Sensing ionic liquids for chemoselective detection of acyclic and cyclic ketone gases†

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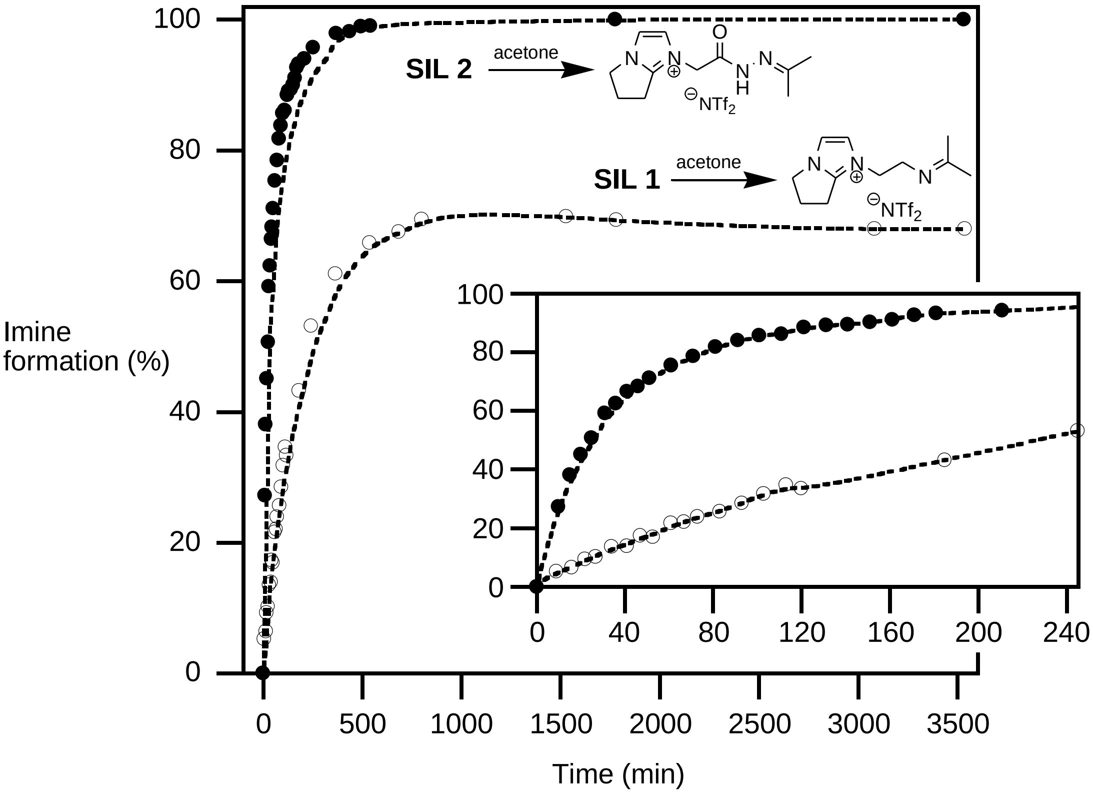


Fig. S1 Kinetic measurements of imine forming reactions of sensing ionic liquids (**SIL 1** and **SIL 2**, 0.20 M each) with acetone (0.22 M) in DMSO-d_6 solvent at ambient temperature. Inset: details of early conversions of the reactions. The progress of the imine forming reactions could be readily monitored at the methyl protons on both acetone (δ 2.08 ppm) and the imine product (δ 1.75 and 1.90 ppm for **SIL 1**; δ 1.90 and 1.97 ppm for **SIL 2**) by ^{1}H NMR.

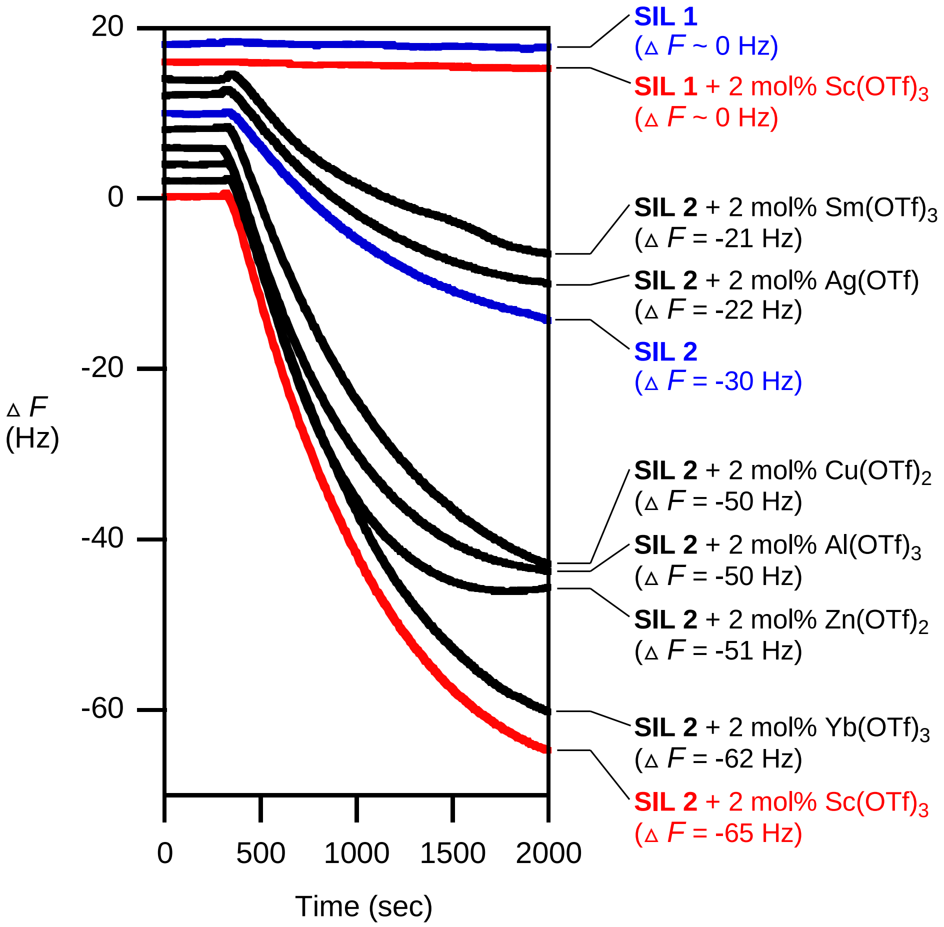


Fig. S2 Ultrasensitive, Lewis acid-catalyzed detection of acetone gas (58 ppb) by 9 MHz QCM thin-coated with **SIL 1** and **SIL 2** (3.3 nL each, 300 nm thickness) containing various metal triflates (2 mol%). The QCM response curves were vertically shifted (2 Hz in between) for clarity. Gas samples were injected at 300 s. The resonance frequency drop, △*F*, is the QCM response on the quartz chip surface.

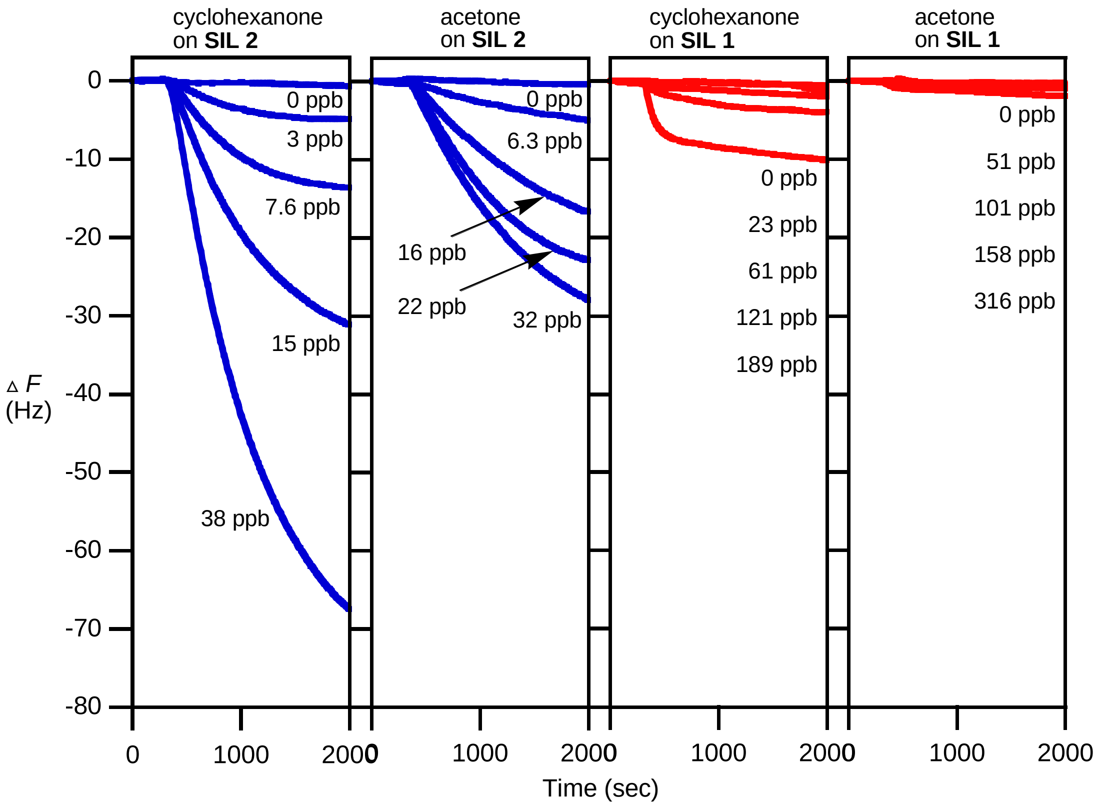


Fig. S3 Sensitivity detection of acetone and cyclohexanone gases using 9 MHz QCM thin-coated with **SIL 1** and **SIL 2** (3.3 nL each, 300 nm thickness) containing 2 mol% Sc(OTf)$_3$. Ketone gas samples were injected at 300 s. The resonance frequency drop, △*F*, is the QCM response on the quartz chip surface.

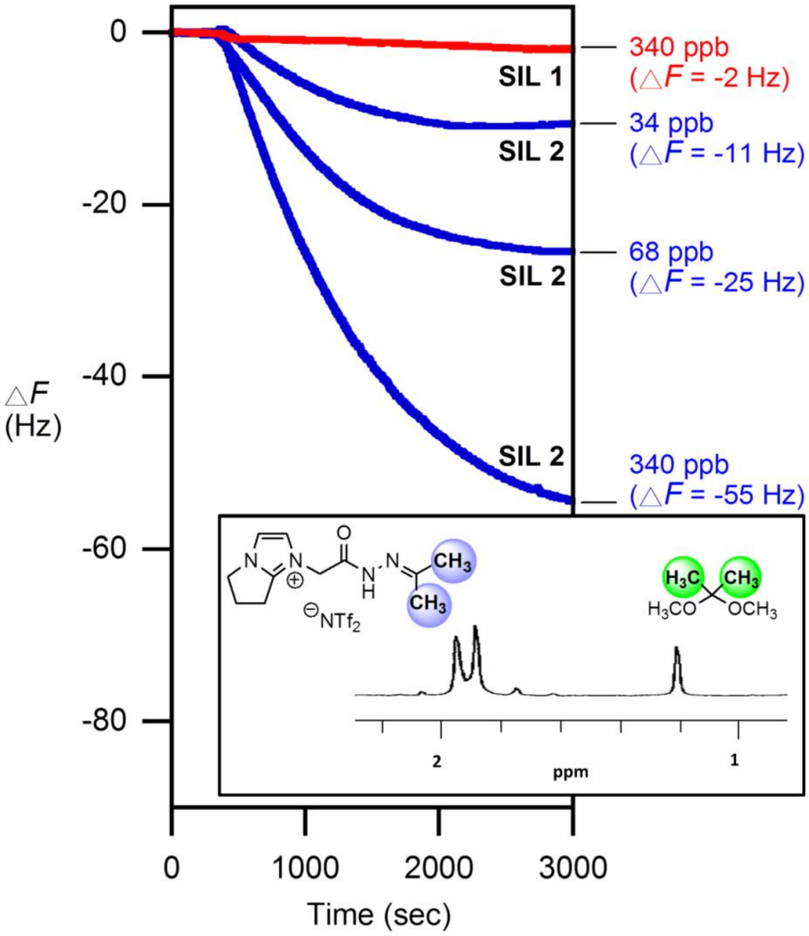
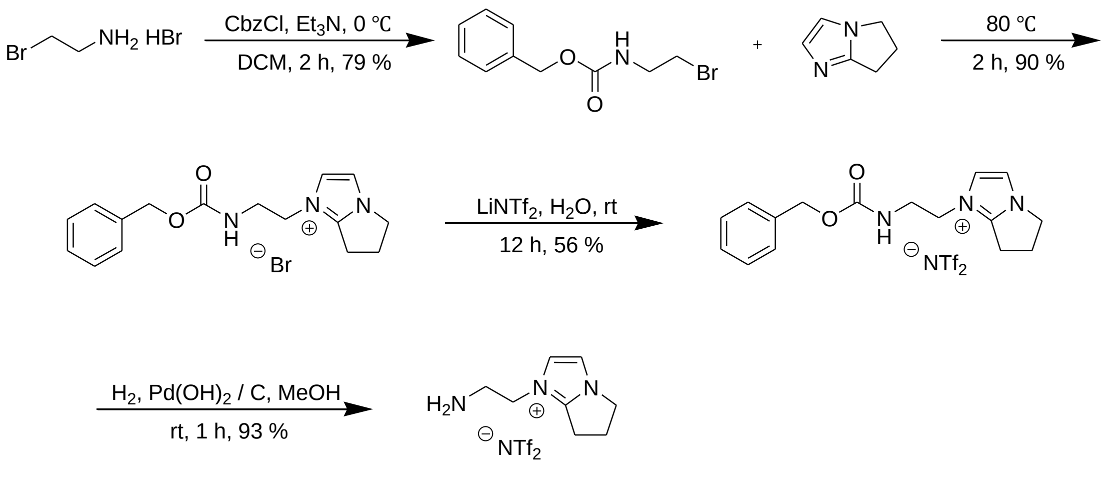


Fig. S4 Sensitive detection of 2,2-dimethoxypropane gas, a masked acetone, by 9 MHz QCM thin-coated with **SIL 2** (3.3 nL each, 300 nm thickness) containing 2 mol% $Sc(OTf)_3$. Gas samples were injected at 300 s. The resonance frequency drop, △*F*, is the QCM response on the quartz chip surface. Inset: ^{1}H NMR detail of the conversion confirmation of the imine forming reaction.



SIL 1

Scheme S1. Synthesis of **SIL 1**.

Synthesis of SIL 1

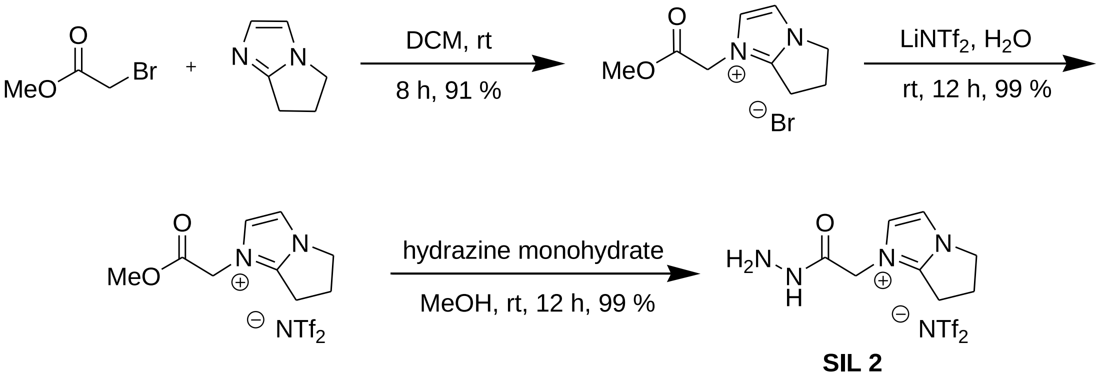
To a solution of 2-bromoethylamine hydrobromide (1.0 g, 4.88 mmol) and triethylamine (1.5 g, 14.85 mmol) in dichloromethane (20 mL), benzyl chloroformate (1.3 g, 7.62 mmol) was added portion-wise at 0 ℃. The resultant mixture was stirred at 0 °C for 2 h. The mixture was then washed with 10% sodium bicarbonate (3×10 mL) and 10% citric acid (3×10 mL) and dried over anhydrous sodium sulfate. After filtration, dichloromethane was evaporated to obtain crude product. The residue was then purified by silica gel column chromatography with ethyl acetate/hexane (1/7, v/v) as the eluent to afford the pure product (0.99 g, 79 % yield) as a white crystal solid.

6,7-dihydro-5H-pyrrolo[1,2-*a*]imidazole was prepared as described previously.[1] To a round-bottomed flask containing 6,7-dihydro-5H-pyrrolo[1,2-*a*]imidazole (0.82 g, 7.57 mmol) was added *N*-benzyloxycarbonyl-2-bromoethylamine (1.96 g, 7.57 mmol). The mixture was stirred and heated at 80 ^{o}C for 2 h. The crude product was then purified by silica gel column chromatography with methanol/dichloromethane (1/10, v/v) as the eluent to afford the desired product (2.48 g, 90% yield) as a colorless viscous liquid.

A mixture of bistrifluoromethanesulfonimide lithium salt (2.17 g, 7.56 mmol), water (10 mL) and the bromide salt (2.48 g, 6.77 mmol) was allowed to proceed the ion exchange for 12 h at room temperature. The resulting solution was added dichloromethane (10 mL) and then washed with water (3×3 mL). After removal of the solvent under reduced pressure, the residue was purified by silica gel column chromatography with ethyl acetate/ dichloromethane (1/3, v/v) as the eluent to afford the pure product (2.13 g, 56 % yield) as viscous liquid.

The Cbz-protected ionic liquid (2.13 g, 3.76 mmol) was then dissolved in methanol (10 mL) and catalytic amount of $Pd(OH)_2/C$ was added. The resulting mixture was bubbled with hydrogen. Reaction was carried out at room temperature for 1 h.

$Pd(OH)_2/C$ was filtered off, and the methanol was removed under reducing pressure to give the desired product **SIL 1** (1.51 g, 93% yield) as viscous liquid. ^{1}H NMR (400 MHz, DMSO-d_6) δ 2.66 (qn, J = 7.5 Hz, CCH_2C, 2H), 2.90 (t, J = 5.7 Hz, NCH_2C, 2H), 3.16 (t, J = 7.6 Hz, $N{=}CCH_2$, 2H), 4.01 (t, J = 5.7 Hz, $NCCH_2$, 2H), 4.19 (t, J = 7.3 Hz, NCH_2, 2H), 7.61 (s, Im, 2H); ^{13}C NMR (100 MHz, DMSO-d_6) δ 22.8, 25.5, 41.2, 47.8, 51.3, 117.7, 119.5 (q, J_{CF} = 320 Hz, CF_3), 125.8, 152.8; FAB-HRMS m/z $[M]^+$ calcd for $C_8H_{14}N_3$ 152.1188, found 152.1191.



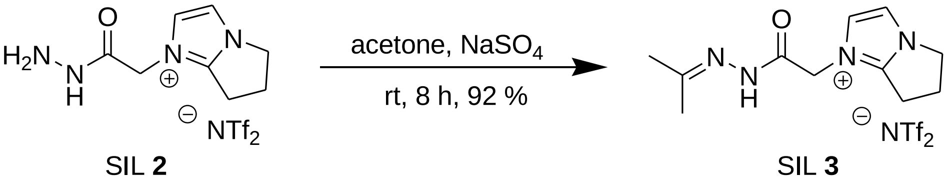
Scheme S2. Synthesis of **SIL 2**.

Synthesis of SIL 2

6,7-dihydro-5H-pyrrolo[1,2-*a*]imidazole was prepared as described previously.[1] To a solution of 6,7-dihydro-5H-pyrrolo[1,2-*a*]imidazole (203 mg, 1.87 mmol) in dichloromethane (2 mL), methyl bromoacetate (374 mg, 2.44 mmol) was added portion-wise at room temperature. The resultant mixture was stirred at room temperature for 8 h and the product was precipitated as white solid. The mixture was filtered and the pellet was washed with dichloromethane (3 × 1 mL) and dried under vacuum to obtain pure product (443 mg, 91 % yield) as a white solid.

A mixture of bistrifluoromethanesulfonimide lithium salt (250 mg, 0.87 mmol), water (1 mL) and the bromide salt (189 mg, 0.72 mmol) was allowed to proceed the ion exchange for 12 h at room temperature. The mixture was then washed with dichloromethane (3 × 2 mL) and dried over anhydrous sodium sulfate. Solvent was evaporated to obtain pure product (330 mg, 99% yield) as viscous liquid.

The methyl ester ionic liquid (113 mg, 0.25 mmol) was then dissolved in methanol (1 mL) and hydrazine monohydrate (25 mg, 0.50 mmol) was added. The resultant mixture was stirred at room temperature for 12 h. The methanol and hydrazine monohydrate was removed under reducing pressure to give the desired product **SIL 2** (113 mg, 99% yield) as viscous liquid. ^{1}H NMR (400 MHz, DMSO-d_6) δ 2.50-2.71 (m, CCH_2C, 2H), 3.04-3.11 (m, $N{=}CH_2C$, 2H), 4.23-4.27 (m ,NCH_2C, 2H), 4.45, 4.54 (br, NH_2-hydrazide, 2H), 4.82, 5.17 (s, CH_2-hydrazide, 2H), 7.57-7.63 (m, Im, 2H), 9.00, 9.48 (br, H-amide, 1H); ^{13}C NMR (100 MHz, DMSO-d_6) δ 22.7, 22.8, 25.6, 48.0, 48.1, 48.8, 49.0, 117.3, 117.7, 119.5 (q, J_{CF} = 320 Hz, CF_3), 126.8, 127.3, 153.4, 153.5, 164.1, 168.4; FAB-HRMS m/z $[M]^+$ calcd for $C_8H_{13}N_4O$ 181.1089, found 181.1088.



Synthesis of SIL 3

To a round-bottomed flask containing **SIL 2** (18 mg, 0.04 mmol) was added anhydrous sodium sulfate in acetone (2 mL). The solution was allowed to stand at room temperature for 12 h. The mixture was filtered to remove the sodium sulfate and the filtered solution was concentrated under vacuum to afford the pure product **SIL 3** (18 mg, 92% yield). ^{1}H NMR (400 MHz, DMSO-d_6) δ 1.90-1.96 (m, 2×CH_3-hydrazone, 6H), 2.64-2.72 (m, CCH_2C, 2H), 3.08-3.12 (m, N=CH_2C, 2H), 4.24-4.29 (m, NCH_2C, 2H), 5.01, 5.33 (s, CH_2-hydrazone, 2H), 7.60-7.66 (m, Im, 2H), 10.64, 10.78 (br, H-amide, 1H); ^{13}C NMR (100 MHz, DMSO-d_6) δ 17.3, 17.8, 22.7, 22.9, 24.9, 25.1, 25.5, 25.6, 48.1, 48.2, 48.5, 49.7, 117.4, 117.6, 117.8, 119.5 (q, J_{CF} =

320 Hz, CF_3), 126.9, 127.0, 127.4, 152.9, 153.6, 153.7, 157.4, 161.4, 164.4, 166.7; FAB-HRMS m/z $[M]^+$ calcd for $C_{11}H_{17}N_4O$ 221.1402, found 221.1397.

QCM measurements

The PSS QCM system (9 MHz) available from the ANT Technology Co. (Taipei, Taiwan, ROC) (http://www.anttech.com.tw/) was operated under room temperature and using air 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 (1.26 L). A rapid initial frequency decrease was typically detected within 5 sec after sample injection. The QCMs employed 9-MHz AT-cut quartz deposited with gold electrodes (area 11 mm^2) on both sides were commercially available (ANT Technology Co., Taipei, Taiwan). The gold electrodes on chips were cleaned with NaOH (2 N) for 30 min, water for 10 min, and HCl (1 N) for 5 min to remove organic absorbent impurities. Finally, quartz chips were rinsed with water thoroughly and dried under nitrogen.

Chemoselective detection of various gases using SIL 1 and 2

The SIL coating solutions were prepared by dissolving **SIL** (1 μL) in acetonitrile (HPLC grade) with concentration of 1/300 (v/v). 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 °C) for 1 min to remove residual acetonitrile. The freshly prepared sensor chips were then mounted in the gas flow chamber (100 cm ^{3}) and used air as carrier gas at flow rate of 3.0 mL/min. Until a stable baseline was obtained, numbers of target organic vapors (98 ppb), hexane, ethanol, ethyl acetate, water, acetone and propionaldehyde were injected into the chamber, respectively.

General procedure for imine / hydrazone formation reaction of SIL 1 and 2 with acetone

The ^{1}H NMR of a DMSO-d_6 solution containing **SIL 1** or **2** (0.2 M, 500 μL) was recorded first. Subsequently, acetone (0.22 M) was added to the NMR tube and then placed on a rotating shaker. The resulting solution was allowed to react at ambient temperature. The ^{1}H NMR spectrum was therefore collected at regular intervals. The area of the integrals of the CH_3 hydrogens of acetone and those of product were recorded to determine reaction rate.

Screening of metal triflates as catalysts for hydrazone formation reaction

The coating solutions were prepared by dissolving **SIL 2** (1 μL) and 2 mol% of metal triflate (Ag(OTf), $Al(OTf)_3$, $Cu(OTf)_2$, $Sc(OTf)_3$, $Sm(OTf)_3$, $Yb(OTf)_3$, and $Zn(OTf)_2$) in acetonitrile with final concentration of 1/300 (v/v). The **SIL 2** coating solutions (1 μL) were applied to the center of the gold electrodes using a micropipet. The coated chips were then placed in a heating oven (110 °C) for 1 min to evaporate residual acetonitrile. The freshly prepared sensor chips were then set in the gas flow chamber (100 cm^3) and flowing with air continuously under flow condition (3.0 mL/min). Until a stable baseline was obtained, acetone (58 ppb) was then injected into the chamber. The resonance frequency drop versus time curves was recorded.

Chemoselective gas detection of ketone compounds

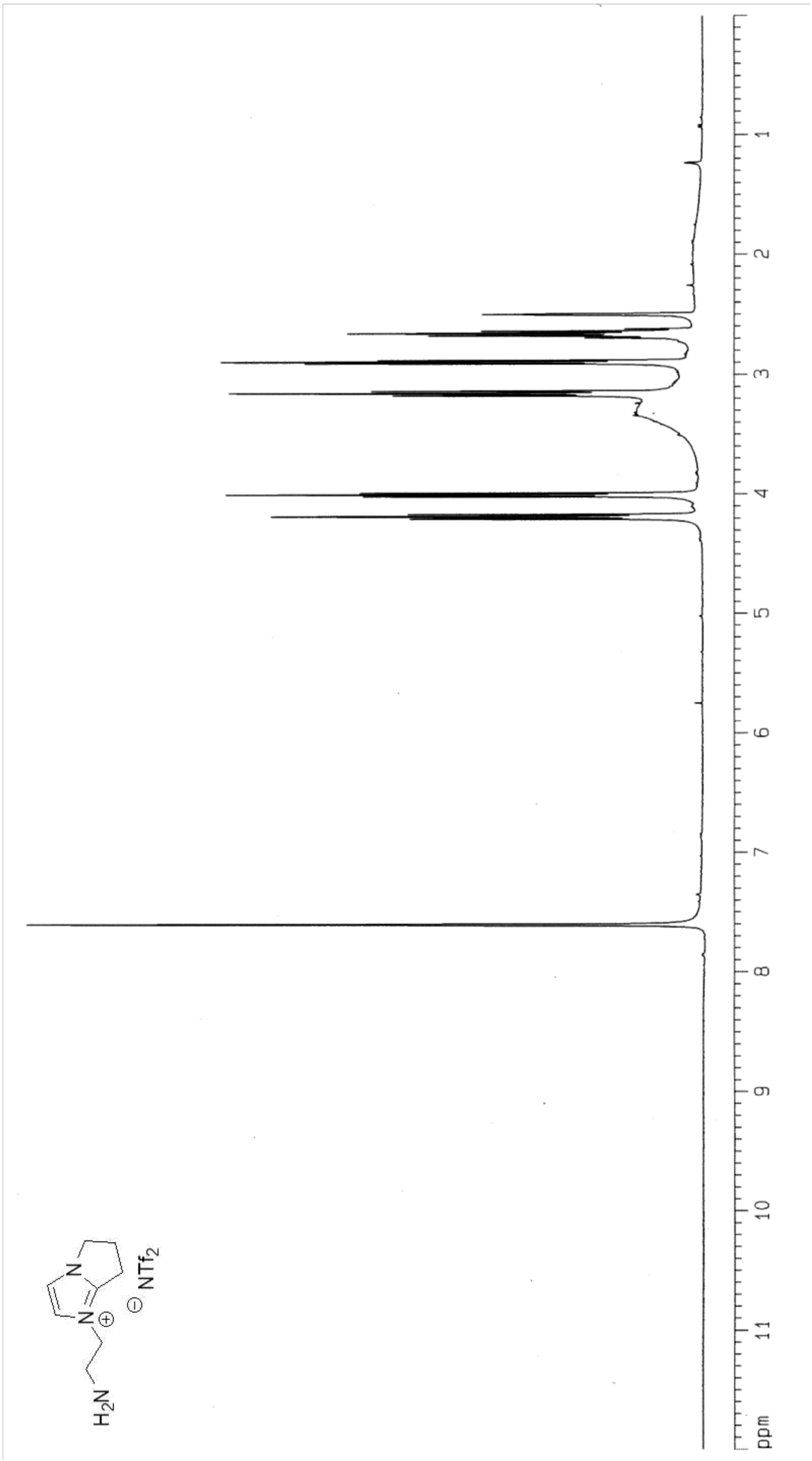
The coating solution was prepared by dissolving **SIL 2** (1 μL) and 2 mol% of $Sc(OTf)_3$ in acetonitrile (300 μL, HPLC grade). A micropipet was used to applied the coating solution (1 μL) onto the center of the gold electrodes. The chip was then placed in a heating oven (110 °C) for 1 min to remove residual acetonitrile. The freshly prepared sensor chip coated with **SIL 2** containing 2 mol% $Sc(OTf)_3$ was set in the flow chamber (100 cm^3) and used air as carrier gas at flow rate of 3.0 mL/min. After baseline was stable, a series of ketone vapors (76 ppb), 3-pentanone, 2-butanone, acetone, cycloheptanone, cyclohexanone and cyclopentanone were injected into the chamber, respectively. The resonance frequency drop versus time curves were recorded.

Detection of 2,2-dimethoxypropane

A freshly prepared **SIL 2** chip and a control chip coated with **SIL 1** containing 2 mol% Sc(OTf)$_3$ were mounted into the gas flow chamber and continuously flowing with air until system was stable under flow condition (3.0 mL/min). And then various concentrations of 2,2-dimethoxypropane (34, 68, 340 ppb) were injected into the chamber. The resonance frequency drop versus time curves were recorded.

References:

1. H.-C. Kan, M.-C. Tseng and Y.-H. Chu, *Tetrahedron* 2007, **63**, 1644-1653.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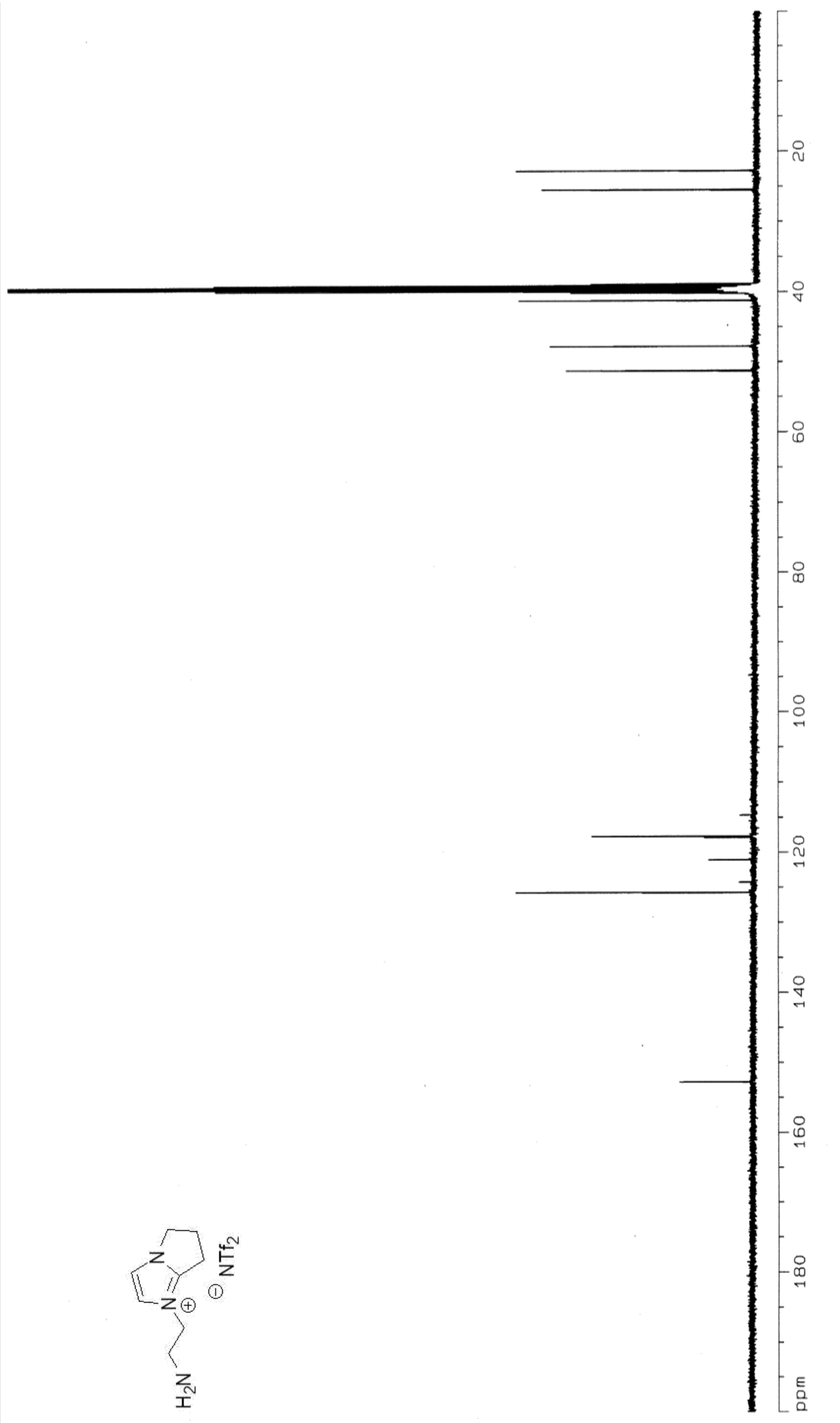
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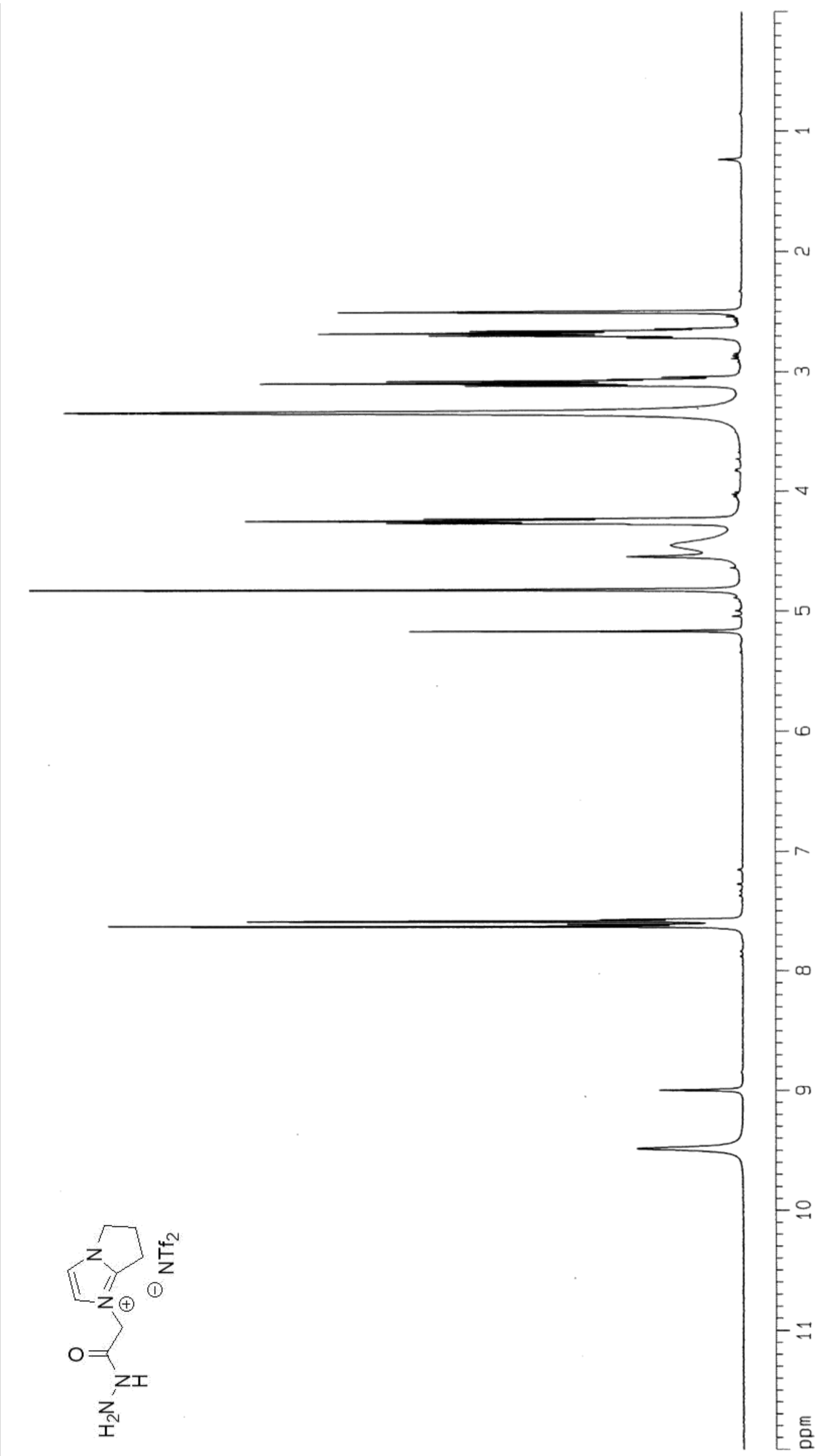
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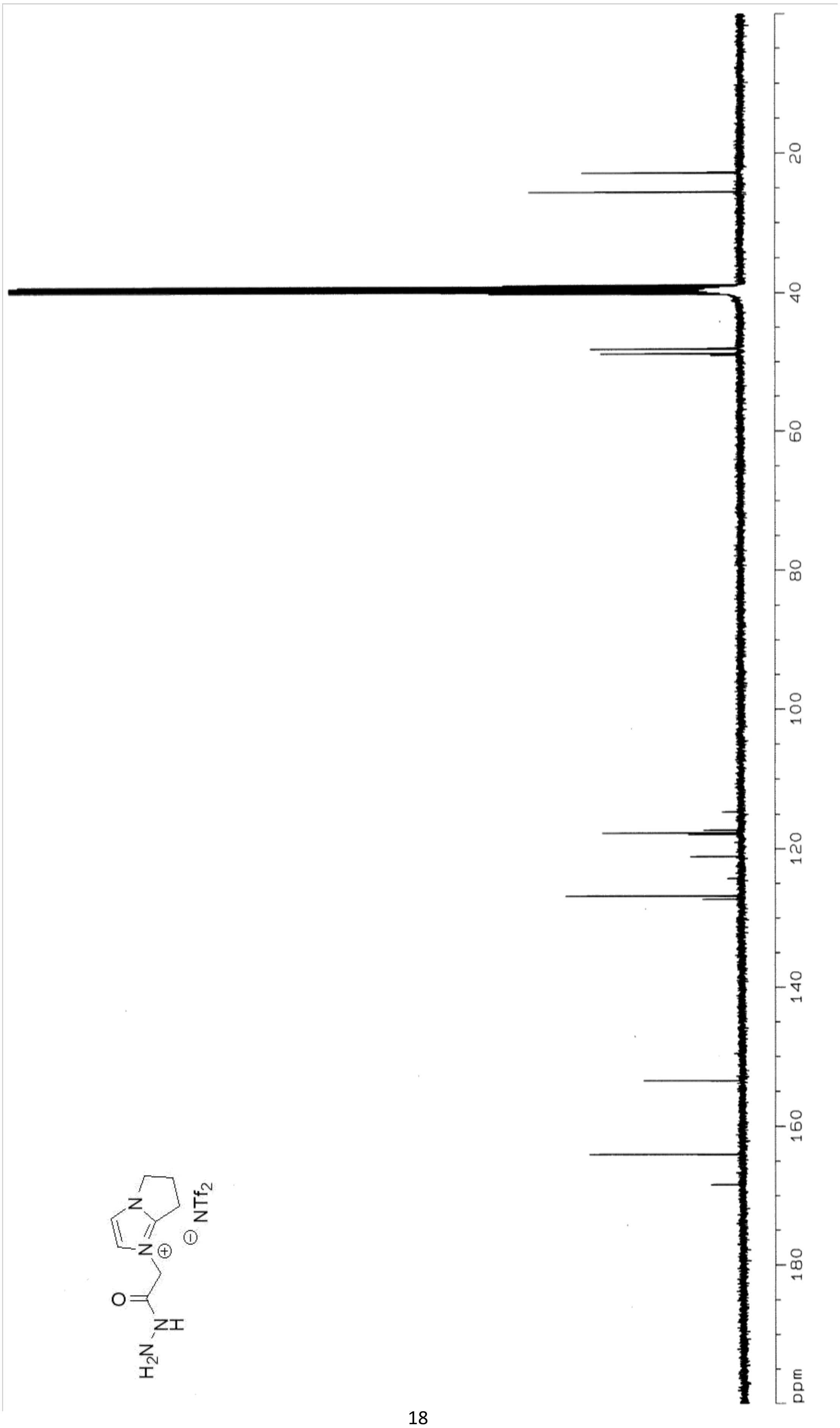
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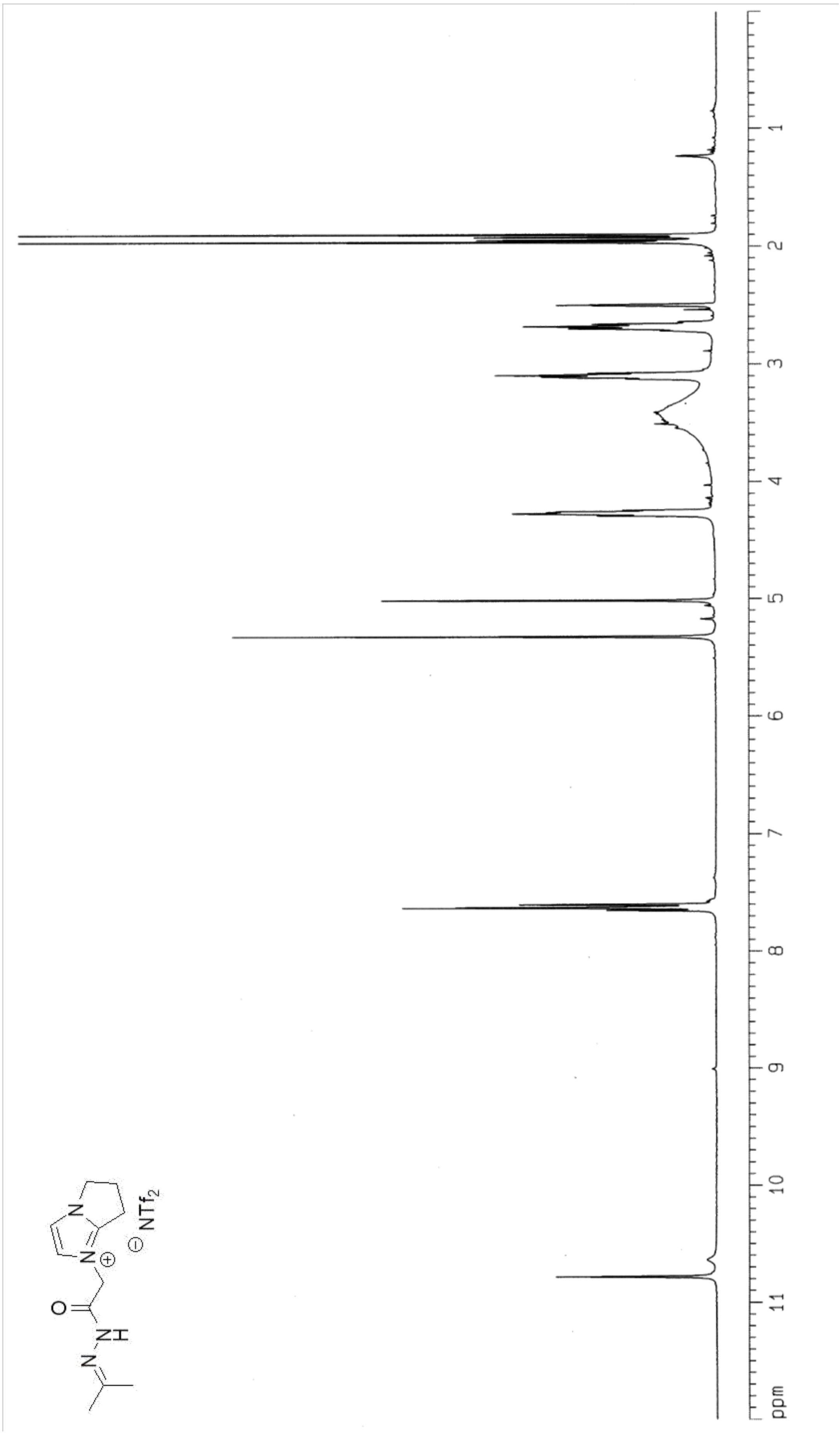
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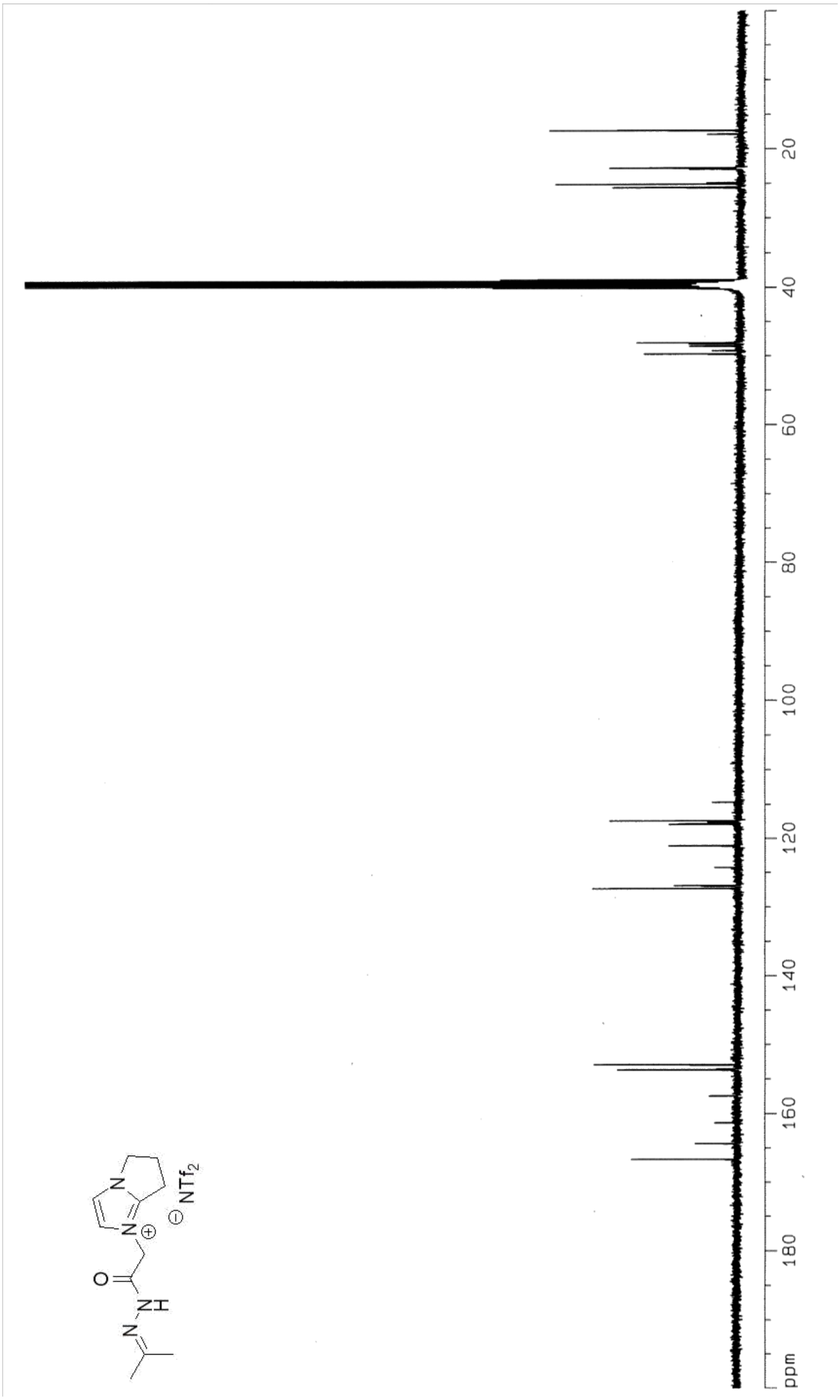
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