Electronic Supplementary Material (ESI) for Analyst.

Supporting Information

Exploring Silver Ionic Liquids for Reaction-Based Gas Sensing on Quartz Crystal Microbalance†

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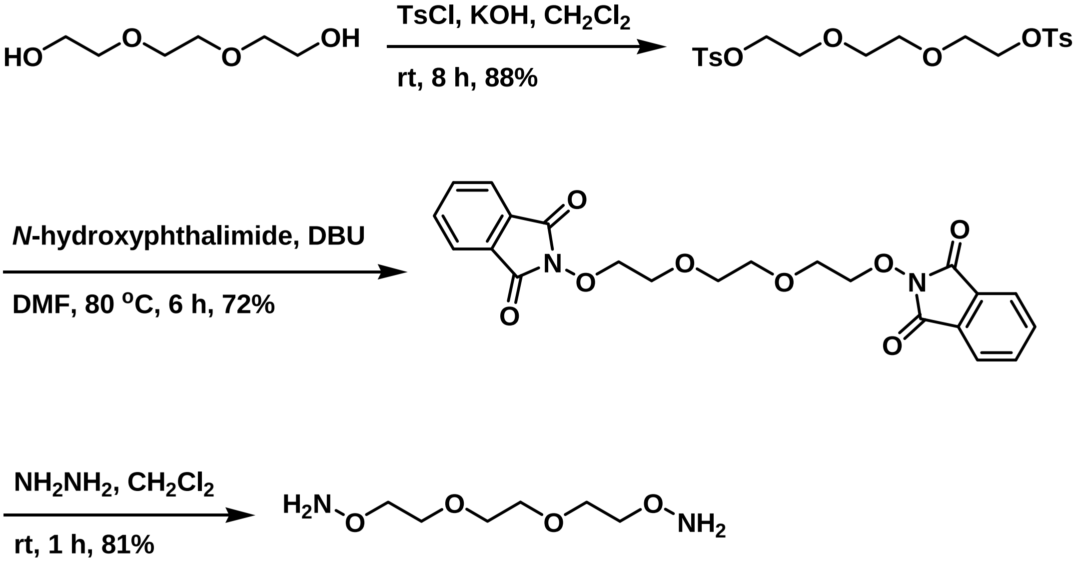


Fig. S1 Synthesis of 1,2-bis(2-aminooxyethoxy)ethane used as the ligand for synthesizing silver ionic liquid **SIL 4**.

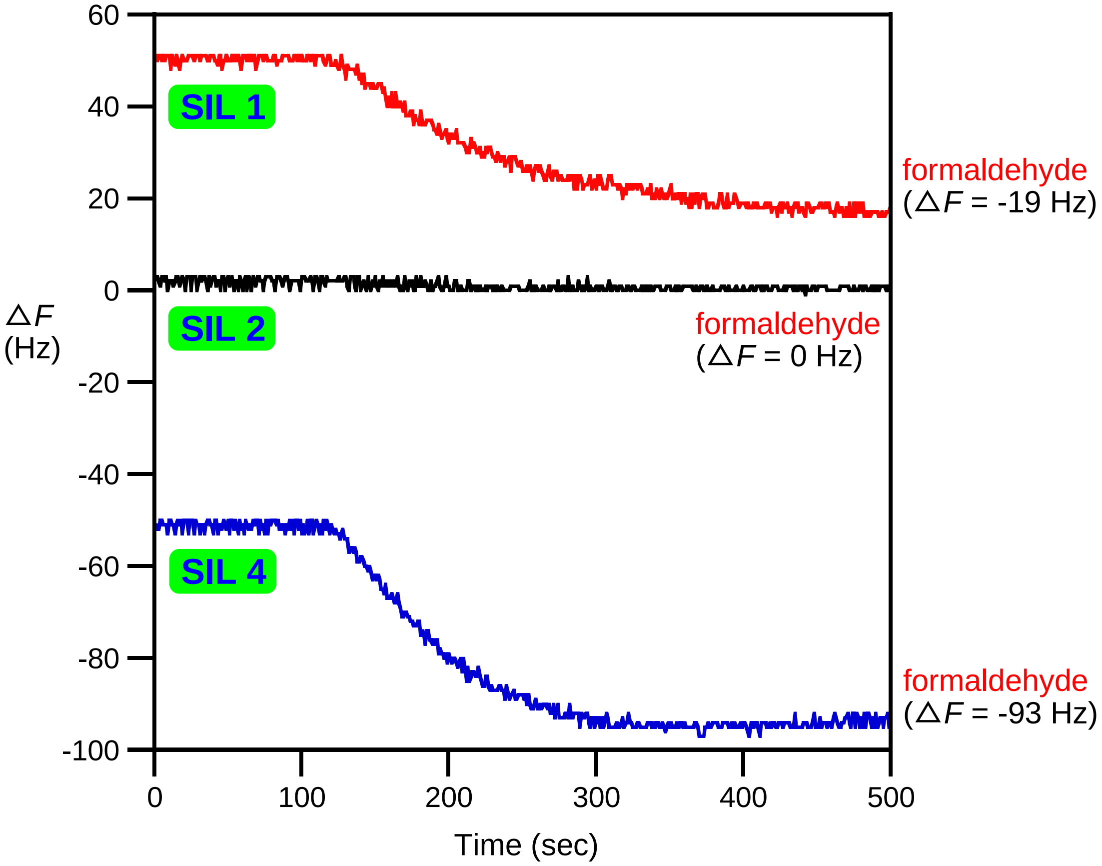


Fig. S2 Chemoselective detection of formaldehyde gas (100 ppb) by a multi-channel QCM thin-coated with **SIL 1**, **SIL 2** and **SIL 4**. The QCM sensorgrams with **SIL 1**, **SIL 2** and **SIL 4** for formaldehyde gas were vertically shifted (50 Hz in between) for clarity. Nitrogen was used as the carrier gas with a flow rate of 3 mL/min, and gaseous samples were injected at 100 s. The resonance frequency drop, Δ*F*, in Hz is the QCM response on the quartz chip surface.

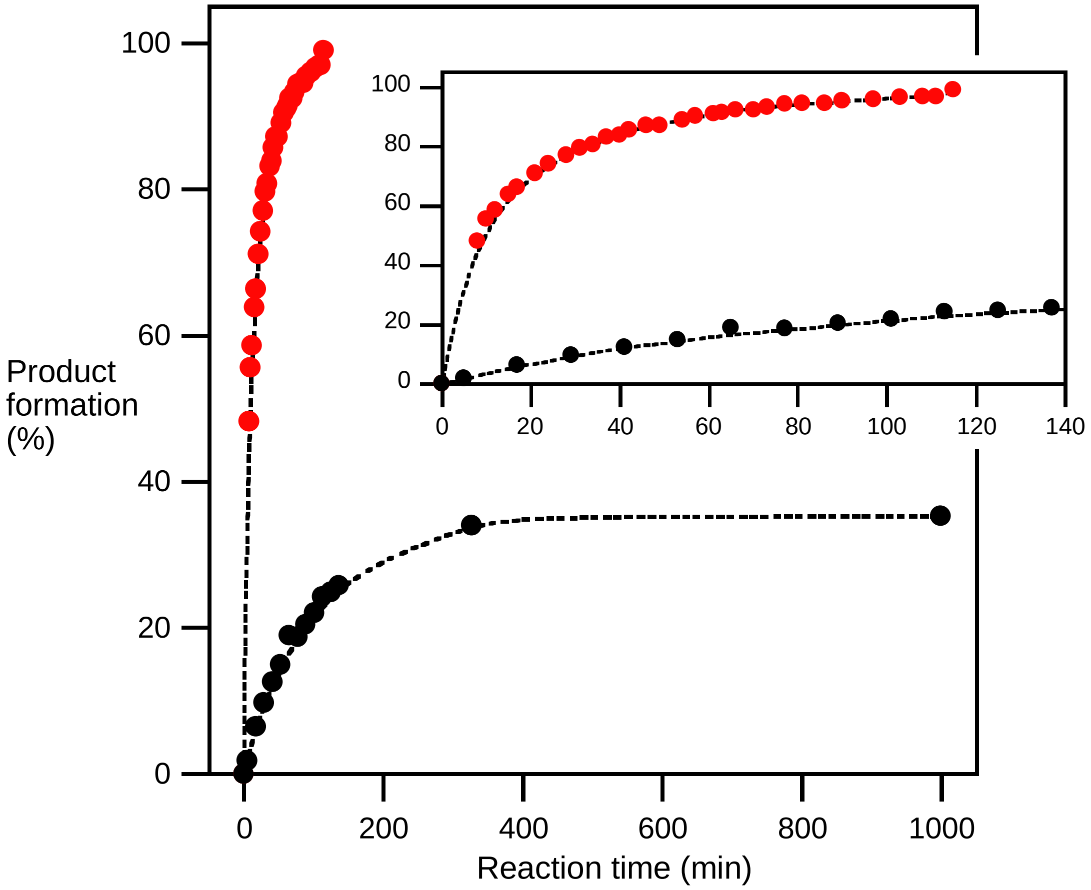


Fig. S3 Kinetic measurements of imine forming reactions of amine ligands (0.50 M each) of **SIL 1** (1,2-bis(2-aminoethoxy)ethane, black circle ●) and **SIL 4** (1,2-bis(2-aminooxyethoxy)ethane, red circle ●) with acetone (1.0 M) in $CDCl_3$ solvent at ambient temperature. Inset: details of early conversions of the reactions (0-140 min). The progress of formation reactions of the imine adducts could be readily monitored at the methylene protons on 1,2-bis(2-aminoethoxy)ethane (δ 3.52 ppm for $C\mathit{H}_2NH_2$) and 1,2-bis(2-aminooxyethoxy)ethane (δ 3.83 ppm for $C\mathit{H}_2ONH_2$) and corresponding imine adducts (δ 3.74 ppm for for $C\mathit{H}_2N{=}C$; δ 4.17 ppm for for $C\mathit{H}_2ON{=}C$) by ^{1}H NMR.

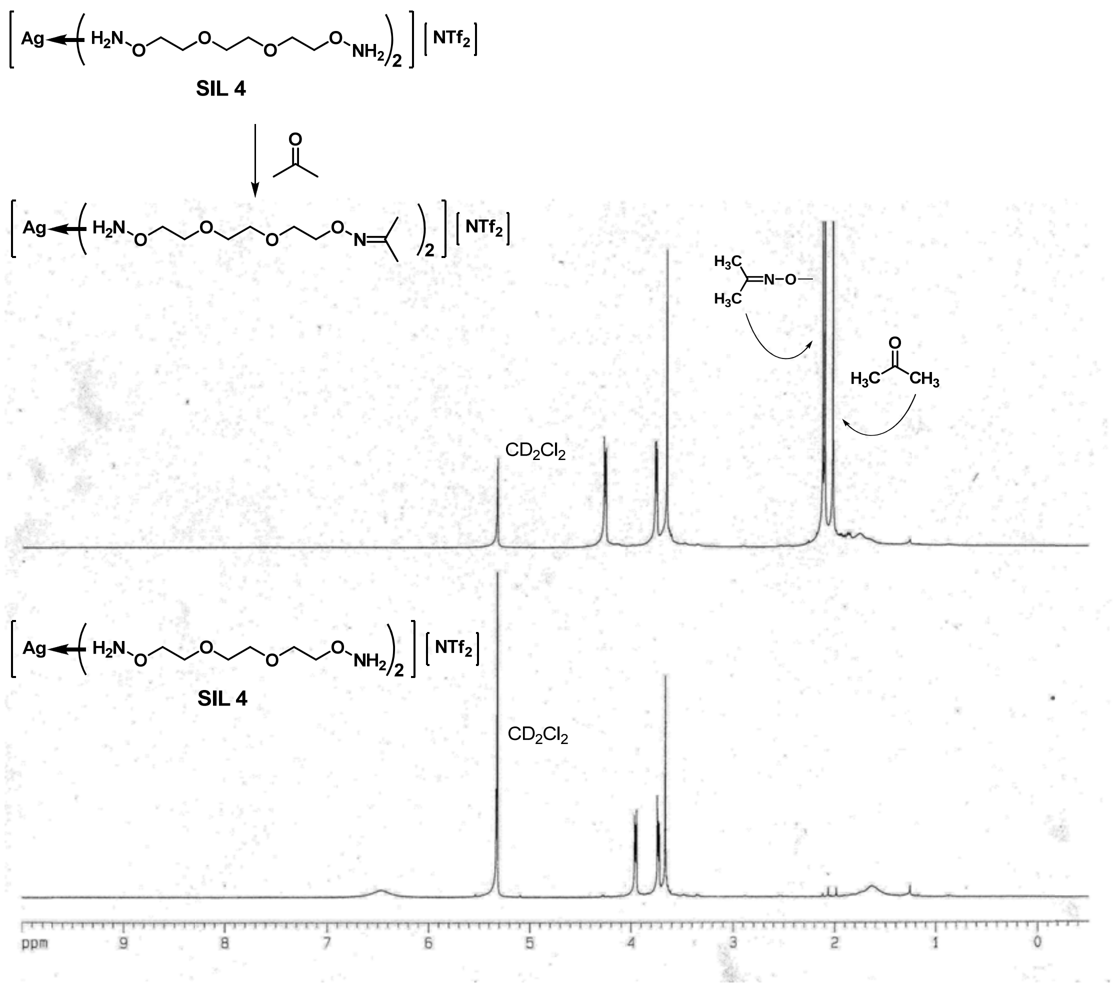


Fig. S4 ^{1}H NMR analysis of the formation of oxime adduct upon silver ionic liquid **SIL 4** reaction with acetone. The measurement was carried out in CD_2Cl_2 solvent at ambient temperature.

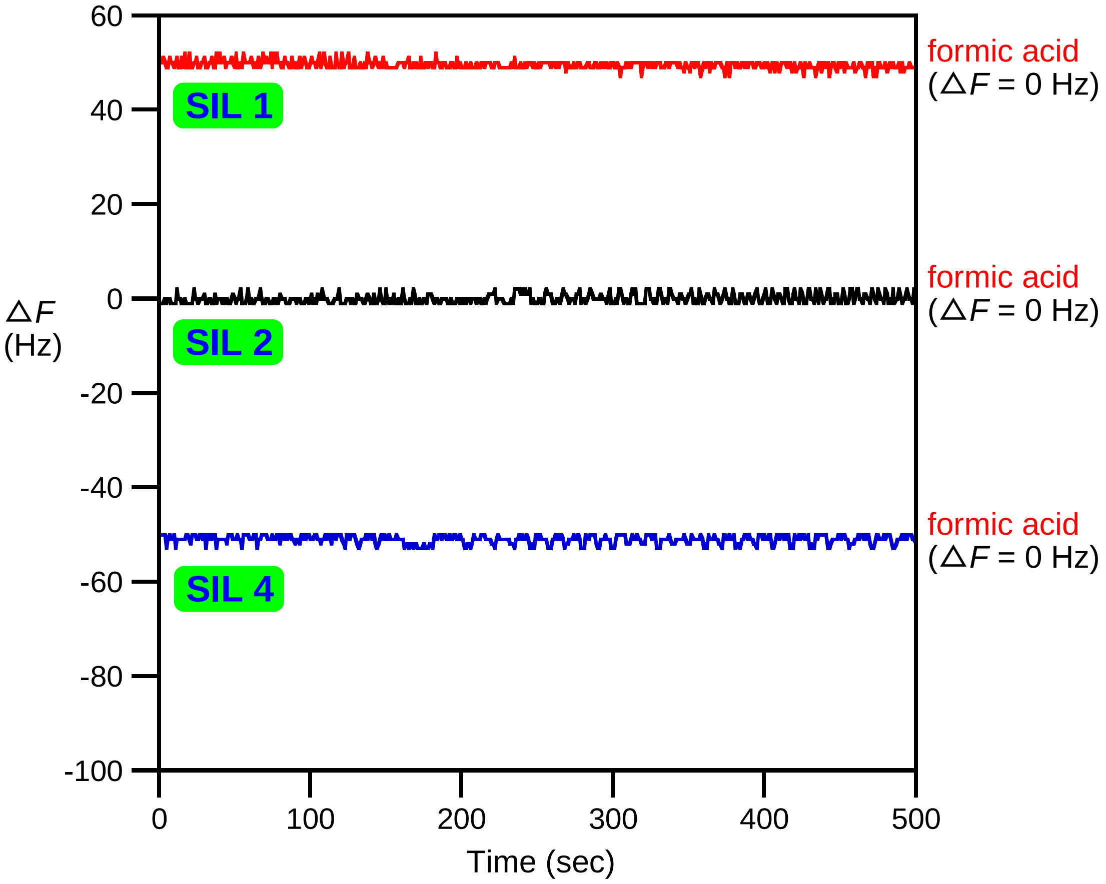


Fig. S5 Chemoselective detection of formic acid gas (100 ppb) by a multi-channel QCM thin-coated with **SIL 1**, **SIL 2** and **SIL 4**. The QCM sensorgrams with **SIL 1**, **SIL 2** and **SIL 4** for formic acid gas were vertically shifted (50 Hz in between) for clarity. Nitrogen was used as the carrier gas with a flow rate of 3 mL/min, and gaseous samples were injected at 100 s. The resonance frequency drop, Δ*F*, in Hz is the QCM response on the quartz chip surface.

Synthesis of 1,2-bis(2-aminooxyethoxy)ethane as SIL 4 ligand

To a precooled solution of triethylene glycol (3.0 g, 19.9 mmol) and potassium hydroxide (9.0 g, 160 mmol) in dichloromethane (100 mL) was added slowly neat *p*-toluenesulfonyl chloride (7.6 g, 40 mmol). The resulting solution was stirred at ambient temperature for 8 h and, after the tosylation reaction was completed, washed sequentially with citric acid (10 wt%, 15 mL), sodium bicarbonate (10 wt%, 15 mL), brine (15 mL) and then dried over Na_2SO_4. After filtration, the solvent was removed under reduced pressure to afford high purity triethylene glycol di-*p*-tosylate (8.11 g, 88% yield) as white solid.

The obtained triethylene glycol di-*p*-tosylate (1.0 g, 2.18 mmol) was dissolved in DMF (20 mL), and then *N*-hydroxyphthalimide (711 mg, 4.36 mmol) and DBU (0.66 mL, 4.36 mmol) were added. The substitution reaction was carried out at 80 ^{o}C for 6 h. After completion of reaction, DMF solvent was removed *in vacuo*, ethyl acetate solvent was added, and the resulting organic phase was washed with sodium bicarbonate (10 wt%), brine and finally dried over Na_2SO_4. After filtration and solvent evaporation under reduced pressure, the crude product mixture was purified by flash column chromatography to afford the desired 1,8-diphthalimidooxy-3,6-dioxaoctane (743.2 mg, 72% yield) as white solid.

To a solution of 1,8-diphthalimidooxy-3,6-dioxaoctane (743 mg, 1.76 mmol) in dichloromethane (3 mL) was added hydrazine monohydrate (1.3 mL, 17.6 mmol). The deprotection reaction was readily carried out at room temperature for 1 h. After filtering off the precipitate (2,3-dihydrophthalazine-1,4-dione) and removing the dichloromethane solvent, a yellow viscous liquid was resulted. Diethyl ether solvent was added to this viscous liquid to filter off residual 2,3-dihydrophthalazine-1,4-dione. The ether solvent was evaporated off under reduced pressure. High vacuum was then applied to remove residual hydrazine, if any, to finally afford the desired yellow liquid product, 1,2-bis(2-aminooxyethoxy)ethane, with high isolated yield (295 mg, 81%). Yellow liquid; ^{1}H NMR (400 MHz, $CDCl_3$) δ 3.65-3.77 (m, $NOCCH_2$, 4H), 3.67 (s, $COCH_2$, 4H), 3.82-3.92 (m, $NOCH_2$, 4H), 5.29-5.79 (bs, NH_2, 4H); ^{13}C NMR (100 MHz, CD_3OD) δ 70.6, 71.4, 75.8.

Synthesis of silver ionic liquid SIL 1

To a precooled 1,2-bis(aminoethoxy)ethane (352.3 mg, 2.38 mmol) in 4-mL reaction vessel was delivered slowly by a syringe pump a solution of silver nitrate (201.7 mg, 1.19 mmol) in deionized water (250 μL) for a time period of 2 h. The reaction mixture was kept in dark to avoid light exposure and stirred at 4 °C for 2 h and subsequently at room temperature for another 1 h to afford a solution containing silver ionic liquid nitrate salt.

To the solution of silver ionic liqiuid nitrate salt was added a solution of lithium bistrifluoromethanesulfonimide (377.7 mg, 1.32 mmol) in water (250 μL). This metathesis reaction was allowed to proceed for 2 h at room temperature. The formation of two phases was observed usually within first 30 min. The resulting solution was then added dichloromethane (750 μL) for extraction to afford the ionic liquid product. This organic phase was further washed three times with deionized water (500 μL each time) to remove any unreactive water miscible diamine ligand and silver nitrate residue. After removal of the solvent under reduced pressure, the desired **SIL 1** product was obtained (537.2 mg, 66% yield) as light yellow liquid.

Light yellow liquid; ^{1}H NMR (400 MHz, $CDCl_3$) δ 2.57 (s, NH_2, 8H), 3.06 (t, J = 4.6 Hz, NCH_2, 8H) δ 3.58 (t, J = 4.6 Hz, OCH_2CN, 8H) δ 3.66 (s, $COCH_2$, 8H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 42.3, 69.5, 69.6, 119.7 (q, J_{CF} = 319 Hz, CF_3); ESI-HRMS *m/z* $[M]^+$ calcd for $C_{12}H_{32}N_4O_4Ag$ 403.1474, found 403.1470.

Synthesis of silver ionic liquid SIL 2

To a precooled 2-methoxyethylamine (178.1 mg, 2.37 mmol) in 4-mL reaction vessel was added slowly a solution of silver nitrate (200.2 mg, 1.18 mmol) in deionized water (250 μL). The reaction mixture was kept in dark to avoid light exposure and stirred at 4 °C for 2 h and subsequently at room temperature for another 1 h to afford a solution containing silver ionic liquid nitrate salt.

To the solution of silver ionic liqiuid nitrate salt was added a solution of lithium bistrifluoromethanesulfonimide (372.4 mg, 1.30 mmol) in water (250 μL). Since two phases was formed almost instantaneously, this metathesis reaction was vigorously stirred for 6 h at room temperature. The resulting solution was then added dichloromethane (750 μL) for extraction to afford the ionic liquid product. This organic phase was further washed three times with deionized water (500 μL each time) to remove any unreactive water miscible amine ligand and silver nitrate residue. After removal of the solvent under reduced pressure, the desired **SIL 2** product was obtained (598.6 mg, 94% yield) as colorless liquid.

Colorless liquid; ^{1}H NMR (400 MHz, $CDCl_3$) δ 2.53-2.98 (bs, NH_2, 4H), 3.05 (t, J = 4.8 Hz, CH_2N, 4H), 3.39 (s, CH_3O, 6H), 3.50 (t, J = 4.8 Hz, OCH_2, 4H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 43.5, 58.9, 72.1, 119.7 (q, J_{CF} = 319 Hz, CF_3); ESI-HRMS *m/z* $[M]^+$ calcd for $C_6H_{18}N_2O_2Ag$ 257.0419, found 257.0421.

Synthesis of silver ionic liquid SIL 4

To a precooled 1,2-bis(2-aminooxyethoxy)ethane (215.8 mg, 1.20 mmol) in 4-mL reaction vessel was delivered slowly by a syringe pump a solution of silver nitrate (100.7 mg, 0.59 mmol) in deionized water (125 μL) for a time period of 2 h. The reaction mixture was kept in dark to avoid light exposure and stirred at 4 ^{o}C for 2 h and subsequently at room temperature for another 1 h to afford a solution containing silver ionic liquid nitrate salt.

To the solution of silver ionic liqiuid nitrate salt was added a solution of lithium bistrifluoromethanesulfonimide (187.1 mg, 0.65 mmol) in water (125 μL). This metathesis reaction was allowed to proceed for 2 h at room temperature. The formation of two phases was observed usually within first 30 min. The resulting solution was then added dichloromethane (750 μL) for extraction to afford the ionic liquid product. This organic phase was further washed three times with deionized water (500 μL each time) to remove any unreactive water miscible diamine ligand and silver nitrate residue. After removal of the solvent under reduced pressure, the desired **SIL 4** product was obtained (346.3 mg, 78% yield) as bright yellow liquid.

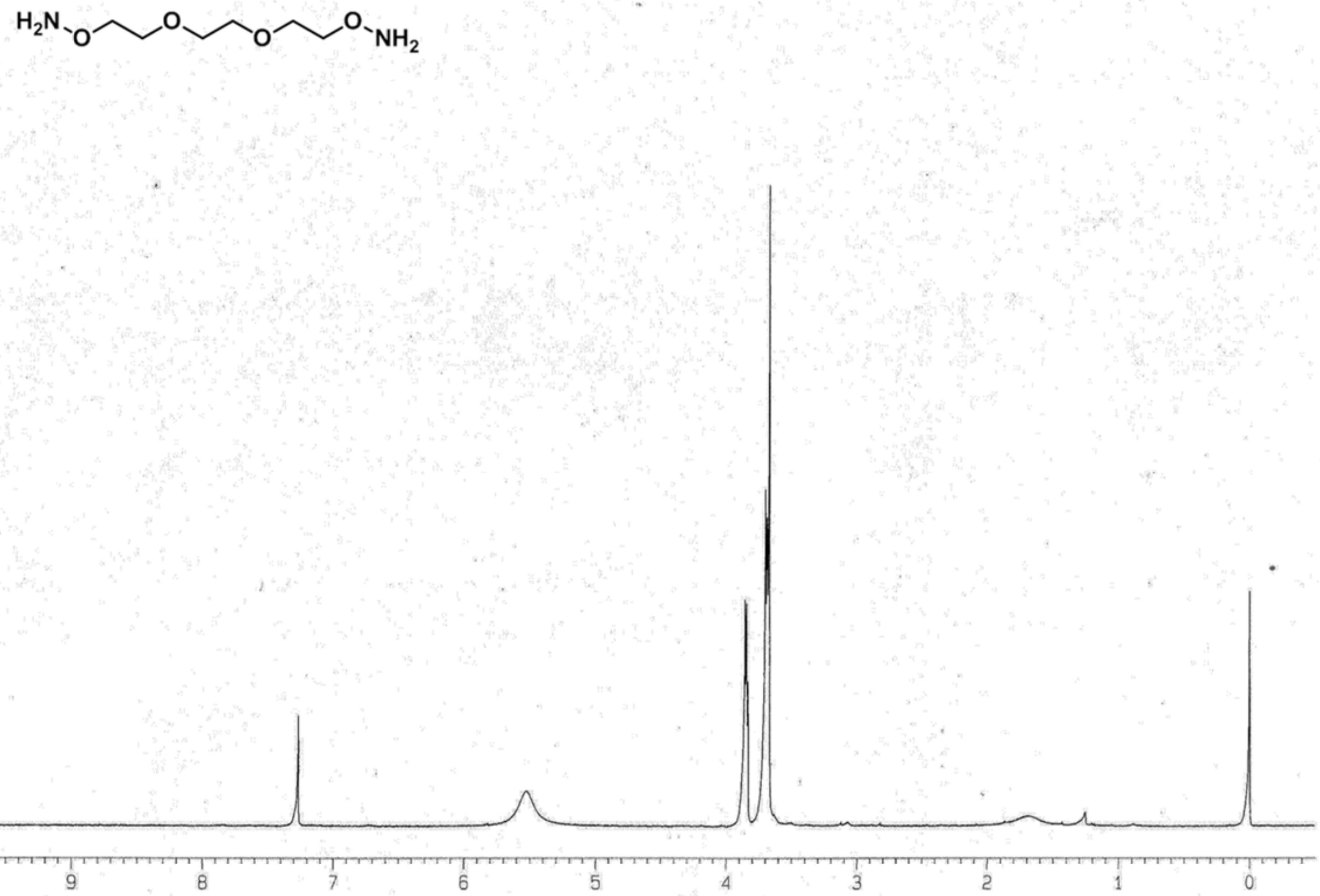
^{1}H NMR (400 MHz, CD_2Cl_2) δ 3.66 (s, $COCH_2$, 8H), 3.73 (t, *J* = 4.0 Hz, $NOCCH_2$, 8H), 3.96 (t, *J* = 4.0 Hz, $NOCH_2$, 8H), 6.11-6.89 (bs, NH_2, 8H); ^{13}C NMR (100 MHz, CD_2Cl_2) δ 69.6, 70.4, 75.5, 119.4 (q, J_{CF} = 319 Hz, CF_3); ESI-HRMS *m/z* $[M]^+$ calcd for $C_{12}H_{32}AgN_4O_8$ 467.1271, found 467.1273.

QCM measurements

A 9 MHz QCM prototype device used in this work was composed of an outer metal chassis of ADS (affinity detection system) (ANT Technology Co., Taipei, Taiwan; http://www.anttech.com.tw/) and a QCM SB01B Analyzer core unit (Smart Biotechnology, Taipei, Taiwan). This QCM system was operated at room temperature and using nitrogen as carrier gas. The flow rate of the carrier gas was controlled by a commercial flow meter (Supelco Inc.). Organic vapors were obtained by gasifying the chemicals in the sealed glass container (1.25 L). The QCM system employed commercially available 9-MHz AT-cut quartz chips (ANT Technology Co., Taipei, Taiwan) deposited with gold electrodes (area 11 mm^2) on both sides. The gold electrodes on chips were cleaned with HCl (1 N) for 5 min, water for 5 min, and NaOH (5 N) for 5 min twice to remove organic absorbent impurities. Finally, quartz chips were rinsed with methanol thoroughly and dried.

The SIL coating solutions were prepared by dissolving silver ionic liquids in methanol with a volume ratio of 1:300. The freshly prepared coating solutions (1 μL) were carefully pipetted onto the cleaned bare gold electrodes, at the center of quartz chip.

The SIL coated chips were placed in a heating oven (110 ^{o}C) for 30 sec to remove residual methanol. The freshly prepared sensor chips were then mounted inside the gas flow chamber and used nitrogen as carrier gas at a flow rate of 3.0 mL/min. Until a stable baseline was obtained, targeted aldehyde or ketone gases were injected into the chamber.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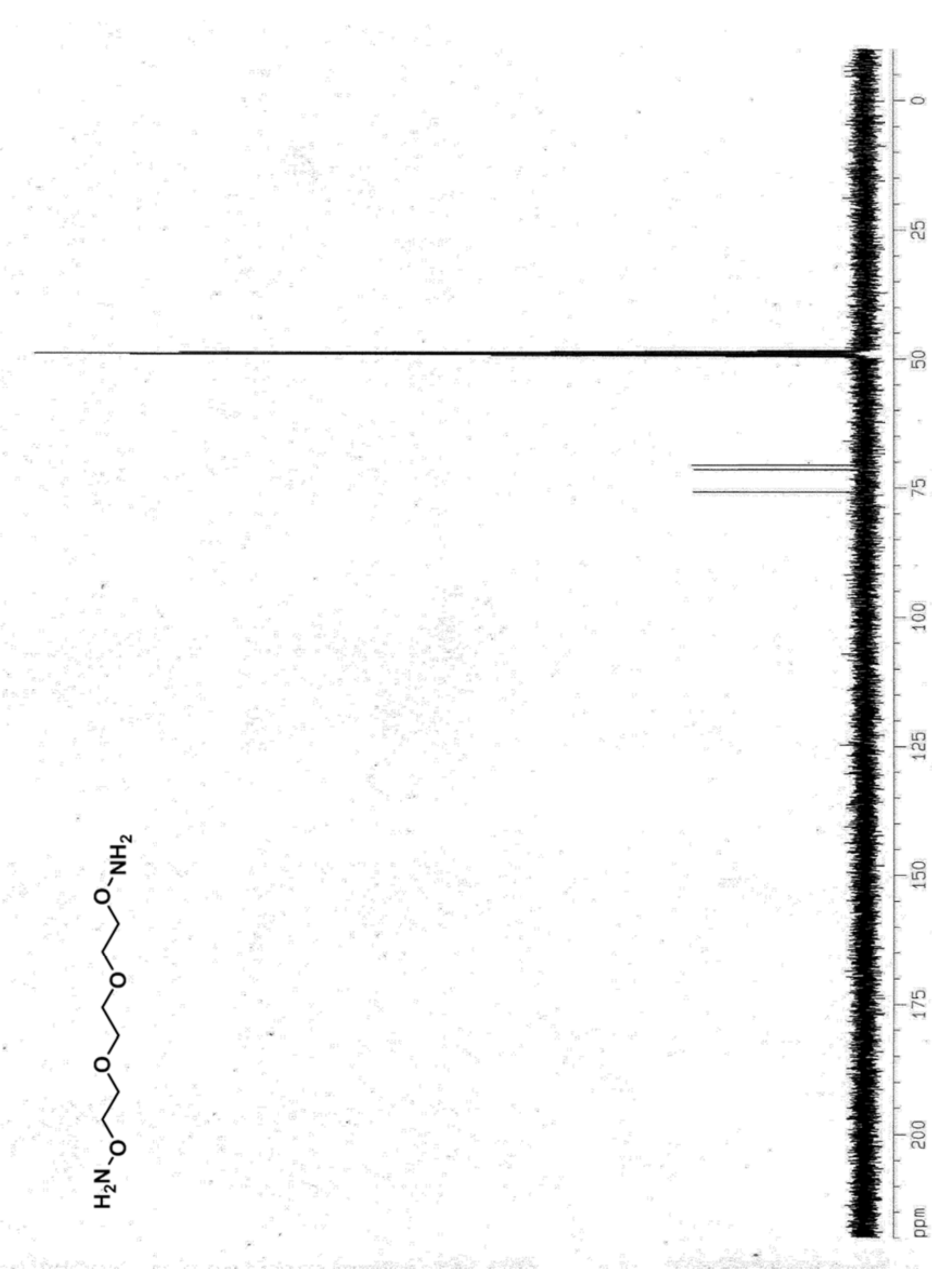

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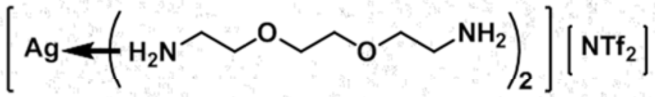

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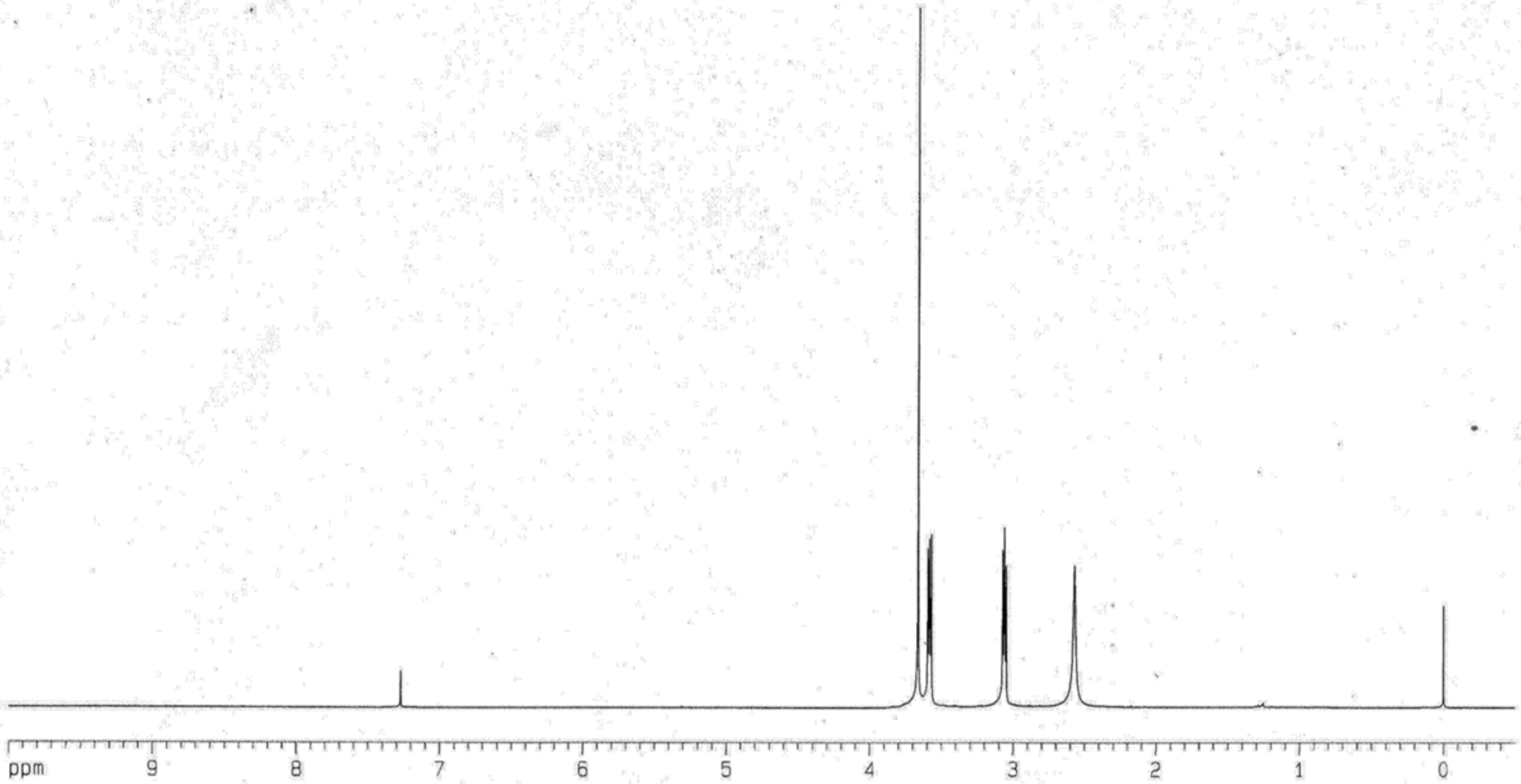

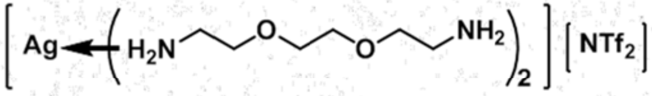

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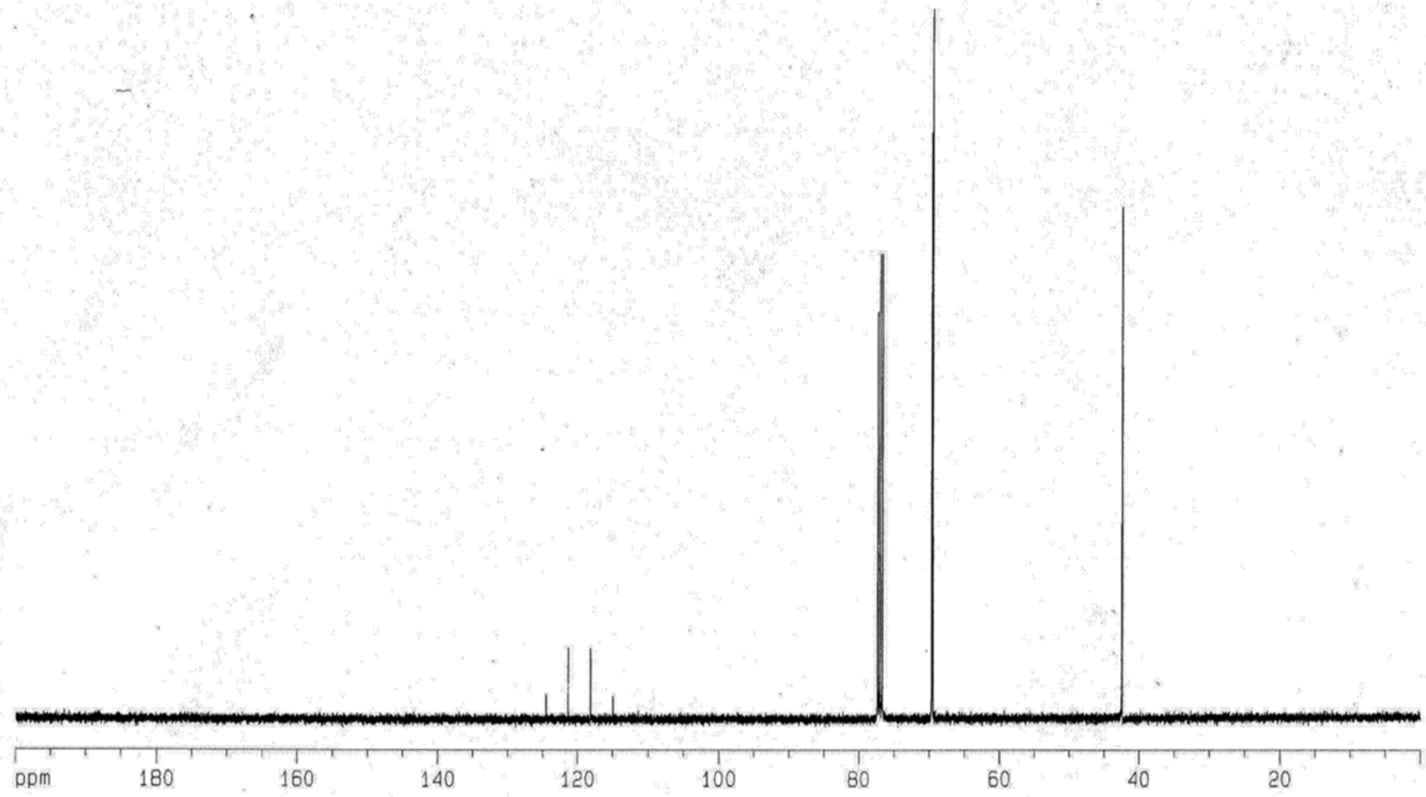
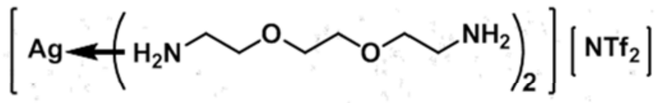


Elemental Composition Report



SIL 1

Single Mass Analysis

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Monoisotopic Mass, Even Electron Ions
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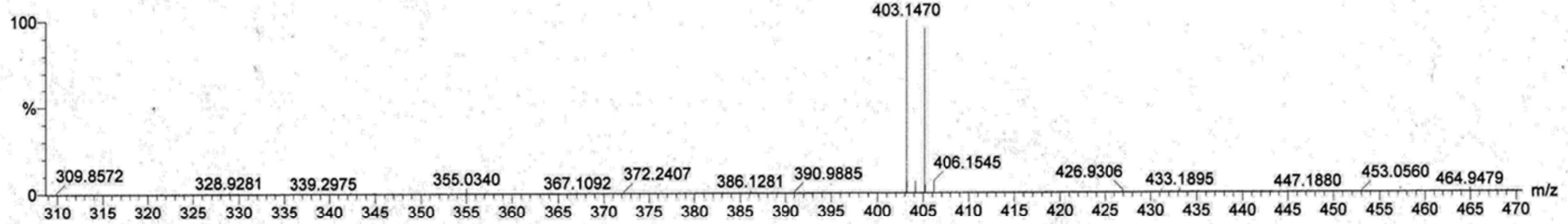

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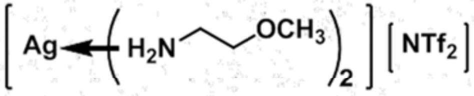

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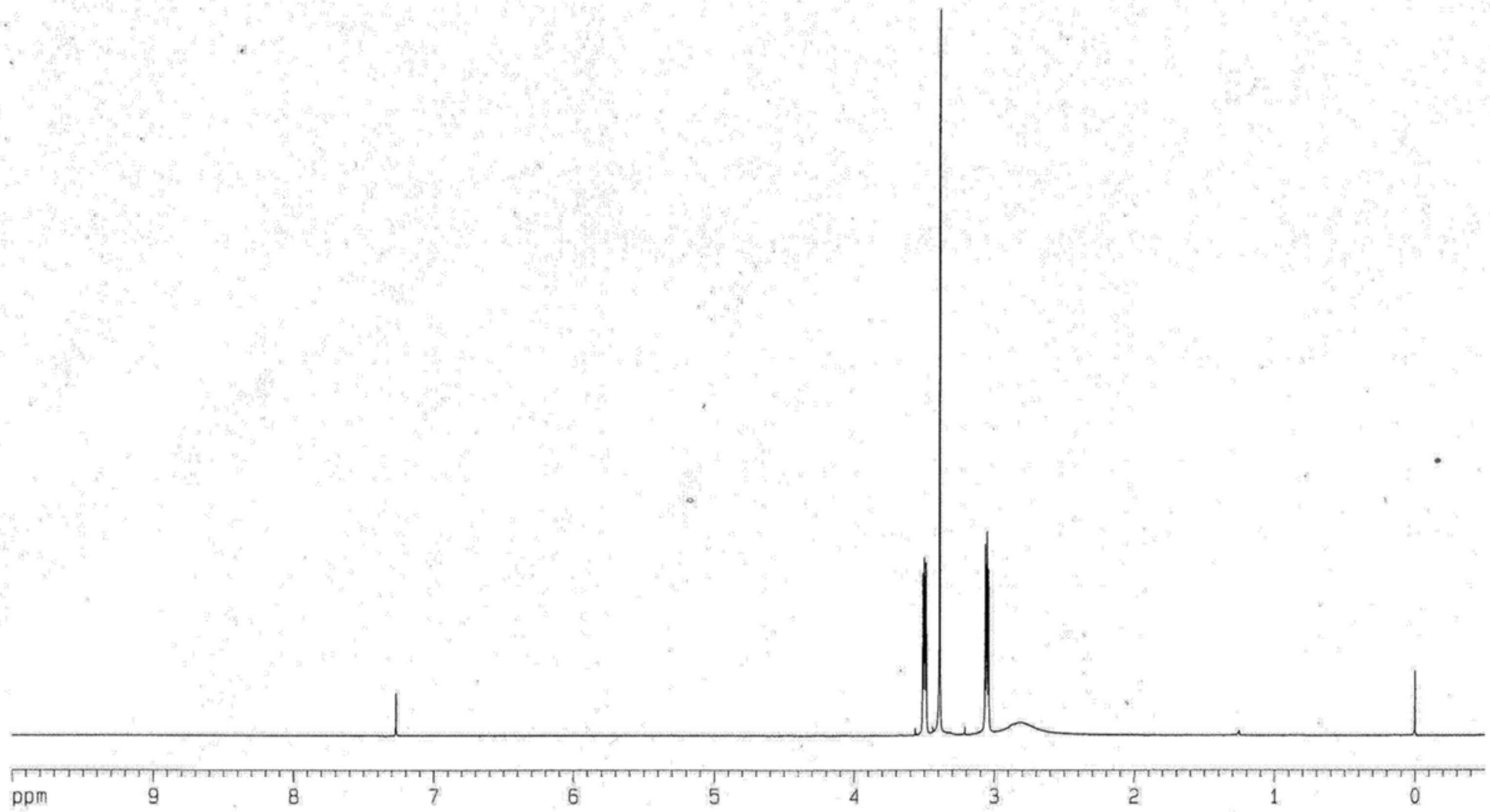

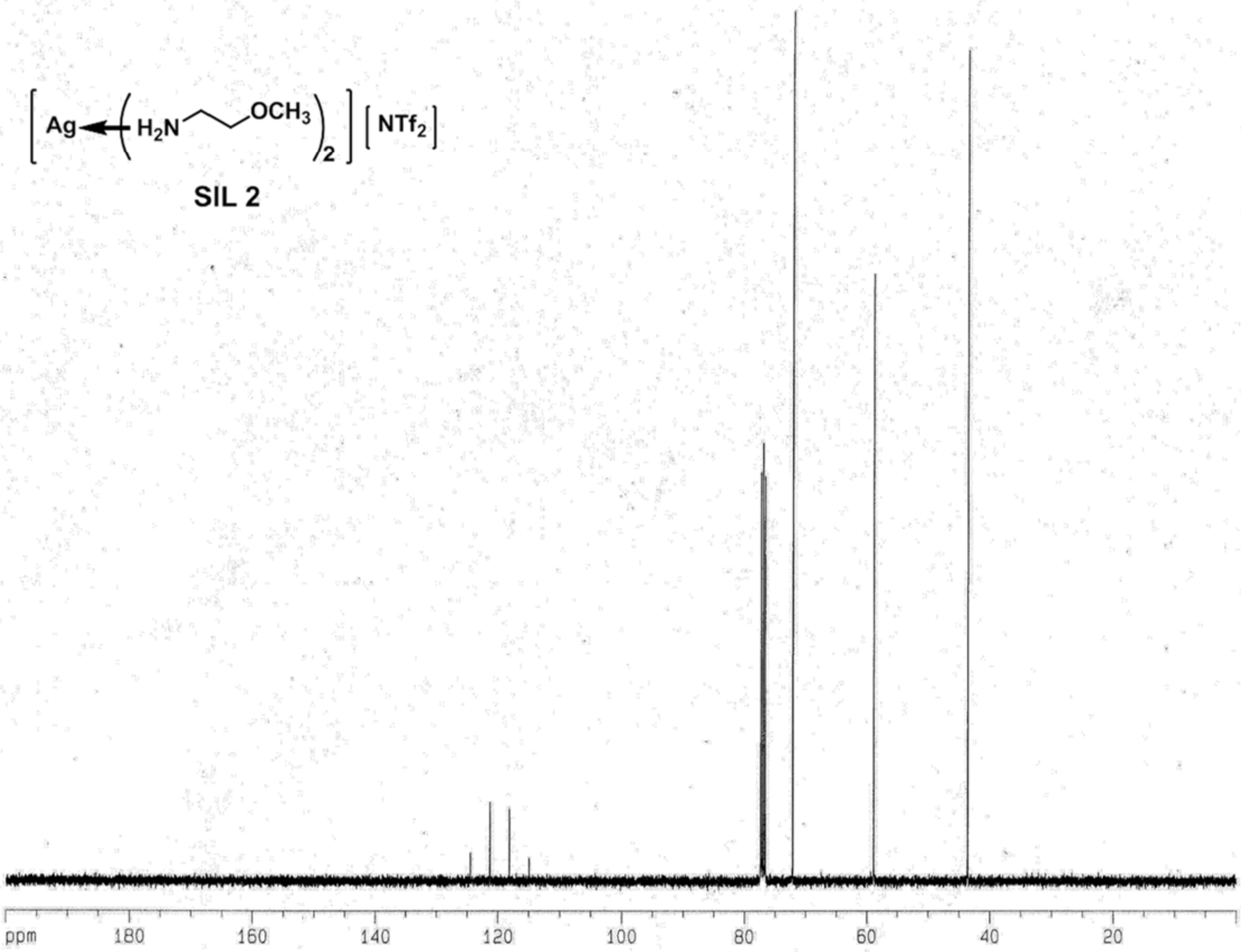

SIL 2

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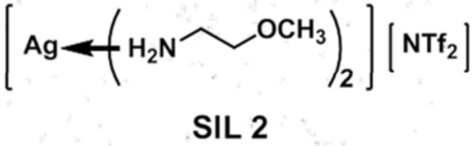

SIL 2

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Number of isotope peaks used for i-FIT = 2

Monoisotopic Mass, Even Electron Ions
5 formula(e) evaluated with 1 results within limits (up to 50 best isotopic matches for each mass)
Elements Used:
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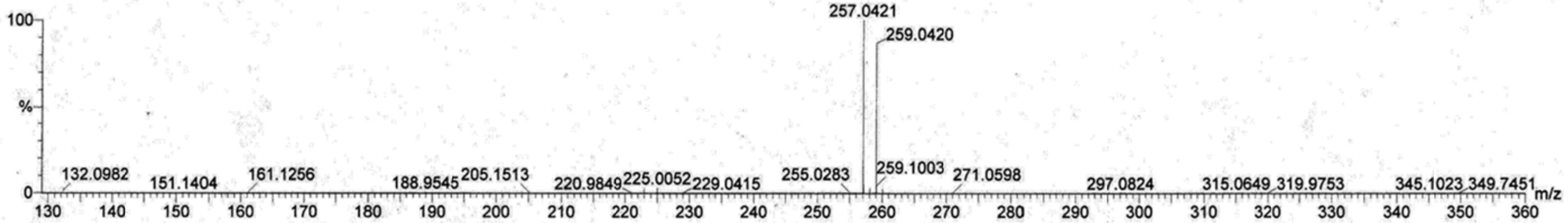

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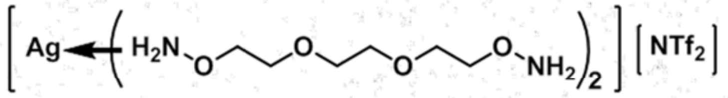

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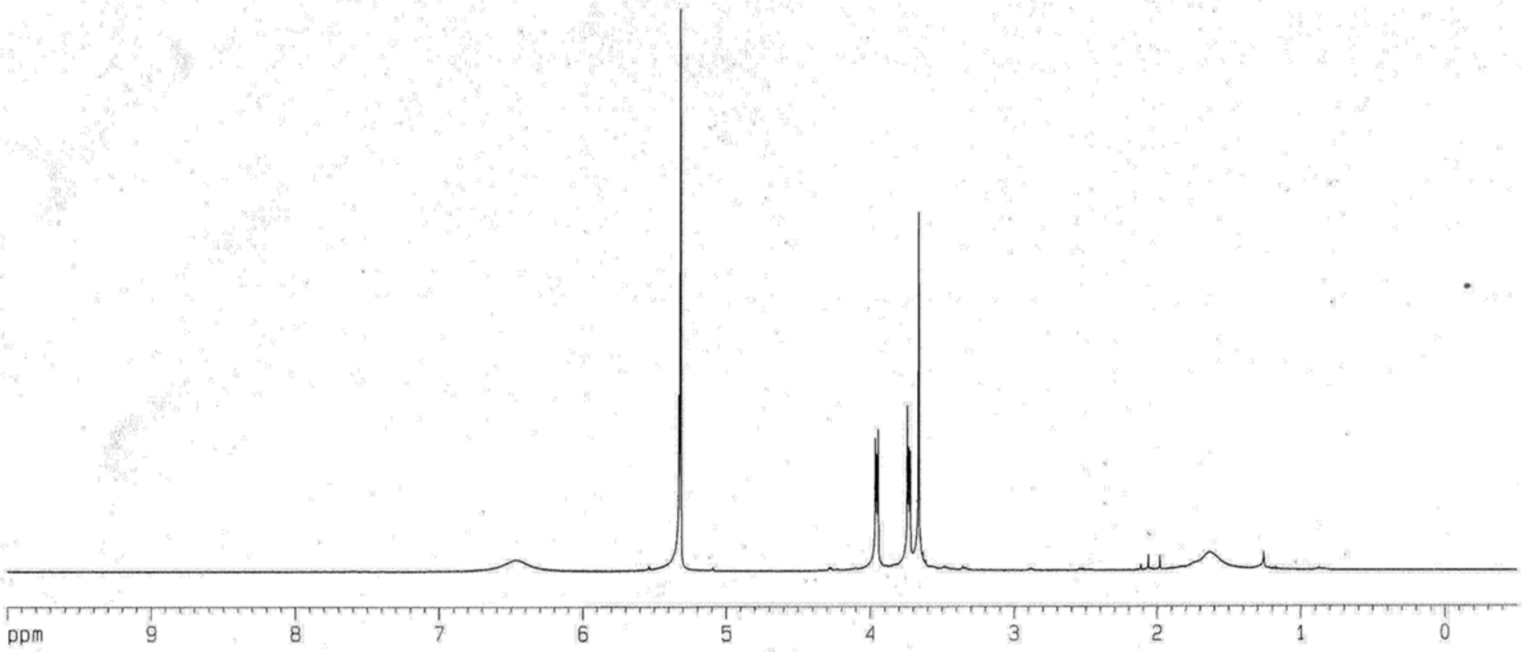

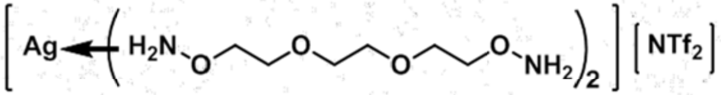

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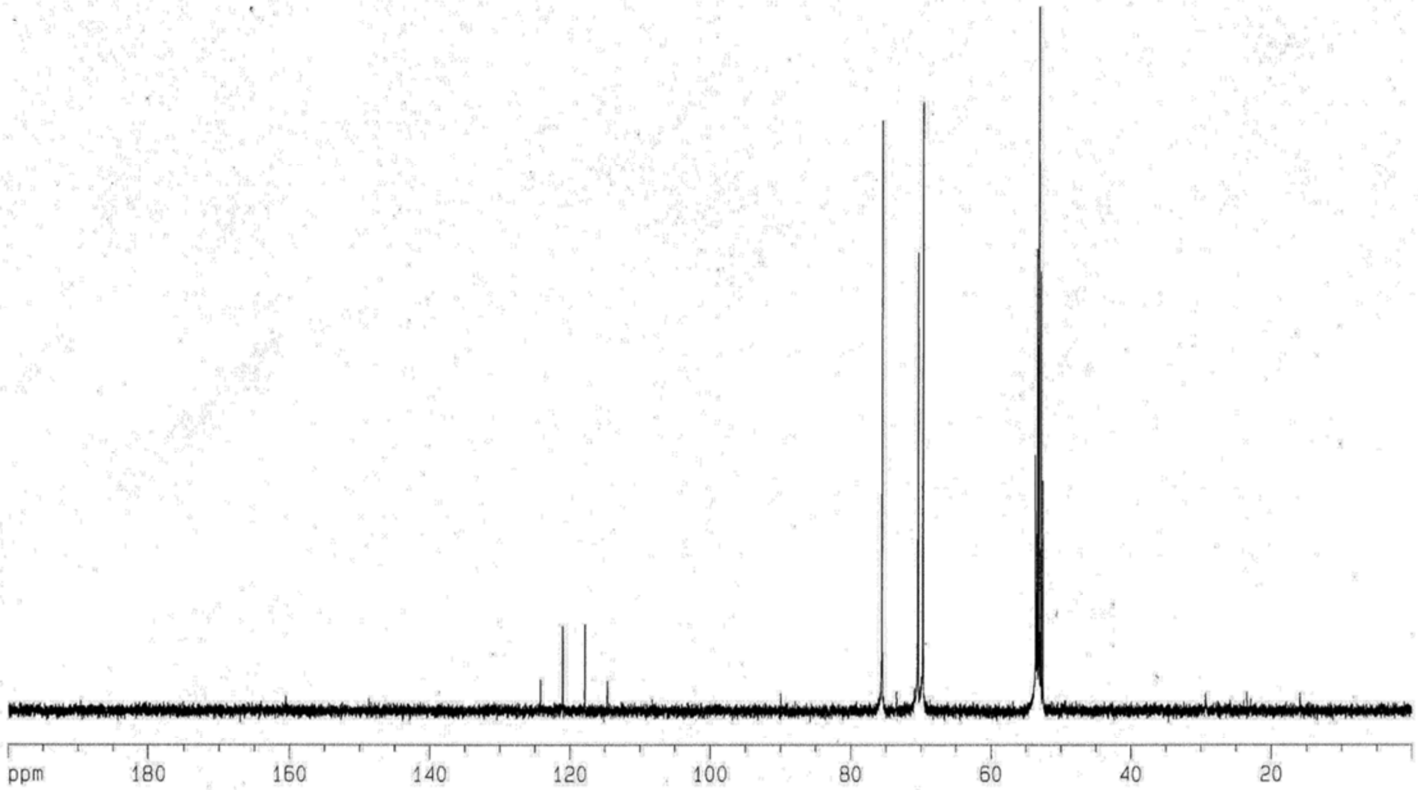

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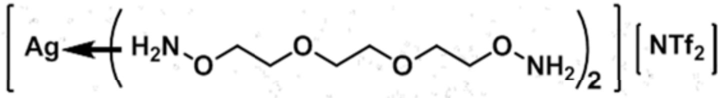

SIL 4

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Monoisotopic Mass, Even Electron Ions
3 formula(e) evaluated with 1 results within limits (up to 50 best isotopic matches for each mass)
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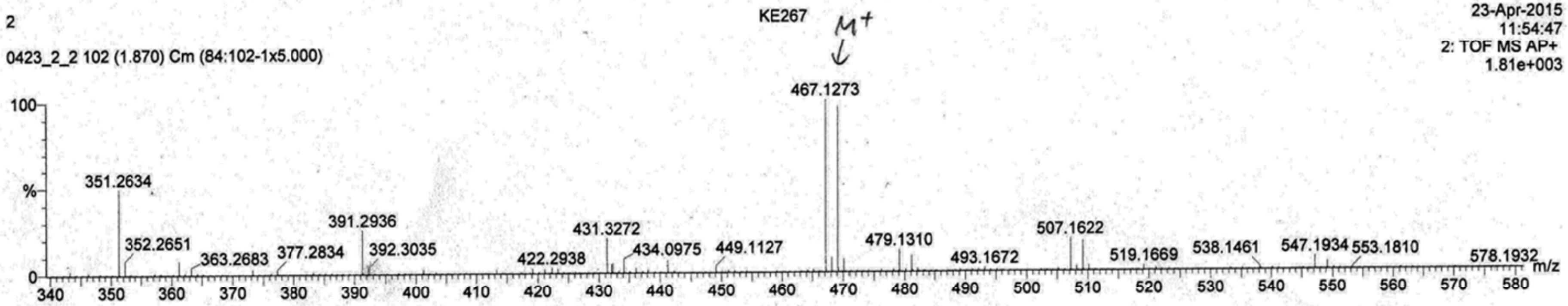

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