

Generation of Cobalt-Containing Nanoparticles on Carbon via Pyrolysis of a Cobalt Corrole and Its Application in the Hydrogenation of Nitroarenes

Jessica Michalke ¹, Michael Haas ², Dominik Krisch ², Thomas Bögl ³, Stephan Bartling ⁴, Nils Rockstroh ⁴, Wolfgang Schöfberger ² and Christoph Topf ^{1,*}

¹ Institute of Catalysis (INCA), Johannes Kepler University (JKU), Altenberger Straße 69, 4040 Linz, Austria; jessica.michalke@jku.at

² Institute of Organic Chemistry, Johannes Kepler University (JKU), Altenberger Straße 69, 4040 Linz, Austria; michael.haas@jku.at (M.H.); dominik.krisch@jku.at (D.K.); wolfgang.schoefberger@jku.at (W.S.)

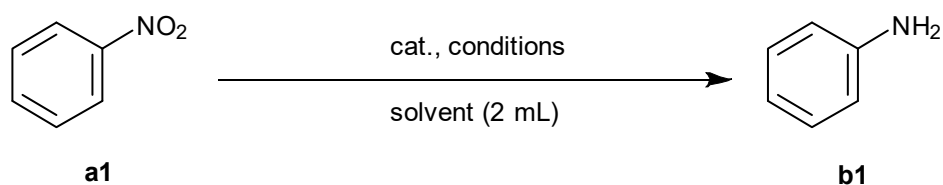
³ Department of Analytical Chemistry, Johannes Kepler University (JKU), Altenberger Straße 69, 4040 Linz, Austria; thomas.boegl@jku.at

⁴ Leibniz Institute for Catalysis e. V. (LIKAT Rostock), Albert-Einstein-Straße 29a, 18059 Rostock, Germany; stephan.bartling@catalysis.de (S.B.); nils.rockstroh@catalysis.de (N.R.)

* Correspondence: christoph.topf@jku.at

1. Effect of Temperature and H₂ Pressure on the Nitrobenzene Conversion Catalyzed by CoCorrPPh₃@Vulcan-800.....	2
2. Dependence of the CoCorrPPh₃@Vulcan-800-Catalyzed Nitrobenzene Hydrogenation on the Reaction Time.....	3
3. Control Experiments for the Nitrobenzene Hydrogenation.....	4
4. Maitlis' Hot Filtration Test	4
5. Catalyst Characterization	5
a. Elemental Analysis (EA) of CoCorrPPh ₃ @Vulcan-800	5
b. X-Ray Photoelectron Spectroscopy (XPS) and Energy-Dispersive X-Ray Spectroscopy (EDX) Data of CoCorrPPh ₃ @Vulcan-800	5
c. Thermogravimetric Analysis (TGA) of the Precursor CoCorrPPh ₃	6
6. Synthesis and Characterization of the CoCorrPPh₃ Precursor.....	7
7. Characterization Data of the Isolated Products.....	10
8. ¹H NMR, ¹³C{¹H} NMR, ¹⁹F NMR, and HR-MS Spectra of the Isolated Products.....	18

1. 1.Effect of Temperature and H₂ Pressure on the Nitrobenzene Conversion Catalyzed by CoCor-rPPh₃@Vulcan-800



Entry	H ₂ (bar)	T (°C)	Reaction time (h)	Solvent	Conversion (%)
1	20	80	20	MeOH	7
2	40	80	20	MeOH	16
3	60	80	20	MeOH	7
4	20	100	20	MeOH	21
5	40	100	16	H ₂ O	74
6	20	120	16	H ₂ O	84
7	40	120	16	H ₂ O	93
8	40	120	16	MeOH	79

Table S1: Hydrogenation of nitrobenzene; variation of temperature and pressure. Reaction conditions: nitrobenzene (0.25 mmol), catalyst (1 mol%), solvent (2 mL), reaction time as indicated, *n*-hexadecane (in case of MeOH) or chlorobenzene (in case of H₂O) applied as internal standards (18 mg), respectively.

2. Dependence of the CoCorrPPh₃@Vulcan-800-Catalyzed Nitrobenzene Hydrogenation on the Reaction Time

Entry	Reaction time (h)	Conversion (%)
1	5	26
2	7	43
3	9	66
4	13	74
5	16	79
6	20	>99

Table S2: Hydrogenation of nitrobenzene; influence of the reaction time on the substrate conversion. Reaction conditions: nitrobenzene (0.25 mmol), catalyst (0.5 mol%), H₂ (40 bar), MeOH (2 mL), 120 °C, reaction time as indicated, and *n*-hexadecane used as the internal standard (18 mg).

3. Control Experiments for the Nitrobenzene Hydrogenation

Entry	Catalyst	Pyrolysis T (°C)	Aniline amount (%)
1	Vulcan	no pyrolysis	0
2	Vulcan	800	0
3	-	-	0
4	components@Vulcan ^a	no pyrolysis	0
5	components@Vulcan ^a	800	0

Table S3: Hydrogenation of nitrobenzene; reaction conditions: nitrobenzene (0.25 mmol), catalyst (0.5 mol%), H₂ (40 bar), MeOH (2 mL), 120 °C, and applying a reaction time of 20 h. In neither case was it possible to detect any aniline product via GC-MS analysis.

^aThe material components@Vulcan was prepared according to the standard procedure as described in the main text, with the exception that the molecularly well-defined CoCorrPPh₃ precursor was not applied as such but instead the constituents of this phosphine-tagged cobalt corrolate, *i.e.* aldehyde, pyrrole, triphenylphosphine, and cobalt(II)acetate tetrahydrate were added consecutively (in the listed order) to the pertinent suspension.

4. Maitlis' Hot Filtration Test

Entry	Reaction time (t)	Conversion (%)
1	1	4
2 ^a	16	4

Table S4: Maitlis' hot filtration test; reaction conditions: 4-nitrobenzonitrile (0.25 mmol), catalyst (0.5 mol%), H₂ (40 bar), MeOH (2 mL), 120 °C, 16 h reaction time, and *n*-hexadecane as the internal standard (18 mg).

^a Following the general hydrogenation procedure the hot filtration test was performed with 4-nitrobenzonitrile. After 1 h the reaction was interrupted and the reaction mixture was filtered through a 0.2 µm Teflon filter whereupon the clear filtrate was analyzed via GC (Entry 1). Afterwards, the hydrogenation reaction was re-enacted with the filtrate and it was found that the conversion remained constant (Entry 2). Hence, we conclude that the described CoCorrPPh₃@Vulcan-800-catalyzed nitrobenzene hydrogenation indeed proceeds via a heterogeneous route.

5. Catalyst Characterization

a. Elemental Analysis (EA) of CoCorrPPh₃@Vulcan-800

Entry	Co (%)	C (%)	H (%)	N (%)
1	1,005	95.62	0.3049	0.3629
2	1.311	95.80	0.4252	0.6931

Table S5: EA (% by weight) obtained for the CoCorrPPh₃@Vulcan-800 catalyst.

b. X-Ray Photoelectron Spectroscopy (XPS) and Energy-Dispersive X-Ray Spectroscopy (EDX) Data of CoCorrPPh₃@Vulcan-800

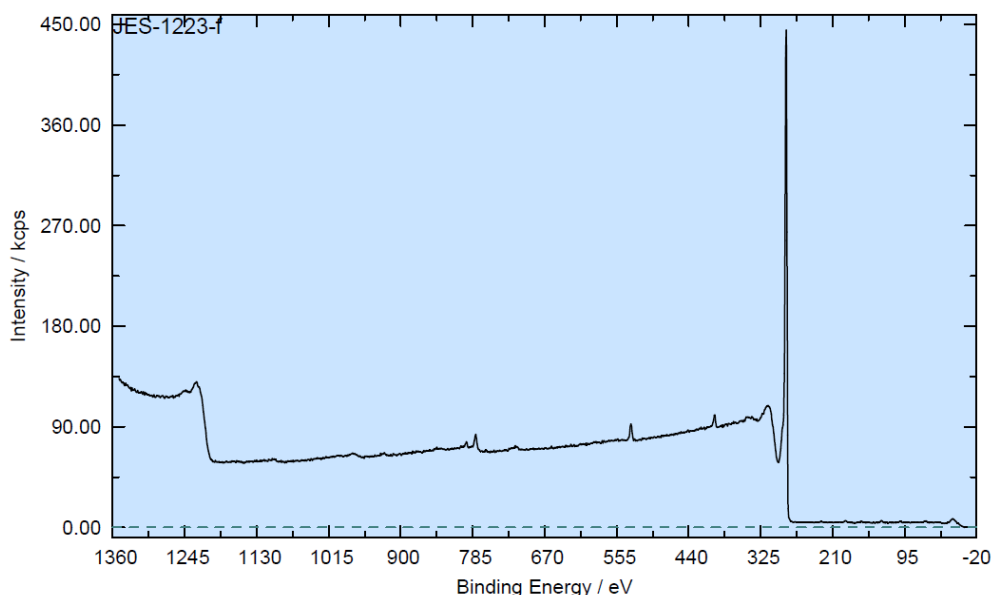


Figure S1: Complete spectra (XPS) of the pyrolytically activated CoCorrPPh₃@Vulcan-800 catalyst.

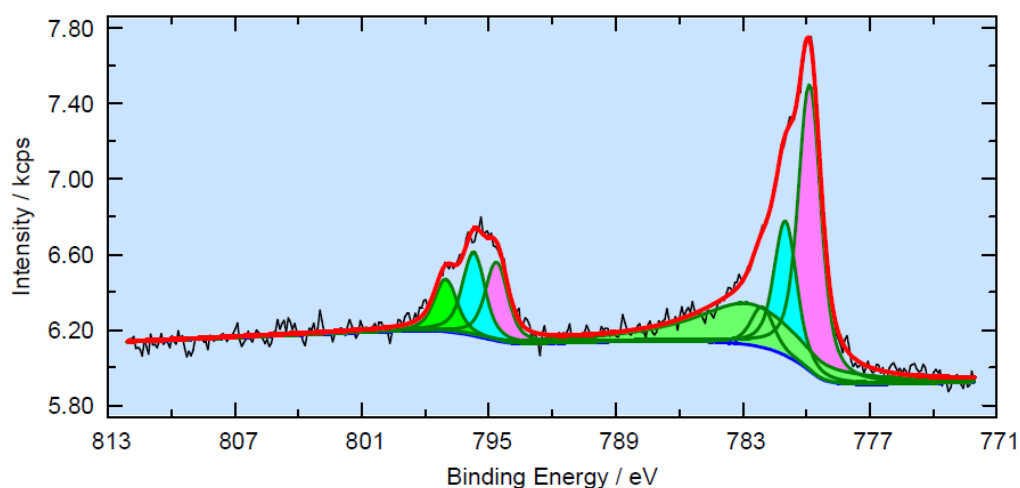


Figure S2: Enlarged excerpt of the complete spectra (XPS) of pyrolytically activated CoCorrPPh₃@Vulcan-800; cobalt region.

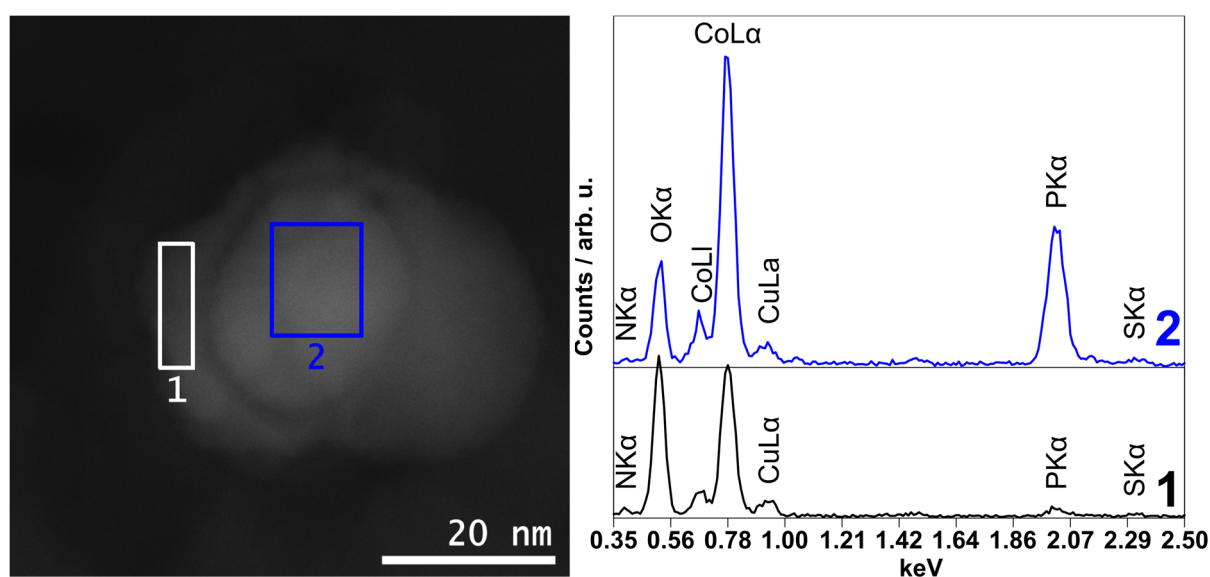


Figure S3: Selected EDX spectra (right) of the highlighted areas of CoCorrPPh₃@Vulcan-800 (STEM-HAADF image on the left). Owing to the different contrast and the different ratios of O and P to Co a typical core-shell structure of the respective particle is deduced, with a phosphidic core and an oxidic shell.

c. Thermogravimetric Analysis (TGA) of the Precursor CoCorrPPh₃

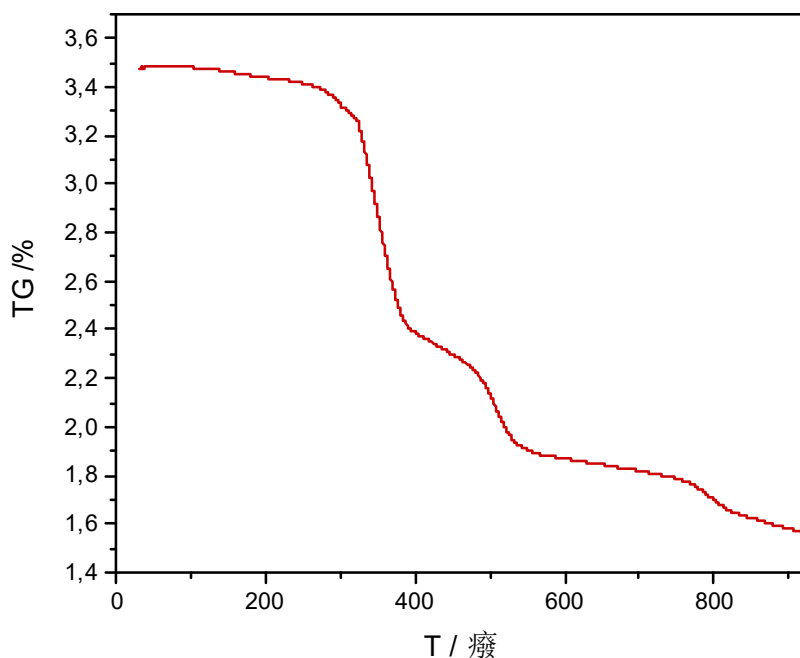


Figure S4: Recorded TGA trace of the non-supported CoCorrPPh₃ complex; the slight bend located at around 800 °C indicates that the thermal conversion of the phosphine-tagged metal corrole precursor into the heterogenized catalytically active material is completed. The impregnated Vulcan[®] support that was pyrolyzed at 800 °C gives rise to the highest active heterogeneous catalyst (see main text, Table 3).

6. Synthesis and Characterization of the CoCorrPPh₃ Precursor

According to the procedure of Gryko 2006 (*J. Org. Chem.* **2006**, 71, 3707–3717; doi: 10.1021/jo060007k) the following synthesis was carried out:

Synthesis of 5,10,15-4-*t*-butylphenylcorrole: 4-*t*-butylbenzaldehyde (836 μ L, 5 mmol) and freshly distilled pyrrole (692 μ L, 10 mmol) were dissolved in methanol (200 mL). Afterwards, water (200 mL) and conc. hydrochloric acid (4.25 mL) were added upon which the solution was stirred at room temperature (2.5 h). The mixture was extracted thrice with dichloromethane while the organic layer was dried over Na₂SO₄ and then concentrated. The crude was diluted with dichloromethane (300 mL) then *p*-chloranil (1.23 g, 5 mmol) was added, and the mixture was allowed to stir overnight at room temperature. Subsequent evaporation to dryness and purification *via* column chromatography (silica, dichloromethane/heptane 1:1 by volume) afforded the pure product as a green solid (234 mg, 20 % yield).

The phosphine-tagged cobalt corrole was then prepared following the procedure of Chen 2013 (*Tetrahedron Letters* **2013**, 54, 4143–4147; doi: 10.1016/j.tetlet.2013.05.083):

Synthesis of Cobalt(III)-triphenylphospine-5,10,15-4-*t*-butylphenylcorrole: Co(OAc)₂·4 H₂O (327 mg, 1.31 mmol) and triphenylphospine (88 mg, 0.337 mmol) were dissolved in a mixture of methanol and dichloromethane (150 mL, 1:2 by volume). Subsequently, the freebase corrole (234 mg, 0.337 mmol) was added and the solution was stirred under reflux conditions (45 min, Ar atmosphere). Afterwards, the mixture was extracted thrice with dichloromethane upon which the organic layer was dried over Na₂SO₄ and then concentrated. Purification *via* column chromatography (silica, dichloromethane/heptane 1:1 by volume) afforded the product as a red solid (300 mg, 88 %). ¹H-NMR (300 MHz, CDCl₃, 25 °C): δ = 8.55 (d, *J* = 4.5 Hz,

2H), 8.35 (d, $J = 4.8$ Hz, 2H), 8.11 (d, $J = 4.8$ Hz, 2H), 7.92 – 8.04 (m, 5H), 7.53 – 7.63 (m, 8H), 7.34 (dd, $J_1 = 8.0$ Hz, $J_2 = 1.8$ Hz, 1H), 7.05 (t, $J = 7.4$ Hz, 3H), 6.71 (td, $J_1 = 7.8$ Hz, $J_2 = 2.3$ Hz, 6H), 4.71 – 4.76 (m, 6H), 1.54 (s, 27H) ppm;

^{13}C -NMR (125 MHz, CDCl_3 , 25 °C): $\delta = 149.8, 146.2, 145.8, 145.1, 140.5, 138.9, 136.6, 131.8, 131.2, 130.4, 129.5, 129.2, 128.6, 127.0, 125.4, 124.3, 124.1, 123.8, 118.3, 31.6$ ppm; ^{31}P -NMR (202 MHz, CDCl_3 , 25 °C): $\delta = 37.1$ ppm; HRMS m/z : calcd.. for $\text{C}_{67}\text{H}_{62}\text{CoN}_4\text{P}$: 1012.4044; found 1012.4060 $[\text{M}]^+$.

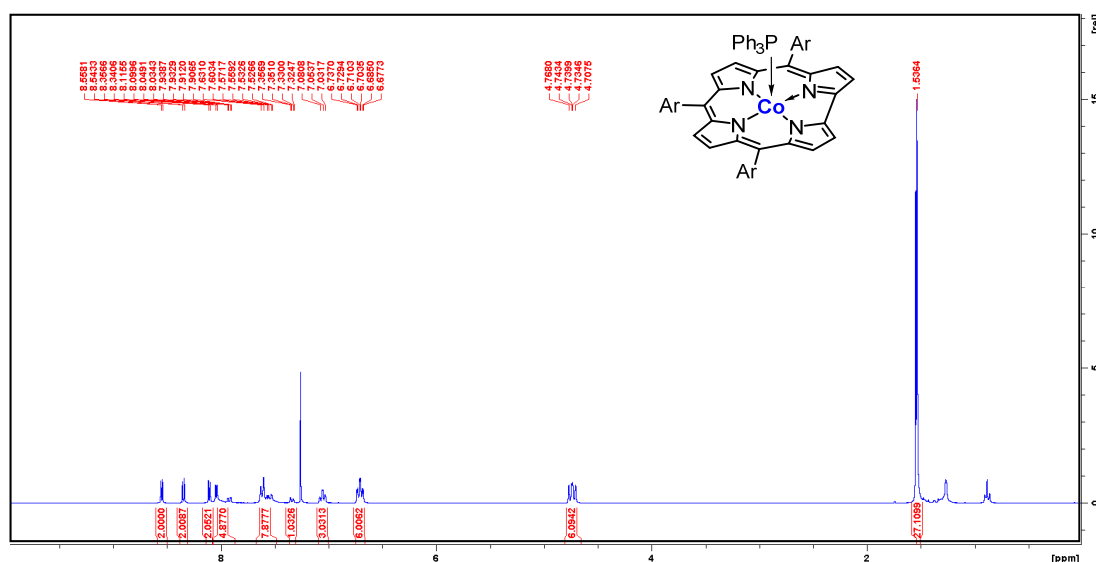


Figure S5: ^1H NMR of CoCorrPPh_3 in CDCl_3 .

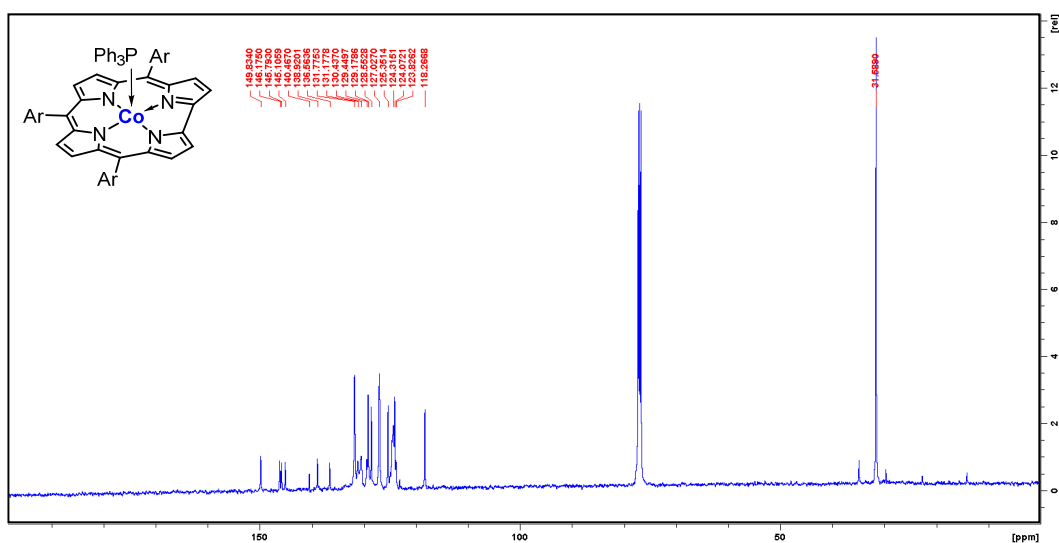


Figure S6: $^{13}\text{C}\{^1\text{H}\}$ NMR of CoCorrPPh_3 in CDCl_3 .

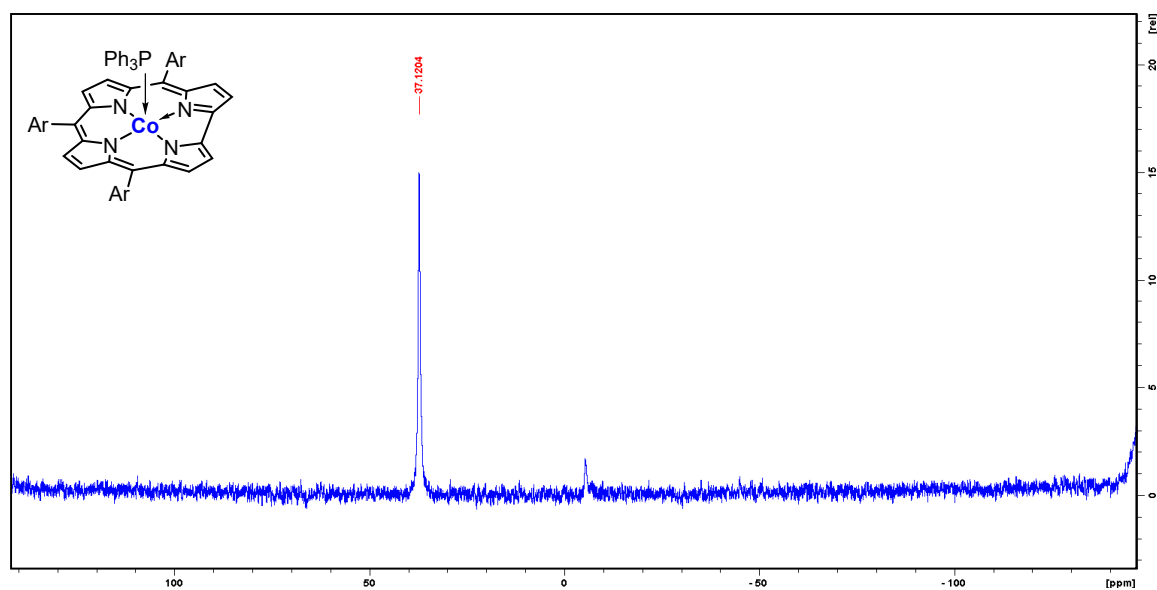


Figure S7: ^{31}P NMR of CoCorrPPh_3 in CDCl_3 .

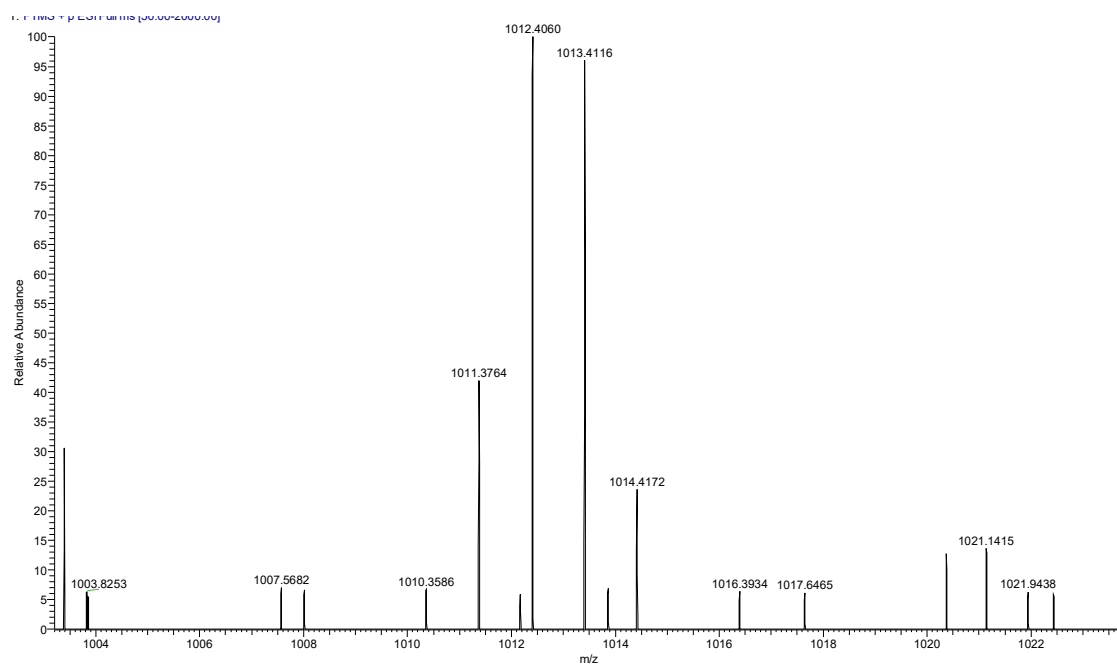


Figure S8: HR-MS of CoCorrPPh_3 .

7. Characterization Data of the Isolated Products

Anilinium chloride (c1). The title compound was synthesized according to the standard procedure. 62 mg (0.501 mmol) of **a1** was used. Appearance: white crystalline powder: 63 mg (0.482 mmol, 96% yield). Analytical data: ^1H NMR (500 MHz, D_2O , 25 °C): δ = 7.42 – 7.40 (m, 3H), 7.29 – 7.28 (m, 2H) ppm; $^{13}\text{C}\{^1\text{H}\}$ NMR (125 MHz, D_2O , 25 °C): δ = 130.1, 129.7, 129.2, 122.8 ppm; HR-MS (ESI-Orbitrap) m/z : $[\text{M}-\text{Cl}]^+$ calcd. for $\text{C}_6\text{H}_8\text{N}$: 94.0651; found: 94.0650.

1,1'-Biphenyl-2,2'-diaminium dichloride (c2). The title compound was synthesized according to the standard procedure. 122 mg (0.501 mmol) of **a2** was used. Appearance: off-white powder, 125 mg (0.485 mmol, 97% yield). Analytical data: ^1H NMR (300 MHz, D_2O , 25 °C): δ = 7.65 – 7.56 (m, 6 H), 7.47 – 7.44 (m, 2 H) ppm; $^{13}\text{C}\{^1\text{H}\}$ NMR (75.5 MHz, D_2O , 25 °C): δ = 131.5, 131.0, 129.9, 129.5, 129.2, 124.0 ppm; HR-MS (ESI-Orbitrap) m/z : $[\text{M}-2\text{Cl}-\text{H}]^+$ calcd. for $\text{C}_{12}\text{H}_{13}\text{N}_2$: 185.1073; found: 185.1076.

Benzene-1,2-diaminium dichloride (c3). The title compound was synthesized according to the standard procedure. 70 mg (0.507 mmol) of **a3** was used. Appearance: light-pink crystalline powder, 82 mg (0.454 mmol, 90% yield). Analytical data: ^1H NMR (300 MHz, D_2O , 25 °C): δ = 7.30 (s, 4 H) ppm; $^{13}\text{C}\{^1\text{H}\}$ NMR (75.5 MHz, D_2O , 25 °C): δ = 127.5, 126.7, 123.2 ppm; HR-MS (ESI-Orbitrap) m/z : $[\text{M}-2\text{Cl}-\text{H}]^+$ calcd. for $\text{C}_6\text{H}_9\text{N}_2$: 109.0760; found: 109.0759.

4,5-Dimethylbenzene-1,2-diaminium dichloride (c4). The title compound was synthesized according to the standard procedure. 83 mg (0.500 mmol) of **a4** was used. Appearance: brown crystalline powder, 83 mg (0.396 mmol, 79% yield). Analytical data: ^1H NMR (300 MHz, D_2O , 25 °C): δ = 7.17 (s, 2H), 2.25 (s, 6H) ppm; $^{13}\text{C}\{^1\text{H}\}$ NMR (75.5 MHz, D_2O , 25 °C): δ = 138.0, 124.4, 123.1, 18.3 ppm; HR-MS (ESI-Orbitrap) m/z : $[\text{M}-2\text{Cl}-\text{H}]^+$ calcd. for $\text{C}_8\text{H}_{13}\text{N}_2$: 137.1073; found: 137.1074.

2,3-Dimethylbenzenaminium chloride (c5). The title compound was synthesized according to the standard procedure. 76 mg (0.500 mmol) of **a5** was used. Appearance: reddish black powder, 78 mg (0.462 mmol, 98% yield). Analytical data: ^1H NMR (300 MHz, D_2O , 25 °C): δ = 7.31 – 7.24 (m, 1 H), 7.22 – 7.21 (m, 2 H),

2.32 (s, 1 H), 2.25 (s, 1 H) ppm; $^{13}\text{C}\{^1\text{H}\}$ NMR (75.5 MHz, D_2O , 25 °C): δ = 139.7, 130.5, 130.4, 128.3, 126.7, 120.6, 19.2, 12.7 ppm; HR-MS (ESI-Orbitrap) m/z : $[\text{M}-\text{Cl}]^+$ calcd. for $\text{C}_8\text{H}_{12}\text{N}$: 122.0964; found: 122.0964.

*N*¹-Methylbenzene-1,2-diaminium dichloride (**c6**). The title compound was synthesized according to the standard procedure. 76 mg (0.502 mmol) of **a6** was used. Appearance: light-pink crystalline powder, 73 mg (0.378 mmol, 75% yield). Analytical data: ^1H NMR (300 MHz, D_2O , 25 °C): δ = 7.25 – 7.21 (m, 2H), 7.13 – 7.10 (m, 2H), 3.01 (s, 3H) ppm; $^{13}\text{C}\{^1\text{H}\}$ NMR (75.5 MHz, D_2O , 25 °C): δ = 131.3, 128.6, 128.4, 124.8, 121.8, 121.4, 34.7 ppm; HR-MS (ESI-Orbitrap) m/z : $[\text{M}-2\text{Cl}-\text{H}]^+$ calcd. for $\text{C}_7\text{H}_{11}\text{N}_2$: 123.0917; found: 123.0918.

4-Aminobenzonitrile (**b7**). The title compound was synthesized according to the standard procedure. 74 mg (0.500 mmol) of **a7** was used. Appearance: colorless crystals, 56 mg (476 mmol, 95% yield). Analytical data: ^1H NMR (300 MHz, D_2O , 20 °C): δ = 7.40 (d, J = 8.5 Hz, 2 H), 6.64 (d, J = 8.5 Hz, 2 H), 4.18 (br, 2 H) ppm; $^{13}\text{C}\{^1\text{H}\}$ NMR (75.5 MHz, D_2O , 20 °C): δ = 150.4, 133.8, 120.2, 114.5, 100.2 ppm; HR-MS (ESI-Orbitrap) m/z : $[\text{M}+\text{H}]^+$ calcd. for $\text{C}_7\text{H}_7\text{N}_2$: 119.0604; found 119.0588.

2-(Hydroxymethyl)benzeneaminium chloride (**c8**). The title compound was synthesized according to the standard procedure. 77 mg (0.501 mmol) of **a8** was used. Appearance: sand-colored solid, 16 mg (0.098 mmol, 20% yield). Analytical data: ^1H NMR (300 MHz, D_2O , 25 °C): δ = 7.50 – 7.48 (m, 3 H), 7.44 – 7.42 (m, 1 H), 4.82 (s, 2 H) ppm; $^{13}\text{C}\{^1\text{H}\}$ NMR (75.5 MHz, D_2O , 25 °C): δ = 133.4, 129.7, 129.5, 129.4, 128.7, 123.8, 60.9 ppm; HR-MS (ESI-Orbitrap) m/z : $[\text{M}-\text{Cl}]^+$ calcd. for $\text{C}_7\text{H}_{10}\text{NO}$: 124.0757; found: 124.0749.

2-Hydroxybenzeneaminium chloride (**c9**). The title compound was synthesized according to the standard procedure. 70 mg (0.500 mmol) of **a9** was used. Appearance: red-brown powder, 62 mg (0.425 mmol, 85% yield). Analytical data: ^1H NMR (300 MHz, D_2O , 25 °C): δ = 7.19 – 7.11 (m, 2 H), 7.01 – 6.92 (m, 2 H) ppm; $^{13}\text{C}\{^1\text{H}\}$ NMR (75.5 MHz, D_2O , 25 °C): δ = 149.1, 129.1, 123.1, 120.6, 116.3 ppm; HR-MS (ESI-Orbitrap) m/z : $[\text{M}-\text{Cl}]^+$ calcd. for $\text{C}_6\text{H}_8\text{NO}$: 110.0600; found: 110.0616.

3-Hydroxybenzeneaminium chloride (**c10**). The title compound was synthesized according to the standard procedure. 70 mg (0.502 mmol) of **a10** was used. Appearance: olive-green powder, 56 mg (0.382 mmol,

76% yield). Analytical data: ^1H NMR (300 MHz, D_2O , 25 °C): δ = 7.43 – 7.38 (m, 1 H), 7.01 – 6.88 (m, 3 H) ppm; $^{13}\text{C}\{^1\text{H}\}$ NMR (75.5 MHz, D_2O , 25 °C): δ = 156.8, 131.2, 130.9, 116.1, 114.6, 110.1 ppm; HR-MS (ESI-Orbitrap) m/z : $[\text{M}-\text{Cl}]^+$ calcd. for $\text{C}_6\text{H}_8\text{NO}$: 110.0600; found 110.0650.

4-Hydroxybenzeneaminium chloride (c11). The title compound was synthesized according to the standard procedure. 70 mg (0.502 mmol) of **a11** was used. Appearance: dark violet-black powder, 55 mg (0.379 mmol, 76% yield). Analytical data: ^1H NMR (300 MHz, D_2O , 25 °C): δ = 7.28 (d, J = 8.8 Hz, 2 H), 6.98 (d, J = 8.8 Hz, 2 H) ppm; $^{13}\text{C}\{^1\text{H}\}$ NMR (75.5 MHz, D_2O , 25 °C): δ = 156.0, 124.3, 122.0, 116.5 ppm; HR-MS (ESI-Orbitrap) m/z : $[\text{M}-\text{Cl}]^+$ calcd. for $\text{C}_6\text{H}_8\text{NO}$: 110.0600; found: 110.0599.

2-Aminoacetophenone (b12). The title compound was synthesized according to the standard procedure. 83 mg (0.500 mmol) of **a12** was used. Appearance: white crystalline powder, 67 mg (0.496 mmol, 99% yield). Analytical data: ^1H NMR (300 MHz, D_2O , 25 °C): δ = 7.76 – 7.73 (m, 1 H), 7.33 – 7.30 (m, 1 H), 6.72 – 6.69 (m, 2 H), 2.61 (s, 3 H) ppm; $^{13}\text{C}\{^1\text{H}\}$ NMR (75.5 MHz, D_2O , 25 °C): δ = 200.7, 150.0, 134.3, 132.0, 118.3, 117.2, 115.8, 27.8 ppm; HR-MS (ESI-Orbitrap) m/z : $[\text{M}+\text{H}]^+$ calcd. for $\text{C}_8\text{H}_{10}\text{NO}$: 136.0757; found: 136.0758.

3-Acetylbenzenaminium chloride (c13). The title compound was synthesized according to the standard procedure. 82 mg (0.497 mmol) of **a13** was used. Appearance: sand-colored solid, 59 mg (0.344 mmol, 69% yield). Analytical data: ^1H -NMR (300 MHz, D_2O , 20 °C): δ = 8.02 – 8.00 (m, 1H), 7.85 (s, 1H), 7.64 – 7.56 (m, 2H), 2.60 (s, 3H) ppm; $^{13}\text{C}\{^1\text{H}\}$ NMR (75.5 MHz, D_2O , 20 °C): δ = 202.0, 138.1, 131.0, 130.7, 129.1, 127.8, 122.3, 26.30 ppm; HR-MS (ESI-Orbitrap) m/z : $[\text{M}-\text{Cl}]^+$ calcd. for $\text{C}_8\text{H}_{10}\text{NO}$: 136.0757; found: 136.0758.

4-Acetylbenzenaminium chloride (c14). The title compound was synthesized according to the standard procedure. 83 mg (0.501 mmol) of **a14** was used. Appearance: grey powder, 80 mg (0.463 mmol, 92% yield). Analytical data: ^1H NMR (300 MHz, D_2O , 25 °C): δ = 7.93 (d, J = 8.7 Hz, 2H), 7.35 (d, J = 8.7 Hz, 2H), 2.52 (s, 3H) ppm; $^{13}\text{C}\{^1\text{H}\}$ NMR (75.5 MHz, D_2O , 25 °C): δ = 202.2, 136.2, 135.9, 130.4, 122.6, 26.2 ppm; HR-MS (ESI-Orbitrap) m/z : $[\text{M}-\text{Cl}]^+$ calcd. for $\text{C}_8\text{H}_{10}\text{NO}$: 136.0757; found: 136.0758.

2-Chloroanilinium chloride (c15). The title compound was synthesized according to the standard procedure. 79 mg (0.500 mmol) of **a15** was used. Appearance: off-white powder, 69 mg (0.420 mmol, 84% yield). Analytical data: ^1H NMR (300 MHz, D_2O , 25 °C): δ = 7.61 – 7.59 (m, 1 H), 7.47 – 7.42 (m, 3 H) ppm; $^{13}\text{C}\{^1\text{H}\}$ NMR (125.8 MHz, D_2O , 25 °C): δ = 130.5, 129.8, 128.8, 128.5, 127.0, 124.1 ppm; HR-MS (ESI-Orbitrap) m/z : $[\text{M}-\text{Cl}]^+$ calcd. for $\text{C}_6\text{H}_7\text{ClN}$: 128.0262; found: 128.0262.

3-Chloroanilinium chloride (c16). The title compound was synthesized according to the standard procedure. 79 mg (0.500 mmol) of **a16** was used. Appearance: off-white powder, 75 mg (0.454 mmol, 91% yield). Analytical data: ^1H NMR (300 MHz, D_2O , 25 °C): δ = 7.51 – 7.45 (m, 3 H), 7.33 – 7.32 (m, 1 H) ppm; $^{13}\text{C}\{^1\text{H}\}$ -NMR (125.8 MHz, D_2O , 25 °C): δ = 134.9, 131.5, 131.3, 129.0, 123.0, 121.2 ppm; HR-MS (ESI-Orbitrap) m/z : $[\text{M}-\text{Cl}]^+$ calcd. for $\text{C}_6\text{H}_7\text{ClN}$: 128.0262; found: 128.0262.

4-Chloroanilinium chloride (c17). The title compound was synthesized according to the standard procedure. 79 mg (0.501 mmol) of **a17** was used. Appearance: white powder, 77 mg (0.468 mmol, 93% yield). Analytical data: ^1H NMR (300 MHz, D_2O , 25 °C): δ = 7.54 (d, J = 9.0 Hz, 2 H), 7.37 (d, J = 9.0 Hz, 2 H) ppm; $^{13}\text{C}\{^1\text{H}\}$ NMR (125.8 MHz, D_2O , 25 °C): δ = 134.3, 130.0, 128.8, 124.4 ppm; HR-MS (ESI-Orbitrap) m/z : $[\text{M}-\text{Cl}]^+$ calcd. for $\text{C}_6\text{H}_7\text{ClN}$: 128.0262; found: 128.0263.

2-Bromoanilinium chloride (c18). The title compound was synthesized according to the standard procedure. 101 mg (0.498 mmol) of **a18** was used. Appearance: brownish solid, 64 mg (0.306 mmol, 61% yield). Analytical data: ^1H NMR (300 MHz, D_2O , 25 °C): δ = 7.77 (d, J = 8.3 Hz, 1 H), 7.50 – 7.44 (m, 2 H), 7.36 – 7.33 (m, 1 H) ppm; $^{13}\text{C}\{^1\text{H}\}$ NMR (125.8 MHz, D_2O , 25 °C): δ = 133.7, 130.7, 129.7, 129.1, 123.9, 116.0 ppm; HR-MS (ESI-Orbitrap) m/z : $[\text{M}-\text{Cl}]^+$ calcd. for $\text{C}_6\text{H}_7\text{BrN}$: 171.9756; found: 171.9761.

3-Bromoanilinium chloride (c19). The title compound was synthesized according to the standard procedure. 102 mg (0.502 mmol) of **a19** was used. Appearance: off-white powder, 99 mg (0.475 mmol, 95% yield). Analytical data: ^1H NMR (300 MHz, D_2O , 25 °C): δ = 7.66 (d, J = 8.4 Hz, 1 H), 7.61 (s, 1 H), 7.45 – 7.36 (m, 2 H) ppm; $^{13}\text{C}\{^1\text{H}\}$ NMR (125.8 MHz, D_2O , 25 °C): δ = 132.0, 131.6, 131.5, 125.9, 122.6, 121.7 ppm; HR-MS (ESI-Orbitrap) m/z : $[\text{M}-\text{Cl}]^+$ calcd. for $\text{C}_6\text{H}_7\text{BrN}$: 171.9756; found: 171.9761.

4-Bromoanilinium chloride (c20). The title compound was synthesized according to the standard procedure. 102 mg (0.504 mmol) of **a20** was used. Appearance: white powder, 87 mg (0.416 mmol, 83% yield). Analytical data: ^1H NMR (300 MHz, D_2O , 25 °C): δ = 7.67 (d, J = 8.6 Hz, 2 H), 7.30 (d, J = 8.6 Hz, 2 H) ppm; $^{13}\text{C}\{^1\text{H}\}$ NMR (125.8 MHz, D_2O , 25 °C): δ = 133.1, 129.1, 124.7, 122.3 ppm; HR-MS (ESI-Orbitrap) m/z : $[\text{M}-\text{Cl}]^+$ calcd. for $\text{C}_6\text{H}_7\text{BrN}$: 171.9756; found: 171.9759.

2-Fluoroanilinium chloride (c21). The title compound was synthesized according to the standard procedure. 70 mg (0.498 mmol) of **a21** was used. Appearance: off-white powder, 40 mg (0.271 mmol, 54% yield). Analytical data: ^1H NMR (300 MHz, D_2O , 25 °C): δ = 7.51 – 7.44 (m, 2 H), 7.39 – 7.30 (m, 2 H) ppm; $^{13}\text{C}\{^1\text{H}\}$ NMR (75.5 MHz, D_2O , 25 °C): δ = 156.4, 154.4, 130.6, 130.5, 125.4, 124.5, 166.7, 116.6 ppm; ^{19}F NMR (470.5 MHz, D_2O , 20 °C) δ = -126.7 ppm; HR-MS (ESI-Orbitrap) m/z : $[\text{M}-\text{Cl}]^+$ calcd. for $\text{C}_6\text{H}_7\text{FN}$: 112.0557; found: 112.0557.

2-Iodoanilinium chloride (c22). The title compound was synthesized according to the standard procedure. 125 mg (0.501 mmol) of **a22** was used. Appearance: light brownish powder, 51 mg (0.200 mmol, 40% yield). Analytical data: ^1H NMR (300 MHz, D_2O , 25 °C): δ = 7.99 (d, J = 8.4 Hz, 1 H), 7.52 – 7.40 (m, 2 H), 7.18 – 7.13 (m, 1 H) ppm; $^{13}\text{C}\{^1\text{H}\}$ NMR (75.5 MHz, D_2O , 25 °C): δ = 140.4, 133.6, 129.9, 129.8, 123.4, 89.9 ppm; HR-MS (ESI-Orbitrap) m/z : $[\text{M}-\text{Cl}]^+$ calcd. for $\text{C}_6\text{H}_7\text{IN}$: 219.9618; found: 219.9608.

3-Iodoanilinium chloride (c23). The title compound was synthesized according to the standard procedure. 125 mg (0.501 mmol) of **a23** was used. Appearance: white powder, 84 mg (0.329 mmol, 66% yield). Analytical data: ^1H NMR (300 MHz, D_2O , 25 °C): δ = 7.86 (d, J = 8.1 Hz, 1 H), 7.79 (s, 1 H), 7.40 (d, J = 8.11 Hz, 1 H), 7.29 – 7.26 (m, 1 H) ppm; $^{13}\text{C}\{^1\text{H}\}$ NMR (75.5 MHz, D_2O , 25 °C): δ = 138.1, 131.7, 131.4, 131.2, 122.3, 93.8 ppm; HR-MS (ESI-Orbitrap) m/z : $[\text{M}-\text{Cl}]^+$ calcd. for $\text{C}_6\text{H}_7\text{IN}$: 219.9618; found: 219.9622.

4-Iodoanilinium chloride (c24). The title compound was synthesized according to the standard procedure. 125 mg (0.500 mmol) of **a24** was used. Appearance: off-white powder, 36 mg (0.139 mmol, 28% yield). Analytical data: ^1H NMR (300 MHz, D_2O , 25 °C): δ = 7.90 (d, J = 8.5 Hz, 2H), 7.18 (d, J = 8.5 Hz, 2H) ppm; $^{13}\text{C}\{^1\text{H}\}$ NMR (75.5 MHz, D_2O , 25 °C): δ = 139.1, 130.0, 124.7, 92.7 ppm; HR-MS (ESI-Orbitrap) m/z : $[\text{M}-\text{Cl}]^+$ calcd. for $\text{C}_6\text{H}_7\text{IN}$: 219.9618; found: 219.9622.

Benzylamine hydrochloride (c25). The title compound was synthesized according to the standard procedure. 72 mg (0.523 mmol) of **a25** was used. Appearance: colorless crystals, 9 mg (0.062 mmol, 12% yield). Analytical data: ^1H NMR (300 MHz, D_2O , 25 °C): δ = 7.53 – 7.46 (m, 4 H), 4.20 (s, 2 H) ppm; $^{13}\text{C}\{^1\text{H}\}$ NMR (75.5 MHz, D_2O , 25 °C): δ = 132.6, 129.2, 128.8, 43.1 ppm; HR-MS (ESI-Orbitrap) m/z : $[\text{M}-\text{Cl}]^+$ calcd. for $\text{C}_7\text{H}_{10}\text{N}$: 108.0808; found: 108.0807.

4-Ethylanilinium chloride (c26). The title compound was synthesized according to the standard procedure. 74 mg (0.500 mmol) of **a26** was used. Appearance: brown powder, 9 mg (0.057 mmol, 11% yield). Analytical data: ^1H NMR (300 MHz, D_2O , 25 °C): δ = 7.42 – 7.31 (m, 4 H), 2.72 – 2.64 (m, 2 H), 1.23 – 1.18 (m, 3 H) ppm; $^{13}\text{C}\{^1\text{H}\}$ NMR (75.5 MHz, D_2O , 25 °C): δ = 146.0, 129.4, 127.2, 122.8, 27.8, 14.8 ppm; HRMS (ESI-Orbitrap) m/z : $[\text{M}-\text{Cl}]^+$ calcd. for $\text{C}_8\text{H}_{12}\text{N}$: 122.0964; found: 122.0965.

3-Ethynylanilinium chloride (c27). The title compound was synthesized according to the standard procedure. 74 mg (0.501 mmol) of **a27** was used. Appearance: off-white powder, 8 mg (0.055 mmol, 11% yield). Analytical data: ^1H NMR (300 MHz, D_2O , 25 °C): δ = 7.66 – 7.42 (m, 4 H), 3.63 (s, 1 H) ppm; $^{13}\text{C}\{^1\text{H}\}$ NMR (75.5 MHz, D_2O , 25 °C): δ = 132.4, 130.6, 130.3, 126.1, 123.4, 123.4, 82.0, 79.8 ppm; HR-MS (ESI-Orbitrap) m/z : $[\text{M}-\text{Cl}]^+$ calcd. for $\text{C}_8\text{H}_8\text{N}$: 118.0651; found: 118.0650.

Cyclopentanamine hydrochloride (c28). The title compound was synthesized according to the standard procedure. 58 mg (0.501 mmol) of **a28** was used. Appearance: light-brownish solid, 21 mg (0.175 mmol, 35% yield). Analytical data: ^1H NMR (300 MHz, D_2O , 25 °C): δ = 3.68 – 3.64 (m, 1 H), 2.09 – 2.00 (m, 2 H), 1.79 – 1.58 (m, 6 H) ppm; $^{13}\text{C}\{^1\text{H}\}$ NMR (75.5 MHz, D_2O , 25 °C): δ = 52.1, 30.5, 23.5 ppm; HRMS (ESI-Orbitrap) m/z : $[\text{M}-\text{Cl}]^+$ calcd. for $\text{C}_5\text{H}_{12}\text{N}$: 86.0964; found: 86.0962.

2,3-Diammonio-4-methylpyridinium trichloride (c29). The title compound was synthesized according to the standard procedure. 77 mg (0.500 mmol) of **a29** was used. Appearance: auburn powder, 66 mg (0.284 mmol, 57% yield). Analytical data: ^1H NMR (300 MHz, D_2O , 25 °C): δ = 7.24 (d, J = 6.5 Hz, 1H), 6.70 (d, J = 6.4 Hz, 1H), 2.19 (s, 3H) ppm; $^{13}\text{C}\{^1\text{H}\}$ NMR (75.5 MHz, D_2O , 25 °C): δ = 144.7, 137.5, 127.6, 124.9, 116.5, 17.1 ppm; HR-MS (ESI-Orbitrap) m/z : $[\text{M}-3\text{Cl}-2\text{H}]^+$ calcd. for $\text{C}_6\text{H}_{10}\text{N}_3$: 124.0869; found: 124.0869.

6-Ammonioquinolinium dichloride (c30). The title compound was synthesized according to the standard procedure. 87 mg (0.500 mmol) of **a30** was used. Appearance: olive-green powder, 86 mg (0.396 mmol, 79% yield). Analytical data: ^1H NMR (300 MHz, D_2O , 20 °C): δ = 8.72 – 8.66 (m, 2 H), 7.91 – 7.79 (m, 2 H), 7.57 (dd, J = 9.1, 2.6 Hz, 1 H), 7.28 (d, J = 2.6 Hz, 1 H) ppm; $^{13}\text{C}\{^1\text{H}\}$ NMR (75.5 MHz, D_2O , 20 °C): δ = 145.5, 144.4, 139.7, 132.5, 130.6, 127.3, 121.6, 121.3 ppm; HR-MS (ESI-Orbitrap) m/z : $[\text{M}-2\text{Cl}-\text{H}]^+$ calcd. for $\text{C}_9\text{H}_9\text{N}_2$: 145.0760; found: 145.0763.

8-Aminoquinoline (b31). The title compound was synthesized according to the standard procedure. 87 mg (0.501 mmol) of **a31** was used. Appearance: auburn solid, 67 mg (0.467 mmol, 93% yield). Analytical data: ^1H NMR (300 MHz, CDCl_3 , 20 °C): δ = 8.67 – 8.65 (m, 1 H), 7.98 – 7.95 (m, 1 H), 7.28 – 7.16 (m, 2 H), 7.05 (d, J = 8.1 Hz, 1 H), 6.83 (d, J = 8.1 Hz, 1 H), 4.88 (br, 1 H) ppm; $^{13}\text{C}\{^1\text{H}\}$ NMR (75.5 MHz, CDCl_3 , 20 °C): δ = 147.5, 144.0, 138.5, 136.0, 128.9, 127.4, 121.4, 116.1, 110.0 ppm; HRMS (ESI-Orbitrap) m/z : $[\text{M}+\text{H}]^+$ calcd. for $\text{C}_9\text{H}_9\text{N}_2$: 145.0760; found: 145.0761.

4-Sulfamoylanilinium chloride (c32). The title compound was synthesized according to the standard procedure. 101 mg (0.500 mmol) of **a32** was used. Appearance: brown-grey solid, 84 mg (0.406 mmol, 81% yield). Analytical data: ^1H NMR (300 MHz, D_2O , 20 °C): δ = 7.90 (d, J = 8.4 Hz, 2 H), 7.34 (d, J = 8.4 Hz, 2 H) ppm; $^{13}\text{C}\{^1\text{H}\}$ NMR (75.5 MHz, D_2O , 20 °C): δ = 140.6, 137.4, 127.9, 127.4, 124.6, 120.9 ppm; HRMS (ESI-Orbitrap) m/z : $[\text{M}-\text{Cl}]^+$ calcd. for $\text{C}_6\text{H}_9\text{N}_2\text{O}_2\text{S}$: 173.0379; found: 173.0380.

4-Carboxybenzenaminium chloride (c33). The title compound was synthesized according to the standard procedure. 84 mg (0.501 mmol) of **a33** was used. Appearance: grey powder, 72 mg (0.415 mmol, 83% yield). Analytical data: ^1H NMR (300 MHz, D_2O , 25 °C): δ = 8.12 – 8.09 (m, 1 H), 7.99 (s, 1 H), 7.70 – 7.63 (m, 2 H) ppm; $^{13}\text{C}\{^1\text{H}\}$ NMR (75.5 MHz, D_2O , 25 °C): δ = 168.9, 131.9, 130.5, 130.4, 130.2, 127.8, 124.4, 124.0 ppm; HR-MS (ESI-Orbitrap) m/z : $[\text{M}-\text{Cl}]^+$ calcd. for $\text{C}_7\text{H}_8\text{NO}_2$: 138.0550; found: 138.0550.

(E)-3-(2-Carboxyvinyl)benzenaminium chloride (**c34**). The title compound was synthesized according to the standard procedure. 97 mg (0.502 mmol) of **a34** was used. Appearance: light brownish solid, 56 mg (0.280 mmol, 56% yield). Analytical data: ^1H NMR (300 MHz, D_2O , 25 °C): δ = 7.70 – 7.64 (m, 2 H), 7.58 – 7.52 (m, 2 H), 7.43 – 7.40 (m, 1 H), 6.54 (d, J = 15.9 Hz, 1 H) ppm; $^{13}\text{C}\{^1\text{H}\}$ NMR (75.5 MHz, D_2O , 25 °C): δ = 170.5, 144.2, 136.0, 130.8, 130.6, 128.6, 124.5, 122.3, 119.5 ppm; HR-MS (ESI-Orbitrap) m/z : $[\text{M}-\text{Cl}]^+$ calcd. for $\text{C}_9\text{H}_{10}\text{NO}_2$: 164.0706; found: 164.0710.

(E)-Disodium 4,4'-diamino-2,2'-stilbenedisulfonate (**b35**). The title compound was synthesized according to the standard procedure. 475 mg (1.00 mmol) of **a35** was used. Appearance: red-brownish powder, 372 mg (0.897 mmol, 90% yield). Analytical data: ^1H NMR (300 MHz, D_2O , 20 °C): δ = 7.73 – 7.72 (m, 4 H), 7.33 (s, 2 H), 6.98 (d, J = 8.7 Hz, 2 H) ppm; $^{13}\text{C}\{^1\text{H}\}$ NMR (75.5 MHz, D_2O , 20 °C): δ = 146.0, 140.4, 128.2, 125.7, 125.1, 119.2, 114.1 ppm; HR-MS (ESI-Orbitrap) m/z : $[\text{M}-2\text{Na}+3\text{H}]^+$ calcd. for $\text{C}_{14}\text{H}_{15}\text{N}_2\text{O}_6\text{S}_2$: 371.0366; found: 371.0367.

2-Acetamido-5-methoxybenzenaminium chloride (**c36**). The title compound was synthesized according to the standard procedure. 105 mg (0.500 mmol) of **a36** was used. Appearance: light brown powder, 83 mg (0.384 mmol, 77% yield). Analytical data: ^1H -NMR (300 MHz, D_2O , 25 °C): δ = 7.27 (d, J = 9.0 Hz, 1 H), 7.08 – 7.01 (m, 2 H), 3.85 (s, 3 H), 2.21 (s, 3 H) ppm; $^{13}\text{C}\{^1\text{H}\}$ -NMR (75.5 MHz, D_2O , 25 °C): δ = 174.3, 158.7, 128.4, 122.5, 114.7, 109.2, 55.8, 21.9 ppm; HRMS (ESI-Orbitrap) m/z : $[\text{M}-\text{Cl}]^+$ calcd. for $\text{C}_9\text{H}_{13}\text{N}_2\text{O}_2$: 181.0972; found: 181.0974.

8. ^1H NMR, $^{13}\text{C}\{^1\text{H}\}$ NMR, ^{19}F NMR, and HR-MS Spectra of the Isolated Products

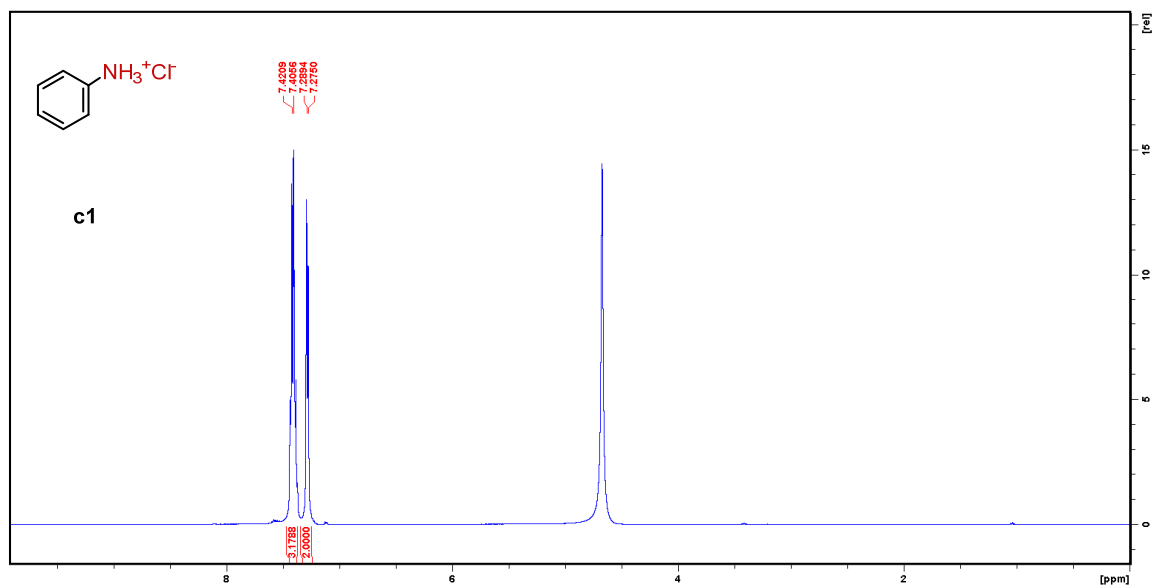


Figure S9: ^1H NMR of anilinium chloride (**c1**) in D_2O .

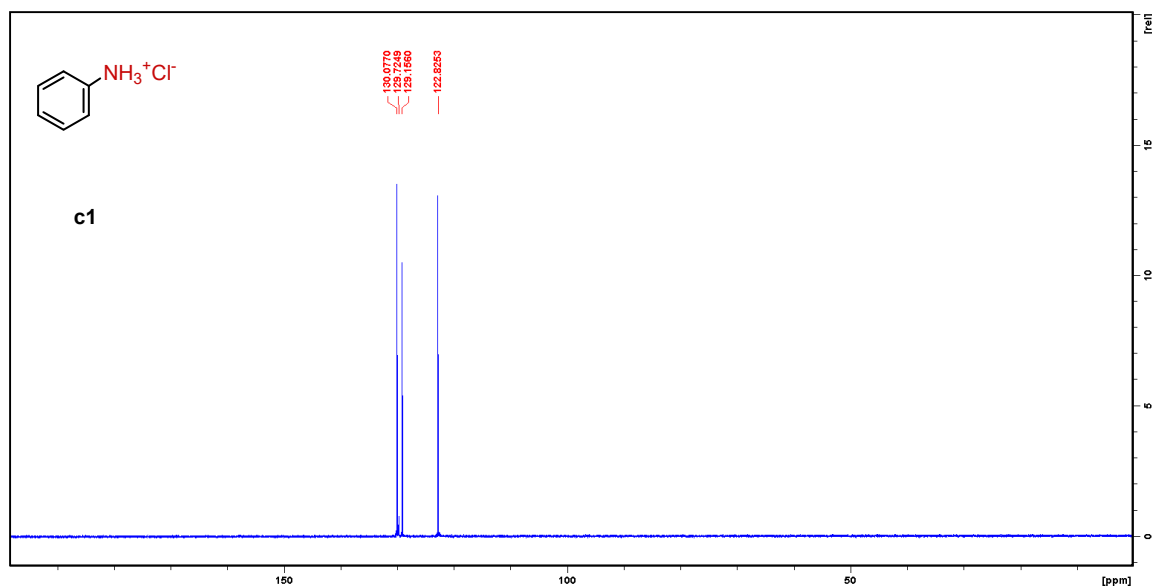


Figure S10: $^{13}\text{C}\{^1\text{H}\}$ NMR of anilinium chloride (**c1**) in D_2O .

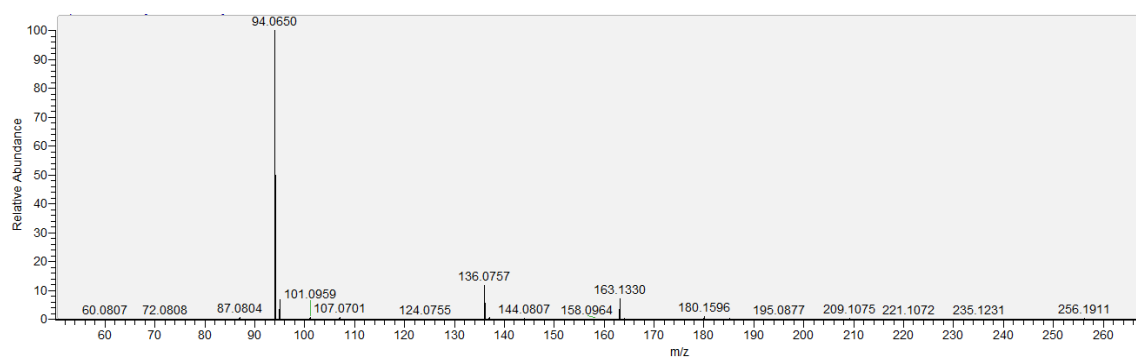


Figure S11: HR-MS of anilinium chloride (**c1**).

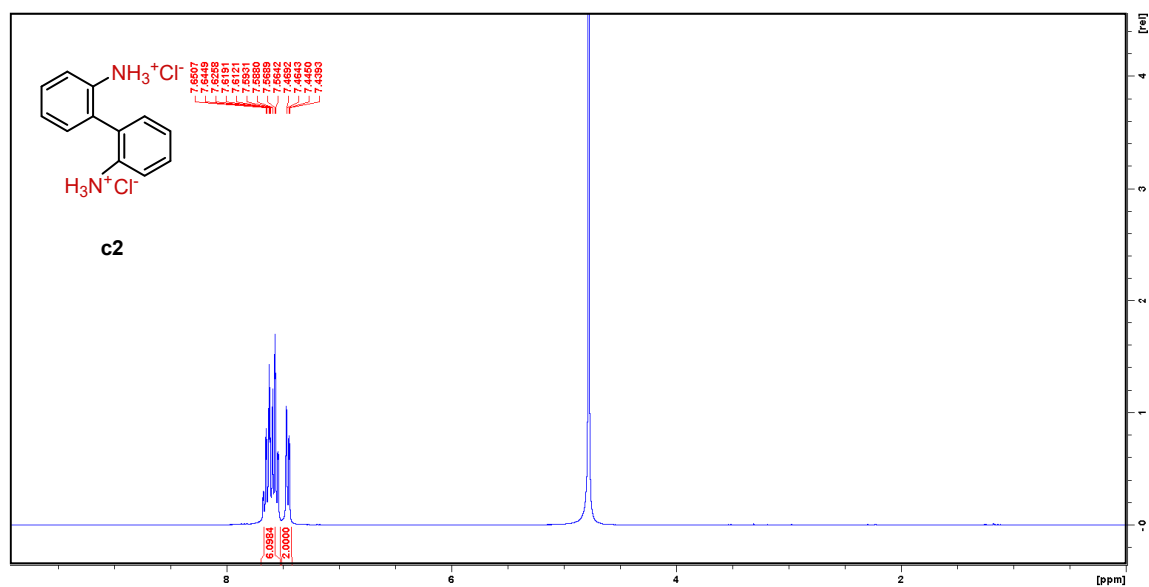


Figure S12: ^1H NMR of 1,1'-biphenyl-2,2'-diaminium dichloride (**c2**) in D_2O .

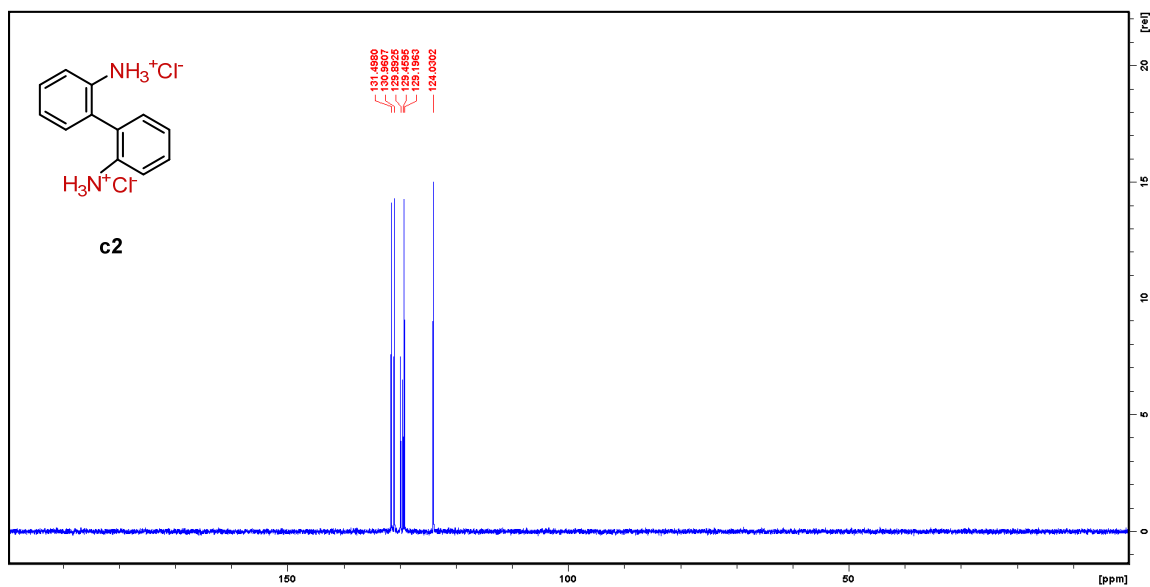


Figure S13: $^{13}\text{C}\{^1\text{H}\}$ NMR of 1,1'-biphenyl-2,2'-diaminium dichloride (**c2**) in D_2O .

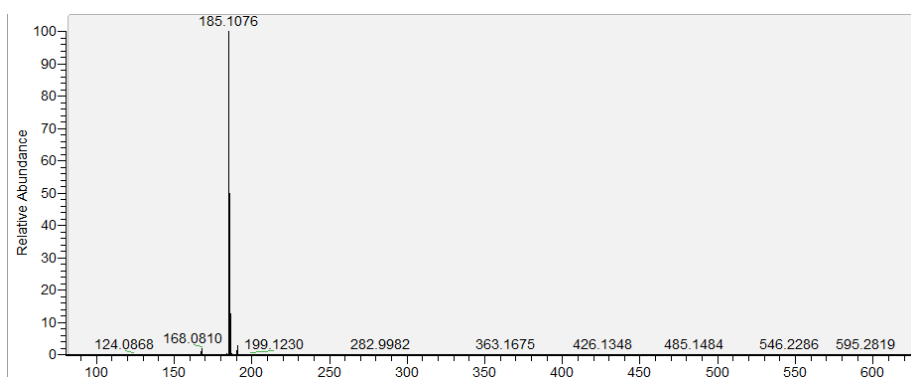


Figure S14: HR-MS of 1,1'-biphenyl-2,2'-diaminium dichloride (**c2**).

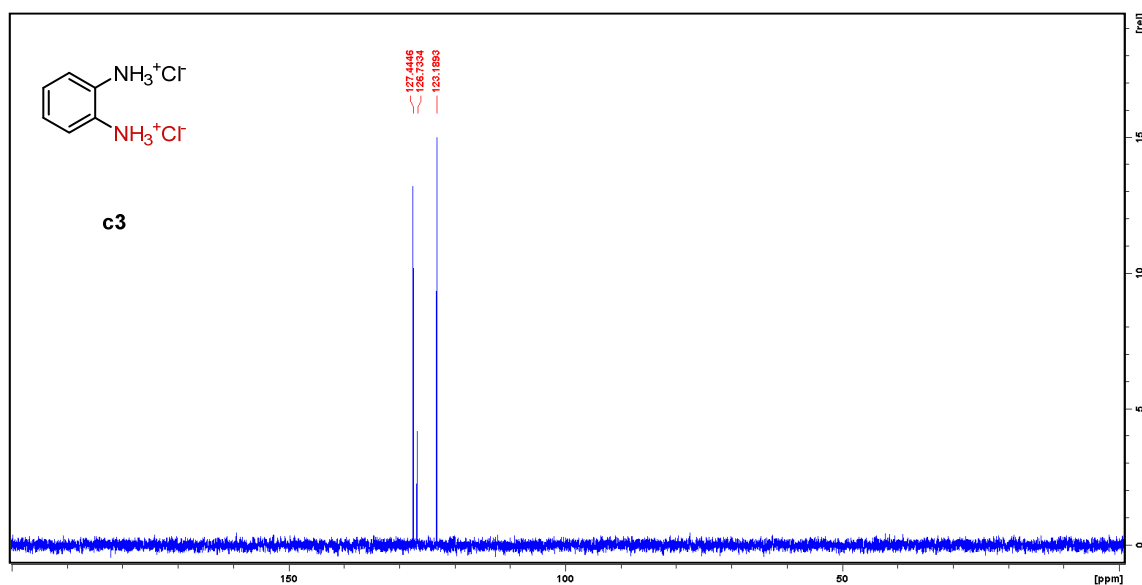


Figure S15: ^1H NMR of benzene-1,2-diaminium dichloride (**c3**) in D_2O .

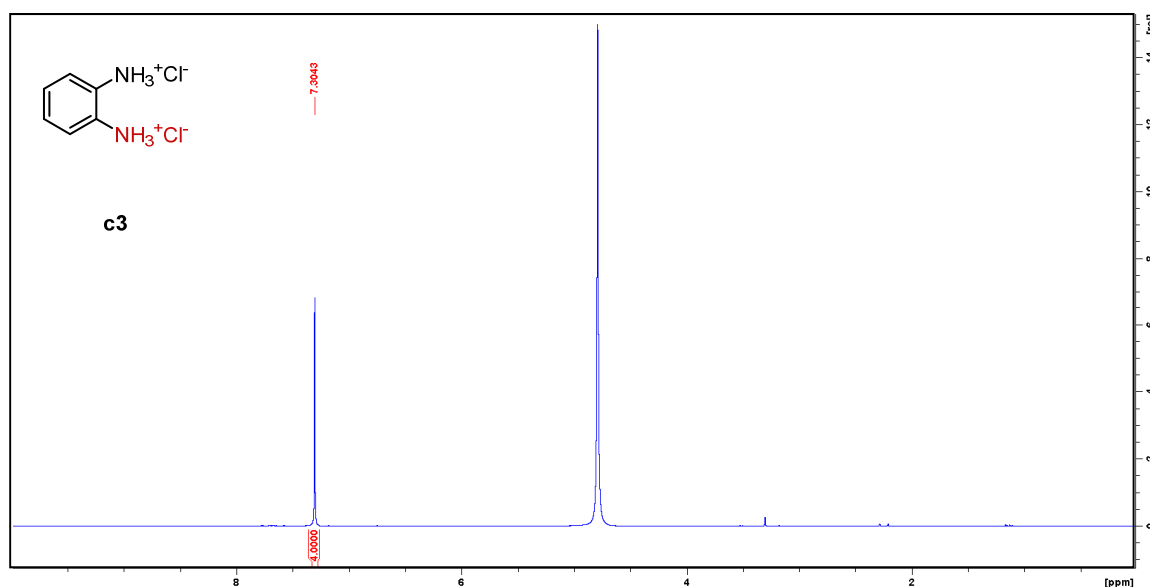


Figure S16: $^{13}\text{C}\{^1\text{H}\}$ NMR of benzene-1,2-diaminium dichloride (**c3**) in D_2O .

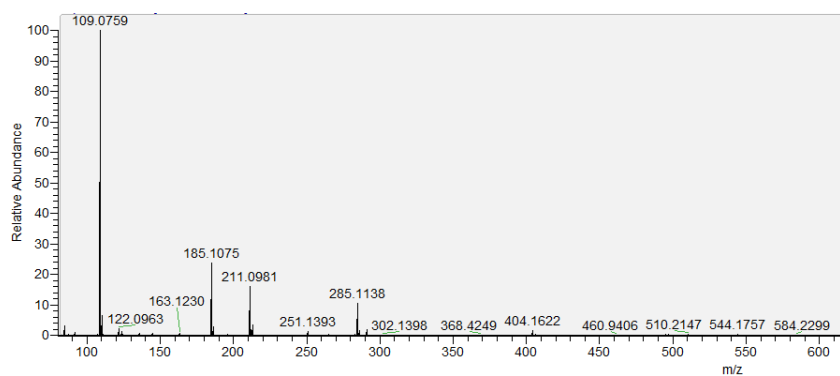


Figure S17: HR-MS of benzene-1,2-diaminium dichloride (**c3**).

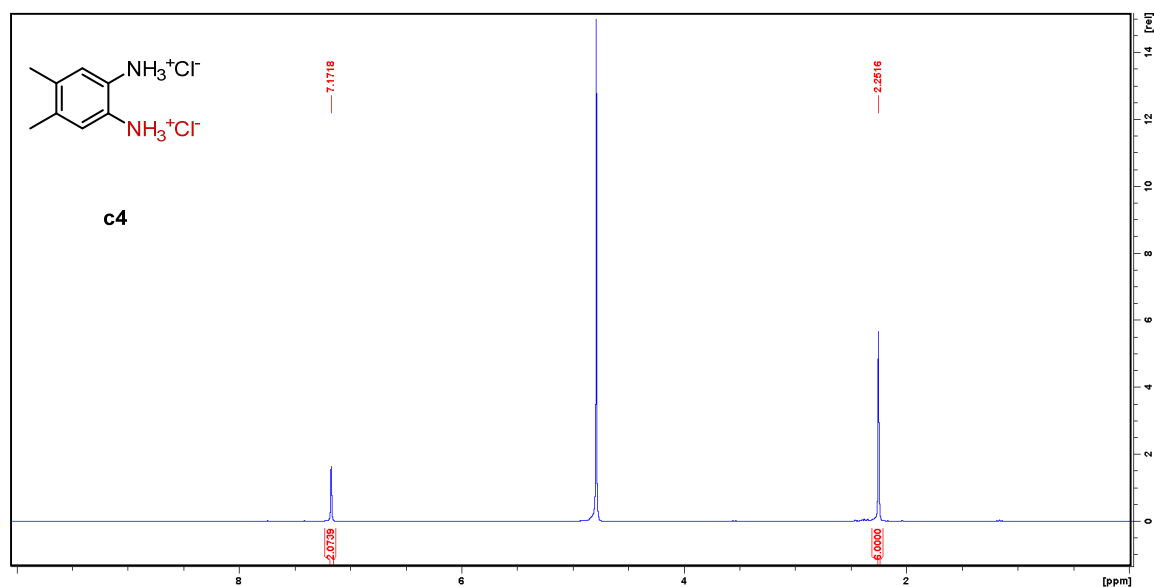


Figure S18: ^1H NMR of 4,5-dimethylbenzene-1,2-diaminium dichloride (**c4**) in D_2O .

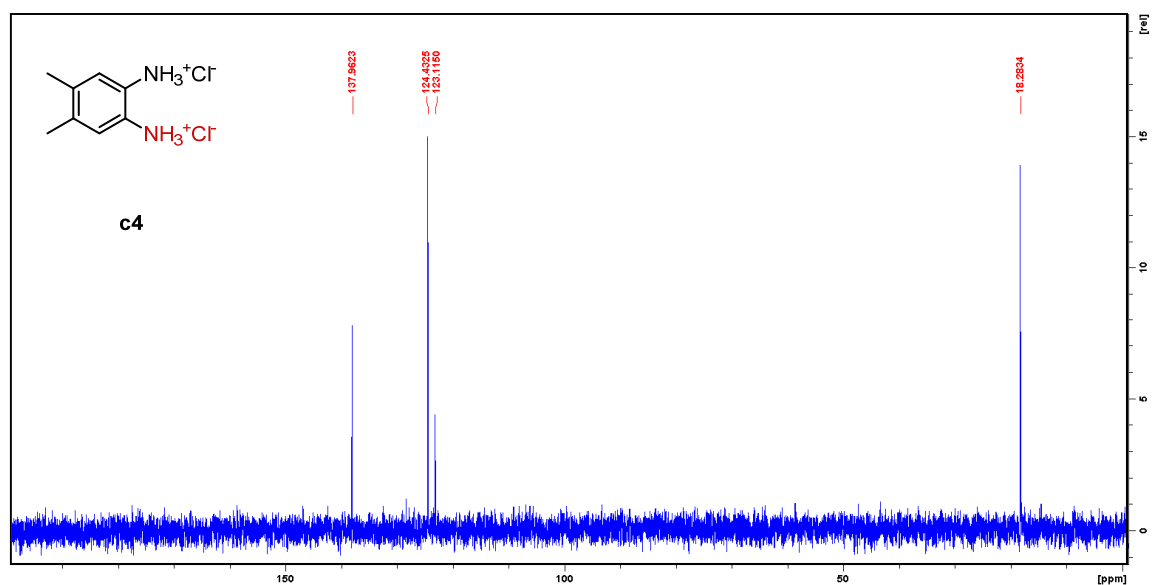


Figure S19: $^{13}\text{C}\{^1\text{H}\}$ NMR of 4,5-dimethylbenzene-1,2-diaminium dichloride (**c4**) in D_2O .

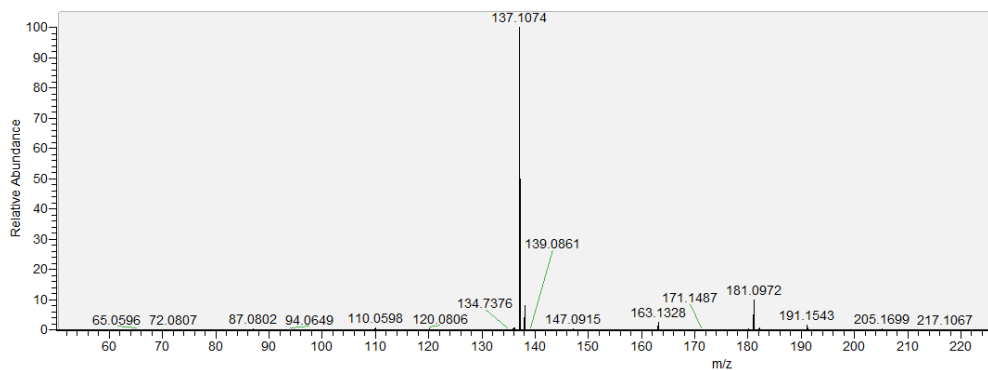


Figure S20: HR-MS of 4,5-dimethylbenzene-1,2-diaminium dichloride (**c4**).

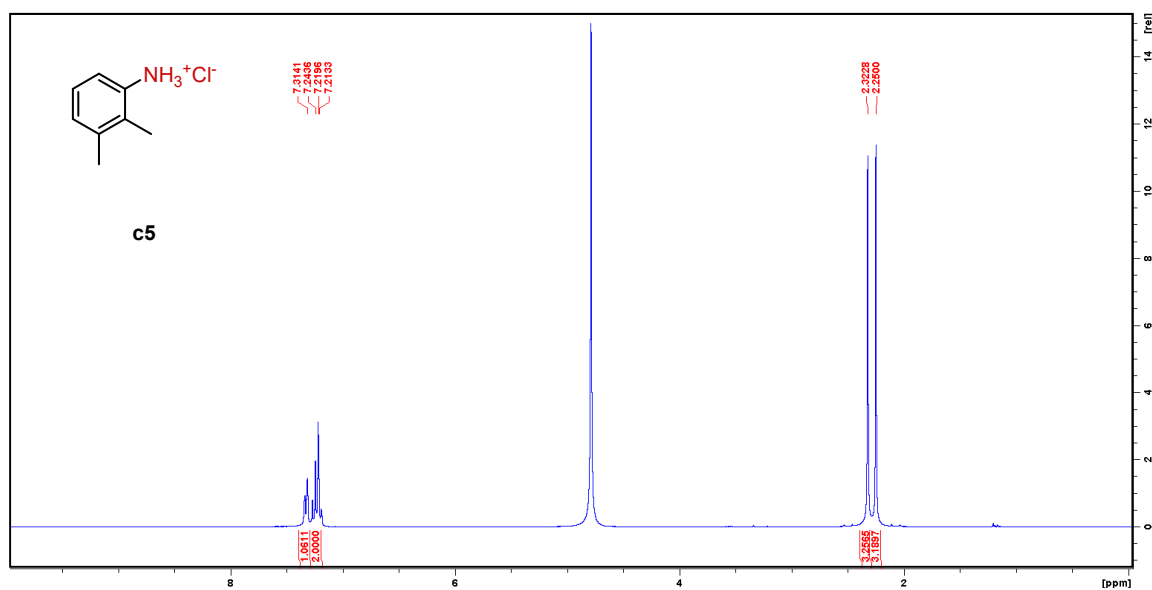


Figure S21: ¹H NMR of 2,3-dimethylbenzenaminium chloride (**c5**) in D₂O.

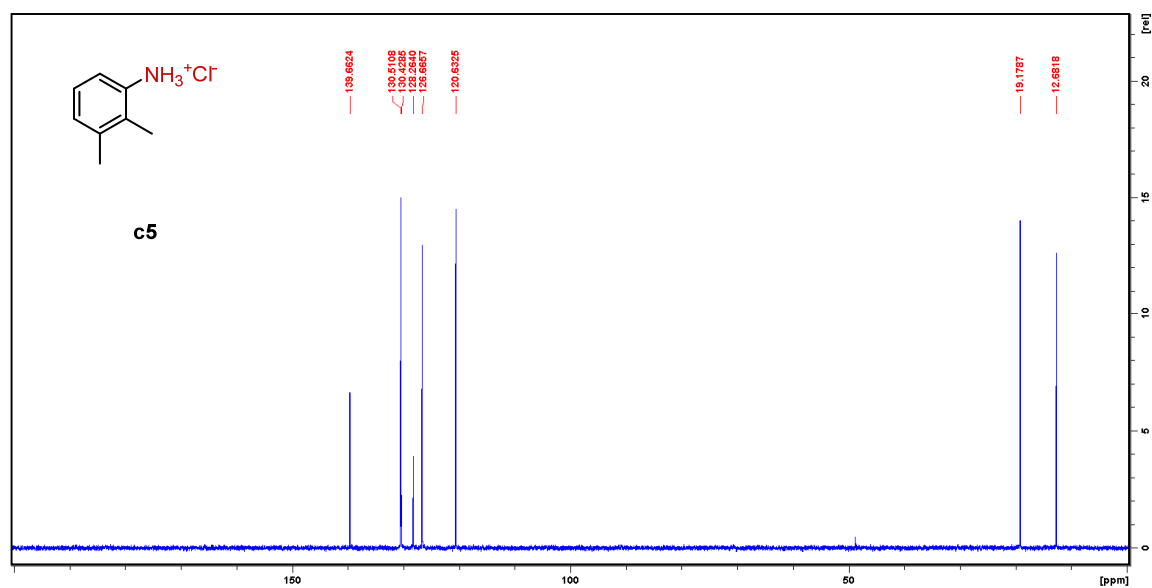


Figure S22: ¹³C{¹H} NMR of 2,3-dimethylbenzenaminium chloride (**c5**) in D₂O.

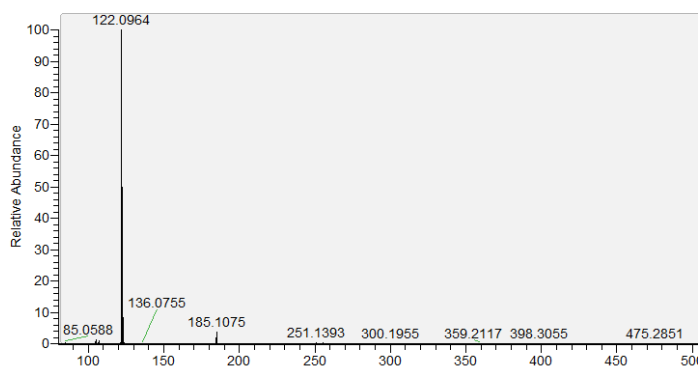


Figure S23: HR-MS of 2,3-dimethylbenzenaminium chloride (**c5**).

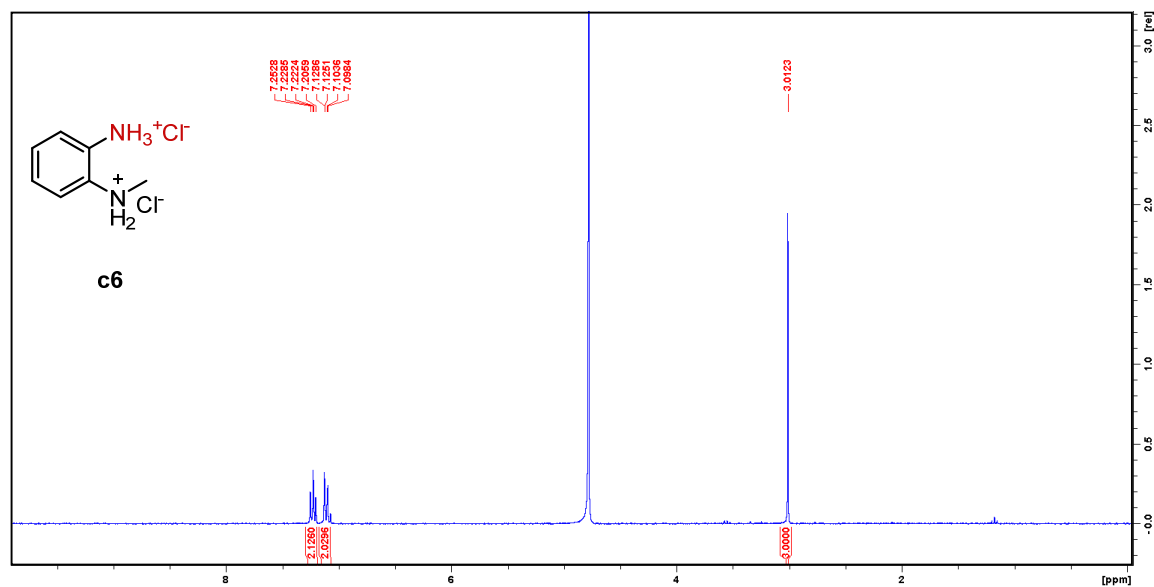


Figure S24: ¹H NMR of *N*¹-methylbenzene-1,2-diaminium dichloride (**c6**) in D₂O.

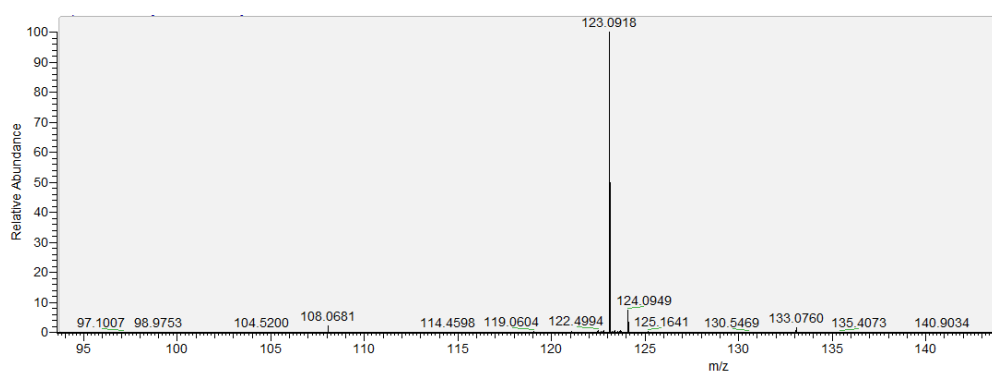


Figure S25: ¹³C{¹H} NMR of *N*¹-methylbenzene-1,2-diaminium dichloride (**c6**) in D₂O.

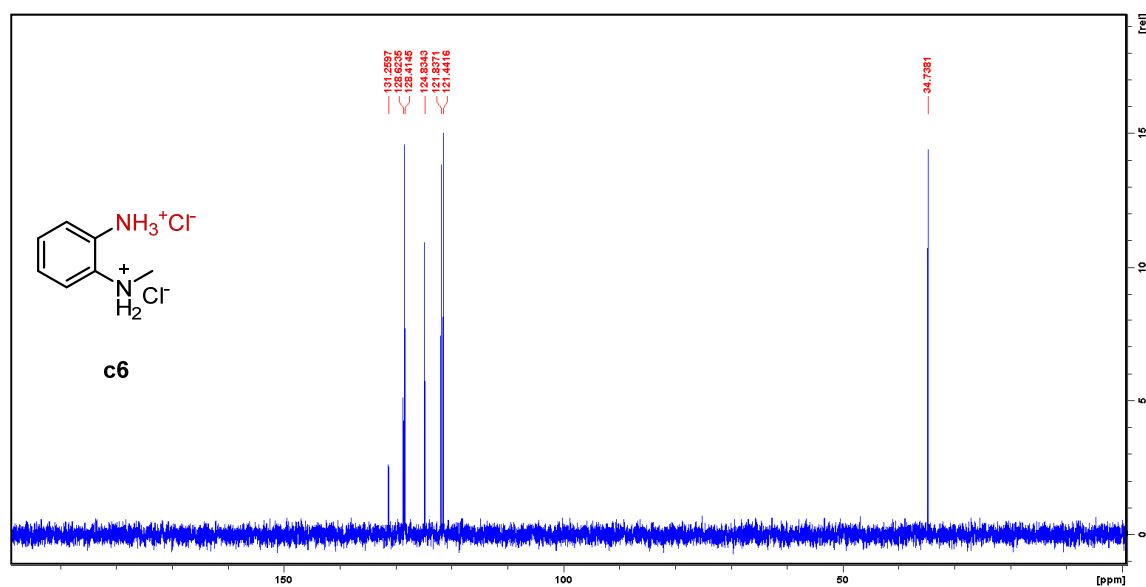


Figure S26: HR-MS of *N*¹-methylbenzene-1,2-diaminium dichloride (**c6**).

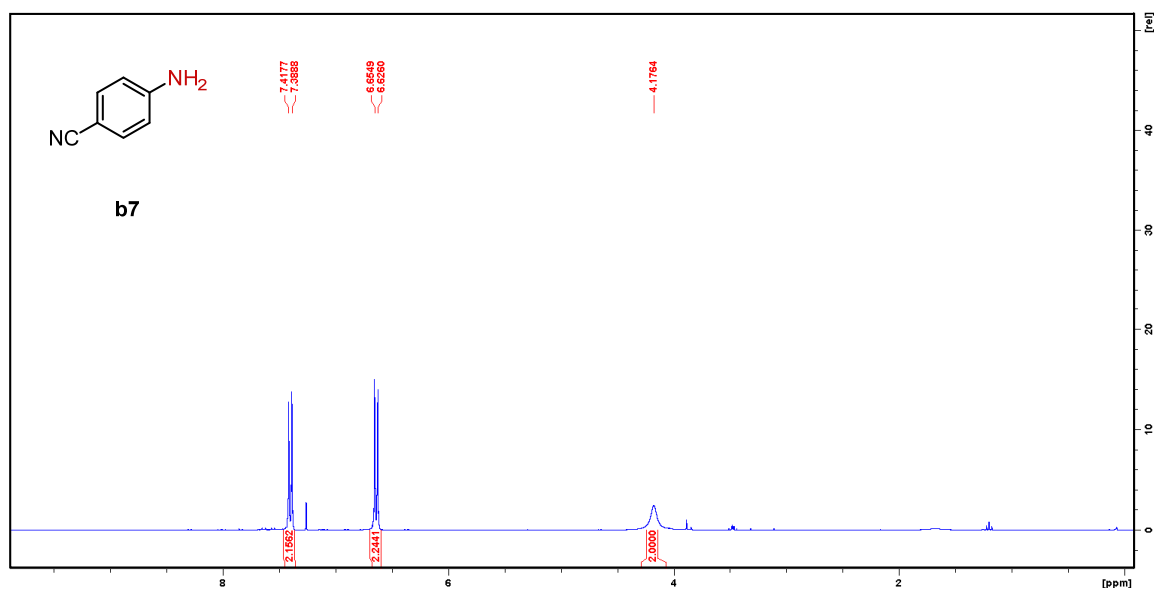


Figure S27: ^1H NMR of 4-aminobenzonitrile (**b7**) in CDCl_3 .

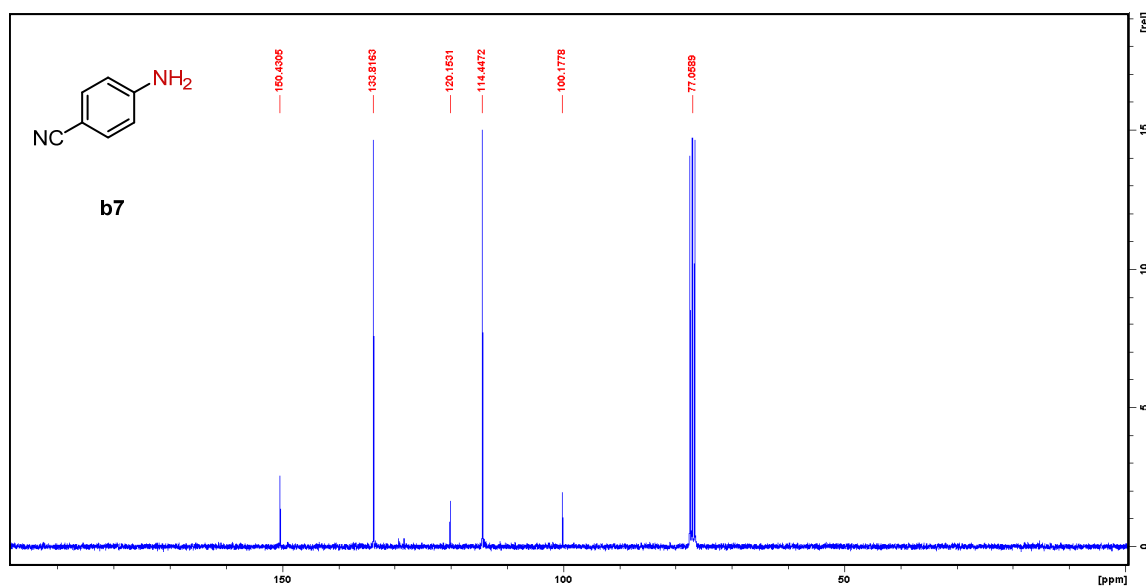


Figure S28: $^{13}\text{C}\{^1\text{H}\}$ NMR of 4-aminobenzonitrile (**b7**) in CDCl_3 .

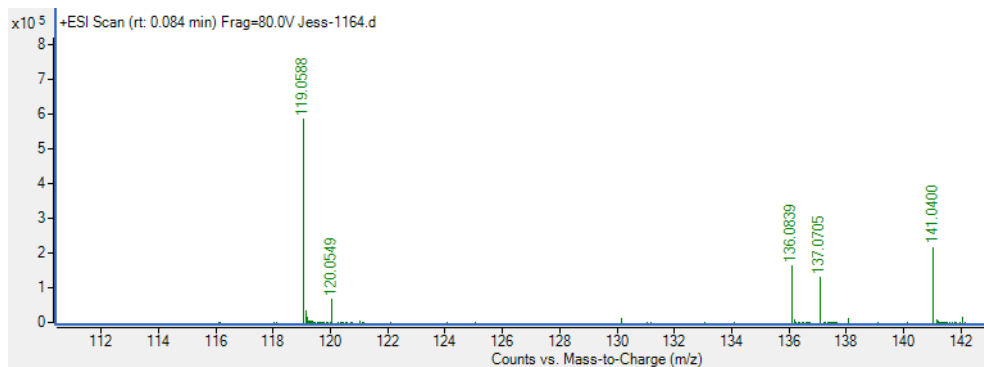


Figure S29: HR-MS of 4-aminobenzonitrile (**b7**).

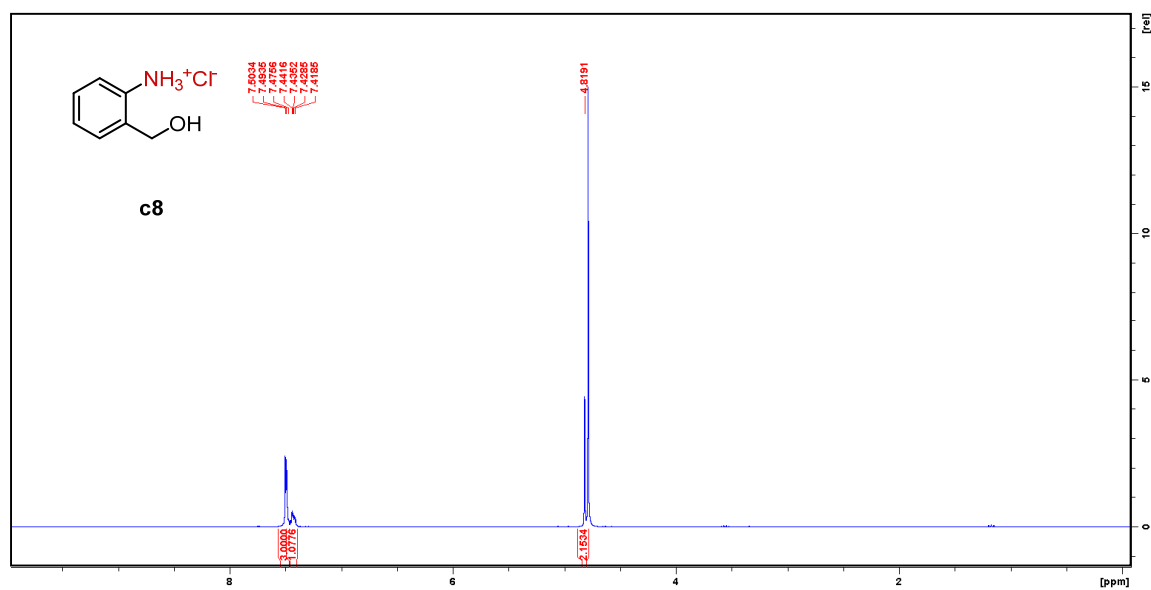


Figure S30: ^1H NMR of 2-(hydroxymethyl)benzeneaminium chloride (**c8**) in D_2O .

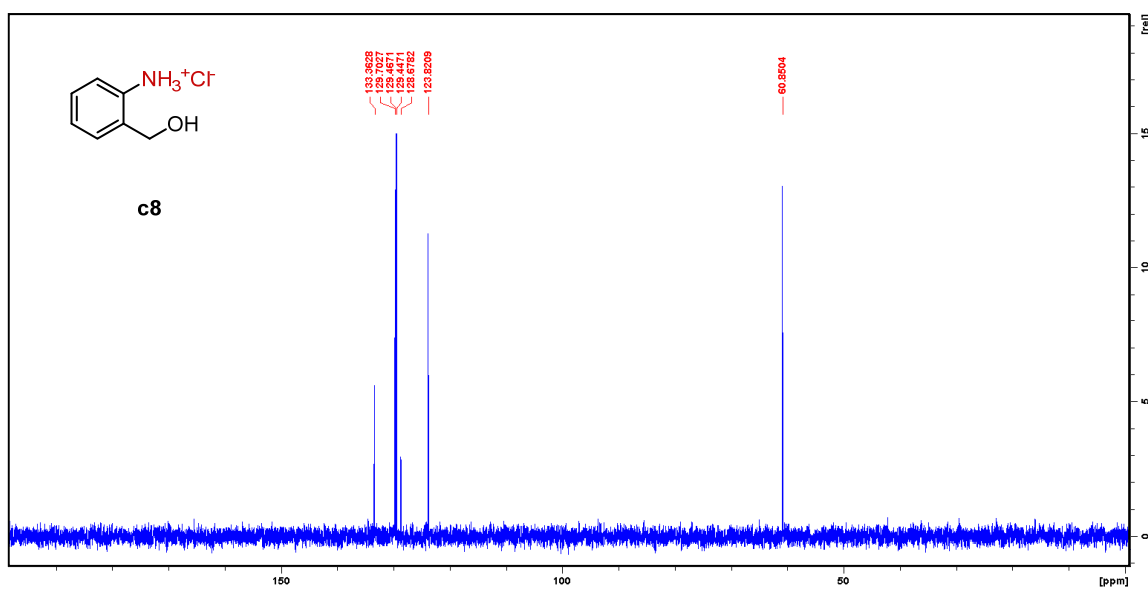


Figure S31: $^{13}\text{C}\{^1\text{H}\}$ NMR of 2-(hydroxymethyl)benzeneaminium chloride (**c8**) in D_2O .

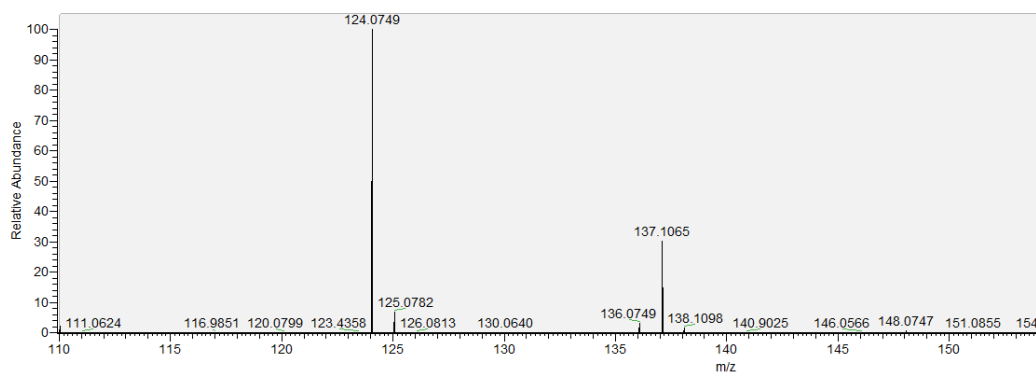


Figure S32: HR-MS of 2-(hydroxymethyl)benzeneaminium chloride (**c8**).

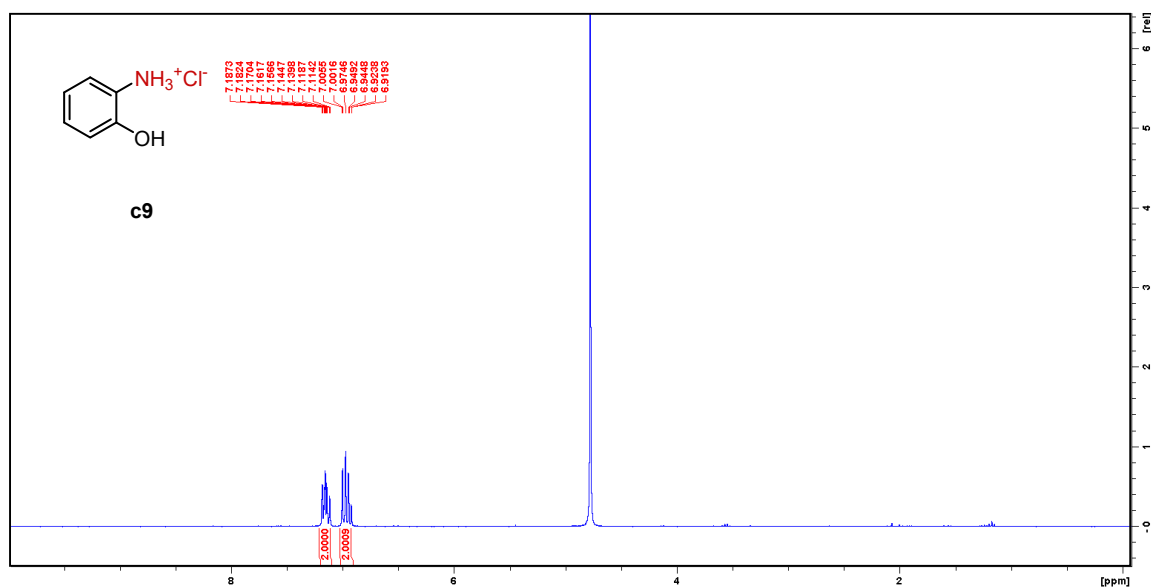


Figure S33: ¹H NMR of 2-hydroxybenzeneaminium chloride (**c9**) in D₂O.

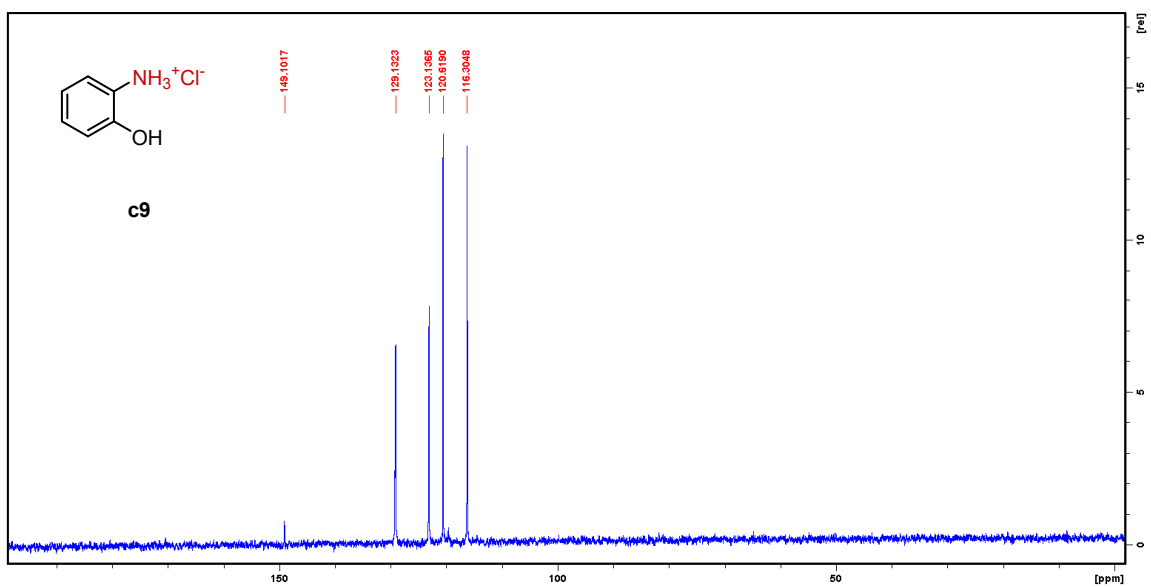


Figure S34: ¹³C{¹H} NMR of 2-hydroxybenzeneaminium chloride (**c9**) in D₂O.

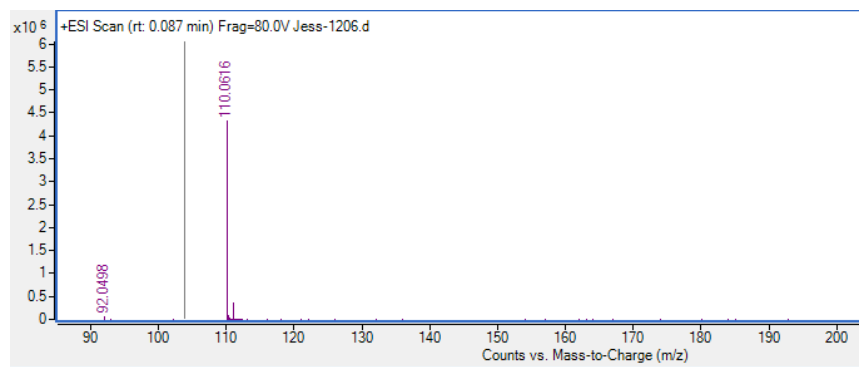


Figure S35: HR-MS of 2-hydroxybenzeneaminium chloride (**c9**).

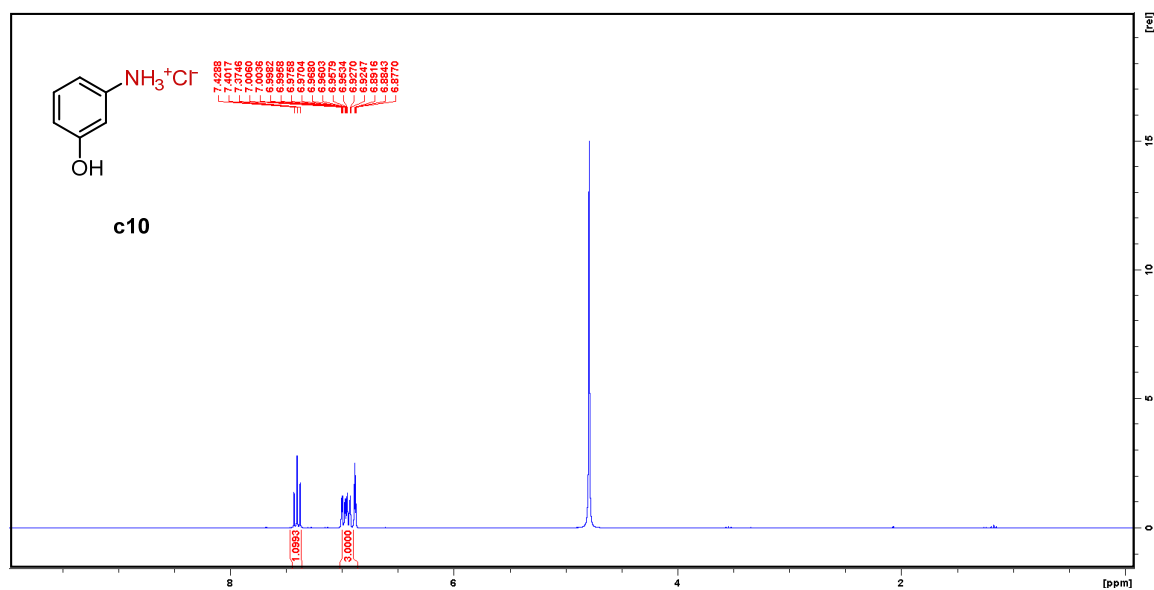


Figure S36: ¹H NMR of 3-hydroxybenzeneaminium chloride (**c10**) in D₂O.

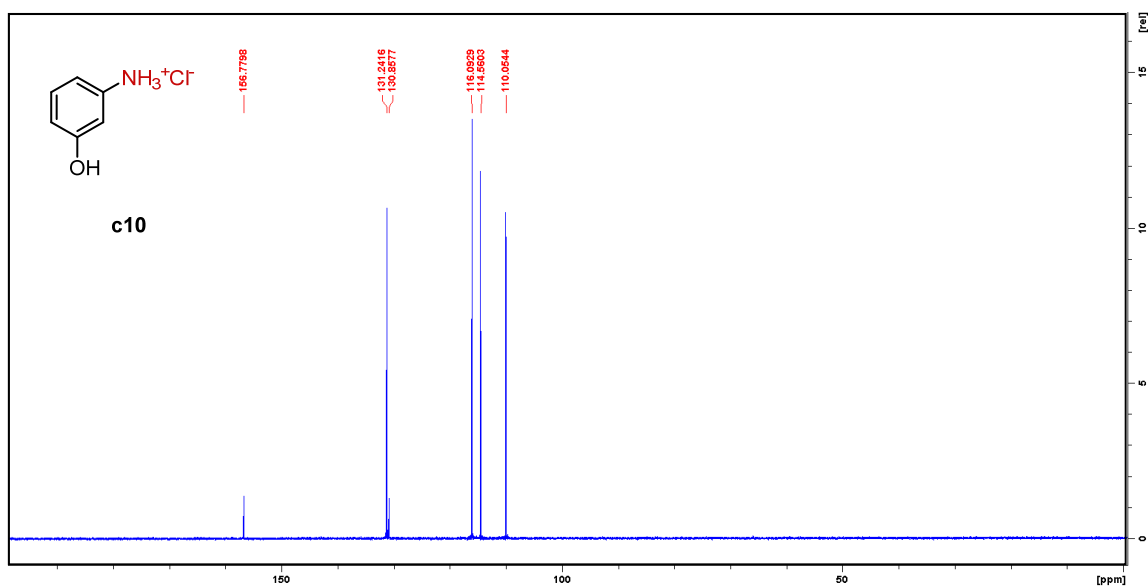


Figure S37: ¹³C{¹H} NMR of 3-hydroxybenzeneaminium chloride (**c10**) in D₂O.

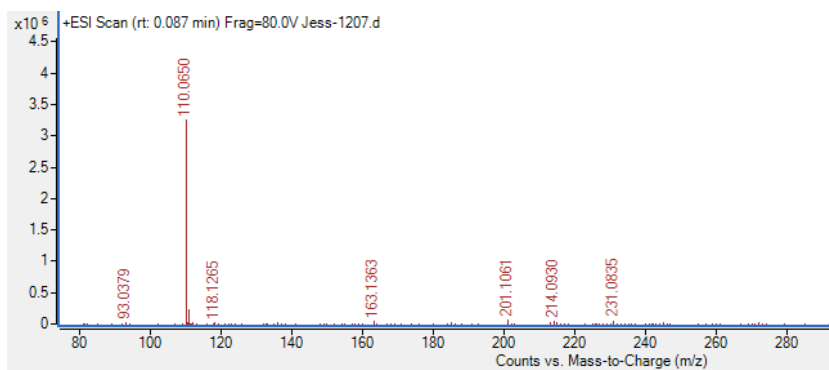


Figure S38: HR-MS of 3-hydroxybenzeneaminium chloride (**c10**).

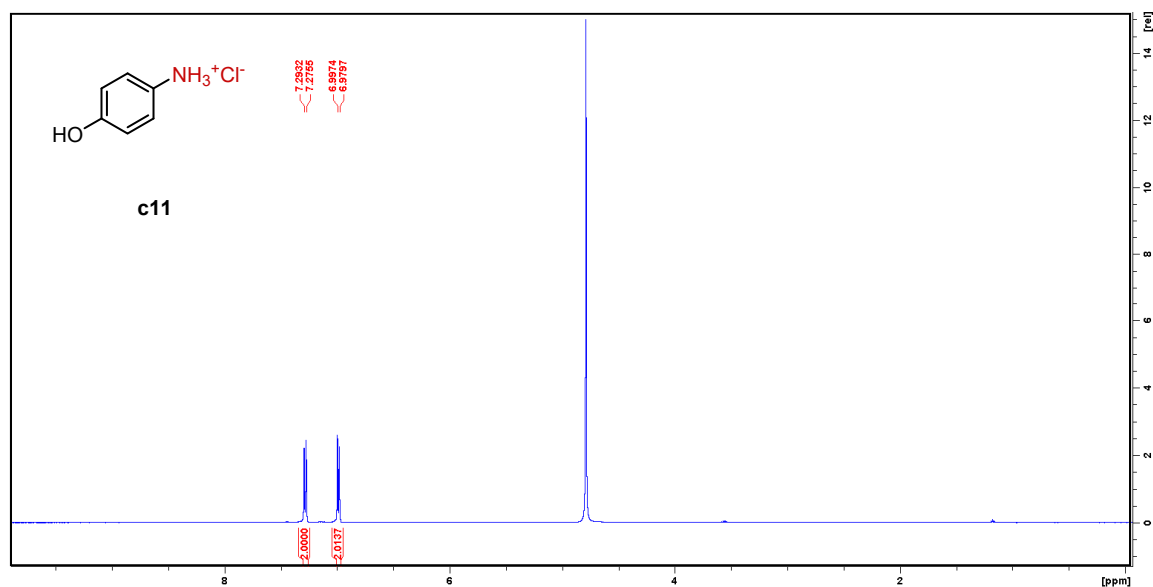


Figure S39: ¹H NMR of 4-hydroxybenzeneaminium chloride (c11) in D₂O.

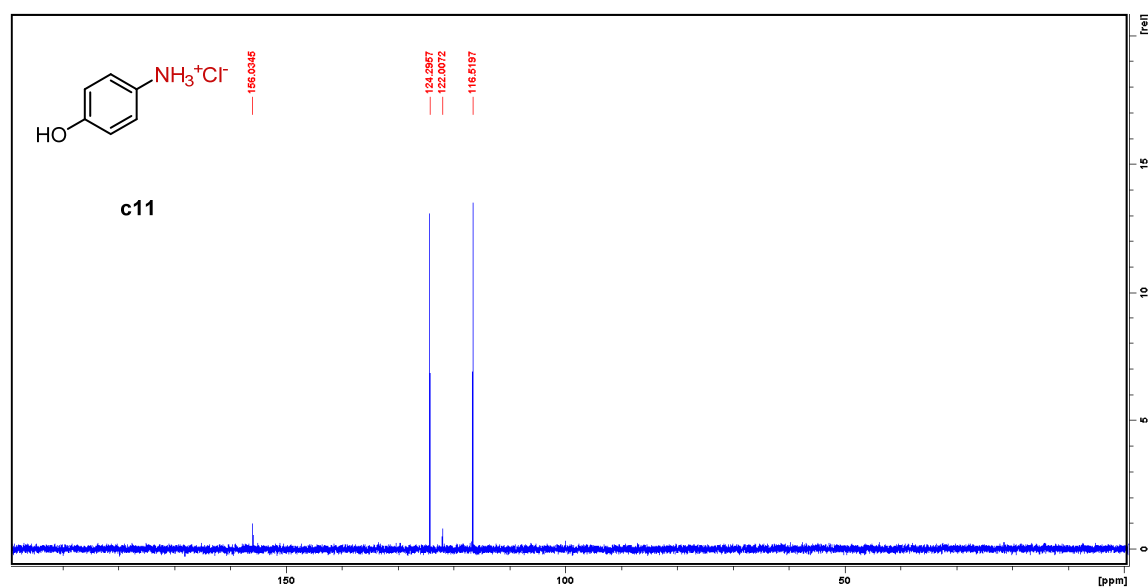


Figure S40: ¹³C{¹H} NMR of 4-hydroxybenzeneaminium chloride (c11) in D₂O.

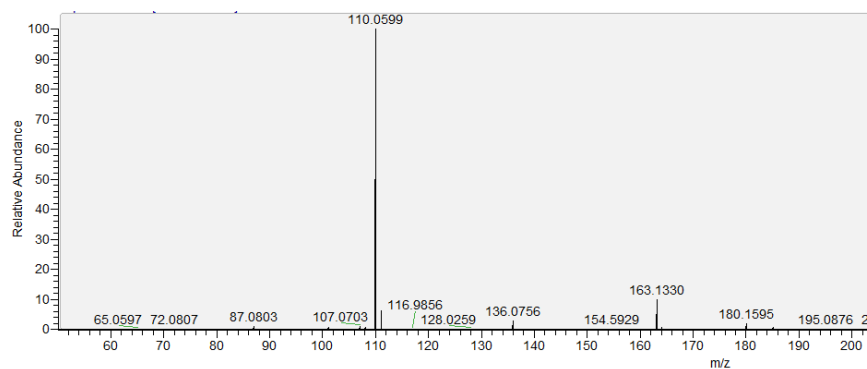


Figure S41: HR-MS of 4-hydroxybenzeneaminium chloride (c11).

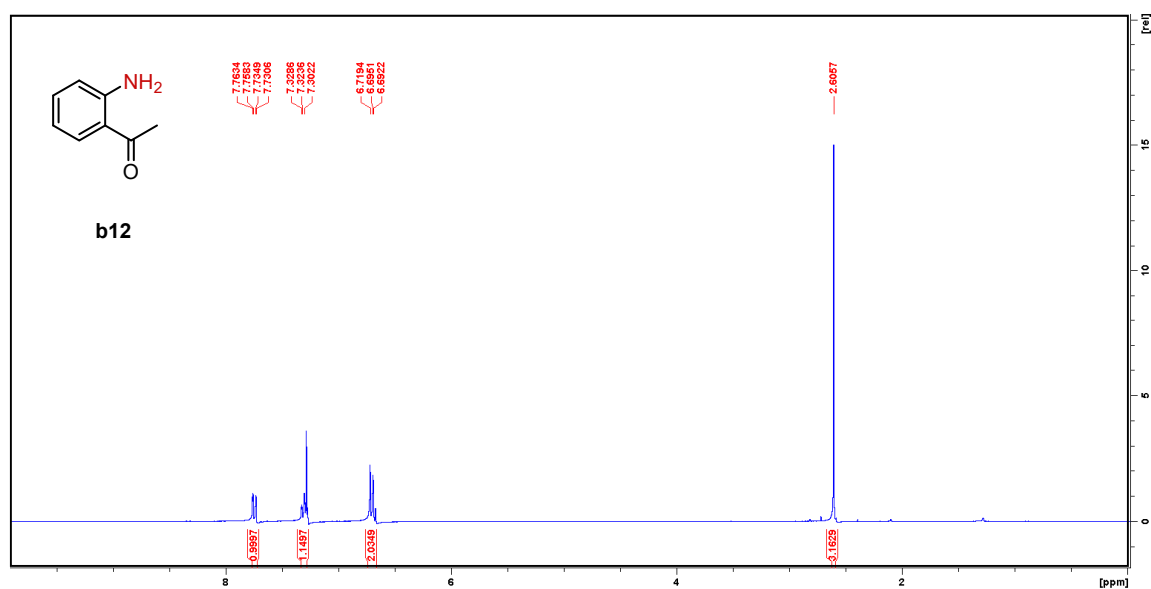


Figure S42: ¹H NMR of 2-aminoacetophenone (**b12**) in CDCl₃.

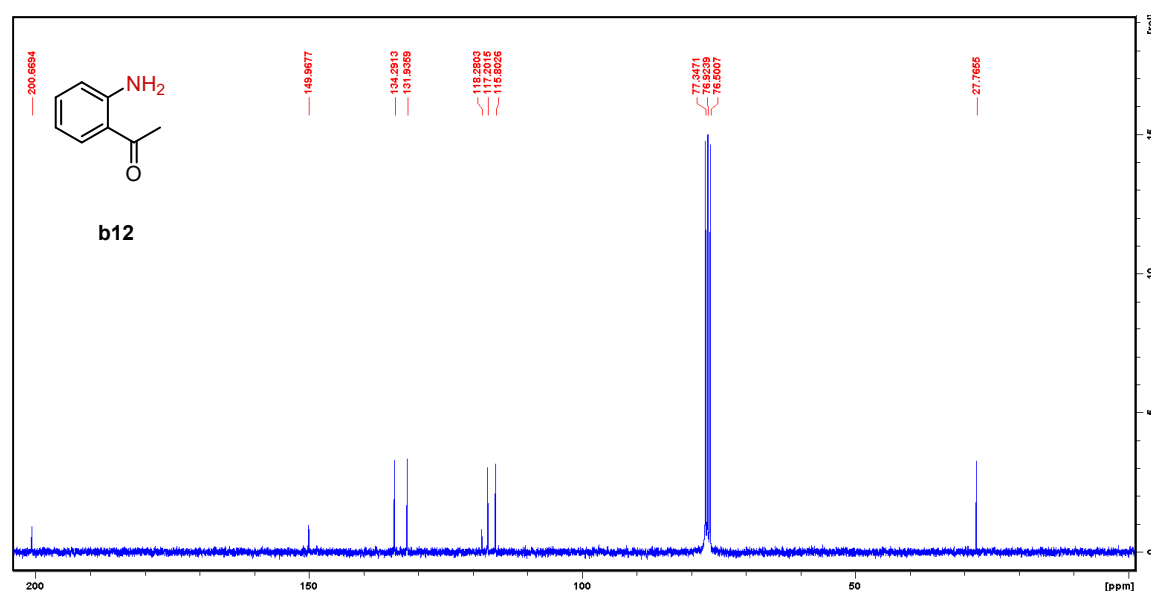


Figure S43: ¹³C{¹H} NMR of 2-aminoacetophenone (**b12**) in CDCl₃.

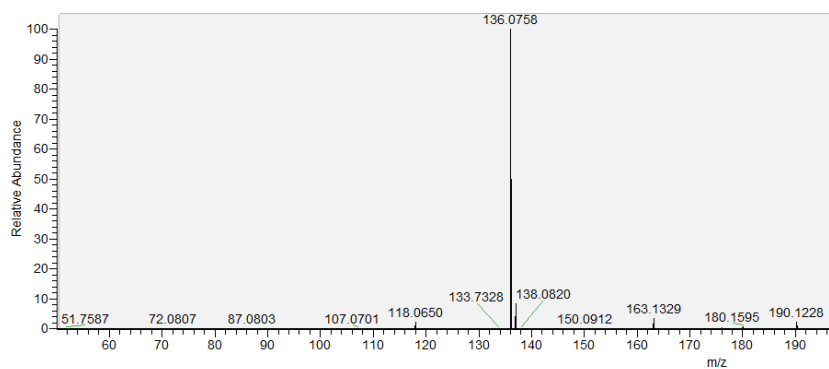


Figure S44: HR-MS of 2-aminoacetophenone (**b12**).

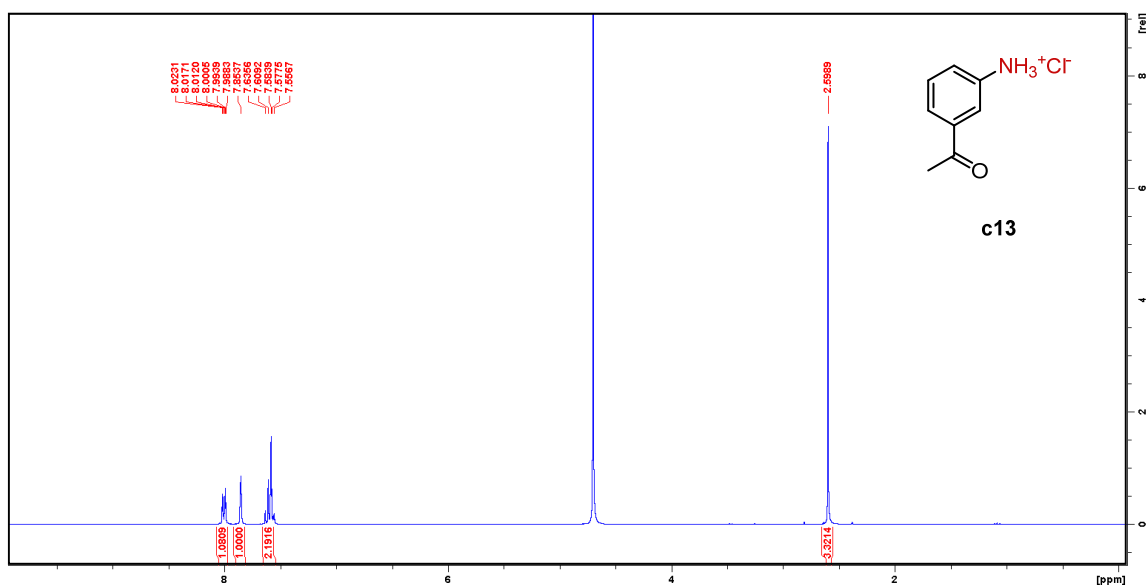


Figure S45: ¹H NMR of 3-acetylbenzenaminium chloride (**c13**) in D₂O.

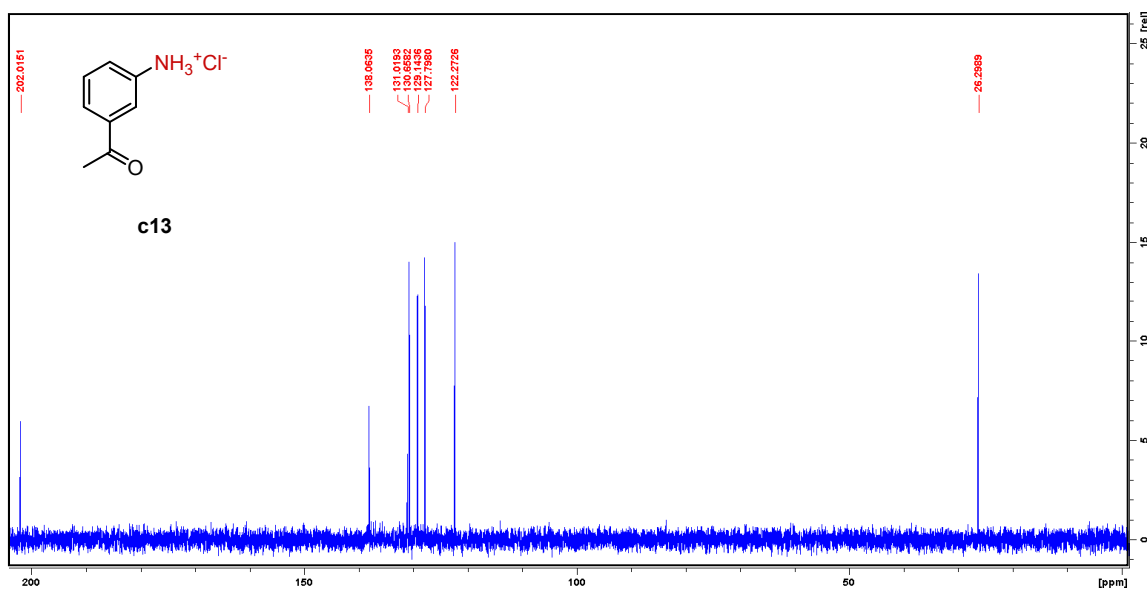


Figure S46: ¹³C{¹H} NMR of 3-acetylbenzenaminium chloride (**c13**) in D₂O.

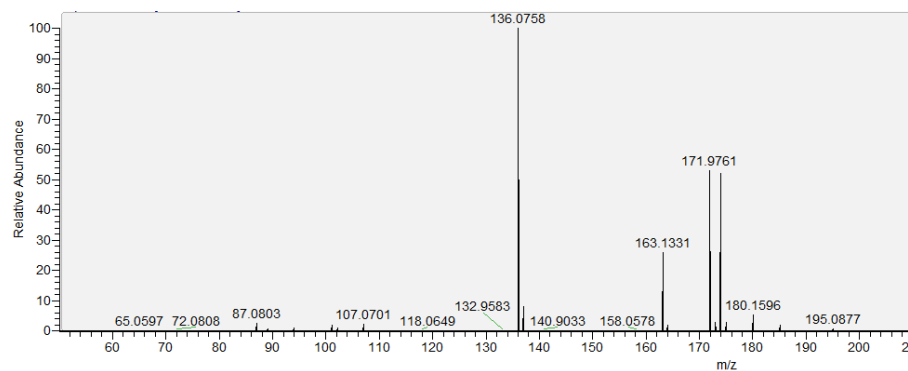


Figure S47: HR-MS of 3-acetylbenzenaminium chloride (**c13**).

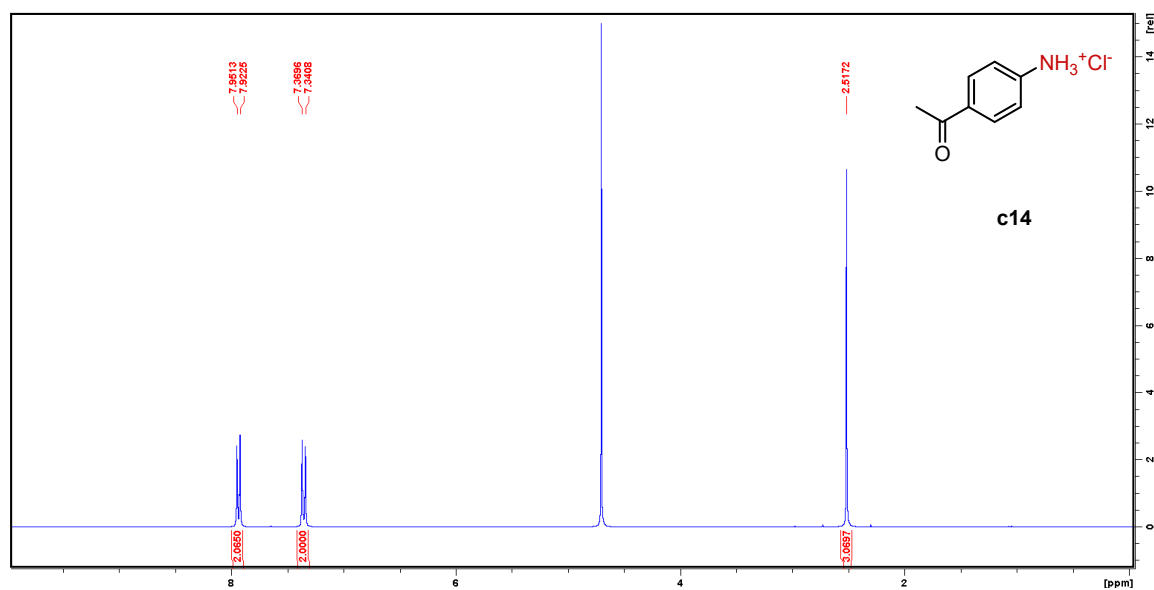


Figure S48: ¹H NMR of 4-acetylbenzenaminium chloride (**c14**) in D₂O.

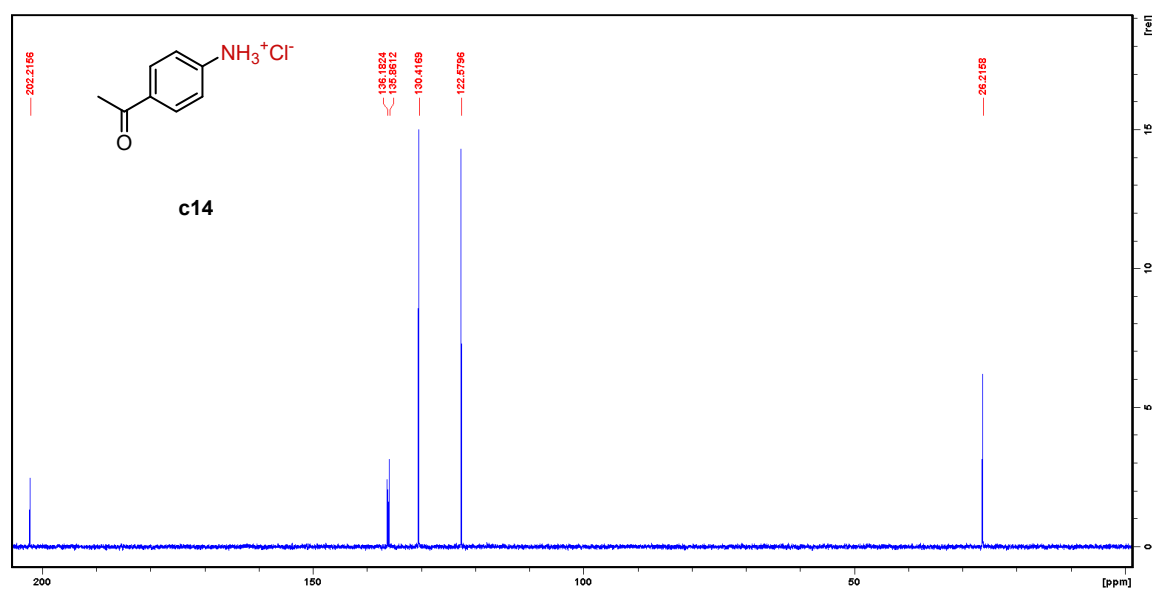


Figure S49: ¹³C{¹H} NMR of 4-acetylbenzenaminium chloride (**c14**) in D₂O.

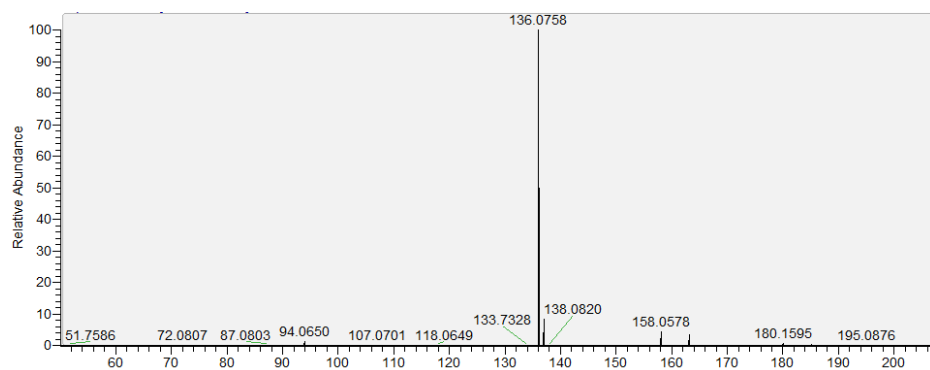


Figure S50: HR-MS of 4-acetylbenzenaminium chloride (**c14**).

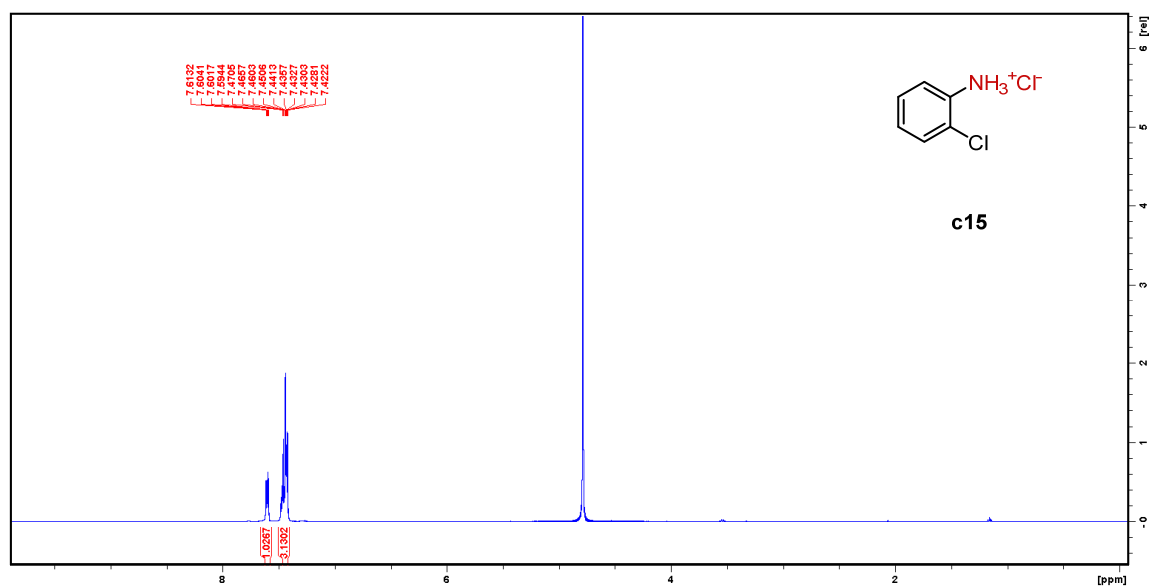


Figure S51: ¹H NMR of 2-chloroanilinium chloride (c15) in D₂O.

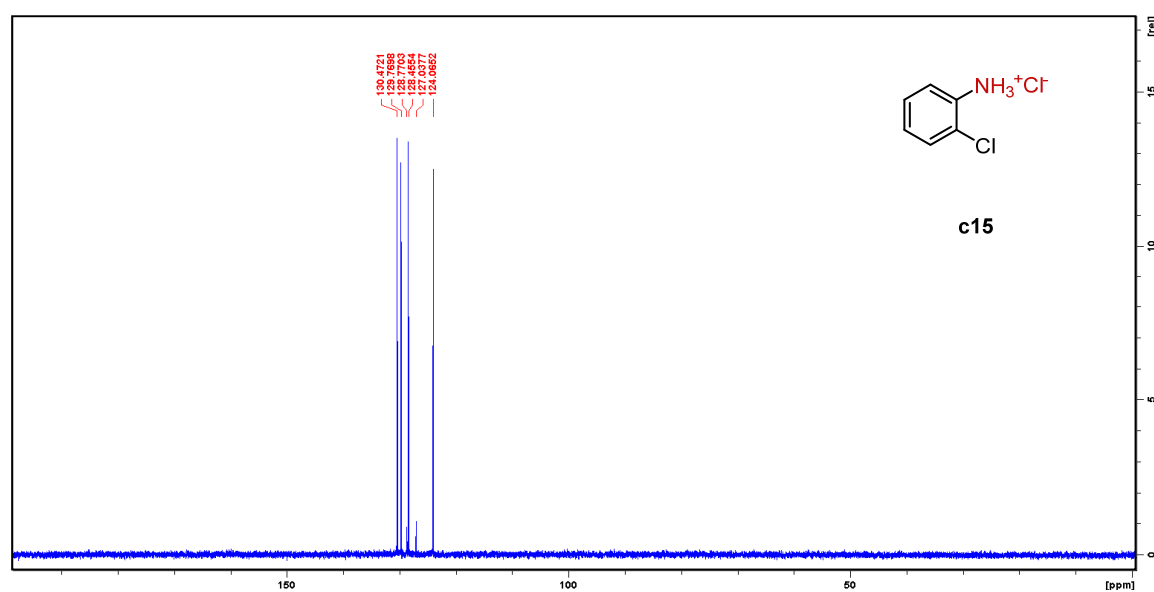


Figure S52: ¹³C{¹H} NMR of 2-chloroanilinium chloride (c15) in D₂O.

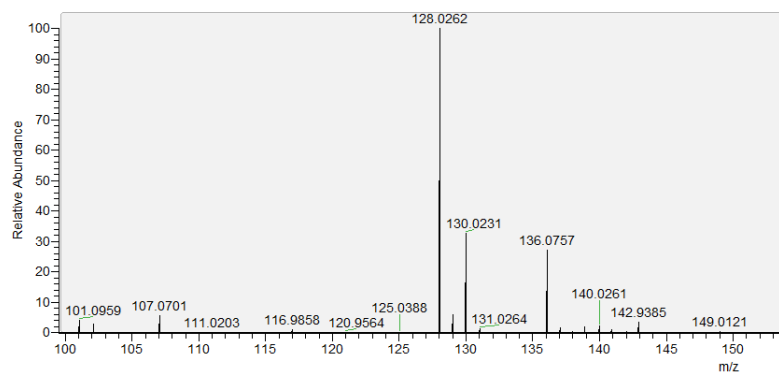


Figure S53: HR-MS of 2-chloroanilinium chloride (c15).

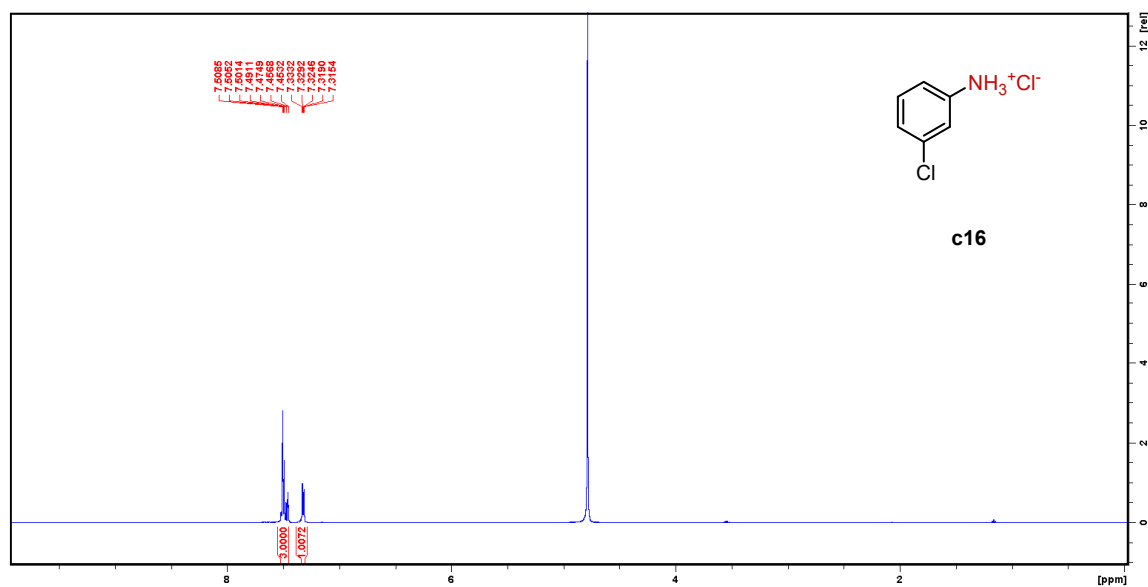


Figure S54: ¹H NMR of 3-chloroanilinium chloride (c16) in D₂O.

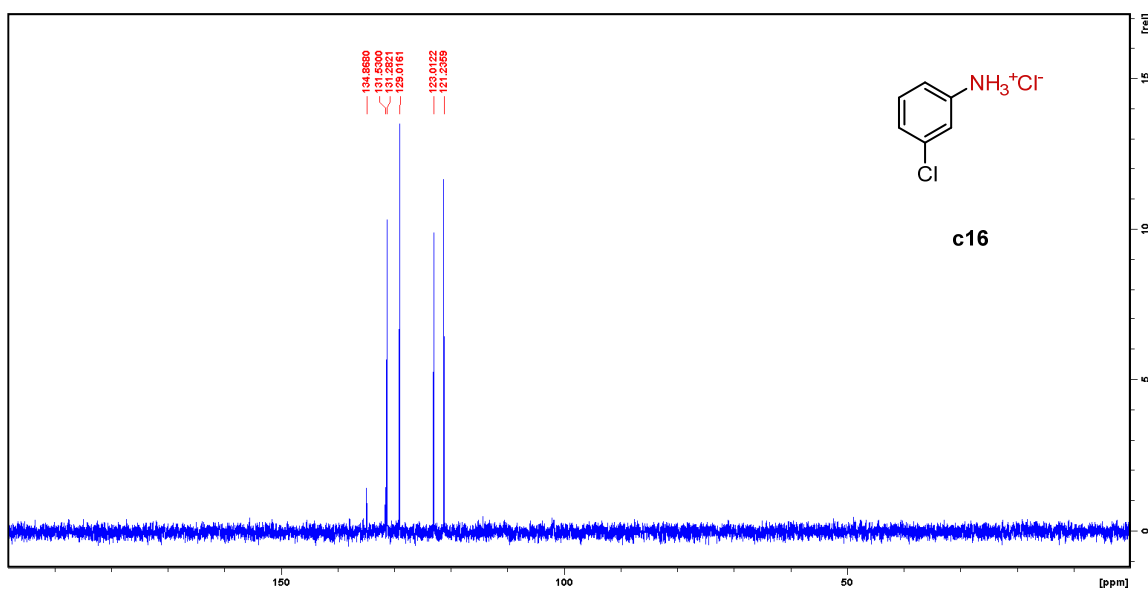


Figure S55: ¹³C{¹H} NMR of 3-chloroanilinium chloride (c16) in D₂O.

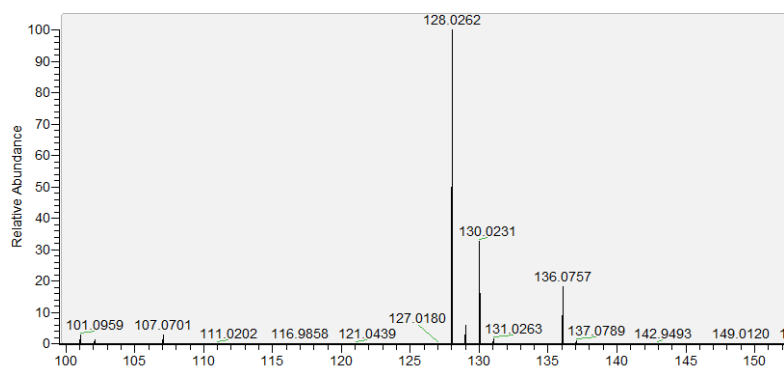


Figure S56: HR-MS of 3-chloroanilinium chloride (c16)

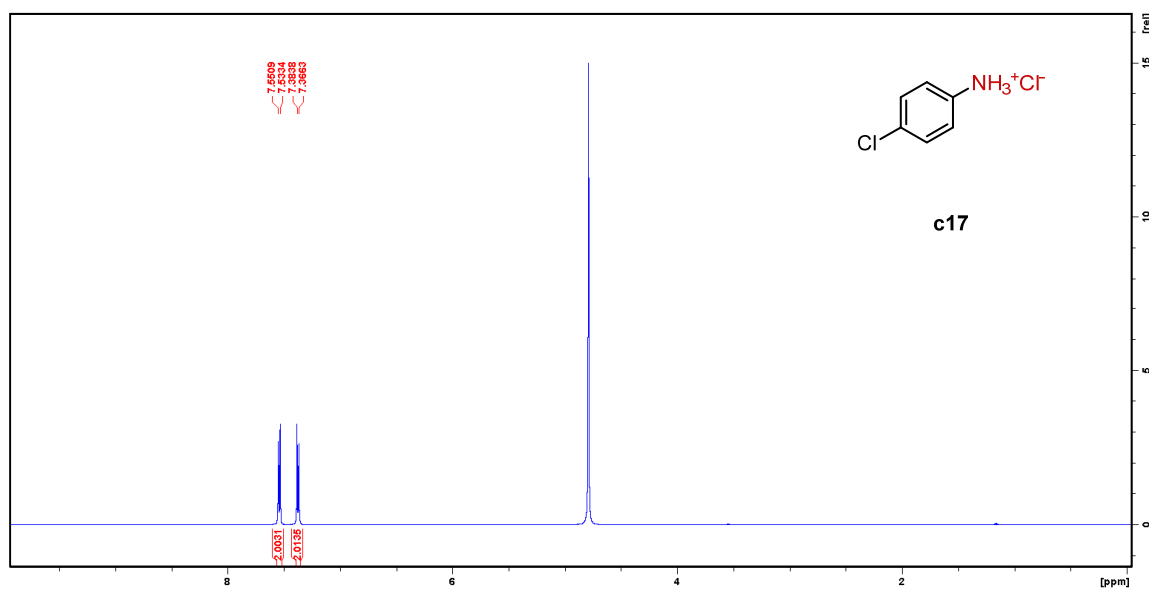


Figure S57: ¹H NMR of 4-chloroanilinium chloride (c17) in D₂O.

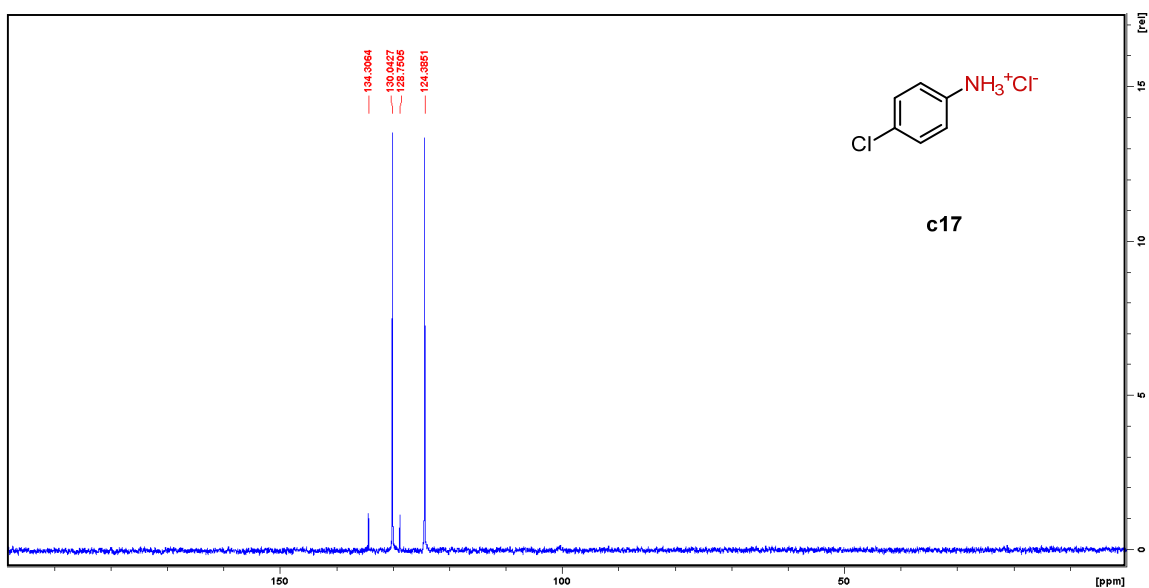


Figure S58: ¹³C{¹H} NMR of 4-chloroanilinium chloride (c17) in D₂O.

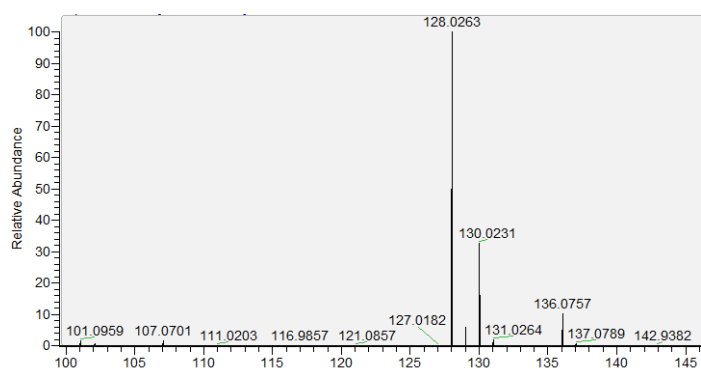


Figure S59: HR-MS of 4-chloroanilinium chloride (c17).

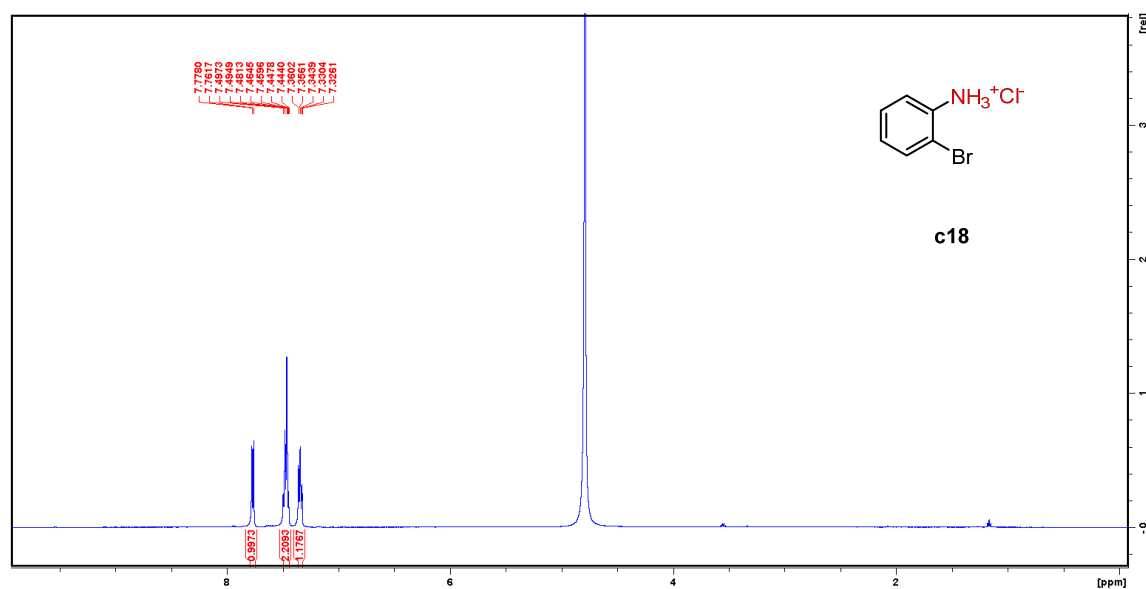


Figure S60: ¹H NMR of 2-bromoanilinium chloride (**c18**) in D₂O.

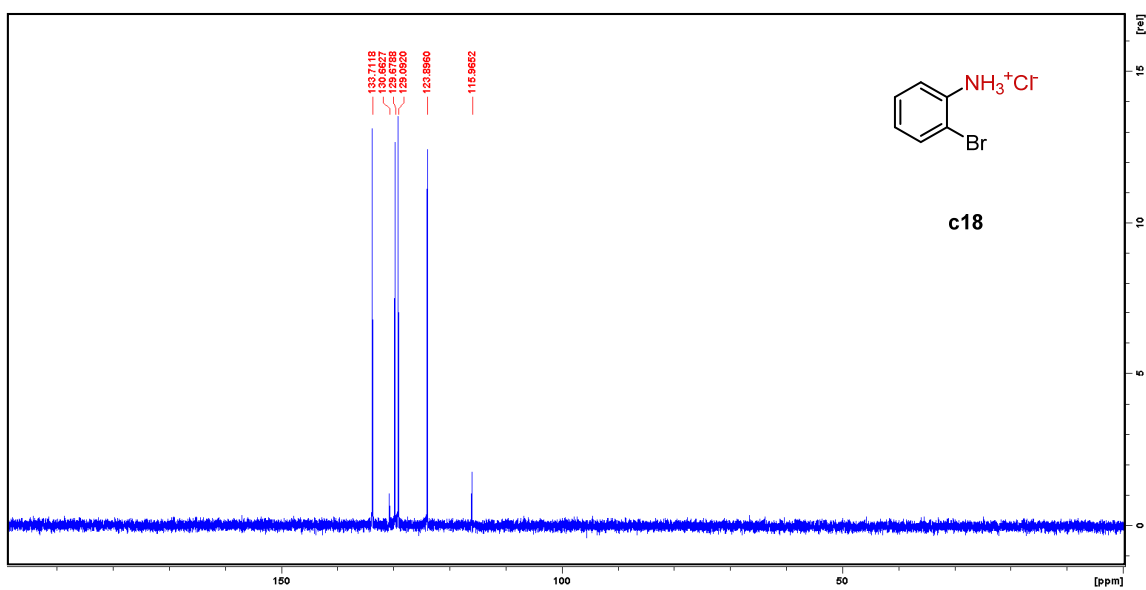


Figure S61: ¹³C{¹H} NMR of 2-bromoanilinium chloride (**c18**) in D₂O.

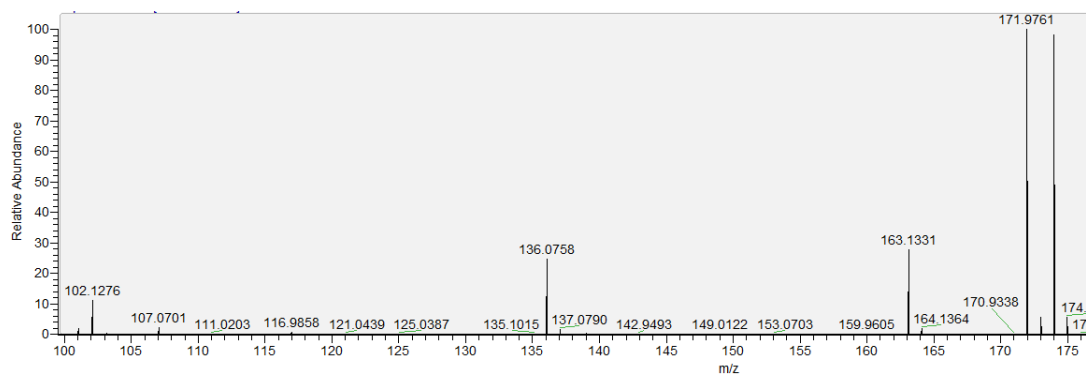


Figure S62: HR-MS of 2-bromoanilinium chloride (**c18**).

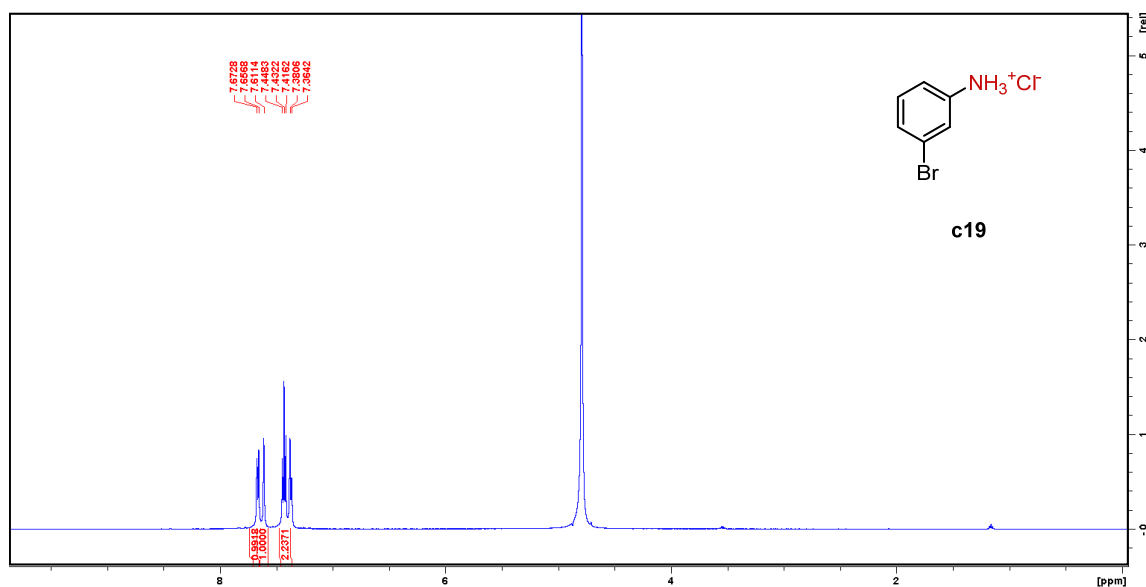


Figure S63: ¹H NMR of 3-bromoanilinium chloride (c19) in D₂O.

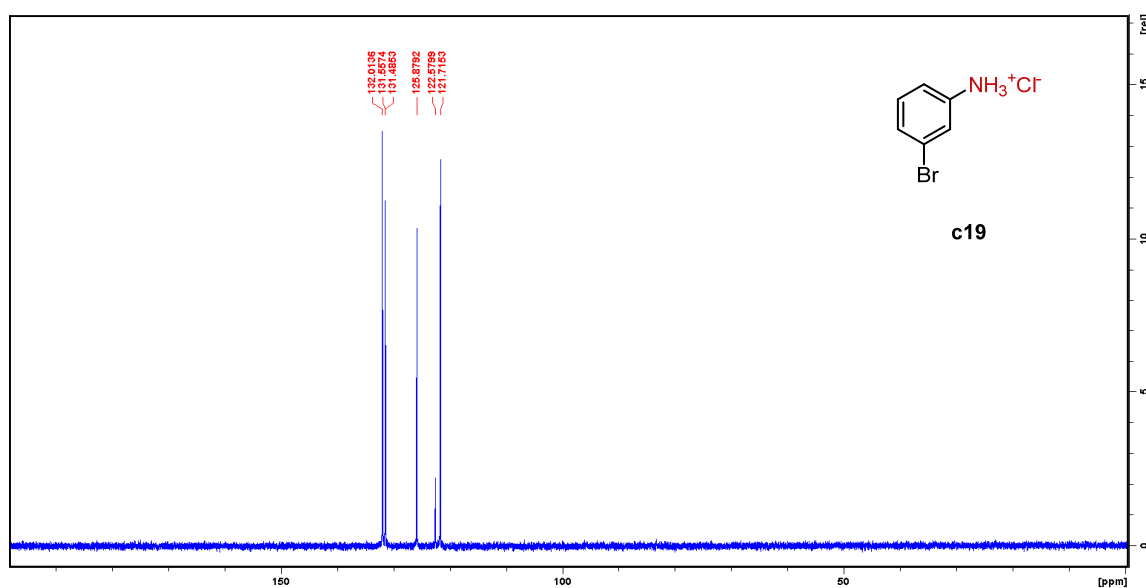


Figure S64: ¹³C{¹H} NMR of 3-bromoanilinium chloride (c19) in D₂O.

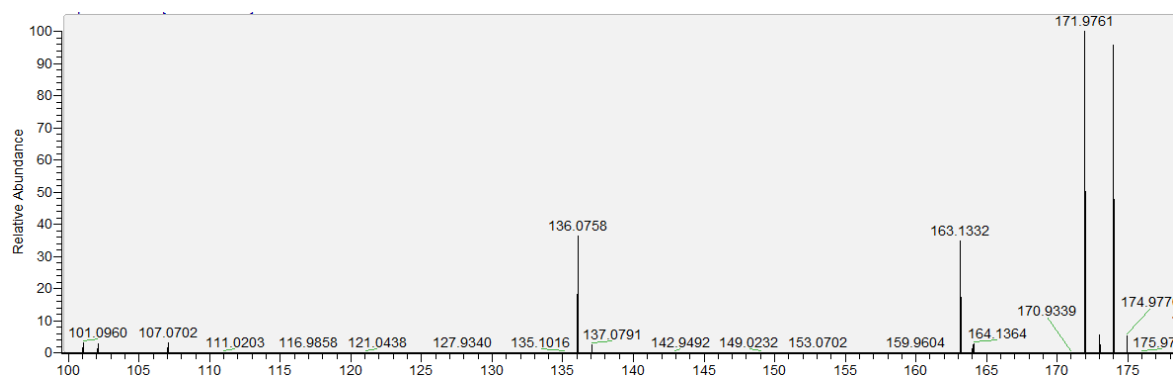


Figure S65: HR-MS of 3-bromoanilinium chloride (c19).

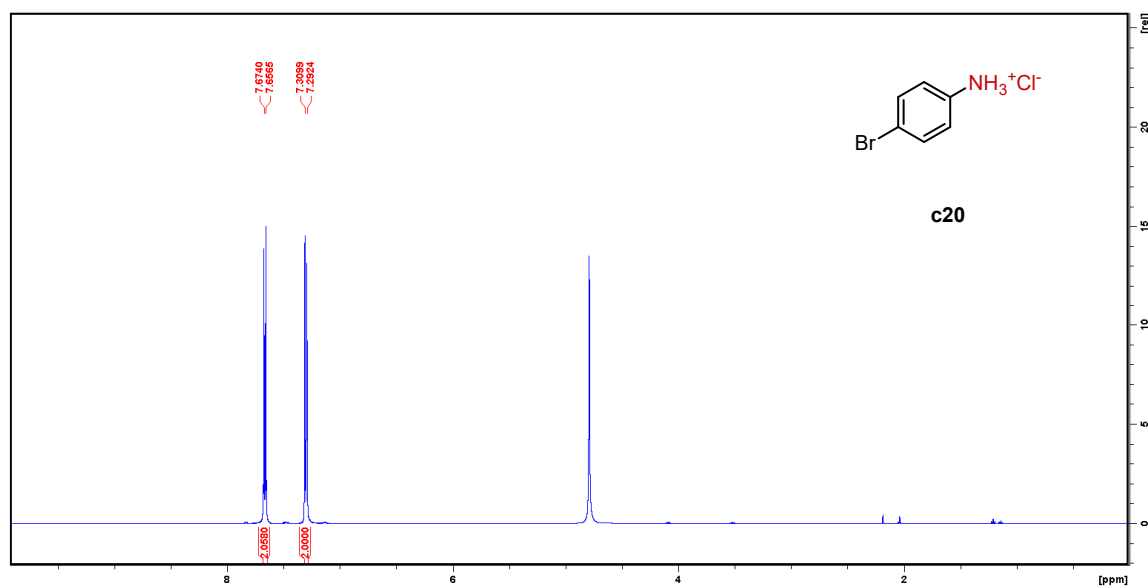


Figure S66: ¹H NMR of 4-bromoanilinium chloride (c20) in D₂O.

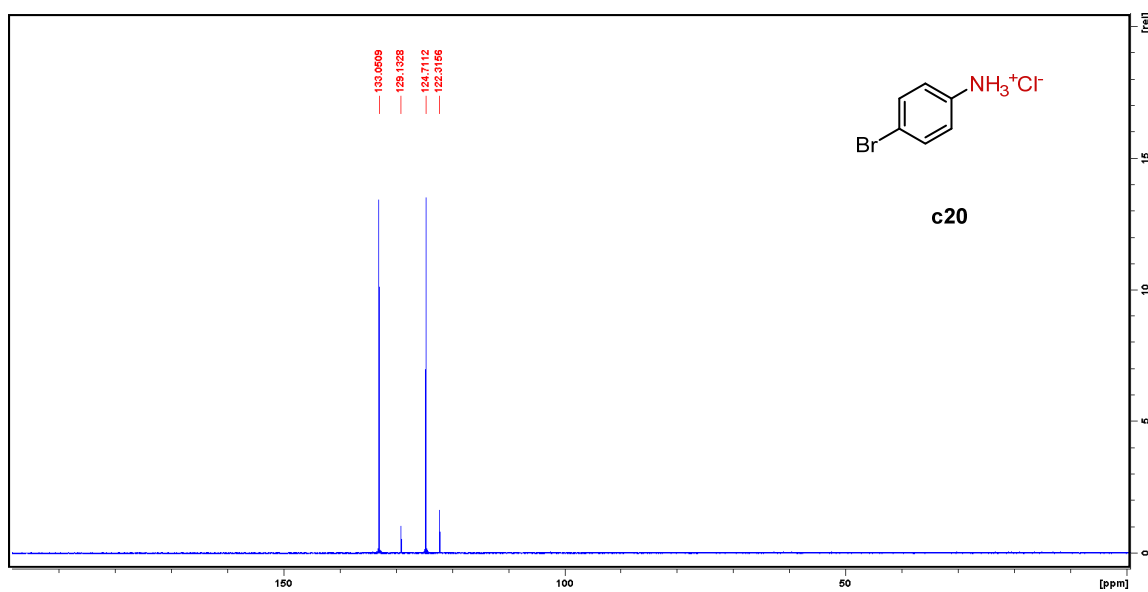


Figure S67: ¹³C{¹H} NMR of 4-bromoanilinium chloride (c20) in D₂O.

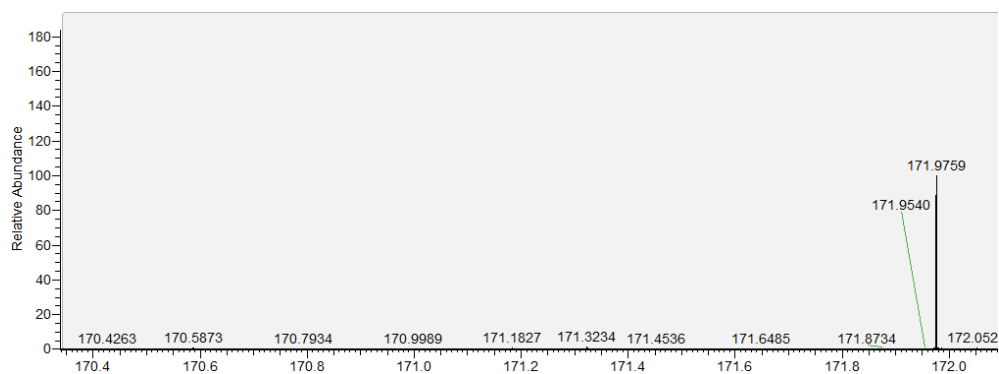


Figure S68: HR-MS of 4-bromoanilinium chloride (c20).

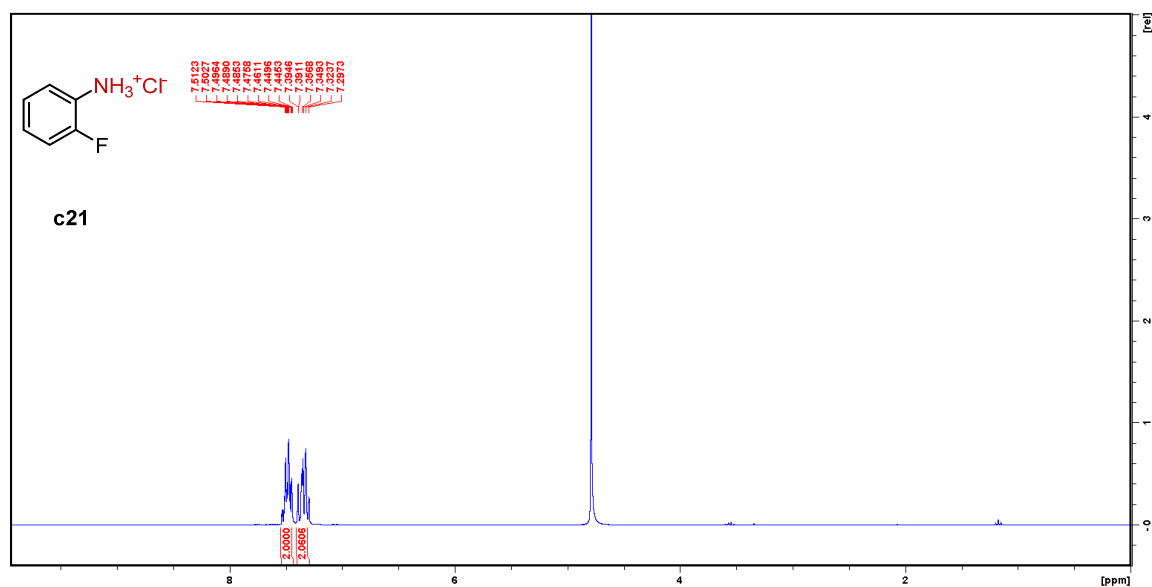


Figure S69: ^1H NMR of 2-fluoroanilinium chloride (**c21**) in D_2O .

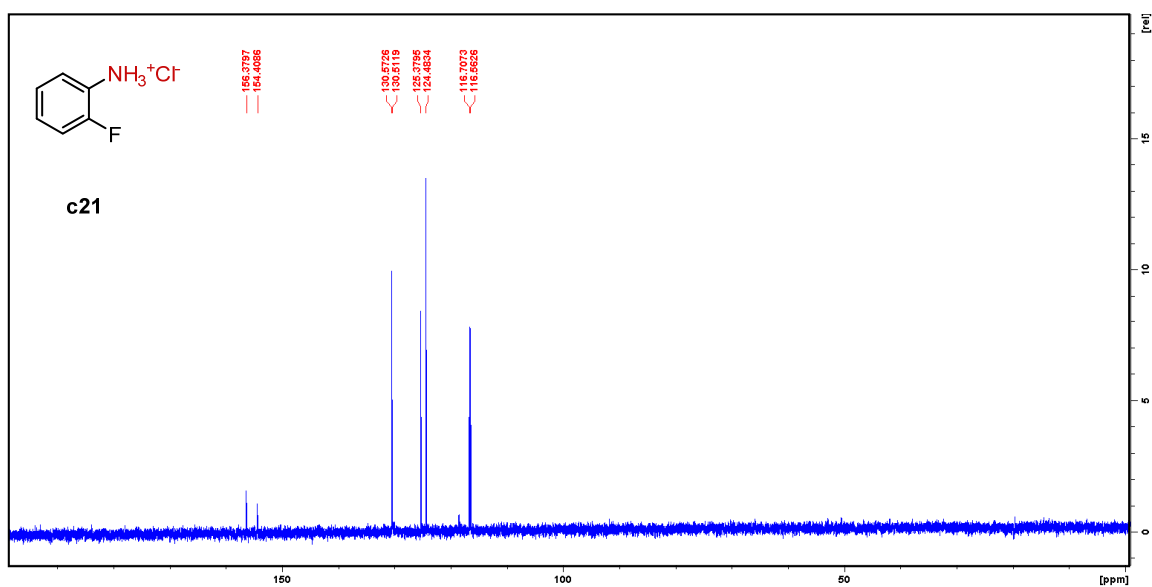


Figure S70: $^{13}\text{C}\{^1\text{H}\}$ NMR of 2-fluoroanilinium chloride (**c21**) in D_2O .

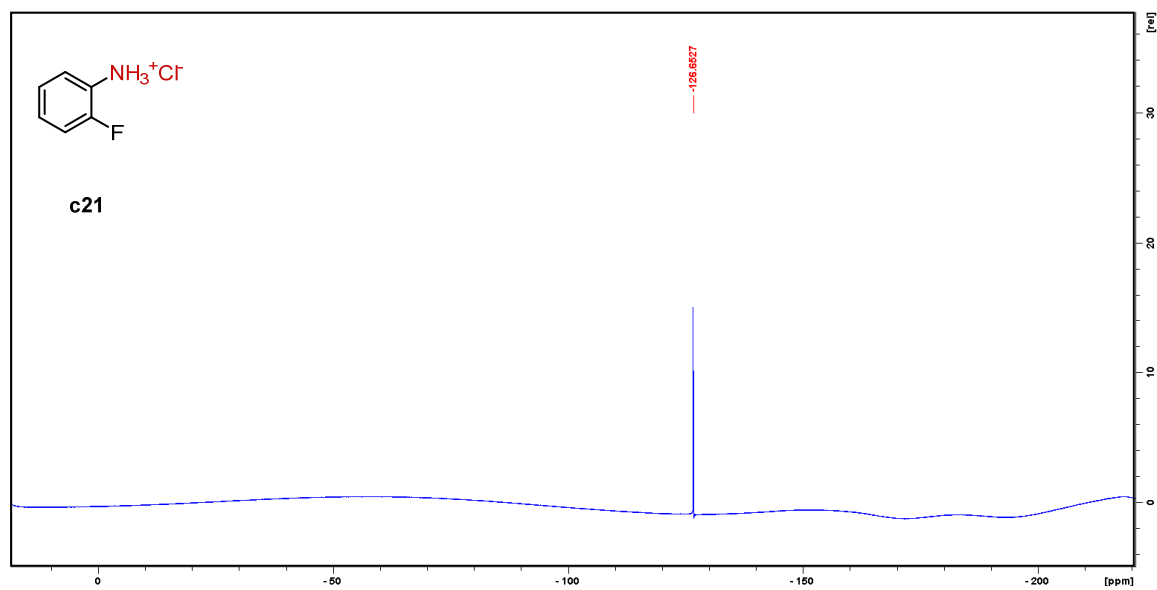


Figure S71: ^{19}F NMR of 2-fluoroanilinium chloride (**c21**) in D₂O.

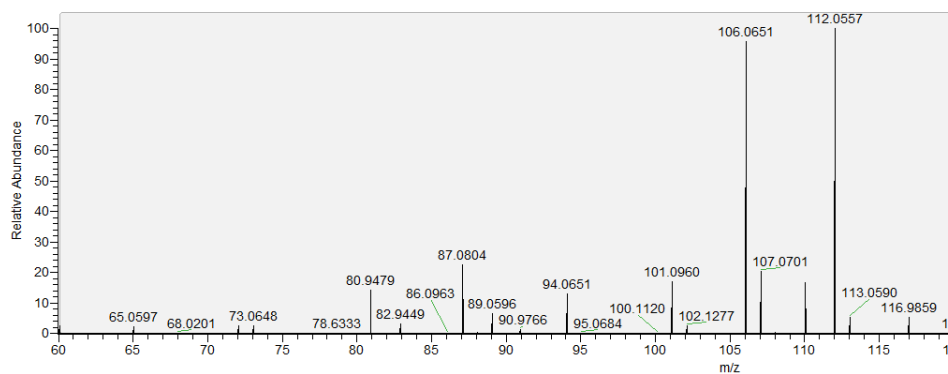


Figure S72: HR-MS of 2-fluoroanilinium chloride (**c21**).

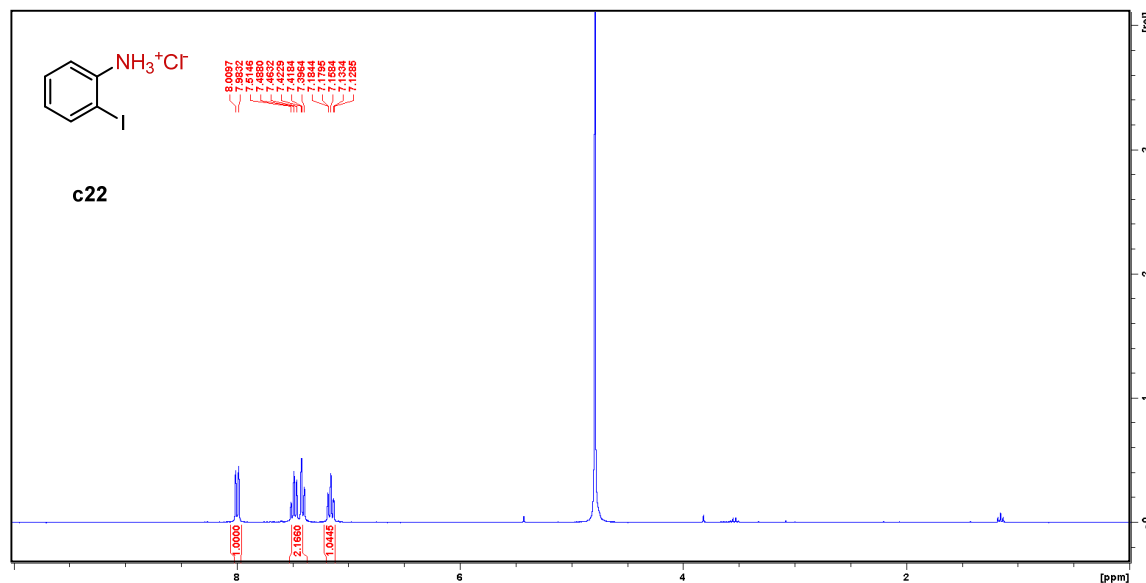


Figure S73: ^1H NMR of 2-iodoanilium chloride (**c22**) in D_2O .

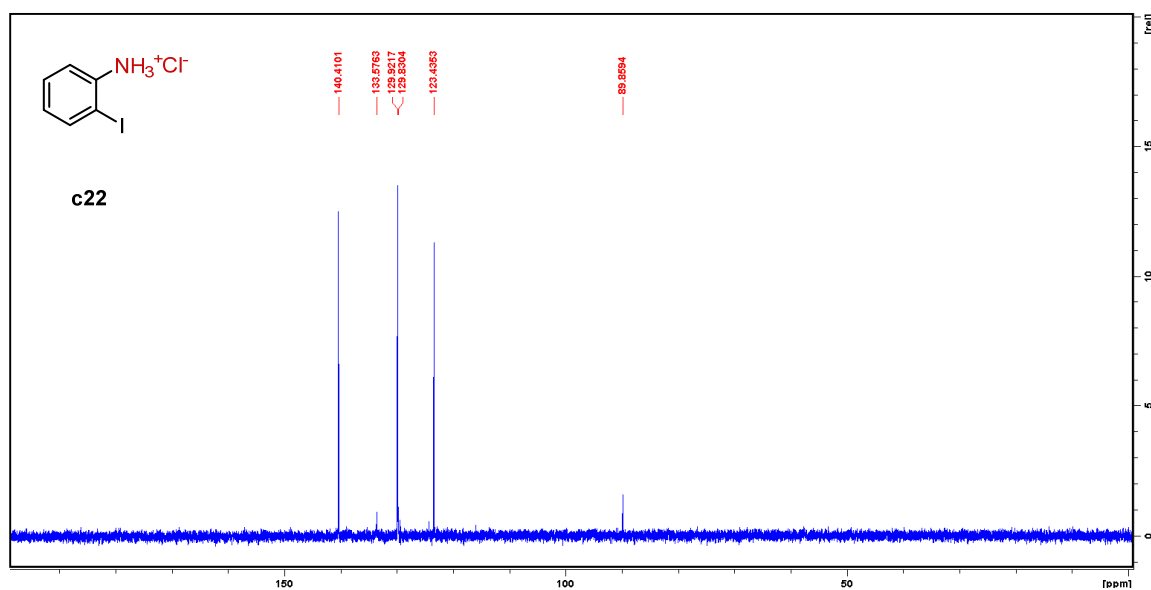


Figure S74: $^{13}\text{C}\{^1\text{H}\}$ NMR of 2-iodoanilium chloride (**c22**) in D_2O .

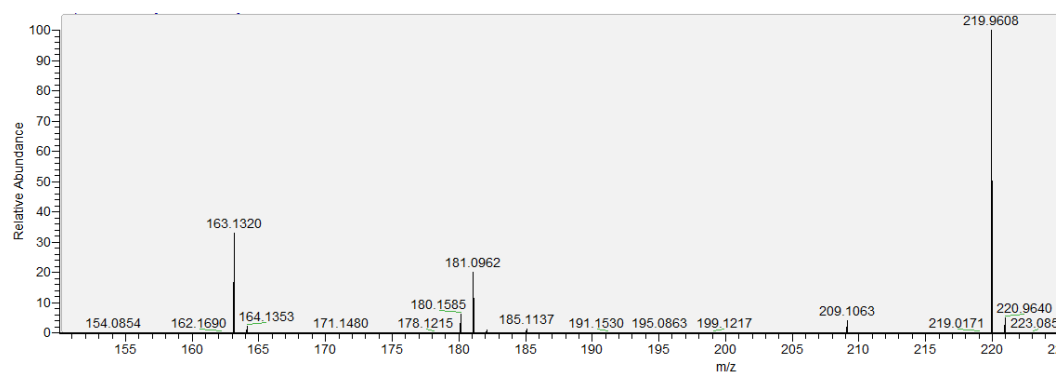
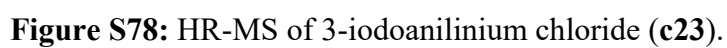
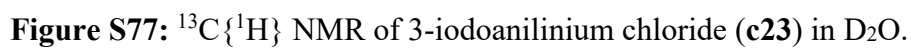


Figure S75: HR-MS of 2-iodoanilium chloride (**c22**).



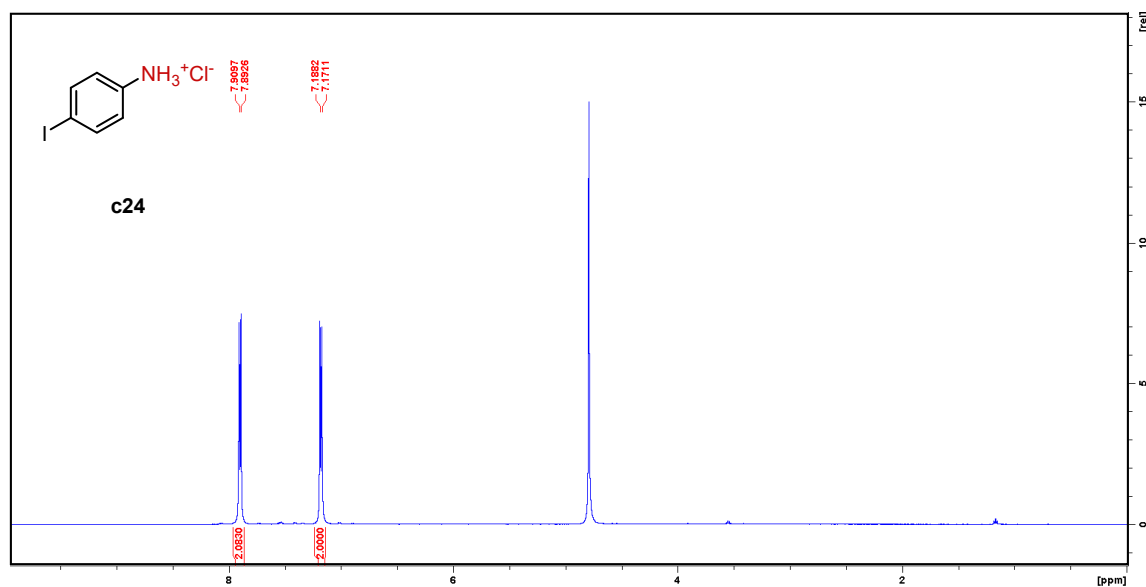


Figure S79: ^1H NMR of 4-iodoanilinium chloride (**c24**) in D_2O .

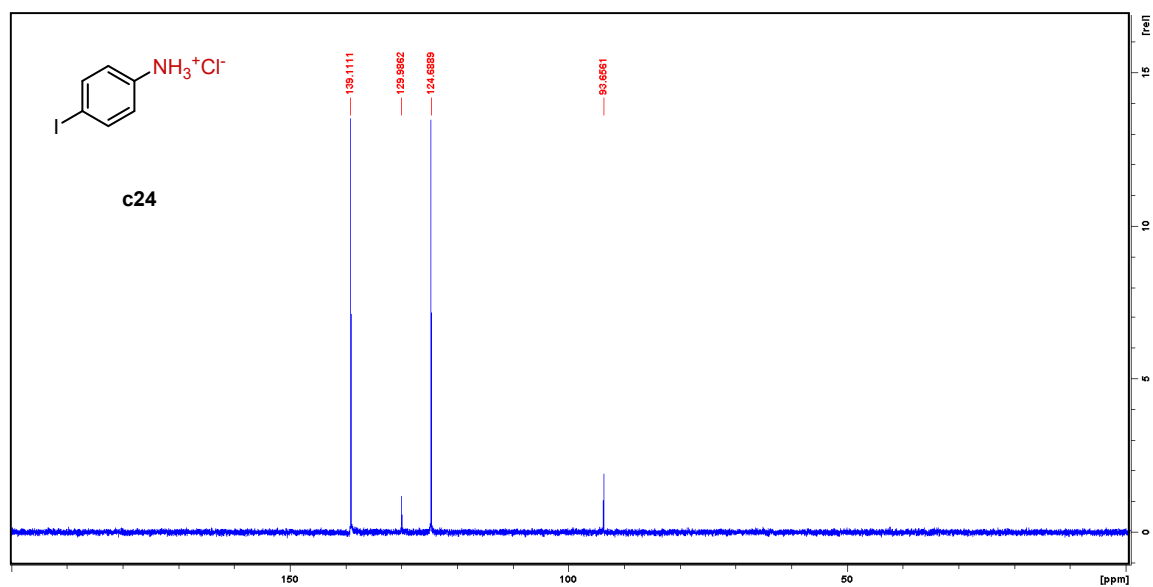


Figure S80: $^{13}\text{C}\{^1\text{H}\}$ NMR of 4-iodoanilinium chloride (**c24**) in D_2O .

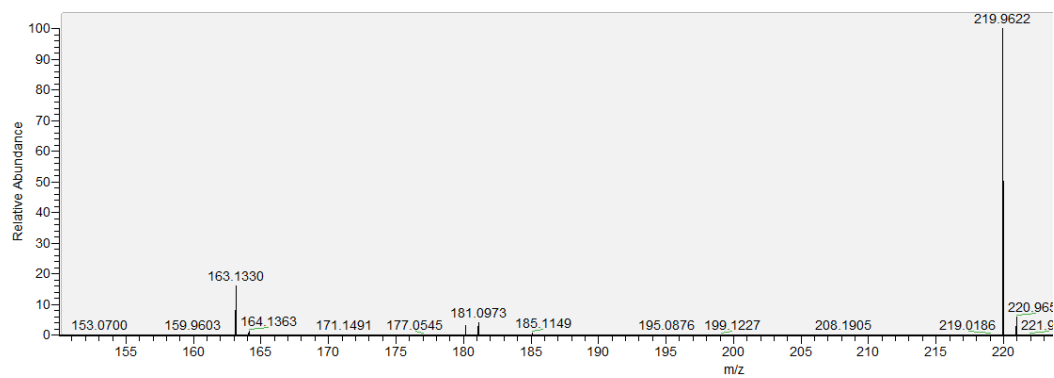


Figure S81: HR-MS of 4-iodoanilinium chloride (**c24**).

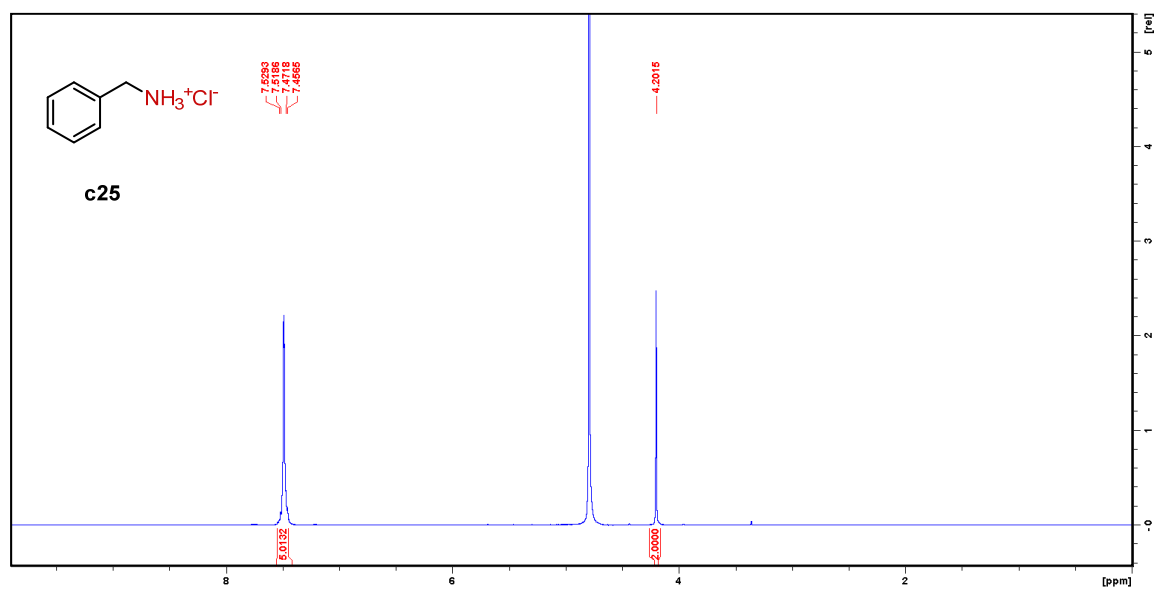


Figure S82: ^1H NMR of benzylamine hydrochloride (**c25**) in D_2O .

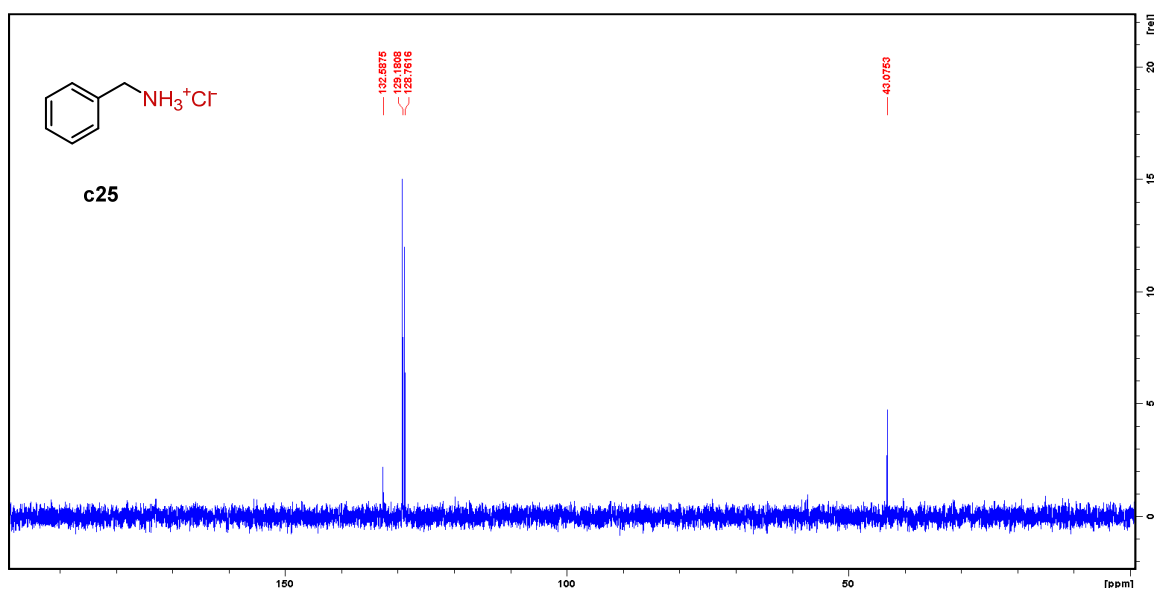


Figure S83: $^{13}\text{C}\{^1\text{H}\}$ NMR of benzylamine hydrochloride (**c25**) in D_2O .

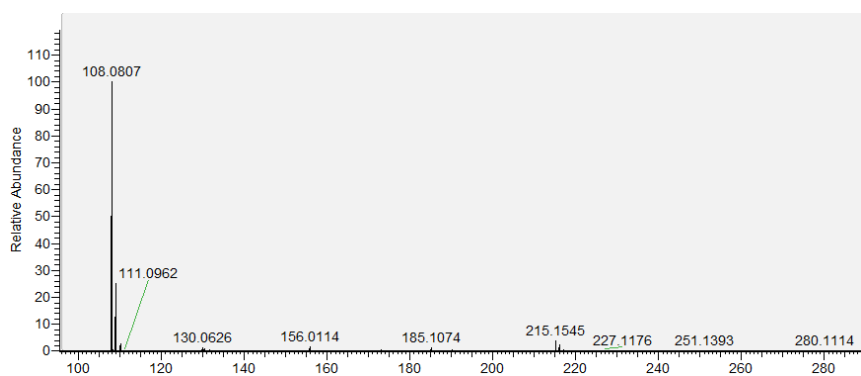


Figure S84: HR-MS of benzylamine hydrochloride (**c25**).

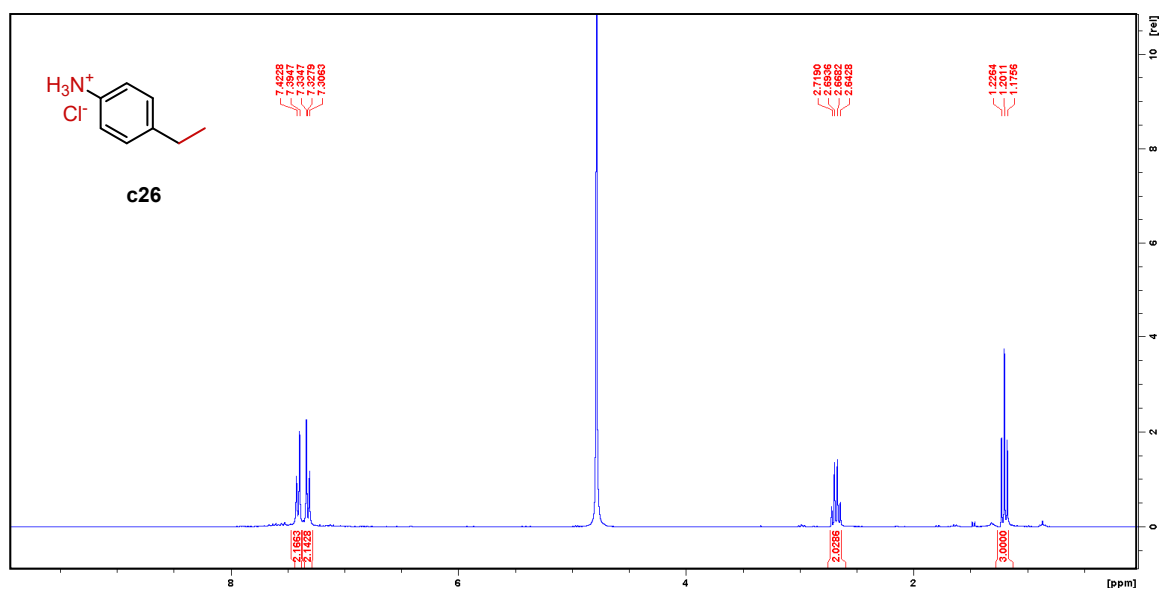


Figure S85: ^1H NMR of 4-ethylanilinium chloride (**c26**) in D_2O .

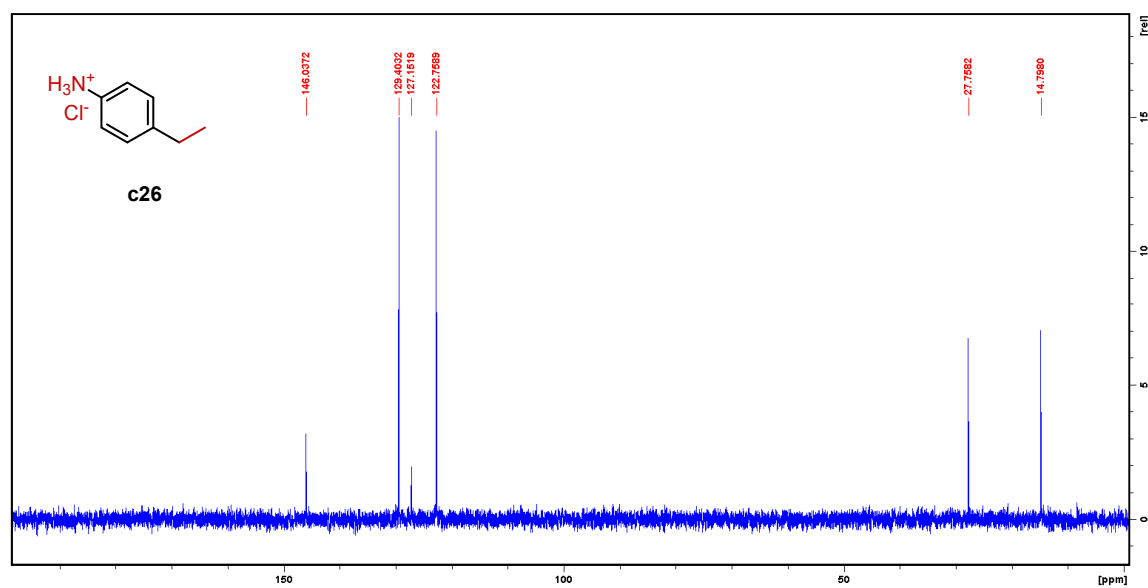


Figure S86: $^{13}\text{C}\{^1\text{H}\}$ NMR of 4-ethylanilinium chloride (**c26**) in D_2O .

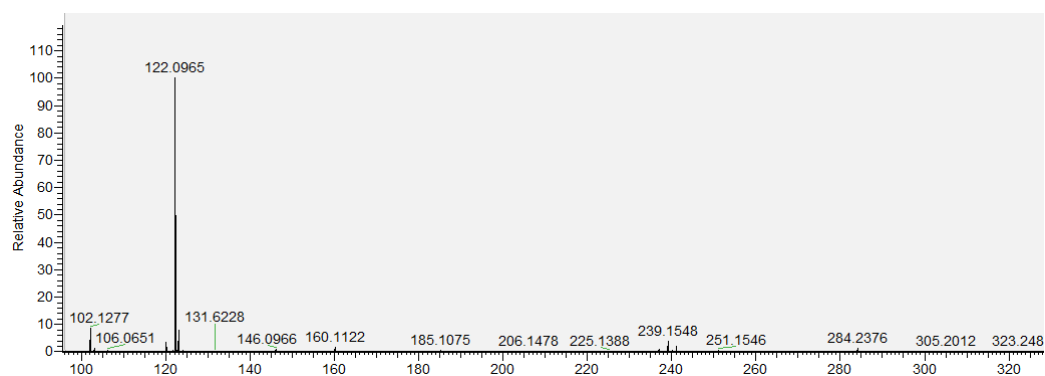


Figure S87: HR-MS of 4-ethylanilinium chloride (**c26**).

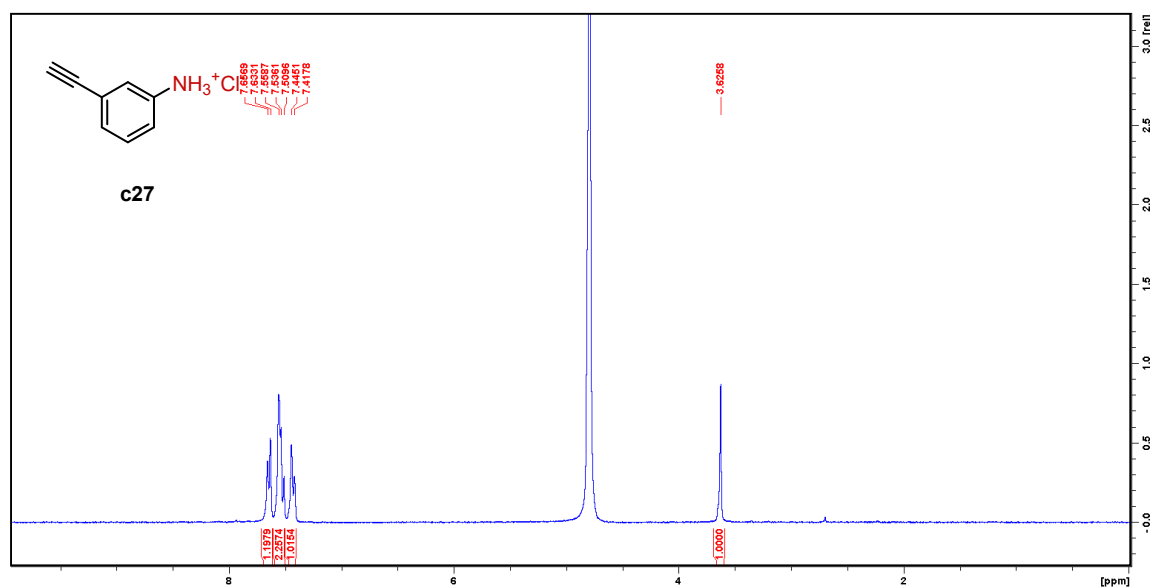


Figure S88: ^1H NMR of 3-ethynylanilinium chloride (c27) in D_2O .

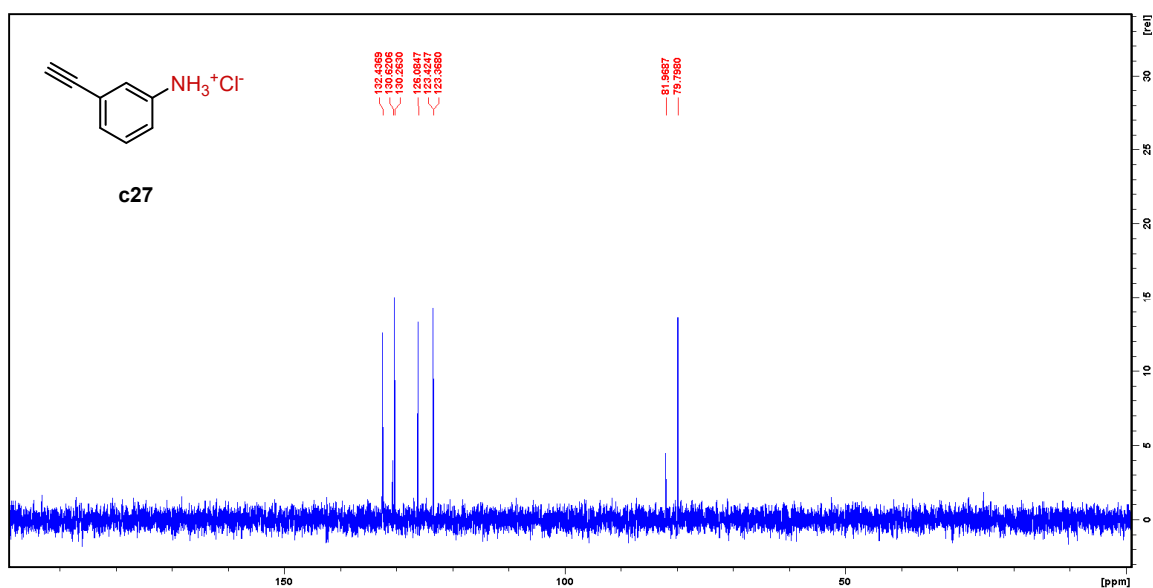


Figure S89: $^{13}\text{C}\{^1\text{H}\}$ NMR of 3-ethynylanilinium chloride (c27) in D_2O .

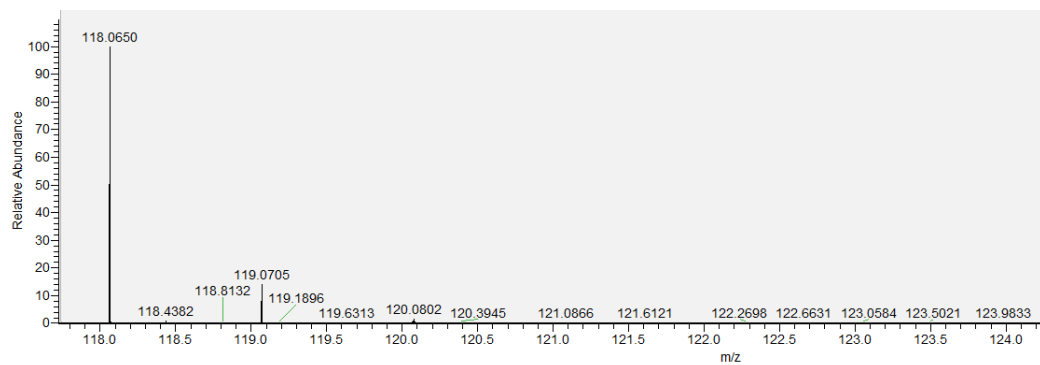


Figure S90: HR-MS of 3-ethynylanilinium chloride (c27).

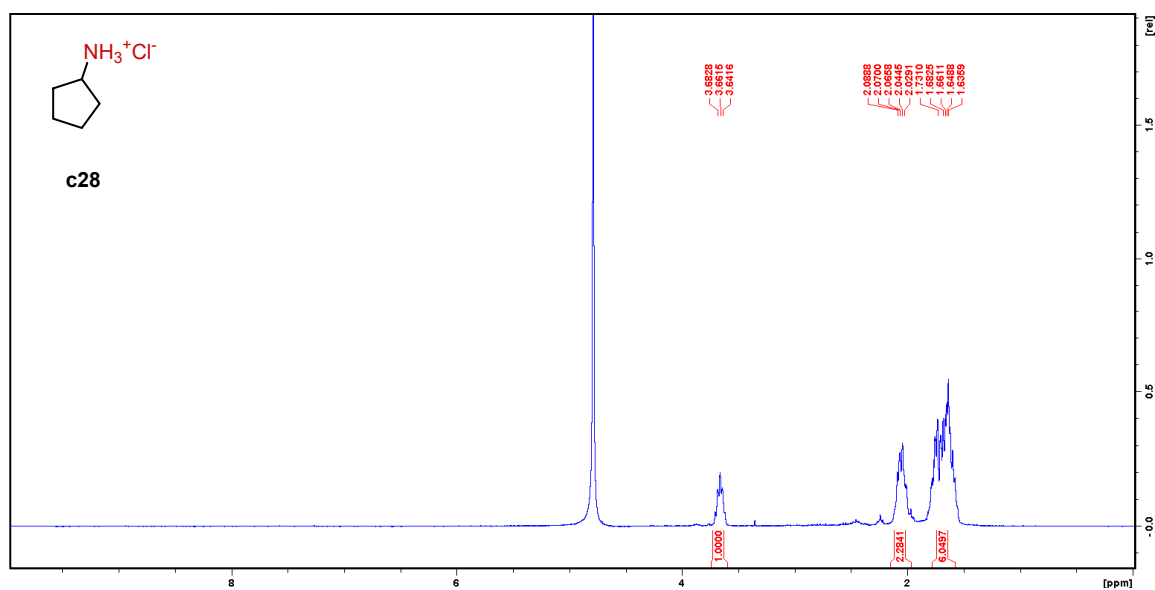


Figure S91: ^1H NMR of cyclopentanamine hydrochloride (**c28**) in D_2O .

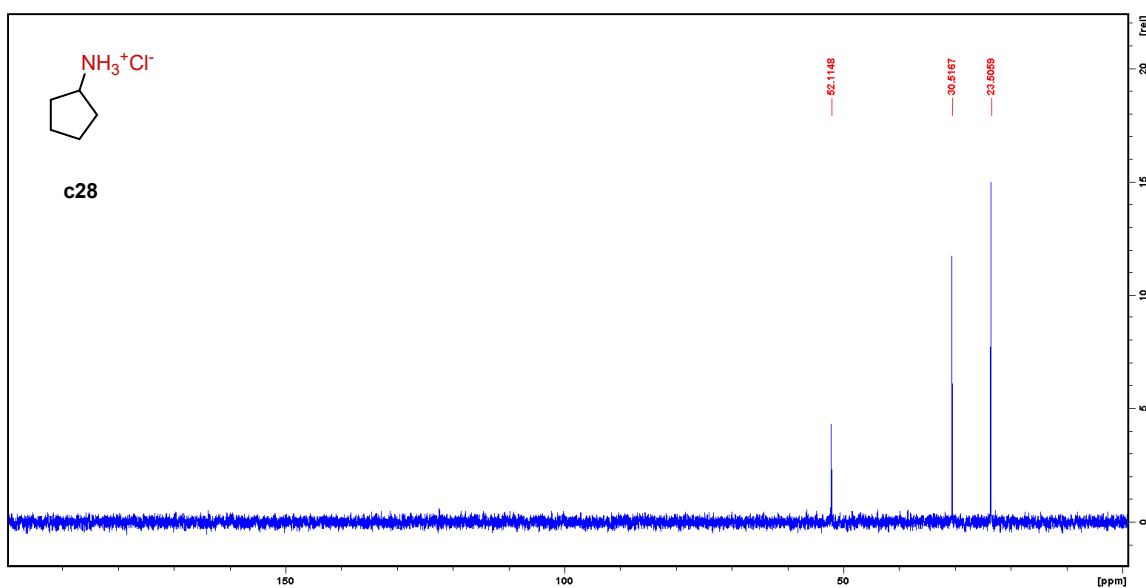


Figure S92: $^{13}\text{C}\{^1\text{H}\}$ NMR of cyclopentanamine hydrochloride (**c28**) in D_2O .

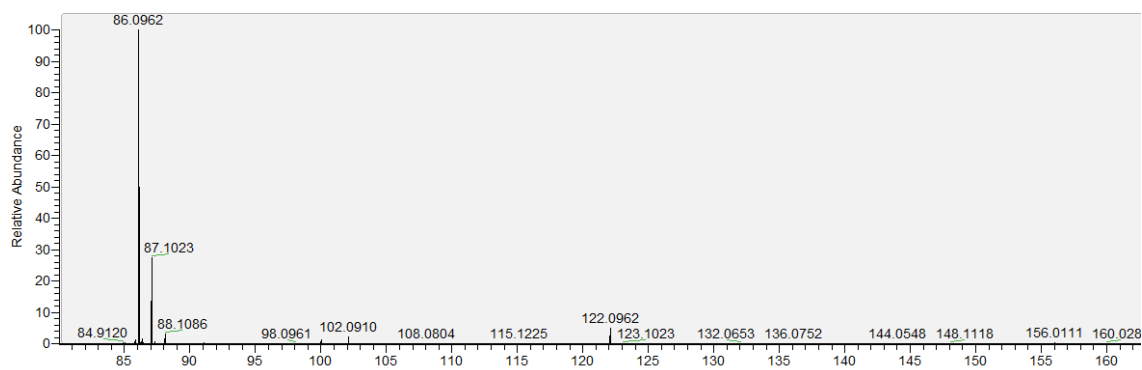


Figure S93: HR-MS of cyclopentanamine hydrochloride (**c28**).

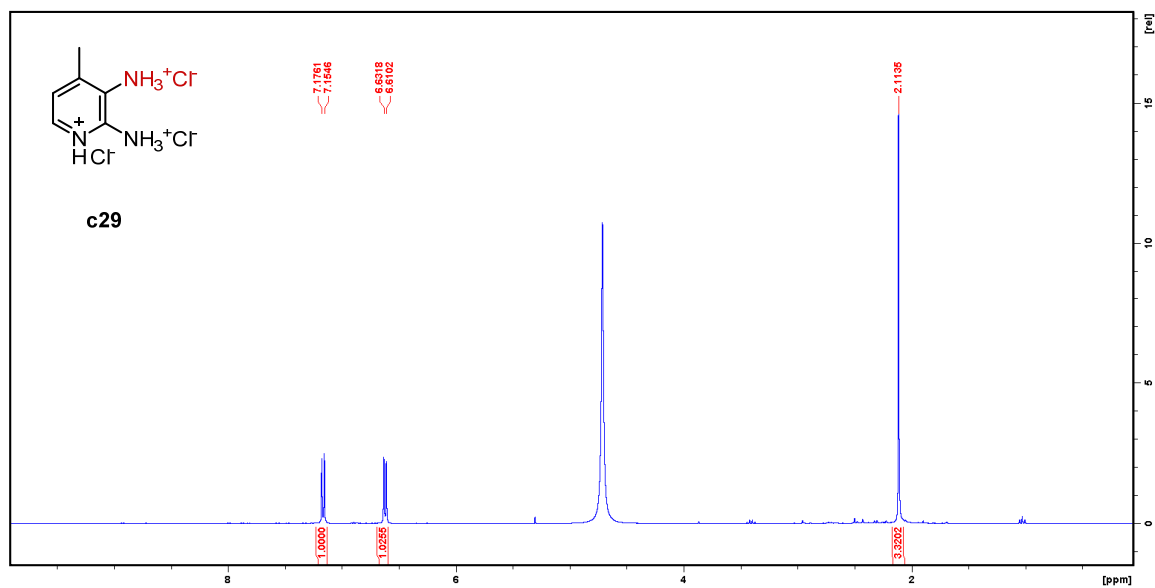


Figure S94: ^1H NMR of 2,3-diammonio-4-methylpyridinium trichloride (**c29**) in D_2O .

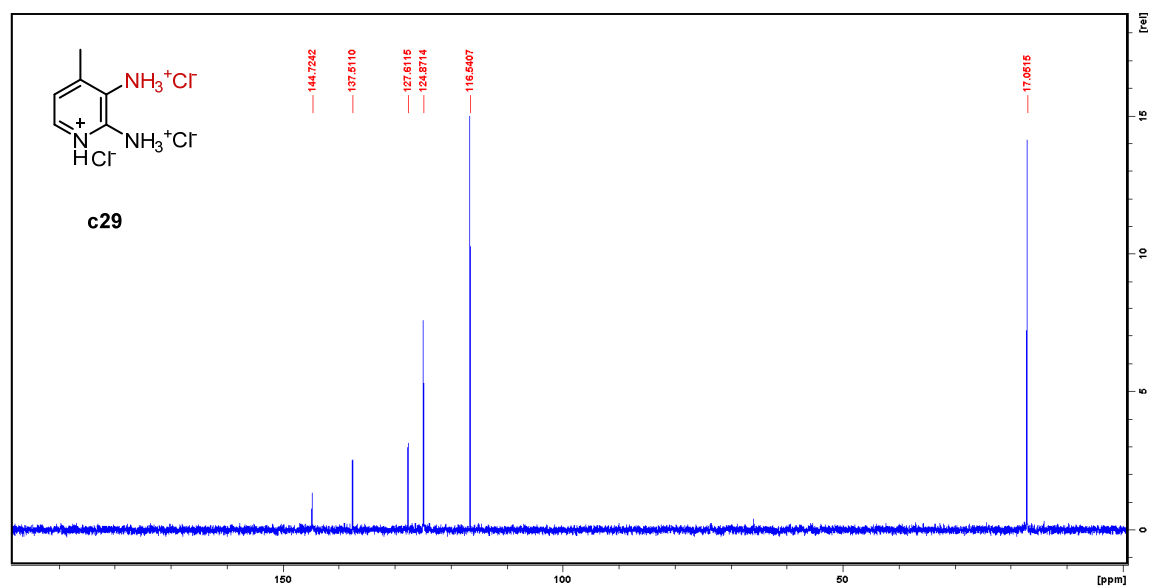


Figure S95: $^{13}\text{C}\{^1\text{H}\}$ NMR of 2,3-diammonio-4-methylpyridinium trichloride (**c29**) in D_2O .

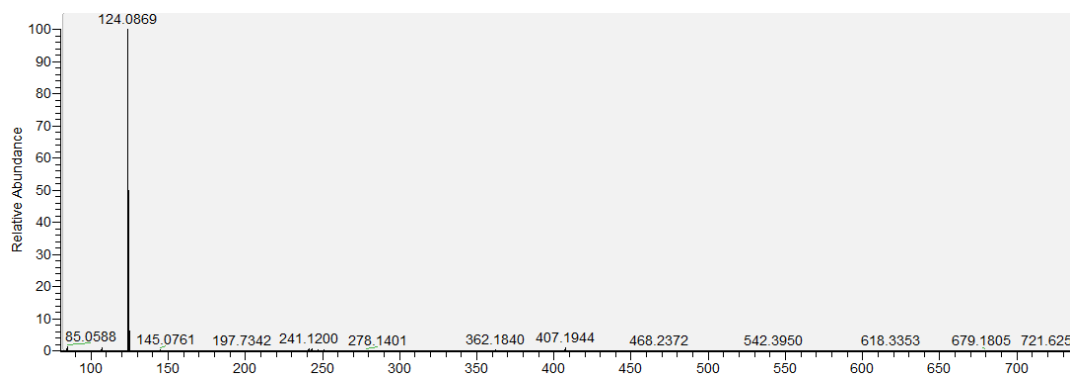


Figure S96: HR-MS of 2,3-diammonio-4-methylpyridinium trichloride (**c29**).

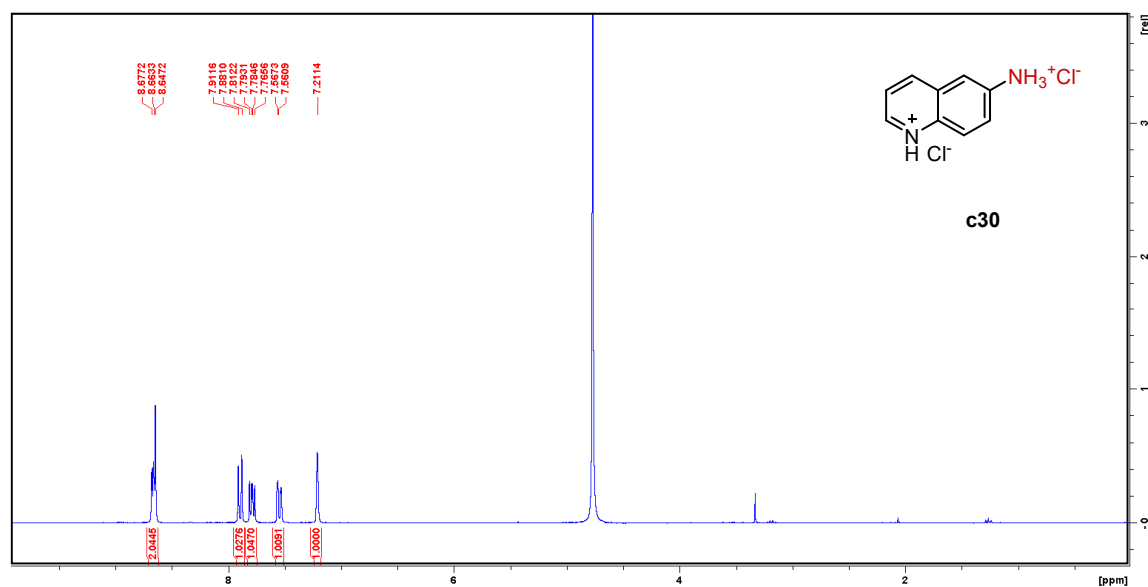


Figure S97: ¹H NMR of 6-ammonioquinolinium dichloride (**c30**) in D₂O.

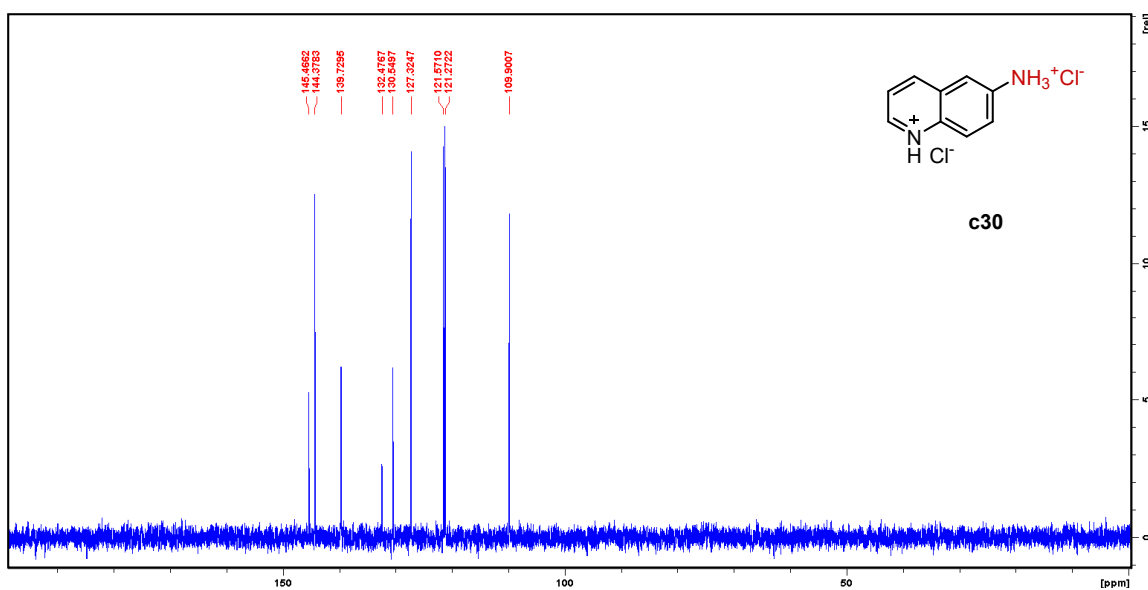


Figure S98: ¹³C{¹H} NMR of 6-ammonioquinolinium dichloride (**c30**) in D₂O.

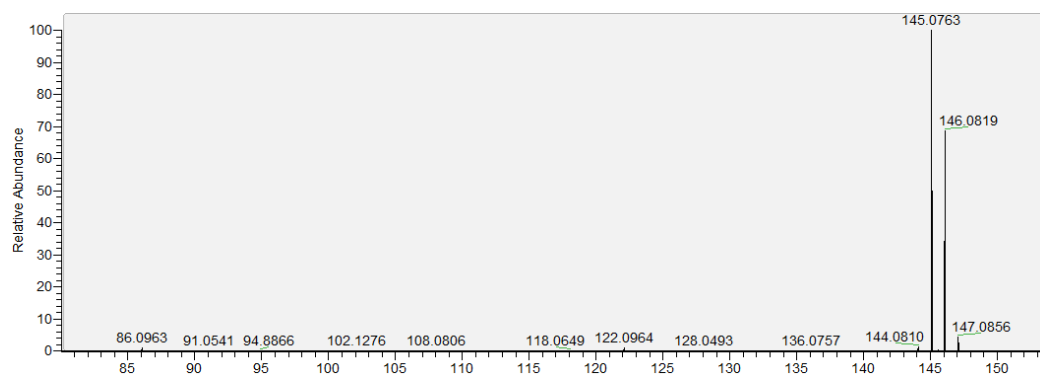


Figure S99: HR-MS of 6-ammonioquinolinium dichloride (**c30**).

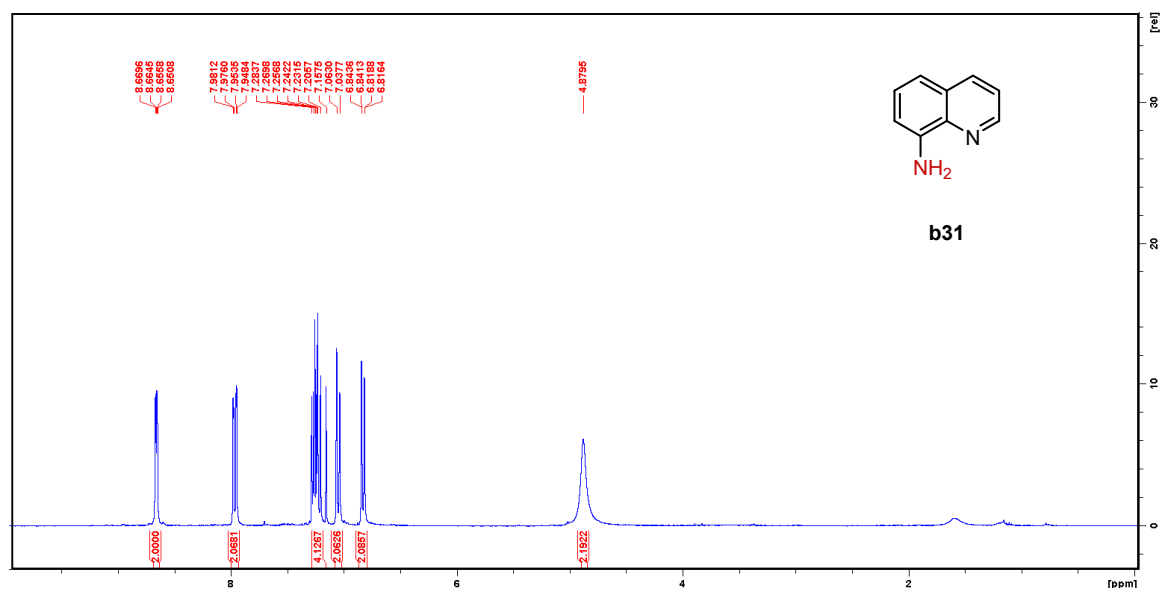


Figure S100: ¹H NMR of 8-aminoquinoline (**b31**) in CDCl₃.

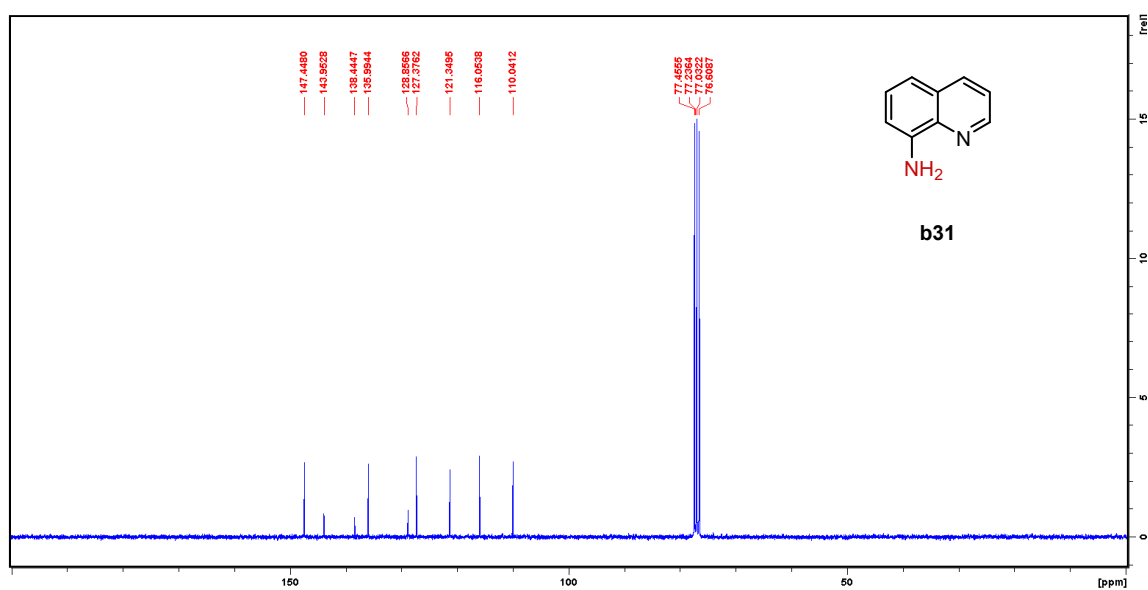


Figure S101: ¹³C{¹H} NMR of 8-aminoquinoline (**b31**) in CDCl₃.

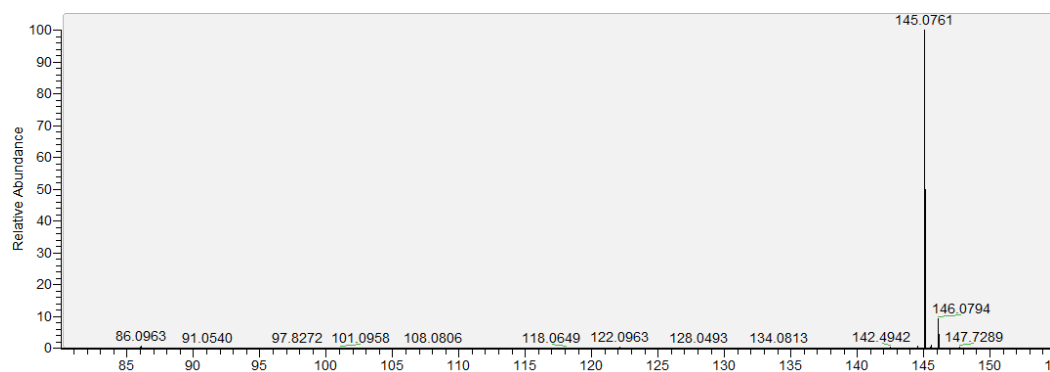


Figure S102: HR-MS of 8-aminoquinoline (**b31**).

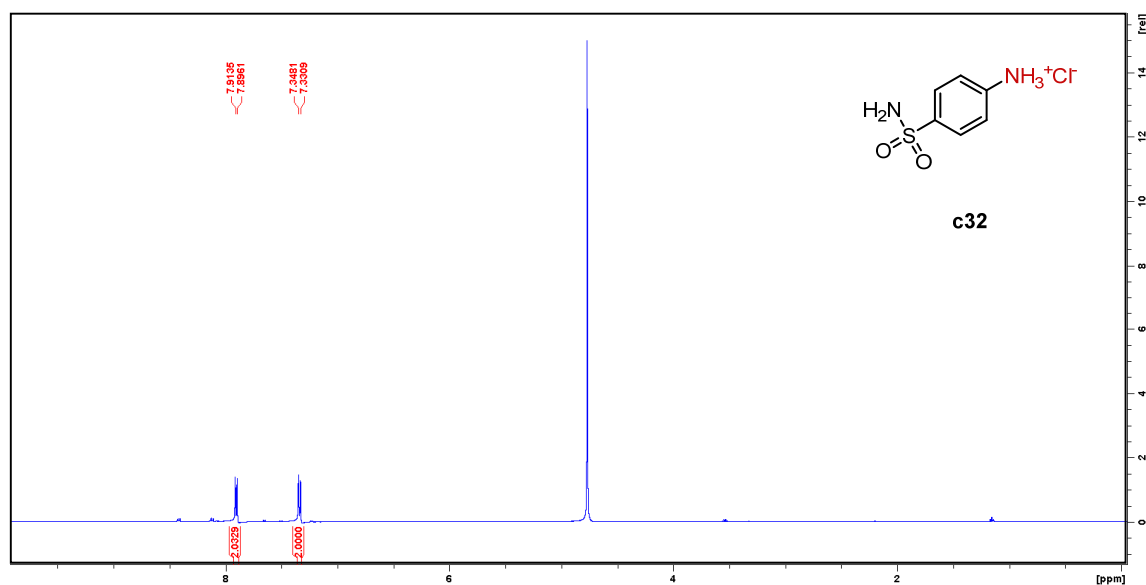


Figure S103: ¹H NMR of 4-sulfamoylanilinium chloride (c32) in D₂O.

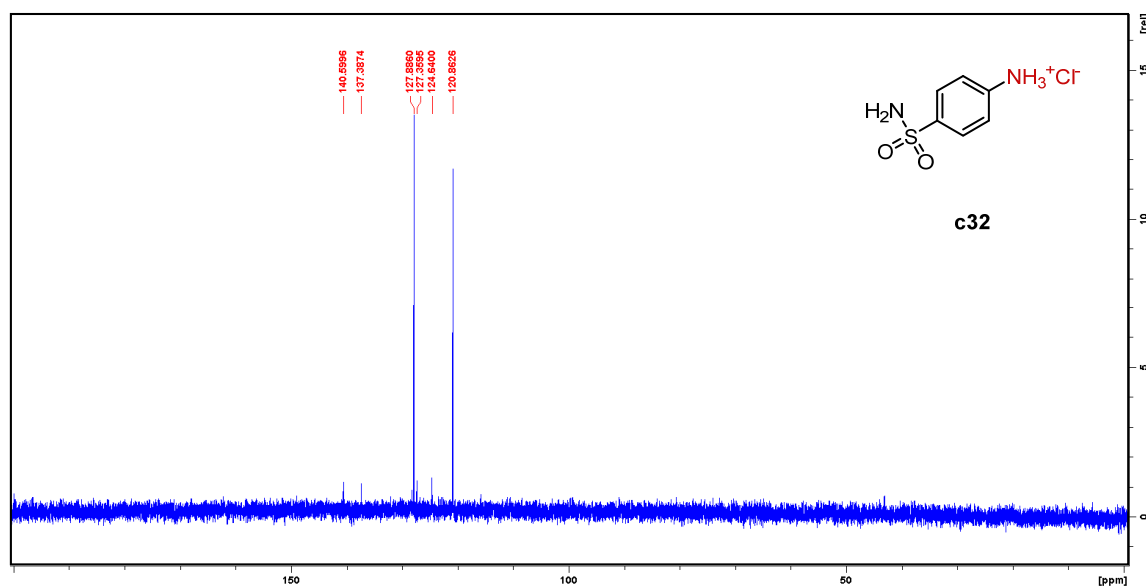


Figure S104: ¹³C{¹H} NMR of 4-sulfamoylanilinium chloride (c32) in D₂O.

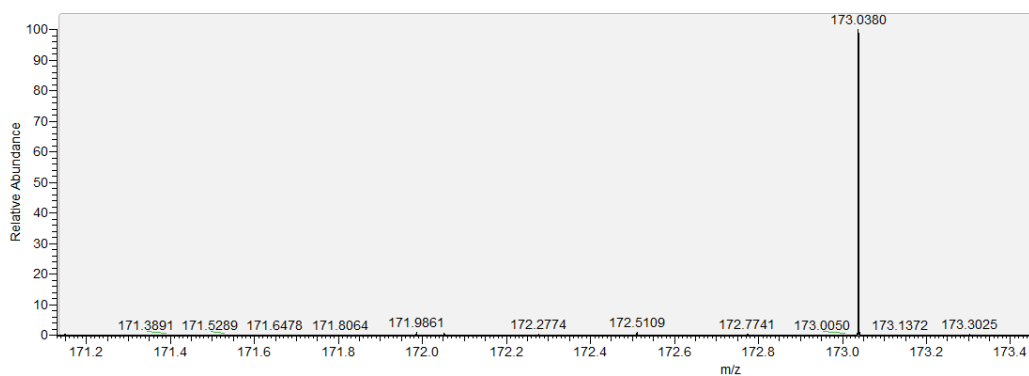


Figure S105: HR-MS of 4-sulfamoylanilinium chloride (c32).

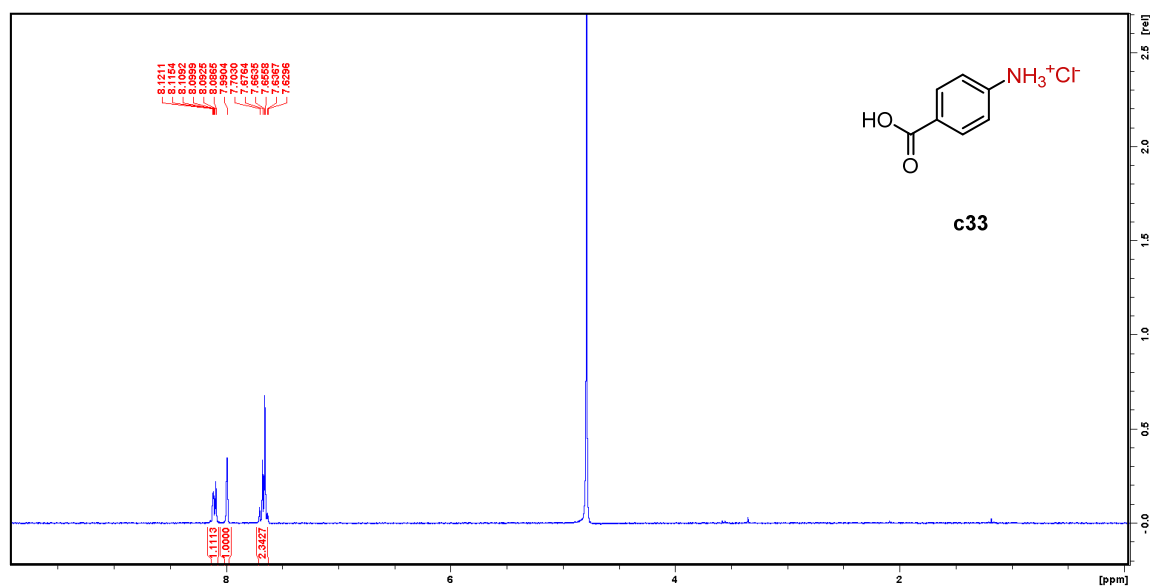


Figure S106: ¹H NMR of 4-carboxybenzenaminium chloride (**c33**) in D₂O.

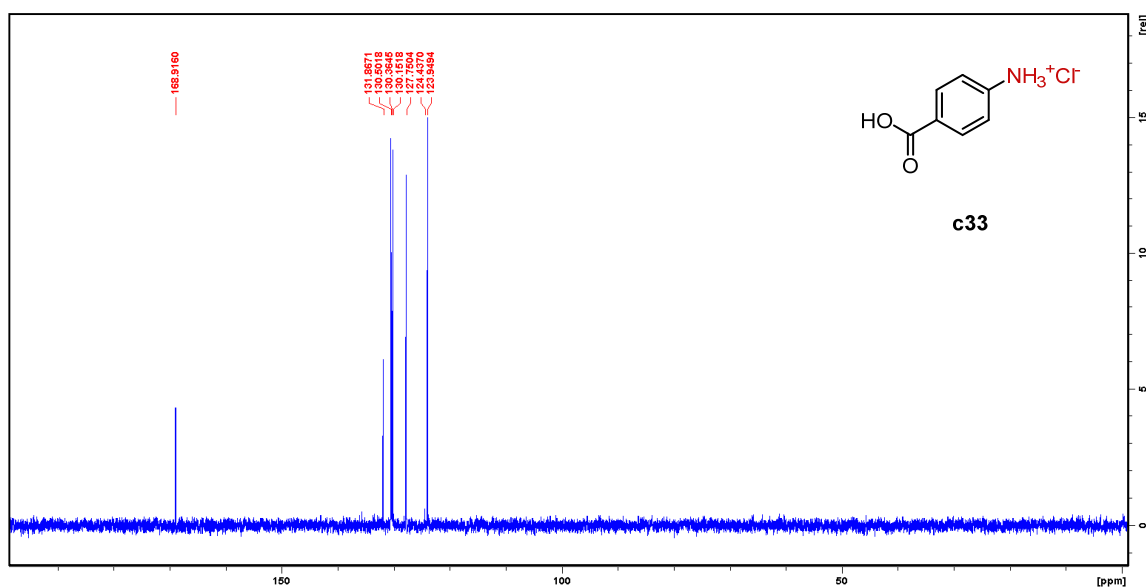


Figure S107: ¹³C {¹H} NMR of 4-carboxybenzenaminium chloride (**c33**) in D₂O.

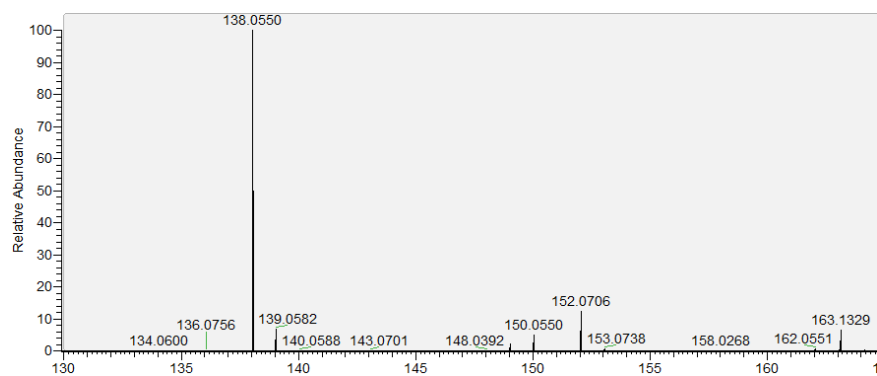


Figure S108: HR-MS of 4-carboxybenzenaminium chloride (**c33**).

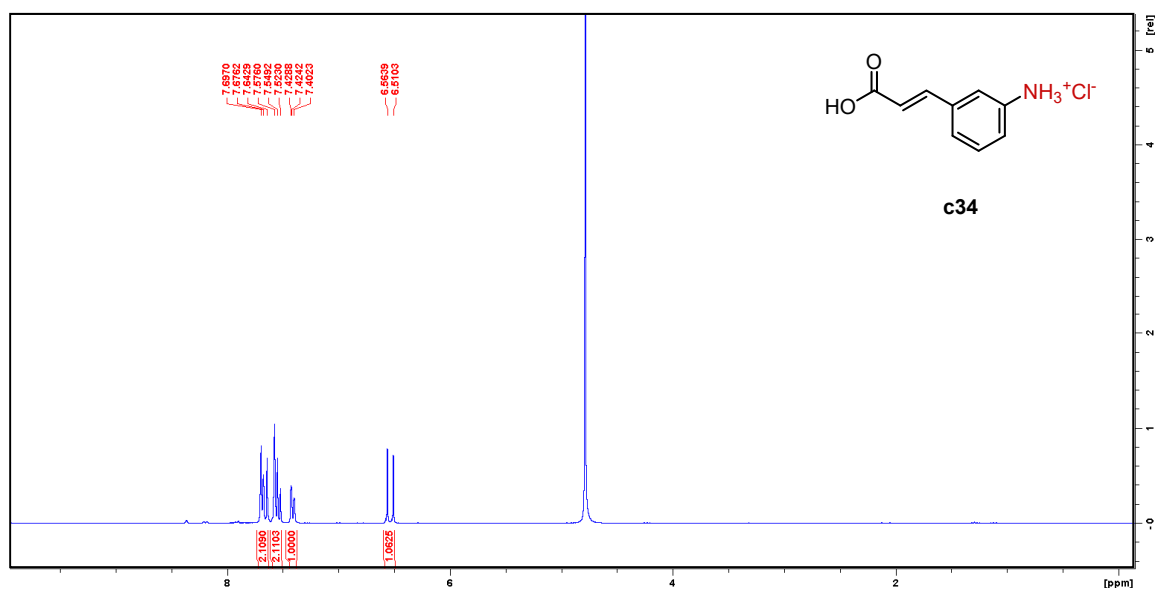


Figure S109: ¹H NMR of (E)-3-(2-carboxyvinyl)benzenaminium chloride (**c34**) in D₂O.

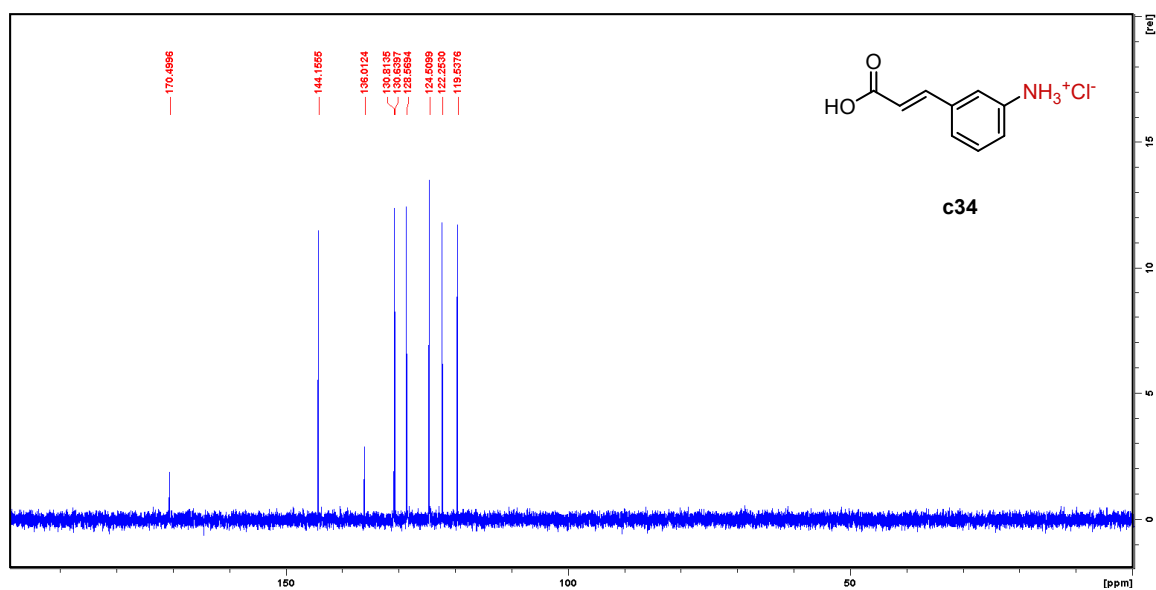


Figure S110: ¹³C {¹H} NMR of (E)-3-(2-carboxyvinyl)benzenaminium chloride (**c34**) in D₂O.

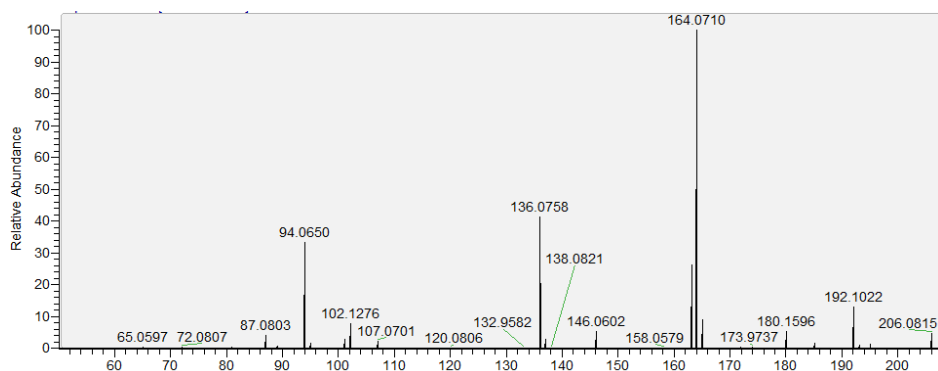


Figure S111: HR-MS of (E)-3-(2-carboxyvinyl)benzenaminium chloride (**c34**).

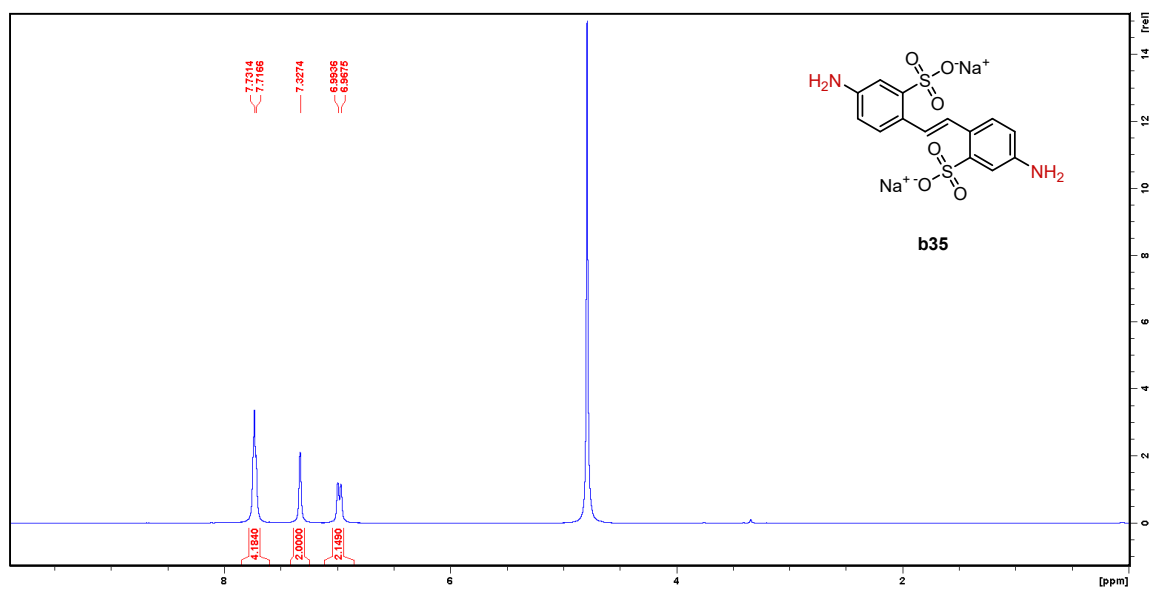


Figure S112: ¹H NMR of (E)-disodium 4,4'-diamino-2,2'-stilbenedisulfonate (**b35**) in CDCl₃.

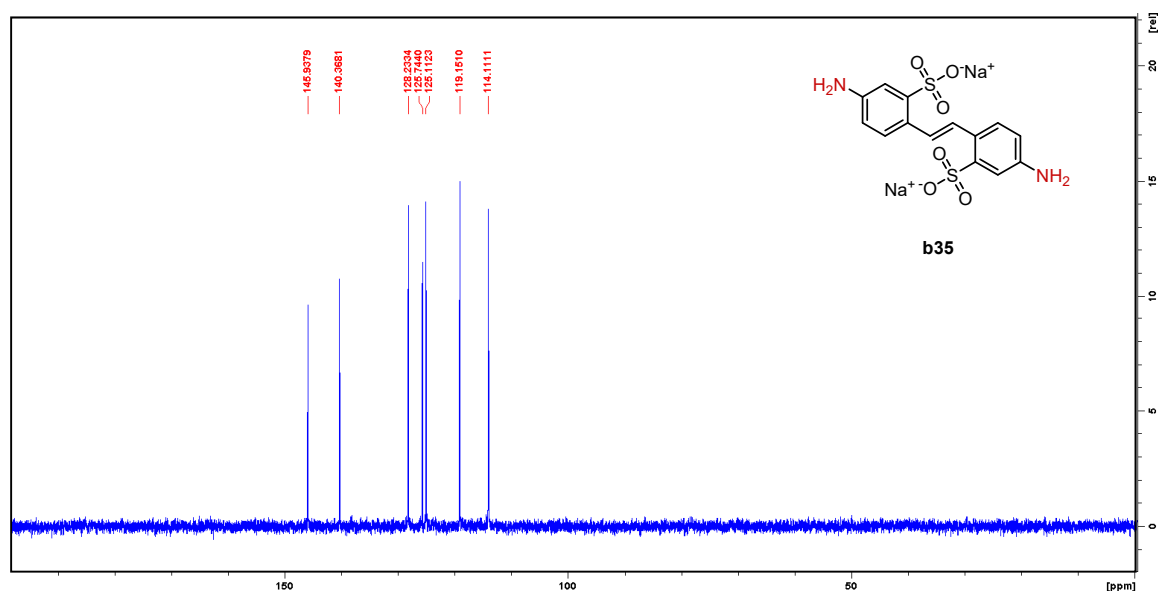


Figure S113: ¹³C {¹H} NMR of (E)-disodium 4,4'-diamino-2,2'-stilbenedisulfonate (**b35**) in CDCl₃.

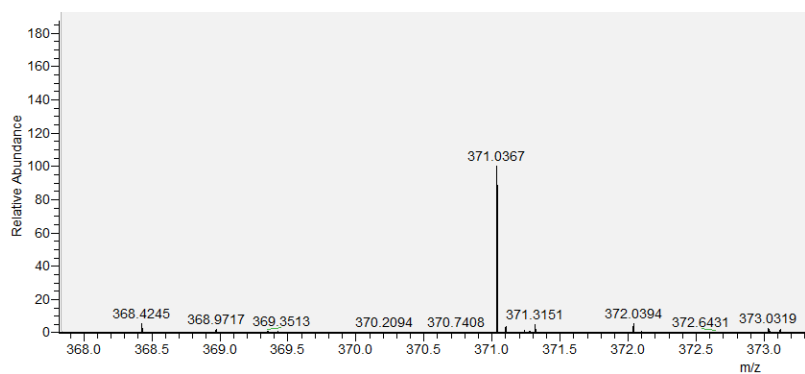


Figure S114: HR-MS of (E)-disodium 4,4'-diamino-2,2'-stilbenedisulfonate (**b35**).

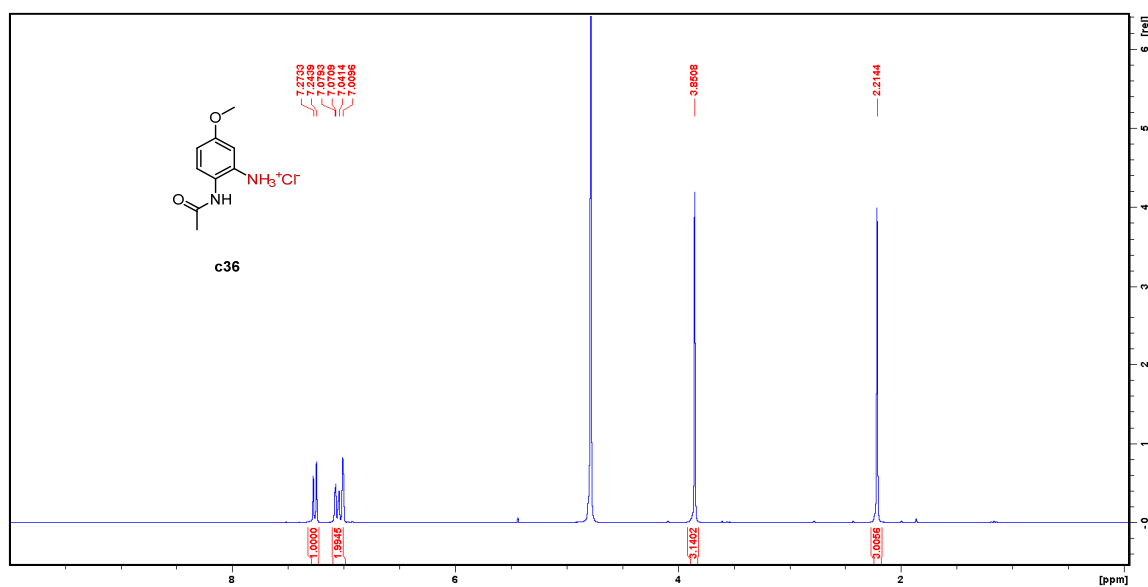


Figure S115: ^1H NMR of 2-acetamido-5-methoxybenzenaminium chloride (**c36**) in D_2O .

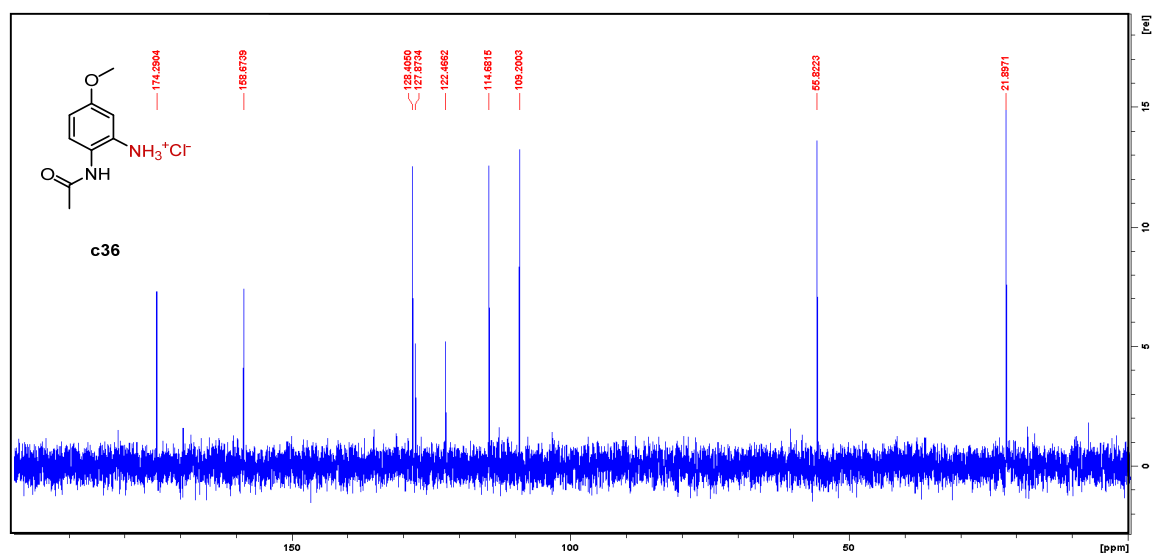


Figure S116: $^{13}\text{C}\{^1\text{H}\}$ NMR of 2-acetamido-5-methoxybenzenaminium chloride (**c36**) in D_2O .

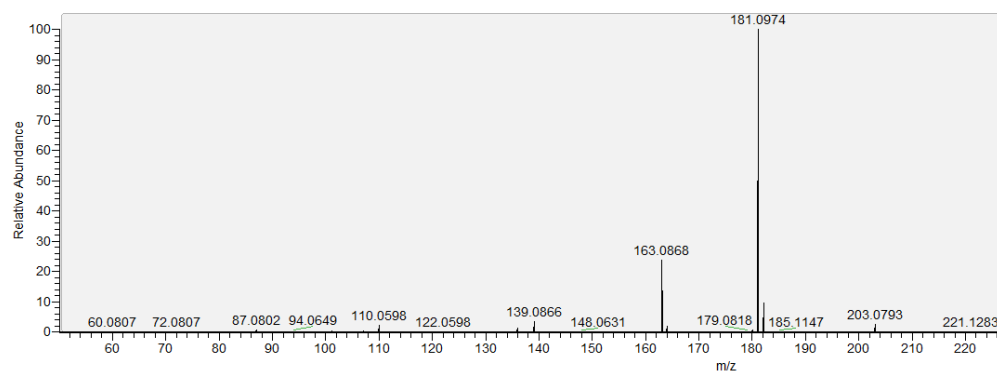


Figure S117: HR-MS of 2-acetamido-5-methoxybenzenaminium chloride (**c36**).