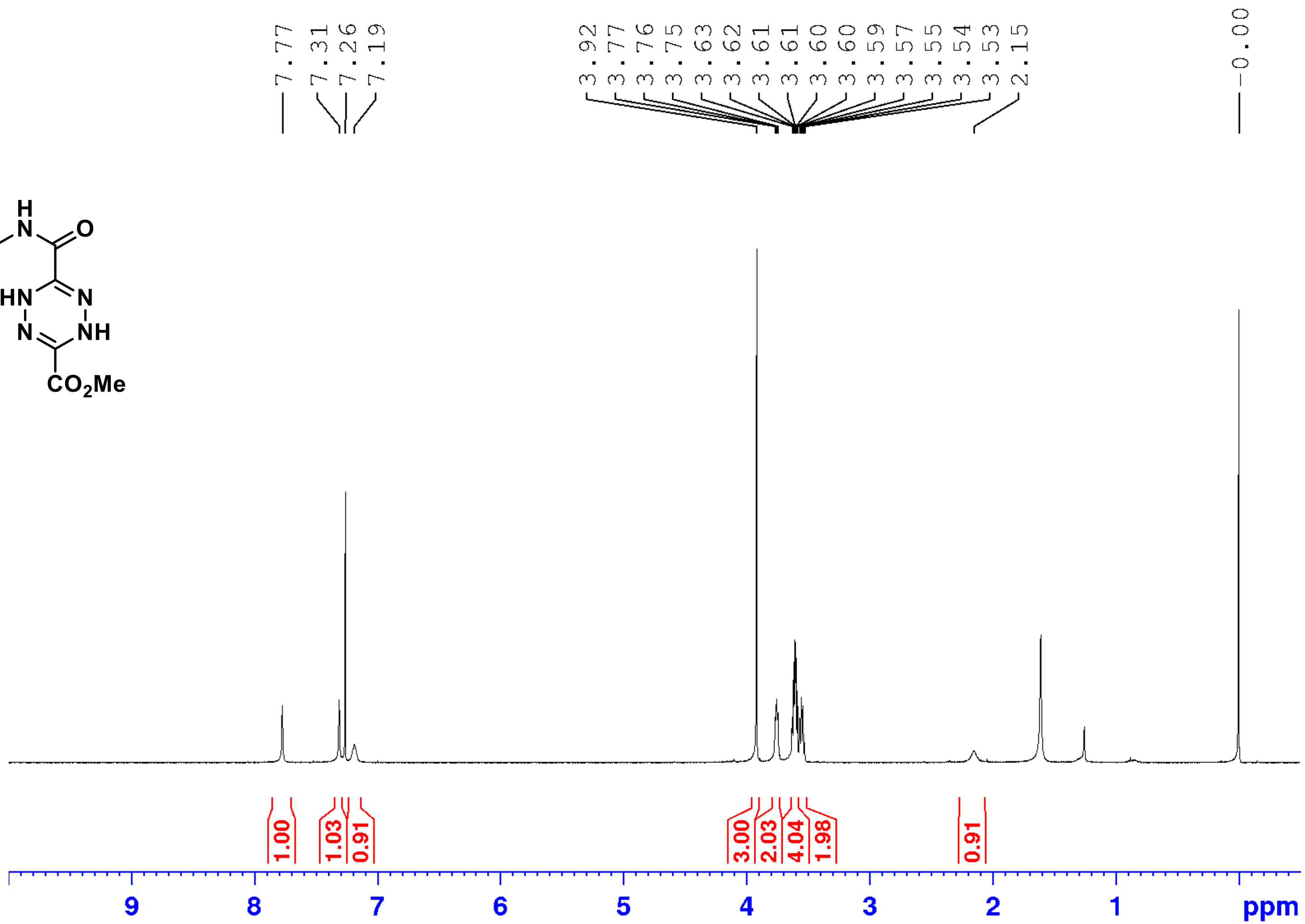
20241231_1_NEG_1 235 (4.012)
TOF MS ES-
1.90e3



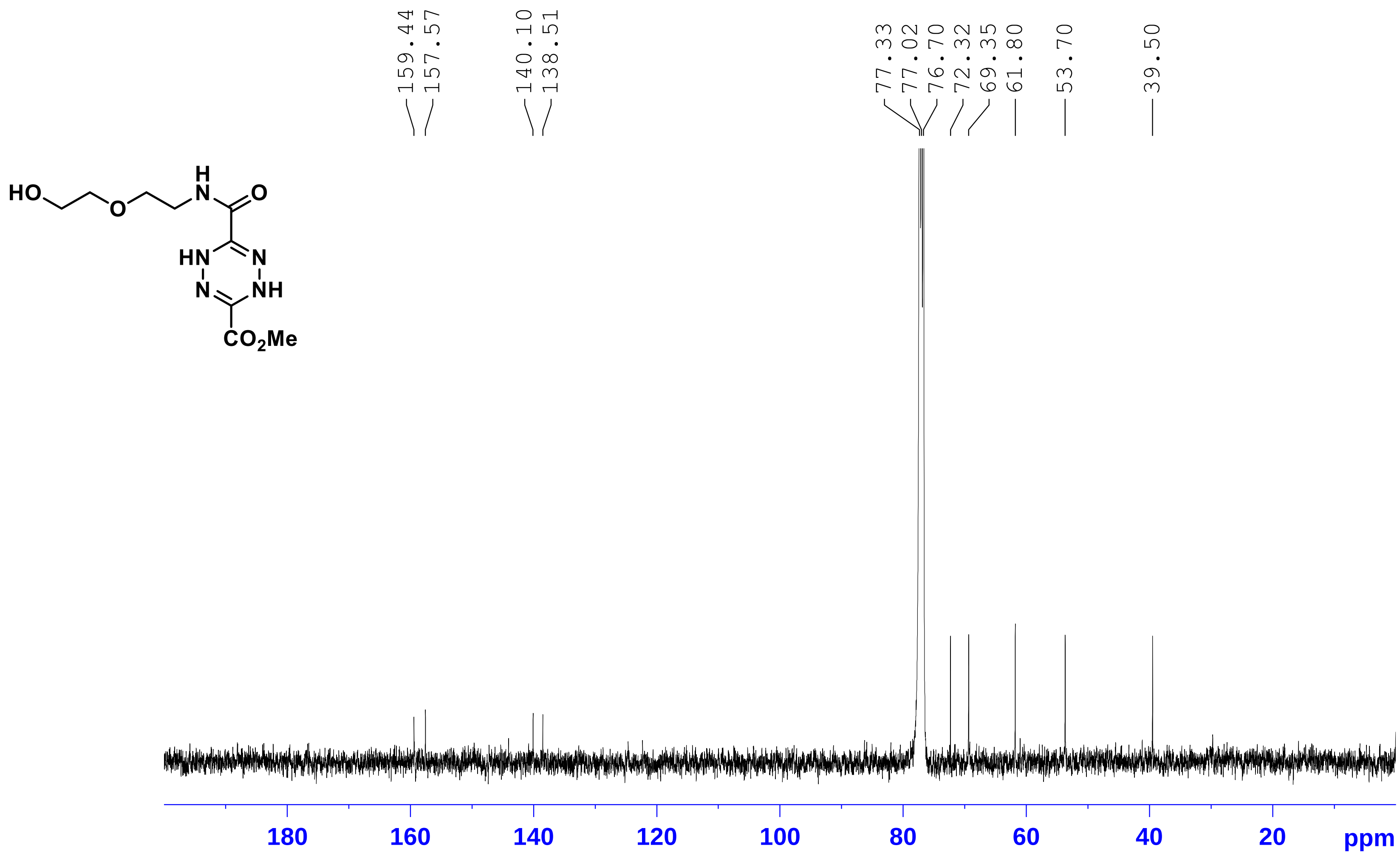
Minimum:				-1.5	
Maximum:		5.0	30.0	100.0	
Mass	Calc. Mass	mDa	PPM	DBE	Formula
171.0158	171.0154	0.4	2.3	5.5	C4 H3 N4 O4

[1]H NMR spectrum of methyl 6-((2-(2-hydroxyethoxy)ethyl)carbamoyl)-1,4-dihydro-1,2,4,5-tetrazine-3-carboxylate

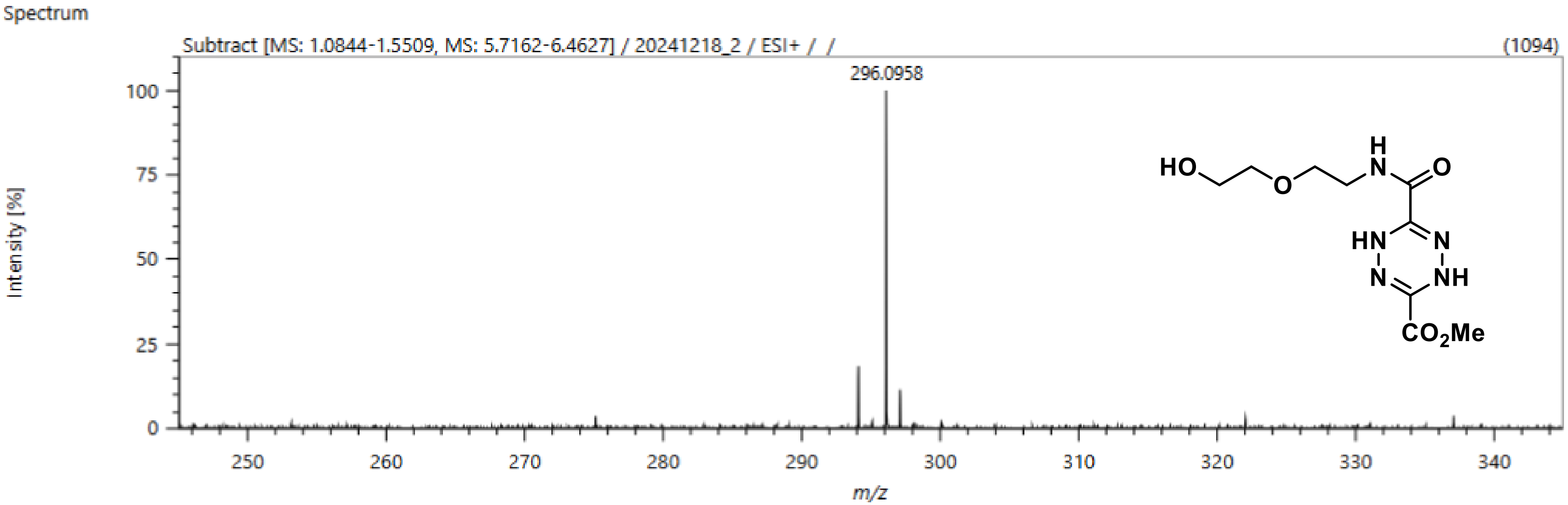




^{13}C NMR spectrum of methyl 6-((2-(2-hydroxyethoxy)ethyl)carbamoyl)-1,4-dihydro-1,2,4,5-tetrazine-3-carboxylate



High-resolution mass spectrum of methyl 6-((2-(2-hydroxyethoxy)ethyl)carbamoyl)-1,4-dihydro-1,2,4,5-tetrazine-3-carboxylate



Elemental Composition

Parameters

Tolerance:	±3.00 ppm
Electron:	Odd/Even
Charge:	+1
DBE:	-99.0 - 999.0

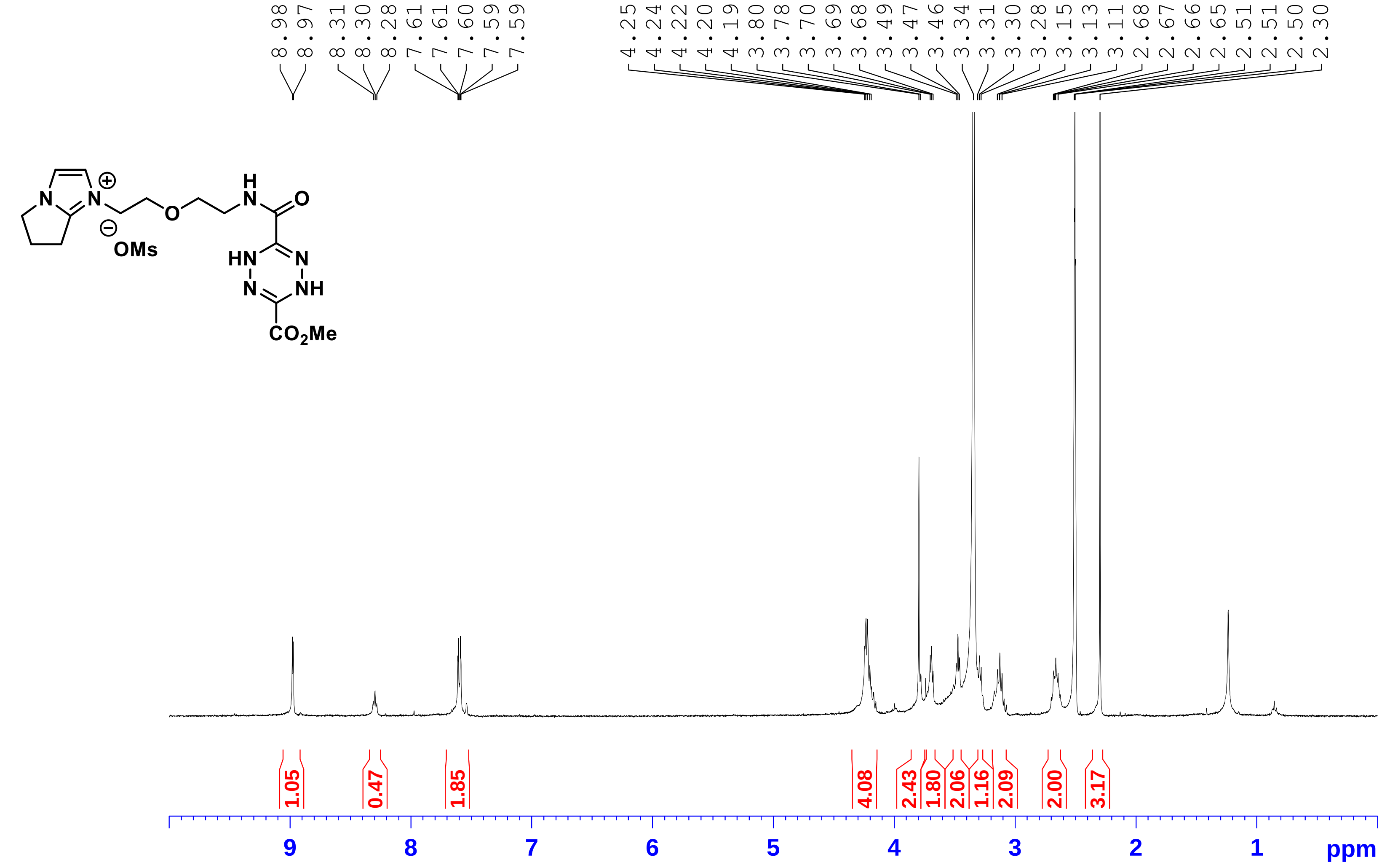
Elements Set 2:

Symbol	C	H	O	N	Na
Min	0	0	5	5	1
Max	400	1000	5	5	1

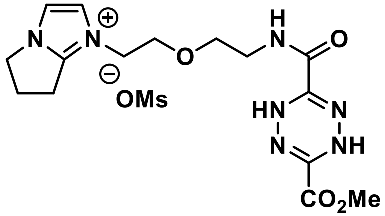
Results

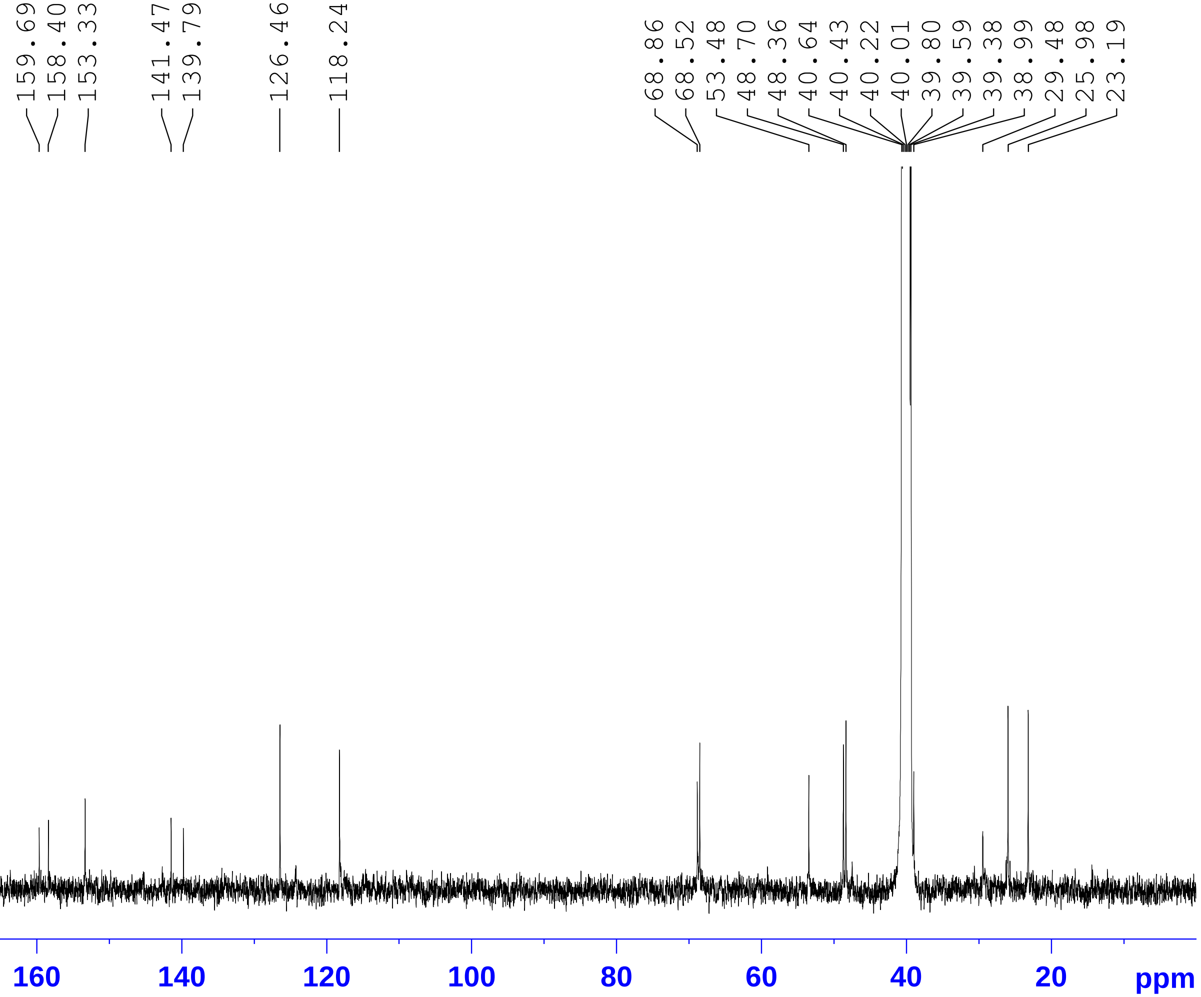
Mass	Formula	Calculated Mass	Mass Difference [mDa]	Mass Difference [ppm]	DBE
296.09584	C9 H15 N5 O5 Na	296.09654	-0.70	-2.37	4.5

^1H NMR spectrum of [DHTz-3C-im][OMs]

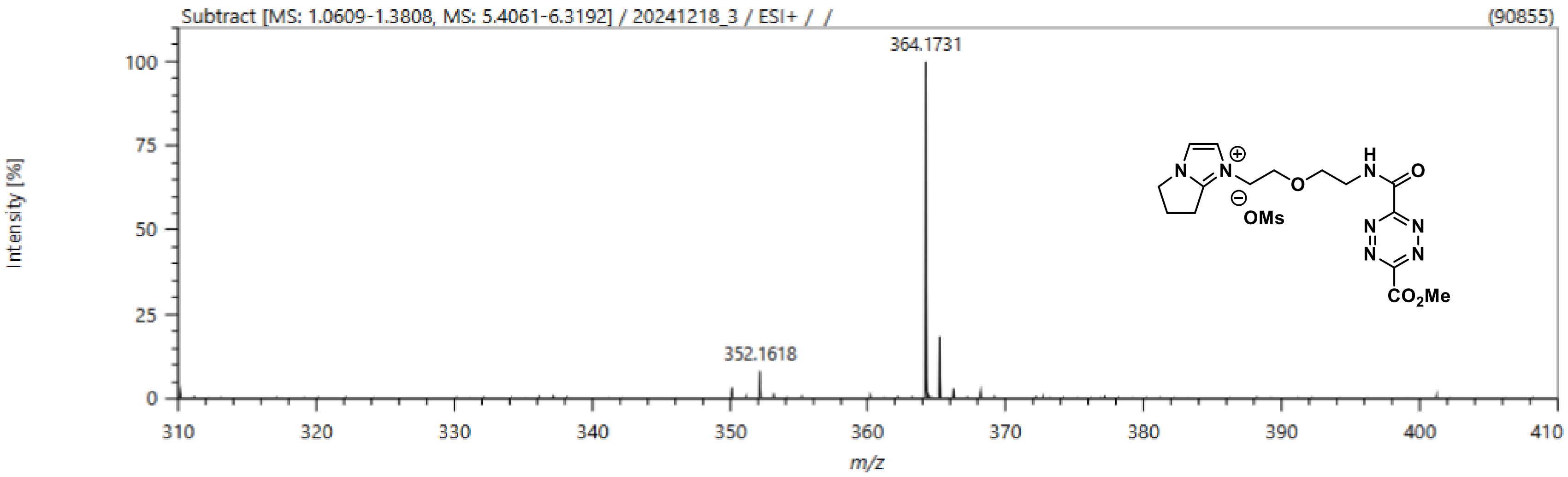


^{13}C NMR spectrum of [DHTz-3C-im][OMs]





High-resolution mass spectrum of [DHTz-3C-im][OMs]



Elemental Composition

Parameters	
Tolerance:	±2.00 ppm
Electron:	Odd/Even
Charge:	+1
DBE:	-99.0 - 999.0

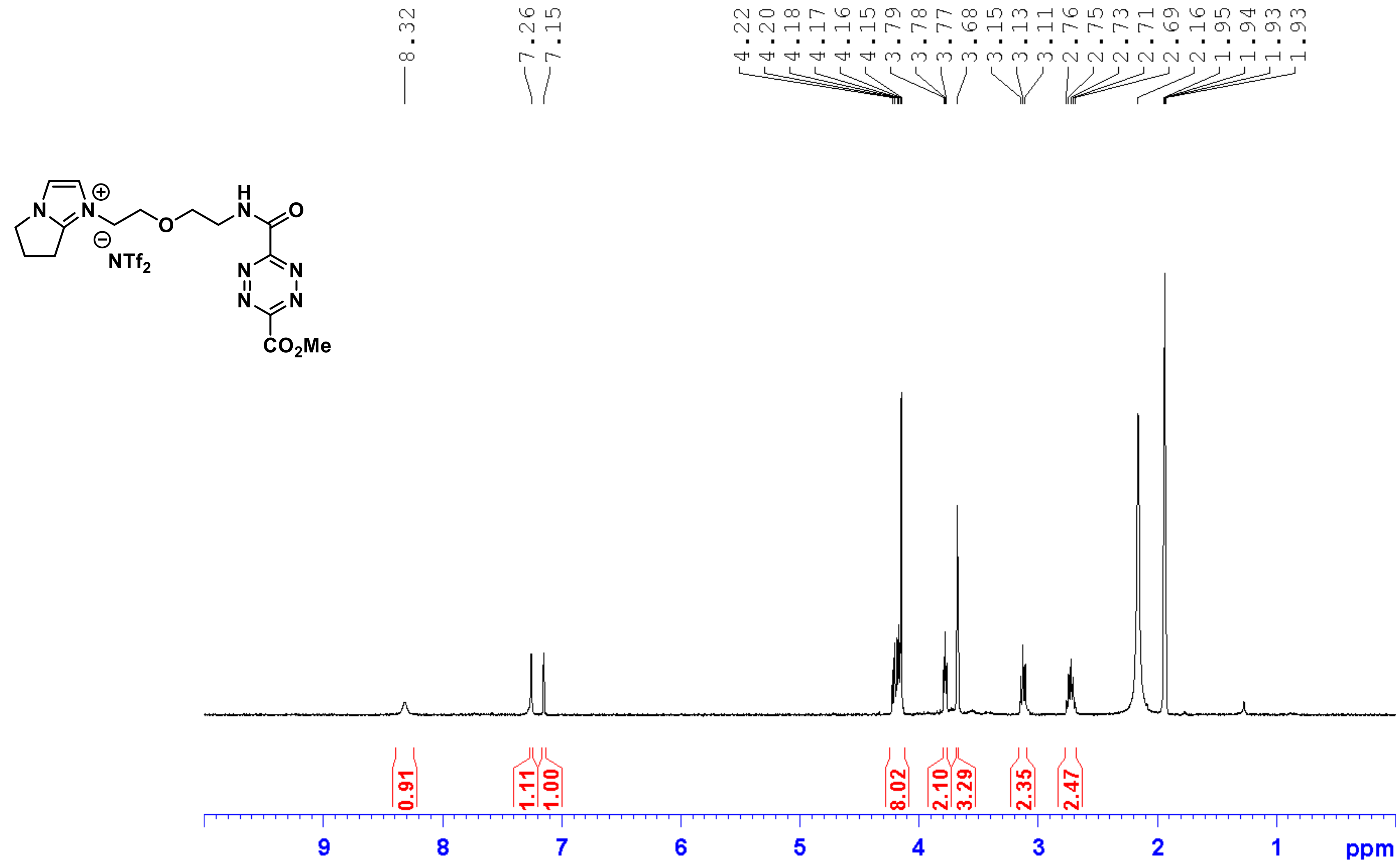
Elements Set 2:

Symbol	C	H	O	N	S
Min	0	0	4	7	0
Max	400	1000	7	7	1

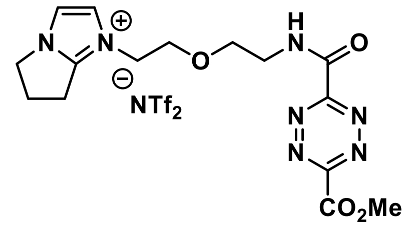
Results

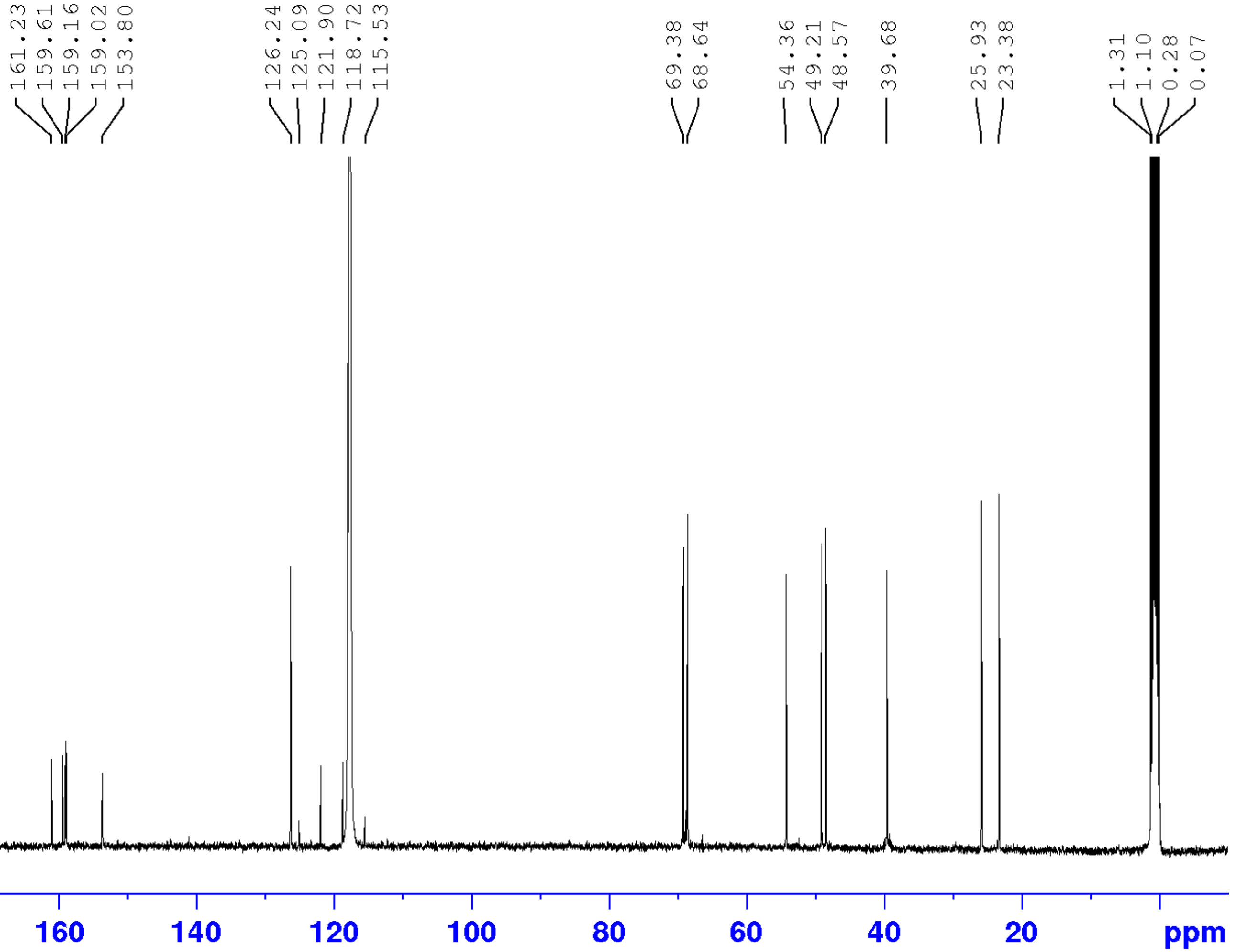
Mass	Formula	Calculated Mass	Mass Difference [mDa]	Mass Difference [ppm]	DBE
364.17308	C15 H22 N7 O4	364.17278	0.30	0.83	8.5

^{1}H NMR spectrum of **TIL**



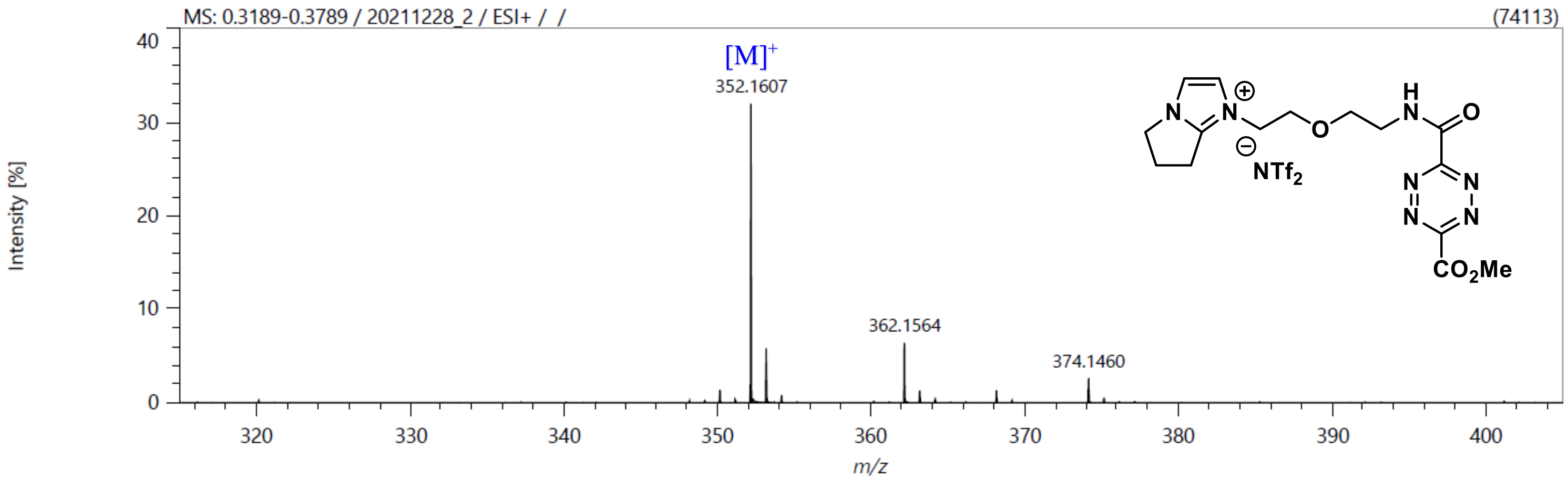
[13]C NMR spectrum of **TIL**





High-resolution mass spectrum of **TIL**

Spectrum



Elemental Composition

Parameters	
Tolerance:	±5.00 ppm
Electron:	Odd/Even
Charge:	+1
DBE:	-99.0 - 999.0

Elements Set 1:

Symbol	C	H	N	O
Min	0	0	7	4
Max	400	1000	7	4

Results

Mass	Formula	Calculated Mass	Mass Difference [mDa]	Mass Difference [ppm]	DBE
362.15637	C15 H20 N7 O4	362.15713	-0.76	-2.09	9.5

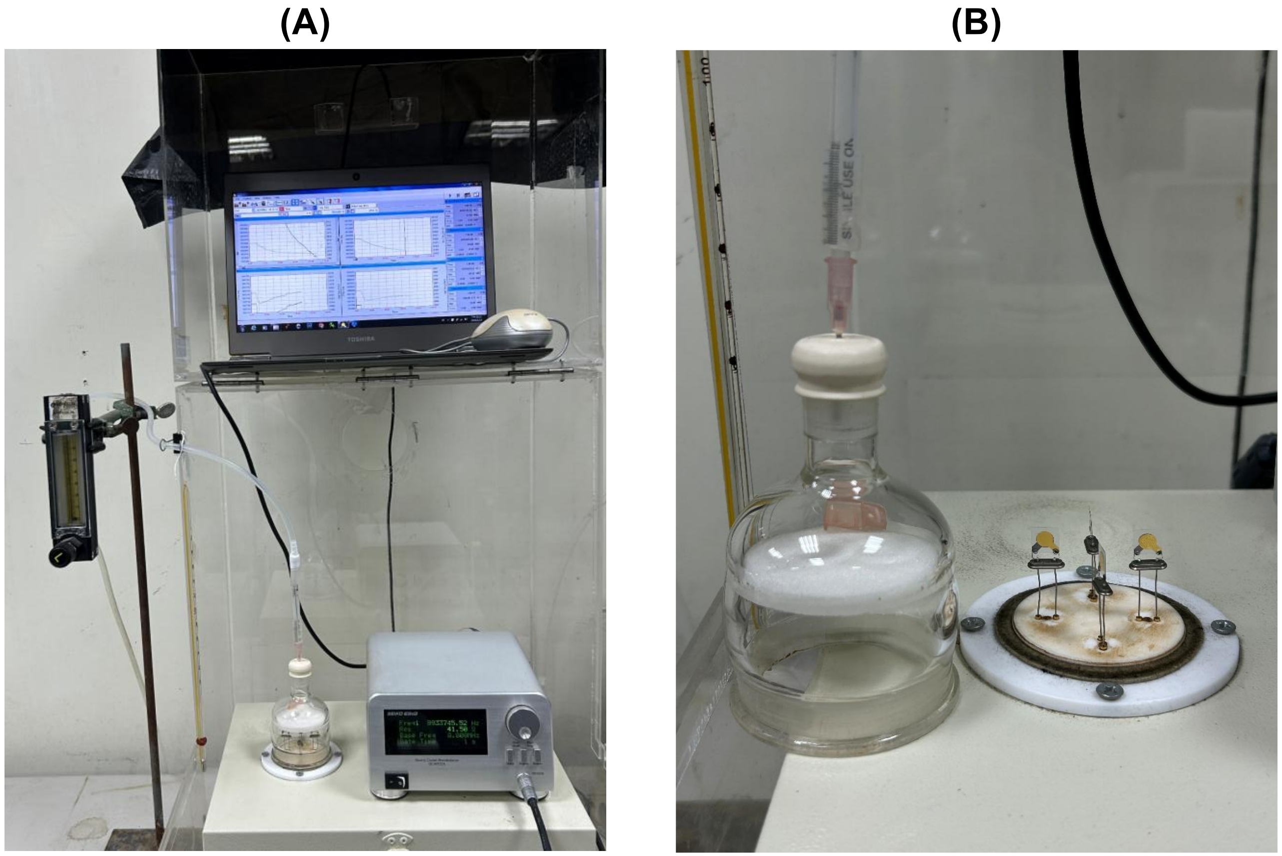
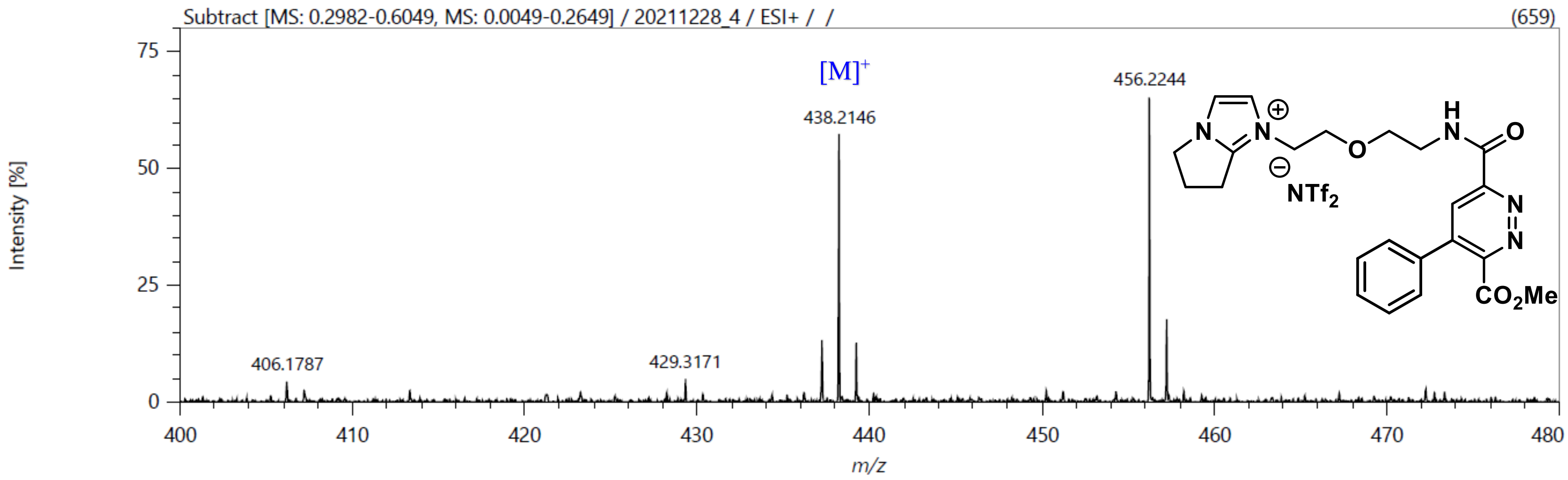


Fig. S1 (A) Photo of our lab-built **TIL**-on-QCM gas analysis setup and (B) detail of the QCM reaction chamber housed with four quartz sensor chips.

Spectrum



Elemental Composition

Parameters	
Tolerance:	±5.00 ppm
Electron:	Odd/Even
Charge:	+1
DBE:	-99.0 - 999.0

Elements Set 1:

Symbol	C	H	N	O
Min	0	0	5	4
Max	400	1000	5	4

Results

Mass	Formula	Calculated Mass	Mass Difference [mDa]	Mass Difference [ppm]	DBE
438.21458	C23 H28 N5 O4	438.21358	1.00	2.29	12.5

Fig. S2 A adduct of **TIL** with styrene isolated from QCM chip.

Procedure for QCM measurements

A Princeton Applied Research QCM922A detector (Oak Ridge, TN, USA) was operated at room temperature and nitrogen was used as carrier gas. The flow rate of the carrier gas was controlled by a Supelco 23324 flowmeter (Merck KGaA, Darmstadt, Germany). The 9 MHz AT-cut quartz chips deposited with gold electrodes (area 11 mm^2) on both sides were also available from ANT Technology Co. (Taipei, Taiwan). Sample vapors were obtained by gasifying the chemicals in CH_2Cl_2 in the sealed screw cap septum vials (4 mL). Before use, the gold electrodes on chips were cleaned with NaOH (5 N), water, and HCl to remove organic absorbent impurities. Finally, quartz chips were rinsed with water thoroughly and dried under nitrogen.

The coating solutions were prepared by dissolving individual AIL (1 μL) in acetonitrile (HPLC grade, 300 μL). The freshly prepared solutions (1 μL) were carefully pipetted onto the cleaned bare gold electrode situated at the center of quartz chips. The AIL coated chips were placed in a heating oven (110 ^{o}C) for 30 sec to remove residual acetonitrile. The freshly prepared sensor chips were then mounted in the gas flow chamber (100 cm^{3}) and used nitrogen as carrier gas at flow rate of 3.0 mL/min. Until a stable baseline was obtained, target gas samples were injected into the chamber. The resonance frequency drops versus time curves were measured in real time and recorded. Typically, the used quartz chips could be readily regenerated by a simple wash with acetonitrile or methanol solvent.

Reactions of AIL 1 and AIL 2 toward styrene in CH_3CN measured by NanoDrop UV-Vis spectrophotometer

Stock solutions of **AIL 1** (50 mM), **AIL 2** (50 mM) and styrene (500 mM) were prepared by weighing out a portion of pure compound in a microtube and diluting by CH_3CN. To a microtube containing a portion of **AIL 1** or **AIL 2** stock solution (10 μL, 50 mM), then styrene stock solution (10 μL, 500 mM) was added and mixed evenly. The progress of click reactions were monitored by NanoDrop 2000 spectrophotometer (Thermo Scientific, Waltham, MA, USA).