

Supporting information

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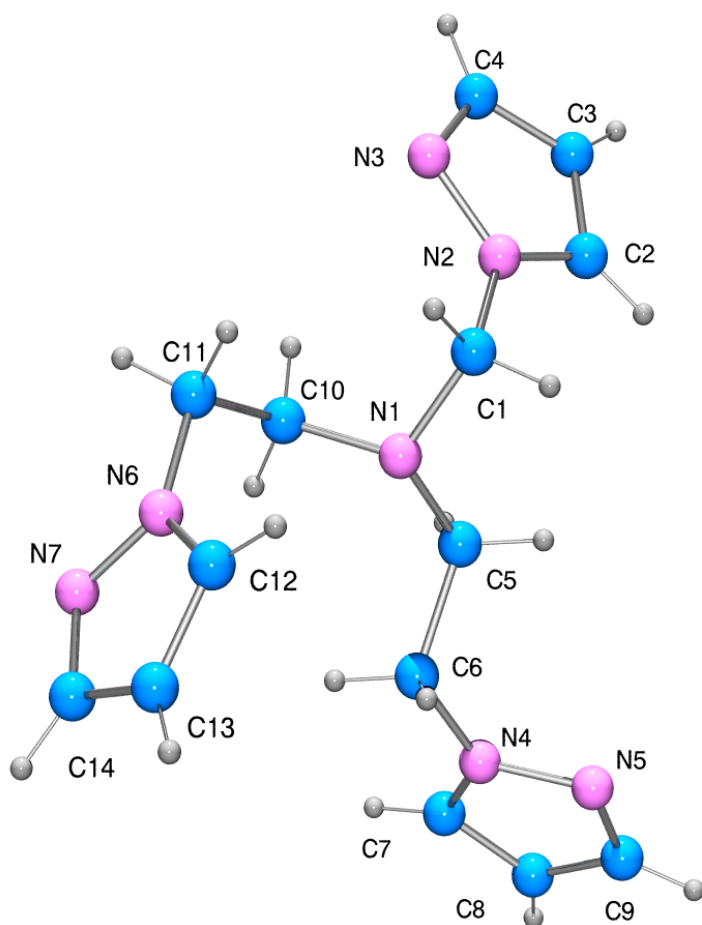


Fig. S1 The X-ray structure of bepz (**6**). Bond lengths (Å) and angles (°): N6 C12 1.346(2), N6 N7 1.3560(18), N6 C11 1.4522(19), N3 C4 1.329(2), N3 N2 1.3579(18), N2 C2 1.348(2), N2 C1 1.4685(19), N1 C1 1.4401(19), N1 C5 1.4631(19), N1 C10 1.4663(19), N4 C7 1.347(2), N4 N5 1.3580(18), N4 C6 1.4545(19), N5 C9 1.335(2), N7 C14 1.330(2), C10 C11 1.520(2), C6 C5 1.526(2), C14 C13 1.394(2), C9 C8 1.395(2), C4 C3 1.391(2), C8 C7 1.374(2), C3 C2 1.366(2), C12 C13 1.369(2). C12 N6 N7 112.18(13), C12 N6 C11 128.22(14), N7 N6 C11 119.42(13), C4 N3 N2 104.26(13), C2 N2 N3 111.75(13), C2 N2 C1 128.54(13), N3 N2 C1 119.71(12), C1 N1 C5 114.78(12), C1 N1 C10 115.05(12), C5 N1 C10 113.93(12), C7 N4 N5 112.18(13), C7 N4 C6 128.22(13), N5 N4 C6 119.43(13), C9 N5 N4 104.29(13), C14 N7 N6 104.03(13), N1 C10 C11 112.03(13), N4 C6 C5 110.87(12), N1 C5 C6 109.71(12), N6 C11 C10 111.72(12), N1 C1 N2 116.48(13), N7 C14 C13 112.09(14), N5 C9 C8 111.67(14), N3 C4 C3 111.97(15), C7 C8 C9 104.98(14), N4 C7 C8 106.87(14), C2 C3 C4 104.85(15), N2 C2 C3 107.18(15), N6 C12 C13 107.07(14), C12 C13 C14 104.62(14).

Compound reference	bepz
Chemical formula	C ₁₄ H ₁₉ N ₇
Formula Mass	285.36
Crystal system	Triclinic
<i>a</i> /Å	8.6809(14)
<i>b</i> /Å	9.4471(16)
<i>c</i> /Å	10.1041(16)
<i>α</i> /°	80.019(8)
<i>β</i> /°	66.216(7)
<i>γ</i> /°	87.123(8)
Unit cell volume/Å ³	746.6(2)
Temperature/K	89(2)
Space group	P-1
No. of formula units per unit cell, Z	2
No. of reflections measured	14062
No. of independent reflections	3031
<i>R</i> _{int}	0.0415
Final <i>R</i> _i values (<i>I</i> > 2σ(<i>I</i>))	0.0457
Final <i>wR</i> (<i>F</i> ²) values (<i>I</i> > 2σ(<i>I</i>))	0.1146
Final <i>R</i> _i values (all data)	0.0583
Final <i>wR</i> (<i>F</i> ²) values (all data)	0.1239
Goodness of fit on <i>F</i> ²	1.082

Table S1 Details of the solid state structure of 6

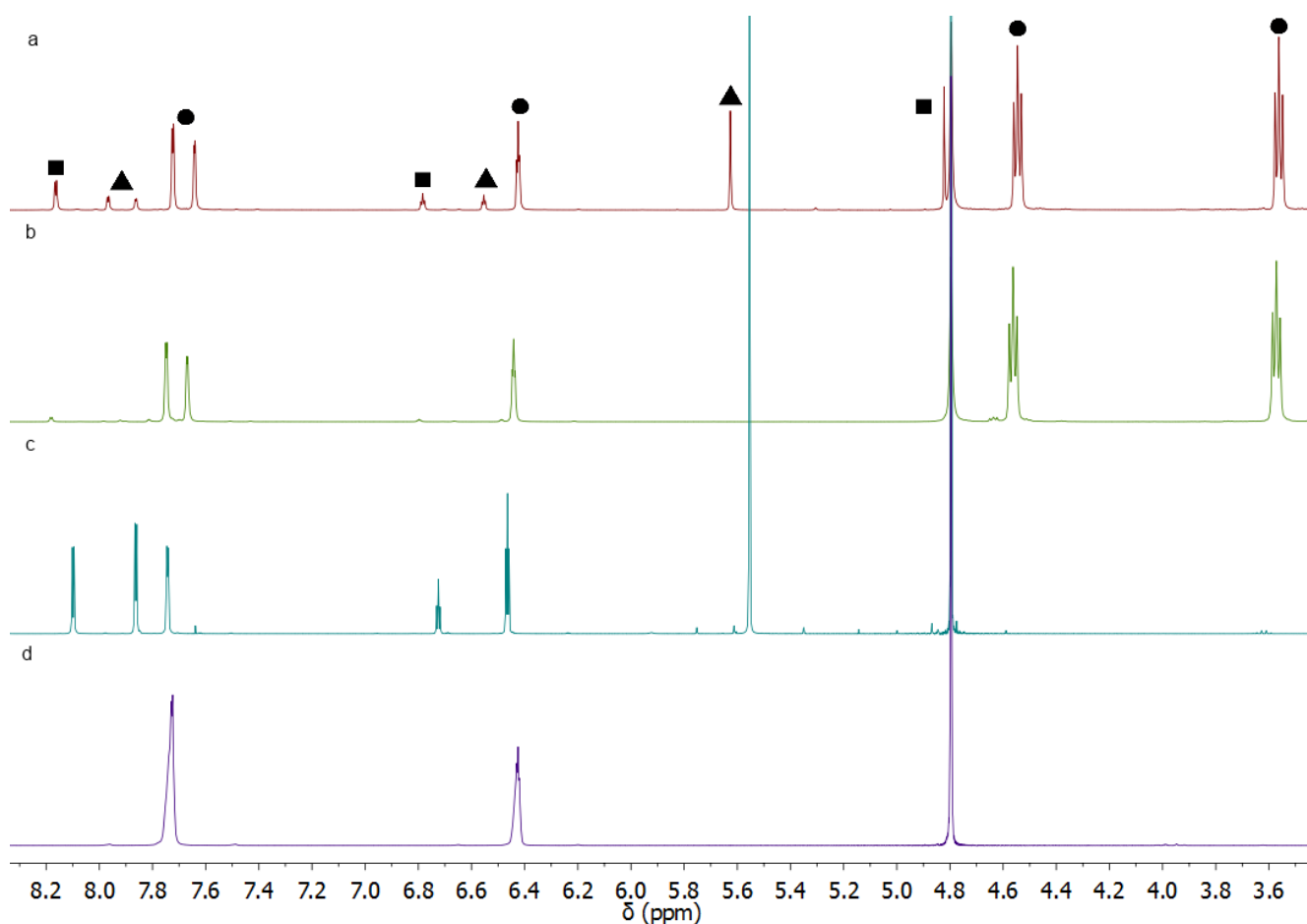


Fig. S2 ¹H NMR spectra of bepz (a), 8 (●, b), 10 (▲, c), and pyrazole (■, d) in D₂O. [D₃O⁺] = 0.014M for all samples.

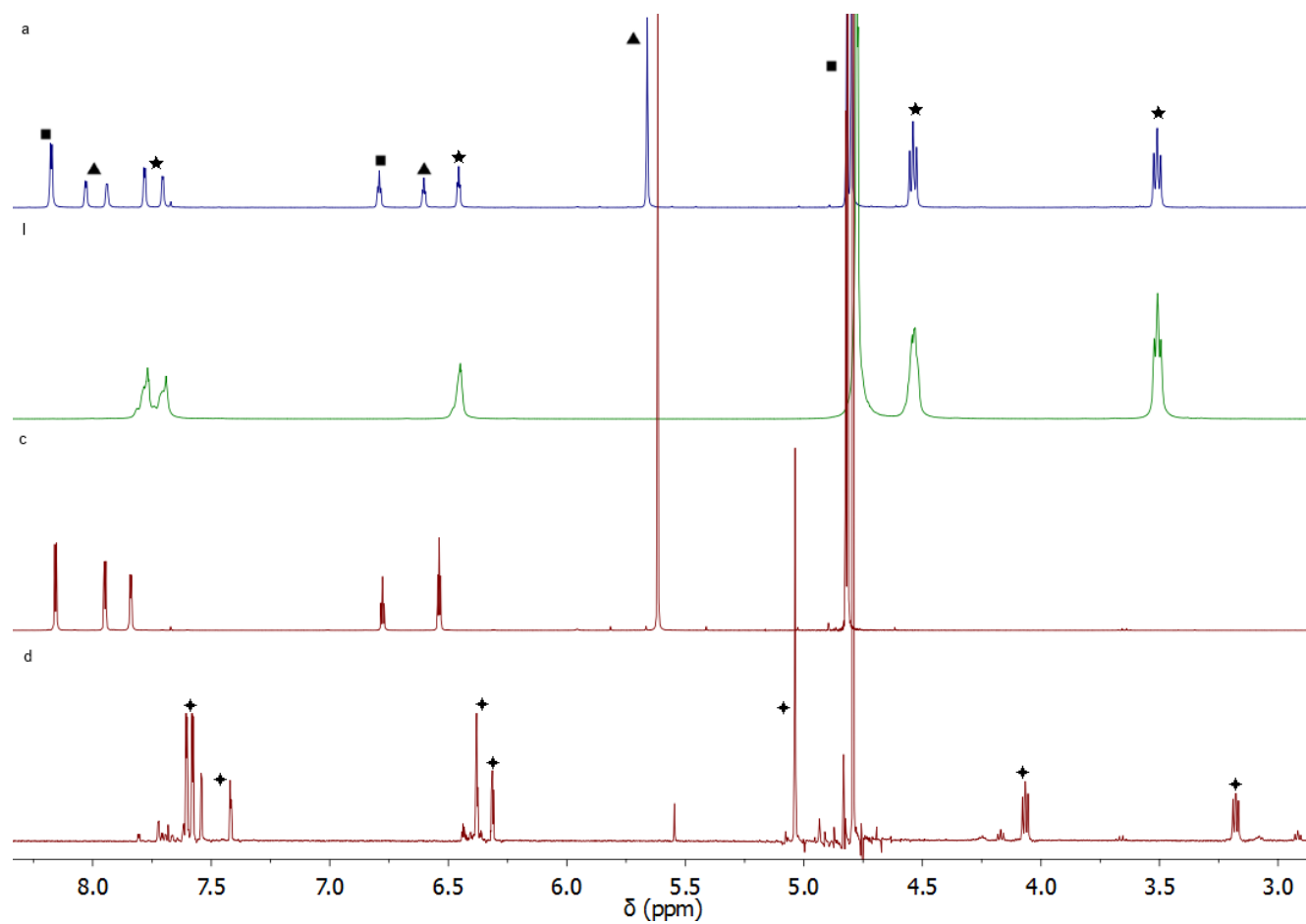


Fig. S3 ^1H NMR spectra of bmpz ($\blacklozenge$, a), **9** ($\star$, b), and **10** ($\blacktriangle$, c) in D_2O with $[\text{D}_3\text{O}^+] = 0.014\text{M}$ ($\blacksquare$ = pyrazole). Also, ^1H NMR spectrum of bmpz in D_2O at neutral pD (d).

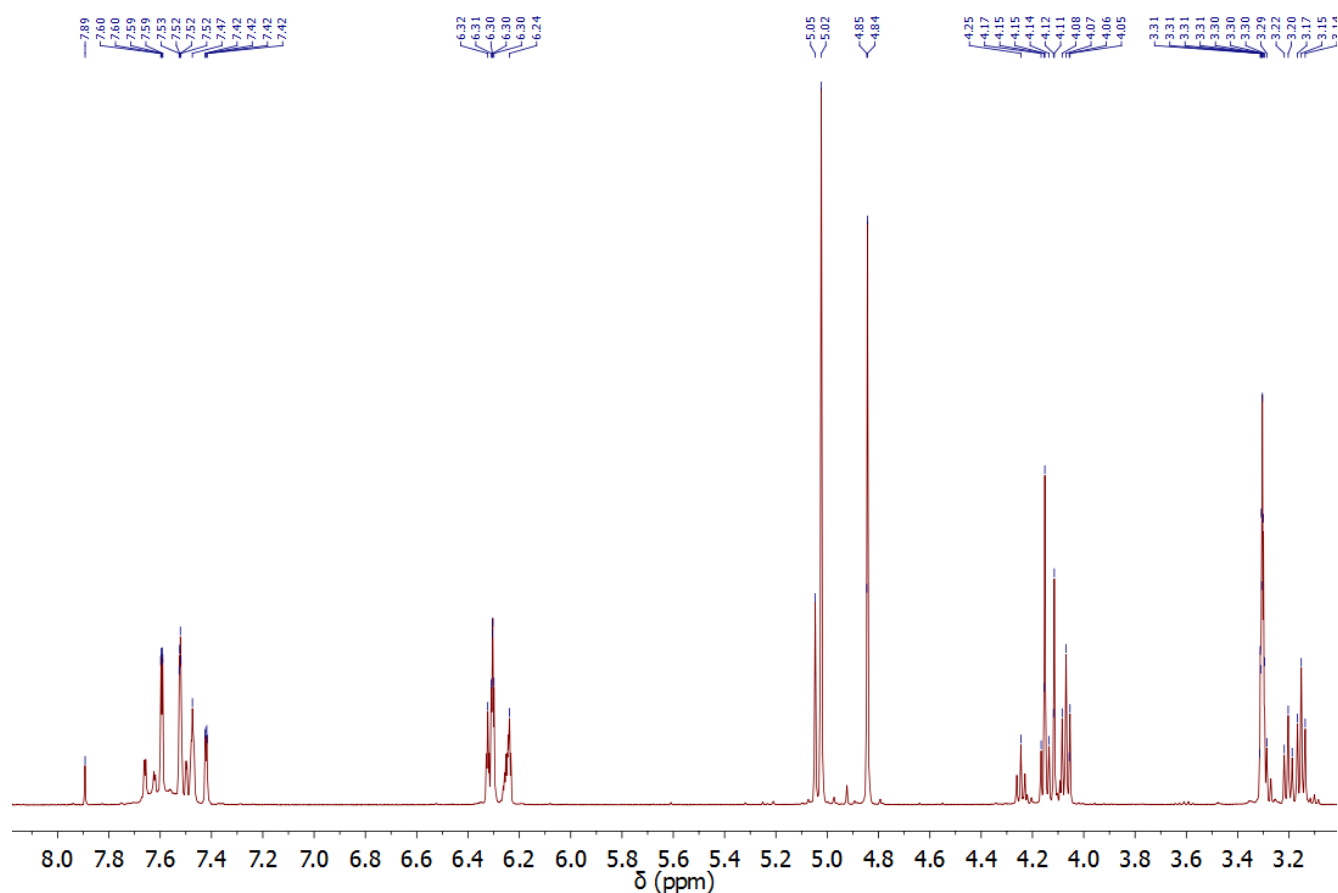


Fig. S4 ^1H NMR spectrum of bmpz in CD_3OD

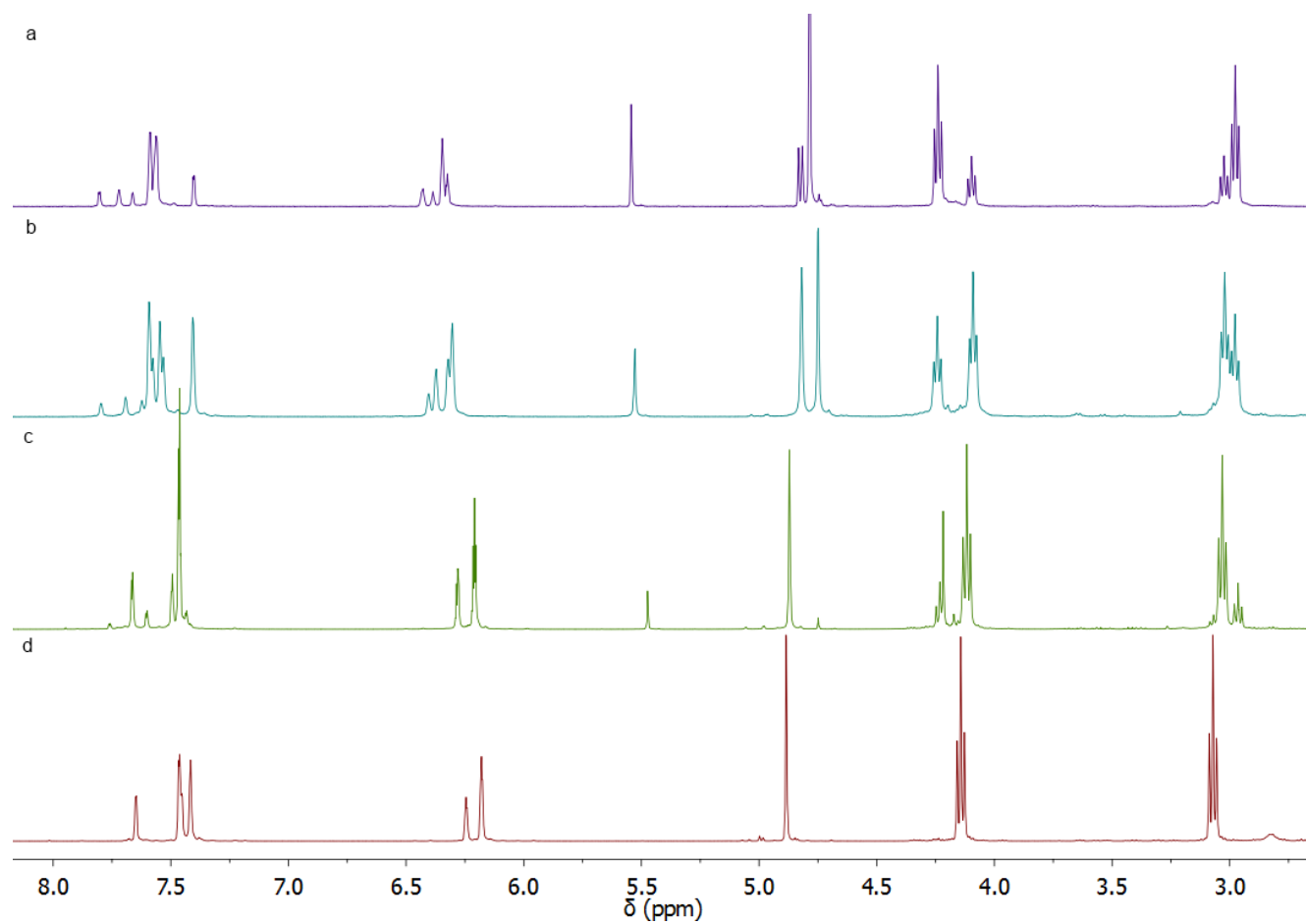


Fig. S5 ^1H NMR spectra of bepz in D_2O (a), $\text{D}_2\text{O}:\text{d}_6\text{-acetone}$ 3:1 (b), $\text{d}_6\text{-acetone}:\text{D}_2\text{O}$ 3:1 (c) and $\text{d}_6\text{-acetone}$ (d).

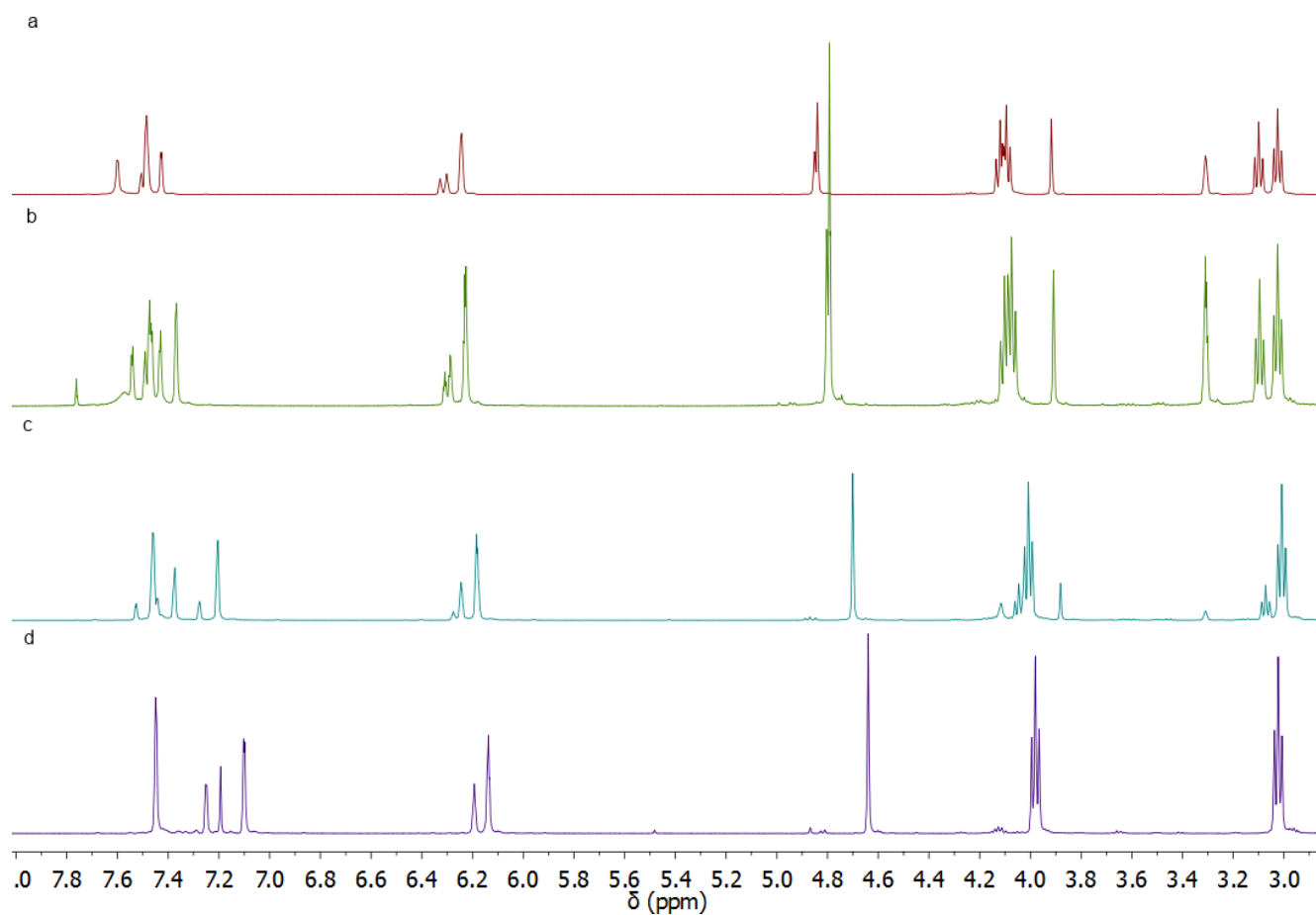


Fig. S6 ^1H NMR spectra of bepz in CD_3OD (a), $\text{CD}_3\text{OD}:\text{CDCl}_3$ 3:1 (b), $\text{CDCl}_3:\text{CD}_3\text{OD}$ 3:1 (c) and CDCl_3 (d).

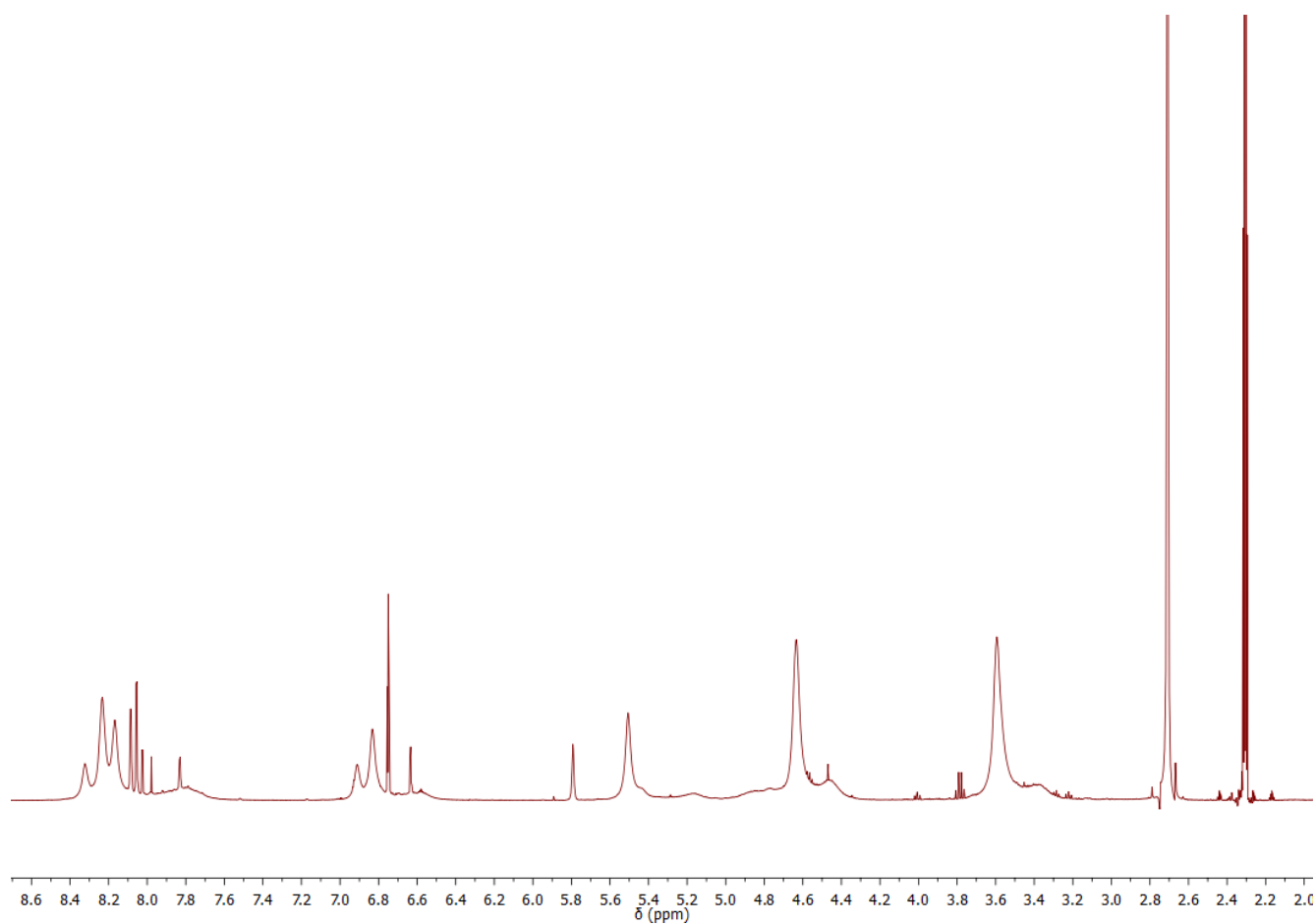


Fig. S7 ^1H NMR spectrum of bepz combined with one equivalent of $\text{Zn}(\text{ClO}_4)_2 \cdot 6\text{H}_2\text{O}$ in CD_3CN .

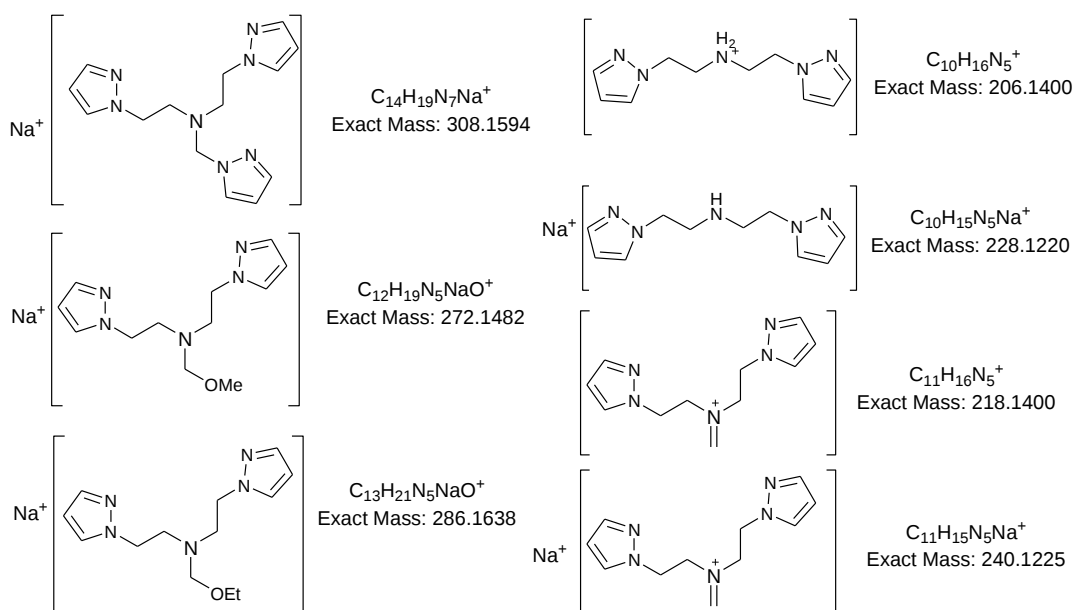


Fig. S8 Assignment of relevant peaks observed in the mass spectra of bepz collected in methanol, ethanol and isopropanol (Figs. S9-S12).

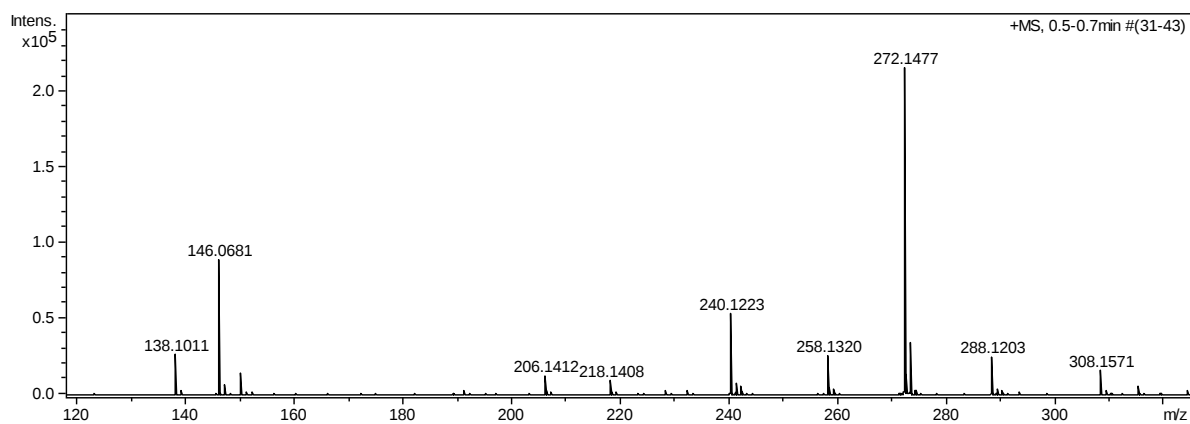


Fig. S9 The mass spectrum of bepz collected in methanol. Relevant peaks assigned in Fig. S7.

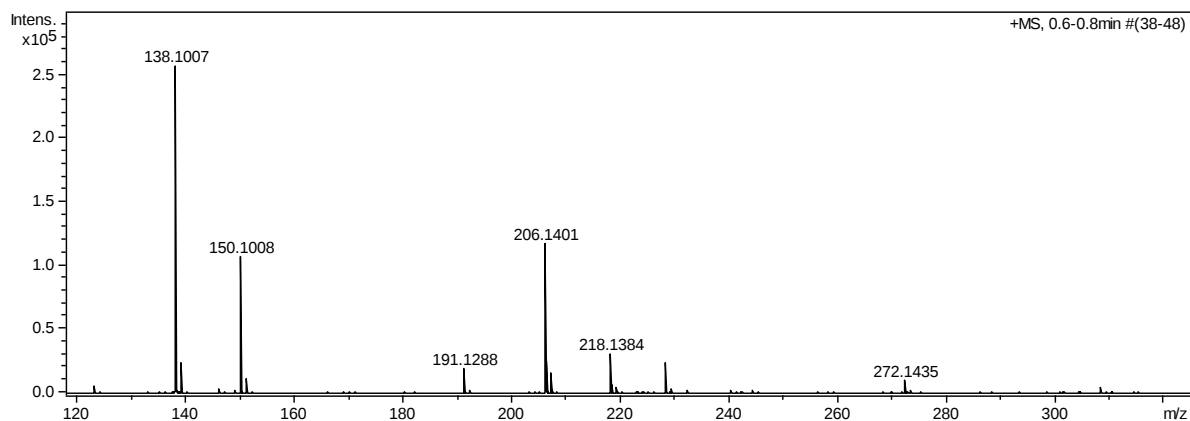


Fig. S10 The mass spectrum of bepz collected in methanol, with one drop of 0.1% formic acid in methanol added.

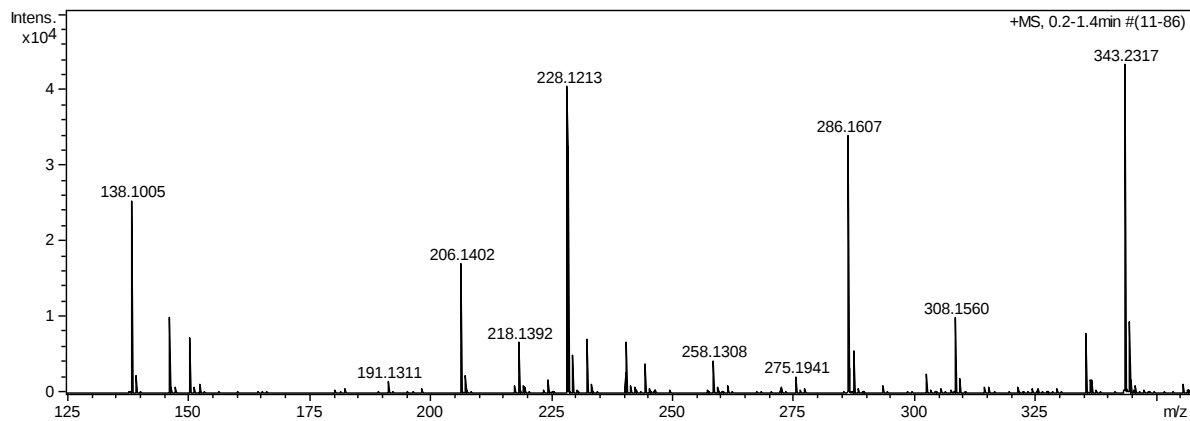


Fig. S11 The mass spectrum of bepz collected in rectified spirits. Relevant peaks assigned in Fig. S7.

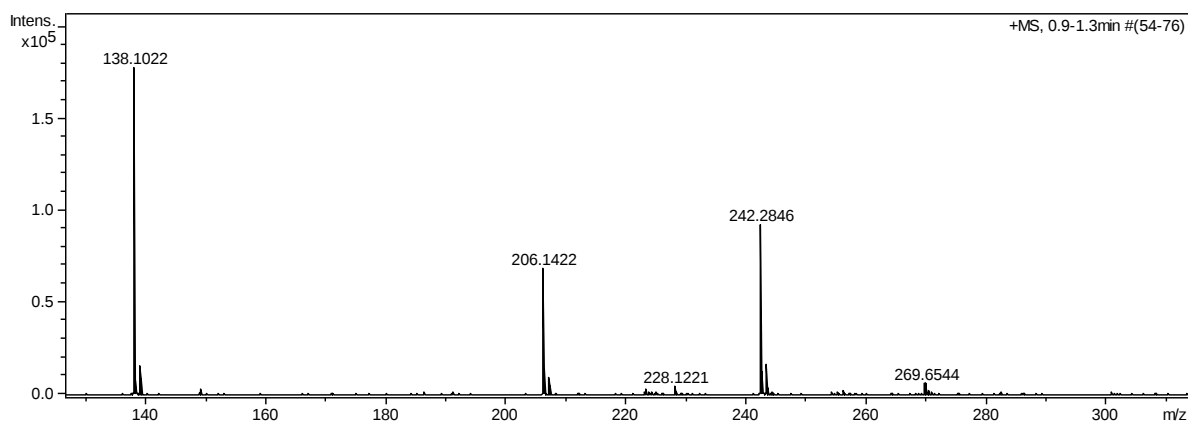


Fig. S12 The mass spectrum of bepz collected in isopropanol:acetonitrile 1:1. Relevant peaks assigned in Fig. S7.

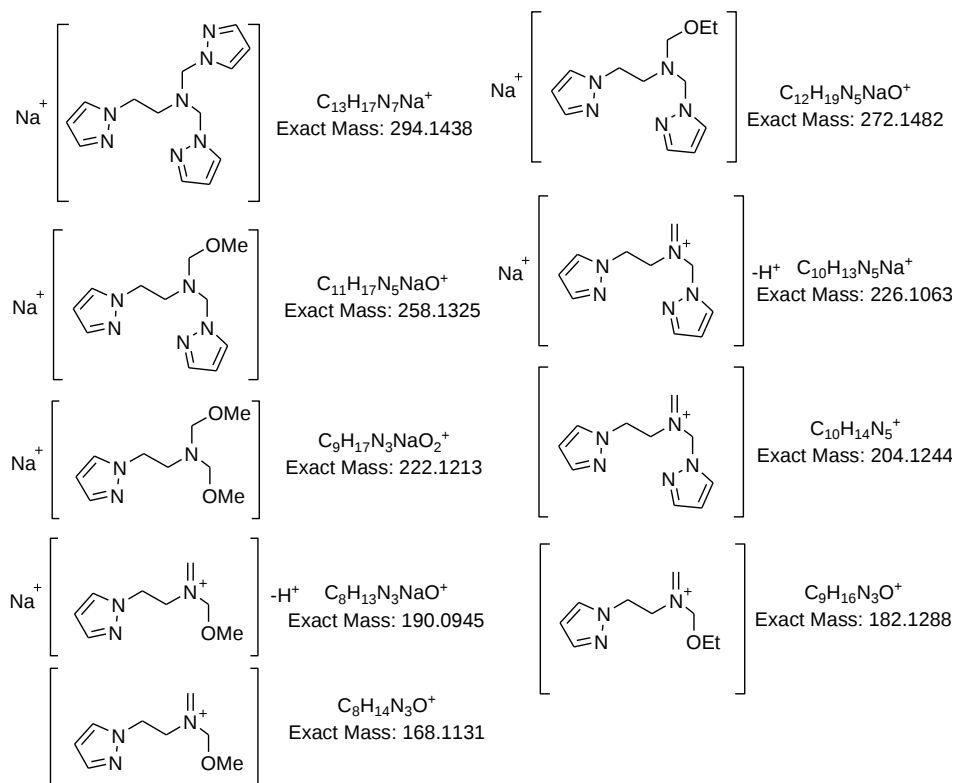


Fig. S13 Assignments of peaks observed in the mass spectra of bmpz collected in methanol (left column, corresponds to Figs. S14, S15) and in ethanol (right column, corresponds to Fig. S16).

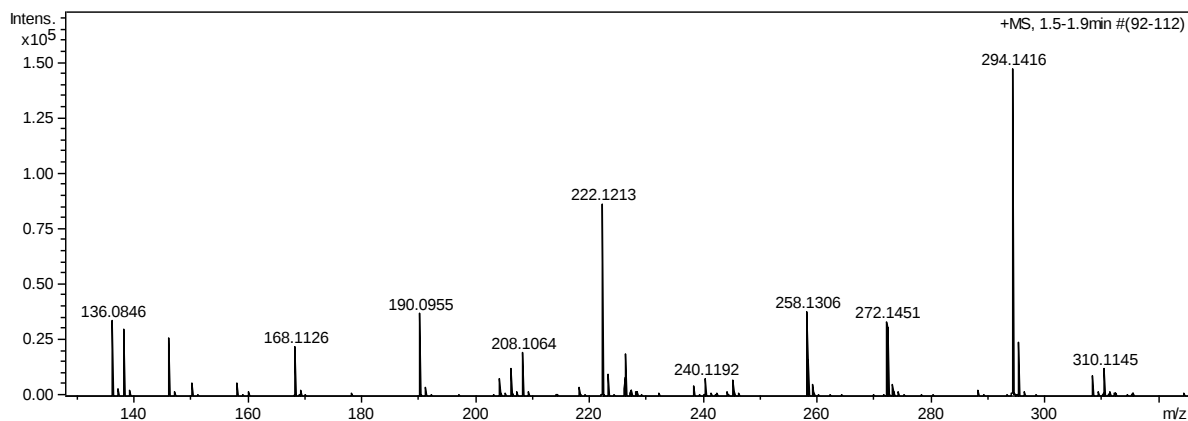


Fig. S14 The mass spectrum of bmpz collected in methanol. Relevant peaks assigned in Fig. S11.

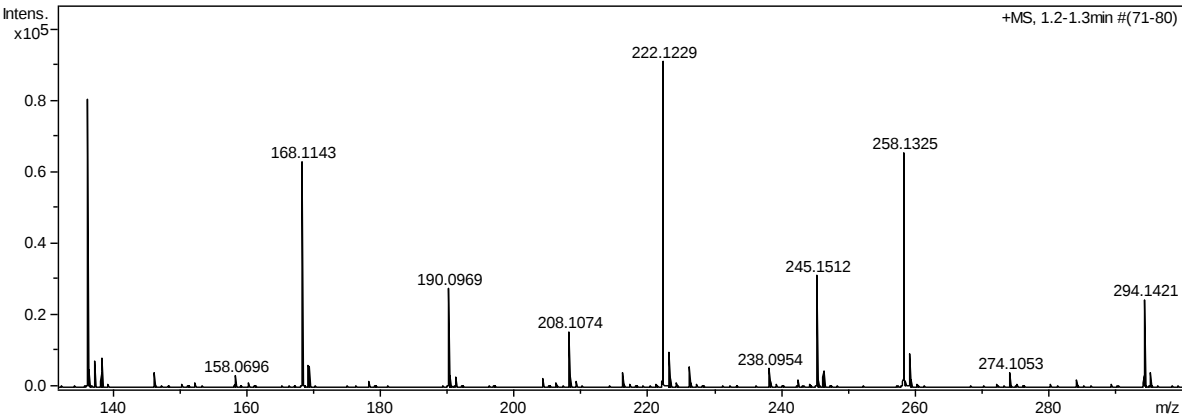


Fig. S15 The mass spectrum of bmpz collected in methanol with one drop of 0.1% formic acid in methanol added.

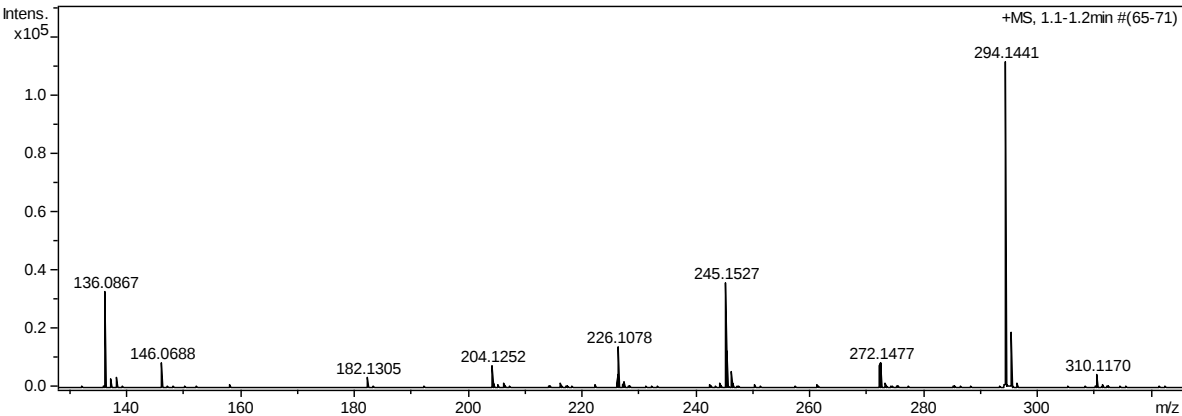


Fig. S16 The mass spectrum of bmpz collected in rectified spirits. Relevant peaks assigned in Fig. S11.

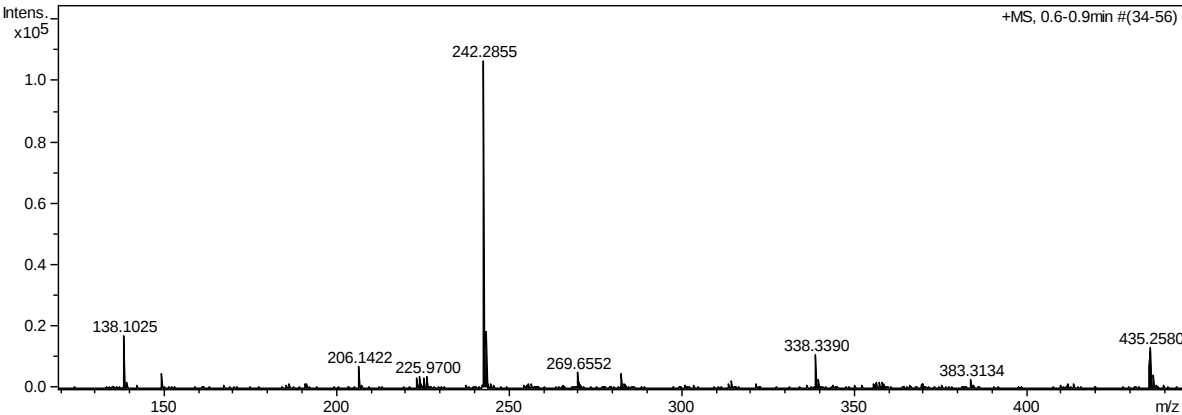


Fig. S17 The mass spectrum of bmpz collected in 1:1 isopropanol:water.